Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Divergent synthesis of nitrocyclopropanes and isoxazoline *N*-oxides from nitro compounds and vinyl sulfonium salts

Ushakov P. Yu., Golovanov I. S., Ioffe S. L., Tabolin A. A.

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1. General information

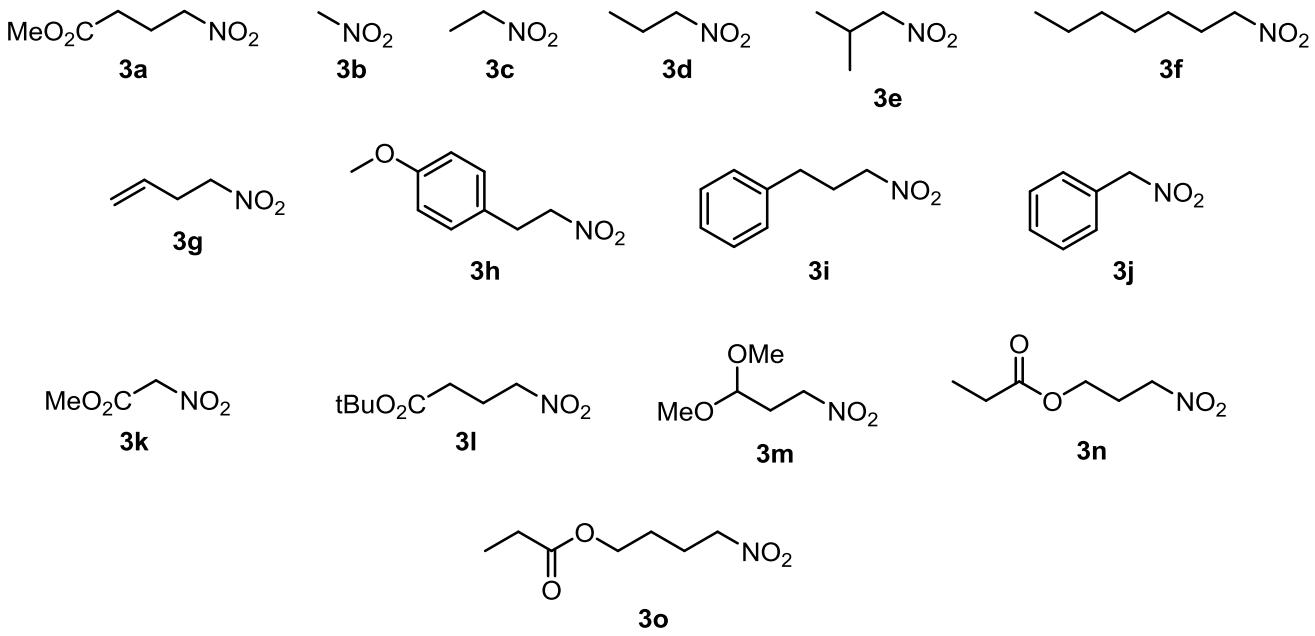
All reactions were carried out in oven-dried (150°C) glassware.

NMR spectra were recorded at 298K with residual solvents peaks as an internal standard. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), br (broad). Assignment of ^{1}H and ^{13}C NMR spectra is based on 2D NMR (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{1}H NOESY) for characteristic compounds. HRMS were measured on electrospray ionization (ESI) instrument with a time-of-flight (TOF) detector. IR spectra were recorded in ATR mode. Relative intensities are indicated as follows: s (strong), m (medium), w (weak), br (broad), sh (shoulder).

Column chromatography was performed using Kieselgel 40–60 μm 60 A using ethyl acetate – petroleum ether (PE) mixture, ethyl acetate, and MeOH. Analytical thin layer chromatography was performed on silica gel plates with F 254 indicator. Visualization was accomplished with UV light and/or solution of anisaldehyde/H_2SO_4 in ethanol and/or ninhydrin stain. Melting points were determined on a Koffler apparatus and are uncorrected.

Brine refers to a saturated aqueous solution of NaCl. TFE refers to 2,2,2-trifluoroethanol. Petroleum ether, ethyl acetate, MeOH, diethyl ether, $CHCl_3$, DMF, DMSO, THF, MeCN, PhMe, Et_2O, 1,4-dioxane, tBuOMe, TFE, EtOH, DME, AcMe, CCl_4 were distilled without drying agents. CH_2Cl_2 and Et_3N were distilled from CaH_2, DBU and TMG were distilled from CaH_2 under reduced pressure Most of the chemicals were acquired from commercial sources and used as received.

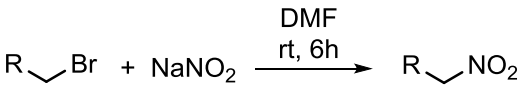
2. Synthesis of nitro compounds 3



Nitro compounds **3b**, **3c**, **3d**, **3j** and **3k** were received from commercial sources.

Methyl 4-nitrobutanoate **3a**[1], 2-methyl-1-nitropropane **3e**[2], 2-(4-Methoxyphenyl)-1-nitroethane **3h**[3], *tert*-butyl 4-nitrobutanoate **3l**[4], 3-nitropropanal dimethylacetal **3m**[5], 3-nitropropyl propionate **3o**[6] were synthesized according to literature procedures.

Synthesis of nitro compounds 3f,g,i[7]:



3f,g,i

To a stirred solution of $NaNO_2$ (10.35 g, 150 mmol, 1.5 equiv.) a corresponding alkyl bromide (100 mmol, 1 equiv.) was added. Reaction mixture was stirred for 6h at room temperature. Then the mixture was diluted with water (500 mL) and extracted with Et_2O (3 × 150 mL). Combined organic phase was dried over anhydrous Na_2SO_4. The solvent was evaporated and crude material was purified by vacuum distillation or flash column chromatography.

1-Nitroheptane **3f** was synthesized from heptyl bromide (17.9 g, 100 mmol) and sodium nitrite (10.35 g, 100 mmol), yield – 7.15 g (49%). Colorless liquid. Bp 54 – 59°C/1.0 mmHg (lit.[8] 60°C/1 mmHg).

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.36 (t, J = 7.1 Hz, 2H, C$\underline{H}_2$NO$_2$), 1.99 (p, J = 7.1 Hz, 2H, C$\underline{H}_2$), 1.41 – 1.21 (m, 8H, 4C$\underline{H}_2$), 0.92 – 0.83 (m, 3H, C$\underline{H}_3$). ^{1}H NMR spectrum was in accordance with literature data.[9]

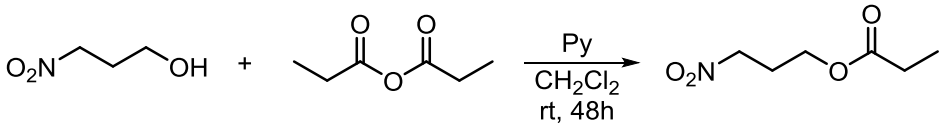
4-Nitro-1-butene **3g** was synthesized from homoallyl bromide (5.05 g, 37 mmol) and sodium nitrite (3.8 g, 56 mmol), yield – 0.90 g (24%). Colorless liquid. Bp 64 – 66°C/9 mmHg.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.77 (ddt, J = 17.0, 10.2, 7.0 Hz, 1H, C$\underline{H}$=CH$_2$), 5.25 – 5.12 (m, 2H, CHC$\underline{H}_2$), 4.44 (t, J = 7.0 Hz, 2H, CH$_2$C$\underline{H}_2$NO$_2$), 2.75 (q, J = 7.0 Hz, 2H, C$\underline{H}_2$CH$_2$NO$_2$) ppm. ^{1}H NMR spectrum was in accordance with literature data.[10]

3-Phenyl-1-nitropropane **3i** was synthesized from 3-phenylpropyl bromide (8.7 g, 44 mmol) and sodium nitrite (5.18 g, 75 mmol). Column chromatography (PE/EtOAc 50:1) afforded **3i** as colorless oil, yield – 1.5 g (21%). R_f = 0.62 (PE/EtOAc = 10:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 – 7.11 (m, 5H, C<u>H</u>$_{Ph}$), 4.31 (t, J = 7.1 Hz, 2H, $PhCH_2CH_2C\underline{H}_2$), 2.68 (t, J = 7.1 Hz, 2H, $PhC\underline{H}_2CH_2CH_2$), 2.28 (p, J = 7.1 Hz, 2H, $PhCH_2C\underline{H}_2CH_2$) ppm. ^{1}H NMR spectrum was in accordance with literature data.[11]

Synthesis of acylated nitroalcohol 3n[6]:



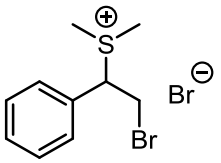
To a stirred solution of 3-nitropropanol[5] (202 mg, 1.9 mmol, 1 equiv.) in 4 mL of freshly distilled CH_2Cl_2 propionic anhydride (245 µL, 245 mg, 1.9 mmol, 1 equiv.) and freshly distilled pyridine (169 µL, 165 mg, 5.7 mmol, 3 equiv.) were added. Reaction mixture was stirred for 48h at room temperature. Then the mixture was diluted with 50 mL of EtOAc and washed with 50 mL of water and 50 mL of 0.25M solution of $NaHSO_4$. Organic phase was dried over anhydrous Na_2SO_4. The solvent was evaporated and crude material was purified by flash column chromatography (PE/EtOAc 6:1 to 3:1), yield – 243 mg (79%). Colorless oil. R_f = 0.71 (PE/EtOAc = 3:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.47 (t, *J* = 6.8 Hz, 2H, $C\underline{H}_2NO_2$), 4.17 (t, *J* = 6.0 Hz, 1H, $C\underline{H}_2O$), 2.40 – 2.24 (m, 4H, $C\underline{H}_2$ and $C\underline{H}_2CH_3$), 1.11 (t, *J* = 7.6 Hz, 3H, $CH_2C\underline{H}_3$) ppm.

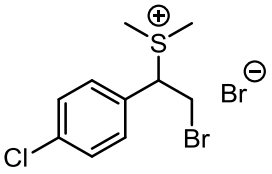
^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 174.2 (1C, <u>C</u>=O), 72.5 (1C, $\underline{C}H_2NO_2$), 60.7 (1C, $\underline{C}H_2O$), 27.4 and 26.6 (2C, $\underline{C}H_2$ and $\underline{C}H_2CH_3$), 9.1 (1C, $CH_2\underline{C}H_3$) ppm.

HRMS (ESI): m/z calcd for $C_6H_{11}NaNO_4^+$ $[M+Na]^+$: 184.0580, found 184.0587.

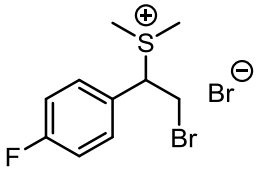
3. Synthesis of sulfonium salts 4



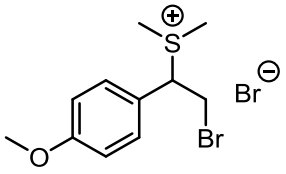
4a



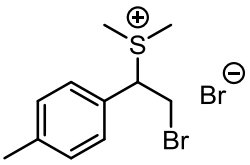
4b



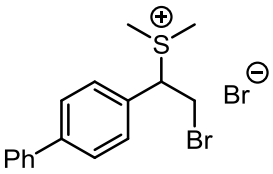
4c



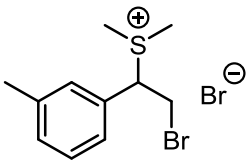
4d



4e



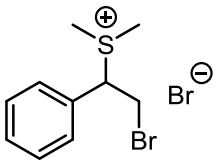
4f



4g

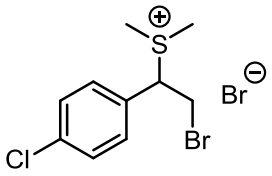
General procedure 1 (GP1) for the preparation of sulfonium salts 4:[12,13]

To a stirred solution of Me_2S (7.7 mL, 6.51 g, 105 mmol, 3.5 equiv.) in 60 mL of MeCN a solution of bromine (1.6 mL, 4.8 g, 30 mmol, 1 equiv.) in 10 mL of CCl_4 was added at 0 °C. The mixture was stirred for 10 minutes at 0 °C. Orange solid was formed. Then corresponding styrene (60 mmol, 2 equiv.) was added and the resulting mixture was stirred at 0 °C for 30 minutes. During the reaction orange solid dissolved and white solid precipitated. To this suspension 100 mL of Et_2O was added. After 30 minutes at rt resulted precipitate was filtered off, washed with Et_2O and dried on filter to give pure sulfonium salt **4**.



(2-Bromo-1-phenylethyl)dimethylsulfonium bromide 4a

Sulfonium bromide **4a** was synthesized by GP1 from styrene (6.9 mL, 6.24 g, 60 mmol), yield – 5.98 g (61%). White solid. Mp 143 – 145 °C (Et_2O) (lit.[13] 145 – 148 °C). ^{1}H NMR spectrum was in accordance with literature data.[13]

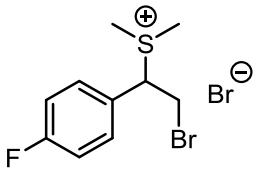


(2-Bromo-1-(4-chlorophenyl)ethyl)dimethylsulfonium bromide 4b

Sulfonium bromide **4b** was synthesized by GP1 from 4-chlorostyrene (508 µL, 554 mg, 4 mmol), yield – 535 mg (74%). White solid. Mp 140 – 143 °C (Et_2O).

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.62 (s, 4H, C$\underline{H}_{Ar}$), 5.43 (dd, *J* = 9.6, 6.1 Hz, 1H, C$\underline{H}$–Ar), 4.44 – 4.31 (m, 2H, C$\underline{H}_2$Br), 2.97 (s, 3H, S$\underline{Me}_2$), 2.71 (s, 3H, S$\underline{Me}_2$) ppm.

^{13}C NMR (75 MHz, DMSO-d_6, DEPT): δ 135.4 (1C, $\underline{C}_{Ar}$), 131.6 and 129.5 (4C, $\underline{C}H_{Ar}$), 129.1 (1C, $\underline{C}_{Ar}$), 57.6 (1C, $\underline{C}$H–Ar), 29.1 (1C, $\underline{C}H_2$Br), 24.0 and 22.7 (2C, S$\underline{Me}_2$) ppm.



(2-Bromo-1-(4-fluorophenyl)ethyl)dimethylsulfonium bromide 4c

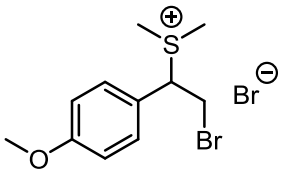
Sulfonium bromide **4c** was synthesized by GP1 from 4-fluorostyrene (477 µL, 488 mg, 4 mmol), yield – 647 mg (94%). White solid. Mp 143 – 145 °C (Et_2O).

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.66 (dd, *J* = 8.8, 5.4 Hz, 2H, C$\underline{H}_{Ar}$), 7.40 (t, *J* = 8.8 Hz, 2H, C$\underline{H}_{Ar}$), 5.45 (dd, *J* = 9.7, 6.1 Hz, 1H, C$\underline{H}$–Ar), 4.46 – 4.31 (m, 2H, C$\underline{H}_2$Br), 2.97 (s, 3H, S$\underline{Me}_2$), 2.71 (s, 3H, S$\underline{Me}_2$) ppm.

^{13}C NMR (75 MHz, DMSO-d_6, DEPT): δ 163.2 (d, *J* = 248.0 Hz, 1C, $\underline{C}_{Ar}$), 132.1 (d, *J* = 9.0 Hz, 2C, $\underline{C}H_{Ar}$), 126.4 (d, *J* = 3.0 Hz, 1C, $\underline{C}_{Ar}$), 116.5 (d, *J* = 21.8 Hz, 2C, $\underline{C}H_{Ar}$), 57.7 (1C, $\underline{C}$H–Ar), 29.3 (1C, $\underline{C}H_2$Br), 24.0 and 22.6 (2C, S$\underline{Me}_2$) ppm.

^{19}F NMR (282 MHz, DMSO-d_6): δ -109.78 (tt, *J* = 8.8, 5.4 Hz) ppm.

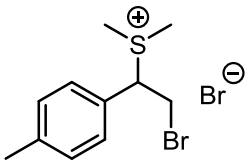
FTIR (ATR): 1605 (s), 1516 (s), 1421 (m), 1236 (s), 1172 (m), 1051 (m), 859 (s), 827 (m), 753 (m), 611 (s) cm^{-1}.



(2-Bromo-1-(4-methoxyphenyl)ethyl)dimethylsulfonium bromide 4d

Sulfonium bromide **4d** was synthesized by GP1 from 4-methoxystyrene (508 µL, 554 mg, 4 mmol), yield – 535 mg (74%). White solid. Mp 107 – 109 °C (Et_2O).

We were unable to characterize this compound by NMR due to its decomposition in DMSO-d_6 (cf.[12])



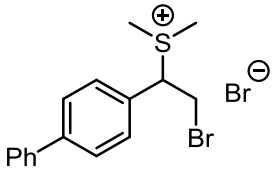
(2-Bromo-1-(*p*-tolyl)ethyl)dimethylsulfonium bromide 4e

Sulfonium bromide **4e** was synthesized by GP1 from 4-methylstyrene (526 µL, 472 mg, 4 mmol), yield – 616 mg (91%). White solid. Mp 139 – 141 °C (Et_2O) (lit.[14] 145 – 148 °C).

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.45 (d, *J* = 8.1 Hz, 2H, C$\underline{H}_{Ar}$), 7.34 (d, *J* = 8.1 Hz, 2H, C$\underline{H}_{Ar}$), 5.36 (dd, *J* = 9.8, 6.0 Hz, 1H, C$\underline{H}$–Ar), 4.42 – 4.28 (m, 2H, C$\underline{H}_2$Br), 2.94 (s, 3H, S$\underline{Me}_2$), 2.66 (s, 3H, S$\underline{Me}_2$), 2.35 (s, 3H, $\underline{Me}_{Ar}$) ppm.

^{13}C NMR (75 MHz, DMSO-d_6, DEPT): δ 140.3 (1C, $\underline{C}_{Ar}$), 130.0 and 129.6 (4C, $\underline{C}H_{Ar}$), 126.9 (1C, $\underline{C}_{Ar}$), 58.5 (1C, $\underline{C}$H–Ar), 29.4 (1C, $\underline{C}H_2$Br), 24.0 and 22.6 (2C, S$\underline{Me}_2$), 20.9 (1C, $\underline{Me}_{Ar}$) ppm.

FTIR (ATR): 2976 (m), 1610 (w), 1514 (m), 1450 (m), 1211 (m), 1189 (m), 1051 (s), 1005 (s), 827 (s), 744 9s), 620 (s) cm^{-1}.

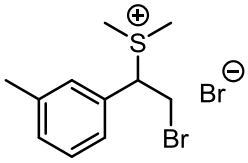


(1-([1,1'-Biphenyl]-4-yl)-2-bromoethyl)dimethylsulfonium bromide 4f

Sulfonium bromide **4f** was synthesized by GP1 from 4-phenylstyrene (720 mg, 4 mmol), yield – 662 mg (82%). White solid. Mp 131 – 133 °C (Et_2O).

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.84 (d, *J* = 8.3 Hz, 2H, C$\underline{H}_{Ar}$), 7.74 (d, *J* = 7.3 Hz, 2H, C$\underline{H}_{Ar}$), 7.67 (d, *J* = 8.3 Hz, 2H, $\underline{H}_{Ar}$), 7.49 (t, *J* = 7.3 Hz, 3H, $\underline{H}_{Ar}$), 7.42 (d, *J* = 7.3 Hz, 2H, $\underline{H}_{Ar}$), 5.47 (dd, *J* = 9.0, 6.6 Hz, 1H, C$\underline{H}$–Ar), 4.49 – 4.35 (m, 2H, C$\underline{H}_2$Br), 2.99 (s, 3H, S$\underline{Me}_2$), 2.74 (s, 3H, S$\underline{Me}_2$) ppm.

^{13}C NMR (75 MHz, DMSO-d_6, DEPT): δ 142.0 and 138.9 (2C, $\underline{C}_{Ar}$), 130.3 (2C, $\underline{C}H_{Ar}$), 129.2 (2C, $\underline{C}H_{Ar}$), 129.1 (1C, $\underline{C}_{Ar}$), 128.2 (1C, $\underline{C}H_{Ar}$), 127.6 (2C, $\underline{C}H_{Ar}$), 126.9 (2C, $\underline{C}H_{Ar}$), 58.3 (1C, $\underline{C}$H–Ar), 29.3 (1C, $\underline{C}H_2$Br), 24.0 and 22.7 (2C, S$\underline{Me}_2$) ppm.



(2-Bromo-1-(*m*-tolyl)ethyl)dimethylsulfonium bromide 4g

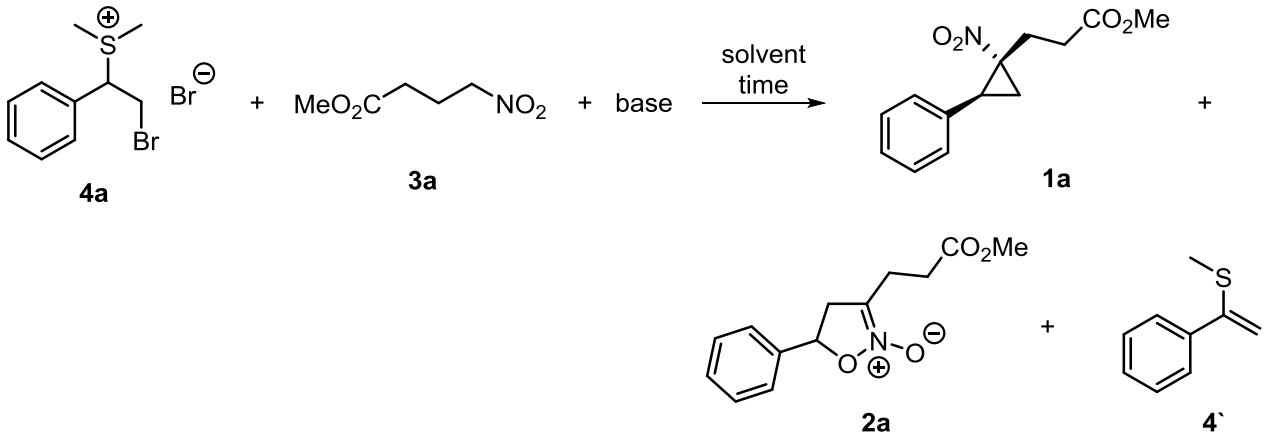
Sulfonium bromide **4g** was synthesized by GP1 from 3-methylstyrene (530 µL, 472 mg, 4 mmol), yield – 433 mg (64%). White solid. Mp 122 – 125 °C (Et_2O).

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.46 – 7.31 (m, 4H, C$\underline{H}_{Ar}$), 5.31 (dd, *J* = 9.8, 5.8 Hz, 1H, C$\underline{H}$–Ar), 4.42 – 4.29 (m, 2H, C$\underline{H}_2$Br), 2.95 (s, 3H, S$\underline{Me}_2$), 2.67 (s, 3H, S$\underline{Me}_2$), 2.36 (s, 3H, $\underline{Me}_{Ar}$) ppm.

^{13}C NMR (75 MHz, DMSO-d_6, DEPT): δ 139.0 (2C, $\underline{C}_{Ar}$), 131.2, 130.0, 129.3 and 126.8 (4C, $\underline{C}H_{Ar}$), 58.6 (1C, $\underline{C}$H–Ar), 29.3 (1C, $\underline{C}H_2$Br), 24.0 and 22.8 (2C, S$\underline{Me}_2$), 21.1 (1C, $\underline{Me}_{Ar}$) ppm.

FTIR (ATR): 3010 (w), 22987 (m), 2953 (m), 1606 (m), 1491 (m), 1437 (s), 1416 (m), 1233 (m), 1209 (s), 1152 (w), 1047 (s), 1101 9s), 855 (w), 797 (s), 739 (s), 723 (s), 711 (s), 693 (s), 567 (m) cm^{-1}.

4. Optimization study



General procedure for optimization studies:

To a stirred suspension or solution of sulfonium salt **4a** (indicated amount) in 0.4 mL of solvent nitro compound **3a** (29 mg, 0.2 mmol, 1 equiv.) and base (indicated amount) were added and the reaction mixture was stirred under indicated conditions (temperature and time). Then dimethyl terephthalate (0.5 equiv., 0.1 mmol, 19 mg) was added to the mixture as internal standard. This mixture was diluted with 5 mL of EtOAc and washed with 5 mL of 0.25M aq. solution of $NaHSO_4$. Aqueous layer was back extracted with 5 mL of EtOAc. Combined organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude material was analyzed by ^1H NMR using signal of dimethyl terephthalate at 8.09 ppm as standard.

Table 1.

Entry	4a	Base	Solvent	Time	Tempe-rature	3a, %	4`, %	2a, %	1a
1	1 equiv.	DBU, 2 equiv.	$CHCl_3$, 0.5M	14h	rt	**0**	**0**	**39**	**59**
2	1 equiv.	DBU, 2 equiv.	DMF, 0.5M	14h	rt	**0**	**0**	**32**	**58**
3	1 equiv.	DBU, 2 equiv.	THF, 0.5M	14h	rt	**7**	**0**	**10**	**74**
4	1 equiv.	DBU, 2 equiv.	MeCN, 0.5M	14h	rt	**9**	**0**	**41**	**42**
5	1 equiv.	DBU, 2 equiv.	CH_2Cl_2, 0.5M	14h	rt	**6**	**0**	**35**	**56**
6	1 equiv.	DBU, 2 equiv.	PhMe, 0.5M	14h	rt	**5**	**0**	**18**	**78**
7	1 equiv.	DBU, 2 equiv.	EtOAc, 0.5M	14h	rt	**5**	**0**	**9**	**78**
8	1 equiv.	DBU, 2 equiv.	Et_2O, 0.5M	14h	rt	**5**	**2**	**33**	**53**
9	1 equiv.	DBU, 2 equiv.	1,4-dioxane, 0.5M	14h	rt	**10**	**4**	**26**	**56**
10	1 equiv.	DBU, 2 equiv.	tBuOMe, 0.5M	14h	rt	**25**	**5**	**35**	**40**

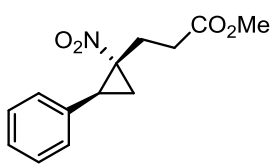
Table 1. (continued)

Entry	4a	Base	Solvent	Time	Tempe-rature	3a, %	4`, %	2a, %	1a
11	1 equiv.	DBU, 2 equiv.	TFE, 0.5M	14h	rt	**24**	**0**	**60**	**10**
12	1 equiv.	DBU, 2 equiv.	EtOH, 0.5M	14h	rt	**5**	**0**	**64**	**26**
13	1 equiv.	DBU, 2 equiv.	DME, 0.5M	14h	rt	**7**	**0**	**14**	**66**
14	1 equiv.	DBU, 2 equiv.	AcMe, 0.5M	14h	rt	**8**	**2**	**31**	**48**
15	1 equiv.	DBN, 2 equiv.	EA, 0.5M	14h	rt	**8**	**0**	**40**	**40**
16	1 equiv.	Et_3N, 2 equiv.	EA, 0.5M	14h	rt	**27**	**14**	**26**	**36**
17	1 equiv.	DBU, 2.2 equiv.	EA, 0.5M	14h	rt	**2**	**0**	**10**	**85**
18	1.1 equiv.	DBU, 2.3 equiv.	EA, 0.5M	14h	rt	**0**	**0**	**10**	**90**
19	1.2 equiv.	DBU, 2.4 equiv.	EA, 0.5M	14h	rt	**0**	**9**	**10**	**86**
20	1.5 equiv.	DBU, 2.7 equiv.	EA, 0.5M	14h	rt	**0**	**30**	**11**	**84**
21	1.1 equiv.	DBU, 2.3 equiv.	EA, 0.5M	1h	rt	**0**	**3**	**9**	**84**
22	1.1 equiv.	DBU, 2.3 equiv.	EA, 0.5M	2h	rt	**0**	**3**	**10**	**83**
23	1.1 equiv.	DBU, 2.3 equiv.	EA, 0.5M	4h	rt	**0**	**5**	**11**	**85**
24	1.5 equiv.	DBU, 2.7 equiv.	TFE, 0.5M	14h	rt	**0**	**0**	**74**	**10**
25	1.5 equiv.	PS, 2.7 equiv.	TFE, 0.5M	14h	rt	**0**	**0**	**82**	**10**
26	1.5 equiv.	TMG, 2.7 equiv.	TFE, 0.5M	14h	rt	**0**	**0**	**80**	**10**
27	1.5 equiv.	DBN, 2.7 equiv.	TFE, 0.5M	14h	rt	**10**	**1**	**74**	**10**
28	1.5 equiv.	Et_3N, 2.7 equiv.	TFE, 0.5M	14h	rt	**15**	**6**	**80**	**10**
29	1.7 equiv.	Et_3N, 2.9 equiv.	TFE, 0.5M	14h	rt	**4**	**9**	**80**	**10**
30	2.0 equiv.	Et_3N, 3.2 equiv.	TFE, 0.5M	14h	rt	**4**	**16**	**80**	**10**
31	2.0 equiv.	Et_3N, 3.2 equiv.	TFE, 0.5M	1h	rt	**11**	**4**	**75**	**10**

Table 1. (continued)

Entry	4a	Base	Solvent	Time	Tempe-rature	3a, %	4`, %	2a, %	1a
32	2.0 equiv.	Et_3N, 3.2 equiv.	TFE, 0.5M	2h	rt	**9**	**7**	**84**	**10**
33	2.0 equiv.	Et_3N, 3.2 equiv.	TFE, 0.5M	4h	rt	**4**	**2**	**89**	**10**
34	1.0 equiv.	K_2CO_3, 5 equiv.	$CHCl_3/H_2O$ (3:1), 0.5M	14h	rt	**68**	**55**	**0**	**6**
35	1.0 equiv.	K_2CO_3, 5 equiv.	AcMe/H_2O (3:1), 0.5M	14h	rt	**57**	**57**	**5**	**11**
36	1.0 equiv.	tBuONa, 2 equiv.	THF, 0.5M	14h	rt	**36**	**19**	**12**	**42**
37	1.0 equiv.	Cs_2CO_3, 5 equiv.	DMF, 0.5M	14h	rt	**14**	**23**	**12**	**45**
38	1.0 equiv.	K_2CO_3, 2 equiv.	DMSO, 0.5M	14h	rt	**24**	**20**	**14**	**35**

5. Synthesis of nitro cyclopropanes 1



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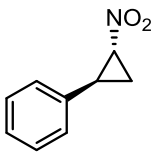

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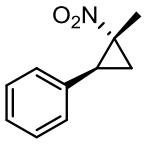

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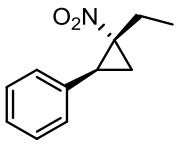

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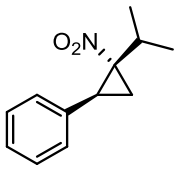

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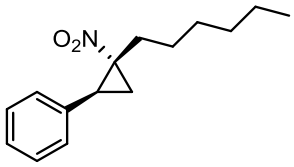

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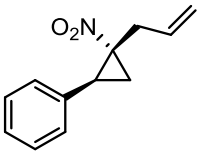

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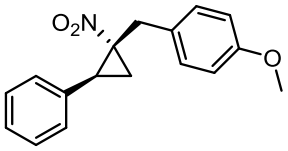

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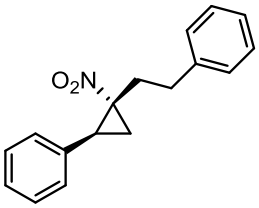

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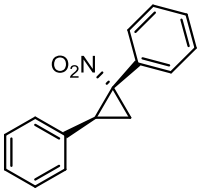

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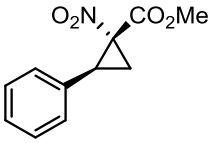

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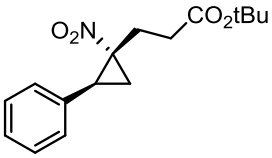

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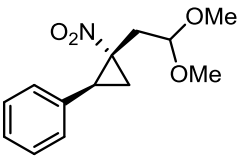

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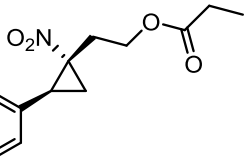

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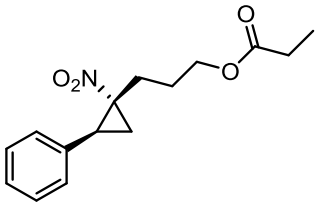

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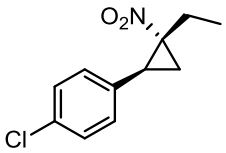

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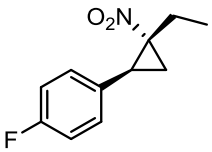

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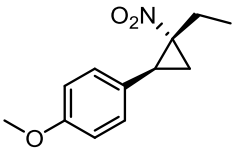

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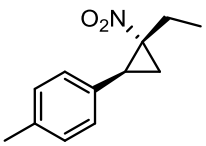

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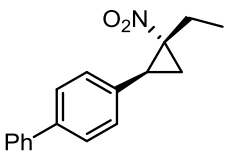

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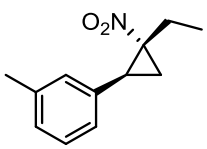
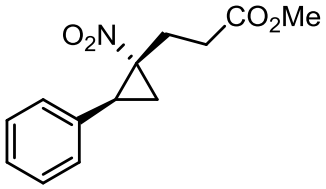


1u

General procedure 2 (GP2) for preparation of nitro cyclopropanes 1:

To a stirred suspension of sulfonium salt **4** (0.55 mmol, 1.1 equiv) in 1 mL of EtOAc nitro compound **3** (0.5 mmol, 1 equiv.) and DBU (172 µL, 175 mg, 1.15 mmol, 2.3 equiv.) were added and the reaction mixture was stirred for 1 h at rt. Then the mixture was diluted with 25 mL of EtOAc and washed with 25 mL of 0.25M solution of $NaHSO_4$. Aqueous layer was back extracted with 25 mL of EtOAc. Combined organic layers were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude material was subjected to column chromatography (PE/EtOAc 100:1 to 5:1) to give pure nitro cyclopropane **1**.



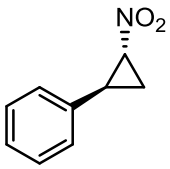
***Rel* methyl 3-((*1R*,*2S*)-1-nitro-2-phenylcyclopropyl)propanoate 1a**

Cyclopropane **1a** was synthesized by **GP2** from methyl nitrobutyrate **3a** (147 mg, 1 mmol) and sulfonium bromide **4a** (359 mg, 1.1 mmol), yield – 210 mg (84%). Colorless oil. R_f = 0.76 (PE/EtOAc = 3:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 7.41 – 7.29 (m, 3H, C$\underline{H}_{Ph}$), 7.25 – 7.18 (m, 2H, C$\underline{H}_{Ph}$), 3.63 (s, 3H, OC$\underline{H}_3$), 3.38 (dd, *J* = 10.4, 8.4 Hz, 1H, C$\underline{H}$–Ph), 2.53 – 2.42 and 2.42 – 2.31 (2m, 4H, C$\underline{H}_{2a}$ and C$\underline{H}_{2a}$C$\underline{H}_2$CO$_2$Me), 1.80 – 1.60 (m, 2H, C$\underline{H}_{2b}$ and C$\underline{H}_{2b}$CH$_2$CO$_2$Me) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 172.9 (1C, $\underline{C}$=O), 134.0 (1C, $\underline{C}_{Ph}$), 128.9, 128.8 and 128.1 (5C, $\underline{C}H_{Ph}$), 69.2 (1C, $\underline{C}NO_2$), 51.8 (1C, O$\underline{C}H_3$), 35.7 (1C, $\underline{C}$H–Ph), 30.4 (1C, $\underline{C}H_2\underline{C}H_2CO_2Me$), 24.1 (1C, $\underline{C}H_2\underline{C}H_2CO_2Me$), 20.5 (1C, $\underline{C}H_2$) ppm.

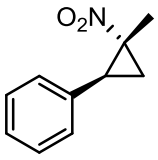
HRMS (ESI): m/z calcd for $C_{13}H_{16}NO_4^+$ $[M+H]^+$: 250.1074, found 250.1071.



***Rel* ((*1S*,*2R*)-2-nitrocyclopropyl)benzene 1b**

Cyclopropane **1a** was synthesized by **GP2** from nitromethane **3b** (61 mg, 1 mmol) and sulfonium bromide **4a** (359 mg, 1.1 mmol), yield – 115 mg (71%). Colorless oil. R_f = 0.76 (PE/EtOAc = 5:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 7.40 – 7.28 (m, 3H, C$\underline{H}_{Ph}$), 7.13 (dd, J = 7.8, 1.7 Hz, 2H, C$\underline{H}_{Ph}$), 4.42 (ddd, J = 7.1, 4.0, 3.0 Hz, 1H, C$\underline{H}NO_2$), 3.14 (ddd, J = 10.7, 7.9, 3.0 Hz, 1H, C$\underline{H}_{2a}$), 2.25 (ddd, J = 10.7, 6.3, 4.0 Hz, 1H, $\underline{C}$H–Ph), 1.68 (ddd, J = 7.9, 7.3, 6.3 Hz, 1H, C$\underline{H}_{2a}$). ^{1}H NMR spectrum was in accordance with literature data.[15]



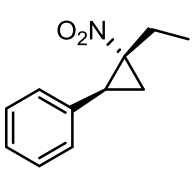
***Rel* ((*1S*,*2R*)-2-methyl-2-nitrocyclopropyl)benzene 1c**

Cyclopropane **1a** was synthesized by **GP2** from nitroethane **3c** (75 mg, 1 mmol) and sulfonium bromide **4a** (359 mg, 1.1 mmol), yield – 210 mg (83%). Colorless oil. R_f = 0.77 (PE/EtOAc = 3:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.60 – 6.46 (m, 3H, C$\underline{H}_{Ph}$), 6.42 – 6.35 (m, 2H, C$\underline{H}_{Ph}$), 2.57 (m, 1H, C$\underline{H}$–Ph), 1.55 (dd, *J* = 10.7, 5.7 Hz, 1H, C$\underline{H}_{2a}$), 0.77 (dt, *J* = 8.2, 5.7 Hz, 1H, C$\underline{H}_{2b}$), 0.64 (s, 3H, CH_3) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 134.6 (1C, $\underline{C}_{Ph}$), 128.9, 128.8 and 127.9 (5C, $\underline{C}H_{Ph}$), 65.6 (1C, $\underline{C}NO_2$), 34.9 (1C, $\underline{C}$H–Ph), 22.1 (1C, C$\underline{H}_2$), 15.3 (1C, C$\underline{H}_3$) ppm.

HRMS (ESI): m/z calcd for $C_{10}H_{12}NO_2^+$ $[M+H]^+$: 178.0863, found 178.0868.



***Rel* ((*1S*,*2R*)-2-ethyl-2-nitrocyclopropyl)benzene 1d**

Cyclopropane **1d** was synthesized by **GP2** from 1-nitropropane **3d** (89 mg, 1 mmol) and sulfonium bromide **4a** (359 mg, 1.1 mmol), yield – 168 mg (88%). White solid. Mp 48 – 50 °C (from Et_2O). R_f = 0.82 (PE/EtOAc = 3:1, anisaldehyde).

Scale up procedure: cyclopropane **1a** was synthesized by **GP2** from 1-nitropropane **3d** (623 mg, 7 mmol) and sulfonium bromide **4a** (2.51 g, 7.7 mmol), yield – 1.02 g (76%).

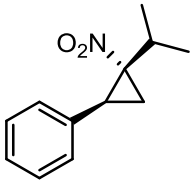
^{1}H NMR (300 MHz, $CDCl_3$, NOESY): δ 7.41 – 7.31 (m, 3H, C$\underline{H}_{Ph}$), 7.24 – 7.18 (m, 2H, C$\underline{H}_{Ph}$), 3.38 (dd, *J* = 10.3, 8.3 Hz, 1H, C$\underline{H}$–Ph), 2.35 (ddd, *J* = 10.3, 6.0, 1.7 Hz, 1H, C$\underline{H}_{2a}$ anti to Ph), 2.16 (dqd, *J* = 14.5, 7.1, 1.7 Hz, 1H, C$\underline{H}_{2a}CH_3$), 1.56 (dd, *J* = 8.3, 6.0 Hz, 1H, C$\underline{H}_{2b}$ syn to Ph), 1.30 (dq, *J* = 14.5

7.3 Hz, 1H, C$\underline{H}_{2b}$CH$_3$), 0.98 (t, *J* = 7.2 Hz, 3H, CH$_2$C$\underline{H}_3$) ppm. **Characteristic NOESY correlations**: C$\underline{H}_2$CH$_3$/C$\underline{H}_{Ph}$; C$\underline{H}_{Ph}$/C$\underline{H}_{2b}$ syn to Ph; C$\underline{H}_2$CH$_3$/C$\underline{H}_{2b}$ syn to Ph.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 134.7 (1C, $\underline{C}_{Ph}$), 128.9, 128.7 and 127.9 (5C, $\underline{C}H_{Ph}$), 71.0 (1C, $\underline{C}NO_2$), 35.6 (1C, $\underline{C}$H–Ph), 22.2 (1C, $\underline{C}H_2CH_3$), 20.1 (1C, $\underline{C}H_2$), 10.2 (1C, CH$_2\underline{C}H_3$) ppm.

FTIR (ATR): 2979 (br), 2945 (br), 1821 (br), 1524 (s), 1497 (m), 1458 (m), 1448 (m), 1350 (s), 1276 (m), 1080 (w), 1055 (w), 869 (m), 787 (m), 765 (s), 697 (s), 605 (m) cm^{-1}.

HRMS (ESI): m/z calcd for $C_{11}H_{13}NaNO_2^+$ $[M+Na]^+$: 214.0838, found 214.0830.



***Rel* ((*1S*,*2S*)-2-isopropyl-2-nitrocyclopropyl)benzene 1e**

Cyclopropane **1e** was synthesized by **GP2** from 2-methyl-1-nitropropane **3e** (103 mg, 1 mmol) and sulfonium bromide **4a** (359 mg, 1.1 mmol). Column chromatography (PE/EtOAc, 100:1, then 3:1, then 1:1) afforded target cyclopropane **1e** (93 mg, 45%) and isoxazoline *N*-oxide **2e** (98 mg, 48%) as colorless oils.

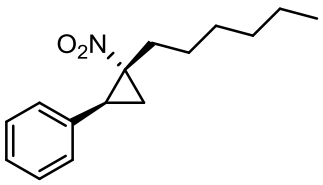
Mixture of diastereomers with dr = 7:1.

R_f = 0.56 (PE/EtOAc = 100:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$, COSY, NOESY): δ 7.42 – 7.19 (m, 5H, C$\underline{H}_{Ph}$), 3.48 (dd, *J* = 10.4, 8.3 Hz, 1H, C$\underline{H}$–Ph), 2.21 (dd, *J* = 10.4, 6.0 Hz, 1H, C$\underline{H}_{2a}$), 1.59 (dd, *J* = 8.3, 6.0 Hz, 1H, C$\underline{H}_{2b}$), 1.47 – 1.32 (m, 1H, C$\underline{H}$Me$_2$), 1.25 (d, *J* = 6.9 Hz, 3H, C$\underline{H}_3$), 0.98 (d, *J* = 6.9 Hz, 3H, C$\underline{H}_3$) ppm. Characteristic signals of minor diastereomer: 3.32 (dd, J = 10.5, 8.4 Hz, 1H, C$\underline{H}$-Ph), 2.40 (ddd, J = 10.5, 6.1, 1.7 Hz, 1H, C$\underline{H}_{2a}$), 0.83 (m, 3H, C$\underline{H}_3$) ppm. **Characteristic NOESY correlations**: C$\underline{H}$Me$_2$/C$\underline{H}_{Ph}$; C$\underline{H}_{2b}$/C$\underline{H}_{Ph}$; CH$_3$/C$\underline{H}_{Ph}$.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 134.2 (1C, $\underline{C}_{Ph}$), 129.0, 128.6 and 127.8 (5C, $\underline{C}H_{Ph}$), 73.9 (1C, $\underline{C}NO_2$), 35.4 (1C, $\underline{C}$H–Ph), 29.7 (1C, C$\underline{H}$Me$_2$), 20.9 (1C, $\underline{C}H_2$), 18.7 and 17.2 (2C, CH$\underline{Me}_2$) ppm.

HRMS (ESI): m/z calcd for $C_{12}H_{16}NO_2^+$ $[M+H]^+$: 206.1176, found 206.1170.



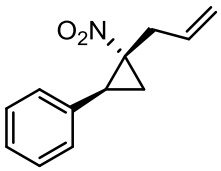
***Rel* ((*1S*,*2R*)-2-hexyl-2-nitrocyclopropyl)benzene 1f**

Cyclopropane **1f** was synthesized by **GP2** from 1-nitroheptane **3f** (145 mg, 1 mmol) and sulfonium bromide **4a** (359 mg, 1.1 mmol), yield – 193 mg (78%). Colorless oil. R_f = 0.89 (PE/EtOAc = 20:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 – 7.30 (m, 3H, C$\underline{H}_{Ph}$), 7.23 – 7.18 (m, 2H, C$\underline{H}_{Ph}$), 3.33 (dd, *J* = 10.4, 8.3 Hz, 1H, C$\underline{H}$–Ph), 2.37 (ddd, *J* = 10.4, 6.1, 1.7 Hz, 1H, C$\underline{H}_{2a}$), 2.18 – 2.07 (m, 1H, C$\underline{H}_2$ of hexyl), 1.57 (dd, *J* = 8.3, 6.1 Hz, 1H, C$\underline{H}_{2b}$), 1.46 – 1.31 (m, 2H, C$\underline{H}_2$ of hexyl), 1.29 – 1.11 (m, 7H, C$\underline{H}_2$ of hexyl), 0.85 (t, *J* = 6.8 Hz, 3H, C$\underline{H}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 134.7 (1C, $\underline{C}_{Ph}$), 128.9, 128.7 and 127.9 (5C, $\underline{C}H_{Ph}$), 70.3 (1C, $\underline{C}NO_2$), 35.3 (1C, $\underline{C}$H–Ph), 31.5, 29.1, 28.7, 25.8 and 22.5 (5C, $\underline{C}H_2$ of hexyl), 20.2 (1C, $\underline{C}H_2$), 14.1 (1C, $\underline{C}H_3$) ppm.

HRMS (ESI): m/z calcd for $C_{15}H_{22}NO_2^+$ $[M+H]^+$: 248.1645, found 248.1646.



***Rel* ((*1S*,*2R*)-2-allyl-2-nitrocyclopropyl)benzene 1g**

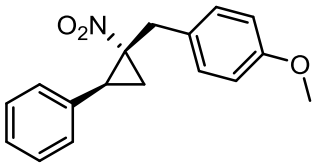
Cyclopropane **1g** was synthesized by **GP2** from 4-nitro-1-butene **3g** (101 mg, 1 mmol) and sulfonium bromide **4a** (359 g, 1.1 mmol), yield – 150 mg (75%). Colorless oil. R_f = 0.61 (PE/EtOAc = 50:1, anisaldehyde). Mixture of diastereomers with dr = 16:1.

^{1}H NMR (300 MHz, $CDCl_3$, COSY, NOESY): δ 7.39 – 7.30 (m, 3H, C$\underline{H}_{Ph}$), 7.23 – 7.17 (m, 2H, C$\underline{H}_{Ph}$), 5.76 (ddt, *J* = 17.0, 10.4, 6.5 Hz, 1H, C$\underline{H}$=CH$_2$), 5.04 (dq, *J* = 10.4, 1.5 Hz, 1H, CH=C$\underline{H}_{2a}$), 4.98 (dq, *J* = 17.0, 1.5 Hz, 1H, CH=C$\underline{H}_{2b}$), 3.39 (dd, *J* = 10.4, 8.4 Hz, 1H, C$\underline{H}$–Ph), 2.94 (ddd, *J* = 16.1, 6.1, 1.5 Hz, 1H, C$\underline{H}_{2a}$CH=CH$_2$), 2.38 (ddd, *J* = 10.5, 6.2, 1.7 Hz, 1H, C$\underline{H}_{2a}$), 1.92 (ddt, *J* = 16.1, 6.8, 1.5 Hz, 1H, C$\underline{H}_{2b}$CH=CH$_2$), 1.62 (dd, *J* = 8.4, 6.2 Hz, 1H, C$\underline{H}_{2b}$) ppm. Characteristic signals of minor diastereomer: δ 6.00 – 5.86 (m, 1H, C$\underline{H}$=CH$_2$), 5.32 – 5.18 (m, 2H, 1H, CH=C$\underline{H}_2$), 2.76 – 2.68 (m, 1H), 2.68 – 2.57 (m, 1H) ppm.

Characteristic NOESY correlations: C$\underline{H}_2$CH=CH$_2$/C$\underline{H}_{Ph}$; C$\underline{H}_{2b}$/C$\underline{H}_{Ph}$; C$\underline{H}_{2a}$/C$\underline{H}$–Ph; C$\underline{H}_{2b}$/C$\underline{H}_{2b}$CH=CH$_2$.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 134.4 (1C, $\underline{C}_{Ph}$), 132.4 (1C, $\underline{C}$H=CH$_2$), 129.0, 128.8 and 128.0 (5C, $\underline{C}H_{Ph}$), 118.2 (1C, CH=$\underline{C}$H$_2$), 69.2 (1C, $\underline{C}$NO$_2$), 35.2 (1C, $\underline{C}$H–Ph), 32.6 (1C, $\underline{C}$H$_2$CH=CH$_2$), 20.0 (1C, $\underline{C}$H$_2$) ppm.

HRMS (ESI): m/z calcd for $C_{12}H_{14}NO_2^+$ $[M+H]^+$: 204.1019, found 204.1027.



***Rel* 1-methoxy-4-(((*1S*,*2S*)-1-nitro-2-phenylcyclopropyl)methyl)-benzene 1h**

Cyclopropane **1h** was synthesized by **GP2** from 2-(4-methoxyphenyl)-1-nitroethane **3h** (181 mg, 1 mmol) and sulfonium bromide **4a** (359 g, 1.1 mmol), yield – 206 mg (73%). Colorless oil. R_f = 0.56 (PE/EtOAc = 5:1, anisaldehyde).

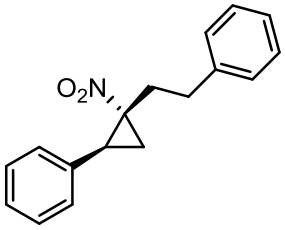
^{1}H NMR (300 MHz, $CDCl_3$, NOESY) 7.46 – 7.33 (m, 3H, C$\underline{H}_{Ph}$), 7.31 – 7.24 (m, 2H, C$\underline{H}_{Ph}$), 7.09 (d, *J* = 8.7 Hz, 2H, C$\underline{H}_{Ar}$), 6.82 (d, *J* = 8.7 Hz, 2H, C$\underline{H}_{Ar}$), 3.80 (s, 3H, OC$\underline{H}_3$), 3.71 (dd, *J* = 16.2, 1.8 Hz, 1H, C$\underline{H}_{2a}$Ar), 3.38 (dd, *J* = 10.5, 8.4 Hz, 1H, C$\underline{H}$–Ph), 2.54 (ddd, *J* = 10.5, 6.4, 1.8 Hz, 1H, C$\underline{H}_{2a}$ anti to Ph), 2.31 (d, *J* = 16.2 Hz, 1H, C$\underline{H}_{2b}$Ar), 1.79 (dd, *J* = 8.4, 6.4 Hz, 1H, C$\underline{H}_{2b}$ syn to Ph) ppm.

Characteristic NOESY correlations: C$\underline{H}_2$Ar/C$\underline{H}_{Ph}$; C$\underline{H}_{2b}$Ar/C$\underline{H}_{2b}$ syn to Ph; C$\underline{H}_{Ph}$/C$\underline{H}_{2b}$ syn to Ph.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 158.6 (1C, $\underline{C}_{Ar}$), 134.5 (1C, $\underline{C}_{Ph}$), 129.9, 129.0, 128.95, 128.92 and 128.1 (7C, $\underline{C}H_{Ar}$ and $\underline{C}H_{Ph}$), 125.9 (1C, $\underline{C}_{Ar}$), 114.0 (2C, $\underline{C}H_{Ar}$), 70.7 (1C, $\underline{C}$NO$_2$), 55.3 (1C, O$\underline{C}$H$_3$), 35.8 (1C, $\underline{C}$H–Ph), 32.9 (1C, $\underline{C}$H$_2$Ar), 19.9 (1C, $\underline{C}$H$_2$) ppm.

FTIR (ATR): 3011 (br), 2928 (br), 1611 (w), 1527 (s), 1511 (s), 1451 (m), 1422 (m), 1344 (s), 1304 (m), 1244 (s), 1178 (m), 1030 (s), 876 (m), 830 9m), 811 (m), 802 (m), 741 (m), 702 (s), 590 (m) cm^{-1}.

HRMS (ESI): m/z calcd for $C_{17}H_{18}NO_3^+$ $[M+H]^+$: 284.1281, found 284.1275



***Rel* ((*1S*,*2R*)-2-nitro-2-phenethylcyclopropyl)benzene 1i**

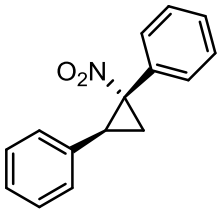
Cyclopropane **1i** was synthesized by **GP2** from 3-phenyl-1-nitropropane **3i** (165 mg, 1 mmol) and sulfonium bromide **4a** (359 g, 1.1 mmol), yield – 191 mg (72%). Colorless oil. R_f = 0.78 (PE/EtOAc = 10:1, anisaldehyde).

Mixture of diastereomers with dr = 17:1.

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 7.44 – 7.34 (m, 3H, C$\underline{H}_{Ph}$), 7.30 – 7.15 (m, 5H, C$\underline{H}_{Ph}$), 7.02 – 6.97 (m, 2H, C$\underline{H}_{Ph}$), 3.42 (dd, *J* = 10.4, 8.3 Hz, 1H, C$\underline{H}$–Ph), 2.83 – 2.65 (m, 2H, $CH_2C\underline{H}_2Ph$), 2.41 – 2.29 (m, 2H, $C\underline{H}_{2a}CH_2Ph$ and $C\underline{H}_{2a}$), 1.71 (ddd, *J* = 15.2, 10.0, 7.2 Hz, 1H, $C\underline{H}_{2b}CH_2Ph$), 1.54 (dd, *J* = 8.3, 6.2 Hz, 1H, $C\underline{H}_{2b}$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 141.0 and 134.4 (2C, $\underline{C}_{Ph}$), 128.8, 128.5, 128.5, 128.0 and 126.5 (10C, $\underline{C}H_{Ph}$), 69.6 (1C, $\underline{C}NO_2$), 35.1 (1C, $\underline{C}$H–Ph), 32.3 (1C, $\underline{C}H_2CH_2Ph$), 31.2 (1C, $CH_2\underline{C}H_2Ph$), 20.7 (1C, $\underline{C}H_2$) ppm.

HRMS (ESI): m/z calcd for $C_{17}H_{18}NO_3^+$ $[M+H]^+$: 268.1332, found 268.1339.



***Rel* ((*1R,2S*)-1-nitrocyclopropane-1,2-diyl)dibenzene 1j**

Cyclopropane **1j** was synthesized by **GP2** from phenynitromethane **3j** (137 mg, 1 mmol) and sulfonium bromide **4a** (359 mg, 1.1 mmol). Column chromatography (PE/EtOAc, 20:1, then 5:1) afforded target cyclopropane **1j** (42 mg, 18%) as colorless oil and isoxazoline *N*-oxide **2j** (137 mg, 57%) as white solid.

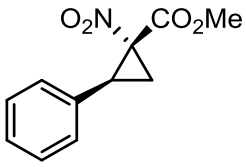
Mixture of diastereomers with dr = 14:1.

R_f = 0.75 (PE/EtOAc = 5:1, anisaldehyde).

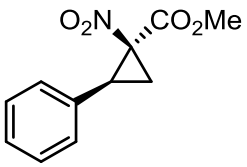
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 – 7.14 (m, 8H, C$\underline{H}_{Ph}$), 6.93 – 6.78 (m, 2H, C$\underline{H}_{Ph}$), 3.70 (dd, *J* = 10.7, 8.4 Hz, 1H, C$\underline{H}$–Ph), 2.78 (dd, *J* = 10.7, 6.3 Hz, 1H, $C\underline{H}_{2a}$), 2.18 (dd, *J* = 8.4, 6.3 Hz, 1H, $C\underline{H}_{2b}$) ppm. Characteristic signals of minor diastereomer: 3.19 (t, *J* = 9.1 Hz, 1H, C$\underline{H}$–Ph), 2.98 (dd, *J* = 8.6, 6.5 Hz, 1H, $C\underline{H}_{2a}$), 1.94 (dd, *J* = 9.7, 6.5 Hz, 1H, $C\underline{H}_{2b}$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 134.4 and 129.8 (2C, $\underline{C}_{Ph}$), 132.5, 129.5, 128.4, 128.3, 128.1 and 127.5 (10C, $\underline{C}H_{Ph}$), 73.7 (1C, $\underline{C}NO_2$), 35.2 (1C, $\underline{C}$H–Ph), 21.7 (1C, $\underline{C}H_2$) ppm.

HRMS (ESI): m/z calcd for $C_{15}H_{14}NO_2^+$ $[M+H]^+$: 240.1019, found 240.1022.



1k, *Rel (1R,2S)*



1k`, *Rel (1S,2S)*

***Rel* methyl (*1R,2S*)-1-nitro-2-phenylcyclopropane-1-carboxylate 1k** and ***Rel* methyl (*1S,2S)*-1-nitro-2-phenylcyclopropane-1-carboxylate 1k`**

Cyclopropanes **1k** and **1k`** were synthesized by **GP2** from methyl nitroacetate **3k** (119 mg, 1 mmol) and sulfonium bromide **4a** (359 g, 1.1 mmol). Column chromatography (PE/EtOAc, 30:1, then 1:1) afforded **1k** (68 mg, 31%), **1k`** (56 mg, 25%), and isoxazoline *N*-oxide **2k** (77 mg, 35%) as colorless oils.

***Rel* methyl (*1R,2S*)-1-nitro-2-phenylcyclopropane-1-carboxylate 1k**

R_f = 0.51 (PE/EtOAc = 10:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 – 7.27 (m, 3H, C$\underline{H}_{Ph}$), 7.23 – 7.17 (m, 2H, C$\underline{H}_{Ph}$), 3.77 (dd, *J* = 10.7, 9.2 Hz, 1H, C$\underline{H}$–Ph), 3.50 (s, 3H, $OC\underline{H}_3$), 2.45 (dd, *J* = 9.2, 6.6 Hz, 1H, $C\underline{H}_{2a}$), 2.22 (dd, *J* = 10.7, 6.6 Hz, 1H, $C\underline{H}_{2b}$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 162.5 (1C, $\underline{C}$=O), 132.1 (1C, $\underline{C}_{Ph}$), 128.6 and 128.4 (4C, $\underline{C}H_{Ph}$), 128.4 (1C, $\underline{C}H_{Ph}$), 71.8 (1C, $\underline{C}NO_2$), 53.2 (1C, $O\underline{C}H_3$), 34.3 (1C, $\underline{C}$H–Ph), 21.0 (1C, $\underline{C}H_2$) ppm.

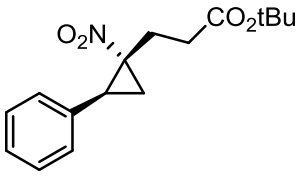
***Rel* methyl (*1S*,*2S*)-1-nitro-2-phenylcyclopropane-1-carboxylate 1k`**

R_f = 0.32 (PE/EtOAc = 10:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 – 7.18 (m, 5H, C$\underline{H}_{Ph}$), 3.89 (s, 3H, OC$\underline{H}_3$), 3.49 (t, *J* = 9.6 Hz, 1H, C$\underline{H}$–Ph), 2.69 (dd, *J* = 9.2, 7.0 Hz, 1H, C$\underline{H}_{2a}$), 2.04 (dd, *J* = 9.9, 7.0 Hz, 1H, C$\underline{H}_{2b}$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 165.9 (1C, C=O), 131.4 (1C, $\underline{C}_{Ph}$), 128.8, 128.7 and 128.4 (5C, $\underline{C}H_{Ph}$), 72.58 (1C, $\underline{C}NO_2$), 53.8 (1C, O$\underline{C}H_3$), 33.9 (1C, $\underline{C}$H–Ph), 20.1 (1C, $\underline{C}H_2$) ppm.

NMR spectra were in accordance with literature data.[16]



***Rel tert*-butyl 3-((*1R*,*2S*)-1-nitro-2-phenylcyclopropyl)propanoate 1l**

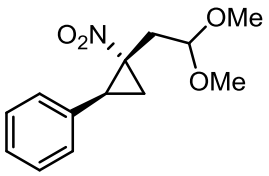
Cyclopropane **1l** was synthesized by **GP2** from *tert*-butyl 4-nitro-butanoate **3l** (378 mg, 3 mmol) and sulfonium bromide **4a** (717 g, 3.3 mmol), yield – 432 mg (74%). Colorless oil. R_f = 0.56 (PE/EtOAc = 20:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 – 7.28 (m, 3H, C$\underline{H}_{Ph}$), 7.23 – 7.18 (m, 2H, C$\underline{H}_{Ph}$), 3.33 (dd, *J* = 10.5, 8.4 Hz, 1H, C$\underline{H}$–Ph), 2.42 – 2.31 (m, 4H, C$\underline{H}_{2a}$ and $CH_2C\underline{H}_2CO_2$tBu and C$\underline{H}_{2a}CH_2CO_2$tBu), 1.69 (dd, *J* = 8.4, 6.1 Hz, 1H, C$\underline{H}_{2b}$), 1.65 – 1.54 (m, 1H, C$\underline{H}_{2b}CH_2CO_2$tBu), 1.39 (s, 9H, t$\underline{Bu}$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 171.8 (1C, $\underline{C}$=O), 134.1 (1C, $\underline{C}_{Ph}$), 128.88, 128.85 and 128.1 (5C, $\underline{C}H_{Ph}$), 80.8 (1C, $\underline{C}Me_3$), 69.4 (1C, $\underline{C}NO_2$), 35.8 (1C, $\underline{C}$H–Ph), 31.9 (1C, $CH_2\underline{C}H_2CO_2$tBu), 28.1 (3C, C$\underline{Me}_3$), 24.0 (1C, $\underline{C}H_2CH_2CO_2$tBu), 20.4 (1C, $\underline{C}H_2$) ppm.

FTIR (ATR): 2976 (br), 1730 (s), 1529 9s), 1428 (m), 1347 (s), 1331 (s), 1281 (m), 1148 (s), 1136 (s), 950 (m), 880 (m), 789 (m), 758 (m), 698 (s), 575 (m) cm^{-1}.

HRMS (ESI): m/z calcd for $C_{16}H_{22}NO_4^+$ $[M+H]^+$: 292.1543, found 292.1534.



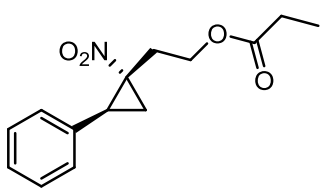
***Rel* ((*1S*,*2S*)-2-(2,2-dimethoxyethyl)-2-nitrocyclopropyl)benzene 1m**

Cyclopropane **1m** was synthesized by **GP2** from 3-nitropropanal dimethylacetal **3m** (149 mg, 1 mmol) and sulfonium bromide **4a** (359 mg, 1.1 mmol), yield – 181 mg (72%). Colorless oil. R_f = 0.74 (PE/EtOAc = 5:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$, COSY, NOESY): δ 7.39 – 7.30 (m, 3H, C$\underline{H}_{Ph}$), 7.22 – 7.16 (m, 2H, C$\underline{H}_{Ph}$), 4.61 (dd, *J* = 7.7, 3.1 Hz, 1H, $CH_2C\underline{H}(OMe)_2$), 3.34 and 3.32 (2s, 6H, 2 OC$\underline{H}_3$), 3.25 (dd, *J* = 10.5, 8.6 Hz, 1H, C$\underline{H}$–Ph), 2.70 (ddd, *J* = 15.6, 3.1, 1.9 Hz, 1H, C$\underline{H}_{2a}CH(OMe)_2$), 2.45 (ddd, *J* = 10.5, 6.4, 1.9 Hz, 1H, C$\underline{H}_{2a}$), 1.91 (dd, *J* = 8.6, 6.4 Hz, 1H, C$\underline{H}_{2b}$), 1.23 (dd, *J* = 15.6, 7.7 Hz, 1H, C$\underline{H}_{2b}CH(OMe)_2$) ppm. **Characteristic NOESY correlations**: $C\underline{H}_2CH(OMe)_2$/C$\underline{H}_{Ph}$; C$\underline{H}_{2b}$/C$\underline{H}_{Ph}$.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 134.3 (1C, $\underline{C}_{Ph}$), 128.9, 128.8 and 128.0 (5C, $\underline{C}H_{Ph}$), 103.4 (1C, $CH_2\underline{C}H(OMe)_2$, 67.1 (1C, $\underline{C}NO_2$), 54.9 and 54.0 (2C, O$\underline{C}H_3$), 34.9 (1C, $\underline{C}$H–Ph), 32.1 (1C, $\underline{C}H_2CH(OMe)_2$), 19.9 (1C, $\underline{C}H_2$) ppm.

HRMS (ESI): m/z calcd for $C_{13}H_{17}NaNO_4^+$ $[M+Na]^+$: 274.1050, found 274.1044.



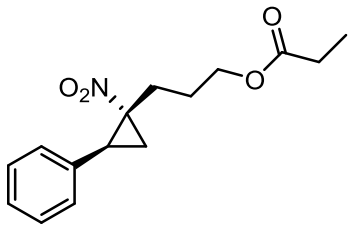
***Rel* 2-((*1S*,*2S*)-1-nitro-2-phenylcyclopropyl)ethyl propionate 1n**

Cyclopropane **1n** was synthesized by **GP2** from 3-nitropropyl propionate **3n** (175 mg, 1 mmol) and sulfonium bromide **4a** (359 mg, 1.1 mmol), yield – 168 mg (64%). Colorless oil. R_f = 0.40 (PE/EtOAc = 5:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$, COSY, NOESY): δ 7.42 – 7.31 (m, 3H, C$\underline{H}_{Ph}$), 7.23 – 7.17 (m, 2H, C$\underline{H}_{Ph}$), 4.28 (dt, *J* = 11.1, 6.8 Hz, 1H, $CH_2C\underline{H}_{2a}O$), 4.16 (ddd, *J* = 11.1, 7.1, 5.6 Hz, 1H, $CH_2C\underline{H}_{2b}O$), 3.33 (dd, *J* = 10.5, 8.5 Hz, 1H, C$\underline{H}$–Ph), 2.65 (dddd, *J* = 15.6, 6.5, 5.6, 1.8 Hz, 1H, C$\underline{H}_{2a}CH_2O$), 2.45 (ddd, *J* = 10.6, 6.3, 1.8 Hz, 1H, C$\underline{H}_{2a}$ anti to Ph), 2.28 (q, *J* = 7.6 Hz, 2H, $CH_3C\underline{H}_2$), 1.72 (dd, *J* = 8.4, 6.3 Hz, 1H, C$\underline{H}_{2b}$ syn to Ph), 1.44 (dt, *J* = 15.6, 7.1 Hz, 1H, C$\underline{H}_{2b}CH_2O$), 1.12 (t, *J* = 7.6 Hz, 3H, C$\underline{H}_3CH_2$) ppm. **Characteristic NOESY correlations**: C$\underline{H}_2CH_2O$/C$\underline{H}_{Ph}$; C$\underline{H}_{Ph}$/C$\underline{H}_{2b}$ syn to Ph; C$\underline{H}_{2b}CH_2O$/ C$\underline{H}_{2b}$ syn to Ph.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 174.2 (1C, C=O), 134.1 (1C, $\underline{C}_{Ph}$), 129.0, 128.9 and 128.2 (5C, $\underline{C}H_{Ph}$), 67.5 (1C, $\underline{C}NO_2$), 61.2 (1C, $CH_2\underline{C}H_2O$), 35.1 (1C, $\underline{C}$H–Ph), 27.9 (1C, $\underline{C}H_2CH_2O$), 27.5 (1C, $CH_3\underline{C}H_2$), 20.0 (1C, $\underline{C}H_2$), 9.1 (1C, $\underline{C}H_3CH_2$) ppm.

HRMS (ESI): m/z calcd for $C_{14}H_{18}NO_4^+$ $[M+H]^+$: 264.1230, found 264.1238.



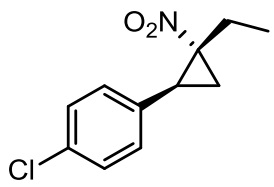
***Rel* 3-((*1R*,*2S*)-1-nitro-2-phenylcyclopropyl)propyl propionate 1o**

Cyclopropane **1o** was synthesized by **GP2** from 4-nitrobutyl propionate **3o** (175 mg, 1 mmol) and sulfonium bromide **4a** (359 mg, 1.1 mmol), yield – 140 mg (51%). Colorless oil. R_f = 0.56 (PE/EtOAc = 5:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$, COSY, NOESY): δ 7.41 – 7.30 (m, 3H, C$\underline{H}_{Ph}$), 7.22 – 7.16 (m, 2H, C$\underline{H}_{Ph}$), 4.04 – 3.88 (m, 2H, $CH_2CH_2C\underline{H}_2O$), 3.38 (dd, *J* = 10.4, 8.3 Hz, 1H, C$\underline{H}$–Ph), 2.37 (ddd, *J* = 10.4, 6.1, 1.5 Hz, 1H, C$\underline{H}_{2a}$ anti to Ph), 2.24 (q, *J* = 7.5 Hz, 2H, $CH_3C\underline{H}_2$), 2.19 – 2.09 (m, 1H, C$\underline{H}_{2a}CH_2CH_2O$), 1.83 – 1.70 (m, 2H, $CH_2C\underline{H}_2CH_2O$), 1.61 (dd, *J* = 8.3, 6.1 Hz, 1H, C$\underline{H}_{2b}$ syn to Ph), 1.44 – 1.29 (m, 1H, C$\underline{H}_{2b}CH_2CH_2O$), 1.08 (t, *J* = 7.6 Hz, 3H, C$\underline{H}_3CH_2$) ppm. **Characteristic NOESY correlations**: C$\underline{H}_2CH_2CH_2O$/C$\underline{H}_{Ph}$; C$\underline{H}_{Ph}$/C$\underline{H}_{2b}$ syn to Ph; C$\underline{H}_2CH_2CH_2O$/C$\underline{H}_{2b}$ syn to Ph

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 174.3 (1C, C=O), 134.3 (1C, $\underline{C}_{Ph}$), 128.8 and 128.0 (5C, $\underline{C}H_{Ph}$), 69.6 (1C, $\underline{C}NO_2$), 63.4 (1C, $CH_2CH_2\underline{C}H_2O$), 35.4 (1C, $\underline{C}$H–Ph), 27.6 (1C, $CH_3\underline{C}H_2$), 25.5 (1C, $\underline{C}H_2CH_2CH_2O$), 25.2 (1C, $CH_2\underline{C}H_2CH_2O$), 20.5 (1C, $\underline{C}H_2$), 9.2 (1C, $\underline{C}H_3CH_2$) ppm.

HRMS (ESI): m/z calcd for $C_{15}H_{20}NO_4^+$ $[M+H]^+$: 278.1387, found 278.1385.



***Rel* 1-chloro-4-((*1S*,*2R*)-2-ethyl-2-nitrocyclopropyl)benzene 1p**

Cyclopropane **1p** was synthesized by **GP2** from 1-nitropropane **3d** (45 mg, 0.5 mmol) and sulfonium bromide **4b** (198 g, 0.55 mmol). Column chromatography (PE/EtOAc, 100:1, then 1:1) afforded target cyclopropane **1p** (25 mg, 22%) and isoxazoline *N*-oxide **2p** (64 mg, 57%) as colorless oils.

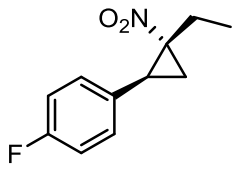
Mixture of diastereomers with dr = 4:1.

R_f = 0.55 (major) and 0.32 (minor) (PE/EtOAc = 20:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 7.34 (d, *J* = 8.4 Hz, 2H, C$\underline{H}_{Ar}$), 7.15 (d, *J* = 8.4 Hz, 2H, C$\underline{H}_{Ar}$), 3.33 (dd, *J* = 10.4, 8.2 Hz, 1H, C$\underline{H}$–Ar), 2.35 (ddd, *J* = 10.4, 6.2, 1.7 Hz, 1H, C$\underline{H}_{2a}$ anti to Ar), 2.14 (dqd, *J* = 15.7, 7.1, 1.7 Hz, 1H, C$\underline{H}_{2a}CH_3$), 1.51 (dd, *J* = 8.1, 6.1 Hz, 1H, C$\underline{H}_{2b}$ syn to Ar), 1.29 (dq, *J* = 15.7, 7.3 Hz, 1H, C$\underline{H}_{2b}CH_3$), 0.98 (t, *J* = 7.2 Hz, 3H, $CH_2C\underline{H}_3$) ppm. Characteristic signals of minor diastereomer: 7.28 (d, *J* = 8.5 Hz, 2H, C$\underline{H}_{Ar}$) 2.79 – 2.65 (m, 1H, C$\underline{H}_{2a}CH_3$), 2.68 – 2.60 (m, 1H, C$\underline{H}$–Ar) 2.53 (ddd, *J* = 8.1, 6.4, 1.5 Hz, 1H, C$\underline{H}_2$), 1.79 (dq, *J* = 14.7, 7.3 Hz, 1H, C$\underline{H}_{2b}CH_3$), 1.17 (t, *J* = 7.3 Hz, 3H, $CH_2C\underline{H}_3$).

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 133.9 and 133.3 (2C, $\underline{C}_{Ar}$), 130.2 and 129.0 (4C, C$\underline{H}_{Ar}$), 70.9 (1C, $\underline{C}NO_2$), 34.7 (1C, $\underline{C}$H–Ar), 22.3 (1C, $\underline{C}H_2CH_3$), 20.2 (1C, $\underline{C}H_2$), 10.2 (1C, $CH_2\underline{C}H_3$) ppm. Characteristic signals of minor diastereomer: 130.3 and 128.7 (4C, C$\underline{H}_{Ar}$), 33.4 (1C, $\underline{C}$H–Ar), 28.2 (1C, $\underline{C}H_2CH_3$), 18.4 (1C, $\underline{C}H_2$), 10.5 (1C, $CH_2\underline{C}H_3$) ppm.

HRMS (ESI): m/z calcd for $C_{11}H_{13}{}^{35}ClNO_2^+$ $[M+H]^+$: 226.0629, found 226.0635.



***Rel* 1-((*1S*,*2R*)-2-ethyl-2-nitrocyclopropyl)-4-fluorobenzene 1q**

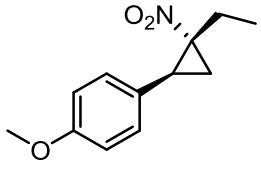
Cyclopropane **1q** was synthesized by **GP2** from 1-nitropropane **3d** (45 mg, 0.5 mmol) and sulfonium bromide **4c** (189 mg, 0.55 mmol), yield – 74 mg (71%). Colorless oil. R_f = 0.74 (PE/EtOAc = 20:1, anisaldehyde). Mixture of diastereomers with dr = 14:1.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (dd, *J* = 8.6, 5.2 Hz, 2H, C$\underline{H}_{Ar}$), 7.05 (t, *J* = 8.6 Hz, 2H, C$\underline{H}_{Ar}$), 3.41 – 3.27 (m, 1H, C$\underline{H}$–Ar), 2.34 (ddd, *J* = 10.5, 6.1, 1.7 Hz, 1H, C$\underline{H}_{2a}$ anti to Ar), 2.15 (dqd, *J* = 14.5, 7.2, 1.7 Hz, 1H, $CH_3C\underline{H}_{2a}$), 1.50 (dd, *J* = 8.2, 6.1 Hz, 1H, C$\underline{H}_{2b}$ syn to Ar), 1.27 (dq, *J* = 14.5, 7.2 Hz, 1H, $CH_3C\underline{H}_{2b}$), 0.98 (t, *J* = 7.2 Hz, 3H, $C\underline{H}_3CH_2$) ppm. Characteristic signals of minor diastereomer: 2.79 – 2.60 (m, 2H, C$\underline{H}_{2a}CH_3$ and C$\underline{H}$–Ar), 2.52 (ddd, *J* = 8.2, 6.5, 1.5 Hz, 1H, C$\underline{H}_{2a}$), 1.78 (dq, *J* = 14.7, 7.3 Hz, 1H, C$\underline{H}_{2b}CH_3$), 1.17 (t, *J* = 7.3 Hz, 3H, $CH_2C\underline{H}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HMBC): δ 162.4 (d, *J* = 247.0 Hz, 1C, $\underline{C}_{Ar}$), 130.5 (d, *J* = 8.2 Hz, 2C, C$\underline{H}_{Ar}$), 115.7 (d, *J* = 21.6 Hz, 2C, C$\underline{H}_{Ar}$), 100.1 (1C, $\underline{C}_{Ar}$), 70.8 (1C, $\underline{C}NO_2$), 34.7 (1C, $\underline{C}$H–Ar), 22.2 (1C, $CH_3\underline{C}H_2$), 20.3 (1C, $\underline{C}H_2$), 10.2 (1C, $\underline{C}H_3CH_2$) ppm.

^{19}F NMR (282 MHz, $CDCl_3$): δ -114.07 (tt, *J* = 8.6, 5.2 Hz) ppm.

HRMS (ESI): m/z calcd for $C_{11}H_{13}FNO_2^+$ $[M+H]^+$: 210.0925, found 210.0929.



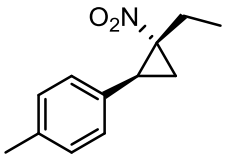
***Rel* 1-((*1S*,*2R*)-2-ethyl-2-nitrocyclopropyl)-4-methoxybenzene 1r**

Cyclopropane **1r** was synthesized by **GP2** from 1-nitropropane **3d** (45 mg, 0.5 mmol) and sulfonium bromide **4d** (196 mg, 0.55 mmol), yield – 70 mg (64%). Colorless oil. R_f = 0.42 (PE/EtOAc = 20:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 7.12 (d, *J* = 8.4 Hz, 2H, C$\underline{H}_{Ar}$), 6.88 (d, *J* = 8.7 Hz, 2H, C$\underline{H}_{Ar}$), 3.82 (s, 3H, O$C\underline{H}_3$), 3.31 (dd, *J* = 10.4, 8.2 Hz, 1H, C$\underline{H}$–Ar), 2.32 (ddd, *J* = 10.3, 6.0, 1.7 Hz, 1H, C$\underline{H}_{2a}$ anti to Ar), 2.15 (dqd, *J* = 15.8, 7.0, 1.7 Hz, 1H, $CH_3C\underline{H}_{2a}$), 1.49 (dd, *J* = 8.2, 6.0 Hz, 1H, C$\underline{H}_{2b}$ syn to Ar), 1.29 (dq, *J* = 15.1, 7.3 Hz, 1H, $CH_3C\underline{H}_{2b}$), 0.98 (t, *J* = 7.2 Hz, 3H, $C\underline{H}_3CH_2$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 159.3 (1C, $\underline{C}$-OCH_3), 130.0 (2C, C$\underline{H}_{Ar}$), 126.7 (1C, $\underline{C}_{Ar}$), 114.1 (2C, C$\underline{H}_{Ar}$), 71.0 (1C, $\underline{C}NO_2$), 55.4 (1C, O$\underline{C}H_3$), 35.3 (1C, $\underline{C}$H–Ar), 22.2 (1C, $CH_3\underline{C}H_2$), 20.4 (1C, $\underline{C}H_2$), 10.2 (1C, $\underline{C}H_3CH_2$) ppm.

HRMS (ESI): m/z calcd for $C_{12}H_{16}NO_3^+$ [M+H]$^+$: 222.1125, found 222.1121.



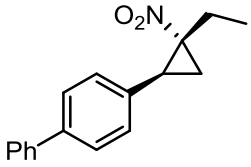
***Rel* 1-((*1S*,*2R*)-2-ethyl-2-nitrocyclopropyl)-4-methylbenzene 1s**

Cyclopropane **1s** was synthesized by **GP2** from 1-nitropropane **3d** (45 mg, 0.5 mmol) and sulfonium bromide **4e** (187 mg, 0.55 mmol), yield – 83 mg (81%). Colorless oil. R_f = 0.74 (PE/EtOAc = 20:1, anisaldehyde). Mixture of diastereomers with dr = 17:1.

^{1}H NMR (300 MHz, $CDCl_3$, COSY, NOESY): δ 7.17 (d, *J* = 8.0 Hz, 2H, C$\underline{H}_{Ar}$), 7.10 (d, *J* = 8.0 Hz, 2H, C$\underline{H}_{Ar}$), 3.34 (dd, *J* = 10.4, 8.3 Hz, 1H, C$\underline{H}$–Ar), 2.41 – 2.29 (m, 4H, C$\underline{H}_3$-Ar and C$\underline{H}_{2a}$), 2.15 (dtd, *J* = 15.6, 7.1, 1.7 Hz, 1H, $CH_3C\underline{H}_{2a}$), 1.53 (dd, *J* = 8.3, 6.0 Hz, 1H, C$\underline{H}_{2b}$), 1.37 – 1.23 (m, 1H, $CH_3C\underline{H}_{2b}$), 0.99 (t, *J* = 7.1 Hz, 3H, C$\underline{H}_3CH_2$) ppm. **Characteristic NOESY correlations**: C$\underline{H}_{2a}CH_3$/C$\underline{H}_{Ar}$; $CH_3C\underline{H}_{2b}$/C$\underline{H}_{Ar}$; C$\underline{H}_{2b}$/C$\underline{H}_{Ar}$; C$\underline{H}_{2b}$/$CH_3C\underline{H}_{2b}$.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 137.6 and 131.7 (2C, $\underline{C}_{Ar}$), 129.4 and 128.8 (4C, $\underline{C}H_{Ar}$), 71.0 (1C, $\underline{C}NO_2$), 35.5 (1C, $\underline{C}$H–Ar), 22.2 (1C, $CH_3C\underline{H}_2$), 21.2 (1C, $\underline{C}H_{3Ar}$), 20.2 (1C, $\underline{C}H_2$), 10.2 (1C, $\underline{C}H_3CH_2$) ppm.

HRMS (ESI): m/z calcd for $C_{12}H_{15}NaNO_2^+$ [M+Na]$^+$: 228.0995, found 228.0997.



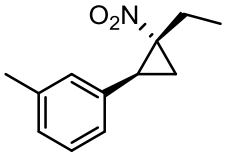
***Rel* 4-((*1S*,*2R*)-2-ethyl-2-nitrocyclopropyl)-1,1'-biphenyl 1t**

Cyclopropane **1t** was synthesized by **GP2** from 1-nitropropane **3d** (45 mg, 0.5 mmol) and sulfonium bromide **4f** (221 mg, 0.55 mmol), yield – 51 mg (38%). Colorless oil. R_f = 0.39 (major) and 0.24 (minor) (PE/EtOAc = 100:1, anisaldehyde). Mixture of diastereomers with dr = 6:1.

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 7.62 – 7.30 (m, 9H, C$\underline{H}_{Ar}$), 3.43 (dd, *J* = 10.4, 8.3 Hz, 1H, C$\underline{H}$–Ar), 2.40 (ddd, *J* = 10.4, 6.1, 1.7 Hz, 1H, C$\underline{H}_{2a}$), 2.32 – 2.15 (m, 1H, C$\underline{H}_{2a}CH_3$), 1.61 (dd, *J* = 8.3, 6.1 Hz, 1H, C$\underline{H}_{2b}$), 1.46 – 1.30 (m, 1H, C$\underline{H}_{2b}CH_3$), 1.03 (t, *J* = 7.2 Hz, 3H, $CH_2C\underline{H}_3$) ppm. Characteristic signals of minor diastereomer: 2.85 – 2.70 (m, 2H, C$\underline{H}_{2a}CH_3$ and C$\underline{H}$–Ar), 2.63 (ddd, J = 8.2, 6.4, 1.5 Hz, 1H, C$\underline{H}_{2a}$), 1.83 (dq, J = 14.8, 7.3 Hz, 1H, C$\underline{H}_{2b}CH_3$), 1.55 (dd, J = 9.3, 6.4 Hz, 1H, C$\underline{H}_{2b}$), 1.22 (t, J = 7.3 Hz, 3H, $CH_2C\underline{H}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 140.8, 140.4 and 133.8 (3C, $\underline{C}_{Ar}$), 129.3, 129.0, 127.6, 127.4 and 127.1 (9C, $\underline{C}H_{Ar}$), 71.1 (1C, $\underline{C}NO_2$), 35.3 (1C, $\underline{C}$H–Ar), 22.3 (1C, $CH_3\underline{C}H_2$), 20.3 (1C, $\underline{C}H_2$), 10.3 (1C, $\underline{C}H_3CH_2$) ppm. Characteristic signals of minor diastereomer: 128.8 and 127.2 ($\underline{C}H_{Ar}$), 33.9 (1C, $\underline{C}$H–Ar), 28.3 (1C, $CH_3\underline{C}H_2$), 18.4 (1C, $\underline{C}H_2$), 10.5 (1C, $\underline{C}H_3CH_2$) ppm.

HRMS (ESI): m/z calcd for $C_{17}H_{18}NO_2^+$ [M+H]$^+$: 268.1332, found 268.1332.



***Rel* 1-((*1S*,*2R*)-2-ethyl-2-nitrocyclopropyl)-3-methylbenzene 1u**

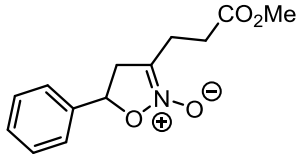
Cyclopropane **1u** was synthesized by **GP2** from 1-nitropropane **3d** (45 mg, 1 mmol) and sulfonium bromide **4g** (187 g, 1.1 mmol). Column chromatography (PE/EtOAc, 100:1, then 3:1) afforded target cyclopropane **1u** (20 mg, 20%) and isoxazoline *N*-oxide **2u** (49 mg, 48%) as colorless oils.

R_f = 0.76 (PE/EtOAc = 20:1, anisaldehyde).

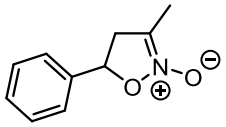
Mixture of diastereomers with dr = 6:1.

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 7.26 – 6.95 (m, 4H, C$\underline{H}_{Ar}$), 3.32 (dd, *J* = 10.4, 8.3 Hz, 1H, C$\underline{H}$–Ar), 2.35 (s, 3H, $\underline{Me}_{Ar}$), 2.34 – 2.27 (m, 1H, C$\underline{H}_{2a}$), 2.16 (dqd, *J* = 15.7, 7.1, 1.8 Hz, 1H, C$\underline{H}_{2a}CH_3$), 1.52 (dd, *J* = 8.3, 6.0 Hz, 1H, C$\underline{H}_{2b}$), 1.32 – 1.19 (m, 1H, C$\underline{H}_{2b}CH_3$), 0.97 (t, *J* = 7.2 Hz, 3H, $CH_2C\underline{H}_3$) ppm. Characteristic signals of minor diastereomer: δ 2.78 – 2.69 (m, 1H, C$\underline{H}_2CH_3$), 2.68 – 2.60 (m, 1H, C$\underline{H}$–Ar), 2.53 (ddd, *J* = 8.2, 6.3, 1.5 Hz, 1H, C$\underline{H}_2$), 2.32 (s, 3H, $\underline{Me}_{Ar}$), 1.77 (dq, *J* = 14.8, 7.3 Hz, 1H, C$\underline{H}_2CH_3$), 1.46 (dd, *J* = 9.2, 6.3 Hz, 1H, C$\underline{H}_2$), 1.16 (t, *J* = 7.3 Hz, 3H, $CH_2C\underline{H}_3$) ppm.
^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 138.4 and 134.7 (2C, $\underline{C}_{Ar}$), 129.7, 128.6, 128.6 and 125.9 (4C, $\underline{C}H_{Ar}$), 71.0 (1C, $\underline{C}NO_2$), 35.7 (1C, $\underline{C}$H–Ar), 22.2 (1C, $\underline{C}H_2CH_3$), 21.5 (1C, $\underline{Me}_{Ar}$), 20.1 (1C, $\underline{C}H_2$), 10.3 (1C, $CH_2\underline{C}H_3$) ppm. Characteristic signals of minor diastereomer: δ 129.7 and 128.3 (2C, $\underline{C}H_{Ar}$), 34.2 (1C, $\underline{C}$H–Ar), 28.4 (1C, $\underline{C}H_2CH_3$), 18.3 (1C, $\underline{C}H_2$), 10.5 (1C, $CH_2\underline{C}H_3$).
HRMS (ESI): m/z calcd for $C_{12}H_{16}NO_2^+$ $[M+H]^+$: 206.1176, found 206.1182.

6. Synthesis of isoxazoline *N*-oxides 2



2a



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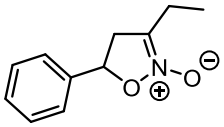

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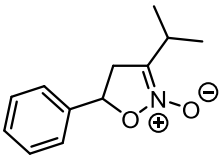

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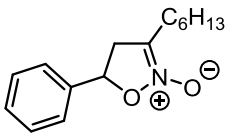
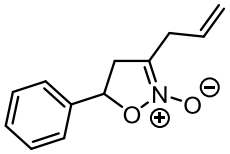


2f



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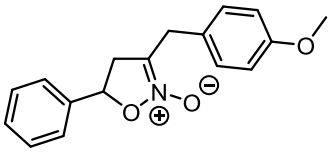

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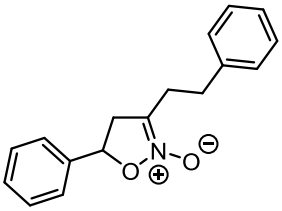
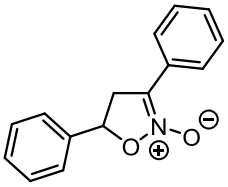


2i



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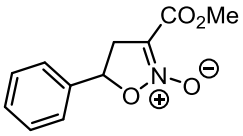
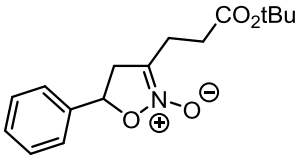


2k



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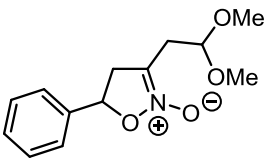

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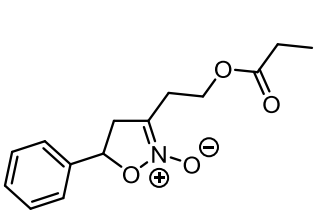

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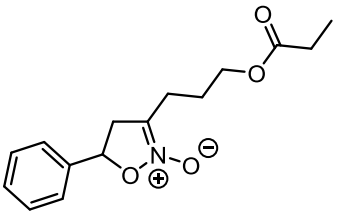
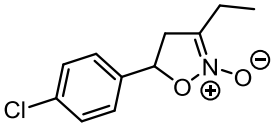
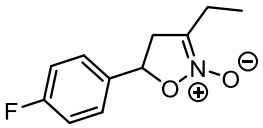


2o



2p



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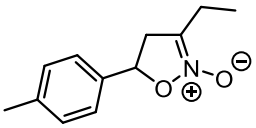

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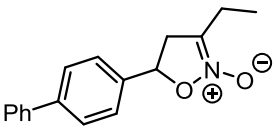
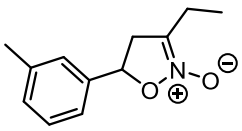


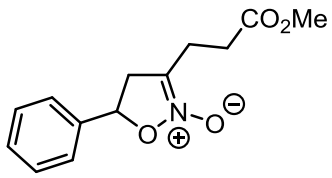
2t



2u

General procedure 3 (GP3) for preparation of isoxazoline *N*-oxides 2:

To a stirred solution of sulfonium salt **4** (1.0 mmol, 2 equiv.) in 1 mL of TFE (2,2,2-trifluoroethanol) nitro compound **3** (0.5 mmol, 1 equiv.) and Et_3N (160 µL, 116 mg, 1.15 mmol, 2.3 equiv.) were added and the reaction mixture was stirred for 4h at rt. Then the mixture was diluted with 25 mL of EtOAc and washed with 25 mL of 0.25M aq. solution of $NaHSO_4$. Aqueous layer was back extracted with 25 mL of EtOAc. Combined organic layers were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude material was subjected to column chromatography (PE/EtOAc 10:1 to 1:1) to give pure isoxazoline *N*-oxide **2**.



3-(3-Methoxy-3-oxopropyl)-5-phenyl-4,5-dihydroisoxazole 2-oxide 2a

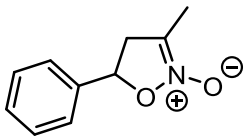
N-oxide **2a** was synthesized by **GP3** from methyl 3-nitrobutyrate **3a** (74 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 94 mg (75%). White solid. Mp 39 – 40 °C (Et_2O). R_f = 0.38 (PE/EtOAc = 1:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 – 7.30 (m, 5H, C$\underline{H}_{Ph}$), 5.56 (dd, *J* = 9.5, 7.6 Hz, 1H, C$\underline{H}$–Ph), 3.62 (s, 3H, OC$\underline{H}_3$), 3.51 (dd, *J* = 17.1, 9.6 Hz, 1H, C$\underline{H}_{2a}$), 3.10 (dd, *J* = 17.1, 7.6 Hz, 1H, C$\underline{H}_{2b}$), 2.64 (s, 4H, C$\underline{H}_2$C$\underline{H}_2$$CO_2$Me) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 172.5 (1C, $\underline{C}$=O), 138.8 (1C, $\underline{C}_{Ph}$), 128.9, 128.7 and 125.6 (5C, $\underline{C}H_{Ph}$), 114.6 (1C, $\underline{C}$=N-O), 76.0 (1C, $\underline{C}$H–Ph), 51.9 (1C, O$\underline{C}H_3$), 41.3 (1C, $\underline{C}H_2$), 28.9 and 21.5 (2C, $\underline{C}H_2\underline{C}H_2CO_2$Me) ppm.

FTIR (ATR): 2949 (br), 1728 (s), 1638 (s), 1498 (w), 1437 (m), 1354 (m), 1309 (m), 1244 (m), 1202 (m), 1176 (s), 1157 (s), 1075 (m), 973 (w), 867 (s), 828 (m), 767 (s), 750 (m), 698 (s), 655 (w), 625 (m),602 (w) cm^{-1}.

HRMS (ESI): m/z calcd for $C_{13}H_{16}NO_4^+$ $[M+H]^+$: 250.1074, found 250.1082.

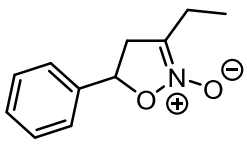


3-Methyl-5-phenyl-4,5-dihydroisoxazole 2-oxide 2c

N-oxide **2c** was synthesized by **GP3** from nitroethane **3c** (38 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 50 mg (56%). Colorless oil. R_f = 0.42 (PE/EtOAc = 1:1, anisaldehyde).

Scale up procedure: *N*-oxide **2c** was synthesized by **GP3** from nitroethane **3c** (380 mg, 5 mmol) and sulfonium bromide **4a** (3.26 g, 10 mmol), yield – 724 mg (82%).

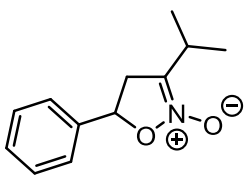
^{1}H NMR (300 MHz, $CDCl_3$): δ δ 7.43 – 7.33 (m, 5H, C$\underline{H}_{Ph}$), 5.59 (dd, *J* = 9.6, 7.6 Hz, 1H, C$\underline{H}$–Ph), 3.49 (ddq, *J* = 17.2, 9.6, 1.8 Hz, 1H, C$\underline{H}_{2a}$), 3.09 (ddq, *J* = 17.2, 7.6, 1.8 Hz, 1H, C$\underline{H}_{2b}$), 2.03 (br s, 3H, C$\underline{H}_3$) ppm. ^{1}H NMR spectrum was in accordance with literature data.[17]



3-Ethyl-5-phenyl-4,5-dihydroisoxazole 2-oxide 2d

N-oxide **2d** was synthesized by **GP3** from 1-nitropropane **3d** (45 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 80 mg (83%). White solid. Mp 44 – 46 °C. R_f = 0.70 (PE/EtOAc = 1:1, anisaldehyde).

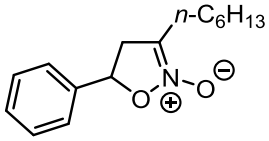
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 – 7.29 (m, 5H, C$\underline{H}_{Ph}$), 5.59 (dd, *J* = 9.6, 7.6 Hz, 1H, C$\underline{H}$–Ph), 3.49 (ddt, *J* = 17.1, 9.6, 1.6 Hz, 1H, C$\underline{H}_{2a}$), 3.07 (ddt, *J* = 17.1, 7.6, 1.6 Hz, 1H, C$\underline{H}_{2b}$), 2.51 – 2.42 (m, 2H, C$\underline{H}_2$$CH_3$), 1.14 (t, *J* = 7.7 Hz, 3H, CH_2C$\underline{H}_3$) ppm. ^{1}H NMR spectrum was in accordance with literature data.[17]



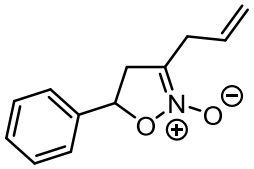
3-Isopropyl-5-phenyl-4,5-dihydroisoxazole 2-oxide 2e

N-oxide **2e** was synthesized by **GP3** from 2-methyl-1-nitropropane **3e** (52 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 40 mg (40%). Colorless oil. R_f = 0.38 (PE/EtOAc = 3:1, anisaldehyde).

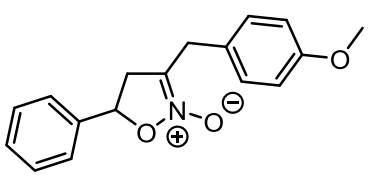
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 – 7.29 (m, 5H, C$\underline{H}_{Ph}$), 5.55 (dd, *J* = 9.5, 7.5 Hz, 1H, C$\underline{H}$–Ph), 3.44 (ddd, *J* = 17.1, 9.5, 1.0 Hz, 1H, C$\underline{H}_{2a}$), 3.05 – 2.94 (m, 2H, C$\underline{H}_{2b}$ and C$\underline{H}Me_2$), 1.15 (d, *J* = 7.0 Hz, 3H, CH$\underline{Me}_2$), 1.10 (d, *J* = 7.0 Hz, 3H, CH$\underline{Me}_2$) ppm.
^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 139.2 (1C, 1-$\underline{C}_{Ph}$), 129.0, 128.7 and 125.5 (5C, $\underline{C}H_{Ph}$), 119.9 (1C, $\underline{C}$=N-O), 75.7 (1C, $\underline{C}$H–Ph), 38.5 (1C, $\underline{C}H_2$), 26.4 (1C, $\underline{C}HMe_2$), 18.8 (1C, CH$\underline{Me}_2$), 18.6 (1C, CH$\underline{Me}_2$).
HRMS (ESI): m/z calcd for $C_{12}H_{16}NO_2^+$ $[M+H]^+$: 206.1176, found 206.1182.



3-Hexyl-5-phenyl-4,5-dihydroisoxazole 2-oxide 2f
N-oxide **2f** was synthesized by **GP3** from 1-nitroheptane **3f** (73 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 99 mg (80%). White solid. Mp 42 – 44 °C. R_f = 0.39 (PE/EtOAc = 3:1, anisaldehyde).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.28 (m, 5H, C$\underline{H}_{Ph}$), 5.57 (dd, *J* = 9.5, 7.4 Hz, 1H, C$\underline{H}$–Ph), 3.53 – 3.40 (m, 1H, C$\underline{H}_{2a}$), 3.13 – 2.95 (m, 1H, C$\underline{H}_{2b}$), 2.44 – 2.35 (m, 2H, C$\underline{H}_2$ of hexyl), 1.52 (p, *J* = 7.7 Hz, 2H, C$\underline{H}_2$ of hexyl), 1.39 – 1.20 (m, 6H, C$\underline{H}_2$ of hexyl), 0.92 – 0.82 (m, 3H, C$\underline{H}_3$ of hexyl) ppm.
^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 139.2 (1C, 1-$\underline{C}_{Ph}$), 129.0, 128.7 and 125.6 (5C, $\underline{C}H_{Ph}$), 115.9 (1C, $\underline{C}$=N-O), 75.5 (1C, $\underline{C}$H–Ph), 41.1 (1C, $\underline{C}H_2$), 31.5, 29.0, 26.2, 25.5 and 22.6 (5C, $\underline{C}H_2$ of hexyl), 14.1 (1C, $\underline{C}H_3$) ppm.
HRMS (ESI): m/z calcd for $C_{15}H_{22}NO_2^+$ $[M+H]^+$: 248.1645, found 248.1646.

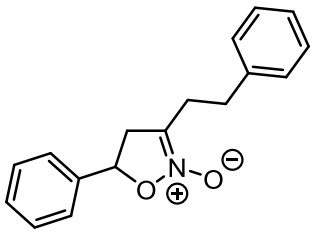


3-Allyl-5-phenyl-4,5-dihydroisoxazole 2-oxide 2g
N-oxide **2g** was synthesized by **GP3** from 4-nitro-1-butene **3g** (51 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 32 mg (30%). Colorless oil. R_f = 0.22 (PE/EtOAc = 3:1, anisaldehyde).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 – 7.31 (m, 5H, C$\underline{H}_{Ph}$), 5.76 (ddt, *J* = 16.8, 10.0, 6.7 Hz, 1H, C$\underline{H}$=CH_2), 5.59 (dd, *J* = 9.6, 7.6 Hz, 1H, C$\underline{H}$–Ph), 5.23 – 5.17 (m, 1H, CH=C$\underline{H}_2$), 5.16 – 5.14 (m, 1H, CH=C$\underline{H}_2$), 3.46 (ddt, *J* = 17.1, 9.6, 1.5 Hz, 1H, C$\underline{H}_{2a}$), 3.20 – 3.13 (m, 2H, C$\underline{H}_2$CH=CH_2), 3.06 (ddt, *J* = 17.1, 7.6, 1.5 Hz, 1H, C$\underline{H}_{2b}$) ppm.
^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 139.0 (1C, 1-$\underline{C}_{Ph}$), 130.0 (1C, $\underline{C}$H=CH_2), 129.0, 128.8 and 125.6 (5C, $\underline{C}H_{Ph}$), 119.3 (1C, CH=$\underline{C}H_2$), 113.9 (1C, $\underline{C}$=N-O), 75.8 (1C, $\underline{C}$H–Ph), 40.7 (1C, $\underline{C}H_2$), 30.6 (1C, $\underline{C}H_2$CH=CH_2) ppm.
HRMS (ESI): m/z calcd for $C_{12}H_{14}NO_2^+$ $[M+H]^+$: 204.1019, found 204.1024.

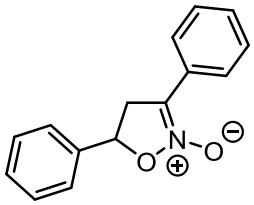


3-(4-Methoxybenzyl)-5-phenyl-4,5-dihydroisoxazole 2-oxide 2h
N-oxide **2h** was synthesized by **GP3** from 2-(4-methoxyphenyl)-1-nitroethane **3h** (91 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 110 mg (77%). Colorless oil. R_f = 0.29 (PE/EtOAc = 3:1, anisaldehyde).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 – 7.29 (m, 5H, C$\underline{H}_{Ph}$), 7.14 (d, *J* = 8.6 Hz, 2H, 2,6-C$\underline{H}_{Ar}$), 6.84 (d, *J* = 8.6 Hz, 2H, 3,5-C$\underline{H}_{Ar}$), 5.55 (dd, *J* = 9.5, 7.7 Hz, 1H, C$\underline{H}$–Ph), 3.78 (s, 3H, OC$\underline{H}_3$), 3.73 (d, *J* = 15.8 Hz, 1H, C$\underline{H}_{2a}$Ar), 3.64 (d, *J* = 15.8 Hz, 1H, C$\underline{H}_{2b}$Ar), 3.34 (ddt, *J* = 17.1, 9.5, 1.5 Hz, 1H, C$\underline{H}_{2a}$), 2.95 (ddt, *J* = 17.1, 7.7, 1.5 Hz, 1H, C$\underline{H}_{2b}$) ppm.

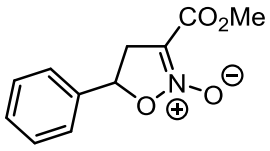
^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 159.0 (1C, 4-$\underline{C}_{Ar}$), 138.9 (1C, 1-$\underline{C}_{Ph}$), 129.9 (2C, 2,6-$\underline{C}H_{Ar}$), 129.0, 128.8 and 125.7 (5C, $\underline{C}H_{Ph}$), 127.0 (1C, 1-$\underline{C}_{Ar}$), 115.3 (1C, $\underline{C}$=N-O), 114.5 (2C, 3,5-$\underline{C}H_{Ar}$), 75.9 (1C, $\underline{C}$H–Ph), 55.4 (1C, O$\underline{C}H_3$), 40.7 (1C, $\underline{C}H_2$), 31.8 (1C, $\underline{C}H_2$Ar) ppm.
HRMS (ESI): m/z calcd for $C_{17}H_{18}NO_3^+$ $[M+H]^+$: 284.1281, found 284.1279.



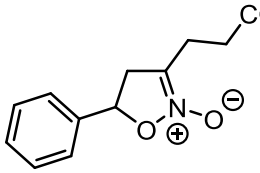
3-Phenethyl-5-phenyl-4,5-dihydroisoxazole 2-oxide 2i
N-oxide **2i** was synthesized by **GP3** from 3-phenyl-1-nitropropane **3i** (83 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 94 mg (75%). White solid. Mp 64 – 66 °C (Et_2O/PE 1:1). R_f = 0.28 (PE/EtOAc = 3:1, anisaldehyde).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 – 7.16 (m, 10H, $\underline{H}_{Ph}$), 5.51 (dd, *J* = 9.6, 7.3 Hz, 1H, $\underline{H}$–Ph), 3.27 (br dd, *J* = 17.1, 9.6 Hz, 1H, $\underline{H}_{2a}$), 2.97 – 2.73 (m, 5H, $\underline{H}_{2b}$ and $\underline{H}_2\underline{H}_2$Ph) ppm.
^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 139.8 and 139.0 (2C, $\underline{C}_{Ph}$), 128.9, 128.8, 128.7, 128.3, 126.7 and 125.7 (10C, $\underline{C}H_{Ph}$), 115.1 (1C, $\underline{C}$=N-O), 75.6 (1C, $\underline{C}$H–Ph), 41.4 (1C, $\underline{C}H_2$), 31.1 and 27.6 (2C, $\underline{C}H_2\underline{C}H_2$Ph).
FTIR (ATR): 3029 (br), 1630 (s), 1495 (m), 1457 (m), 1302 (m), 1217 (s), 1136 (m), 1077 (w), 1026 (w), 870 (s), 739 (s), 697 (s), 657 (s), 568 (m) cm^{-1}.
HRMS (ESI): m/z calcd for $C_{17}H_{18}NO_2^+$ $[M+H]^+$: 268.1332, found 268.1328.



3,5-Diphenyl-4,5-dihydroisoxazole 2-oxide 2j
N-oxide **2j** was synthesized by **GP3** from phenylnitromethane **3j** (69 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 75 mg (63%). White solid. Mp 89 – 91 °C (Et_2O). R_f = 0.70 (PE/EtOAc = 3:1, anisaldehyde).
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 – 7.89 (m, 2H, $\underline{H}_{Ph}$), 7.50 – 7.36 (m, 8H, $\underline{H}_{Ph}$), 5.74 (dd, *J* = 9.5, 7.7 Hz, 1H, $\underline{H}$–Ph), 3.93 (dd, *J* = 16.2, 9.5 Hz, 1H, $\underline{H}_{2a}$), 3.55 (dd, *J* = 16.2, 7.7 Hz, 1H, $\underline{H}_{2b}$) ppm.
^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 138.8 (1C, $\underline{C}_{Ph}$), 129.6, 129.1, 128.94, 128.85, 126.3 and 125.8 (10C, $\underline{C}H_{Ph}$), 126.8 (1C, $\underline{C}_{Ph}$), 114.1 (1C, $\underline{C}$=N-O), 75.8 (1C, $\underline{C}$–HPh), 40.4 (1C, $\underline{C}H_2$) ppm.
HRMS (ESI): m/z calcd for $C_{15}H_{14}NO_2^+$ $[M+H]^+$: 240.1019, found 240.1021.



3-(Methoxycarbonyl)-5-phenyl-4,5-dihydroisoxazole 2-oxide 2k
N-oxide **2k** was synthesized by **GP3** from methyl nitroacetate **3k** (60 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 101 mg (91%). Colorless oil. R_f = 0.64 (PE/EtOAc = 2:1, anisaldehyde).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 – 7.34 (m, 5H, $\underline{H}_{Ph}$), 5.71 (dd, *J* = 9.6, 7.8 Hz, 1H, $\underline{H}$–Ph), 3.85 (s, 3H, O$\underline{H}_3$), 3.79 (dd, *J* = 16.9, 9.6 Hz, 1H, $\underline{H}_{2a}$), 3.42 (dd, *J* = 16.9, 7.8 Hz, 1H, $\underline{H}_{2b}$) ppm. ^{1}H NMR spectrum was in accordance with literature data.[18]



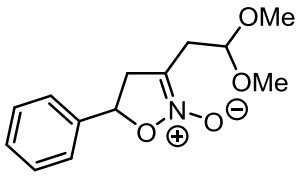
3-(3-(*tert*-Butoxy)-3-oxopropyl)-5-phenyl-4,5-dihydroisoxazole 2-oxide 2l

N-oxide **2l** was synthesized by **GP3** from *tert*-butyl 4-nitrobutanoate **3l** (95 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 107 mg (73%). White solid. Mp 76 – 78 °C (Et_2O/PE 1:1). R_f = 0.28 (PE/EtOAc = 3:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 – 7.31 (m, 5H, C$\underline{H}_{Ph}$), 5.57 (dd, *J* = 9.6, 7.5 Hz, 1H, C$\underline{H}$–Ph), 3.52 (ddt, *J* = 17.2, 9.6, 1.4 Hz, 1H, C$\underline{H}_{2a}$), 3.12 (ddt, *J* = 17.1, 7.5, 1.4 Hz, 1H, C$\underline{H}_{2b}$), 2.66 – 2.61 (m, C$\underline{H}_2$CH$_2$CO$_2$tBu), 2.56 – 2.52 (m, 2H, CH$_2$C$\underline{H}_2$CO$_2$tBu), 1.41 (s, 9H, OC$\underline{Me}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 171.4 (1C, $\underline{C}$=O), 139.0 (1C, $\underline{C}_{Ph}$), 129.0, 128.8 and 125.7 (5C, $\underline{C}H_{Ph}$), 114.8 (1C, $\underline{C}$=N-O), 81.2 (1C, O$\underline{C}$Me$_3$), 75.9 (1C, $\underline{C}$H–Ph), 41.3 (1C, C$\underline{H}_2$), 30.6 (1C, CH$_2\underline{C}$H$_2$CO$_2$tBu), 21.7 (1C, $\underline{C}$H$_2$CH$_2$CO$_2$tBu), 28.1 (3C, OC$\underline{Me}_3$) ppm.

HRMS (ESI): m/z calcd for $C_{16}H_{22}NO_4^+$ $[M+H]^+$: 292.1543, found 292.1549.



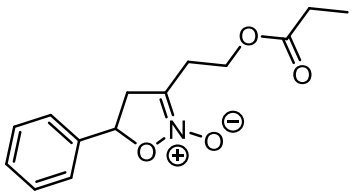
3-(2,2-Dimethoxyethyl)-5-phenyl-4,5-dihydroisoxazole 2-oxide 2m

N-oxide **2n** was synthesized by **GP3** from 3-nitropropanal dimethylacetal **3m** (75 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 50 mg (40%). Colorless oil. R_f = 0.25 (PE/EtOAc = 2:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 – 7.29 (m, 5H, C$\underline{H}_{Ph}$), 5.56 (dd, *J* = 9.6, 7.5 Hz, 1H, C$\underline{H}$–Ph), 4.59 (t, *J* = 5.4 Hz, 1H, CH$_2$C$\underline{H}$(OMe)$_2$), 3.52 (ddt, *J* = 17.3, 9.6, 1.4 Hz, 1H, C$\underline{H}_{2a}$), 3.34 (s, 3H, O$\underline{Me}$), 3.35 – 3.28 (m, 3H, O$\underline{Me}$), 3.12 (ddt, *J* = 17.3, 7.5, 1.5 Hz, 1H, C$\underline{H}_{2b}$), 2.72 (br d, *J* = 5.4 Hz, 3H, C$\underline{H}_2$CH(OMe)$_2$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 139.0 (1C, C_{Ph}), 128.9, 128.7 and 125.7 (5C, $\underline{C}H_{Ph}$), 112.6 (1C, $\underline{C}$=N), 101.2 (1C, CH$_2\underline{C}$H(OMe)$_2$), 76.1 (1C, $\underline{C}$H–Ph), 53.94 and 53.91 (2C, 2O$\underline{Me}$), 41.4 (1C, C$\underline{H}_2$), 30.5 (1C, $\underline{C}$H$_2$CH(OMe)$_2$) ppm.

HRMS (ESI): m/z calcd for $C_{13}H_{18}NO_4^+$ $[M+H]^+$: 252.1230, found 252.1240.



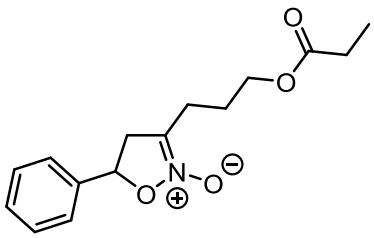
5-Phenyl-3-(2-(propionyloxy)ethyl)-4,5-dihydroisoxazole 2-oxide 2n

N-oxide **2n** was synthesized by **GP3** from 3-nitropropyl propionate **3n** (81 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 87 mg (66%). Colorless oil. R_f = 0.26 (PE/EtOAc = 2:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 7.45 – 7.30 (m, 5H, C$\underline{H}_{Ph}$), 5.61 (dd, *J* = 9.6, 7.3 Hz, 1H, C$\underline{H}$–Ph), 4.33 – 4.20 (m, 2H, CH$_2$C$\underline{H}_2$O), 3.55 (dd, *J* = 17.1, 9.6 Hz, 1H, C$\underline{H}_{2a}$), 3.12 (dd, *J* = 17.0, 7.3 Hz, 1H, C$\underline{H}_{2b}$), 2.77 (t, *J* = 6.1 Hz, 2H, C$\underline{H}_2$CH$_2$O), 2.28 (q, *J* = 7.6 Hz, 2H, C$\underline{H}_2$CH$_3$), 1.11 (t, *J* = 7.6 Hz, 3H, CH$_2$C$\underline{H}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 174.1 (1C, $\underline{C}$=O), 138.9 (1C, $\underline{C}_{Ph}$), 129.0, 128.8 and 125.6 (5C, $\underline{C}H_{Ph}$), 112.8 (1C, $\underline{C}$=N-O), 75.9 (1C, $\underline{C}$H–Ph), 59.8 (1C, CH$_2\underline{C}$H$_2$O), 41.1 (1C, C$\underline{H}_2$), 27.4 (1C, $\underline{C}$H$_2$CH$_3$), 26.2 (1C, $\underline{C}$H$_2$CH$_2$O), 9.0 (1C, CH$_2\underline{C}$H$_3$) ppm.

HRMS (ESI): m/z calcd for $C_{14}H_{18}NO_4^+$ $[M+H]^+$: 264.1230, found 264.1236.



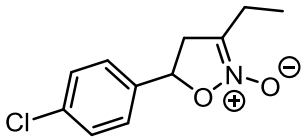
5-Phenyl-3-(3-(propionyloxy)propyl)-4,5-dihydroisoxazole 2-oxide 2o

N-oxide **2o** was synthesized by **GP3** from 4-nitrobutyl propionate **3o** (88 mg, 0.5 mmol) and sulfonium bromide **4a** (326 mg, 1 mmol), yield – 98 mg (71%). Colorless oil. R_f = 0.34 (PE/EtOAc = 2:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 – 7.32 (m, 5H, C$\underline{H}_{Ph}$), 5.59 (dd, *J* = 9.5, 7.5 Hz, 1H, C$\underline{H}$–Ph), 4.09 (t, *J* = 6.3 Hz, 2H, $CH_2CH_2C\underline{H}_2O$), 3.49 (ddt, *J* = 17.0, 9.5, 1.5 Hz, 1H, C$\underline{H}_{2a}$), 3.08 (ddt, *J* = 17.0, 7.5, 1.5 Hz, 1H, C$\underline{H}_{2b}$), 2.56 – 2.43 (m, 2H, $C\underline{H}_2CH_2CH_2O$), 2.31 (q, *J* = 7.6 Hz, 2H, $C\underline{H}_2CH_3$), 1.89 (tt, *J* = 7.7, 6.3 Hz, 2H, $CH_2C\underline{H}_2CH_2O$), 1.12 (t, *J* = 7.6 Hz, 3H, $CH_2C\underline{H}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 174.5 (1C, $\underline{C}$=O), 138.9 (1C, $\underline{C}_{Ph}$), 129.0, 128.8 and 125.6 (5C, $\underline{C}H_{Ph}$), 114.7 (1C, $\underline{C}$=N-O), 75.7 (1C, $\underline{C}$H–Ph), 63.3 (1C, $CH_2CH_2\underline{C}H_2O$), 41.1 (1C, $\underline{C}H_2$), 27.6 (1C, $\underline{C}H_2CH_3$), 24.6 (1C, $CH_2\underline{C}H_2CH_2O$), 23.1 (1C, $\underline{C}H_2CH_2CH_2O$), 9.2 (1C, $CH_2\underline{C}H_3$) ppm.

HRMS (ESI): m/z calcd for $C_{15}H_{20}NO_4^+$ $[M+H]^+$: 278.1387, found 278.1386.



5-(4-Chlorophenyl)-3-ethyl-4,5-dihydroisoxazole 2-oxide 2p

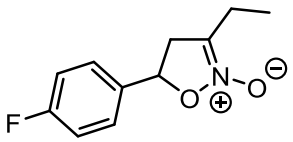
N-oxide **2p** was synthesized by **GP3** from 1-nitropropane **3d** (22 mg, 0.25 mmol) and sulfonium bromide **4b** (181 mg, 1 mmol), yield – 40 mg (71%). Colorless oil. R_f = 0.38 (PE/EtOAc = 2:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 – 7.30 (m, 4H, C$\underline{H}_{Ar}$), 5.55 (dd, *J* = 9.5, 7.3 Hz, 1H, C$\underline{H}$–Ar), 3.49 (ddt, *J* = 17.1, 9.5, 1.5 Hz, 1H, C$\underline{H}_{2a}$), 3.01 (ddt, *J* = 17.1, 7.3, 1.6 Hz, 1H, C$\underline{H}_{2b}$), 2.49 – 2.39 (m, 2H, $C\underline{H}_2CH_3$), 1.12 (t, *J* = 7.6 Hz, 3H, $CH_2C\underline{H}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 137.8 and 134.6 (2C, $\underline{C}_{Ar}$), 129.2 and 127.0 (4C, $\underline{C}H_{Ar}$), 116.4 (1C, $\underline{C}$=N-O), 74.8 (1C, $\underline{C}$H–Ph), 40.6 (1C, $\underline{C}H_2$), 19.7 (1C, $\underline{C}H_2CH_3$), 9.9 (1C, $CH_2\underline{C}H_3$) ppm.

FTIR (ATR): 2976 (br), 1636 (s), 1491 (m), 1438 (w), 1415 (w), 1351 (w), 1265 (m), 1212 (s), 1159 (m), 1091 (s), 1014 (m), 862 (s), 833 (s), 686 (m), 621 (m), 596 (m) cm^{-1}.

HRMS (ESI): m/z calcd for $C_{11}H_{13}{}^{35}ClNO_2^+$ $[M+H]^+$: 226.0629, found 226.0622.



3-Ethyl-5-(4-fluorophenyl)-4,5-dihydroisoxazole 2-oxide 2q

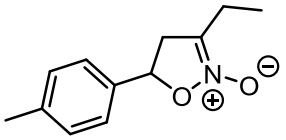
N-oxide **2q** was synthesized by **GP3** from 1-nitropropane **3d** (22 mg, 0.25 mmol) and sulfonium bromide **4c** (172 mg, 0.5 mmol), yield – 42 mg (81%). White solid. Mp 56 – 58 °C (Et_2O). R_f = 0.32 (PE/EtOAc = 2:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (dd, *J* = 8.6, 5.3 Hz, 2H, 2,6-C$\underline{H}_{Ar}$), 7.08 (t, *J* = 8.6 Hz, 2H, 3,5-C$\underline{H}_{Ar}$), 5.56 (dd, *J* = 9.5, 7.5 Hz, 1H, C$\underline{H}$–Ar), 3.47 (dd, *J* = 17.1, 9.5 Hz, 1H, C$\underline{H}_{2a}$), 3.03 (dd, *J* = 17.1, 7.5 Hz, 1H, C$\underline{H}_{2b}$), 2.52 – 2.38 (m, 2H, $C\underline{H}_2CH_3$), 1.13 (t, *J* = 7.6 Hz, 3H, $CH_2C\underline{H}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HMBC): δ 162.9 (d, *J* = 247.6 Hz, 1C, 4-$\underline{C}_{Ar}$), 134.9 (d, *J* = 3.2 Hz, 1C, 1-$\underline{C}_{Ar}$), 127.6 (d, *J* = 8.4 Hz, 2C, 2,6-C$\underline{H}_{Ar}$), 116.6 (1C, $\underline{C}$=N-O), 116.0 (d, *J* = 21.8 Hz, 2C, 3,5-C$\underline{H}_{Ar}$), 75.1 (1C, C$\underline{H}$–Ar), 40.7 (1C, $\underline{C}H_2$), 19.8 (1C, $\underline{C}H_2CH_3$), 9.9 (1C, $CH_2\underline{C}H_3$) ppm.

^{19}F NMR (282 MHz, $CDCl_3$): δ -112.93 (tt, *J* = 8.5, 5.2 Hz) ppm.

HRMS (ESI): m/z calcd for $C_{11}H_{13}FNO_2^+$ $[M+H]^+$: 210.0925, found 210.0926.



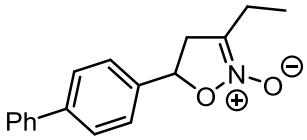
3-Ethyl-5-(*p*-tolyl)-4,5-dihydroisoxazole 2-oxide 2s

N-oxide **2s** was synthesized by **GP3** from 1-nitropropane **3d** (22 mg, 0.25 mmol) and sulfonium bromide **4e** (170 mg, 0.5 mmol), yield – 44 mg (86%). White solid. Mp 79 – 81 °C (Et_2O/PE 1:1). R_f = 0.46 (PE/EtOAc = 2:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.1 Hz, 2H, 2,6-C$\underline{H}_{Ar}$), 7.21 (d, *J* = 8.1 Hz, 2H, 3,5-C$\underline{H}_{Ar}$), 5.57 (dd, *J* = 9.4, 7.7 Hz, 1H, C$\underline{H}$–Ar), 3.47 (dd, *J* = 17.1, 9.5 Hz, 1H, C$\underline{H}_{2a}$), 3.07 (dd, *J* = 17.1, 7.7 Hz, 1H, C$\underline{H}_{2b}$), 2.53 – 2.43 (m, 2H, C$\underline{H}_2$CH$_3$), 2.37 (s, 3H, C$\underline{H}_3$), 1.15 (t, *J* = 7.6 Hz, 3H, CH$_2$C$\underline{H}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 138.7 and 136.0 (2C, $\underline{C}_{Ar}$), 129.6 and 125.7 (4C, $\underline{C}H_{Ar}$), 116.9 (1C, $\underline{C}$=N-O), 75.7 (1C, $\underline{C}$H–Ph), 40.5 (1C, $\underline{C}H_2$), 21.3 (1C, $\underline{C}H_3$), 19.7 (1C, $\underline{C}H_2CH_3$), 9.9 (1C, $CH_2\underline{C}H_3$) ppm.

HRMS (ESI): m/z calcd for $C_{12}H_{16}NO_2^+$ $[M+H]^+$: 206.1176, found 206.1168.



5-([1,1'-Biphenyl]-4-yl)-3-ethyl-4,5-dihydroisoxazole 2-oxide 2t

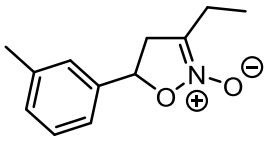
N-oxide **2t** was synthesized by **GP3** from 1-nitropropane **3d** (22 mg, 0.25 mmol) and sulfonium bromide **4f** (201 mg, 0.5 mmol), yield – 45 mg (67%). Colorless oil. R_f = 0.42 (PE/EtOAc = 2:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 – 7.56 (m, 4H, C$\underline{H}_{Ar}$), 7.50 – 7.33 (m, 5H, C$\underline{H}_{Ar}$), 5.64 (dd, *J* = 9.5, 7.5 Hz, 1H, C$\underline{H}$–Ar), 3.52 (dd, *J* = 17.1, 9.5 Hz, 1H, C$\underline{H}_{2a}$), 3.11 (dd, *J* = 17.1, 7.5 Hz, 1H, C$\underline{H}_{2b}$), 2.56 – 2.41 (m, 2H, C$\underline{H}_2$CH$_3$), 1.16 (t, *J* = 7.6 Hz, 3H, CH$_2$C$\underline{H}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 141.8, 140.5 and 138.1 (3C, $\underline{C}_{Ar}$), 129.0, 127.7, 127.7, 127.2 and 126.1 (9C, $\underline{C}H_{Ar}$), 116.7 (1C, $\underline{C}$=N-O), 75.5 (1C, C$\underline{H}$–Ar), 40.6 (1C, $\underline{C}H_2$), 19.8 (1C, $\underline{C}H_2CH_3$), 9.9 (1C, $CH_2\underline{C}H_3$) ppm.

FTIR (ATR): 2975 (w), 1632 (s), 1484 (m), 1449 (m), 1362 (m), 1269 (m), 1212 (s), 1158 (m), 1074 (m), 1006 (m), 927 (w), 865 (s), 839 9s), 822 (s), 765 (s), 699 (s), 589 (m) cm^{-1}.

HRMS (ESI): m/z calcd for $C_{17}H_{18}NO_2^+$ $[M+H]^+$: 268.1332, found 268.1334.



3-Ethyl-5-(*m*-tolyl)-4,5-dihydroisoxazole 2-oxide 2u

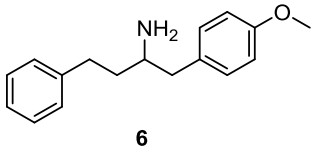
N-oxide **2u** was synthesized by **GP3** from 1-nitropropane **3d** (22 mg, 0.25 mmol) and sulfonium bromide **4g** (170 mg, 0.5 mmol), yield – 39 mg (76%). Colorless oil. R_f = 0.46 (PE/EtOAc = 2:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 – 7.12 (m, 4H, C$\underline{H}_{Ar}$), 5.54 (dd, *J* = 9.5, 7.6 Hz, 1H, C$\underline{H}$–Ar), 3.47 (dd, *J* = 17.1, 9.6 Hz, 1H, C$\underline{H}_{2a}$), 3.06 (dd, *J* = 17.1, 7.6 Hz, 1H, C$\underline{H}_{2b}$), 2.51 – 2.40 (m, 2H, C$\underline{H}_2$CH$_3$), 2.36 (s, 3H, CH$_3$), 1.13 (t, *J* = 7.6 Hz, 3H, CH$_2$C$\underline{H}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 139.1 and 138.8 (2C, $\underline{C}_{Ar}$), 129.5, 128.9, 126.2 and 122.7 (4C, $\underline{C}H_{Ar}$), 116.8 (1C, $\underline{C}$=N-O), 75.6 (1C, C$\underline{H}$–Ar), 40.6 (1C, $\underline{C}H_2$), 21.5 (1C, $\underline{C}H_3$), 19.8 (1C, $\underline{C}H_2CH_3$), 9.9 (1C, $CH_2\underline{C}H_3$) ppm.

HRMS (ESI): m/z calcd for $C_{12}H_{16}NO_2^+$ $[M+H]^+$: 206.1176, found 206.1179.

