Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

NBS-Promoted Halosulfonylation of Terminal Alkynes: Highly Regio- and Stereoselective Synthesis of (E)-*β*-Halo Vinylsulfones

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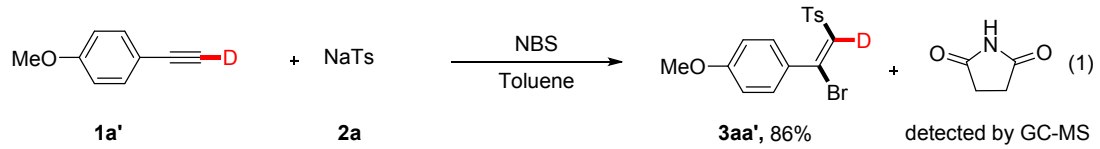
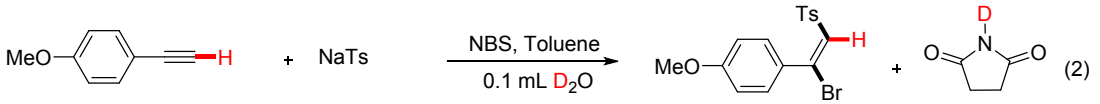
General Information

^{1}H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Gas chromatograph mass spectra were obtained with a SHIMADZU model GC-MS-QP5000 spectrometer. High-resolution mass spectra (ESI) were obtained with a LCMS-IT-TOF mass spectrometer. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification.

Control Experiments

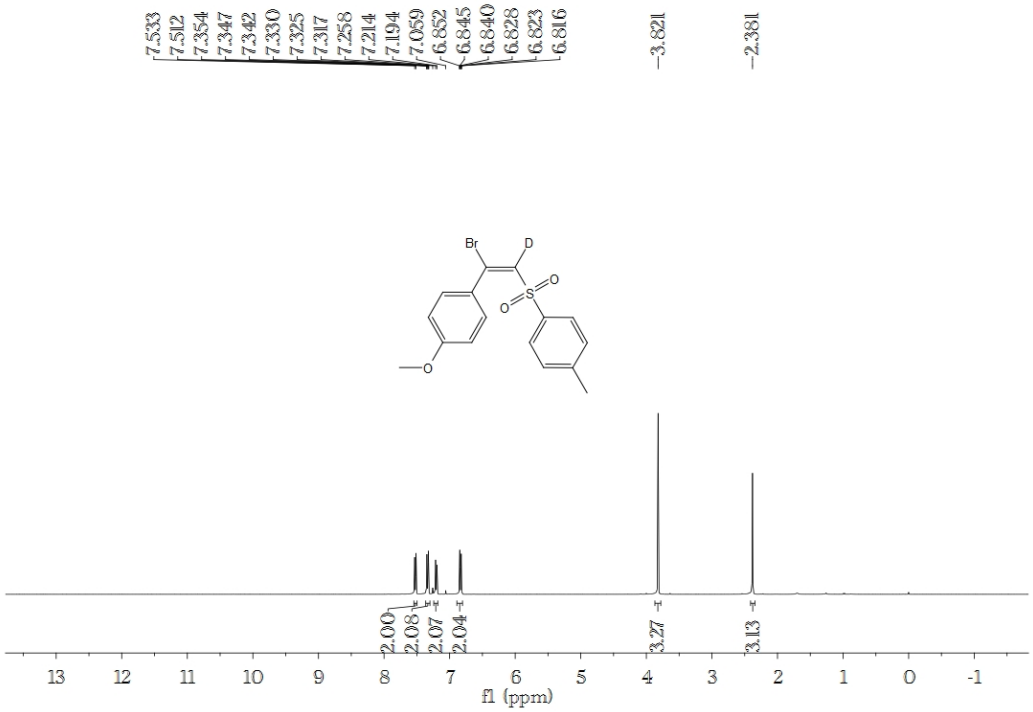


1a' **2a** **3aa',** 86% detected by GC-MS

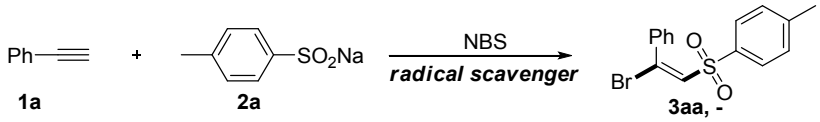


1a' **2a** **3aa,** 82% detected by GC-MS

First, two deuterated experiments were carried out to distinguish the hydrogen position of the terminal alkyne. As depicted in [eqn. (1)], deuterium product **3aa'** was obtained exclusively in 86% isolated yield and the deuterium atom (98% examined by ^{1}H NMR spectroscopy) was still present. When 0.1 mL D_2O was added, there was no deuterium in the halosulfonylation product and deuterium pyrrolidine-2,5-dione was detected by GC-MS [eqn. (2)].



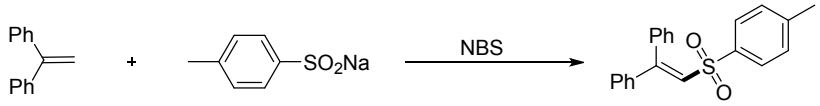
Radical-trapping Experiments[a]



1a **2a** **3aa**, -

Scavenger	Yield[b] (%)
none	88
TMEPO (1.2 equiv)	0
BHT (1.2 equiv)	0

[a] Radical-trapping experiments were carried out by adding 1.2 equiv radical scavengers TEMPO and BHT in the reaction system under the standard reaction condition. [b] Determined by GC based on **1a**. TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl. BHT = 2,6-di-tert-butyl-4-methylphenol.



1a' **2a** **5a**, 86%

When ethene-1,1-diyl dibenzene was employed as the substrate under the standard reaction conditions, (2-tosylethene-1,1-diyl)dibenzene was produced in good yield, thus providing an evidence for this radical process.

Analysis Data for Compounds 3aa-3ga, 4a-6a

(E)-1-(2-bromo-2-phenylvinylsulfonyl)-4-methylbenzene (3aa) [1]

white solid (142.8 mg, 85%); mp 97−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.36 (dd, *J* = 8.5, 4.1 Hz, 1H), 7.31 (d, *J* = 4.4 Hz, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.14 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 138.2, 137.3, 136.0, 134.2, 130.2, 129.6, 128.5, 127.8, 127.7, 21.48.

(E)-1-(2-bromo-2-(4-fluorophenyl)vinylsulfonyl)-4-methylbenzene (3ab) [1]

white solid (145.1 mg, 82%); mp 90−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.30 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.13 (s, 1H), 7.02 (t, *J* = 8.6 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, *J* = 250.5 Hz), 144.8, 137.2, 136.8, 134.5, 132.0 (d, *J*= 3.4 Hz), 130.9 (d, *J*= 8.8 Hz), 129.7, 127.77, 115.1 (d, *J*= 22 Hz), 21.5.

(E)-1-(2-bromo-2-(4-chlorophenyl)vinylsulfonyl)-4-methylbenzene (3ac) [1]

white solid (149.8 mg, 81%); mp 119−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.27 (m, 4H), 7.26 – 7.24 (m, 2H), 7.12 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.94, 137.28, 136.66, 136.53, 134.73, 134.47, 130.03, 129.79, 128.30, 127.82, 21.63.

(E)-1-bromo-4-(1-bromo-2-tosylvinyl)benzene (3ad) [1]

white solid (165.6 mg, 80%); mp 133−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.22 (tt, *J* = 4.1, 2.6 Hz, 4H), 7.12 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 137.2, 136.5, 134.9, 134.8, 131.2, 130.2, 129.8, 127.8, 125.0, 21.6.

(E)-1-(2-bromo-2-p-tolylvinylsulfonyl)-4-methylbenzene (3ae) [1]

white solid (154.0 mg, 88%); mp 121−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.08 (s, 1H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 140.9, 138.6, 137.6, 133.6, 133.2, 129.6, 128.76, 128.6, 127.8, 21.6, 21.4.

(E)-1-(2-bromo-2-(4-tert-butylphenyl)vinylsulfonyl)-4-methylbenzene (3af)

white solid (156.8 mg, 80%); mp 107−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.26 – 7.22 (m, 2H), 7.14 (t, *J* = 4.0 Hz, 3H), 2.37 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 144.3, 138.6, 137.4, 134.2, 133.0, 129.4, 128.6, 127.8, 124.9, 34.8, 31.2, 21.5. IR (KBr, cm^{-1}): 3046, 2961, 1601, 1320, 1149, 828, 651, 555; ESI-HRMS calcd for $C_{19}H_{21}BrO_2S$ $(M + Na)^+$ 415.0338; found, 415.0336.

(E)-1-methoxy-4-(2-tosylvinyl)benzene (3ag) [1]

white solid (150.1 mg, 82%); mp 110−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.06 (s, 1H), 6.86 – 6.83 (m, 2H), 3.84 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 144.5, 138.6, 137.7, 133.1, 130.8, 129.6, 128.2, 127.7, 113.3, 55.4, 21.6.

(E)-4-(1-bromo-2-tosylvinyl)biphenyl (3ah)

white solid (173.0 mg, 84%); mp 123−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 2H), 7.56 – 7.51 (m, 4H), 7.46 (dd, *J* = 10.2, 4.7 Hz, 2H), 7.40 (dd, *J* = 7.7, 5.9 Hz, 3H), 7.19 (t, *J* = 6.6 Hz, 2H), 7.16 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 143.3, 139.9, 138.0, 137.4, 134.8, 134.3, 133.2, 129.6, 129.2, 128.9, 127.8, 127.1, 126.5, 21.6. IR (KBr, cm^{-1}): 3047, 2924, 2177, 1600, 1485, 1324, 1152, 1085, 760, 551; ESI-HRMS calcd for $C_{21}H_{17}BrO_2S$ $(M + Na)^+$ 435.0025; found, 435.0019.

(E)-1-(1-bromo-2-tosylvinyl)-3-methylbenzene (3ai)

white solid (150.5 mg, 86%); mp 102−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.16 (m, 4H), 7.12 (t, *J* = 3.4 Hz, 2H), 7.02 (s, 1H), 2.39 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 138.6, 137.7, 136.0, 134.3, 131.1, 129.5, 128.9, 127.9, 127.8, 125.7, 21.5, 21.2. IR (KBr, cm^{-1}): 3046, 1594, 1322, 1149, 1085, 930, 793, 694, 553; ESI-HRMS calcd for $C_{16}H_{15}BrO_2S$ $(M + Na)^+$ 372.9868; found, 372.9864.

(E)-1-(1-bromo-2-(phenylsulfonyl)vinyl)-2,4-dimethylbenzene (3aj)

white solid (145.6 mg, 80%); mp 97−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.21 – 7.16 (m, 3H), 6.98 – 6.92 (m, 3H), 2.40 (s, 3H), 2.34 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 140.3, 138.8, 137.3, 135.3, 132.7, 130.9, 129.9, 129.5, 127.9, 127.2, 126.2, 21.6, 21.3, 19.1. IR (KBr, cm^{-1}): 3045, 2357, 2169, 1605, 1449, 1325, 1150, 1084, 814, 550; ESI-HRMS calcd for $C_{17}H_{17}BrO_2S$ $(M + Na)^+$ 387.0025; found, 387.0022.

(E)-3-(1-bromo-2-tosylvinyl)pyridine (3ak)

white solid (128.1 mg, 76%); mp 115−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 36.1 Hz, 2H), 7.76 – 7.72 (m, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.35 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.24 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 148.3, 145.2, 137.1, 136.2, 135.9, 134.0, 130.0, 127.8, 122.8, 21.63. IR (KBr, cm^{-1}): 3049, 2358, 2170, 1605, 1450, 1318, 1150, 1086, 815, 552; ESI-HRMS calcd for $C_{14}H_{12}BrNO_2S$ $(M + H)^+$ 337.9845; found, 337.9836.

(E)-1-(2-bromooct-1-enylsulfonyl)-4-methylbenzene (3al) [1]

colorless oil (132.4 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.75 (s, 1H), 3.10 – 2.90 (m, 2H), 2.45 (s, 3H), 1.58 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.39 – 1.20 (m, 6H), 0.90 (dd, *J* = 9.3, 4.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 144.8, 138.2, 132.1, 130.0, 127.4, 36.8, 31.4, 28.4, 28.3, 22.4, 21.6, 14.0.

(E)-5-bromo-6-tosylhex-5-enenitrile (3am)

colorless oil (140.6 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.83 (s, 1H), 3.26 – 3.18 (m, 2H), 2.48 – 2.44 (m, 5H), 2.04 (p, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 142.3, 137.6, 134.0, 130.2, 127.5, 118.8, 35.6, 24.3, 21.7, 16.2. IR (KBr, cm^{-1}): 3045, 2357, 2169, 1605, 1419, 1270, 1148, 1079, 754, 545; ESI-HRMS calcd for $C_{13}H_{14}BrNO_2S$ $(M + Na)^+$ 349.9821; found, 349.9816.

(E)-(2-bromo-2-cyclohexylvinylsulfonyl)benzene (3an)

colorless oil (138.5 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 3.56 (ddd, *J* = 10.6, 7.1, 3.5 Hz, 1H), 2.45 (s, 3H), 1.80 – 1.65 (m, 4H), 1.51 (s, 1H), 1.44 – 1.35 (m, 4H), 1.22 – 1.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 144.7, 138.5, 131.3, 130.0, 127.4, 42.4, 31.2, 25.3, 25.1, 21.6. IR (KBr, cm^{-1}): 2929, 2856, 2357, 1758, 1596, 1450, 1321, 1148, 1072, 813, 549; ESI-HRMS calcd for $C_{15}H_{19}BrO_2S$ $(M + Na)^+$ 365.0181; found, 365.0170.

(E)-1-(2-bromo-4-phenylbut-1-enylsulfonyl)-4-methylbenzene (3ao)

colorless oil (160.1 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.23 (m, 7H), 6.72 (s, 1H), 3.39 (dd, *J* = 8.8, 6.7 Hz, 2H), 2.94 (dd, *J* = 8.7, 6.8 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 144.7, 139.5, 137.9, 132.5, 130.0, 128.7, 128.6, 127.4, 126.5, 38.6, 34.6, 21.6. IR (KBr, cm^{-1}): 3046, 2358, 2170, 1604, 1419, 1271, 1148, 1078, 754, 545; ESI-HRMS calcd for $C_{17}H_{17}BrO_2S$ $(M + Na)^+$ 387.0025; found, 387.0027.

(E)-(1-bromo-2-(phenylsulfonyl)vinyl)benzene (3ba) [1]

white solid (138.4 mg, 86%); mp 79−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.3, 0.9 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 3H), 7.34 – 7.29 (m, 4H), 7.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 138.8, 136.0, 134.2, 133.5, 130.4, 129.0, 128.6, 128.0, 127.8.

(E)-1-(2-bromo-2-phenylvinylsulfonyl)-4-fluorobenzene (3ca)

white solid (142.8 mg, 84%); mp 87−89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (ddd, *J* = 8.1, 5.0, 2.5 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.35 – 7.26 (m, 4H), 7.17 (s, 1H), 7.07 – 7.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 164.3, 139.0, 136.3, 136.3, 135.9, 134.2, 132.7, 130.7, 130.6, 130.5, 128.5, 128.1, 116.3, 116.1. IR (KBr, cm^{-1}): 3047, 2960, 1605, 1321, 1150, 820, 651, 555; ESI-HRMS calcd for $C_{14}H_{10}BrFO_2S$ $(M + Na)^+$ 362.9461; found, 362.9453.

(E)-1-(2-bromo-2-phenylvinylsulfonyl)-4-chlorobenzene (4da) [1]

white solid (142.4 mg, 80%); mp 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.42 – 7.34 (m, 2H), 7.33 – 7.28 (m, 3H), 7.17 (s, 1H), 7.07 – 7.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 135.9, 134.3, 130.7, 130.6, 130.5, 128.6, 128.1, 116.3, 116.1.

(E)-1-bromo-4-(2-bromo-2-phenylvinylsulfonyl)benzene (3ea) [1]

white solid (166.0 mg, 83%); mp 120−121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.43 – 7.37 (m, 3H), 7.36 – 7.31 (m, 2H), 7.28 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 139.3, 135.9, 134.0, 132.2, 130.6, 129.3, 128.9, 128.5, 128.1.

(E)-2-(2-bromo-2-phenylvinylsulfonyl)naphthalene (3fa)

white solid (158.1 mg, 85%); mp 104−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.3 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.59 – 7.54 (m, 1H), 7.32 – 7.19 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 136.9, 135.9, 135.0, 134.3, 131.9, 130.4, 129.8, 129.3, 129.3, 129.3, 128.5, 127.9, 127.8, 127.5, 122.3. IR (KBr, cm^{-1}): 3046, 2367, 2158, 1615, 1420, 1272, 1148, 1080, 754, 545; ESI-HRMS calcd for $C_{18}H_{13}BrO_2S$ $(M + Na)^+$ 394.9712; found, 394.9710.

(E)-2-(2-bromo-2-phenylvinylsulfonyl)thiophene (3ga)

white solid (134.5 mg, 82%); mp 85−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.42 – 7.35 (m, 5H), 7.33 – 7.30 (m, 1H), 7.22 (s, 1H), 6.98 (dd, *J* = 4.9, 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 139.0, 135.9, 134.4, 134.3, 134.2, 130.5, 128.5, 128.0, 127.6. IR (KBr, cm^{-1}): 3050, 2357, 1629, 1327, 1144, 1081, 1013, 872, 573; ESI-HRMS calcd for $C_{12}H_9BrO_2S$ $(M + Na)^+$ 350.9120; found, 350.9120.

(E)-1-(2-iodo-2-phenylvinylsulfonyl)-4-methylbenzene (4a)

white solid (168.9 mg, 88%); mp 90−92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.36 (s, 1H), 7.31 – 7.24 (m, 3H), 7.22 (dt, *J* = 8.2, 2.1 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 141.2, 139.6, 137.2, 129.7, 129.6, 127.8, 127.8, 127.6, 114.1, 21.5. IR (KBr, cm^{-1}): 3040, 2964, 16001, 1322, 1152, 823, 658, 556; ESI-HRMS calcd for $C_{15}H_{13}IO_2S$ $(M + Na)^+$ 406.9573; found, 406.9586.

(E)-1-chloro-4-(1-iodo-2-tosylvinyl)benzene (4b)

white solid (179.7 mg, 86%); mp 104−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.9 Hz, 2H), 7.35 (s, 1H), 7.30 – 7.17 (m, 4H), 6.97 (t, *J* = 8.4 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 161.8, 144.7, 141.5, 137.1, 135.6, 135.6, 129.9, 129.8, 129.6, 127.7, 115.1, 114.8, 112.5, 21.5. IR (KBr, cm^{-1}): 3040, 2958, 1590, 1327, 1150, 828, 651, 555; ESI-HRMS calcd for $C_{15}H_{12}ClIO_2S$ $(M + Na)^+$ 440.9183; found, 440.9211.

(E)-1-fluoro-4-(1-iodo-2-tosylvinyl)benzene (4c)

white solid (178.9 mg, 89%); mp 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.35 (s, 1H), 7.28 – 7.18 (m, 4H), 6.97 (t, *J* = 8.5 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, J = 294.8) 144.7, 141.5, 137.1, 135.6 (d, J = 3.4), 129.9 (d, J = 8.6), 129.6, 127.6, 115.0 (d, J = 2.2), 112.5, 21.5. IR (KBr, cm^{-1}): 3038, 2954, 1587, 1326, 1153, 827, 652, 558; ESI-HRMS calcd for $C_{15}H_{12}FIO_2S$ $(M + Na)^+$ 424.9478; found, 424.9475.

(E)-1-(1-iodo-2-tosylvinyl)-3,5-bis(trifluoromethyl)benzene (4d)

white solid (226.2 mg, 87%); mp 107−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.60 (s, 2H), 7.51 (s, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.49, 144.03, 141.55, 136.62, 131.5 (q, *J* = 33.7 Hz), 129.99, 127.7 (d, *J* = 3.6 Hz), 127.65, 122.7 (d, *J* = 271.3 Hz), 123.2 (m), 107.69, 21.51. IR (KBr, cm^{-1}): 3042, 2948, 1592, 1328, 1150, 828, 651, 556; ESI-HRMS calcd for $C_{15}H_{12}ClIO_2S$ $(M + Na)^+$ 542.9320; found, 542.9324.

(2-tosylethene-1,1-diyl)dibenzene (5a) [2]

colorless oil (74.3 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.88 (m, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.36 (dt, *J* = 7.0, 6.3 Hz, 4H), δ 7.20 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.09 (dd, *J* = 5.2, 3.3 Hz, 2H), 6.99 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 143.7, 139.2, 138.6, 135.5, 130.2, 129.7, 129.3, 128.9, 128.8, 128.5, 128.1, 127.7, 127.6, 21.47.

(E)-(4-tosylbut-3-en-1-yne-1,3-diyl)dibenzene (5b)

white solid (80.6 mg, 90%); mp 96−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.1 Hz, 2H), 7.47 – 7.33 (m, 8H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.99 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 137.9, 136.7, 135.3, 134.1, 131.8, 129.5, 129.4, 129.4, 128.9, 128.4,

127.8, 127.6, 121.4, 97.3, 88.3, 21.4. IR (KBr, cm^{-1}): 3046, 2961, 1601, 1320, 1149, 828, 651, 555; ESI-HRMS calcd for $C_{23}H_{18}O_2S$ $(M + Na)^+$ 381.0920; found, 381.0920.

