Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper-Catalyzed Regioselective 1,4-Sulfonylcyanation of 1,3-Enynes with Sulfonyl Chlorides and TMSCN

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1. General Information

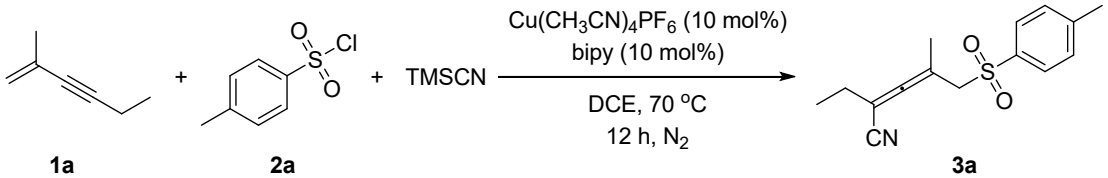
All deuterated solvents were purchased from Cambridge Isotope Laboratories. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 25 ºC on a Brüker Advance 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz, and ^{19}F: 376 MHz). ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.00 ppm or to the signal of the residual protonated solvent: $CDCl_3$ at δ 7.26 ppm. ^{13}C NMR chemical shifts were determined relative to the signal of the solvent: $CDCl_3$ at δ 77.00 ppm. Data for ^{1}H, ^{13}C, ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet of doublets), coupling constants (Hz) and integration. Melting points were obtained with a micro melting point XT4A Beijing Keyi electrooptic apparatus and are uncorrected. High-resolution mass data were recorded on a Waters LCT PremierxeTM (USA). Single-crystal X-ray diffraction was carried out on a Bruker Smart Apex II diffractometer system.

Materials and Methods:

Unless otherwise stated, starting materials were purchased from Aldrich or Energy-Chemical Limited and used as supplied without further purification. Solvents were used directly without further purification. Enynes (**1b-1w**, **1y**) was synthesized following literature procedures.[1, 2] The 1,4-sulfonylcyanation of 1,3-enynes were performed under a nitrogen atmosphere in flame dried flasks. All reactions were monitored by thin layer chromatography (TLC) with Taizhou GF254 silica gel coated plates. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure.

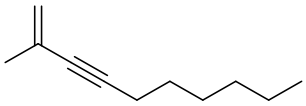
2. General Procedure for 1,4-Sulfonylcyanation of 1,3-Enynes

Typical Procedure for the Copper-Catalyzed Regioselective 1,4-Sulfonylcyanation of 1,3-Enynes with Sulfonyl Chlorides and TMSCN (**3a** as an example)



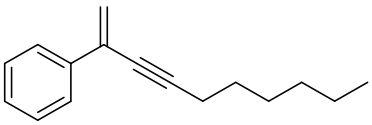
To a solution of the *p*-tosyl chloride **2a** (86.7 mg, 0.45 mmol) in 1,2-dichloroethane (DCE, 1.0 mL) was added the 2-methylhex-1-en-3-yne **1a** (39 μL, 0.3 mmol), TMSCN (59 μL, 0.45 mmol), $Cu(CH_3CN)_4PF_6$ (11.5 mg, 0.03 mmol) and bipy (4.8 mg, 0.03 mmol) under a N_2 atmosphere in a Schlenck tube. The reaction mixture was stirred at 70 °C for 12 h. After the reaction finished, the reaction mixture was purified by column chromatography to give the corresponding products **3a** (58.5 mg, 71%).

3. Analytical Data of Compounds 1, 3, 4 and 5



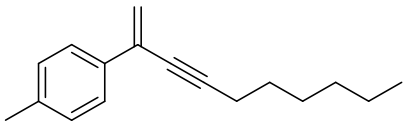
2-methyldec-1-en-3-yne 1b

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.18 (s, 1H), 5.12 (s, 1H), 2.28 (t, J = 7.2 Hz, 2H), 1.86 (s, 3H), 1.56-1.49 (m, 2H), 1.43-1.25 (m, 6H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.4, 120.2, 89.5, 81.8, 31.3, 28.7, 28.6, 23.8, 22.5, 19.2, 14.0.



dec-1-en-3-yn-2-ylbenzene 1c

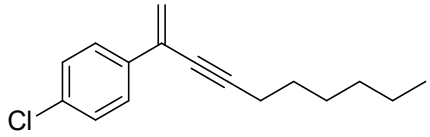
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.64 (m, 2H), 7.34-7.27 (m, 3H), 5.82 (d, J = 1.2 Hz, 1H), 5.57 (s, 1H), 2.39 (t, J = 7.2 Hz, 2H), 1.63-1.56 (m, 2H), 1.48-1.41 (m, 2H), 1.35-1.27 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 131.0, 128.2, 128.0, 126.0, 119.2, 92.0, 79.7, 31.3, 28.7, 28.6, 22.6, 19.4, 14.0.



1-(dec-1-en-3-yn-2-yl)-4-methylbenzene 1d

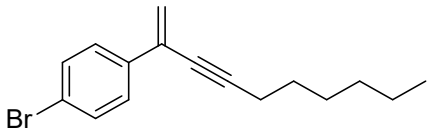
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 5.80 (s, 1H), 5.52 (s, 1H), 2.41 (t, J = 7.2 Hz, 2H), 2.35 (s, 3H), 1.64-1.57 (m, 2H), 1.49-1.42 (m,

2H), 1.36-1.31 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 135.0, 130.8, 128.9, 125.9, 118.4, 91.8, 79.9, 31.3, 28.7, 28.6, 22.6, 21.1, 19.4, 14.0.



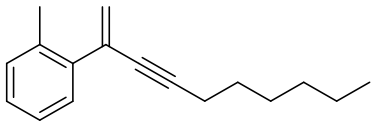
1-chloro-4-(dec-1-en-3-yn-2-yl)benzene 1e

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 5.81 (s, 1H), 5.58 (s, 1H), 2.40 (t, J = 7.2 Hz, 2H), 1.64-1.55 (m, 2H), 1.48-1.41 (m, 2H), 1.37-1.26 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.3, 133.9, 129.9, 128.4, 127.4, 119.6, 92.5, 79.3, 31.3, 28.6, 22.6, 19.4, 14.0.



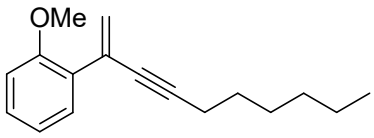
1-bromo-4-(dec-1-en-3-yn-2-yl)benzene 1f

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 5.81 (s, 1H), 5.58 (s, 1H), 2.40 (t, J = 7.2 Hz, 2H), 1.62-1.56 (m, 2H), 1.46-1.41 (m, 2H), 1.35-1.25 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 131.3, 130.0, 127.7, 122.1, 119.7, 92.6, 79.3, 31.3, 28.6, 22.6, 19.4, 14.0.



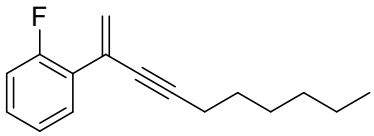
1-(dec-1-en-3-yn-2-yl)-2-methylbenzene 1g

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.15 (m, 4H), 5.67 (s, 1H), 5.37 (s, 1H), 2.42 (s, 3H), 2.32 (t, J = 7.2 Hz, 2H), 1.57-1.49 (m, 2H), 1.42-1.33 (m, 2H), 1.31-1.25 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 135.4, 132.2, 130.3, 128.6, 127.6, 125.8, 123.8, 92.0, 80.6, 31.3, 28.6, 22.5, 20.2, 19.4, 14.0.



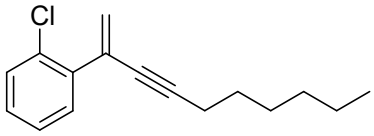
1-(dec-1-en-3-yn-2-yl)-2-methoxybenzene 1h

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, J_1 = 2.0 Hz, J_2 = 7.6 Hz, 1H), 7.25 (dd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1H), 6.96-6.89 (m, 2H), 5.87 (d, J = 2.0 Hz, 1H), 5.75 (d, J = 2.0 Hz, 1H), 3.85 (s, 3H), 2.35 (t, J = 7.2 Hz, 2H), 1.59-1.52 (m, 2H), 1.46-1.38 (m, 2H), 1.34-1.26 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 130.3, 128.9, 128.3, 127.9, 124.3, 120.4, 111.3, 90.1, 81.0, 55.5, 31.4, 28.7, 28.6, 22.6, 19.4, 14.0.



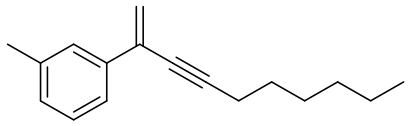
1-(dec-1-en-3-yn-2-yl)-2-fluorobenzene 1i

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dt, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 7.25-7.20 (m, 1H), 7.13-7.01 (m, 2H), 5.92 (s, 1H), 5.80 (s, 1H), 2.37 (t, J = 7.2 Hz, 2H), 1.61-1.53 (m, 2H), 1.47-1.40 (m, 2H), 1.34-1.26 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2 (d, J = 249.0 Hz), 130.5 (d, J = 3.0 Hz), 129.2 (d, J = 8.0 Hz), 126.1 (d, J = 11.0 Hz), 125.9, 124.9 (d, J = 10.0 Hz), 123.8 (d, J = 4.0 Hz), 116.0 (d, J = 23.0 Hz), 90.9, 80.1, 31.3, 28.6, 28.6, 22.6, 19.3, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.4.



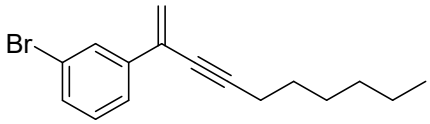
1-chloro-2-(dec-1-en-3-yn-2-yl)benzene 1j

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.36 (m, 2H), 7.23-7.20 (m, 2H), 5.77 (s, 1H), 5.55 (s, 1H), 2.33 (t, J = 7.2 Hz, 2H), 1.58-1.50 (m, 2H), 1.43-1.38 (m, 2H), 1.29-1.27 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 132.1, 130.3, 129.9, 129.7, 128.8, 126.6, 125.1, 92.1, 79.9, 31.3, 28.6, 28.5, 22.5, 19.4, 14.0.



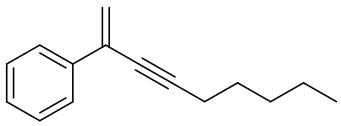
1-(dec-1-en-3-yn-2-yl)-3-methylbenzene 1k

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 5.81 (s, 1H), 5.55 (s, 1H), 2.40 (t, J = 7.2 Hz, 2H), 2.36 (s, 3H), 1.62-1.57 (m, 2H), 1.50-1.42 (m, 2H), 1.33-1.30 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 131.0, 128.8, 128.1, 126.8, 123.2, 119.2, 91.9, 79.9, 31.4, 28.7, 28.6, 22.6, 21.4, 19.4, 14.0.



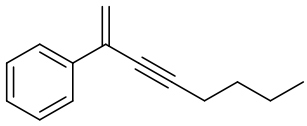
1-bromo-3-(dec-1-en-3-yn-2-yl)benzene 1l

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 5.83 (s, 1H), 5.60 (s, 1H), 2.41 (t, J = 7.2 Hz, 2H), 1.64-1.55 (m, 2H), 1.49-1.42 (m, 2H), 1.36-1.31 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 131.0, 129.8, 129.7, 129.3, 124.6, 122.5, 120.3, 92.7, 79.1, 31.3, 28.6, 28.6, 22.6, 19.4, 14.1.



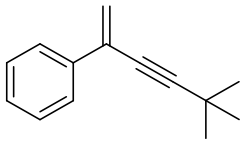
non-1-en-3-yn-2-ylbenzene 1m

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.64 (m, 2H), 7.36-7.29 (m, 3H), 5.84 (s, 1H), 5.58 (s, 1H), 2.41 (t, J = 7.2 Hz, 2H), 1.64-1.60 (m, 2H), 1.44-1.35 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 131.0, 128.2, 128.1, 126.1, 119.3, 92.1, 79.7, 31.2, 28.4, 22.2, 19.4, 14.0.



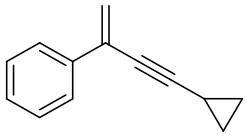
oct-1-en-3-yn-2-ylbenzene 1n

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.63 (m, 2H), 7.33-7.25 (m, 3H), 5.81 (s, 1H), 5.56 (s, 1H), 2.39 (t, J = 7.2 Hz, 2H), 1.59-1.43 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 131.0, 128.2, 128.0, 126.0, 119.2, 91.9, 79.7, 30.8, 22.0, 19.0, 13.6.



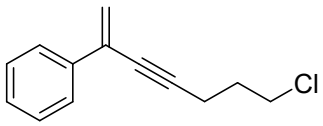
(5,5-dimethylhex-1-en-3-yn-2-yl)benzene 1o

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 7.2 Hz, 2H), 7.36-7.25 (m, 3H), 5.83 (s, 1H), 5.56 (s, 1H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 130.8, 128.2, 128.0, 126.0, 119.1, 100.1, 78.2, 31.0, 28.0.



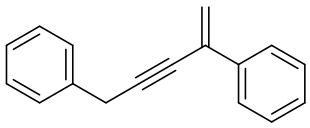
(4-cyclopropylbut-1-en-3-yn-2-yl)benzene 1p

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.2 Hz, 2H), 7.25-7.16 (m, 3H), 5.72 (s, 1H), 5.47 (s, 1H), 1.40-1.31 (m, 1H), 0.78-0.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.7, 130.8, 128.2, 128.0, 126.0, 119.4, 95.0, 75.0, 8.6, 0.1.



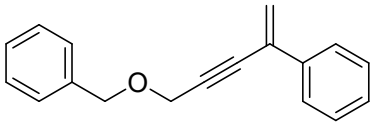
(7-chlorohept-1-en-3-yn-2-yl)benzene 1q

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.62 (m, 2H), 7.36-7.29 (m, 3H), 5.85 (s, 1H), 5.59 (s, 1H), 3.69 (t, J = 6.4 Hz, 2H), 2.60 (t, J = 7.2 Hz, 2H), 2.07-2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 130.6, 128.3, 128.2, 125.9, 119.9, 89.6, 80.7, 43.7, 31.4, 16.8.



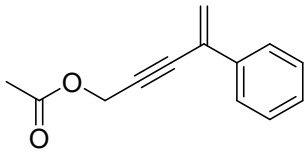
pent-4-en-2-yne-1,4-diyldibenzene 1r

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 7.2 Hz, 2H), 7.41-7.23 (m, 8H), 5.89 (s, 1H), 5.65 (s, 1H), 3.84 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 136.6, 130.7, 128.6, 128.3, 128.2, 127.9, 126.6, 126.1, 120.1, 89.0, 81.8, 25.7.



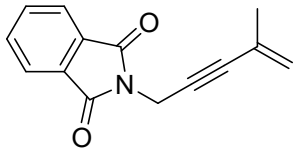
(5-(benzyloxy)pent-1-en-3-yn-2-yl)benzene 1s

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 7.2 Hz, 2H), 7.39-7.29 (m, 8H), 5.94 (s, 1H), 5.69 (s, 1H), 4.67 (s, 2H), 4.40 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 137.1, 130.2, 128.5, 128.4, 128.4, 128.1, 127.9, 126.0, 121.2, 86.6, 85.7, 71.7, 57.9.



4-phenylpent-4-en-2-yn-1-yl acetate 1t

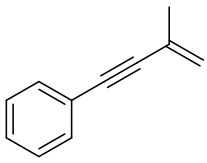
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 6.8 Hz, 2H), 7.37-7.28 (m, 3H), 5.95 (s, 1H), 5.70 (s, 1H), 4.89 (s, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 136.7, 129.8, 128.4, 128.4, 126.0, 121.8, 85.6, 84.4, 52.6, 20.7.



2-(4-methylpent-4-en-2-yn-1-yl)isoindoline-1,3-dione 1u

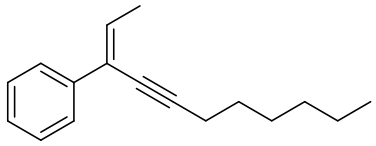
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, J_1 = 3.2 Hz, J_2 = 5.2 Hz, 2H), 7.73 (dd, J_1 = 3.2 Hz, J_2 = 5.2 Hz, 2H), 5.27 (s, 1H), 5.20 (s, 1H), 4.56 (s, 2H), 1.83 (s, 3H). ^{13}C NMR (100

MHz, $CDCl_3$): δ 167.1, 134.1, 132.0, 126.0, 123.5, 122.7, 84.1, 81.5, 27.7, 23.2.



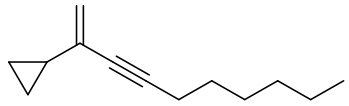
(3-methylbut-3-en-1-yn-1-yl)benzene 1v

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.46 (m, 2H), 7.34-7.32 (m, 3H), 5.43 (d, J = 0.8 Hz, 1H), 5.32 (t, J = 1.6 Hz, 1H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.5, 128.2, 128.1, 126.8, 123.2, 121.9, 90.5, 88.4, 23.5.



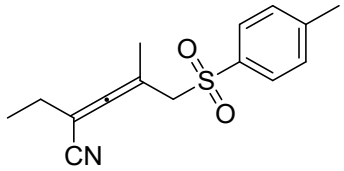
(*Z*)-undec-2-en-4-yn-3-ylbenzene 1w

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.25-7.21 (m, 1H), 6.39 (q, J = 7.2 Hz, 1H), 2.46 (t, J = 7.2 Hz, 2H), 2.04 (d, J = 7.2 Hz, 1H), 1.64-1.59 (m, 2H), 1.53-1.46 (m, 2H), 1.34-1.31 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 131.5, 128.2, 127.1, 125.8, 124.7, 96.8, 77.7, 31.4, 28.9, 28.6, 22.6, 19.6, 16.8, 14.0.



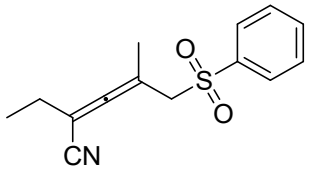
dec-1-en-3-yn-2-ylcyclopropane 1y

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.24 (d, J = 2.0 Hz, 1H), 5.16 (d, J = 2.0 Hz, 1H), 2.25 (t, J = 7.2 Hz, 2H), 1.54-1.46 (m, 3H), 1.42-1.25 (m, 6H), 0.89 (t, J = 6.8 Hz, 3H), 0.70-0.60 (m, 4H), . ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.3, 117.2, 90.4, 77.4, 31.3, 28.7, 28.5, 22.5, 19.1, 16.5, 13.9, 5.6.



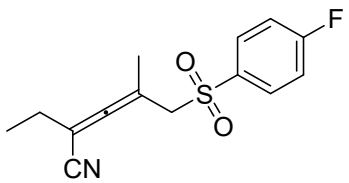
2-ethyl-4-methyl-5-tosylpenta-2,3-dienenitrile 3a

Colorless oil (58.5 mg, 71%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 3.73 (dd, J_1 = 14.0 Hz, J_2 = 30.0 Hz, 2H), 2.44 (s, 3H), 2.05-1.94 (m, 2H), 1.92 (s, 3H), 0.95 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 145.4, 134.8, 130.1, 128.1, 114.3, 96.6, 84.2, 59.8, 24.5, 21.6, 18.4, 12.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{18}NO_2S$ 276.1058; Found 276.1055.



2-ethyl-4-methyl-5-(phenylsulfonyl)penta-2,3-dienenitrile 3b

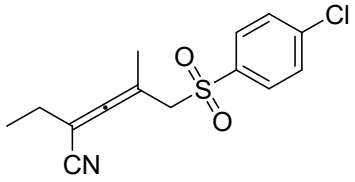
Colorless oil (58.7 mg, 75%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.6 Hz, 2H), 7.70 (t, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 3.77 (dd, J_1 = 14.0 Hz, J_2 = 31.2 Hz, 2H), 2.03-1.92 (m, 2H), 1.95 (s, 3H), 0.97 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 137.9, 134.2, 129.5, 128.2, 114.3, 96.5, 84.4, 59.8, 24.8, 18.5, 12.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{16}NO_2S$ 262.0902; Found 262.0911.



2-ethyl-5-((4-fluorophenyl)sulfonyl)-4-methylpenta-2,3-dienenitrile 3c

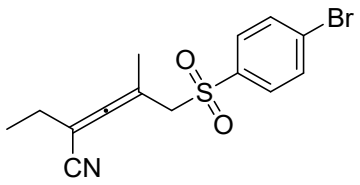
Colorless oil (58.6 mg, 70%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.92 (m, 2H), 7.30 (t, J = 8.4 Hz, 2H), 3.78 (dd, J_1 = 14.0 Hz, J_2 = 25.2 Hz, 2H), 2.10-1.99 (m, 2H), 1.97 (s, 3H), 1.00 (t, J = 7.2 Hz, 3H). ^{13}C

NMR (100 MHz, $CDCl_3$): δ 211.7, 166.1 (d, J = 256.0 Hz), 133.8 (d, J = 3.0 Hz), 131.1 (d, J = 10.0 Hz), 116.9 (d, J = 22.0 Hz), 114.2, 96.4, 84.5, 59.9, 24.8, 18.6, 12.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}FNO_2S$ 280.0808; Found 280.0821.



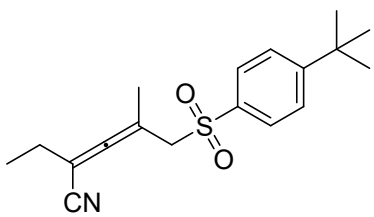
5-((4-chlorophenyl)sulfonyl)-2-ethyl-4-methylpenta-2,3-dienenitrile 3d

Colorless oil (63.6 mg, 72%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 3.76 (dd, J_1 = 14.0 Hz, J_2 = 25.6 Hz, 2H), 2.08-1.97 (m, 2H), 1.95 (s, 3H), 0.98 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 141.1, 136.2, 129.9, 129.7, 114.2, 96.3, 84.6, 59.8, 24.8, 18.6, 12.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}ClNO_2S$ 296.0512; Found 296.0507.



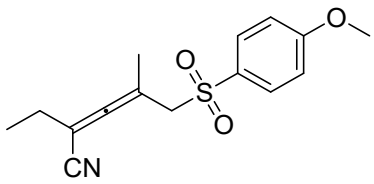
5-((4-bromophenyl)sulfonyl)-2-ethyl-4-methylpenta-2,3-dienenitrile 3e

Colorless oil (71.5 mg, 70%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77-7.73 (m, 4H), 3.76 (dd, J_1 = 14.0 Hz, J_2 = 26.4 Hz, 2H), 2.05-1.97 (m, 2H), 1.95 (s, 3H), 0.98 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 136.8, 132.9, 129.8, 129.7, 114.2, 96.3, 84.6, 59.8, 24.9, 18.6, 12.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}BrNO_2S$ 340.0007, 341.9986; Found 340.0016, 341.9998.



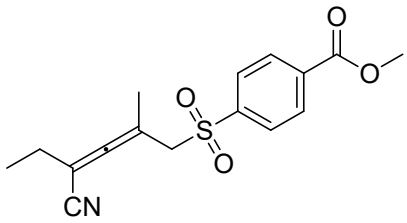
5-((4-(*tert*-butyl)phenyl)sulfonyl)-2-ethyl-4-methylpenta-2,3-dienenitrile 3f

Colorless oil (64.6 mg, 68%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 3.76 (dd, J_1 = 14.0 Hz, J_2 = 33.2 Hz, 2H), 1.96 (s, 3H), 1.94-1.88 (m, 2H), 1.34 (s, 9H), 0.95 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 158.2, 134.9, 128.1, 126.5, 114.4, 96.6, 84.2, 59.8, 35.3, 31.0, 24.8, 18.5, 12.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{24}NO_2S$ 318.1528; Found 318.1521.



2-ethyl-5-((4-methoxyphenyl)sulfonyl)-4-methylpenta-2,3-dienenitrile 3g

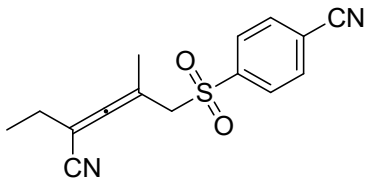
Colorless oil (70.5 mg, 81%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 3.72 (dd, J_1 = 14.0 Hz, J_2 = 28.0 Hz, 2H), 2.06-1.95 (m, 2H), 1.92 (s, 3H), 0.96 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 164.1, 130.3, 129.1, 114.7, 114.4, 96.8, 84.2, 60.0, 55.7, 24.8, 18.5, 12.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{18}NO_3S$ 292.1007; Found 292.1012.



methyl 4-((4-cyano-2-methylhexa-2,3-dien-1-yl)sulfonyl)benzoate 3h

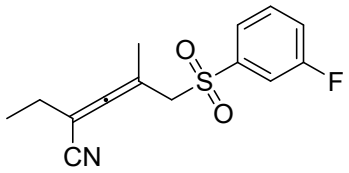
Colorless oil (64.1 mg, 67%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 7.6 Hz, 2H), 3.96 (s, 3H), 3.79 (dd, J_1 = 14.0 Hz, J_2 = 28.0 Hz, 2H), 2.05-1.97 (m, 2H), 1.94 (s, 3H), 0.96 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 165.2, 141.7, 135.3, 130.6, 128.3, 114.2, 96.1, 84.6, 59.7, 52.8, 24.8, 18.6, 12.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{18}NO_4S$

320.0957; Found 320.0962.



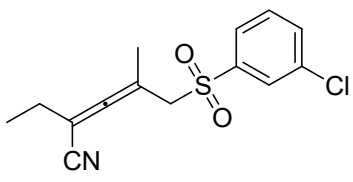
4-((4-cyano-2-methylhexa-2,3-dien-1-yl)sulfonyl)benzonitrile 3i

White solid (56.5 mg, 66%). Petroleum ether/ethyl acetate = 4/1 as eluent for column chromatography. Mp: 109−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 3.80 (dd, J_1 = 14.0 Hz, J_2 = 20.0 Hz, 2H), 2.08-1.99 (m, 2H), 1.97 (s, 3H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 141.8, 133.3, 128.9, 118.1, 116.9, 114.1, 96.0, 84.9, 59.6, 24.8, 18.6, 12.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{15}N_2O_2S$ 287.0854; Found 287.0866.



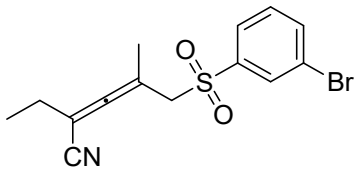
2-ethyl-5-((3-fluorophenyl)sulfonyl)-4-methylpenta-2,3-dienenitrile 3j

Colorless oil (50.1 mg, 60%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.0 Hz, 1H), 7.64-7.60 (m, 2H), 7.43-7.39 (m, 1H), 3.78 (dd, J_1 = 14.0 Hz, J_2 = 28.0 Hz, 2H), 2.08-1.99 (m, 2H), 1.97 (s, 3H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 162.6 (d, J = 253.0 Hz), 139.8 (d, J = 7.0 Hz), 131.5 (d, J = 8.0 Hz), 124.1 (d, J = 3.0 Hz), 121.6 (d, J = 21.0 Hz), 115.6 (d, J = 24.0 Hz), 114.2, 96.2, 84.6, 59.7, 24.9, 18.5, 12.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -108.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}FNO_2S$ 280.0808; Found 280.0815.



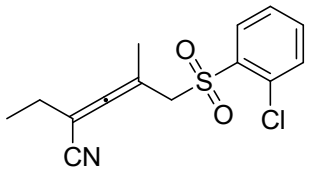
5-((3-chlorophenyl)sulfonyl)-2-ethyl-4-methylpenta-2,3-dienenitrile 3k

Colorless oil (52.2 mg, 59%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 3.78 (dd, J_1 = 14.0 Hz, J_2 = 30.0 Hz, 2H), 2.08-1.94 (m, 2H), 1.97 (s, 3H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 139.6, 135.8, 134.4, 130.9, 128.2, 126.4, 114.2, 96.2, 84.6, 59.8, 24.9, 18.6, 12.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}ClNO_2S$ 296.0512; Found 296.0517.



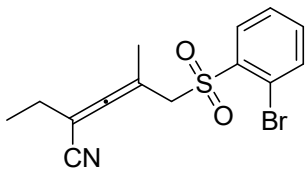
5-((3-bromophenyl)sulfonyl)-2-ethyl-4-methylpenta-2,3-dienenitrile 3l

Colorless oil (58.1 mg, 57%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (t, J = 1.2 Hz, 1H), 7.85-7.81 (m, 2H), 7.50 (t, J = 8.0 Hz, 1H), 3.78 (dd, J_1 = 14.0 Hz, J_2 = 31.6 Hz, 2H), 2.08-1.96 (m, 2H), 1.98 (s, 3H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 139.7, 137.4, 131.1, 131.1, 126.8, 123.5, 114.2, 96.2, 84.6, 59.8, 24.9, 18.6, 12.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}BrNO_2S$ 340.0007, 341.9986; Found 340.0013, 341.9994.



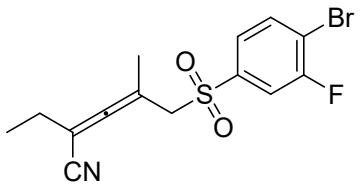
5-((2-chlorophenyl)sulfonyl)-2-ethyl-4-methylpenta-2,3-dienenitrile 3m

Colorless oil (62.6 mg, 71%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.11 (m, 1H), 7.64-7.58 (m, 1H), 7.53-7.49 (m, 1H), 4.11 (dd, J_1 = 14.0 Hz, J_2 = 18.0 Hz, 2H), 2.04-1.92 (m, 2H), 1.93 (s, 3H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.6, 135.4, 132.5, 132.1, 132.0, 127.8, 114.2, 96.2, 84.5, 57.5, 24.9, 18.6, 12.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}ClNO_2S$ 296.0512; Found 296.0519.



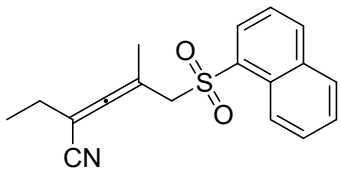
5-((2-bromophenyl)sulfonyl)-2-ethyl-4-methylpenta-2,3-dienenitrile 3n

Colorless oil (66.3 mg, 65%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J_1 = 2.0 Hz, J_2 = 7.6 Hz, 1H), 7.80 (dd, J_1 = 0.8 Hz, J_2 = 7.6 Hz, 1H), 7.58-7.49 (m, 2H), 4.15 (dd, J_1 = 14.0 Hz, J_2 = 20.8 Hz, 2H), 2.03-1.91 (m, 2H), 1.93 (s, 3H), 1.00 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 137.0, 135.7, 135.3, 132.3, 128.3, 120.7, 114.3, 96.1, 84.4, 56.9, 24.9, 18.6, 12.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}BrNO_2S$ 340.0007, 341.9986; Found 340.0011, 341.9993.



5-((4-bromo-3-fluorophenyl)sulfonyl)-2-ethyl-4-methylpenta-2,3-dienenitrile 3o

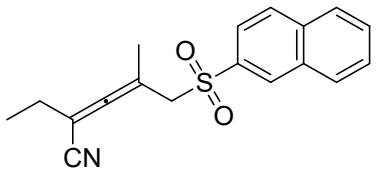
Colorless oil (70.6 mg, 66%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.81 (m, 1H), 7.64 (d, J = 7.2 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 3.78 (dd, J_1 = 14.0 Hz, J_2 = 24.0 Hz, 2H), 2.11-2.01 (m, 2H), 1.97 (s, 3H), 1.00 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 159.1 (d, J = 253.0 Hz), 138.8 (d, J = 5.0 Hz), 135.1, 124.9 (d, J = 4.0 Hz), 117.0 (d, J = 21.0 Hz), 116.4 (d, J = 25.0 Hz), 114.1, 96.1, 84.8, 59.8, 24.9, 18.6, 12.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ -101.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{14}BrFNO_2S$ 357.9913, 359.9892; Found 357.9921, 359.9899.



2-ethyl-4-methyl-5-(naphthalen-1-ylsulfonyl)penta-2,3-dienenitrile 3p

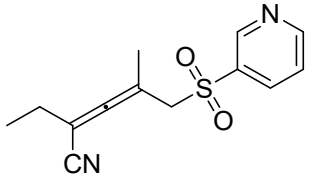
Colorless oil (69.8 mg, 75%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, J = 8.8 Hz, 1H), 8.30 (d, J = 7.2 Hz, 1H),

8.16 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.75-7.71 (m, 1H), 7.66-7.60 (m, 2H), 3.99 (dd, J_1 = 14.0 Hz, J_2 = 42.0 Hz, 2H), 1.91 (s, 3H), 1.83-1.74 (m, 1H), 1.68-1.58 (m, 1H), 0.77 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.6, 135.7, 134.2, 132.9, 131.2, 129.4, 129.0, 128.7, 127.1, 124.5, 123.6, 114.3, 96.3, 84.1, 59.4, 24.7, 18.5, 12.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{18}NO_2S$ 312.1058; Found 312.1050.



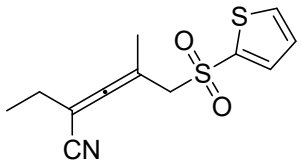
2-ethyl-4-methyl-5-(naphthalen-2-ylsulfonyl)penta-2,3-dienenitrile 3q

Colorless oil (71.0 mg, 76%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.05-8.00 (m, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.85 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 7.71-7.63 (m, 2H), 3.85 (dd, J_1 = 14.0 Hz, J_2 = 36.0 Hz, 2H), 1.97 (s, 3H), 1.89-1.72 (m, 2H), 0.79 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 135.4, 134.8, 132.0, 130.2, 129.8, 129.6, 129.4, 128.0, 127.9, 122.5, 114.3, 96.4, 84.3, 59.8, 24.7, 18.7, 11.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{18}NO_2S$ 312.1058; Found 312.1055.



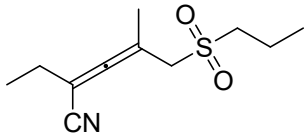
2-ethyl-4-methyl-5-(pyridin-3-ylsulfonyl)penta-2,3-dienenitrile 3r

Colorless oil (51.1 mg, 65%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.92 (d, J = 4.4 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 7.57 (dd, J_1 = 4.8 Hz, J_2 = 8.0 Hz, 1H), 3.82 (dd, J_1 = 14.0 Hz, J_2 = 26.4 Hz, 2H), 2.07-1.95 (m, 2H), 1.99 (s, 3H), 0.98 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.7, 154.8, 149.2, 136.0, 134.3, 124.2, 114.1, 96.1, 84.9, 60.2, 24.8, 18.6, 12.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{15}N_2O_2S$ 263.0854; Found 263.0845.



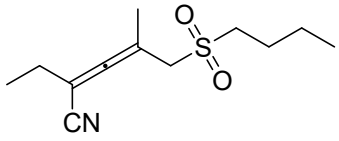
2-ethyl-4-methyl-5-(thiophen-2-ylsulfonyl)penta-2,3-dienenitrile 3s

Colorless oil (68.0 mg, 85%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, J_1 = 0.8 Hz, J_2 = 4.2 Hz, 1H), 7.71-7.70 (m, 1H), 7.20 (t, J = 4.4 Hz, 1H), 3.86 (dd, J_1 = 14.0 Hz, J_2 = 28.8 Hz, 2H), 2.12-2.01 (m, 2H), 1.96 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 138.4, 135.0, 134.9, 128.3, 114.4, 96.6, 84.5, 61.1, 24.9, 18.4, 12.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{14}NO_2S_2$ 268.0466; Found 268.0472.



2-ethyl-4-methyl-5-(propylsulfonyl)penta-2,3-dienenitrile 3t

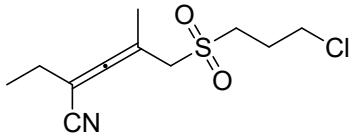
Colorless oil (37.5 mg, 55%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.63 (dd, J_1 = 14.0 Hz, J_2 = 22.0 Hz, 2H), 3.02 (t, J = 8.0 Hz, 2H), 2.28 (q, J = 7.6 Hz, 2H), 2.05 (s, 3H), 1.94-1.84 (m, 2H), 1.49 (t, J = 7.2 Hz, 3H), 1.16 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.5, 114.5, 97.1, 84.8, 56.3, 53.8, 24.9, 18.8, 16.0, 13.2, 12.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{18}NO_2S$ 228.1058; Found 228.1068.



5-(butylsulfonyl)-2-ethyl-4-methylpenta-2,3-dienenitrile 3u

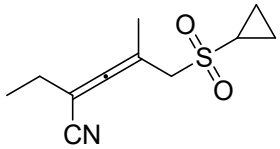
Colorless oil (48.3 mg, 67%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.63 (dd, J_1 = 14.0 Hz, J_2 = 20.8 Hz, 2H), 3.05-3.00 (m, 2H), 2.27 (q, J = 7.6 Hz, 2H), 2.03 (s, 3H), 1.84-1.79 (m, 2H), 1.52-1.48 (m, 2H), 1.14 (t, J = 7.2 Hz, 3H), 0.97 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.4, 114.5, 97.0, 84.8, 56.3, 51.9, 24.9, 23.9, 21.7, 18.7, 13.5, 12.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for

$C_{12}H_{20}NO_2S$ 242.1215; Found 242.1216.



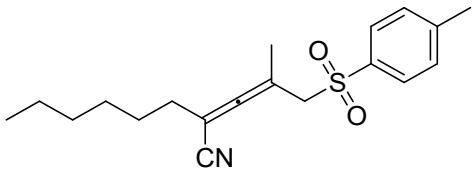
5-((3-chloropropyl)sulfonyl)-2-ethyl-4-methylpenta-2,3-dienenitrile 3v

Colorless oil (48.5 mg, 62%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73-3.68 (m, 4H), 3.22 (t, J = 7.6 Hz, 2H), 2.37-2.26 (m, 4H), 2.05 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.5, 114.4, 96.7, 85.1, 57.0, 49.4, 42.7, 24.9, 24.9, 18.8, 12.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{17}ClNO_2S$ 262.0669; Found 262.0678.



5-(cyclopropylsulfonyl)-2-ethyl-4-methylpenta-2,3-dienenitrile 3w

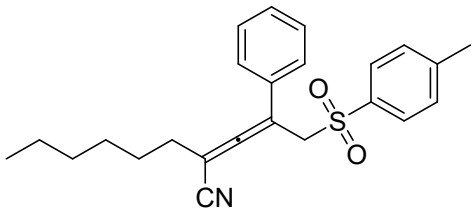
Colorless oil (41.1 mg, 61%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (dd, J_1 = 14.0 Hz, J_2 = 23.6 Hz, 2H), 2.50-2.44 (m, 1H), 3.27 (q, J = 7.2 Hz, 2H), 2.05 (s, 3H), 1.35-1.30 (m, 1H), 1.25-1.09 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 114.7, 97.0, 84.6, 57.5, 29.0, 24.9, 18.6, 12.1, 5.2, 4.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{16}NO_2S$ 226.0902; Found 226.0894.



2-(2-methyl-3-tosylprop-1-en-1-ylidene)octanenitrile 4b

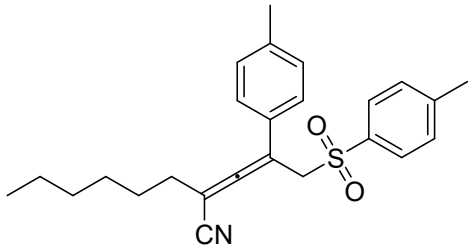
Colorless oil (59.5 mg, 60%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 3.73 (dd, J_1 = 14.0 Hz, J_2 = 27.2 Hz, 2H), 2.45 (s, 3H), 1.94-1.89 (m, 5H), 1.36-1.23 (m, 8H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.2, 145.4, 134.8, 130.1, 128.2, 114.4, 96.0,

82.8, 59.9, 31.3, 31.3, 28.2, 27.4, 22.5, 21.7, 18.4, 14.0. HRMS (ESI-TOF). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{26}NO_2S$, 332.1684; Found 332.1680.



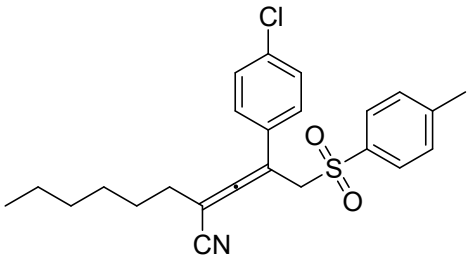
2-(2-phenyl-3-tosylprop-1-en-1-ylidene)octanenitrile 4c

Colorless oil (88.4 mg, 75%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.33-7.25 (m, 7H), 4.23 (dd, J_1 = 14.4 Hz, J_2 = 22.0 Hz, 2H), 2.42 (s, 3H), 2.16 (t, J = 7.6 Hz, 2H), 1.54-1.50 (m, 2H), 1.30-1.26 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.9, 145.3, 134.9, 131.3, 130.0, 128.8, 128.4, 126.8, 113.7, 102.0, 86.5, 57.0, 31.5, 31.3, 28.4, 27.4, 22.5, 21.6, 13.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{28}NO_2S$ 394.1841; Found 394.1827.



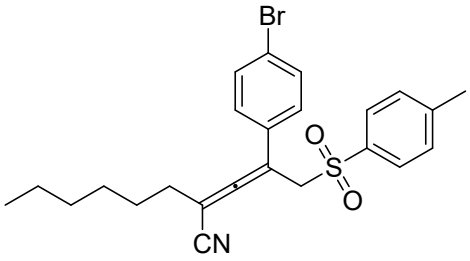
2-(2-(*p*-tolyl)-3-tosylprop-1-en-1-ylidene)octanenitrile 4d

Colorless oil (97.5 mg, 80%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.16-7.11 (m, 4H), 4.21 (dd, J_1 = 14.4 Hz, J_2 = 23.6 Hz, 2H), 2.42 (s, 3H), 2.34 (s, 3H), 2.13 (t, J = 7.6 Hz, 2H), 1.52-1.47 (m, 2H), 1.29-1.26 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.8, 145.3, 139.0, 134.9, 130.0, 129.5, 128.4, 128.2, 126.7, 113.8, 102.0, 86.3, 57.0, 31.6, 31.3, 28.3, 27.4, 22.4, 21.6, 21.1, 13.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{30}NO_2S$ 408.1997; Found 408.1987.



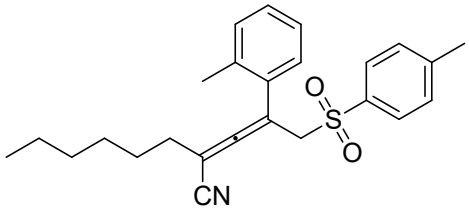
2-(2-(4-chlorophenyl)-3-tosylprop-1-en-1-ylidene)octanenitrile 4e

Colorless oil (92.2 mg, 72%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 4.19 (dd, J_1 = 14.4 Hz, J_2 = 25.6 Hz, 2H), 2.44 (s, 3H), 2.16 (t, J = 7.6 Hz, 2H), 1.51-1.49 (m, 2H), 1.28-1.26 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.8, 145.6, 135.0, 134.8, 130.1, 129.9, 129.1, 128.4, 128.2, 113.5, 101.3, 87.0, 57.1, 31.6, 31.3, 28.4, 27.5, 22.5, 21.6, 13.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{27}ClNO_2S$ 428.1451; Found 428.1441.



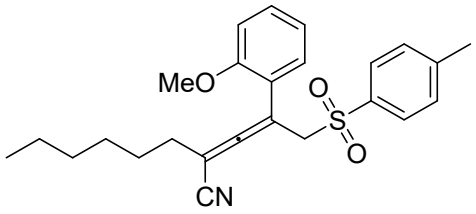
2-(2-(4-bromophenyl)-3-tosylprop-1-en-1-ylidene)octanenitrile 4f

Colorless oil (100.5 mg, 71%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 4.19 (dd, J_1 = 14.4 Hz, J_2 = 25.6 Hz, 2H), 2.44 (s, 3H), 2.16 (t, J = 7.6 Hz, 2H), 1.51-1.49 (m, 2H), 1.28-1.26 (m, 6H), 0.87 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.8, 145.6, 134.8, 132.0, 130.4, 130.1, 128.4, 128.4, 123.2, 113.4, 101.4, 87.0, 57.0, 31.5, 31.3, 28.4, 27.4, 22.5, 21.6, 13.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{27}BrNO_2S$ 472.0946, 474.0925; Found 472.0940, 474.0909.



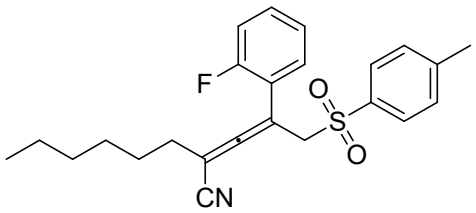
2-(2-(*o*-tolyl)-3-tosylprop-1-en-1-ylidene)octanenitrile 4g

Colorless oil (98.9 mg, 81%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.22-7.12 (m, 3H), 7.07 (d, J = 7.6 Hz, 1H), 4.14 (dd, J_1 = 14.0 Hz, J_2 = 24.8 Hz, 2H), 2.43 (s, 3H), 2.28 (s, 3H), 2.20-2.15 (m, 2H), 1.52-1.49 (m, 2H), 1.27-1.24 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.3, 145.2, 135.8, 135.5, 132.1, 130.9, 130.0, 128.7, 128.1, 128.1, 126.3, 114.1, 99.8, 84.4, 59.4, 31.3, 31.2, 28.3, 27.4, 22.4, 21.6, 20.4, 13.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{30}NO_2S$ 408.1997; Found 408.2008.



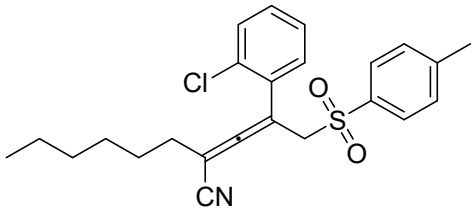
2-(2-(2-methoxyphenyl)-3-tosylprop-1-en-1-ylidene)octanenitrile 4h

Colorless oil (96.5 mg, 76%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.0 Hz, 2H), 7.27-7.23 (m, 3H), 7.01 (dd, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1H), 6.87 (t, J = 7.6 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 4.31 (dd, J_1 = 14.4 Hz, J_2 = 18.0 Hz, 2H), 3.77 (s, 3H), 2.40 (s, 3H), 2.12 (t, J = 7.6 Hz, 2H), 1.50-1.47 (m, 2H), 1.34-1.25 (m, 6H), 0.86 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.0, 156.4, 144.8, 135.2, 130.2, 130.0, 129.7, 128.2, 120.7, 114.3, 111.0, 99.6, 83.6, 58.0, 55.4, 31.3, 31.3, 28.3, 27.4, 22.4, 21.5, 13.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{30}NO_3S$ 424.1946; Found 424.1935.



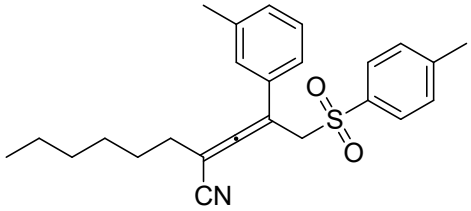
2-(2-(2-fluorophenyl)-3-tosylprop-1-en-1-ylidene)octanenitrile 4i

Colorless oil (92.5 mg, 75%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 2H), 7.31-7.27 (m, 3H), 7.18 (dt, J_1 = 1.6 Hz, J_2 = 7.6 Hz, 1H), 7.11 (dt, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1H), 7.04-6.99 (m, 1H), 4.23 (s, 2H), 2.41 (s, 3H), 2.14 (t, J = 7.6 Hz, 2H), 1.50-1.48 (m, 2H), 1.30-1.26 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.3, 159.7 (d, J = 249.0 Hz), 145.3, 134.8, 130.7 (d, J = 9.0 Hz), 130.0, 129.6 (d, J = 2.0 Hz), 128.3, 124.5 (d, J = 4.0 Hz), 120.0 (d, J = 11.0 Hz), 116.2 (d, J = 22.0 Hz), 113.6, 96.9, 85.1 (d, J = 1.0 Hz), 58.0 (d, J = 3.0 Hz), 31.3, 31.3, 28.3, 27.3, 22.5, 21.6, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ -112.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{27}FNO_2S$ 412.1747; Found 412.1735.



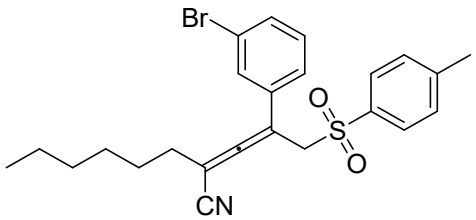
2-(2-(2-chlorophenyl)-3-tosylprop-1-en-1-ylidene)octanenitrile 4j

Colorless oil (89.7 mg, 70%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.4 Hz, 2H), 7.37-7.32 (m, 3H), 7.28-7.18 (m, 3H), 4.21 (dd, J_1 = 14.4 Hz, J_2 = 15.6 Hz, 2H), 2.43 (s, 3H), 2.17-2.14 (m, 2H), 1.49-1.47 (m, 2H), 1.25-1.22 (m, 6H), 0.85 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.0, 145.2, 135.1, 132.5, 131.6, 130.4, 130.2, 130.0, 128.3, 127.1, 113.7, 99.3, 85.2, 58.6, 31.2, 31.2, 28.2, 27.2, 22.4, 21.6, 13.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{27}ClNO_2S$ 428.1451; Found 428.1440.



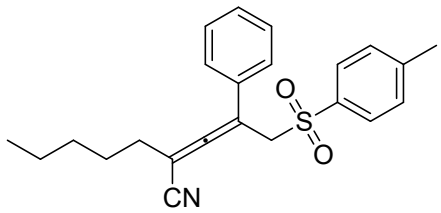
2-(2-(*m*-tolyl)-3-tosylprop-1-en-1-ylidene)octanenitrile 4k

Colorless oil (97.7 mg, 80%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.20 (t, J = 7.6 Hz, 3H), 7.09 (d, J = 7.6 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.97 (s, 1H), 4.21 (dd, J_1 = 14.4 Hz, J_2 = 22.0 Hz, 2H), 2.42 (s, 3H), 2.30 (s, 3H), 2.18 (t, J = 7.6 Hz, 2H), 1.55-1.51 (m, 2H), 1.30-1.21 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.9, 145.3, 138.6, 135.0, 131.3, 130.0, 129.6, 128.7, 128.5, 127.4, 124.0, 113.8, 102.1, 86.4, 57.2, 31.6, 31.3, 28.4, 27.5, 22.5, 21.6, 21.3, 14.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{30}NO_2S$ 408.1997; Found 408.1986.