7. Post transformations of nitro cyclopropanes and isoxazoline *N*-oxides



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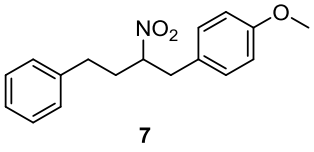

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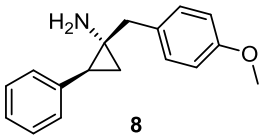

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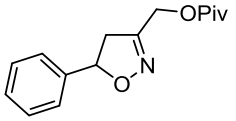
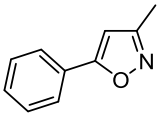
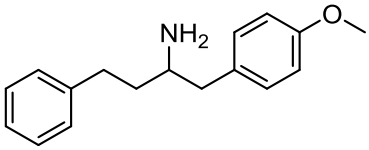


9



10

Hydrogenation to amine 6 (Scheme 6, Part B):



1-(4-Methoxyphenyl)-4-phenylbutan-2-amine 6

To a stirred solution of nitrocyclopropane **1h** (56 mg, 0.2 mmol) in 2 mL of MeOH 5% Pd/C (50 mg) was added. Resulted mixture was hydrogenated under atmospheric pressure (balloon) of H_2 for 6h. After that solid catalyst was filtered off. The solvent was evaporated and the crude product was purified by flash column chromatography (eluent MeOH) to give pure amine **6**, yield – 37 mg (73%). Colorless oil. R_f = 0.50 (MeOH, ninhydrin).

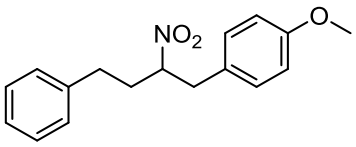
^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 7.36 – 7.28 (m, 2H, C$\underline{H}_{Ph}$), 7.24 – 7.19 (m, 3H, C$\underline{H}_{Ph}$), 7.13 (d, *J* = 8.5 Hz, 2H, 2,6-C$\underline{H}_{Ar}$), 6.88 (d, *J* = 8.5 Hz, 2H, 3,5-C$\underline{H}_{Ar}$), 3.82 (s, 3H, OC$\underline{H}_3$), 3.01 (tt, *J* = 8.5, 4.8 Hz, 1H, C$\underline{H}$NH$_2$), 2.90 – 2.77 (m, 2H, C$\underline{H}_{2a}$Ar and PhC$\underline{H}_{2a}$CH$_2$), 2.70 (ddd, *J* = 13.7, 10.0, 6.1 Hz, 1H, PhC$\underline{H}_{2b}$CH$_2$), 2.47 (dd, *J* = 13.5, 8.6 Hz, 1H, C$\underline{H}_{2b}$Ar), 1.85 (dddd, *J* = 13.5, 10.6, 6.1, 4.8 Hz, 1H, PhCH$_2$C$\underline{H}_{2a}$), 1.68 (dddd, *J* = 13.5, 10.0, 7.8, 5.9 Hz, 1H, PhCH$_2$C$\underline{H}_{2b}$), 1.30 (br s, 2H, NH$_2$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 158.2 (1C, 4-$\underline{C}_{Ar}$), 142.3 (1C, $\underline{C}_{Ph}$), 131.5 (1C, $\underline{C}_{Ar}$), 130.3 (2C, 2,6-$\underline{C}H_{Ar}$), 128.5, 128.5 and 125.9 (5C, $\underline{C}H_{Ph}$), 114.0 (2C, 3,5-$\underline{C}H_{Ar}$), 55.3 (1C, O$\underline{C}$H$_3$), 52.5 (1C, $\underline{C}$HNH$_2$), 43.9 (1C, $\underline{C}$H$_2$Ar), 39.4 (1C, PhCH$_2\underline{C}$H$_2$), 32.8 (1C, Ph$\underline{C}$H$_2$CH$_2$) ppm.

FTIR (ATR): 3332 (w), 3173 (br), 2912 (br), 1609 (m), 1582 (w), 1509 (s), 1452 (m), 1296 (w), 1244 (s), 1174 (m), 1105 (w), 1032 (s), 808 (m), 740 (s), 696 (s), 602 (w) cm^{-1}.

HRMS (ESI): m/z calcd for $C_{17}H_{22}NO^+$ $[M+H]^+$: 256.1696, found 256.1691.

Hydrogenation to nitro compound 7 (Scheme 6, Part C):



1-Methoxy-4-(2-nitro-4-phenylbutyl)benzene 7

To a stirred solution of nitrocyclopropane **1h** (43 mg, 0.15 mmol) in 1 mL of MeOH PtO_2 (10 mg) was added. Resulted mixture was hydrogenated under atmospheric pressure (balloon) of H_2 for 2h. After that solid catalyst was filtered off. The solvent was evaporated and the crude product was purified by flash column chromatography (eluent PE/EtOAc, 20:1) to give pure nitro compound **7**, yield – 29 mg (67%). Colorless oil. R_f = 0.62 (PE/EtOAc = 5:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$, COSY): δ 7.37 – 7.22 (m, 3H, C$\underline{H}_{Ph}$), 7.20 – 7.14 (m, 2H, C$\underline{H}_{Ph}$), 7.07 (d, *J* = 8.6 Hz, 2H, C$\underline{H}_{Ar}$), 6.85 (d, *J* = 8.6 Hz, 2H, C$\underline{H}_{Ar}$), 4.69 (dddd, *J* = 9.8, 8.5, 5.9, 3.9 Hz, 1H, C$\underline{H}$NO$_2$), 3.81 (s, 3H, OC$\underline{H}_3$), 3.24 (dd, *J* = 14.3, 8.5 Hz, 1H, C$\underline{H}_{2a}$Ar), 3.01 (dd, *J* = 14.3, 5.9 Hz, 1H, C$\underline{H}_{2b}$Ar),

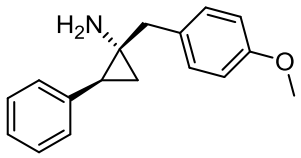
2.73 (ddt, *J* = 13.4, 9.3, 4.6 Hz, 1H, PhC$\underline{H}_{2a}$CH$_2$), 2.66 – 2.57 (m, 1H, PhC$\underline{H}_{2b}$CH$_2$), 2.46 – 2.27 (m, 1H, PhCH$_2$C$\underline{H}_{2a}$), 2.17 – 1.95 (m, 1H, PhCH$_2$C$\underline{H}_{2b}$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 159.0 (1C, 4-$\underline{C}_{Ar}$), 139.8 (1C, $\underline{C}_{Ph}$), 127.4 (1C, $\underline{C}_{Ar}$), 130.0 (2C, $\underline{C}H_{Ar}$), 128.8 and 128.5 (4C, $\underline{C}H_{Ph}$), 126.6 (1C, $\underline{C}H_{Ph}$), 114.3 (2C, $\underline{C}H_{Ar}$), 89.5 (1C, $\underline{C}HNO_2$), 55.4 (1C, O$\underline{C}H_3$), 39.4 (1C, $\underline{C}H_2$Ar), 35.0 (1C, PhCH$_2\underline{C}H_2$), 32.1 (1C, PhCH$_2\underline{C}H_2$) ppm.

FTIR (ATR): 2996 (br), 2927 (br), 2833 (w), 1611 (w), 1544 (s), 1509 (s), 1450 (m), 1379 (m), 1302 (m), 1245 (s), 1179 (s), 1110 (m), 1034 (s), 836 (m), 745 (s), 699 (s) 595 (w) cm^{-1}.

HRMS (ESI): m/z calcd for $C_{17}H_{19}NaNO_3^+$ [M+Na]$^+$: 308.1257, found 308.1256.

Reduction to amino cyclopropane 8 (Scheme 6, Part D):



***Rel* (*1S*,*2S*)-1-(4-methoxybenzyl)-2-phenylcyclopropan-1-amine 8**

To a stirred solution of nitrocyclopropane **1h** (28 mg, 0.1 mmol, 1 equiv.) in 1 mL of MeOH 1M aq. HCl (2 mL, 2 mmol, 20 equiv.) was added followed by Zn dust (activated[19] by consecutive washing with 1M aq. HCl, water, EtOH and Et_2O prior to use) (130 mg, 2 mmol, 20 equiv.) in one portion. Reaction mixture was stirred for 14h, diluted with 10 mL of CH_2Cl_2 and washed with 10 mL of saturated aq. solution of $NaHCO_3$. Aqueous phase was washed with 10 mL of CH_2Cl_2. Combined organic phase was dried over anhydrous Na_2SO_4. Then the solvent was evaporated, and crude material was purified by flash column chromatography (EtOAc) to give pure amino cyclopropane **8**, yield – 17 mg (68%). Colorless oil. R_f = 0.50 (EtOAc, ninhydrin).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 – 7.20 (m, 5H, C$\underline{H}_{Ph}$), 6.99 (d, *J* = 8.6 Hz, 2H, 2,6-C$\underline{H}_{Ar}$), 6.82 (d, *J* = 8.6 Hz, 2H, 3,5-C$\underline{H}_{Ar}$), 3.80 (s, 3H, OC$\underline{H}_3$), 2.60 (dd, *J* = 14.7, 1.2 Hz, 1H, C$\underline{H}_{2a}$Ar), 2.38 – 2.30 (m, 2H, C$\underline{H}_{2b}$Ar and C$\underline{H}$Ph), 1.66 (br s, 2H, N$\underline{H}_2$), 1.31 – 1.21 (m, 1H, C$\underline{H}_{2a}$), 1.16 (ddd, *J* = 9.2, 5.3, 1.0 Hz, 1H, C$\underline{H}_{2b}$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, HSQC): δ 158.3 (1C, 4-$\underline{C}_{Ar}$), 139.2 (1C, $\underline{C}_{Ph}$), 131.4 (1C, $\underline{C}_{Ar}$), 130.3 (2C, $\underline{C}H_{Ar}$), 128.8, 128.3 and 126.1 (5C, $\underline{C}H_{Ph}$), 113.9 (2C, $\underline{C}H_{Ar}$), 55.4 (1C, O$\underline{C}H_3$), 41.5 (1C, $\underline{C}NH_2$), 40.5 (1C, $\underline{C}H_2$Ar), 31.8 (1C, $\underline{C}$HPh), 19.0 (1C, $\underline{C}H_2$) ppm.

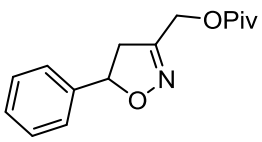
FTIR (ATR): 1709 (w), 1511 (w), 1052 (br s), 795 (br m), 699 (w) cm^{-1}.

HRMS (ESI): m/z calcd for $C_{17}H_{20}NO^+$ [M+H]$^+$: 254.1539, found 254.1540.

Cyclopropane – *N*-oxide rearrangement (Scheme 6, Part E):

To a mixture of nitro cyclopropane **1d** (57 mg, 0.3 mmol, 1 equiv.), $Yb(OTf)_3 \cdot 6H_2O$ (66 mg, 0.09 mmol, 0.3 equiv.) and MS4Å (90 mg) 0.6 mL of CH_2Cl_2 was added under Ar atmosphere at rt. The mixture was stirred for 14h. After that the reaction mass was diluted with 25 mL of EtOAc and washed with 25 mL of Brine. Aqueous layer was back extracted with 25 mL of EtOAc. Combined organic phase was dried over anhydrous Na_2SO_4. The solvent was evaporated, and crude material was purified by flash column chromatography (eluent PE/EtOAc, 2:1) to give pure isoxazoline *N*-oxide **2d**, yield – 50 mg (88%).

Acylation of *N*-oxide 2c (Scheme 6, Part F):



(5-Phenyl-4,5-dihydroisoxazol-3-yl)methyl pivalate 9 and 3-Methyl-5-phenylisoxazole 10

To a stirred solution of isoxazoline *N*-oxide **2c** (177 mg, 1 mmol, 1 equiv.) in 2 mL of CH_2Cl_2 Et_3N (417 µL, 303 mg, 3 mmol, 3 equiv.) and PivCl (246 µL, 241 mg, 2 mmol, 2 equiv.) were added at -15 °C. Reaction mixture was warmed up to rt and stirred for 72h. Then the mixture was diluted with 50 mL of EtOAc and washed with 50 mL of 0.25M aq. solution of $NaHSO_4$. Aqueous layer was back extracted with 25 mL of EtOAc. Combined organic layers were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude material was subjected to column chromatography (eluent PE/EtOAc, 4:1) to give target isoxazoline **9** (217 mg, 83%) and isoxazole **10** (20 mg, 13%) as colorless oils.

Isoxazoline 9:

R_f = 0.49 (PE/EtOAc = 3:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 – 7.28 (m, 5H, C$\underline{H}_{Ph}$), 5.63 (dd, *J* = 11.1, 8.3 Hz, 1H, C$\underline{H}$Ph), 4.90 (s, 2H, C$\underline{H}_2$OPiv), 3.42 (dd, *J* = 17.3, 11.1 Hz, 1H, C$\underline{H}_{2a}$), 2.97 (dd, *J* = 17.3, 8.3 Hz, 1H, C$\underline{H}_{2b}$), 1.21 (s, 9H, C$\underline{Me}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT): δ 177.9 (1C, $\underline{C}$=O), 154.4 (1C, $\underline{C}$=N), 140.6 (1C, $\underline{C}_{Ph}$), 128.9, 128.4 and 125.6 (5C, $\underline{C}H_{Ph}$), 82.5 (1C, $\underline{C}$HPh), 58.7 (1C, $\underline{C}H_2$OPiv), 43.3 (1C, $\underline{C}H_2$), 39.0 (1C, $\underline{C}Me_3$), 27.2 (3C, C$\underline{Me}_3$) ppm.

FTIR (ATR): 2972 (w), 1731 (s), 1479 (w), 1397 (w), 1278 (m), 1137 (s), 1031 (w), 885 (br m), 757 (m), 697 (m) cm^{-1}.

HRMS (ESI): m/z calcd for $C_{15}H_{20}NO_3^+$ $[M+H]^+$: 262.1438, found 262.1442.

Isoxazole 10:

R_f = 0.49 (PE/EtOAc = 3:1, anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$, characteristic signals): δ 7.77 – 7.73 (m, 2H, C$\underline{H}_{Ph}$), 6.36 (s, 1H, 4-C$\underline{H}$), 2.35 (s, 3H, C$\underline{H}_3$) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, DEPT, characteristic signals) δ 160.4 (1C, 5-$\underline{C}$), 130.1 and 129.0 (4C, $\underline{C}H_{Ph}$), 100.3 (4-$\underline{C}$H), 11.6 (1C, $\underline{C}H_3$) ppm.

NMR spectra were in accordance with literature data.[20]

8. DFT calculations

DFT calculations were performed with the Gaussian 16 Rev C.01.[21] M11 DFT functional with cc-pvdz+d basis set was used for geometry optimization, calculations of thermodynamics and kinetics. Calculations were performed in gas phase, 2,2,2-trifluoroethanol or ethyl acetate (SMD model). The approach of Martin and co-workers was followed for free energy correction in solution,[22,23] particularly, pressures of p = 251 and 336 atm were used for solvents EtOAc and TFE, respectively. Cartesian coordinates are given in angstroms; absolute energies for all substances are given in hartrees. Analysis of vibrational frequencies was performed for all optimized structures. All compounds, except transition state structures, were characterized by only real vibrational frequencies. TS were characterized by one imaginary frequency. Wavefunction stability, using stable keyword, was also checked for each molecule.

For calculations of optimized geometries, frequencies and thermodynamics, following keywords were used (calculations in 2,2,2-trifluoroethanol as an example):

 # opt=calcfc freq cc-pvdz+d m11 scf=xqc nosymm scrf=(smd,solvent=2,2,2-TriFluoroEthanol) pressure=336 test

The same parameters were calculated for transition state structures with keywords:

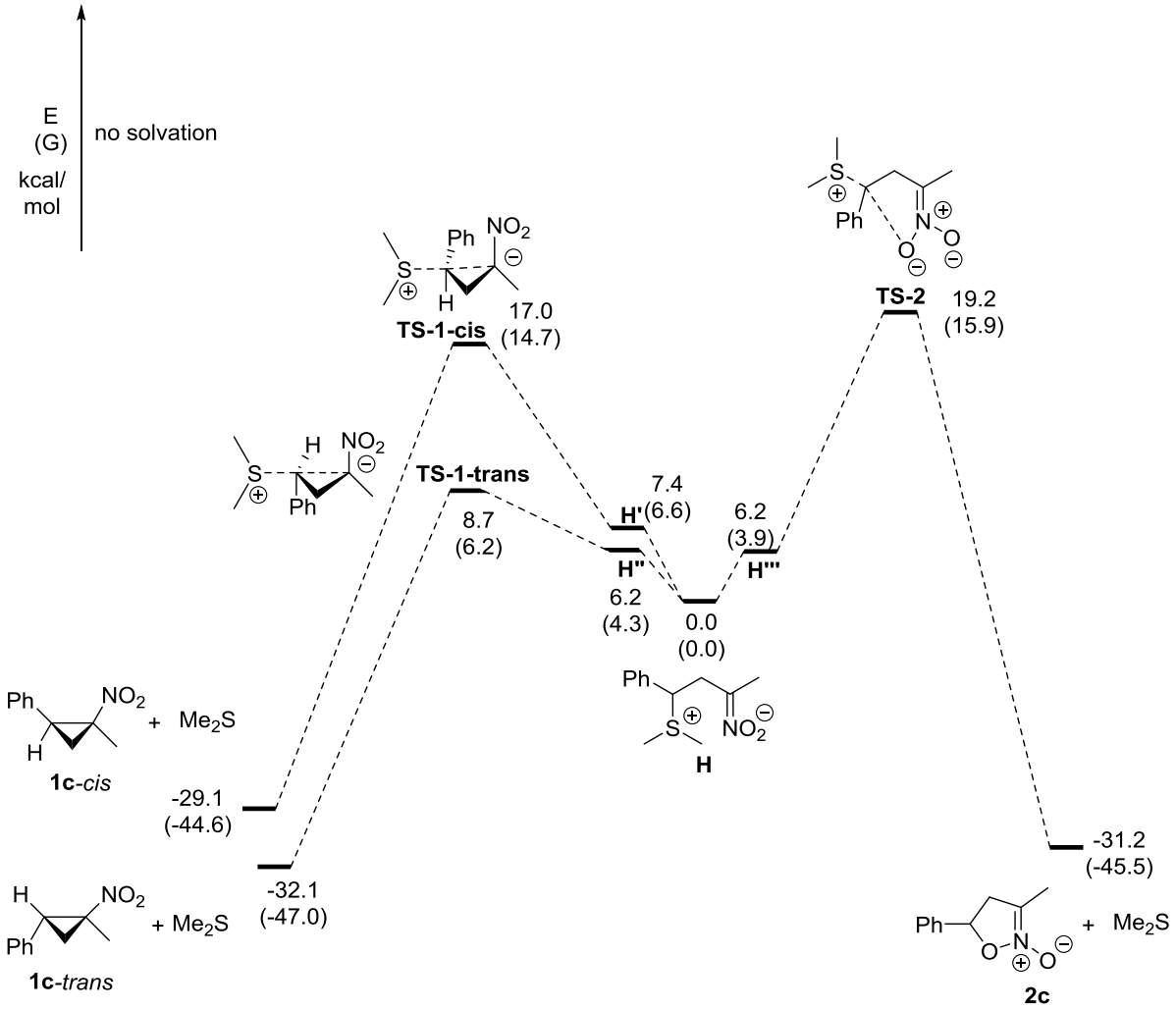
 # opt=(calcfc,ts,noeigentest) freq scf=xqc cc-pvdz+d m11 nosymm scrf=(smd,solvent=2,2,2-TriFluoroEthanol) pressure=336 test

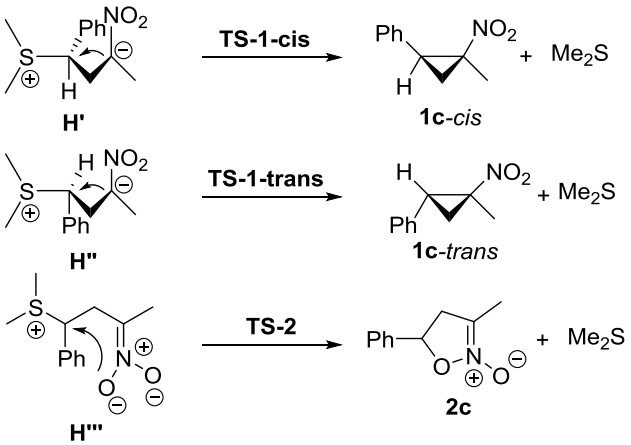
IRC calculation was performed for TS and proved that TS connects products and reactants:

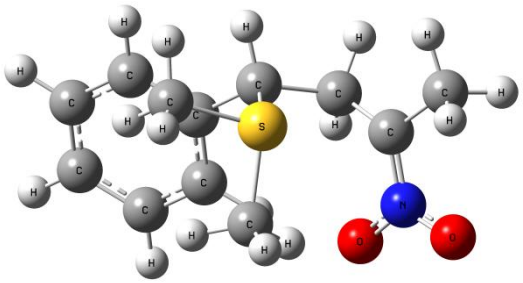
 # irc=(forward,calcfc,maxcycle=150,MaxPoints=10,HPC) scf=xqc cc-pvdz+d m11 nosymm scrf=(smd,solvent=2,2,2-TriFluoroEthanol) pressure=336 test

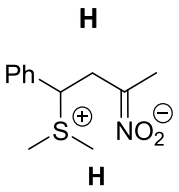
 # irc=(reverse,calcfc,maxcycle=150,MaxPoints=10,HPC) scf=xqc cc-pvdz+d m11 nosymm scrf=(smd,solvent=2,2,2-TriFluoroEthanol) pressure=336 test

8.1 Calculations in gas phase









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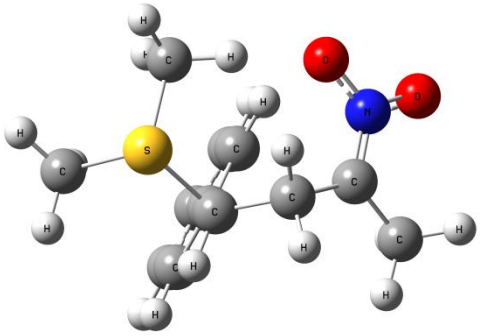
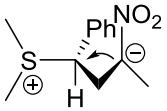
C -1.63163800 4.47070200 -1.33943300
C -2.34749600 3.15882500 -1.42879000
C -3.12958500 2.77153200 -0.13226700
N -0.31119100 4.45107900 -1.04434500
O 0.36347700 5.49073100 -1.13099100
O 0.21636500 3.36645500 -0.60253200
S -2.85990700 4.19535200 1.03279400
H -4.22449500 2.84185400 -0.28525300
C -3.97635000 3.69211700 2.37308000
C -1.27996100 3.90721300 1.83706400
H -1.93580300 6.60204500 -1.24497600
H -1.70904400 5.99134000 -2.89104900
H -3.26217900 5.68585500 -2.04083800
H -1.62300900 2.35739000 -1.64468500
H -5.01319800 3.75597500 2.00207100
H -3.83799500 4.41445500 3.19433100
H -3.74360700 2.66785400 2.71025500
H -0.52417300 3.65767400 1.04997300
H -1.01796400 4.85068600 2.34281000
H -1.39130500 3.07830000 2.55494500
H -3.08267600 3.18656300 -2.25355500
C -2.80838500 1.43789000 0.49517200
C -1.48366700 0.98365900 0.56012600
C -3.83793100 0.64043800 1.01038900
C -1.20518900 -0.24723300 1.15268500
H -0.68242200 1.60789700 0.13396100
C -3.55395900 -0.59166800 1.59756400
H -4.87971700 0.98466100 0.93765800
C -2.23364000 -1.03413900 1.67298900
H -0.16756800 -0.59871900 1.20032800
H -4.36863800 -1.21187700 1.98995000
H -2.00594600 -2.00400900 2.13154000

DFT M11; cc-pvdz+d, gas phase
Total electronic energy= -1070.371148 E_0
Sum of electronic and zero-point Energies= -1070.100177 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.083679 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.082735 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.143610 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.270971
Number of imaginary vibrational frequencies = 0



Pre-reaction conformation **H'**

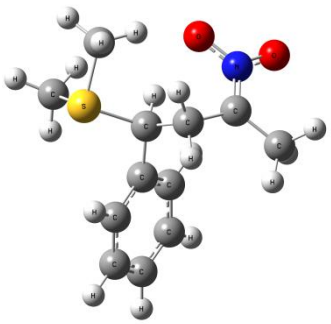


H'

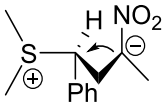
Charge 0; multiplicity 1

C 0.81791500 -1.97173700 0.23759300
C 2.10553200 -1.94778900 0.99593500
H 2.07295300 -1.20307600 1.81906600
H 2.95044700 -1.69916400 0.32793900
H 2.30233900 -2.92453600 1.47636600
C 0.66232000 -1.53466000 -1.17057400
H -0.18251400 -2.09034800 -1.61884800
H 1.57152000 -1.78765400 -1.74559100
C 0.44226500 0.01937300 -1.39356700
H 1.22034500 0.39956200 -2.08284200
C 0.39091200 0.93201500 -0.19357500
C -0.42793600 0.67037500 0.91649600
H -1.07164700 -0.21969900 0.94629100
C -0.41878000 1.55023000 1.99785000
H -1.04869800 1.32941200 2.86744800
C 0.39229700 2.68584600 1.99019600
H 0.39596000 3.36485200 2.85142000
C 1.20697000 2.94841000 0.89064100
H 1.85599100 3.83202300 0.87868400
C 1.20498800 2.07160700 -0.19342300
H 1.86343700 2.26742900 -1.05184700
N -0.27899600 -2.31084700 0.91875400
O -1.44065500 -2.23750900 0.34474200
O -0.20469600 -2.63956100 2.11969400
S -1.05256800 0.20733500 -2.47039500
C -1.20171100 1.98942200 -2.65055700
H -2.13239100 2.19014200 -3.20586300
H -1.22232100 2.45358400 -1.64979900
H -0.33542500 2.34988800 -3.22950000
C -2.43316900 -0.19281500 -1.40208700
H -2.09939700 -1.07904500 -0.78529400
H -2.64151800 0.66905800 -0.74722100
H -3.29061600 -0.42736500 -2.05260900

DFT M11; cc-pvdz+d, gas phase
Total electronic energy= -1070.359276 E_0
Sum of electronic and zero-point Energies= -1070.088755 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.072102 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.071158 $E_0 + H_{corr}$
Zero-point correction (*unscaled*) = 0.270521
Number of imaginary vibrational frequencies = 0



Pre-reaction conformation **H''**



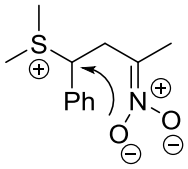
H"

Charge 0; multiplicity 1

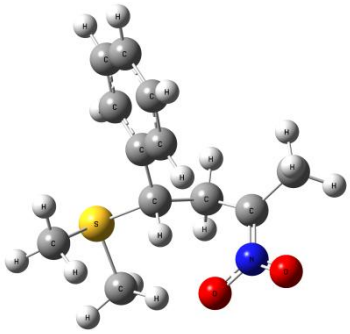
C 1.12238300 -0.74779800 -1.67366400
C 2.43350400 -1.42863100 -1.44777400
N 0.14139900 -1.46645100 -2.23651700
C 0.75482300 0.62505000 -1.21571700
O -1.02716500 -0.92611800 -2.39300400
O 0.33439200 -2.65215600 -2.57304600
C -0.29704400 0.43261900 -0.09608100
S -1.50278500 1.83784000 -0.03094100
C -2.81669400 1.01949600 0.88699900
C -2.16099500 1.76319100 -1.71740000
H 2.30640700 -2.36360800 -0.86534100
H 2.90163200 -1.73372300 -2.40436100
H 3.13129200 -0.76347200 -0.90825000
H 0.32385500 1.22187000 -2.04522400
H -2.41517800 0.79574000 1.88936800
H -3.67656300 1.70407500 0.96042700
H -3.08423800 0.08952800 0.35620900
H -1.71935000 2.60059600 -2.27931600
H -3.25289600 1.89353900 -1.64903000
H -1.85816200 0.77511000 -2.14259800
H 1.63373500 1.16075000 -0.81590500
C 0.28433100 0.18108200 1.26981000
C 0.46332800 -1.15051800 1.66046900
C 0.71561700 1.21050700 2.11405300
C 1.06474400 -1.44697000 2.88256600
H 0.14418700 -1.95220200 0.98000500
C 1.30242300 0.91133500 3.34272400
H 0.60380100 2.26024700 1.80728400
C 1.47819000 -0.41777900 3.72804600
H 1.21071100 -2.49331900 3.17575400
H 1.63434800 1.72357200 4.00034200
H 1.94562000 -0.65218100 4.69179300
H -0.95336200 -0.39054400 -0.43612800

DFT M11; cc-pvdz+d, gas phase
Total electronic energy= -1070.361314 E_0
Sum of electronic and zero-point Energies= -1070.090963 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.073958 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.073014 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.136775 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.270351
Number of imaginary vibrational frequencies = 0

Pre-reaction conformation **H'''**



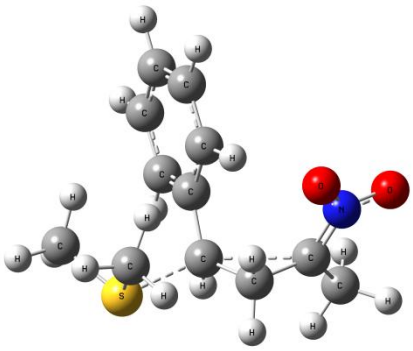
H'''



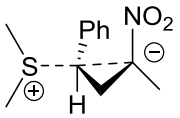
Charge 0; multiplicity 1

C -0.90499400 -1.78982500 -0.84971200
C -0.13839500 -2.33099900 -2.01289100
N -0.96977300 -2.54600400 0.25460900
C -1.50561500 -0.42630200 -0.75141100
O -1.57587100 -2.08164100 1.30296800
O -0.42386700 -3.66716800 0.29090500
C -0.66629000 0.33368400 0.30444800
S -1.68002400 1.58354700 1.22236900
H 0.89184600 -2.61553100 -1.71792200
H -0.60205000 -3.25562400 -2.40976900
H -0.08426500 -1.58500600 -2.82592000
H -2.56580200 -0.47831100 -0.42990700
H -1.45660000 0.10198700 -1.71983600
C 0.58577300 0.97253800 -0.23472100
C 1.77235600 0.23513500 -0.15715400
C 0.59062300 2.22087200 -0.86734000
C 2.94952100 0.74301400 -0.70430500
H 1.75365400 -0.75493000 0.31924300
C 1.77266800 2.73344700 -1.39976800
H -0.34046600 2.79846600 -0.95679500
C 2.95330300 1.99472200 -1.31934000
H 3.87235300 0.15365600 -0.64832000
H 1.76924800 3.71421100 -1.89013000
H 3.88123600 2.39595400 -1.74384400
C -2.96386000 0.50301800 1.90597000
H -3.12249400 0.80469600 2.95370200
H -3.88234500 0.67602800 1.32418200
H -2.59816400 -0.54742400 1.79780600
C -0.61078200 1.79555900 2.65442500
H -0.42640400 0.80295300 3.10039700
H 0.32962300 2.24029500 2.28857200
H -1.10532000 2.47329900 3.36821700
H -0.45707300 -0.39745900 1.10794100

DFT M11; cc-pvdz+d, gas phase
Total electronic energy= -1070.361297 E_0
Sum of electronic and zero-point Energies= -1070.091032 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.073954 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.073009 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.137331 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.270265
Number of imaginary vibrational frequencies = 0



TS-1-cis

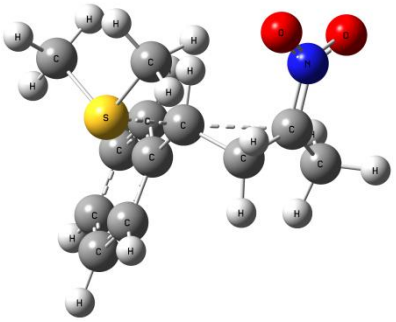


TS-1-cis

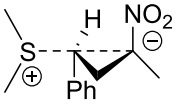
Charge 0; multiplicity 1

C 4.95385600 4.26327400 7.08152400
C 6.41154300 3.95789600 6.95636000
H 7.03442700 4.61028500 7.59940700
H 6.74295400 4.07594300 5.90688000
H 6.62800000 2.91982400 7.27703800
C 4.06277200 4.65938400 5.96328500
H 3.02507600 4.55116300 6.31608100
H 4.21337300 4.07401100 5.03015100
C 4.45257100 6.10056700 5.72830600
H 5.44639500 6.18177200 5.25159500
C 4.24574500 7.15619600 6.75667600
C 3.22410500 7.08135400 7.71540000
H 2.67641600 6.13729400 7.85605200
C 3.01557900 8.15456900 8.58245900
H 2.23210800 8.08032600 9.34593800
C 3.80888700 9.29885100 8.50593200
H 3.63595200 10.13537500 9.19370300
C 4.84718200 9.36407800 7.57411100
H 5.49715000 10.24614300 7.53139000
C 5.06397100 8.29693600 6.70873400
H 5.88946700 8.33825300 5.98348800
N 4.37942000 4.07694700 8.30423000
O 3.13258900 4.25362000 8.46114000
O 5.10314800 3.72062600 9.25002300
S 3.30867300 6.67923000 4.05688600
C 3.16111000 8.46982500 4.17759200
H 2.43283700 8.80541900 3.42026000
H 2.83934900 8.74818800 5.19631000
H 4.14901400 8.90802500 3.96324500
C 1.68479500 6.21699800 4.68013700
H 1.57809000 5.12665900 4.57194300
H 1.60639800 6.50954800 5.74267900
H 0.92262400 6.73061800 4.07158500

DFT M11; cc-pvdz+d, gas phase
Total electronic energy= -1070.344102 E_0
Sum of electronic and zero-point Energies= -1070.075322 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.058502 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.057558 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.120131 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.268780
Number of imaginary vibrational frequencies = 1; 240*i*



TS-1-trans

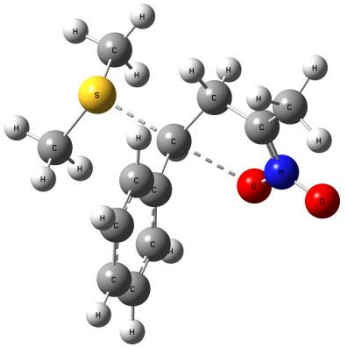


TS-1-trans

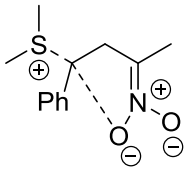
Charge 0; multiplicity 1

C 1.89765700 -0.17067200 -0.49066200
C 3.14567700 -0.83931800 -0.01762700
N 1.00299900 -0.91023100 -1.20156800
C 1.47761300 1.23080100 -0.18990700
O -0.09452900 -0.36905300 -1.55982000
O 1.25673400 -2.09769900 -1.46404800
C 0.52131500 0.84154500 0.90085100
S -0.92067500 2.34231600 1.17955900
C -2.05262100 1.33915100 2.15482400
C -1.65525200 2.17344100 -0.46335100
H 2.91300800 -1.79211700 0.49595100
H 3.81887800 -1.09652500 -0.85930400
H 3.69170000 -0.18018300 0.68132900
H 0.98280100 1.71586300 -1.04982000
H -1.61083700 1.23119900 3.15943100
H -3.02909200 1.84553300 2.22233400
H -2.16029400 0.34729600 1.67995200
H -1.28757200 3.01300000 -1.07468200
H -2.75107700 2.24282800 -0.36911600
H -1.32885900 1.20574100 -0.90387100
H 2.31141800 1.84612700 0.18701700
C 1.07337900 0.57058200 2.26464500
C 0.88055200 -0.68737100 2.84529900
C 1.78907300 1.54908300 2.96460400
C 1.40028900 -0.96547200 4.10862100
H 0.34345200 -1.46022700 2.27841100
C 2.30124500 1.27373500 4.23028600
H 1.94168500 2.53839600 2.51098300
C 2.10733300 0.01567400 4.80337600
H 1.25771000 -1.95879500 4.55031500
H 2.85971900 2.04517100 4.77368400
H 2.51580500 -0.20227900 5.79740200
H -0.21392300 0.10388700 0.54142800

DFT M11; cc-pvdz+d, gas phase
Total electronic energy= -1070.357291 E_0
Sum of electronic and zero-point Energies= -1070.088287 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.071327 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.070383 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.133676 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.269005
Number of imaginary vibrational frequencies = 1; 357*i*



TS-2

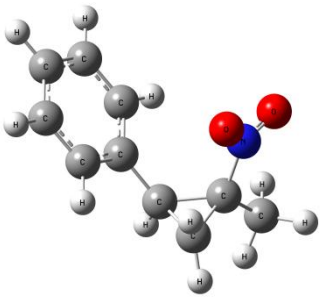


TS-2

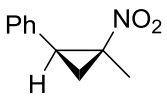
Charge 0; multiplicity 1

C 2.13020500 -0.59548500 -0.37052400
C 1.88233300 -0.79376400 -1.82646000
N 3.05924400 -1.30739200 0.26628000
C 1.33159100 0.30037100 0.52144400
O 3.19073900 -1.06379000 1.54044600
O 3.79231400 -2.15003600 -0.28111600
C 2.24641000 0.94641100 1.56303700
S 1.16591700 2.69952400 2.07557200
H 2.71594900 -1.39378700 -2.22499100
H 0.93825500 -1.33717600 -2.04167700
H 1.83961000 0.17037800 -2.37305200
H 0.52900200 -0.24033700 1.07309800
H 0.84232300 1.07798000 -0.09945900
C 3.53124600 1.57367500 1.11385000
C 4.70414000 1.34735900 1.83894300
C 3.55890000 2.40260900 -0.01152600
C 5.88800000 1.97425800 1.45835300
H 4.68053100 0.62460500 2.66288200
C 4.74580600 3.02588500 -0.39347500
H 2.64238200 2.55753500 -0.59833600
C 5.90927400 2.81897300 0.34711900
H 6.80884200 1.78569300 2.02282800
H 4.76354600 3.66949100 -1.28081700
H 6.84468200 3.30546800 0.04553300
C -0.13674300 1.94236100 3.06051200
H -0.64195200 2.71417300 3.66396400
H -0.85771300 1.49249200 2.35871300
H 0.29374100 1.15884400 3.70891200
C 2.25482500 3.30406700 3.37267100
H 2.58781500 2.45716800 3.99922500
H 3.12564000 3.75742400 2.87074700
H 1.72562800 4.05887800 3.97665000
H 2.23184600 0.54470800 2.58312300

DFT M11; cc-pvdz+d, gas phase
Total electronic energy= -1070.340495 E_0
Sum of electronic and zero-point Energies= -1070.072411 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.055194 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.054250 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.118245 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.268083
Number of imaginary vibrational frequencies = 1; 396*i*



1c-*cis*

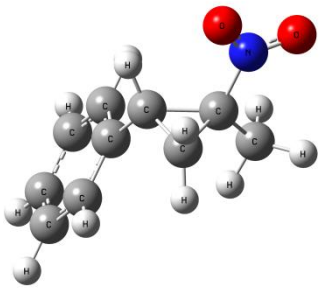


1c-*cis*

Charge 0; multiplicity 1

C 1.24129500 -1.89241200 0.43294300
C 2.31193800 -2.63000700 -0.32549100
H 3.22019400 -2.01442600 -0.42311500
H 1.93181900 -2.87957100 -1.33047400
H 2.58310900 -3.56675800 0.19126000
C -0.22574900 -2.14206700 0.23606600
H -0.83737400 -2.08228100 1.14245400
H -0.49813400 -2.91206500 -0.49369500
C 0.37156400 -0.84989000 -0.24772000
H 0.57764100 -0.78025500 -1.32548000
C 0.05351500 0.45913800 0.41153800
C -1.26377500 0.80322600 0.71880900
H -2.06998400 0.08938600 0.50575700
C -1.55383200 2.03917700 1.29474400
H -2.59206400 2.29935100 1.53351500
C -0.52599000 2.93925600 1.57226300
H -0.75296300 3.90940200 2.03018700
C 0.79340600 2.59850100 1.27351200
H 1.60735000 3.29759300 1.49954700
C 1.08096900 1.36515400 0.69353900
H 2.12131100 1.08879100 0.47210500
N 1.64600200 -1.53066300 1.81838900
O 0.77795100 -1.27088000 2.62411500
O 2.84170200 -1.48554400 2.03548600

DFT M11; cc-pvdz+d, gas phase
Total electronic energy= -592.481950 E_0
Sum of electronic and zero-point Energies= -592.288658 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -592.277294 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -592.276349 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -592.327181 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.193292
Number of imaginary vibrational frequencies = 0



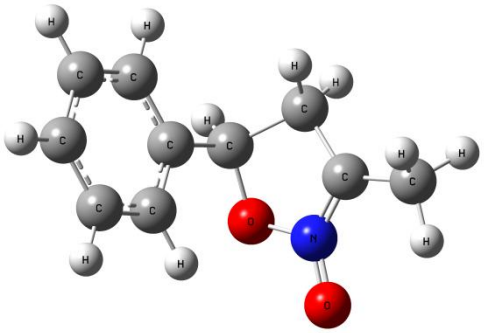
1c-*trans*

1c-*trans*

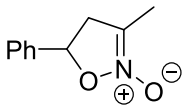
Charge 0; multiplicity 1

C 1.10326900 -0.75978700 -1.47317500
C 2.45236800 -1.31648000 -1.11468600
N 0.43659000 -1.47126200 -2.59413800
C 0.78060300 0.70997500 -1.40215200
O -0.64881500 -1.06021600 -2.96077100
O 1.02030500 -2.42297800 -3.06890900
C 0.13083200 -0.23129000 -0.43353800
H 2.36922400 -2.36868000 -0.79356600
H 3.13244000 -1.27248100 -1.98131400
H 2.87529700 -0.72575300 -0.28518800
H 0.15459500 1.11047700 -2.20512900
H 1.59681900 1.34943100 -1.04566400
C 0.52600500 -0.28957600 1.00955600
C 0.45316800 -1.50813100 1.69572700
C 0.96665100 0.84624000 1.69211500
C 0.81855800 -1.58884300 3.03682600
H 0.10653200 -2.40430500 1.16355500
C 1.33246400 0.76795000 3.03656400
H 1.01311000 1.80845300 1.16626300
C 1.26154000 -0.44934000 3.71075700
H 0.75881400 -2.54985200 3.56170900
H 1.67318200 1.66842800 3.56165700
H 1.55005700 -0.51186800 4.76678100
H -0.91539800 -0.47262900 -0.66159200

DFT M11; cc-pvdz+d, gas phase
Total electronic energy= -592.486656 E_0
Sum of electronic and zero-point Energies= -592.292973 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -592.281758 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -592.280813 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -592.330926 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.193683
Number of imaginary vibrational frequencies = 0



2c



2c

Charge 0; multiplicity 1

C -0.70126000 -1.90905400 -1.33021100
C -0.94260900 -2.55017500 -2.65122800
N 0.01312900 -2.52011000 -0.42690300
C -1.18581100 -0.59279200 -0.80690000
O 0.10074700 -1.74761900 0.77494100
O 0.59504100 -3.59340100 -0.40799100
C -0.22704900 -0.41276800 0.38925700
H -0.42331400 -3.52128800 -2.67281200
H -2.02272100 -2.71459500 -2.82029400
H -0.56388600 -1.91612000 -3.47333100
H -2.24764900 -0.64617900 -0.49643000
H -1.07497200 0.22234800 -1.54250700
C 1.02625900 0.35306200 -0.00156500
C 2.24435000 -0.30725100 -0.16901400
C 0.95157200 1.73236400 -0.21572000
C 3.37568300 0.41094200 -0.55922400
H 2.30360400 -1.38800300 0.01244800
C 2.08316500 2.44801800 -0.59915400
H -0.00572500 2.25483600 -0.07635400
C 3.29943500 1.78569300 -0.77408900
H 4.32966900 -0.11332700 -0.69255300
H 2.01725200 3.53090000 -0.75943200
H 4.19209700 2.34649700 -1.07592000
H -0.71881100 0.05536500 1.25847700

DFT M11; cc-pvdz+d, gas phase
Total electronic energy= -592.485295 E_0
Sum of electronic and zero-point Energies= -592.290918 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -592.279925 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -592.278981 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -592.328560 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.194376
Number of imaginary vibrational frequencies = 0

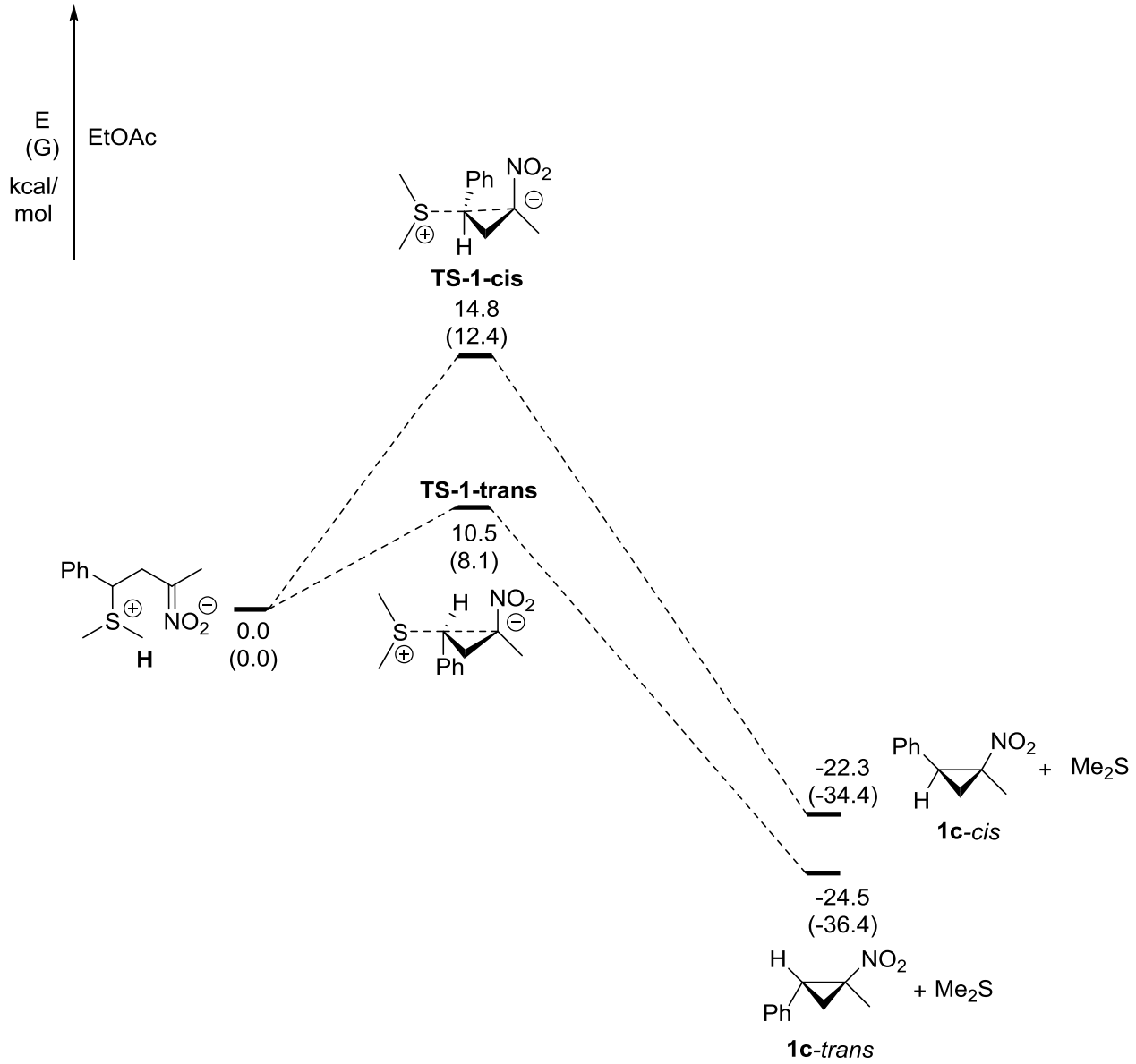
Me_2S

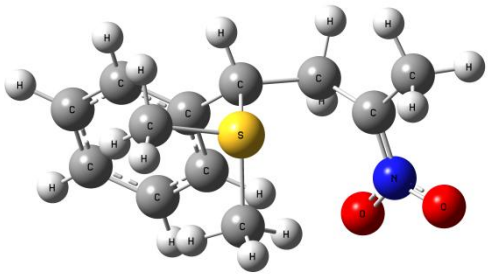
Charge 0; multiplicity 1

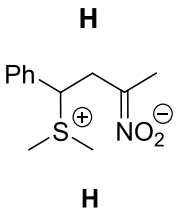
S -1.93670700 2.57604300 0.01958500
C -2.64414300 1.35277000 1.14530600
C -2.61482800 1.93464200 -1.52743100
H -2.31484100 1.61211100 2.16509800
H -3.74777400 1.37500200 1.11102800
H -2.28486000 0.33708000 0.90249000
H -2.26357900 2.59156000 -2.34029100
H -3.71901600 1.94742600 -1.51097000
H -2.25753800 0.90756700 -1.72009200

DFT M11; cc-pvdz+d, gas phase
Total electronic energy= -477.935584 E_0
Sum of electronic and zero-point Energies= -477.860500 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -477.855594 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -477.854650 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -477.887552 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.075084
Number of imaginary vibrational frequencies = 0

8.2 Calculations of competitive formation of *cis*- and *trans*- nitrocyclopropanes 1c in EtOAc



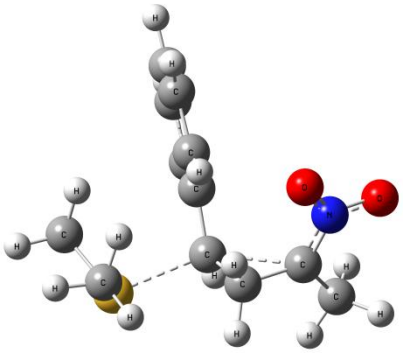




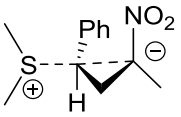
Charge 0; multiplicity 1

C -2.18092600 5.73422300 -1.92447400
C -1.59435500 4.44825700 -1.43128200
C -2.32640800 3.14301500 -1.42783500
C -3.10640500 2.78729000 -0.11829700
N -0.29908200 4.46226800 -1.10075700
O 0.36490000 5.52876400 -1.18597500
O 0.26912200 3.39268600 -0.65389900
S -2.86253700 4.18308000 1.07429800
H -4.19800300 2.86088200 -0.28381000
C -3.99990300 3.72282900 2.38975400
C -1.28509900 3.88007600 1.87218900
H -2.01377700 6.55395100 -1.19840300
H -1.71608800 6.06815600 -2.87500300
H -3.26847600 5.62547500 -2.08949700
H -1.60902900 2.33041700 -1.62360700
H -5.02743100 3.79419200 1.99449100
H -3.86421800 4.46049000 3.19873600
H -3.77800700 2.70472500 2.75103800
H -0.52389100 3.69577700 1.08058100
H -1.04939500 4.79509800 2.44164000
H -1.38059000 3.01077700 2.54395100
H -3.07208800 3.14036100 -2.24292700
C -2.79442800 1.44631100 0.50063500
C -1.47376400 0.97913200 0.56065200
C -3.83060200 0.65820100 1.01595200
C -1.20261000 -0.25962100 1.14100500
H -0.66860600 1.60332800 0.14241000
C -3.55512400 -0.58264700 1.59138400
H -4.86674400 1.01979800 0.95386900
C -2.23900400 -1.04116300 1.65675400
H -0.16798800 -0.62190100 1.18576000
H -4.37452400 -1.19671200 1.98504800
H -2.01965700 -2.01756000 2.10669100

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1070.402777 E_0
Sum of electronic and zero-point Energies= -1070.131560 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.115083 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.114138 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.169911 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.271217
Number of imaginary vibrational frequencies = 0



TS-1-cis

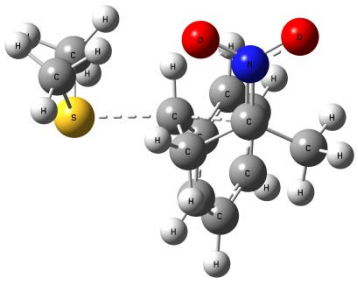


TS-1-cis

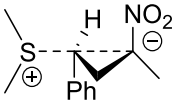
Charge 0; multiplicity 1

C 5.01779200 4.26286700 7.09852000
C 6.40758600 3.84256700 6.74085900
H 7.17334400 4.50256700 7.19305200
H 6.53785300 3.85087900 5.64324600
H 6.62664900 2.81940700 7.10703300
C 3.96406100 4.60763700 6.09571800
H 2.95866600 4.53992700 6.53631700
H 4.03350600 4.00515100 5.17140400
C 4.43986900 6.00694900 5.88570400
H 5.42540600 6.06298900 5.39737800
C 4.19762300 7.09885600 6.85211600
C 3.05205000 7.15328900 7.66059500
H 2.34370200 6.32048600 7.66495700
C 2.83106900 8.26102200 8.48061400
H 1.93464700 8.29579400 9.11188200
C 3.74605700 9.31289200 8.50983800
H 3.56718700 10.17777600 9.16091300
C 4.89517300 9.26119900 7.71499700
H 5.62203700 10.08223100 7.74126600
C 5.11467200 8.16378200 6.88985200
H 6.01182500 8.11933000 6.25638000
N 4.69972100 4.31804700 8.42117300
O 3.53233400 4.62071600 8.78578700
O 5.59005900 4.04929100 9.26170400
S 3.33895400 6.71139100 4.02875700
C 3.17392600 8.48925600 4.25251500
H 2.47179500 8.87548500 3.49347100
H 2.80452400 8.70941900 5.27020500
H 4.16664200 8.94477000 4.10004200
C 1.67999100 6.19659600 4.49586000
H 1.61540800 5.10296200 4.37266100
H 1.47709000 6.48011000 5.54351400
H 0.95435700 6.68356200 3.82221000

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1070.379180 E_0
Sum of electronic and zero-point Energies= -1070.110758 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.093766 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.092822 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.150181 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.268422
Number of imaginary vibrational frequencies = 1; 444*i*



TS-1-trans

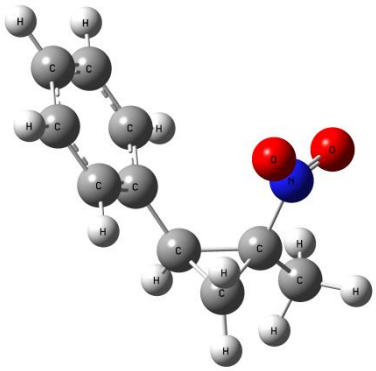


TS-1-trans

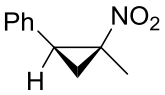
Charge 0; multiplicity 1

C 1.91861100 -0.13801500 -0.46804100
C 3.17783300 -0.73862800 0.06361900
N 1.10235100 -0.92717400 -1.22303600
C 1.44596600 1.26307300 -0.22872700
O 0.00952700 -0.45797000 -1.65848300
O 1.44114400 -2.10683700 -1.46028600
C 0.55572800 0.78427500 0.86137000
S -0.99289000 2.35614600 1.24137700
C -2.10975800 1.28732700 2.16258100
C -1.71256900 2.21952200 -0.40580200
H 2.97476900 -1.66339800 0.63845100
H 3.87108200 -1.02002800 -0.75400800
H 3.69272400 -0.01836800 0.72347200
H 0.90810900 1.68336500 -1.09290300
H -1.72337300 1.20657200 3.19269700
H -3.11645000 1.73813000 2.18018100
H -2.14765600 0.28879400 1.68909400
H -1.29372000 3.03132900 -1.02367700
H -2.80588400 2.34660100 -0.33381800
H -1.45149900 1.23575800 -0.84557900
H 2.25088600 1.92911500 0.11806600
C 1.10517900 0.52388100 2.22152200
C 0.76227500 -0.66168800 2.88352700
C 1.95425300 1.44326500 2.85198000
C 1.26921800 -0.93050100 4.15479000
H 0.10468900 -1.38561000 2.38291000
C 2.45582200 1.17610100 4.12379300
H 2.21608800 2.38192700 2.34511400
C 2.11575500 -0.01168800 4.77620600
H 1.00347200 -1.86601800 4.66219300
H 3.11821900 1.90134500 4.61223400
H 2.51459000 -0.22132600 5.77650400
H -0.22918200 0.09215000 0.51920700

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1070.385997 E_0
Sum of electronic and zero-point Energies= -1070.117206 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.100243 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.099299 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.157059 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.268791
Number of imaginary vibrational frequencies = 1; 519*i*



1c-*cis*

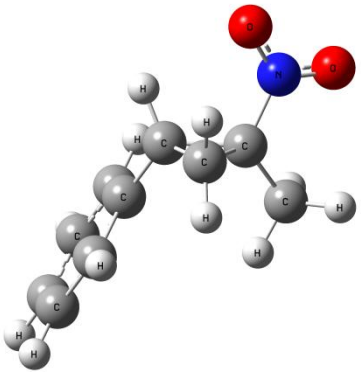


1c-*cis*

Charge 0; multiplicity 1

C 1.22748900 -1.90325400 0.44213500
C 2.32445500 -2.63482900 -0.28119000
H 3.24151400 -2.02554000 -0.33531500
H 1.98244400 -2.85976400 -1.30543800
H 2.56370500 -3.58582200 0.22627300
C -0.23107500 -2.12419900 0.15723900
H -0.89671500 -2.08513100 1.02598600
H -0.46357300 -2.87405400 -0.60673300
C 0.40424000 -0.83188200 -0.26244800
H 0.68391800 -0.74648000 -1.32192400
C 0.07403200 0.47181000 0.40092000
C -1.22873900 0.76664500 0.81005900
H -2.02084700 0.01951700 0.66905100
C -1.52406200 1.99844000 1.39495800
H -2.55117600 2.21905000 1.71167300
C -0.51609800 2.94523000 1.58106700
H -0.74729900 3.91231600 2.04474100
C 0.78885300 2.65559400 1.17790700
H 1.58735200 3.39351500 1.32527200
C 1.08123200 1.42593700 0.58936800
H 2.10922500 1.19650200 0.27576200
N 1.55824700 -1.58335800 1.85141400
O 0.65778000 -1.27563800 2.60778300
O 2.73500000 -1.62245100 2.16169300

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -592.498252 E_0
Sum of electronic and zero-point Energies= -592.305119 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -592.293856 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -592.292912 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -592.337878 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.193132
Number of imaginary vibrational frequencies = 0



1c-*trans*

1c-*trans*

Charge 0; multiplicity 1

C 1.11074400 -0.74011300 -1.46901800
C 2.47866400 -1.24810200 -1.11396000
N 0.46574000 -1.47417900 -2.58290100
C 0.73602300 0.71733500 -1.39067100
O -0.63343500 -1.10371800 -2.95690500
O 1.07353500 -2.41263000 -3.05987500
C 0.12134900 -0.24612200 -0.42379800
H 2.43714400 -2.29780400 -0.77509300
H 3.15547500 -1.18599500 -1.98285200
H 2.88771500 -0.62930000 -0.29800800
H 0.09620900 1.10379300 -2.19017200
H 1.53543100 1.37991100 -1.03790700
C 0.51981500 -0.30260500 1.01898500
C 0.41243300 -1.51406300 1.71527100
C 0.99706000 0.82596900 1.69112400
C 0.77966000 -1.59470500 3.05705800
H 0.03659100 -2.40445300 1.19282400
C 1.36451400 0.74693500 3.03609700
H 1.07447400 1.78260400 1.15830800
C 1.25893700 -0.46299300 3.72120000
H 0.69245800 -2.54976400 3.59008500
H 1.73454000 1.64143300 3.55268600
H 1.54862700 -0.52572400 4.77750200
H -0.91533300 -0.53062900 -0.64508100

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -592.501729 E_0
Sum of electronic and zero-point Energies= -592.308362 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -592.297142 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -592.296198 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -592.341132 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.193367
Number of imaginary vibrational frequencies = 0

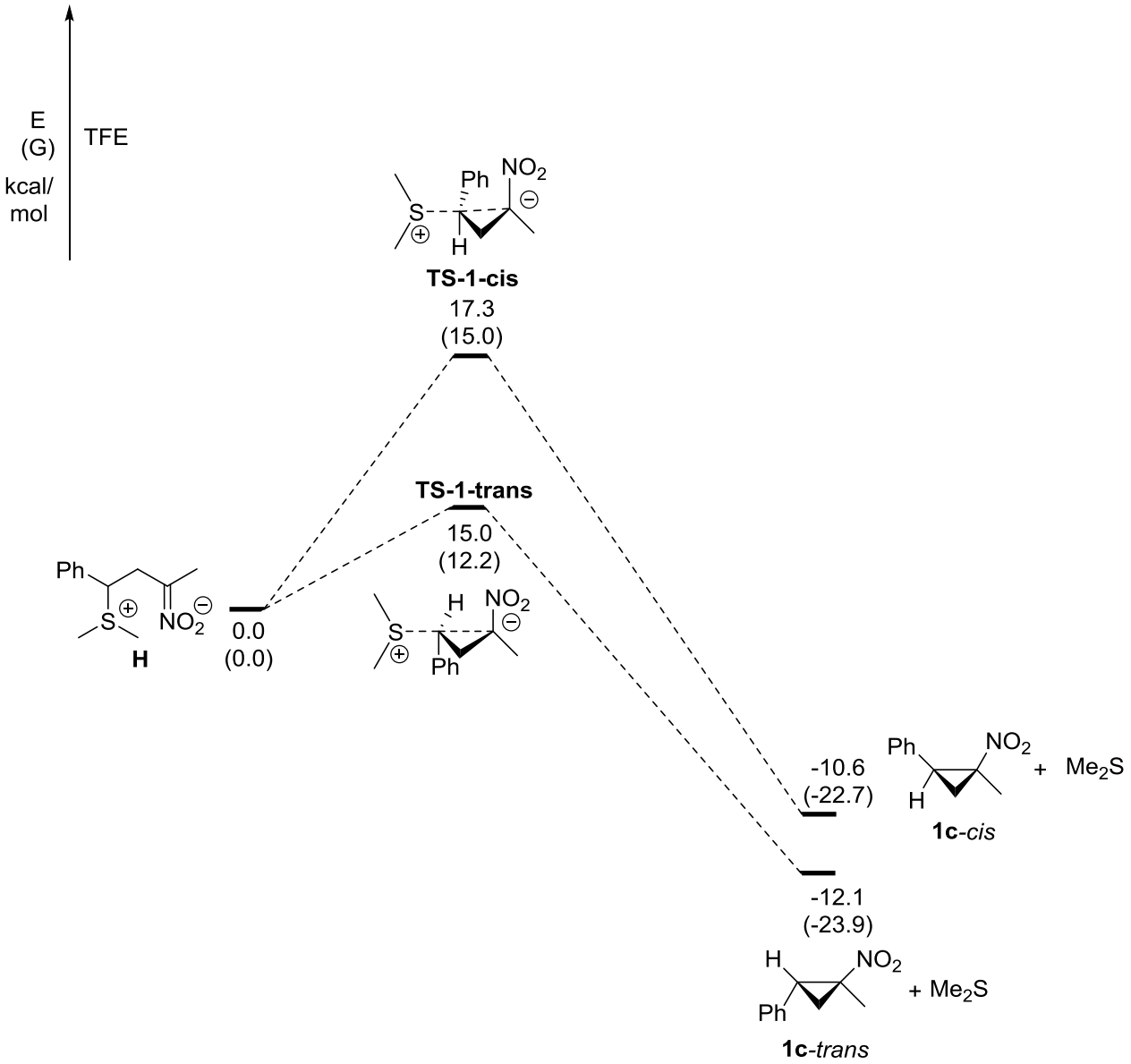
Me_2S

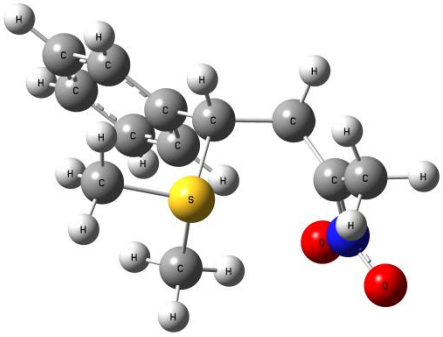
Charge 0; multiplicity 1

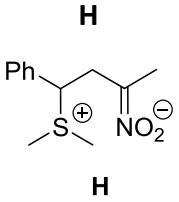
S -1.99520000 2.60720400 0.00558000
C -2.71513100 1.39651600 1.13883200
C -2.64550900 1.94385200 -1.54533500
H -2.40559200 1.66979300 2.16225700
H -3.81838400 1.41299000 1.08379700
H -2.34729800 0.37923600 0.91454800
H -2.28715400 2.59207300 -2.36343800
H -3.75026200 1.94927600 -1.54358100
H -2.27938200 0.91602600 -1.71828600

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -477.940106 E_0
Sum of electronic and zero-point Energies= -477.865010 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -477.860128 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -477.859184 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -477.886806 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.075096
Number of imaginary vibrational frequencies = 0

8.3 Calculations of competitive formation of *cis*- and *trans*- nitrocyclopropanes 1c in TFE



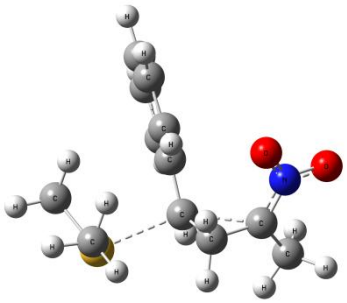




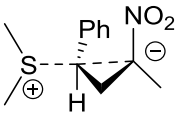
Charge 0; multiplicity 1

C -2.25561700 5.70532200 -1.92277600
C -1.57941400 4.44901400 -1.47048800
C -2.26492700 3.11864900 -1.41920200
C -3.06231700 2.79997200 -0.11486500
N -0.29705500 4.52605600 -1.15928500
O 0.32338500 5.64131900 -1.24530300
O 0.36338500 3.49419500 -0.73543200
S -2.82192300 4.18208300 1.09355600
H -4.14819200 2.89761300 -0.29990200
C -3.97041100 3.73083400 2.39655400
C -1.25062200 3.86778600 1.89734800
H -2.11994100 6.51867600 -1.18363700
H -1.83459000 6.07449500 -2.87964200
H -3.33682700 5.52981500 -2.06220700
H -1.51704600 2.32652000 -1.57239300
H -4.99140300 3.79068900 1.98329400
H -3.84689100 4.48060800 3.19634600
H -3.74185700 2.71893600 2.77055500
H -0.47478100 3.76499900 1.11331300
H -1.05212900 4.74803000 2.53238200
H -1.32953000 2.95262800 2.50740300
H -2.99238100 3.05983300 -2.24777200
C -2.78532800 1.45056700 0.50204100
C -1.47444100 0.96242300 0.59612400
C -3.84658300 0.67585500 0.98497400
C -1.23473500 -0.28373100 1.17356600
H -0.64318900 1.57121600 0.21092300
C -3.60376800 -0.57338900 1.55729300
H -4.87439400 1.05591000 0.90185400
C -2.29717100 -1.05338300 1.65358200
H -0.20674900 -0.66035500 1.24489300
H -4.44248000 -1.17682700 1.92625700
H -2.10480900 -2.03640500 2.10171700

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1070.418027 E_0
Sum of electronic and zero-point Energies= -1070.146737 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.130174 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.129228 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.185002 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.271290
Number of imaginary vibrational frequencies = 0



TS-1-cis

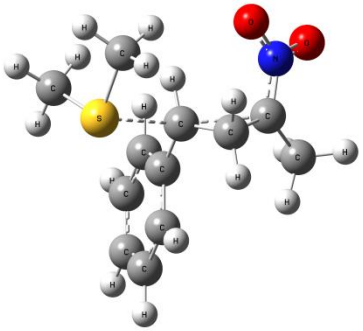


TS-1-cis

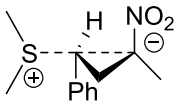
Charge 0; multiplicity 1

C 5.03844600 4.26095100 7.10672800
C 6.39440700 3.78430100 6.69304100
H 7.19836200 4.42277700 7.10527100
H 6.47299600 3.78061900 5.59205000
H 6.58016900 2.75536000 7.05939100
C 3.94161500 4.59334300 6.13765900
H 2.94202400 4.53559500 6.59015700
H 4.00899100 3.99521800 5.21417900
C 4.47988400 5.96570600 5.97944500
H 5.44515400 6.02289100 5.45555800
C 4.21071300 7.08152700 6.89685800
C 3.02877500 7.17564800 7.64908700
H 2.29082500 6.36775700 7.61899700
C 2.78837100 8.30688300 8.42975100
H 1.86170100 8.37650500 9.01257300
C 3.71999700 9.34436100 8.47139900
H 3.52523700 10.23086900 9.08821700
C 4.90060800 9.25733900 7.72664900
H 5.63388800 10.07255400 7.75785100
C 5.14080400 8.13562600 6.94127700
H 6.05866400 8.06400600 6.34126600
N 4.78763100 4.35419400 8.43084700
O 3.64972900 4.69271400 8.86125100
O 5.71354300 4.08616400 9.24850700
S 3.34999200 6.76268900 3.99745400
C 3.13472500 8.52197900 4.31197200
H 2.40986800 8.93054900 3.58647700
H 2.77332000 8.68202200 5.34435600
H 4.11192500 9.01402400 4.17094200
C 1.70144000 6.18127800 4.42677800
H 1.67508200 5.08952500 4.27269500
H 1.47399600 6.42328600 5.48020900
H 0.96269200 6.66094300 3.76164600

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1070.390431 E_0
Sum of electronic and zero-point Energies= -1070.121986 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.105015 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.104071 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.161062 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.268445
Number of imaginary vibrational frequencies = 1; 542*i*



TS-1-trans

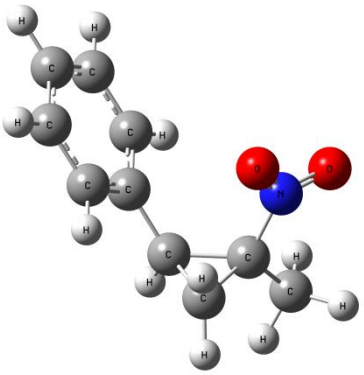


TS-1-trans

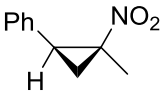
Charge 0; multiplicity 1

C 1.94338800 -0.13753500 -0.45189000
C 3.21574600 -0.68338500 0.10740000
N 1.18594800 -0.95875200 -1.22004600
C 1.44457800 1.26656800 -0.26840700
O 0.09701000 -0.54825300 -1.71873600
O 1.56699300 -2.14114300 -1.42422600
C 0.59255000 0.73286200 0.81514200
S -1.02324600 2.37636800 1.27210600
C -2.11164200 1.27768400 2.19351800
C -1.78370400 2.26740900 -0.35681200
H 3.03427800 -1.58114800 0.72973900
H 3.90564400 -0.98280300 -0.70546200
H 3.71482500 0.08238500 0.72474800
H 0.89367700 1.64759300 -1.14064800
H -1.72029200 1.20196400 3.22225200
H -3.12933600 1.70356700 2.21818700
H -2.13013200 0.27897700 1.71890900
H -1.30434500 3.02142600 -1.00351200
H -2.86120300 2.49036100 -0.27503300
H -1.63153400 1.25614300 -0.78039700
H 2.23640300 1.95258800 0.06507000
C 1.12184700 0.49056600 2.18038700
C 0.70971300 -0.65561800 2.87283100
C 2.01469900 1.38347600 2.78929100
C 1.19316900 -0.91316400 4.15550400
H 0.01291700 -1.35449000 2.39001300
C 2.49210000 1.12642100 4.07209800
H 2.32707400 2.29384600 2.26030900
C 2.08436700 -0.02257000 4.75577300
H 0.87245900 -1.81638000 4.68920300
H 3.18774100 1.83004600 4.54594900
H 2.46404500 -0.22281700 5.76562600
H -0.23042600 0.07923500 0.48763900

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1070.3941689 E_0
Sum of electronic and zero-point Energies= -1070.125660 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.108585 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.107640 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.16530 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.268509
Number of imaginary vibrational frequencies = 1; 607*i*



1c-*cis*

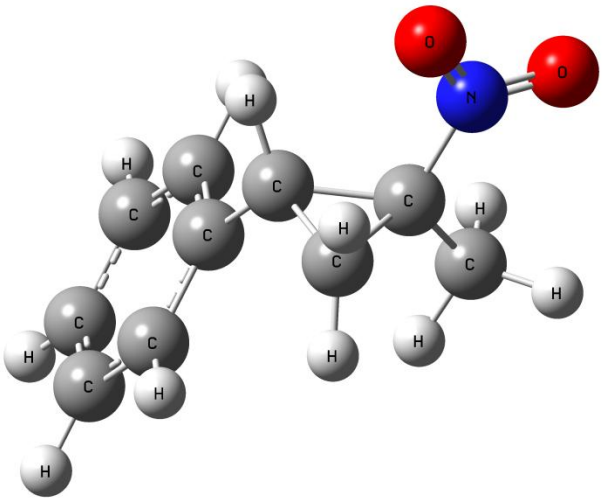


1c-*cis*

Charge 0; multiplicity 1

C 1.23221200 -1.90372400 0.44295300
C 2.32837900 -2.63422300 -0.28045600
H 3.24614300 -2.02462100 -0.33264400
H 1.98583300 -2.85201600 -1.30580200
H 2.56259900 -3.58783000 0.22448200
C -0.22934500 -2.11920500 0.15442800
H -0.89859500 -2.08789500 1.02140000
H -0.45422000 -2.86940200 -0.61152100
C 0.40589600 -0.82869600 -0.25962300
H 0.69585200 -0.74407900 -1.31631800
C 0.07403700 0.47566400 0.40056200
C -1.22804400 0.76389200 0.81851300
H -2.01797300 0.01300400 0.68365500
C -1.52533900 1.99574600 1.40367500
H -2.55167000 2.21183100 1.72660500
C -0.52082000 2.94843700 1.58053100
H -0.75389000 3.91558900 2.04357000
C 0.78306000 2.66490800 1.16787300
H 1.57846100 3.40808600 1.30688000
C 1.07804900 1.43546400 0.57944300
H 2.10436000 1.21032600 0.25727400
N 1.55607400 -1.59947200 1.84943600
O 0.67149600 -1.21103100 2.59012100
O 2.71734900 -1.72859700 2.19521600

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -592.495059 E_0
Sum of electronic and zero-point Energies= -592.302073 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -592.290818 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -592.289874 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -592.334735 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.192986
Number of imaginary vibrational frequencies = 0



1c-*trans*

1c-*trans*

Charge 0; multiplicity 1

C 1.11665700 -0.72517400 -1.46998000
C 2.47532600 -1.24215100 -1.09671400
N 0.47913900 -1.46314900 -2.57716400
C 0.74890800 0.73583500 -1.40699200
O -0.61194900 -1.09169100 -2.97502400
O 1.07718000 -2.41689500 -3.03914900
C 0.11668400 -0.21361200 -0.44040500
H 2.41819400 -2.28541600 -0.73917200
H 3.15891100 -1.19916500 -1.96195700
H 2.88476800 -0.61195100 -0.28976500
H 0.12410900 1.12156100 -2.21912500
H 1.55305900 1.39192000 -1.05270600
C 0.50234000 -0.27073400 1.00536400
C 0.35867700 -1.47662800 1.70504600
C 1.00349900 0.84893500 1.67524900
C 0.71370500 -1.56074400 3.05021800
H -0.03539600 -2.35920100 1.18253500
C 1.35839700 0.76593500 3.02371200
H 1.11103900 1.80107200 1.13942600
C 1.21665300 -0.43821800 3.71322000
H 0.59873600 -2.51123300 3.58654800
H 1.74807300 1.65291000 3.53918500
H 1.49694300 -0.50368300 4.77211000
H -0.91841300 -0.49948300 -0.66856700

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -592.497399 E_0
Sum of electronic and zero-point Energies= -592.304158 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -592.292975 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -592.292031 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -592.336584 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.193241
Number of imaginary vibrational frequencies = 0

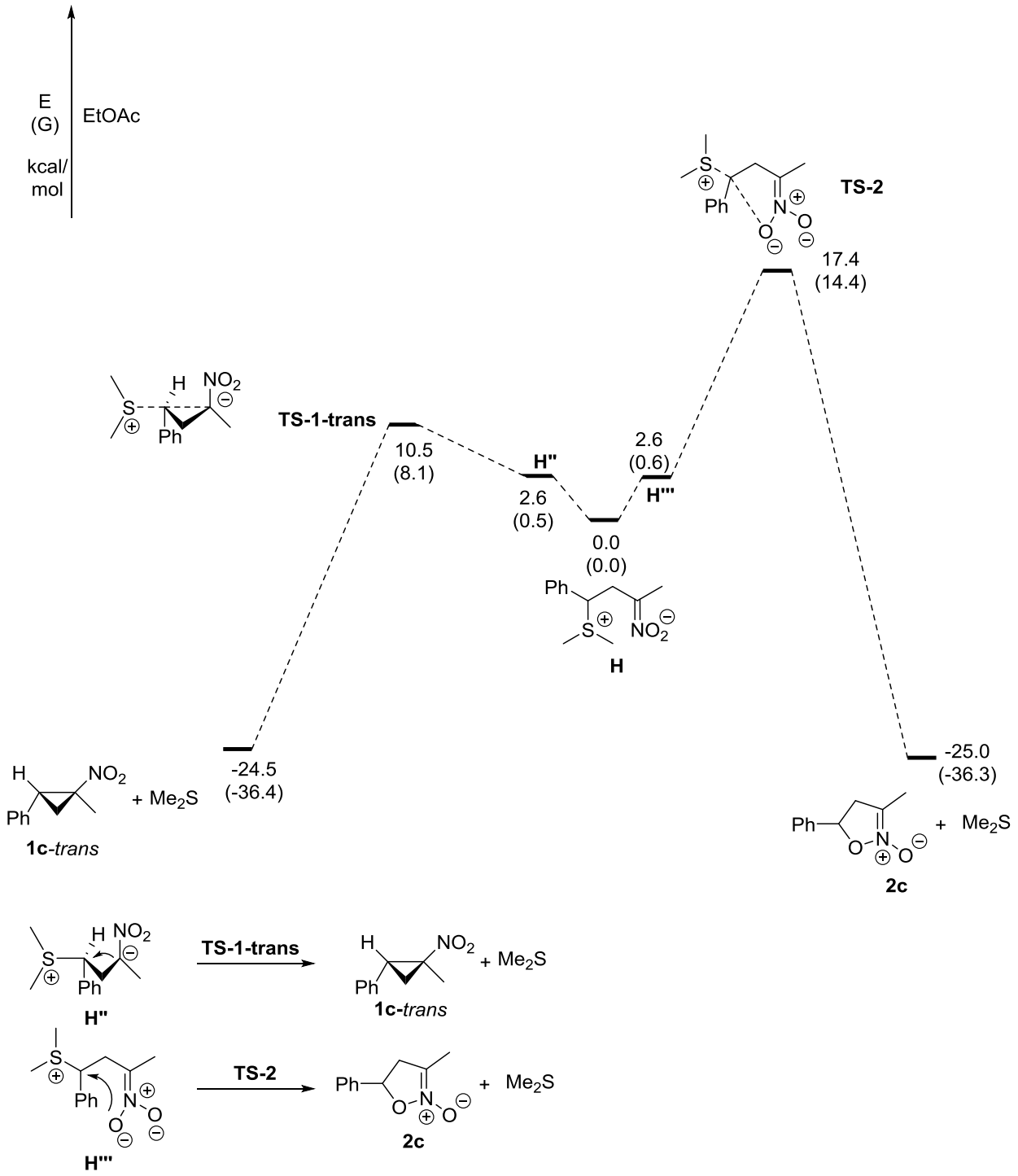
Me_2S

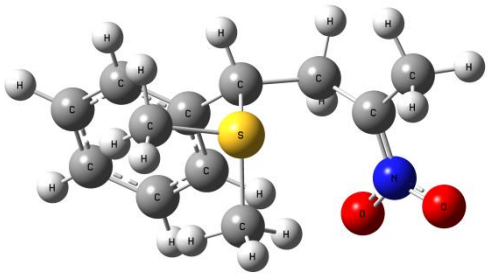
Charge 0; multiplicity 1

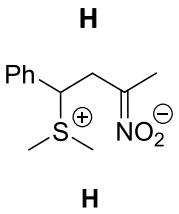
S -2.63823800 2.20471200 1.26977200
C -3.37823000 0.76629900 2.07787100
H -3.83940600 1.05109900 3.04051900
H -4.16221500 0.37106200 1.40904000
H -2.62200000 -0.02110500 2.24700200
C -1.43128000 2.63734800 2.54469300
H -0.71499200 1.81141200 2.70352700
H -0.87912300 3.52741500 2.19689500
H -1.93634000 2.87929400 3.49696700

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -477.939926 E_0
Sum of electronic and zero-point Energies= -477.864936 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -477.860021 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -477.859077 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -477.886519 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.074990
Number of imaginary vibrational frequencies = 0

8.4 Calculations of competitive formation of *trans*-cyclopropane 1c-*trans* and *N*-oxide 2c in EtOAc



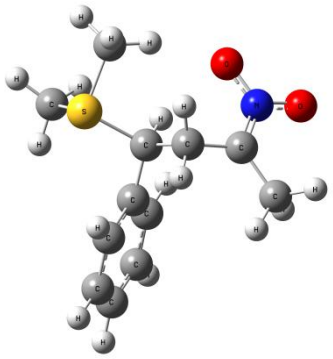




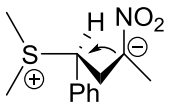
Charge 0; multiplicity 1

C -2.18092600 5.73422300 -1.92447400
C -1.59435500 4.44825700 -1.43128200
C -2.32640800 3.14301500 -1.42783500
C -3.10640500 2.78729000 -0.11829700
N -0.29908200 4.46226800 -1.10075700
O 0.36490000 5.52876400 -1.18597500
O 0.26912200 3.39268600 -0.65389900
S -2.86253700 4.18308000 1.07429800
H -4.19800300 2.86088200 -0.28381000
C -3.99990300 3.72282900 2.38975400
C -1.28509900 3.88007600 1.87218900
H -2.01377700 6.55395100 -1.19840300
H -1.71608800 6.06815600 -2.87500300
H -3.26847600 5.62547500 -2.08949700
H -1.60902900 2.33041700 -1.62360700
H -5.02743100 3.79419200 1.99449100
H -3.86421800 4.46049000 3.19873600
H -3.77800700 2.70472500 2.75103800
H -0.52389100 3.69577700 1.08058100
H -1.04939500 4.79509800 2.44164000
H -1.38059000 3.01077700 2.54395100
H -3.07208800 3.14036100 -2.24292700
C -2.79442800 1.44631100 0.50063500
C -1.47376400 0.97913200 0.56065200
C -3.83060200 0.65820100 1.01595200
C -1.20261000 -0.25962100 1.14100500
H -0.66860600 1.60332800 0.14241000
C -3.55512400 -0.58264700 1.59138400
H -4.86674400 1.01979800 0.95386900
C -2.23900400 -1.04116300 1.65675400
H -0.16798800 -0.62190100 1.18576000
H -4.37452400 -1.19671200 1.98504800
H -2.01965700 -2.01756000 2.10669100

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1070.402777 E_0
Sum of electronic and zero-point Energies= -1070.131560 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.115083 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.114138 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.169911 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.271217
Number of imaginary vibrational frequencies = 0



Pre-reaction conformation **H''**



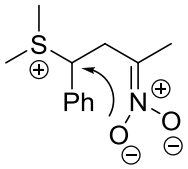
H"

Charge 0; multiplicity 1

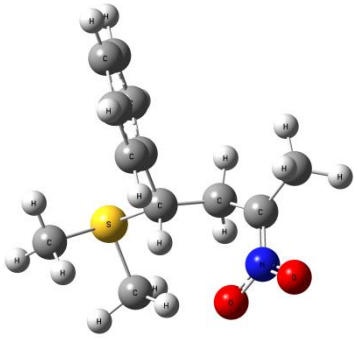
C 1.19949900 -0.64184300 -1.72616900
C 2.51994800 -1.24821900 -1.37367000
N 0.32816400 -1.39714300 -2.39773200
C 0.69529300 0.68065000 -1.24078200
O -0.85818000 -0.94867800 -2.63736200
O 0.65248800 -2.55371400 -2.78718500
C -0.34141300 0.39879200 -0.13238200
S -1.54887500 1.79190500 -0.00078900
C -2.81265500 1.01810700 1.01493600
C -2.30022200 1.70162300 -1.64320800
H 2.39230700 -2.20639000 -0.82898200
H 3.12110100 -1.49045700 -2.27362200
H 3.10635300 -0.55900500 -0.73943800
H 0.21421800 1.23257500 -2.07127300
H -2.39708600 0.90311300 2.02996600
H -3.68304800 1.69438400 1.03783000
H -3.07671300 0.03956400 0.57820100
H -1.91866900 2.55032800 -2.23308900
H -3.39110500 1.79450400 -1.51513300
H -2.00276600 0.73327500 -2.09697100
H 1.51776700 1.29766200 -0.83757100
C 0.25227700 0.12567100 1.22679300
C 0.10605000 -1.14404600 1.79295800
C 0.97388500 1.10911300 1.91573900
C 0.67890600 -1.43151500 3.03288900
H -0.45265200 -1.91547100 1.24591200
C 1.53621700 0.82448900 3.15870400
H 1.10106600 2.10800900 1.47405800
C 1.39065800 -0.44715500 3.71824800
H 0.56737100 -2.43349300 3.46520600
H 2.09776500 1.60031300 3.69363200
H 1.83875300 -0.67151100 4.69415200
H -0.97611900 -0.43751700 -0.47716100

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1070.398590 E_0
Sum of electronic and zero-point Energies= -1070.128273 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.111141 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.110197 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.169161 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.270318
Number of imaginary vibrational frequencies = 0

Pre-reaction conformation **H'''**



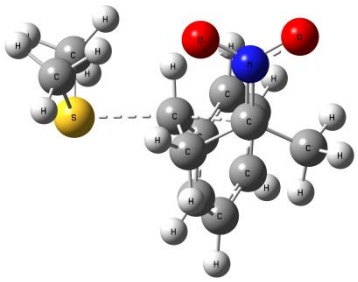
H'''



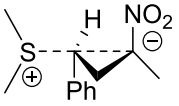
Charge 0; multiplicity 1

C -0.99052900 -1.79295400 -0.94686400
C -0.16690300 -2.19622000 -2.12780100
N -1.10288700 -2.66231900 0.05908800
C -1.56536100 -0.43154100 -0.71489500
O -1.72598700 -2.31910700 1.13597100
O -0.59120800 -3.81338500 -0.03063200
C -0.69288900 0.26584100 0.35095700
S -1.67756400 1.54240100 1.25257600
H 0.84929000 -2.51823800 -1.82045900
H -0.60633000 -3.05957100 -2.66802500
H -0.06949200 -1.35538700 -2.83822800
H -2.60670400 -0.51486800 -0.34744700
H -1.56719000 0.16383800 -1.64510700
C 0.56787100 0.89570500 -0.18549500
C 1.80714100 0.37114400 0.19310600
C 0.51889000 1.97264700 -1.08007000
C 2.98666300 0.91410300 -0.31892800
H 1.84124500 -0.47972800 0.88696100
C 1.69753100 2.52121400 -1.58206700
H -0.45201700 2.38434000 -1.39140200
C 2.93329700 1.99165500 -1.20277500
H 3.95442500 0.49049800 -0.02348700
H 1.65198400 3.36636700 -2.27994000
H 3.86012600 2.42134100 -1.60251500
C -2.91252100 0.48136000 2.03838500
H -2.99836500 0.79522600 3.09159300
H -3.87067300 0.64398400 1.51942300
H -2.57167400 -0.56952400 1.93045100
C -0.56772300 1.89037000 2.62134100
H -0.27137900 0.93986800 3.09704100
H 0.30718100 2.41977000 2.20799600
H -1.10331500 2.54348100 3.32976100
H -0.47481100 -0.47473100 1.14169600

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1070.398619 E_0
Sum of electronic and zero-point Energies= -1070.128245 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.111148 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.110204 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.168902 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.270374
Number of imaginary vibrational frequencies = 0



TS-1-trans

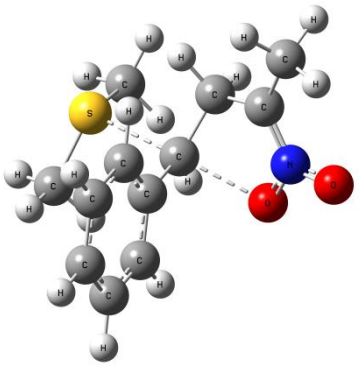


TS-1-trans

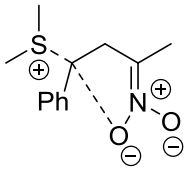
Charge 0; multiplicity 1

C 1.91861100 -0.13801500 -0.46804100
C 3.17783300 -0.73862800 0.06361900
N 1.10235100 -0.92717400 -1.22303600
C 1.44596600 1.26307300 -0.22872700
O 0.00952700 -0.45797000 -1.65848300
O 1.44114400 -2.10683700 -1.46028600
C 0.55572800 0.78427500 0.86137000
S -0.99289000 2.35614600 1.24137700
C -2.10975800 1.28732700 2.16258100
C -1.71256900 2.21952200 -0.40580200
H 2.97476900 -1.66339800 0.63845100
H 3.87108200 -1.02002800 -0.75400800
H 3.69272400 -0.01836800 0.72347200
H 0.90810900 1.68336500 -1.09290300
H -1.72337300 1.20657200 3.19269700
H -3.11645000 1.73813000 2.18018100
H -2.14765600 0.28879400 1.68909400
H -1.29372000 3.03132900 -1.02367700
H -2.80588400 2.34660100 -0.33381800
H -1.45149900 1.23575800 -0.84557900
H 2.25088600 1.92911500 0.11806600
C 1.10517900 0.52388100 2.22152200
C 0.76227500 -0.66168800 2.88352700
C 1.95425300 1.44326500 2.85198000
C 1.26921800 -0.93050100 4.15479000
H 0.10468900 -1.38561000 2.38291000
C 2.45582200 1.17610100 4.12379300
H 2.21608800 2.38192700 2.34511400
C 2.11575500 -0.01168800 4.77620600
H 1.00347200 -1.86601800 4.66219300
H 3.11821900 1.90134500 4.61223400
H 2.51459000 -0.22132600 5.77650400
H -0.22918200 0.09215000 0.51920700

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1070.385997 E_0
Sum of electronic and zero-point Energies= -1070.117206 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.100243 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.099299 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.157059 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.268791
Number of imaginary vibrational frequencies = 1; 519*i*



TS-2

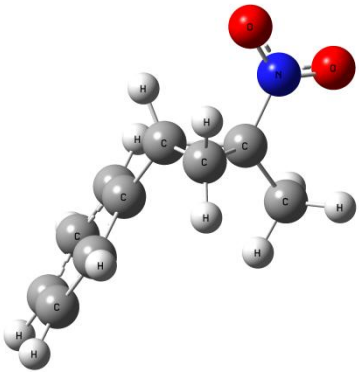


TS-2

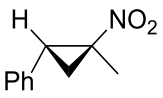
Charge 0; multiplicity 1

C 2.07577100 -0.60287400 -0.41668000
C 1.72457900 -0.82042800 -1.84855400
N 3.04458700 -1.29129300 0.16008800
C 1.36056800 0.33502800 0.50864800
O 3.26949600 -1.01984100 1.42302800
O 3.75314200 -2.15727400 -0.41246600
C 2.33961300 0.88212800 1.54340200
S 1.20352400 2.73493200 2.12204400
H 2.51378100 -1.43656900 -2.30830800
H 0.75695900 -1.34832600 -1.97764700
H 1.64844900 0.13839600 -2.39864800
H 0.53252500 -0.16336100 1.05553500
H 0.91308200 1.15496700 -0.08466500
C 3.59861300 1.55668900 1.11021800
C 4.72218600 1.52372300 1.94503400
C 3.66638800 2.23043300 -0.11302600
C 5.89528300 2.17053400 1.56709000
H 4.67257700 0.95727400 2.88382000
C 4.84453700 2.87569300 -0.49273800
H 2.78917000 2.26000200 -0.77357200
C 5.95758100 2.85026200 0.34712400
H 6.77359400 2.13696400 2.22354400
H 4.89178000 3.40091800 -1.45455700
H 6.88335600 3.35720900 0.04758700
C -0.13767300 1.93383000 3.01626900
H -0.62173300 2.66709200 3.68321400
H -0.87158200 1.57699700 2.27466900
H 0.25504200 1.08364800 3.60317000
C 2.23997900 3.24303800 3.50017200
H 2.56663800 2.35575000 4.07311600
H 3.11443700 3.76999400 3.08321500
H 1.66962800 3.92922200 4.14882100
H 2.27845300 0.54380600 2.58351900

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1070.375040 E_0
Sum of electronic and zero-point Energies= -1070.106710 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.089574 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.088630 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.146890 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.268331
Number of imaginary vibrational frequencies = 1; 532*i*



1c-*trans*

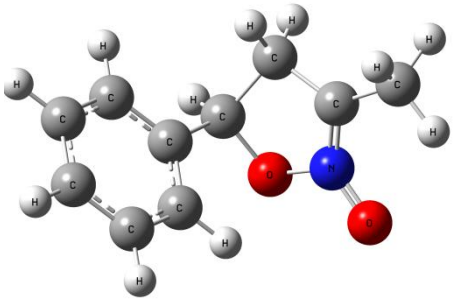


1c-*trans*

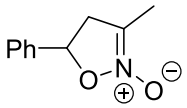
Charge 0; multiplicity 1

C 1.11074400 -0.74011300 -1.46901800
C 2.47866400 -1.24810200 -1.11396000
N 0.46574000 -1.47417900 -2.58290100
C 0.73602300 0.71733500 -1.39067100
O -0.63343500 -1.10371800 -2.95690500
O 1.07353500 -2.41263000 -3.05987500
C 0.12134900 -0.24612200 -0.42379800
H 2.43714400 -2.29780400 -0.77509300
H 3.15547500 -1.18599500 -1.98285200
H 2.88771500 -0.62930000 -0.29800800
H 0.09620900 1.10379300 -2.19017200
H 1.53543100 1.37991100 -1.03790700
C 0.51981500 -0.30260500 1.01898500
C 0.41243300 -1.51406300 1.71527100
C 0.99706000 0.82596900 1.69112400
C 0.77966000 -1.59470500 3.05705800
H 0.03659100 -2.40445300 1.19282400
C 1.36451400 0.74693500 3.03609700
H 1.07447400 1.78260400 1.15830800
C 1.25893700 -0.46299300 3.72120000
H 0.69245800 -2.54976400 3.59008500
H 1.73454000 1.64143300 3.55268600
H 1.54862700 -0.52572400 4.77750200
H -0.91533300 -0.53062900 -0.64508100

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -592.501729 E_0
Sum of electronic and zero-point Energies= -592.308362 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -592.297142 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -592.296198 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -592.341132 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.193367
Number of imaginary vibrational frequencies = 0



2c



2c

Charge 0; multiplicity 1

C -0.74039700 -1.90276000 -1.30416600
C -1.03775700 -2.51260900 -2.62694900
N -0.01742700 -2.53651700 -0.42880500
C -1.18425500 -0.58344400 -0.75316600
O 0.11896300 -1.78525200 0.77997200
O 0.54412800 -3.63152100 -0.43284600
C -0.19949100 -0.43467500 0.42352400
H -0.54890300 -3.49745600 -2.69302000
H -2.12800900 -2.63893200 -2.76053400
H -0.67071800 -1.86635600 -3.44493900
H -2.23818000 -0.62633600 -0.41826700
H -1.08060400 0.23510900 -1.48529300
C 1.05977700 0.31713200 0.02501500
C 2.25956300 -0.35964200 -0.20544900
C 1.00822100 1.70587100 -0.13540200
C 3.39579300 0.34913100 -0.60243800
H 2.30489600 -1.44795000 -0.06871000
C 2.14439800 2.41225900 -0.52594300
H 0.06555100 2.23971400 0.05094800
C 3.34228000 1.73327900 -0.76271400
H 4.33425700 -0.18936500 -0.78492100
H 2.09643100 3.50202700 -0.64435600
H 4.23768100 2.28767800 -1.07021600
H -0.66915500 0.02689300 1.30762800

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -592.502485 E_0
Sum of electronic and zero-point Energies= -592.308450 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -592.297411 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -592.296466 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -592.340985 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.194035
Number of imaginary vibrational frequencies = 0

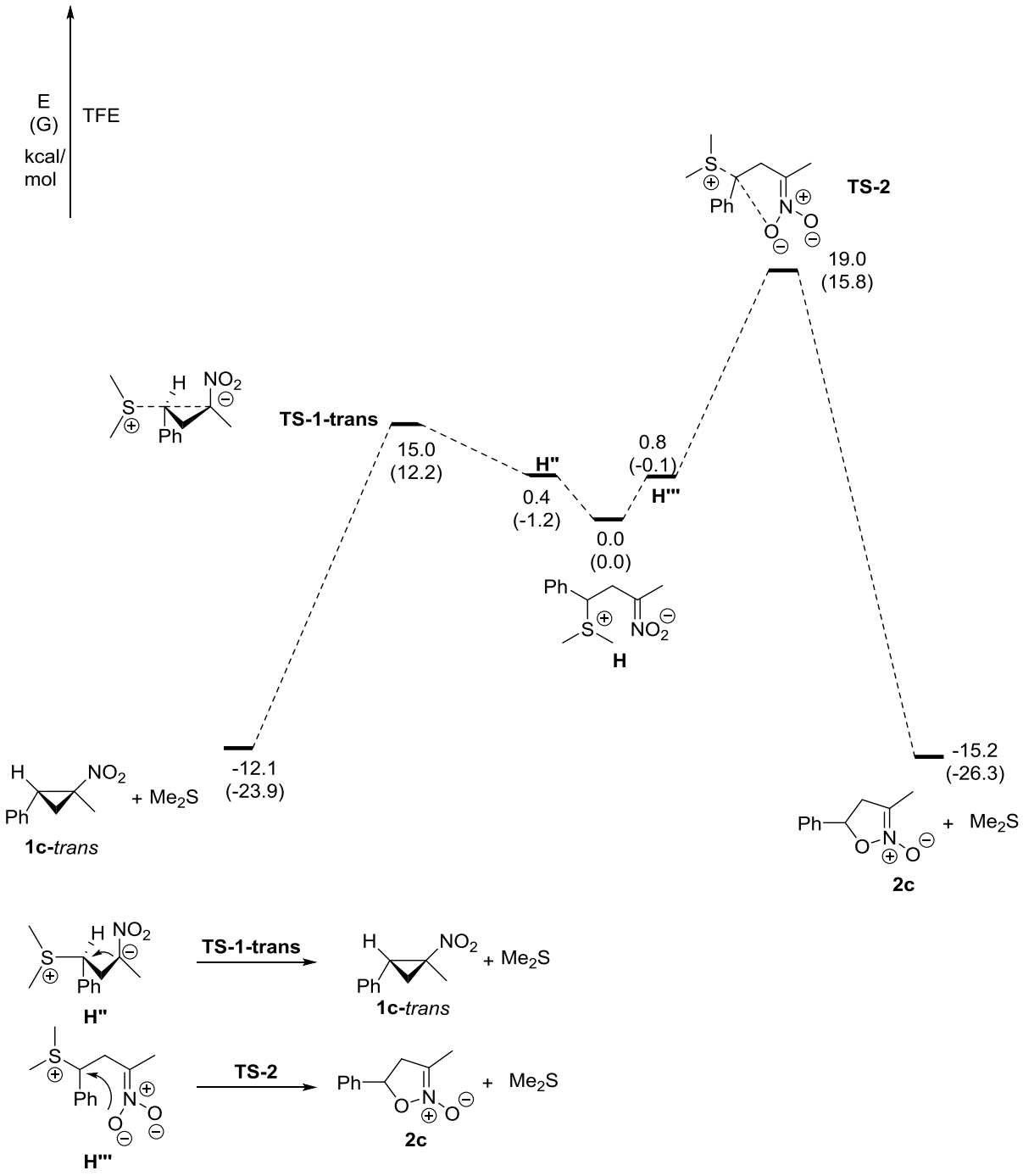
Me_2S

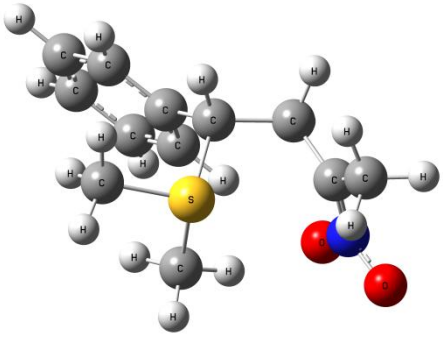
Charge 0; multiplicity 1

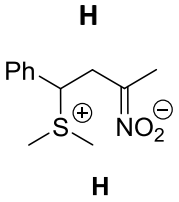
S -1.99520000 2.60720400 0.00558000
C -2.71513100 1.39651600 1.13883200
C -2.64550900 1.94385200 -1.54533500
H -2.40559200 1.66979300 2.16225700
H -3.81838400 1.41299000 1.08379700
H -2.34729800 0.37923600 0.91454800
H -2.28715400 2.59207300 -2.36343800
H -3.75026200 1.94927600 -1.54358100
H -2.27938200 0.91602600 -1.71828600

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -477.940106 E_0
Sum of electronic and zero-point Energies= -477.865010 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -477.860128 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -477.859184 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -477.886806 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.075096
Number of imaginary vibrational frequencies = 0

8.5 Calculations of competitive formation of *trans*-cyclopropane 1c-*trans* and *N*-oxide 2c in 2,2,2-trifluoroethanol (TFE)



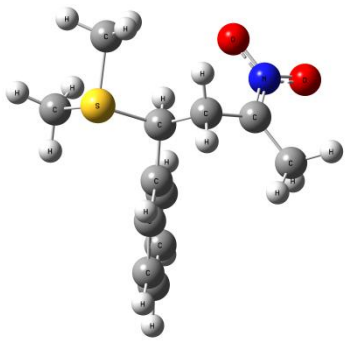




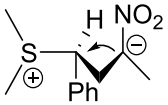
Charge 0; multiplicity 1

C -2.25561700 5.70532200 -1.92277600
C -1.57941400 4.44901400 -1.47048800
C -2.26492700 3.11864900 -1.41920200
C -3.06231700 2.79997200 -0.11486500
N -0.29705500 4.52605600 -1.15928500
O 0.32338500 5.64131900 -1.24530300
O 0.36338500 3.49419500 -0.73543200
S -2.82192300 4.18208300 1.09355600
H -4.14819200 2.89761300 -0.29990200
C -3.97041100 3.73083400 2.39655400
C -1.25062200 3.86778600 1.89734800
H -2.11994100 6.51867600 -1.18363700
H -1.83459000 6.07449500 -2.87964200
H -3.33682700 5.52981500 -2.06220700
H -1.51704600 2.32652000 -1.57239300
H -4.99140300 3.79068900 1.98329400
H -3.84689100 4.48060800 3.19634600
H -3.74185700 2.71893600 2.77055500
H -0.47478100 3.76499900 1.11331300
H -1.05212900 4.74803000 2.53238200
H -1.32953000 2.95262800 2.50740300
H -2.99238100 3.05983300 -2.24777200
C -2.78532800 1.45056700 0.50204100
C -1.47444100 0.96242300 0.59612400
C -3.84658300 0.67585500 0.98497400
C -1.23473500 -0.28373100 1.17356600
H -0.64318900 1.57121600 0.21092300
C -3.60376800 -0.57338900 1.55729300
H -4.87439400 1.05591000 0.90185400
C -2.29717100 -1.05338300 1.65358200
H -0.20674900 -0.66035500 1.24489300
H -4.44248000 -1.17682700 1.92625700
H -2.10480900 -2.03640500 2.10171700

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1070.418027 E_0
Sum of electronic and zero-point Energies= -1070.146737 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.130174 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.129228 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.185002 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.271290
Number of imaginary vibrational frequencies = 0



Pre-reaction conformation **H''**

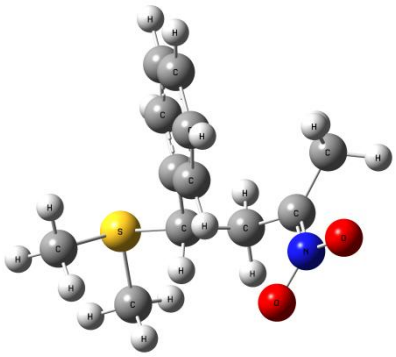


H"

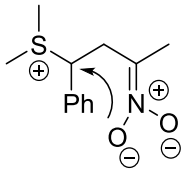
Charge 0; multiplicity 1

C 1.23957400 -0.63425000 -1.63532000
C 2.59461900 -1.04926200 -1.15882500
N 0.52077400 -1.51315700 -2.30730000
C 0.58089000 0.67122200 -1.30676400
O -0.68577500 -1.23801300 -2.68540800
O 1.00303200 -2.66671200 -2.59586200
C -0.44179600 0.40013300 -0.18853700
S -1.58629900 1.82899300 0.01710700
C -2.83631900 1.09002200 1.07271000
C -2.42575300 1.82699300 -1.57440400
H 2.53565700 -1.95415700 -0.52009300
H 3.26229300 -1.30749000 -2.00470200
H 3.06408600 -0.23739100 -0.57669300
H 0.06429000 1.06077300 -2.20243200
H -2.38548900 0.94860800 2.06910400
H -3.67479900 1.80344100 1.13536700
H -3.15594600 0.12945500 0.63385000
H -1.83341400 2.44223300 -2.27033300
H -3.41523900 2.28822200 -1.41827300
H -2.51460800 0.78664900 -1.93340400
H 1.32908200 1.41073600 -0.97131800
C 0.19064800 0.08935100 1.14808500
C -0.02652800 -1.16153000 1.73310200
C 1.01883300 1.01939700 1.78897100
C 0.58515900 -1.48480400 2.94551800
H -0.67510100 -1.88860800 1.22573700
C 1.62226100 0.69795700 3.00376700
H 1.19856200 2.00405700 1.33387300
C 1.40808100 -0.55542400 3.58224100
H 0.41595200 -2.47103700 3.39543400
H 2.26918400 1.43105200 3.50144400
H 1.88790900 -0.80844900 4.53600600
H -1.10079000 -0.42518400 -0.51616200

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1070.417393 E_0
Sum of electronic and zero-point Energies= -1070.146820 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.129740 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.128796 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.186899 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.270573
Number of imaginary vibrational frequencies = 0



Pre-reaction conformation **H'''**

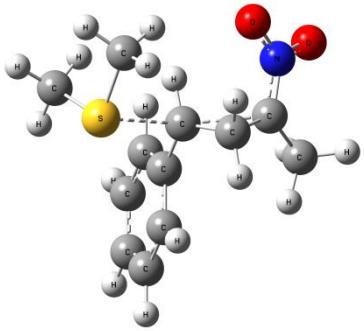


H'''

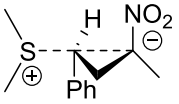
Charge 0; multiplicity 1

C -0.69985700 -1.67966000 -1.01878300
C -0.20472400 -1.55849000 -2.42481100
N -0.10806600 -2.56201100 -0.24015500
C -1.62548100 -0.69091600 -0.37313200
O -0.40412600 -2.65179300 1.01621900
O 0.80887700 -3.33035700 -0.70444600
C -0.82171200 0.18598900 0.61813500
S -1.83315100 1.59881000 1.18802900
H 0.86984100 -1.27366600 -2.44388400
H -0.28258100 -2.52039200 -2.96692600
H -0.78033400 -0.79460200 -2.97542700
H -2.43120800 -1.20355500 0.18483800
H -2.07985300 -0.05746300 -1.15755100
C 0.47503500 0.68881100 0.02203600
C 1.64498100 -0.02002300 0.31961700
C 0.51681500 1.74182200 -0.89723800
C 2.84860900 0.32941900 -0.29075200
H 1.59237800 -0.87582400 1.00835900
C 1.72582200 2.09558500 -1.49930200
H -0.39911200 2.28980400 -1.16137200
C 2.89178500 1.39106500 -1.19757700
H 3.76027700 -0.23532200 -0.05881700
H 1.75344700 2.92550900 -2.21640400
H 3.83981800 1.66740800 -1.67591900
C -3.16936900 0.75919400 2.04337400
H -3.68740900 1.52002900 2.65072400
H -3.85692900 0.35815100 1.28128700
H -2.75214700 -0.04226400 2.67634400
C -0.84280600 2.18817800 2.56421900
H -0.59865200 1.33745300 3.22235200
H 0.06747100 2.64349100 2.13949100
H -1.43650300 2.95190200 3.09378200
H -0.61361100 -0.40925400 1.52358900

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1070.416707 E_0
Sum of electronic and zero-point Energies= -1070.146028 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.129143 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.128199 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.185084 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.270680
Number of imaginary vibrational frequencies = 0



TS-1-trans

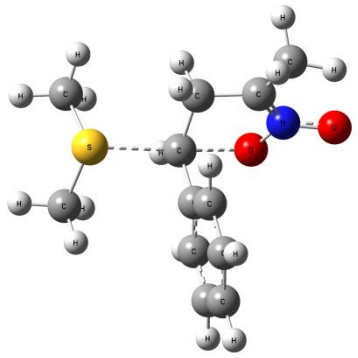


TS-1-trans

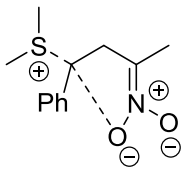
Charge 0; multiplicity 1

C 1.94338800 -0.13753500 -0.45189000
C 3.21574600 -0.68338500 0.10740000
N 1.18594800 -0.95875200 -1.22004600
C 1.44457800 1.26656800 -0.26840700
O 0.09701000 -0.54825300 -1.71873600
O 1.56699300 -2.14114300 -1.42422600
C 0.59255000 0.73286200 0.81514200
S -1.02324600 2.37636800 1.27210600
C -2.11164200 1.27768400 2.19351800
C -1.78370400 2.26740900 -0.35681200
H 3.03427800 -1.58114800 0.72973900
H 3.90564400 -0.98280300 -0.70546200
H 3.71482500 0.08238500 0.72474800
H 0.89367700 1.64759300 -1.14064800
H -1.72029200 1.20196400 3.22225200
H -3.12933600 1.70356700 2.21818700
H -2.13013200 0.27897700 1.71890900
H -1.30434500 3.02142600 -1.00351200
H -2.86120300 2.49036100 -0.27503300
H -1.63153400 1.25614300 -0.78039700
H 2.23640300 1.95258800 0.06507000
C 1.12184700 0.49056600 2.18038700
C 0.70971300 -0.65561800 2.87283100
C 2.01469900 1.38347600 2.78929100
C 1.19316900 -0.91316400 4.15550400
H 0.01291700 -1.35449000 2.39001300
C 2.49210000 1.12642100 4.07209800
H 2.32707400 2.29384600 2.26030900
C 2.08436700 -0.02257000 4.75577300
H 0.87245900 -1.81638000 4.68920300
H 3.18774100 1.83004600 4.54594900
H 2.46404500 -0.22281700 5.76562600
H -0.23042600 0.07923500 0.48763900

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1070.3941689 E_0
Sum of electronic and zero-point Energies= -1070.125660 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.108585 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.107640 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.16530 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.268509
Number of imaginary vibrational frequencies = 1; 607*i*



TS-2

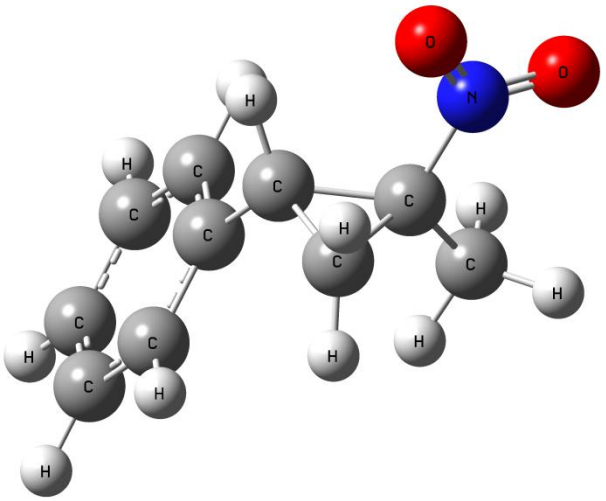


TS-2

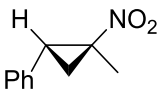
Charge 0; multiplicity 1

C 2.06240800 -0.61056200 -0.43911000
C 1.66107900 -0.82893100 -1.85647200
N 3.03357500 -1.28641900 0.11712100
C 1.38166700 0.34778600 0.49334600
O 3.29565500 -1.00813900 1.38058200
O 3.75071800 -2.17139000 -0.45314300
C 2.38463000 0.84602700 1.52539200
S 1.19384900 2.75992700 2.14564900
H 2.35930400 -1.53334200 -2.33381700
H 0.63682900 -1.24436700 -1.92587900
H 1.66878200 0.12412000 -2.41925400
H 0.54093500 -0.14038100 1.02529500
H 0.96337600 1.18305700 -0.09631600
C 3.62490600 1.55316400 1.10353400
C 4.71662800 1.60060800 1.98092100
C 3.71896100 2.15981800 -0.15362100
C 5.88603100 2.25743700 1.60852100
H 4.64289400 1.09881500 2.95520400
C 4.89338300 2.81659800 -0.52497900
H 2.86657100 2.13262300 -0.84603700
C 5.97539200 2.86835400 0.35409100
H 6.73834500 2.28937300 2.29860400
H 4.96167400 3.29226500 -1.51115200
H 6.89732600 3.38575800 0.06010000
C -0.13524900 1.91426900 3.01833900
H -0.61813200 2.61647500 3.71906200
H -0.87295700 1.58125000 2.26921900
H 0.26853800 1.04447300 3.56835700
C 2.22611900 3.23158800 3.54084600
H 2.56422300 2.32924800 4.08319600
H 3.09362700 3.78577600 3.14491900
H 1.64738700 3.88661400 4.21424600
H 2.29585200 0.54667300 2.57570500

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1070.387772 E_0
Sum of electronic and zero-point Energies= -1070.119528 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1070.102320 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1070.101376 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1070.159791 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.268243
Number of imaginary vibrational frequencies = 1; 581*i*



1c-*trans*

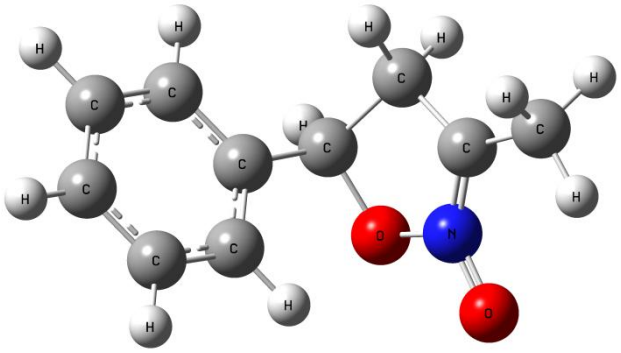


1c-*trans*

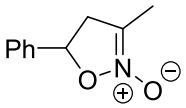
Charge 0; multiplicity 1

C 1.11665700 -0.72517400 -1.46998000
C 2.47532600 -1.24215100 -1.09671400
N 0.47913900 -1.46314900 -2.57716400
C 0.74890800 0.73583500 -1.40699200
O -0.61194900 -1.09169100 -2.97502400
O 1.07718000 -2.41689500 -3.03914900
C 0.11668400 -0.21361200 -0.44040500
H 2.41819400 -2.28541600 -0.73917200
H 3.15891100 -1.19916500 -1.96195700
H 2.88476800 -0.61195100 -0.28976500
H 0.12410900 1.12156100 -2.21912500
H 1.55305900 1.39192000 -1.05270600
C 0.50234000 -0.27073400 1.00536400
C 0.35867700 -1.47662800 1.70504600
C 1.00349900 0.84893500 1.67524900
C 0.71370500 -1.56074400 3.05021800
H -0.03539600 -2.35920100 1.18253500
C 1.35839700 0.76593500 3.02371200
H 1.11103900 1.80107200 1.13942600
C 1.21665300 -0.43821800 3.71322000
H 0.59873600 -2.51123300 3.58654800
H 1.74807300 1.65291000 3.53918500
H 1.49694300 -0.50368300 4.77211000
H -0.91841300 -0.49948300 -0.66856700

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -592.497399 E_0
Sum of electronic and zero-point Energies= -592.304158 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -592.292975 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -592.292031 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -592.336584 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.193241
Number of imaginary vibrational frequencies = 0



2c



2c

Charge 0; multiplicity 1

C -0.75196800 -1.89939100 -1.29319900
C -1.09374400 -2.48157100 -2.61558300
N 0.00351900 -2.53679800 -0.45590600
C -1.18672500 -0.59578800 -0.69897100
O 0.18222700 -1.82020100 0.75461900
O 0.58267200 -3.63769000 -0.50028500
C -0.16434300 -0.45893400 0.44496600
H -0.62031600 -3.47020100 -2.72189800
H -2.18967100 -2.58680700 -2.71160400
H -0.74581600 -1.81647700 -3.42638100
H -2.22705600 -0.66503000 -0.33002800
H -1.12028800 0.23521900 -1.42067300
C 1.07565800 0.30941300 0.02229400
C 2.27345600 -0.35033700 -0.26377500
C 1.00516200 1.70102600 -0.10409200
C 3.38988200 0.37912900 -0.68039300
H 2.33761100 -1.44145900 -0.15777000
C 2.12155600 2.42719600 -0.51522900
H 0.06352900 2.21968800 0.12493600
C 3.31801300 1.76613300 -0.80614100
H 4.32673100 -0.14577700 -0.90649700
H 2.05901500 3.51890200 -0.60742100
H 4.19763000 2.33663900 -1.12984800
H -0.60690400 -0.02964500 1.35792100

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -592.502283 E_0
Sum of electronic and zero-point Energies= -592.308244 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -592.297268 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -592.296324 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -592.340326 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.194039
Number of imaginary vibrational frequencies = 0

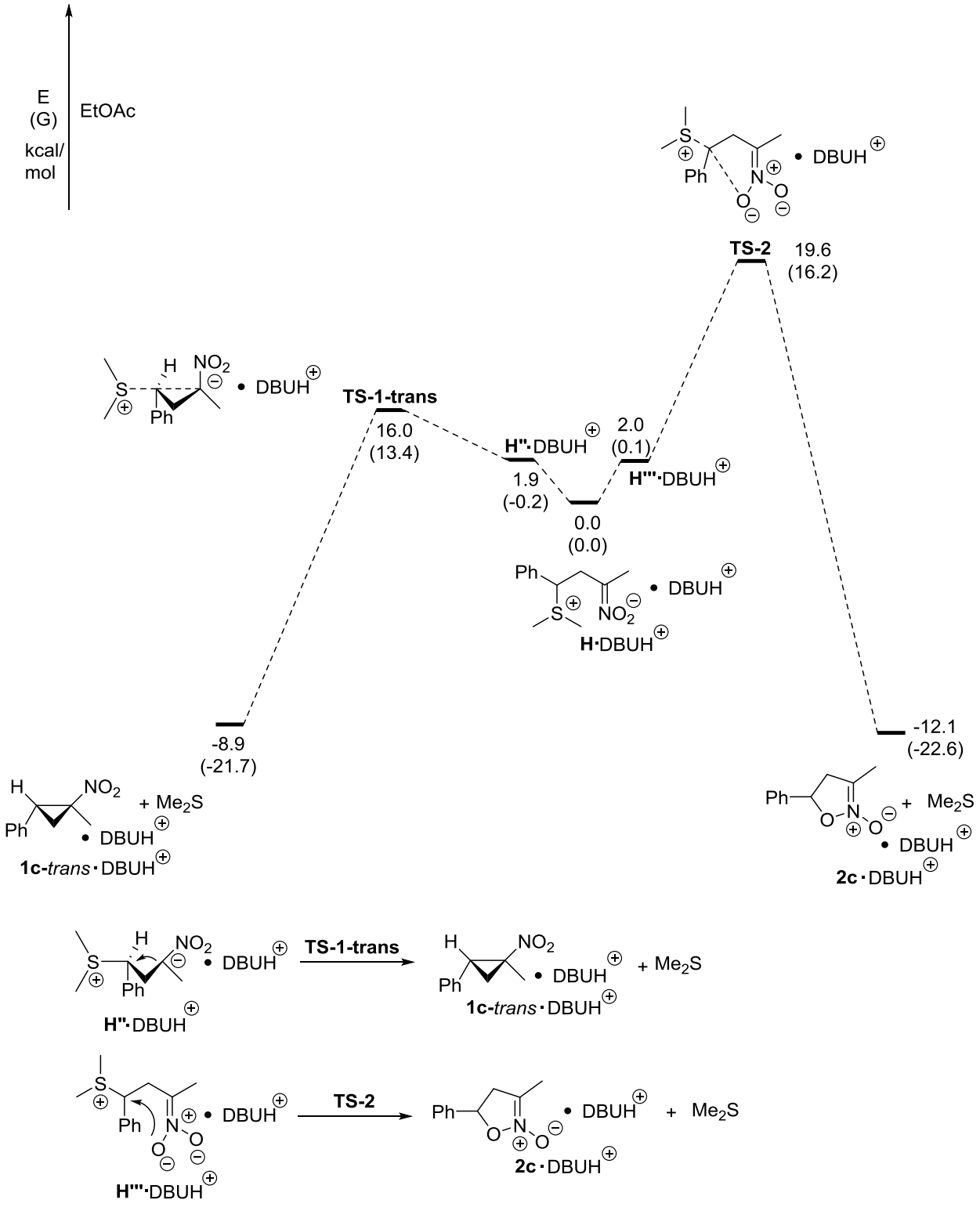
Me_2S

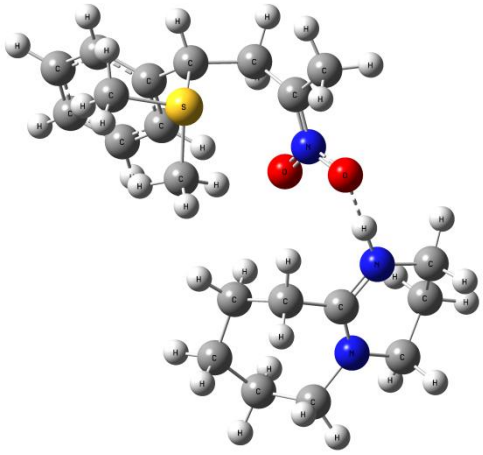
Charge 0; multiplicity 1

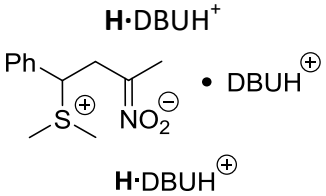
S -2.63823800 2.20471200 1.26977200
C -3.37823000 0.76629900 2.07787100
H -3.83940600 1.05109900 3.04051900
H -4.16221500 0.37106200 1.40904000
H -2.62200000 -0.02110500 2.24700200
C -1.43128000 2.63734800 2.54469300
H -0.71499200 1.81141200 2.70352700
H -0.87912300 3.52741500 2.19689500
H -1.93634000 2.87929400 3.49696700

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -477.939926 E_0
Sum of electronic and zero-point Energies= -477.864936 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -477.860021 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -477.859077 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -477.886519 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.074990
Number of imaginary vibrational frequencies = 0

8.6 Calculations in EtOAc with $DBUH^+$ as HBD





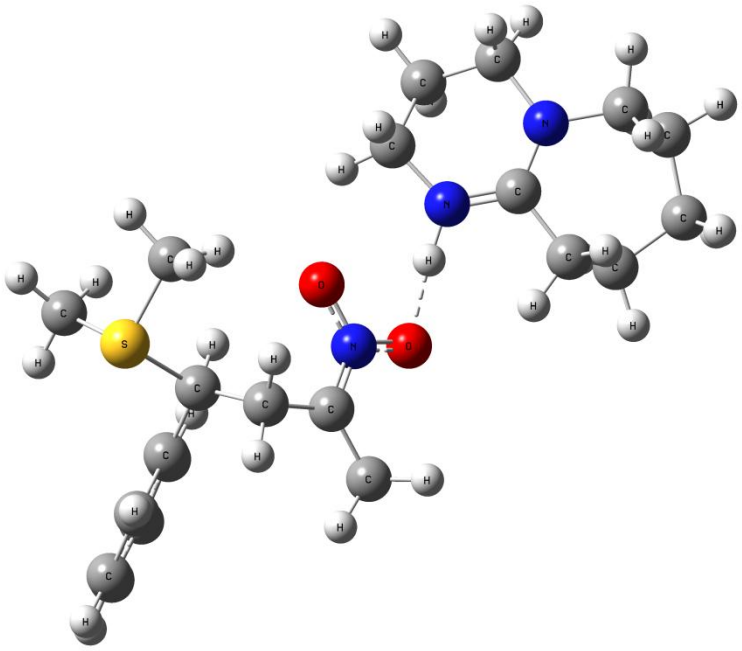


Charge 1; multiplicity 1

C -3.20893400 6.30589000 -1.28120700
C -2.54882400 4.99023100 -1.55694400
C -3.21045200 3.66454800 -1.32490300
C -3.04201100 3.03388600 0.09566200
N -1.35040200 5.00544500 -2.10898700
O -0.69437600 3.93016300 -2.36735000
S -2.02625400 4.18630500 1.13299300
H -4.00086000 3.06850700 0.64611200
C -2.13922000 3.42625500 2.75602700
C -0.32348300 3.82364500 0.69581600
H -2.54691400 6.96538100 -0.68976000
H -3.43971000 6.84890100 -2.21872000
H -4.15047900 6.15152000 -0.72561400
H -2.82965600 2.94492100 -2.06617600
H -3.18545600 3.50484000 3.09608400
H -1.48768700 4.01434100 3.42443600
H -1.80543200 2.37632800 2.70808100
H -0.25335300 3.81739800 -0.41157000
H 0.29080000 4.63013400 1.13137400
H -0.04534300 2.84194200 1.11450000
H -4.29557200 3.78019900 -1.49033400
C -2.50468600 1.62305800 0.13136300
C -1.46680500 1.22598300 -0.72392100
C -3.04898600 0.69967100 1.03153600
C -0.97712100 -0.07804200 -0.66174000
H -1.05232500 1.95103800 -1.44066900
C -2.55952900 -0.60560500 1.08680500
H -3.87381100 1.00737000 1.68925200
C -1.51974400 -0.99425800 0.24200300
H -0.16548200 -0.38485200 -1.33308100
H -2.99787300 -1.32402300 1.79023100
H -1.13471500 -2.02076300 0.28197600
O -0.78720800 6.13796500 -2.37548700
H 0.43090200 5.80507500 -3.39831700
N 1.25913700 5.63959600 -4.04081300
C 1.13013200 5.90252900 -5.46697500
C 2.34003200 5.11811400 -3.50732600
H 1.45618200 6.93723900 -5.68835200
H 0.06298800 5.82016200 -5.72994500
C 1.97655700 4.89654500 -6.23323100
N 3.41085100 4.80920300 -4.23530100
C 2.32027800 4.83375000 -2.02829400
H 1.55210900 3.88451400 -6.09934600
H 1.97924000 5.12938800 -7.31054800

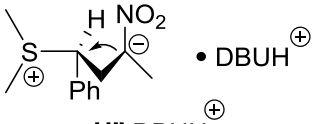
C 3.40031700 4.92968700 -5.69920200
C 4.64707100 4.31482300 -3.61713600
C 2.41957800 3.32860000 -1.72051000
H 1.36774700 5.23904000 -1.65023300
H 3.15104100 5.38340100 -1.54526500
H 3.98735700 4.08571800 -6.10147500
H 3.91260200 5.86791000 -5.98890900
H 4.93842200 4.98768000 -2.78886100
H 5.42791600 4.40137400 -4.39068800
C 4.53751700 2.87249100 -3.11906800
C 3.84161800 2.76470900 -1.76168400
H 1.75220400 2.78132400 -2.41340800
H 2.01129100 3.16885200 -0.70572600
H 5.55807600 2.45604600 -3.03602900
H 4.00475400 2.27266400 -3.88343000
H 3.81880800 1.70530400 -1.44603800
H 4.45588900 3.30352800 -1.01106700

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1532.766559 E_0
Sum of electronic and zero-point Energies= -1532.235179 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1532.207161 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1532.206217 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1532.289258 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.531379
Number of imaginary vibrational frequencies = 0



