Supporting Information

Tunable [3+2] and [4+2] Annulations for Pyrrolidine and Piperidine Synthesis

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Content

1. General Information

Commercial reagents and solvents were purchased from Sigma Aldrich, Oakwood Chemicals, Alfa Aesar, Matrix Scientific, Acros Organic and were used as received. Organic solutions were concentrated under reduced pressure on an IKA rotary evaporator using an acetone-dry ice bath. Chromatographic purification of products was accomplished using flash chromatography on 230-400 mesh silica gel. Thin-layer chromatography (TLC) was performed on Analtech 250 mm silica gel HLF UV-250 plates. Visualization of the developed plates was performed by fluorescent quenching and potassium permanganate. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker instrument (600 and 150 MHz) or INOVA 600 (600 and 150 MHz) and are internally referenced to residual protio solvent signals (for CDCl3, 7.27 and 77.0 ppm, respectively). Data for ^{1}H NMR are reported as follows: chemicals shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were recorded and reported as chemical shifts in ppm and multiplicity where appropriate. IR spectra were recorded on a PerkinElmer FT-IR spectrophotometer and reported in terms of wavenumber of absorption (cm^{-1}). High resolution mass spectra were obtained on Waters Synapt High-Definition Mass Spectrometer (HDMS) by electrospray ionization at the University of Toledo, OH, USA and Maxis Ultra High-resolution ESI LC/MS at the University of Wisconsin-Madison, WI, USA.

2. Experimental Procedures

General Procedure A for Pyrrolidine Synthesis

To an 8 mL vial equipped with a stir bar was added NIS (62 mg, 0.275 mmol) and *N*-allyl-4-methylbenzenesulfonamide (0.25 mmol). The vial was evacuated and backfilled with nitrogen. Then the solvent (DCM, 4.0 mL) was added via a syringe, followed by alkene (0.5 mmol). The reaction mixture was then stirred for 16 h under compact fluorescent light (CFL) or Blue LED light. The reaction was quenched with 2 mL of saturated $Na_2S_2O_3$. Organic layer was separated, aqueous layer was extracted with DCM (2×2 mL). Combined organic layer was concentrated under reduced pressure to give the crude product, which was purified by column chromatography on silica gel to afford the pure product.

General Procedure B for the Elimination Reaction

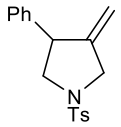
In an 8 mL vial equipped with a stir bar, NaH (32 mg, 1.25 mmol) and THF (0.5 mL) were added. Pyrrolidine compound dissolved in THF (0.5 mL) was added to the above mixture at 0 °C. After stirring at room temperature for 16 h the reaction was diluted with EtOAc and quenched with saturated NH_4Cl (2 mL). Organic layer was separated, aqueous layer was extracted with EtOAc (2×2 mL). Combined organic layer was filtered through a short column of silica and concentrated under reduced pressure to give the pure product without further purification.

General Procedure C for Piperidine Synthesis

To an 8 mL vial equipped with a stir bar was added NBS (49 mg, 0.275 mmol) and *N*-allyl-4-methylbenzenesulfonamide (0.25 mmol). The vial was evacuated and backfilled with nitrogen. Then the solvent (DCM, 0.25 mL) was added via a syringe, followed by alkene (0.5 mmol). The reaction mixture was then stirred for 1 h under fluorescent light, HFIP (0.5 mL) was added and

stirred under ambient light at room temperature for 36 h. The reaction was diluted with EtOAc (2 mL) and quenched with saturated $Na_2S_2O_3$ (2 mL). Organic layer was separated, aqueous layer was extracted with EtOAc (2×2 mL). Combined organic layer was concentrated under reduced pressure to give the crude product, which was purified by column chromatography on silica gel to afford the pure product.

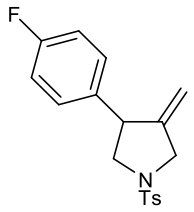
3. Spectral Characterization of Products



3-methylene-4-phenyl-1-tosylpyrrolidine (4): This compound was prepared according to the General Procedure A and B using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and styrene (58 μL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the pyrrolidine compound **4** was isolated as a white solid (73 mg, 66% yield).[1-3] For procedure B, in an 8 mL vial equipped with a stir bar, NaH (32 mg, 1.25 mmol) and THF (0.5 mL) were added. Pyrrolidine compound **4** dissolved in THF (0.5 mL) was added to the above mixture at 0 °C (ice-bath) and temperature was maintained for 2 hours. After stirring for 16 h the reaction was diluted with EtOAc and quenched with saturated NH_4Cl (2 mL). Organic layer was separated, aqueous layer was extracted with EtOAc (2×2 mL). Combined organic layer was concentrated under reduced pressure and purified by column chromatography (10% EtOAc/hexanes) to give the title compound as a white solid (53 mg, 68% yield).[4]

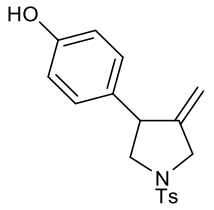
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.3 Hz, 2 H), 7.37 (d, *J* = 7.3 Hz, 2 H), 7.35-7.22 (m, 3 H), 7.14 (d, *J* = 7.0 Hz, 2 H), 5.05 (br.s., 1 H), 4.68 (br. s., 1 H), 4.12 (d, *J* = 13.9 Hz, 1 H), 3.94 (d, *J* = 13.9 Hz, 1 H), 3.81 (br. s., 2 H), 3.31-3.17 (m, 1 H), 2.48 (br. s., 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.0, 143.7, 139.5, 132.6, 129.7, 128.6, 128.1, 127.7, 127.1, 109.1, 77.2, 76.8, 55.4,

52.4, 49.2, 21.5; IR (neat): 2923, 1344, 1158, 1092, 700, 661, 587, 546 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{20}NO_2S$ $[(M+H)^+]$ 314.1215, found 314.1197.



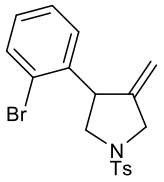
3-(4-fluorophenyl)-4-methylene-1-tosylpyrrolidine (5): This compound was prepared according to the General Procedure A and B using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and 4-fluorostyrene (61 μL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the pyrrolidine compound was isolated as a white solid (74 mg, 64% yield) and the title compound was obtained as a white solid (50 mg, 60% yield).

^1H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2 H), 7.36 (d, J = 7.8 Hz, 2 H), 7.12-7.05 (m, 2 H), 6.98 (t, J = 8.5 Hz, 2 H), 5.04 (d, J = 2.0 Hz, 1 H), 4.65 (d, J = 2.0 Hz, 1 H), 4.08 (d, J = 14.4 Hz, 1 H), 3.91 (d, J = 14.2 Hz, 1 H), 3.83-3.73 (m, 2 H), 3.19-3.10 (m, 1 H), 2.47 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.9 ($J_{c\text{-}f}$ = 243.0 Hz), 148.0, 143.8, 135.3 ($J_{c\text{-}f}$ = 3.0 Hz), 132.7, 129.8, 129.7, 127.8, 115.6, 115.5, 109.4, 55.5, 52.3, 48.6, 21.6; ^{19}F NMR (375 MHz, $CDCl_3$): δ -116.2 (m, 1 F); IR (neat): 2920, 1596, 1510, 1338, 1220, 1153, 1064 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{19}FNO_2S$ $[(M+H)^+]$ 332.1121, found 332.1114.



4-(4-methylene-1-tosylpyrrolidin-3-yl)phenol (6): This compound was prepared according to the General Procedure A and B using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and 4-acetoxystyrene (76 μL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (20%-30% EtOAc/hexanes), the pyrrolidine compound was isolated as a colorless oil (88 mg, 70% yield). and the title compound was obtained after purification by column chromatography SiO_2 (30%-40% EtOAc/hexanes) as a white solid (56 mg, 68% yield). [Note: the acetyl group has been deprotected during the elimination step].

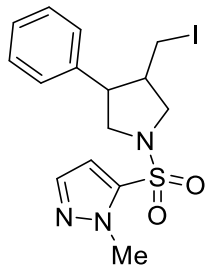
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 6.97 (d, *J* = 8.1 Hz, 2 H), 6.76 (d, *J* = 8.3 Hz, 2 H), 5.22 (br. s., 1 H), 5.01 (br. s., 1 H), 4.65 (br. s., 1 H), 4.08 (d, *J* = 14.2 Hz, 1 H), 3.88 (d, *J* = 14.2 Hz, 1 H), 3.80-3.69 (m, 2 H), 3.11 (t, *J* = 8.4 Hz, 1 H), 2.46 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.8, 148.3, 143.8, 132.7, 131.4, 129.9, 129.7, 129.4, 127.8, 115.6, 115.5, 109.0, 55.5, 52.4, 48.6, 30.9; IR (neat): 3415, 1614, 1596, 1514, 1331, 1212, 1150, 1090 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{20}NO_3S$ [$(M+H)^+$] 330.1164, found 330.1154.



3-(2-bromophenyl)-4-methylene-1-tosylpyrrolidine (7): This compound was prepared according to the General Procedure A and B using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and *o*-bromostyrene (91 μL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the pyrrolidine compound was isolated as a

colorless oil (109 mg, 82% yield) and the title compound was obtained as a white solid (80 mg, 82% yield).

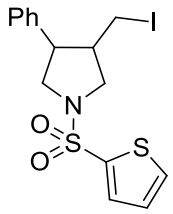
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2 H), 7.54 (d, *J* = 7.8 Hz, 1 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.22 (t, *J* = 7.6 Hz, 1 H), 7.15 (d, *J* = 7.8 Hz, 1 H), 7.12-7.06 (m, 1 H), 5.09 (d, *J* = 2.0 Hz, 1 H), 4.79 (d, *J* = 2.2 Hz, 1 H), 4.30 (t, *J* = 7.2 Hz, 1 H), 4.09-3.97 (m, 2 H), 3.82-3.73 (m, 1 H), 3.22 (dd, *J* = 9.8, 7.6 Hz, 1 H), 2.45 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.7, 143.8, 139.7, 132.9, 132.5, 129.8, 129.1, 128.6, 127.8, 127.8, 124.8, 109.6, 54.7, 52.7, 48.1, 21.6.; IR (neat): 2922, 1614, 1596, 1514, 1332, 1213, 1150, 1090, 1058 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{19}BrNO_2S$ [$(M+H)^+$] 392.0320, found 392.0298.



5-((3-(iodomethyl)-4-phenylpyrrolidin-1-yl)sulfonyl)-1-methyl-1*H*-pyrazole (8): This compound was prepared according to the General Procedure A using *N*-allyl-1-methyl-1*H*-pyrazole-5-sulfonamide (50 mg, 0.25 mmol) and styrene (58 μL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (5%–10% EtOAc/hexanes). The title compound was isolated as a thick colorless liquid (65mg, 60% yield, 2.8:1 d.r.).

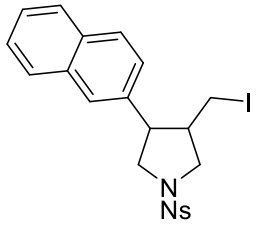
^{1}H NMR (600MHz , $CDCl_3$) δ 7.96-7.80 (d, *J* = 8.3 Hz, 2 H_{Maj} + 2 H_{Min}), 7.37-7.27 (m, 3 H_{Maj} + 3 H_{Min}), 7.20-7.10 (d, *J* = 8.4 Hz, 2 H_{Maj} + 2 H_{Min}), 4.02 (s, 3 H_{Maj} + 3 H_{Min}), 3.78 (dd, *J* = 10.5, 8.3 Hz, 1 H_{Maj} + 1 H_{Min}), 3.72 (dd, *J* = 10.5, 7.5 Hz, 1 H_{Maj} + 1 H_{Min}), 3.67-3.58 (m, 1 H_{Maj} + 1 H_{Min}), 3.38 (m, *J* = 9.9 Hz, 1 H_{Maj} + 1 H_{Min}), 3.19-3.08 (m, 2 H_{Maj} + 2 H_{Min}), 2.93 (m, *J* = 10.7, 7.9 Hz, 2

H_{Maj} + 2 H_{Min}); ^{13}C NMR (150MHz , $CDCl_3$) δ 138.8, 138.7, 137.8, 132.2, 129.1, 128.9, 128.0, 127.8, 127.6, 127.5, 118.2, 55.0, 54.4, 52.8, 52.5, 50.2, 47.5, 47.0, 46.2, 39.8, 6.1; IR (neat): 2925, 2854, 1522, 1452, 1343, 1116, 1091, 847 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{20}BrN_3O_2S$ $[(M+H)^+]$ 432.0181, found 432.0239.



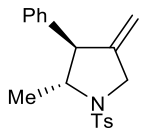
3-(iodomethyl)-4-phenyl-1-(thiophen-2-ylsulfonyl)pyrrolidine (9): This compound was prepared according to the General Procedure A using *N*-allylthiophene-2-sulfonamide (51 mg, 0.25 mmol) and styrene (58 μL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (5%–10% EtOAc/hexanes). The title compound was isolated as a thick colorless liquid (60 mg, 55% yield, 2.2:1 d.r.).

^1H NMR (600MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.3, 1.3 Hz, 1 H_{Min}), 7.91-7.87 (m, 2 H_{Maj}), 7.69-7.64 (m, 1.5 H_{Min}), 7.62-7.57 (m, 3 H_{Maj}), 7.32-7.28 (m, 2 $H_{Maj+Min}$), 7.27-7.22 (m, 3 H_{Maj}), 7.11-7.07 (m, 2 H_{Maj}), 7.06-7.01 (m, 1 H_{Min}), 3.81 (dd, *J* = 10.3, 8.1, Hz 1 H_{Maj}), 3.77 (dd, *J* = 10.3, 7.5 Hz, 1 H_{Maj}), 3.73-3.65 (m, 1.4 $H_{Maj+Min}$), 3.47-3.43 (m, 0.5 H_{Min}), 3.39 (t, *J* = 10.0 Hz 1 H_{Maj}), 3.28 (dd, *J* = 11.9, 8.8 Hz, 1 H_{Min}), 3.15 (dd, *J* = 10.3, 9.2 Hz, 1 H_{Maj}), 3.10 (dd, *J* = 10.3, 3.9 Hz, 1 H_{Maj}), 2.92-2.84 (m, 2 $H_{Maj+Min}$), 2.73-2.66 (m, 0.5 H_{Min}), 2.63 (dd, *J* = 9.1, 5.9 Hz, 0.5 H_{Min}), 2.41 (t, *J* = 9.1 Hz, 0.5 H_{Min}), 2.28-2.19 (m, 1 H_{Maj}); δ ^{13}C NMR (150MHz, $CDCl_3$) δ 137.9, 137.4, 136.8, 136.6, 133.0, 129.3, 129.3, 129.0, 128.8, 127.8, 127.7, 127.5, 127.4, 127.4, 77.2, 76.8, 54.9, 54.3, 52.6, 52.5, 50.2, 47.6, 46.8, 46.3, 5.8, 3.2; IR (neat): 3028, 2880, 1601, 1426, 1445, 1339, 1159, 1018, 716 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{17}INO_2S_2$ $[(M+H)^+]$ 433.9745, found 433.9755.



3-(iodomethyl)-4-(naphthalen-2-yl)-1-((4-nitrophenyl)sulfonyl)pyrrolidine (10): This compound was prepared according to the General Procedure A using *N*-allyl-4-nitrobenzenesulfonamide (61 mg, 0.25 mmol) and 4-vinylnaphthalene (77 mg, 0.5 mmol) with Blue LED light. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the pyrrolidine compound was isolated as a yellow solid (112 mg, 86% yield, 1.5:1 d.r).

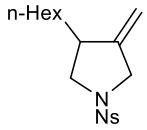
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (d, J = 8.1 Hz, 2 H_{Maj} + 2 H_{Min}), 8.19-8.12 (m, 1 H_{Maj} + 1 H_{Min}), 8.10 (d, J = 8.1 Hz,1 H_{Maj} + 1 H_{Min}), 7.89-7.81 (m, 2 H_{Maj} + 2 H_{Min}), 7.81-7.75 (m, 1 H_{Maj} + 1 H_{Min}), 7.56-7.45 (m, 3 H_{Maj} + 3 H_{Min}), 7.26-7.19 (m, 1 H_{Maj} + 1 H_{Min}), 4.01-3.73 (m, 3 H_{Maj} + 3 H_{Min}), 3.73-3.64 (m, 1 H_{Min}), 3.64-3.51 (m, 1 H_{Maj}), 3.46 (br. s., 1 H_{Min}), 3.29-3.20 (m, 1 H_{Maj}), 3.17 (dd, J = 3.8, 10.3 Hz, 1 H_{Maj}), 3.14-3.06 (m, 1 H_{Min}), 3.04-2.91 (m, 1 H_{Maj}), 2.70 (br. s., 1 H_{Min}), 2.55-2.36 (m, 1 H_{Maj} + 1 H_{Min}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.5, 150.4, 143.2, 143.1, 134.7, 134.6, 133.5, 133.4, 133.0, 132.8, 129.3, 129.0, 128.8, 128.8, 127.9, 127.9, 127.8, 127.8, 126.9, 126.6, 126.5, 125.9, 124.8, 124.8, 124.8, 55.0, 54.5, 53.0, 52.9, 50.6, 47.4, 47.2, 46.6; IR (neat): 2988, 1597, 1473, 1338, 1297, 1161, 1087 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{22}H_{23}BrNO_2S$ [$(M+H)^+$] 523.0188, found 523.0189.



2-methyl-4-methylene-3-phenyl-1-tosylpyrrolidine (11): This compound was prepared according to the General Procedure A and B using *N*-allyl-4-methylbenzenesulfonamide (53 mg,

0.25 mmol) and *β*-methylstyrene (65 µL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the pyrrolidine compound was isolated as a colorless oil (55 mg, 54% yield) and the title compound was obtained as a white solid (43 mg, 53% yield, >20:1 d.r.).

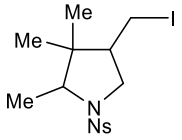
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 2 H), 7.28 (d, *J* = 8.3 Hz, 2 H), 7.22-7.17 (m, 3 H), 6.91-6.85 (m, 2 H), 5.02 (d, *J* = 2.0 Hz, 1 H), 4.65 (d, *J* = 2.0 Hz, 1 H), 4.25 (d, *J* = 14.6 Hz, 1 H), 4.01 (dd, *J* = 14.5, 1.8 Hz, 1 H), 3.53 (quin, *J* = 6.3 Hz, 1 H), 3.44 (d, *J* = 6.3 Hz, 1 H), 2.45 (s, 3 H), 1.43 (d, *J* = 6.1 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.5, 143.4, 139.6, 134.0, 129.6, 128.5, 128.3, 127.6, 127.0, 109.3, 64.1, 58.2, 53.4, 21.5, 21.0.; IR (neat): 2864, 1598, 1495, 1448, 1420, 1334, 1178, 1154, 1084 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{19}H_{22}NO_2S$ [$(M+H)^+$] 328.1371, found 328.1356.



3-hexyl-4-methylene-1-((4-nitrophenyl)sulfonyl)pyrrolidine (12): This compound was prepared according to the General Procedure A and B using *N*-allyl-4-nitrobenzenesulfonamide (61 mg, 0.25 mmol) and 1-octene (78 µL, 0.5 mmol) with Blue LED light. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the pyrrolidine compound was isolated as a colorless oil (43 mg, 44% yield) and the title compound was obtained as a white solid (35 mg, 40% yield).

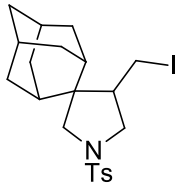
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.3 Hz, 2 H), 8.02 (d, *J* = 8.5 Hz, 2 H), 4.93 (d, *J* = 17.8 Hz, 2 H), 3.95 (d, *J* = 13.9 Hz, 1 H), 3.82 (d, *J* = 13.9 Hz, 1 H), 3.58 (t, *J* = 8.3 Hz, 1 H), 2.94-2.86 (m, 1 H), 2.60 (br. s., 1 H), 1.36-1.17 (m, 10 H), 0.88 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (150 MHz,

$CDCl_3$) δ 150.2, 147.1, 142.2, 128.7, 124.3, 107.3, 53.6, 52.1, 43.0, 32.0, 31.6, 29.2, 27.4, 22.6, 14.0; IR (neat): 2957, 2926, 2855, 1664, 1604, 1527, 1345, 1313, 1159, 1090, 1057 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{25}N_2O_4S$ [$(M+H)^+$] 353.1535, found 353.1515.



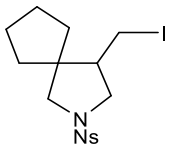
4-(iodomethyl)-2,3,3-trimethyl-1-((4-nitrophenyl)sulfonyl)pyrrolidine (13): This compound was prepared according to the General Procedure A using *N*-allyl-4-nitrobenzenesulfonamide (61 mg, 0.25 mmol) and 2-methylbut-2-ene (53 µL, 0.5 mmol) with Blue LED light. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), The title compound was isolated as a colorless oil (72 mg, 66% yield, 1.3:1 d.r.).

^1H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.8 Hz, 2 H_{Maj} + 2 H_{Min}), 8.04 (t, *J* = 8.9 Hz, 2 H_{Maj} + 2 H_{Min}), 3.91-3.78 (m, 1 H_{Maj} + 1 H_{Min}), 3.57 (q, *J* = 6.6 Hz, 1 H_{Min}), 3.17 (t, *J* = 11.2 Hz, 1 H_{Maj}), 3.15-3.10 (m, 1 H_{Maj} + 1 H_{Min}), 3.08 (q, *J* = 6.4 Hz, 1 H_{Maj}), 2.86 (t, *J* = 9.0 Hz, 1 H_{Maj} + 1 H_{Min}), 2.71 (t, *J* = 11.4 Hz, 1 H_{Min}), 2.49-2.38 (m, 1 H_{Min}), 1.73-1.64 (m, 1 H_{Maj}), 1.30 (d, *J* = 6.6 Hz, 3 H_{Maj}), 1.24 (d, *J* = 6.6 Hz, 3 H_{Min}), 0.94 (s, 3 H_{Min}), 0.86 (s, 3 H_{Maj}), 0.74 (s, 3 H_{Maj}), 0.35 (s, 3 H_{Min}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.1, 150.0, 143.6, 143.2, 128.6, 128.4, 124.4, 124.3, 67.8, 67.3, 54.5, 53.3, 50.9, 48.6, 44.5, 44.0, 29.7, 24.4, 21.7, 21.2, 19.0, 15.9, 15.0, 0.7, 0.6; IR (neat): 2969, 1603, 1522, 1470, 1345, 1303, 1159, 1090, 1062 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{14}H_{20}IN_2O_4S$ [$(M+H)^+$] 439.0188, found 439.0179.



(1r,3r,5r,7r)-4'-(Iodomethyl)-1'-tosylspiro[adamantane-2,3'-pyrrolidine] (14): This compound was prepared according to the General Procedure A using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and 2-methyleneadamantane (74 mg, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (2%–6% EtOAc/hexanes), The title compound was isolated as a white solid (55 mg, 45% yield).

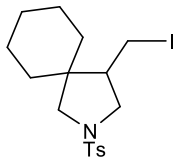
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2 H), 7.33 (d, *J* = 7.9 Hz, 2 H), 3.73 (d, *J* = 10.6 Hz, 1 H), 3.59 (d, *J* = 10.8 Hz, 1 H), 3.38 (ddd, *J* = 10.9, 5.7, 1.9 Hz, 1 H), 3.27 (dt, *J* = 9.7, 2.3 Hz, 1 H), 2.79 (d, *J* = 10.5 Hz, 1 H), 2.68 (ddd, *J* = 12.6, 5.5, 2.8 Hz, 1 H), 2.44 (s, 3 H), 2.34 (dd, *J* = 12.6, 9.6 Hz, 1 H), 1.86-1.81 (m, 3 H), 1.79 (br. s., 1 H), 1.68-1.60 (m, 6 H), 1.58-1.46 (m, 3 H), 1.23 (br. s., 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.5, 133.6, 129.7, 127.4, 53.5, 51.9, 51.8, 47.0, 37.9, 34.4, 33.9, 33.6, 33.4, 31.9, 31.9, 27.0, 26.9, 21.6, 7.3; IR (neat): 2895, 2877, 1596, 1456, 1344, 1325, 1160, 1088, 1054, 815 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{21}H_{29}INO_2S$ [$(M+H)^+$] 486.0964, found 486.0968.



4-(iodomethyl)-2-((4-nitrophenyl)sulfonyl)-2-azaspiro[4.4]nonane (15): This compound was prepared according to the General Procedure A using *N*-allyl-4-nitrobenzenesulfonamide (61 mg, 0.25 mmol) and methylenecyclopentane (53 μL, 0.5 mmol) with Blue LED light. After purification by column chromatography SiO_2 (5%-10% EtOAc/hexanes), The title compound was isolated as a colorless oil (59 mg, 52% yield).

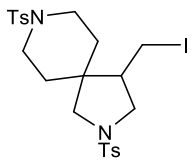
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.5 Hz, 2 H), 8.04 (d, *J* = 8.8 Hz, 2 H), 3.65 (dd, *J* = 10.4, 7.0 Hz, 1 H), 3.29 (dd, *J* = 10.4, 6.2 Hz, 1 H), 3.24 (d, *J* = 9.5 Hz, 1 H), 3.17 (dd, *J* = 9.8, 3.2

Hz, 1 H), 3.09 (d, *J* = 9.5 Hz, 1 H), 2.65 (dd, *J* = 12.0, 10.0 Hz, 1 H), 3.34-2.26 (m, 1 H), 1.70-1.50 (m, 4 H), 1.50-1.37 (m, 3 H), 1.32-1.20 (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.1, 142.9, 128.4, 124.4, 58.7, 54.0, 53.3, 50.0, 36.2, 30.6, 24.5, 23.9, 3.3; IR (neat): 2952, 1604, 1526, 1473, 1346, 1160, 1105, 1089, 1054 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{20}IN_2O_4S$ [$(M+H)^+$] 451.0188, found 451.0162.



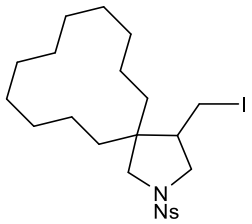
4-(iodomethyl)-2-tosyl-2-azaspiro[4.5]decane (16): This compound was prepared according to the General Procedure A using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and methylenecyclohexane (60 µL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (5%-10% EtOAc/hexanes), The title compound was isolated as a colorless oil (78 mg, 72% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 3.68 (dd, *J* = 10.3, 7.6 Hz, 1 H), 3.47 (d, *J* = 10.0 Hz, 1 H), 3.19 (dd, *J* = 9.6, 3.3 Hz, 1 H), 3.11 (dd, *J* = 10.1, 8.2 Hz, 1 H), 3.02 (d, *J* = 10.0 Hz, 1 H), 2.71 (dd, *J* = 12.0, 9.8 Hz, 1 H), 2.44 (s, 3 H), 2.17-2.06 (m, 1 H), 1.66-1.46 (m, 3 H), 1.39-1.30 (m, 1 H), 1.28-1.10 (m, 4 H), 1.10-1.05 (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.5, 133.7, 129.7, 127.4, 56.4, 53.1, 51.3, 45.6, 35.3, 28.2, 25.7, 23.3, 22.5, 21.5, 3.2; IR (neat): 2924, 2857, 1738, 1596, 1449, 1337, 1159, 1118, 1091, 1044 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{25}INO_2S$ [$(M+H)^+$] 434.0651, found 434.0625.



4-(iodomethyl)-2,8-ditosyl-2,8-diazaspiro[4.5]decane (17): This compound was prepared according to the General Procedure A using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and 4-methylene-1-tosylpiperidine (125 mg, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (20%-40% EtOAc/hexanes), The title compound was isolated as a colorless oil (102 mg, 69% yield).

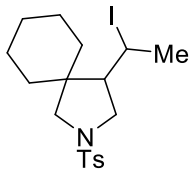
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 2 H), 7.61 (d, *J* = 8.1 Hz, 2 H), 7.37 (d, *J* = 7.7 Hz, 2 H), 7.33 (d, *J* = 7.3 Hz, 2 H), 3.70 - 3.51 (m, 3 H), 3.34-3.24 (m, 1 H), 3.18-3.02 (m, 2 H), 2.86 (d, *J* = 9.5 Hz, 1 H), 2.72-2.59 (m, 1 H), 2.50 (s, 3 H), 2.45 (s, 3 H), 2.29-2.13 (m, 2 H), 2.13-2.01 (m, 1 H), 1.83-1.68 (m, 1 H), 1.53 (br. s., 1 H), 1.27 (dd, *J* = 11.4, 11.0 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.1, 144.0, 133.2, 132.6, 129.9, 129.8, 127.6, 127.3, 54.9, 52.8, 50.8, 43.5, 43.3, 42.7, 33.6, 27.3, 21.6, 21.6, 1.1; IR (neat): 2920, 1596, 1492, 1335, 1305, 1154, 1089, 1047 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{23}H_{30}IN_2O_4S_2$ [$(M+H)^+$] 589.0692, found 589.0660.



4-(iodomethyl)-2-((4-nitrophenyl)sulfonyl)-2-azaspiro[4.11]hexadecane (18): This compound was prepared according to the General Procedure A using *N*-allyl-4-nitrobenzenesulfonamide (61 mg, 0.25 mmol) and methylenecyclododecane (90 mg, 0.5 mmol) with Blue LED light. After purification by column chromatography SiO_2 (5%-10% EtOAc/hexanes), The title compound was isolated as a colorless oil (92 mg, 63% yield).

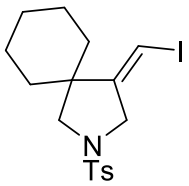
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.8 Hz, 2 H), 8.03 (d, *J* = 8.5 Hz, 2 H), 3.67 (dd, *J* = 10.5, 7.3 Hz, 1 H), 3.36-3.24 (m, 2 H), 3.20 (d, *J* = 9.8 Hz, 1 H), 3.00 (d, *J* = 10.0 Hz, 1 H), 2.64

(dd, J = 11.8, 10.1 Hz, 1 H), 2.37-2.25 (m, 1 H), 1.50-1.10 (m, 22 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.1, 142.7, 128.5, 124.4, 57.5, 54.2, 50.0, 48.3, 32.4, 26.6, 26.5, 25.9, 22.6, 22.5, 22.1, 22.0, 19.7, 19.5, 5.3.; IR (neat): 2930, 2858, 1603, 1527, 1470, 1345, 1161, 1099, 1010 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{22}H_{33}IN_2NaO_4S$ [$(M+Na)^+$] 571.1103, found 571.1084.



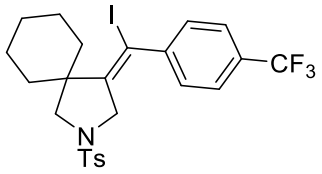
4-(1-iodoethyl)-2-tosyl-2-azaspiro[4.5]decane (19): This compound was prepared according to the General Procedure A using *N*-(but-2-en-1-yl)-4-methylbenzenesulfonamide (56 mg, 0.25 mmol) and methylenecyclohexane (60 µL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the pyrrolidine compound was isolated as a white solid (68 mg, 61% yield, 1.4:1 d.r.).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (dd, J = 8.3, 4.2 Hz, 2 H_{Maj} + 2 H_{Min}), 7.35 (d, J = 8.1 Hz, 2H_{Maj} + 2 H_{Min}), 4.43 (dd, J = 7.0, 4.8 Hz, 1 H_{Min}), 4.19 (t, J = 7.0 Hz, 1 H_{Maj}), 3.70 (dd, J = 10.3,8.1 Hz, 1 H_{Maj}), 3.63 (d, J = 9.9 Hz, 1 H_{Maj}), 3.51 (dd, J = 10.6, 7.7 Hz, 1 H_{Min}), 3.38 (dd, J = 10.6, 5.1 Hz, 1 H_{Min}), 3.28 (d, J = 10.3 Hz, 1 H_{Min}), 3.21 (d, J = 10.6 Hz, 1 H_{Min}), 3.11 (dd, J = 10.3, 8.1 Hz, 1 H_{Maj}), 3.06 (d, J = 9.9 Hz, 1 H_{Maj}), 2.45 (s, 3 H_{Maj} + 3 H_{Min}), 1.98 (d, J = 7.0 Hz, 3 H_{Maj}), 1.78 (d, J = 7.0 Hz, 3 H_{Min}), 1.70-1.59 (m, 1 H_{Maj} + 1 H_{Min}), 1.57-1.50 (m, 2 H_{Maj} + 2 H_{Min}), 1.47-1.43 (m, 1 H_{Maj} + 1 H_{Min}), 1.39-1.29 (m, 2 H_{Maj} + 2 H_{Min}), 1.29-1.19 (m, 4H_{Maj} + 4 H_{Min}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.6, 143.4, 133.8, 129.7, 127.6, 127.4, 56.7, 55.8, 54.9, 49.5, 46.0, 45.0, 37.1, 36.5, 29.7, 29.4, 27.6, 27.5, 25.9, 25.8, 25.5,23.5, 23.1, 23.0, 22.6, 21.6; IR (neat): 2918, 2847, 1595, 1449, 1333, 1157, 1016, 818,cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{27}INO_2S$ [$(M+H)^+$] 448.0807, found 448.0801.



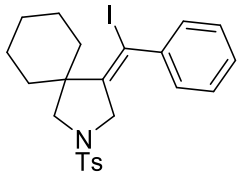
4-(iodomethylene)-2-tosyl-2-azaspiro[4.5]decane (20): This compound was prepared according to the General Procedure A using 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (53 mg, 0.25 mmol) and methylenecyclohexane (60 μL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the pyrrolidine compound was isolated as a yellow solid (69 mg, 64% yield, 1.5:1 *E*:*Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 5.70 (br. s., 1 H), 4.04 (d, *J* = 2.6 Hz, 2 H), 3.68 (s, 2 H), 2.44 (s, 3 H), 2.05-1.99 (m, 4 H), 1.97 (t, *J* = 2.6 Hz, 1 H), 1.68-1.60 (m, 4 H), 0.90 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 136.2, 131.6, 129.6, 129.4, 127.8, 127.7, 127.7, 73.5, 52.8, 35.2, 31.6, 25.9, 25.3, 22.7, 22.5, 22.2, 21.6, 14.2; IR (neat): 2925, 2854, 1596, 1449, 1341, 1158, 1040, 813,cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{23}INO_2S$ [$(M+H)^+$] 432.0494, found 432.0494.



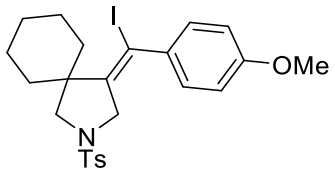
4-(iodo(4-(trifluoromethyl)phenyl)methylene)-2-tosylazaspiro[4.5]decane (21): This compound was prepared according to the General Procedure A using *N*-(3-(4-trifluoromethyl phenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (89 mg, 0.25 mmol) and methylenecyclohexane (60 μL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the pyrrolidine compound was isolated as a white solid (75 mg, 52% yield, 5.6:1 *E*:*Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2 H), 7.58 (d, *J* = 8.1 Hz, 2 H), 7.42 (d, *J* = 7.7 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 3.95 (s, 2 H), 3.33 (s, 2 H), 2.49 (s, 3 H), 1.50 (d, *J* = 12.8 Hz, 3 H), 1.42 (d, *J* = 13.9 Hz, 2 H), 1.21-1.07 (m, 2 H), 1.07-0.98 (m, 2 H), 0.72 (br. s., 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.3, 144.0, 132.2, 129.9, 128.6, 128.0, 125.2, 125.2, 90.2, 61.7, 57.6, 50.0, 34.1, 25.1, 22.8, 21.7; IR (neat): 2923, 2851, 1597, 1503, 1343, 1157, 1030, 833,cm^{-1}; ^{19}F NMR (375 MHz, $CDCl_3$): δ -63.1 (s, 1 F); IR (neat): 3217, 2932, 1676, 1560, 1489, 1324, 1112, 1066, 828,cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{24}H_{26}F_3INO_2S$ [$(M+H)^+$] 576.0681, found 576.0686.



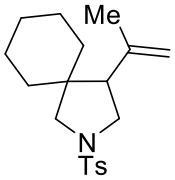
4-(iodo(phenyl)methylene)-2-tosyl-2-azaspiro[4.5]decane (22): This compound was prepared according to the General Procedure A using *N*-(3-phenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (72 mg, 0.25 mmol) and methylenecyclohexane (60 μL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the pyrrolidine compound was isolated as a white solid (66 mg, 52% yield, 6.7:1 *E*:*Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.3 Hz, 2 H), 7.58-7.53 (m, 2 H), 7.46 (s, 2 H), 7.40 (d, *J* = 8.1 Hz, 2 H), 7.03 (s, 1 H), 3.57 (s, 2 H), 2.48 (s, 3 H), 2.24 (t, *J* = 13.2 Hz, 2 H), 1.63 - 1.58 (m, 1 H), 1.32 - 1.24 (m, 6 H), 1.22-1.12 (m, 2 H), 0.89 (br. s., 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.9, 143.8, 140.4, 133.4, 131.6, 130.1, 129.8, 128.4, 127.3, 58.1, 49.9, 33.4, 29.7, 24.8, 22.7, 22.6, 21.7, 21.7, 14.2; IR (neat): 2923, 2851, 1597, 1503, 1343, 1157, 1030, 833,cm^{-1}; IR (neat): 3217, 2932, 1676, 1560, 1489, 1324, 1112, 1066, 828,cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{23}H_{27}INO_2S$ [$(M+H)^+$] 508.0807, found 508.0816.



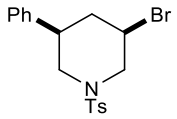
4-(iodo(4-methoxyphenyl)methylene)-2-tosyl-2-azaspiro[4.5]decane (23): This compound was prepared according to the General Procedure A using *N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (80 mg, 0.25 mmol) and methylenecyclohexane (60 μL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the pyrrolidine compound was isolated as a yellow solid (64 mg, 48% yield, 6.3:1 *E*:*Z*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79-7.75 (d, *J* = 8.1 Hz, 2 H), 7.42-7.38 (d, *J* = 8.1 Hz, 2 H), 7.12-7.08 (d, *J* = 8.8 Hz, 2 H), 6.83-6.79 (d, *J* = 8.8 Hz, 2 H), 3.90 (s, 2 H), 3.82 (s, 3 H), 3.30 (s, 2 H), 2.48 (s, 3 H), 1.51-1.43 (m, 3 H), 1.43-1.37 (m, 2 H), 1.26 (s, 2 H), 1.13-1.10 (m, 2 H), 0.89 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 150.1, 143.8, 136.2, 132.3, 129.8, 129.5, 128.0, 113.4, 93.6, 61.7, 57.7, 55.3, 49.7, 33.9, 29.7, 25.2, 22.9, 21.7; IR (neat): 2923, 2851, 1597, 1503, 1343, 1157, 1030, 833,cm^{-1}; IR (neat): 3271, 2933, 1676, 1520, 1488, 1337, 1112, 1064, 846,cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{24}H_{29}INO_3S$ [$(M+H)^+$] 538.0913, found 538.0929.



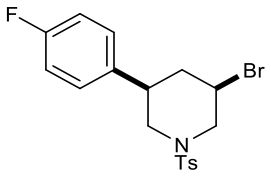
4-(prop-1-en-2-yl)-2-tosyl-2-azaspiro[4.5]decane (24): This compound was prepared according to the General Procedure A using 4-methyl-*N*-(3-methylbut-2-en-1-yl)benzenesulfonamide (60 mg, 0.25 mmol) and methylenecyclohexane (60 μL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the pyrrolidine compound was isolated as a yellow solid (40 mg, 48% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 4.87 (s, 1 H), 4.62 (s, 1 H), 3.48-3.39 (m, 1 H), 3.36 (d, *J* = 10.3 Hz, 1 H), 3.28 (dd, *J* = 9.9, 7.3 Hz, 1 H), 3.11 (d, *J* = 10.3 Hz, 1 H), 2.44 (s, 3 H), 2.31 (d, *J* = 7.7 Hz, 1 H), 1.65 (s, 3 H), 1.56 (td, *J* = 12.5, 3.9 Hz, 1 H), 1.33-1.21 (m, 4 H), 1.19-1.09 (m, 4 H), 0.88 (d, *J* = 7.0 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.3, 142.2, 134.1, 129.6, 127.4, 114.3, 55.7, 54.9, 50.2, 45.4, 36.0, 29.9, 25.8, 23.6, 23.2, 23.0, 21.6; IR (neat): 2923, 2851, 1597, 1503, 1343, 1157, 1030, 833,cm^{-1}; IR (neat): 2924, 2854, 1676, 1597, 1450, 1341, 1108, 1046, 812,cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{19}H_{28}NO_2S$ [$(M+H)^+$] 334.1841, found 334.1847.



3-bromo-5-phenyl-1-tosylpiperidine (3): This compound was prepared according to the General Procedure C using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and styrene (58 µL, 0.5 mmol). After purification by column chromatography SiO_2 (3%-5% EtOAc/hexanes), the title compound was isolated as a colorless oil (74 mg, 75% yield, >20:1 d.r.).

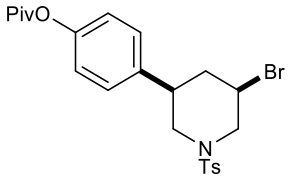
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 3 H), 7.32 (d, *J* = 7.6 Hz, 2 H), 7.30-7.25 (m, 1 H), 7.15 (d, *J* = 7.3 Hz, 2 H), 4.27 (dd, *J* = 11.5, 4.4 Hz, 1 H), 4.16 (tt, *J* = 11.5, 4.3 Hz, 1 H), 4.00-3.93 (m, 1 H), 3.01 (tt, *J* = 12.0, 3.6 Hz, 1 H), 2.55 (d, *J* = 13.2 Hz, 1 H), 2.52 (t, 12.0 Hz, 1 H), 2.46 (s, 3 H), 2.28 (t, *J* = 11.6 Hz, 1 H), 1.89 (q, *J* = 12.5 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.9, 140.3, 133.3, 129.9, 128.8, 127.4, 127.0, 53.1, 51.6, 44.0, 43.4, 42.0, 21.5; IR (neat): 2870, 1597, 1495, 1454, 1324, 1161, 1121, 1110, 1086, 1068 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{21}BrNO_2S$ [$(M+H)^+$] 394.0476, found 394.0472.



3-bromo-5-(4-fluorophenyl)-1-tosylpiperidine (25)

This compound was prepared according to the General Procedure C using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and 4-fluorostyrene (60 µL, 0.5 mmol). After purification by column chromatography SiO_2 (5%-10% EtOAc/hexanes), the title compound was isolated as a colorless oil (79 mg, 77% yield, >20:1 d.r.).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 7.8 Hz, 2 H), 7.12 (dd, *J* = 8.2, 5.5 Hz, 2 H), 7.01 (t, *J* = 8.4 Hz, 2 H), 4.26 (dd, *J* = 11.5, 4.2 Hz, 1 H), 4.18-4.10 (m, 1 H), 3.97-3.89 (m, 1 H), 3.05-2.95 (m, 1 H), 2.54 (d, *J* = 15.2 Hz, 1 H), 2.50 (t, *J* = 11.4 Hz, 2 H), 2.46 (s, 3 H), 2.23 (t, *J* = 11.6 Hz, 1 H), 1.84 (q, *J* = 12.6 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8, 161.1, 144.0, 136.02, 136.0, 133.3, 129.9, 128.53, 128.48, 127.5, 115.7, 115.6, 53.0, 51.7, 43.7, 42.7, 42.1, 21.6; ^{19}F NMR (375 MHz, $CDCl_3$): δ -115.2 (m, 1 F); IR (neat): 2919, 2851, 1596, 1511, 1473, 1341, 1296, 1221, 1160 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{20}BrFNO_2S$ [$(M+H)^+$] 412.0382, found 412.0410.

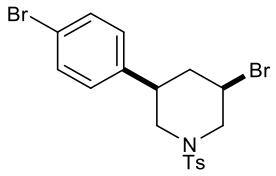


4-(5-bromo-1-tosylpiperidin-3-yl)phenyl pivalate (26)

This compound was prepared according to the General Procedure C using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and 4-vinylphenyl pivalate (102 mg, 0.5 mmol).

After purification by column chromatography SiO_2 (10%-15% EtOAc/hexanes), the title compound was isolated as a colorless oil (84 mg, 68% yield, >20:1 d.r.).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.16 (d, *J* = 8.5 Hz, 2 H), 7.01 (d, *J* = 8.5 Hz, 2 H), 4.26 (dd, *J* = 11.6, 4.5 Hz, 1 H), 4.18-4.10 (m, 1 H), 3.93 (dd, J = 12.0, 3.3 Hz, 1 H), 3.06-2.97 (m, 1 H), 2.54 (d, *J* = 13.2 Hz, 1 H), 2.50 (t, *J* = 11.4 Hz, 1 H), 2.45 (s, 3 H), 2.23 (t, *J* = 11.6 Hz, 1 H), 1.86 (q, *J* = 12.6 Hz, 1 H), 1.36 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 210.5, 141.9, 128.5, 128.4, 128.4, 128.3, 125.7, 83.0, 69.4, 40.5, 34.6, 32.2, 31.3, 27.7, 23.1; IR (neat): 2979, 2931, 1741, 1597, 1508, 1470, 1343, 1160, 1120, 1086 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{23}H_{29}BrNO_4S$ [$(M+H)^+$] 494.1001, found 494.1014.