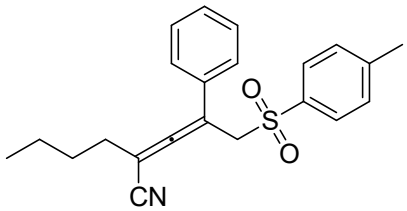
2-(2-(3-bromophenyl)-3-tosylprop-1-en-1-ylidene)octanenitrile 4l

Colorless oil (99.0 mg, 70%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.4 Hz, 2H), 7.41-7.40 (m, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.23-7.17 (m, 3H), 4.18 (dd, J_1 = 14.4 Hz, J_2 = 20.8 Hz, 2H), 2.43 (s, 3H), 2.22 (t, J = 7.6 Hz, 2H), 1.57-1.52 (m, 2H), 1.28-1.17 (m, 6H), 0.87 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.9, 145.6, 134.8, 133.7, 131.8, 130.3, 130.1, 129.7, 128.4, 125.5, 123.0, 113.4, 101.1, 87.2, 57.1, 31.6, 31.3, 28.4, 27.4, 22.5, 21.7, 14.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{27}BrNO_2S$ 472.0946, 474.0925; Found 472.0927, 474.0915.



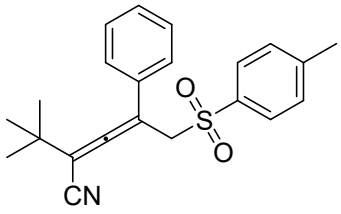
2-(2-phenyl-3-tosylprop-1-en-1-ylidene)heptanenitrile 4m

Colorless oil (88.6 mg, 78%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.33-7.25 (m, 7H), 4.23 (dd, J_1 = 14.4 Hz, J_2 = 21.2 Hz, 2H), 2.42 (s, 3H), 2.16 (t, J = 7.6 Hz, 2H), 1.54-1.50 (m, 2H), 1.30-1.27 (m, 4H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.9, 145.3, 134.9, 131.3, 130.0, 128.8, 128.4, 126.8, 113.7, 102.0, 86.6, 57.1, 31.5, 30.8, 27.2, 22.1, 21.6, 13.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{26}NO_2S$ 380.1684; Found 380.1673.



2-(2-phenyl-3-tosylprop-1-en-1-ylidene)hexanenitrile 4n

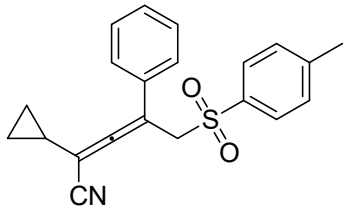
Colorless oil (76.7 mg, 70%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 2H), 7.33-7.25 (m, 7H), 4.23 (dd, J_1 = 14.4 Hz, J_2 = 21.2 Hz, 2H), 2.42 (s, 3H), 2.17 (t, J = 7.6 Hz, 2H), 1.52-1.48 (m, 2H), 1.34-1.32 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.9, 145.4, 134.9, 131.3, 130.0, 128.9, 128.4, 126.8, 113.7, 102.1, 86.6, 57.1, 31.3, 29.6, 21.9, 21.6, 13.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{24}NO_2S$ 366.1528; Found 366.1521.



2-(tert-butyl)-4-phenyl-5-tosylpenta-2,3-dienenitrile 4o

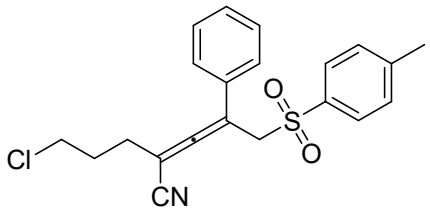
Colorless oil (67.8 mg, 62%). Petroleum ether/ethyl acetate = 15/1 as eluent for column

chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 2H), 7.30-7.22 (m, 7H), 4.24 (dd, J_1 = 14.4 Hz, J_2 = 31.2 Hz, 2H), 2.41 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.8, 145.4, 135.2, 131.6, 130.1, 128.9, 128.7, 128.3, 126.5, 113.0, 103.2, 97.7, 57.3, 36.0, 28.7, 21.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{24}NO_2S$ 366.1528; Found 366.1520.



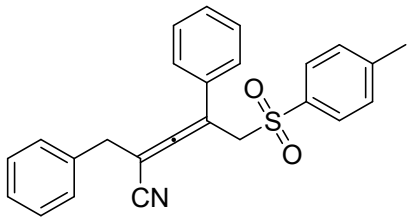
2-cyclopropyl-4-phenyl-5-tosylpenta-2,3-dienenitrile 4p

Colorless oil (69.0 mg, 66%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 2H), 7.32-7.25 (m, 7H), 4.24 (s, 2H), 2.41 (s, 3H), 1.43-1.37 (m, 1H), 0.90-0.81 (m, 2H), 0.73-0.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.7, 145.3, 135.0, 131.4, 130.0, 128.9, 128.9, 128.4, 126.9, 112.4, 103.5, 90.4, 57.2, 21.6, 11.4, 6.5, 6.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{20}NO_2S$ 350.1215; Found 350.1221.



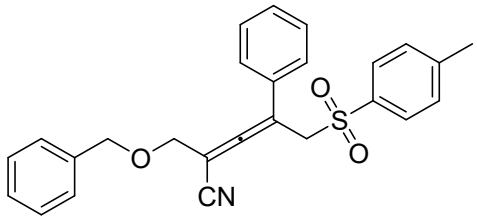
2-(3-chloropropyl)-4-phenyl-5-tosylpenta-2,3-dienenitrile 4q

Colorless oil (86.6 mg, 75%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.0 Hz, 2H), 7.32-7.23 (m, 7H), 4.24 (s, 2H), 3.55 (t, J = 6.4 Hz, 2H), 2.43-2.40 (m, 5H), 2.05-2.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.1, 145.4, 135.0, 131.1, 130.1, 129.0, 128.9, 128.4, 126.8, 113.4, 102.7, 85.2, 57.0, 43.3, 29.8, 28.9, 21.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}ClNO_2S$ 386.0982; Found 386.0971.



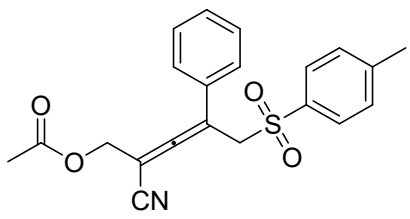
2-benzyl-4-phenyl-5-tosylpenta-2,3-dienenitrile 4r

Colorless oil (78.0 mg, 65%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 2H), 7.35-7.27 (m, 8H), 7.21-7.17 (m, 4H), 4.17 (dd, J_1 = 14.4 Hz, J_2 = 24.4 Hz, 2H), 3.50 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.4, 145.5, 135.6, 134.9, 131.1, 130.1, 129.0, 128.9, 128.9, 128.8, 128.4, 127.6, 126.9, 113.5, 102.9, 86.6, 57.0, 37.9, 21.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{22}NO_2S$ 400.1371; Found 400.1365.



2-((benzyloxy)methyl)-4-phenyl-5-tosylpenta-2,3-dienenitrile 4s

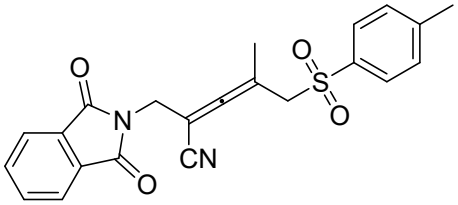
Colorless oil (65.5 mg, 51%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.0 Hz, 2H), 7.36-7.24 (m, 12H), 4.54 (dd, J_1 = 12.0 Hz, J_2 = 20.0 Hz, 2H), 4.22 (dd, J_1 = 14.4 Hz, J_2 = 26.8 Hz, 2H), 4.10 (dd, J_1 = 12.0 Hz, J_2 = 18.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.3, 145.5, 136.8, 134.7, 130.7, 130.0, 129.2, 129.0, 128.5, 128.4, 128.0, 127.8, 127.0, 112.5, 103.4, 84.9, 72.5, 67.8, 56.8, 21.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{24}NO_3S$ 430.1477; Found 430.1465.



2-cyano-4-phenyl-5-tosylpenta-2,3-dien-1-yl acetate 4t

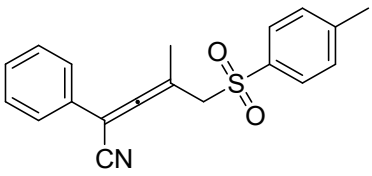
Colorless oil (62.6 mg, 55%). Petroleum ether/ethyl acetate = 15/1 as eluent for column

chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.34-7.25 (m, 7H), 4.57 (dd, J_1 = 12.4 Hz, J_2 = 16.8 Hz, 2H), 4.26 (d, 2H), 2.42 (d, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.8, 170.0, 145.6, 134.7, 130.1, 130.0, 129.4, 129.0, 128.4, 127.0, 111.8, 104.6, 83.4, 61.2, 56.5, 21.6, 20.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{20}NO_4S$ 382.1113; Found 382.1105.



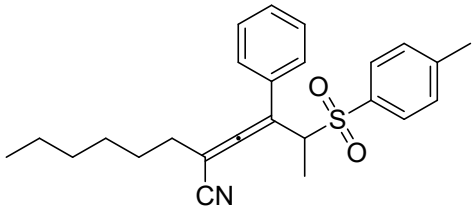
2-((1,3-dioxoisoindolin-2-yl)methyl)-4-methyl-5-tosylpenta-2,3-dienenitrile 4u

Colorless oil (63.5 mg, 52%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, J_1 = 3.2 Hz, J_2 = 5.6 Hz, 2H), 7.77 (dd, J_1 = 3.2 Hz, J_2 = 5.6 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.26 (s, 2H), 3.70 (dd, J_1 = 13.6 Hz, J_2 = 39.2 Hz, 2H), 2.42 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.2, 167.0, 145.6, 134.5, 134.4, 131.7, 130.2, 128.2, 123.7, 112.3, 100.1, 79.2, 59.1, 37.6, 21.7, 18.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{19}N_2O_4S$ 407.1066; Found 407.1058.



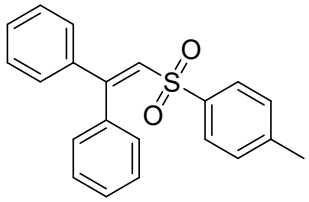
4-methyl-2-phenyl-5-tosylpenta-2,3-dienenitrile 4v

Colorless oil (38.0 mg, 39%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 2H), 7.36-7.33 (m, 7H), 3.89 (dd, J_1 = 14.0 Hz, J_2 = 31.6 Hz, 2H), 2.44 (d, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.5, 145.6, 135.0, 130.3, 129.1, 129.0, 128.8, 128.1, 126.2, 113.0, 100.3, 86.9, 59.7, 21.7, 18.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{18}NO_2S$ 324.1058; Found 324.1051.



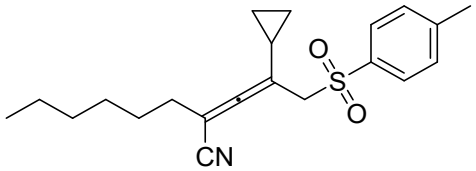
2-(2-phenyl-3-tosylbut-1-en-1-ylidene)octanenitrile 4w

Colorless oil (61.1 mg, 50%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.0 Hz, 2H), 7.31-7.15 (m, 7H), 4.32-4.23 (m, 2H), 2.38 (s, 3H), 2.35-2.19 (m, 2H), 1.68-1.57 (m, 5H), 1.39-1.20 (m, 6H), 0.91-0.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.4, 213.6, 145.2, 145.0, 134.1, 132.7, 132.6, 132.5, 129.8, 129.6, 129.2, 129.1, 128.7, 128.6, 128.5, 126.9 126.8, 114.1, 113.6, 109.5, 108.4, 88.5, 88.3, 60.5, 60.4, 31.8, 31.3, 31.2, 28.5, 28.2, 27.7, 27.3, 22.4, 22.3, 21.5, 15.0, 13.9, 13.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{30}NO_2S$ 408.1997; Found 408.1985.



(2-tosylethene-1,1-diyl)dibenzene 5

Colorless oil (60.1 mg, 60%). Petroleum ether/ethyl acetate = 15/1 as eluent for column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.0 Hz, 2H), 7.39-7.34 (m, 2H), 7.30 (t, J = 7.6 Hz, 4H), 7.20 (d, J = 7.2 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.2 Hz, 2H), 6.99 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 143.7, 139.2, 138.6, 135.6, 130.2, 129.8, 129.3, 129.0, 128.8, 128.5, 128.2, 127.8, 127.7, 21.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{19}O_2S$ 335.1106; Found 335.1121.



2-(2-cyclopropyl-3-tosylprop-1-en-1-ylidene)octanenitrile 4y

Colorless oil (32.1 mg, 30%). Petroleum ether/ethyl acetate = 15/1 as eluent for column

chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 3.86 (dd, J_1 = 14.0 Hz, J_2 = 21.6 Hz, 2H), 2.46 (s, 3H), 1.94-1.90 (m, 2H), 1.50-1.45 (m, 1H), 1.37-1.24 (m, 8H), 0.91-0.83 (m, 5H), 0.39 (d, J = 3.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.2, 145.3, 135.0, 130.1, 128.4, 114.3, 104.6, 85.7, 59.4, 31.5, 31.3, 28.3, 27.5, 22.5, 21.7, 14.0, 12.1, 8.3 8.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{28}NO_2S$ 358.1841; Found 358.1833.

4. Structure Analysis X-Ray Crystallography of 3i

Single crystals for compound **3i** were grown by slow evaporation of concentrated solution in petroleum ether/ethyl acetate in glass vials, which were then sealed by plugs with needles on them.

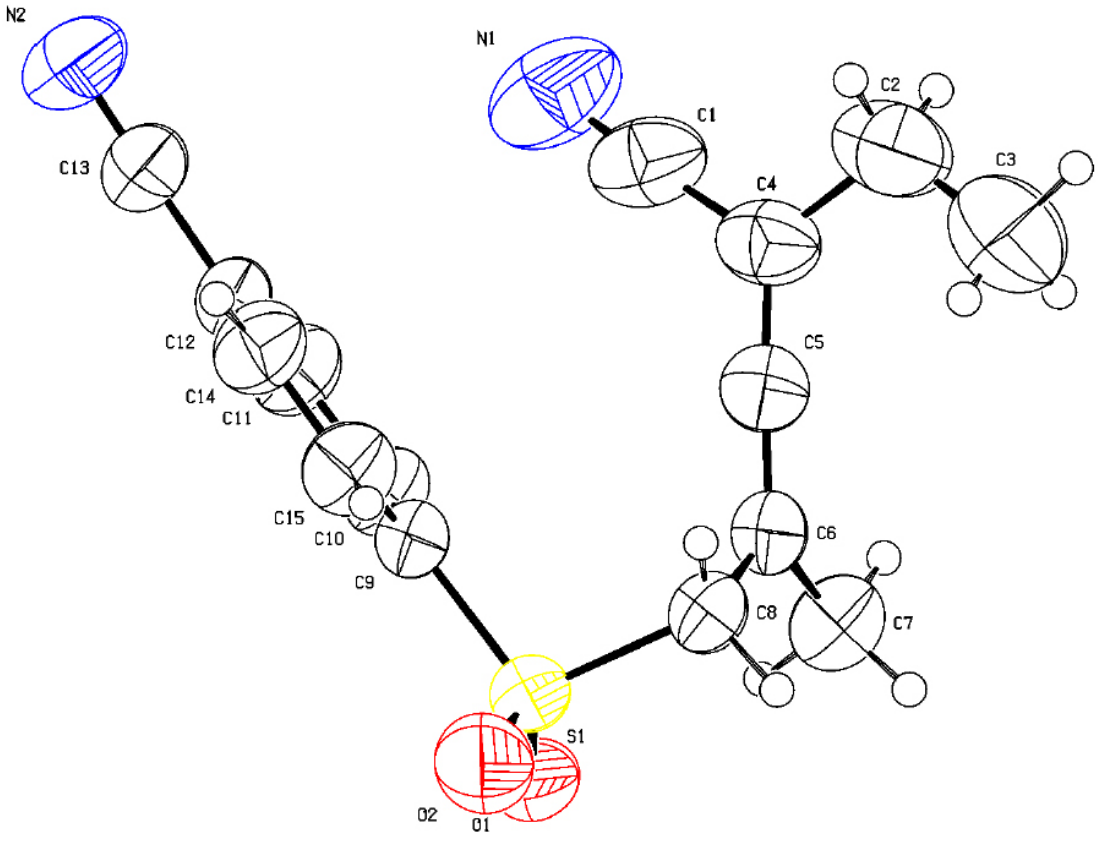


Fig. S1 Thermal ellipsoid plot (30%) of the crystal structure of **3i**

Table S1 The single crystal date of compounds **3i**

Phase	**3i**
Empirical formula	$C_{15}H_{14}N_2O_2S$
Formula weight	286.34
Temperature/K	273 K
Wavelength/ Å	0.71073 Å
Crystal system	Triclinic
Space group	P-1
a (Å)	8.6746(3)
b (Å)	9.5180(4)
c (Å)	10.4880(5)
α (°)	100.7100(15)
β (°)	90.3641(15)
γ (°)	116.6448(14)
V (Å3)	756.52(6)
Z	2
Calculated density ($g \cdot cm^{-3}$)	1.257
Absorption coefficient(mm^{-1})	0.216
F(000)	300.0
θ range (°)	26.429 > θ > 2.656
Reflections collected/unique	3065 / 2358
Completeness to theta	0.989
Refinement method	full-matrix least-squares on F^2
Index range	$-10 \le h \le 10$ $-11 \le k \le 11$ $-13 \le l \le 13$
Goodness-of -fit on F^2	1.060
Final *R* indices [I>2sigma(I)]	0.0484
wR_2 (all data)	0.1476
Largest diff. peak and hole /($e \cdot Å^{-3}$)	0.260, -0.202

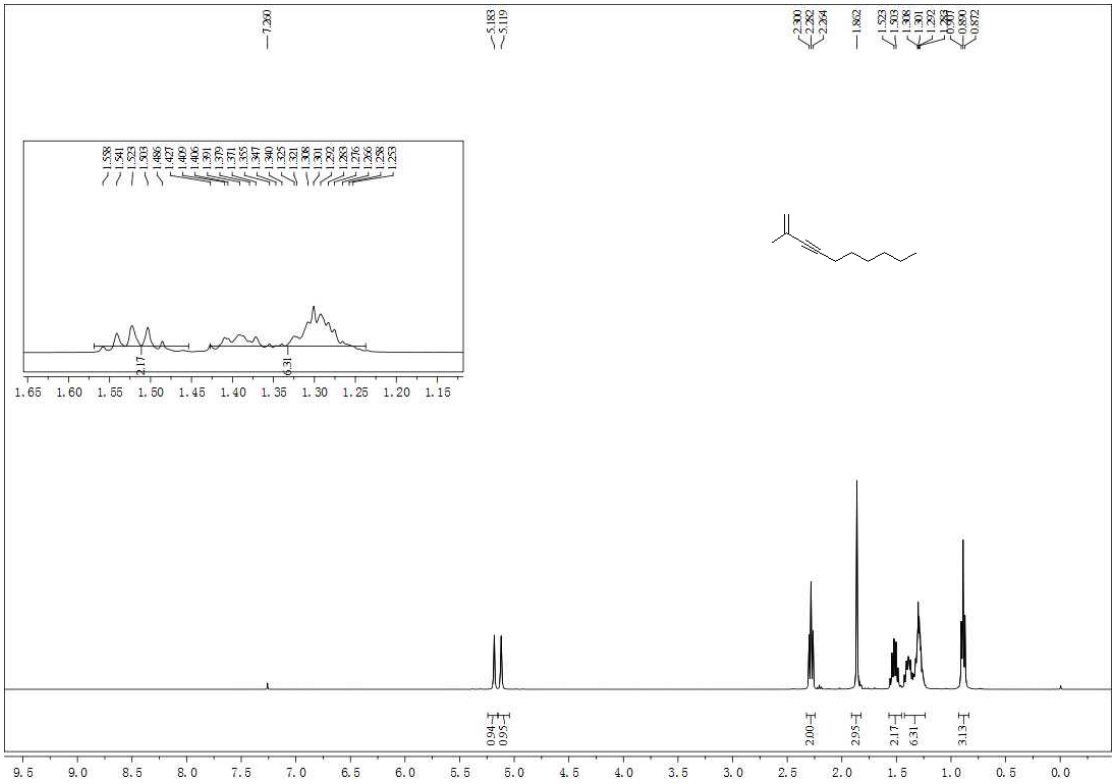
5. References

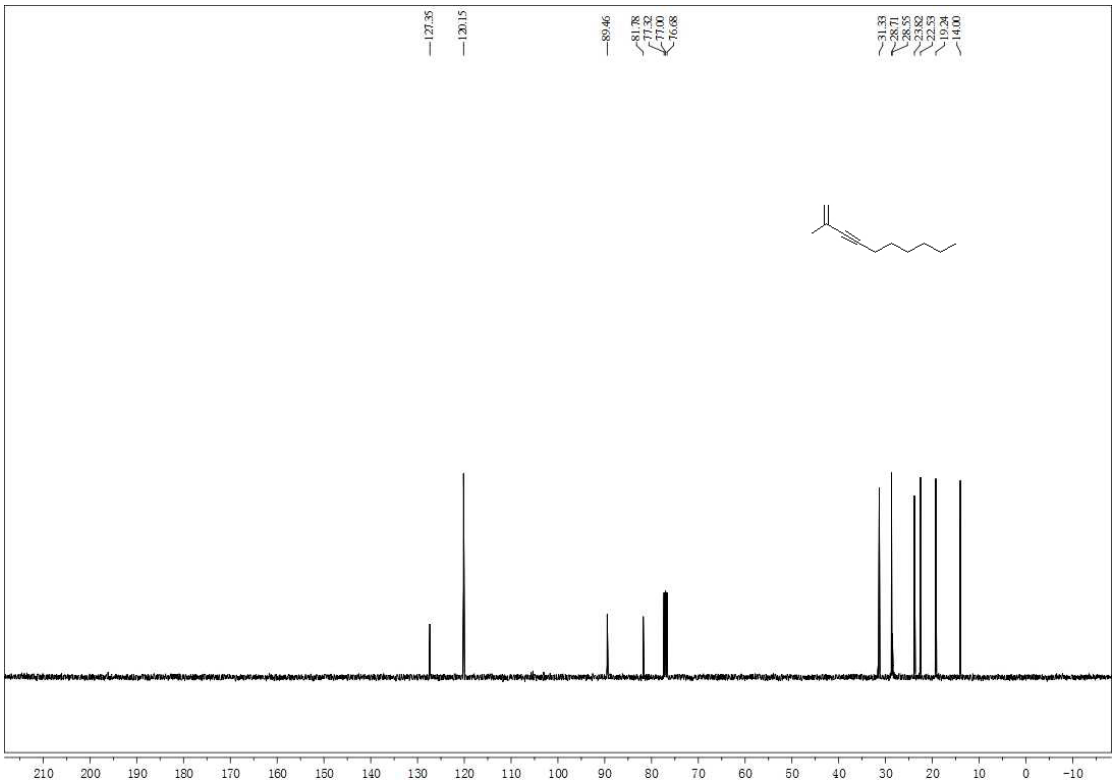
[1] X. Zhu, W. Deng, M.-F. Chiou, C. Ye, W. Jian, Y. Zeng, Y. Jiao, L. Ge, Y. Li, X. Zhang, H. Bao, Copper-Catalyzed Radical 1,4-Difunctionalization of 1,3-Enynes with Alkyl Diacyl Peroxides and *N*-Fluorobenzenesulfonimide. *J. Am. Chem. Soc.,* 2019, **141**, 548−559.

[2] X.-Y. Dong, T.-Y. Zhan, S.-P. Jiang, X.-D. Liu, L. Ye, Z.-L. Li, Q.-S. Gu, X.-Y. Liu, Copper-Catalyzed Asymmetric Coupling of Allenyl Radicals with Terminal Alkynes to Access Tetrasubstituted Allenes. *Angew. Chem., Int. Ed.,* 2021, **60**, 2160−2164.

6. NMR Spectra of Compounds 1, 3, 4 and 5

Product 1b





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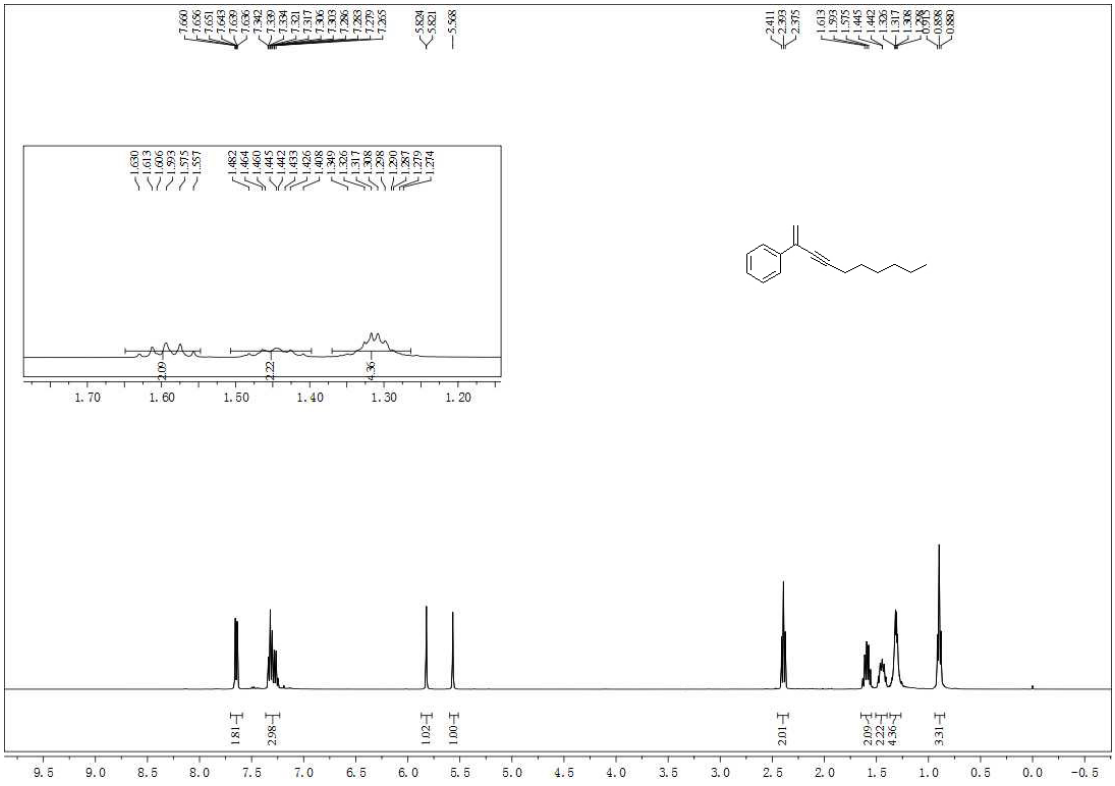

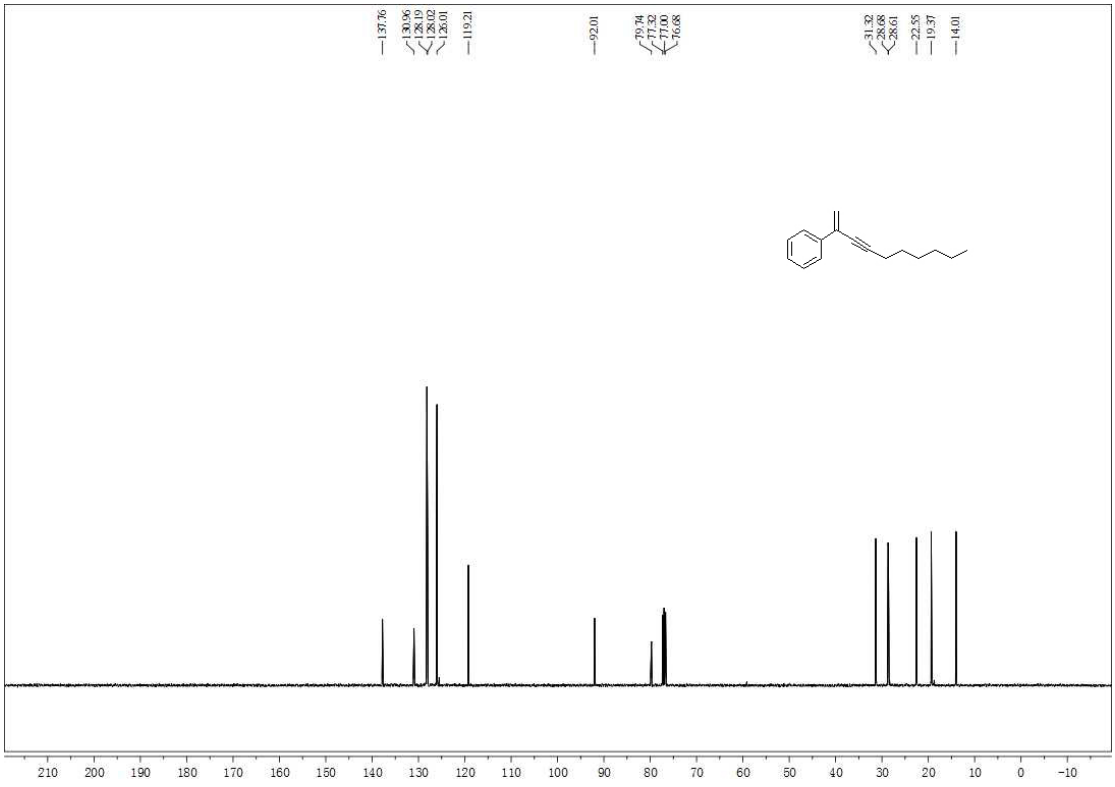

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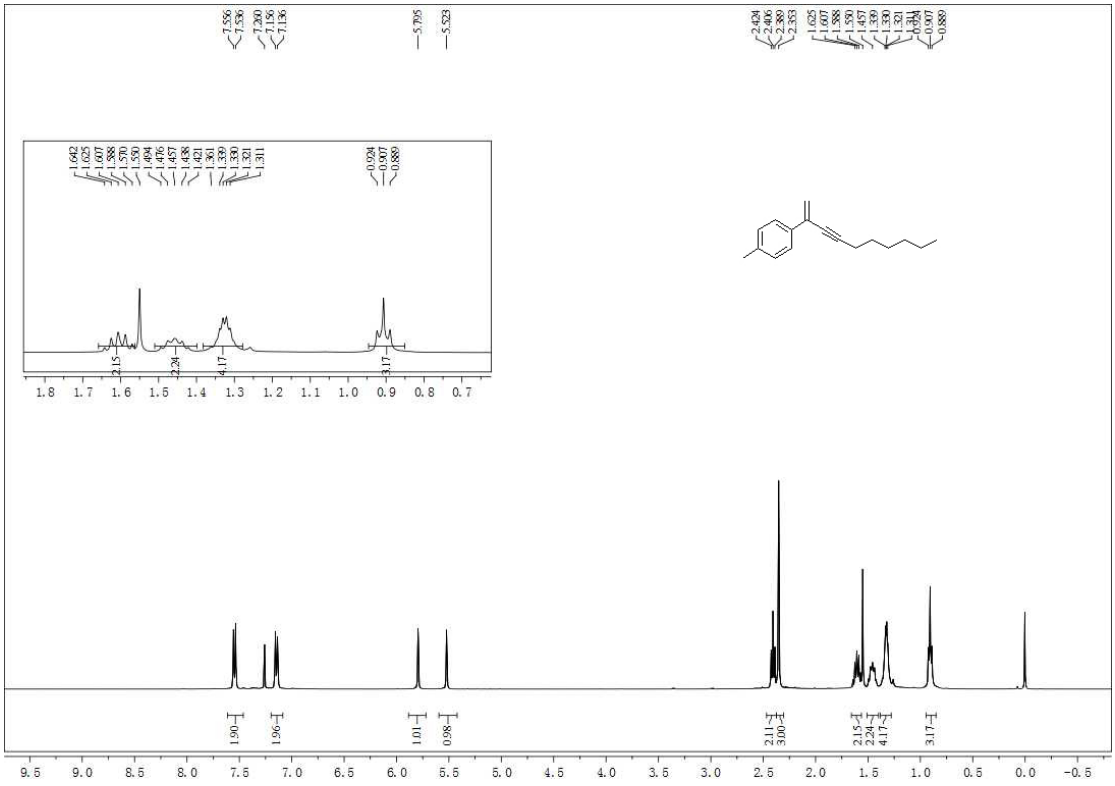

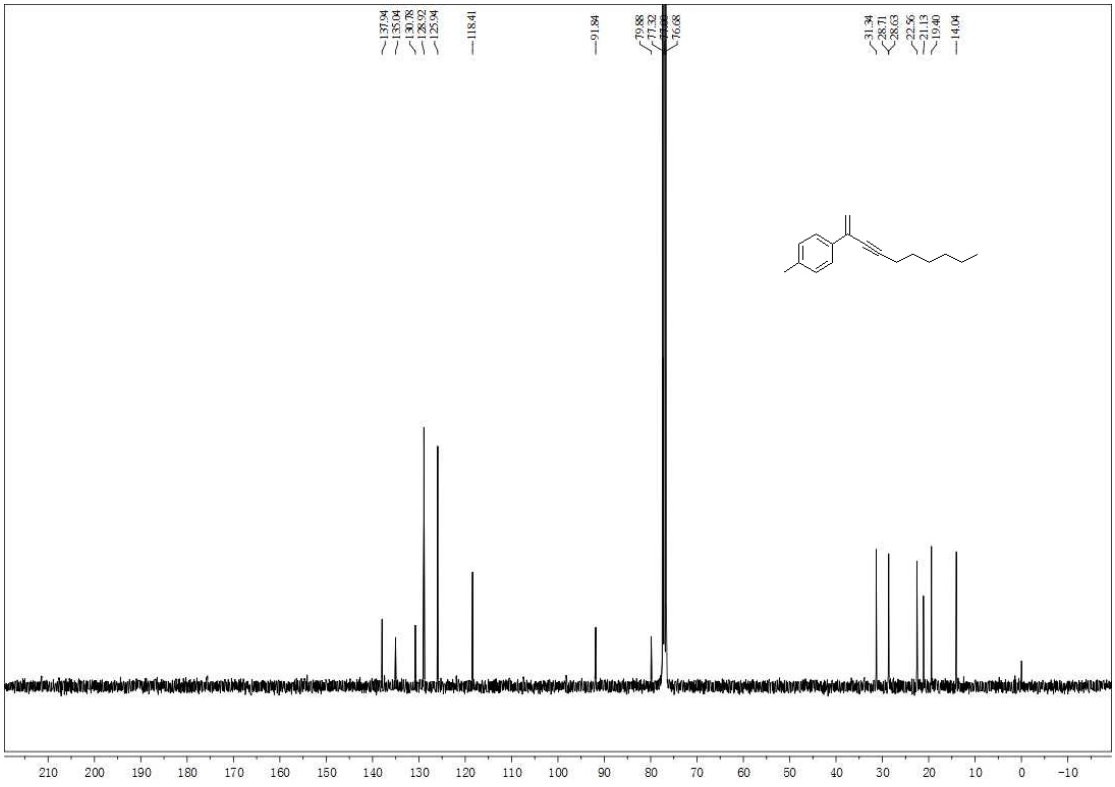

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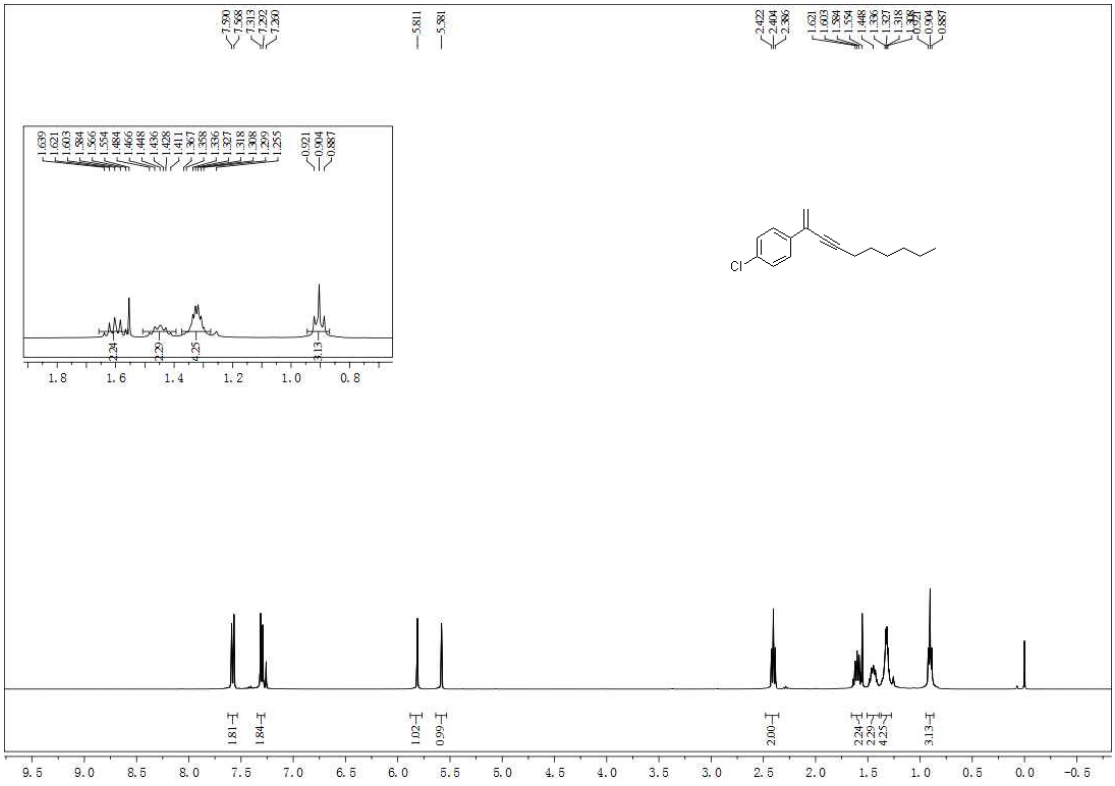

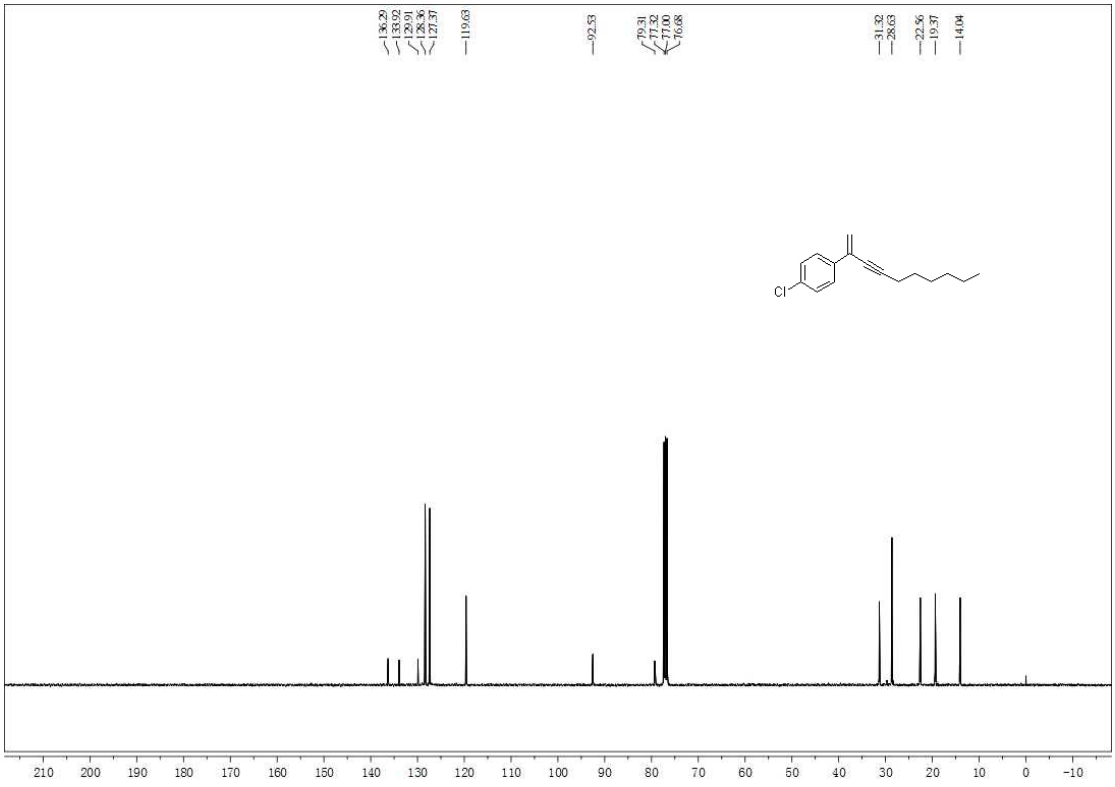

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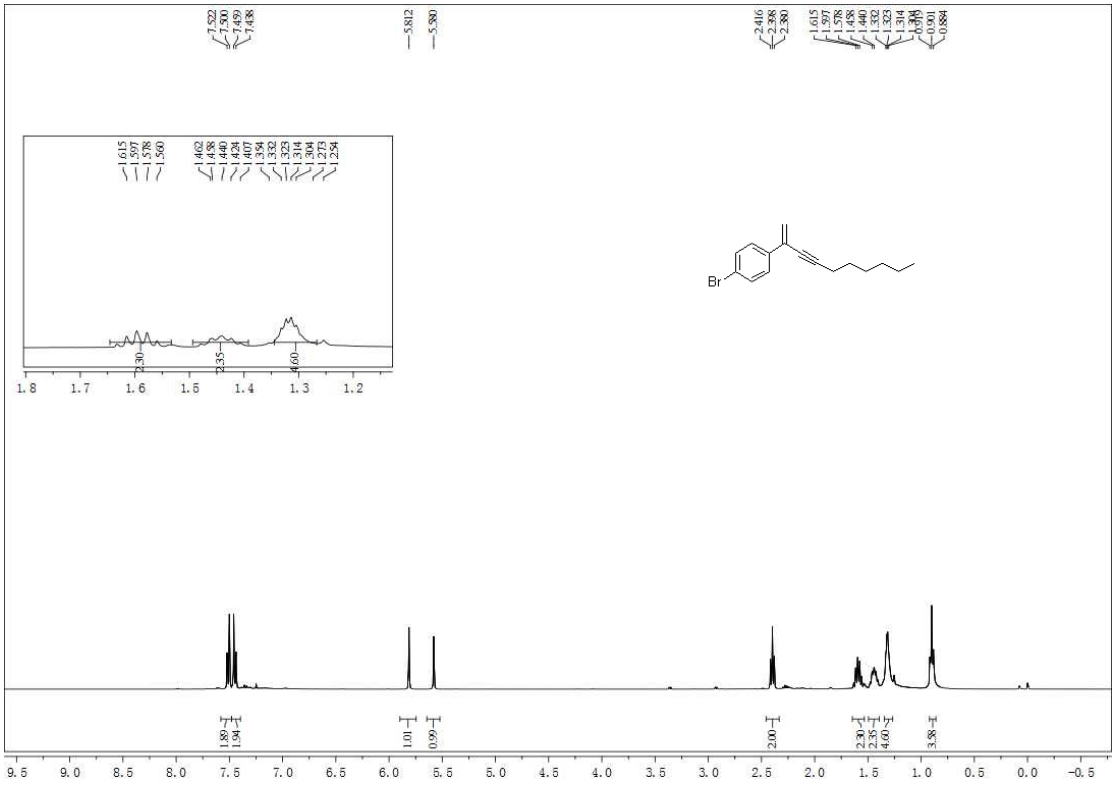
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1.462
1.438
1.440
1.424
1.407
1.354
1.332
1.325
1.314
1.304
1.275
1.254
0.918
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Br
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0.99
2.00
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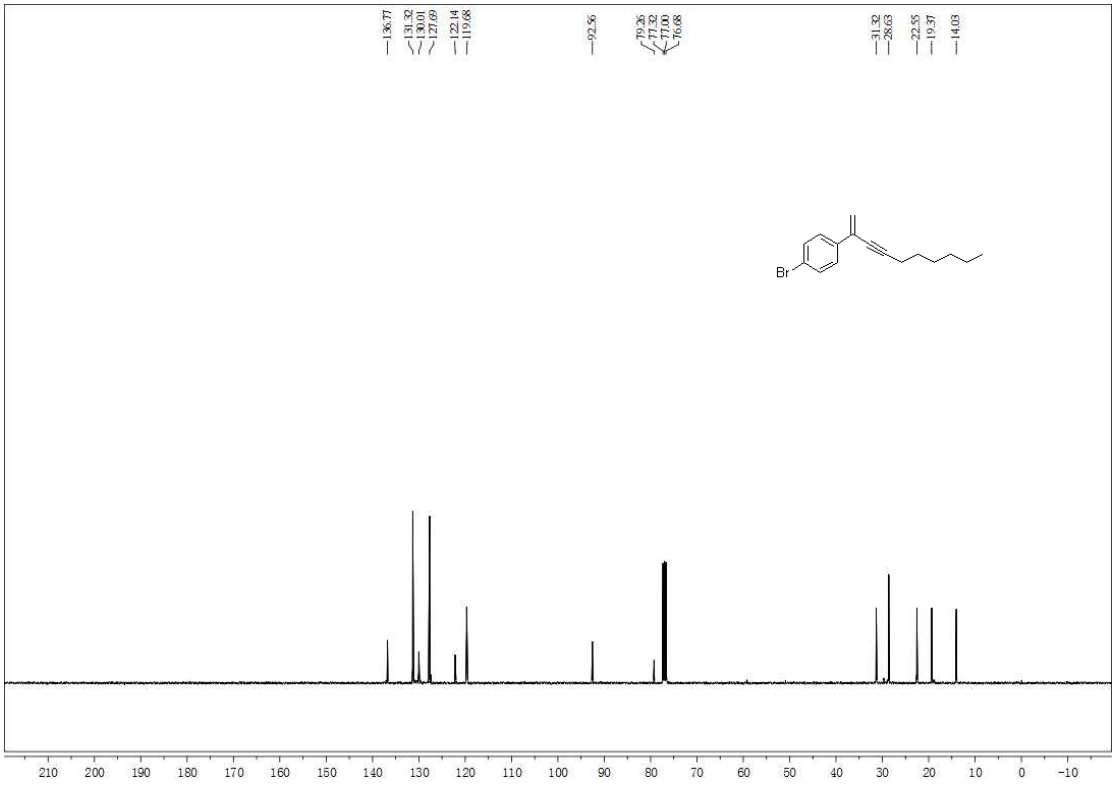
4.60
3.88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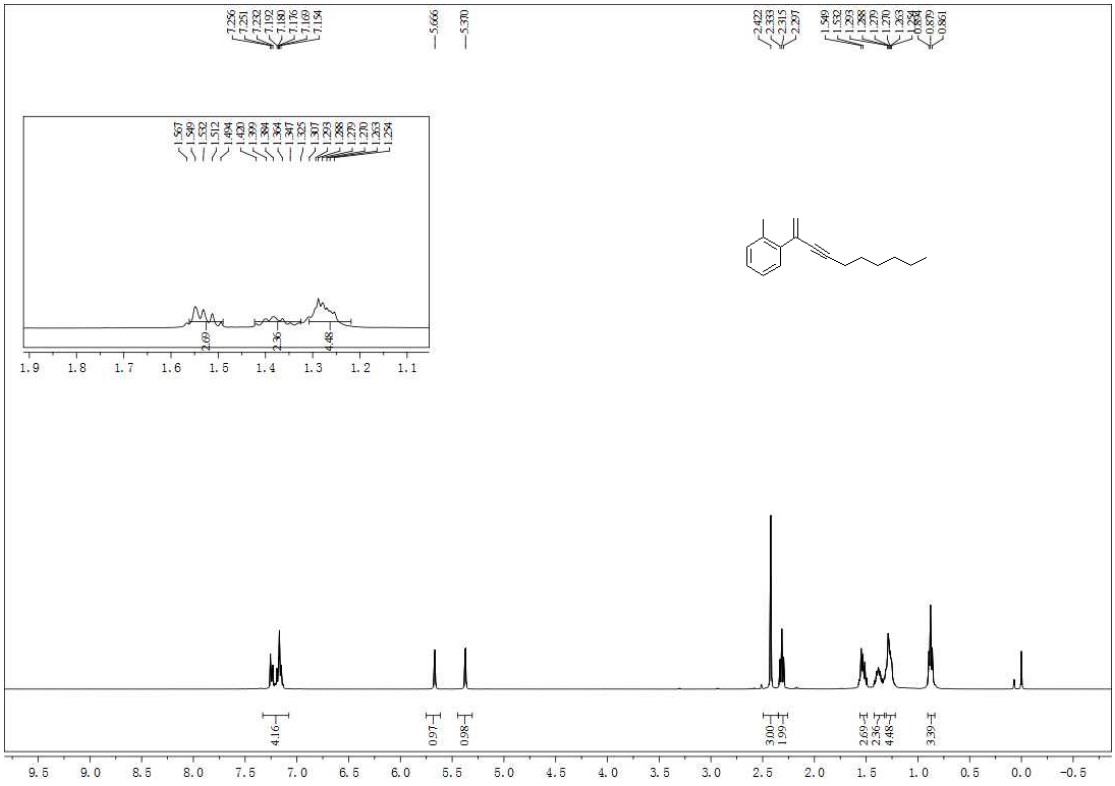
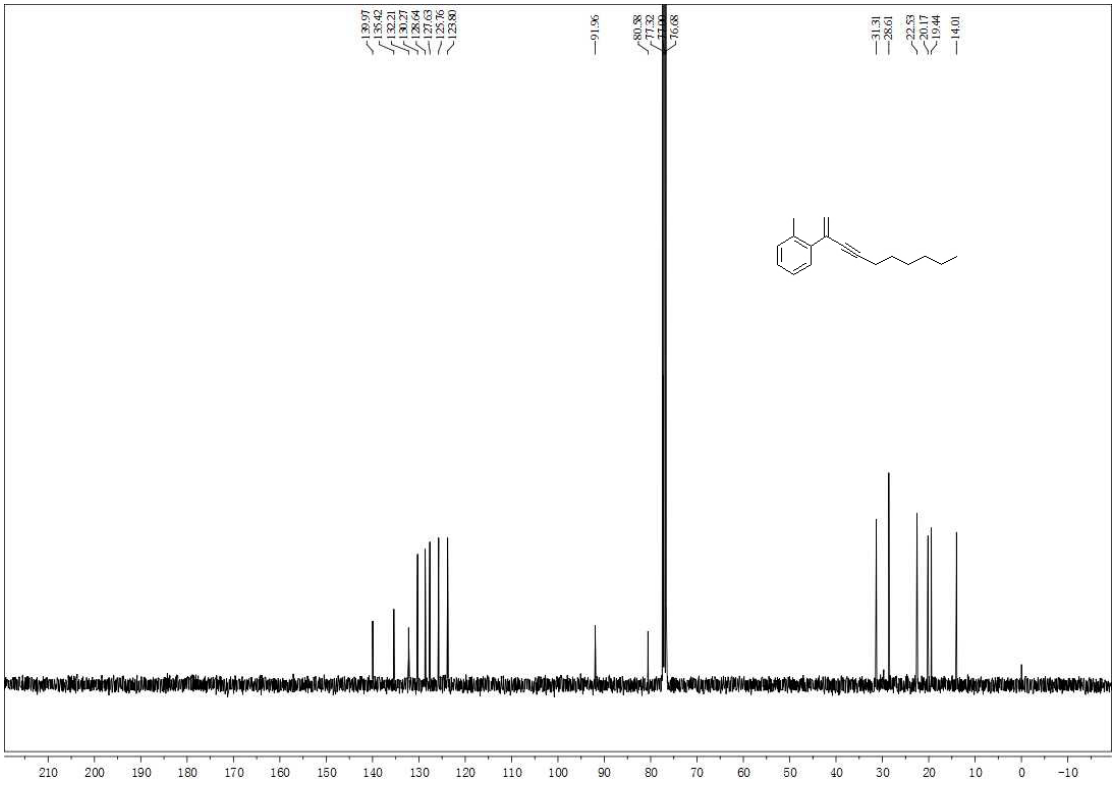
22.55
19.37
14.03
Br

