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Supporting Information

Photoredox-Catalyzed Oxytrifluoromethylation of Alkenes toward CF_3-Containing Five-Membered Cyclic Carbonates

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I. General Information

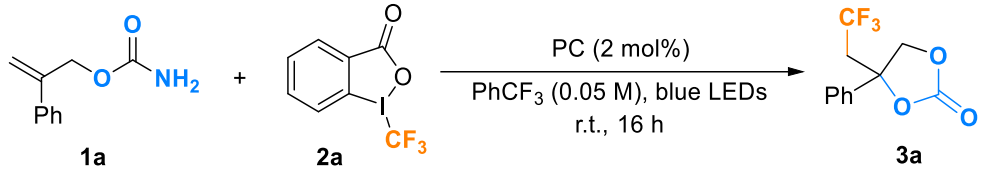
THF, toluene, and 1,4-dioxane were distilled from sodium benzophenoneketyl prior to use. DCM was distilled from Calcium hydride (CaH_2) to use. EA, MeCN, and $PhCF_3$ [Extra Dry, with molecular sieves, Water≤50 ppm (by K.F.)] were purchased from Energy and used as received. The other commercially available chemicals were used as received without mentioned. 5 W blue LEDs were used as the light source. NMR spectra were recorded on a Bruker-400 instrument or Oxford instrument. ^{1}H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm), ^{13}C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, $CDCl_3$), ^{19}F NMR chemical shifts were referenced to the solvent resonance. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quadruplet, PE = petroleum ether, EA = ethyl acetate, THF = tetrahydrofuran, DCM = dichloromethane, $PhCF_3$ = Benzotrifluoride . IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. High-resolution mass spectra (HRMS) were

recorded on LCMS-IT-TOF (ESI-TOF) and EI-TOF (electro-spray ionization-time of flight). Melting points were obtained using an X-4 melting point apparatus (Laboratory Devices, Beijing Taike CO., LTD.).

II. Optimizations of Reaction Conditions.

Optimizations on different photocatalysts were listed in **Table S1**. Most organic photocatalysts cannot catalyze the reaction to produce the target product, and only a small amount of product was observed when Neutral Red was used as the photocatalyst (entries 1-9). The *fac*-Ir(ppy)$_3$ led to **3a** in 75% yield with 13% recovery of **1a** (entry 12). So, *fac*-Ir(ppy)$_3$ was chosen as the photocatalyst.

Table S1. Optimizations of photocatalysts.[a]



Entry	Photocatalyst	3a (%)	Recovery of 1a (%)
1	Nuetral Red	12	13
2	Eosin Y	/	98
3	Eosin Y Disodiulm salt	/	92
4	Rhodamine 6G	/	85
5	Basic Blue 17	/	85
6	Basic Orange 14	/	75
7	Xanthone	/	78
8	Michler's ketone	/	30
9	PTH	/	85
10	Cu(dap)$_2$Cl	/	12
11	Ru(bpy)$_3$(PF$_6$)$_2$	/	93
12	***fac*-Ir(ppy)$_3$**	**75**	**13**

[a]Reaction conditions: 2-phenylallyl carbamate **1a** (0.1 mmol), CF$_3$-reagent (**2a**) (0.15 mmol), photocatalyst (0.002 mmol), PhCF$_3$ (2 mL), under the irradiation of 5 W blue LEDs for 16 h at room temperature. Yields of **3a** and recovery of **1a** were determined by ^{1}H NMR using Trimethyl-phenylsilane (TMSPh) as an internal standard.

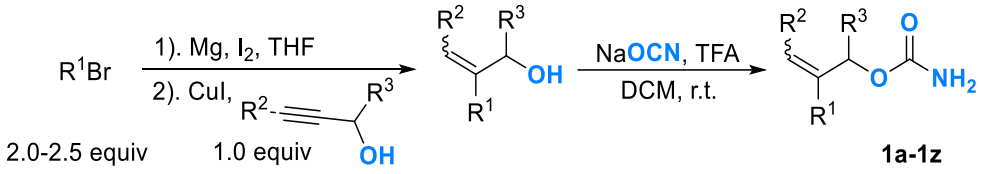
III. Procedures for the Synthesis of Starting Materials

Magnesium, iodine, cuprous iodide, (4-chlorophenyl)magnesium bromide, phenylmagnesium bromide, *p*-tolylmagnesium bromide, and trifluoroacetic acid were purchased from Energy and used as received. Sodium cyanate, but-3-yn-2-ol, but-2-yn-1-ol, bromobenzene, (bromomethyl)benzene, 1-bromo-4-chlorobenzene, 4-bromo-1,1'-biphenyl, (4-bromophenyl)trimethylsilane, 1-bromo-3-(*iso*-propyl)benzene, 1-bromo-3,5-dimethylbenzene, 1-bromo-3,5-di-*tert*-butylbenzene, 1-bromo-3,5-dimethoxybenzene, 2-bromo-4-fluoro-1-methylbenzene, 2-bromo-1,3,5-trimethylbenzene, 1-bromonaphthalene, 2-bromo-naphthalene, 5-bromobenzo[b]thiophene, 2-bromospiro[fluorene-9,9'-xanthene], (2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene, 1-bromo-4-(*tert*-butyl)benzene, 1-bromo-4-metho-xybenzene, (4-bromophenyl)(methyl)sulfane, (4-bromophenyl)triphenylsilane, 4-bromo-1,2-dichlorobenzene, 5-bromobenzo[d][1,3]dioxole, 3-bromobenzo[b]thiophene and 2-bromodibenzo [b,d]thiophene were purchased from Leyan.com and used as received. The prop-2-yn-1-ol was purchased from Alfla and used as received.

The photocatalyst *fac*-Ir(ppy)$_3$ was prepared according to the previously reported procedures.[1]

The substrate **8** were prepared according to the previously reported procedures.[2]

The substrates **1a-1z** were prepared by the following steps: [3,4]

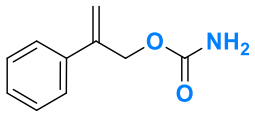


***General Procedures*:**

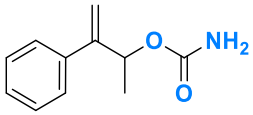
Step 1: The allylic alcohols were prepared according to the previously reported procedures.[3] The obtained crude product was then used directly in the next step without further purification.

Step 2: Allyl carbamates were prepared according to previously reported procedures with some modifications.[4] In a 250 mL Schlenk flask, crude allyl alcohol (1.0 equiv), NaOCN (2.0 equiv), and DCM (0.5 M) were added. Trifluoroacetic acid (2.0 equiv) dissolved in 10-20 mL of dry DCM was then added dropwise to the stirred mixture. The resulting mixture was stirred for 5 hours at room temperature. Once the allyl alcohols were fully consumed (monitored by TLC), 20 mL of water was added and the organic layer was separated. The aqueous phase was extracted with DCM (40 mL x

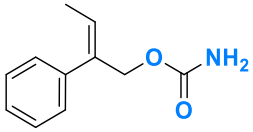
3). The organic extracts were combined, washed with brine, dried over Na_2SO_4, concentrated by rotary evaporation, and further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford allyl carbamates **1a-1z**.



2-Phenylallyl carbamate (**1a**)**:** Prepared according to general procedures using bromobenzene (3.17 mL, ρ = 1.49 g/ml, 30 mmol), magnesium turnings (0.71 g, 30 mmol), a grain of iodine, CuI (0.43 g, 2.3 mmol), prop-2-yn-1-ol (0.92 mL, ρ = 0.96 g/mL, 15 mmol), sodium cyanate (1.91 g, 30 mmol), and TFA (2.30 mL, ρ = 1.49 g/mL, 30 mmol). The crude product was further purified by flash chromato-graphy on silica gel (PE/EA = 10/1-2/1) to afford the **1a** (2.37 g, 89% yield over two steps) as a light yellow solid. M.p. 79-80 °C (PE/EA); IR (neat): 3433, 2951, 1684, 1605, 1401, 1341 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.48-7.41 (m, 2H), 7.38-7.28 (m, 3H), 5.55 (s, 1H), 5.37 (s, 1H), 4.99 (s, 2H), 4.72 (br, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.8, 142.7, 137.9, 128.5, 128.0, 125.9, 115.1, 66.3; HRMS (ESI) calculated for $[C_{10}H_{11}NNaO_2]^+$ ($M+Na^+$) requires m/z 200.0682, found: m/z 200.0682.

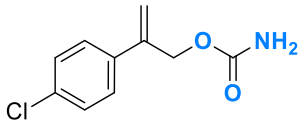


3-Phenylbut-3-en-2-yl carbamate (1b): Prepared according to general procedures[4c] using phenylmagnesium bromide (50 mL, 1.0 M in THF), CuI (0.59 g, 3.0 mmol), but-3-yn-2-ol (1.57 mL, ρ = 0.89, 20 mmol), sodium cyanate (1.30 g, 20 mmol), and TFA (1.53 mL, ρ = 1.49 g/mL, 20 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 20/1-5/1) to afford the **1b** (0.75 g, 20% yield over two steps) as a colorless oil. IR (neat): 3415, 2927, 1708, 1496, 1452, 1375 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.48-7.22 (m, 5H), 5.73 (q, J = 6.4 Hz, 1H), 5.33 (s, 1H), 5.31 (s, 1H), 4.72 (br, 2H), 1.36 (d, J = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.2, 149.5, 139.3, 128.3, 127.7, 126.8, 112.7, 72.1, 20.1; HRMS (ESI) calculated for $[C_{11}H_{13}NNaO_2]^+$ ($M+Na^+$) requires m/z 214.0838, found: m/z 214.0837.

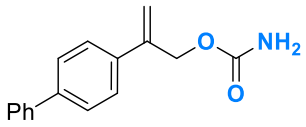


(*E*)-2-phenylbut-2-en-1-yl carbamate (1c): Prepared according to general procedures[4d] using phenylmagnesium bromide (50 mL, 1.0 M in THF), CuI (0.59 g, 3.0 mmol), but-2-yn-1-ol (1.50 mL, ρ = 0.94, 20 mmol), sodium cyanate (0.80 g, 12 mmol), and TFA (0.91 mL, ρ = 1.49 g/mL, 12 mmol). In the first step,

the crude product was purified by flash chromatography on silica gel (PE/EA = 30/1) to afford (*E*)-2-phenylbut-2-en-1-ol (0.85 g, 29% yield). In the second step, the crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1c** (0.91 g, 84% yield) as a light yellow solid. M.p. 138-140 °C (PE/EA); ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.40-7.27 (m, 3H), 7.25-7.20 (m, 2H), 5.91 (q, *J* = 6.8 Hz, 1H), 4.78 (s, 2H), 4.62 (br, 2H), 1.66 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.7, 137.8, 136.5, 128.6, 128.2, 127.1, 126.7, 69.7, 14.6; HRMS (ESI) calculated for $[C_{11}H_{13}NNaO_2]^+$ ($M+Na^+$) requires m/z 214.0838, found: m/z 214.0839.

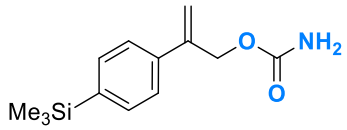


2-(4-Chlorophenyl)allyl carbamate (**1d**)**:** Prepared according to general procedures using (4-chlorophenyl)magnesium bromide (50 mL, 1.0 M in THF), CuI (0.56 g, 3.0 mmol), prop-2-yn-1-ol (1.23 mL, ρ = 0.96 g/mL, 20 mmol), sodium cyanate (1.91 g, 30 mmol), and TFA (3.06 mL, ρ = 1.49 g/mL, 40 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1) to afford the **1d** (3.27 g, 77% yield over two steps) as a light yellow solid. M.p. 79-82 °C (PE/EA); IR (neat): 3437, 2950, 1689, 1607, 1398, 1334 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.54 (s, 1H), 5.39 (s, 1H), 4.96 (s, 2H), 4.66 (br, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.4, 141.7, 136.3, 133.9, 128.6, 127.3, 115.8, 66.2; HRMS (ESI) calculated for $[C_{10}H_{11}ClNO_2]^+$ ($M+H^+$) requires m/z 212.0473, found: m/z 212.0471.

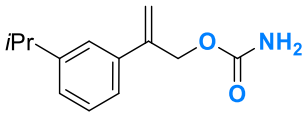


2-([1,1'-Biphenyl]-4-yl)allyl carbamate (**1e**)**:** Prepared according to general procedures using 4-bromo-1,1'-biphenyl ((9.36 g, 40 mmol), magnesium turnings (1.04 g, 40 mmol), a grain of iodine, CuI (0.59 g, 3.0 mmol), prop-2-yn-1-ol (1.23 mL, ρ = 0.96 g/mL, 20 mmol), sodium cyanate (2.62 g, 40 mmol), and TFA (3.20 mL, ρ = 1.49 g/mL, 42 mmol). The crude product was further purified by flash chromatography on silica gel (DCM/PE= 5/1 to DCM/EA= 20/1) to afford the **1e** (3.75 g, 74% yield over two steps) as a yellow solid. M.p. 160-162 °C (PE/EA); IR (neat): 3676, 3445, 2920, 1743, 1699, 1403 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.64-7.50 (m, 6H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 5.62 (s, 1H), 5.40 (s, 1H), 5.03 (s, 2H), 4.69 (br, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.4, 142.2, 140.8, 140.5, 136.7, 128.8, 127.4, 127.2, 127.0, 126.3, 115.3, 66.4; HRMS

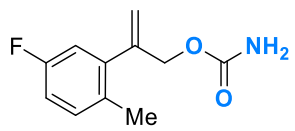
(ESI) calculated for $[C_{16}H_{15}NNaO_2]^+$ ($M+Na^+$) requires m/z 276.0995, found: m/z 276.0997.



2-(4-(Trimethylsilyl)phenyl)allyl carbamate (1f): Prepared according to general procedures using (4-bromophenyl) trimethyl-lsilane (5.77 g, 25 mmol), magnesium turnings (0.74 g, 30 mmol), a grain of iodine, CuI (0.34 g, 1.8 mmol), prop-2-yn-1-ol (0.70 mL, ρ = 0.96 g/mL, 12 mmol), sodium cyanate (2.34 g, 36 mmol), and TFA (1.90 mL, ρ = 1.49 g/mL, 25 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1) to afford the **1f** (2.07 g, 69% yield over two steps) as a yellow solid. M.p. 68-71 °C (PE/EA); IR (neat): 3419, 2955, 1696, 1405, 1342, 1066 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 5.57 (s, 1H), 5.37 (s, 1H), 4.98 (s, 2H), 4.73 (br, 2H), 0.27 (s, 9H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.6, 142.5, 140.4, 138.1, 133.5, 125.2, 115.3, 66.3, -1.2; HRMS (ESI) calculated for $[C_{13}H_{19}NNaO_2Si]^+$ ($M+Na^+$) requires m/z 272.1077, found: m/z 272.1078.

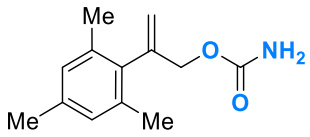


2-(3-*Iso*-propylphenyl)allyl carbamate (1g): Prepared according to general procedures using 1-bromo-3-isopropylbenzene (4.27 mL, ρ = 1.17, 24 mmol), magnesium turnings (0.58 g, 24 mmol), a grain of iodine, CuI (0.27 g, 1.4 mmol), prop-2-yn-1-ol (0.73 mL, ρ = 0.96 g/mL, 12 mmol), sodium cyanate (1.58 g, 24 mmol), and TFA (1.90 mL, ρ = 1.49 g/mL, 25 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1) to afford the **1g** (1.10 g, 42% yield over two steps) as a yellow oil. IR (neat): 3353, 2962, 1709, 1395, 1334, 1061 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 3H), 7.21-7.16 (m, 1H), 5.54 (s, 1H), 5.34 (d, *J* = 0.8 Hz, 1H), 4.98 (s, 2H), 4.92 (br, 2H), 2.98-2.84 (m, 1H), 1.26 (d, *J* = 7.2 Hz, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.7, 149.0, 142.9, 137.8, 128.4, 126.1, 124.1, 123.4, 114.7, 66.3, 34.1, 23.9; HRMS (ESI) calculated for $[C_{13}H_{17}NNaO_2]^+$ ($M+Na^+$) requires m/z 242.1151, found: m/z 242.1149.

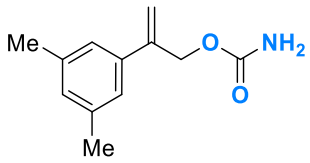


2-(5-Fluoro-2-methylphenyl)allyl carbamate (1h): Prepared according to general procedures using 2-bromo-4-fluoro-1-methyl-benzene (3.80 mL, ρ = 1.50, 30 mmol), magnesium turnings (0.72 g,

30 mmol), a grain of iodine, CuI (0.45 g, 2.3 mmol), prop-2-yn-1-ol (0.92 mL, ρ = 0.96 g/mL, 15 mmol), sodium cyanate (1.56 g, 24 mmol), and TFA (1.84 mL, ρ = 1.49 g/mL, 24 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1) to afford the **1h** (1.30 g, 41% yield over two steps) as a yellow oid. IR (neat): 3364, 2932, 1711, 1494, 1397, 1334 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.18-7.08 (m, 1H), 6.95-6.80 (m, 2H), 5.48 (s, 1H), 5.10 (s, 1H), 4.87 (br, 2H), 4.73 (s, 2H), 2.27 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 160.7 (d, J = 240.0 Hz), 156.4, 143.5 (d, J = 1.6 Hz), 140.6 (d, J = 7.3 Hz), 131.4 (d, J = 8.0 Hz), 131.1 (d, J = 3.7 Hz), 116.3, 115.5 (d, J = 21.2 Hz), 114.2 (d, J = 20.5 Hz), 66.9, 19.0; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -118.2; HRMS (ESI) calculated for $[C_{11}H_{12}FNNaO_2]^+$ ($M+Na^+$) requires m/z 232.0744, found: m/z 232.0745.

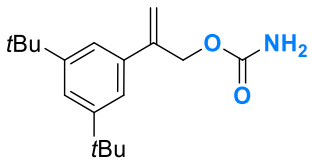


2-Mesitylallyl carbamate (1i): Prepared according to general procedures using 2-bromo-1,3,5-trimethylbenzene (7.60 mL, ρ = 1.30, 50 mmol), magnesium turnings (1.22 g, 50 mmol), a grain of iodine, CuI (0.57 g, 3.0 mmol), prop-2-yn-1-ol (1.20 mL, ρ = 0.96 g/mL, 20 mmol), sodium cyanate (2.60 g, 40 mmol), and TFA (3.20 mL, ρ = 1.49 g/mL, 42 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1) to afford the **1i** (3.26 g, 74% yield over two steps) as a yellow solid. M.p. 99-101 ºC (PE/EA); IR (neat): 3361, 2923, 1712, 1396, 1333, 1062 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 6.88 (s, 2H), 5.51-5.47 (m, 1H), 5.01-4.96 (m, 1H), 4.83 (br, 2H), 4.66-4.60 (m, 2H), 2.27 (s, 3H), 2.23 (s, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ156.6, 143.4, 136.8, 135.9, 135.4, 128.1, 114.6, 66.5, 20.9, 19.6; HRMS (ESI) calculated for $[C_{12}H_{15}NNaO_4]^+$ ($M+Na^+$) requires m/z 242.1151, found: m/z 242.1152.

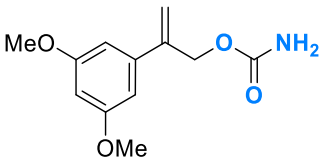


2-(3,5-Dimethylphenyl)allyl carbamate (1j): Prepared according to general procedures using 1-bromo-3,5-dimethylbenzene (6.36 g, 34 mmol), magnesium turnings (0.83 g, 34 mmol), a grain of iodine, CuI (0.38 g, 2.0 mmol), prop-2-yn-1-ol (0.80 mL, ρ = 0.96 g/mL, 13.6 mmol), sodium cyanate (2.60 g, 40 mmol), and TFA (3.20 mL, ρ = 1.49 g/mL, 42 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1) to afford the **1j** (2.26 g, 80% yield over two

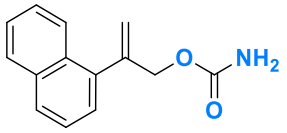
steps) as a yellow solid. M.p. 65-67 °C (PE/EA); IR (neat): 3422, 2915, 1694, 1603, 1396, 1340 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.05 (s, 2H), 6.96 (s, 1H), 5.51 (s, 1H), 5.32 (s, 1H), 4.96 (s, 2H), 4.72 (br, 2H), 2.32 (s, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.8, 142.8, 137.9, 137.8, 129.7, 123.7, 114.5, 66.3, 21.3; HRMS (ESI) calculated for $[C_{12}H_{15}NNaO_2]^+$ ($M+Na^+$) requires m/z 228.0995, found: m/z 228.0996.



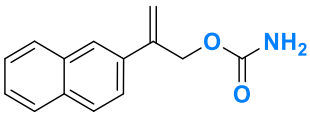
2-(3,5-Di-*tert*-butylphenyl)allyl carbamate (1k): Prepared according to general procedures using 1-bromo-3,5-di-*tert*-butyl-benzene (13.4 g, 50 mmol), magnesium turnings (1.22 g, 50 mmol), a grain of iodine, CuI (0.57 g, 3.0 mmol), prop-2-yn-1-ol (1.20 mL, ρ = 0.96 g/mL, 20 mmol), sodium cyanate (2.60 g, 40 mmol), and TFA (3.20 mL, ρ = 1.49 g/mL, 42 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1) to afford the **1k** (4.99 g, 86% yield over two steps) as a white solid. M.p. 81-82 °C (PE/EA); IR (neat): 3505, 2961, 1717, 1594, 1396, 1340 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.27 (d, J = 1.2 Hz, 1H), 5.53 (s, 1H), 5.34 (s, 1H), 5.01 (s, 2H), 4.70 (br, 2H), 1.34 (s, 18H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.7, 150.7, 143.6, 137.1, 122.3, 120.2, 114.3, 66.5, 34.8, 31.4; HRMS (ESI) calculated for $[C_{18}H_{27}NNaO_2]^+$ ($M+Na^+$) requires m/z 312.1934, found: m/z 312.1932.



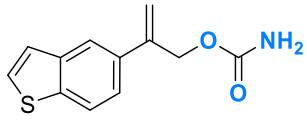
2-(3,5-Dimethoxyphenyl)allyl carbamate (1l): Prepared according to general procedures using 1-bromo-3,5-dimethoxybenzene (10.92 g, 50 mmol), magnesium turnings (1.21 g, 50 mmol), a grain of iodine, CuI (0.55 g, 3.0 mmol), prop-2-yn-1-ol (1.20 mL, ρ = 0.96 g/mL, 20 mmol), sodium cyanate (2.59 g, 40 mmol), and TFA (3.22 mL, ρ = 1.49 g/mL, 42 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1l** (3.87 g, 81% yield over two steps) as a yellow solid. M.p. 95-97 °C (PE/EA); IR (neat): 3441, 2940, 1697, 1594, 1338, 1205 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 6.58 (s, 2H), 6.43 (s, 1H), 5.54 (s, 1H), 5.36 (s, 1H), 4.94 (s, 2H), 4.74 (br, 2H), 3.80 (s, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 160.7, 156.6, 142.7, 140.0, 115.5, 104.2, 99.9, 66.3, 55.3; HRMS (ESI) calculated for $[C_{12}H_{15}NNaO_4]^+$ ($M+Na^+$) requires m/z 260.0893, found: m/z 260.0895.



2-(Naphthalen-1-yl)allyl carbamate (1m): Prepared according to general procedures using 1-bromonaphthalene (10.35 g, 50 mmol), magnesium turnings (1.22 g, 50 mmol), a grain of iodine, CuI (0.57 g, 3.0 mmol), prop-2-yn-1-ol (1.20 mL, ρ = 0.96 g/mL, 20 mmol), sodium cyanate (2.63 g, 40 mmol), and TFA (3.20 mL, ρ = 1.49 g/mL, 42 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1m** (3.15 g, 69% yield over two steps) as a yellow solid. M.p. 81-84 °C (PE/EA); IR (neat): 3502, 3353, 2928, 1714, 1393, 1334 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 8.10-8.00 (m, 1H), 7.88-7.82 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.50-7.40 (m, 3H), 7.34 (dd, *J* = 6.8, 0.8 Hz, 1H), 5.66 (d, *J* = 1.6 Hz, 1H), 5.28 (d, *J* = 1.6 Hz, 1H), 4.89 (br, 4H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.6, 143.2, 137.3, 133.5, 131.4, 128.2, 127.9, 126.1, 125.8, 125.7, 125.4, 125.1, 116.7, 67.7; HRMS (ESI) calculated for $[C_{14}H_{13}NNaO_2]^+$ ($M+Na^+$) requires m/z 250.0838, found: m/z 250.0840.

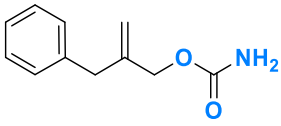


2-(Naphthalen-2-yl)allyl carbamate (1n): Prepared according to general procedures using 2-bromonaphthalene (6.30 g, 30 mmol), magnesium turnings (0.73 g, 30 mmol), a grain of iodine, CuI (0.35 g, 1.8 mmol), prop-2-yn-1-ol (0.70 mL, ρ = 0.96 g/mL, 12 mmol), sodium cyanate (1.55 g, 24 mmol), and TFA (2.00 mL, ρ = 1.49 g/mL, 25 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1n** (1.72 g, 63% yield over two steps) as a yellow solid. M.p. 110-111 °C (PE/EA); IR (neat): 3448, 2921, 1691, 1609, 1408, 1334 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.90-7.78 (m, 4H), 7.61 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.52-7.42 (m, 2H), 5.70 (s, 1H), 5.47 (s, 1H), 5.11 (s, 2H), 4.76 (br, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.5, 142.5, 135.0, 133.2, 133.0, 128.3, 128.1, 127.5, 126.3, 126.2, 124.8, 124.1, 115.6, 66.4; HRMS (ESI) calculated for $[C_{14}H_{13}NNaO_2]^+$ ($M+Na^+$) requires m/z 250.0838, found: m/z 250.0839.

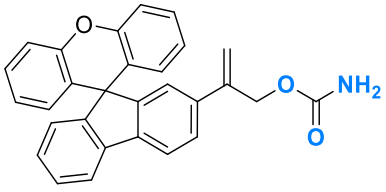


2-(Benzo[b]thiophen-5-yl)allyl carbamate (1o): Prepared according to general procedures using 5-bromobenzo[b]thiophene (1.20 g, 5.6 mmol), magnesium turnings (0.14 g, 5.6 mmol), a grain of iodine, CuI (0.07 g, 0.34 mmol), prop-2-yn-1-ol (0.15 mL, ρ = 0.96 g/mL, 2.3 mmol), sodium cyanate (0.29 g,

4.5 mmol), and TFA (0.36 mL, ρ = 1.49 g/mL, 4.7 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1o** (0.31 g, 58% yield over two steps) as a yellow solid. M.p. 110-113 °C (PE/EA); IR (neat): 3416, 2962, 1694, 1611, 1403, 1327 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.90-7.82 (m, 2H), 7.46 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.34 (d, *J* = 5.6 Hz, 1H), 5.61 (s, 1H), 5.42 (d, *J* = 0.8 Hz, 1H), 5.06 (s, 2H), 4.68 (br, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.4, 142.7, 139.8, 139.3, 134.2, 127.0, 124.0, 122.5, 122.4, 120.9, 115.2, 66.6; HRMS (ESI) calculated for $[C_{12}H_{11}NNaO_2S]^+$ ($M+Na^+$) requires m/z 256.0403, found: m/z 256.0403.

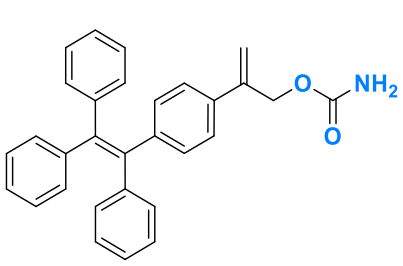


2-Benzylallyl carbamate (1p): Prepared according to general procedures using (bromomethyl)benzene (5.94 mL, ρ = 1.44 g/mL, 50 mmol), magnesium turnings (1.46 g, 60 mmol), a grain of iodine, CuI (1.14 g, 6 mmol), prop-2-yn-1-ol (1.23 mL, ρ = 0.96 g/mL, 20 mmol), sodium cyanate (2.60 g, 40 mmol), and TFA (3.06 mL, ρ = 1.49 g/mL, 40 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1p** (1.04 g, 27% yield over two steps) as a yellow solid. M.p. 45-47 °C (PE/EA); ^1H NMR: (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.25-7.15 (m, 3H), 5.13 (s, 1H), 4.95 (s, 1H), 4.69 (br, 2H), 4.49 (s, 2H), 3.40 (s, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.7, 143.6, 138.5, 128.9, 128.4, 126.3, 113.8, 66.9, 40.0; HRMS (ESI) calculated for $[C_{11}H_{13}NNaO_2]^+$ ($M+Na^+$) requires m/z 214.0838, found: m/z 214.0839.

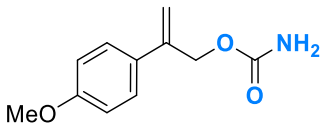


2-(Spiro[fluorene-9,9'-xanthen]-2-yl)allyl carbamate (1q): Prepared according to general procedures using 2-bromo-spiro[fluorene-9,9'-xanthene] (10.00 g, 24 mmol), magnesium turnings (0.68 g, 26 mmol), a grain of iodine, CuI (0.38 g, 1.8 mmol), prop-2-yn-1-ol (0.70 mL, ρ = 0.96 g/mL, 12 mmol), sodium cyanate (1.56 g, 24 mmol), and TFA (1.84 mL, ρ = 1.49 g/mL, 24 mmol).The crude product was further purified by flash chromato-graphy on silica gel (PE/EA = 10/1-2/1) to afford the **1q** (2.36 g, 46% yield over two steps) as a yellow solid. M.p. 162-163 °C (PE/EA); IR (neat): 3357, 2923, 1716, 1447, 1306, 1244 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 7.2 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.2 Hz,

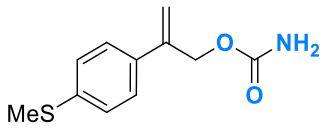
1H), 7.27-7.14 (m, 7H), 6.77 (t, J = 7.2 Hz, 2H), 6.41 (d, J = 7.6 Hz, 2H), 5.47 (s, 1H), 5.27 (s, 1H), 4.89 (s, 2H), 4.49 (br, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.4, 155.31, 155.27, 151.3, 142.3, 139.7, 139.0, 137.8, 128.5, 128.1, 127.9, 125.8, 125.7, 124.7, 123.2, 123.2, 120.0, 119.9, 116.8, 114.7, 66.2, 54.2; HRMS (ESI) calculated for $[C_{29}H_{21}NNaO_3]^+$ ($M+Na^+$) requires m/z 454.1414, found: m/z 454.1415.



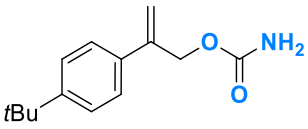
2-(4-(1,2,2-Triphenylvinyl)phenyl)allyl carbamate (1r): Prepared according to general procedures using (2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene (5.0 g, 12.2 mmol), magnesium turnings (0.30 g, 12.2 mmol), a grain of iodine, CuI (0.14 g, 0.73 mmol), prop-2-yn-1-ol (0.28 mL, ρ = 0.96 g/mL, 4.9 mmol), sodium cyanate (0.65g, 10 mmol), and TFA (1.91 mL, ρ = 1.49 g/mL, 25 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1r** (1.14 g, 54% yield over two steps) as a bright yellow solid. M.p. 67-69 °C (PE/EA); IR (neat): 3507, 3021, 1718, 1598, 1395, 1337 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.18 (d, J = 7.6 Hz, 2H), 7.16-6.96 (m, 17H), 5.53 (s, 1H), 5.31 (s, 1H), 4.91 (s, 2H), 4.63 (br, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.4, 143.60, 143.56, 143.5, 142.0, 141.2, 140.3, 135.5, 131.4, 131.32, 131.26, 127.7, 127.64, 127.59, 126.49, 126.46, 126.4, 125.0, 114.5, 66.2; HRMS (ESI) calculated for $[C_{30}H_{25}NNaO_2]^+$ ($M+Na^+$) requires m/z 454.1778, found: m/z 454.1776.



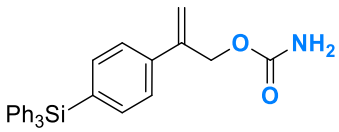
2-(4-Methoxyphenyl)allyl carbamate (1s): Prepared according to general procedures using *p*-tolylmagnesium bromide (20 mL, 1.0 M in THF), CuI (0.27 g, 1.5 mmol), prop-2-yn-1-ol (0.61 mL, ρ = 0.96 g/mL, 10 mmol), sodium cyanate (1.08 g, 16 mmol), and TFA (1.23 mL, ρ = 1.49 g/mL, 16 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1s** (1.00 g, 45% yield over two steps) as a yellow solid. M.p. 106-109°C (PE/EA); IR (neat): 3442, 2917, 1743, 1699, 1512, 1250 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 5.47 (s, 1H), 5.27 (s, 1H), 4.95 (s, 2H), 4.78 (br, 2H), 3.81 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.4, 156.7, 141.9, 130.3, 127.1, 113.8, 113.4, 66.4, 55.2; HRMS (ESI) calculated for $[C_{11}H_{13}NNaO_3]^+$ ($M+Na^+$) requires m/z 230.0788, found: m/z 230.0789.



2-(4-(Methylthio)phenyl)allyl carbamate (1t): Prepared according to general procedures using 1-bromo-4-(tert-butyl)benzene (10.30 g, 50 mmol), magnesium turnings (1.22 g, 50 mmol), a grain of iodine, CuI (0.57 g, 3 mmol), prop-2-yn-1-ol (1.20 mL, ρ = 0.96 g/mL, 20 mmol), sodium cyanate (2.60 g, 40 mmol), and TFA (3.20 mL, ρ = 1.49 g/mL, 42 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1t** (3.33 g, 75% yield over two steps) as a yellow solid. M.p. 108-110 °C (PE/EA); IR (neat): 3447, 3176, 2921, 1738, 1697, 1359 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.53 (s, 1H), 5.33 (s, 1H), 4.95 (s, 2H), 4.91 (br, 2H), 2.48 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.6, 141.9, 138.4, 134.4, 126.3, 126.2, 114.7, 66.2, 15.5; HRMS (ESI) calculated for $[C_{11}H_{13}NNaO_2S]^+$ ($M+Na^+$) requires m/z 246.0559, found: m/z 246.0561.

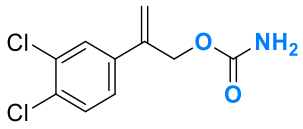


2-(4-(*Tert*-butyl)phenyl)allyl carbamate (1u): Prepared according to general procedures using 1-bromo-4-(*tert*-butyl)benzene (2.10 mL, ρ = 1.26 g/mL, 12 mmol), magnesium turnings (0.30 g, 12.2 mmol), a grain of iodine, CuI (0.17 g, 0.91 mmol), prop-2-yn-1-ol (0.37 mL, ρ = 0.96 g/mL, 6 mmol), sodium cyanate (0.79 g, 12 mmol), and TFA (1.00 mL, ρ = 1.49 g/mL, 13 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1u** (1.19 g, 85% yield over two steps) as a yellow solid. M.p. 83-86 °C (PE/EA); IR (neat): 3359, 2961, 1710, 1605, 1398, 1338 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.46-7.33 (m, 4H), 5.55 (s, 1H), 5.33 (s, 1H), 4.97 (s, 1H), 4.83 (br, 2H), 1,32 (s, 9H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.6, 151.1, 142.2, 134.8, 125.5, 125.4, 114.4, 66.4, 34.5, 31.2; HRMS (ESI) calculated for $[C_{14}H_{19}NNaO_2]^+$ ($M+Na^+$) requires m/z 256.1308, found: m/z 256.1308.

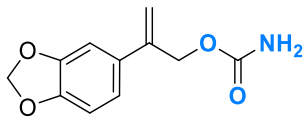


2-(4-(Triphenylsilyl)phenyl)allyl carbamate (1v): Prepared according to general procedures using (4-bromophenyl)triphenylsilane (10.0 g, 24 mmol), magnesium turnings (0.59 g, 24 mmol), a grain of iodine, CuI (0.29 g, 1.5 mmol), prop-2-yn-1-ol (0.58 mL, ρ = 0.96 g/mL, 10 mmol), sodium cyanate (3.02 g, 48 mmol), and TFA (3.82 mL, ρ = 1.49 g/mL, 50 mmol). The crude product

was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1v** (3.24 g, 74% yield over two steps) as a yellow solid. M.p. 126-129 °C (PE/EA); IR (neat): 3365, 3063, 1716, 1394, 1336, 1108 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.65-7.52 (m, 8H), 7.48-7.30 (m, 12H), 5.61 (s, 1H), 5.39 (s, 1H), 4.98 (s, 2H), 4.78 (br, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.5, 142.4, 138.8, 136.5, 136.3, 134.1, 133.9, 129.6, 127.9, 125.2, 115.8, 66.2; HRMS (ESI) calculated for $[C_{28}H_{25}NNaO_2Si]^+$ ($M+Na^+$) requires m/z 458.1547, found: m/z 458.1549.

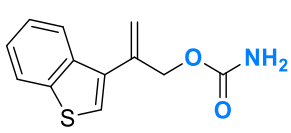


2-(3,4-Dichlorophenyl)allyl carbamate (**1w**)**:** Prepared according to general procedures using 4-bromo-1,2-dichlorobenzene (13.25 g, 58 mmol), magnesium turnings (1.22 g, 50 mmol), a grain of iodine, CuI (0.55 g, 3 mmol), prop-2-yn-1-ol (1.20 mL, ρ = 0.96 g/mL, 20 mmol), sodium cyanate (2.57 g, 40 mmol), and TFA (3.20 mL, ρ = 1.49 g/mL, 42 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1w** (2.95 g, 60% yield over two steps) as a yellow solid. M.p. 88-89 °C (PE/EA); IR (neat): 3425, 2946, 1683, 1612, 1412, 1338 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 6.8 Hz, 1H), 5.56 (s, 1H), 5.44 (s, 1H), 4.93 (s, 2H), 4.67 (br, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.3, 140.9, 138.0, 132.6, 132.0, 130.4, 128.0, 125.3, 116.9, 65.9; HRMS (ESI) calculated for $[C_{28}H_{25}NNaO_2Si]^+$ ($M+Na^+$) requires m/z 267.9903, found: m/z 267.9905.

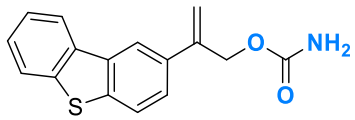


2-(Benzo[d][1,3]dioxol-5-yl)allyl carbamate (**1x**)**:** Prepared according to general procedures using 5-bromobenzo[d][1,3]dioxole (4.50 mL, 37.2 mmol), magnesium turnings (0.88 g, 37 mmol), a grain of iodine, CuI (0.42 g, 2.2 mmol), prop-2-yn-1-ol (0.87 mL, ρ = 0.96 g/mL, 15 mmol), sodium cyanate (1.82 g, 28 mmol), and TFA (2.30 mL, ρ = 1.49 g/mL, 29 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1x** (1.51 g, 49% yield over two steps) as a yellow solid. M.p. 93-94 °C (PE/EA); IR (neat): 3432, 2903, 1685, 1608, 1499, 1243 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 5.96 (s, 2H), 5.44 (s, 1H), 5.28 (s, 1H), 4.92 (s, 2H), 4.74 (br, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.6, 147.8, 147.4, 142.2, 132.1, 119.6, 114.2, 108.1, 106.5, 101.1, 66.5;

HRMS (ESI) calculated for $[C_{11}H_{11}NNaO_4]^+$ (M+Na^+) requires m/z 244.0580, found: m/z 244.0581.



2-(Benzo[b]thiophen-3-yl)allyl carbamate (**1y**)**:** Prepared according to general procedures using 3-bromobenzo[b]thiophene (10.72 g, 50 mmol), magnesium turnings (1.24 g, 50 mmol), a grain of iodine, CuI (0.57 g, 3 mmol), prop-2-yn-1-ol (1.20 mL, ρ = 0.96 g/mL, 20 mmol), sodium cyanate (2.60 g, 40 mmol), and TFA (3.22 mL, ρ = 1.49 g/mL, 42 mmol). The crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1y** (1.88 g, 40% yield over two steps) as a yellow solid. M.p. 63-66 °C (PE/EA); IR (neat): 3358, 2933, 1707, 1599, 1396, 1326 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 2H), 7.44-7.32 (m, 3H), 5.62 (s, 1H), 5.55 (s, 1H), 4.95 (s, 2H), 4.67 (br, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.6, 140.3, 138.1, 137.7, 134.6, 124.4, 124.3, 123.6, 123.0, 122.8, 116.5, 67.1; HRMS (ESI) calculated for $[C_{12}H_{11}NNaO_2S]^+$ (M+Na^+) requires m/z 256.0403, found: m/z 256.0402.



2-(Dibenzo[b,d]thiophen-2-yl)allyl carbamate (**1z**)**:** Prepared according to general procedures using 2-bromodibenzo[b,d]-thiophene (13.11 g, 50 mmol), magnesium turnings (1.22 g, 50 mmol), a grain of iodine, CuI (0.57 g, 3 mmol), prop-2-yn-1-ol (1.20 mL, ρ = 0.96 g/mL, 20 mmol), sodium cyanate (1.35 g, 19 mmol), and TFA (1.30 mL, ρ = 1.49 g/mL, 20 mmol). In the first step, the crude product was purified by flash chromatography on silica gel (PE/EA = 30/1-5/1) to afford 2-(dibenzo[b,d]thiophen-2-yl)prop-2-en-1-ol (2.33 g, 48% yield). In the second step, the crude product was further purified by flash chromatography on silica gel (PE/EA = 10/1-2/1) to afford the **1z** (1.84 g, 67% yield) as a yellow solid. M.p. 137-139 °C (PE/EA); IR (neat): 3434, 2911, 1685, 1605, 1403, 1337 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 8.25-8.15 (m, 2H), 7.90-7.80 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.52-7.42 (m, 2H), 5.67 (s, 1H), 5.46 (s, 1H), 5.11 (s, 2H), 4.67 (br, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 156.4, 142.7, 139.8, 139.1, 135.7, 135.3, 134.4, 126.9, 124.8, 124.5, 122.9, 122.7, 121.6, 118.9, 115.4, 66.5; HRMS (ESI) calculated for $[C_{12}H_{11}NNaO_2S]^+$ (M+Na^+) requires m/z 306.0559, found: m/z 306.0559.

IV. Photoredox-Catalyzed Oxytrifluoromethylation of Alkenes

Materials used to set up the reaction device: 25 mL Schlenk flask. IKA RCT basic. Blue LED lamp strip (457 nm, 5 W/m, 1 m). Oil bath (125 mm). The LED lamp strip was wrapped around the outside of the oil bath, with a distance of 2.3-2.4 cm from the Schlenk flask. (**Figure S1)**. We directly measured the emission spectrum of the blue LEDs (**Figure S2)** using OHSP-350 produced by Hangzhou Hopoo Light and Color Technology Co., Ltd.

Figure S1. Blue LEDs system

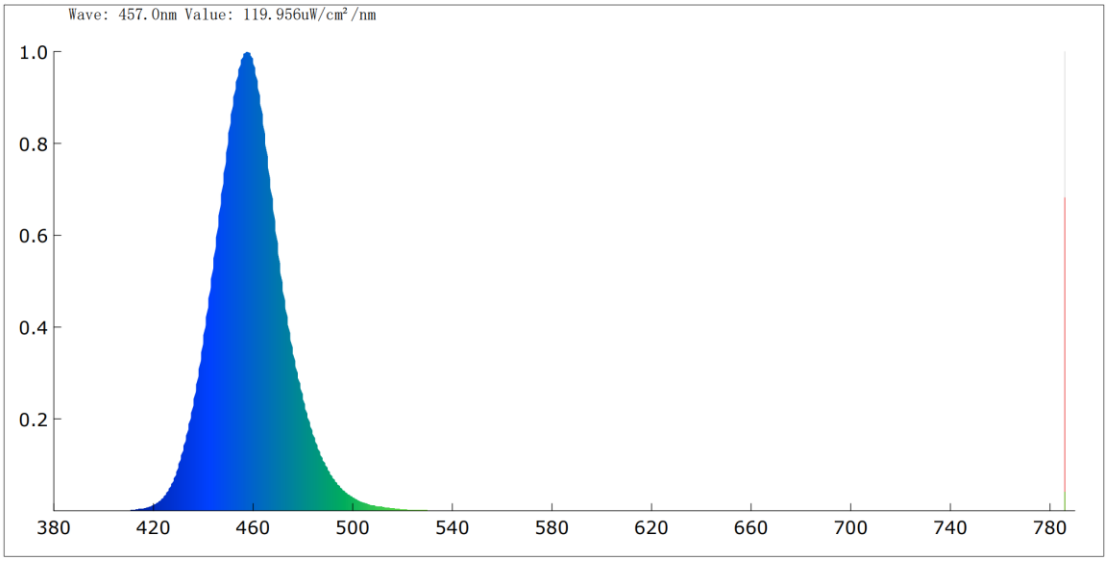
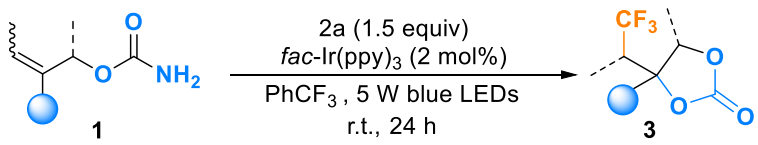
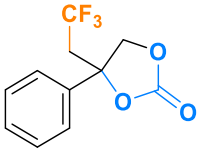


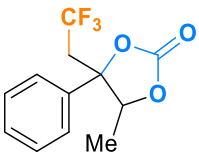
Figure S2. Emission spectrum of blue LEDs



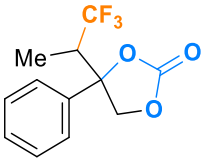
General procedure for the photoredox-catalyzed oxytrifluoromethylation of alkenes: A 25 mL flame-dried Schlenk flask was cooled at room temperature under nitrogen, then charged with 0.2 mmol of allyl carbamate **1a-1r**, 0.3 mmol of 1-trifluoroMethyl-1,2-benziodoxol-3(1H)-one (Togni reagent II) **2a**, 0.004 mmol of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$ or MeCN. The mixture was degassed three times, warmed to room temperature under nitrogen, and stirred at room temperature (30-35 °C) under the irradiation of 5 W blue LEDs for 24 hours. The reaction mixture was then concentrated by rotary evaporation, monitored by ^{1}H NMR using trimethylphenylsilane (TMSPh) as an internal standard, and further purified by flash chromatography on silica gel to afford the corresponding cyclic carbonates **3a-3r**.



4-Phenyl-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3a): Prepared according to the general procedure, using 0.0353 g of **1a** (0.20 mmol), 0.0948 g of **2a** (0.30 mmol), 0.0024 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1, 1% Et_3N) to afford 0.0374 g (0.152 mmol, 76% yield) of **3a** (monitored by $KMnO_4$) as a white soild. M.p. 77-79 °C (PE/EA); IR (neat): 2919, 1809, 1388, 1262, 1222, 1130 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.50-7.38 (m, 3H), 7.35 (d, J = 7.2 Hz, 2H), 4.79 (d, J = 8.8 Hz, 1H), 4.62 (d, J = 8.8 Hz, 1H), 3.05-2.81 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.1, 138.5, 129.3, 129.2, 124.1 (q, J = 276.6 Hz), 124.0, 81.8, 74.0, 43.6 (q, J = 28.5 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -60.7; HRMS (ESI) calculated for $[C_{11}H_9F_3NaO_3]^+$ (M+Na$^+$) requires m/z 269.0396, found m/z 269.0395.

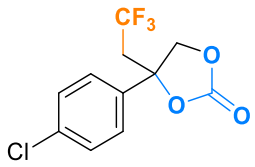


5-Methyl-4-phenyl-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3b): Prepared according to the general procedure, using 0.0388 g of **1b** (0.20 mmol), 0.0936 g of **2a** (0.30 mmol), 0.0022 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR (15% recovery of **1b**). The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1, 1% Et_3N) to afford 0.0386 g (0.148 mmol, 74% yield, 2:1 *dr*) of **3b** (monitored by $KMnO_4$) as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.50-7.25 (m, 5H), 4.88 (q, *J* = 6.4 Hz, 0.33H), 4.70 (q, *J* = 6.4 Hz, 0.67H), 3.00 (q, *J* = 10.0 Hz, 0.66H), 2.95-2.80 (m, 1.34H), 1.58 (d, *J* = 6.4 Hz, 2H), 0.99 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 152.8, 152.6, 137.5, 134.6, 129.13, 129.08, 129.0, 128.8, 124.9, 124.4 (q, *J* = 276.4 Hz), 124.2 (q, *J* = 277.0 Hz) 123.8, 84.7 (q, *J* = 2.2 Hz), 84.1 (q, *J* = 2.2 Hz), 82.9, 81.1, 42.7 (q, *J* = 28.5 Hz), 38.4 (q, *J* = 28.5 Hz), 17.3, 14.3; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -59.2, -59.8; HRMS (ESI) calculated for $[C_{12}H_{11}F_3NaO_3]^+$ ($M+Na^+$) requires m/z 283.0552, found m/z 283.0550.

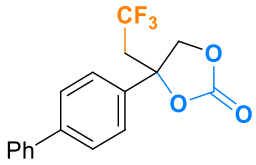


4-Phenyl-4-(1,1,1-trifluoropropan-2-yl)-1,3-dioxolan-2-one (3c): Prepared according to the general procedure, using 0.0381 g of **1c** (0.20 mmol), 0.0992 g of **2a** (0.30 mmol), 0.0033 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of MeCN. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1, 1% Et_3N) to afford 0.0395 g (0.152 mmol, 76% yield, 1.5:1 *dr*) of **3c** (monitored by $KMnO_4$) as a colorless oil. Major product: ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.50-7.38 (m, 3H), 7.36-7.30 (m, 2H), 4.97 (d, *J* = 8.8 Hz, 1H), 4.58 (d, *J* = 8.8 Hz, 1H), 2.95-2.80 (m, 1H), 1.18 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.2, 139.0, 129.2, 126.2 (q, *J* = 279.4 Hz), 124.3, 84.6, 72.8 (q, *J* = 2.4 Hz), 46.2 (q, *J* = 25.5 Hz), 9.5 (q, *J* = 2.9 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -65.98; Minor product: ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.48-7.33 (m, 5H), 4.87-4.78 (m, 2H), 3.05-2.92 (m, 1H), 1.25 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.0, 136.1, 129.4, 128.6, 125.8 (q, *J* = 278.6 Hz), 125.7, 84.7, 74.5 (q, *J* = 3.3 Hz), 47.2 (q, *J* = 25.5 Hz), 8.9 (q, *J* = 2.5

Hz);^{19}F NMR: (376 MHz, $CDCl_3$) δ -66.03; HRMS (ESI) calculated for $[C_{12}H_{11}F_3NaO_3]^+$ ($M+Na^+$) requires m/z 283.0552, found m/z 283.0553.

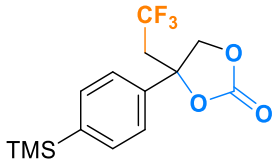


4-(4-Chlorophenyl)-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3d): Prepared according to the general procedure Conditions, using 0.0455 g of **1d** (0.20 mmol), 0.0975 g of **2a** (0.30 mmol), 0.0024 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1, 1% Et_3N) to afford 0.0382 g (0.136 mmol, 68% yield) of **3d** (monitored by $KMnO_4$) as a colorless soild. M.p. 84-86 °C (PE/EA); IR (neat): 2920, 1808, 1392, 1261, 1218, 1131 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.77 (d, J = 8.8 Hz, 1H), 4.58 (d, J = 8.8 Hz, 1H), 2.92 (q, J = 9.6 Hz, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 152.8, 136.8, 135.5, 129.5, 125.6, 124.0 (q, J = 276.6 Hz), 81.4, 74.0, 43.5 (q, J = 28.5 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -60.6; HRMS (EI) calculated for $[C_{11}H_8ClF_3O_3]^+$ (M^+) requires m/z 280.0109, found m/z 280.0110.

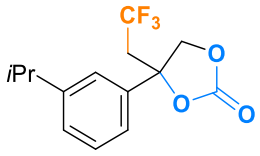


4-([1,1'-Biphenyl]-4-yl)-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3e): Prepared according to the general procedure, using 0.0559 g of **1e** (0.20 mmol), 0.0952 g of **2a** (0.30 mmol), 0.0032 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of MeCN. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1, 1% Et_3N) to afford 0.0496 g (0.154 mmol, 77% yield) of **3e** as a white soild. M.p. 160-162 °C (PE/EA); IR (neat): 2918, 1788, 1699, 1459, 1235, 1128 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.50-7.35 (m, 5H), 4.82 (d, J = 8.8 Hz, 1H), 4.66 (d, J = 8.8 Hz, 1H), 3.05-2.87 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.1, 142.3, 139.7, 137.3, 128.9, 127.95, 127.87, 127.1, 124.5, 124.1 (q, J = 276.6 Hz), 81.8, 73.9, 43.6 (q, J = 28.0 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -60.6; HRMS (ESI) calculated

for $[C_{17}H_{13}F_3NaO_3]^+$ ($M+Na^+$) requires m/z 345.0709, found m/z 345.0705.

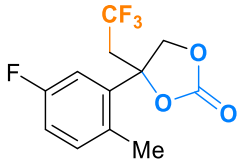


4-(2,2,2-Trifluoroethyl)-4-(4-(trimethylsilyl)phenyl)-1,3-dioxolan-2-one (3f): Prepared according to the general procedure, using 0.0503 g of **1f** (0.20 mmol), 0.0952 g of **2a** (0.30 mmol), 0.0026 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1, 1% Et_3N) to afford 0.0407 g (0.128 mmol, 64% yield) of **3f** (monitored by $KMnO_4$) as a colorless soild. M.p. 52-55 °C (PE/EA); IR (neat): 2957, 1810, 1388, 1258, 1221, 1137 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 4.81 (d, J = 8.8 Hz, 1H), 4.61 (d, J = 8.8 Hz, 1H), 3.02-2.83 (m, 2H), 0.28 (s, 9H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.1, 142.3, 138.9, 134.1, 124.1 (q, J = 277.0 Hz), 123.1, 81.8 (q, J = 2.2 Hz), 73.8 (q, J = 1.5 Hz), 43.5 (q, J = 28.5 Hz), -1.3; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -60.7; HRMS (ESI) calculated for $[C_{14}H_{17}F_3NaO_3Si]^+$ ($M+Na^+$) requires m/z 341.0791, found m/z 341.0792.

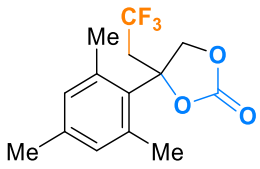


4-(3-*Iso*-propylphenyl)-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3g): Prepared according to the general procedure, using 0.0462 g of **1g** (0.20 mmol), 0.0943 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1, 1% Et_3N) to afford 0.0430 g (0.149 mmol, 75% yield) of **3g** (monitored by $KMnO_4$) a colorless oil. IR (neat): 2916, 1808, 1391, 1264, 1134 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.37 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.20 (s, 1H), 7.12 (d, J = 7.6 Hz, 1H), 4.81 (d, J = 8.8 Hz, 1H), 4.62 (d, J = 8.8 Hz, 1H), 3.02-2.80 (m, 3H), 1.26 (d, J = 6.8 Hz, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.2, 150.2, 138.6, 129.2, 127.3, 124.1 (q, J = 277.1 Hz), 122.0, 121.3, 81.9 (q, J = 2.1 Hz), 73.9 (q, J = 1.5 Hz), 43.7 (q, J = 27.7 Hz), 34.2, 23.9; ^{19}F NMR:

(376 MHz, $CDCl_3$) δ -60.8; HRMS (ESI) calculated for $[C_{14}H_{15}F_3NaO_3]^+$ ($M+Na^+$) requires m/z 311.0866, found m/z 311.0864.

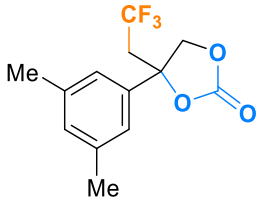


4-(5-Fluoro-2-methylphenyl)-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (**3h**)**:** Prepared according to the general procedure, using 0.0456 g of **1h** (0.20 mmol), 0.0949 g of **2a** (0.30 mmol), 0.0027 g of *fac*-$Ir(ppy)_3$ (0.004 mmol), and 4 mL of MeCN. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^1H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1, 1% Et_3N) to afford 0.0458 g (0.165 mmol, 82% yield) of **3h** (monitored by $KMnO_4$) as a colorless soild. M.p. 84-86 ºC (PE/EA); IR (neat): 2978, 1820, 1651, 1380, 1261, 1132 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 1H), 7.24-7.17 (m, 1H), 7.06-6.96 (m, 1H), 4.95 (d, J = 8.8 Hz, 1H), 4.57 (d, J = 8.8 Hz, 1H), 3.01-2.82 (m, 2H), 2.78 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 161.3 (d, J = 245.2 Hz), 152.4, 139.0 (d, J = 6.6 Hz), 134.1 (d, J = 7.8 Hz), 127.6 (d, J = 3.7 Hz), 124.2 (q, J = 277.0 Hz), 116.1 (d, J = 21.0 Hz), 112.4 (d, J = 24.8 Hz), 81.7, 73.0, 42.1 (q, J = 28.0 Hz), 19.7; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -61.3, -114.6; HRMS (ESI) calculated for $[C_{12}H_{10}F_4NaO_3]^+$ ($M+Na^+$) requires m/z 301.0458, found m/z 301.0459.

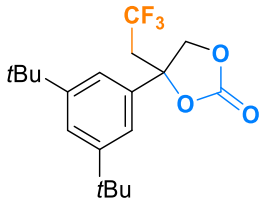


4-Mesityl-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (**3i**)**:** Prepared according to the general procedure, using 0.0442 g of **1i** (0.20 mmol), 0.0967 g of **2a** (0.30 mmol), 0.0028 g of *fac*-$Ir(ppy)_3$ (0.004 mmol), and 4 mL of MeCN. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^1H NMR (18% recovery of **1i**). The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1, 1% Et_3N) to afford 0.0369 g (0.128 mmol, 64% yield) of **3i** (monitored by $KMnO_4$) as a colorless oil. IR (neat): 2954, 1817, 1374, 1260, 1215, 1130 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 6.89 (s, 2H), 5.07 (d, J = 8.8 Hz, 1H), 4.60 (d, J = 8.8 Hz, 1H), 3.06-2.70 (m, 2H), 2.37 (br, 6H), 2.26 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 152.8, 138.4, 133.9, 131.91, 131.88, 124.5 (q, J = 277.0 Hz), 84.4, 73.8, 41.9 (q, J = 27.6 Hz), 23.3-22.4 (m), 20.4; ^{19}F

NMR: (376 MHz, $CDCl_3$) δ -61.7; HRMS (ESI) calculated for $[C_{14}H_{15}F_3NaO_3]^+$ ($M+Na^+$) requires m/z 311.0866, found m/z 311.0865.

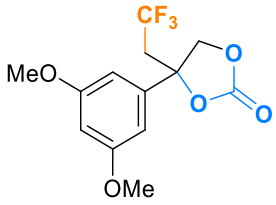


4-(3,5-Dimethylphenyl)-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3j): Prepared according to the general procedure, using 0.0420 g of **1j** (0.20 mmol), 0.0950 g of **2a** (0.30 mmol), 0.0025 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^1H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1, 1% Et_3N) to afford 0.0395 g (0.144 mmol, 72% yield) of **3j** (monitored by $KMnO_4$) as a colorless oil. IR (neat): 2984, 1813, 1389, 1263, 1135 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.03 (s, 1H), 6.93 (s, 2H), 4.77 (d, J = 8.8 Hz, 1H), 4.58 (d, J = 8.8 Hz, 1H), 3.00-2.78 (m, 2H), 2.34 (s, 6H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.2, 139.0, 138.7, 130.8, 124.2 (q, J = 276.6 Hz), 121.6, 81.8, 73.9, 43.5 (q, J = 28.5 Hz), 21.3; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -60.8; HRMS (ESI) calculated for $[C_{13}H_{13}F_3NaO_3]^+$ ($M+Na^+$) requires m/z 297.0709, found m/z 297.0711.

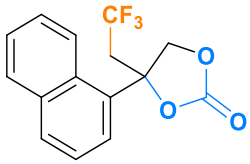


4-(3,5-Di-*tert*-butylphenyl)-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3k): Prepared according to the general procedure, using 0.0581 g of **1k** (0.20 mmol), 0.0948 g of **2a** (0.30 mmol), 0.0026 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^1H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1, 1% Et_3N) to afford 0.0530 g (0.148 mmol, 74% yield) of **3k** (monitored by $KMnO_4$) as a light yellow soild. M.p. 72-74 °C (PE/EA); IR (neat): 2962, 1809, 1472, 1387, 1254, 1132 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.13 (s, 2H), 4.87 (d, J = 8.8 Hz, 1H), 4.64 (d, J = 8.8 Hz, 1H), 3.03-2.79 (m, 2H), 1.33 (s, 18H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.3, 152.0, 138.1, 124.2 (q, J = 276.4 Hz), 123.2, 117.9, 82.3 (q, J = 2.2 Hz), 73.8 (q, J = 1.4 Hz), 43.9 (q, J = 28.4 Hz), 35.1, 31.3; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -60.8; HRMS (ESI)

calculated for $[C_{19}H_{25}F_3NaO_3]^+$ (M+Na^+) requires m/z 386.1648, found m/z 386.1647.

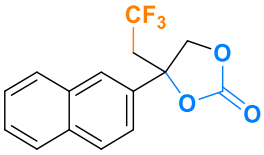


4-(3,5-Dimethoxyphenyl)-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3l): Prepared according to the general procedure, using 0.0494 g of **1l** (0.20 mmol), 0.0942 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1, 1% Et_3N) to afford 0.0412 g (0.135 mmol, 67% yield) of **3l** (monitored by $KMnO_4$) as a light yellow soild. M.p. 71-73 ^{o}C (PE/EA); IR (neat): 2932, 1815, 1605, 1462, 1262, 1156 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 6.45 (s, 3H), 4.76 (d, J = 8.8 Hz, 1H), 4.56 (d, J = 8.8 Hz, 1H), 3.81 (s, 6H), 3.00-2.80 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 161.4, 153.0, 141.0, 124.1 (q, J = 276.9 Hz), 102.2, 100.4, 81.6, 73.9, 55.5, 43.4 (q, J = 28.1 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -60.8; HRMS (ESI) calculated for $[C_{13}H_{13}F_3NaO_5]^+$ (M+Na^+) requires m/z 329.0607, found m/z 329.0607.

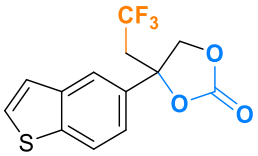


4-(Naphthalen-1-yl)-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3m): Prepared according to the general procedure, using 0.0454 g of **1m** (0.20 mmol), 0.0960 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of MeCN. After the reaction was stirred at stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1, 1% Et_3N) to afford 0.0462 g (0.156 mmol, 78% yield) of **3m** as a colorless oil. IR (neat): 2914, 1815, 1514, 1388, 1261, 1133 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.65-7.49 (m, 3H), 7.42 (d, J = 8.4 Hz, 1H), 5.26 (d, J = 8.8 Hz, 1H), 4.78 (d, J = 8.8 Hz, 1H), 3.32-3.02 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 152.7, 134.7, 134.5, 130.4, 130.3, 127.5, 127.4, 126.1, 125.3, 124.5 (q, J = 276.9 Hz), 123.1, 122.0, 82.3, 73.1, 42.9 (q, J = 28.0 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -61.1; HRMS (ESI) calculated for $[C_{15}H_{11}F_3O_3]^+$ (M+Na^+) requires m/z 319.0552, found

m/z 319.0553.

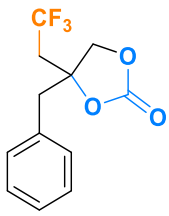


4-(Naphthalen-2-yl)-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3n): Prepared according to the general procedure Conditions, using 0.0467 g of **1n** (0.20 mmol), 0.0959 g of 2a (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR (17% recovery of **1n**). The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1, 1% Et_3N) to afford 0.0394 g (0.133 mmol, 66% yield) of **3n** as a white soild. M.p. 154-156 °C (PE/EA); IR (neat): 2922, 1814, 1388, 1265, 1133 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.8 Hz, 1H), 7.92-7.84 (m, 3H), 7.61-7.53 (m, 2H), 7.35 (dd, J = 8.4, 1.6 Hz, 1H), 4.86 (d, J = 8.8 Hz, 1H), 4.71 (d, J = 8.8 Hz, 1H), 3.10-2.95 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.1, 135.4, 133.1, 132.7, 129.5, 128.3, 127.7, 127.3, 127.2, 124.1 (q, J = 277.0 Hz), 123.5, 121.0, 81.9 (q, J = 2.1 Hz), 73.9 (q, J = 2.2 Hz), 43.5 (q, J = 28.5 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -60.7; HRMS (ESI) calculated for $[C_{15}H_{11}F_3NaO_3]^+$ ($M+Na^+$) requires m/z 319.0552, found m/z 319.0551.

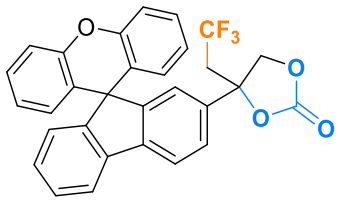


4-(Benzo[b]thiophen-5-yl)-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3o): Prepared according to the general procedure, using 0.0474 g of **1o** (0.20 mmol), 0.0960 g of **2a** (0.30 mmol), 0.0026 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1, 1% Et_3N) to afford 0.0367 g (0.121 mmol, 61% yield) of **3o** as a white soild. M.p. 168-170 °C (PE/EA); IR (neat): 2922, 1815, 1516, 1391, 1260, 1137 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.8 Hz, 1H), 7.87 (s, 1H), 7.56 (d, J = 5.6 Hz, 1H), 7.38 (d, J = 5.6 Hz, 1H), 7.26 (s, 1H), 4.85 (d, J = 8.8 Hz, 1H), 4.68 (d, J = 8.8 Hz, 1H), 3.06-2.92 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.1, 140.4, 139.8, 134.7, 128.5, 124.1 (q, J = 276.4 Hz), 123.9, 123.5, 119.7, 119.2, 82.0, 74.2, 43.8 (q, J = 28.4 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$)

δ -60.6; HRMS (ESI) calculated for $[C_{13}H_9F_3NaO_3S]^+$ ($M+Na^+$) requires m/z 325.0117, found m/z 325.0116.

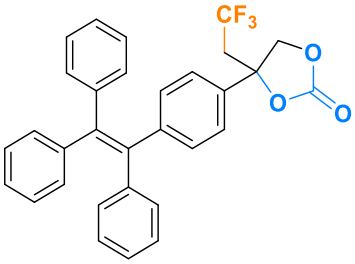


4-Benzyl-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3p): Prepared according to the general procedure, using 0.0394 g of **1p** (0.20 mmol), 0.0968 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR (32% recovery of **1p**). The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1, 1% Et_3N) to afford 0.0156 g (0.060 mmol, 30% yield) of **3p** as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 3H), 7.29-7.24 (m, 2H), 4.43 (d, J = 9.2 Hz, 1H), 4.36 (d, J = 9.2 Hz, 1H), 3.18 (d, J = 14.8 Hz, 1H), 3.08 (d, J = 14.8 Hz, 1H), 2.69 (q, J = 10.4 Hz, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.1, 132.1, 130.5, 129.0, 128.2, 124.6 (q, J = 275.7 Hz), 80.7, 70.9, 43.4, 40.9 (q, J = 28.4 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -60.1; HRMS (ESI) calculated for $[C_{12}H_{11}F_3NaO_3]^+$ ($M+Na^+$) requires m/z 283.0552, found m/z 283.0552.

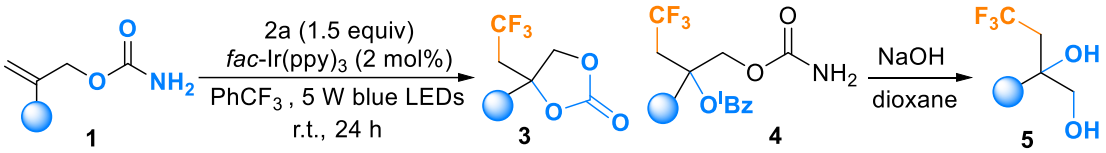


4-(Spiro[fluorene-9,9'-xanthen]-2-yl)-4-(2,2,2-trifluoroethyl)-1,3-dioxolan-2-one (3q): Prepared according to the general procedure, using 0.0881 g of **1q** (0.20 mmol), 0.0957 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR (18% recovery of **1q**). The reaction mixture was further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1, 1% Et_3N) to afford 0.0641 g (0.128 mmol, 64% yield) of **3q** as a colorless oil. IR (neat): 2917, 1813, 1478, 1390, 1259, 1130 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.45-7.32 (m, 2H), 7.25-7.16 (m, 6H), 7.09 (s, 1H), 6.77 (dd, J = 12.4, 6.8 Hz, 2H), 6.34 (t, J = 6.8 Hz, 2H), 4.67 (d, J = 8.8 Hz, 1H), 4.48 (d, J = 8.8 Hz, 1H), 2.90-2.70 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 155.7, 155.6, 152.9, 151.3, 151.2, 141.5, 138.3, 137.7, 129.2, 128.45, 128.43, 128.0, 127.6, 125.7, 124.02, 123.95, 123.9 (q, J = 276.6 Hz), 123.8, 123.4, 121.5, 120.7,

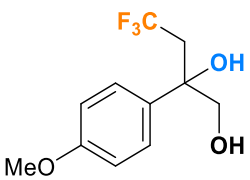
120.4, 117.0, 81.9, 73.9, 54.4, 43.8 (q, J = 28.0 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -60.8; HRMS (ESI) calculated for $[C_{30}H_{19}F_3NaO_4]^+$ ($M+Na^+$) requires m/z 523.1128, found m/z 523.1131.



4-(2,2,2-Trifluoroethyl)-4-(4-(1,2,2-triphenylvinyl)phenyl)-1,3-dioxolan-2-one (3r): Prepared according to the general procedure, using 0.0864 g of **1r** (0.20 mmol), 0.0980 g of **2a** (0.30 mmol), 0.0026 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1, 1% Et_3N) to afford 0.0514 g (0.103 mmol, 51% yield) of **3r** as a white soild. M.p. 97-99 °C (PE/EA); IR (neat): 2926, 1819, 1700, 1514, 1391, 1263 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.18-6.94 (m, 19H), 4.70 (d, J = 8.8 Hz, 1H), 4.57 (d, J = 8.8 Hz, 1H), 2.95-2.75 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 153.1, 145.1, 143.1, 143.04, 142.99, 142.1, 139.4, 135.9, 132.0, 131.22, 131.18, 127.8, 127.72, 127.66, 126.8, 126.7, 124.0 (q, J = 276.4 Hz), 123.4, 81.7 (q, J = 2.1 Hz), 73.8, 43.6 (q, J = 28.4 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -60.7; HRMS (ESI) calculated for $[C_{31}H_{23}F_3NaO_3]^+$ ($M+Na^+$) requires m/z 523.1492, found m/z 523.1495.

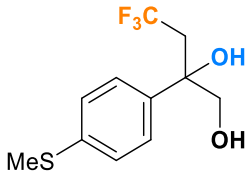


Additional basic hydrolysis for the synthesis of 1,2-diols: The reaction mixture was redissolved in 4 mL dioxane under the atmosphere of nitrogen, and 4 mL NaOH (1M) was added. The mixture was stirred at 80 °C for 2 hours. After cooling to room temperature, it was concentrated by rotary evaporation, and then further purified by flash chromatography on silica gel to afford 1,2-diols **5**.

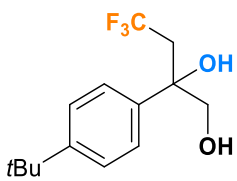


4,4,4-Trifluoro-2-(4-methoxyphenyl)butane-1,2-diol (5s): Prepared according to the general procedure, using 0.0411 g of **1s** (0.20 mmol), 0.0998 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the

irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR (26% yield of **3s,** 59% yield of **4s**). Then additional basic hydrolysis was carried out. The mixure was concentrated by rotary evaporation and further purified by flash chromatography on silica gel (PE/EA = 4/1-2/1) to afford 0.0410 g (0.164 mmol, 82% yield) of **5s** (monitored by phosphomolybdic acid) as a colorless soild. M.p. 61-63 °C (PE/EA); IR (neat): 3611, 2960, 1514, 1370, 1252, 1125 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 3.79-3.65 (m, 2H), 3.13 (brs, 1H), 2.88-2.58 (m, 2H), 2.37 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 159.0, 133.2, 126.3, 125.8 (q, J = 276.3 Hz), 113.8, 74.1 (q, J = 1.5 Hz), 69.6 (q, J = 1.4 Hz), 55.2, 41.5 (q, J = 26.2 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -59.2; HRMS (EI) calculated for $[C_{11}H_{13}F_3O_3]^+$ (M^+) requires m/z 250.0811, found m/z 250.0816.

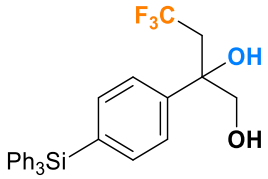


4,4,4-Trifluoro-2-(4-(methylthio)phenyl)butane-1,2-diol (5t): Prepared according to the general procedure using 0.0447 g of **1t** (0.20 mmol), 0.0963 g of **2a** (0.30 mmol), 0.0024 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR (10% recovery of **1t,** 27% yield of **3t,** 54% yield of **4t**). Then additional basic hydrolysis was carried out. The mixure was concentrated by rotary evaporation and further purified by flash chromatography on silica gel (PE/EA = 5/1-7/3) to afford 0.0425 g (0.160 mmol, 80% yield) of **5t** (monitored by phosphomolybdic acid) as a light yellow soild. M.p. 53-56 °C (PE/EA); IR (neat): 3565, 2955, 1498, 1372, 1261, 1126 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 3.82-3.67 (m, 2H), 2.99 (brs, 1H), 2.88-2.60 (m, 2H), 2.48 (s, 3H), 2.03 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 138.3, 137.9, 126.3, 125.7 (q, J = 276.4 Hz), 125.6, 74.2 (q, J = 1.5 Hz), 69.6 (q, J = 1.5 Hz), 41.4 (q, J = 26.2 Hz), 15.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -59.1; HRMS (EI) calculated for $[C_{11}H_{13}F_3O_2S]^+$ (M^+) requires m/z 266.0583, found m/z 266.0585.

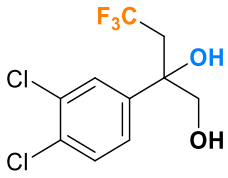


2-(4-(*Tert*-butyl)phenyl)-4,4,4-trifluorobutane-1,2-diol (5u): Prepared according to the general procedure, using 0.0482 g of **1u** (0.20 mmol), 0.0942 g of **2a** (0.30 mmol), 0.0025 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4

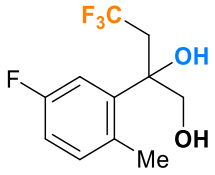
mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^1H NMR (72% yield of **3u**, 14% yield of **4u**). Then additional basic hydrolysis was carried out. The mixure was concentrated by rotary evaporation and further purified by flash chromatography on silica gel (PE/EA = 5/1) to afford 0.0490 g (0.177 mmol, 89% yield) of **5u** (monitored by phosphomolybdic acid) as a white soild. M.p. 100-101 ºC (PE/EA); IR (neat): 3620, 2961, 1514, 1369, 1262, 1128 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 3.84-3.69 (m, 2H), 3.00 (brs, 1H), 2.88-2.60 (m, 2H), 2.07 (br, 1H), 1.31 (s, 9H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 150.8, 138.4, 125.8 (q, J = 276.6 Hz), 125.5, 124.7, 74.3, 69.6, 41.5 (q, J = 26.3 Hz), 34.5, 31.2; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -59.1; HRMS (EI) calculated for $[C_{14}H_{19}F_3O_2]^+$ (M^+) requires m/z 276.1332, found m/z 276.1334.



4,4,4-Trifluoro-2-(4-(triphenylsilyl)phenyl)butane-1,2-diol (5v): Prepared according to the general procedure, using 0.0892 g of **1v** (0.20 mmol), 0.0954 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^1H NMR (6% recovery of **1v**, 63% yield of **3v**, 16% yield of **4v**). Then additional basic hydrolysis was carried out. The mixure was concentrated by rotary evaporation and further purified by flash chromatography on silica gel (PE/EA = 5/1-7/3) to afford 0.0621 g (0.130 mmol, 65% yield) of **5v** as a colorless oil. IR (neat): 3377, 2918, 1711, 1428, 1261, 1107 cm^{-1}; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.64-7.50 (m, 8H), 7.46-7.30 (m, 11H), 3.83-3.67 (m, 2H), 3.14 (brs, 1H), 2.88-2.60 (m, 2H), 2.23 (t, J = 6.4 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 142.8, 136.6, 136.3, 133.9, 133.8, 129.7, 127.9, 125.8 (q, J = 276.4 Hz), 124.5, 74.4 (q, J = 2.2 Hz), 69.4, 41.5 (q, J = 26.2 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -59.1; HRMS (EI) calculated for $[C_{28}H_{25}F_3O_2Si]^+$ (M^+) requires m/z 478.1570, found m/z 478.1572.

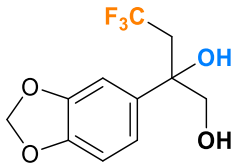


2-(3,4-Dichlorophenyl)-4,4,4-trifluorobutane-1,2-diol (5w): Prepared according to the general procedure, using 0.0503 g of **1w** (0.20 mmol), 0.0942 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR (8% recovery of **1w**, 58% yield of **3w**, 16% yield of **4w**). Then additional basic hydrolysis was carried out. The mixure was concentrated by rotary evaporation and further purified by flash chromatography on silica gel (PE/EA = 5/1) to afford 0.0399 g (0.138 mmol, 69% yield) of **5w** (monitored by phosphomolybdic acid) as a colorless soild. M.p. 56-58 °C (PE/EA); IR (neat): 3614, 2951, 1699, 1377, 1261, 1130 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.26 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.74 (s, 2H), 3.13 (br, 1H), 2.92-2.76 (m, 1H), 2.74-2.58 (m, 1H), 2.14 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 141.7, 132.9, 132.0, 130.5, 127.6, 125.5 (q, *J* = 276.4 Hz), 124.6, 73.8 (q, *J* = 1.4 Hz), 69.3 (q, *J* = 1.4 Hz), 41.3 (q, *J* = 27.0 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -59.2; HRMS (EI) calculated for $[C_{10}H_9Cl_2F_3O_2]^+$ (M^+) requires m/z 287.9926, found m/z 287.9927.

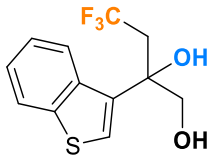


4,4,4-Trifluoro-2-(5-fluoro-2-methylphenyl)butane-1,2-diol (5h): Prepared according to the general procedure, using 0.0424 g of **1h** (0.20 mmol), 0.0979 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of MeCN. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR (85% yield of **3h**, 11% yield of **4h**). Then additional basic hydrolysis was carried out. The mixure was concentrated by rotary evaporation and further purified by flash chromatography on silica gel (PE/EA = 5/1) to afford 0.0464 g (0.184 mmol, 92% yield) of **5h** (monitored by phosphor-molybdic acid) as a colorless soild. M.p. 75-77 °C (PE/EA); IR (neat): 3626, 2954, 1494, 1368, 1262, 1136 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 10.8, 2.4 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.91 (td, *J* = 8.0, 2.4 Hz, 1H), 4.02-3.87 (m, 2H), 3.23 (brs, 1H), 2.95-2.75 (m, 2H), 2.46 (s, 3H), 2.12 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 161.3 (d, *J* = 242.0 Hz), 141.0 (d, *J* = 6.2 Hz), 134.1 (d, *J* = 7.4 Hz), 130.2 (d, *J* = 3.3 Hz), 125.7 (q, *J* = 276.6 Hz), 114.6 (d, *J* = 20.6 Hz), 114.0

(d, J = 23.9 Hz), 74.8, 67.6, 40.1 (q, J = 26.4 Hz), 21.4; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -59.9; HRMS (EI) calculated for $[C_{11}H_{12}F_4O_2]^+$ (M^+) requires m/z 252.0768, found m/z 252.0770.

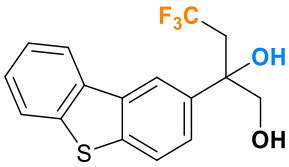


2-(Benzo[d][1,3]dioxol-5-yl)-4,4,4-trifluorobutane-1,2-diol (5x): Prepared according to the general procedure, using 0.0447 g of **1x** (0.20 mmol), 0.0937 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR (5% recovery of **1x,** 28% yield of **3x,** 46% yield of **4x**). Then additional basic hydrolysis was carried out. The mixure was concentrated by rotary evaporation and further purified by flash chromatography on silica gel (PE/EA = 4/1-2/1) to afford 0.0380 g (0.144 mmol, 72% yield) of **5x** (monitored by phosphomolybdic acid) as a colorless soild. M.p. 80-82 °C (PE/EA); IR (neat): 3442, 2911, 1493, 1372, 1243, 1150 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 6.95 (s, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 5.98 (s, 2H), 3.80-3.67 (m, 2H), 2.96 (brs, 1H), 2.86-2.57 (m, 2H), 1.98 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 148.0, 147.1, 135.3, 125.7 (q, J = 277.1 Hz), 118.4, 108.2, 106.0, 101.3, 74.3 (q, J = 2.2 Hz), 69.7 (q, J = 1.5 Hz), 41.6 (q, J = 26.3 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -59.2; HRMS (ESI) calculated for $[C_{11}H_{11}F_3O_4]^+$ (M+Na^+) requires m/z 264.0604, found m/z 264.0605.