Pre-reaction conformation

H''·DBUH$^+$



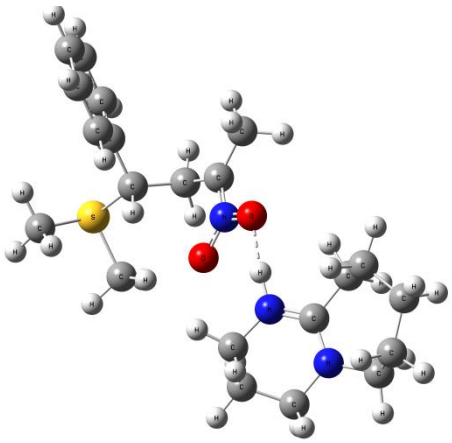
H"·DBUH$^+$

Charge 1; multiplicity 1

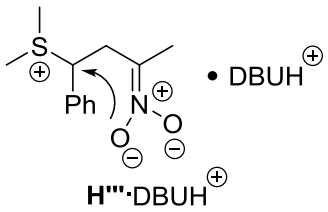
C 1.74065500 0.43353500 -0.92115900
C 2.99344700 0.86645500 -0.22905000
H 2.76714100 1.56949900 0.59539100
H 3.67278100 1.36233900 -0.94353800
H 3.52587200 0.00895500 0.22672000
C 1.45084300 0.61674900 -2.37979200
H 1.00919200 -0.31374700 -2.78234800
H 2.37434200 0.84712900 -2.93814700
C 0.44696700 1.77935600 -2.51264900
H -0.33939300 1.64712700 -1.74682000
C 1.07291700 3.15039900 -2.42677100
C 0.74471400 3.98754900 -1.35673300
H 0.02331400 3.64277500 -0.60353400
C 1.34131000 5.24398000 -1.24050400
H 1.08641700 5.89188600 -0.39294300
C 2.25774800 5.67337200 -2.20007900
H 2.72401000 6.66222500 -2.11033600
C 2.58369500 4.84237600 -3.27445900
H 3.30466400 5.17725900 -4.03009100
C 1.99752100 3.58331200 -3.38586700
H 2.26450700 2.92909400 -4.22823100
N 0.76147200 -0.07444700 -0.20234700
O -0.36515400 -0.40874900 -0.72748800
O 0.91445500 -0.23586500 1.07357900
S -0.48083600 1.63633200 -4.09953200
C -1.78771900 2.83433200 -3.81424400
H -2.50819000 2.74212000 -4.64387600
H -2.26598700 2.62621600 -2.84193000
H -1.32443100 3.83506500 -3.82700900
C -1.34774600 0.07603600 -3.82416800
H -0.81601700 -0.70688400 -4.38812300
H -1.33404900 -0.13937800 -2.73836600
H -2.37050600 0.19150600 -4.21895500
H -0.31780300 -1.17574000 1.46223000
N -1.08247000 -1.85572100 1.76512300
C -2.41941600 -1.70715800 1.21449400
C -0.77112400 -2.79074100 2.63058300
H -2.51050300 -2.32173500 0.29829500

H -2.53896600 -0.65415600 0.91604900
C -3.43104300 -2.13972900 2.26550300
N -1.67142700 -3.65564600 3.09612000
C 0.65270700 -2.83619300 3.12040700
H -3.39407800 -1.43861200 3.11980700
H -4.45450600 -2.12670000 1.85594200
C -3.09281300 -3.54589000 2.74030100
C -1.29341500 -4.75139500 3.99714100
C 0.77780500 -2.53235500 4.62396100
H 1.21294700 -2.09874800 2.52186000
H 1.07496600 -3.83521900 2.89960300
H -3.67815700 -3.80394800 3.64036600
H -3.32725400 -4.29423900 1.95821200
H -0.45043300 -5.31685500 3.55677200
H -2.15841800 -5.43455400 4.01973600
C -0.94475600 -4.28103600 5.41126700
C 0.47660700 -3.72823200 5.52961700
H 0.12096300 -1.67803300 4.88001100
H 1.81332000 -2.19706400 4.81191600
H -1.05431000 -5.14096300 6.09715700
H -1.68839600 -3.52179200 5.72522600
H 0.67140100 -3.44455400 6.58022700
H 1.19010800 -4.54167800 5.28537800

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1532.763475 E_0
Sum of electronic and zero-point Energies= -1532.232941 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1532.204347 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1532.203403 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1532.289524 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.530534
Number of imaginary vibrational frequencies = 0



Pre-reaction conformation **H'''**·DBUH$^+$

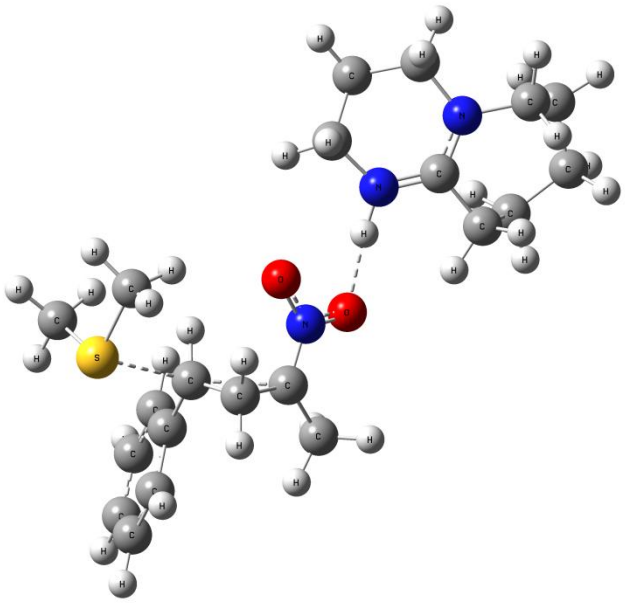


Charge 1; multiplicity 1

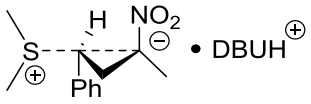
C -0.36280400 1.56498300 -1.28845000
C 0.31495700 1.66104200 -2.61784400
C -1.02344700 2.70324800 -0.57243600
O -0.81176100 0.29592200 0.54806100
O 0.28431800 -0.59641500 -1.15815900
C -0.07669500 3.15134300 0.55802000
S -1.03556500 4.02023500 1.87221700
H 1.37805600 1.36154700 -2.54268800
H -0.14930900 0.98607800 -3.36289100
H 0.26266400 2.69526100 -2.99932600
H -1.98404100 2.35824500 -0.14581500
H -1.21898800 3.54151600 -1.26280400
C 1.06480300 4.03019900 0.10767100
C 2.37658300 3.56656300 0.24310700
C 0.83083200 5.28825300 -0.46228500
C 3.44666900 4.34931400 -0.19267900
H 2.55562800 2.57712300 0.68499200
C 1.90111400 6.07272200 -0.88770600
H -0.19767200 5.65995800 -0.57692000
C 3.21004400 5.60337100 -0.75498400
H 4.47267300 3.97510500 -0.09085000
H 1.71249900 7.05806700 -1.33114700
H 4.05080100 6.22065600 -1.09476800
C -2.08105000 2.66230000 2.44462900
H -2.09765900 2.69704600 3.54629500
H -3.09554300 2.83008700 2.04928400
H -1.65731800 1.71472300 2.05900600
C 0.20443200 4.10342400 3.16965100
H 0.64116000 3.10096300 3.31917000
H 0.96889000 4.82993800 2.84692200
H -0.29634200 4.46456700 4.08309200
H 0.29443500 2.24738100 1.07557800
N -0.30592700 0.42705100 -0.62856100
H -0.22446300 -1.80949200 -0.24514400
N -0.58553000 -2.66596100 0.27810800
C -0.78405000 -2.58512000 1.71609600
C -0.81246400 -3.75835100 -0.41217600
H -1.82182100 -2.26251400 1.92712200
H -0.11216300 -1.80070300 2.09753700
C -0.50318000 -3.95039200 2.32616000
N -1.21948200 -4.88955800 0.16169100
C -0.55947200 -3.70560500 -1.89624100
H 0.56860500 -4.19347300 2.20389300
H -0.73451700 -3.95455400 3.40402500
C -1.35005500 -5.00031700 1.62107500

C -1.54057600 -6.08351500 -0.63048200
C 0.59487100 -4.62261500 -2.33847300
H -0.34005700 -2.65262200 -2.13879800
H -1.48963800 -3.98287300 -2.42817400
H -1.02585100 -6.01720200 1.90338100
H -2.41801300 -4.89726100 1.89606600
H -2.25813900 -5.81500500 -1.42879900
H -2.06687000 -6.76828800 0.05456100
C -0.30722300 -6.76615700 -1.22657300
C 0.19812300 -6.09122200 -2.50285100
H 1.43272000 -4.52670700 -1.62019100
H 0.96930400 -4.24570400 -3.30684400
H -0.57119400 -7.81494100 -1.45515100
H 0.48911800 -6.79481300 -0.45649800
H 1.06230000 -6.65712600 -2.89679400
H -0.59797700 -6.15595500 -3.27254000

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1532.763433 E_0
Sum of electronic and zero-point Energies= -1532.232560 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1532.204018 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1532.203074 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1532.289102 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.530873
Number of imaginary vibrational frequencies = 0



TS-1-trans



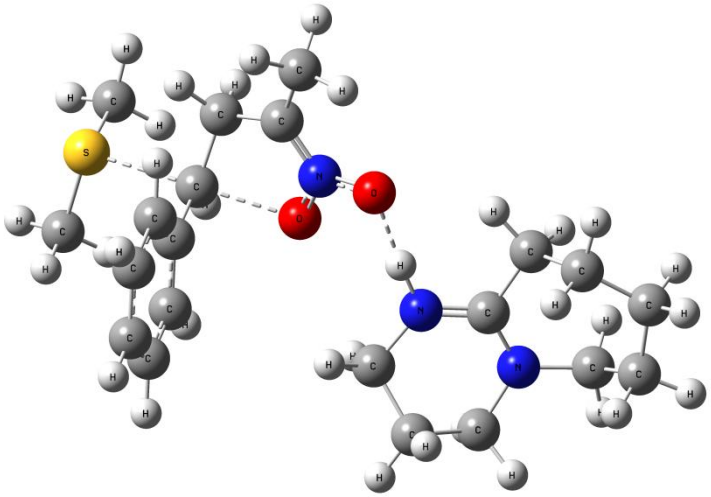
TS-1-trans

Charge 1; multiplicity 1

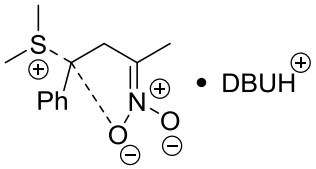
C 7.00074800 4.86749100 7.68563800
C 8.23943500 5.37720100 8.34575400
H 7.99888100 6.08933500 9.15669000
H 8.87654500 5.88440400 7.60171900
H 8.81810400 4.54837900 8.79680900
C 6.72729200 4.88893200 6.20905000
H 6.13452600 4.02610900 5.87215700
H 7.64037800 5.03786800 5.61522900
C 5.94222100 6.11584200 6.45908600
H 5.00796500 5.96544500 7.02183900
C 6.57930600 7.44976900 6.57371700
C 6.11418700 8.34109000 7.54933200
H 5.29717700 8.03067300 8.21492100
C 6.69543400 9.60117600 7.68423700
H 6.33227100 10.29139200 8.45534200
C 7.73860000 9.98011600 6.83869600
H 8.19560000 10.97201000 6.94250300
C 8.20073700 9.09837300 5.85791100
H 9.01589400 9.39922000 5.18869500
C 7.62553900 7.83756500 5.72520100
H 7.97969000 7.15228800 4.94359100
N 6.04294300 4.30321900 8.45836300
O 4.97218700 3.86713400 7.95601700
O 6.22838400 4.23090100 9.71226700
S 4.59313400 6.43070900 4.54692900
C 3.49447300 7.62019600 5.33399800
H 2.54186000 7.66860300 4.77939200
H 3.30741500 7.32912200 6.38432700
H 3.99004300 8.60527000 5.29907500
C 3.66592600 4.91009200 4.82290500
H 4.11940700 4.12345800 4.19659700
H 3.72193000 4.61749400 5.89014500
H 2.61689800 5.05598400 4.51400800
H 4.94494000 3.18739200 10.19805800
N 4.23490100 2.49692300 10.52701400
C 2.91426900 2.49632500 9.91485900
C 4.58802500 1.66351400 11.48178100
H 2.91422600 1.81970200 9.03903100
H 2.71612100 3.51561000 9.54860500
C 1.89987900 2.04674000 10.95534900

N 3.74311800 0.76852100 11.98091700
C 5.98669400 1.78151000 12.02646000
H 1.83341800 2.80642500 11.75589700
H 0.90054300 1.93591800 10.50378600
C 2.33911700 0.71562000 11.54717300
C 4.16784500 -0.21315700 12.98884600
C 6.01789300 2.21967000 13.50191600
H 6.51575300 2.51040000 11.39064900
H 6.49888400 0.80773400 11.90877700
H 1.73229900 0.46409100 12.43405800
H 2.22274800 -0.10412000 10.81200900
H 5.07393400 -0.73748400 12.63057600
H 3.36227400 -0.96389700 13.03578600
C 4.41118800 0.40136700 14.36885800
C 5.77539600 1.08098900 14.49456600
H 5.28226800 3.03299200 13.65725300
H 7.01323100 2.65630000 13.69788900
H 4.34083200 -0.40606900 15.12034000
H 3.59412600 1.11706100 14.58772900
H 5.89790600 1.46656300 15.52322900
H 6.56396900 0.31462400 14.34857900

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1532.741042 E_0
Sum of electronic and zero-point Energies= -1532.211724 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1532.183072 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1532.182127 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1532.267887 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.529318
Number of imaginary vibrational frequencies = 1; 550*i*



TS-2



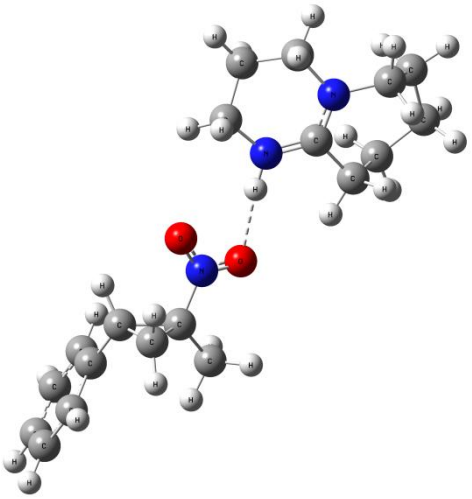
TS-2

Charge 1; multiplicity 1

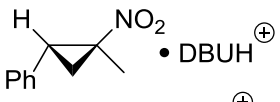
C 1.44884400 0.08029600 -1.32784900
C 1.48957600 0.37216400 -2.78754100
C 1.01037600 1.05493700 -0.27361300
O 1.72241100 -1.24902300 0.45113000
O 2.18875100 -2.07844400 -1.55637500
C 1.72191600 0.74516400 1.03809100
S 1.35038900 2.82951300 2.02192300
H 1.96704300 -0.46950500 -3.31194100
H 0.47269800 0.51697300 -3.20118000
H 2.06219000 1.29780500 -2.98663500
H -0.08305900 0.99546100 -0.10416300
H 1.23858400 2.08012800 -0.61795700
C 3.20539500 0.76855100 1.12849900
C 3.83692400 0.13236000 2.20594500
C 3.97809300 1.40243600 0.14998400
C 5.22489900 0.13607900 2.30626700
H 3.22595800 -0.38351500 2.95921000
C 5.36997800 1.40163800 0.25076700
H 3.49285500 1.90730700 -0.69586200
C 5.99406900 0.77187500 1.32697000
H 5.71413300 -0.36443100 3.15098700
H 5.97083900 1.89898700 -0.52022200
H 7.08833700 0.77359900 1.40419500
C -0.43748000 2.69005800 2.19271300
H -0.78142300 3.36426800 2.99564400
H -0.89559500 3.00105700 1.23914200
H -0.71644800 1.64622800 2.42734800
C 1.84666600 2.39824900 3.69581500
H 1.47196300 1.39039200 3.95242800
H 2.94840400 2.41897000 3.73649000
H 1.43928300 3.14497600 4.39848200
H 1.16267500 0.32725600 1.88198800
N 1.78325400 -1.08604500 -0.84802800
H 2.45269900 -3.26948100 -0.45867500
N 2.57466100 -4.07624400 0.21135200
C 3.23519700 -3.83946500 1.48511200
C 2.09478200 -5.24591900 -0.14279200
H 2.48634700 -3.51750000 2.23400800
H 3.94511100 -3.00815700 1.34461000
C 3.93174500 -5.12098600 1.91828900
N 2.20179000 -6.32040100 0.63444400

C 1.44511100 -5.34684300 -1.49736700
H 4.75968700 -5.34199800 1.21978300
H 4.35696800 -5.01211400 2.92945100
C 2.93318500 -6.26967600 1.90808500
C 1.59996200 -7.60610500 0.25694300
C 2.22695800 -6.25690300 -2.46209000
H 1.37840100 -4.31943900 -1.89202600
H 0.41212100 -5.72335700 -1.37248900
H 3.45146000 -7.23689000 2.02799800
H 2.20510600 -6.16996900 2.73677300
H 0.53371300 -7.45295700 0.00316100
H 1.62572700 -8.22956200 1.16551000
C 2.33157700 -8.30148600 -0.89342800
C 1.95413100 -7.75033600 -2.26958700
H 3.30986400 -6.04554200 -2.36570000
H 1.94385400 -5.97437700 -3.49160600
H 2.08455100 -9.37824400 -0.85750300
H 3.42286500 -8.21528400 -0.72177700
H 2.49202100 -8.31904300 -3.05019300
H 0.87267400 -7.93323600 -2.43559700

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1532.735360 E_0
Sum of electronic and zero-point Energies= -1532.206755 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1532.177993 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1532.177049 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1532.263412 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.528605
Number of imaginary vibrational frequencies = 1; 552*i*



1c-*trans*·DBUH$^+$



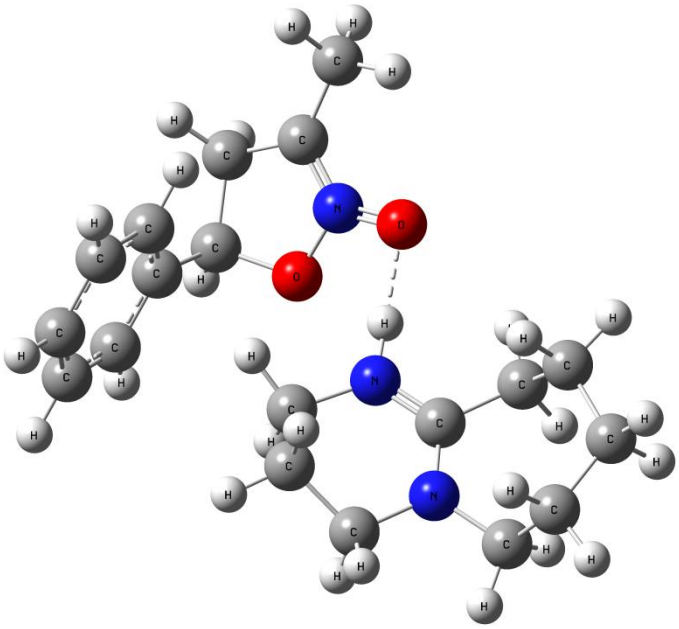
1c-*trans*·DBUH$^+$

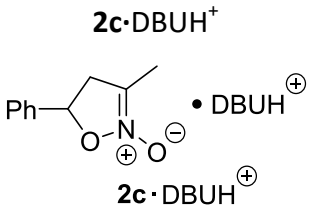
Charge 1; multiplicity 1

C 1.53501900 0.83807500 -0.96379200
C 2.84792400 1.18696100 -0.32453900
H 2.70023900 1.79932000 0.58167200
H 3.44700000 1.76485000 -1.04753400
H 3.40429000 0.27462700 -0.05054700
C 1.38649200 0.55795100 -2.44052500
H 0.71418700 -0.25827200 -2.72323100
H 2.31924400 0.64685100 -3.01024500
C 0.77467100 1.79776800 -1.87719600
H -0.31248500 1.76117800 -1.73001400
C 1.35854000 3.15677700 -2.11278400
C 1.18864300 4.15729700 -1.14704900
H 0.62872000 3.93248700 -0.22894400
C 1.72656900 5.42746800 -1.34378100
H 1.59018200 6.20270200 -0.57953300
C 2.43934400 5.71232300 -2.51093800
H 2.86327300 6.71210100 -2.66648600
C 2.60755900 4.72220500 -3.47828200
H 3.16093900 4.94193900 -4.39979900
C 2.07010200 3.44886800 -3.27938500
H 2.19782800 2.67425500 -4.04666600
N 0.64438000 0.03432200 -0.11065800
O -0.42894000 -0.33492800 -0.55096300
O 1.02668900 -0.22643300 1.02281500
H -0.43586100 -1.40651400 1.60215400
N -1.13461300 -2.09772200 1.88769600
C -2.45793200 -2.05988200 1.27508100
C -0.77025000 -2.98684500 2.79450700
H -2.45461600 -2.66597900 0.34945900
H -2.67244300 -1.01583100 0.99822700
C -3.46344700 -2.59899400 2.28031500
N -1.60608300 -3.91634700 3.22824000
C 0.62191800 -2.88265600 3.35663500
H -3.54299700 -1.89904500 3.13217000
H -4.45921800 -2.69144700 1.81758300
C -3.00596100 -3.96190000 2.77603200
C -1.17639900 -4.95729900 4.17587300
C 0.63348100 -2.53789700 4.85763500
H 1.15103600 -2.10658300 2.77942000
H 1.15090000 -3.83830500 3.18000700
H -3.61447700 -4.28795000 3.63664800
H -3.09766700 -4.72825800 1.98266700

H -0.26131800 -5.44436500 3.78988100
H -1.97334300 -5.71816000 4.16579600
C -0.95215600 -4.42902800 5.59372500
C 0.40146900 -3.74092200 5.77354000
H -0.11542100 -1.74684100 5.05725300
H 1.62085000 -2.10044700 5.08789900
H -1.01655600 -5.28456600 6.29017800
H -1.78093100 -3.74072400 5.85202700
H 0.51050100 -3.41854700 6.82502400
H 1.20248200 -4.48470100 5.58590000

DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1054.840660 E_0
Sum of electronic and zero-point Energies= -1054.386959 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1054.363912 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1054.362968 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1054.437084 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.453701
Number of imaginary vibrational frequencies = 0





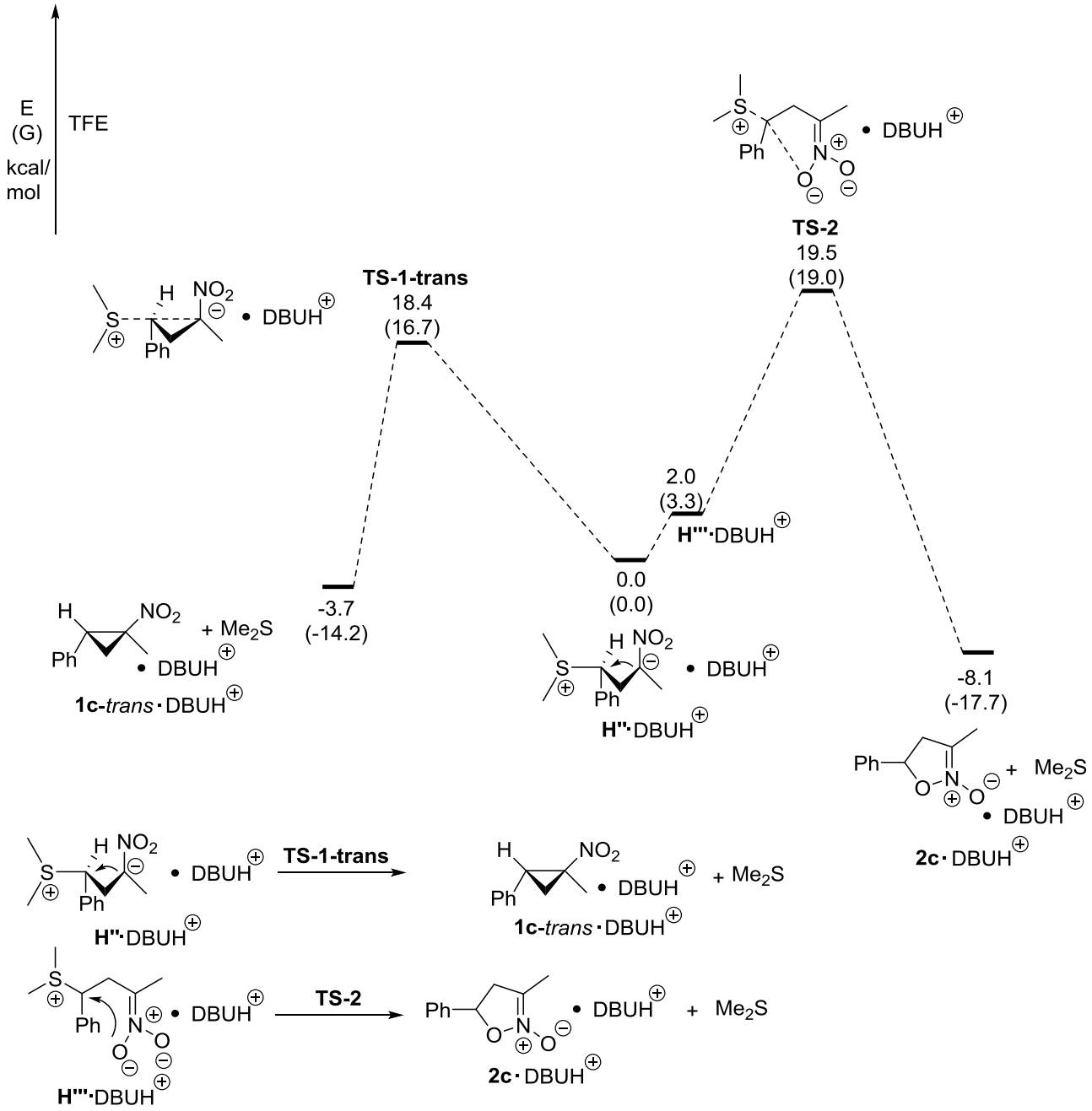
Charge 1; multiplicity 1

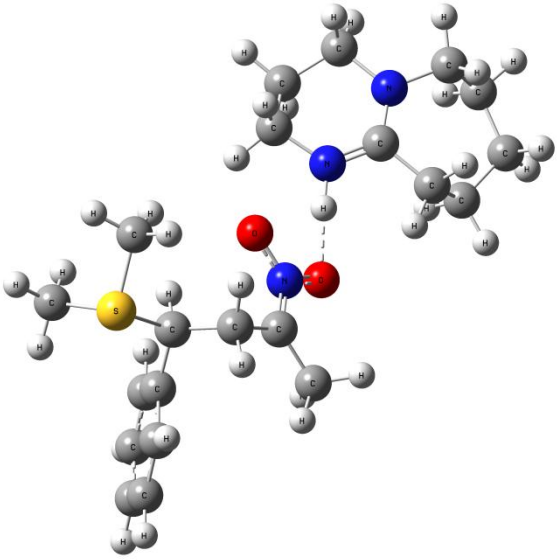
C -1.19491400 2.10903000 -1.88490000
C -1.18856100 2.43728800 -3.33314600
C -1.16616000 3.03928100 -0.71234200
O -1.25483300 0.76750300 -0.07450700
O -1.26563500 -0.20746400 -2.09191000
C -0.85223900 2.07366600 0.44269400
H -1.17791100 1.50849400 -3.92414600
H -2.08634100 3.02693900 -3.59316000
H -0.30183100 3.04726000 -3.58273800
H -2.14537200 3.53613100 -0.58668900
H -0.39536400 3.82101000 -0.82453200
C 0.60247600 1.97783400 0.84742900
C 0.91402600 1.65410400 2.17067000
C 1.63370100 2.08698300 -0.09357300
C 2.23650600 1.42528100 2.55177900
H 0.10415400 1.57033500 2.90831000
C 2.95603100 1.85472500 0.28510300
H 1.41113600 2.34875700 -1.13695700
C 3.25888100 1.51833400 1.60629800
H 2.47038800 1.17494400 3.59402200
H 3.75852200 1.94030700 -0.45798800
H 4.30006400 1.33907900 1.90205200
H -1.48492400 2.25122000 1.32600200
N -1.23369200 0.88267500 -1.47389800
H -0.50631500 -1.37264100 -1.00033500
N -0.04430200 -2.05638600 -0.37387600
C 0.87851800 -1.57604400 0.64679900
C -0.31415900 -3.33110600 -0.57022500
H 0.31891500 -1.35615700 1.57657800
H 1.32120400 -0.63117600 0.29016400
C 1.93904100 -2.64038200 0.88169300
N 0.25437100 -4.28671000 0.15167200
C -1.27251500 -3.67526600 -1.67849300
H 2.57399000 -2.73018900 -0.01882500
H 2.58457400 -2.35920400 1.73000100
C 1.26862300 -3.97533000 1.17042300
C -0.09476500 -5.70244700 -0.03771300
C -0.60132000 -4.44849900 -2.82816100
H -1.69798600 -2.72589600 -2.04408000

H -2.10559000 -4.26746500 -1.25473500
H 2.00852300 -4.79402200 1.15533000
H 0.78462500 -3.97175200 2.16600900
H -1.19328200 -5.81943000 0.02154500
H 0.33287400 -6.23539200 0.82677200
C 0.43807900 -6.28494600 -1.34858500
C -0.43472100 -5.94494900 -2.55779900
H 0.37781100 -3.98407500 -3.05646400
H -1.22814700 -4.31673100 -3.72767600
H 0.48802700 -7.38348000 -1.23925100
H 1.47642300 -5.92885900 -1.49949800
H -0.01498000 -6.42902400 -3.45849600
H -1.43944400 -6.38758800 -2.40099700

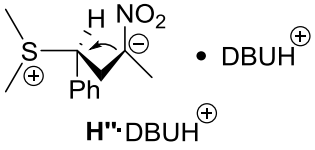
DFT M11; cc-pvdz+d, solvent EtOAc, SMD model
Total electronic energy= -1054.845799 E_0
Sum of electronic and zero-point Energies= -1054.391162 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1054.368630 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1054.367686 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1054.438473 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.454637
Number of imaginary vibrational frequencies = 0

8.7 Calculations in 2,2,2-trifluoroethanol (TFE) with $DBUH^+$ as HBD





Pre-reaction conformation **H''**·DBUH$^+$



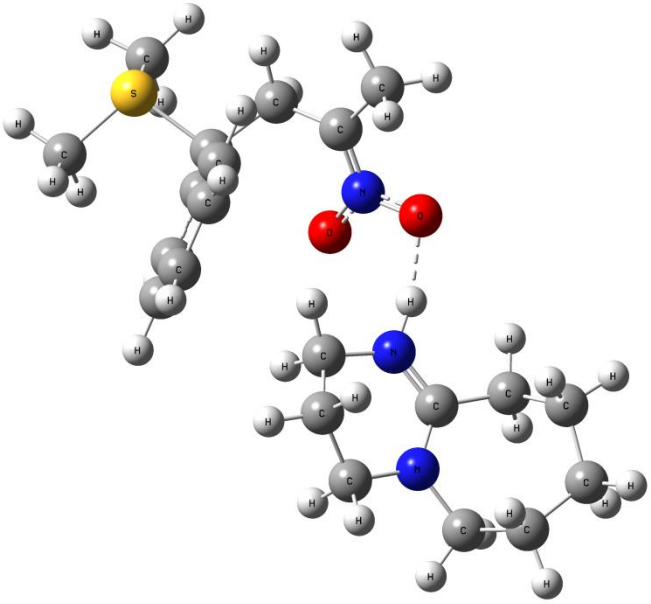
H''·DBUH$^+$

Charge 1; multiplicity 1

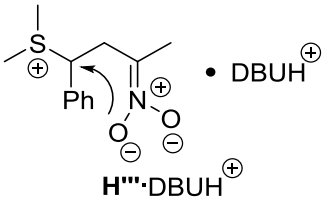
C 1.68237200 0.35904300 -1.09205900
C 2.95452900 0.82877500 -0.46193100
H 2.75197400 1.58087500 0.32597200
H 3.61324600 1.28042600 -1.22283100
H 3.49553000 -0.00551300 0.02529400
C 1.33959300 0.52319500 -2.54257900
H 0.85791400 -0.39998500 -2.91173700
H 2.25192300 0.71709300 -3.13284200
C 0.36304100 1.70723100 -2.65770000
H -0.49297100 1.52432600 -1.98161600
C 0.99708000 3.04801600 -2.36789500
C 0.52569900 3.80828400 -1.29372000
H -0.31545700 3.43336400 -0.69504000
C 1.12763300 5.02813500 -0.98059600
H 0.75789500 5.61627500 -0.13149700
C 2.19515800 5.49700500 -1.74666400
H 2.66759700 6.45658800 -1.50202300
C 2.66288900 4.74378300 -2.82619400
H 3.50128800 5.11038400 -3.43134800
C 2.06906200 3.52109300 -3.13503200
H 2.44704100 2.92849500 -3.98042900
N 0.75377300 -0.15906800 -0.32456300
O -0.39297700 -0.53146200 -0.78680800
O 0.96989200 -0.30372600 0.95131300
S -0.38814900 1.75490300 -4.33664600
C -1.68458900 2.96875100 -4.07689200
H -2.31192400 2.97473700 -4.98369400
H -2.26888100 2.68710700 -3.18436600
H -1.19620900 3.94906200 -3.94807000
C -1.33370100 0.22474000 -4.33071600
H -0.66793400 -0.58755600 -4.66318800
H -1.71632100 0.04040100 -3.31155000
H -2.15615800 0.35296800 -5.05391100
H -0.32208500 -1.23413100 1.47144500
N -1.10121200 -1.82994600 1.85138300
C -2.46861000 -1.54610400 1.44199400
C -0.79211600 -2.79014600 2.69556300
H -2.71699400 -2.13924000 0.54070100
H -2.52220700 -0.48041800 1.16696900
C -3.40211000 -1.88844400 2.59208300
N -1.71699000 -3.56392500 3.25311200

C 0.66141000 -2.96988000 3.03900400
H -3.21301000 -1.19804600 3.43486000
H -4.45523400 -1.77821700 2.28575000
C -3.15131900 -3.32102200 3.03718800
C -1.35464500 -4.67307100 4.14626700
C 0.96210100 -2.64988300 4.51416300
H 1.23009200 -2.30230900 2.37097700
H 0.95797400 -4.00971400 2.80320900
H -3.66657700 -3.52634900 3.99167500
H -3.52821600 -4.04221000 2.28645900
H -0.61099900 -5.31997300 3.64401900
H -2.27085300 -5.27364800 4.26741000
C -0.83110300 -4.21159900 5.50749300
C 0.63988700 -3.79391100 5.47748700
H 0.41324500 -1.73244000 4.80495300
H 2.03790400 -2.41161200 4.59234900
H -0.95286800 -5.04719800 6.22097000
H -1.46873700 -3.38162000 5.87140900
H 0.95918700 -3.50803800 6.49683000
H 1.24860700 -4.67560000 5.19030700

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1532.776704 E_0
Sum of electronic and zero-point Energies= -1532.246396 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1532.217577 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1532.216633 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1532.303663 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.530308
Number of imaginary vibrational frequencies = 0



Pre-reaction conformation **H'''**·DBUH$^+$



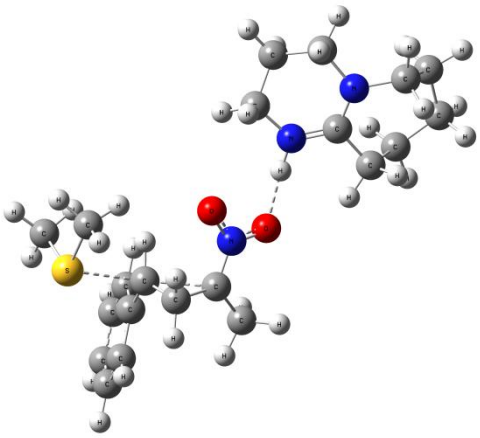
H'''·DBUH

Charge 1; multiplicity 1

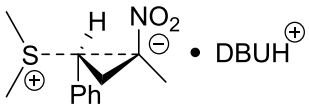
C -0.95534300 2.15094900 -1.60538300
C -0.33242700 2.40206900 -2.94287000
C -1.33322800 3.24601900 -0.65139800
O -1.73246200 0.60277500 -0.13215300
O -0.95367300 -0.05021600 -2.10932200
C -0.80894800 3.07166400 0.79510000
S -0.72058600 4.76672100 1.52273700
H 0.61907500 1.84417800 -3.04497800
H -0.98995600 2.05933600 -3.76526200
H -0.13089900 3.47787200 -3.07888000
H -2.43583600 3.33428500 -0.58646000
H -0.95657200 4.19339000 -1.08091300
C 0.55723800 2.44657100 0.95688600
C 0.79997600 1.62224700 2.06118800
C 1.58674200 2.69565000 0.04144100
C 2.05958100 1.05537400 2.25496200
H -0.01456100 1.42145700 2.77148100
C 2.84111100 2.11329300 0.22605600
H 1.40974300 3.35091900 -0.82281500
C 3.07980900 1.29517300 1.33311900
H 2.24147700 0.41313000 3.12618600
H 3.64198300 2.30593200 -0.49851000
H 4.06947600 0.84341700 1.47784200
C -2.44526200 5.26776300 1.48883700
H -2.52860100 6.16656400 2.12263000
H -2.70592100 5.51958100 0.44821000
H -3.07078500 4.44607400 1.87721300
C -0.50393900 4.43618100 3.27232300
H -1.25116100 3.69546600 3.60381300
H 0.52584300 4.07312200 3.42118900
H -0.63952400 5.39925900 3.79311100
H -1.54284800 2.53367600 1.41676300
N -1.22196400 0.91393400 -1.27208700
H -0.69079900 -1.37026400 -1.16092600
N -0.23094400 -2.04523000 -0.49632900
C 0.68684400 -1.45026400 0.46215000
C -0.40065900 -3.34002300 -0.63325700
H 0.14906100 -1.22224600 1.40243800
H 1.03140600 -0.49309100 0.03049800

C 1.83461400 -2.41691400 0.70633500
N 0.24718100 -4.21574000 0.12824000
C -1.33473700 -3.80972300 -1.71478100
H 2.43928100 -2.50936800 -0.21494800
H 2.49042600 -2.05107000 1.51400800
C 1.27220400 -3.77864200 1.08798200
C -0.00859200 -5.65885000 0.03056900
C -0.60963900 -4.60259900 -2.81687400
H -1.81232800 -2.90996300 -2.13776300
H -2.13354200 -4.42564300 -1.25946800
H 2.06890800 -4.54260000 1.08545200
H 0.82869100 -3.75411200 2.10223800
H -1.09589200 -5.84424500 0.11528000
H 0.46209900 -6.10950000 0.91951500
C 0.54445300 -6.29045300 -1.24787600
C -0.35386500 -6.06953600 -2.46571400
H 0.34182800 -4.09171500 -3.06418900
H -1.23598300 -4.55942700 -3.72573600
H 0.65237200 -7.37666200 -1.07280600
H 1.56150600 -5.89078600 -1.43145000
H 0.08846200 -6.57756600 -3.34263900
H -1.33055400 -6.55952000 -2.27495800

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1532.773504 E_0
Sum of electronic and zero-point Energies= -1532.243416 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1532.214848 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1532.213904 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1532.298410 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.530087
Number of imaginary vibrational frequencies = 0



TS-1-trans



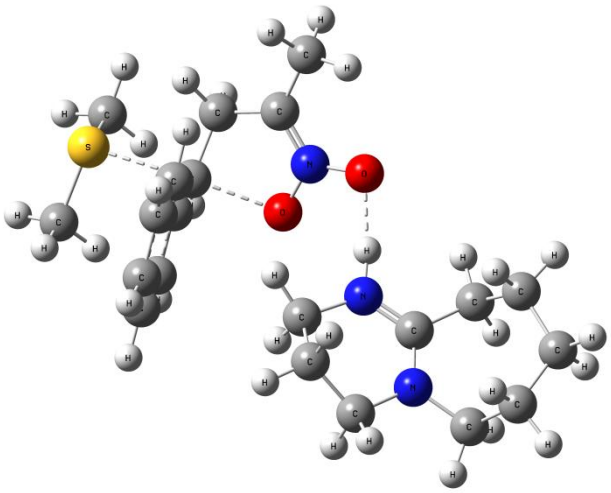
TS-1-trans

Charge 1; multiplicity 1

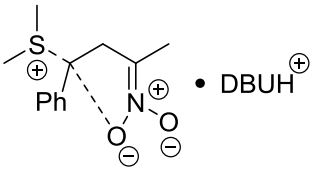
C 6.97959400 4.81899900 7.60328000
C 8.25556000 5.29139700 8.21900200
H 8.06846800 6.04579100 9.00648400
H 8.90275200 5.73446300 7.44409100
H 8.79627200 4.44731200 8.68825500
C 6.66073300 4.84094600 6.13380800
H 6.02252700 4.00284200 5.81965000
H 7.56023200 4.95531100 5.51291600
C 5.93852000 6.09119900 6.43306700
H 4.99602300 5.97807600 6.99114800
C 6.61547400 7.40314200 6.54014300
C 6.15712800 8.31927300 7.49667200
H 5.31684400 8.04155800 8.14772100
C 6.77146000 9.56418700 7.62711600
H 6.41247000 10.27451100 8.38196900
C 7.84089300 9.90254600 6.79689900
H 8.32396300 10.88267200 6.89673100
C 8.29690600 8.99508900 5.83629500
H 9.13364700 9.26385400 5.17985000
C 7.68921800 7.74919600 5.70726900
H 8.04193800 7.04466700 4.94251500
N 6.04277300 4.27890100 8.41281800
O 4.94483000 3.85574200 7.95536100
O 6.26913900 4.21008300 9.66165600
S 4.55237600 6.51159400 4.49730400
C 3.52155100 7.73365900 5.32594100
H 2.55624000 7.82341000 4.79871200
H 3.35239300 7.43735400 6.37798900
H 4.05141000 8.70066600 5.28706800
C 3.54492100 5.03947200 4.74795600
H 3.99819900 4.21916100 4.16625400
H 3.51968500 4.76899700 5.82113800
H 2.52181900 5.22410400 4.37801700
H 4.94662300 3.14813700 10.23170800
N 4.23274700 2.47997900 10.57591000
C 2.89904400 2.50473200 9.98993400
C 4.58664100 1.64480300 11.53255300
H 2.86701500 1.83178600 9.11170700
H 2.70556000 3.53026500 9.63733700
C 1.89866300 2.06926400 11.04813900
N 3.73800000 0.76142100 12.03967500
C 5.98880200 1.74860900 12.06541800
H 1.86039900 2.82847000 11.85110300
H 0.89036000 1.97617900 10.61294000
C 2.32568500 0.73083400 11.62933500

C 4.15502000 -0.20190900 13.06915800
C 6.02312400 2.22596200 13.52877100
H 6.53163600 2.45158400 11.41272200
H 6.48186700 0.76277800 11.97222500
H 1.73055000 0.48840200 12.52634700
H 2.18403200 -0.08593900 10.89578100
H 5.05743200 -0.73966500 12.72273500
H 3.34406500 -0.94554700 13.13077900
C 4.40045500 0.44035300 14.43527300
C 5.76868800 1.11435000 14.54864200
H 5.29199000 3.04796000 13.65966600
H 7.02192400 2.65893700 13.71561800
H 4.32573000 -0.35226800 15.20215200
H 3.58655400 1.16397200 14.63959100
H 5.89005700 1.52519200 15.56797700
H 6.55231000 0.33931200 14.42383800

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1532.747359 E_0
Sum of electronic and zero-point Energies= -1532.219214 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1532.190187 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1532.189242 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1532.277108 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.528145
Number of imaginary vibrational frequencies = 1; 601*i*



TS-2



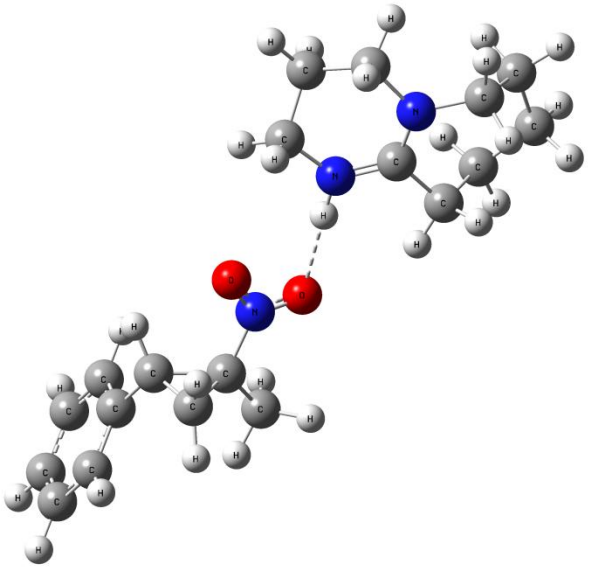
TS-2

Charge 1; multiplicity 1

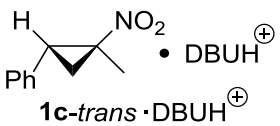
C 1.33561000 0.26065200 -1.40117800
C 1.58119700 0.54055200 -2.84235200
C 1.17994700 1.32597900 -0.35680400
O 0.99279000 -1.10869400 0.34174500
O 1.26721500 -2.01668700 -1.67377100
C 1.53218000 0.77619700 1.01684900
S 1.71793200 2.92943200 2.04240600
H 1.84274900 -0.39120400 -3.36652100
H 0.68359500 0.97714100 -3.32132900
H 2.40476800 1.26953500 -2.95430500
H 0.13747600 1.69770400 -0.34114900
H 1.83537100 2.17567600 -0.62030200
C 2.90732300 0.32768700 1.34587100
C 3.13686200 -0.32240900 2.56662400
C 3.96634900 0.51332500 0.44834500
C 4.41233400 -0.77793900 2.88944500
H 2.29771000 -0.48210100 3.25725700
C 5.24073900 0.04454200 0.77048100
H 3.80302300 1.03101700 -0.50591700
C 5.46618100 -0.59869700 1.98868500
H 4.58570300 -1.28507600 3.84703300
H 6.06687100 0.18887900 0.06333000
H 6.47114100 -0.96101000 2.23985500
C -0.00299700 3.42740600 1.84547800
H -0.23992500 4.21776200 2.57817500
H -0.12598900 3.82859600 0.82564000
H -0.66857000 2.55750900 1.99620100
C 1.67404100 2.40038200 3.76200000
H 0.95017600 1.57430500 3.88610900
H 2.68738000 2.06761200 4.04138000
H 1.38407200 3.25716000 4.39414300
H 0.74398200 0.59727700 1.75680300
N 1.19827500 -0.95062400 -0.94848700
H 1.77968100 -3.23676400 -0.63268400
N 2.26174400 -3.91161900 0.00596000
C 3.21397500 -3.36733800 0.96227800
C 2.04743500 -5.20013700 -0.14717600
H 2.70017400 -3.16072600 1.92068800
H 3.57653300 -2.40581700 0.55954200
C 4.34139800 -4.36866800 1.15399100
N 2.68828400 -6.10803700 0.57941800
C 1.06713400 -5.62072100 -1.20753200
H 4.92177100 -4.45265600 0.21649900

H 5.02422700 -4.03669900 1.95398900
C 3.75479000 -5.72446300 1.51735100
C 2.39170000 -7.54193000 0.45524500
C 1.73676100 -6.40457400 -2.35058500
H 0.59628900 -4.70074000 -1.59241200
H 0.27007700 -6.22885700 -0.73916000
H 4.52960000 -6.50910400 1.46899800
H 3.34286100 -5.71653000 2.54489000
H 1.30267300 -7.70092500 0.56622300
H 2.87496300 -8.02513300 1.31989600
C 2.89365100 -8.15481700 -0.85299400
C 1.96698800 -7.88475300 -2.03944400
H 2.69219800 -5.91099100 -2.61698800
H 1.08278300 -6.32553100 -3.23724400
H 2.98081800 -9.24702500 -0.70629700
H 3.91438300 -7.77432900 -1.05592000
H 2.37184000 -8.38310200 -2.93966600
H 0.98452100 -8.35565100 -1.83126200

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1532.745575 E_0
Sum of electronic and zero-point Energies= -1532.217401 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1532.188576 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1532.187632 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1532.273433 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.528174
Number of imaginary vibrational frequencies = 1; 577*i*



1c-*trans*·DBUH$^+$



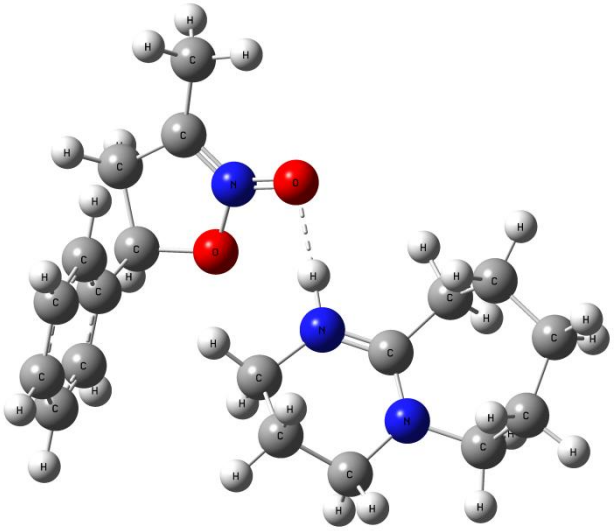
1c-*trans*·DBUH$^+$

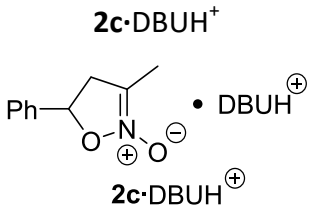
Charge 1; multiplicity 1

C 1.56671000 0.84320400 -0.96972200
C 2.88334700 1.21288700 -0.35160600
H 2.73948000 1.85850500 0.53257700
H 3.48044500 1.76126300 -1.09900100
H 3.43852400 0.30866800 -0.04855400
C 1.40457600 0.51707200 -2.43526200
H 0.73096100 -0.30973200 -2.68350000
H 2.33245700 0.58705200 -3.01556200
C 0.79597900 1.77254800 -1.90414700
H -0.28913400 1.74117500 -1.74027200
C 1.37348400 3.12679200 -2.17735600
C 1.18118200 4.15414900 -1.24404900
H 0.61010100 3.95027900 -0.32782200
C 1.71094100 5.42310600 -1.47083800
H 1.55677000 6.21937500 -0.73167400
C 2.43833000 5.67981900 -2.63595900
H 2.85598500 6.67853800 -2.81536300
C 2.62934000 4.66232600 -3.57072700
H 3.19520500 4.85900800 -4.49015200
C 2.10024200 3.39004900 -3.34173100
H 2.24798900 2.59393100 -4.08307500
N 0.68598100 0.06654100 -0.08413200
O -0.39453100 -0.30971100 -0.50080100
O 1.08122000 -0.16630900 1.04942200
H -0.38664600 -1.31964900 1.70360600
N -1.12805600 -1.96270600 1.99370400
C -2.47264900 -1.78055800 1.45966600
C -0.80159400 -2.92586600 2.83711800
H -2.57753300 -2.34726300 0.51498700
H -2.60508200 -0.71076400 1.23306600
C -3.46778400 -2.26499500 2.50139700
N -1.69598700 -3.79975300 3.26988200
C 0.61970600 -2.97948500 3.32409800
H -3.42863000 -1.59947500 3.38331300
H -4.49220500 -2.24120200 2.09588800
C -3.11973000 -3.68584100 2.91459100
C -1.31909600 -4.91505500 4.15233100
C 0.73230900 -2.69989300 4.83408200
H 1.19285700 -2.23267700 2.74997200
H 1.04191700 -3.97342800 3.08386900

H -3.70099800 -3.98541900 3.80344100
H -3.34206400 -4.40445800 2.10284900
H -0.47110500 -5.46474600 3.70303700
H -2.18193000 -5.60054800 4.15156100
C -0.98338600 -4.47258900 5.57674100
C 0.43348200 -3.91394900 5.71530800
H 0.06554600 -1.85538100 5.09728900
H 1.76461100 -2.36129800 5.03270200
H -1.09031500 -5.35093000 6.23915300
H -1.73496700 -3.72768700 5.90522400
H 0.61913700 -3.64625900 6.77181600
H 1.15387200 -4.71763400 5.46006900

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1054.842614 E_0
Sum of electronic and zero-point Energies= -1054.389217 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1054.366067 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1054.365123 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1054.439821 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.453398
Number of imaginary vibrational frequencies = 0





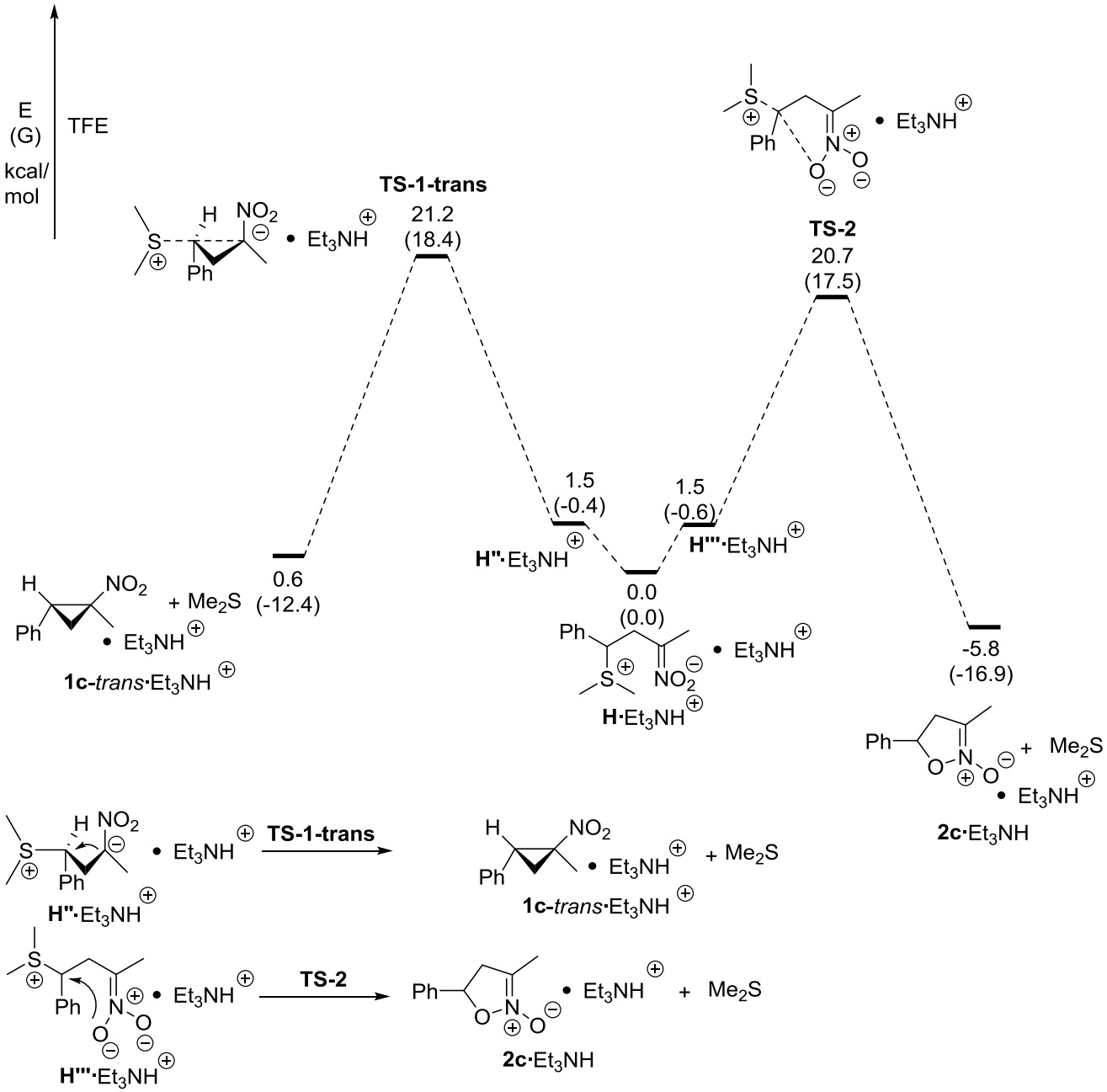
Charge 1; multiplicity 1

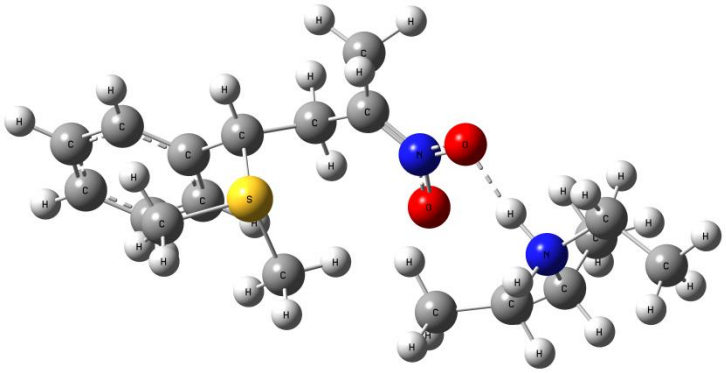
C -0.91574000 2.26307500 -2.13643800
C -0.89014400 2.58050100 -3.58546600
C -0.89366100 3.20528100 -0.97443500
O -1.01387100 0.94300400 -0.31524900
O -1.02887000 -0.05775700 -2.32019000
C -0.60219500 2.25227300 0.19498500
H -0.91134500 1.65137800 -4.17564600
H -1.76348400 3.20475900 -3.84733900
H 0.02115900 3.15588900 -3.82870200
H -1.87371800 3.70516900 -0.87073700
H -0.11868600 3.98201700 -1.08865800
C 0.84778500 2.14279600 0.61276000
C 1.14322000 1.81840100 1.93988200
C 1.88915900 2.24253800 -0.31843000
C 2.45993500 1.57787600 2.33398400
H 0.32515400 1.74205400 2.66932100
C 3.20589800 2.00049100 0.07424000
H 1.68098100 2.50522300 -1.36477500
C 3.49270900 1.66186900 1.39859500
H 2.68113500 1.32344900 3.37821900
H 4.01620600 2.07752300 -0.66154700
H 4.52925700 1.47169700 1.70449100
H -1.24379800 2.44186000 1.06887800
N -0.97934400 1.04444500 -1.71174200
H -0.29891200 -1.25936500 -1.18066600
N 0.09647900 -1.91773200 -0.48954400
C 1.02882800 -1.41992100 0.51425800
C -0.28453300 -3.17832700 -0.56199000
H 0.46645000 -1.07816700 1.40459100
H 1.55466600 -0.54922100 0.08804600
C 1.99246400 -2.53896100 0.87392900
N 0.17424600 -4.09554700 0.27667200
C -1.23813000 -3.55505400 -1.66111400
H 2.62981300 -2.76882400 0.00025700
H 2.64619600 -2.23065000 1.70653700
C 1.20666300 -3.77721100 1.27581300
C -0.29163200 -5.48935900 0.22155300
C -0.59144900 -4.49212400 -2.69749300
H -1.57281400 -2.61814500 -2.13610300
H -2.12902200 -4.03371000 -1.21307600
H 1.87235000 -4.65451400 1.34593700
H 0.71953900 -3.63885700 2.26000700

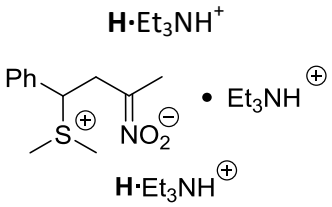
H -1.39723700 -5.50740800 0.25416200
H 0.06408600 -5.96018600 1.15224600
C 0.22563500 -6.25144400 -0.99934700
C -0.56915200 -5.96205800 -2.27375100
H 0.43405100 -4.13580700 -2.91834600
H -1.16682100 -4.40058200 -3.63578800
H 0.16495900 -7.33232100 -0.77605400
H 1.29807600 -6.01122900 -1.14057800
H -0.16280300 -6.56998200 -3.10307400
H -1.61506200 -6.29682600 -2.11811400

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1054.849741 E_0
Sum of electronic and zero-point Energies= -1054.396066 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1054.373138 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1054.372193 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1054.445278 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.453675
Number of imaginary vibrational frequencies = 0

8.8 Calculations in 2,2,2-trifluoroethanol (TFE) with Et_3NH^+ as HBD





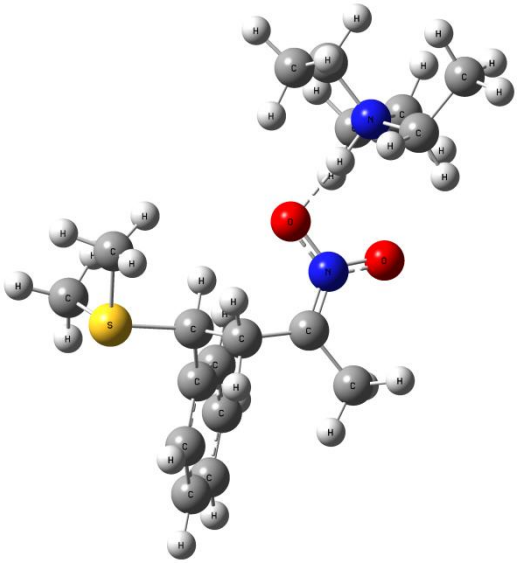


Charge 1; multiplicity 1

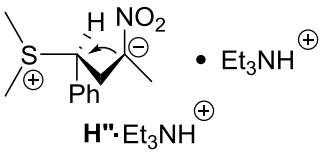
C -4.00451900 4.88301100 -2.08087900
C -2.80511500 3.99062900 -2.14684200
C -2.68086100 2.74642200 -1.32023700
C -2.69599300 3.02858500 0.19313200
N -1.83839700 4.31916200 -2.97085500
O -0.75488700 3.63352500 -3.12137500
S -1.54710900 4.45295200 0.51005300
H -3.66428400 3.47974400 0.48208700
C -1.36010300 4.44954800 2.29334600
C 0.05496400 3.86096800 -0.03003600
H -3.73172000 5.90199200 -1.74377600
H -4.46911000 4.99064200 -3.07923900
H -4.75466800 4.46694400 -1.38639800
H -1.76505800 2.21107000 -1.61222600
H -2.35587800 4.62380900 2.73529600
H -0.69092100 5.29275100 2.53495700
H -0.92950200 3.49118000 2.62747700
H -0.01302400 3.68616900 -1.12160200
H 0.76911500 4.67489200 0.18439900
H 0.32656200 2.95058200 0.53023000
H -3.54129100 2.07433900 -1.50626800
C -2.41354700 1.83835300 1.07635300
C -1.42332300 0.90010000 0.75679100
C -3.15730200 1.67408300 2.25230200
C -1.17616600 -0.17637900 1.60953800
H -0.83918200 0.99812000 -0.16696800
C -2.91225900 0.59549400 3.10052500
H -3.94154100 2.40241800 2.50001000
C -1.91691800 -0.32984700 2.78202000
H -0.39808400 -0.90488900 1.35036200
H -3.50447800 0.47667100 4.01628000
H -1.72126000 -1.17899700 3.44872600
O -1.96005900 5.40108200 -3.68835100
H -0.76938600 7.70962000 -5.44176700
C -0.19428500 6.90347900 -5.92935300
N 0.36259300 6.07305900 -4.81735900
C 0.86716100 7.46663200 -6.85709500
H -0.91429300 6.26840700 -6.47274100
C 1.13312700 6.89194500 -3.83045500
C 1.14958900 4.89462100 -5.28726400
H 1.38825300 6.67072400 -7.41799700
H 1.61589400 8.06369000 -6.30605200
H 0.37959800 8.13112900 -7.59104300
C 1.09501000 6.27801600 -2.43951400
H 0.67305900 7.89486800 -3.81700500
H 2.16733300 6.99275200 -4.20520600

C 0.34196800 4.00930400 -6.22108600
H 1.43464400 4.33588000 -4.38156400
H 2.07038600 5.27323100 -5.76564200
H 1.63490400 6.94151200 -1.74166900
H 0.04974900 6.17998300 -2.09170300
H 1.57600800 5.28495500 -2.40825800
H 0.88125200 3.05814700 -6.37082400
H -0.64248600 3.78186300 -5.77353900
H 0.19230500 4.47399100 -7.21148100
H -0.50998800 5.69991700 -4.31001700

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1363.157299 E_0
Sum of electronic and zero-point Energies= -1362.665398 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1362.638070 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1362.637126 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1362.717621 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.491902
Number of imaginary vibrational frequencies = 0



Pre-reaction conformation **H''**·Et_3NH^+



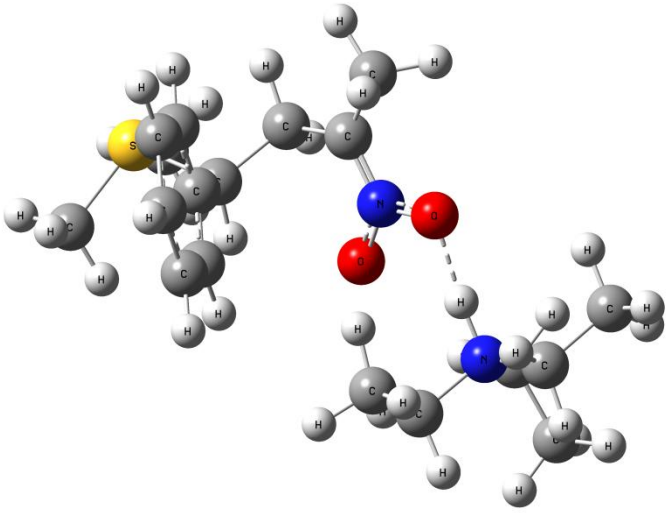
H''·Et_3NH^+

Charge 1; multiplicity 1

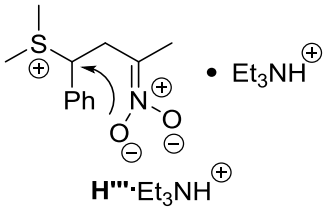
C 1.56127500 -0.60901000 -0.01747200
C 2.93166300 -0.35690700 0.52387400
H 2.92180300 0.48459300 1.24498200
H 3.63016300 -0.11686800 -0.29507600
H 3.31095200 -1.24106200 1.07149000
C 1.17608100 -0.46796600 -1.46076700
H 0.50093500 -1.29468700 -1.74294200
H 2.07665800 -0.50094000 -2.09856200
C 0.45406400 0.88157200 -1.62276200
H -0.41626400 0.90412100 -0.94148400
C 1.34984400 2.07536500 -1.38244100
C 1.06590100 2.93909700 -0.32047200
H 0.17955300 2.75639000 0.30256300
C 1.91117200 4.01610100 -0.04850200
H 1.68741100 4.68581900 0.79109100
C 3.03585200 4.23936000 -0.84333100
H 3.69915800 5.08708800 -0.63078500
C 3.31775600 3.38246100 -1.90987500
H 4.20111800 3.55580500 -2.53682400
C 2.48011300 2.30094500 -2.17784900
H 2.71314600 1.62404300 -3.01241800
N 0.61105500 -0.89319300 0.83686900
O -0.62600600 -1.06978600 0.42993200
O 0.84170600 -1.00246500 2.09551200
S -0.28394600 1.01968600 -3.30248300
C -1.30650900 2.47874500 -3.08319400
H -1.93643900 2.57313700 -3.98323400
H -1.91878500 2.35671600 -2.17334300
H -0.62980000 3.34556600 -3.00303500
C -1.51941800 -0.28573200 -3.24261900
H -1.02599000 -1.23319400 -3.51250400
H -1.95070500 -0.32782000 -2.22702100
H -2.28649200 -0.03769100 -3.99480600
N -1.82923700 -2.25894300 2.51536500
C -1.78699700 -1.40648200 3.74181400
C -2.06948800 0.05250700 3.42091600
H -0.77316700 -1.51343500 4.16167700
H -2.51375500 -1.81599000 4.46583300
H -1.90982800 0.65620100 4.33097500
H -1.37382500 0.40916300 2.64044800
H -3.10774000 0.21953400 3.08612700

C -3.22777100 -2.46906000 2.03670400
C -3.28731700 -3.31201000 0.77329100
H -3.64020000 -1.46460100 1.84448700
H -3.80615600 -2.92144700 2.86244000
H -4.30869400 -3.26132700 0.35870600
H -2.58478100 -2.92833800 0.01081300
H -3.05412000 -4.37303200 0.96983600
H -1.32400100 -1.72285300 1.73493000
C -1.04718400 -3.52237300 2.67776200
H -0.03572700 -3.20237900 2.97891400
C -1.65619200 -4.49328300 3.67299900
H -2.64457000 -4.85929000 3.34200700
H -1.76094400 -4.04159200 4.67551200
H -0.96202500 -3.97372900 1.67422000
H -0.98855700 -5.36718400 3.76653200

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1363.154892 E_0
Sum of electronic and zero-point Energies= -1362.663710 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1362.635802 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1362.634858 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1362.718317 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.491183
Number of imaginary vibrational frequencies = 0



Pre-reaction conformation **H'''**·Et_3NH^+



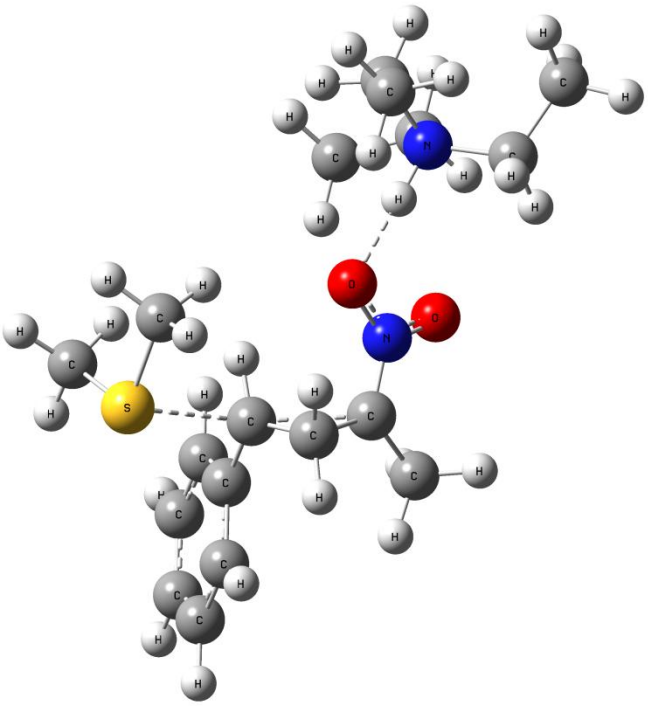
H'''·Et_3NH^+

Charge 1; multiplicity 1

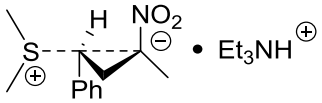
C -0.39678000 0.99551800 -1.60518600
C 0.31765900 1.13630200 -2.91188900
C -0.86404700 2.15325900 -0.77017500
O -1.15258700 -0.42268800 0.00875900
O -0.19497300 -1.24954300 -1.81637800
C -0.17312300 2.17911400 0.61240600
S -0.33628400 3.86131100 1.32754900
H -0.22741800 0.61908900 -3.72459700
H 0.42596900 2.20068400 -3.17836600
H 1.32433300 0.67659600 -2.85941600
H -1.95754800 2.09562200 -0.60762800
H -0.64558900 3.08409200 -1.32533700
C 1.29638300 1.82605800 0.56762000
C 1.75041000 0.71554200 1.28358600
C 2.19303400 2.56519100 -0.21455600
C 3.09461000 0.34341400 1.21851700
H 1.03634500 0.13134700 1.88057300
C 3.53556400 2.19547600 -0.27240300
H 1.83918700 3.43378800 -0.78921800
C 3.98753300 1.08388500 0.44370100
H 3.44595600 -0.53312900 1.77766400
H 4.23531400 2.77759400 -0.88480000
H 5.04426300 0.79285200 0.39409000
C -2.11543200 4.00078600 1.52235700
H -2.30074500 4.87920100 2.16294900
H -2.55044700 4.16925600 0.52365300
H -2.50509100 3.07818800 1.98491300
C 0.18362900 3.56493000 3.01884600
H -0.36391200 2.69493200 3.41925700
H 1.27143600 3.38537100 3.00158400
H -0.03898800 4.48040000 3.59242000
H -0.70087300 1.51349200 1.31435000
N -0.59014700 -0.20727600 -1.13371000
H -0.75194400 -2.46265000 -0.92714000
N -1.04982300 -3.36994100 -0.43099400
C -0.37782300 -3.36612400 0.90252500
C 1.08848700 -2.97320000 0.79249800
H -0.50073200 -4.36688500 1.35356000
H -0.92337200 -2.63138600 1.51798600
H 1.48156900 -2.77205300 1.80450000
H 1.70657000 -3.77192700 0.34700700
H 1.19248700 -2.05765400 0.18272300

C -0.55150700 -4.47226000 -1.30516700
C -1.20859000 -4.46064700 -2.67589800
H -0.70835300 -5.42913100 -0.77493700
H 0.53474500 -4.31179800 -1.40753100
H -0.66849300 -5.16041100 -3.33639000
H -2.26488000 -4.77913300 -2.63598700
H -1.15562400 -3.45180300 -3.12489300
C -2.53753500 -3.31126800 -0.31404600
H -2.92739900 -3.08908800 -1.32201800
C -3.15893400 -4.57734900 0.24929900
H -2.77000200 -4.81610800 1.25499100
H -2.99473600 -5.44704800 -0.41183900
H -4.24845600 -4.42472900 0.33847600
H -2.75104300 -2.43346900 0.31824000

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1363.154972 E_0
Sum of electronic and zero-point Energies= -1362.664320 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1362.636314 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1362.635370 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1362.718632 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.490653
Number of imaginary vibrational frequencies = 0



TS-1-trans



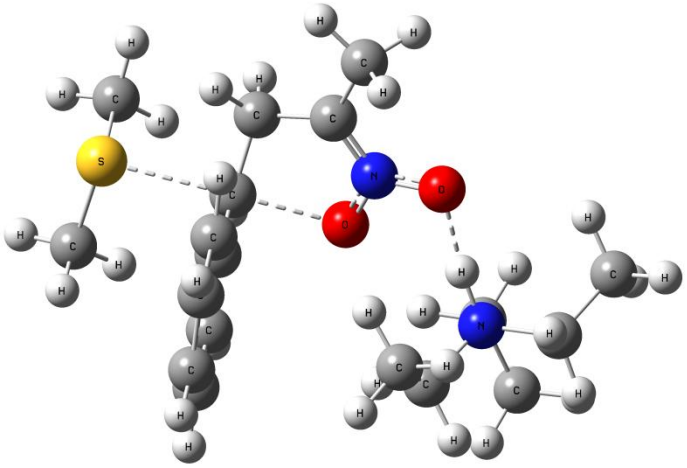
TS-1-trans

Charge 1; multiplicity 1

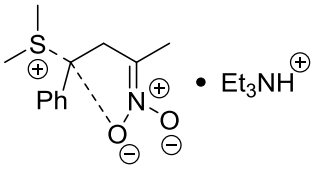
C 6.67575500 4.82366800 7.61515300
C 7.98839000 5.15661600 8.24417600
H 7.88007800 5.95464800 9.00309000
H 8.70117700 5.48808800 7.47139000
H 8.40695400 4.26764300 8.75335800
C 6.38388400 4.85421900 6.13928900
H 5.65816400 4.09054000 5.82641100
H 7.30144700 4.85406300 5.53490000
C 5.80875700 6.18354800 6.40897600
H 4.84374600 6.19254800 6.93772300
C 6.62489100 7.41151700 6.50612900
C 6.23175000 8.40782400 7.41086000
H 5.33624500 8.25166600 8.02786400
C 6.97933000 9.57806300 7.53361800
H 6.67105600 10.35173700 8.24738000
C 8.11784400 9.76136200 6.74756200
H 8.70583900 10.68304500 6.84101000
C 8.50995100 8.77385600 5.83883000
H 9.40162200 8.92207900 5.21743200
C 7.76890900 7.60182200 5.71745200
H 8.07217400 6.83302100 4.99455700
N 5.67952900 4.41520700 8.42735700
O 4.53484700 4.10990500 7.94517100
O 5.86044500 4.34447900 9.67035400
S 4.49619800 6.71554300 4.41696300
C 3.58581900 8.05420700 5.20638000
H 2.64859200 8.24230100 4.65477800
H 3.35948900 7.79383900 6.25728800
H 4.21883800 8.95720300 5.17062300
C 3.33741900 5.36201100 4.68358700
H 3.71486500 4.48234500 4.13538900
H 3.26283700 5.12752300 5.76272200
H 2.34588200 5.63847200 4.28583800
N 3.18438700 3.13061800 10.16708800
C 3.14669500 4.15701300 11.25651300

C 2.87659000 5.54765500 10.70598100
H 4.13255100 4.12681200 11.75004200
H 2.37690300 3.84526600 11.98414700
H 2.95630400 6.27811500 11.52930200
H 3.62795700 5.80808500 9.93845300
H 1.86716200 5.64133300 10.27028900
C 1.81710000 2.82797100 9.64193600
C 1.84804200 1.82565800 8.50044300
H 1.40007200 3.78898000 9.29880000
H 1.20444800 2.47369100 10.48972400
H 0.85014600 1.79131000 8.03098100
H 2.58138700 2.12806300 7.73006600
H 2.09493000 0.80724900 8.84762500
H 3.71919900 3.55546700 9.36485900
C 3.96315800 1.91361700 10.56062000
H 4.94950500 2.28620000 10.88356000
C 3.29020600 1.08997200 11.64332500
H 2.33007800 0.66301600 11.30296200
H 3.11451600 1.68124600 12.55942100
H 4.11728700 1.32486600 9.64056100
H 3.95595400 0.25051700 11.90798700

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1363.123566 E_0
Sum of electronic and zero-point Energies= -1362.633956 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1362.605859 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1362.604915 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1362.688358 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.489611
Number of imaginary vibrational frequencies = 1; 597*i*



TS-2



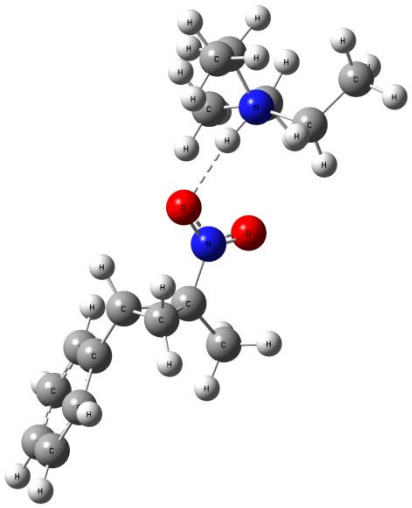
TS-2

Charge 1; multiplicity 1

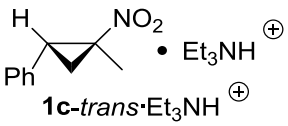
C 1.37724100 0.26380500 -1.43366300
C 1.70436300 0.46431700 -2.87322400
C 1.17726800 1.33822200 -0.40567900
O 0.93638200 -1.08748900 0.30708000
O 1.33669500 -2.00570900 -1.68854100
C 1.47812700 0.78013400 0.97857600
S 1.66466900 2.93865800 2.02382000
H 0.87141900 0.12313900 -3.51699500
H 1.89959500 1.52884300 -3.07924300
H 2.59571500 -0.12943000 -3.14911300
H 0.13401600 1.70739000 -0.42963600
H 1.84084400 2.18763600 -0.64393900
C 2.83896800 0.31901200 1.34713700
C 3.01042800 -0.40534100 2.53615200
C 3.94086300 0.56991400 0.52130300
C 4.27374900 -0.85982000 2.90232300
H 2.13691700 -0.61392500 3.16916300
C 5.20512100 0.10616200 0.88901100
H 3.82100300 1.13998400 -0.40934600
C 5.37420900 -0.60275500 2.07843000
H 4.40347600 -1.42284400 3.83506200
H 6.06683900 0.30710500 0.24061400
H 6.37054900 -0.96109800 2.36655700
C -0.05703600 3.43093400 1.82021500
H -0.30546500 4.21072700 2.56041800
H -0.17325200 3.84438300 0.80433500
H -0.72021300 2.55631500 1.95332800
C 1.61151800 2.37402500 3.73154600
H 0.88743300 1.54496000 3.83437900
H 2.62355700 2.03432200 4.00789200
H 1.31839600 3.21600700 4.38184100
H 0.66812400 0.62285100 1.69953100
N 1.21484200 -0.93663200 -0.97179000
H 1.17764700 -3.19966000 -0.57444800
N 1.12098000 -4.06541400 0.04494900
C 2.23292900 -3.96220000 1.04116600
C 3.50623400 -3.40916200 0.41990800
H 2.39263800 -4.96732700 1.47063600
H 1.87692300 -3.29178900 1.84306700
H 4.29361900 -3.38079400 1.19252500
H 3.87624900 -4.03804000 -0.40848800
H 3.34607200 -2.38182400 0.04421200
C 1.31274900 -5.22235700 -0.88174900

C 0.22579900 -5.29163400 -1.94164300
H 1.35929900 -6.14195700 -0.27173600
H 2.29787800 -5.07761900 -1.35500800
H 0.52126800 -6.02885500 -2.70756900
H -0.74510100 -5.60886400 -1.52279300
H 0.09878100 -4.31144600 -2.43713600
C -0.22662800 -4.03180600 0.69241200
H -0.96515200 -3.88510800 -0.11389700
C -0.53654900 -5.27301400 1.50990900
H 0.21749800 -5.44320200 2.29909800
H -0.60399300 -6.17776500 0.87999500
H -1.51390300 -5.13360100 2.00330600
H -0.23419300 -3.12232200 1.31523000

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1363.124293 E_0
Sum of electronic and zero-point Energies= -1362.635469 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1362.607322 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1362.606377 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1362.689736 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.488824
Number of imaginary vibrational frequencies = 1; 581*i*



1c-*trans*·Et_3NH^+



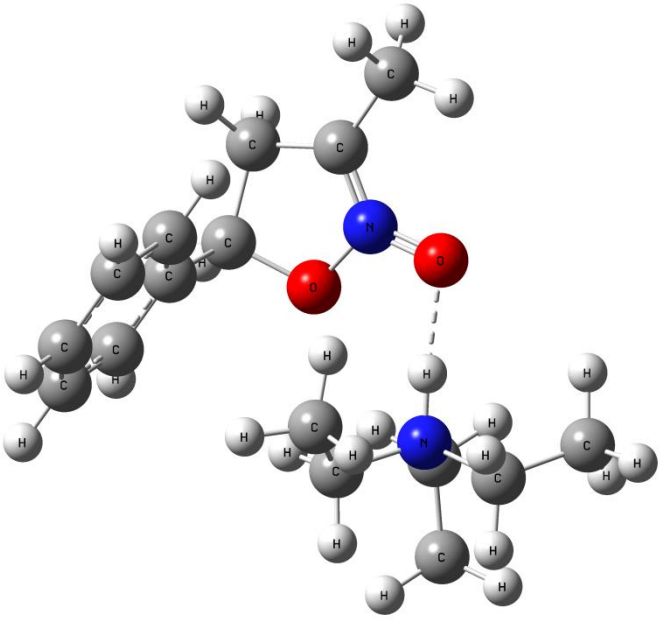
1c-*trans*·Et_3NH

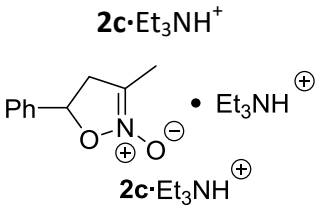
Charge 1; multiplicity 1

C 1.46966500 -0.14525900 0.12639500
C 2.75350000 0.05087300 0.87901400
H 2.60669200 0.71879700 1.74601000
H 3.49384900 0.50633300 0.20071500
H 3.14690500 -0.91675100 1.23479400
C 1.41394900 -0.44985400 -1.35211900
H 0.66540000 -1.18012000 -1.67652800
H 2.39749100 -0.50860000 -1.83361300
C 0.92569000 0.87615300 -0.87206800
H -0.16511500 0.98894900 -0.81949900
C 1.69888400 2.14404800 -1.06352600
C 1.52856300 3.19103000 -0.14779400
H 0.83166000 3.06459100 0.69216600
C 2.23583900 4.38252000 -0.29688400
H 2.09611300 5.19477000 0.42759100
C 3.12216600 4.54100000 -1.36540200
H 3.67975200 5.47859900 -1.48380200
C 3.29259400 3.50405200 -2.28255500
H 3.98328900 3.62398500 -3.12678000
C 2.58470200 2.30938500 -2.13171900
H 2.71765100 1.49956300 -2.86081400
N 0.41465400 -0.79213900 0.91660100
O -0.66275000 -1.03347900 0.38202400
O 0.64534700 -1.05777000 2.08042000
N -2.00394000 -2.47274000 2.58065700
C -1.85564500 -1.68764800 3.85040100
C -2.21111900 -0.22500500 3.64558900
H -0.80220600 -1.79187100 4.15905800
H -2.49737000 -2.16613100 4.61008000
H -1.95183500 0.33397000 4.56093100
H -1.63245900 0.20435000 2.80601200
H -3.28684100 -0.07398200 3.45352800
C -3.44354700 -2.69950200 2.23277800
C -3.60560300 -3.43011200 0.91203100
H -3.90723300 -1.70114800 2.18317600
H -3.89929600 -3.24853500 3.07492700
H -4.66910100 -3.40009300 0.62016900
H -3.01768100 -2.93812300 0.11453700
H -3.30179900 -4.48909800 0.98010100
H -1.60418400 -1.88862400 1.82050300
C -1.17802300 -3.72659200 2.58914400
H -0.15255100 -3.40353700 2.83651300

C -1.68579600 -4.77159900 3.56498500
H -2.68123900 -5.15530100 3.27985600
H -1.73204600 -4.38279200 4.59755000
H -1.16962700 -4.10820500 1.55442500
H -0.98288700 -5.62224500 3.55699300

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -885.216356 E_0
Sum of electronic and zero-point Energies= -884.802122 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -884.779696 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -884.778751 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -884.850818 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.414234
Number of imaginary vibrational frequencies = 0





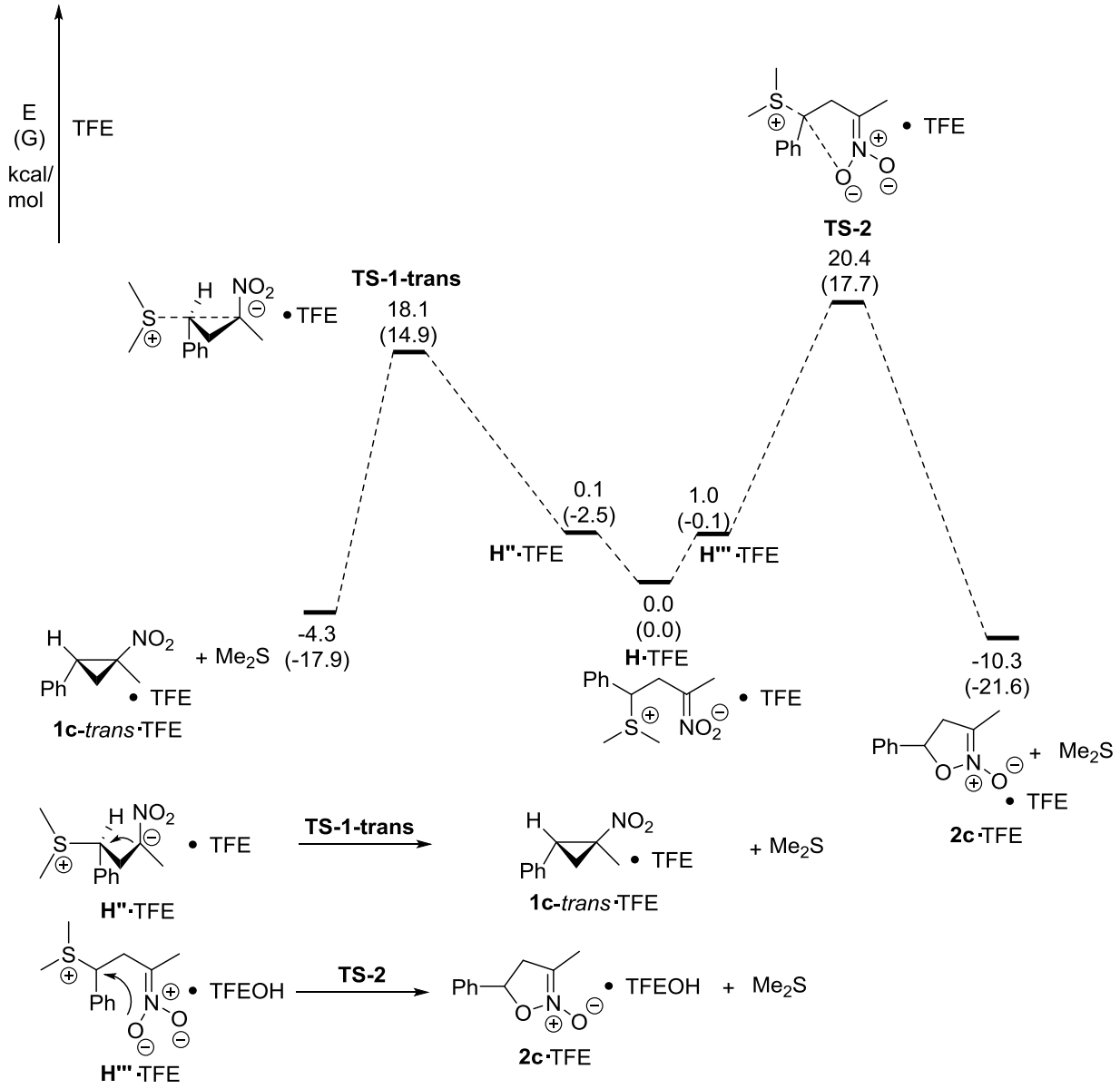
Charge 1; multiplicity 1

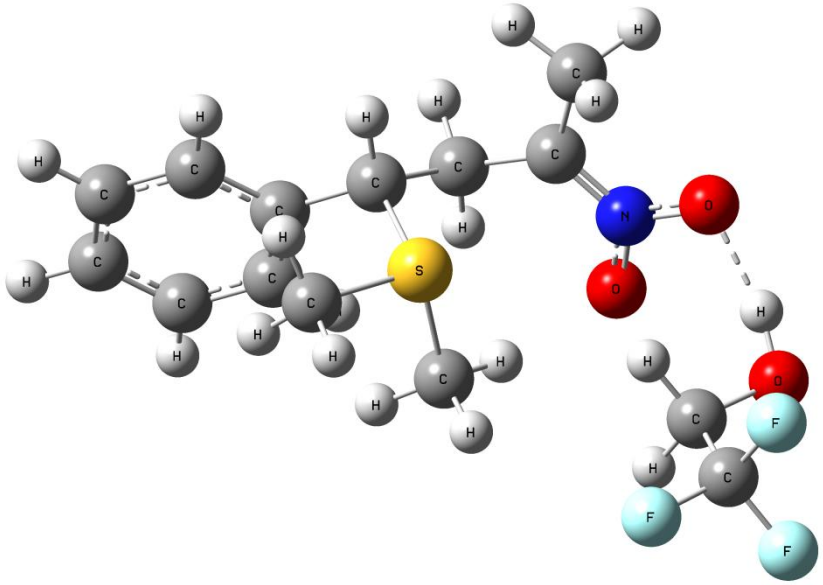
C -0.52072800 1.21543400 -2.20974100
C -0.37096700 1.57707700 -3.64054600
C -0.54384500 2.11793800 -1.01579800
O -0.82359200 -0.15152200 -0.44829900
O -0.75247600 -1.09215000 -2.47737900
C -0.37890300 1.11636700 0.13723900
H -1.18110200 2.26740000 -3.93679500
H 0.59069900 2.09810600 -3.79652600
H -0.40900900 0.67232200 -4.26651500
H -1.50985700 2.65237700 -0.96716900
H 0.26496900 2.86689200 -1.04655700
C 1.03234100 0.92781400 0.65198900
C 1.21355700 0.49972800 1.97142700
C 2.15068900 1.09911000 -0.17276300
C 2.49379300 0.24678500 2.46509700
H 0.33626000 0.36925000 2.62012700
C 3.43106300 0.84261200 0.31902500
H 2.03337900 1.43806500 -1.21130400
C 3.60500600 0.41711300 1.63736800
H 2.62464800 -0.08141400 3.50391300
H 4.30197700 0.98075800 -0.33383700
H 4.61367100 0.22237500 2.02318500
H -1.07161900 1.30988200 0.97025800
N -0.68267800 -0.00813000 -1.83186400
H -0.72472600 -2.34841100 -1.27799900
N -0.75806500 -3.15310600 -0.60239600
C 0.31911400 -2.91516500 0.41044500
C 1.62645100 -2.50592300 -0.24997600
H 0.43078800 -3.83784700 1.00614100
H -0.05089200 -2.11121100 1.06907900
H 2.30933100 -2.10961100 0.52241700
H 2.13106700 -3.35383600 -0.74400100
H 1.45263500 -1.70990700 -0.99789800
C -0.49623900 -4.37878400 -1.41975900
C -1.54837500 -4.58522300 -2.49574000
H -0.43389500 -5.23513600 -0.72515300
H 0.49590800 -4.23463800 -1.87769400
H -1.20678400 -5.38350000 -3.17643400

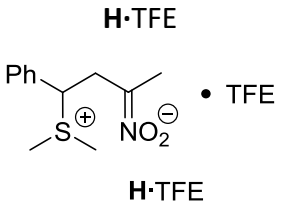
H -2.52166900 -4.89159700 -2.07476800
H -1.68937300 -3.66354000 -3.09047100
C -2.12793700 -3.10770400 0.00333000
H -2.84295600 -3.03989100 -0.83398100
C -2.43424300 -4.29184900 0.90222700
H -1.70793900 -4.38097500 1.72923100
H -2.45685600 -5.24259800 0.34090000
H -3.43290500 -4.14074500 1.34699200
H -2.17547600 -2.15566300 0.55870500

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -885.226672 E_0
Sum of electronic and zero-point Energies= -884.811648 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -884.789681 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -884.788737 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -884.857987 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.415025
Number of imaginary vibrational frequencies = 0

8.9 Calculations in 2,2,2-trifluoroethanol (TFE) with 2,2,2-trifluoroethanol (TFE) as HBD





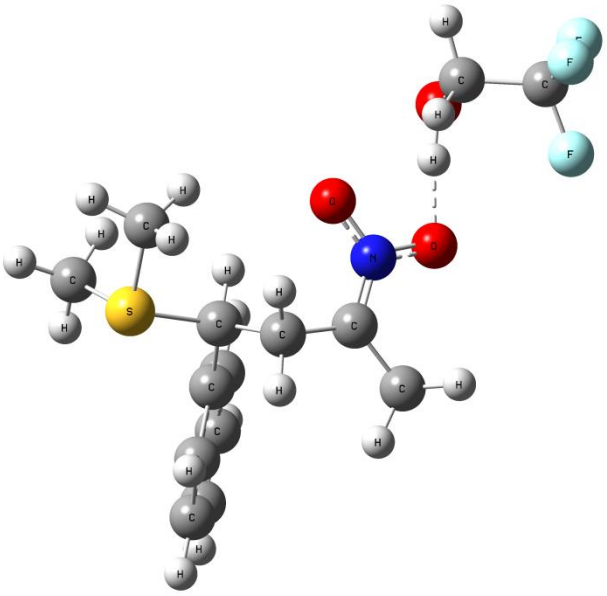


Charge 0; multiplicity 1

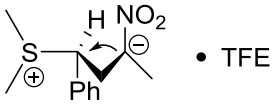
C -3.76503900 5.71160600 -1.53931200
C -2.95822300 4.55762600 -2.04643200
C -3.02515200 3.19316700 -1.42902800
C -2.59191500 3.18271900 0.04885000
N -2.16133400 4.76683700 -3.07162200
O -1.41726200 3.85520700 -3.59664000
S -1.05956100 4.22131500 0.19104900
H -3.30040900 3.77979700 0.65368800
C -0.45517300 3.84348000 1.83667200
C 0.14554400 3.38369600 -0.83792000
H -3.11460900 6.53752200 -1.19042200
H -4.40575700 6.12813800 -2.33972400
H -4.41192000 5.39124800 -0.70405500
H -2.40841800 2.50220700 -2.02244100
H -1.21700700 4.17825300 2.56081400
H 0.46950900 4.43056300 1.96874500
H -0.25535000 2.76280600 1.92665100
H -0.25134200 3.38026600 -1.87268100
H 1.06697300 3.99018900 -0.78463800
H 0.32459100 2.36675200 -0.45015800
H -4.06496300 2.81152300 -1.43659400
C -2.43288600 1.81716100 0.66953300
C -1.82617100 0.75879300 -0.01953600
C -2.89472100 1.60826900 1.97557000
C -1.67986200 -0.48500000 0.59559400
H -1.46659600 0.89534100 -1.04723600
C -2.75120500 0.36391800 2.58696500
H -3.37680400 2.43547100 2.51437000
C -2.13979900 -0.68477400 1.89786900
H -1.20404600 -1.30758700 0.04757800
H -3.12130300 0.21242800 3.60853100
H -2.02537800 -1.66520400 2.37698100
O -2.10402400 5.95867400 -3.59130700
H -0.66972000 6.04271600 -4.37228500
O 0.30860000 6.09771100 -4.57778400
C 0.93699700 5.74258500 -3.37766300
C 2.05117700 6.71760800 -3.09818500
H 1.38971500 4.72946900 -3.40358100
H 0.24384200 5.79892600 -2.51453600

F 2.70484400 6.39811500 -1.95346600
F 2.97248300 6.73940900 -4.08848200
F 1.60249900 7.98534600 -2.96006800

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1523.102948 E_0
Sum of electronic and zero-point Energies= -1522.772579 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1522.748999 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1522.748054 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1522.822011 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.330370
Number of imaginary vibrational frequencies = 0



Pre-reaction conformation **H''**·TFE



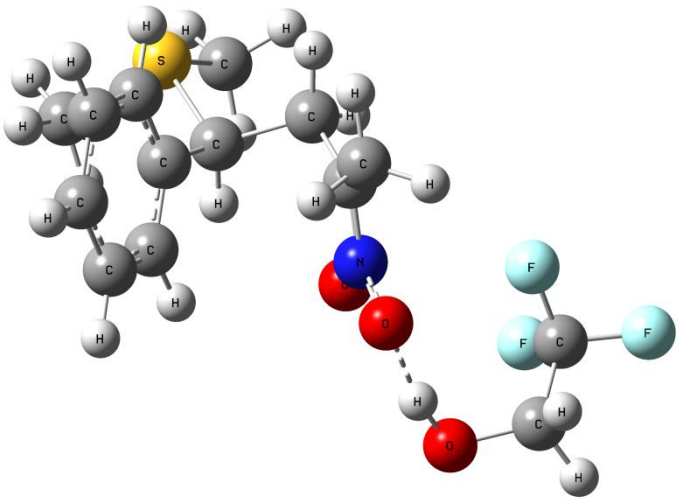
H"·TFE

Charge 0; multiplicity 1

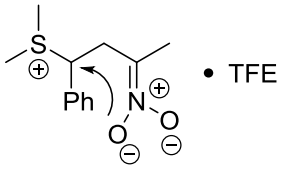
C 1.12971500 -0.51503600 -0.40717100
C 2.54599600 -0.42756800 0.06379500
H 2.65923100 0.36085100 0.83368300
H 3.21601500 -0.19700700 -0.78191400
H 2.87587800 -1.37668400 0.52905900
C 0.68253700 -0.29522500 -1.82132500
H -0.09595700 -1.03613800 -2.07700000
H 1.53237300 -0.40526900 -2.51685000
C 0.10189800 1.12791300 -1.90190900
H -0.66611700 1.24081000 -1.11427800
C 1.14648700 2.21466300 -1.79359800
C 1.09092300 3.11386900 -0.72482400
H 0.27436200 3.03384700 0.00559200
C 2.07211700 4.09678300 -0.58399800
H 2.02682800 4.79456300 0.26138400
C 3.10524100 4.19097900 -1.51673000
H 3.87495800 4.96529800 -1.40771600
C 3.15965200 3.29829600 -2.58988900
H 3.97058300 3.37011100 -3.32527800
C 2.18617100 2.31016100 -2.72715000
H 2.23968400 1.60442500 -3.56856600
N 0.18430800 -0.71712800 0.47917500
O -1.06410200 -0.74405400 0.15498200
O 0.49605400 -0.89616500 1.72920500
S -0.83140800 1.35998500 -3.47136600
C -1.67256200 2.90535100 -3.11641500
H -2.39492700 3.07826500 -3.93141700
H -2.17877600 2.82289300 -2.13959500
H -0.91012700 3.70225700 -3.11158800
C -2.16688800 0.17398900 -3.25259300
H -1.82068200 -0.80004200 -3.63354600
H -2.42855400 0.11732600 -2.18135800
H -3.01704600 0.53088500 -3.85757600
H -0.87836000 -0.86351700 2.57519400
O -1.73981900 -1.05357400 3.05641700
C -2.05056900 -2.37549400 2.71474400
C -1.36271200 -3.32668700 3.66633200
H -1.72379900 -2.63147200 1.68750000
H -3.13781100 -2.55877700 2.80308500
F -1.62302900 -4.62118900 3.36506200

F -1.75178400 -3.13246500 4.94904600
F -0.01729300 -3.17591400 3.64853400

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1523.102787 E_0
Sum of electronic and zero-point Energies= -1522.773245 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1522.749011 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1522.748067 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1522.826007 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.329542
Number of imaginary vibrational frequencies = 0



Pre-reaction conformation **H'''**·TFE

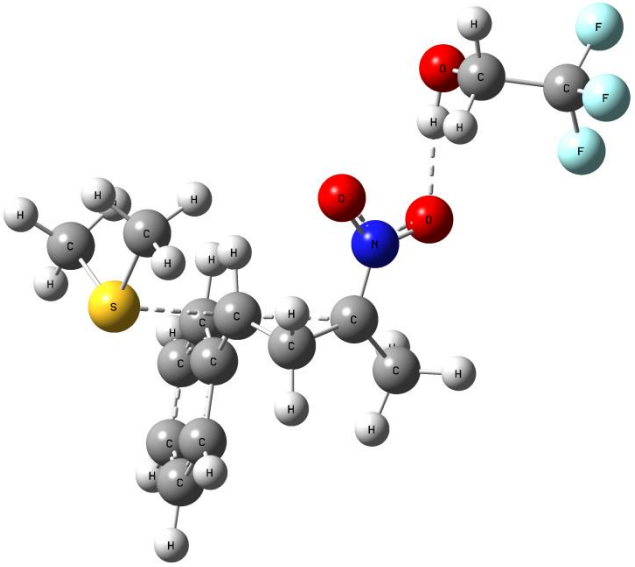


H'''·TFE

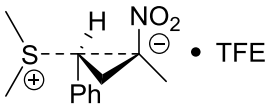
Charge 0; multiplicity 1

C -0.67325800 0.08007700 -1.05427900
C -0.52936400 0.14275000 -2.54160400
C -1.18807100 1.21158500 -0.21213900
O -0.17546600 -1.04395800 0.86030400
O 0.40976300 -1.90437900 -1.09588300
C 0.00886600 1.85274500 0.52514400
S -0.51052700 3.36822000 1.40807100
H 0.54070400 0.18737800 -2.83502700
H -0.95512200 -0.75871000 -3.02134100
H -1.04090200 1.03474100 -2.94106700
H -1.91385900 0.83896800 0.53406800
H -1.68169200 1.95634000 -0.86250400
C 1.15233800 2.17107400 -0.41214500
C 2.24402100 1.29622600 -0.43419600
C 1.08745700 3.22577800 -1.32864800
C 3.26744500 1.47913400 -1.36370900
H 2.26675600 0.44745800 0.26506000
C 2.11812900 3.41216400 -2.25084600
H 0.22196100 3.90403600 -1.33788000
C 3.20768700 2.53983200 -2.27003900
H 4.11715400 0.78532400 -1.38203900
H 2.06449200 4.24248700 -2.96594900
H 4.01386600 2.68477600 -3.00005400
C -1.64665900 2.69726800 2.62621300
H -1.79458600 3.47986700 3.38914500
H -2.60090200 2.48495200 2.11726800
H -1.20920500 1.78527300 3.06714900
C 0.94243200 3.67759700 2.41510000
H 1.21620800 2.75041500 2.94648500
H 1.74714500 4.00772300 1.73728500
H 0.68598300 4.48628300 3.11946800
H 0.34692700 1.15776500 1.31356700
N -0.15828300 -0.94525800 -0.42279100
C -0.76792800 -4.58760800 0.06478800
O 0.37962700 -3.94153900 0.53339200
H 0.48726700 -3.11454100 -0.02625200
H -0.80552700 -4.68469200 -1.04016600
H -0.83226800 -5.59885000 0.50656400
C -2.03353700 -3.85909800 0.47691100
F -3.12703800 -4.63899200 0.28336200
F -2.02061000 -3.50732300 1.78110800
F -2.24484800 -2.72374800 -0.23144400

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1523.101408 E_0
Sum of electronic and zero-point Energies= -1522.771753 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1522.747748 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1522.746804 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1522.822172 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.329655
Number of imaginary vibrational frequencies = 0



TS-1-trans·



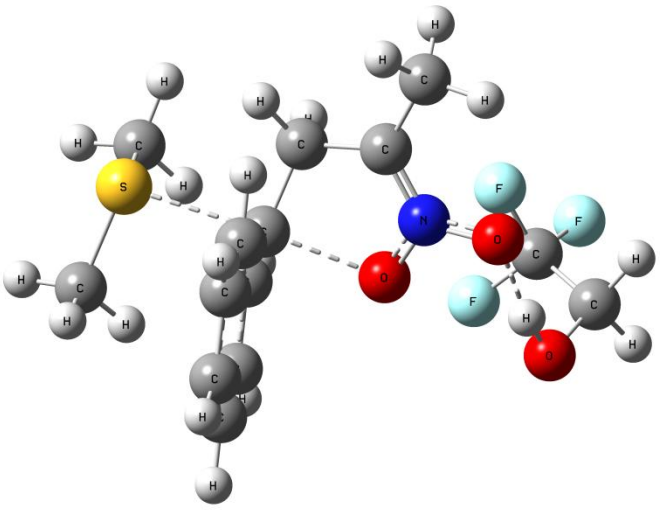
TS-1-trans

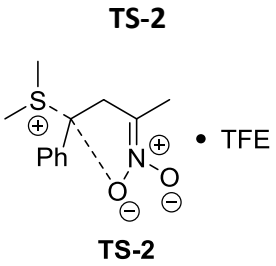
Charge 0; multiplicity 1

C 6.54561800 4.51737400 7.18469600
C 7.92269400 4.70954800 7.72921300
H 7.95641800 5.54380000 8.45530500
H 8.62430000 4.92227000 6.90565700
H 8.26278800 3.79710200 8.25526200
C 6.17852100 4.50417000 5.72682400
H 5.34830700 3.82038800 5.49915200
H 7.05208700 4.35444000 5.07719800
C 5.78315200 5.90917400 5.93537600
H 4.86831100 6.06629900 6.52686000
C 6.75392000 7.02623000 5.91268000
C 6.57163700 8.09202800 6.80438000
H 5.72262400 8.07095600 7.50138700
C 7.46857100 9.15951200 6.81455000
H 7.32530500 9.98720200 7.51998600
C 8.54636200 9.17090400 5.92804700
H 9.25160200 10.01155300 5.93300400
C 8.72758300 8.11405100 5.03105700
H 9.57140100 8.12683800 4.33019500
C 7.83732500 7.04356900 5.02256600
H 7.97547000 6.22108500 4.30830700
N 5.54305000 4.28094900 8.05866400
O 4.35672600 4.10971300 7.66609500
O 5.80838800 4.24210000 9.30122100
S 4.44285200 6.48792700 4.01354100
C 3.75856200 7.97511300 4.76424000
H 2.82364500 8.25428500 4.24871400
H 3.56042700 7.80138200 5.83827200
H 4.49931000 8.78389300 4.64321700
C 3.13973100 5.31203400 4.41952900
H 3.36181800 4.36857100 3.89291600
H 3.10961600 5.13424000 5.51166400
H 2.16835600 5.70211200 4.07037000
H 4.32920300 4.11516100 10.12879400
O 3.47732100 3.81392900 10.53534800
C 3.37441900 2.45187700 10.21834300
C 4.16826100 1.63384600 11.21066400
H 3.75972200 2.21844800 9.20599600
H 2.32213200 2.12146300 10.28820100
F 4.11698300 0.31111000 10.92945100

F 3.71501600 1.78981300 12.47634200
F 5.47441400 1.99024300 11.22446000

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1523.074169 E_0
Sum of electronic and zero-point Energies= -1522.746365 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1522.722086 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1522.721142 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1522.798326 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.327804
Number of imaginary vibrational frequencies = 1; 602*i*

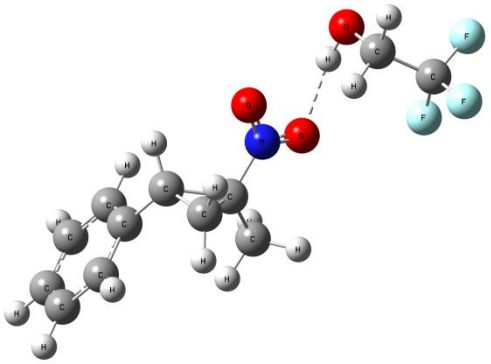




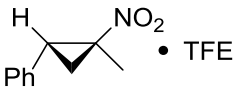
Charge 0; multiplicity 1

C 1.10259800 -0.18896600 -0.48973400
C 0.32166500 -0.17513700 -1.75643900
C 0.96249500 0.82918200 0.60436700
O 2.57114400 -1.06273600 0.95101600
O 2.21267300 -2.14921500 -0.95501100
C 2.27432600 0.92833800 1.36998800
S 1.83181500 3.04233600 2.34114600
H 0.63873600 -1.00819000 -2.40160300
H -0.76120500 -0.27459800 -1.55020800
H 0.47095900 0.77957600 -2.29469100
H 0.16117900 0.52862200 1.30785700
H 0.67792700 1.79862000 0.15925100
C 3.53108000 1.32908000 0.68418300
C 4.76064000 1.02218600 1.28287700
C 3.50493500 1.98594400 -0.55106700
C 5.95167900 1.37703500 0.65629400
H 4.77152500 0.48332400 2.23995000
C 4.70115300 2.33820500 -1.17781700
H 2.54669200 2.23694500 -1.02593100
C 5.92311400 2.03711900 -0.57576700
H 6.91128800 1.13216300 1.12822700
H 4.67625900 2.85355600 -2.14586500
H 6.86190500 2.31503200 -1.07126100
C 0.52876700 2.49212500 3.45679200
H 0.42777200 3.21197400 4.28706300
H -0.41390600 2.46098600 2.88498800
H 0.76783400 1.48733400 3.85133100
C 3.22466800 3.05413400 3.47997600
H 3.38882100 2.03962000 3.88810500
H 4.11425500 3.38735600 2.91966600
H 3.01872400 3.76461000 4.29866200
H 2.34049600 0.57373800 2.40442500
N 1.94479600 -1.13615500 -0.20204100
C 1.86730200 -4.65216900 0.94971300
O 3.06983100 -3.96995600 0.73809200
H 2.87526800 -3.23958000 0.08728600
H 1.31281800 -4.87793100 0.01585900
H 2.06979600 -5.60219600 1.47690900
C 0.92156400 -3.86552800 1.83833800
F -0.08203200 -4.65386400 2.29643100
F 1.54787000 -3.34644900 2.91623900
F 0.32853300 -2.82897500 1.19627800

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1523.070472 E_0
Sum of electronic and zero-point Energies= -1522.742944 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1522.718650 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1522.717706 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1522.793838 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.327529
Number of imaginary vibrational frequencies = 1; 582*i*



1c-*trans*·TFE

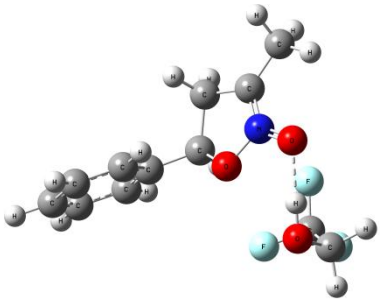


1c-*trans*·TFE

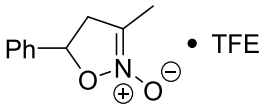
Charge 0; multiplicity 1

C 0.93790400 -0.03867200 -0.13697300
C 2.32962600 -0.08567900 0.42316400
H 2.43575700 0.60273500 1.27997800
H 3.03746600 0.21731600 -0.36602300
H 2.58162200 -1.10835900 0.75238200
C 0.61838100 -0.33506800 -1.58216500
H -0.29324900 -0.90959200 -1.77655500
H 1.49371200 -0.58148300 -2.19487600
C 0.46070600 1.06253300 -1.08128200
H -0.57130400 1.38024600 -0.88243600
C 1.42326300 2.15864800 -1.41862200
C 1.58101300 3.22607500 -0.52450100
H 0.99584200 3.24108600 0.40527200
C 2.47232500 4.25947100 -0.80705300
H 2.58905900 5.08870400 -0.09786600
C 3.21608000 4.23821000 -1.98979100
H 3.91785600 5.05149300 -2.21362900
C 3.06065700 3.18046400 -2.88557900
H 3.63804300 3.16009200 -3.81853800
C 2.16878200 2.14379300 -2.60075100
H 2.04610200 1.31766900 -3.31325200
N -0.10292200 -0.46793800 0.80920700
O -1.26134600 -0.51211800 0.44052100
O 0.24980300 -0.76261200 1.94319800
H -1.33791800 -1.09895000 2.91934200
O -2.15290900 -1.58212700 3.15357600
C -2.05169100 -2.84930800 2.55639600
C -1.13592800 -3.73058600 3.37567200
H -1.65286400 -2.81483700 1.52280100
H -3.04659000 -3.32751500 2.53932800
F -0.99041900 -4.95493200 2.82226600
F -1.59800600 -3.91012400 4.63345600
F 0.10141100 -3.19241400 3.49344200

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1045.169799 E_0
Sum of electronic and zero-point Energies= -1044.917619 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1044.898828 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1044.897884 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1044.963956 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.252180
Number of imaginary vibrational frequencies = 0



2c·TFE



2c·TFE

Charge 0; multiplicity 1

C -1.65453900 0.50863500 -1.62879200
C -3.07951000 0.52723300 -2.04270600
C -0.76646500 1.66010400 -1.27607400
O 0.35463600 -0.40897900 -1.20095400
O -1.29762100 -1.78521700 -1.82339500
C 0.43486100 0.93080000 -0.64782000
H -3.43475400 -0.49965400 -2.21981200
H -3.69366900 1.00423000 -1.25855800
H -3.19262200 1.12041800 -2.96837300
H -1.24516500 2.35464700 -0.56717700
H -0.48931600 2.22226900 -2.18875100
C 1.78645200 1.51150100 -0.97409500
C 2.49215800 2.22463700 -0.00361300
C 2.32497800 1.36352800 -2.25686300
C 3.72593200 2.79995300 -0.31541000
H 2.07178700 2.32774000 1.00576900
C 3.56026700 1.93038400 -2.56459300
H 1.77181100 0.79122600 -3.01350800
C 4.26159300 2.65254200 -1.59486000
H 4.27535000 3.36085700 0.45109700
H 3.98176200 1.80731900 -3.57023300
H 5.23387400 3.09902600 -1.83865600
H 0.30135100 0.84338100 0.44602400
N -0.97849500 -0.59051900 -1.58121700
C 0.00574300 -3.39683500 0.80544900
O 0.53937900 -3.24783700 -0.48053300
H -0.12343100 -2.77337200 -1.03708200
H -1.01895000 -3.82002200 0.81838600
H 0.66647500 -4.05506800 1.39695100
C -0.05831800 -2.07293100 1.54137600
F -0.33901700 -2.25397200 2.85156400
F 1.10288600 -1.38520000 1.46721200
F -1.02334200 -1.25108700 1.04923400

DFT M11; cc-pvdz+d, solvent TFE, SMD model
Total electronic energy= -1045.179441 E_0
Sum of electronic and zero-point Energies= -1044.926398 $E_0 + E_{ZPE}$
Sum of electronic and thermal Energies= -1044.908035 $E_0 + E_{tot}$
Sum of electronic and thermal Enthalpies= -1044.907091 $E_0 + H_{corr}$
Sum of electronic and thermal Free Energies= -1044.969924 $E_0 + G_{corr}$
Zero-point correction (*unscaled*) = 0.253042
Number of imaginary vibrational frequencies = 0

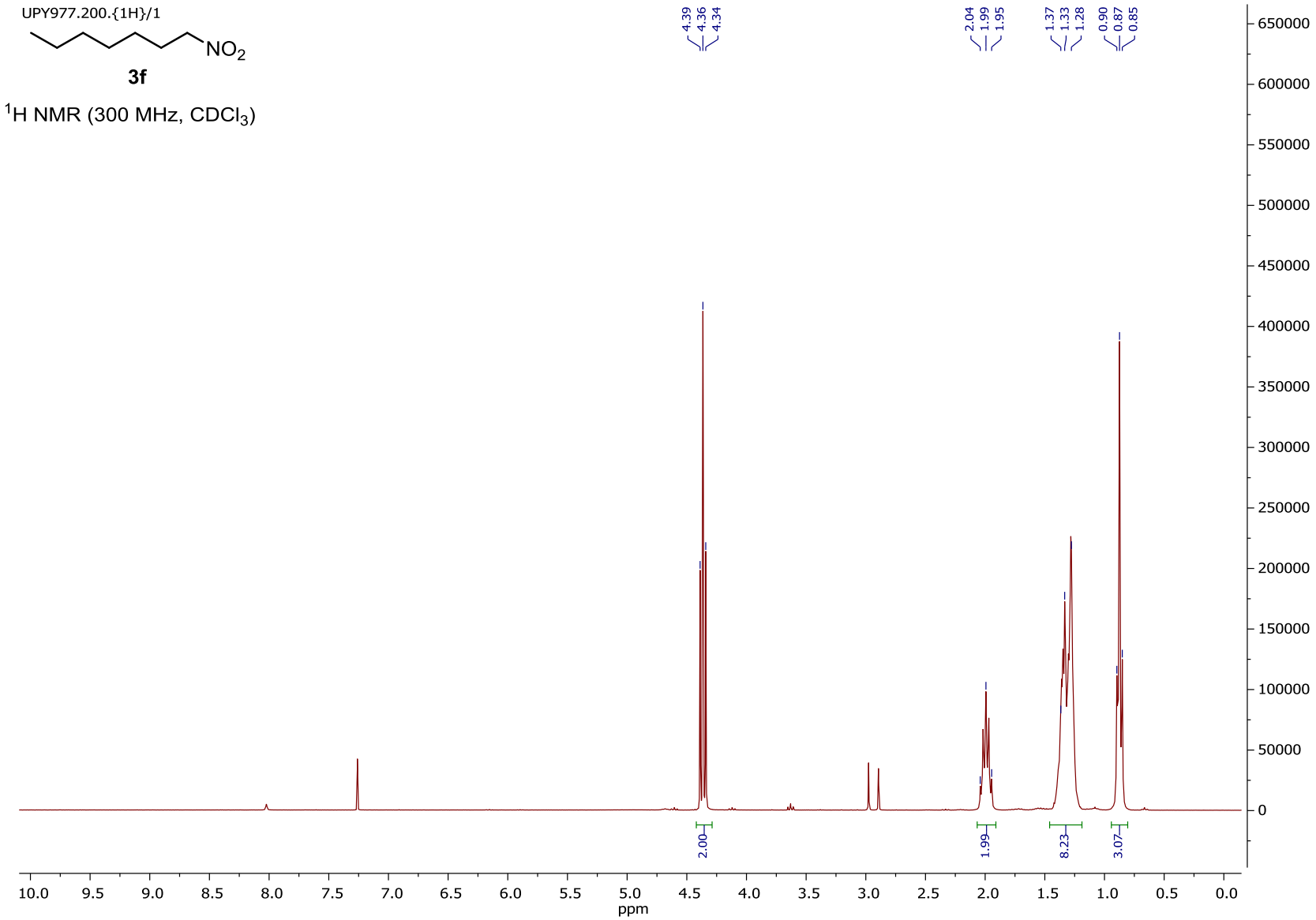
9. References

1. M. A. Drinan, T. D. Lash, *J. Heterocyclic Chem*., 1994, **31**, 255.
2. C. A. Citron, P. Rabe, J. S. Dickschat, *J. Nat. Prod*., 2012, **75**, 10, 1765.
3. A. Bhattacharjya, R. Mukhopadhyay, S. C. Pakrashi, *Synthesis*, 1985, **9**, 886.
4. S. Hajra, B. Jana, *Org. Lett*., 2017, **19**, 4778.
5. H. Griesser, R. Öhrlein, W. Schwab, R. Ehrler, V. Jäger, *Org. Synth*., 2000, **77**, 236.
6. Y. A. Antonova, S. L. Ioffe, A. Y. Sukhorukov, A. A. Tabolin, *Eur. J. Org. Chem*., 2021, **2021**, 3197.
7. R. Ballini, G. Bosica, G. Rafaiani, *Helvetica Chim. Acta*, 1995, **78**, 879.
8. D. Seebach, F. Lehr, *Helvetica Chim. Acta*, 1979, **62**, 2239.
9. S. Cai, X. Zhao, X. Wang, Q. Liu, Z. Li, D.Z. Wang, *Angew. Chem. Int. Ed*., 2012, **51**, 8050.
10. G. P. Marsh, P. J. Parsons, C. McCarthy, X. G. Corniquet, *Org. Lett*., 2007, **9**, 2613.
11. J. Li, M. J. Lear, Y. Hayashi, *Chem. Commun*., 2018, **54**, 6360.
12. J. V. Matlock, S. P. Fritz, S. A. Harrison, D. M. Coe, E. M. McGarrigle, V. K. Aggarwal*, J. Org. Chem.*, 2014, **79**, 10226.
13. Y. L. Chow, B. H. Bakker, *Synthesis*, 1982, **8**, 648.
14. P. Gopinath, S. Chandrasekaran, *J. Org. Chem*., 2011, **76**, 700.
15. A. Reichle, M. Koch, H. Sterzel, L. J. Großkopf, J. Floss, J. Rehbein, O. Reiser, *Angew. Chem. Int. Ed.*, 2023, **62**, e202219086.
16. A. B. Charette, R. Wurz, *J. Mol. Catal. A: Chemical*, 2003, **196**, 83.
17. R. A. Kunetsky, A. D. Dilman, S. L. Ioffe, M. I. Struchkova, Y. A. Strelenko, V. A. Tartakovsky, *Org. Lett*., 2003, **5**, 4907.
18. O. Lifchits, A.B. Charette, *Org. Lett*., 2008, **10**, 2809.
19. S. Yamamura, M. Toda, Y. Hirata, *Org. Synth*. 1973, **53**, 86.
20. A. Baglieri, L. Meschisi, F. De Sarlo, F. Machetti, *Eur. J. Org. Chem*., 2016, **2016**, 4643.
21. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
22. R. L. Martin, P. J. Hay, L. R. Pratt, *J. Phys. Chem. A*, 1998, **102**, 3565.
23. a) A. Poater, E. Pump, S. V. C. Vummaleti, L. Cavallo, *J. Chem. Theory Comput.*, 2014, **10**, 4442. b) D. G. Gusev, *ACS Catal.*, 2016, **6**, 6967. c) P. Pandey, P. Daw, N. U D. Reshi, K. R.

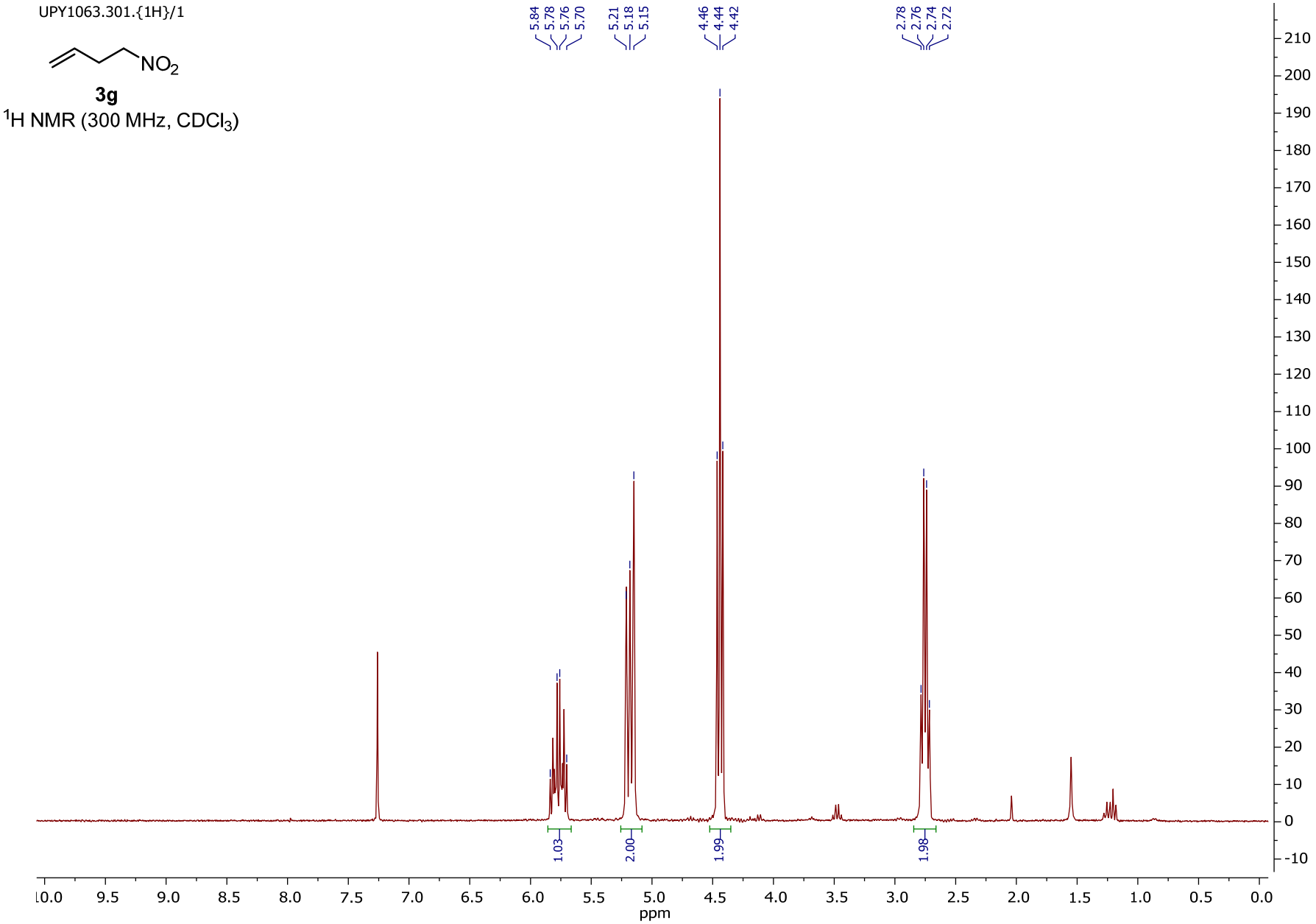
Ehmann, M. Hoelscher, W. Leitner, J. K. Bera, *Organometallics*, 2020, **39**, 3849. d) Z. Alassad, A. Nandi, S. Kozuch, A. Milo, *J. Am. Chem. Soc.*, 2023, **145**, 89. e) M. Wodrich, M. Chang, S. Gallarati, L. Wozniak, N. Cramer, C. Corminboeuf, *Chem. Eur. J.*, 2022, **28**, e202200399.

