Supplementary Information

Bis(phenylsulfonyl)methane mediated synthesis of olefins via a halogen elimination and double bond migration

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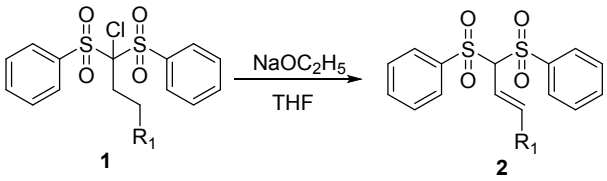
Contents:

1. Materials and Methods:

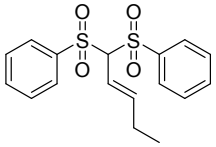
^{1}H and ^{13}C NMR spectra were obtained from a solution in $CDCl_3$ or d^6-DMSO with TMS as internal standard using a 600/151 MHz ($^{1}H/^{13}C$) or 400/101 MHz ($^{1}H/^{13}C$) spectrometer. Spin multiplicity are reported as singlet (s), doublet (d), triplet (t), doublet of doublet (dd) and multiplet (m). Coupling constant *J* is given in Hertz (Hz). Mass spectra were obtained in ESI mode. Chemicals, reagents and solvents were purchased from commercial suppliers and used without special instructions. Thin layer chromatography (TLC) was performed on silica gel HSGF254 plates. Column chromatography was performed using either 200-300 Mesh silica gel. Visualization of spots on TLC plate was accomplished with UV light (254 nm).

2. Synthesis of 2a-2s, 3-8



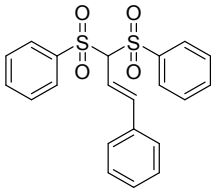
1 2

General procedure for synthesis of olefins. To a solution of compound **1** (1 mmol) in anhydrous THF (5 mL) was added $NaOC_2H_5$ (340 mg, 5 mmol). The resulting mixture was then stirred at 70 °C until the reaction was completed monitored by TLC (generally 0.5-2 h). After cooling to room temperature, water (15 mL) was added and extracted with EtOAc (10 mL ×3). The combined organic layers were washed with water and brine and dried over sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography to give desired product **2**.



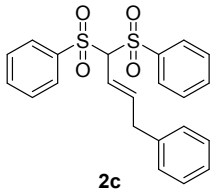
2a

Compound 2a: white solid, isolated yield 73 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 4H), 7.69 (t, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 4H), 5.75-5.68 (m, 1H), 5.40-5.30 (m, 1H), 4.84 (d, *J* = 10.4 Hz, 1H), 2.02 (p, *J* = 7.3 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.42, 137.75, 134.53, 129.73, 128.92, 113.38, 87.12, 25.84, 12.25. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{17}H_{19}S_2O_4$ 351.1, found 351.1.



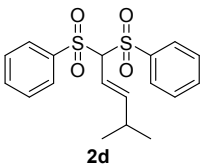
2b

Compound 2b. white solid, isolated yield 86 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 4H), 7.69 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 4H), 7.32-7.31 (m, 3H), 7.23 (dd, *J* = 6.4, 3.1 Hz, 2H), 6.50 (d, *J* = 15.7 Hz, 1H), 5.99 (dd, *J* = 15.7, 10.3 Hz, 1H), 5.04 (d, *J* = 10.3 Hz, 1H).^{13}C NMR (400 MHz, $CDCl_3$) δ 143.33, 137.75, 134.68, 129.76, 129.47, 129.04, 128.77, 127.01, 112.35, 87.44. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{21}H_{19}S_2O_4$ 399.1, found 399.1.



2c

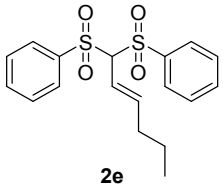
Compound 2c. white solid, isolated yield 65 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 4H), 7.67 (t, *J* = 7.1 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 4H), 7.25-7.19 (m, 3H), 6.92 (d, *J* = 7.2 Hz, 2H), 5.86-5.83 (m, 1H), 5.43 (dd, *J* = 15.4, 9.8 Hz, 1H), 4.87 (d, *J* = 10.3 Hz, 1H), 3.33 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 145.10, 137.67, 134.52, 129.67, 128.98, 128.57, 128.52, 126.58, 115.66, 86.90, 38.99. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{22}H_{21}S_2O_4$ 413.1, found 413.1.



2d

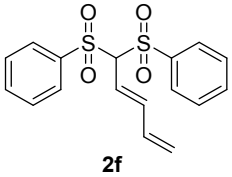
Compound 2d. white solid, isolated yield 67 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.7 Hz, 4H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 4H), 5.51 (dd, *J* = 15.4,

6.6 Hz, 1H), 5.24 (dd, *J* = 15.7, 10.0 Hz, 1H), 4.75 (d, *J* = 10.3 Hz, 1H), 2.16 (dq, *J* = 13.3, 6.6 Hz, 1H), 0.74 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 153.28, 137.80, 134.50, 129.73, 128.92, 111.91, 87.12, 31.41, 21.13. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{18}H_{20}S_2O_4$ 365.1, found 365.1.



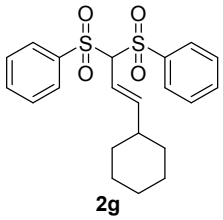
2e

Compound 2e. white solid, isolated yield 78 %.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 4H), 7.69 (t, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 4H), 5.72-5.65 (m, 1H), 5.41-5.30 (m, 1H), 4.84 (d, *J* = 10.4 Hz, 1H), 1.98 (q, *J* = 7.1 Hz, 2H), 1.27-1.20 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 147.13, 137.79, 134.51, 129.70, 128.94, 114.26, 87.19, 34.73, 21.36, 13.48. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{18}H_{21}S_2O_4$ 365.1, found 365.1.



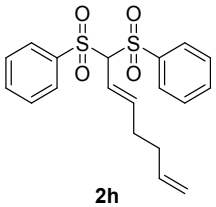
2f

Compound 2f. white solid, isolated yield 64 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 4H), 7.70 (t, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 4H), 6.26 (dt, *J* = 16.4, 10.2 Hz, 1H), 6.16 (dd, *J* = 15.0, 10.6 Hz, 1H), 5.54 (dd, *J* = 14.8, 10.5 Hz, 1H), 5.26 (dd, *J* = 13.1, 8.2 Hz, 2H), 4.90 (d, *J* = 10.3 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 143.37, 137.19, 134.23, 134.12, 129.29, 128.57, 122.23, 115.38, 86.66. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{17}H_{17}S_2O_4$ 349.0, found 349.0.



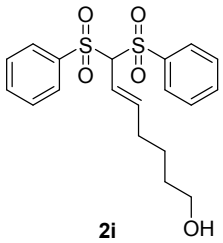
2g

Compound 2g. white solid, isolated yield 62 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 4H), 7.69 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.7 Hz, 4H), 5.55 (dd, *J* = 15.5, 6.7 Hz, 1H), 5.31 (dd, *J* = 15.4, 10.4 Hz, 1H), 4.80 (d, *J* = 10.2 Hz, 1H), 1.91 (dd, *J* = 11.3, 4.1 Hz, 1H), 1.64 (d, *J* = 11.1 Hz, 2H), 1.49 (d, *J* = 13.4 Hz, 2H), 1.26-1.05 (m, 4H), 0.83 (dd, *J* = 24.2, 11.9 Hz, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 151.72, 137.35, 134.05, 129.29, 128.47, 111.75, 86.80, 40.33, 31.13, 25.33, 25.04. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{21}H_{25}S_2O_4$ 405.1, found 405.1.



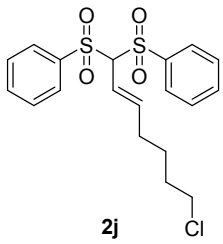
2h

Compound 2h. white solid, isolated yield 73 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.5 Hz, 4H), 7.69 (t, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 4H), 5.72-5.59 (m, 2H), 5.41 (dd, *J* = 15.3, 10.3 Hz, 1H), 4.95 (s, 1H), 4.92-4.90 (m, 1H), 4.84 (d, *J* = 10.3 Hz, 1H), 2.10 (q, *J* = 7.4 Hz, 2H), 1.97 (q, *J* = 7.1 Hz, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 146.20, 137.78, 136.84, 134.55, 129.71, 128.96, 115.52, 114.65, 87.08, 32.08, 31.99. LRMS (ESI) m/z $[M+H]^+$ calcd for $C_{19}H_{21}S_2O_4$ 376.1, found 376.1.



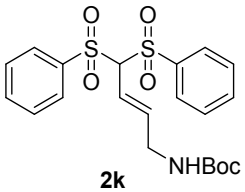
2i

Compound 2i. white solid, isolated yield 58 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 4H), 7.69 (t, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 4H), 5.73-5.69 (m, 1H), 5.41 (dd, *J* = 15.3, 10.3 Hz, 1H), 4.85 (d, *J* = 10.3 Hz, 1H), 3.58 (t, *J* = 6.3 Hz, 2H), 2.05 (q, *J* = 7.1 Hz, 2H), 1.44-1.39 (m, 2H), 1.36-1.29 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 146.93, 137.75, 134.57, 129.67, 128.99, 114.42, 87.08, 62.30, 32.41, 31.76, 24.29. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{19}H_{23}S_2O_5$ 395.1, found 395.1.



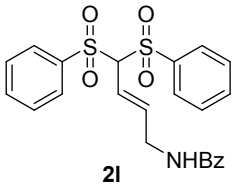
2j

Compound 2j. white solid, isolated yield 61 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 4H), 7.69 (t, *J* = 7.5 Hz, 2H), 7.58 (q, *J* = 7.2 Hz, 4H), 5.70-5.66 (m, 1H), 5.41 (dd, *J* = 15.3, 10.3 Hz, 1H), 4.86 (d, *J* = 10.3 Hz, 1H), 3.46 (t, *J* = 6.5 Hz, 2H), 2.03 (q, *J* = 7.2 Hz, 2H), 1.63-1.56 (m, 2H), 1.37 (dt, *J* = 14.5, 7.3 Hz, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 145.83, 137.28, 134.18, 129.21, 128.92, 128.58, 128.38, 114.43, 86.51, 44.12, 31.42, 31.09, 24.86. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{19}H_{22}S_2O_4Cl$ 413.1, found 413.1.



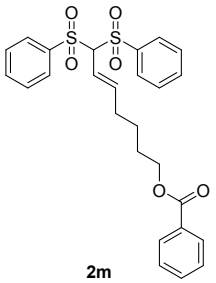
2k

Compound 2k. white solid, isolated yield 57 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 4H), 7.70 (t, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 4H), 5.71 (dt, *J* = 15.4, 4.8 Hz, 1H), 5.61 (dd, *J* = 15.6, 9.7 Hz, 1H), 4.87 (d, *J* = 9.8 Hz, 1H), 4.59 (s, 1H), 3.68 (t, *J* = 4.9 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 155.39, 142.84, 137.56, 134.69, 129.76, 129.05, 115.05, 86.39, 79.78, 41.69, 28.32. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{21}H_{26}NS_2O_6$ 452.1, found 452.1.



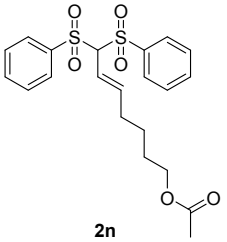
2l

Compound 2l. white solid, isolated yield 52 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 4H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 5H), 7.45 (t, *J* = 7.4 Hz, 2H), 6.32 (s, 1H), 5.87-5.83 (m, 1H), 5.66 (dd, *J* = 15.3, 10.6 Hz, 1H), 4.93 (d, *J* = 10.2 Hz, 1H), 4.03 (t, *J* = 5.4 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 165.99, 143.35, 137.73, 134.47, 134.04, 131.34, 129.29, 128.91, 128.34, 127.17, 114.44, 83.21. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{21}H_{19}S_2O_4$ 456.1, found 456.1.



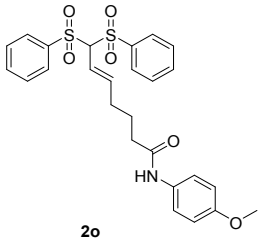
2m

Compound 2m. white solid, isolated yield 58 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.92 (d, *J* = 7.3 Hz, 4H), 7.65 (t, *J* = 7.5 Hz, 2H), 7.59-7.52 (m, 5H), 7.46 (t, *J* = 7.6 Hz, 2H), 5.72-5.69 (m, 1H), 5.42 (dd, *J* = 15.2, 10.3 Hz, 1H), 4.85 (d, *J* = 10.2 Hz, 1H), 4.25 (t, *J* = 6.4 Hz, 2H), 2.09 (q, *J* = 7.0 Hz, 2H), 1.64-1.61 (m, 2H), 1.41-1.33 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 166.09, 145.93, 137.30, 134.12, 132.54, 129.78, 129.23, 129.04, 128.52, 127.95, 114.34, 86.62, 63.92, 31.84, 27.54, 24.21. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{23}H_{27}S_2O_6$ 499.1, found 499.1.



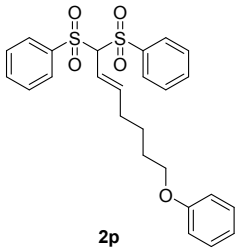
2n

Compound 2n. white solid, isolated yield 63 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.5 Hz, 4H), 7.69 (t, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 4H), 5.70-5.67 (m, 1H), 5.40 (dd, *J* = 15.2, 10.3 Hz, 1H), 4.86 (d, *J* = 10.2 Hz, 1H), 3.98 (q, *J* = 6.7 Hz, 2H), 2.08-2.01 (m, 5H), 1.48-1.44 (m, 2H), 1.32-1.25 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 171.04, 146.44, 137.75, 134.55, 129.58, 128.97, 114.74, 86.80, 63.89, 32.16, 27.74, 24.46, 20.93. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{21}H_{25}S_2O_6$ 437.1, found 437.1.



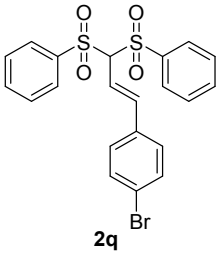
2o

Compound 2o. white solid, isolated yield 47 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.66 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 4H), 7.74 (t, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.7 Hz, 4H), 7.48 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 6.22 (d, *J* = 10.1 Hz, 1H), 5.75-5.65 (m, 1H), 5.34 (dd, *J* = 15.1, 10.1 Hz, 1H), 3.71 (s, 3H), 2.08 (t, *J* = 7.4 Hz, 2H), 1.93 (dd, *J* = 14.3, 7.1 Hz, 2H), 1.38 (dt, *J* = 14.7, 7.1 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 170.56, 155.45, 146.74, 138.38, 134.96, 132.86, 129.48, 121.06, 115.23, 114.20, 84.25, 55.58, 35.75, 31.96, 24.25. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{26}H_{28}NS_2O_6$ 514.1, found 514.1.



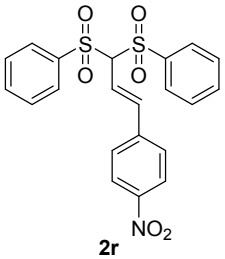
2p

Compound 2p. white solid, isolated yield 51 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 4H), 7.67 (t, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 4H), 7.29 (t, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 5.73-5.69 (m, 1H), 5.44 (dd, *J* = 15.3, 10.2 Hz, 1H), 4.86 (d, *J* = 10.3 Hz, 1H), 3.88 (t, *J* = 6.2 Hz, 2H), 2.08 (q, *J* = 7.7 Hz, 2H), 1.65-1.58 (m, 2H), 1.45-1.37 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 158.43, 146.25, 137.31, 134.13, 129.23, 129.02, 128.56, 120.19, 114.23, 113.92, 86.61, 66.72, 31.92, 28.00, 24.26. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{25}H_{27}S_2O_5$ 471.1, found 471.1.



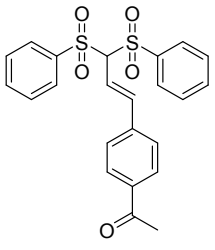
2q

Compound 2q. white solid, isolated yield 82 %. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 (d, *J* = 7.6 Hz, 4H), 7.75 (t, *J* = 7.1 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 4H), 7.31 (d, *J* = 9.6 Hz, 4H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.45 (d, *J* = 10.1 Hz, 1H), 6.05-5.94 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 143.32, 137.76, 134.67, 129.76, 129.47, 129.04, 128.77, 127.02, 112.35, 87.45. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{21}H_{18}S_2O_4Br$ 476.9, found 476.9.



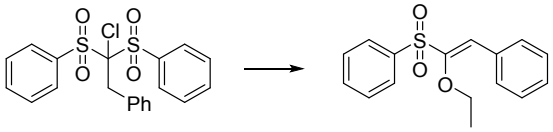
2r

Compound 2r. white solid, isolated yield 74 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 7.6 Hz, 4H), 7.72 (t, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 4H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.19 (dd, *J* = 15.6, 10.3 Hz, 1H), 5.10 (d, *J* = 10.2 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.05, 140.63, 137.54, 134.96, 129.73, 129.19, 127.64, 124.16, 117.17, 86.99. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{21}H_{18}S_2O_6N$ 444.0, found 444.0.



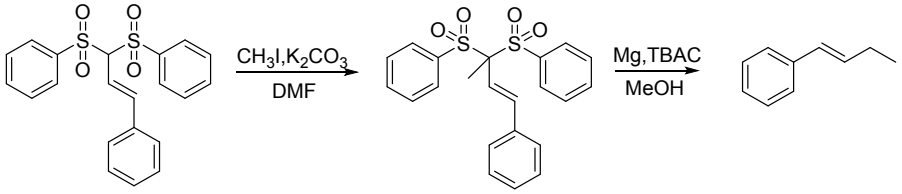
2s

Compound 2s. white solid, isolated yield 81 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 4H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.70 (t, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 15.7 Hz, 1H), 6.12 (dd, *J* = 15.6, 10.4 Hz, 1H), 5.07 (d, *J* = 10.3 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.24, 141.94, 138.96, 137.63, 134.83, 129.75, 129.12, 128.81, 127.12, 115.19, 87.22, 26.63. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{23}H_{21}S_2O_5$ 441.1, found 441.1.



1t 2t

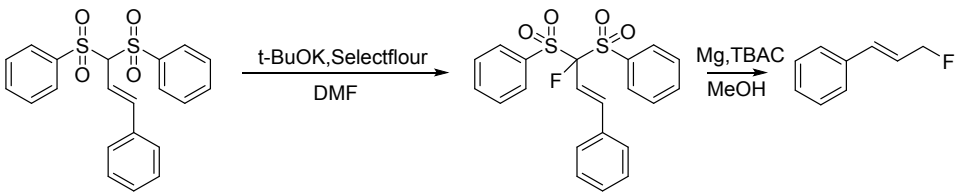
Compound 2t. yellow solid, isolated yield 37 %. ^{1}H NMR (400 MHz, CDCl3) δ 7.97 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 6.4 Hz, 3H), 7.55 (t, J = 7.4 Hz, 2H), 7.37 (d, J = 7.1 Hz, 3H), 7.23 (s, 1H), 4.15 (q, J = 6.9 Hz, 2H), 1.32 (t, J = 7.0 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 152.24, 139.00, 133.55, 131.71, 129.80, 129.66, 129.09, 128.76, 128.40, 122.58, 70.80, 15.37. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{16}H_{16}S_2O_3$ 289.1, found 289.1.



2b 3 4

(*E*)-but-1-en-1-ylbenzene (4). To a solution of compound **2b** (199 mg, 0.5 mmol) in 5 mL DMF was added K_2CO_3 (104 mg, 0.75 mmol). CH_3I (142 mg, 1 mmol) was added slowly at room temperature. The reaction mixture was then stirred at 70 °C until the reaction was completed monitored by TLC. Water (15 mL) was added and extrated with EtOAc (10 mL×3). The combined organic layers were washed with water and brine and dried over sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography to give desired product **3**. Yield 93 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.5 Hz, 4H), 7.67 (t, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.0 Hz, 4H), 7.32 (d, *J* = 13.1 Hz, 5H), 6.50 (s, 2H), 1.89 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 138.89, 136.45, 135.00, 134.57, 131.04, 129.35, 128.84, 128.62, 127.05, 118.06, 87.86, 15.13. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{22}H_{21}S_2O_4$ 413.1, found 413.1.

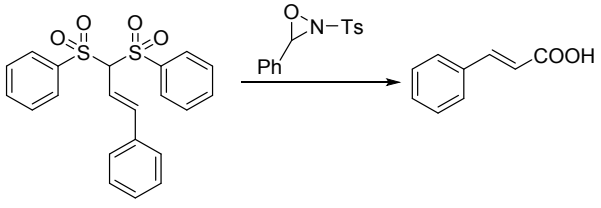
Compound **3** (206 mg, 0.5 mmol) was dissolved in 5 mL MeOH. Activated Mg (1.2 g, 50 mmol) and tetrabutylammonium chloride (TBAC, 1.4 g, 5 mmol) was added to this solution and the mixture was stirred at room temperature for 3 h. HCl (100 mL, 1 mol/L) was added and extrated with EtOAc (25 mL×3). The combined organic layers were washed with water and brine and dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography to give desired product **4**. Yield 69 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 6.5 Hz, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.8, 6.3 Hz, 1H), 2.27 (p, *J* = 6.4 Hz, 2H), 1.14 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 137.50, 132.17, 128.36, 128.02, 126.30, 125.47, 25.63, 13.21. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{10}H_{13}$ 133.1, found 133.1.



2b **5** **6**

(*E*)-(3-fluoroprop-1-en-1-yl) benzene (6). To a solution of compound **2b** (239 mg, 0.6 mmol) in 3 mL DMF was added *t*-BuOK (202 mg, 1.8 mmol) in one portion. The reaction was stirred at room temperature for 20 min before a solution of Selectflour (637 mg, 1.8 mmol) in 2 mL DMF was added slowly. The reaction mixture was then stirred at room temperature for 30 min. Water (15 mL) was added and extrated with EtOAc (10 mL×3). The combined organic layers were washed with water and brine and dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography to give desired product **5**. Yield 80 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 4H), 7.68 (t, *J* = 7.1 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 4H), 7.35 (s, 5H), 6.78 (dd, *J* = 42.0, 15.3 Hz, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 140.10, 140.03, 135.26, 130.85, 129.89, 129.07, 128.97, 128.88, 128.83, 128.63, 128.16, 127.34, 126.52, 112.55, 112.45. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{21}H_{18}S_2O_4F$ 417.1, found 417.1.