2-(Benzo[b]thiophen-3-yl)-4,4,4-trifluorobutane-1,2-diol (5y): Prepared according to the general procedure, using 0.0472 g of **1y** (0.20 mmol), 0.0949 g of **2a** (0.30 mmol), 0.0026 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of MeCN. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR (46% yield of **3y,** 21% yield of **4y**). Then additional basic hydrolysis was carried out. The mixure was concentrated by rotary evaporation and further purified by flash chromatography on silica gel (PE/EA = 5/1-7/3) to afford 0.0287 g (0.104 mmol, 52% yield) of **5y** (monitored by phosphomolybdic acid) as a colorless oil. IR (neat): 3416, 2926, 1746, 1371, 1261, 1144 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.6 Hz, 2H), 7.88 (d, J = 7.6 Hz, 2H), 7.50 (s, 1H), 7.44-

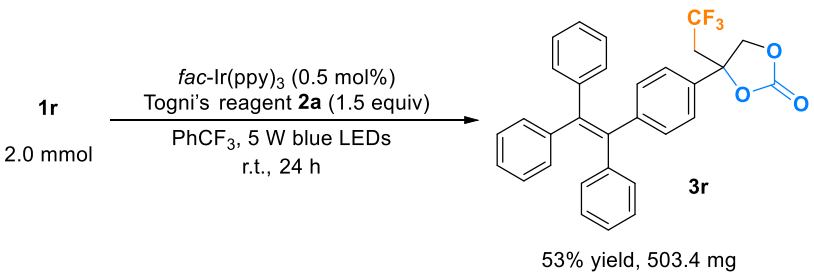
7.32 (m, 2H), 4.13 (d, J = 11.2 Hz, 1H), 4.05-3.93 (m, 1H), 3.25 (brs, 1H), 3.08-2.88 (m, 2H), 1.94 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 141.5, 136.1, 136.0, 125.6 (q, J = 276.3 Hz), 124.5, 124.34, 124.30, 123.4, 123.1, 74.1 (q, J = 1.4 Hz), 67.7, 40.3 (q, J = 26.9 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -59.8; HRMS (ESI) calculated for $[C_{12}H_{11}F_3O_2S]^+$ (M^+) requires m/z 276.0426, found m/z 276.0427.



2-(Dibenzo[b,d]thiophen-2-yl)-4,4,4-trifluorobutane-1,2-diol (5z): Prepared according to the general procedure, using 0.0572 g of **1z** (0.20 mmol), 0.0955 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of MeCN. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR (65% yield of **3z,** 10% yield of **4z**). Then additional basic hydrolysis was carried out. The mixure was concentrated by rotary evaporation and further purified by flash chromatography on silica gel (PE/EA = 5/1-7/3) to afford 0.0361 g (0.111 mmol, 55% yield) of **5z** as a white soild. M.p. 61-63 ºC (PE/EA); IR (neat): 3415, 2921, 1743, 1372, 1261, 1123 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) 8.31 (s, 1H), 8.24-8.16 (m, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.54-7.42 (m, 3H), 3.95-3.81 (m, 1H), 3.16 (brs, 1H), 3.04-2.74 (m, 2H), 1.98 (t, J = 5.6 Hz, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 139.8, 138.9, 137.9, 135.8, 135.2, 127.0, 125.8 (q, J = 276.5 Hz), 124.5, 123.6, 122.9, 121.7, 118.4, 74.6, 69.8, 41.8 (q, J = 26.4 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -59.1; HRMS (ESI) calculated for $[C_{16}H_{13}F_3O_2S]^+$ (M^+) requires m/z 326.0583, found m/z 326.0588.

V. Synthetic Applications

a) Scaled up reaction:



53% yield, 503.4 mg

A 100 mL flame-dried Schlenk flask was cooled at room temperature under nitrogen, then charged with **1r** (0.85 g, 2.0 mmol), Togni's reagent **2a** (0.95 g, 3.0 mmol), *fac*-Ir(ppy)$_3$ (0.0065 g, 0.01 mmol), and $PhCF_3$ (40 mL). The mixture was degassed for three times, warmed to room temperature under nitrogen, and stirred at room temperature (30-35°C) while being irradiated with 5 W blue LEDs for 24 hours. The reaction mixture was concentrated by rotary evaporation, monitored by ^1H NMR, and then further purified by flash chromatography on silica gel (PE/EA = 10/1-5/1, 1% Et_3N) to afford 0.53 g **3r** in 53% yield. The **3r** exhibits a significant aggregation-induced luminescence effect under ultraviolet light irradiation, displaying blue fluorescence. (**Figure S3)**.

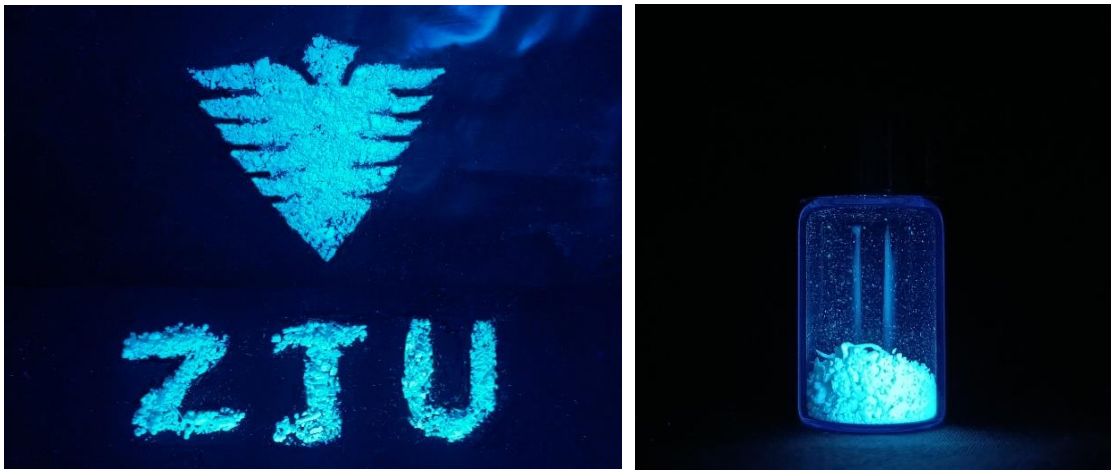
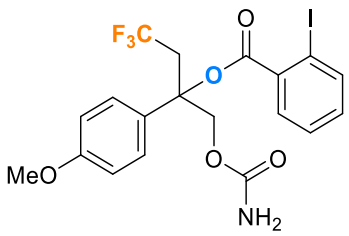


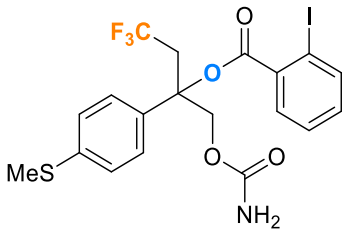
Figure S3. The product **3r** under UV-365 nm irradiation

b) Synthesis of acyclic carbamates by intermolecular oxytrifluoromethylation:



2-Iodobenzoate1-(carbamoyloxy)-4,4,4-trifluoro-2-(4-methoxyphenyl)butan-2-yl (4s): Prepared according to the general procedure, using 0.0438 g of **1s** (0.20 mmol), 0.0944 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and

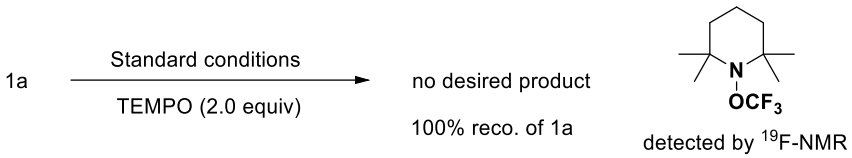
monitored by ^{1}H NMR. Then 30-50 mL of EA was added to dilute the reaction mixture, and the excess 2-iodobenzoic acid was washed with saturated sodium bicarbonate. The organic layers were combined, dried over Na_2SO_4, concentrated by rotary evaporation, and further purified by flash chromatography on silica gel (PE/EA = 5/1-7/3) to afford 0.0586 g (0.112 mmol, 56% yield) of **4s** as a colorless oil. IR (neat): 2921, 1730, 1515, 1376, 1254, 1110 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.92-4.79 (m, 2H), 4.61 (br, 2H), 3.81 (s, 3H), 3.45-3.25 (m, 2H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 164.5, 159.3, 155.5, 141.6, 134.7, 133.0, 131.2, 130.5, 128.0, 126.2, 125.2 (q, *J* = 276.5 Hz), 113.9, 94.1, 81.3, 66.9, 55.2, 38.2 (q, *J* = 27.6 Hz); ^{19}F NMR: (376 MHz, $CDCl_3$) δ -59.8; HRMS (ESI) calculated for $[C_{19}H_{17}F_3INNaO_5]^+$ ($M+Na^+$) requires m/z 545.9996, found m/z 545.9996.



2-Iodobenzoate1-(carbamoyloxy)-4,4,4-trifluoro-2-(4-(methylthio)phenyl)butan-2-yl 2-iodobenzoate (**4t**)**:** Prepared according to the general procedure, using 0.0484 g of **1t** (0.20 mmol), 0.0936 g of **2a** (0.30 mmol), 0.0027 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR. Then 30-50 mL of EA was added to dilute the reaction mixture, and the excess 2-iodobenzoic acid was washed with saturated sodium bicarbonate. The organic layers were combined, dried over Na_2SO_4, concentrated by rotary evaporation, and further purified by flash chromatography on silica gel (PE/EA = 5/1-7/3) to afford 0.0525 g (0.097 mmol, 49% yield) of **4t** as a colorless oil. IR (neat): 3412, 1728, 1597, 1337, 1257, 1126 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.28-7.22 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 4.91-4.77 (m, 2H), 4.61 (br, 2H), 3.42-3.28 (m, 2H), 2.48 (s, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 164.5, 155.4, 141.6, 139.1, 135.2, 134.5, 133.1, 131.2, 128.1, 126.2, 125.4, 125.1 (q, *J* = 275.6 Hz), 94.2, 81.2, 66.9, 38.1 (q, *J* = 27.8 Hz), 15.3; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -59.8; HRMS (ESI) calculated for $[C_{19}H_{17}F_3INNaO_4S]^+$ ($M+Na^+$) requires m/z 561.9767, found m/z 561.9768.

VI. Mechanistic Studies

a) Radical-inhibition experiments:



According to the general procedure, a 25 mL flame-dried Schlenk flask was cooled at room temperature under nitrogen, then charged with 0.0363 g of **1a** (0.2 mmol), 0.0966 g of **2a** (0.30 mmol), 0.0670 g of TEMPO (0.4 mmol), 0.0024 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. The mixture was degassed three times, warmed to room temperature under nitrogen, and stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours. The reaction mixture was then concentrated by rotary evaporation and monitored by ^{1}H NMR (100% recovery of **1a** and 0% yield of **3a**). In addition, the reaction mixture was analyzed using ^{19}F-NMR, revealing a signal peak corresponding to the product formed by trapping the trifluoromethyl radical with TEMPO (**Figure S4)**. ^{19}F NMR: (376 MHz, $CDCl_3$) δ -55.3. The chemical shift of the fluorine spectrum signal peak of the product is consistent with the reported literature.[5]

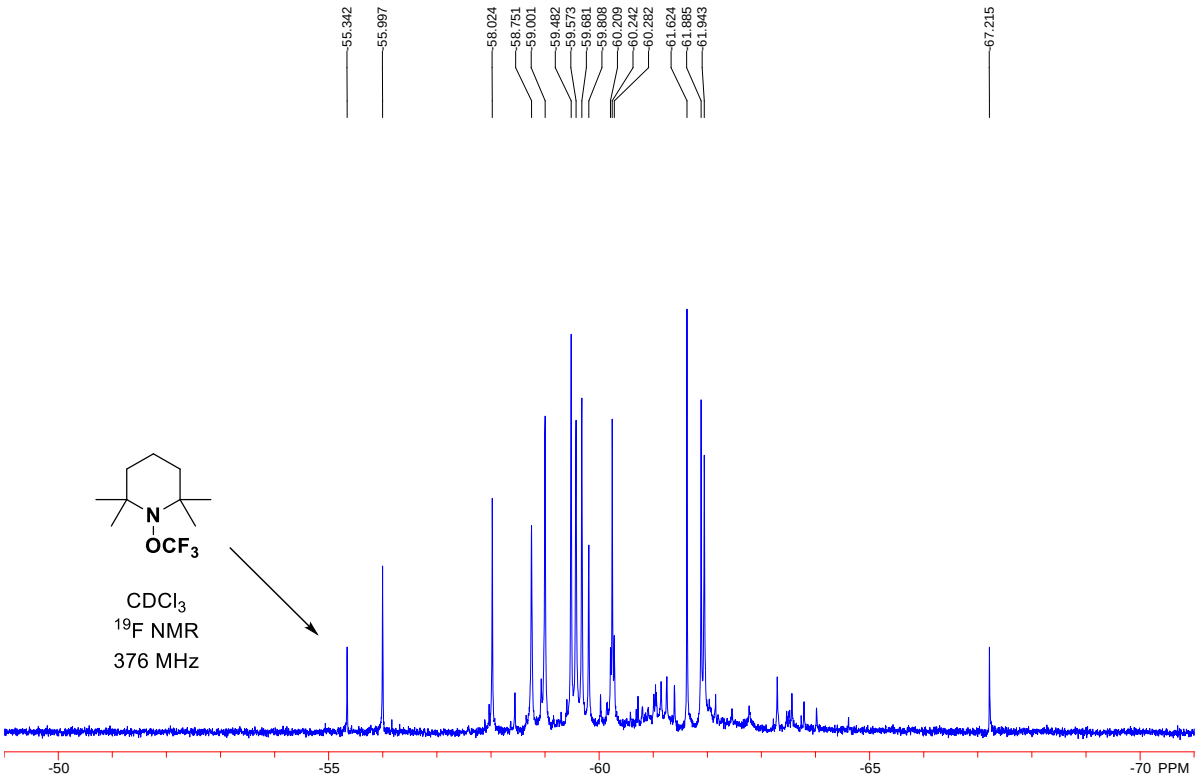
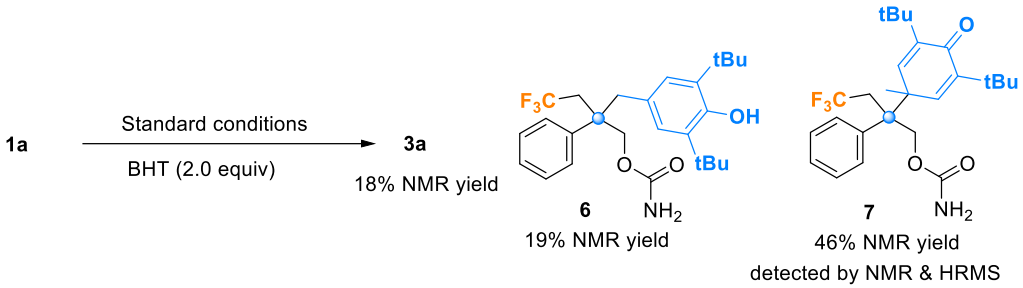


Figure S4. ^{19}F-NMR of the reaction solution with TEMPO added.



According to the general procedure, a 25 mL flame-dried Schlenk flask was cooled at room temperature under nitrogen, then charged with 0.0382 g of **1a** (0.2 mmol), 0.0969 g of **2a** (0.30 mmol), 0.0886 g of BHT (0.4 mmol), 0.0023 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. The mixture was degassed three times, warmed to room temperature under nitrogen, and stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours. The reaction mixture was then concentrated by rotary evaporation and monitored by ^{1}H NMR (18% yield of **3a**, 19% yield of **8** and 46% yield of **9**). The mixture of **8** and **9** (**8**:**9** = 1:7.5) was obtained by silica gel plate (20×20 cm) separation **(Figure S4)**. ^{1}H NMR of **9**: (400 MHz, $CDCl_3$) δ 7.40-7.30 (m, 3H), 7.19 (d, J = 7.6 Hz, 2H), 6.50-6.44 (m, 1H), 6.24 (s, 1H), 4.96 (d, J = 12.0 Hz, 1H), 4.80 (br, 2H), 4.56 (d, J = 12.0 Hz, 1H), 2.92-2.56 (m, 2H), 1.24 (s, 9H), 1.20 (s, 9H), 1.09 (s, 3H); In addition, the products **8** and **9** of BHT capturing benzylic radicals were further confirmed by high-resolution mass spectrometry (**Figure S5)**.

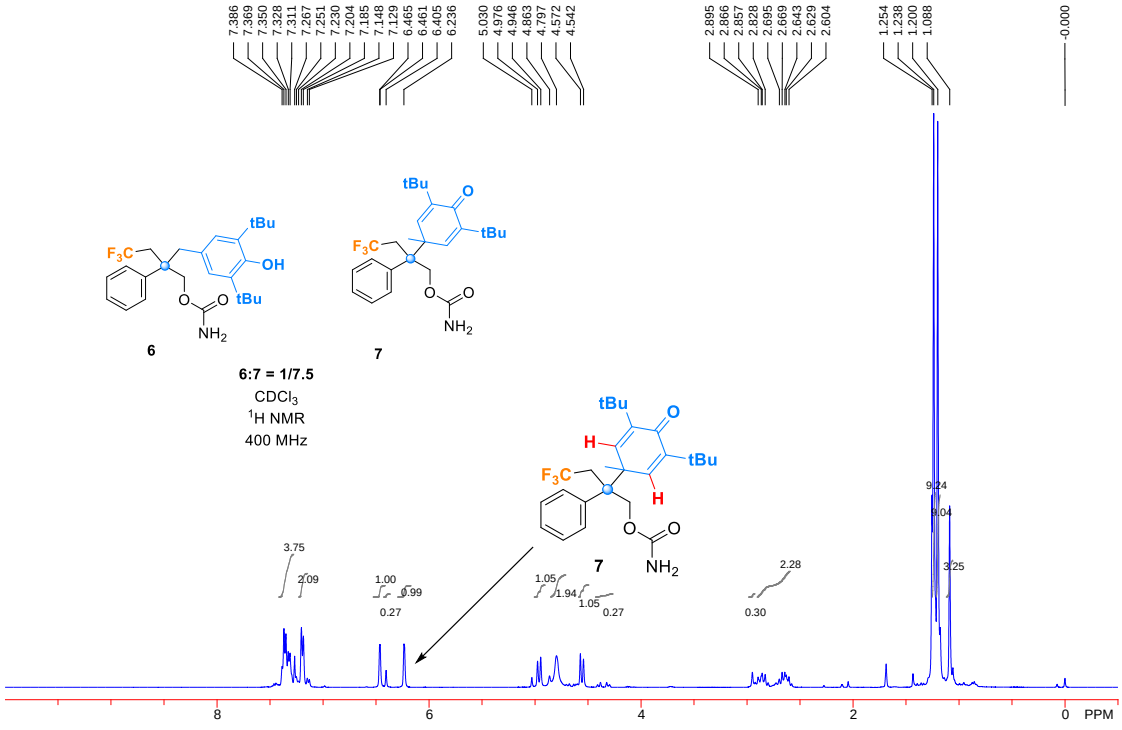
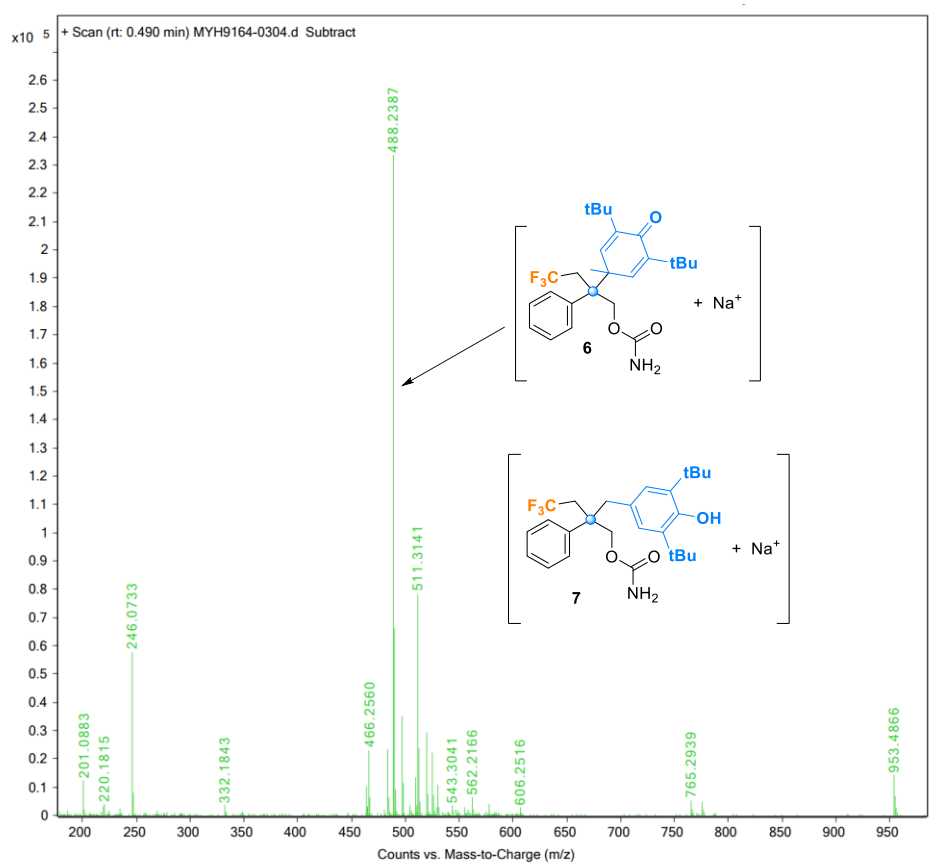
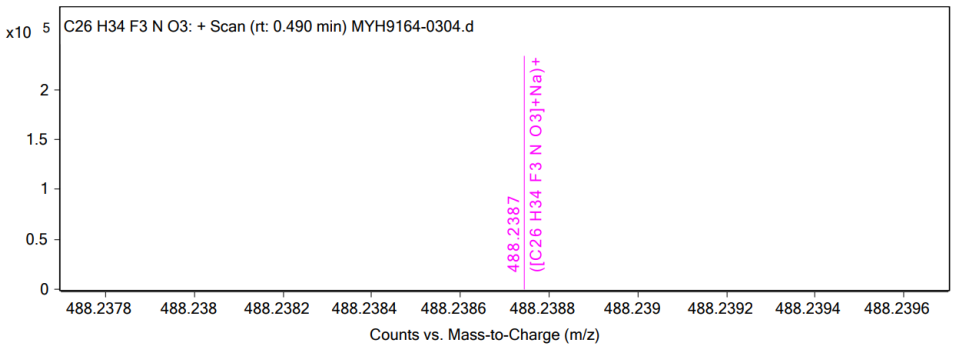


Figure S5. ^{1}H-NMR of the mixture of **8** and **9**.





Formula Calculator Element Limits

Element	Min	Max
C	0	100
H	0	100
O	0	5
F	3	3
N	0	5

Formula Calculator Results

Formula	Best	Measured Mass	Tgt Mass	Diff (ppm)	Score
C26 H34 F3 N Na O3	True	488.2387	488.2383	-0.72	99.5

--- End Of Report ---

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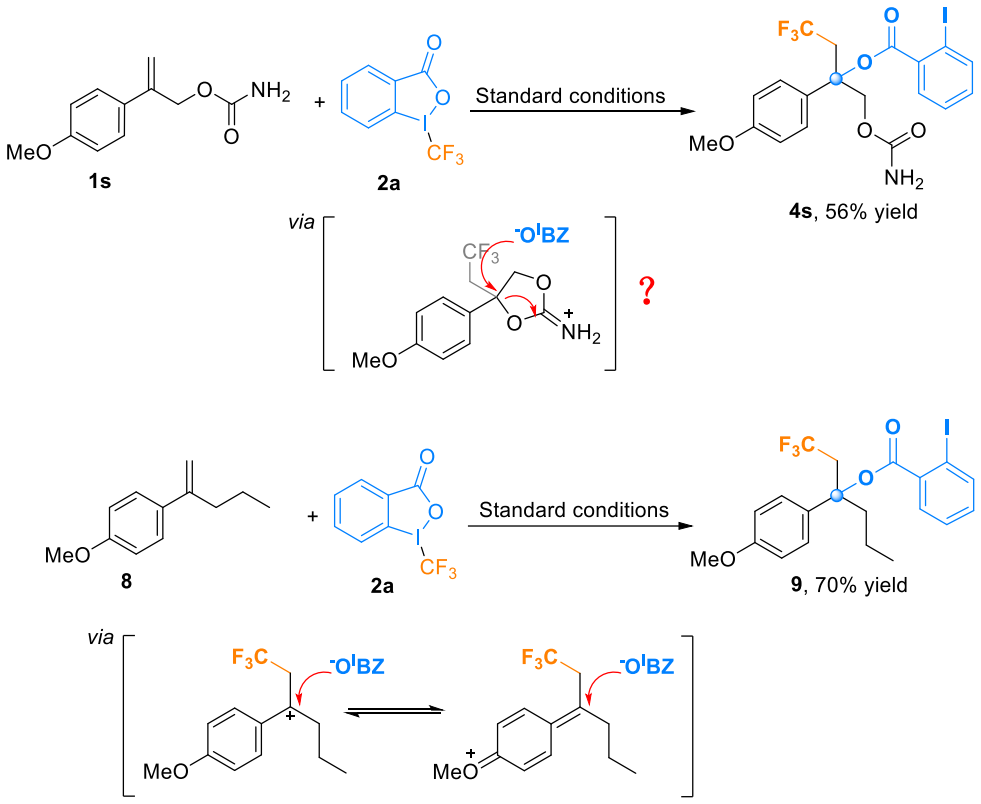
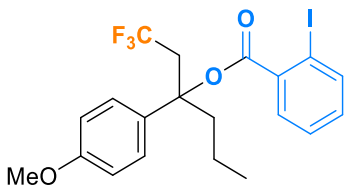
Figure S6. ESI-HRMS report of the mixture of **6** and **7**.

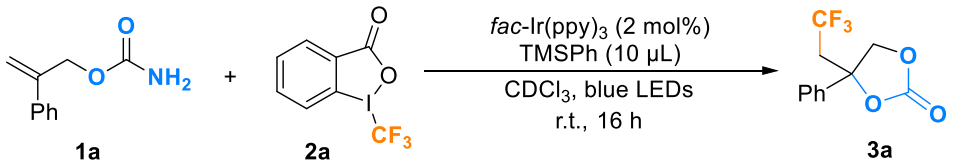
b) Trapping benzylic carbocations experiments:





1,1,1-Trifluoro-3-(4-methoxyphenyl)hexan-3-yl 2-iodobenzoate (9): Prepared according to the general procedure, using 0.0350 g of **8** (0.20 mmol), 0.0946 g of **2a** (0.30 mmol), 0.0024 g of *fac*-Ir(ppy)$_3$ (0.004 mmol), and 4 mL of $PhCF_3$. After the reaction was stirred at room temperature under the irradiation of 5 W blue LEDs for 24 hours, it was concentrated by rotary evaporation and monitored by ^{1}H NMR. The reaction mixture was then further purified by flash chromatography on silica gel (PE/EA = 50/1) to afford 0.0689 g (0.140 mmol, 70% yield) of **9** as a colorless oil. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H), 3.59-3.44 (m, 1H), 3.29-3.13 (m, 1H), 2.63 (td, J = 12.8, 4.4 Hz, 1H), 2.13 (td, J = 12.8, 4.4 Hz, 1H), 1.27-1.03 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 165.2, 158.7, 141.4, 135.7, 133.3, 132.6, 130.8, 128.0, 126.0, 125.4 (q, J = 276.5 Hz), 113.7, 93.9, 84.1, 55.2, 41.2, 40.1 (q, J = 27.4 Hz), 16.2, 13.9; ^{19}F NMR: (376 MHz, $CDCl_3$) δ -60.1; HRMS (ESI) calculated for $[C_{20}H_{20}F_3INaO_3]^+$ (M+Na$^+$) requires m/z 515.0301, found m/z 515.0304.

c) Light on and off experiments.



According to the general procedure, a 25 mL flame-dried Schlenk flask was cooled at room temperature under nitrogen, then charged with 0.0360 g of **1a** (0.2 mmol), 0.0961 g of **2a** (0.30 mmol), 0.0025 g of fac-Ir(ppy)$_3$ (0.004 mmol), 4 mL of $CDCl_3$, and 10 uL of trimethylphenylsilane. The mixture was degassed for three times, warmed to room temperature under nitrogen, and stirred at room temperature under the irradiation of 5 W blue LEDs. Samples were taken every hour, and the reaction yield was detected by nuclear magnetic resonance (**Table S2**). The experimental results show that when the reaction is shielded from light, the reaction does not proceed, indicating that the photocatalytic reaction is not a radical chain reaction (**Figure S6**). This reaction also indicates that the benzylic radical generated during the reaction process is not oxidized to a benzylic carbocation by **2a** with a single electron.

Table S2. Light on and off experiments.

Entry	Time (h)	Light	Yiled of 3a (%)	Recovery of 1a (%)
1	0	**On**	0	100
2	1	**Off**	54	26
3	2	**On**	54	26
4	3	**Off**	60	9
5	4	**On**	61	9
6	5	**Off**	68	0
7	6	/	68	0

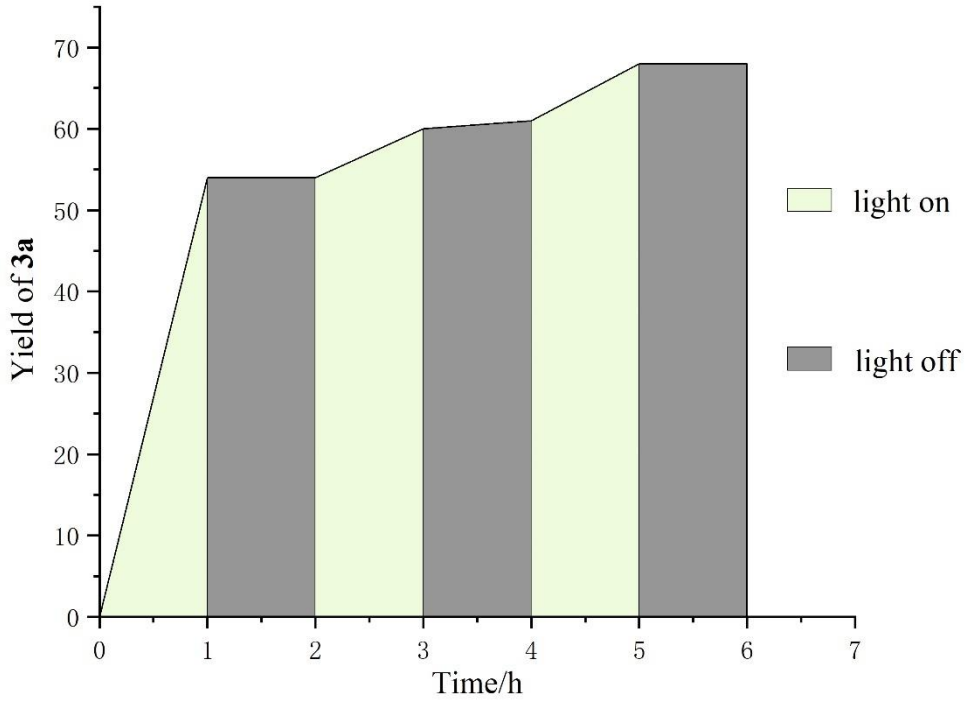


Figure S7. Light on and off experiments.

VII. References

(1) (a) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647–6653. (b) Rackl, D.; Kais, V.; Lutsker, E.; Reiser, O. *Eur. J. Org. Chem.* **2017**, 2130–2138.

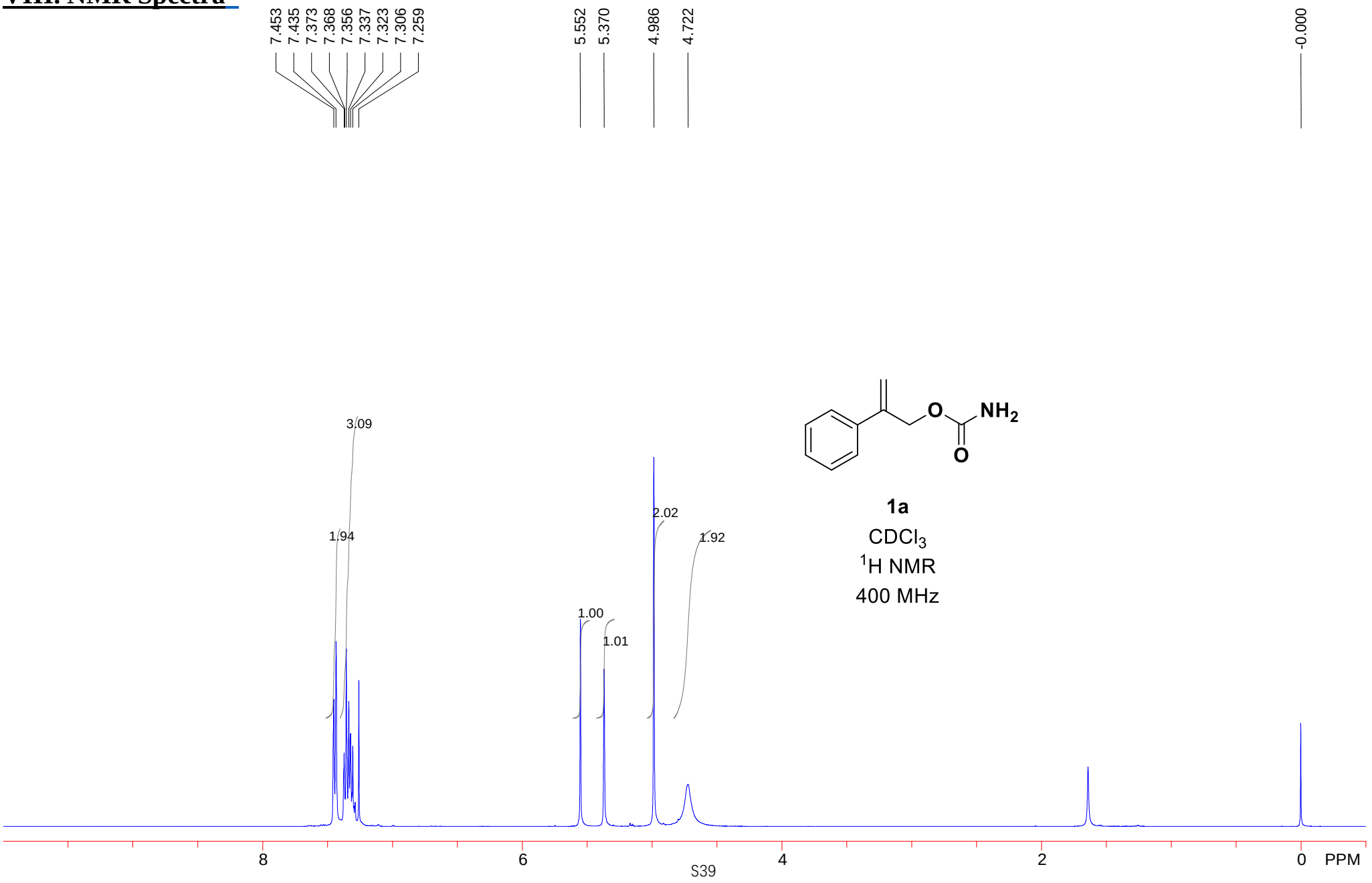
(2) Lu, P.; Ren, X.; Xu, H.; Lu, D.; Sun, Y.; Lu, Z. *J. Am. Chem. Soc.* **2021**, *143*, 12433–12438.

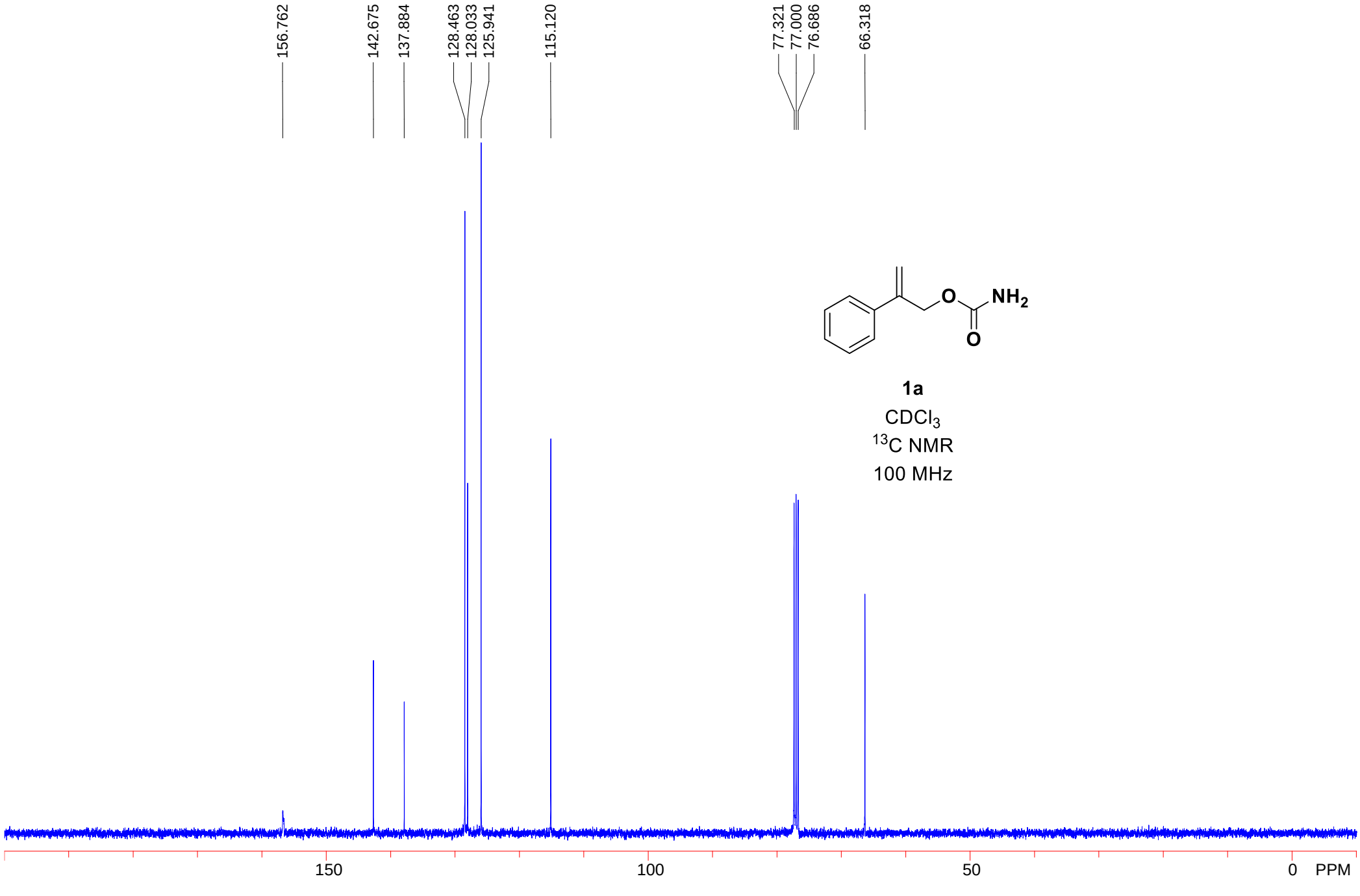
(3) (a) Kawato, Y.; Kubota, A.; Ono, H.; Egami, H.; Hamashima, Y. *Org. Lett.* **2015**, *17*, 1244–1247. (b) Xu, B.; Tambar, U. K. *ACS Catal.* **2019**, *9*, 4627–4631. (c) Lu, Z.; Ma, S. *J. Org. Chem.* **2006**, *71*, 2655–2660. (d) Schwarz, K. J.; Pearson, C. M.; Cintron-Rosado, G. A.; Liu, P.; Snaddon, T. N. *Angew. Chem., Int. Ed.* **2018**, *57*, 7800–7803.

(4) (a) Gwon, D.; Hwang, H.; Kim, H. K.; Marder, S. R.; Chang, S. *Chem. - Eur. J.* **2015**, *21*, 17200–17204. (b) Hen, N.; Bialer, M.; Yagen, B. *J. Med. Chem.* **2012**, *55*, 2835–2845.

(5) Cheng, Y.-F.; Liu, J.-R.; Gu, Q.-S.; Yu, Z.-L.; Wang, J.; Li, Z.-L.; Bian, J.-Q.; Wen, H.T.; Wang, X.-J.; Hong, X.; Liu, X.-Y. *Nat. Catal.* **2020**, *3*, 401–410.

VIII. NMR Spectra

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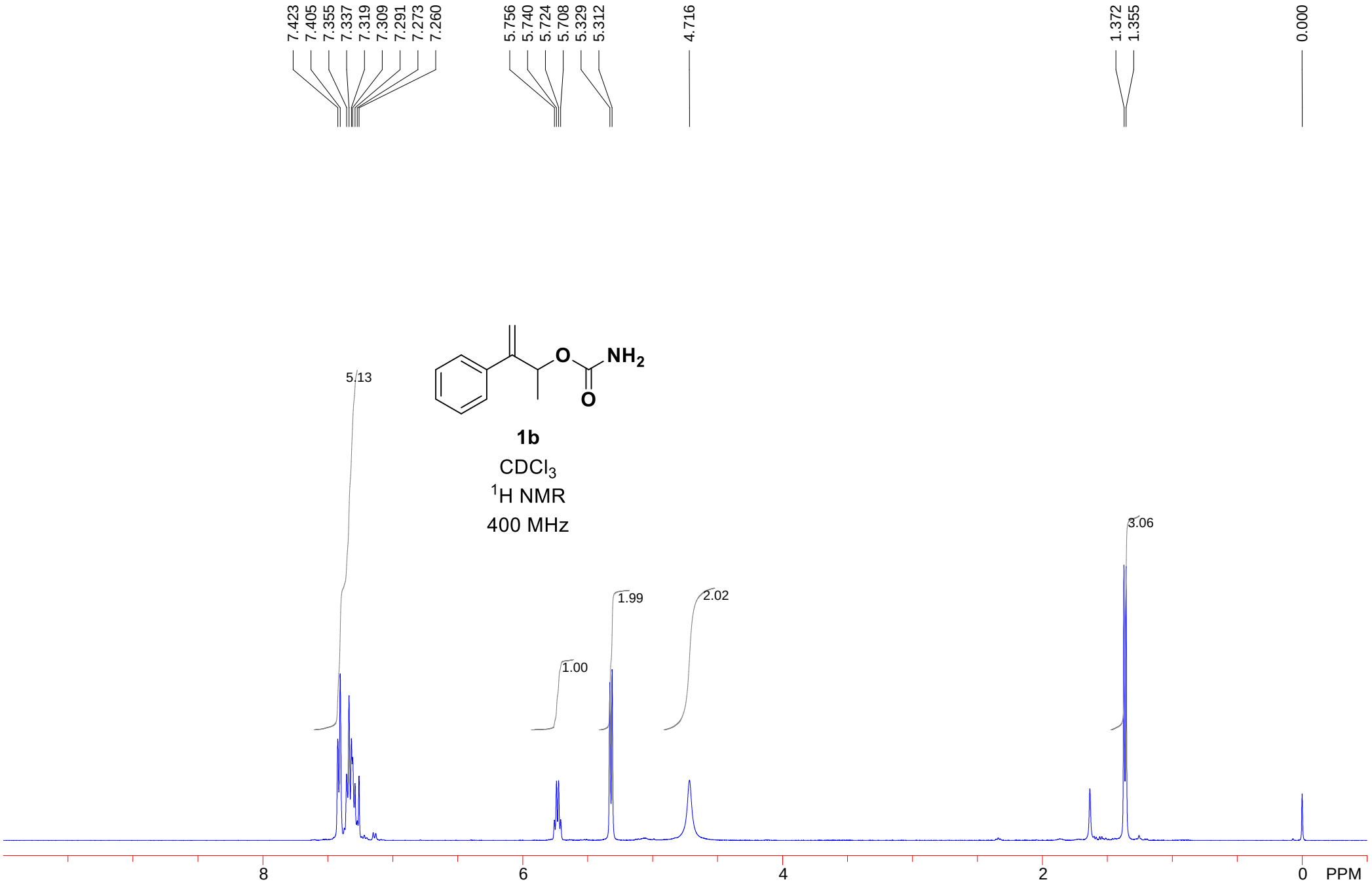
PPM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5.329
5.312
4.716
1.372
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0.000
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O
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8
6
4
2
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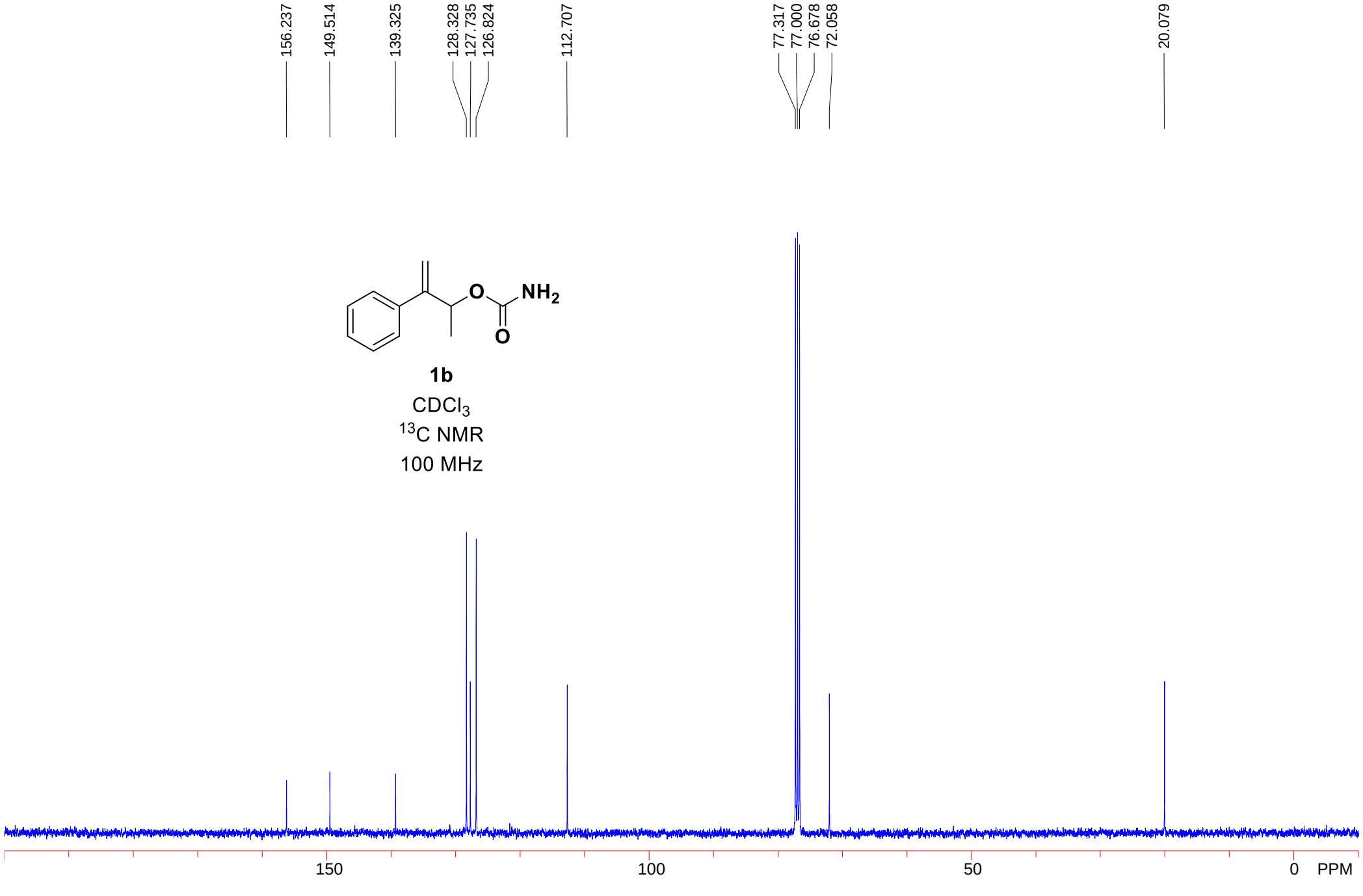
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100 MHz
150
100
50
0
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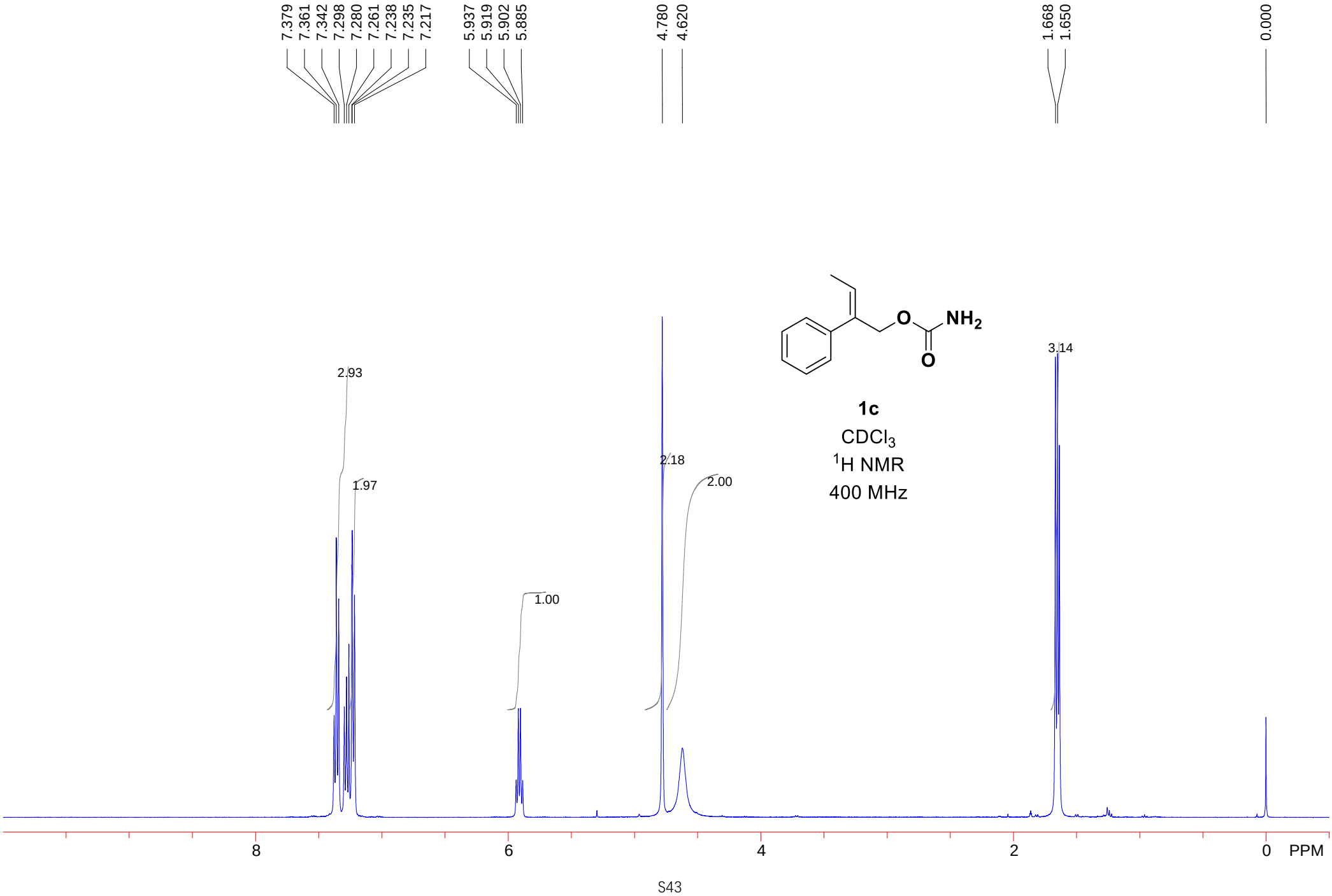
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7.235
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5.919
5.902
5.885
4.780
4.620
1.668
1.650
0.000
2.93
1.97
1.00
2.18
2.00
3.14
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NH2
O
1c
CDCl3
1H NMR
400 MHz
8
6
4
2
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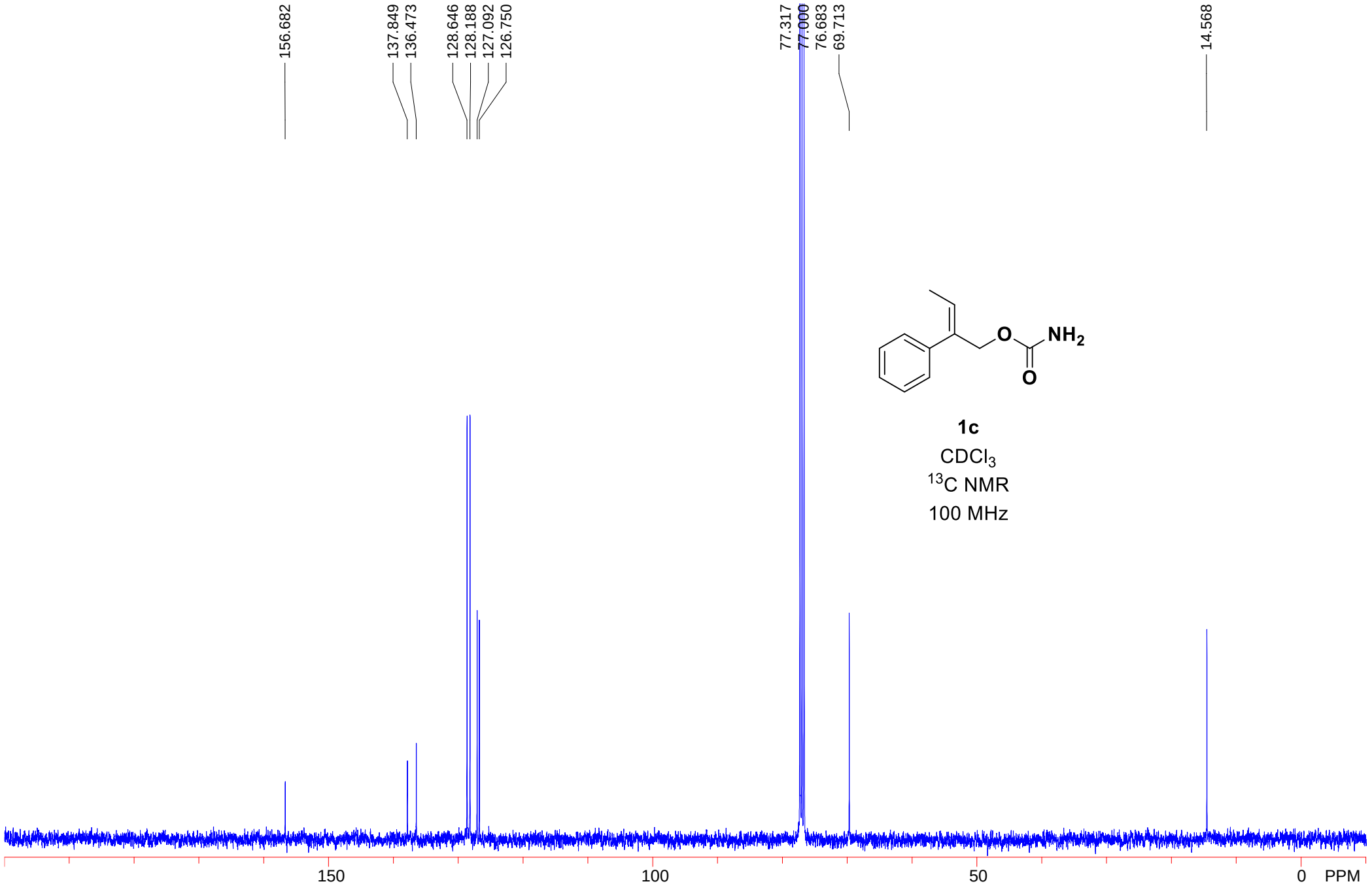
PPM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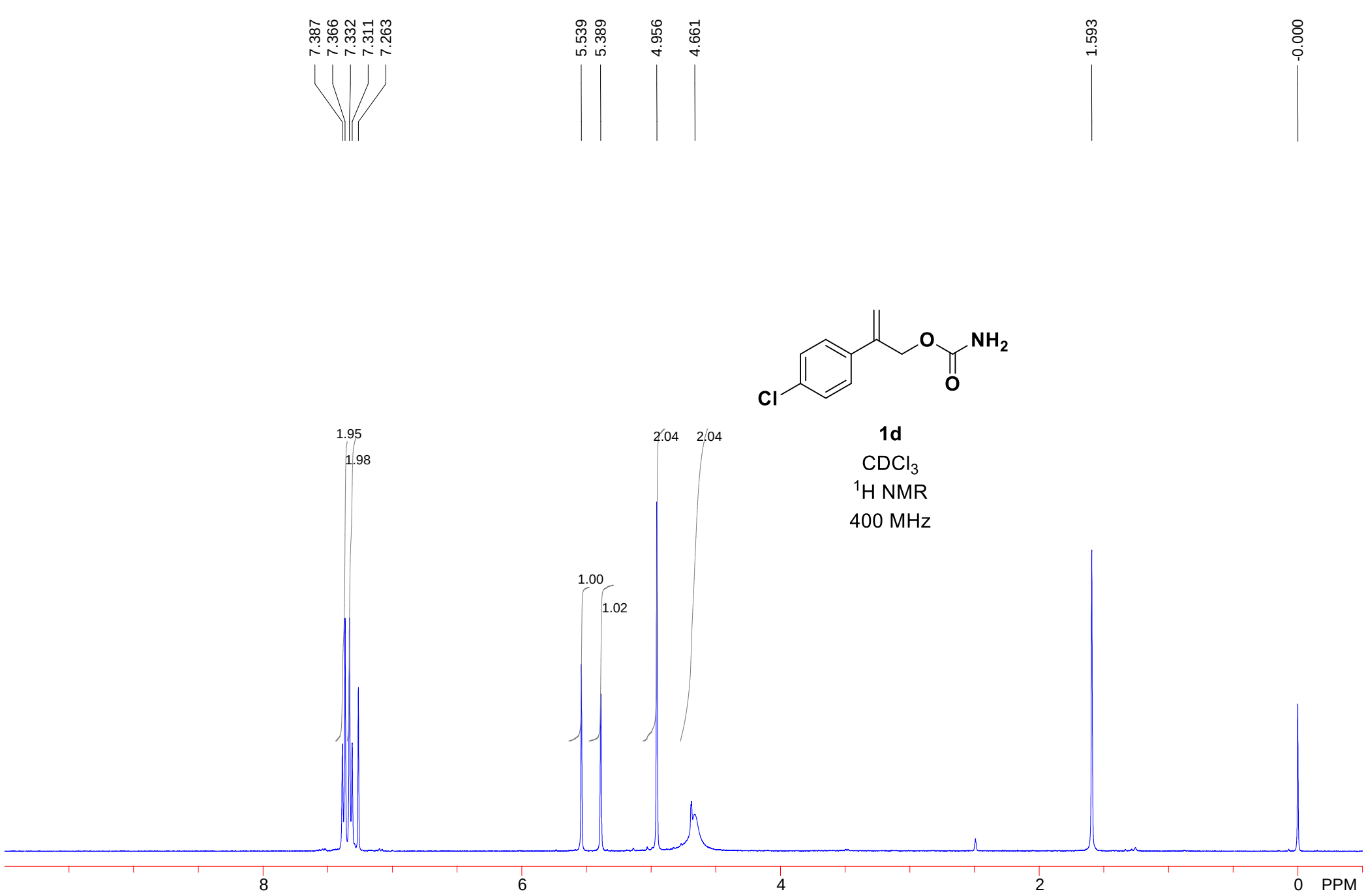
PPM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4
2
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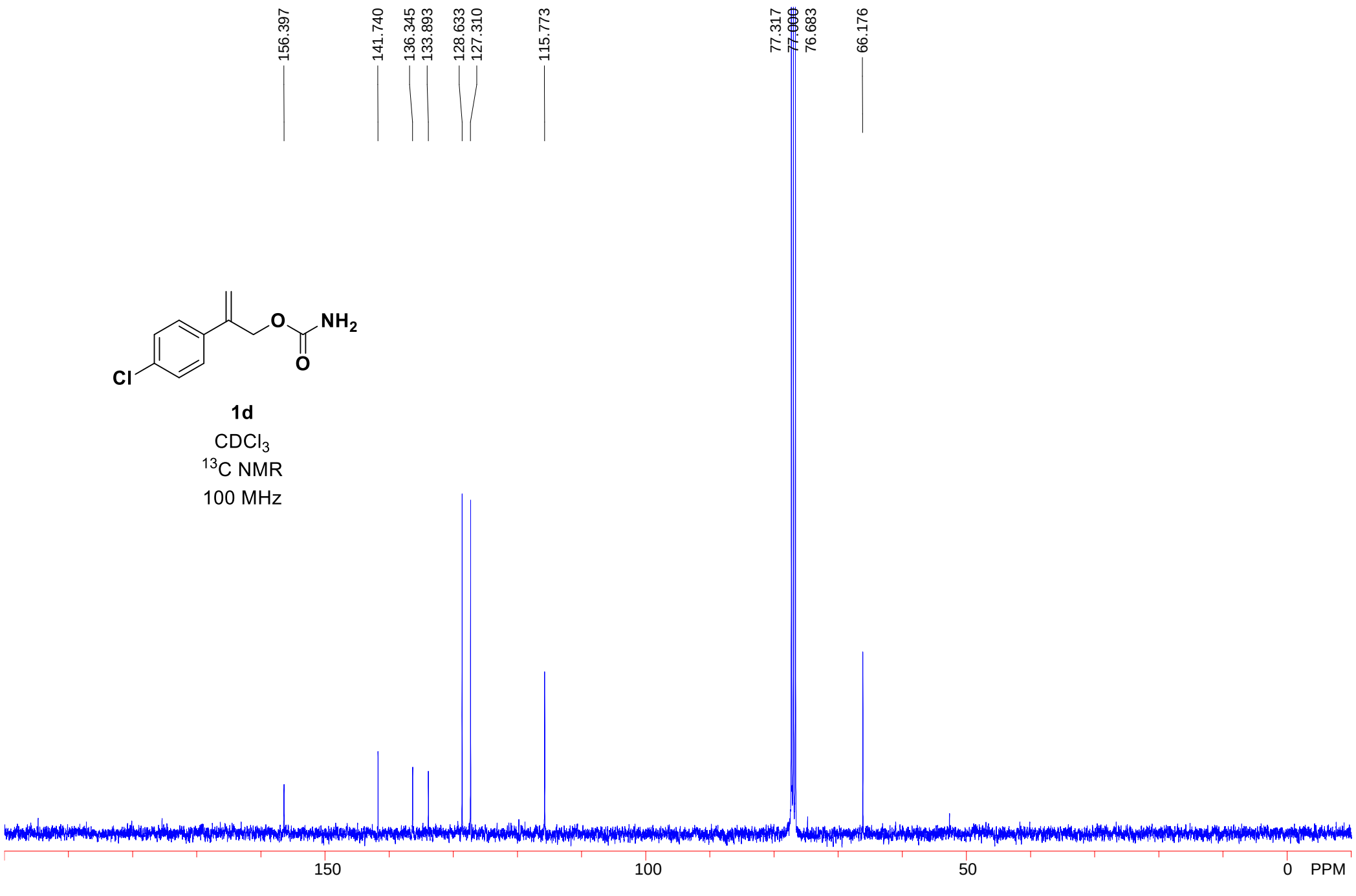
PPM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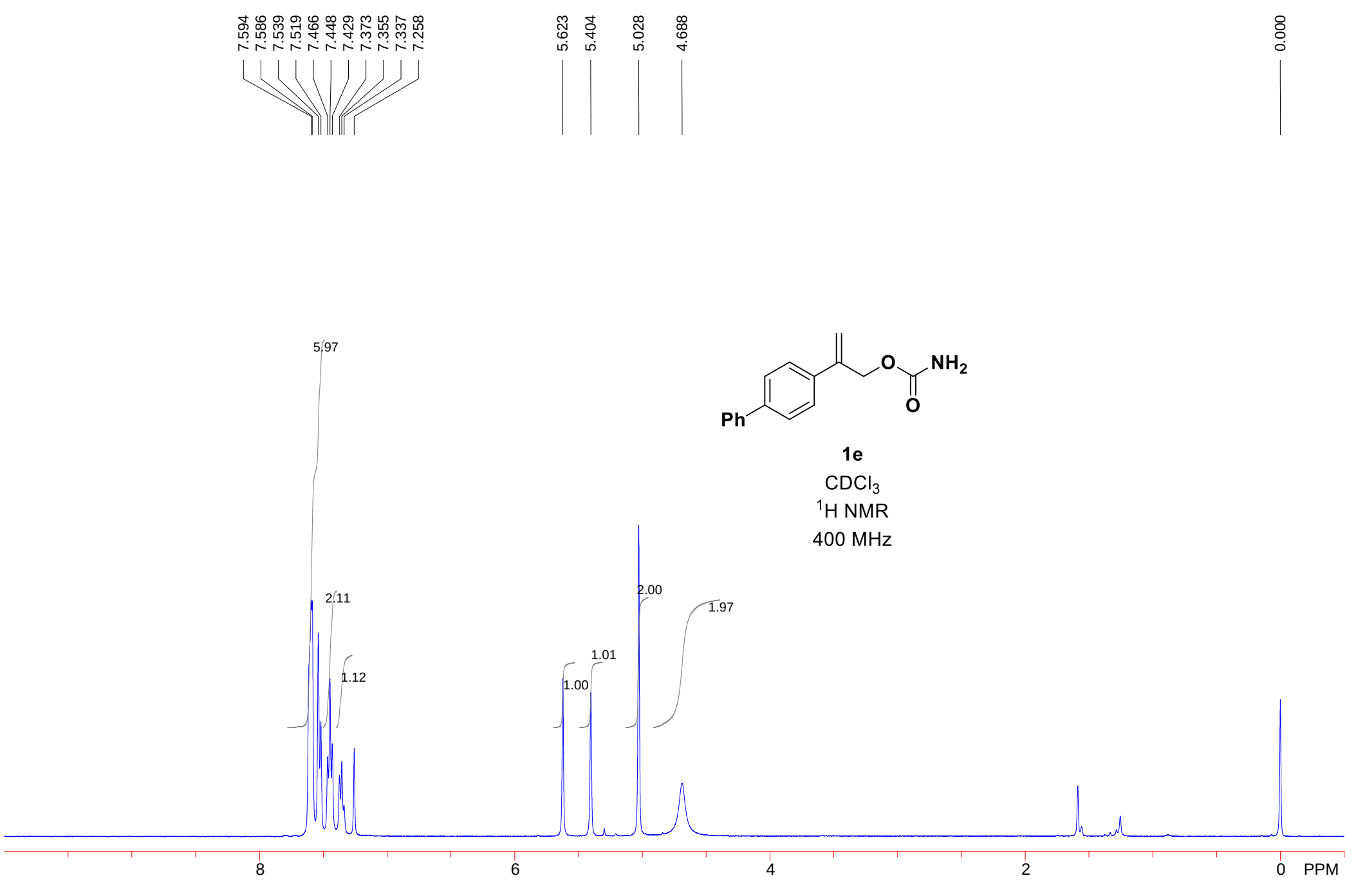
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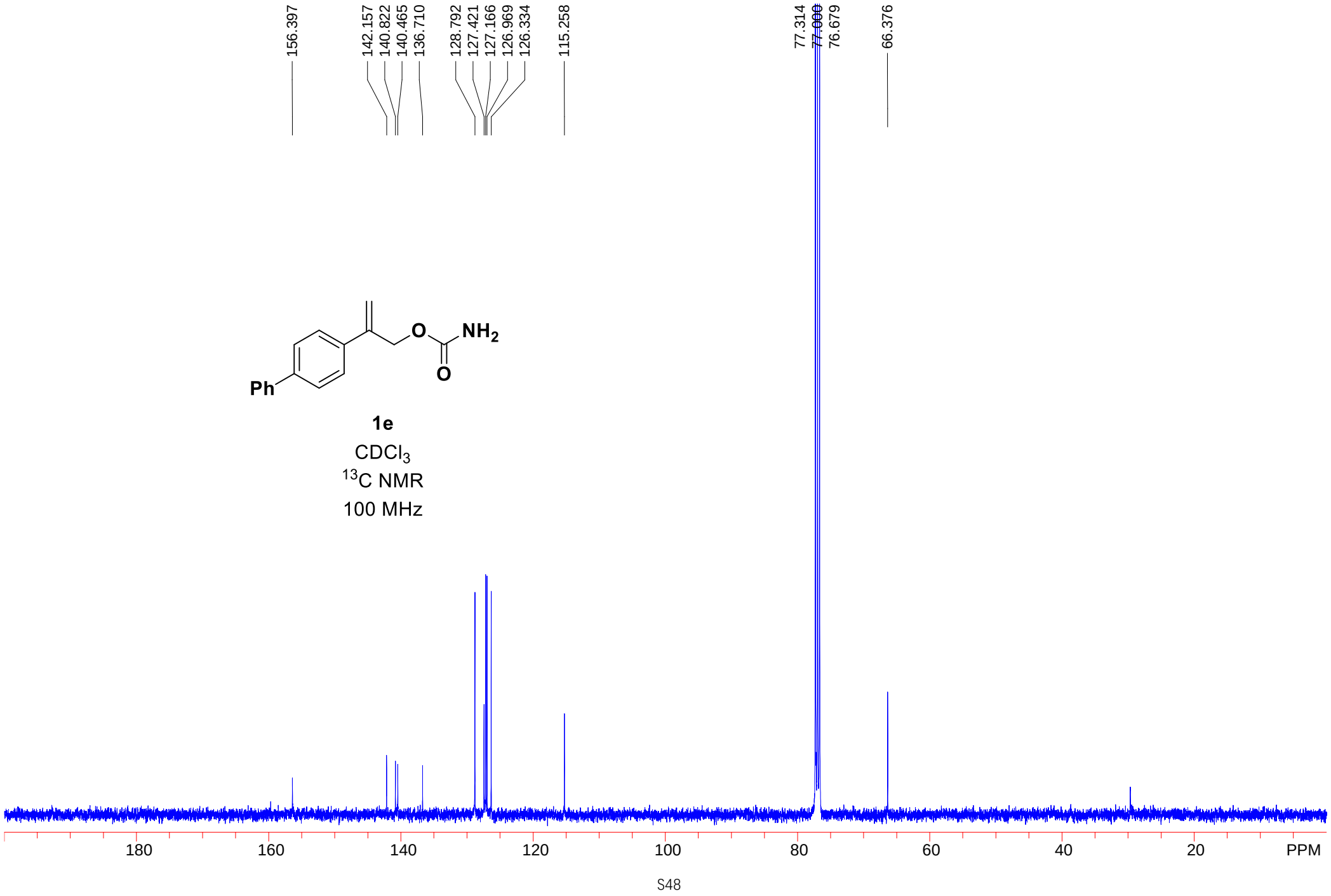
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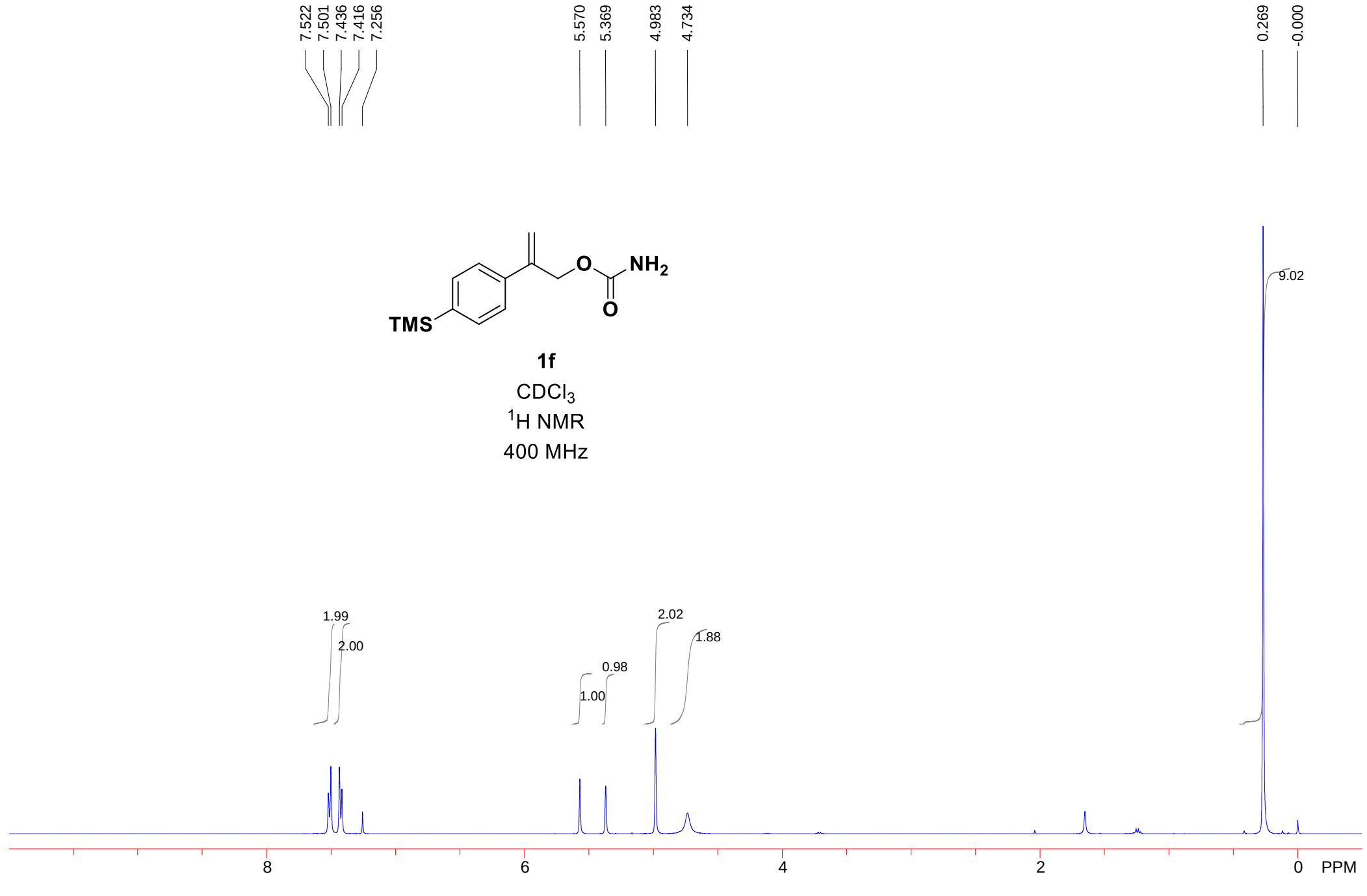
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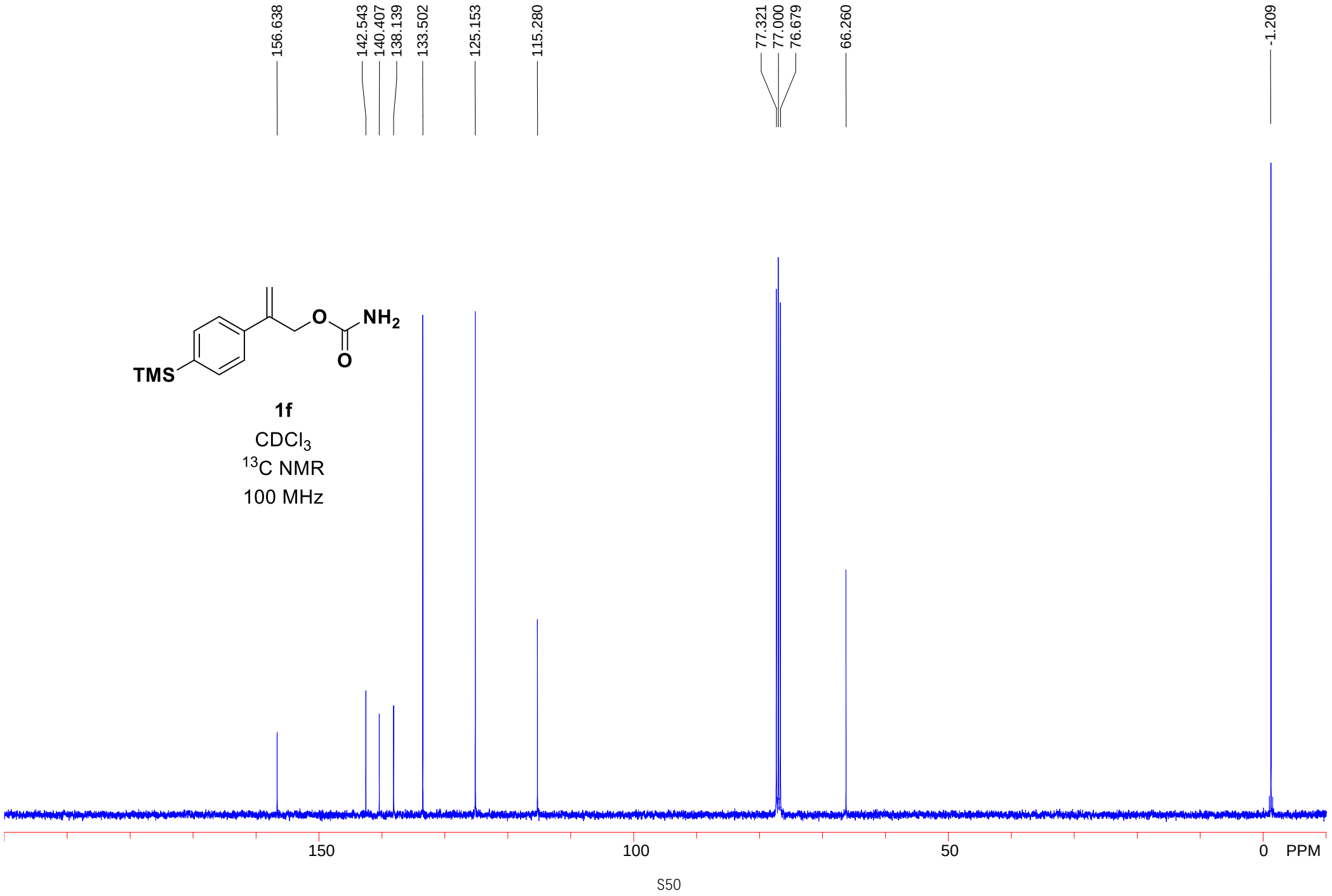
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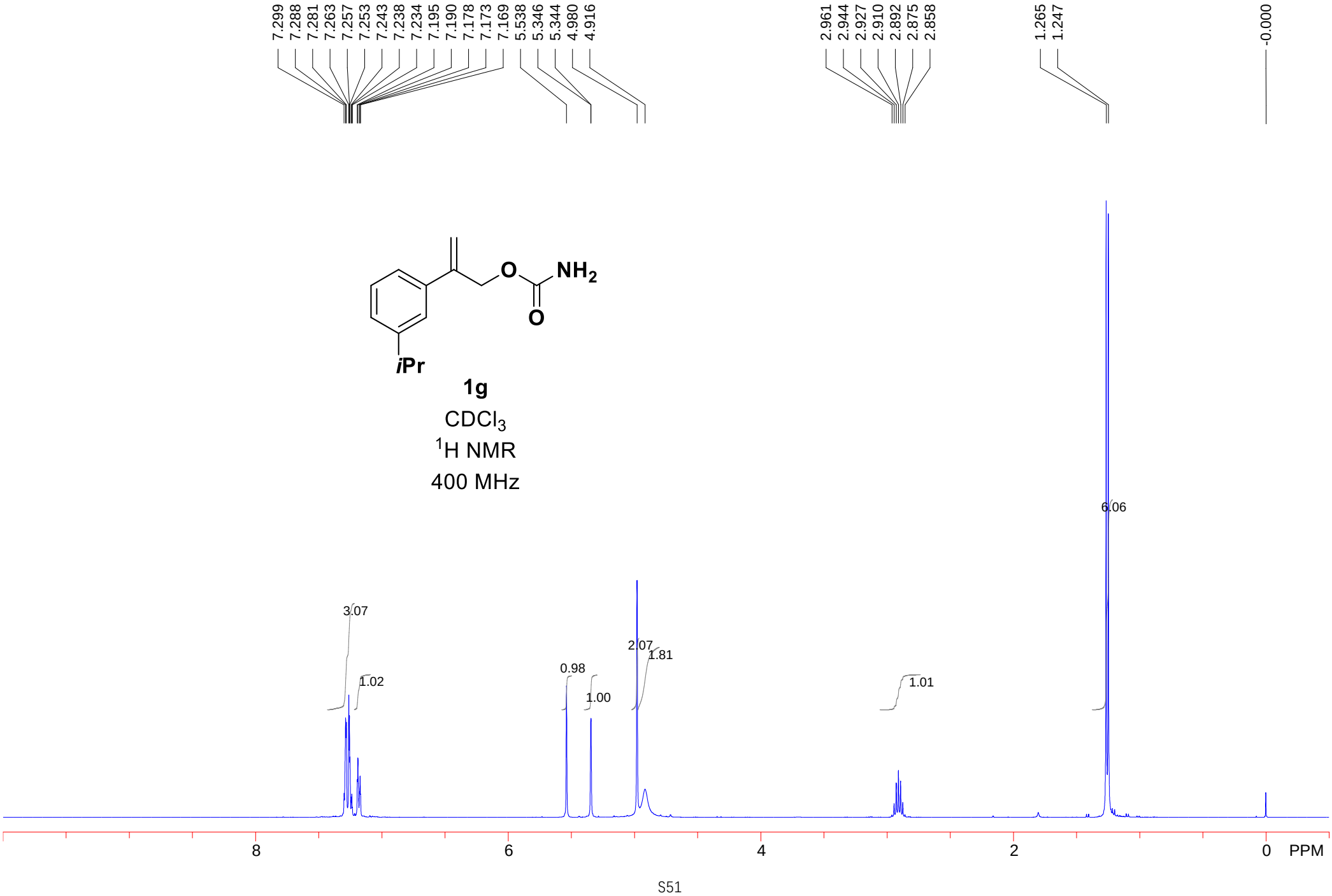
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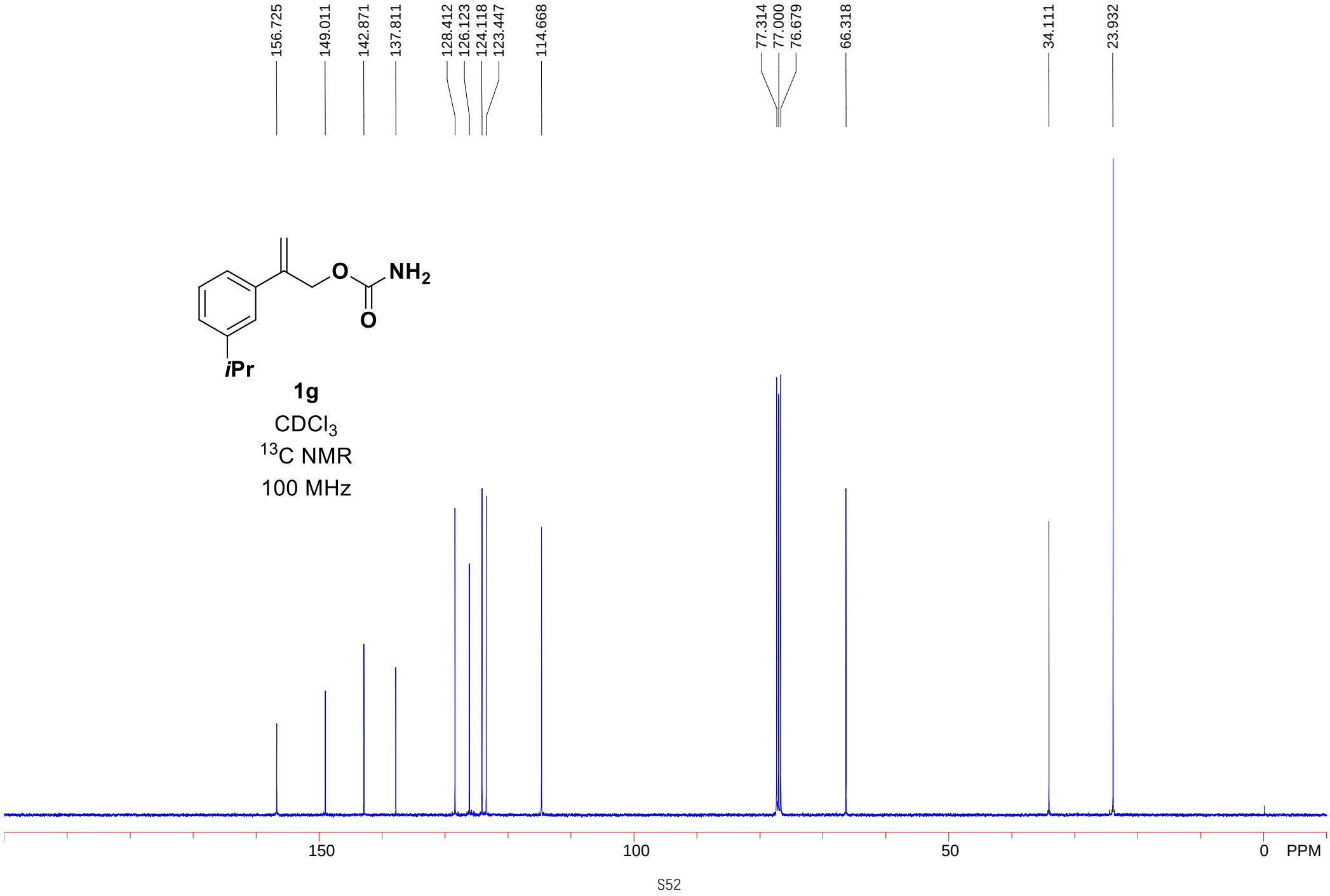
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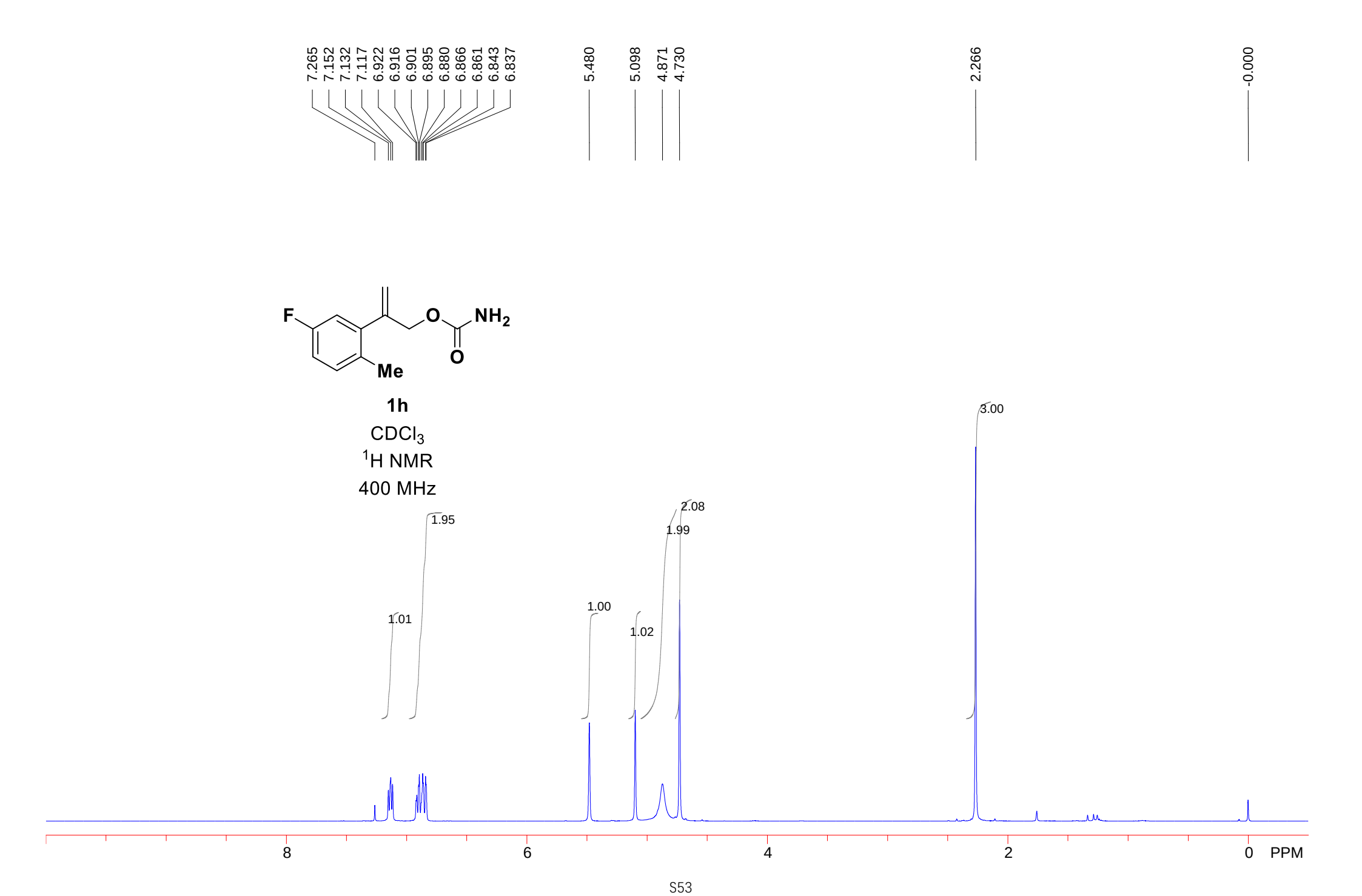
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Me
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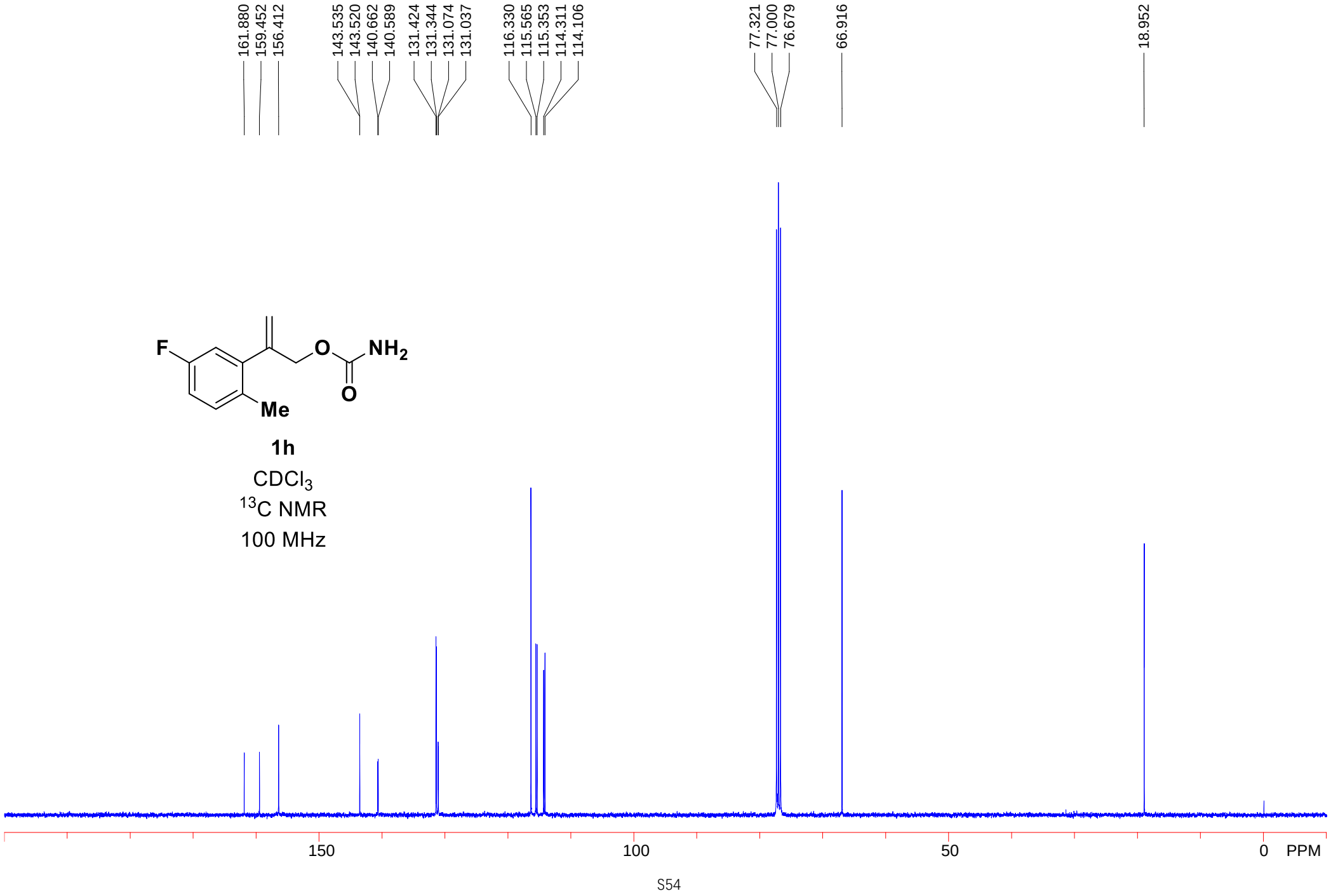
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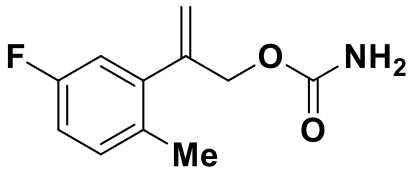
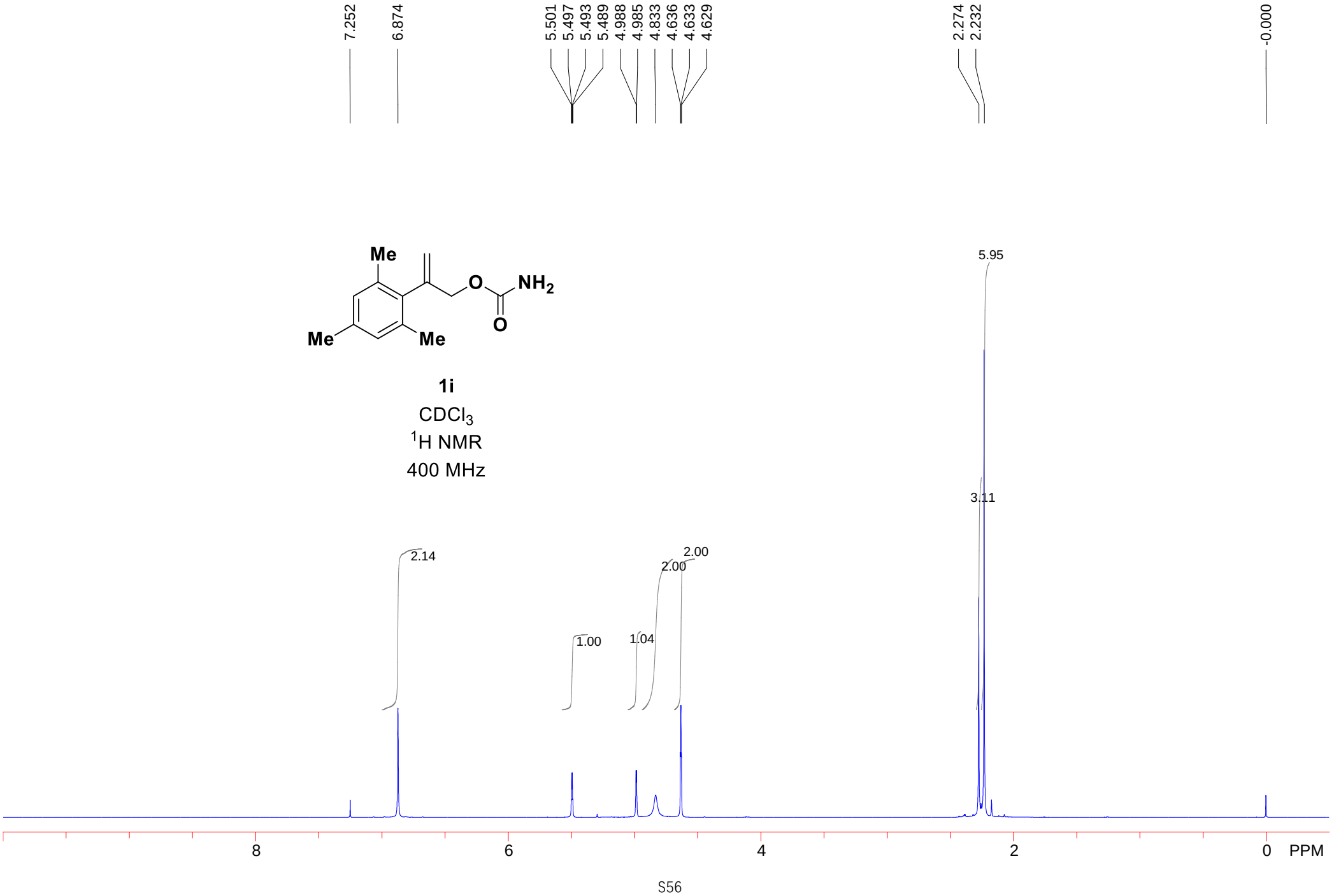