10. Spectra copies

NMR of **3f**

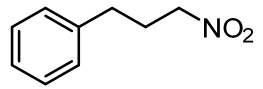


NMR of **3g**


UPY1063.301.{1H}/1
NO2
3g
1H NMR (300 MHz, CDCl3)
5.84
5.78
5.76
5.70
5.21
5.18
5.15
4.46
4.44
4.42
2.78
2.76
2.74
2.72
1.03
2.00
1.99
1.98
ppm

NMR of **3i**

UPY1019.201.{1H}/1

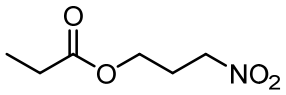


3i

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **3n**

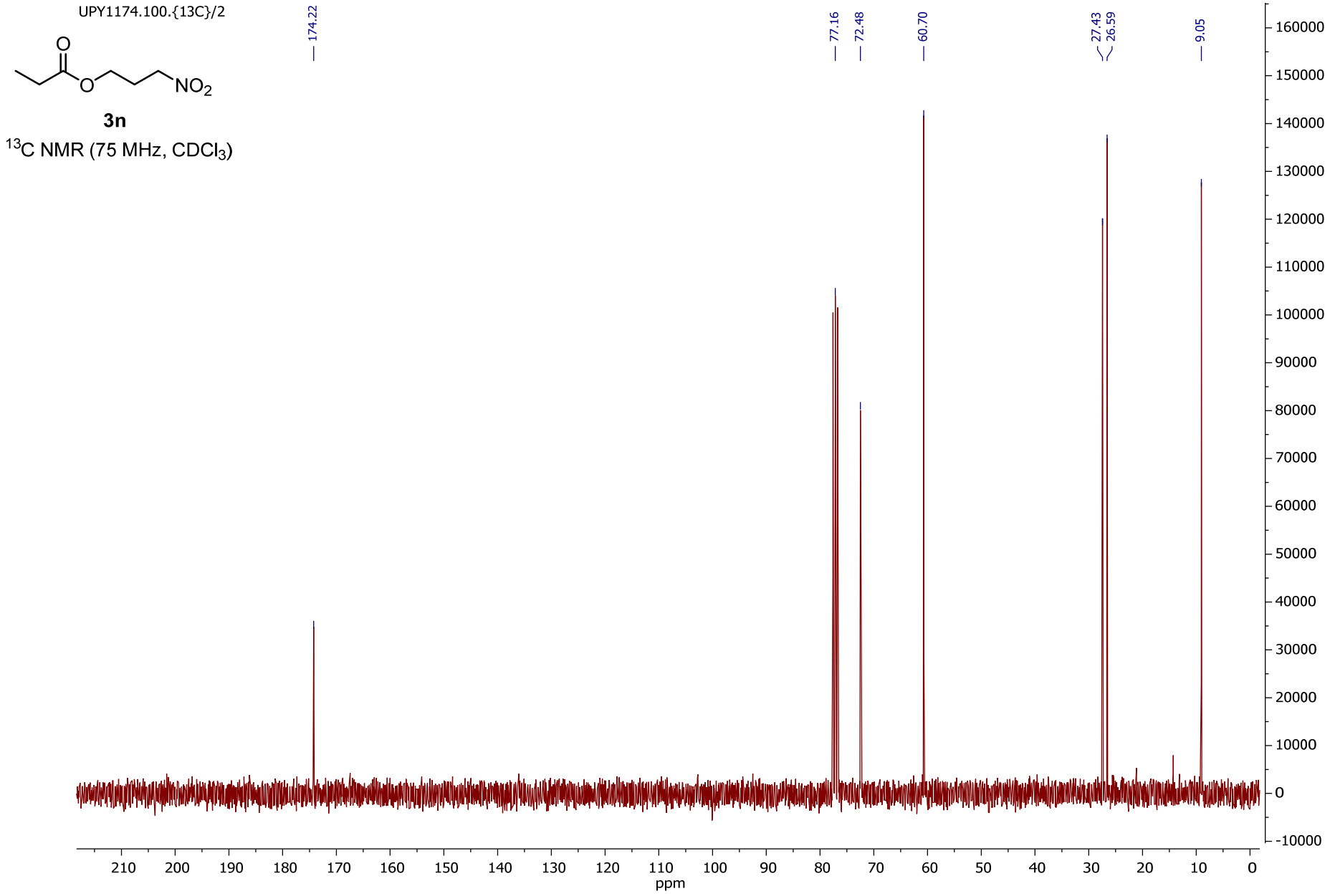
UPY1174.100.{1H}/1



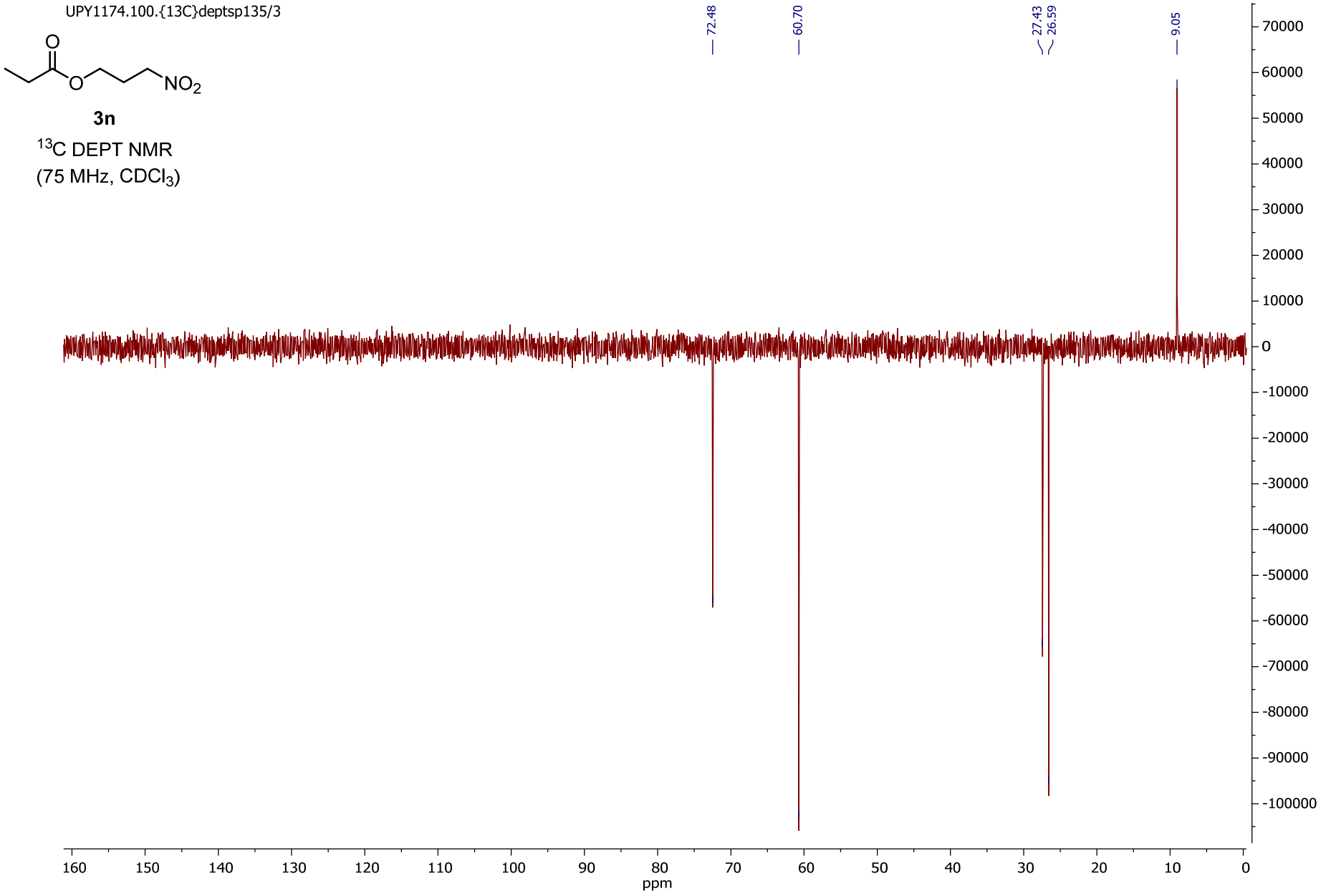
3n

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **3n**

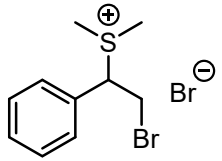

UPY1174.100.{13C}/2
O
O
NO2
3n
13C NMR (75 MHz, CDCl3)
174.22
77.16
72.48
60.70
27.43
26.59
9.05
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

NMR of **3n**


UPY1174.100.{13C}deptsp135/3
O
O
NO2
3n
13C DEPT NMR
(75 MHz, CDCl3)
72.48
60.70
27.43
26.59
9.05
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
-50000
-60000
-70000
-80000
-90000
-100000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

NMR of **4a**

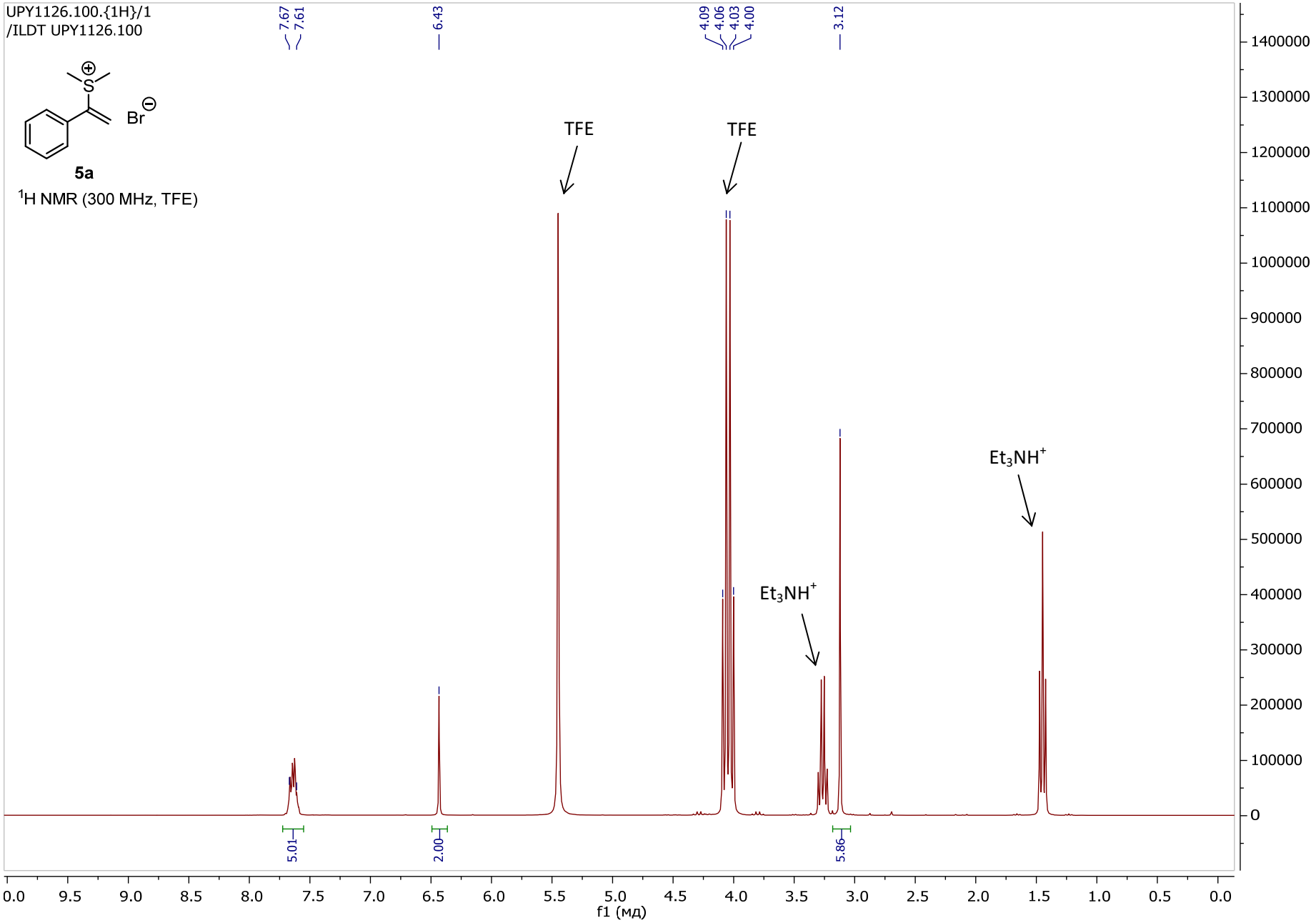
UPY929.100.{1H}/1



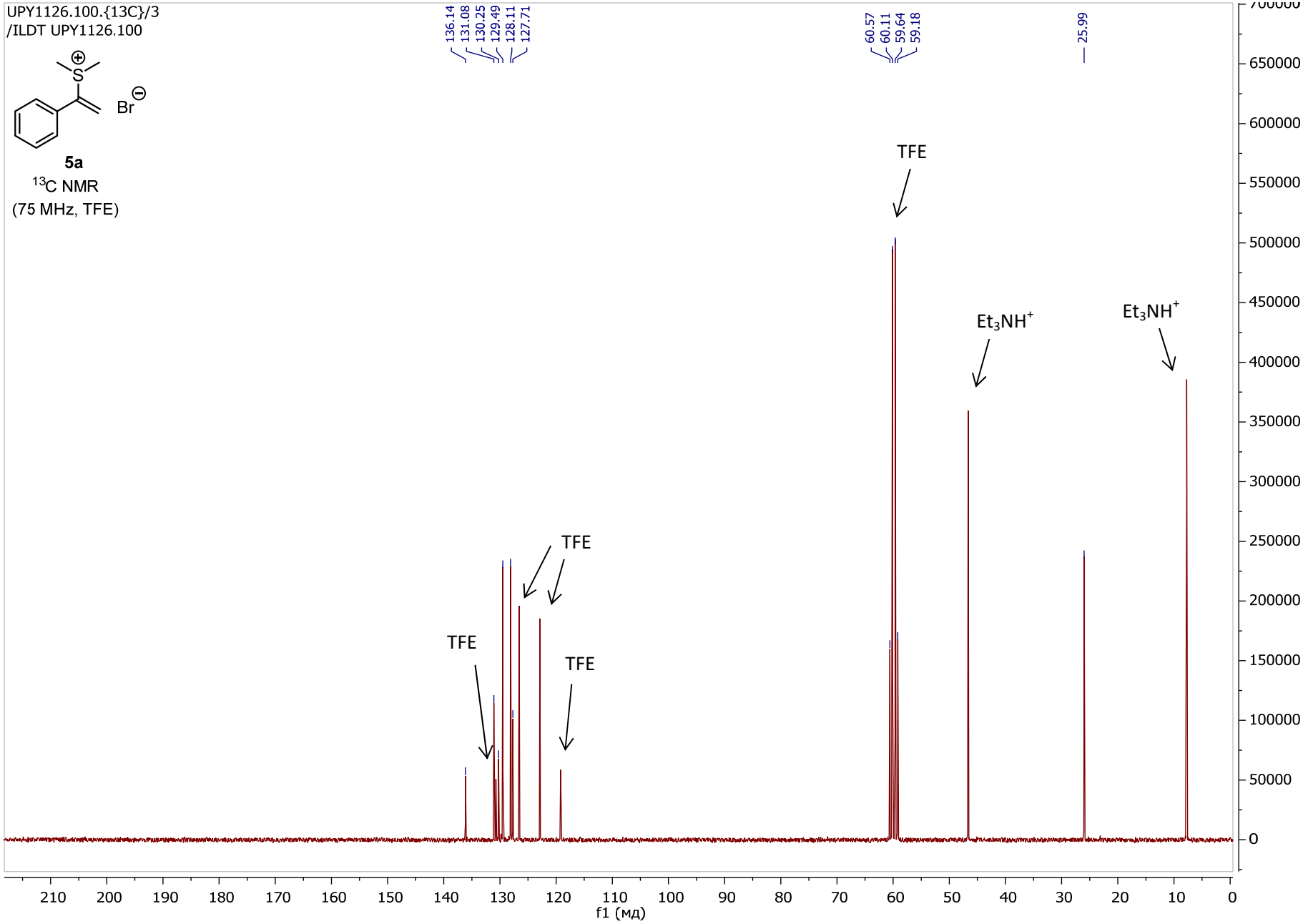
4a

^{1}H NMR (300 MHz, DMSO-d_6)

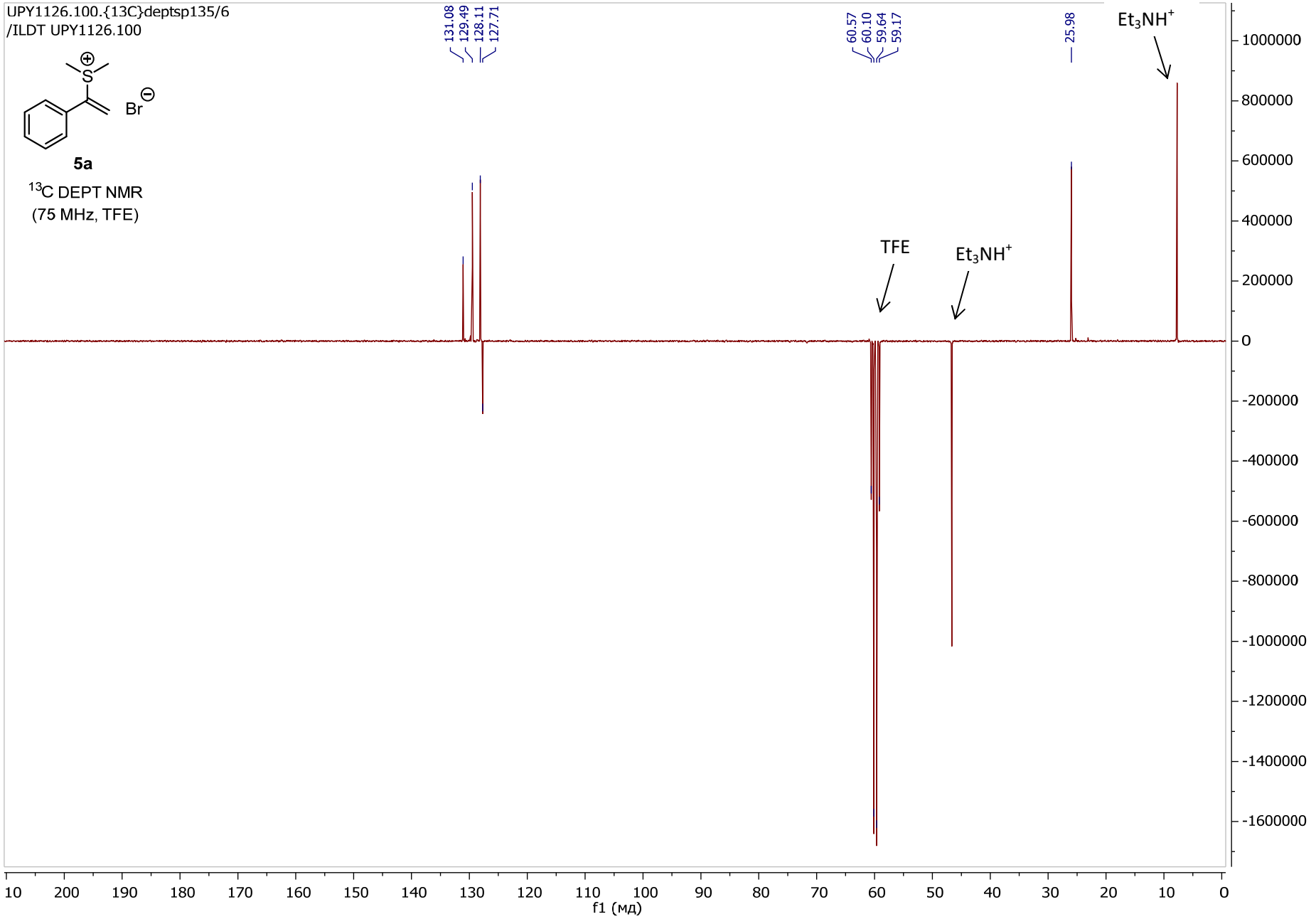
NMR of **5a** (reaction mixture of **4a** + NEt_3 in TFE)



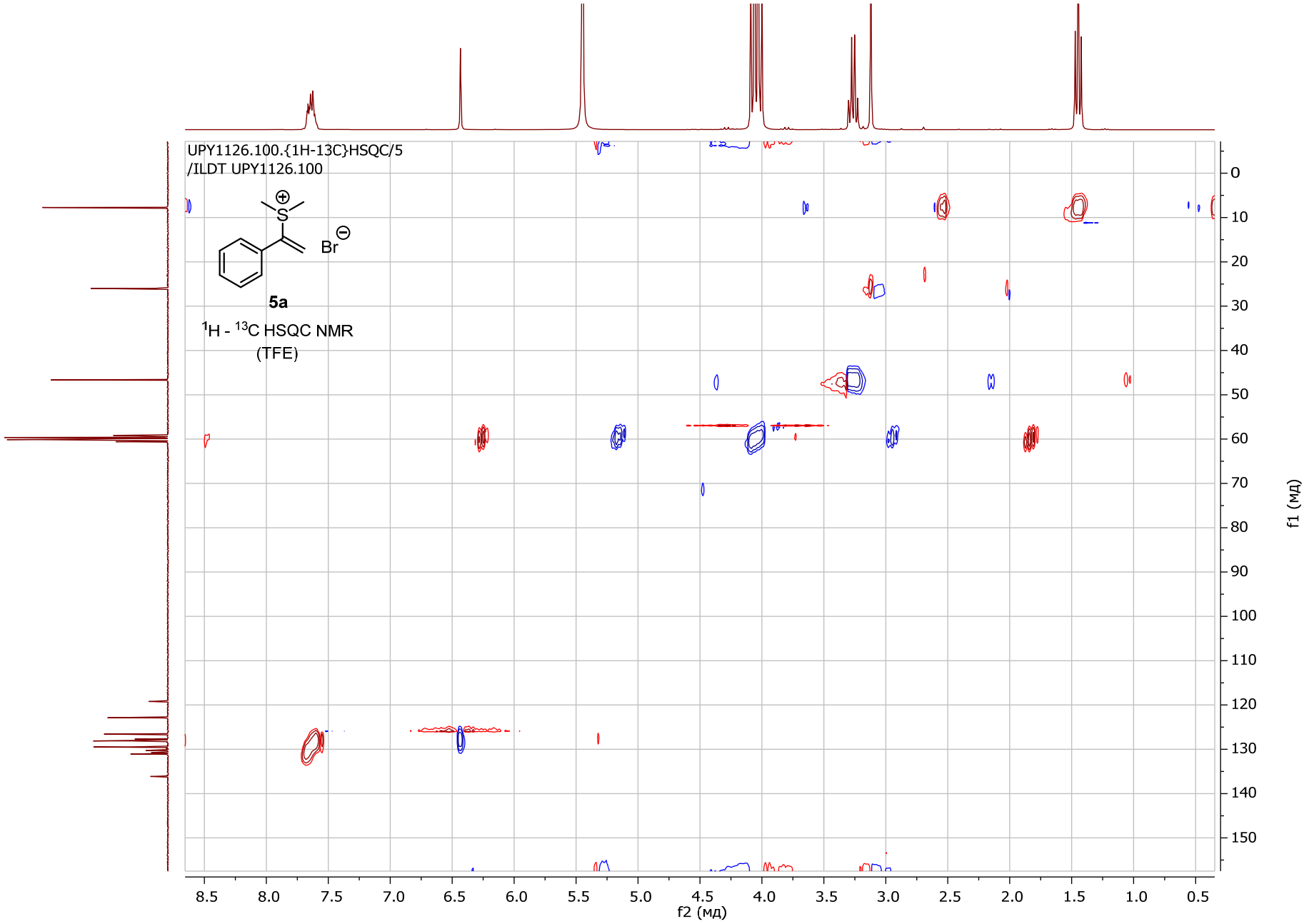
NMR of **5a** (reaction mixture of **4a** + NEt_3 in TFE)



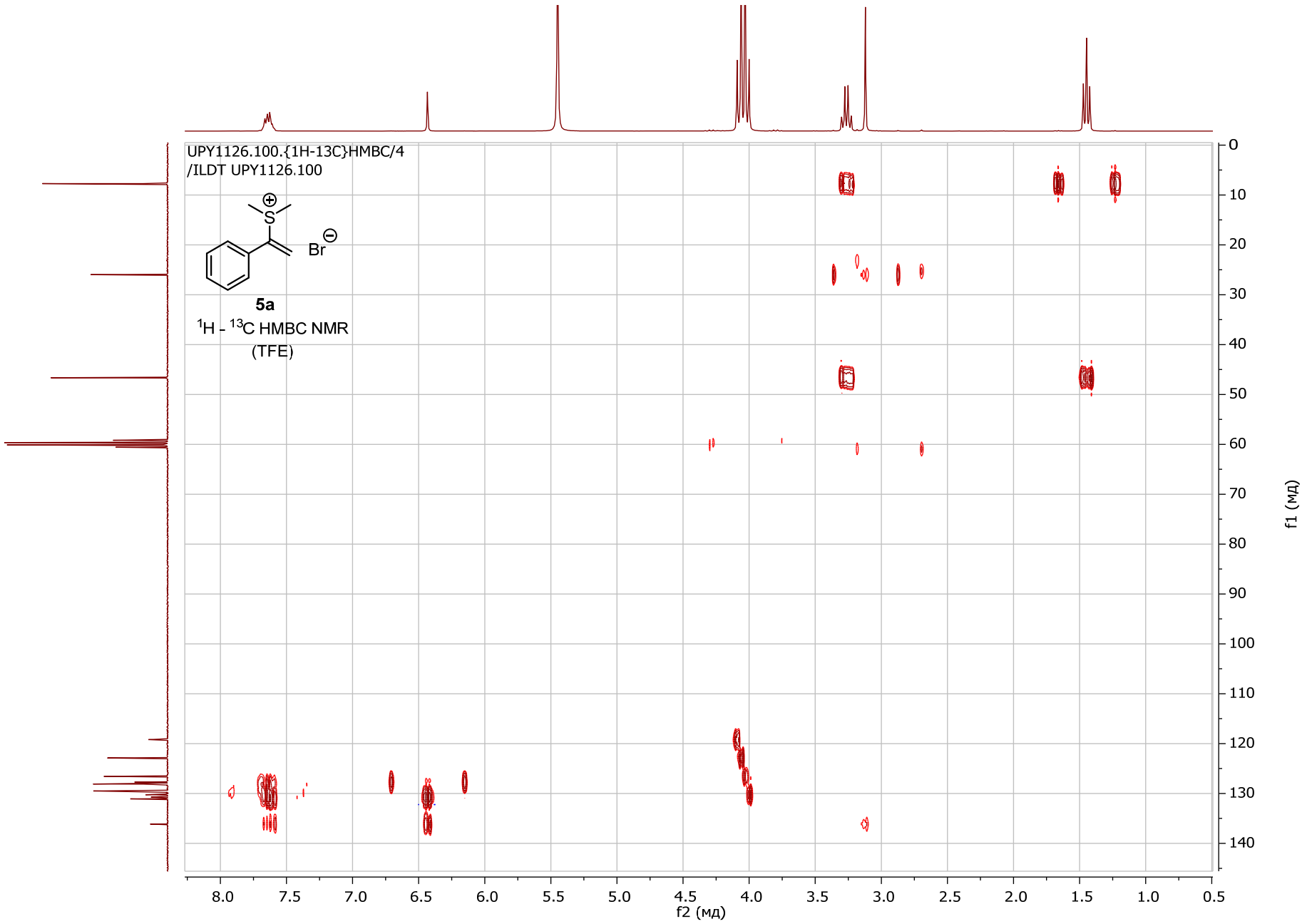
NMR of **5a** (reaction mixture of **4a** + NEt_3 in TFE)



NMR of **5a** (reaction mixture of **4a** + NEt_3 in TFE)

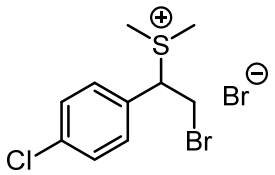


NMR of **5a** (reaction mixture of **4a** + NEt_3 in TFE)



NMR of **4b**

UPY982.200.{1H}/1

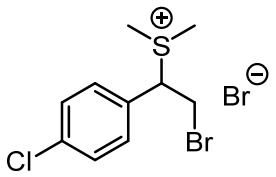


4b

^{1}H NMR (300 MHz, DMSO-d_6)

NMR of **4b**

UPY982.200.{13C}/2

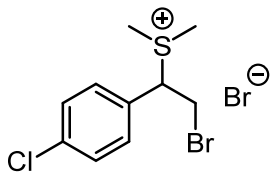


4b

^{13}C NMR

(75 MHz, DMSO-d_6)

NMR of **4b**

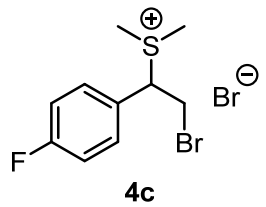


4b

^{13}C DEPT NMR
(75 MHz, DMSO-d_6)

NMR of **4c**

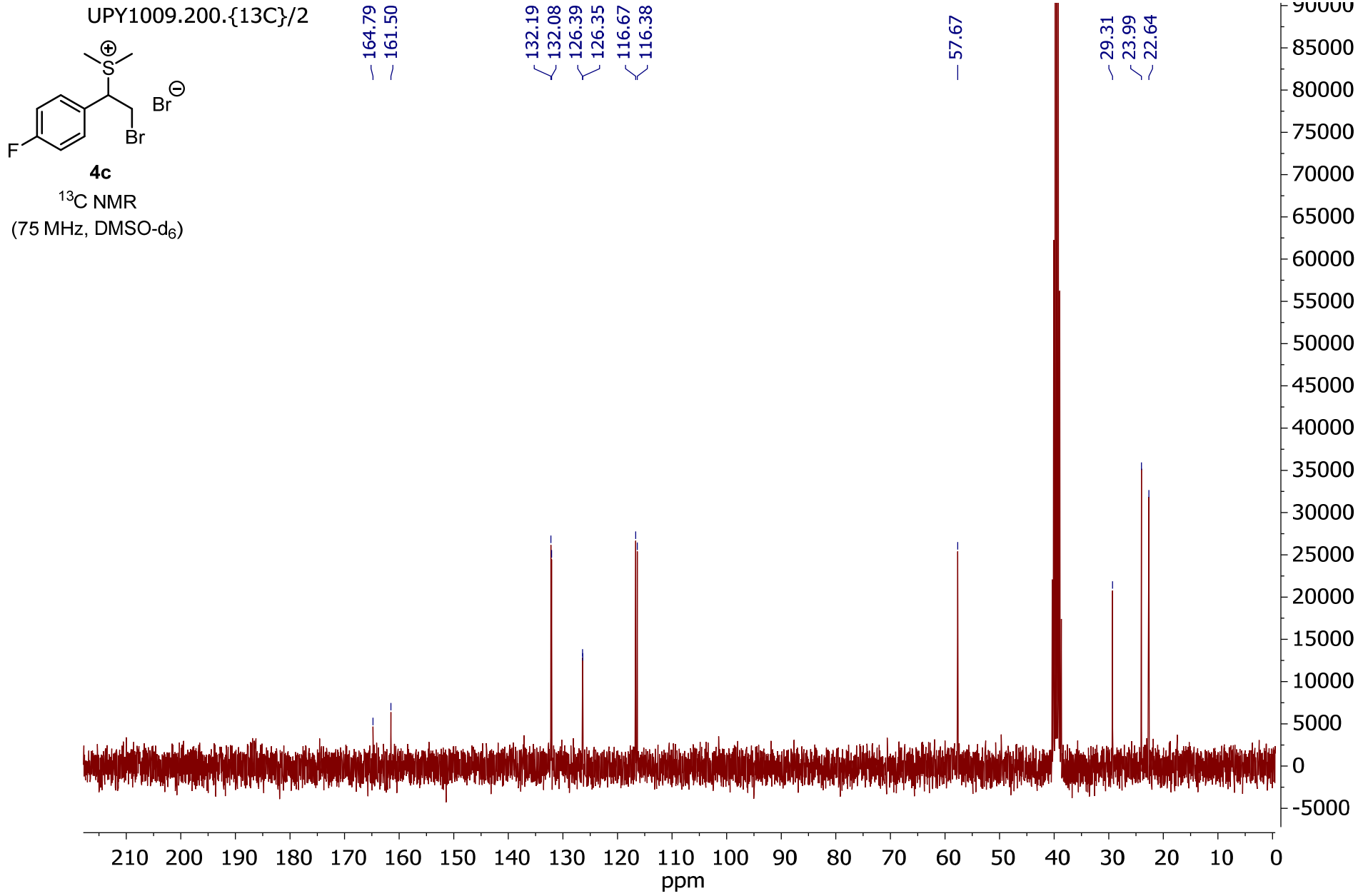
UPY1009.200.{1H}/1



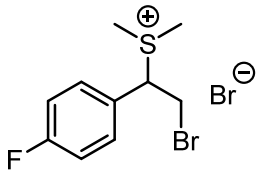
4c

^{1}H NMR (300 MHz, DMSO-d_6)

NMR of **4c**


UPY1009.200.{13C}/2
164.79
161.50
132.19
132.08
126.39
126.35
116.67
116.38
57.67
29.31
23.99
22.64
Br
Br
F
4c
13C NMR
(75 MHz, DMSO-d6)
ppm

NMR of **4c**



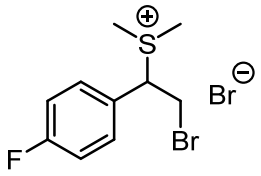
4c

^{13}C DEPT NMR

(75 MHz, DMSO-d_6)

NMR of **4c**

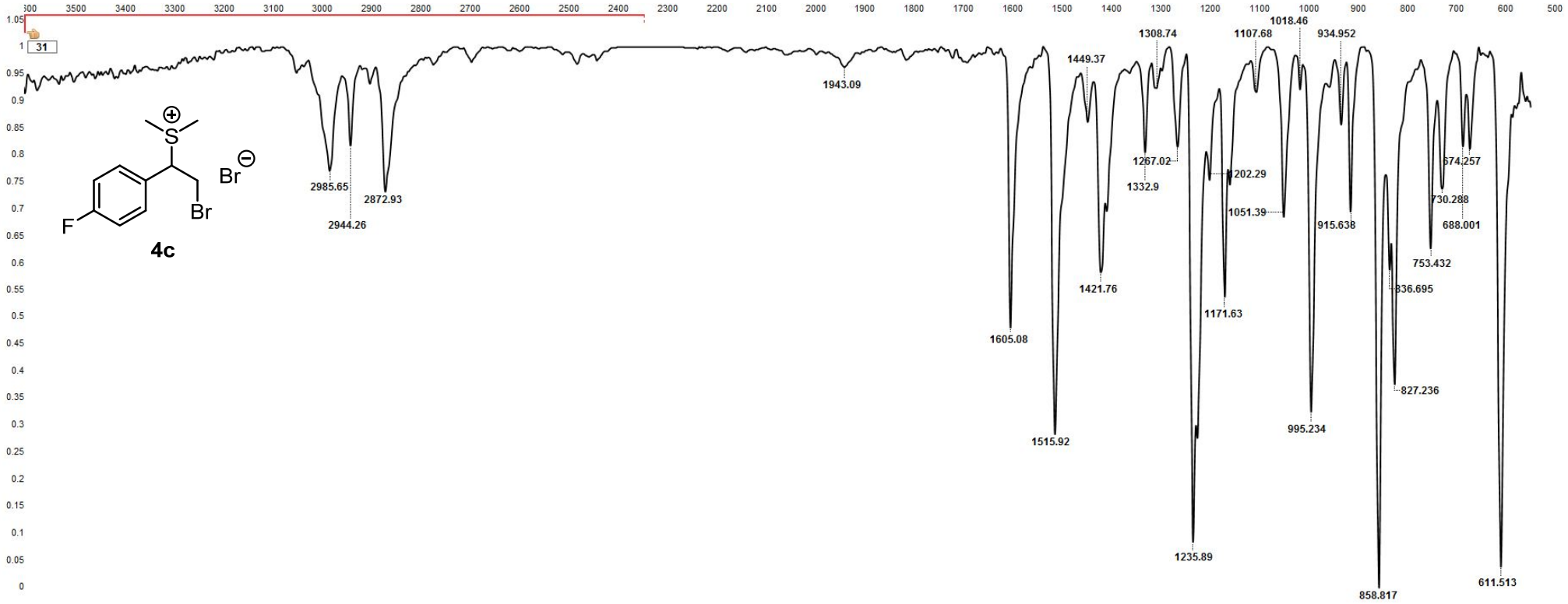
UPY1009.200.{19F}/19



4c

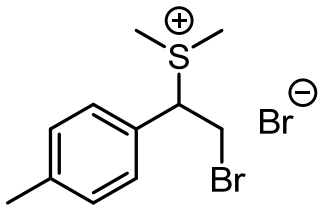
^{19}F NMR (282 MHz, DMSO-d_6)

FTIR (ATR) of **4c**



NMR of **4e**

UPY1005.200.{1H}/1

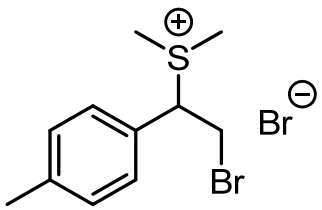


4e

^{1}H NMR (300 MHz, DMSO-d_6)

NMR of **4e**

UPY1005.200.{13C}/2

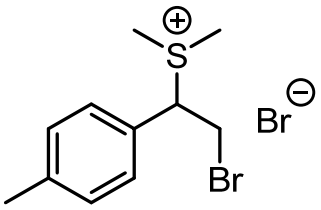


4e

^{13}C NMR

(75 MHz, DMSO-d_6)

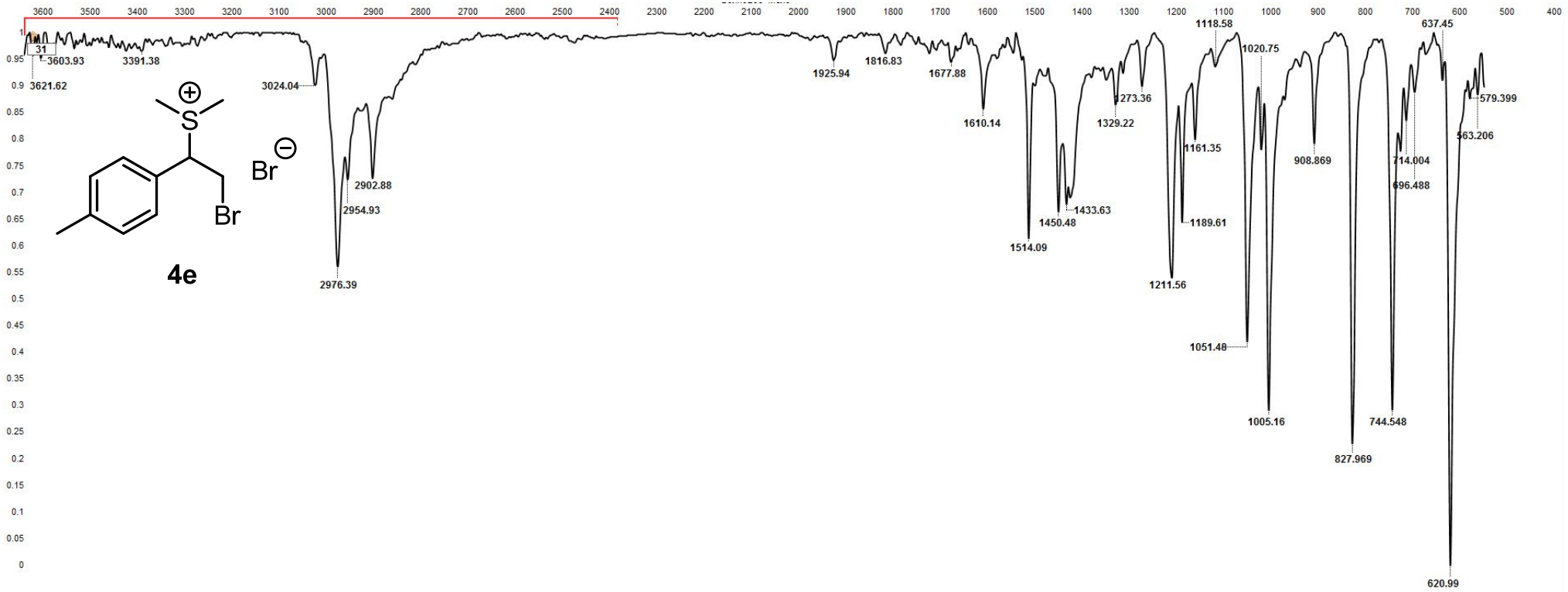
NMR of **4e**



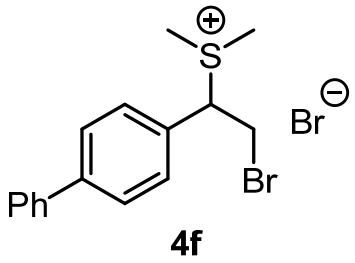
4e

^{13}C DEPT NMR
(75 MHz, DMSO-d_6)

FTIR (ATR) of **4e**



NMR of **4f**

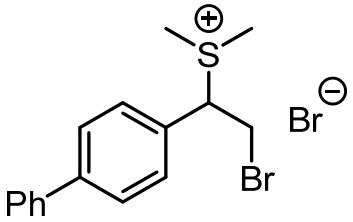


4f

^{1}H NMR (300 MHz, DMSO-d_6)

NMR of **4f**

UPY1017.200.{13C}/2

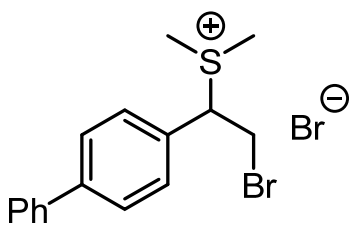


4f

^{13}C NMR

(75 MHz, DMSO-d_6)

NMR of **4f**

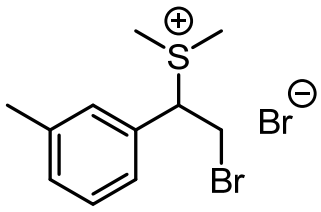


4f

^{13}C DEPT NMR

(75 MHz, DMSO-d_6)

NMR of **4g**

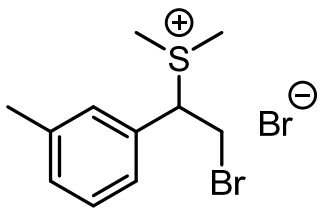


4g

^{1}H NMR (300 MHz, DMSO-d_6)

NMR of **4g**

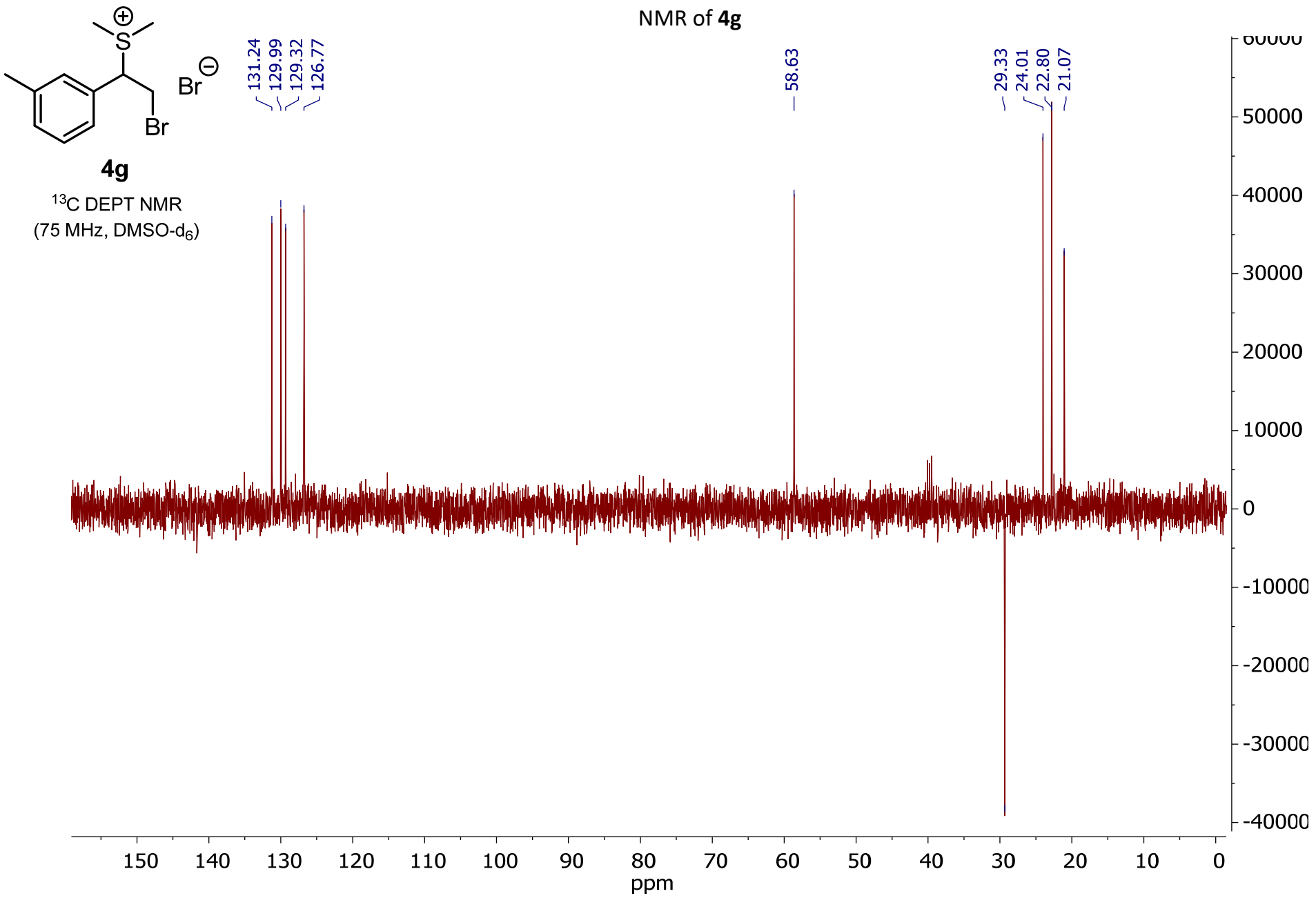
UPY1006.200.{13C}/2



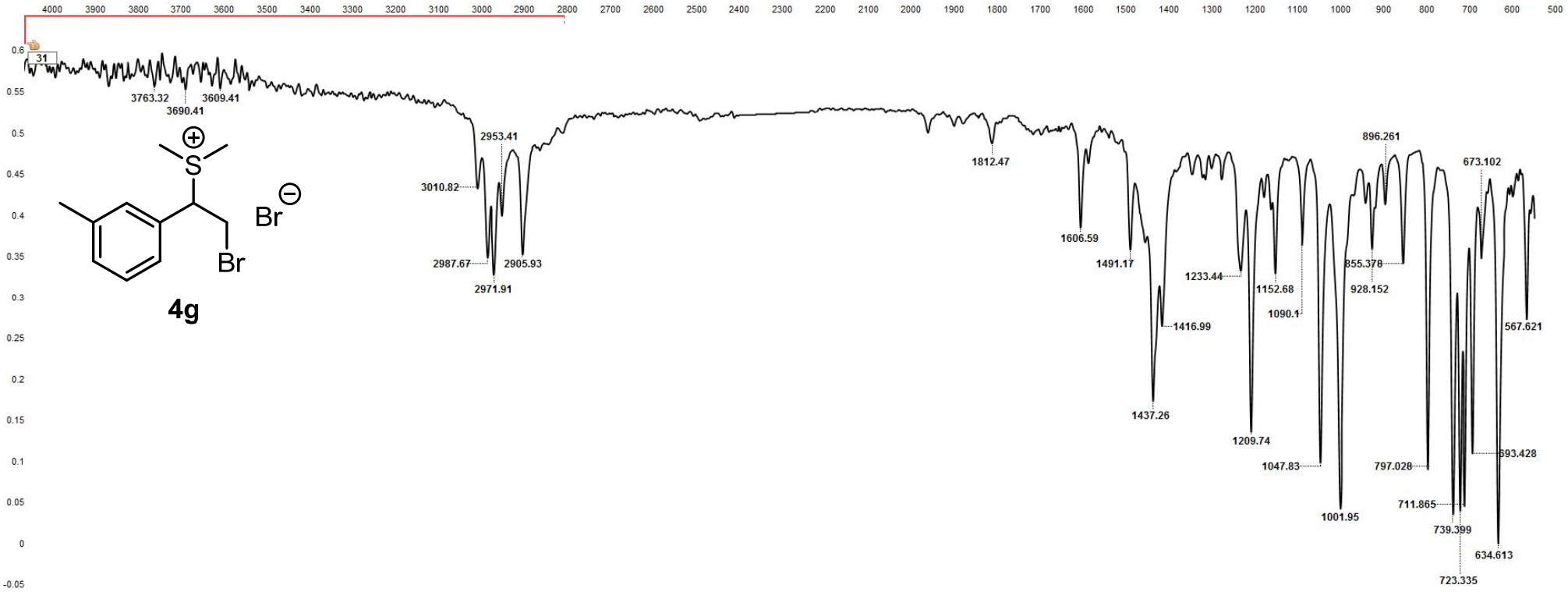
4g

^{13}C NMR

(75 MHz, DMSO-d_6)

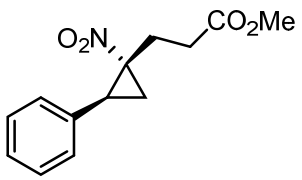

NMR of 4g
4g
13C DEPT NMR
(75 MHz, DMSO-d6)
Br
Br
131.24
129.99
129.32
126.77
58.63
29.33
24.01
22.80
21.07
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

FTIR (ATR) of **4g**



NMR of **1a**

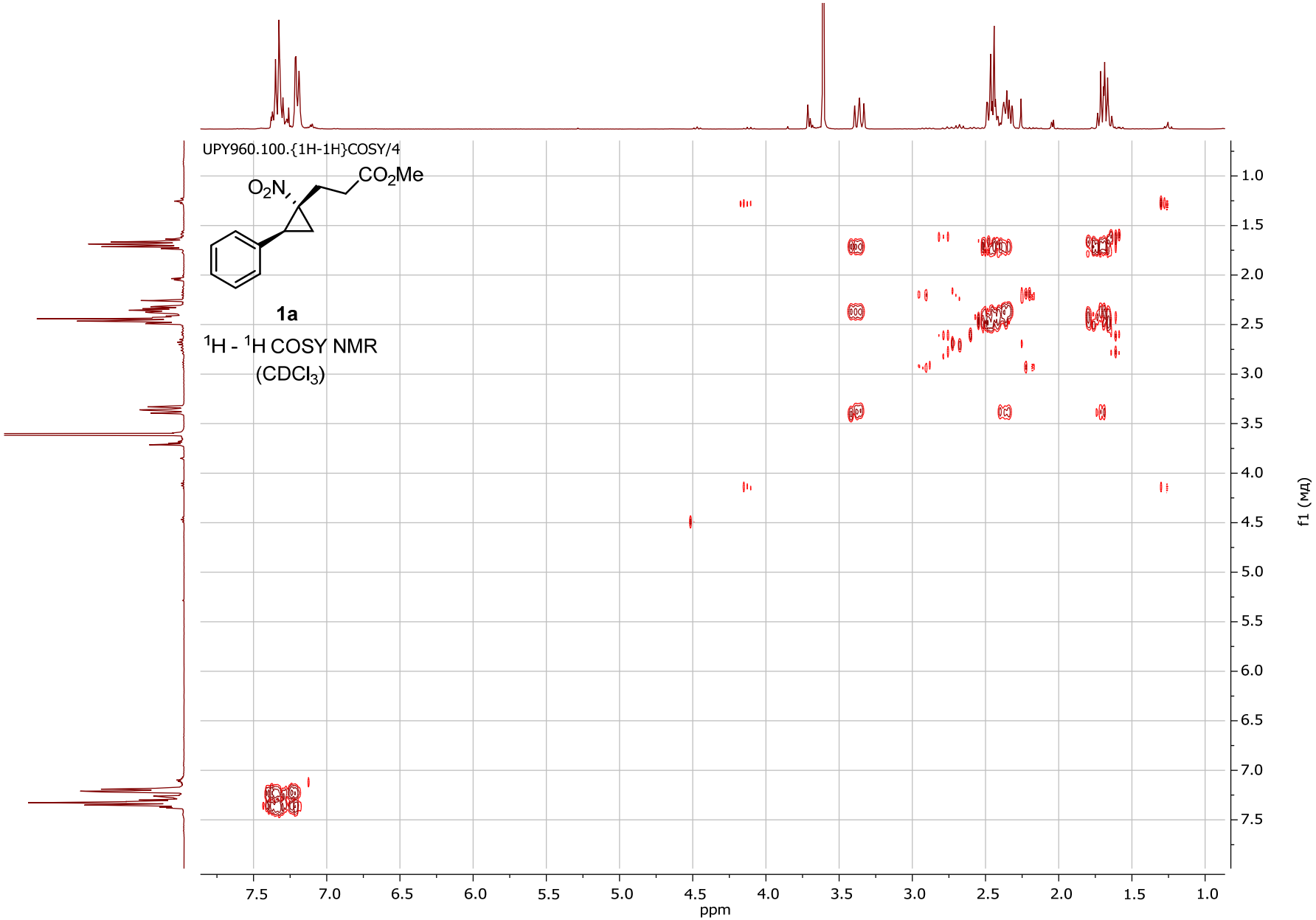
UPY960.100.{1H}/1



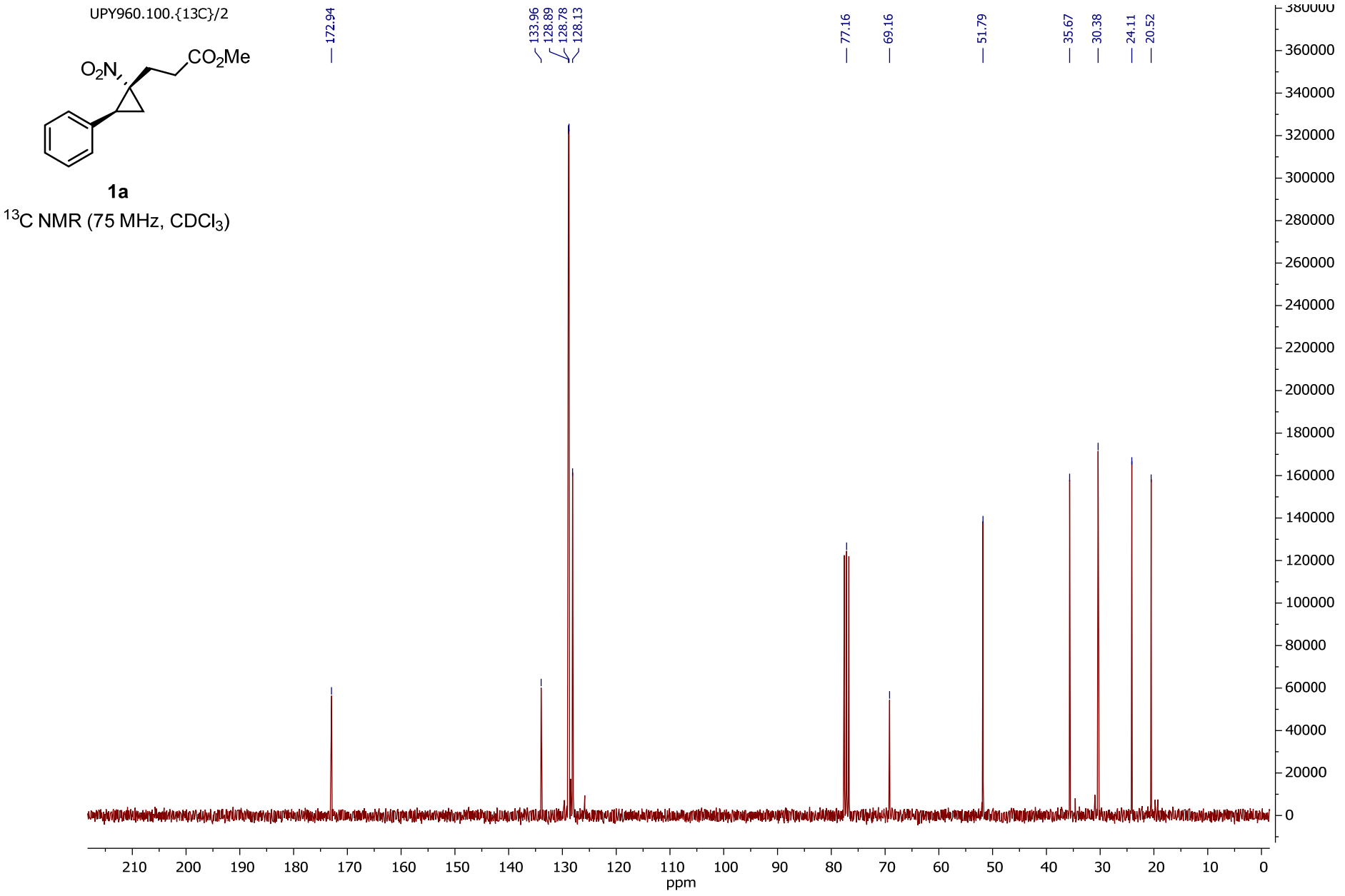
1a

^{1}H NMR (300 MHz, $CDCl_3$)

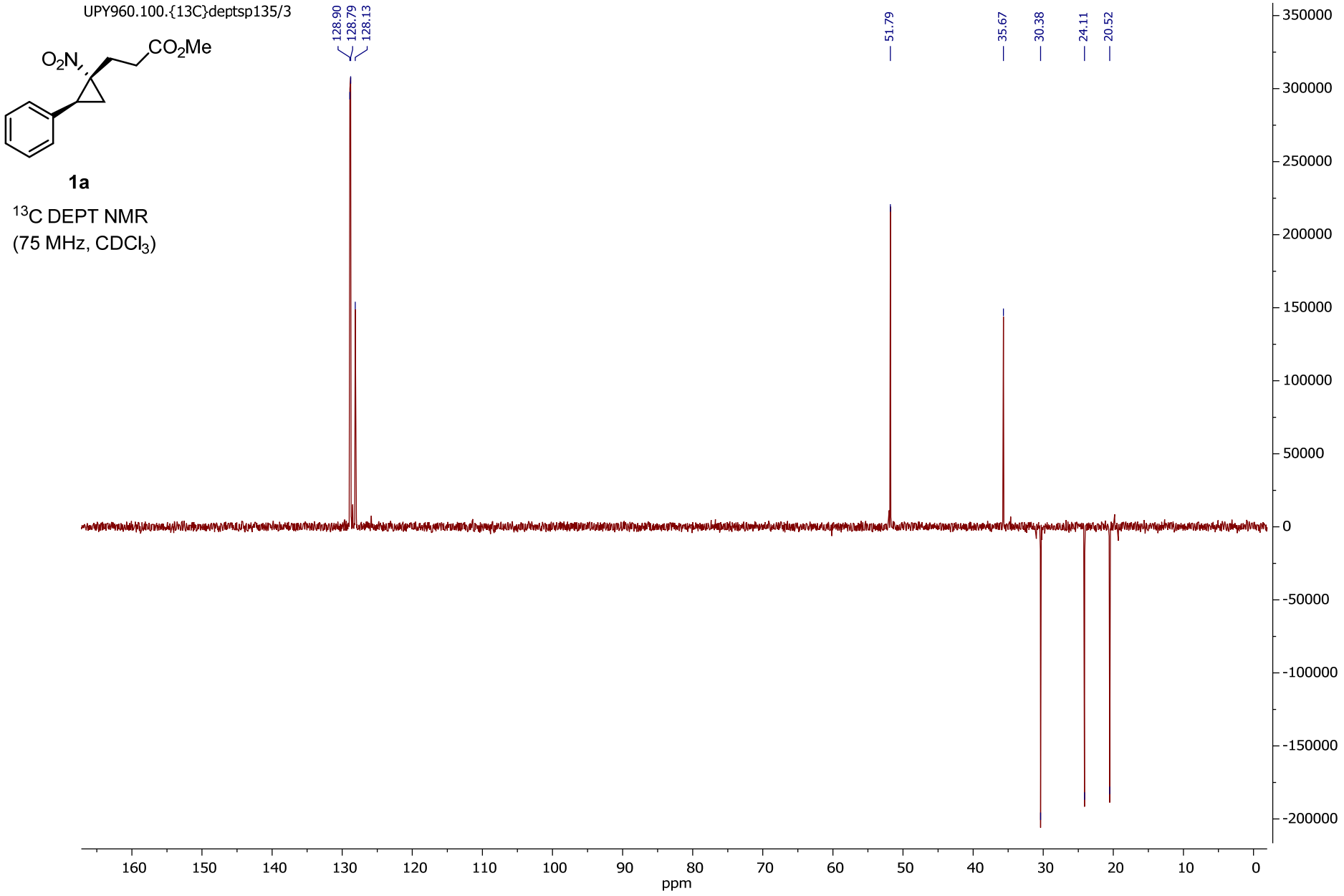
NMR of **1a**


UPY960.100.{1H-1H}COSY/4
O2N
CO2Me
1a
1H - 1H COSY NMR
(CDCl3)
ppm
f1 (мд)

NMR of **1a**

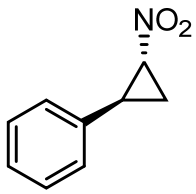

UPY960.100.{13C}/2
O2N
CO2Me
1a
13C NMR (75 MHz, CDCl3)
172.94
133.96
128.89
128.78
128.13
77.16
69.16
51.79
35.67
30.38
24.11
20.52
ppm

NMR of **1a**


UPY960.100.{13C}deptsp135/3
O_2N
CO_2Me
1a
^{13}C DEPT NMR
(75 MHz, $CDCl_3$)
128.90
128.79
128.13
51.79
35.67
30.38
24.11
20.52
350000
300000
250000
200000
150000
100000
50000
0
-50000
-100000
-150000
-200000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

NMR of **1b**

UPY968.100.{1H}/1

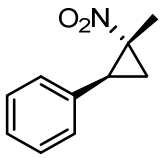


1b

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **1c**

UPY961.100.{1H}/1

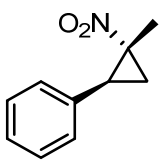


1c

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **1c**

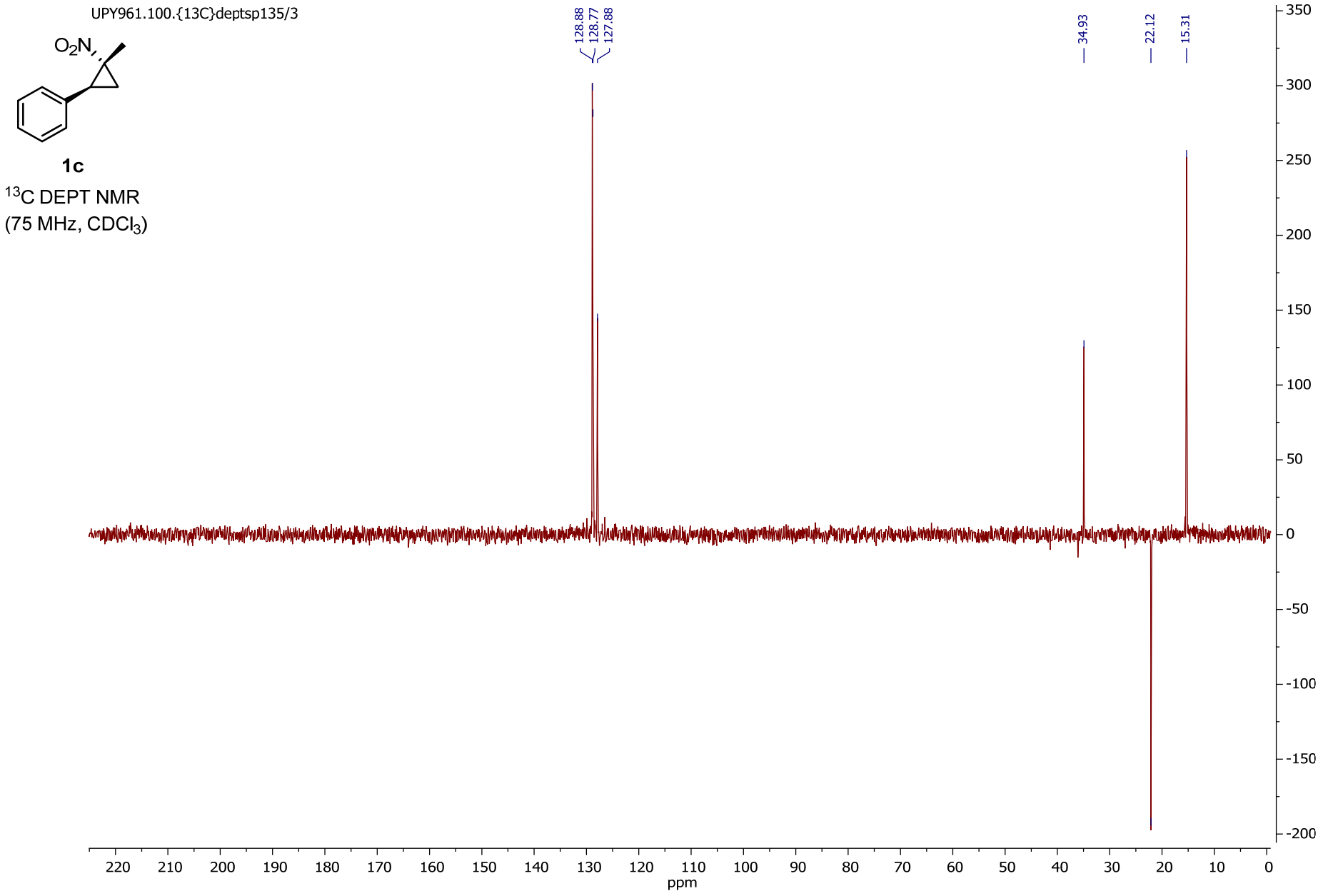
UPY961.100.{13C}/2



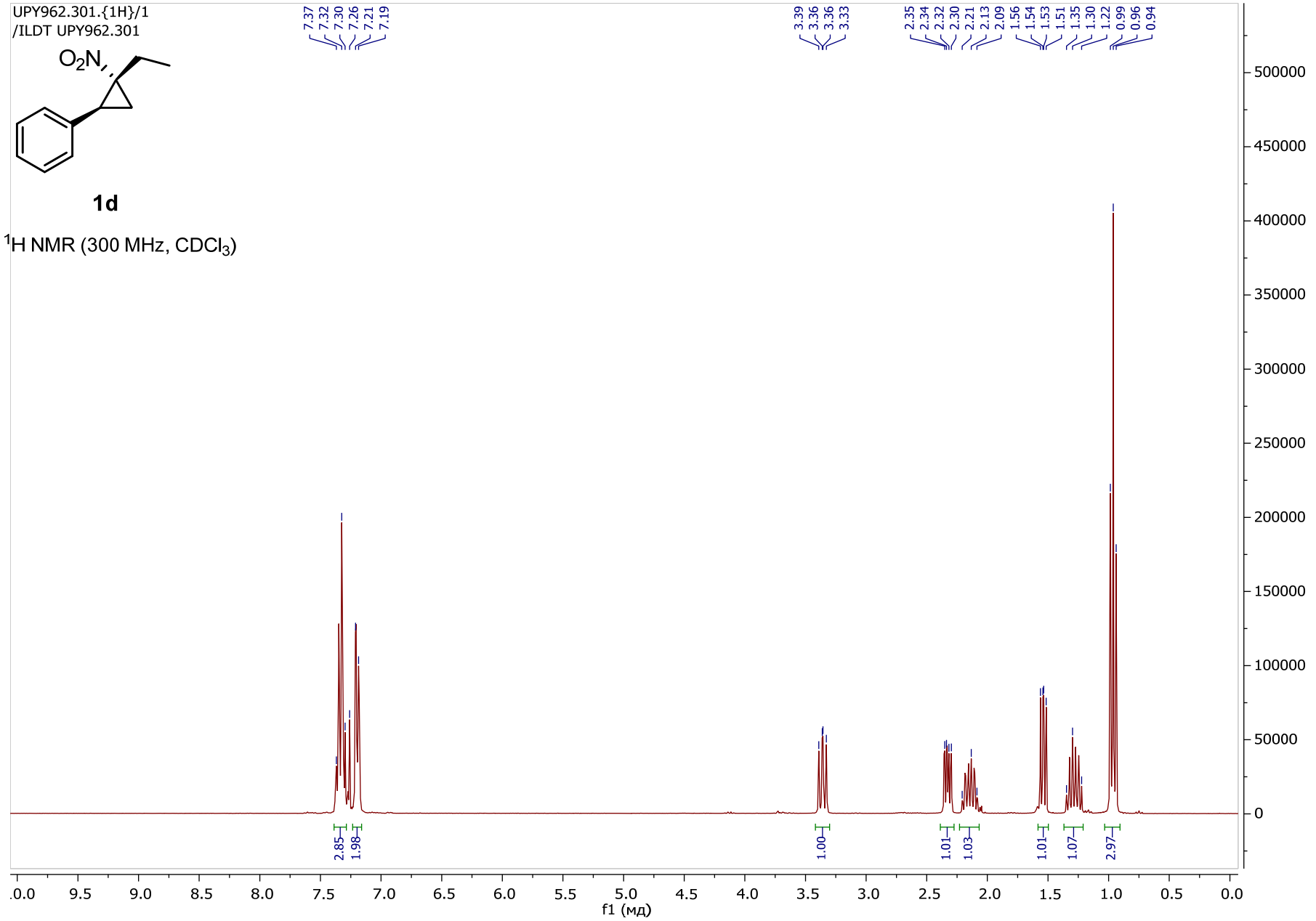
1c

^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **1c**

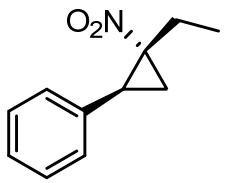

UPY961.100.{13C}deptsp135/3
O2N
1c
13C DEPT NMR
(75 MHz, CDCl3)
128.88
128.77
127.88
34.93
22.12
15.31
350
300
250
200
150
100
50
0
-50
-100
-150
-200
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

NMR of **1d**


UPY962.301.{1H}/1
/ILDT UPY962.301
O2N
1d
1H NMR (300 MHz, CDCl3)
7.37
7.32
7.30
7.26
7.21
7.19
3.39
3.36
3.36
3.33
2.35
2.34
2.32
2.30
2.21
2.13
2.09
1.56
1.54
1.53
1.51
1.35
1.30
1.22
0.99
0.96
0.94
2.85
1.98
1.00
1.01
1.03
1.01
1.07
2.97
f1 (мд)

NMR of **1d**

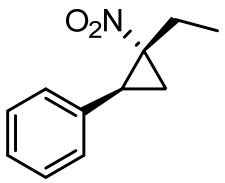
UPY962.301.{13C}/2



1d

^{13}C NMR (75 MHz, $CDCl_3$)

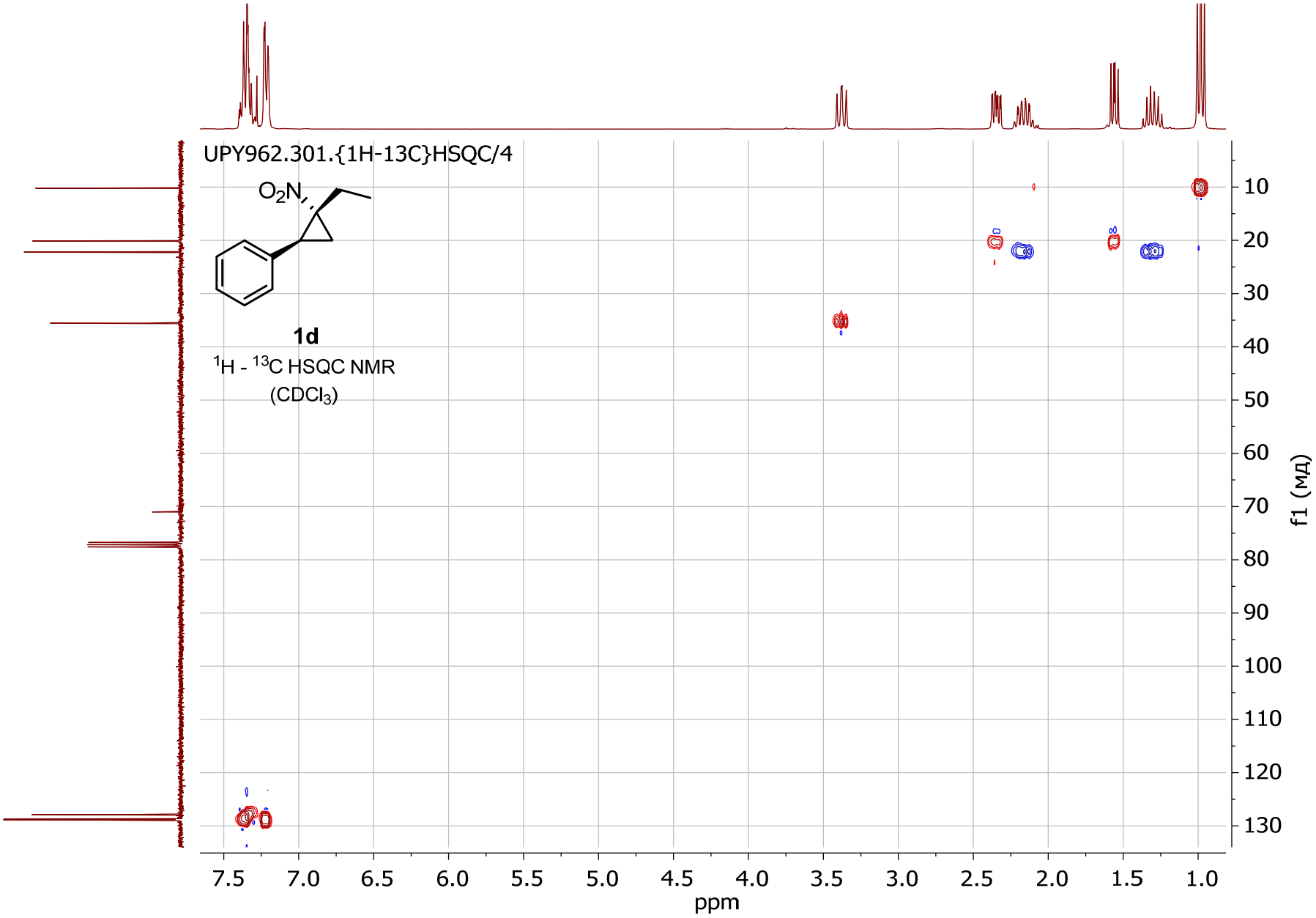
NMR of **1d**



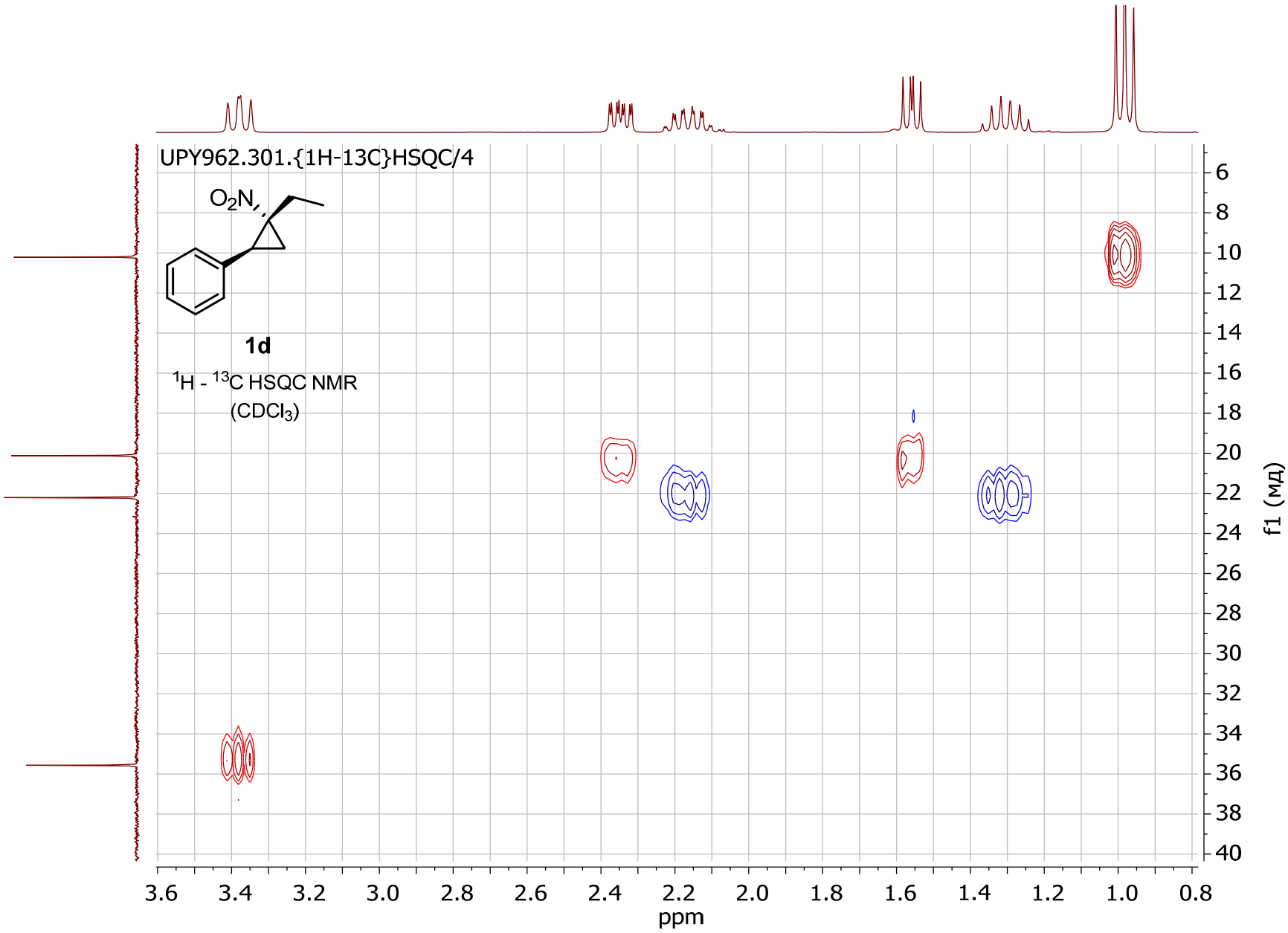
1d

^{13}C DEPT NMR
(75 MHz, $CDCl_3$)

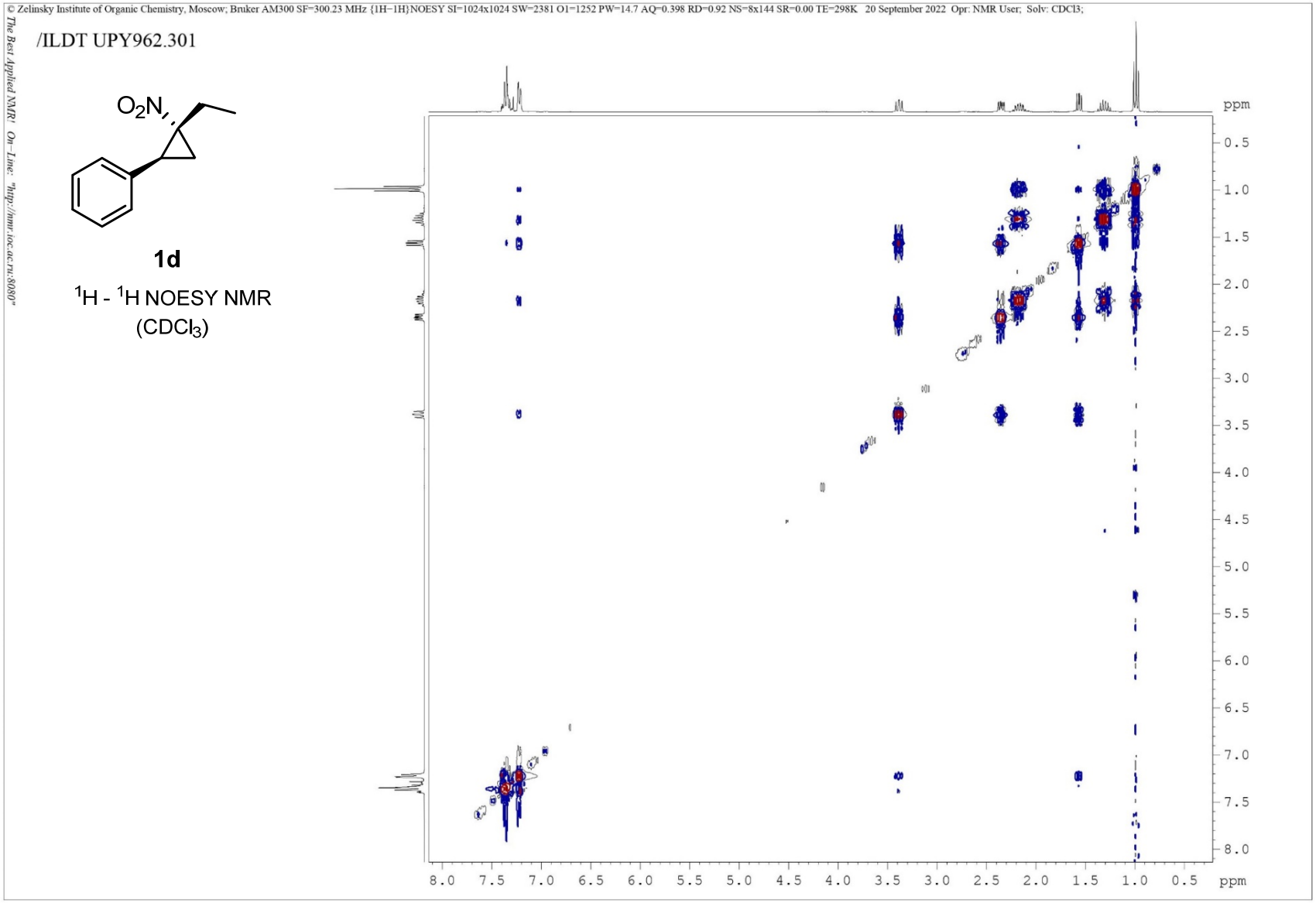
NMR of **1d**


UPY962.301.{1H-13C}HSQC/4
O2N
1d
1H - 13C HSQC NMR
(CDCl3)
10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (мд)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

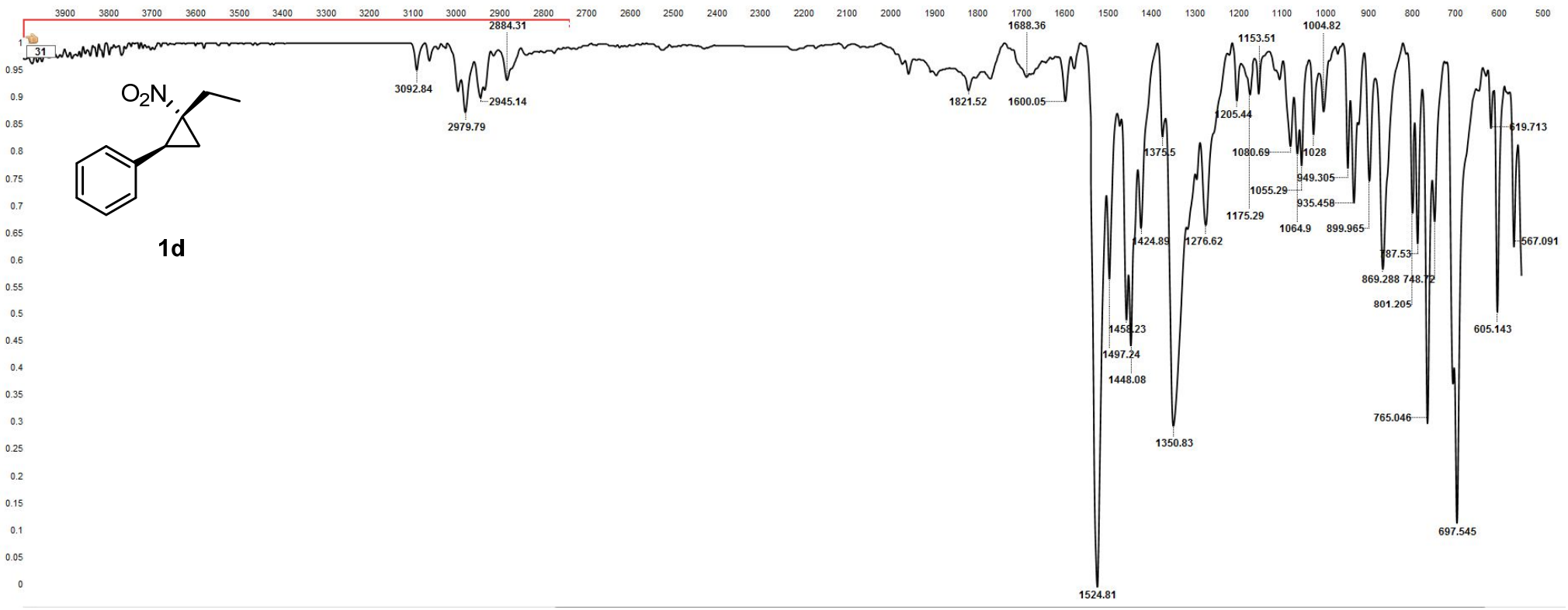
NMR of **1d**


UPY962.301.{1H-13C}HSQC/4
O2N
1d
1H - 13C HSQC NMR
(CDCl3)
f1 (мд)
ppm
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40

NMR of **1d**

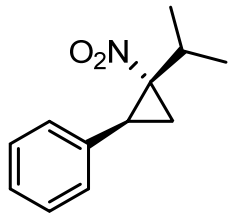

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.23 MHz {1H−1H}NOESY SI=1024x1024 SW=2381 O1=1252 PW=14.7 AQ=0.398 RD=0.92 NS=8x144 SR=0.00 TE=298K 20 September 2022 Opr: NMR User; Solv: CDCl3;
The Best Applied NMR! On−Line: "http://nmr.ioc.ac.ru:8080"
/ILDT UPY962.301
O2N
1d
1H - 1H NOESY NMR
(CDCl3)
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

FTIR (ATR) of **1d**



NMR of **1e**

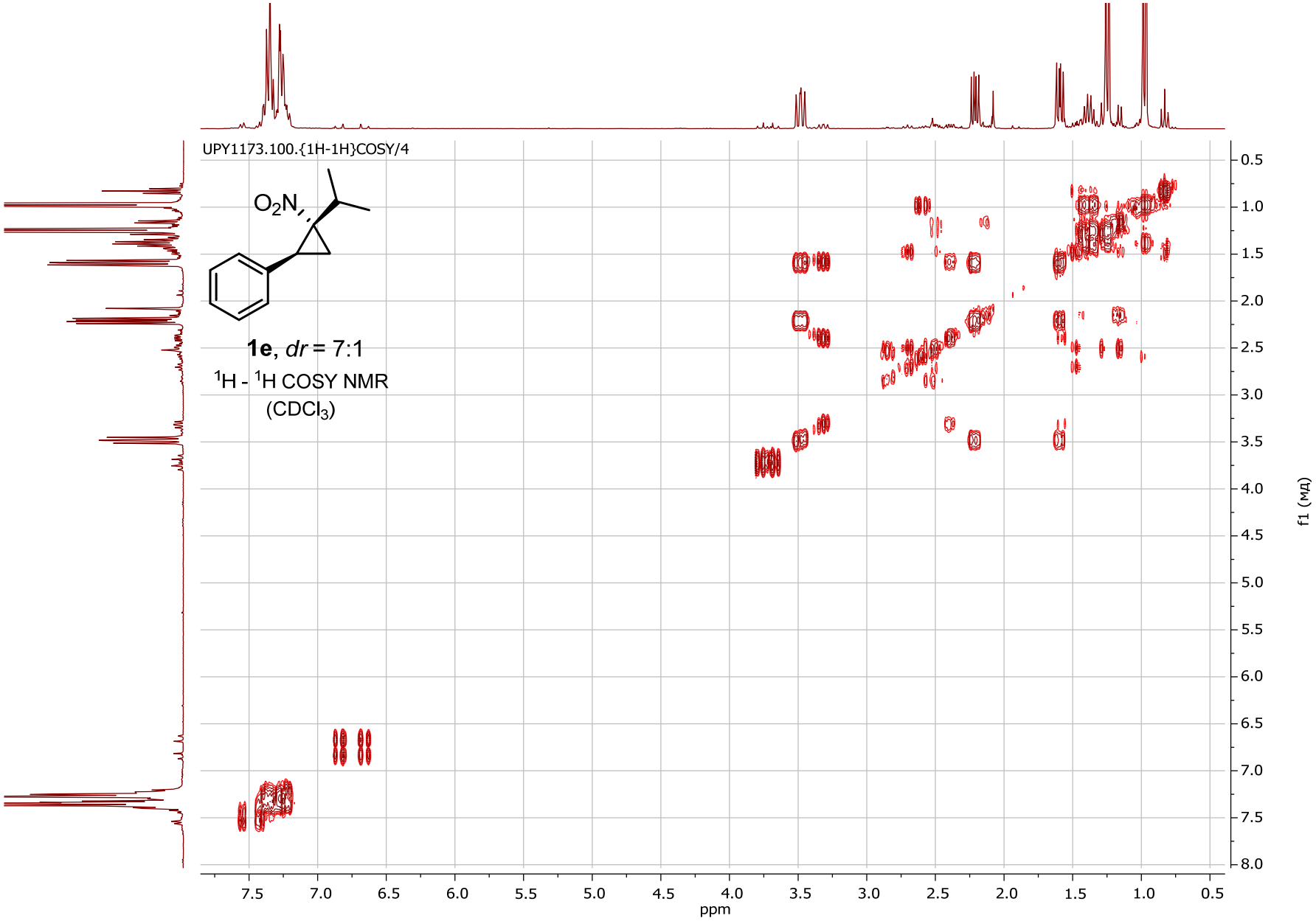
UPY1173.100.{1H}/1



1e, *dr* = 7:1

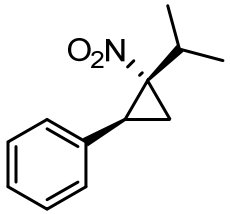
^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **1e**


UPY1173.100.{1H-1H}COSY/4
O2N
1e, dr = 7:1
1H - 1H COSY NMR
(CDCl3)
ppm
f1 (мд)

NMR of **1e**

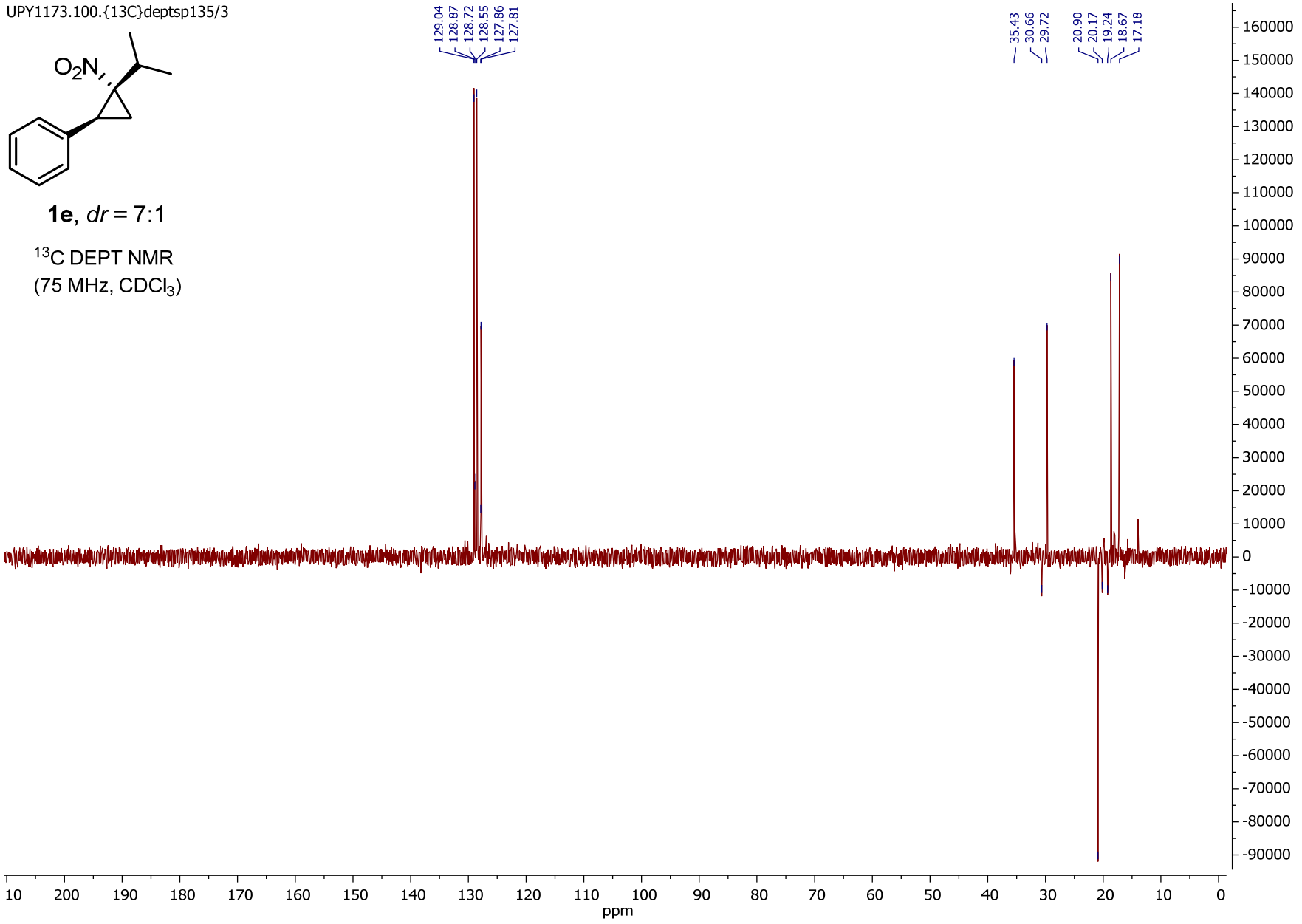
UPY1173.100.{13C}/2



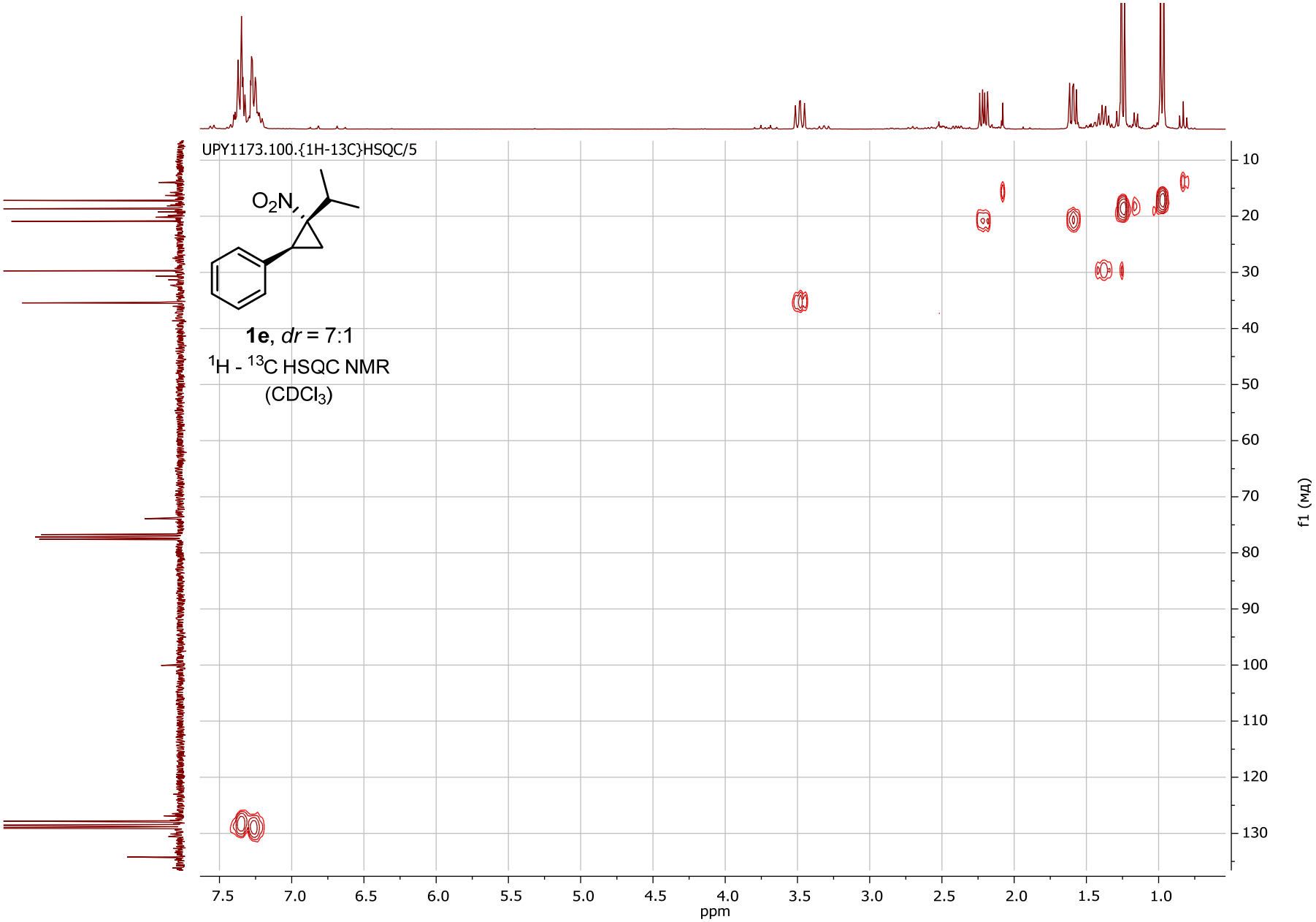
1e, *dr* = 7:1

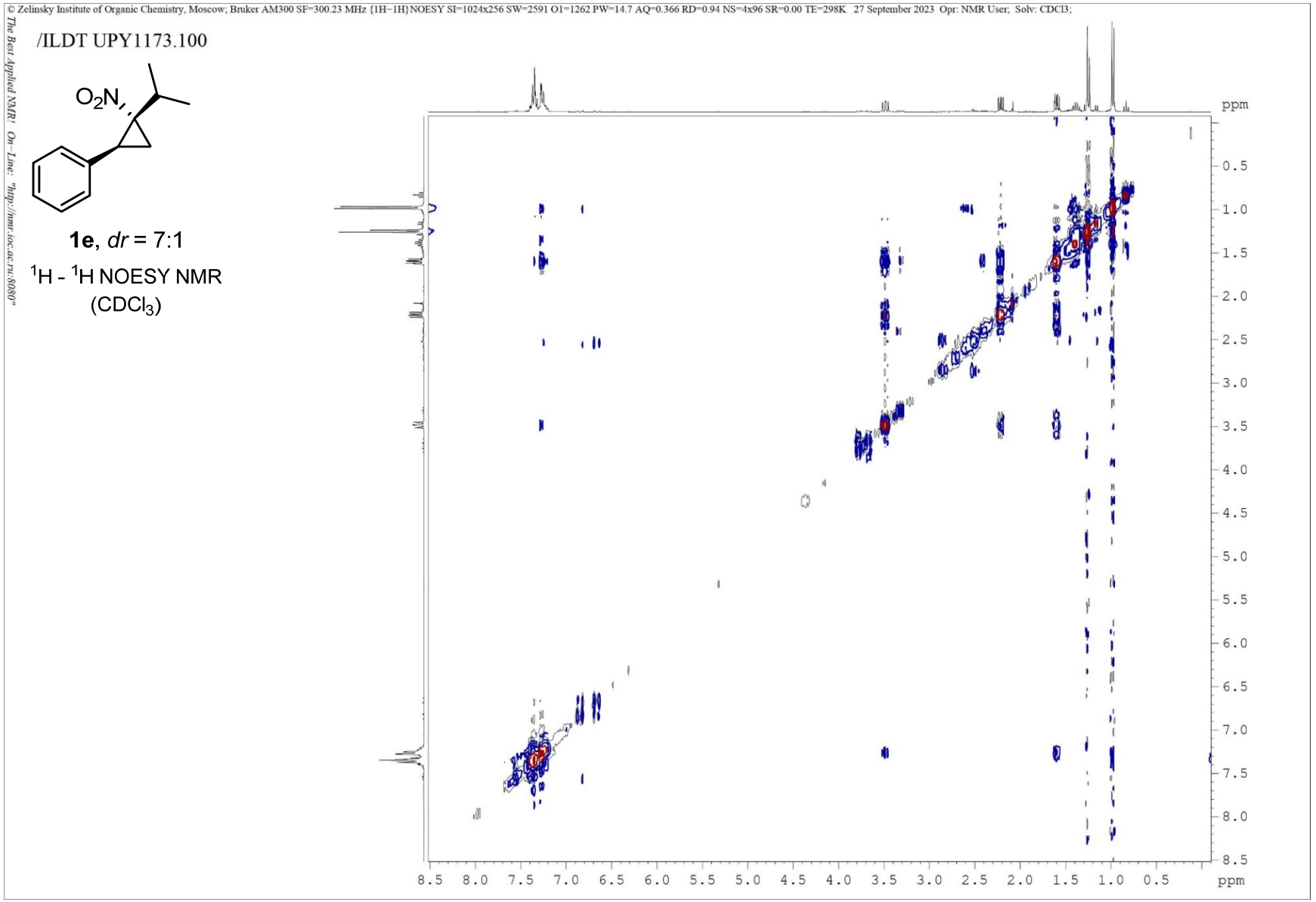
^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **1e**

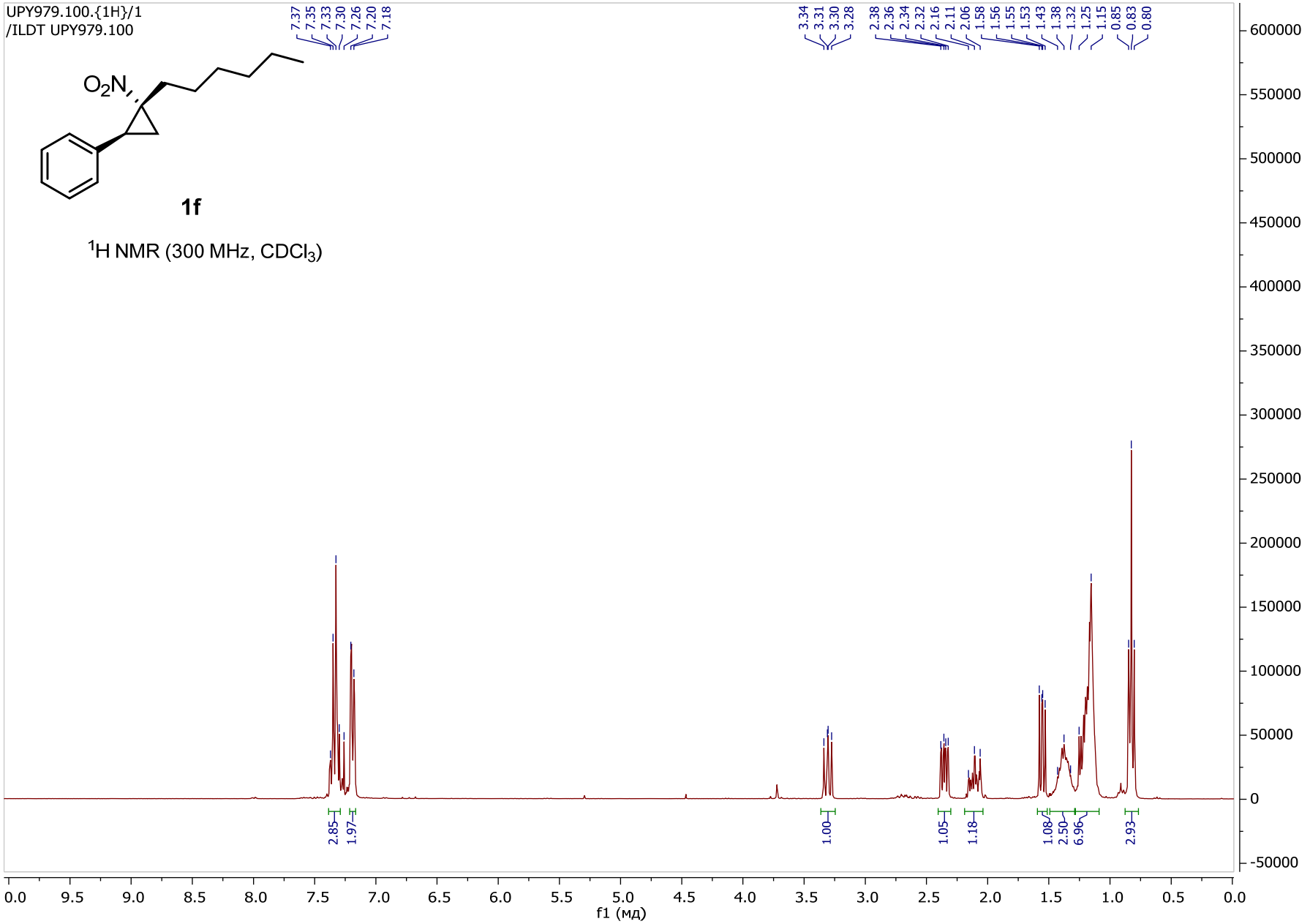

UPY1173.100.{13C}deptsp135/3
O2N
1e, dr = 7:1
13C DEPT NMR
(75 MHz, CDCl3)
129.04
128.87
128.72
128.55
127.86
127.81
35.43
30.66
29.72
20.90
20.17
19.24
18.67
17.18
ppm

NMR of **1e**


UPY1173.100.{1H-13C}HSQC/5
O2N
1e, dr = 7:1
1H - 13C HSQC NMR
(CDCl3)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (мд)

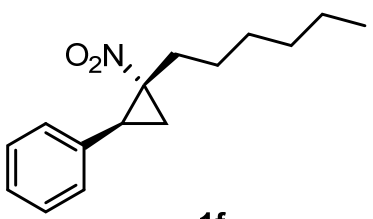

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.23 MHz {1H−1H}NOESY SI=1024x256 SW=2591 O1=1262 PW=14.7 AQ=0.366 RD=0.94 NS=4x96 SR=0.00 TE=298K 27 September 2023 Opr: NMR User; Solv: CDCl3;
The Best Applied NMR! On−Line: "http://nmr.ioc.ac.ru:8080"
/ILDT UPY1173.100
O2N
1e, dr = 7:1
1H - 1H NOESY NMR
(CDCl3)
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

NMR of **1f**


UPY979.100.{1H}/1
/ILDT UPY979.100
7.37
7.35
7.33
7.30
7.26
7.20
7.18
3.34
3.31
3.30
3.28
2.38
2.36
2.34
2.32
2.16
2.11
2.06
1.58
1.56
1.55
1.53
1.43
1.38
1.32
1.25
1.15
0.85
0.83
0.80
O2N
1f
1H NMR (300 MHz, CDCl3)
2.85
1.97
1.00
1.05
1.18
1.08
2.50
6.96
2.93
f1 (мд)

NMR of **1f**

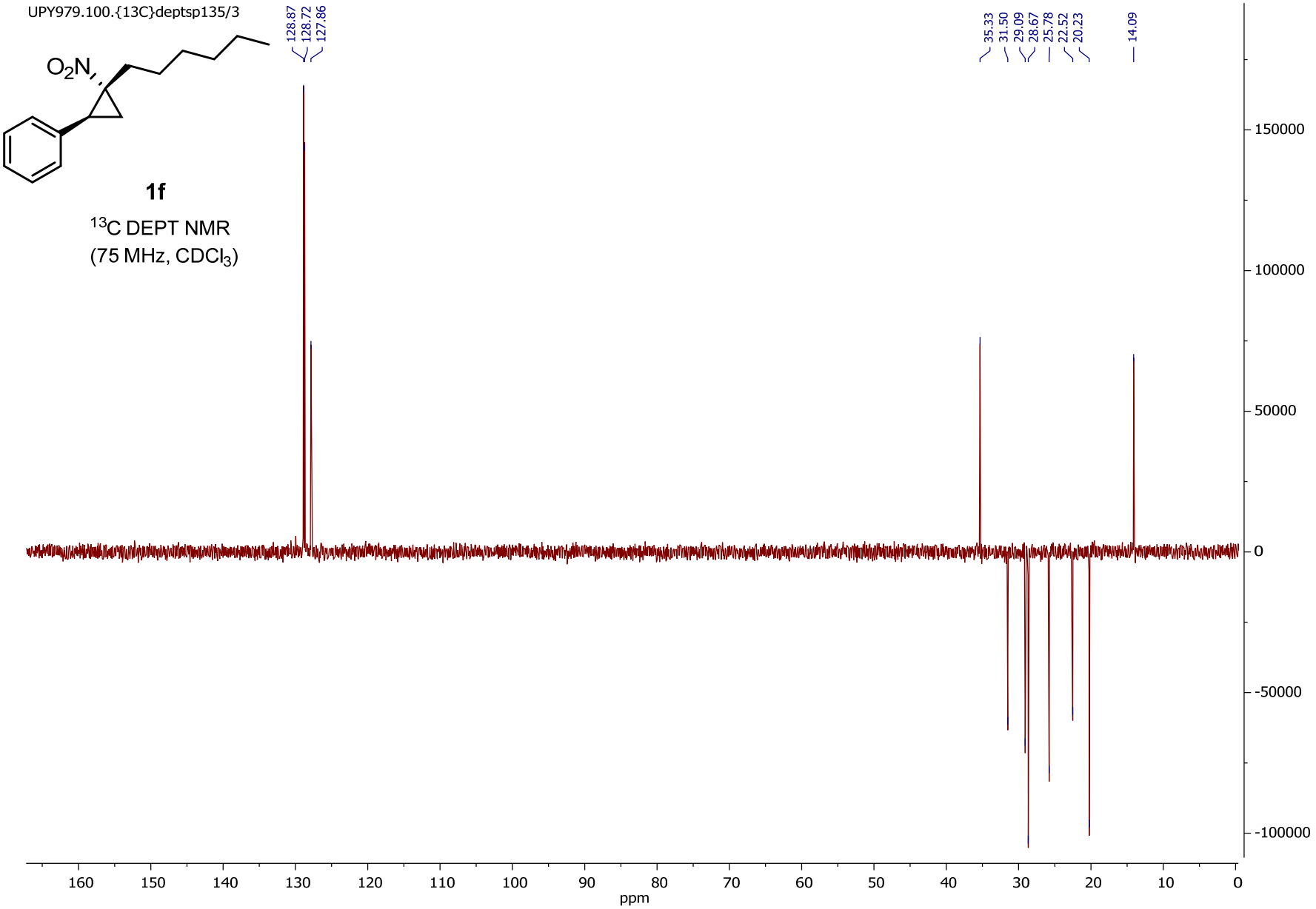
UPY979.100.{13C}/2



1f

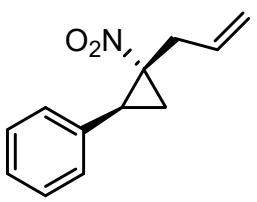
^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **1f**


UPY979.100.{13C}deptsp135/3
128.87
128.72
127.86
35.33
31.50
29.09
28.67
25.78
22.52
20.23
14.09
O_2N
1f
^{13}C DEPT NMR
(75 MHz, $CDCl_3$)
150000
100000
50000
0
-50000
-100000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

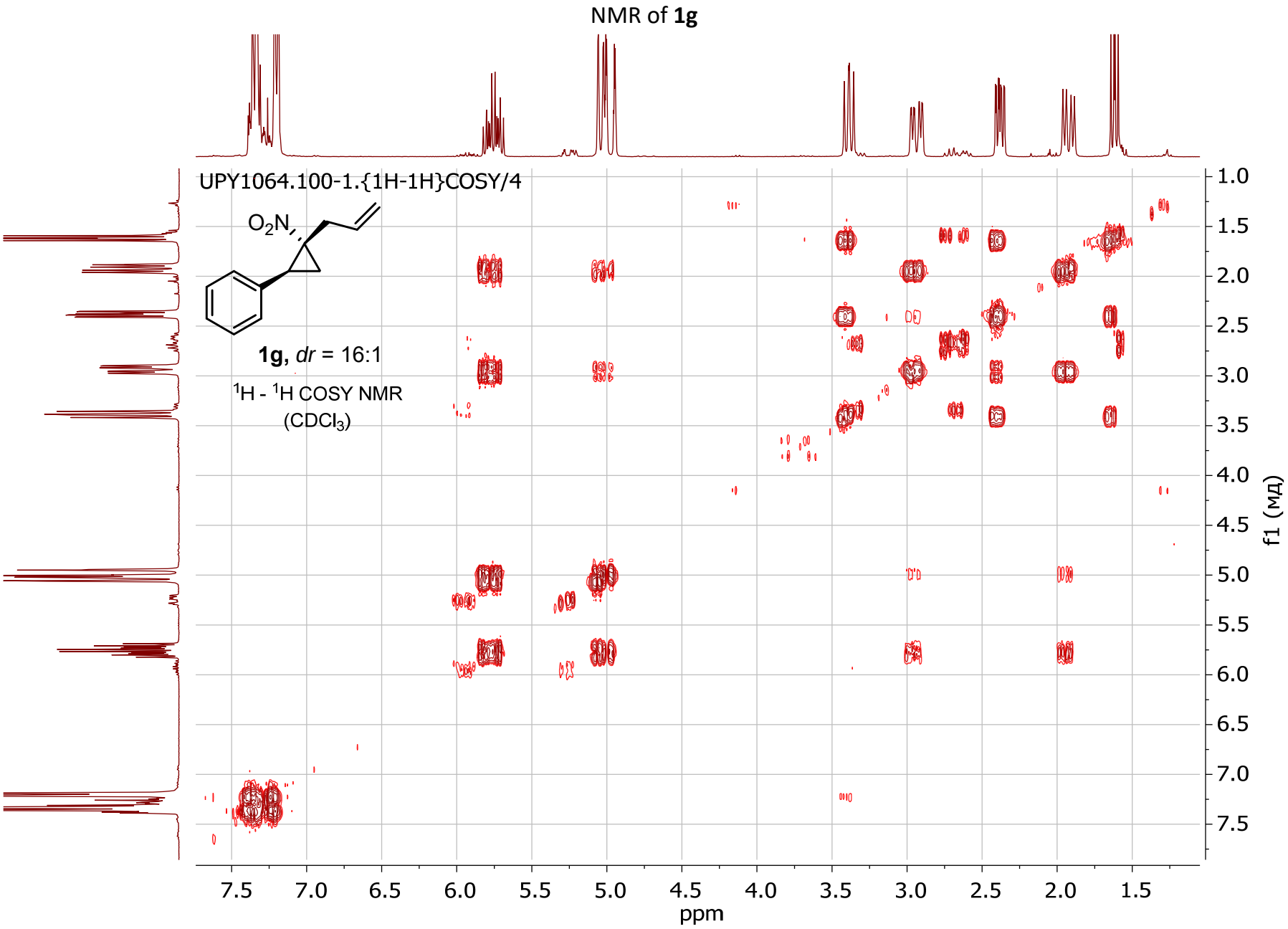
NMR of **1g**

UPY1064.100-1.{1H}/1



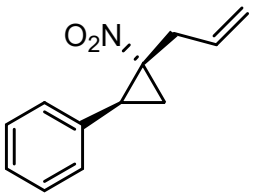
1g, *dr* = 16:1

^{1}H NMR (300 MHz, $CDCl_3$)


NMR of **1g**
UPY1064.100-1.{1H-1H}COSY/4
O_2N
1g, *dr* = 16:1
^1H - ^1H COSY NMR
($CDCl_3$)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
ppm
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5
f1 (мд)

NMR of **1g**

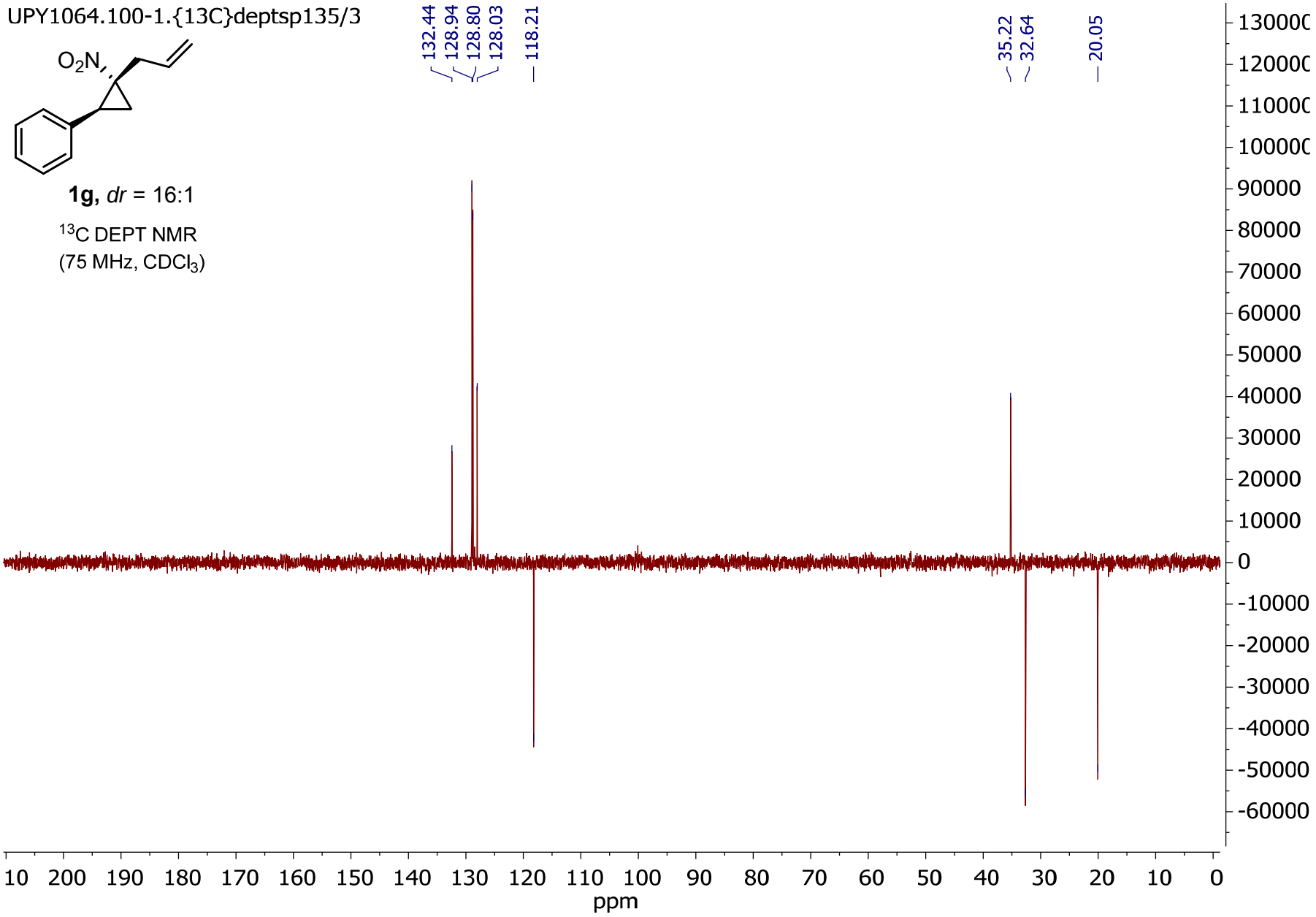
UPY1064.100-1.{13C}/2



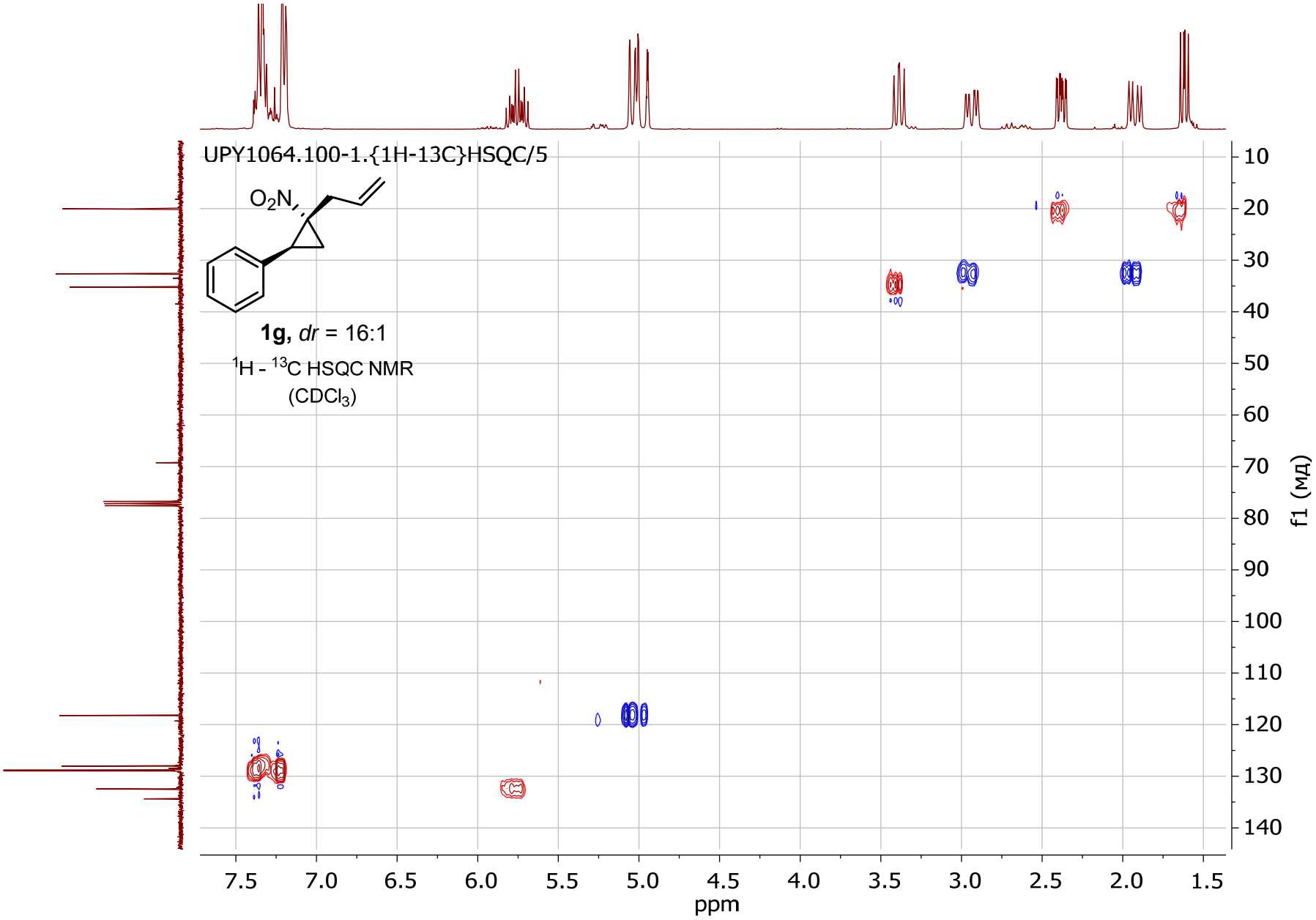
1g, *dr* = 16:1

^{13}C NMR (75 MHz, $CDCl_3$)

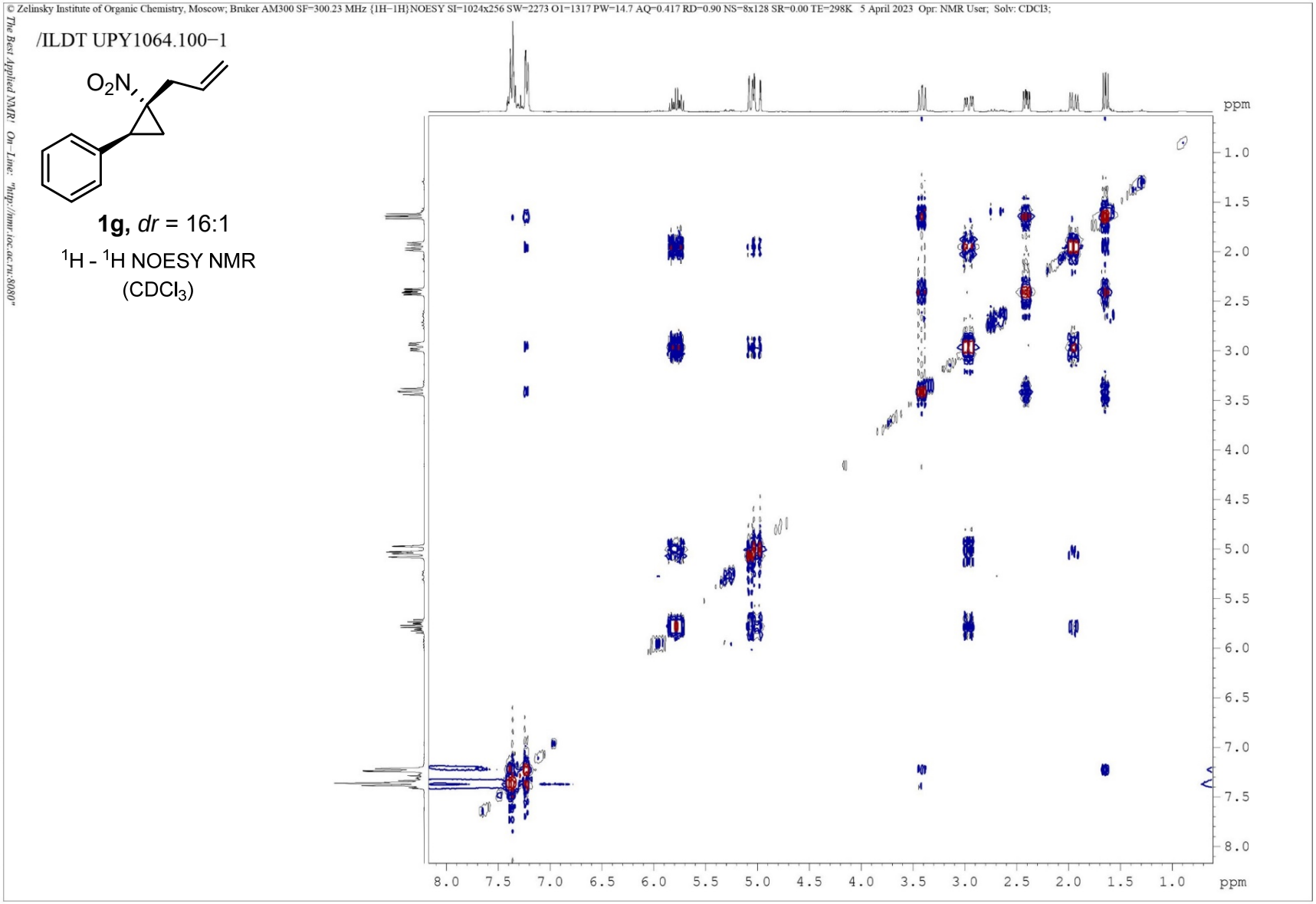
NMR of **1g**


UPY1064.100-1.{13C}deptsp135/3
O2N
1g, dr = 16:1
13C DEPT NMR
(75 MHz, CDCl3)
132.44
128.94
128.80
128.03
118.21
35.22
32.64
20.05
ppm

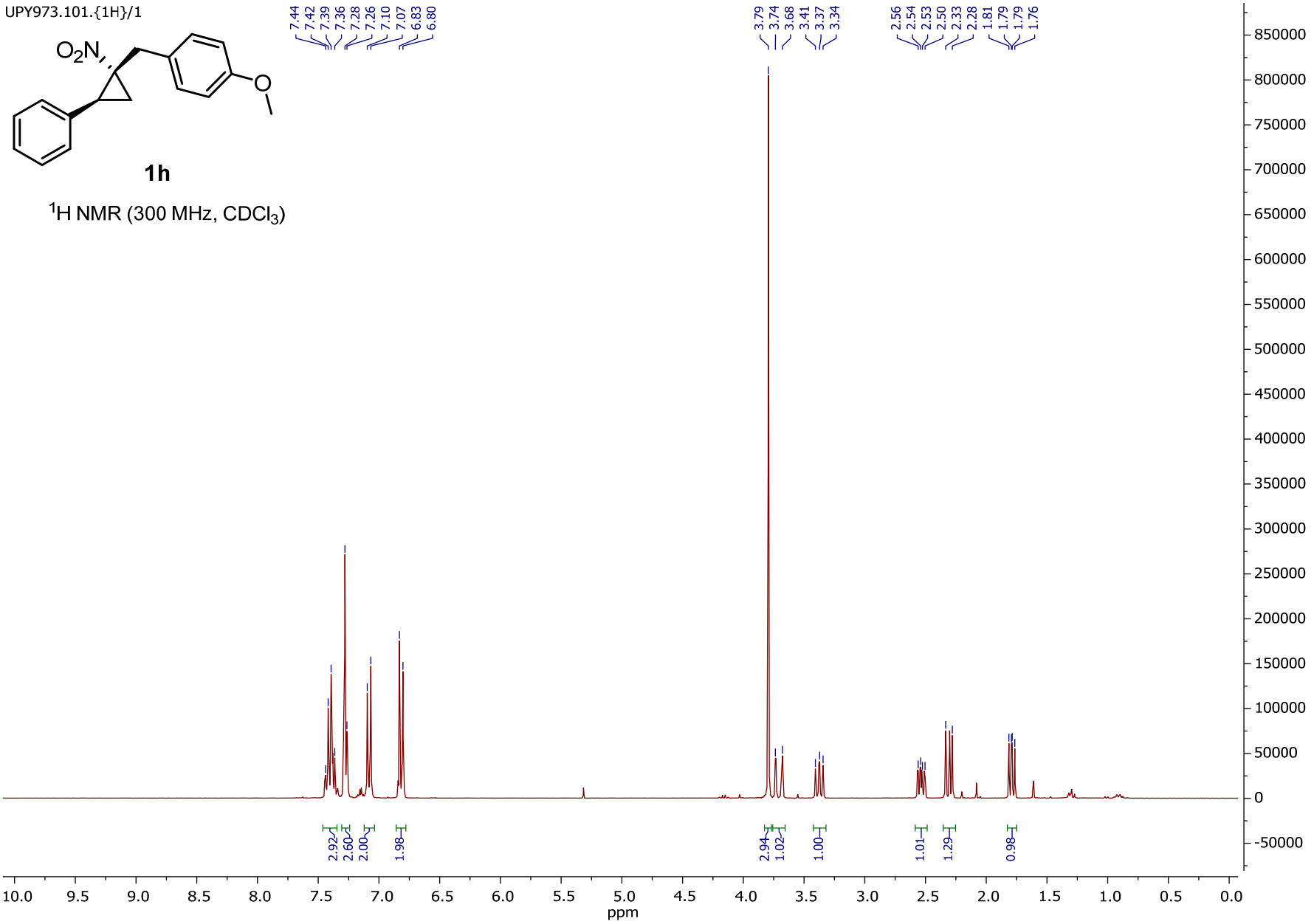
NMR of **1g**


UPY1064.100-1.{1H-13C}HSQC/5
O2N
1g, dr = 16:1
1H - 13C HSQC NMR
(CDCl3)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (м.д)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