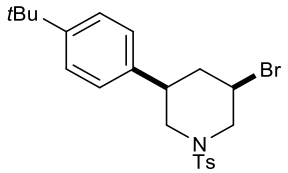


3-bromo-5-(4-bromophenyl)-1-tosylpiperidine (27)

This compound was prepared according to the General Procedure C using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and 4-bromostyrene (65 μL, 0.5 mmol). After purification by column chromatography SiO_2 (3%-5% EtOAc/hexanes), the title compound was isolated as a colorless oil (79 mg, 67% yield, >20:1 d.r.).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2 H), 7.45 (d, *J* = 8.3 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.03 (d, *J* = 8.3 Hz, 2 H), 4.25 (dd, *J* = 11.5, 4.4 Hz, 1 H), 4.19-4.08 (m, 1 H), 3.97-3.86 (m, 1 H), 3.03-2.92 (m, 1 H), 2.52 (d, *J* = 12.6 Hz,1 H), 2.49 (t, *J* = 11.1 Hz, 1 H), 2.45 (s, 3 H), 2.22 (t, *J* = 11.6 Hz, 1 H), 1.83 (q, *J* = 12.5 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.0, 139.2, 133.2, 131.9, 129.9, 128.7, 127.4, 121.3, 53.0, 51.4, 43.5, 42.8, 41.8, 21.6; IR (neat): 2998, 1596,

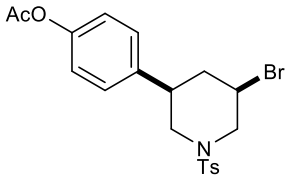
1491, 1470, 1340, 1161, 1137, 1087, 1073 cm^{-1}. HRMS (ESI) *m/z* calcd for $C1_8H_{20}Br_2NO_2S$ $[(M+H)^+]$ 471.9581, found 471.9602.



3-bromo-5-(4-(tert-butyl)phenyl)-1-tosylpiperidine (28)

This compound was prepared according to the General Procedure C using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and 4-*tert*-butylstyrene (78 μL, 0.5 mmol). After purification by column chromatography SiO_2 (3%-5% EtOAc/hexanes), the title compound was isolated as a colorless oil (92 mg, 82% yield, >20:1 d.r.).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2 H), 7.35 (d, *J* = 8.3 Hz, 4 H), 7.10 (d, *J* = 8.3 Hz, 2 H), 4.27 (dd, *J* = 12.0, 4.8 Hz, 1 H), 4.15 (tt, *J* = 11.5, 4.3 Hz, 1 H), 3.99-3.91 (m, 1 H), 2.99 (tt, *J* = 12.1, 3.7 Hz, 1 H), 2.55 (d, *J* = 12.6 Hz, 1 H), 2.52 (t, *J* = 11.4 Hz, 1 H), 2.46 (s, 3 H), 2.28 (t, *J* = 11.6 Hz, 1 H), 1.88 (q, *J* = 12.5 Hz, 1 H), 1.32 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.4, 143.9, 137.2, 133.4, 129.9, 127.5, 126.7, 125.6, 53.1, 51.7, 44.1, 42.9, 42.0, 34.4, 31.3, 21.5; IR (neat): 2955, 1597, 1512, 1467, 1343, 1162, 1138, 1108, 1086 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{22}H_{29}BrNO_2S$ $[(M+H)^+]$ 450.1102, found 450.1102.

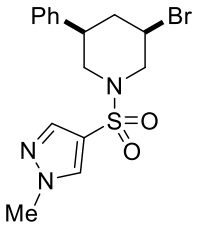


4-(5-bromo-1-tosylpiperidin-3-yl)phenyl acetate (29)

This compound was prepared according to the General Procedure C using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and 4-vinylphenyl acetate (71 μL, 0.5 mmol).

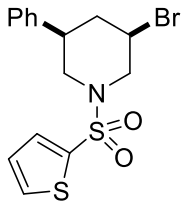
After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the title compound was isolated as a colorless oil (87 mg, 77% yield, >20:1 d.r.).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.17 (d, *J* = 8.3 Hz, 2 H), 7.04 (d, *J* = 8.5 Hz, 2 H), 4.26 (dd, *J* = 11.4, 4.3 Hz, 1 H), 4.20-4.09 (m, 1 H), 3.93 (dd, *J* = 11.7, 3.7 Hz, 1 H), 3.07-2.97 (m, 1 H), 2.54 (d, *J* = 12.9 Hz, 1 H), 2.49 (t, *J* = 11.4 Hz, 1 H), 2.45 (s, 3 H), 2.31 (s, 3 H), 2.22 (t, *J* = 11.6 Hz, 1 H), 1.86 (q, *J* = 12.5 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 149.8, 144.0, 137.8, 133.2, 129.9, 128.1, 127.5, 121.9, 53.1, 51.7, 43.8, 42.8, 41.9, 21.6, 21.1; IR (neat): 2966, 1752, 1595, 1507, 1341, 1219, 1188, 1161, 1086 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{20}H_{23}BrNO_4S$ $[(M+H)^+]$ 452.0531, found 452.0541.



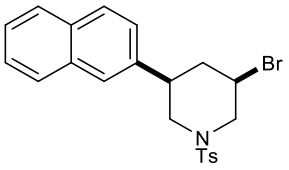
3-bromo-1-((1-methyl-1*H*-pyrazol-5-yl)sulfonyl)-5-phenylpiperidine (30): This compound was prepared according to the General Procedure C using *N*-allyl-1-methyl-1H-imidazole-4-sulfonamide using (50 mg, 0.25 mmol) and styrene (58 µL, 0.5 mmol). After purification by column chromatography SiO_2 (30%-40% EtOAc/hexanes), the title compound was isolated as a white solid (49 mg, 51% yield, >20:1 d.r.).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (s, 1 H), 7.72 (s, 1 H), 7.37-7.25 (m, 3 H), 7.19-7.13 (m, 2H), 4.25-4.13 (m, 2 H), 3.95 (s, 3 H), 3.88 (dd, *J* = 11.5, 4.2 Hz, 1 H), 3.02 (br. s., 1 H), 2.59-2.52 (m, 1 H), 2.48 (t, *J* = 10.9 Hz, 1 H), 2.24 (t, *J* = 11.6 Hz, 1 H), 1.89 (d, *J* = 12.2 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.3, 138.8, 132.0, 128.9, 127.6, 127.1, 118.0, 53.1, 51.7, 43.8, 43.2, 41.9, 39.8. HRMS (ESI) *m/z* calcd for $C_{15}H_{19}BrN_3O_2S$ $[(M+H)^+]$ 384.0381, found 384.0381.



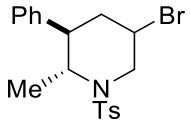
3-Bromo-5-phenyl-1-(thiophen-2-ylsulfonyl)piperidine (31): This compound was prepared according to the General Procedure C using *N*-allylthiophene-2-sulfonamide (51 mg, 0.25 mmol) and styrene (58 μL, 0.5 mmol). After purification by column chromatography SiO_2 (3%-5% EtOAc/hexanes), the title compound was isolated as a colorless oil (60 mg, 62% yield, >20:1 d.r.).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 5.0, 1.1 Hz, 1 H), 7.56 (dd, *J* = 3.7, 1.1 Hz, 1 H), 7.36-7.31 (m, 2 H), 7.28 (d, *J* = 7.5 Hz, 1 H), 7.19-7.14 (m, 3 H), 4.32-4.26 (m, 1 H), 4.17 (tt, *J* = 11.6, 4.4 Hz, 1 H), 4.01-3.95 (m, 1 H), 3.03 (tt, *J* = 12.1, 3.7 Hz, 1 H), 2.61 (t, *J* = 11.5 Hz, 1 H), 2.59-2.54 (m, 1 H), 2.38 (t, *J* = 11.7 Hz, 1 H), 1.92 (q, *J* = 12.7 Hz, 1 H); ^{13}C NMR (150MHz, $CDCl_3$) δ 140.1, 136.7, 132.6, 132.4, 128.9, 127.8, 127.6, 127.0, 53.1, 51.7, 43.7, 43.3, 41.9; IR (neat): 2921, 1601, 1470, 1405, 1348, 1235, 1154, 1135, 1022, 979, 699 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{17}BrNO_2S_2$ [$(M+H)^+$] 385.9884, found 385.9894.



3-bromo-5-(naphthalen-2-yl)-1-tosylpiperidine (32): This compound was prepared according to the General Procedure C using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and 4-vinylnaphthalene (77 mg, 0.5 mmol). After purification by column chromatography SiO_2 (5%-10% EtOAc/hexanes), the title compound was isolated as a colorless oil (91 mg, 82% yield, >20:1 d.r.).

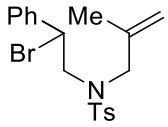
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86-7.77 (m, 3 H), 7.68 (d, *J* = 8.3 Hz, 2 H), 7.60 (s, 1 H), 7.53-7.45 (m, 2 H), 7.35 (m, *J* = 8.1 Hz, 2 H), 7.29 (dd, *J* = 8.5, 1.5 Hz, 1 H), 4.31 (dd, *J* = 11.6, 4.5 Hz, 1 H), 4.21 (tt, *J* = 11.5, 4.3 Hz, 1 H), 4.09-4.02 (m, 1 H), 3.18 (tt, *J* = 12.0, 3.7 Hz, 1 H), 2.65 (d, *J* = 12.9 Hz, 1 H), 2.57 (t, *J* = 11.4 Hz, 1 H), 2.46 (s, 3 H), 2.37 (t, *J* = 11.6 Hz, 1 H), 2.03 (q, *J* = 12.5 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.0, 137.6, 133.3, 132.6, 129.9, 128.5, 127.6, 127.5, 126.4, 126.0, 125.5, 125.3, 53.1, 51.7, 44.0, 43.4, 41.8, 21.6; IR (neat): 2988, 1597, 1473, 1338, 1297, 1161, 1087 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{22}H_{23}BrNO_2S$ [$(M+H)^+$] 444.0633, found 444.0639.



5-bromo-2-methyl-3-phenyl-1-tosylpiperidine (33): This compound was prepared according to the General Procedure C, using *N*-allyl-4-methylbenzenesulfonamide (56 mg, 0.25 mmol) and *β*-methylstyrene (64 μL, 0.5 mmol). After purification by column chromatography SiO_2 (3%-5% EtOAc/hexanes), the title compound was isolated as a white solid (42 mg, 41% yield, 3.4:1 d.r.).

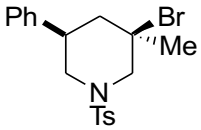
^{1}H NMR (600MHz , $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2 H), 7.41 (d, *J* = 8.1 Hz, 3 H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.32-7.24 (m, 10 H), 7.10 (s, 1 H), 6.94-6.85 (m, 2 H), 6.69-6.60 (m, 1 H), 3.93 (dd, *J* = 6.7, 11.8 Hz, 1 H), 3.68-3.59 (m, 1 H), 3.36 (t, *J* = 11.2 Hz, 1 H), 3.24-3.17 (m, 1 H), 3.09-3.00 (m, 1 H), 2.62 (t, *J* = 10.3 Hz, 1 H), 2.54-2.49 (m, 4 H), 2.48-2.42 (m, 1 H), 1.50 (d, *J* = 6.1 Hz, 1 H), 1.37 (d, *J* = 6.1 Hz, 3 H);^{13}C NMR (150 MHz, $CDCl_3$) δ 143.8, 137.6, 135.0, 130.0, 129.9, 129.8, 129.0, 128.6, 128.5, 128.3, 127.9, 127.8, 127.6, 127.6, 127.5, 127.4, 127.3, 64.1, 61.4, 58.2, 55.3, 53.4, 52.1, 46.5, 44.2, 32.1, 31.2, 29.7, 23.2, 21.7, 20.8IR (neat): 2870, 1591, 1491, 1453, 1324, 1167, 1122, 1117, 1087, 1063 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{19}H_{22}Br_1NO_2S$ [$(M+H)^+$] 407.0555, found 407.0552.

Preparation of bromo-intermediate of product 34:



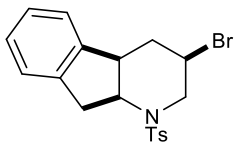
***N*-(2-bromo-2-phenylethyl)-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (34a)**: To an 8 mL vial equipped with a stir bar was added NBS (98 mg, 0.55 mmol) and 4-methyl-*N*-(2-methylallyl)benzenesulfonamide (113 mg, 0.5 mmol). The vial was evacuated and backfilled with nitrogen. Then the solvent (DCM, 0.5 mL) was added via a syringe, followed by styrene (116 µL, 1.0 mmol). The reaction mixture was then stirred for 16 h under fluorescent light. The reaction was diluted with EtOAc (2 mL) and quenched with saturated $Na_2S_2O_3$ (2 mL). Organic layer was separated, aqueous layer was extracted with EtOAc (2×2 mL). Combined organic layer was concentrated under reduced pressure to give the crude product. After purification by column chromatography SiO_2 (7% EtOAc/hexanes), the bromo-intermediate was isolated as a colorless thick liquid (188 mg, 92% yield).

^{1}H NMR (600MHz , $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2 H), 7.40-7.28 (m, 7 H), 5.25 (dd, *J* = 8.7, 6.3 Hz, 1 H), 4.85 (s, 1 H), 4.67 (s, 1 H), 3.83 (d, *J* = 6.3 Hz, 1 H), 3.71–3.61 (m, 2 H), 3.25 (d, *J* = 15.1 Hz, 1 H), 2.44 (s, 3 H), 1.37 (s, 3 H);^{13}C NMR (150 MHz, $CDCl_3$) δ 143.7, 140.1, 139.2, 136.6, 129.7, 128.9, 128.7, 127.4, 115.5, 77.3, 77.1, 76.9, 55.4, 51.6, 21.6, 19.7; IR (neat): 3000, 1567, 1491, 1451, 1320, 1160, 1123, 1112, 1089, 1063 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{19}H_{23}BrNO_2S$ [$(M+H)^+$] 408.0627, found 408.0633.



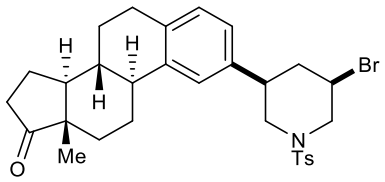
3-bromo-3-methyl-5-phenyl-1-tosylpiperidine (34): To an 8 mL vial equipped with a stir bar was added bromo-intermediate (102 mg, 0.25 mmol) followed by $AlBr_3$ (20 mg, 0.075 mmol) from the glovebox. Then the solvent (DCM, 0.25 mL) was added via a syringe. The reaction mixture was then stirred for 16 h under room temperature. The reaction was diluted with EtOAc (2 mL) and quenched with water (2 mL). Organic layer was separated, aqueous layer was extracted with EtOAc (2×2 mL). Combined organic layer was concentrated under reduced pressure to give the crude product, which was purified by column chromatography SiO_2 (5%-7% EtOAc/hexanes) to afford the pure product. The title compound was isolated as a white solid (62 mg, 61% yield, >20:1 d.r.).

^{1}H NMR (600MHz , $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 2 H), 7.38-7.28 (m, 5 H), 7.18 (d, *J* = 8.4 Hz, 2 H), 4.04 (d, *J* = 12.8 Hz, 1 H), 3.97 (d, *J* = 11.7 Hz, 1 H), 2.44 (s, 3 H), 2.33-2.24 (m, 3 H), 1.85 (s, 3 H), 1.55 (dd, *J* = 12.3, 14.5 Hz, 1 H);^{13}C NMR (150 MHz, $CDCl_3$) δ 143.7, 140.9, 129.8, 128.8, 127.6, 127.4, 127.3, 61.8, 58.4, 51.6, 47.0, 39.3, 32.2, 21.6; IR (neat): 2871, 1593, 1492, 1451, 1320, 1160, 1123, 1112, 1089, 1063 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{19}H_{22}Br_1NO_2S$ [$(M+H)^+$] 407.0555, found 407.0553.



3-bromo-1-tosyl-2,3,4,4a,9,9a-hexahydro-1H-indeno[2,1-b]pyridine (35): This compound was prepared according to the General Procedure C using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and indene (58 µL, 0.5 mmol). After purification by column chromatography SiO_2 (5%-10% EtOAc/hexanes), the title compound was isolated as a colorless oil (53 mg, 52% yield, 3.6:1 d.r.).

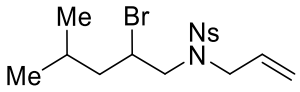
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2 H_{Maj}), 7.75 (d, J = 8.3 Hz, 2 H_{Min}), 7.40-7.33 (m, 2 H_{Maj} + 2 H_{Min}), 7.28-7.21 (m, 4 H_{Maj} + 1 H_{Min}), 7.19-7.14 (m, 2 H_{Min}), 7.14-7.11 (m, 1 H_{Min}), 4.67 (td, J = 10.6, 7.5 Hz, 1 H_{Min}), 4.36 (t, J = 6.1 Hz, 1 H_{Maj}), 4.30 (dd, J = 13.1, 2.3 Hz, 1 H_{Min}), 4.00-3.90 (m, 1 H_{Maj}), 3.86 (tt, J = 3.9, 12.0 Hz, 1 H_{Min}), 3.70 (t, J = 7.1 Hz, 1 H_{Maj}), 3.49 (d, J = 17.1 Hz, 1 H_{Maj}), 3.38 (dd, J = 9.5, 3.9 Hz, 1 H_{Maj}), 3.30 (dd, J = 17.1, 5.9 Hz, 1 H_{Maj}), 3.14-3.06 (m, 2 H_{Min}), 2.90 (dd, J = 15.1, 11.0 Hz, 1 H_{Min}), 2.76 (dd, J = 15.1, 11.0 Hz, 1 H_{Min}), 2.51-2.42 (m, 3 H_{Maj} + 3 H_{Min}), 2.26 (dd, J = 11.2, 9.8 Hz, 1 H_{Maj}), 1.87 (td, J = 13.9, 8.1 Hz, 1 H_{Maj}), 1.60 (q, J = 12.0 Hz, 2 H_{Min}); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.9, 143.8, 143.7, 143.5, 141.0, 138.8, 137.1, 134.5, 130.0, 129.9, 127.8, 127.5, 127.4, 127.3, 127.1, 127.0, 125.5, 125.4, 123.5, 123.3, 66.5, 62.6, 55.1, 49.1, 47.7, 43.9, 43.3, 41.2, 39.5, 35.6, 33.1, 30.7, 29.7, 21.6; IR (neat): 2921, 1736, 1597, 1460, 1341, 1159, 1090, 1041 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{19}H_{21}BrNO_2S$ [$(M+H)^+$] 406.0476, found 406.0471.



(8R,9S,13S,14S)-2-(5-bromo-1-tosylpiperidin-3-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (36): This compound was prepared according to the General Procedure C using *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol) and (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (140 mg, 0.5 mmol). After purification by column chromatography SiO_2 (10%-20% EtOAc/hexanes), the title compound was isolated as a colorless oil (93 mg, 65% yield, >20:1 d.r.).

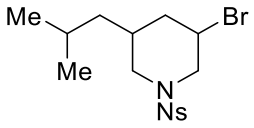
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.25 (d, *J* = 8.1 Hz, 1 H), 6.95 (d, *J* = 8.1 Hz, 1 H), 6.91 (s, 1 H), 4.26 (dd, *J* = 11.4, 4.3 Hz, 1 H), 4.19-4.10 (m, 1 H), 3.94 (dd, *J* = 3.8, 11.6 Hz, 1 H), 3.00- .92 (m, 1 H), 2.92-2.86 (m, 2 H), 2.57-2.47 (m, 3 H), 2.45 (s, 3 H), 2.44-2.38 (m, 1 H), 2.32-2.20 (m, 2 H), 2.20-2.12 (m, 1 H), 2.11-2.00 (m, 2 H), 1.97 (d, *J* = 11.7 Hz, 1 H), 1.88 (q, *J* = 12.5 Hz, 1 H), 1.68-1.56 (m, 4 H), 1.56-1.39 (m, 4 H), 0.91 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.9, 139.1, 137.8, 137.0, 133.4, 129.9, 127.8, 127.5, 125.8, 124.3, 53.1, 51.8, 50.4, 47.9, 44.3, 44.1, 42.9, 41.9, 38.1, 35.8, 31.5, 29.4, 26.4, 25.6, 21.6, 21.5, 13.8; IR (neat): 2921, 1734, 1493, 1450, 1339, 1161, 1088, 1051 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{30}H_{37}BrNO_3S$ [$(M+H)^+$] 570.1678, found 570.1667.

Preparation of bromo-intermediate of product 37:



***N*-allyl-*N*-(2-bromo-4-methylpentyl)-4-nitrobenzenesulfonamide (37a):** To an 8 mL vial equipped with a stir bar was added NBS (49 mg, 0.275 mmol) and *N*-allyl-4-nitrobenzenesulfonamide (61 mg, 0.25 mmol). The vial was evacuated and backfilled with nitrogen. Then the solvent (DCM, 0.25 mL) was added via a syringe, followed by 4-methyl-1-pentene (63 μL, 0.5 mmol). The reaction mixture was then stirred for 20 h under fluorescent light. The reaction was diluted with EtOAc (2 mL) and quenched with saturated $Na_2S_2O_3$ (2 mL). Organic layer was separated, aqueous layer was extracted with EtOAc (2×2 mL). Combined organic layer was concentrated under reduced pressure to give the crude product. After purification by column chromatography SiO_2 (2%-5% EtOAc/hexanes), the bromo-intermediate was isolated as a viscous colorless liquid (53 mg, 52% yield).

^{1}H NMR (600 MHz ,$CDCl_3$) δ 8.40 (d, *J* = 6.0 Hz, 2H), 8.08 (d, *J* = 12 Hz, 2H), 5.65-5.57 (m, 1H), 5.24 (brs, 1H), 5.21 (dd, *J* = 1.0, 7.8 Hz, 1H), 4.25-4.19 (m, 1H), 4.05 (dd, *J* = 6.5, 15.7 Hz, 1H), 3.90 (dd, *J* = 6.6, 15.8 Hz, 1H), 3.61 (dd, *J* = 6.7, 14.8 Hz, 1H), 3.44 (dd, *J* = 7.5, 14.7 Hz, 1H), 1.97-1.88 (m, 1H), 1.74-1.63 (m, 2H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150MHz, $CDCl_3$) δ 150.1, 145.5, 131.8, 128.5, 124.4, 120.5, 54.3, 52.1, 51.4, 44.7, 26.2, 23.1, 20.8; IR (neat): 2982, 1525, 1342, 1305, 1159, 1089, 915, 770 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{22}BrN_2O_4S$ [$(M+H)^+$] 405.0478, found 405.0483.

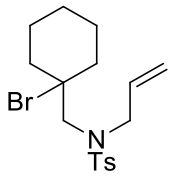


3-Bromo-5-isobutyl-1-((4-nitrophenyl)sulfonyl)piperidine (37): To an 8 mL vial equipped with a stir bar was added bromo-intermediate (40 mg, 0.10 mmol) and vial was evacuated and backfilled with nitrogen followed by $FeBr_3$ (15 mg, 0.050 mmol) from the glove box. Then the solvent (DCM, 0.4 mL) was added via a syringe. The reaction mixture was then stirred for 24 h under room temperature. The reaction was diluted with EtOAc (2 mL) and quenched with saturated ammonium chloride (2 mL). Organic layer was separated, aqueous layer was extracted with EtOAc (2×2 mL). Combined organic layer was concentrated under reduced pressure to give the crude product, which was purified by column chromatography on silica gel (5%-7% EtOAc/hexanes) to afford the pure product. The title compound was isolated as a viscous colorless liquid (16 mg, 39% yield, >20:1 d.r.).

^{1}H NMR (600 MHz ,$CDCl_3$) 8.36 (d, *J* = 12.0 Hz, 2 H), 8.07 (d, *J* = 12.0 Hz, 2 H), 4.31-4.24 (m, 1 H), 3.78-3.70 (m, 1 H), 3.56 (dd, *J* = 10.9, 5.5 Hz, 1 H), 3.39 (dd, J = 10.4, 1.6 Hz, 1 H), 3.32-3.25 (m, 1 H), 1.95 (dd, *J* = 14.9, 12.5 Hz, 1 H), 1.81-1.70 (m, 1 H), 1.67-1.61 (m, 2 H), 1.51-1.44

(m, 1 H), 1.31-1.26 (m, 1 H), 0.98 (d, J = 9.8 Hz, 6 H); ^{13}C NMR (150MHz, $CDCl_3$) δ 149.8, 146.9, 128.2, 124.4, 53.9, 45.6, 43.7, 42.0, 38.7, 33.9, 33.1, 26.8, 23.2; IR (neat): 2922, 2854, 1713, 1606, 1530, 1347, 1306, 1156, 1088, 741 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{22}BrN_2O_4S$ $[(M+H)^+]$ 405.0484, found 405.0478.

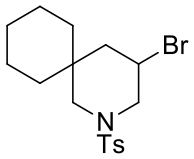
Preparation of bromo-intermediate of product 38:



N-Allyl-N-((1-bromocyclohexyl)methyl)-4-methylbenzenesulfonamide (38a): To an 8 mL vial equipped with a stir bar was added NBS (49 mg, 0.275 mmol) and *N*-allyl-4-methylbenzenesulfonamide (53 mg, 0.25 mmol). The vial was evacuated and backfilled with nitrogen. Then the solvent (DCM, 0.25 mL) was added via a syringe, followed by methylenecyclohexane (60 μL, 0.5 mmol). The reaction mixture was then stirred for 1 h under fluorescent light. The reaction was diluted with EtOAc (2 mL) and quenched with saturated $Na_2S_2O_3$ (2 mL). Organic layer was separated, aqueous layer was extracted with EtOAc (2×2 mL). Combined organic layer was concentrated under reduced pressure to give the crude product. After purification by column chromatography SiO_2 (2%-5% EtOAc/hexanes), the bromo-intermediate was isolated as a viscous colorless liquid (34 mg, 35% yield).

^{1}H NMR (600MHz, $CDCl_3$) δ 7.73 (d, J = 6.0 Hz, 2H), 7.33 (d, J = 6.0 Hz, 2H), 5.36-5.26 (m, 1H), 5.22-5.11 (m, 2 H), 4.12 (d, J = 6.6 Hz, 2 H), 3.70 (s, 2 H), 2.45 (s, 3 H), 2.07 (d, J = 12.9 Hz, 2 H), 1.85-1.65 (m, 7H), 1.29-1.16 (m, 1H); ^{13}C NMR (150MHz, $CDCl_3$) δ 143.6, 137.1, 132.0, 129.8, 127.4, 120.4, 75.72, 59.3, 52.6, 38.7, 25.1, 22.6, 21.5; IR (neat): 2940, 1653, 1506,

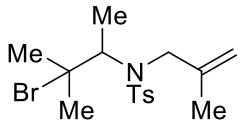
1323, 1339, 1157, 1089, 891, 746 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{25}BrNO_2S$ $[(M+H)^+]$ 386.0784, found 386.0789.



4-Bromo-2-tosyl-2-azaspiro[5.5]undecane (38): To an 8 mL vial equipped with a stir bar was added bromo-intermediate (39 mg, 0.10 mmol) and vial was evacuated and backfilled with nitrogen, followed by $AlBr_3$ (8 mg, 0.03 mmol) in the glovebox. Then the solvent (DCM, 0.4 mL) was added via a syringe. The reaction mixture was then stirred for 16 h under room temperature. The reaction was diluted with EtOAc (2 mL) and quenched with water (2 mL). Organic layer was separated and the aqueous layer was extracted with EtOAc (2×2 mL). Combined organic layer was concentrated under reduced pressure to give the crude product. After purification by column chromatography SiO_2 (5%-7% EtOAc/hexanes), the title compound was isolated as a white solid (24 mg, 62% yield).

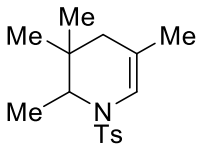
^1H NMR (600MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 4.25-4.18 (m, 1 H), 4.18-4.12 (m, 1 H), 3.76 (d, *J* = 11.7 Hz, 1 H), 2.44 (s, 3 H), 2.33 (t, *J* = 11.1 Hz, 1 H), 2.24 (d, *J* = 13.0 Hz, 1 H), 1.90 (d, *J* = 11.7 Hz, 1 H), 1.76-1.68 (m, 1 H), 1.52-1.38 (m, 7 H), 1.33 (t, *J* = 12.7 Hz, 1 H), 1.25-1.20 (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.7, 133.6, 129.8, 127.4, 53.9, 43.0, 37.5, 37.0, 31.4, 26.2, 21.5, 21.4, 21.1; IR (neat): 2935, 2847, 1595, 1451, 1338, 1163, 1088, 959, 816, 654 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{25}BrNO_2S$ $[(M+H)^+]$ 386.0789, found 386.0807.

Preparation of bromo-intermediate of product 39:



N-(3-bromo-3-methylbutan-2-yl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (39a): To an 8 mL vial equipped with a stir bar was added NBS (177 mg, 1.0 mmol) and 4-methyl-*N*-(2-methylallyl)benzenesulfonamide (113 mg, 0.50 mmol). The vial was evacuated and backfilled with nitrogen. Then the solvent (DCM, 0.25 mL) was added via a syringe, followed by 2-methylbut-2-ene (265 μL, 2.5 mmol). The reaction mixture was then stirred for 1 h under fluorescent light. The reaction was diluted with EtOAc (2 mL) and quenched with saturated $Na_2S_2O_3$ (2 mL). Organic layer was separated, aqueous layer was extracted with EtOAc (2×2 mL). Combined organic layer was concentrated under reduced pressure to give the crude product. After purification by column chromatography SiO_2 (3%-10% EtOAc/hexanes), the bromo-intermediate was isolated as a viscous colorless liquid (121 mg, 65% yield).

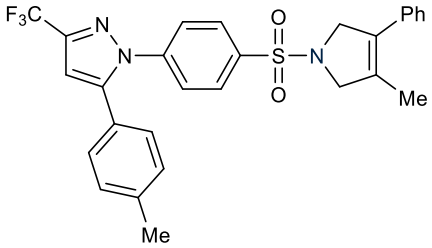
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, J = 8.3 Hz, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 5.04 (s, 1 H), 4.94 (s, 1 H), 3.97 (d, J = 6.8 Hz, 1 H), 3.81 (d, J = 16.6 Hz, 1 H), 3.57 (d, J = 16.6 Hz, 1 H), 2.45 (s, 3 H), 1.91 (s, 3 H), 1.83 (s, 3 H), 1.80 (s, 3 H), 1.02 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 136.2, 129.6, 127.4, 116.7, 69.8, 62.9, 33.5, 30.4, 22.8, 21.5, 19.8, 12.6; IR (neat): 2875, 1343, 1159, 1070, 755, 657, 583, 552, 540 cm^{-1}. . HRMS (ESI) m/z calcd for $C_{16}H_{25}BrNO_2S$ [$(M+H)^+$] 374.0784, found 374.0789.



2,3,3,5-tetramethyl-1-tosyl-1,2,3,4-tetrahydropyridine (39): To an 8 mL vial equipped with a stir bar was added bromo-intermediate (44.8 mg, 0.12 mmol) and vial was evacuated and

backfilled with nitrogen followed by $Zn(OTf)_2$ (13 mg, 0.04 mmol) was added. Then the solvent ($MeNO_2$, 0.25 mL) was added via a syringe. The reaction mixture was then stirred for 16 h under room temperature. The reaction was diluted with EtOAc (2 mL) and quenched with water (2 mL). Organic layer was separated, aqueous layer was extracted with EtOAc (2×2 mL). Combined organic layer was concentrated under reduced pressure to give the crude product. After purification by column chromatography SiO_2 (3%-10% EtOAc/hexanes), the title compound was isolated as a viscous colorless liquid (7.1 mg, 20% yield).

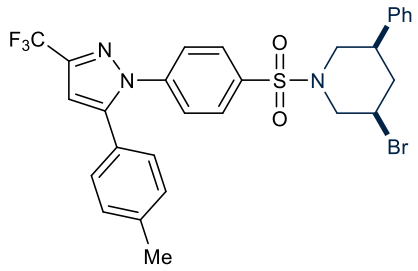
^{1}H NMR (600MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.1 Hz, 2 H), 6.37 (s, 1 H), 3.56 (q, *J* = 6.6 Hz, 1 H), 2.41 (s, 3 H), 1.86 (d, *J* = 17.6 Hz, 1 H), 1.65 (s, 3 H), 1.40 (d, *J* = 17.6 Hz, 1 H), 1.03 (d, *J* = 6.6 Hz, 3 H), 0.89 (s, 3 H), 0.42 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.1, 137.8, 129.6, 126.8, 115.9, 113.0, 57.9, 37.3, 31.9, 27.2, 27.0, 21.6, 20.8, 15.8; IR (neat): 2982, 2872, 1340, 1160, 1090, 1074, 991, 762, 662, 587, 558, 541 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{16}H_{24}NO_2S$ [$(M+H)^+$] 294.1528, found 294.1526.



1-(4-((3-methyl-4-phenyl-2,5-dihydro-1H-pyrrol-1-yl)sulfonyl)phenyl)-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazole (46): This compound was prepared according to the General Procedure A and B using *N*-allyl-4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (105 mg, 0.25 mmol) and styrene (58 µL, 0.5 mmol) with CFL. After purification by column chromatography SiO_2 (5%-15% EtOAc/hexanes), the pyrrolidine

compound was isolated as a colorless oil (127 mg, 78% yield) and the title compound was obtained as a white solid (98 mg, 75% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J = 8.8 Hz, 2 H), 7.52 (d, J = 8.8 Hz, 2 H), 7.35 (t, J = 7.6 Hz, 2 H), 7.29 (t, J = 7.4 Hz, 1 H), 7.22 - 7.13 (m, 4 H), 7.10 (d, J = 8.4 Hz, 2 H), 6.76 (s, 1 H), 4.42 (br. s., 2 H), 4.19 (br. s., 2 H), 2.38 (s, 4 H), 1.79 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 144.1 ($J_{C\text{-}F}$ = 39.0 Hz), 142.6, 139.8, 136.4, 133.4, 129.9, 129.7, 128.8, 128.6, 128.5, 128.4, 127.7, 127.4, 125.7, 121.0 ($J_{C\text{-}F}$ = 268.5 Hz), 106.1, 59.9, 57.7, 21.3, 12.6; ^{19}F NMR (375 MHz, $CDCl_3$): δ -62.9 (m, 3F) ; IR (neat): 2924, 1733, 1596, 1494, 1455, 1402, 1346, 1158, 1092, 1042, 1012 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{25}F_3N_3O_2S$ [$(M+H)^+$] 524.1620, found 524.1616.

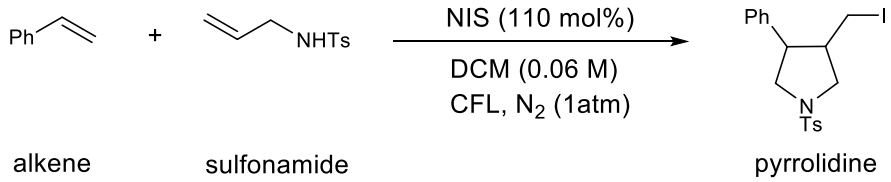


3-bromo-5-phenyl-1-((4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)phenyl) sulfonyl)piperidine (47): This compound was prepared according to the General Procedure C, using N-allyl-4-(5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (105 mg, 0.25 mmol) and Styrene (58 µL, 0.5 mmol). After purification by column chromatography SiO_2 (5%-15% EtOAc/hexanes), the title compound was isolated as a colorless oil (85 mg, 56% yield, >20:1 d.r.).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 8.5 Hz, 2 H), 7.52 (d, J = 8.5 Hz, 2 H), 7.36-7.30 (m, 2 H), 7.30-7.25 (m, 2 H), 7.18 (d, J = 7.8 Hz, 2 H), 7.15 (d, J = 7.3 Hz, 2 H), 7.11 (d, J = 8.1 Hz, 2 H), 4.25 (dd, J = 11.4, 4.0 Hz, 1 H), 4.17-4.08 (m, 1 H), 3.93 (dd, J = 12.0, 3.0 Hz, 1 H), 3.04-2.95 (m, 1 H), 2.56 (d, J = 12.9 Hz, 1 H), 2.50 (t, J = 11.5 Hz, 1 H), 2.39 (s, 3 H), 2.28 (t, J = 11.7

Hz, 1 H), 1.89 (q, J = 12.5 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.3, 144.2 ($J_{C\text{-}F}$ = 37.5 Hz), 142.9, 140.0, 139.9, 135.8, 129.8, 128.9, 128.7, 128.4, 127.6, 127.0, 125.7, 125.5, 121.0 ($J_{C\text{-}F}$ = 268.5 Hz), 106.3, 53.0, 51.6, 43.4, 43.4, 41.9, 21.3; ^{19}F NMR (375 MHz, $CDCl_3$): δ -62.8 (m, 3F); IR (neat): 2921, 1735, 1597, 1497, 1345, 1235, 1231, 1159, 1095 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{26}BrF_3N_3O_2S$ [$(M+H)^+$] 604.0881, found 604.0888.

4. Procedure for collection of NMR time studies for the pyrrolidine synthesis



To a 50 mL round bottomed flask with a stir bar was added NIS (248 mg, 1.1 mmol), *p*-toluenesulfonyl-protected allylic amine (211 mg, 1 mmol), and 1,3-dinitrobenzene (168 mg, 1 mmol) as an internal standard. The reaction was evacuated and backfill with N_2 three times. Then DCM (16 mL) was added via syringe, followed by Styrene (232 μL, 2.0 mmol). The reaction was then stirred under fluorescent light. At each time point, 50 μL reaction solution was taken with syringe, diluted with EtOAc (1 mL), washed with aqueous $Na_2S_2O_3$ solution (20%, 0.5 mL). The organic layer was concentrated under reduced pressure. The yield of pyrrolidine at each time point was determined by crude NMR and plot against time. See the collected data in **Table S1** and the plot in **Figure S1**.

Time	Intermediate (%)	Product (%)
15	23	0
30	59	6
45	65	8
60	65	16

75	65	19
105	62	25
135	59	30
165	54	32
225	45	42
285	42	46
345	39	49
405	37	54

Table S1. Time study of the pyrrolidine synthesis reaction

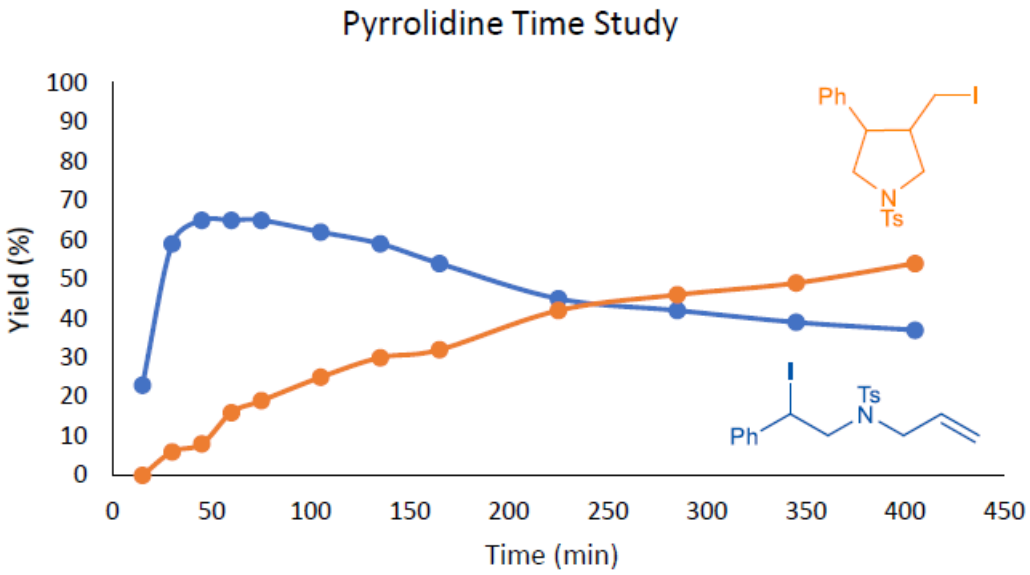


Figure S1. Plot of time study for pyrrolidine synthesis

5. Procedure for Collection of ^{15}N NMR Study

In an NMR sample tube covered with an aluminum foil, *N*-allyl-4-methylbenzenesulfonamide (211 mg, 1 mmol) and NIS (225 mg 1 mmol) were dissolved in MeCN-D. ^{15}N NMR data acquisition was performed overnight. The same procedure was followed to obtain the ^{15}N NMR data with 50%, 25% and 0% NIS loading. NMR spectra were overlayed using ACDLABS NMR processing software **Figure S1** and **Figure S2**.

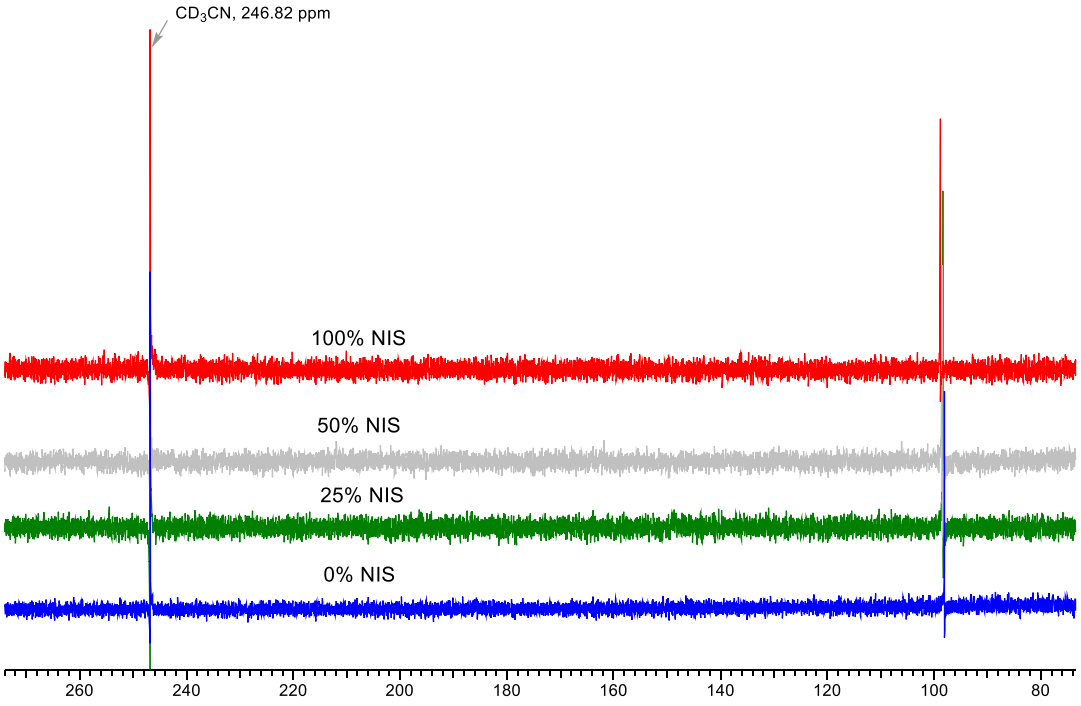


Figure S1. ^{15}N NMR study of allylic sulfonamide and NIS

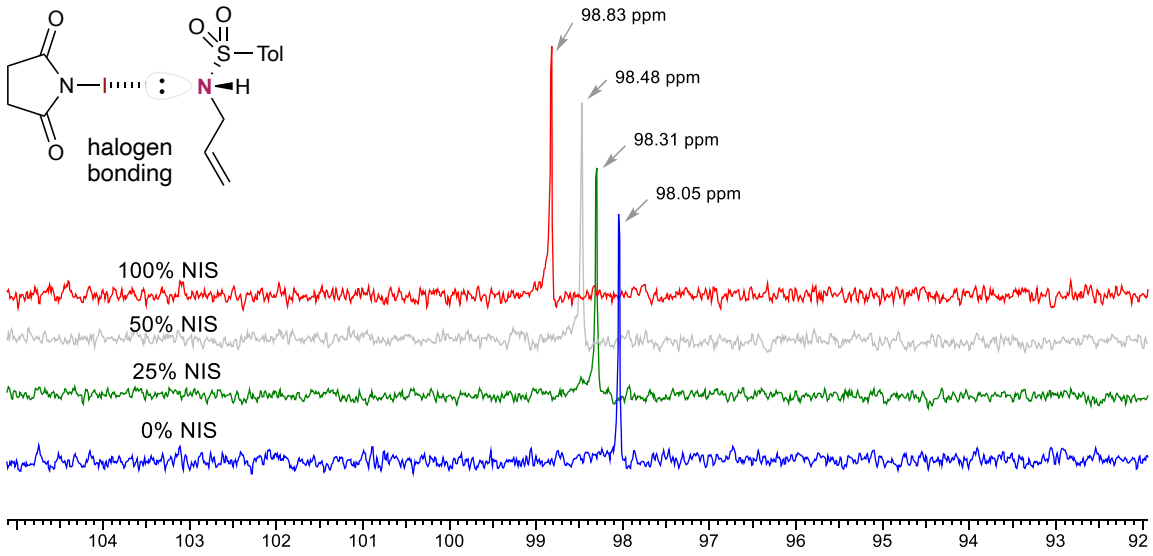


Figure S2. Expanded figure for the ^{15}N NMR study of allylic sulfonamide and NIS

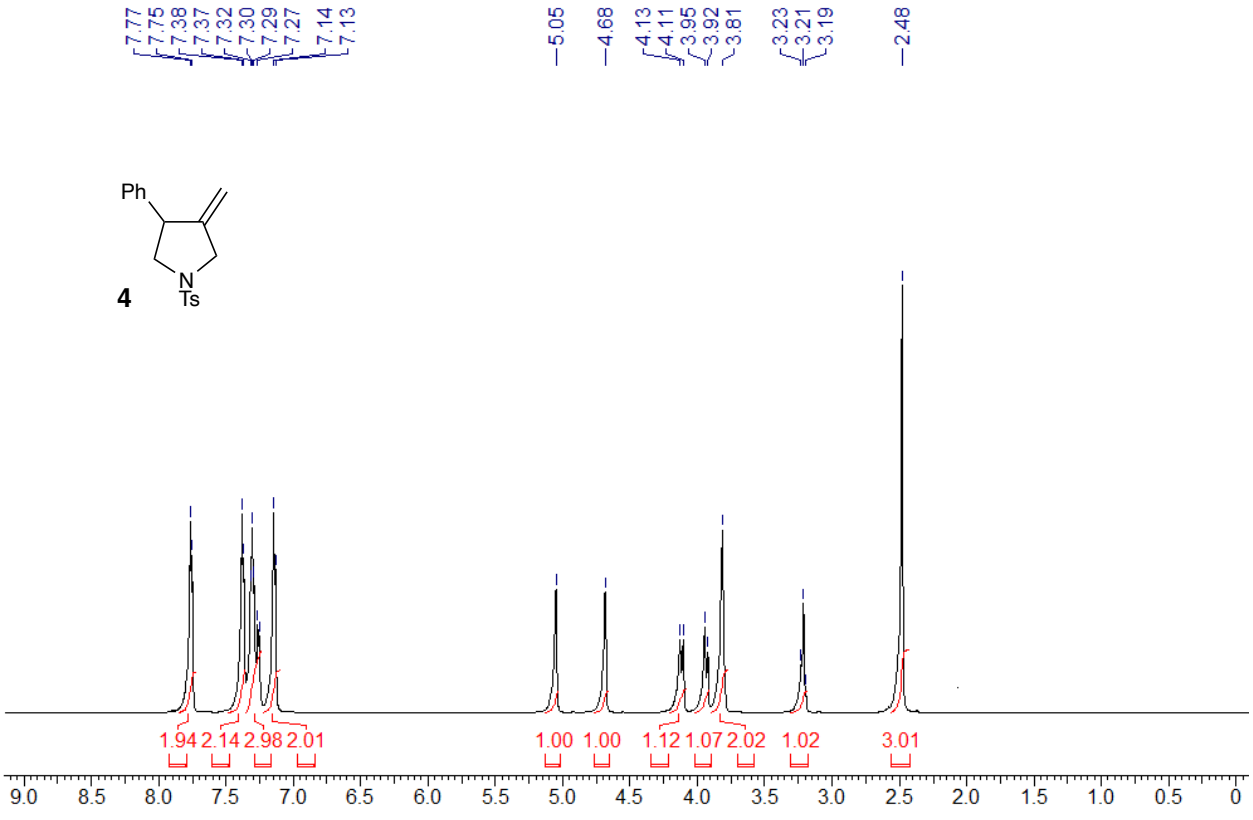
References

1) Similar chloro-pyrrolidines can be found in: T. Tsuritani, H. Shinokubo, K. Oshima, *Org. Lett.* 2001, **3**, 2709-2711.