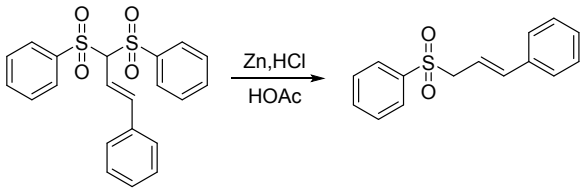
Compound **5** (208 mg, 0.5 mmol) was dissolved in 5 mL MeOH. Activated Mg (1.2 g, 50 mmol) and tetrabutylammonium chloride (TBAC, 1.4 g, 5 mmol) was added to this solution and the mixture was stirred at room temperature for 3 h. HCl (100 mL, 1 mol/L) was added and extrated with EtOAc (25 mL×3). The combined organic layers were washed with water and brine and dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography to give desired product **6**. Yield 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.32-7.28 (m, 1H), 6.72 (dd, *J* = 15.9, 5.0 Hz, 1H), 6.39 (ddd, *J* = 22.1, 12.1, 6.1 Hz, 1H), 5.10 (d, *J* = 6.1 Hz, 1H), 4.98 (d, *J* = 6.1 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 131.22, 129.61, 129.53, 123.89, 123.52, 121.99, 118.82, 118.72, 79.23, 78.15. LRMS (ESI) m/z $[M+H]^+$calcd for $C_9H_{10}F$ 137.1, found 137.1.



2b **7**

Cinnamic acid (7). To a solution of compound **2b** (199 mg, 0.5 mmol) in 5 mL of dry THF was added *t*-BuOK (168 mg, 1.5 mmol) at 0 ºC and stirred at same temperature for another 20 min before 3-phenyl-2-tosyl-1,2-oxaziridine (275 mg, 1.0 mmol) in 2 mL of THF was added slowly. The reaction was then stirred at 0 ºC for 15 min. The mixture was poured into 20 mL of MeOH (including 1 mL of concentrated HCl) and stirred at 0 ºC for 15 min. The solvent was removed under vacuum and water (15 mL) was added and extrated with EtOAc (10 mL×3). The combined organic layers were

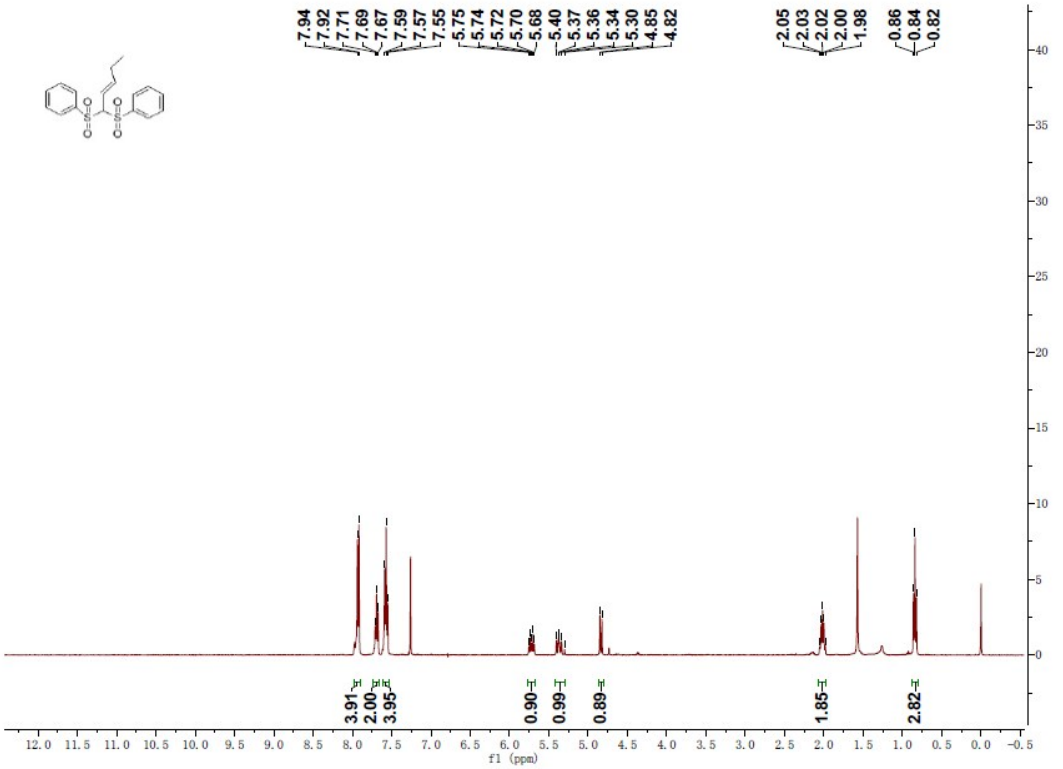
washed with water and brine and dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography to give desired product **7**. Yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 16.0 Hz, 1H), 7.56 (dd, J = 6.4, 2.6 Hz, 2H), 7.42-7.41 (m, 3H), 6.47 (d, J = 16.0 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 172.03, 147.03, 134.02, 130.71, 128.94, 128.33, 117.24. LRMS (ESI) m/z $[M+H]^+$calcd for $C_9H_{10}O_2$ 149.1, found 149.1.

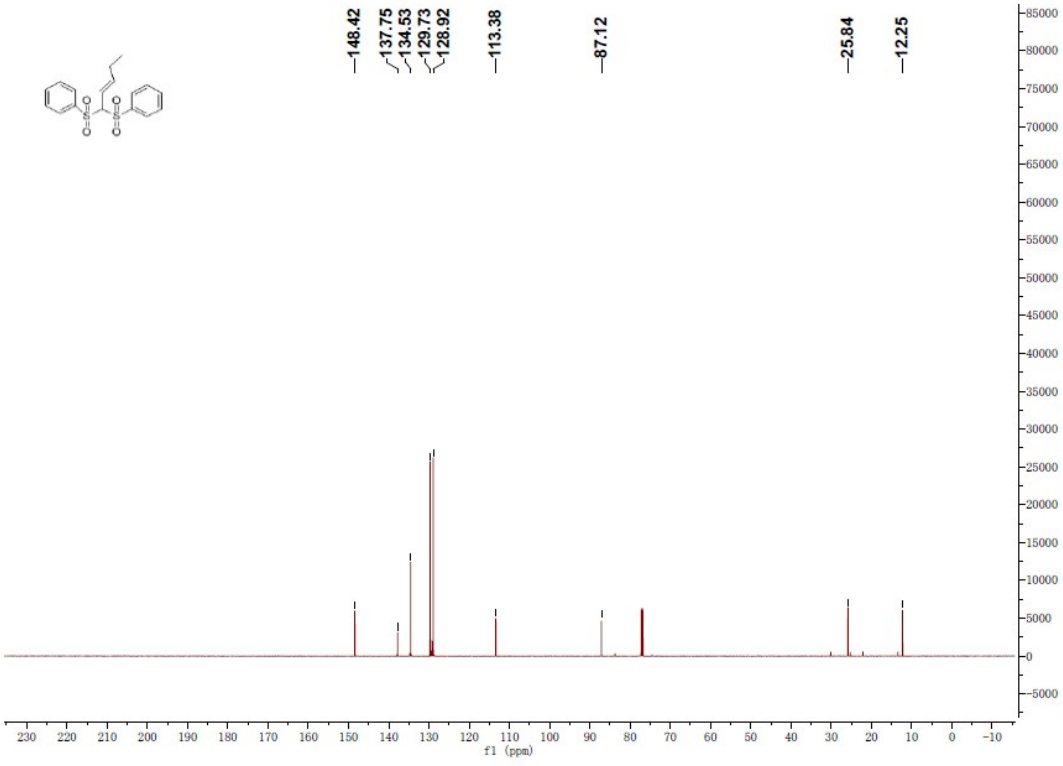


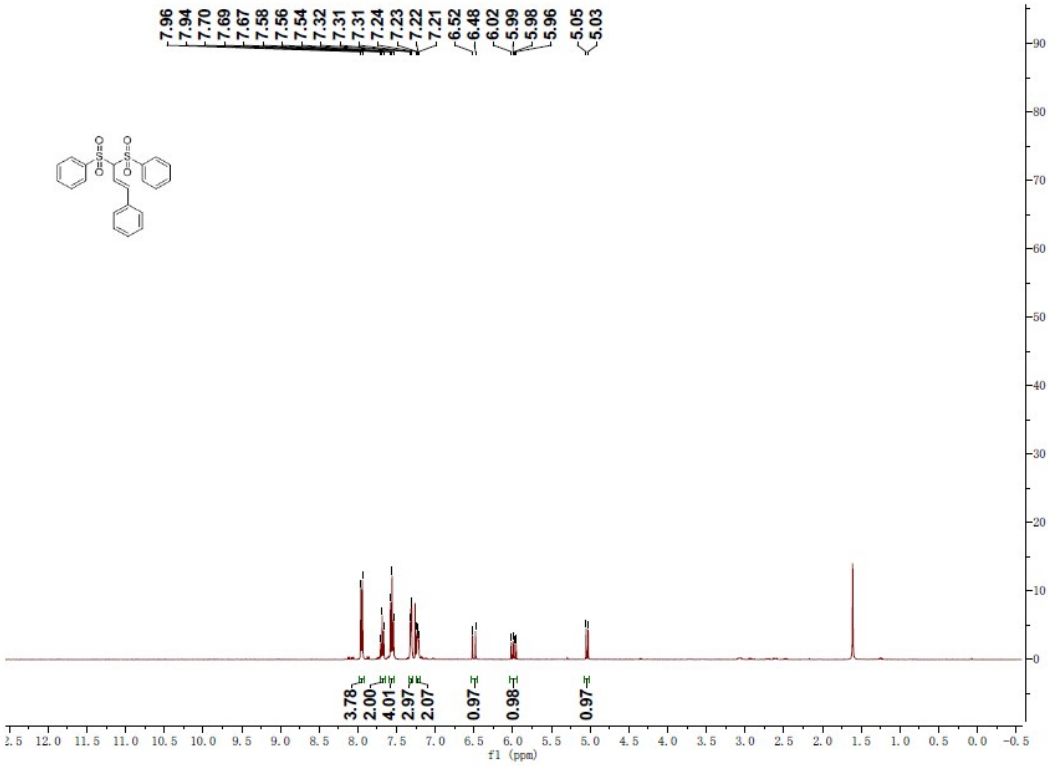
2b **8**

(Cinnamylsulfonyl) benzene (8). Compound **2b** (199 mg, 0.5 mmol) was dissolved in 2 mL AcOH. Zn (97.5 mg, 1.5 mmol) and concentrated HCl (1.0 mL) was added to this solution and the mixture was refluxed for 1 h. The reaction was completed monitored by TLC, if the material did not have the reaction finished, the corresponding hydrochloric acid and zinc powder was added. After the reaction completed, cooling to room temperature, water (15 mL) was added and extracted with EtOAc (10 mL×3). The combined organic layers were washed with water and brine and dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography to give desired product **8**. Yield 75%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (d, J = 7.0 Hz, 2H), 7.73 (d, J = 6.6 Hz, 1H), 7.65 (d, J = 6.9 Hz, 2H), 7.34-7.27 (m, 5H), 6.48 (d, J = 15.7 Hz, 1H), 6.13-6.05 (m, 1H), 4.26 (d, J = 6.9 Hz, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 138.76, 137.88, 135.26, 133.32, 128.63, 128.19, 128.05, 126.14, 114.61, 60.02. LRMS (ESI) m/z $[M+H]^+$calcd for $C_{15}H_{14}SO_2$ 259.1, found 259.1.