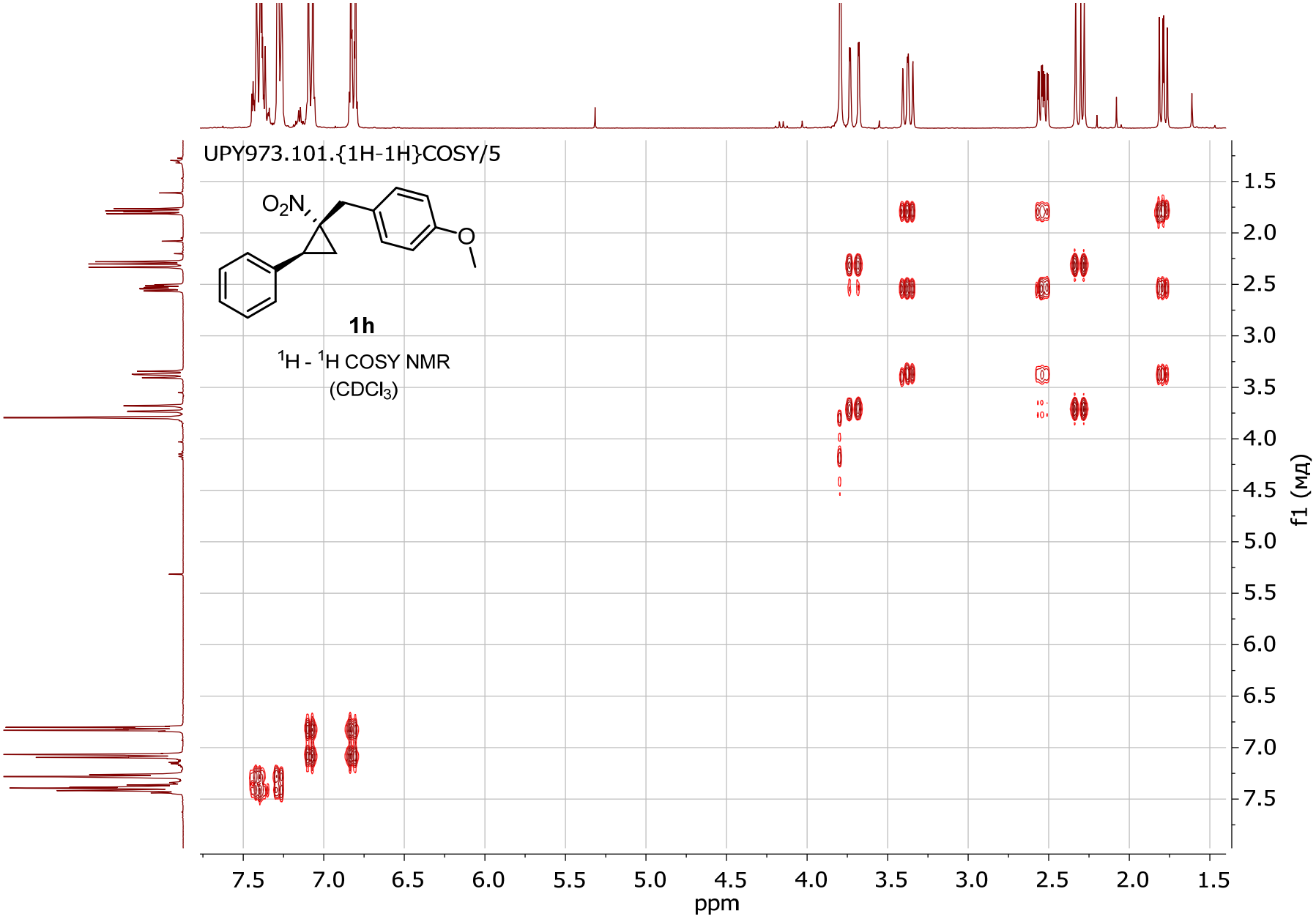
NMR of **1g**


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.23 MHz {1H−1H}NOESY SI=1024x256 SW=2273 O1=1317 PW=14.7 AQ=0.417 RD=0.90 NS=8x128 SR=0.00 TE=298K 5 April 2023 Opr: NMR User; Solv: CDCl3;
The Best Applied NMR' On−Line: "http://nmr.ioc.ac.ru:8080"
/ILDT UPY1064.100−1
O2N
1g, dr = 16:1
1H - 1H NOESY NMR
(CDCl3)
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

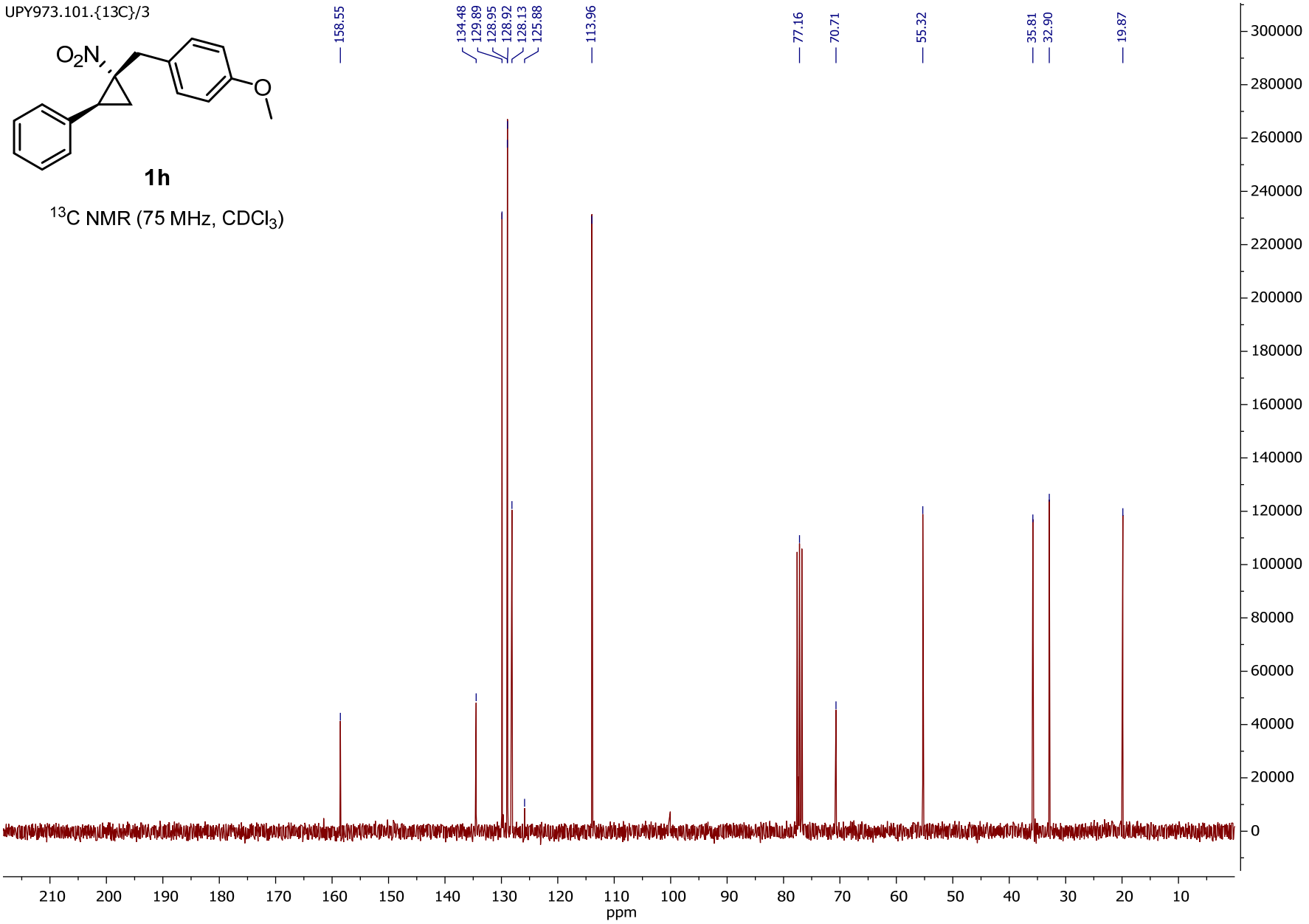
NMR of **1h**


UPY973.101.{1H}/1
O2N
O
1h
1H NMR (300 MHz, CDCl3)
7.44
7.42
7.39
7.36
7.28
7.26
7.10
7.07
6.83
6.80
3.79
3.74
3.68
3.41
3.37
3.34
2.56
2.54
2.53
2.50
2.33
2.28
1.81
1.79
1.79
1.76
2.92
2.60
2.00
1.98
2.94
1.02
1.00
1.01
1.29
0.98
ppm

NMR of **1h**


UPY973.101.{1H-1H}COSY/5
O2N
O
1h
1H - 1H COSY NMR
(CDCl3)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
f1 (мд)

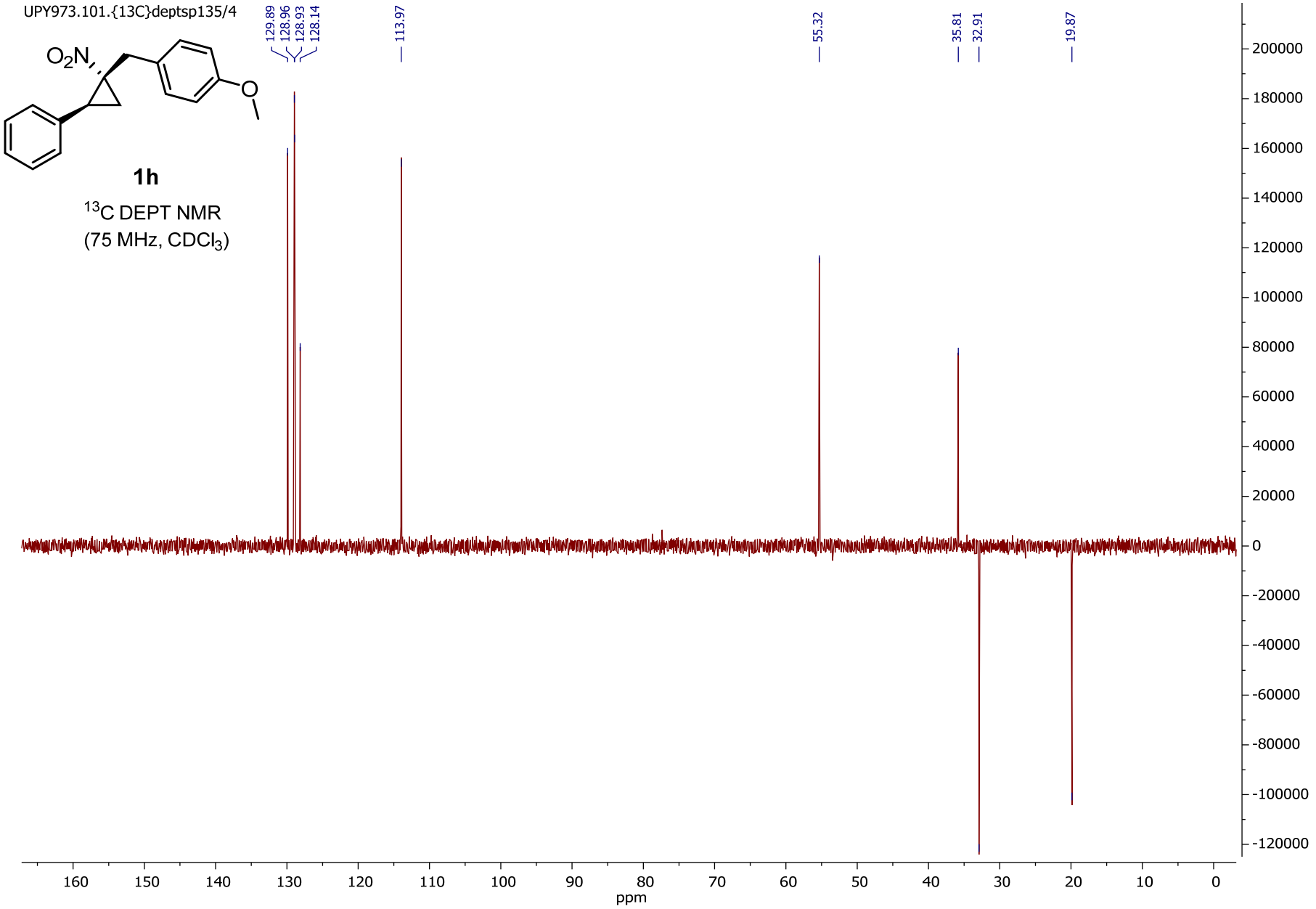
NMR of **1h**



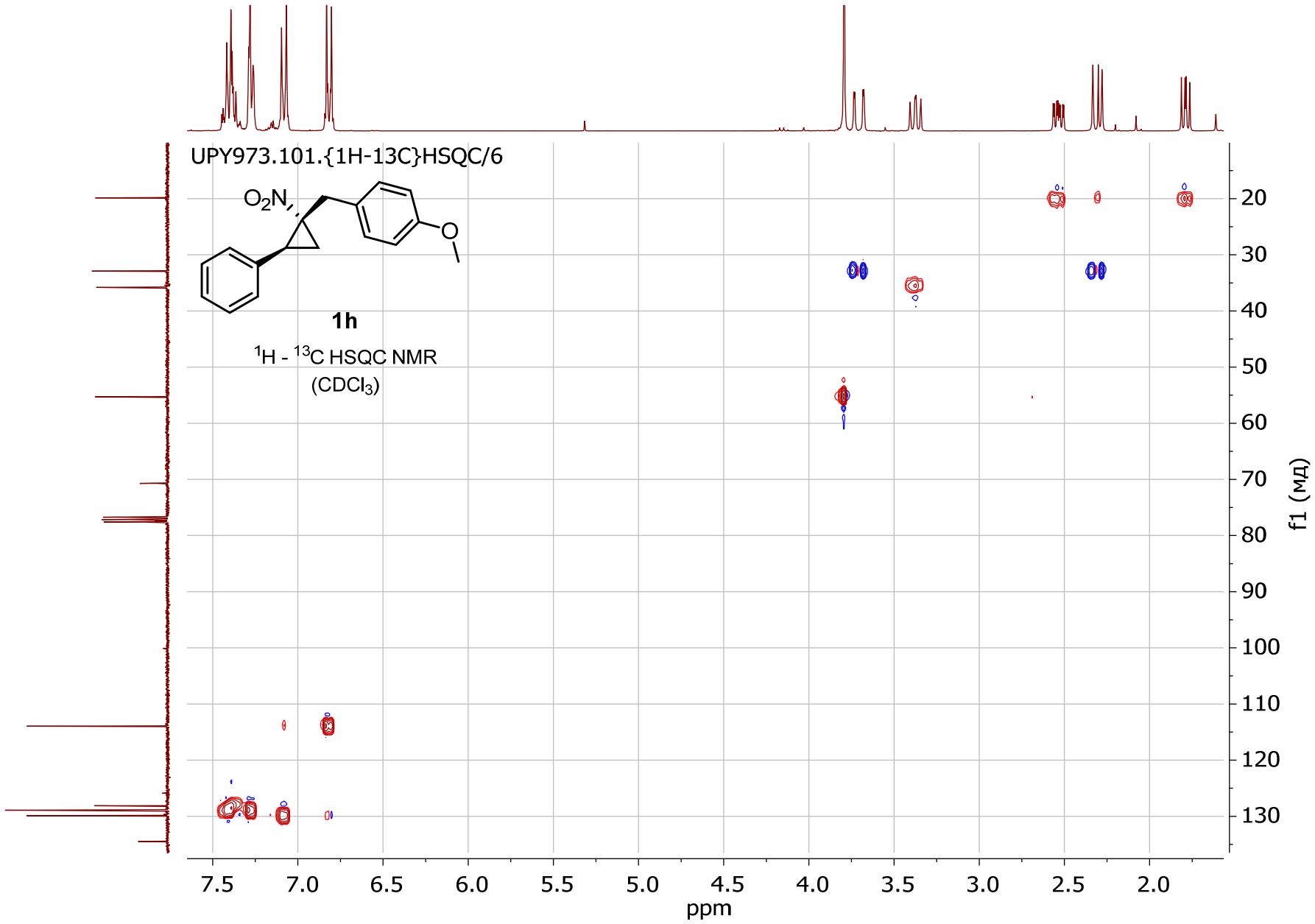
1h

^{13}C NMR (75 MHz, $CDCl_3$)

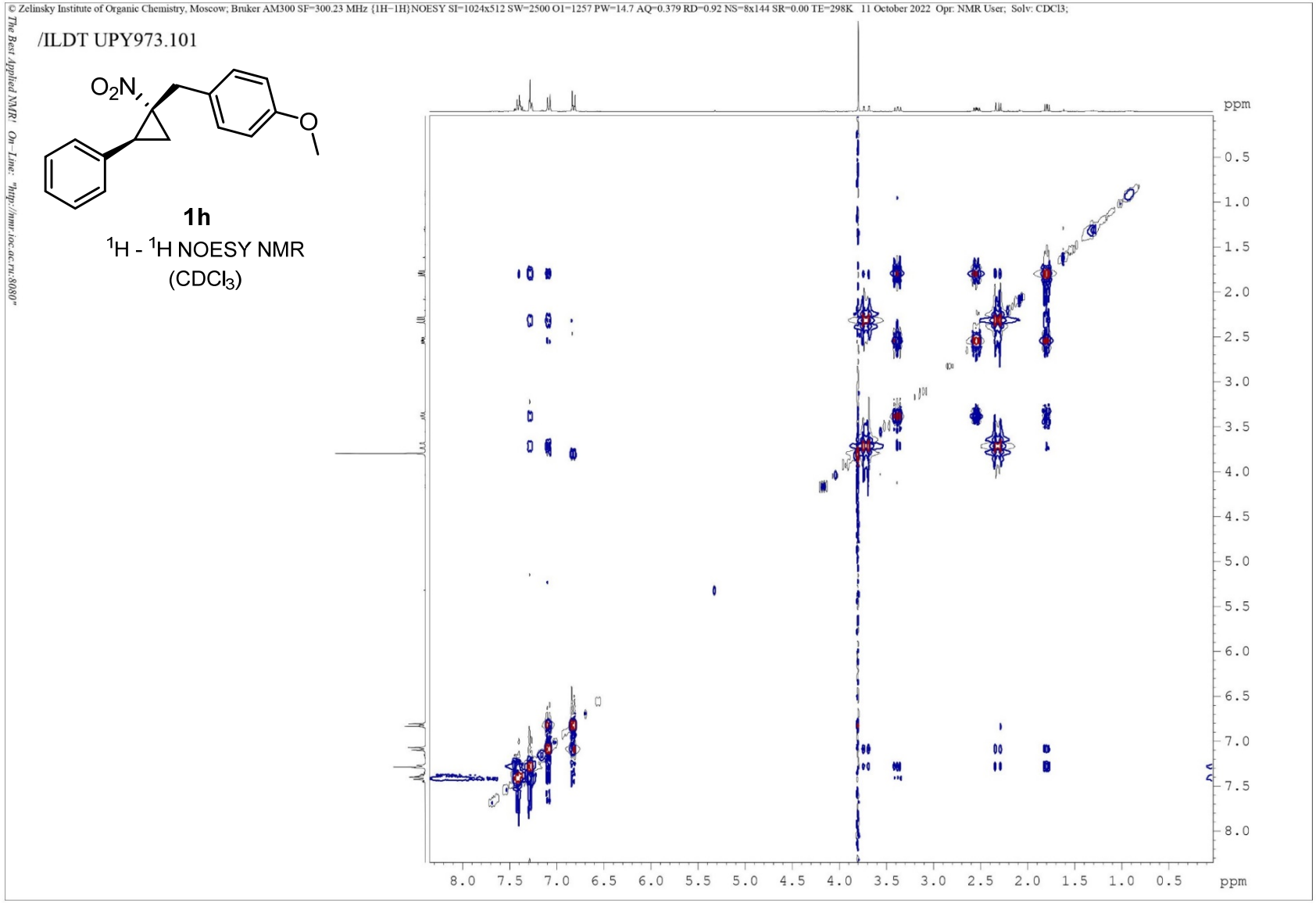
NMR of **1h**


UPY973.101.{13C}deptsp135/4
129.89
128.96
128.93
128.14
113.97
55.32
35.81
32.91
19.87
O2N
O
1h
13C DEPT NMR
(75 MHz, CDCl3)
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
-60000
-80000
-100000
-120000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

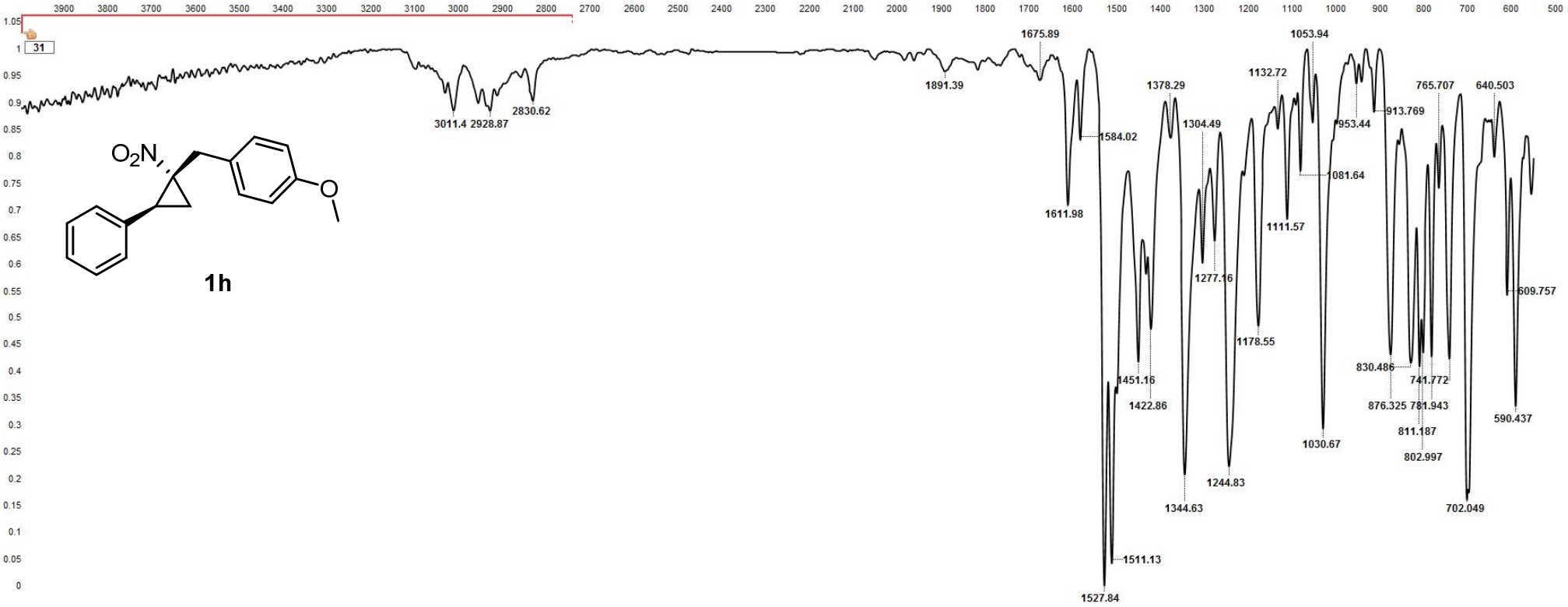
NMR of **1h**


UPY973.101.{1H-13C}HSQC/6
O2N
O
1h
1H - 13C HSQC NMR
(CDCl3)
20
30
40
50
60
70
80
90
100
110
120
130
f1 (мд)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

NMR of **1h**

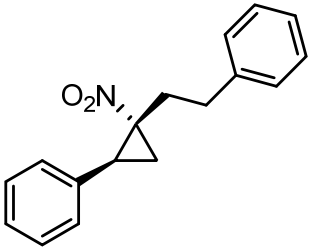

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.23 MHz {1H−1H}NOESY SI=1024x512 SW=2500 O1=1257 PW=14.7 AQ=0.379 RD=0.92 NS=8x144 SR=0.00 TE=298K 11 October 2022 Opr: NMR User; Solv: CDCl3;
The Best Applied NMR! On−Line: "http://nmr.ioc.ac.ru:8080"
/ILDT UPY973.101
O2N
O
1h
1H - 1H NOESY NMR
(CDCl3)
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

FTIR (ATR) of **1h**



NMR of **1i**

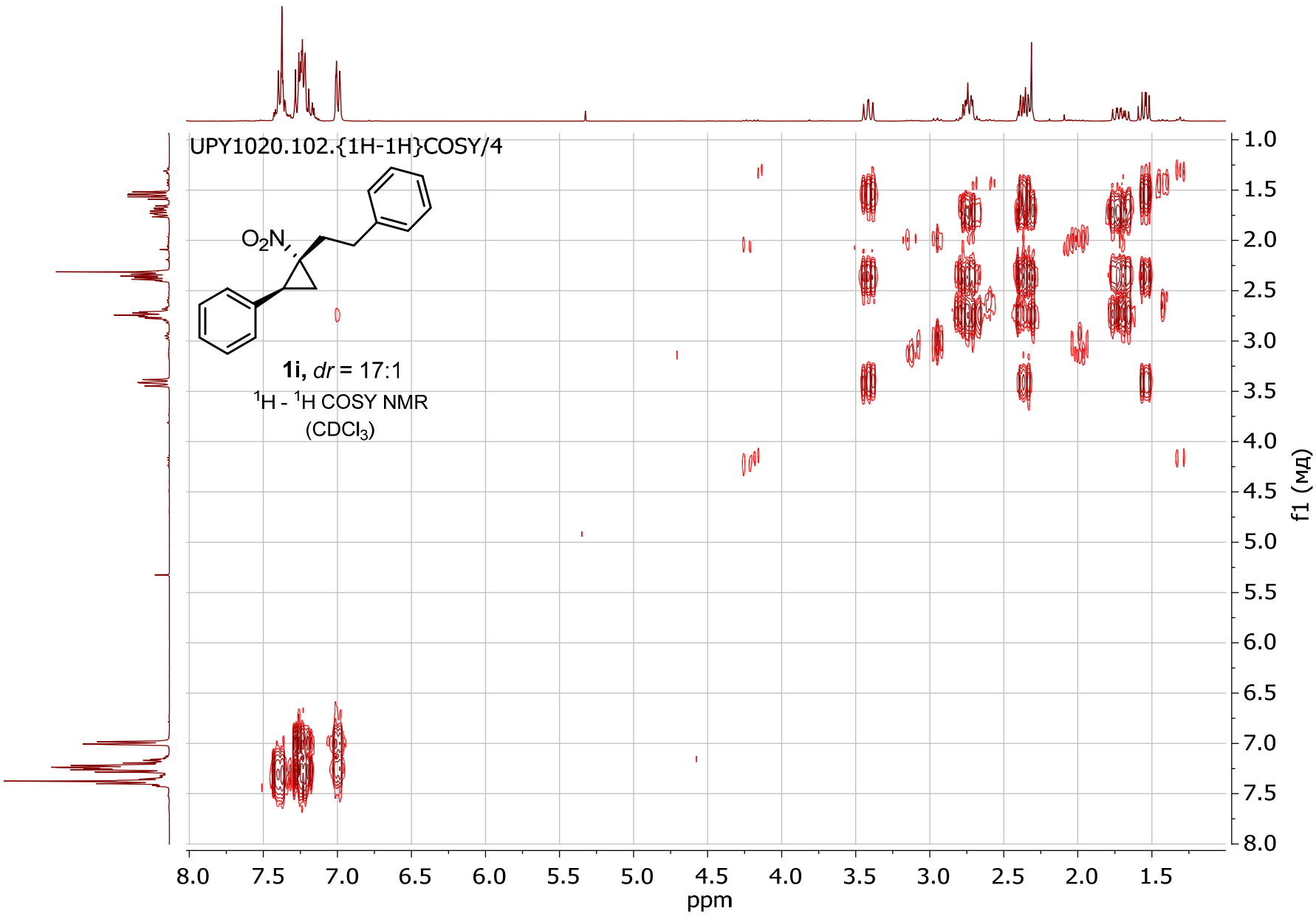
UPY1020.102.{1H}/1



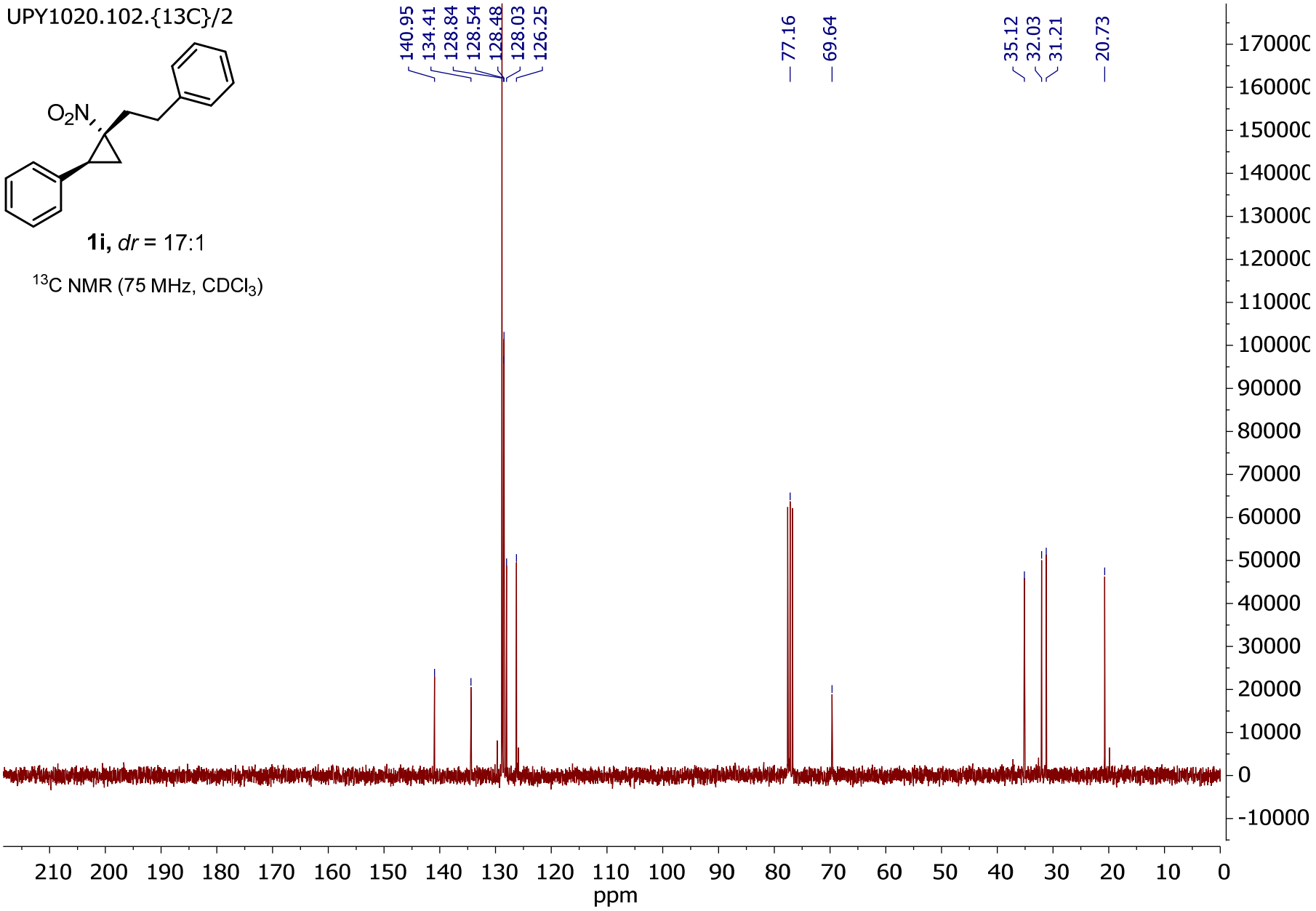
1i, *dr* = 17:1

^{1}H NMR (300 MHz, $CDCl_3$)

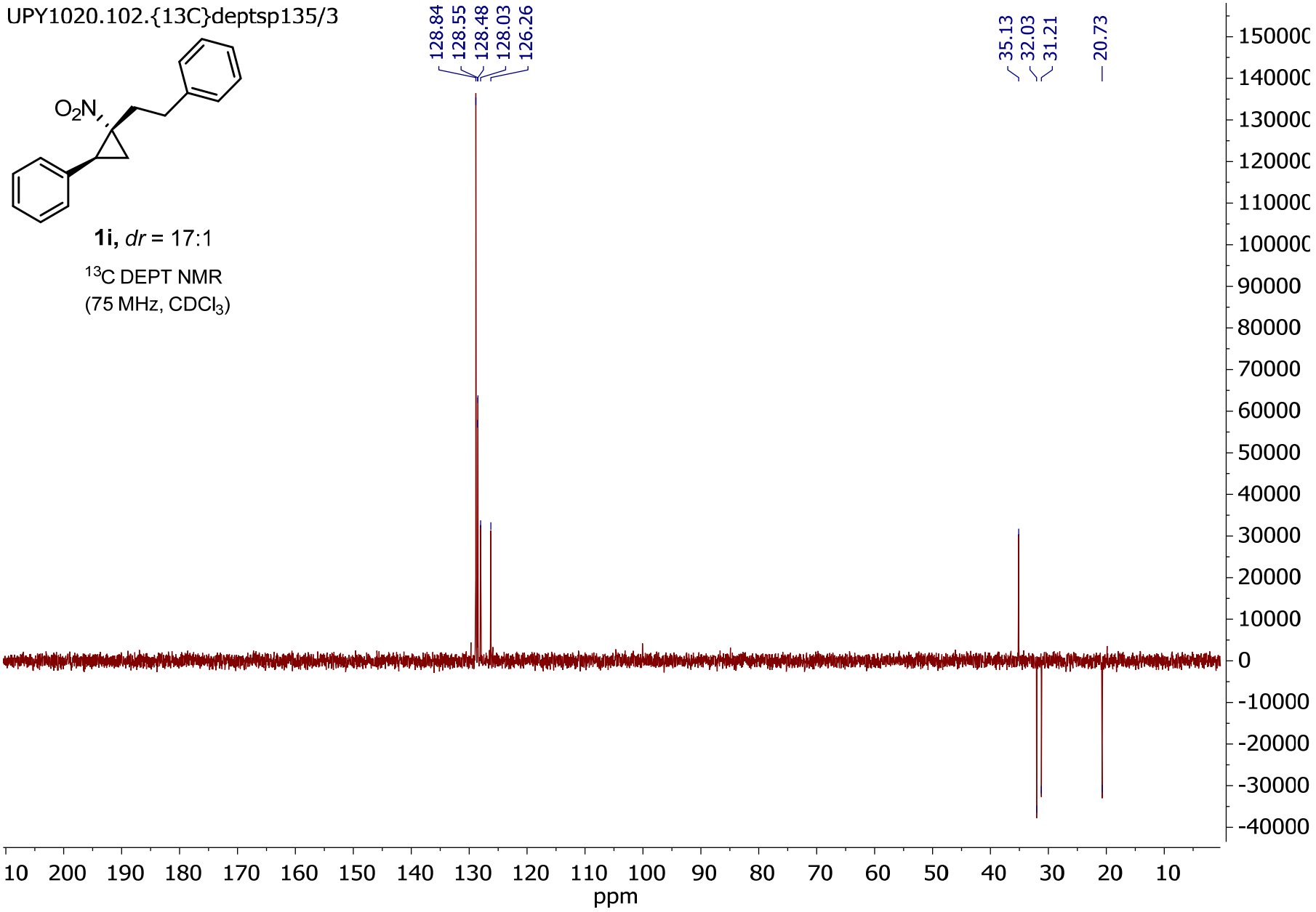
NMR of **1i**


UPY1020.102.{1H-1H}COSY/4
O2N
1i, dr = 17:1
1H - 1H COSY NMR
(CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (мд)

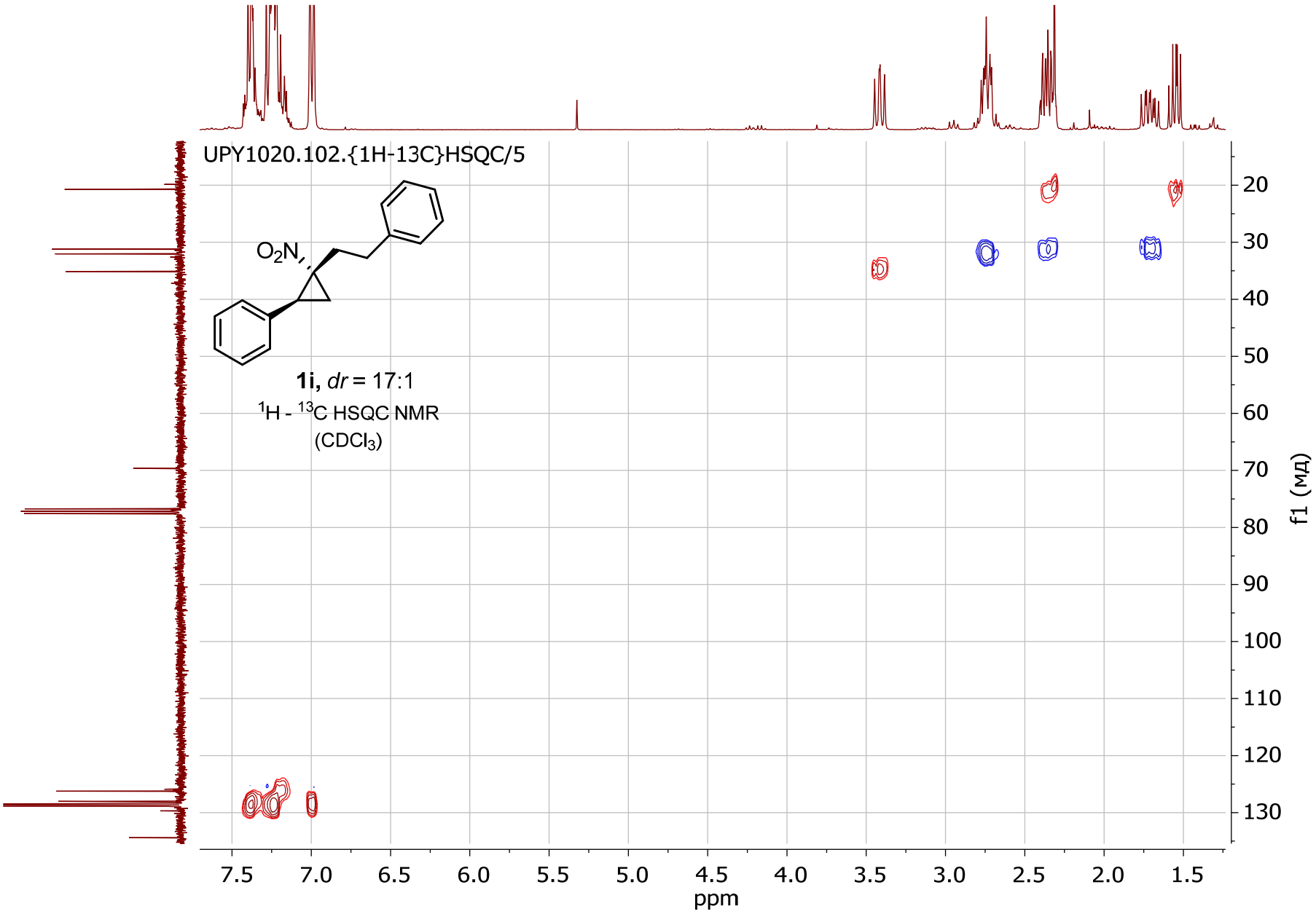
NMR of **1i**


UPY1020.102.{13C}/2
O2N
1i, dr = 17:1
13C NMR (75 MHz, CDCl3)
140.95
134.41
128.84
128.54
128.48
128.03
126.25
77.16
69.64
35.12
32.03
31.21
20.73
ppm

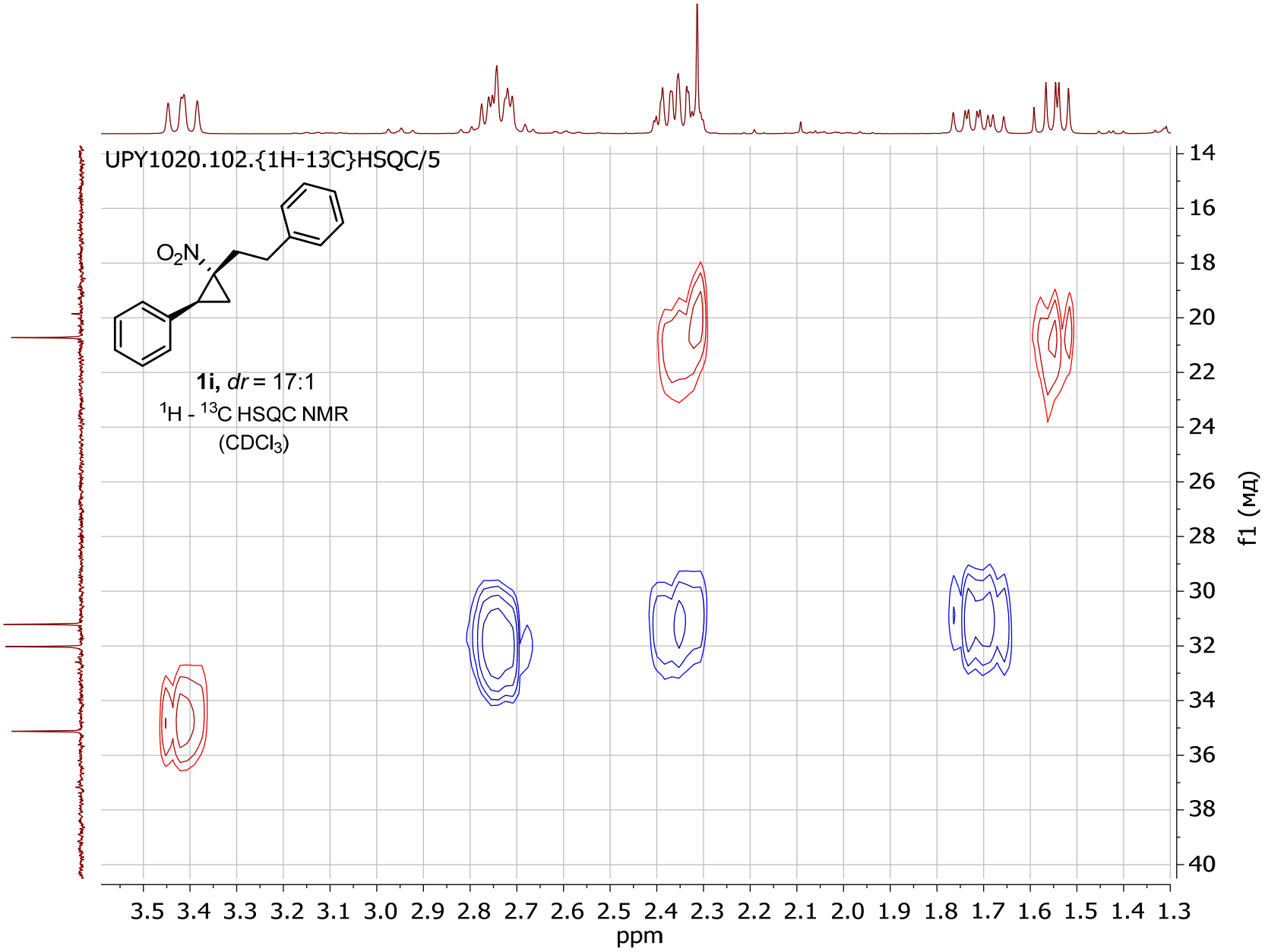
NMR of **1i**


UPY1020.102.{13C}deptsp135/3
O2N
1i, dr = 17:1
13C DEPT NMR
(75 MHz, CDCl3)
128.84
128.55
128.48
128.03
126.26
35.13
32.03
31.21
20.73
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

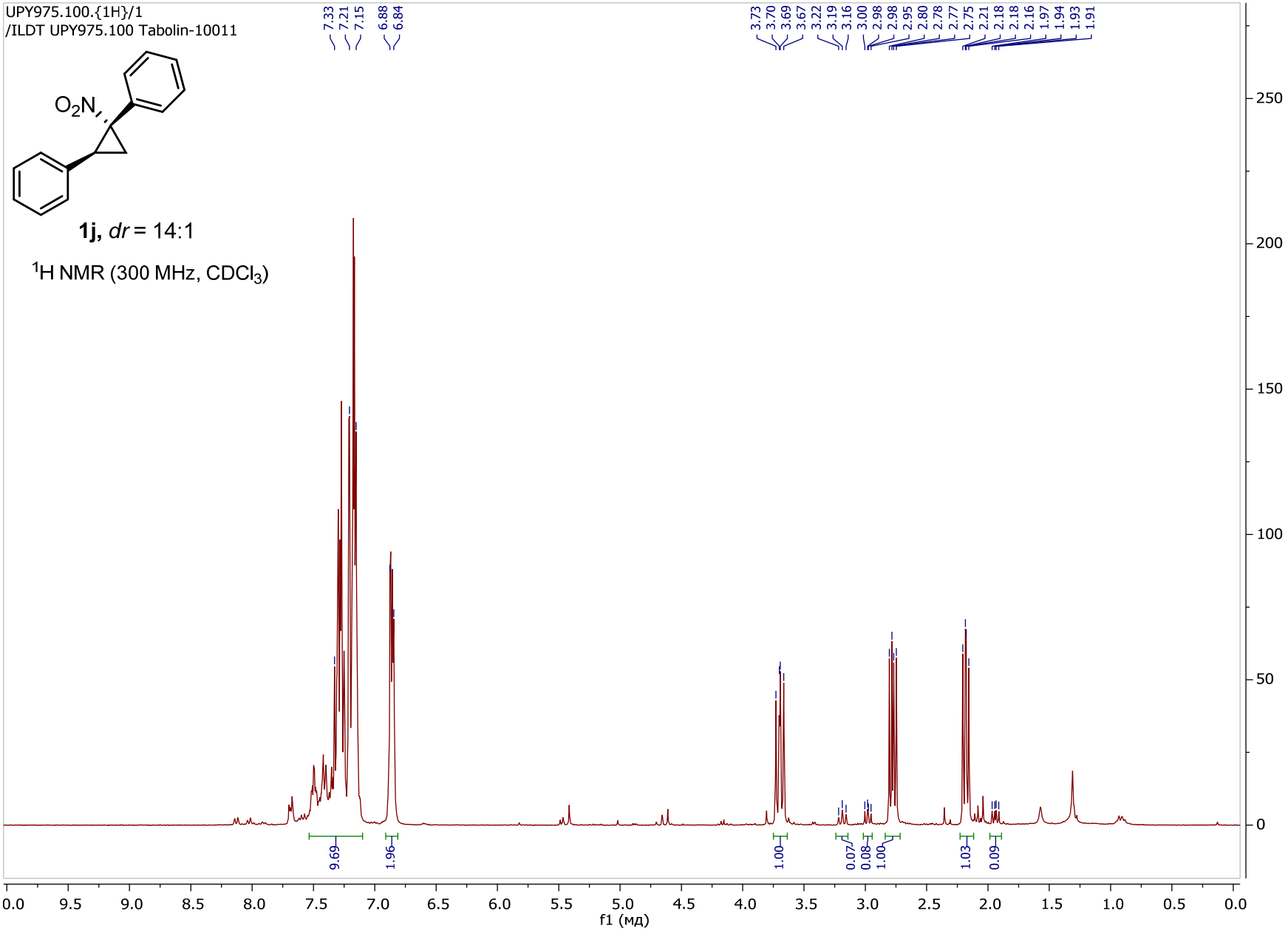
NMR of **1i**


UPY1020.102.{1H-13C}HSQC/5
O2N
1i, dr = 17:1
1H - 13C HSQC NMR
(CDCl3)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
20
30
40
50
60
70
80
90
100
110
120
130
f1 (мд)

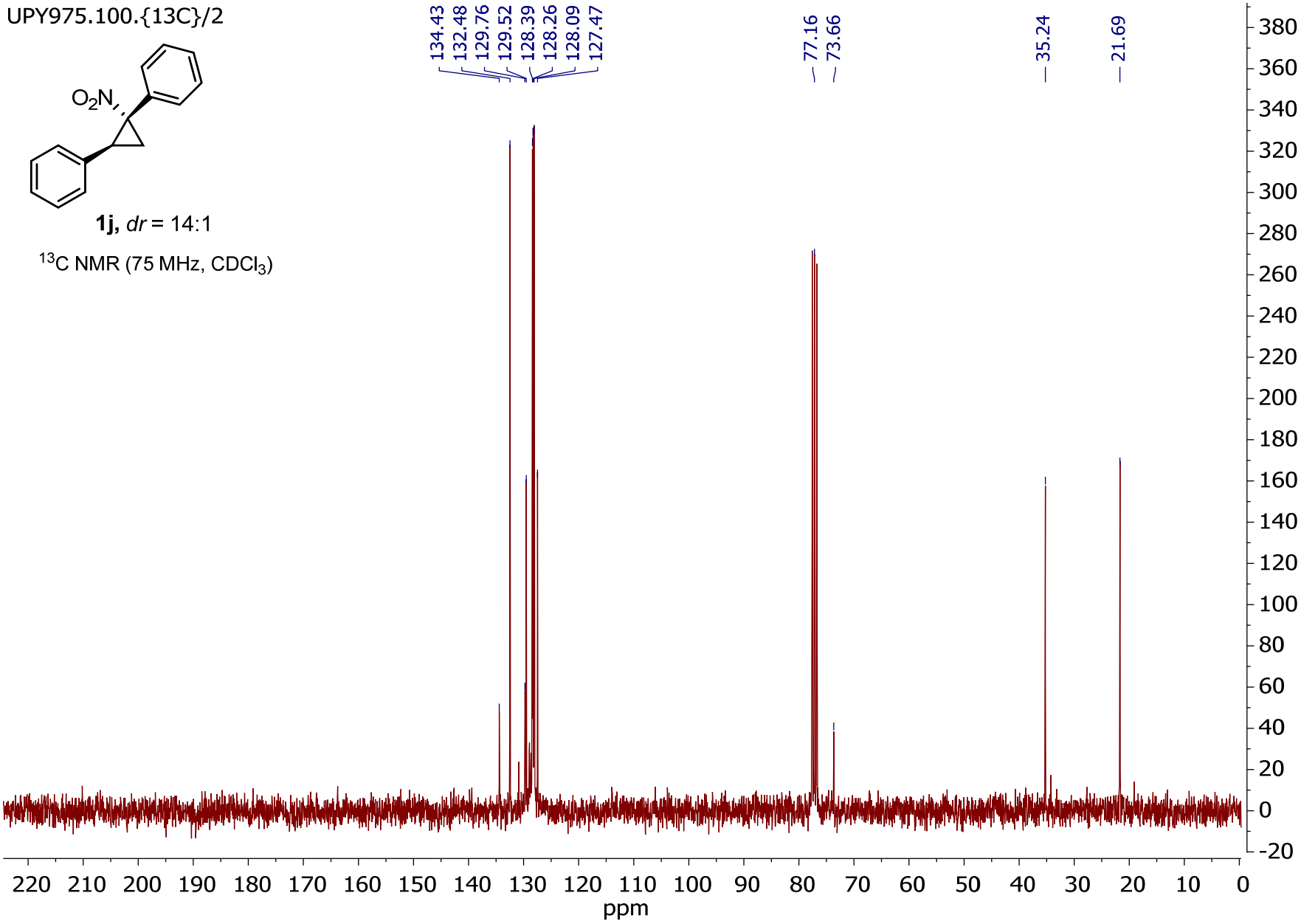
NMR of **1i**


UPY1020.102.{1H-13C}HSQC/5
O2N
1i, dr = 17:1
1H - 13C HSQC NMR
(CDCl3)
f1 (мд)
ppm

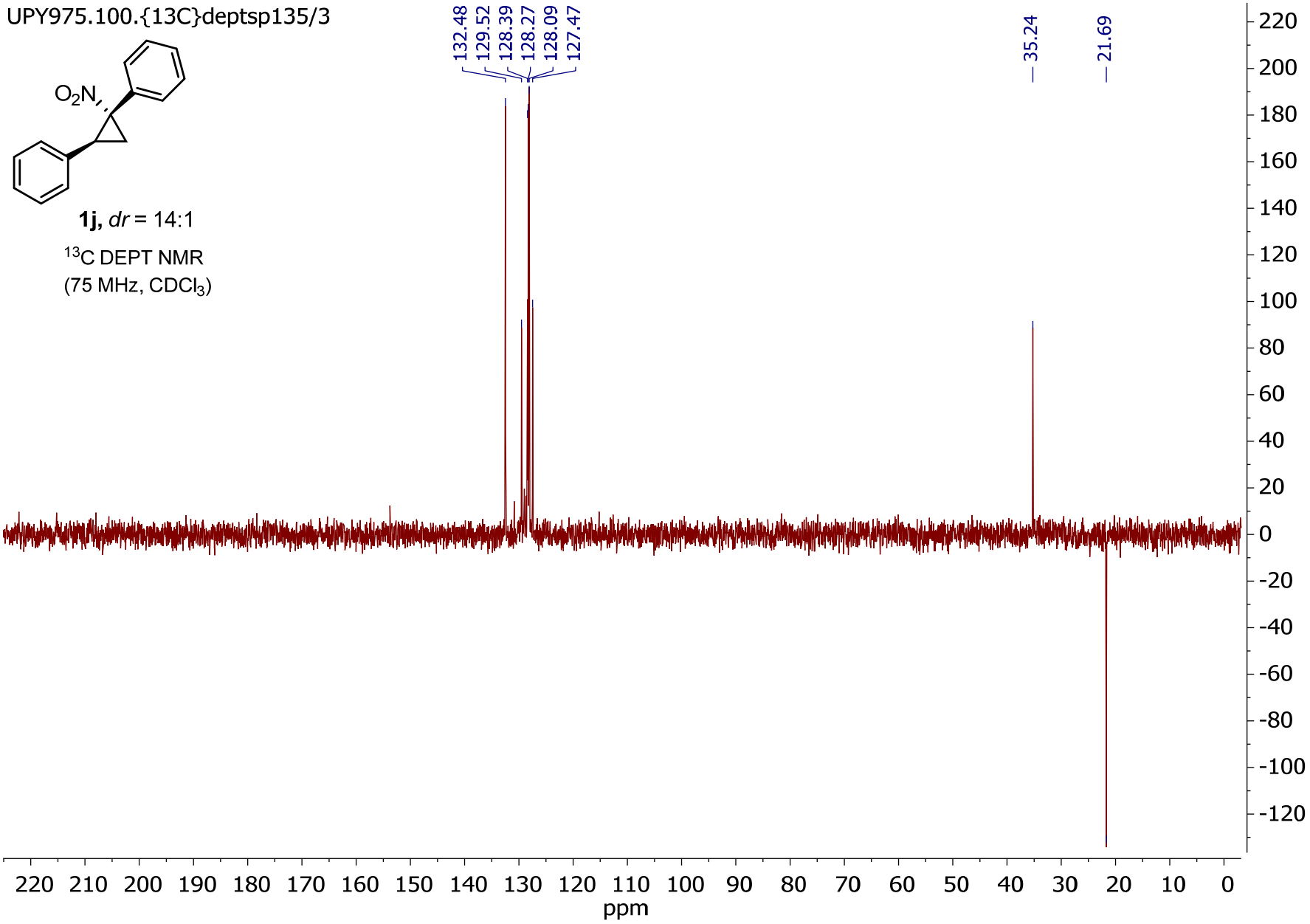
NMR of **1j**


UPY975.100.{1H}/1
/ILDT UPY975.100 Tabolin-10011
7.33
7.21
7.15
6.88
6.84
3.73
3.70
3.69
3.67
3.22
3.19
3.16
3.00
2.98
2.98
2.95
2.80
2.78
2.77
2.75
2.21
2.18
2.18
2.16
1.97
1.94
1.93
1.91
O2N
1j, dr = 14:1
1H NMR (300 MHz, CDCl3)
9.69
1.96
1.00
0.07
0.08
1.00
1.03
0.09
250
200
150
100
50
0
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (мд)

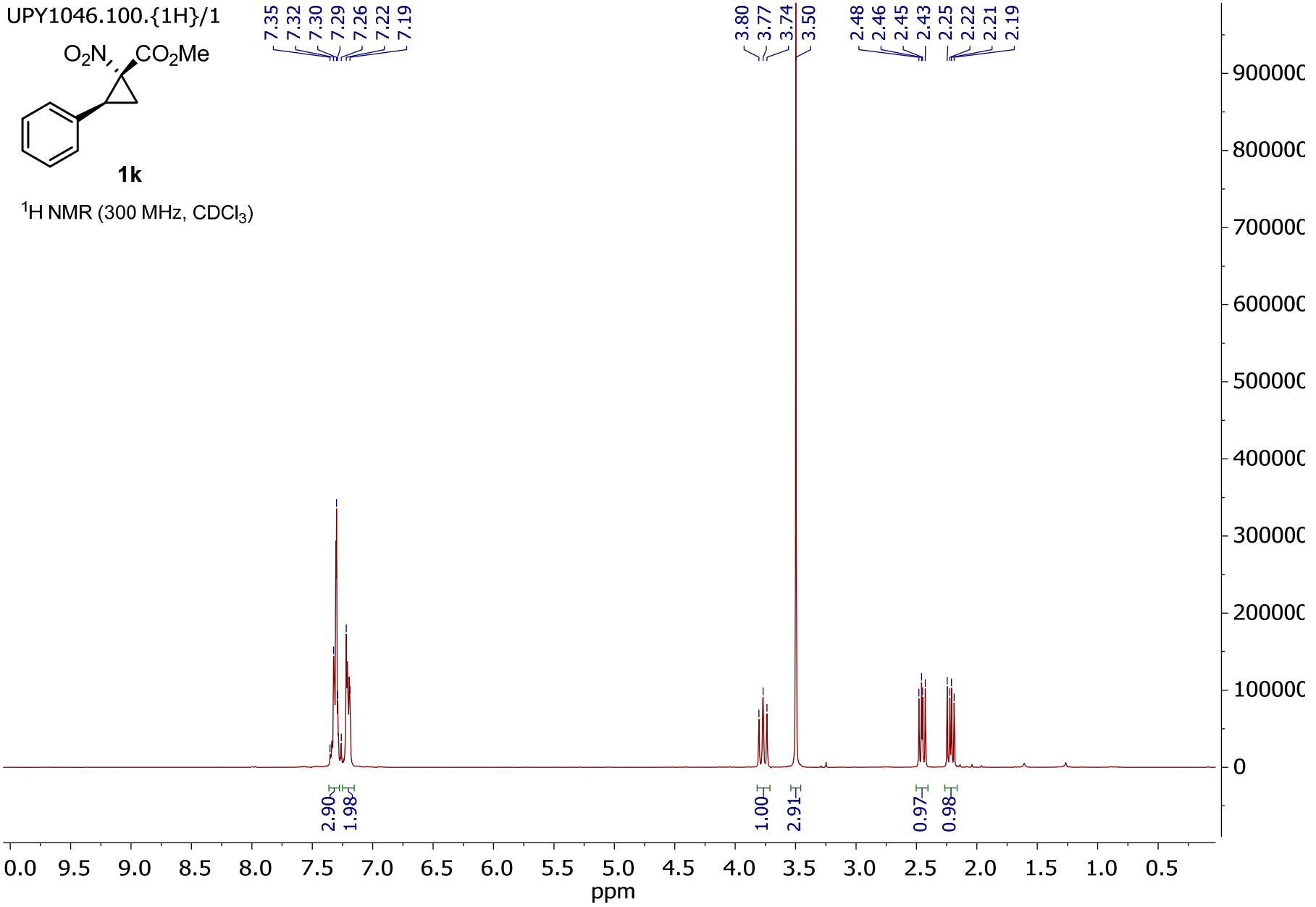
NMR of **1j**


UPY975.100.{13C}/2
O2N
1j, dr = 14:1
13C NMR (75 MHz, CDCl3)
134.43
132.48
129.76
129.52
128.39
128.26
128.09
127.47
77.16
73.66
35.24
21.69
ppm

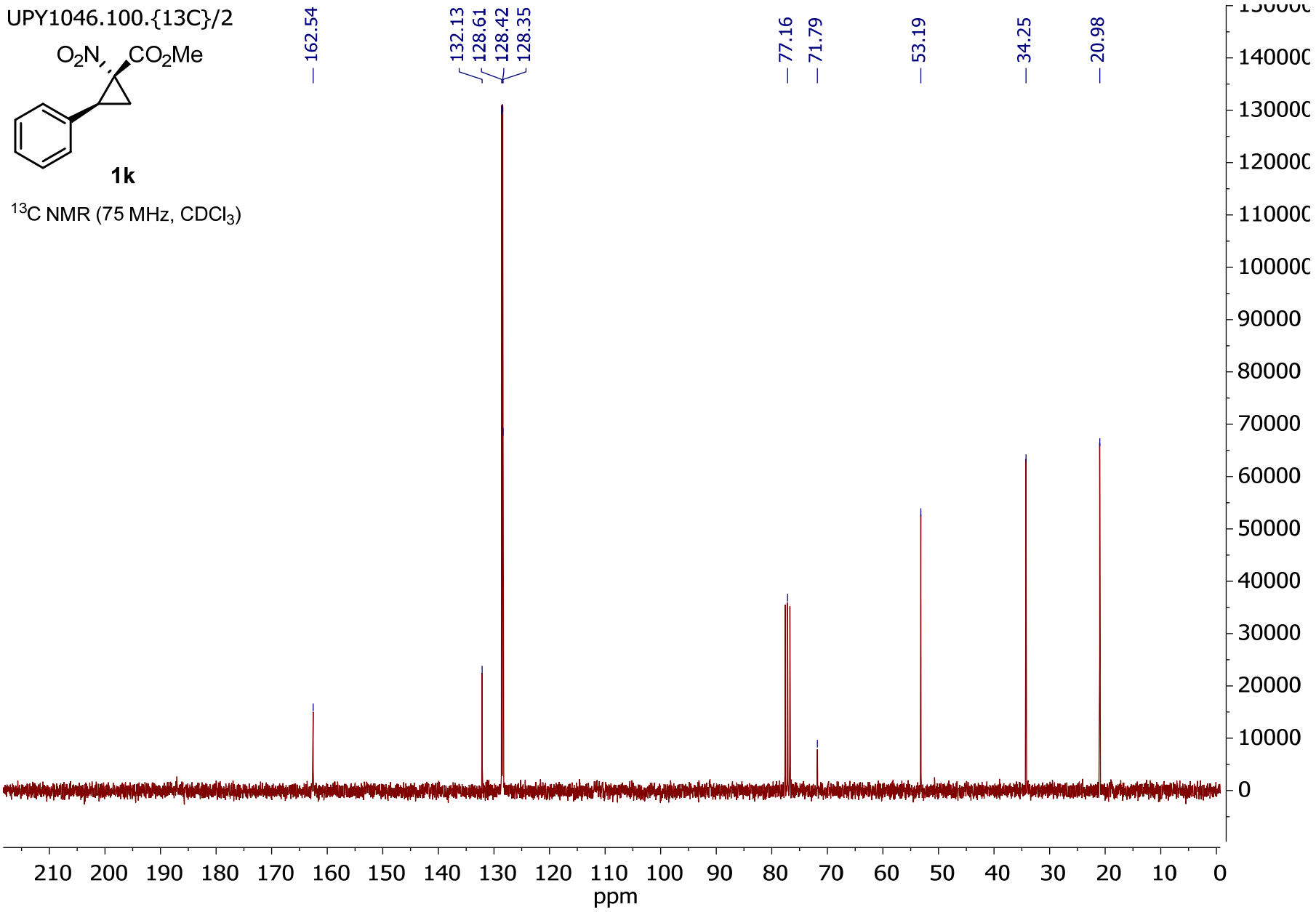
NMR of **1j**


UPY975.100.{13C}deptsp135/3
O2N
1j, dr = 14:1
13C DEPT NMR
(75 MHz, CDCl3)
132.48
129.52
128.39
128.27
128.09
127.47
35.24
21.69
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
220 200 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120

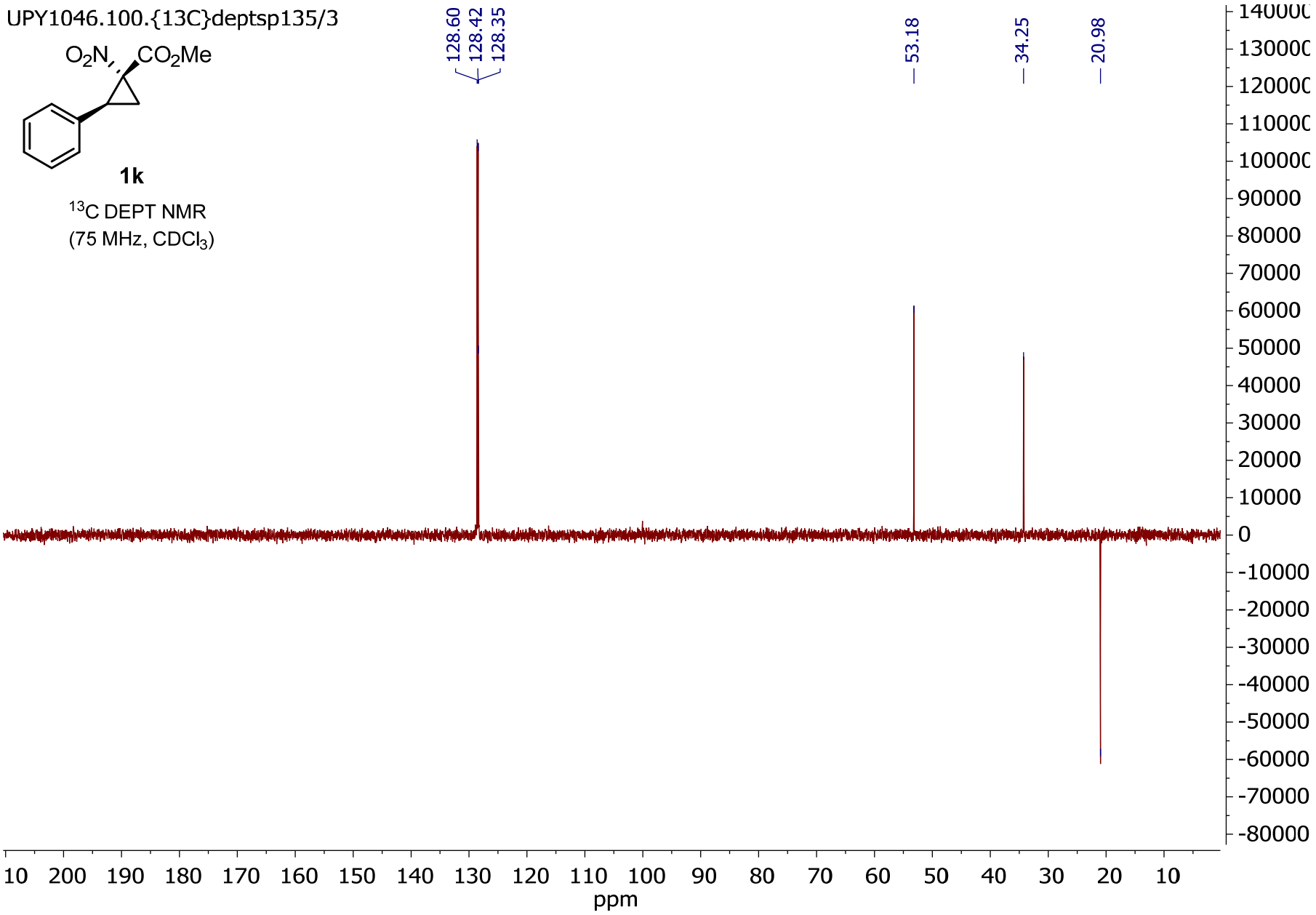
NMR of **1k**


UPY1046.100.{1H}/1
O_2N
CO_2Me
1k
^{1}H NMR (300 MHz, $CDCl_3$)
7.35
7.32
7.30
7.29
7.26
7.22
7.19
3.80
3.77
3.74
3.50
2.48
2.46
2.45
2.43
2.25
2.22
2.21
2.19
2.90
1.98
1.00
2.91
0.97
0.98
ppm

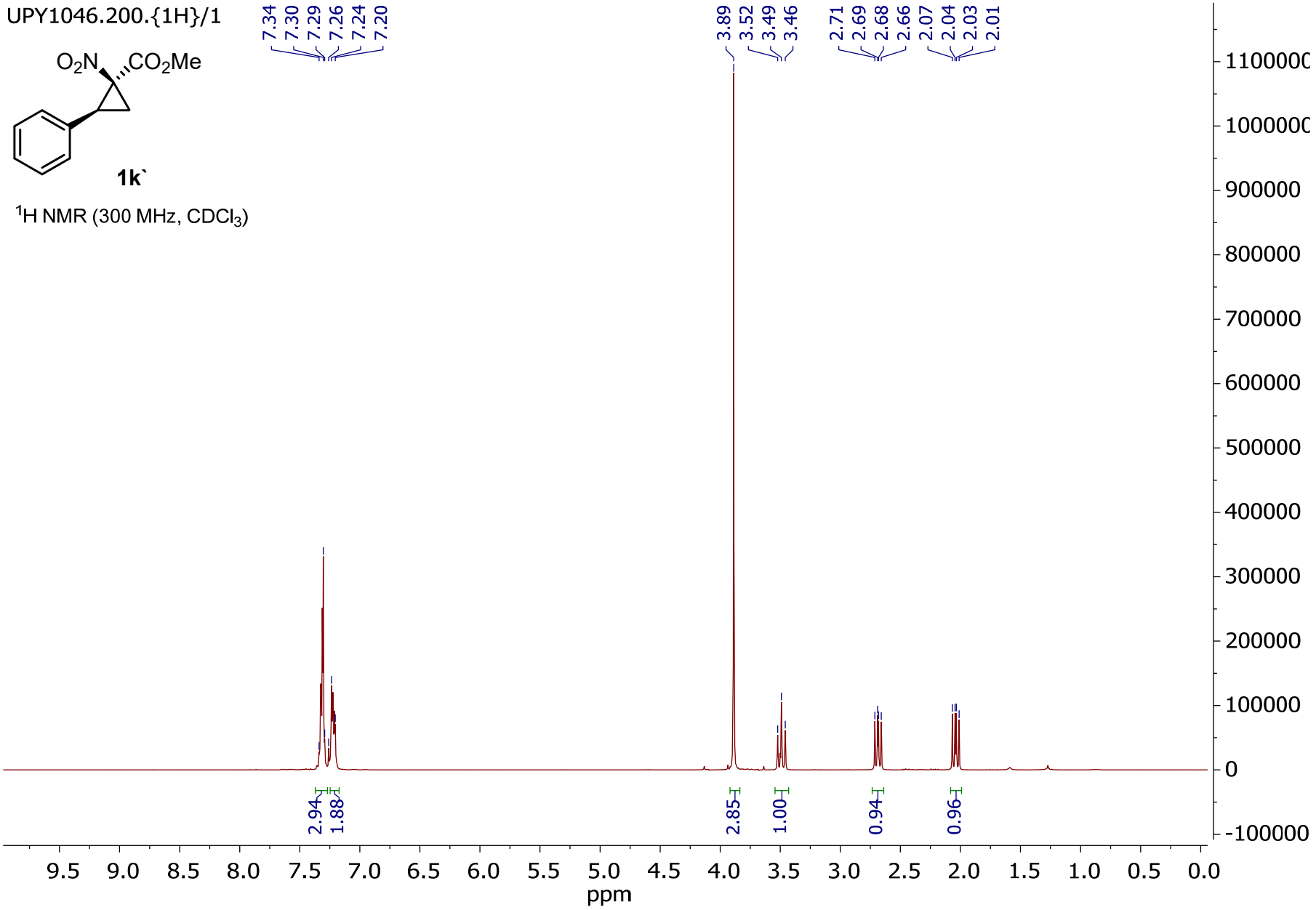
NMR of **1k**


UPY1046.100.{13C}/2
O_2N
CO_2Me
1k
^{13}C NMR (75 MHz, $CDCl_3$)
162.54
132.13
128.61
128.42
128.35
77.16
71.79
53.19
34.25
20.98
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

NMR of **1k**

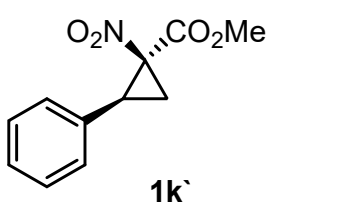

UPY1046.100.{13C}deptsp135/3
O_2N
CO_2Me
1k
^{13}C DEPT NMR
(75 MHz, $CDCl_3$)
128.60
128.42
128.35
53.18
34.25
20.98
ppm

NMR of **1k`**


UPY1046.200.{1H}/1
O2N
CO2Me
1k`
1H NMR (300 MHz, CDCl3)
7.34
7.30
7.29
7.26
7.24
7.20
3.89
3.52
3.49
3.46
2.71
2.69
2.68
2.66
2.07
2.04
2.03
2.01
2.94
1.88
2.85
1.00
0.94
0.96
ppm

NMR of **1k`**

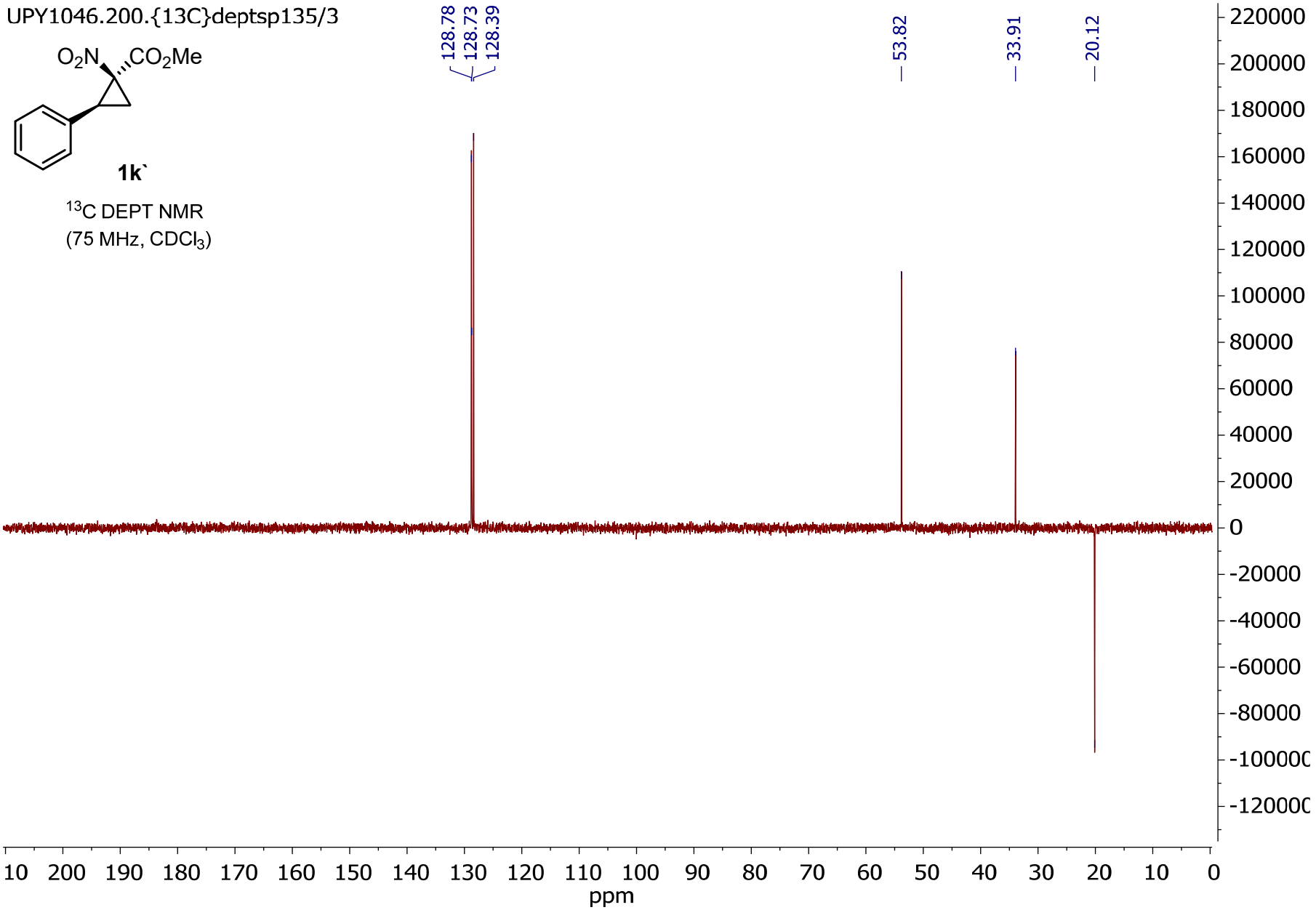
UPY1046.200.{13C}/2



1k`

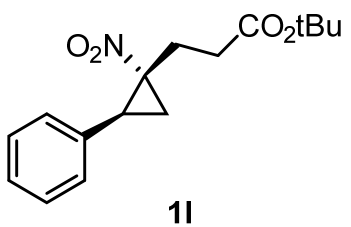
^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **1k`**


UPY1046.200.{13C}deptsp135/3
O_2N
CO_2Me
1k`
^{13}C DEPT NMR
(75 MHz, $CDCl_3$)
128.78
128.73
128.39
53.82
33.91
20.12
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
-60000
-80000
-100000
-120000
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

NMR of **1l**

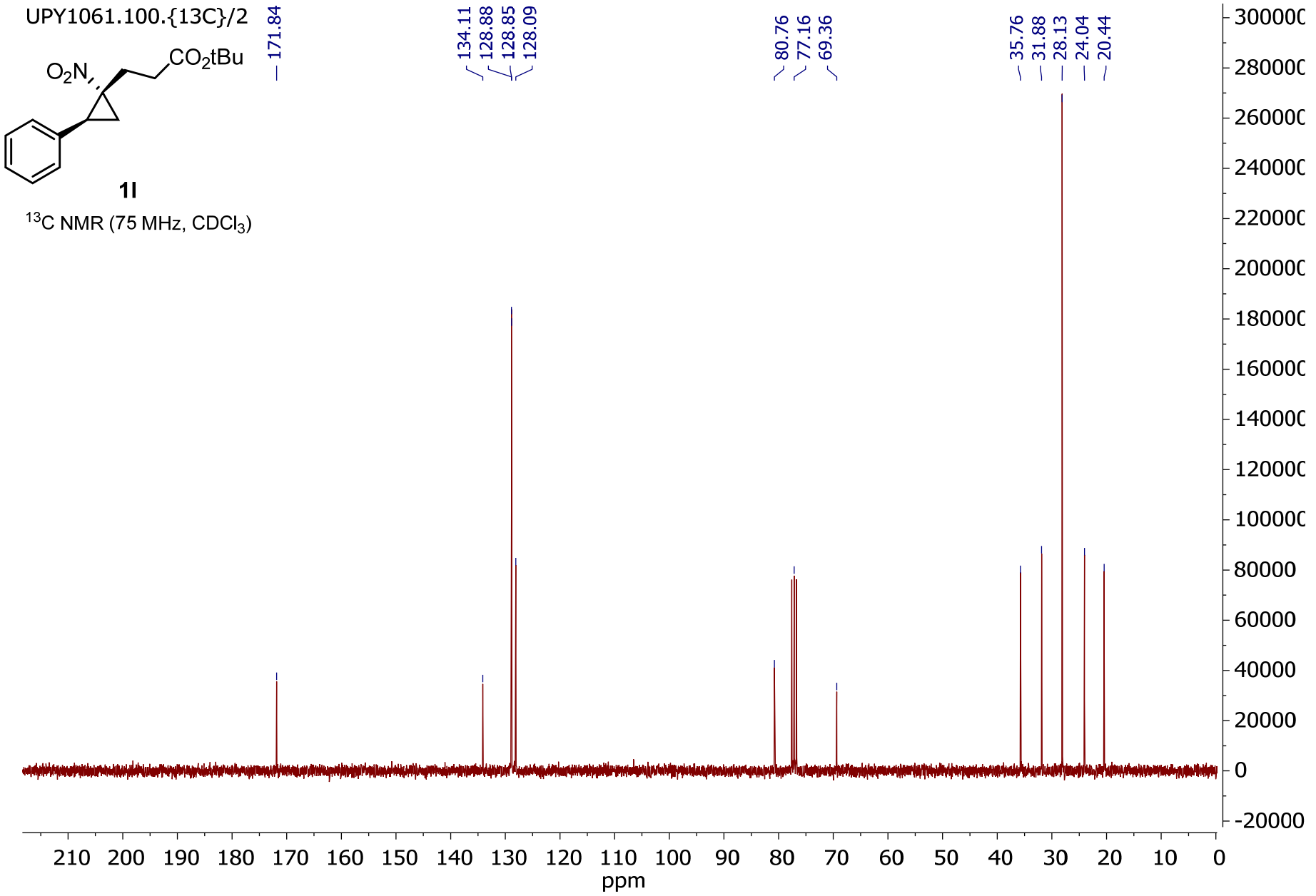
UPY1061.100.{1H}/1



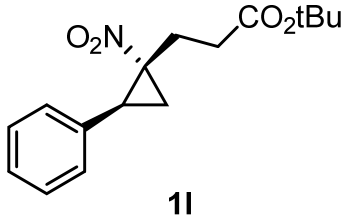
1l

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **1l**


UPY1061.100.{13C}/2
O2N
CO2tBu
1l
13C NMR (75 MHz, CDCl3)
171.84
134.11
128.88
128.85
128.09
80.76
77.16
69.36
35.76
31.88
28.13
24.04
20.44
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

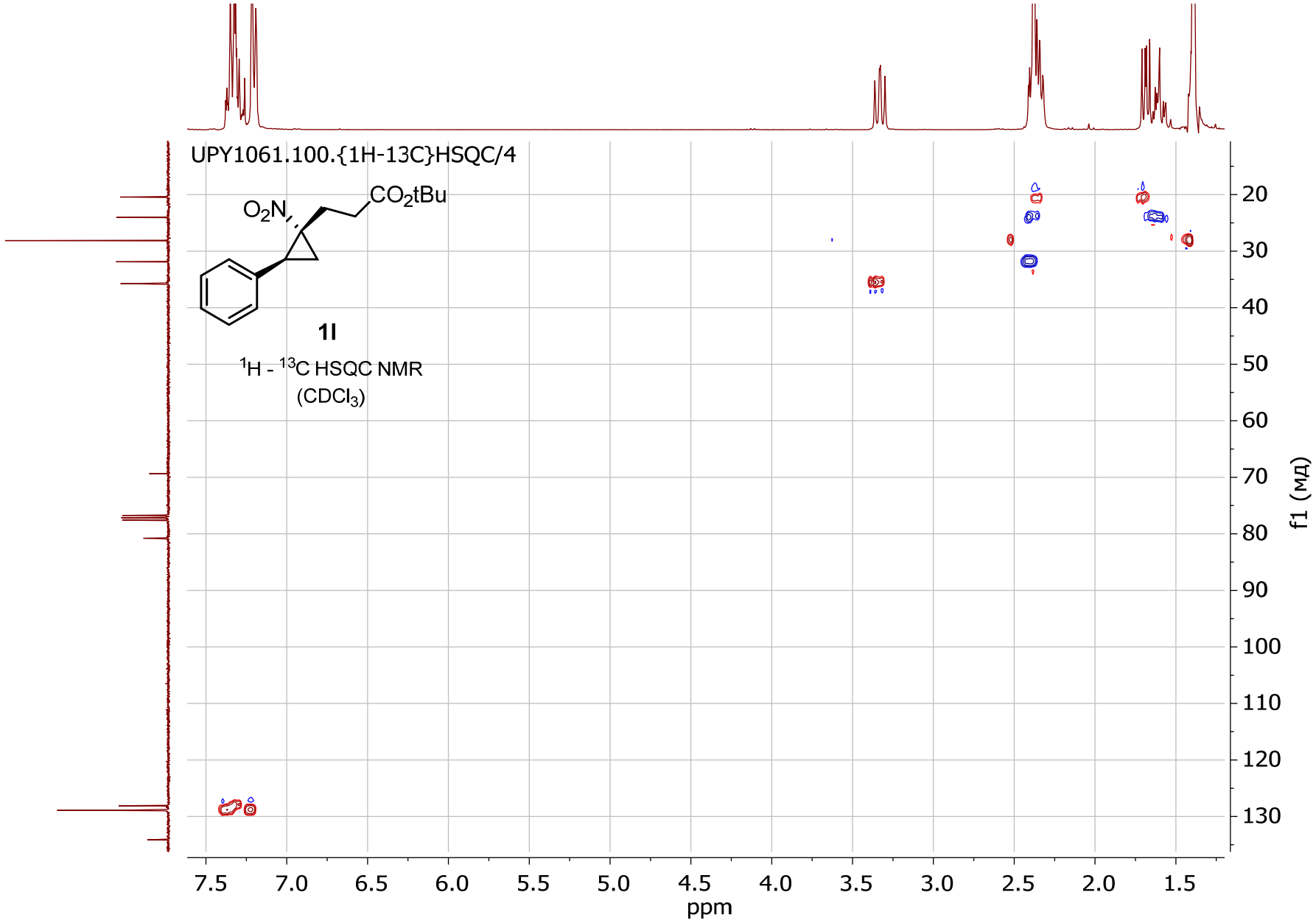
NMR of **1l**



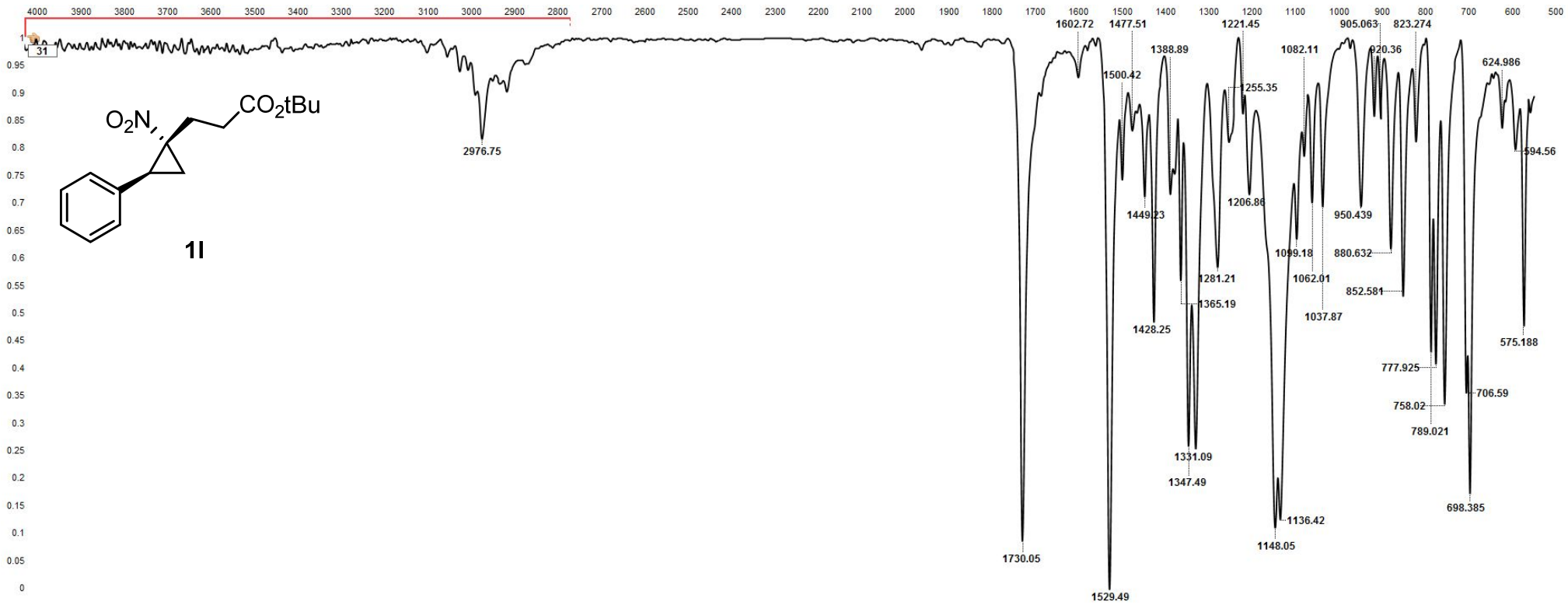
1l

^{13}C DEPT NMR
(75 MHz, $CDCl_3$)

NMR of **1l**

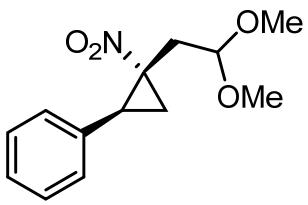

UPY1061.100.{1H-13C}HSQC/4
O2N
CO2tBu
1l
1H - 13C HSQC NMR
(CDCl3)
20
30
40
50
60
70
80
90
100
110
120
130
f1 (мд)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

FTIR (ATR) of **1l**



NMR of **1m**

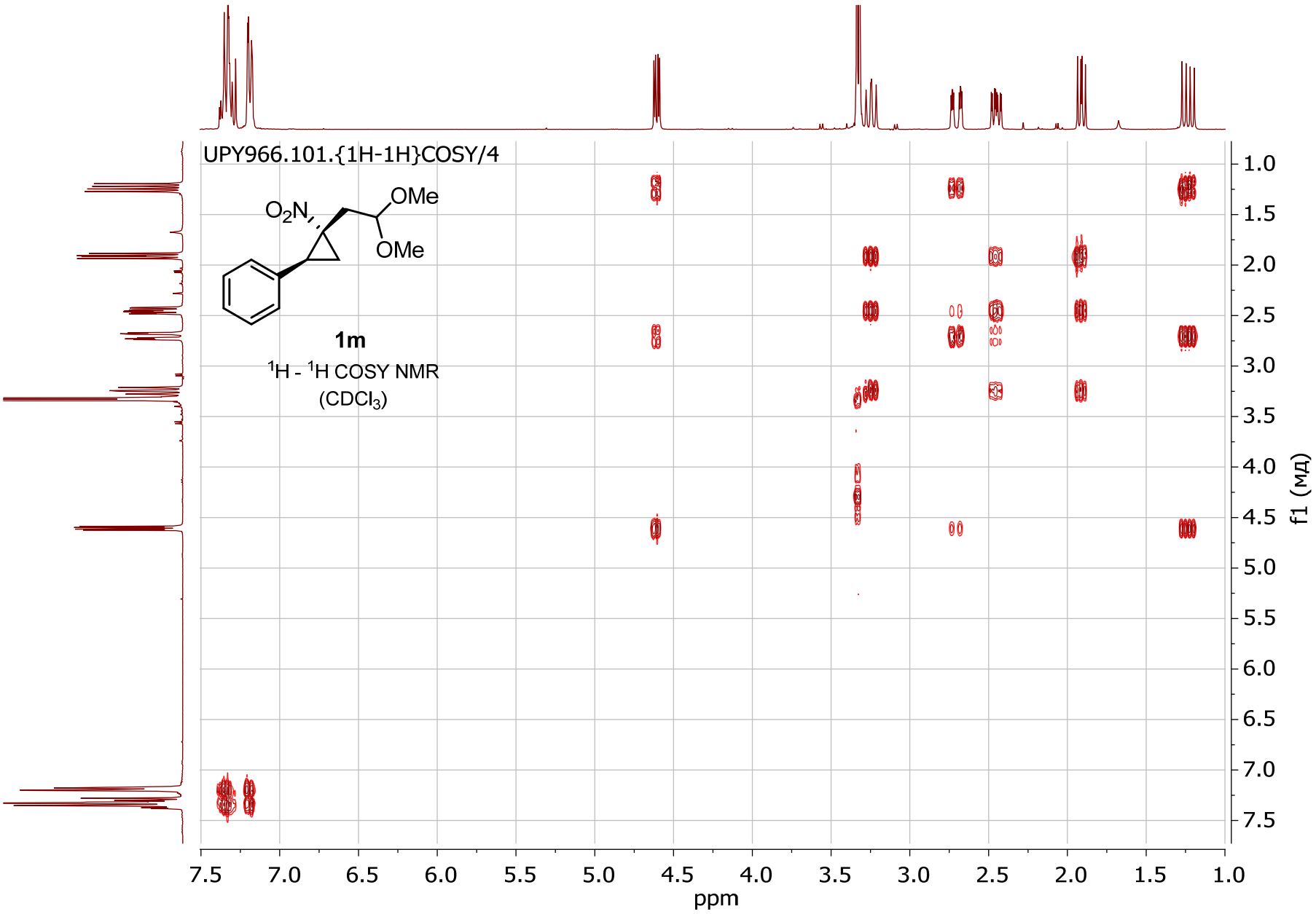
UPY966.101.{1H}/1



1m

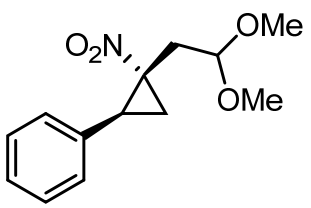
^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **1m**


UPY966.101.{1H-1H}COSY/4
O2N
OMe
OMe
1m
1H - 1H COSY NMR
(CDCl3)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
f1 (мд)

NMR of **1m**

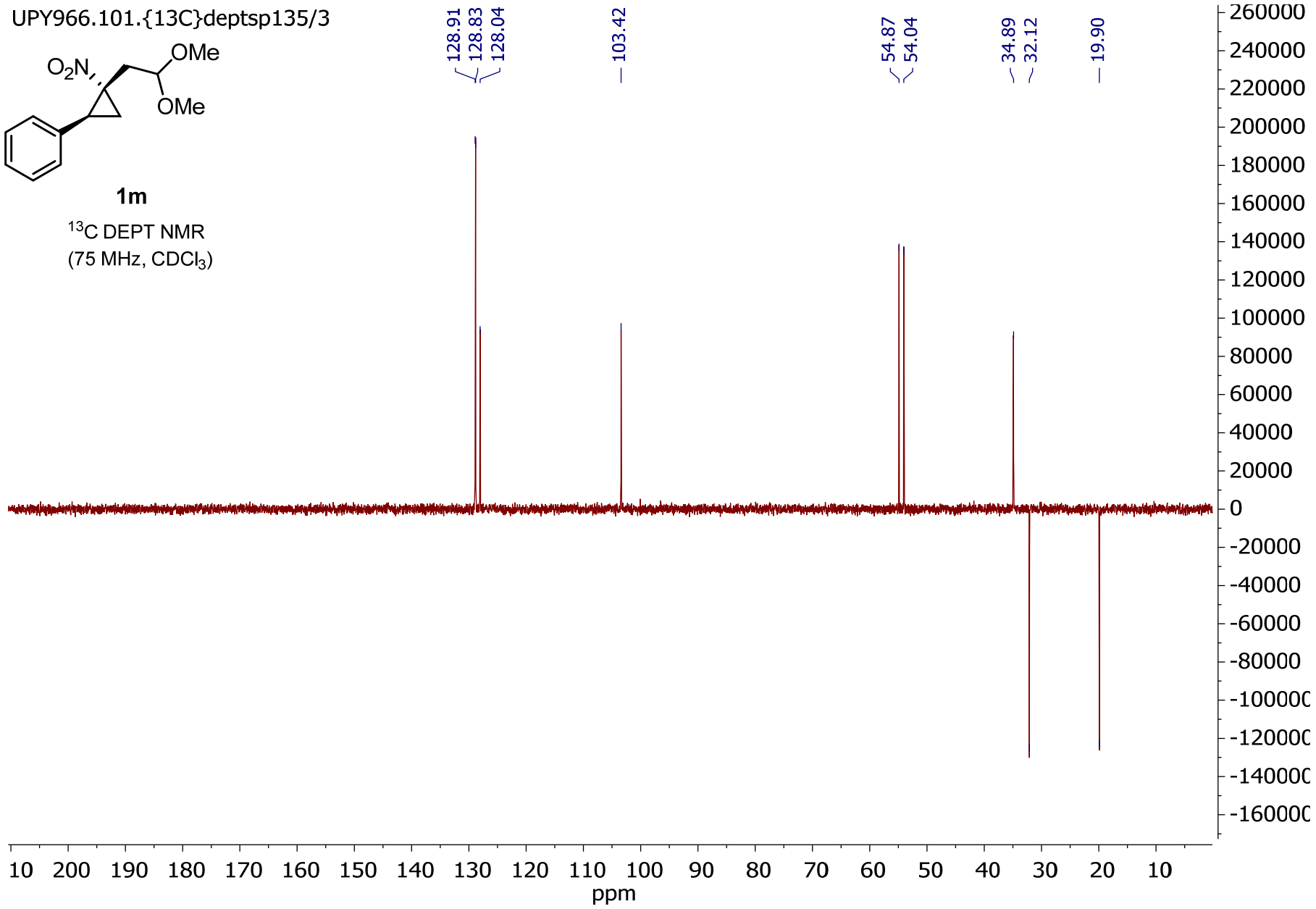
UPY966.101.{13C}/2



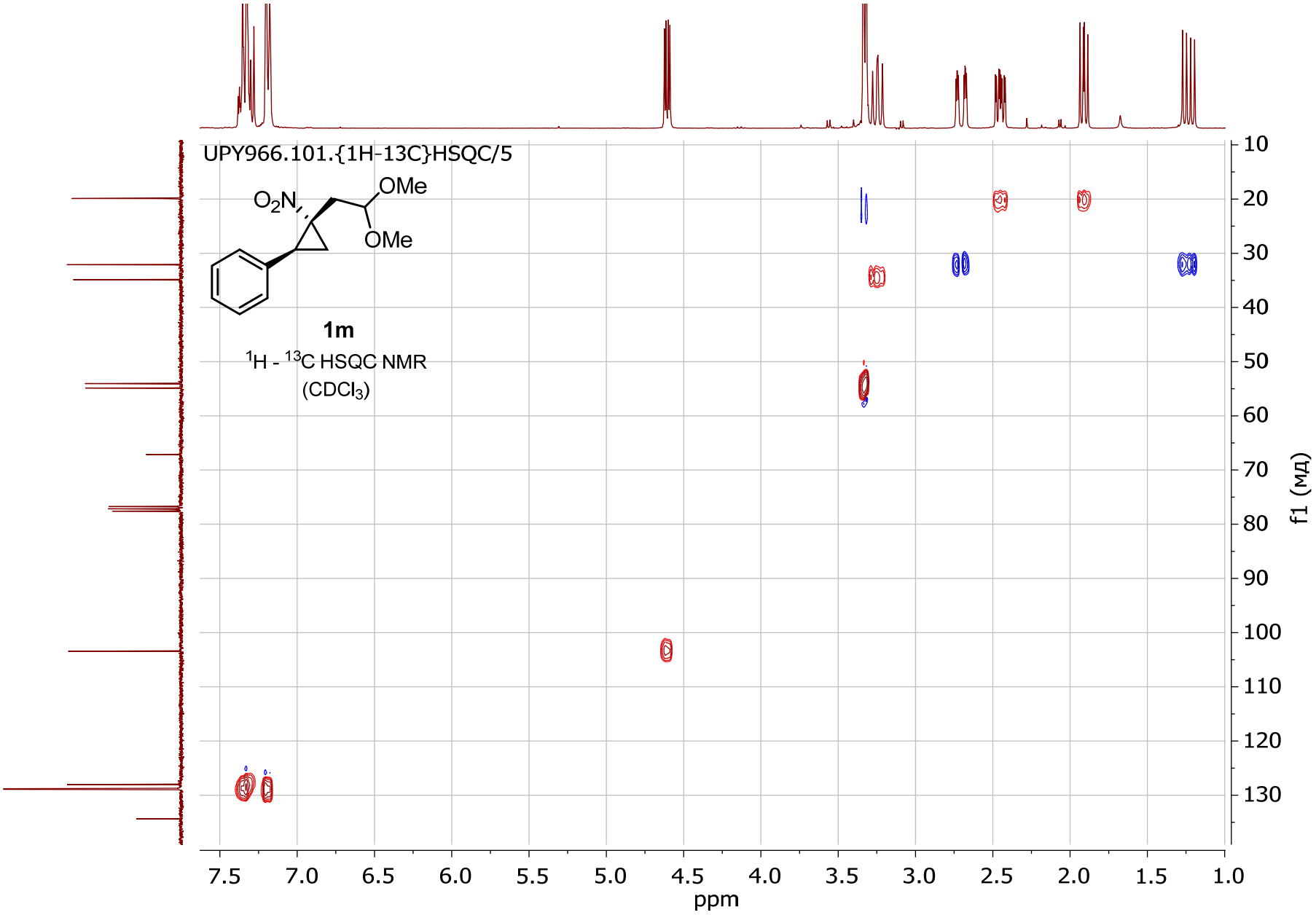
1m

^{13}C NMR (75 MHz, $CDCl_3$)

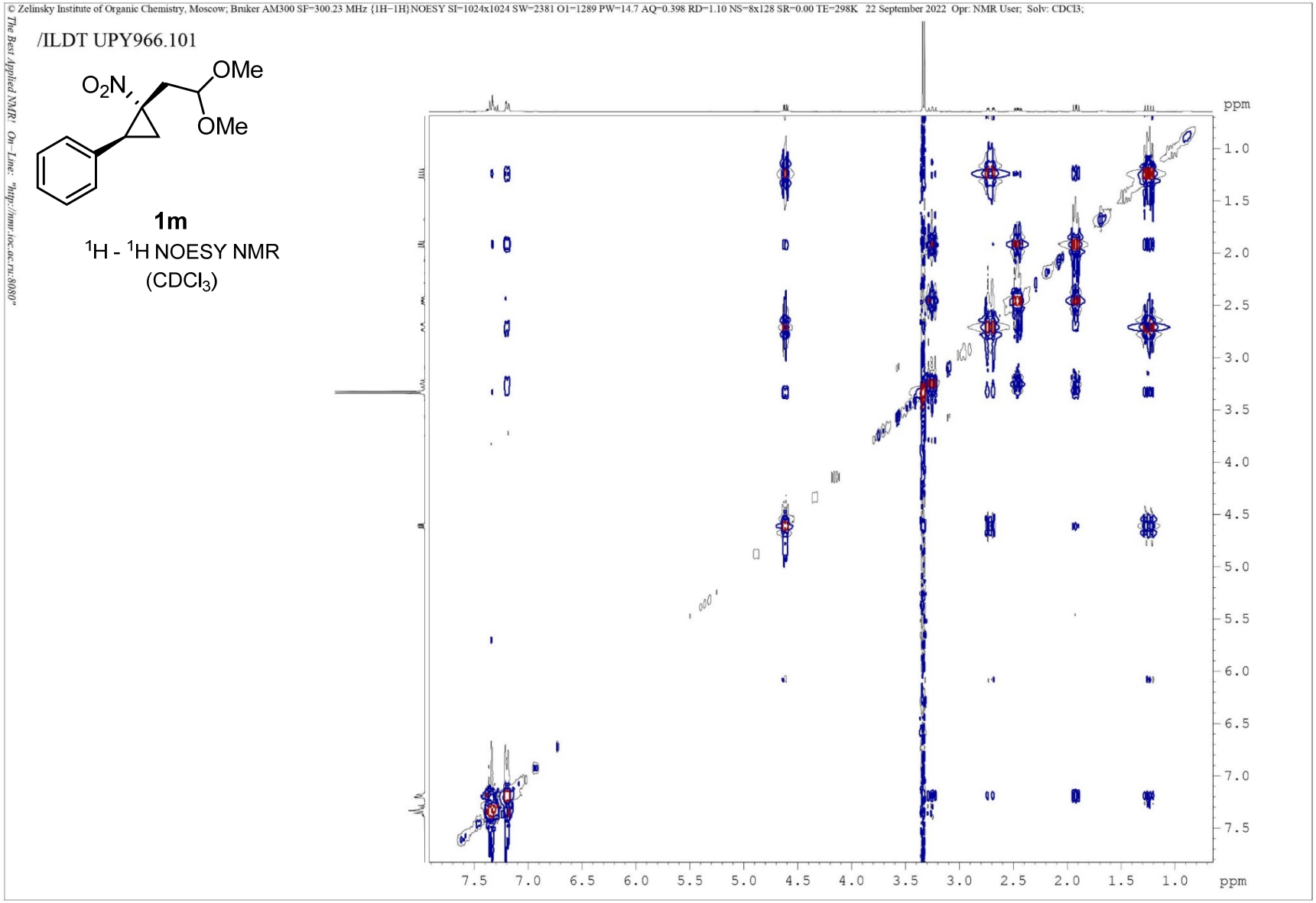
NMR of **1m**


UPY966.101.{13C}deptsp135/3
O2N
OMe
OMe
1m
13C DEPT NMR
(75 MHz, CDCl3)
128.91
128.83
128.04
103.42
54.87
54.04
34.89
32.12
19.90
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
-60000
-80000
-100000
-120000
-140000
-160000
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

NMR of **1m**

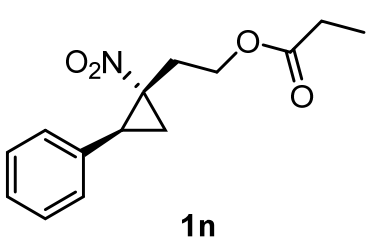

UPY966.101.{1H-13C}HSQC/5
O2N
OMe
OMe
1m
1H - 13C HSQC NMR
(CDCl3)
10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (мд)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

NMR of **1m**


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.23 MHz {1H−1H}NOESY SI=1024x1024 SW=2381 O1=1289 PW=14.7 AQ=0.398 RD=1.10 NS=8x128 SR=0.00 TE=298K 22 September 2022 Opr: NMR User; Solv: CDCl3;
The Best Applied NMR! On−Line: "http://nmr.ioc.ac.ru:8080"
/ILDT UPY966.101
O2N
OMe
OMe
1m
1H - 1H NOESY NMR
(CDCl3)
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

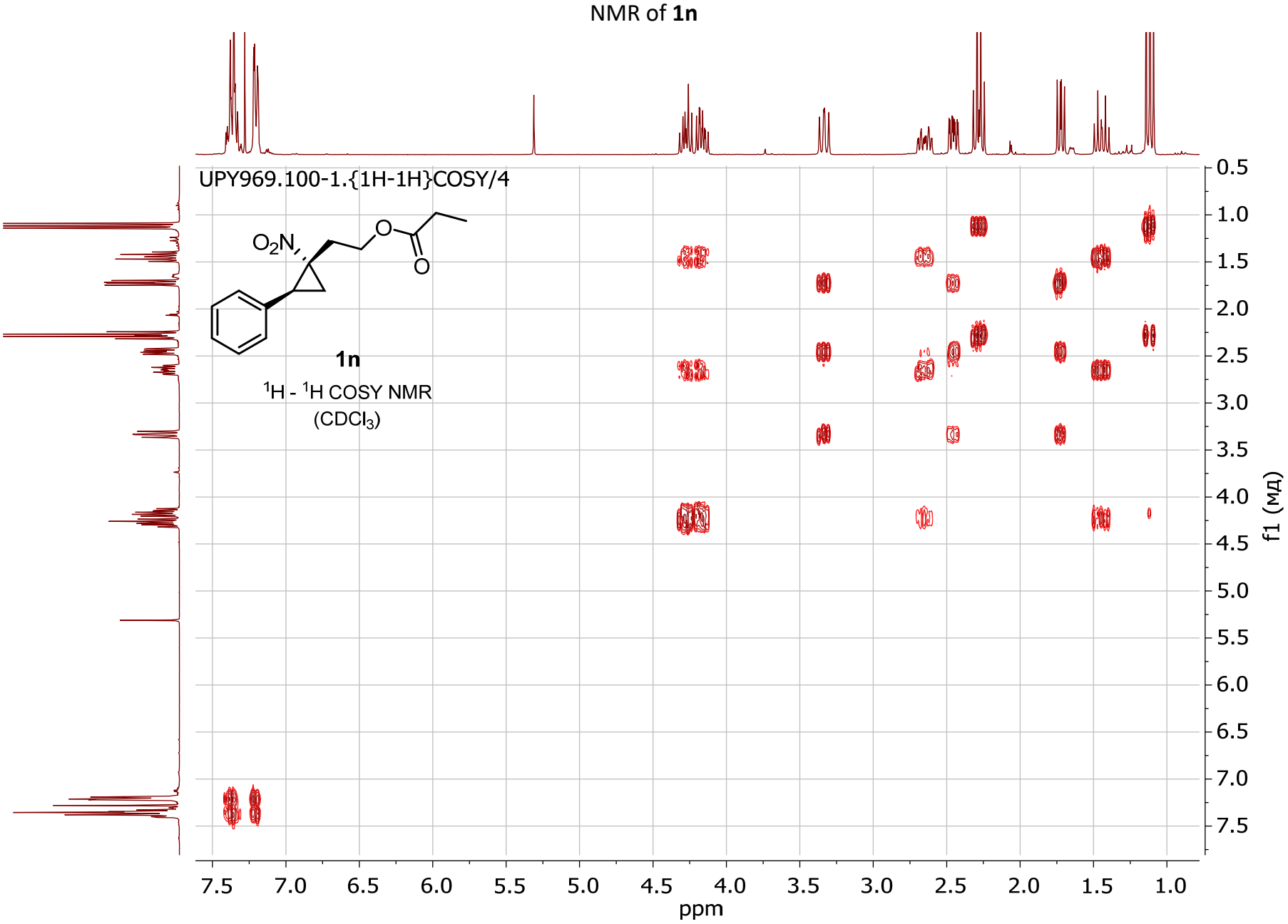
NMR of **1n**

UPY969.100-1.{1H}/1

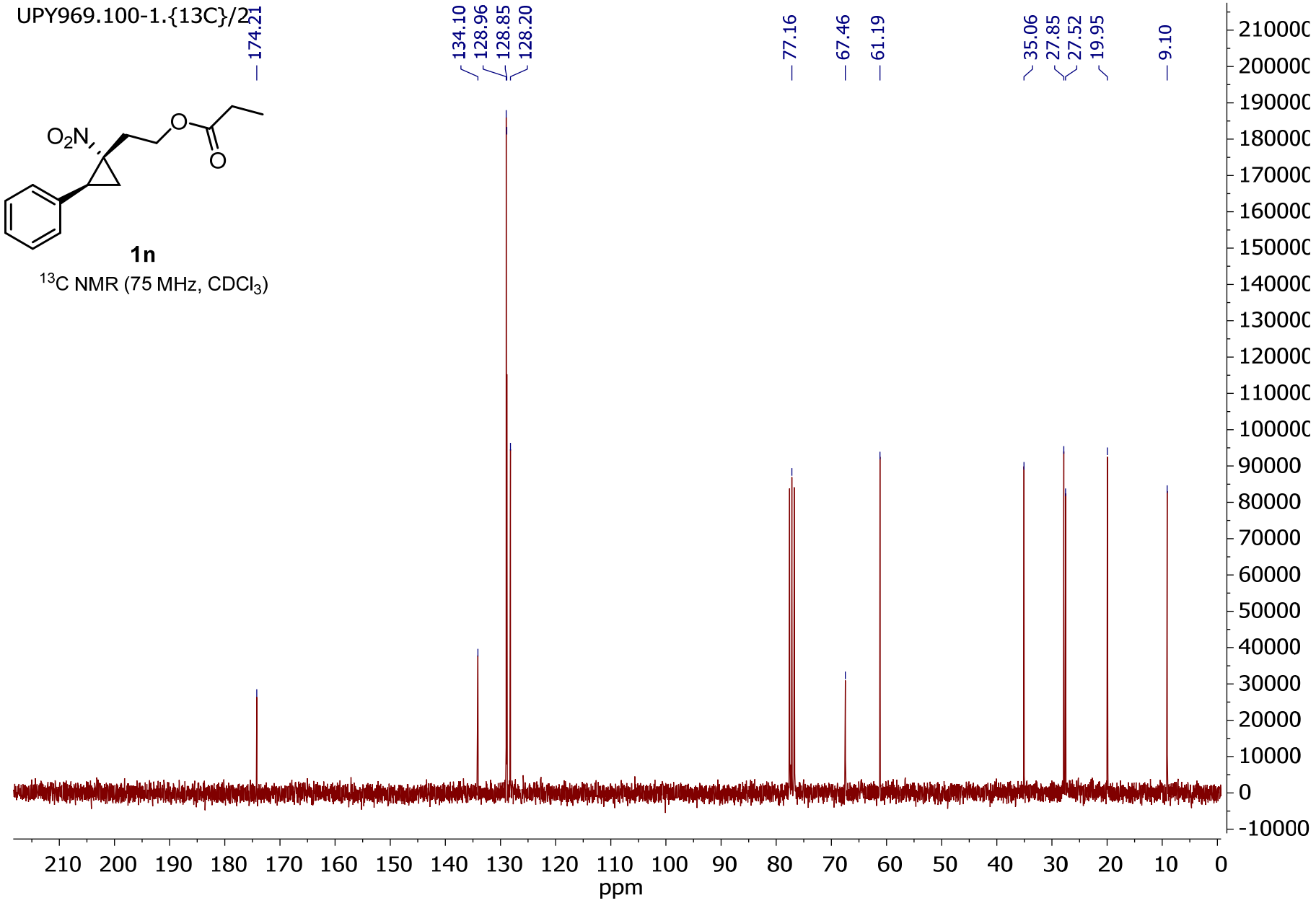


1n

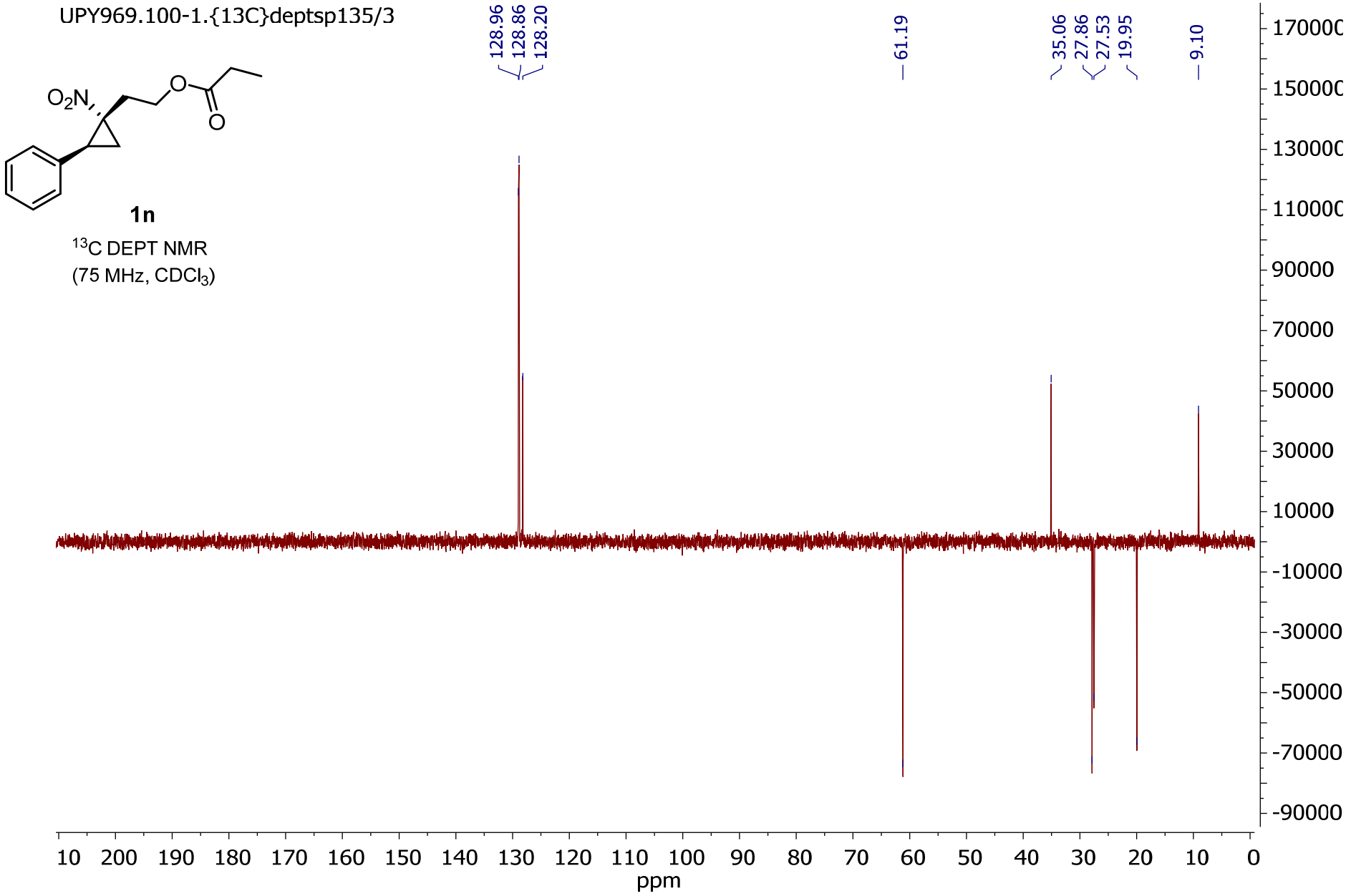
^{1}H NMR (300 MHz, $CDCl_3$)

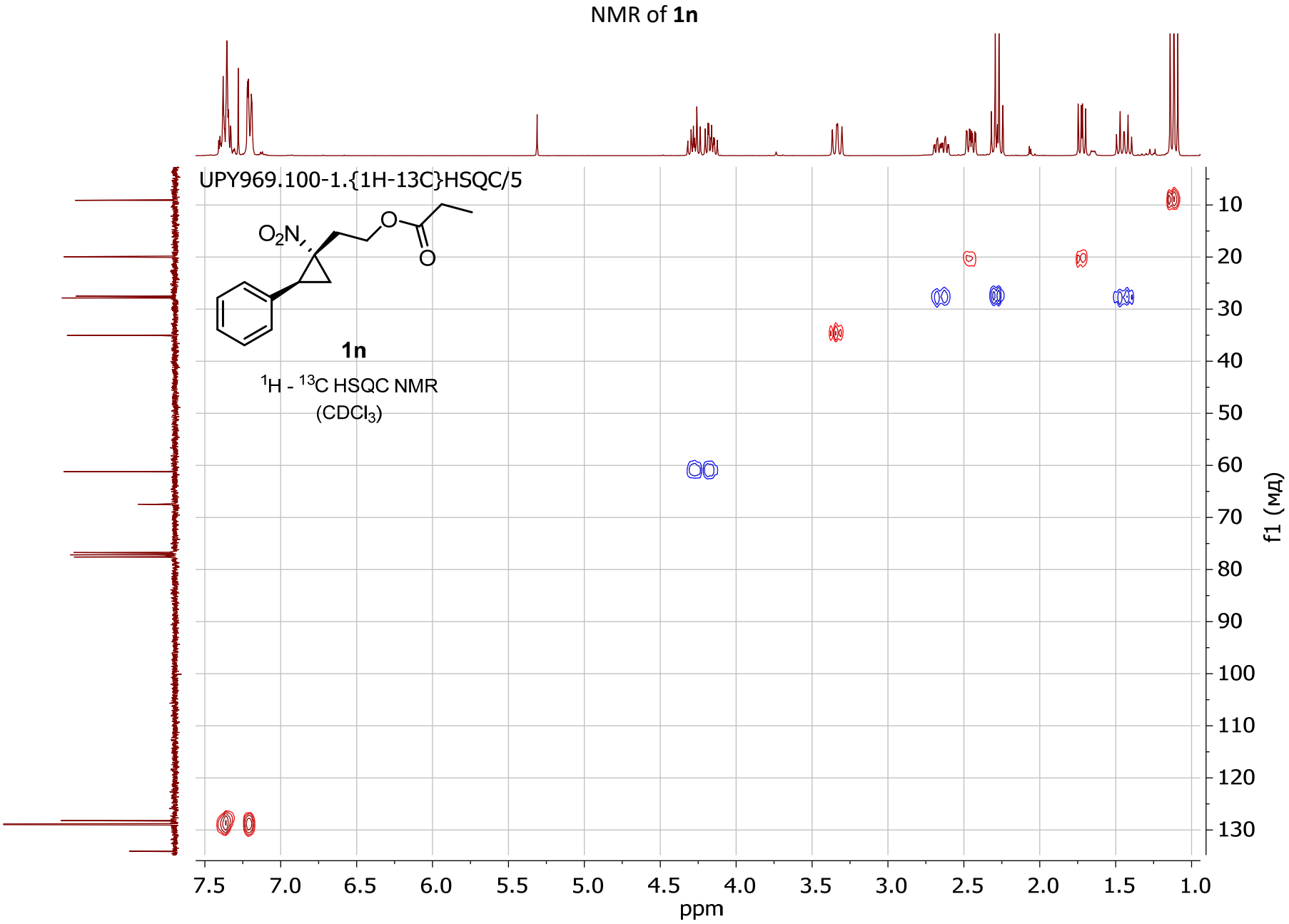

NMR of 1n
UPY969.100-1.{1H-1H}COSY/4
O2N
O
O
1n
1H - 1H COSY NMR
(CDCl3)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (мд)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

NMR of **1n**

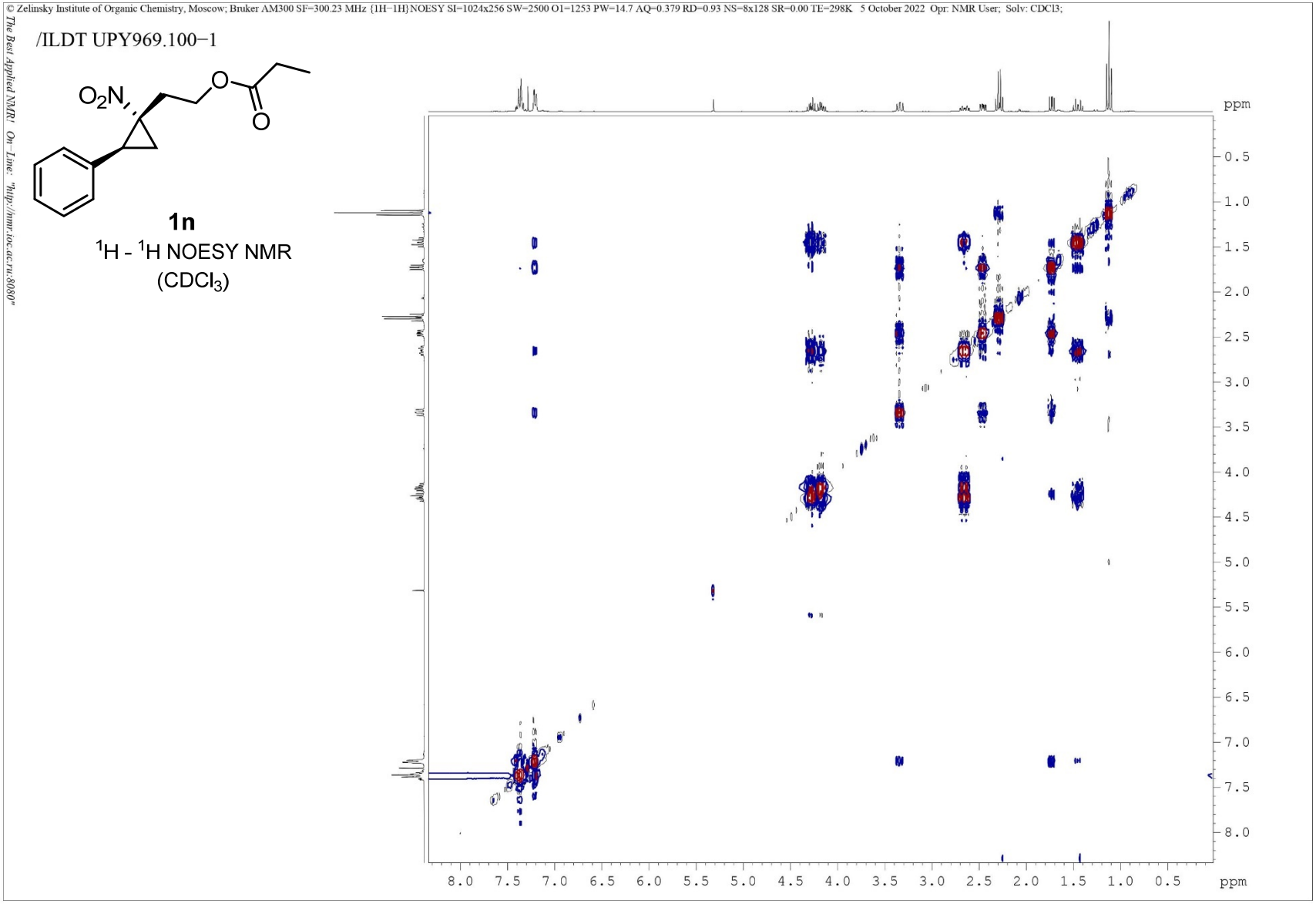

UPY969.100-1.{13C}/2
174.21
134.10
128.96
128.85
128.20
77.16
67.46
61.19
35.06
27.85
27.52
19.95
9.10
O_2N
O
O
1n
^{13}C NMR (75 MHz, $CDCl_3$)
ppm