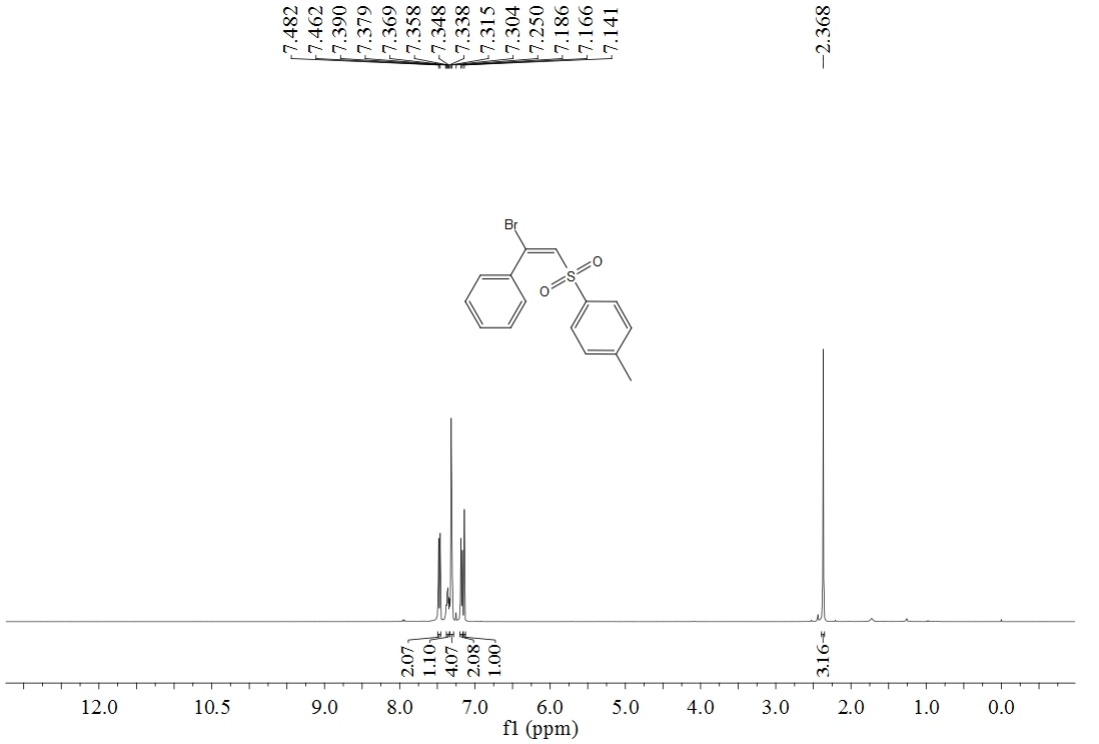
(E)-1-methyl-4-(styrylsulfonyl)benzene (6a) [2]

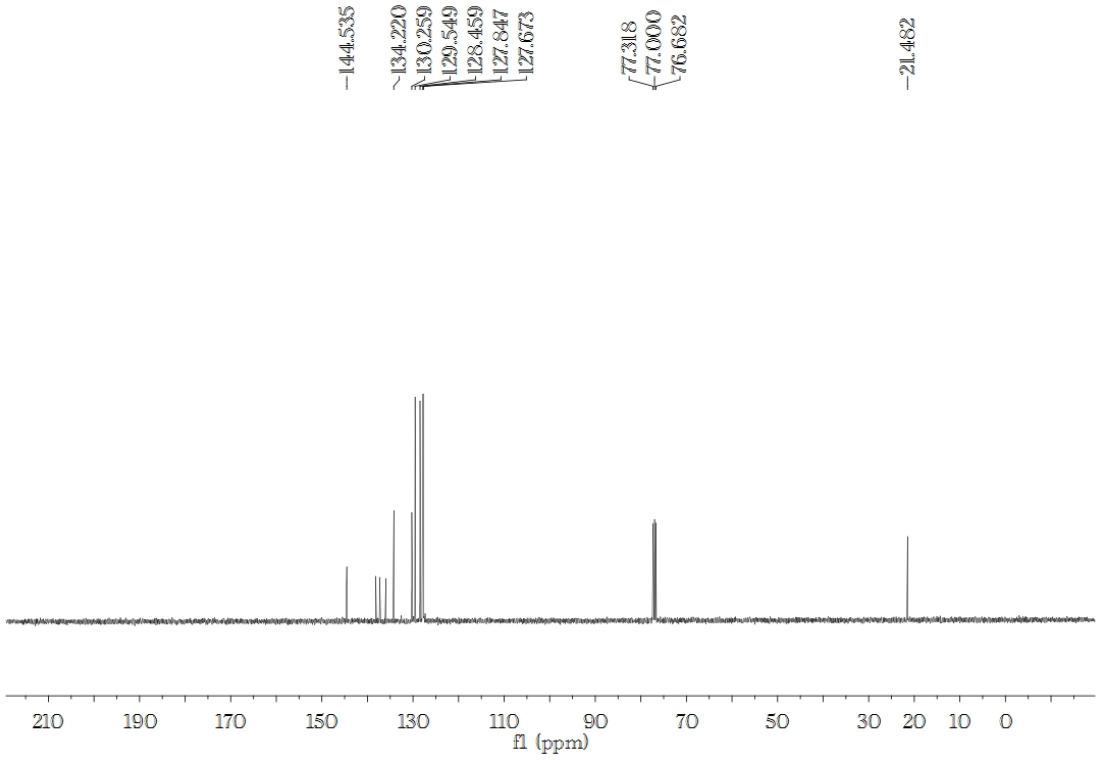
colorless oil (103.2 mg, 80%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 15.4 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.42 – 7.36 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 15.4 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 141.9, 137.7, 132.4, 131.0, 129.9, 129.0, 128.5, 127.7, 127.6, 21.55.

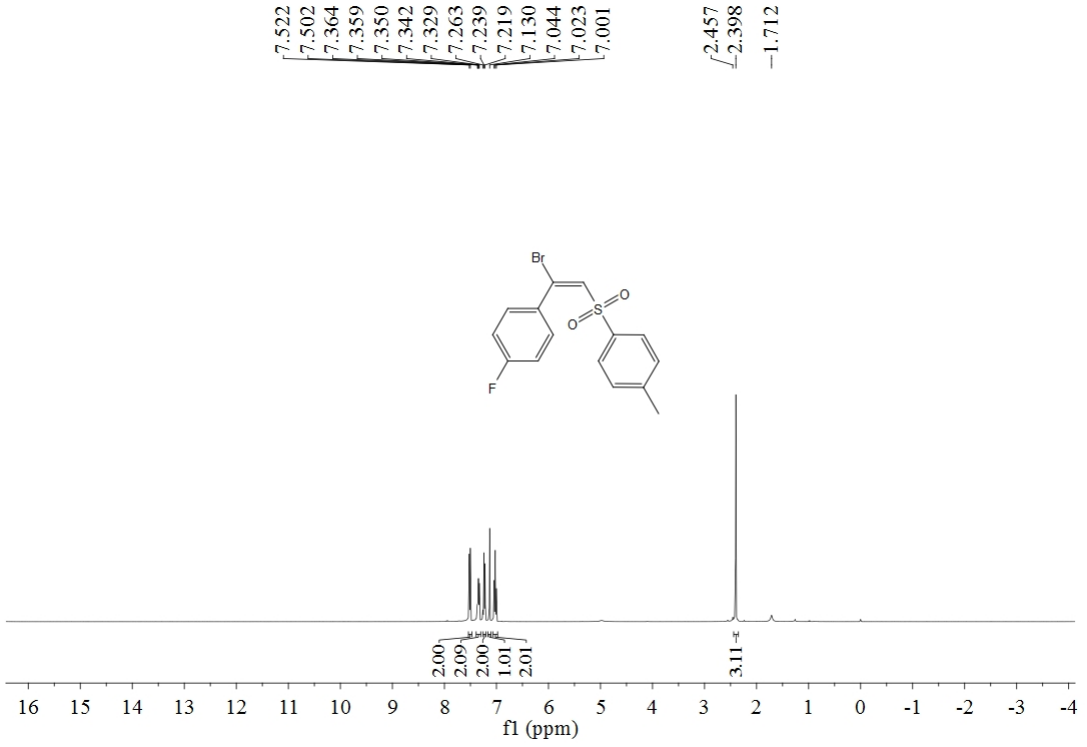
Reference:

1. Taniguchi, N. *Synlett* **2012**, 1245.
2. Li. X.; Shi, X.; Fang, M.; Xu, X. *J. Org. Chem.*, **2013**, *78*, 9499.

NMR Spectra for Compounds 3aa-3ga, 4a-6a



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7.023
7.001
2.457
2.398
1.712
Br
O
S
O
F
2.00
2.09
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1.01
2.01
3.11
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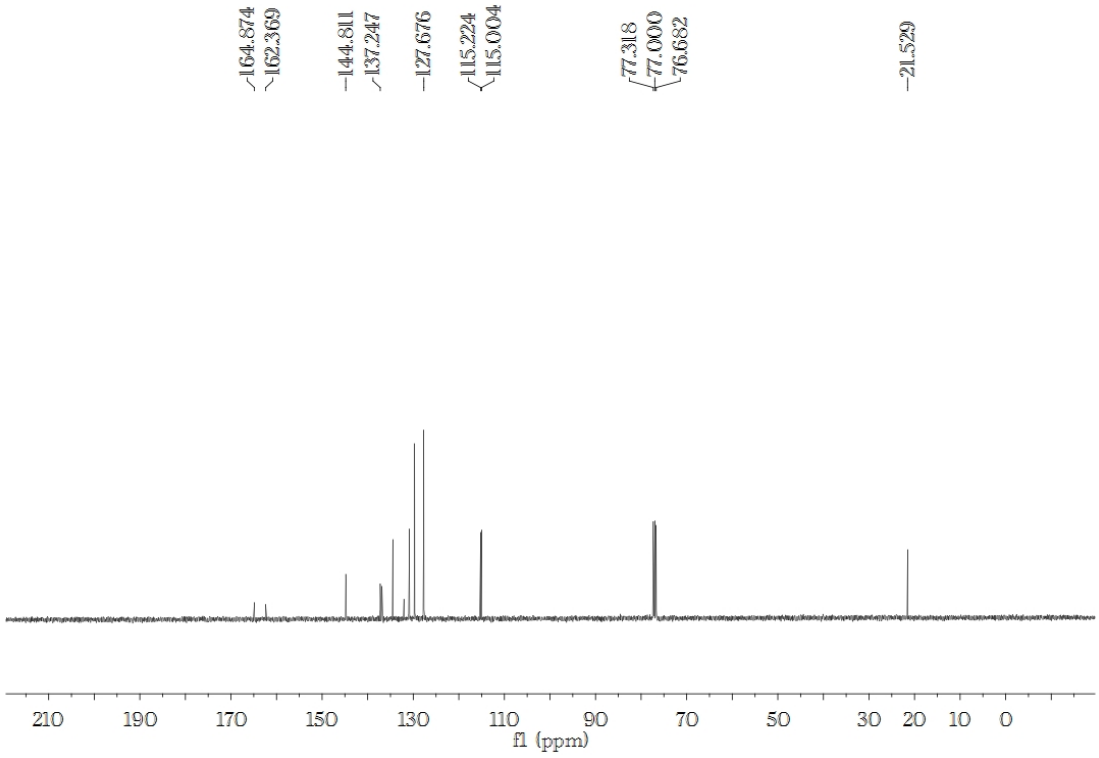
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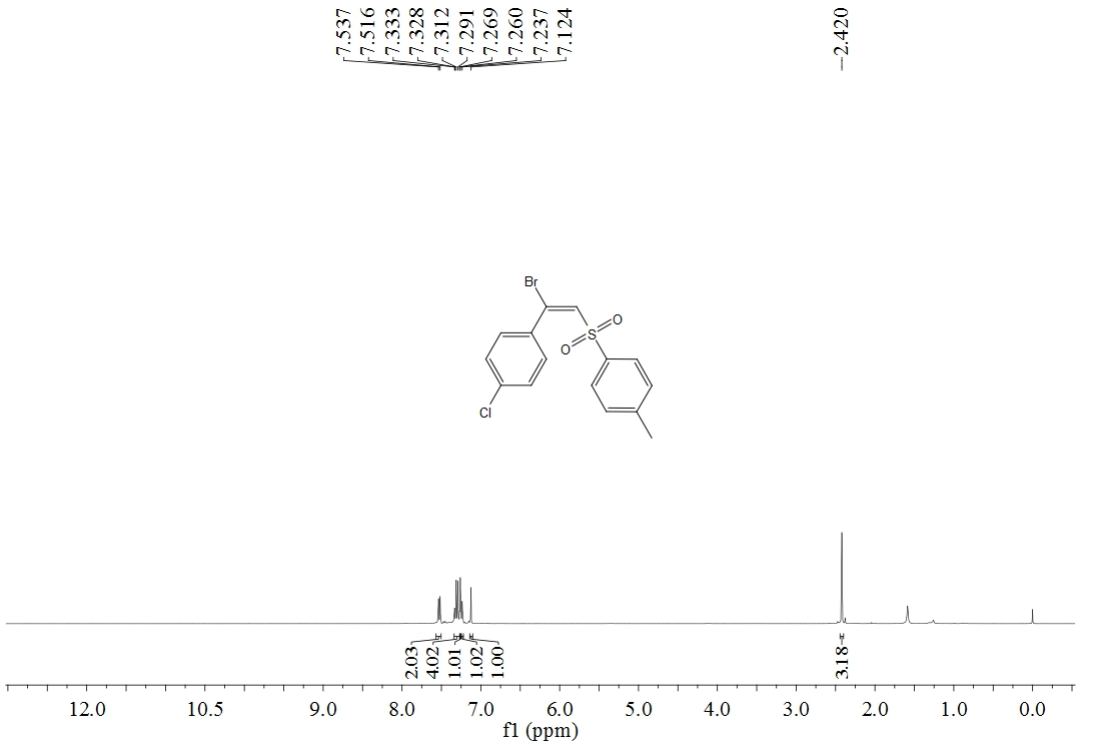
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S
O
Cl
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4.02
1.01
1.02
1.00
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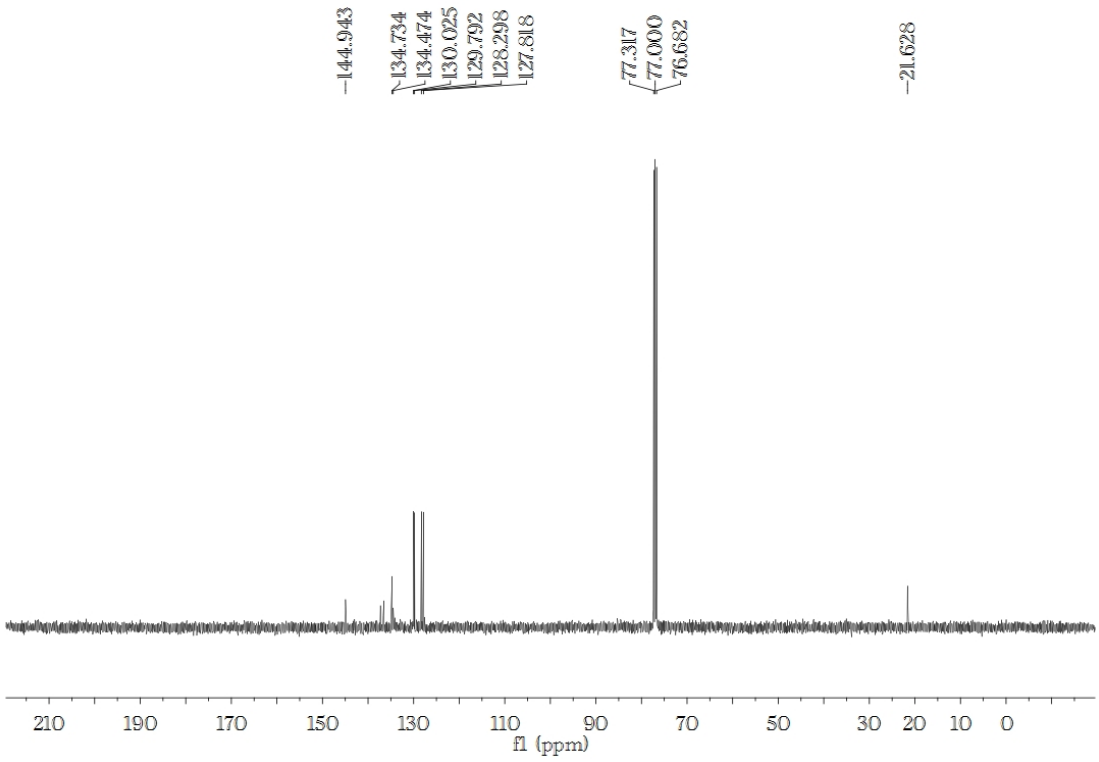
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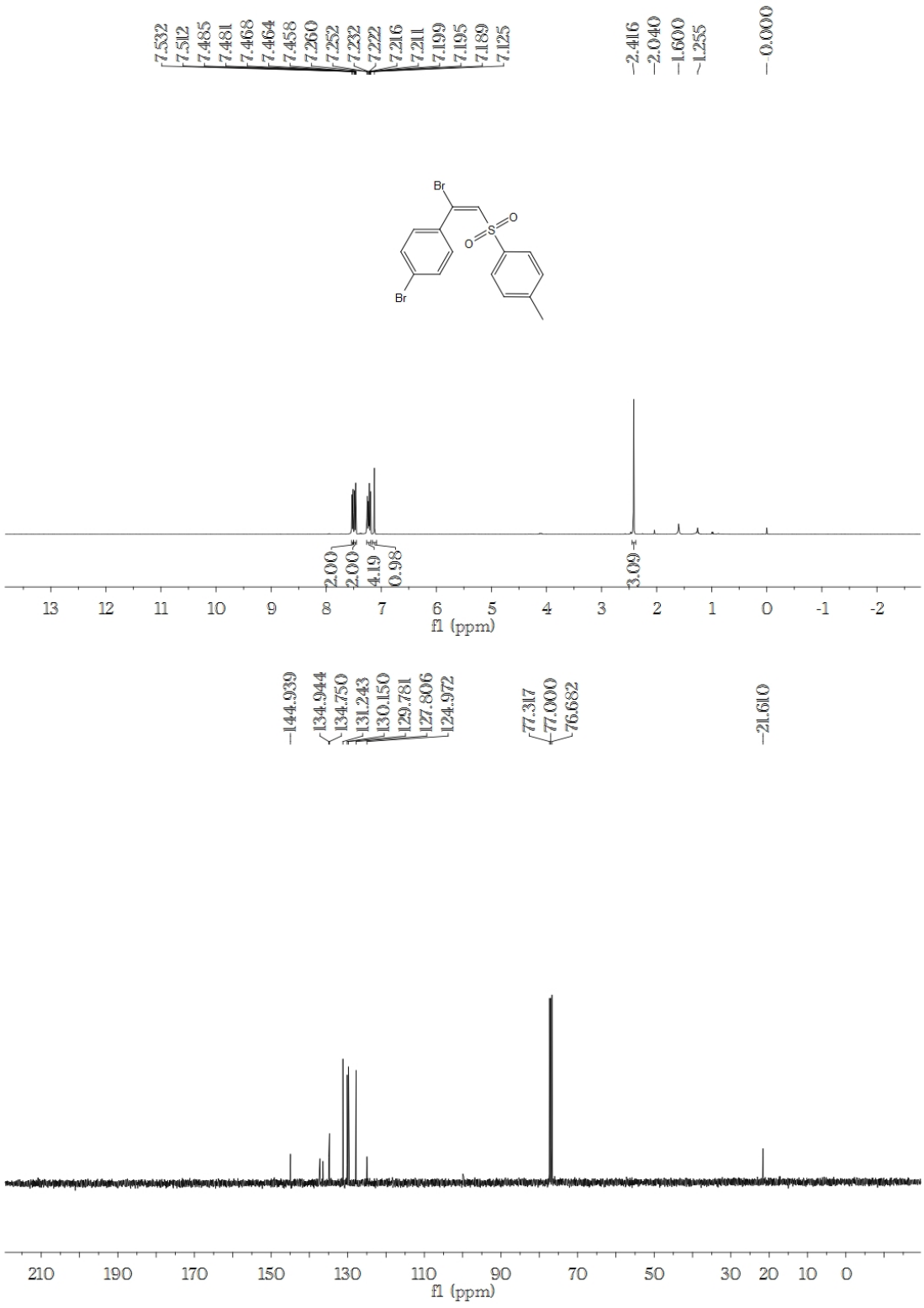
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7.195
7.189
7.125
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Br
O
O
S
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2.00
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3.09
fl (ppm)
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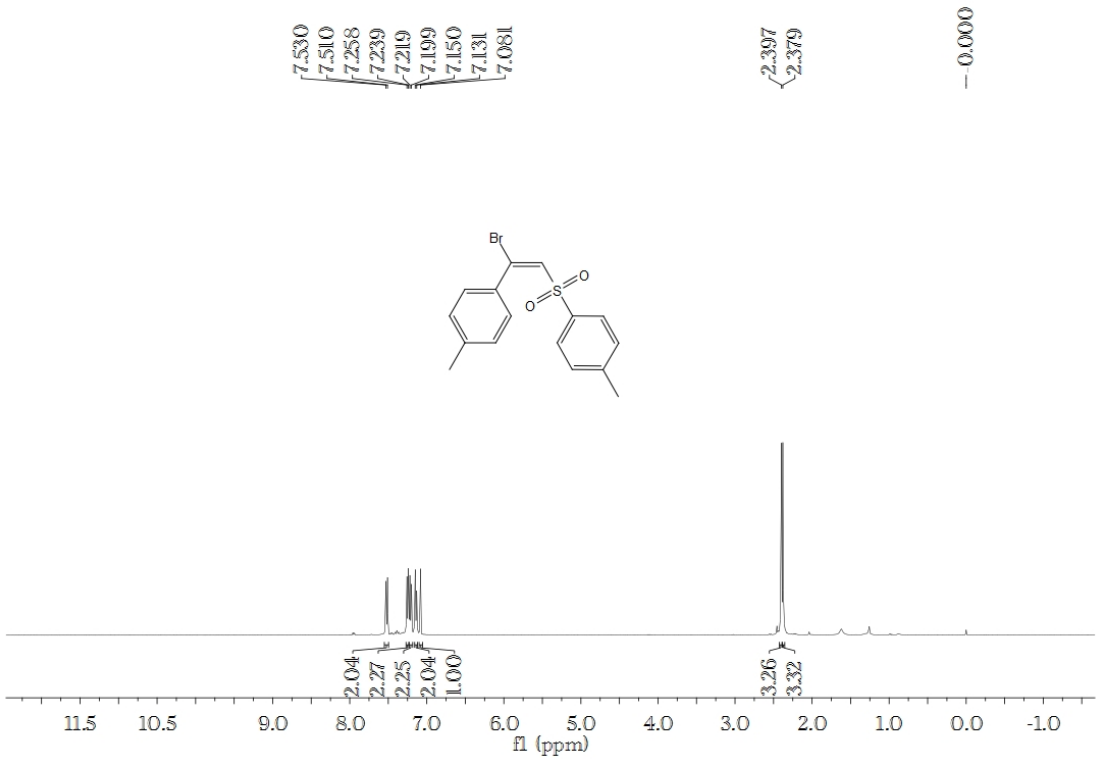
fl (ppm)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O
S
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2.27
2.25
2.04
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10.5
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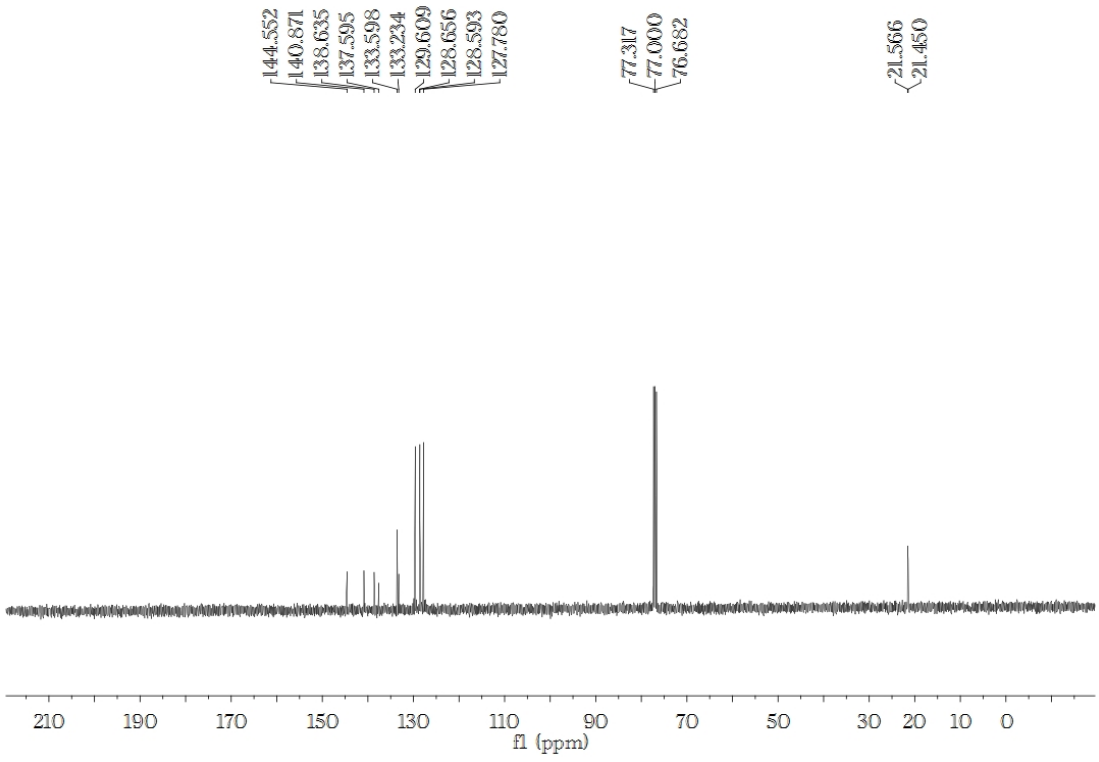
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150