1h

$CDCl_3$

^{19}F NMR

376 MHz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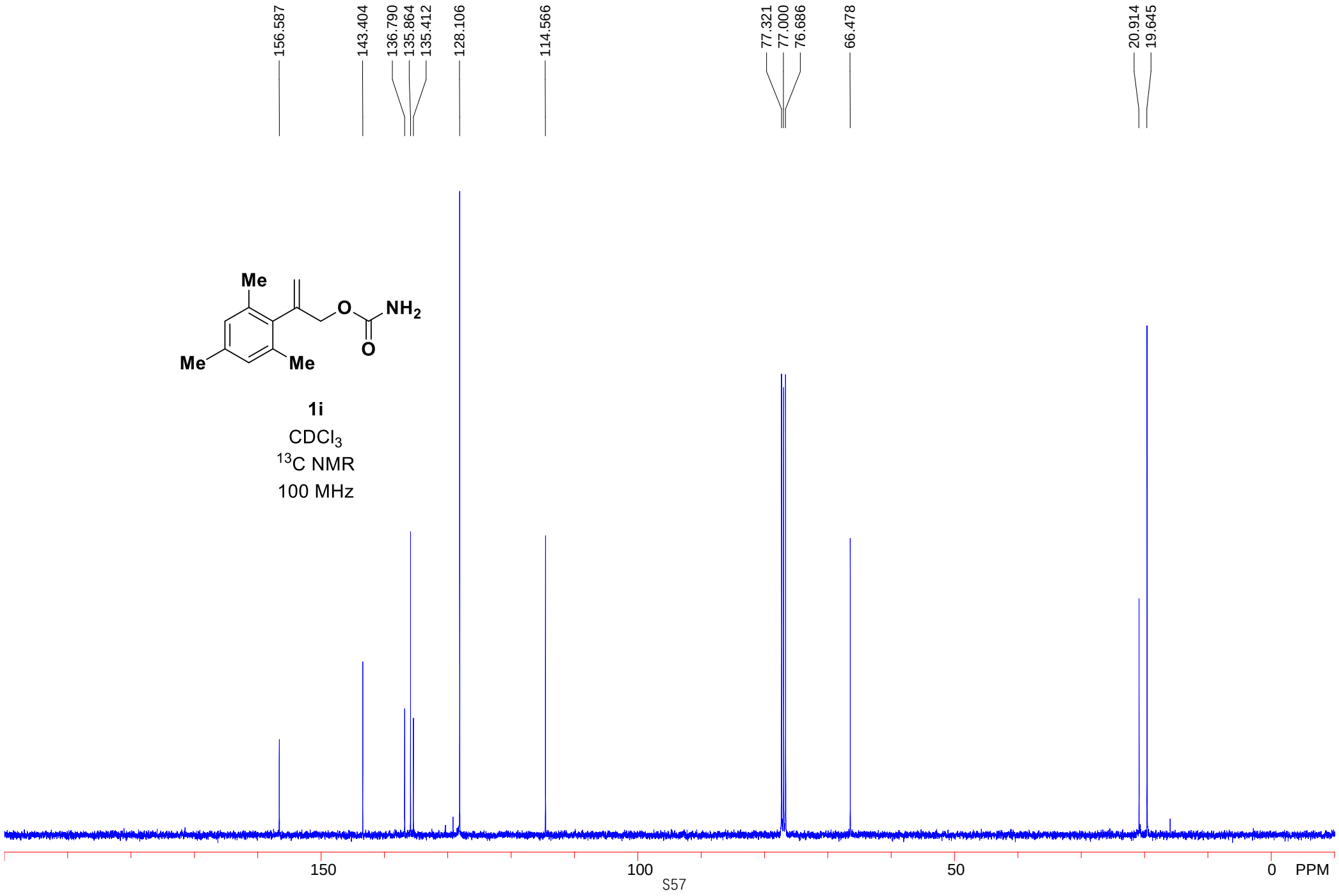
6.874
5.501
5.497
5.493
5.489
4.988
4.985
4.833
4.636
4.633
4.629
2.274
2.232
-0.000
Me
O
NH2
O
Me
Me
1i
CDCl3
1H NMR
400 MHz
5.95
3.11
2.14
1.00
1.04
2.00
2.00
8
6
4
2
0
PPM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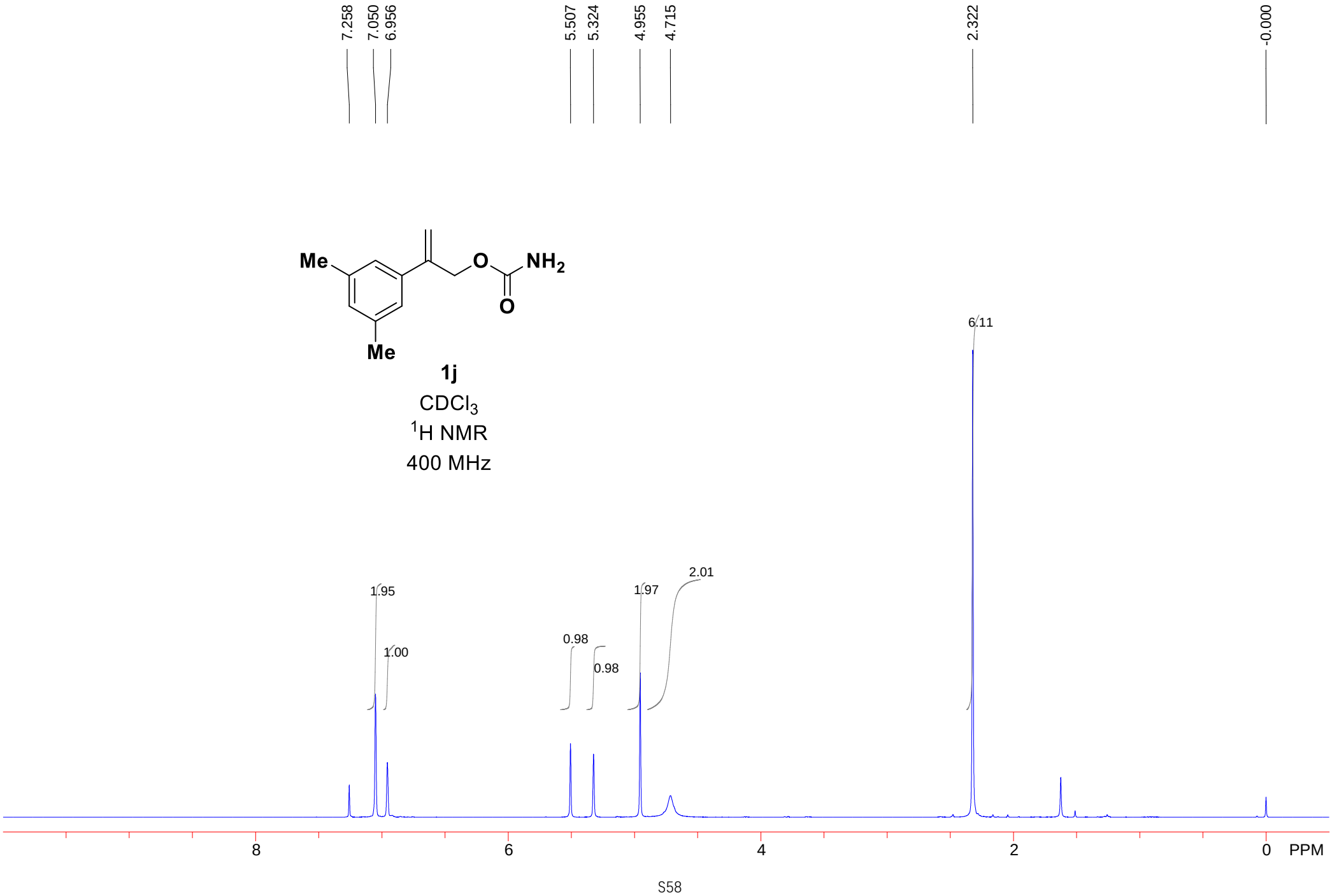
143.404
136.790
135.864
135.412
128.106
114.566
77.321
77.000
76.686
66.478
20.914
19.645
Me
O
NH2
O
Me
Me
1i
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM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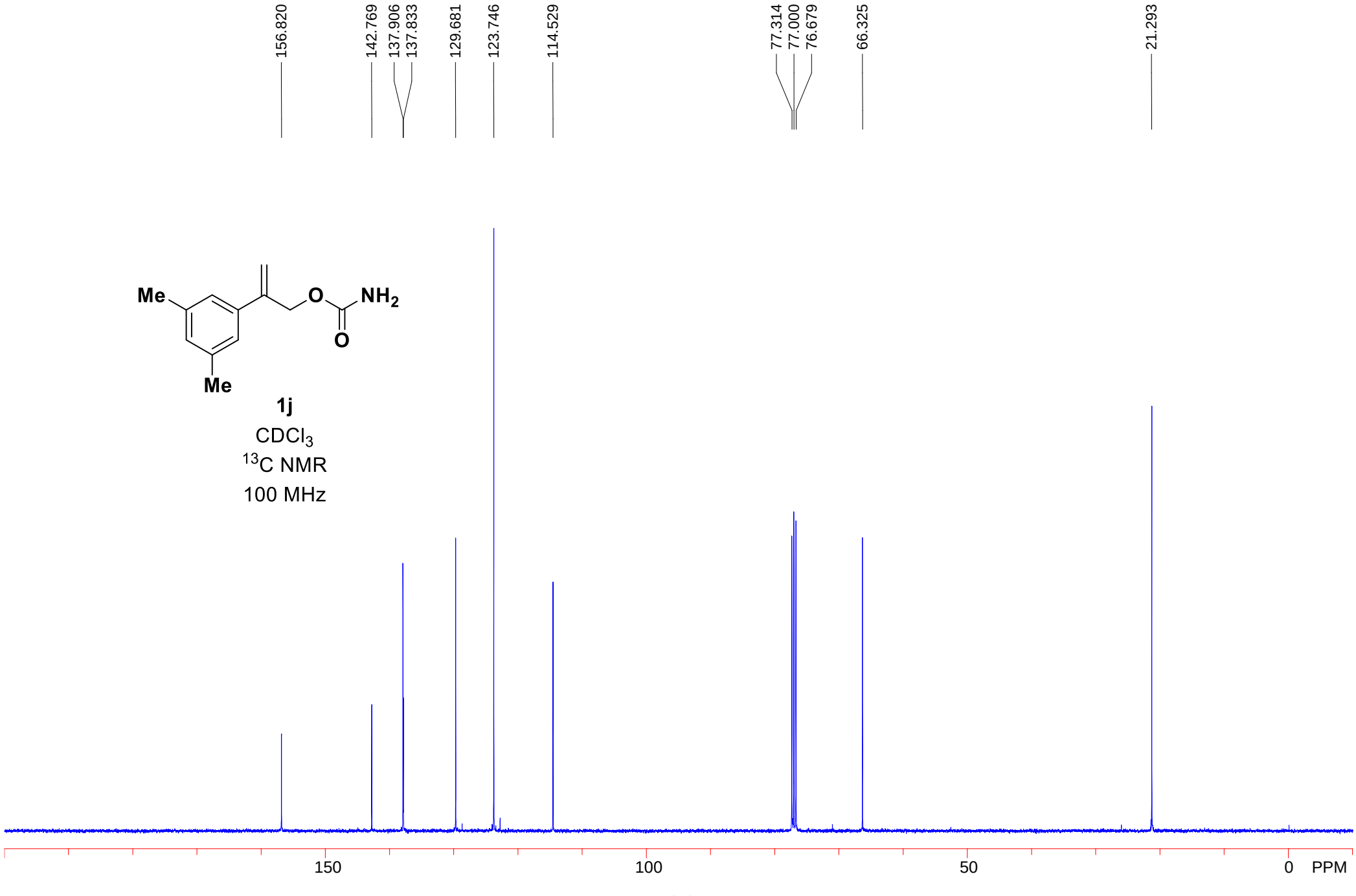
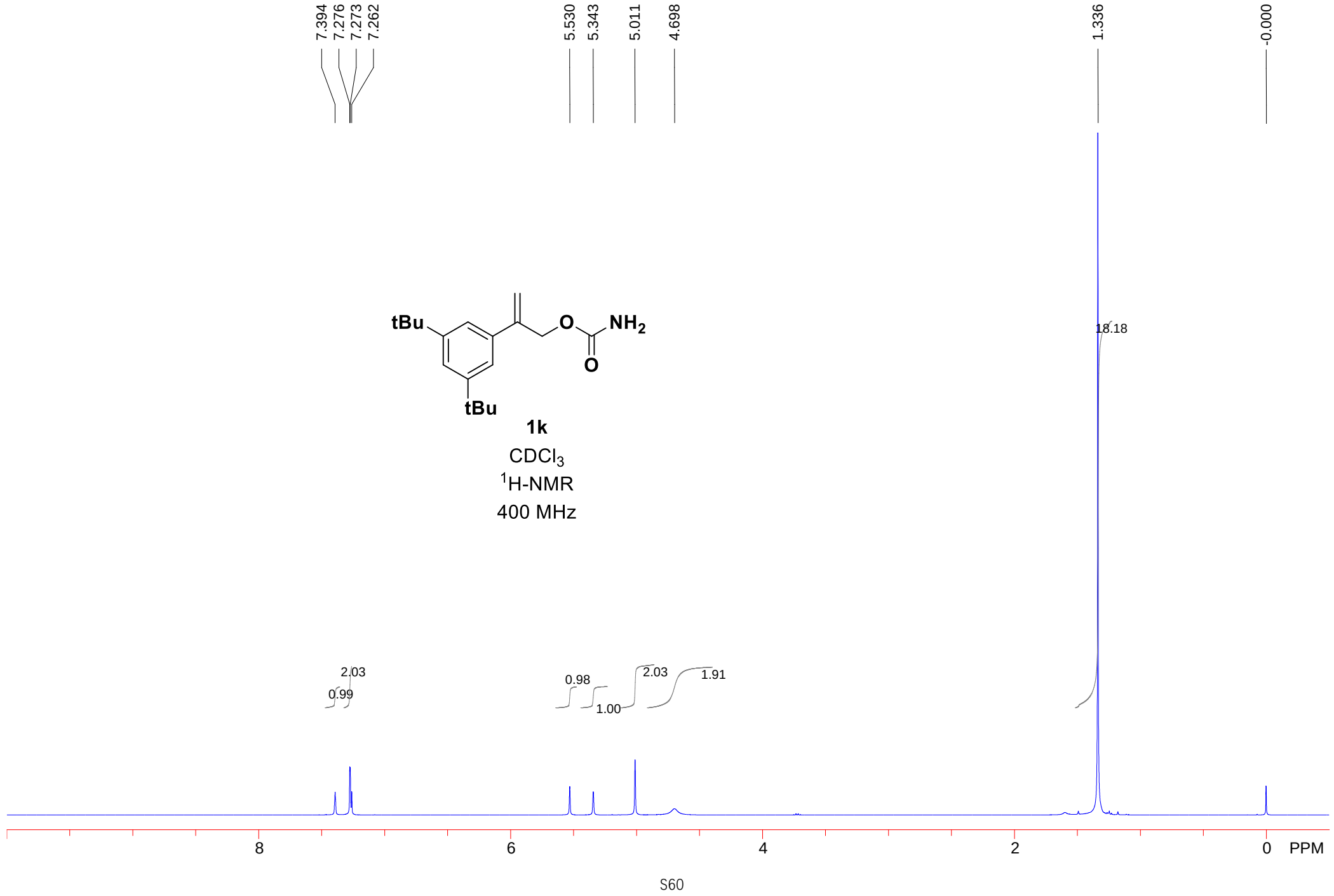
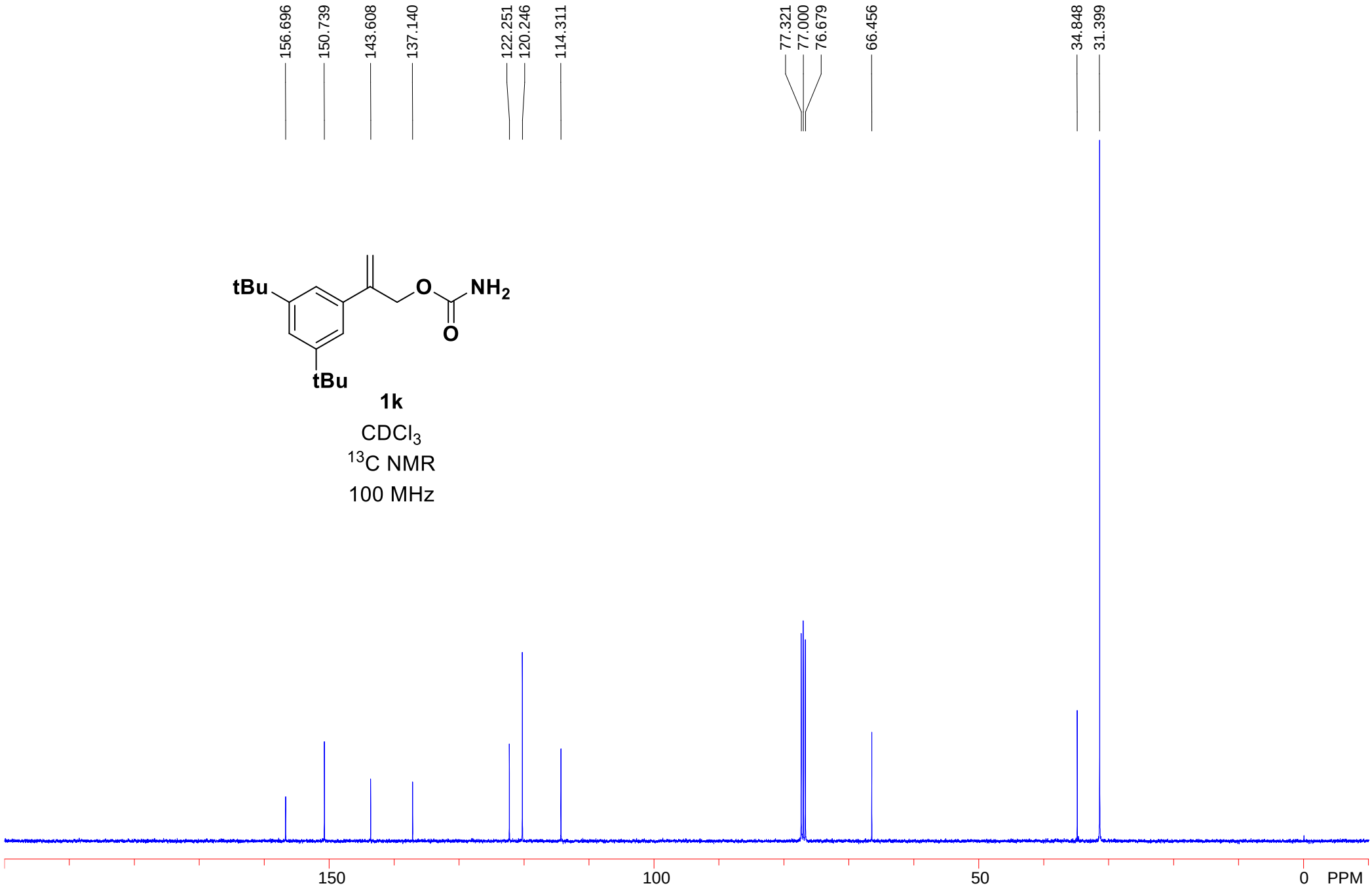
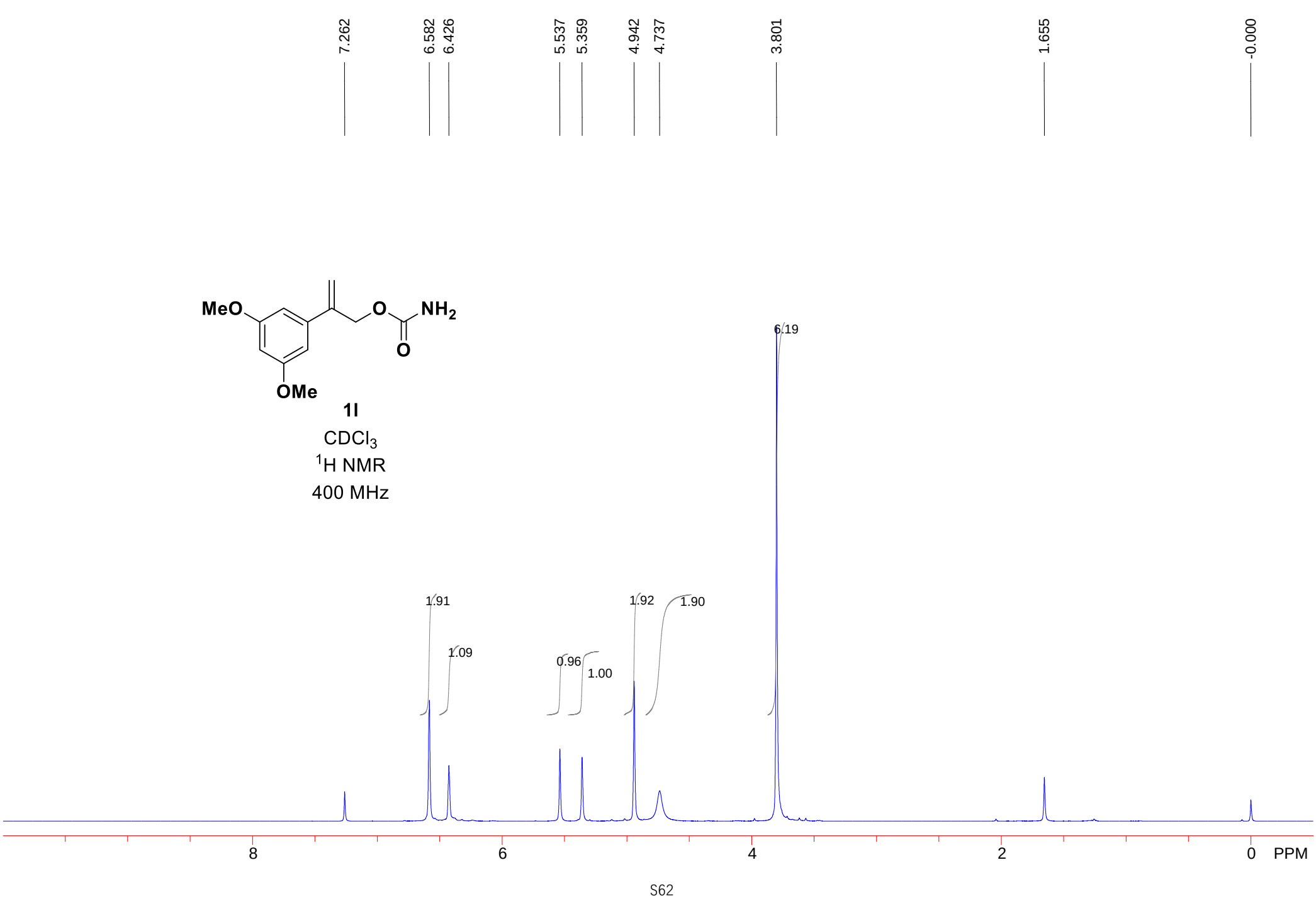
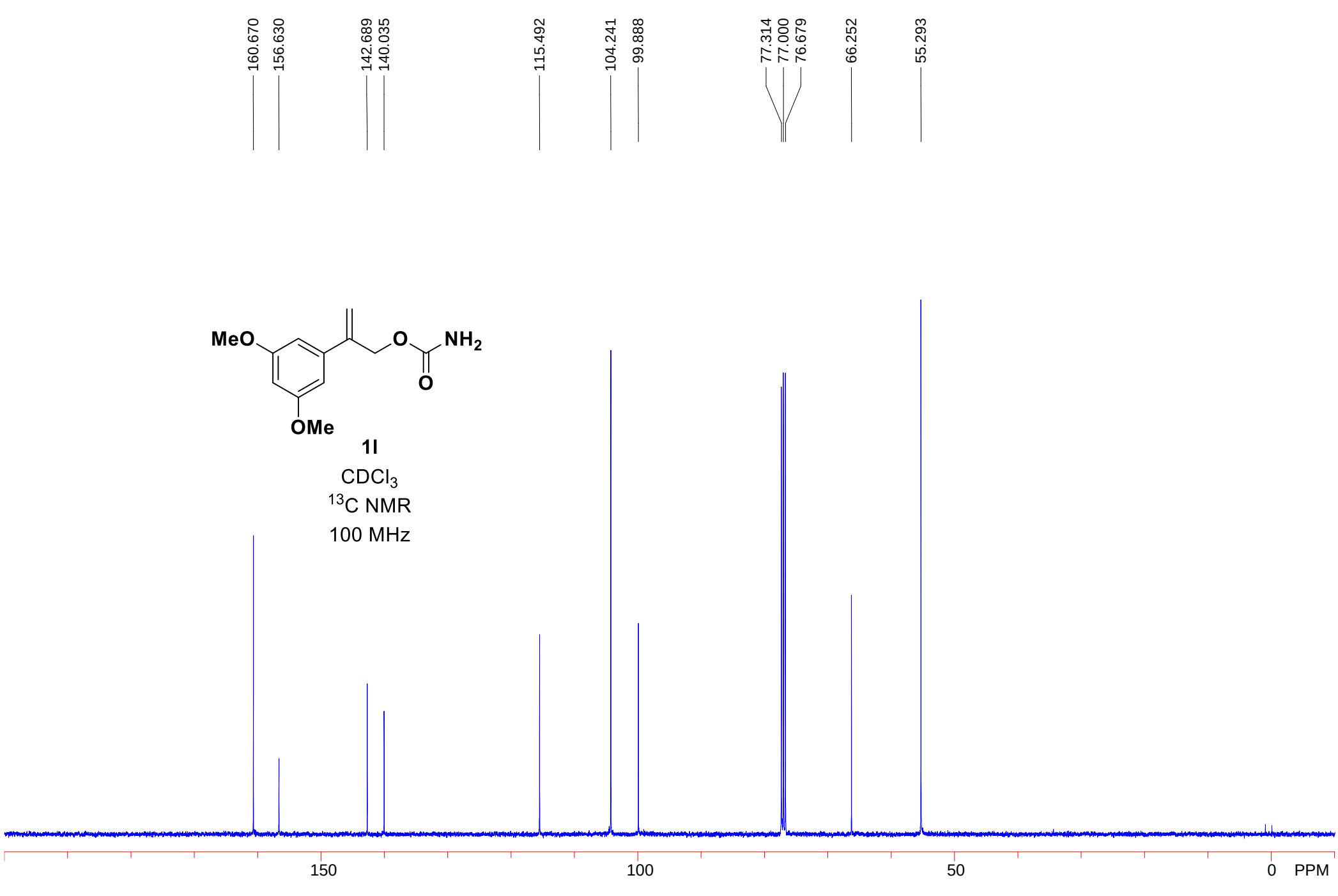
7.050
6.956
5.507
5.324
4.955
4.715
2.322
-0.000
Me
O
NH2
O
Me
1j
CDCl3
1H NMR
400 MHz
6.11
1.95
1.00
0.98
0.98
1.97
2.01
8
6
4
2
0
PPM

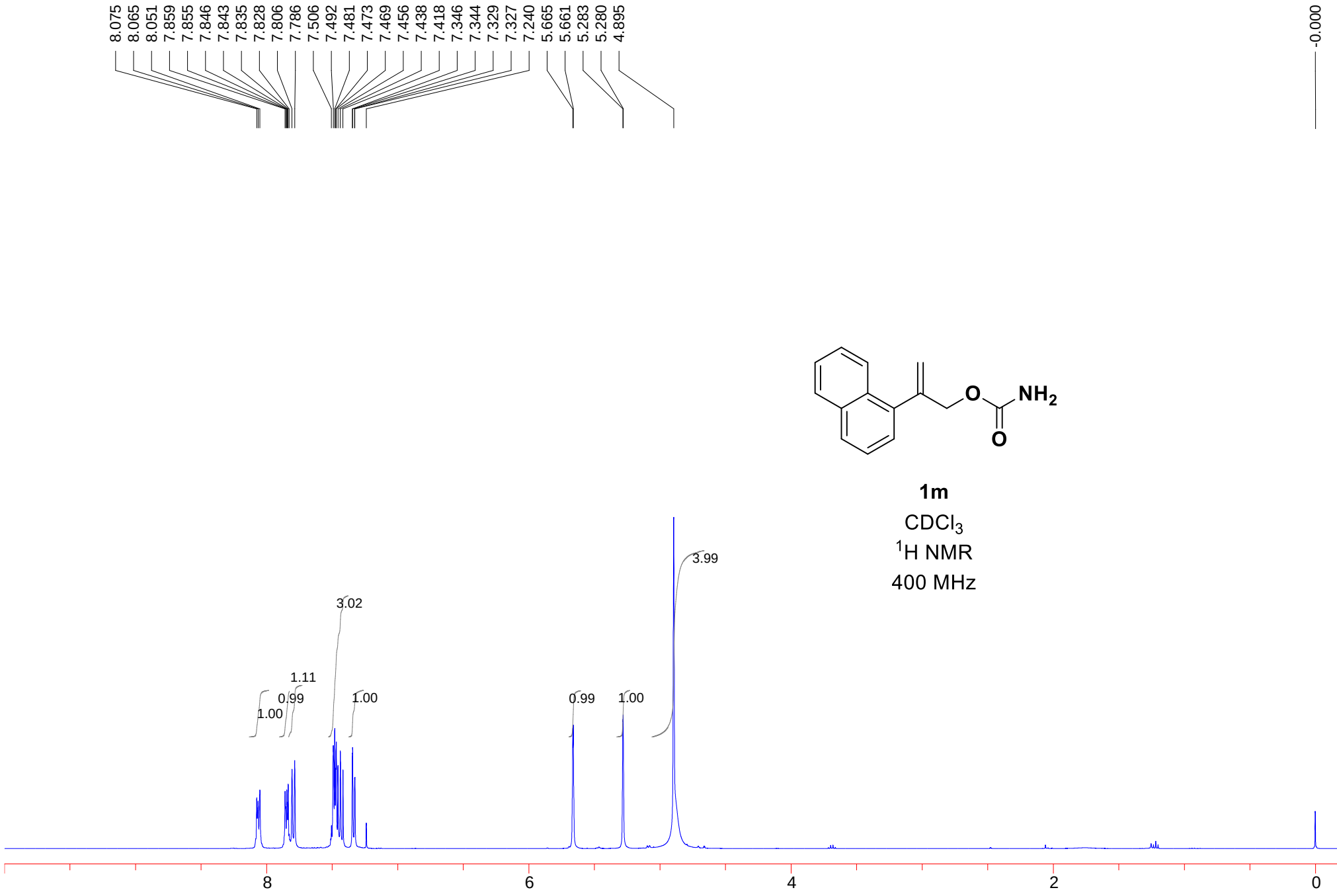

156.820
142.769
137.906
137.833
129.681
123.746
114.529
77.314
77.000
76.679
66.325
21.293
Me
O
NH2
O
Me
1j
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM

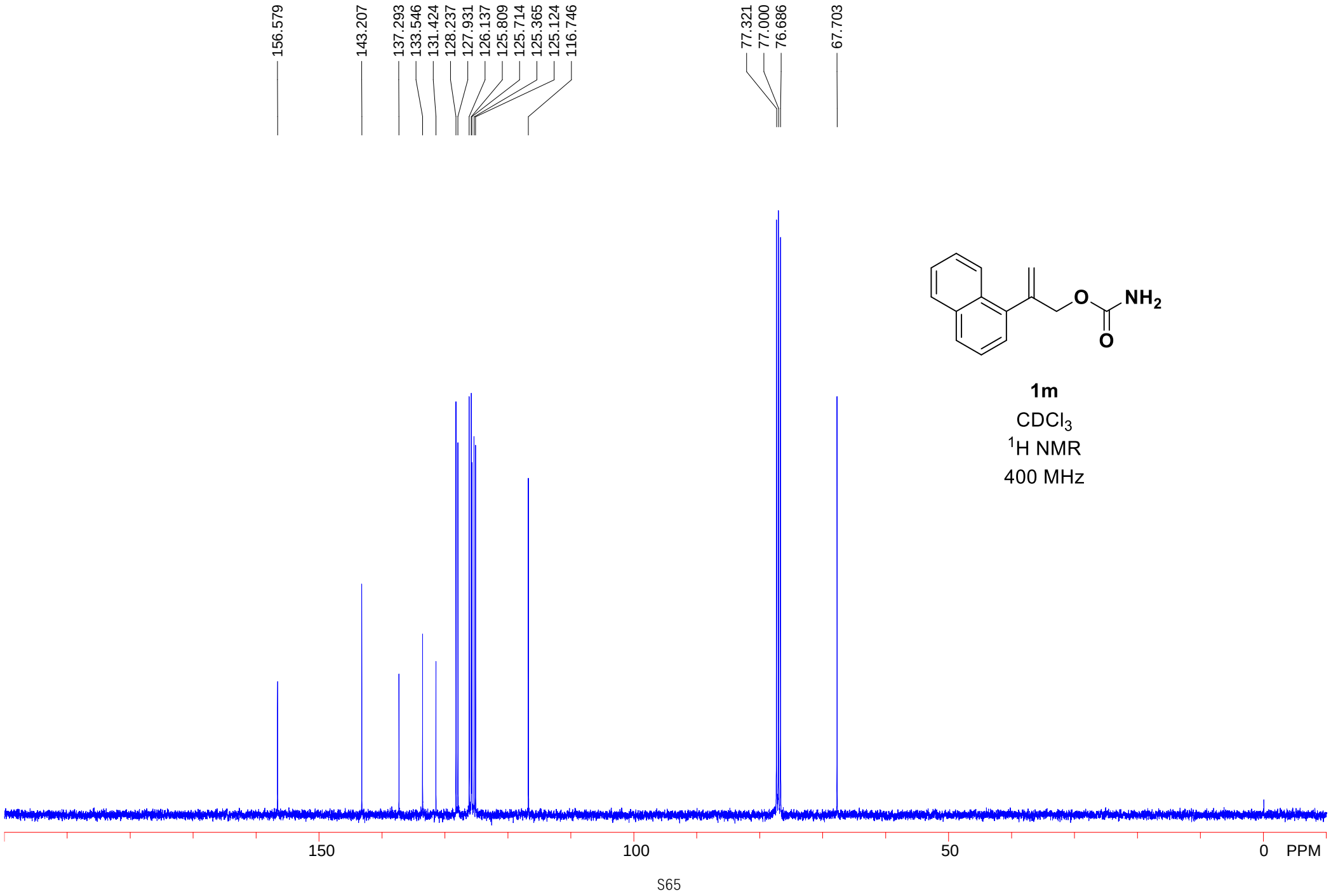

7.394
7.276
7.273
7.262
5.530
5.343
5.011
4.698
1.336
-0.000
tBu
O
NH2
O
tBu
1k
CDCl3
1H-NMR
400 MHz
18.18
2.03
0.99
0.98
1.00
2.03
1.91
8
6
4
2
0
PPM

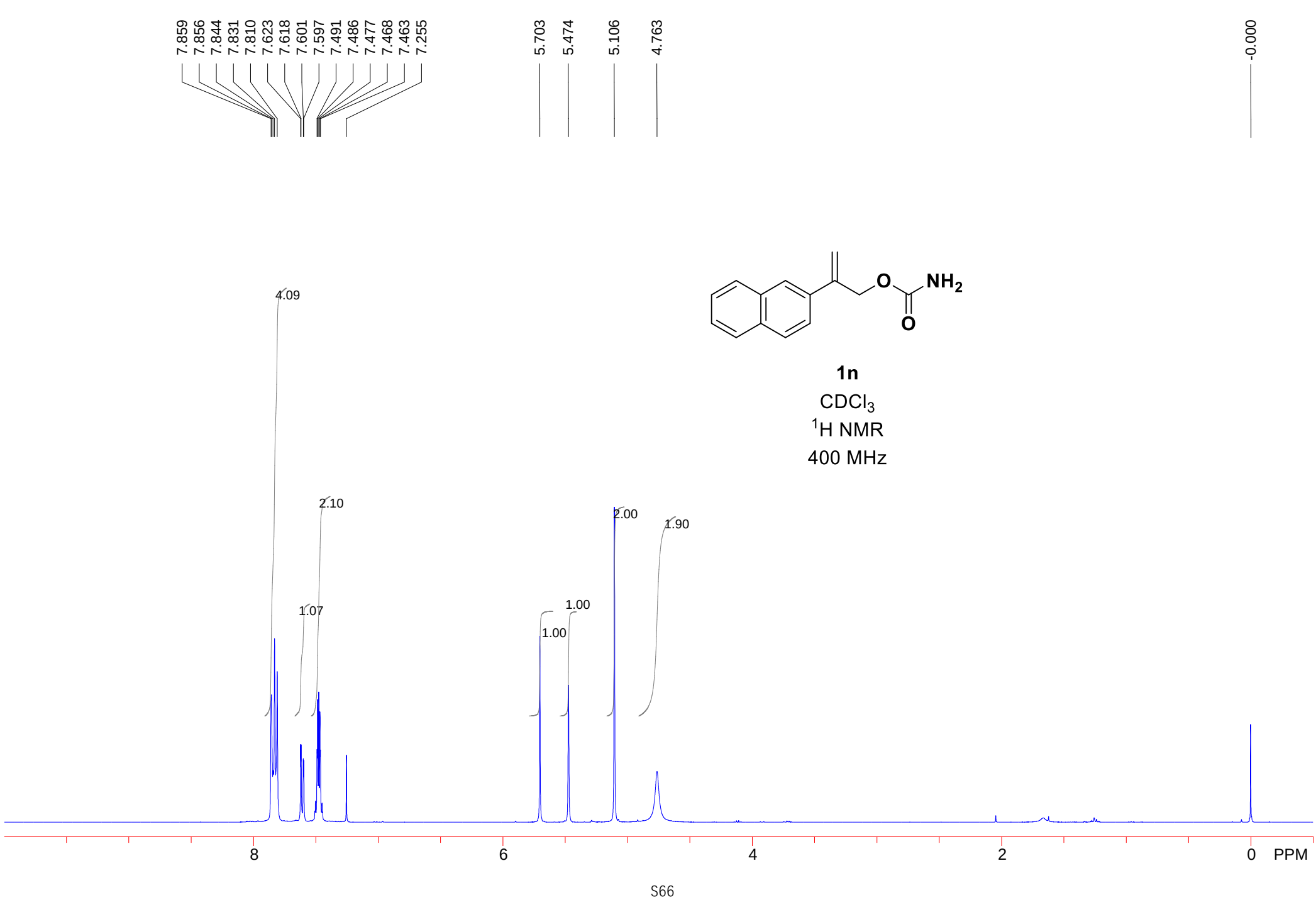

156.696
150.739
143.608
137.140
122.251
120.246
114.311
77.321
77.000
76.679
66.456
34.848
31.399
tBu
O
NH2
O
tBu
1k
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM

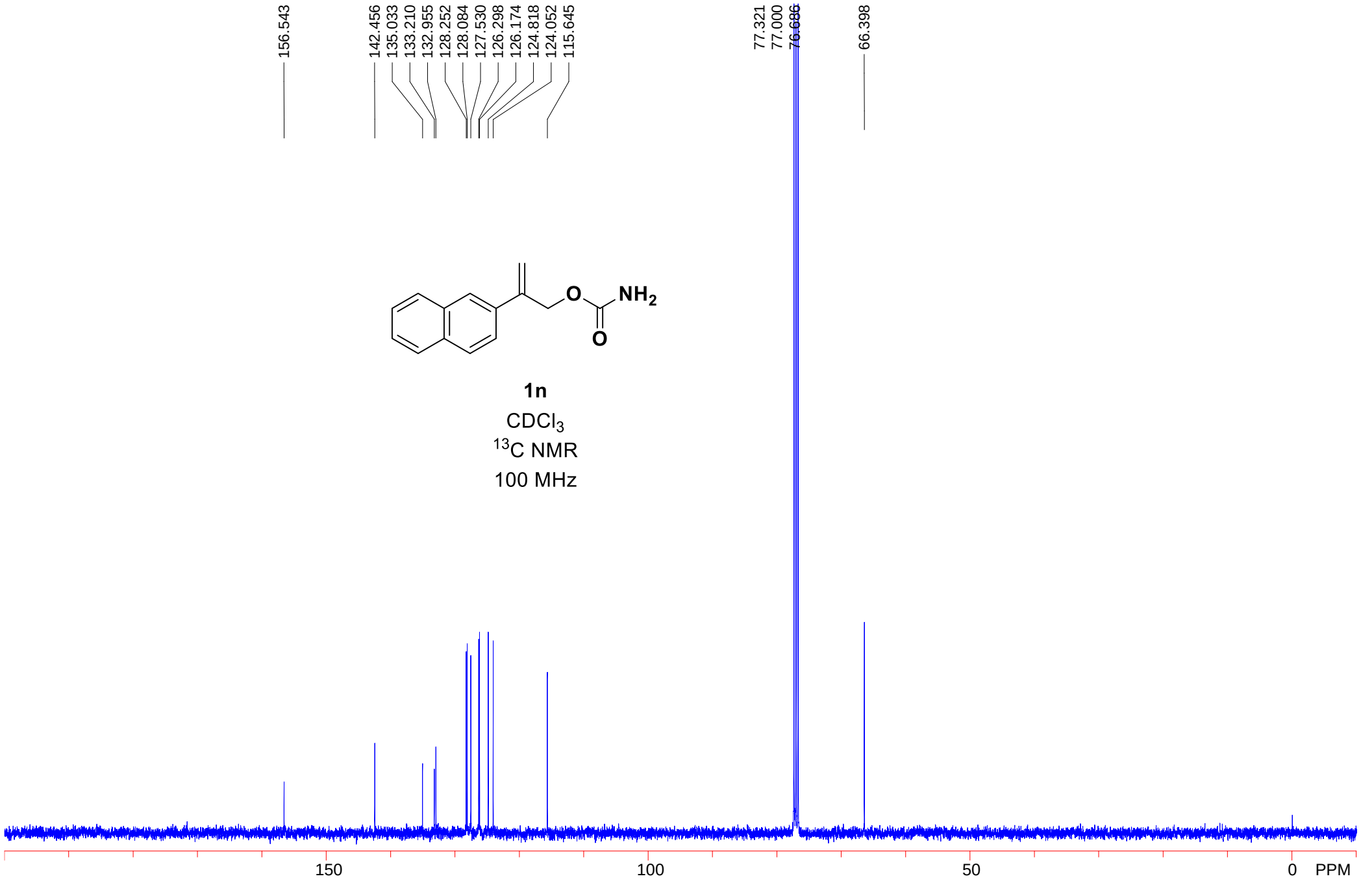

7.262
6.582
6.426
5.537
5.359
4.942
4.737
3.801
1.655
-0.000
MeO
O
NH2
O
OMe
1l
CDCl3
1H NMR
400 MHz
6.19
1.91
1.09
0.96
1.00
1.92
1.90
8
6
4
2
0
PPM

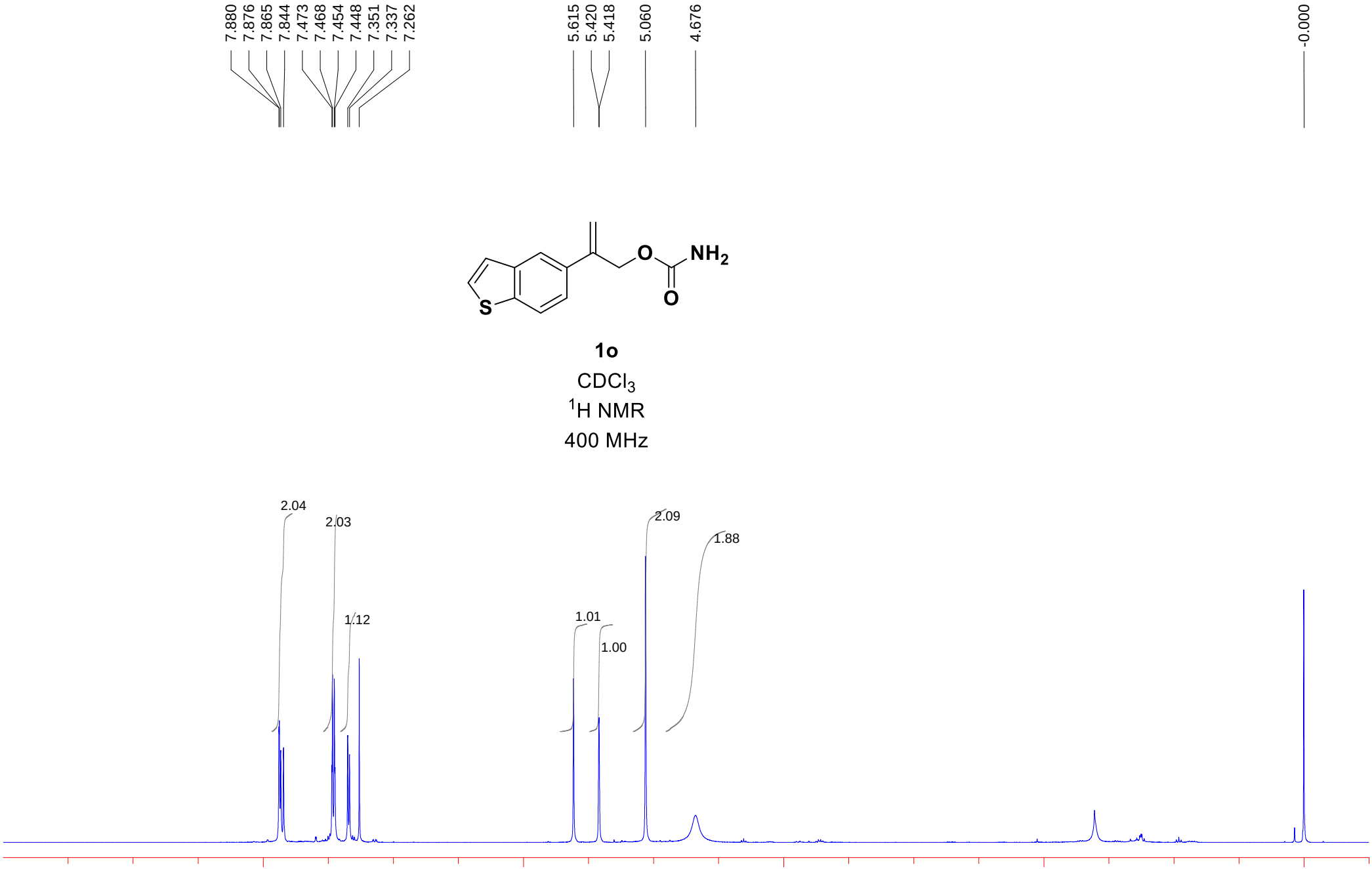

160.670
156.630
142.689
140.035
115.492
104.241
99.888
77.314
77.000
76.679
66.252
55.293
MeO
O
NH2
O
OMe
1l
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM

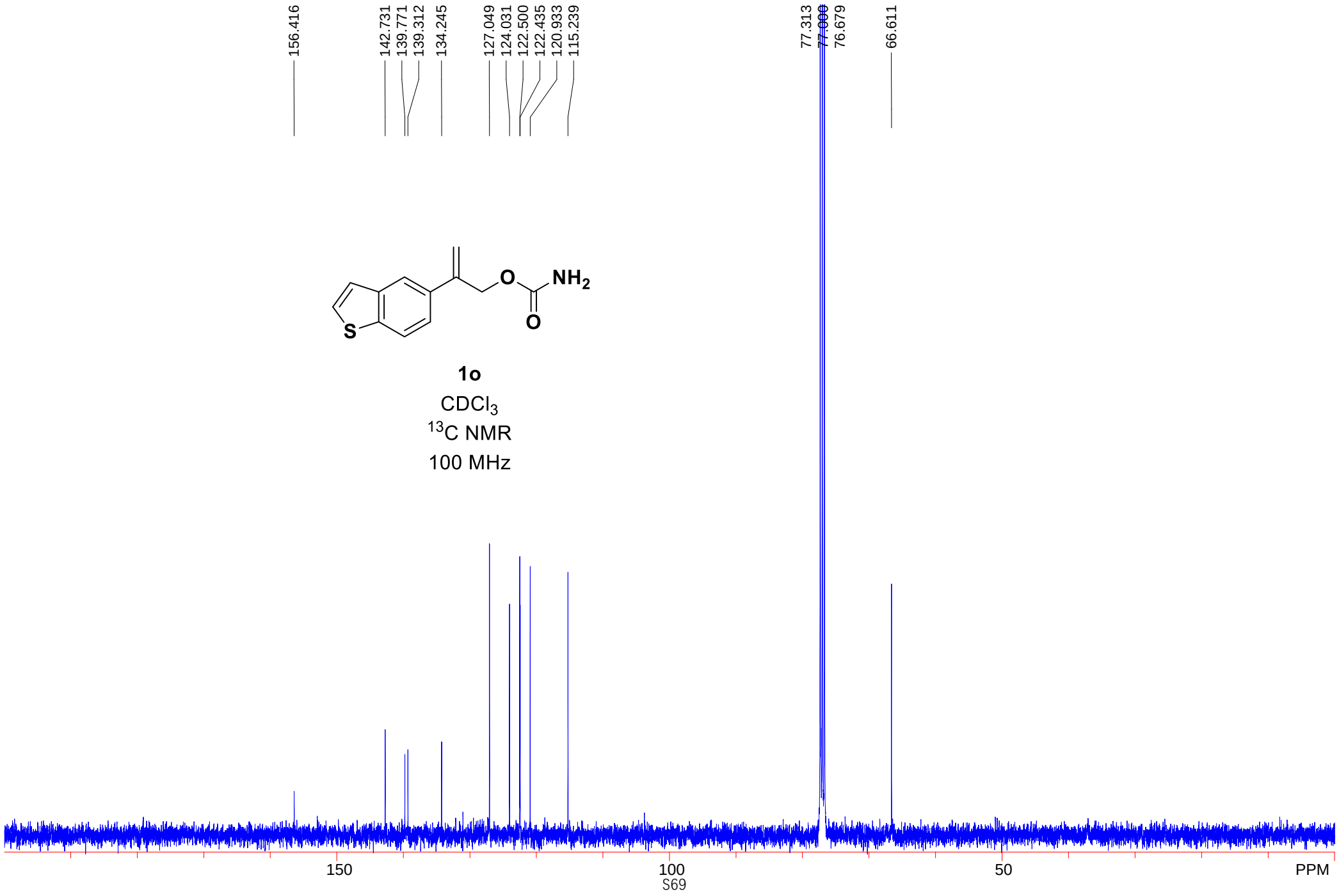

8.075
8.065
8.051
7.859
7.855
7.846
7.843
7.835
7.828
7.806
7.786
7.506
7.492
7.481
7.473
7.469
7.456
7.438
7.418
7.346
7.344
7.329
7.327
7.240
5.665
5.661
5.283
5.280
4.895
-0.000
O
NH2
O
1m
CDCl3
1H NMR
400 MHz
3.99
3.02
1.11
0.99
1.00
1.00
0.99
1.00
8
6
4
2
0
PPM

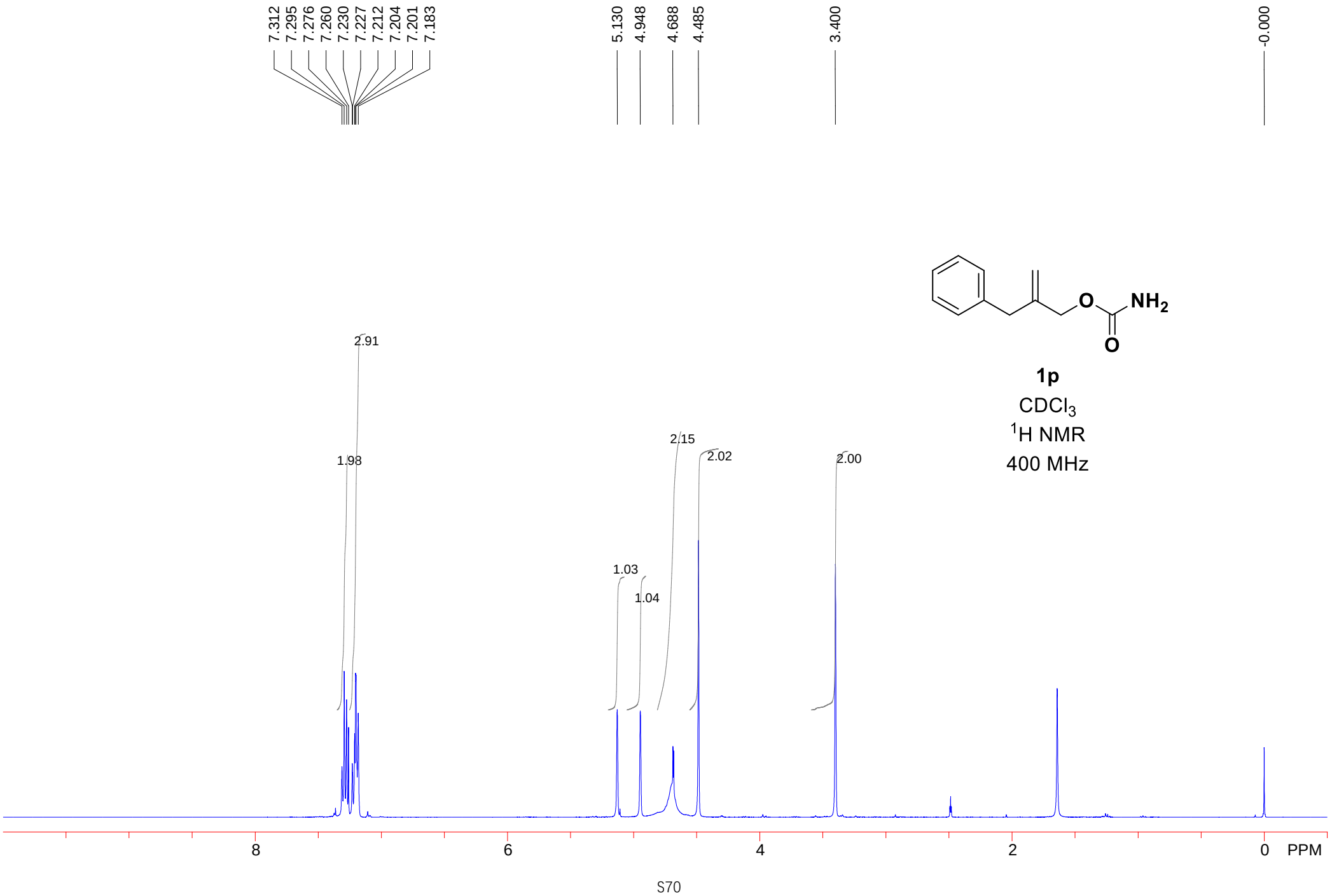

156.579
143.207
137.293
133.546
131.424
128.237
127.931
126.137
125.809
125.714
125.365
125.124
116.746
77.321
77.000
76.686
67.703
O
NH2
O
1m
CDCl3
1H NMR
400 MHz
150
100
50
0
PPM

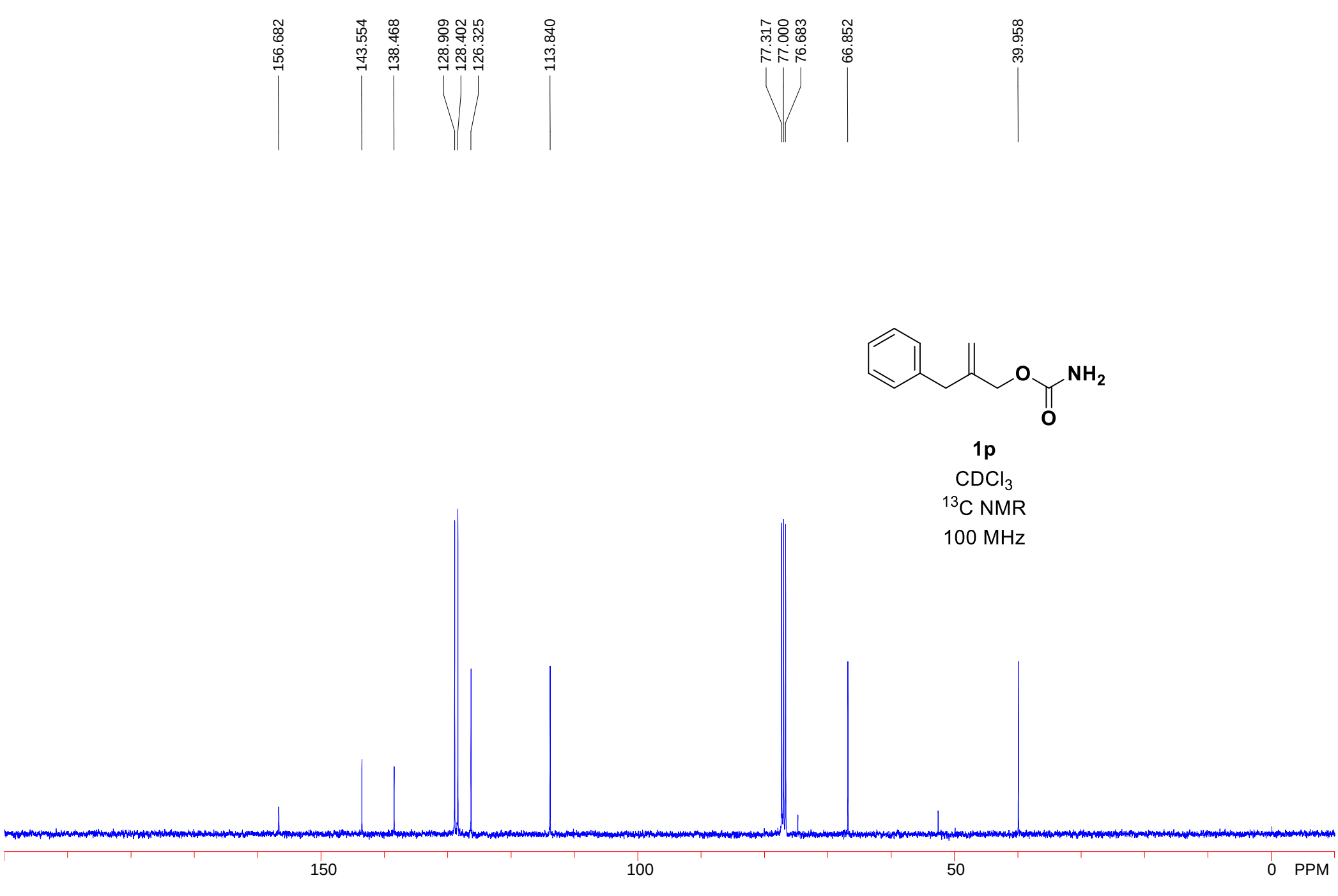

7.859
7.856
7.844
7.831
7.810
7.623
7.618
7.601
7.597
7.491
7.486
7.477
7.468
7.463
7.255
5.703
5.474
5.106
4.763
-0.000
O
NH2
O
1n
CDCl3
1H NMR
400 MHz
4.09
2.10
1.07
1.00
1.00
2.00
1.90
8
6
4
2
0
PPM

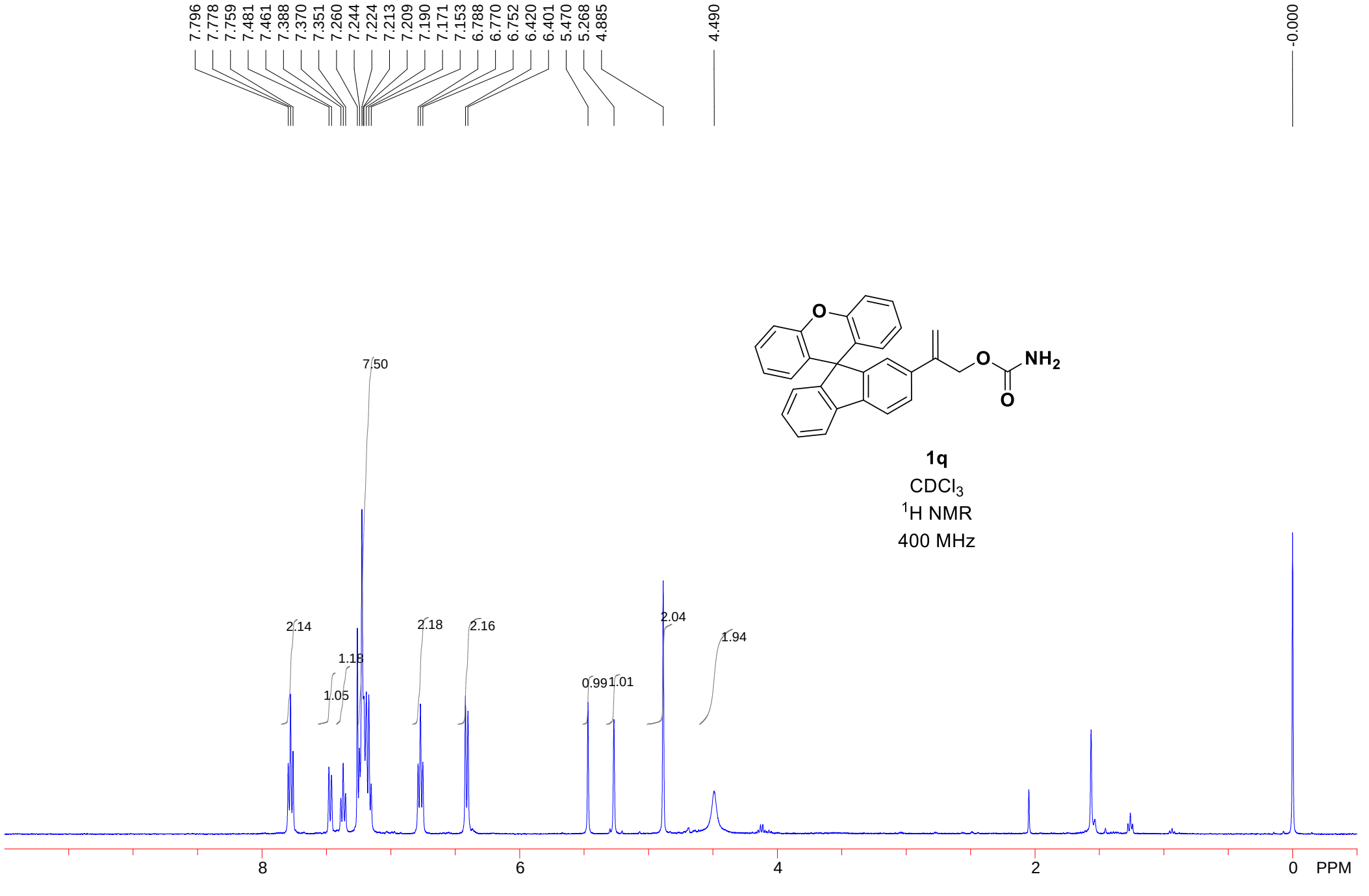

156.543
142.456
135.033
133.210
132.955
128.252
128.084
127.530
126.298
126.174
124.818
124.052
115.645
77.321
77.000
76.680
66.398
O
NH2
O
1n
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM

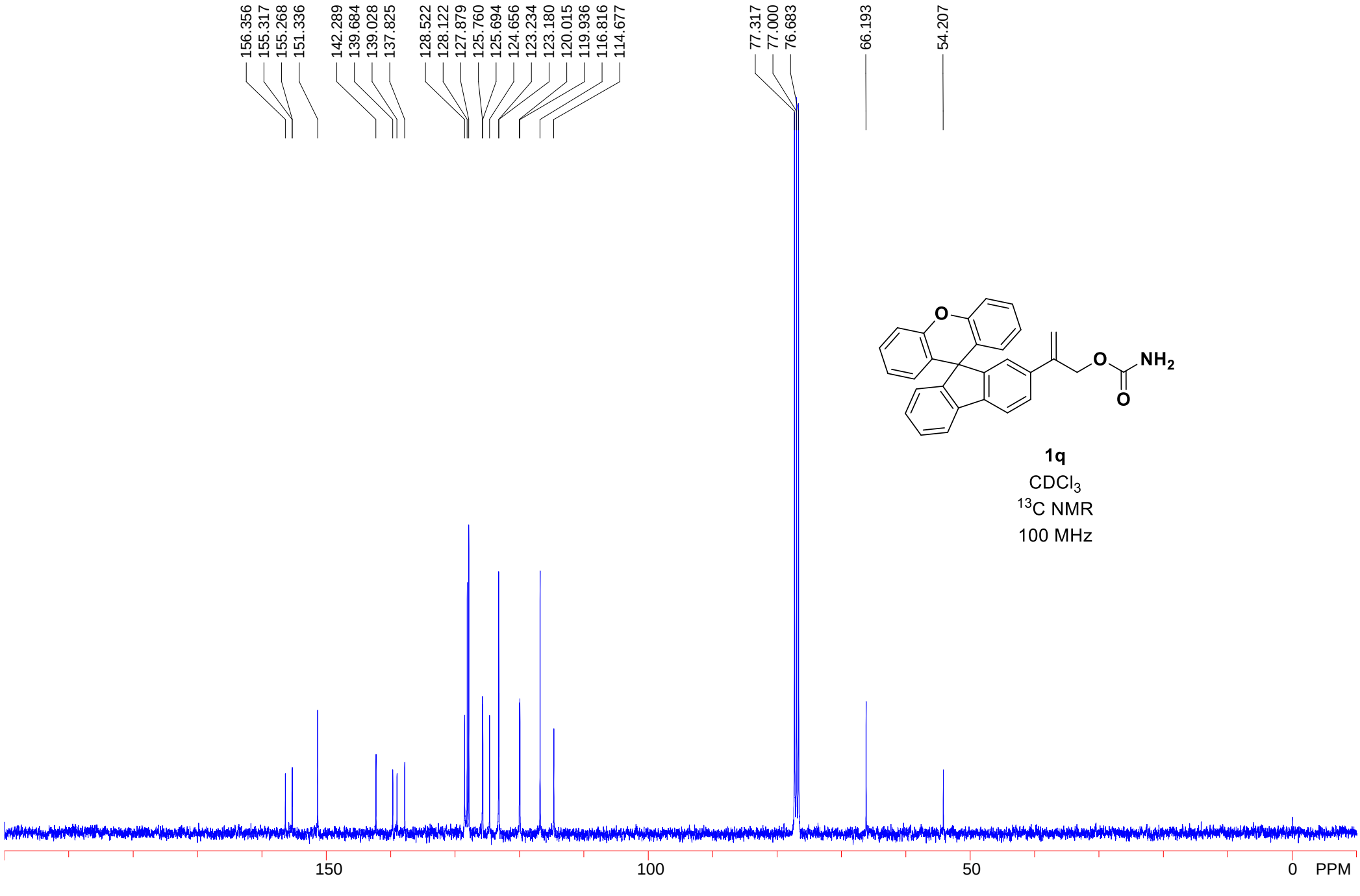

7.880
7.876
7.865
7.844
7.473
7.468
7.454
7.448
7.351
7.337
7.262
5.615
5.420
5.418
5.060
4.676
-0.000
O
NH2
O
S
1o
CDCl3
1H NMR
400 MHz
2.04
2.03
1.12
1.01
1.00
2.09
1.88
8
6
4
2
0
PPM