Product 1g





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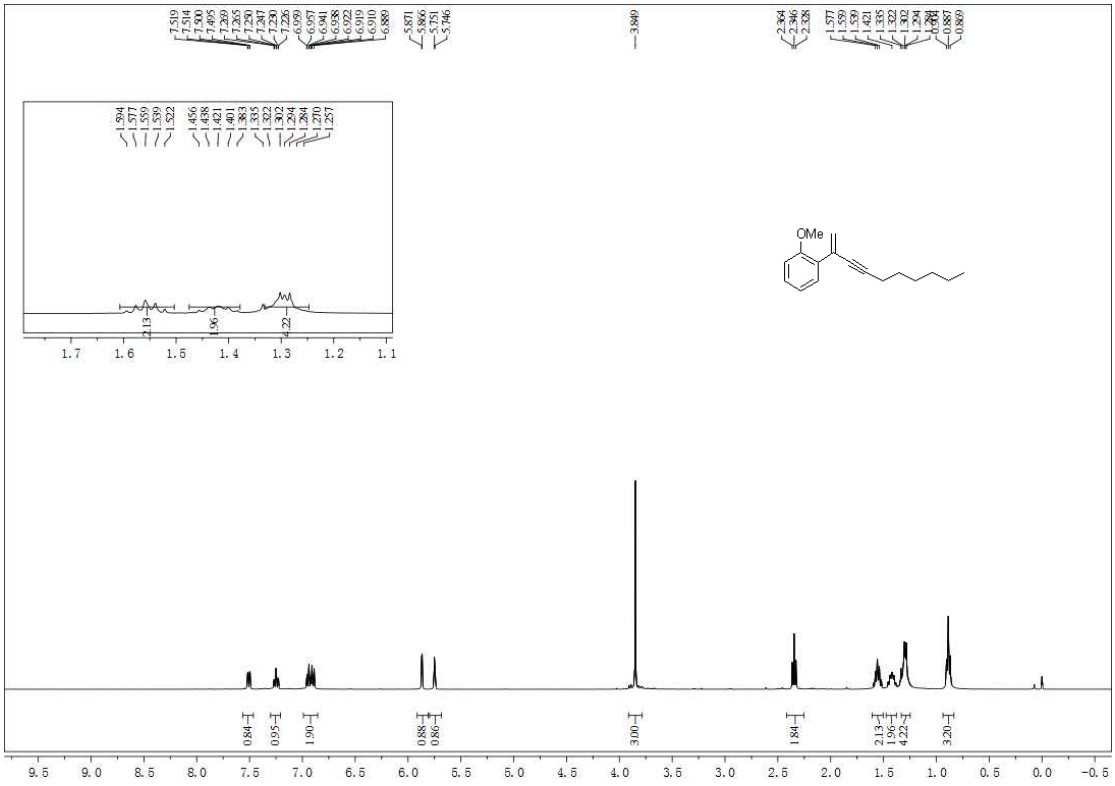

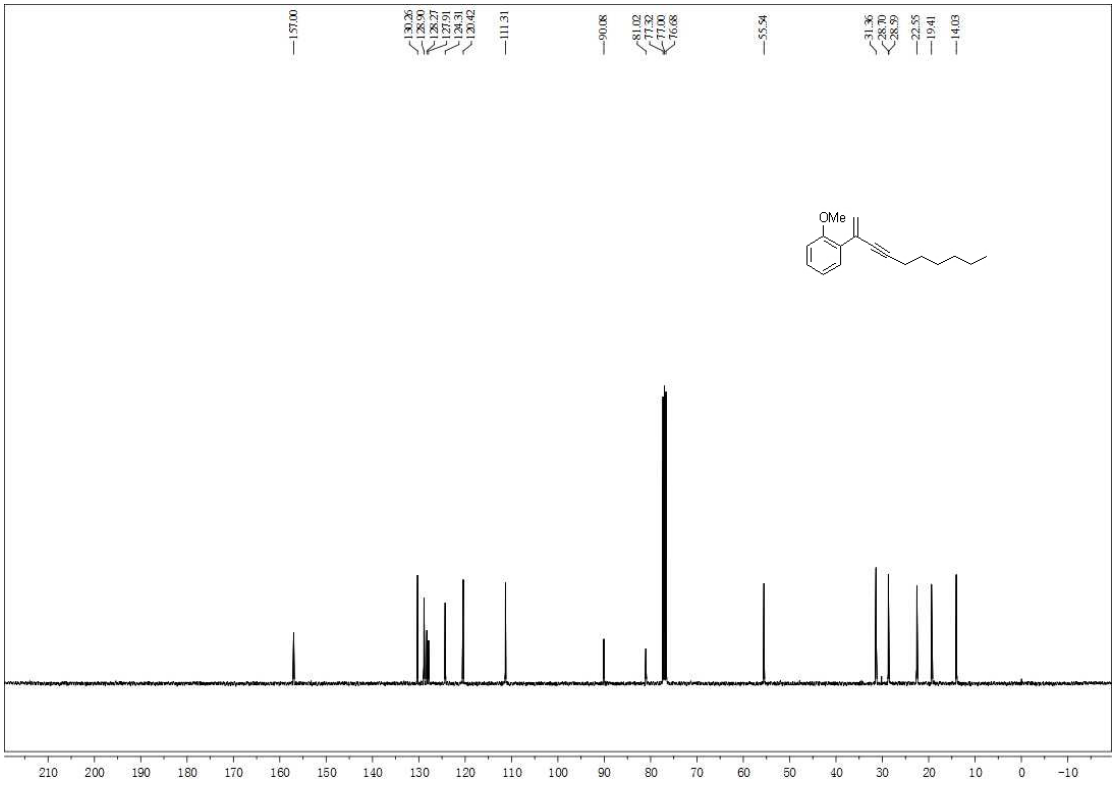

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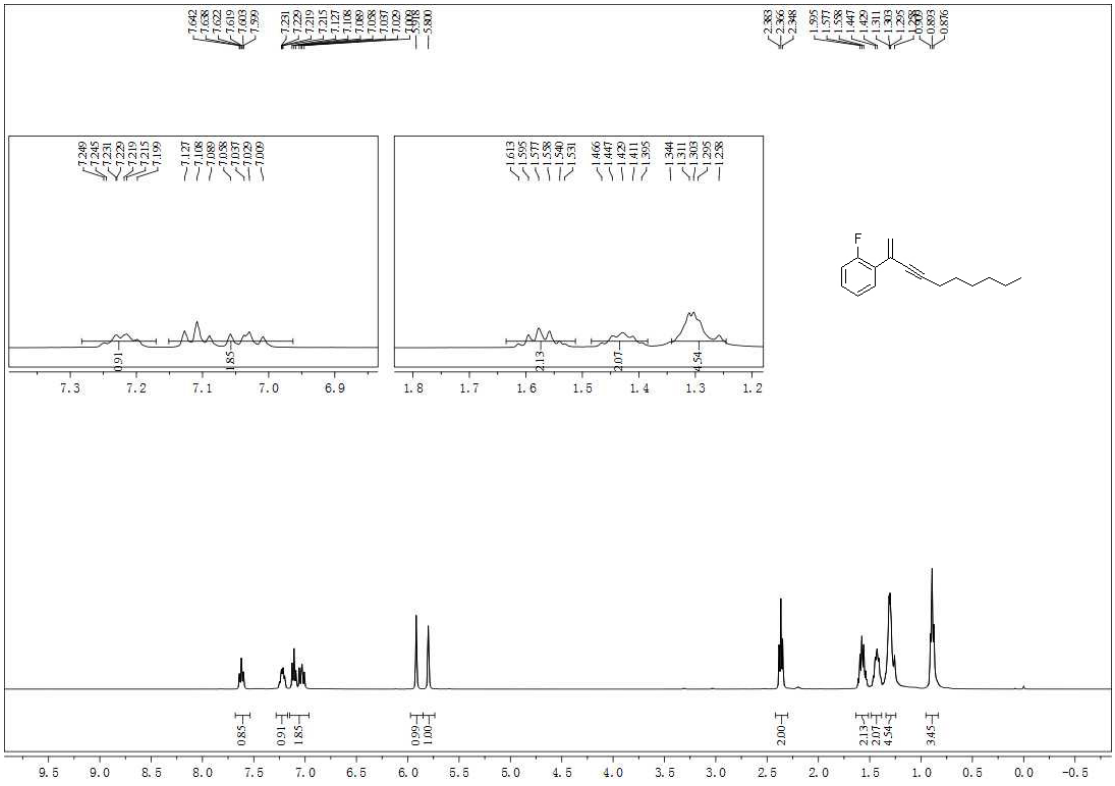

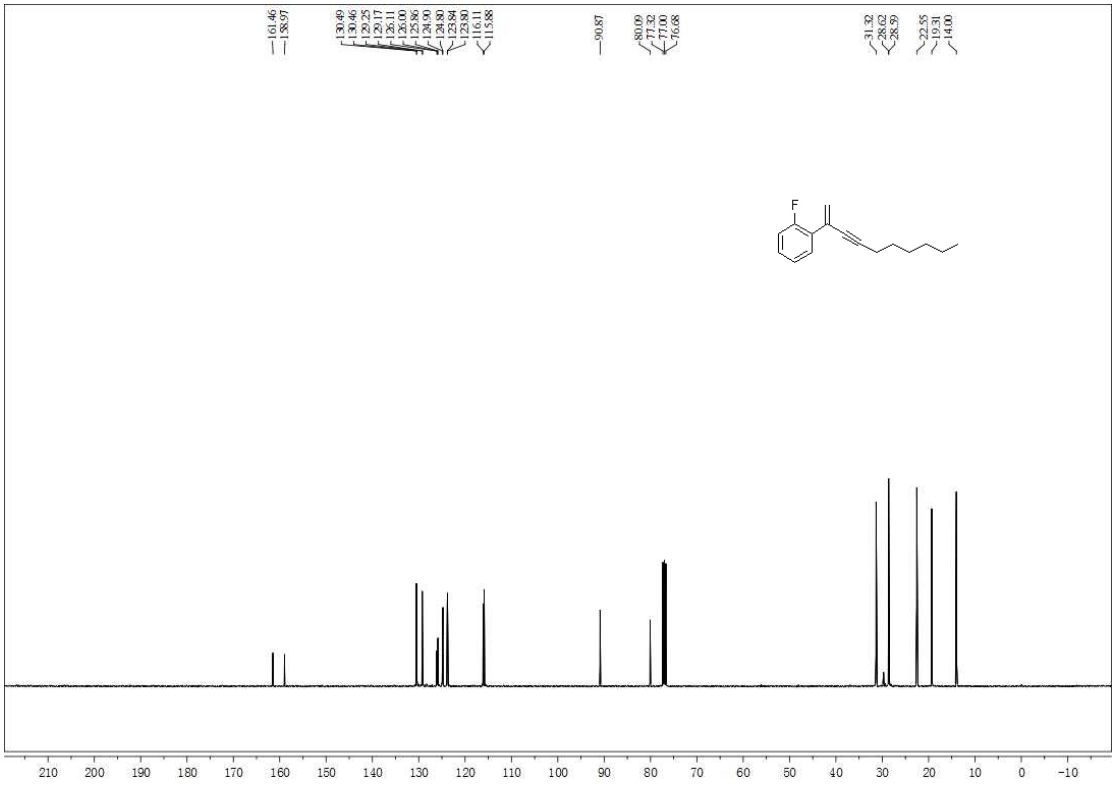

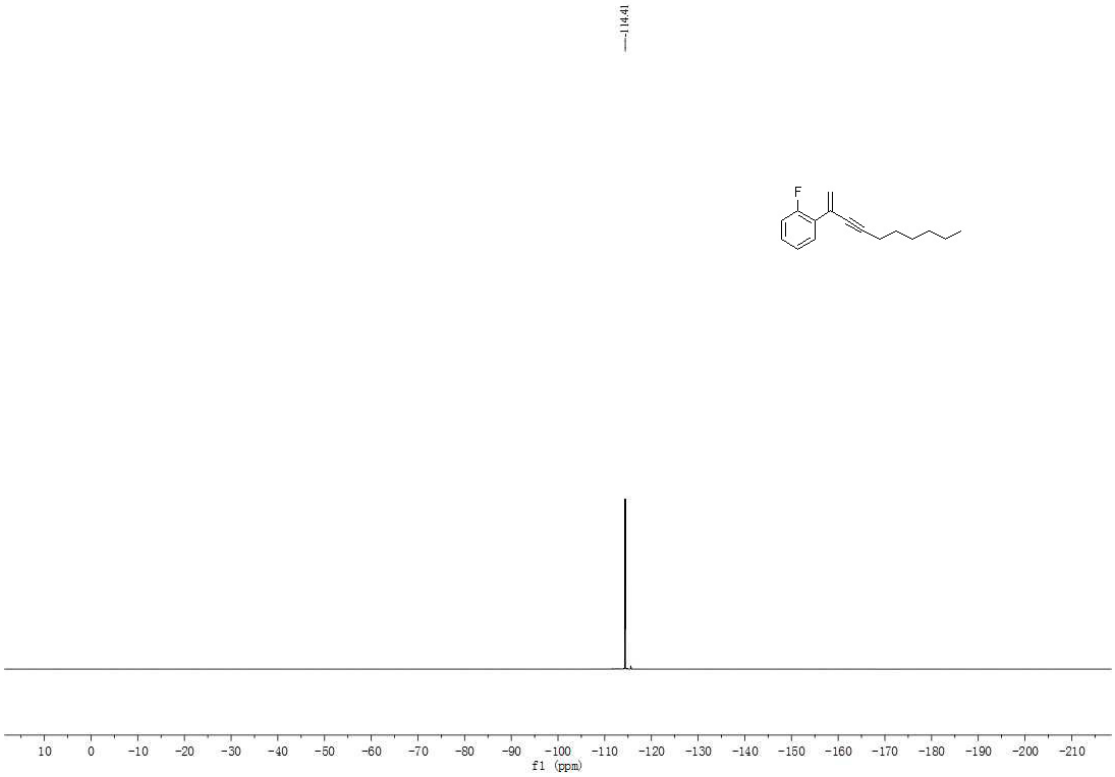
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F
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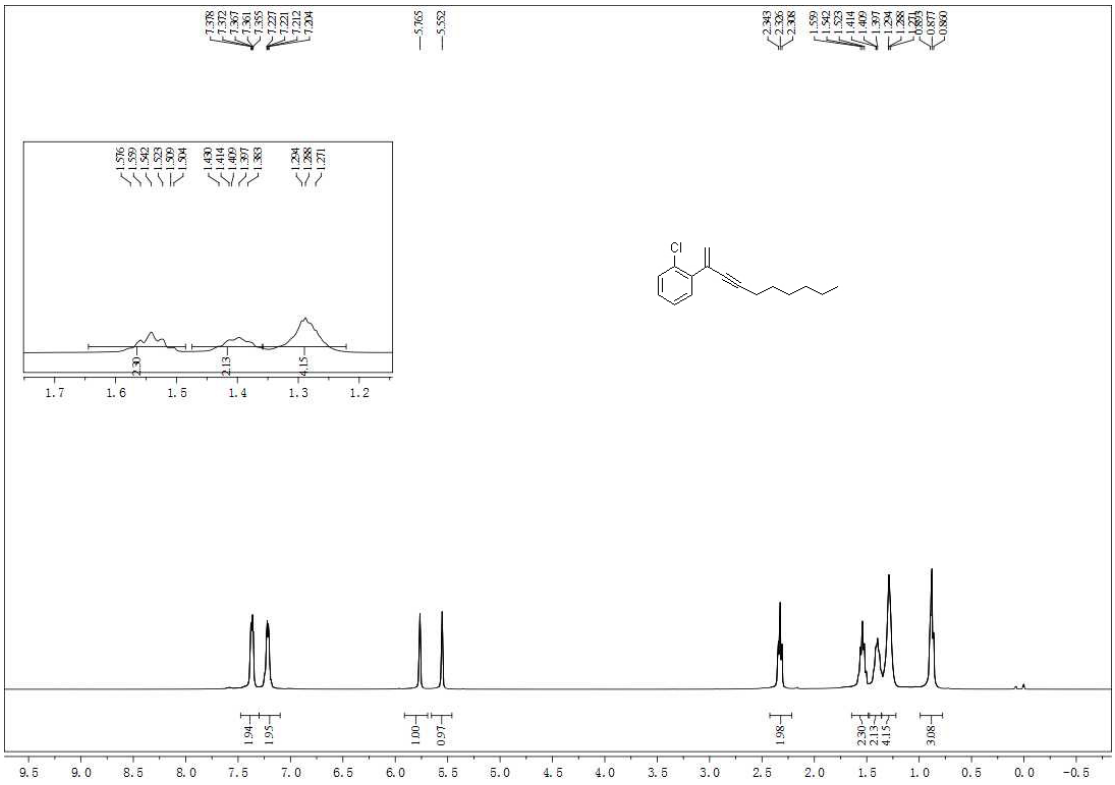
f1 (ppm)

Product 1j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1.409
1.397
1.294
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0.877
0.860
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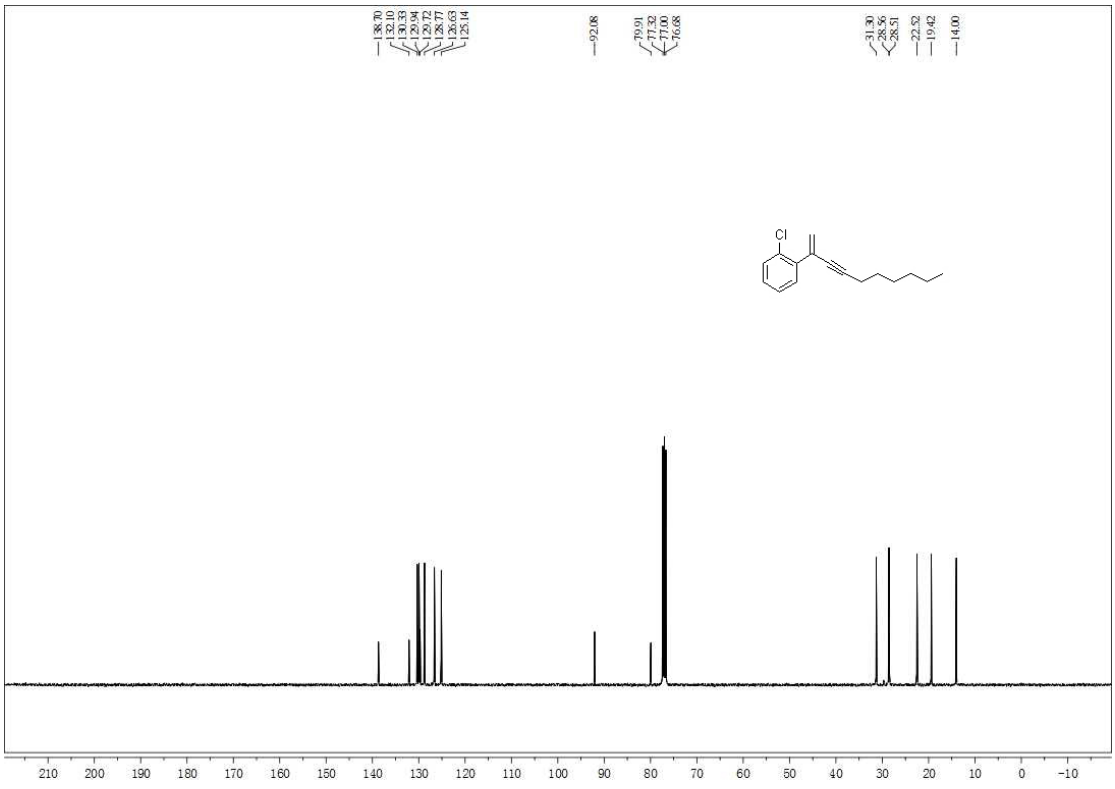
1.559
1.542
1.523
1.509
1.504
1.430
1.414
1.409
1.397
1.388
1.294
1.288
1.271
2.30
2.13
4.15
1.7 1.6 1.5 1.4 1.3 1.2
Cl
1.94
1.95
1.00
0.97
1.98
2.30
2.13
4.15
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5



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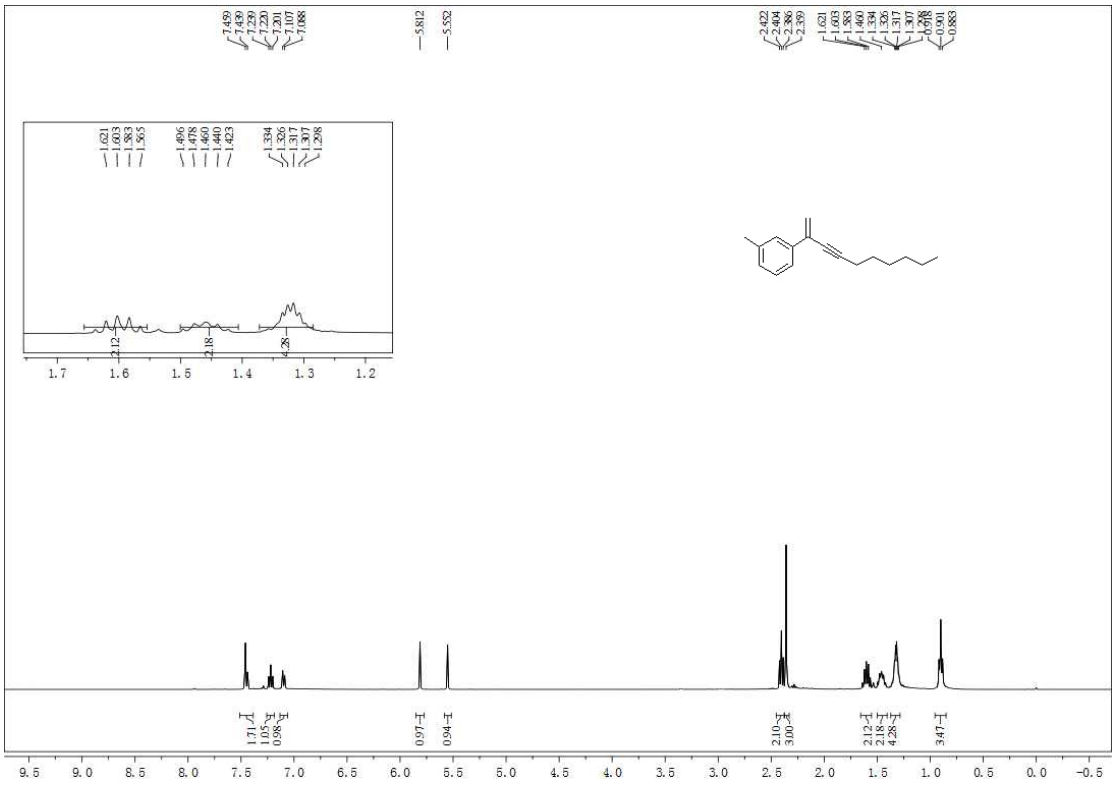
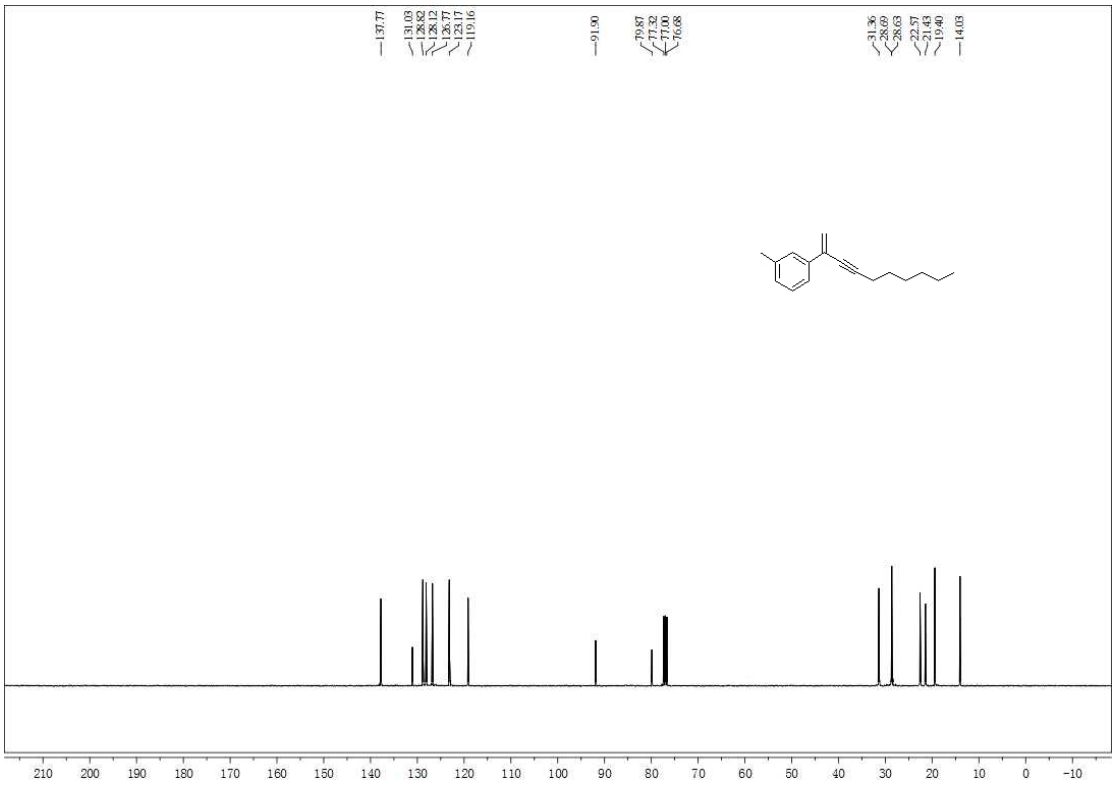
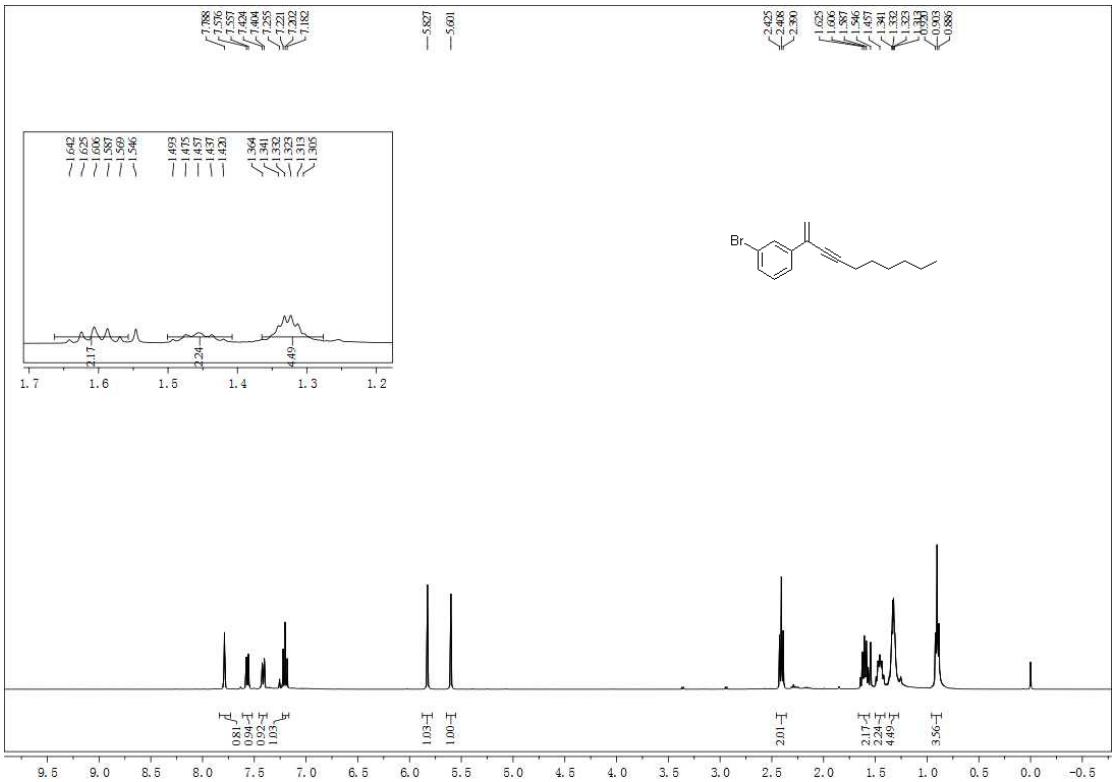
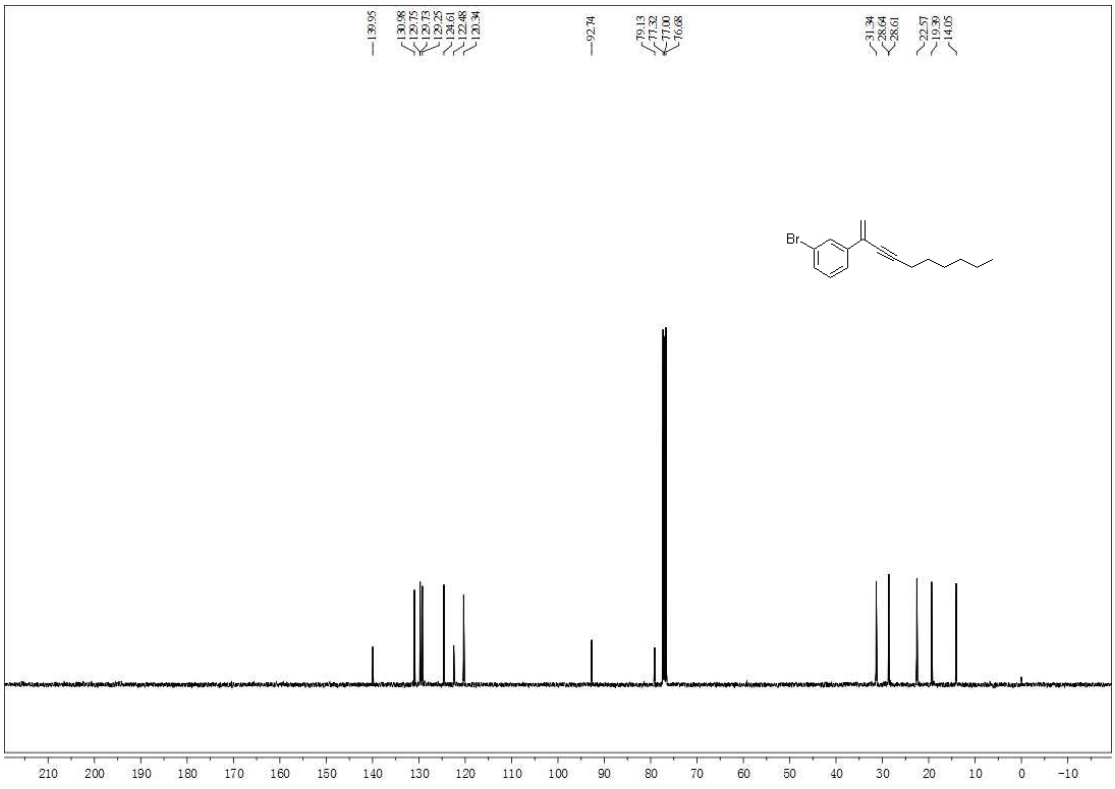




Product 1l

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76.68
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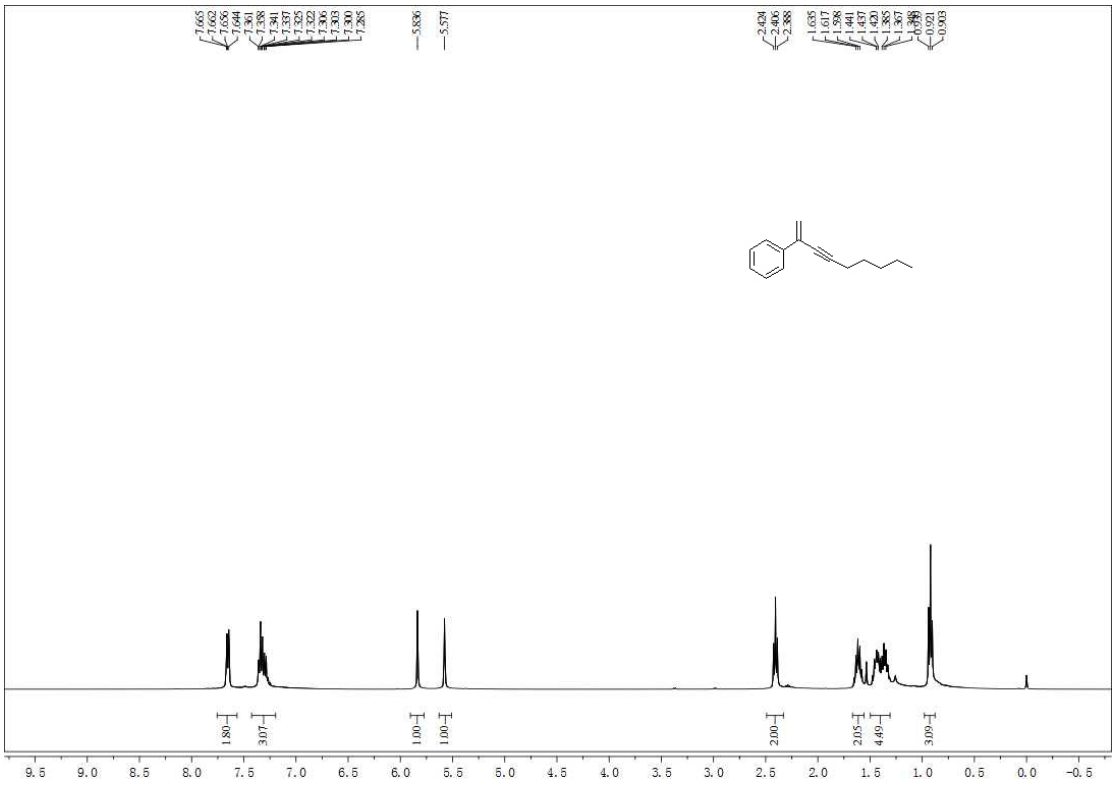
22.57
19.39
14.05
Br