3. ^{1}H and ^{13}C NMR spectra of all compounds



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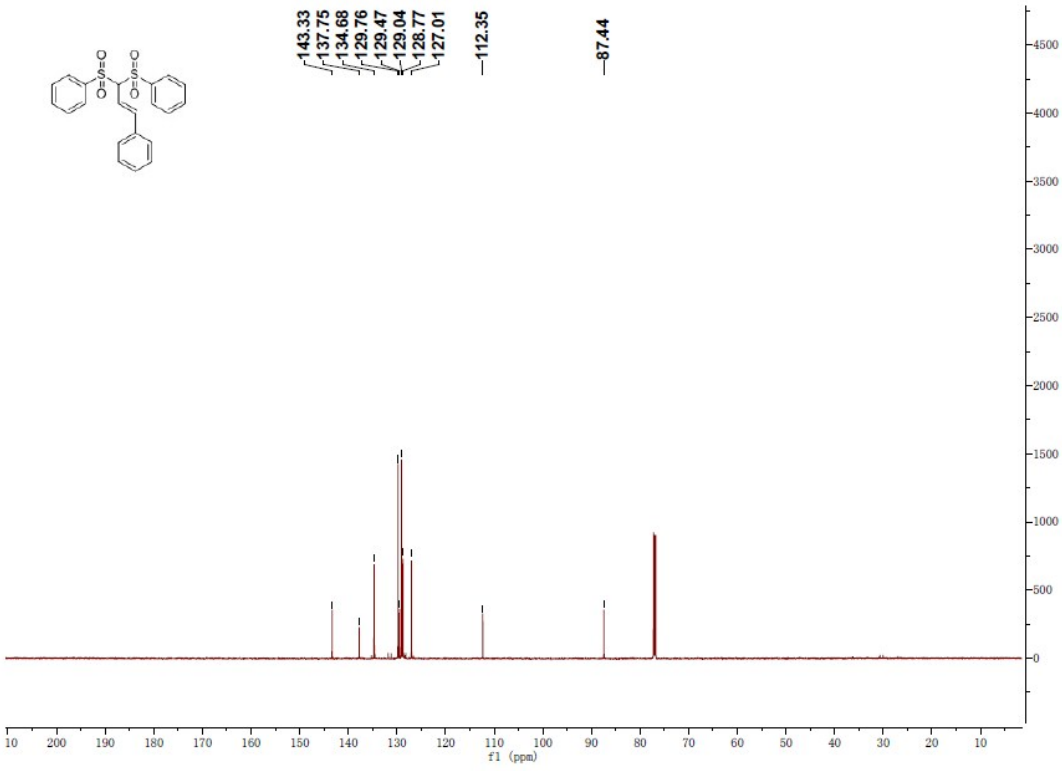
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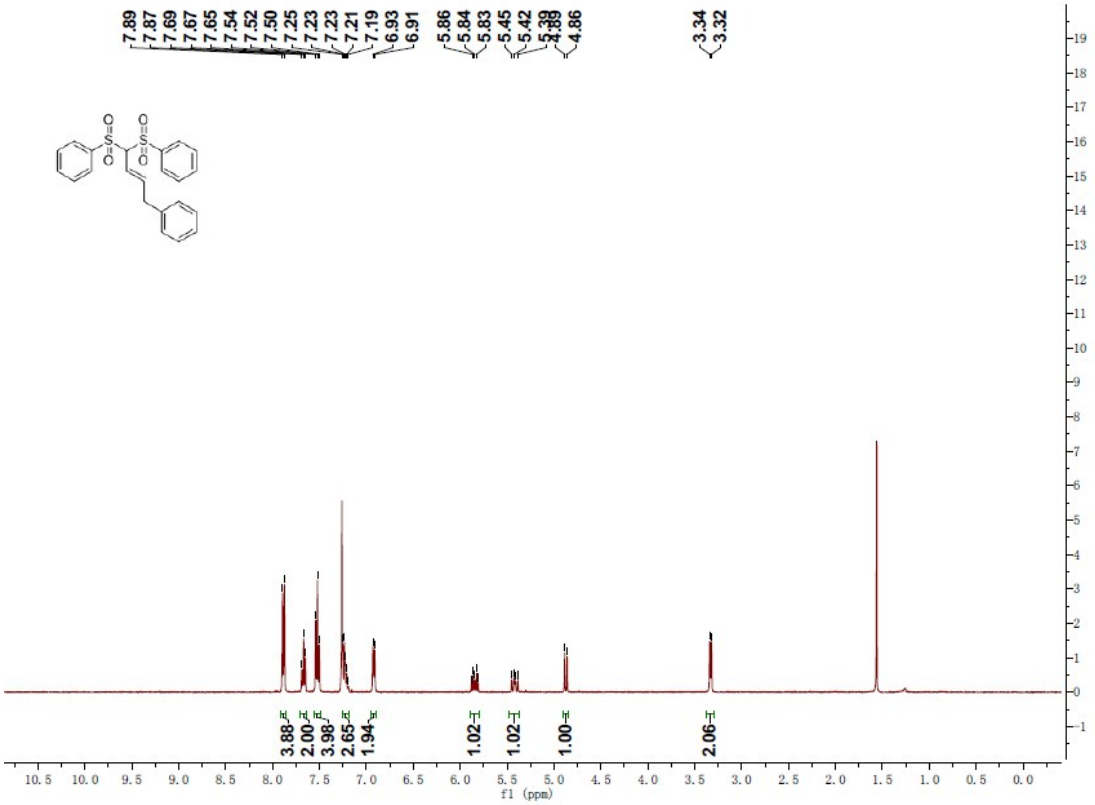
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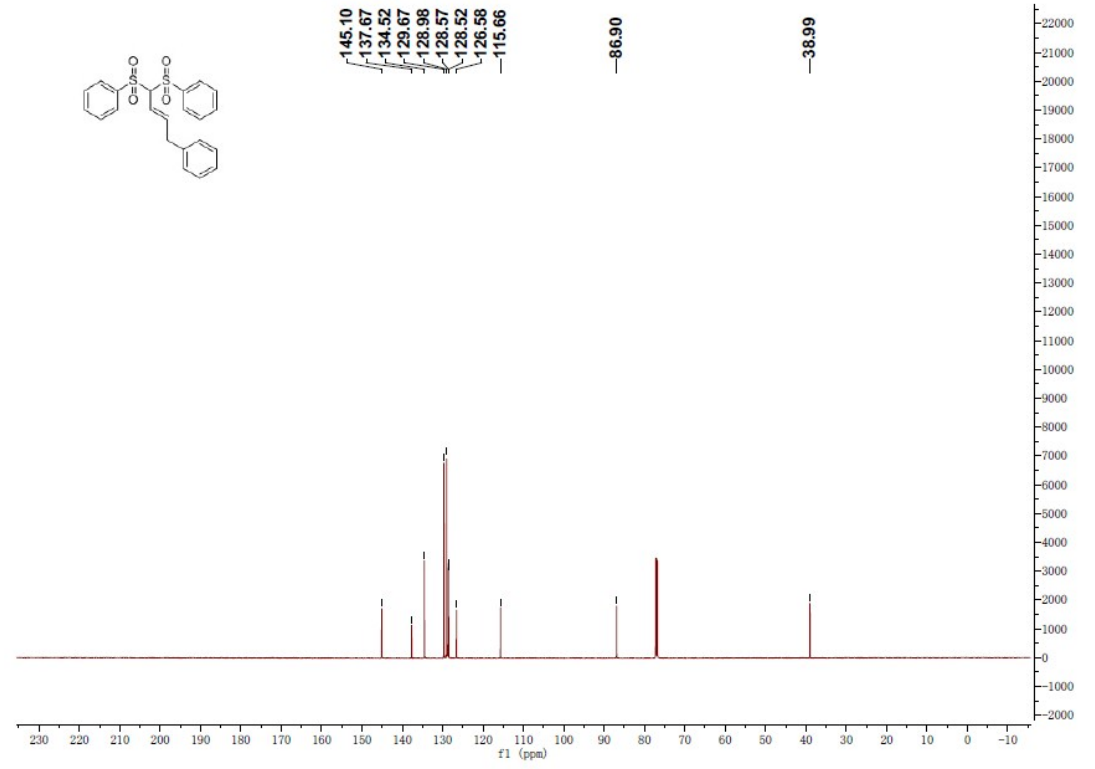
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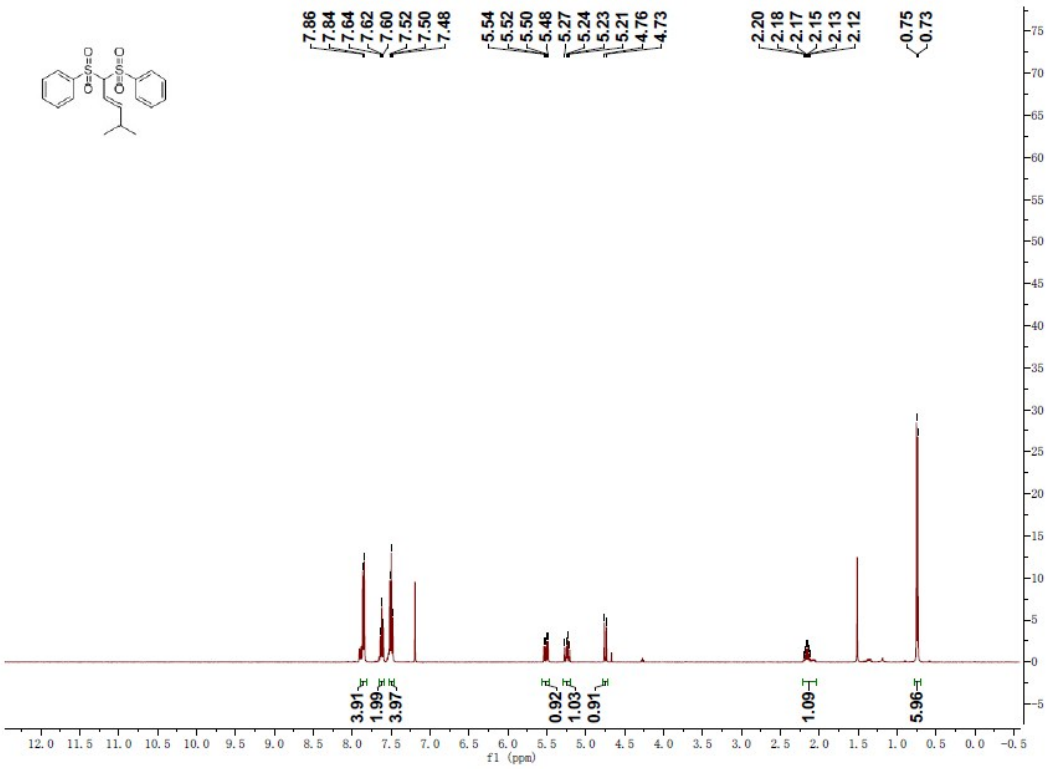
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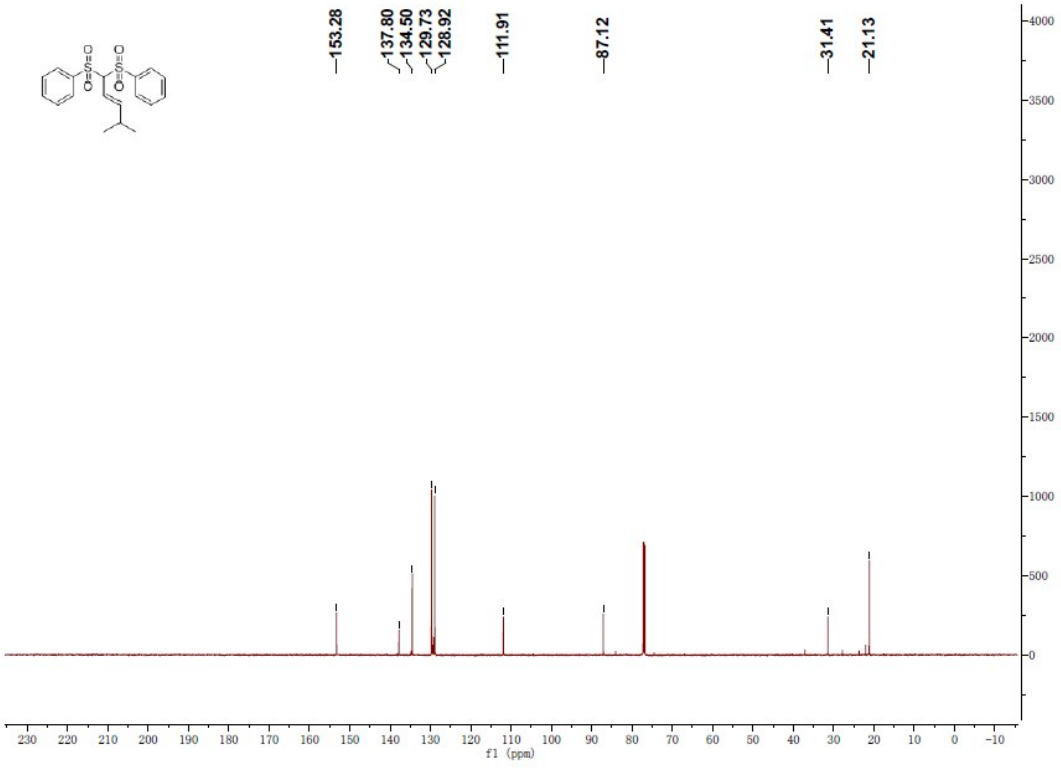
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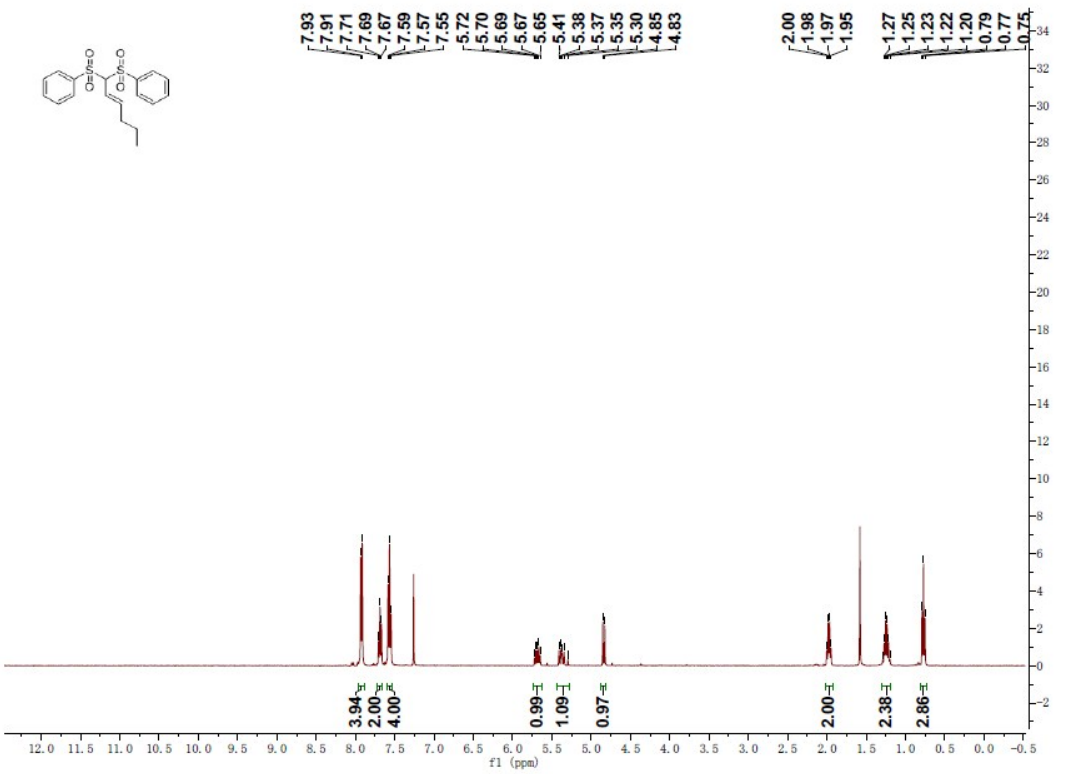
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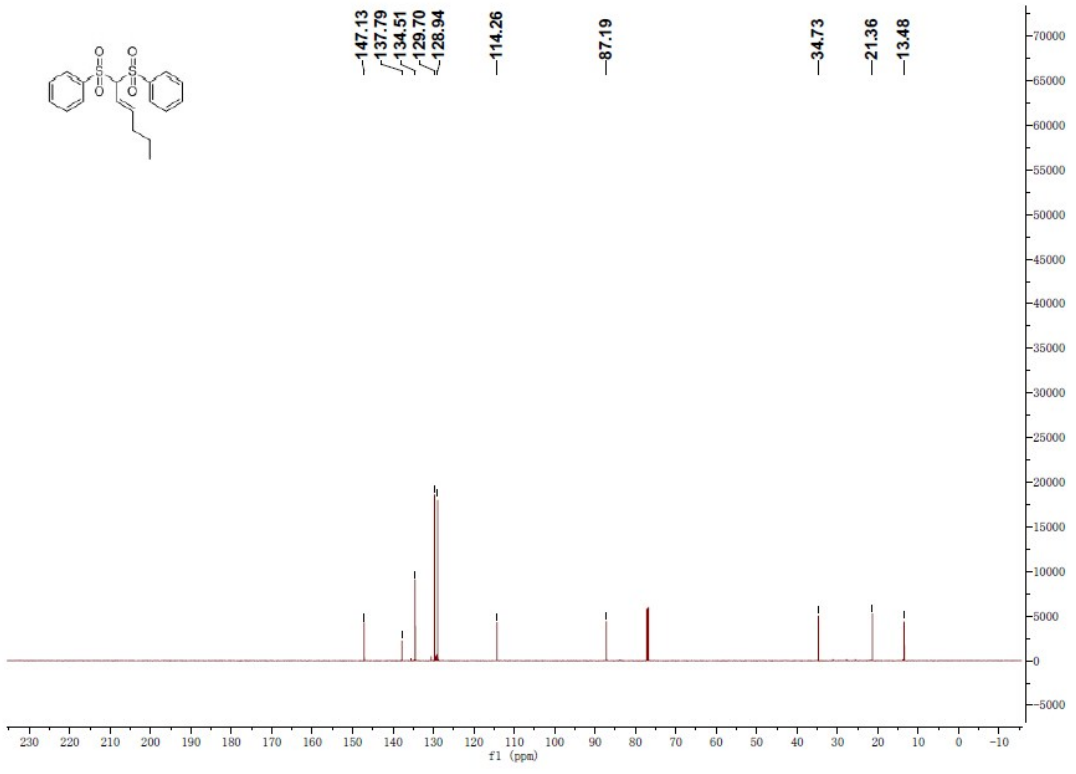
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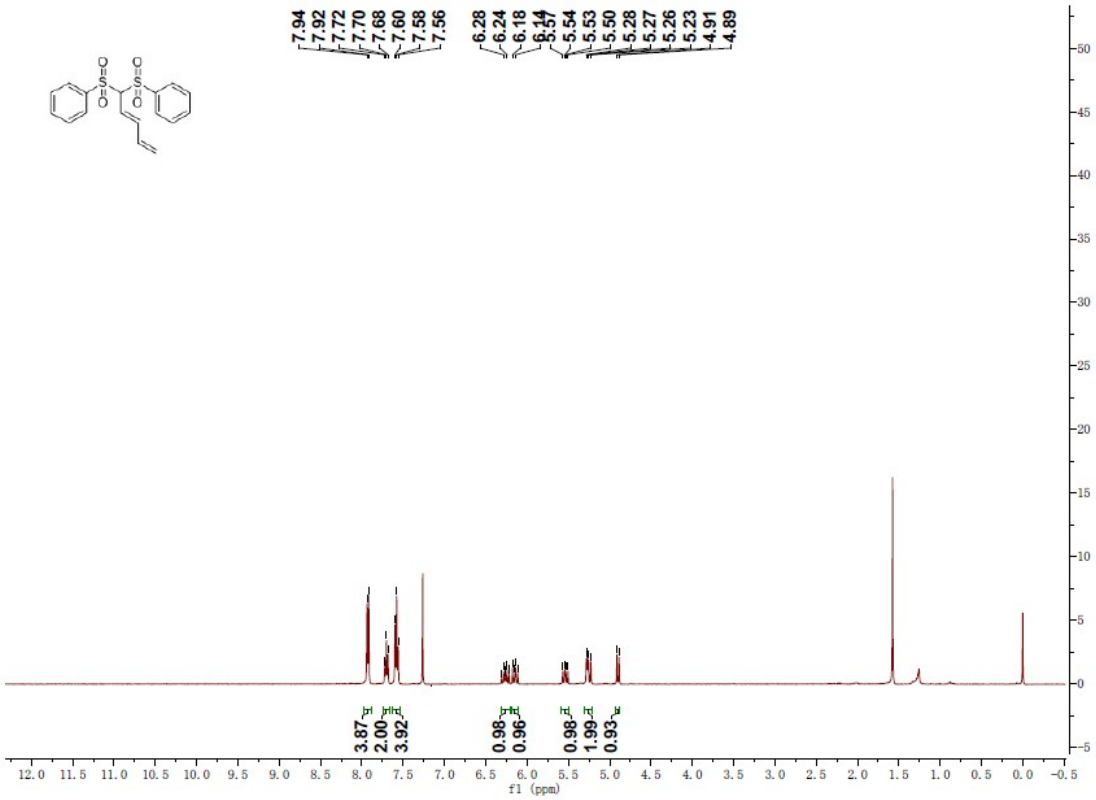
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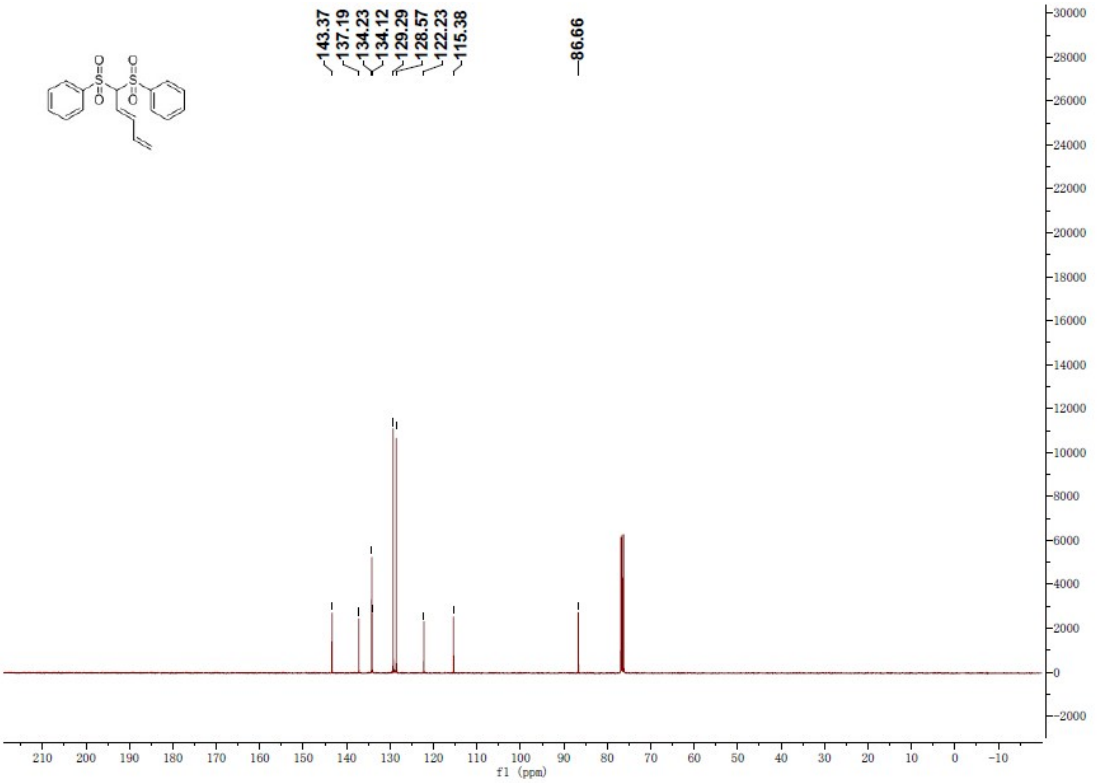
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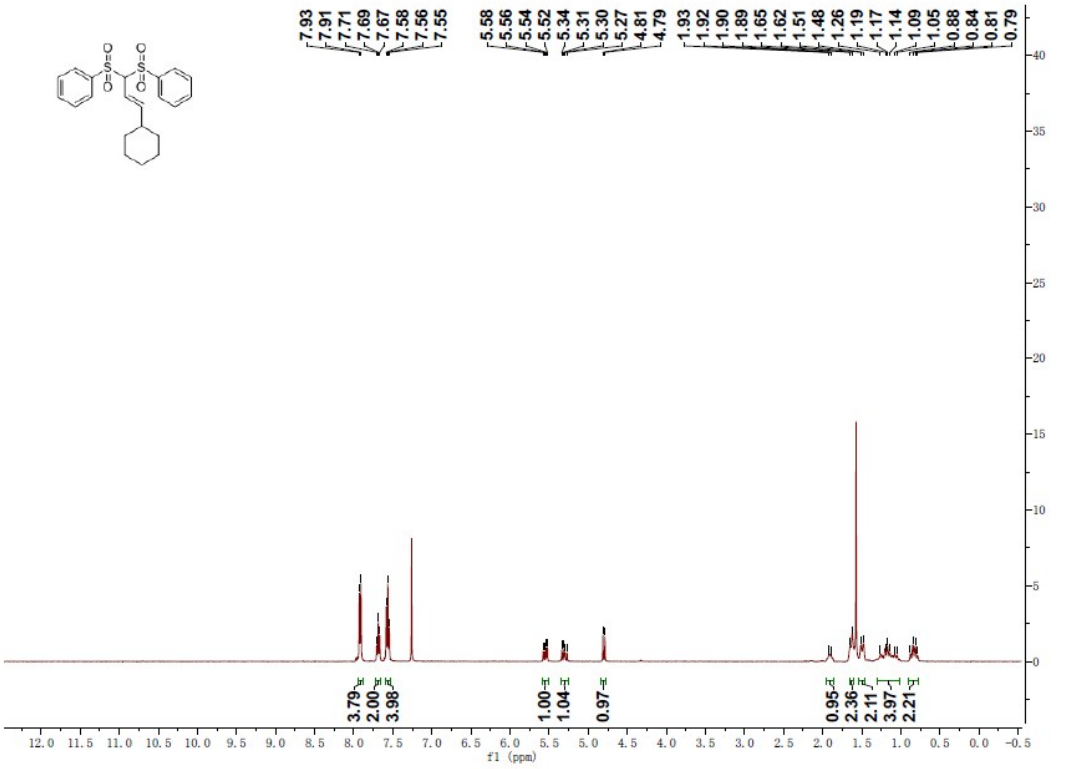
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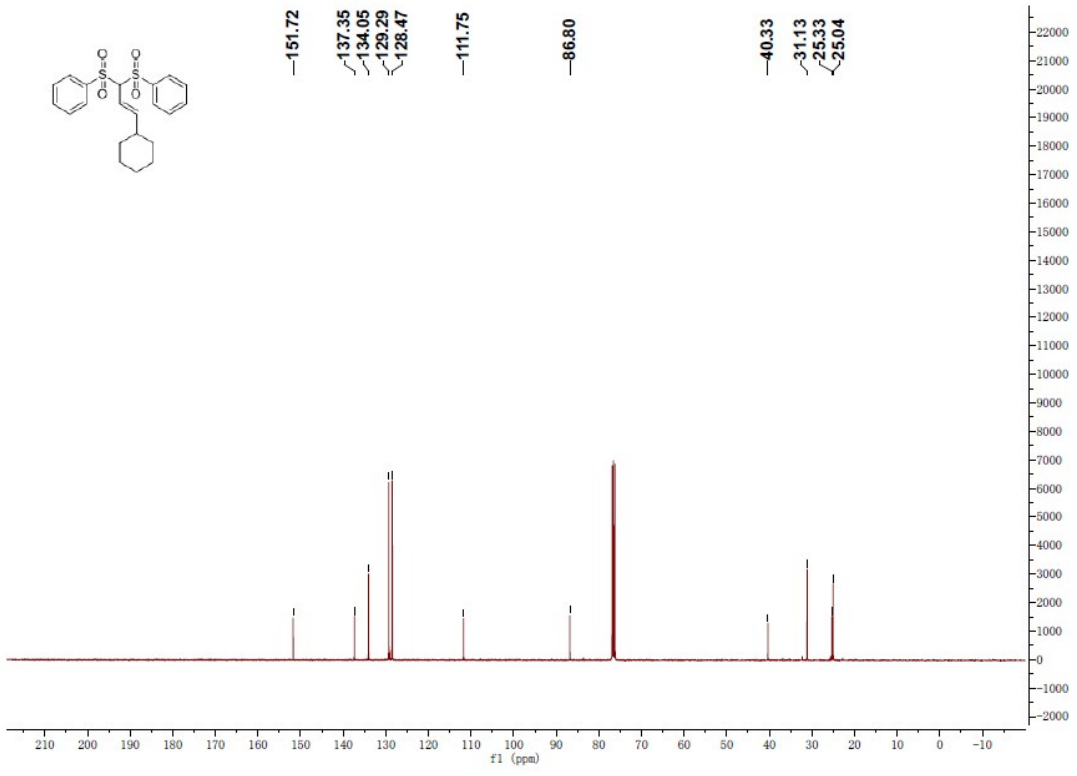
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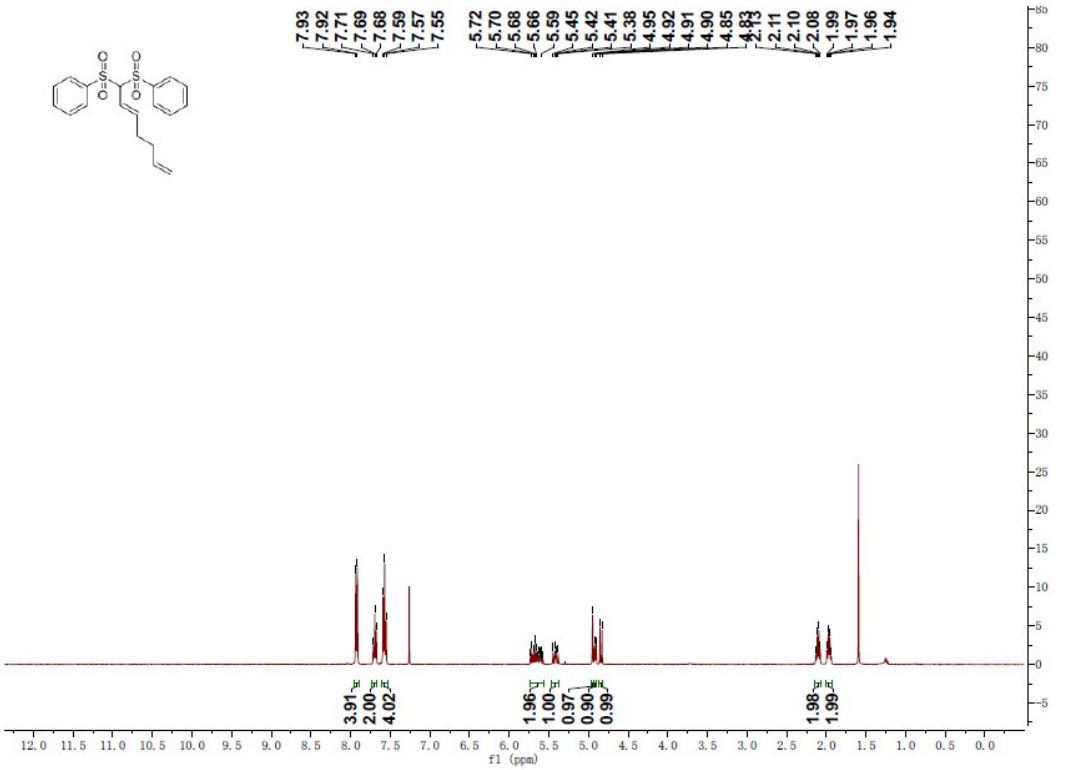
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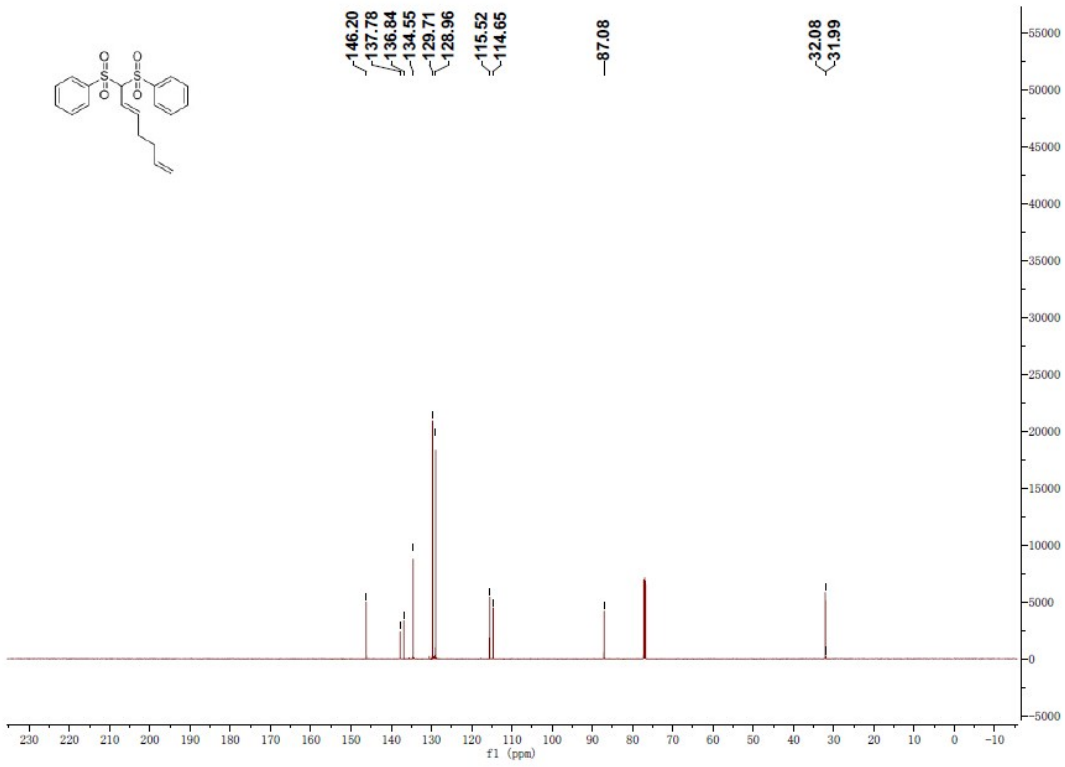
f1 (ppm)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115.52
114.65
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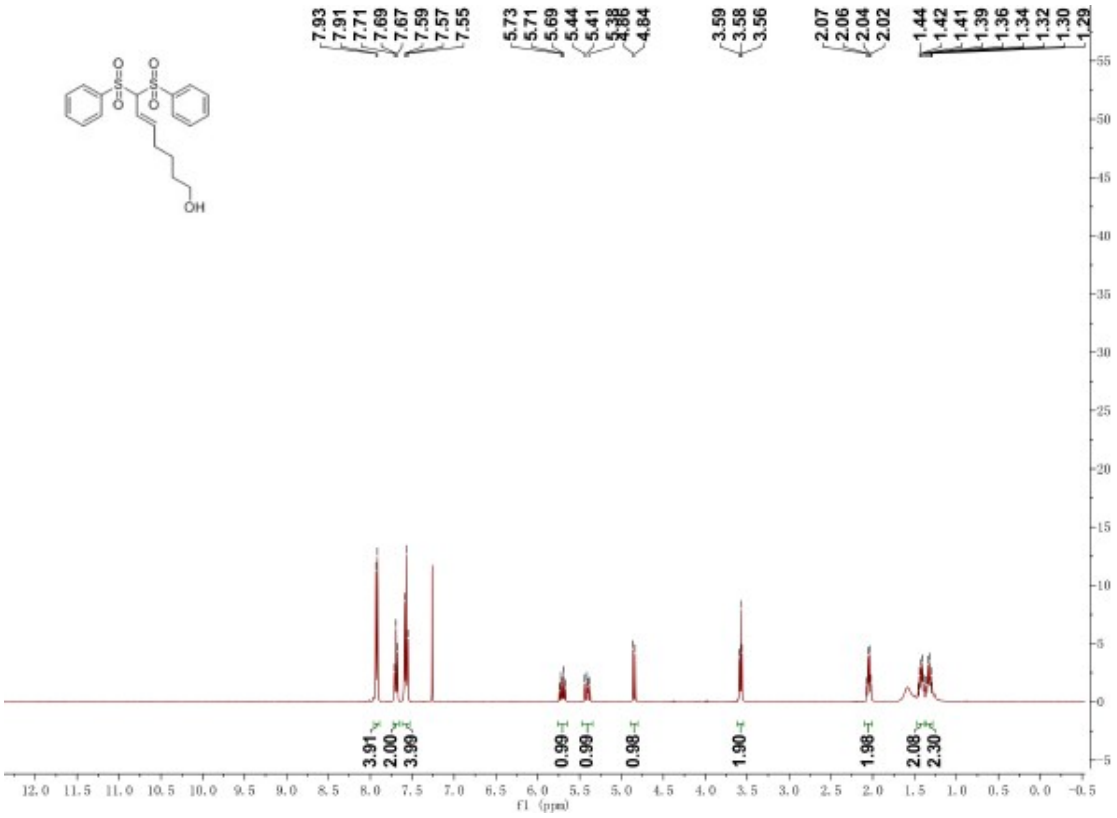
32.08
31.99
f1 (ppm)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7.57
7.55