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70
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30
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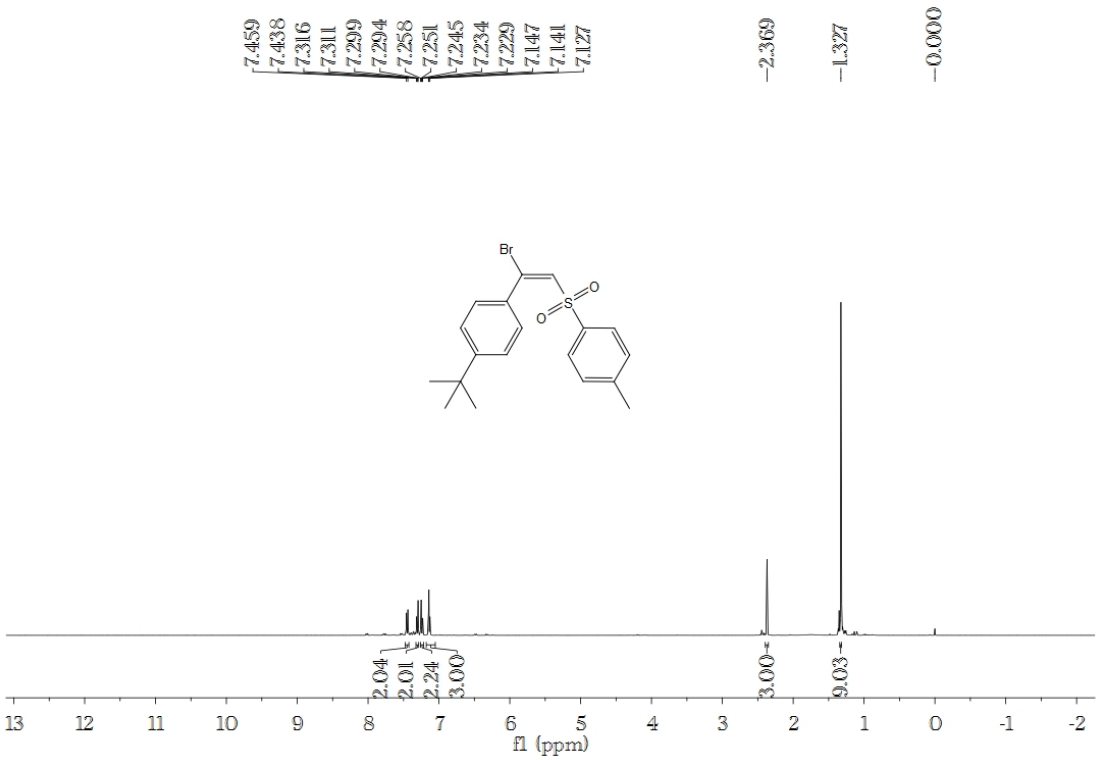
10
0
f1 (ppm)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7.141
7.127
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O
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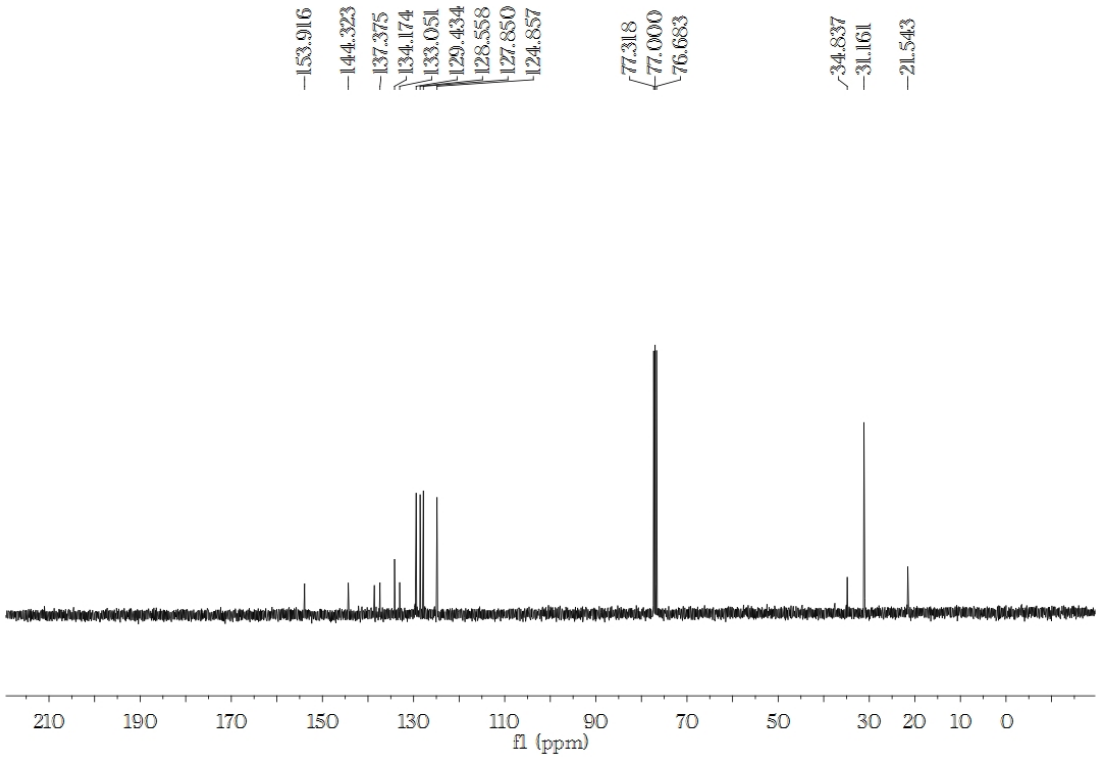
fl (ppm)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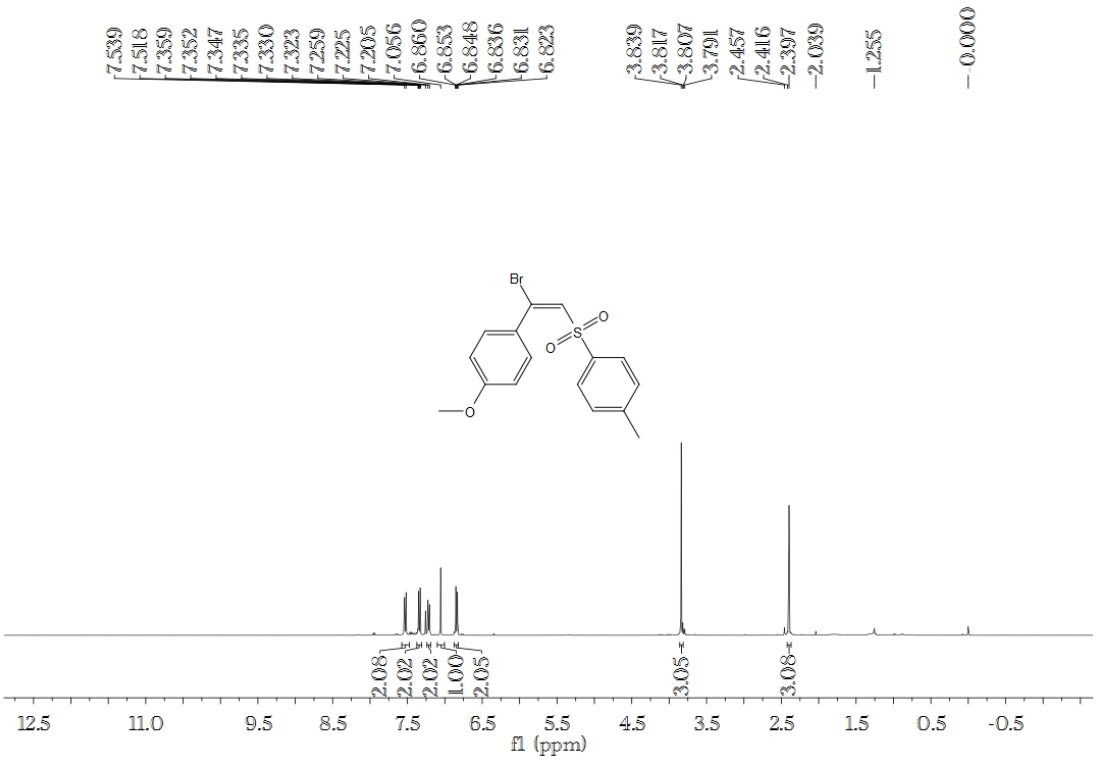
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6.823
3.839
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S
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2.02
1.00
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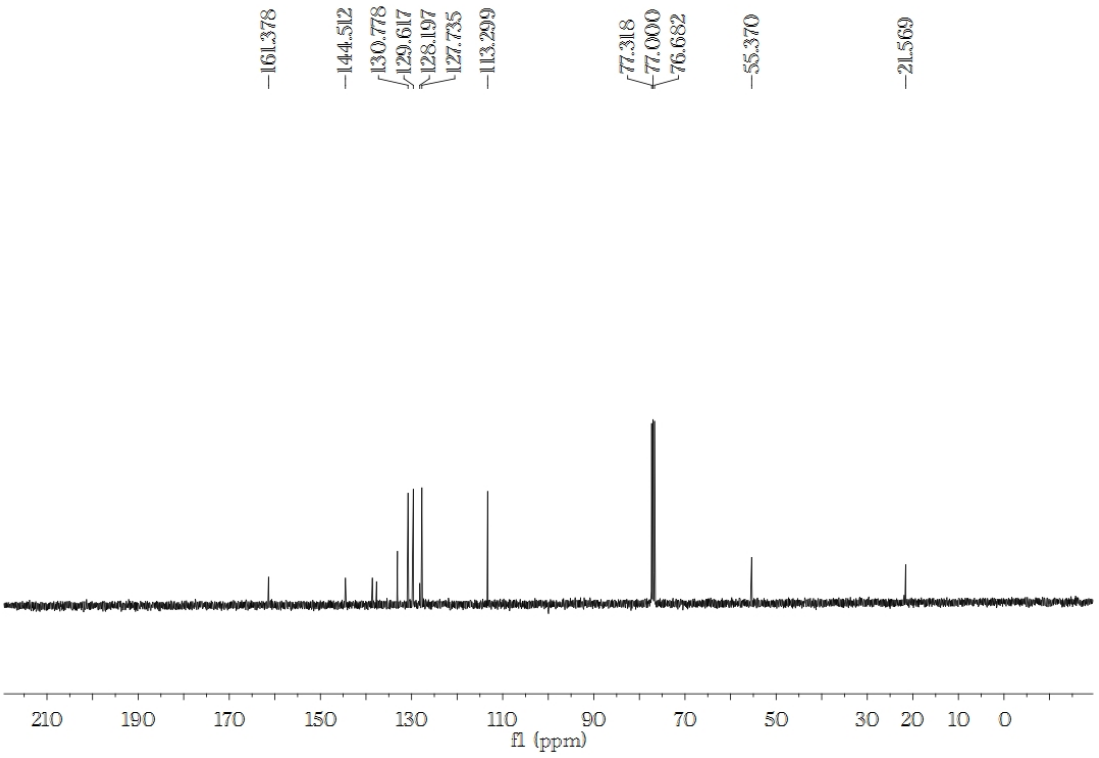
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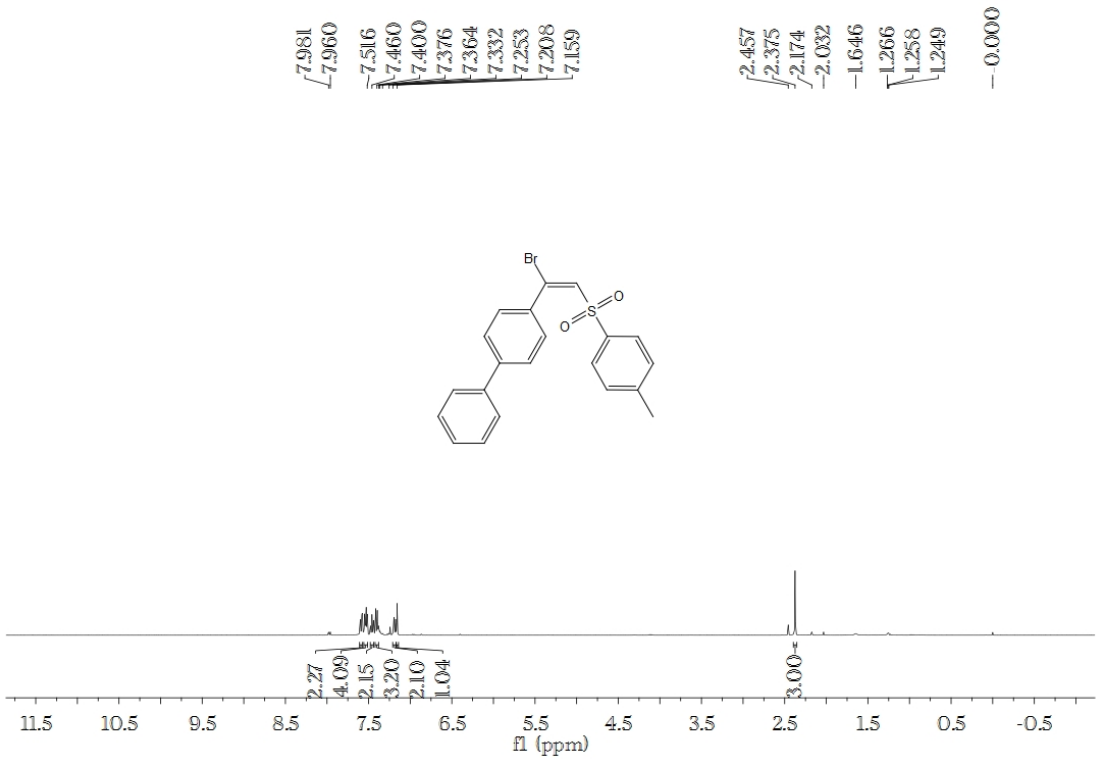
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S
O
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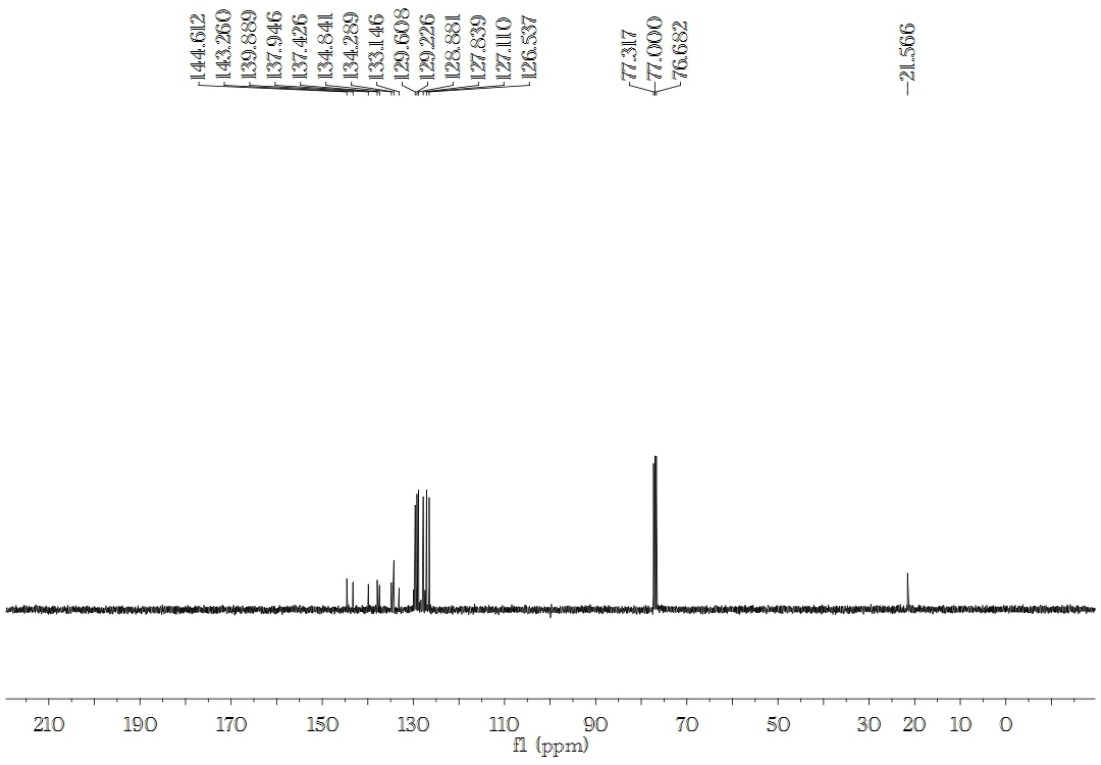
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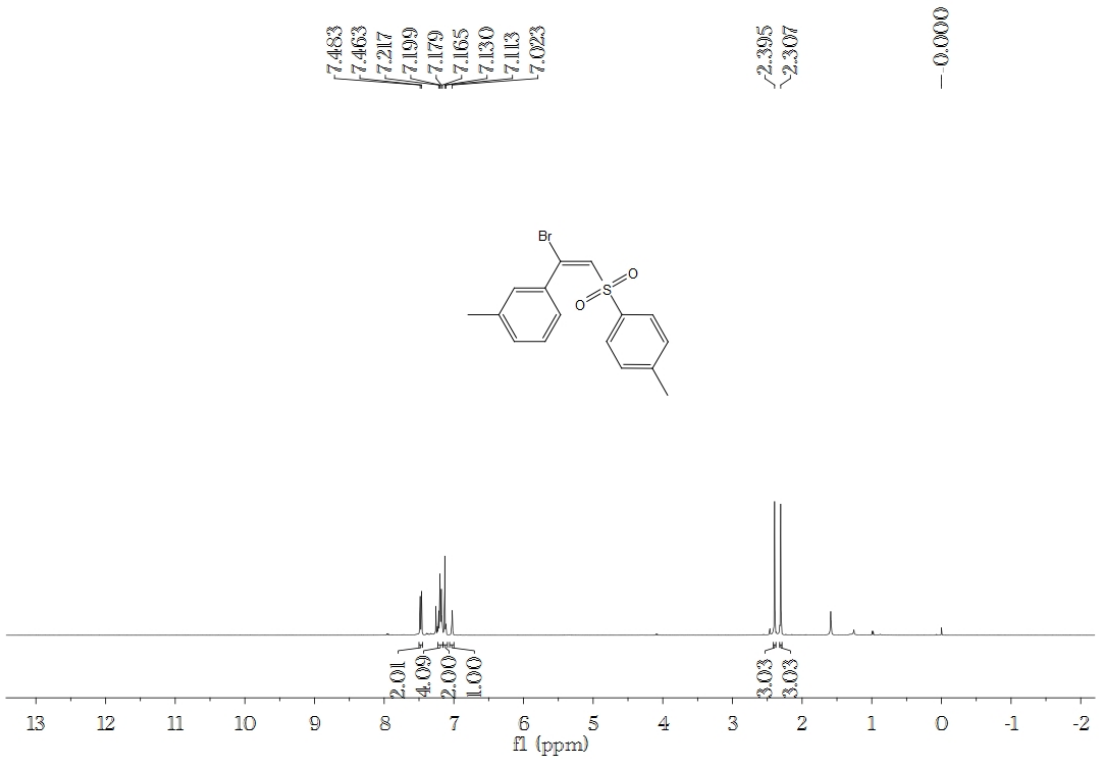
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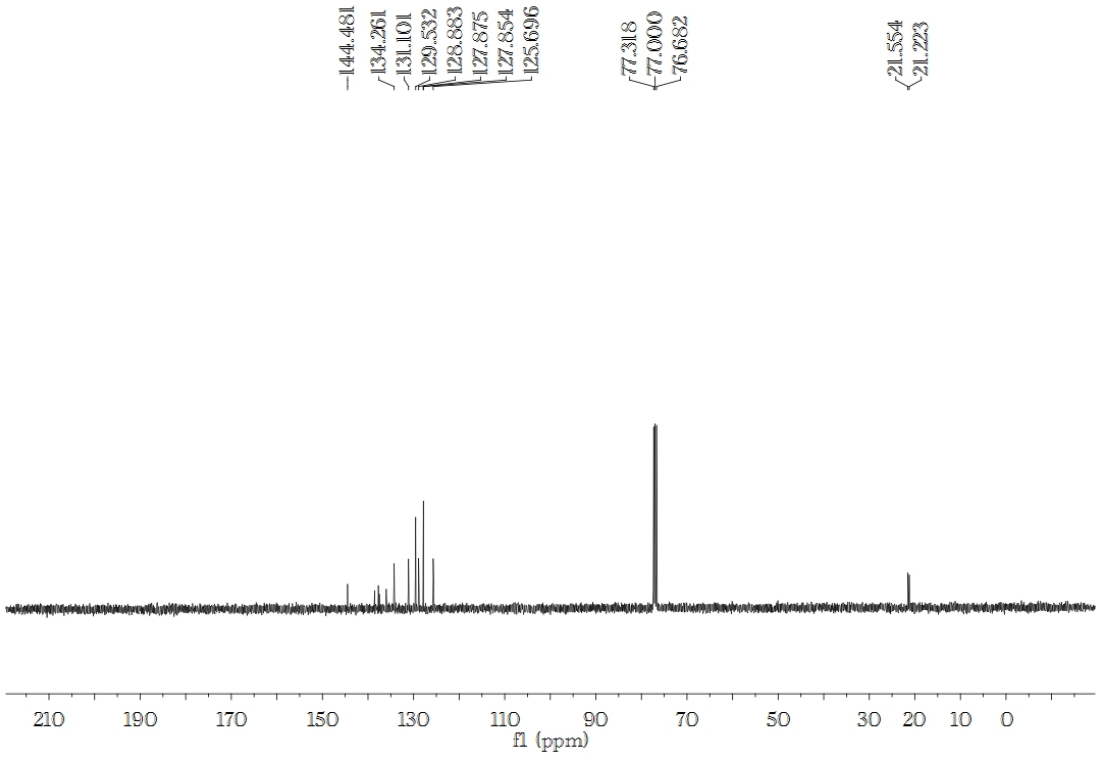
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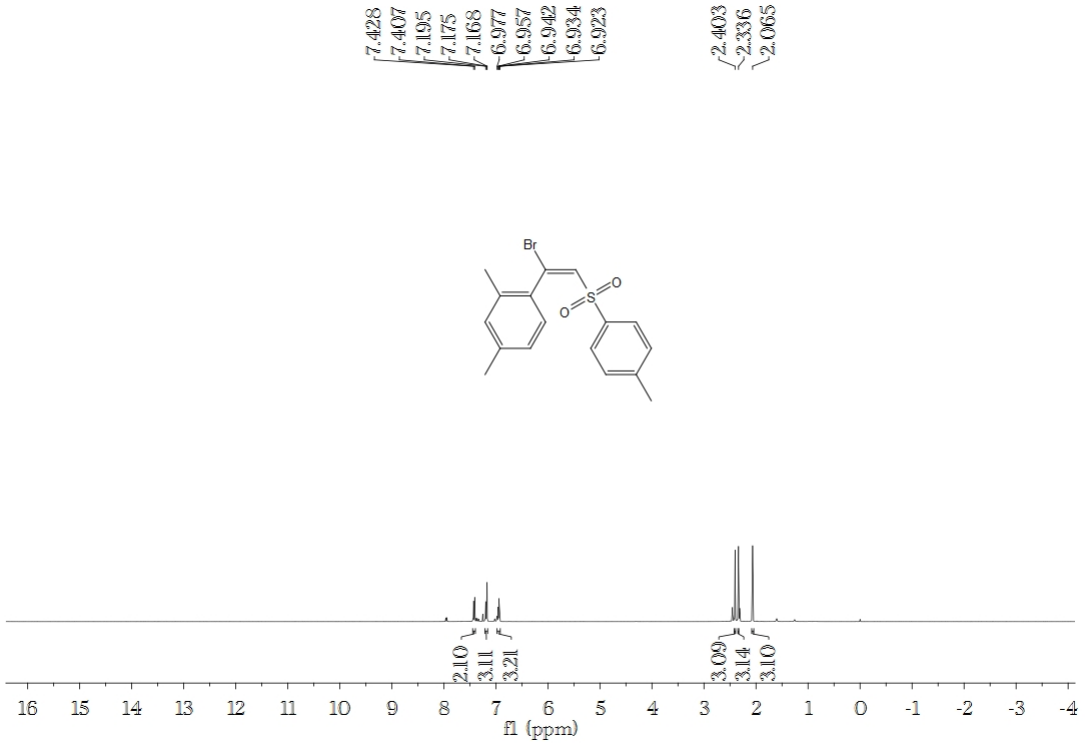
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Br
O
O
S
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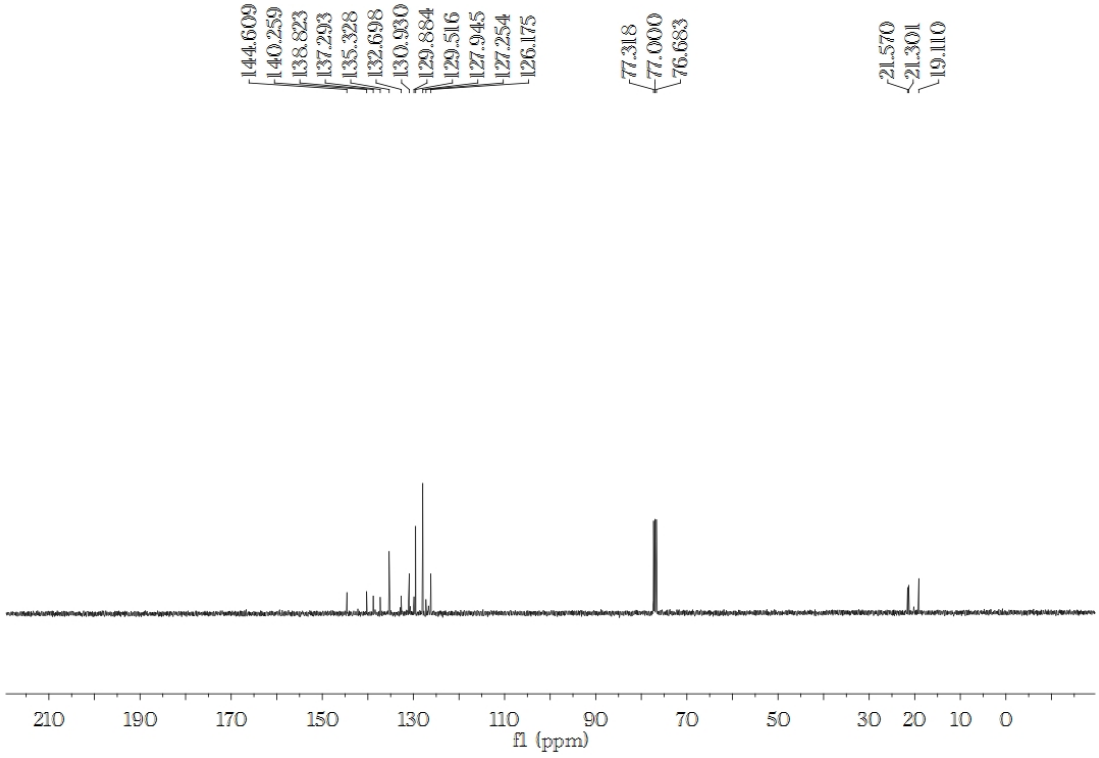
f1 (ppm)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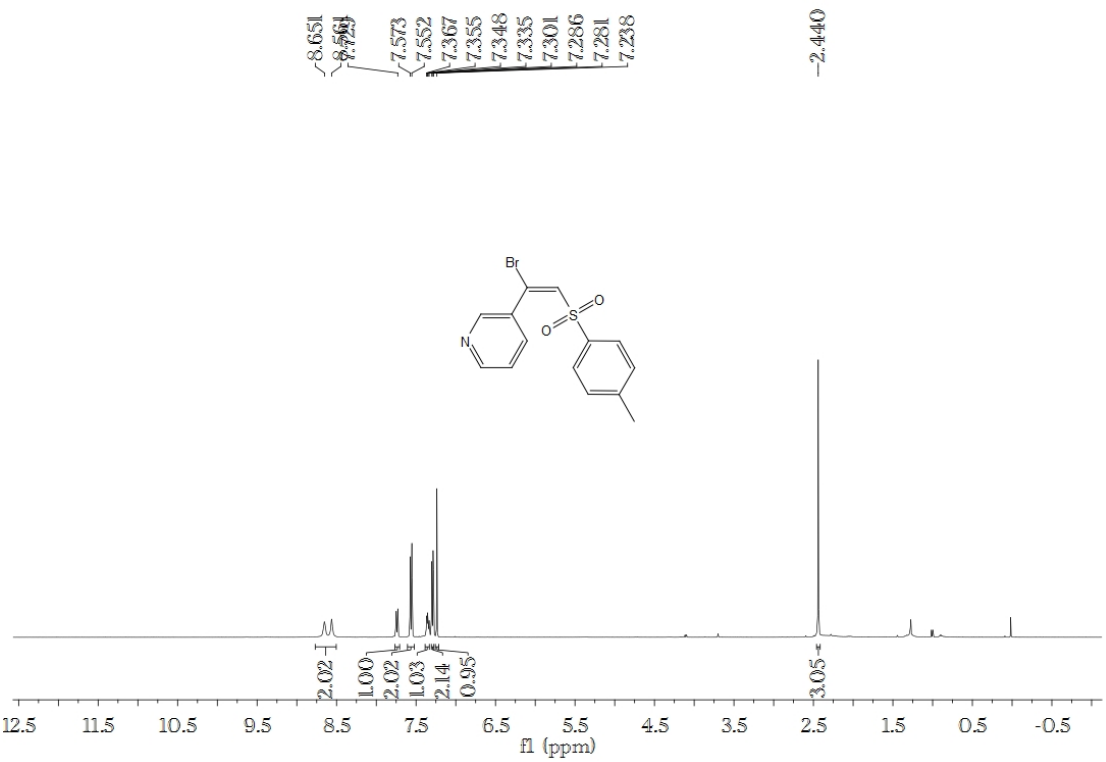