Product 1m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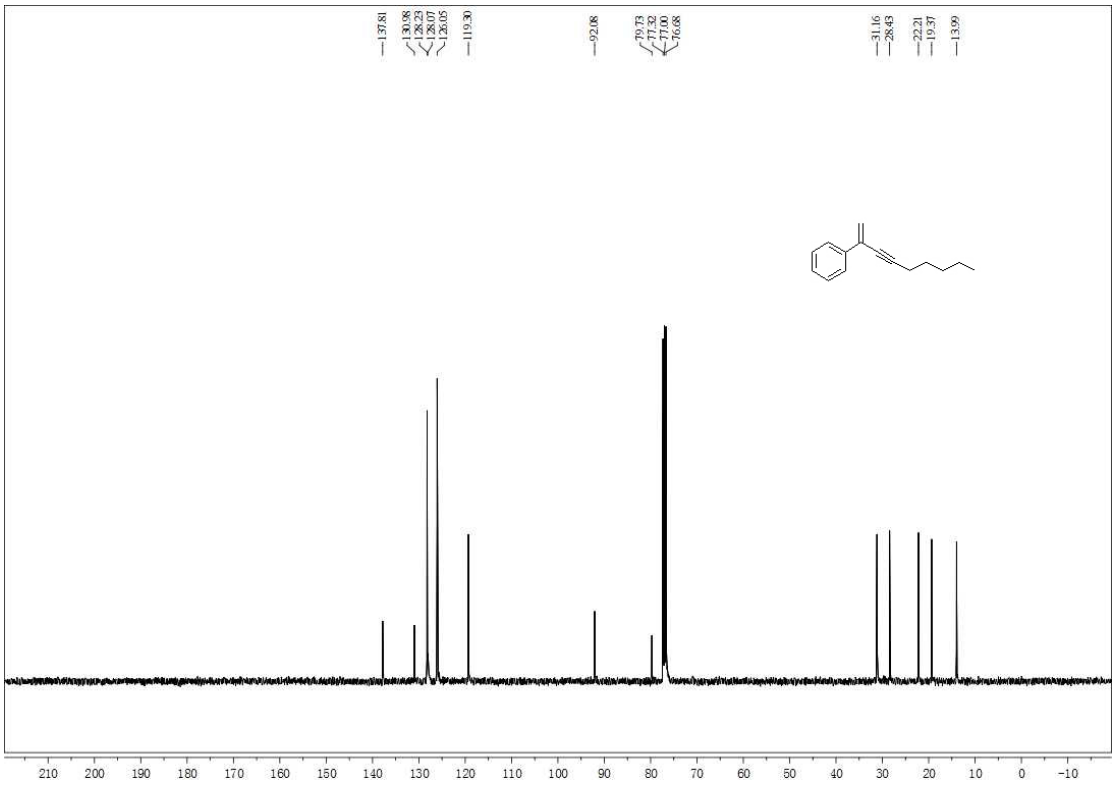
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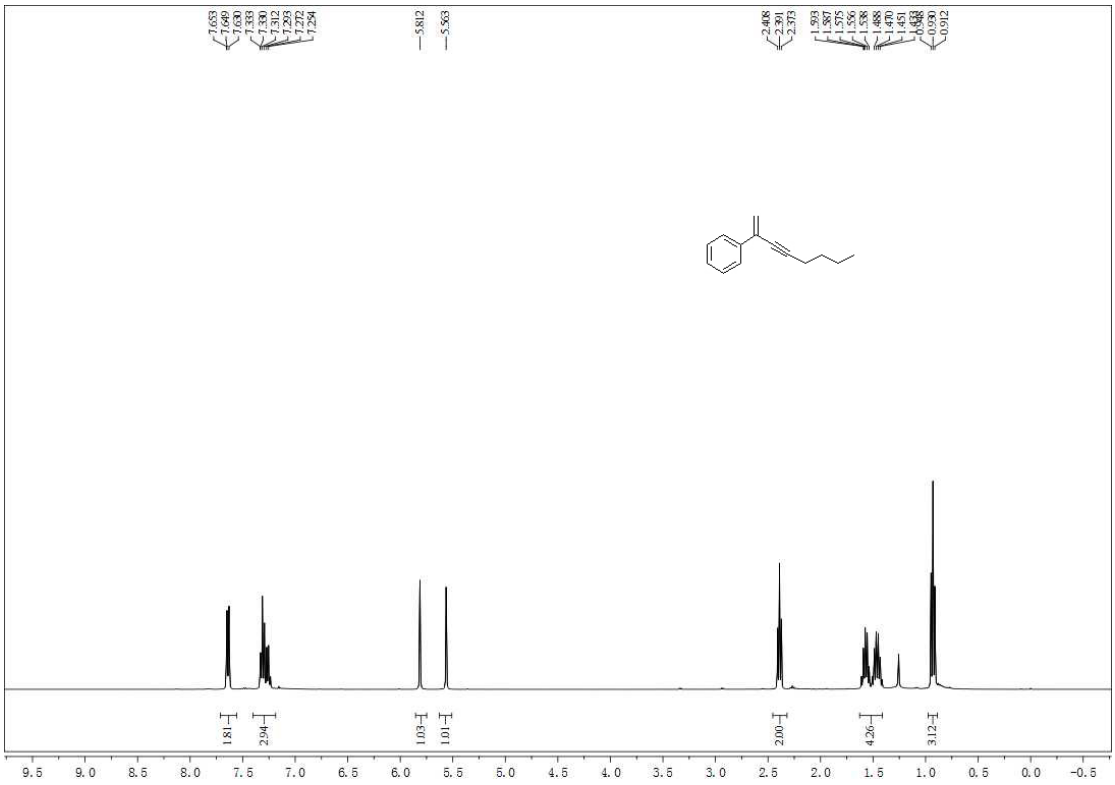
Product 1n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1.538
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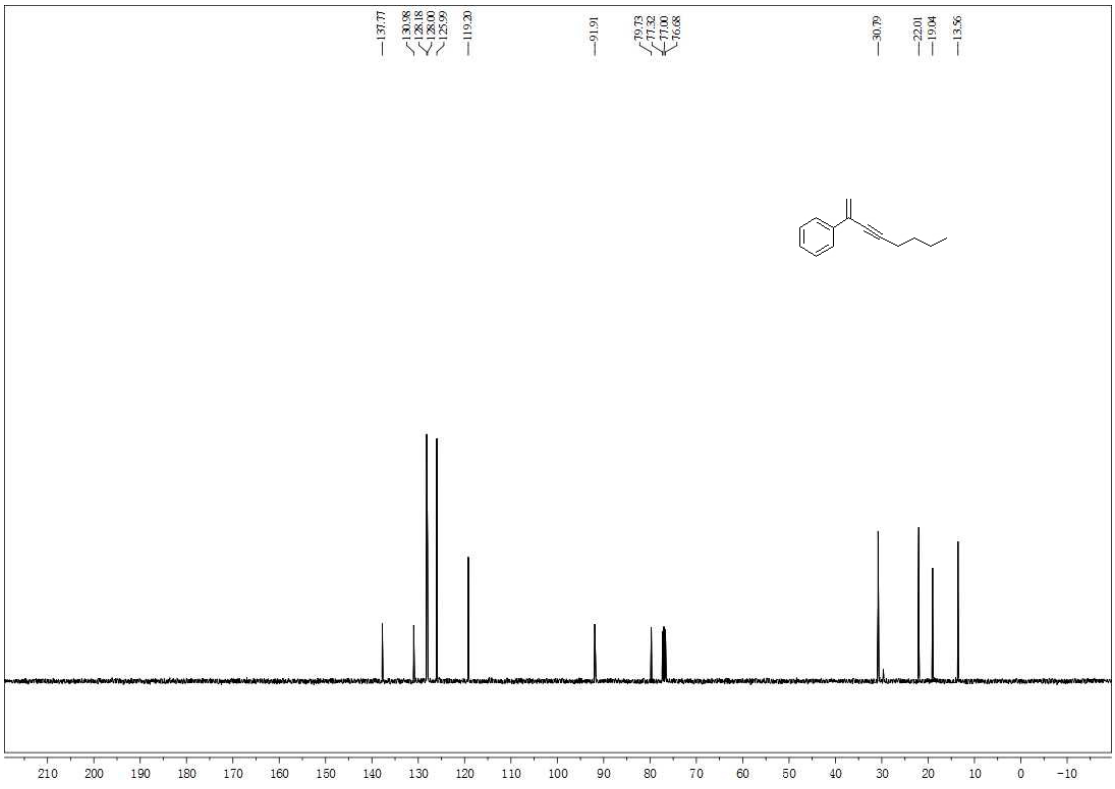
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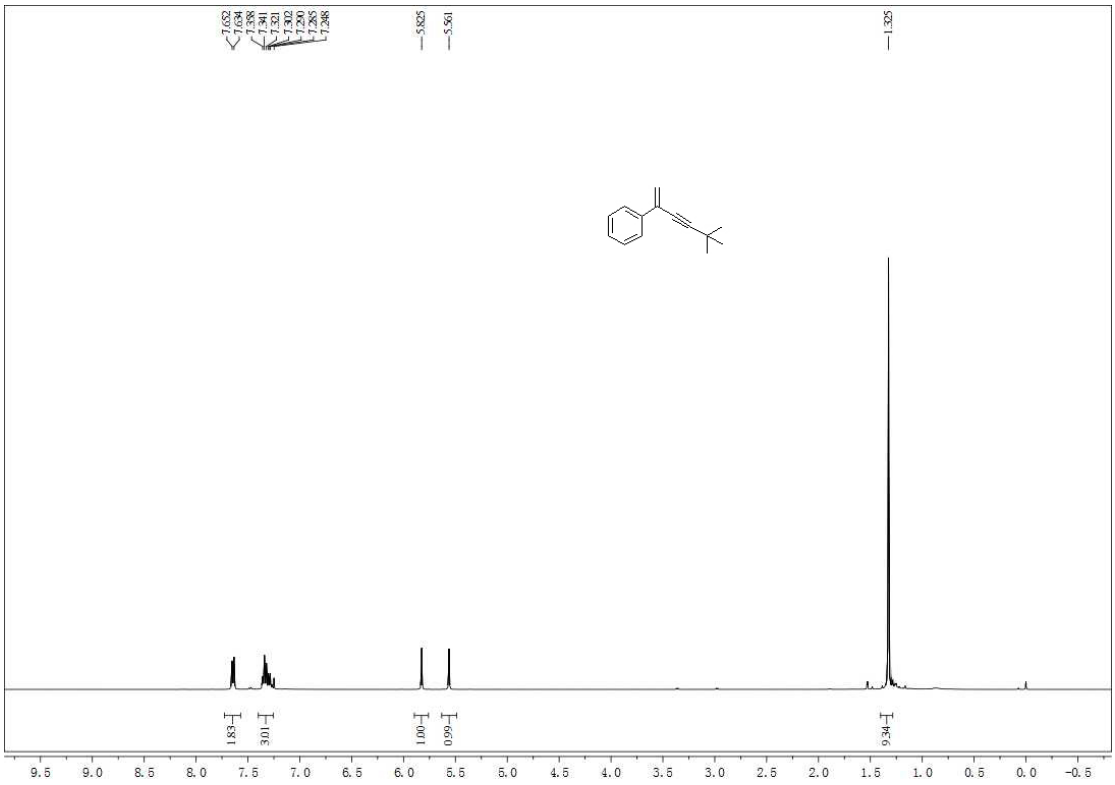
Product 1o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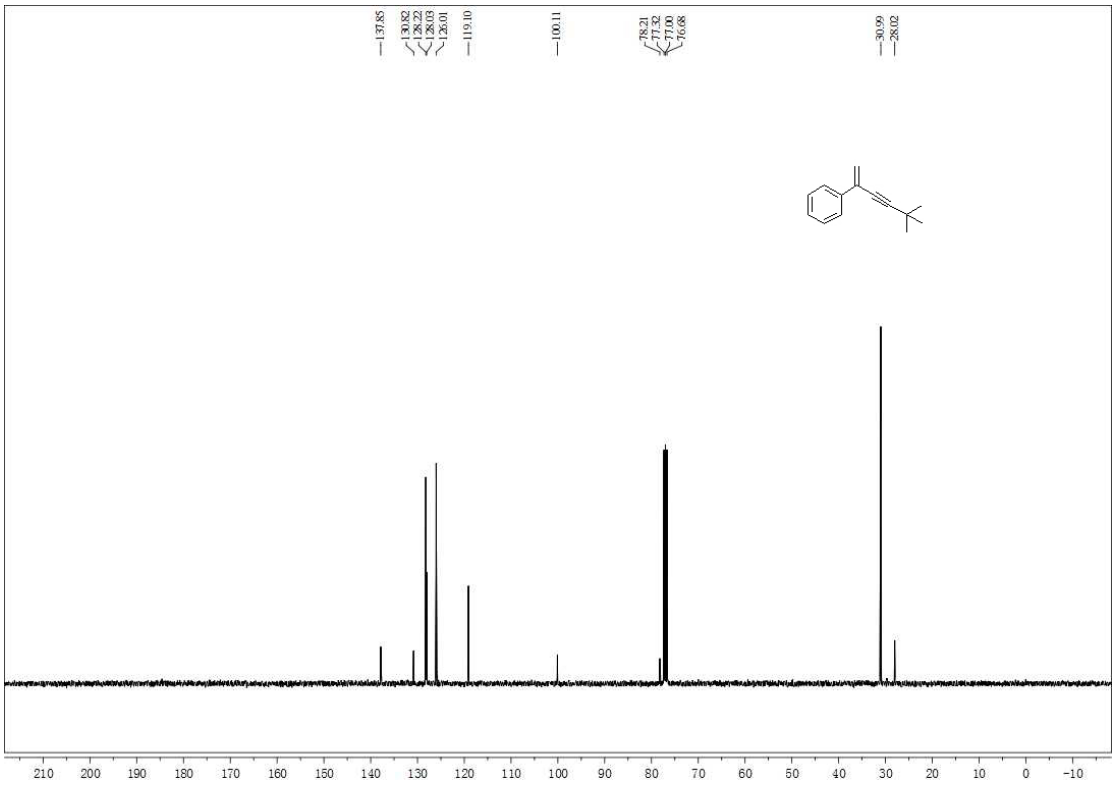
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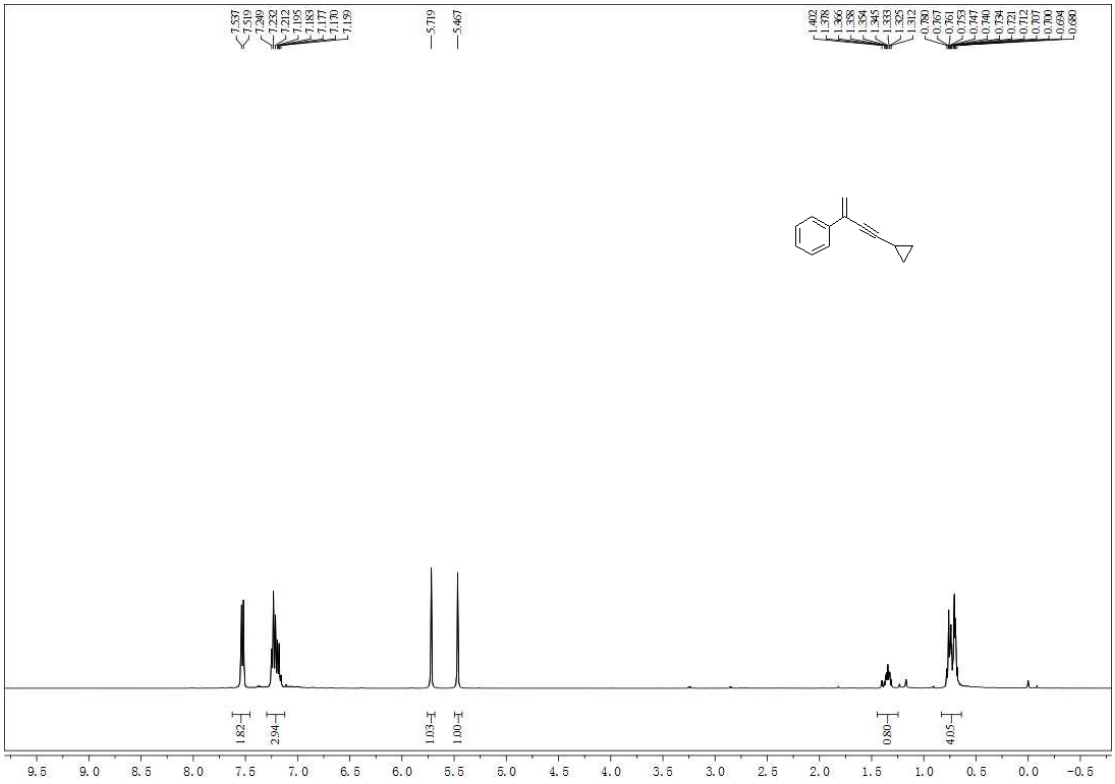
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1.354
1.345
1.333
1.325
1.312
0.780
0.767
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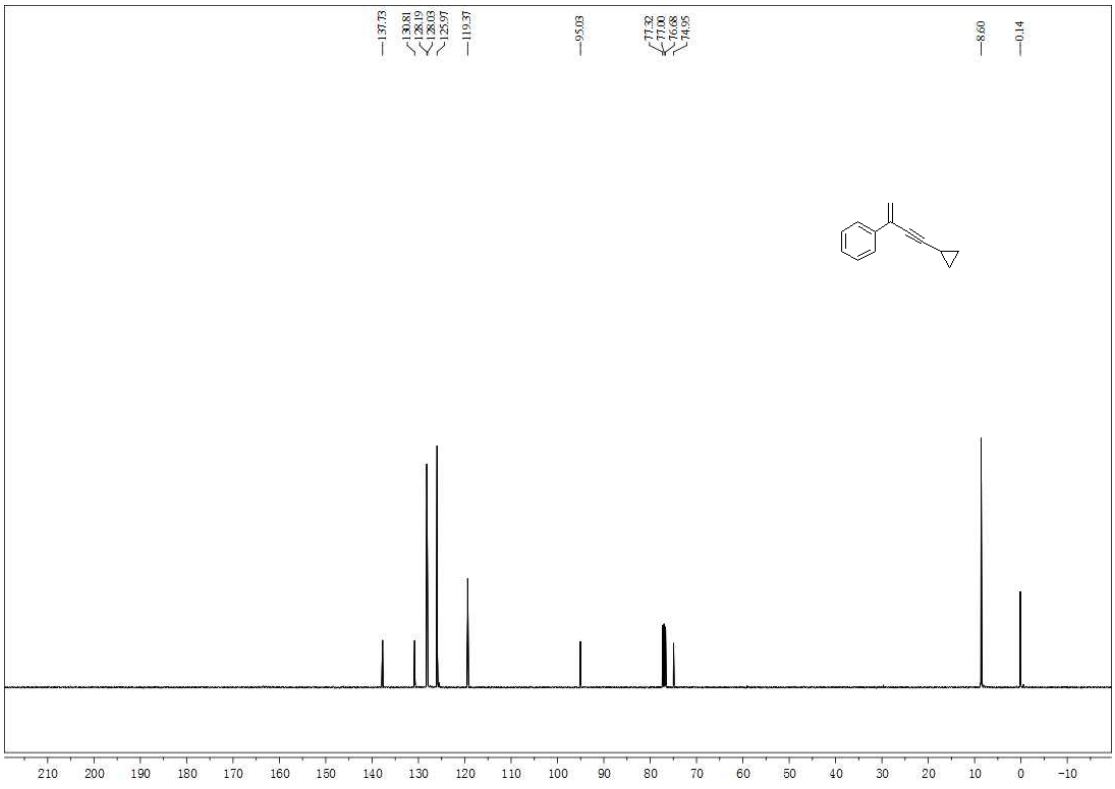
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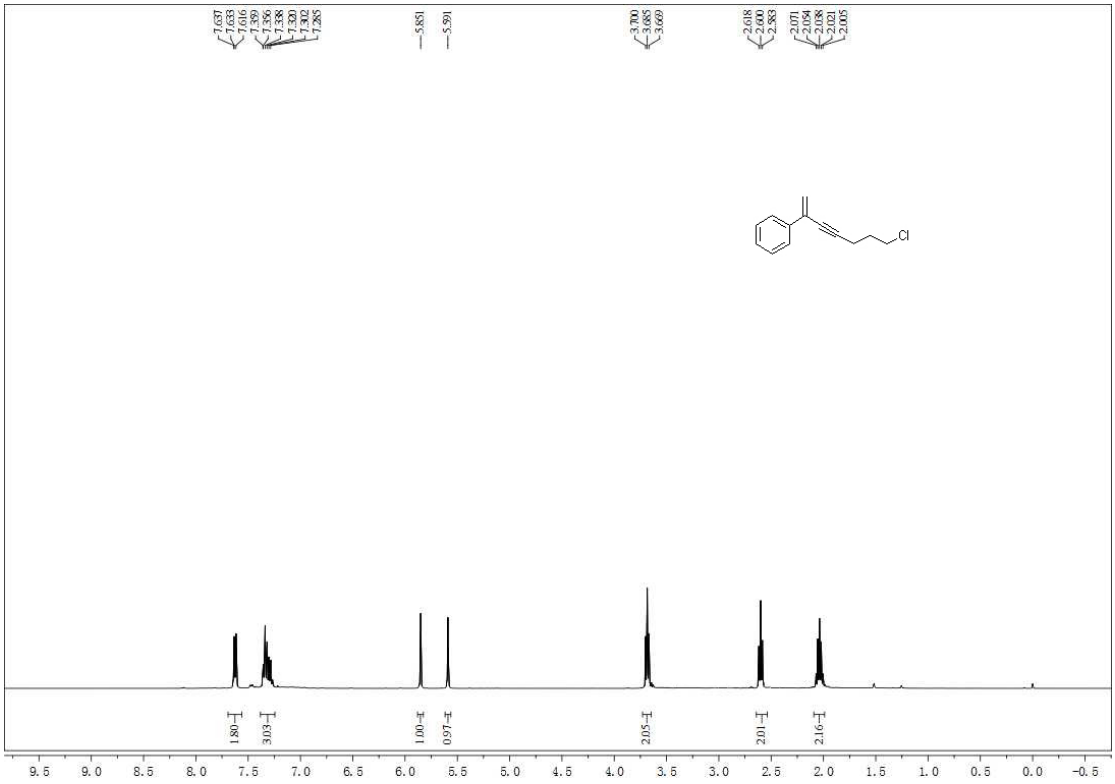
Product 1q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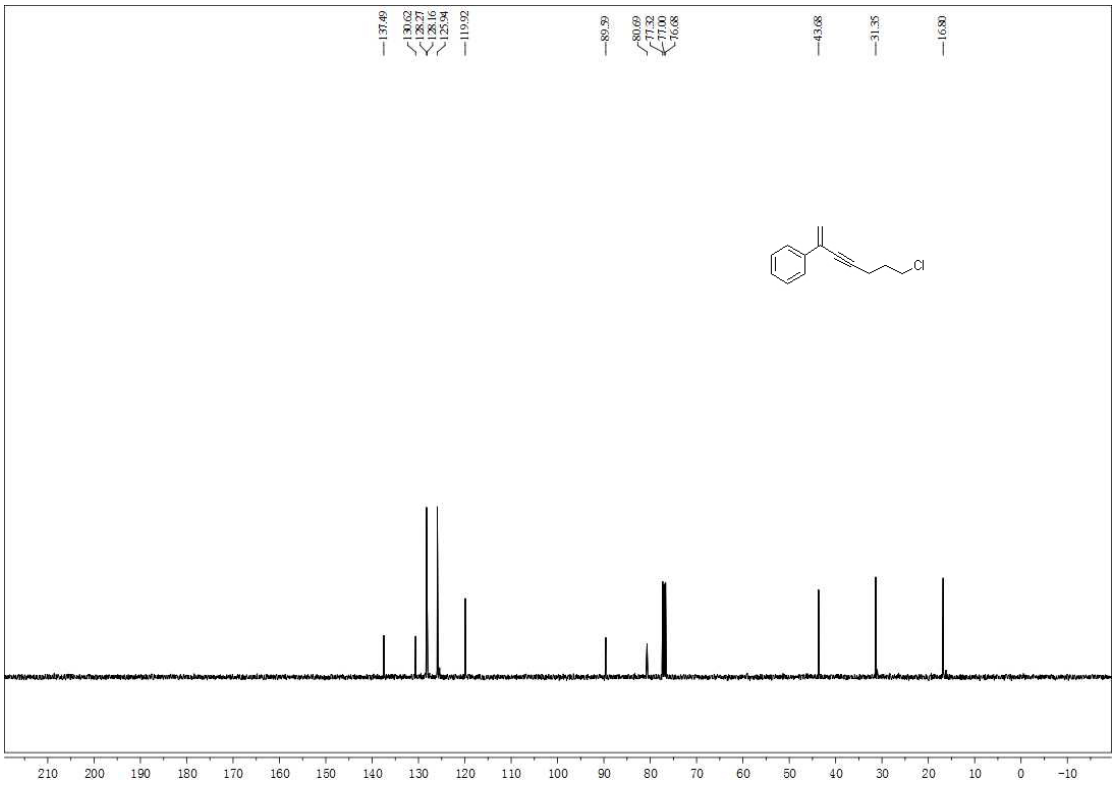
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Cl
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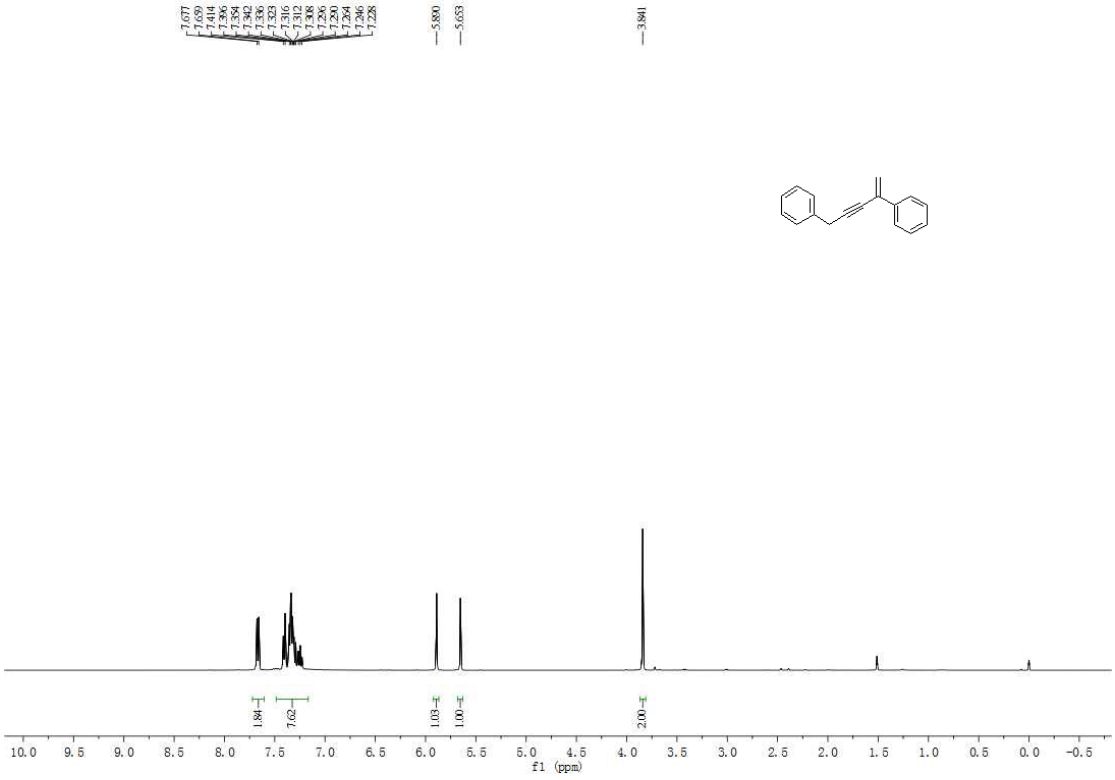
Product 1r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7.246
7.228
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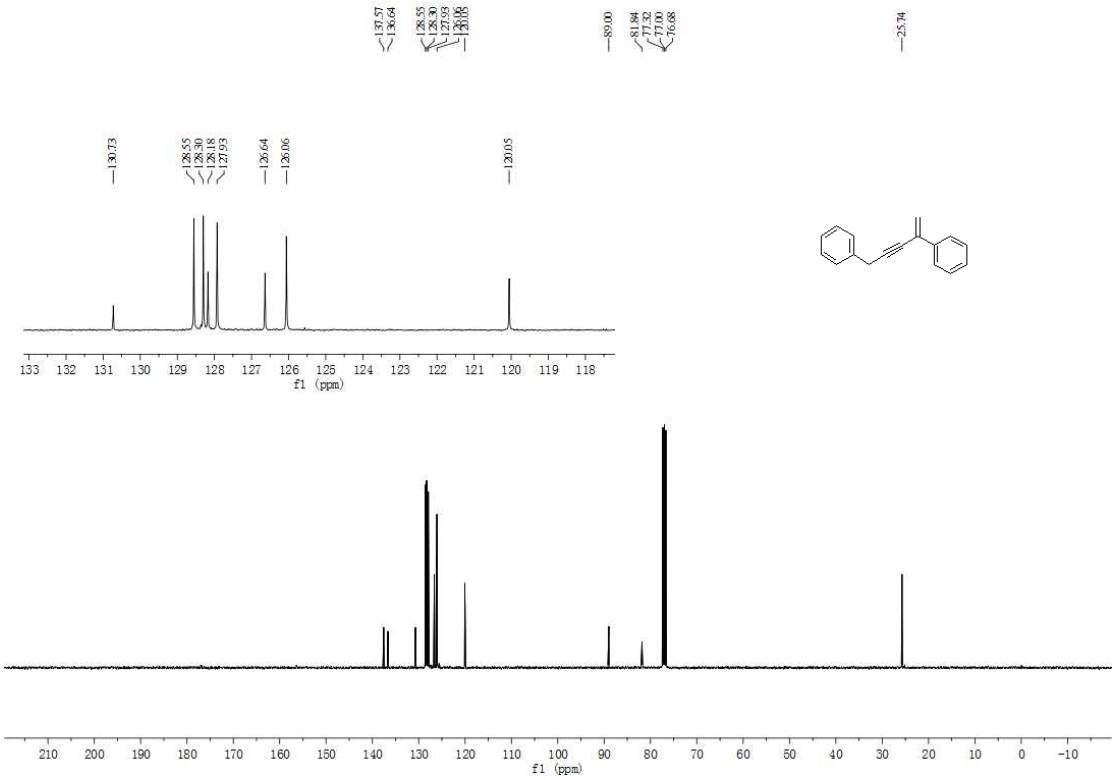
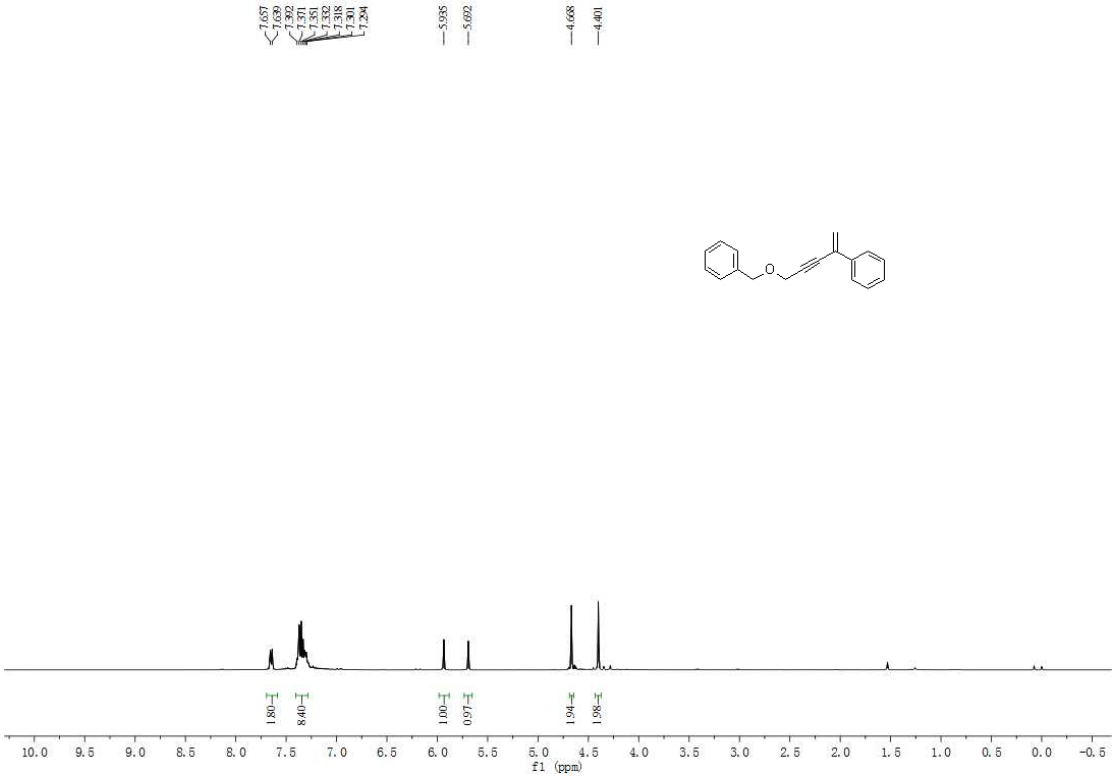
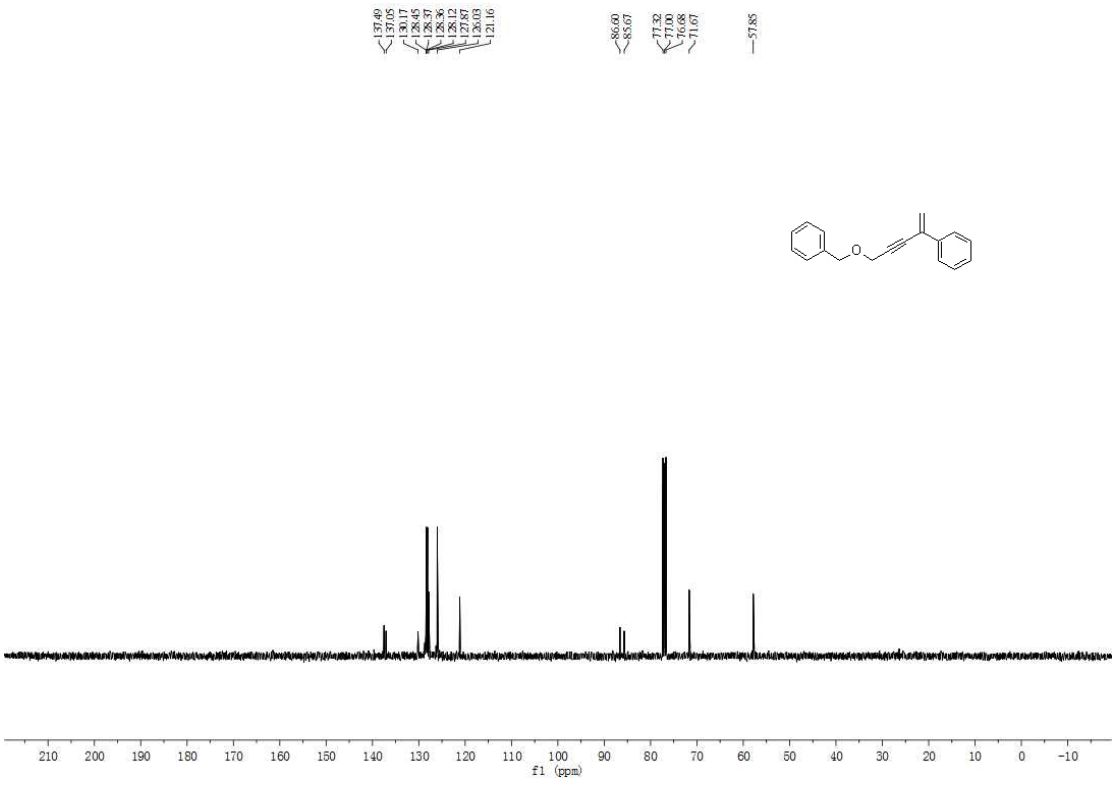
5.653
3.841
1.84
7.62
1.03
1.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



Product 1s

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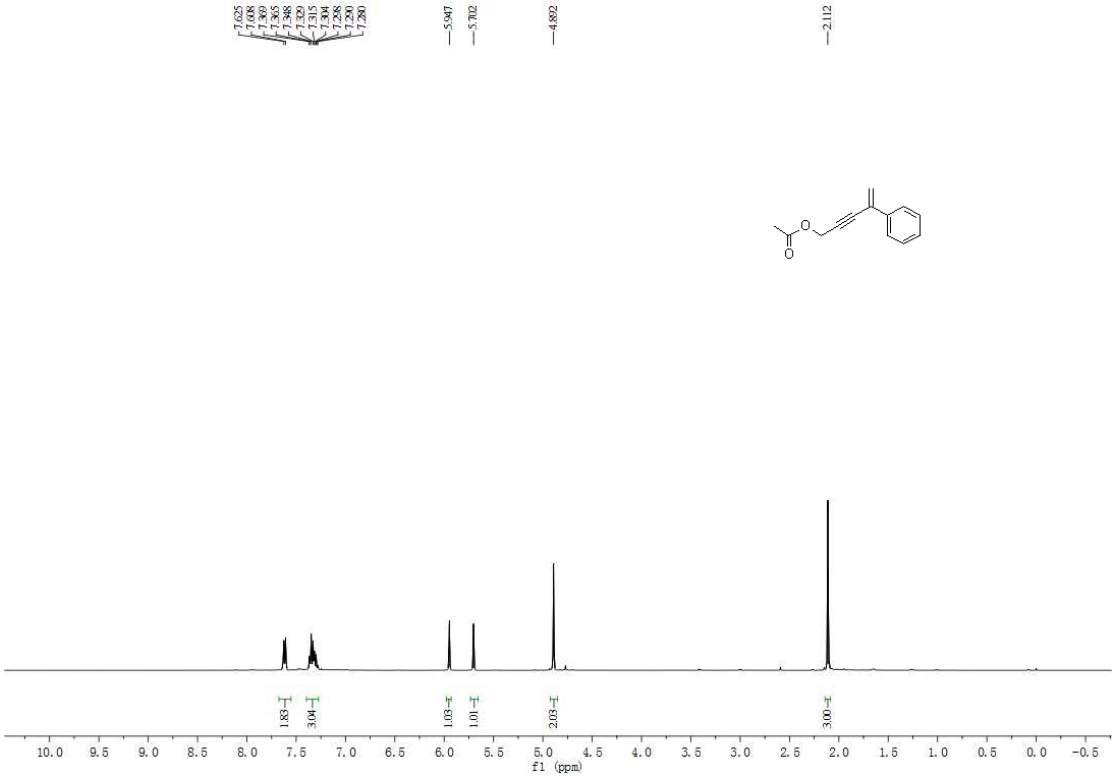
127.87
127.67
121.16
86.60
85.67
71.32
77.00
76.68
71.67
57.85
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Product 1t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7.230
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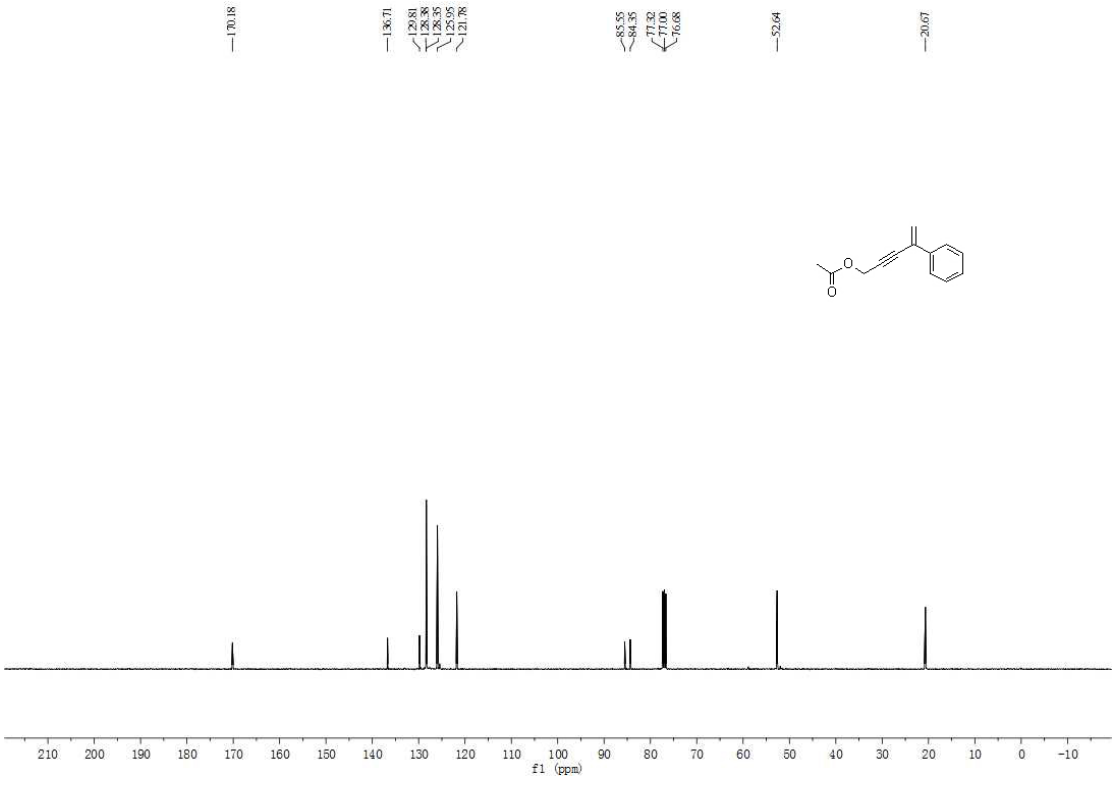
5.702
4.892
2.112
O
O
1.83
3.04
1.03
1.01
2.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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O
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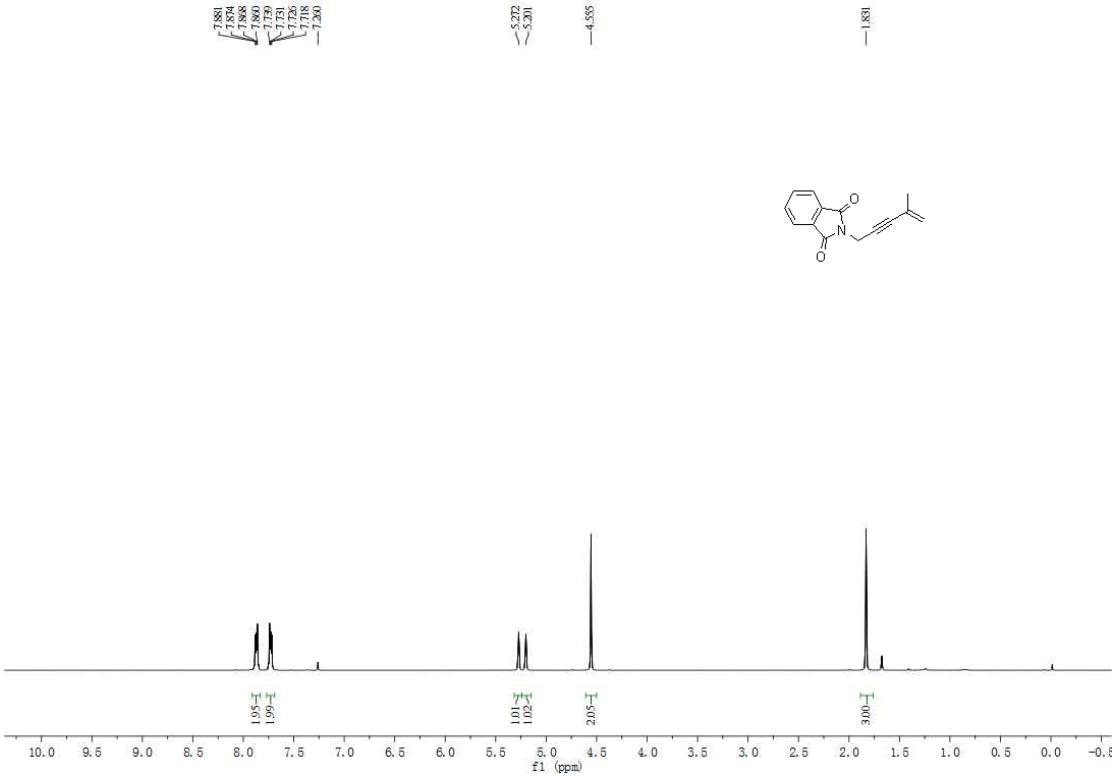
f1 (ppm)

Product 1u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O
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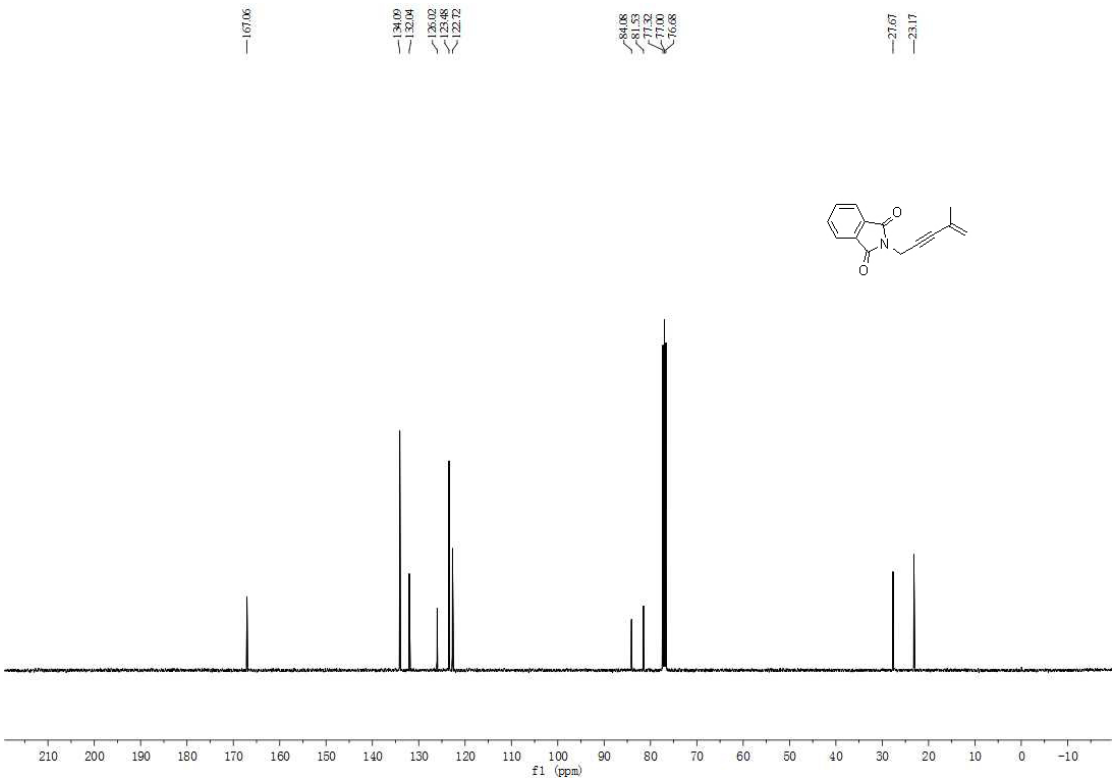
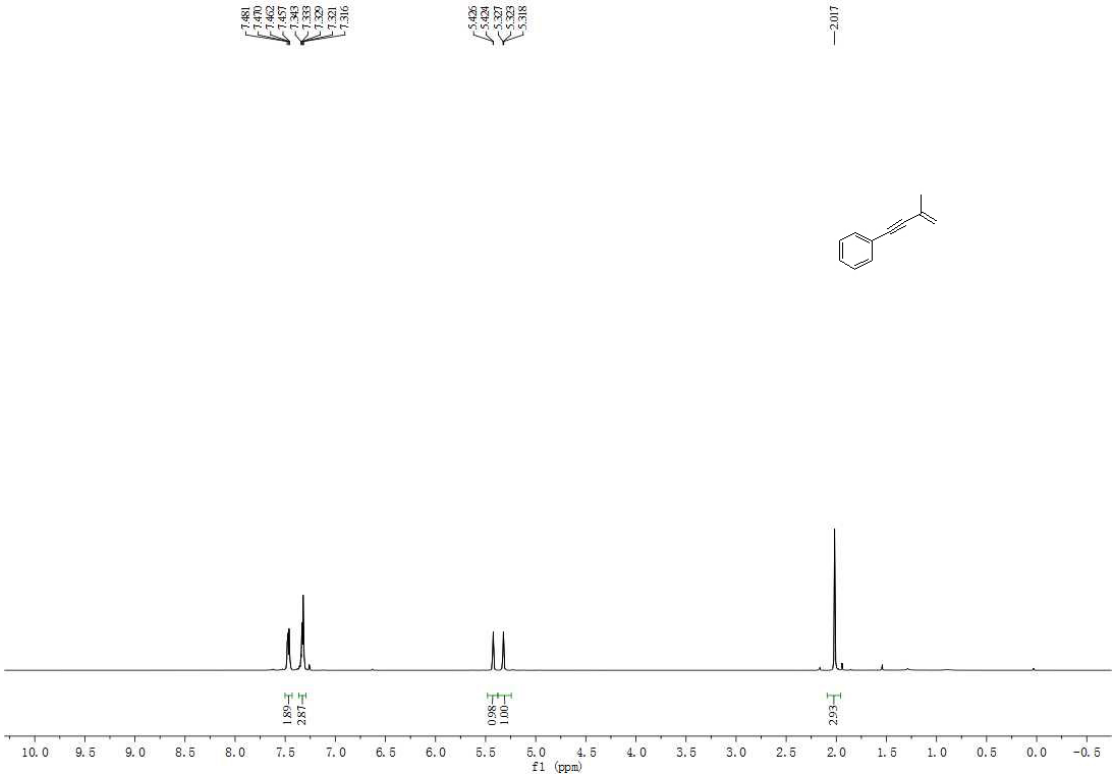
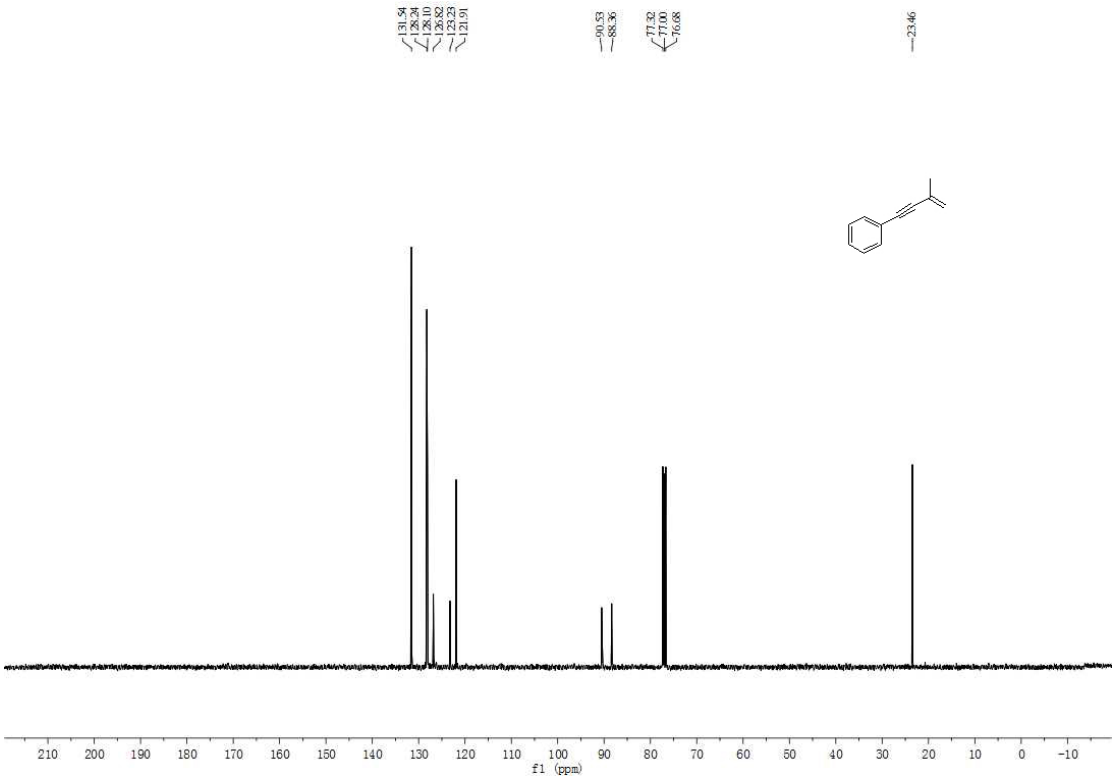
1.02
2.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

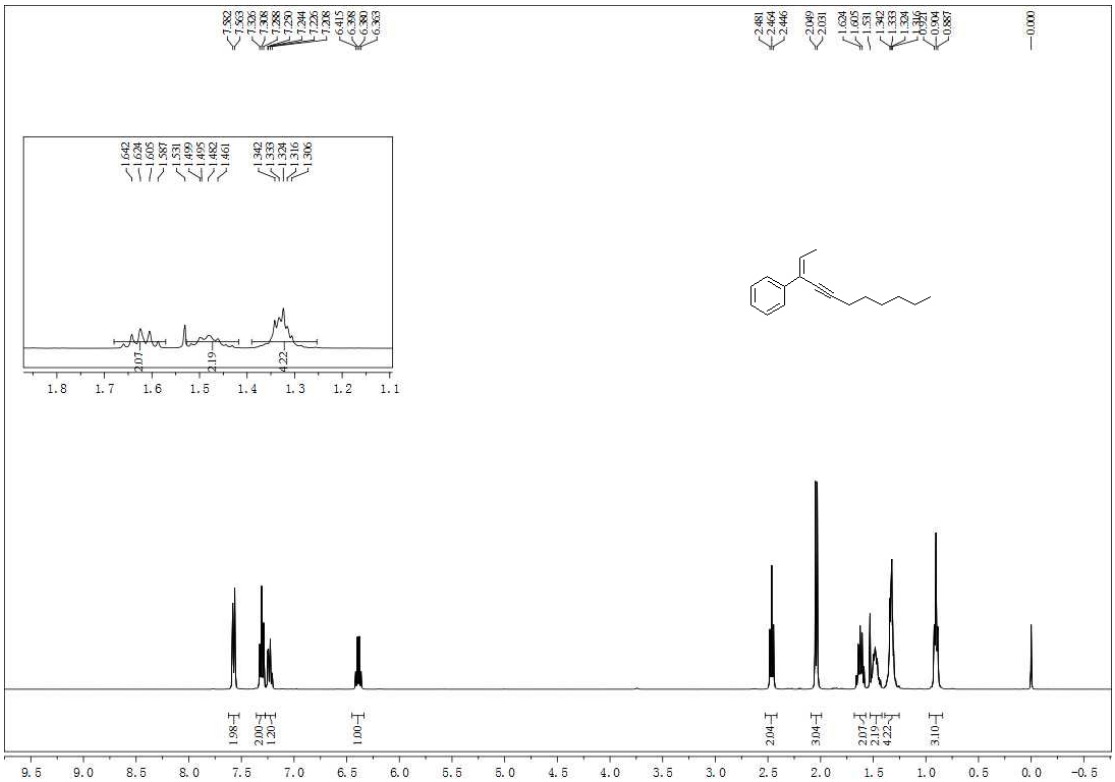

167.06
134.09
132.04
126.02
123.48
122.72
84.08
81.53
77.32
77.00
76.68
27.67
23.17
f1 (ppm)

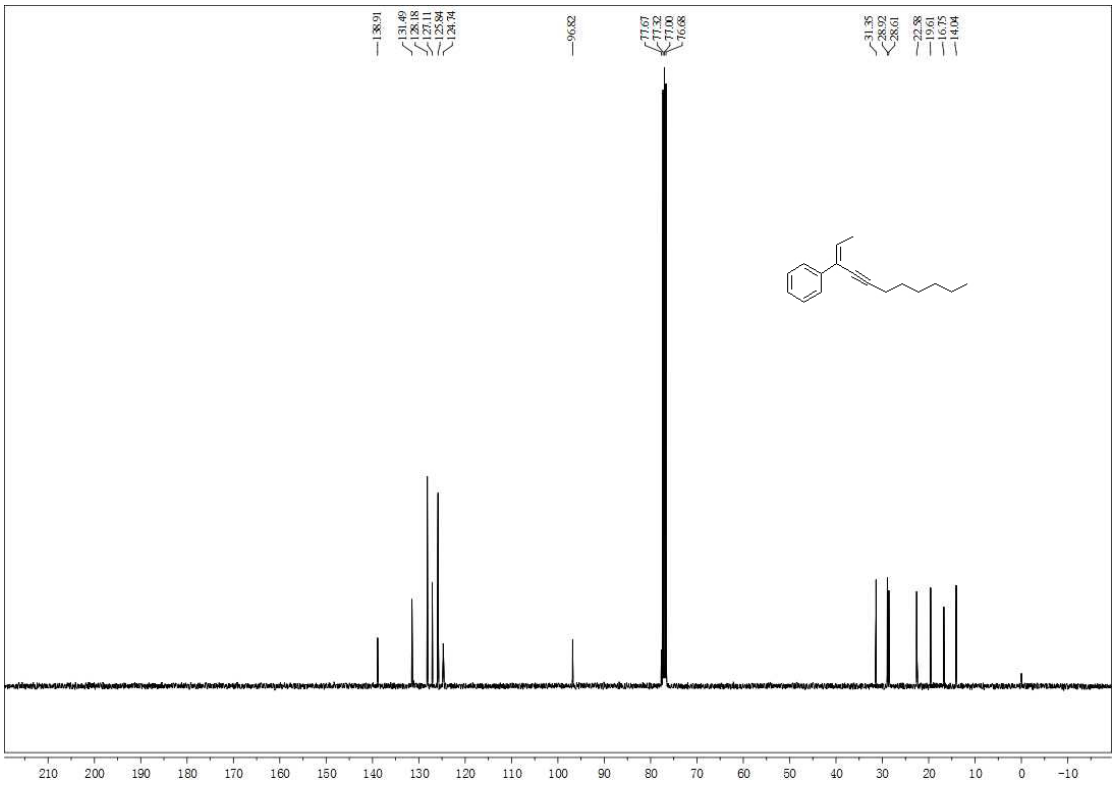
Product 1v


7.481
7.470
7.462
7.457
7.343
7.339
7.329
7.321
7.316
5.406
5.424
5.327
5.323
5.318
2.017
1.89
2.87
0.98
1.00
2.93
f1 (ppm)

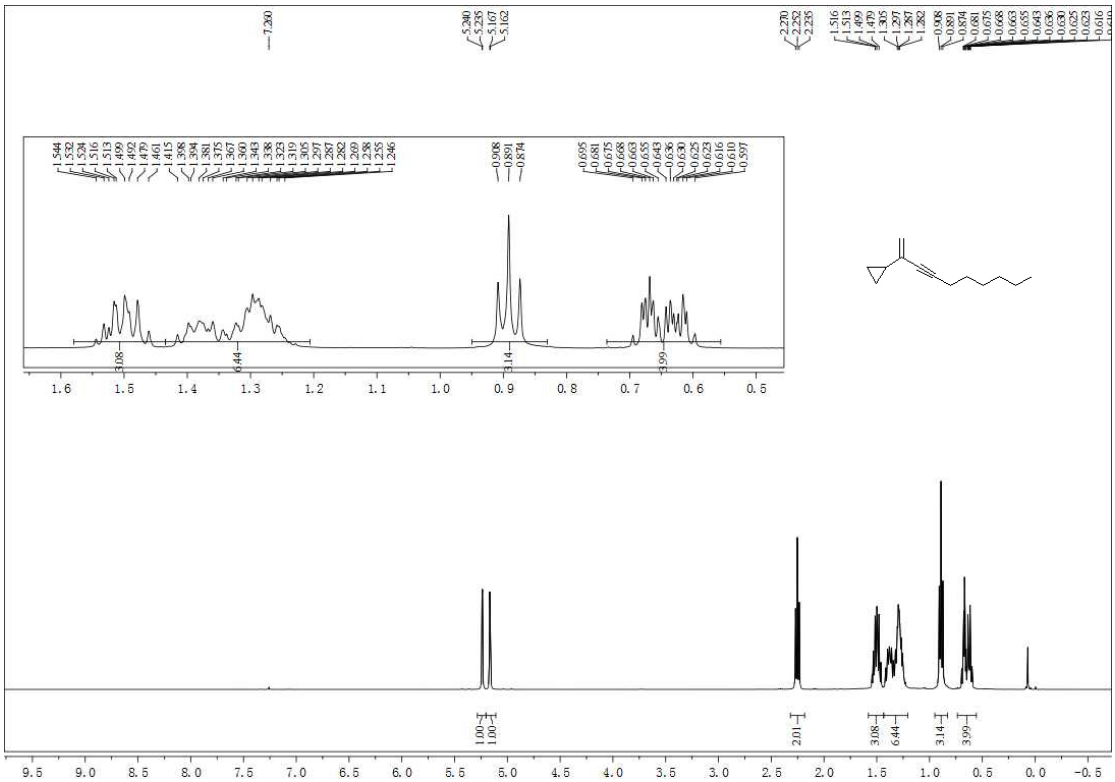

131.54
128.24
128.10
126.82
123.23
121.91
90.53
88.36
77.32
77.00
76.68
23.46
f1 (ppm)

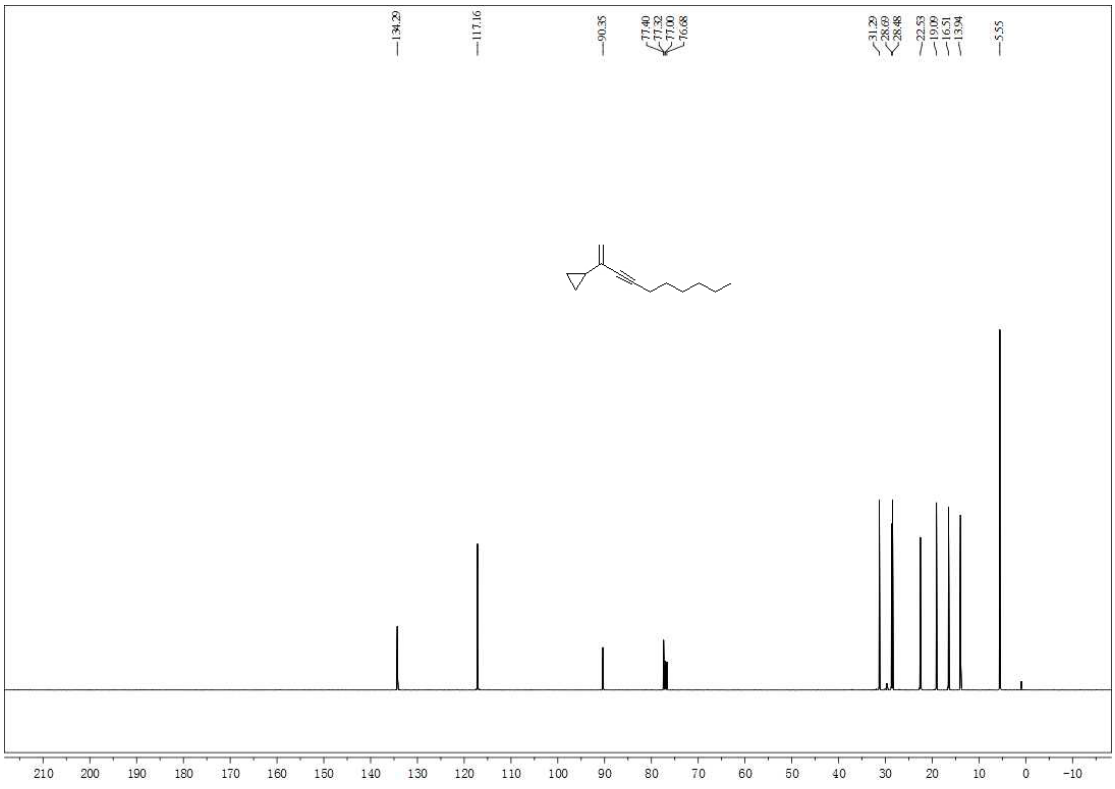
Product 1w


7.582
7.565
7.330
7.308
7.288
7.250
7.244
7.226
7.208
6.415
6.398
6.380
6.303
2.481
2.464
2.446
2.049
2.031
1.624
1.605
1.531
1.342
1.333
1.324
0.904
0.887
0.000
1.642
1.624
1.605
1.587
1.531
1.499
1.495
1.482
1.461
1.342
1.333
1.324
1.316
1.306
2.07
2.19
4.22
1.98
2.00
1.20
1.00
2.04
3.04
2.07
2.19
4.22
3.10

