Transition-metal-free Synthesis of Vinyl Sulfones via a Tandem Cross-decarboxylative/coupling Reaction of Sodium Sulfinates and Cinnamic acids

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Supporting Information

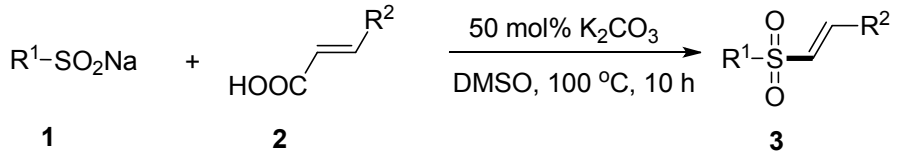
I. General Information

Solvents and all reagents were used as received. ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz and ^{13}C NMR spectra recorded in $CDCl_3$ at 100 MHz. The chemical shifts (d) were referenced to TMS. GC-MS was obtained using electron ionization (EI). 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. Melting points were measured with a micro melting point apparatus. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm.

II. General Procedure for the Preparation of Sodium Sulfinates (1c, 1g-1j).[1]

4-Methoxybenzenesulfinic acid sodium salt (**1c**) was prepared by heating 2.5 g of sodium sulfite, 2.06 g of 4-methoxybenzenesulphonyl chloride, and 1.68 g of sodium bicarbonate in 9.6 mL of water at 70-80 ^{o}C for 4 h. After cooling to room temperature, water was removed under vacuum and the residue was extracted by ethanol, recrystallization as a white solid, the yield was 67% (1.34 g). Similarly, other sodium arenesulfinates (**1g-1j**) was prepared from their corresponding sulphonyl chlorides.

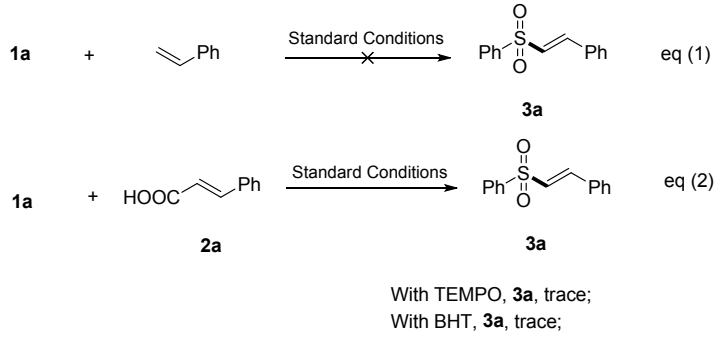
III. General Procedure for the Synthesis of Vinyl Sulfones.



The reaction mixture of sodium sulfinates **1** (0.75 mmol), cinnamic acids **2** (0.5 mmol), K_2CO_3 (0.25 mmol) in 2 mL of anhydrous DMSO in a 25 mL tube was stirred at 100 ^{o}C for 10 h under air atmosphere and monitored periodically by TLC. Upon completion, the crude

product was cooled to room temperature and then quenched by the addition of 5 mL water. The aqueous solution was extracted with ethyl acetate (3 × 5 mL) and the combined extracts were dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure by an aspirator, and the crude product was purified by silica gel column chromatography to give the pure product **3**.

IV. Control Experiments for the Study of Mechanism.



The reaction mixture of **1a** (0.75 mmol), styrene (0.5 mmol), K_2CO_3 (0.25 mmol) in 2 mL of anhydrous DMSO in a 25 mL tube was stirred at 100 ^oC for 10 h under air atmosphere, and then cooled to room temperature, quenched by the addition of 5 mL water. The aqueous solution was extracted with ethyl acetate (3 × 5 mL), dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure by an aspirator, and the crude product was detected by GC-MS.

The reaction mixture of **1a** (0.75 mmol), **2a** (0.5 mmol), K_2CO_3 (0.25 mmol), TEMPO (0.5 mmol) in 2 mL of anhydrous DMSO in a 25 mL tube was stirred at 100 ^oC for 10 h under air atmosphere and then cooled to room temperature, quenched by the addition of 5 mL water. The aqueous solution was extracted with ethyl acetate (3 × 5 mL), dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure by an aspirator, and the crude product was detected by GC-MS.

The reaction mixture of **1a** (0.75 mmol), **2a** (0.5 mmol), K_2CO_3 (0.25 mmol), BHT (0.5 mmol) in 2 mL of anhydrous DMSO in a 25 mL tube was stirred at 100 ^oC for 10 h under air atmosphere and then cooled to room temperature, quenched by the addition of 5 mL water. The aqueous solution was extracted with ethyl acetate (3 × 5 mL), dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure by an aspirator, and the crude product was detected by GC-MS.

V. Analytical Data for 3a-3v.

(*E*)-(2-(phenylsulfonyl)vinyl)benzene (**3a**).[2] Pale Yellow solid, mp 67-68 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.39 (d, *J* = 6.2 Hz, 3H), 6.87 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 140.7, 133.3, 132.3, 131.2, 129.3, 129.0, 128.5, 127.6, 127.3. IR (KBr): 3059, 2924, 1615, 1492, 1447, 1309, 1146, 1084, 975, 817, 749, 689 cm^{-1}. MS (EI) m/z: 244, 179, 125, 102, 92, 77.

(*E*)-1-methyl-4-(styrylsulfonyl)benzene (**3b**).[2] Pale yellow solid, mp 102–103 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 15.4 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.41-7.32 (m, 5H), 6.85 (d, *J* = 15.4 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 141.9, 137.8, 132.5, 131.1, 129.9, 129.0, 128.5, 127.7, 127.6, 21.6. IR (KBr): 3056, 2920, 1659, 1549, 1299, 1120, 973, 815, 748, 685 cm^{-1}. MS (EI) m/z: 258, 193, 179, 139, 119, 102.

(*E*)-1-methoxy-4-(styrylsulfonyl)benzene (**3c**).[2] Pale yellow solid, mp 110–112 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 15.5 Hz, 1H), 7.48-7.46 (m, 2H), 7.43-7.33 (m, 3H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 15.5 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 141.4, 132.5, 132.2, 131.0, 129.9, 129.0, 128.5, 127.9,

114.6, 55.7. IR (KBr): 3058, 2923, 1586, 1496, 1454, 1259, 1139, 1085, 817, 749 cm^{-1}. MS (EI) m/z: 274, 210, 194, 155, 123, 77.

(*E*)-1-fluoro-4-(styrylsulfonyl)benzene (**3d**).[2] Pale yellow solid, mp 95–96 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1Hz, 2H), 7.68 (d, *J* = 15.4 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.43-7.38 (m, 3H), 7.24-7.20 (m, 2H), 6.84 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 164.4, 142.7, 132.2, 131.3, 130.5, 129.11, 128.7, 127.1, 116.7, 116.5. IR (KBr): 3058, 2919, 1654, 1563, 1410, 1272, 1138, 1079, 806, 751 cm^{-1}. MS (EI) m/z: 262, 197, 143, 119, 102, 92, 77.

(*E*)-1-chloro-4-(styrylsulfonyl)benzene (**3e**).[2] Pale yellow solid, mp 107–108 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 6.4 Hz, 2H), 7.40 (q, *J* = 6.4 Hz, 3H), 6.83 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 140.1, 139.3, 132.2, 131.4, 129.7, 129.1, 128.6, 126.9. IR (KBr): 3060, 2925, 1614, 1578, 1476, 1394, 1318, 1147, 1088, 816, 753 cm^{-1}. MS (EI) m/z: 280, 278, 213, 178, 159, 119, 102, 77.

(*E*)-1-bromo-4-(styrylsulfonyl)benzene (**3f**). Yellow solid, mp 115–117 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 15.4 Hz, 1H), 7.48 (d, *J* = 6.6 Hz, 2H), 7.40 (q, *J* = 6.6 Hz, 3H), 6.83 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 139.8, 132.6, 132.2, 131.4, 129.2, 129.1, 128.6, 126.8. IR (KBr): 3055, 2924, 1663, 1516, 1462, 1382, 1247, 1078, 811, 750 cm^{-1}. MS (EI) m/z: 324, 322, 206, 178, 119, 102, 92. ESI-HRMS calcd for $C_{14}H_{11}BrNaO_2S$ $[M+Na]^+$ 344.9555, found 344.9554.

(*E*)-1-(styrylsulfonyl)-4-(trifluoromethyl)benzene (**3g**). Pale yellow solid, mp 77–79 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J*

= 15.4 Hz, 1H), 7.53-7.47 (m, 2H), 7.46-7.36 (m, 3H), 6.86 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 132.0, 131.6, 129.2, 128.7, 128.2, 126.4, 126.3. IR (KBr): 3054, 2925, 1614, 1571, 1451, 1323, 1141, 1061, 816, 746 cm^{-1}. MS (EI) m/z: 312, 227, 178, 145, 119, 102, 91. ESI-HRMS calcd for $C_{15}H_{11}F_3NaO_2S$ $[M+Na]^+$ 335.0324, found 335.0328.

(*E*)-1-chloro-2-(styrylsulfonyl)benzene (**3h**)**.** Pale yellow solid, mp 75–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 15.4 Hz, 1H), 7.56-7.39 (m, 8H), 7.08 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 138.2, 134.5, 132.8, 132.3, 131.9, 131.4, 130.7, 129.1, 128.7, 127.4, 125.2. IR (KBr): 3054, 2925, 1610, 1449, 1319, 1277, 1146, 1040, 820, 766 cm^{-1}. MS (EI) m/z: 280, 278, 213, 178, 119, 102, 91. ESI-HRMS calcd for $C_{14}H_{12}ClO_2S$ $[M+H]^+$ 279.0241, found 279.0235.

(*E*)-2-(styrylsulfonyl)thiophene (**3i**).[3] Pale yellow solid, mp 55–57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 3.6 Hz, 1H), 7.70-7.64 (m, 2H), 7.50 (d, *J* = 15.4 Hz, 1H), 7.49 (d, *J* = 4.9 Hz, 1H),7.44-7.36 (m, 3H), 7.14 (dd, *J* = 4.9, 3.6 Hz, 1H), 6.96 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 142.2, 133.9, 133.4, 132.3, 131.3, 129.1, 128.5, 127.9, 127.9. IR (KBr): 3092, 2922, 1651, 1548, 1396, 1306, 1226, 1137, 1015, 805, 721 cm^{-1}. MS (EI) m/z: 250, 202, 185, 152, 131, 105, 92.

(*E*)-2-(styrylsulfonyl)naphthalene (**3j**).[4] White solid, mp 115–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 15.4 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.50-7.48 (m, 2H), 7.41-7.36 (m, 3H), 6.93 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 137.5, 135.1, 132.4, 132.3, 131.2, 129.7, 129.4, 129.2, 129.1, 129.0, 128.6, 127.9, 127.6, 127.3, 122.5. IR (KBr): 3057, 2959, 1510, 1452, 1378, 1308, 1244, 1136, 810, 749, 661 cm^{-1}. MS (EI) m/z: 294, 229, 192, 175, 127, 92, 77.

(*E*)-(2-(methylsulfonyl)vinyl)benzene (**3k**).[2] Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 15.5 Hz, 1H), 7.52 (d, *J* = 6.7 Hz, 2H), 7.43 (t, *J* = 6.7 Hz, 3H), 6.92 (d, *J* = 15.5 Hz, 1H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 132.1, 131.4, 129.1, 128.5, 126.2, 43.3. IR (KBr): 3054, 2923, 1622, 1545, 1498, 1280, 1125, 946, 820, 752, 687 cm^{-1}. MS (EI) m/z: 182, 167, 119, 102, 91, 77.

(*E*)-(2-(ethylsulfonyl)vinyl)benzene (**3l**). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 15.5 Hz, 1H), 7.52 (d, *J* = 6.7 Hz, 2H), 7.46-7.40 (m, 3H), 6.81 (d, *J* = 15.4 Hz, 1H), 3.09 (q, *J* = 7.4 Hz, 2H), 1.39 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 132.3, 131.4, 129.2, 128.6, 124.1, 49.5, 7.2. IR (KBr): 3054, 2923, 1622, 1545, 1498, 1280, 1125, 946,820, 752, 687 cm^{-1}. MS (EI) m/z: 196, 167, 119, 103, 92, 77. ESI-HRMS calcd for $C_{10}H_{12}NaO_2S$ $[M+Na]^+$ 219.0450, found 219.0454.

(*E*)-(2-(cyclopropylsulfonyl)vinyl)benzene (**3m**). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 15.5 Hz, 1H), 7.53 (d, *J* = 6.3 Hz, 2H), 7.47-7.39 (m, 3H), 6.89 (d, *J* = 15.5 Hz, 1H), 2.47-2.40 (m, 1H), 1.34-1.28 (m, 2H), 1.11-1.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 132.5, 131.1, 129.1, 128.5, 125.7, 31.4, 5.3. IR (KBr): 3054, 2918, 1652, 1544, 1275, 1122, 969, 882, 746, 681 cm^{-1}. MS (EI) m/z: 208, 167, 129, 119, 91, 77. ESI-HRMS calcd for $C_{11}H_{12}NaO_2S$ $[M+Na]^+$ 231.0450, found 231.0457.

(*E*)-1-bromo-4-(2-(phenylsulfonyl)vinyl)benzene (**3n**)**.**[5] Pale yellow solid, mp 106-108 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.65 (d, *J* = 15.4 Hz, 1H), 7.63-7.49 (m, 5H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 15.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.5, 133.5, 132.4, 131.3, 129.9, 129.4, 128.0, 127.7, 125.7. IR (KBr): 3052, 2920, 1653, 1516, 1462, 1382, 1247, 1078, 815, 749 cm^{-1}. MS (EI) m/z: 324, 322, 207, 180, 150, 118, 102.

(*E*)-1,3-dichloro-2-(2-(phenylsulfonyl)vinyl)benzene (3o).[6] Pale yellow solid, mp 80-81

^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.86 (d, *J* = 15.8 Hz, 1H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.25-7.19 (m, 1H), 7.15 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 135.8, 135.5, 135.3, 133.6, 130.7, 129.8, 129.4, 128.9, 127.9. MS (EI) m/z: 314, 312, 277, 207, 171, 159, 125.

(*E*)-4-(2-(phenylsulfonyl)vinyl)benzonitrile (3p). Yellow solid, mp 113-114 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 15.5 Hz, 1H), 7.67–7.61 (m, 3H), 7.58-7.54 (m, 4H), 6.97 (d, *J* = 15.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 139.7, 136.6, 133.8, 132.7, 130.9, 129.5, 128.9, 127.8, 117.9, 114.2. IR (KBr): 3054, 2918, 2230, 1650, 1385, 1277, 1124, 1101, 969, 882, 743, 618 cm^{-1}. MS (EI) m/z: 269, 207, 176, 125, 116, 77. ESI-HRMS calcd for $C_{15}H_{12}NO_2S$ $[M+H]^+$ 270.0583, found 270.0577.

(*E*)-1-nitro-4-(2-(phenylsulfonyl)vinyl)benzene (**3q**). Yellow solid, mp 139-140 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 15.5 Hz, 1H), 7.67-7.53 (m, 5H), 7.04 (d, *J* = 15.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 139.7, 139.2, 138.4, 133.8, 131.7, 129.5, 129.2, 127.8, 124.2. IR (KBr): 3064, 2925, 1595, 1520, 1346, 1308, 1275, 1147, 811, 751 cm^{-1}. MS (EI) m/z: 289, 259, 225, 178, 148, 125. ESI-HRMS calcd for $C_{14}H_{11}NNaO_4S$ $[M+Na]^+$ 312.0301, found 312.0290.

(*E*)-1-methoxy-2-(2-(phenylsulfonyl)vinyl)benzene (3r). Pale yellow solid, mp 97-98 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 15.5 Hz, 1H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.39 (dd, *J* = 19.4, 7.9 Hz, 2H), 7.08 (d, *J* = 15.5 Hz, 1H), 6.98-6.90 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 141.2, 138.6, 133.1, 132.5, 130.8, 129.2, 127.9, 127.6, 121.2, 120.8, 111.2, 55.5. IR (KBr): 3052, 2920, 1648, 1465, 1385, 1277, 1142, 1023, 766, 638 cm^{-1}. MS (EI) m/z: 274, 207, 132, 118, 105, 77. ESI-HRMS calcd for $C_{15}H_{15}O_3S$ $[M+H]^+$ 275.0736, found 275.0742.

(*E*)-1-methoxy-3-(2-(phenylsulfonyl)vinyl)benzene (3s). Pale yellow solid, mp 115-117 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 15.4 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.21 (dd, *J* = 15.0, 7.1 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.93 – 6.84 (m, 2H), 6.78 (d, *J* = 15.4 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 142.4, 140.7, 133.6, 133.4, 130.1, 129.3, 127.6, 127.5, 121.2, 117.1, 113.3, 55.3. IR (KBr): 3050, 2923, 1579, 1460, 1385, 1276, 1143, 1123, 1085, 747, 619 cm^{-1}. MS (EI) m/z: 274, 165, 149, 132, 121, 77. ESI-HRMS calcd for $C_{15}H_{15}O_3S$ $[M+H]^+$ 275.0736, found 275.0742.

(*E*)-1-methyl-3-(2-(phenylsulfonyl)vinyl)benzene (3t). Pale yellow solid, mp 105-106 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.66 (d, *J* = 15.5 Hz, 1H), 7.63-7.51 (m, 3H), 7.33-7.27 (m, 3H), 7.23-7.22 (m, 1H), 6.84 (d, *J* = 15.5 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 140.8, 138.8, 133.3, 132.3, 132.0, 129.3, 129.1, 128.9, 127.6, 127.0, 125.8, 21.2. IR (KBr): 3048, 2923, 1614, 1445, 1384, 1260, 1143, 1084, 747, 621 cm^{-1}. MS (EI) m/z: 258, 207, 177, 133, 105, 77. ESI-HRMS calcd for $C_{15}H_{15}O_2S$ $[M+H]^+$ 259.0787, found 259.0796.