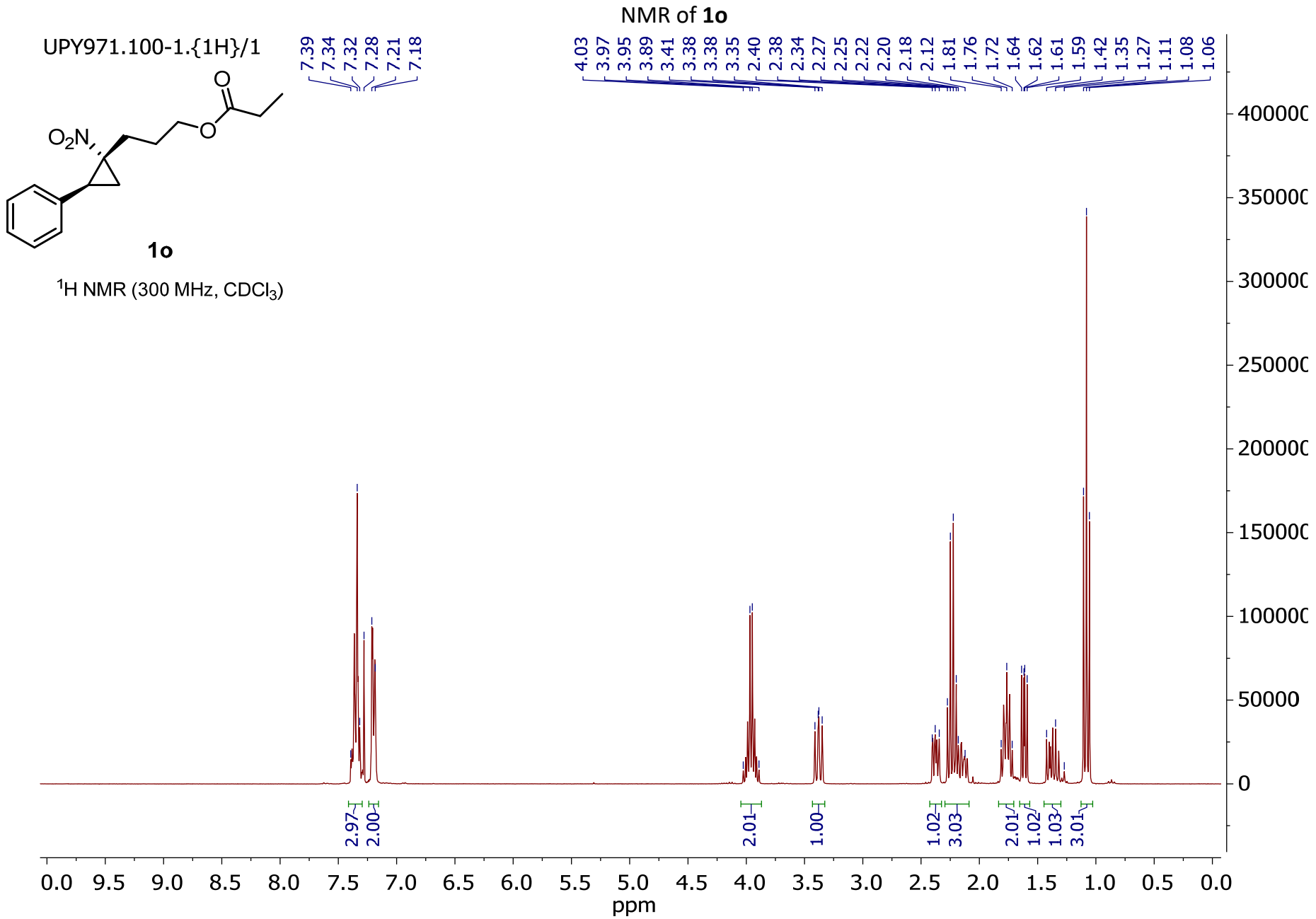
NMR of **1n**


UPY969.100-1.{13C}deptsp135/3
128.96
128.86
128.20
61.19
35.06
27.86
27.53
19.95
9.10
O_2N
O
O
1n
^{13}C DEPT NMR
(75 MHz, $CDCl_3$)
170000
150000
130000
110000
90000
70000
50000
30000
10000
-10000
-30000
-50000
-70000
-90000
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

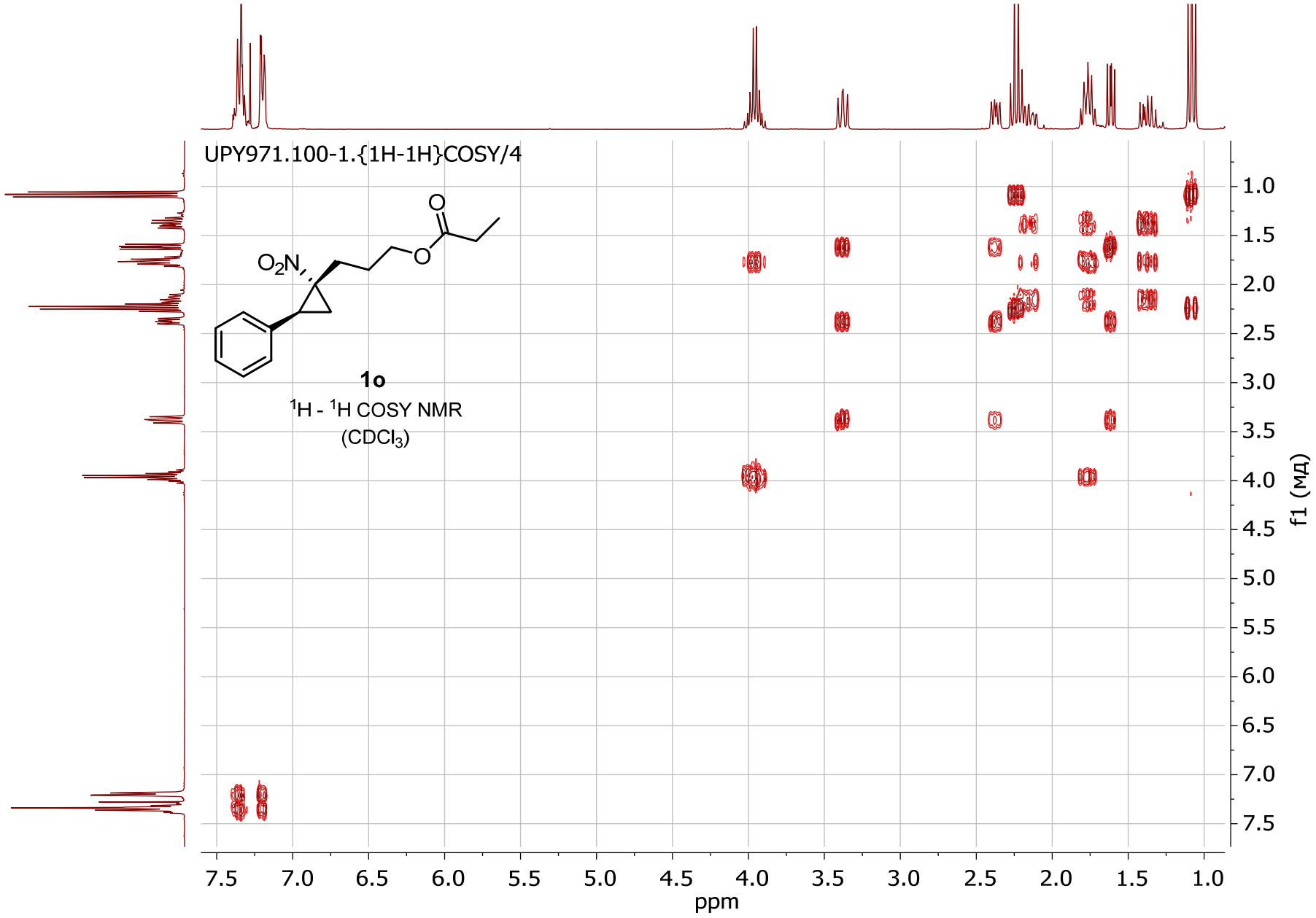

NMR of 1n
UPY969.100-1.{1H-13C}HSQC/5
O2N
O
O
1n
1H - 13C HSQC NMR
(CDCl3)
10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (мд)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

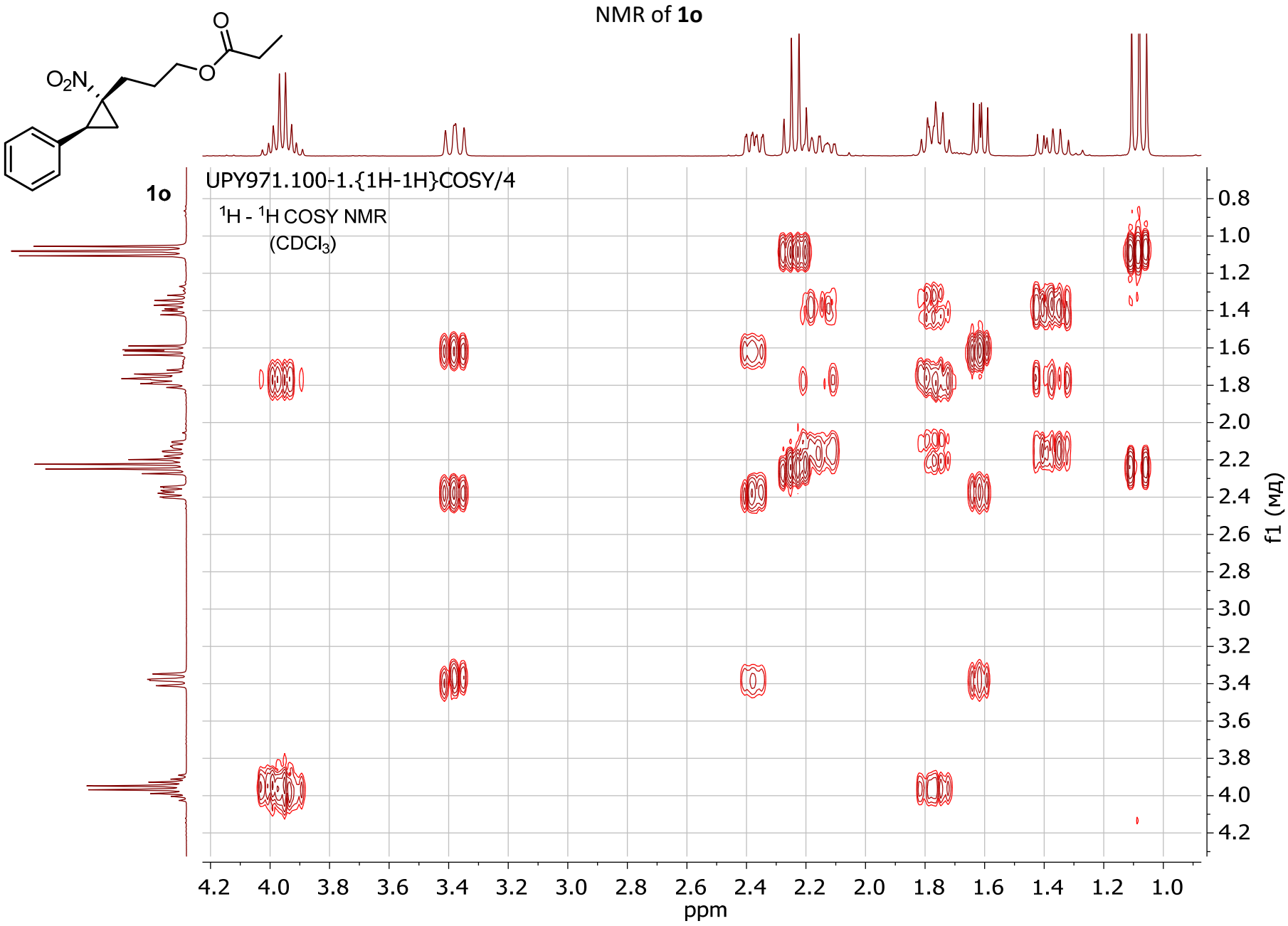
NMR of **1n**


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.23 MHz {1H−1H}NOESY SI=1024x256 SW=2500 O1=1253 PW=14.7 AQ=0.379 RD=0.93 NS=8x128 SR=0.00 TE=298K 5 October 2022 Opr: NMR User; Solv: CDCl3;
The Best Applied NMR! On-Line: "http://nmr.ioc.ac.ru:8080"
/ILDT UPY969.100−1
O2N
O
O
1n
1H - 1H NOESY NMR
(CDCl3)
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

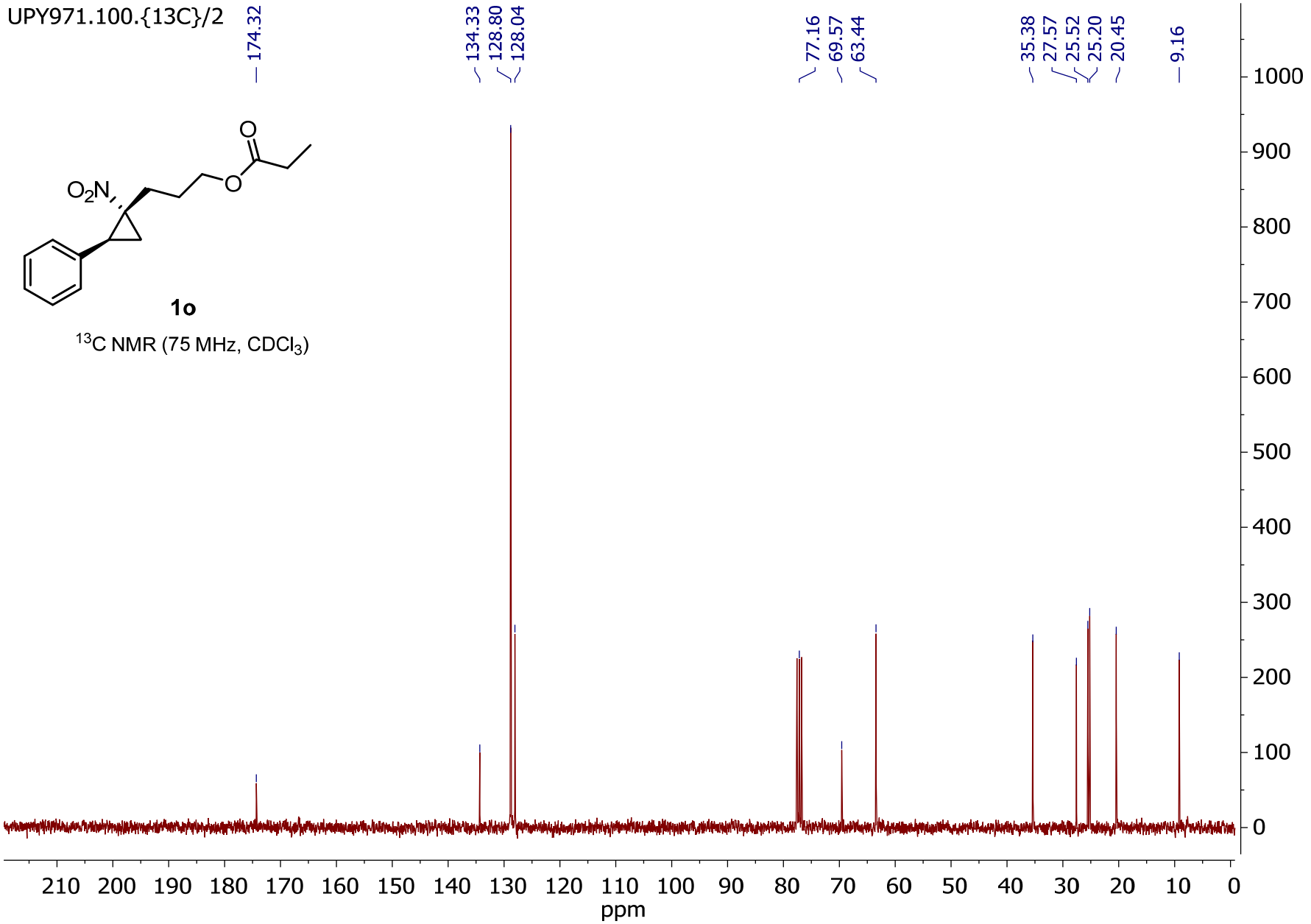

NMR of 1o
UPY971.100-1.{1H}/1
1o
1H NMR (300 MHz, CDCl3)
7.39 7.34 7.32 7.28 7.21 7.18
4.03 3.97 3.95 3.89 3.41 3.38 3.38 3.35 2.40 2.38 2.34 2.27 2.25 2.22 2.20 2.18 2.12 1.81 1.76 1.72 1.64 1.62 1.61 1.59 1.42 1.35 1.27 1.11 1.08 1.06
2.97 2.00 2.01 1.00 1.02 3.03 2.01 1.02 1.03 3.01
ppm

NMR of **1o**


UPY971.100-1.{1H-1H}COSY/4
O2N
O
O
1o
1H - 1H COSY NMR
(CDCl3)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
f1 (мд)

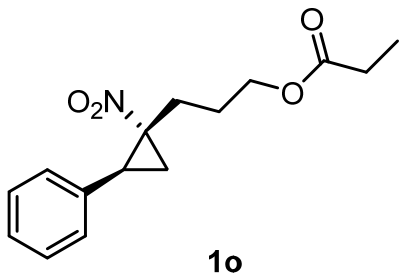

NMR of 1o
1o
UPY971.100-1.{1H-1H}COSY/4
^{1}H - ^{1}H COSY NMR
(CDCl$_3$)
O$_2$N
O
O
4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
ppm
0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2
f1 (мд)

NMR of **1o**


UPY971.100.{13C}/2
174.32
134.33
128.80
128.04
77.16
69.57
63.44
35.38
27.57
25.52
25.20
20.45
9.16
O
O
O2N
1o
13C NMR (75 MHz, CDCl3)
1000
900
800
700
600
500
400
300
200
100
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

NMR of **1o**

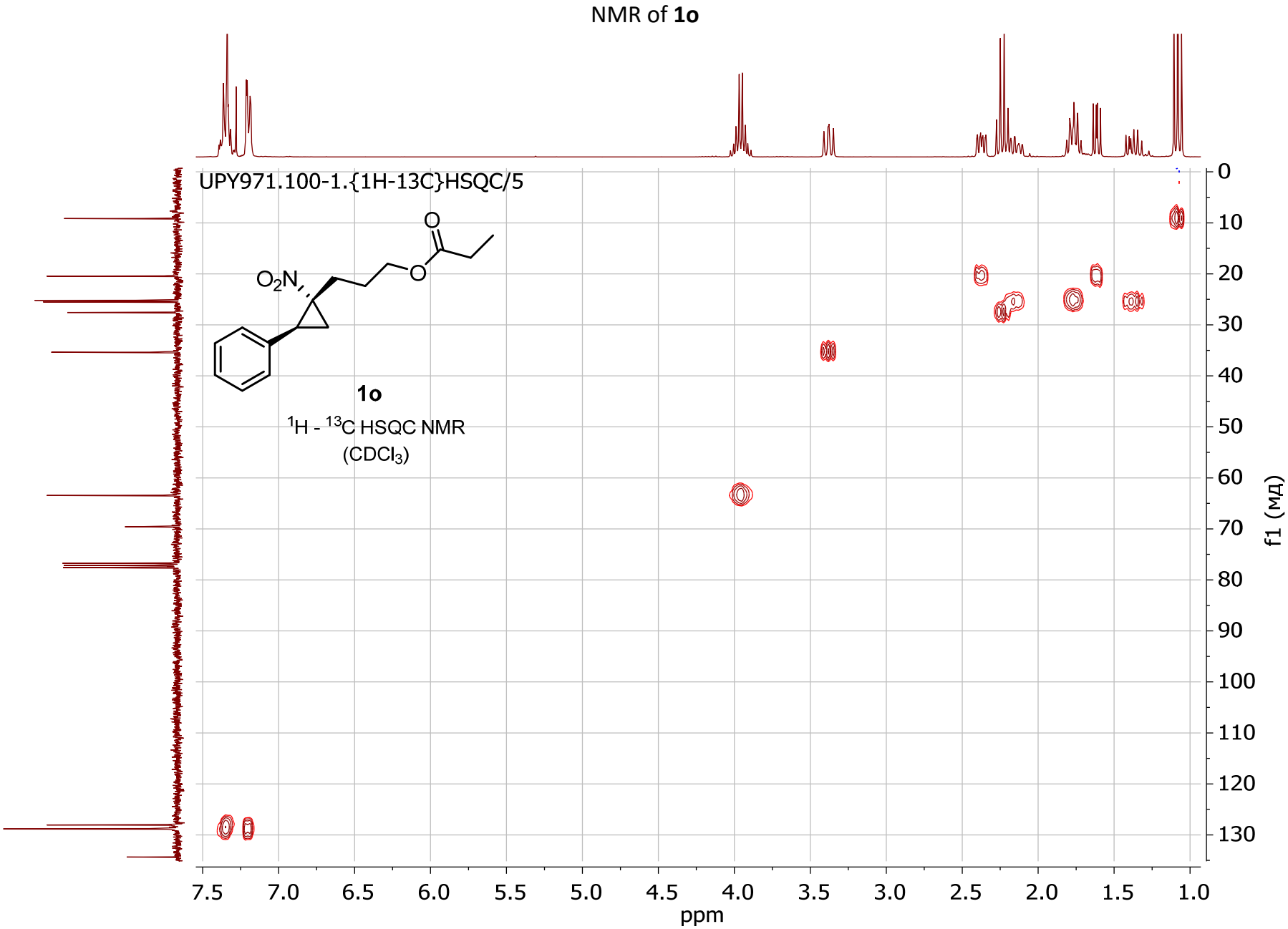
UPY971.100.{13C}deptsp135/3



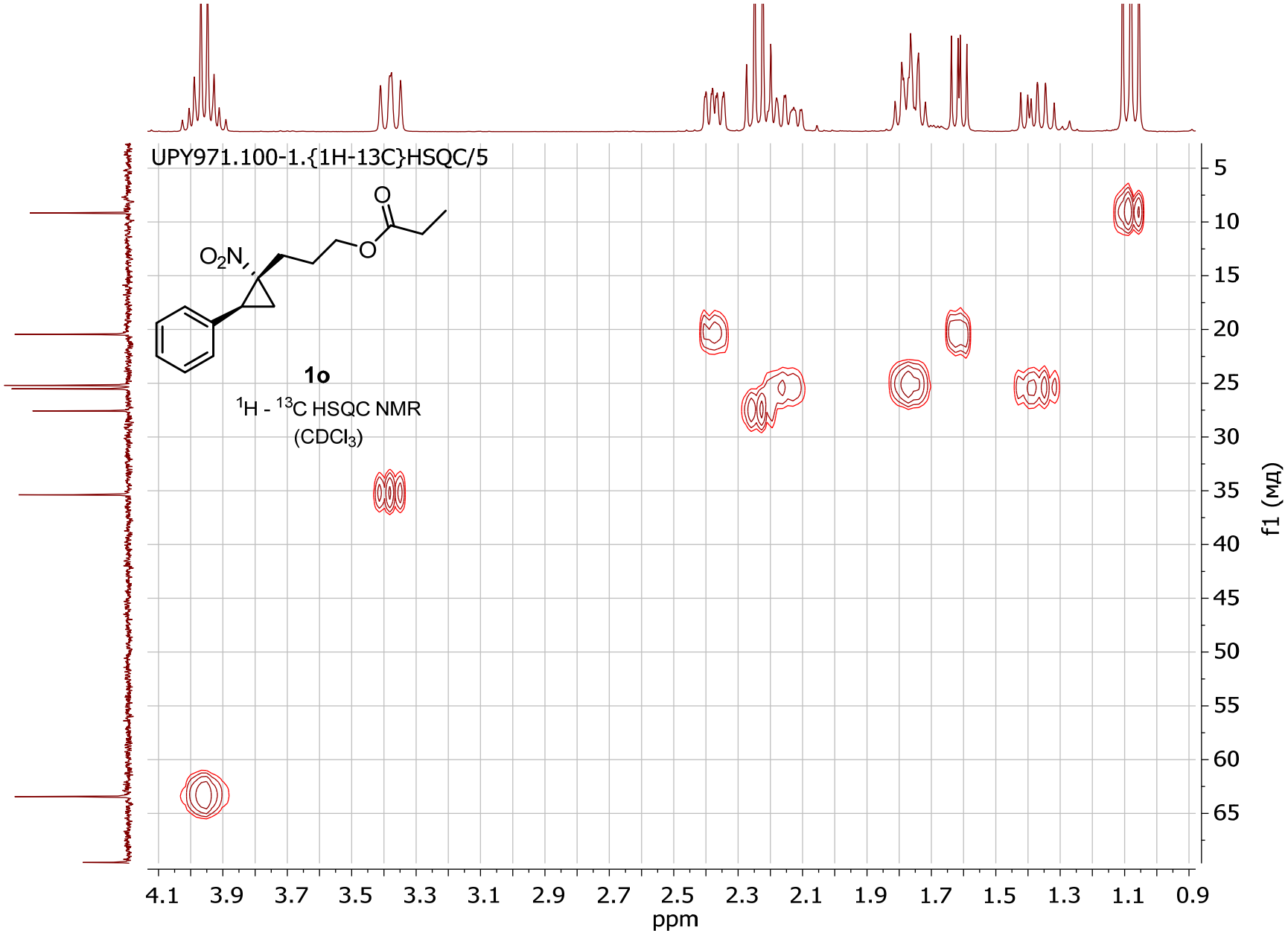
1o

^{13}C DEPT NMR

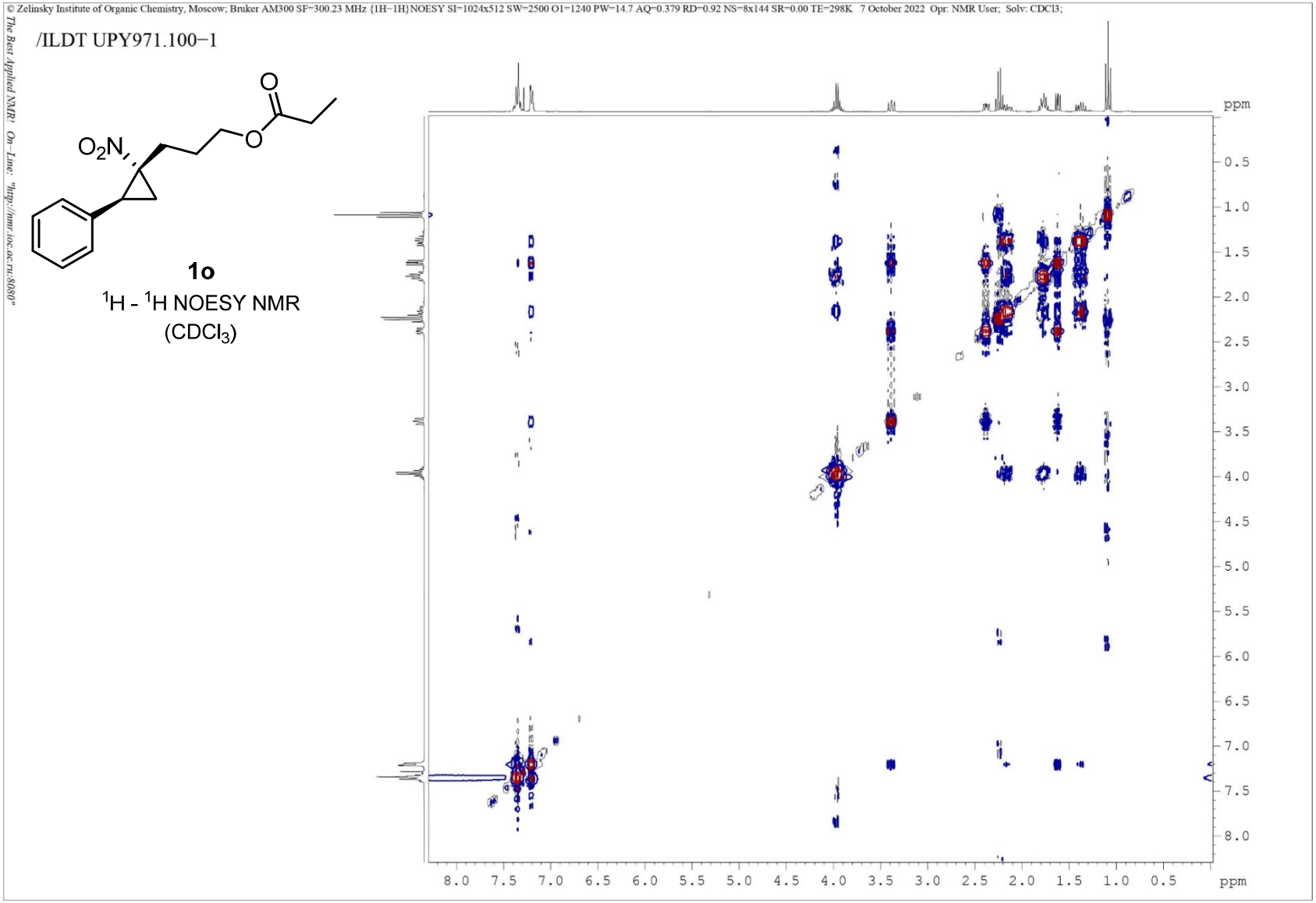
(75 MHz, $CDCl_3$)


NMR of **1o**
UPY971.100-1.{1H-13C}HSQC/5
O_2N
O
O
1o
^{1}H - ^{13}C HSQC NMR
($CDCl_3$)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (мд)

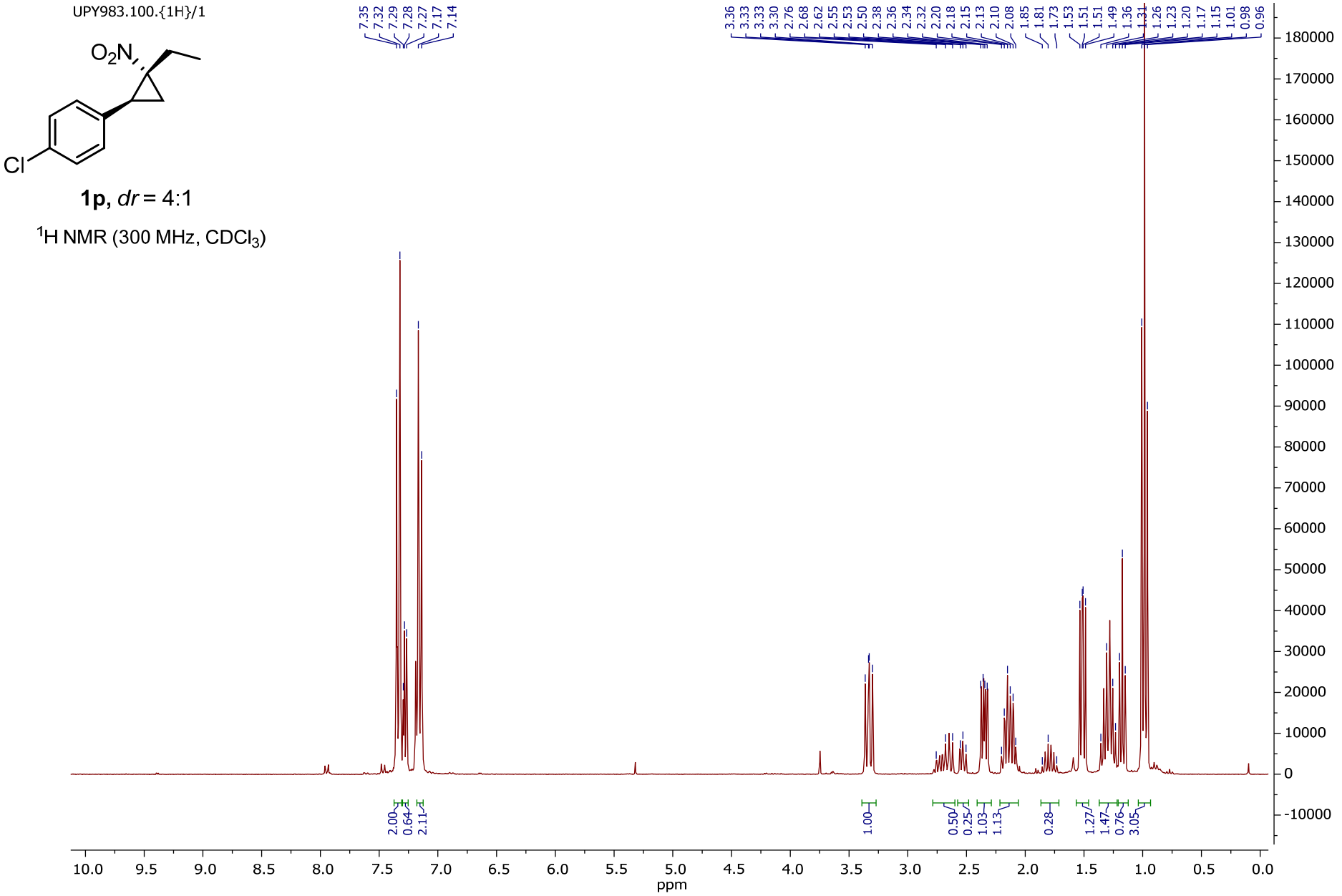
NMR of **1o**


UPY971.100-1.{1H-13C}HSQC/5
O
O
O2N
1o
1H - 13C HSQC NMR
(CDCl3)
5
10
15
20
25
30
35
40
45
50
55
60
65
f1 (мд)
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
ppm

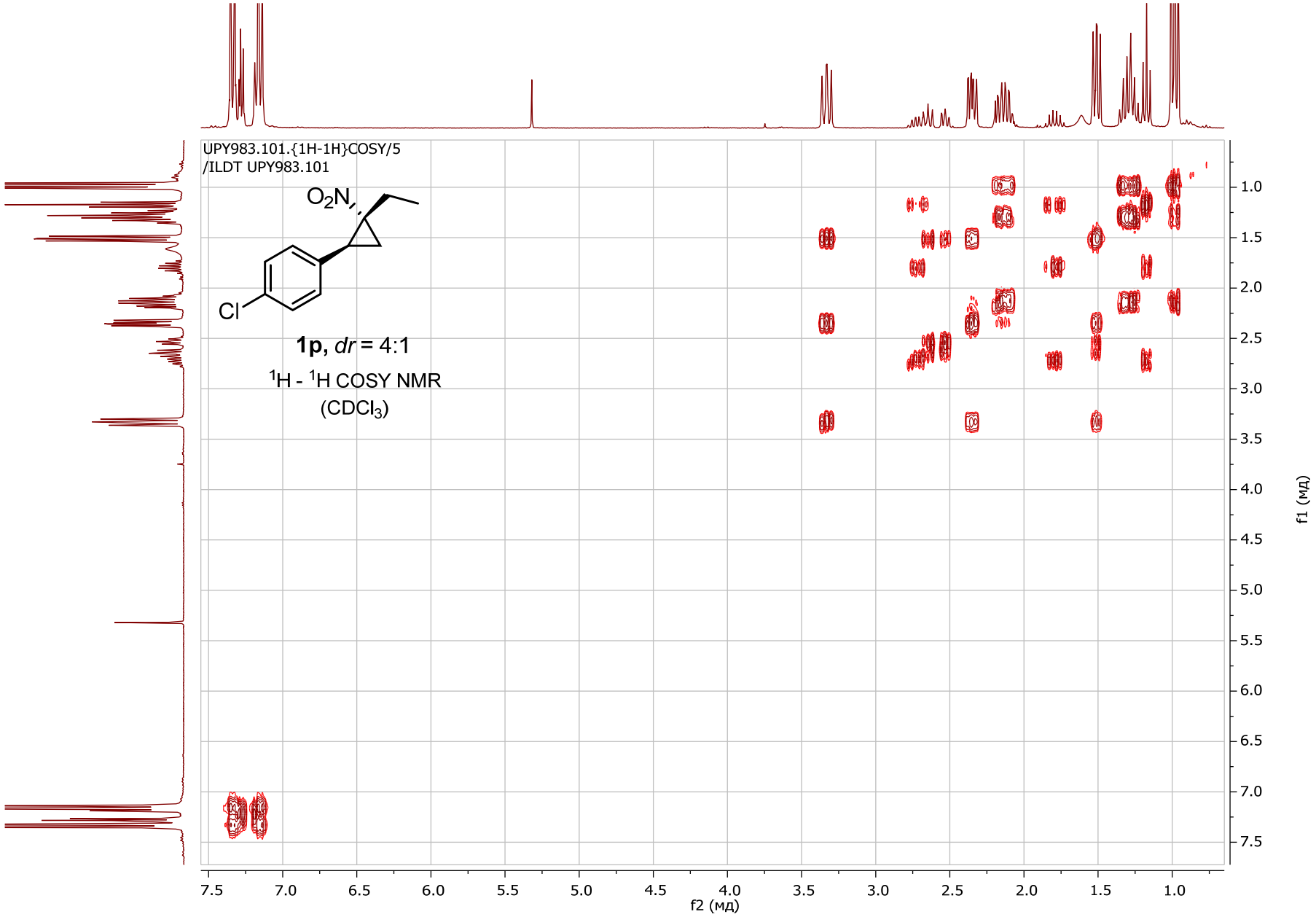
NMR of **1o**


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.23 MHz {1H-1H}NOESY SI=1024x512 SW=2500 O1=1240 PW=14.7 AQ=0.379 RD=0.92 NS=8x144 SR=0.00 TE=298K 7 October 2022 Opr: NMR User; Solv: CDCl3;
/ILDT UPY971.100-1
The Best Applied NMR On-Line: "http://nmr.ioc.ac.ru:8080"
O2N
O
O
1o
1H - 1H NOESY NMR
(CDCl3)
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

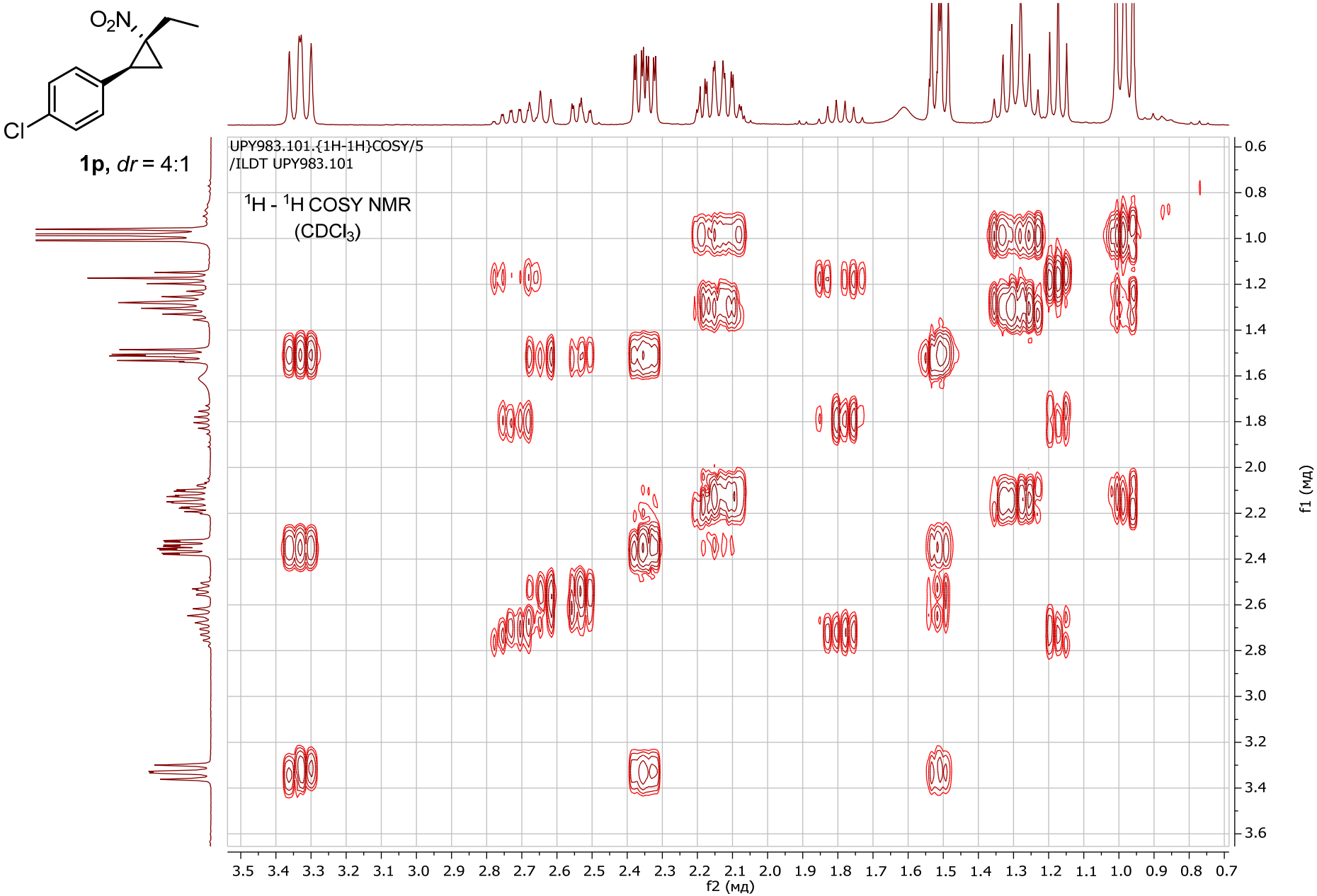
NMR of **1p**


UPY983.100.{1H}/1
O2N
Cl
1p, dr = 4:1
1H NMR (300 MHz, CDCl3)
7.35 7.32 7.29 7.28 7.27 7.17 7.14
3.36 3.33 3.33 3.30 2.76 2.68 2.62 2.55 2.53 2.50 2.38 2.36 2.34 2.32 2.20 2.18 2.15 2.13 2.10 2.08 1.85 1.81 1.73 1.53 1.51 1.51 1.49 1.36 1.31 1.26 1.23 1.20 1.17 1.15 1.01 0.98 0.96
2.00 0.64 2.11 1.00 0.50 0.25 1.03 1.13 0.28 1.27 1.47 0.76 3.05
ppm

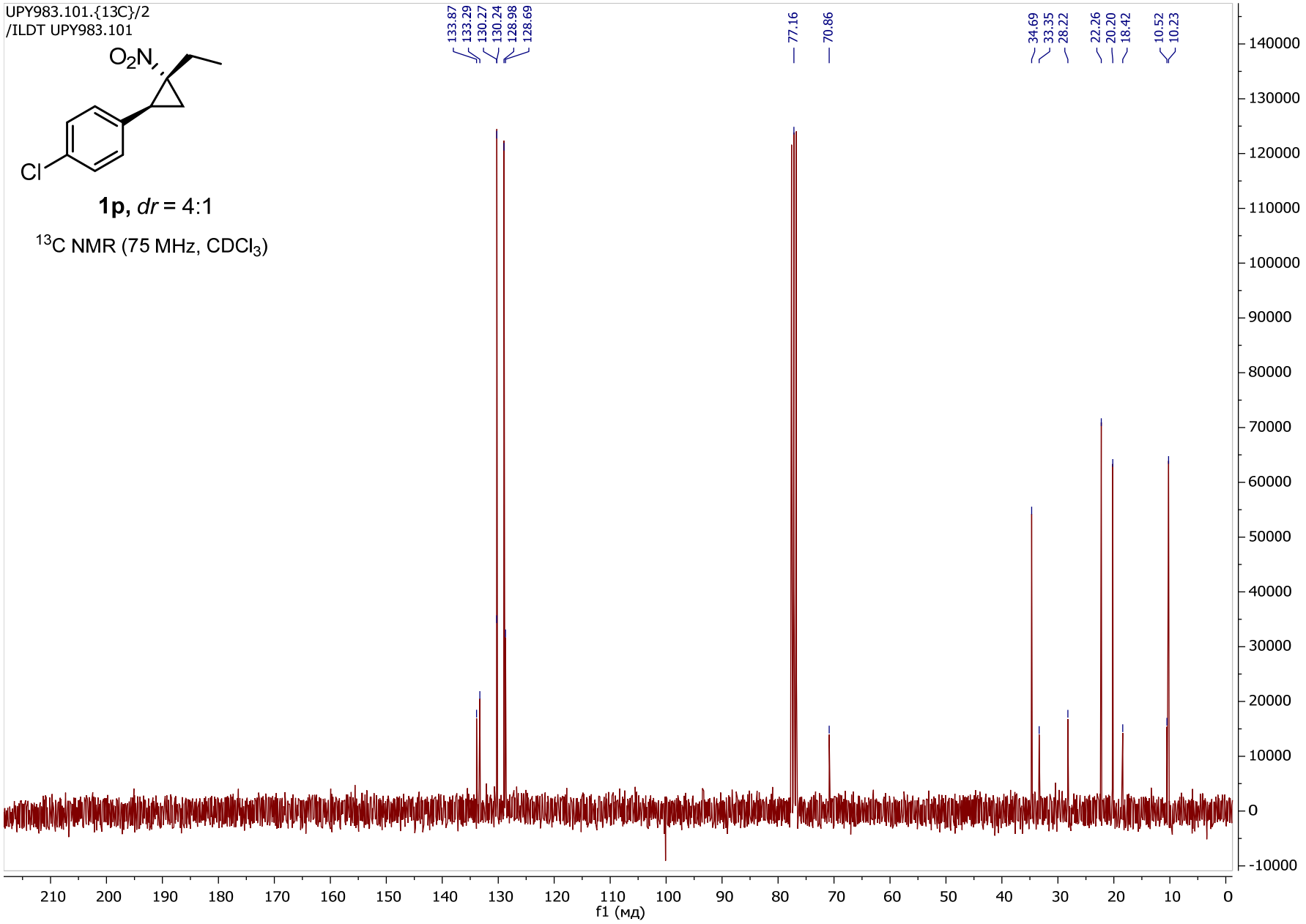
NMR of **1p**


UPY983.101.{1H-1H}COSY/5
/ILDT UPY983.101
O2N
Cl
1p, dr = 4:1
1H - 1H COSY NMR
(CDCl3)
f2 (мд)
f1 (мд)

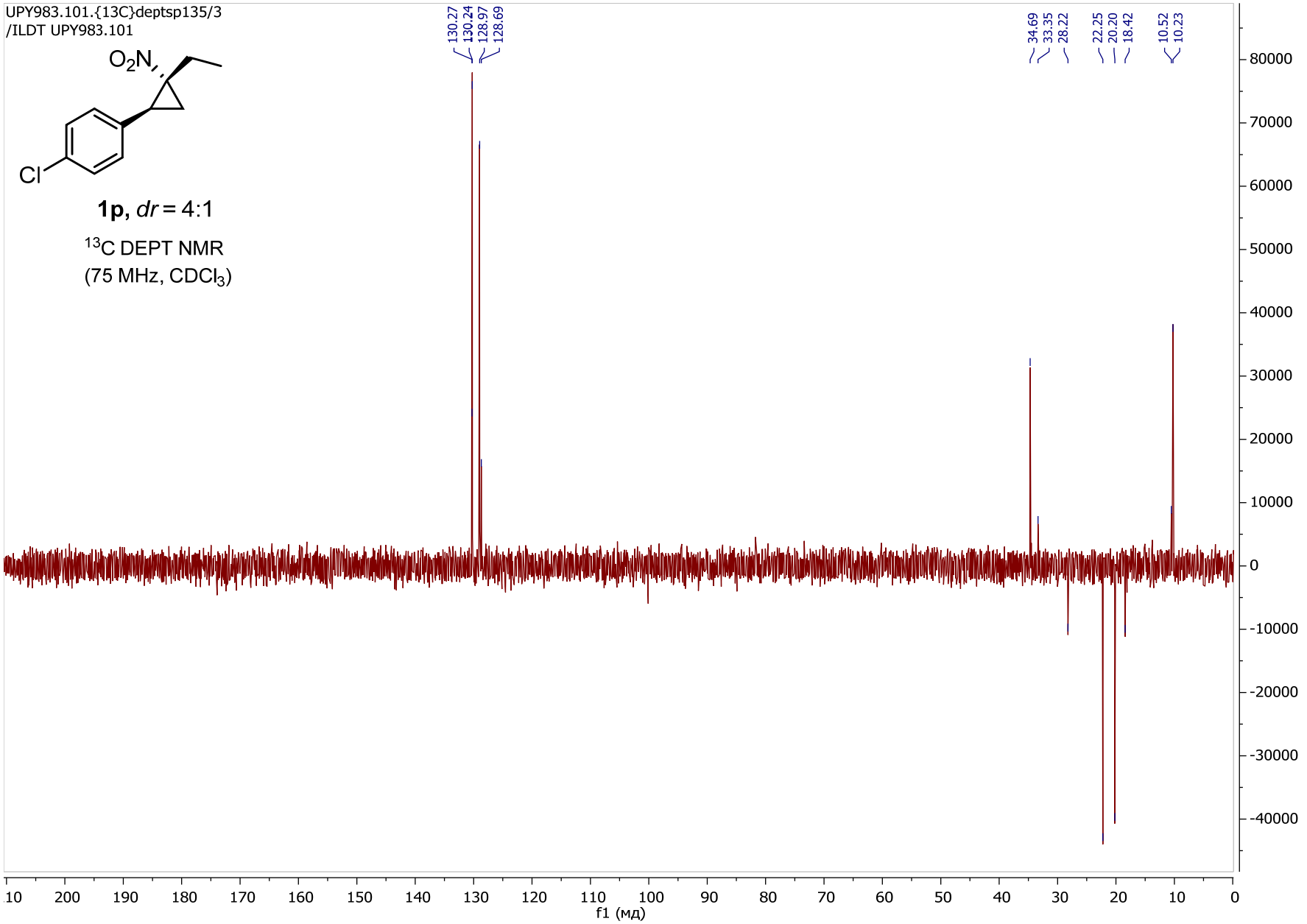
NMR of **1p**


O2N
Cl
1p, dr = 4:1
UPY983.101.{1H-1H}COSY/5
/ILDT UPY983.101
1H - 1H COSY NMR
(CDCl3)
f2 (мд)
f1 (мд)

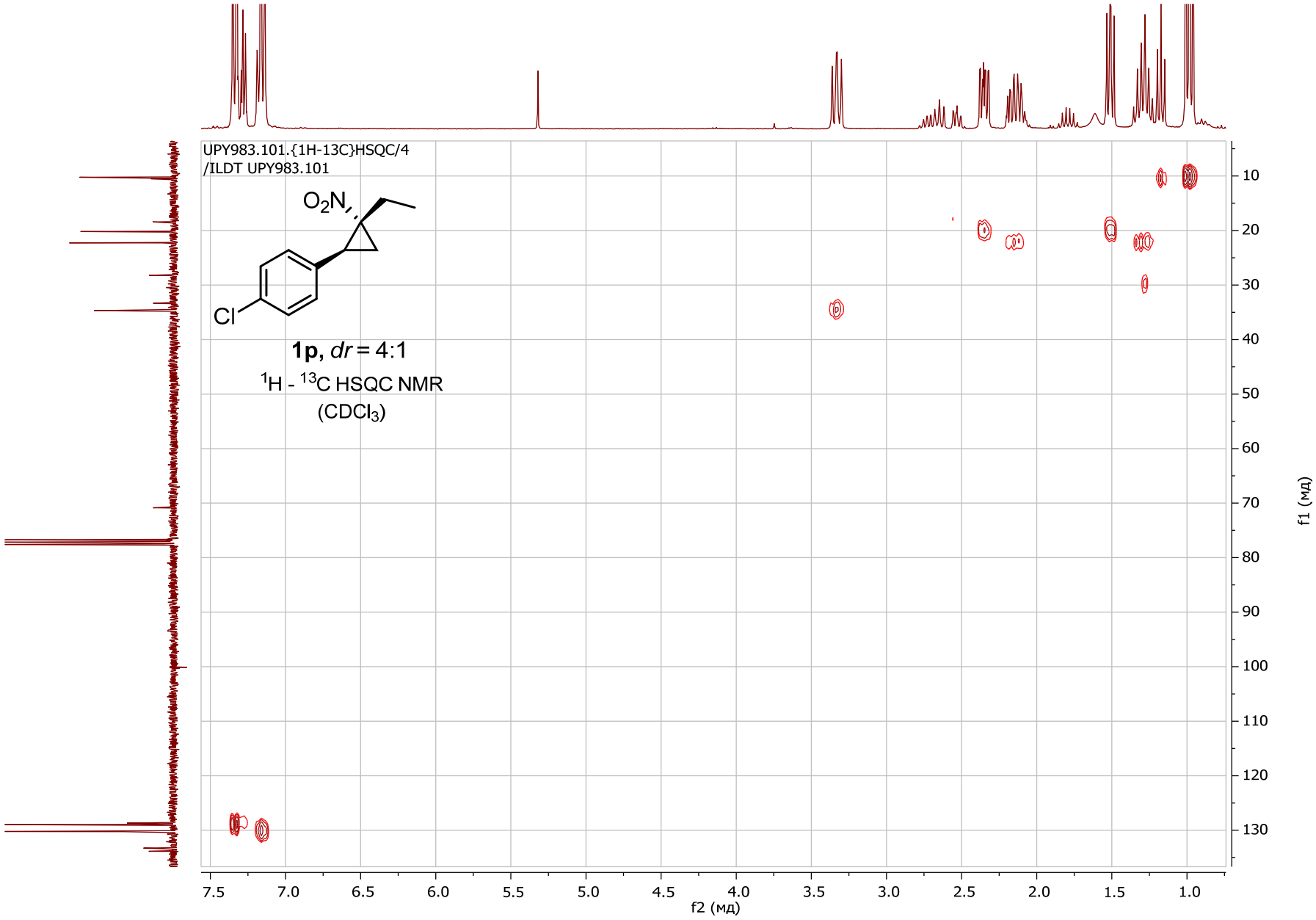
NMR of **1p**


UPY983.101.{13C}/2
/ILDT UPY983.101
O2N
Cl
1p, dr = 4:1
13C NMR (75 MHz, CDCl3)
133.87
133.29
130.27
130.24
128.98
128.69
77.16
70.86
34.69
33.35
28.22
22.26
20.20
18.42
10.52
10.23
f1 (мд)

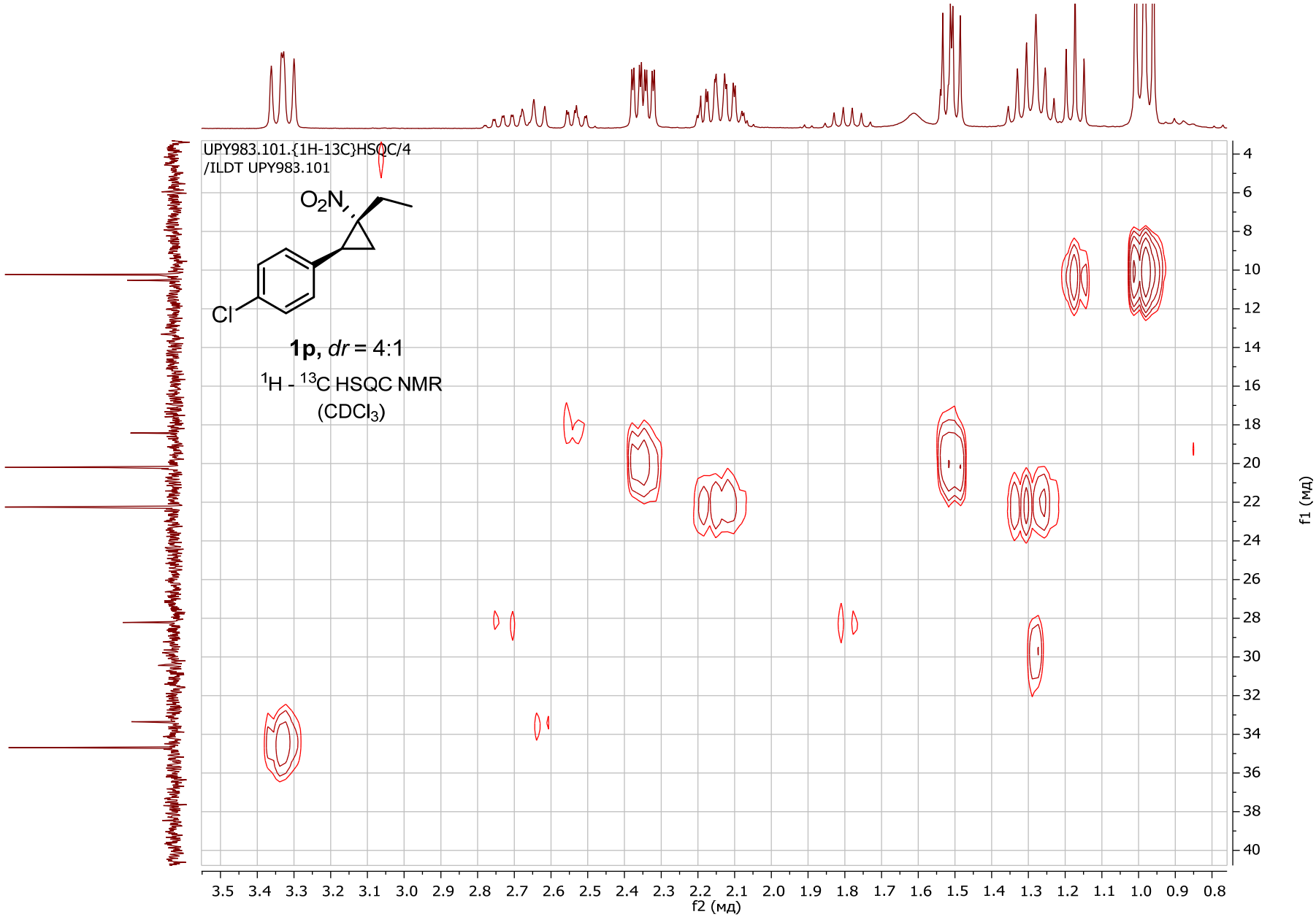
NMR of **1p**


UPY983.101.{13C}deptsp135/3
/ILDT UPY983.101
O2N
Cl
1p, dr = 4:1
13C DEPT NMR
(75 MHz, CDCl3)
130.27
130.24
128.97
128.69
34.69
33.35
28.22
22.25
20.20
18.42
10.52
10.23
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

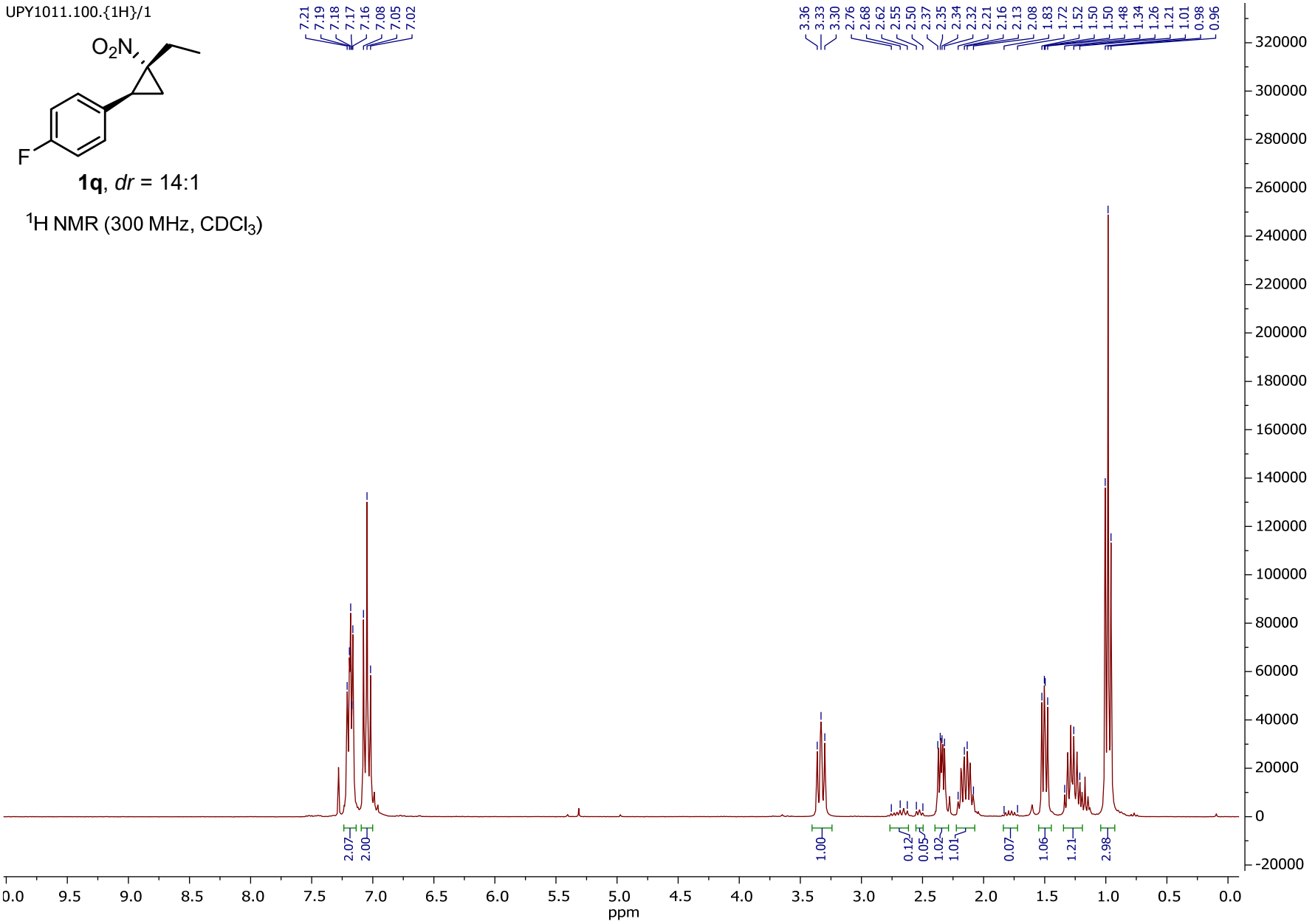
NMR of **1p**


UPY983.101.{1H-13C}HSQC/4
/ILDT UPY983.101
O2N
Cl
1p, dr = 4:1
1H - 13C HSQC NMR
(CDCl3)
f2 (мд)
f1 (мд)

NMR of **1p**

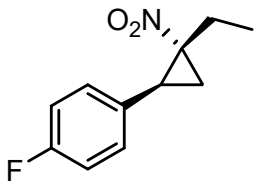

UPY983.101.{1H-13C}HSQC/4
/ILDT UPY983.101
O2N
Cl
1p, dr = 4:1
1H - 13C HSQC NMR
(CDCl3)
f2 (мд)
f1 (мд)

NMR of **1q**


UPY1011.100.{1H}/1
O2N
F
1q, dr = 14:1
1H NMR (300 MHz, CDCl3)
7.21 7.19 7.18 7.17 7.16 7.08 7.05 7.02
3.36 3.33 3.30 2.76 2.68 2.62 2.55 2.50 2.37 2.35 2.34 2.32 2.21 2.16 2.13 2.08 1.83 1.72 1.52 1.50 1.50 1.48 1.34 1.26 1.21 1.01 0.98 0.96
2.07 2.00 1.00 0.12 0.05 1.02 1.01 0.07 1.06 1.21 2.98
ppm

NMR of **1q**

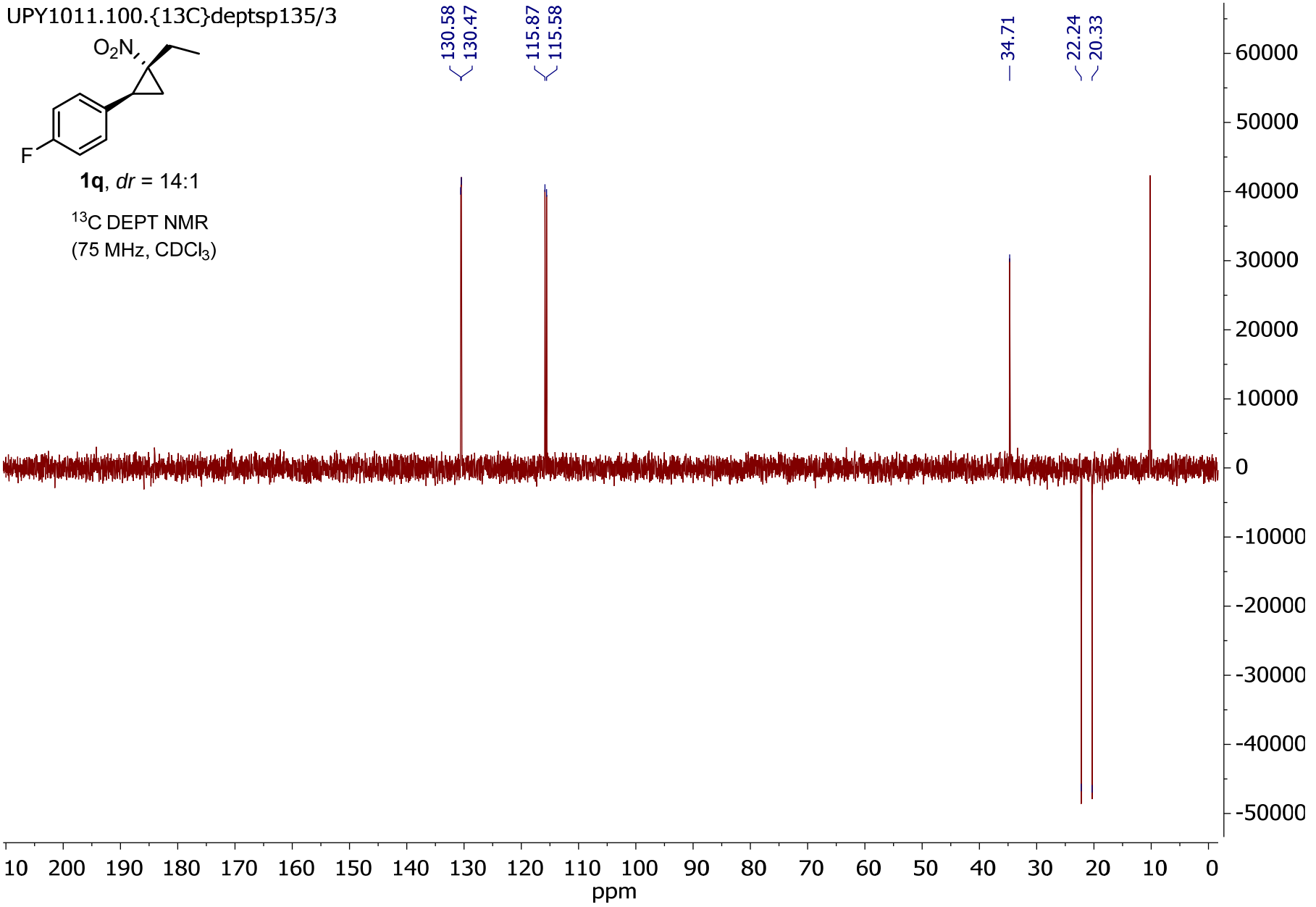
UPY1011.100.{13C}/2



1q, *dr* = 14:1

^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **1q**

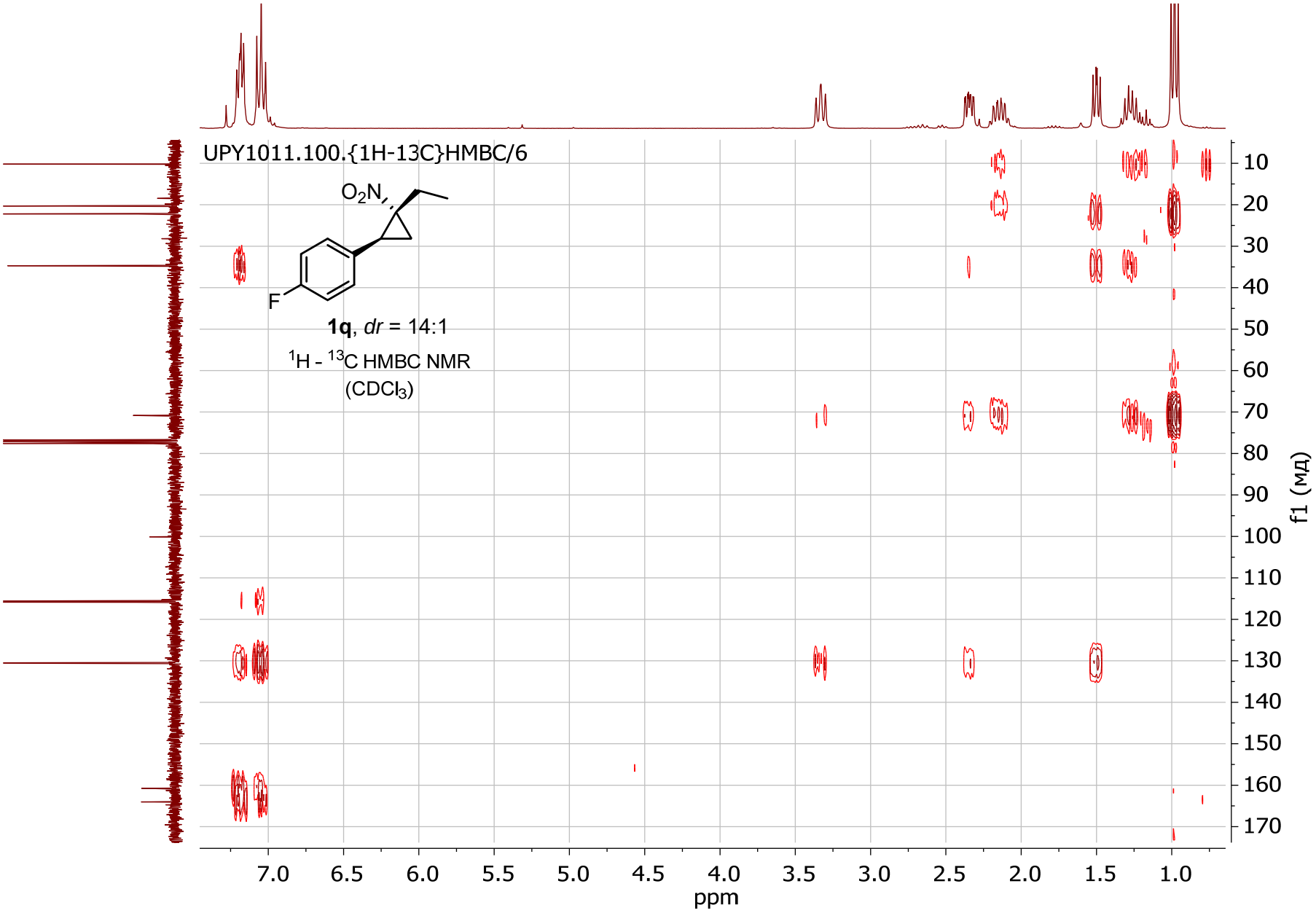


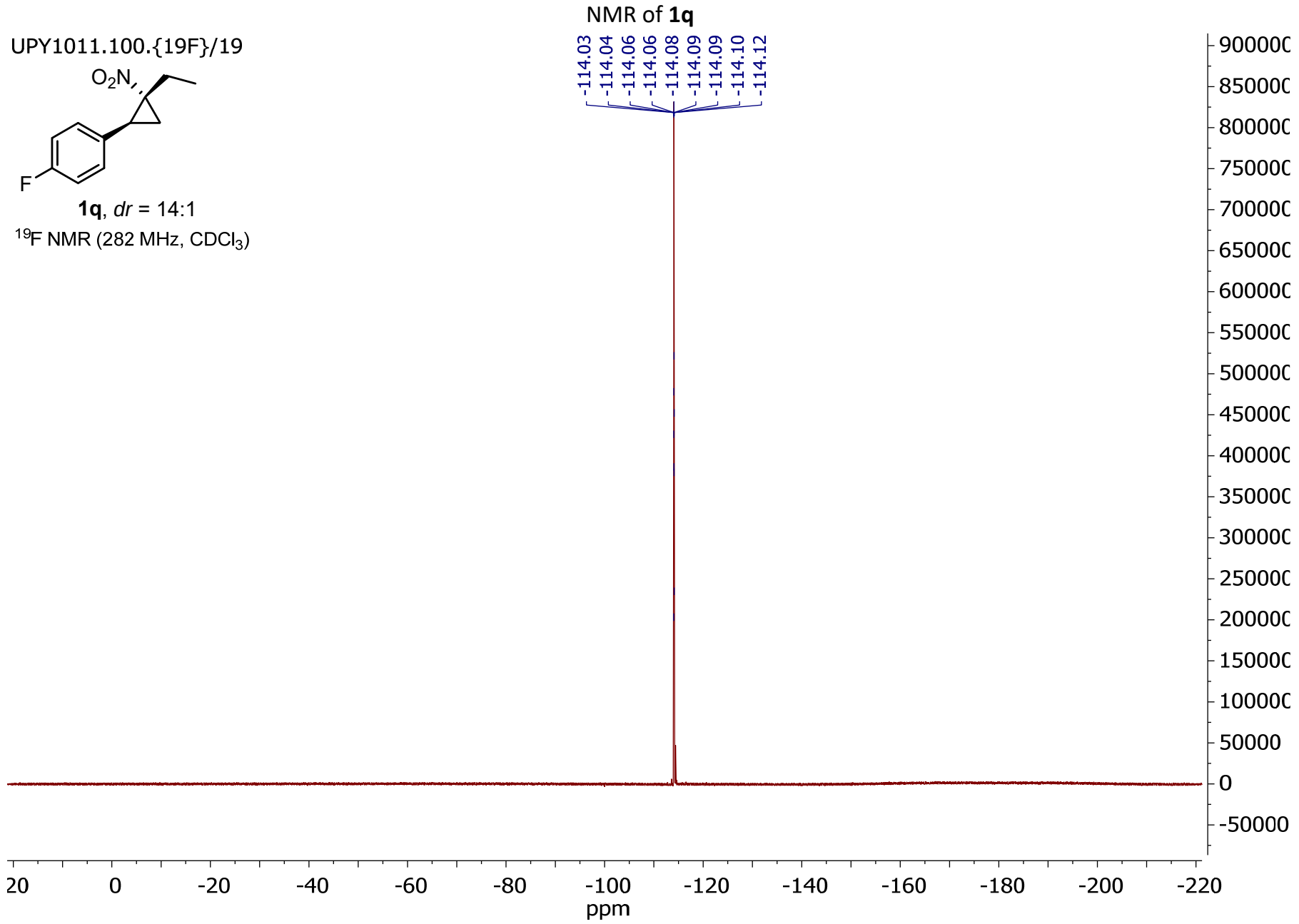
1q, *dr* = 14:1

^{13}C DEPT NMR

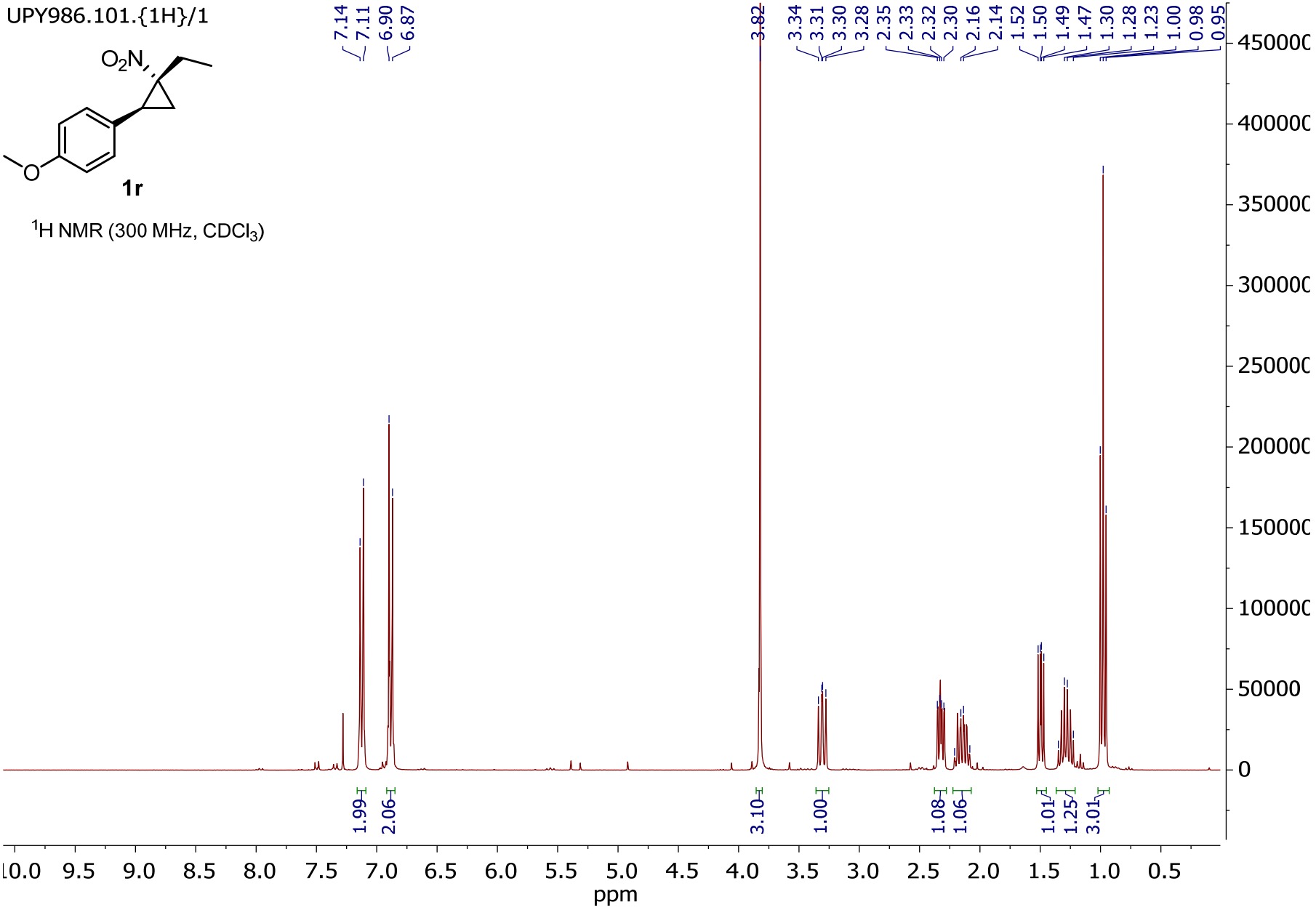
(75 MHz, $CDCl_3$)

NMR of **1q**

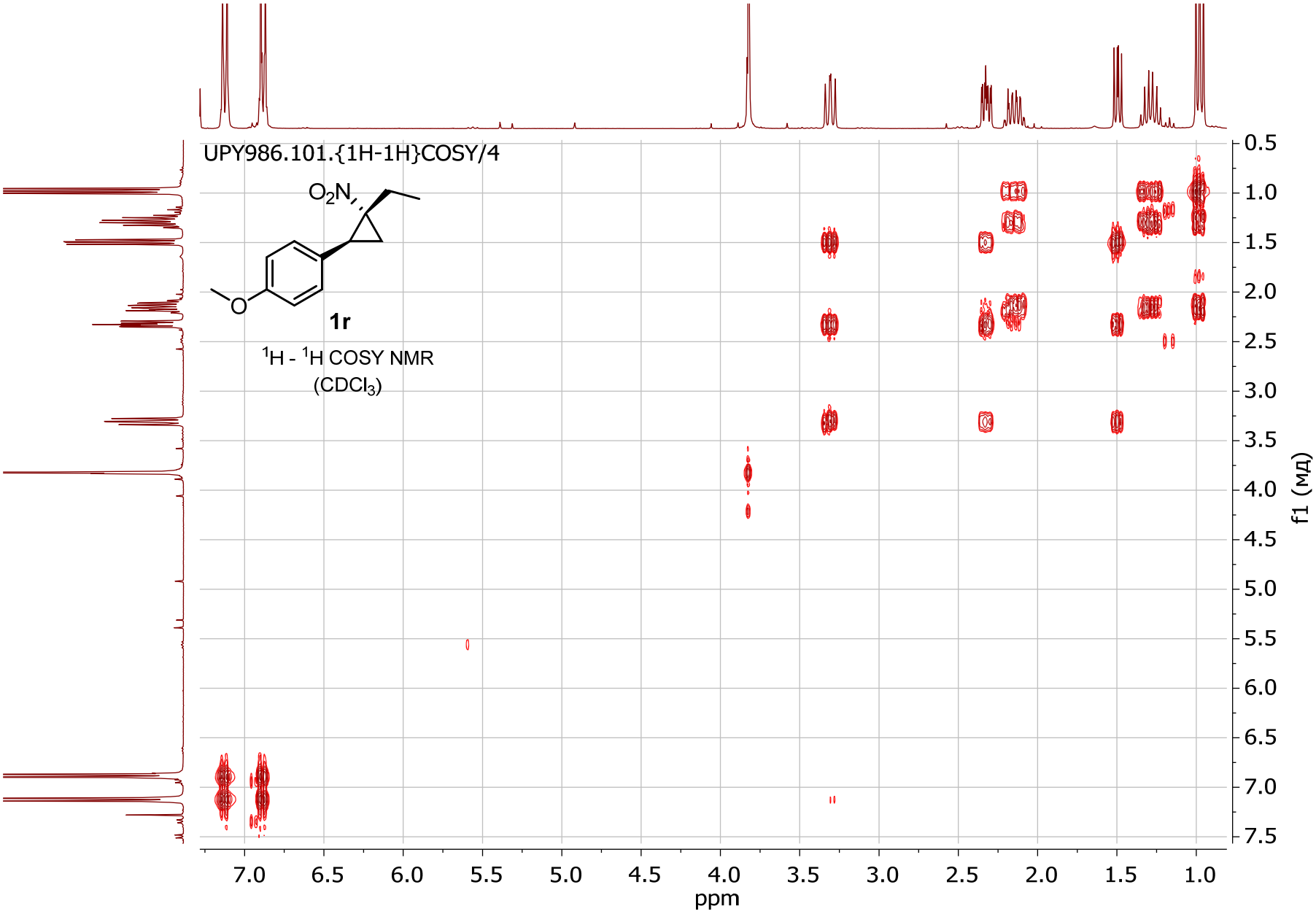

UPY1011.100.{1H-13C}HMBC/6
O2N
F
1q, dr = 14:1
1H - 13C HMBC NMR
(CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (мд)


NMR of 1q
UPY1011.100.{19F}/19
O2N
F
1q, dr = 14:1
19F NMR (282 MHz, CDCl3)
-114.03
-114.04
-114.06
-114.06
-114.08
-114.09
-114.09
-114.10
-114.12
90000
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
50000
0
-50000
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
ppm

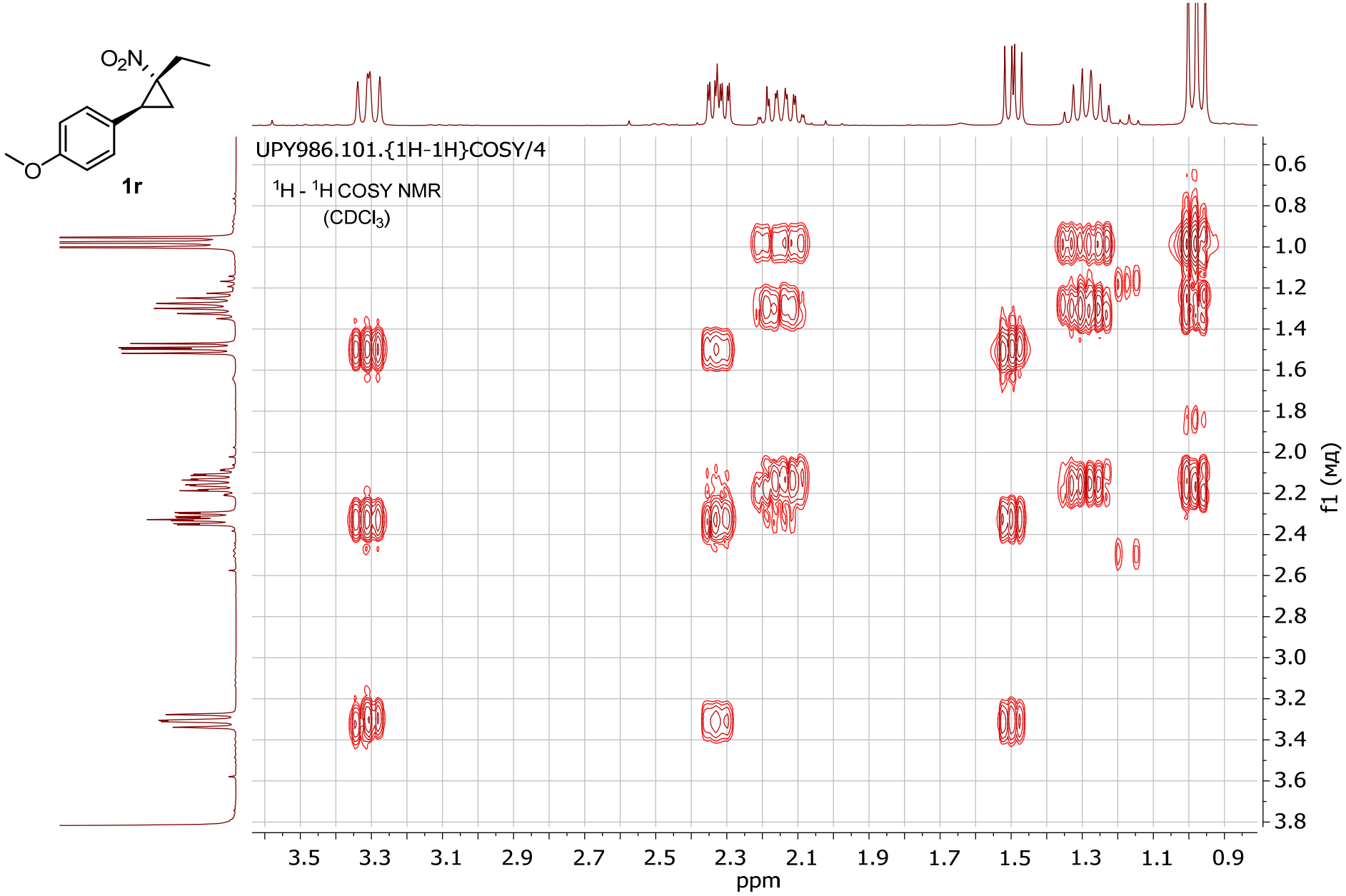
NMR of **1r**


UPY986.101.{1H}/1
O_2N
O
1r
^{1}H NMR (300 MHz, $CDCl_3$)
7.14
7.11
6.90
6.87
3.82
3.34
3.31
3.30
3.28
2.35
2.33
2.32
2.30
2.16
2.14
1.52
1.50
1.49
1.47
1.30
1.28
1.23
1.00
0.98
0.95
1.99
2.06
3.10
1.00
1.08
1.06
1.01
1.25
3.01
45000
40000
35000
30000
25000
20000
15000
10000
50000
0
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

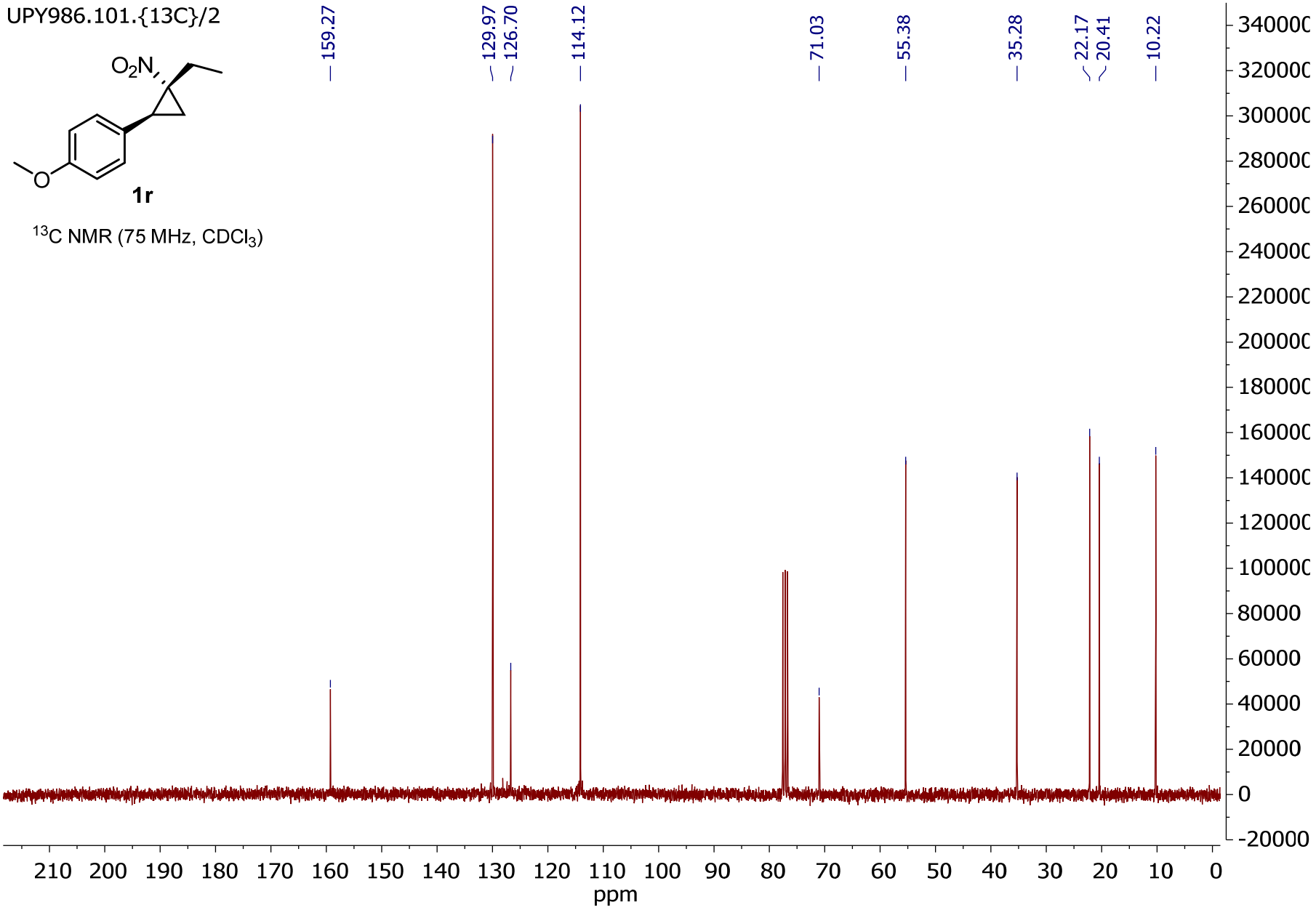
NMR of **1r**



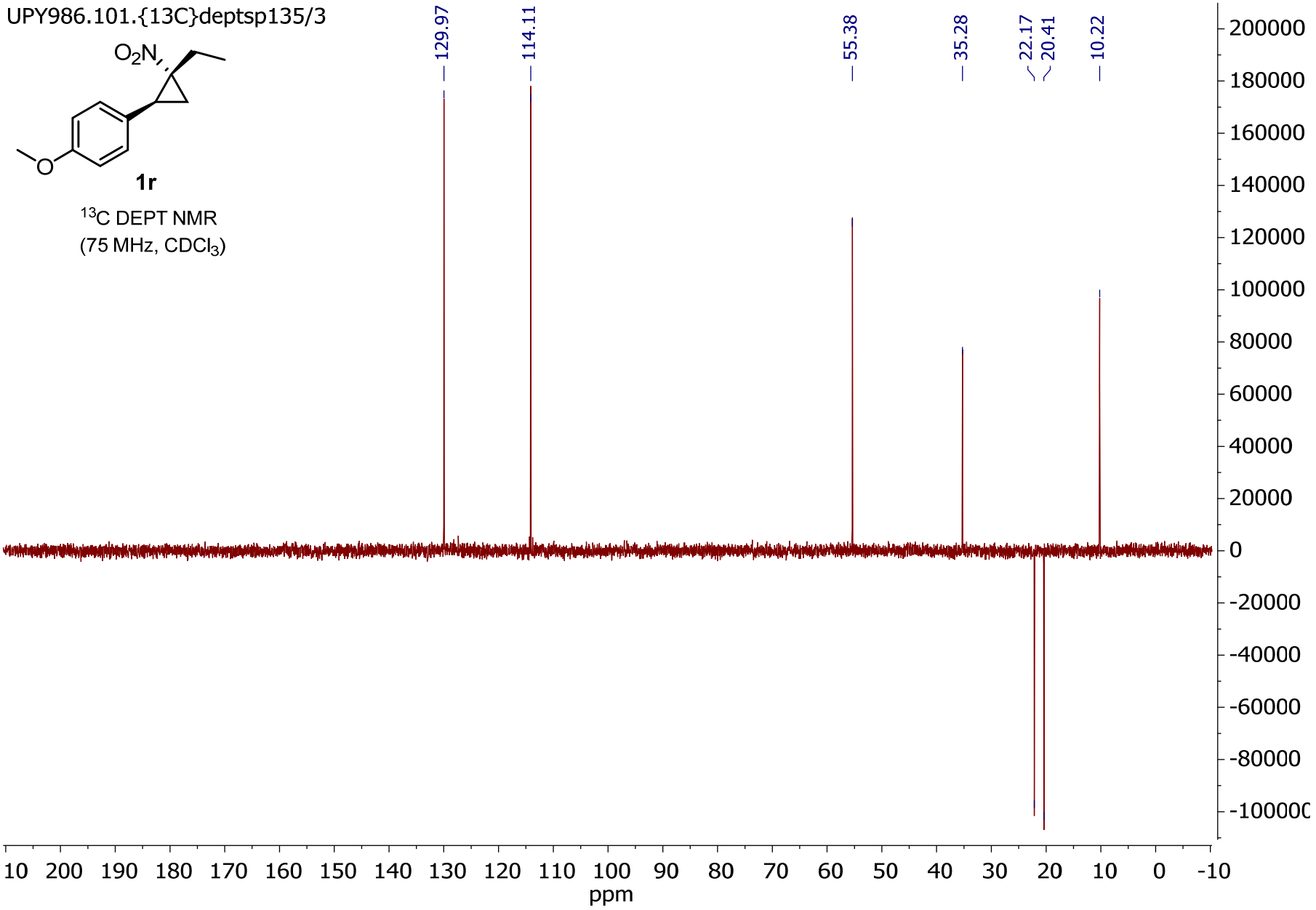
NMR of **1r**


O2N
O
1r
UPY986.101.{1H-1H}COSY/4
1H - 1H COSY NMR
(CDCl3)
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
f1 (мд)
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
ppm

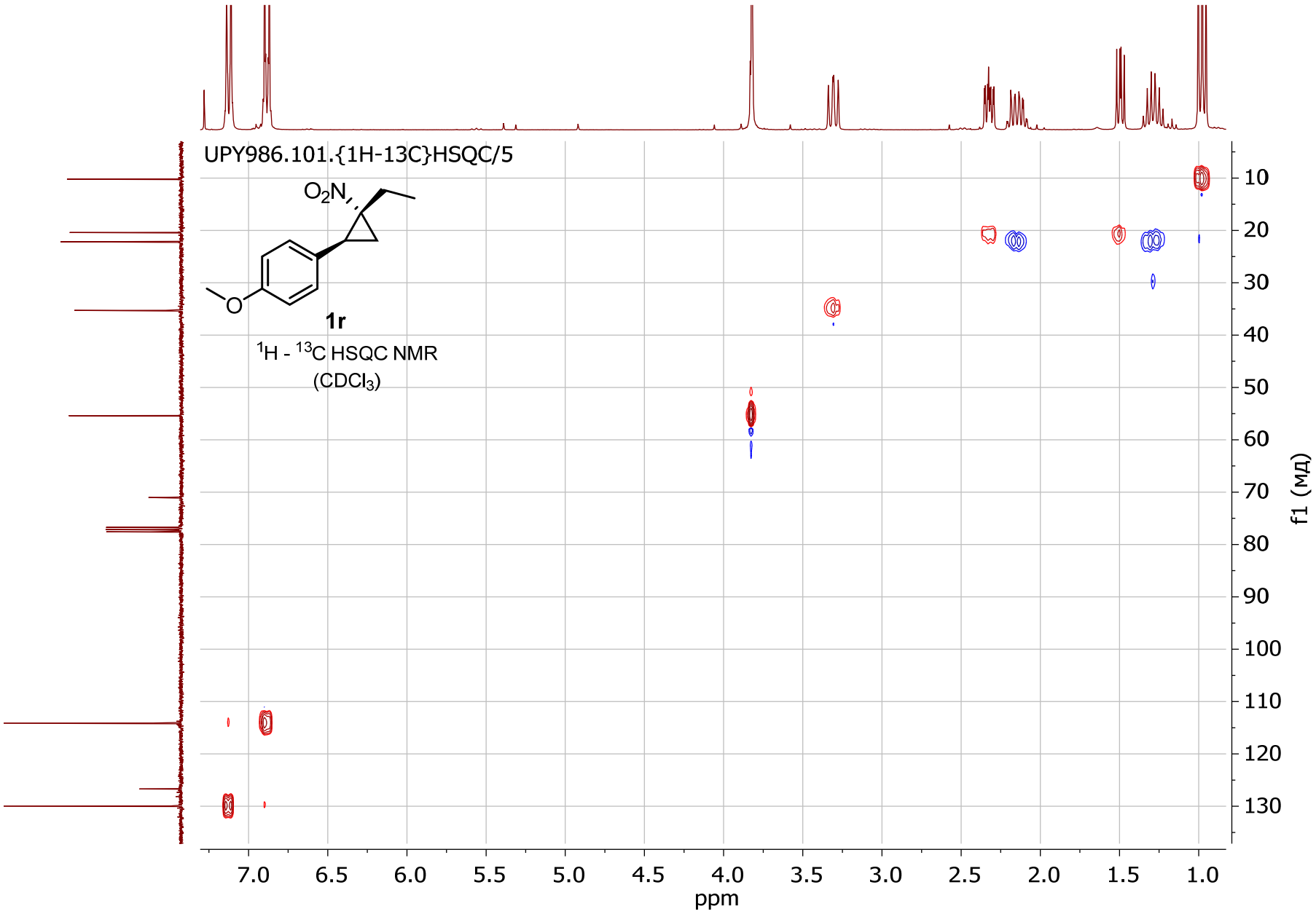
NMR of **1r**


UPY986.101.{13C}/2
O_2N
O
1r
^{13}C NMR (75 MHz, $CDCl_3$)
159.27
129.97
126.70
114.12
71.03
55.38
35.28
22.17
20.41
10.22
ppm

NMR of **1r**

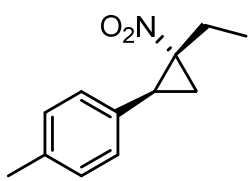

UPY986.101.{13C}deptsp135/3
O_2N
O
1r
^{13}C DEPT NMR
(75 MHz, $CDCl_3$)
129.97
114.11
55.38
35.28
22.17
20.41
10.22
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
-60000
-80000
-100000
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

NMR of **1r**


UPY986.101.{1H-13C}HSQC/5
O2N
O
1r
1H - 13C HSQC NMR
(CDCl3)
10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (мд)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

NMR of **1s**

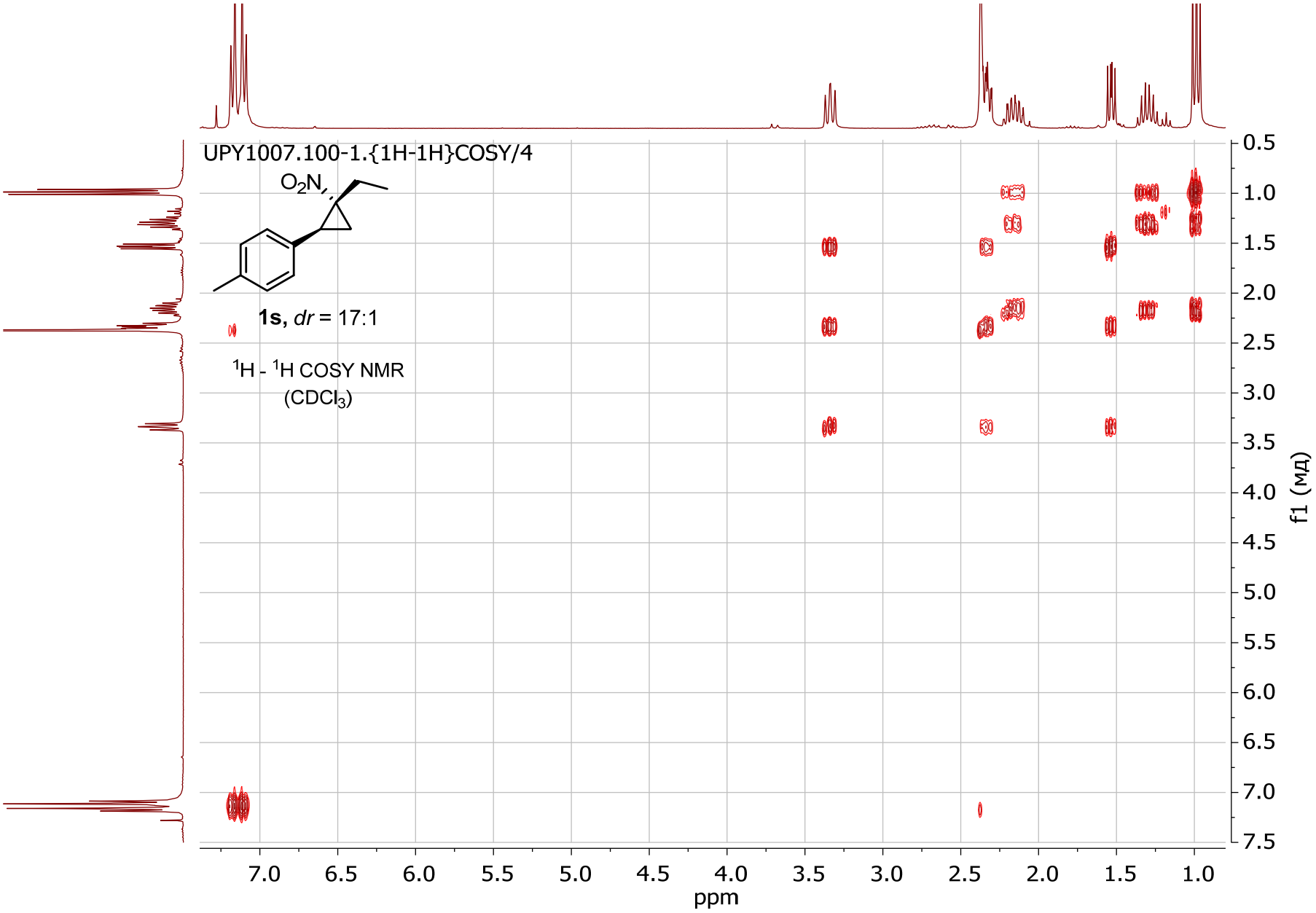
UPY1007.100-1.{1H}/1

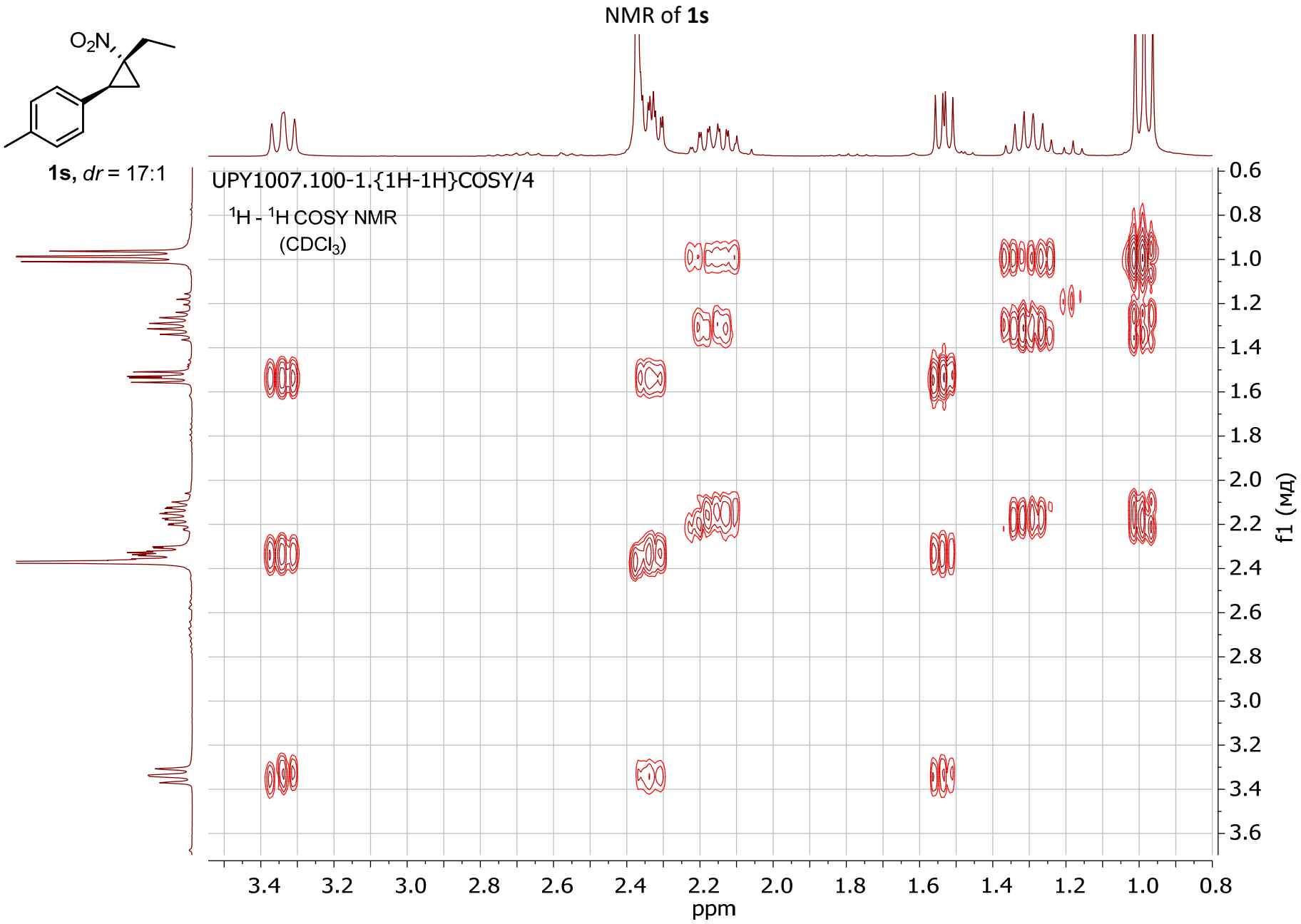


1s, *dr* = 17:1

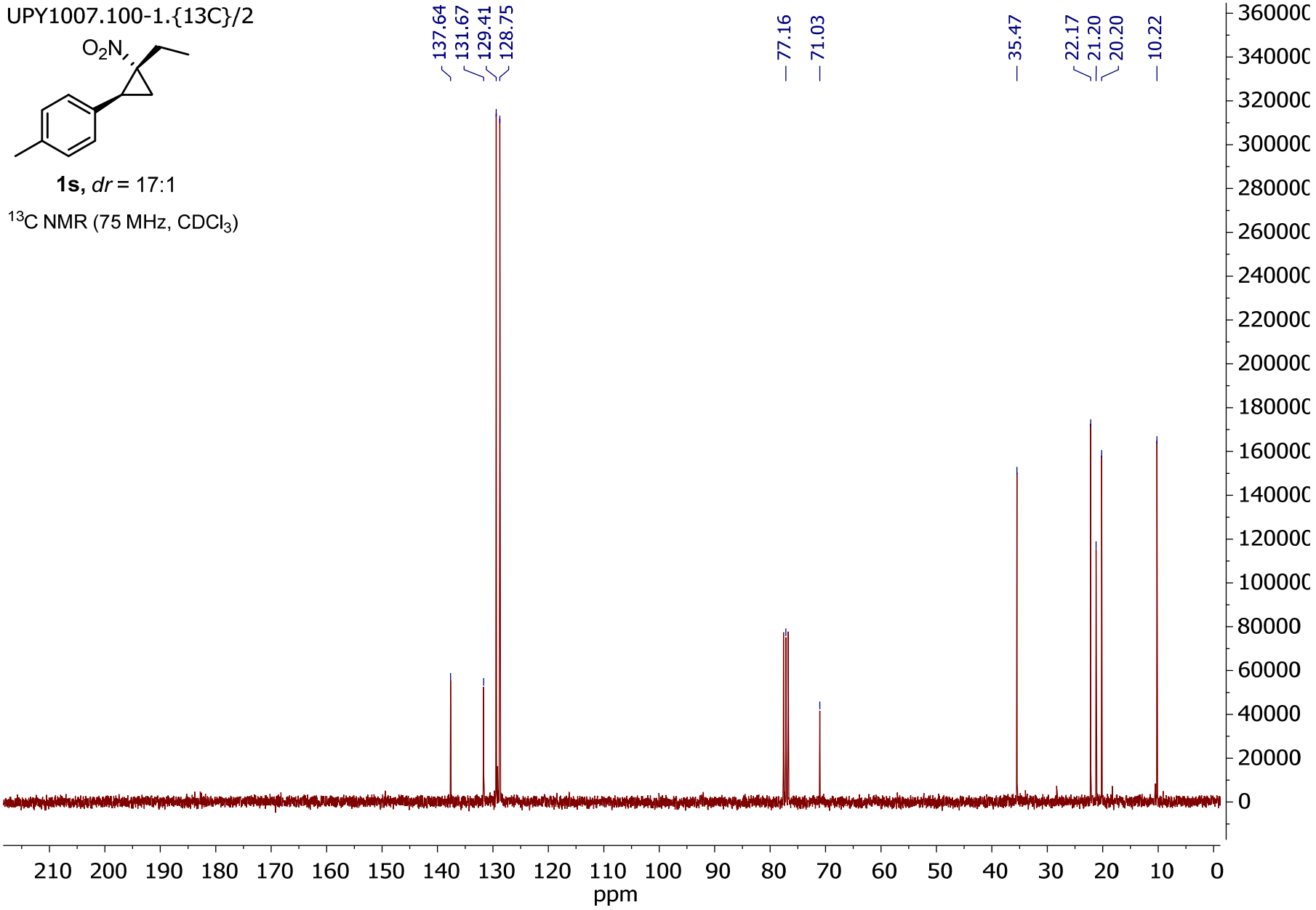
^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **1s**

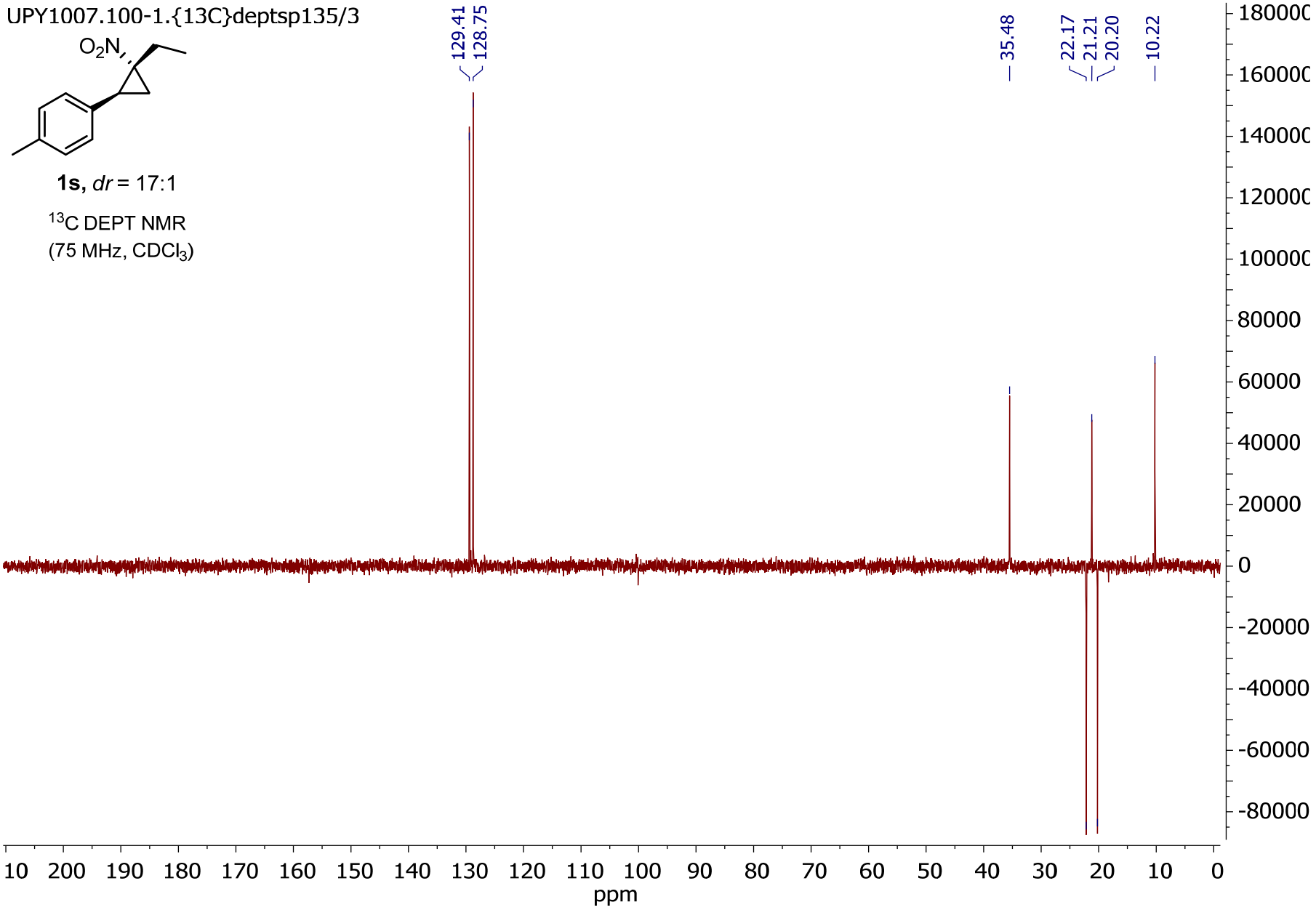

UPY1007.100-1.{1H-1H}COSY/4
O2N
1s, dr = 17:1
1H - 1H COSY NMR
(CDCl3)
ppm
f1 (мд)


NMR of **1s**
O_2N
1s, *dr* = 17:1
UPY1007.100-1.{1H-1H}COSY/4
^1H - ^1H COSY NMR
($CDCl_3$)
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
ppm
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
f1 (мд)

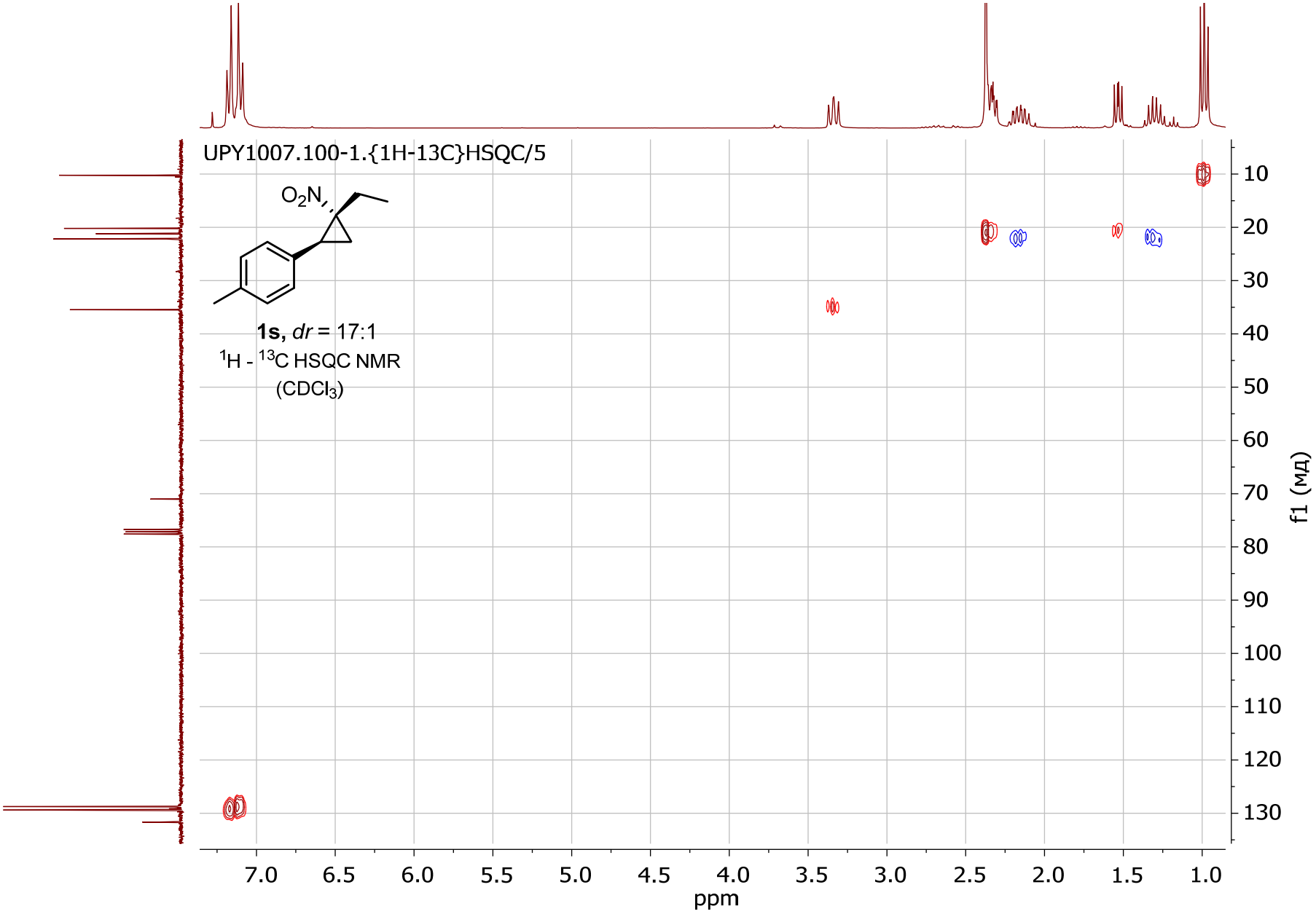
NMR of **1s**

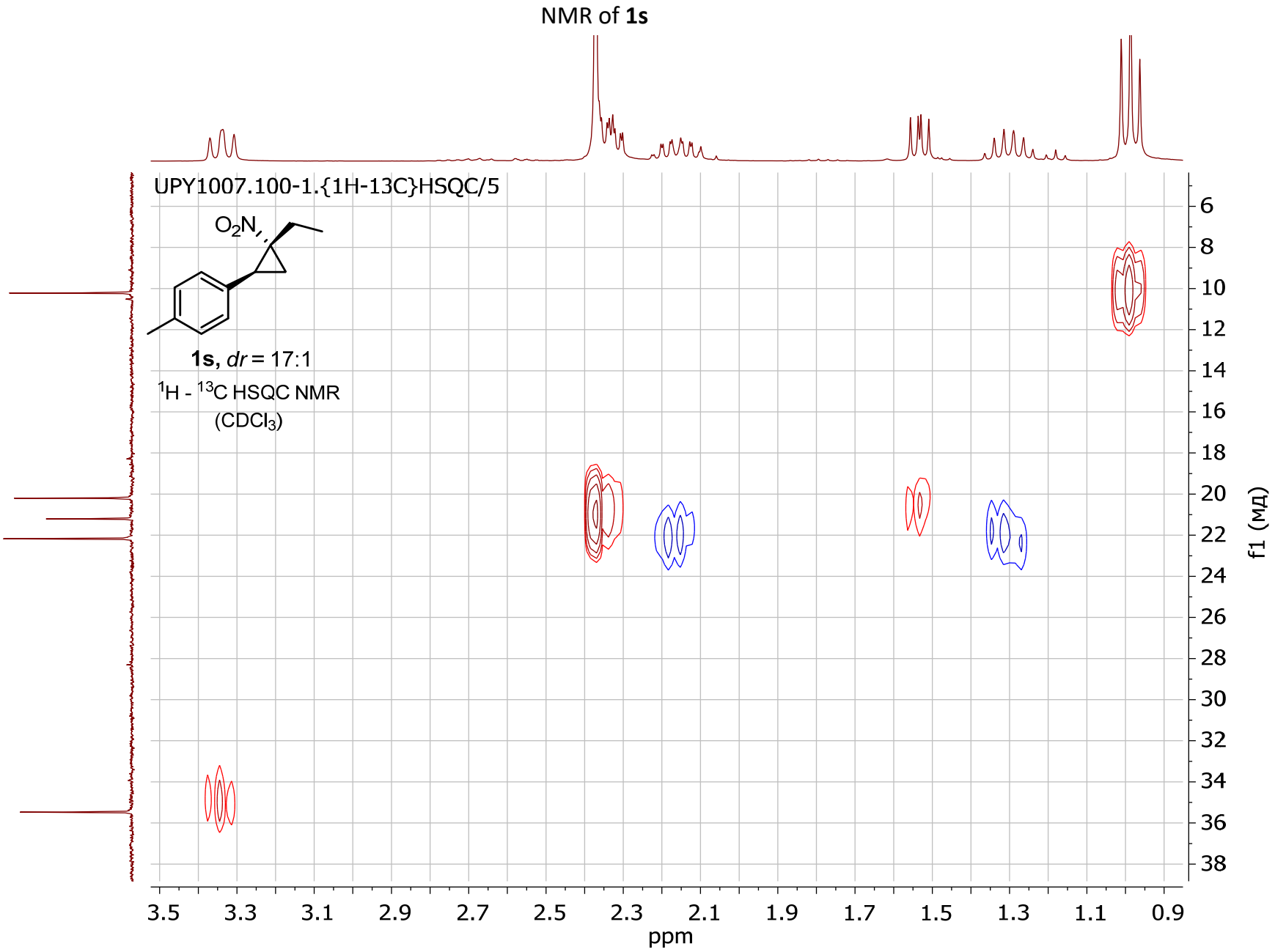

UPY1007.100-1.{13C}/2
O2N
1s, dr = 17:1
13C NMR (75 MHz, CDCl3)
137.64
131.67
129.41
128.75
77.16
71.03
35.47
22.17
21.20
20.20
10.22
ppm

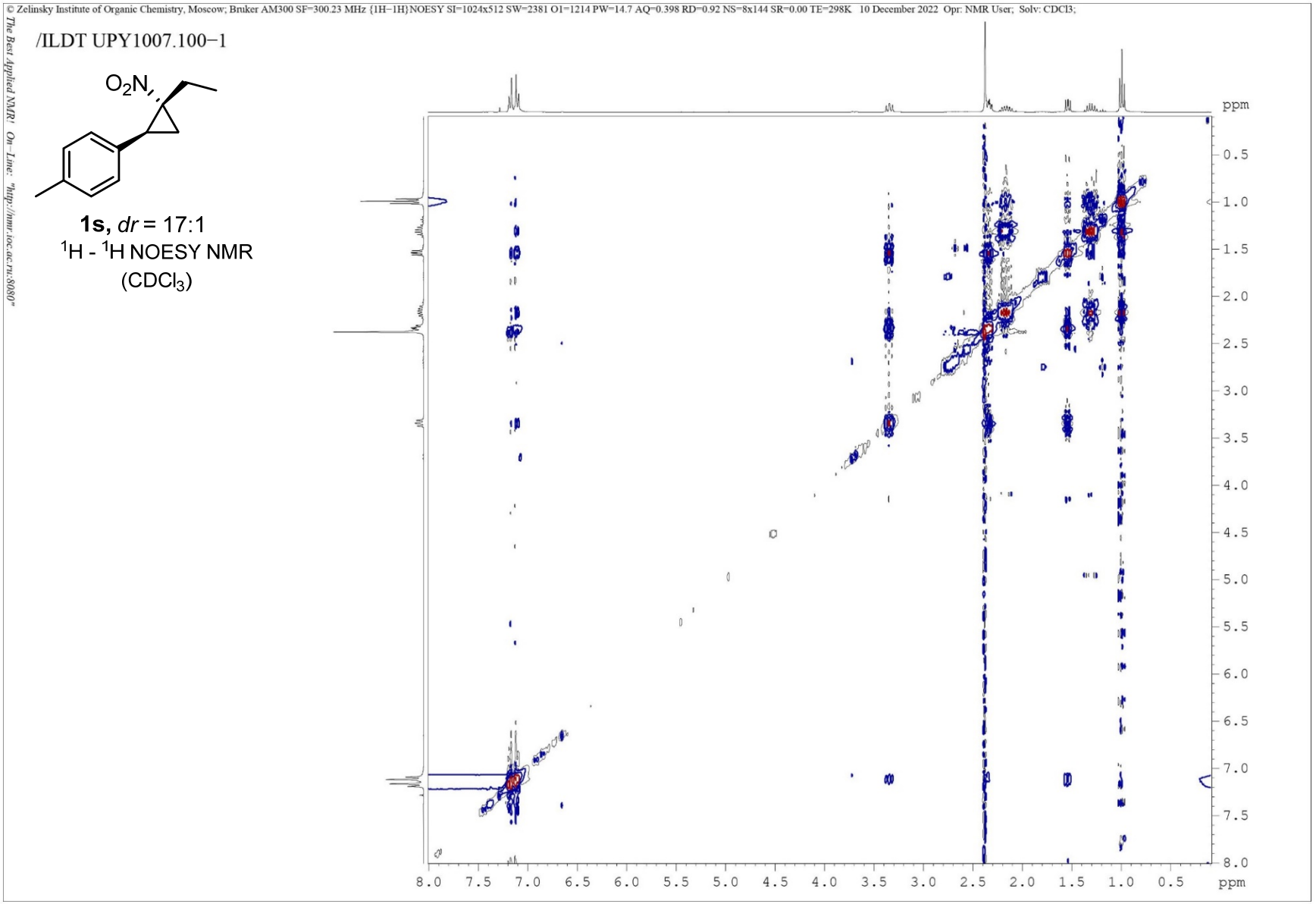
NMR of **1s**


UPY1007.100-1.{13C}deptsp135/3
O2N
1s, dr = 17:1
13C DEPT NMR
(75 MHz, CDCl3)
129.41
128.75
35.48
22.17
21.21
20.20
10.22
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
-60000
-80000
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

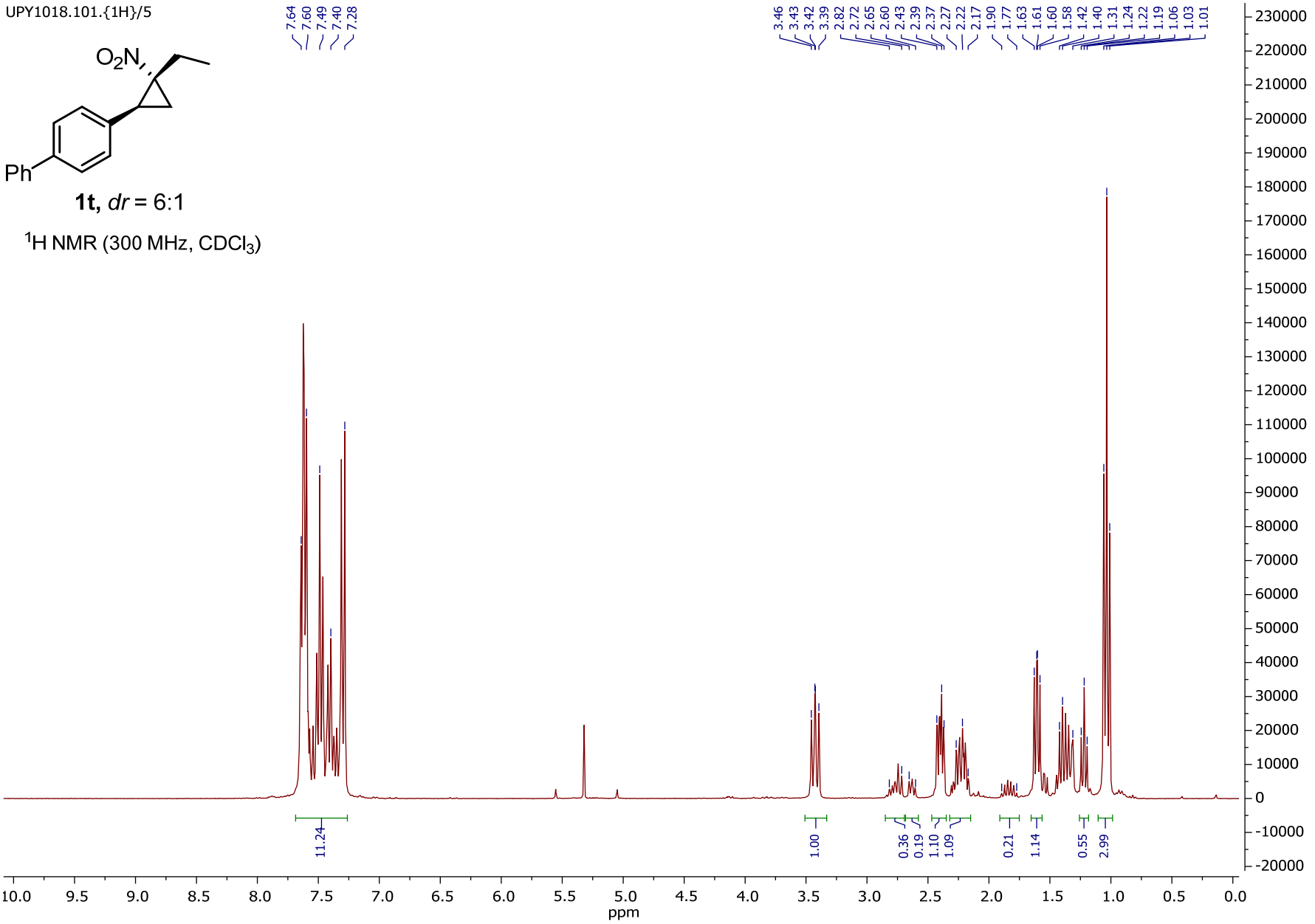
NMR of **1s**


UPY1007.100-1.{1H-13C}HSQC/5
O2N
1s, dr = 17:1
1H - 13C HSQC NMR
(CDCl3)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (мд)