156.416
142.731
139.771
139.312
134.245
127.049
124.031
122.500
122.435
120.933
115.239
77.313
77.000
76.679
66.611
O
NH2
O
S
1o
CDCl3
13C NMR
100 MHz
150
100
50
PPM


7.312
7.295
7.276
7.260
7.230
7.227
7.212
7.204
7.201
7.183
5.130
4.948
4.688
4.485
3.400
-0.000
O
NH2
O
1p
CDCl3
1H NMR
400 MHz
2.91
1.98
2.15
2.02
2.00
1.03
1.04
8
6
4
2
0
PPM


156.682
143.554
138.468
128.909
128.402
126.325
113.840
77.317
77.000
76.683
66.852
39.958
O
NH2
O
1p
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


7.796
7.778
7.759
7.481
7.461
7.388
7.370
7.351
7.260
7.244
7.224
7.213
7.209
7.190
7.171
7.153
6.788
6.770
6.752
6.420
6.401
5.470
5.268
4.885
4.490
-0.000
O
O
NH2
O
1q
CDCl3
1H NMR
400 MHz
7.50
2.14
1.18
1.05
2.18
2.16
0.99
1.01
2.04
1.94
8
6
4
2
0
PPM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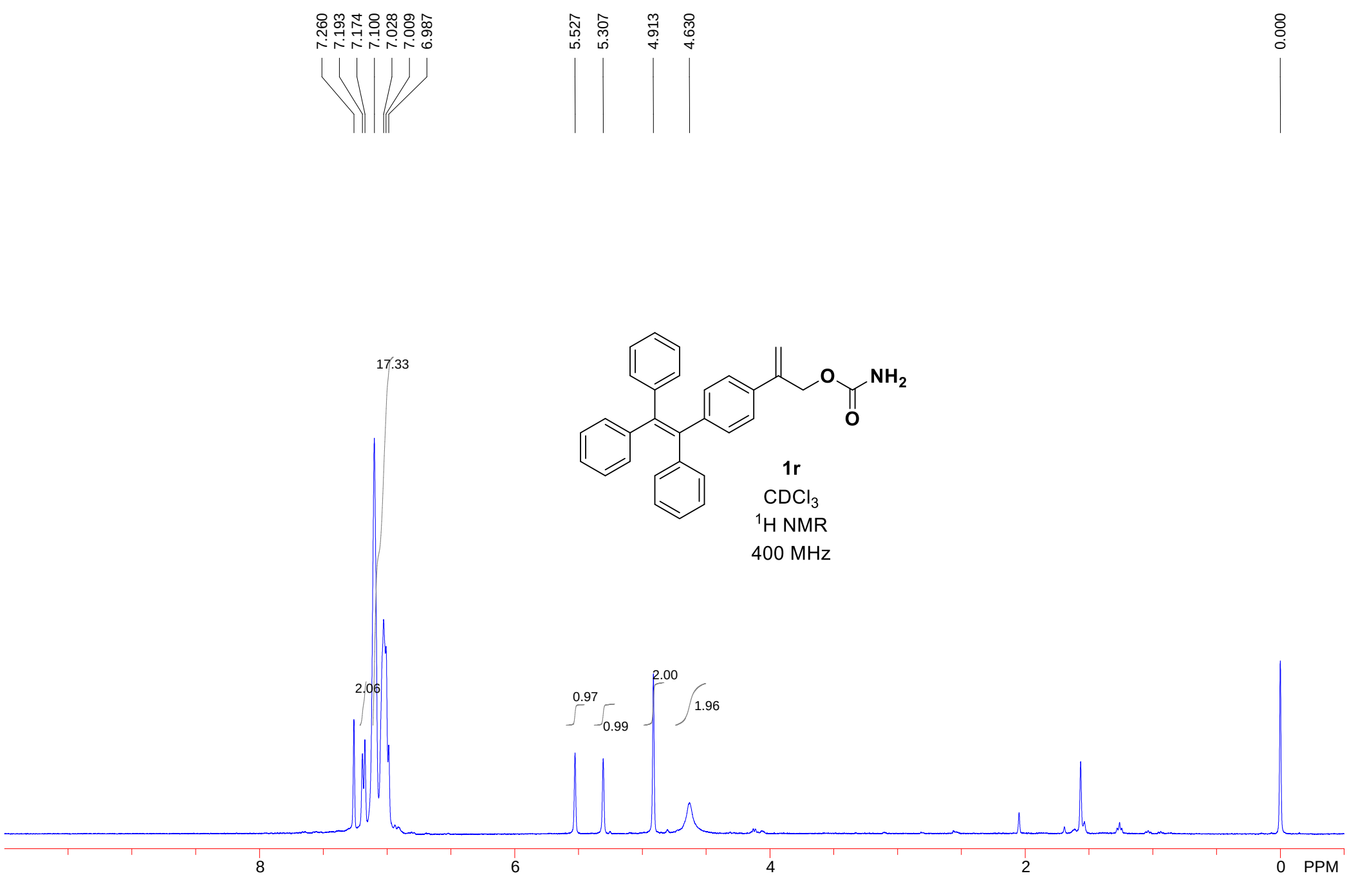
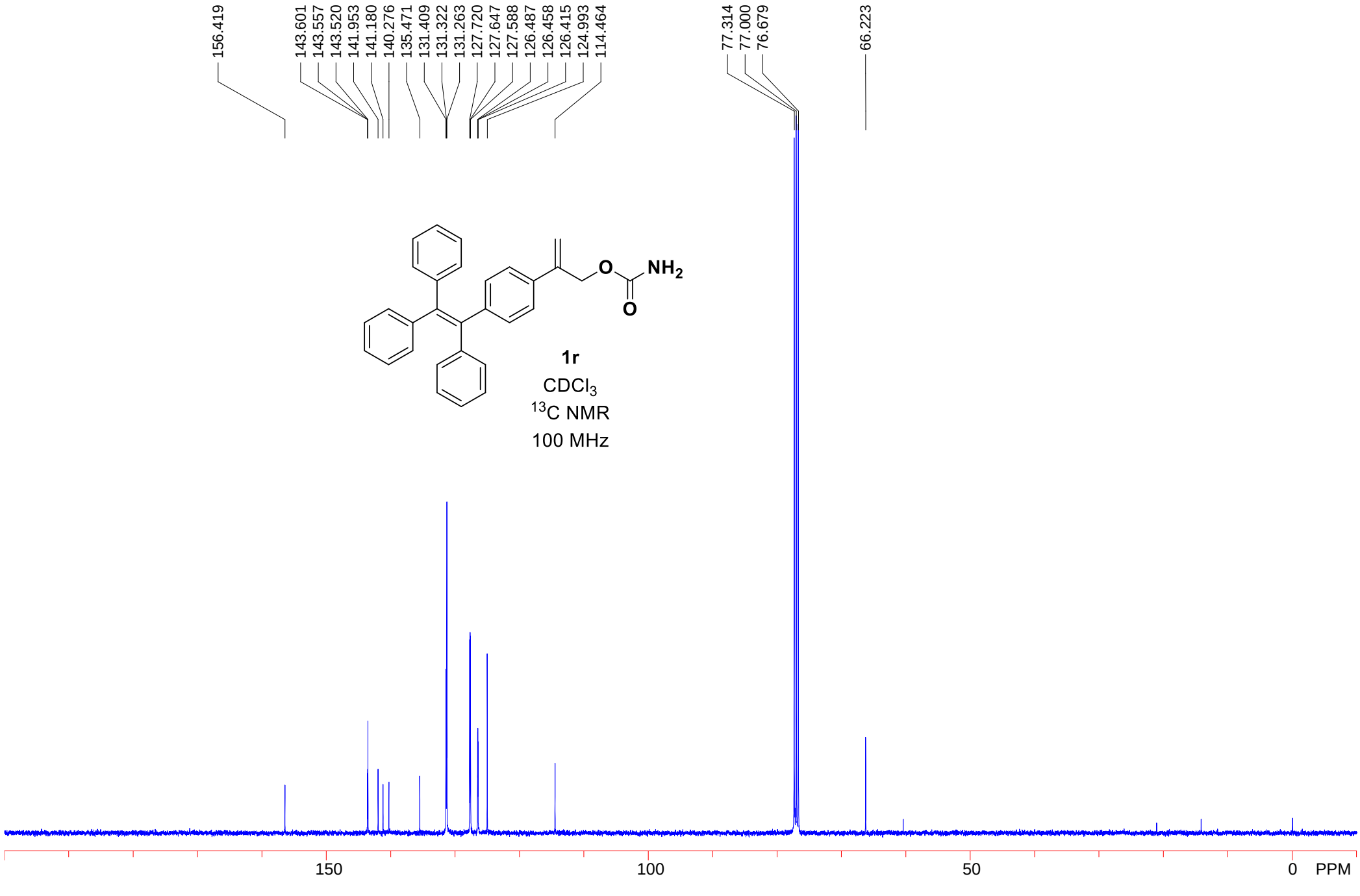
155.317
155.268
151.336
142.289
139.684
139.028
137.825
128.522
128.122
127.879
125.760
125.694
124.656
123.234
123.180
120.015
119.936
116.816
114.677
77.317
77.000
76.683
66.193
54.207
O
O
NH2
O
1q
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


7.260
7.193
7.174
7.100
7.028
7.009
6.987
5.527
5.307
4.913
4.630
0.000
17.33
2.06
0.97
0.99
2.00
1.96
O
NH2
O
1r
CDCl3
1H NMR
400 MHz
8
6
4
2
0
PPM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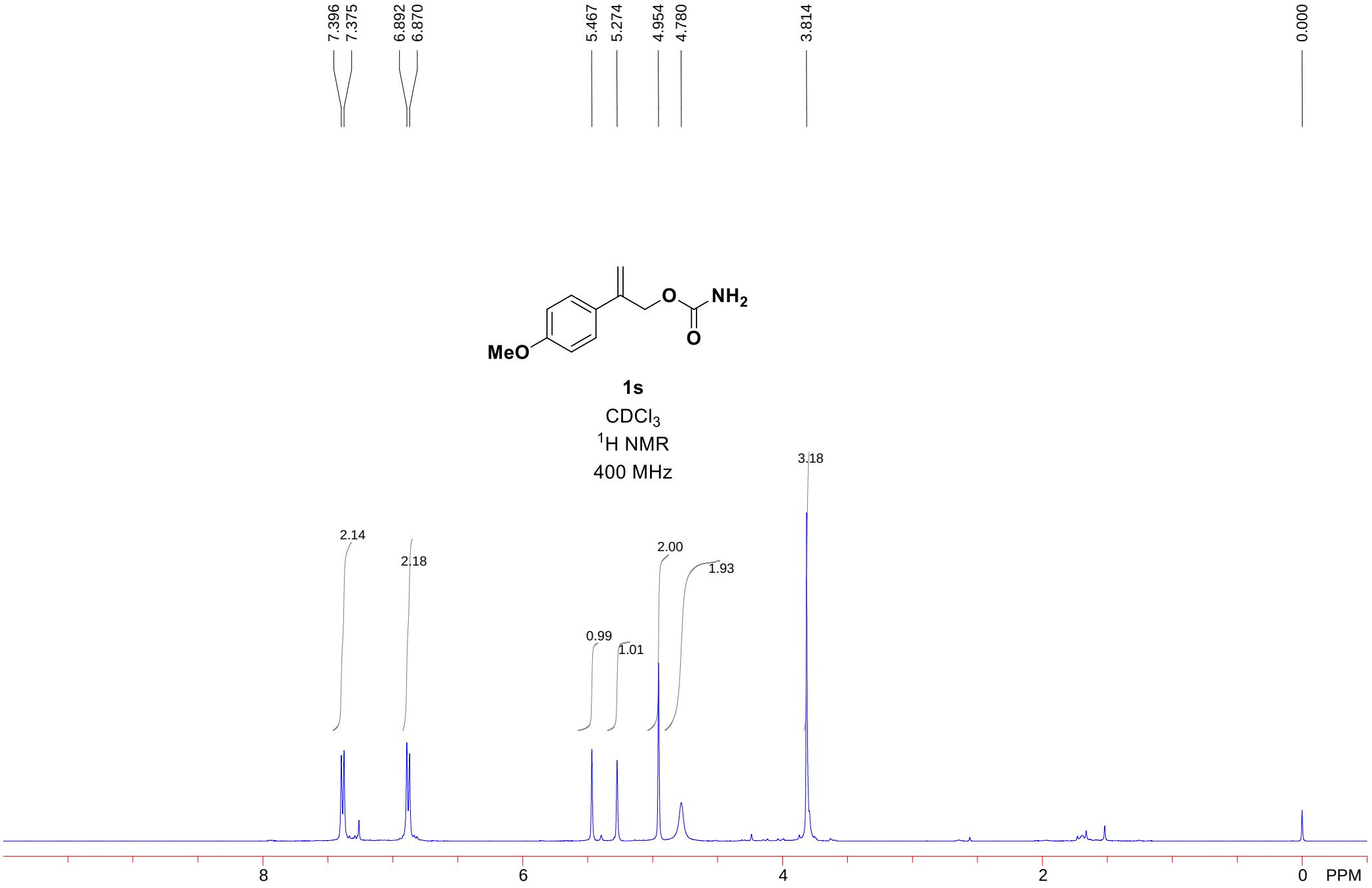
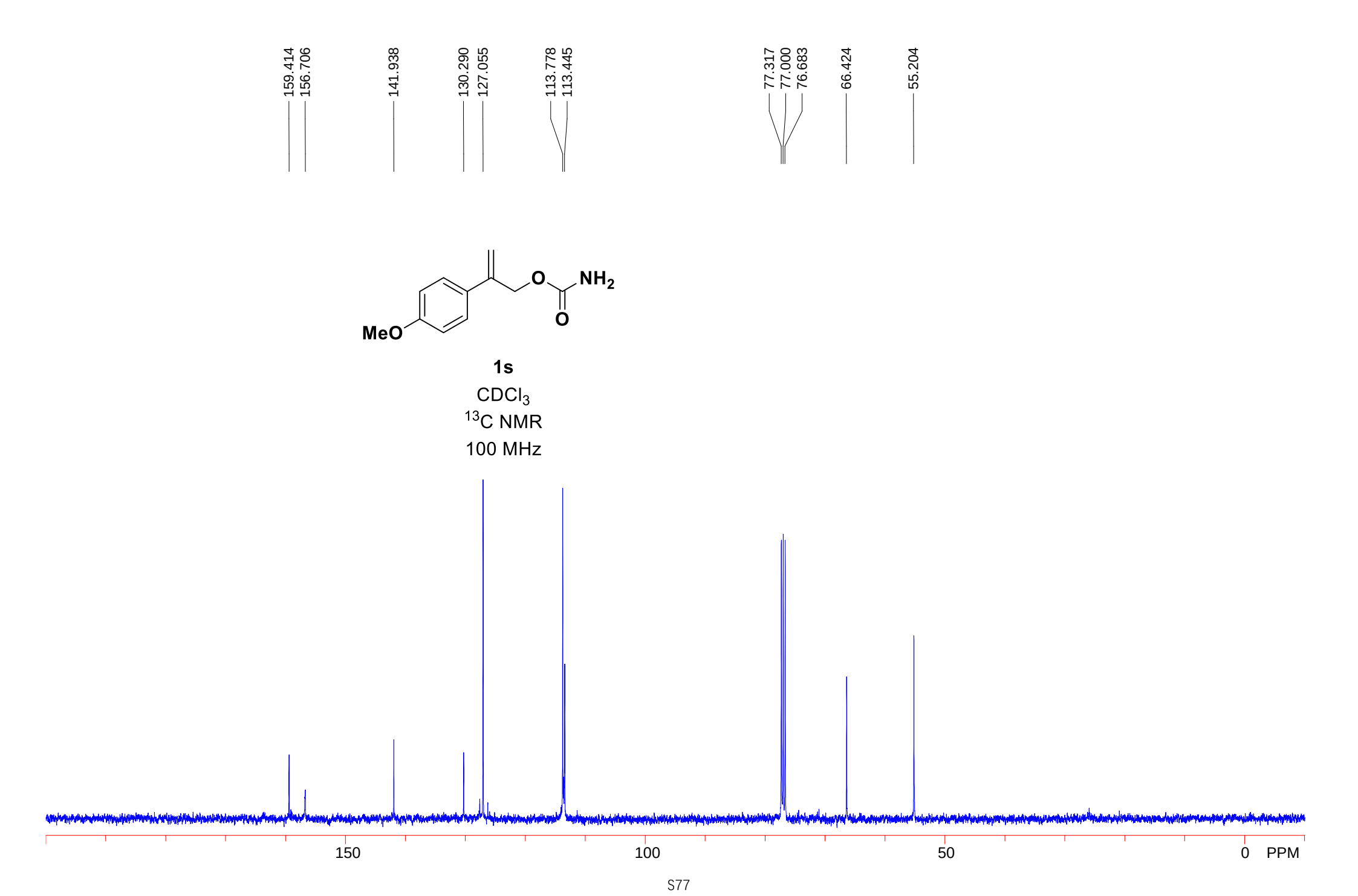
143.520
141.953
141.180
140.276
135.471
131.409
131.322
131.263
127.720
127.647
127.588
126.487
126.458
126.415
124.993
114.464
77.314
77.000
76.679
66.223
O
NH2
O
1r
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


7.396
7.375
6.892
6.870
5.467
5.274
4.954
4.780
3.814
0.000
MeO
O
NH2
O
1s
CDCl3
1H NMR
400 MHz
3.18
2.14
2.18
2.00
1.93
0.99
1.01
8
6
4
2
0
PPM


159.414
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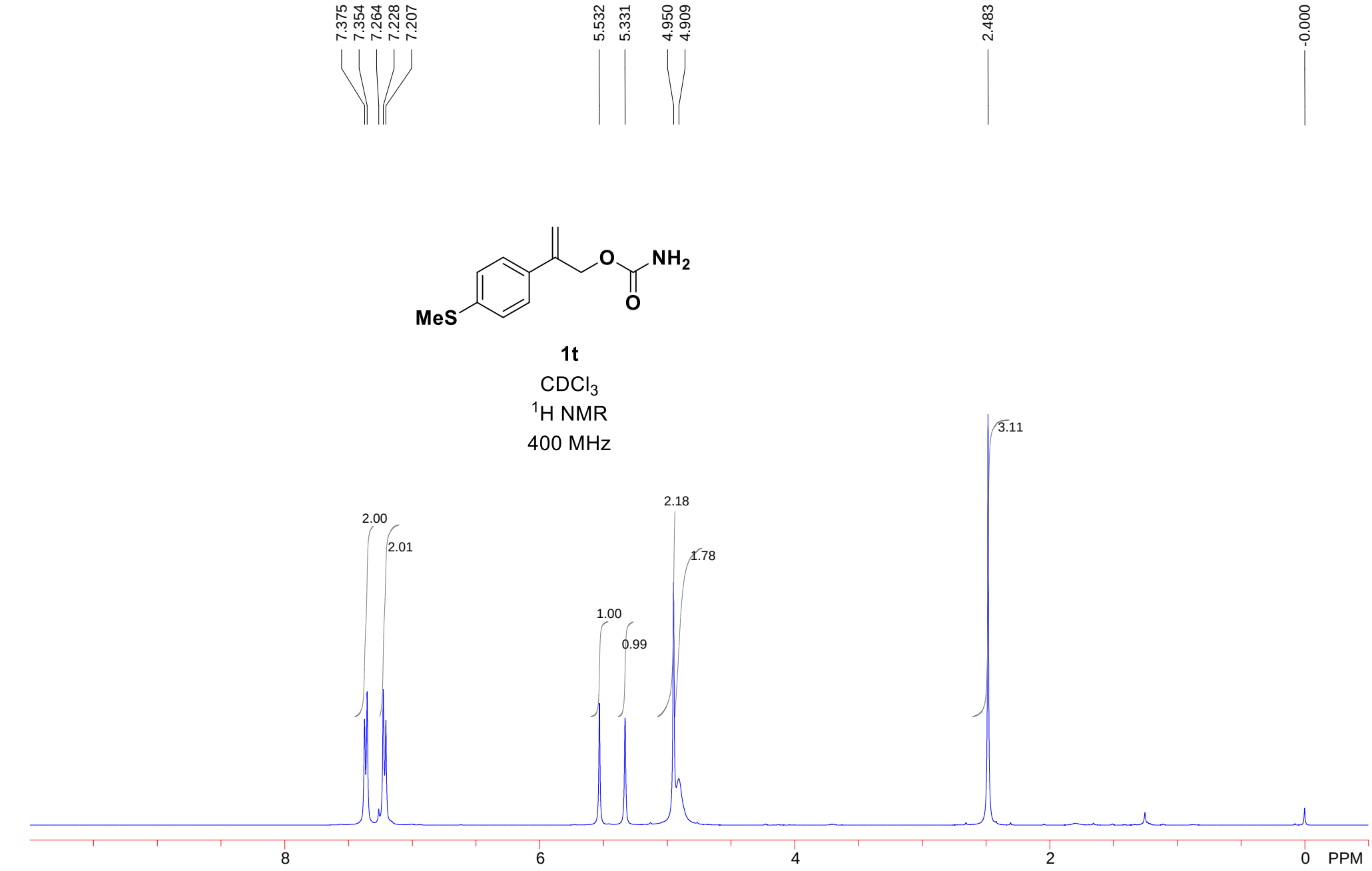
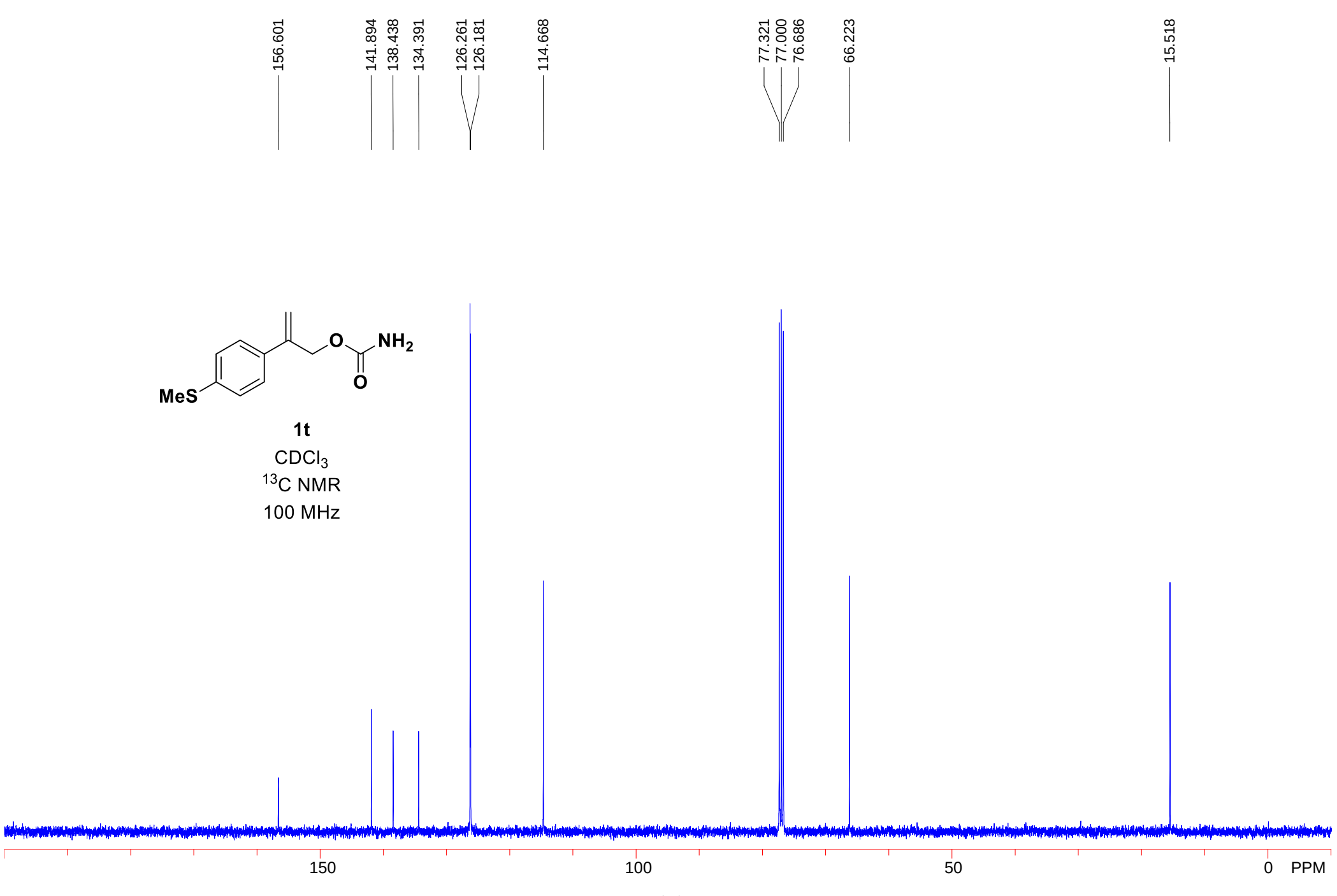
141.938
130.290
127.055
113.778
113.445
77.317
77.000
76.683
66.424
55.204
O
NH2
O
MeO
1s
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


7.375
7.354
7.264
7.228
7.207
5.532
5.331
4.950
4.909
2.483
-0.000
O
NH2
O
MeS
1t
CDCl3
1H NMR
400 MHz
3.11
2.18
2.00
2.01
1.78
1.00
0.99
8
6
4
2
0
PPM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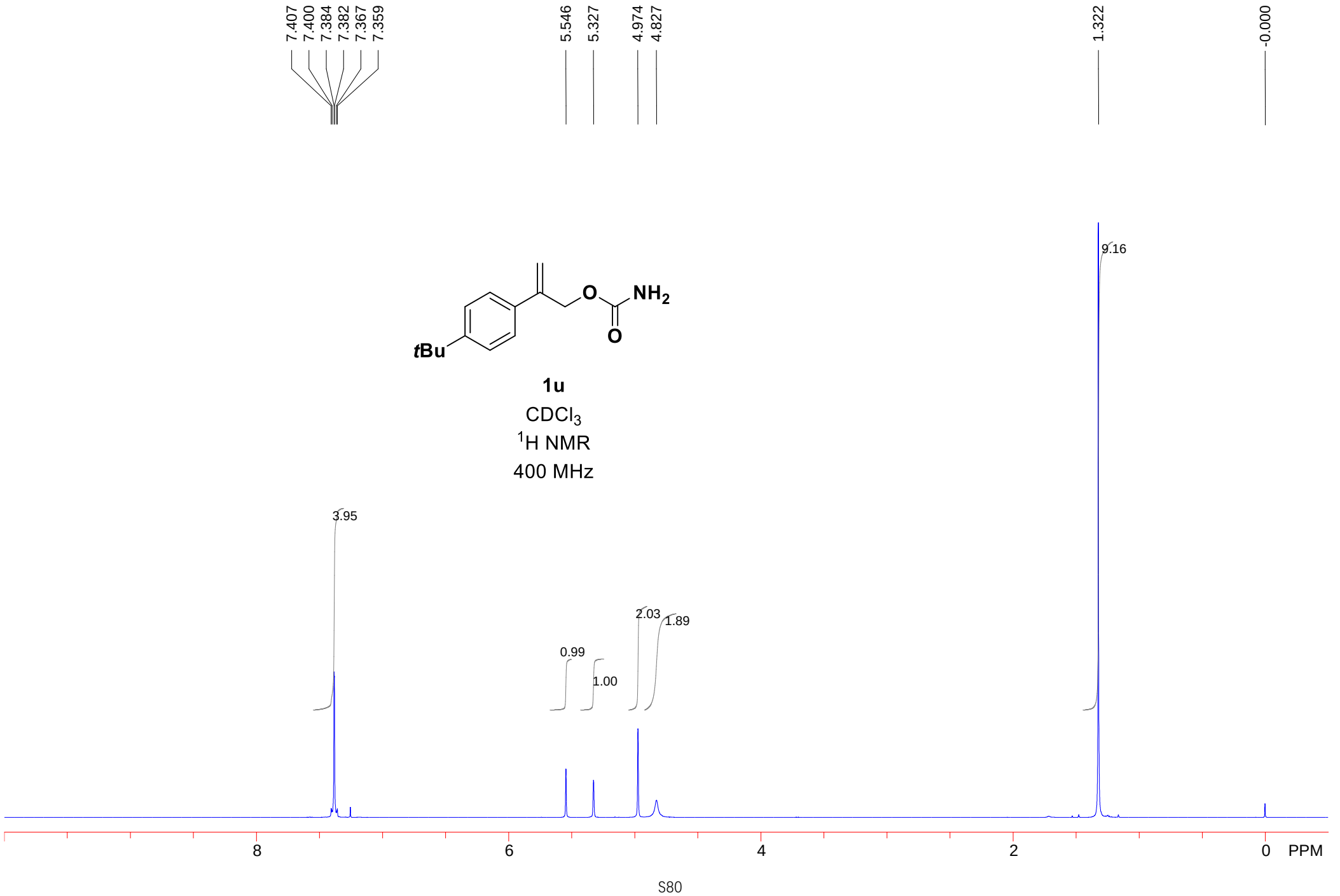
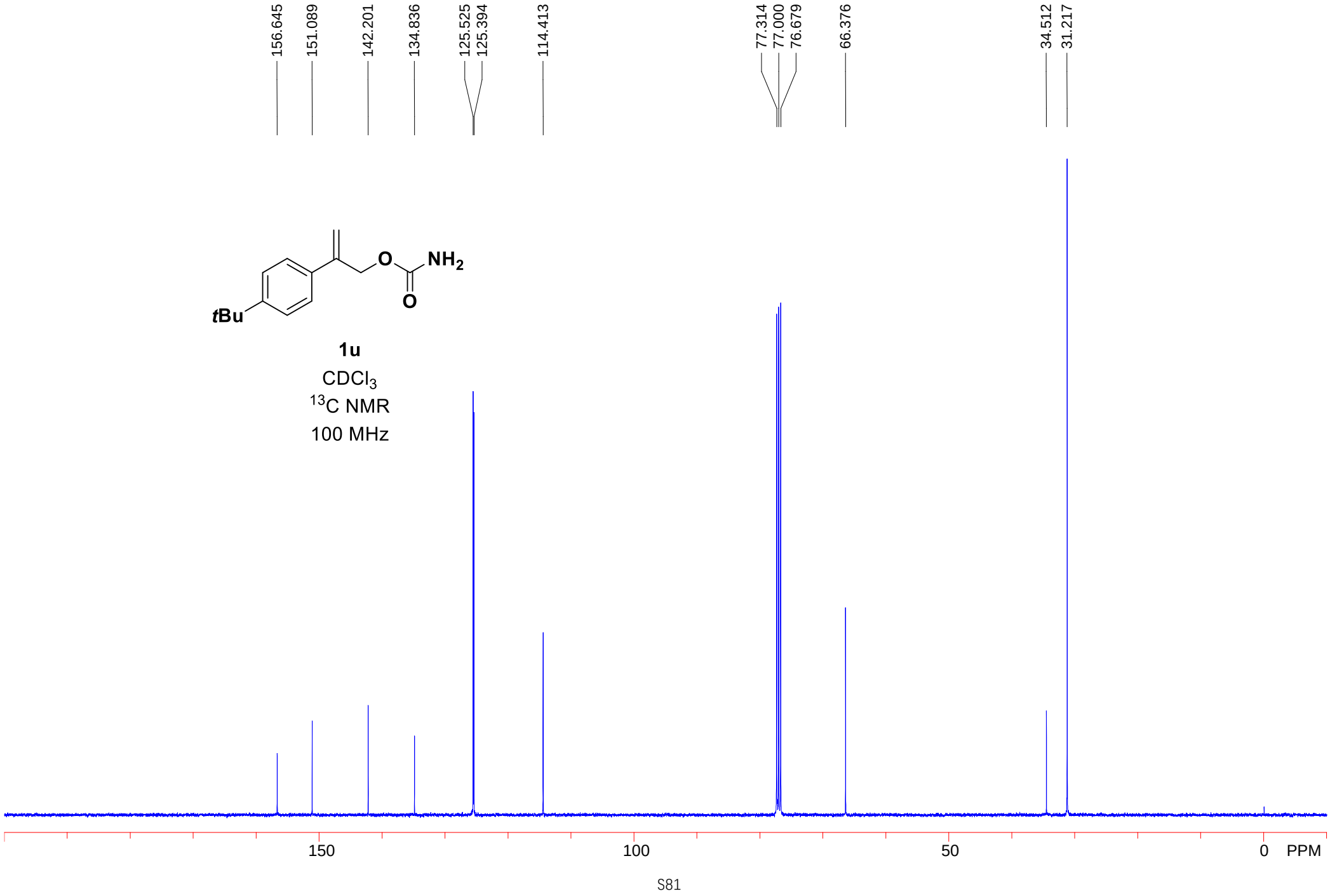
141.894
138.438
134.391
126.261
126.181
114.668
77.321
77.000
76.686
66.223
15.518
O
NH2
O
MeS
1t
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


7.407
7.400
7.384
7.382
7.367
7.359
5.546
5.327
4.974
4.827
1.322
-0.000
O
NH2
O
tBu
1u
CDCl3
1H NMR
400 MHz
3.95
0.99
1.00
2.03
1.89
9.16
8
6
4
2
0
PPM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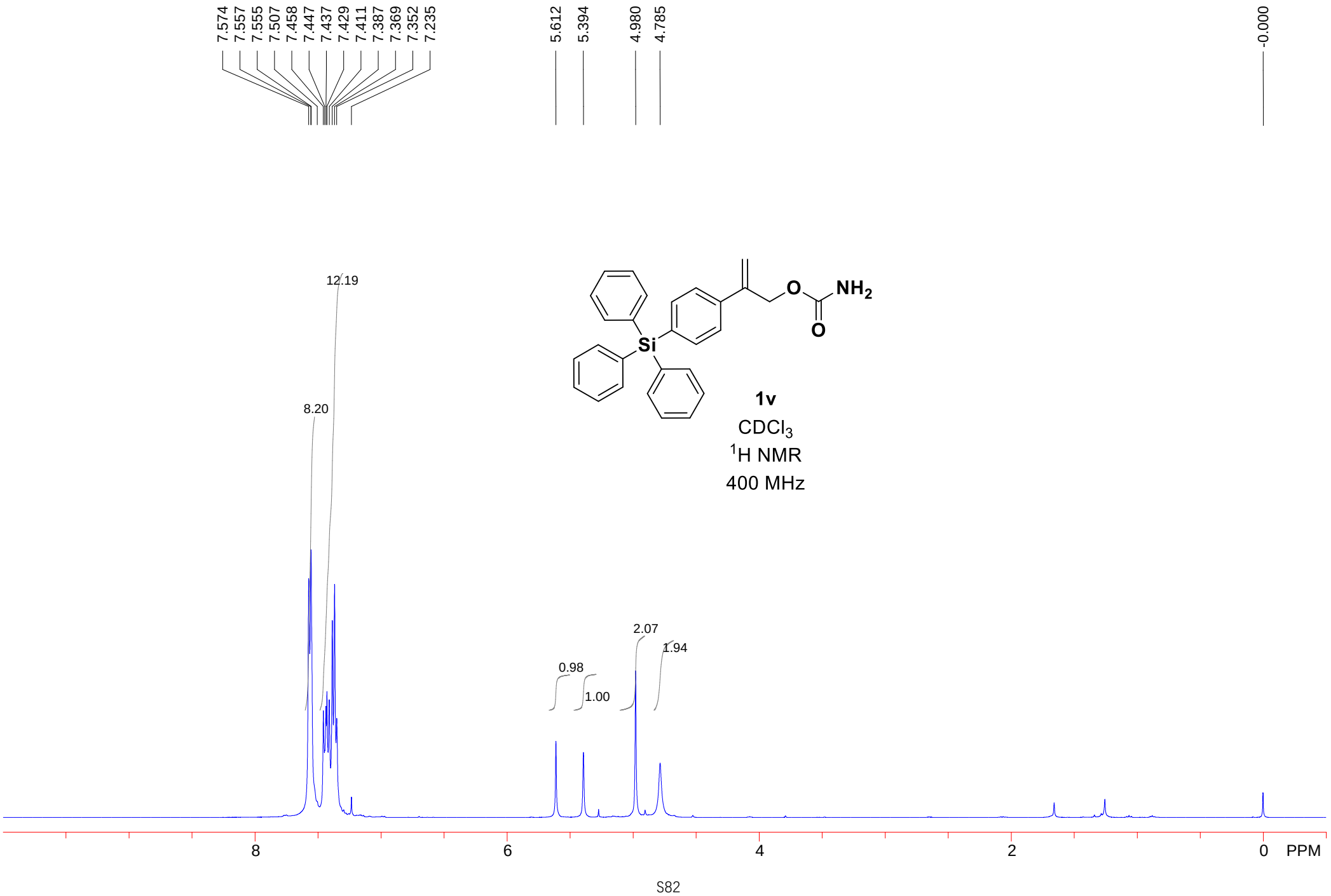
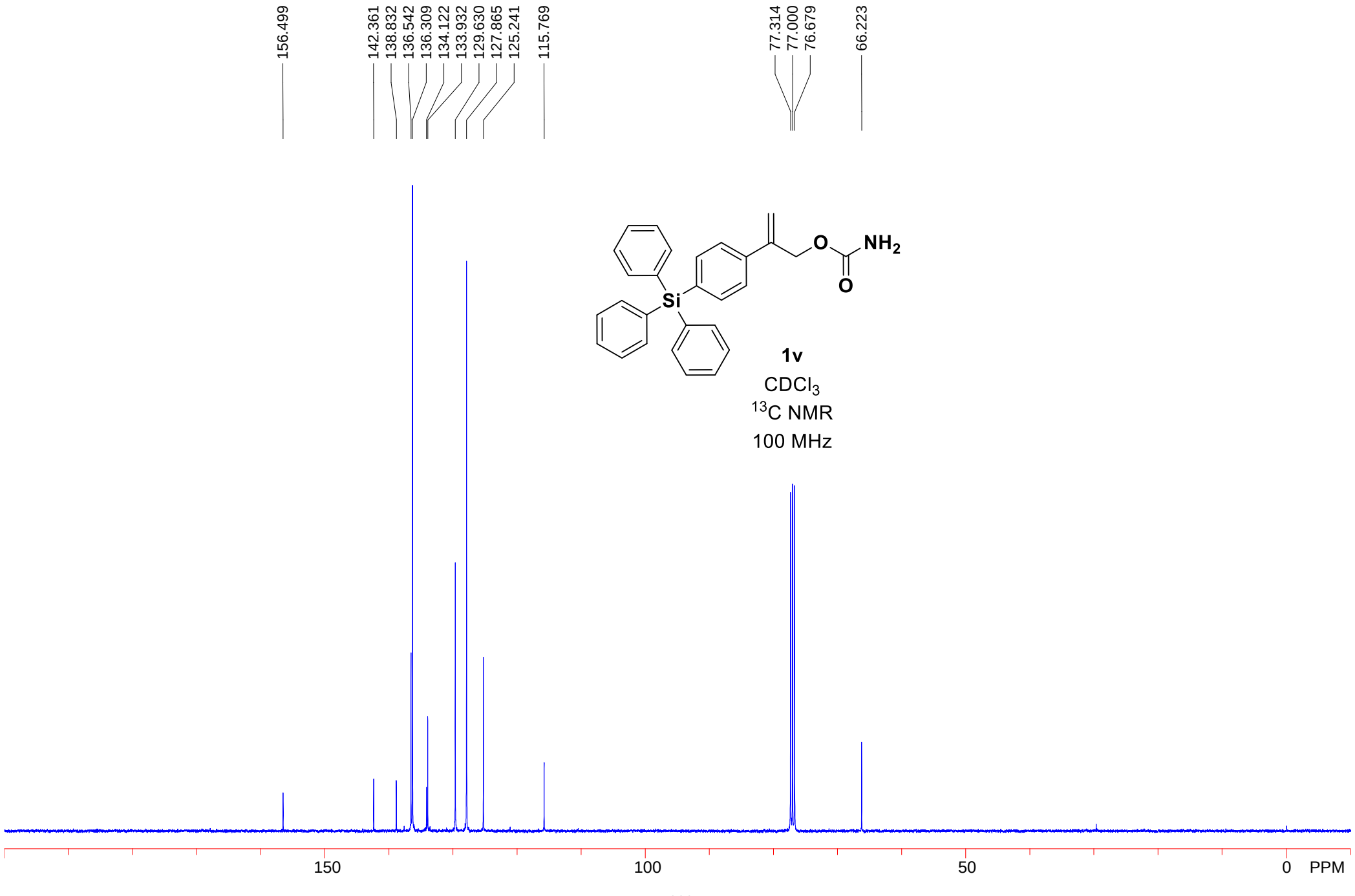
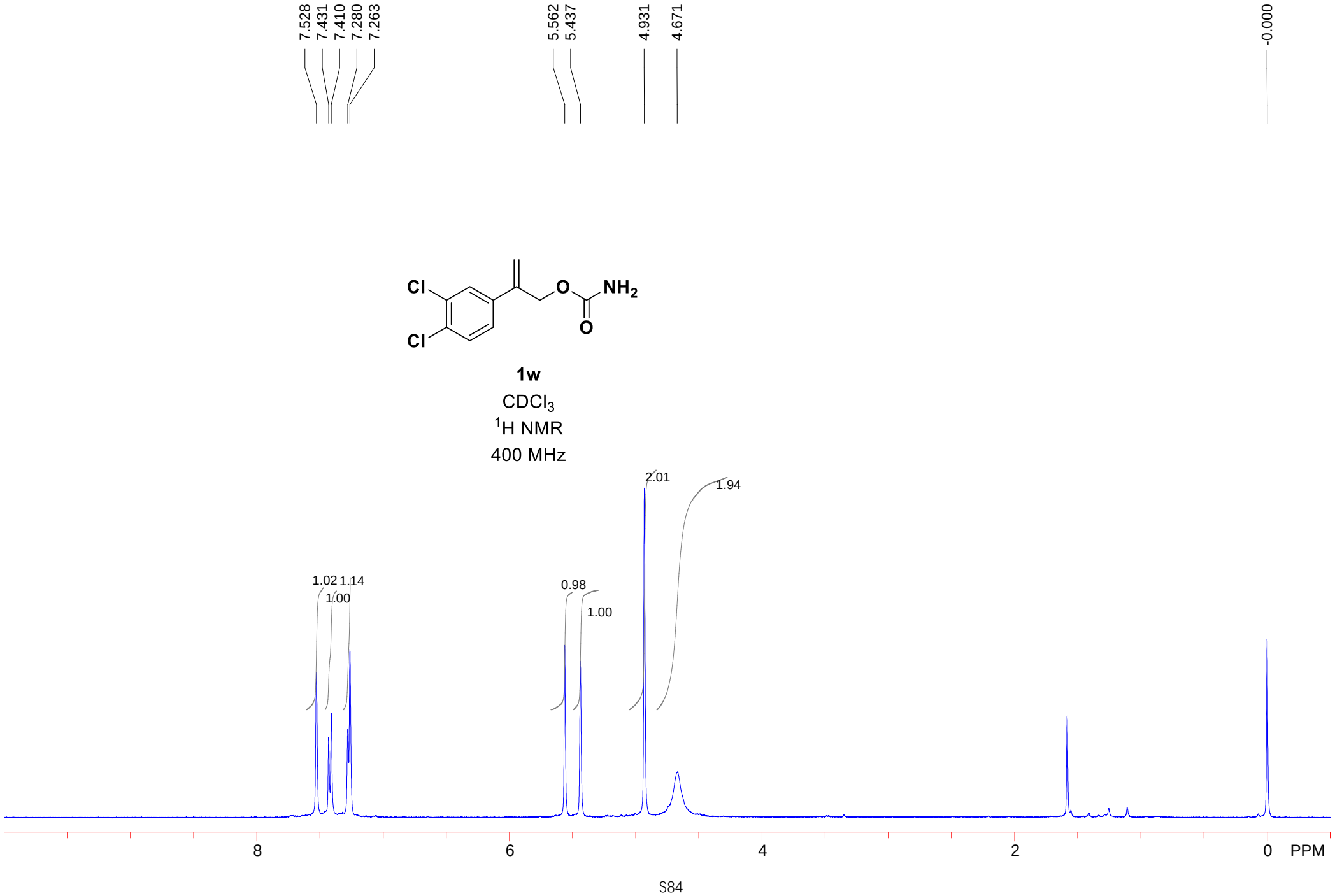
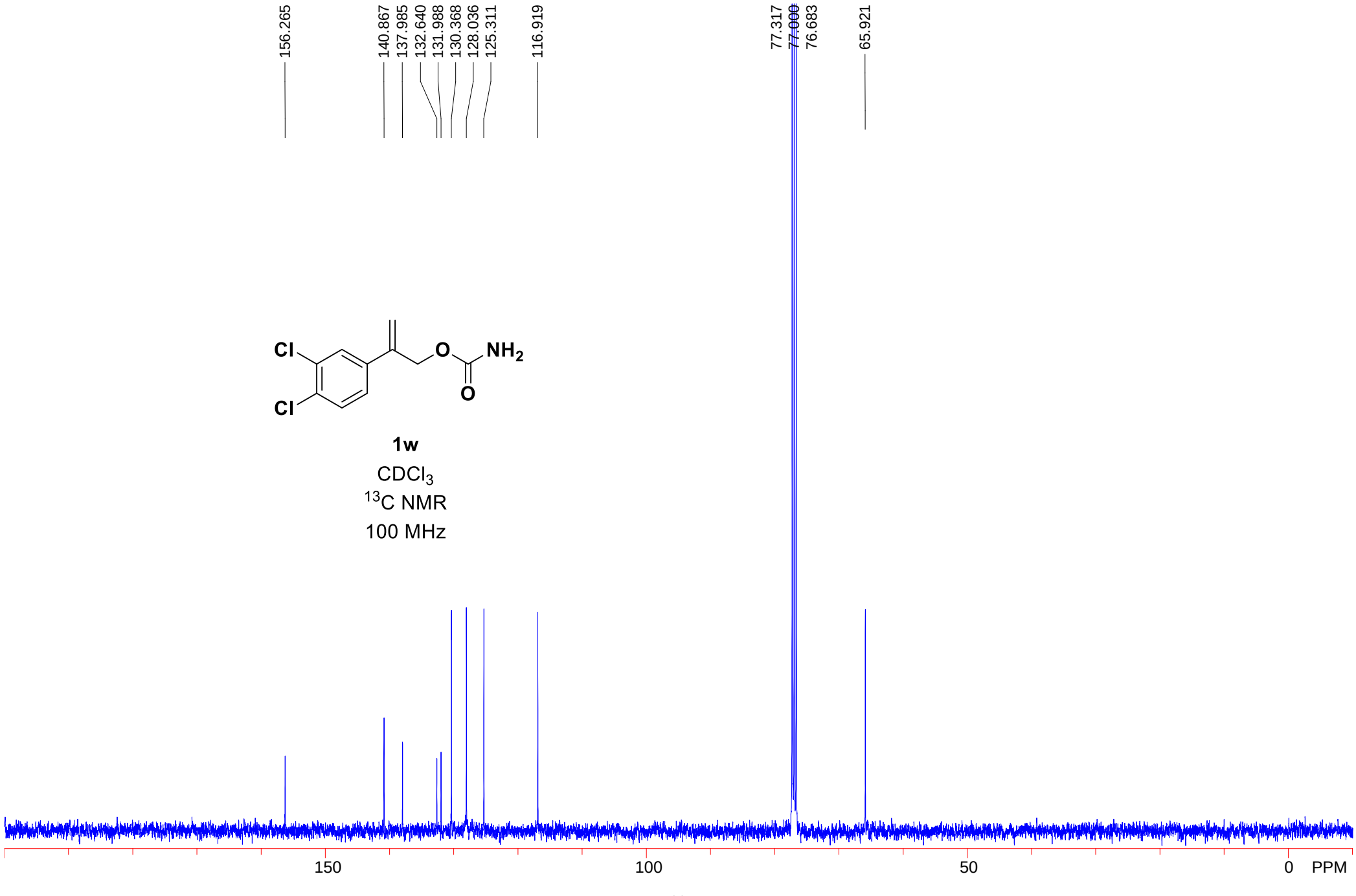
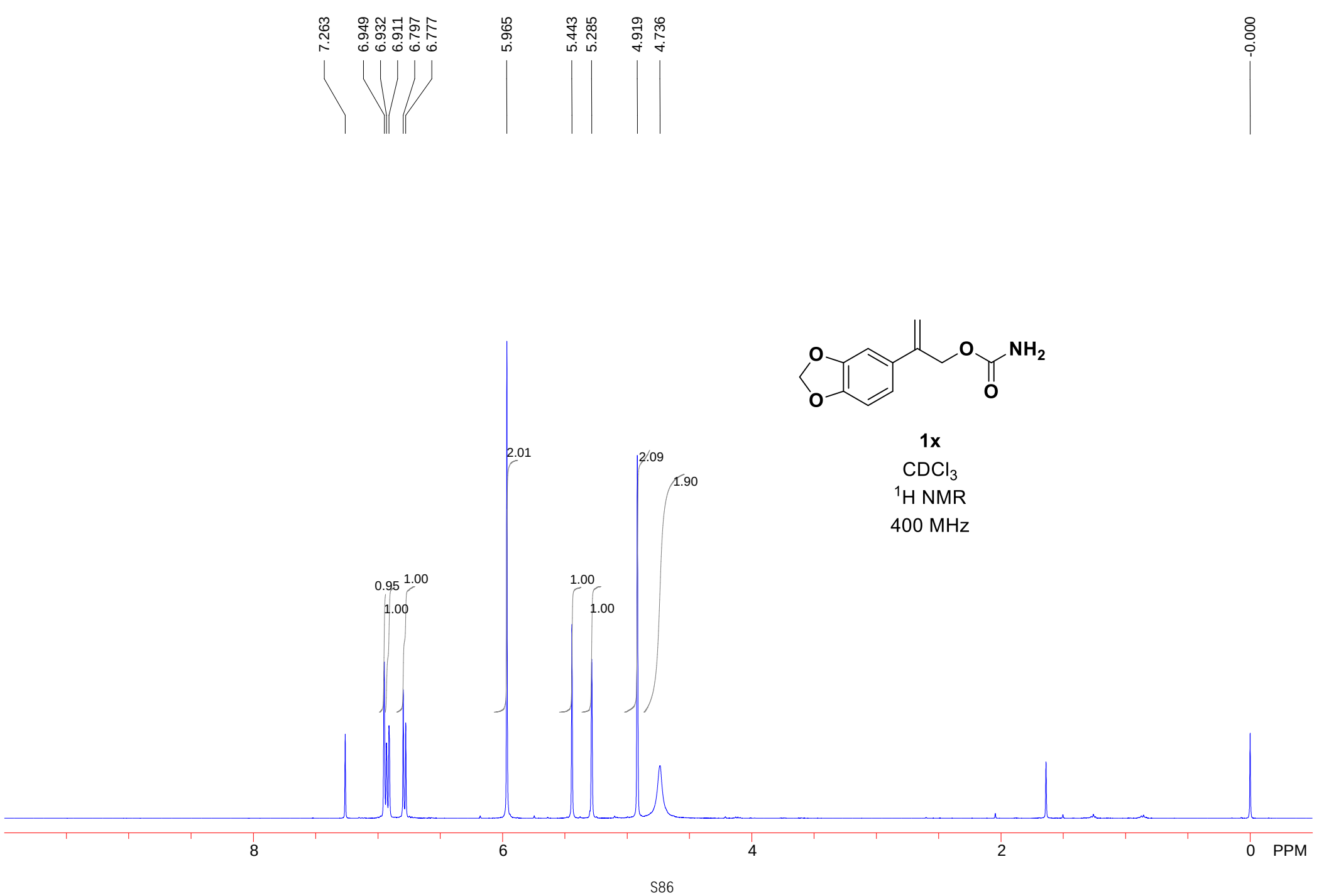
142.201
134.836
125.525
125.394
114.413
77.314
77.000
76.679
66.376
34.512
31.217
O
NH2
O
tBu
1u
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


7.574
7.557
7.555
7.507
7.458
7.447
7.437
7.429
7.411
7.387
7.369
7.352
7.235
5.612
5.394
4.980
4.785
-0.000
12.19
8.20
0.98
1.00
2.07
1.94
O
NH2
O
Si
1v
CDCl3
1H NMR
400 MHz
8
6
4
2
0
PPM


156.499
142.361
138.832
136.542
136.309
134.122
133.932
129.630
127.865
125.241
115.769
77.314
77.000
76.679
66.223
O
NH2
O
Si
1v
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


7.528
7.431
7.410
7.280
7.263
5.562
5.437
4.931
4.671
-0.000
Cl
Cl
O
NH2
O
1w
CDCl3
1H NMR
400 MHz
2.01
1.94
1.02
1.14
1.00
0.98
1.00
8
6
4
2
0
PPM


156.265
140.867
137.985
132.640
131.988
130.368
128.036
125.311
116.919
77.317
77.000
76.683
65.921
Cl
Cl
O
NH2
O
1w
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM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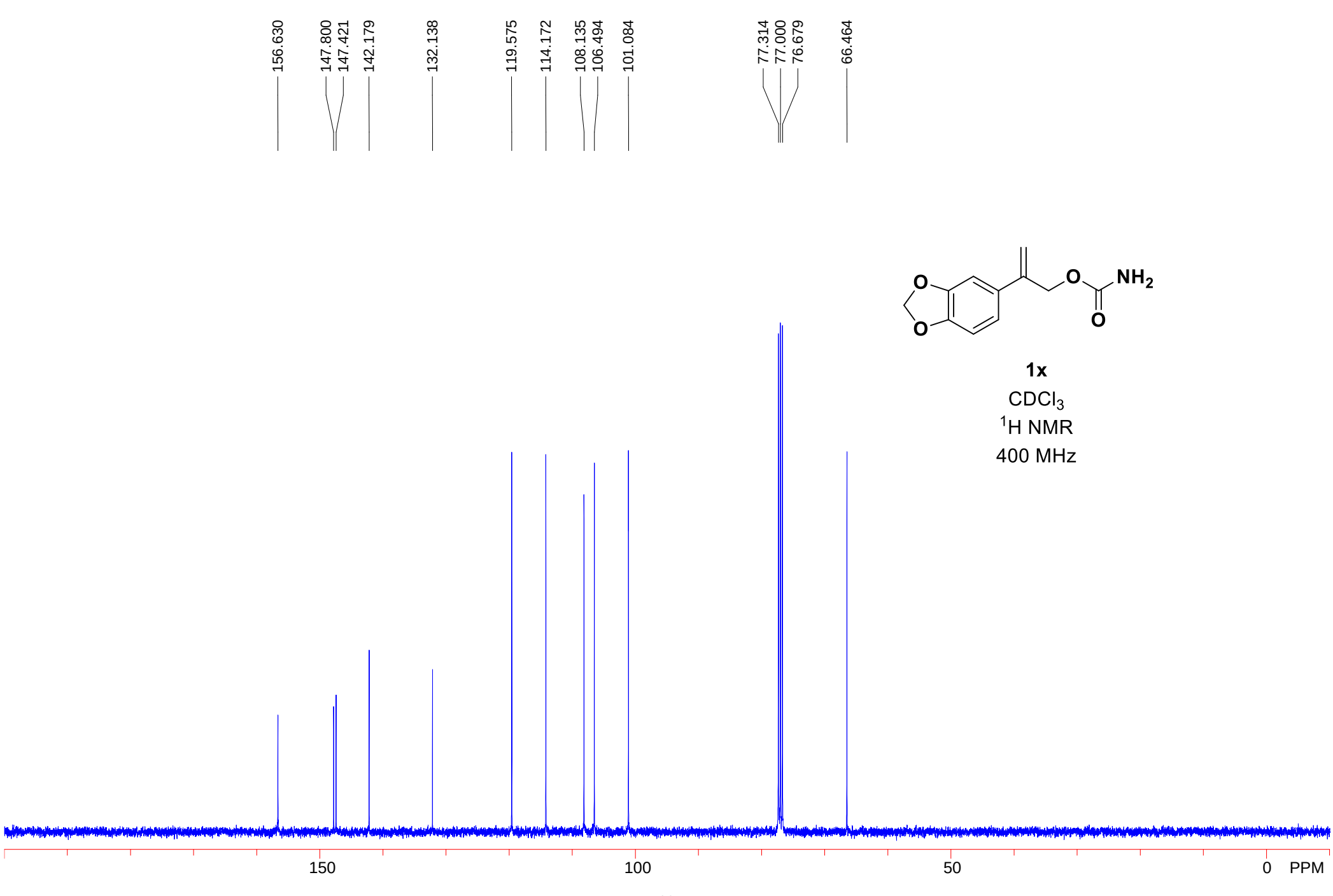
6.949
6.932
6.911
6.797
6.777
5.965
5.443
5.285
4.919
4.736
-0.000
O
O
O
O
NH2
1x
CDCl3
1H NMR
400 MHz
0.95
1.00
1.00
2.01
1.00
1.00
2.09
1.90
8
6
4
2
0
PPM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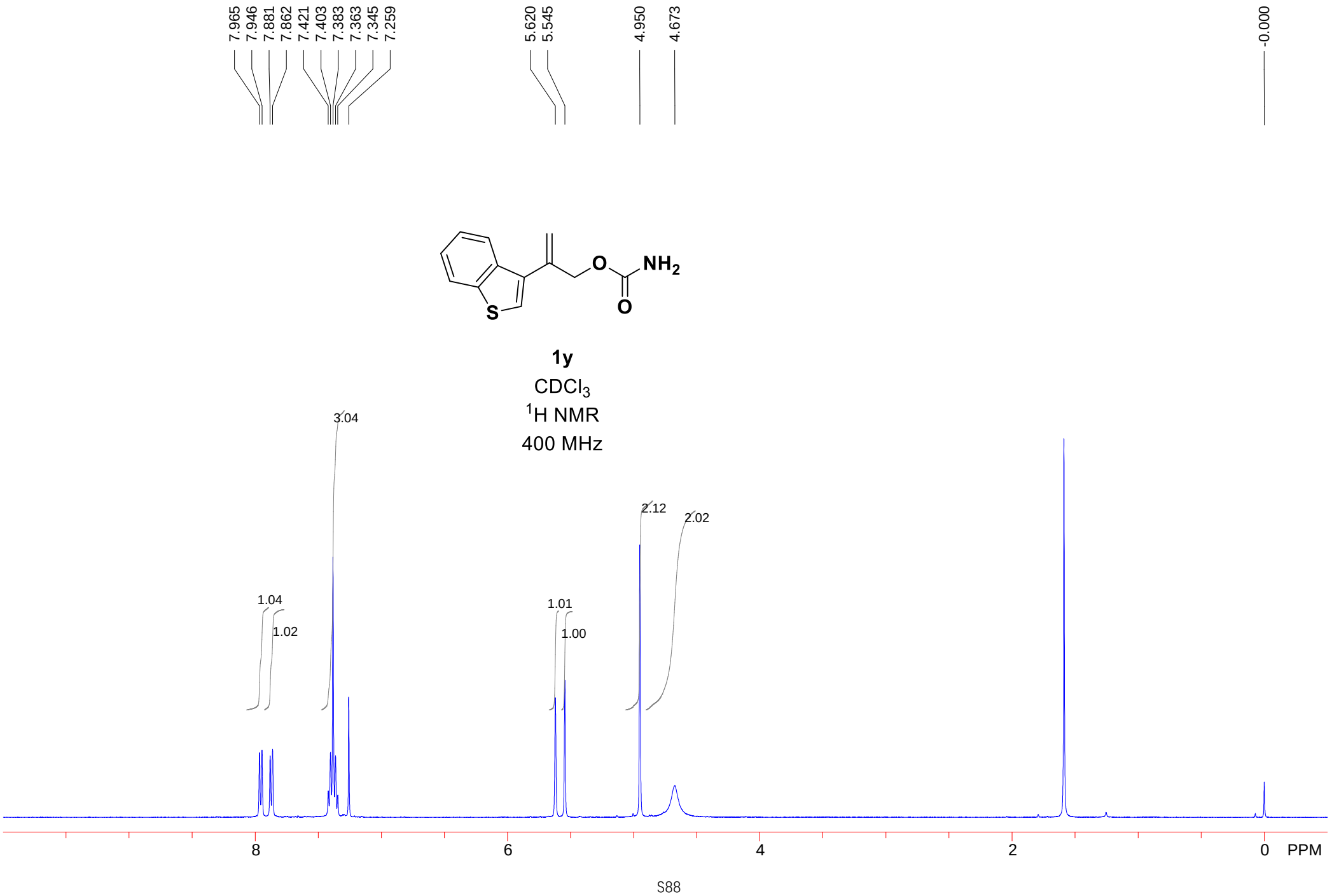
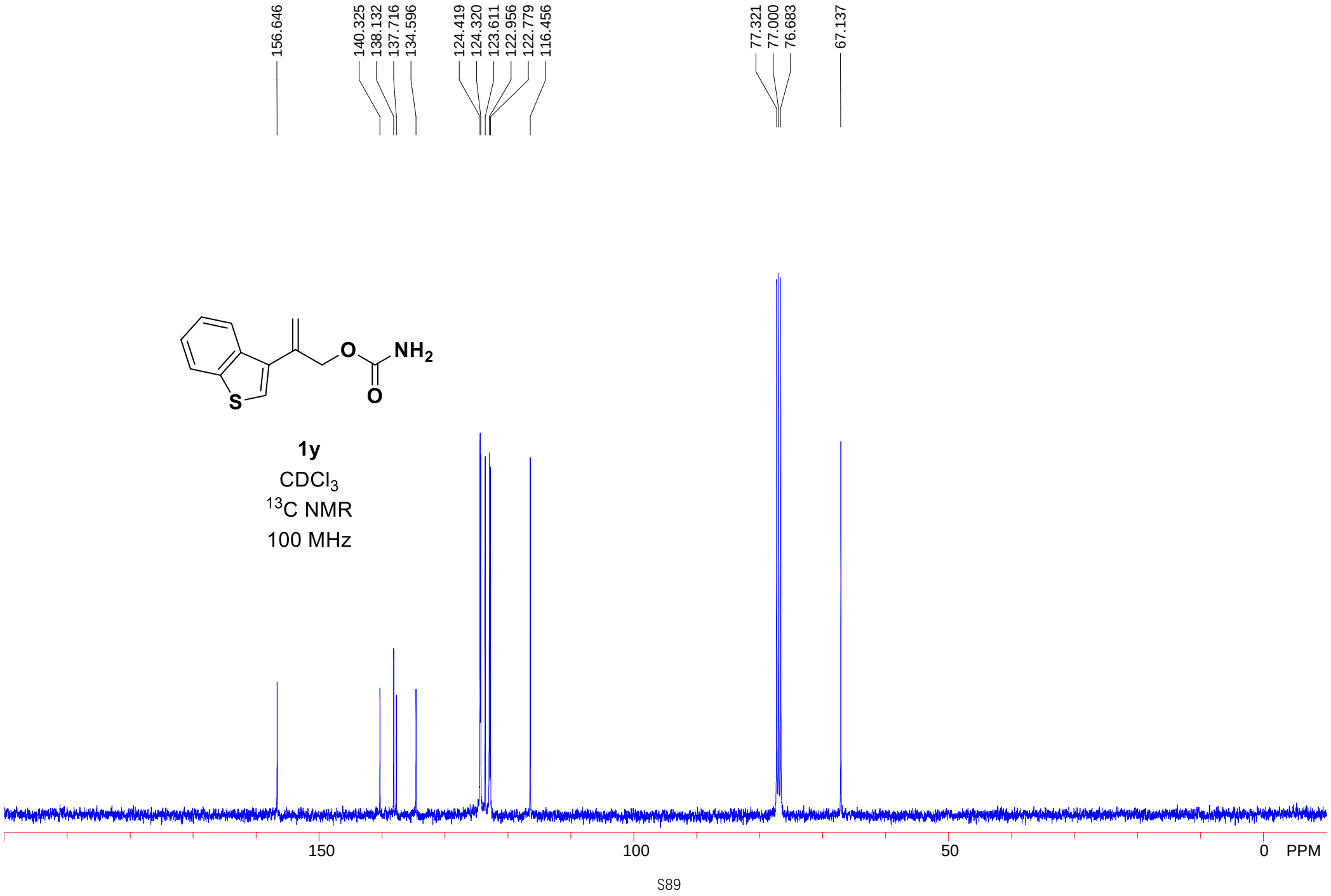
147.800
147.421
142.179
132.138
119.575
114.172
108.135
106.494
101.084
77.314
77.000
76.679
66.464
O
O
O
O
NH2
1x
CDCl3
1H NMR
400 MHz
150
100
50
0
PPM


7.965
7.946
7.881
7.862
7.421
7.403
7.383
7.363
7.345
7.259
5.620
5.545
4.950
4.673
-0.000
O
NH2
O
S
1y
CDCl3
1H NMR
400 MHz
3.04
2.12
2.02
1.04
1.02
1.01
1.00
8
6
4
2
0
PPM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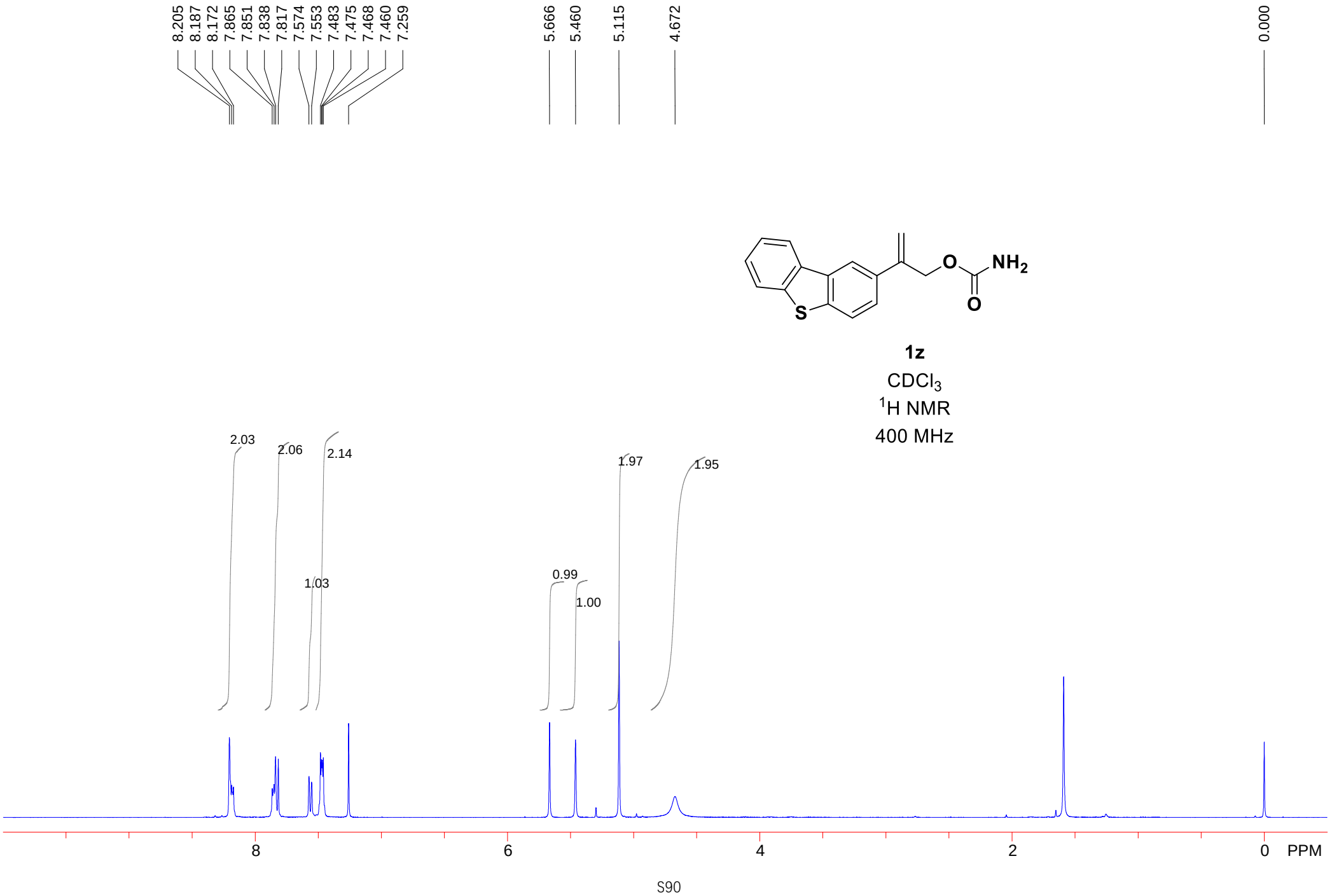
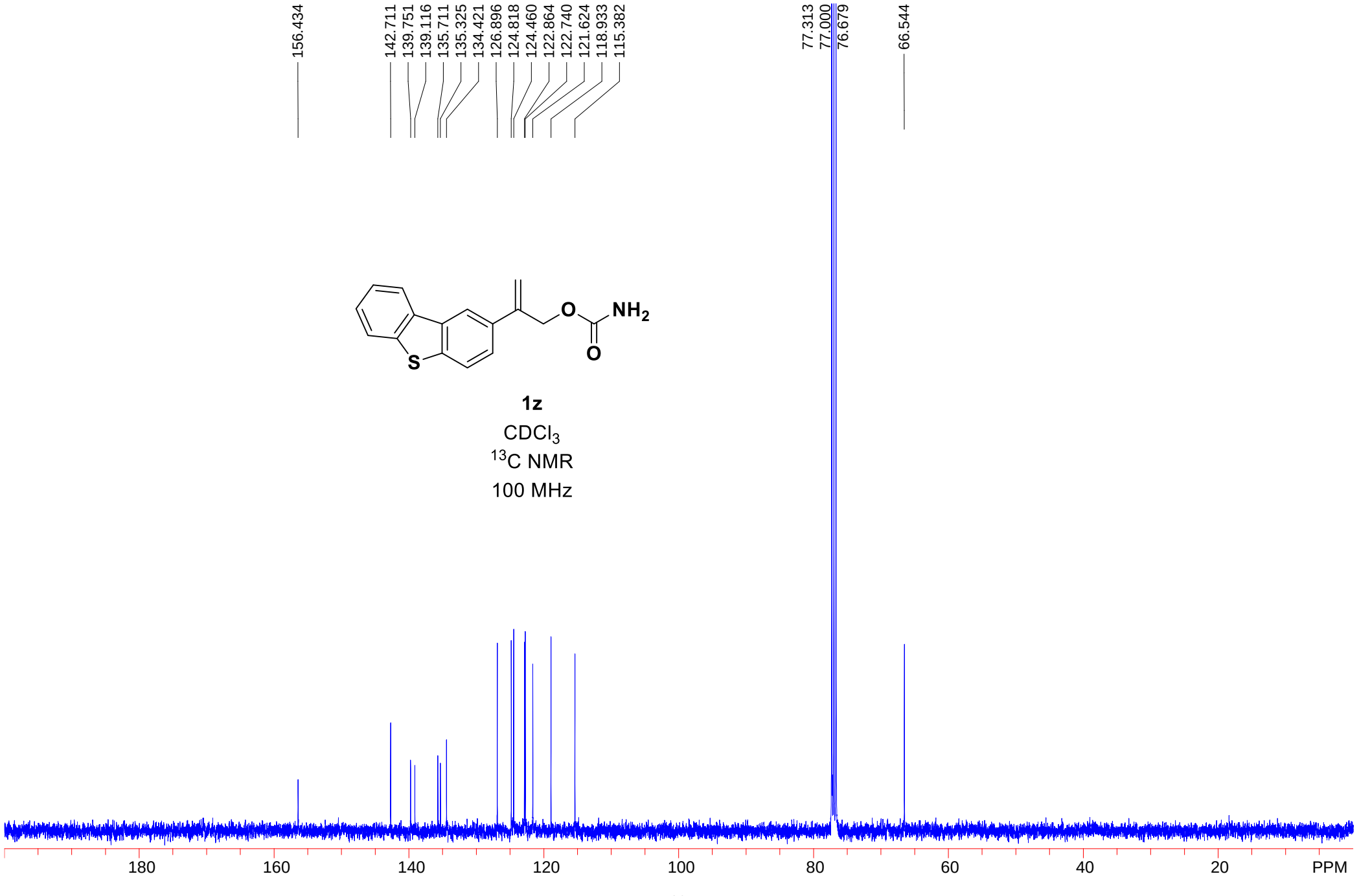
140.325
138.132
137.716
134.596
124.419
124.320
123.611
122.956
122.779
116.456
77.321
77.000
76.683
67.137
O
NH2
O
S
1y
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


8.205
8.187
8.172
7.865
7.851
7.838
7.817
7.574
7.553
7.483
7.475
7.468
7.460
7.259
5.666
5.460
5.115
4.672
0.000
O
NH2
O
S
1z
CDCl3
1H NMR
400 MHz
2.03
2.06
2.14
1.03
0.99
1.00
1.97
1.95
8
6
4
2
0
PPM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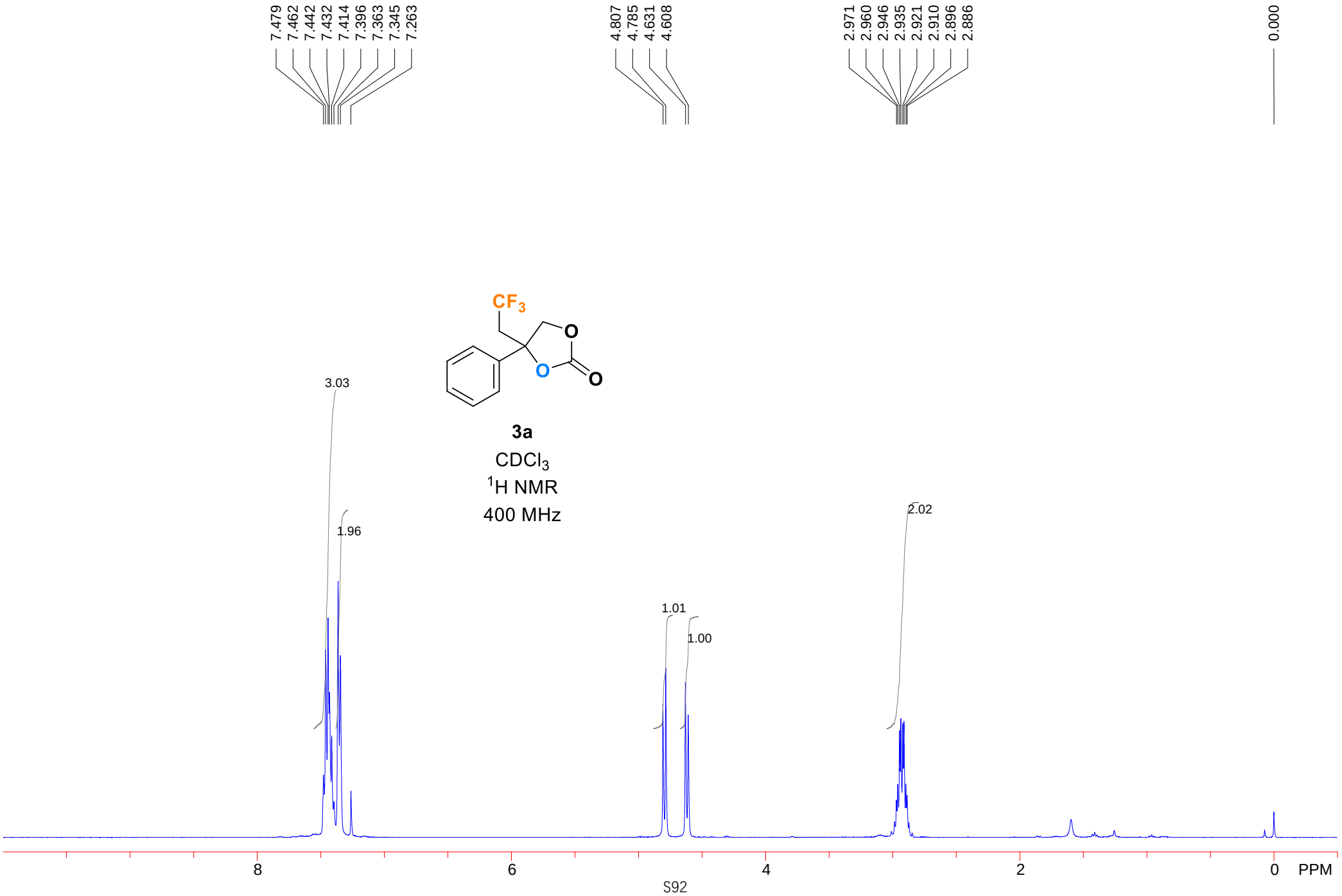
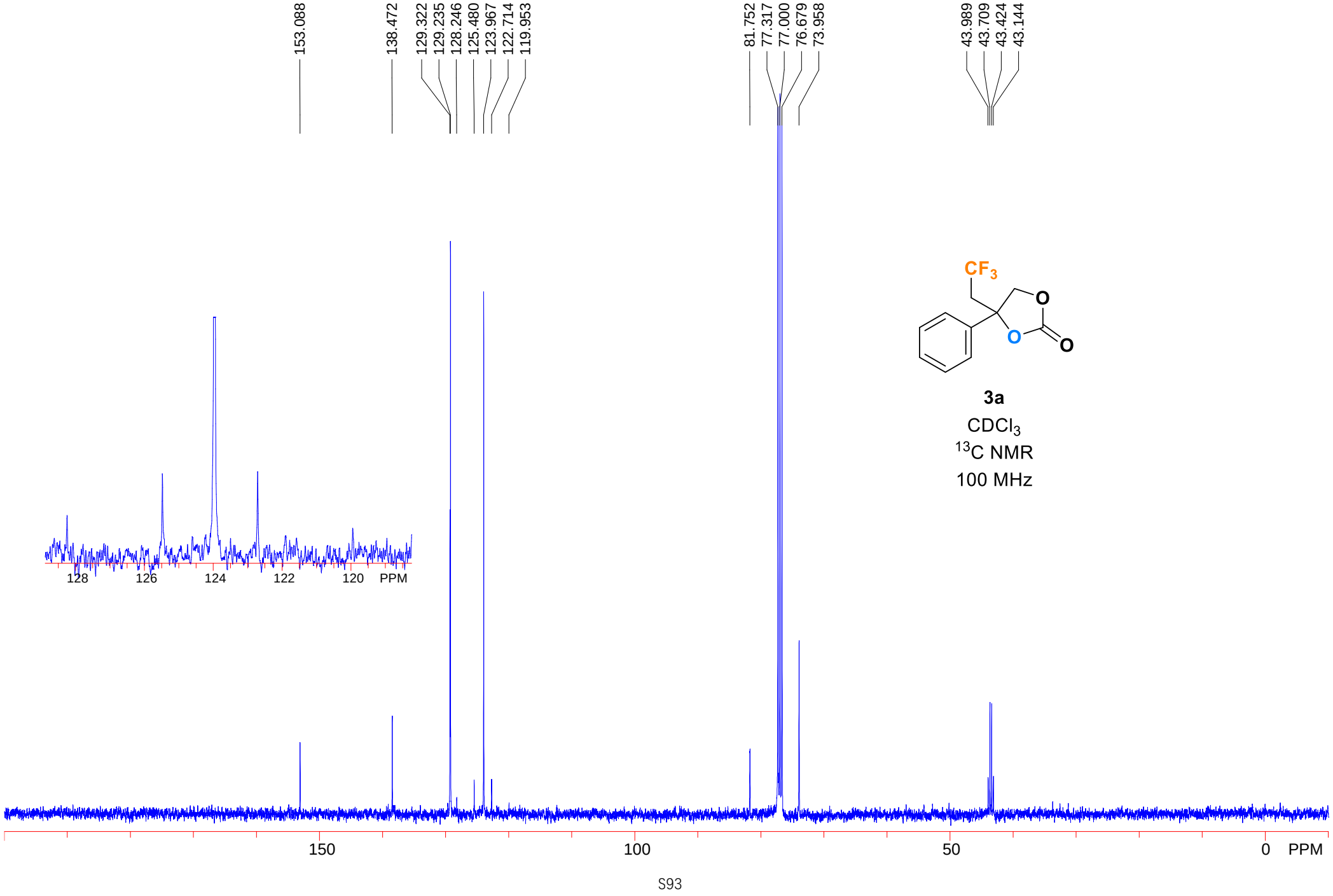
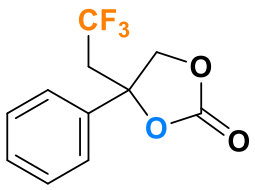
142.711
139.751
139.116
135.711
135.325
134.421
126.896
124.818
124.460
122.864
122.740
121.624
118.933
115.382
77.313
77.000
76.679
66.544
O
NH2
O
S
1z
CDCl3
13C NMR
100 MHz
180
160
140
120
100
80
60
40
20
PPM


7.479
7.462
7.442
7.432
7.414
7.396
7.363
7.345
7.263
4.807
4.785
4.631
4.608
2.971
2.960
2.946
2.935
2.921
2.910
2.896
2.886
0.000
CF3
O
O
O
3a
CDCl3
1H NMR
400 MHz
3.03
1.96
1.01
1.00
2.02
8
6
4
2
0
PPM