(*E*)-2-(2-(phenylsulfonyl)vinyl)pyridine (3u). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.4 Hz, 1H), 7.96 (d, *J* = 7.4 Hz, 2H), 7.74 (td, *J* = 7.7, 1.5 Hz, 1H), 7.65 (d, *J* = 14.9 Hz, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 14.9 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.29 (dd, *J* = 7.1, 5.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 150.2, 140.4, 140.2, 137.1, 133.5, 131.9, 129.3, 127.9, 125.5, 125.0. IR (KBr): 3054, 2920, 1647, 1549, 1463, 1305, 1144, 819, 754 cm^{-1}. MS (EI) m/z: 245, 216, 180, 125, 104, 92. ESI-HRMS calcd for $C_{13}H_{11}NNaO_2S$ $[M+Na]^+$ 268.0403, found 268.0411.

(*E*)-2-(2-(phenylsulfonyl)vinyl)thiophene (3v). Pale yellow solid, mp 93-94 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.80 (d, *J* = 15.1 Hz, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 4.9 Hz, 1H), 7.31 (d, *J* = 3.9 Hz, 1H), 7.07 (dd, *J*

= 4.9, 3.9 Hz, 1H), 6.65 (d, *J* = 15.1 Hz, 1H). MS (EI) m/z: 250, 185, 125, 108, 97, 77. IR (KBr): 3049, 2920, 1602, 1445, 1385, 1277, 1123, 1045, 805, 749 cm^{-1}. ESI-HRMS calcd for $C_{12}H_{11}O_2S_2$ $[M+H]^+$ 251.0195, found 251.0198.

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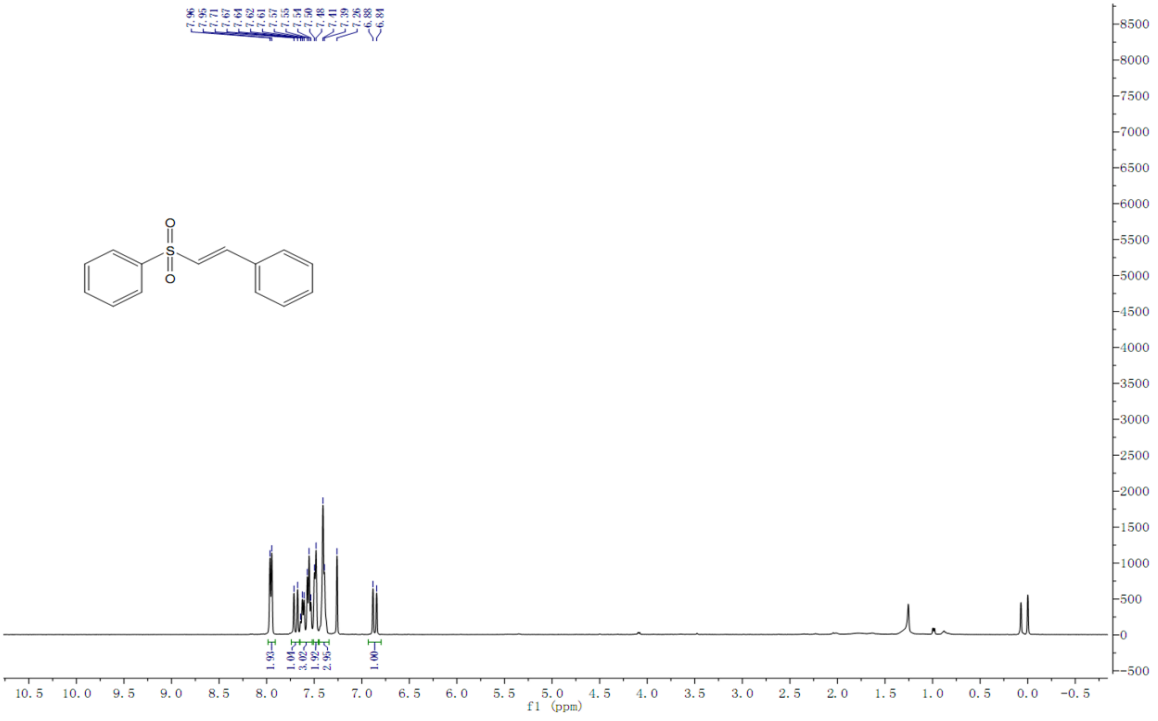
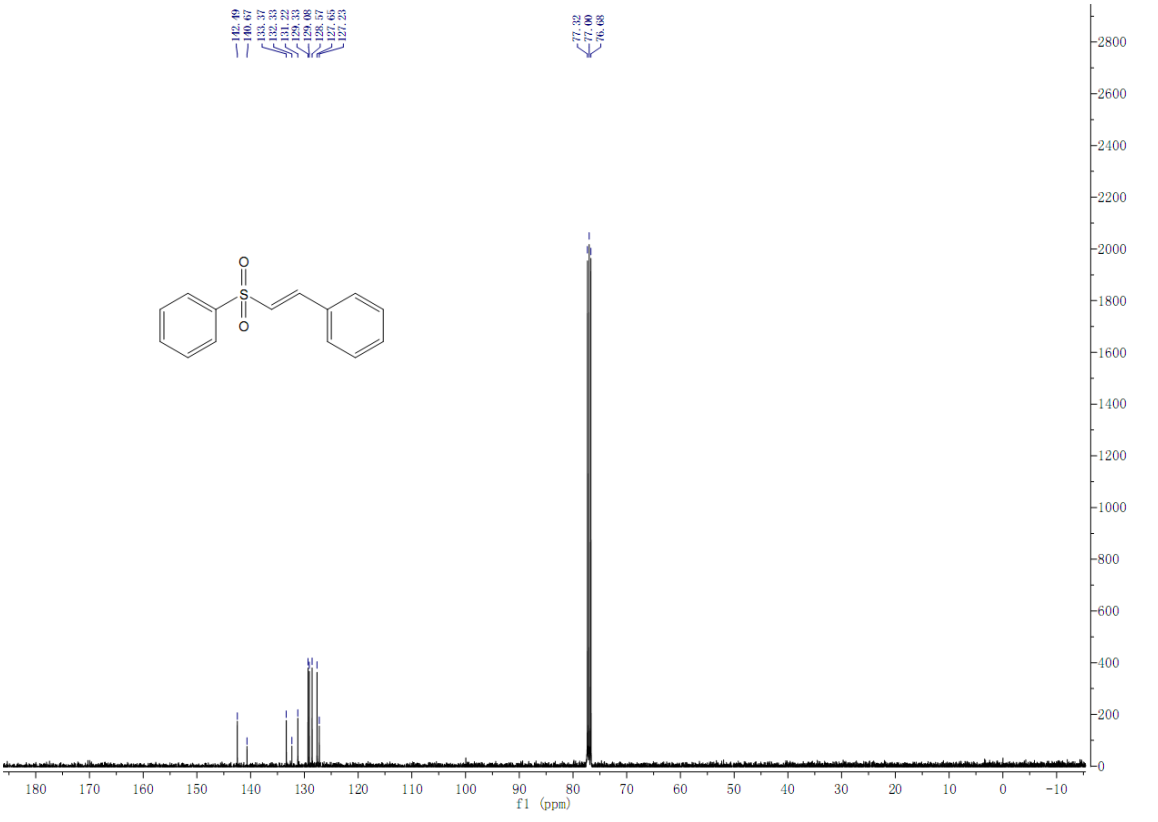
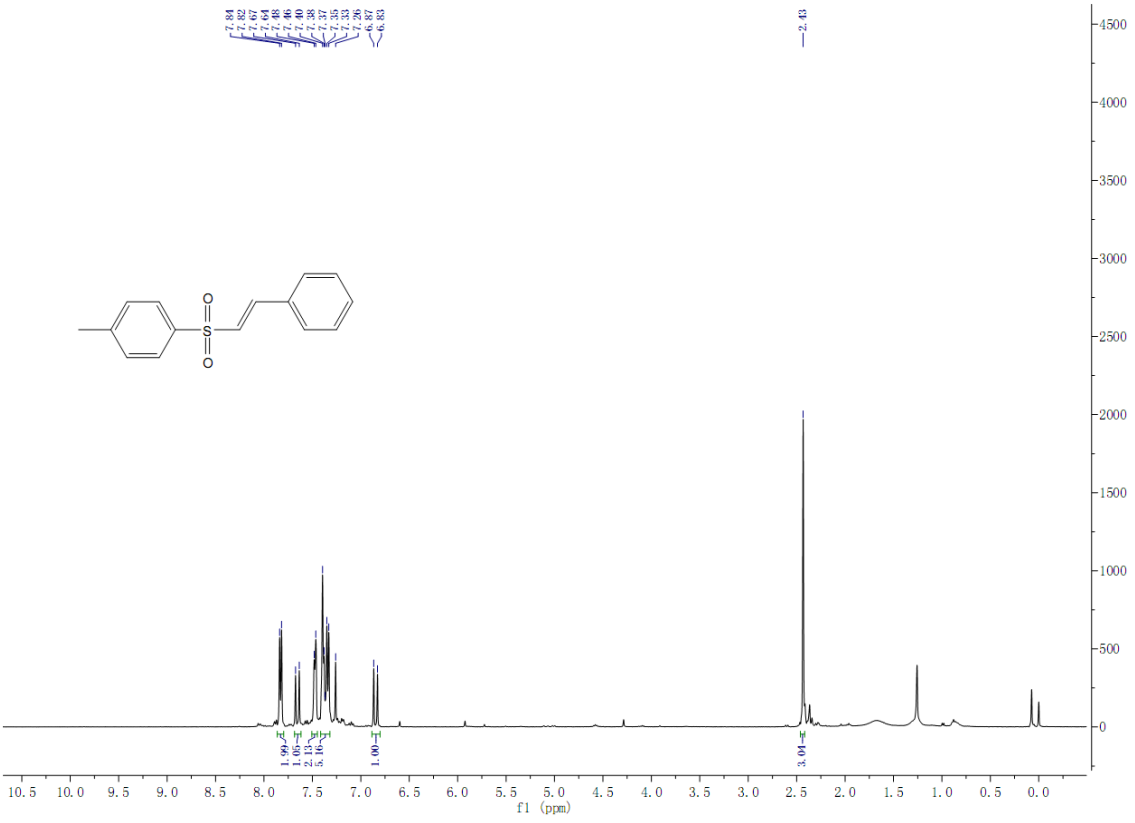
6. M. S. South, A. J. Obiako, R. E. Sykora, D. C. Forbes, *Acta Cryst.* 2011, **67**, 1055.