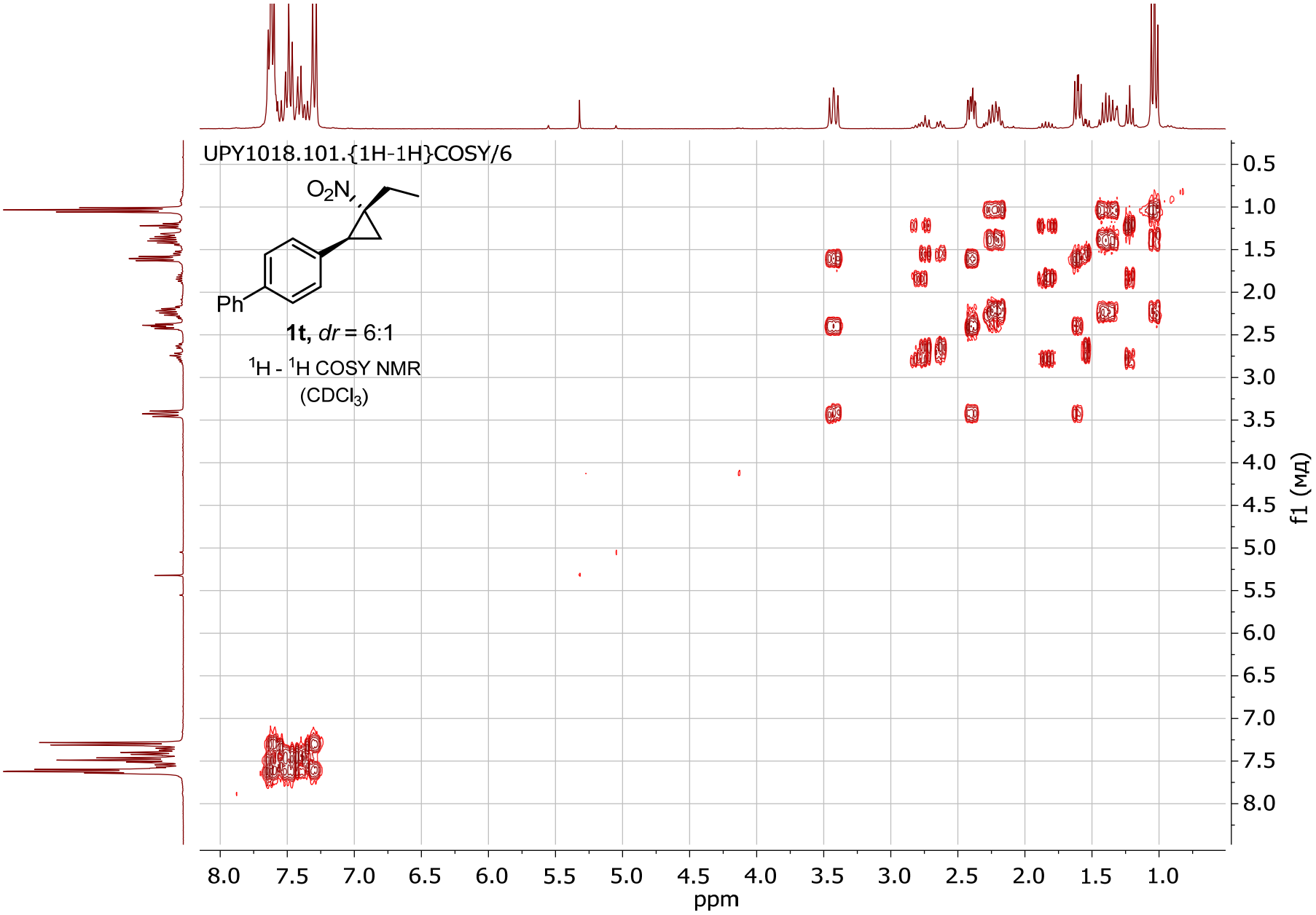

NMR of 1s
UPY1007.100-1.{1H-13C}HSQC/5
O2N
1s, dr = 17:1
1H - 13C HSQC NMR
(CDCl3)
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
ppm
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
f1 (мд)

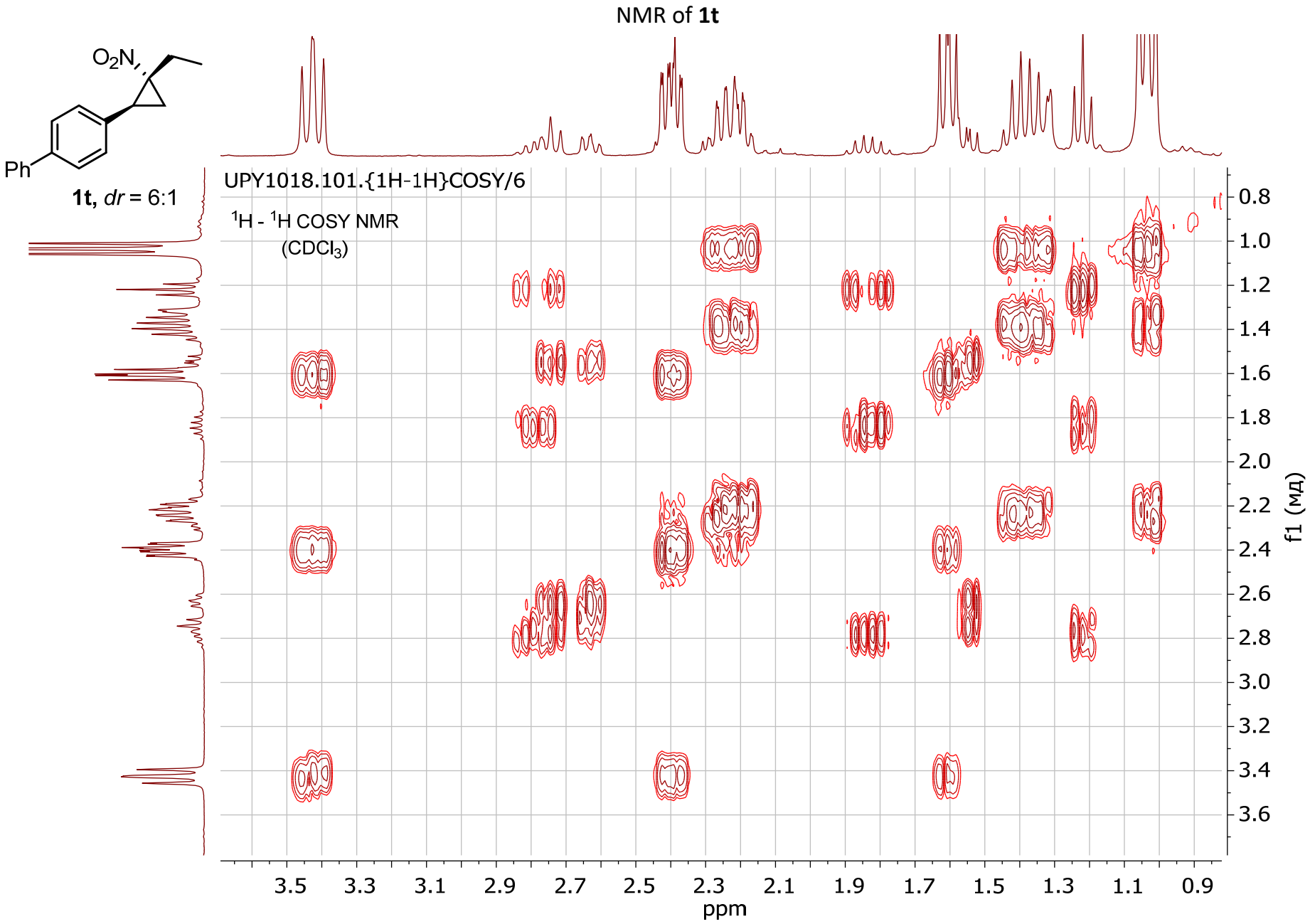

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.23 MHz {1H−1H}NOESY SI=1024x512 SW=2381 O1=1214 PW=14.7 AQ=0.398 RD=0.92 NS=8x144 SR=0.00 TE=298K 10 December 2022 Opr: NMR User; Solv: CDCl3;
The Best Applied NMR! On−Line: "http://nmr.ioc.ac.ru:8080"
/ILDT UPY1007.100−1
O2N
1s, dr = 17:1
1H - 1H NOESY NMR
(CDCl3)
ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

NMR of **1t**

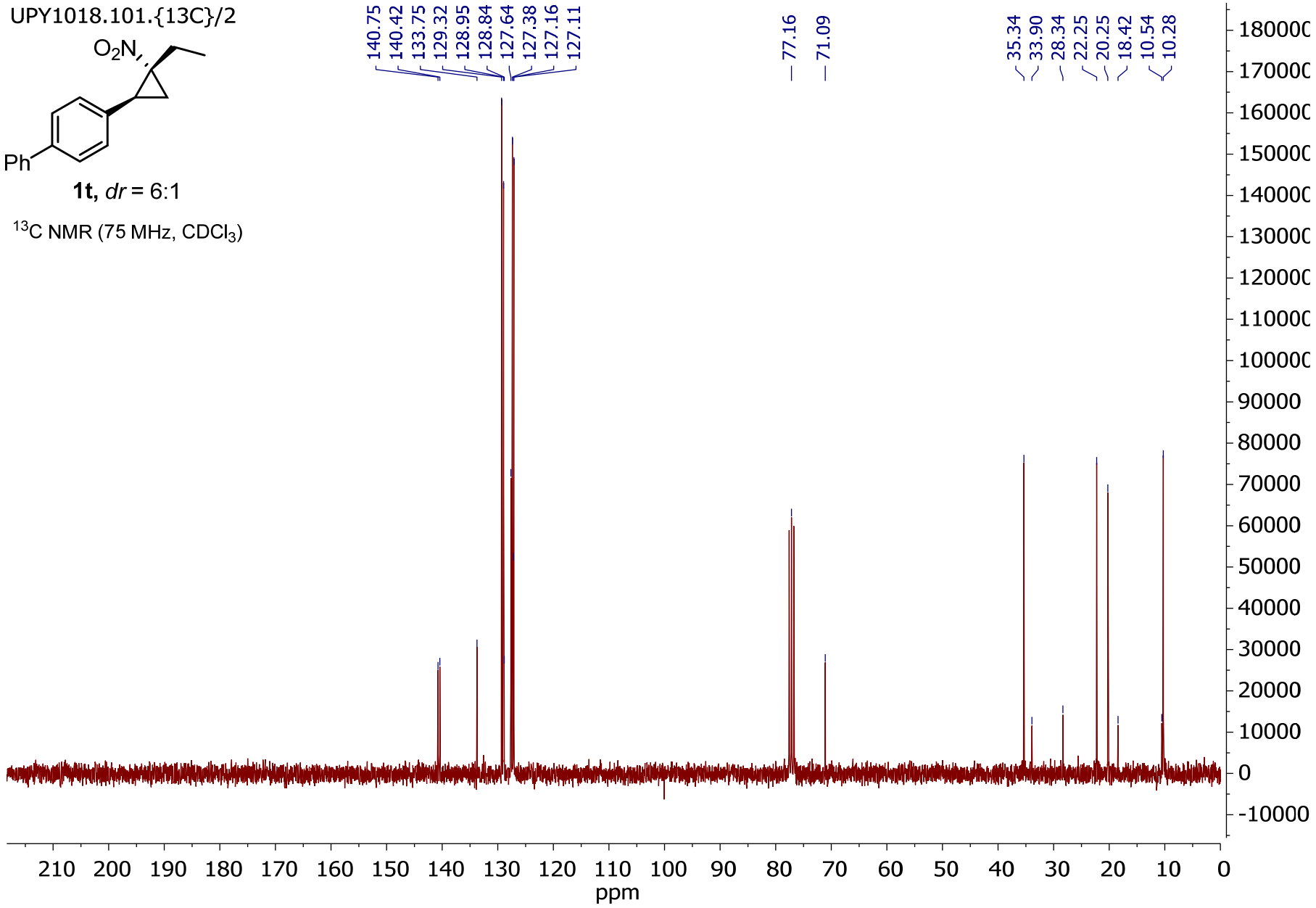

UPY1018.101.{1H}/5
O2N
Ph
1t, dr = 6:1
1H NMR (300 MHz, CDCl3)
7.64
7.60
7.49
7.40
7.28
3.46
3.43
3.42
3.39
2.82
2.72
2.65
2.60
2.43
2.39
2.37
2.27
2.22
2.17
1.90
1.77
1.63
1.61
1.60
1.58
1.42
1.40
1.31
1.24
1.22
1.19
1.06
1.03
1.01
11.24
1.00
0.36
0.19
1.10
1.09
0.21
1.14
0.55
2.99
ppm

NMR of **1t**

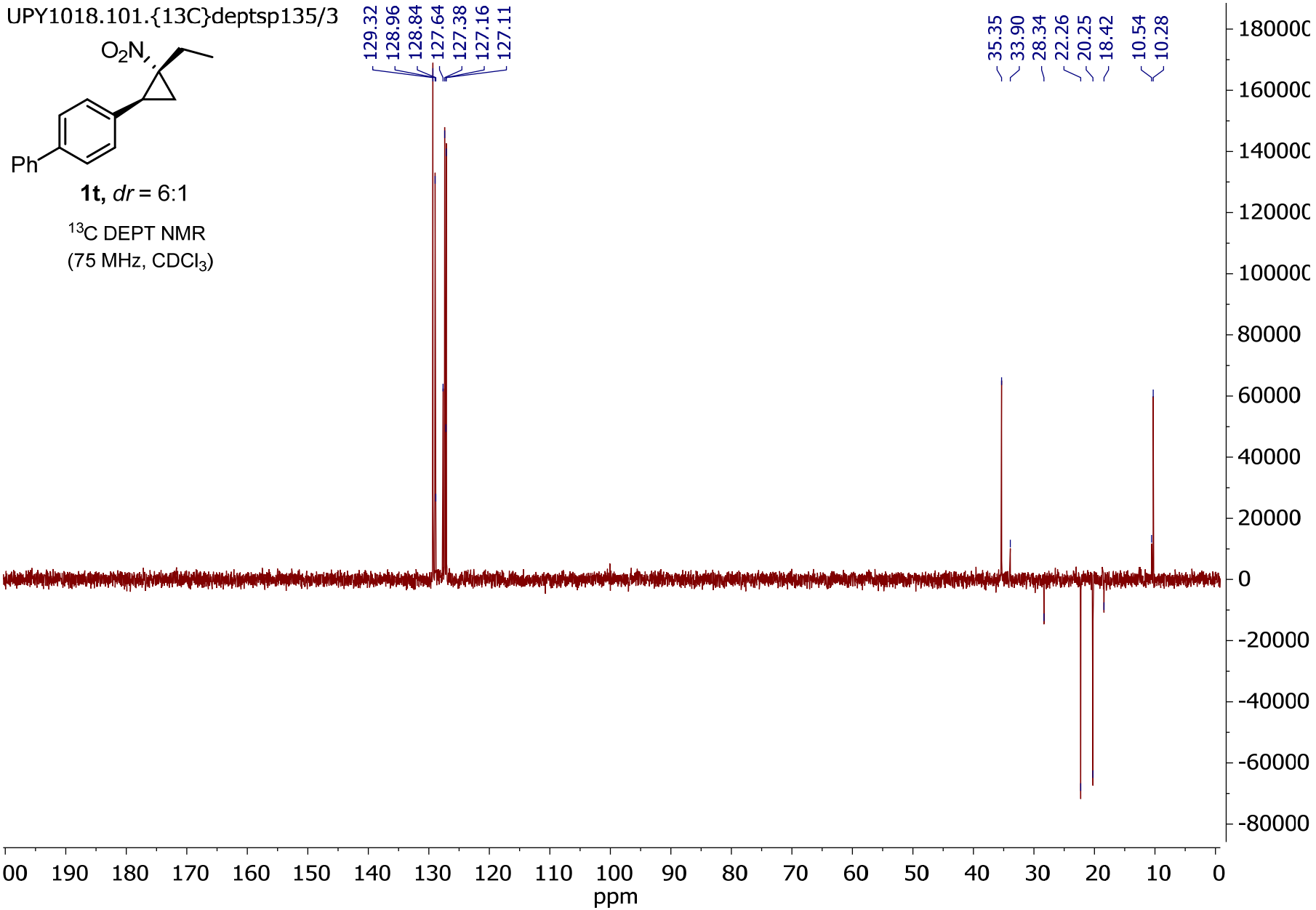

UPY1018.101.{1H-1H}COSY/6
O2N
Ph
1t, dr = 6:1
1H - 1H COSY NMR
(CDCl3)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0
f1 (мд)


NMR of **1t**
O_2N
Ph
1t, *dr* = 6:1
UPY1018.101.{1H-1H}COSY/6
^{1}H - ^{1}H COSY NMR
($CDCl_3$)
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
ppm
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
f1 (мд)

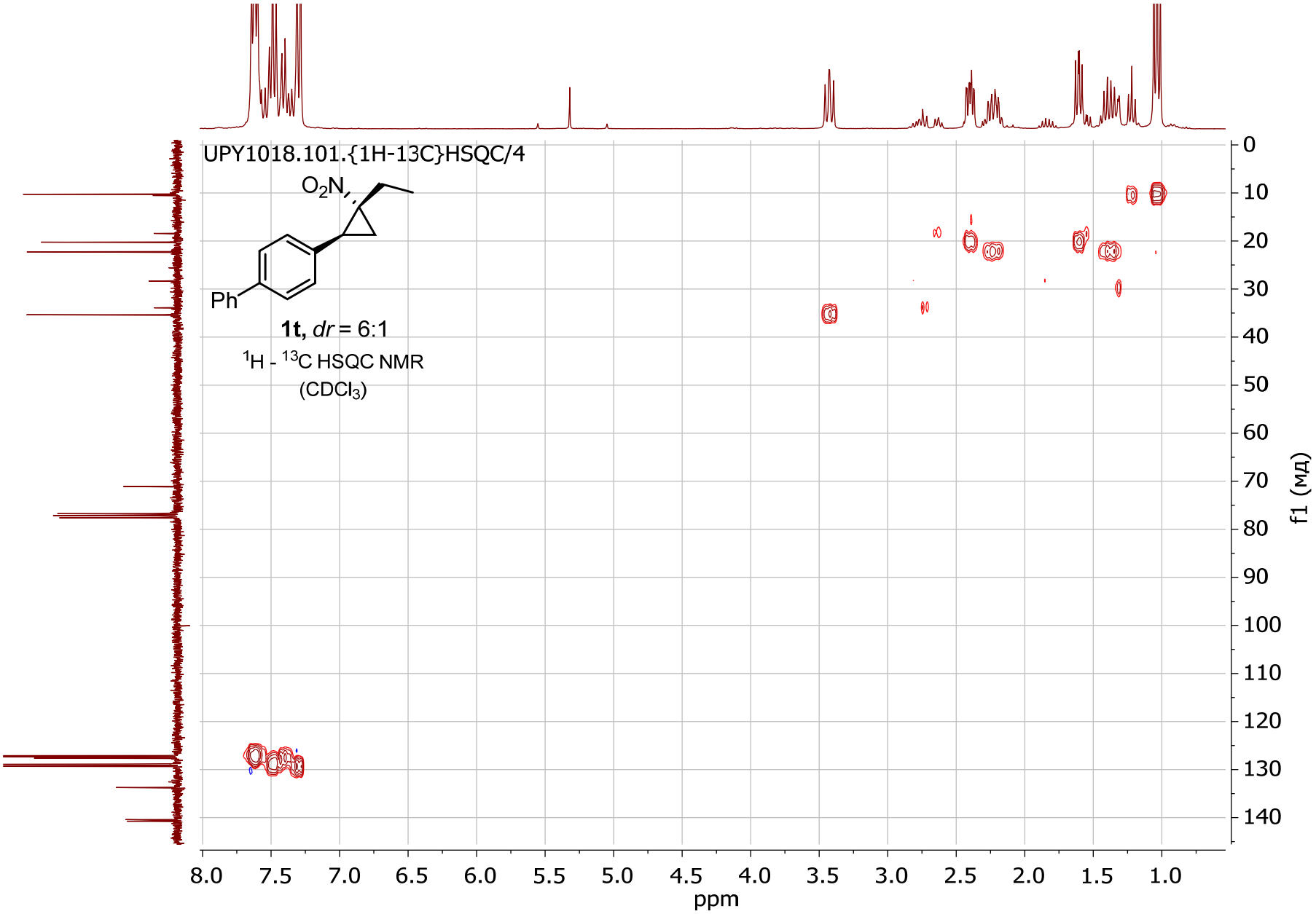
NMR of **1t**


UPY1018.101.{13C}/2
O2N
Ph
1t, dr = 6:1
13C NMR (75 MHz, CDCl3)
140.75
140.42
133.75
129.32
128.95
128.84
127.64
127.38
127.16
127.11
77.16
71.09
35.34
33.90
28.34
22.25
20.25
18.42
10.54
10.28
ppm

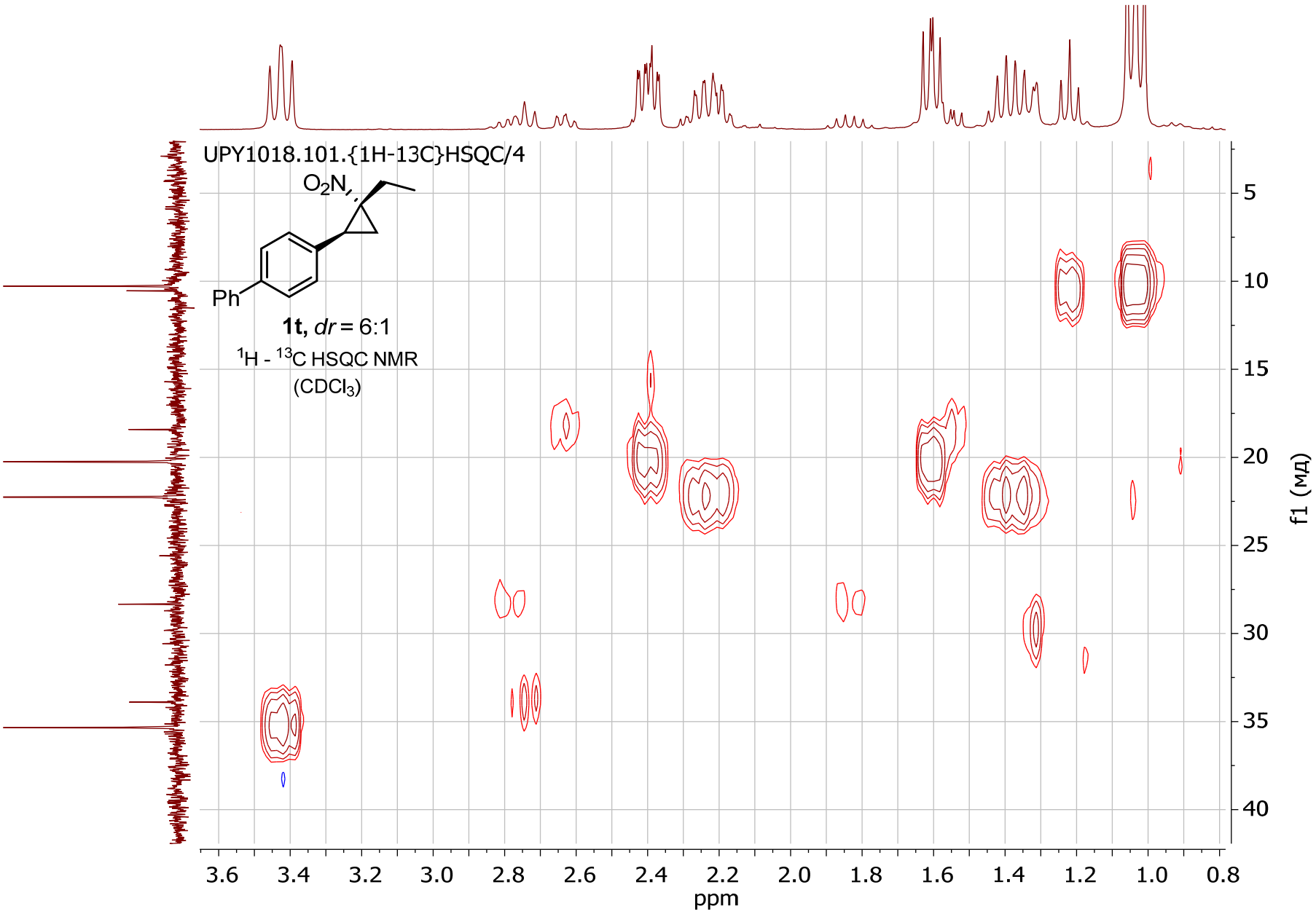
NMR of **1t**


UPY1018.101.{13C}deptsp135/3
O2N
Ph
1t, dr = 6:1
13C DEPT NMR
(75 MHz, CDCl3)
129.32
128.96
128.84
127.64
127.38
127.16
127.11
35.35
33.90
28.34
22.26
20.25
18.42
10.54
10.28
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
-60000
-80000
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

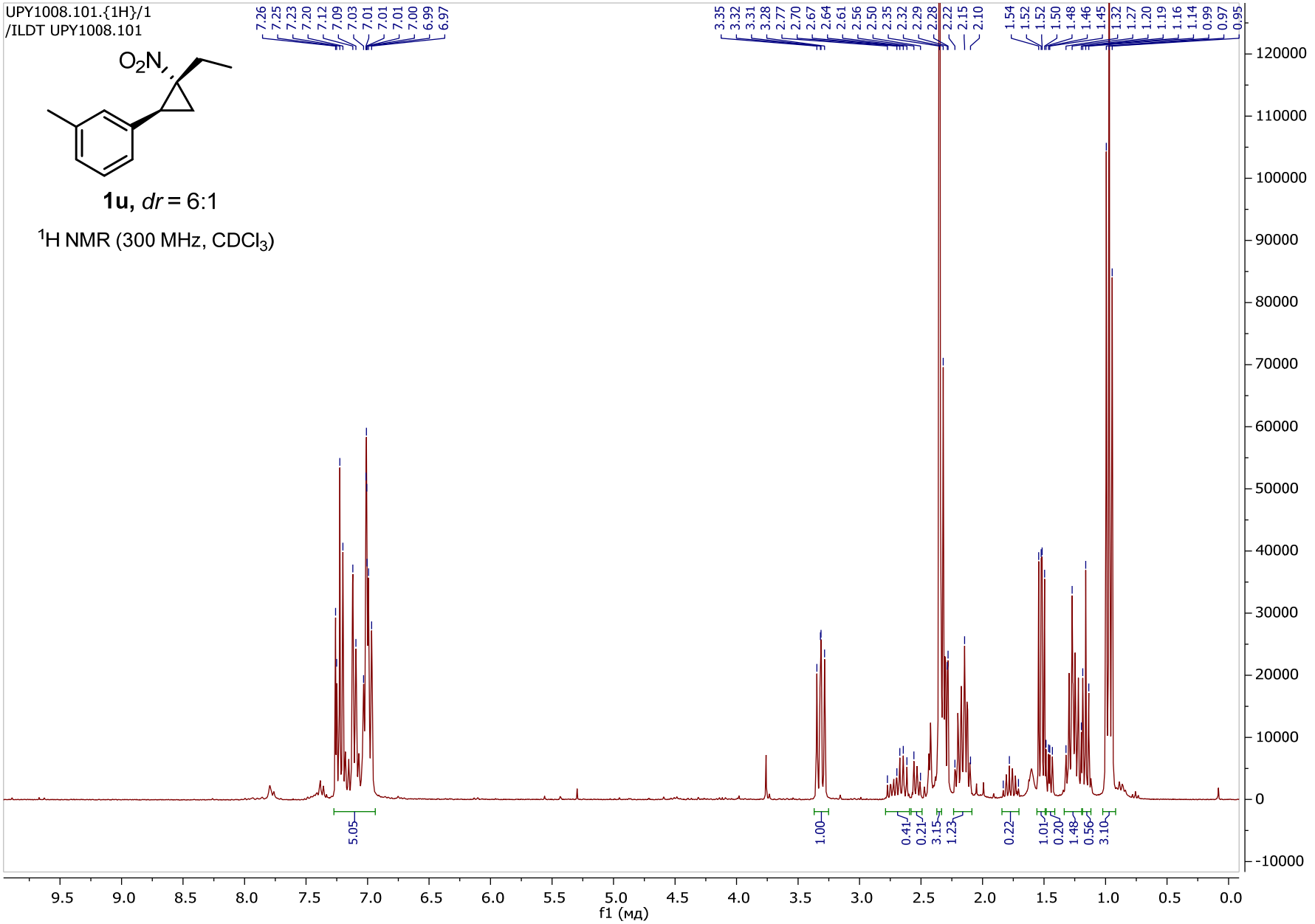
NMR of **1t**


UPY1018.101.{1H-13C}HSQC/4
O2N
Ph
1t, dr = 6:1
1H - 13C HSQC NMR
(CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (мд)

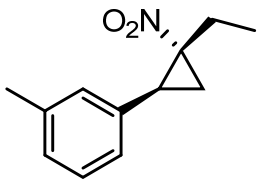
NMR of **1t**


UPY1018.101.{1H-13C}HSQC/4
O2N
Ph
1t, dr = 6:1
1H - 13C HSQC NMR
(CDCl3)
f1 (мд)
ppm
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
5
10
15
20
25
30
35
40

NMR of **1u**

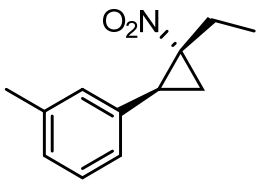

UPY1008.101.{1H}/1
/ILDT UPY1008.101
O2N
1u, dr = 6:1
1H NMR (300 MHz, CDCl3)
f1 (мд)

NMR of **1u**

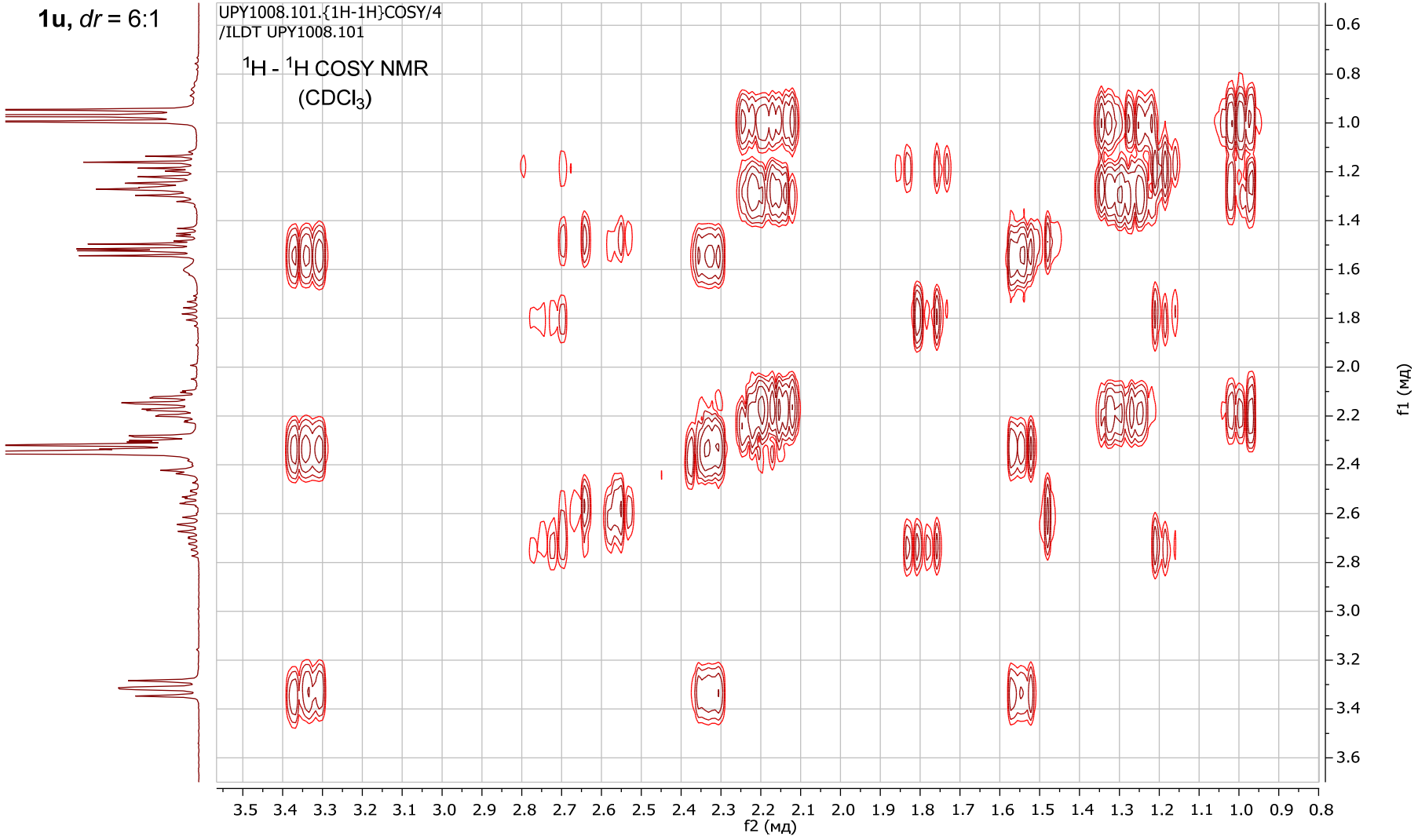


1u, *dr* = 6:1

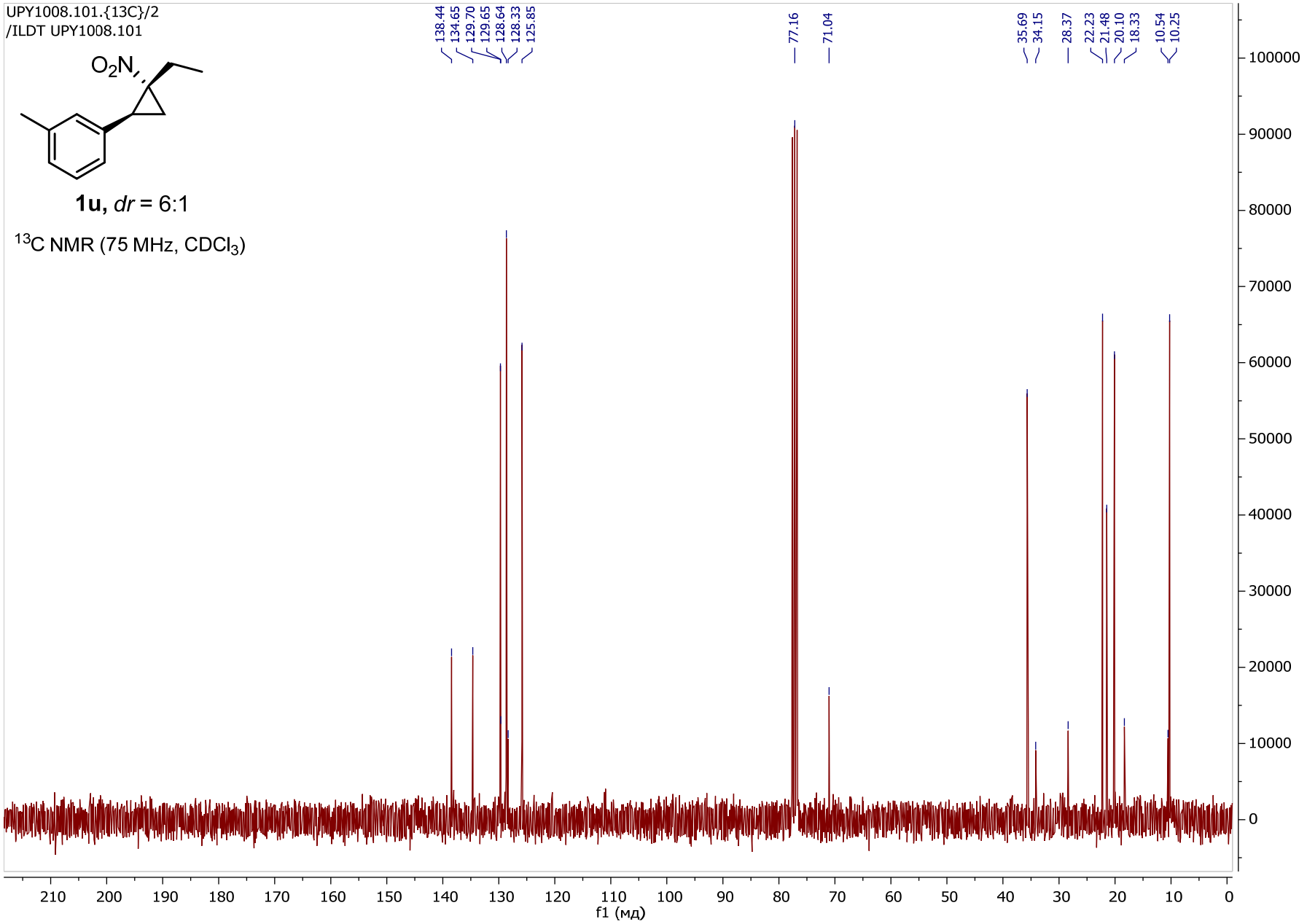
NMR of **1u**



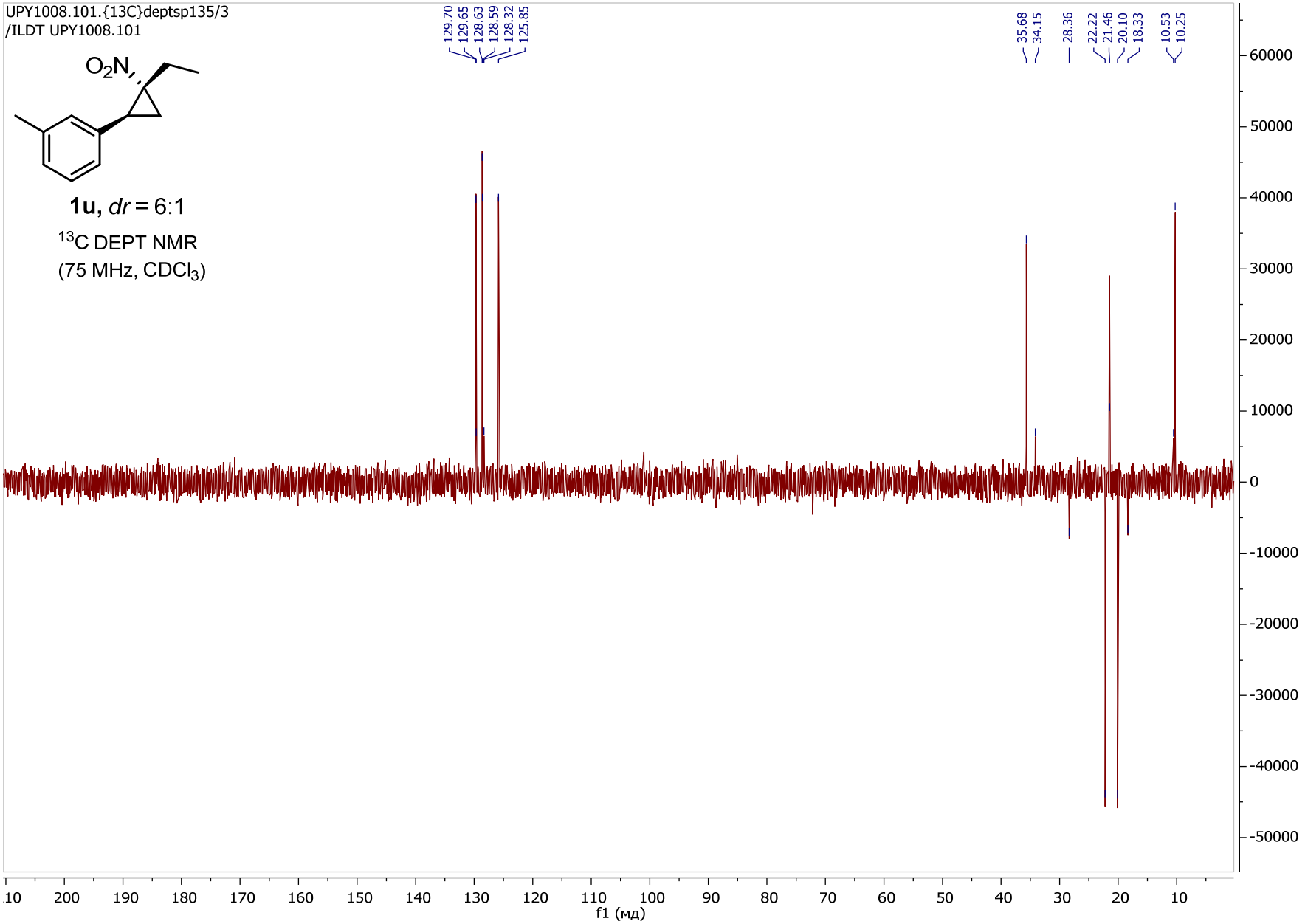
1u, *dr* = 6:1

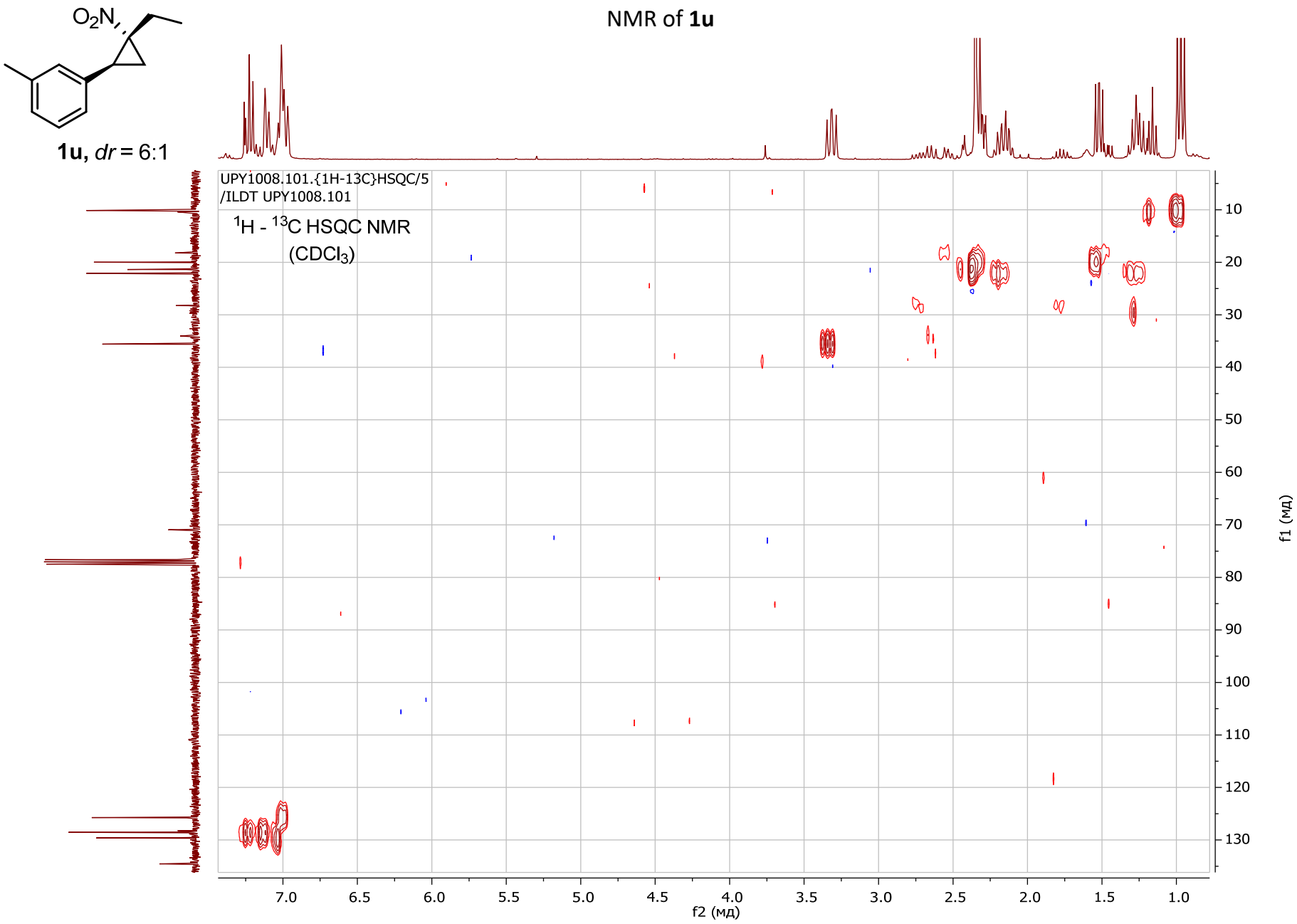


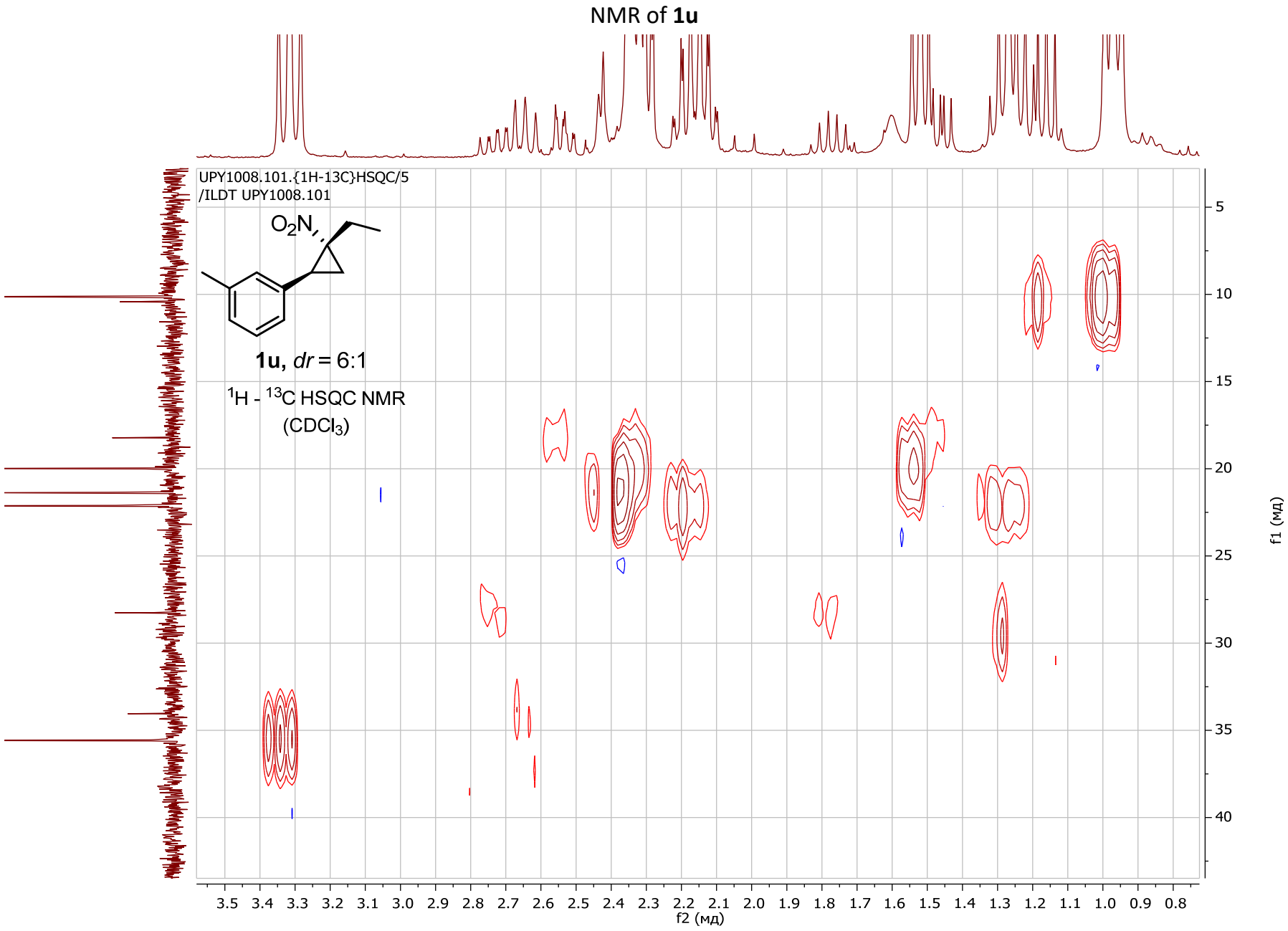
NMR of **1u**


UPY1008.101.{13C}/2
/ILDT UPY1008.101
O_2N
1u, *dr* = 6:1
^{13}C NMR (75 MHz, $CDCl_3$)
138.44
134.65
129.70
129.65
128.64
128.33
125.85
77.16
71.04
35.69
34.15
28.37
22.23
21.48
20.10
18.33
10.54
10.25
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

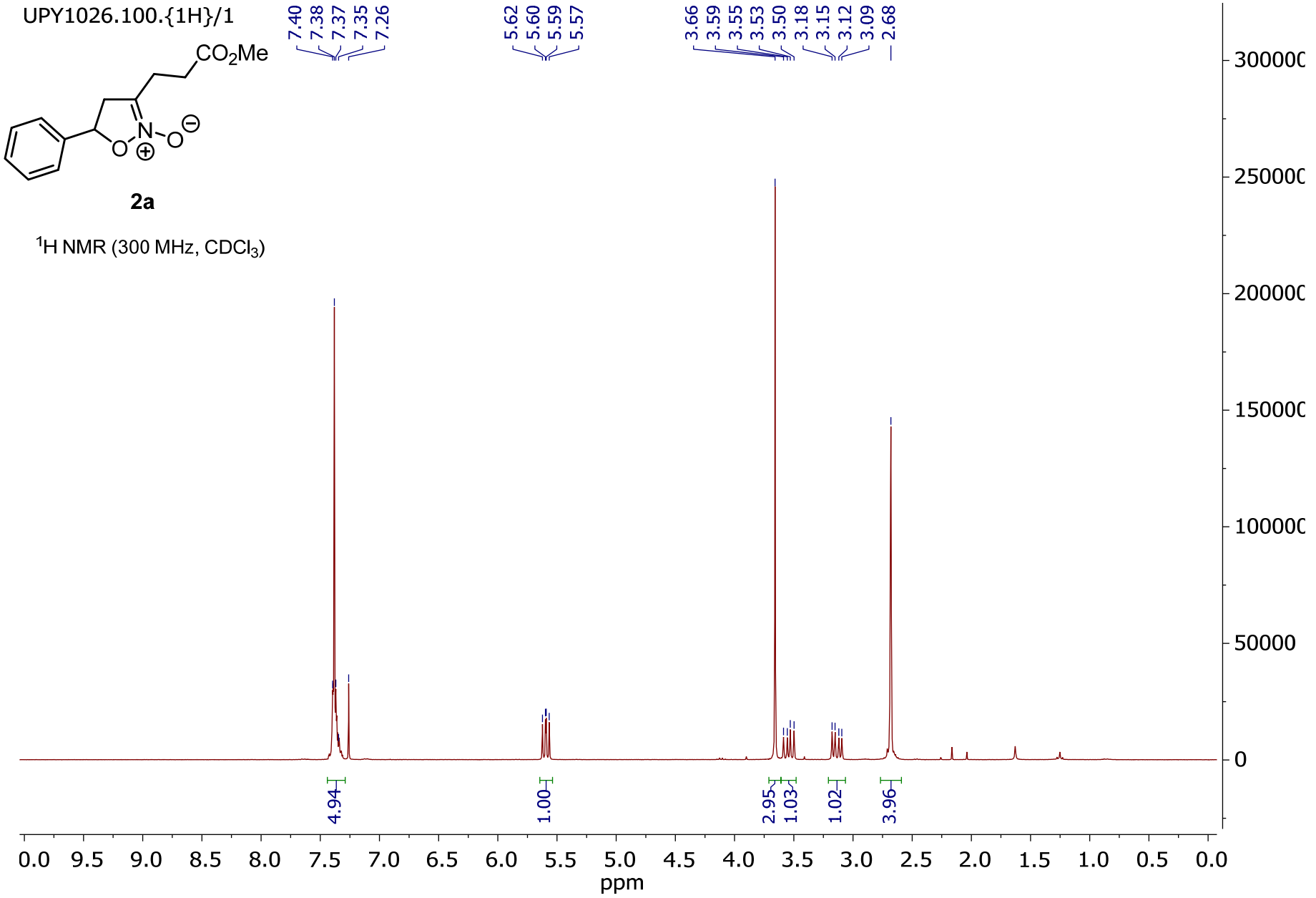
NMR of **1u**


UPY1008.101.{13C}deptsp135/3
/ILDT UPY1008.101
O2N
1u, dr = 6:1
13C DEPT NMR
(75 MHz, CDCl3)
129.70
129.65
128.63
128.59
128.32
125.85
35.68
34.15
28.36
22.22
21.46
20.10
18.33
10.53
10.25
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
-50000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (мд)


O2N
1u, dr = 6:1
NMR of 1u
UPY1008.101.{1H-13C}HSQC/5
/ILDT UPY1008.101
1H - 13C HSQC NMR
(CDCl3)
f2 (мд)
f1 (мд)

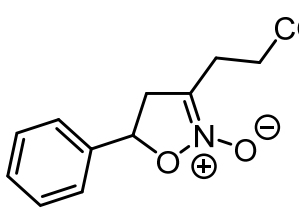

NMR of 1u
UPY1008.101.{1H-13C}HSQC/5
/ILDT UPY1008.101
O2N
1u, dr = 6:1
1H - 13C HSQC NMR
(CDCl3)
f2 (мд)
f1 (мд)

NMR of **2a**


UPY1026.100.{1H}/1
7.40
7.38
7.37
7.35
7.26
5.62
5.60
5.59
5.57
3.66
3.59
3.55
3.53
3.50
3.18
3.15
3.12
3.09
2.68
CO2Me
N
O
O
2a
1H NMR (300 MHz, CDCl3)
300000
250000
200000
150000
100000
50000
0
4.94
1.00
2.95
1.03
1.02
3.96
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

NMR of **2a**

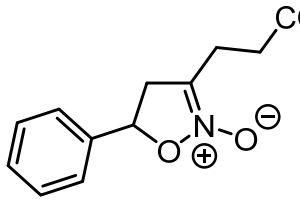
UPY959.100.{13C}/2



2a

^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **2a**

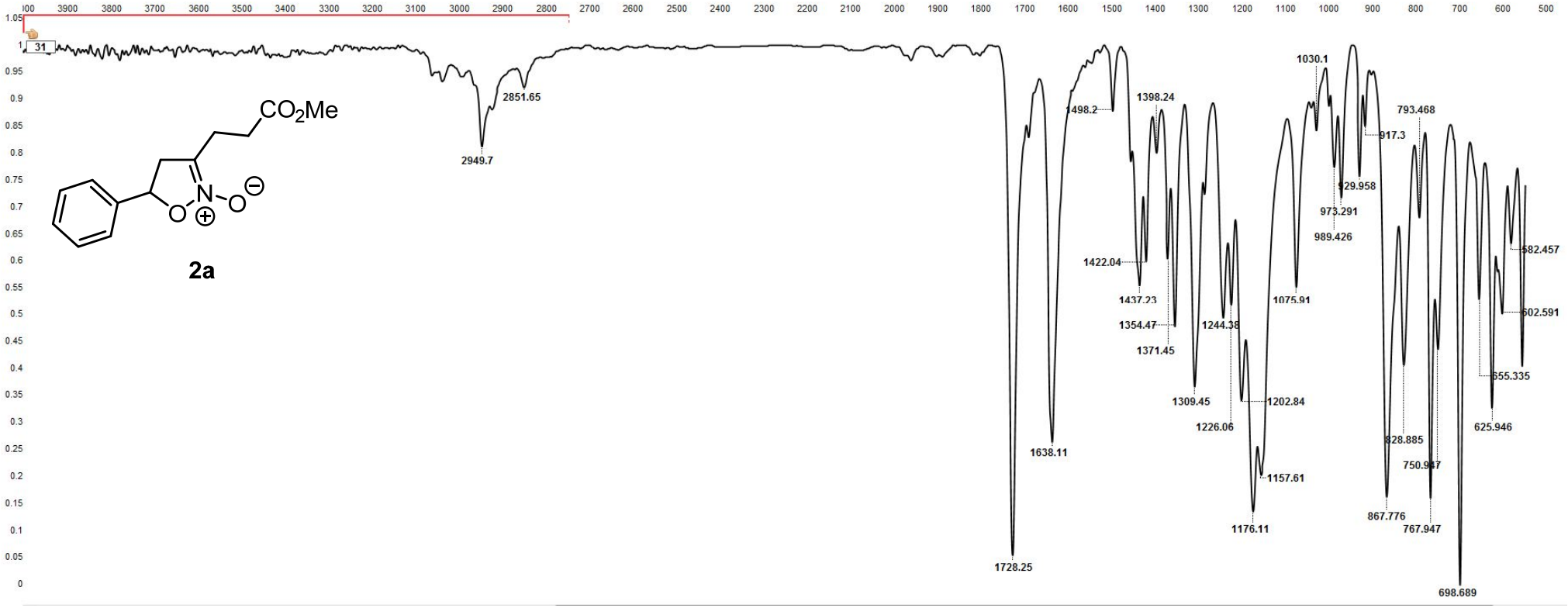


2a

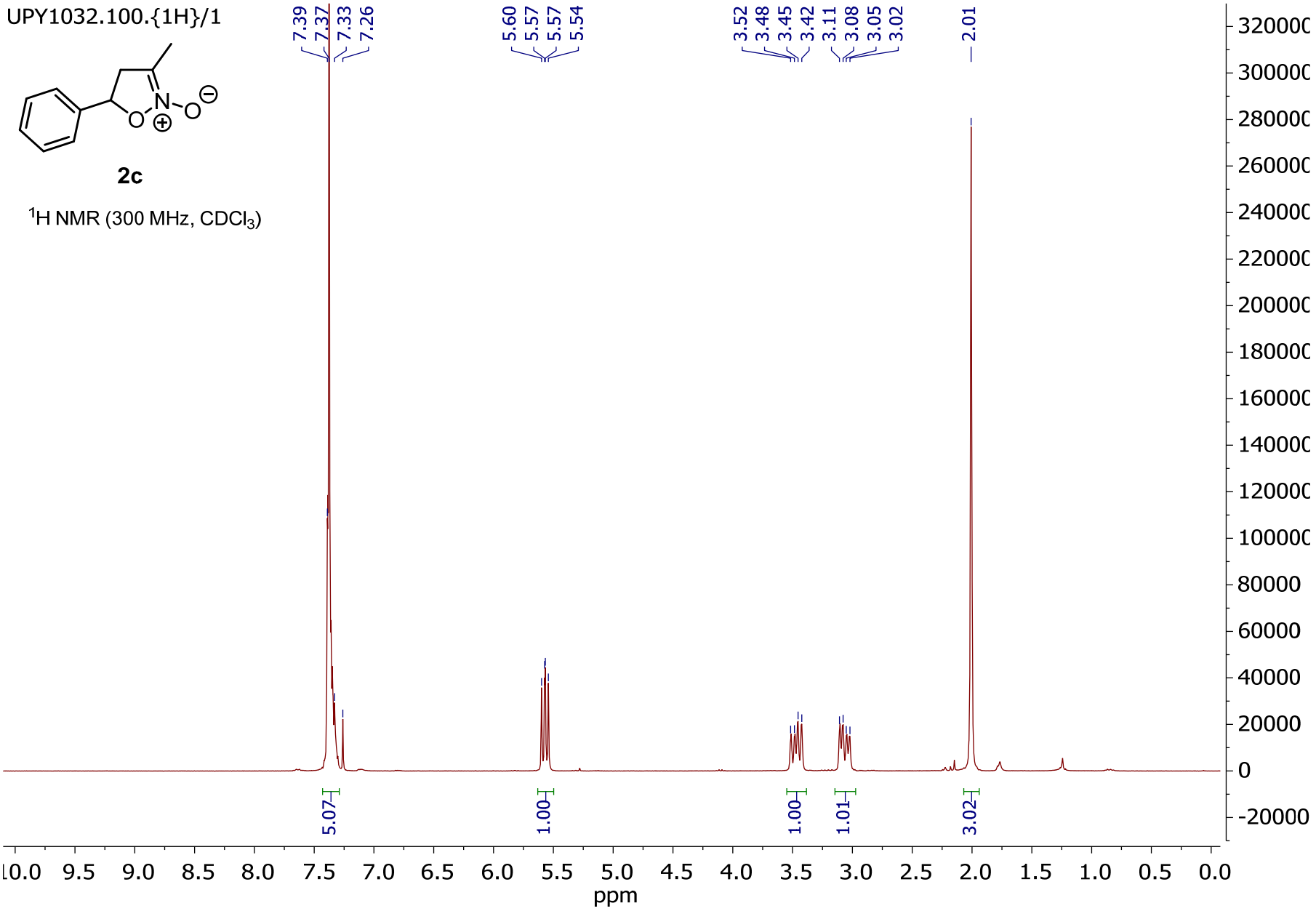
^{13}C DEPT NMR

(75 MHz, $CDCl_3$)

FTIR (ATR) of **2a**

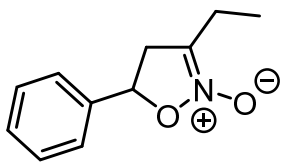


NMR of **2c**


UPY1032.100.{1H}/1
2c
^{1}H NMR (300 MHz, $CDCl_3$)
7.39
7.37
7.33
7.26
5.60
5.57
5.57
5.54
3.52
3.48
3.45
3.42
3.11
3.08
3.05
3.02
2.01
5.07
1.00
1.00
1.01
3.02
ppm

NMR of **2d**

UPY1027.100.{1H}/1

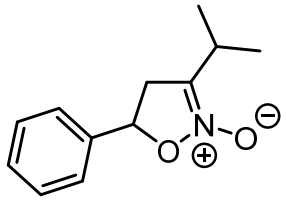


2d

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **2e**

UPY1028.100.{1H}/1

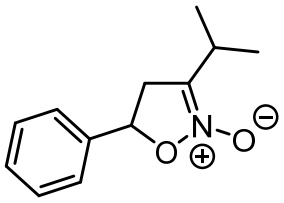


2e

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **2e**

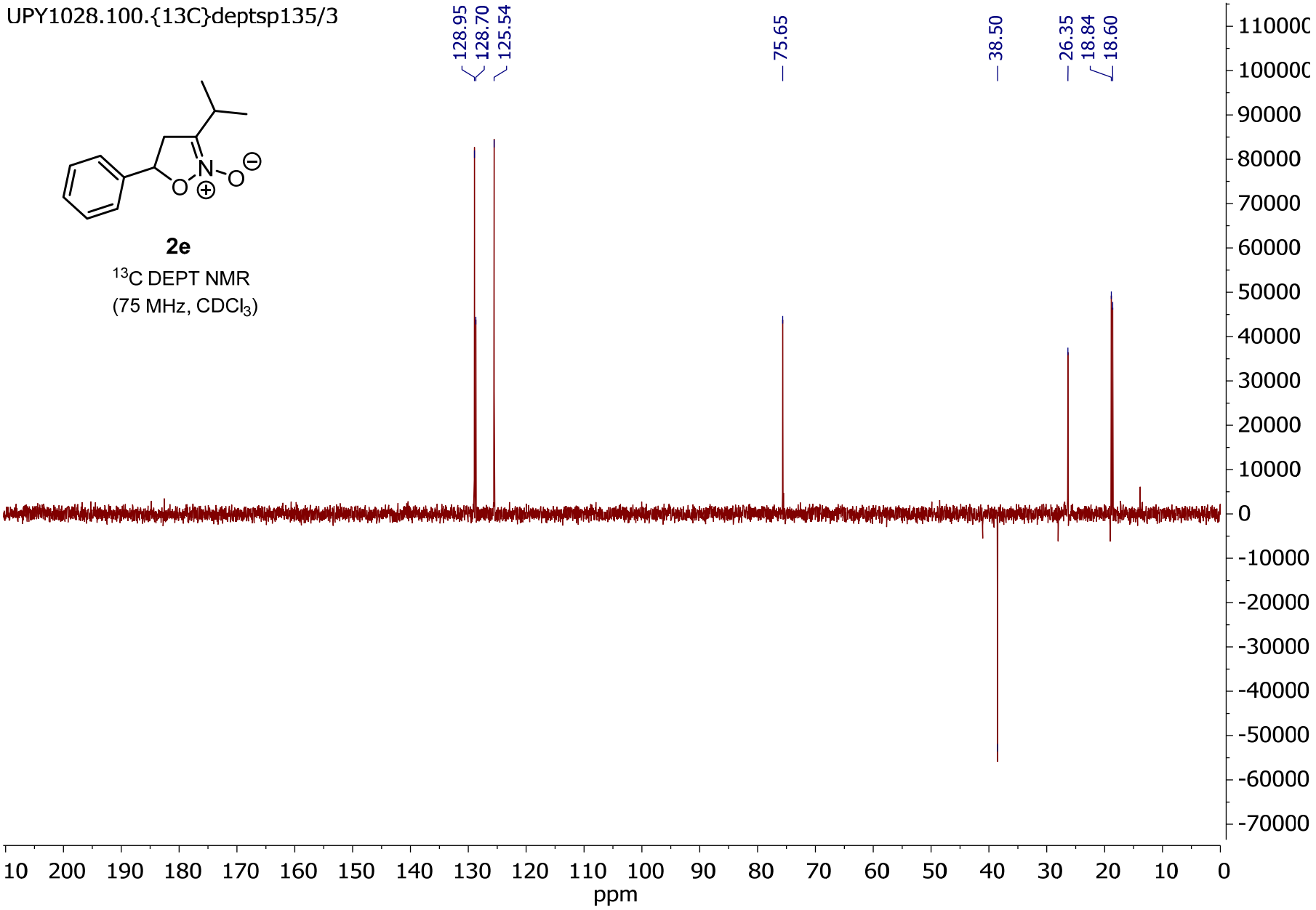
UPY1028.100.{13C}/2



2e

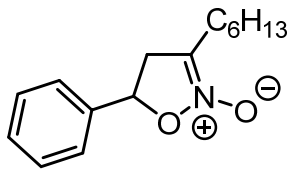
^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **2e**


UPY1028.100.{13C}deptsp135/3
128.95
128.70
125.54
75.65
38.50
26.35
18.84
18.60
2e
13C DEPT NMR
(75 MHz, CDCl3)
ppm

NMR of **2f**

UPY1038.100.{1H}/1

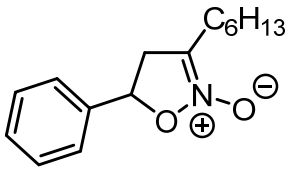


2f

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **2f**

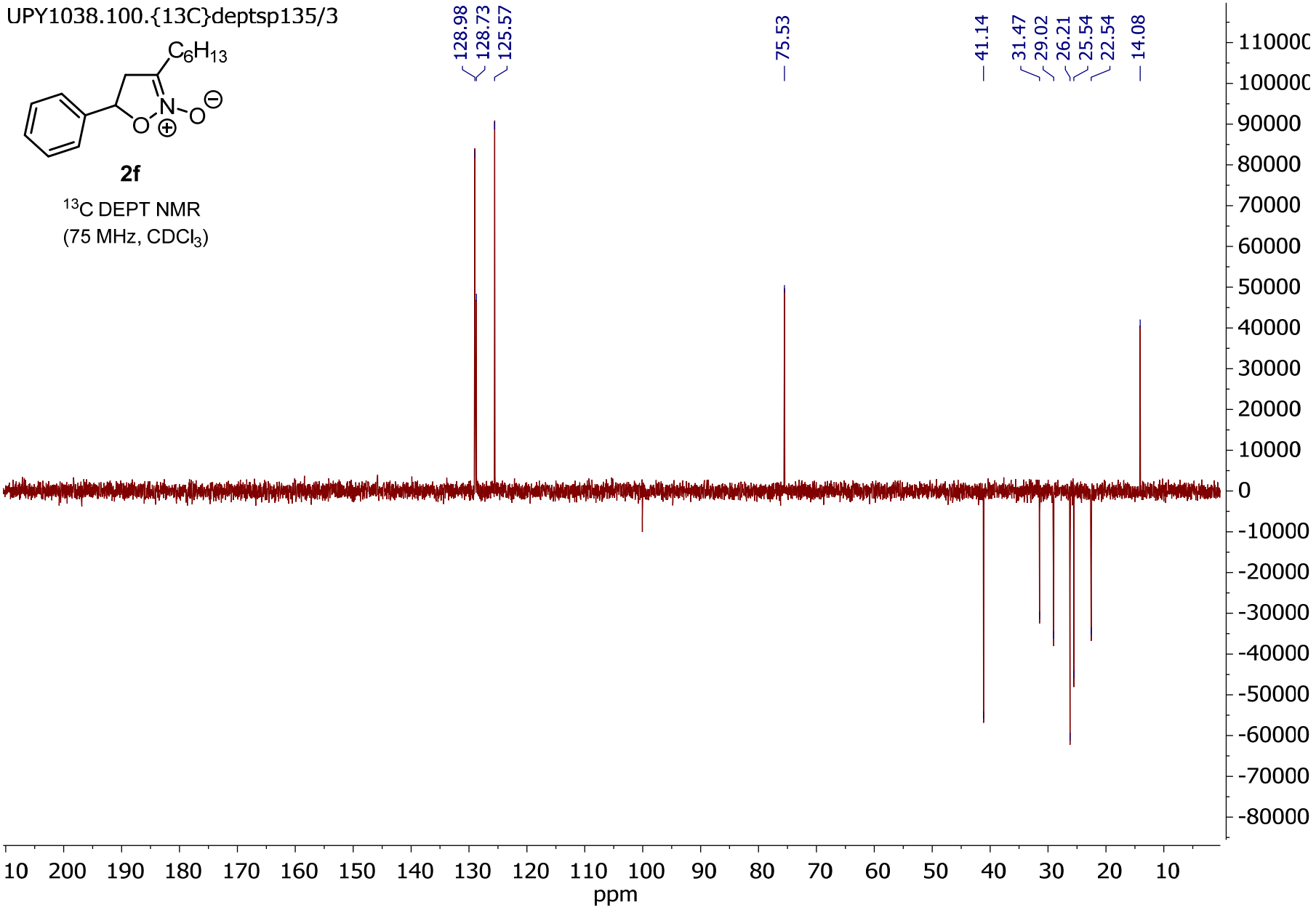
UPY1038.100.{13C}/2



2f

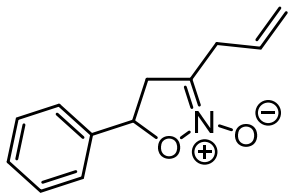
^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **2f**


UPY1038.100.{13C}deptsp135/3
C_6H_{13}
2f
^{13}C DEPT NMR
(75 MHz, $CDCl_3$)
128.98
128.73
125.57
75.53
41.14
31.47
29.02
26.21
25.54
22.54
14.08
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
-50000
-60000
-70000
-80000
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

NMR of **2g**

UPY1065.100.{1H}/1

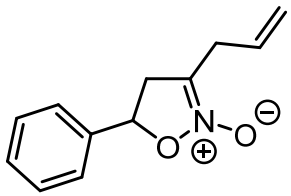


2g

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **2g**

UPY1065.100.{13C}/2

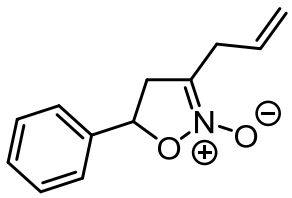


2g

^{13}C NMR (75 MHz, $CDCl_3$)

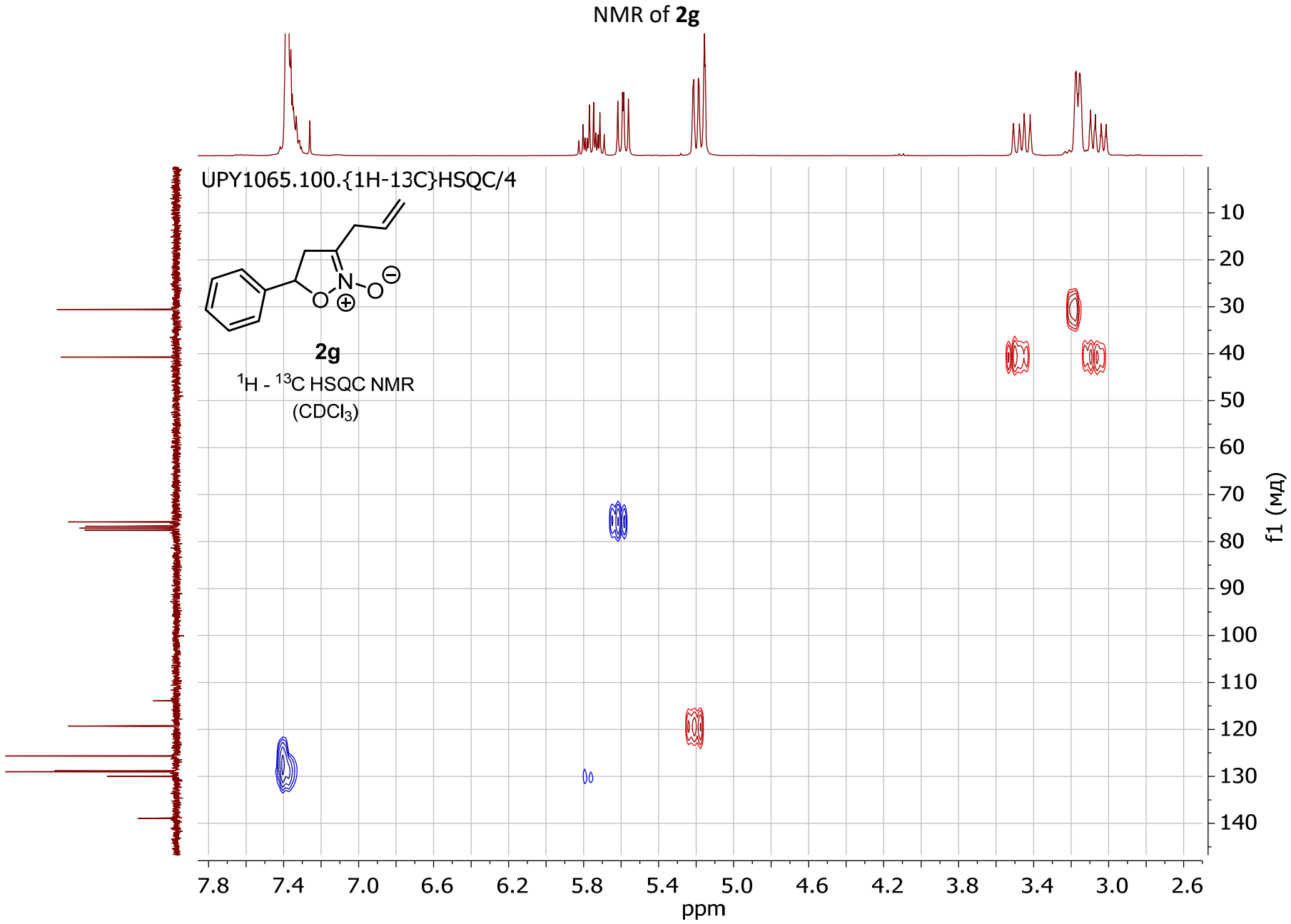
NMR of **2g**

UPY1065.100.{13C}deptsp135/3



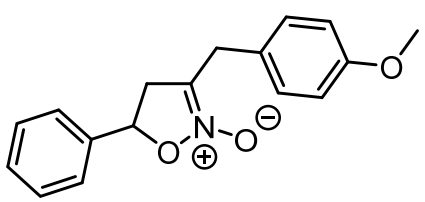
2g

^{13}C DEPT NMR
(75 MHz, $CDCl_3$)


NMR of 2g
UPY1065.100.{1H-13C}HSQC/4
2g
1H - 13C HSQC NMR
(CDCl3)
f1 (мд)
ppm

NMR of **2h**

UPY1030.100.{1H}/1

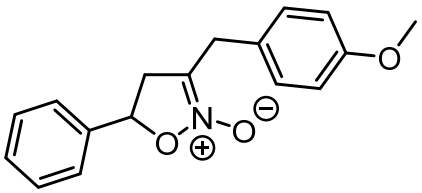


2h

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **2h**

UPY1030.100.{13C}/2

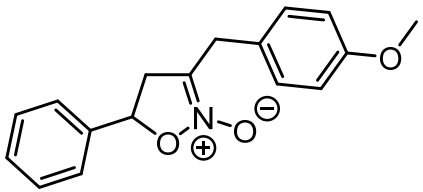


2h

^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **2h**

UPY1030.100.{13C}deptsp135/3

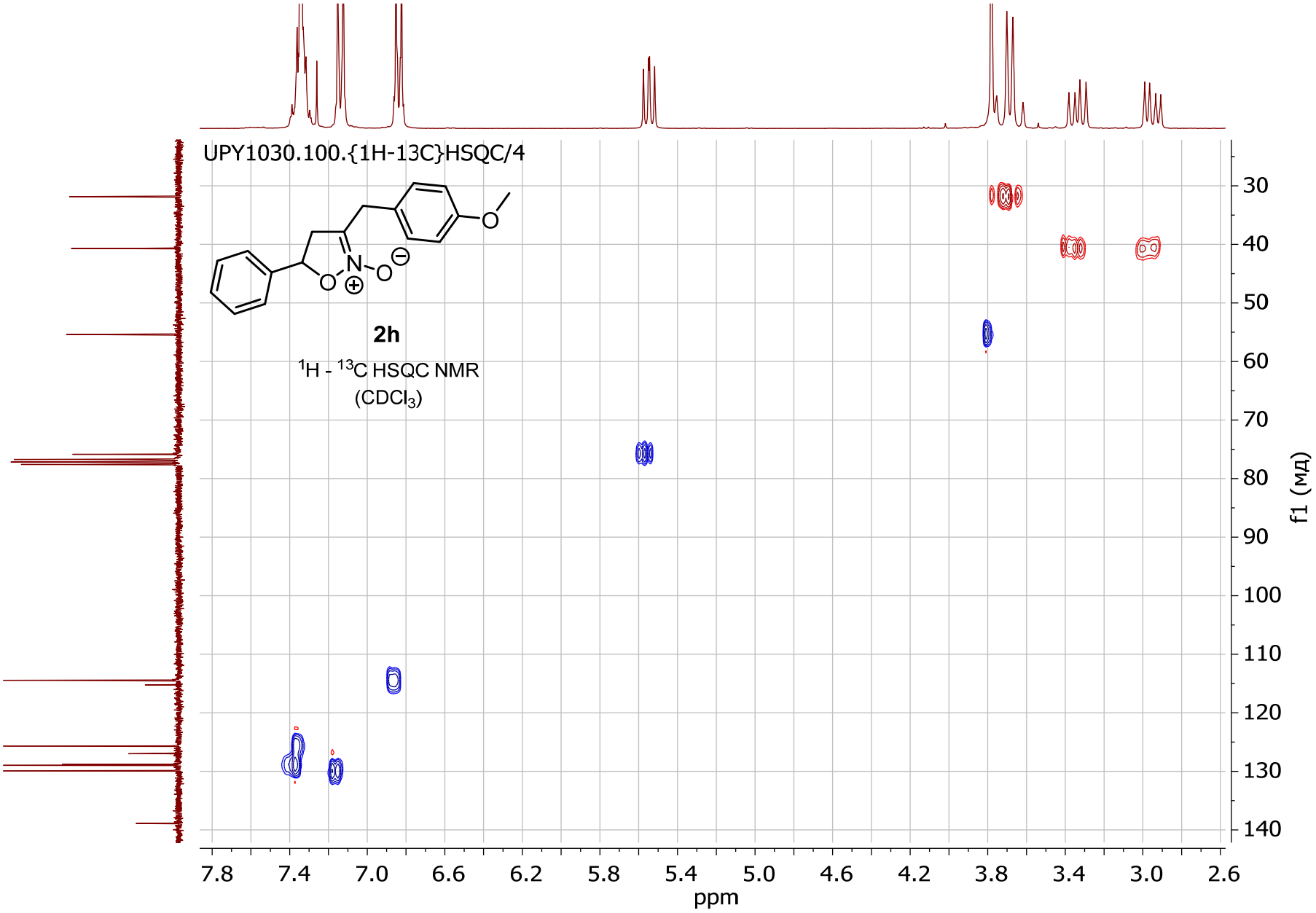


2h

^{13}C DEPT NMR

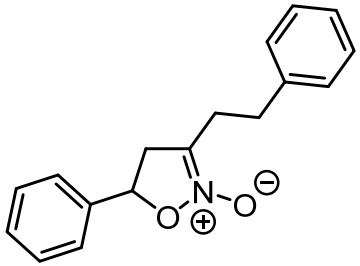
(75 MHz, $CDCl_3$)

NMR of **2h**


UPY1030.100.{1H-13C}HSQC/4
2h
1H - 13C HSQC NMR
(CDCl3)
f1 (мд)
ppm
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
30
40
50
60
70
80
90
100
110
120
130
140

NMR of **2i**

UPY1031.100.{1H}/1

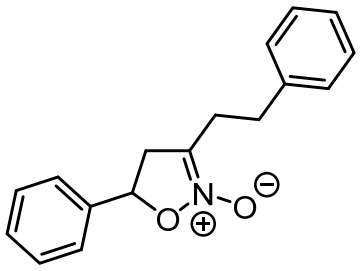


2i

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **2i**

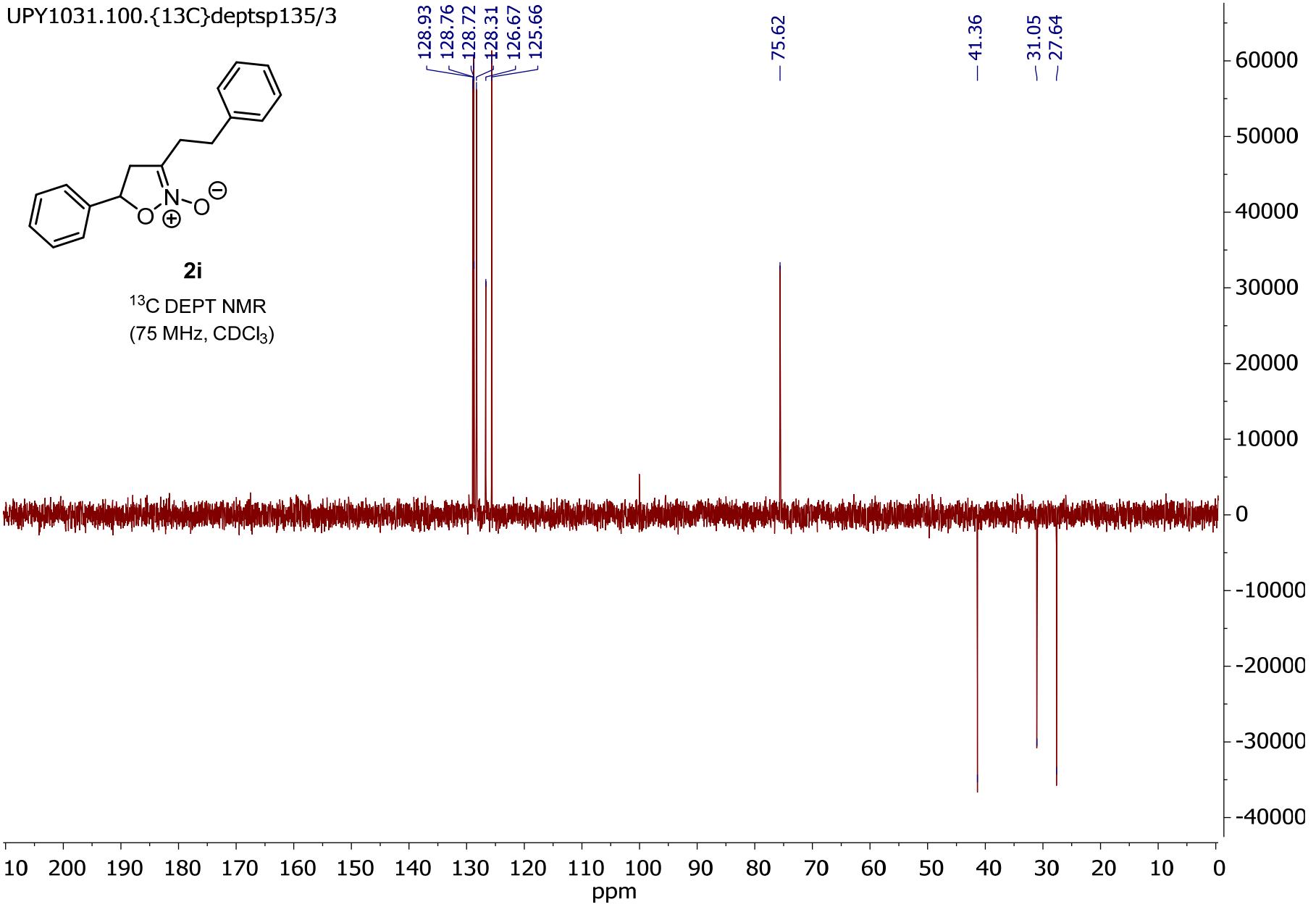
UPY1031.100.{13C}/2



2i

^{13}C NMR (75 MHz, $CDCl_3$)

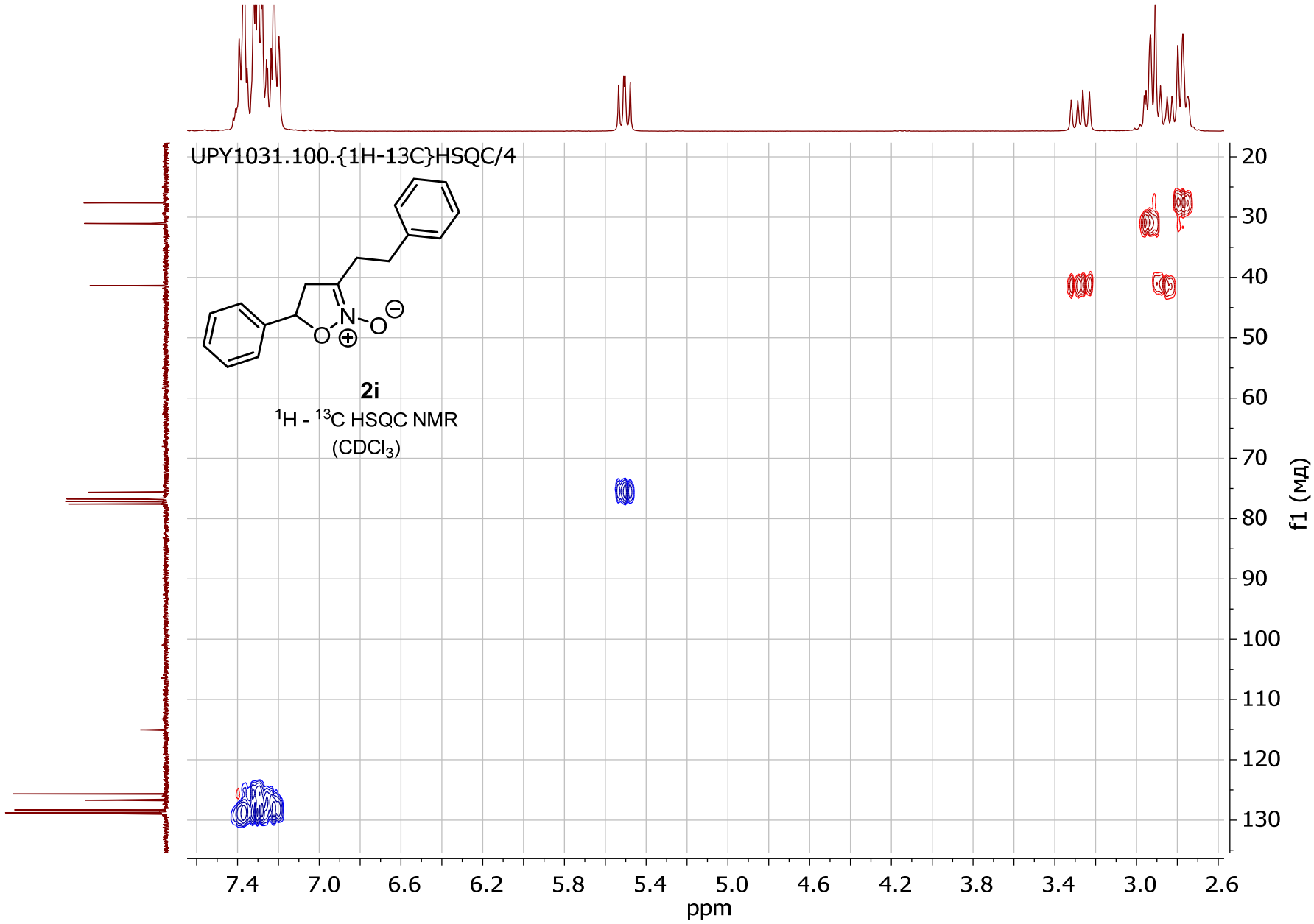
NMR of **2i**



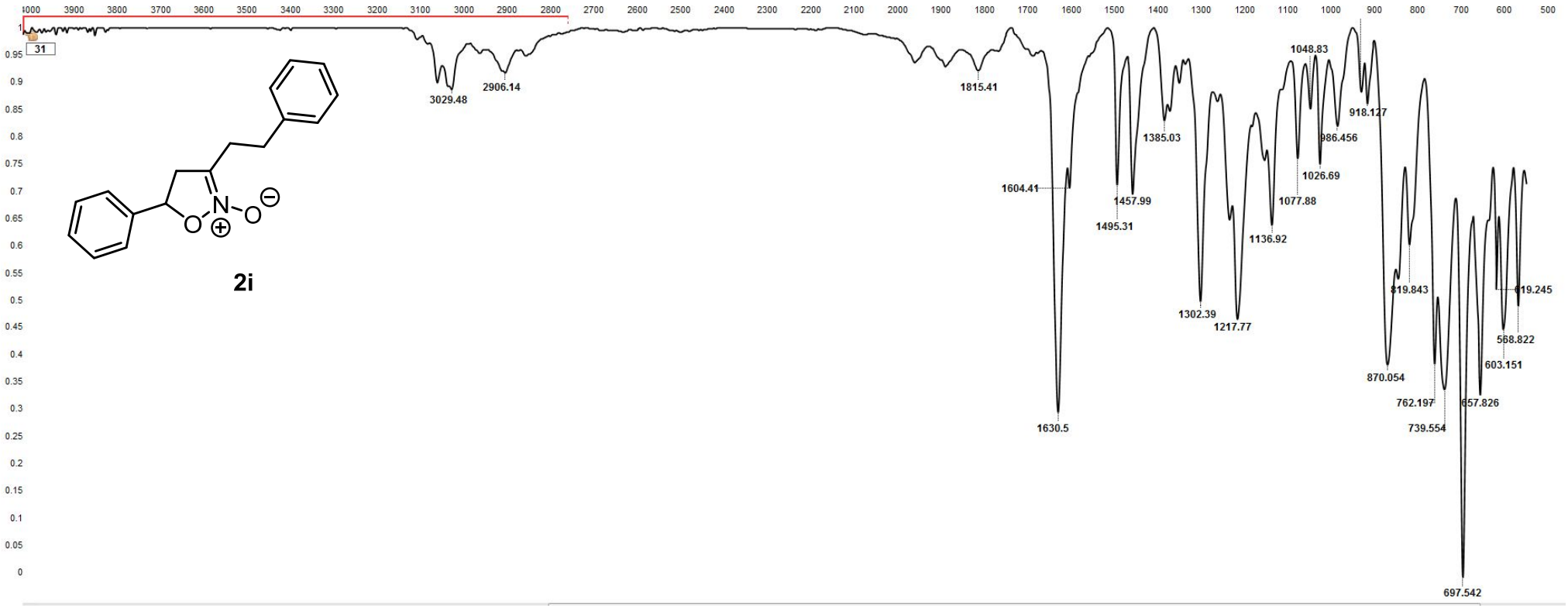
2i

^{13}C DEPT NMR
(75 MHz, $CDCl_3$)

NMR of **2i**

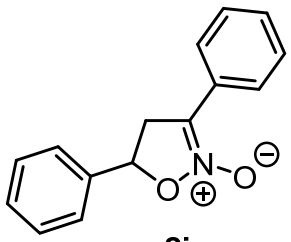

UPY1031.100.{1H-13C}HSQC/4
2i
1H - 13C HSQC NMR
(CDCl3)
20
30
40
50
60
70
80
90
100
110
120
130
f1 (мд)
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0
2.6
ppm

FTIR (ATR) of **2i**



NMR of **2j**

UPY1029.100.{1H}/1

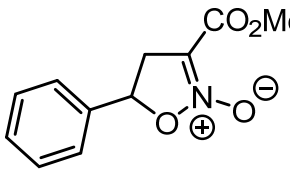


2j

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **2k**

UPY1044.100.{1H}/1

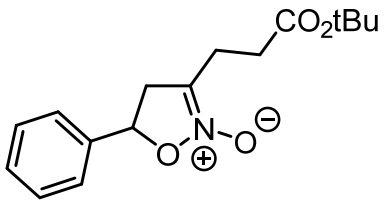


2k

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **2l**

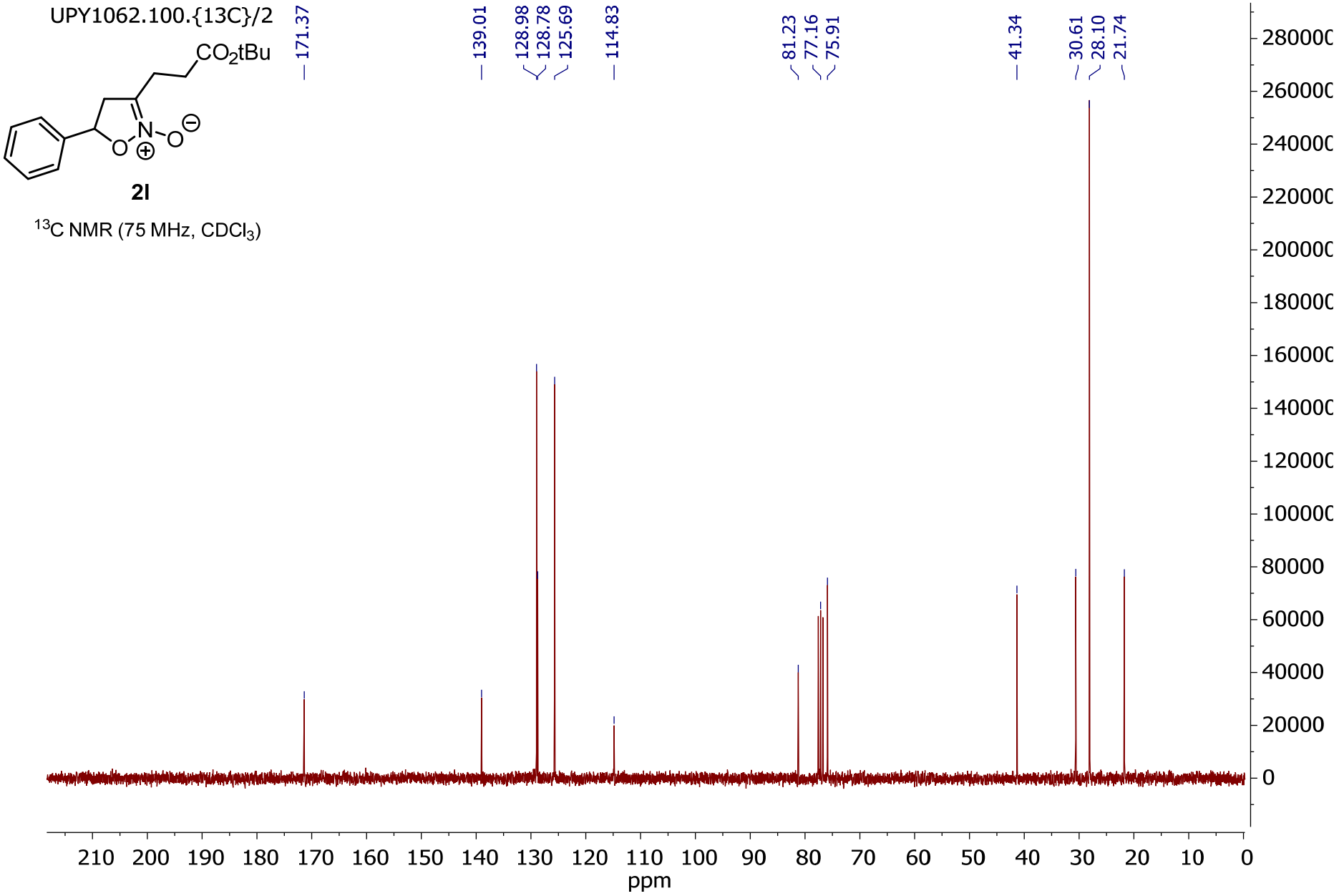
UPY1062.100.{1H}/1



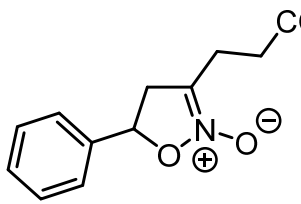
2l

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **2l**


UPY1062.100.{13C}/2
CO2tBu
2l
13C NMR (75 MHz, CDCl3)
171.37
139.01
128.98
128.78
125.69
114.83
81.23
77.16
75.91
41.34
30.61
28.10
21.74
ppm

NMR of **2l**

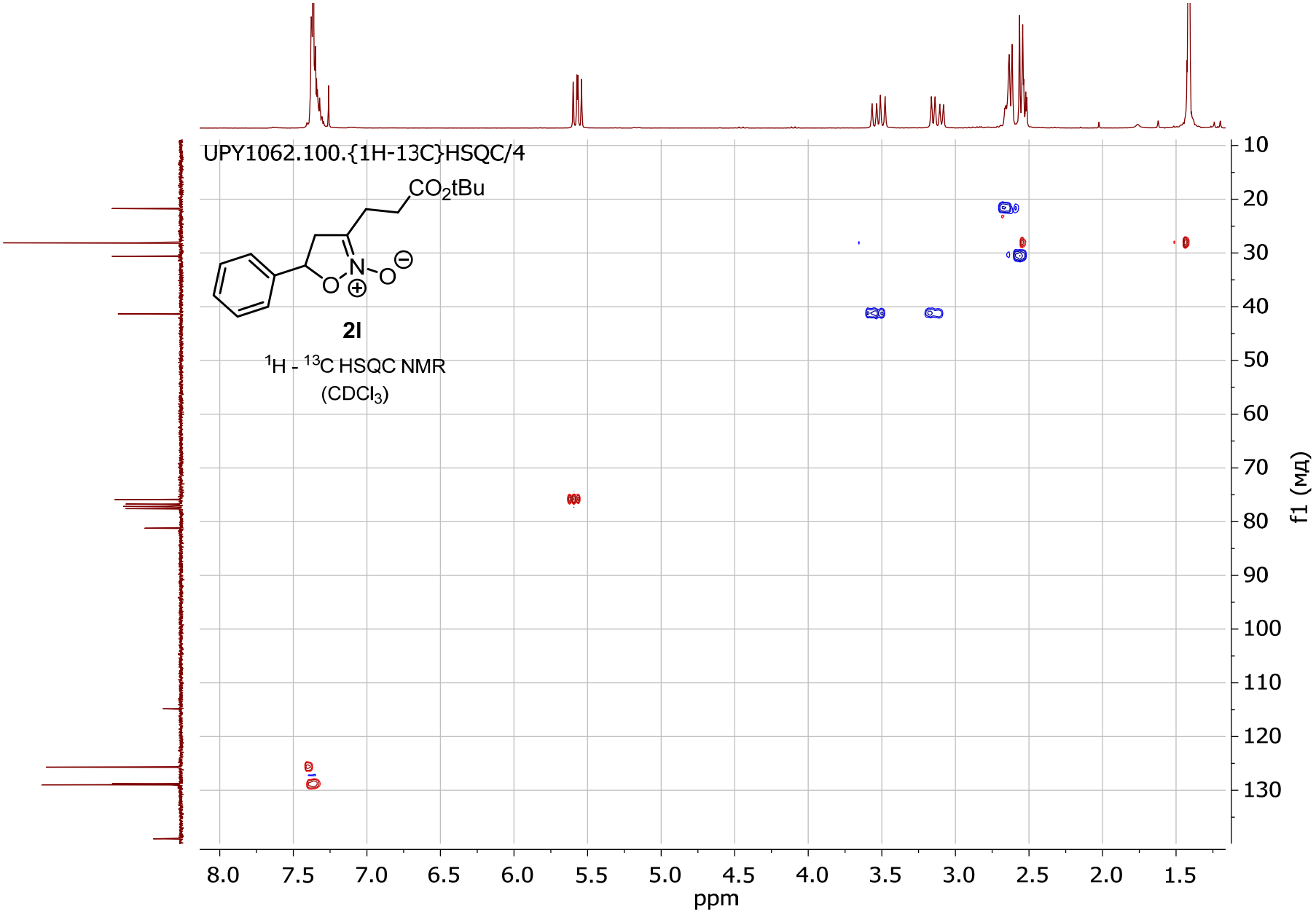


2l

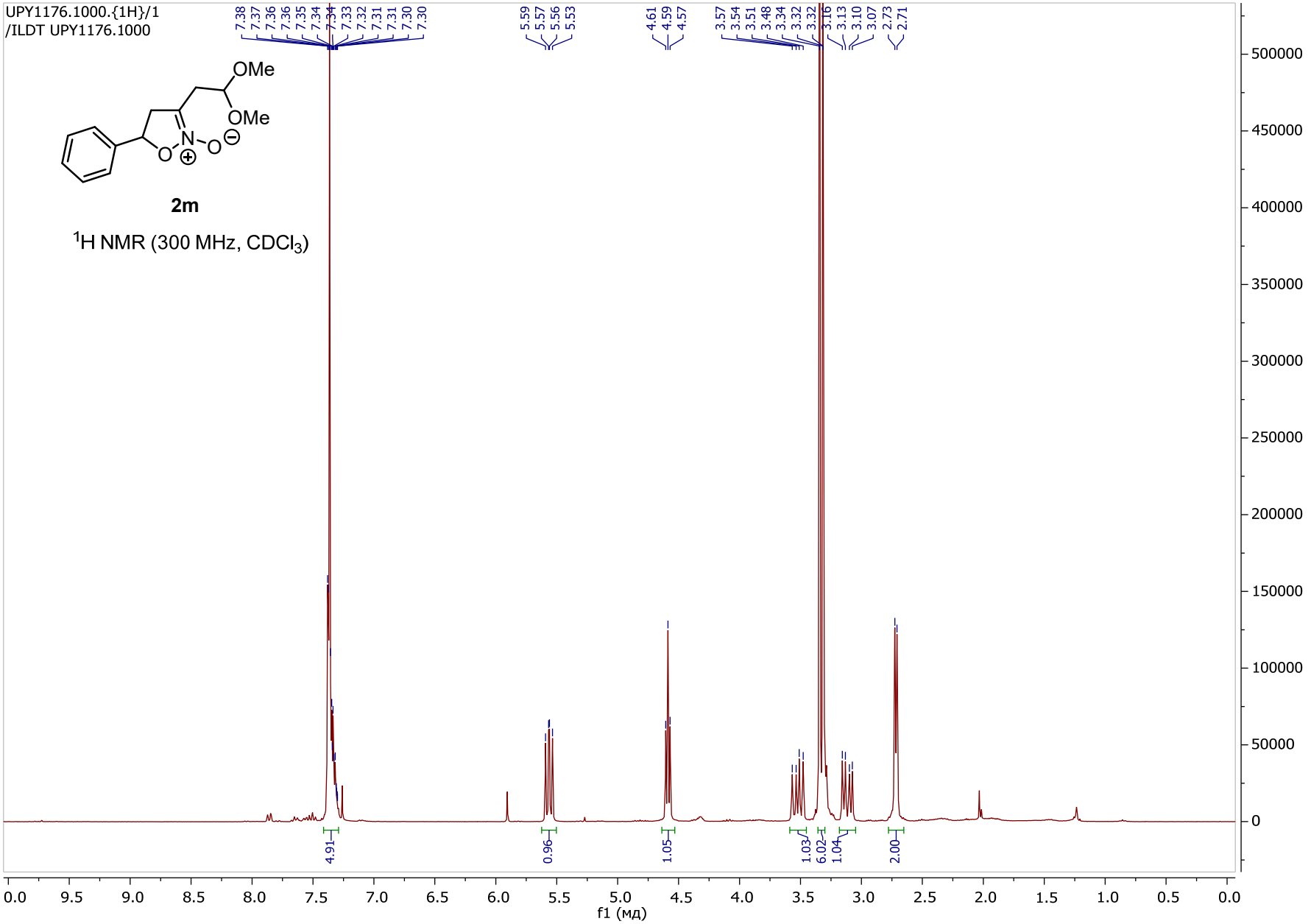
^{13}C DEPT NMR

(75 MHz, $CDCl_3$)

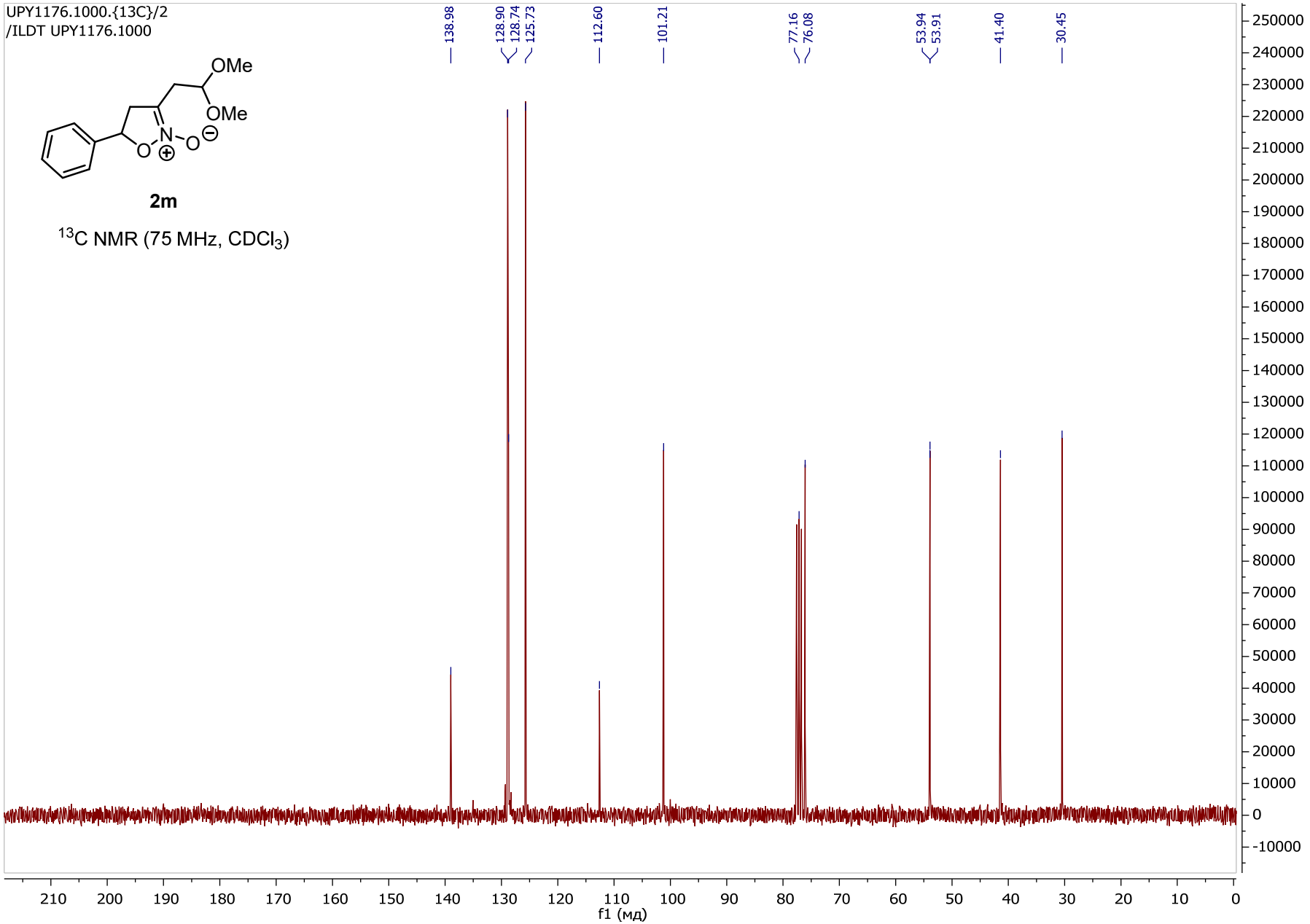
NMR of **2l**


UPY1062.100.{1H-13C}HSQC/4
CO2tBu
2l
1H - 13C HSQC NMR
(CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (мд)

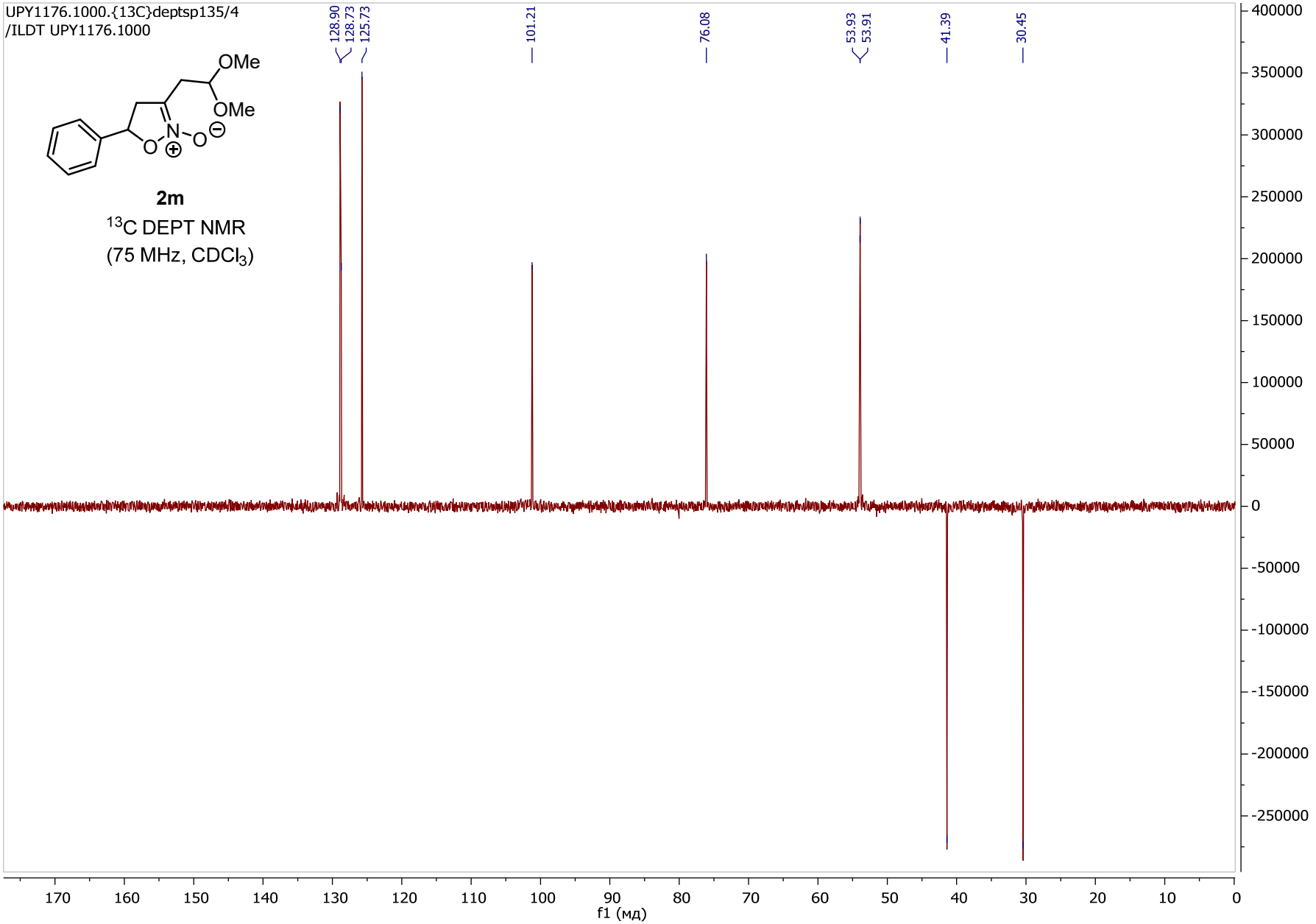
NMR of **2m**


UPY1176.1000.{1H}/1
/ILDT UPY1176.1000
OMe
OMe
N
O
O
2m
1H NMR (300 MHz, CDCl3)
7.38 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.31 7.31 7.30 7.30
5.59 5.57 5.56 5.53
4.61 4.59 4.57
3.57 3.54 3.51 3.48 3.34 3.32 3.32 3.16 3.13 3.10 3.07
2.73 2.71
4.91 0.96 1.05 1.03 6.02 1.04 2.00
f1 (мд)

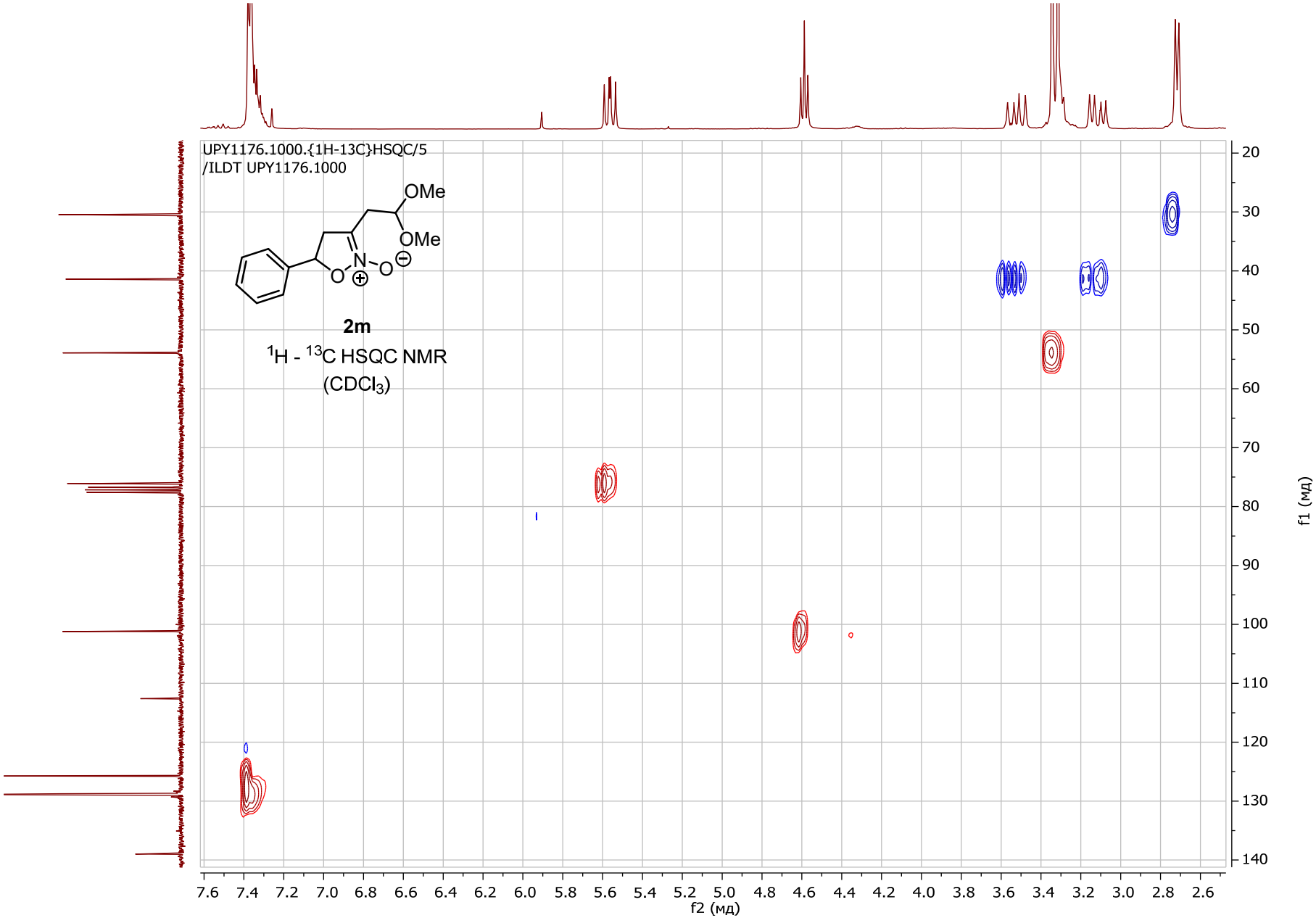
NMR of **2m**


UPY1176.1000.{13C}/2
/ILDT UPY1176.1000
OMe
OMe
N
O
O
2m
^{13}C NMR (75 MHz, $CDCl_3$)
138.98
128.90
128.74
125.73
112.60
101.21
77.16
76.08
53.94
53.91
41.40
30.45
f1 (мд)

NMR of **2m**

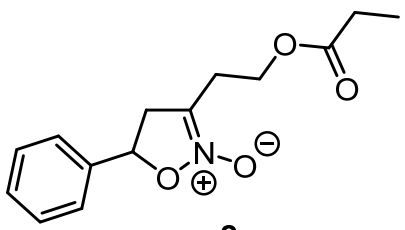

UPY1176.1000.{13C}deptsp135/4
/ILDT UPY1176.1000
OMe
OMe
N
O
O
2m
13C DEPT NMR
(75 MHz, CDCl3)
128.90
128.73
125.73
101.21
76.08
53.93
53.91
41.39
30.45
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
-100000
-150000
-200000
-250000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (мд)

NMR of **2m**


UPY1176.1000.{1H-13C}HSQC/5
/ILDT UPY1176.1000
OMe
OMe
N
O
O
2m
1H - 13C HSQC NMR
(CDCl3)
f2 (мд)
f1 (мд)

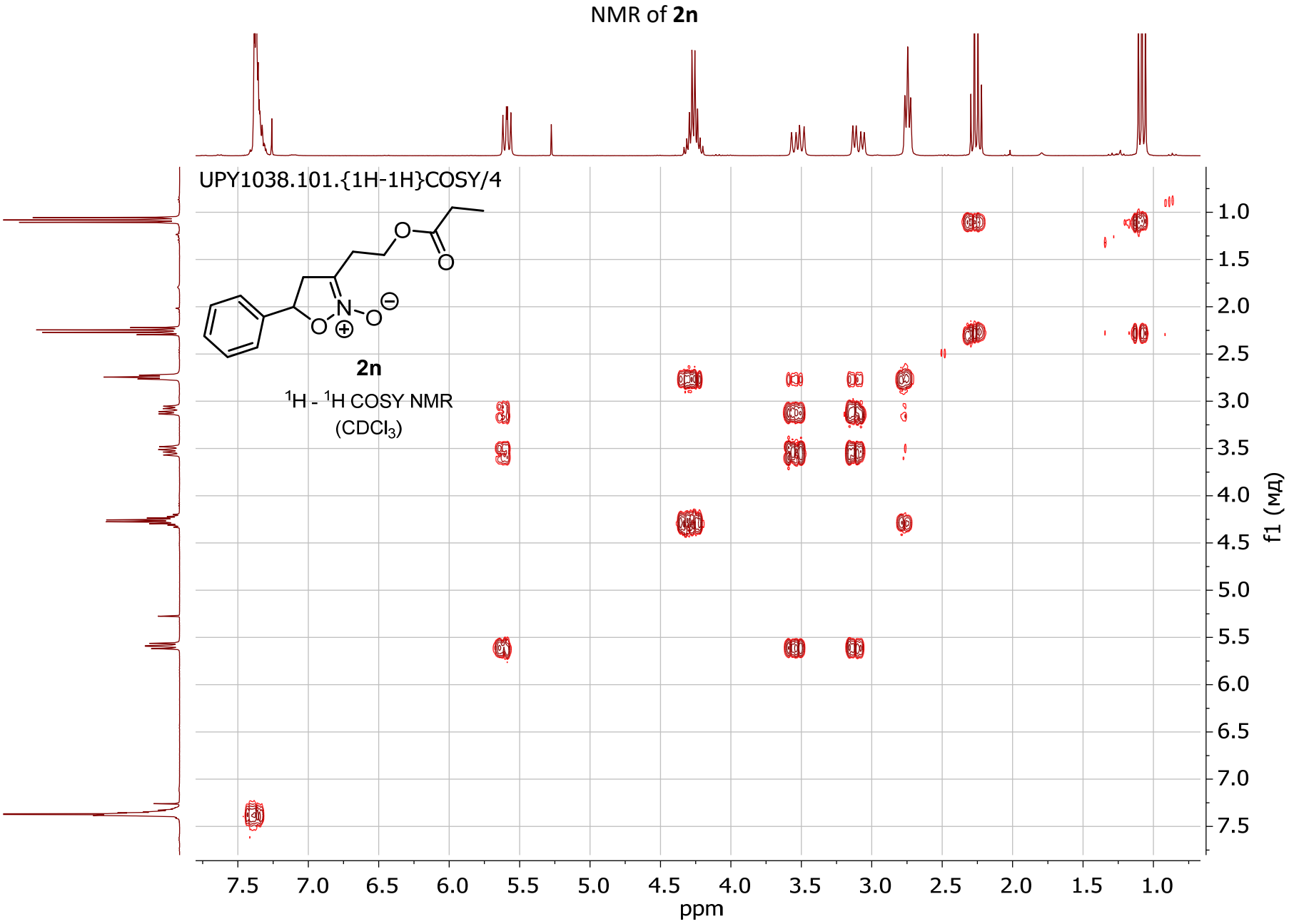
NMR of **2n**

UPY1038.101.{1H}/1



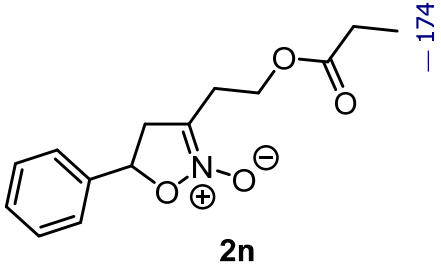
2n

^{1}H NMR (300 MHz, $CDCl_3$)


NMR of **2n**
UPY1038.101.{1H-1H}COSY/4
2n
^{1}H - ^{1}H COSY NMR
($CDCl_3$)
ppm
f1 (мд)

NMR of **2n**

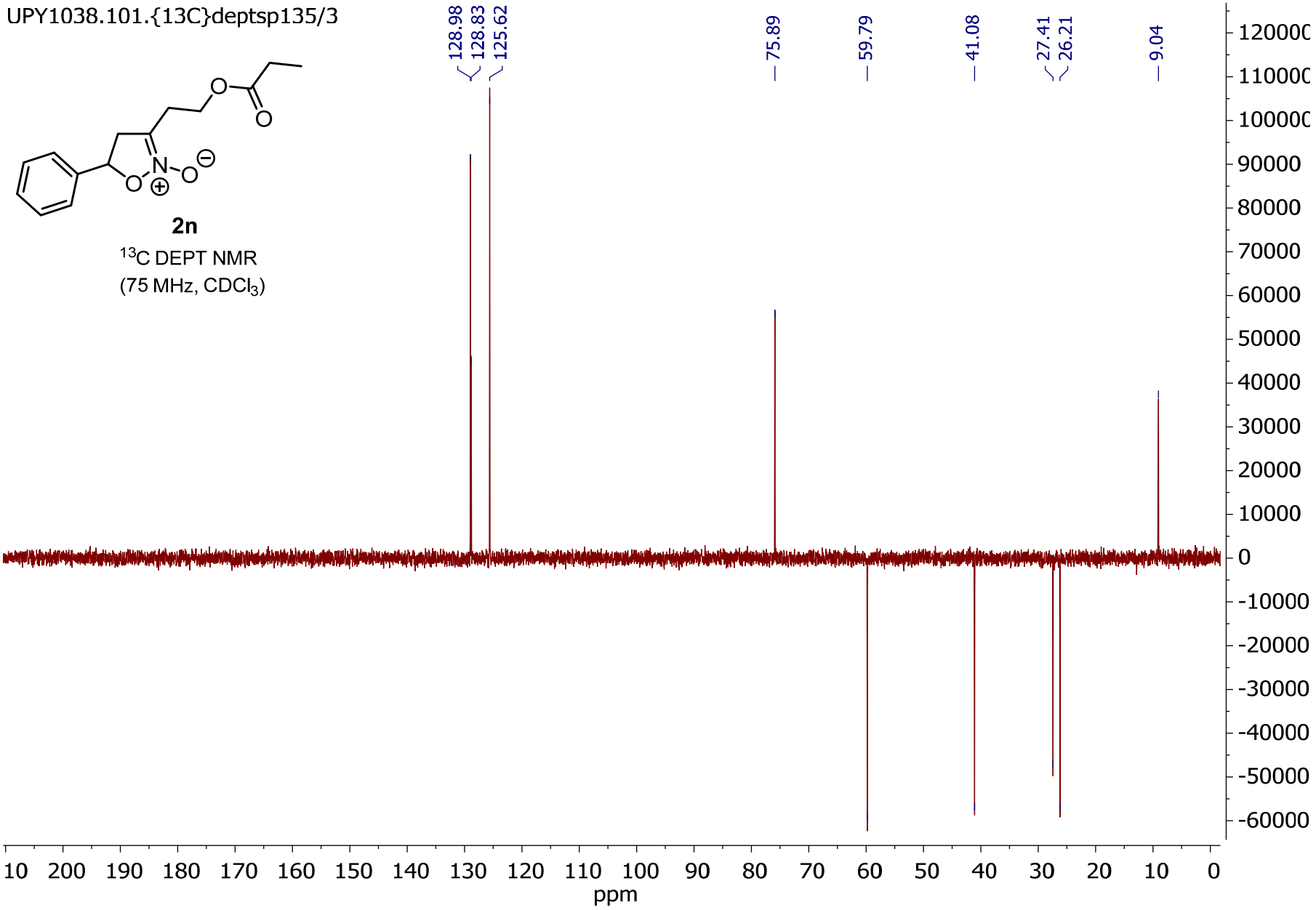
UPY1038.101.{13C}/2

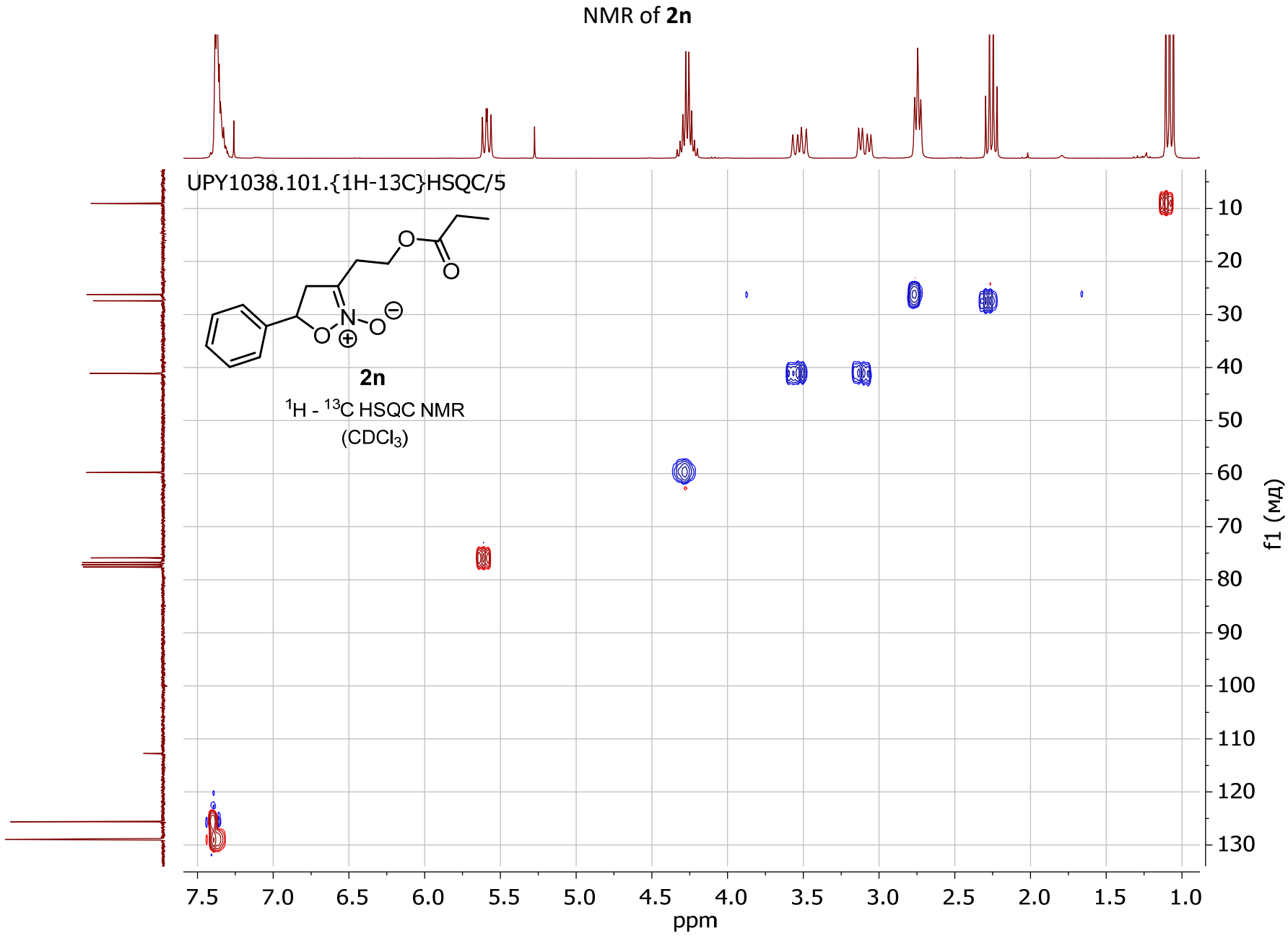


2n

^{13}C NMR (75 MHz, $CDCl_3$)