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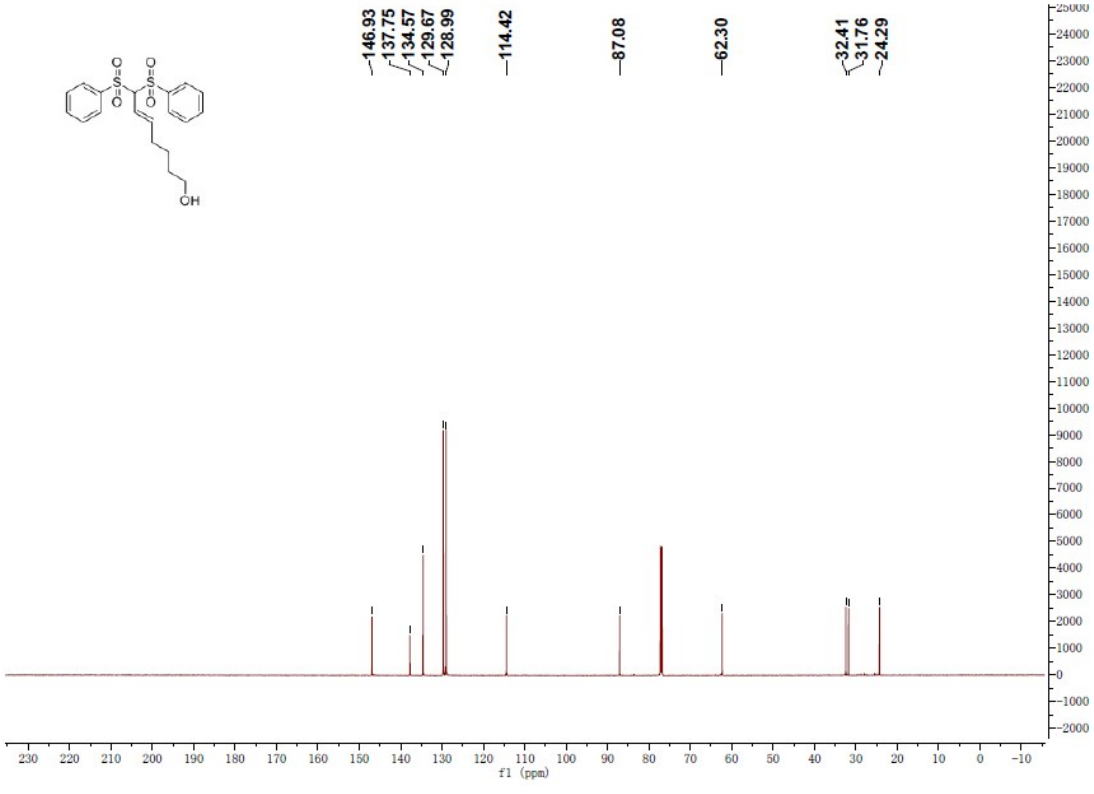
5.71
5.69
5.44
5.41
5.38
4.84
3.59
3.58
3.56
2.07
2.06
2.04
2.02
1.44
1.42
1.41
1.39
1.36
1.34
1.32
1.30
1.29
OH
3.91
2.00
3.99
0.99
0.99
0.98
1.90
1.98
2.08
2.30
f1 (ppm)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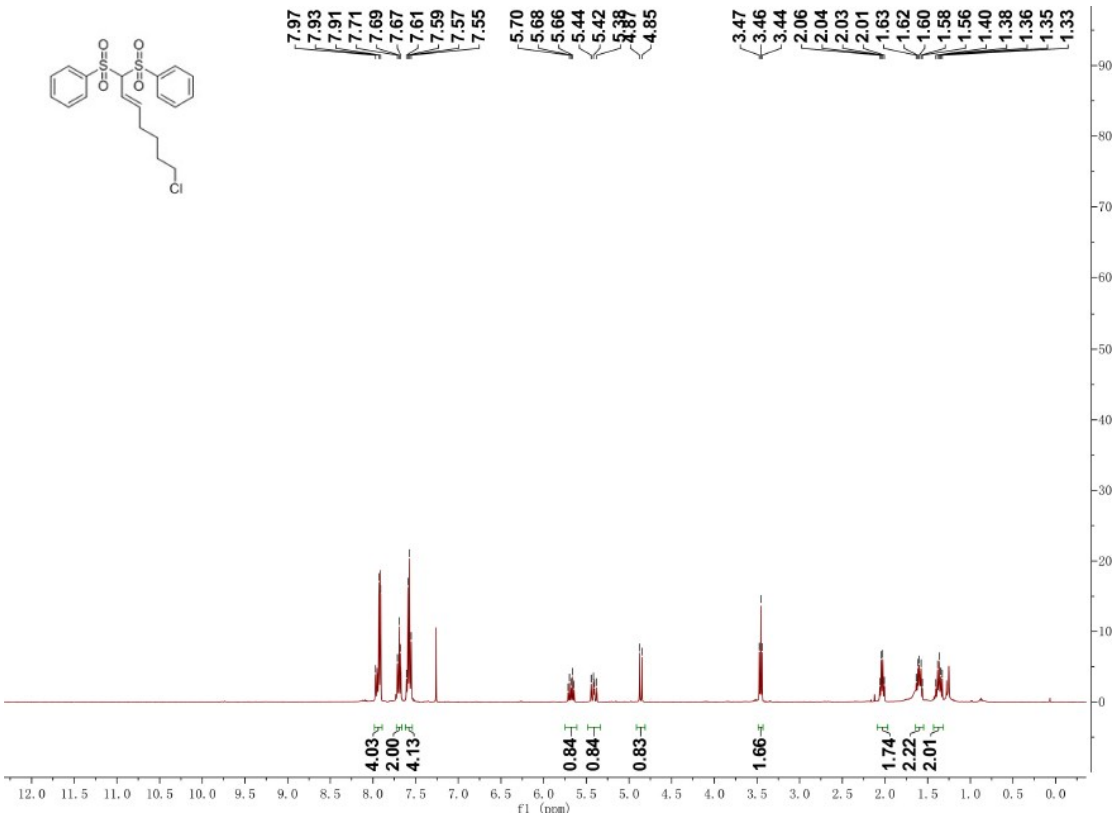
62.30
32.41
31.76
24.29
OH
f1 (ppm)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5.70
5.68
5.66
5.44
5.42
4.87
4.85
3.47
3.46
3.44
2.06
2.04
2.03
2.01
1.63
1.62
1.60
1.58
1.56
1.40
1.38
1.36
1.35
1.33
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4.13
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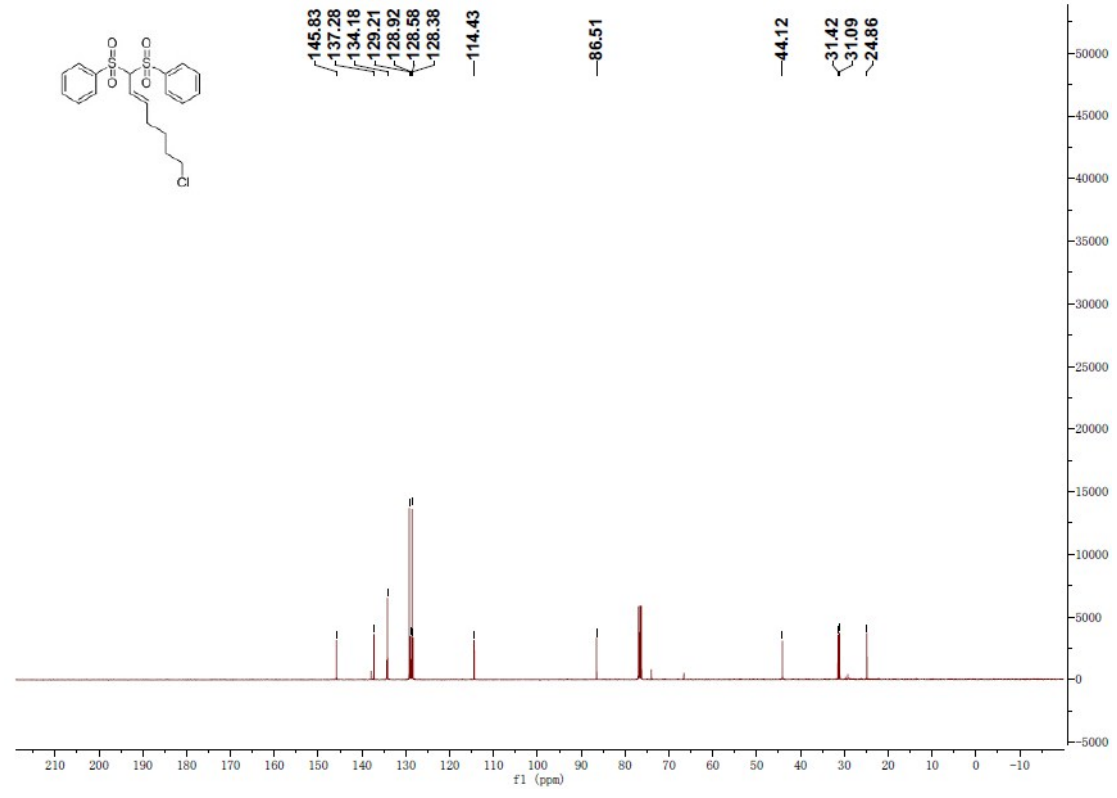
0.84
0.83
1.66
1.74
2.22
2.01
f1 (ppm)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114.43
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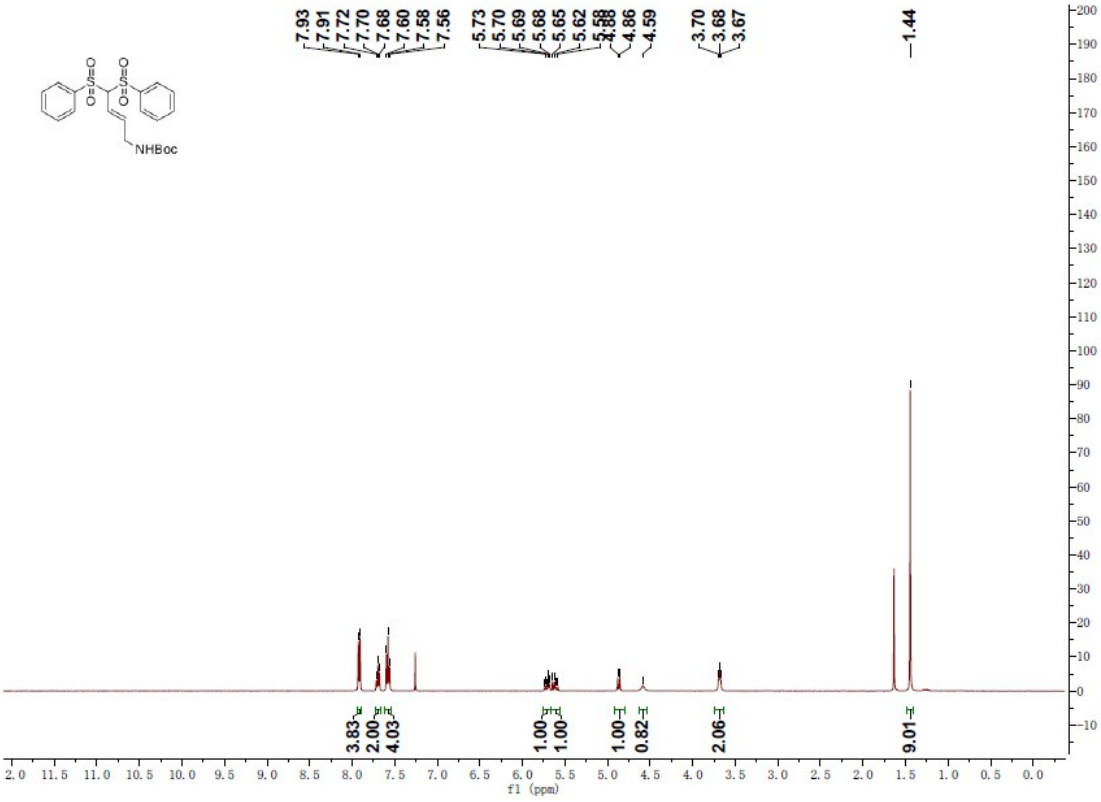
44.12
31.42
31.09
24.86
f1 (ppm)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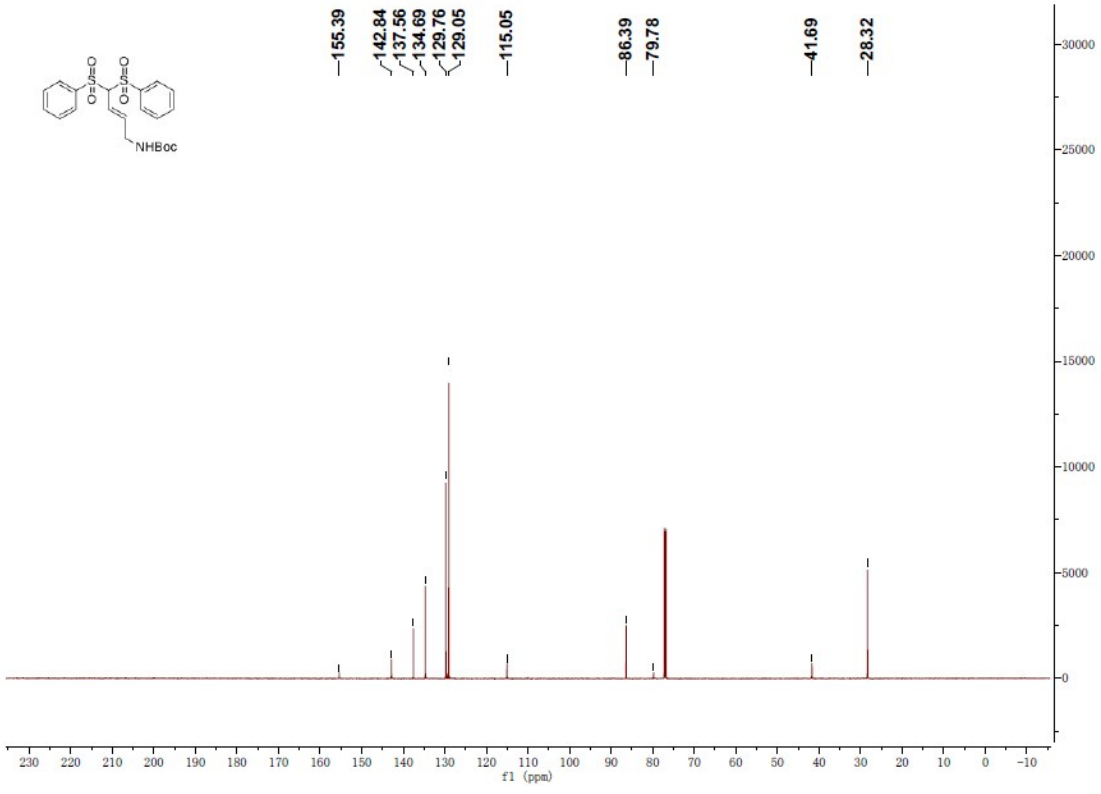
7.91
7.72
7.70
7.68
7.60
7.58
7.56
5.73
5.70
5.69
5.68
5.65
5.62
4.88
4.86
4.59
3.70
3.68
3.67
1.44
NHBoc
3.83
2.00
4.03
1.00
1.00
1.00
0.82
2.06
9.01
f1 (ppm)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137.56
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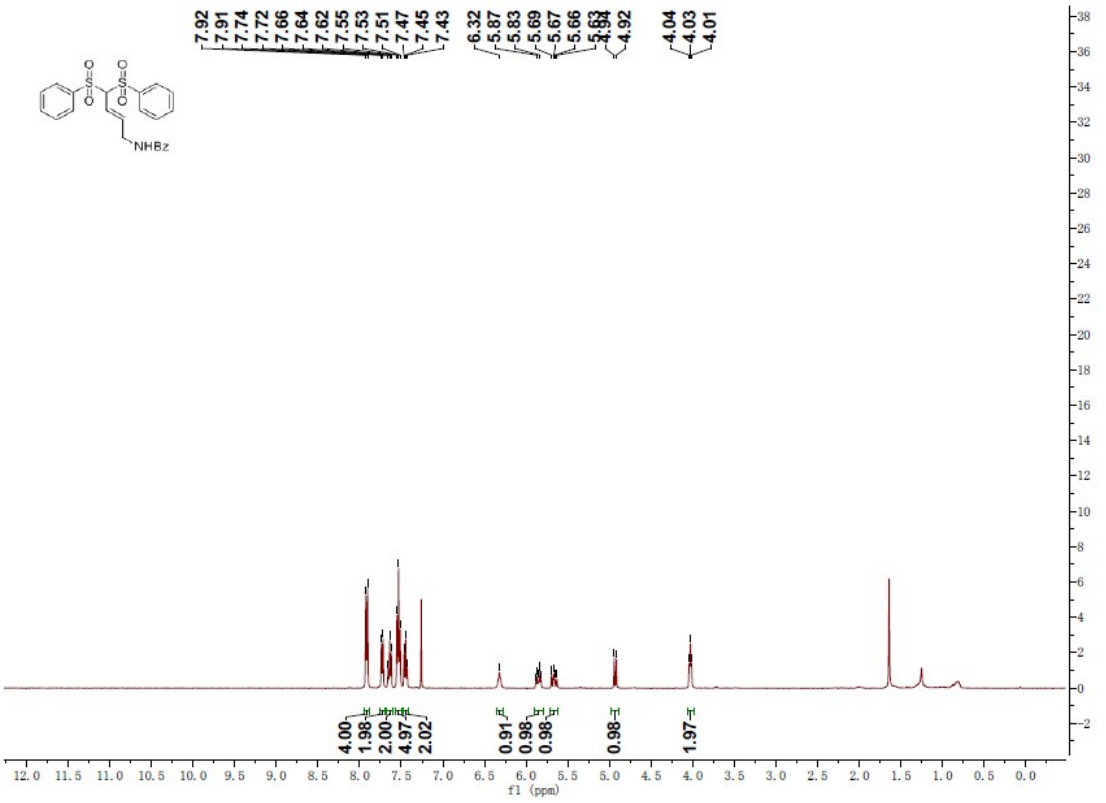
129.05
115.05
86.39
79.78
41.69
28.32
NHBoc
f1 (ppm)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7.64
7.62
7.55
7.53
7.51
7.47
7.45
7.43
6.32
5.87
5.83
5.69
5.67
5.66
5.63
4.92
4.04
4.03
4.01
NHBz