2) L. N. S. Crespin, A. Greb, D. C. Blakemore, S. V. Ley, *J. Org. Chem.* 2017, **82**, 13093-13108.

3) S. Engl, O. Reiser, *Org. Lett.* 2021, **23**, 5581-5586.

4) S. Nocquet-Thibault, P. Retaileau, K. Cariou, R. H. Dodd, *Org. Lett*. 2013, **15**, 1842-1845.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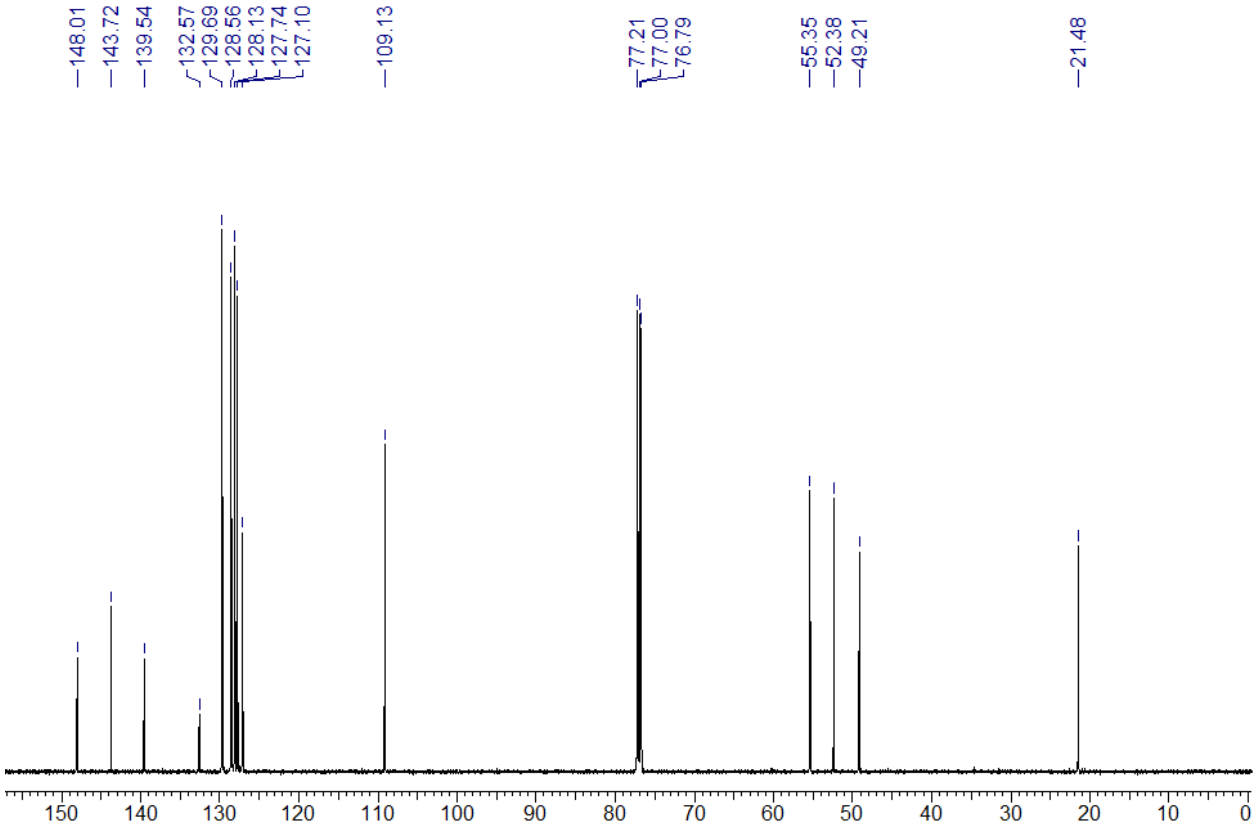
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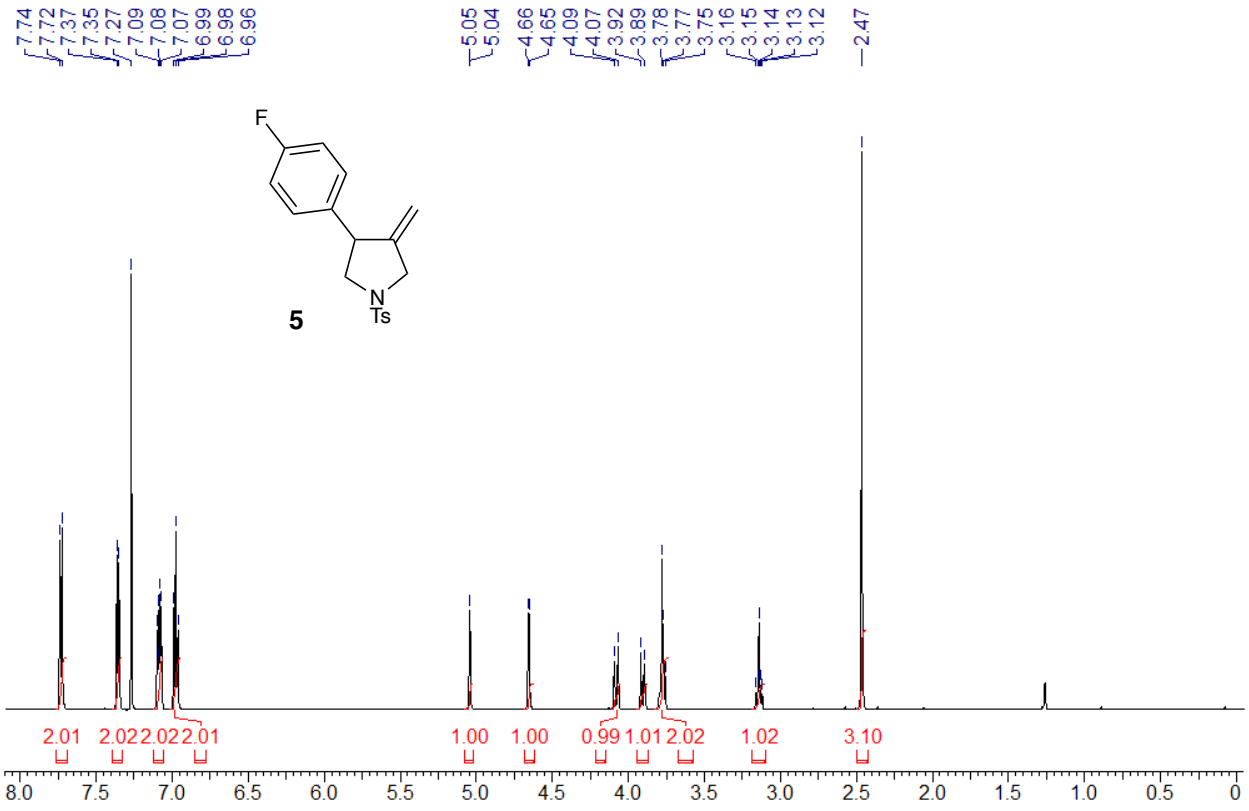
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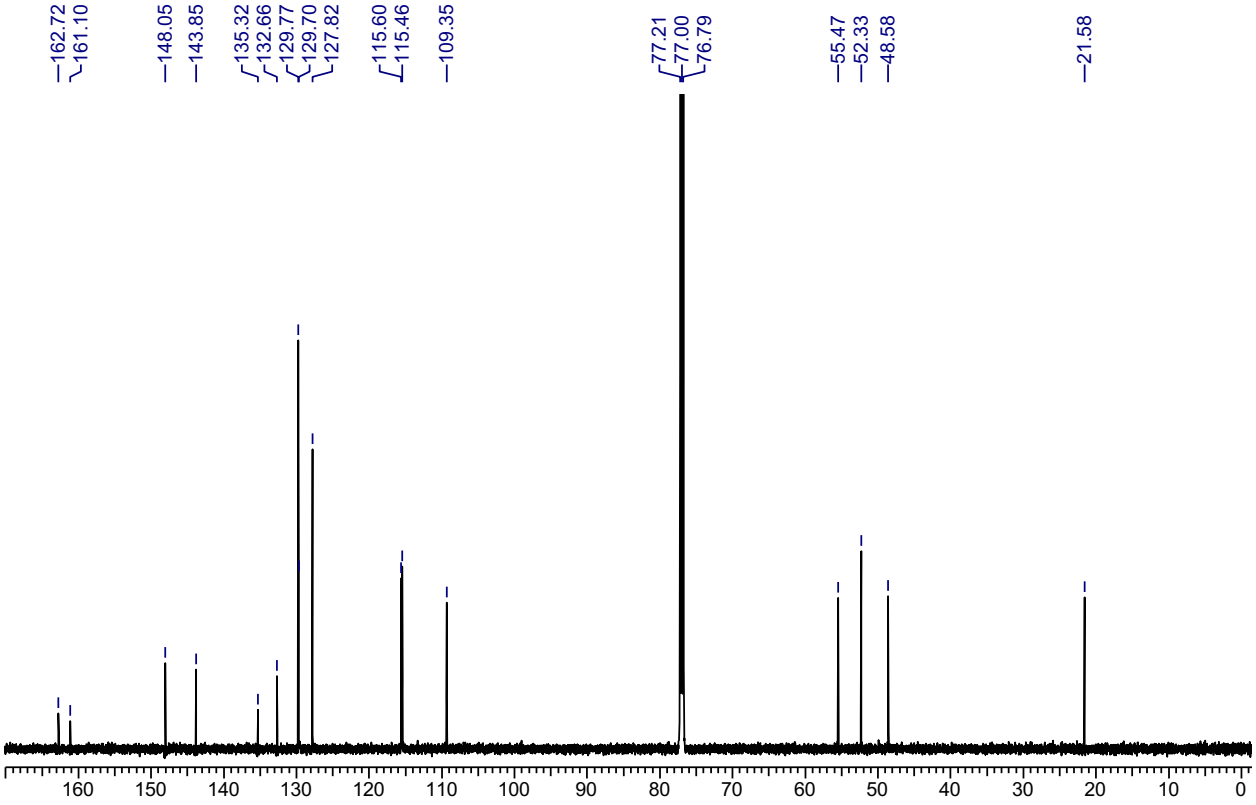
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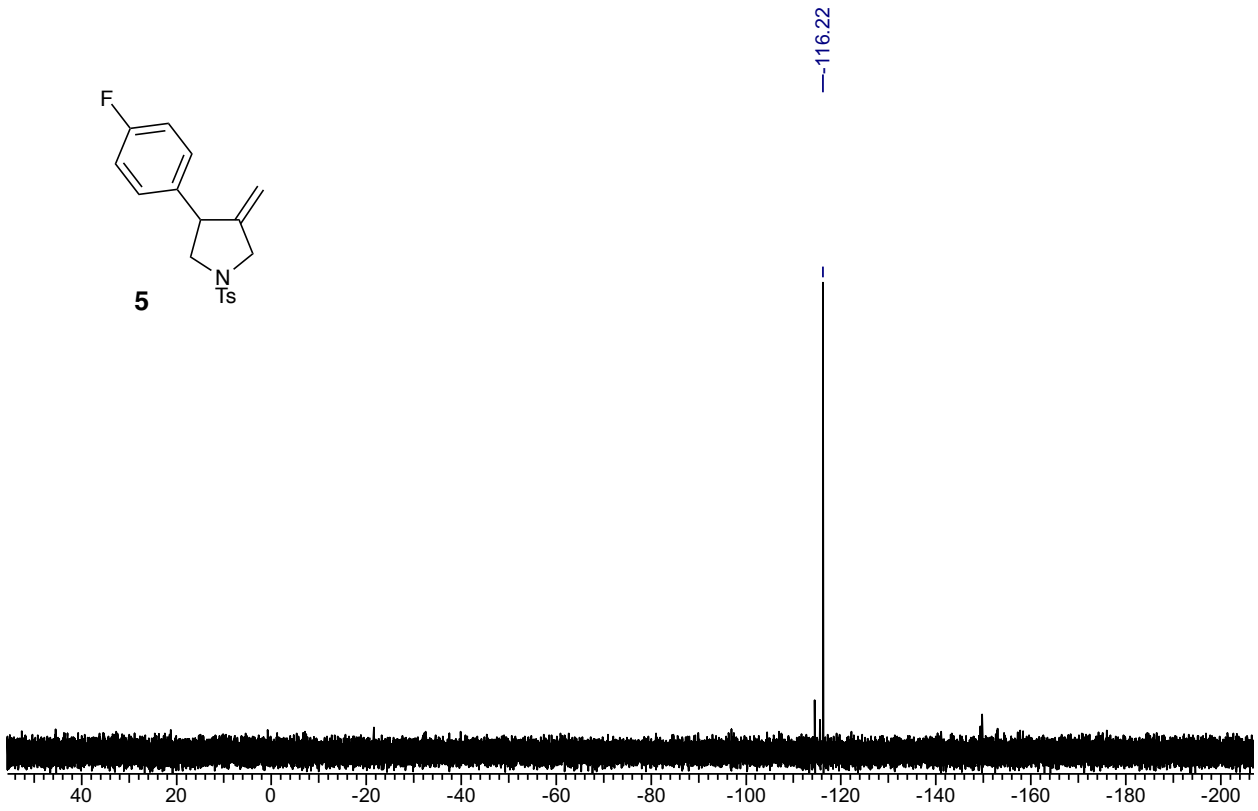
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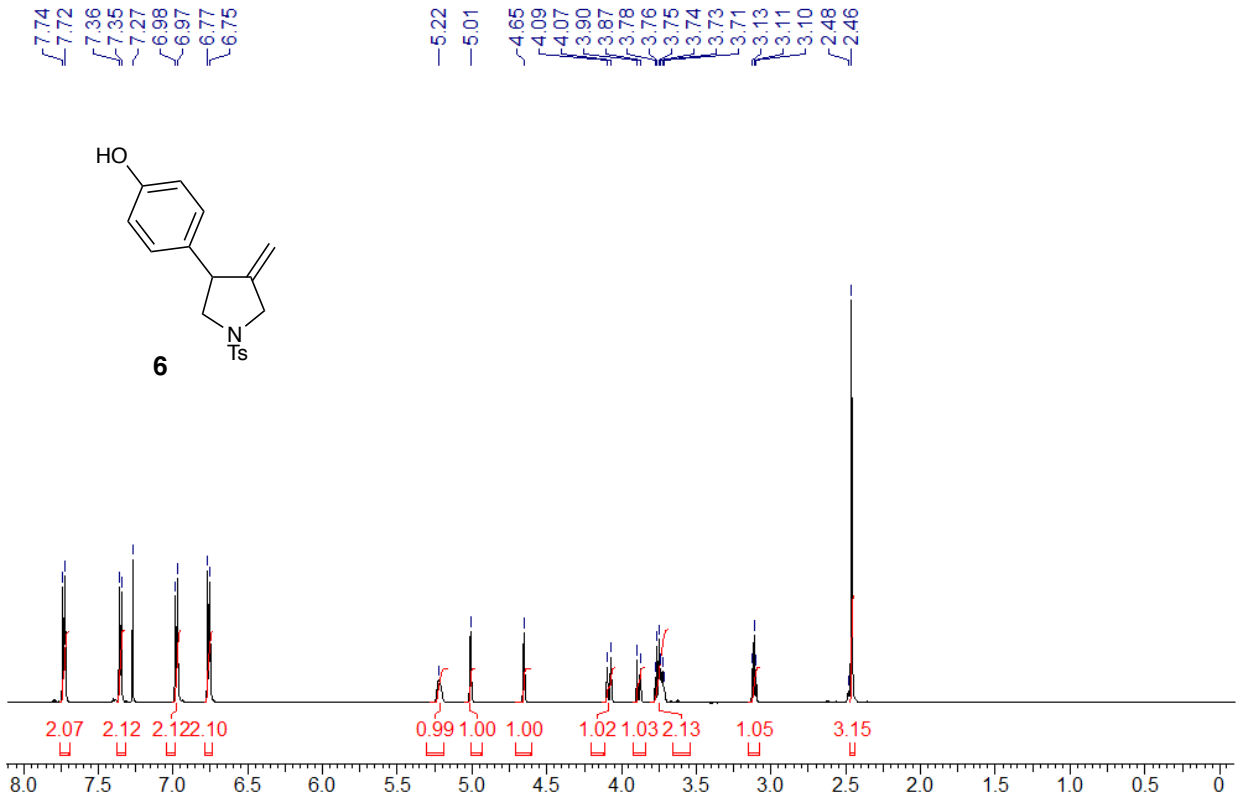
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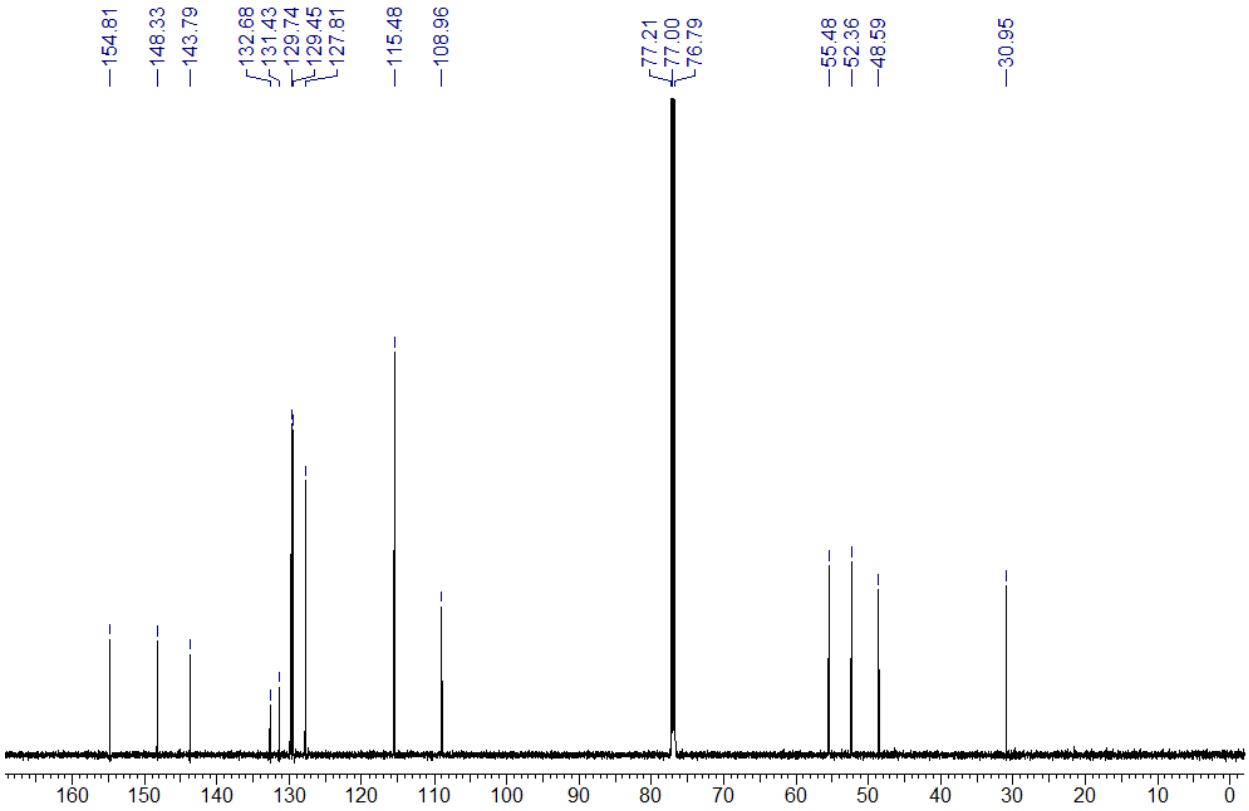
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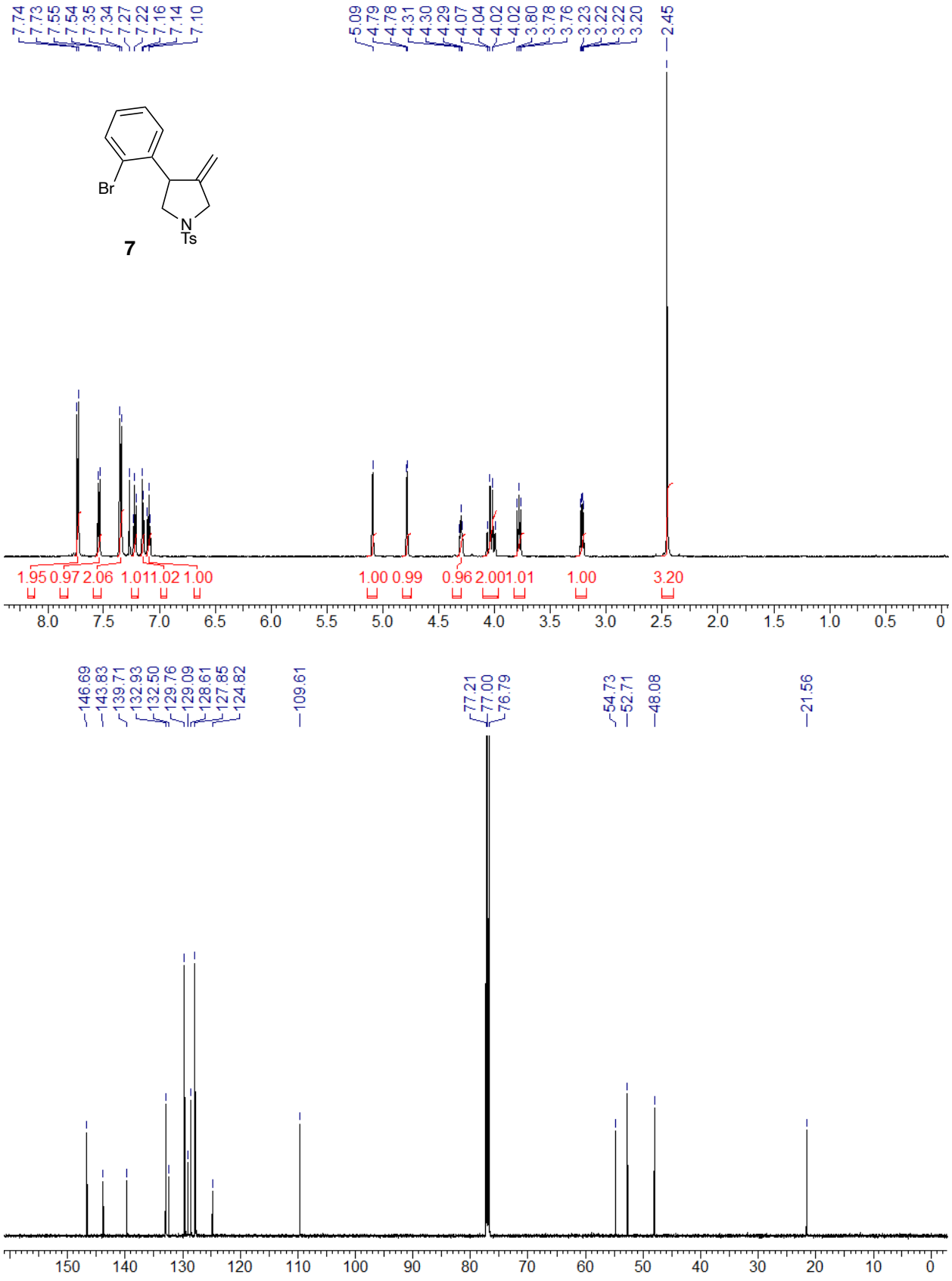
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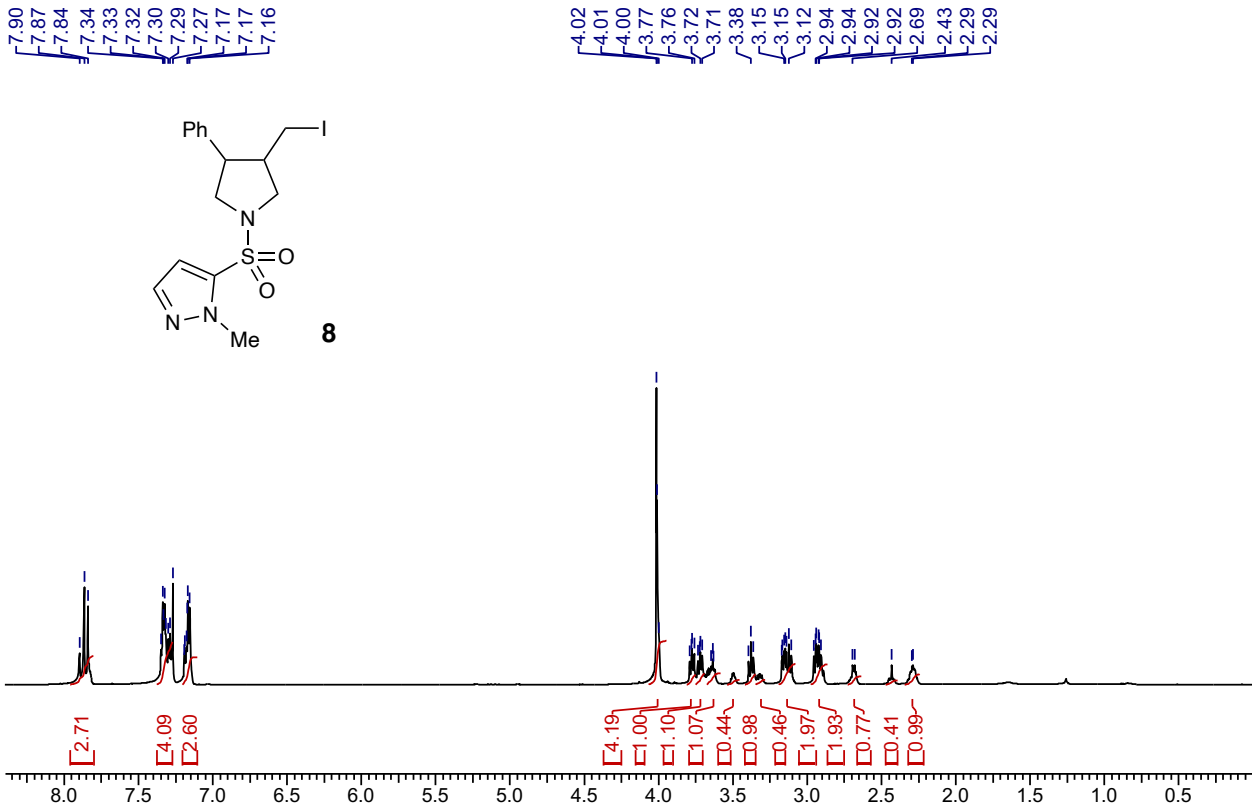
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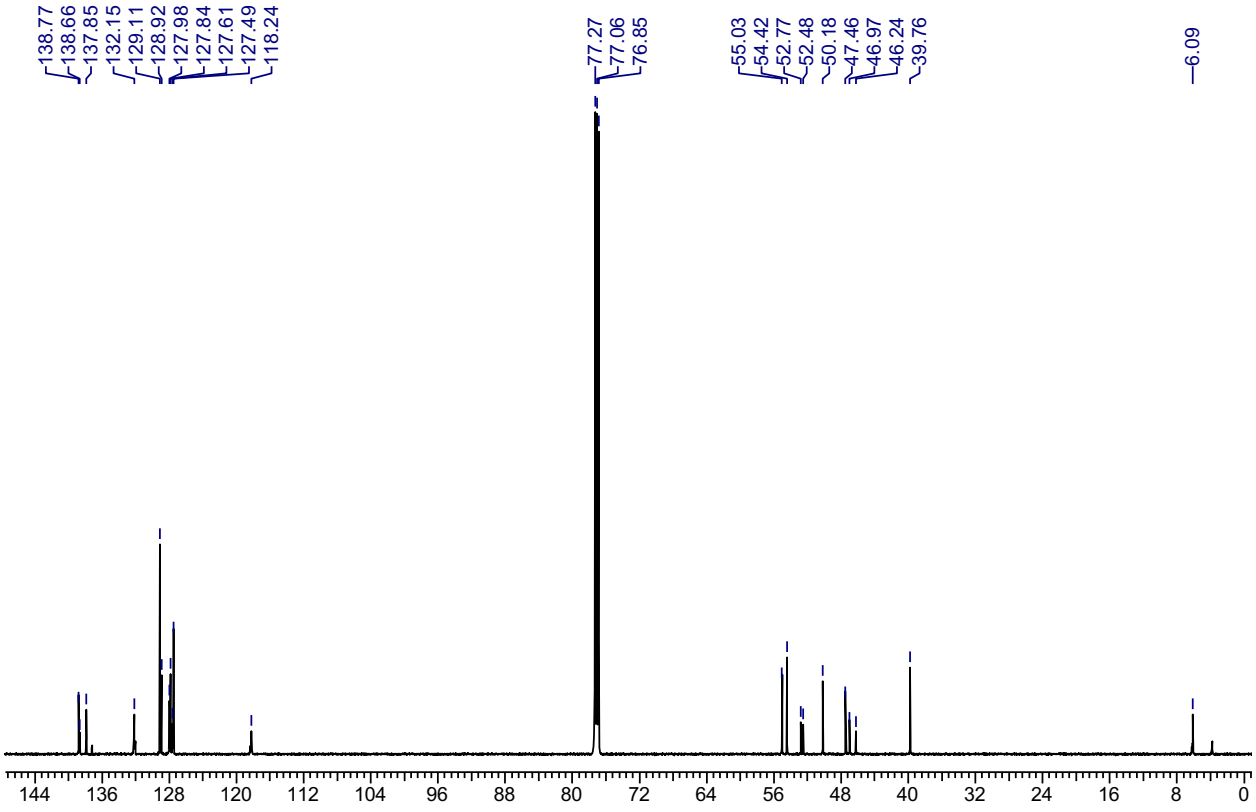
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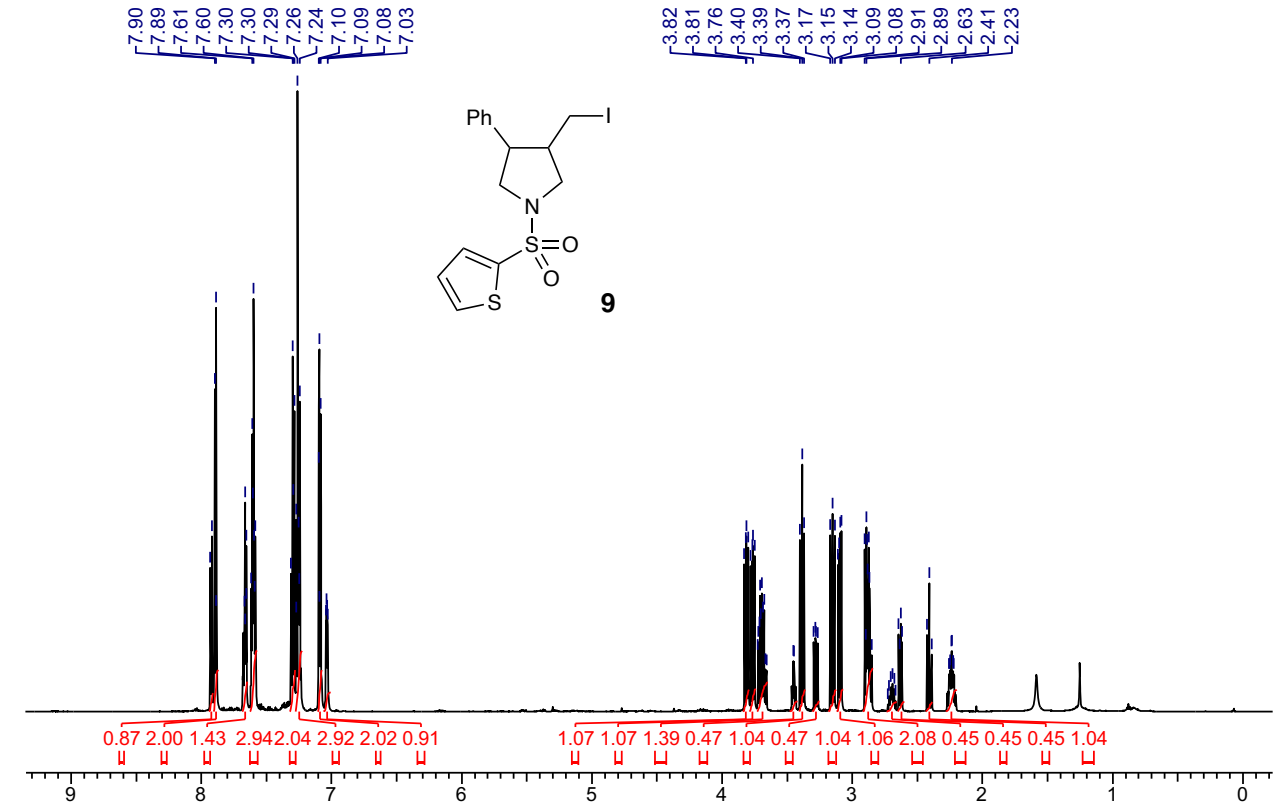
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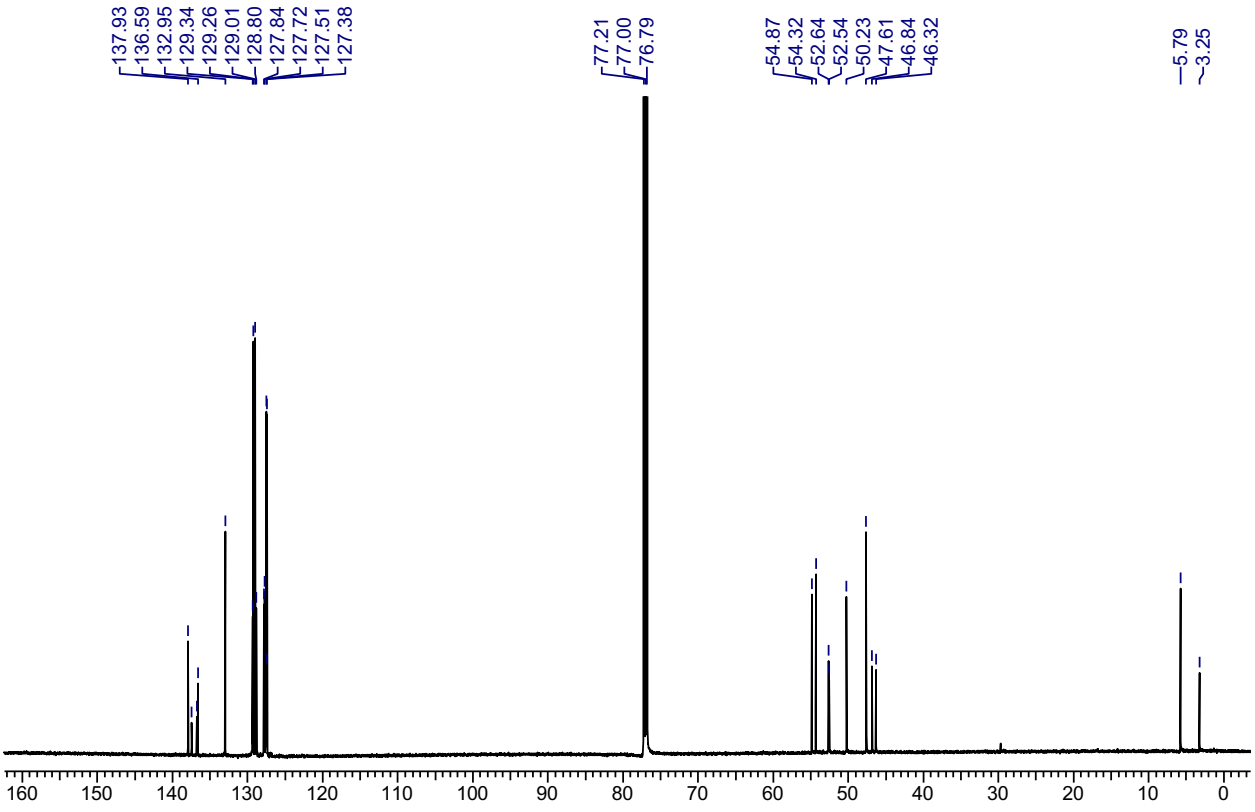
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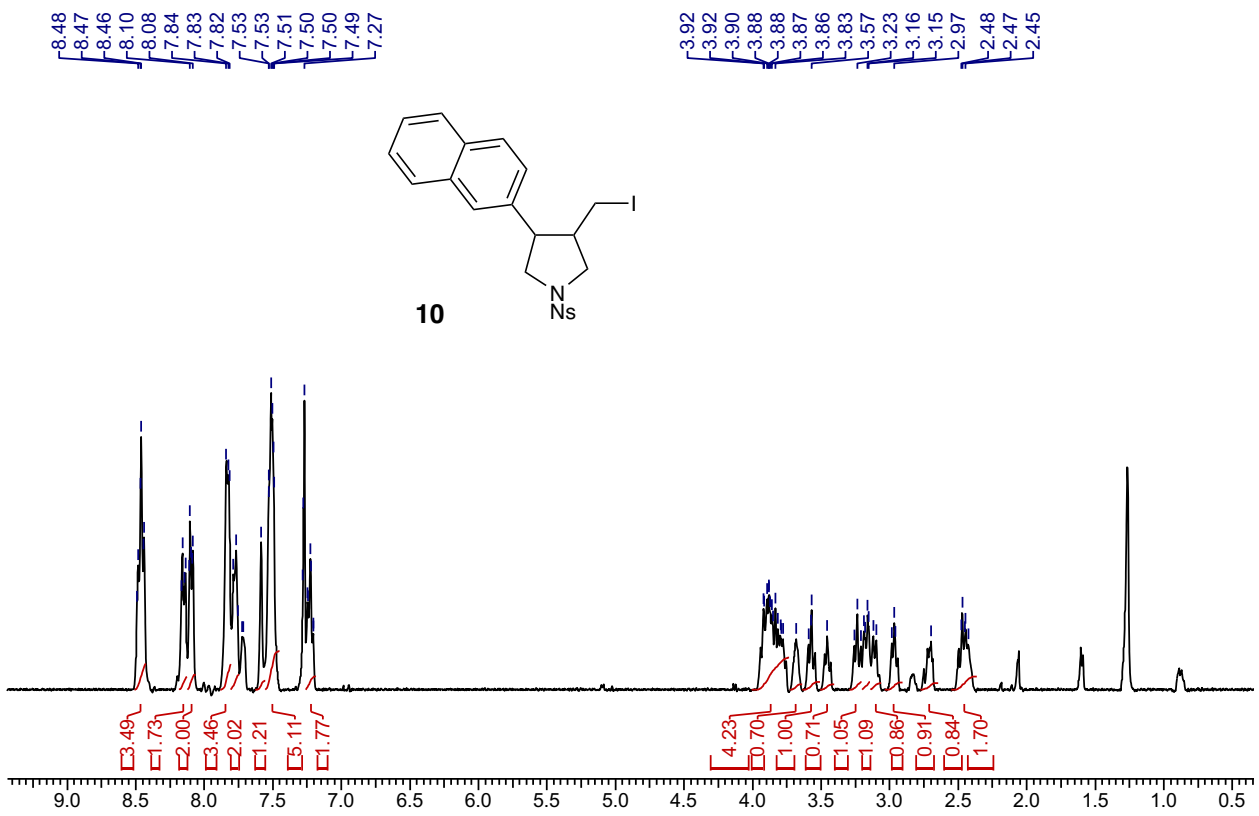
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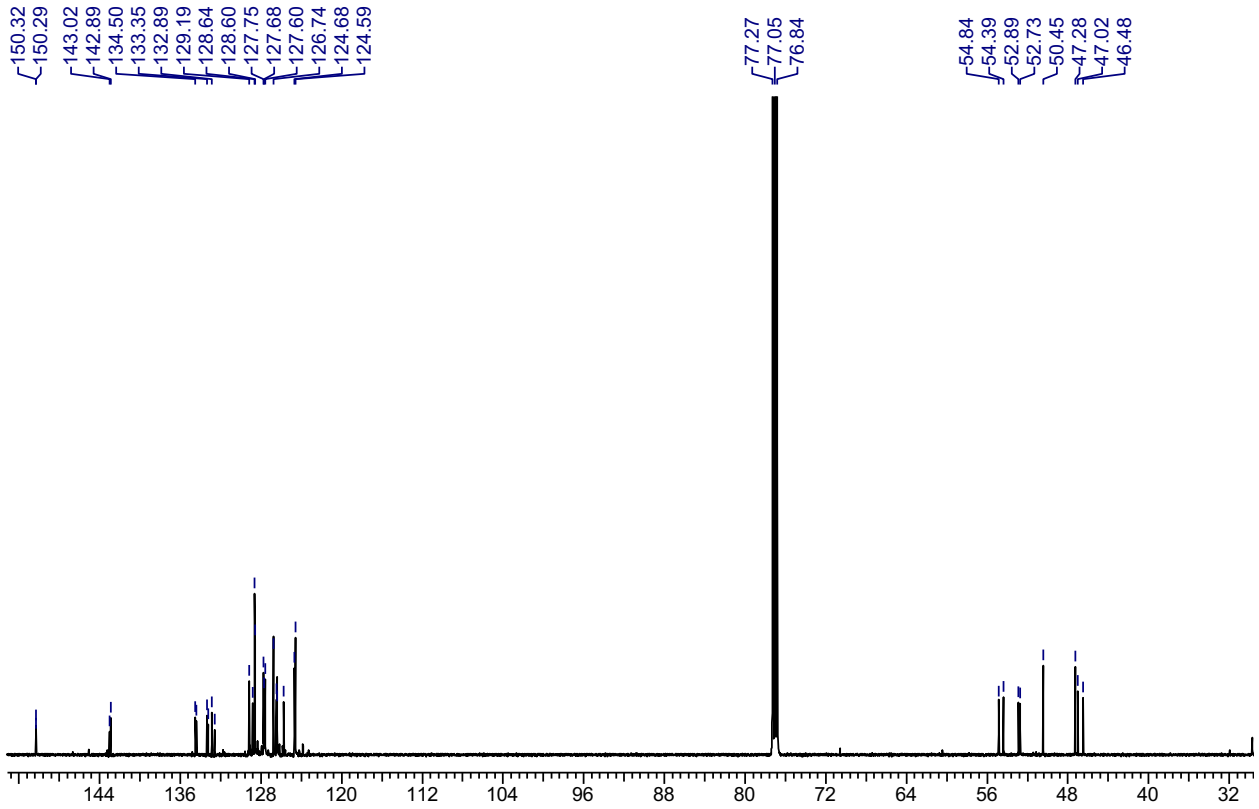
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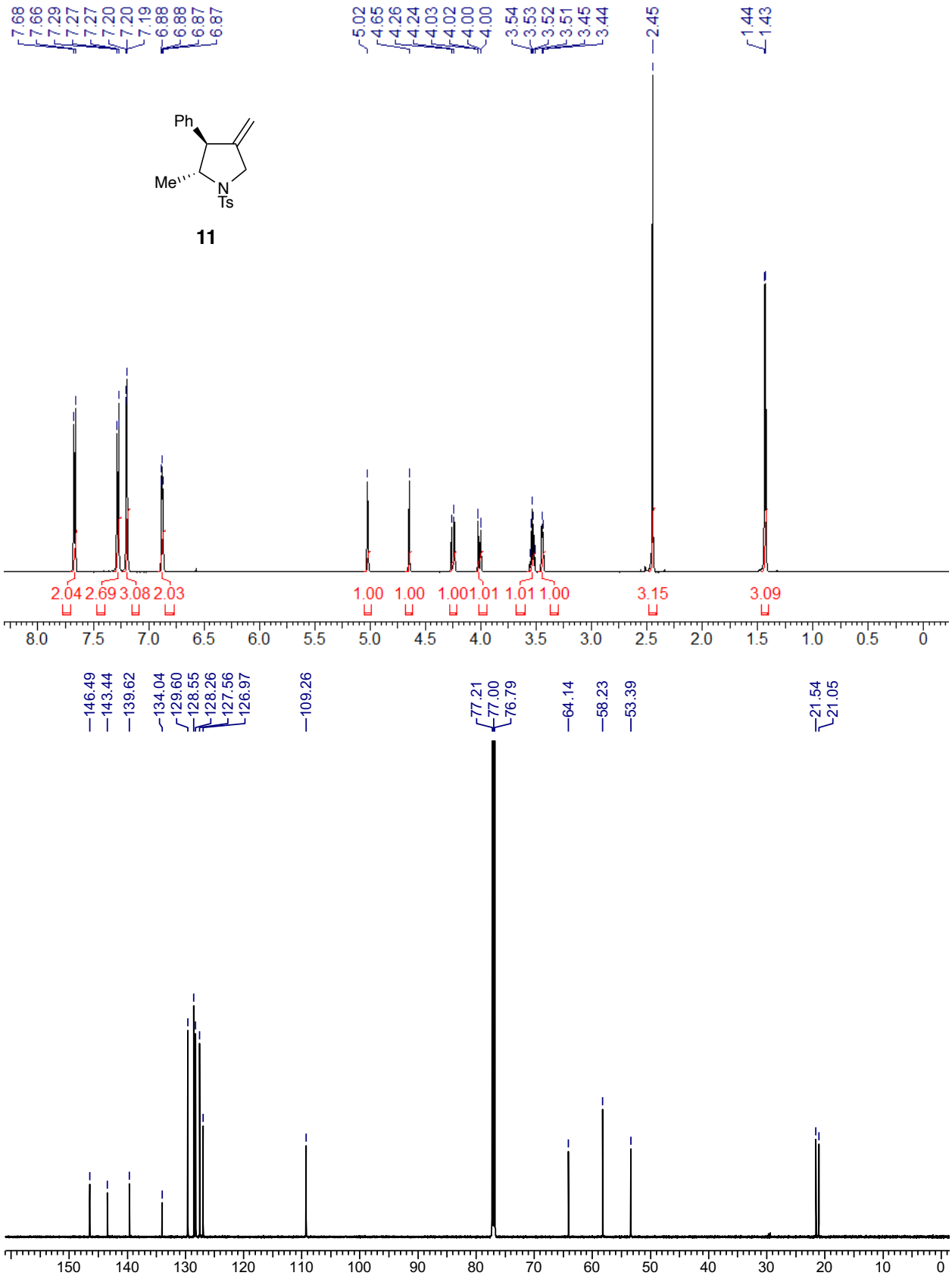
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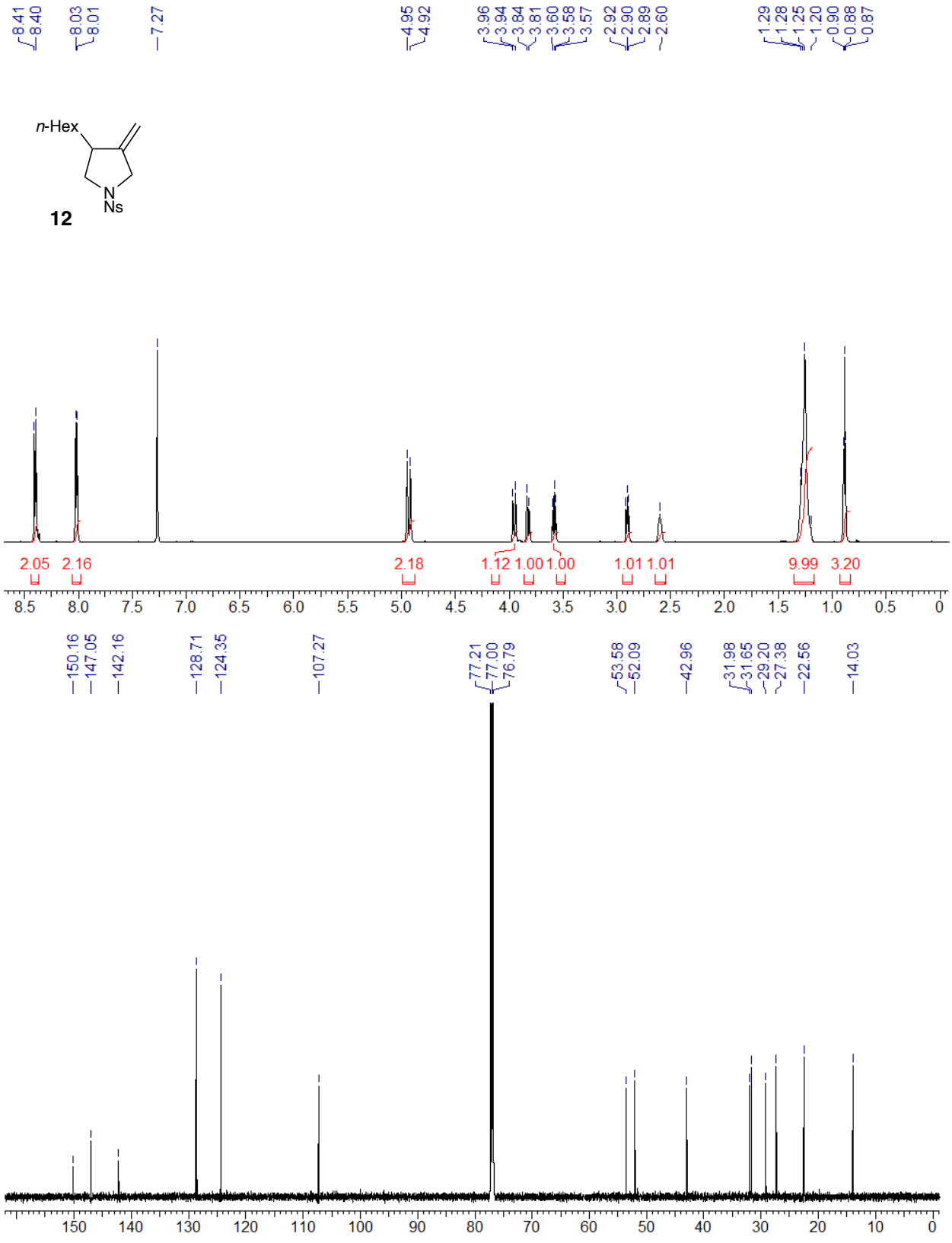
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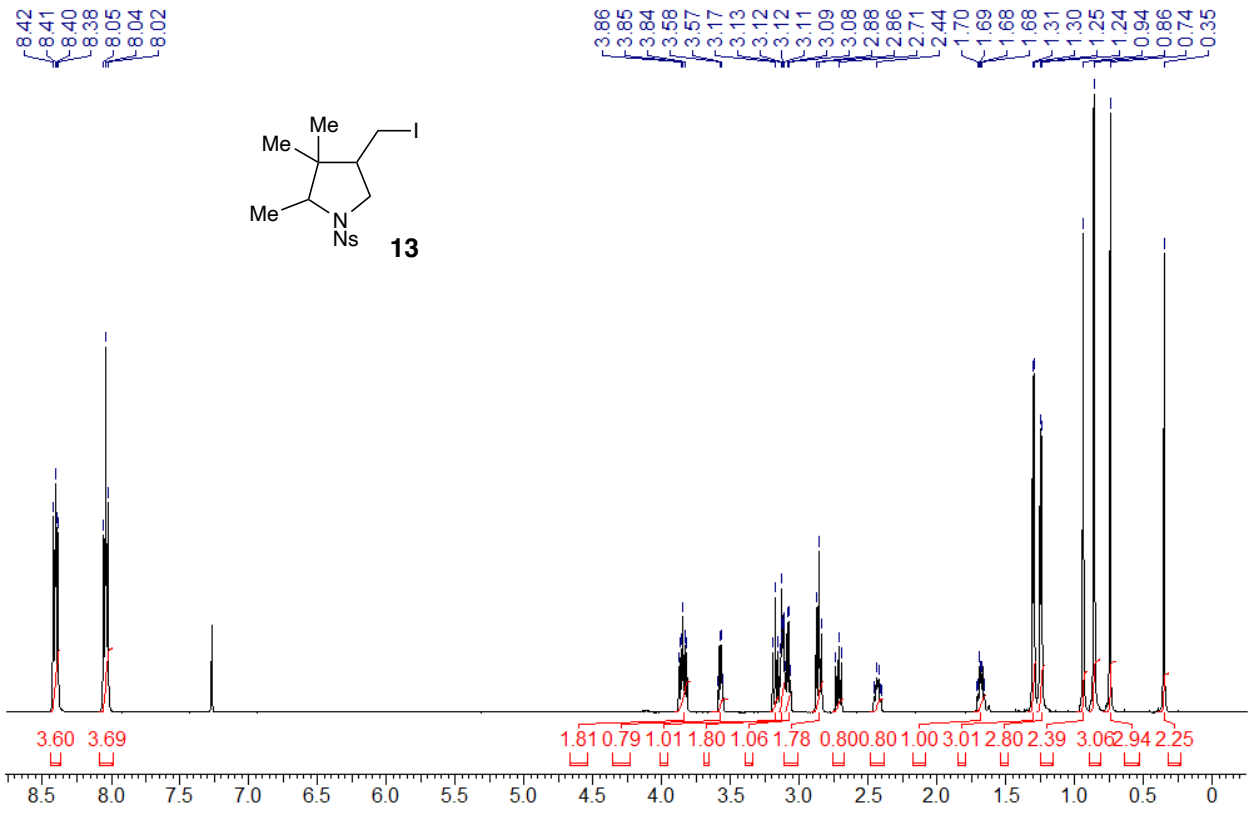
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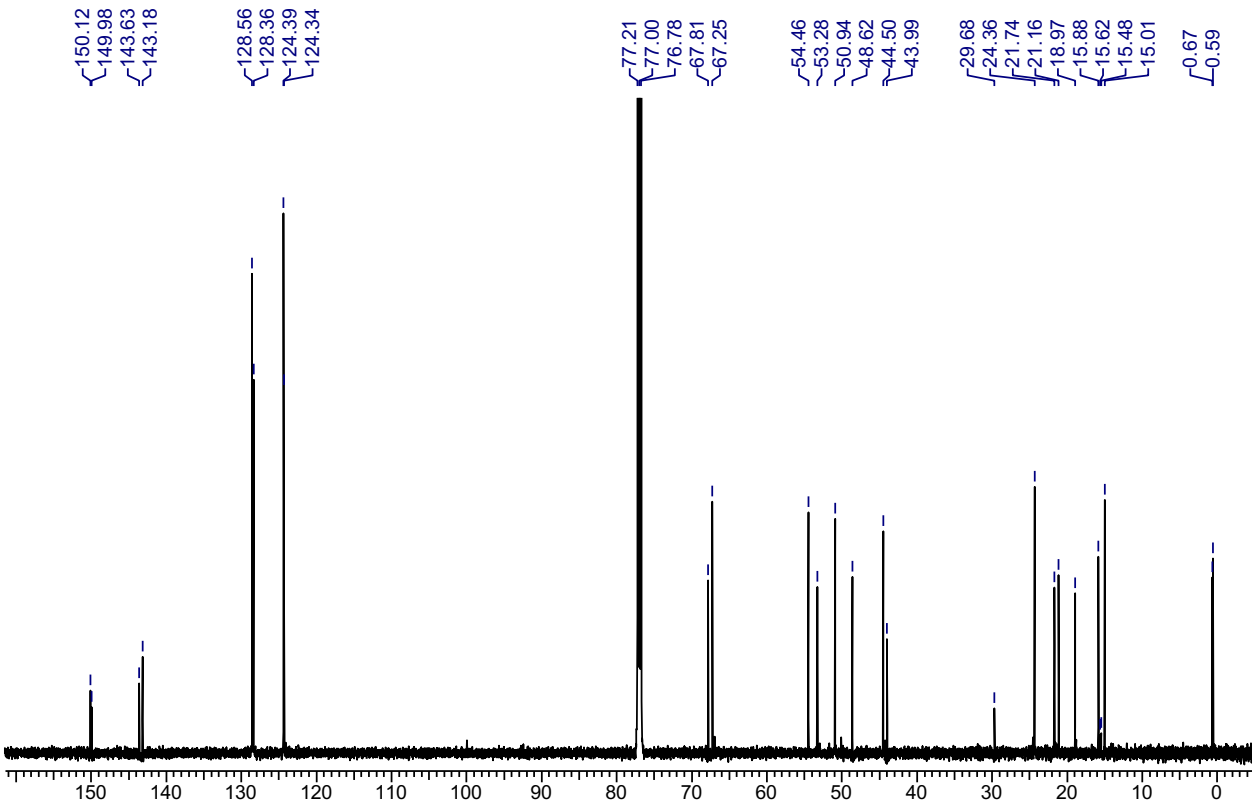
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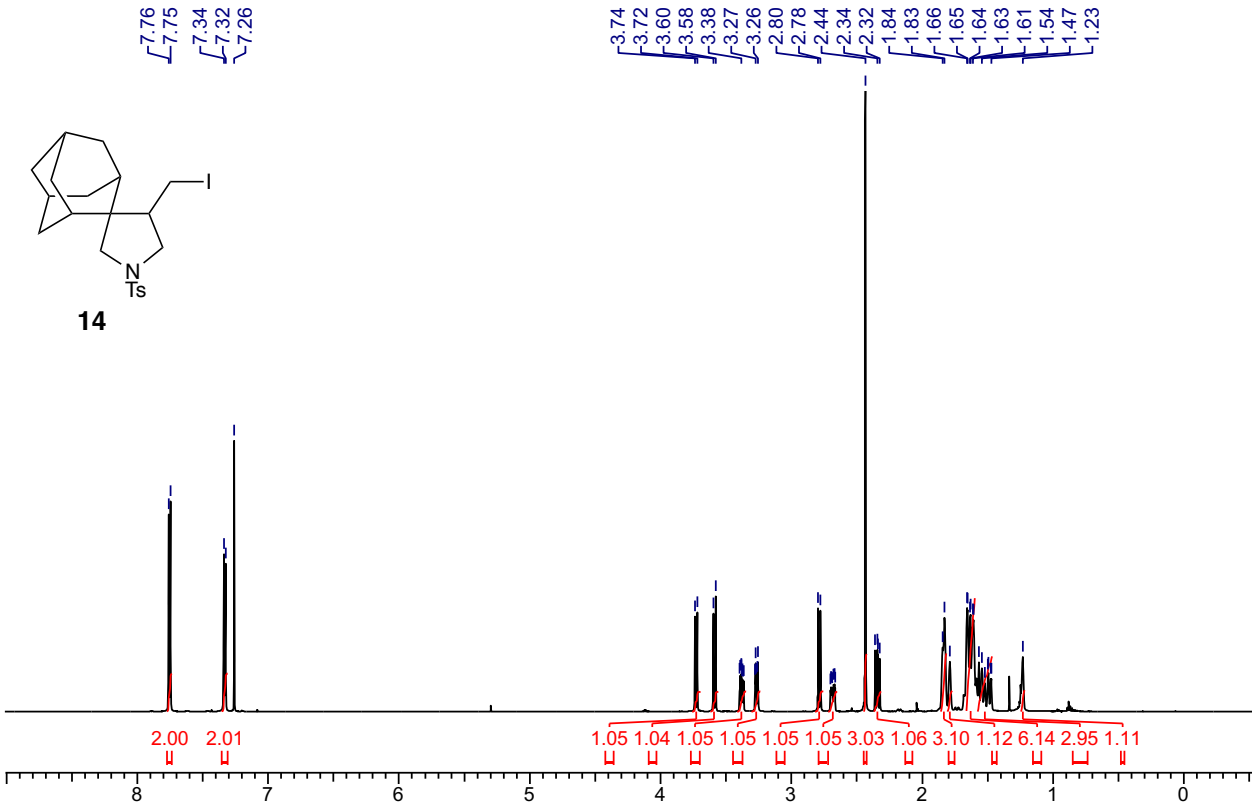
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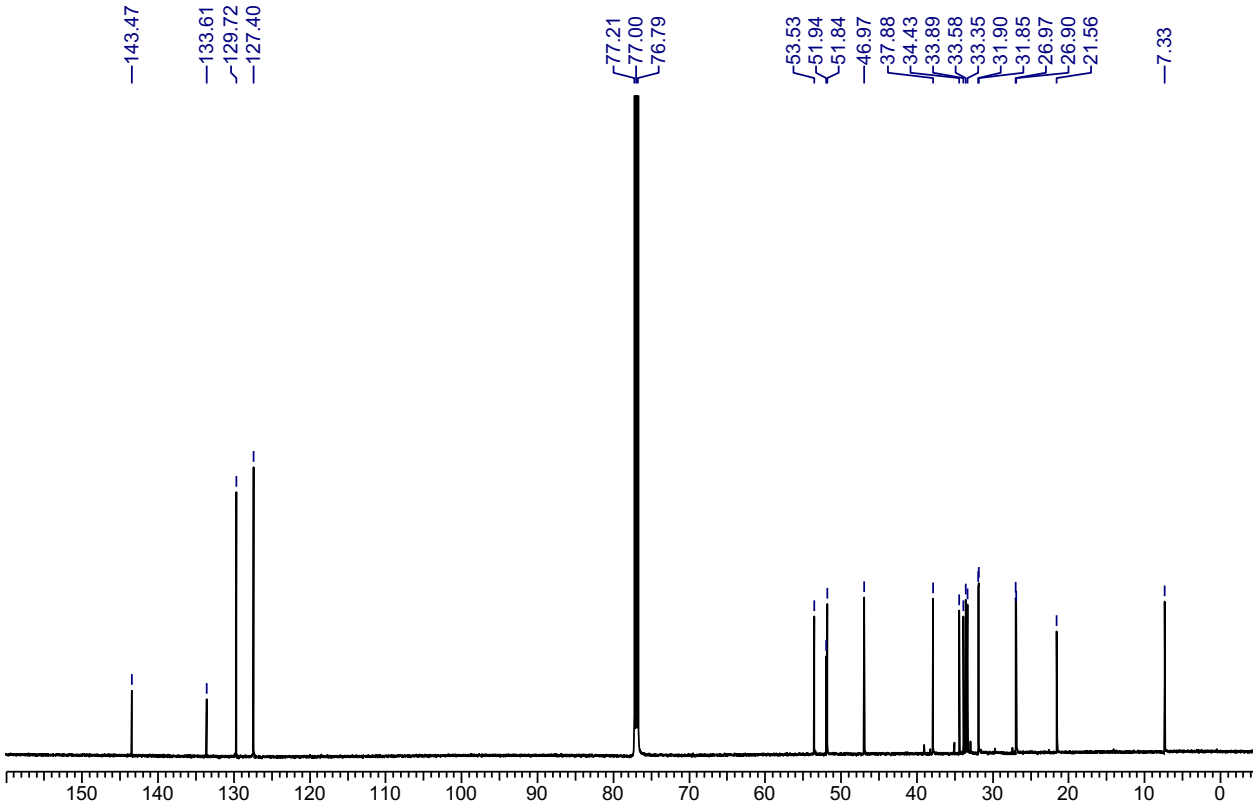
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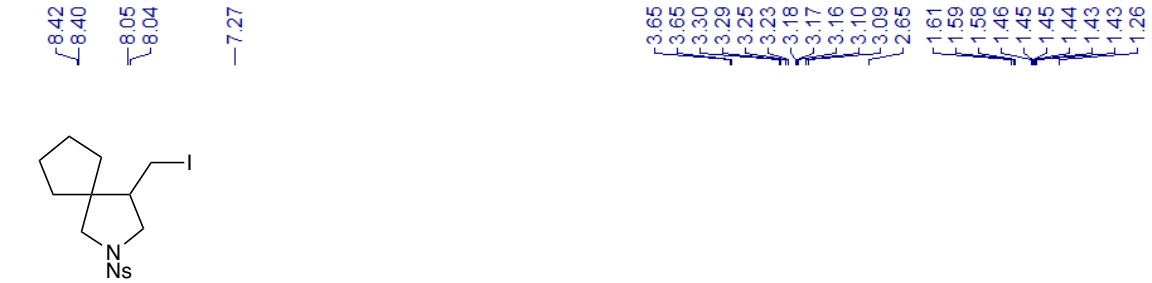
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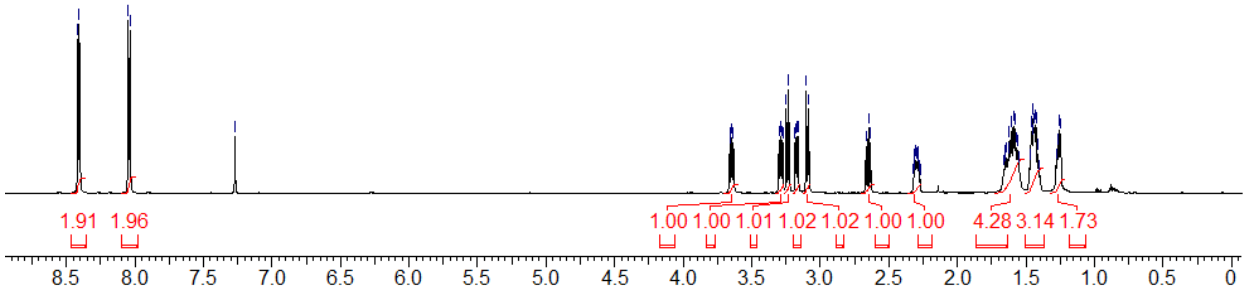
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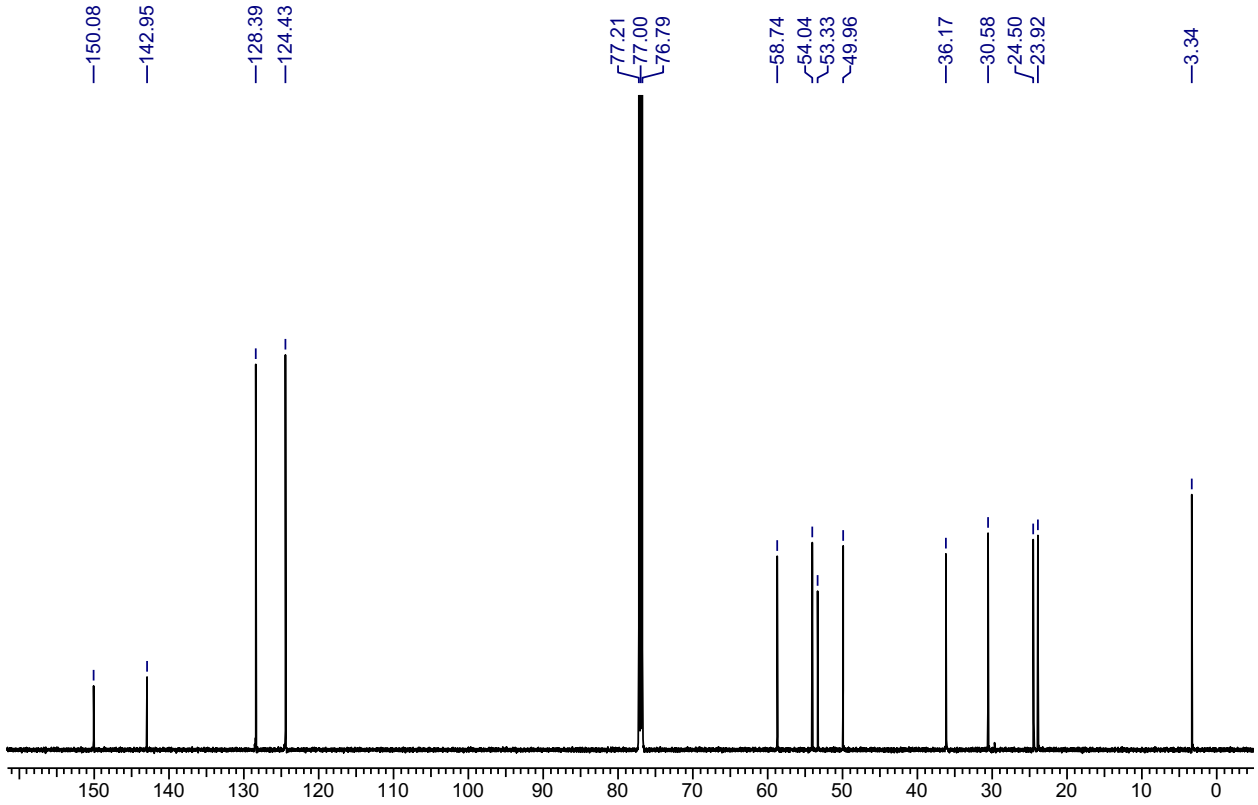
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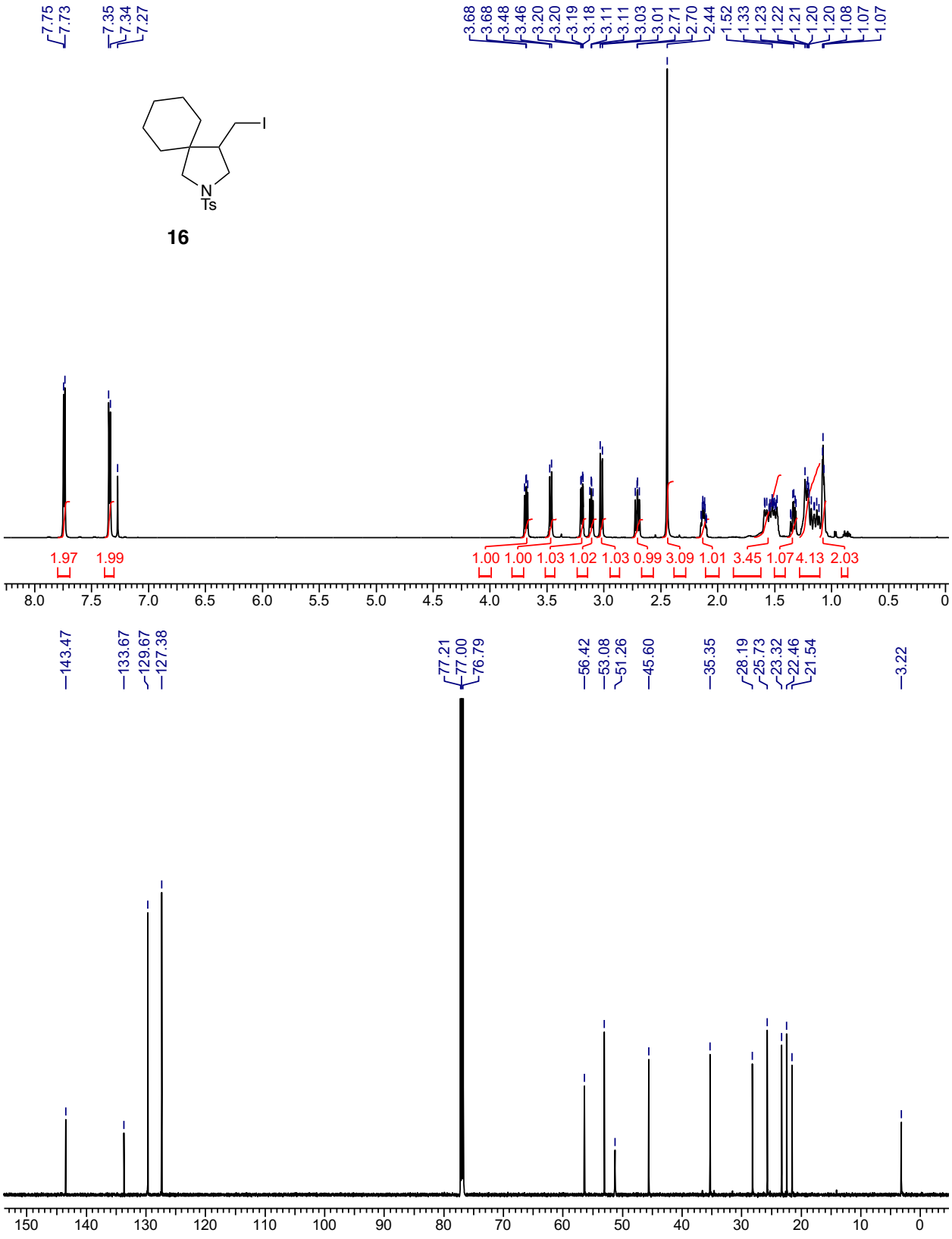