VI. NMR Spectra for All Compounds



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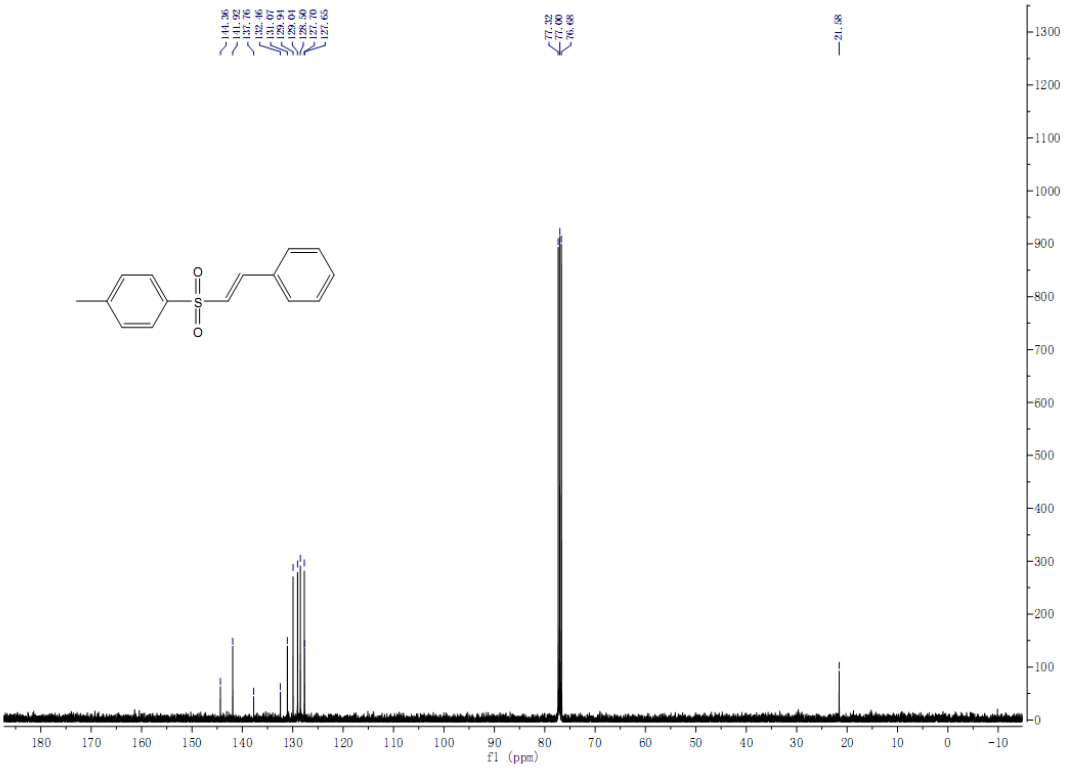
1.99
1.05
2.13
5.16
1.00
3.04
f1 (ppm)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77.00
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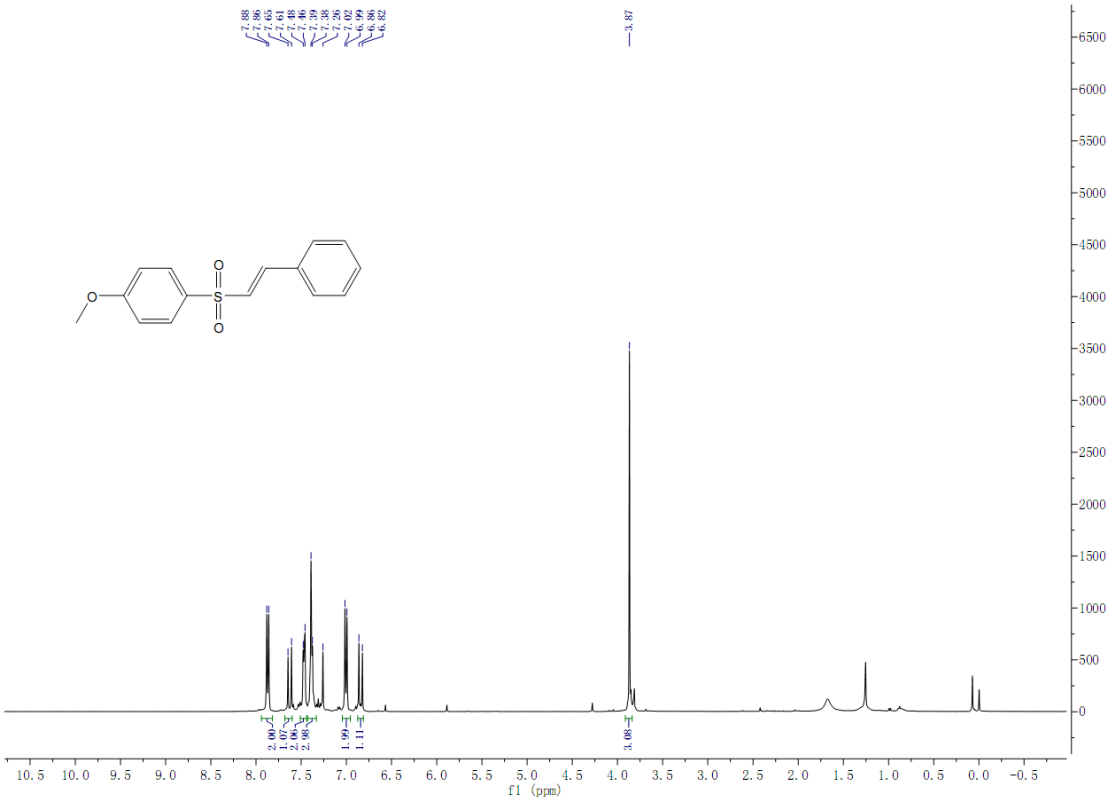
f1 (ppm)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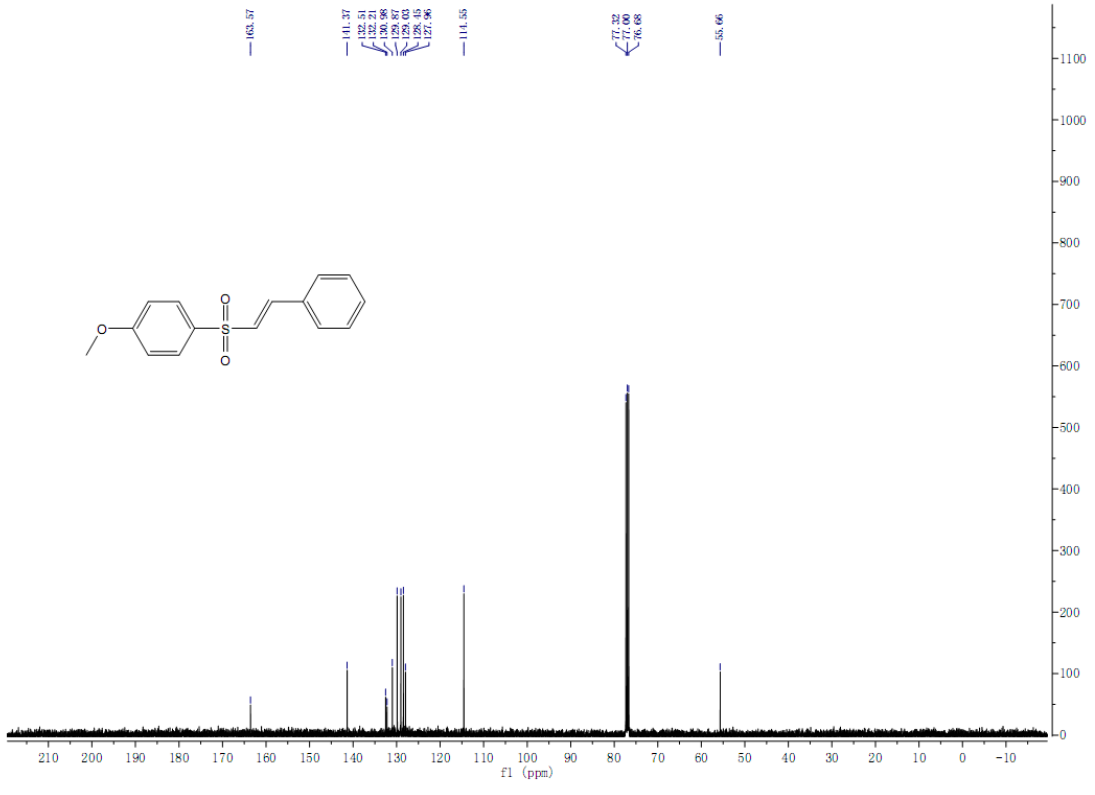
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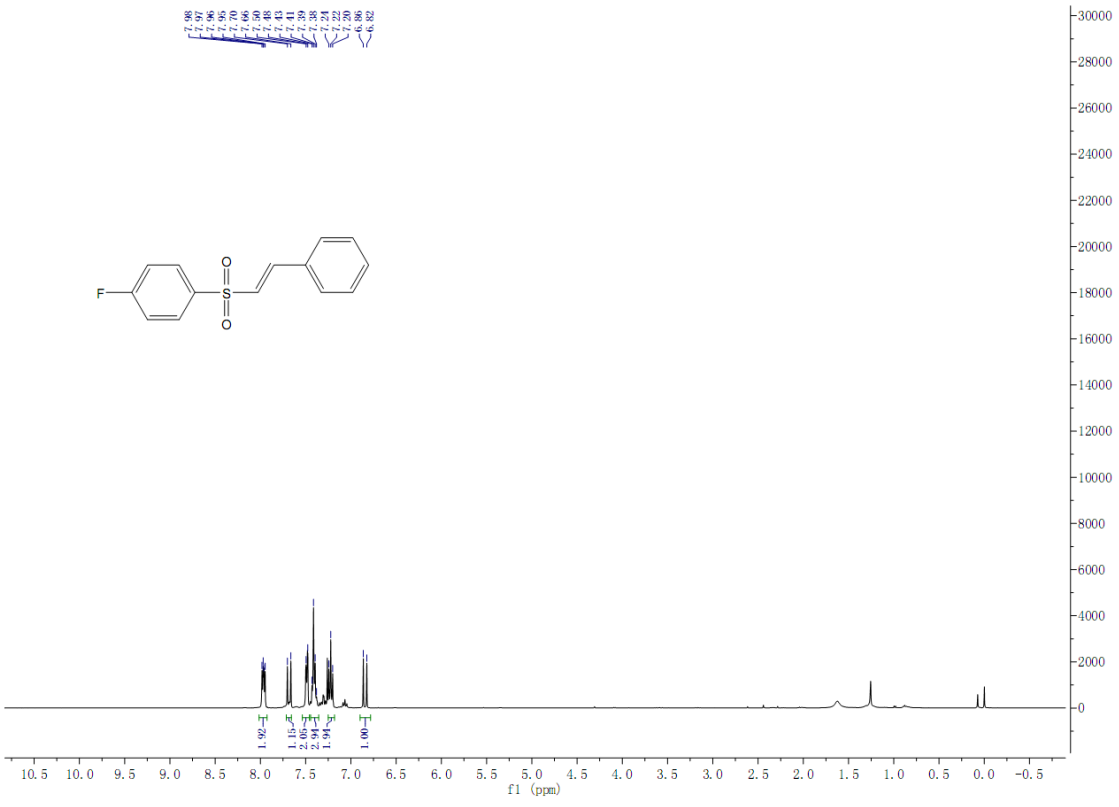
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7.22
7.20
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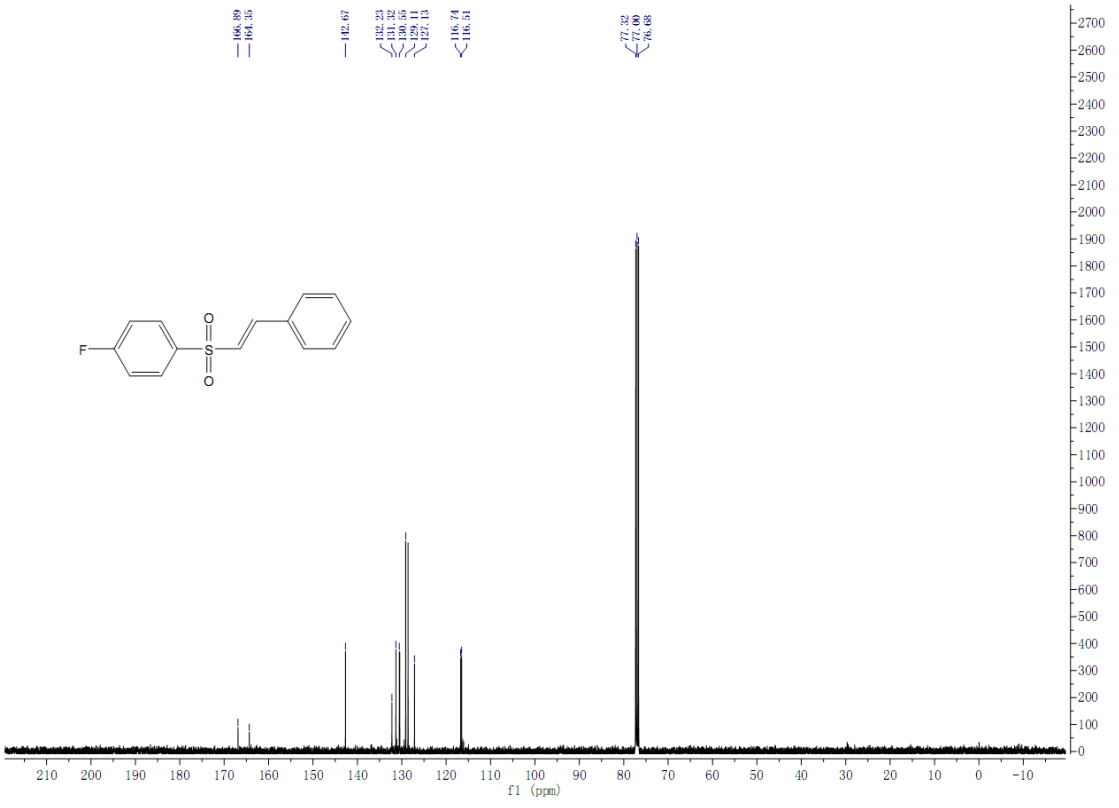
f1 (ppm)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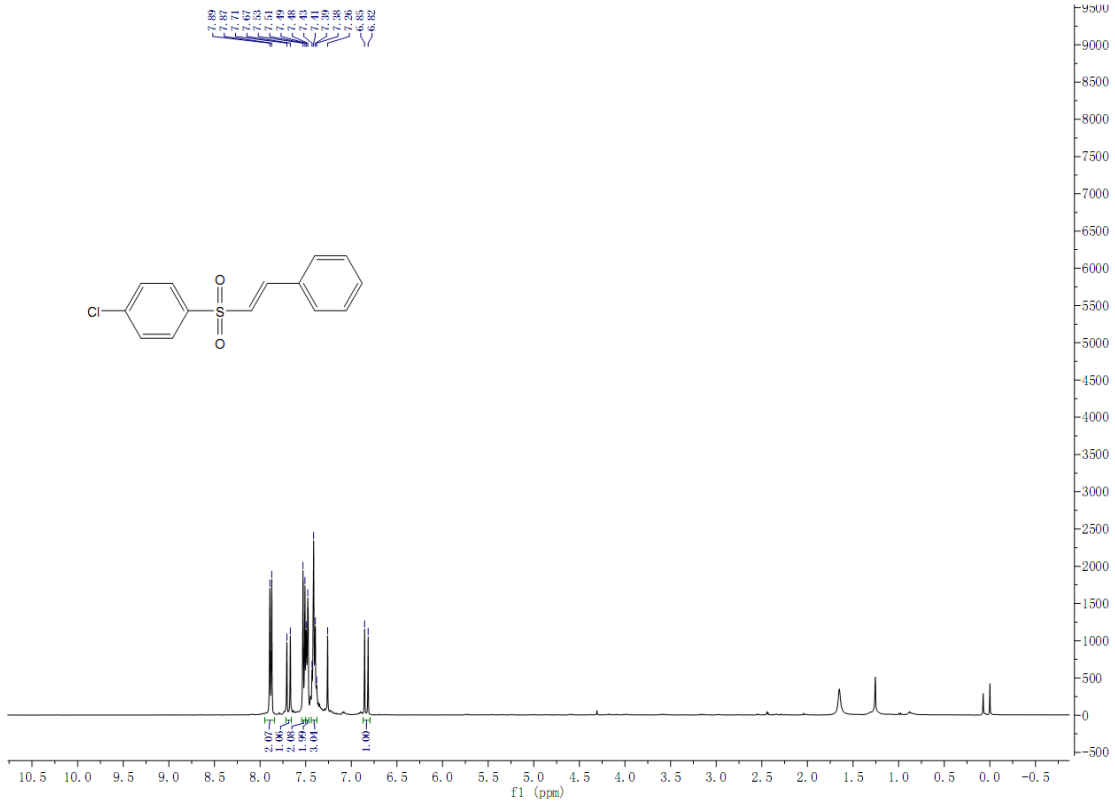
O
f1 (ppm)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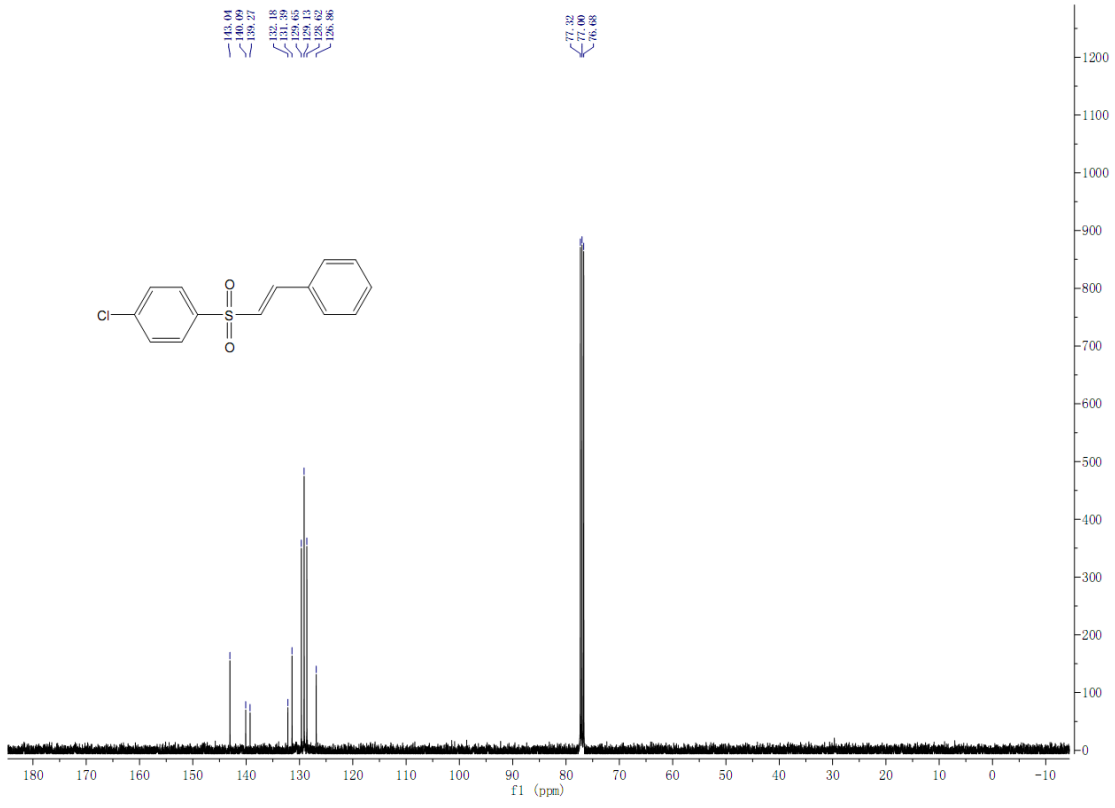