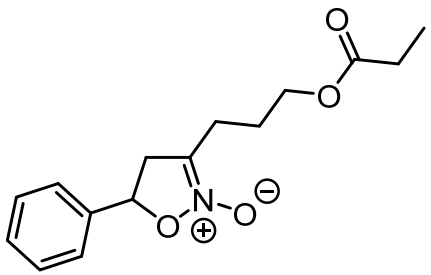
NMR of **2n**


UPY1038.101.{13C}deptsp135/3
128.98
128.83
125.62
75.89
59.79
41.08
27.41
26.21
9.04
2n
13C DEPT NMR
(75 MHz, CDCl3)
ppm


NMR of 2n
UPY1038.101.{1H-13C}HSQC/5
2n
1H - 13C HSQC NMR
(CDCl3)
ppm
f1 (мд)

NMR of **2o**

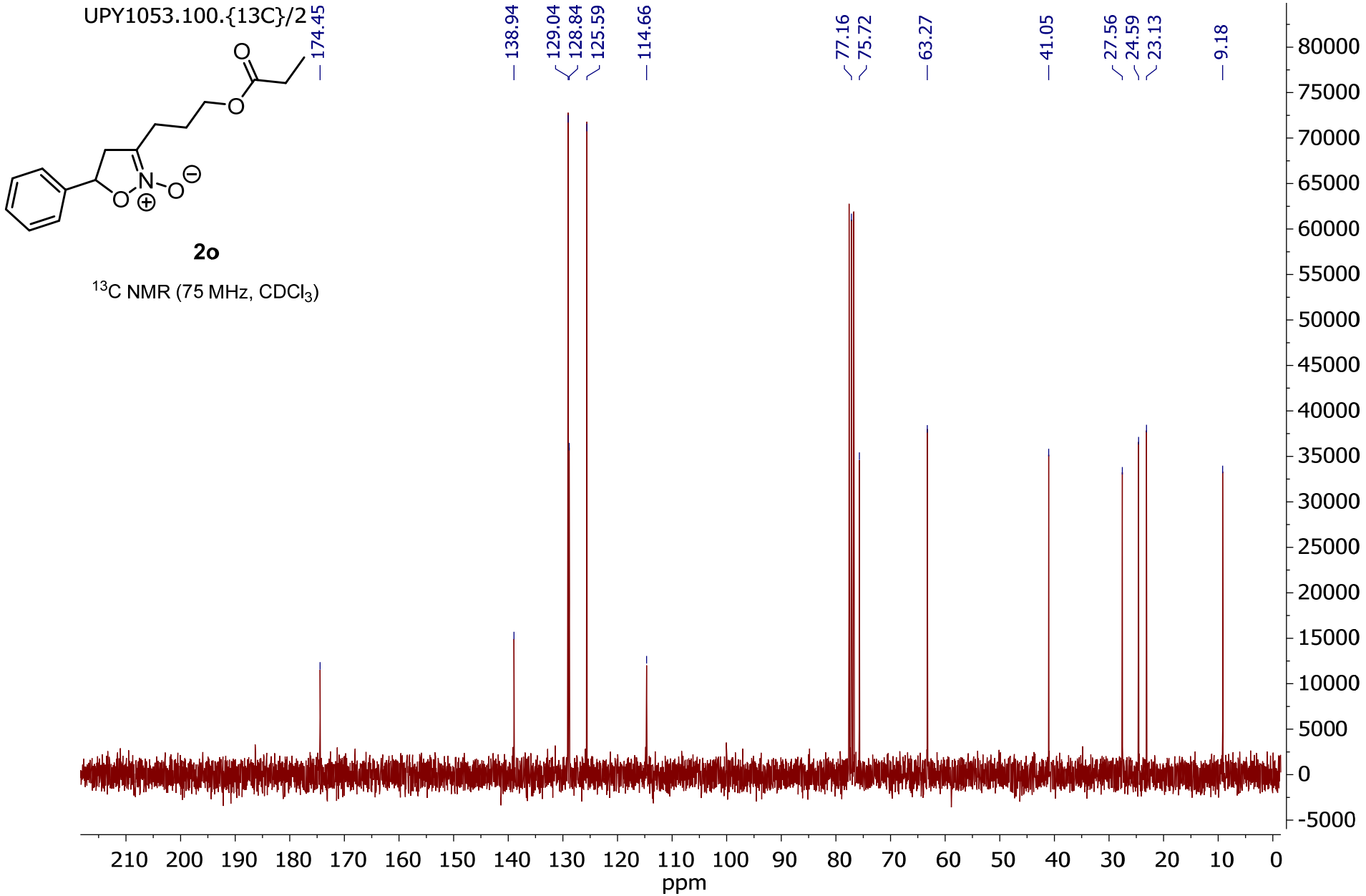
UPY1053.100.{1H}/1



2o

^{1}H NMR (300 MHz, $CDCl_3$)

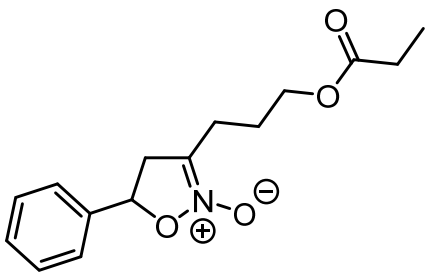
NMR of **2o**



2o

^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **2o**

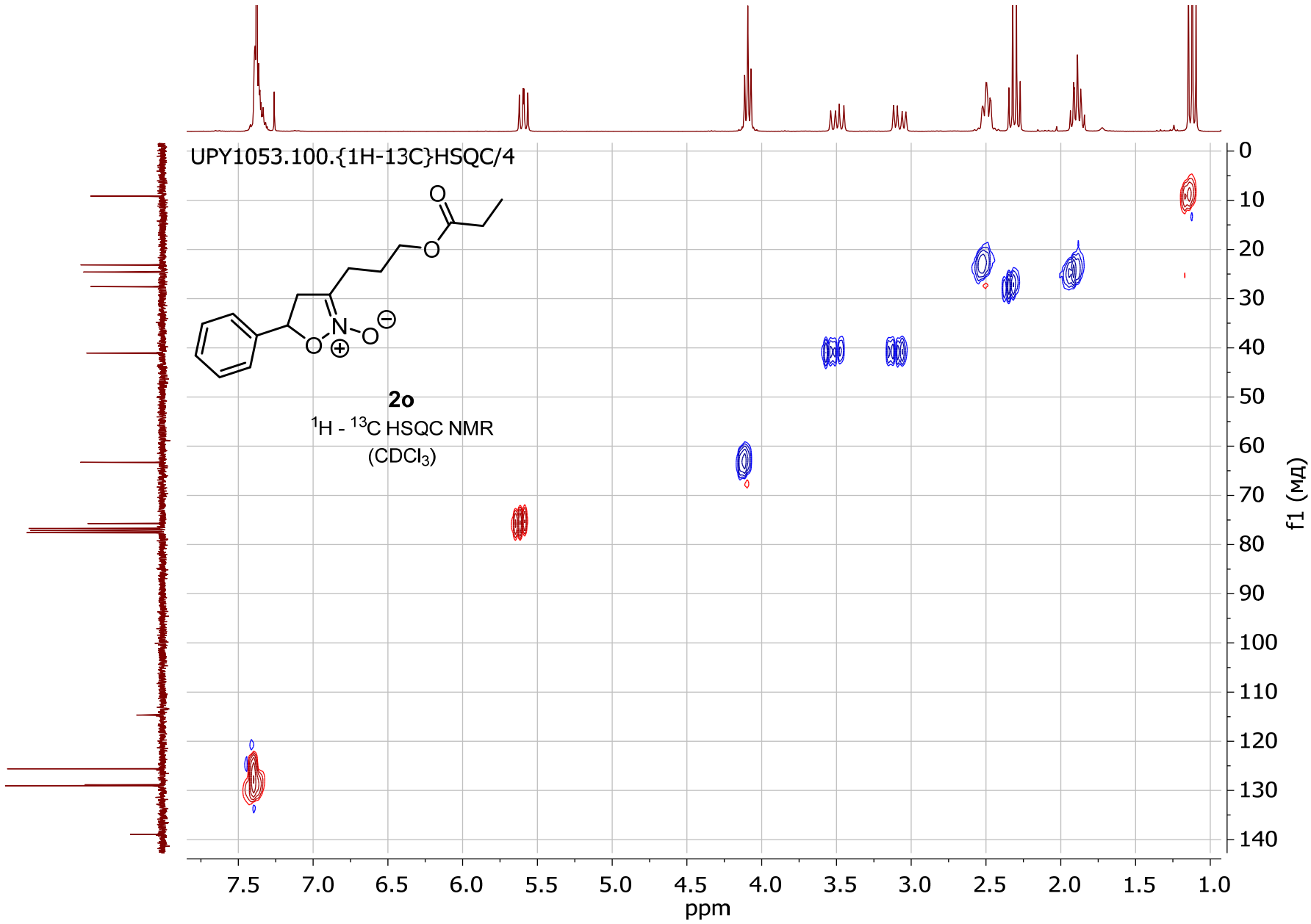


2o

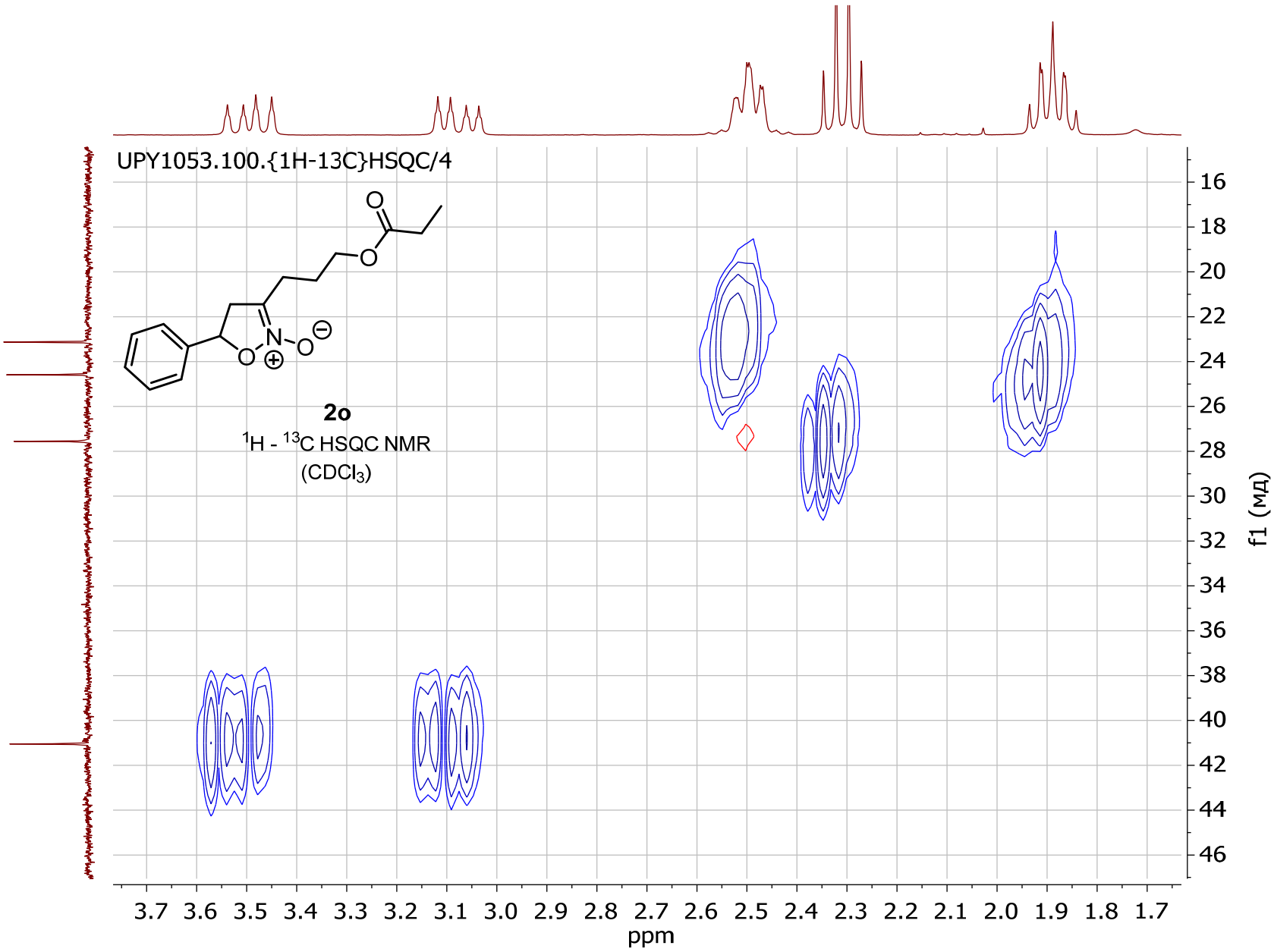
^{13}C DEPT NMR

(75 MHz, $CDCl_3$)

NMR of **2o**

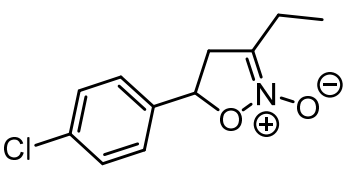


NMR of **2o**



NMR of **2p**

UPY1037.100.{1H}/1

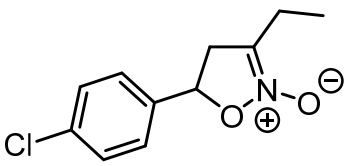


2p

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **2p**

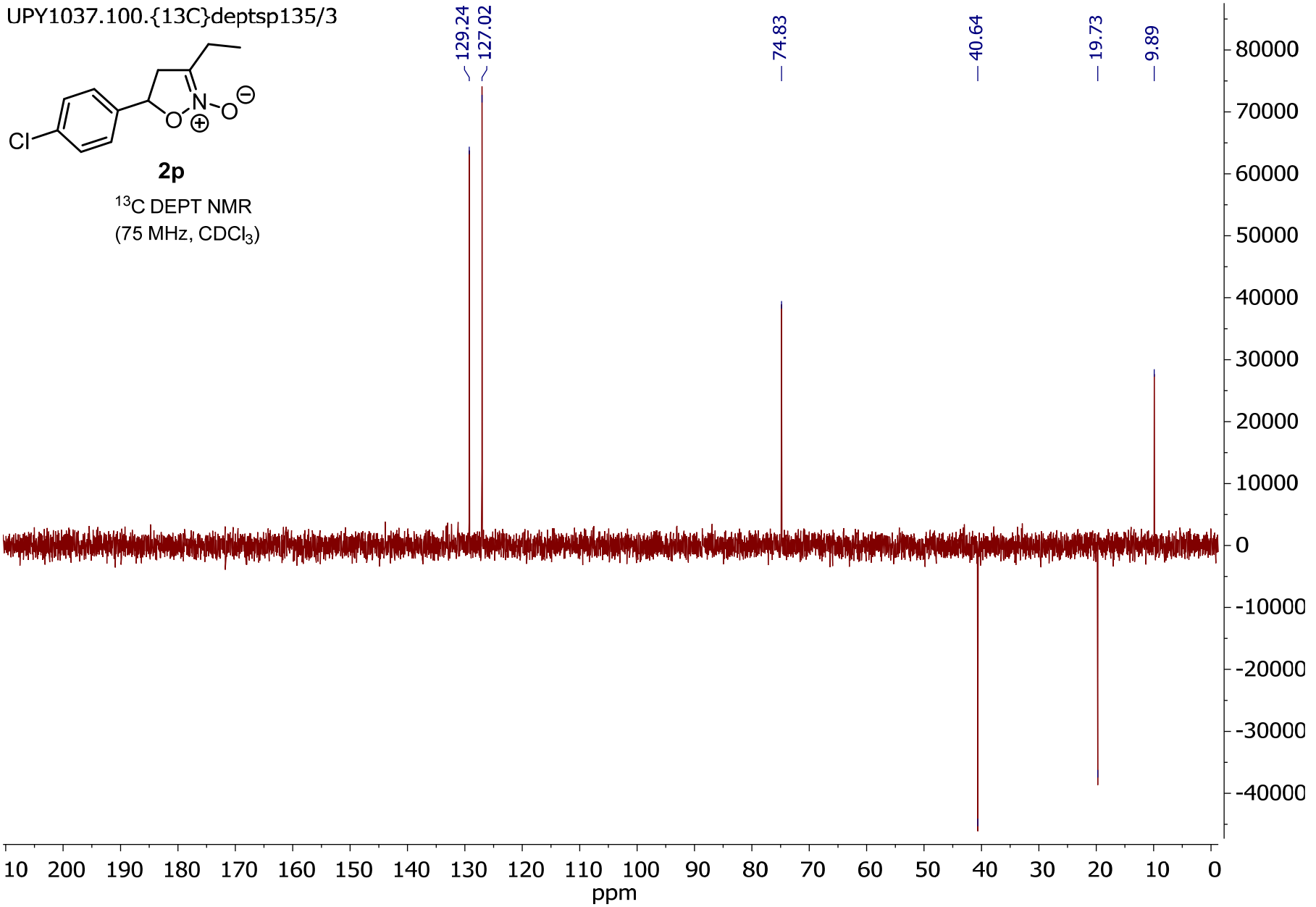
UPY1037.100.{13C}/2



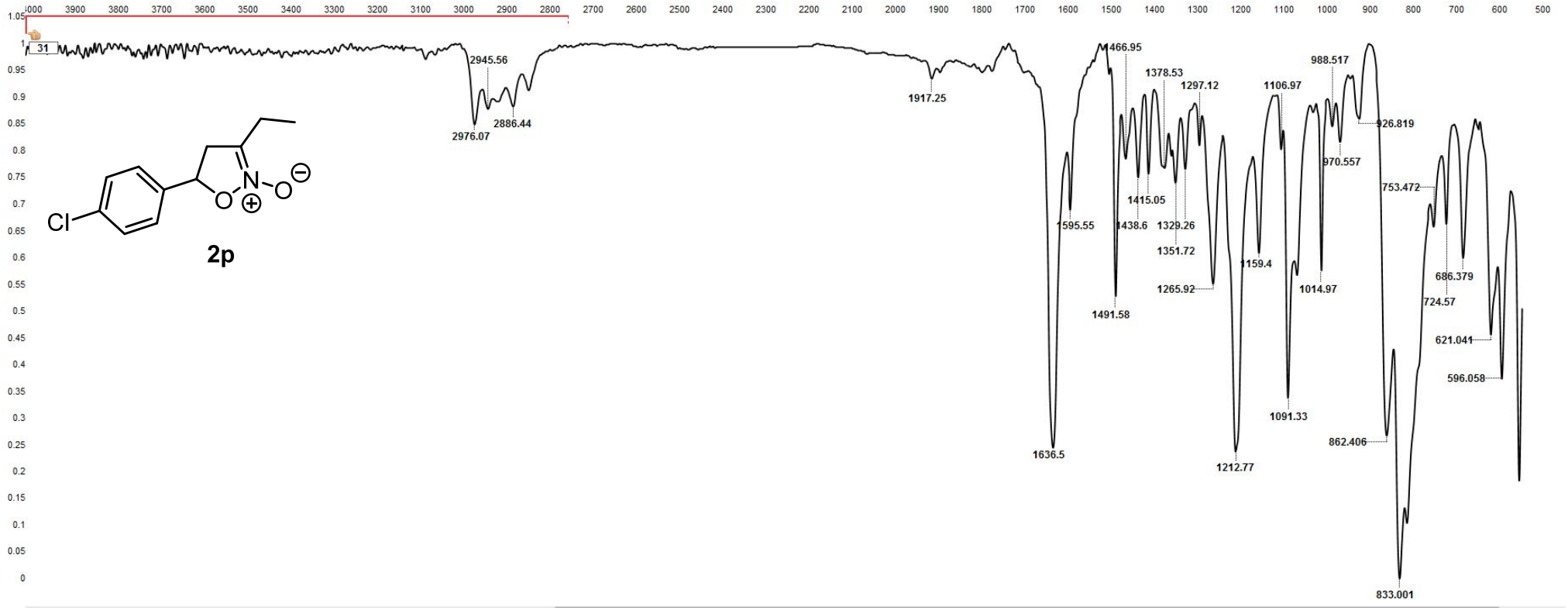
2p

^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **2p**

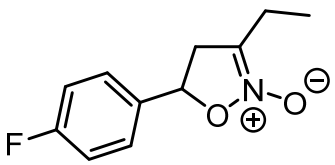

UPY1037.100.{13C}deptsp135/3
129.24
127.02
74.83
40.64
19.73
9.89
Cl
N
O
O
2p
13C DEPT NMR
(75 MHz, CDCl3)
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

FTIR (ATR) of **2p**



NMR of **2q**

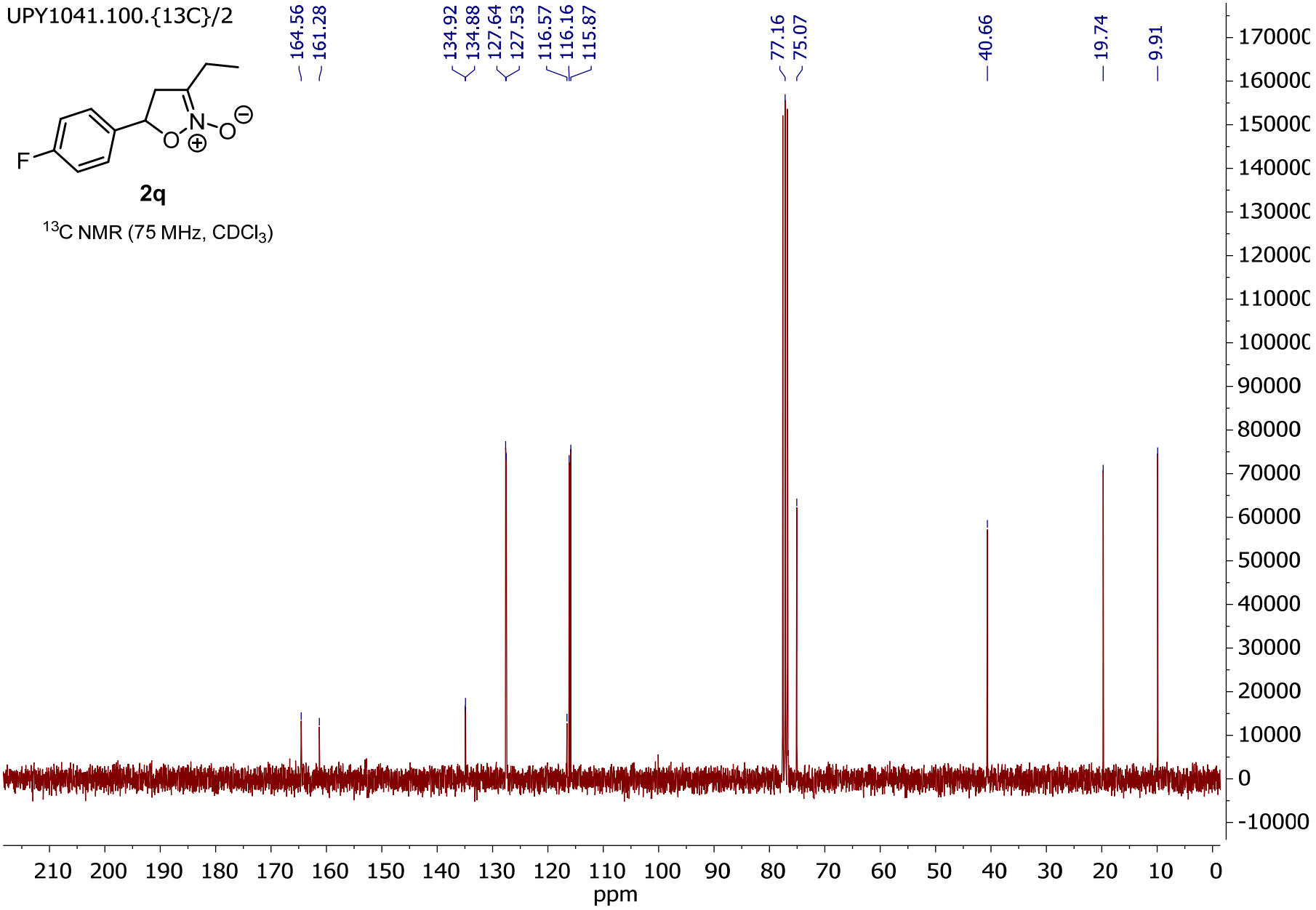
UPY1041.100.{1H}/1



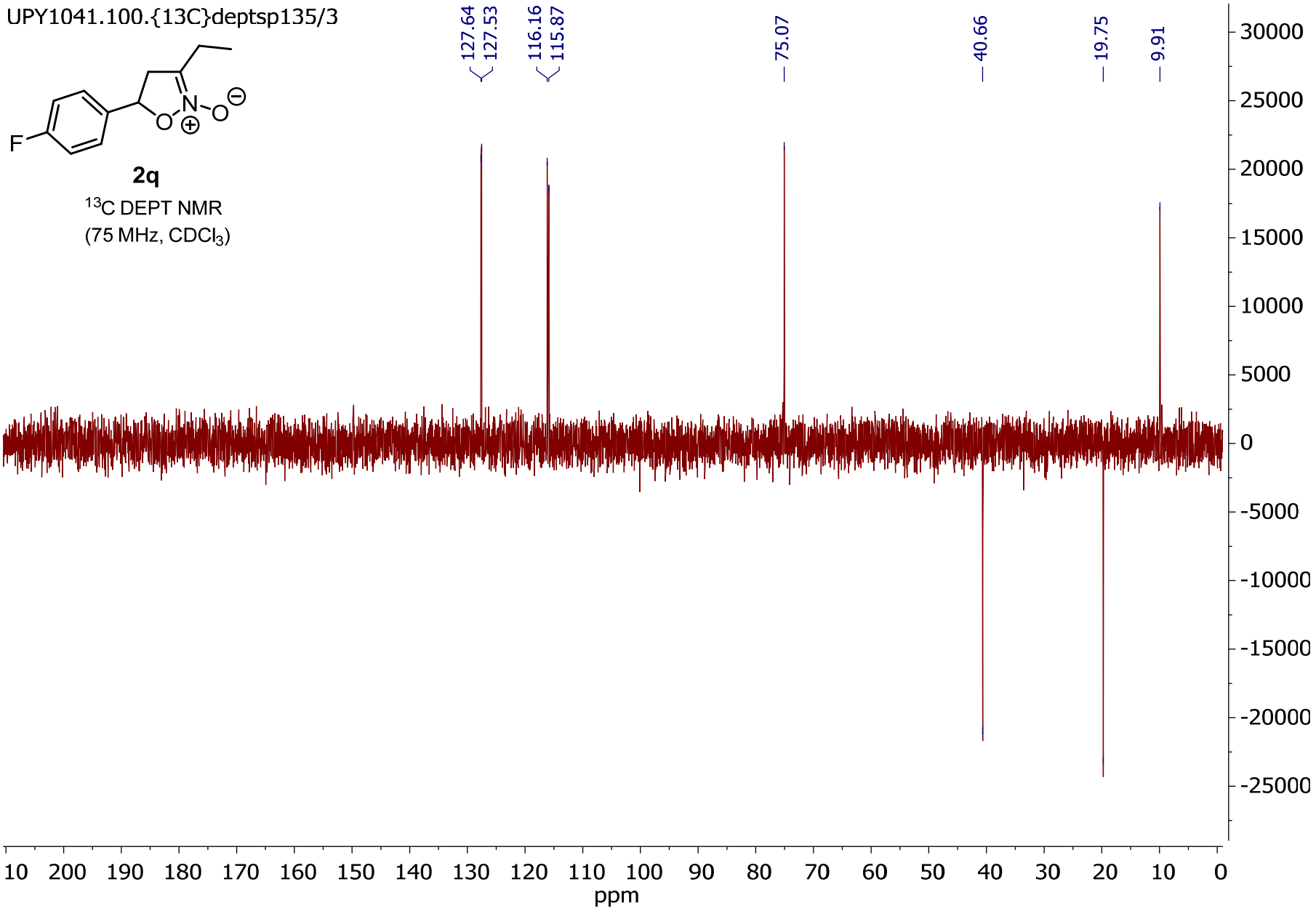
2q

^{1}H NMR (300 MHz, $CDCl_3$)

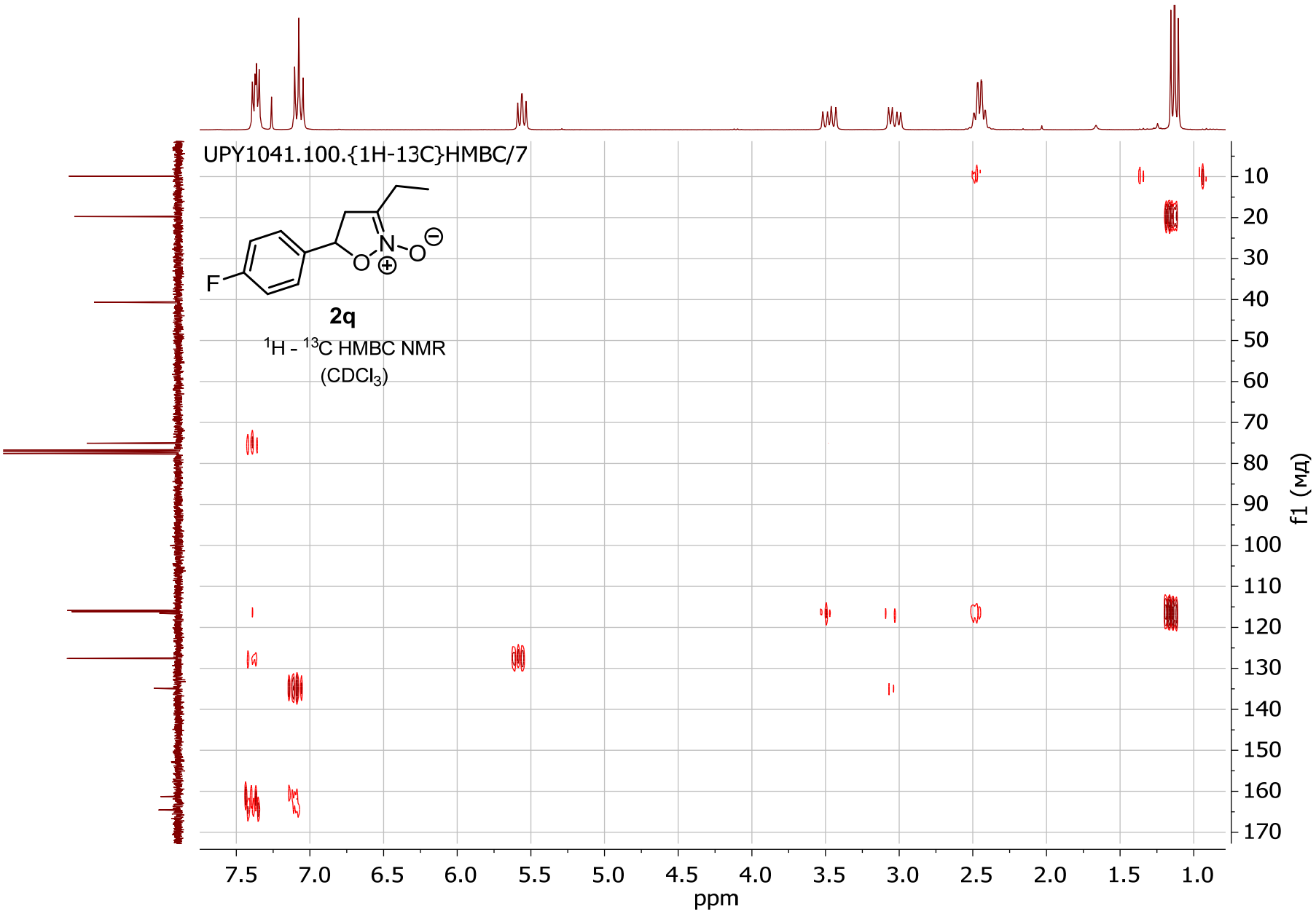
NMR of **2q**


UPY1041.100.{13C}/2
164.56
161.28
134.92
134.88
127.64
127.53
116.57
116.16
115.87
77.16
75.07
40.66
19.74
9.91
F
N
O
O
2q
^{13}C NMR (75 MHz, $CDCl_3$)
ppm

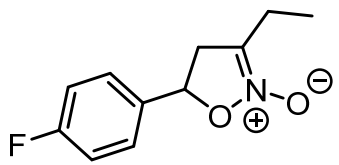
NMR of **2q**


UPY1041.100.{13C}deptsp135/3
127.64
127.53
116.16
115.87
75.07
40.66
19.75
9.91
F
N
O
O
2q
13C DEPT NMR
(75 MHz, CDCl3)
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

NMR of **2q**


UPY1041.100.{1H-13C}HMBC/7
F
N
O
O
2q
1H - 13C HMBC NMR
(CDCl3)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (мд)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

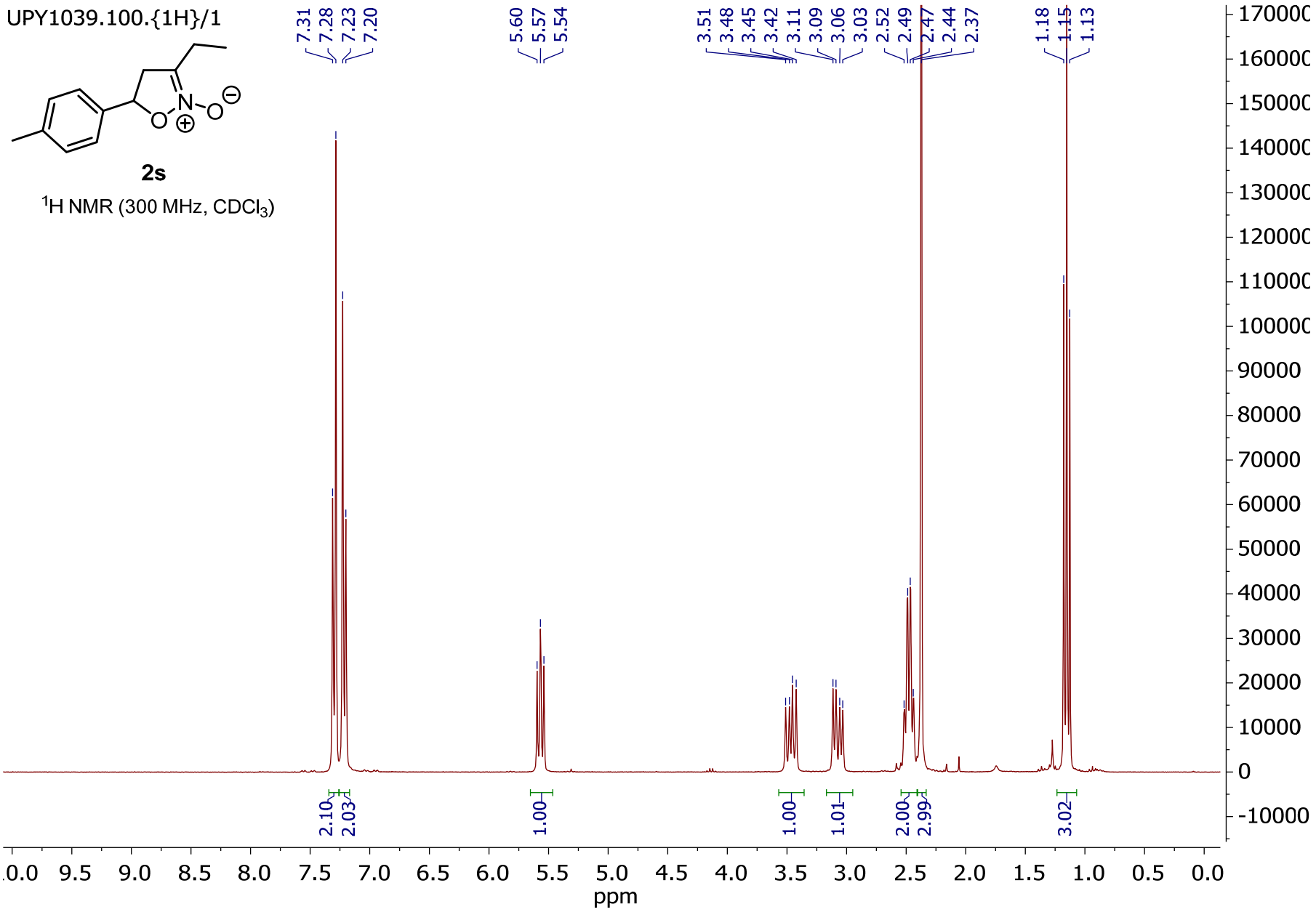
UPY1041.100.{19F}/19



2q

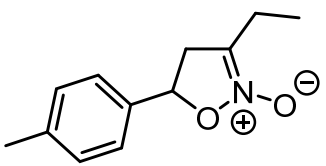
^{19}F NMR (282 MHz, $CDCl_3$)

NMR of **2s**


UPY1039.100.{1H}/1
2s
^{1}H NMR (300 MHz, $CDCl_3$)
7.31
7.28
7.23
7.20
5.60
5.57
5.54
3.51
3.48
3.45
3.42
3.11
3.09
3.06
3.03
2.52
2.49
2.47
2.44
2.37
1.18
1.15
1.13
2.10
2.03
1.00
1.00
1.01
2.00
2.99
3.02
ppm

NMR of **2s**

UPY1039.100.{13C}/2

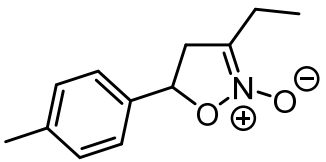


2s

^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **2s**

UPY1039.100.{13C}deptsp135/3

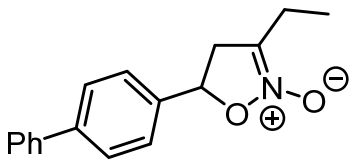


2s

^{13}C DEPT NMR
(75 MHz, $CDCl_3$)

NMR of **2t**

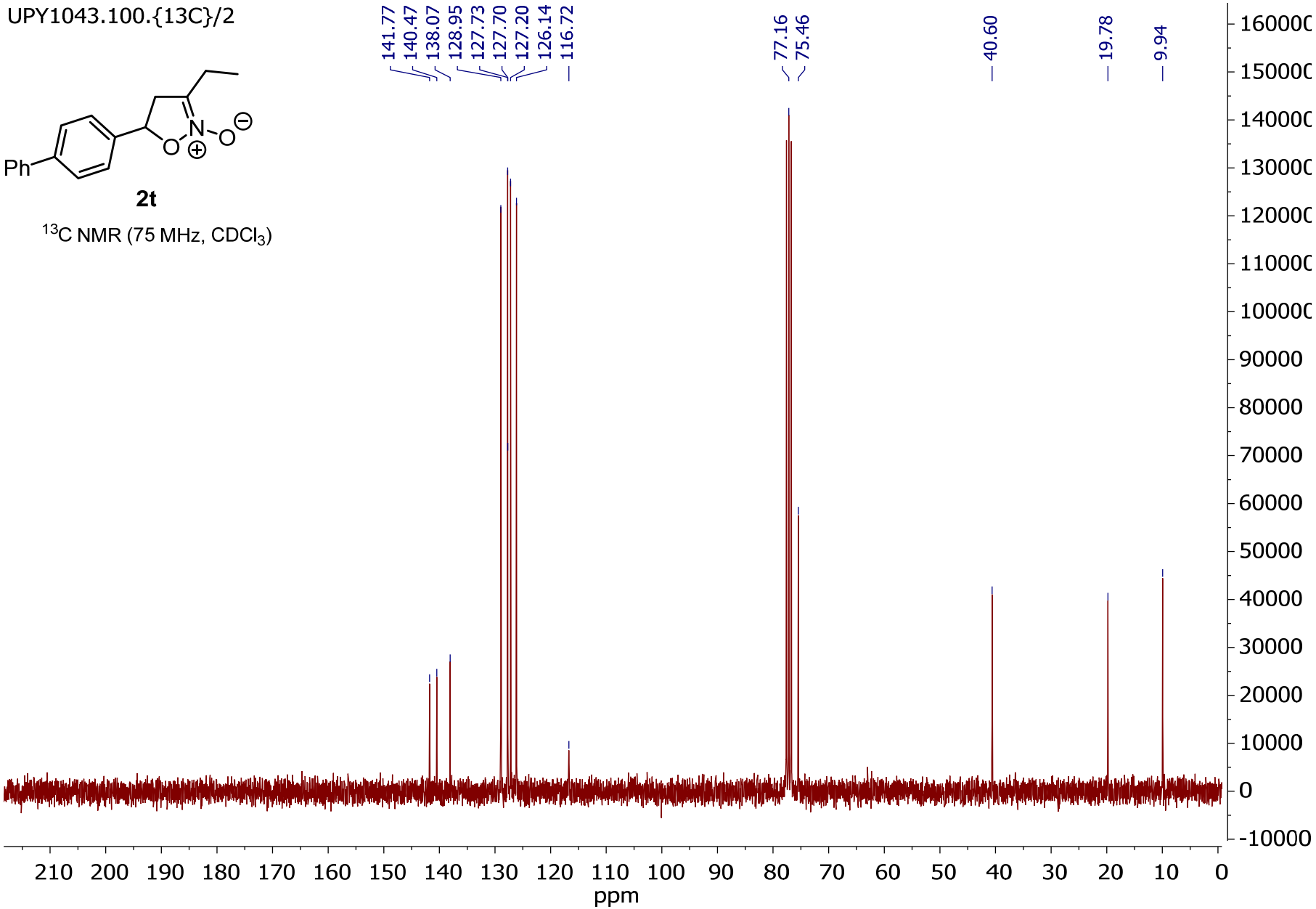
UPY1043.100.{1H}/1



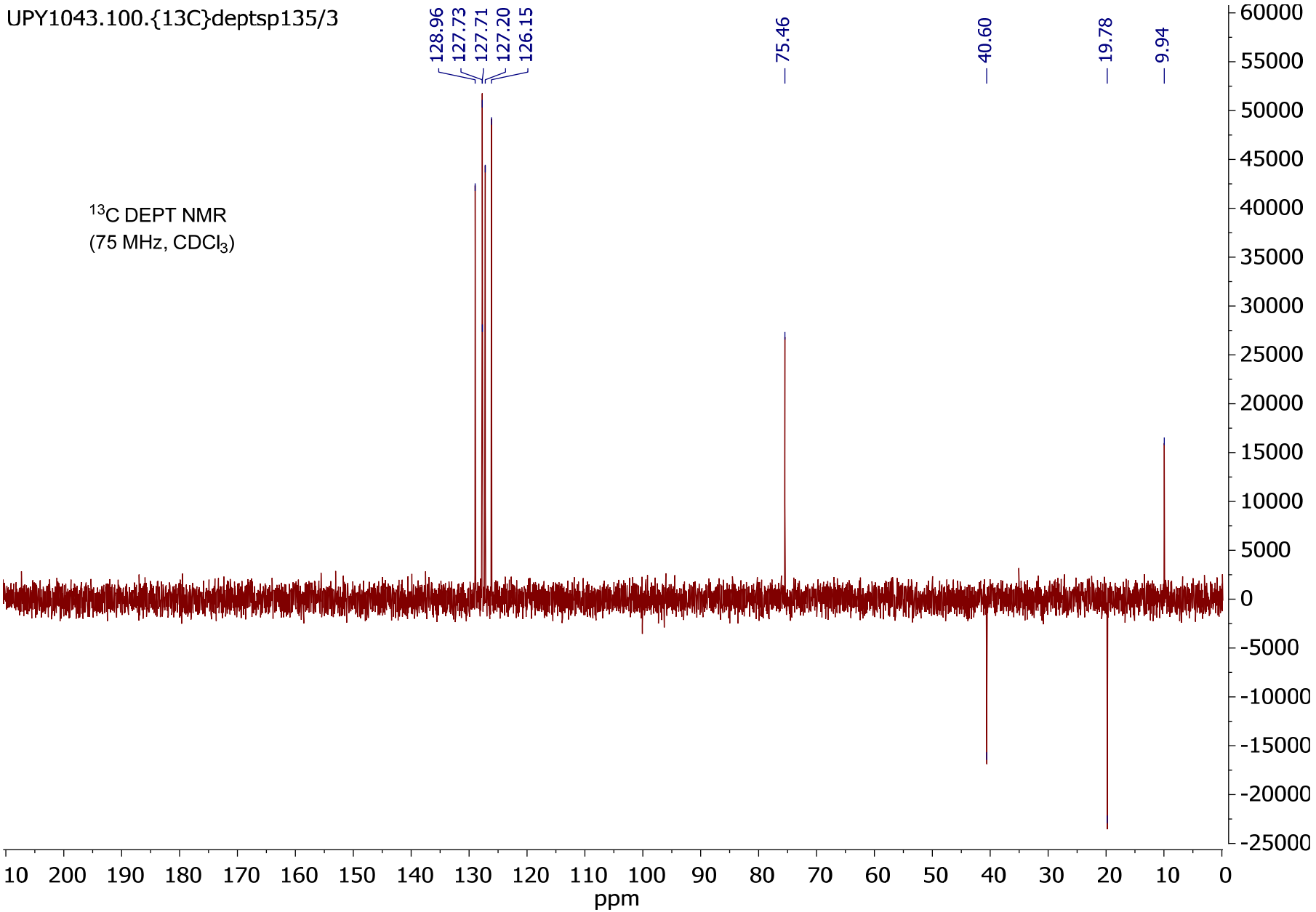
2t

^{1}H NMR (300 MHz, $CDCl_3$)

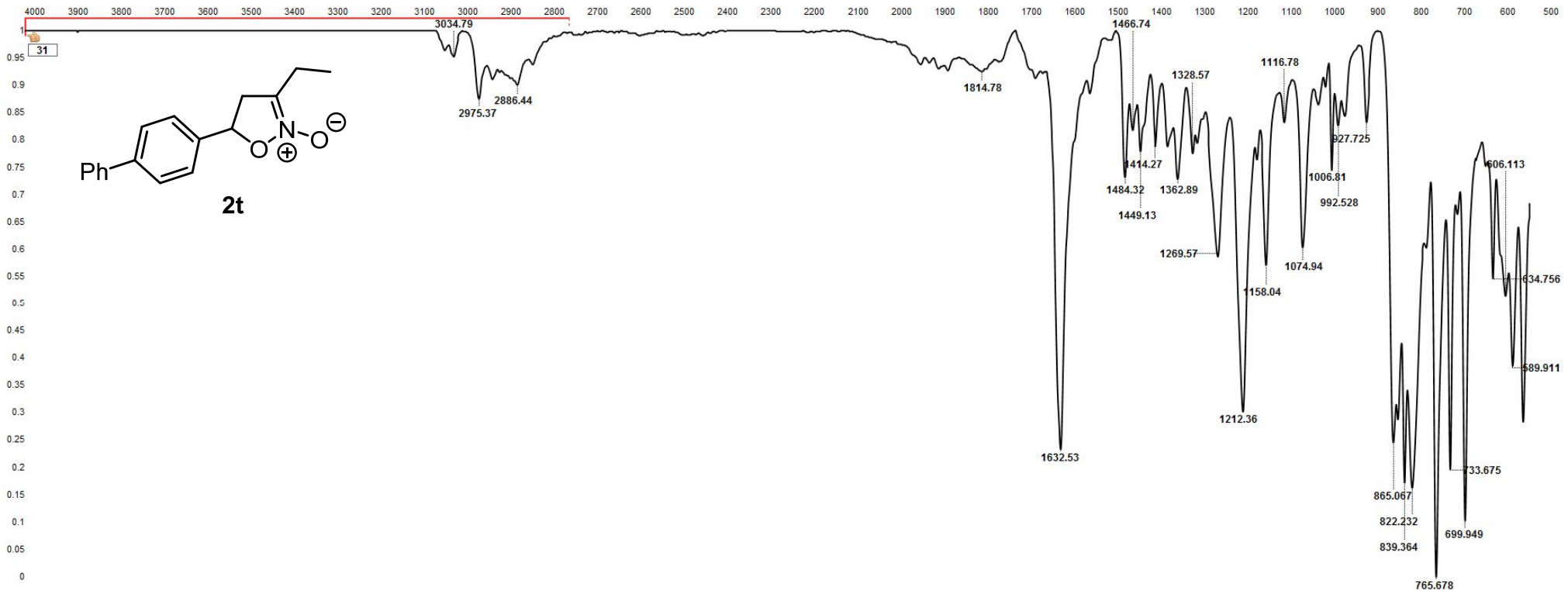
NMR of **2t**


UPY1043.100.{13C}/2
141.77
140.47
138.07
128.95
127.73
127.70
127.20
126.14
116.72
77.16
75.46
40.60
19.78
9.94
Ph
2t
^{13}C NMR (75 MHz, $CDCl_3$)
ppm

NMR of **2t**

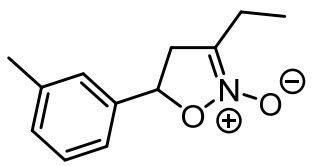

UPY1043.100.{13C}deptsp135/3
128.96
127.73
127.71
127.20
126.15
75.46
40.60
19.78
9.94
^{13}C DEPT NMR
(75 MHz, $CDCl_3$)
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

FTIR (ATR) of **2t**



NMR of **2u**

UPY1040.100.{1H}/1

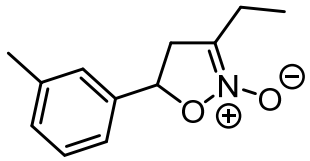


2u

^{1}H NMR (300 MHz, $CDCl_3$)

NMR of **2u**

UPY1040.100.{13C}/2

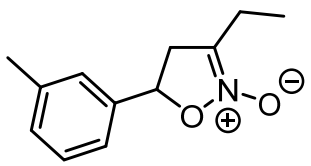


2u

^{13}C NMR (75 MHz, $CDCl_3$)

NMR of **2u**

UPY1040.100.{13C}deptsp135/3

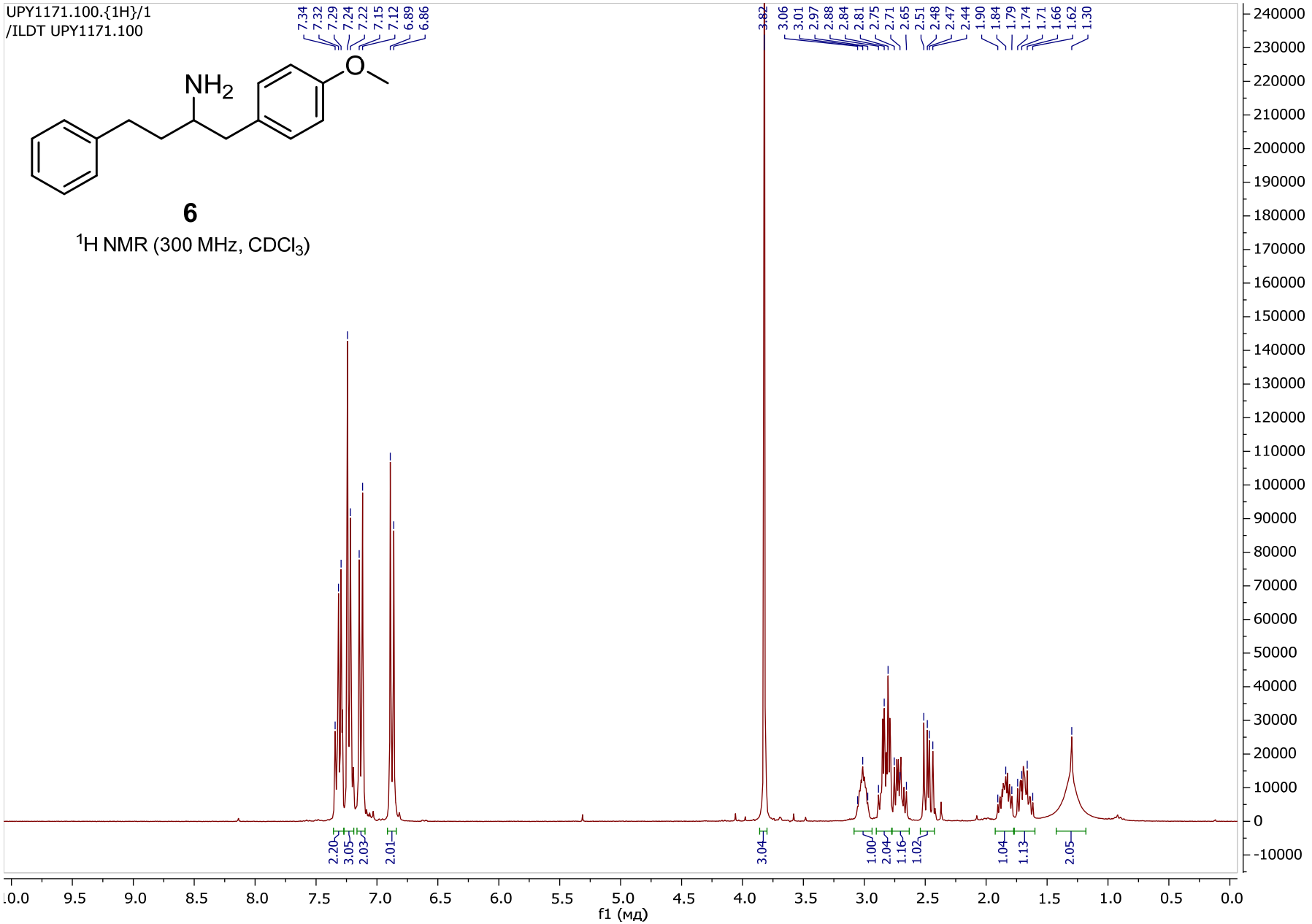


2u

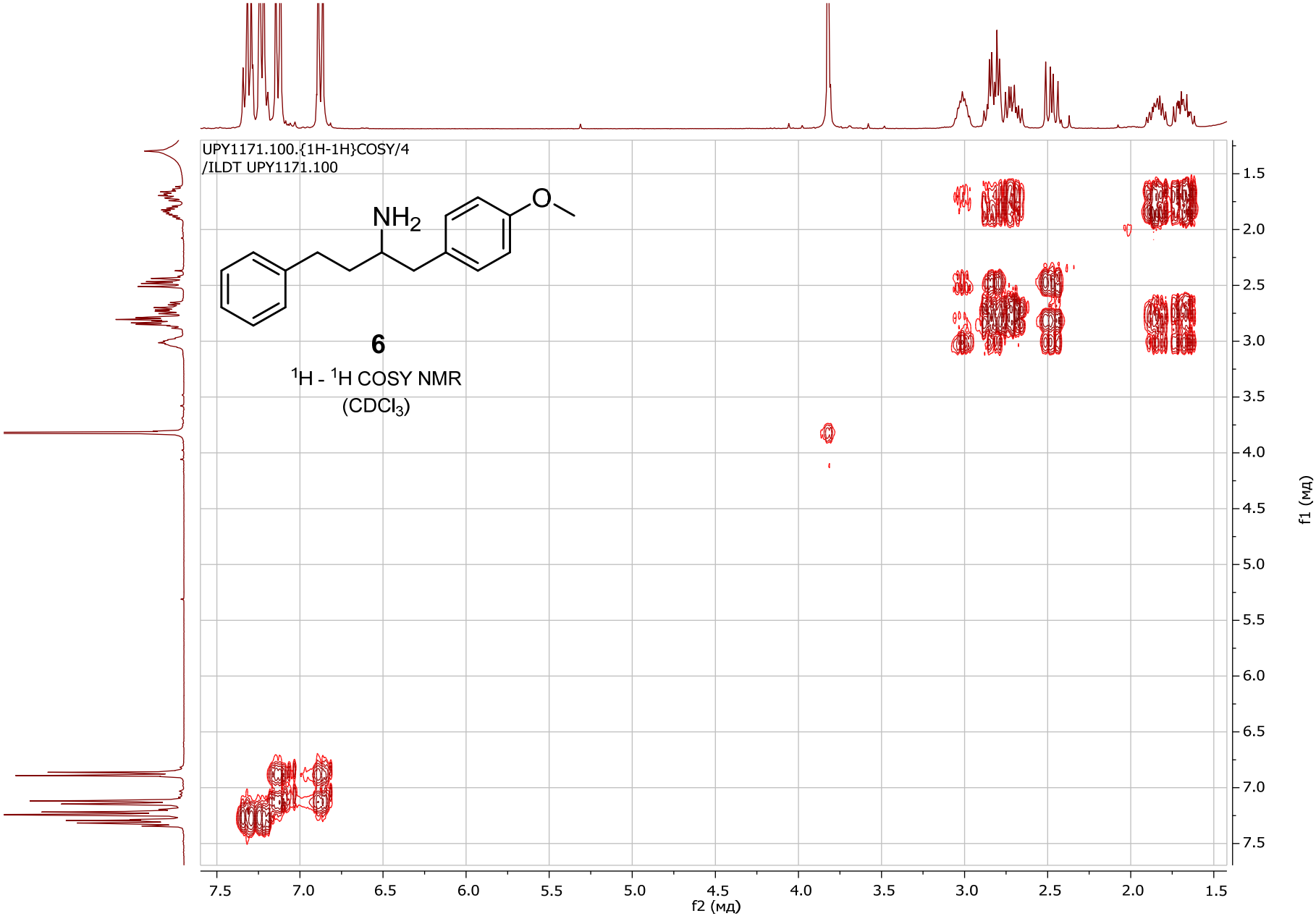
^{13}C DEPT NMR

(75 MHz, $CDCl_3$)

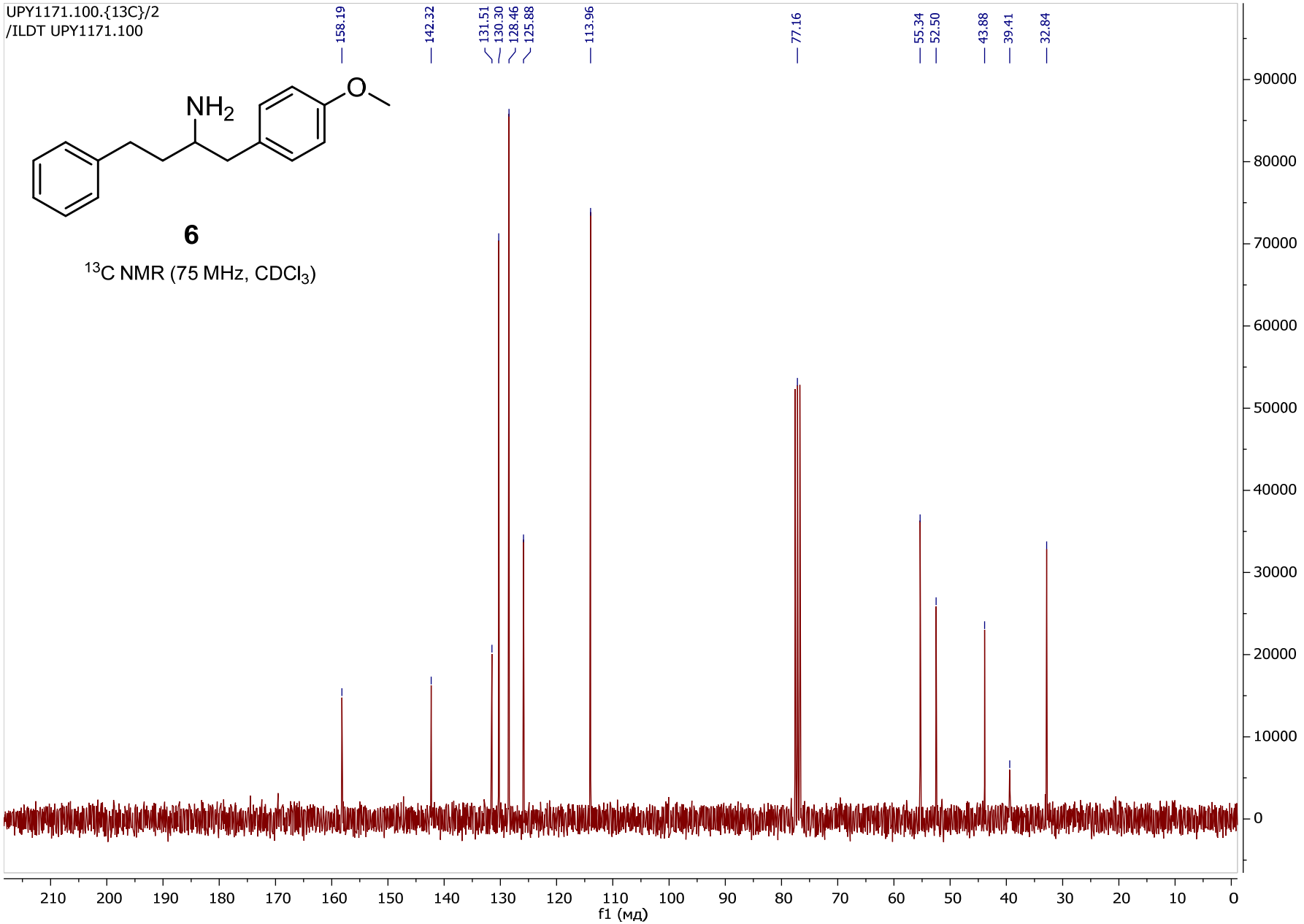
NMR of **6**


UPY1171.100.{1H}/1
/ILDT UPY1171.100
7.34
7.32
7.29
7.24
7.22
7.15
7.12
6.89
6.86
NH2
O
6
1H NMR (300 MHz, CDCl3)
3.82
3.06
3.01
2.97
2.88
2.84
2.81
2.75
2.71
2.65
2.51
2.48
2.47
2.44
1.90
1.84
1.79
1.74
1.71
1.66
1.62
1.30
2.20
3.05
2.03
2.01
3.04
1.00
2.04
1.16
1.02
1.04
1.13
2.05
f1 (мд)

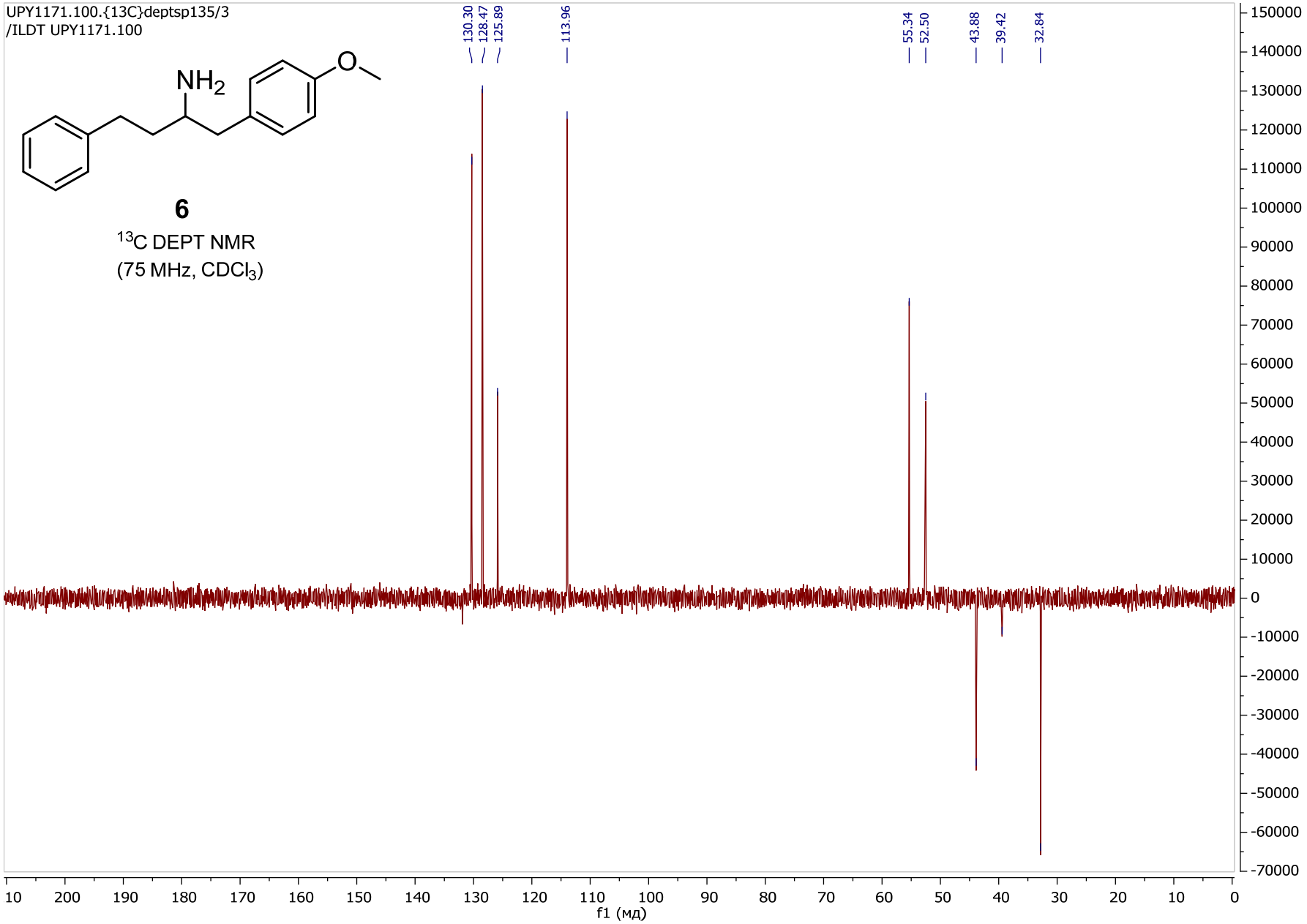
NMR of **6**


UPY1171.100.{1H-1H}COSY/4
/ILDT UPY1171.100
NH2
O
6
1H - 1H COSY NMR
(CDCl3)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (мд)
f1 (мд)

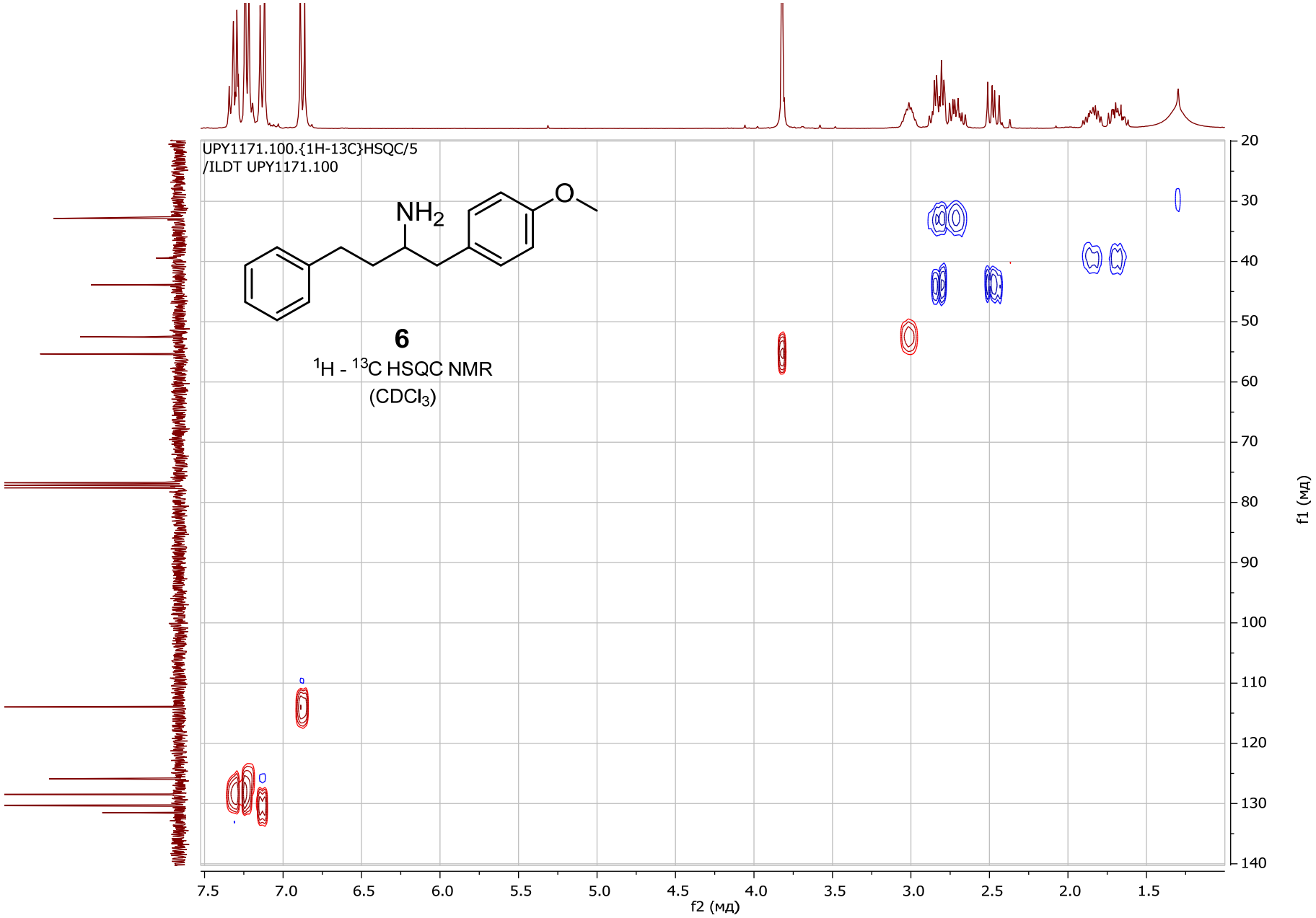
NMR of **6**


UPY1171.100.{13C}/2
/ILDT UPY1171.100
158.19
142.32
131.51
130.30
128.46
125.88
113.96
77.16
55.34
52.50
43.88
39.41
32.84
NH2
O
6
13C NMR (75 MHz, CDCl3)
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (мд)

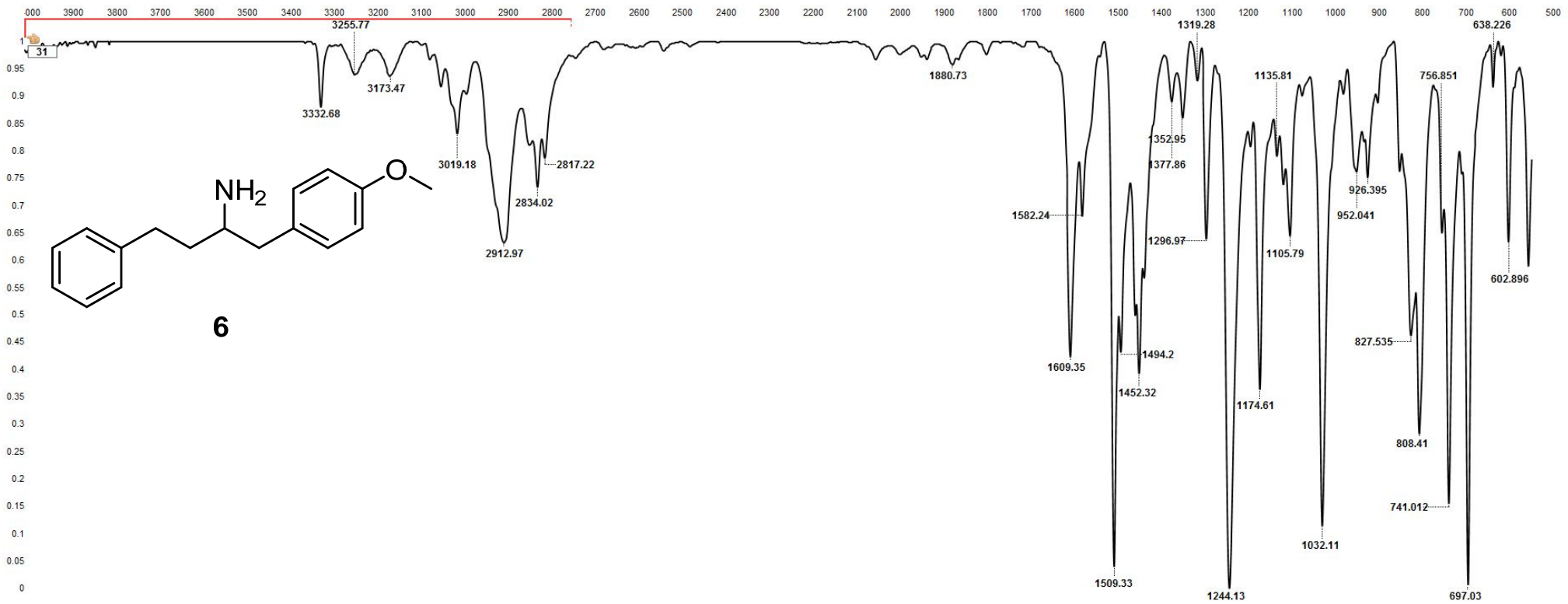
NMR of **6**


UPY1171.100.{13C}deptsp135/3
/ILDT UPY1171.100
NH2
O
6
13C DEPT NMR
(75 MHz, CDCl3)
130.30
128.47
125.89
113.96
55.34
52.50
43.88
39.42
32.84
f1 (мд)

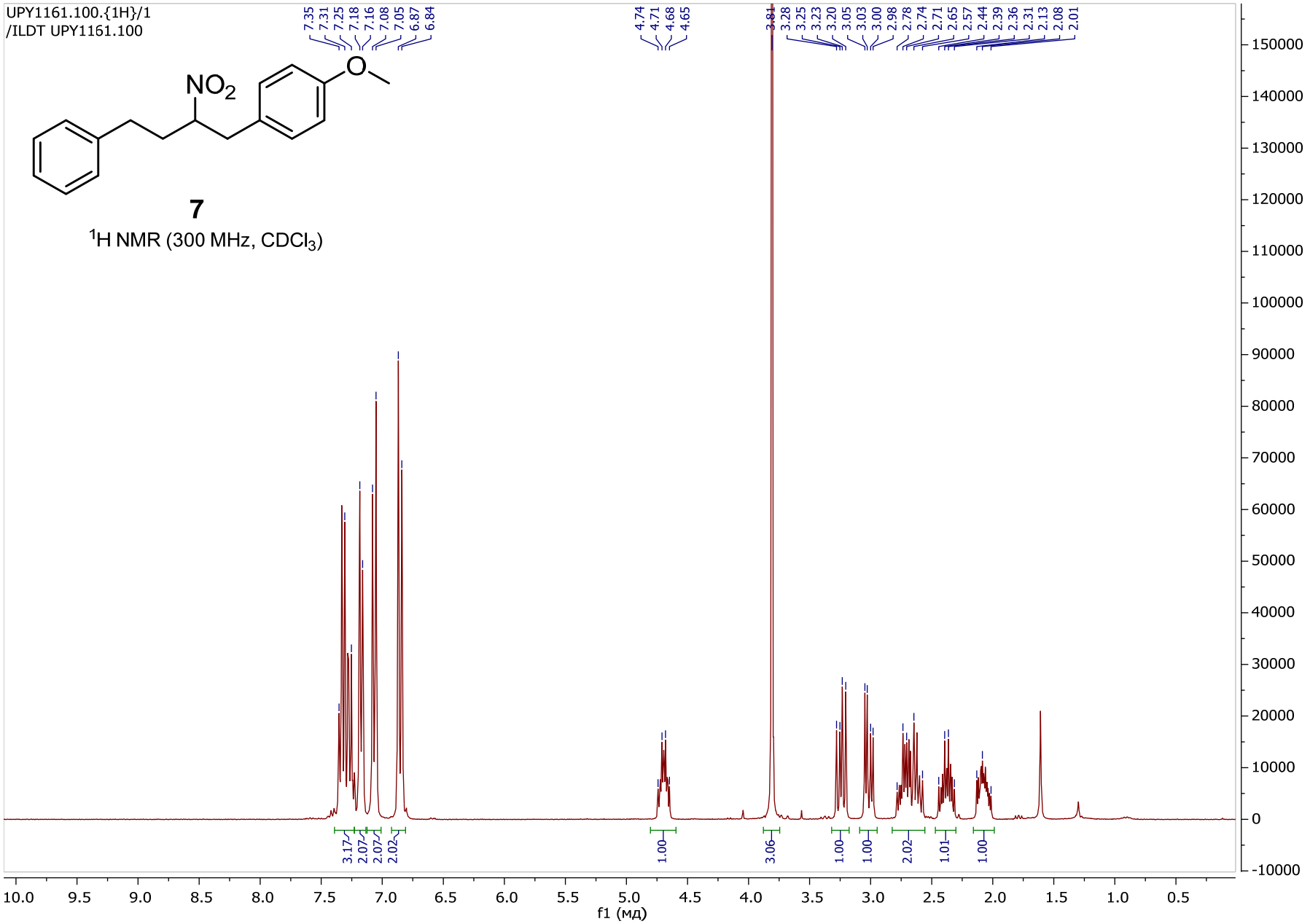
NMR of **6**


UPY1171.100.{1H-13C}HSQC/5
/ILDT UPY1171.100
NH2
O
6
1H - 13C HSQC NMR
(CDCl3)
f2 (мд)
f1 (мд)

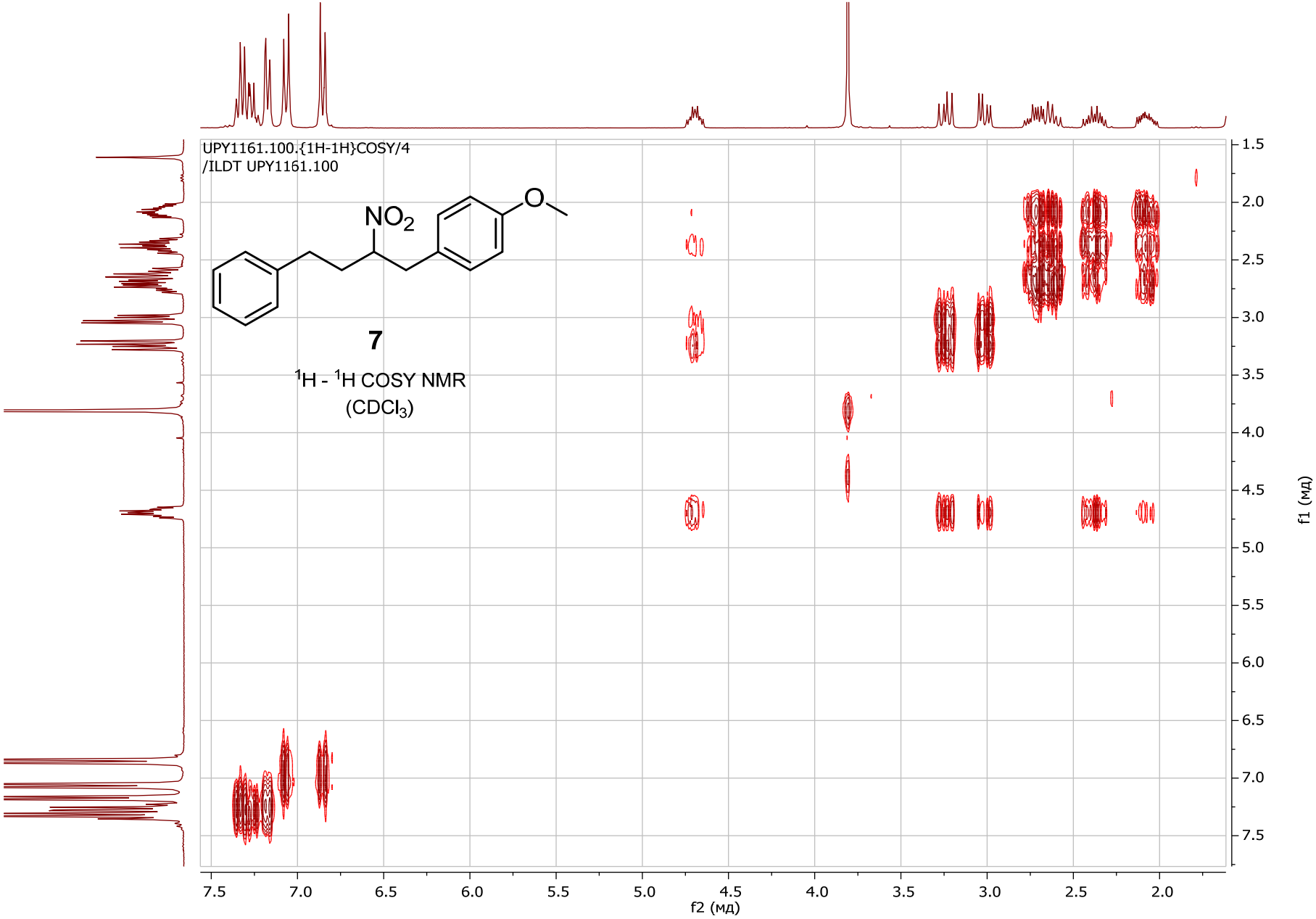
FTIR (ATR) of **6**


3255.77
3332.68
3173.47
3019.18
2912.97
2834.02
2817.22
1880.73
1582.24
1609.35
1509.33
1452.32
1494.2
1352.95
1377.86
1319.28
1296.97
1244.13
1174.61
1135.81
1105.79
1032.11
952.041
926.395
827.535
808.41
756.851
741.012
697.03
638.226
602.896
NH2
O
6

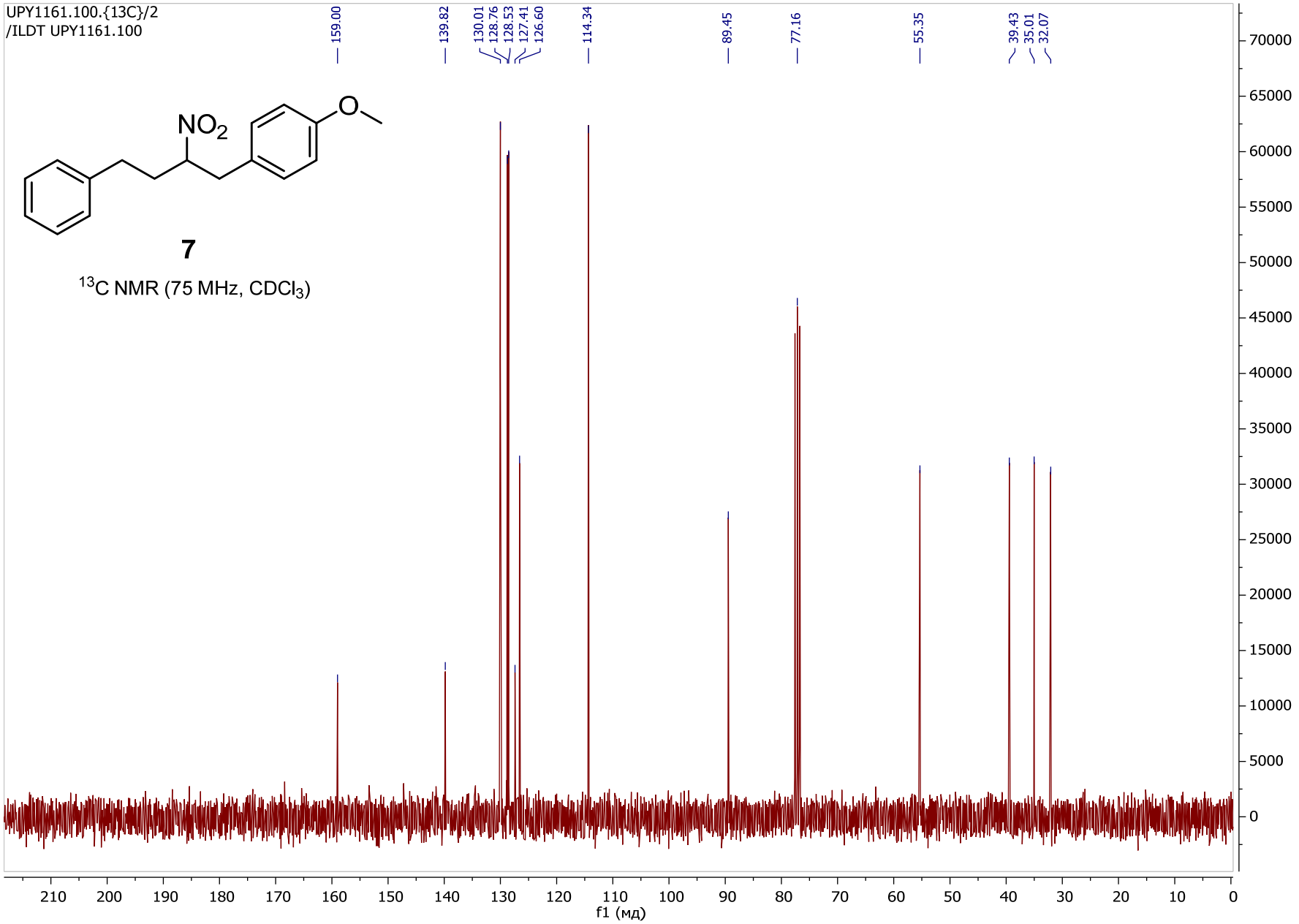
NMR of **7**


UPY1161.100.{1H}/1
/ILDT UPY1161.100
NO2
O
7
1H NMR (300 MHz, CDCl3)
7.35 7.31 7.25 7.18 7.16 7.08 7.05 6.87 6.84
4.74 4.71 4.68 4.65
3.81 3.28 3.25 3.23 3.20 3.05 3.03 3.00 2.98 2.78 2.74 2.71 2.65 2.57 2.44 2.39 2.36 2.31 2.13 2.08 2.01
3.17 2.07 2.07 2.02 1.00 3.06 1.00 1.00 2.02 1.01 1.00
f1 (мд)

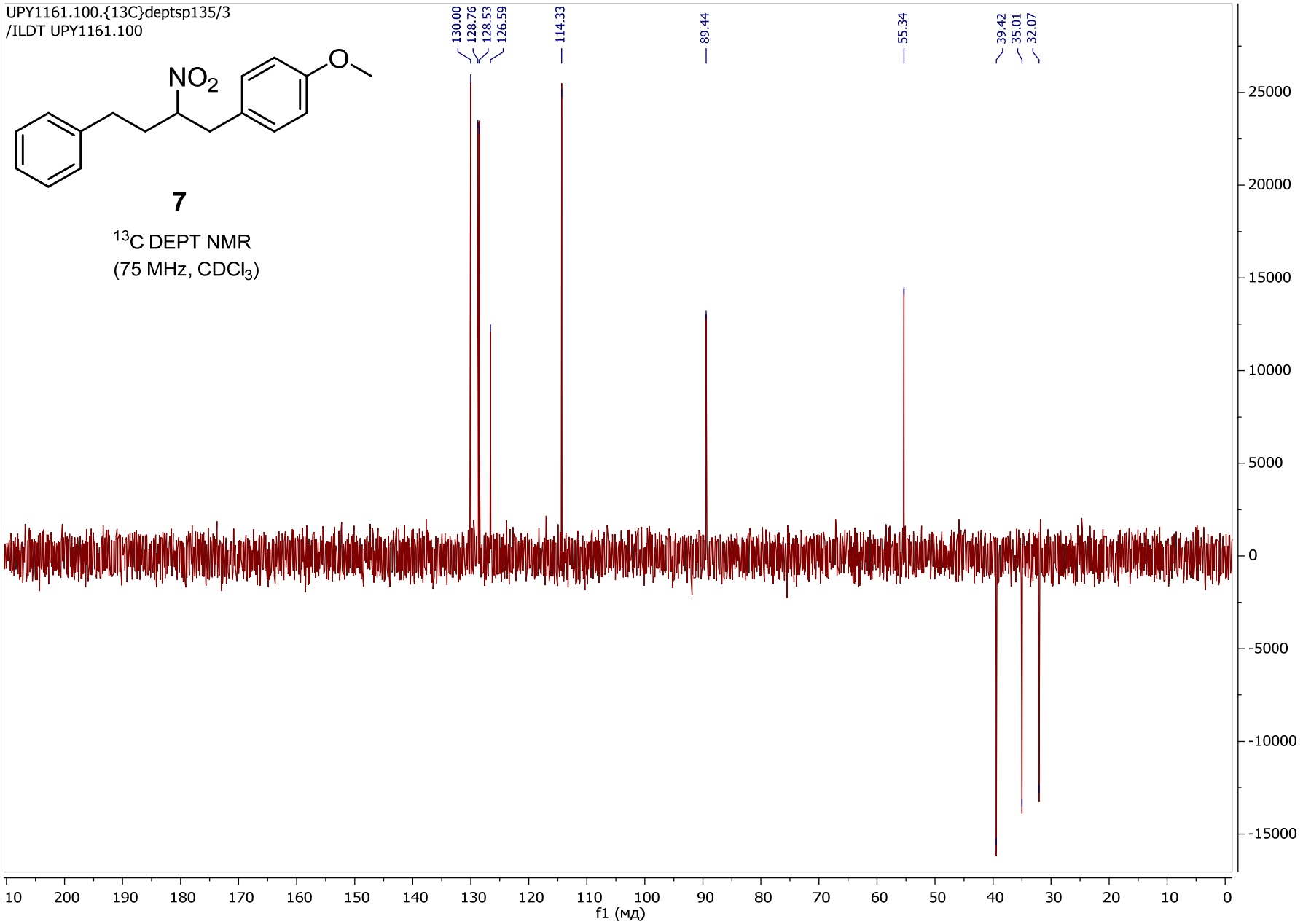
NMR of **7**


UPY1161.100.{1H-1H}COSY/4
/ILDT UPY1161.100
NO2
O
7
1H - 1H COSY NMR
(CDCl3)
f2 (мд)
f1 (мд)

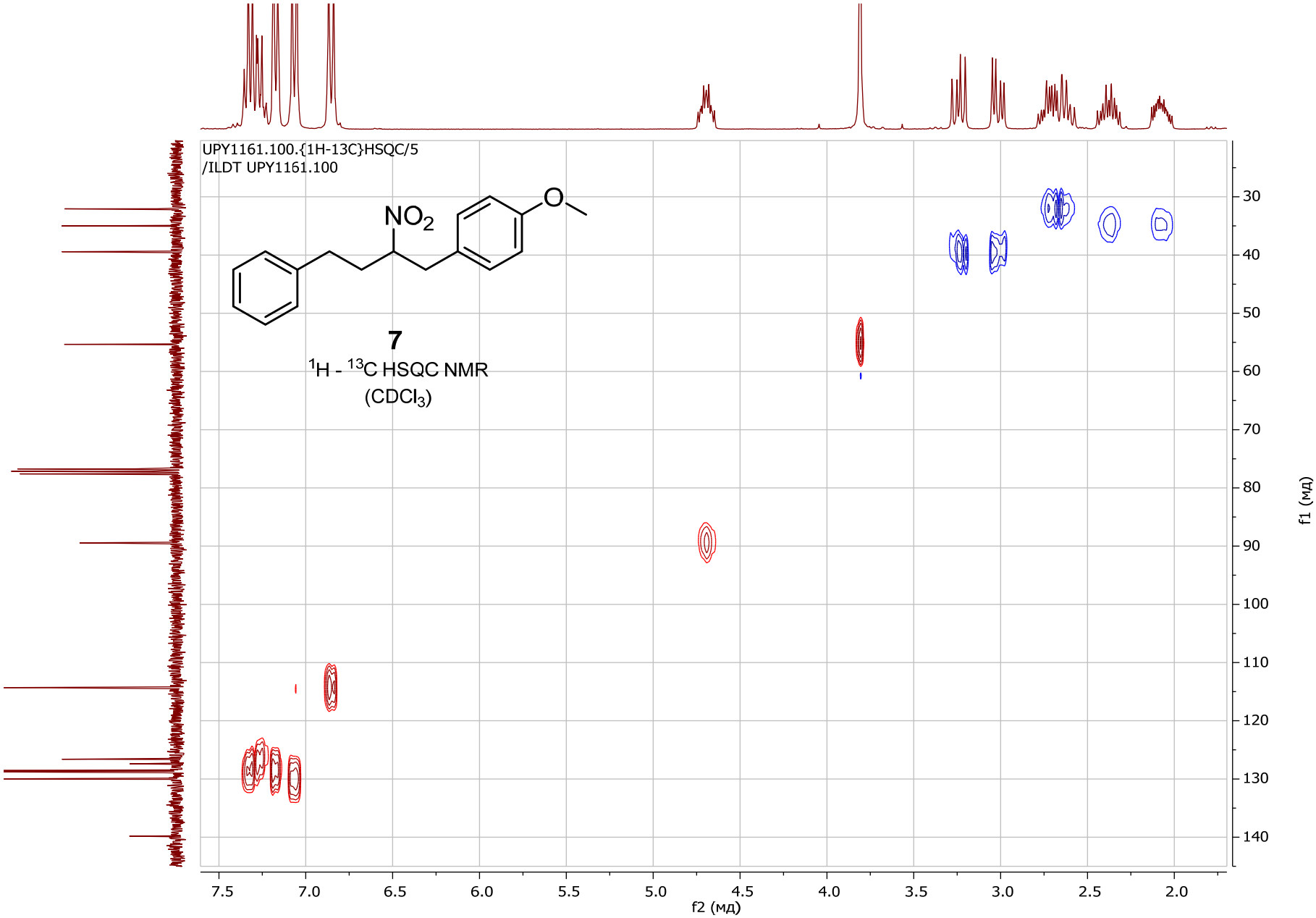
NMR of **7**


UPY1161.100.{13C}/2
/ILDT UPY1161.100
159.00
139.82
130.01
128.76
128.53
127.41
126.60
114.34
89.45
77.16
55.35
39.43
35.01
32.07
NO2
O
7
13C NMR (75 MHz, CDCl3)
f1 (мд)

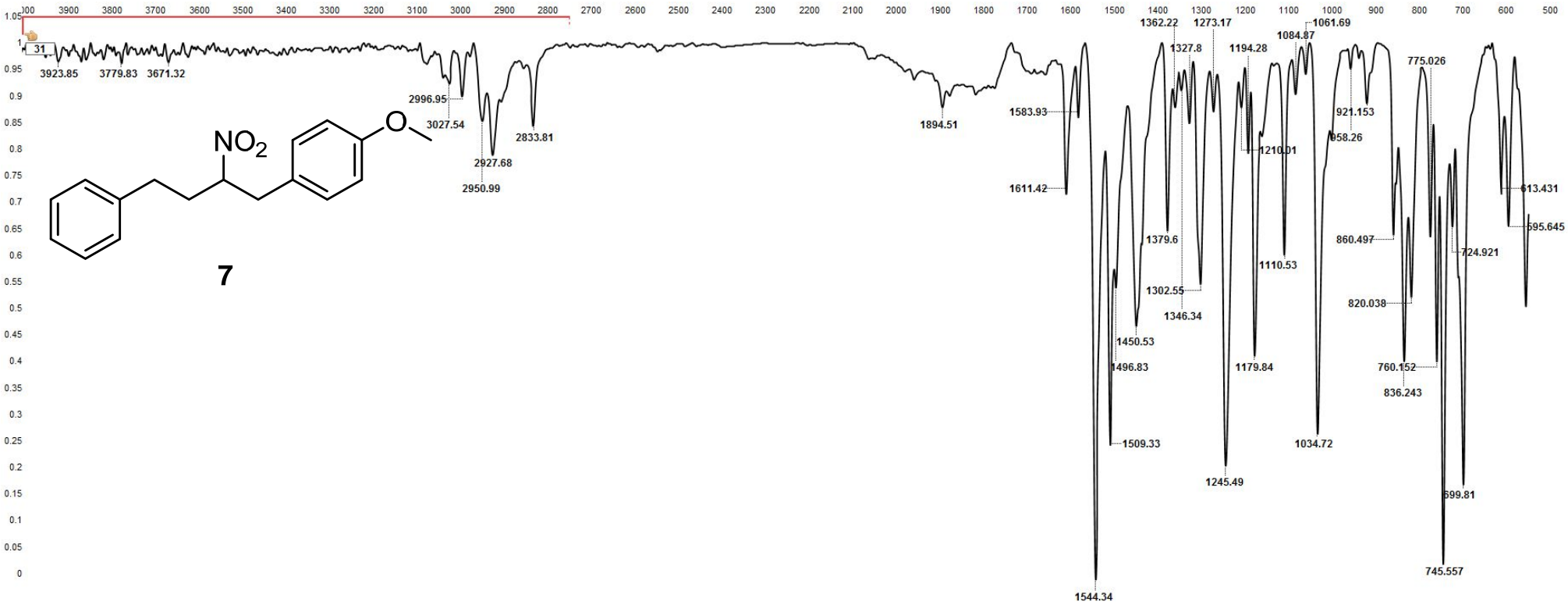
NMR of **7**


UPY1161.100.{13C}deptsp135/3
/ILDT UPY1161.100
NO2
O
7
13C DEPT NMR
(75 MHz, CDCl3)
130.00
128.76
128.53
126.59
114.33
89.44
55.34
39.42
35.01
32.07
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
f1 (мд)

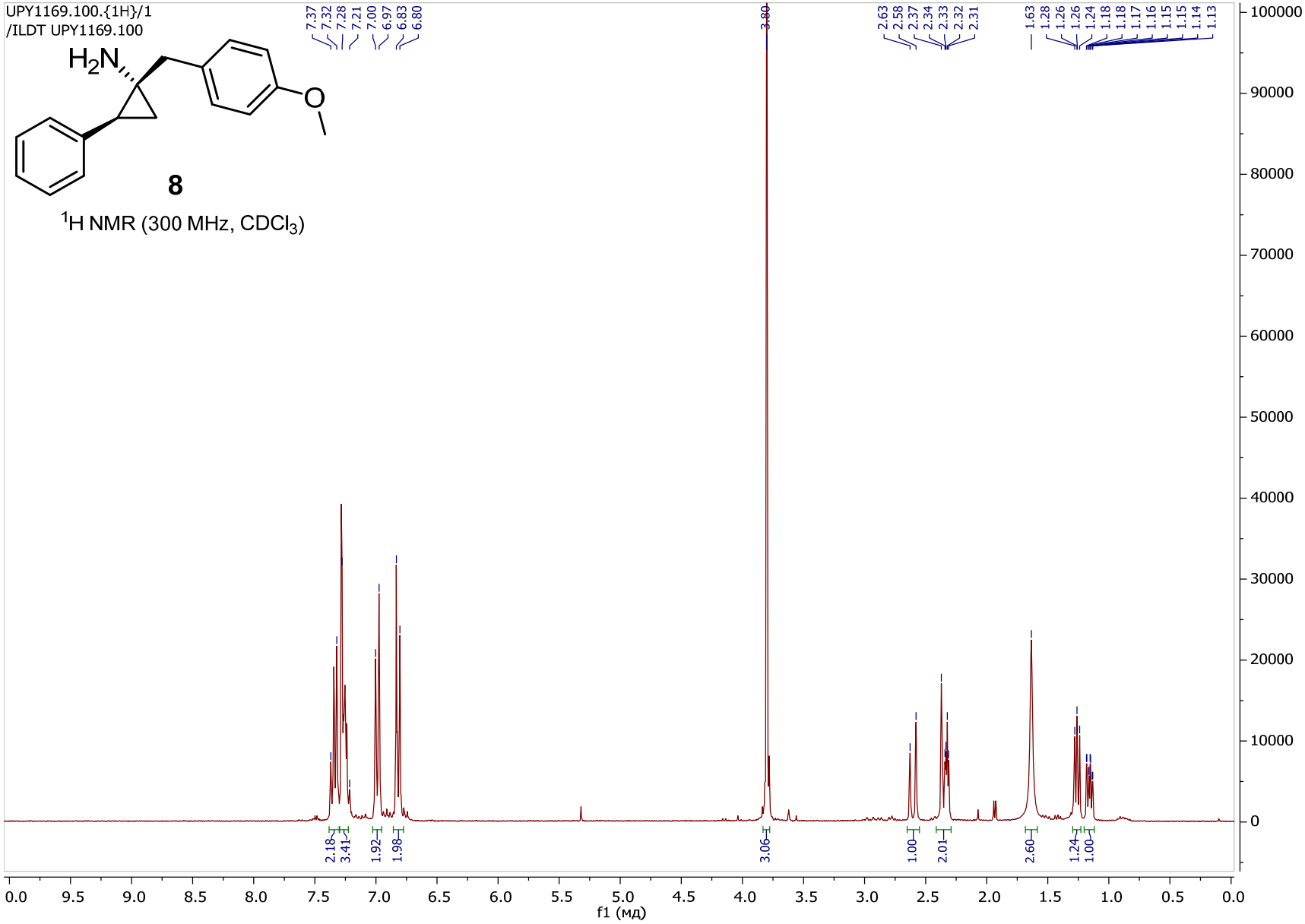
NMR of **7**


UPY1161.100.{1H-13C}HSQC/5
/ILDT UPY1161.100
NO2
O
7
1H - 13C HSQC NMR
(CDCl3)
f2 (мд)
f1 (мд)

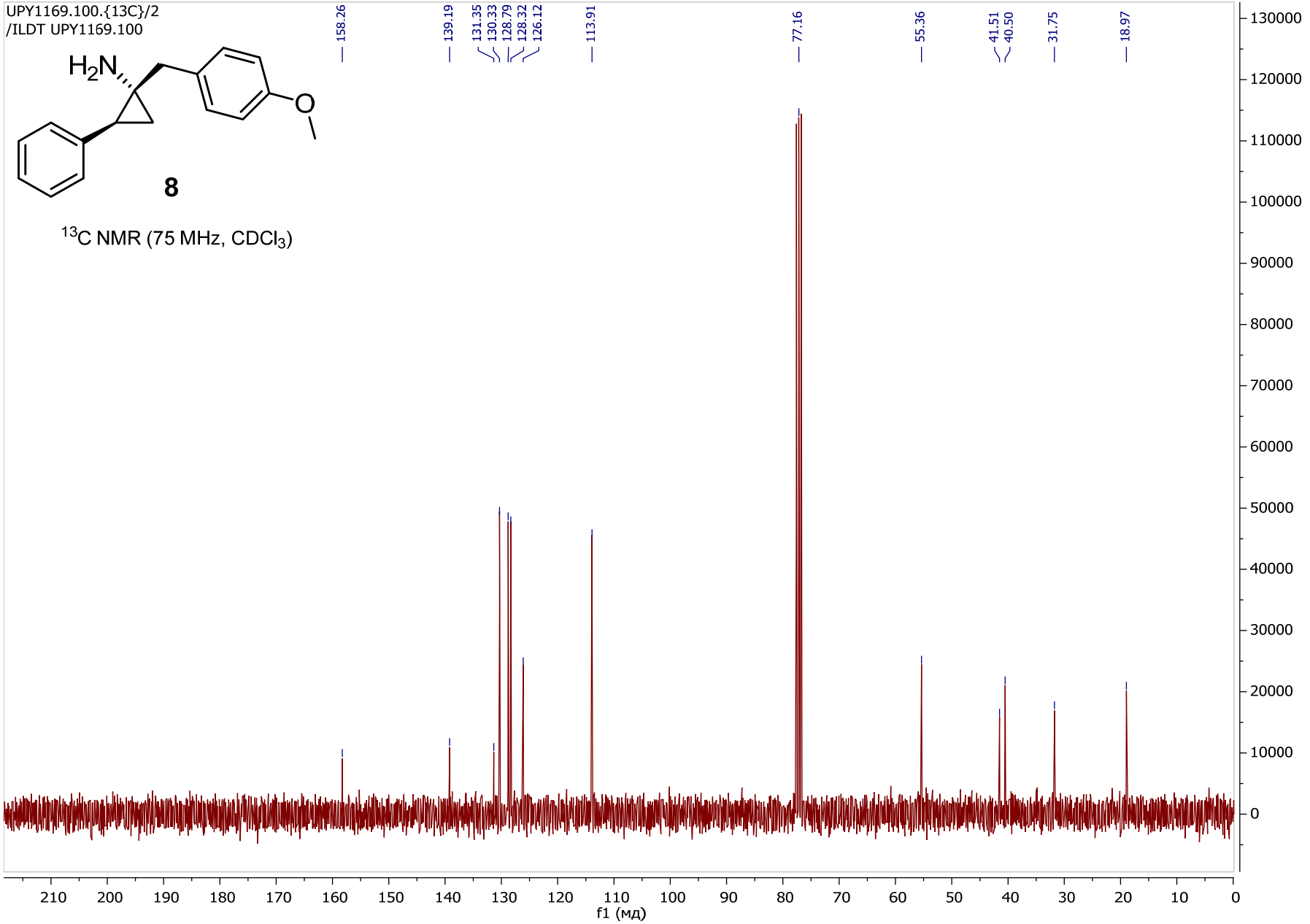
FTIR (ATR) of **7**


3923.85
3779.83
3671.32
2996.95
3027.54
2950.99
2927.68
2833.81
1894.51
1583.93
1611.42
1544.34
1509.33
1496.83
1450.53
1379.6
1362.22
1346.34
1327.8
1302.55
1273.17
1245.49
1210.01
1194.28
1179.84
1110.53
1084.87
1061.69
1034.72
958.26
921.153
860.497
836.243
820.038
775.026
760.152
745.557
724.921
699.81
613.431
595.645
NO2
O
7

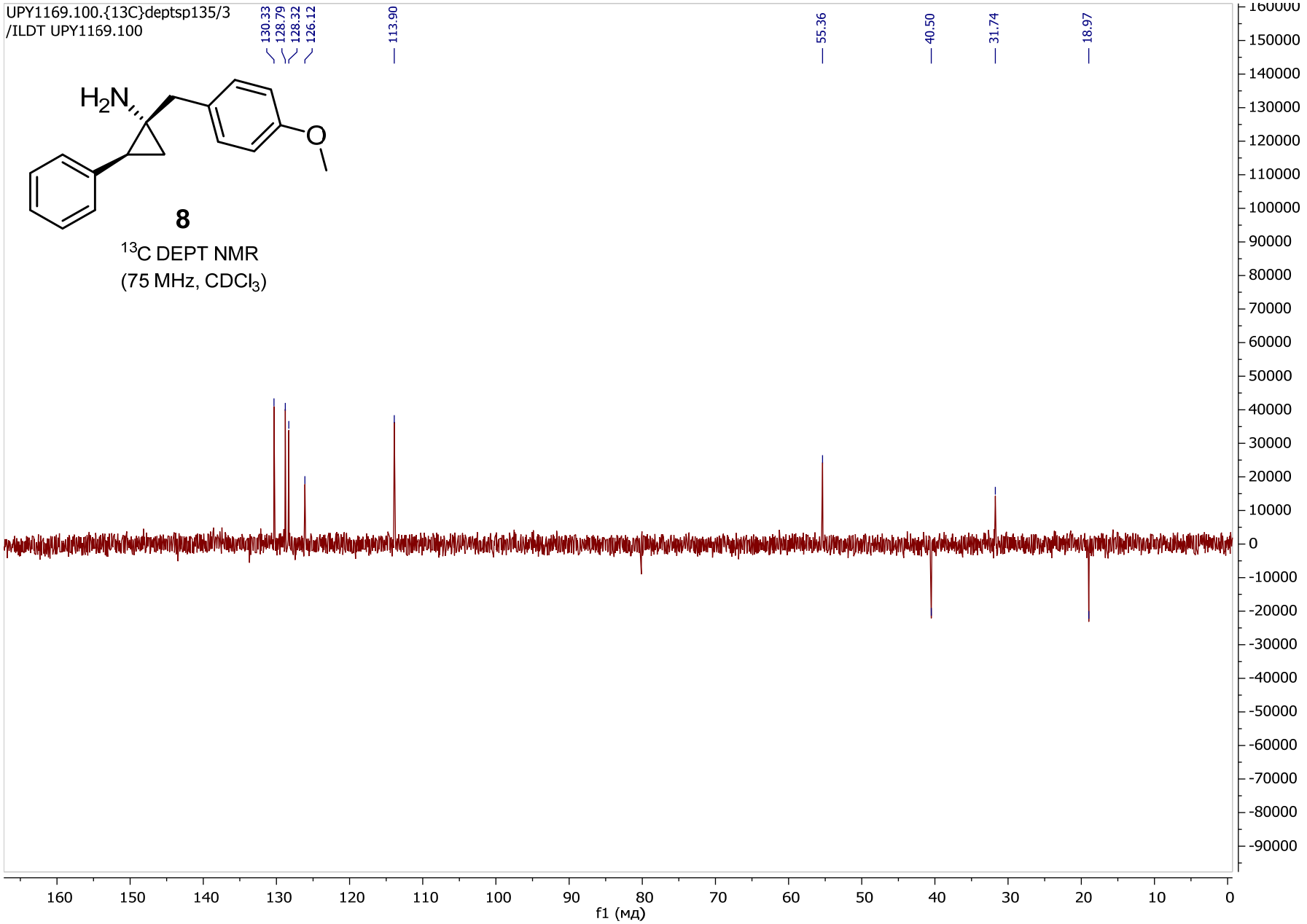
NMR of **8**


UPY1169.100.{1H}/1
/ILDT UPY1169.100
H_2N
O
8
^{1}H NMR (300 MHz, $CDCl_3$)
7.37
7.32
7.28
7.21
7.00
6.97
6.83
6.80
3.80
2.63
2.58
2.37
2.34
2.33
2.32
2.31
1.63
1.28
1.26
1.26
1.24
1.18
1.18
1.17
1.16
1.15
1.15
1.14
1.13
2.18
3.41
1.92
1.98
3.06
1.00
2.01
2.60
1.24
1.00
f1 (мд)

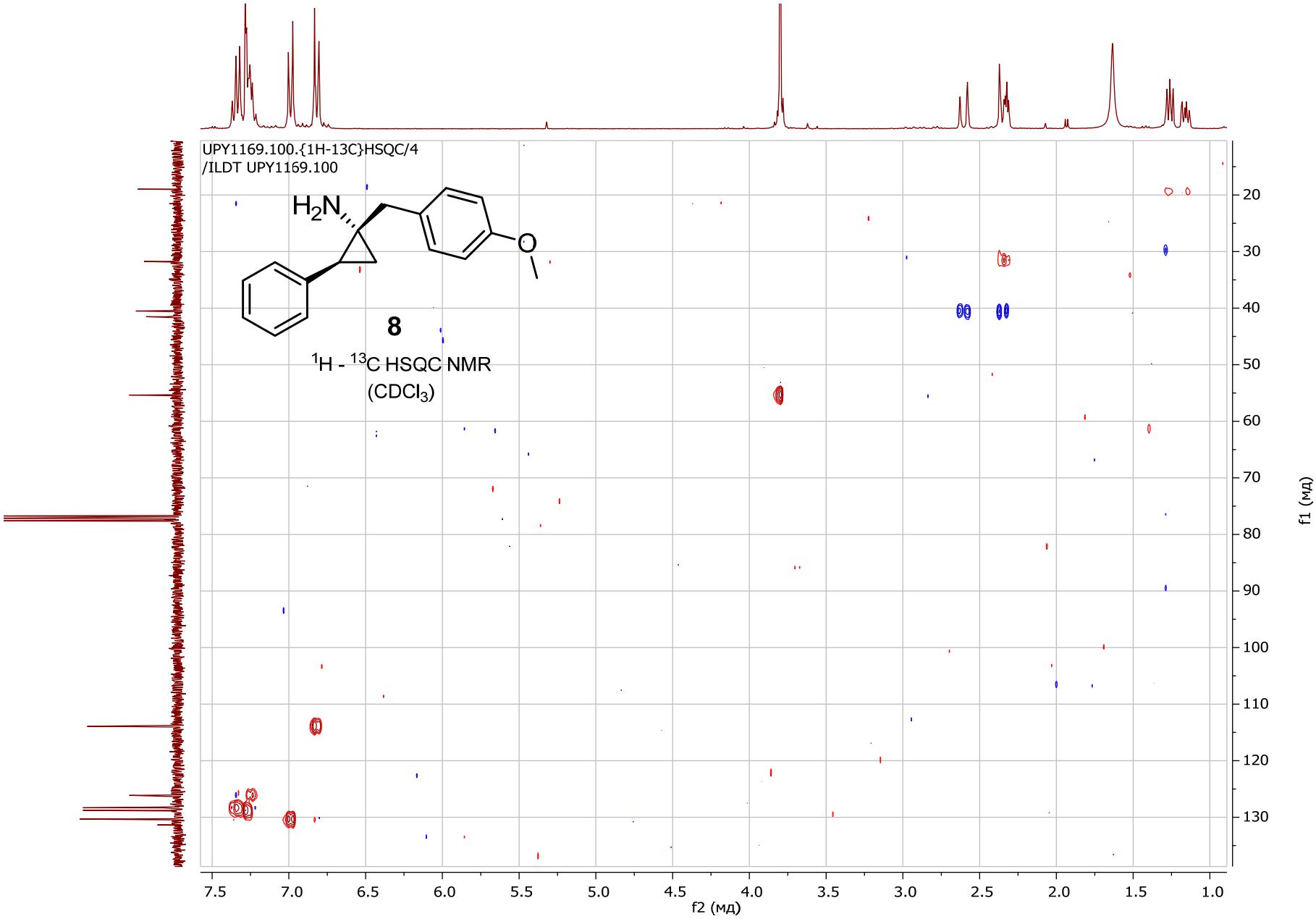
NMR of **8**


UPY1169.100.{13C}/2
/ILDT UPY1169.100
158.26
139.19
131.35
130.33
128.79
128.32
126.12
113.91
77.16
55.36
41.51
40.50
31.75
18.97
8
^{13}C NMR (75 MHz, $CDCl_3$)
f1 (мд)

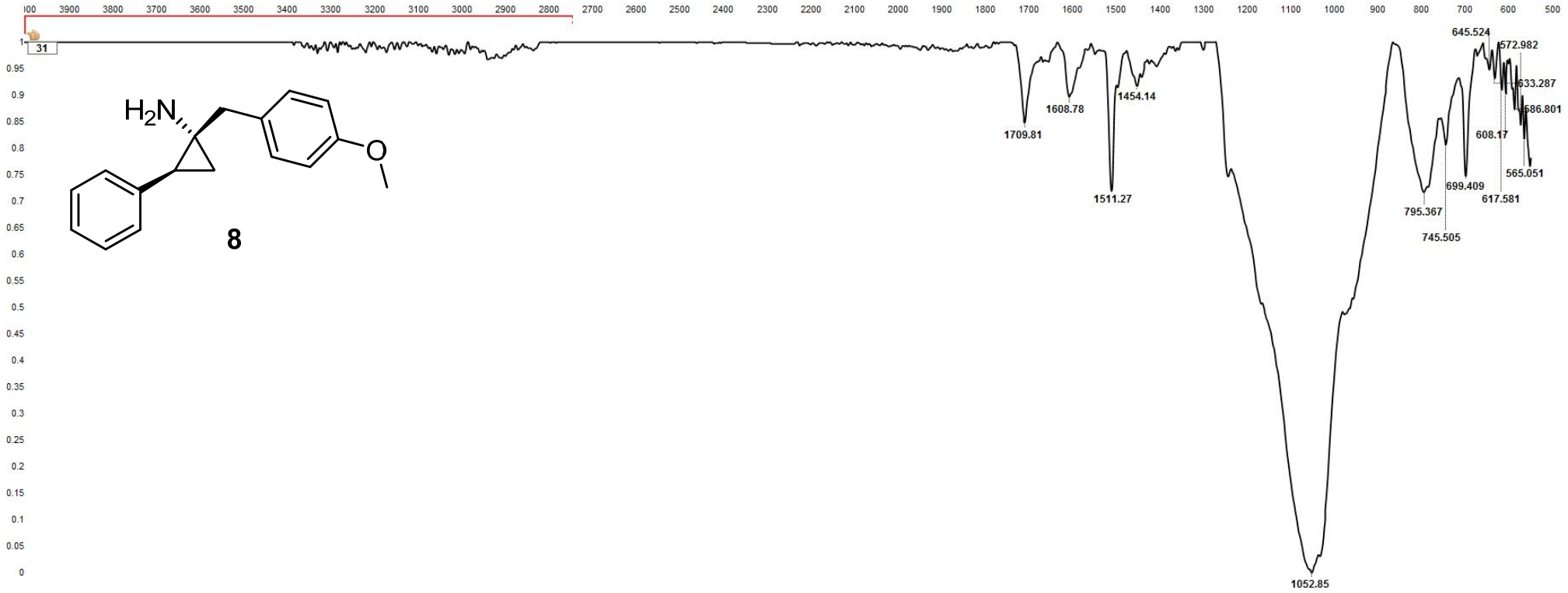
NMR of **8**


UPY1169.100.{13C}deptsp135/3
/ILDT UPY1169.100
130.33
128.79
128.32
126.12
113.90
55.36
40.50
31.74
18.97
H2N
O
8
13C DEPT NMR
(75 MHz, CDCl3)
f1 (мд)

NMR of **8**


UPY1169.100.{1H-13C}HSQC/4
/ILDT UPY1169.100
H2N
O
8
1H - 13C HSQC NMR
(CDCl3)
f2 (мд)
f1 (мд)

FTIR (ATR) of **8**


3900
3800
3700
3600
3500
3400
3300
3200
3100
3000
2900
2800
2700
2600
2500
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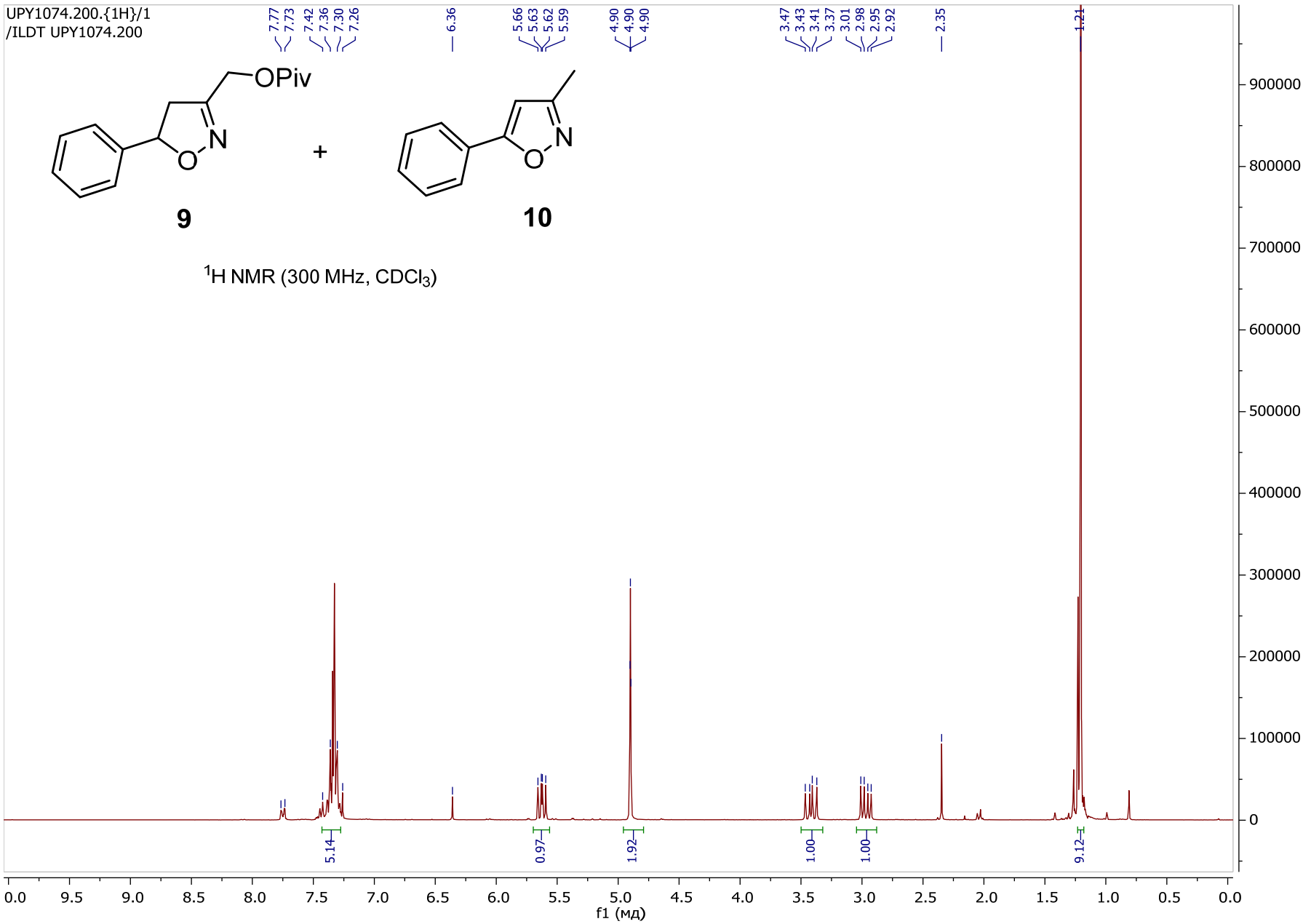
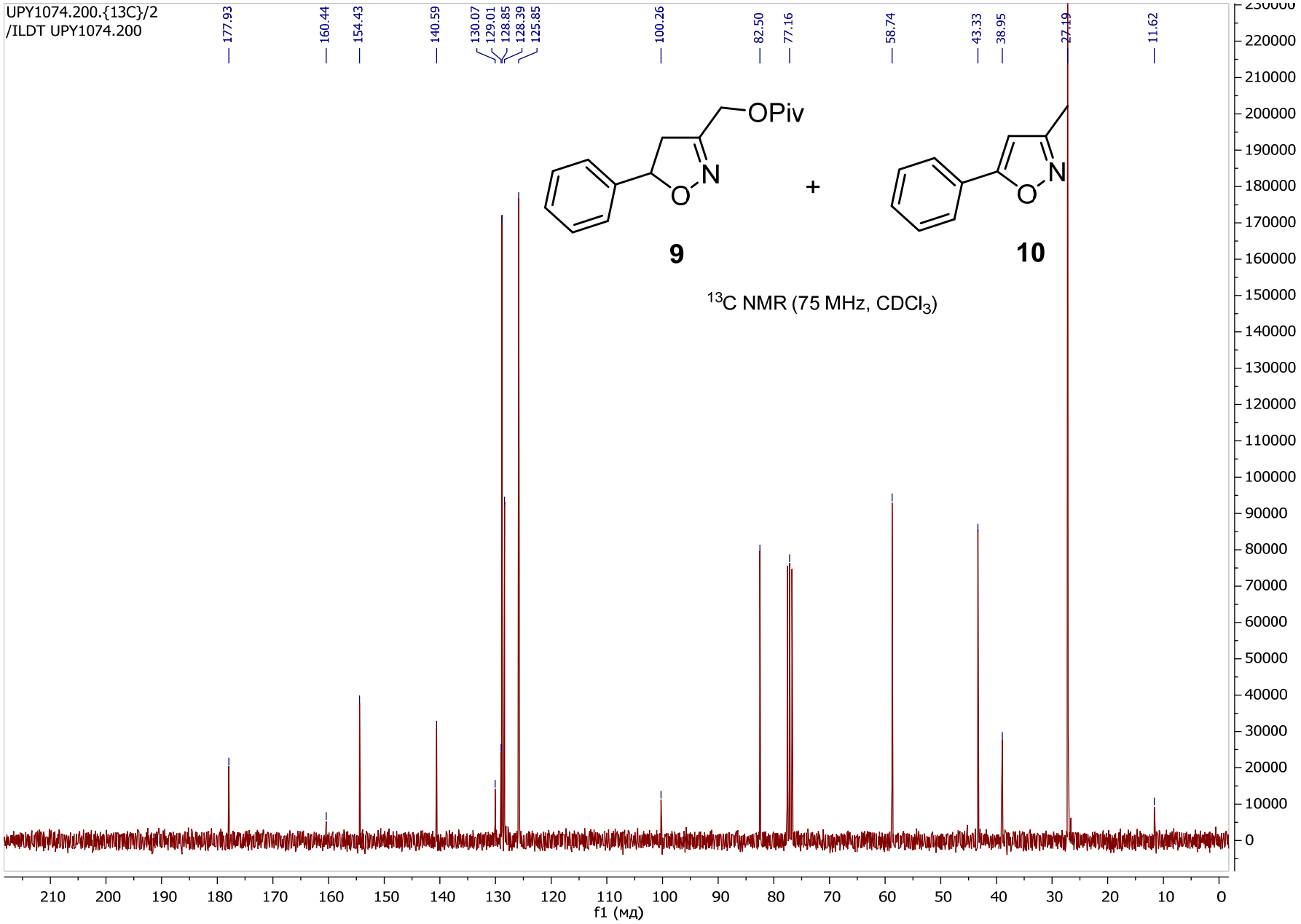
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
31
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
H_2N
O
8
1709.81
1608.78
1454.14
1511.27
1052.85
795.367
745.505
699.409
645.524
617.581
608.17
572.982
565.051
633.287
586.801

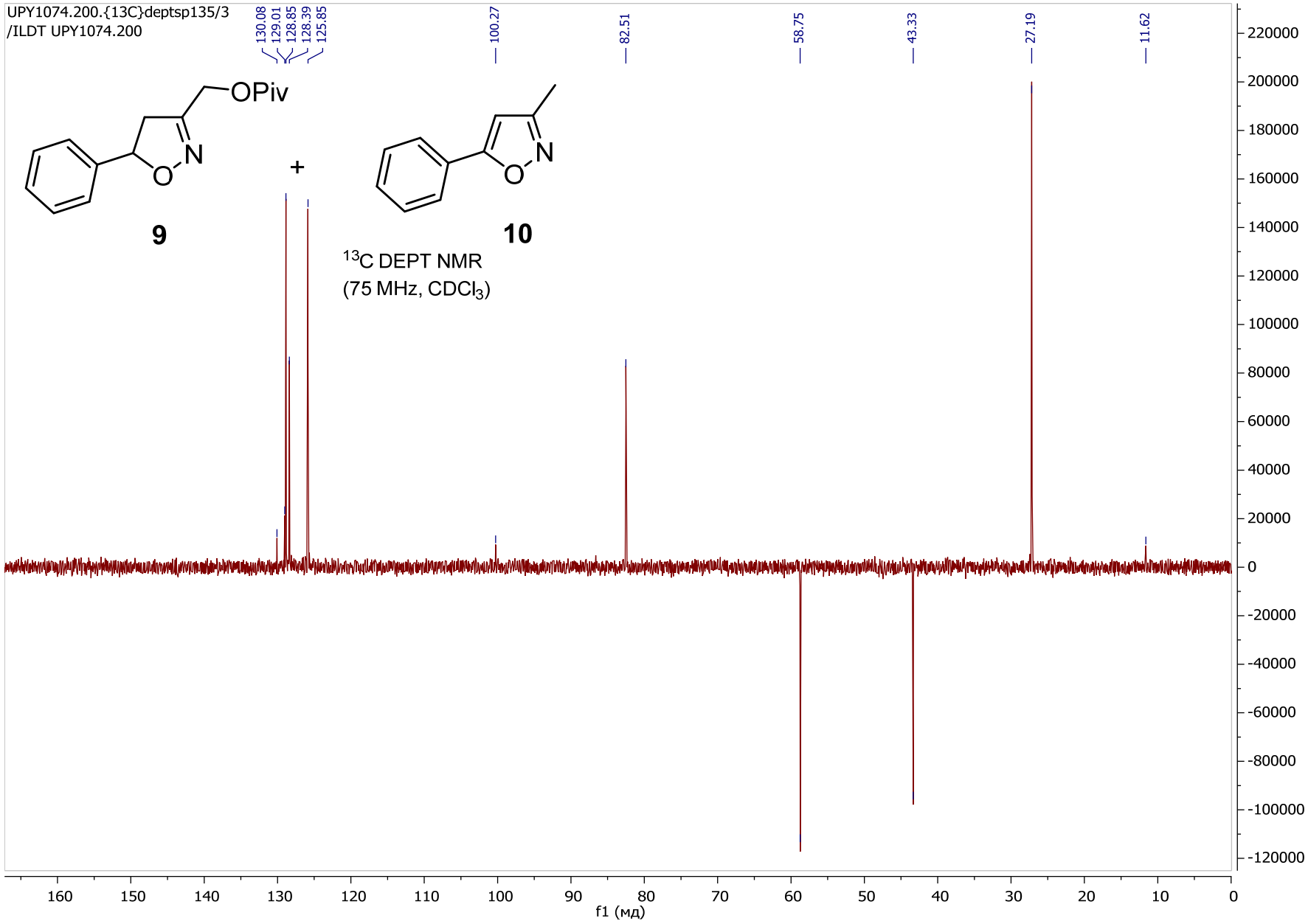
NMR of **9** and **10**



NMR of **9** and **10**



NMR of **9** and **10**



FTIR (ATR) of **9** and **10**