f1 (ppm)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2.02
1.03
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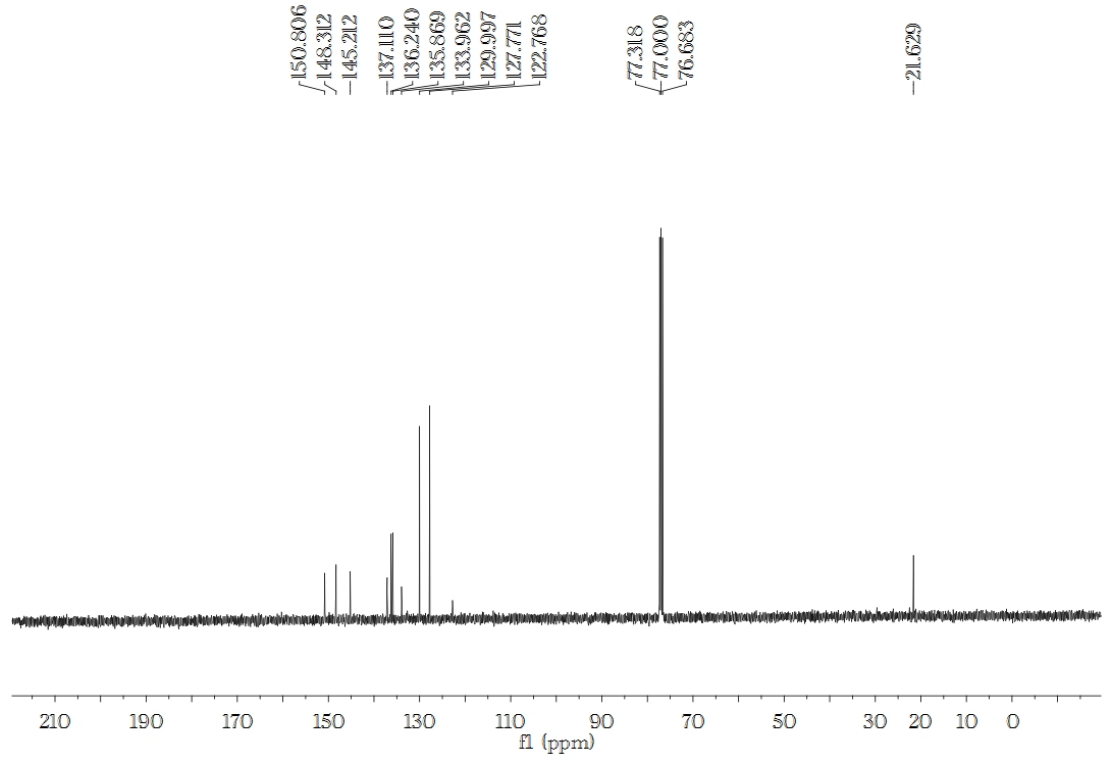
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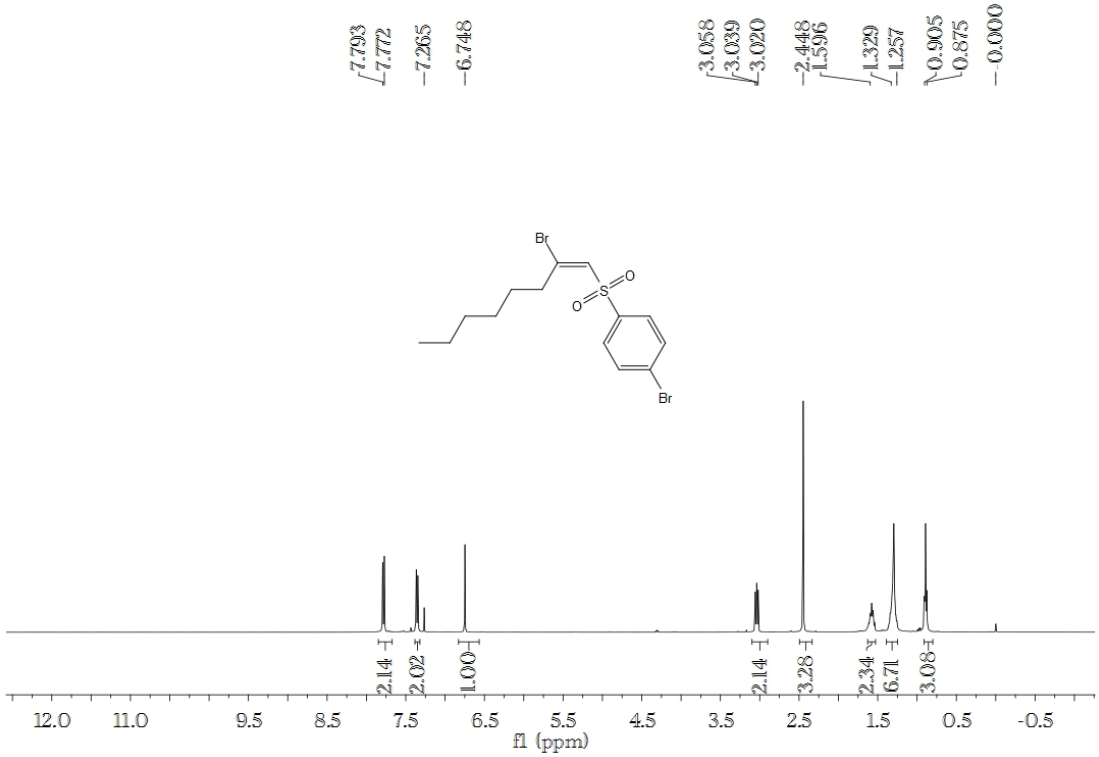
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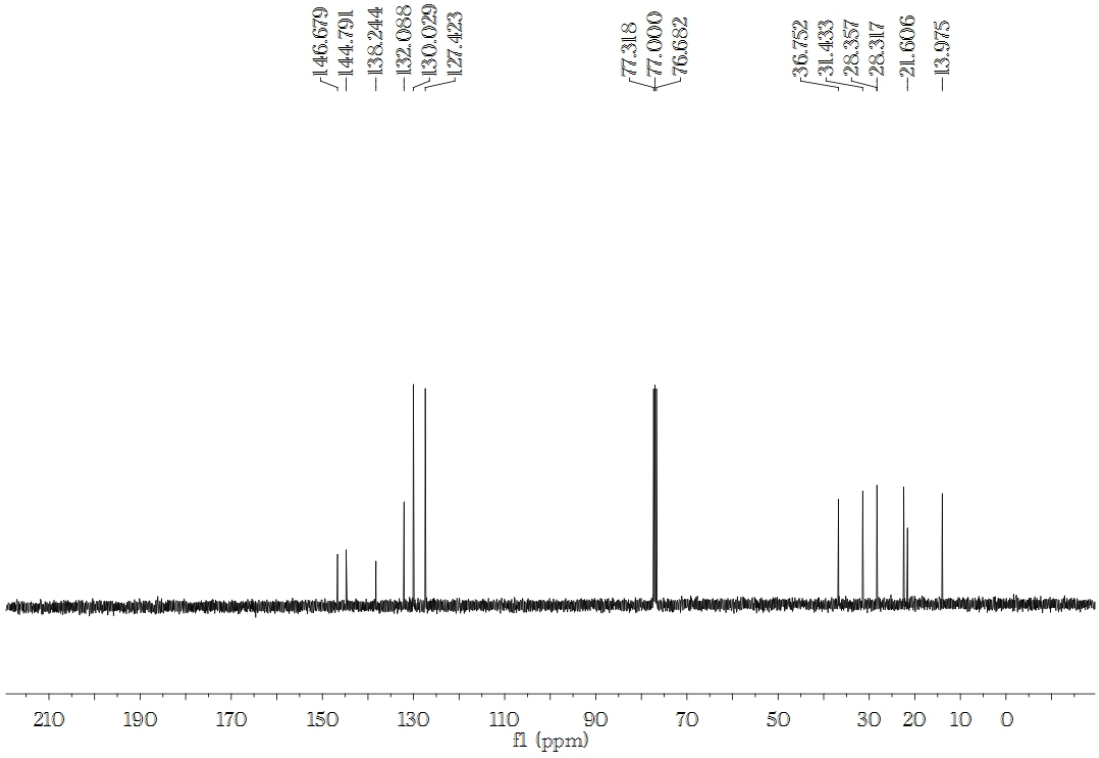
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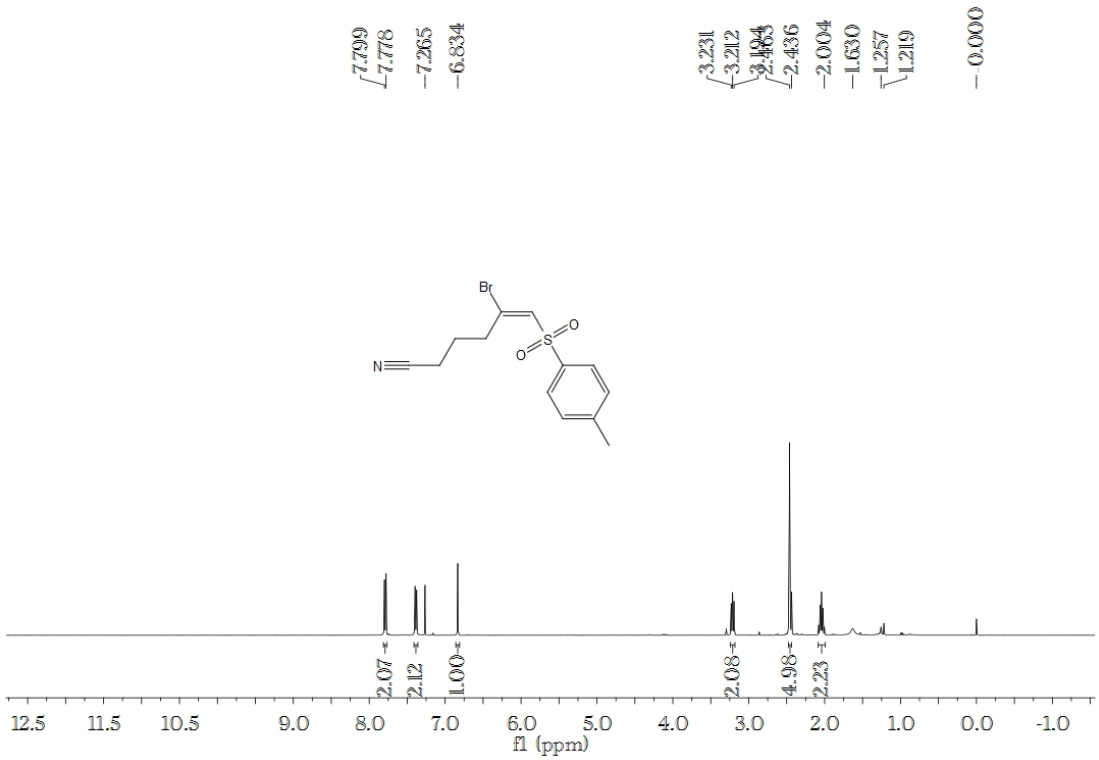
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S
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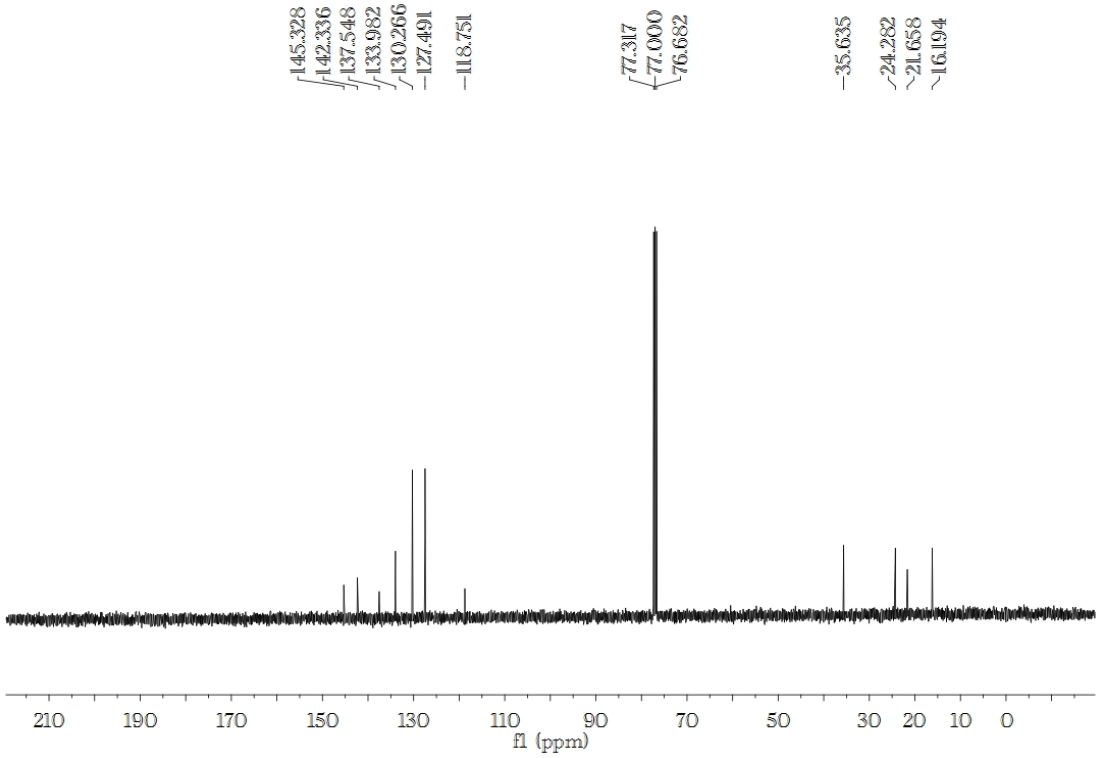
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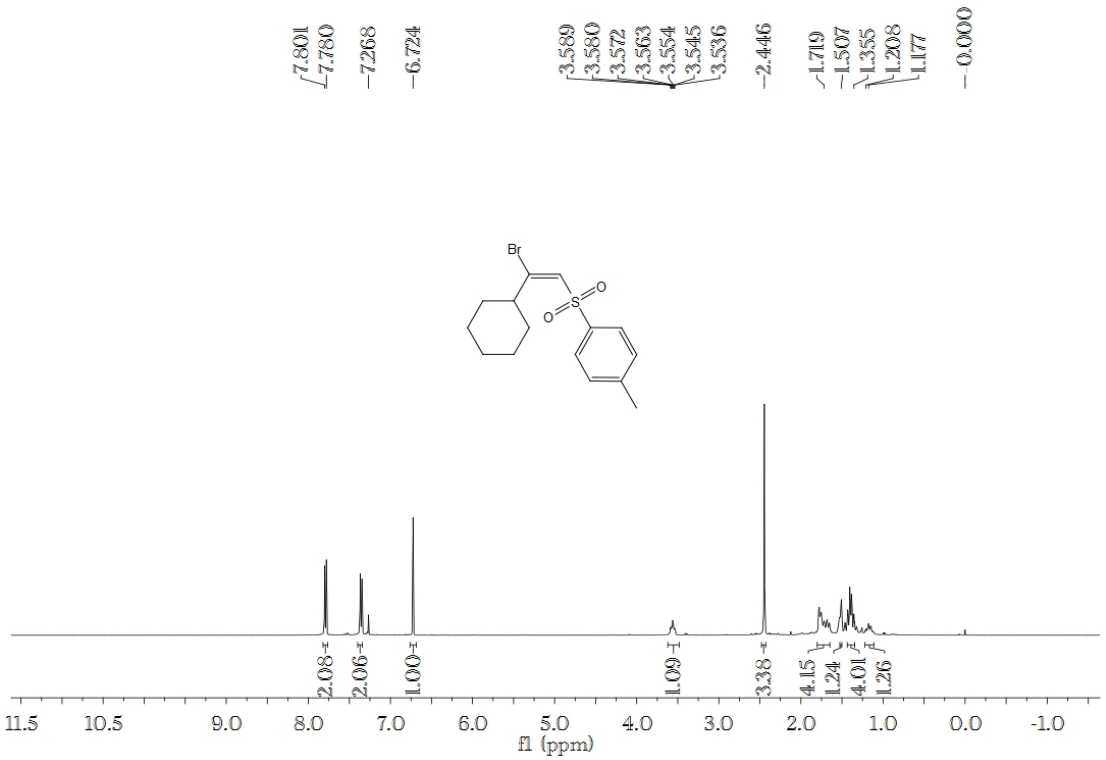
f1 (ppm)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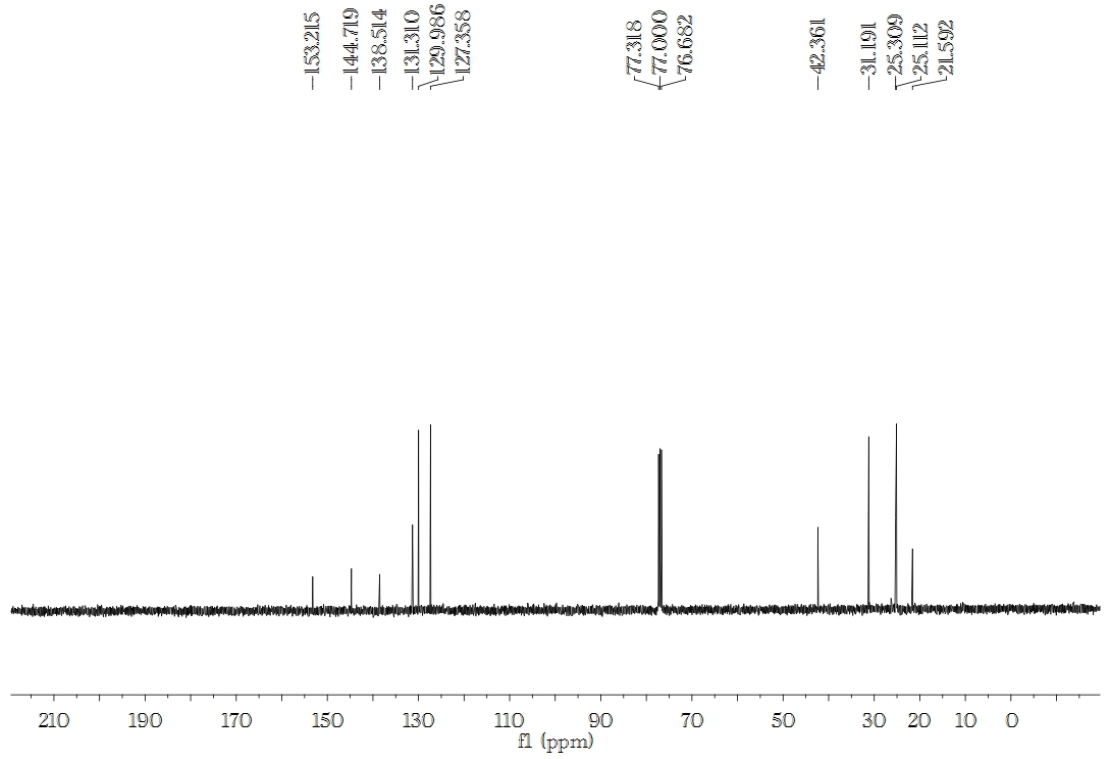
0.0
-1.0
f1 (ppm)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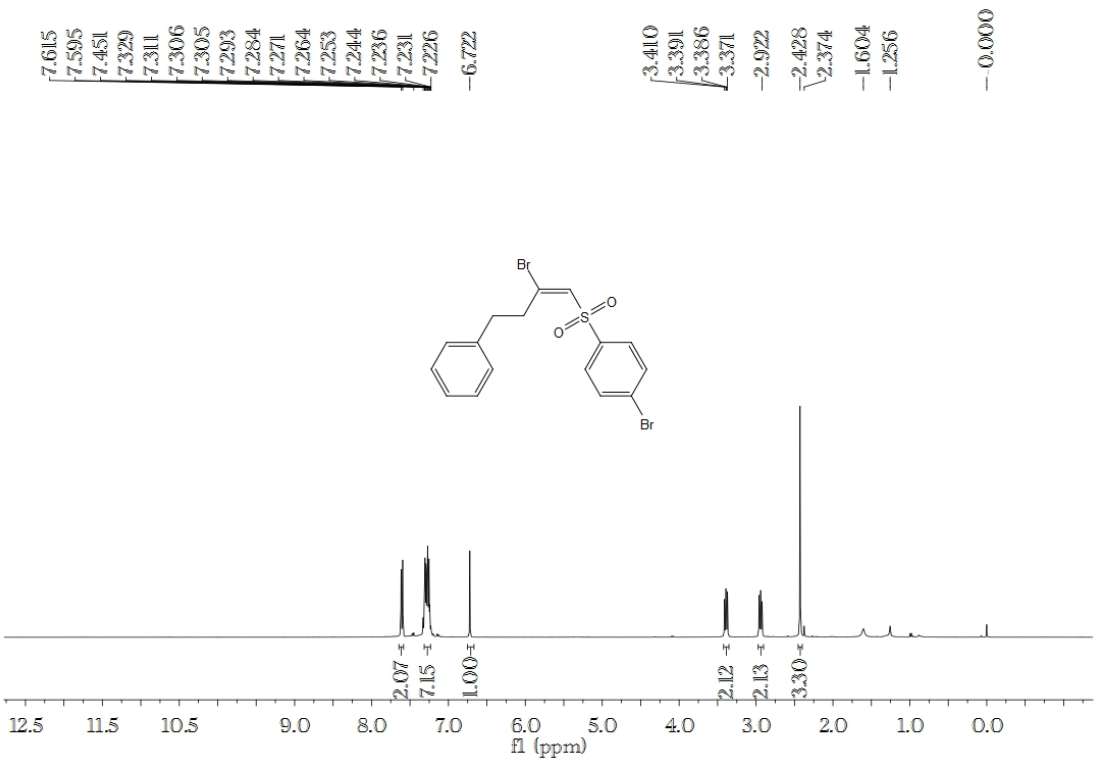
144.719
138.514
131.310
129.986
127.358
77.318
77.000
76.682
42.361
31.191
25.309
25.112
21.592
210
190
170
150
130
110
90
70
50
30
20
10
0
f1 (ppm)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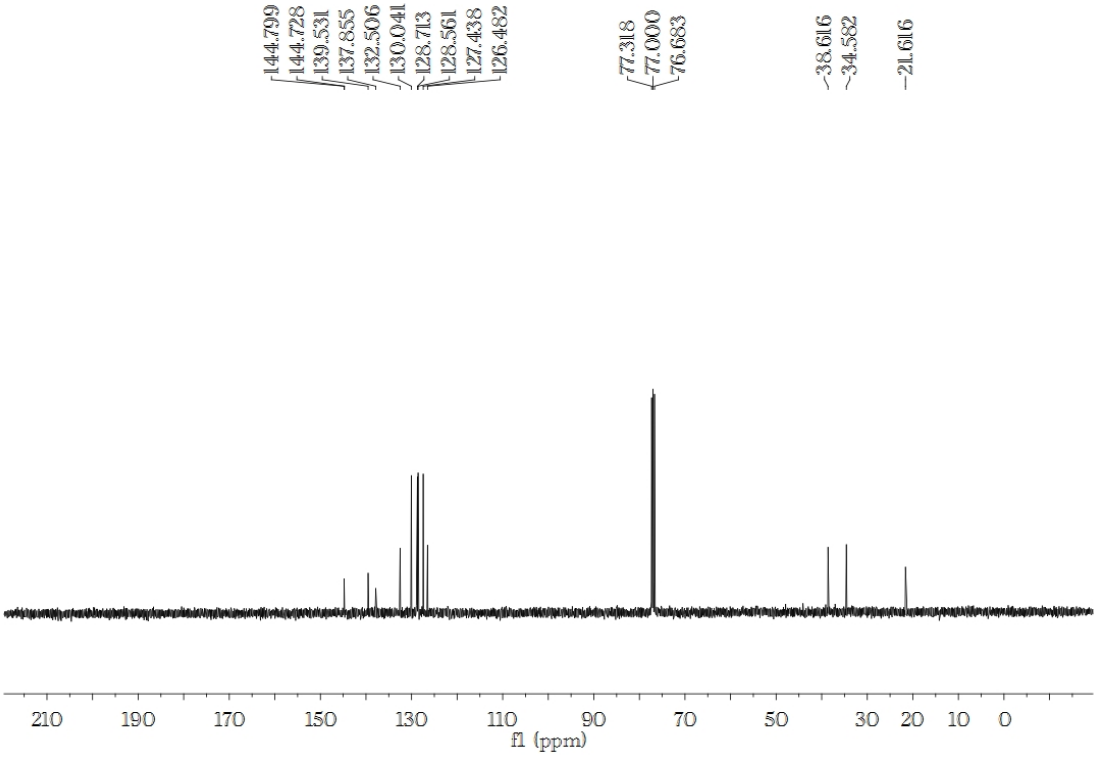
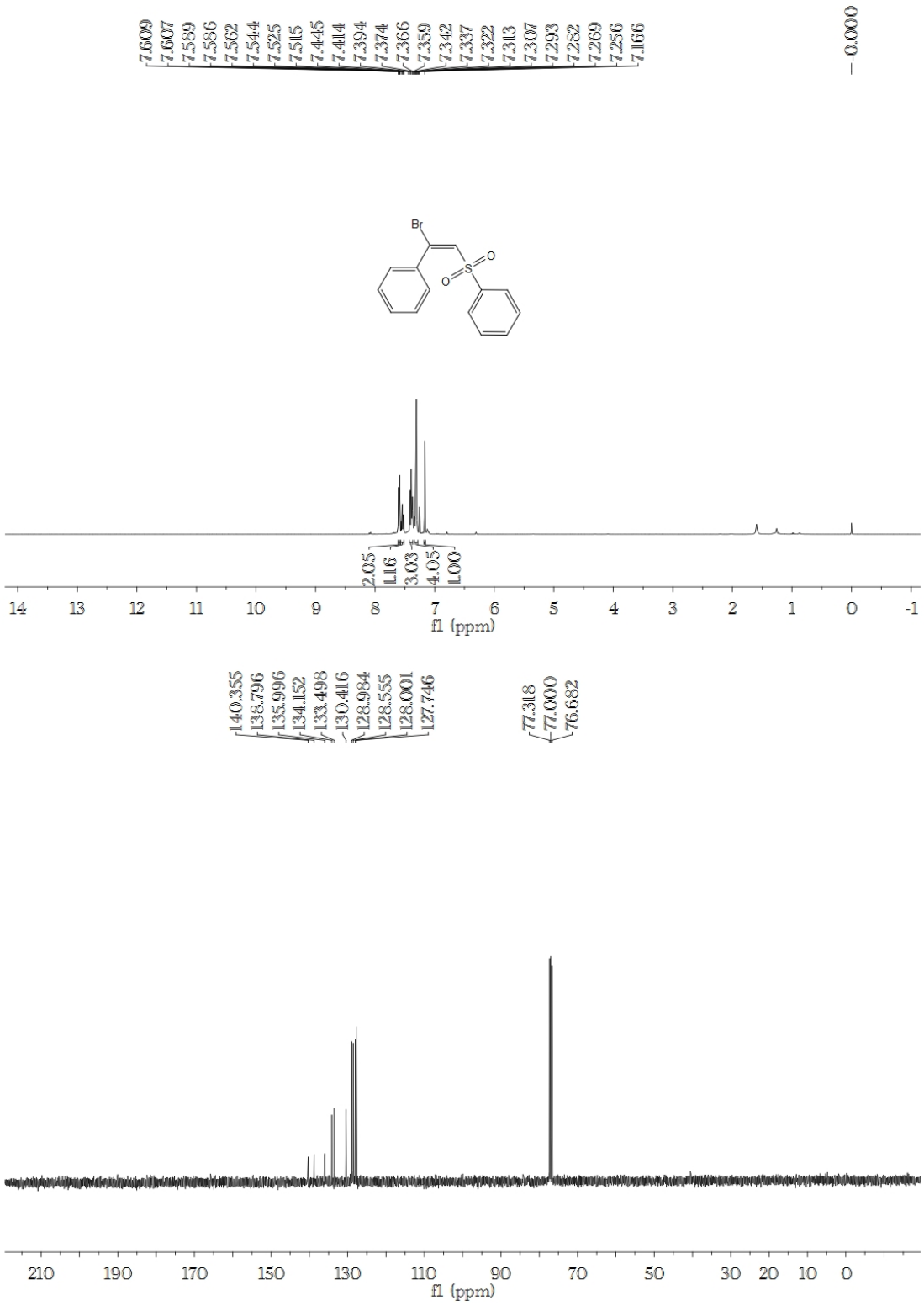
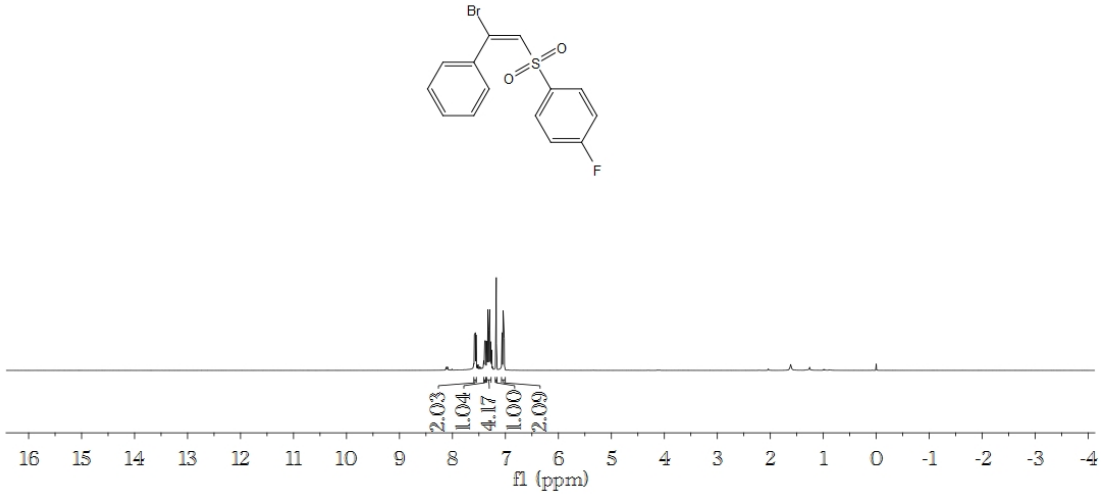
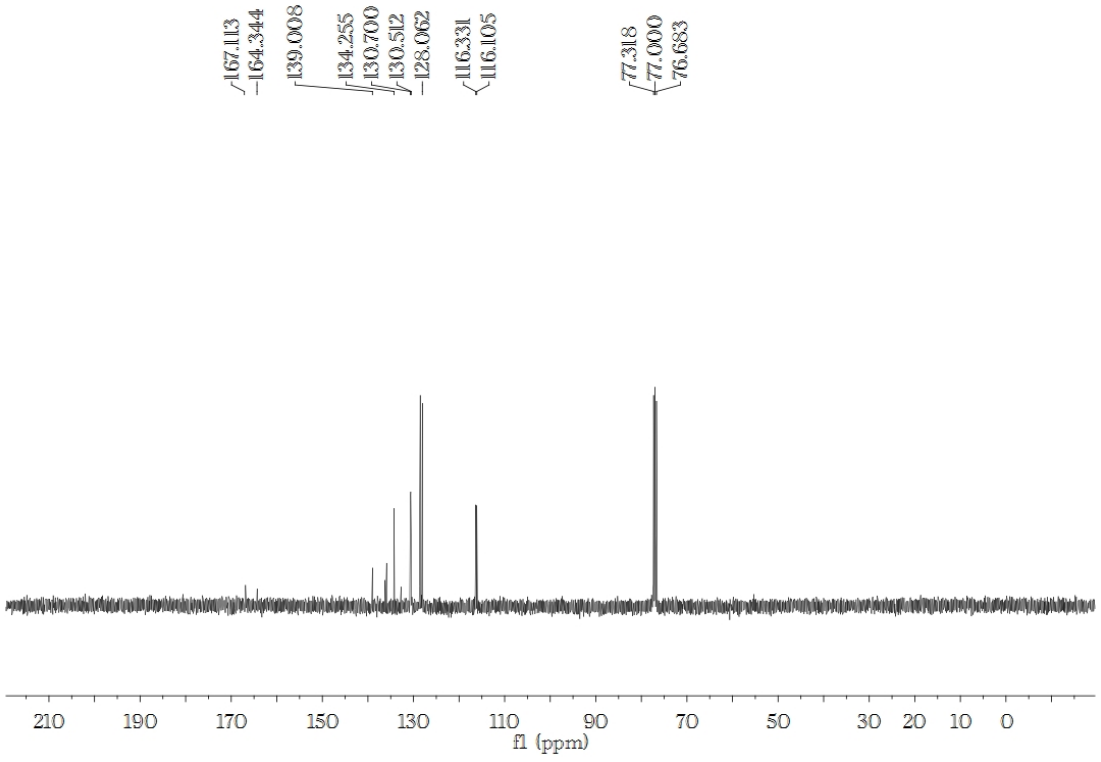
7.595
7.451
7.329
7.311
7.306
7.305
7.293
7.284
7.271
7.264
7.253
7.244
7.236
7.231
7.226
6.722
3.410
3.391
3.386
3.371
2.922
2.428
2.374
1.604
1.256
0.000
Br
O
S
O
Br
2.07
7.15
1.00
2.12
2.13
3.30
12.5
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