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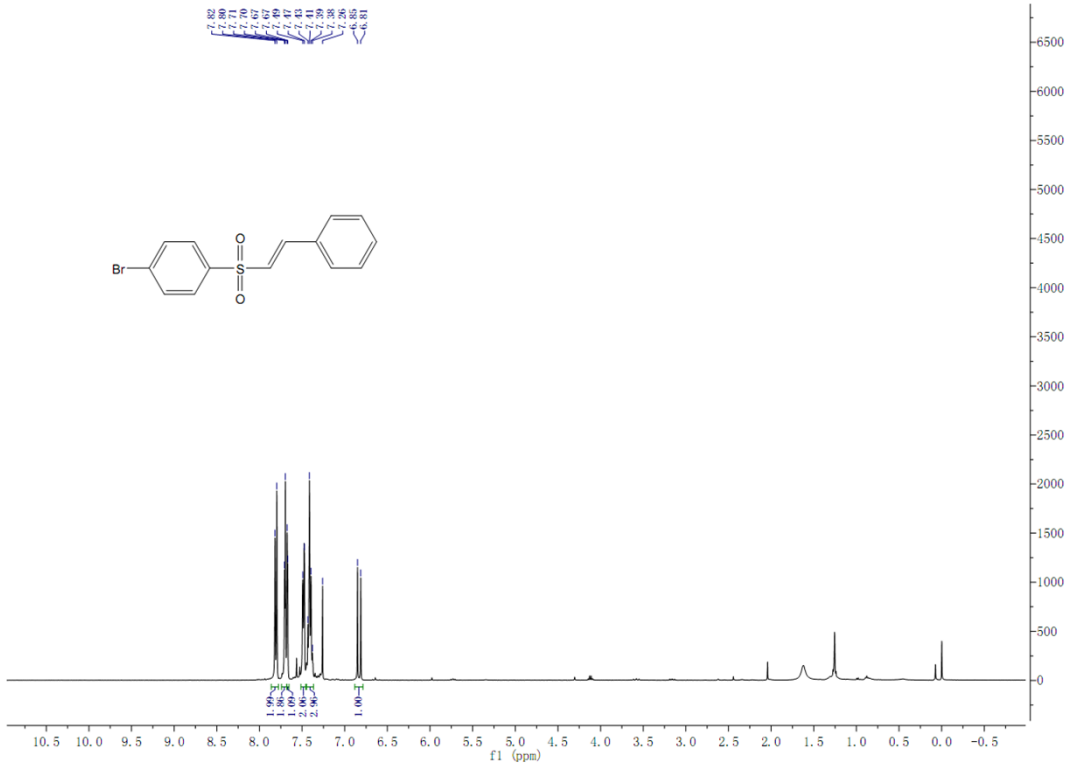
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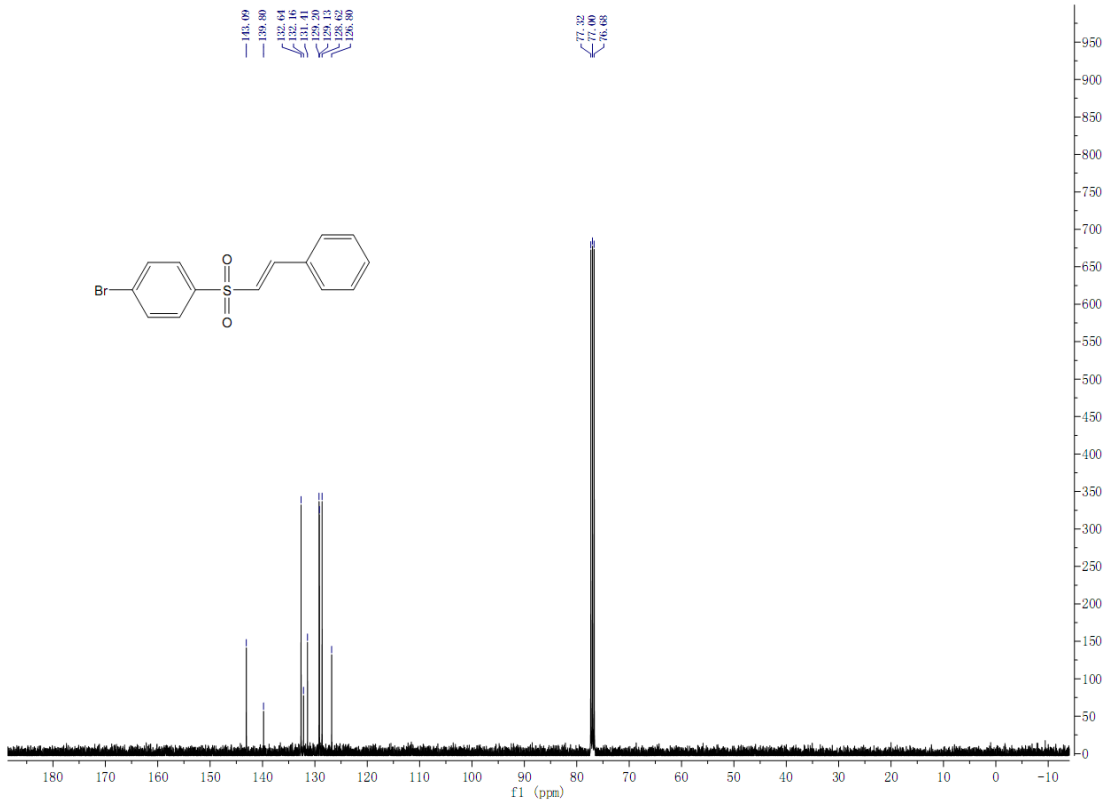
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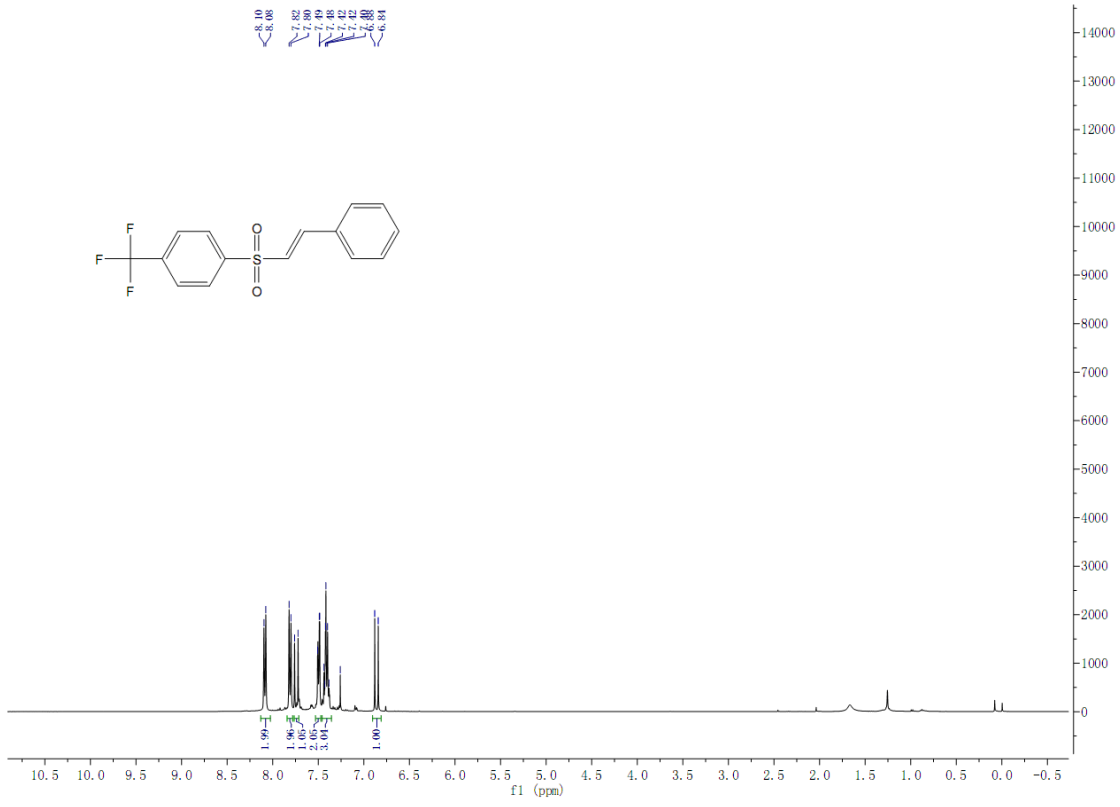
S
O
f1 (ppm)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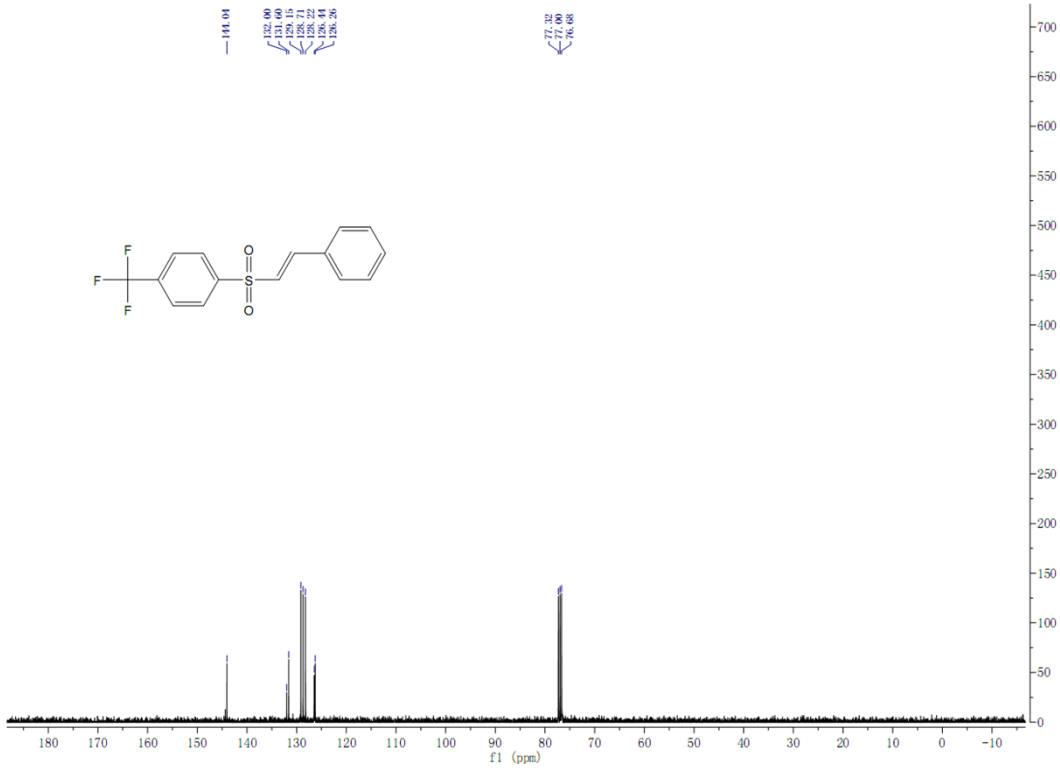
2.05
3.04
1.00
f1 (ppm)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F
F
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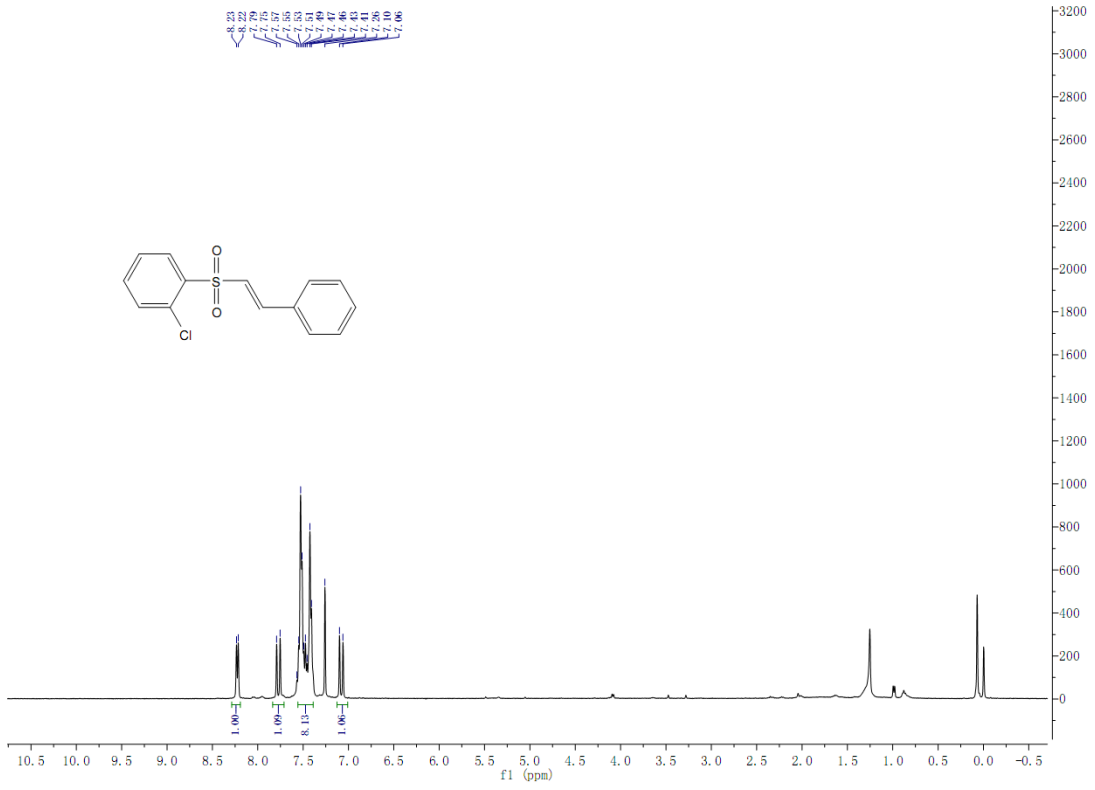
S
O
f1 (ppm)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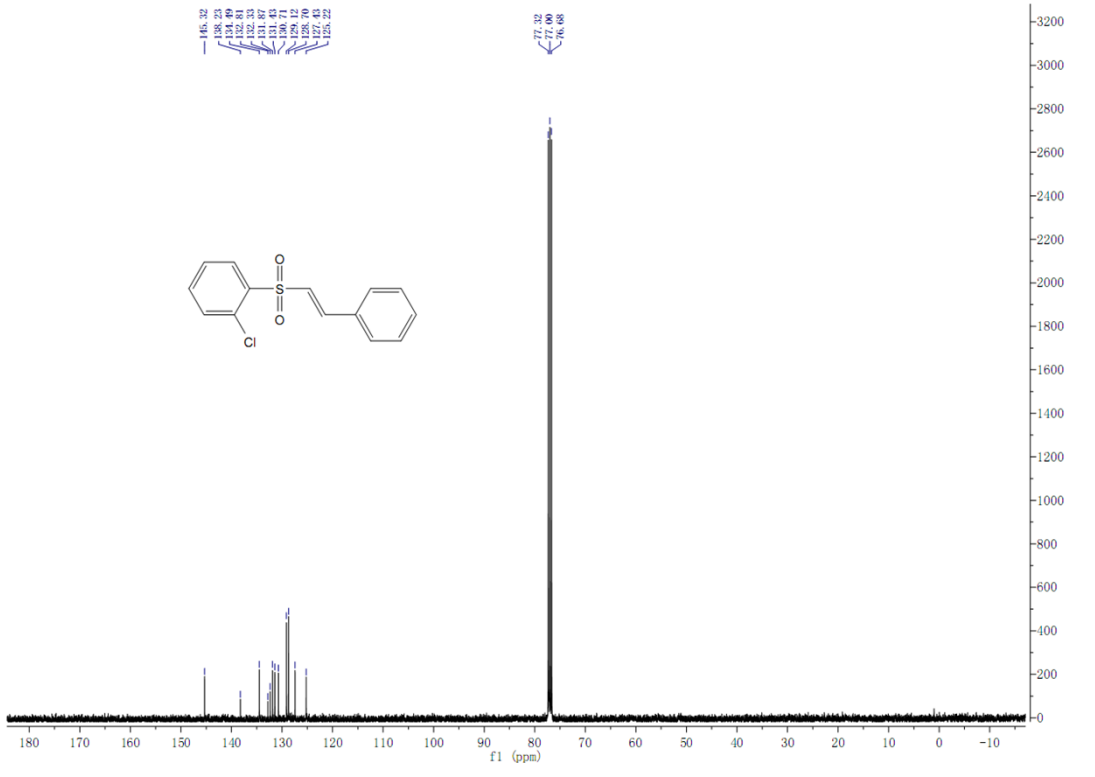
1.06
f1 (ppm)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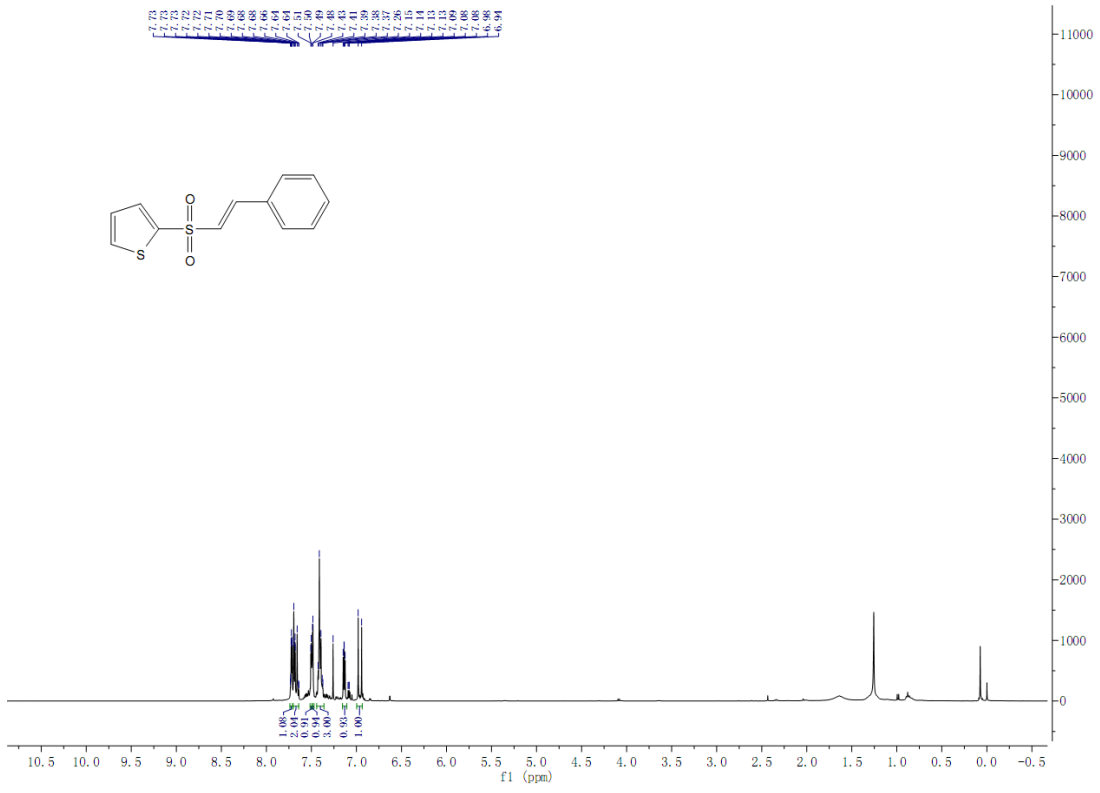
O
Cl