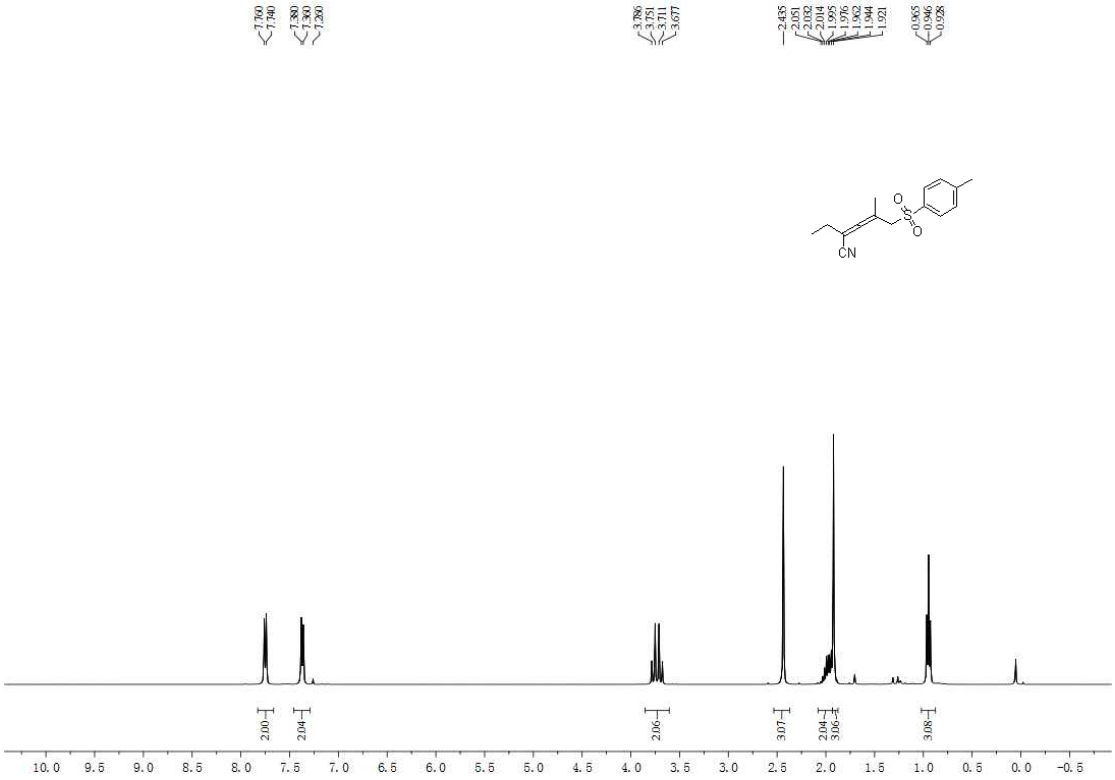


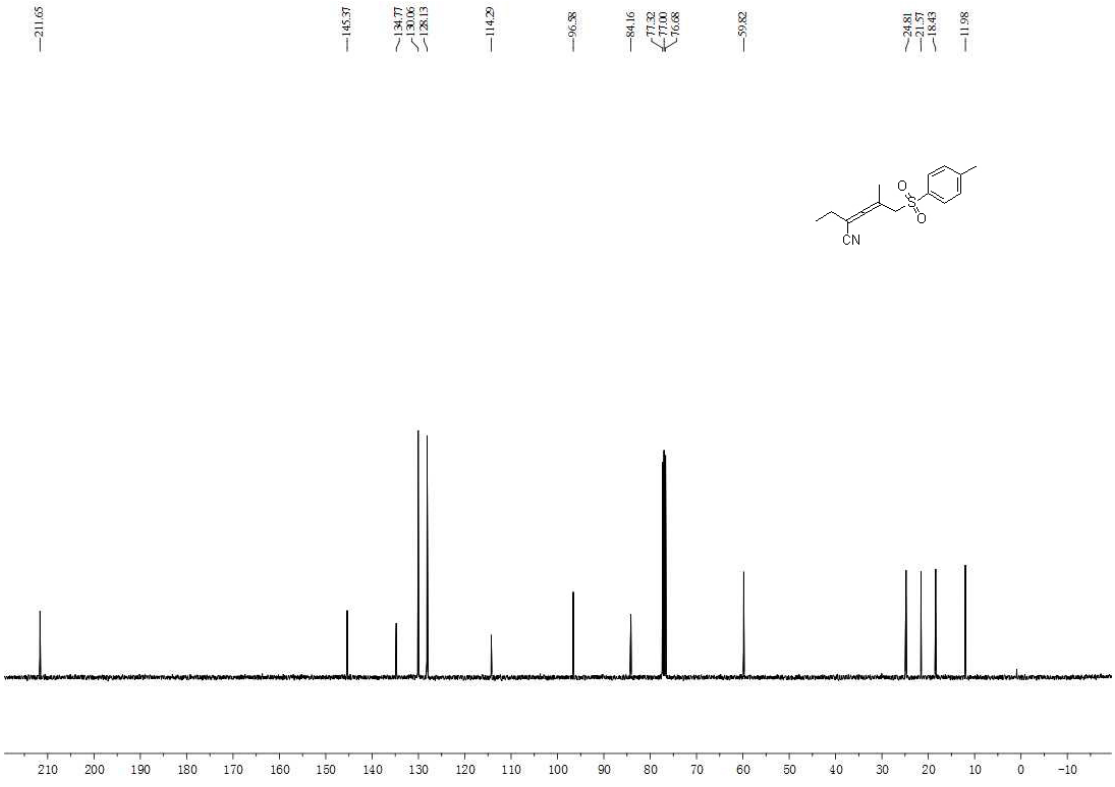
Product 1y



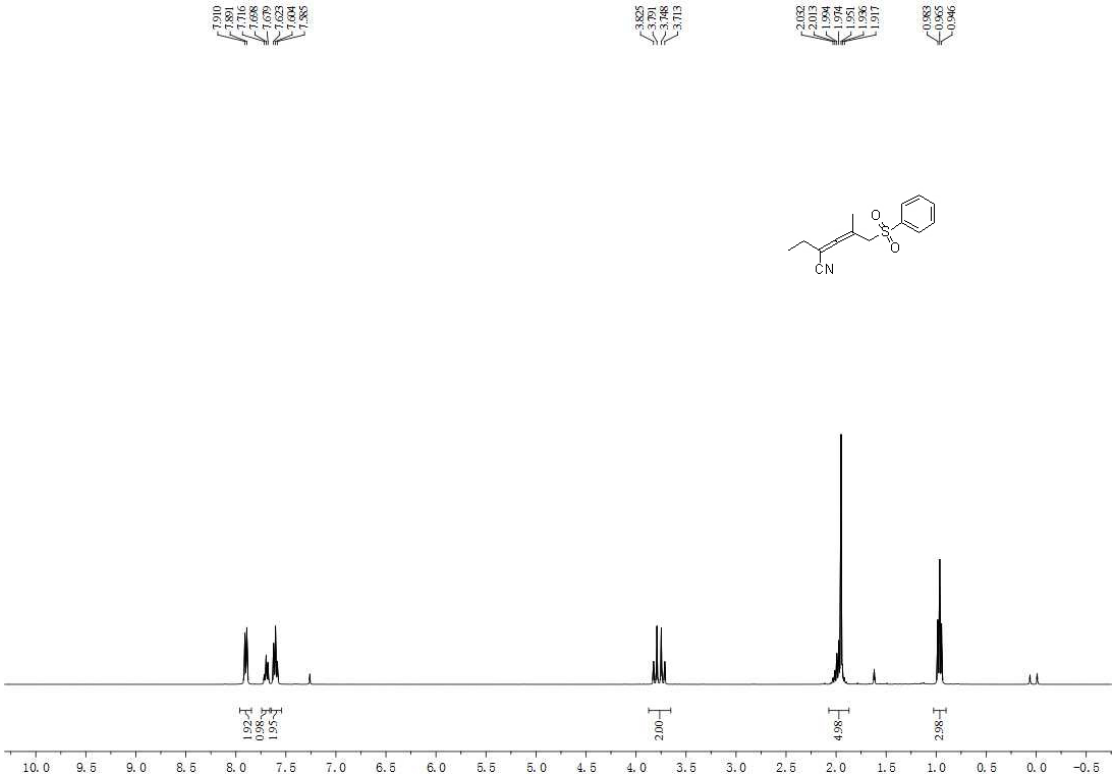

134.29
117.16
90.35
77.40
77.32
77.00
76.68
31.29
28.69
28.48
22.53
19.09
16.51
13.94
5.55

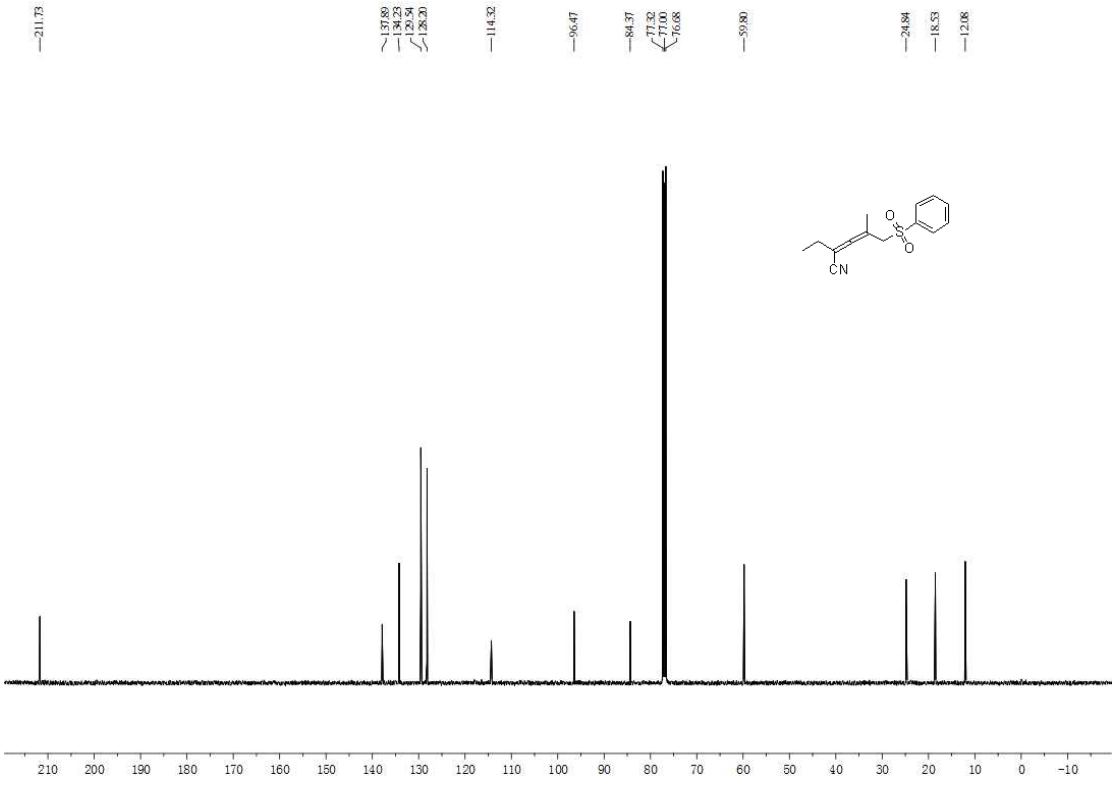
Product 3a


7.760
7.740
7.380
7.300
7.200
3.786
3.751
3.711
3.677
2.435
2.051
2.032
2.014
1.995
1.976
1.942
1.904
1.921
0.965
0.946
0.928
O
S
O
CN
2.00
2.04
2.06
3.07
2.04
3.06
3.08

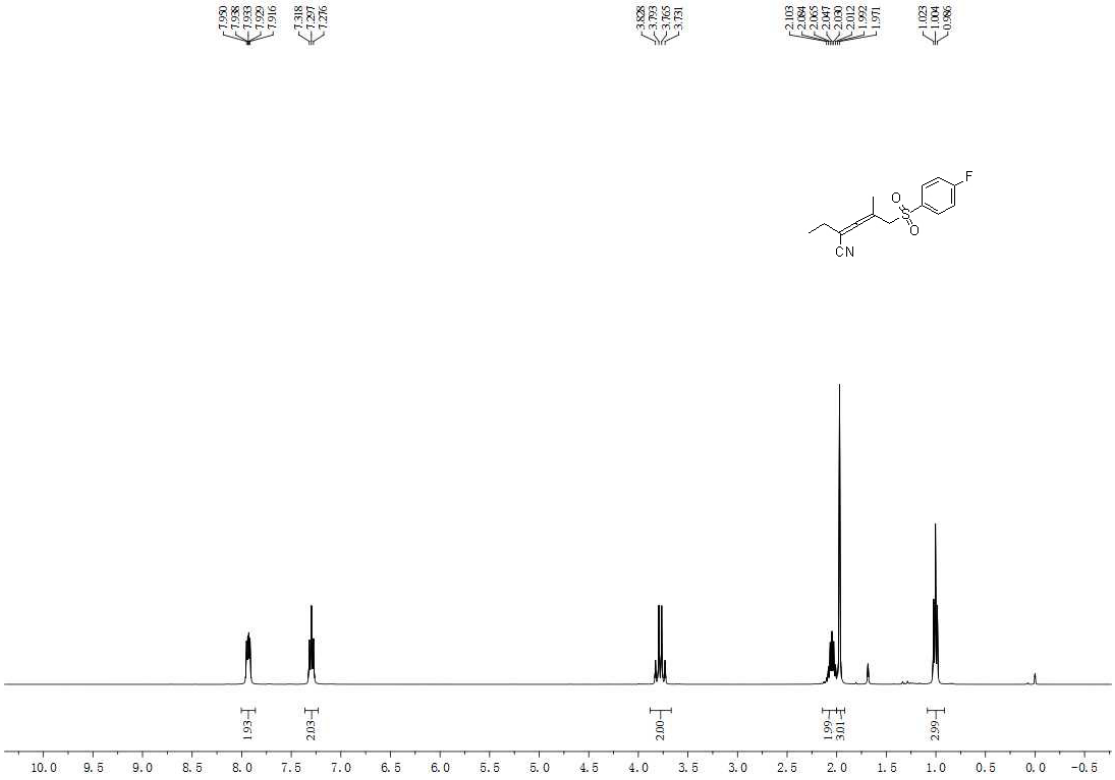

211.65
145.37
134.77
130.06
128.13
114.29
96.38
84.16
77.32
77.00
76.68
59.82
24.81
21.57
18.43
11.98
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

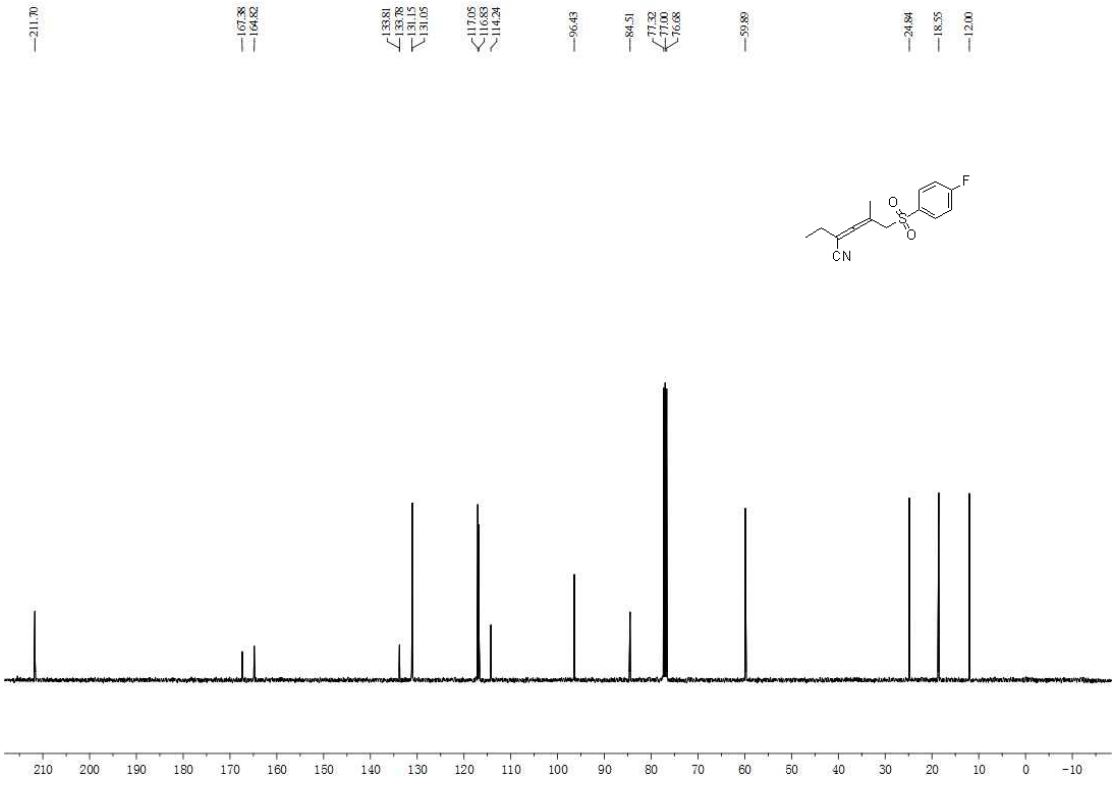
Product 3b

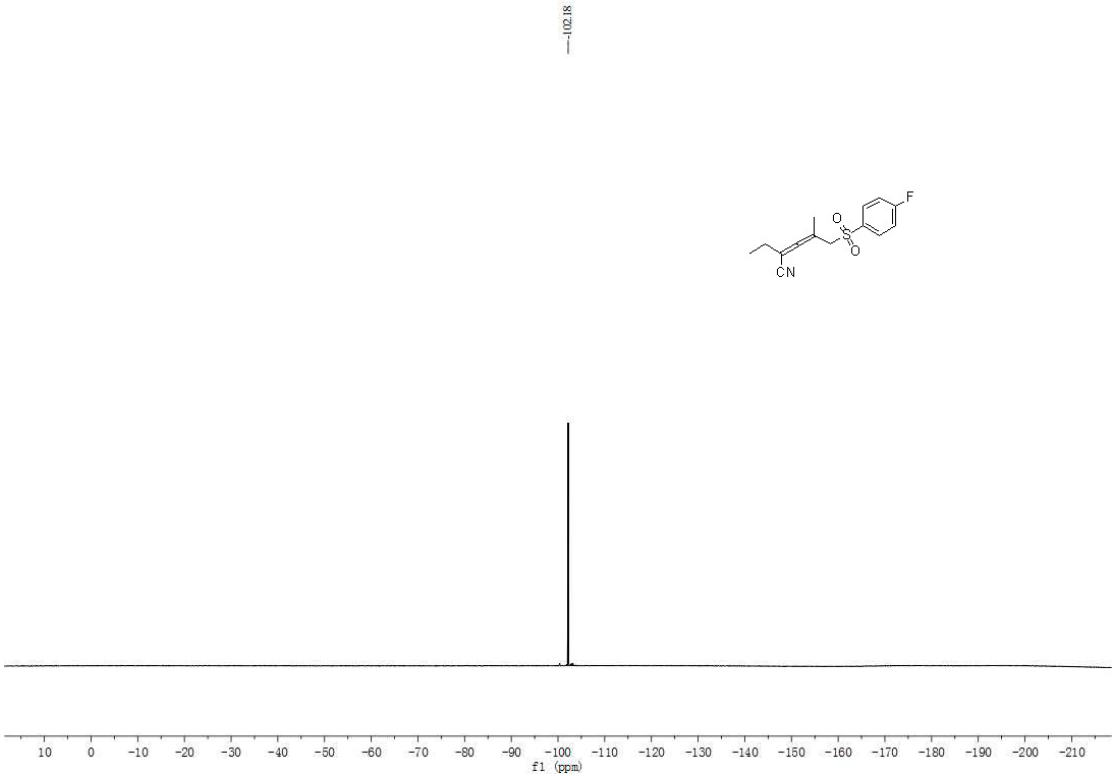

7.910
7.891
7.716
7.696
7.639
7.623
7.604
7.585
3.825
3.791
3.788
3.713
2.032
2.013
1.994
1.974
1.951
1.936
1.917
0.983
0.965
0.946
O
S
O
CN
1.92
0.98
1.95
2.00
4.98
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


211.73
137.89
134.23
129.54
128.20
114.32
96.47
84.37
77.32
77.00
76.68
59.80
24.84
18.53
12.06
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

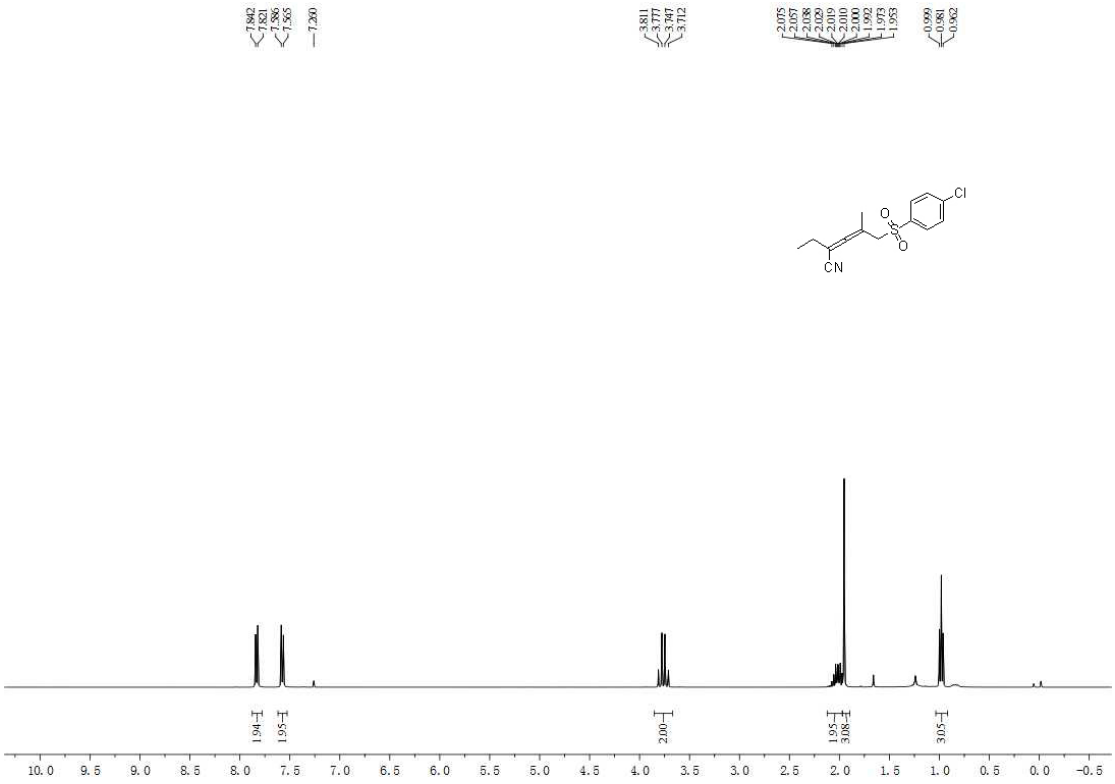
Product 3c

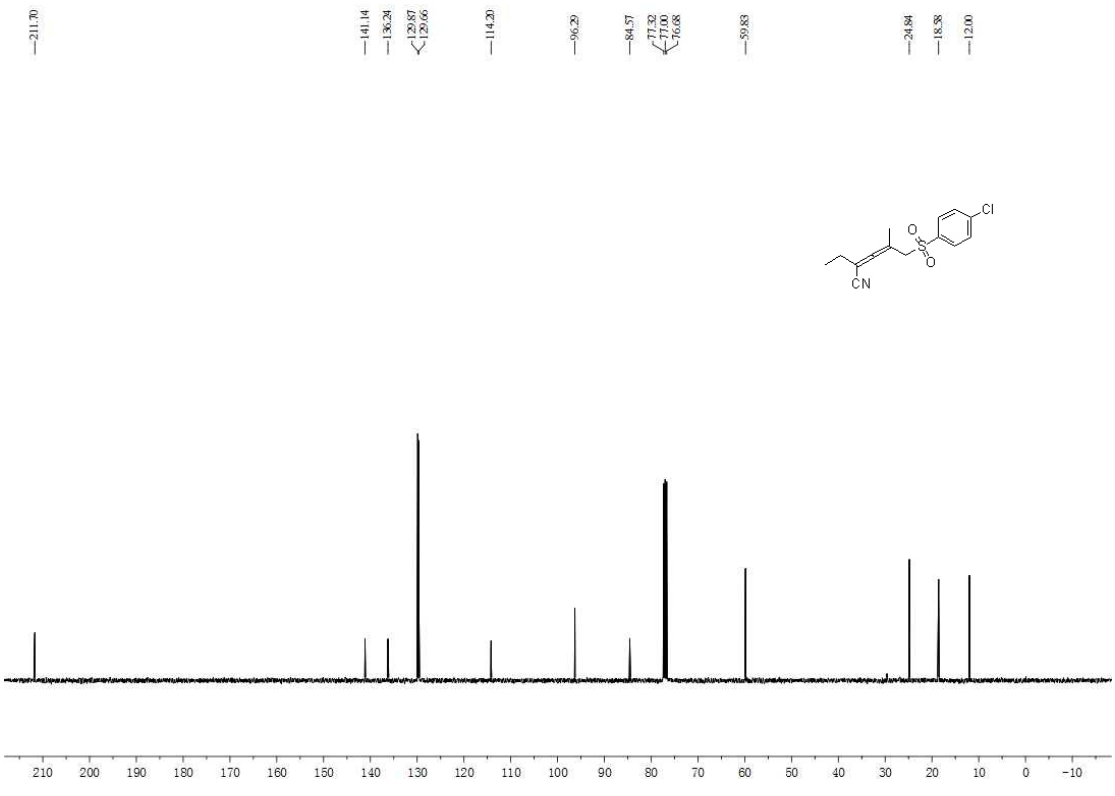

7.990
7.938
7.933
7.929
7.916
7.318
7.297
7.276
3.828
3.793
3.765
3.731
2.103
2.084
2.065
2.047
2.030
2.012
1.992
1.971
1.023
1.004
0.986
F
O
S
O
CN
1.93
2.03
2.00
1.99
3.01
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


211.70
167.38
164.82
133.81
133.78
131.15
131.05
117.05
116.83
114.24
96.43
84.51
77.32
77.00
76.68
59.89
24.84
18.55
12.00
F
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

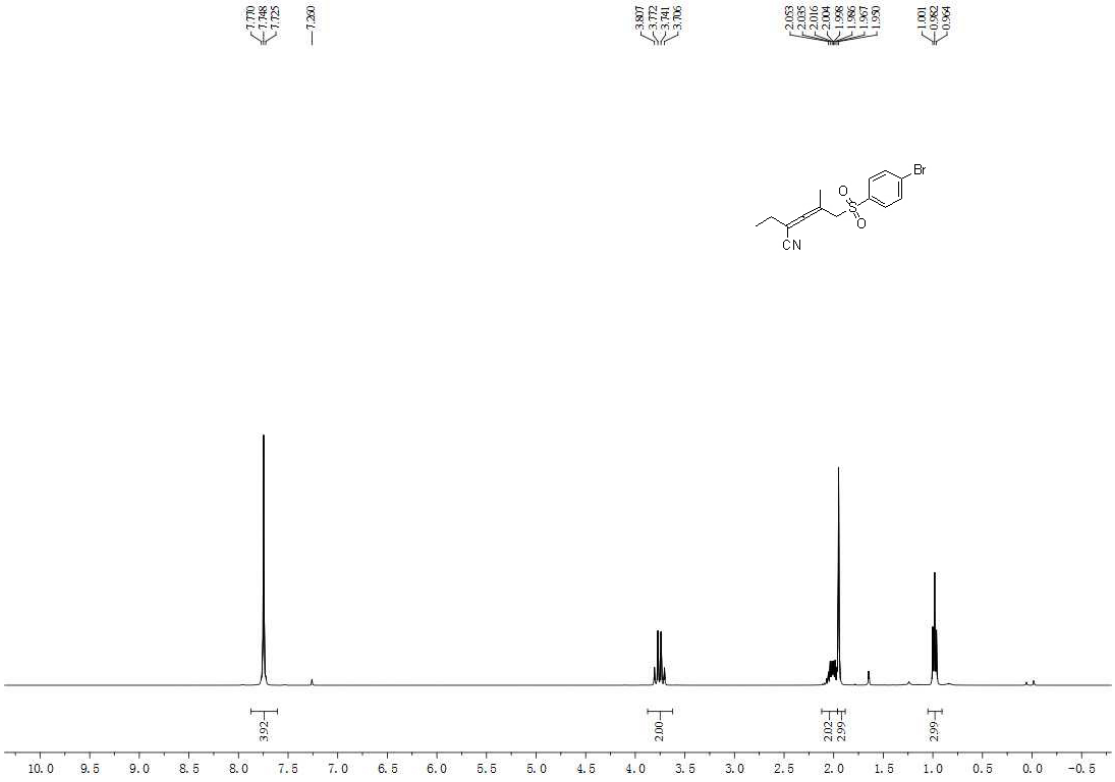

102.18
F
O
S
O
CN
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

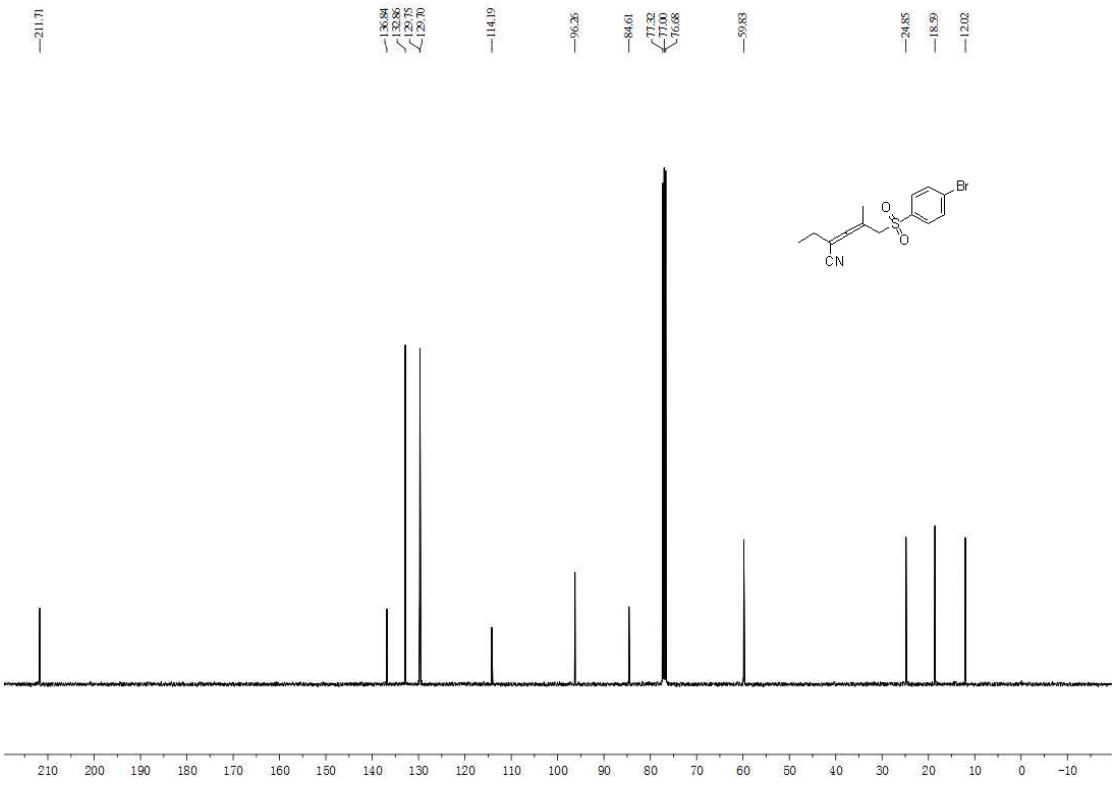
Product 3d


7.842
7.821
7.586
7.565
7.260
3.811
3.777
3.747
3.712
2.075
2.057
2.038
2.029
2.019
2.010
2.000
1.992
1.973
1.953
0.999
0.981
0.962
Cl
O
S
O
CN
1.94
1.95
2.00
1.95
3.08
3.05
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

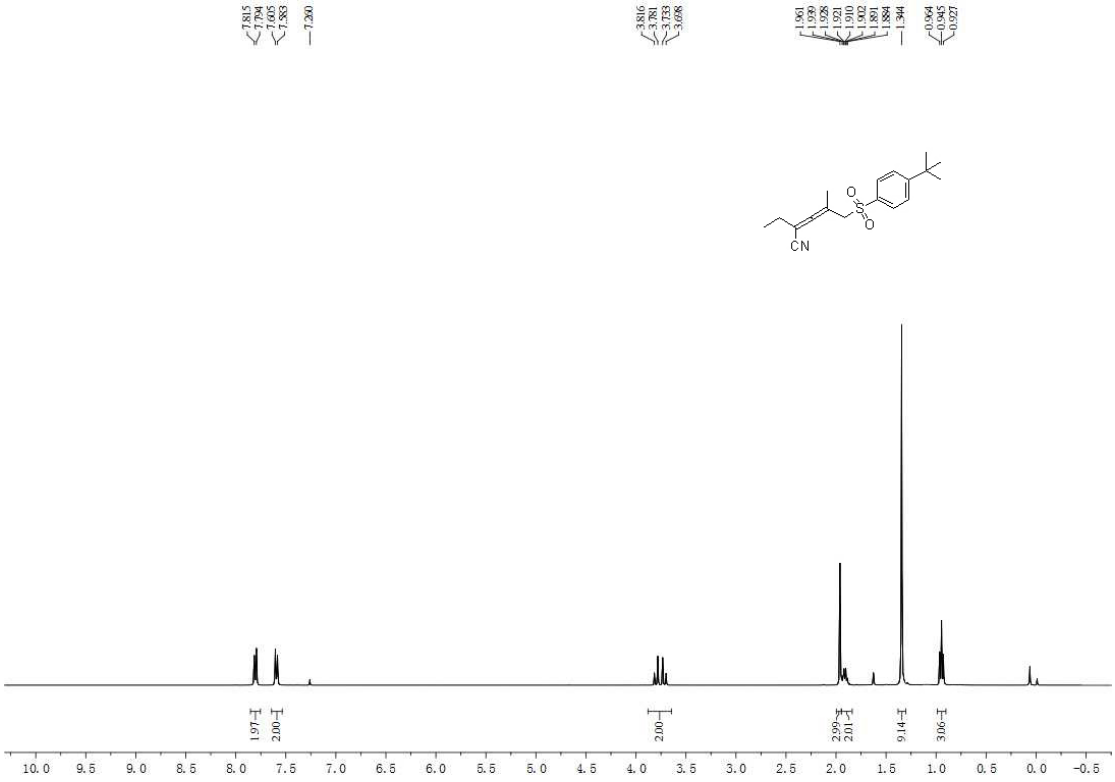

211.70
141.14
136.24
129.87
129.66
114.20
96.29
84.57
77.32
77.00
76.68
59.83
24.84
18.58
12.00
Cl
O
S
O
CN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

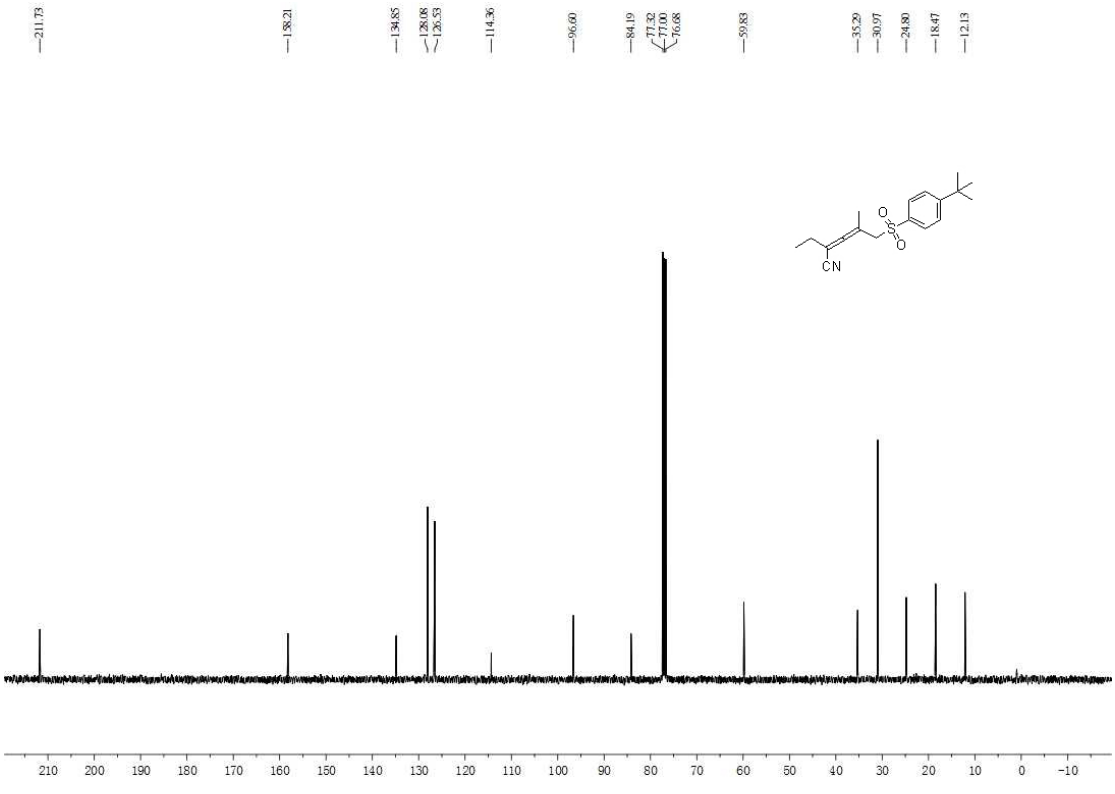
Product 3e


7.770
7.748
7.725
7.260
3.807
3.772
3.741
3.706
2.053
2.035
2.016
2.004
1.998
1.986
1.967
1.950
1.001
0.982
0.964
Br
O
S
O
CN
3.92
2.00
2.02
2.99
2.99
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

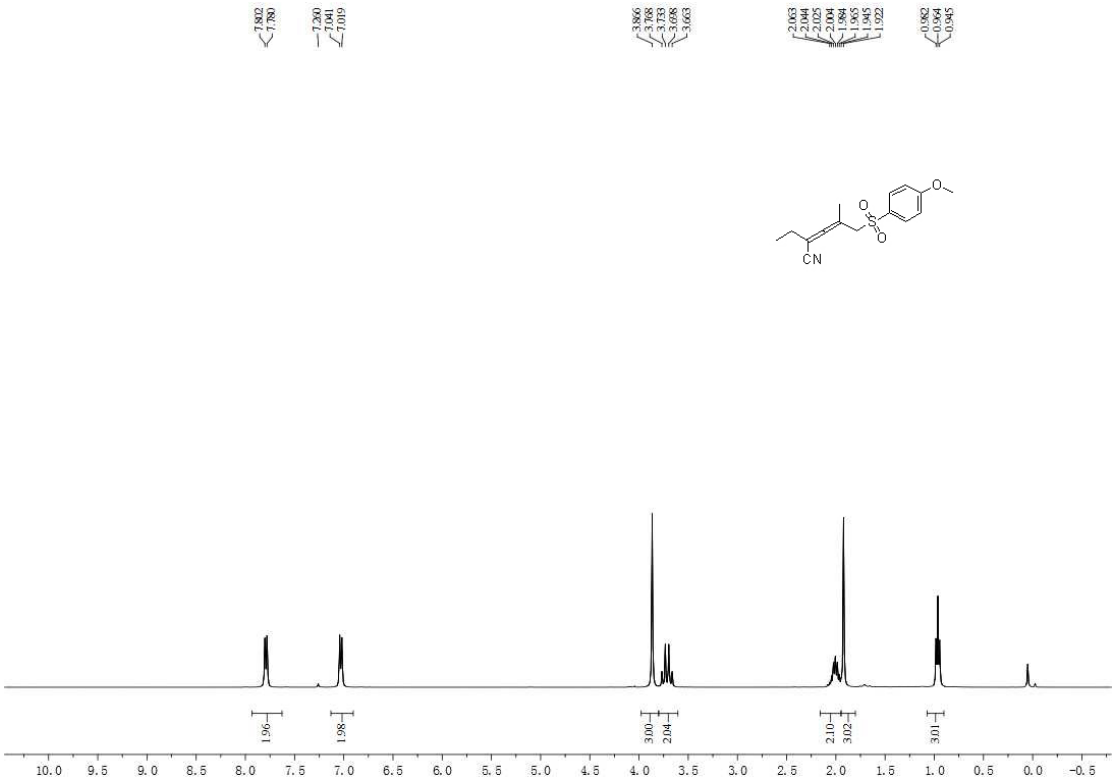

211.71
136.84
132.96
129.35
129.10
114.19
96.26
84.61
77.32
77.00
76.68
59.83
24.85
18.59
12.02
Br
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

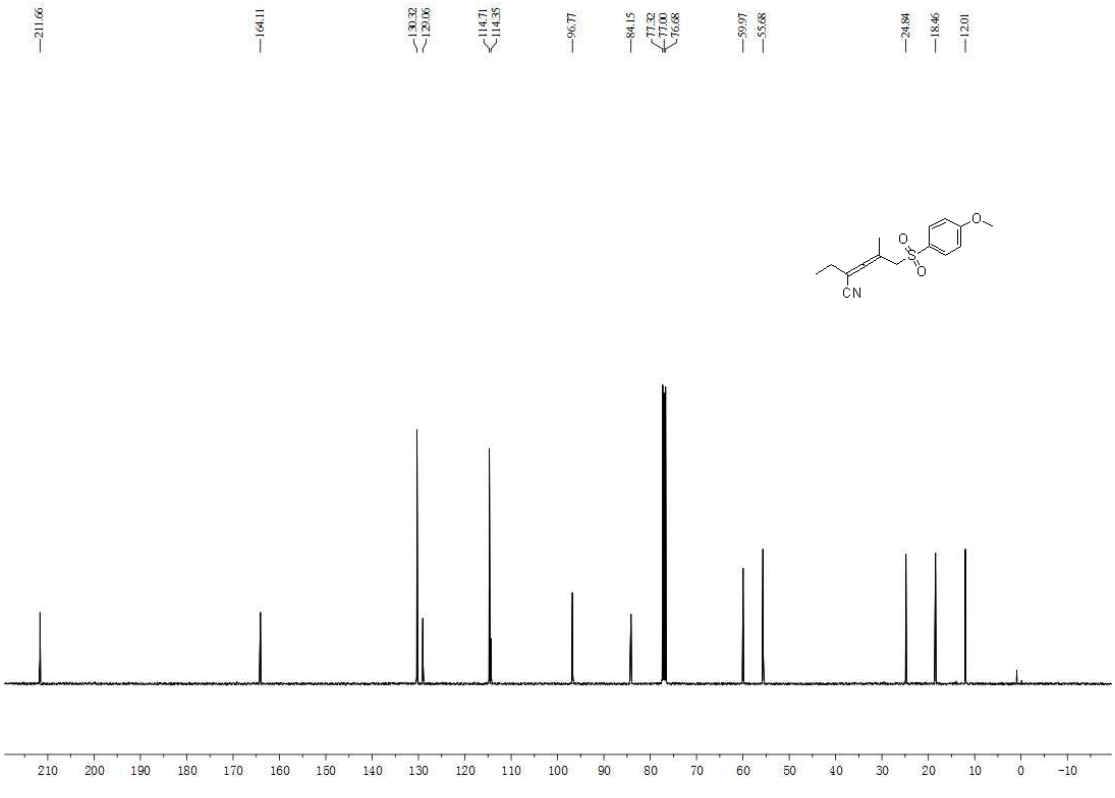
Product 3f


7.815
7.794
7.605
7.583
7.260
3.816
3.781
3.733
3.698
1.961
1.939
1.928
1.921
1.910
1.902
1.891
1.884
1.344
0.964
0.945
0.927
O
S
O
CN
1.97
2.00
2.00
2.99
2.01
9.14
3.06
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

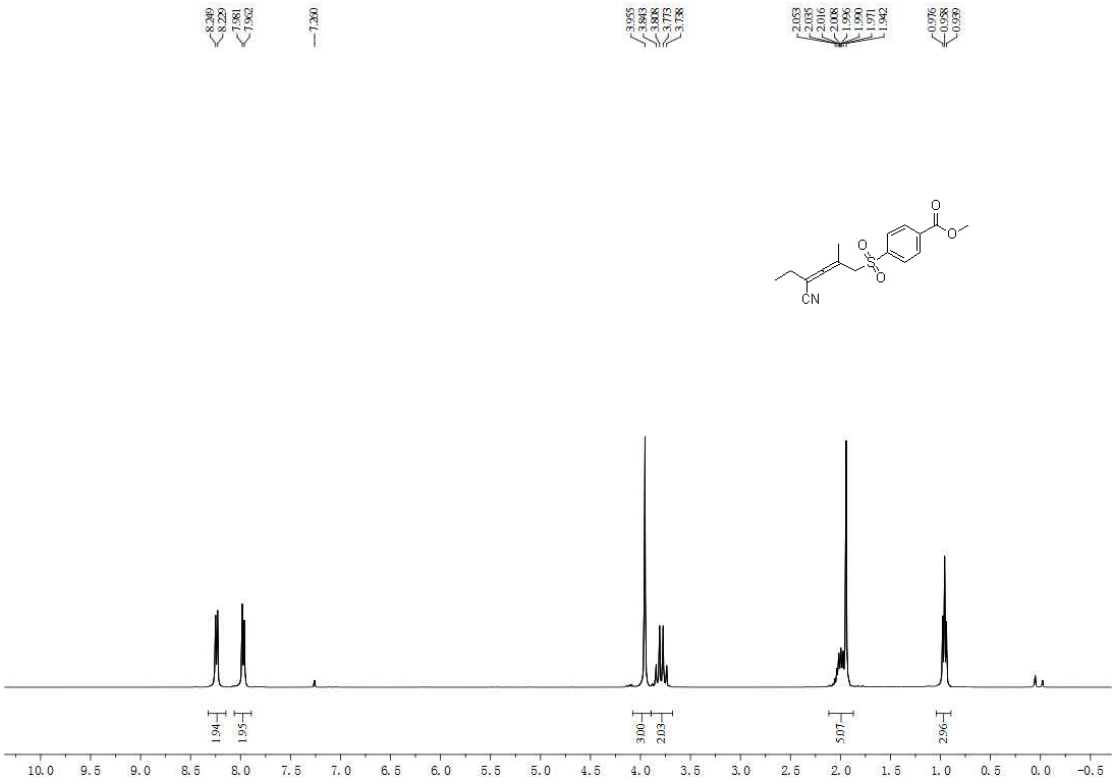

211.73
138.21
134.85
128.08
126.53
114.36
96.60
84.19
77.32
77.00
76.68
59.83
35.29
30.97
24.80
18.47
12.13
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

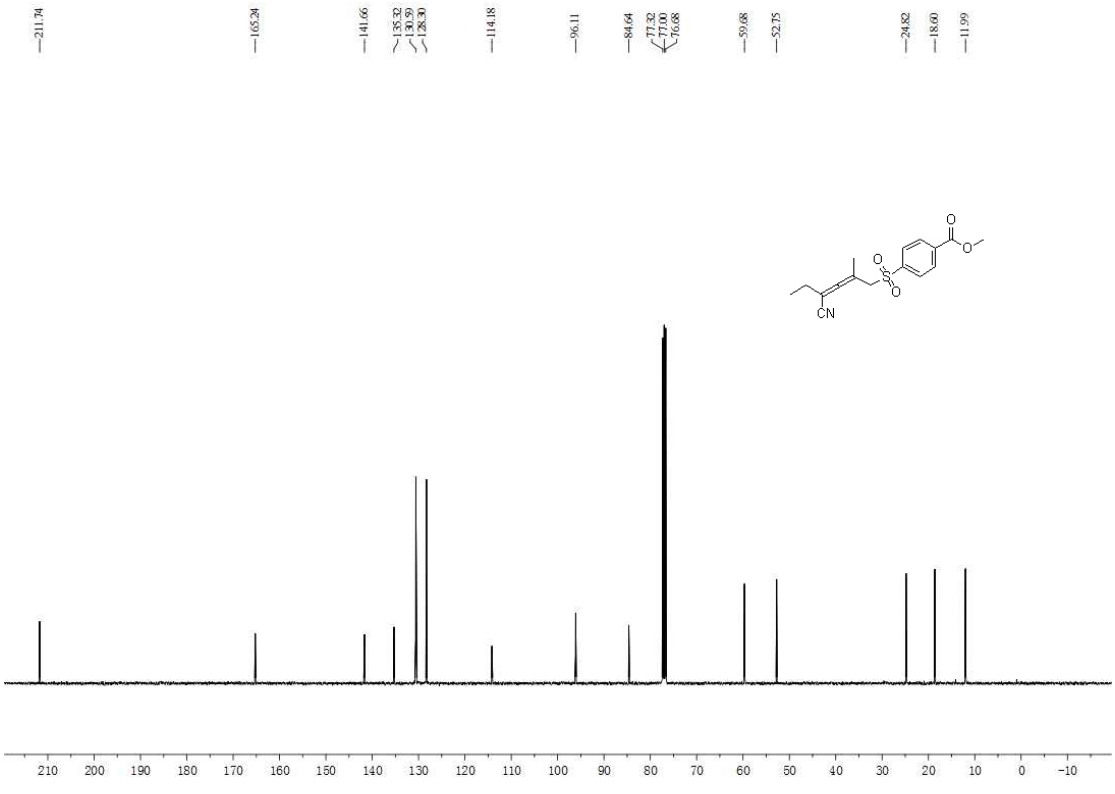
Product 3g


7.802
7.780
7.300
7.041
7.019
3.866
3.788
3.733
3.698
3.663
2.063
2.044
2.025
2.004
1.984
1.965
1.945
1.922
0.982
0.964
0.945
O
O
S
O
CN
1.96
1.98
3.00
2.04
2.10
3.02
3.01
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

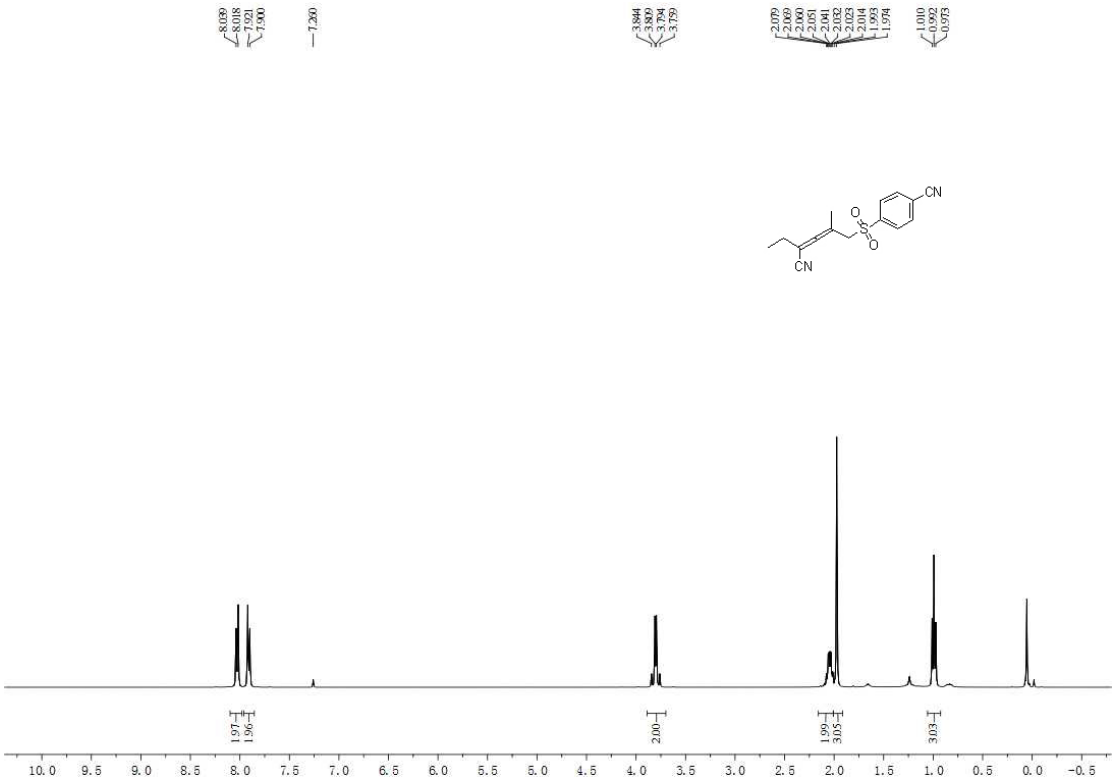

211.66
164.11
130.32
129.06
114.71
114.35
96.77
84.15
77.32
77.00
76.68
59.97
55.68
24.84
18.46
12.01
O
O
S
O
CN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