144.799
144.728
139.531
137.855
132.506
130.041
128.713
128.561
127.438
126.482
77.318
77.000
76.683
38.616
34.582
21.616
210
190
170
150
130
110
90
70
50
30
20
10
0
f1 (ppm)

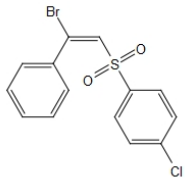

7.609
7.607
7.589
7.586
7.562
7.544
7.525
7.515
7.445
7.414
7.394
7.374
7.366
7.359
7.342
7.337
7.322
7.313
7.307
7.293
7.282
7.269
7.256
7.166
0.000
Br
O
O
S
2.05
1.16
3.03
4.05
1.00
f1 (ppm)
140.355
138.796
135.996
134.152
133.498
130.416
128.984
128.555
128.001
127.746
77.318
77.000
76.682
f1 (ppm)

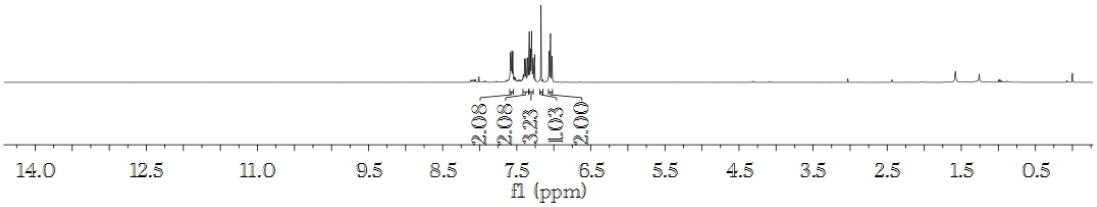

7.587
7.582
7.575
7.570
7.565
7.557
7.552
7.545
7.409
7.405
7.398
7.392
7.385
7.378
7.374
7.370
7.356
7.349
7.333
7.329
7.317
7.312
7.299
7.296
7.283
7.278
7.274
7.269
7.262
7.173
7.064
7.059
7.043
7.026
7.021

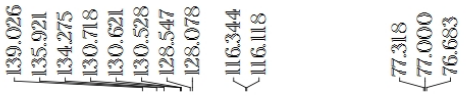

Br
O
O
S
F
2.03
1.04
4.17
1.00
2.09
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

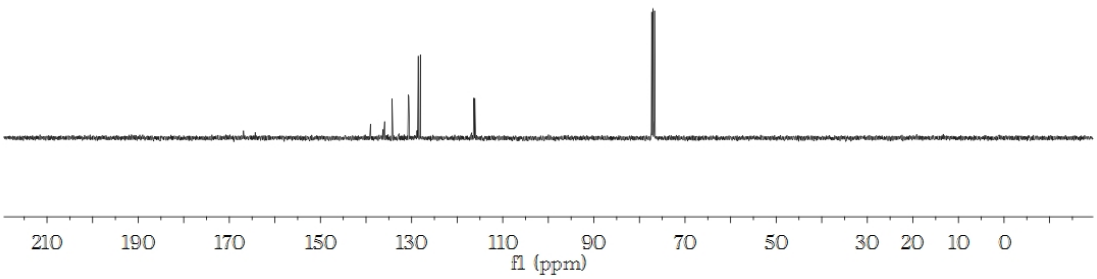

167.113
164.344
139.008
134.255
130.700
130.512
128.062
116.331
116.105
77.318
77.000
76.683
210 190 170 150 130 110 90 70 50 30 20 10 0
f1 (ppm)


7.588
7.583
7.575
7.570
7.565
7.558
7.553
7.415
7.411
7.408
7.401
7.394
7.387
7.380
7.376
7.372
7.351
7.335
7.331
7.318
7.314
7.311
7.300
7.297
7.285
7.280
7.275
7.172
7.072
7.065
7.060
7.044
7.027
7.023
7.015

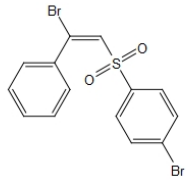

Br
O
S
O
Cl

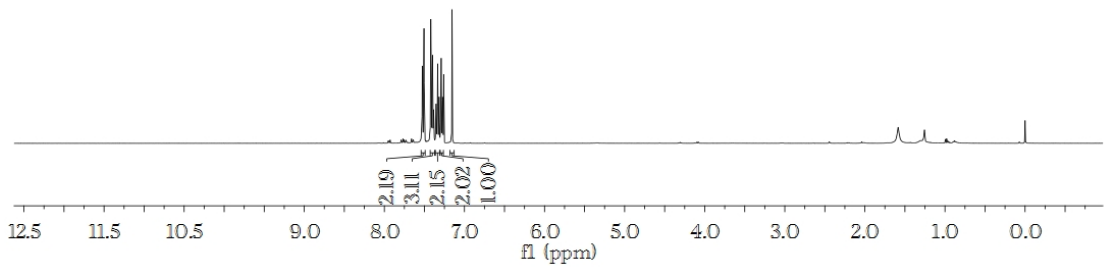

2.08
2.08
3.23
1.03
2.00
14.0
12.5
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


139.026
135.921
134.275
130.718
130.621
130.528
128.547
128.078
116.344
116.118
77.318
77.000
76.683

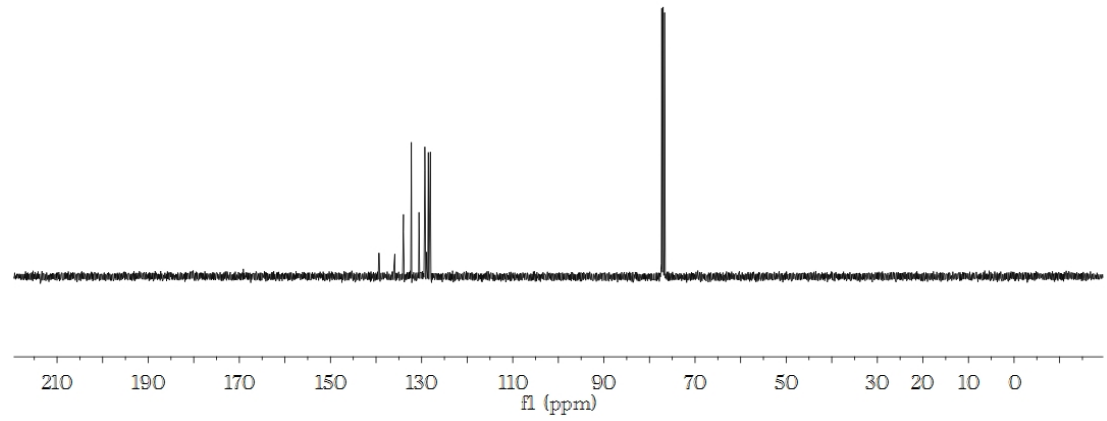

210
190
170
150
130
110
90
70
50
30
20
10
0
f1 (ppm)

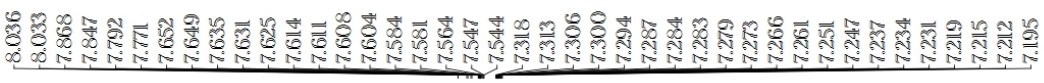

7.532
7.526
7.522
7.510
7.505
7.499
7.420
7.415
7.410
7.403
7.398
7.389
7.385
7.381
7.354
7.338
7.334
7.321
7.316
7.290
7.278
7.273
7.269
7.259
7.155
1.584
1.296
1.256
0.996
0.979
0.880
0.000

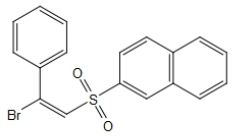

Br
O
S
O
Br

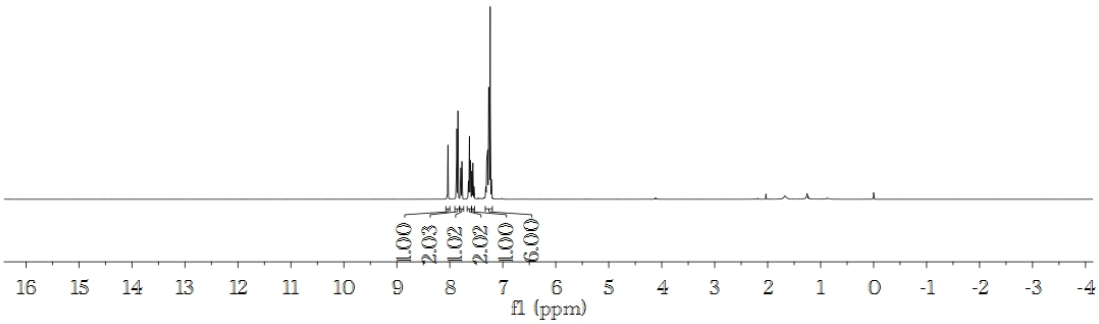

2.19
3.11
2.15
2.02
1.00
12.5
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

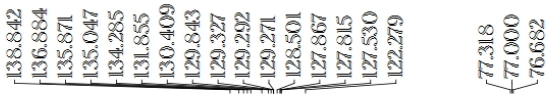

139.418
139.300
135.891
133.987
132.247
130.578
129.287
128.889
128.536
128.087
77.318
77.000
76.683

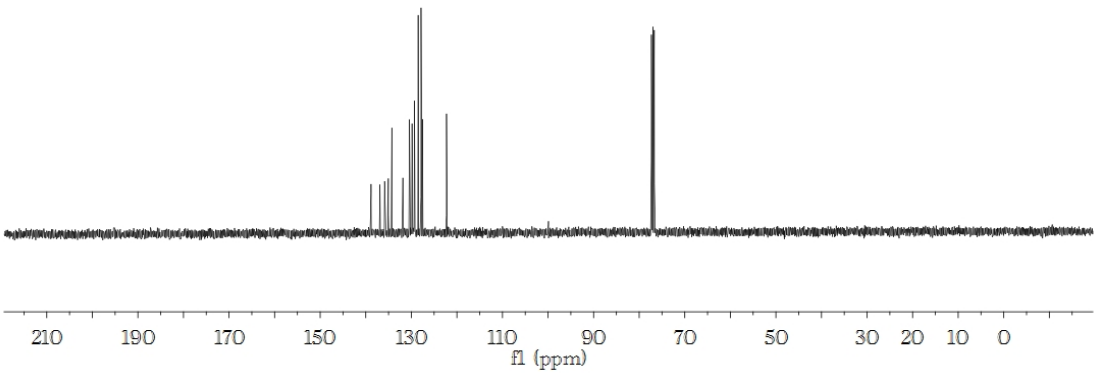

210
190
170
150
130
110
90
70
50
30
20
10
0
f1 (ppm)

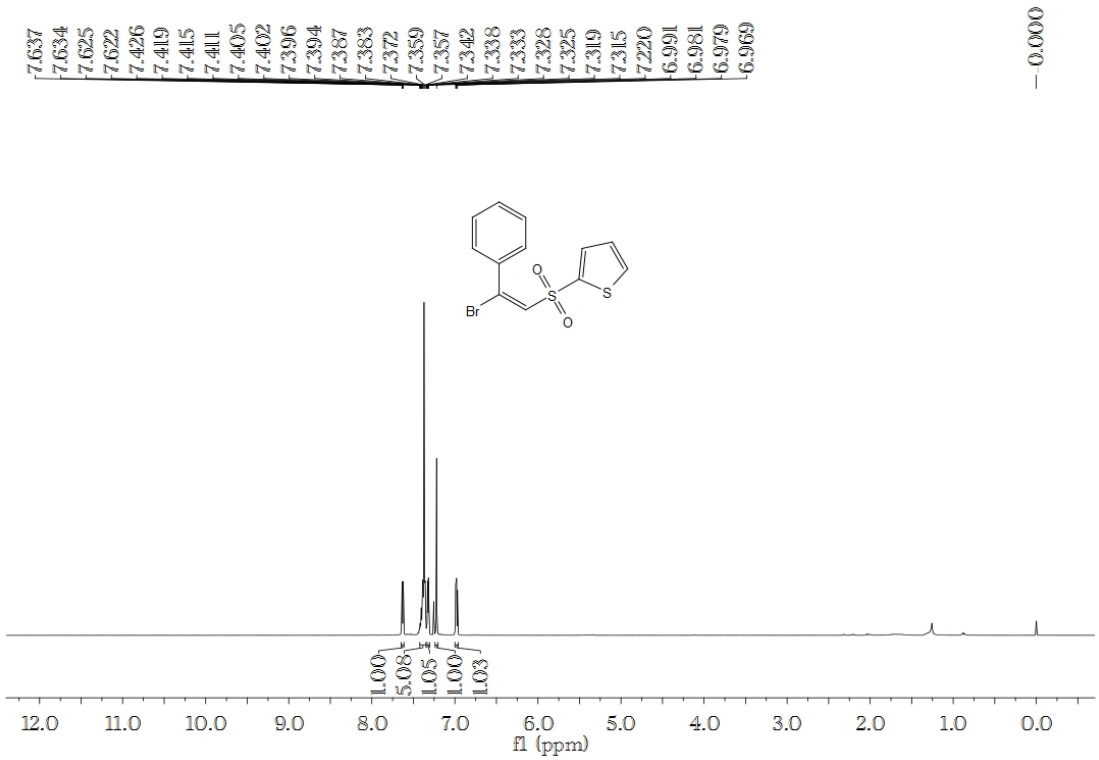

8.036
8.033
7.868
7.847
7.792
7.771
7.652
7.649
7.635
7.631
7.625
7.614
7.611
7.608
7.604
7.584
7.581
7.564
7.547
7.544
7.318
7.313
7.306
7.300
7.294
7.287
7.284
7.283
7.279
7.273
7.266
7.261
7.251
7.247
7.237
7.234
7.231
7.219
7.215
7.212
7.195


Br
O
S
O


1.00
2.03
1.02
2.02
1.00
6.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


138.842
136.884
135.871
135.047
134.285
131.855
130.409
129.843
129.327
129.292
129.271
128.501
127.867
127.815
127.530
122.279
77.318
77.000
76.682


210 190 170 150 130 110 90 70 50 30 20 10 0
f1 (ppm)


7.637
7.634
7.625
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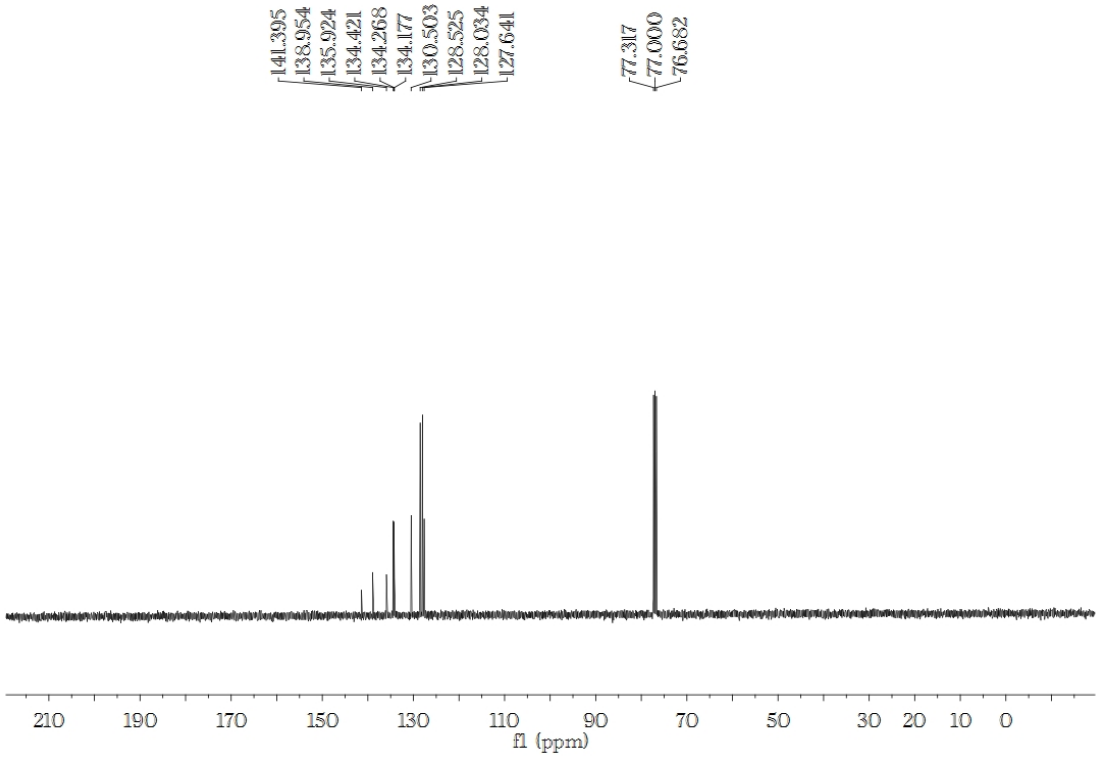
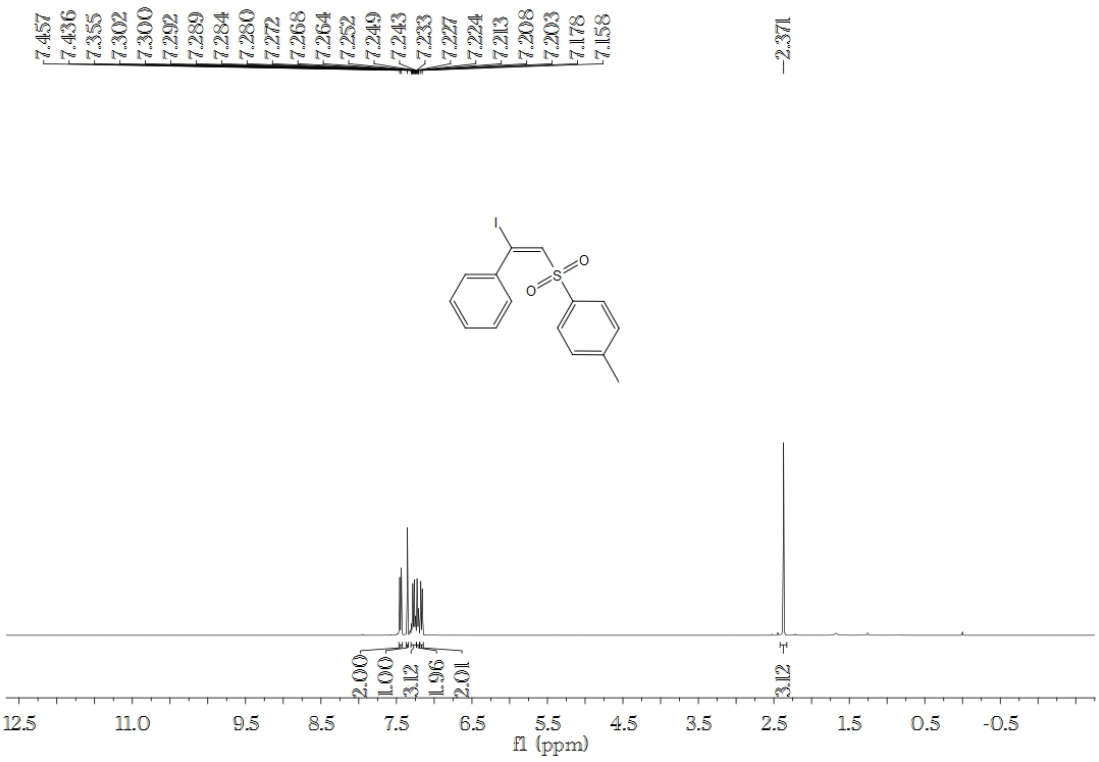
7.426
7.419
7.415
7.411
7.405
7.402
7.396
7.394
7.387
7.383
7.372
7.359
7.357
7.342
7.338
7.333
7.328
7.325
7.319
7.315
7.220
6.991
6.981
6.979
6.969
0.000
Br
O
S
O
S
1.00
5.08
1.05
1.00
1.03
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