f1 (ppm)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7.15
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7.08
7.08
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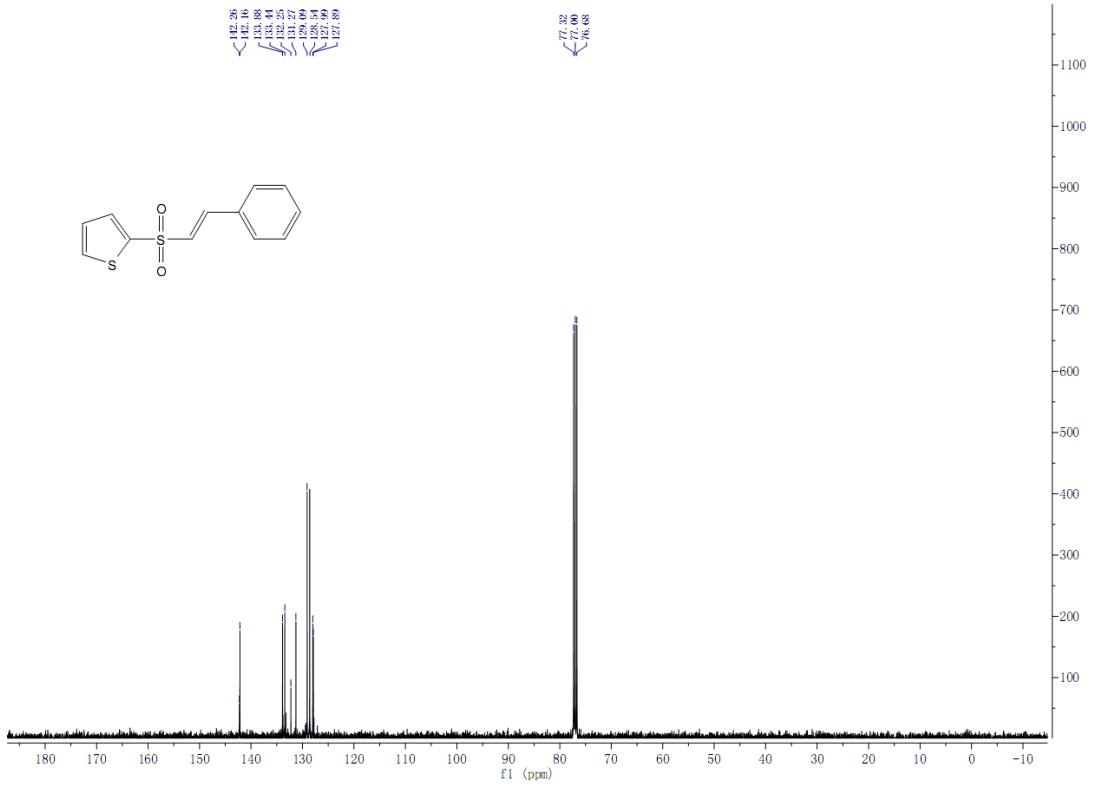
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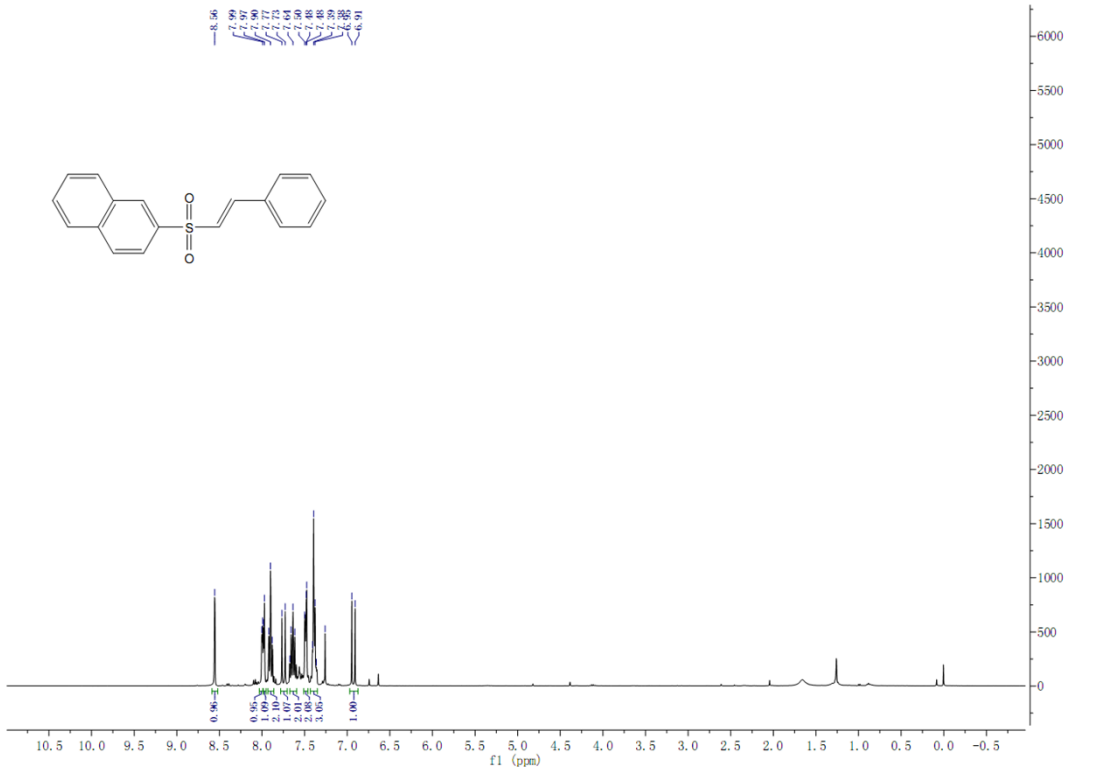
O
S
f1 (ppm)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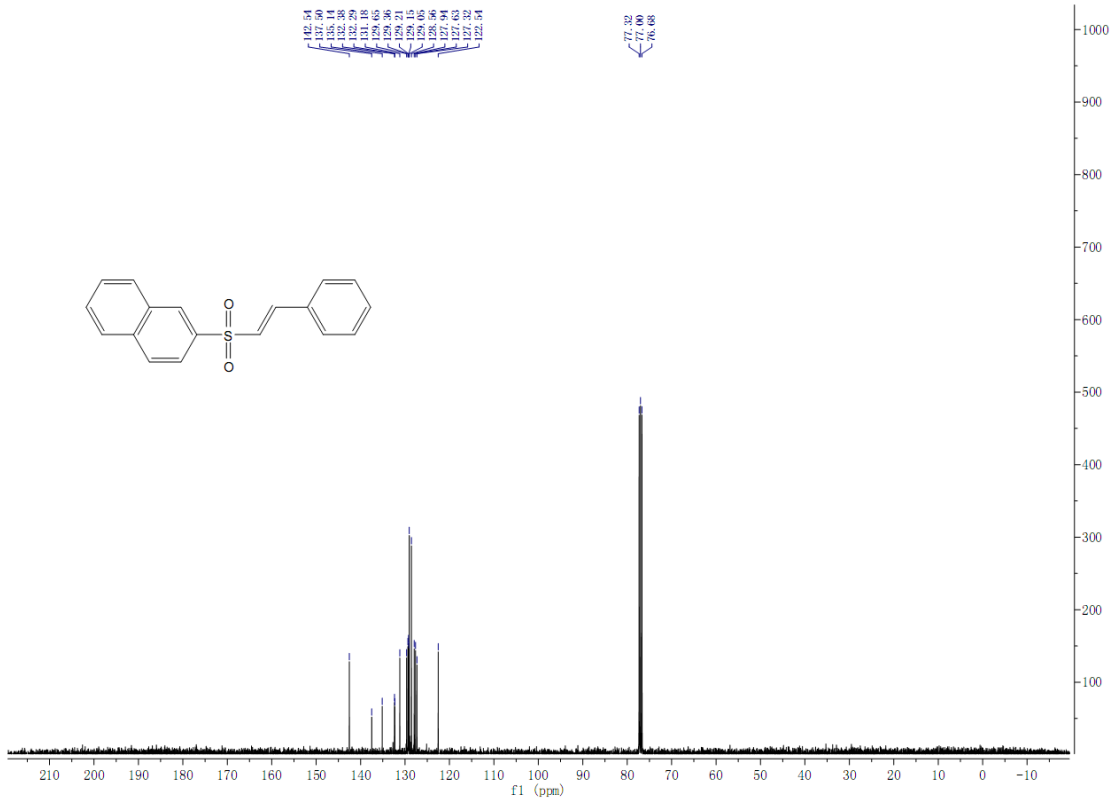
f1 (ppm)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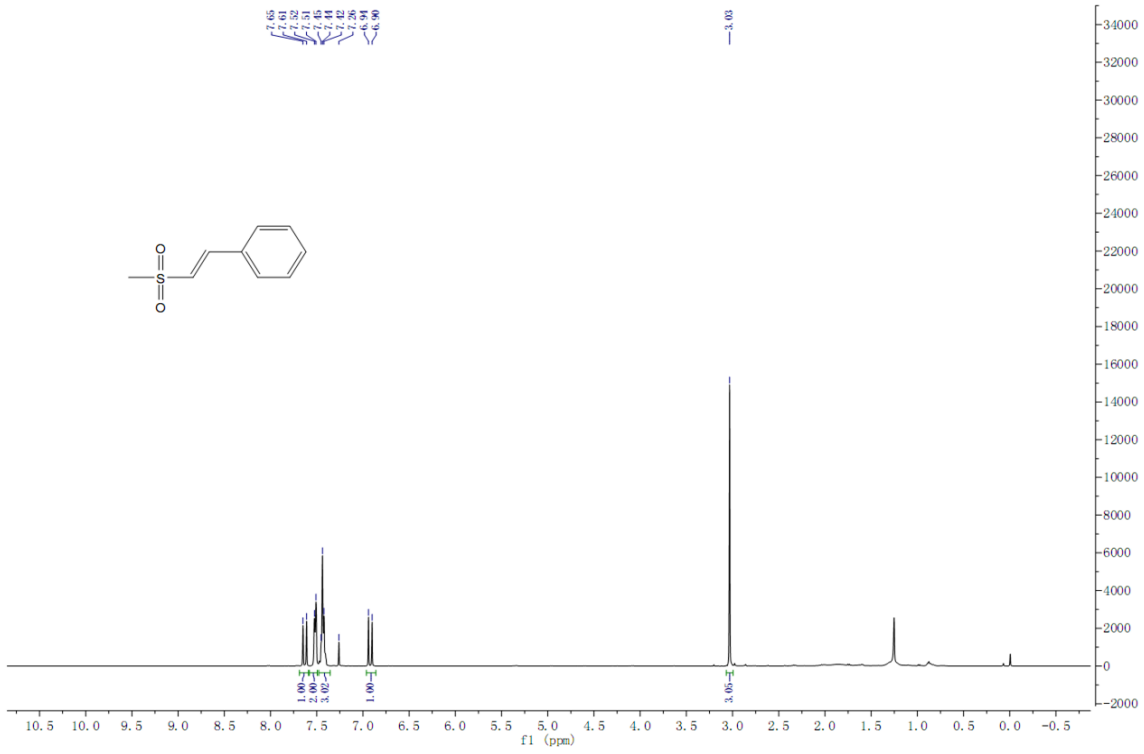
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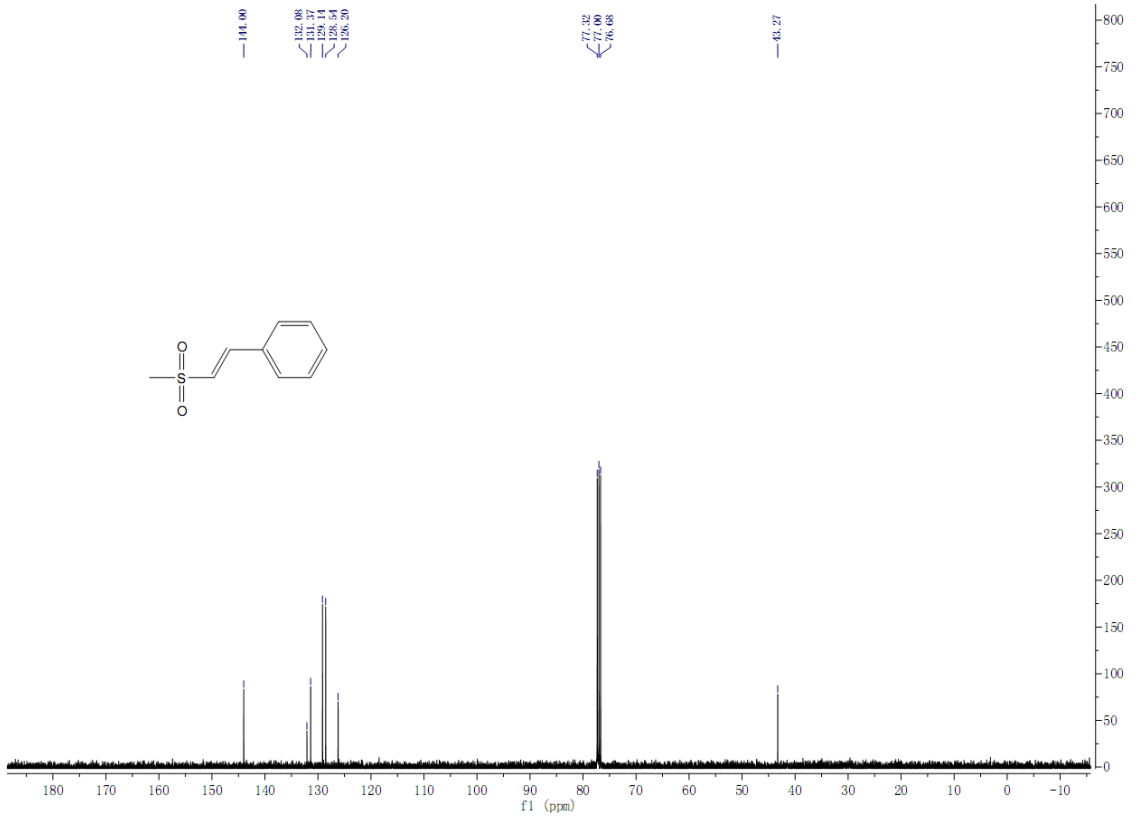
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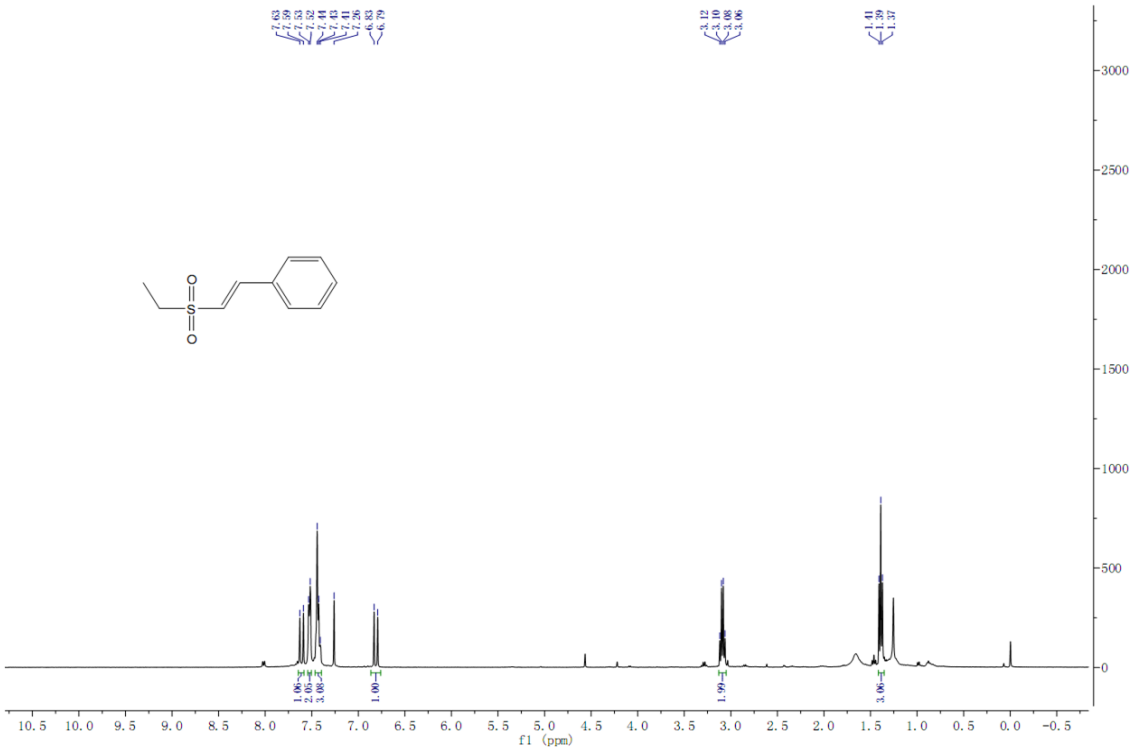
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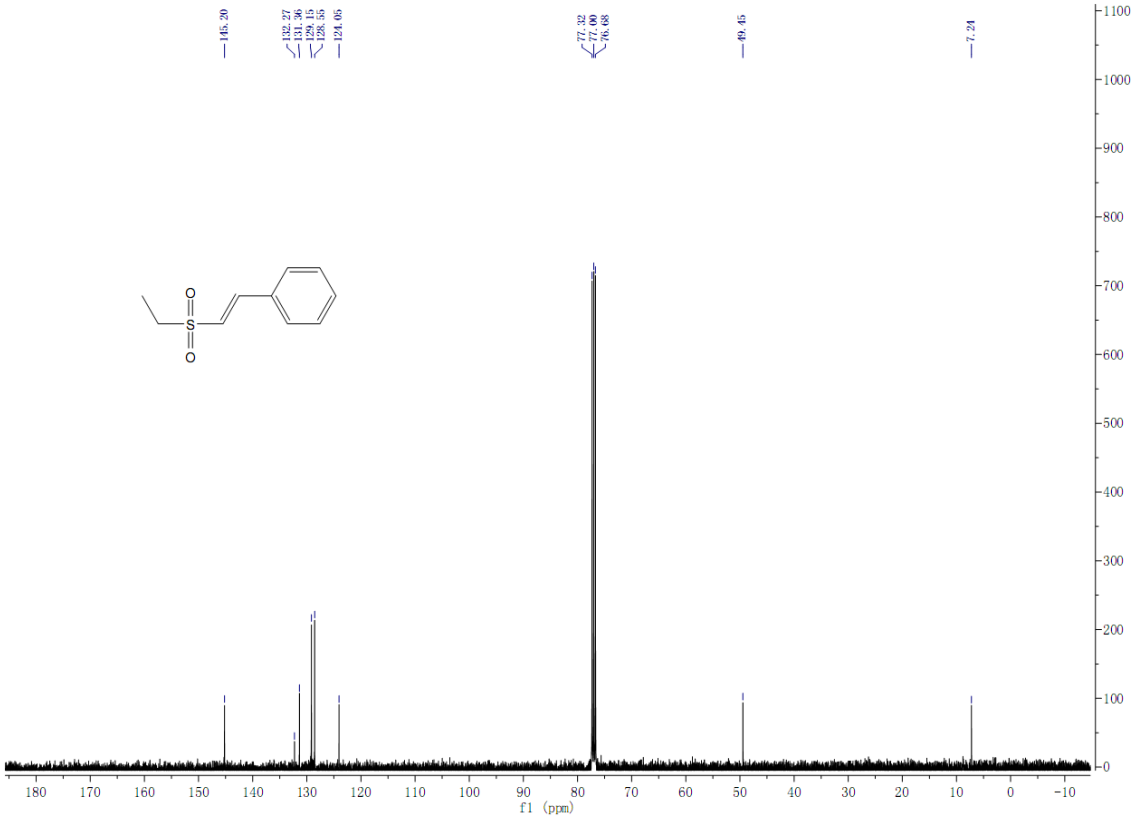
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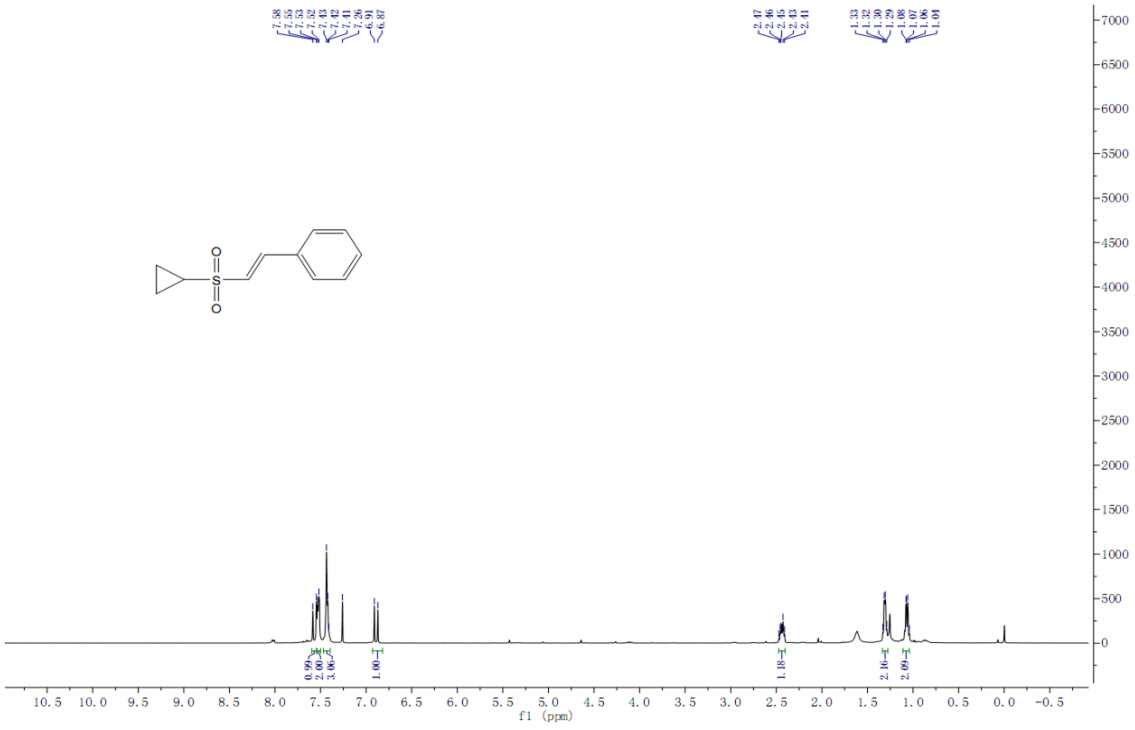