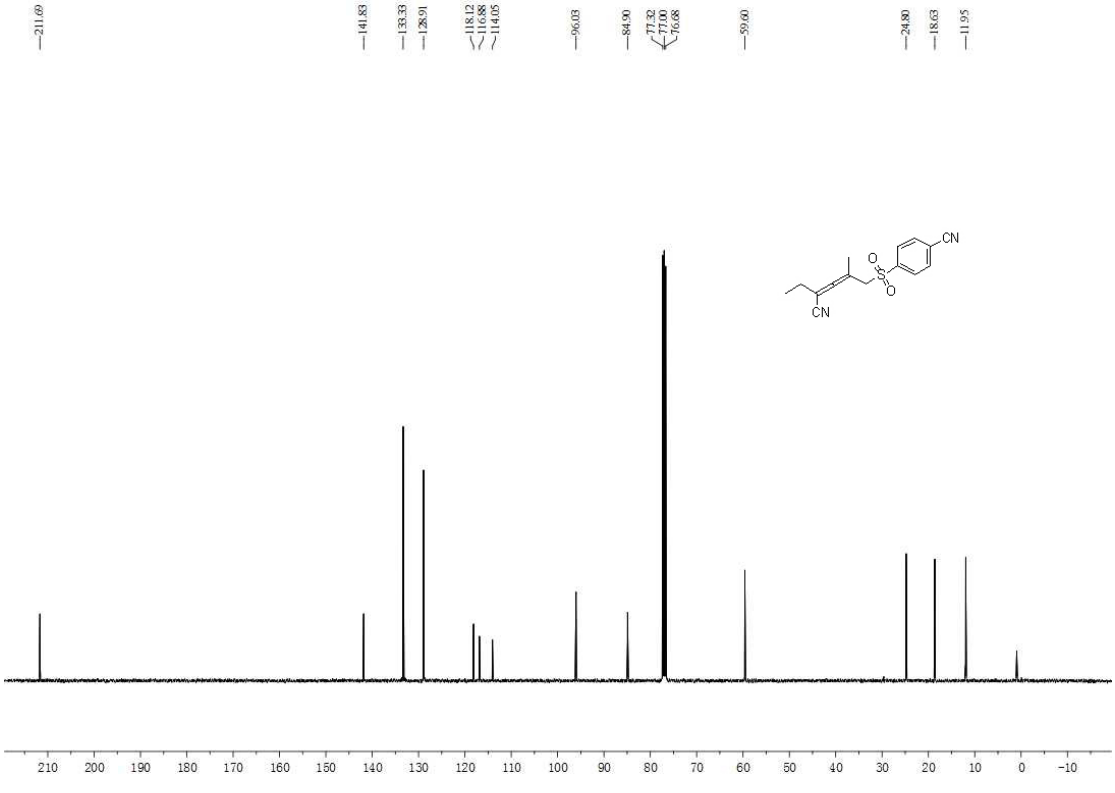
Product 3h


8.249
8.229
7.981
7.962
7.260
3.955
3.843
3.808
3.773
3.738
2.053
2.035
2.016
2.008
1.996
1.990
1.971
1.942
0.976
0.958
0.939
O
O
S
O
O
CN
1.94
1.95
3.00
2.03
5.07
2.96
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

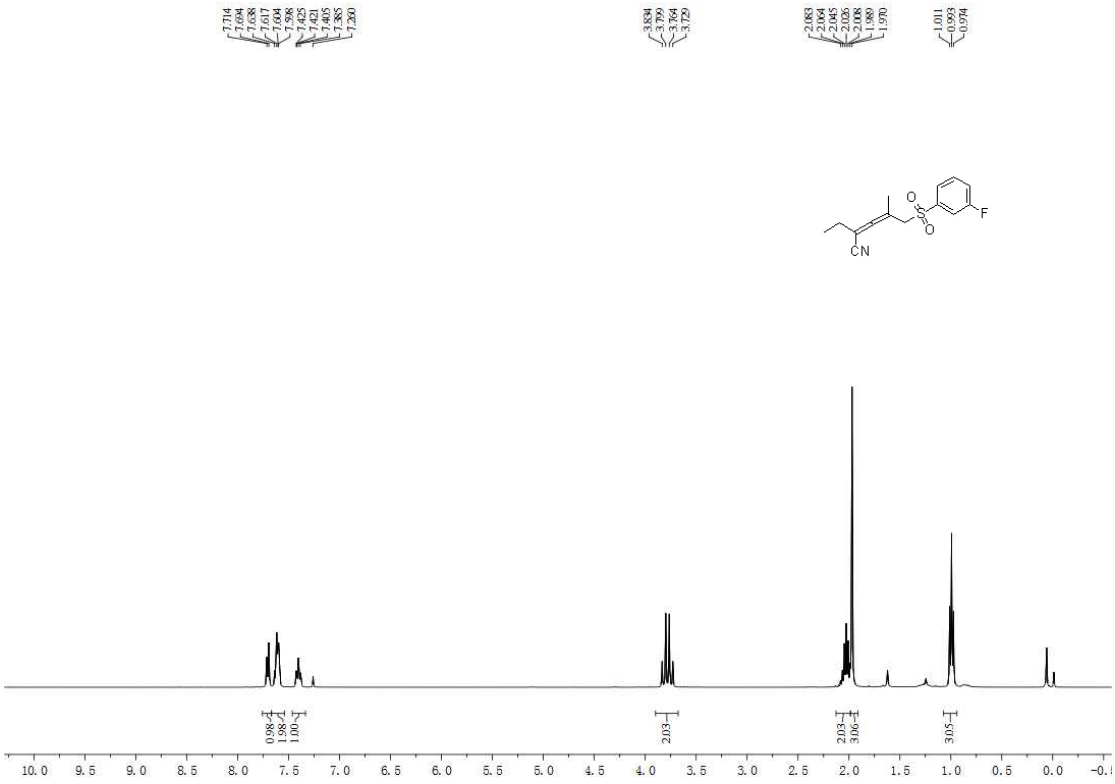

211.74
165.24
141.66
135.32
130.39
128.30
114.18
96.11
84.64
77.32
77.00
76.68
59.68
52.75
24.82
18.60
11.99
O
O
S
O
O
CN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

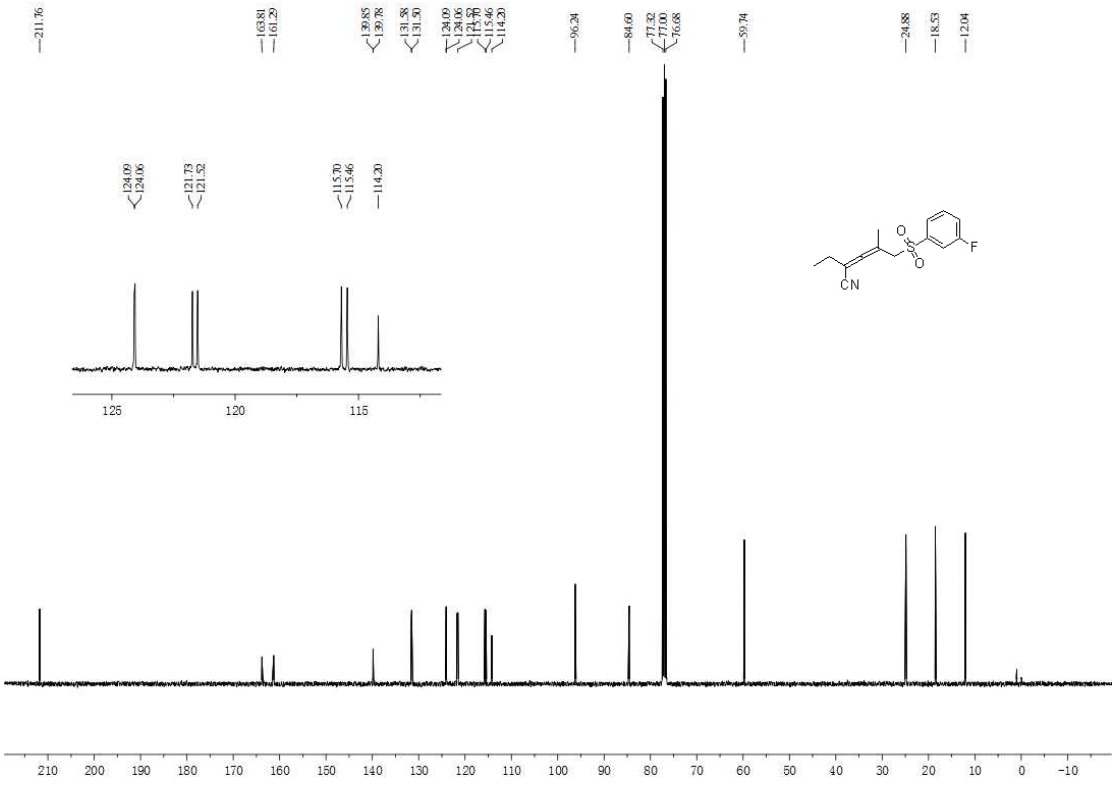
Product 3i

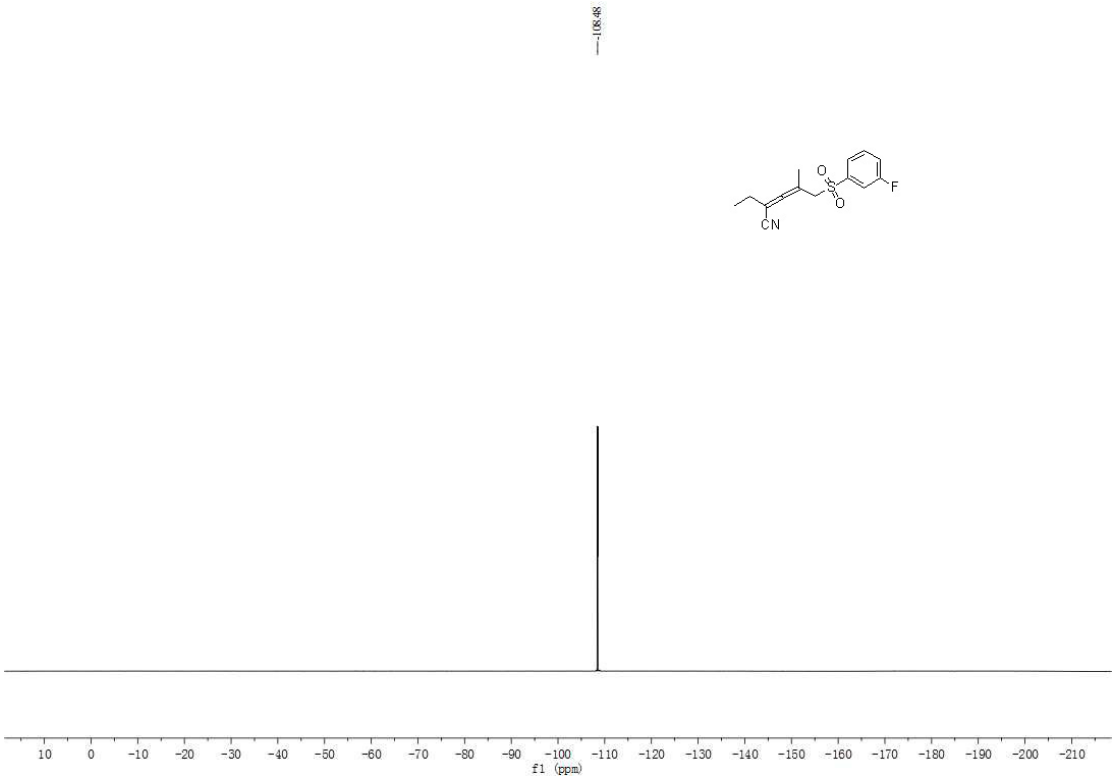

8.039
8.018
7.921
7.900
7.260
3.844
3.820
3.794
3.769
2.079
2.069
2.060
2.051
2.041
2.032
2.023
2.014
1.993
1.974
1.010
0.992
0.973
CN
O
S
O
CN
1.97
1.96
2.00
1.99
3.05
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


211.69
141.83
133.33
128.91
118.12
116.88
114.05
96.03
84.90
77.32
77.00
76.68
59.60
24.80
18.63
11.95
CN
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

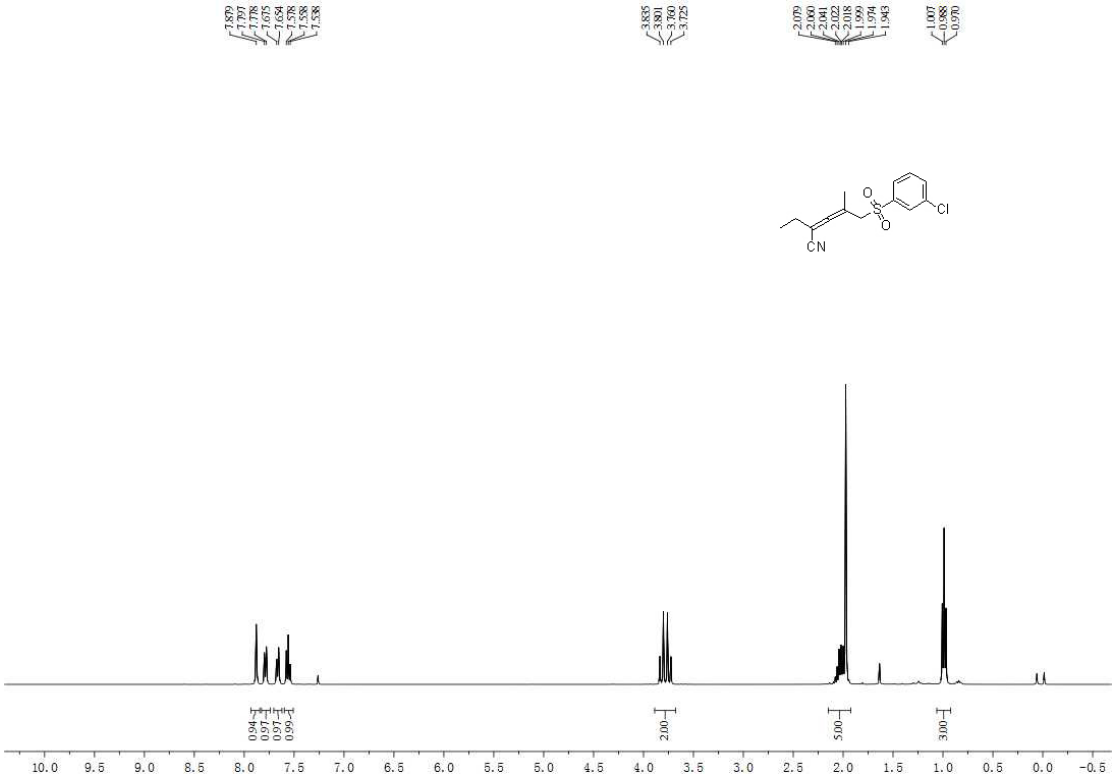
Product 3j

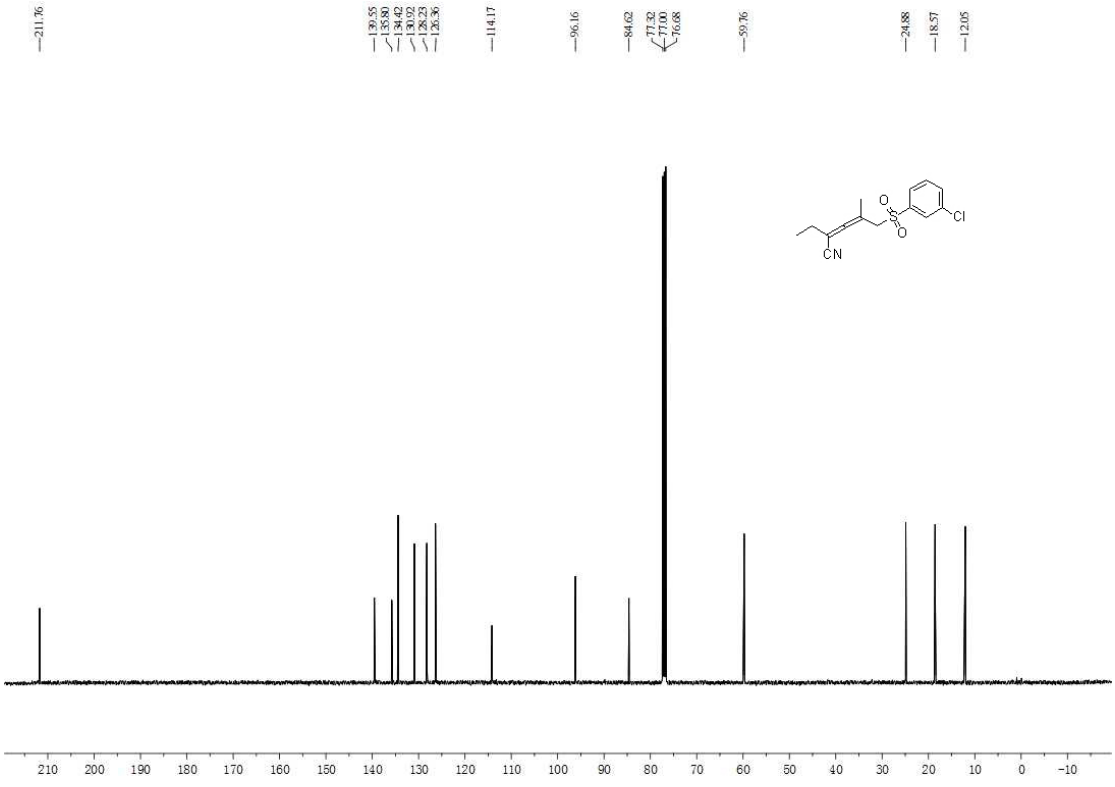





-108.48
O
S
O
F
CN
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Product 3k


7.879
7.797
7.778
7.675
7.654
7.578
7.558
7.538
3.835
3.801
3.760
3.725
2.079
2.060
2.041
2.022
2.018
1.999
1.974
1.943
1.007
0.988
0.970
O
S
O
Cl
CN
0.94
0.97
0.97
0.99
2.00
5.00
3.00
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


211.76
139.55
135.80
134.42
130.92
129.23
128.36
114.17
96.16
84.62
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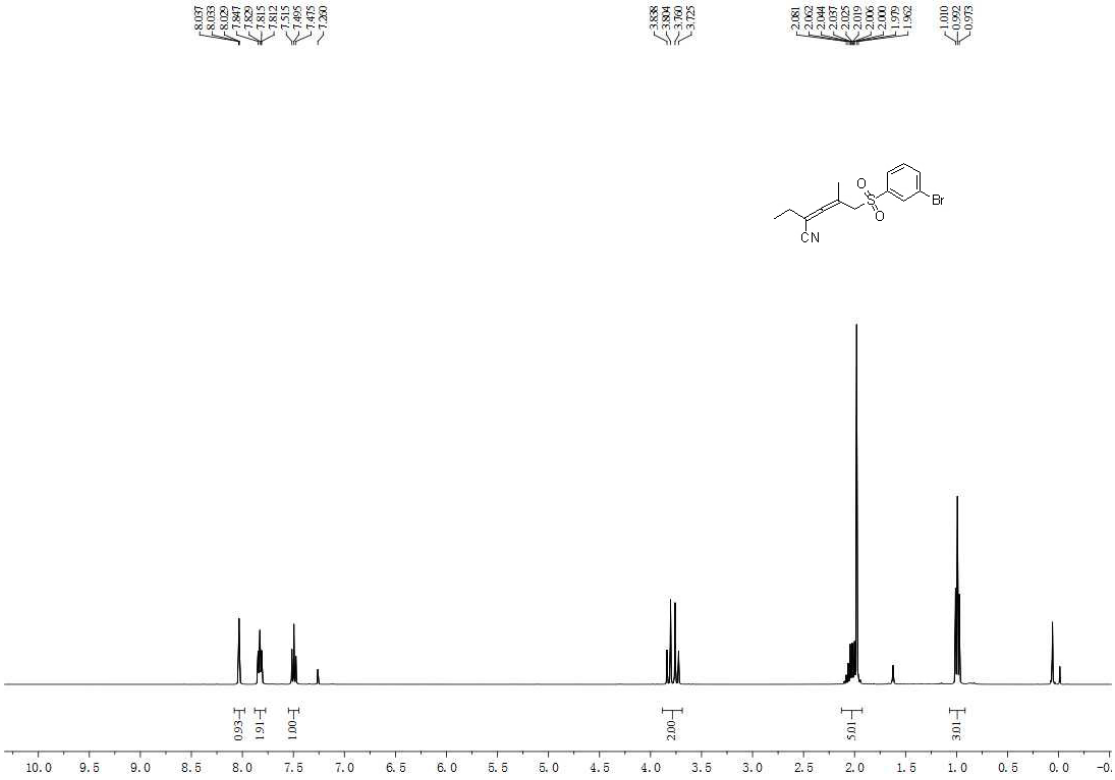
77.00
76.68
59.76
24.88
18.57
12.05
O
S
O
Cl
CN

Product 3l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7.515
7.495
7.475
7.280
3.838
3.804
3.760
3.725
2.081
2.062
2.044
2.037
2.025
2.019
2.006
2.000
1.979
1.962
1.010
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S
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Br
CN
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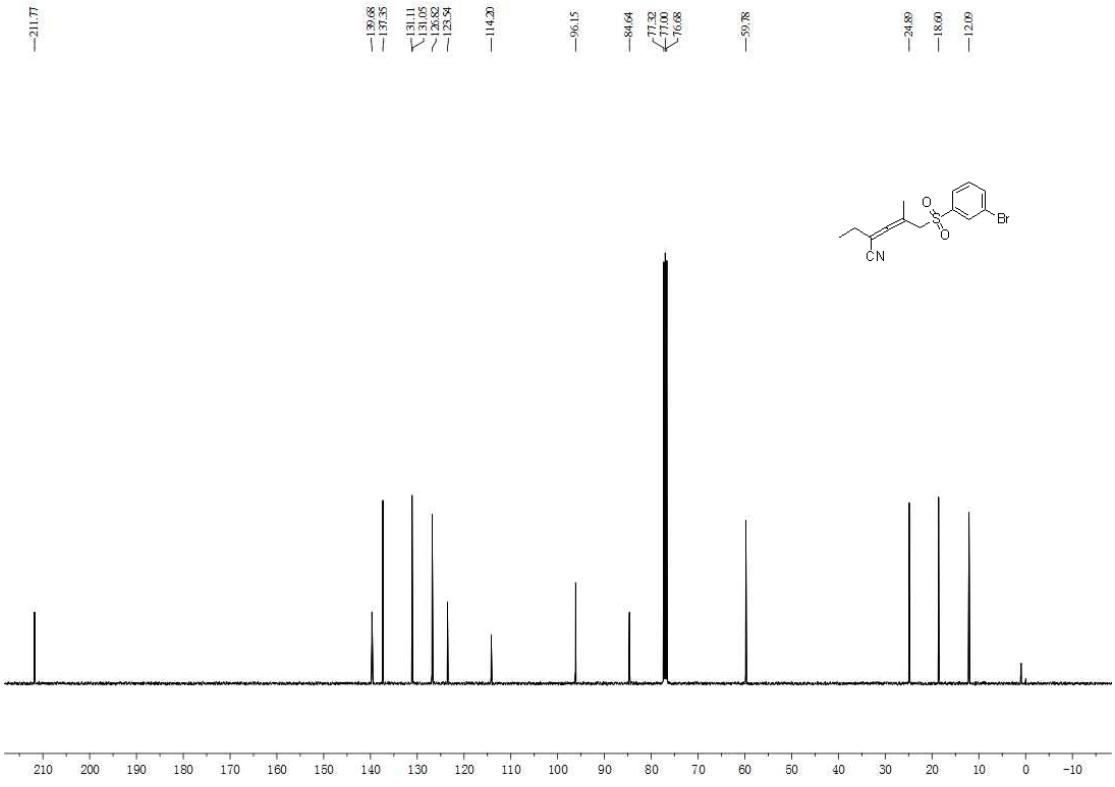
1.91
1.00
2.00
5.01
3.01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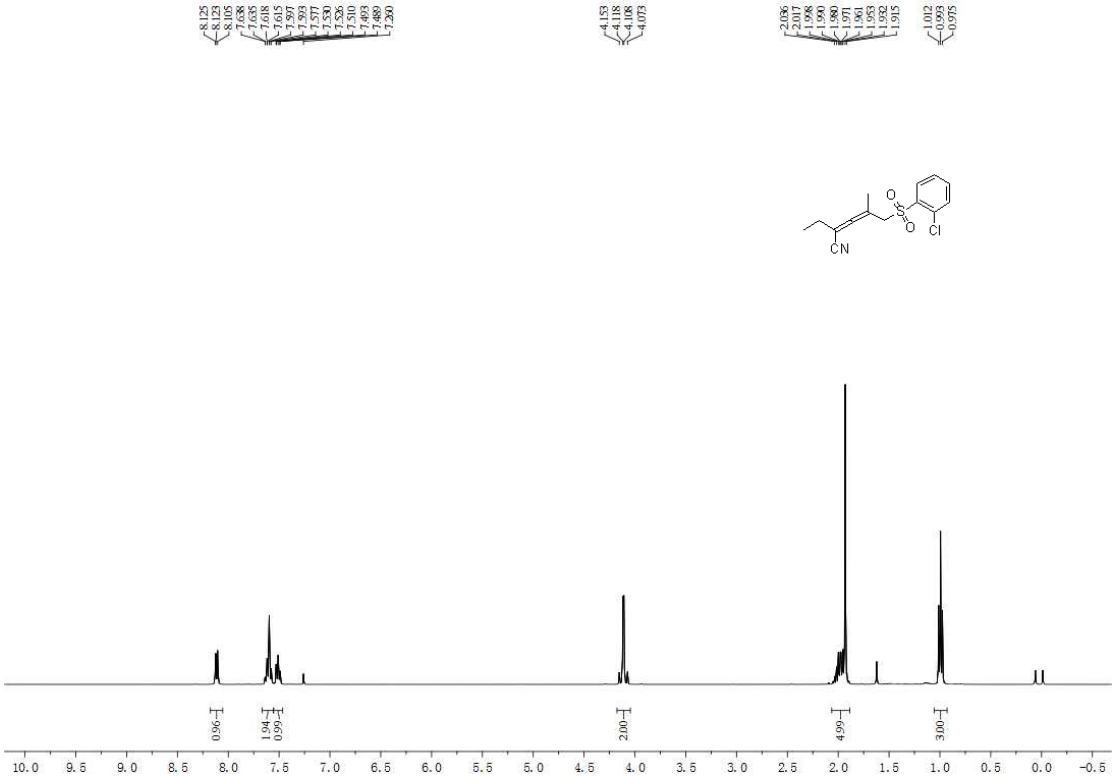
139.68
137.35
131.11
130.05
124.62
123.54
114.20
96.15
84.64
77.32
77.00
76.68
59.78
24.89
18.60
12.09
O
S
O
Br
CN

Product 3m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8.123
8.105
7.638
7.635
7.618
7.615
7.597
7.593
7.577
7.530
7.526
7.510
7.493
7.489
7.200
4.153
4.118
4.118
4.073
2.036
2.017
1.998
1.990
1.980
1.971
1.961
1.955
1.932
1.915
1.012
1.008
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Cl
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1.94
0.99
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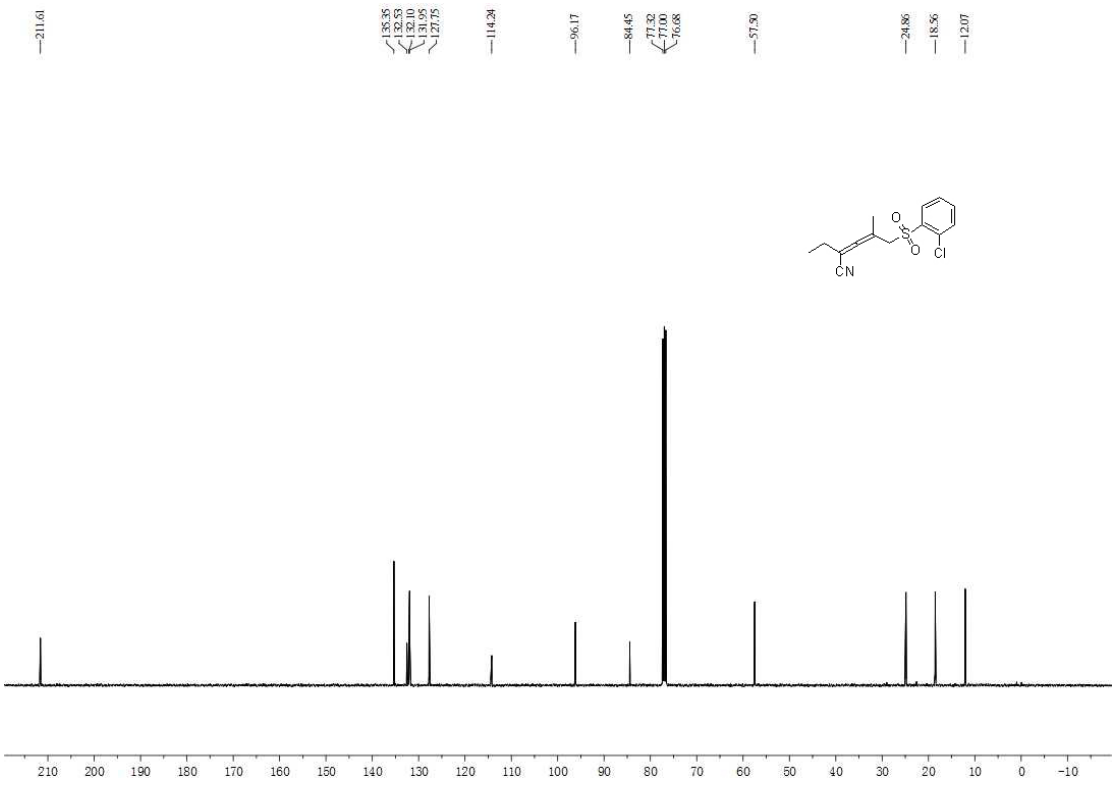
4.99
3.00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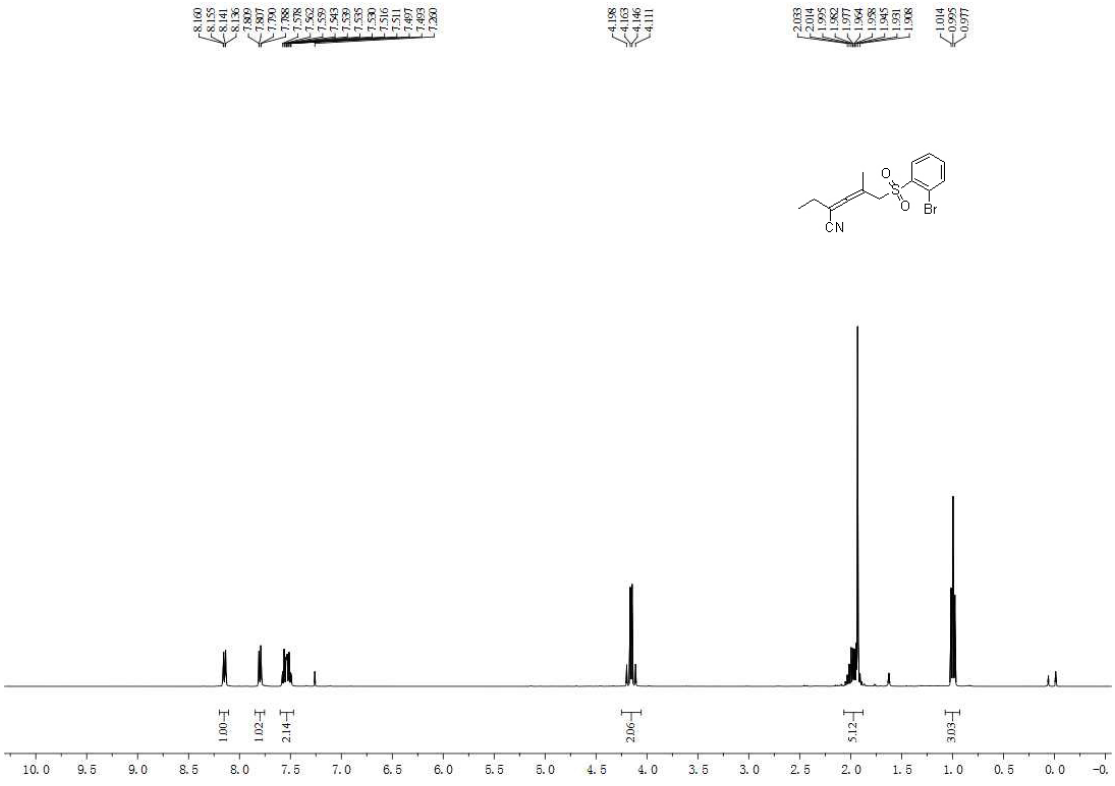
132.53
132.10
131.95
127.75
114.24
96.17
84.45
77.32
77.00
76.68
57.50
24.86
18.56
12.07
O
S
O
Cl
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Product 3n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8.155
8.141
8.136
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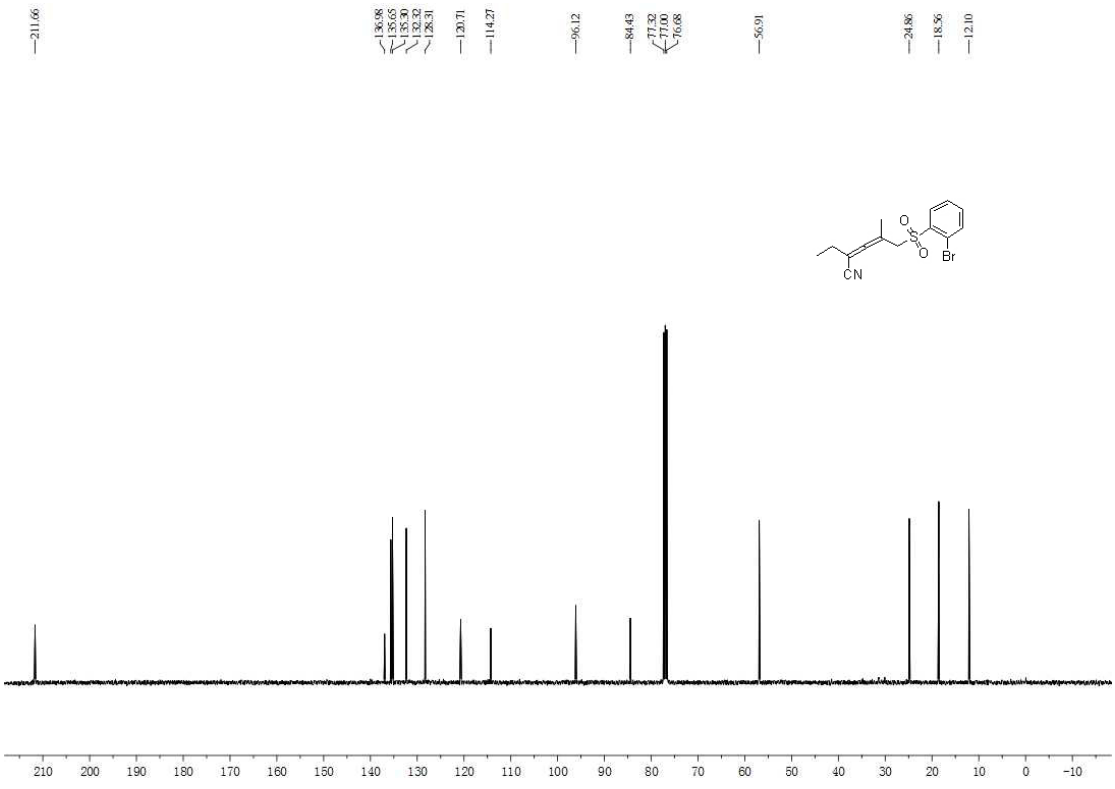
7.807
7.790
7.788
7.578
7.572
7.559
7.543
7.539
7.535
7.530
7.516
7.511
7.497
7.493
7.260
4.188
4.163
4.146
4.111
2.033
2.014
1.995
1.982
1.977
1.964
1.938
1.935
1.931
1.908
1.014
0.995
0.977
O
S
O
Br
CN
1.00
1.02
2.14
2.06
5.12
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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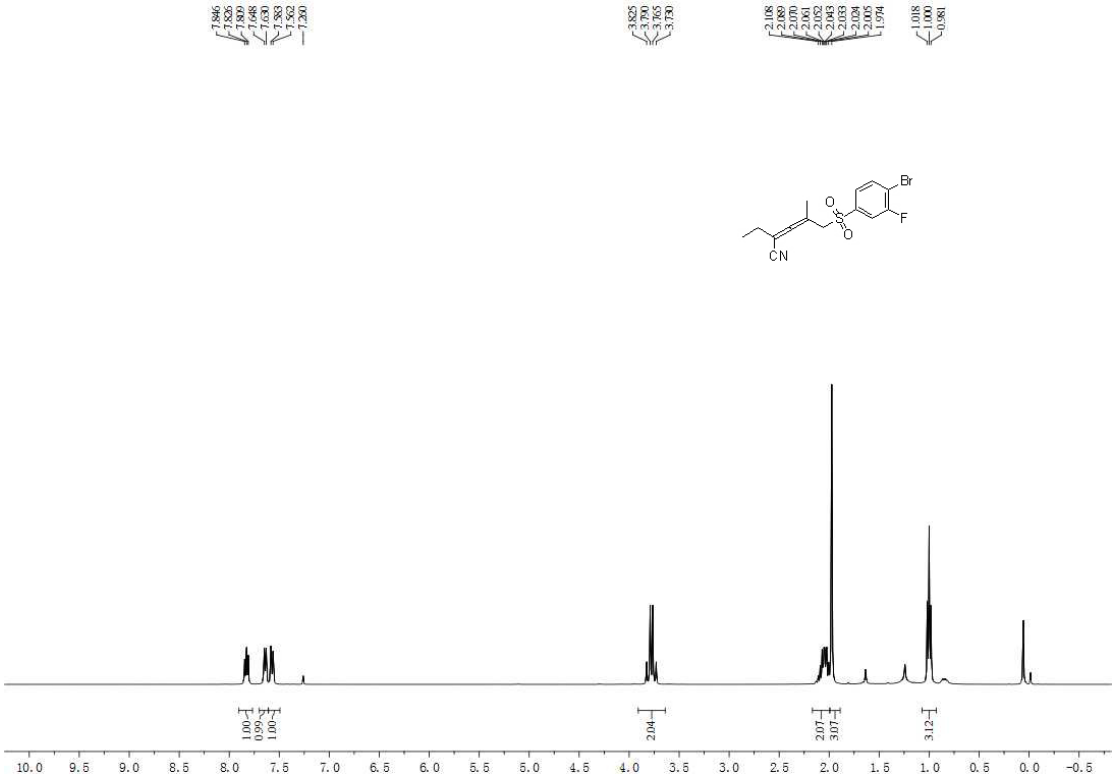
136.98
135.65
135.30
132.32
128.31
120.71
114.27
96.12
84.43
77.32
77.00
76.68
56.91
24.86
18.56
12.10
O
S
O
Br
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Product 3o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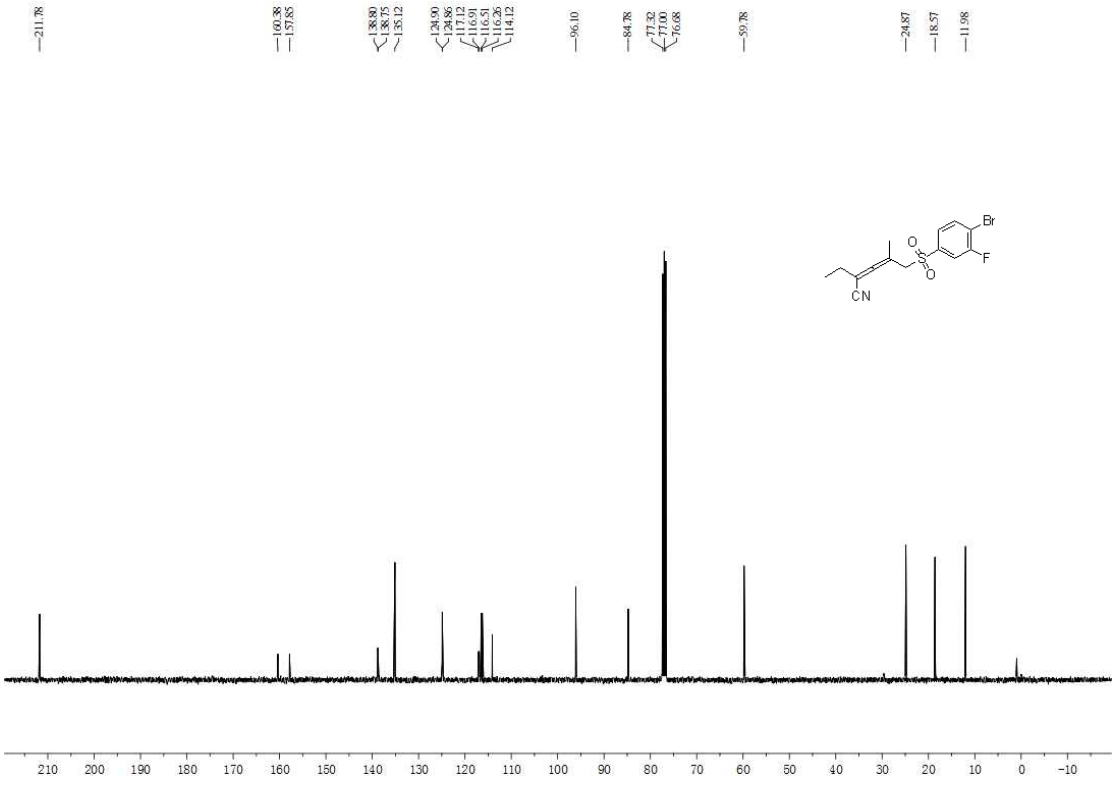
7.835
7.830
7.648
7.630
7.583
7.562
7.260
3.825
3.790
3.765
3.730
2.108
2.089
2.070
2.061
2.052
2.043
2.033
2.024
2.005
1.974
1.018
1.000
0.981
Br
F
O
S
O
CN
1.00
0.99
1.00
2.04
2.07
3.07
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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160.38
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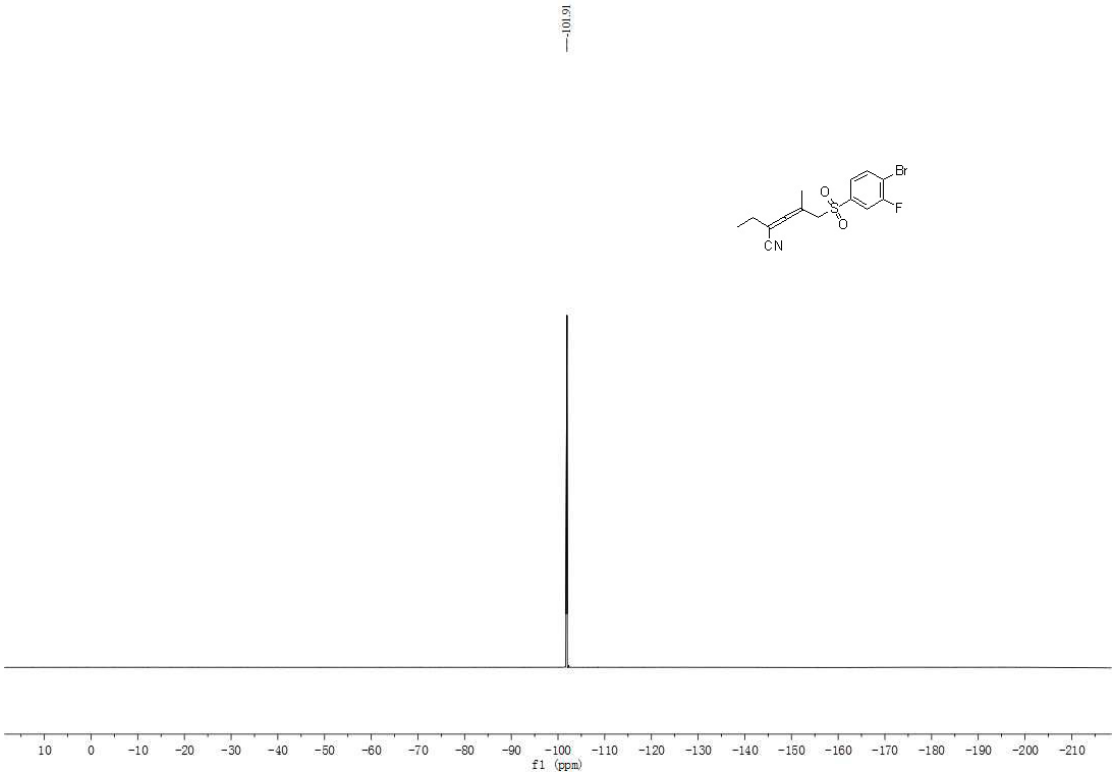
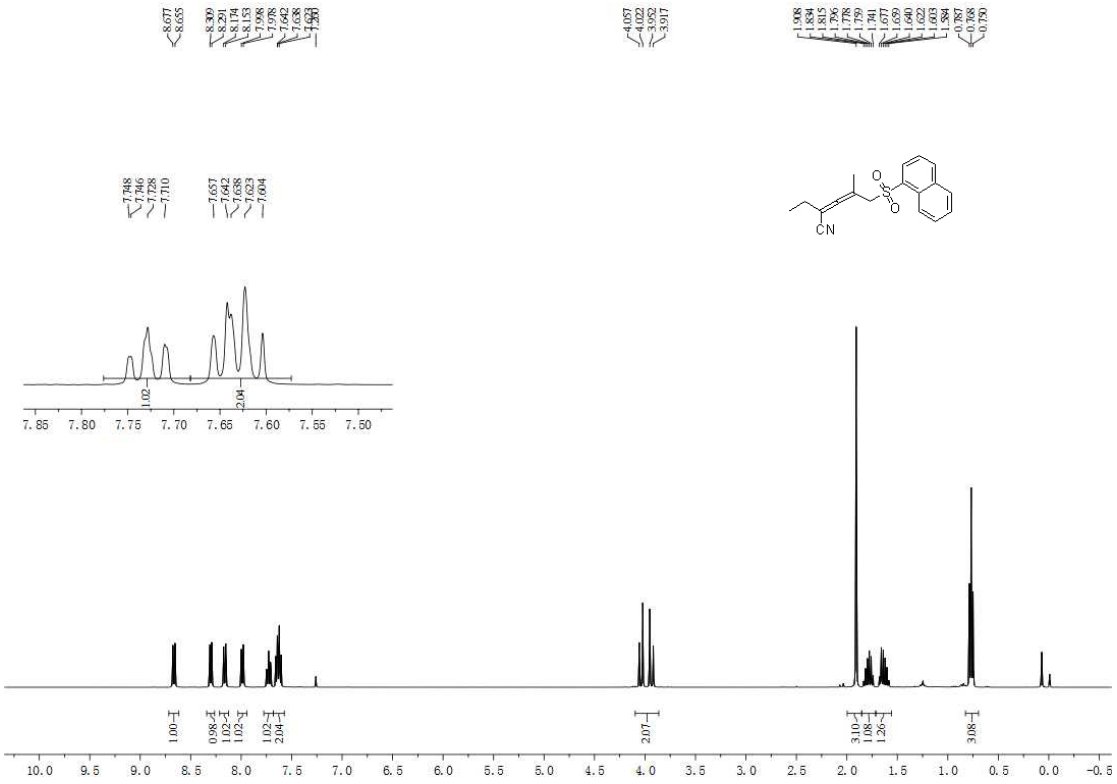
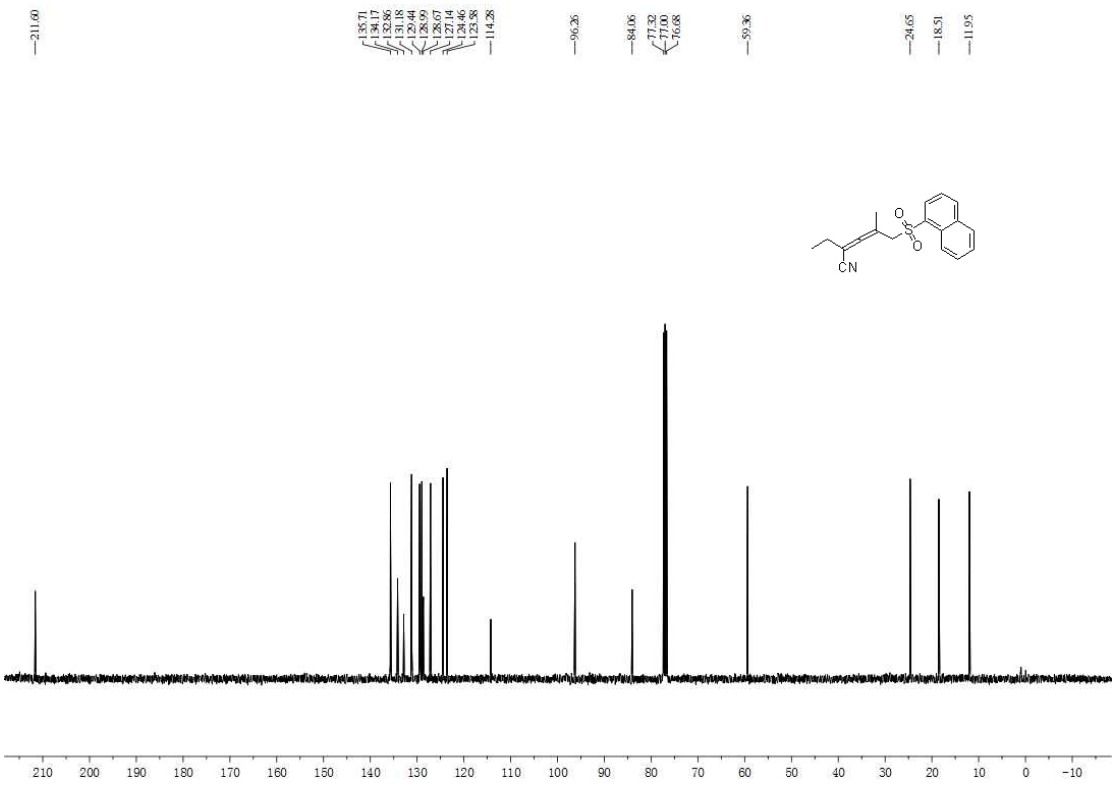
135.12
124.90
124.86
117.12
116.91
116.51
116.26
114.12
96.10
84.78
77.32
77.00
76.68
59.78
24.87
18.57
11.98
Br
F
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