141.395
138.954
135.924
134.421
134.268
134.177
130.503
128.525
128.034
127.641
77.317
77.000
76.682
210
190
170
150
130
110
90
70
50
30
20
10
0
f1 (ppm)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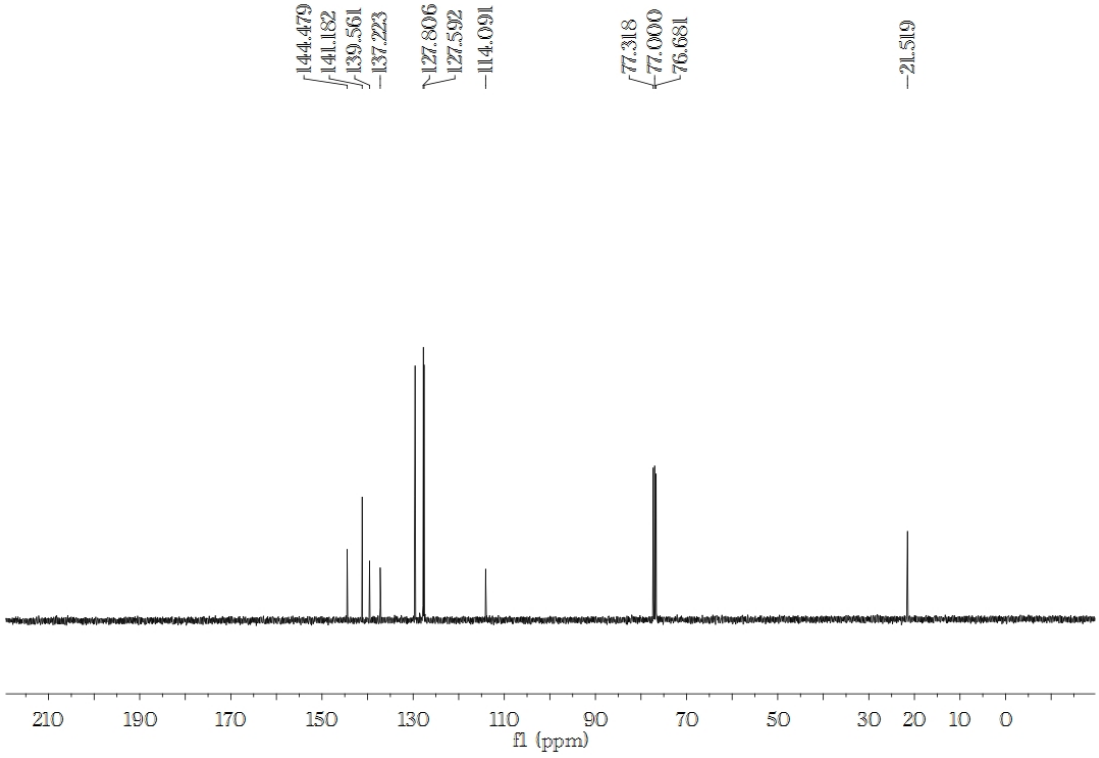
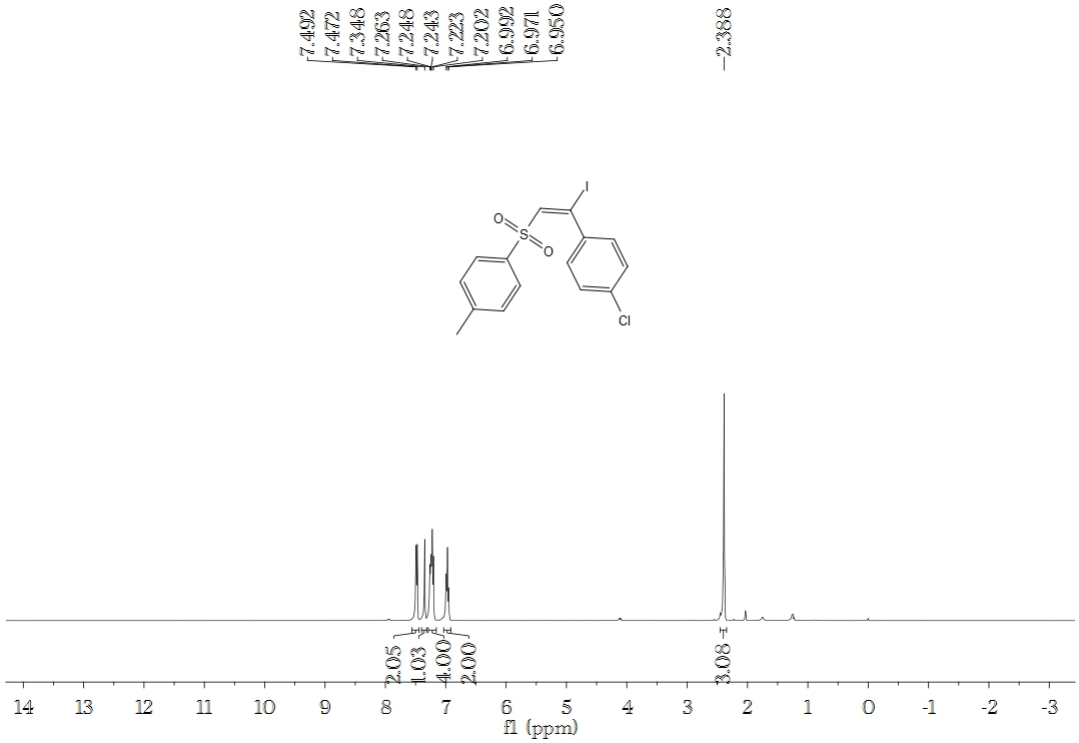
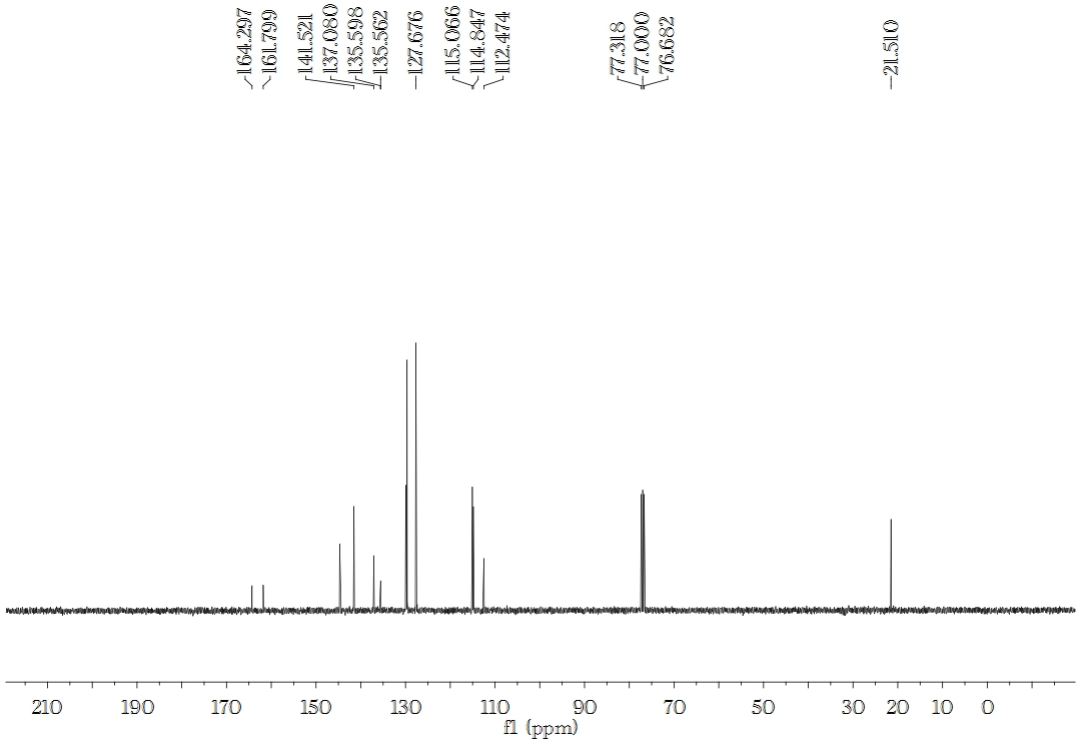
7.302
7.300
7.292
7.289
7.284
7.280
7.272
7.268
7.264
7.252
7.249
7.243
7.233
7.227
7.224
7.213
7.208
7.203
7.178
7.158
2.371
2.00
1.00
3.12
1.96
2.01
3.12
12.5
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


144.479
141.182
139.561
137.223
127.806
127.592
114.091
77.318
77.000
76.681
21.519
210
190
170
150
130
110
90
70
50
30
20
10
0
f1 (ppm)


7.492
7.472
7.348
7.263
7.248
7.243
7.223
7.202
6.992
6.971
6.950
2.388
I
O
S
O
Cl
2.05
1.03
4.00
2.00
3.08
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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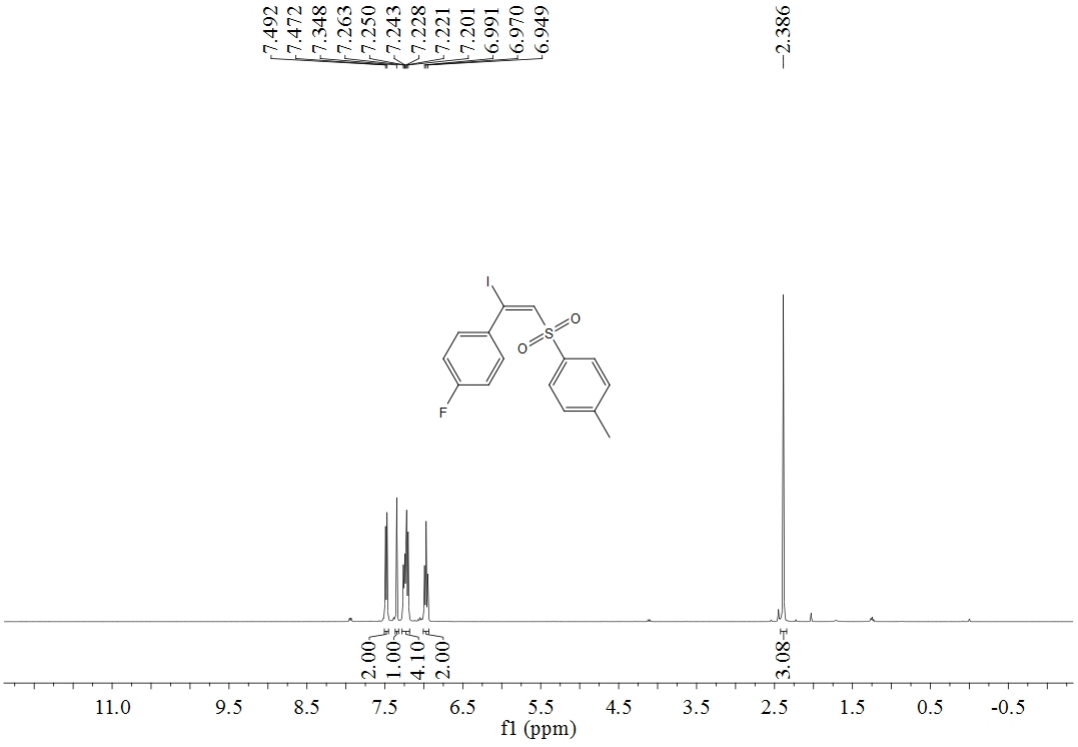
161.799
141.521
137.080
135.598
135.562
127.676
115.066
114.847
112.474
77.318
77.000
76.682
21.510
210 190 170 150 130 110 90 70 50 30 20 10 0
f1 (ppm)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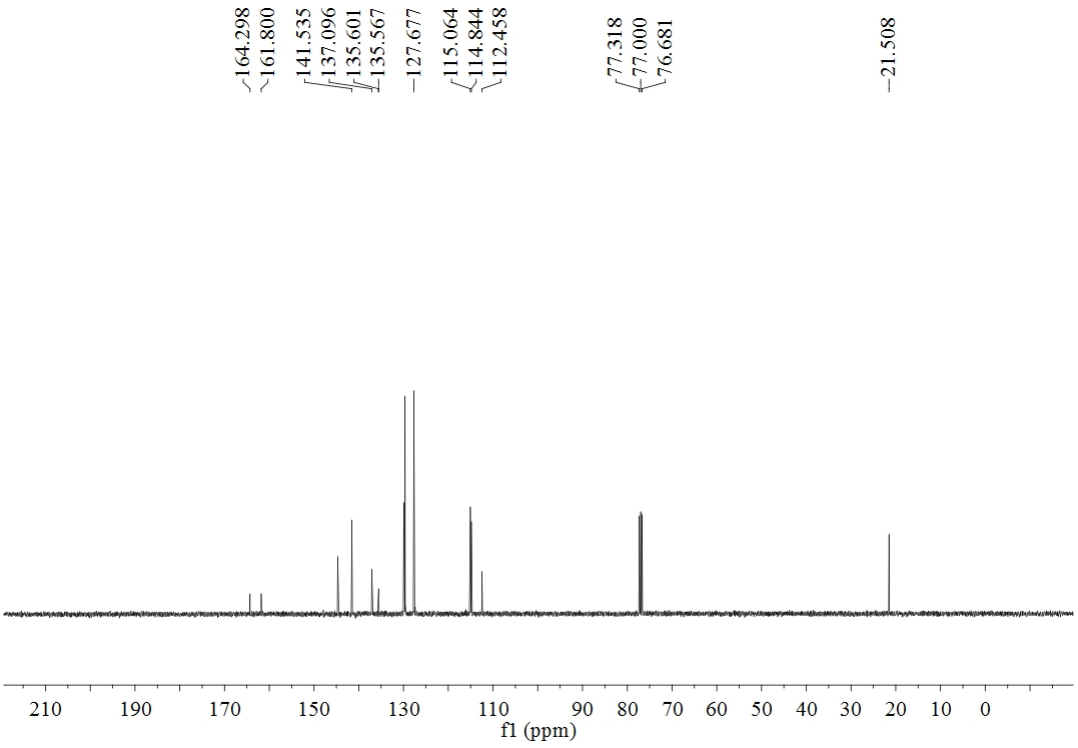
7.472
7.348
7.263
7.250
7.243
7.228
7.221
7.201
6.991
6.970
6.949
2.386
I
O
S
O
F
2.00
1.00
4.10
2.00
3.08
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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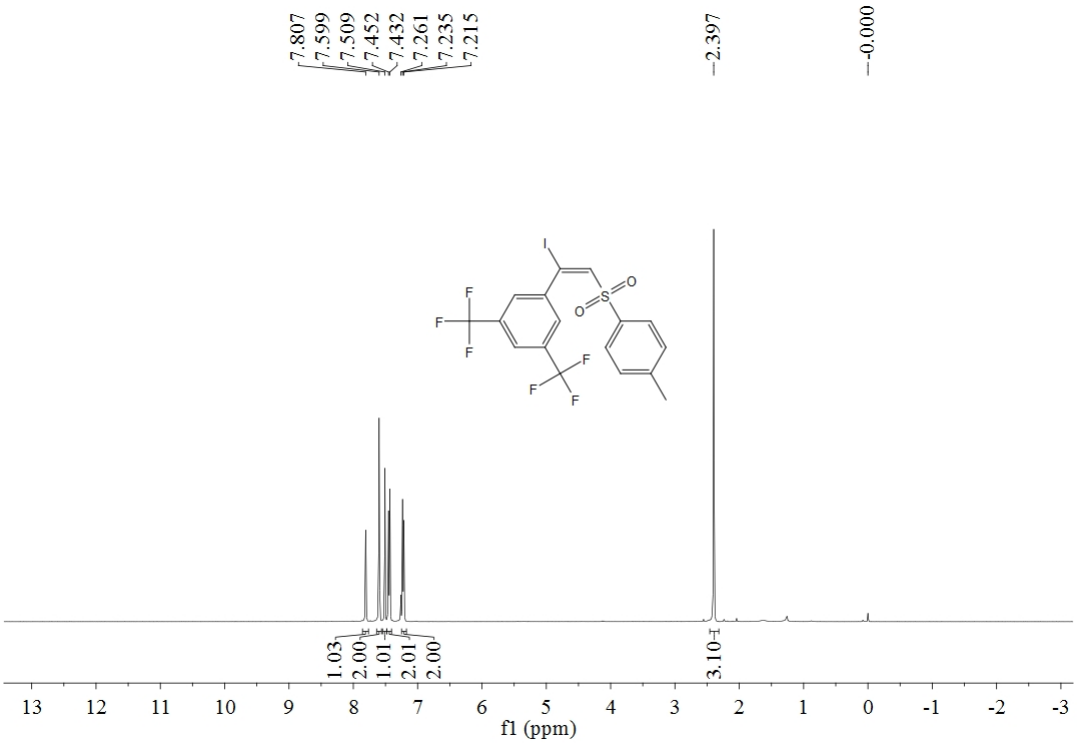
135.601
135.567
127.677
115.064
114.844
112.458
77.318
77.000
76.681
21.508
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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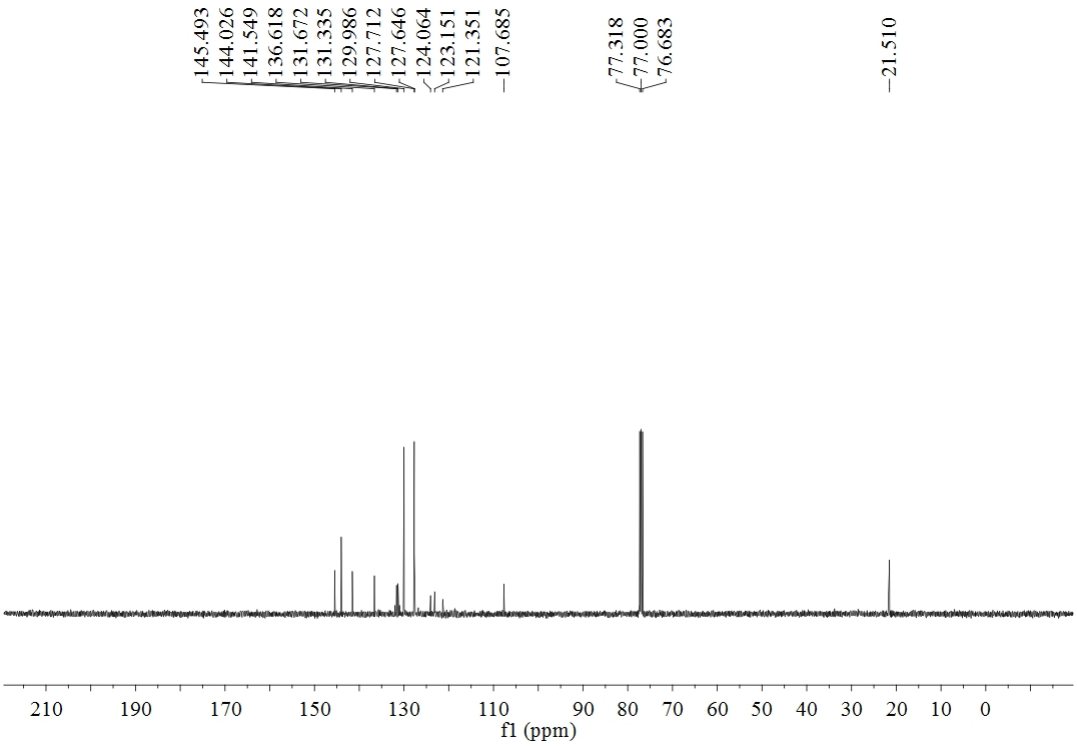
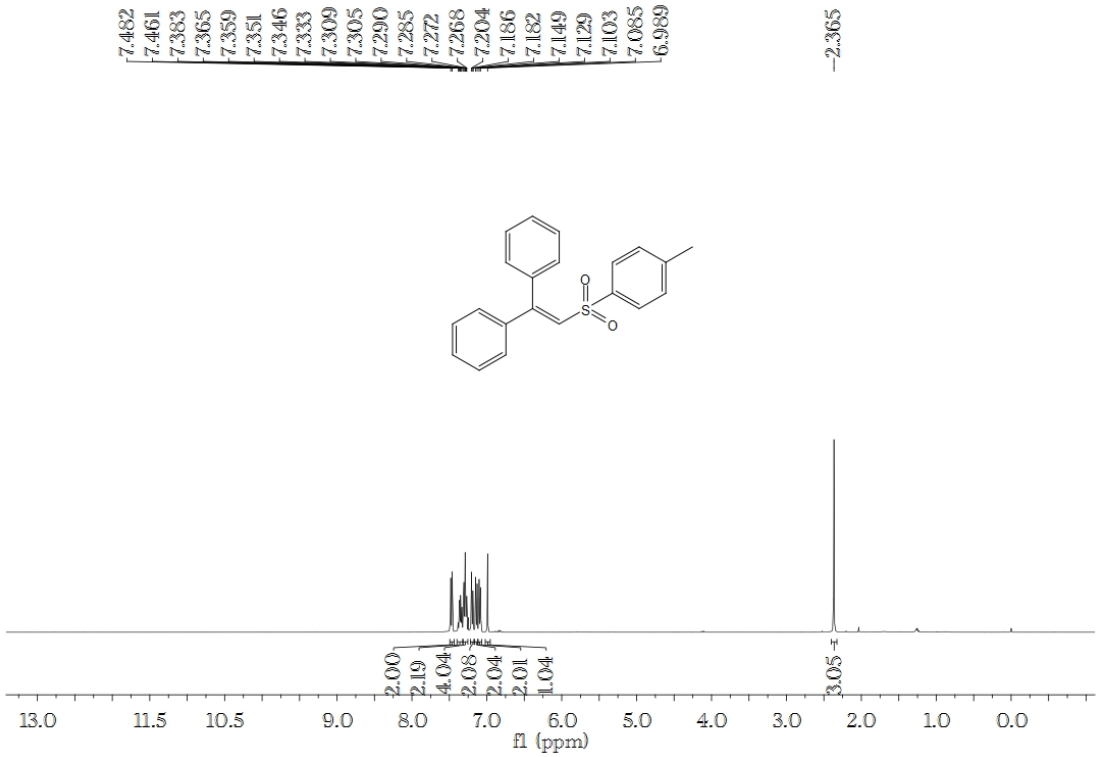
7.599
7.509
7.452
7.432
7.261
7.235
7.215
2.397
0.000
I
O
S
O
F
F
F
F
F
F
1.03
2.00
1.01
2.01
2.00
3.10
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