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2.43
2.41
1.33
1.32
1.30
1.29
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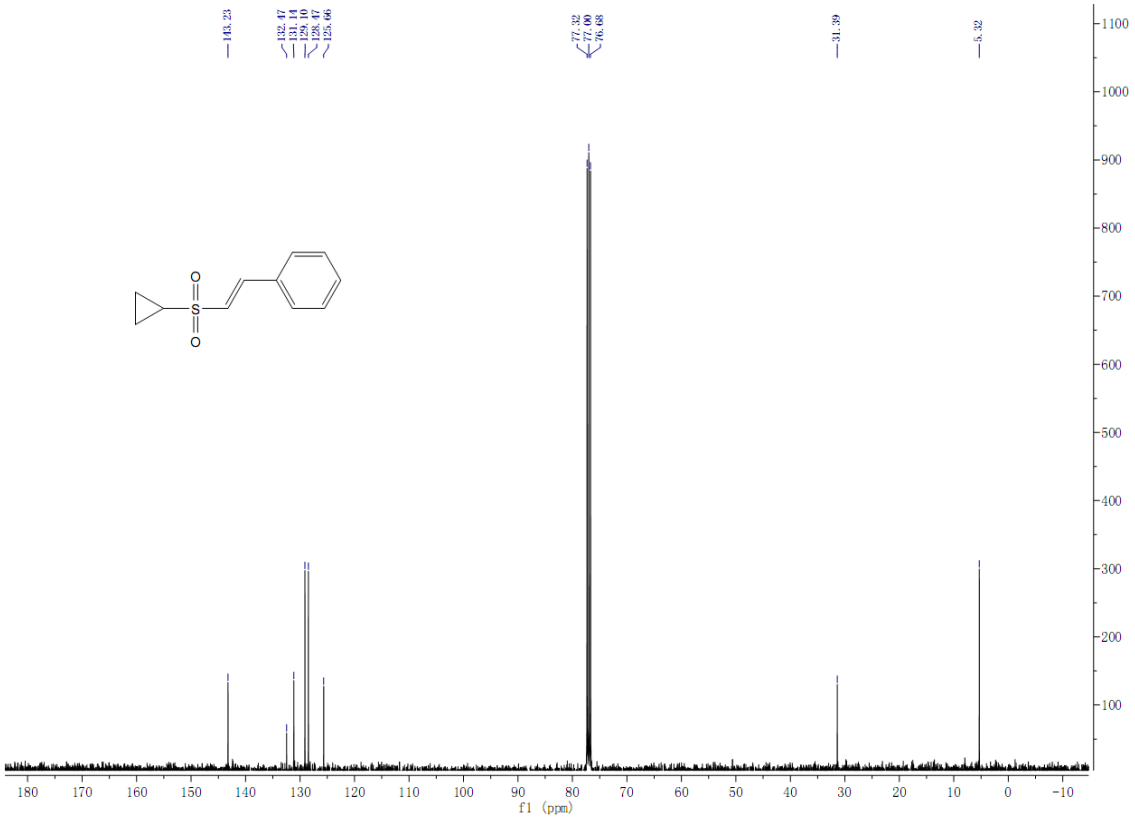
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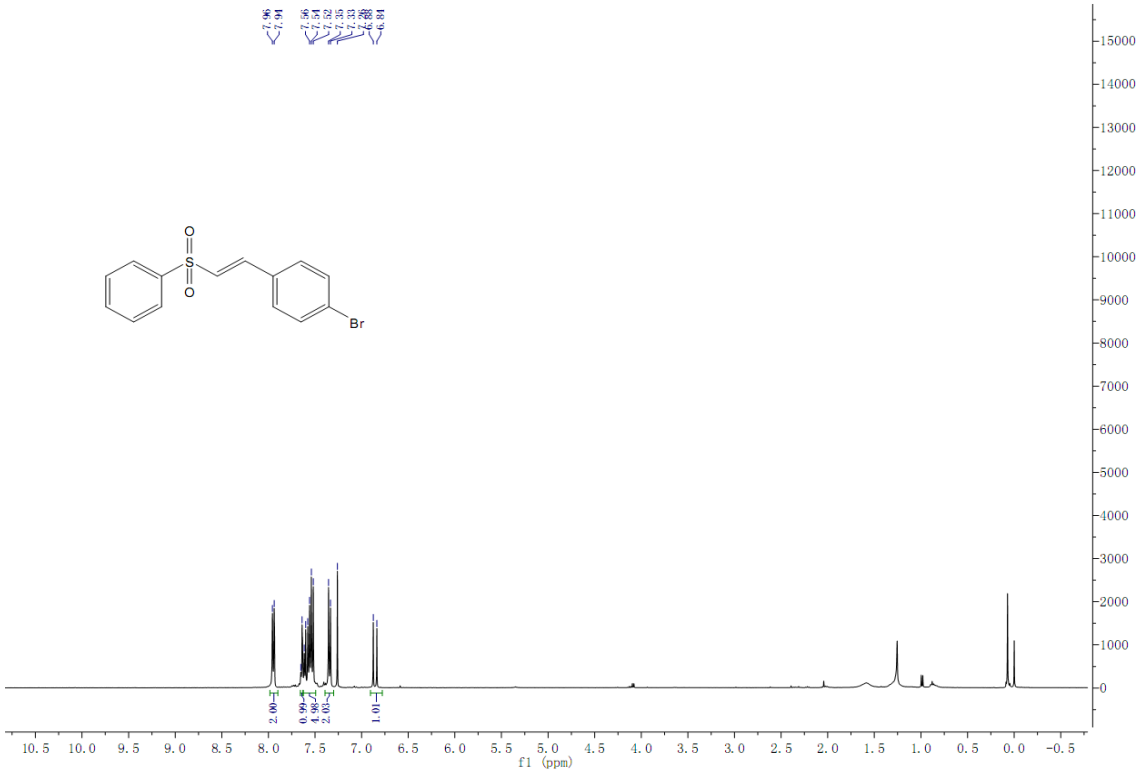
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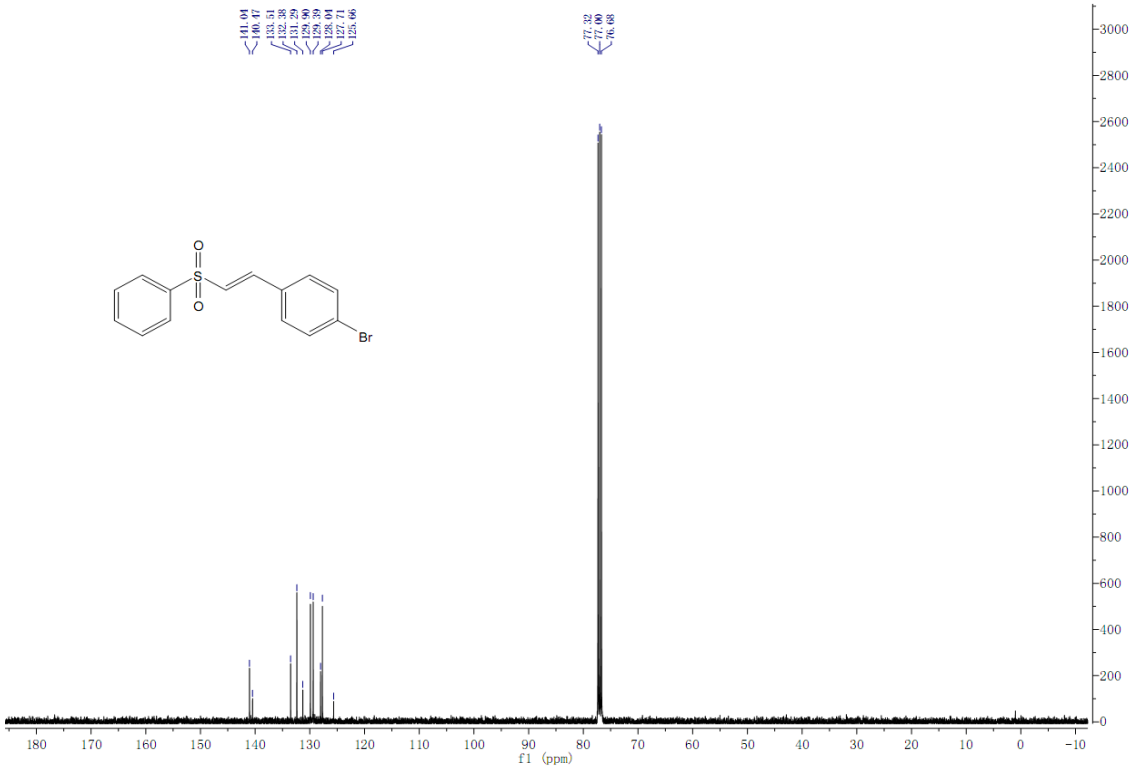
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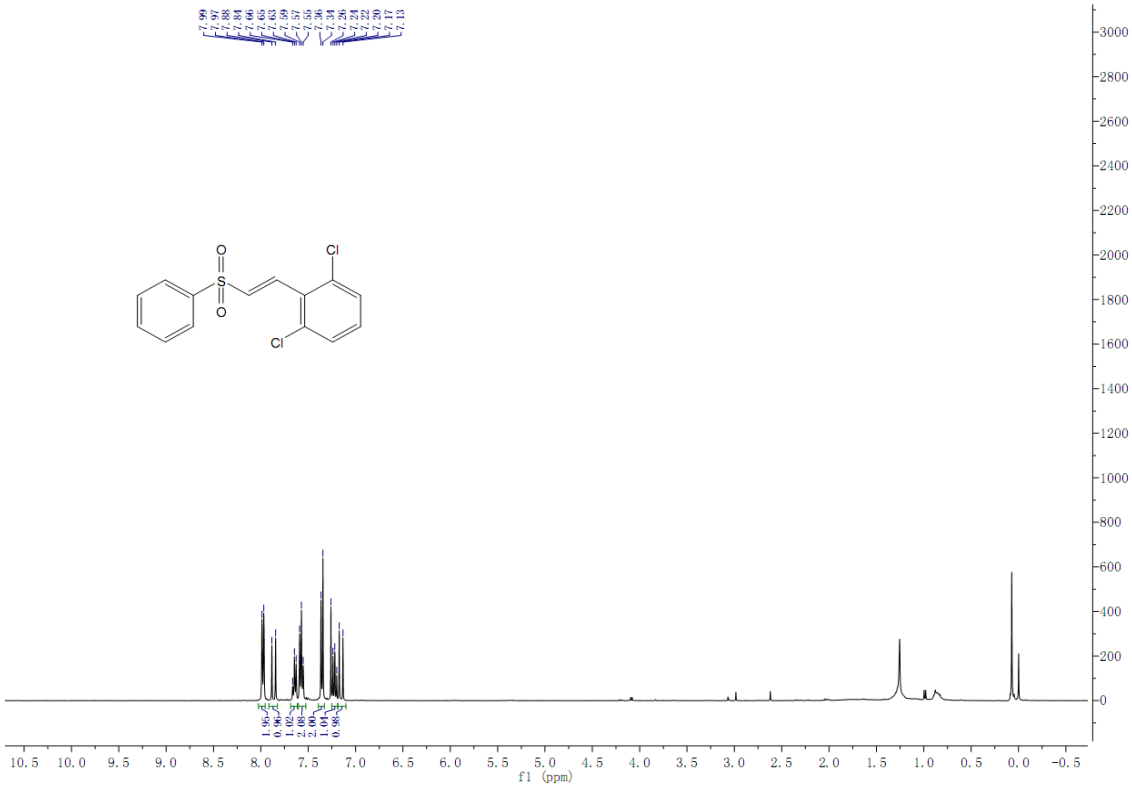
O
Br
f1 (ppm)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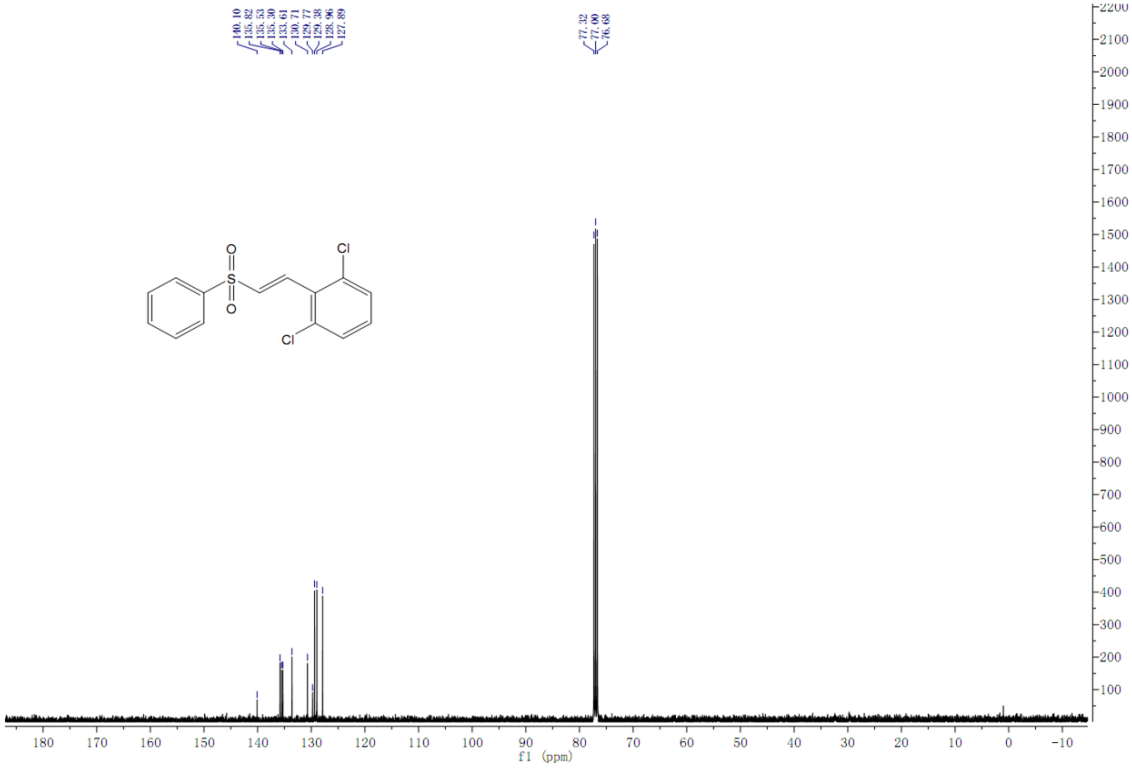
7.26
7.24
7.22
7.20
7.17
7.13
O
S
O
Cl
Cl
1.95
0.94
0.92
2.08
2.00
1.04
0.98
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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S
O
Cl
Cl