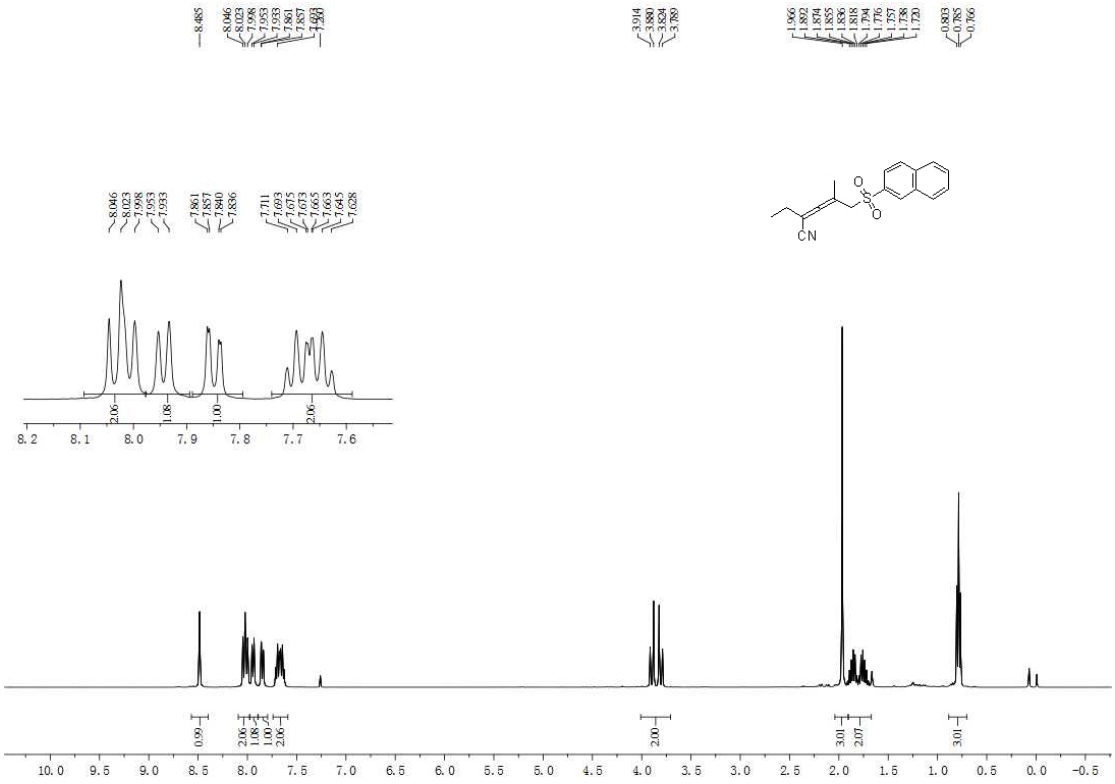

101.91
Br
F
O
S
O
CN
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

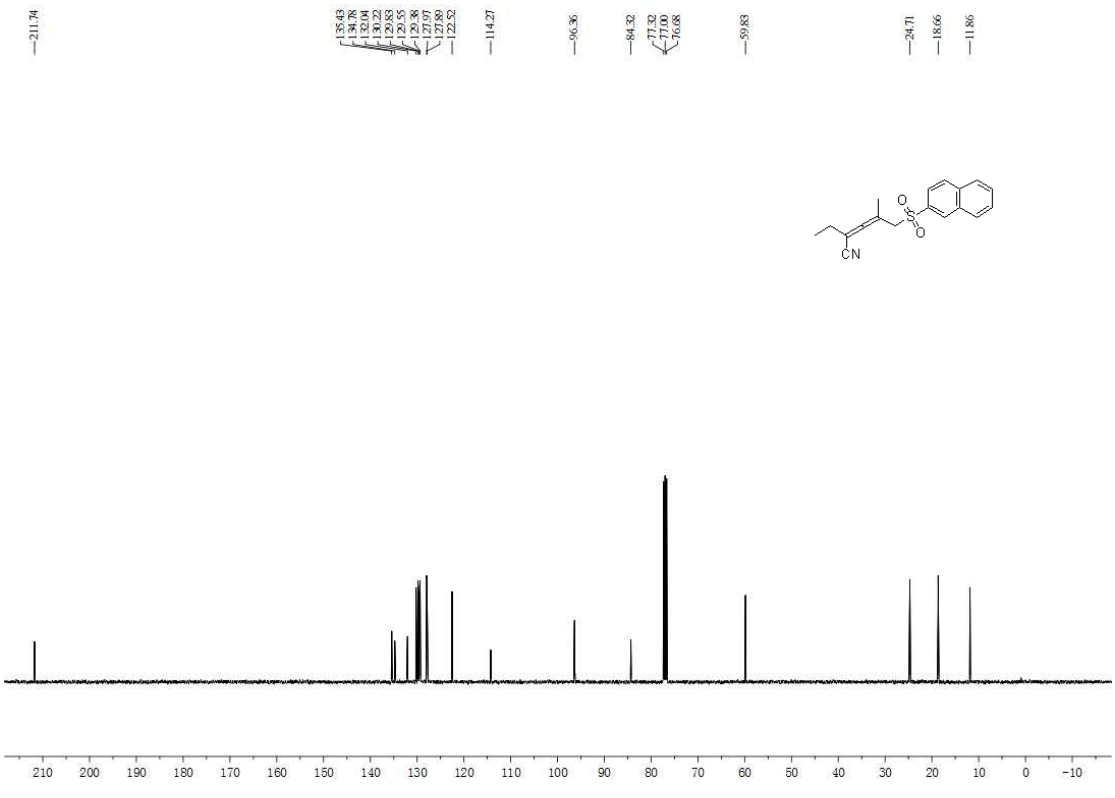
Product 3p



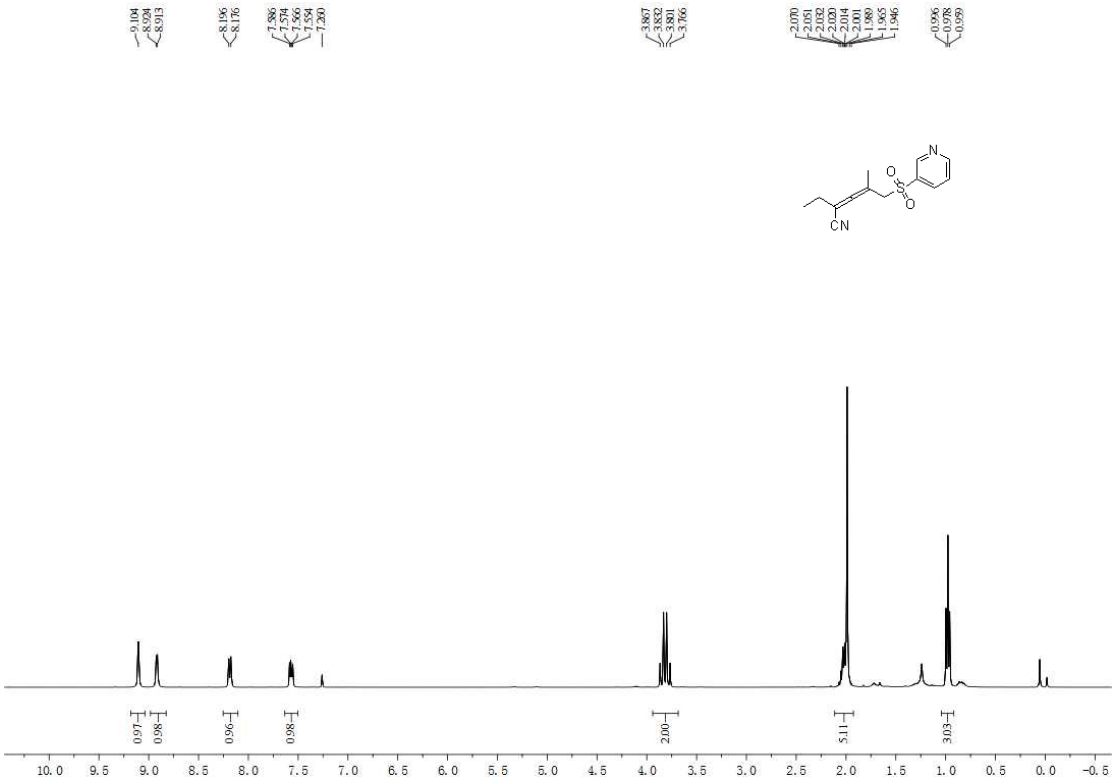


Product 3q





Product 3r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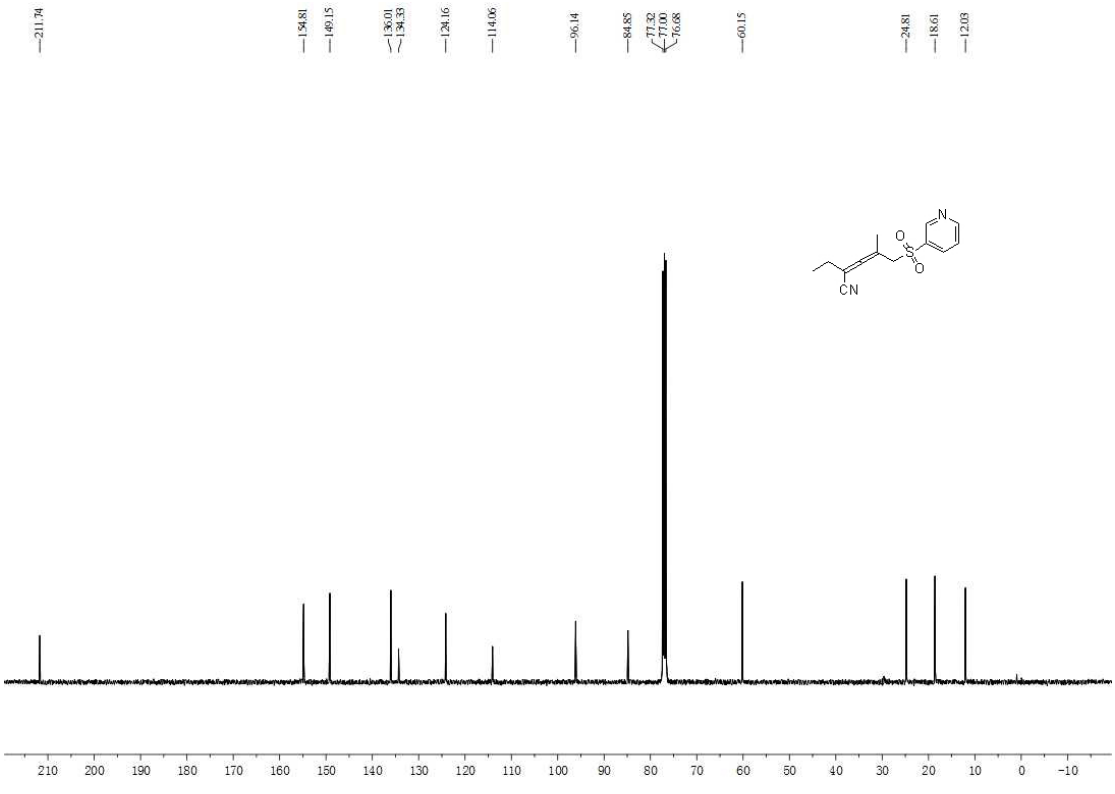
7.574
7.566
7.556
7.200
3.867
3.852
3.801
3.766
2.070
2.051
2.032
2.020
2.014
2.001
1.980
1.965
1.946
0.996
0.978
0.959
N
O
S
O
CN
0.97
0.98
0.96
0.98
2.00
5.11
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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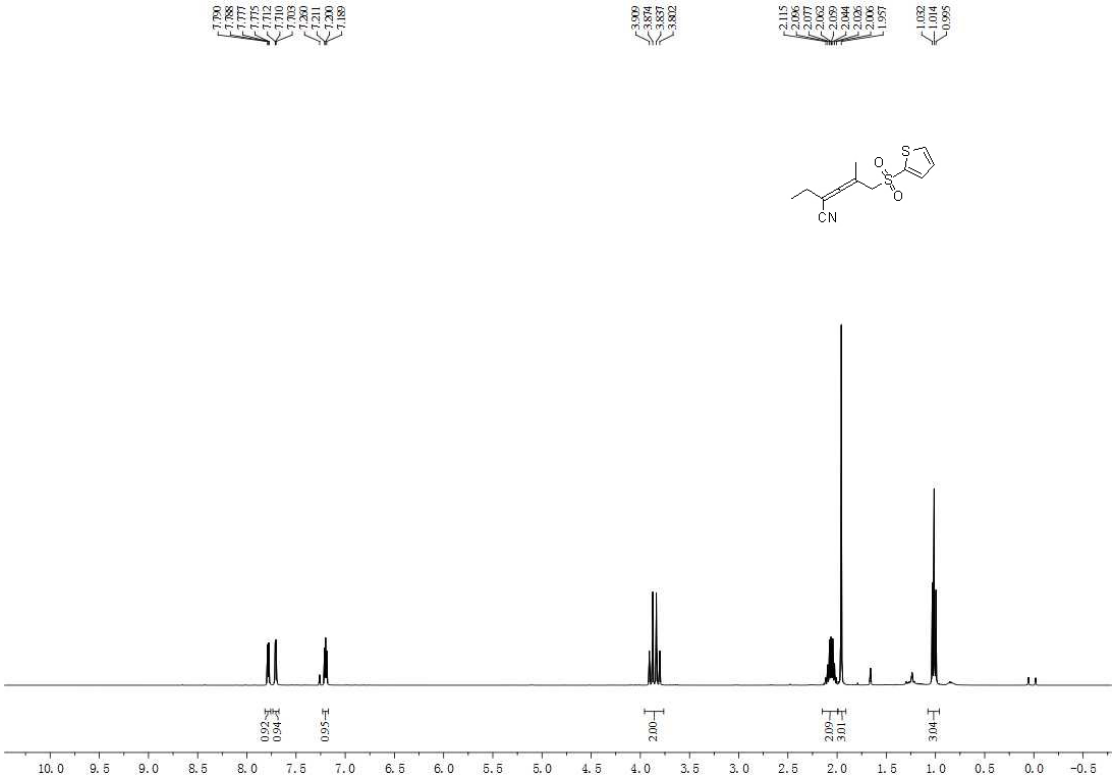
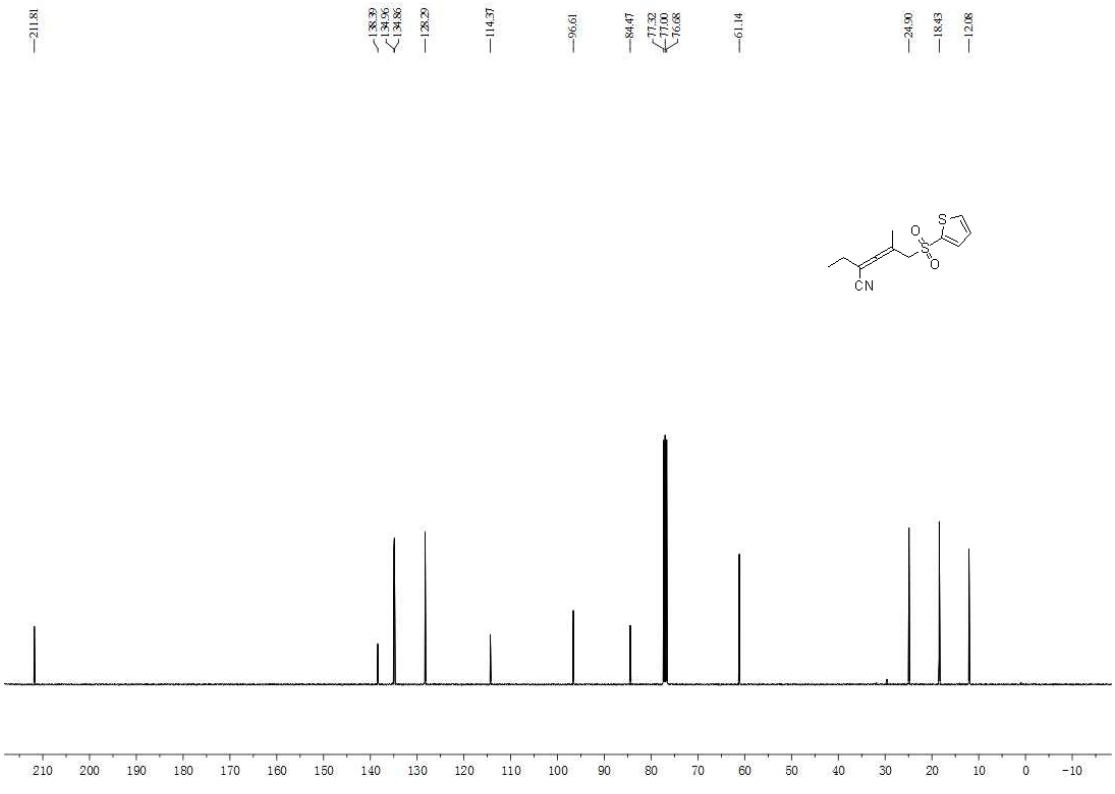
136.01
134.33
124.16
114.06
96.14
84.85
77.32
77.00
76.68
60.15
24.81
18.61
12.03
N
O
S
O
CN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

Product 3s


7.790
7.788
7.777
7.775
7.772
7.710
7.703
7.300
7.211
7.200
7.189
3.909
3.874
3.857
3.802
2.115
2.096
2.077
2.062
2.059
2.044
2.026
2.006
1.997
1.032
1.014
0.995
S
O
O
CN
0.92
0.94
0.95
2.00
2.09
3.01
3.04
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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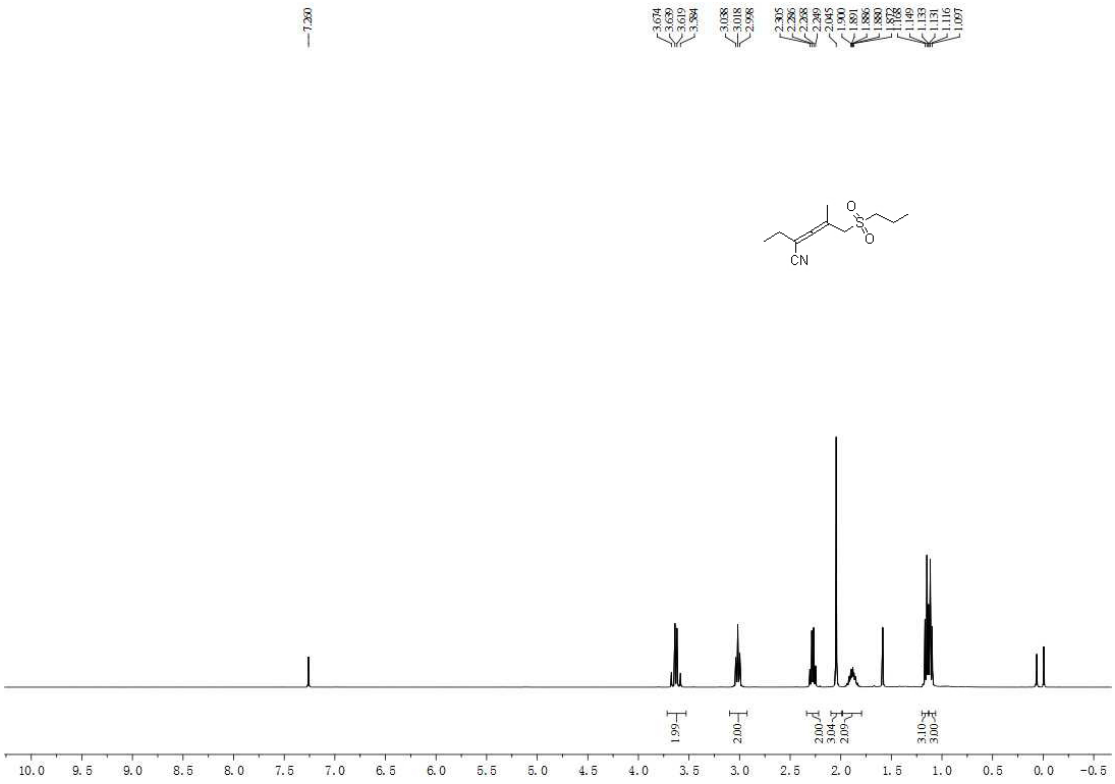
138.39
134.95
134.86
128.29
114.37
96.61
84.47
77.32
77.00
76.68
61.14
24.90
18.43
12.06
S
O
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Product 3t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3.619
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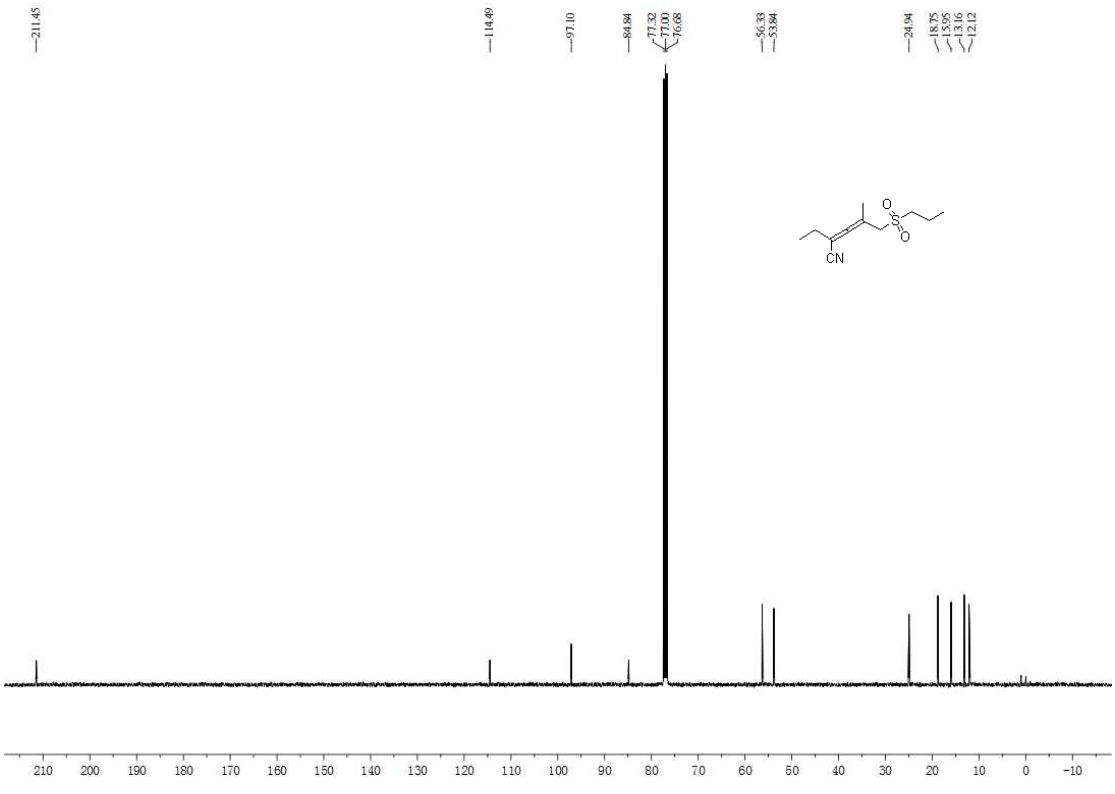
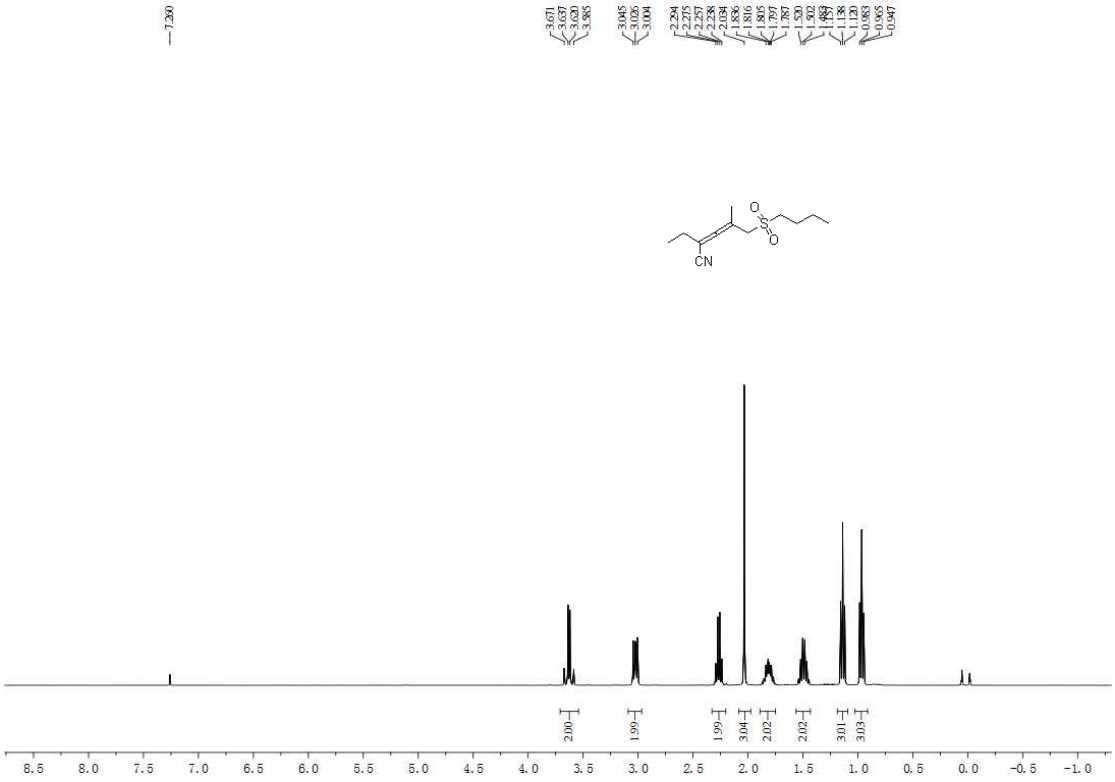
3.038
3.018
2.998
2.305
2.286
2.268
2.249
2.045
1.910
1.891
1.886
1.880
1.872
1.858
1.149
1.133
1.131
1.116
1.097
O
S
O
CN
1.99
2.00
2.00
3.04
2.09
3.10
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


211.45
114.49
97.10
84.84
77.32
77.00
76.68
56.33
53.84
24.94
18.75
15.95
13.16
12.12
O
S
O
CN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

Product 3u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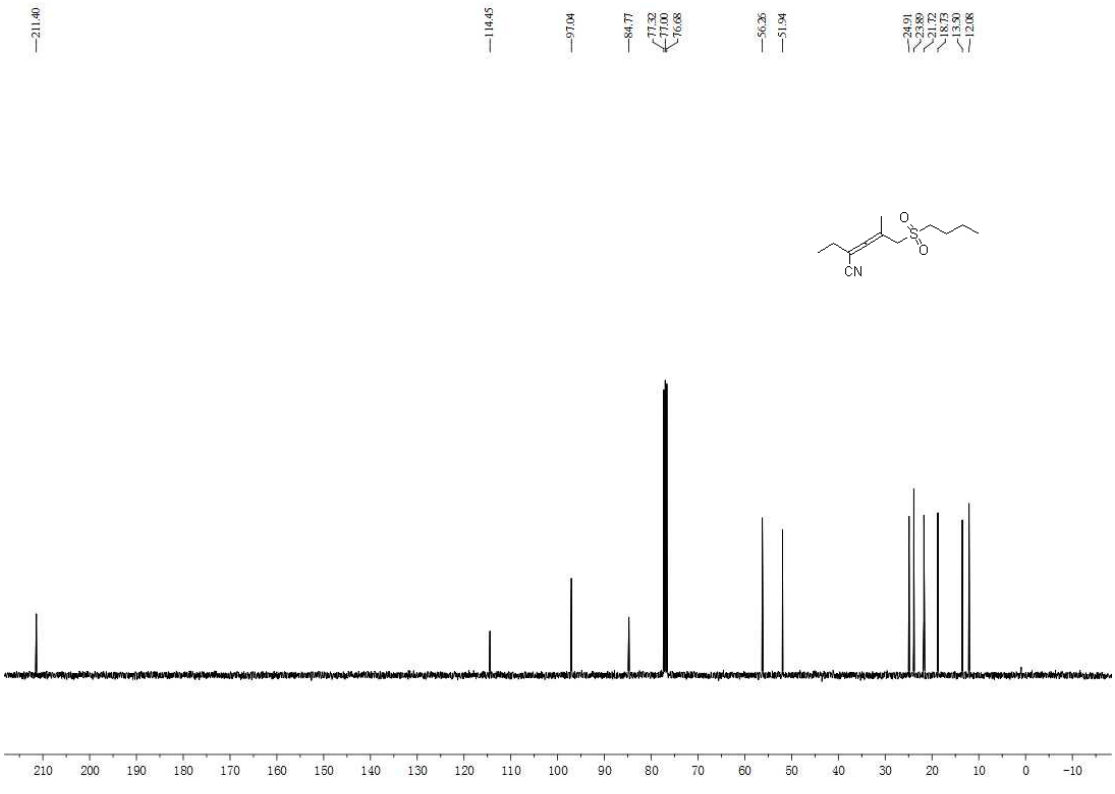
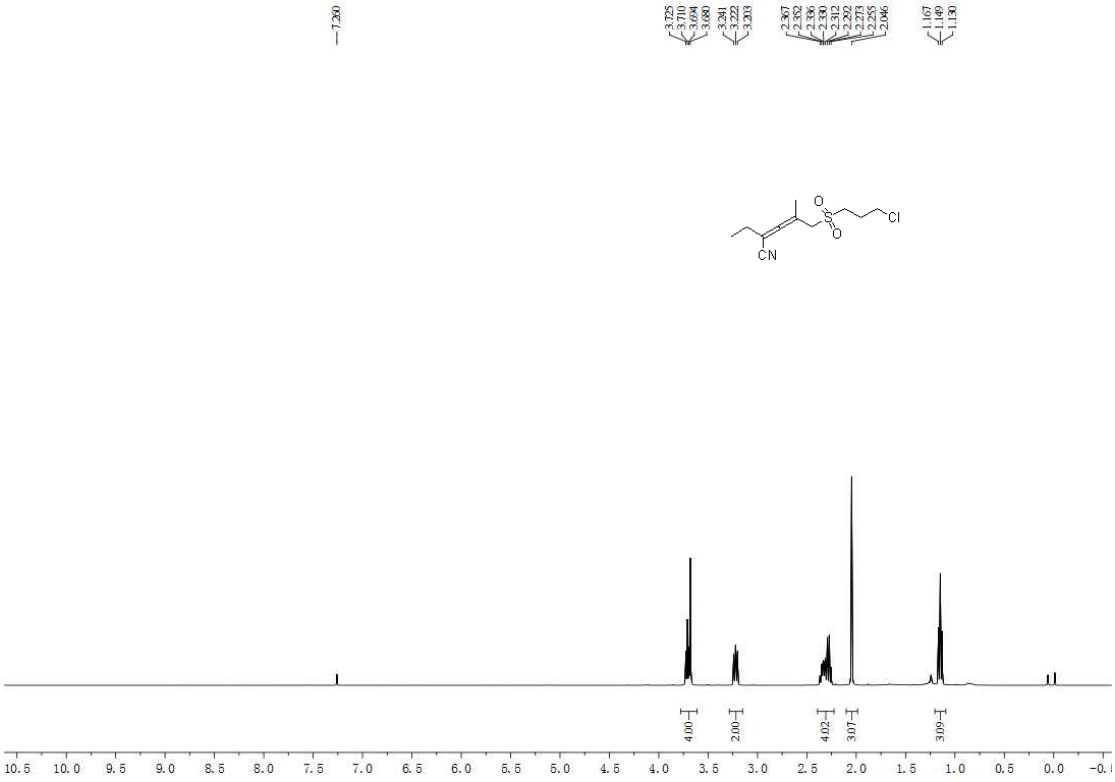
3.657
3.643
3.630
3.045
3.026
3.004
2.294
2.275
2.257
2.238
2.034
1.836
1.816
1.805
1.797
1.787
1.500
1.502
1.483
1.467
1.138
1.120
0.983
0.965
0.947
O
S
O
CN
2.00
1.99
1.99
3.04
2.02
2.02
3.01
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0


211.40
118.45
97.04
84.77
77.32
77.00
76.68
56.26
51.94
24.91
23.80
21.72
18.73
13.50
12.08
O
S
O
CN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

Product 3v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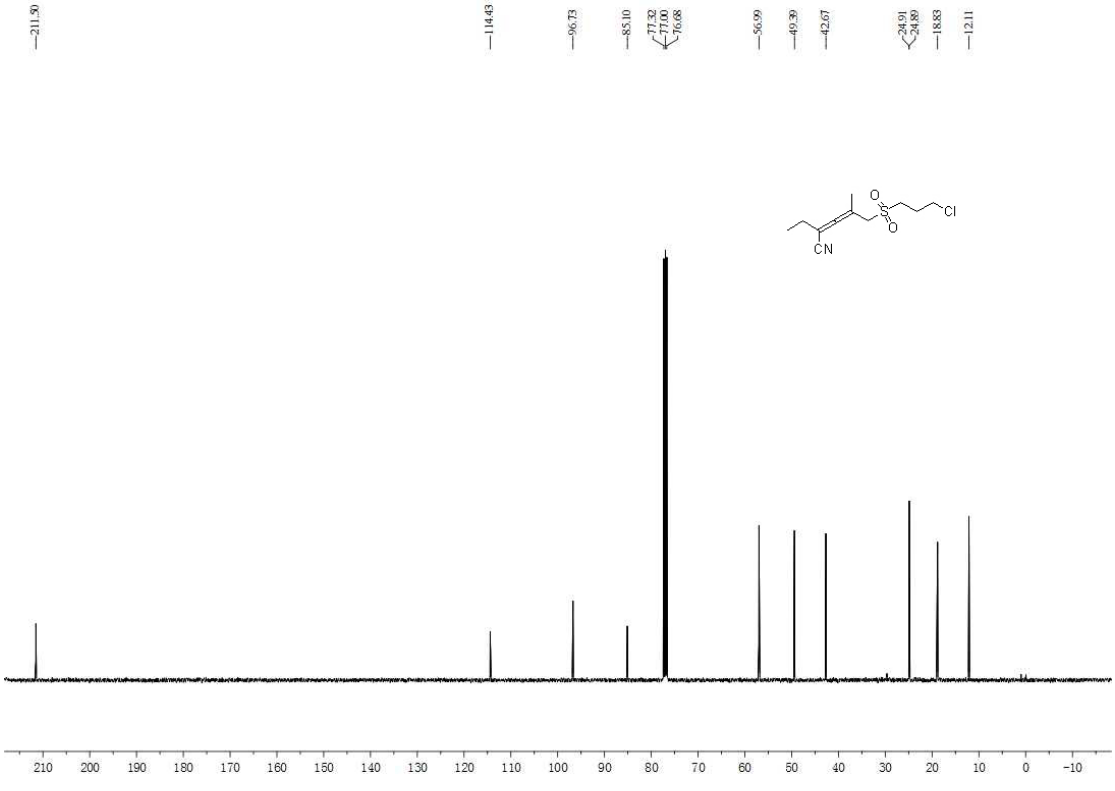
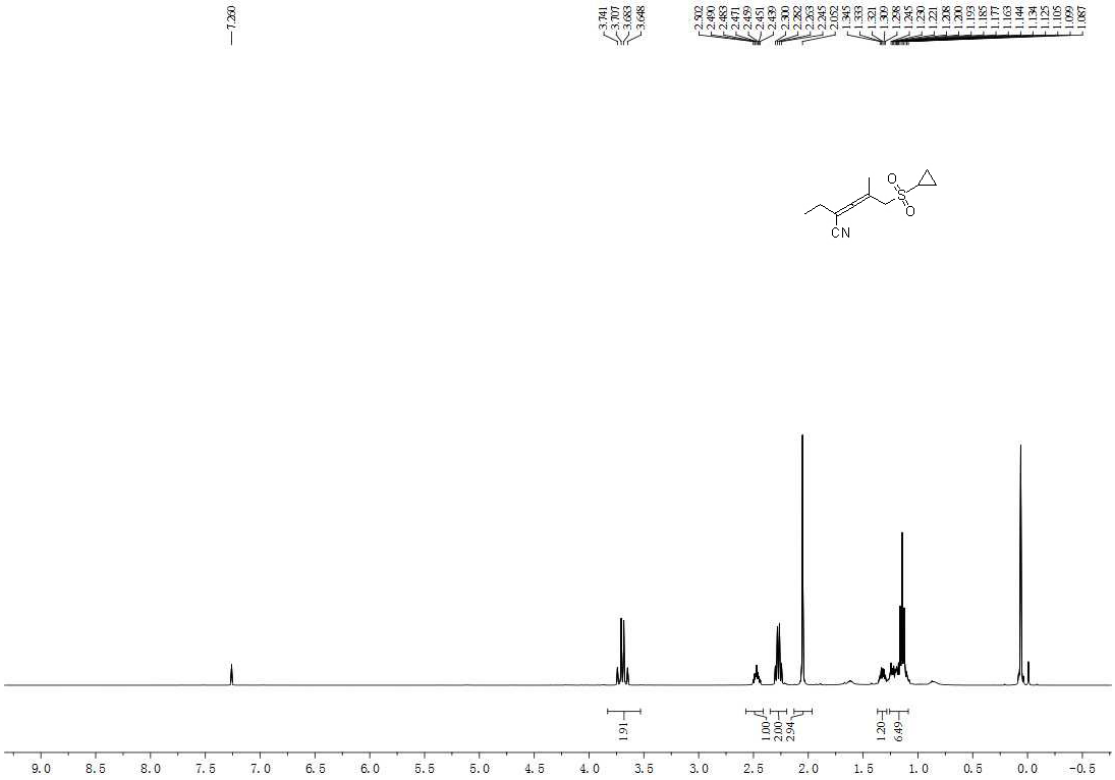
3.680
3.241
3.222
3.203
2.367
2.352
2.336
2.330
2.312
2.292
2.273
2.255
2.046
1.167
1.149
1.130
O
S
O
Cl
CN
4.00
2.00
4.02
3.07
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


211.50
114.43
96.73
85.10
77.32
77.00
76.68
56.99
49.39
42.67
24.91
24.89
18.83
12.11
O
S
O
Cl
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Product 3w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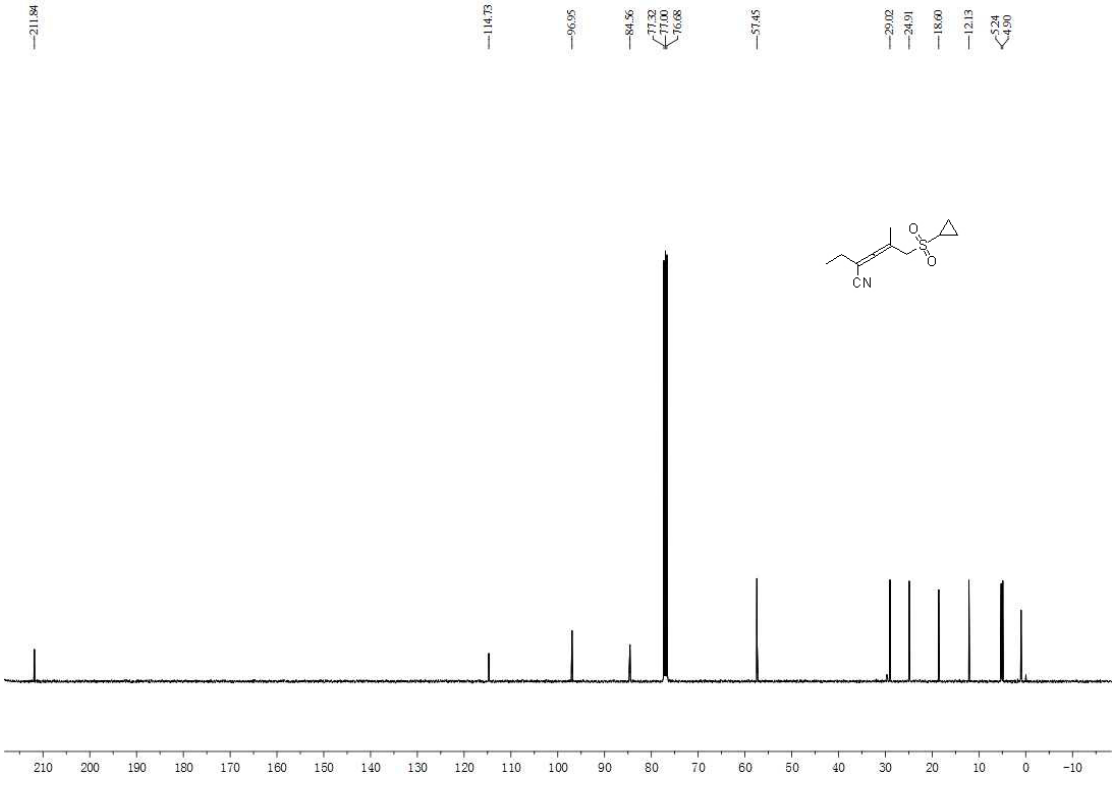
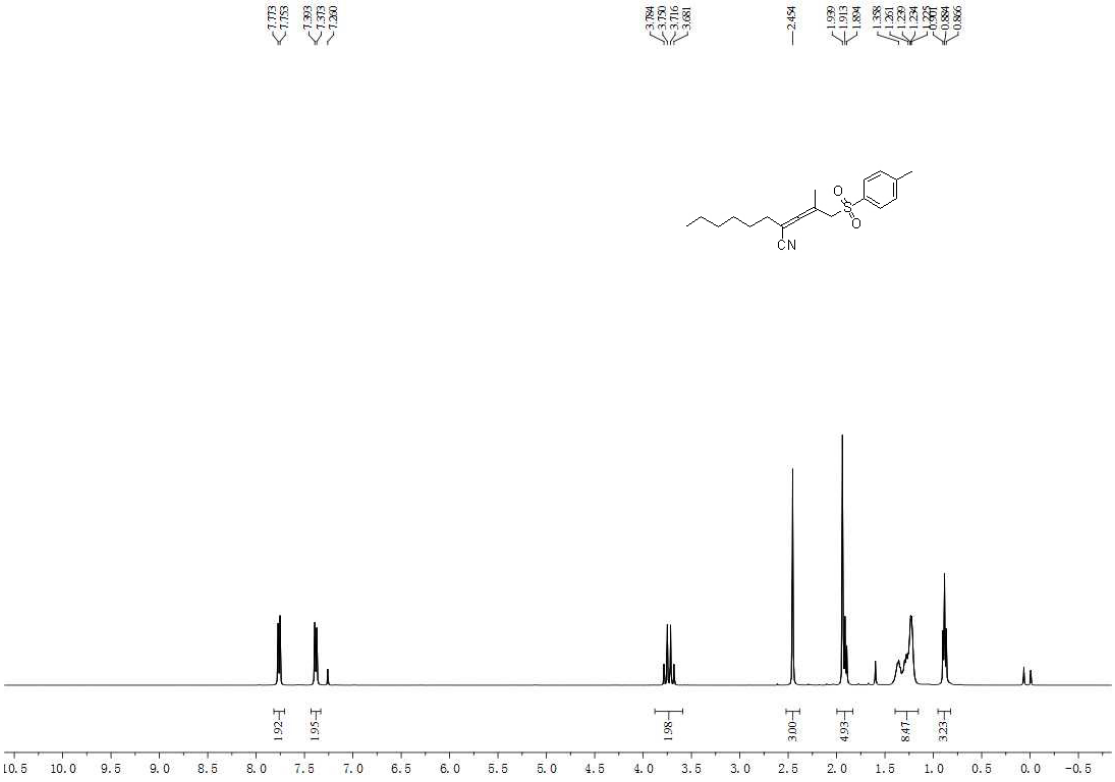
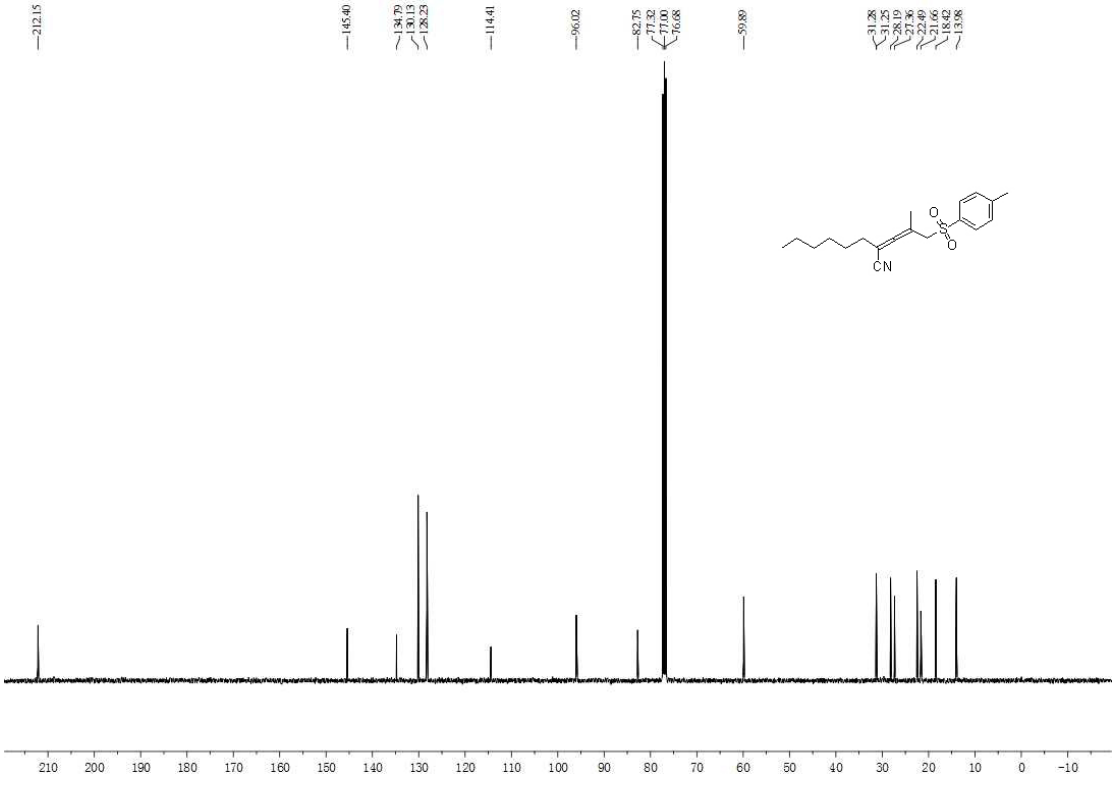
3.741
3.707
3.683
3.648
2.502
2.490
2.483
2.471
2.459
2.451
2.439
2.430
2.382
2.353
2.345
2.052
1.345
1.333
1.321
1.309
1.288
1.245
1.230
1.221
1.208
1.200
1.159
1.165
1.177
1.163
1.144
1.134
1.125
1.105
1.099
1.087
O
S
O
CN
1.91
1.00
2.00
2.94
1.20
6.49
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

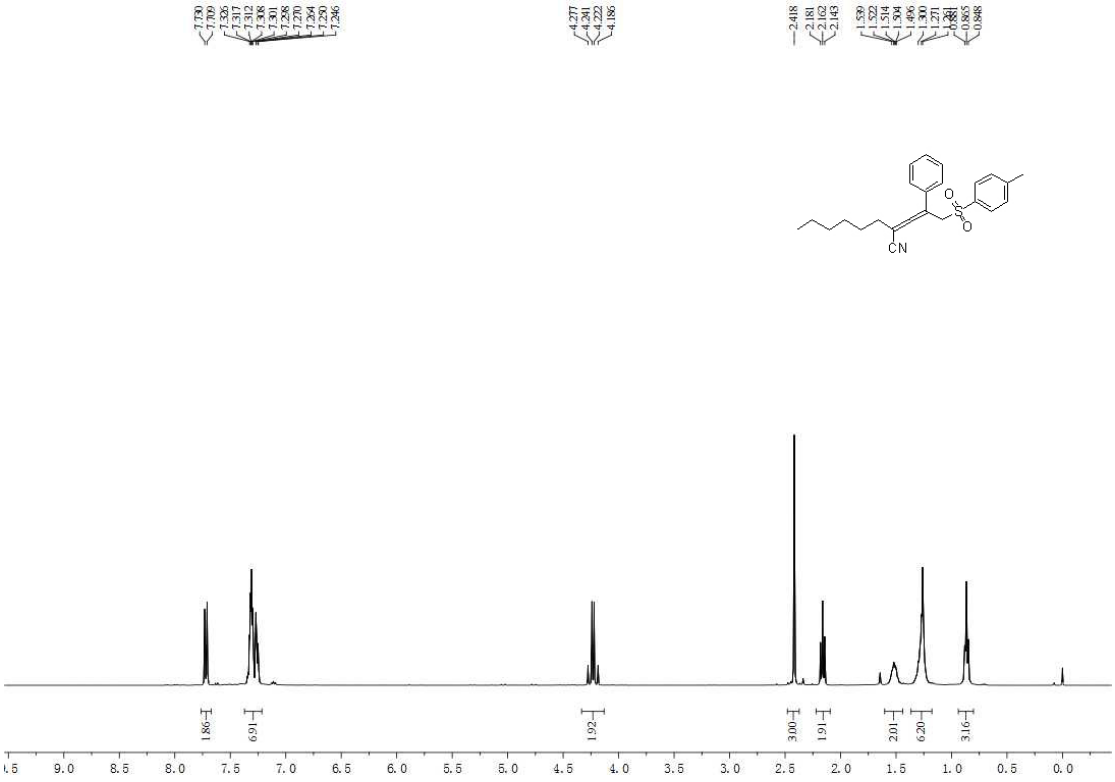

211.84
114.73
96.95
84.56
77.32
77.00
76.68
57.45
29.02
24.91
18.60
12.13
5.24
4.90
O
S
O
CN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