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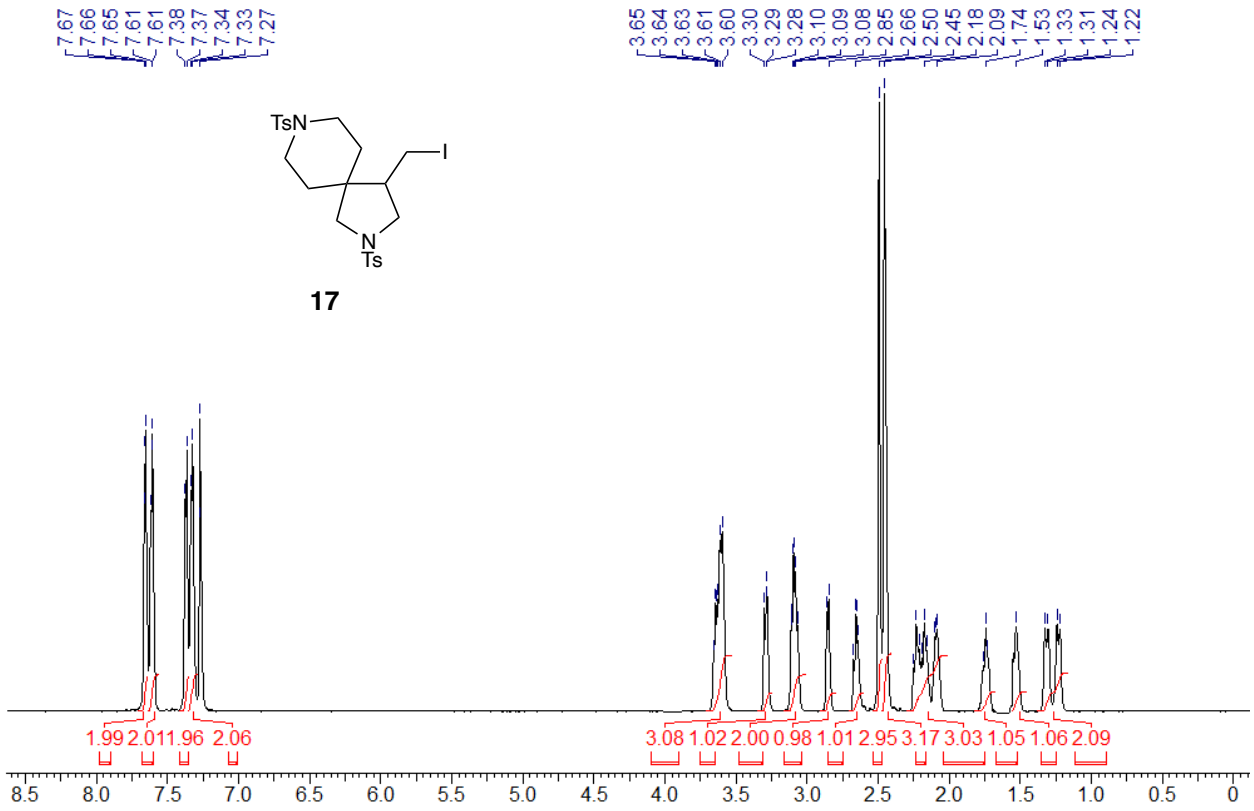
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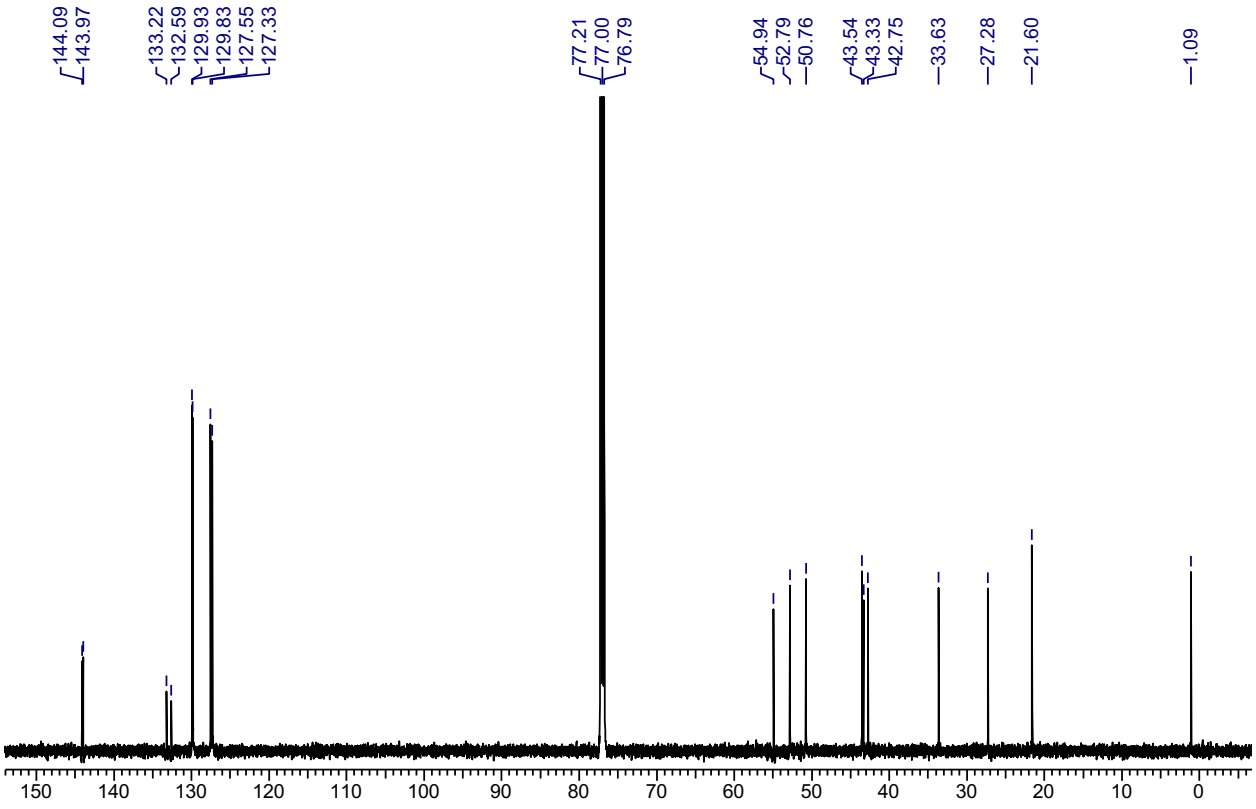
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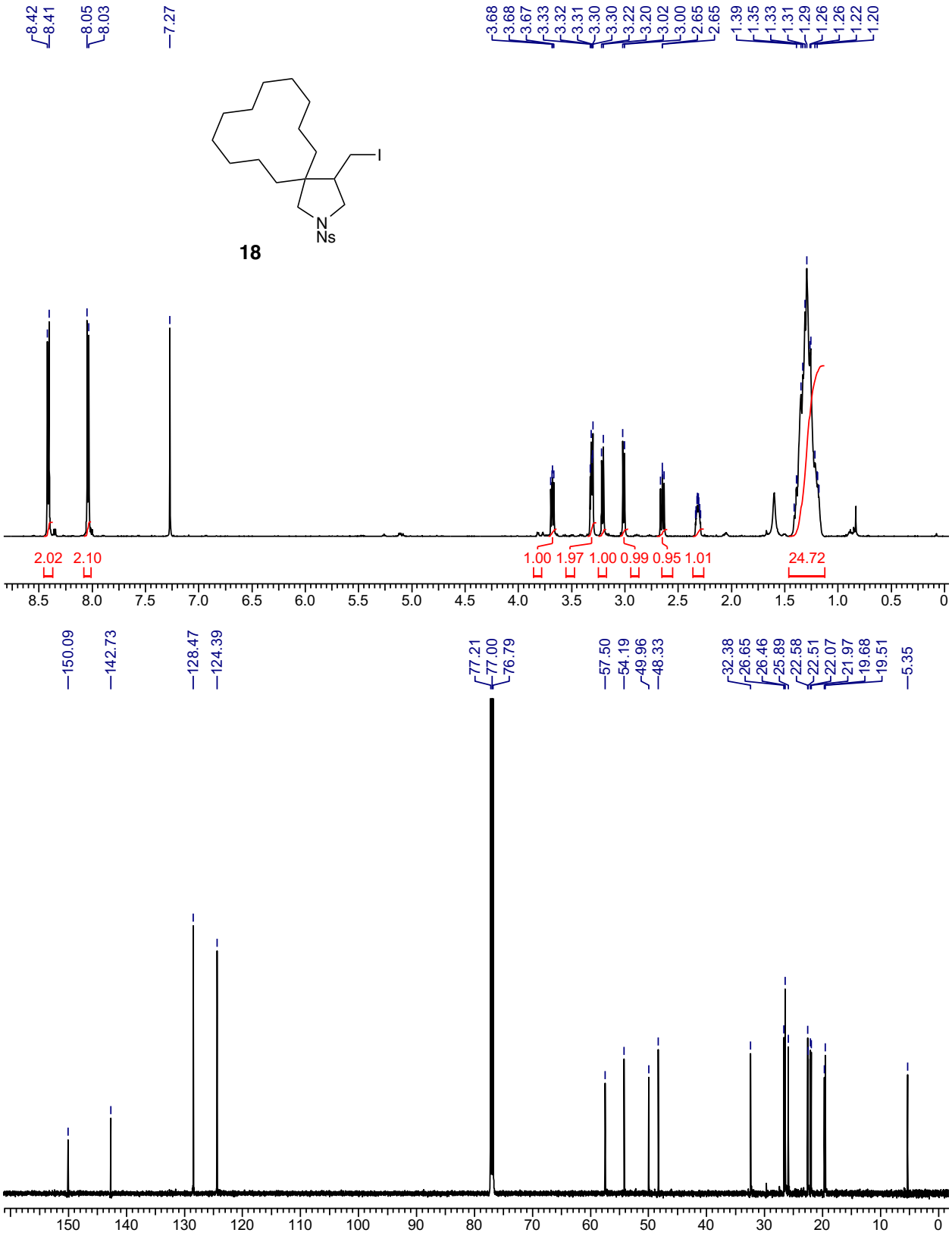
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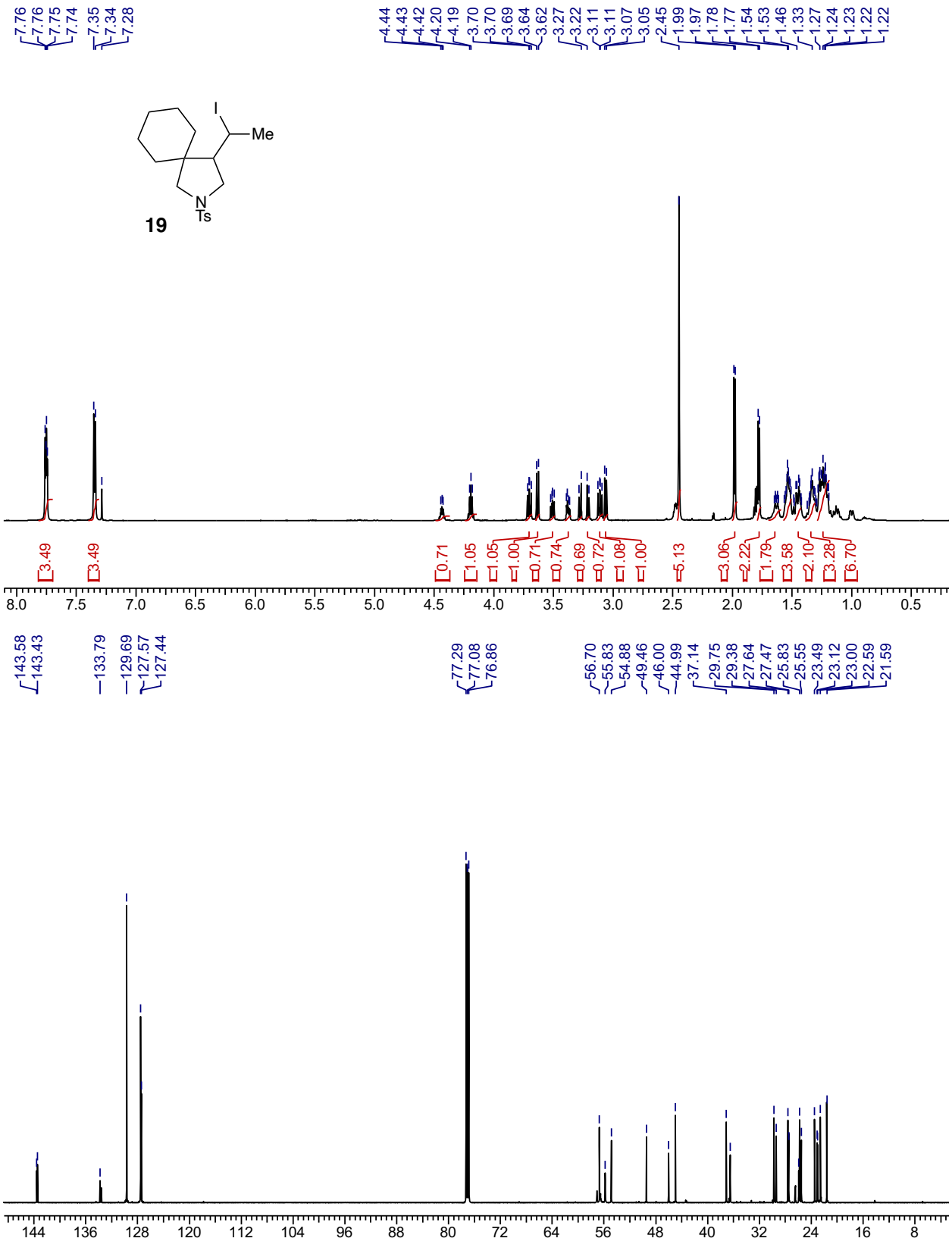
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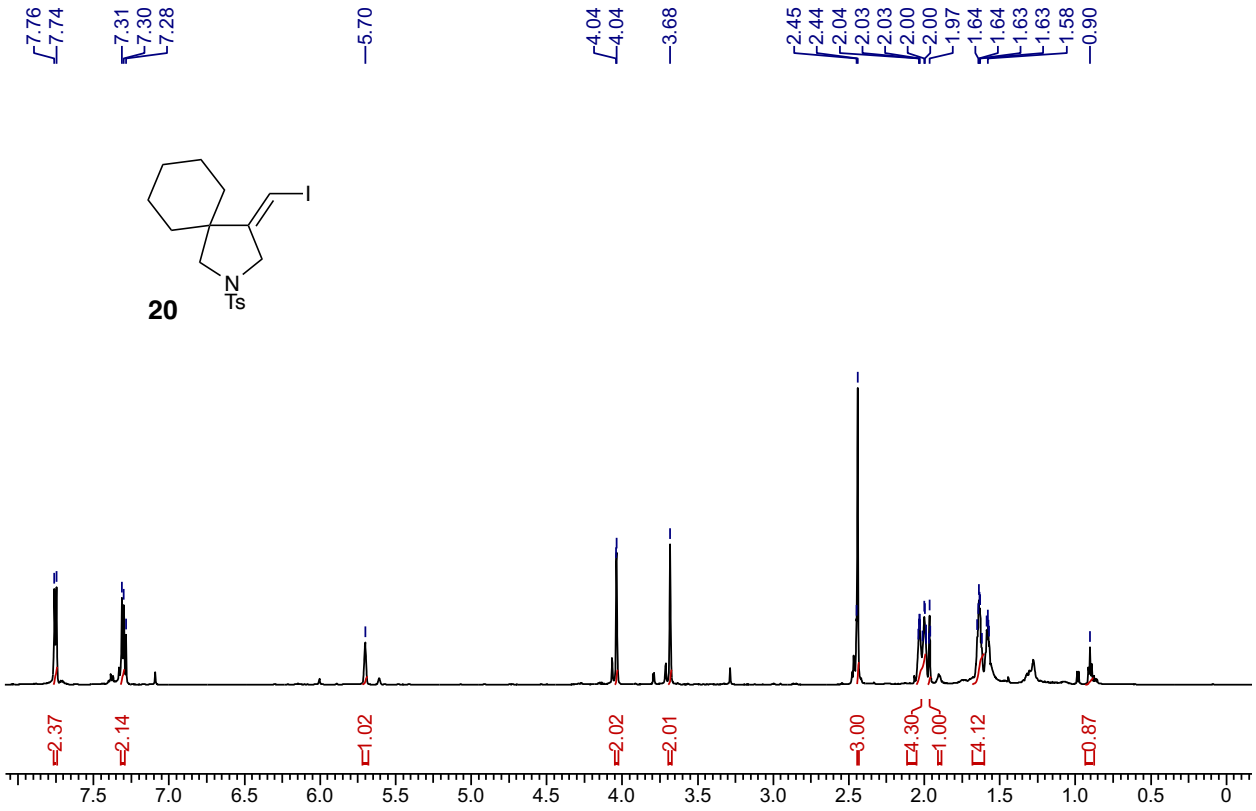
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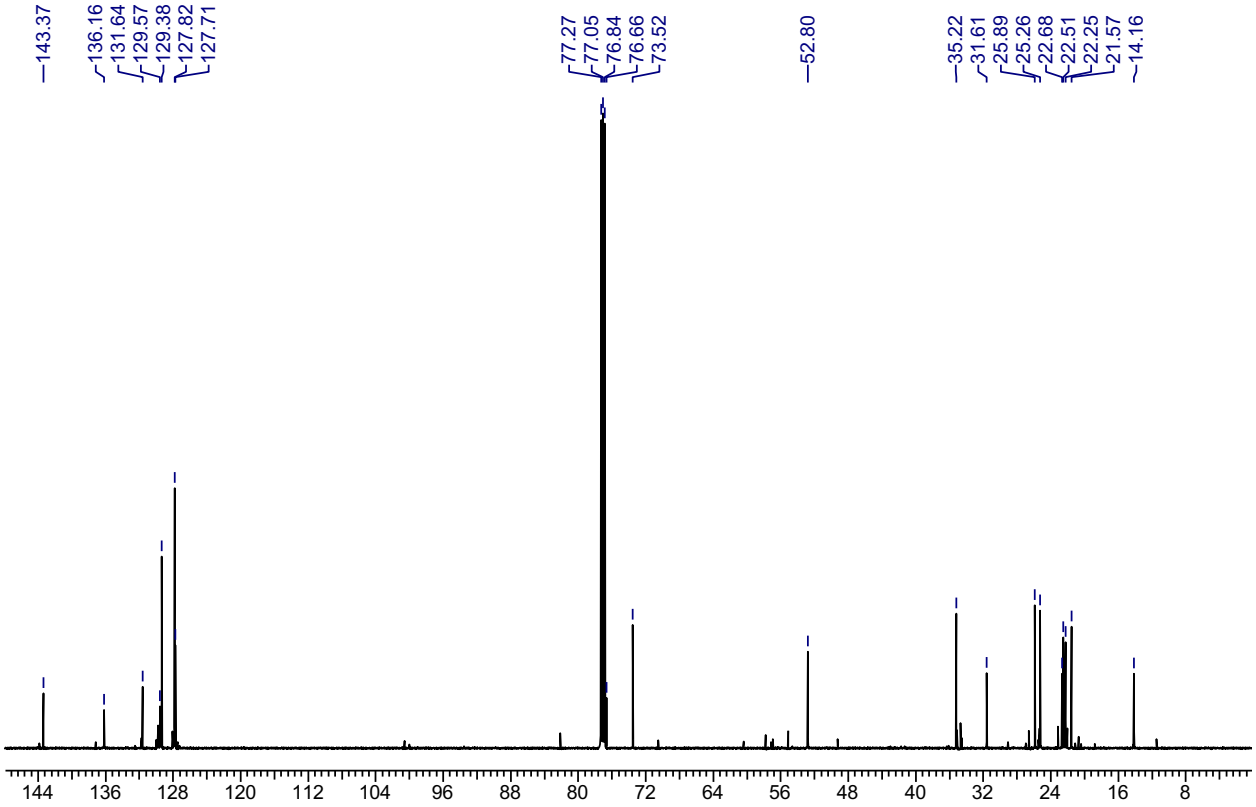
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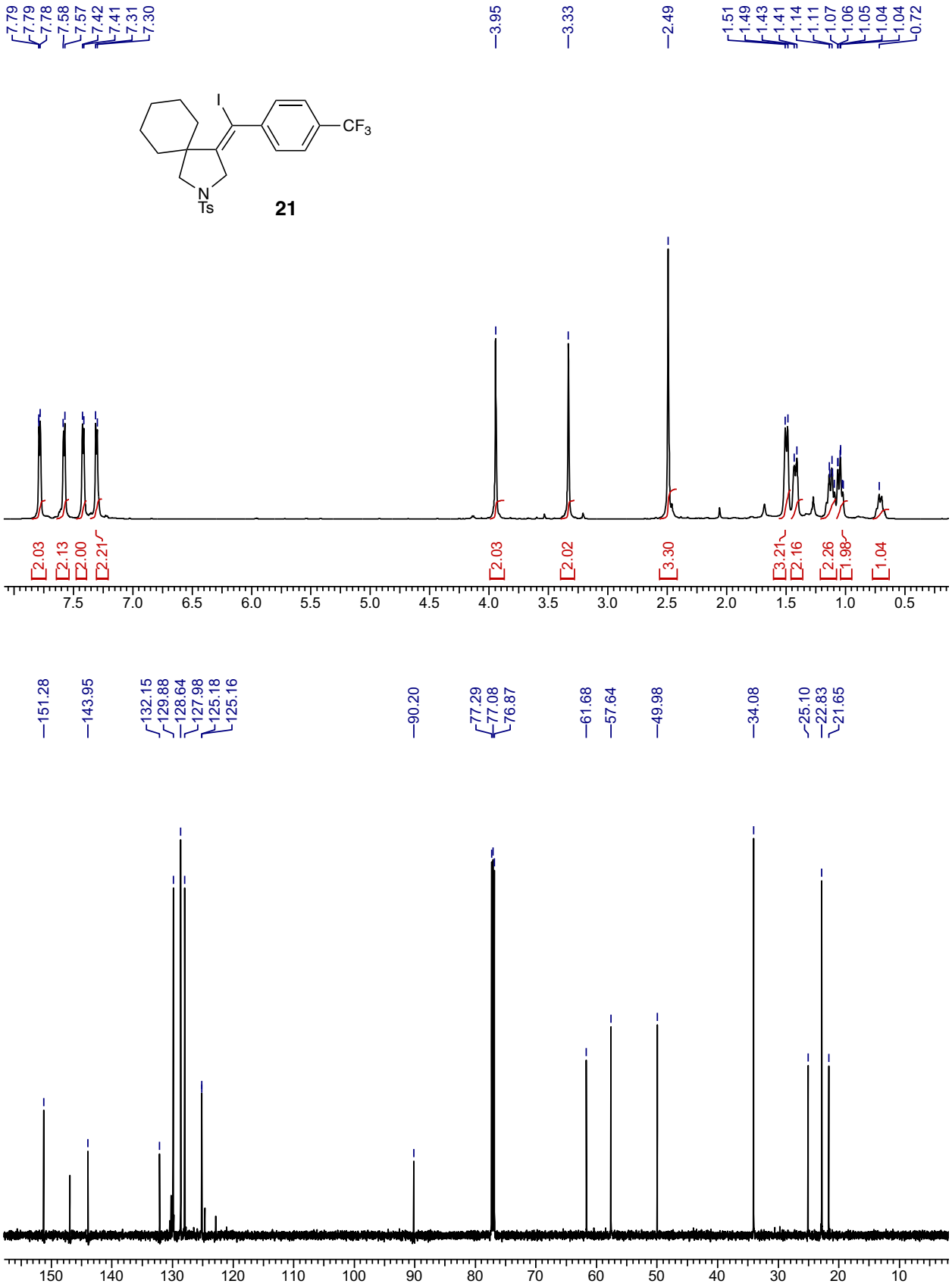
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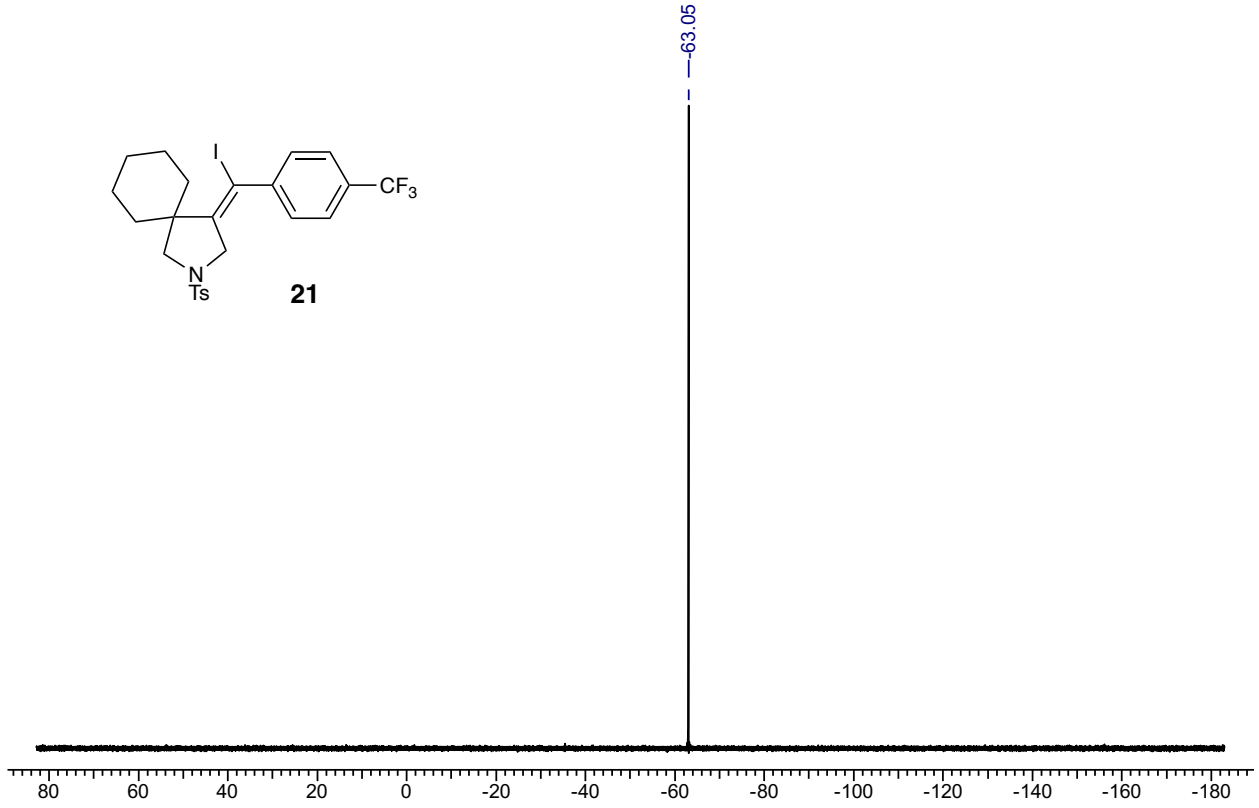
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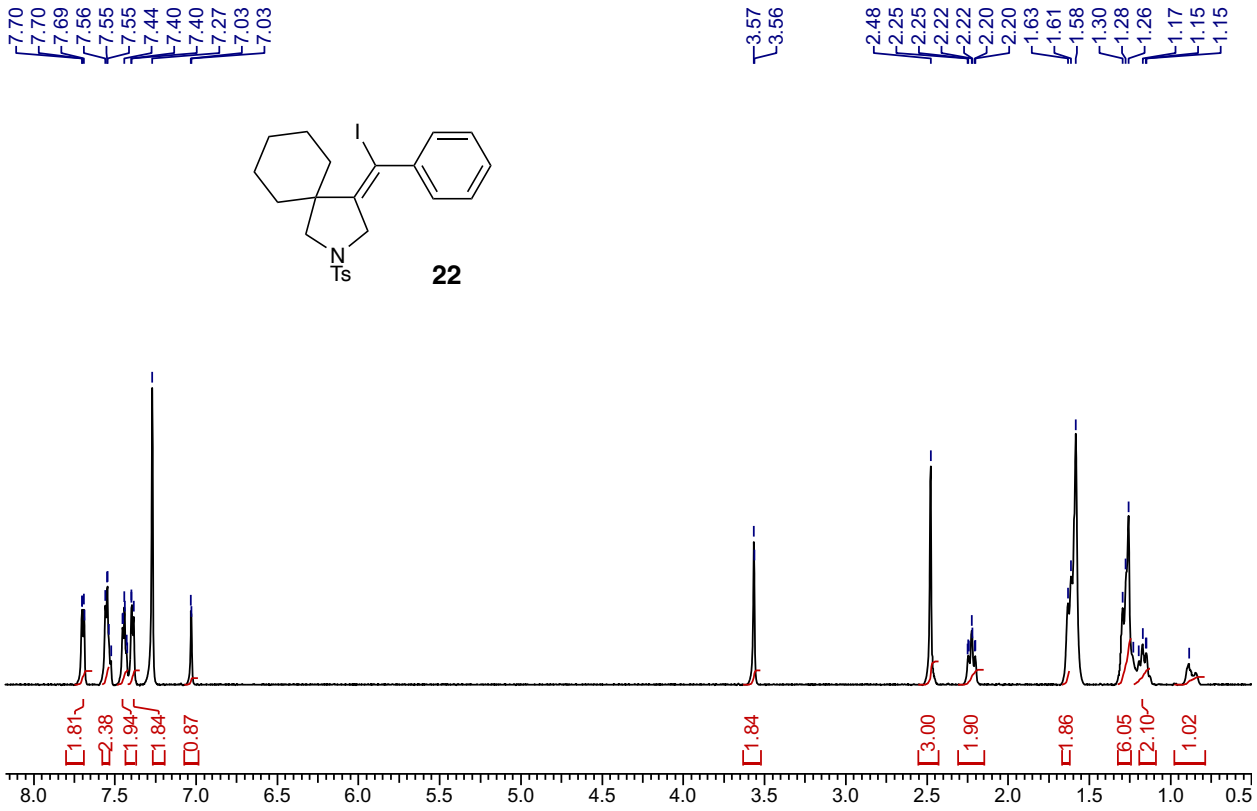
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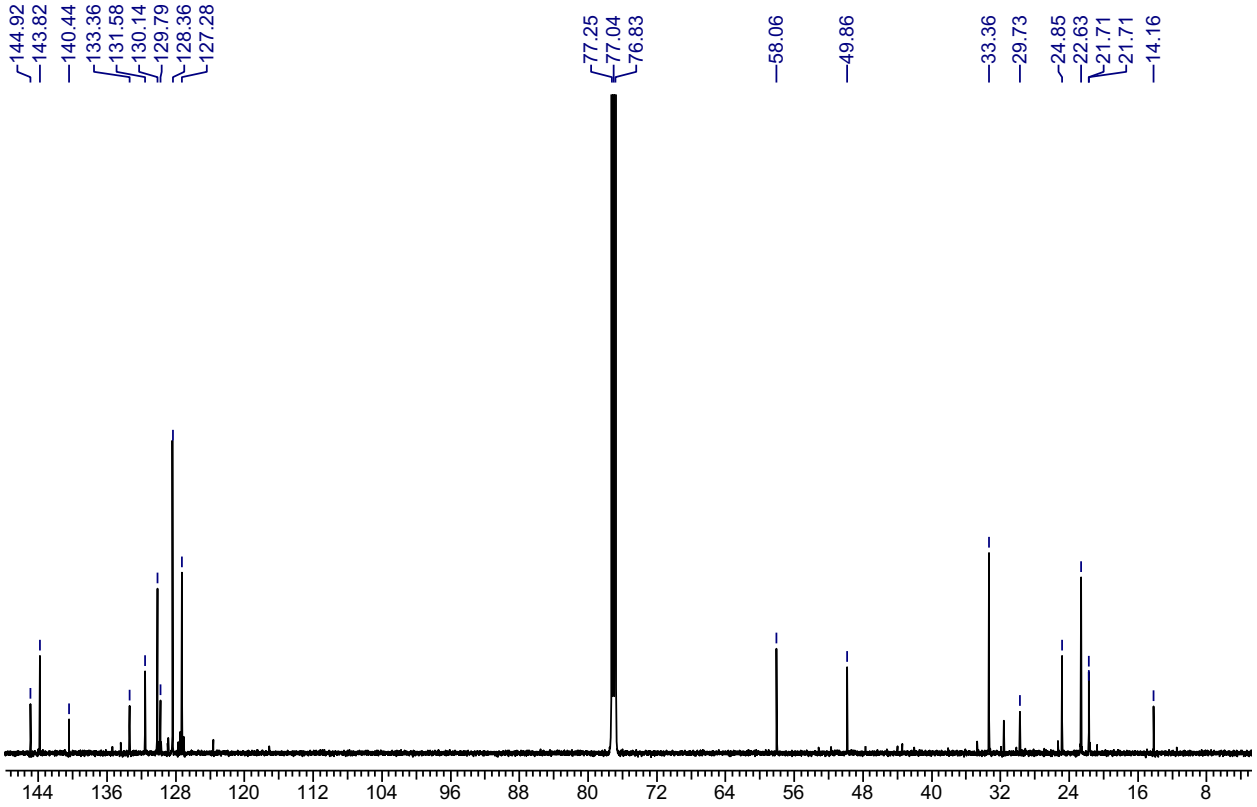
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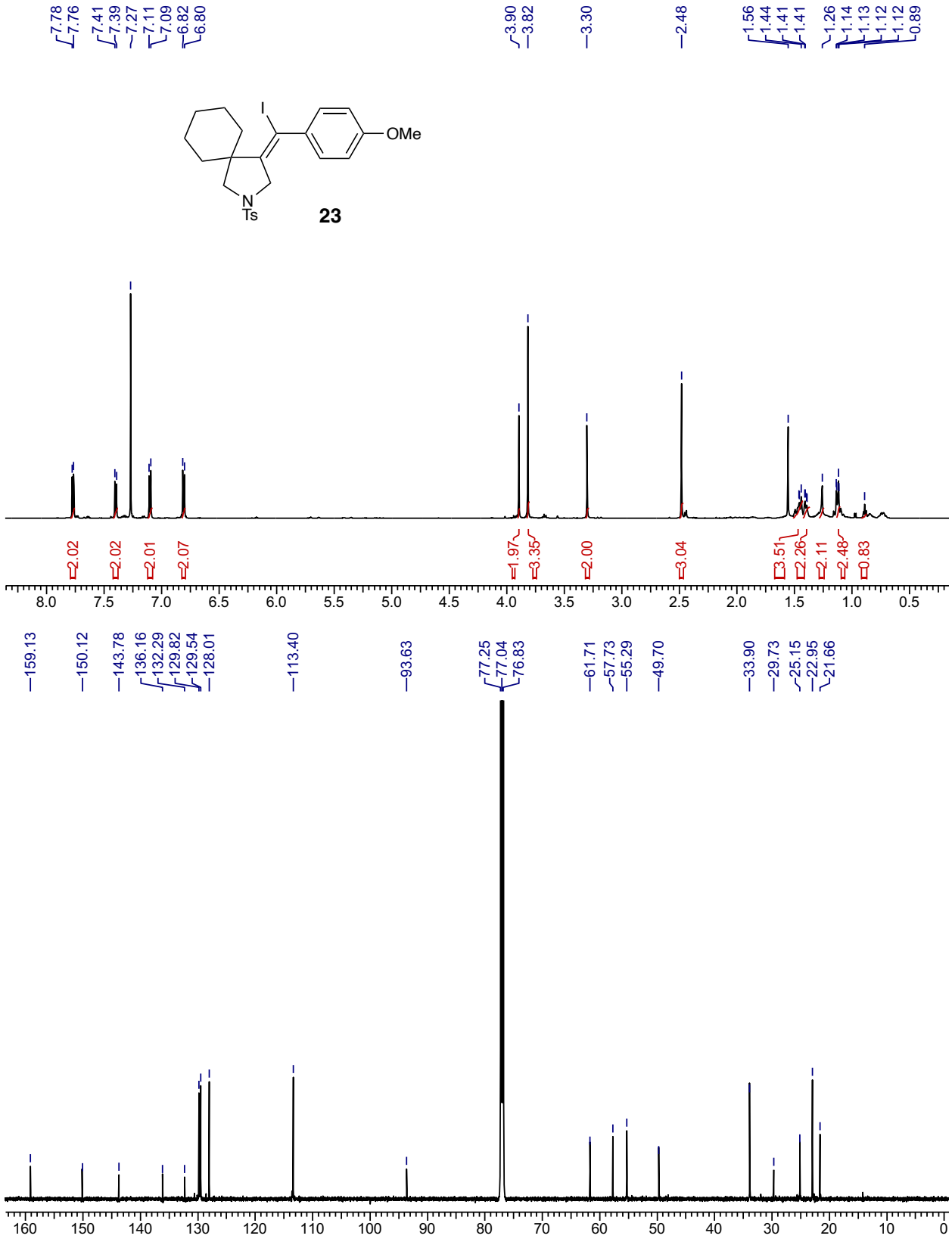
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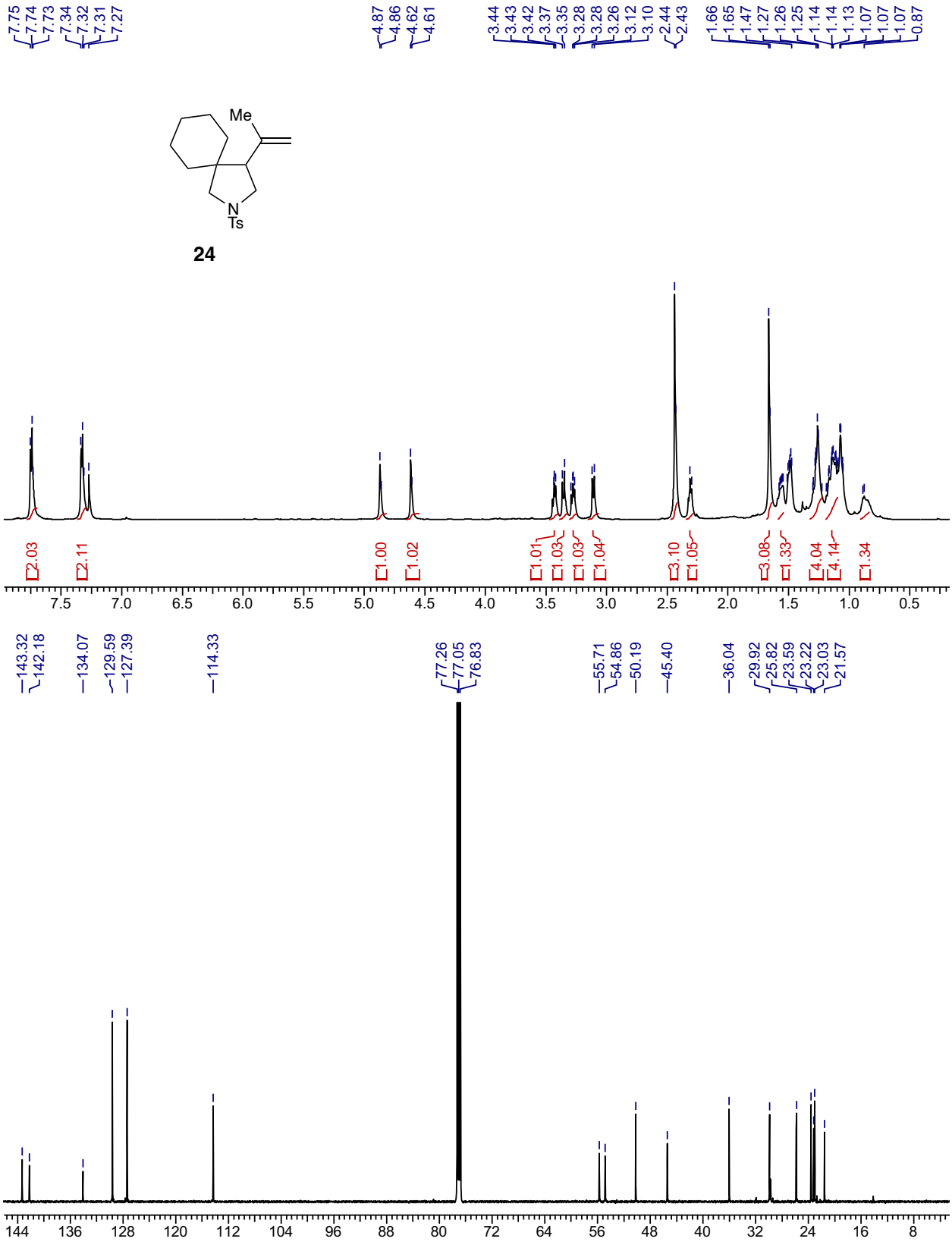
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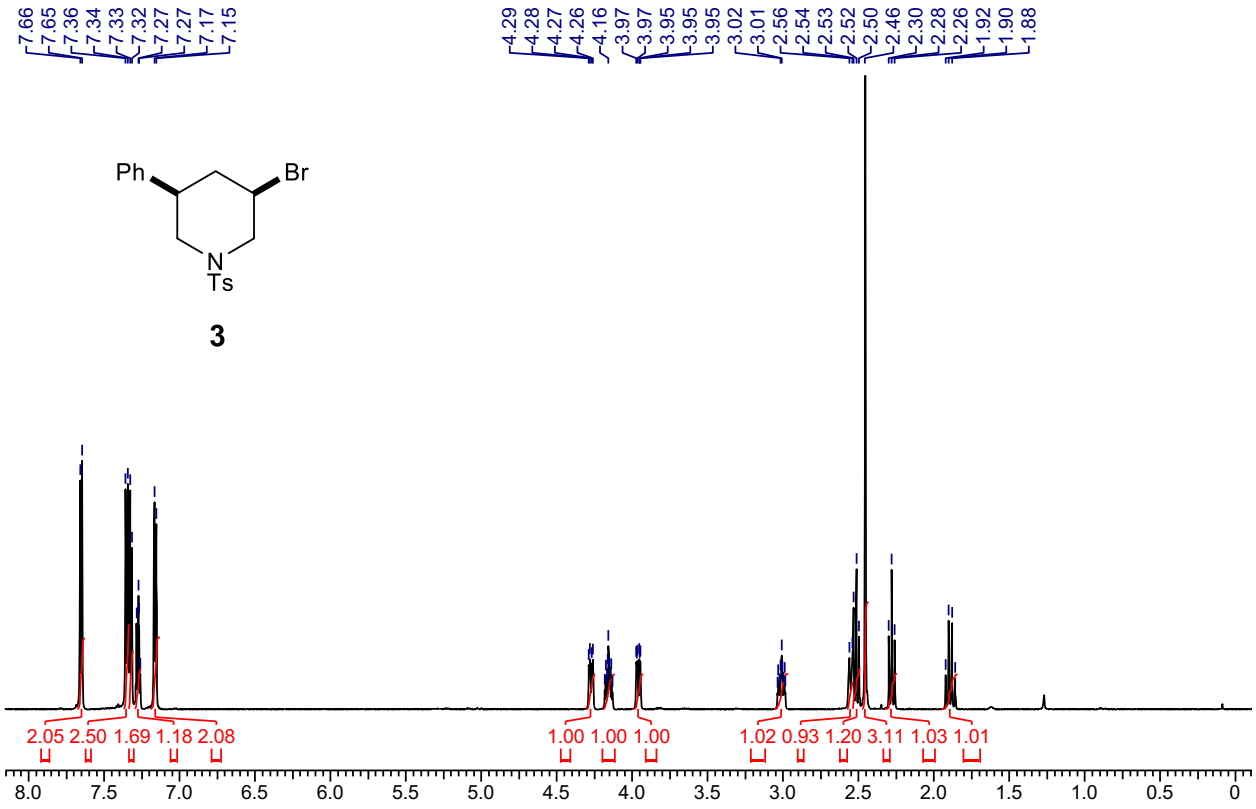
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2.26
1.92
1.90
1.88
Ph
Br
N
Ts
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1.00 1.00 1.00
1.02 0.93 1.20 3.11 1.03 1.01
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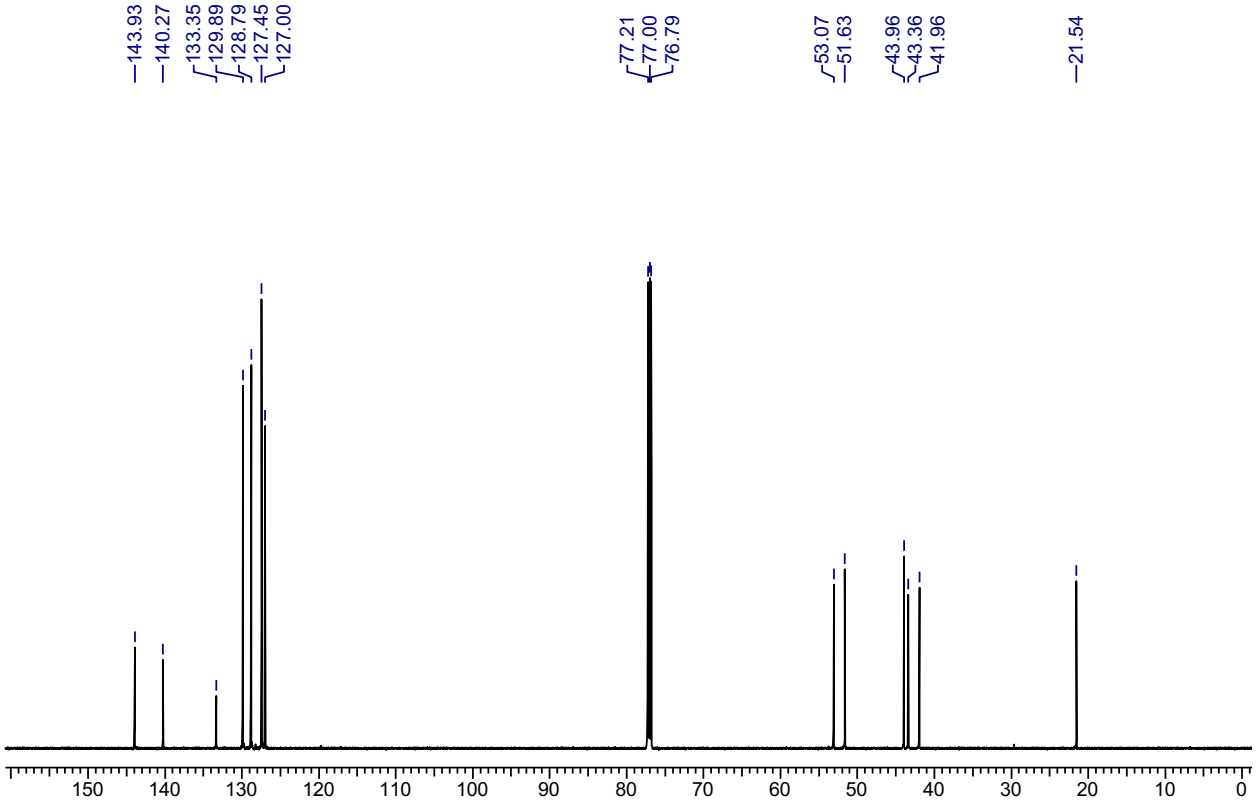
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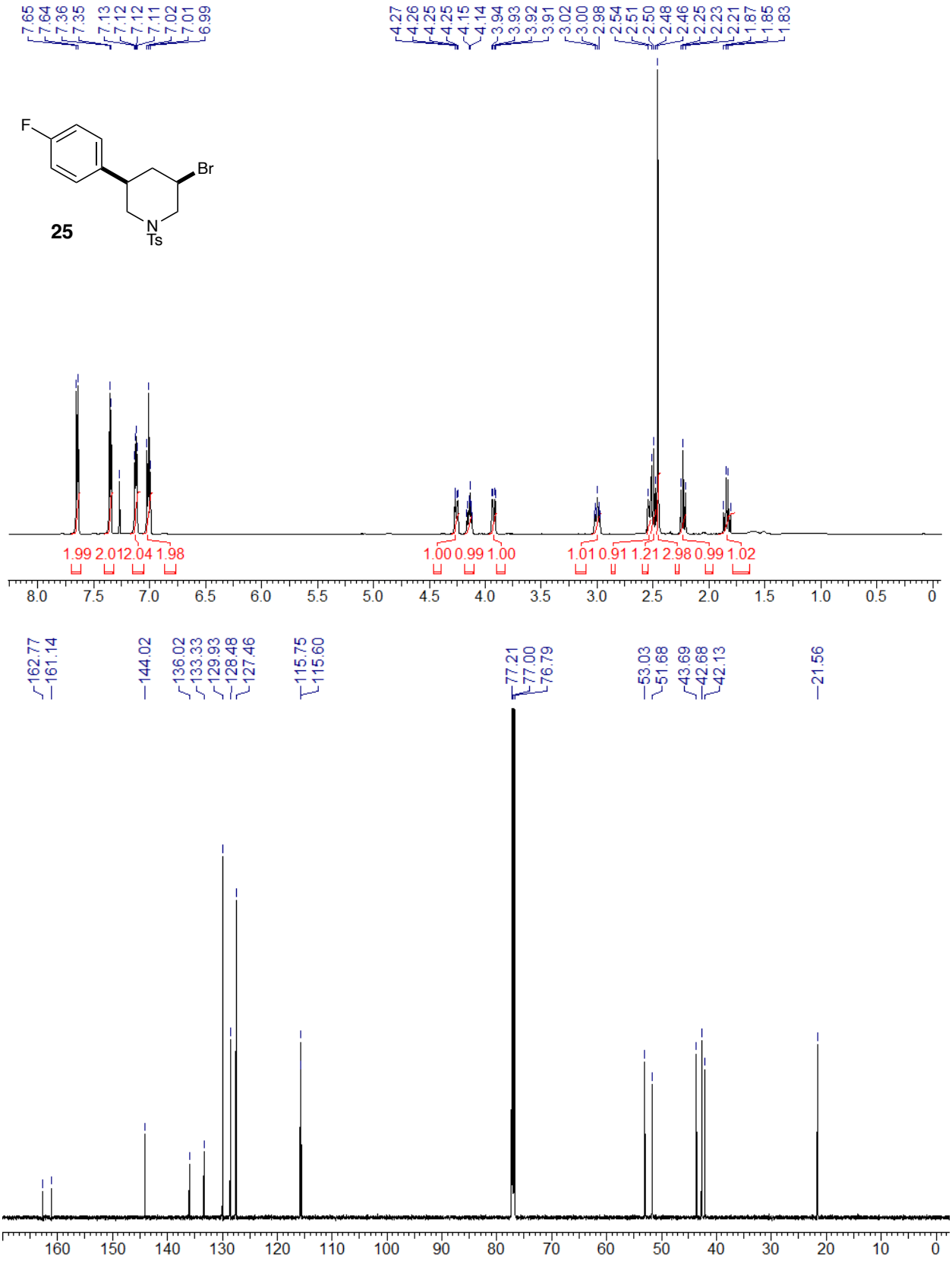
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4.25
4.15
4.14
3.94
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3.92
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3.02
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2.23
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1.85
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F
Br
N
Ts
25
1.99 2.01 2.04 1.98
1.00 0.99 1.00
1.01 0.91 1.21 2.98 0.99 1.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
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144.02
136.02
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127.46
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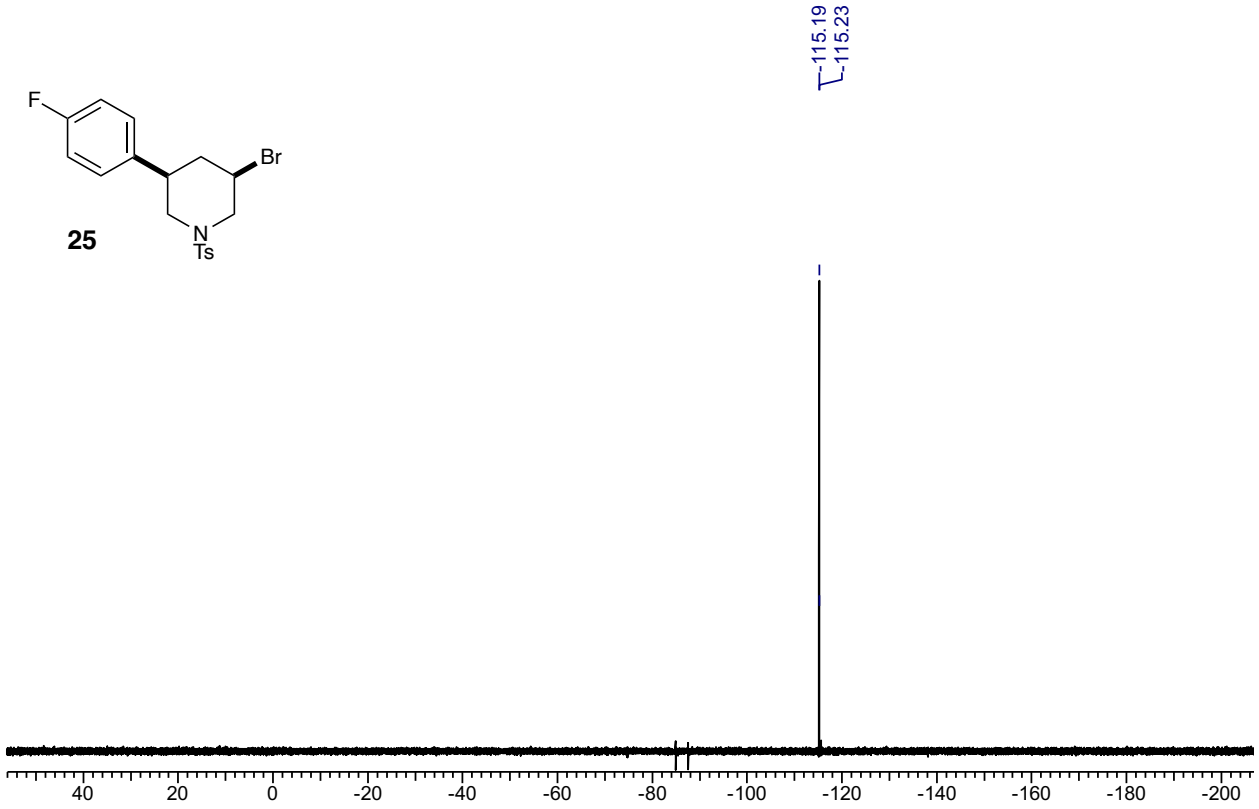
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-200