4.00
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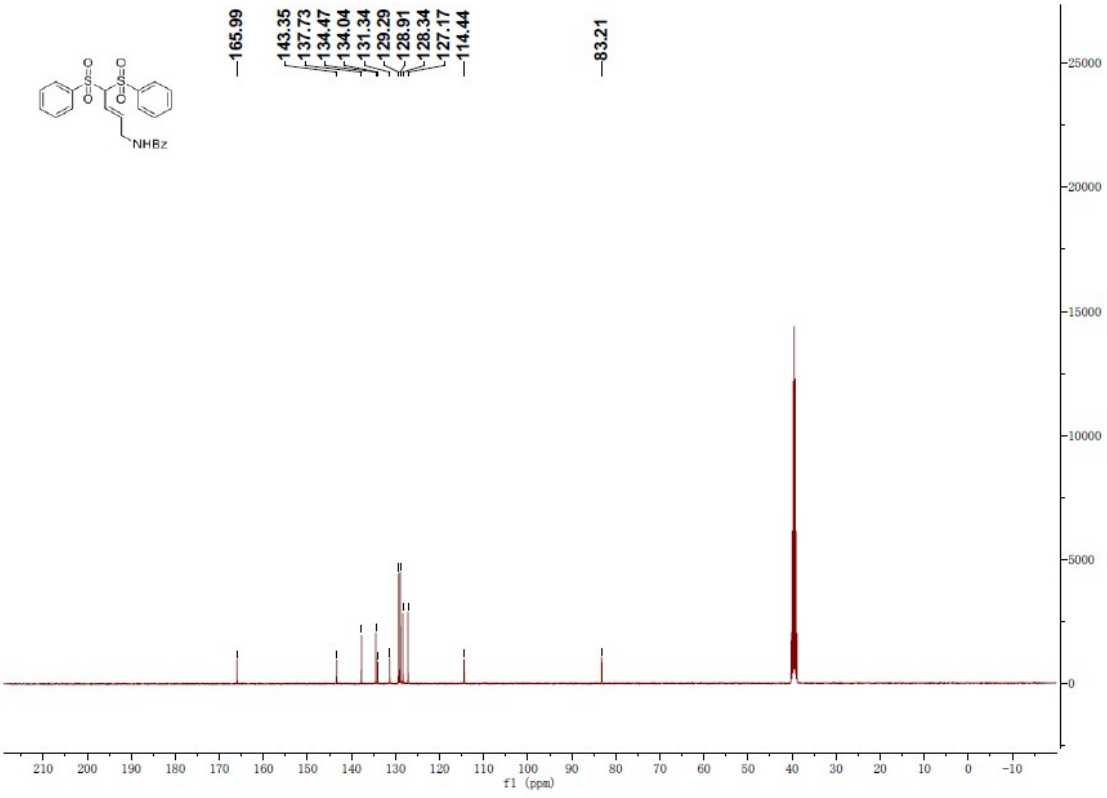
2.00
4.97
2.02
0.91
0.98
0.98
0.98
1.97
f1 (ppm)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131.34
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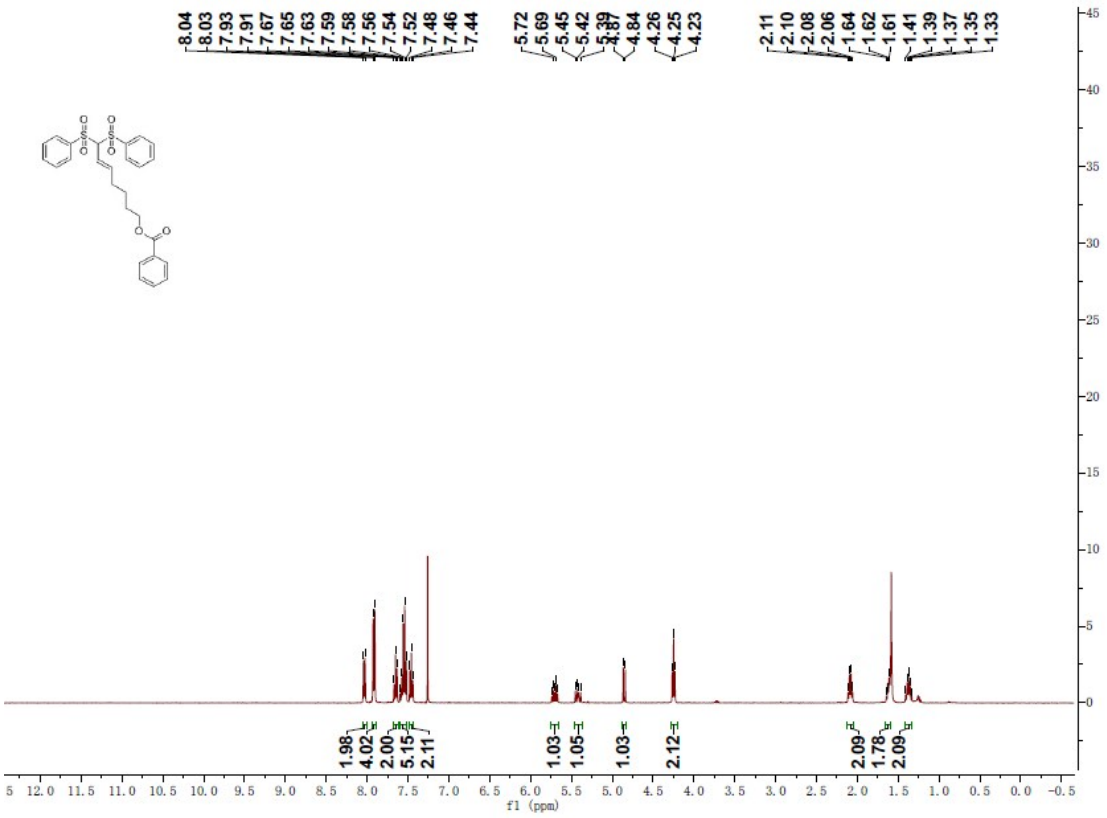
128.91
128.34
127.17
114.44
83.21
NHBz
f1 (ppm)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7.65
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7.59
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7.56
7.54
7.52
7.48
7.46
7.44
5.72
5.69
5.45
5.42
5.39
4.87
4.84
4.26
4.25
4.23
2.11
2.10
2.08
2.06
1.64
1.62
1.61
1.41
1.39
1.37
1.35
1.33
1.98
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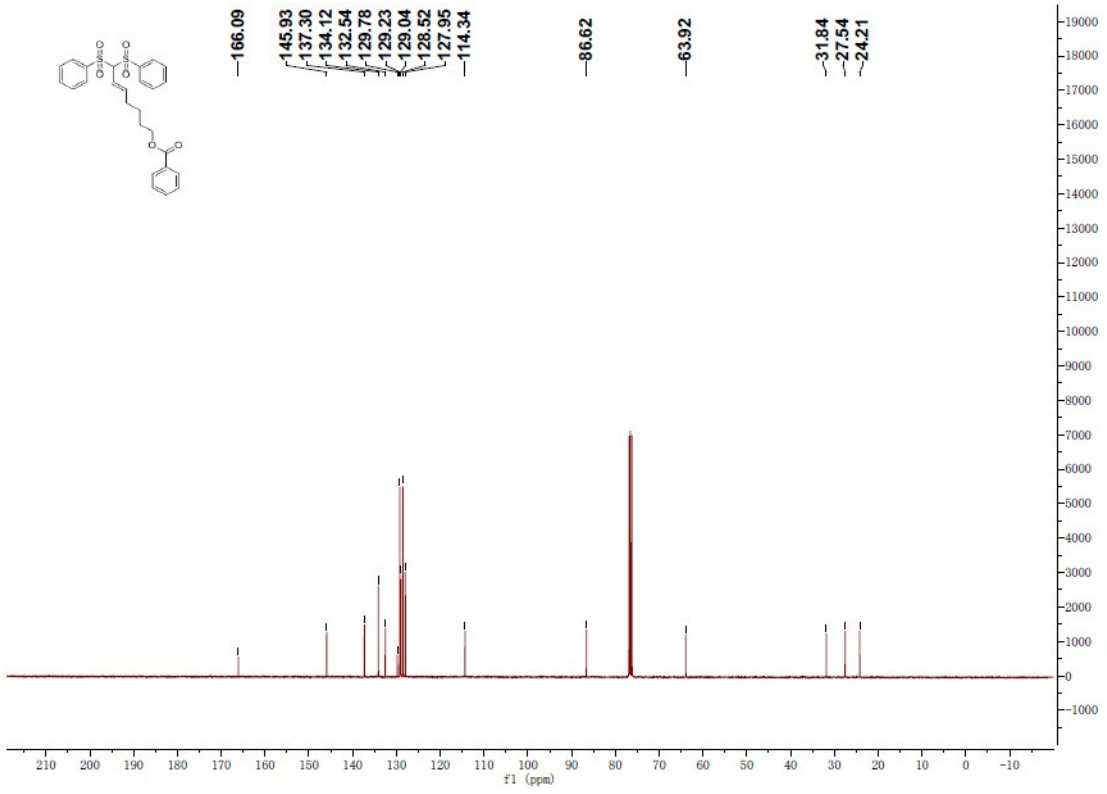
2.00
5.15
2.11
1.03
1.05
1.03
2.12
2.09
1.78
2.09
f1 (ppm)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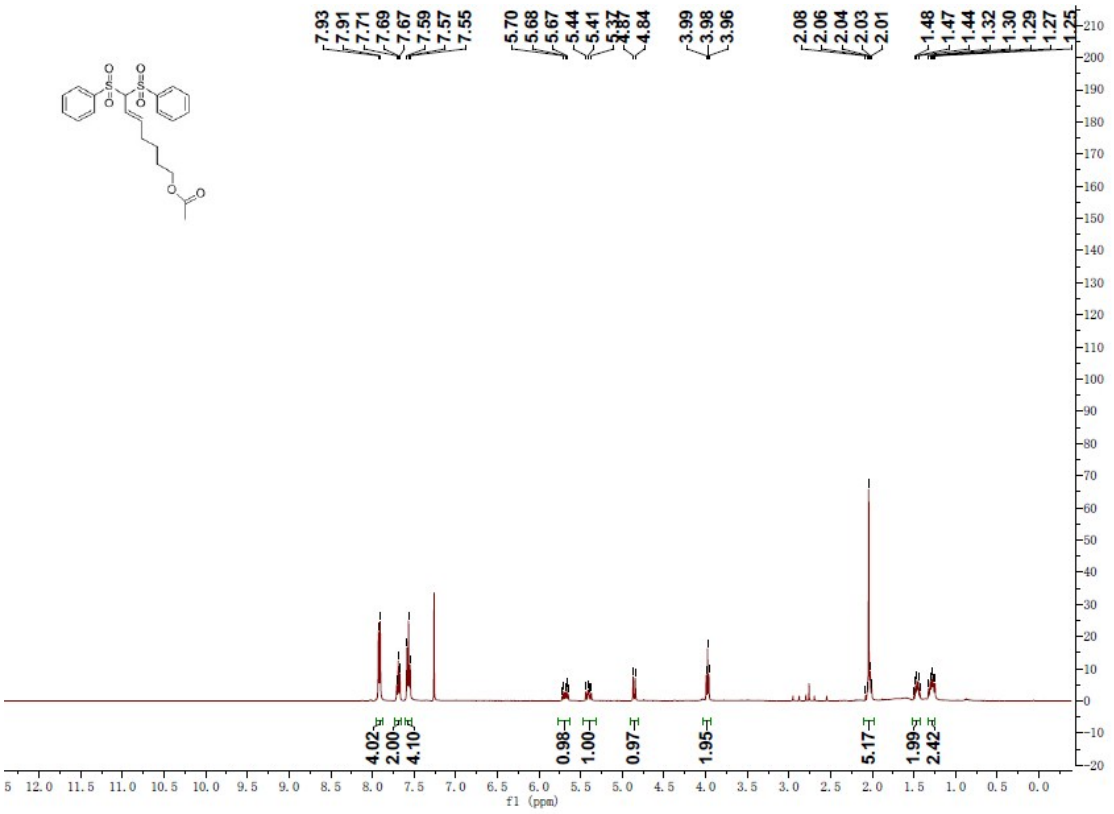
127.95
114.34
86.62
63.92
31.84
27.54
24.21
f1 (ppm)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7.69
7.67
7.59
7.57
7.55
5.70
5.68
5.67
5.44
5.41
5.37
4.87
4.84
3.99
3.98
3.96
2.08
2.06
2.04
2.03
2.01
1.48
1.47
1.44
1.32
1.30
1.29
1.27
1.25
4.02
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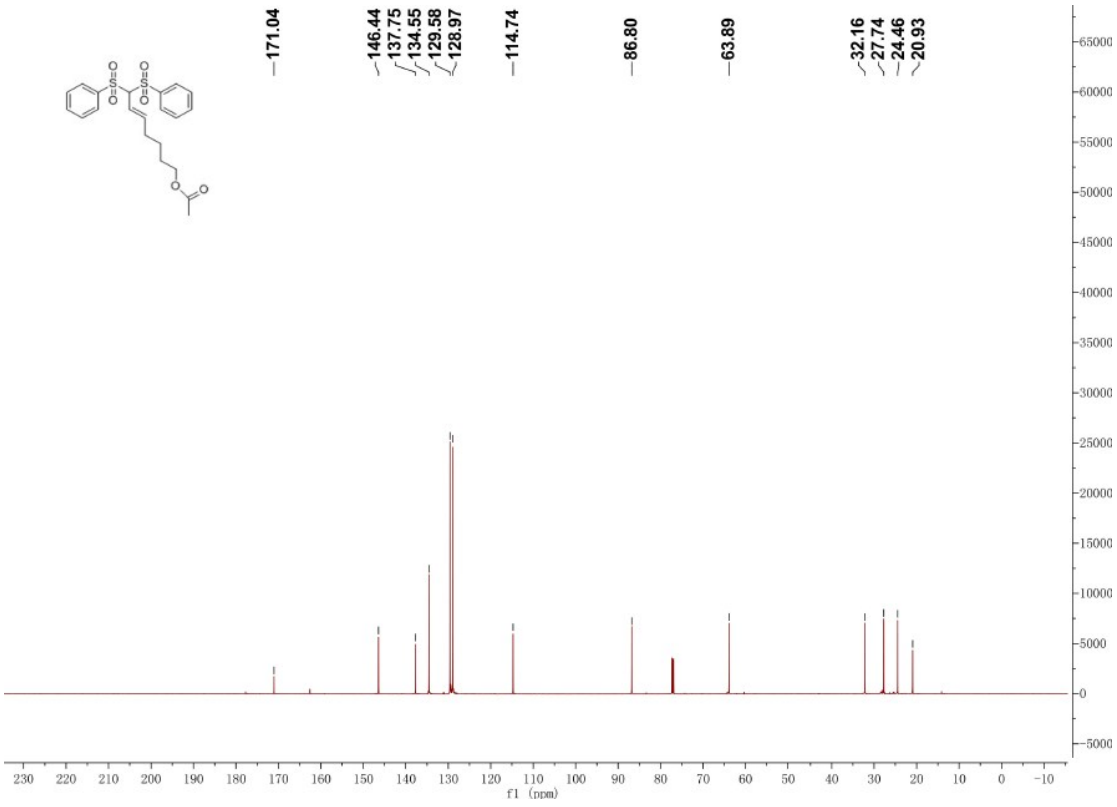
4.10
0.98
1.00
0.97
1.95
5.17
1.99
2.42
f1 (ppm)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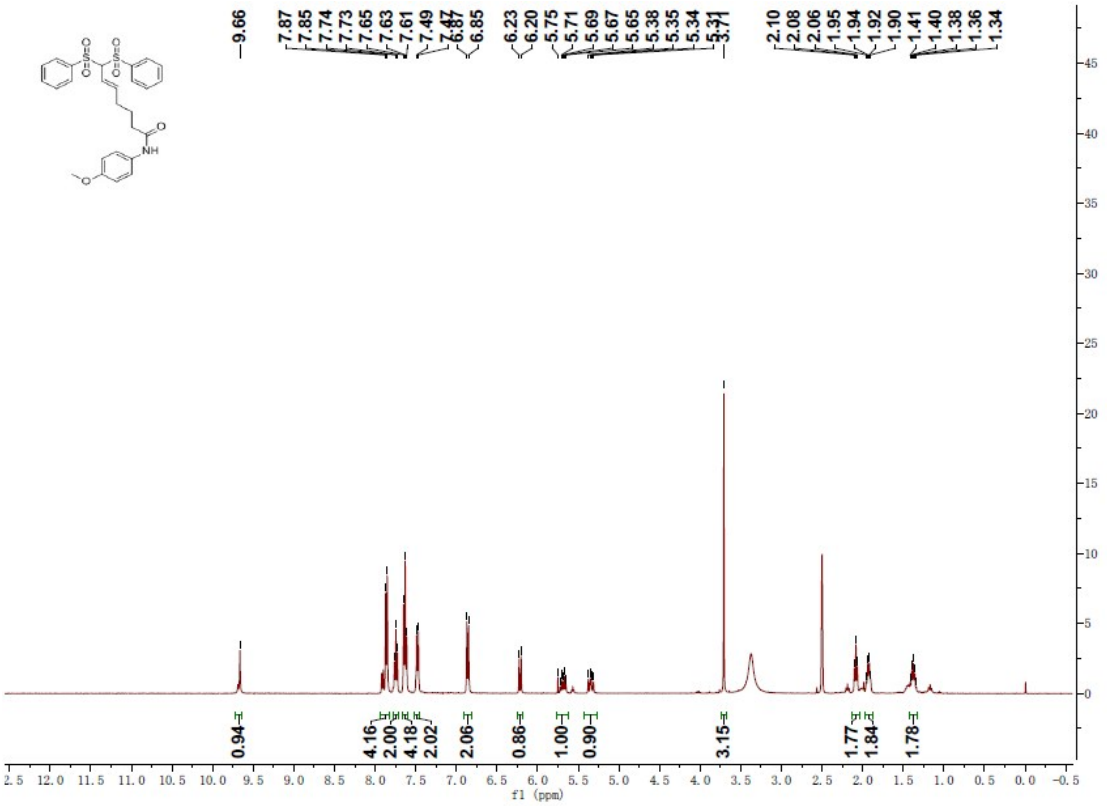
114.74
86.80
63.89
32.16
27.74
24.46
20.93
f1 (ppm)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7.61
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6.87