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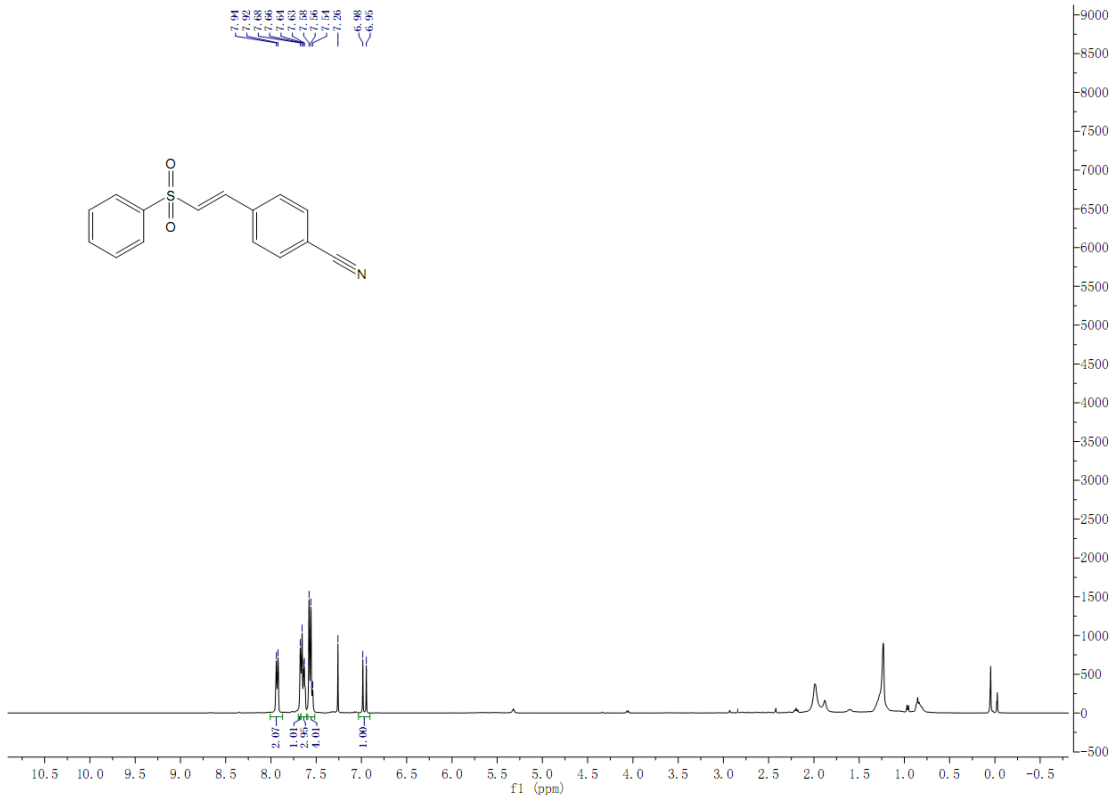
f1 (ppm)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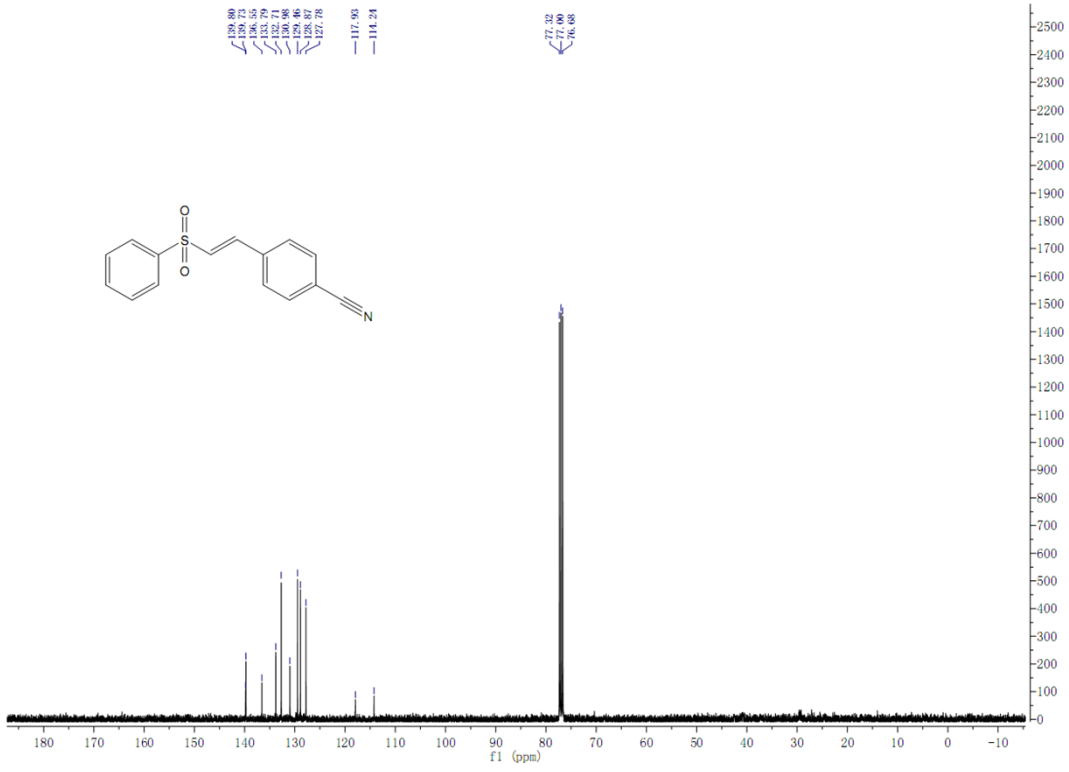
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76.68
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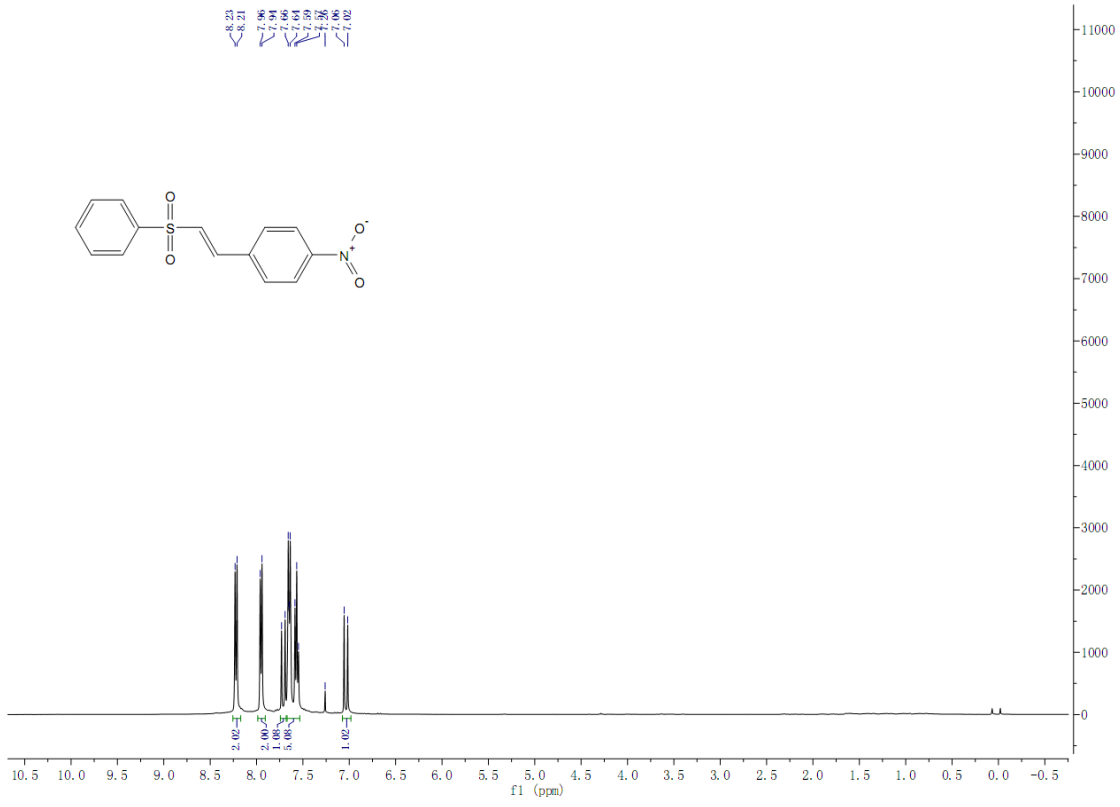
S
O
N
f1 (ppm)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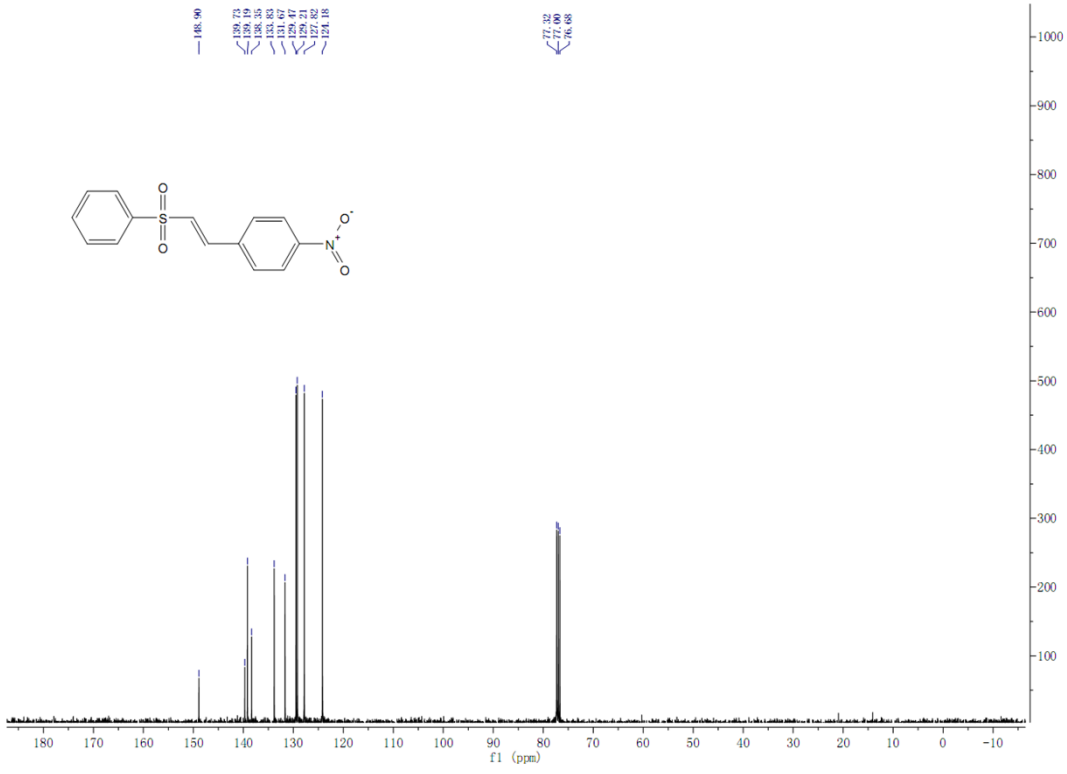
1.08
5.08
1.02
f1 (ppm)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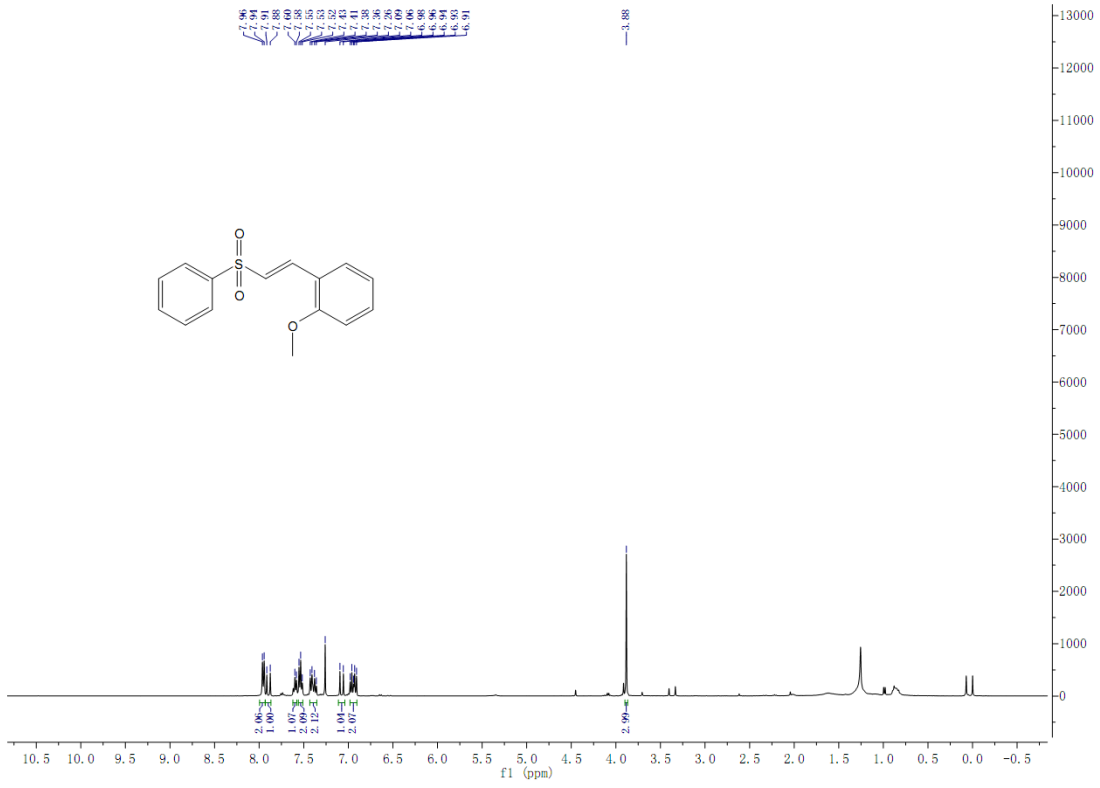
76.68
f1 (ppm)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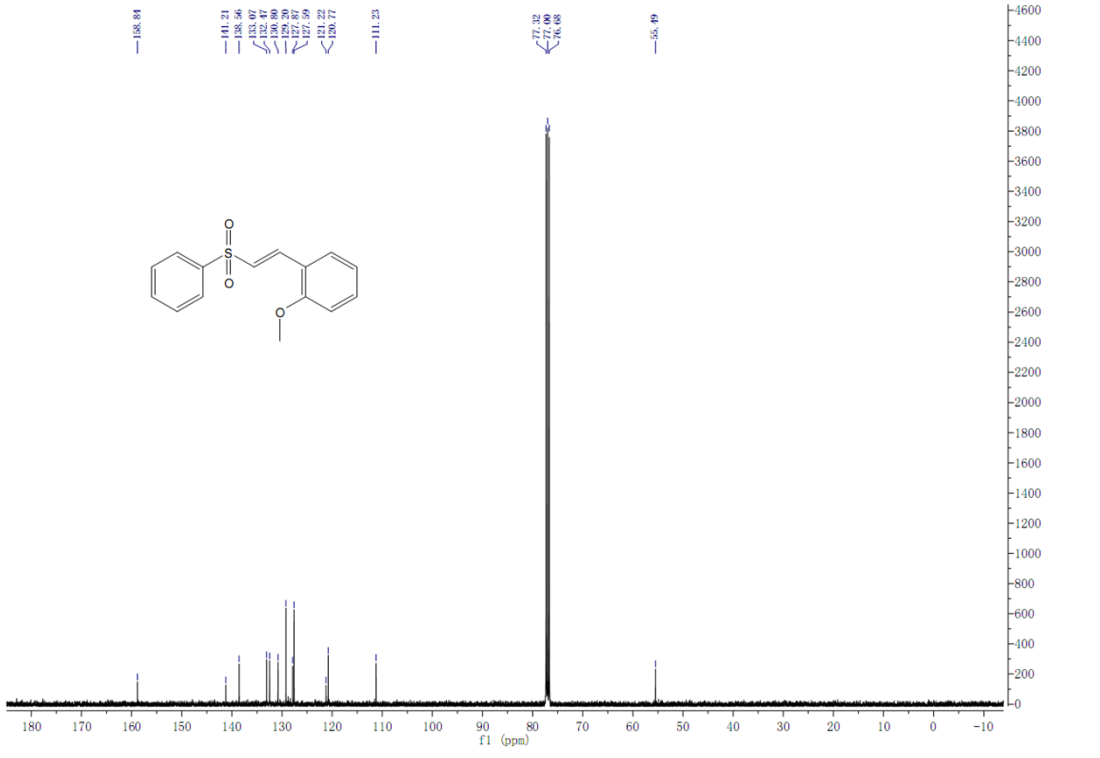
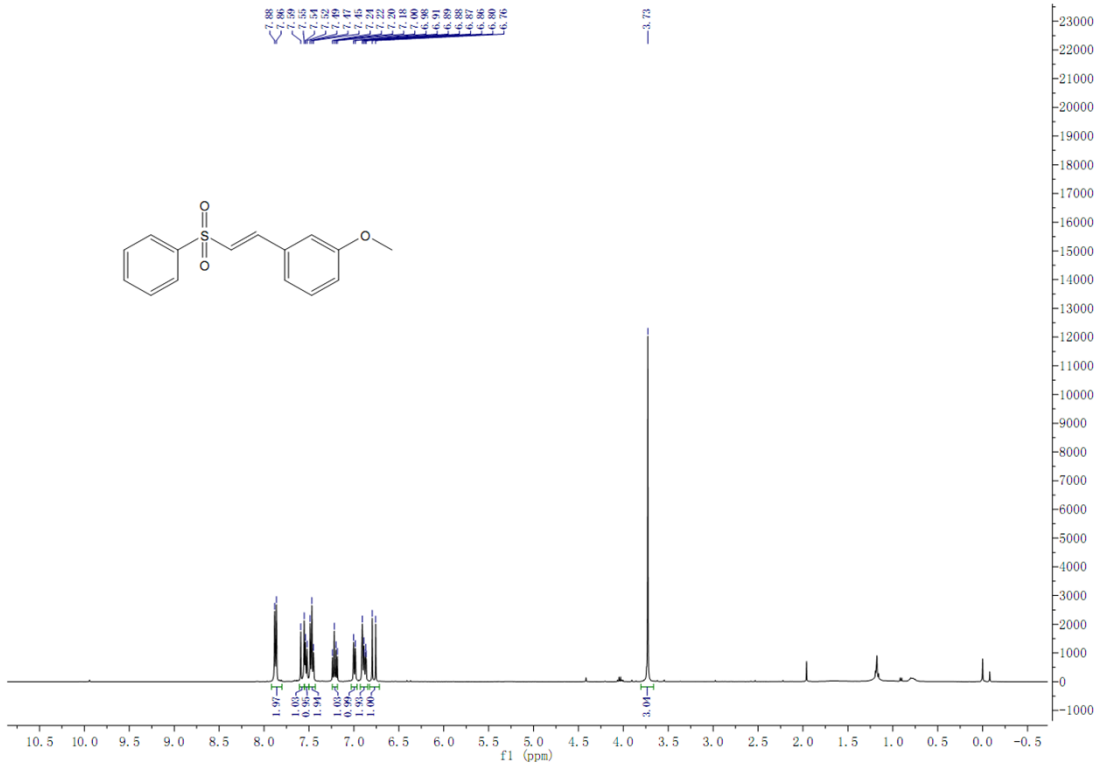
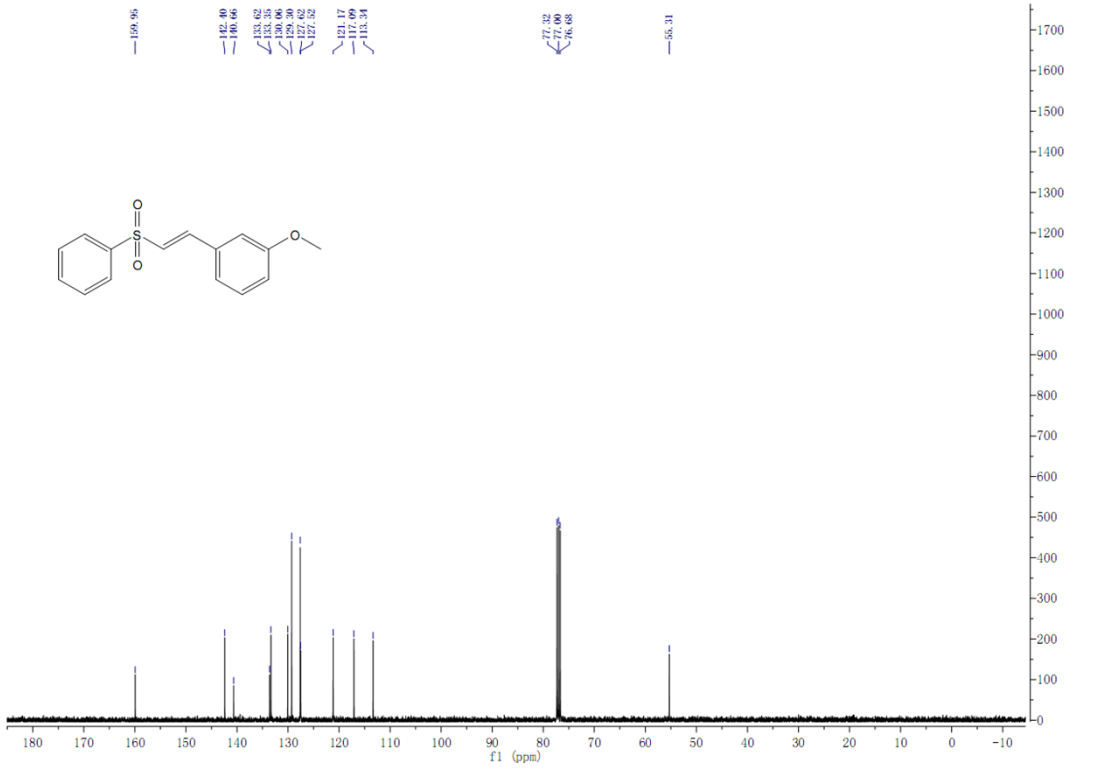
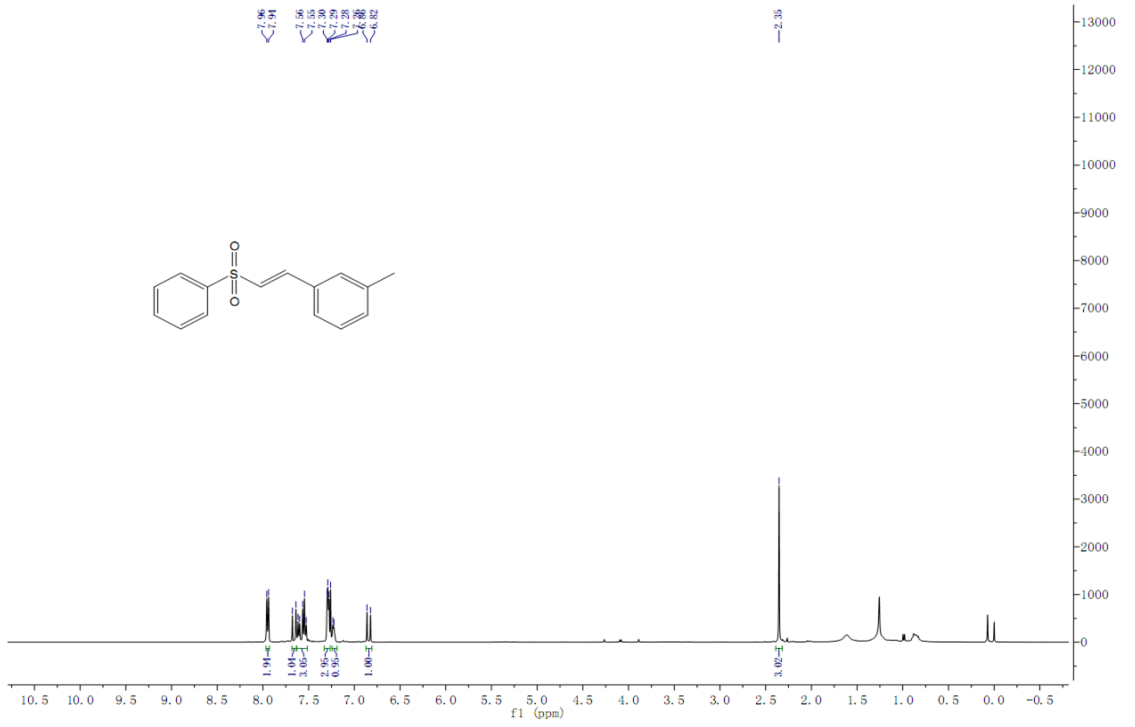
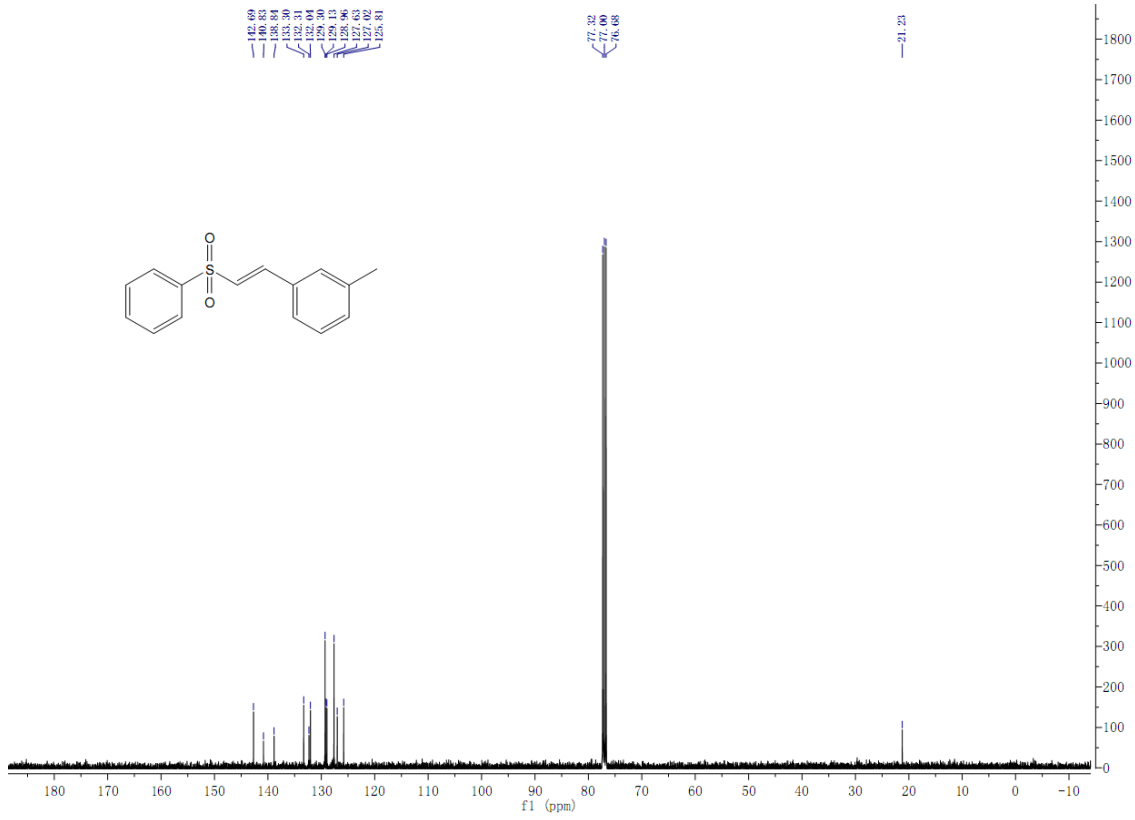
1.04
2.07
2.99
f1 (ppm)