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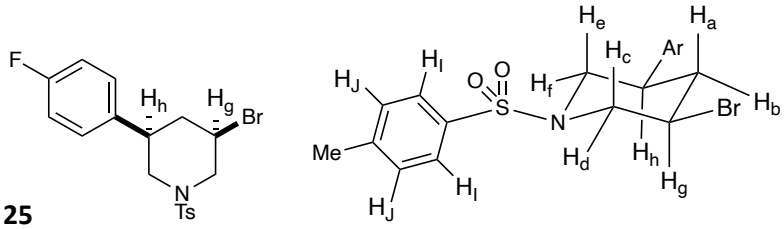
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Hg
Br
N
Ts
HJ
HI
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S
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He
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Hc
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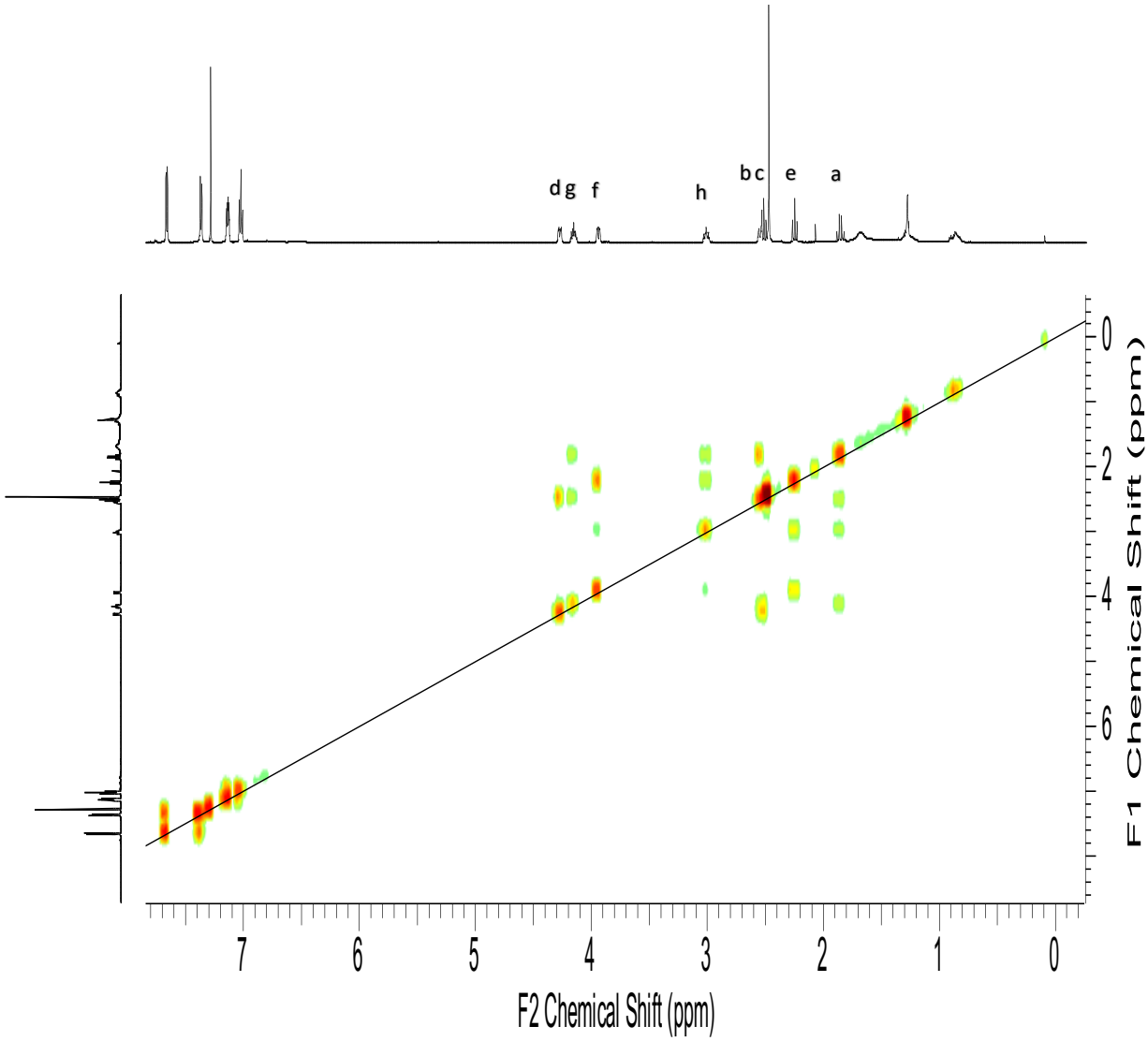
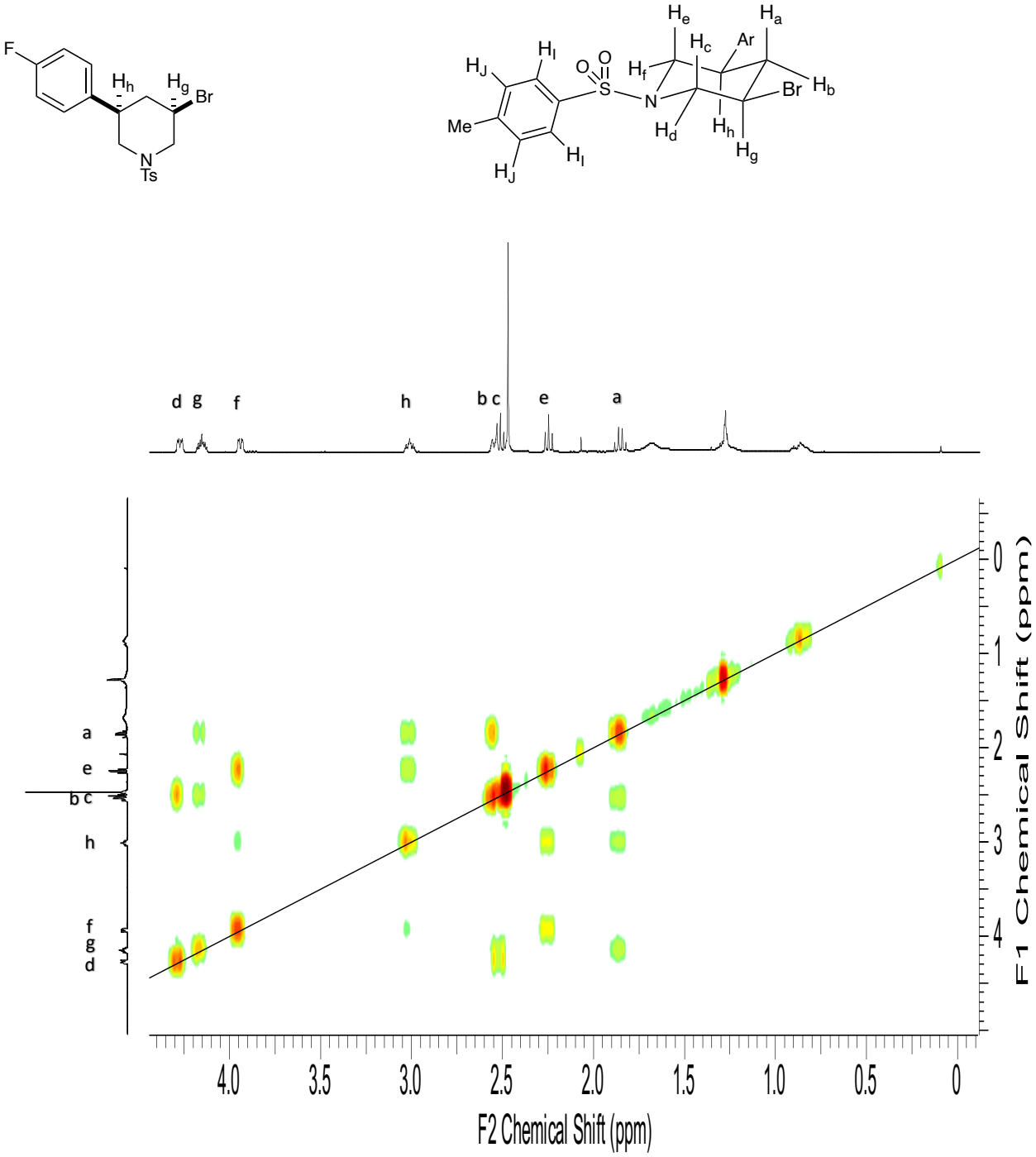
Hf
Br
Hb
Me
Hd
Hh
Hg
HJ
HI


d g f
h
b c
e
a
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)