153.088
138.472
129.322
129.235
128.246
125.480
123.967
122.714
119.953
81.752
77.317
77.000
76.679
73.958
43.989
43.709
43.424
43.144
CF3
O
O
O
3a
CDCl3
13C NMR
100 MHz
128
126
124
122
120
PPM
150
100
50
0
PPM

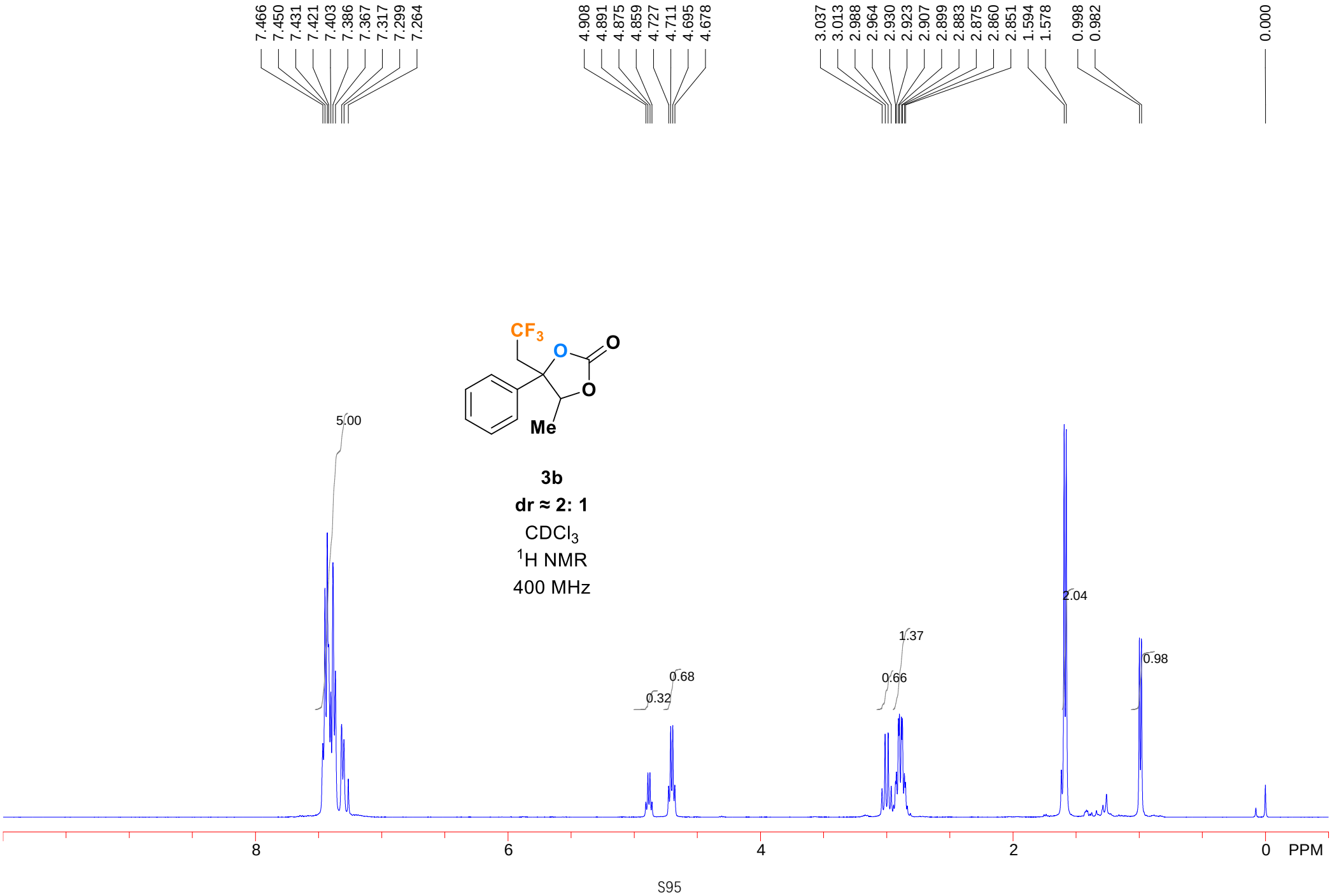


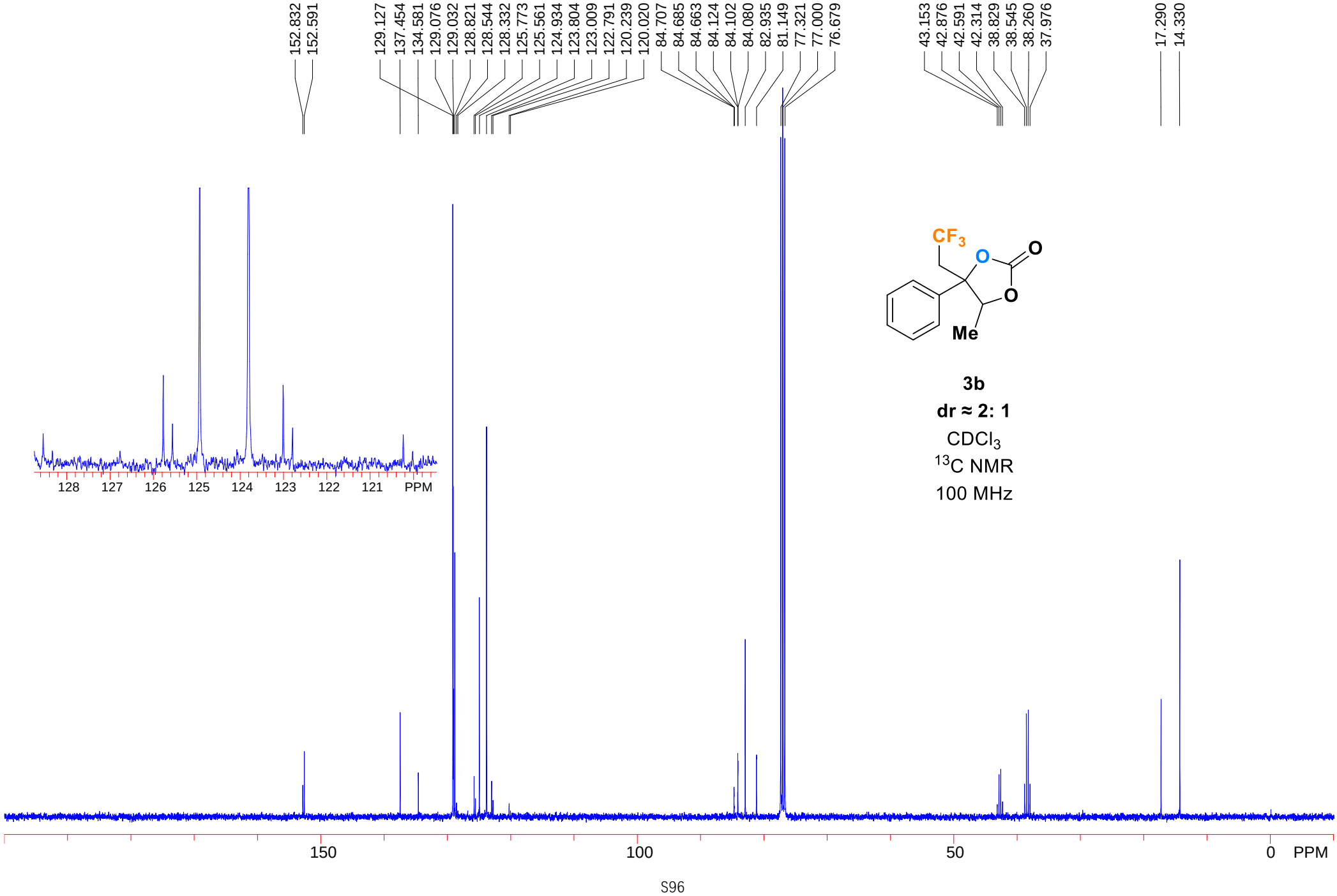
3a

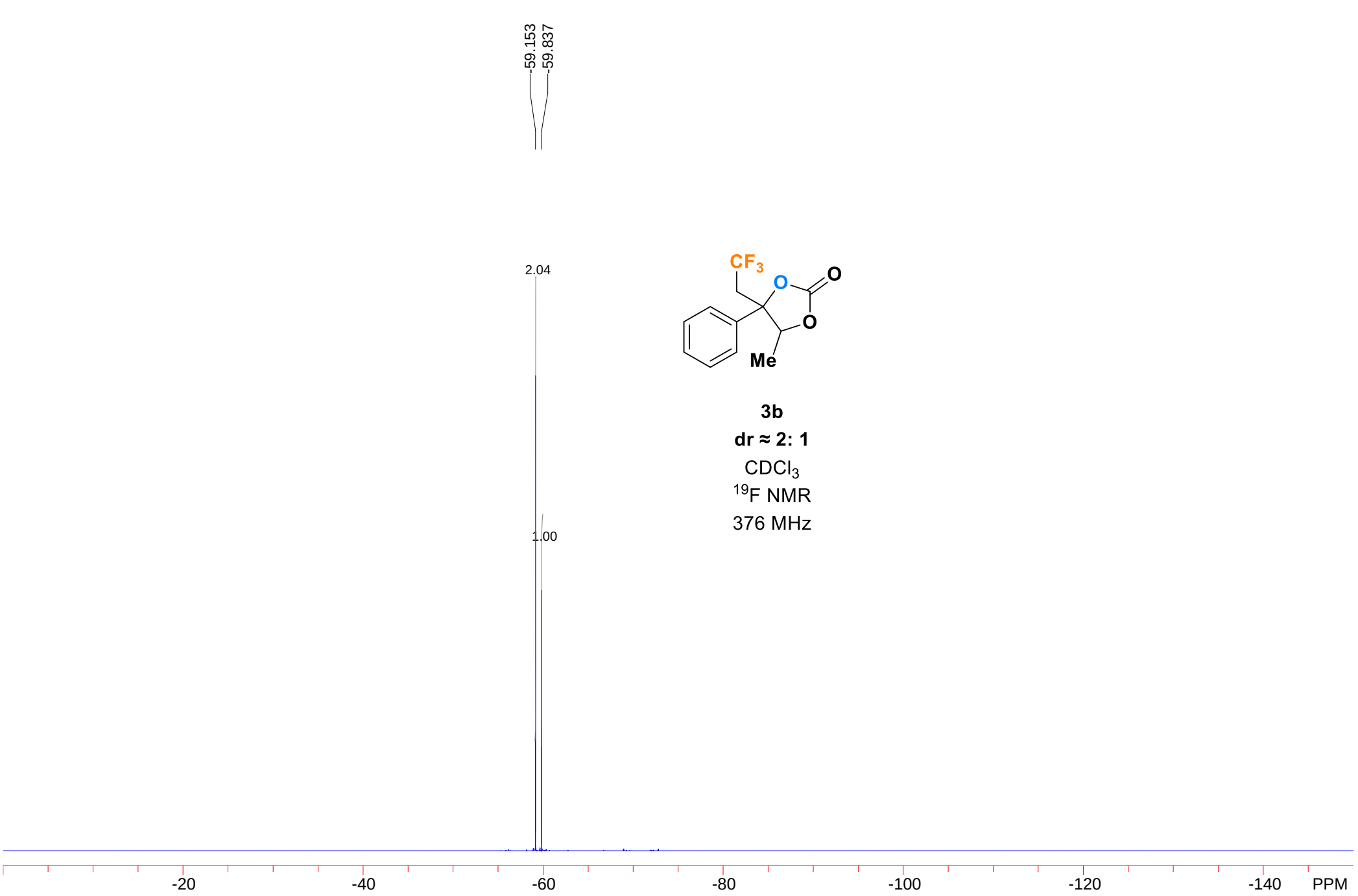
$CDCl_3$

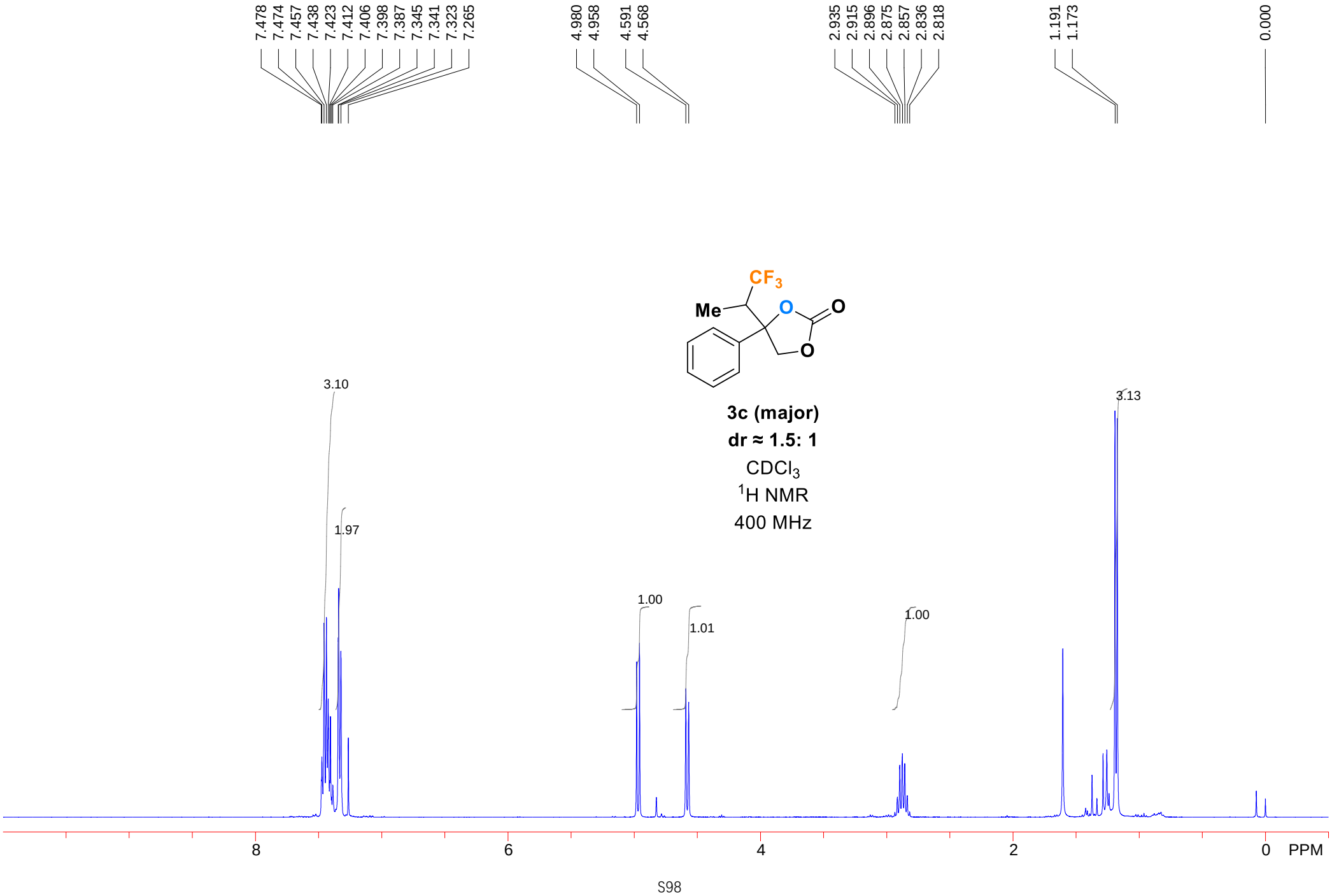
^{19}F NMR

376 MHz


7.466
7.450
7.431
7.421
7.403
7.386
7.367
7.317
7.299
7.264
4.908
4.891
4.875
4.859
4.727
4.711
4.695
4.678
3.037
3.013
2.988
2.964
2.930
2.923
2.907
2.899
2.883
2.875
2.860
2.851
1.594
1.578
0.998
0.982
0.000
CF3
O
O
O
Me
3b
dr ≈ 2: 1
CDCl3
1H NMR
400 MHz
5.00
0.68
0.32
1.37
0.66
2.04
0.98
8
6
4
2
0
PPM


152.832
152.591
129.127
137.454
134.581
129.076
129.032
128.821
128.544
128.332
125.773
125.561
124.934
123.804
123.009
122.791
120.239
120.020
84.707
84.685
84.663
84.124
84.102
84.080
82.935
81.149
77.321
77.000
76.679
43.153
42.876
42.591
42.314
38.829
38.545
38.260
37.976
17.290
14.330
128
127
126
125
124
123
122
121
PPM
CF3
O
O
O
Me
3b
dr ≈ 2: 1
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


-59.153
-59.837
2.04
1.00
CF3
O
O
O
Me
3b
dr ≈ 2: 1
CDCl3
19F NMR
376 MHz
-20
-40
-60
-80
-100
-120
-140
PPM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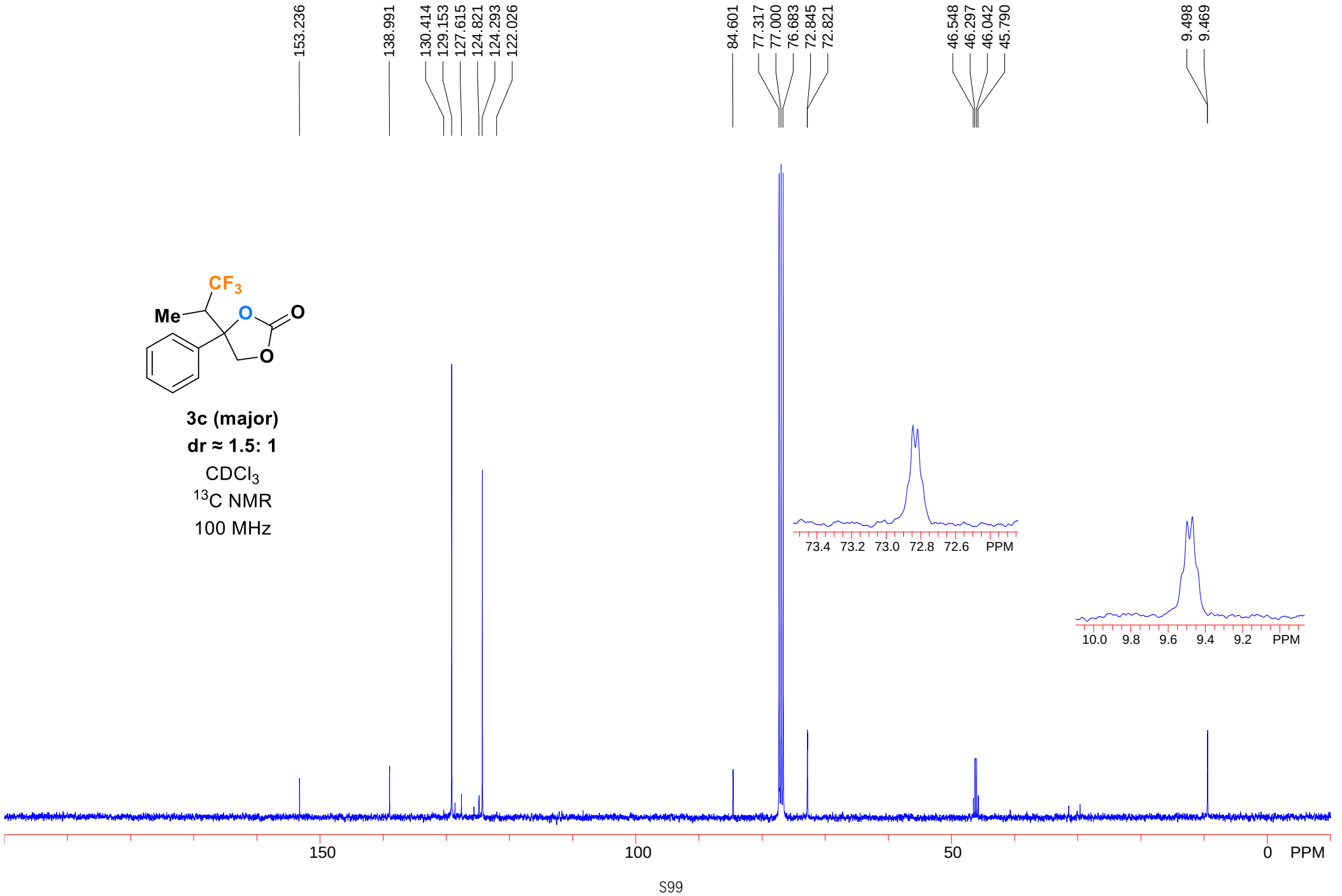
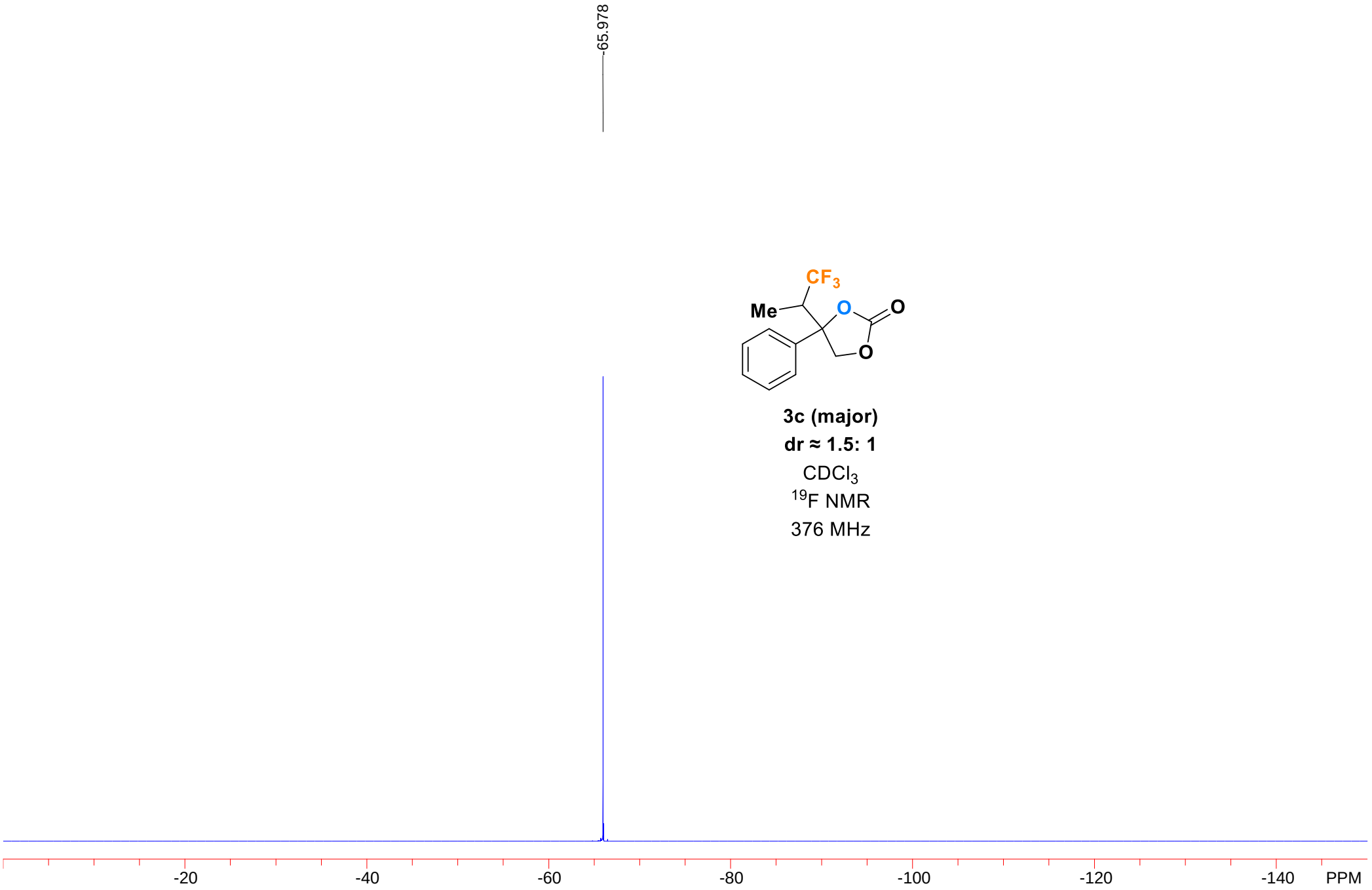
7.474
7.457
7.438
7.423
7.412
7.406
7.398
7.387
7.345
7.341
7.323
7.265
4.980
4.958
4.591
4.568
2.935
2.915
2.896
2.875
2.857
2.836
2.818
1.191
1.173
0.000
CF3
Me
O
O
O
3c (major)
dr ≈ 1.5: 1
CDCl3
1H NMR
400 MHz
3.10
1.97
1.00
1.01
1.00
3.13
8
6
4
2
0
PPM


153.236
138.991
130.414
129.153
127.615
124.821
124.293
122.026
84.601
77.317
77.000
76.683
72.845
72.821
46.548
46.297
46.042
45.790
9.498
9.469
CF3
Me
O
O
O
3c (major)
dr ≈ 1.5: 1
CDCl3
13C NMR
100 MHz
73.4 73.2 73.0 72.8 72.6 PPM
10.0 9.8 9.6 9.4 9.2 PPM
150
100
50
0 PPM



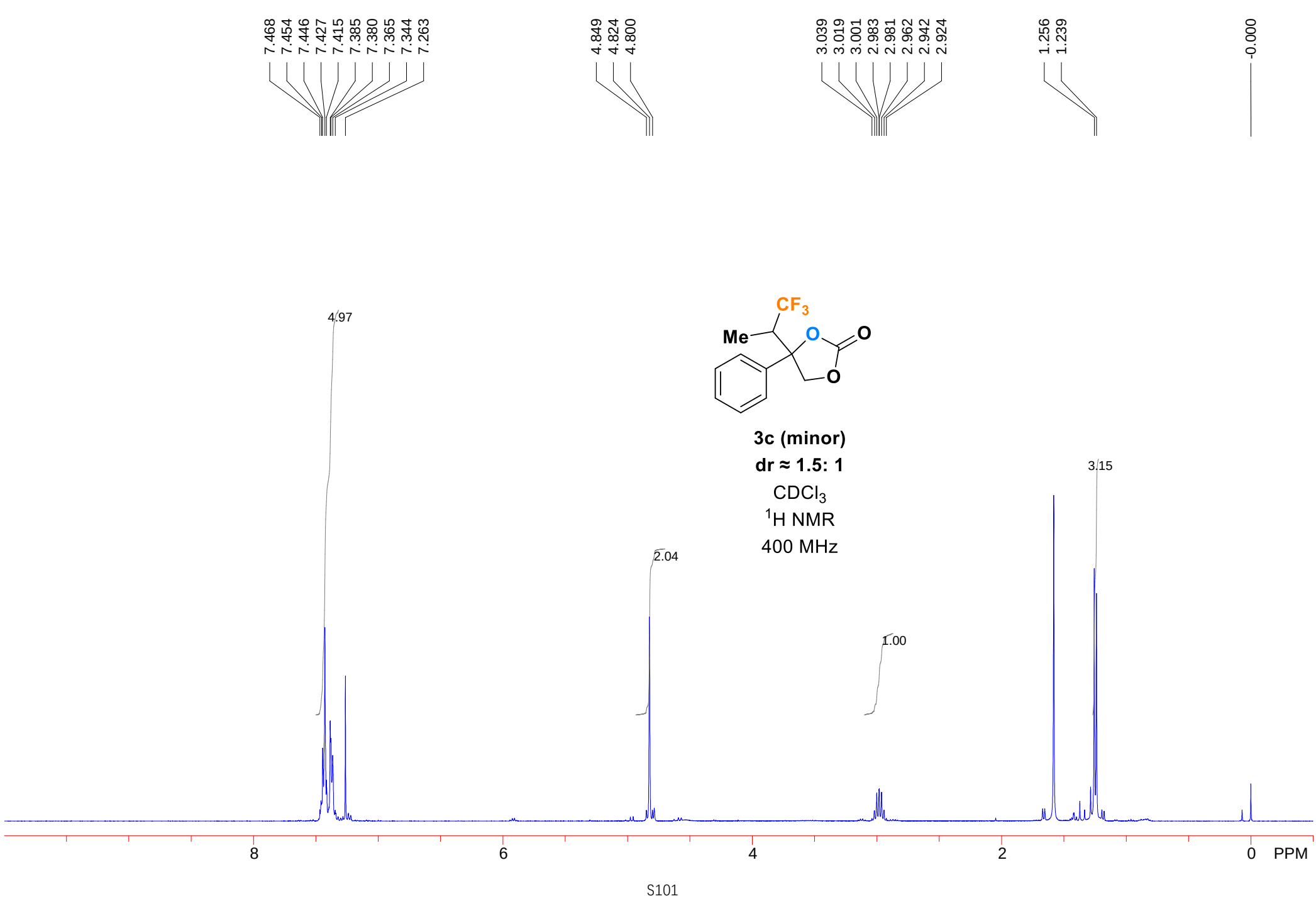
3c (major)

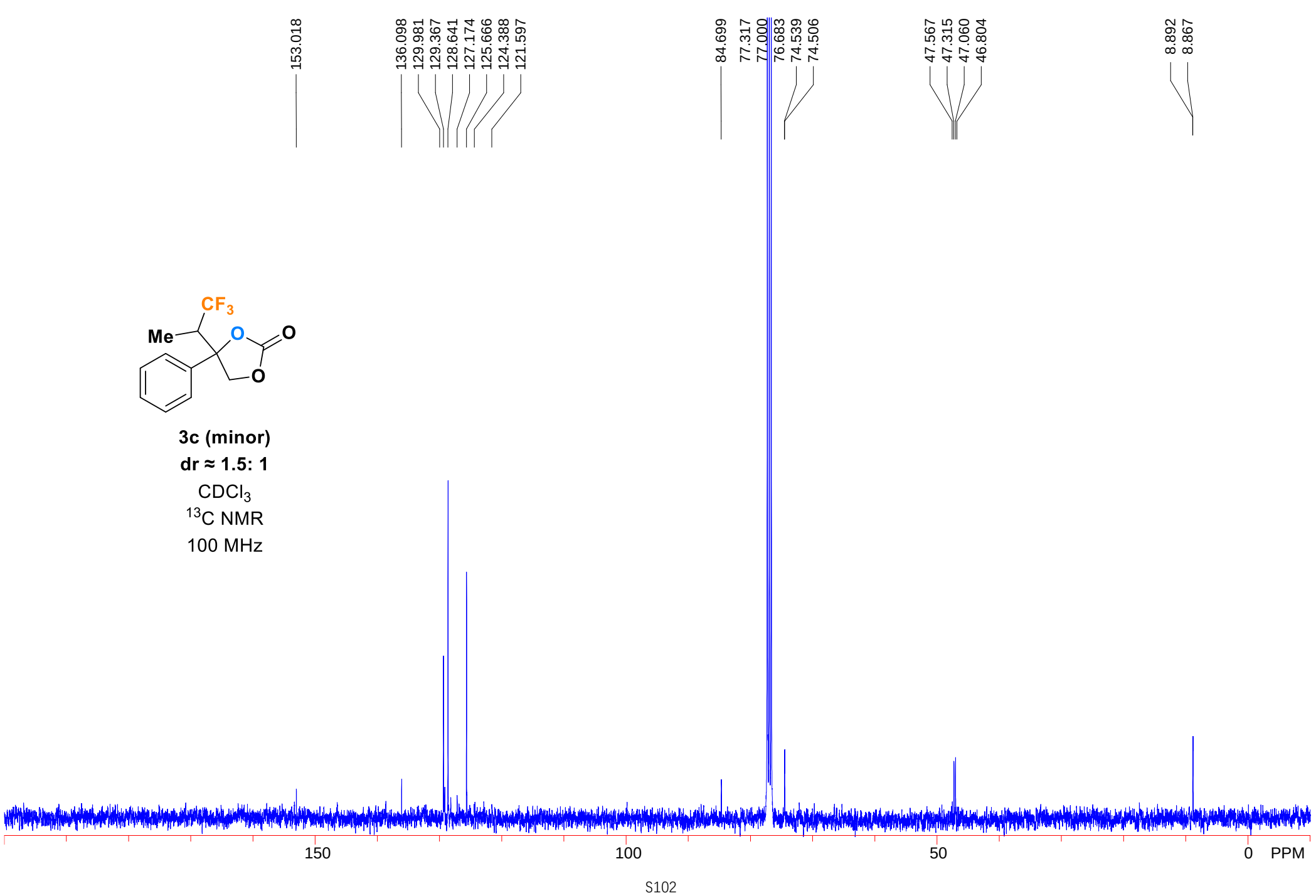
dr ≈ 1.5: 1

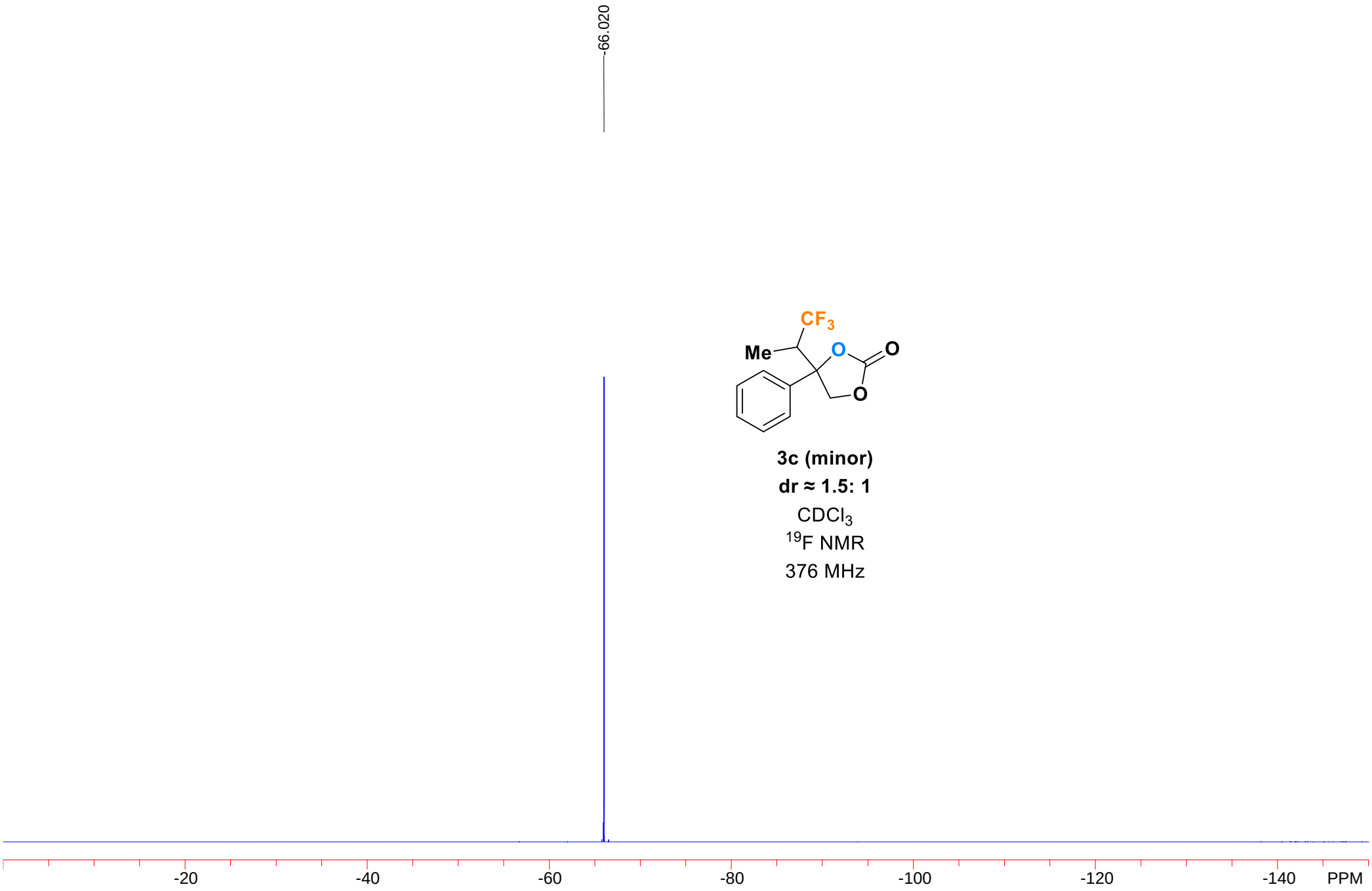
$CDCl_3$

^{19}F NMR

376 MHz


7.468
7.454
7.446
7.427
7.415
7.385
7.380
7.365
7.344
7.263
4.849
4.824
4.800
3.039
3.019
3.001
2.983
2.981
2.962
2.942
2.924
1.256
1.239
-0.000
4.97
2.04
1.00
3.15
CF3
Me
O
O
O
3c (minor)
dr ≈ 1.5: 1
CDCl3
1H NMR
400 MHz
8
6
4
2
0
PPM


153.018
136.098
129.981
129.367
128.641
127.174
125.666
124.388
121.597
84.699
77.317
77.000
76.683
74.539
74.506
47.567
47.315
47.060
46.804
8.892
8.867
CF3
Me
O
O
O
3c (minor)
dr ≈ 1.5: 1
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM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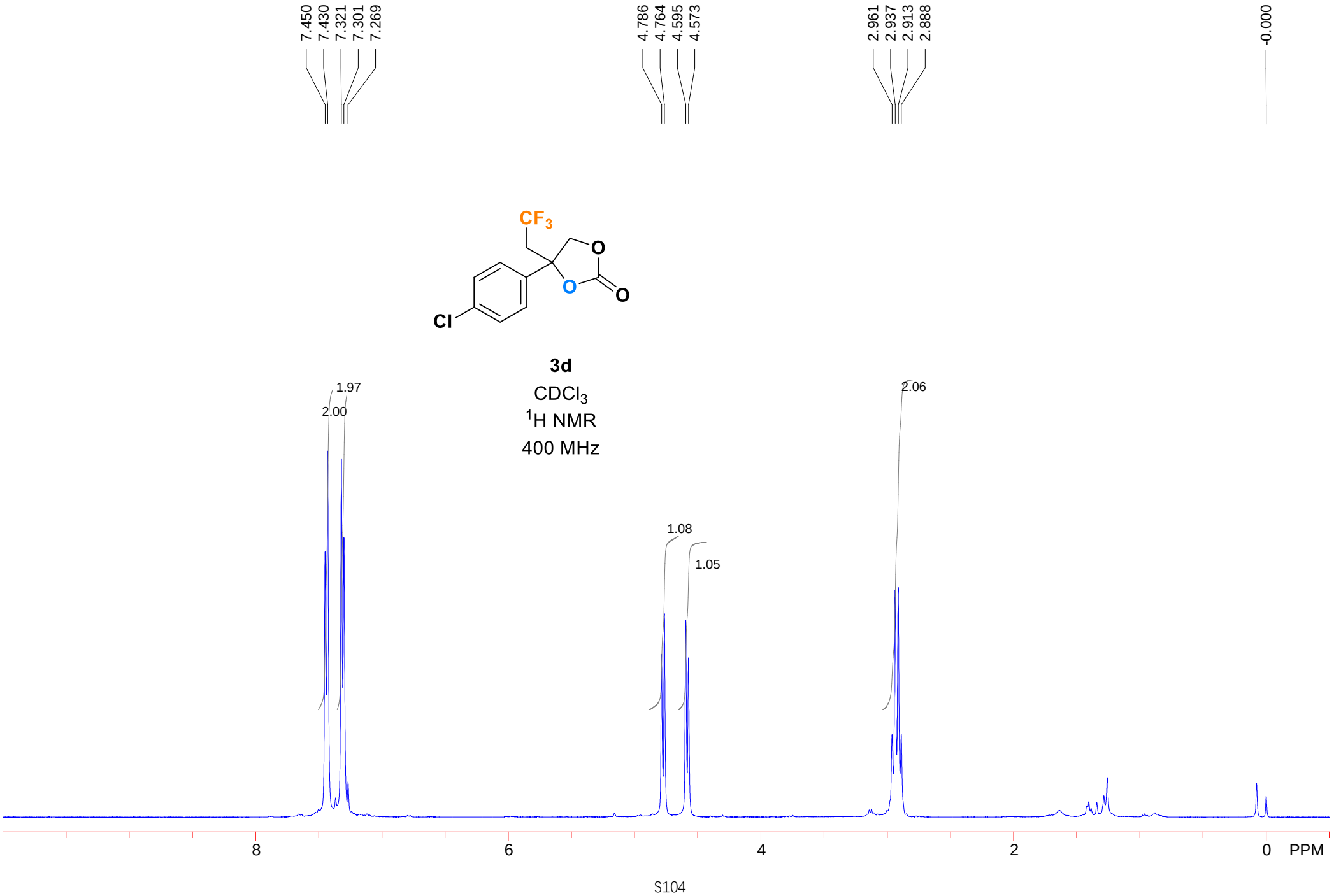
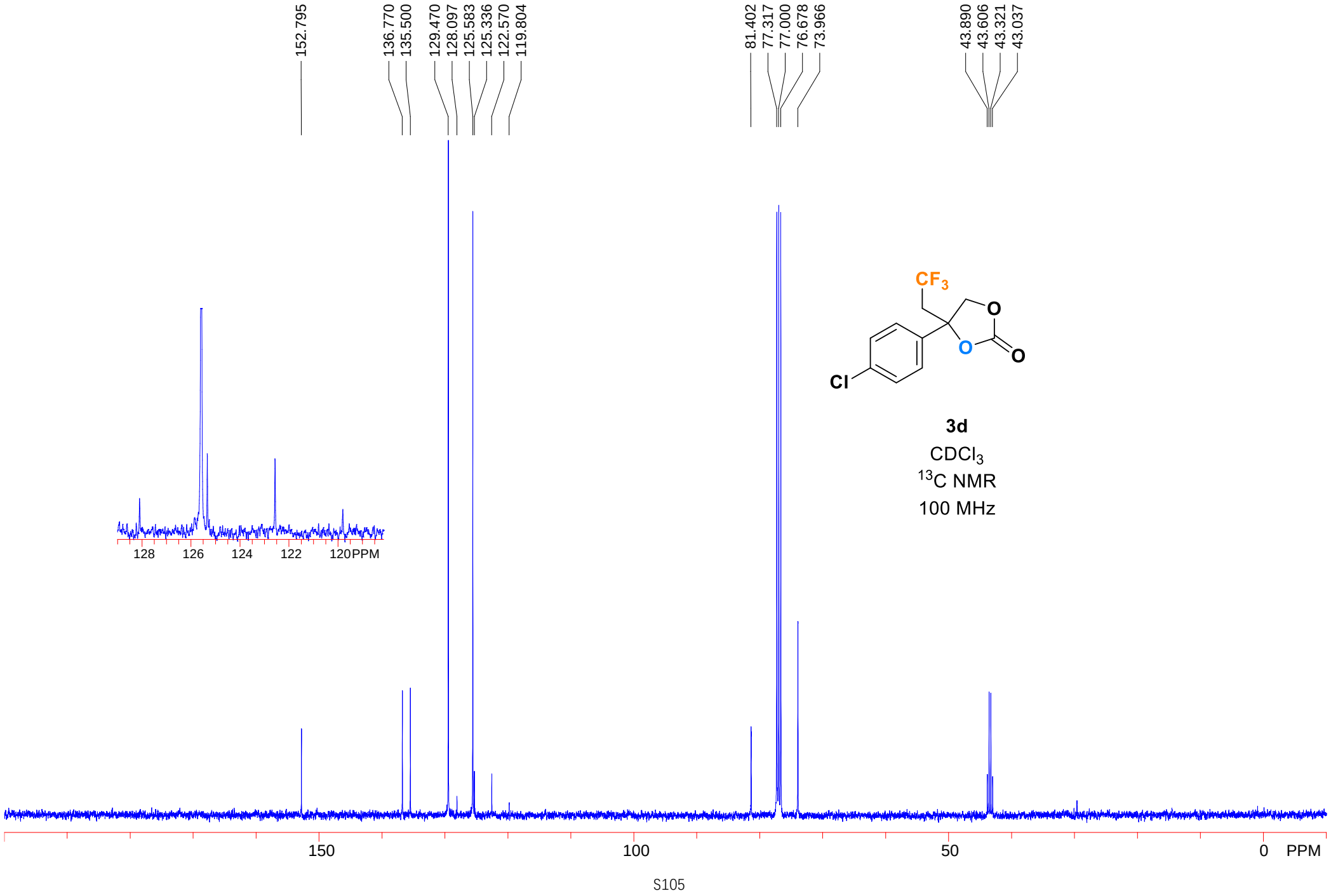
Me
O
O
O
3c (minor)
dr ≈ 1.5: 1
CDCl3
19F NMR
376 MHz
-20
-40
-60
-80
-100
-120
-140
PPM


7.450
7.430
7.321
7.301
7.269
4.786
4.764
4.595
4.573
2.961
2.937
2.913
2.888
-0.000
CF3
O
O
O
Cl
3d
CDCl3
1H NMR
400 MHz
1.97
2.00
1.08
1.05
2.06
8
6
4
2
0
PPM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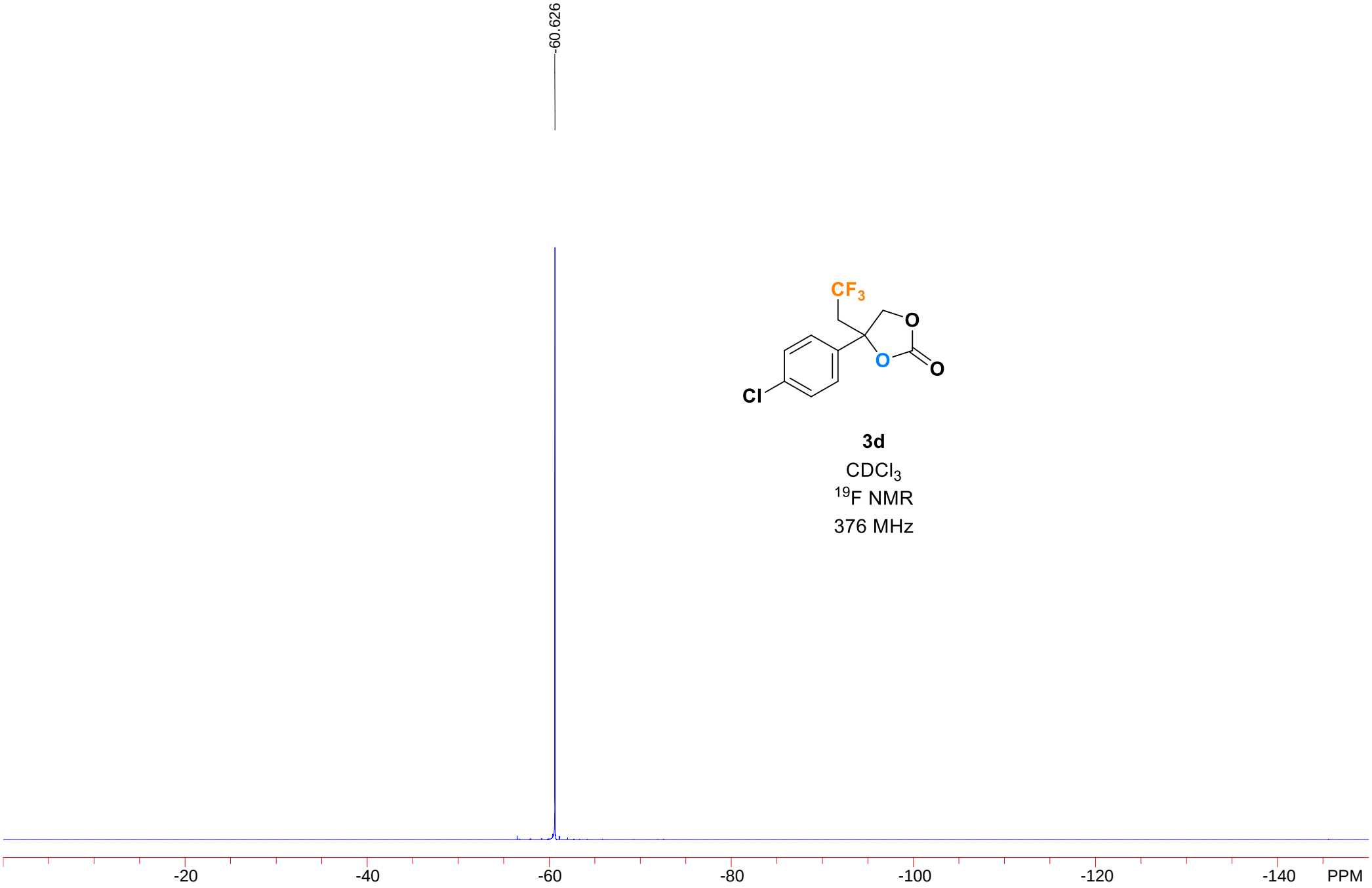
129.470
128.097
125.583
125.336
122.570
119.804
81.402
77.317
77.000
76.678
73.966
43.890
43.606
43.321
43.037
128
126
124
122
120PPM
CF3
O
O
O
Cl
3d
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM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Cl
3d
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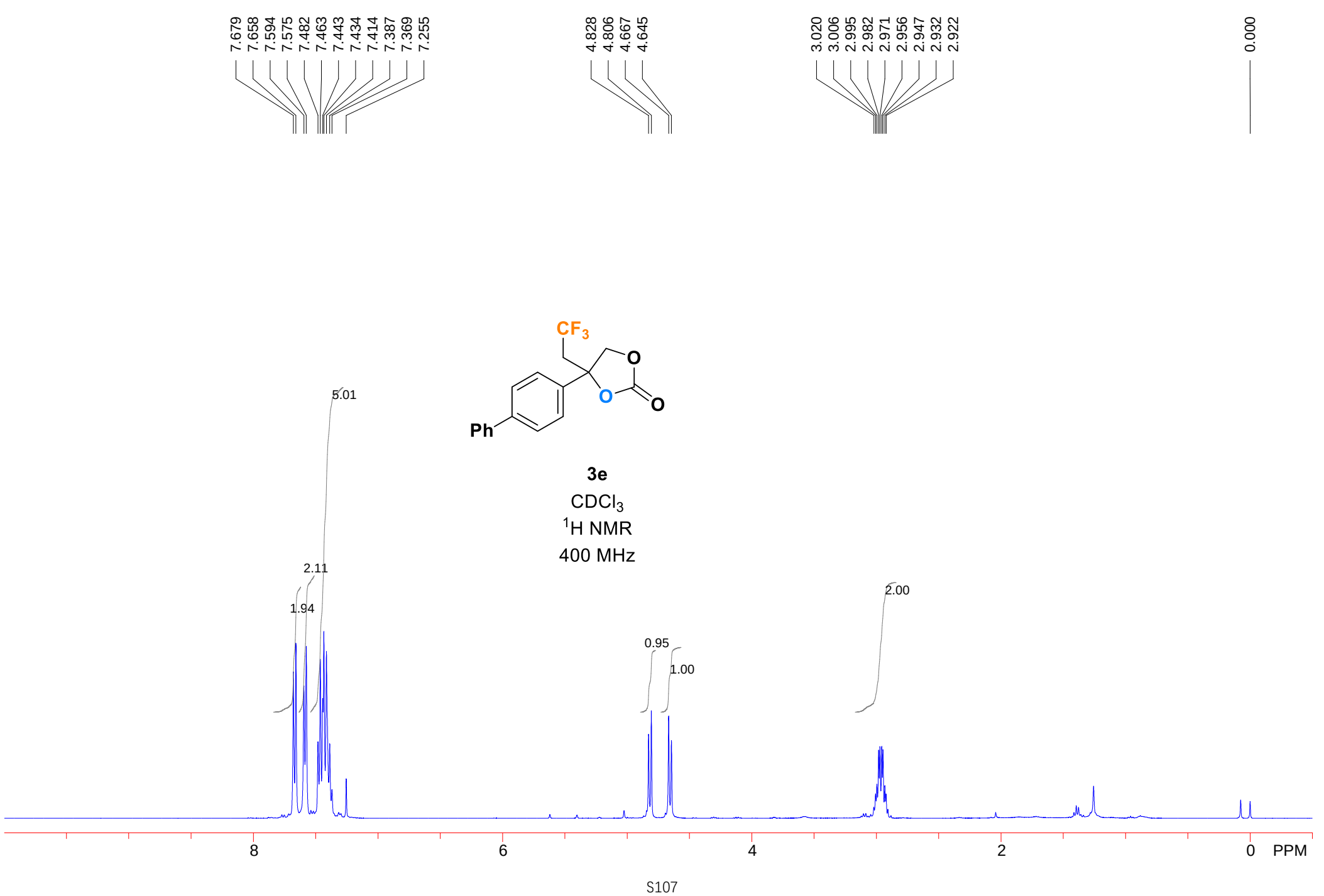
19F NMR
376 MHz
-20
-40
-60
-80
-100
-120
-140
PPM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7.658
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7.575
7.482
7.463
7.443
7.434
7.414
7.387
7.369
7.255
4.828
4.806
4.667
4.645
3.020
3.006
2.995
2.982
2.971
2.956
2.947
2.932
2.922
0.000
CF3
O
O
O
Ph
3e
CDCl3
1H NMR
400 MHz
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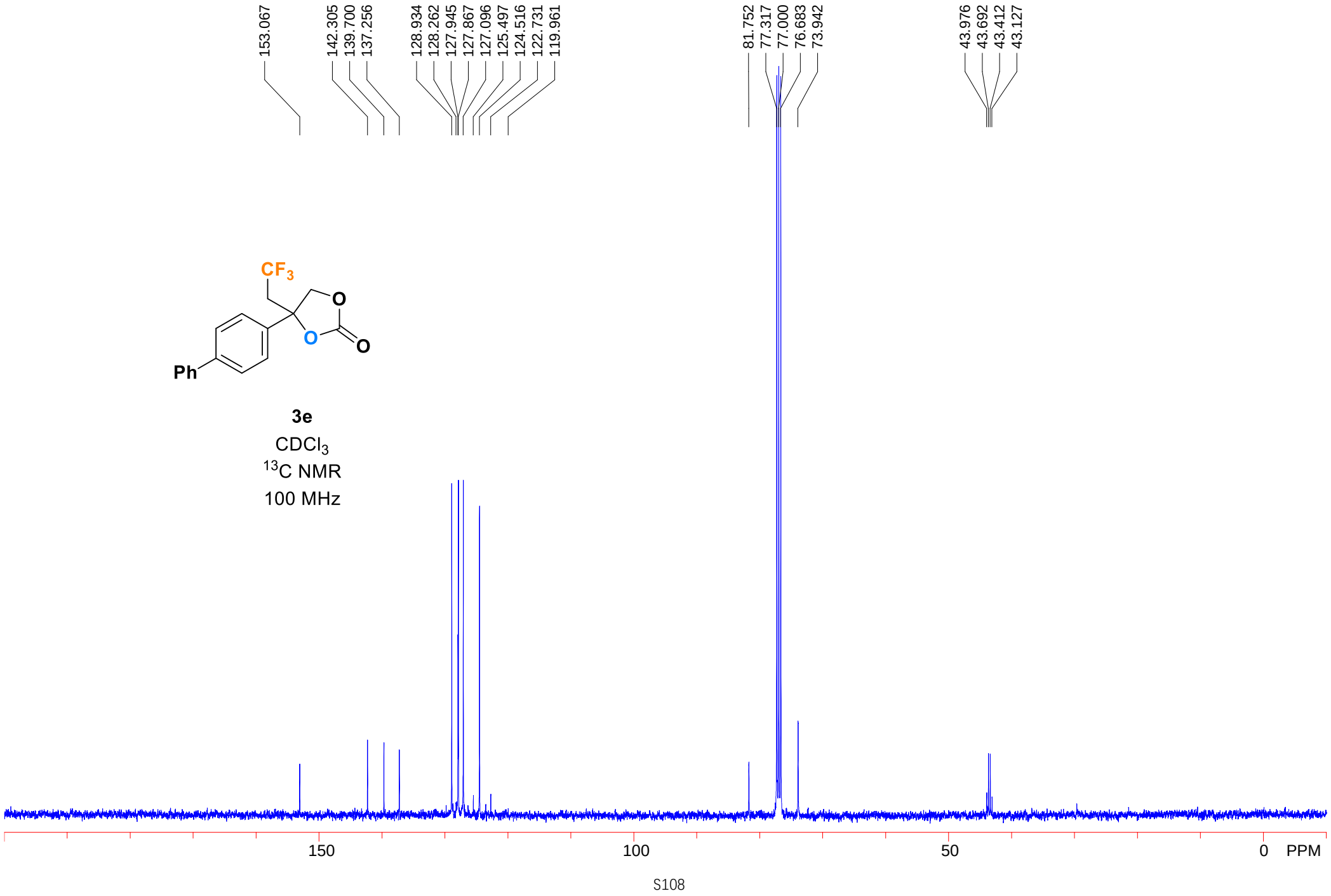
2.11
1.94
0.95
1.00
2.00
8
6
4
2
0
PPM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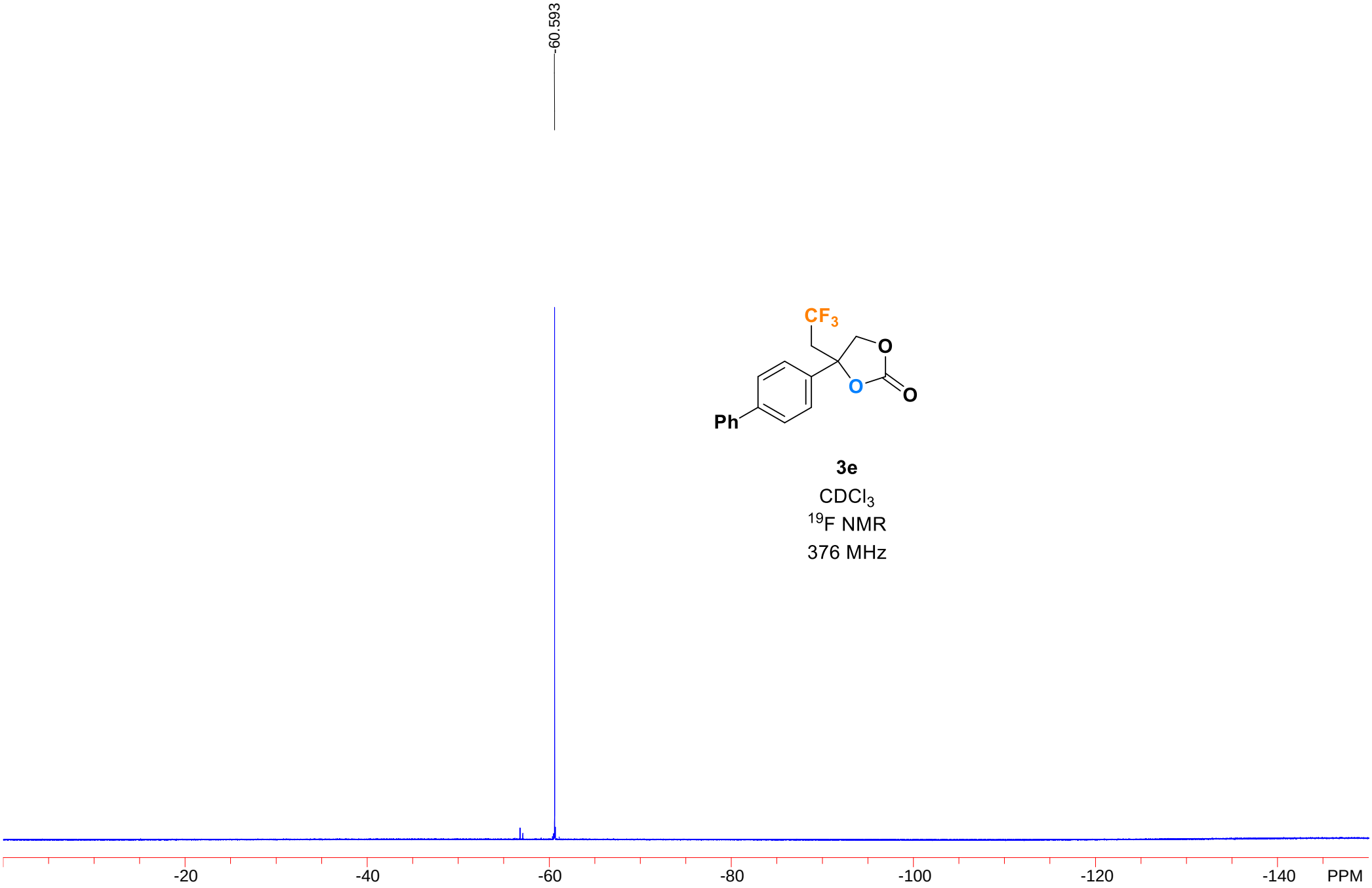
142.305
139.700
137.256
128.934
128.262
127.945
127.867
127.096
125.497
124.516
122.731
119.961
81.752
77.317
77.000
76.683
73.942
43.976
43.692
43.412
43.127
CF3
O
O
O
Ph
3e
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM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CF3
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Ph
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CDCl3
19F NMR
376 MHz
-20
-40
-60
-80
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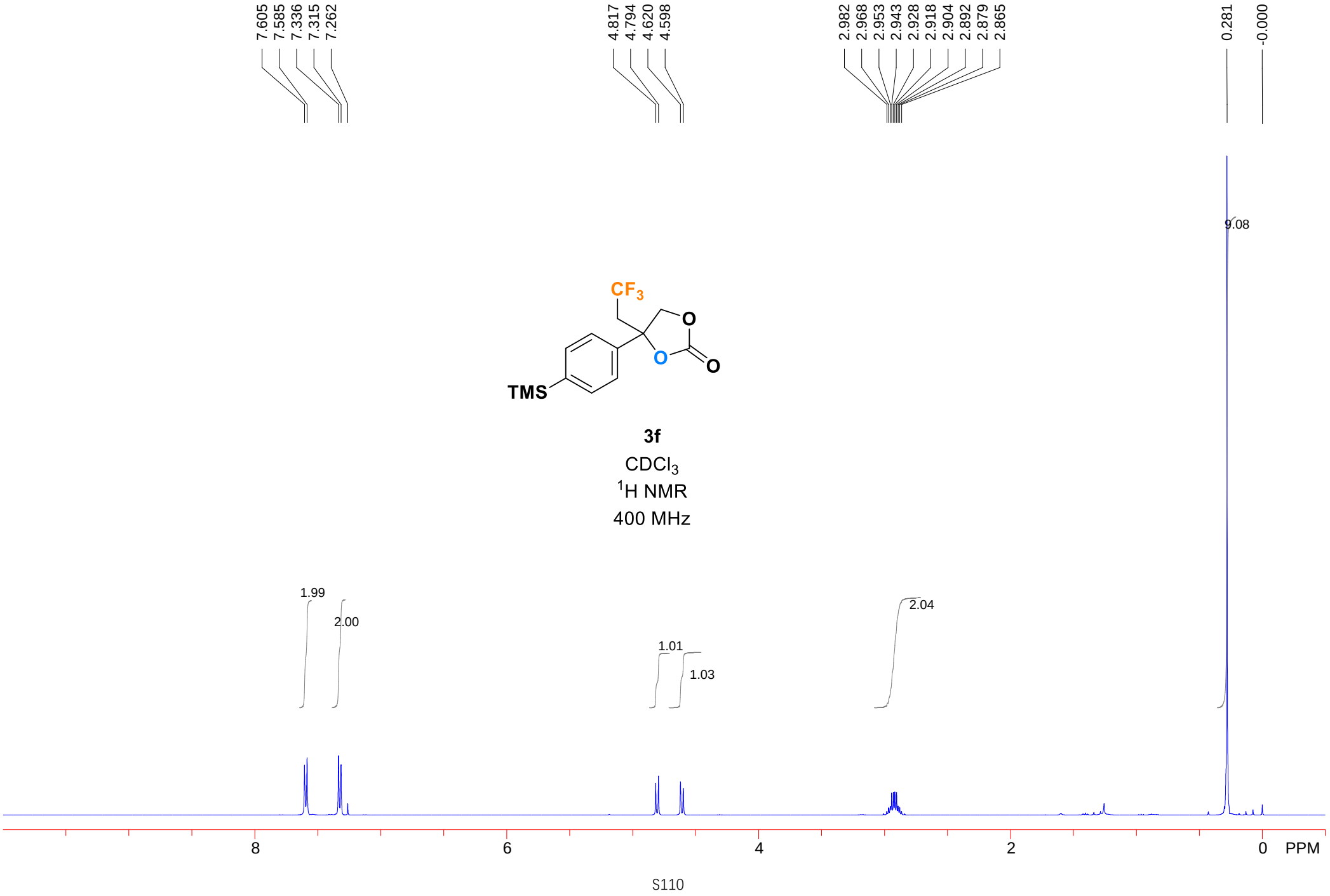
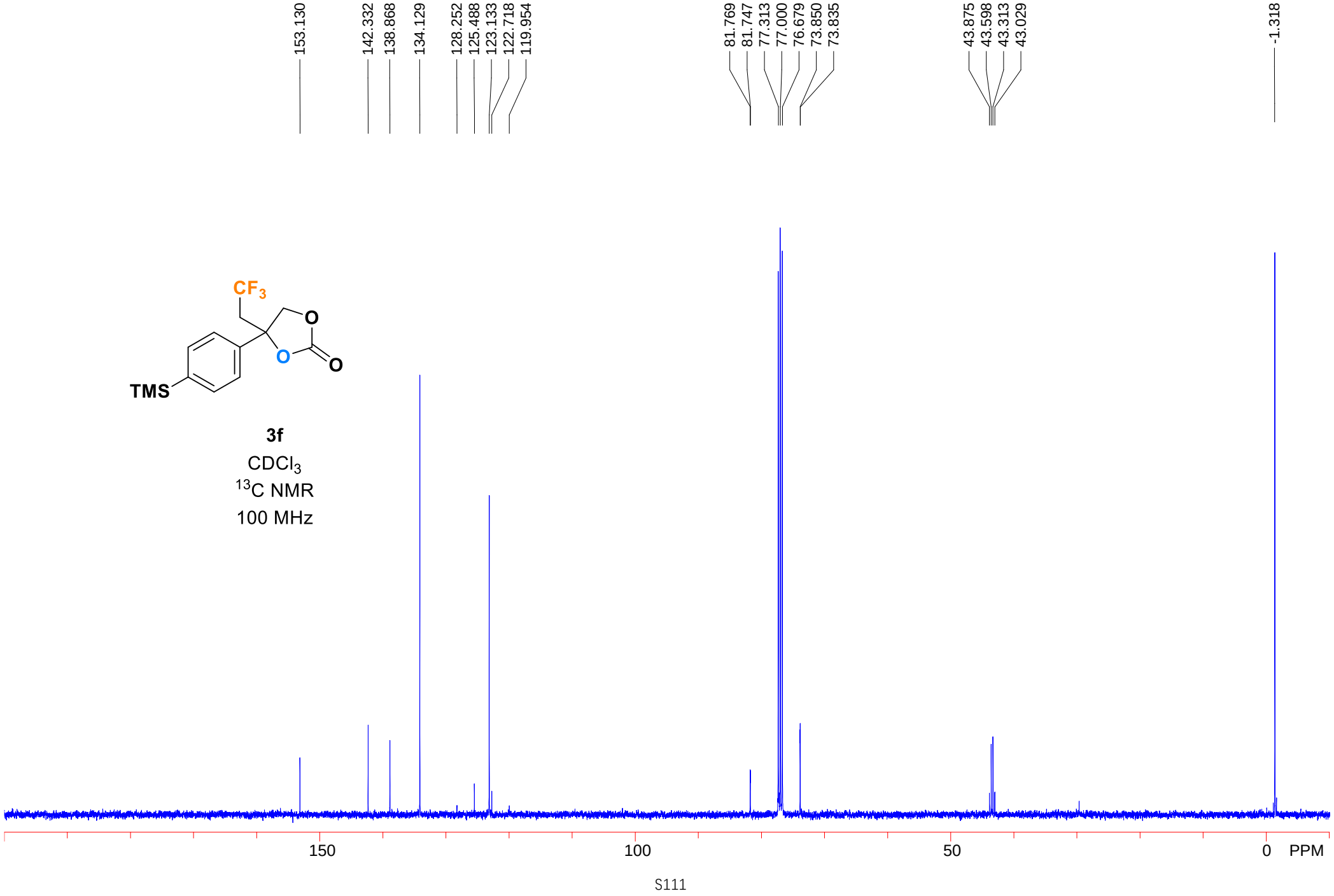
-120
-140
PPM


7.605
7.585
7.336
7.315
7.262
4.817
4.794
4.620
4.598
2.982
2.968
2.953
2.943
2.928
2.918
2.904
2.892
2.879
2.865
0.281
-0.000
9.08
CF3
O
O
O
TMS
3f
CDCl3
1H NMR
400 MHz
1.99
2.00
1.01
1.03
2.04
8
6
4
2
0
PPM


153.130
142.332
138.868
134.129
128.252
125.488
123.133
122.718
119.954
81.769
81.747
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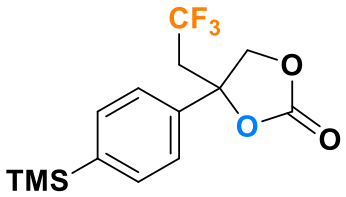
77.000
76.679
73.850
73.835
43.875
43.598
43.313
43.029
-1.318
CF3
O
O
O
TMS
3f
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM

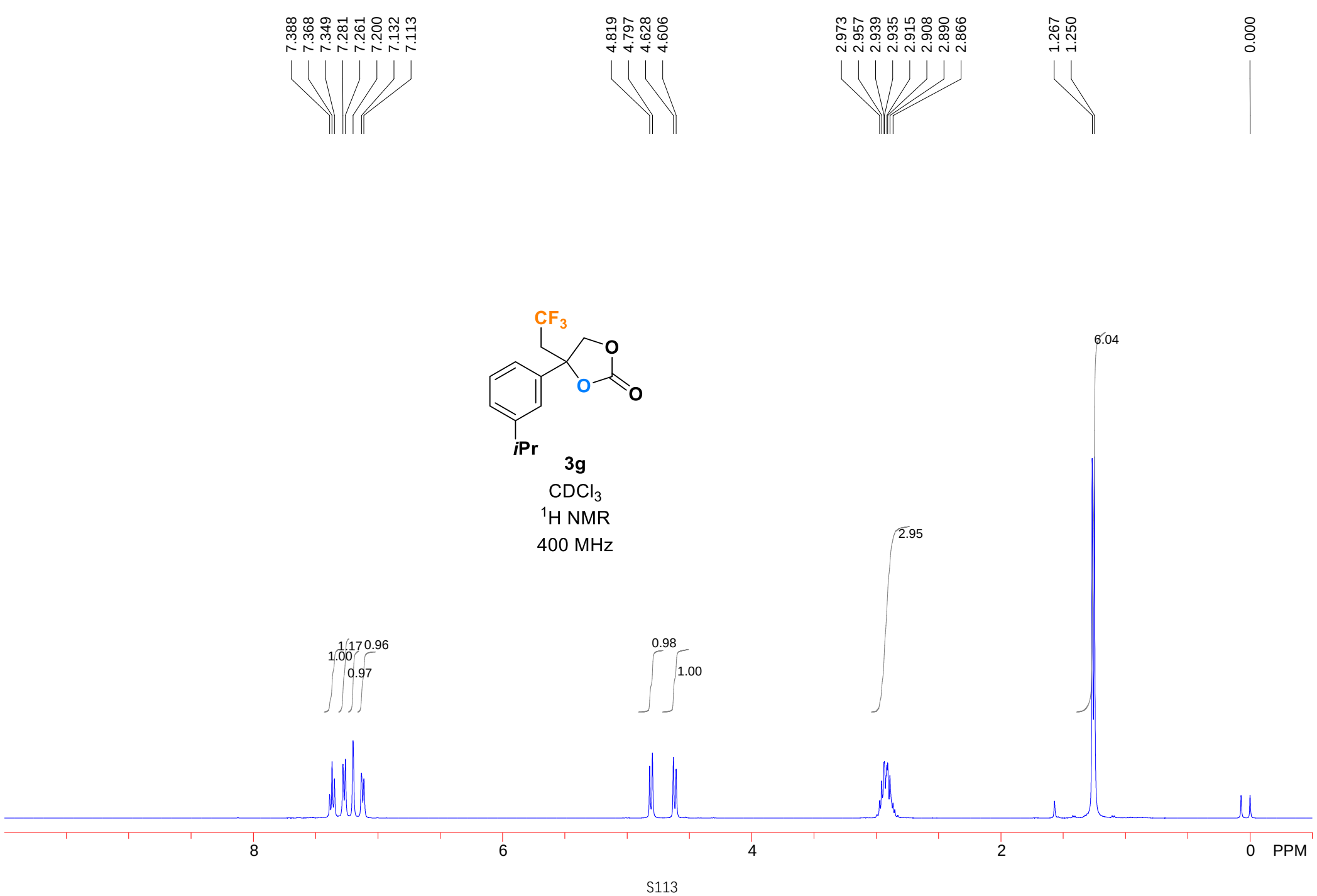


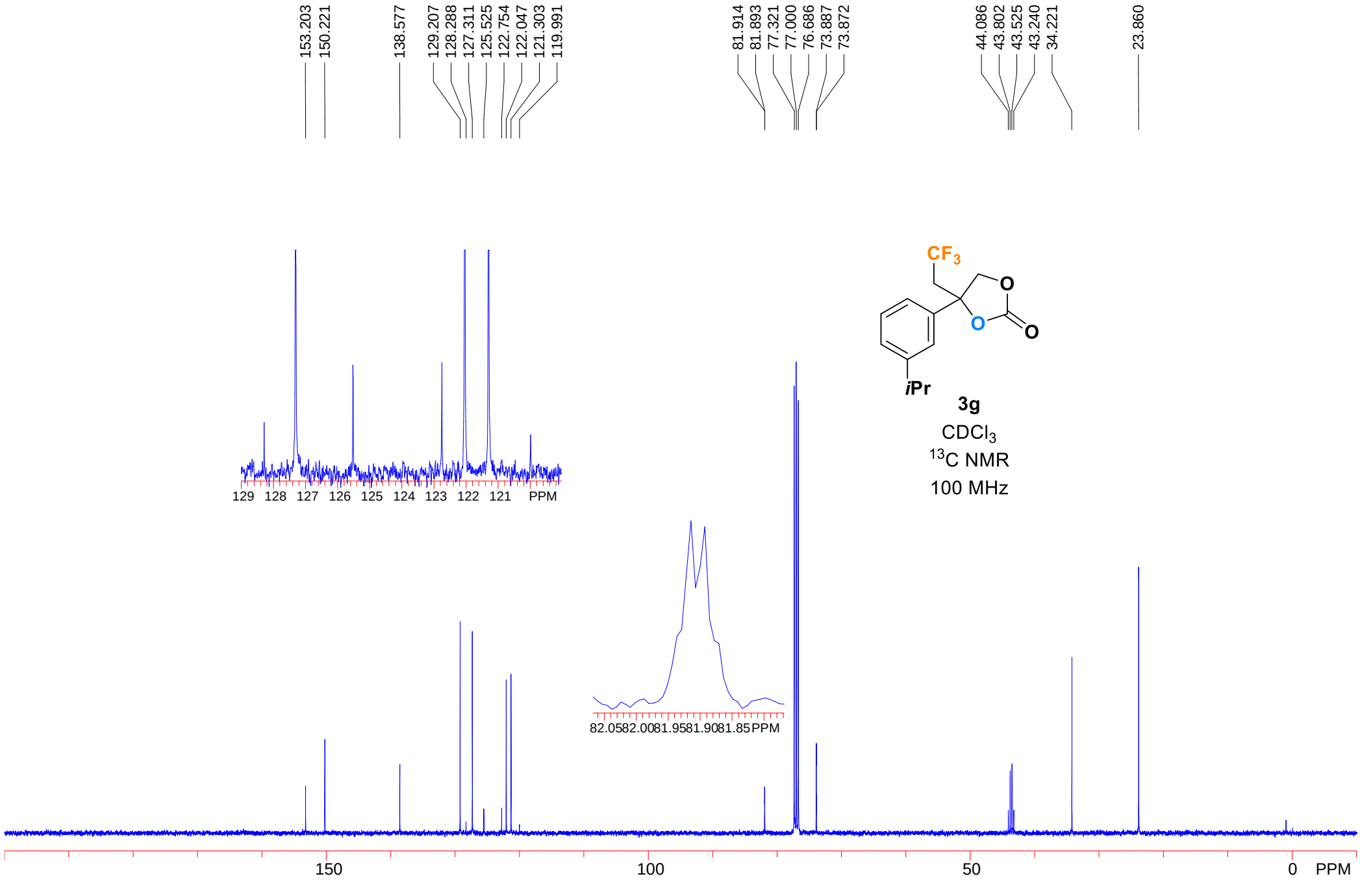
3f

$CDCl_3$

^{19}F NMR

376 MHz


7.388
7.368
7.349
7.281
7.261
7.200
7.132
7.113
4.819
4.797
4.628
4.606
2.973
2.957
2.939
2.935
2.915
2.908
2.890
2.866
1.267
1.250
0.000
CF3
O
O
O
iPr
3g
CDCl3
1H NMR
400 MHz
6.04
2.95
0.98
1.00
1.17
0.96
1.00
0.97
8
6
4
2
0
PPM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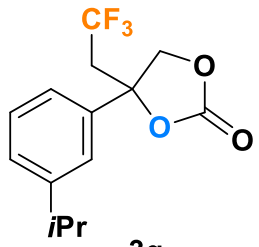
129.207
128.288
127.311
125.525
122.754
122.047
121.303
119.991
81.914
81.893
77.321
77.000
76.686
73.887
73.872
44.086
43.802
43.525
43.240
34.221
23.860
CF3
O
O
O
iPr
3g
CDCl3
13C NMR
100 MHz
129 128 127 126 125 124 123 122 121 PPM
82.05 82.00 81.95 81.90 81.85 PPM
150
100
50
0 PPM