6.85
6.23
6.20
5.75
5.71
5.69
5.67
5.65
5.38
5.35
5.34
5.31
3.71
2.10
2.08
2.06
1.95
1.94
1.92
1.90
1.41
1.40
1.38
1.36
1.34
0.94
4.16
2.00
4.18
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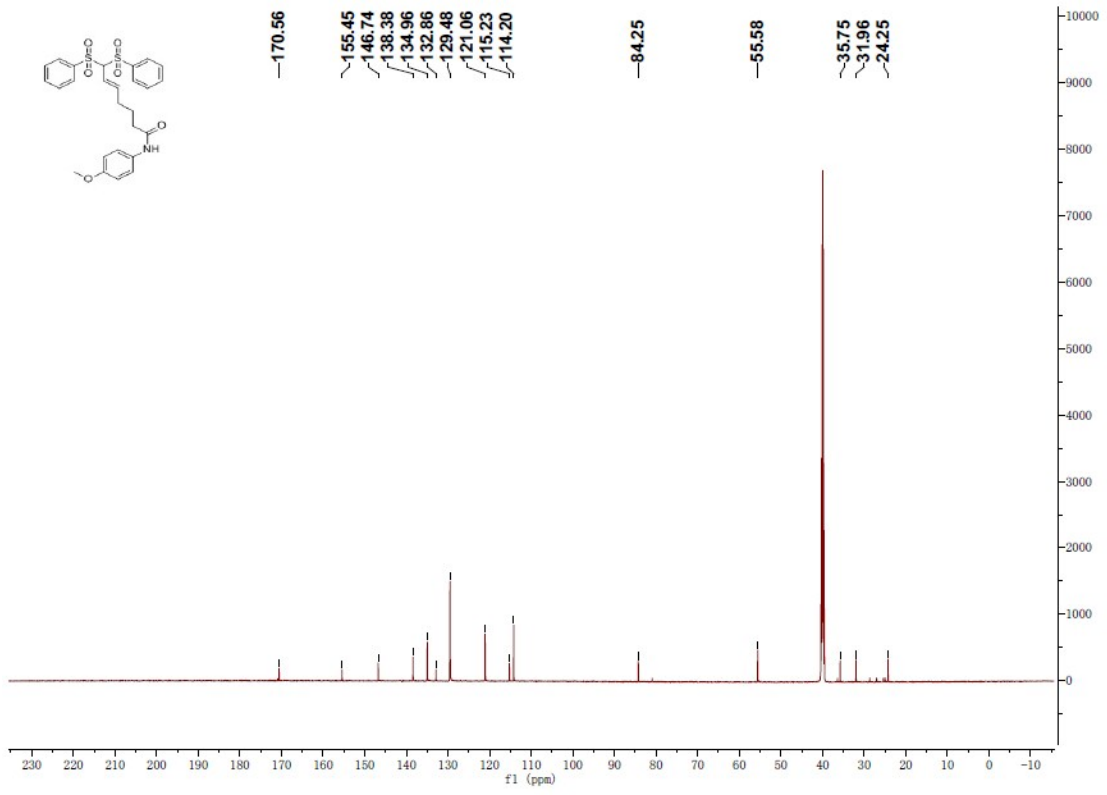
2.06
0.86
1.00
0.90
3.15
1.77
1.84
1.78
f1 (ppm)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121.06
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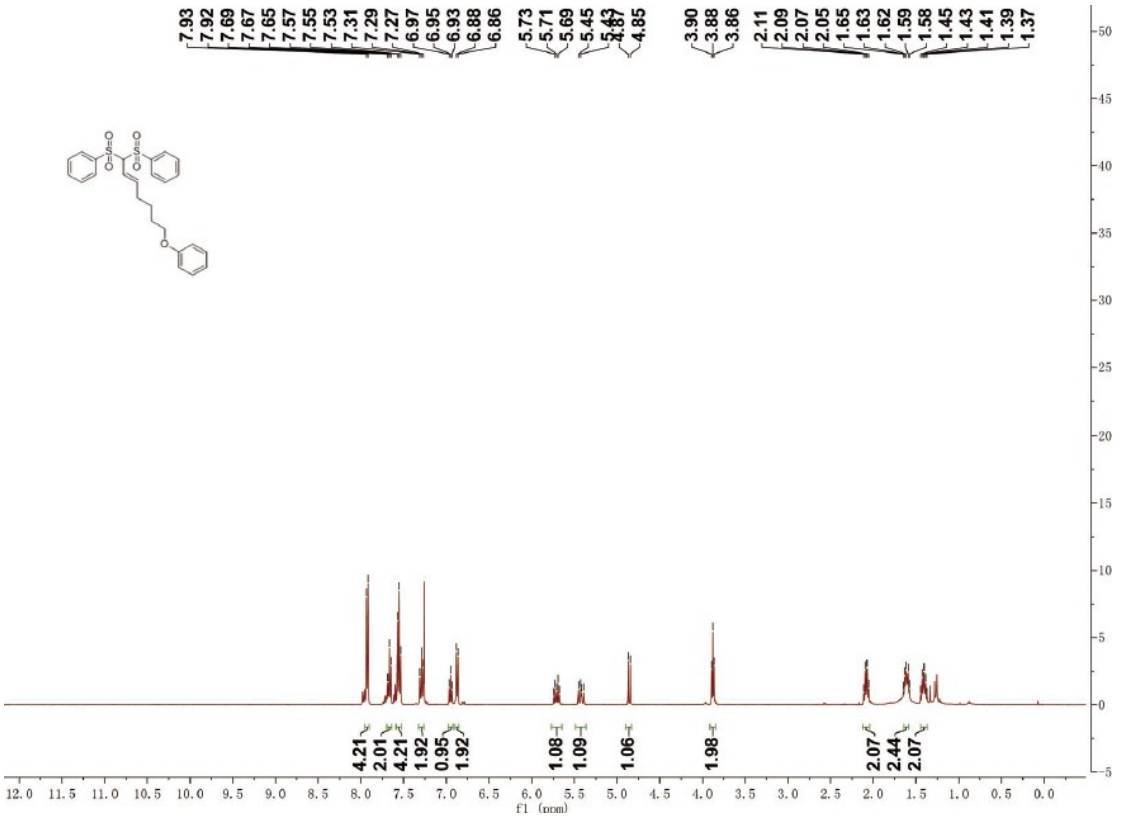
114.20
84.25
55.58
35.75
31.96
24.25
f1 (ppm)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7.92
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7.55
7.53
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6.95
6.93
6.88
6.86
5.73
5.71
5.69
5.45
4.87
4.85
3.90
3.88
3.86
2.11
2.09
2.07
2.05
1.65
1.63
1.62
1.59
1.58
1.45
1.43
1.41
1.39
1.37
4.21
2.01
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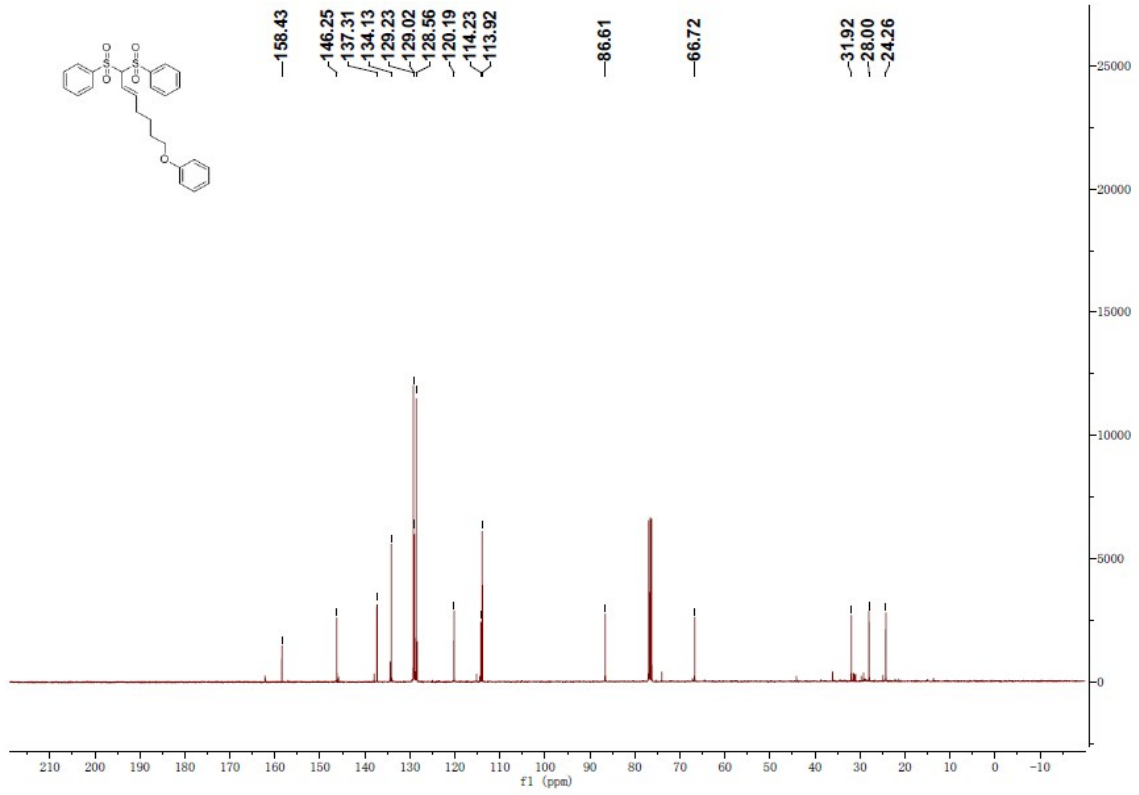
1.92
1.08
1.09
1.06
1.98
2.07
2.44
2.07
f1 (ppm)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134.13
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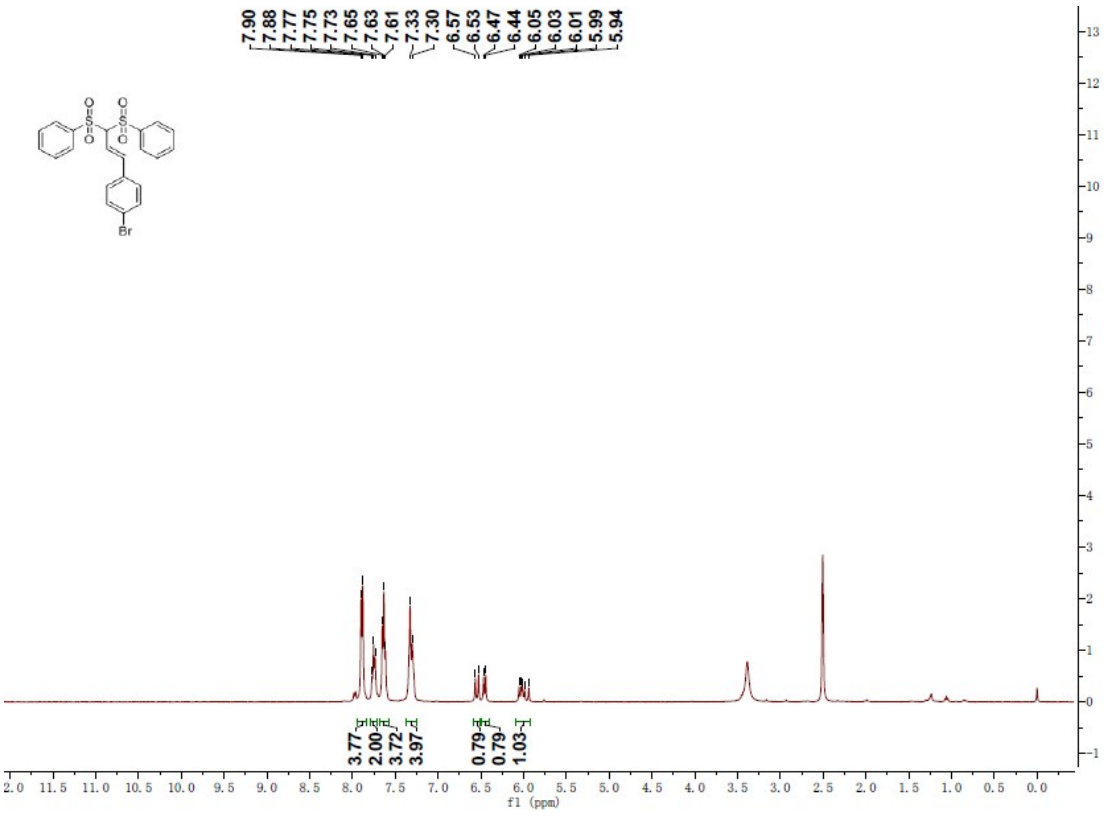
113.92
86.61
66.72
31.92
28.00
24.26
f1 (ppm)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7.88
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7.65
7.63
7.61
7.33
7.30
6.57
6.53
6.47
6.44
6.05
6.03
6.01
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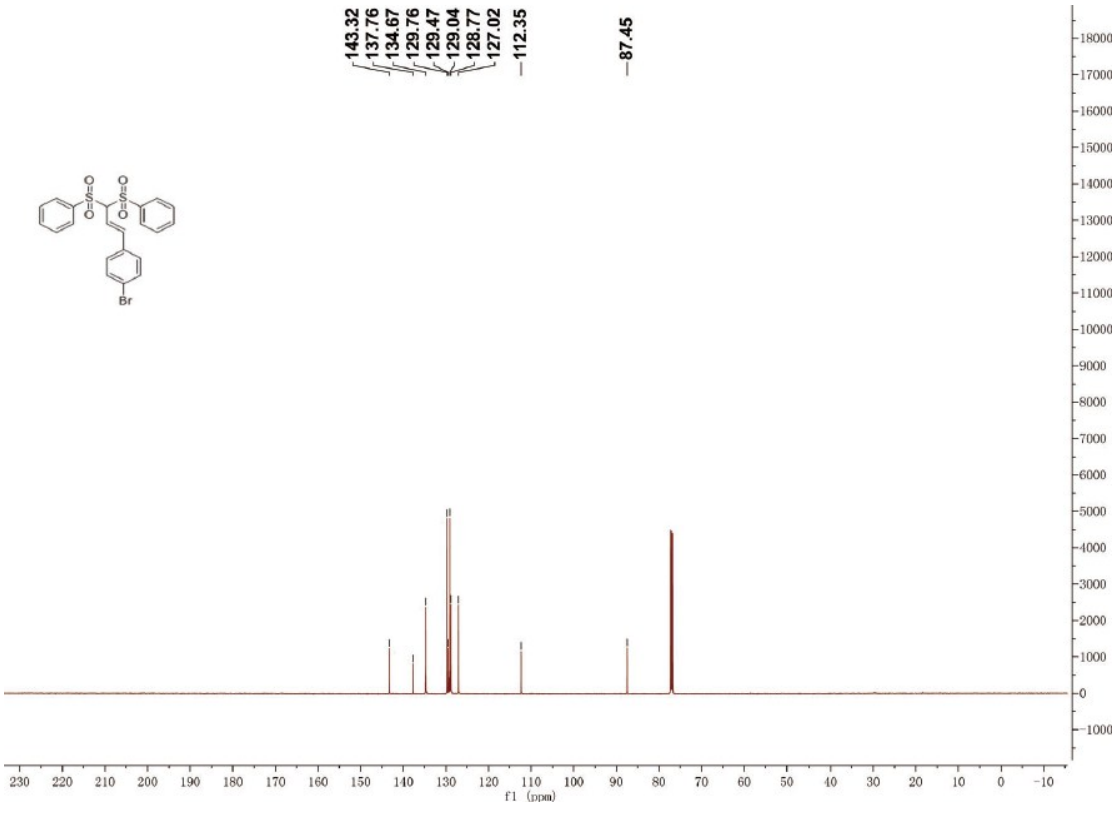
5.94
Br
3.77
2.00
3.72
3.97
0.79
0.79
1.03
f1 (ppm)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127.02