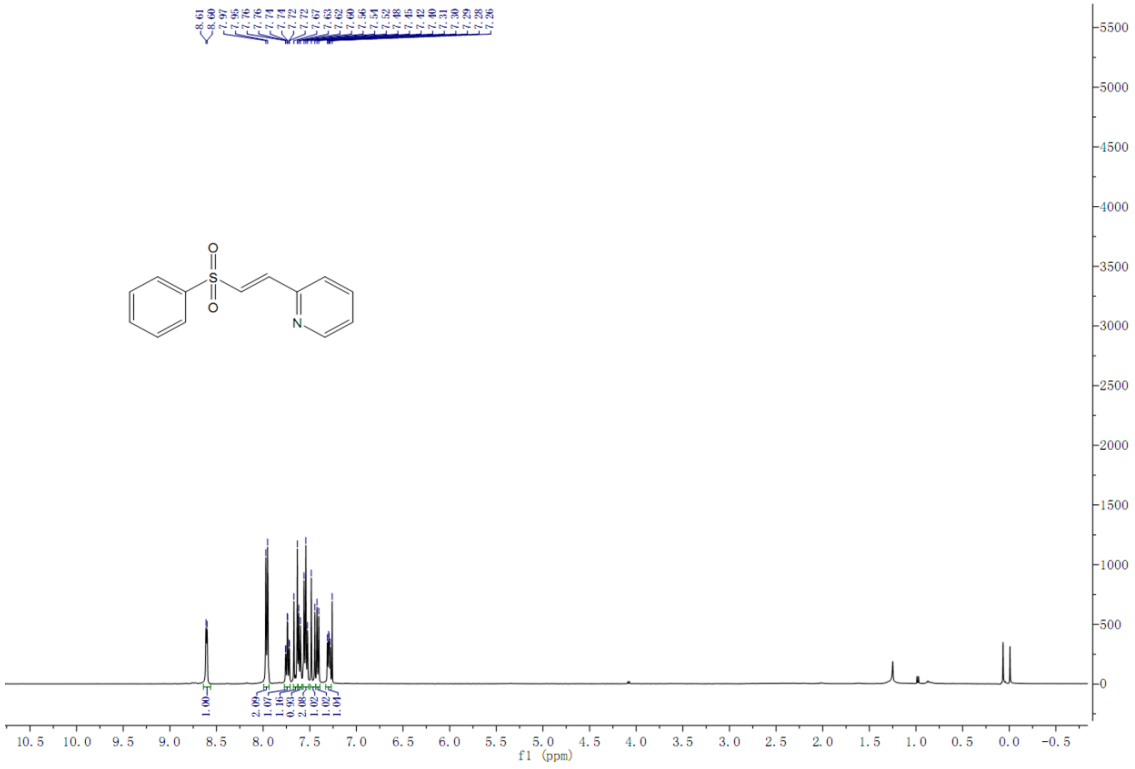

158.84
141.21
138.56
133.67
132.47
130.80
129.20
127.87
127.59
121.22
120.77
111.23
77.32
77.00
76.68
55.49
f1 (ppm)

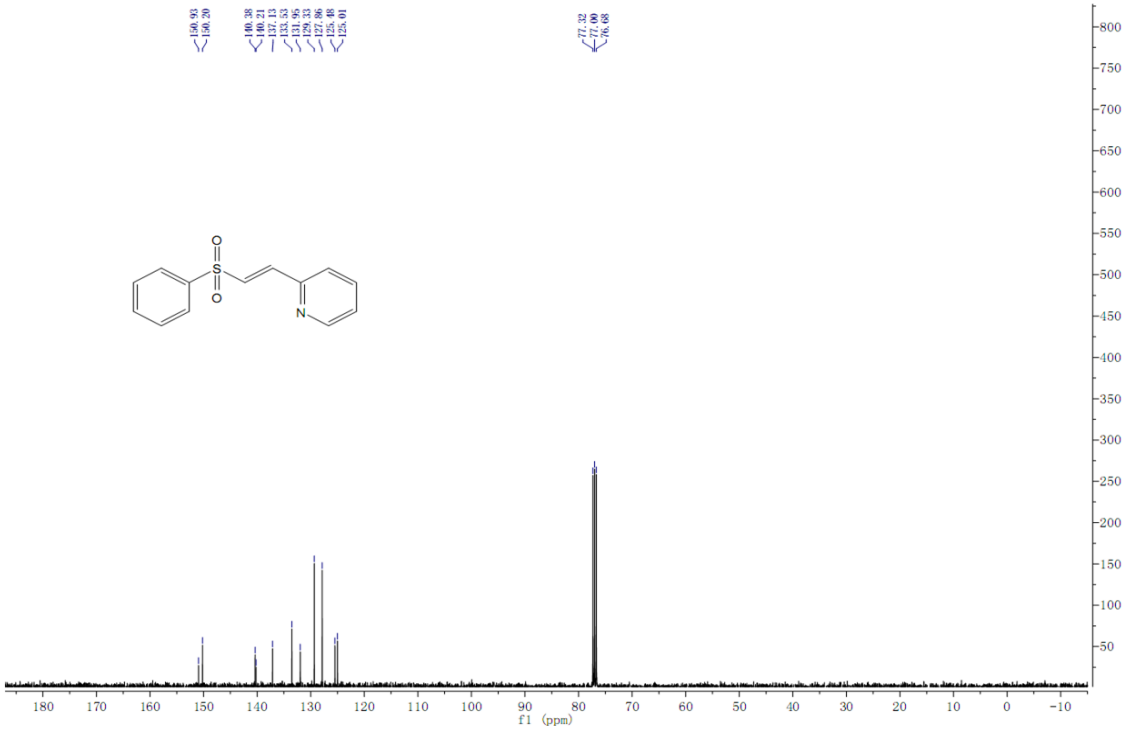

7.88
7.86
7.59
7.55
7.54
7.52
7.49
7.47
7.45
7.24
7.22
7.20
7.18
7.00
6.98
6.91
6.89
6.88
6.87
6.86
6.80
6.76
3.73
1.97
1.03
0.95
1.94
1.03
0.99
1.95
1.00
3.04
f1 (ppm)

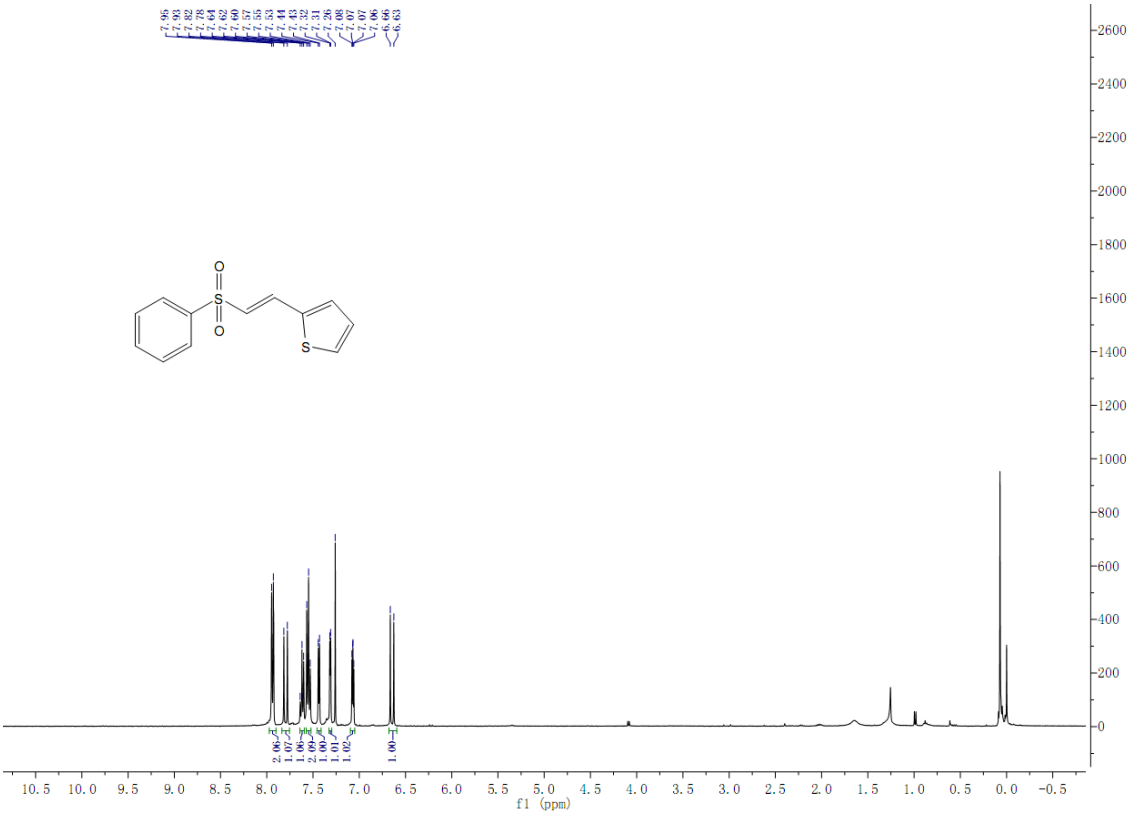

159.95
142.49
140.66
133.62
133.35
130.36
129.30
127.62
127.52
121.17
117.09
113.34
77.32
77.00
76.68
55.31
f1 (ppm)

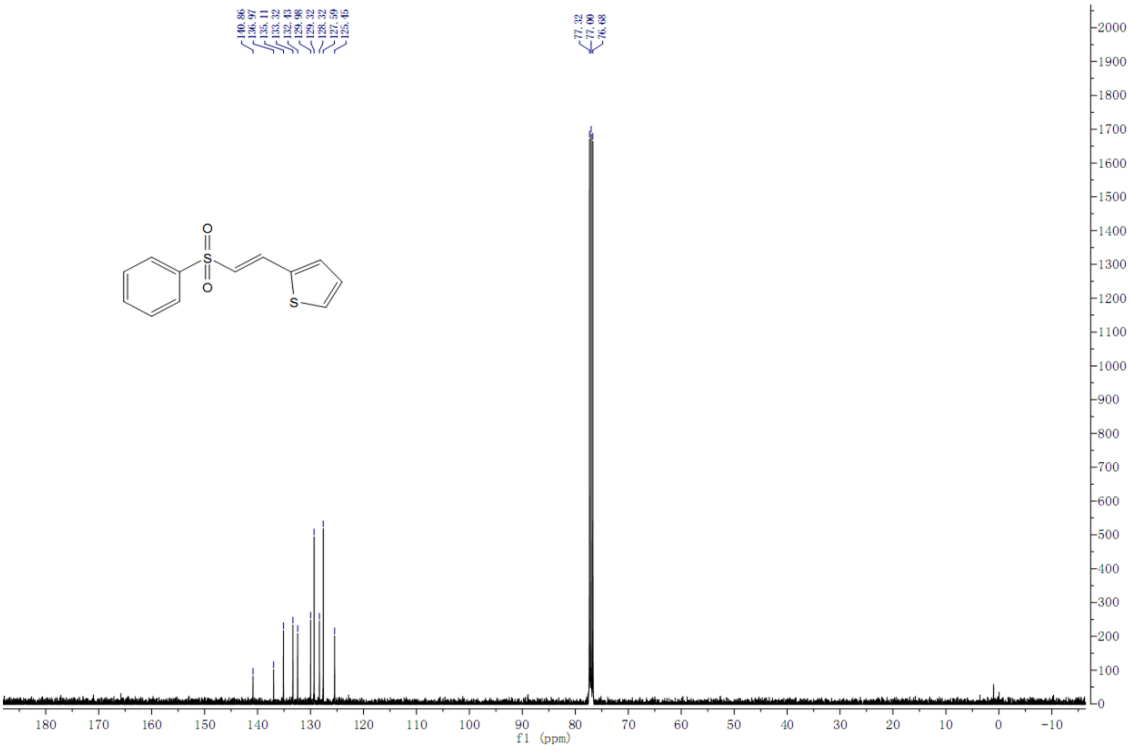

7.96
7.94
7.56
7.55
7.39
7.29
7.28
6.82
2.35
1.94
1.94
3.05
2.96
0.96
1.00
3.02
f1 (ppm)


142.69
140.83
138.84
133.30
132.31
132.04
130.98
129.13
128.96
127.63
127.02
125.81
77.32
77.00
76.68
21.23
f1 (ppm)


8.61
8.60
7.97
7.96
7.76
7.76
7.74
7.74
7.72
7.72
7.67
7.63
7.62
7.60
7.56
7.54
7.52
7.48
7.45
7.42
7.40
7.31
7.30
7.29
7.28
7.26
O
S
O
N
1.00
2.09
1.07
1.05
0.95
2.08
1.02
1.02
1.04
f1 (ppm)


150.93
150.20
140.38
140.21
137.13
133.53
131.95
129.33
127.86
125.48
125.01
77.32
77.00
76.68
O
S
O
N
f1 (ppm)


7.95
7.93
7.82
7.78
7.64
7.62
7.60
7.57
7.55
7.53
7.44
7.43
7.32
7.31
7.26
7.08
7.07
7.07
6.96
6.63
2.06
2.07
1.06
2.09
1.00
1.01
1.02
1.00
f1 (ppm)


140.86
136.97
135.11
133.32
132.43
129.98
129.32
128.32
127.69
125.46
77.32
77.00
76.68
f1 (ppm)