3g

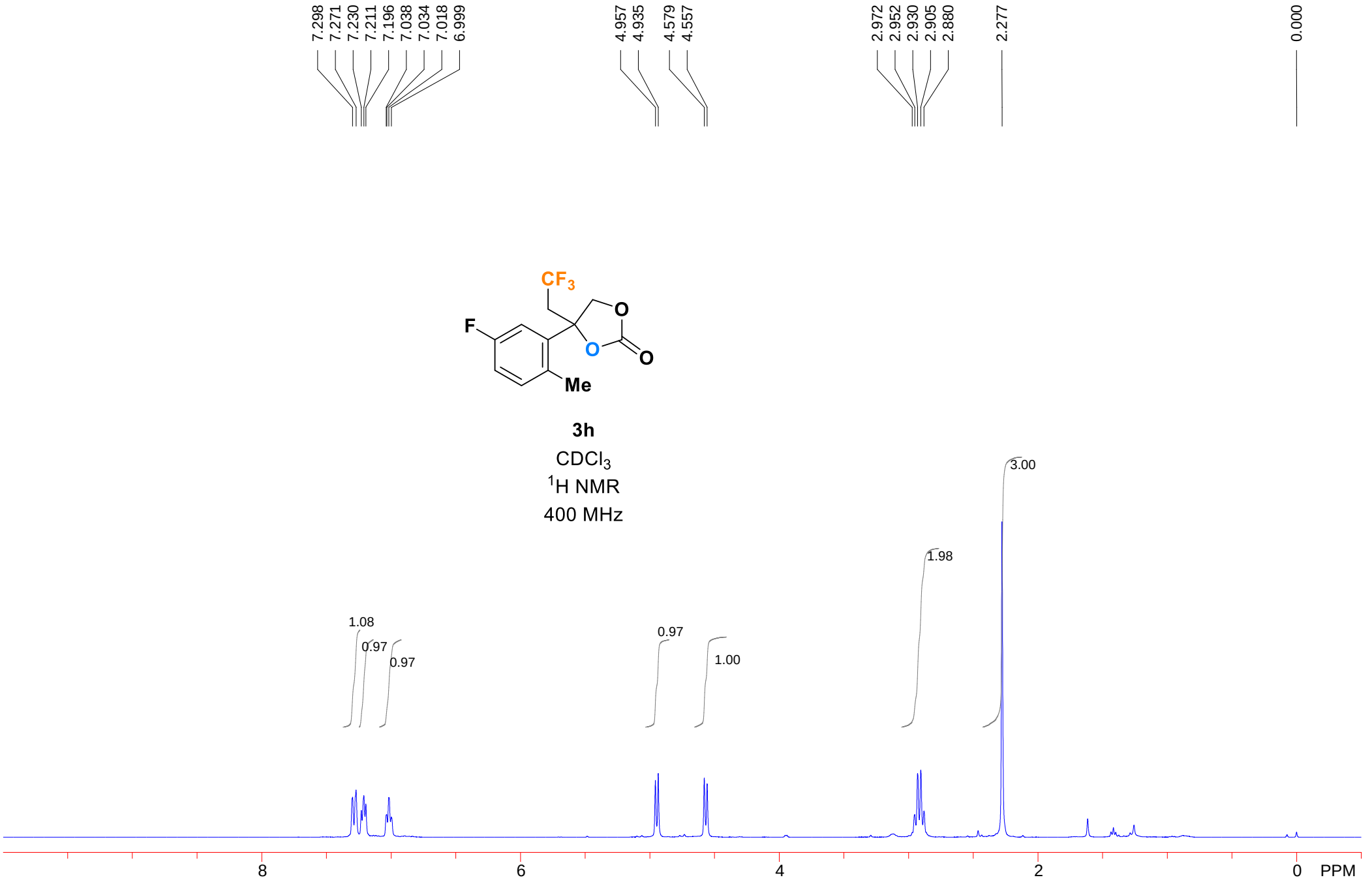
$CDCl_3$

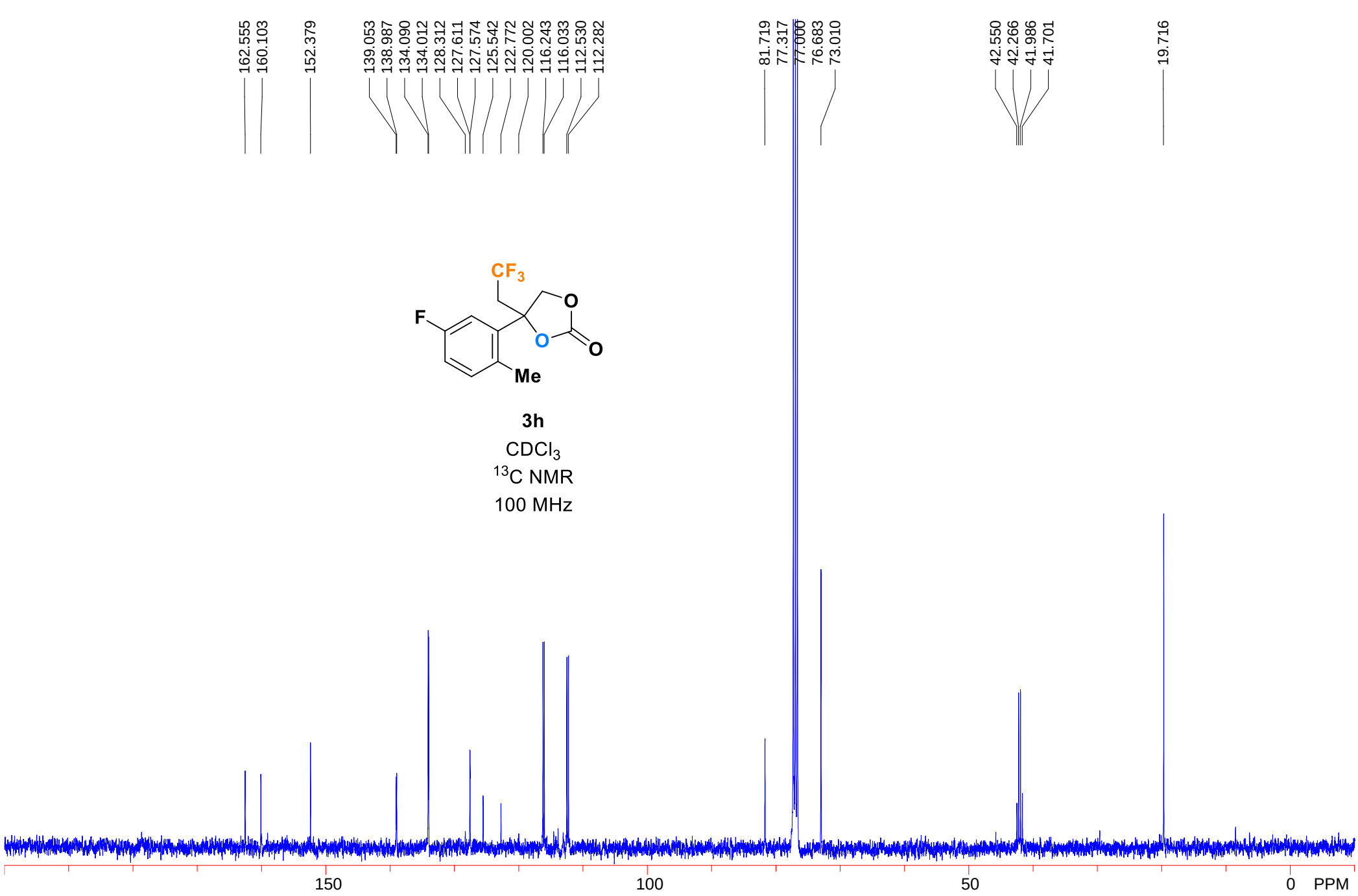
^{19}F NMR

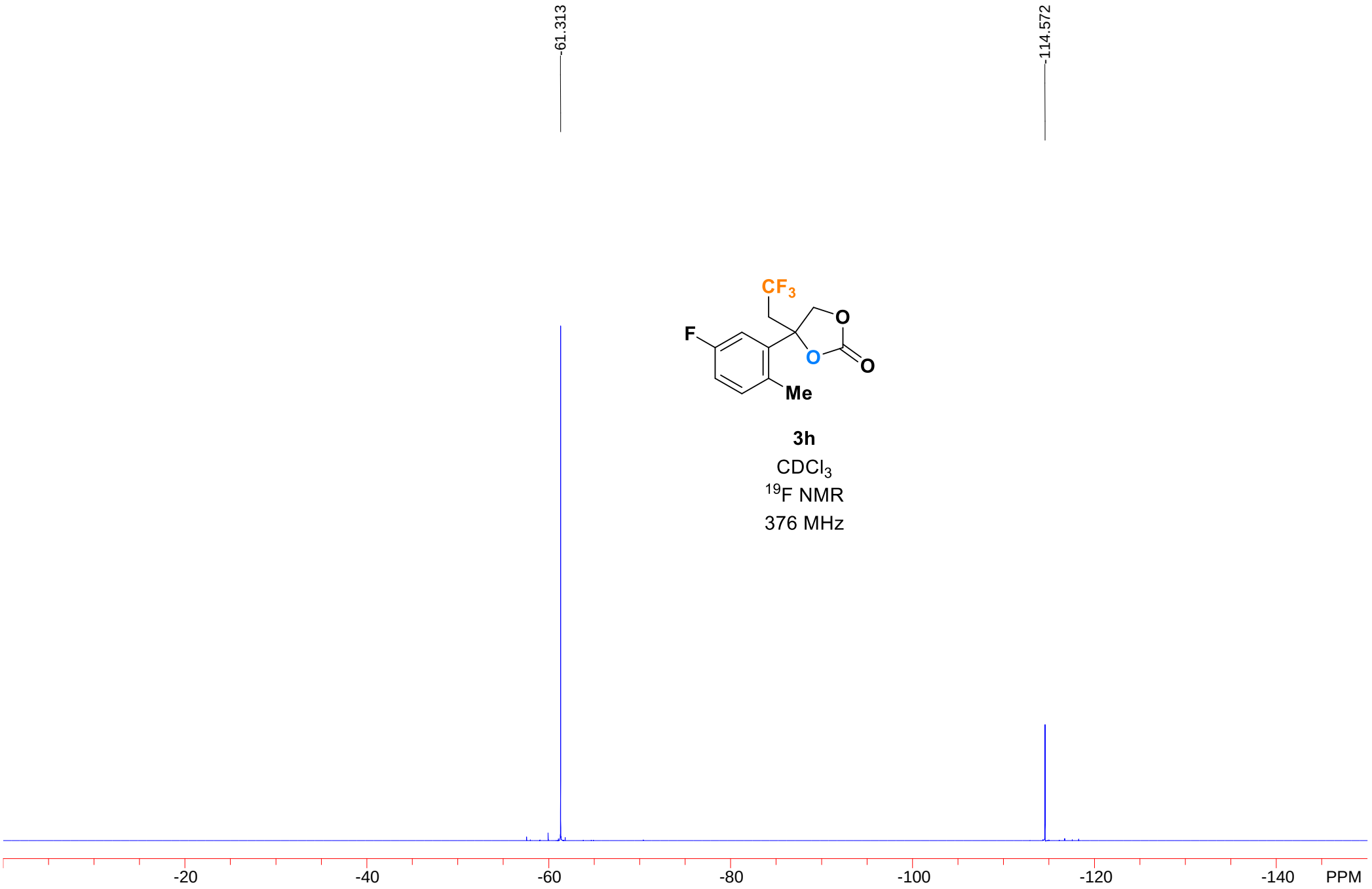
376 MHz

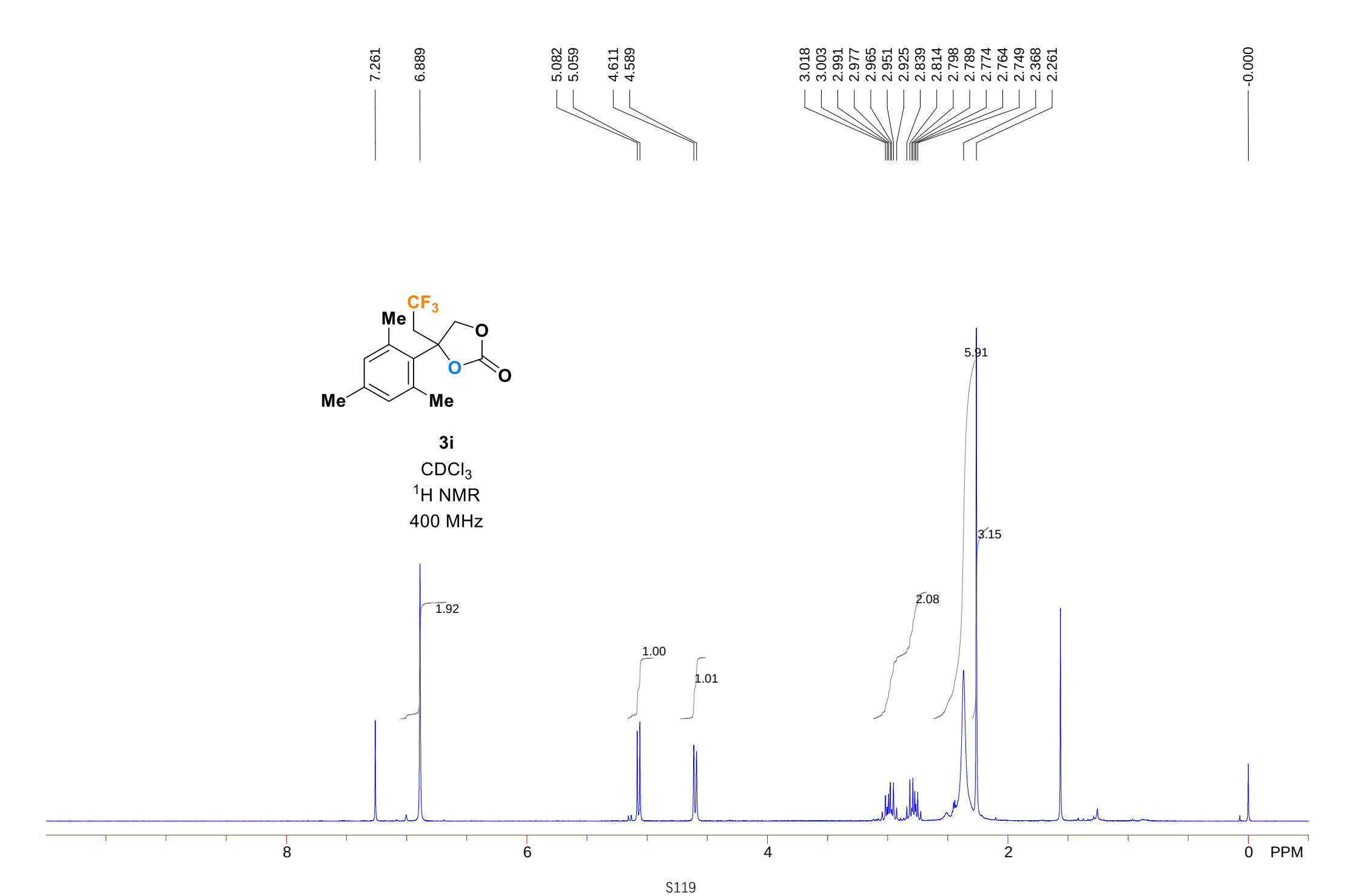
-60.767

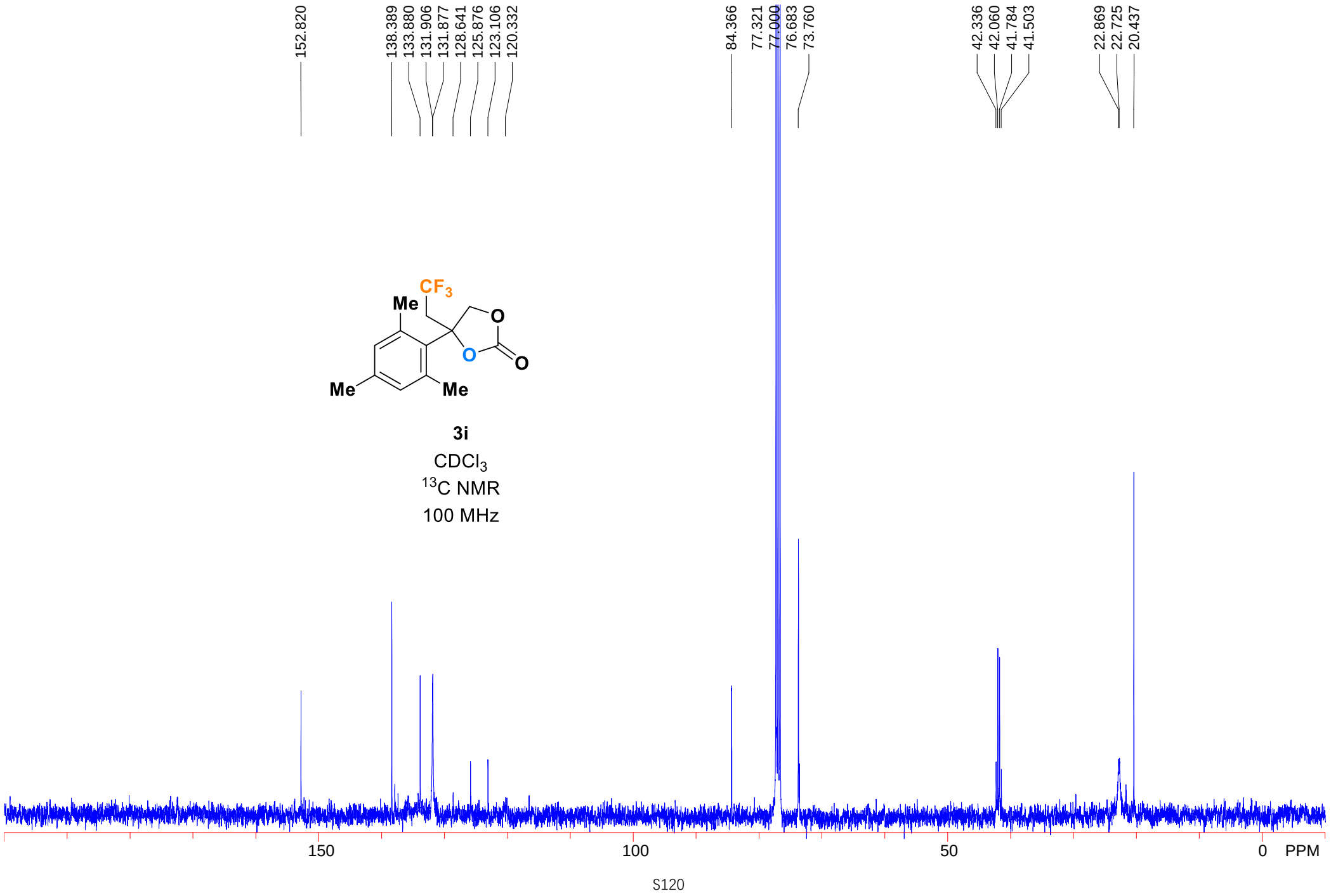
-20 -40 -60 -80 -100 -120 -140 PPM

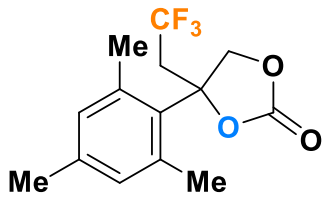

7.298
7.271
7.230
7.211
7.196
7.038
7.034
7.018
6.999
4.957
4.935
4.579
4.557
2.972
2.952
2.930
2.905
2.880
2.277
0.000
CF3
F
O
O
O
Me
3h
CDCl3
1H NMR
400 MHz
3.00
1.98
1.08
0.97
0.97
0.97
1.00
8
6
4
2
0
PPM


162.555
160.103
152.379
139.053
138.987
134.090
134.012
128.312
127.611
127.574
125.542
122.772
120.002
116.243
116.033
112.530
112.282
81.719
77.317
77.000
76.683
73.010
42.550
42.266
41.986
41.701
19.716
CF3
F
O
O
O
Me
3h
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


-61.313
-114.572
CF3
F
O
O
O
Me
3h
CDCl3
19F NMR
376 MHz
-20
-40
-60
-80
-100
-120
-140
PPM


7.261
6.889
5.082
5.059
4.611
4.589
3.018
3.003
2.991
2.977
2.965
2.951
2.925
2.839
2.814
2.798
2.789
2.774
2.764
2.749
2.368
2.261
-0.000
CF3
Me
O
O
O
Me
Me
3i
CDCl3
1H NMR
400 MHz
5.91
3.15
2.08
1.92
1.00
1.01
8
6
4
2
0
PPM


152.820
138.389
133.880
131.906
131.877
128.641
125.876
123.106
120.332
84.366
77.321
77.000
76.683
73.760
42.336
42.060
41.784
41.503
22.869
22.725
20.437
CF3
Me
O
O
O
Me
Me
3i
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM

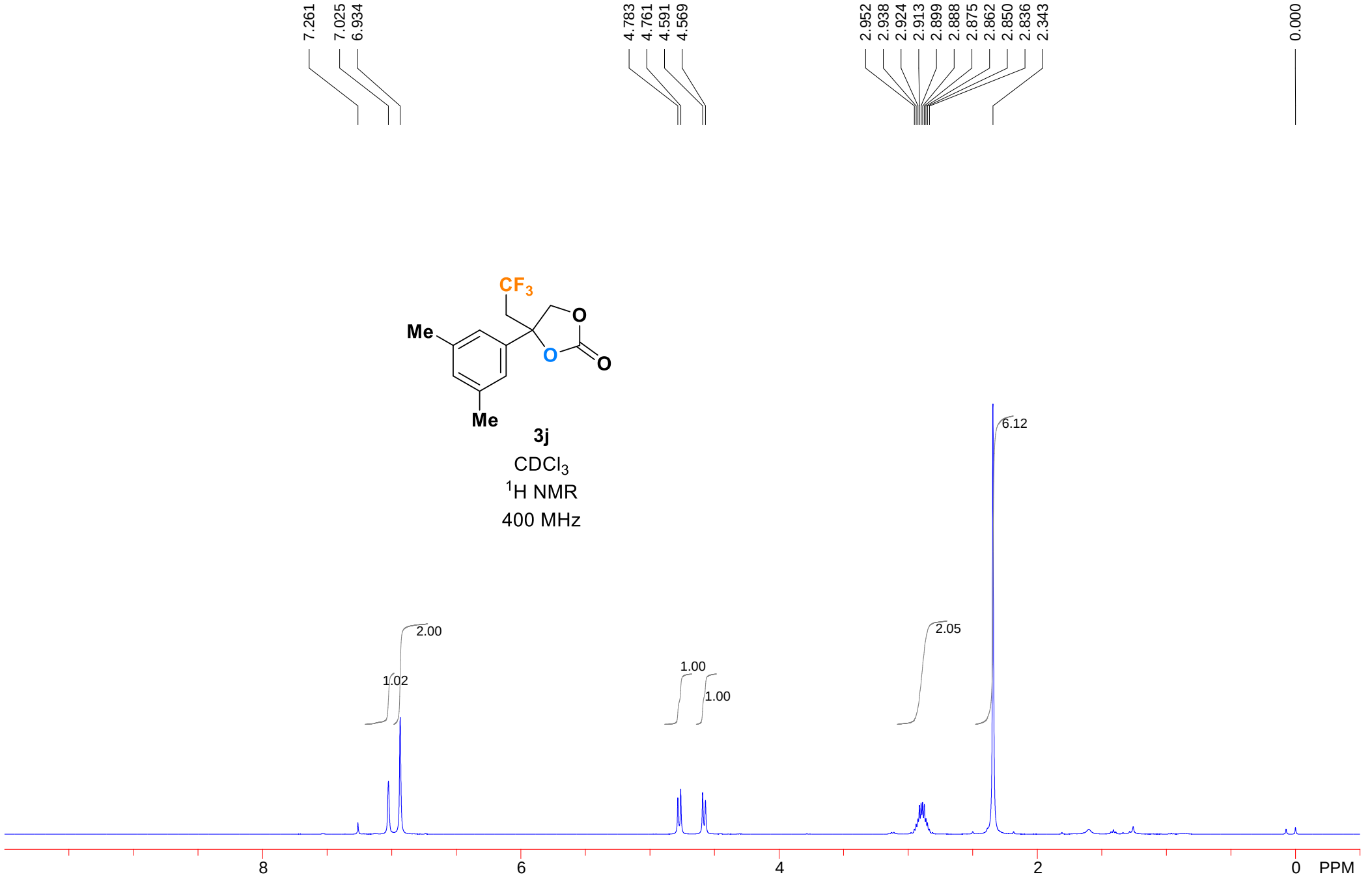


3i

$CDCl_3$

^{19}F NMR

376 MHz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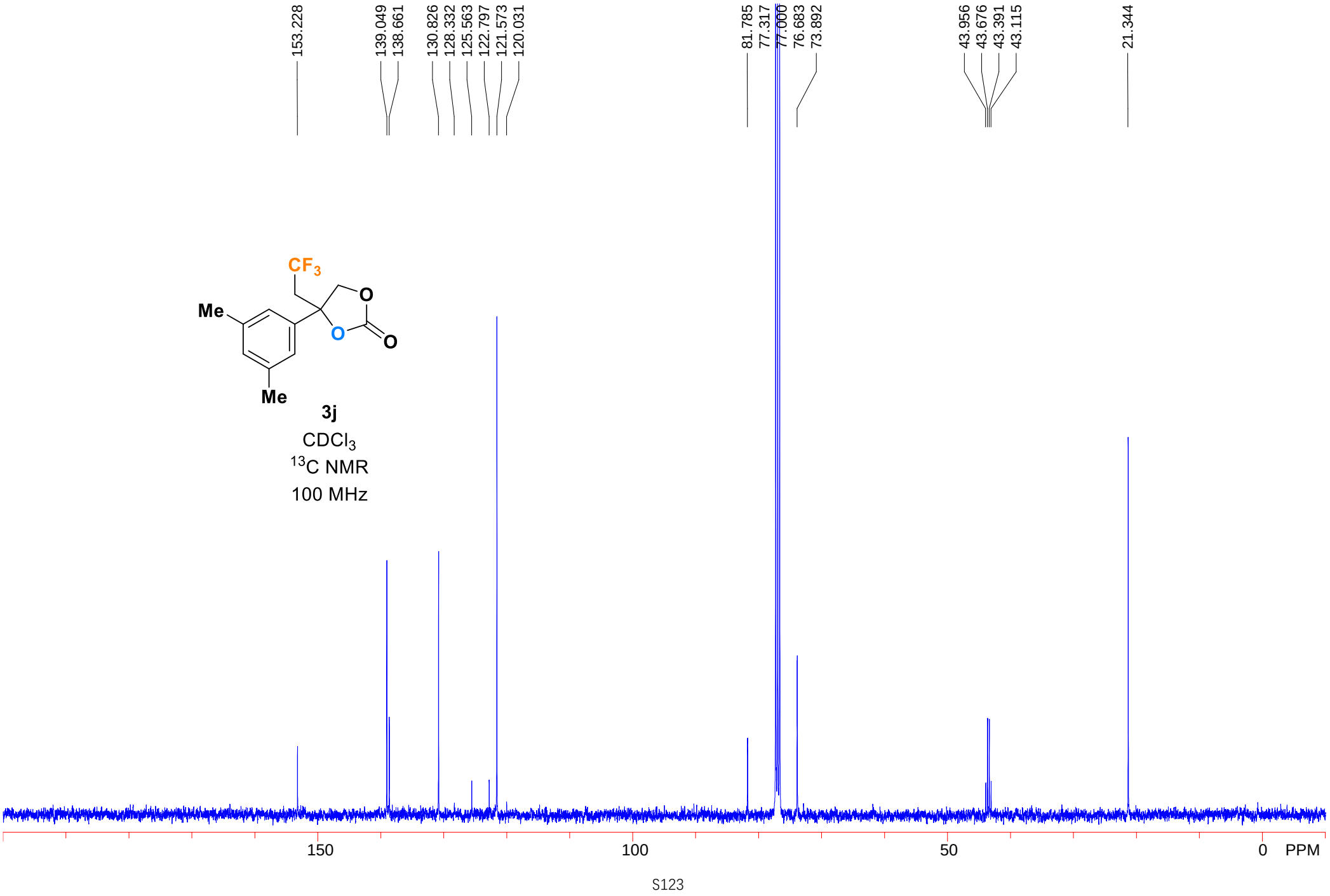
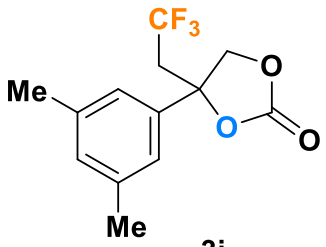
7.025
6.934
4.783
4.761
4.591
4.569
2.952
2.938
2.924
2.913
2.899
2.888
2.875
2.862
2.850
2.836
2.343
0.000
CF3
Me
Me
O
O
O
3j
CDCl3
1H NMR
400 MHz
2.00
1.02
1.00
1.00
2.05
6.12
8
6
4
2
0
PPM


153.228
139.049
138.661
130.826
128.332
125.563
122.797
121.573
120.031
81.785
77.317
77.000
76.683
73.892
43.956
43.676
43.391
43.115
21.344
CF3
O
O
O
Me
Me
3j
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM



3j

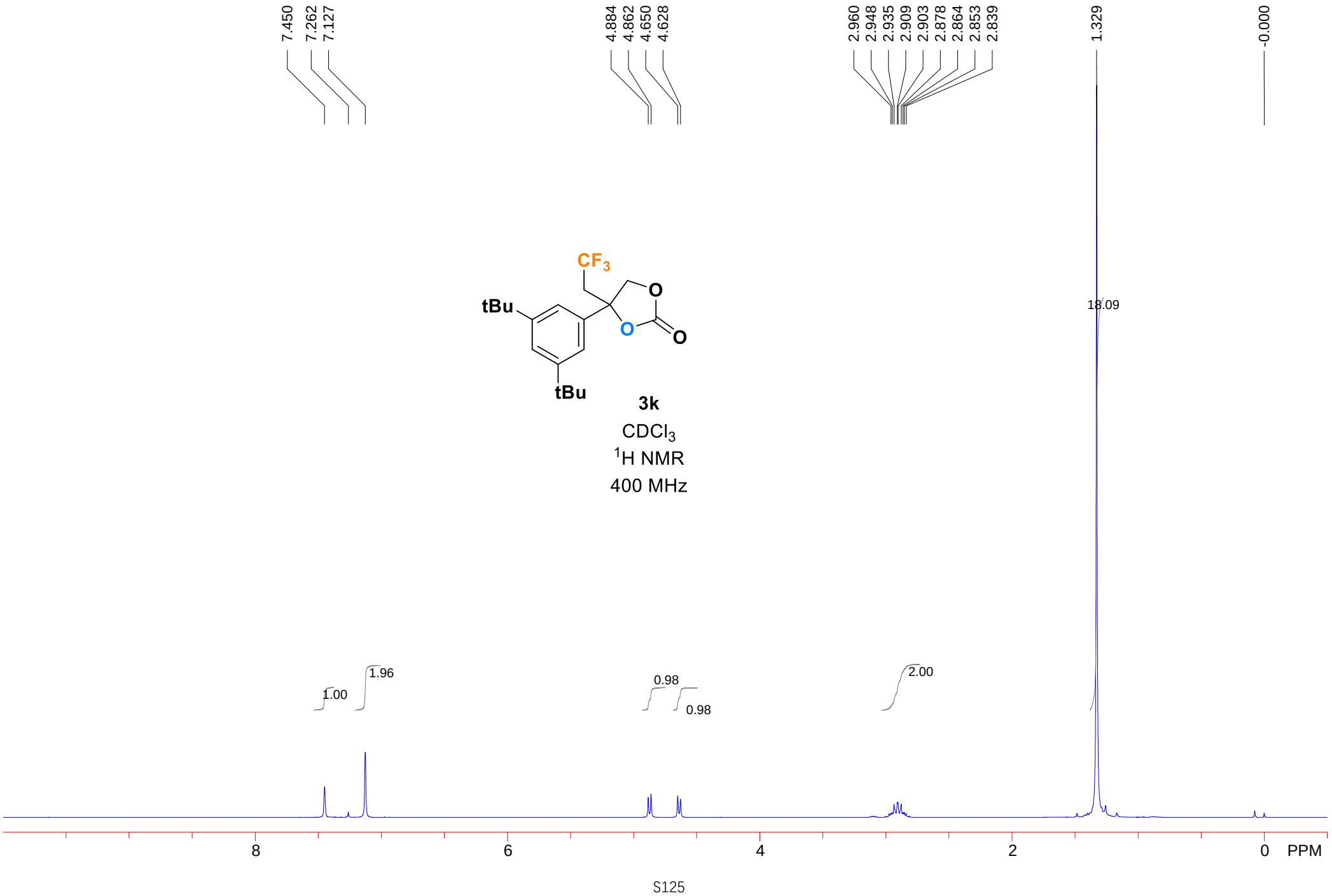
$CDCl_3$

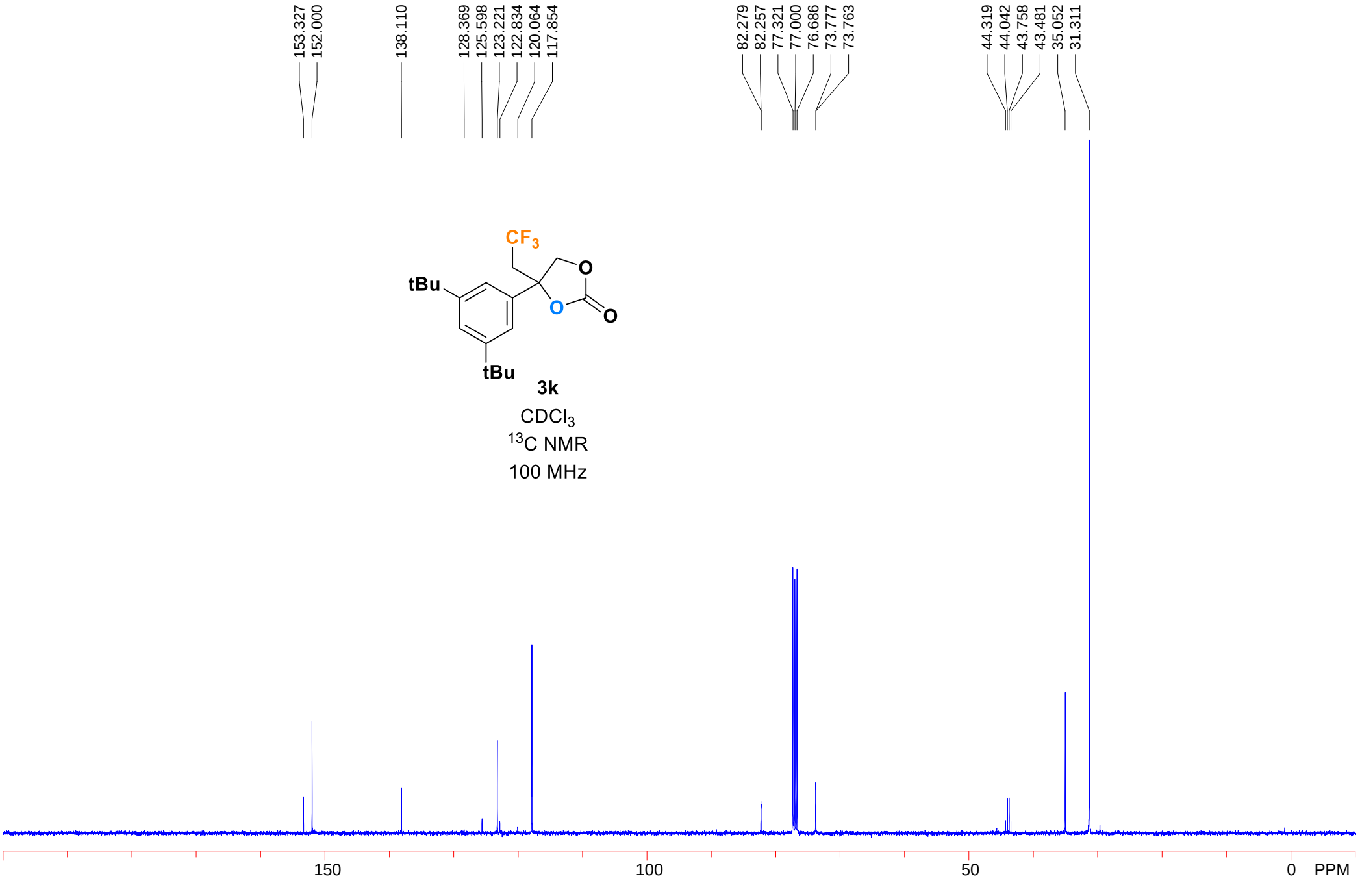
^{19}F NMR

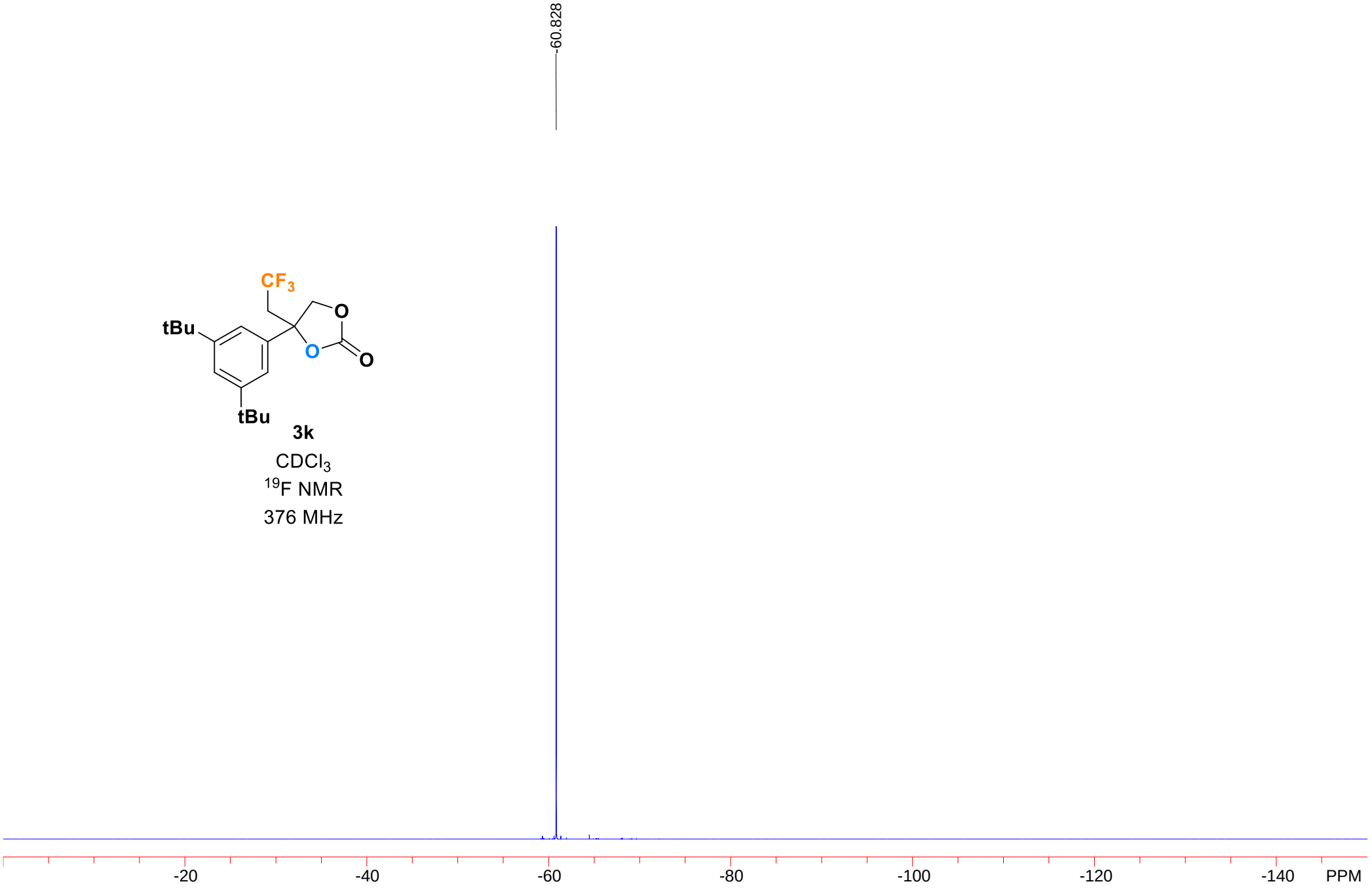
376 MHz

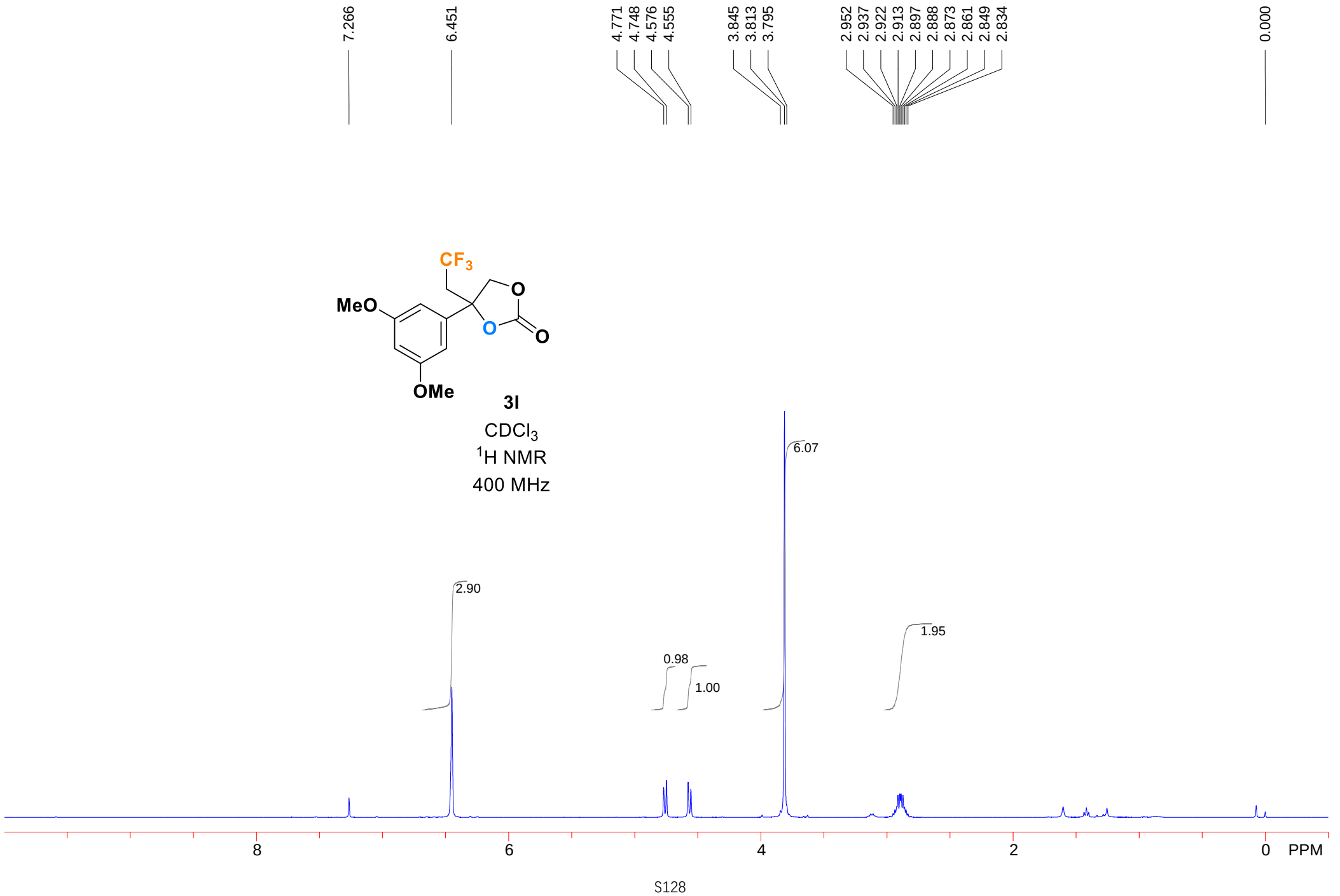
-60.752

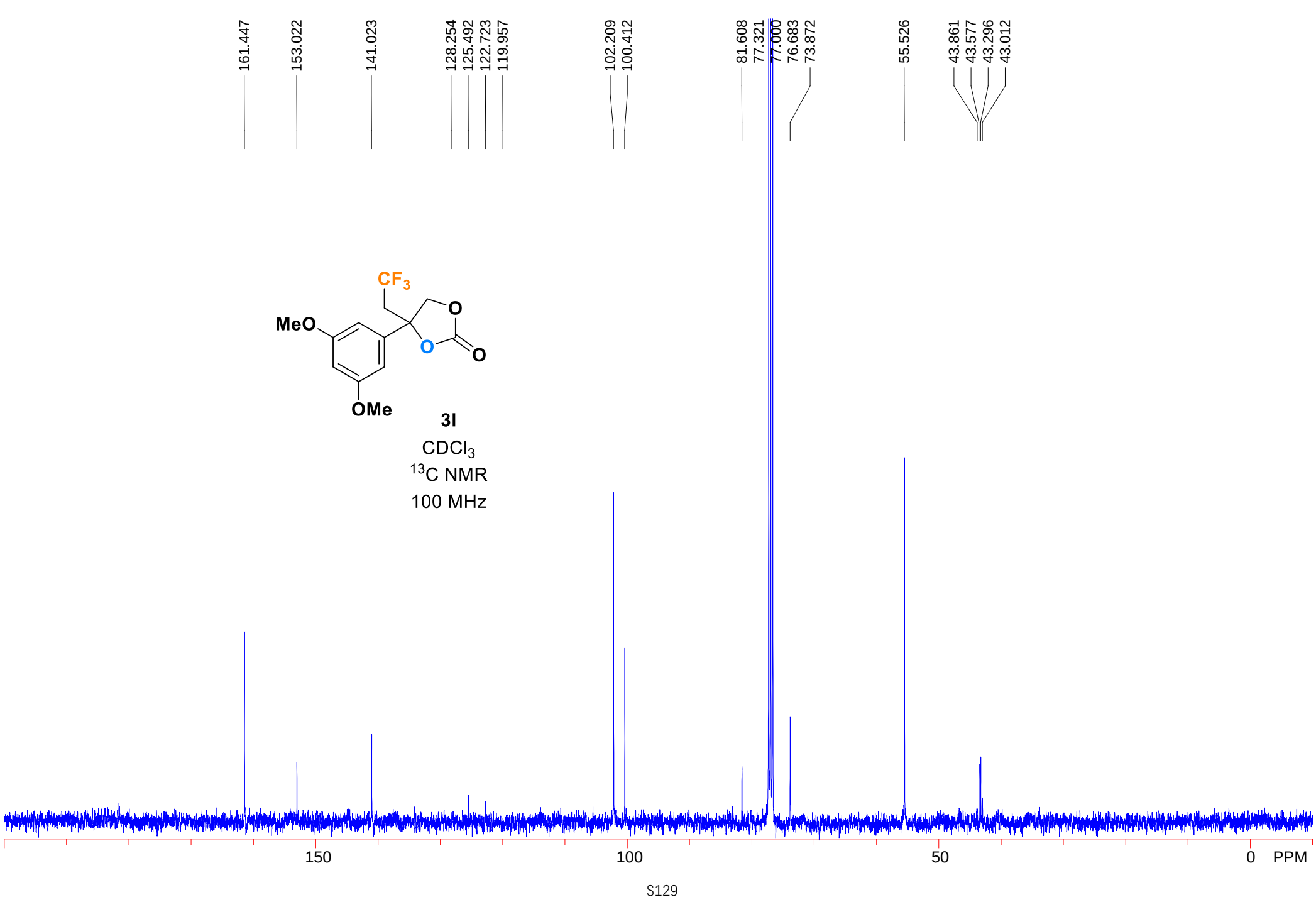
-20 -40 -60 -80 -100 -120 -140 PPM

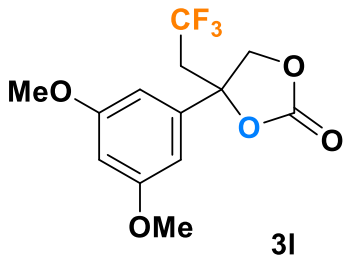

7.450
7.262
7.127
4.884
4.862
4.650
4.628
2.960
2.948
2.935
2.909
2.903
2.878
2.864
2.853
2.839
1.329
-0.000
CF3
O
O
O
tBu
tBu
3k
CDCl3
1H NMR
400 MHz
18.09
1.00
1.96
0.98
0.98
2.00
8
6
4
2
0
PPM


153.327
152.000
138.110
128.369
125.598
123.221
122.834
120.064
117.854
82.279
82.257
77.321
77.000
76.686
73.777
73.763
44.319
44.042
43.758
43.481
35.052
31.311
CF3
O
O
O
tBu
tBu
3k
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


-60.828
CF3
O
O
O
tBu
tBu
3k
CDCl3
19F NMR
376 MHz
-20
-40
-60
-80
-100
-120
-140
PPM


7.266
6.451
4.771
4.748
4.576
4.555
3.845
3.813
3.795
2.952
2.937
2.922
2.913
2.897
2.888
2.873
2.861
2.849
2.834
0.000
CF3
MeO
O
O
O
OMe
3l
CDCl3
1H NMR
400 MHz
6.07
2.90
1.95
0.98
1.00
8
6
4
2
0
PPM


161.447
153.022
141.023
128.254
125.492
122.723
119.957
102.209
100.412
81.608
77.321
77.000
76.683
73.872
55.526
43.861
43.577
43.296
43.012
CF3
MeO
O
O
O
OMe
3l
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM



3l

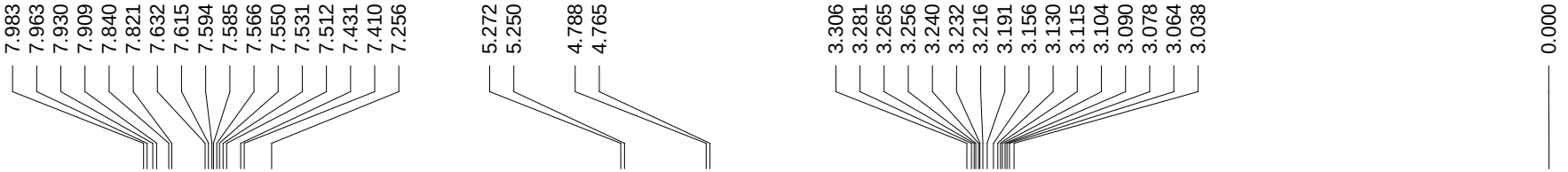
$CDCl_3$

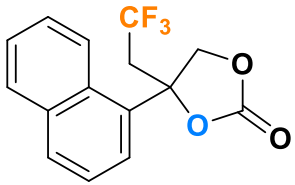
^{19}F NMR

376 MHz

-60.803

-20 -40 -60 -80 -100 -120 -140 PPM



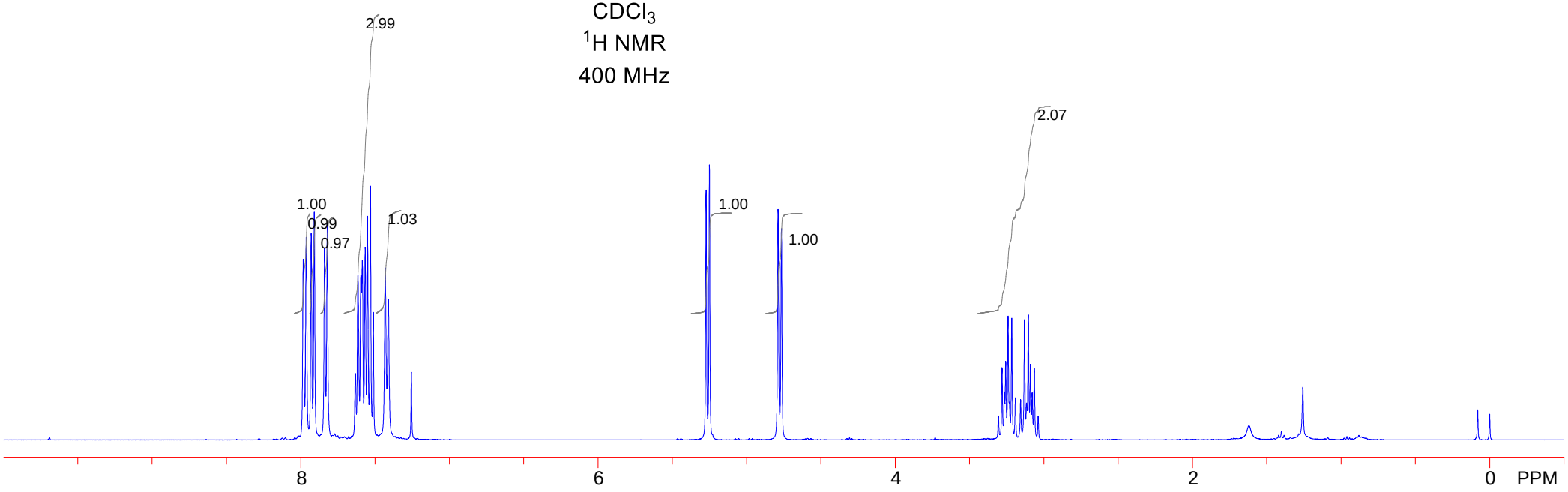


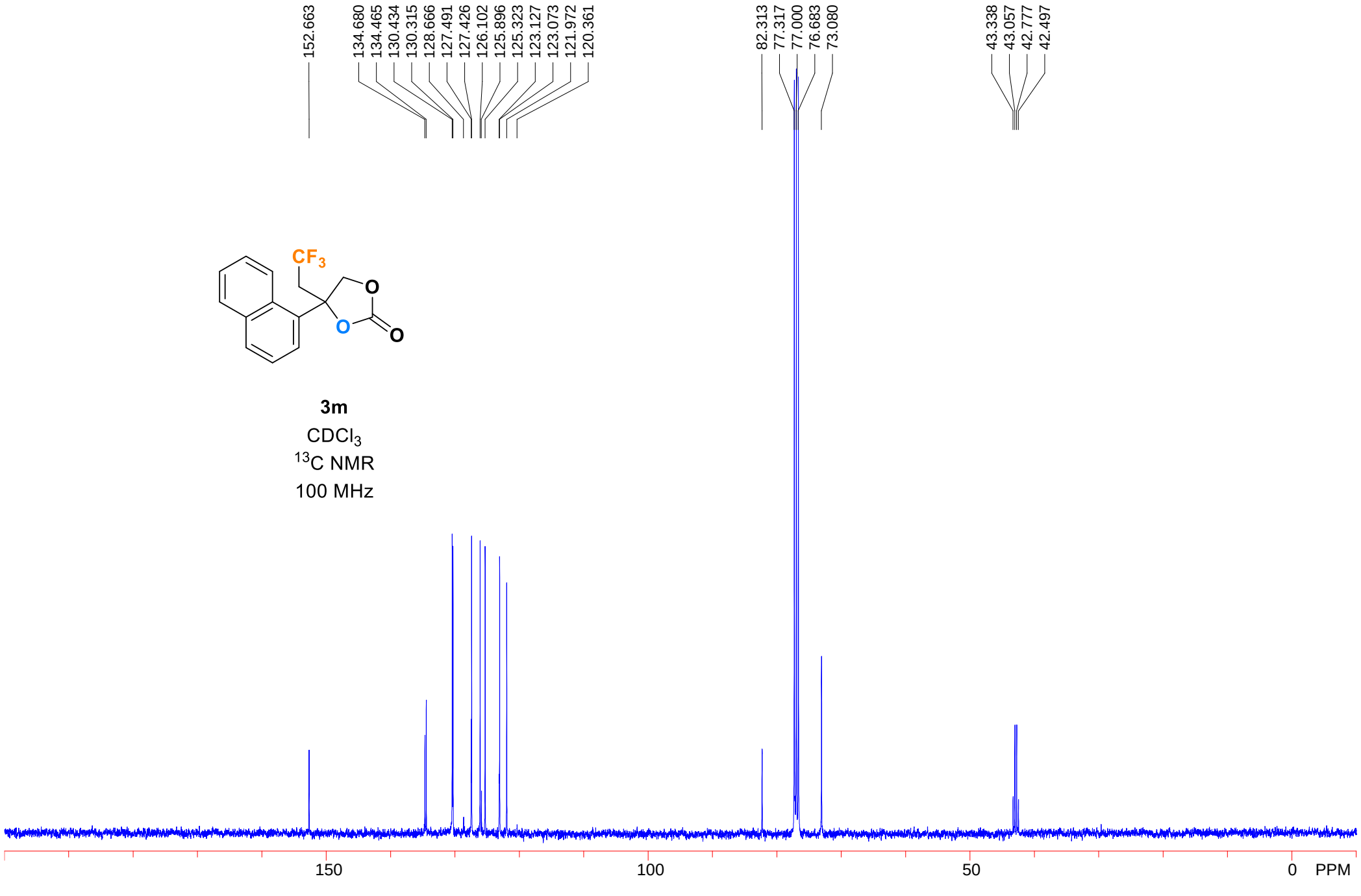
3m

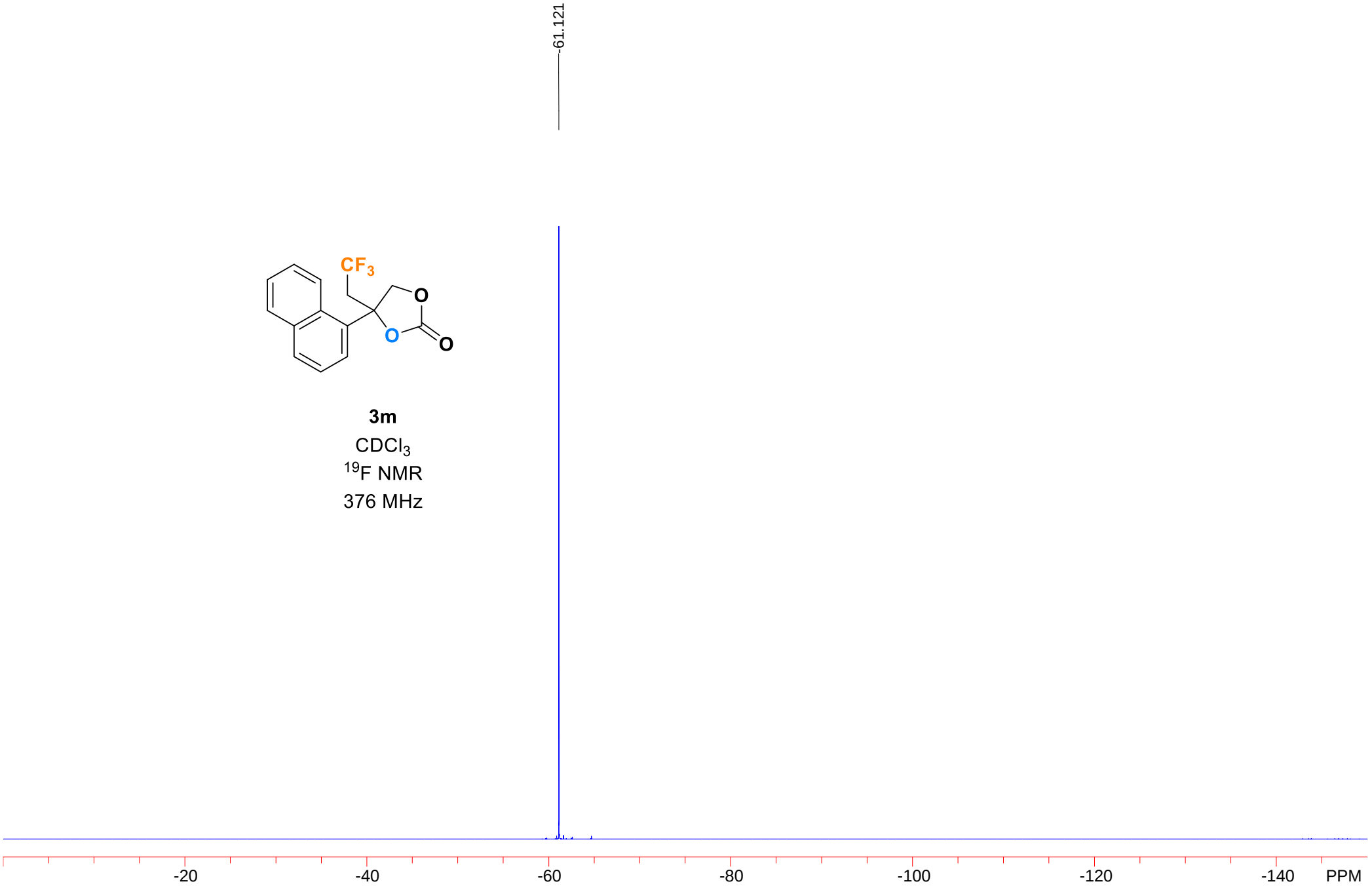
$CDCl_3$

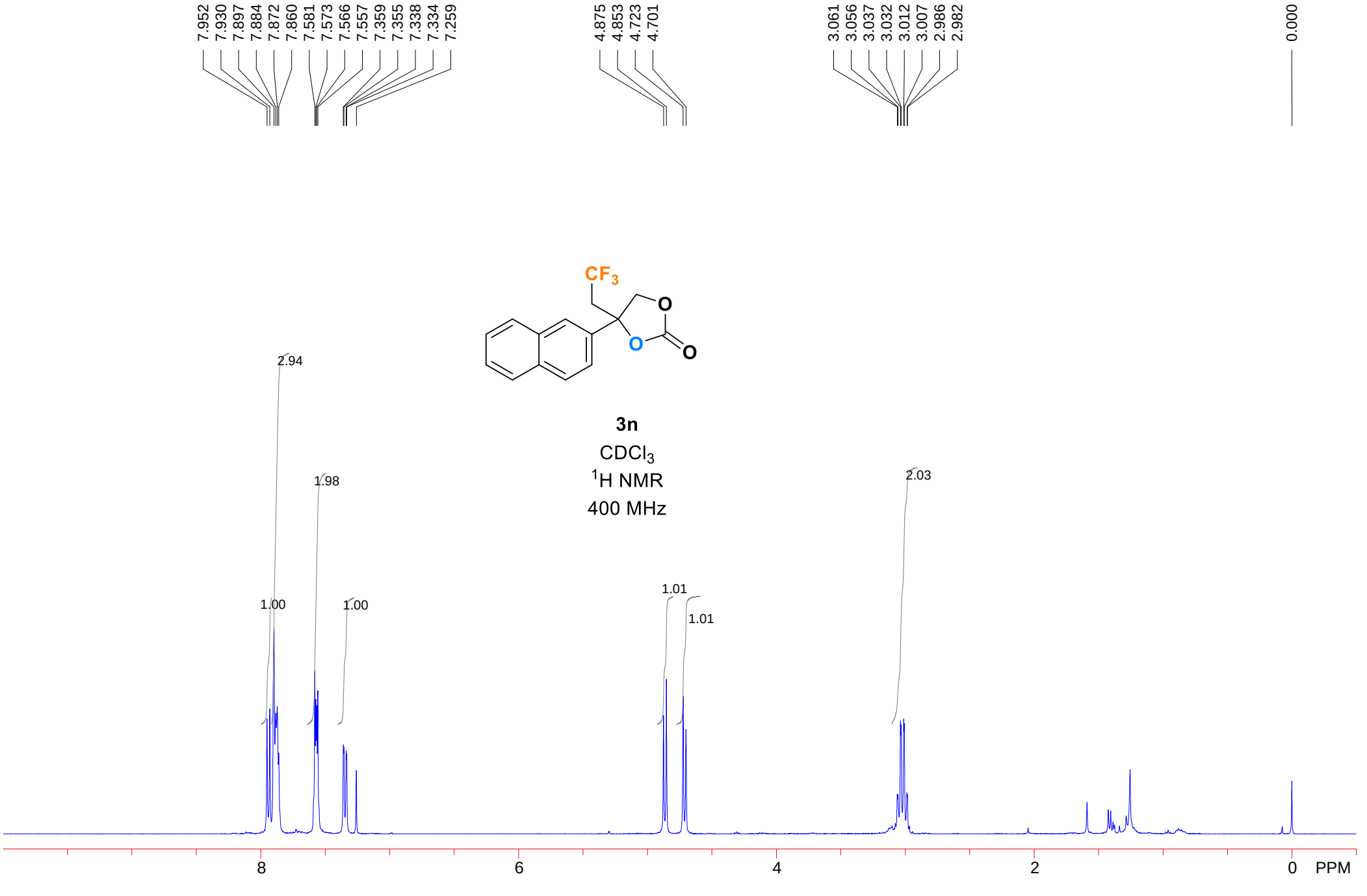
^1H NMR

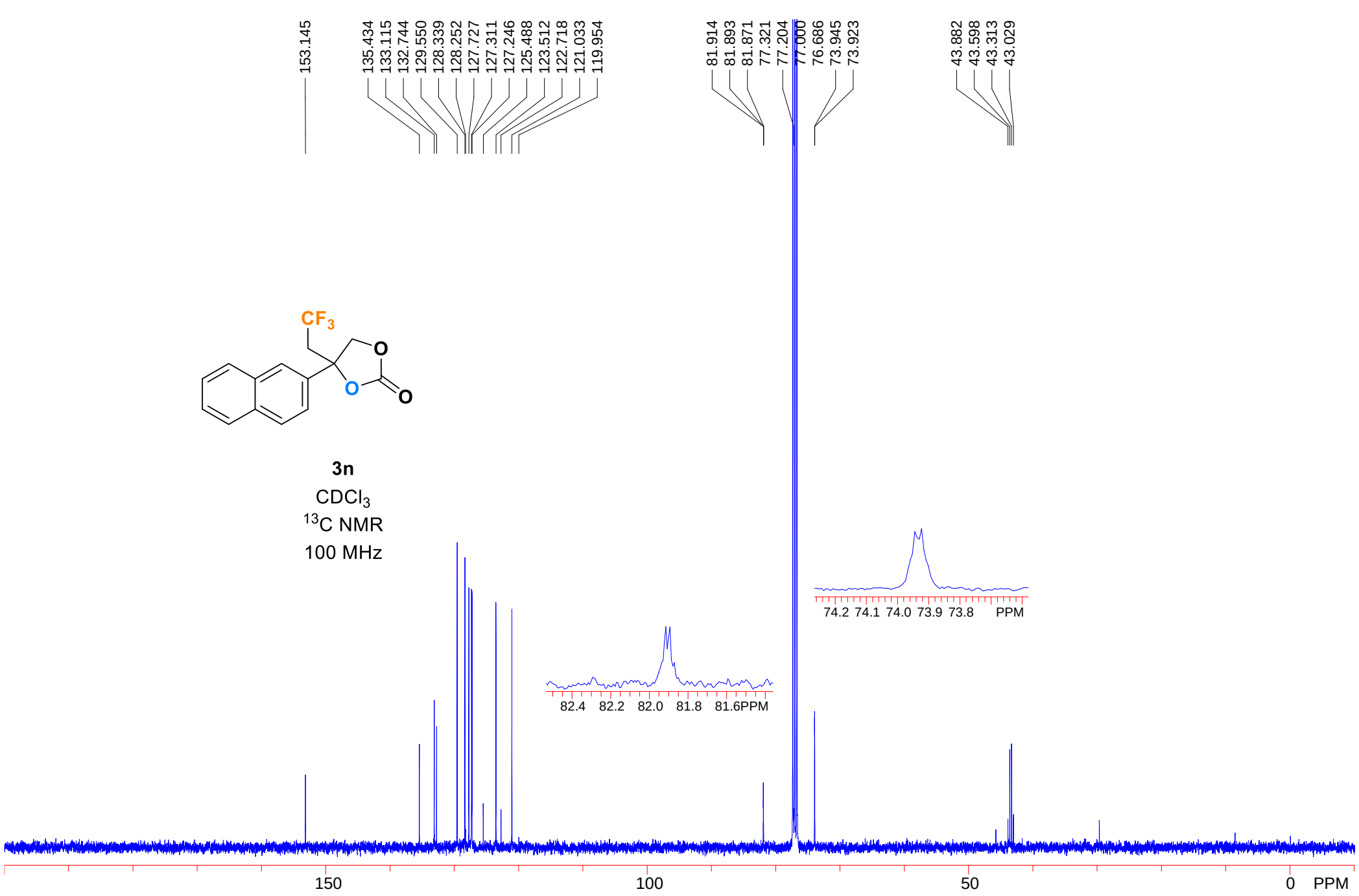
400 MHz

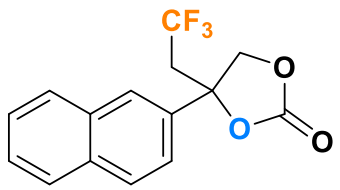



152.663
134.680
134.465
130.434
130.315
128.666
127.491
127.426
126.102
125.896
125.323
123.127
123.073
121.972
120.361
82.313
77.317
77.000
76.683
73.080
43.338
43.057
42.777
42.497
CF3
O
O
O
3m
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


-61.121
CF3
O
O
O
3m
CDCl3
19F NMR
376 MHz
-20
-40
-60
-80
-100
-120
-140
PPM


7.952
7.930
7.897
7.884
7.872
7.860
7.581
7.573
7.566
7.557
7.359
7.355
7.338
7.334
7.259
4.875
4.853
4.723
4.701
3.061
3.056
3.037
3.032
3.012
3.007
2.986
2.982
0.000
CF3
O
O
O
3n
CDCl3
1H NMR
400 MHz
2.94
1.98
1.00
1.00
1.01
1.01
2.03
8
6
4
2
0
PPM


153.145
135.434
133.115
132.744
129.550
128.339
128.252
127.727
127.311
127.246
125.488
123.512
122.718
121.033
119.954
81.914
81.893
81.871
77.321
77.204
77.000
76.686
73.945
73.923
43.882
43.598
43.313
43.029
CF3
O
O
O
3n
CDCl3
13C NMR
100 MHz
74.2 74.1 74.0 73.9 73.8 PPM
82.4 82.2 82.0 81.8 81.6PPM
150
100
50
0 PPM



3n

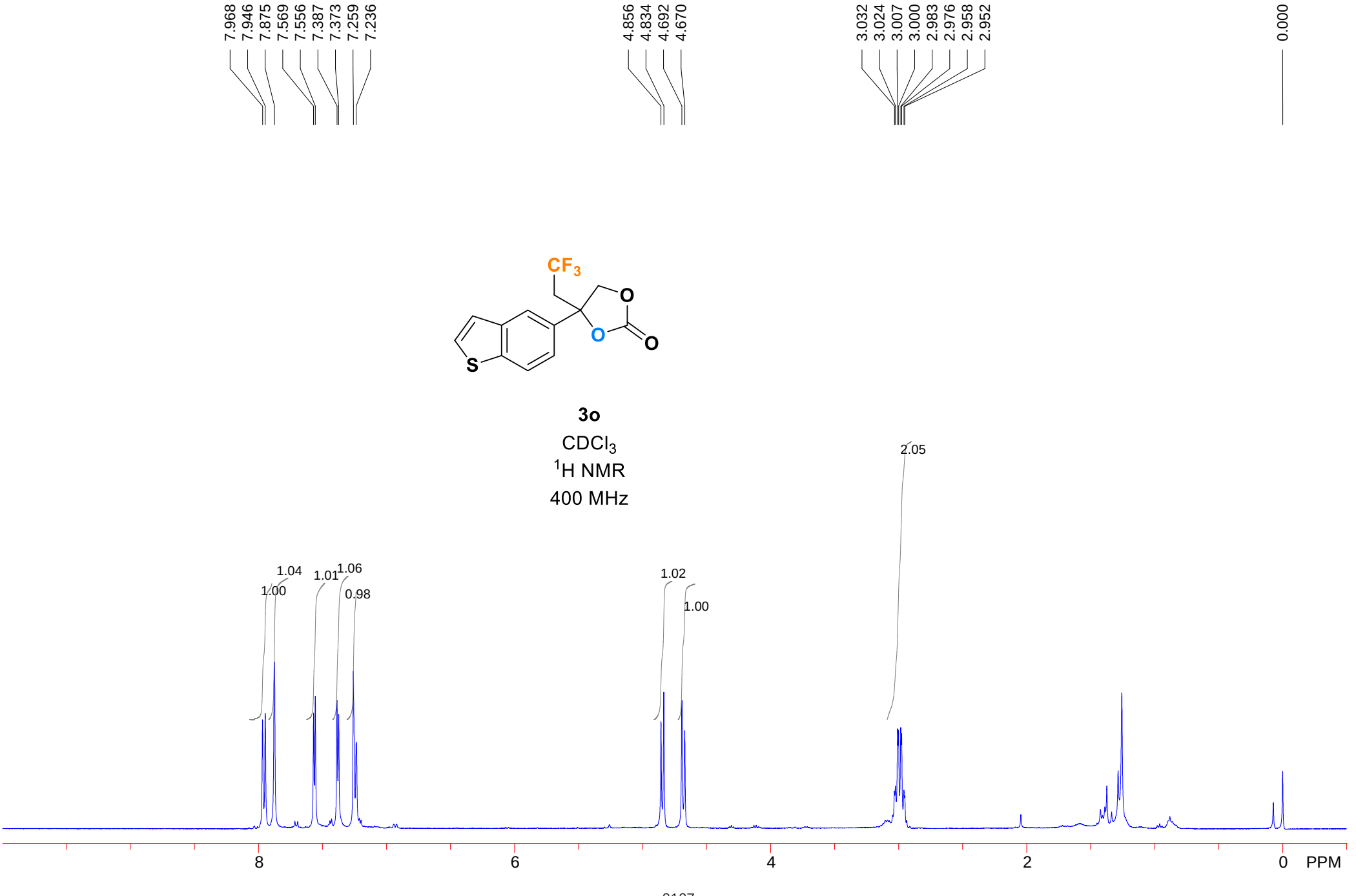
$CDCl_3$

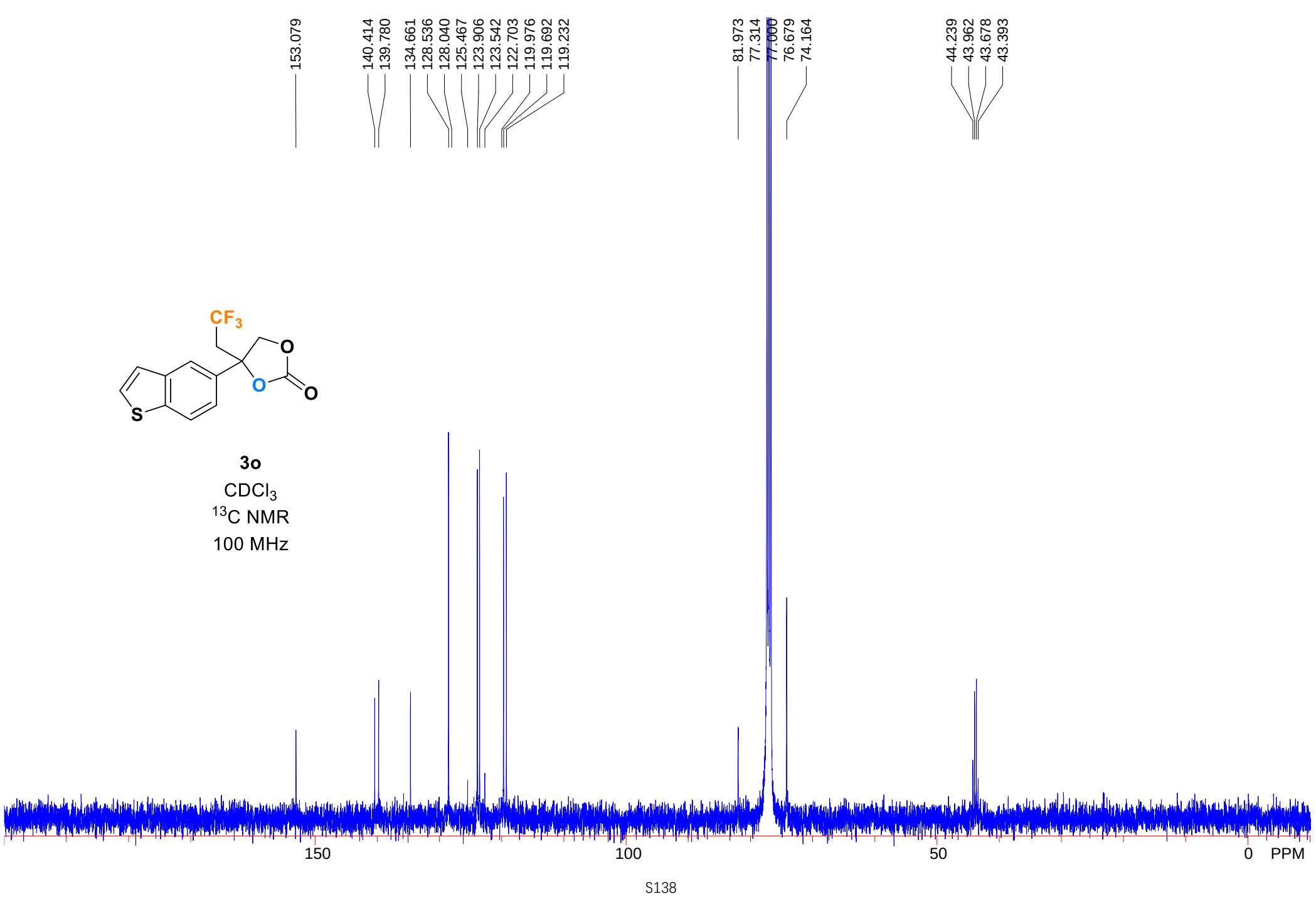
^{19}F NMR

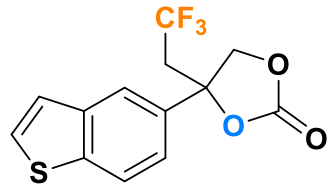
376 MHz

-60.633

-20 -40 -60 -80 -100 -120 -140 PPM


7.968
7.946
7.875
7.569
7.556
7.387
7.373
7.259
7.236
4.856
4.834
4.692
4.670
3.032
3.024
3.007
3.000
2.983
2.976
2.958
2.952
0.000
CF3
O
O
O
S
3o
CDCl3
1H NMR
400 MHz
1.04
1.00
1.01
1.06
0.98
1.02
1.00
2.05
8
6
4
2
0
PPM


153.079
140.414
139.780
134.661
128.536
128.040
125.467
123.906
123.542
122.703
119.976
119.692
119.232
81.973
77.314
77.000
76.679
74.164
44.239
43.962
43.678
43.393
CF3
O
O
O
S
3o
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM

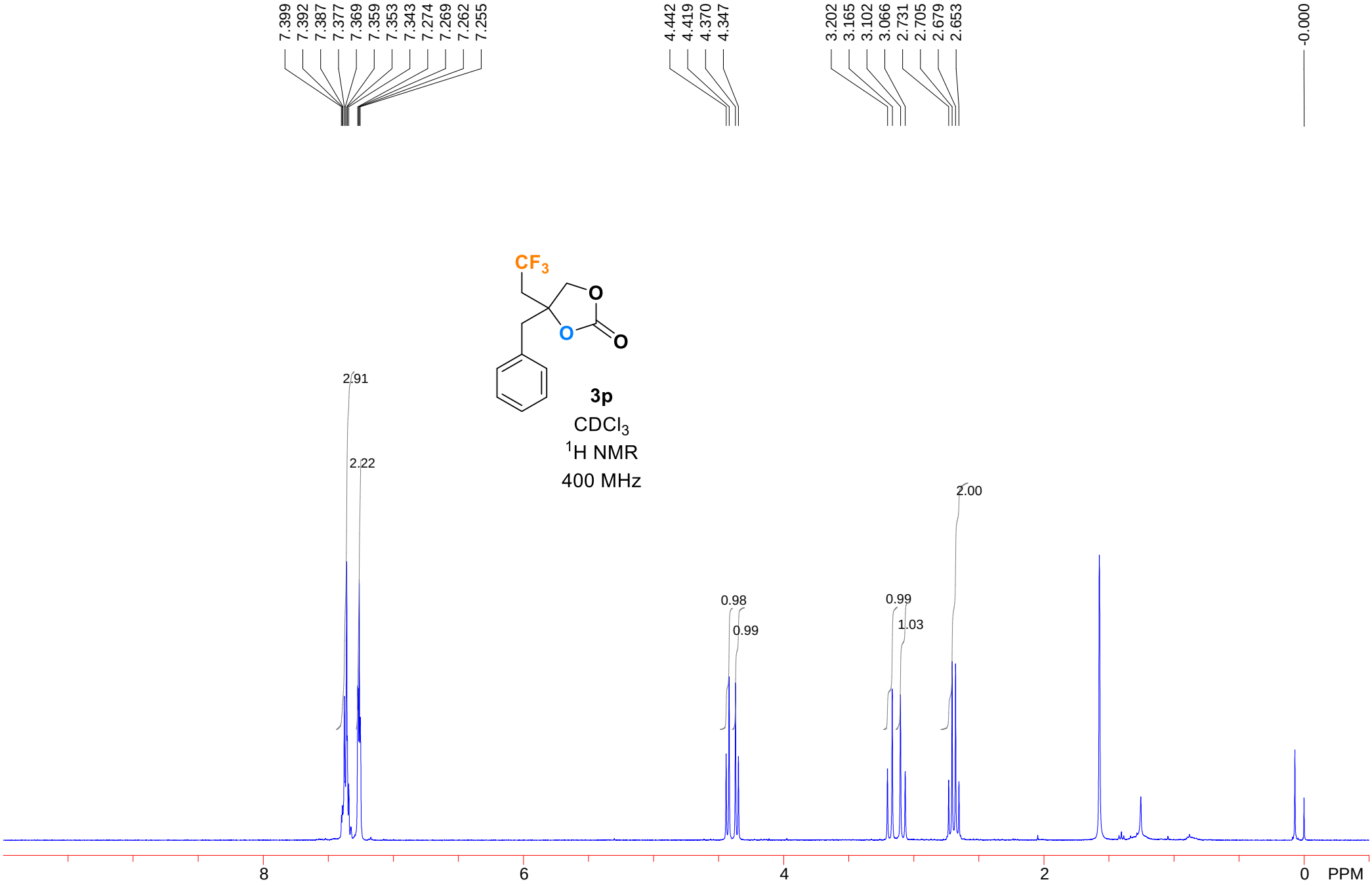


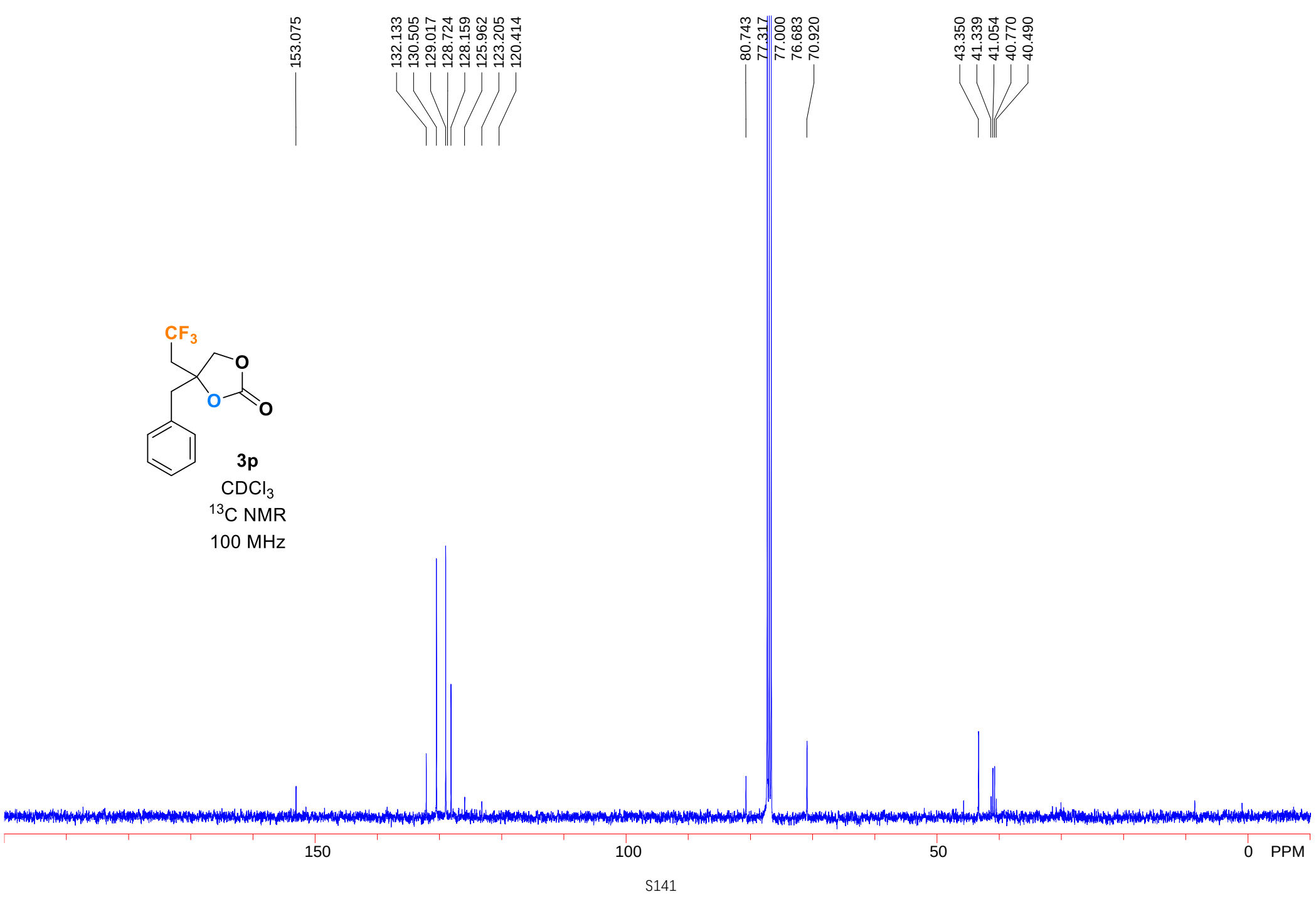
3o

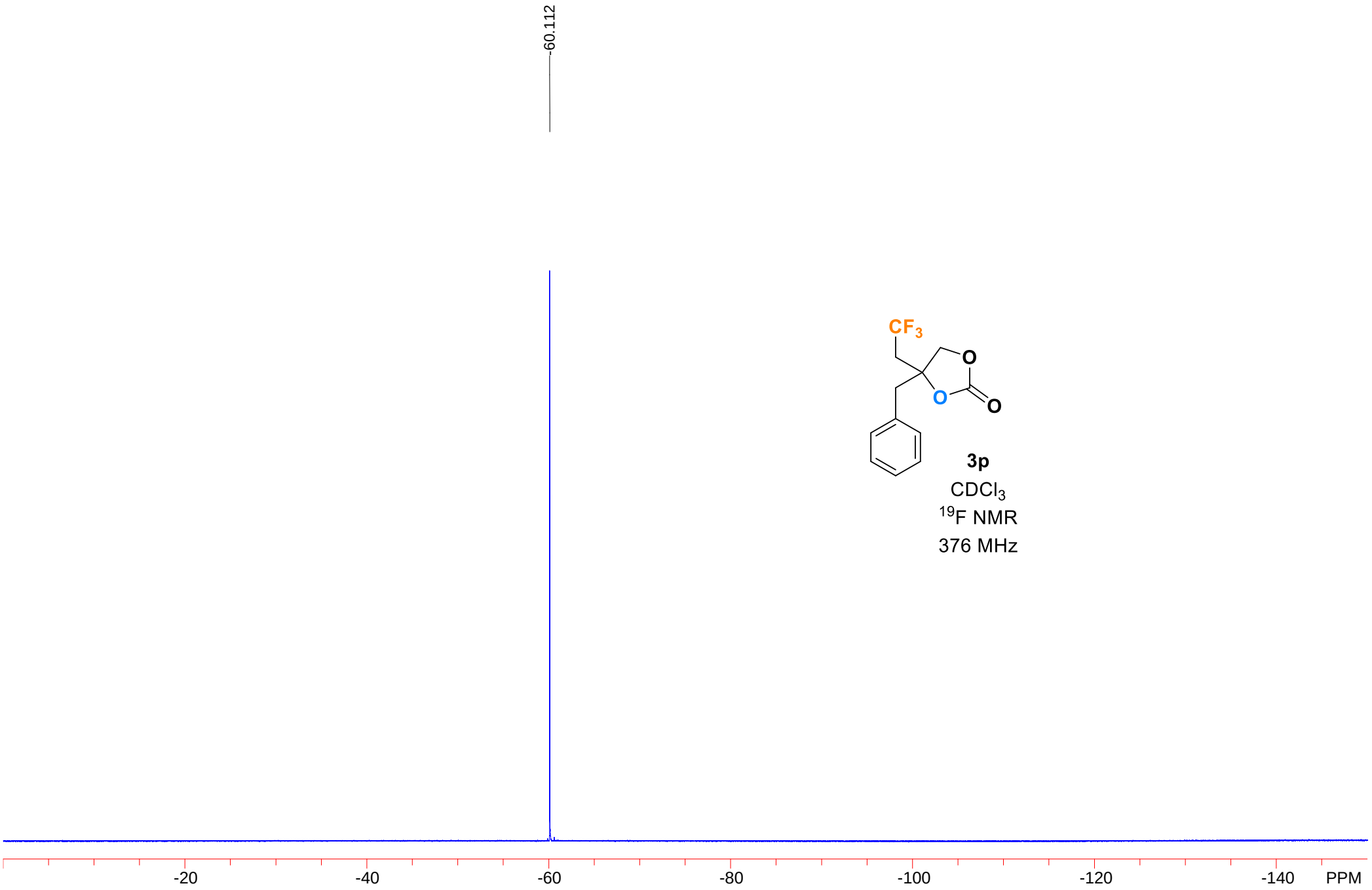
$CDCl_3$

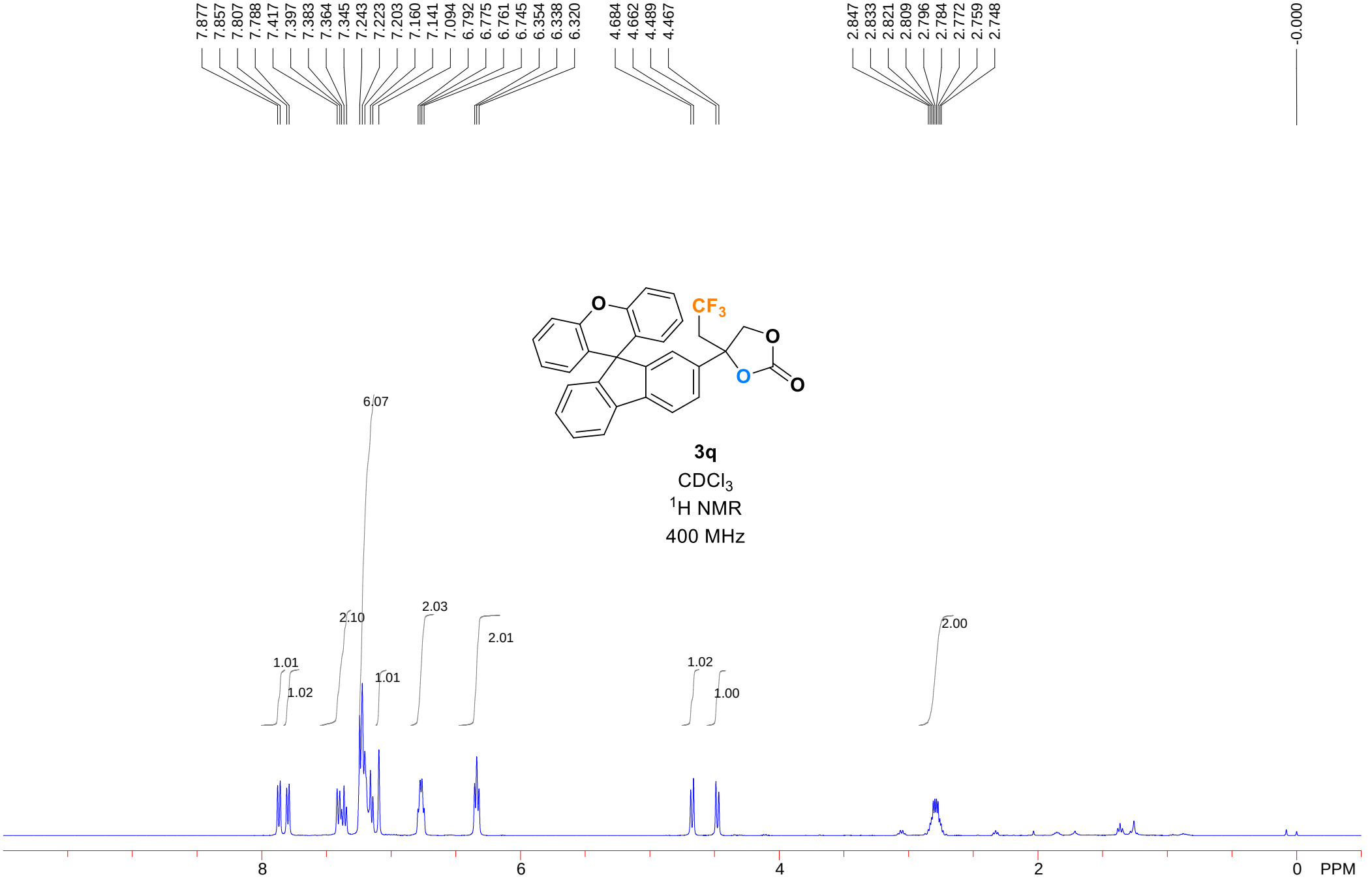
^{19}F NMR

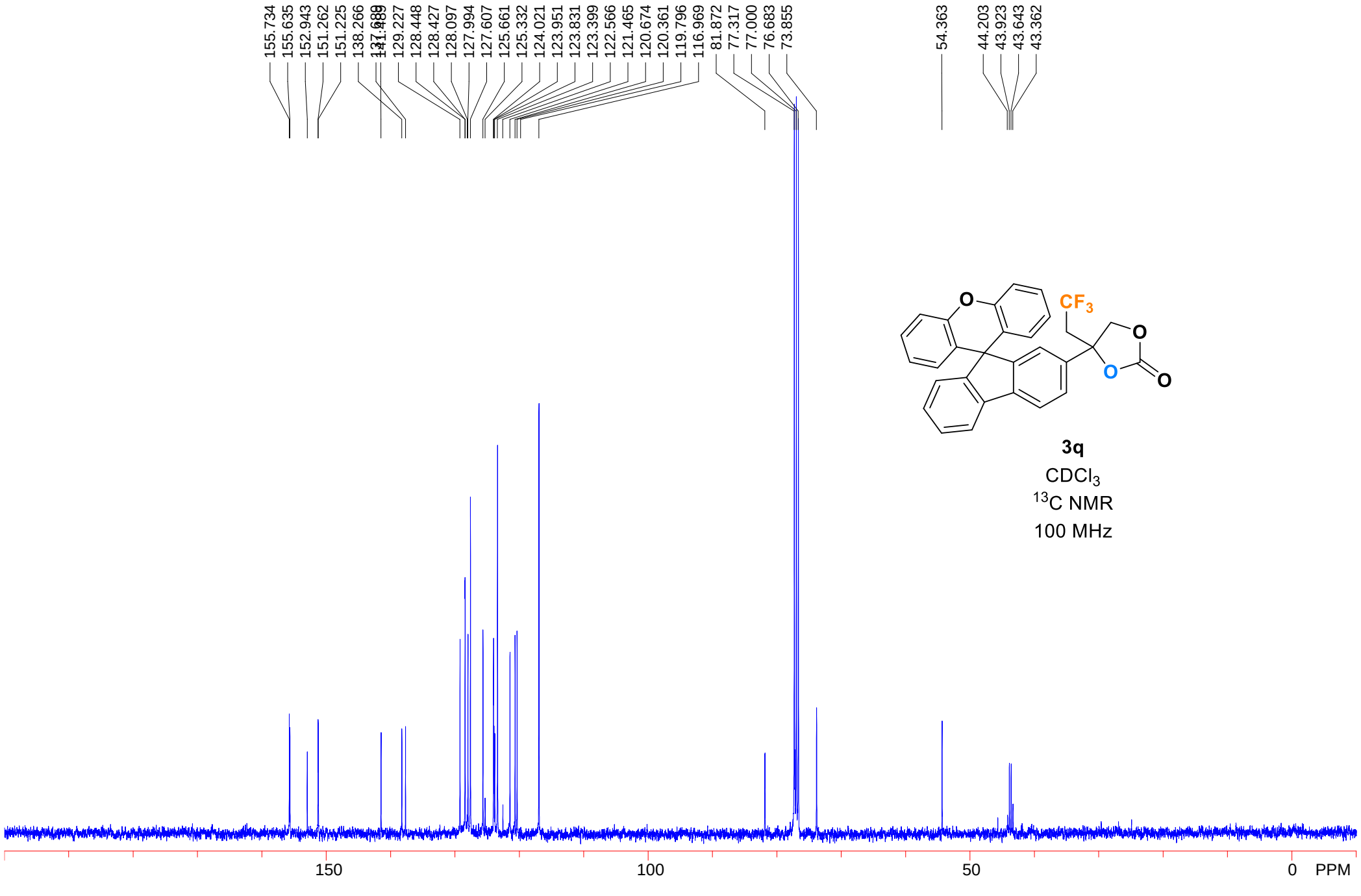
376 MHz


7.399
7.392
7.387
7.377
7.369
7.359
7.353
7.343
7.274
7.269
7.262
7.255
4.442
4.419
4.370
4.347
3.202
3.165
3.102
3.066
2.731
2.705
2.679
2.653
-0.000
CF3
O
O
O
3p
CDCl3
1H NMR
400 MHz
2.91
2.22
0.98
0.99
0.99
1.03
2.00
8
6
4
2
0
PPM


153.075
132.133
130.505
129.017
128.724
128.159
125.962
123.205
120.414
80.743
77.317
77.000
76.683
70.920
43.350
41.339
41.054
40.770
40.490
CF3
O
O
O
3p
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


-60.112
CF3
O
O
O
3p
CDCl3
19F NMR
376 MHz
-20
-40
-60
-80
-100
-120
-140
PPM


7.877
7.857
7.807
7.788
7.417
7.397
7.383
7.364
7.345
7.243
7.223
7.203
7.160
7.141
7.094
6.792
6.775
6.761
6.745
6.354
6.338
6.320
4.684
4.662
4.489
4.467
2.847
2.833
2.821
2.809
2.796
2.784
2.772
2.759
2.748
-0.000
O
CF3
O
O
O
3q
CDCl3
1H NMR
400 MHz
6.07
2.10
2.03
2.01
2.00
1.01
1.02
1.01
1.02
1.00
8
6
4
2
0
PPM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151.262
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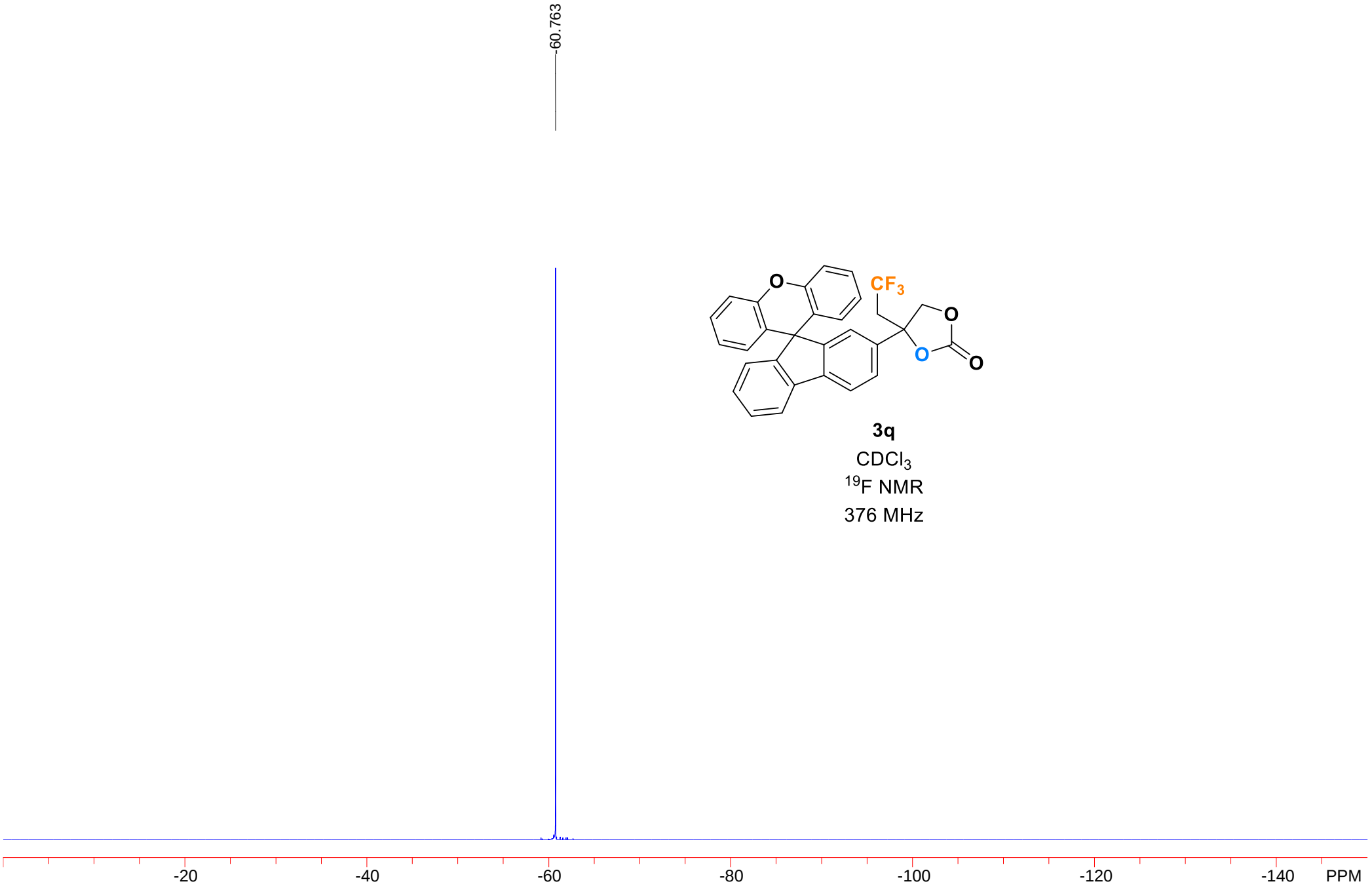
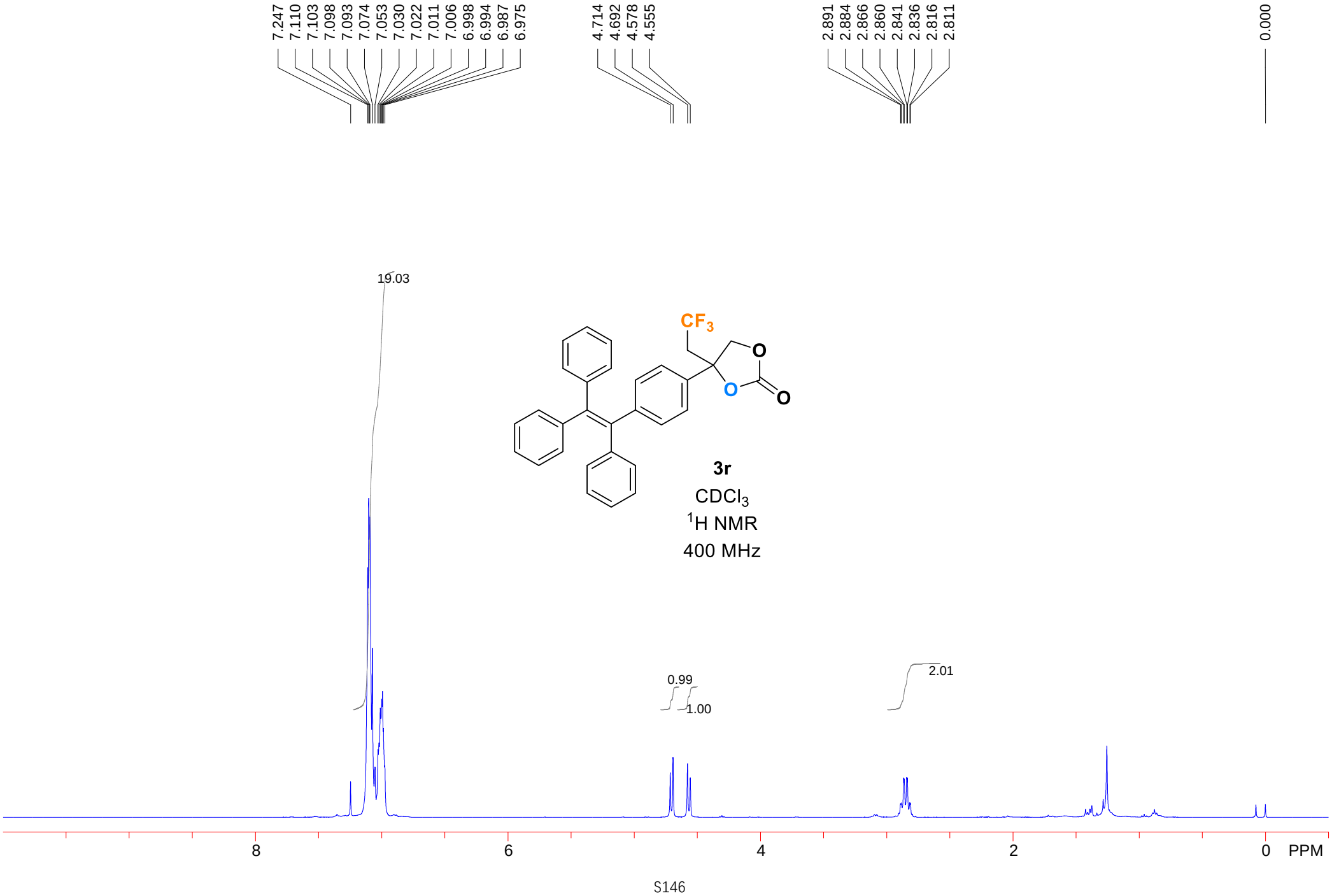
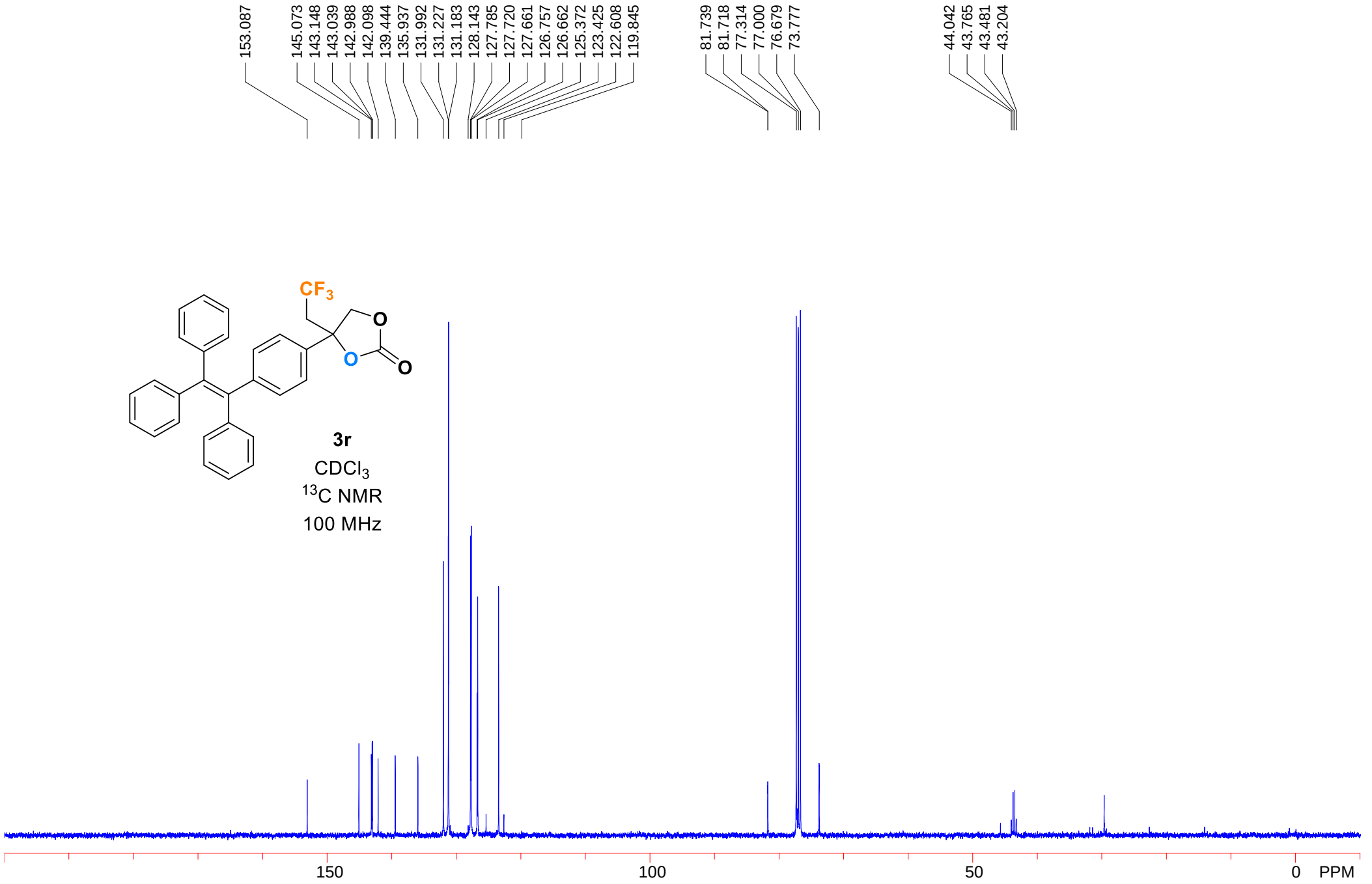
128.448
128.427
128.097
127.994
127.607
125.661
125.332
124.021
123.951
123.831
123.399
122.566
121.465
120.674
120.361
119.796
116.969
81.872
77.317
77.000
76.683
73.855
54.363
44.203
43.923
43.643
43.362
O
CF3
O
O
O
3q
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


-60.763
O
CF3
O
O
O
3q
CDCl3
19F NMR
376 MHz
-20
-40
-60
-80
-100
-120
-140
PPM


7.247
7.110
7.103
7.098
7.093
7.074
7.053
7.030
7.022
7.011
7.006
6.998
6.994
6.987
6.975
4.714
4.692
4.578
4.555
2.891
2.884
2.866
2.860
2.841
2.836
2.816
2.811
0.000
19.03
CF3
O
O
O
3r
CDCl3
1H NMR
400 MHz
0.99
1.00
2.01
8
6
4
2
0
PPM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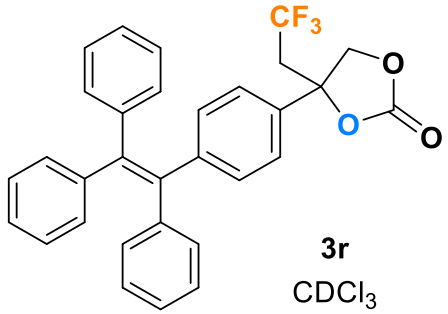
143.148
143.039
142.988
142.098
139.444
135.937
131.992
131.227
131.183
128.143
127.785
127.720
127.661
126.757
126.662
125.372
123.425
122.608
119.845
81.739
81.718
77.314
77.000
76.679
73.777
44.042
43.765
43.481
43.204
CF3
O
O
O
3r
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM



3r

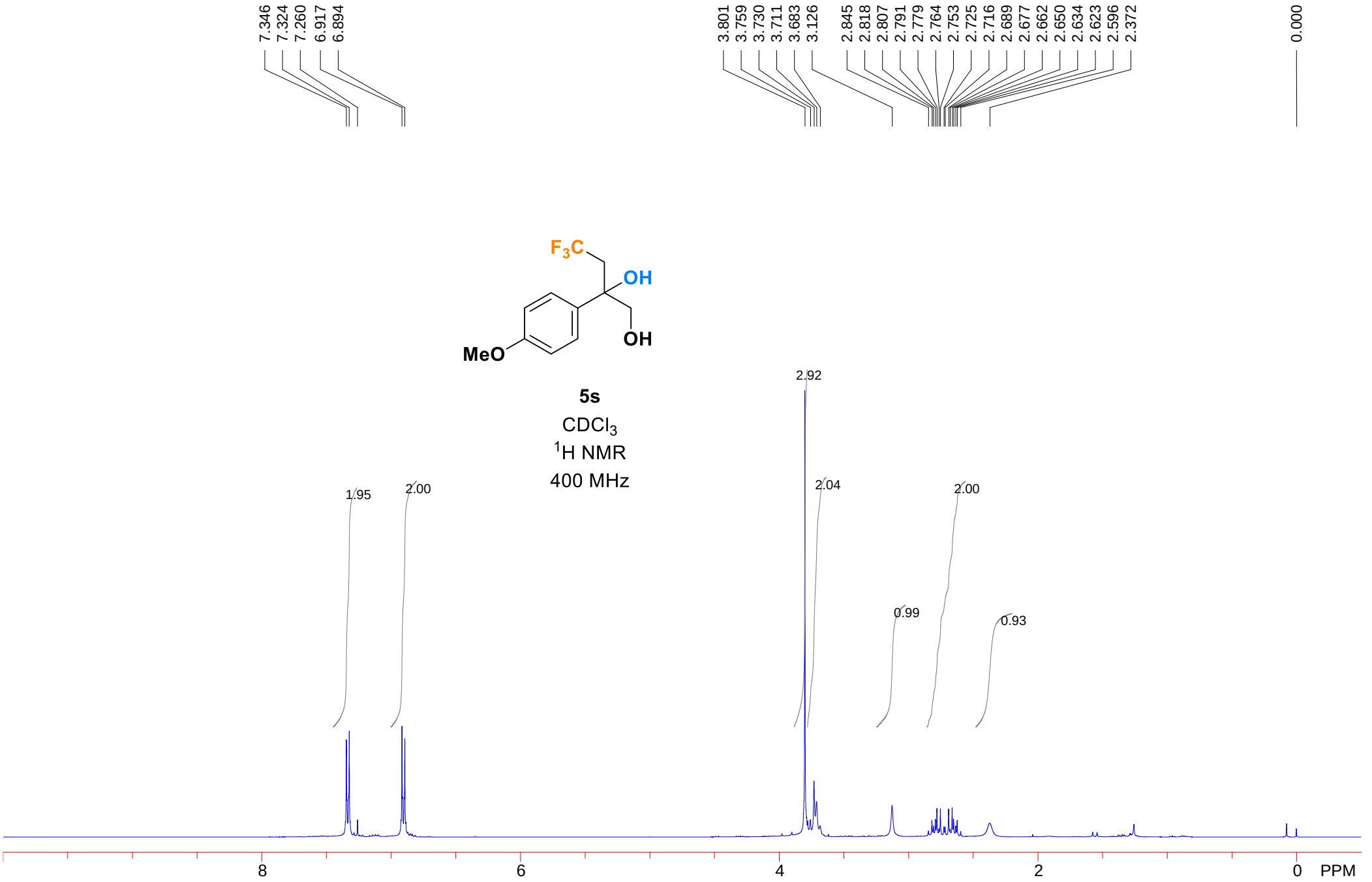
$CDCl_3$

^{19}F NMR

376 MHz

-60.673

-20 -40 -60 -80 -100 -120 -140 PPM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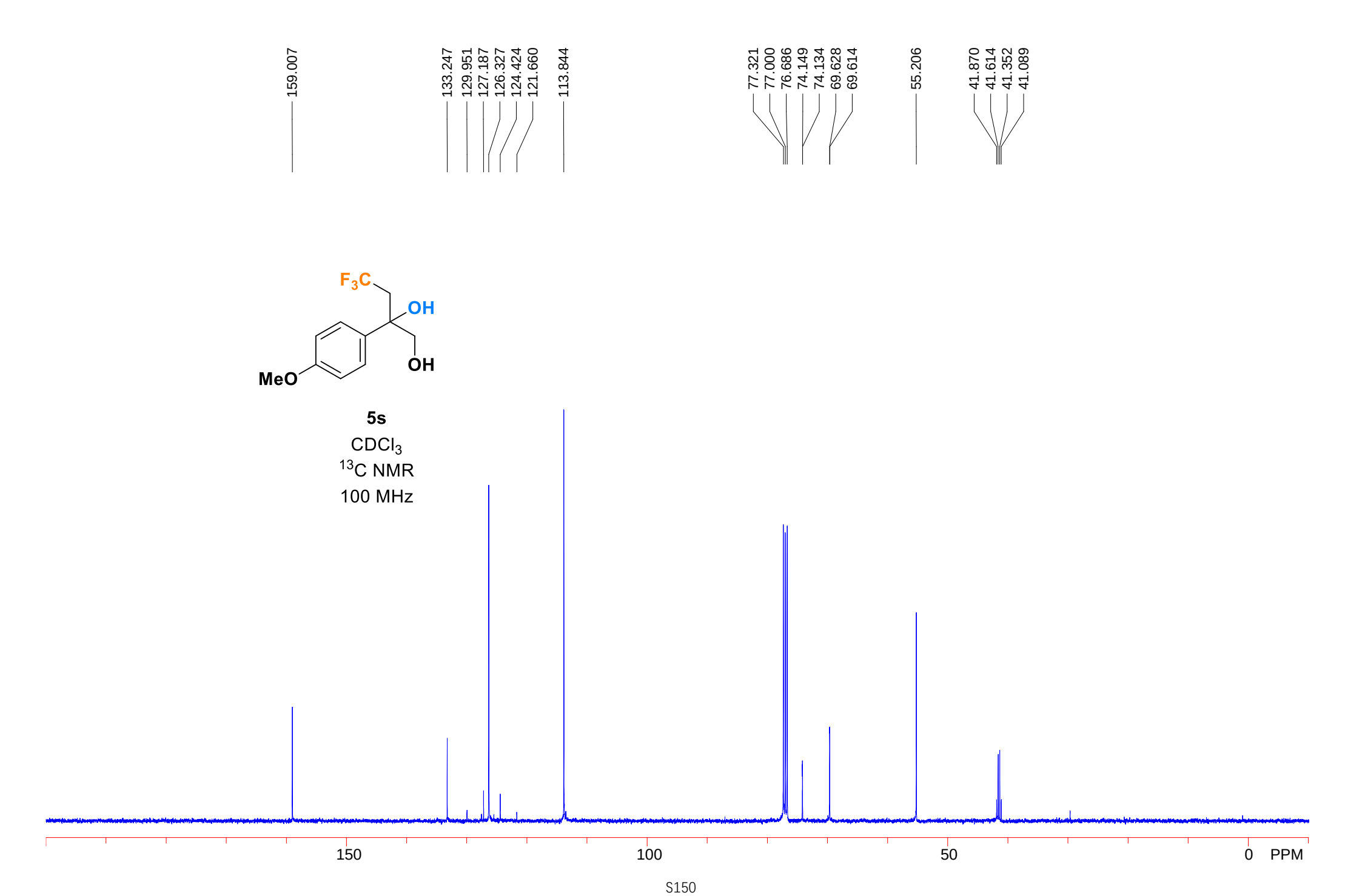
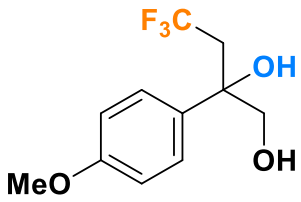
7.324
7.260
6.917
6.894
3.801
3.759
3.730
3.711
3.683
3.126
2.845
2.818
2.807
2.791
2.779
2.764
2.753
2.725
2.716
2.689
2.677
2.662
2.650
2.634
2.623
2.596
2.372
0.000
F3C
OH
OH
MeO
5s
CDCl3
1H NMR
400 MHz
1.95
2.00
2.92
2.04
0.99
2.00
0.93
8
6
4
2
0
PPM


159.007
133.247
129.951
127.187
126.327
124.424
121.660
113.844
77.321
77.000
76.686
74.149
74.134
69.628
69.614
55.206
41.870
41.614
41.352
41.089
F3C
OH
OH
MeO
5s
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM

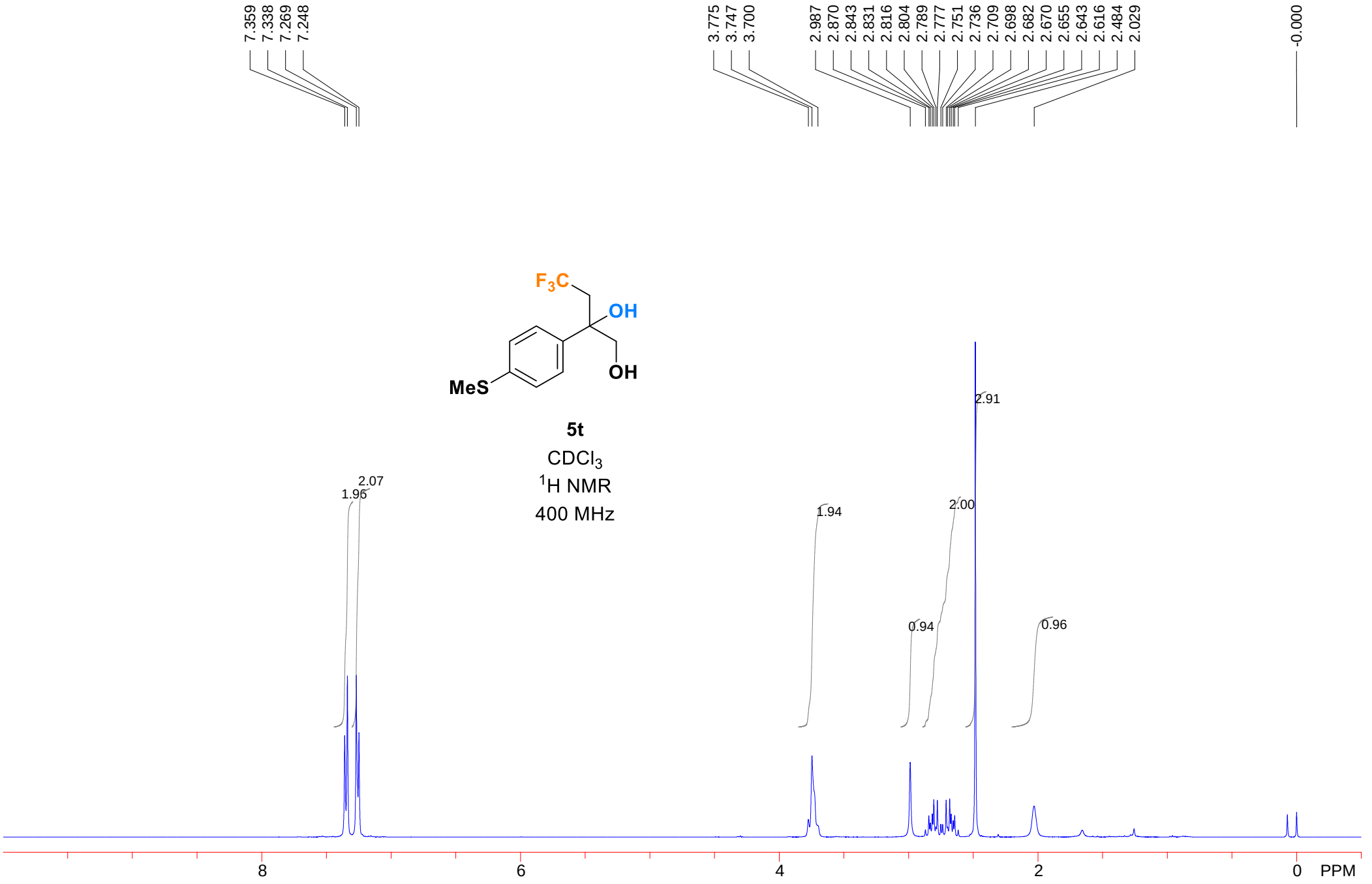


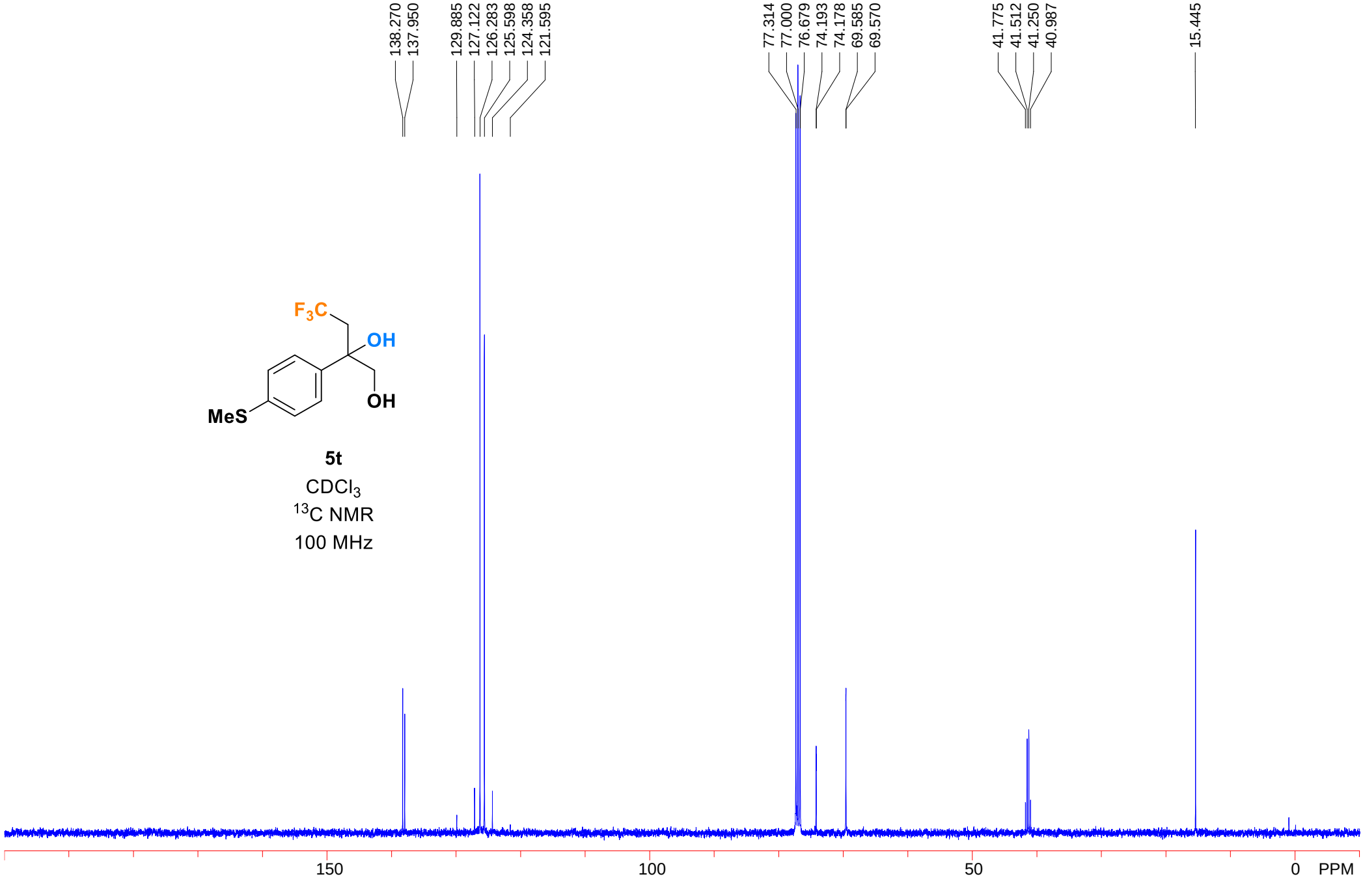
5s

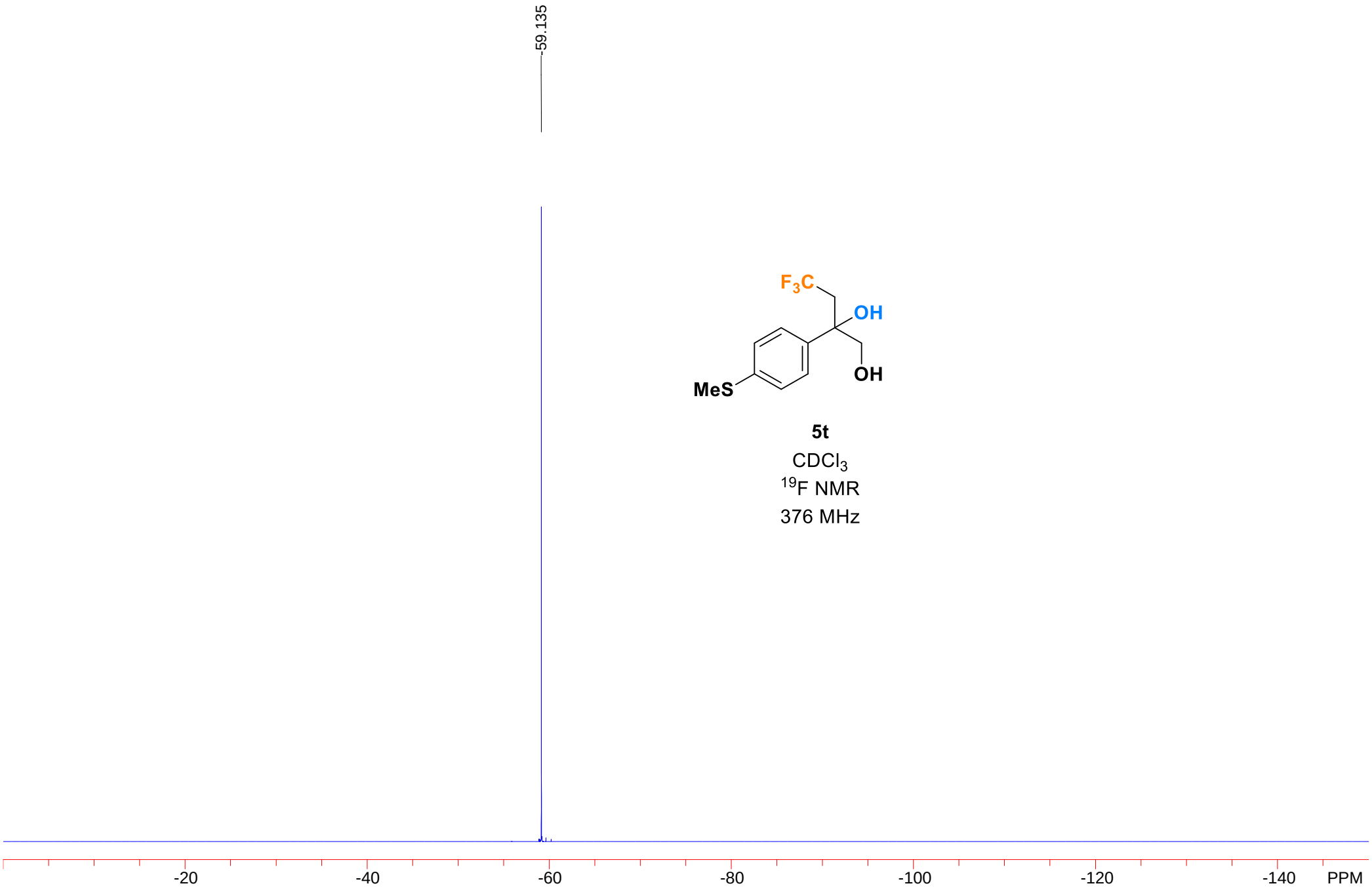
$CDCl_3$

^{19}F NMR

376 MHz


7.359
7.338
7.269
7.248
3.775
3.747
3.700
2.987
2.870
2.843
2.831
2.816
2.804
2.789
2.777
2.751
2.736
2.709
2.698
2.682
2.670
2.655
2.643
2.616
2.484
2.029
-0.000
F3C
OH
OH
MeS
5t
CDCl3
1H NMR
400 MHz
2.07
1.96
1.94
2.00
2.91
0.94
0.96
8
6
4
2
0
PPM


138.270
137.950
129.885
127.122
126.283
125.598
124.358
121.595
77.314
77.000
76.679
74.193
74.178
69.585
69.570
41.775
41.512
41.250
40.987
15.445
F3C
OH
OH
MeS
5t
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM

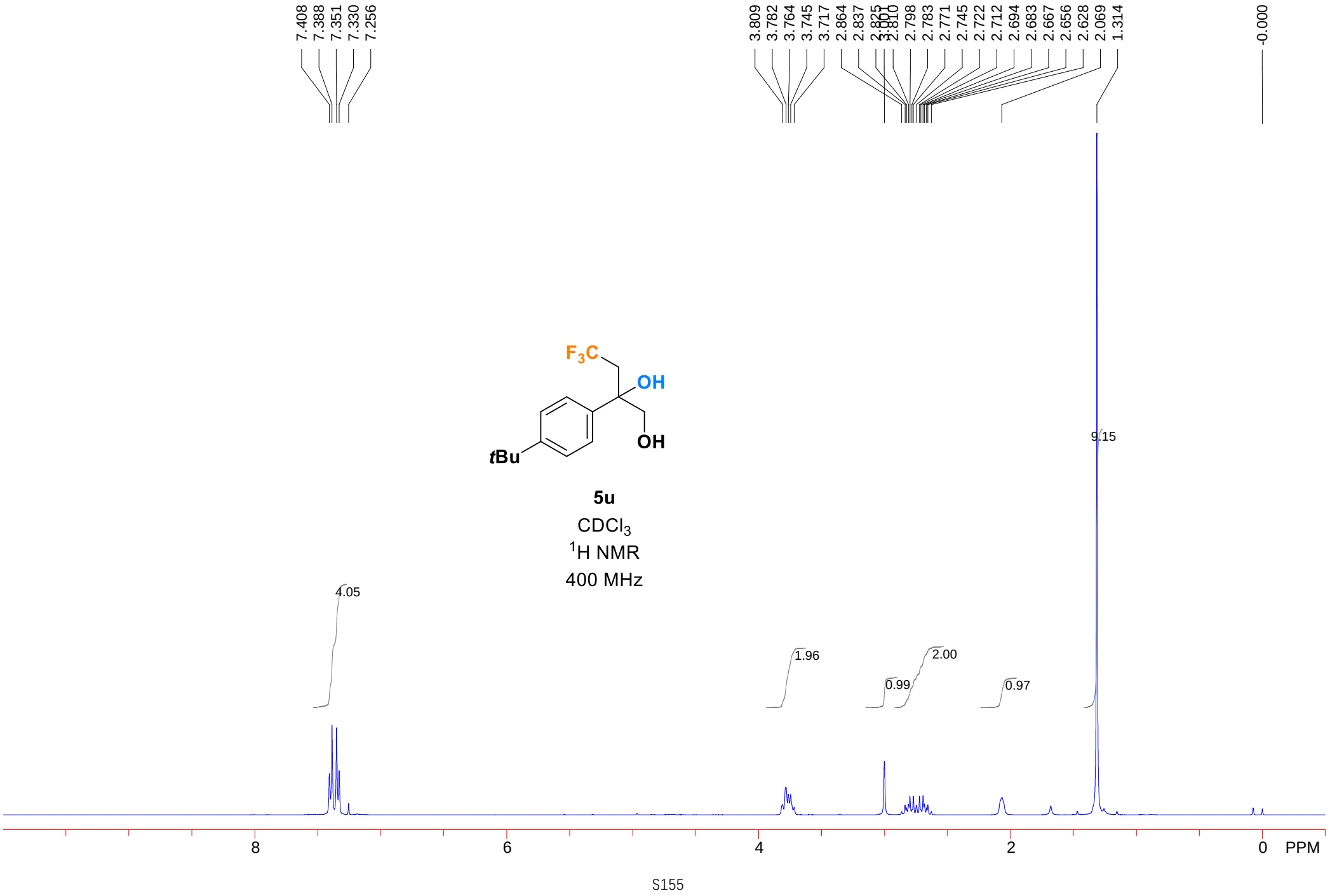


5t

$CDCl_3$

^{19}F NMR

376 MHz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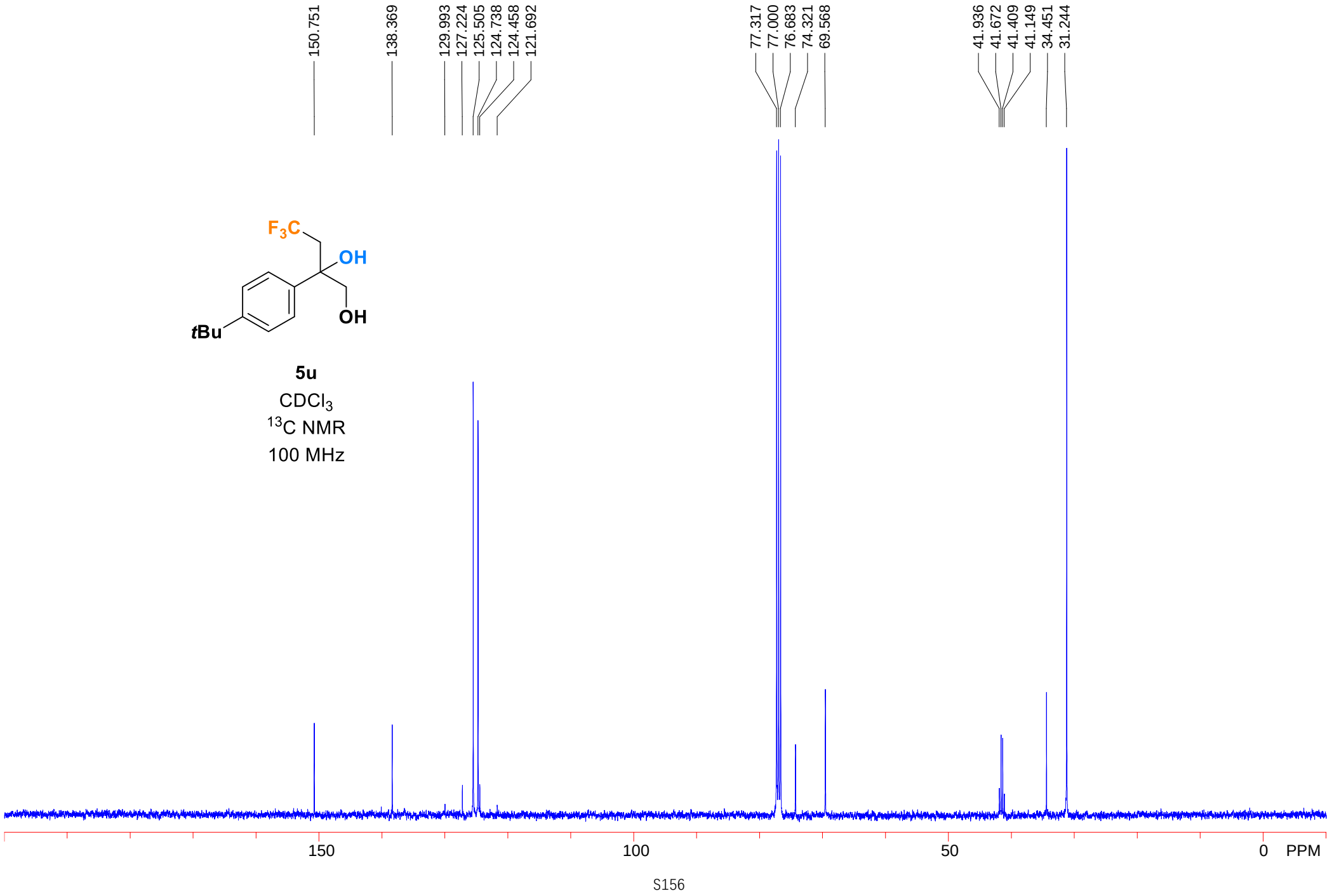
7.388
7.351
7.330
7.256
3.809
3.782
3.764
3.745
3.717
2.864
2.837
2.825
2.810
2.798
2.783
2.771
2.745
2.722
2.712
2.694
2.683
2.667
2.656
2.628
2.069
1.314
-0.000
F3C
OH
OH
tBu
5u
CDCl3
1H NMR
400 MHz
4.05
1.96
0.99
2.00
0.97
9.15
8
6
4
2
0
PPM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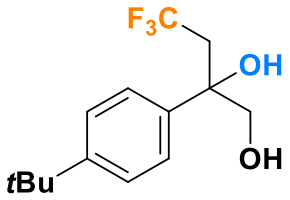
138.369
129.993
127.224
125.505
124.738
124.458
121.692
77.317
77.000
76.683
74.321
69.568
41.936
41.672
41.409
41.149
34.451
31.244
F3C
OH
OH
tBu
5u
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM

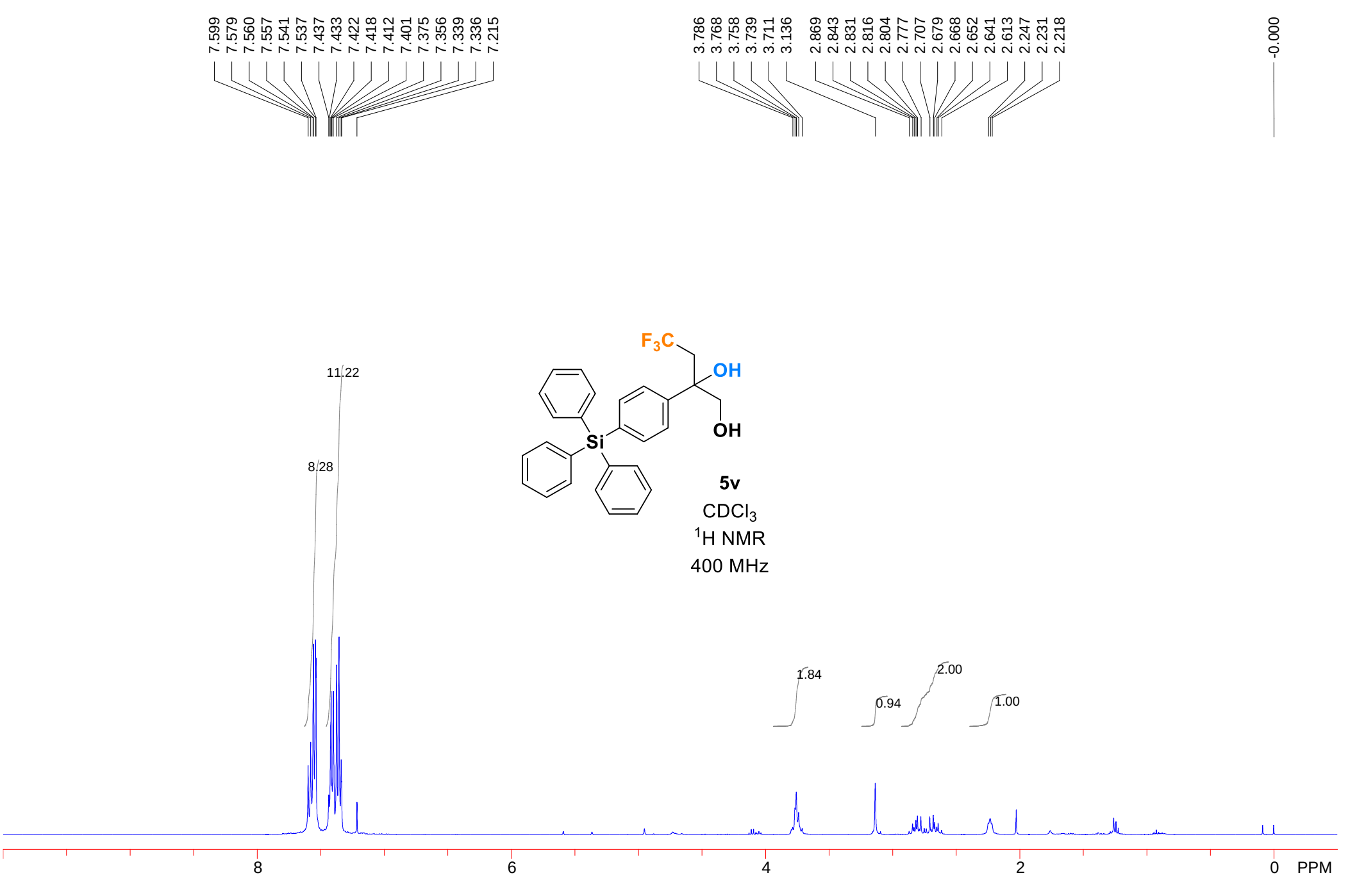


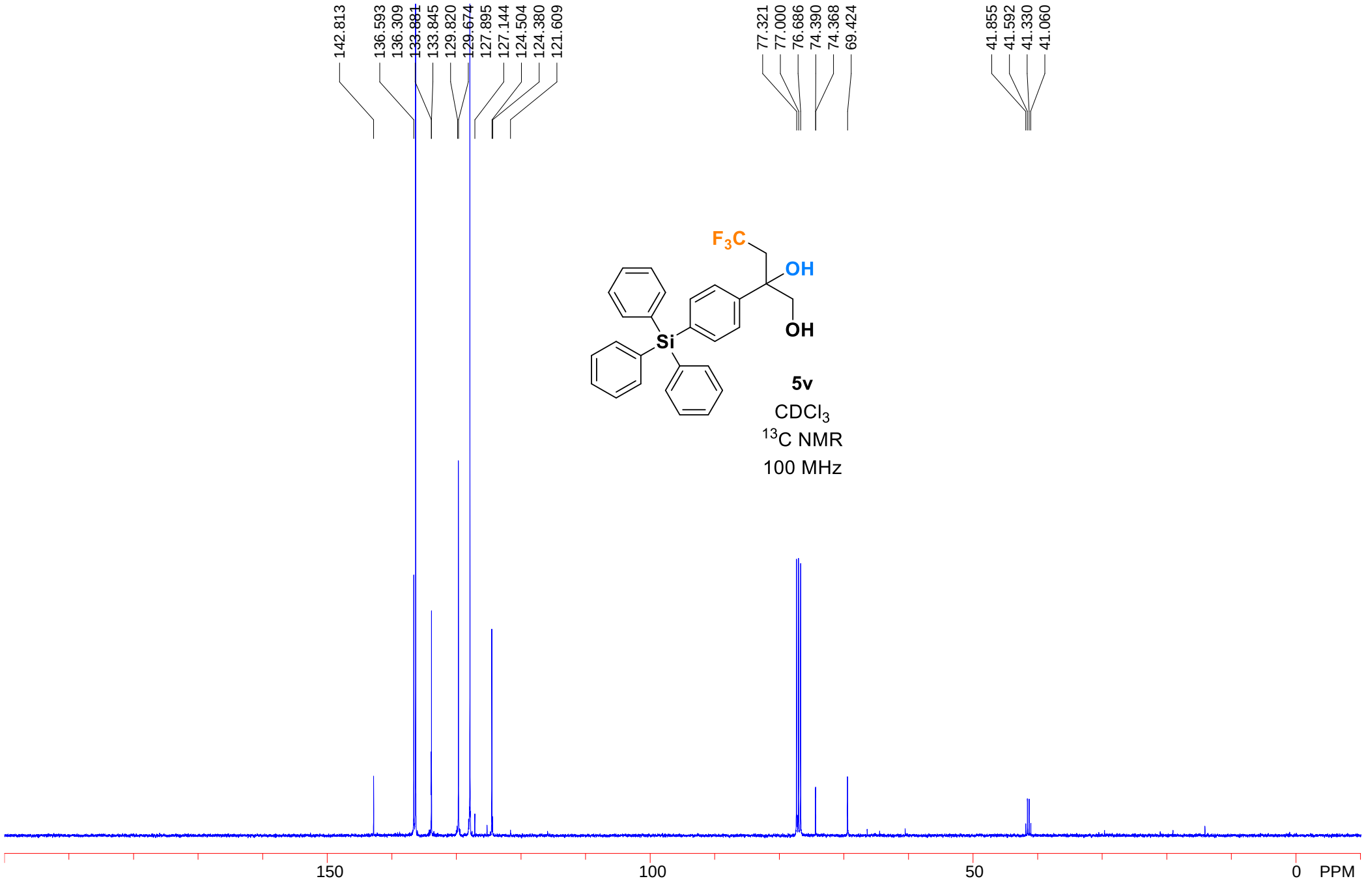
5u

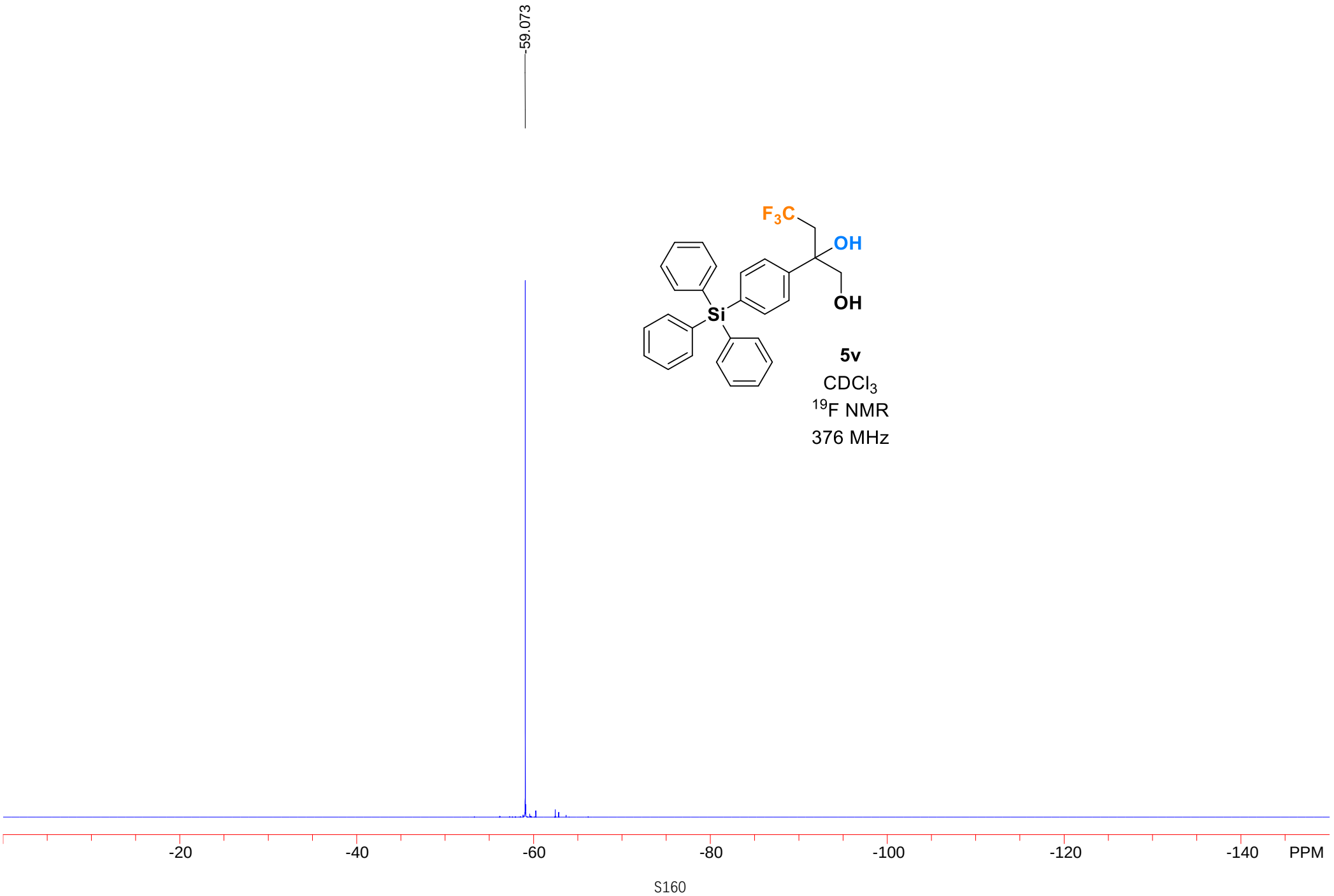
$CDCl_3$

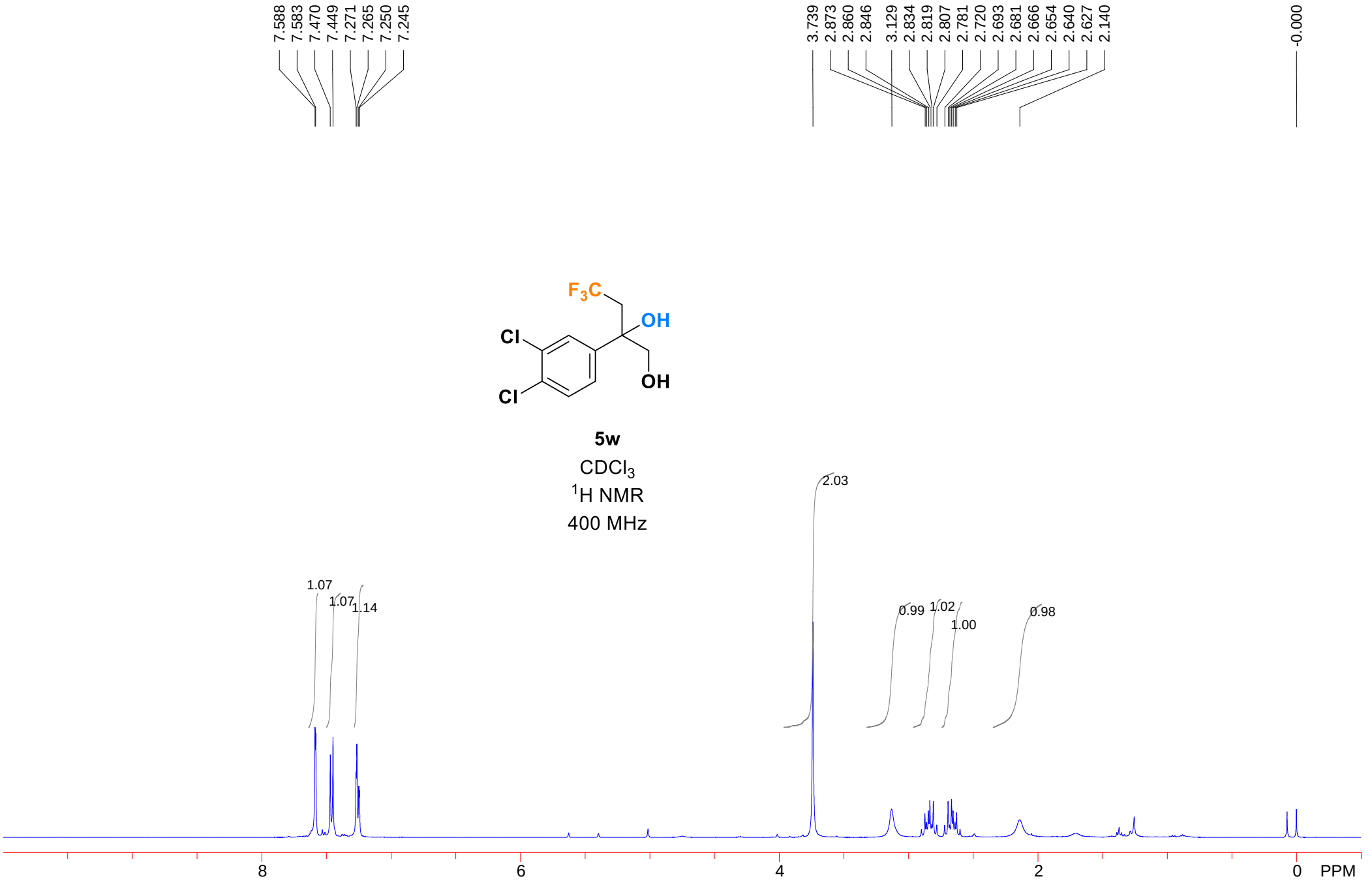
^{19}F NMR

376 MHz


7.599
7.579
7.560
7.557
7.541
7.537
7.437
7.433
7.422
7.418
7.412
7.401
7.375
7.356
7.339
7.336
7.215
3.786
3.768
3.758
3.739
3.711
3.136
2.869
2.843
2.831
2.816
2.804
2.777
2.707
2.679
2.668
2.652
2.641
2.613
2.247
2.231
2.218
-0.000
F3C
OH
OH
Si
5v
CDCl3
1H NMR
400 MHz
11.22
8.28
1.84
0.94
2.00
1.00
8
6
4
2
0
PPM


142.813
136.593
136.309
133.881
133.845
129.820
129.674
127.895
127.144
124.504
124.380
121.609
77.321
77.000
76.686
74.390
74.368
69.424
41.855
41.592
41.330
41.060
F3C
OH
OH
Si
5v
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