112.35
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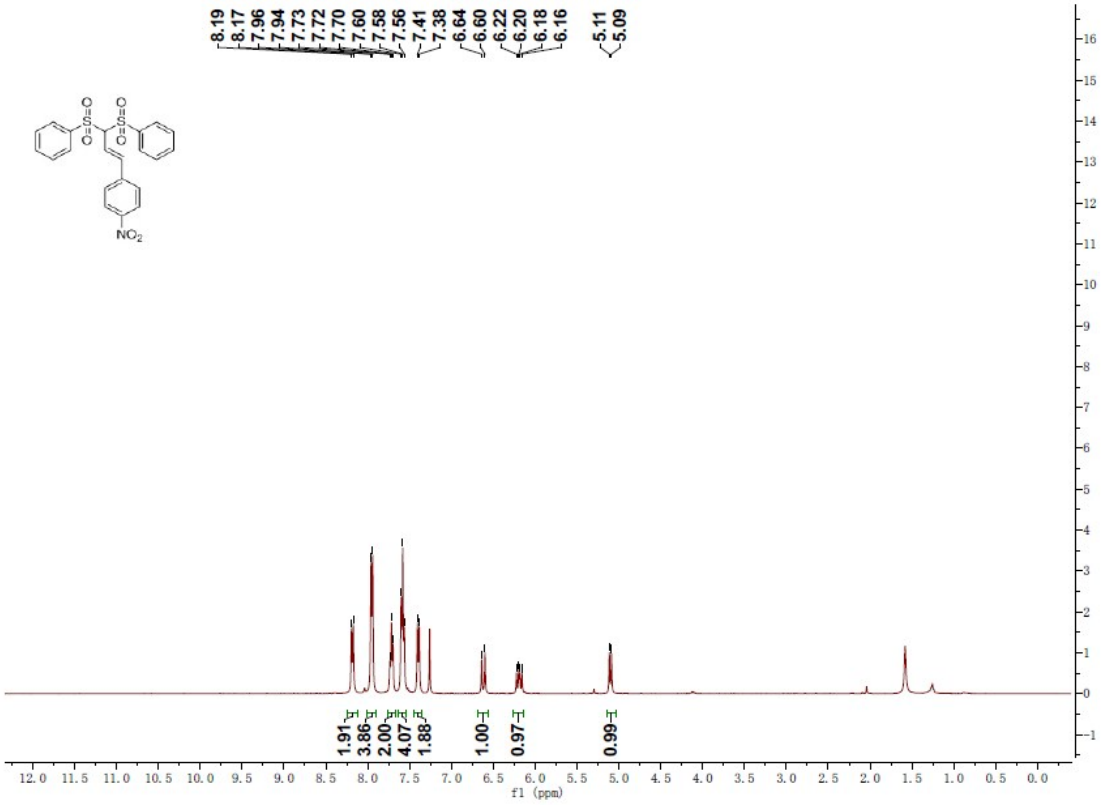
Br
f1 (ppm)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7.70
7.60
7.58
7.56
7.41
7.38
6.64
6.60
6.22
6.20
6.18
6.16
5.11
5.09
1.91
3.86
2.00
4.07
1.88
1.00
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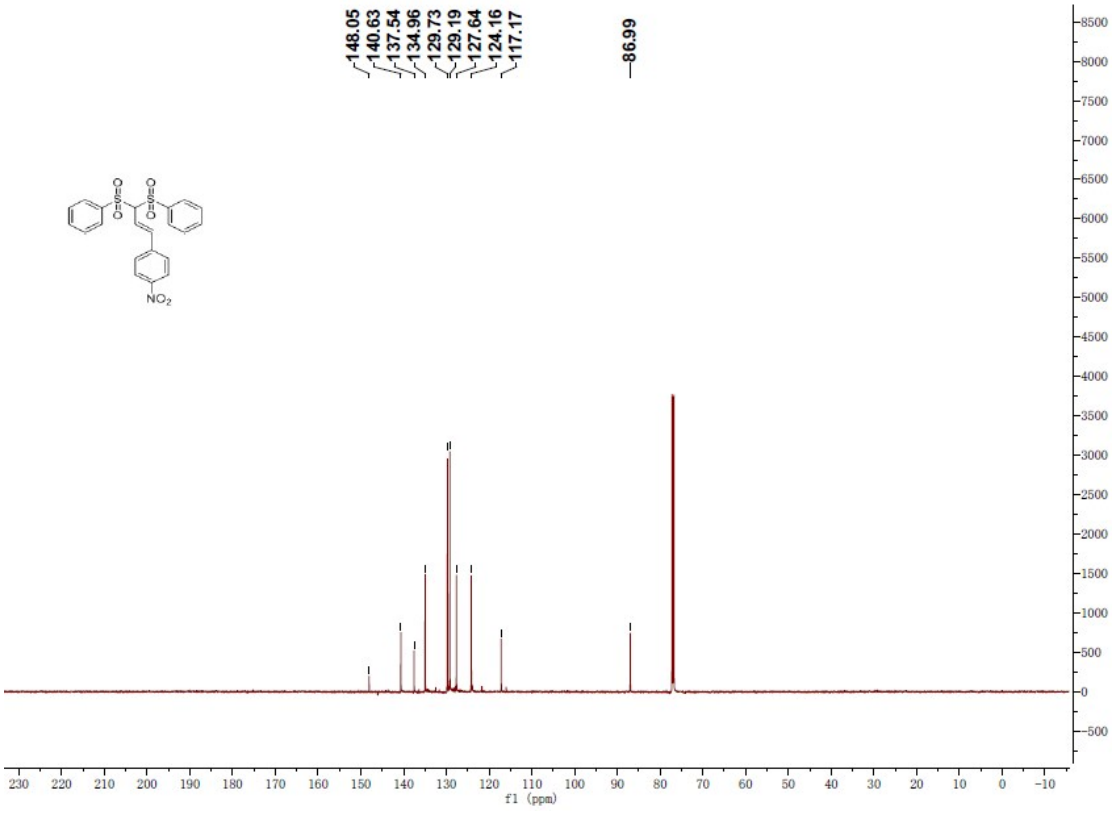
0.99
f1 (ppm)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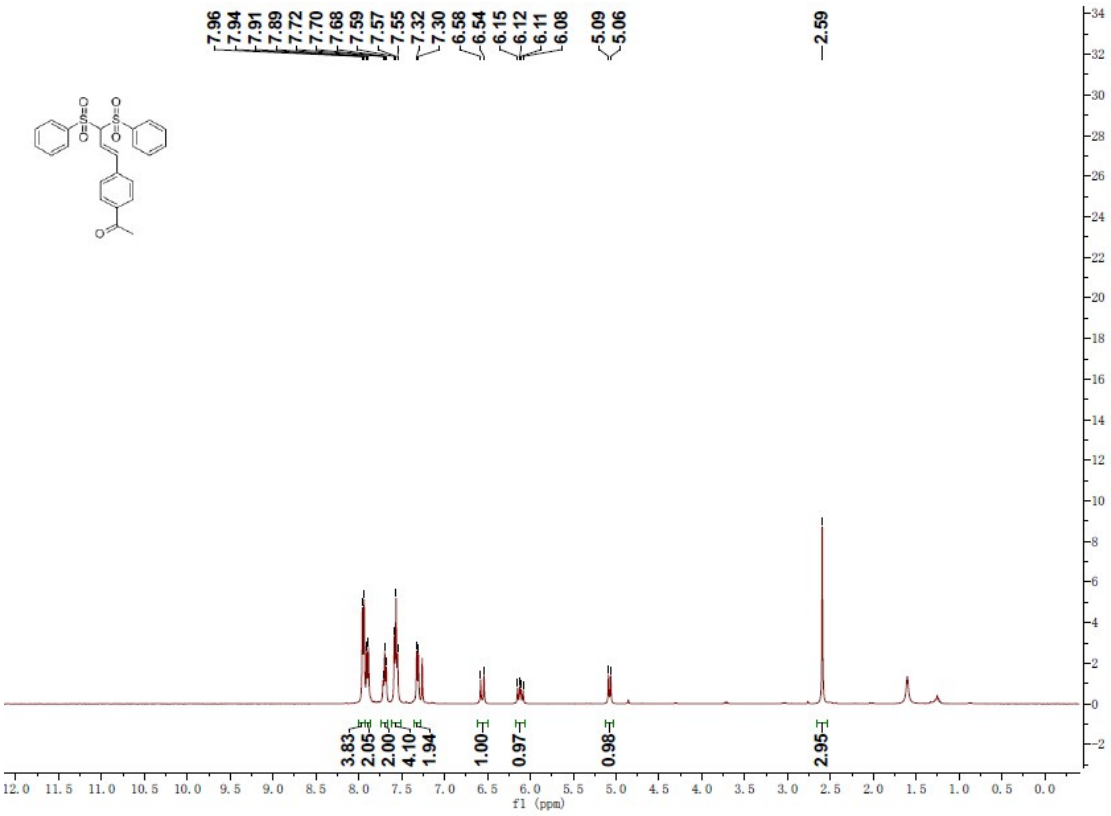
129.19
127.64
124.16
117.17
86.99
f1 (ppm)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7.32
7.30
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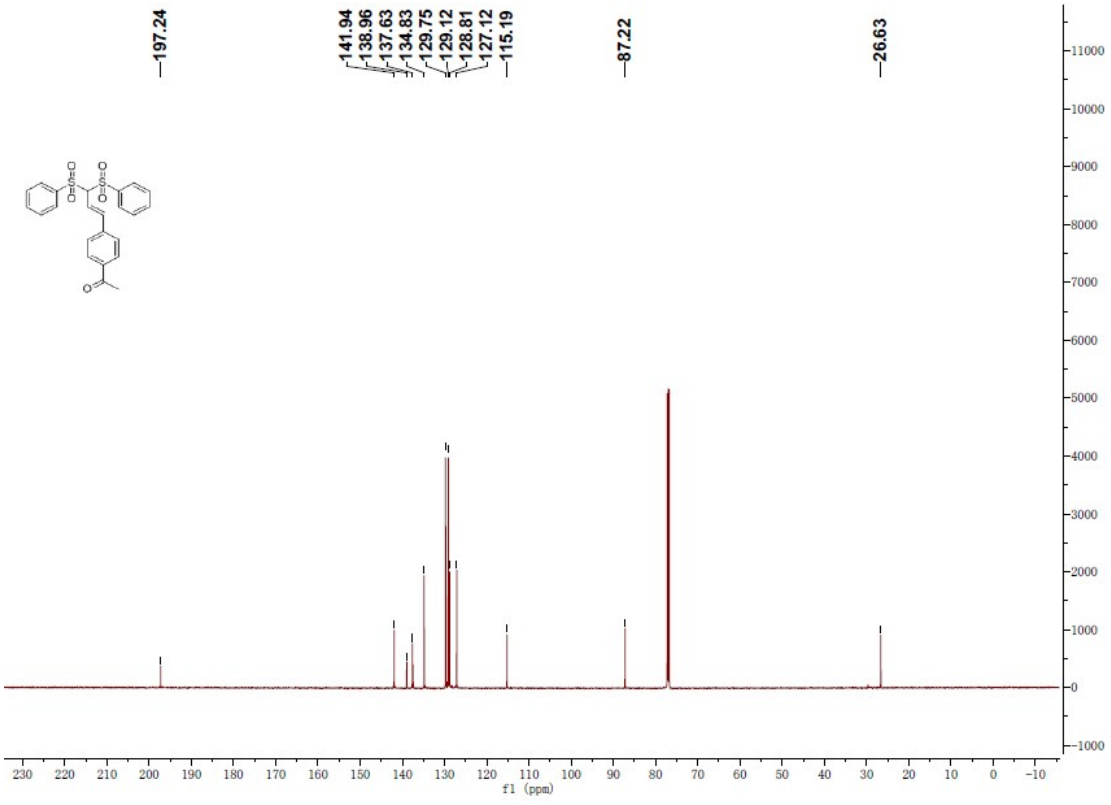
6.54
6.15
6.12
6.11
6.08
5.09
5.06
2.59
3.83
2.05
2.00
4.10
1.94
1.00
0.97
0.98
2.95
f1 (ppm)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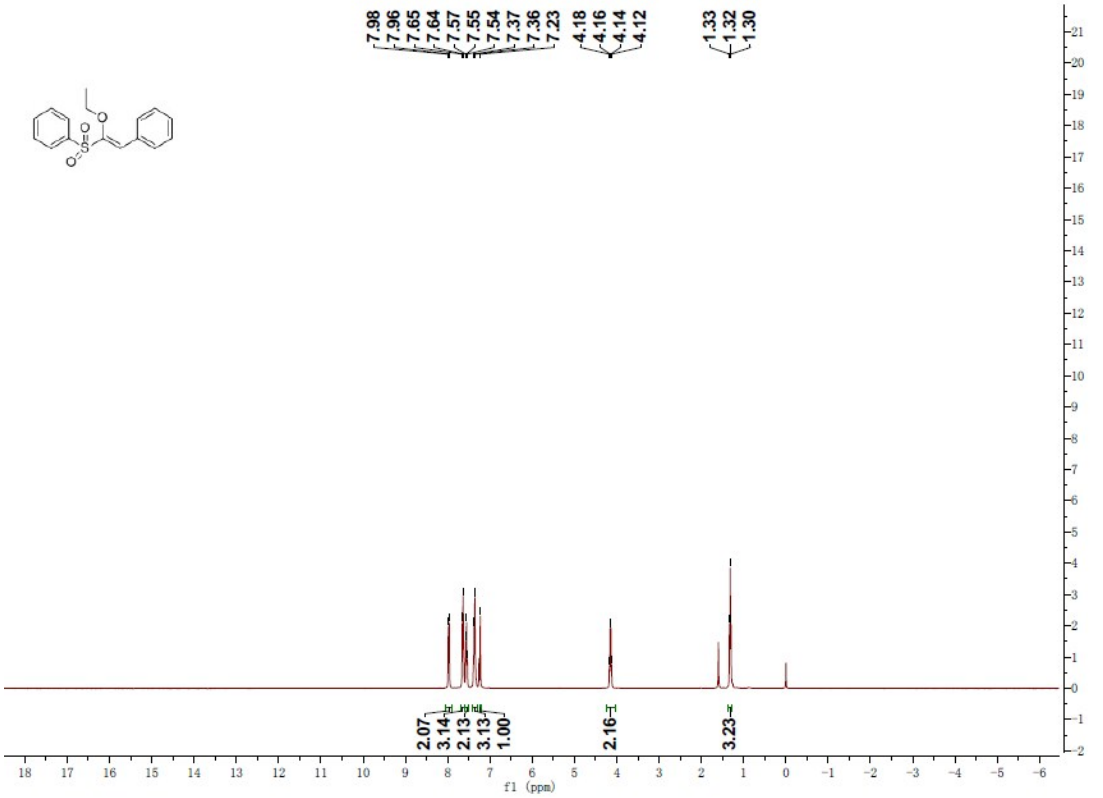
128.81
127.12
115.19
87.22
26.63
f1 (ppm)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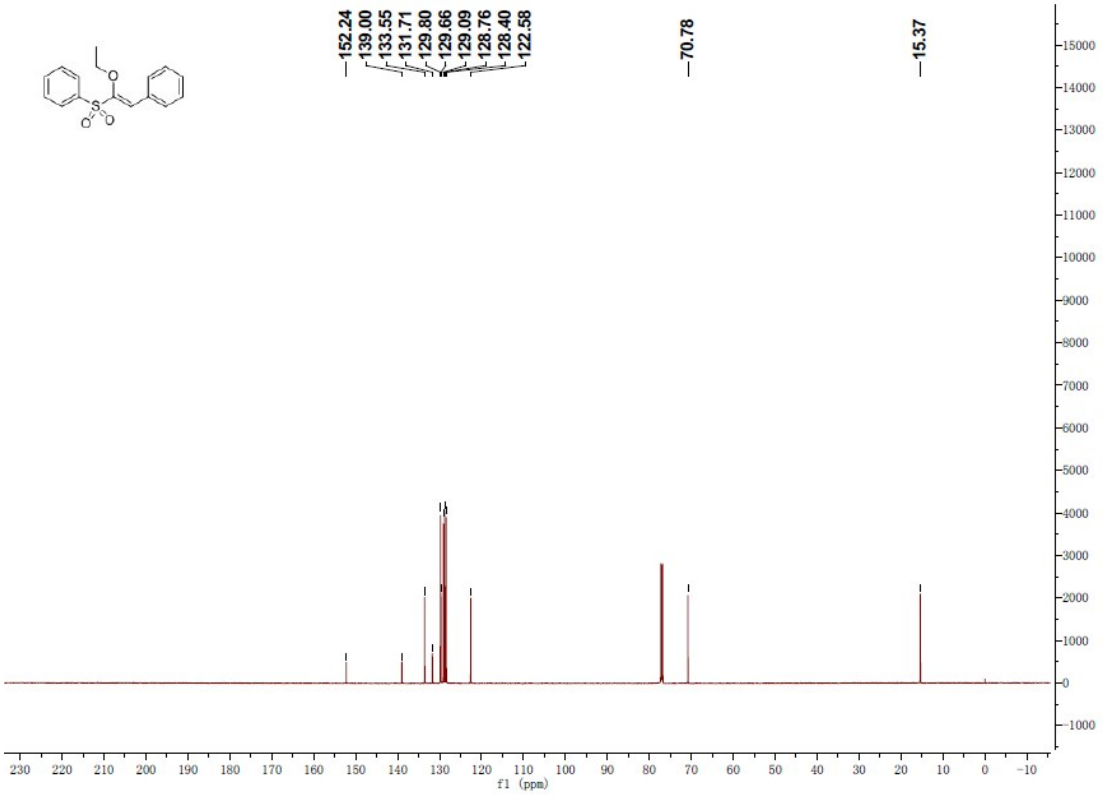
7.57
7.55
7.54
7.37
7.36
7.23
4.18
4.16
4.14
4.12
1.33
1.32
1.30
2.07
3.14
2.13
3.13
1.00
2.16
3.23
f1 (ppm)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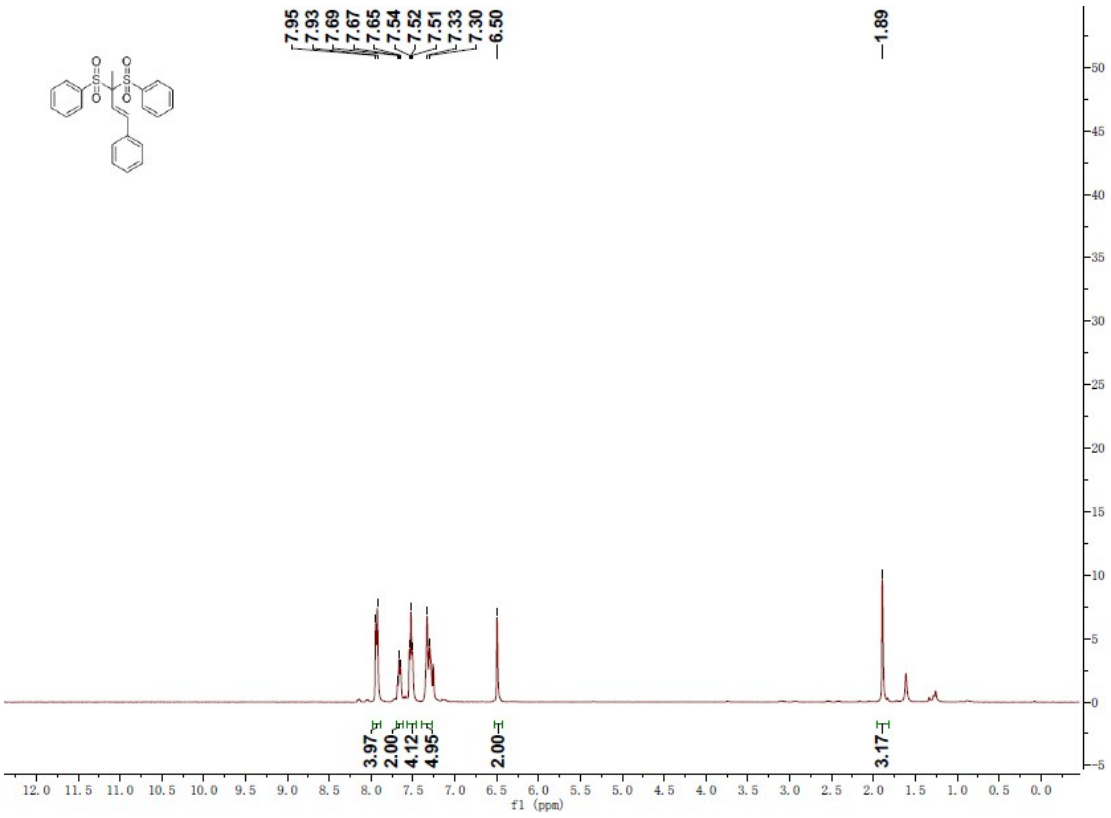
15.37
f1 (ppm)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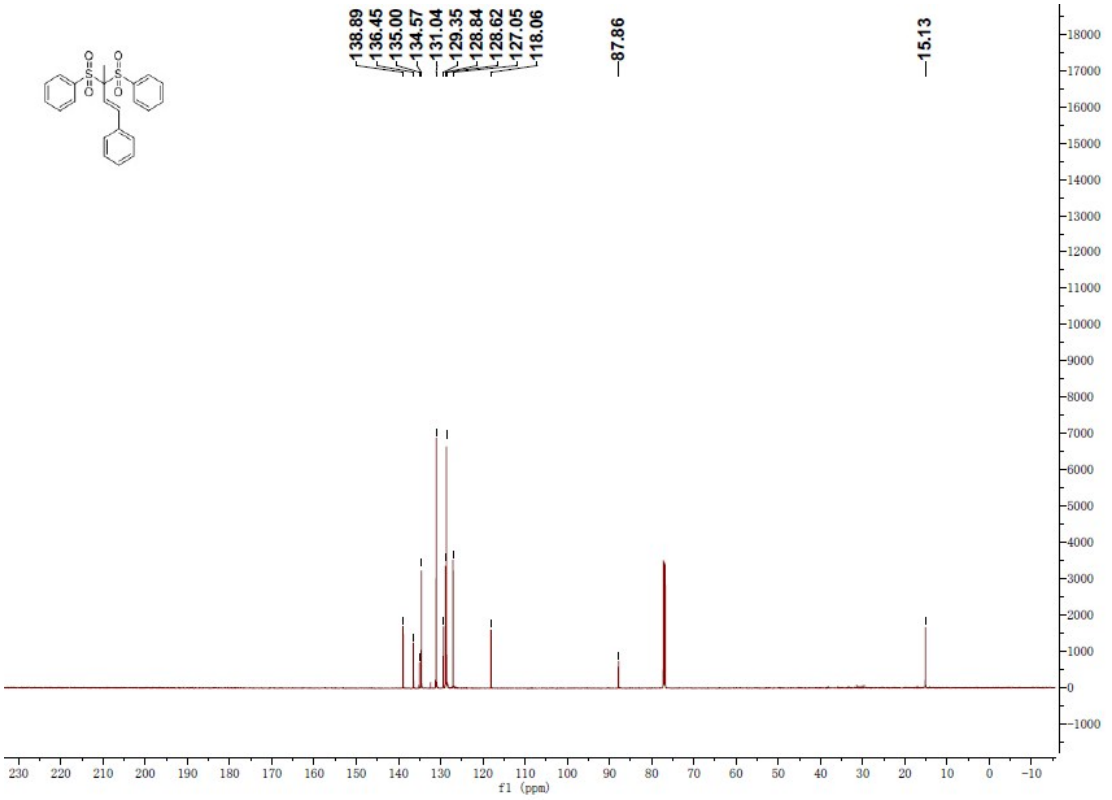
4.12
4.95
2.00
3.17
f1 (ppm)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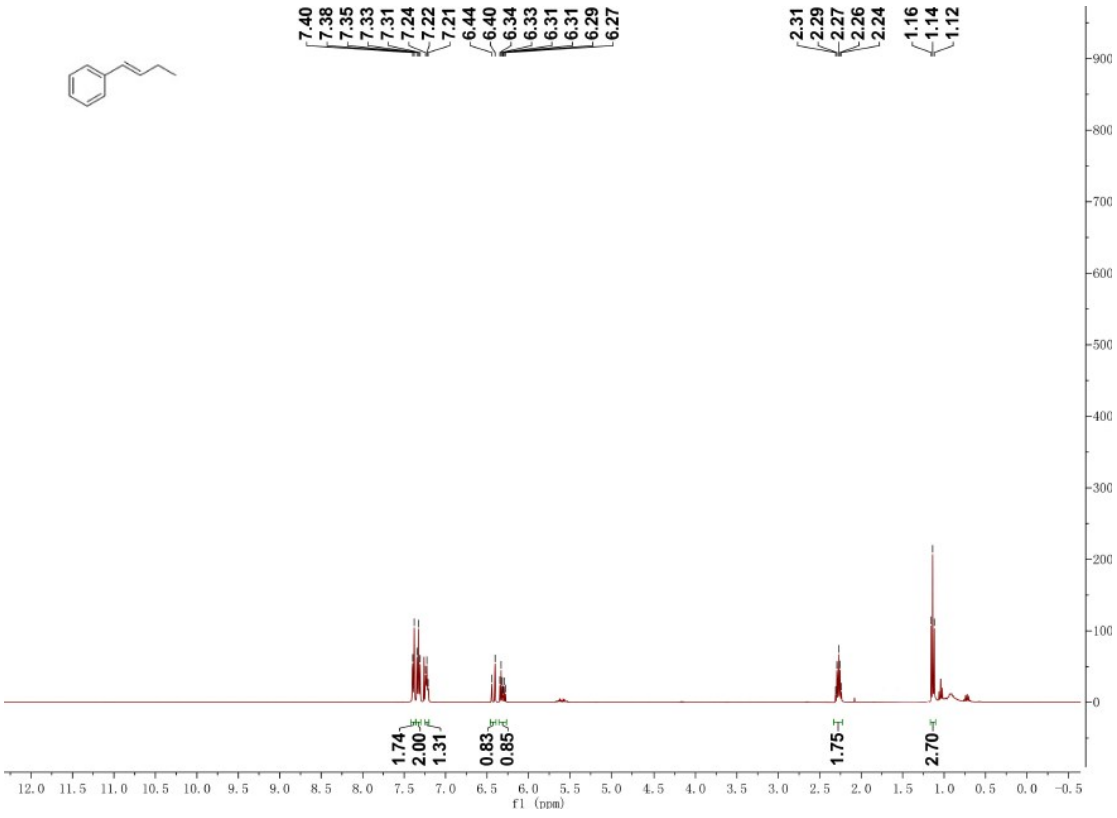
128.62
127.05
118.06
87.86
15.13
f1 (ppm)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6.31
6.31
6.29