F
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Hg
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Ts
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HI
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He
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Ar
Hf
Hb
Br
Me
Hd
Hh
Hg
HI
HJ
d g f
h
b c
e
a
a
e
b c
h
f
g
d
4.0
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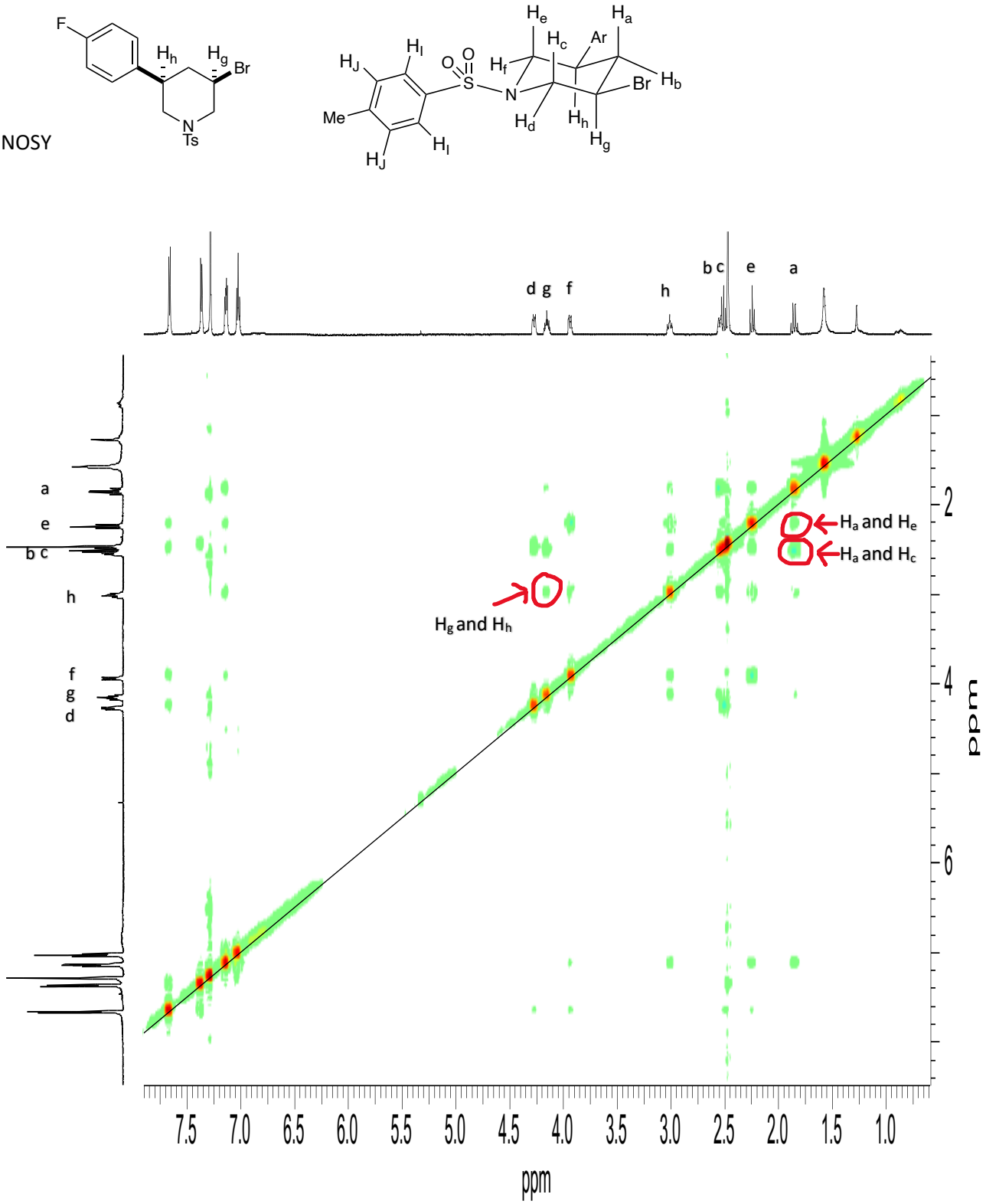
0
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)

NOSY


F
Hh
Hg
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He
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Hc
Ar
Hf
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Hb
Me
Hd
Hh
Hg
HJ
HI
d g f
h
b c
e
a
a
e
b c
h
f
g
d
Hg and Hh
Ha and He
Ha and Hc
2
4
6
ppm
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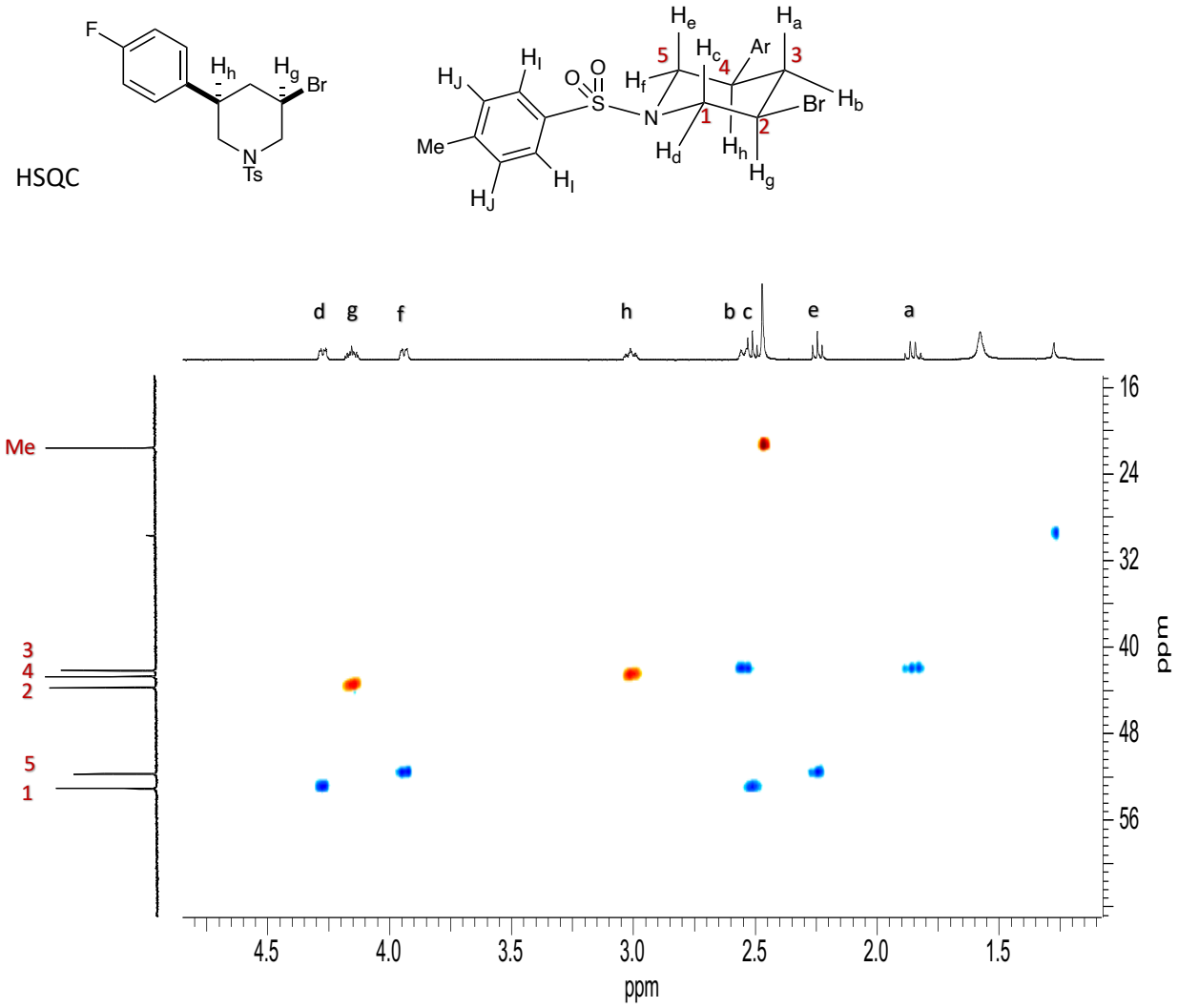
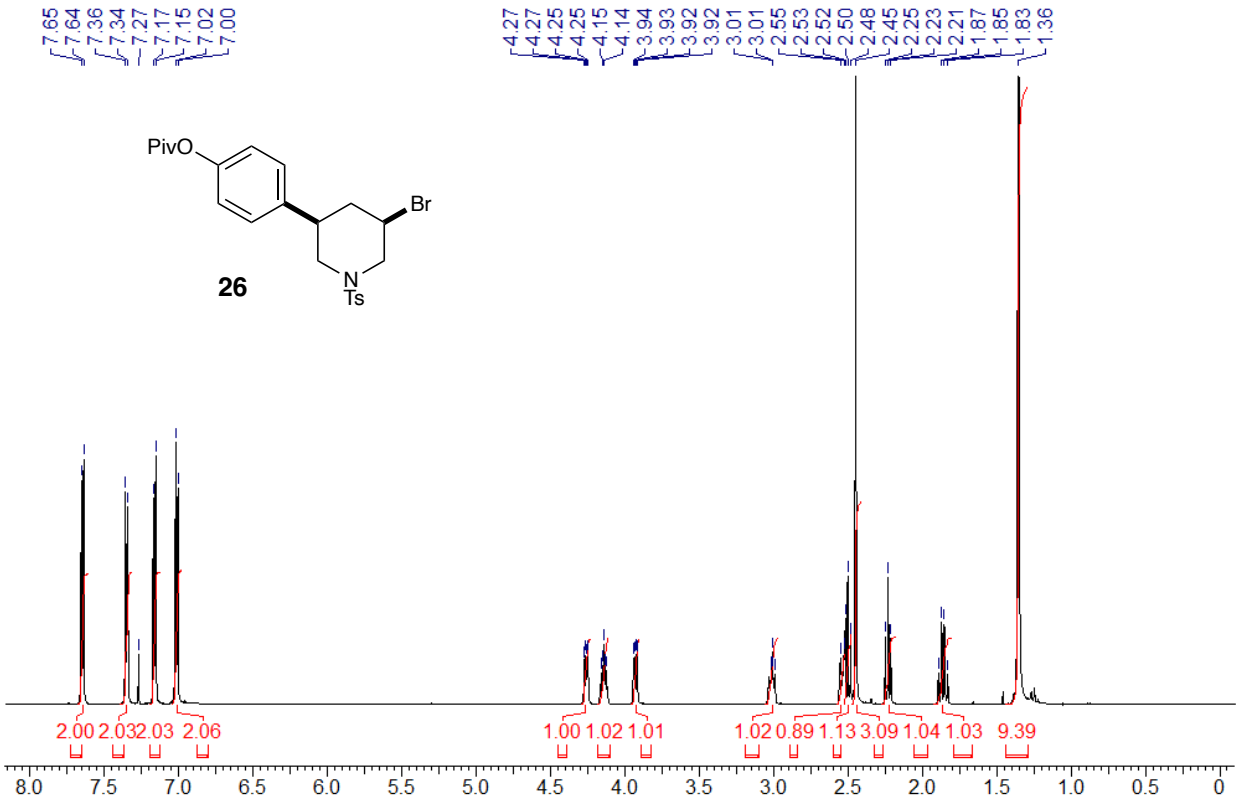
1.0
ppm

HSQC

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4.14
3.94
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3.01
3.01
2.55
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2.23
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1.85
1.83
1.36
PivO
Br
N
Ts
26
2.00 2.03 2.03 2.06
1.00 1.02 1.01
1.02 0.89 1.13 3.09 1.04 1.03 9.39
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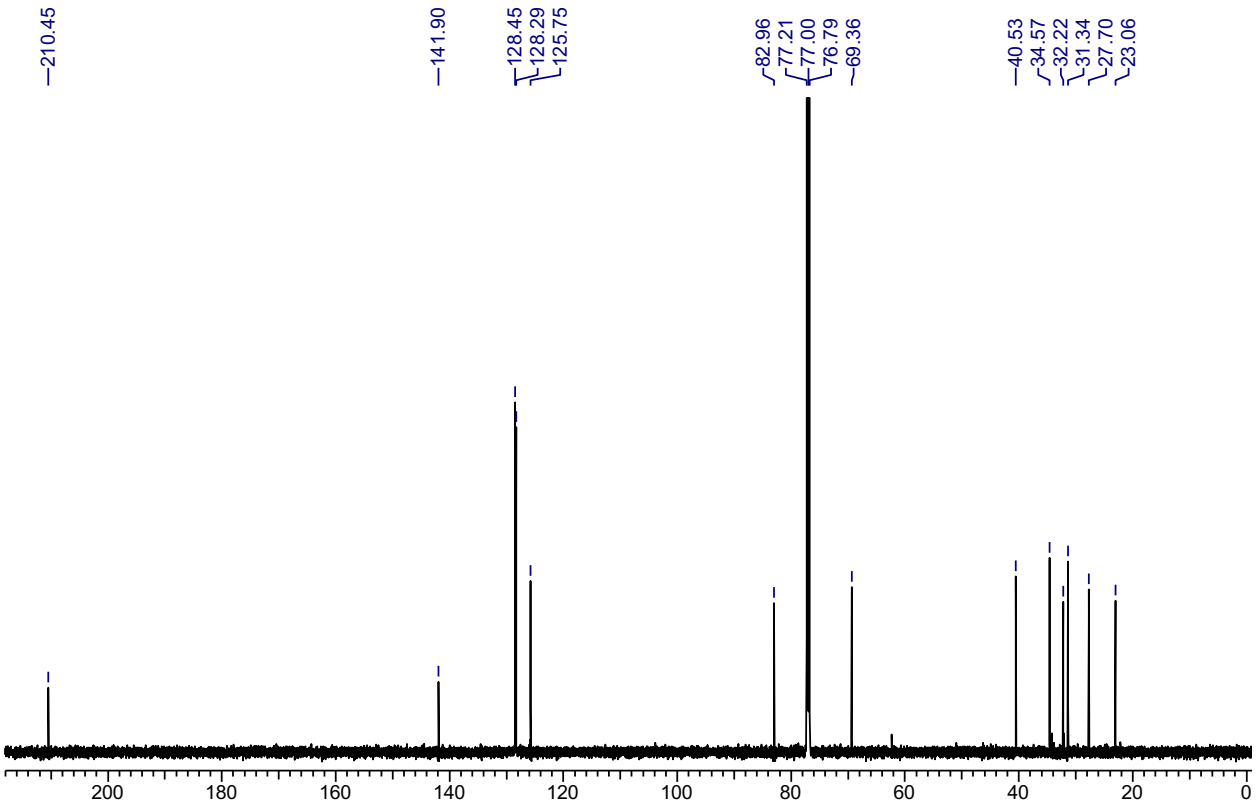
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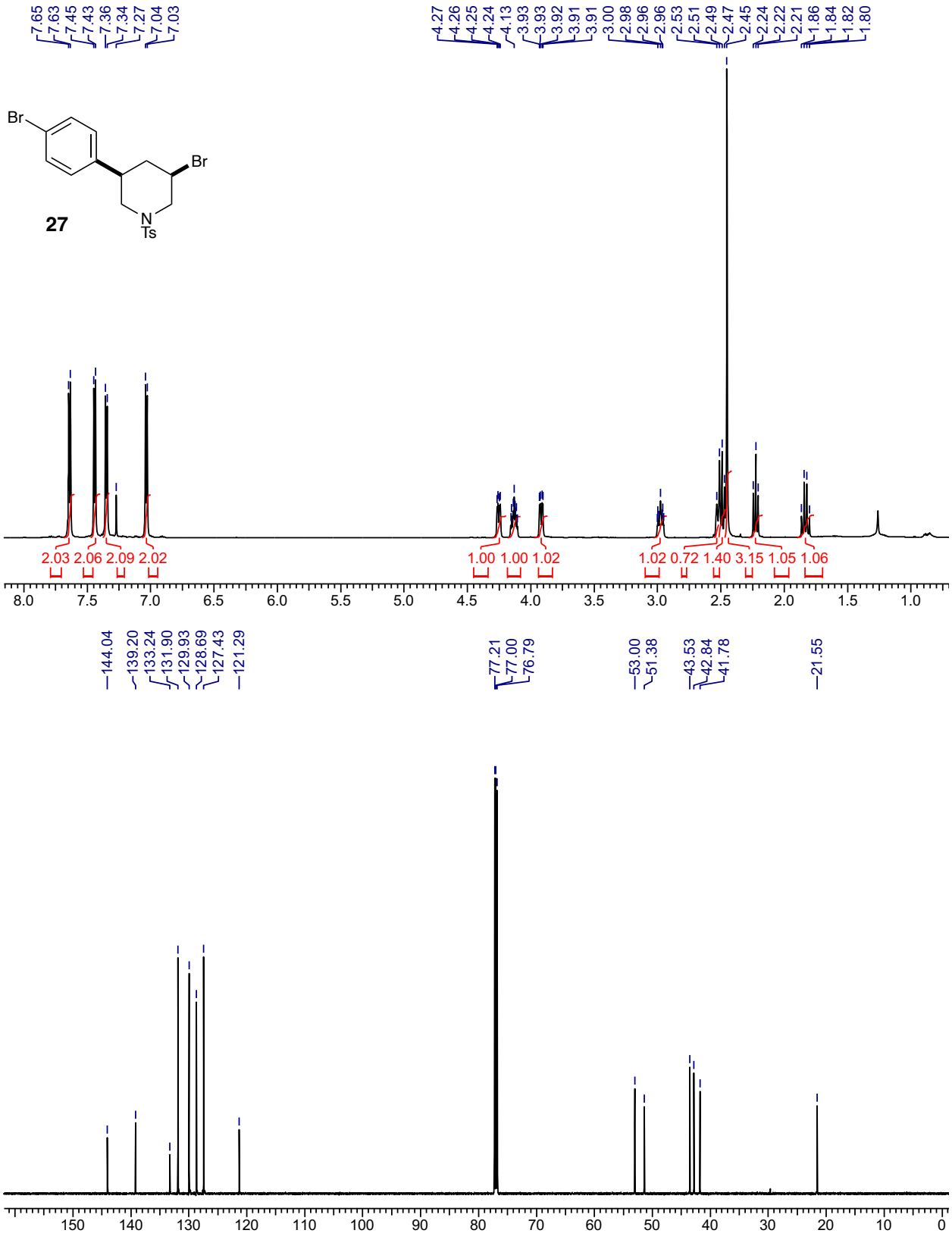
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4.13
3.93
3.93
3.92
3.91
3.91
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2.96
2.96
2.53
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2.49
2.47
2.45
2.24
2.22
2.21
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1.84
1.82
1.80
Br
Br
N
Ts
27
2.03 2.06 2.09 2.02
1.00 1.00 1.02
1.02 0.72 1.40 3.15 1.05 1.06
144.04
139.20
133.24
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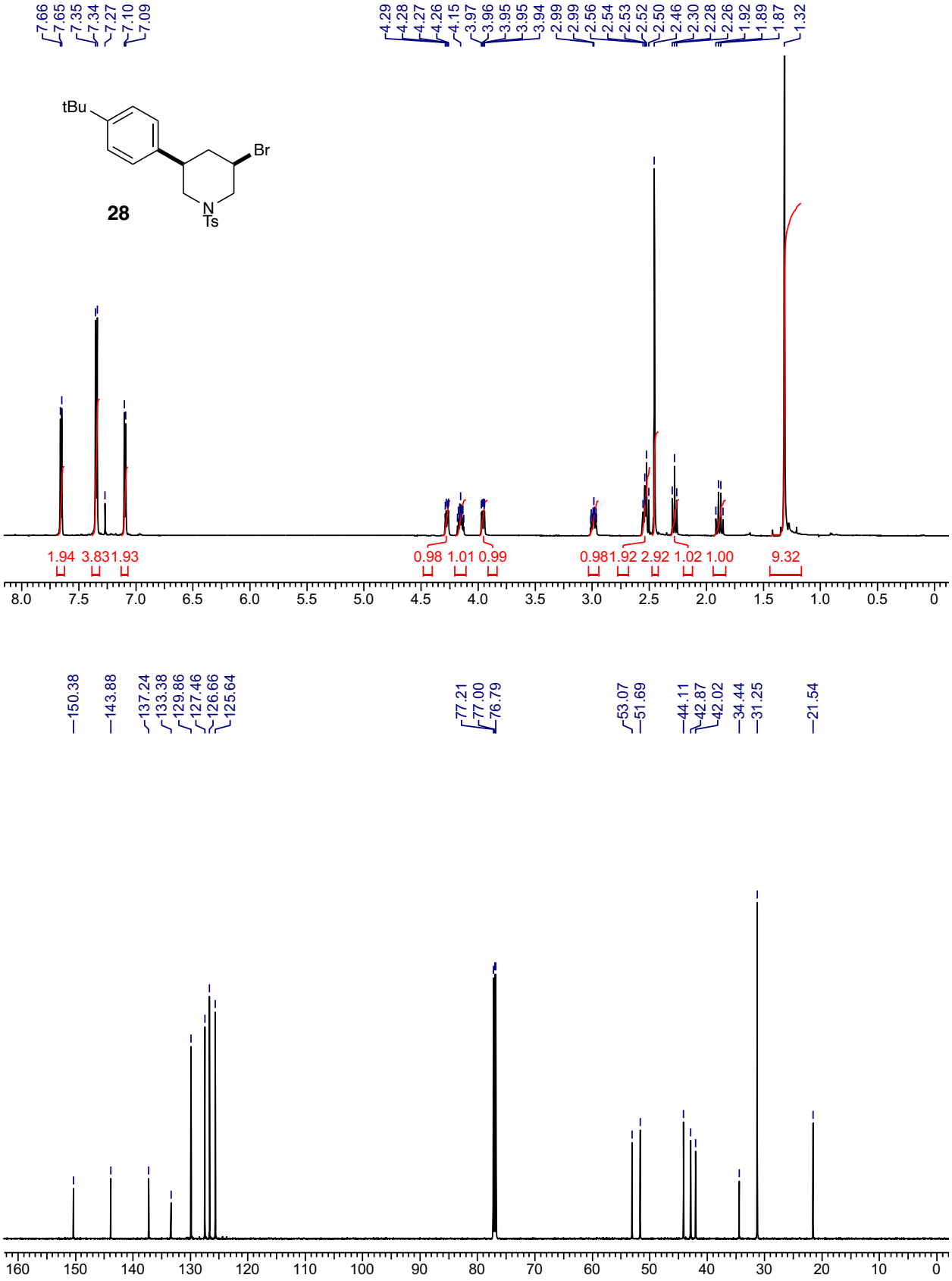
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3.95
3.94
2.99
2.99
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2.53
2.52
2.50
2.46
2.30
2.28
2.26
1.92
1.89
1.87
1.32
tBu
Br
N
Ts
28
1.94 3.83 1.93
0.98 1.01 0.99
0.98 1.92 2.92 1.02 1.00
9.32
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
150.38
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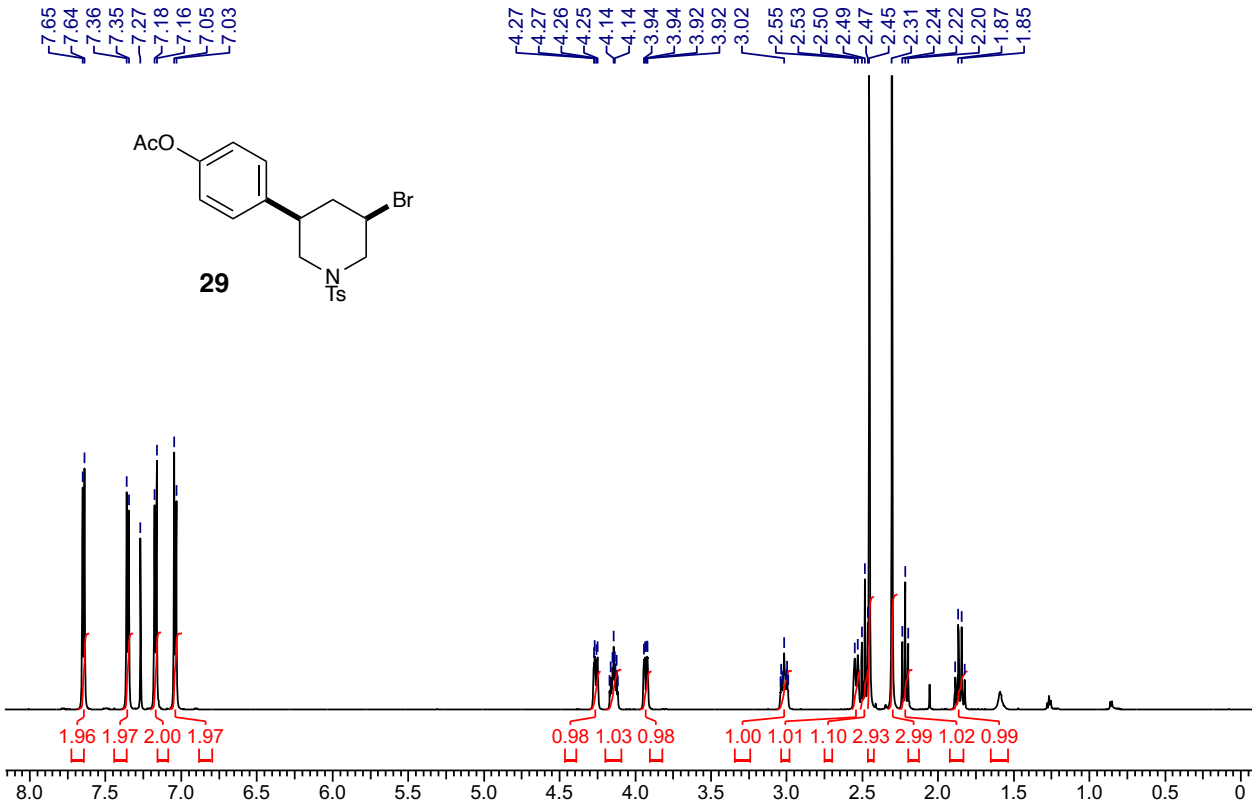
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4.14
3.94
3.94
3.92
3.92
3.02
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2.53
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2.47
2.45
2.31
2.24
2.22
2.20
1.87
1.85
AcO
Br
N
Ts
29
1.96 1.97 2.00 1.97
0.98 1.03 0.98
1.00 1.01 1.10 2.93 2.99 1.02 0.99
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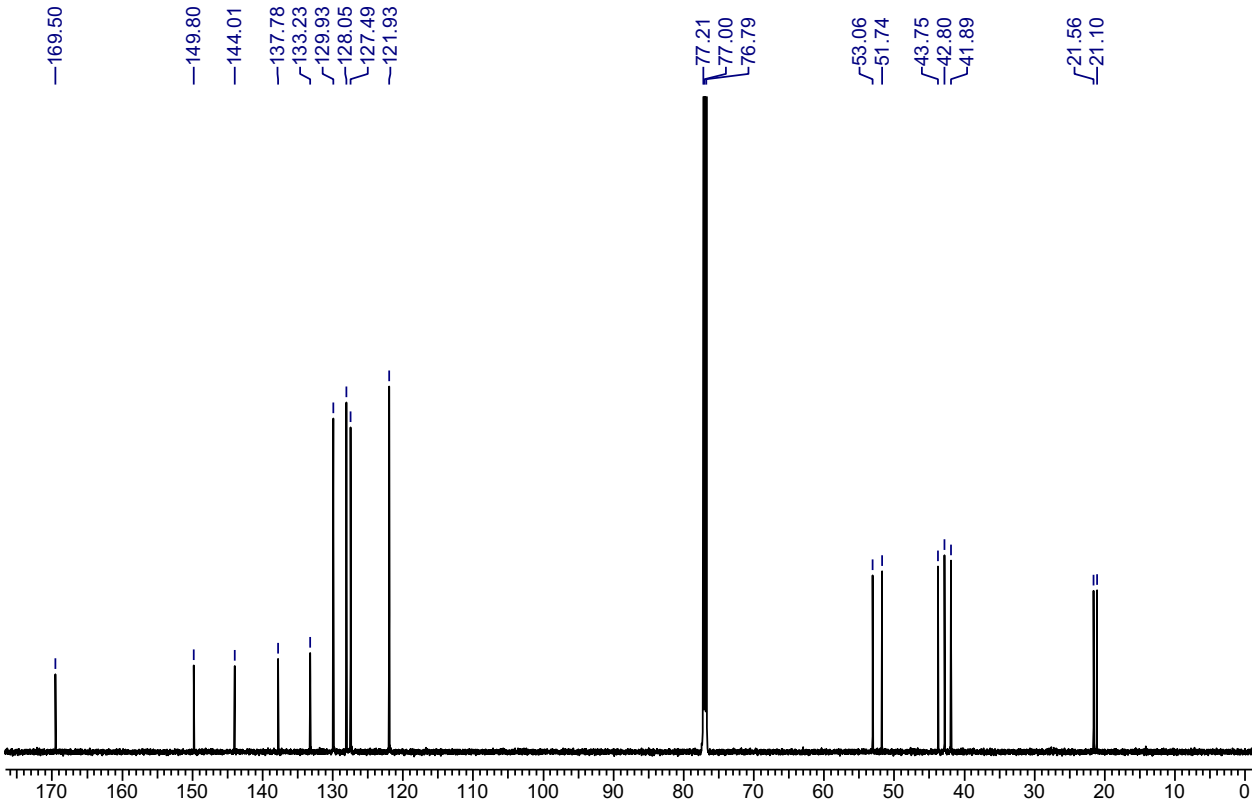
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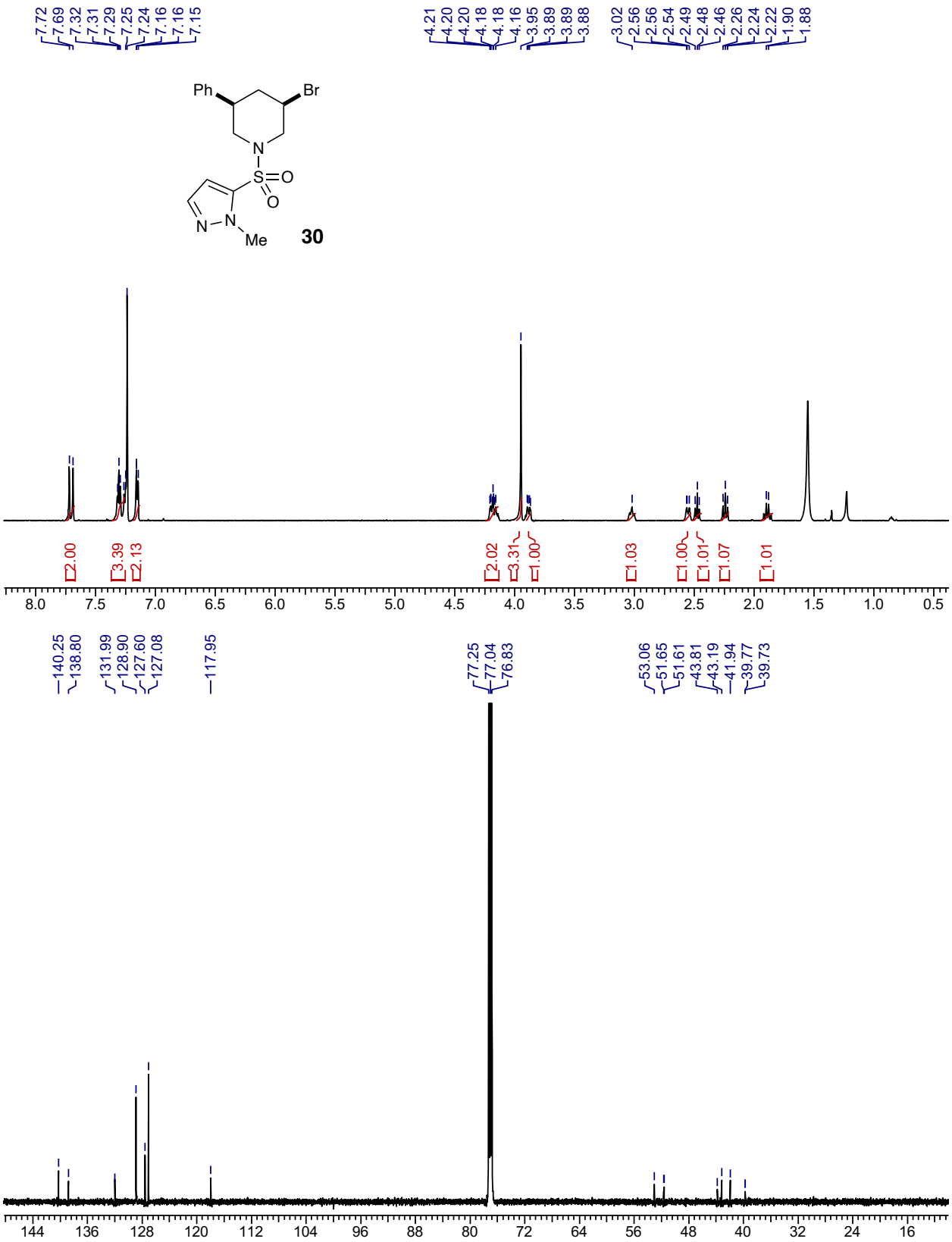
41.89
21.56
21.10
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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4.18
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3.89
3.88
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2.56
2.54
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2.24
2.22
1.90
1.88
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Br
N
S
O
O
N
N
Me
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2.13
2.02
3.31
1.00
1.03
1.00
1.01
1.07
1.01
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7.0
6.5
6.0
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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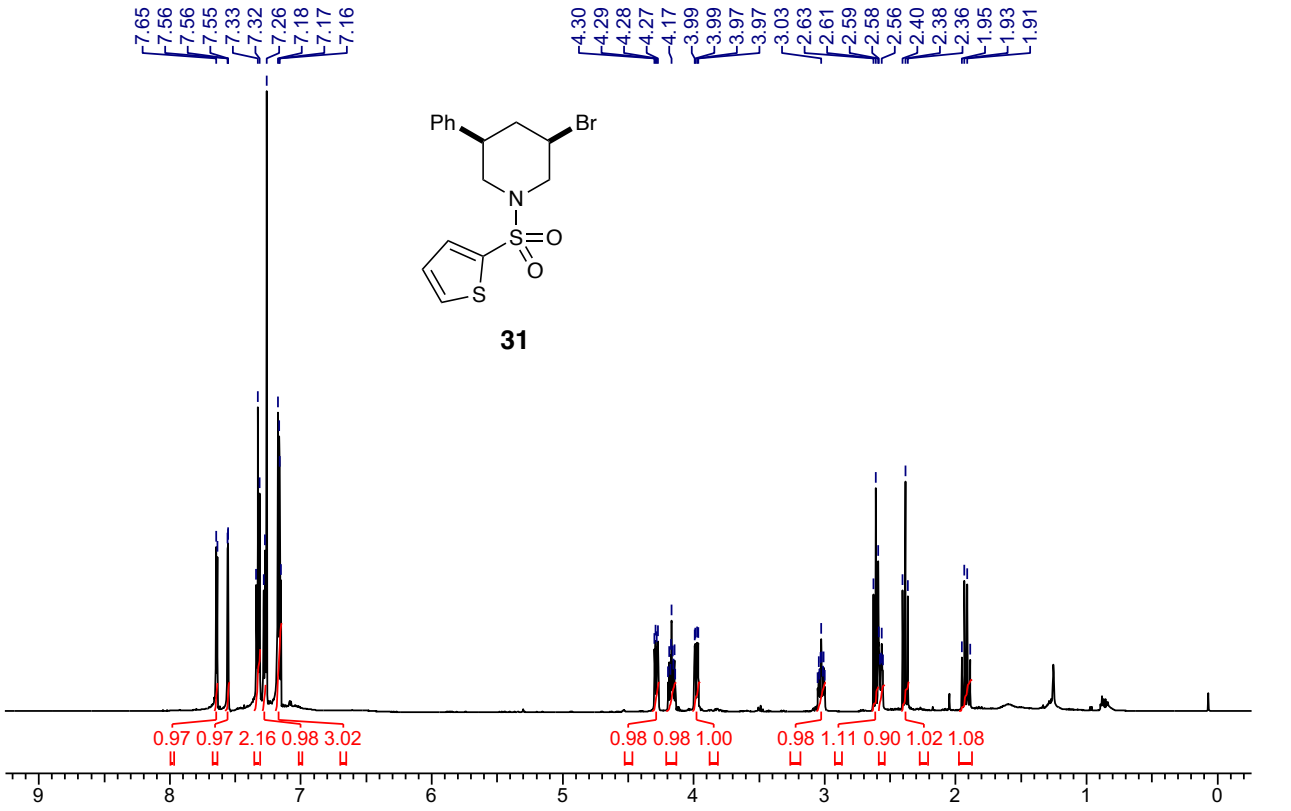
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1.93
1.91
Ph
Br
N
S
O
O
S
0.97 0.97 2.16 0.98 3.02
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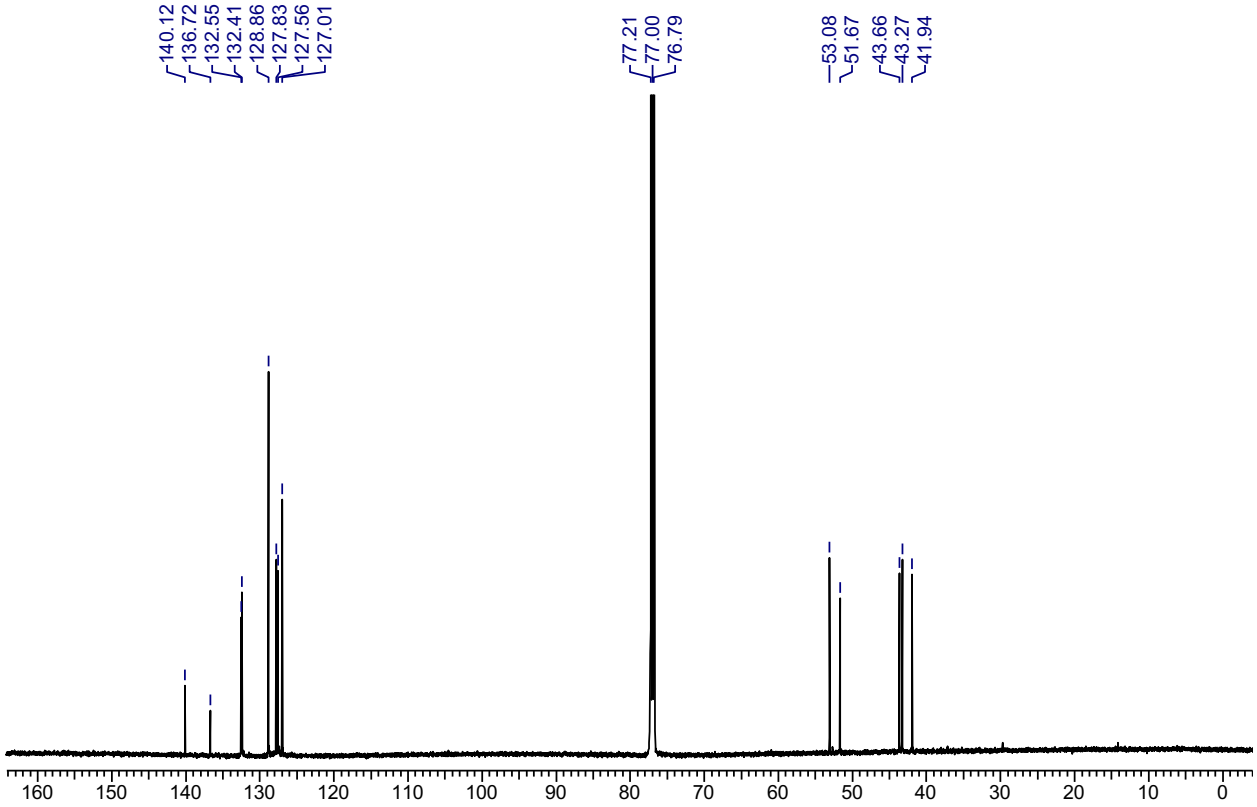
0