145.493
144.026
141.549
136.618
131.672
131.335
129.986
127.712
127.646
124.064
123.151
121.351
107.685
77.318
77.000
76.683
21.510
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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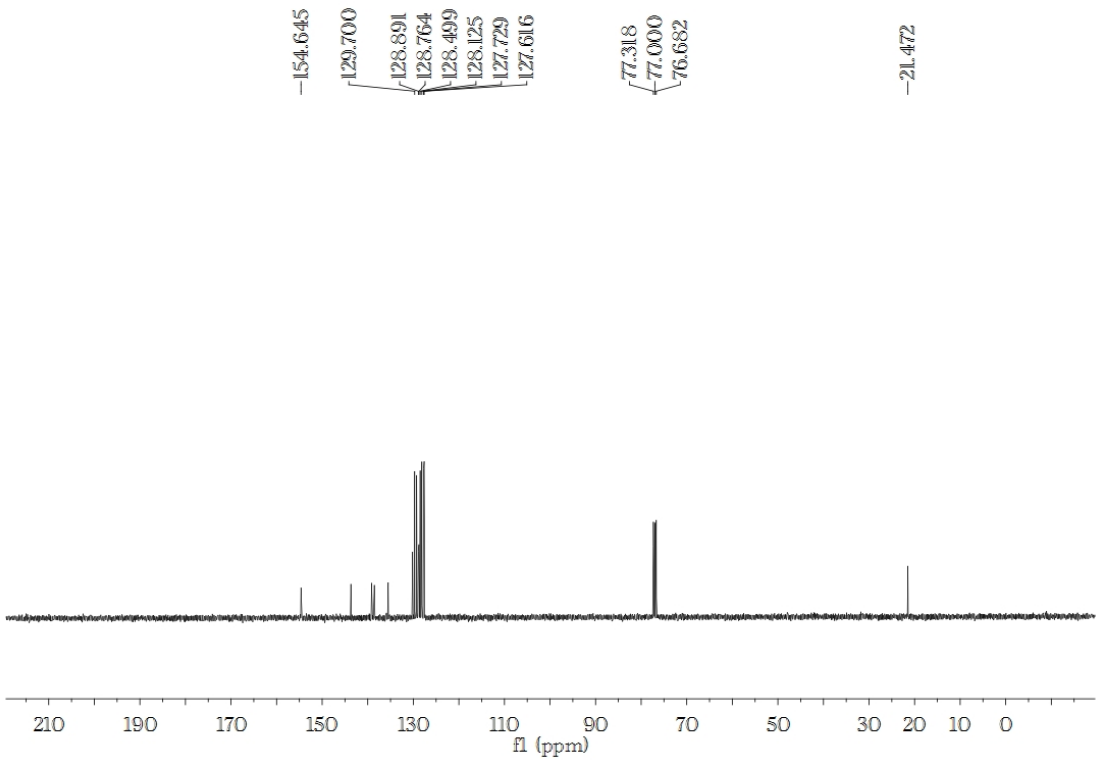
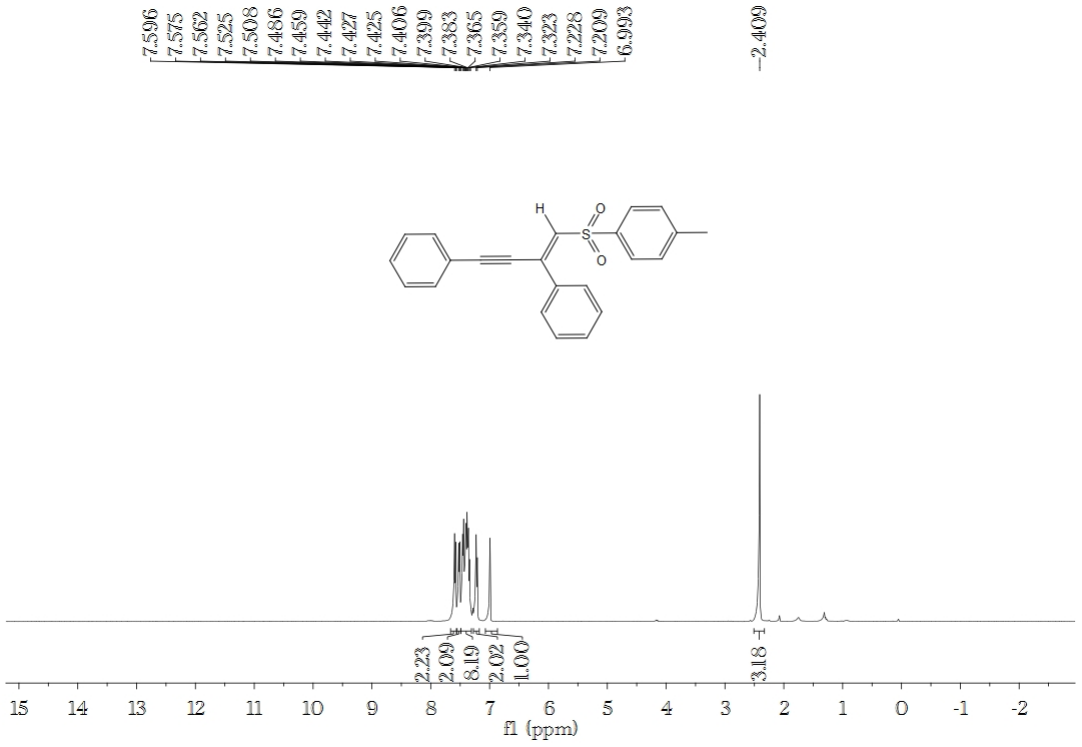
7.383
7.365
7.359
7.351
7.346
7.333
7.309
7.305
7.290
7.285
7.272
7.268
7.204
7.186
7.182
7.149
7.129
7.103
7.085
6.989
2.365
O
S
O
2.00
2.19
4.04
2.08
2.04
2.01
1.04
3.05
13.0
11.5
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


154.645
129.700
128.891
128.764
128.499
128.125
127.729
127.616
77.318
77.000
76.682
21.472
210
190
170
150
130
110
90
70
50
30
20
10
0
f1 (ppm)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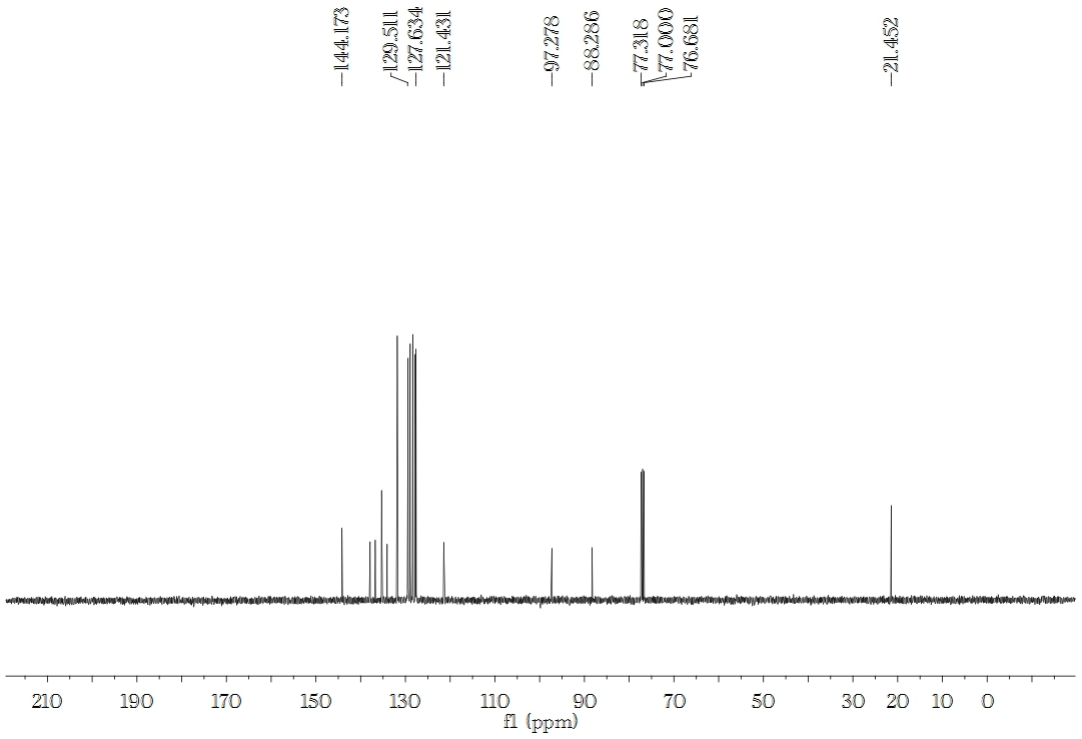
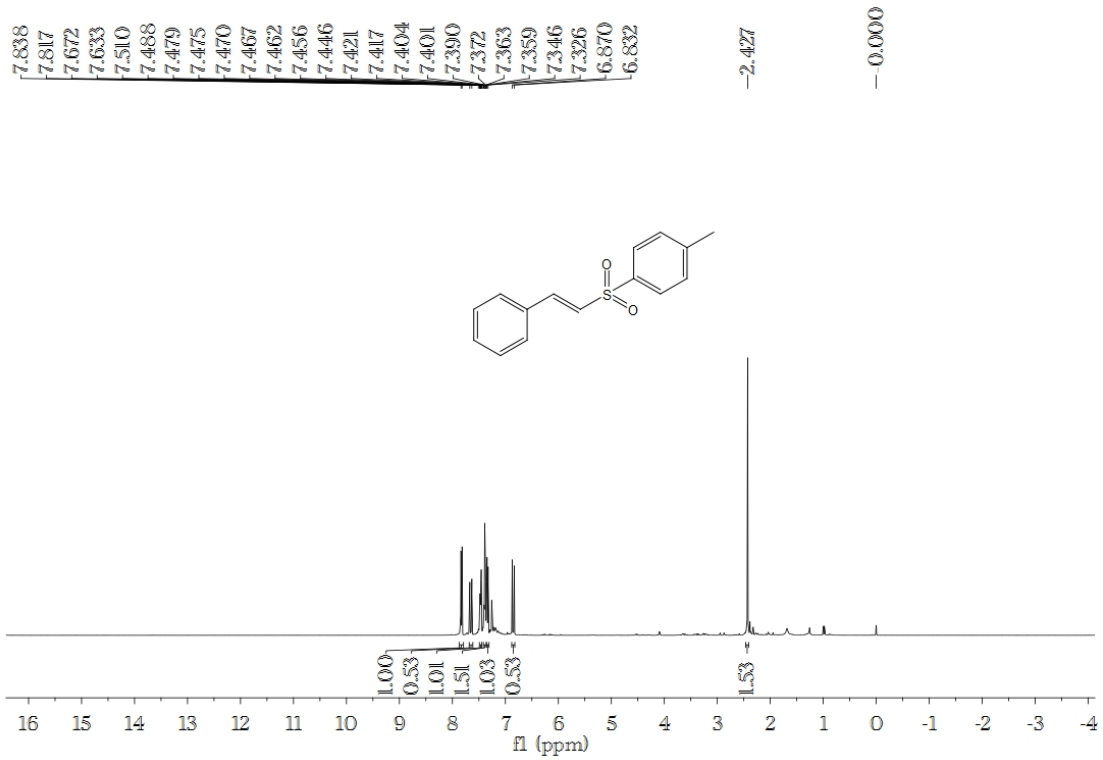
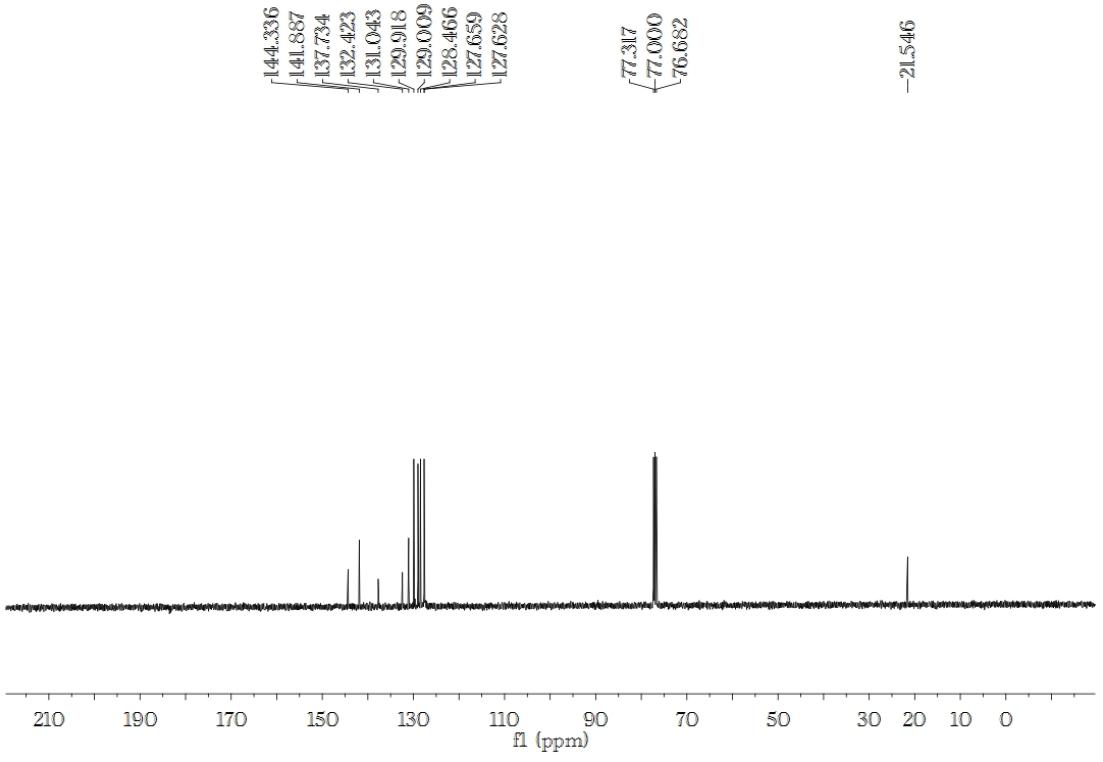
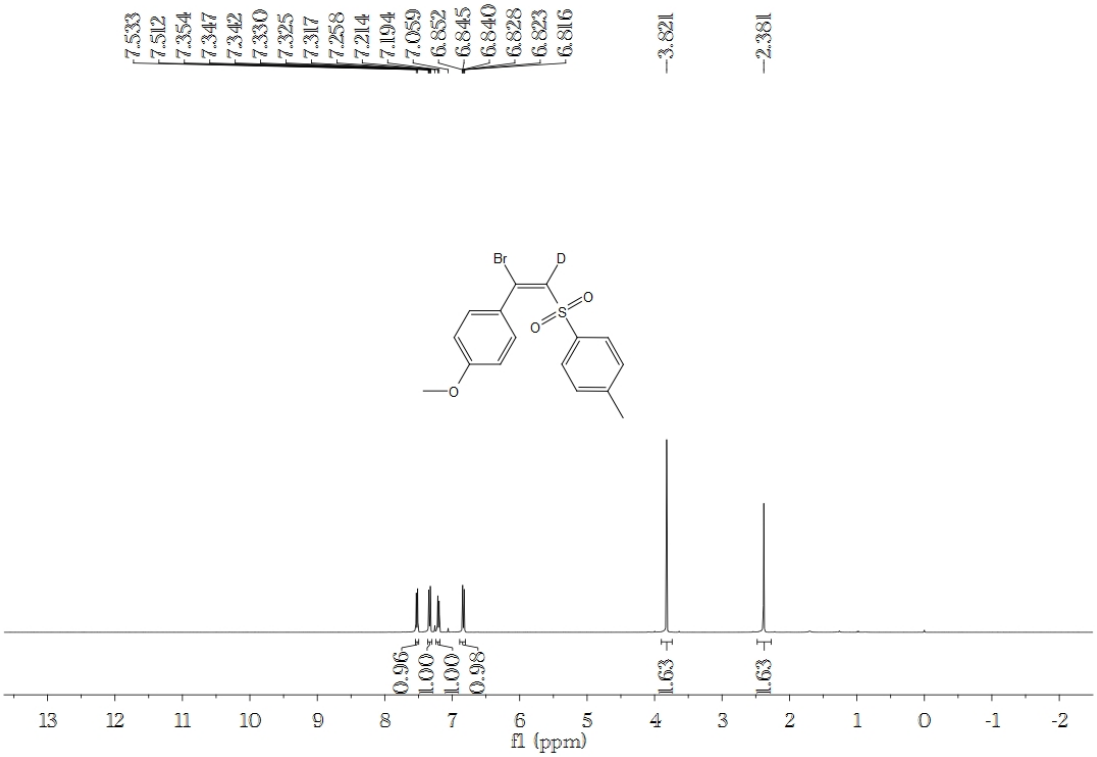
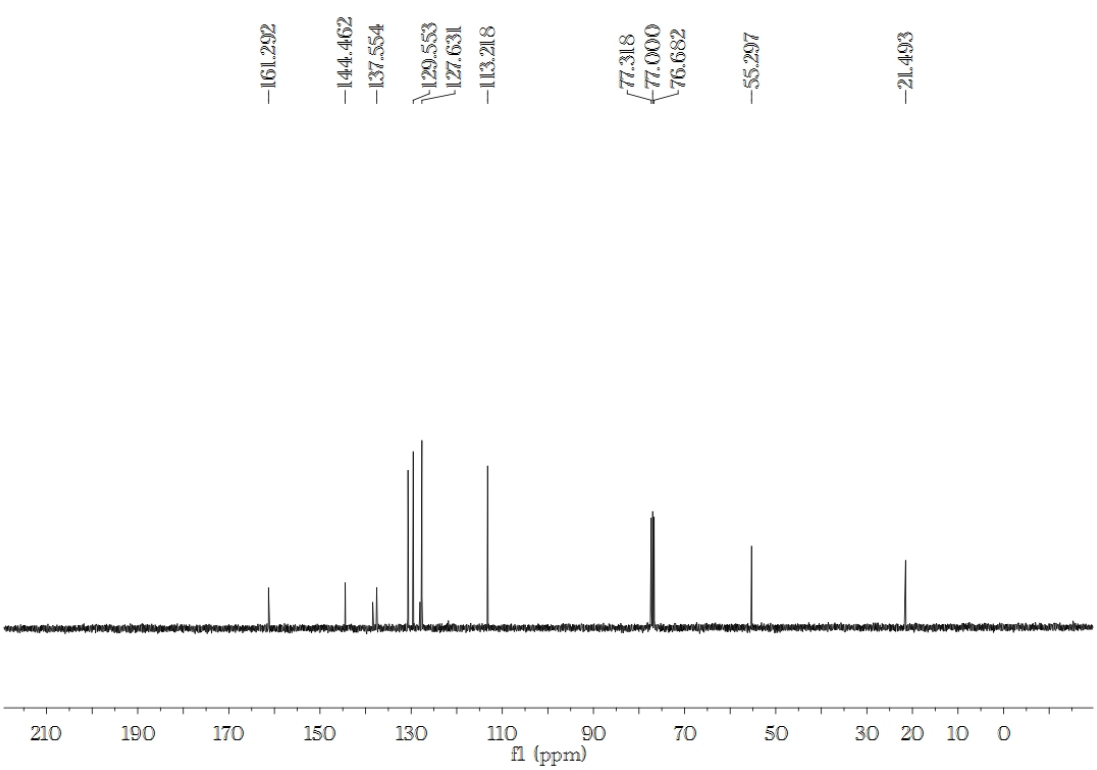
7.442
7.427
7.425
7.406
7.399
7.383
7.365
7.359
7.340
7.323
7.228
7.209
6.993
2.409
H
O
S
O
2.23
2.09
8.19
2.02
1.00
3.18
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


144.173
129.511
127.634
121.431
97.278
88.286
77.318
77.000
76.681
21.452
210 190 170 150 130 110 90 70 50 30 20 10 0
f1 (ppm)


7.838
7.817
7.672
7.633
7.510
7.488
7.479
7.475
7.470
7.467
7.462
7.456
7.446
7.421
7.417
7.404
7.401
7.390
7.372
7.363
7.359
7.346
7.326
6.870
6.832
2.427
0.000
1.00
0.53
1.01
1.51
1.03
0.53
1.53
f1 (ppm)


144.336
141.887
137.734
132.423
131.043
129.918
129.009
128.466
127.659
127.628
77.317
77.000
76.682
21.546
f1 (ppm)


7.533
7.512
7.354
7.347
7.342
7.330
7.325
7.317
7.258
7.214
7.194
7.059
6.852
6.845
6.840
6.828
6.823
6.816
3.821
2.381
Br
D
S
O
O
O
0.96
1.00
1.00
0.98
1.63
1.63
fl (ppm)


161.292
144.462
137.554
129.553
127.631
113.218
77.318
77.000
76.682
55.297
21.493
fl (ppm)