6.27
2.31
2.29
2.27
2.26
2.24
1.16
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1.12
1.74
2.00
1.31
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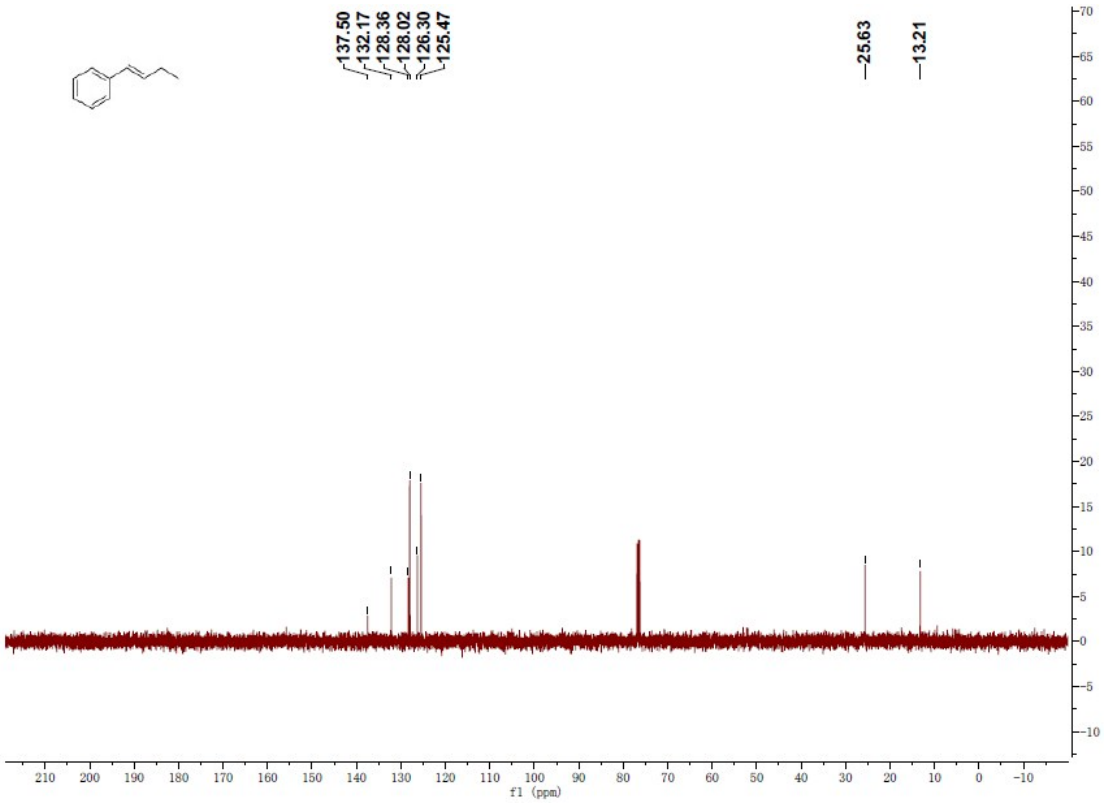
0.85
1.75
2.70
f1 (ppm)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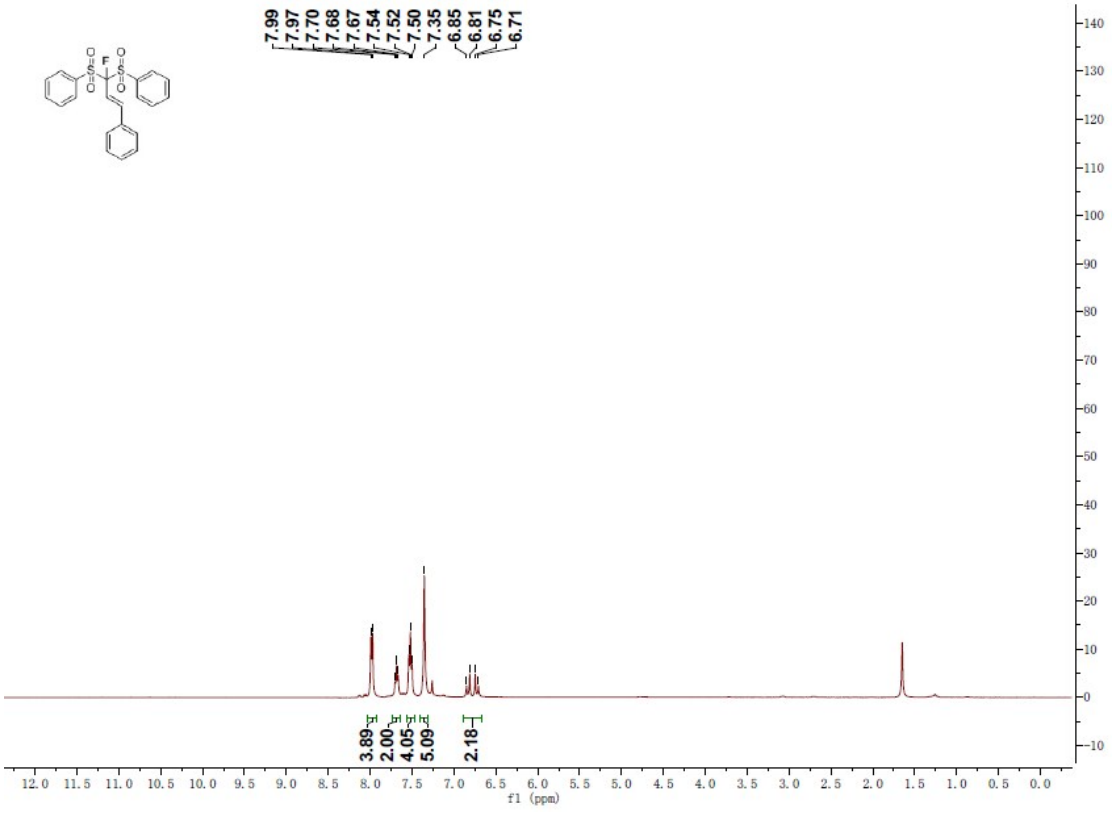
125.47
25.63
13.21
f1 (ppm)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7.35
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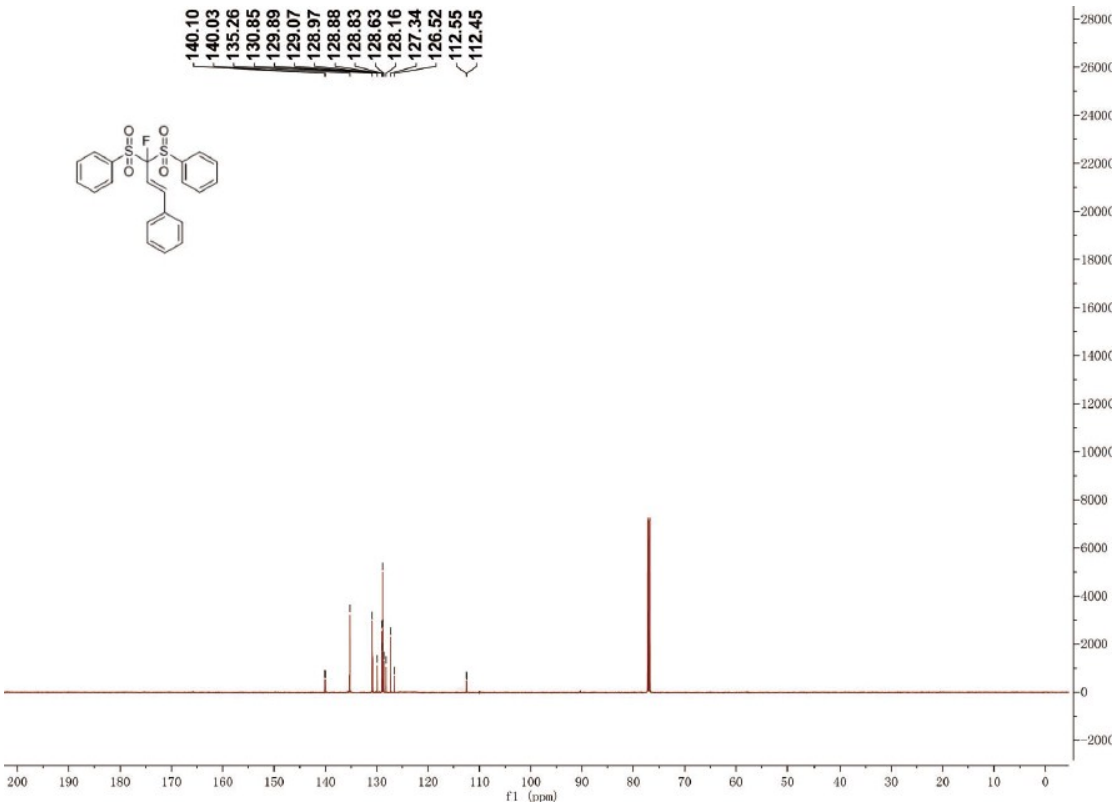
6.75
6.71
3.89
2.00
4.05
5.09
2.18
f1 (ppm)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129.07
128.97
128.88
128.83
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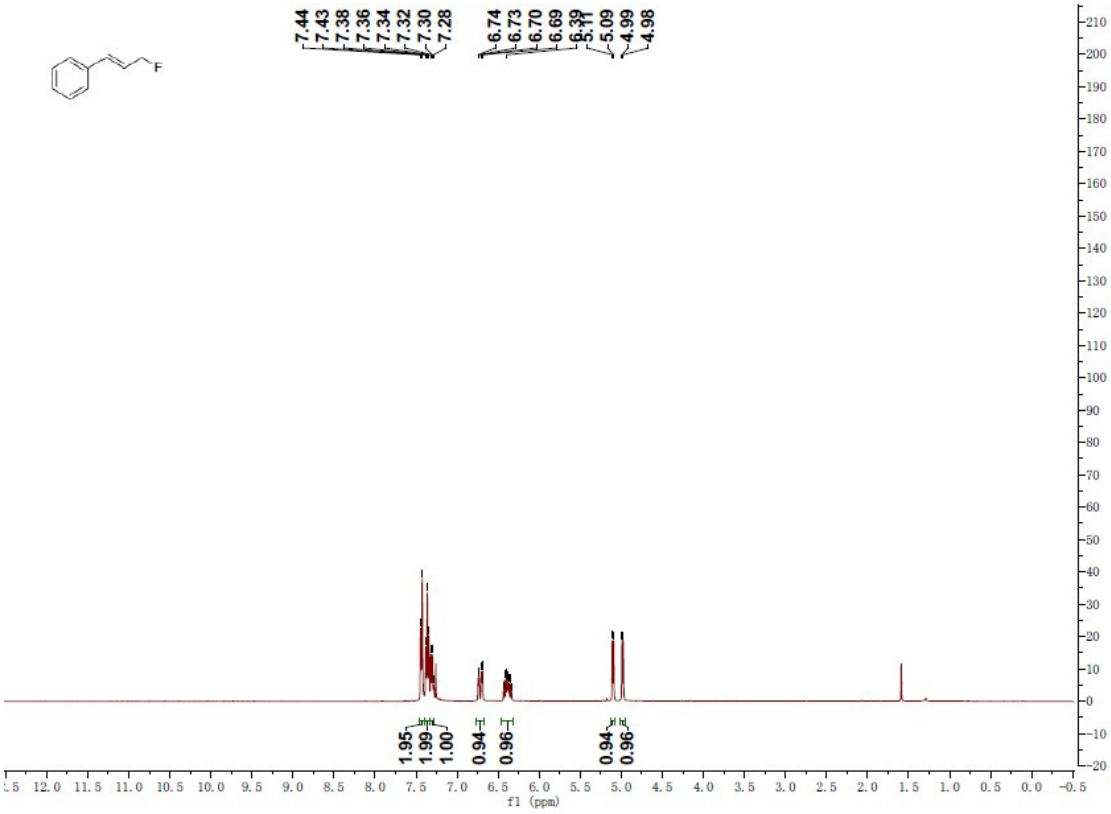
127.34
126.52
112.55
112.45
F
O
S
O
O
S
O
O
f1 (ppm)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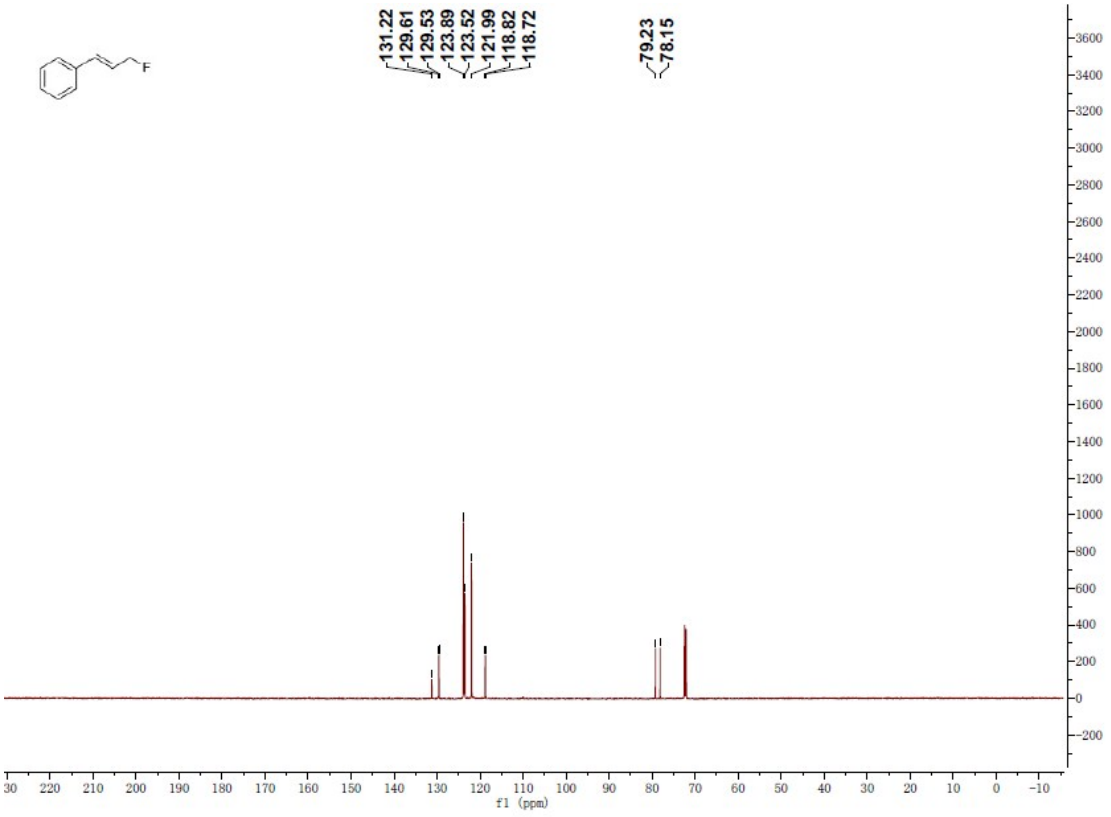
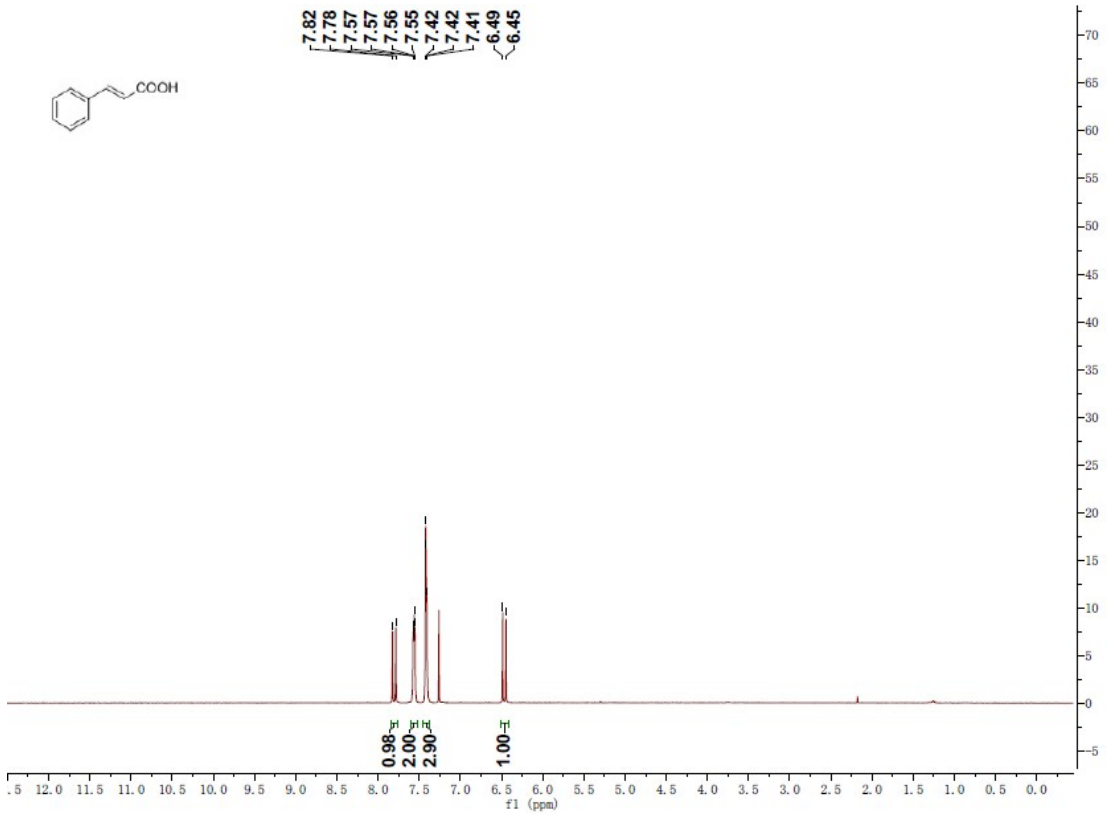
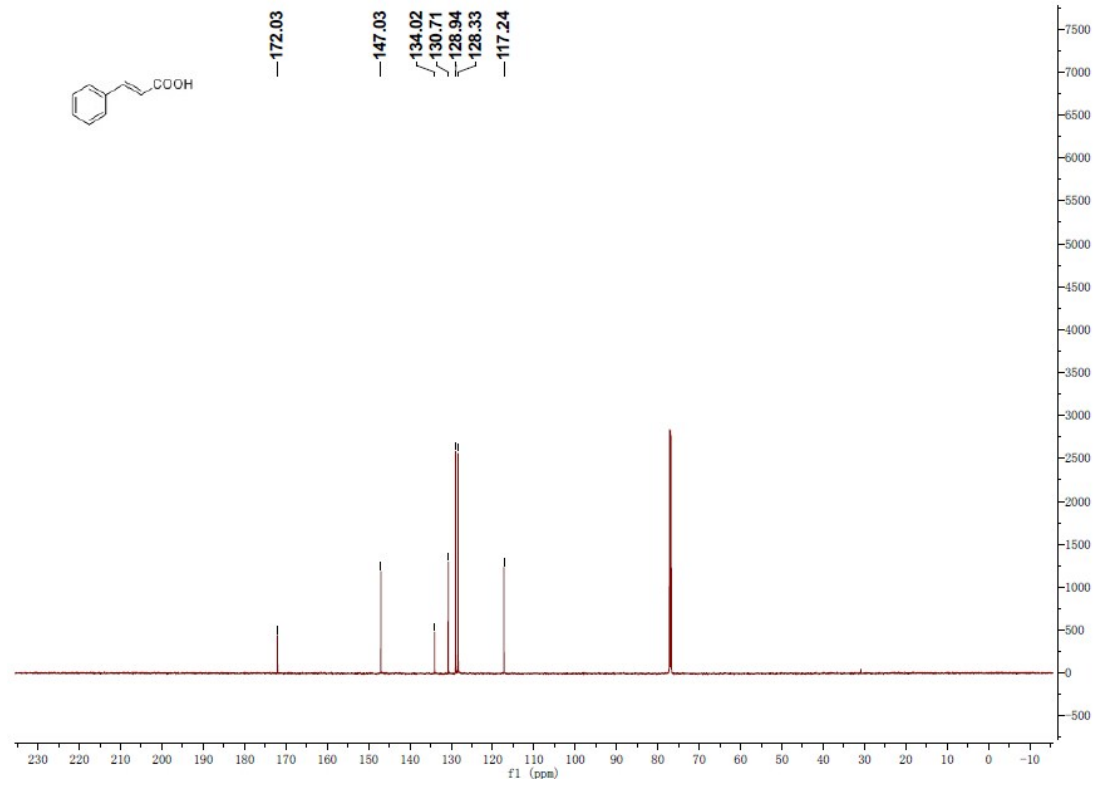
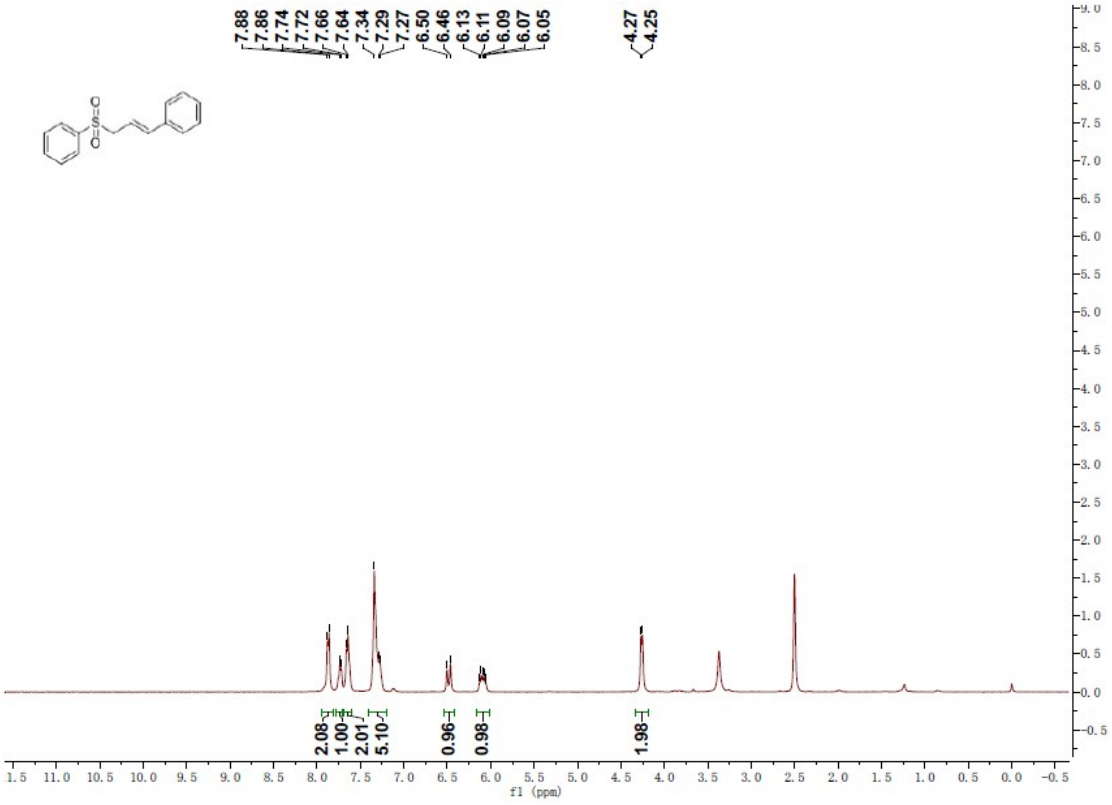
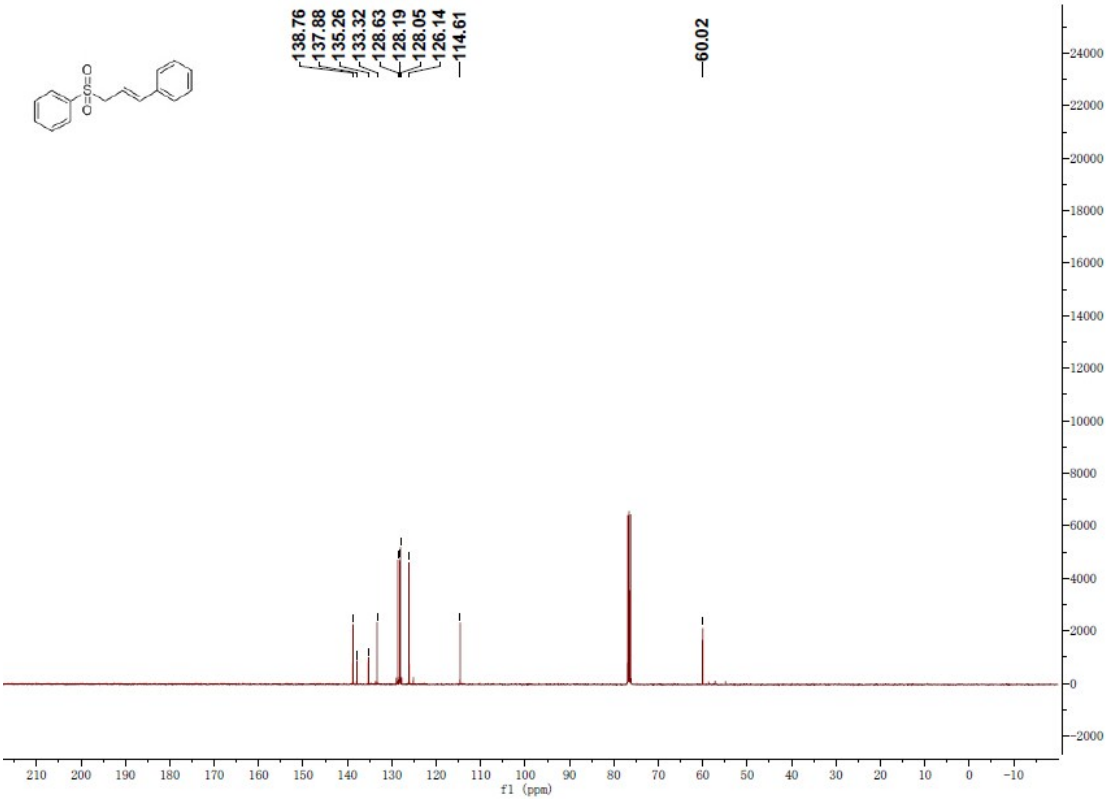
6.69
5.09
4.99
4.98
1.95
1.99
1.00
0.94
0.96
0.94
0.96
f1 (ppm)


131.22
129.61
129.53
123.89
123.52
121.99
118.82
118.72
79.23
78.15
f1 (ppm)


7.82
7.78
7.57
7.57
7.56
7.55
7.42
7.42
7.41
6.49
6.45
COOH
0.98
2.00
2.90
1.00
f1 (ppm)


172.03
147.03
134.02
130.71
128.94
128.33
117.24
COOH
f1 (ppm)


7.88
7.86
7.74
7.72
7.66
7.64
7.34
7.29
7.27
6.50
6.46
6.13
6.11
6.09
6.07
6.05
4.27
4.25
2.08
1.00
2.01
5.10
0.96
0.98
1.98
f1 (ppm)


138.76
137.88
135.26
133.32
128.63
128.19
128.05
126.14
114.61
60.02
f1 (ppm)