31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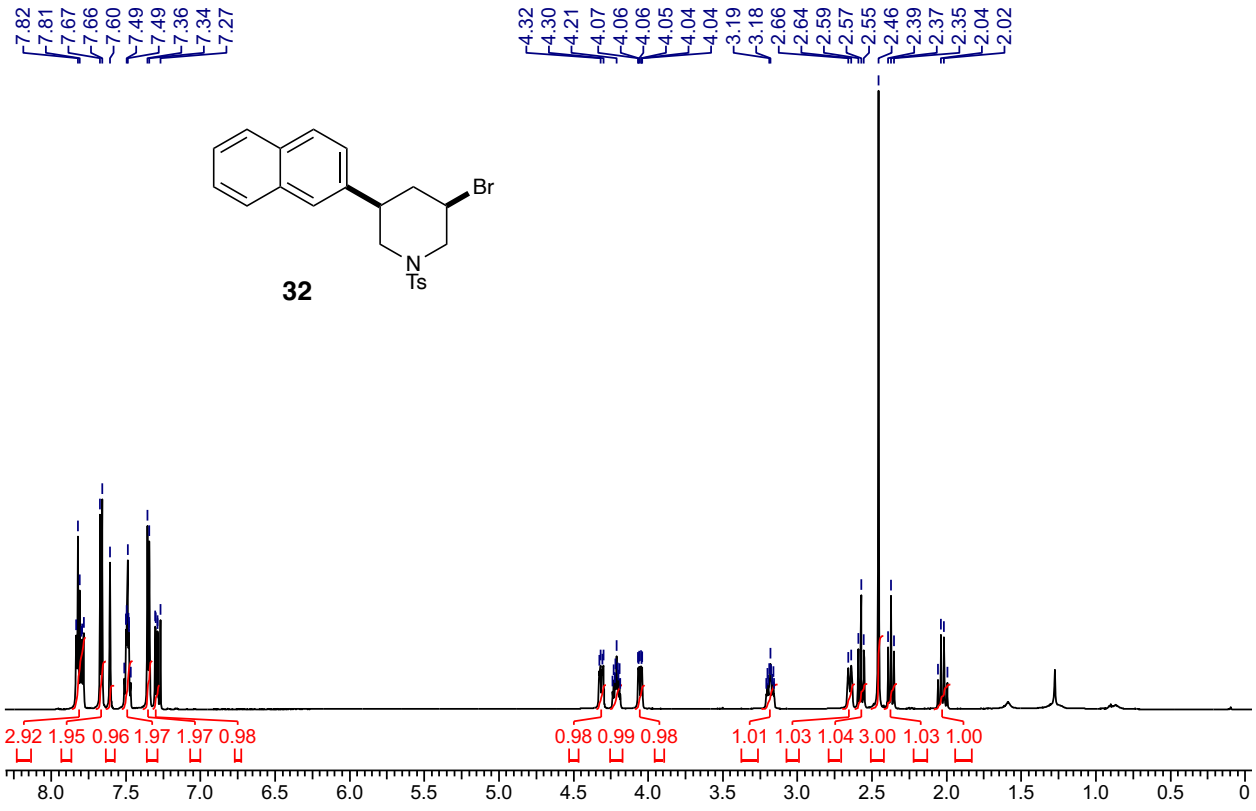
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2.02
Br
N
Ts
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2.92 1.95 0.96 1.97 1.97 0.98
0.98 0.99 0.98
1.01 1.03 1.04 3.00 1.03 1.00
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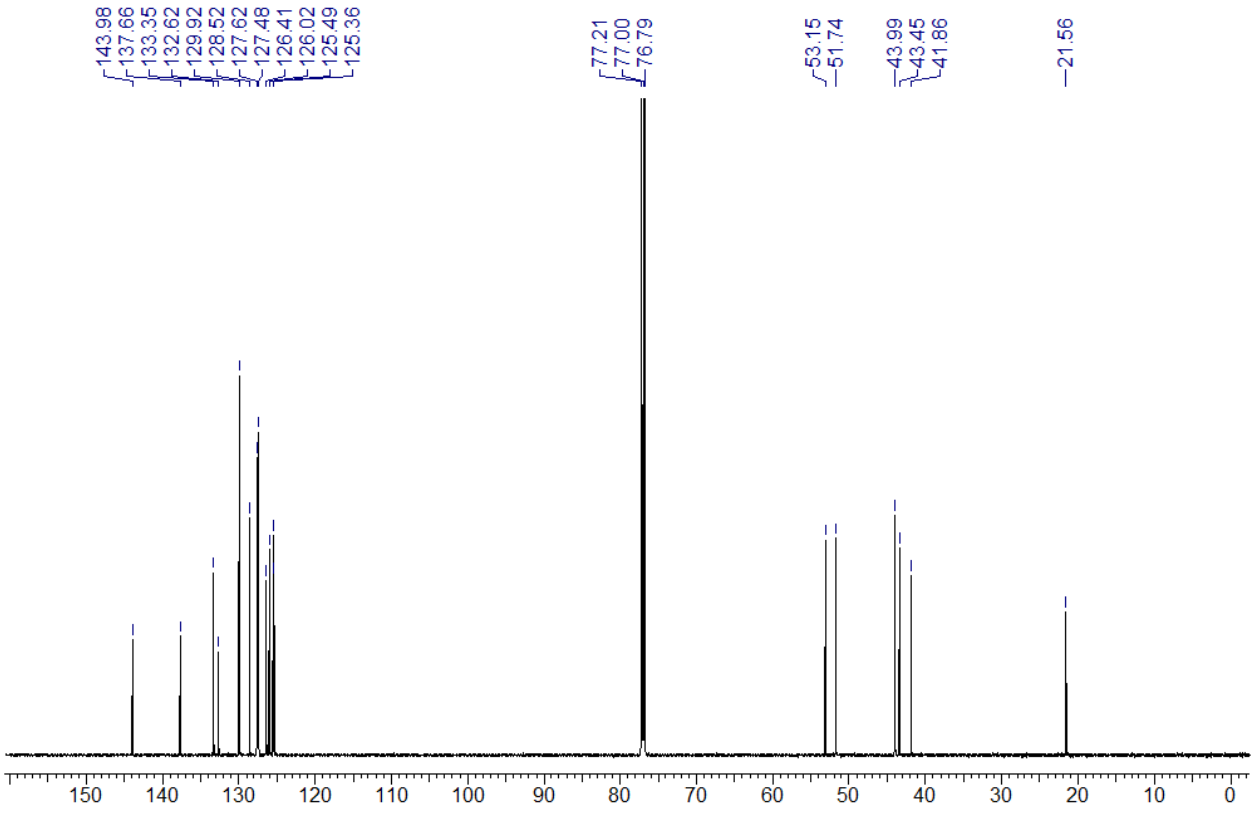
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21.56
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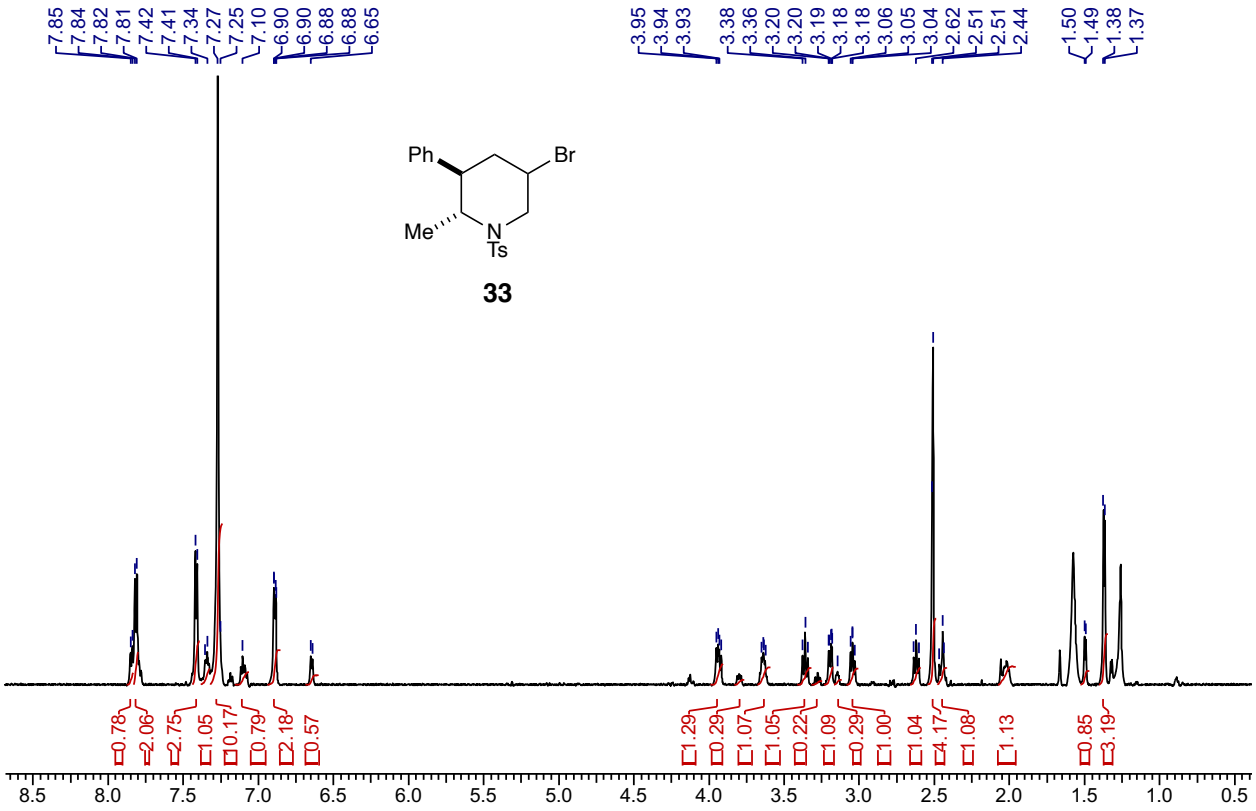
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Ph
Br
Me
N
Ts
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1.08
1.13
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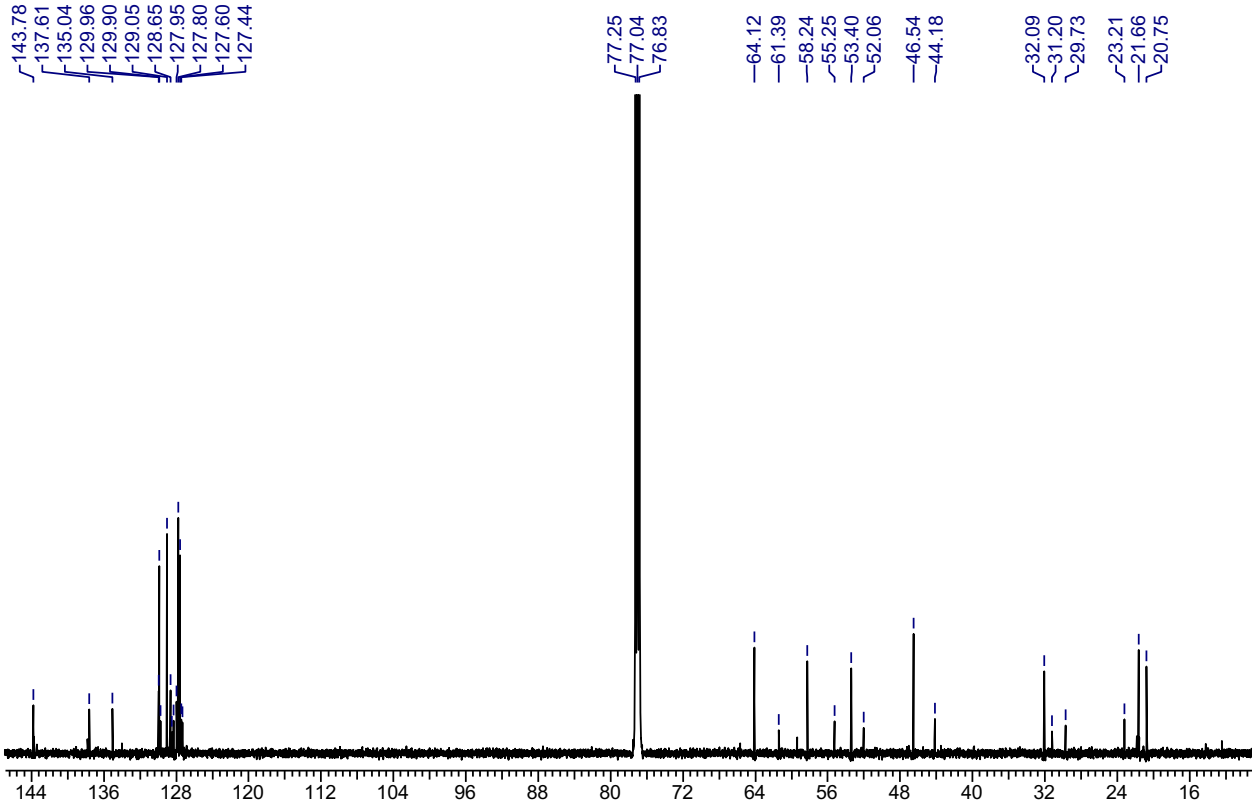
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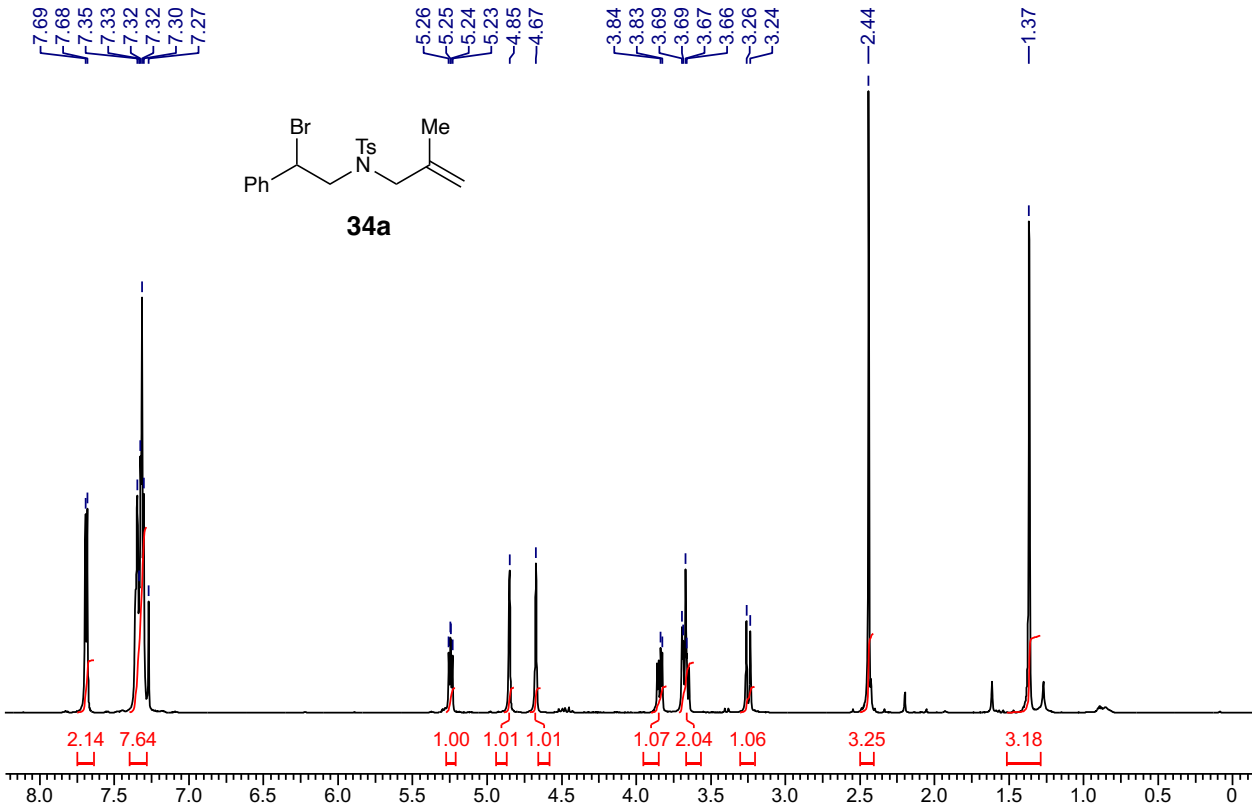
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Me
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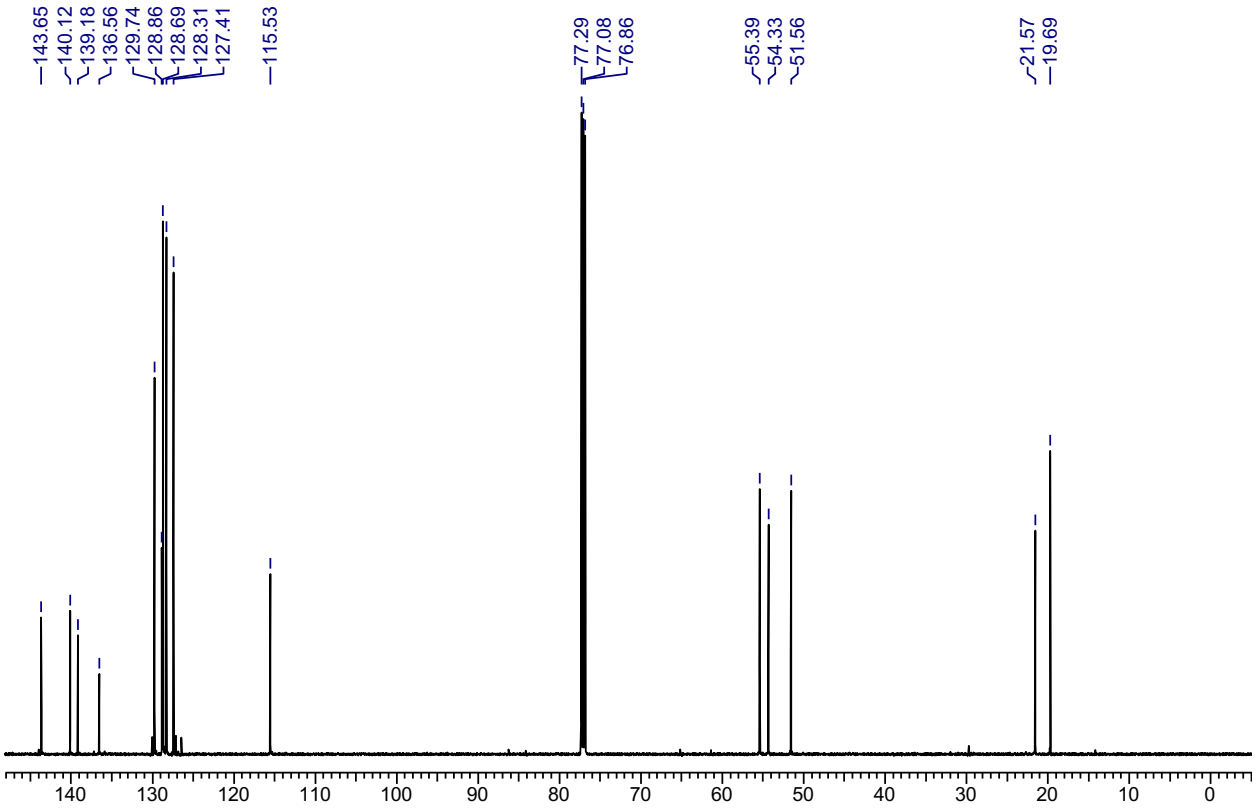
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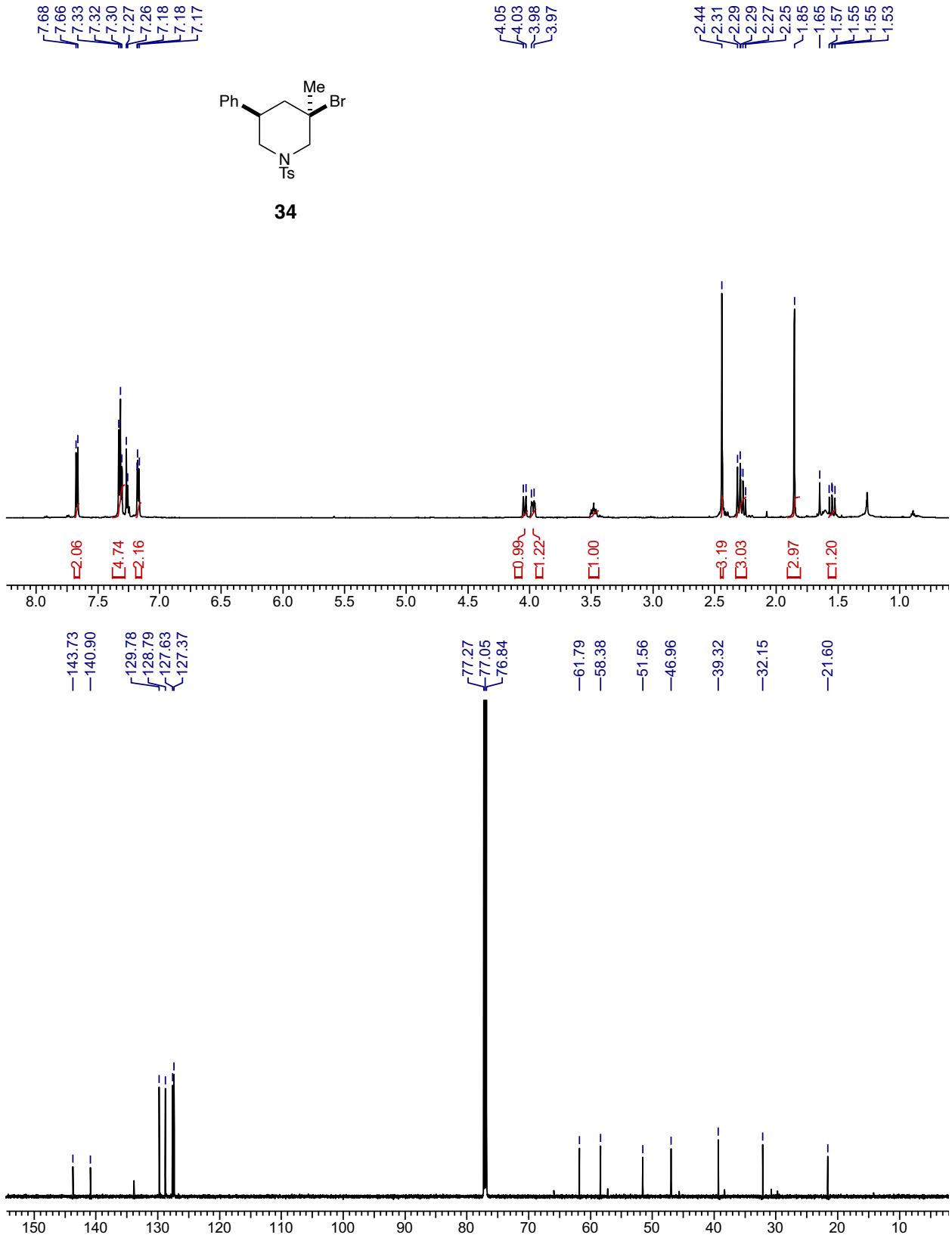
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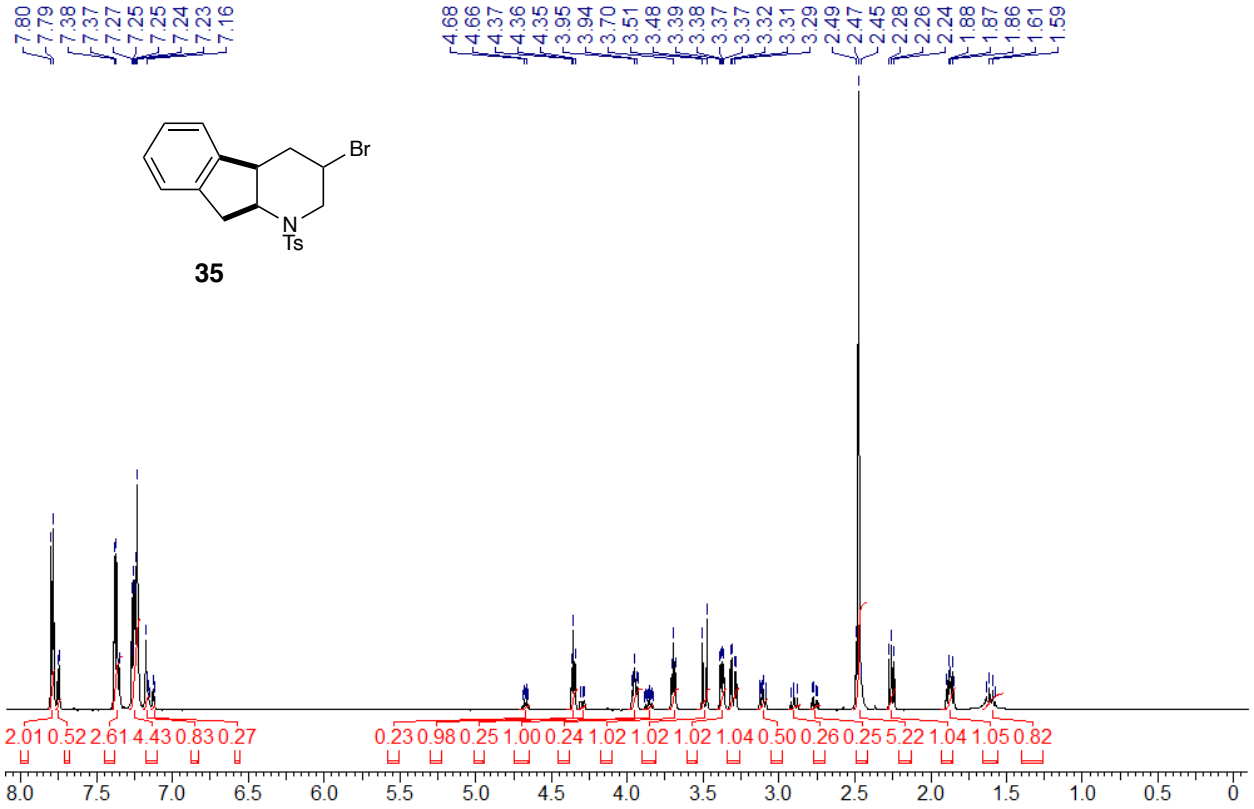
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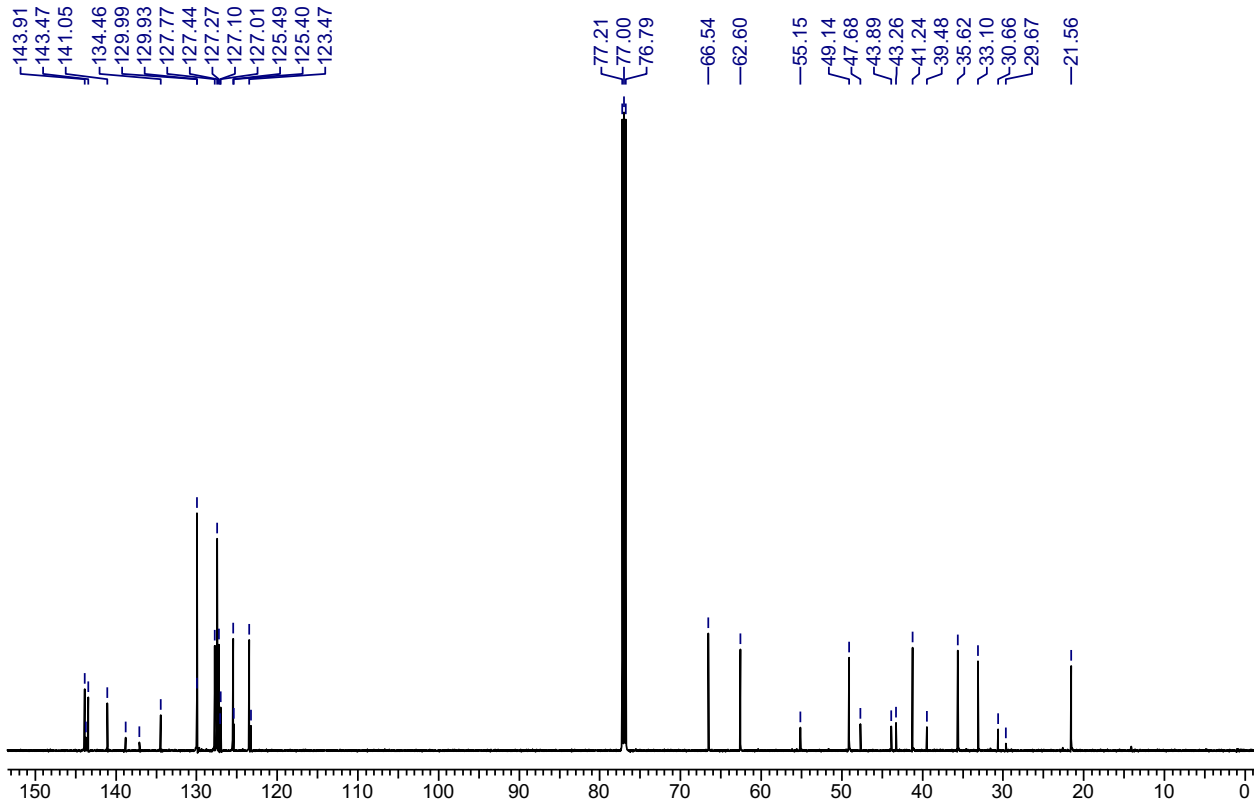
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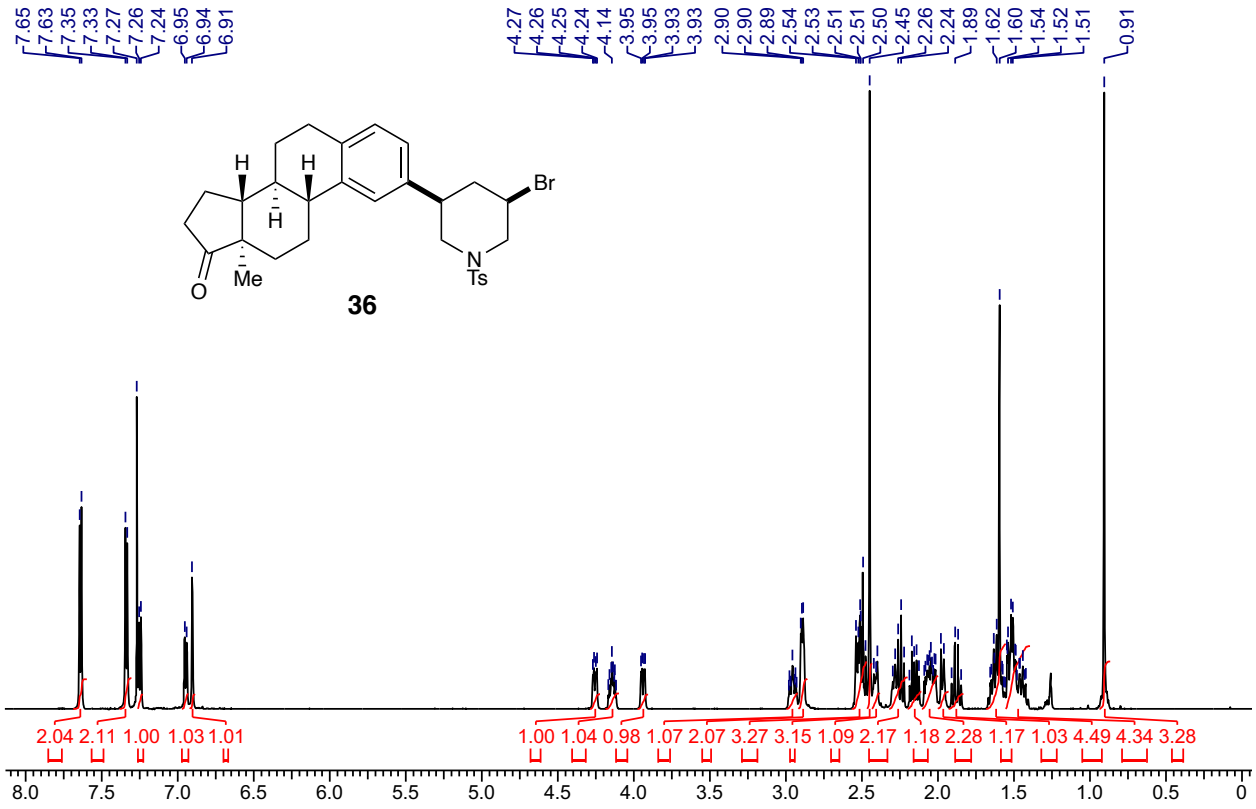
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H
H
Br
N
Ts
Me
O
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1.00 1.04 0.98 1.07 2.07 3.27 3.15 1.09 2.17 1.18 2.28 1.17 1.03 4.49 4.34 3.28
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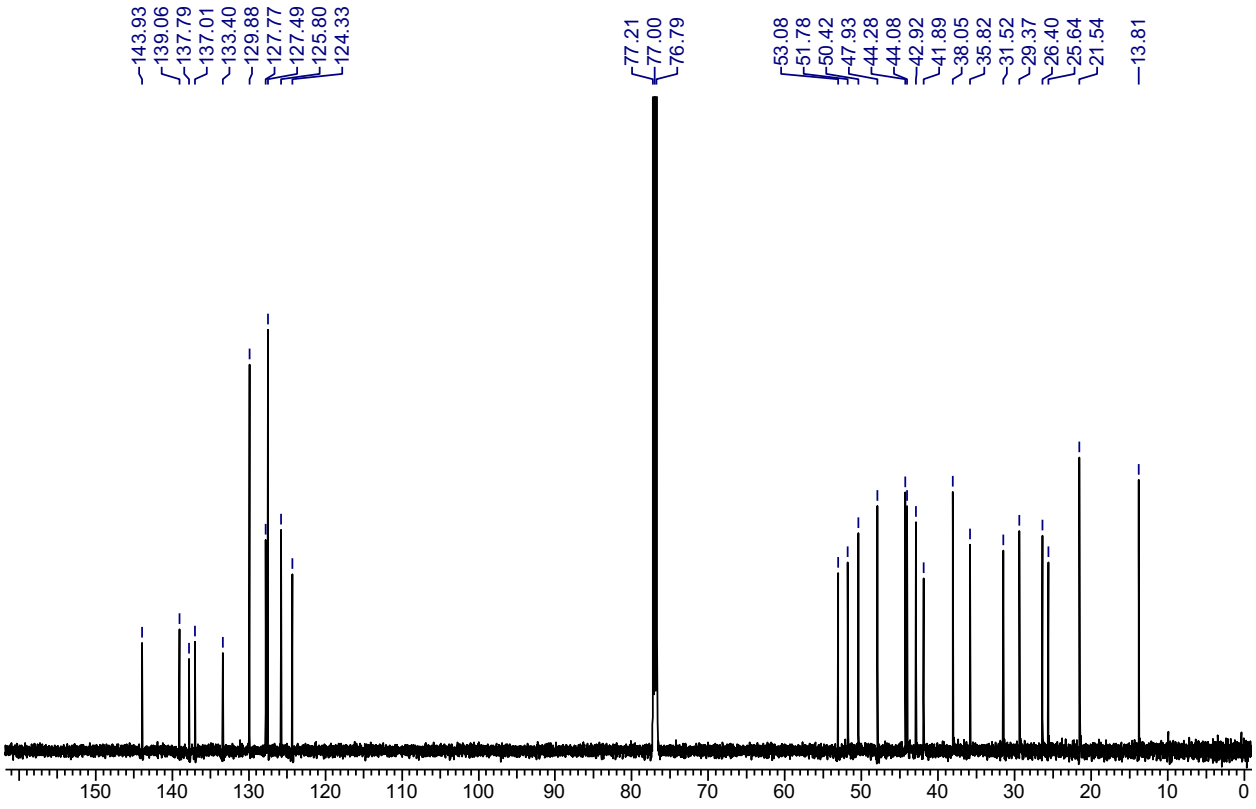
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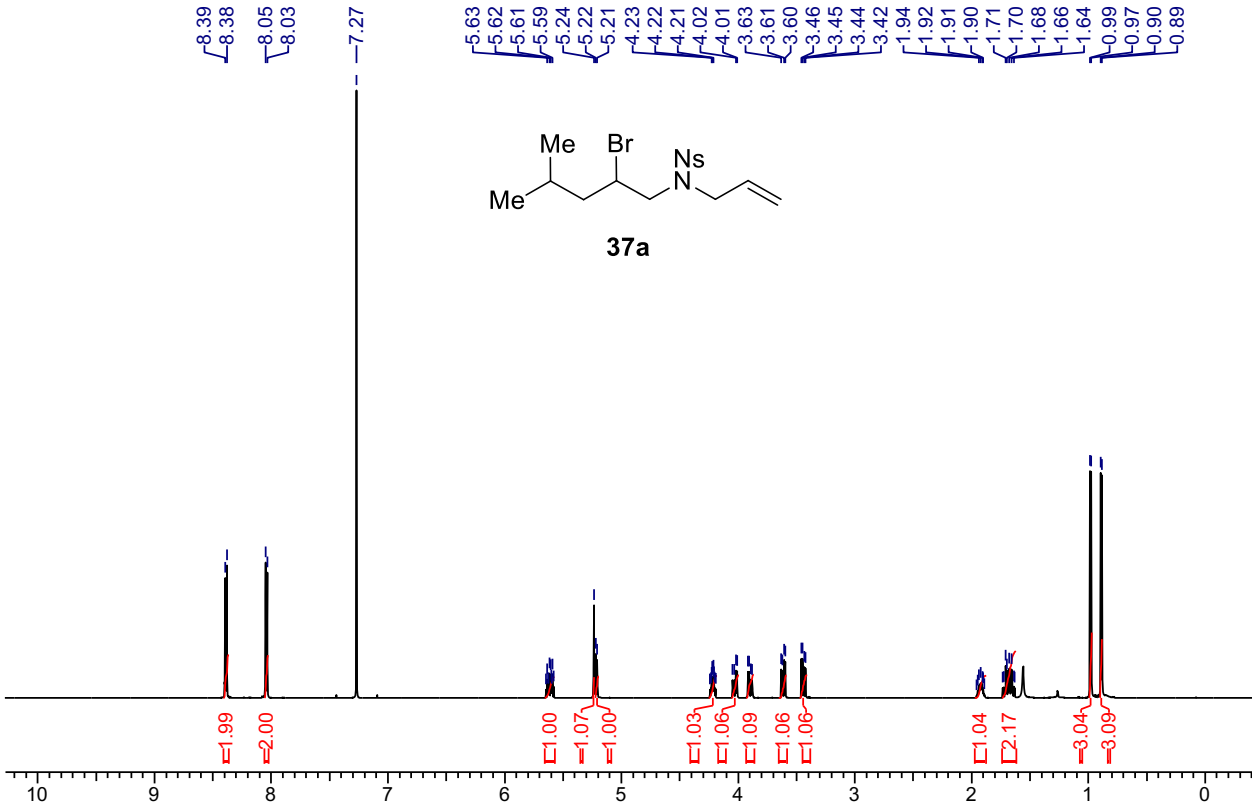
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1.09
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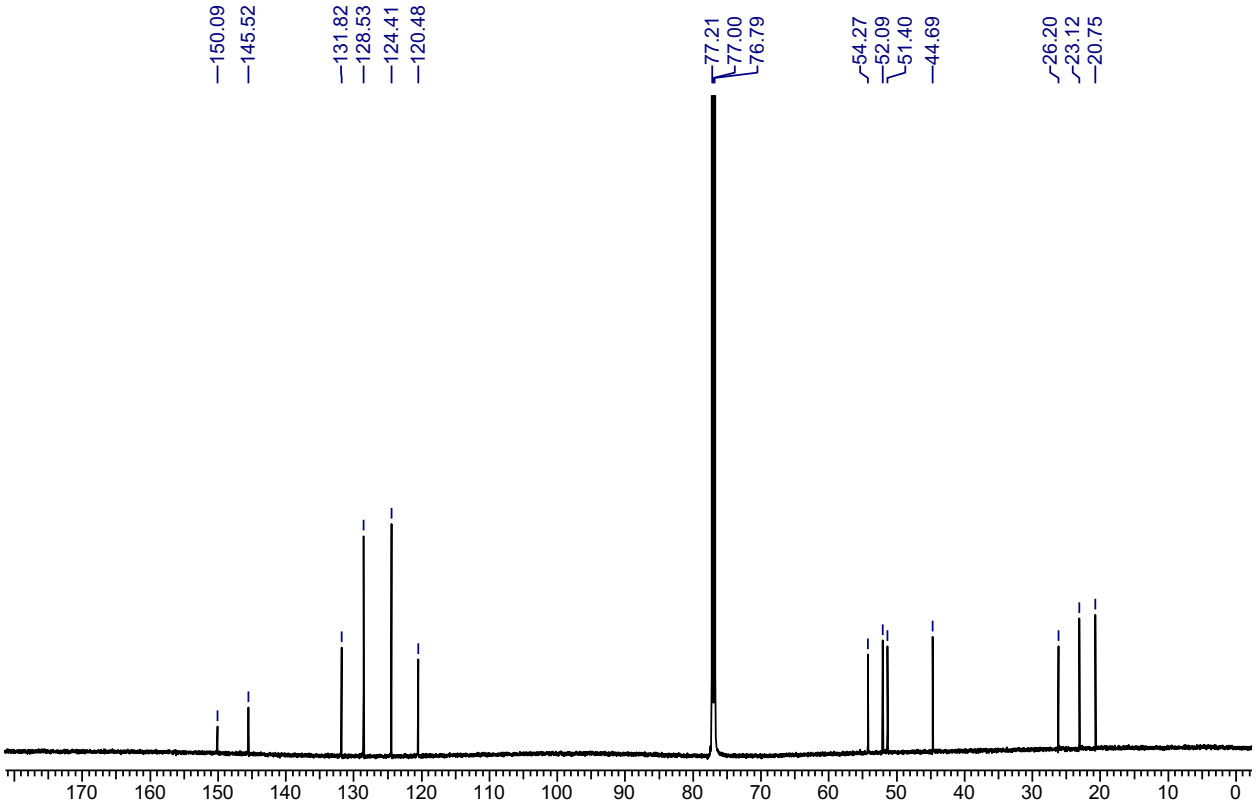
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23.12
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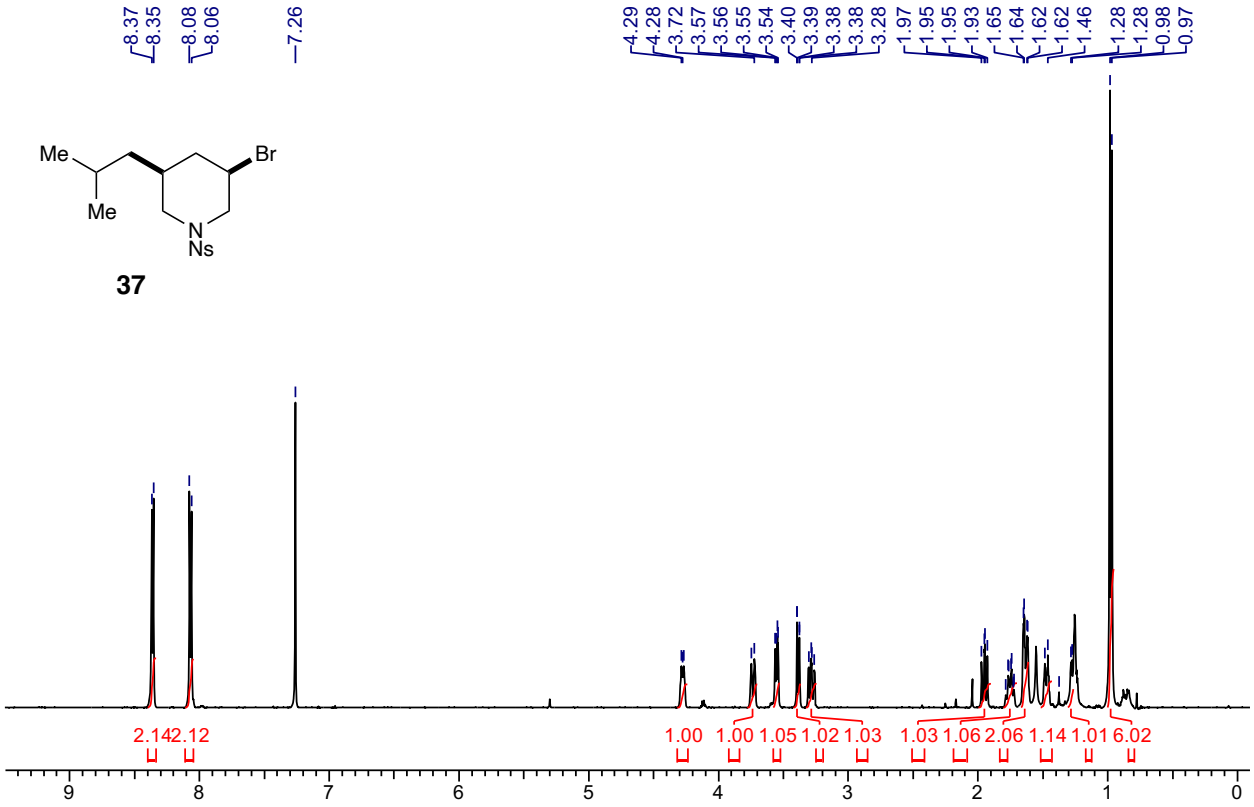
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Me
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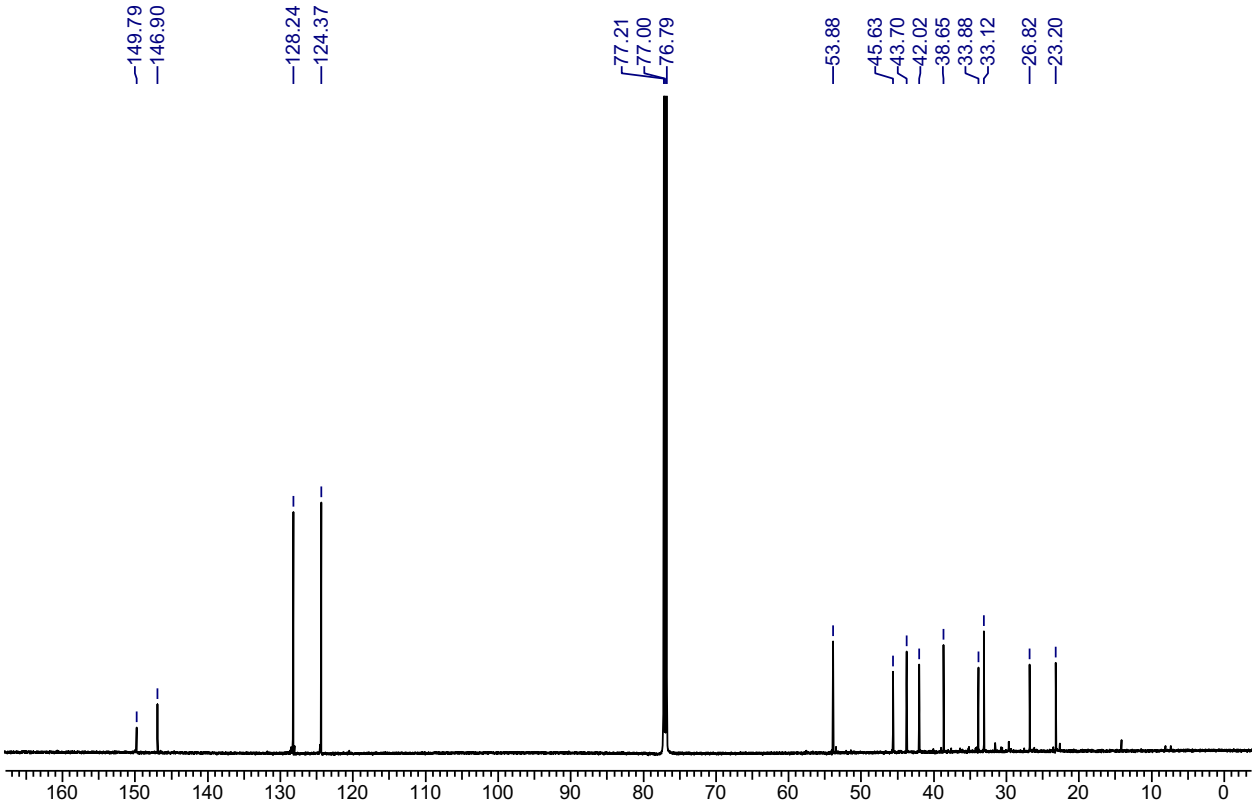
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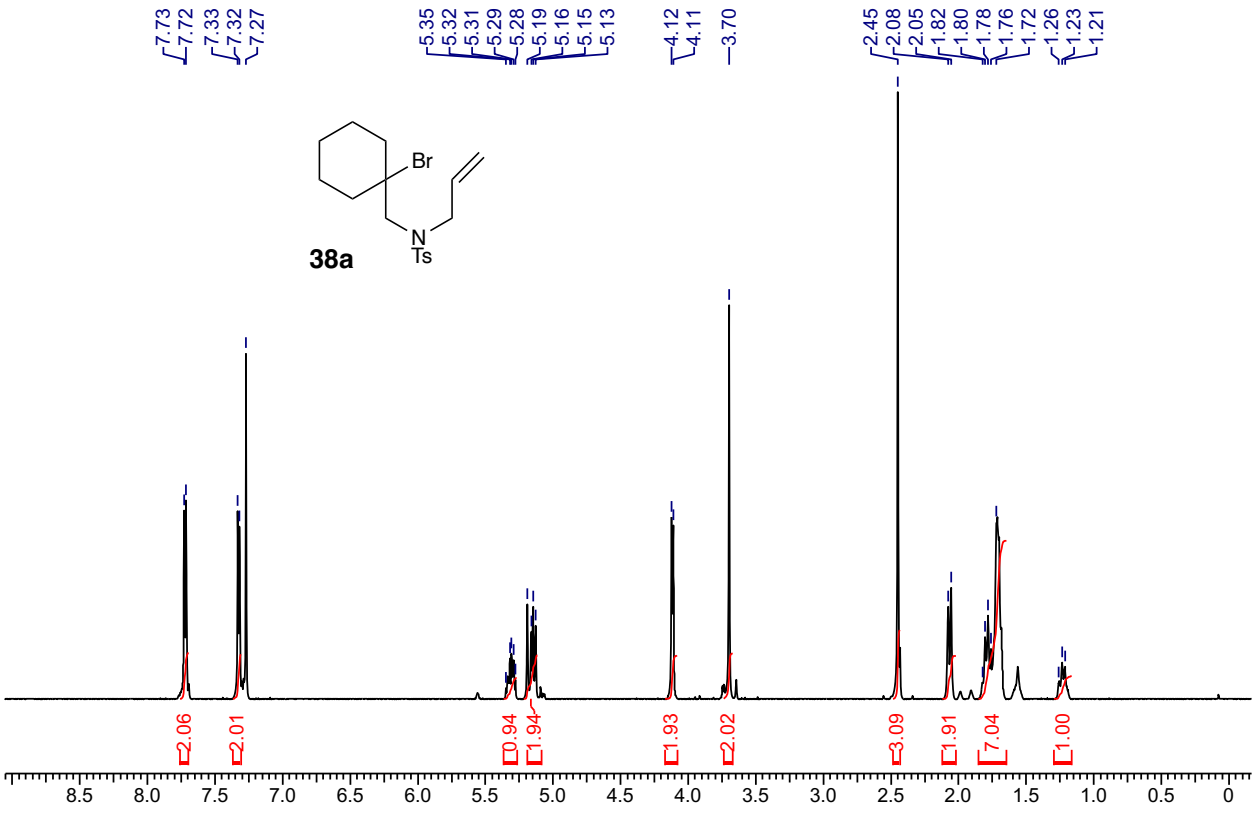
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5.13
4.12
4.11
3.70
2.45
2.08
2.05
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1.80
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1.76
1.72
1.26