-59.073
F3C
OH
OH
Si
5v
CDCl3
19F NMR
376 MHz
-20
-40
-60
-80
-100
-120
-140
PPM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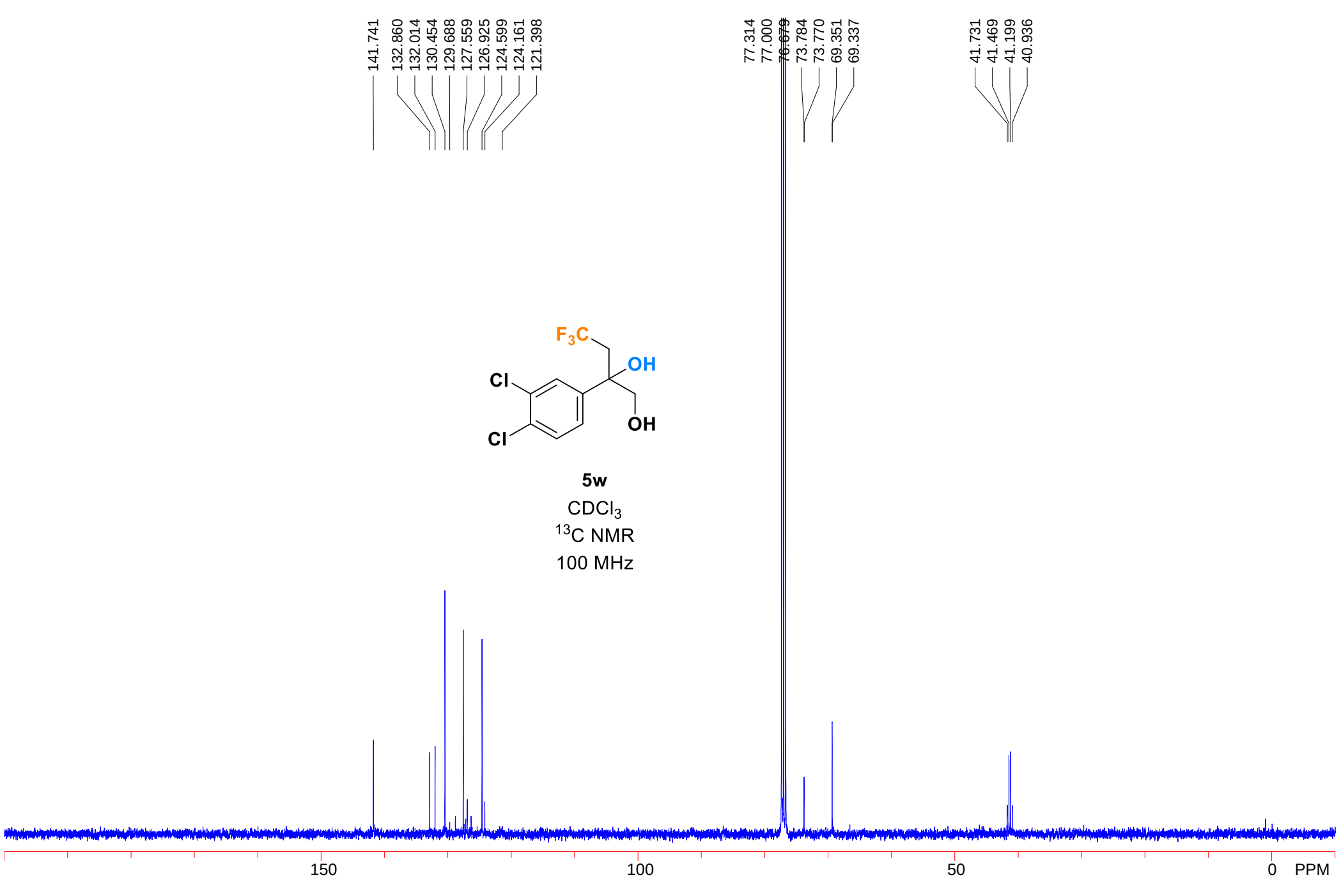
7.583
7.470
7.449
7.271
7.265
7.250
7.245
3.739
2.873
2.860
2.846
3.129
2.834
2.819
2.807
2.781
2.720
2.693
2.681
2.666
2.654
2.640
2.627
2.140
-0.000
F3C
OH
Cl
Cl
OH
5w
CDCl3
1H NMR
400 MHz
1.07
1.07
1.14
2.03
0.99
1.02
1.00
0.98
8
6
4
2
0
PPM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132.014
130.454
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124.599
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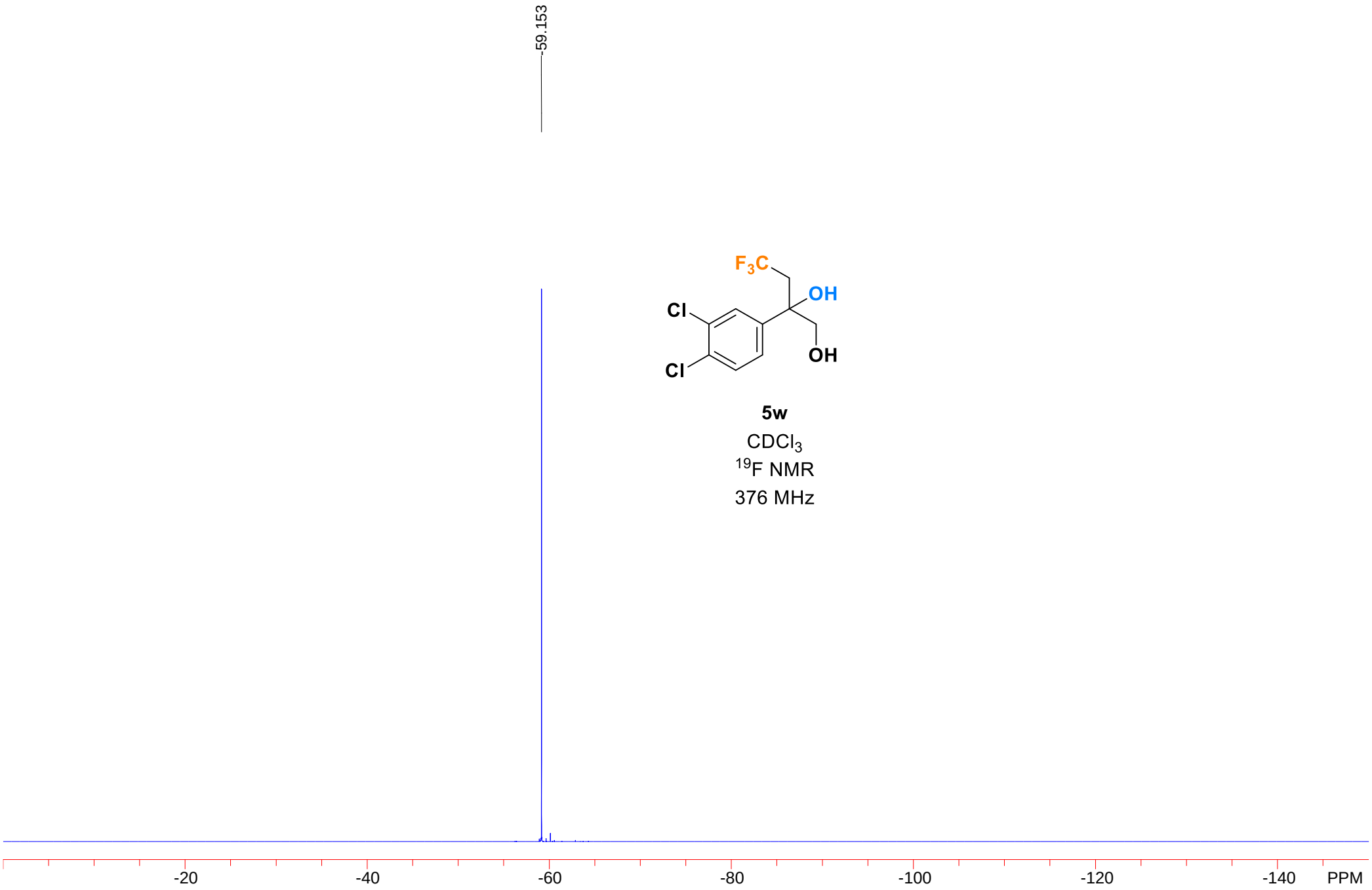
121.398
77.314
77.000
76.679
73.784
73.770
69.351
69.337
41.731
41.469
41.199
40.936
F3C
OH
Cl
Cl
OH
5w
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM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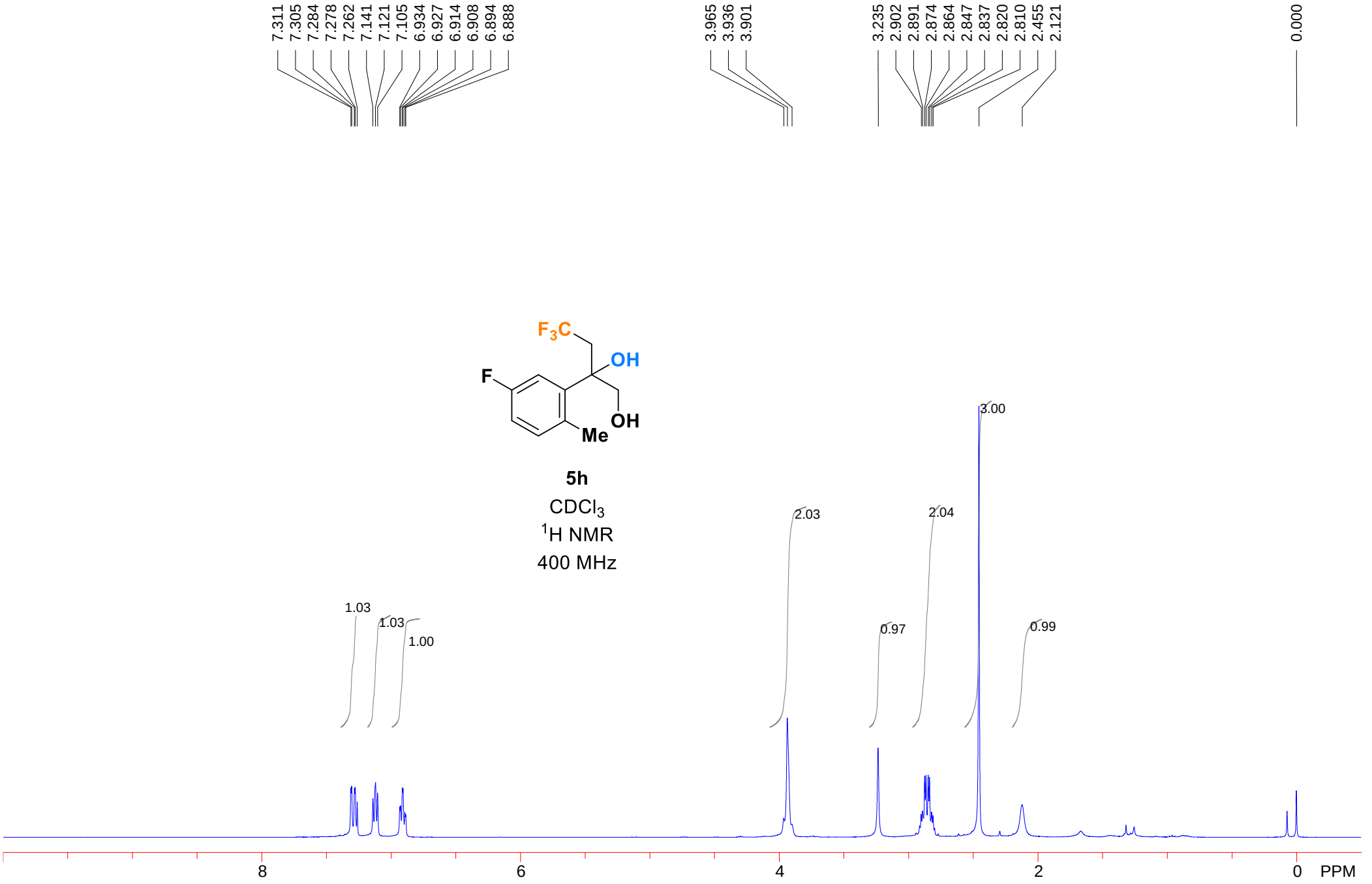
PPM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7.278
7.262
7.141
7.121
7.105
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6.927
6.914
6.908
6.894
6.888
3.965
3.936
3.901
3.235
2.902
2.891
2.874
2.864
2.847
2.837
2.820
2.810
2.455
2.121
0.000
F3C
OH
F
OH
Me
5h
CDCl3
1H NMR
400 MHz
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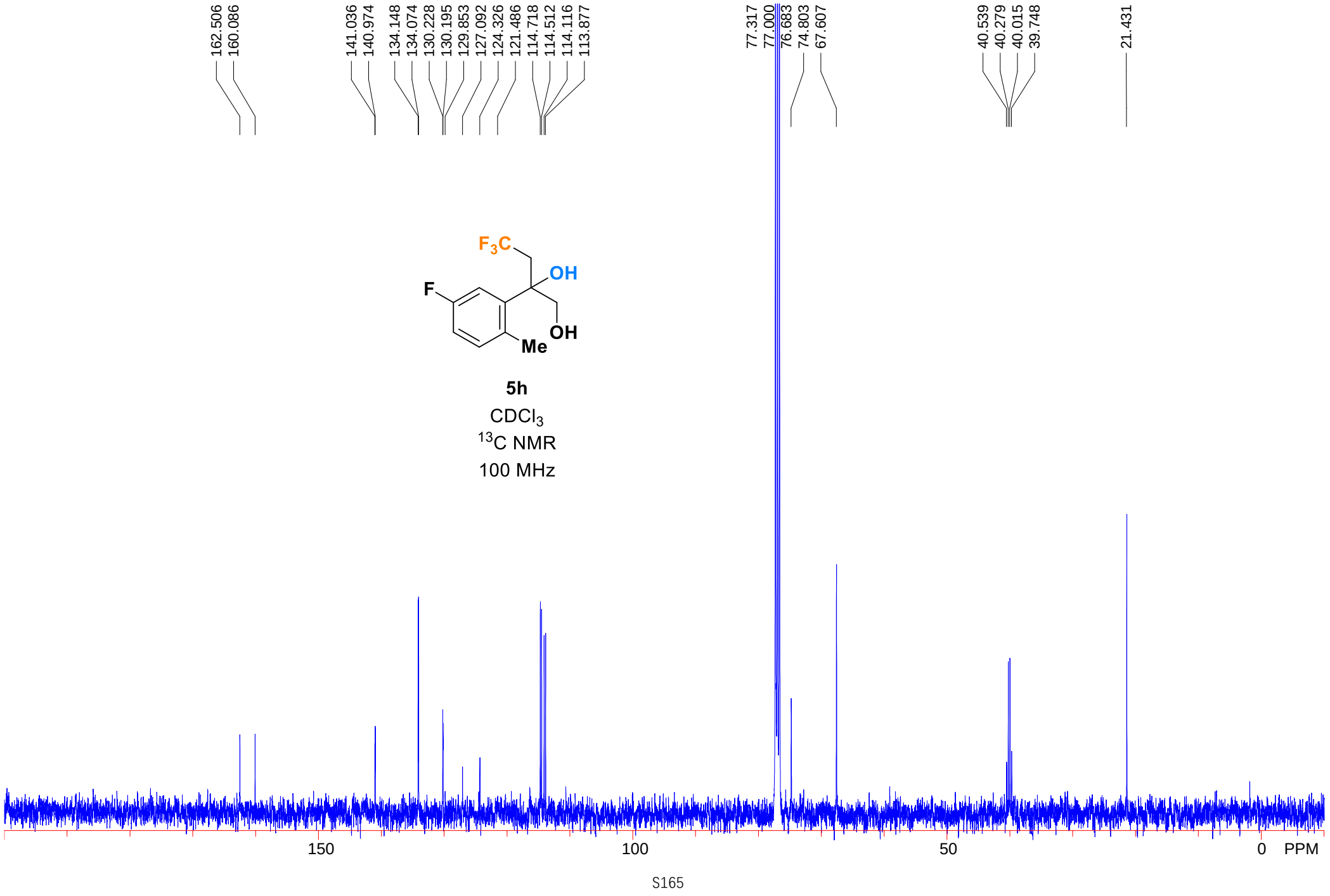
1.03
1.00
2.03
0.97
2.04
3.00
0.99
8
6
4
2
0
PPM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134.074
130.228
130.195
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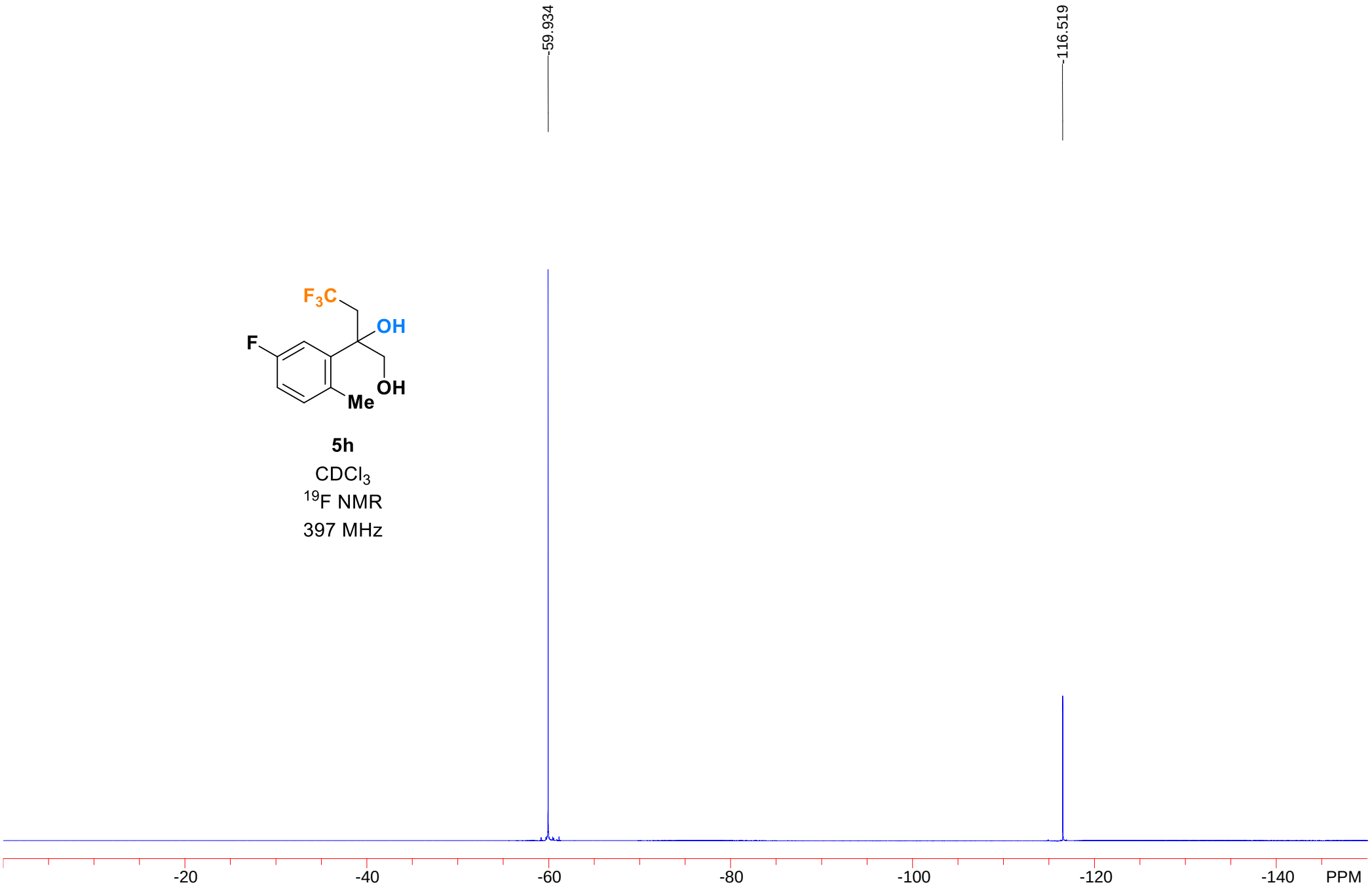
127.092
124.326
121.486
114.718
114.512
114.116
113.877
77.317
77.000
76.683
74.803
67.607
40.539
40.279
40.015
39.748
21.431
F3C
OH
F
OH
Me
5h
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM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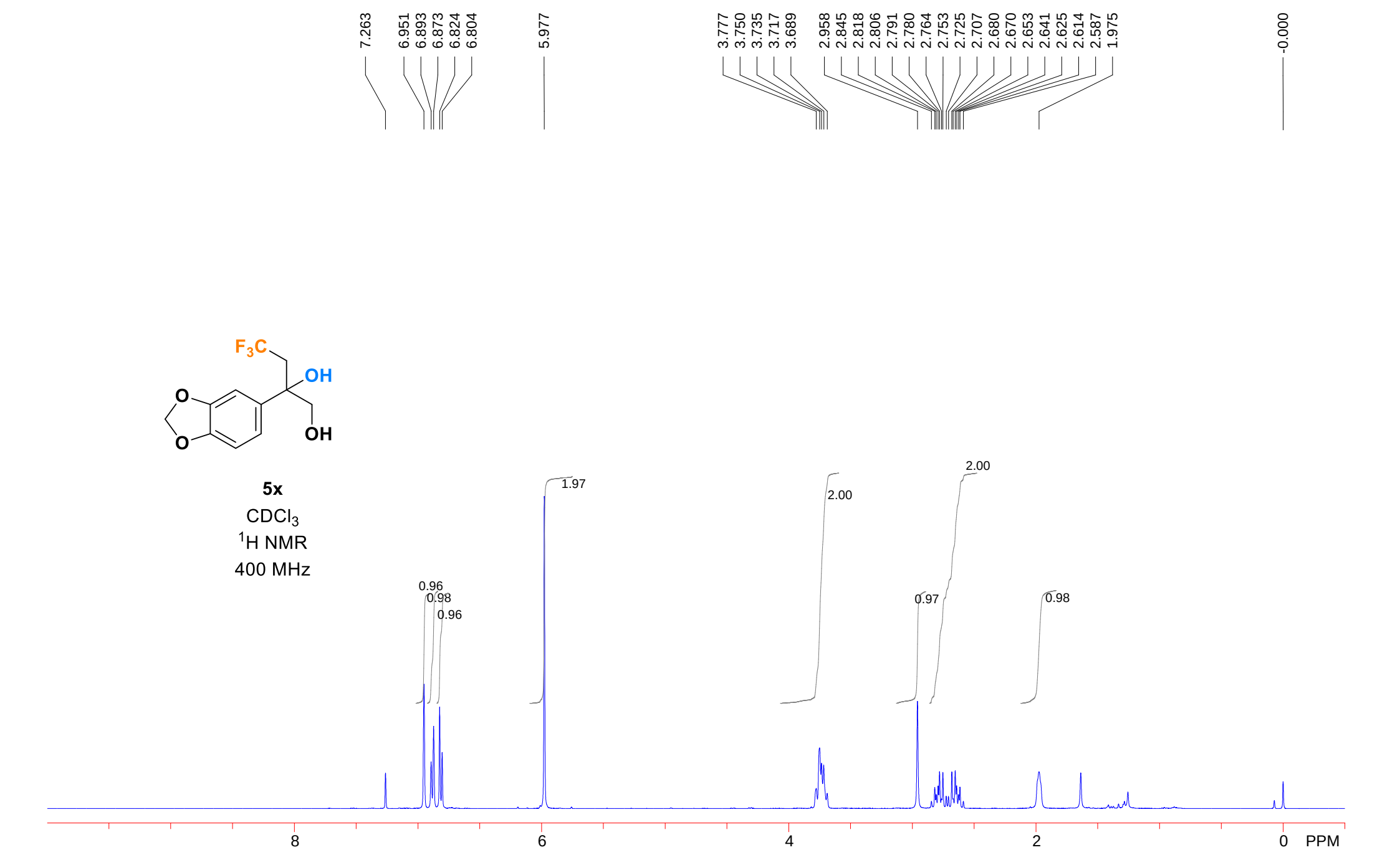
-116.519
F3C
OH
F
OH
Me
5h
CDCl3
19F NMR
397 MHz
-20
-40
-60
-80
-100
-120
-140
PPM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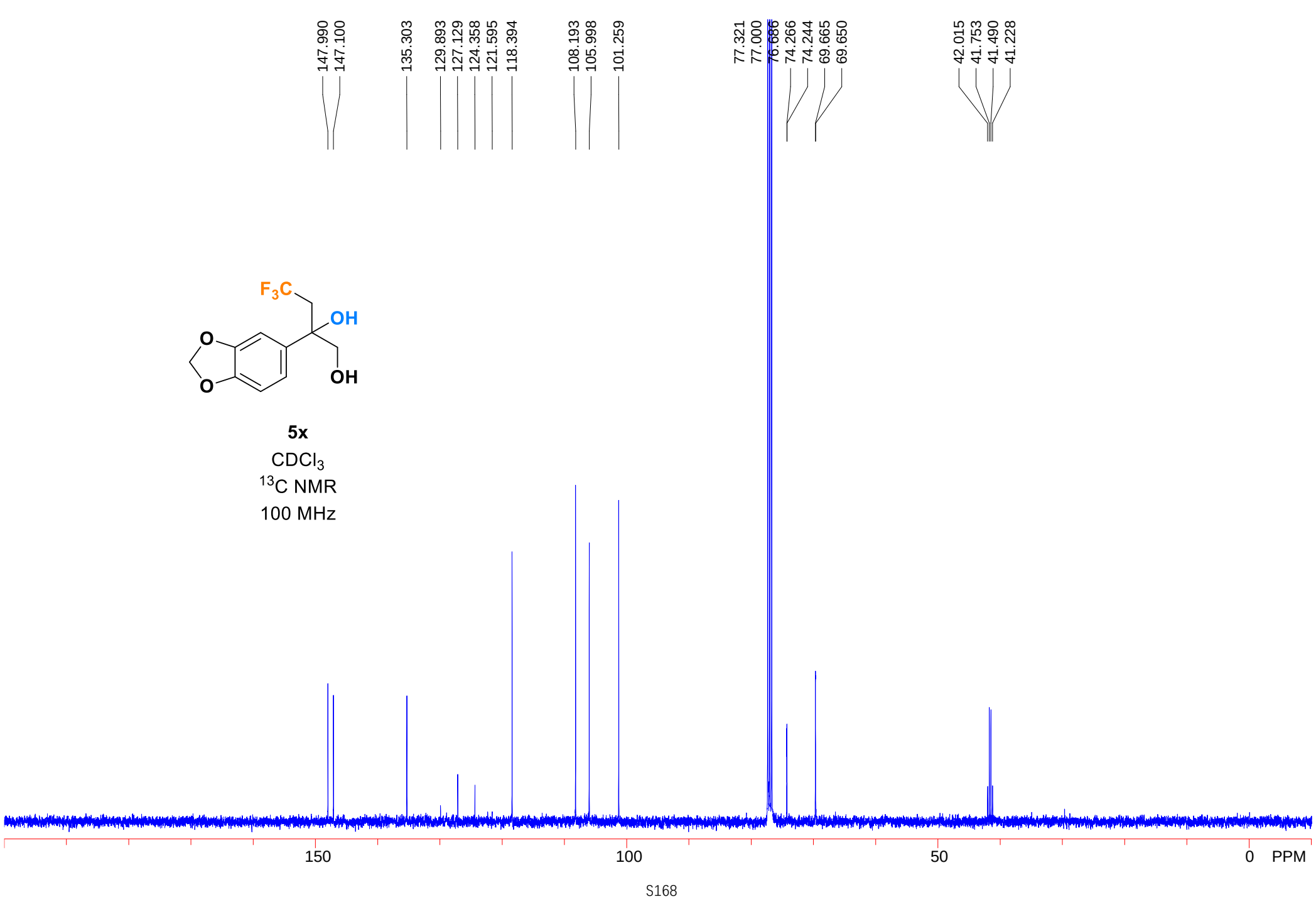
6.951
6.893
6.873
6.824
6.804
5.977
3.777
3.750
3.735
3.717
3.689
2.958
2.845
2.818
2.806
2.791
2.780
2.764
2.753
2.725
2.707
2.680
2.670
2.653
2.641
2.625
2.614
2.587
1.975
-0.000
F3C
OH
O
O
OH
5x
CDCl3
1H NMR
400 MHz
0.96
0.98
0.96
1.97
2.00
0.97
2.00
0.98
8
6
4
2
0
PPM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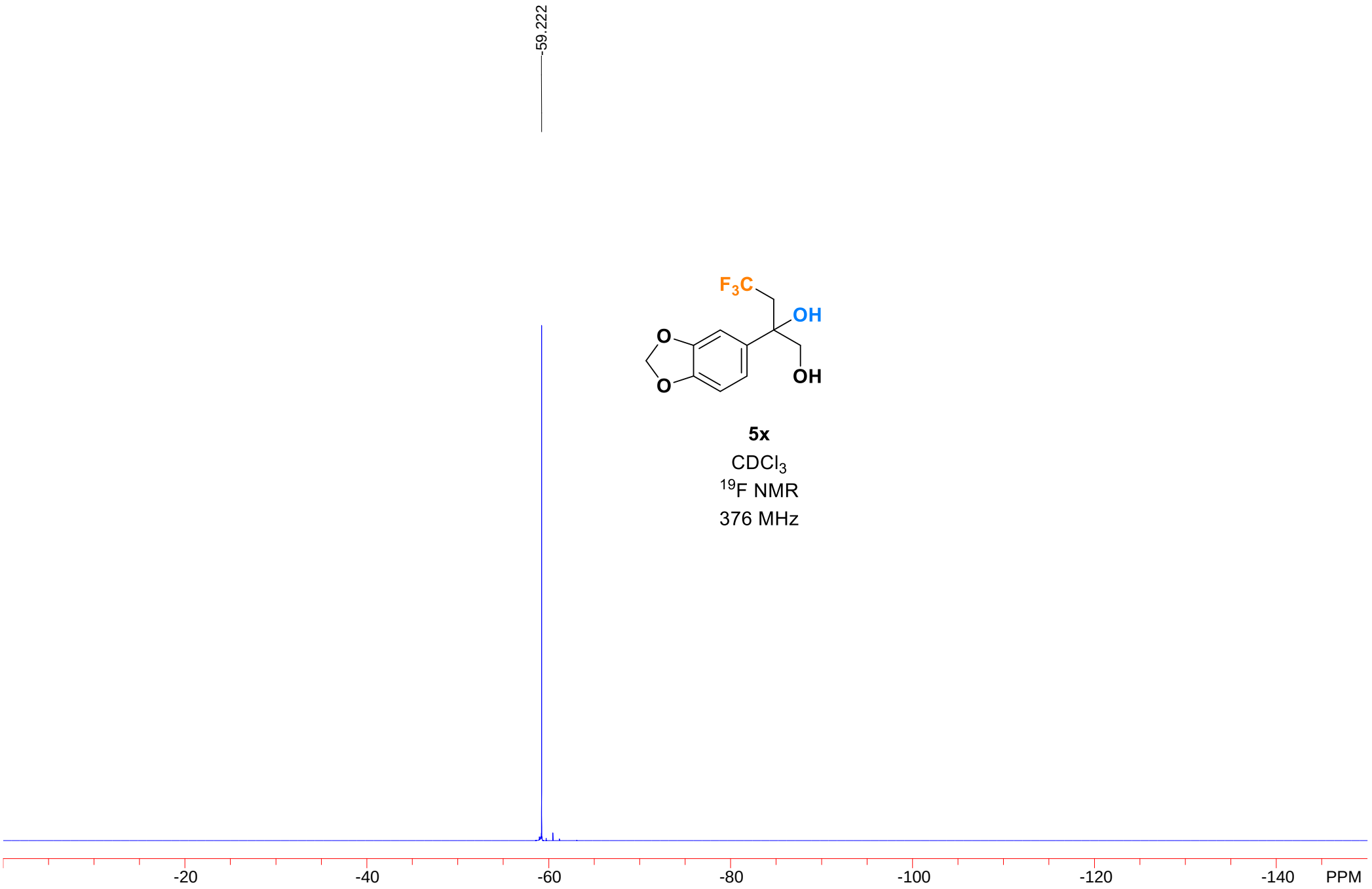
147.100
135.303
129.893
127.129
124.358
121.595
118.394
108.193
105.998
101.259
77.321
77.000
76.686
74.266
74.244
69.665
69.650
42.015
41.753
41.490
41.228
F3C
OH
O
O
OH
5x
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM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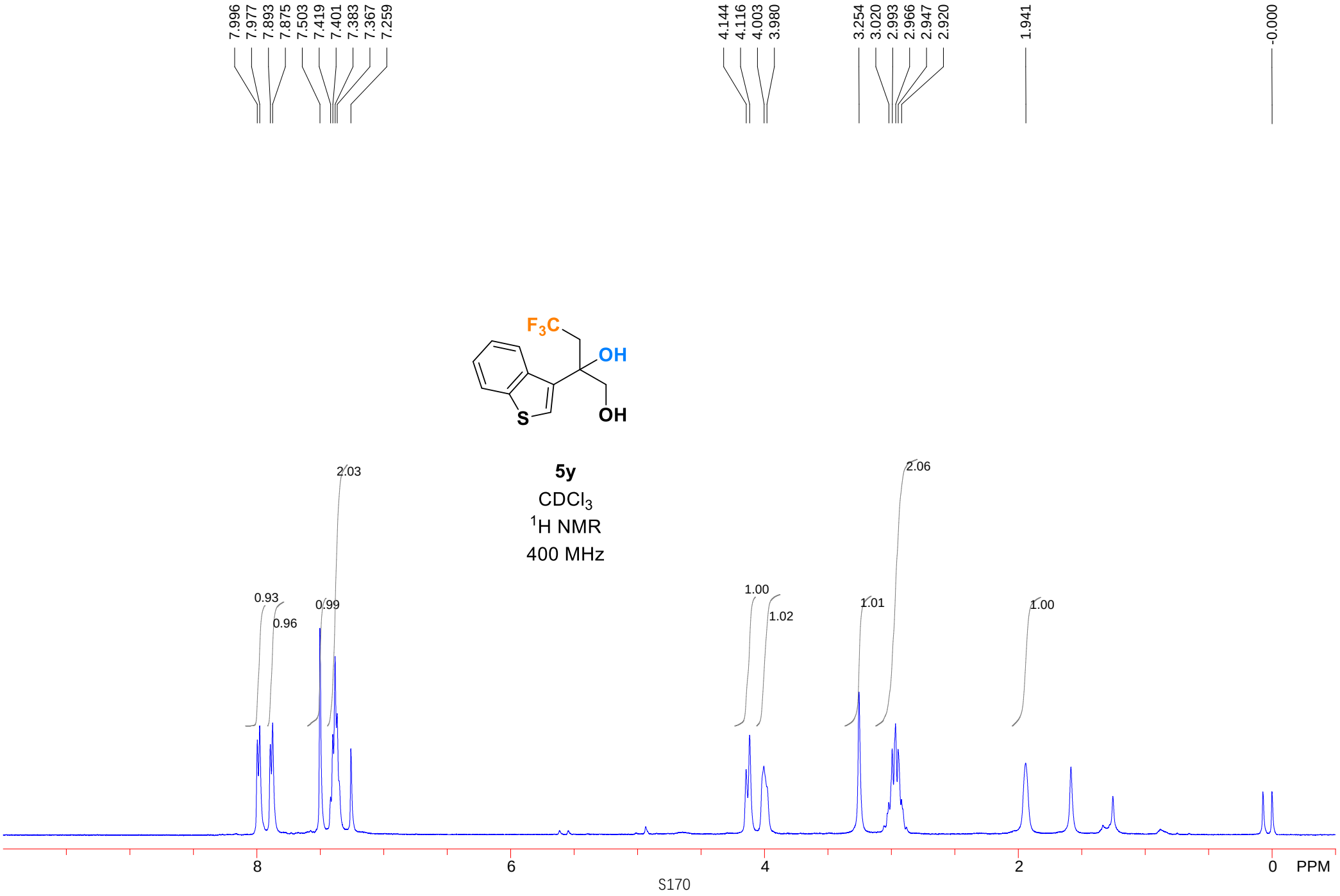
OH
5x
CDCl3
19F NMR
376 MHz
-20
-40
-60
-80
-100
-120
-140
PPM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7.401
7.383
7.367
7.259
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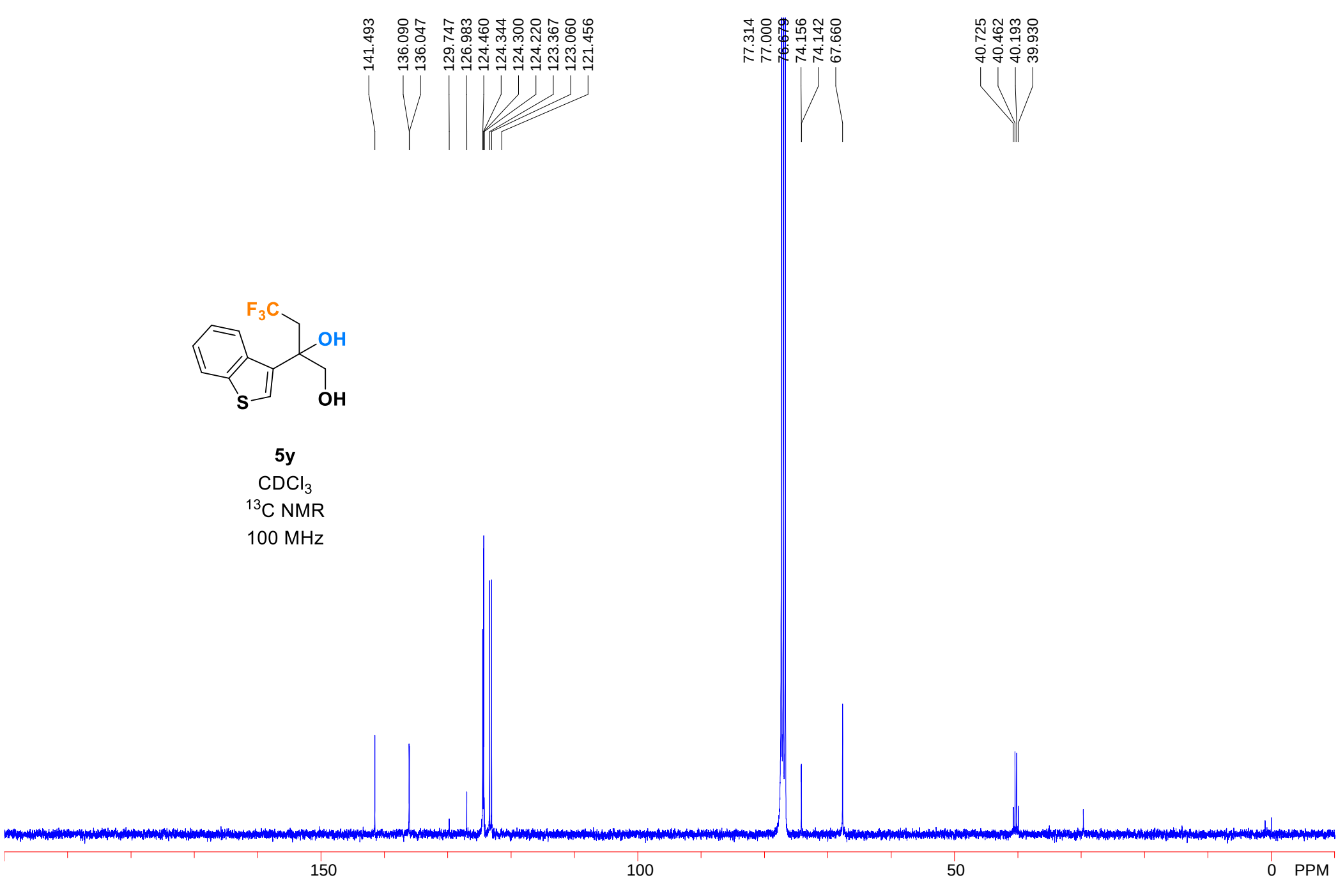
4.003
3.980
3.254
3.020
2.993
2.966
2.947
2.920
1.941
-0.000
F3C
OH
OH
S
5y
CDCl3
1H NMR
400 MHz
0.93
0.96
2.03
0.99
1.00
1.02
1.01
2.06
1.00
8
6
4
2
0
PPM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136.047
129.747
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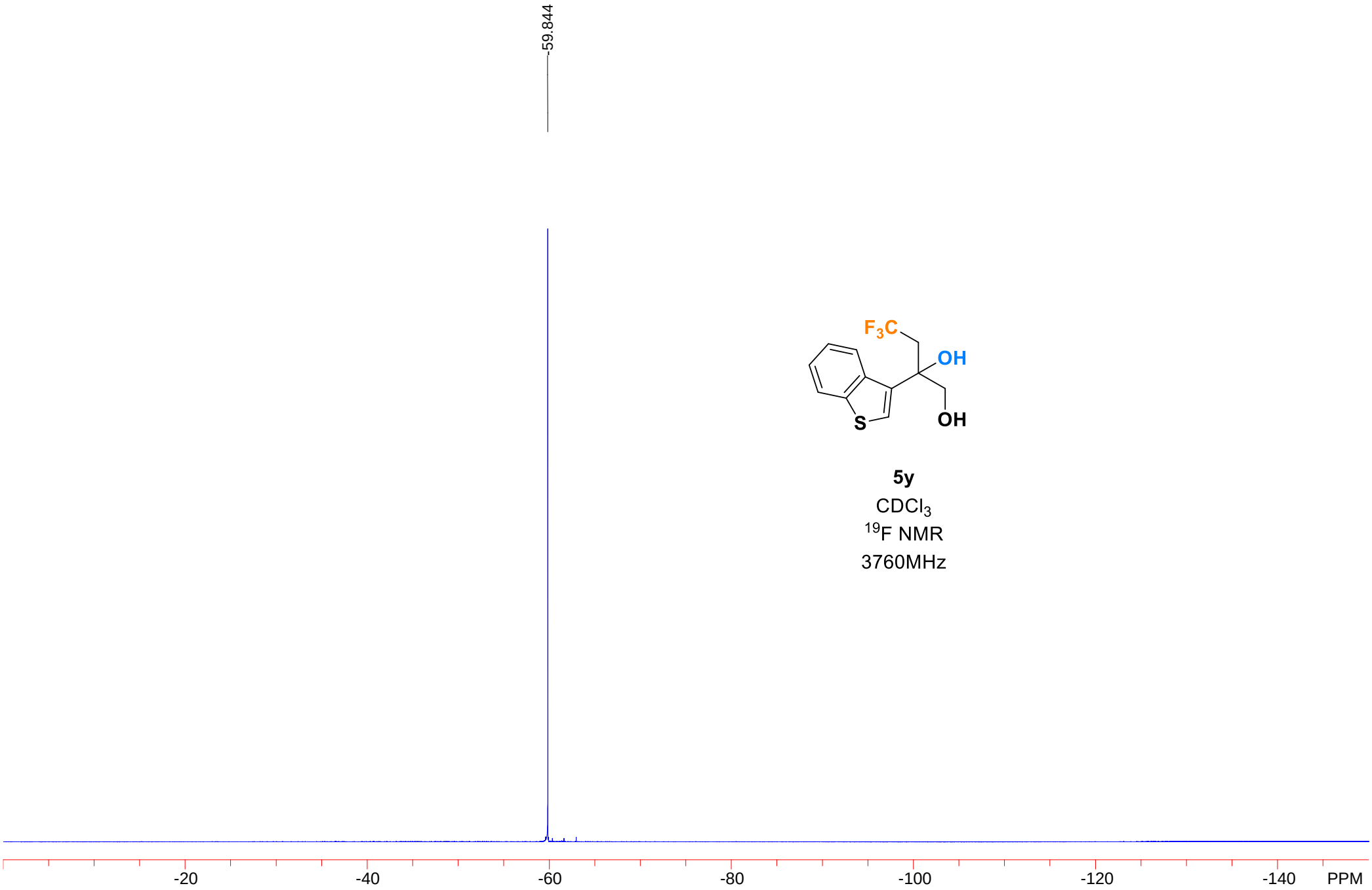
77.314
77.000
76.679
74.156
74.142
67.660
40.725
40.462
40.193
39.930
F3C
OH
OH
S
5y
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM

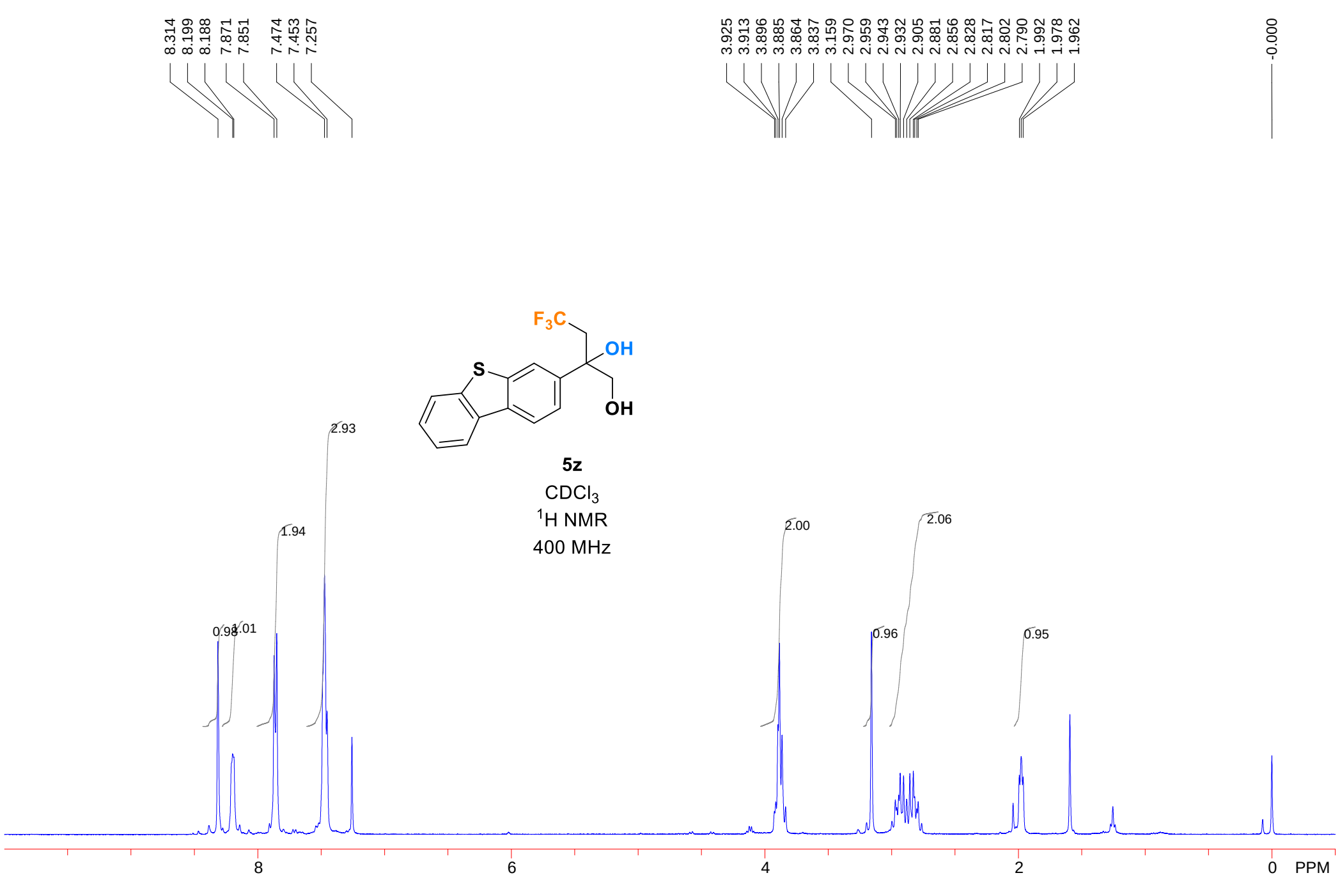


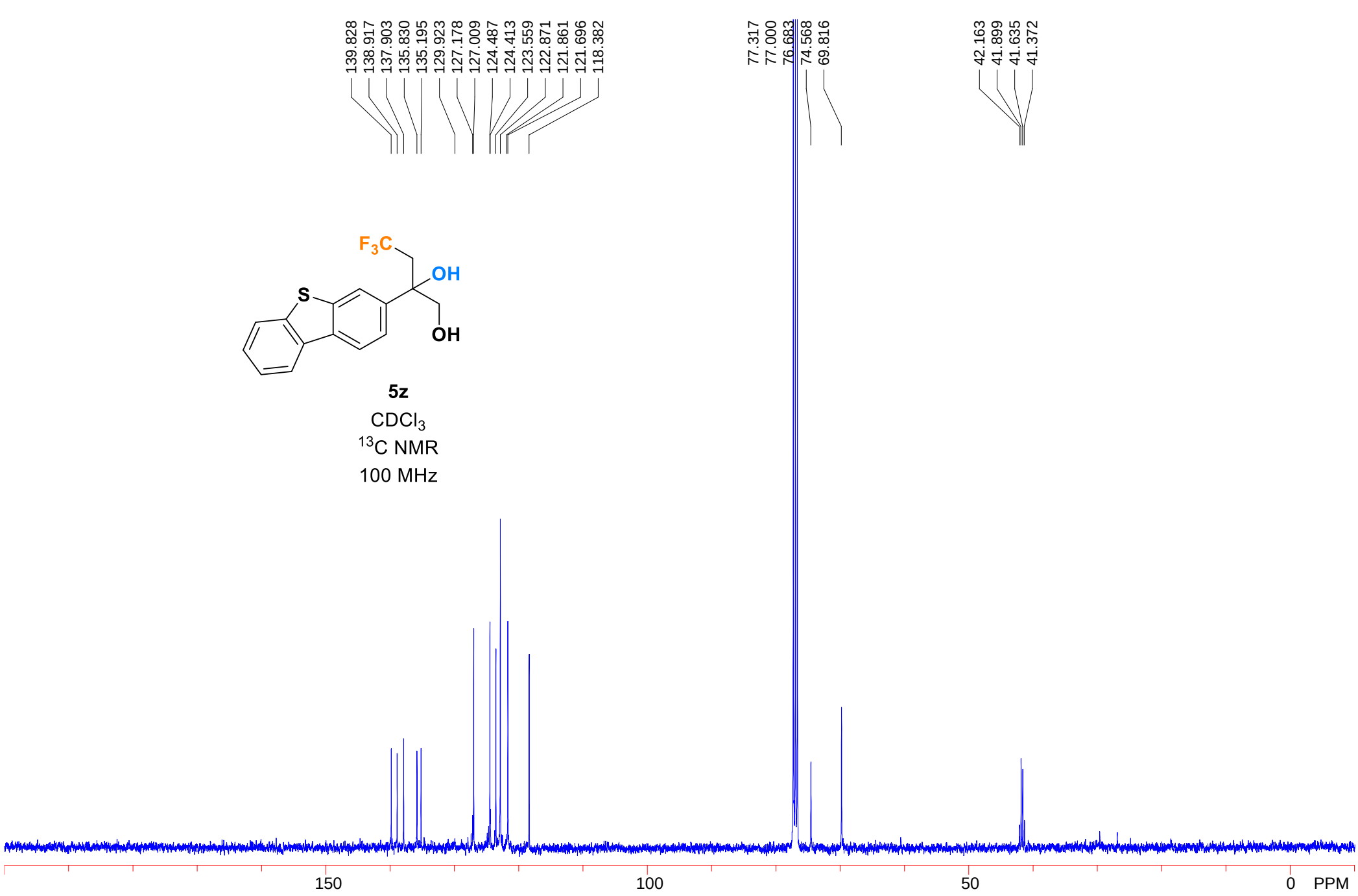
5y

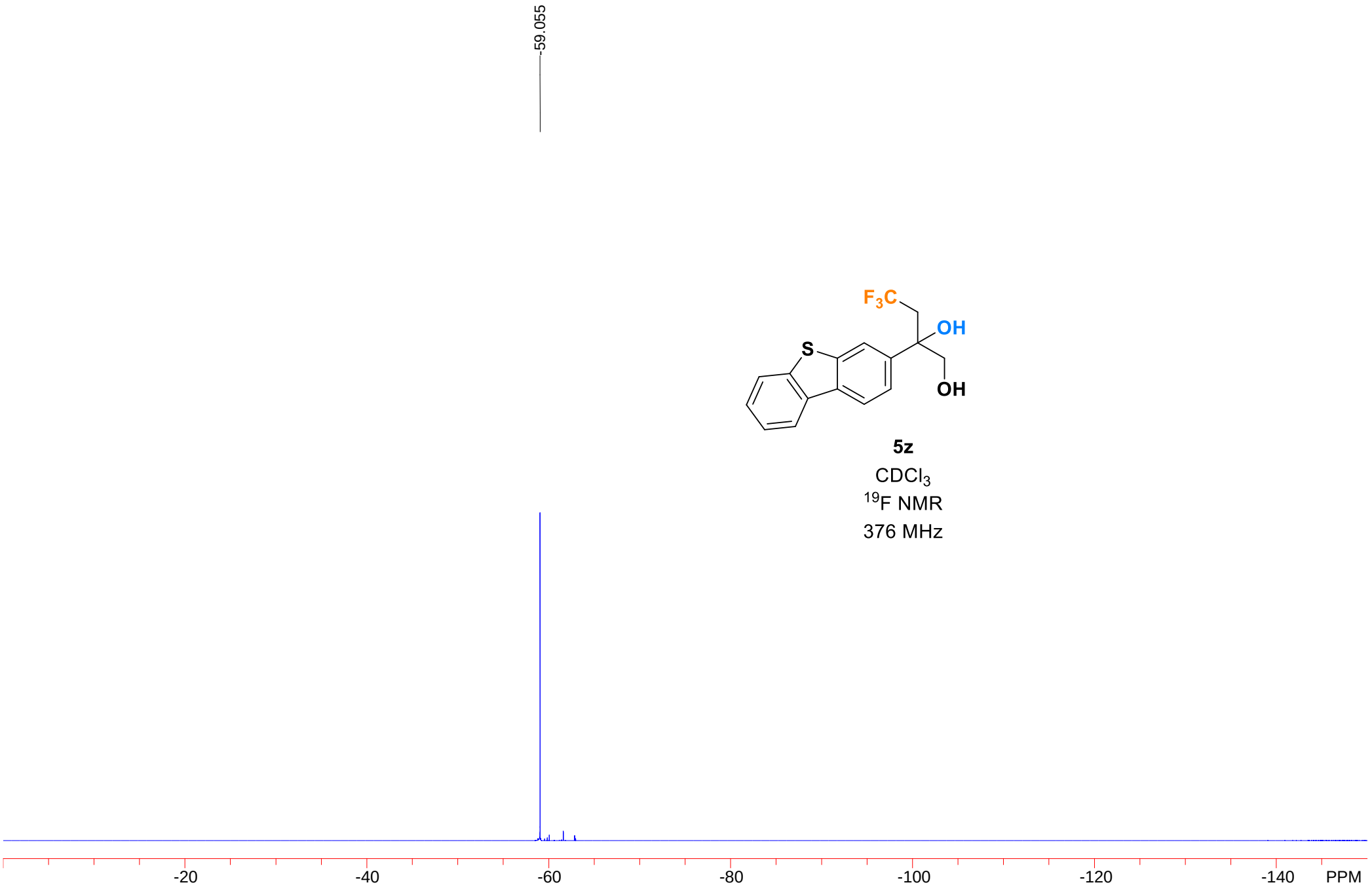
$CDCl_3$

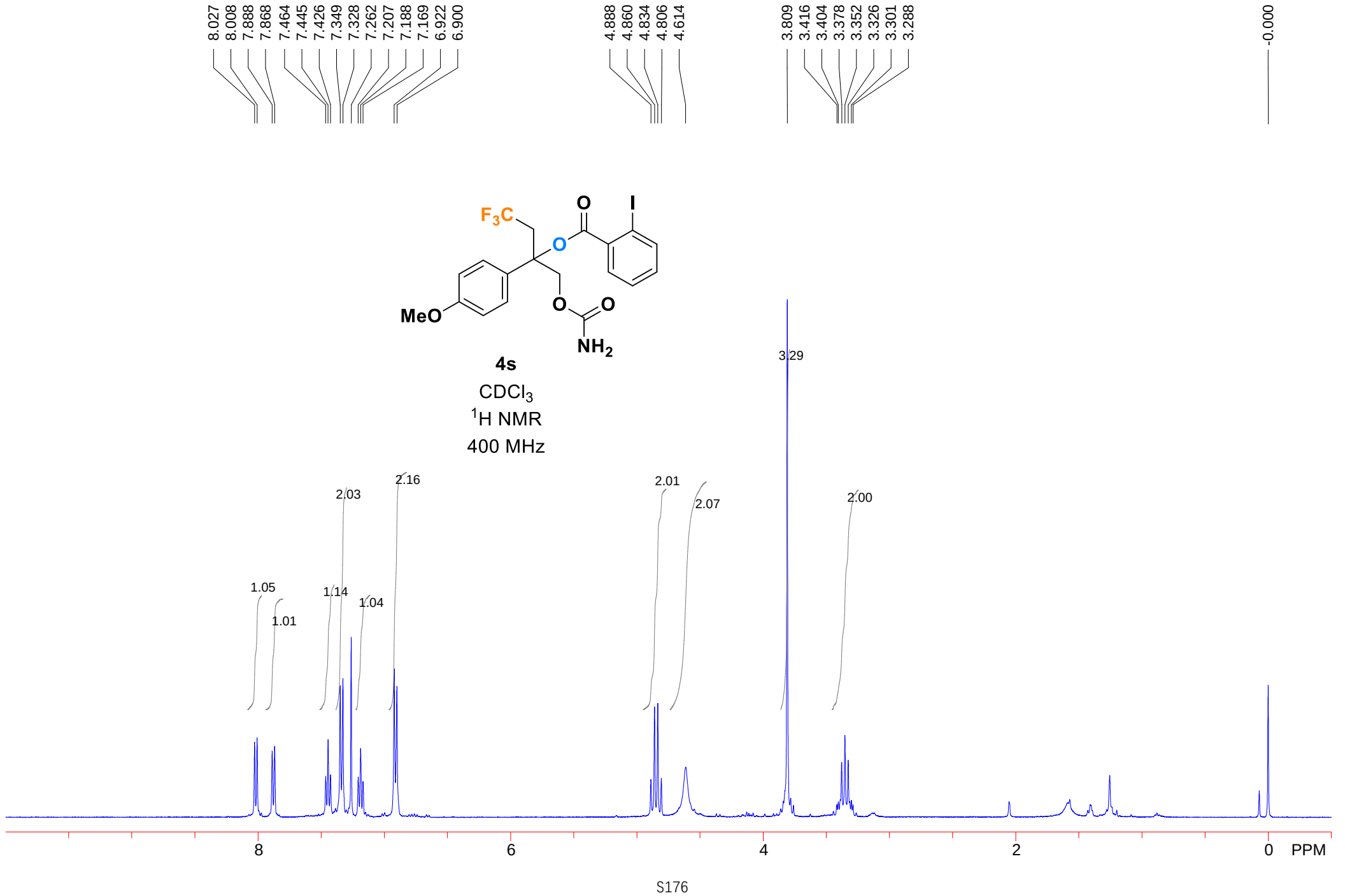
^{19}F NMR

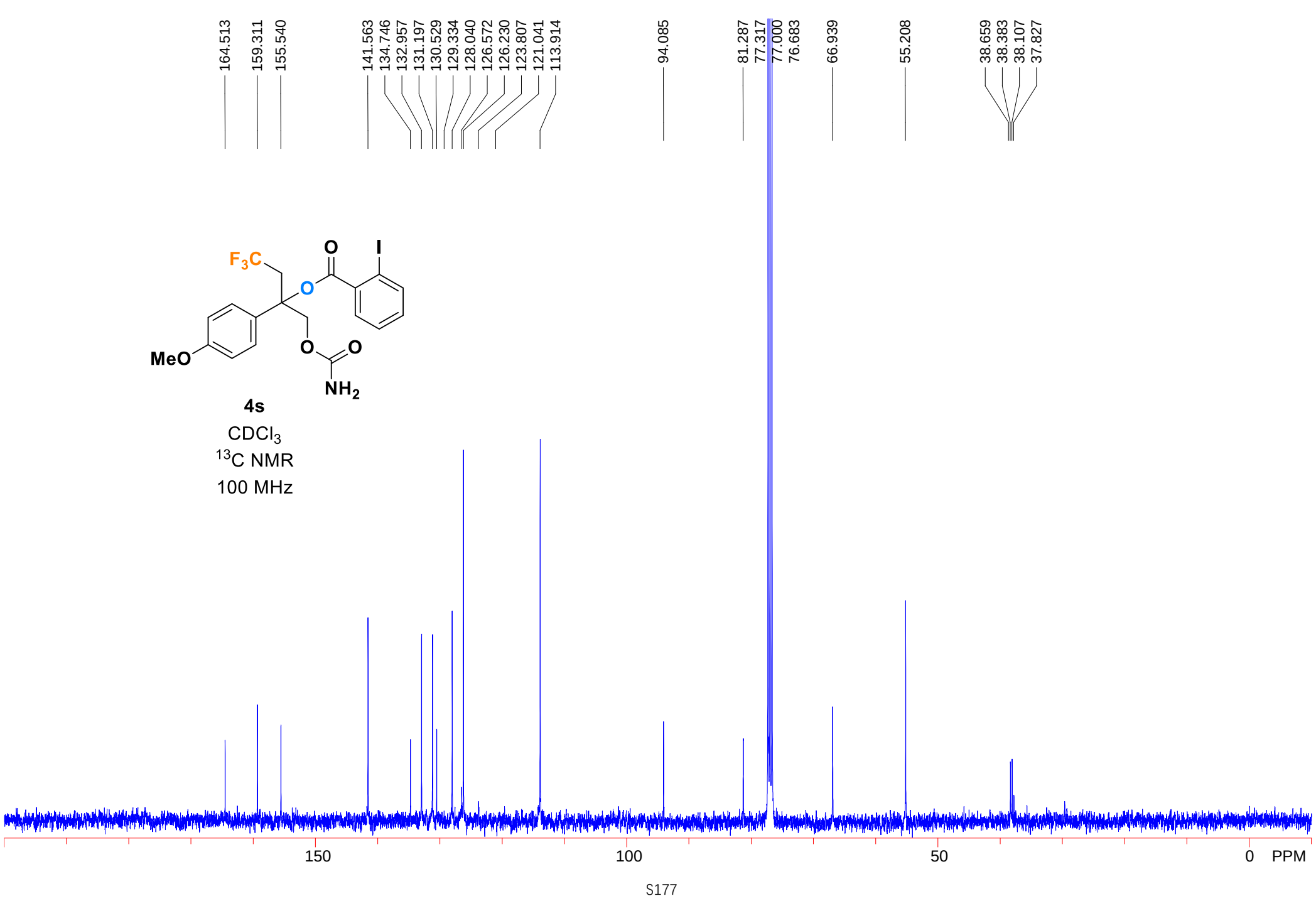
3760MHz

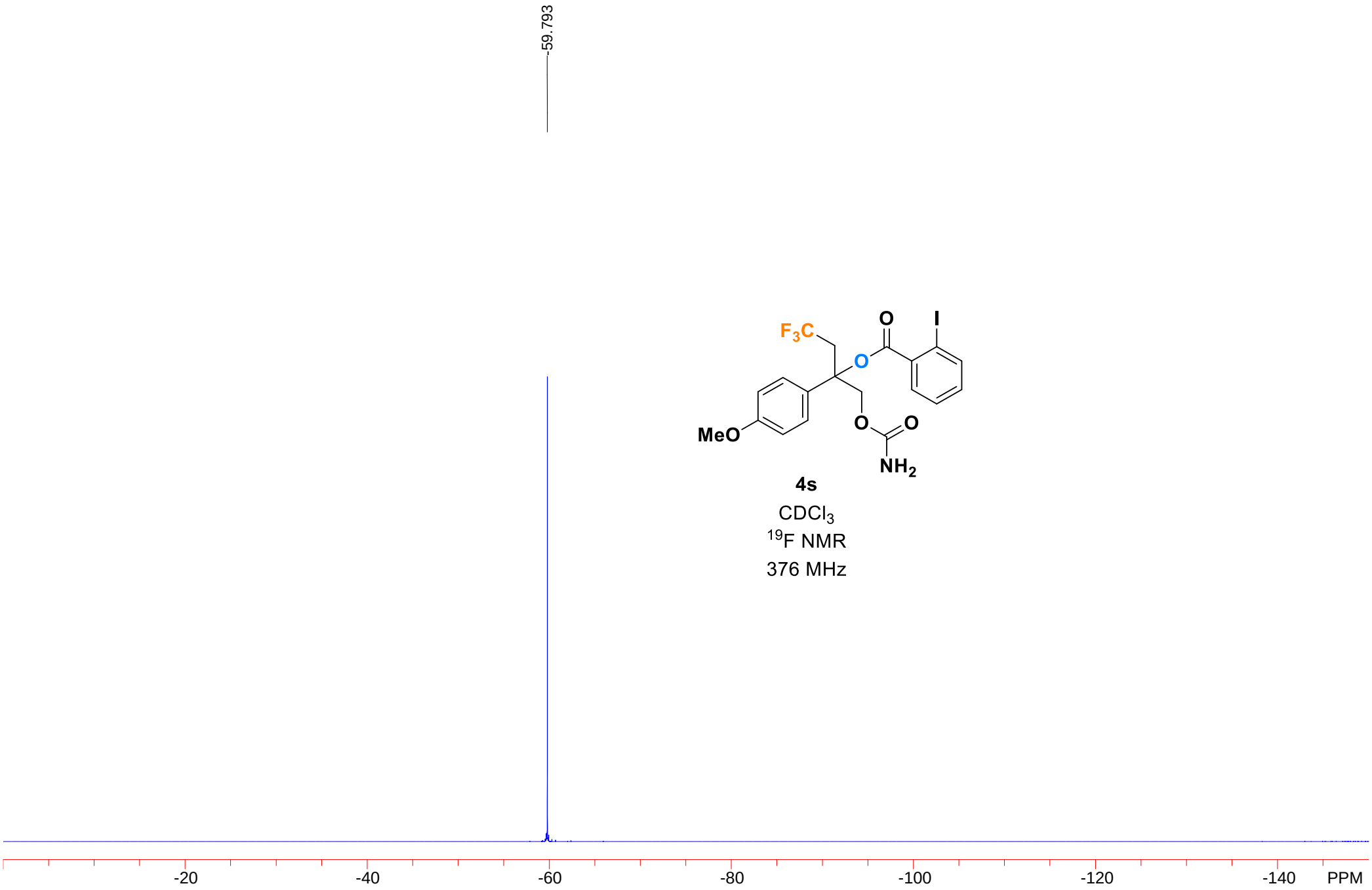

8.314
8.199
8.188
7.871
7.851
7.474
7.453
7.257
3.925
3.913
3.896
3.885
3.864
3.837
3.159
2.970
2.959
2.943
2.932
2.905
2.881
2.856
2.828
2.817
2.802
2.790
1.992
1.978
1.962
-0.000
F3C
OH
S
OH
5z
CDCl3
1H NMR
400 MHz
2.93
1.94
1.01
0.98
2.00
2.06
0.96
0.95
8
6
4
2
0
PPM


139.828
138.917
137.903
135.830
135.195
129.923
127.178
127.009
124.487
124.413
123.559
122.871
121.861
121.696
118.382
77.317
77.000
76.683
74.568
69.816
42.163
41.899
41.635
41.372
F3C
OH
S
OH
5z
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM


-59.055
F3C
OH
S
OH
5z
CDCl3
19F NMR
376 MHz
-20
-40
-60
-80
-100
-120
-140
PPM


8.027
8.008
7.888
7.868
7.464
7.445
7.426
7.349
7.328
7.262
7.207
7.188
7.169
6.922
6.900
4.888
4.860
4.834
4.806
4.614
3.809
3.416
3.404
3.378
3.352
3.326
3.301
3.288
-0.000
F3C
O
I
O
MeO
O
O
NH2
4s
CDCl3
1H NMR
400 MHz
1.05
1.01
2.03
1.14
2.16
1.04
2.01
2.07
3.29
2.00
8
6
4
2
0
PPM


164.513
159.311
155.540
141.563
134.746
132.957
131.197
130.529
129.334
128.040
126.572
126.230
123.807
121.041
113.914
94.085
81.287
77.317
77.000
76.683
66.939
55.208
38.659
38.383
38.107
37.827
F3C
O
I
O
MeO
O
O
NH2
4s
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM

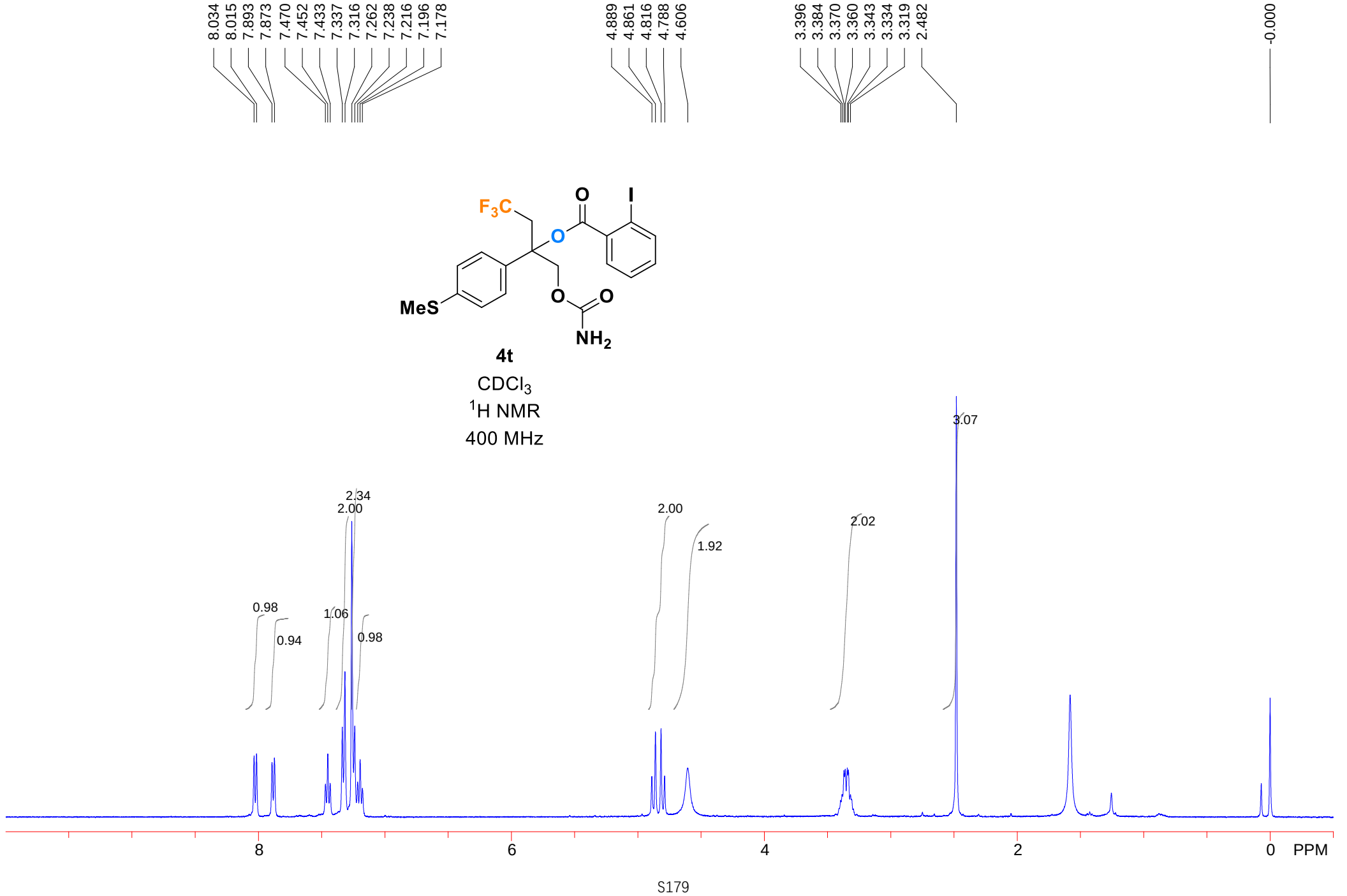


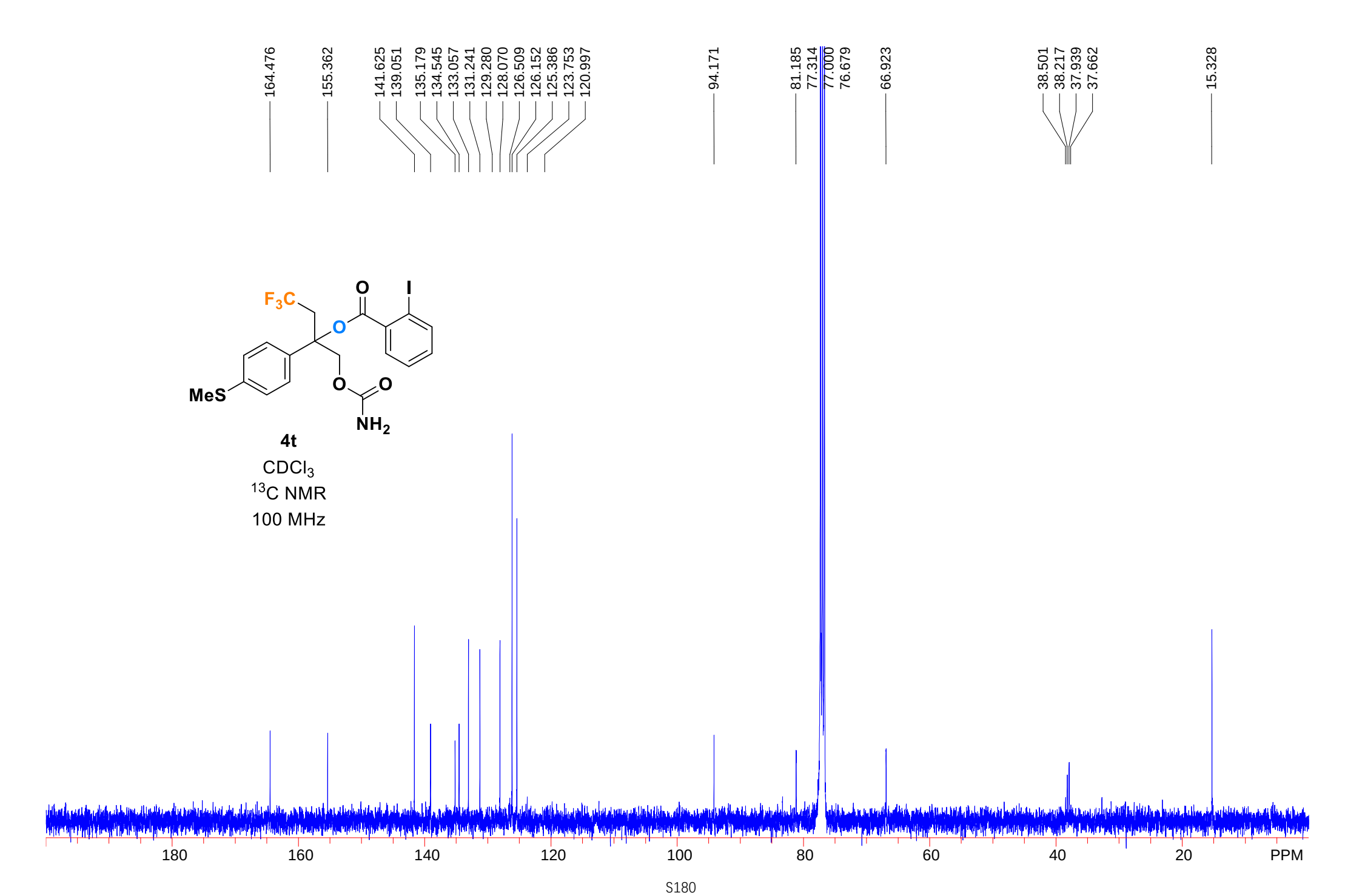
4s

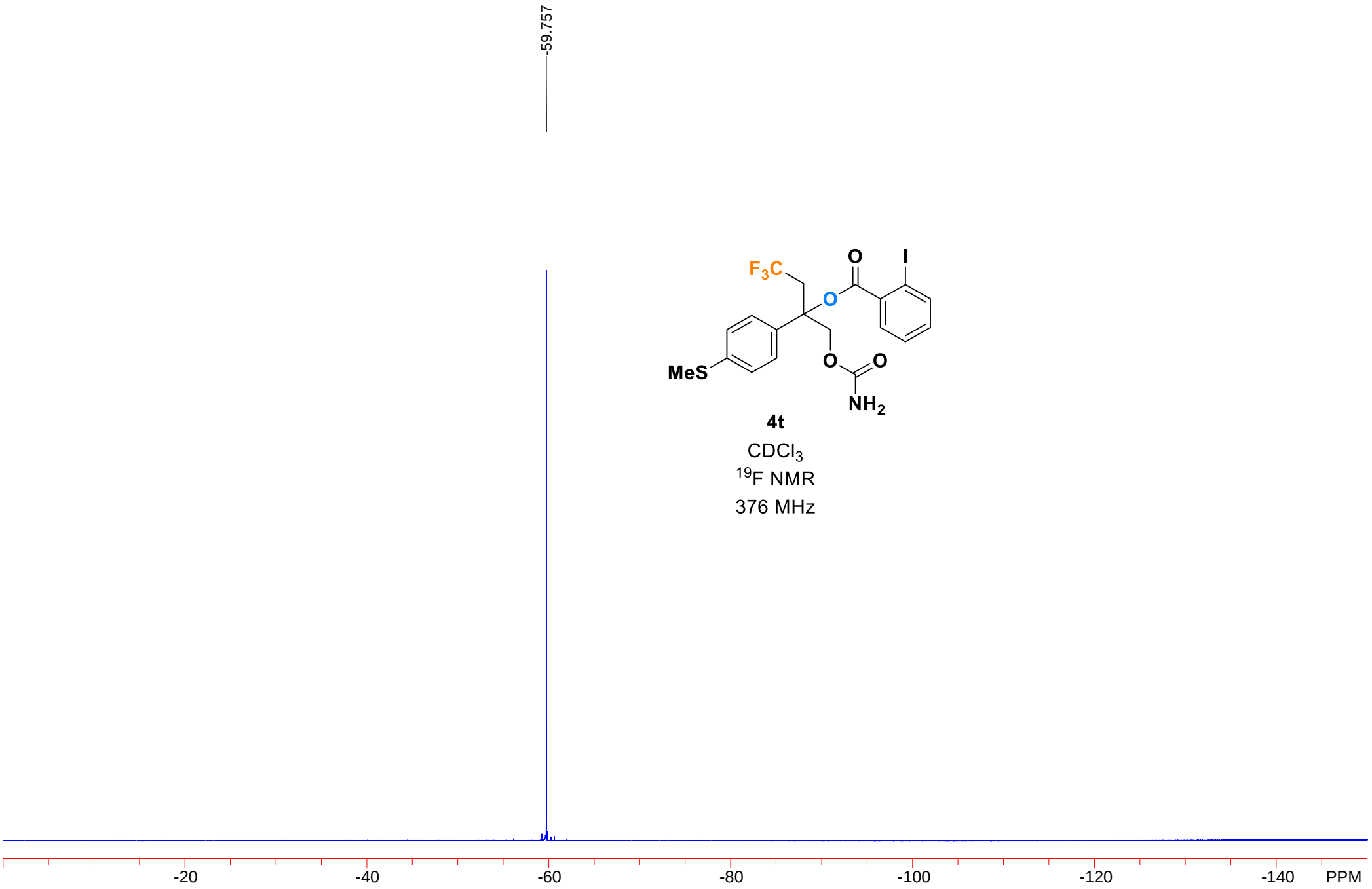
$CDCl_3$

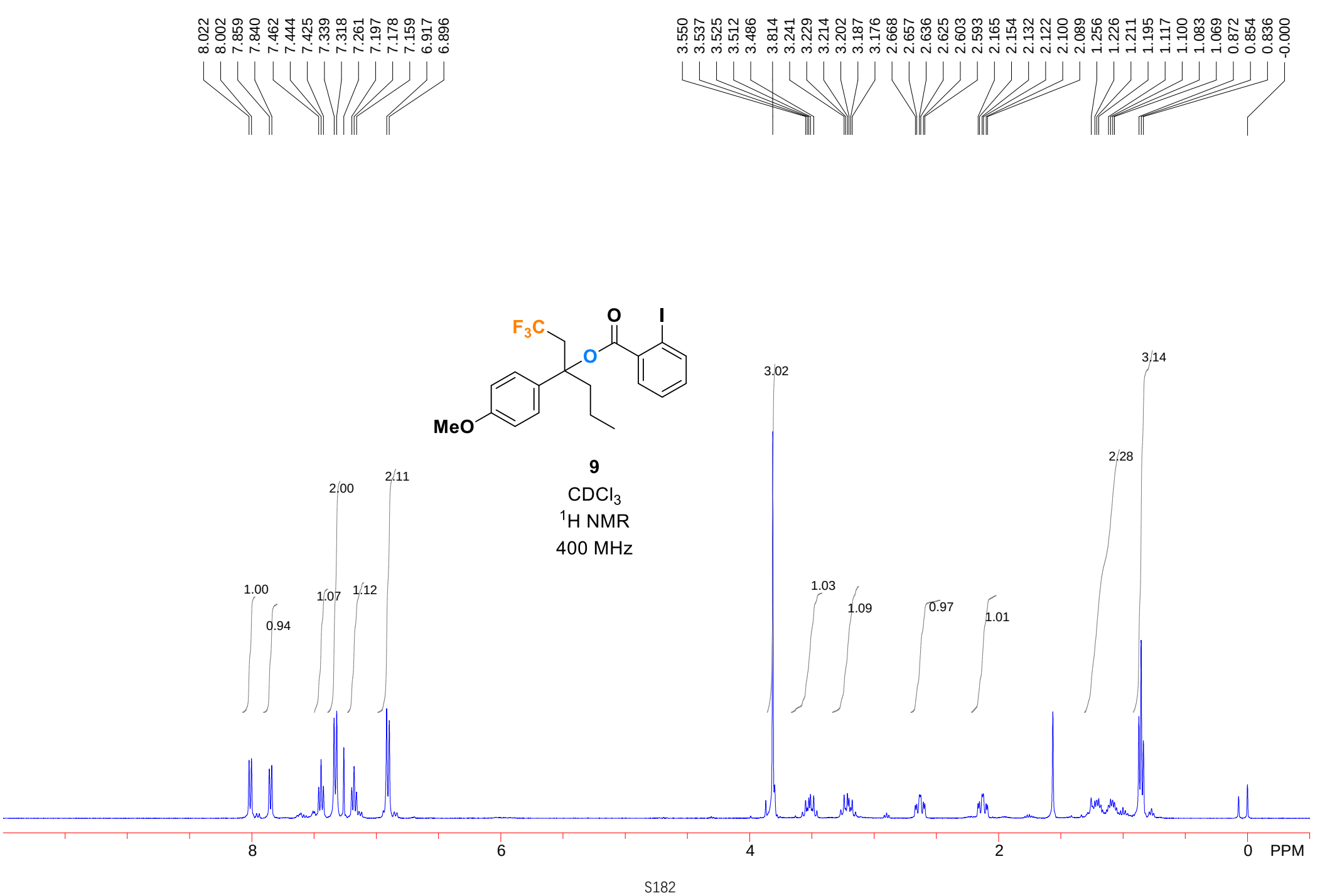
^{19}F NMR

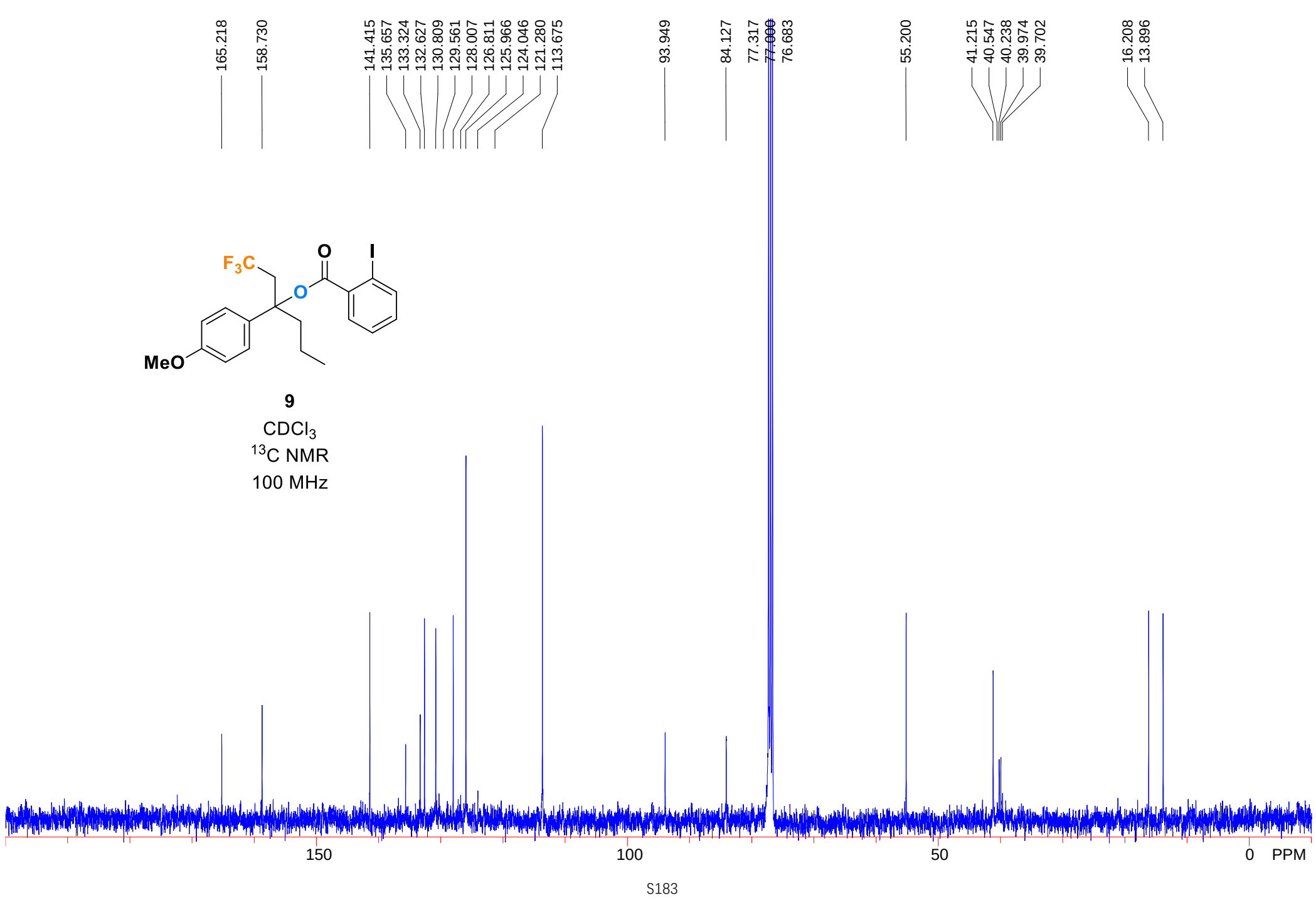
376 MHz

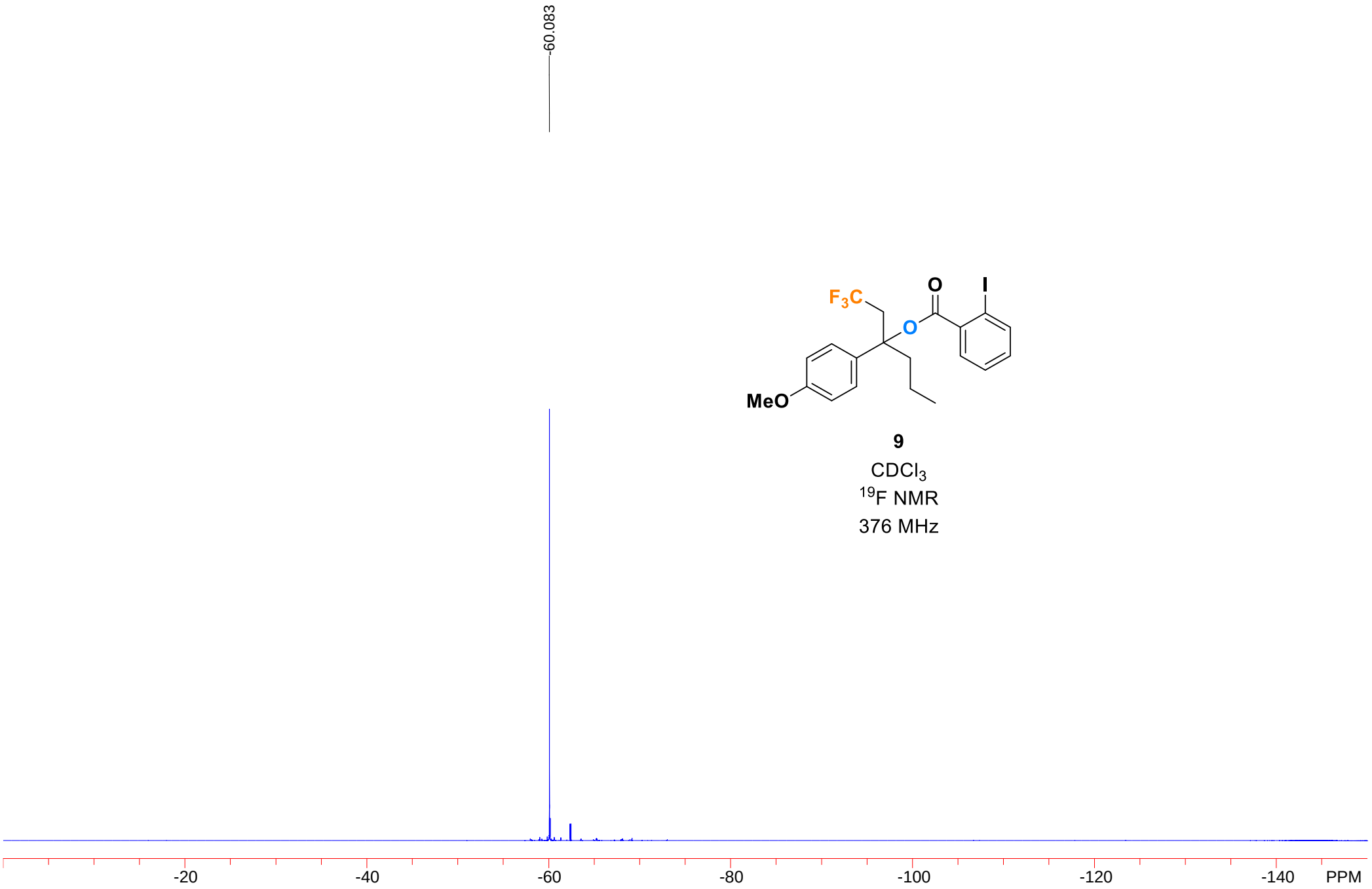

8.034
8.015
7.893
7.873
7.470
7.452
7.433
7.337
7.316
7.262
7.238
7.216
7.196
7.178
4.889
4.861
4.816
4.788
4.606
3.396
3.384
3.370
3.360
3.343
3.334
3.319
2.482
-0.000
F3C
O
I
O
MeS
O
O
NH2
4t
CDCl3
1H NMR
400 MHz
0.98
0.94
2.34
2.00
1.06
0.98
2.00
1.92
2.02
3.07
8
6
4
2
0
PPM


164.476
155.362
141.625
139.051
135.179
134.545
133.057
131.241
129.280
128.070
126.509
126.152
125.386
123.753
120.997
94.171
81.185
77.314
77.000
76.679
66.923
38.501
38.217
37.939
37.662
15.328
F3C
O
I
O
MeS
O
O
NH2
4t
CDCl3
13C NMR
100 MHz
180
160
140
120
100
80
60
40
20
PPM


-59.757
F3C
O
I
O
MeS
O
O
NH2
4t
CDCl3
19F NMR
376 MHz
-20
-40
-60
-80
-100
-120
-140
PPM


8.022
8.002
7.859
7.840
7.462
7.444
7.425
7.339
7.318
7.261
7.197
7.178
7.159
6.917
6.896
3.550
3.537
3.525
3.512
3.486
3.814
3.241
3.229
3.214
3.202
3.187
3.176
2.668
2.657
2.636
2.625
2.603
2.593
2.165
2.154
2.132
2.122
2.100
2.089
1.256
1.226
1.211
1.195
1.117
1.100
1.083
1.069
0.872
0.854
0.836
-0.000
F3C
O
O
I
MeO
9
CDCl3
1H NMR
400 MHz
1.00
0.94
1.07
2.00
1.12
2.11
3.02
1.03
1.09
0.97
1.01
2.28
3.14
8
6
4
2
0
PPM


165.218
158.730
141.415
135.657
133.324
132.627
130.809
129.561
128.007
126.811
125.966
124.046
121.280
113.675
93.949
84.127
77.317
77.000
76.683
55.200
41.215
40.547
40.238
39.974
39.702
16.208
13.896
F3C
O
O
I
MeO
9
CDCl3
13C NMR
100 MHz
150
100
50
0
PPM



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$CDCl_3$

^{19}F NMR

376 MHz