1.23
1.21
Br
N
Ts
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2.01
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1.94
1.93
2.02
3.09
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7.04
1.00
8.5
8.0
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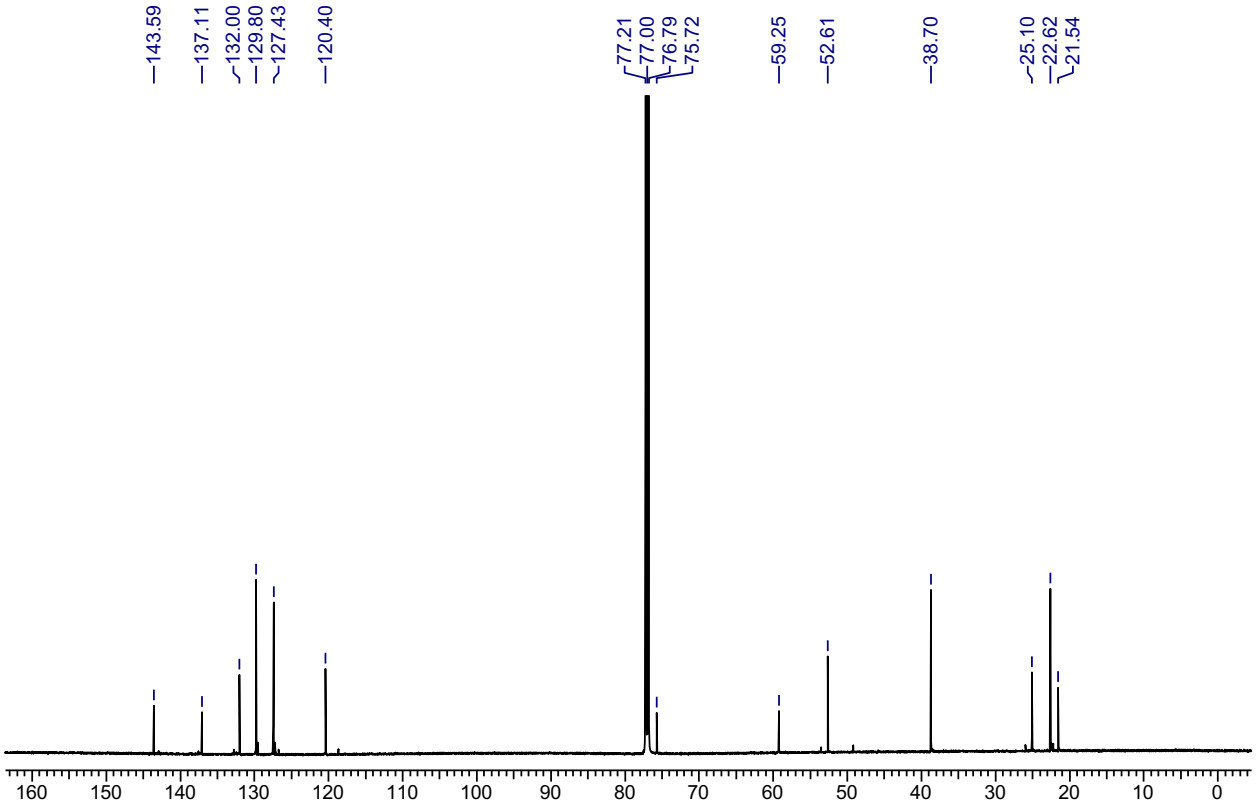
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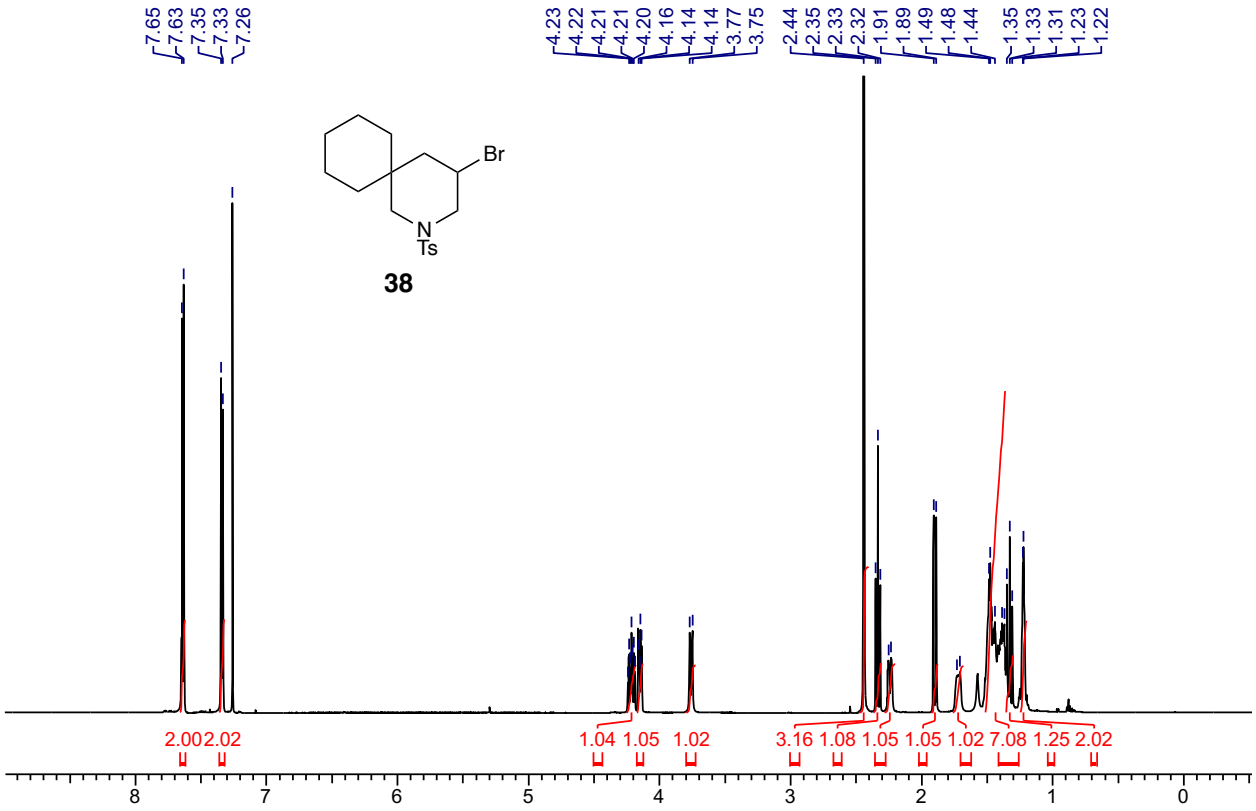
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2.32
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1.89
1.49
1.48
1.44
1.35
1.33
1.31
1.23
1.22
Br
N
Ts
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2.00 2.02
1.04 1.05 1.02
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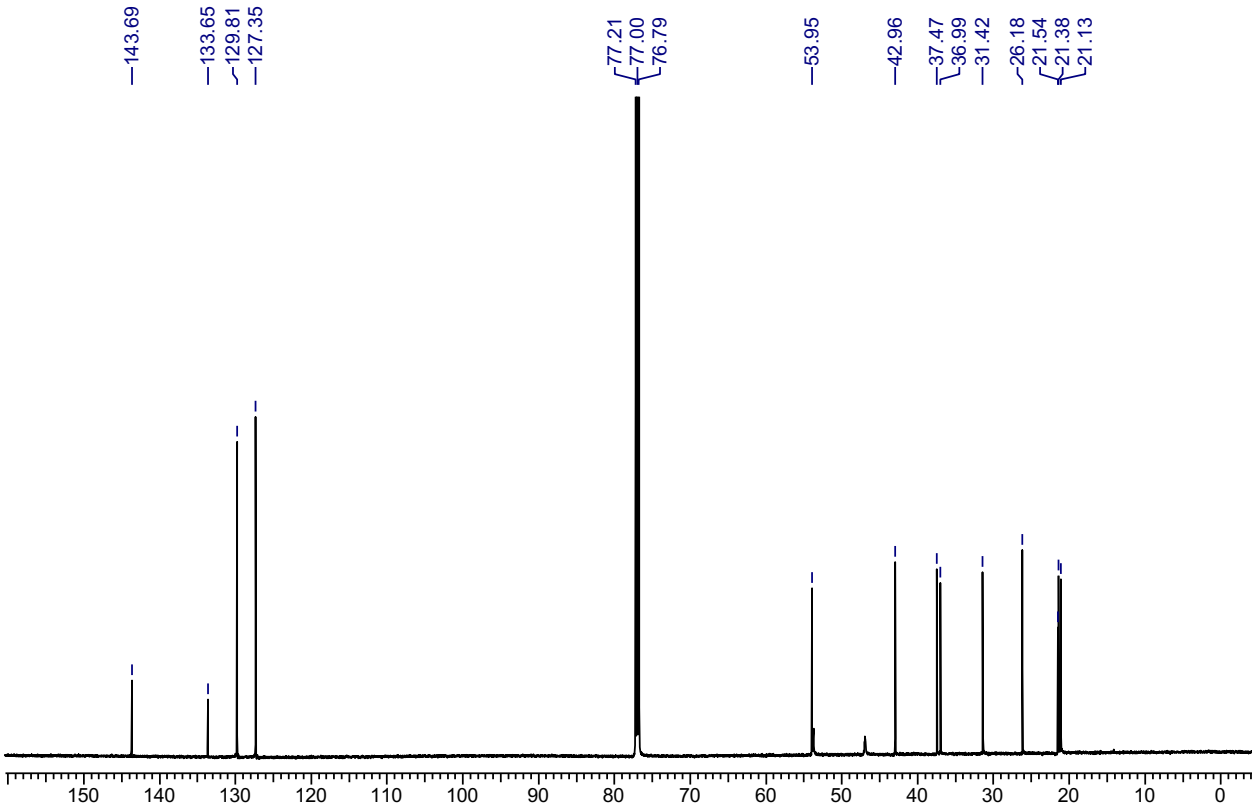
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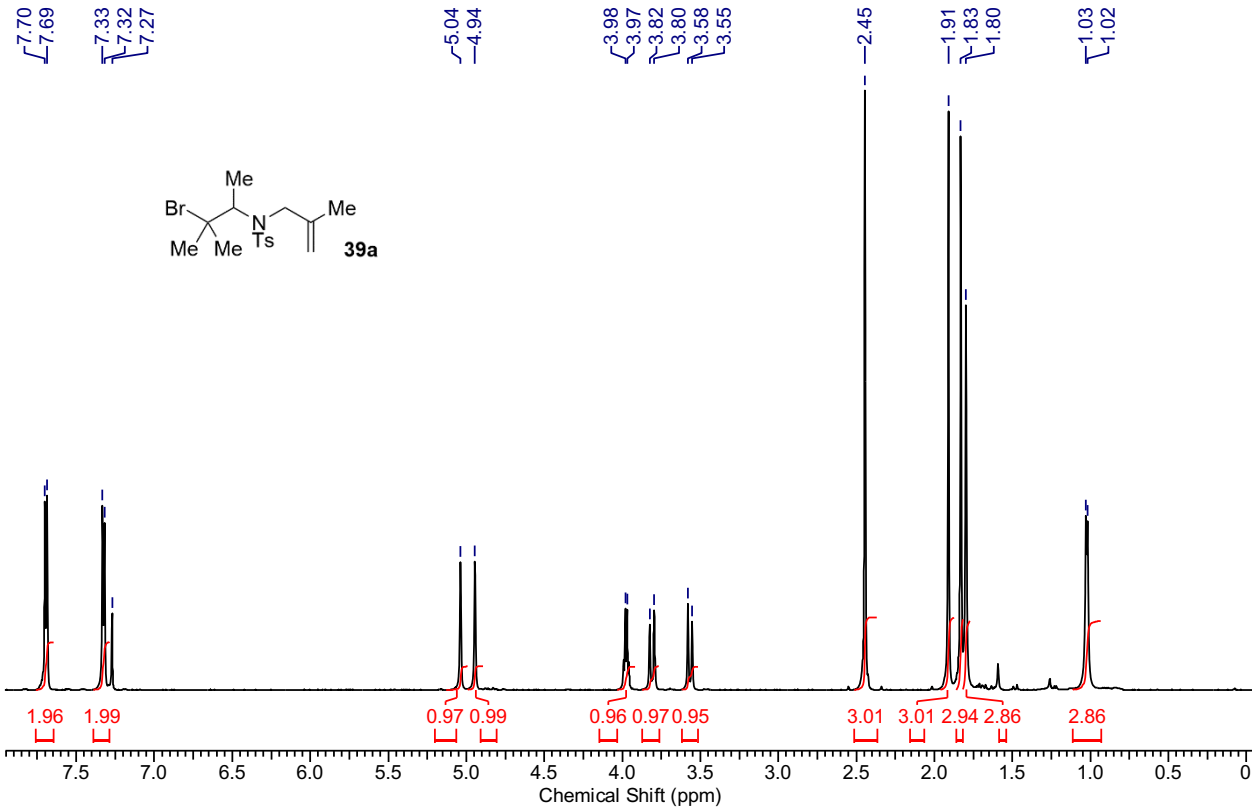
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1.03
1.02
Me
Br
N
Ts
Me
Me
Me
39a
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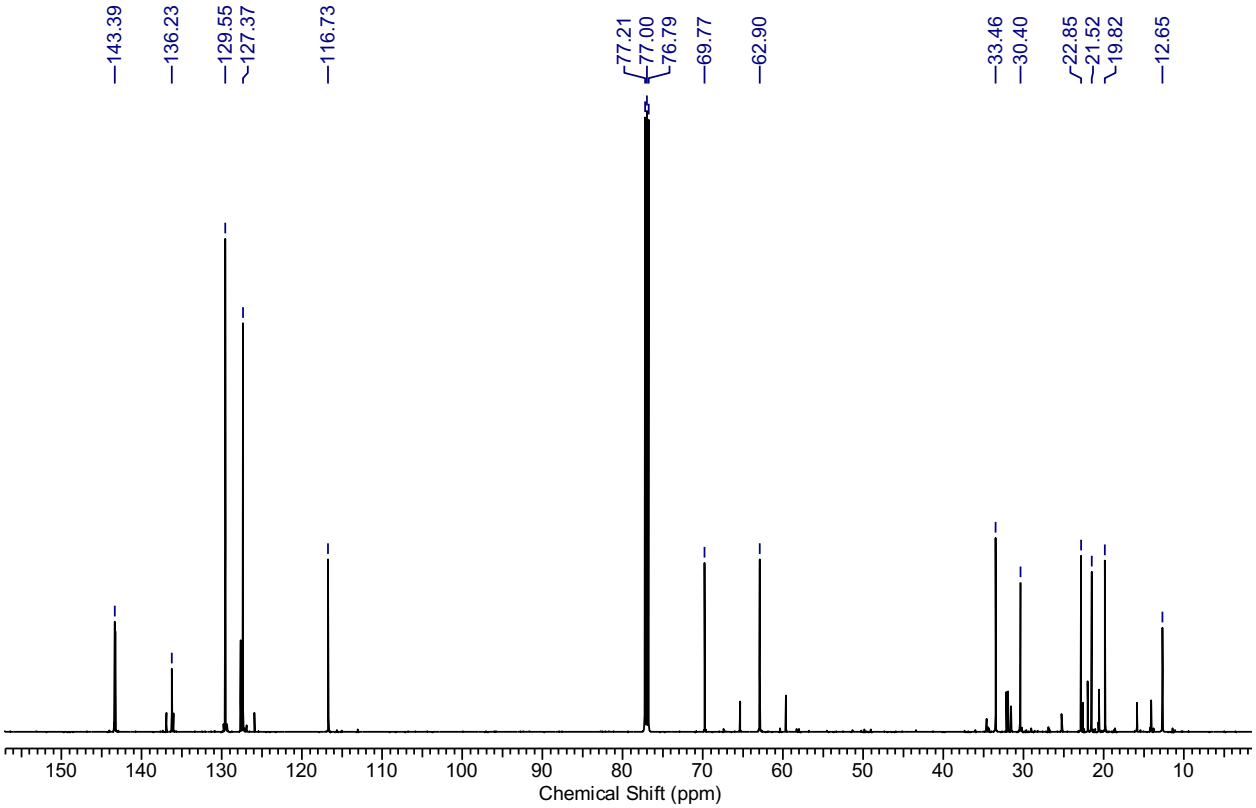
0.96
0.97
0.95
3.01
3.01
2.94
2.86
2.86
Chemical Shift (ppm)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21.52
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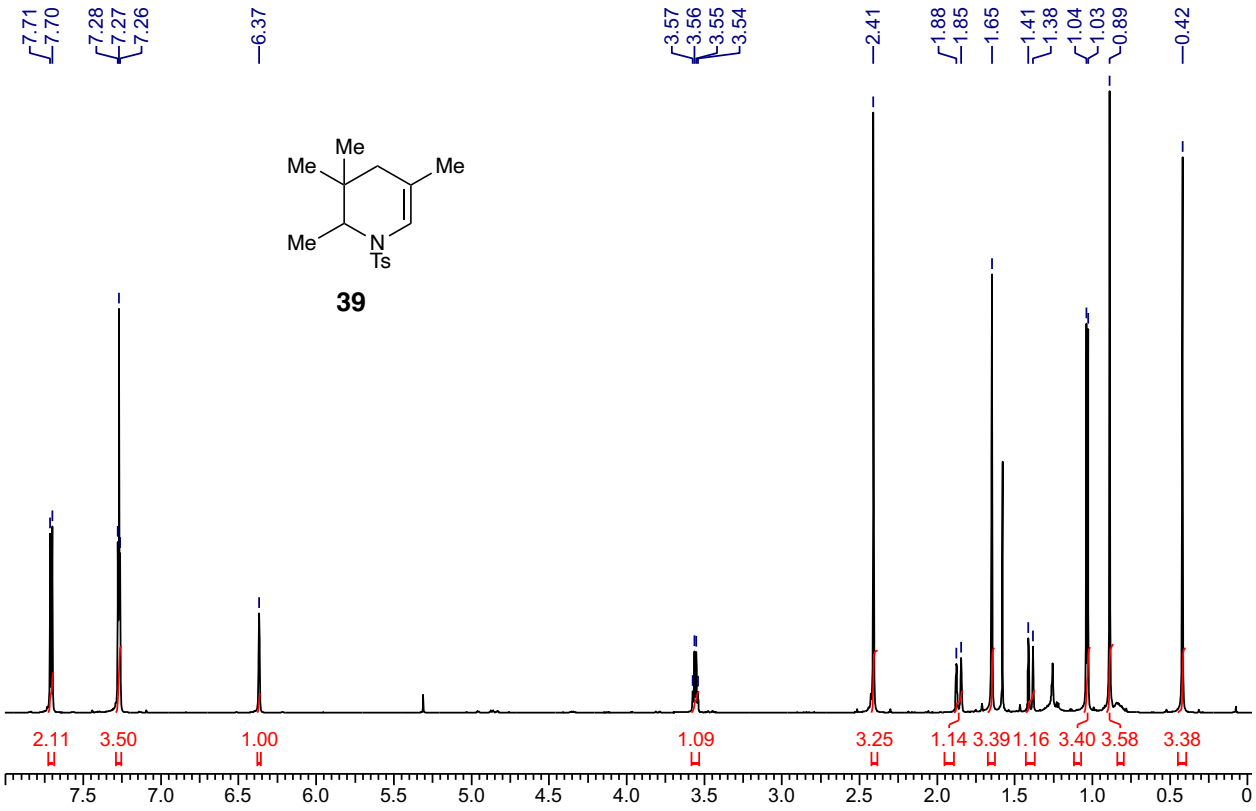
12.65
Chemical Shift (ppm)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Me
Me
Me
N
Ts
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3.39
1.16
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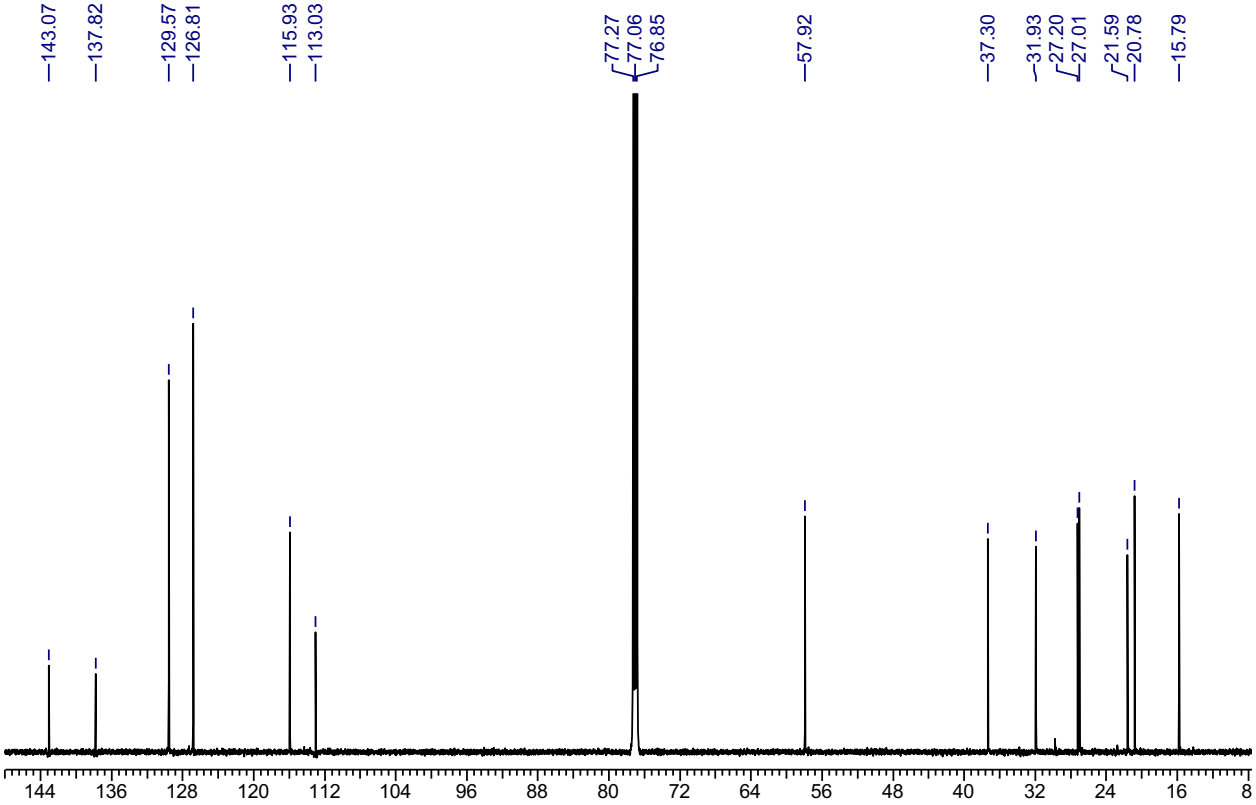
39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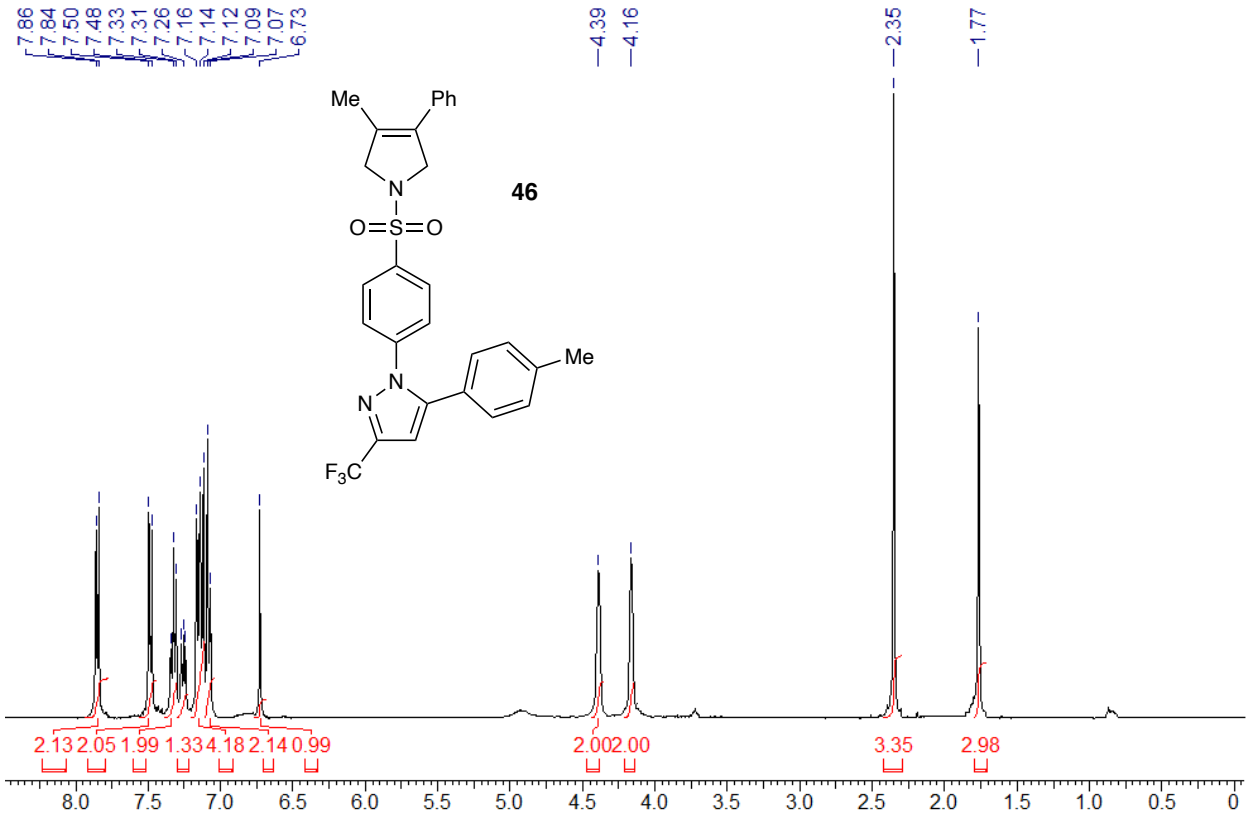
16
8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4.16
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Ph
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N
Me
F3C
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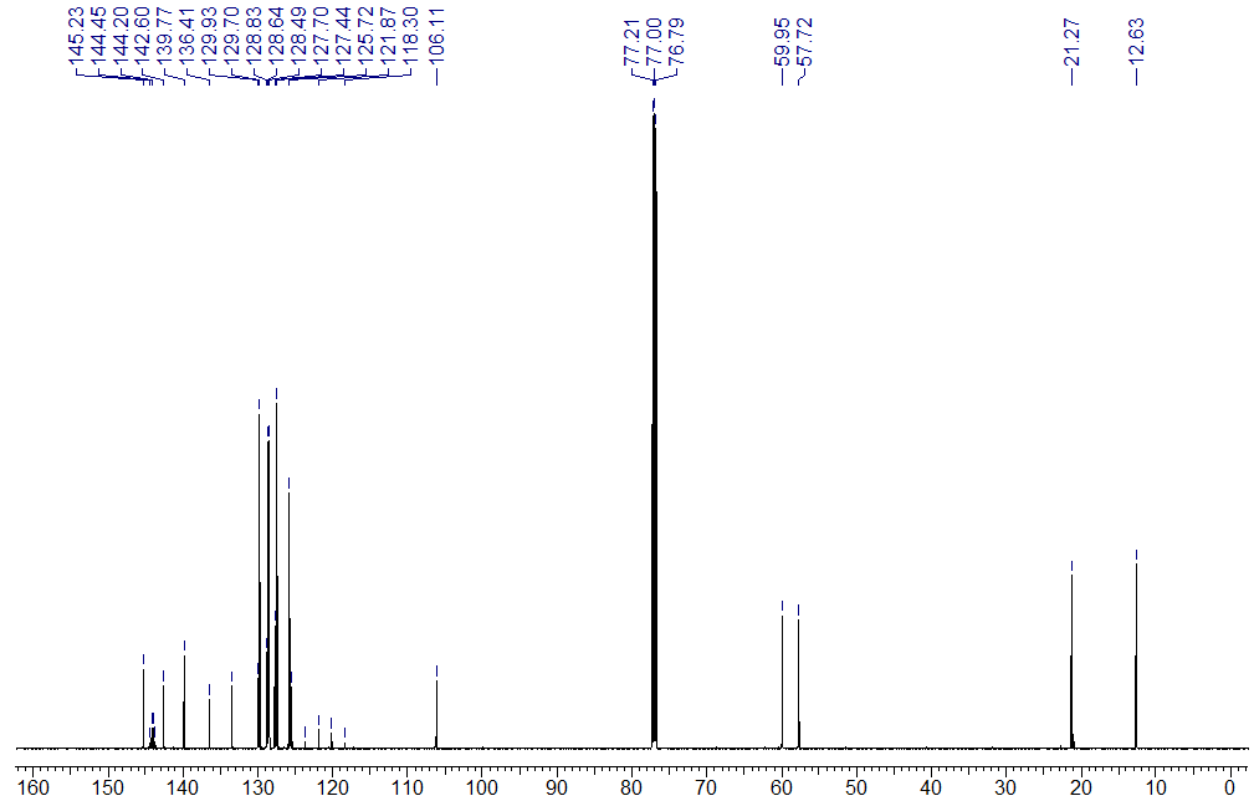
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121.87
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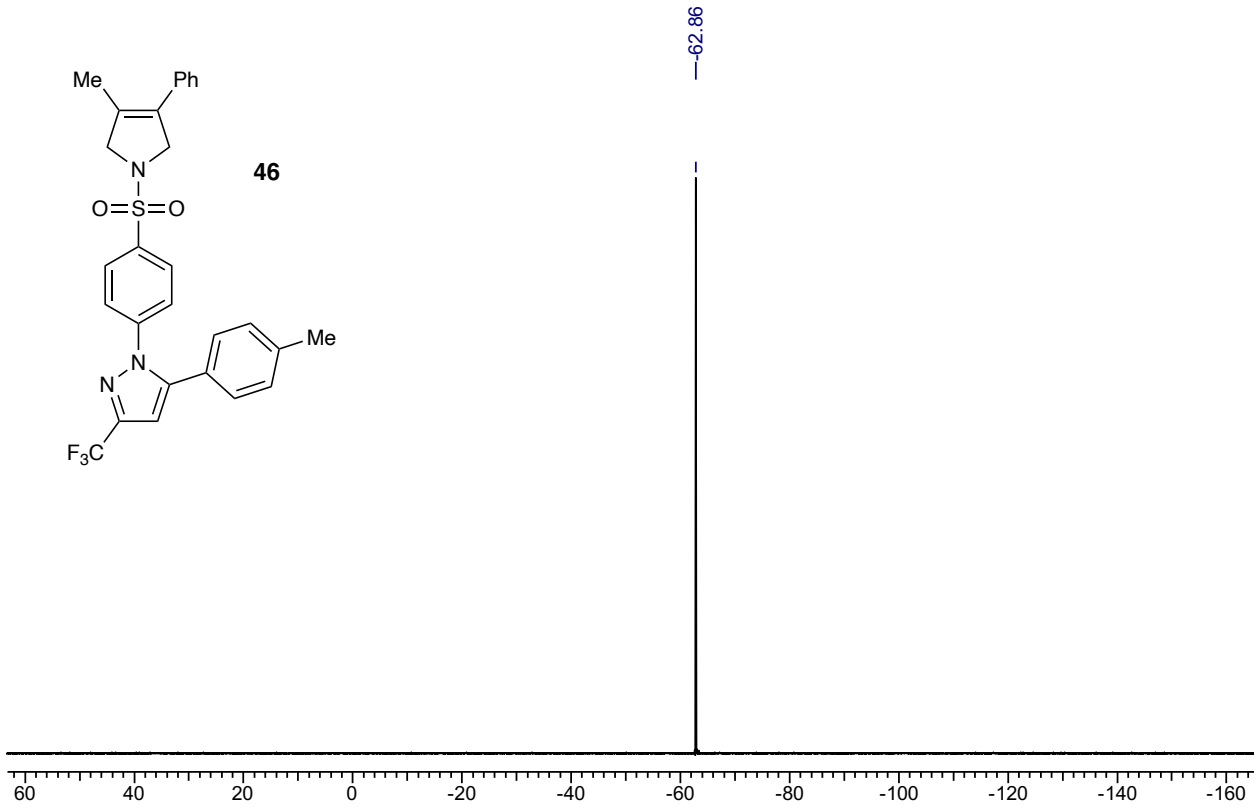
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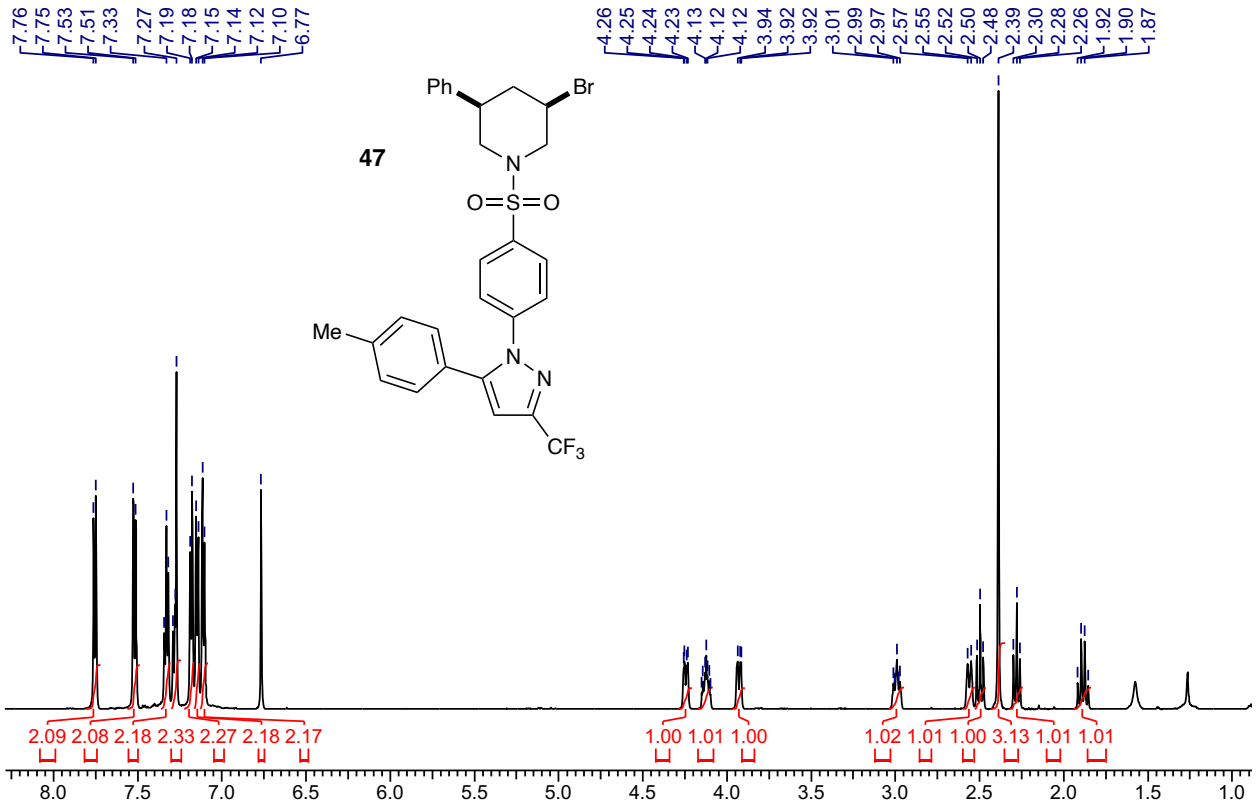
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1.87
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N
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1.02 1.01 1.00 3.13 1.01 1.01
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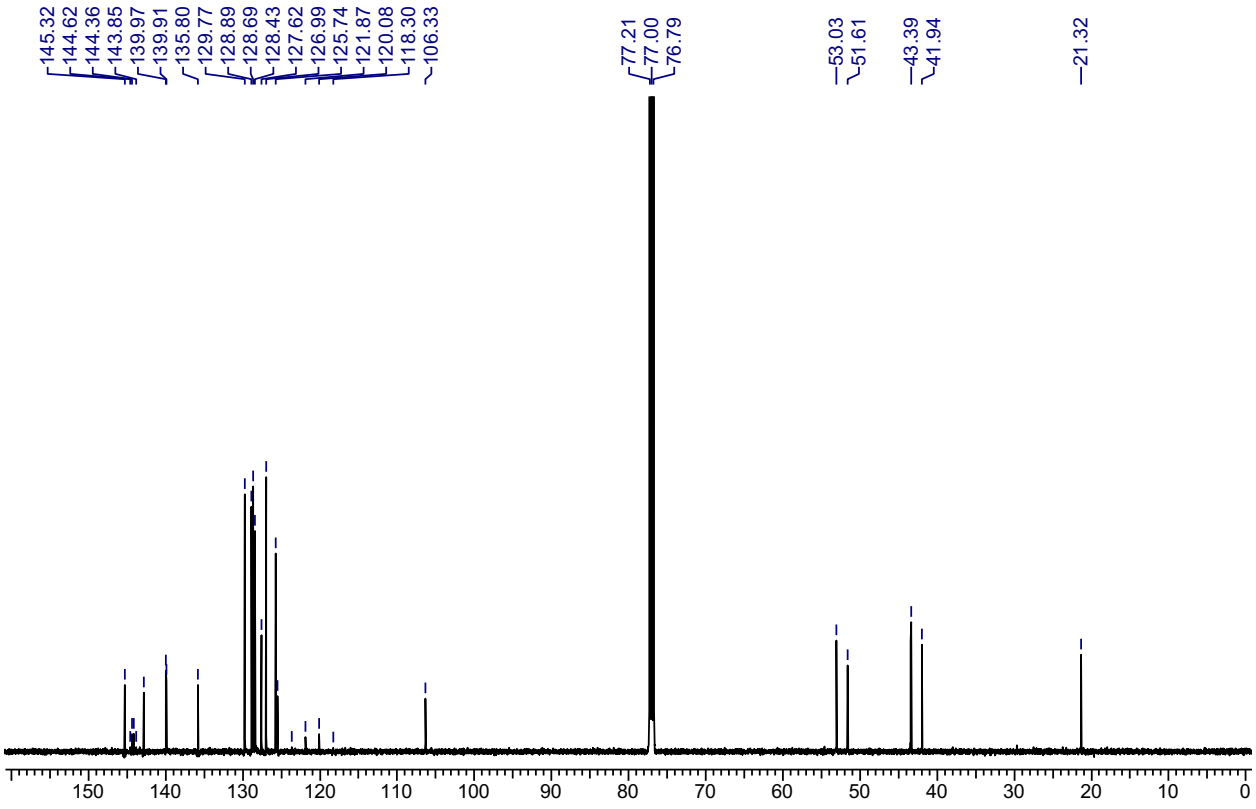
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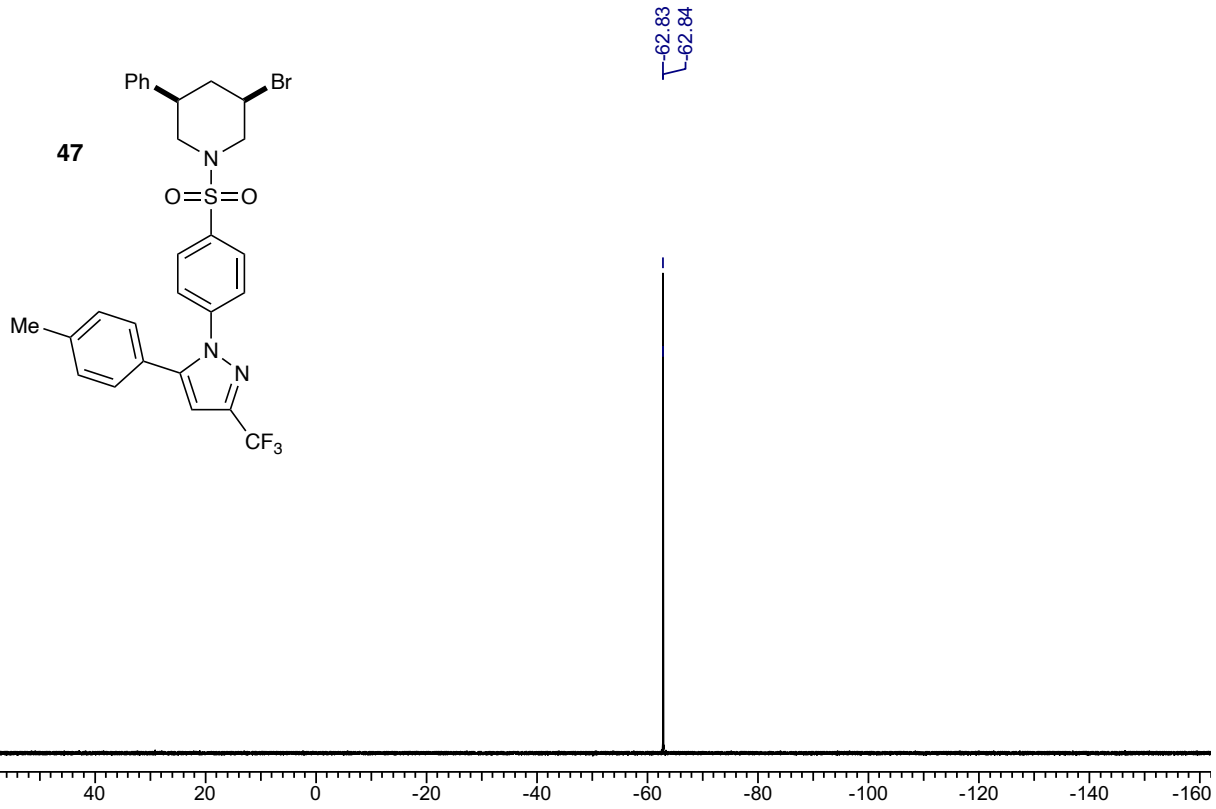
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