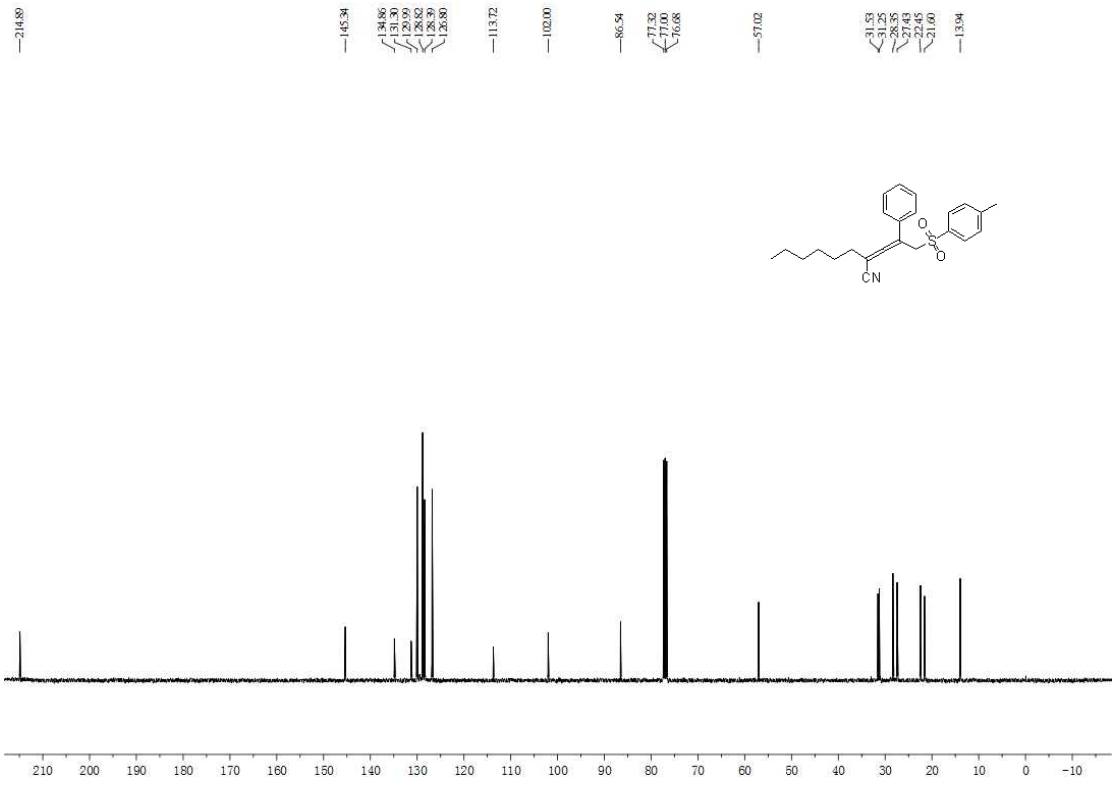
Product 4b



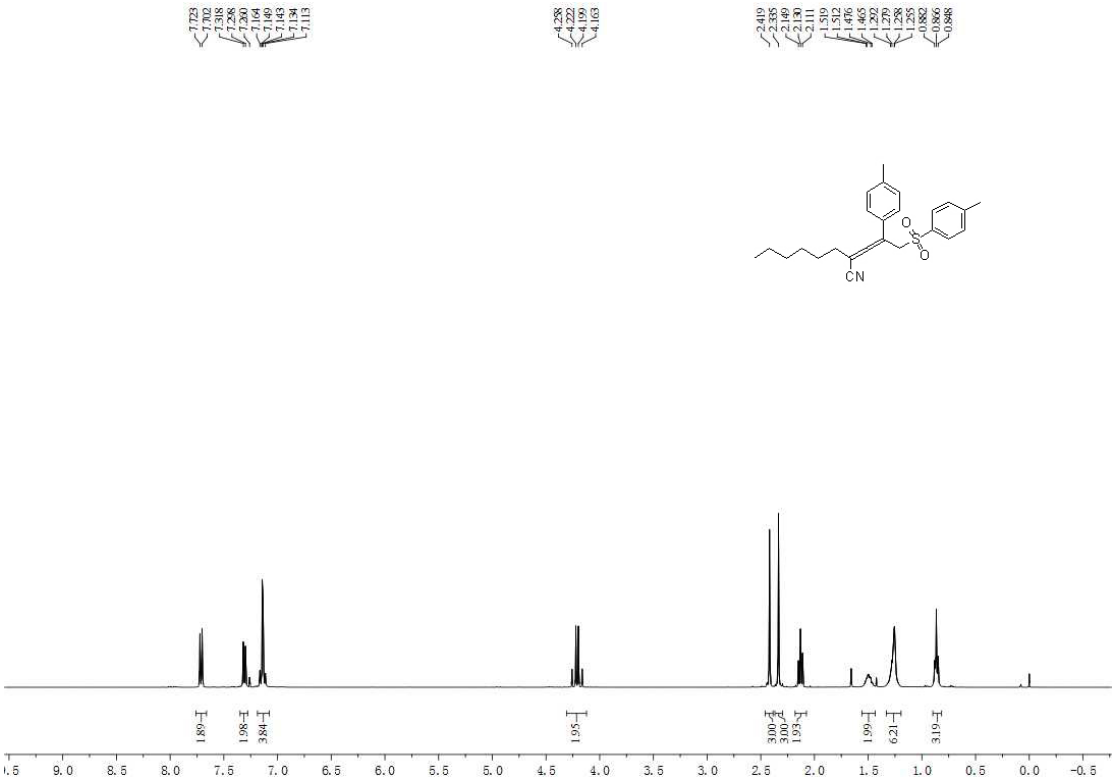


Product 4c





Product 4d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7.143
7.134
7.113
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4.222
4.199
4.163
2.419
2.395
2.369
2.130
2.111
1.519
1.512
1.476
1.465
1.292
1.279
1.258
1.235
0.882
0.866
0.848
O
S
O
CN
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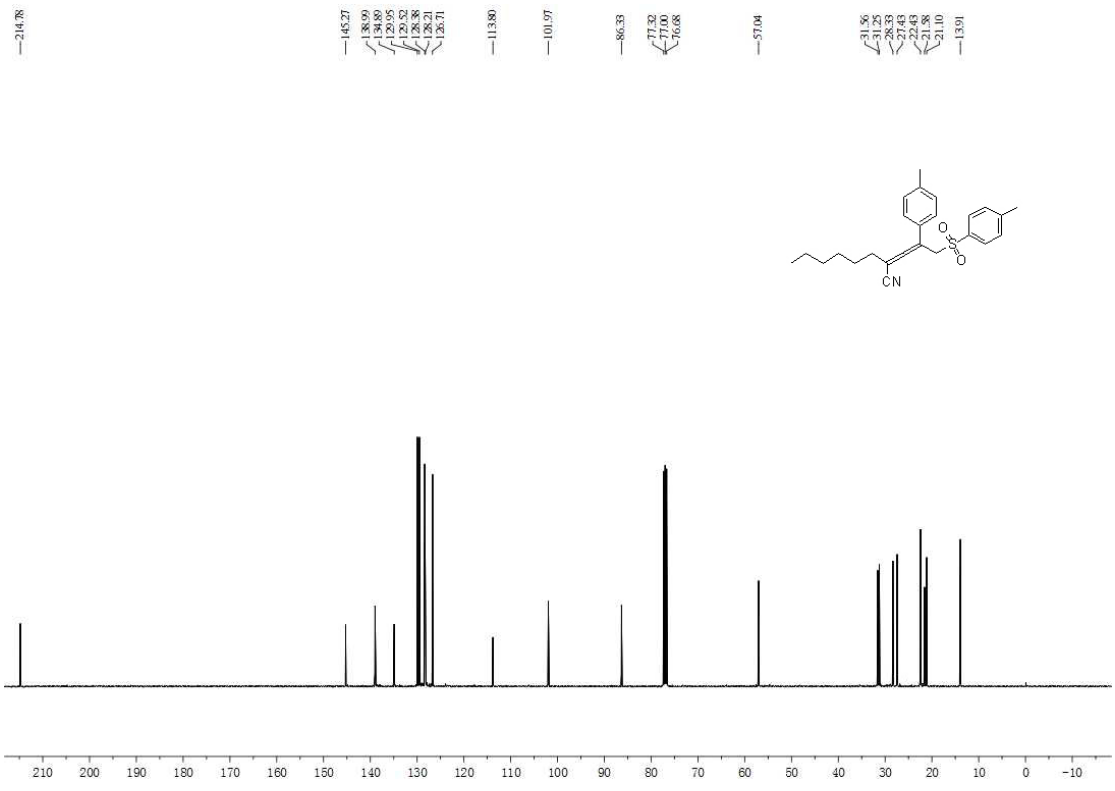
1.98
3.84
1.95
3.00
3.00
1.93
1.99
6.21
3.19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134.89
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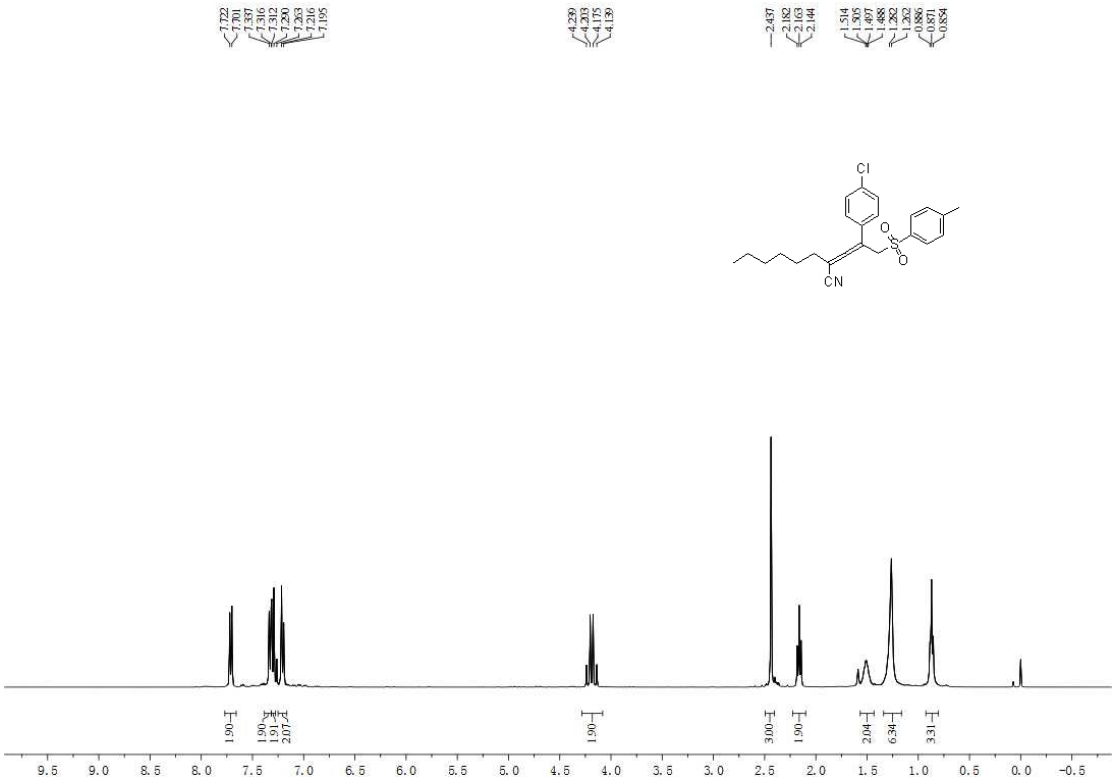
129.52
128.38
128.21
126.71
113.80
101.97
86.33
77.32
77.00
76.68
57.04
31.56
31.25
28.33
27.43
22.43
21.38
21.10
13.91
O
S
O
CN

Product 4e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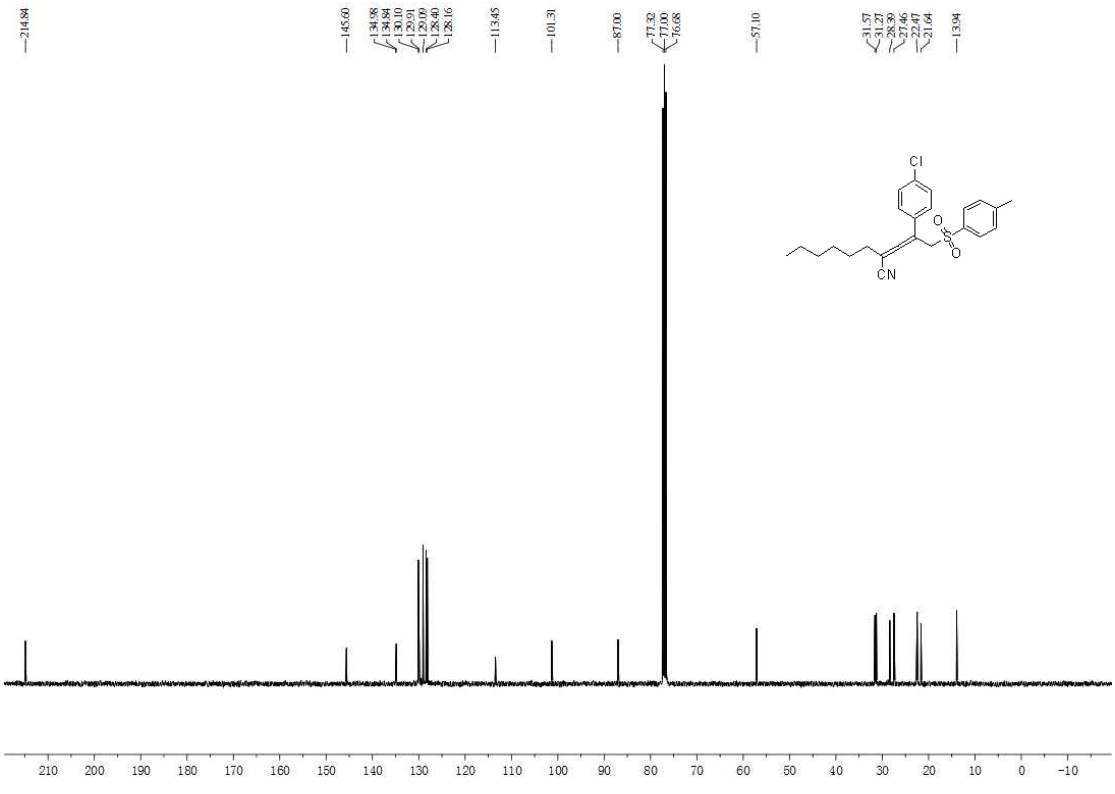
7.701
7.337
7.316
7.312
7.290
7.203
7.206
7.195
4.239
4.203
4.175
4.139
2.437
2.182
2.165
2.144
1.514
1.505
1.497
1.488
1.282
1.202
0.886
0.871
0.854
Cl
O
S
O
CN
1.90
1.90
1.91
2.07
1.90
3.00
1.90
2.04
6.34
3.31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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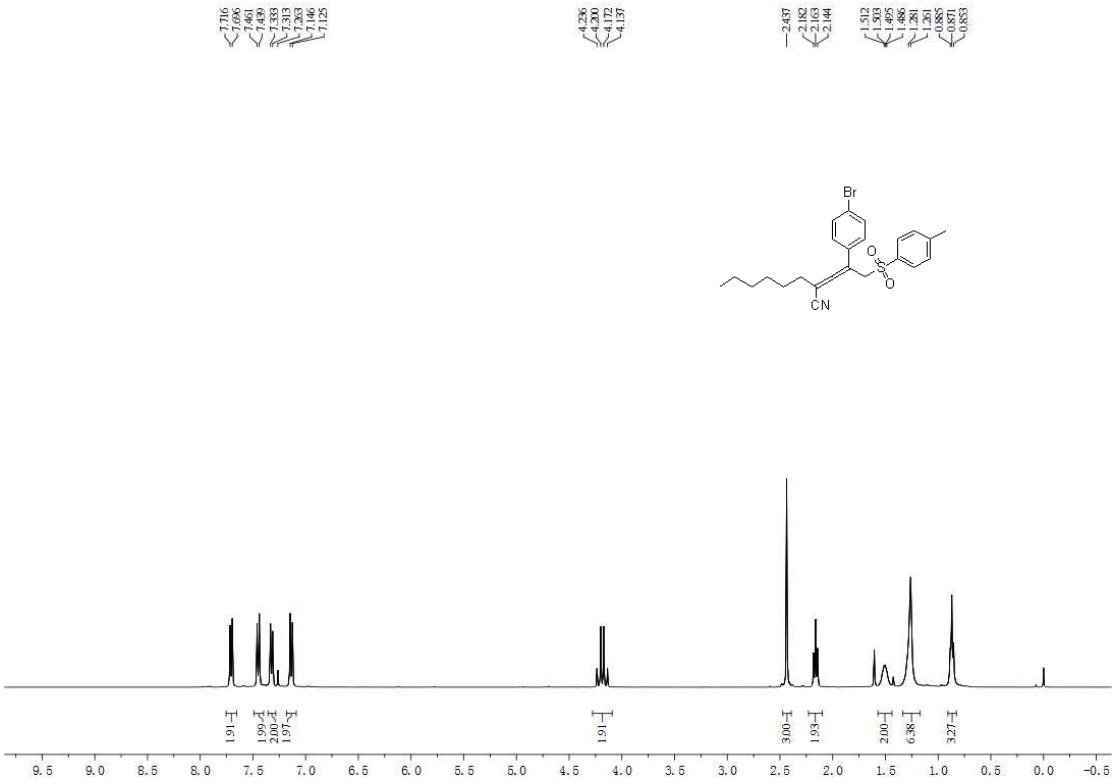
145.60
134.58
134.84
130.10
129.91
129.09
128.40
128.16
113.45
101.31
87.00
77.32
77.00
76.68
57.10
31.57
31.27
28.39
27.46
22.47
21.64
13.94
Cl
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Product 4f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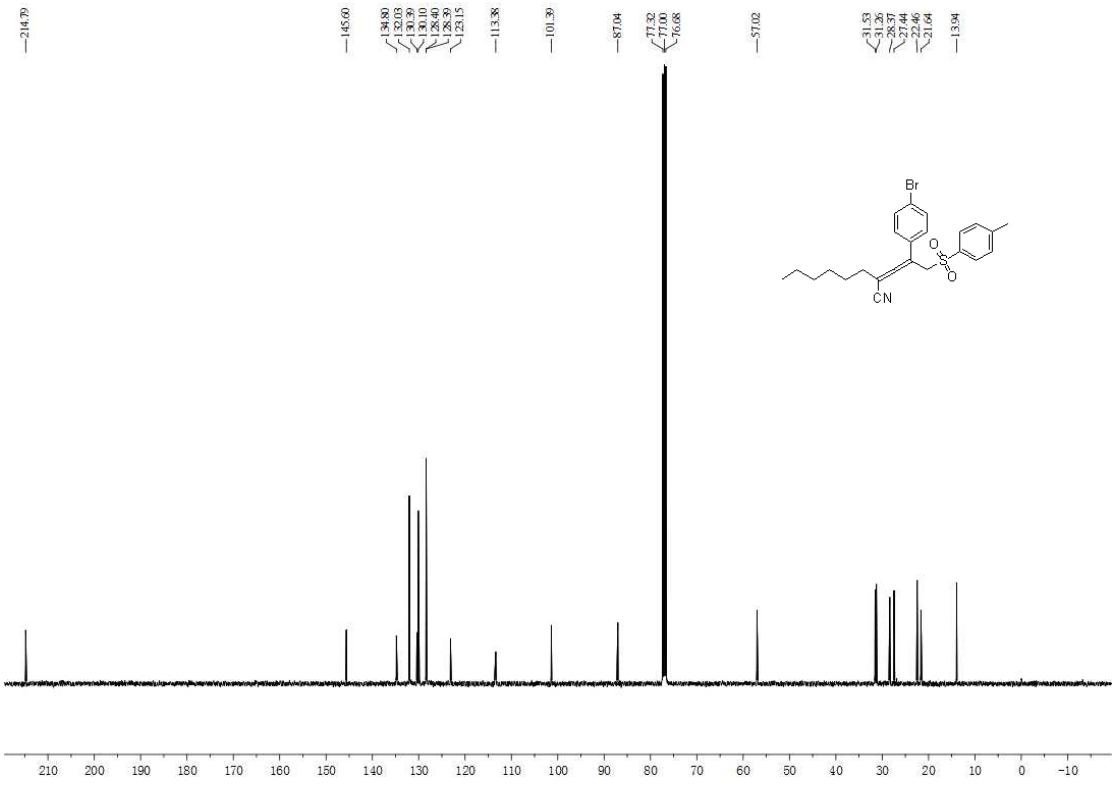
7.461
7.439
7.333
7.313
7.203
7.146
7.125
4.236
4.200
4.172
4.137
2.437
2.182
2.163
2.144
1.512
1.503
1.495
1.486
1.281
1.261
0.865
0.851
0.853
Br
O
S
O
CN
1.91
1.99
2.00
1.97
1.91
3.00
1.93
2.00
6.38
3.27
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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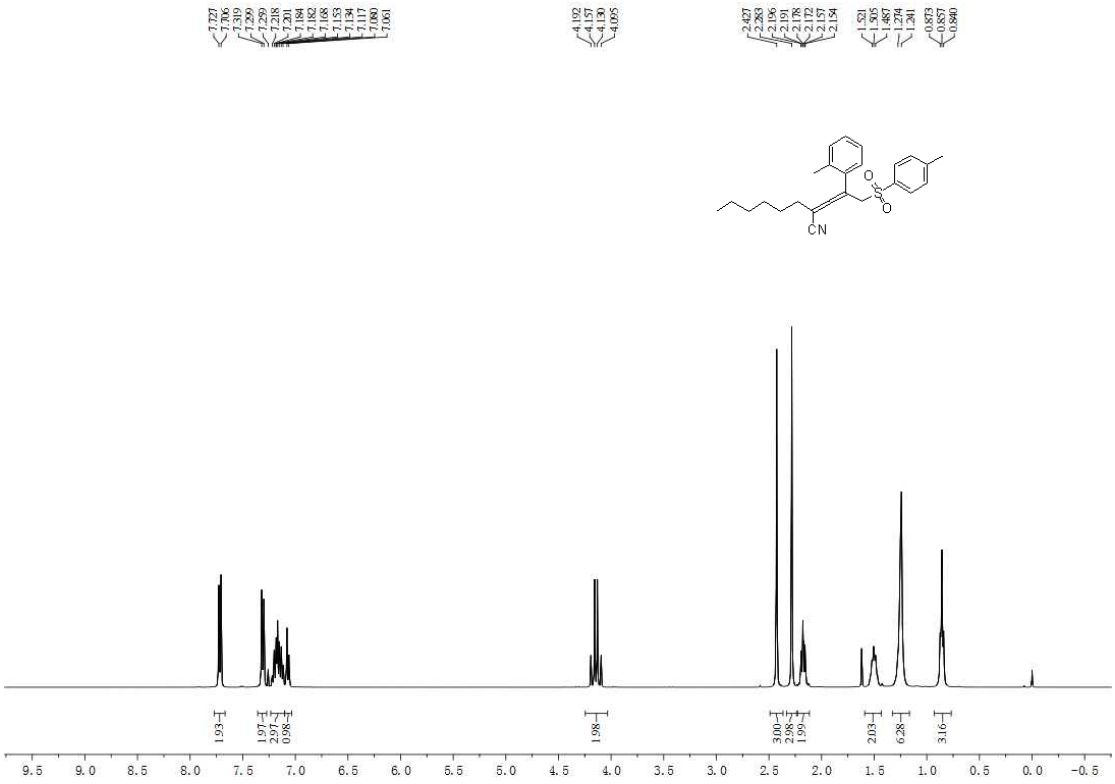
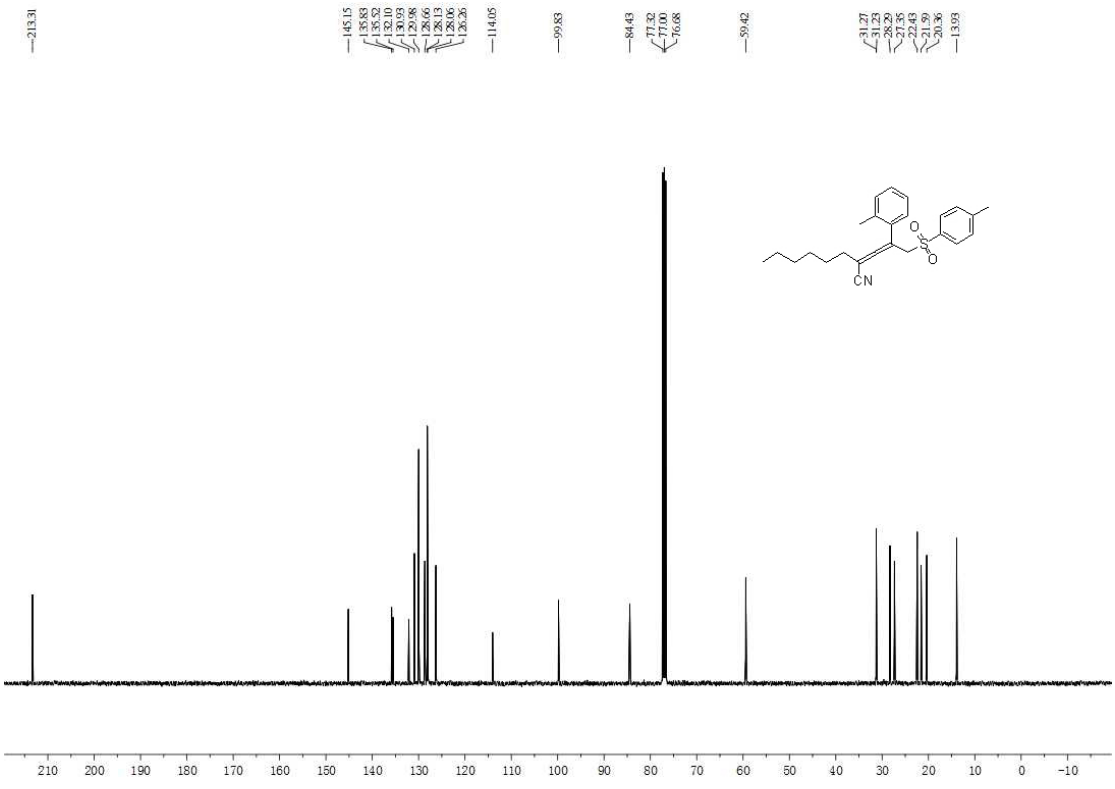
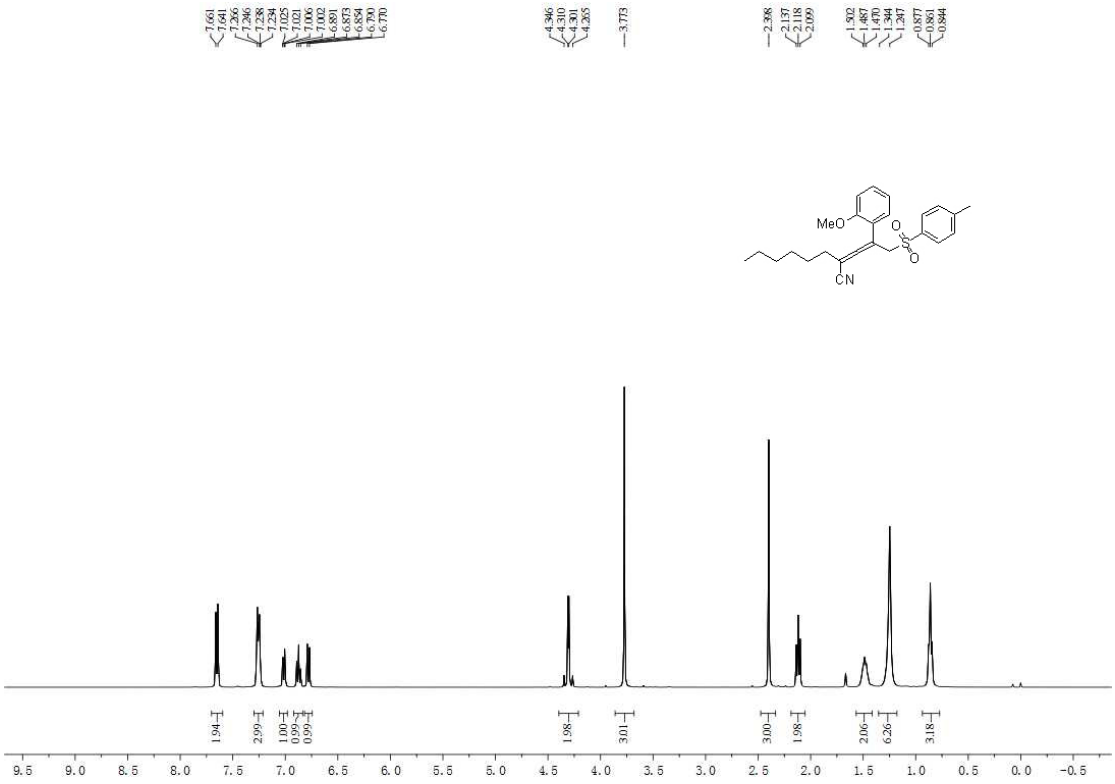
132.03
130.39
130.10
128.64
128.39
123.15
113.38
101.39
87.04
77.32
77.00
76.68
57.02
31.53
31.26
28.37
27.44
22.46
21.64
13.94
Br
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Product 4g





Product 4h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7.366
7.346
7.238
7.234
7.025
7.023
7.006
7.002
6.891
6.873
6.854
6.700
6.770
4.346
4.330
4.301
4.285
3.773
2.388
2.137
2.118
2.099
1.502
1.487
1.470
1.344
1.247
0.877
0.861
0.844
MeO
O
S
O
CN
1.94
2.99
1.00
0.99
0.99
1.98
3.01
3.00
1.98
2.06
6.26
3.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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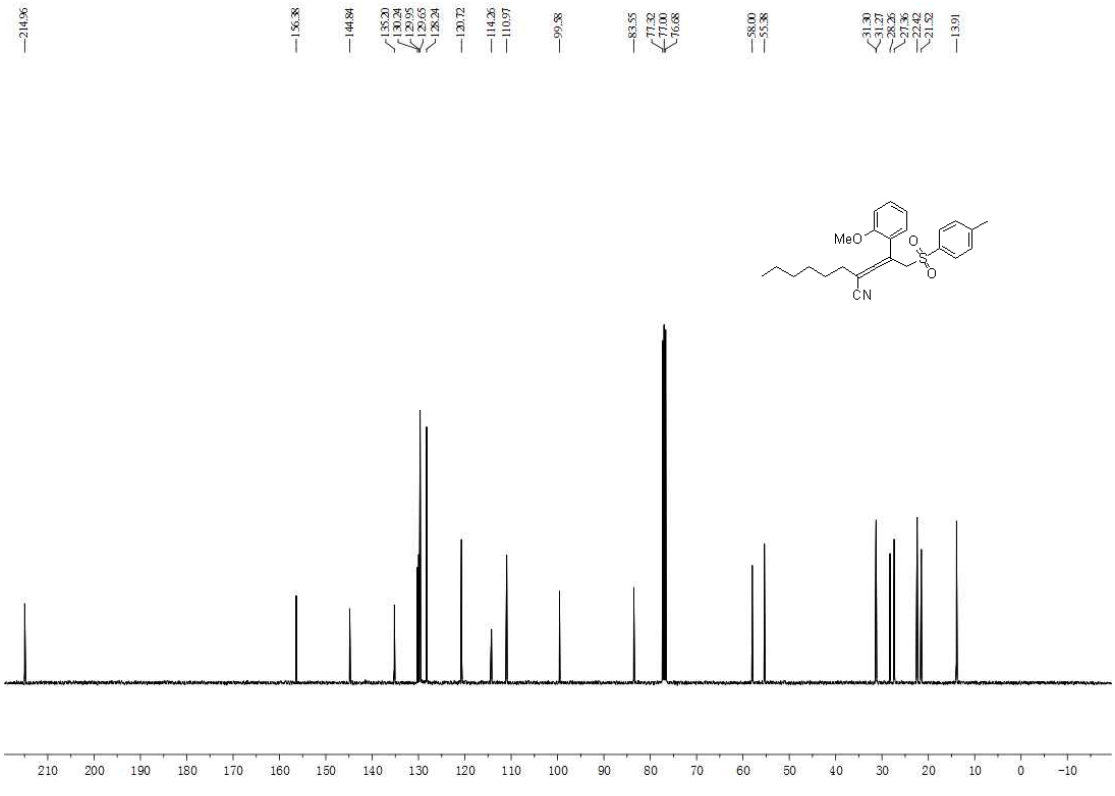
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5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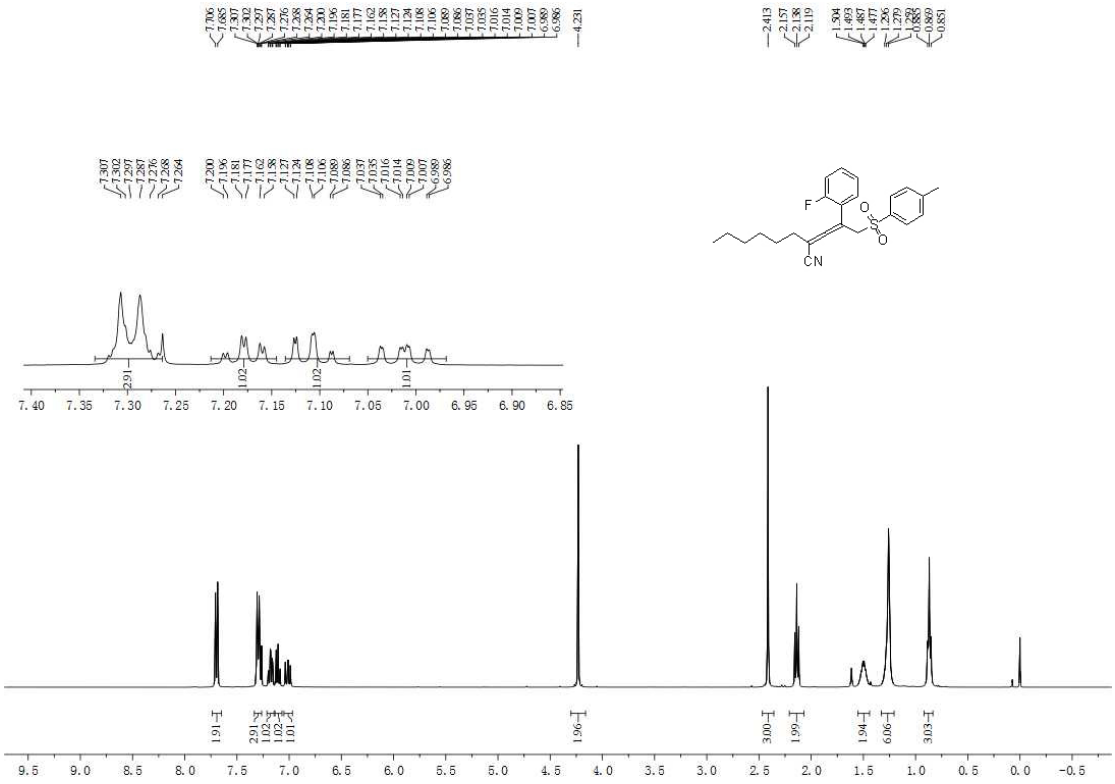
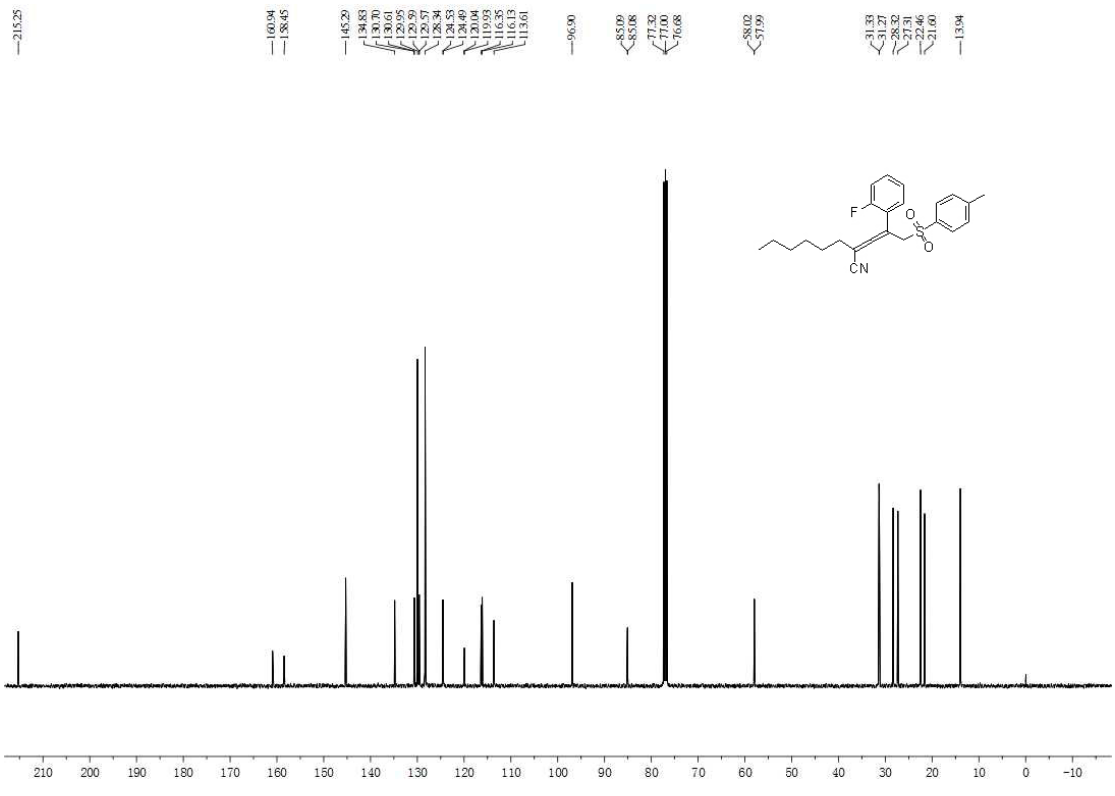
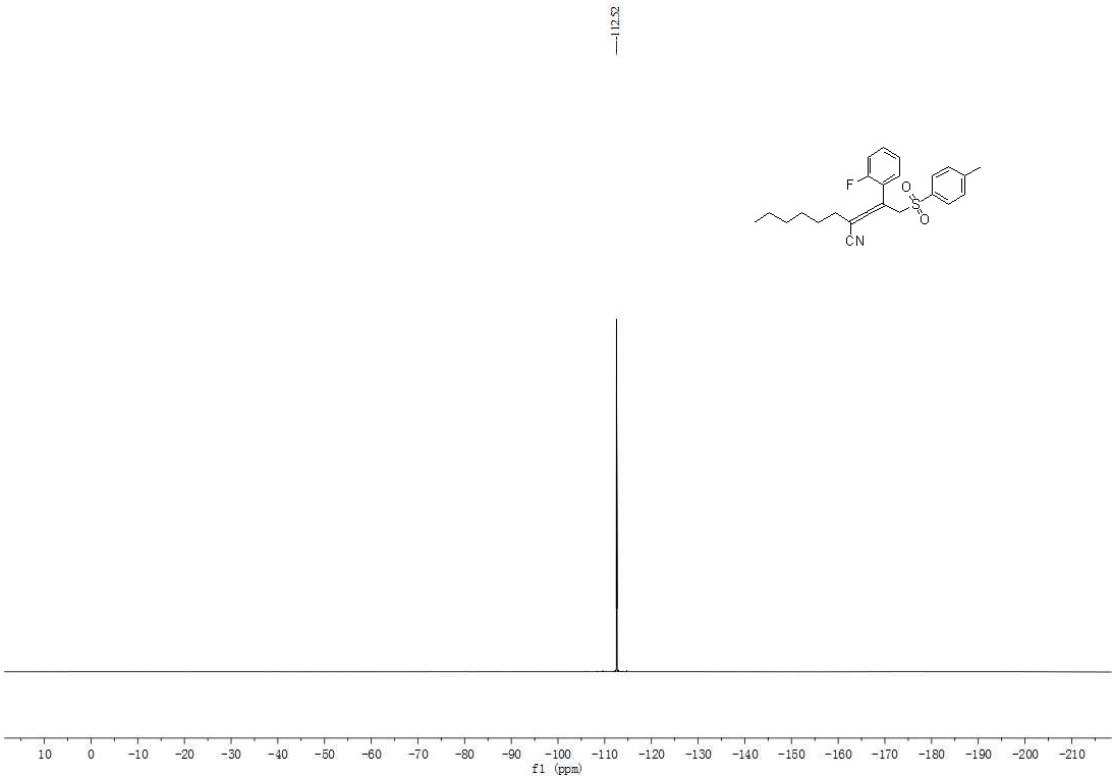
156.38
144.84
135.20
130.24
129.95
129.65
128.24
120.72
114.26
110.97
99.58
83.55
77.32
77.00
76.68
58.00
55.38
31.30
31.27
28.26
27.36
22.42
21.52
13.91
MeO
O
S
O
CN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

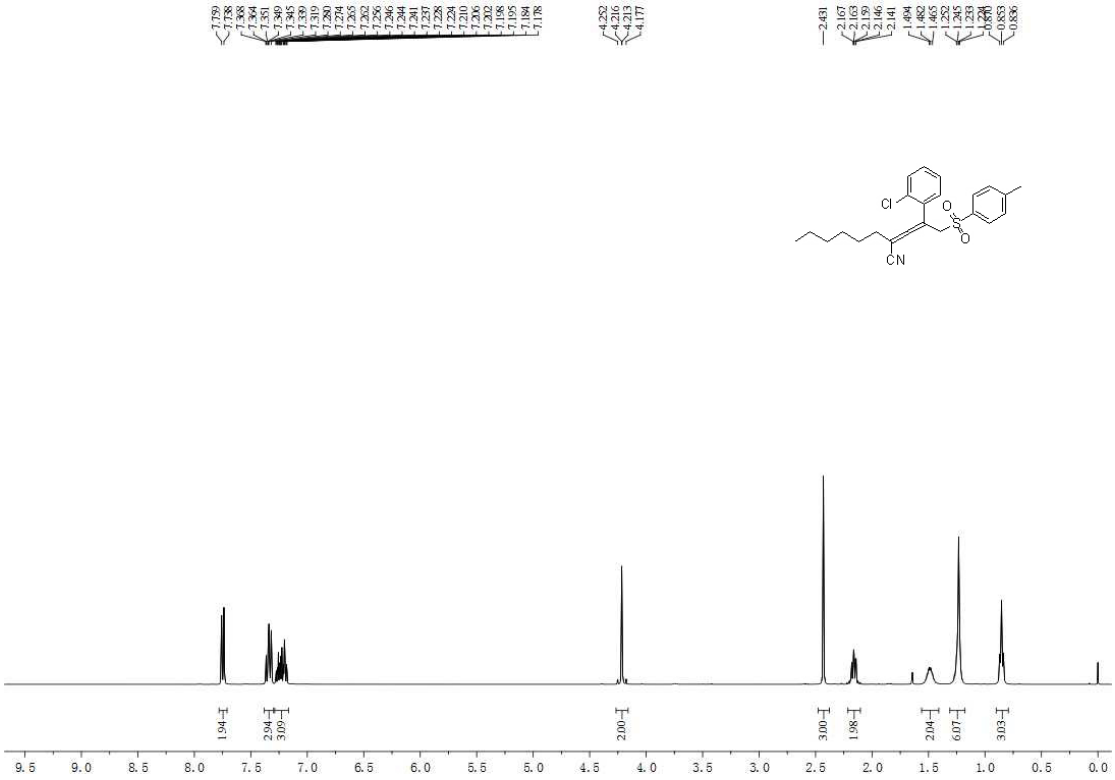
Product 4i






-112.52
F
O
S
O
CN
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Product 4j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7.339
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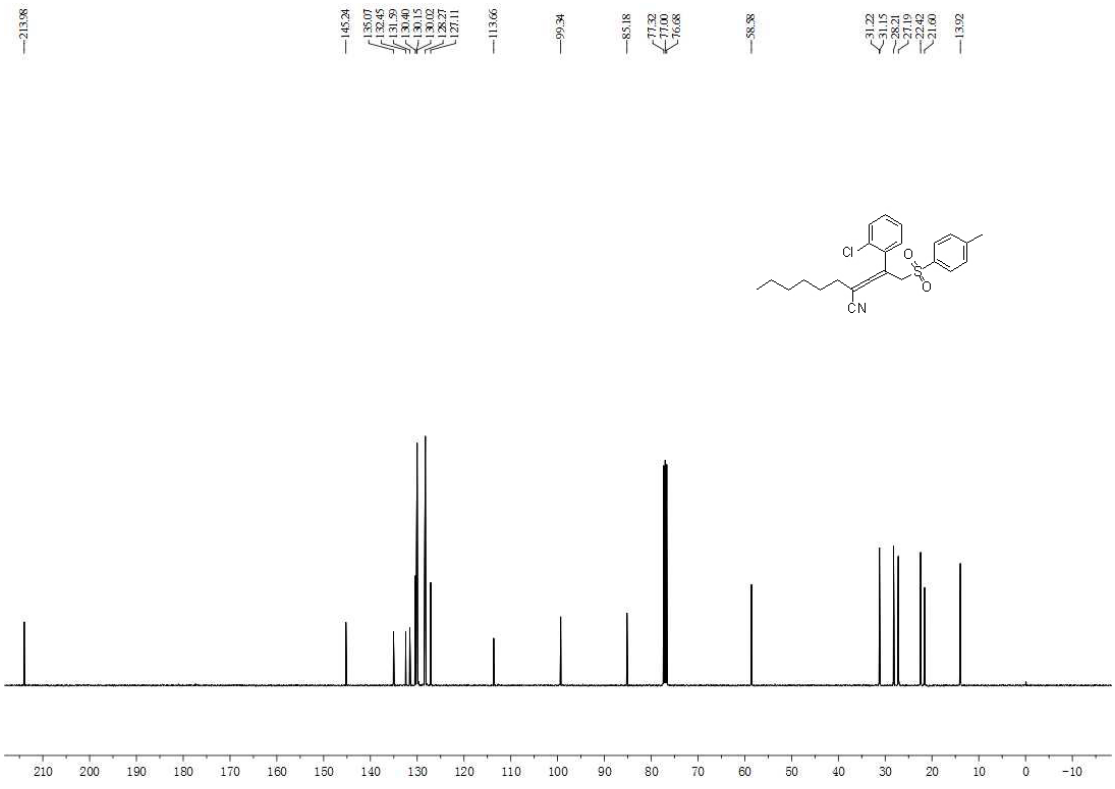
7.280
7.274
7.255
7.252
7.246
7.244
7.241
7.237
7.228
7.224
7.210
7.206
7.202
7.198
7.195
7.194
7.178
4.252
4.216
4.213
4.177
2.431
2.167
2.163
2.159
2.146
2.141
1.494
1.482
1.465
1.252
1.245
1.230
0.870
0.853
0.836
Cl
O
S
O
CN
1.94
2.94
3.09
2.00
3.00
1.98
2.04
6.07
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 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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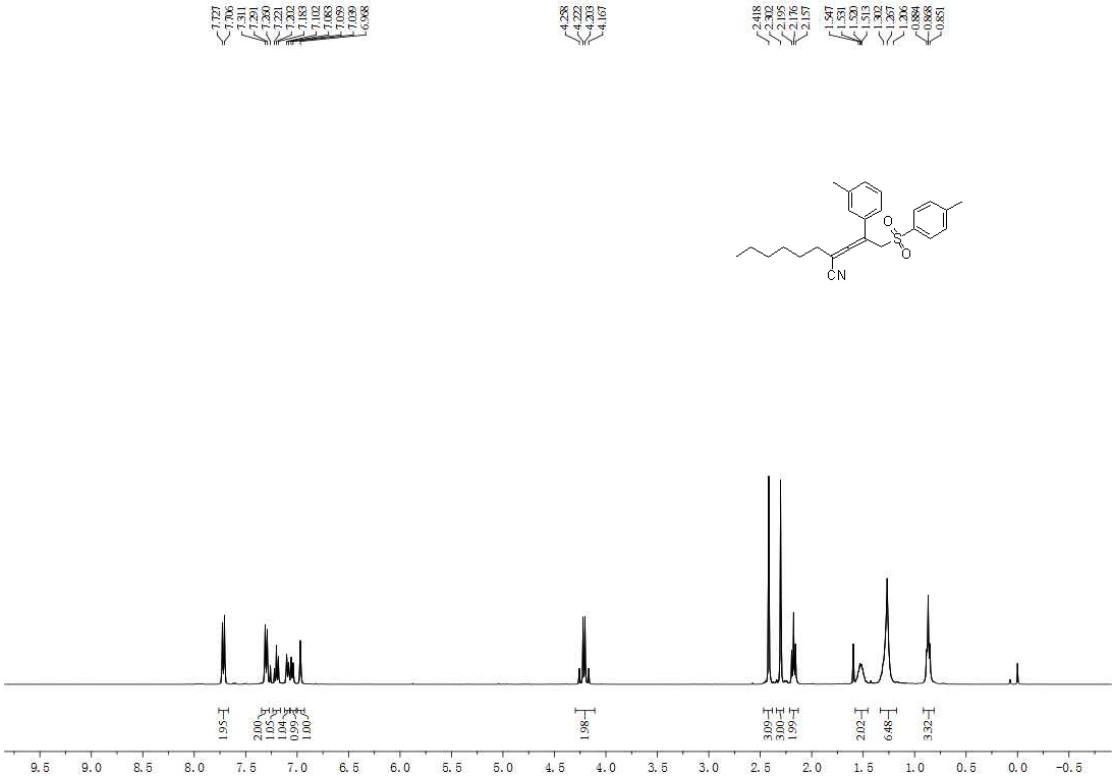
145.24
135.07
132.45
131.59
130.40
130.15
130.02
128.27
127.11
113.66
99.34
85.18
77.32
77.00
76.68
58.58
31.22
31.15
28.21
27.19
22.42
21.60
13.92
Cl
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Product 4k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7.706
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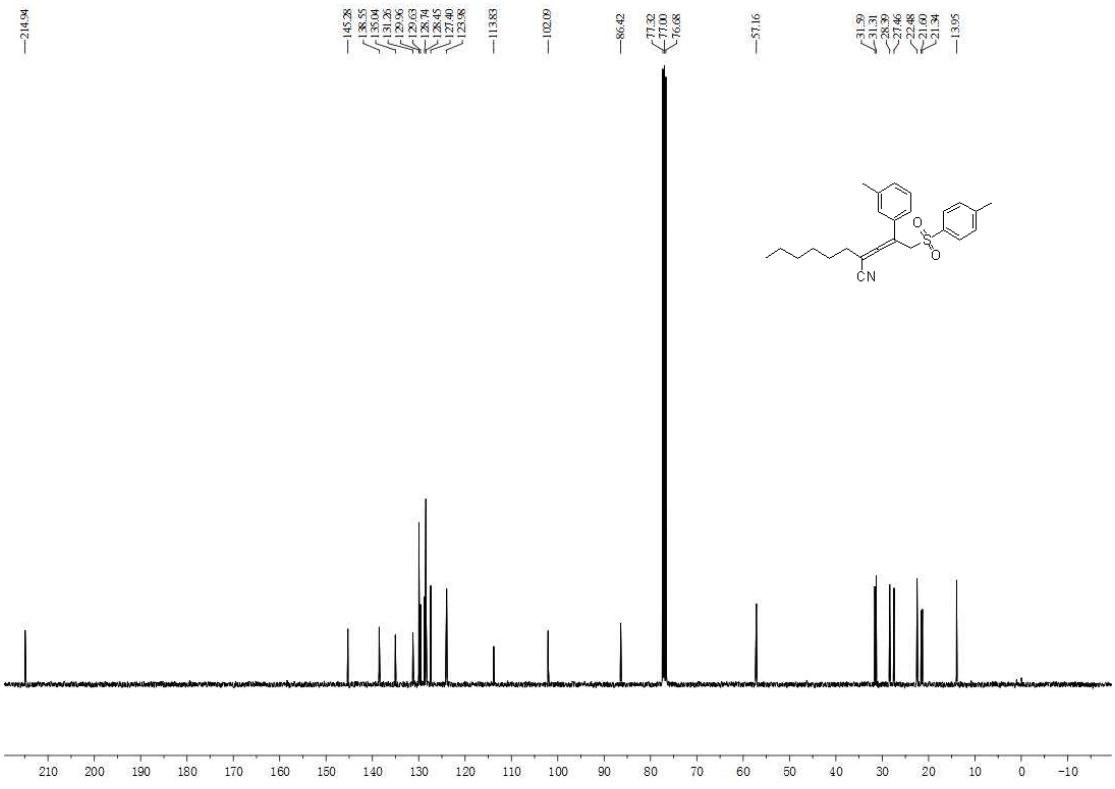
7.291
7.260
7.221
7.202
7.183
7.102
7.083
7.069
7.049
6.968
4.298
4.222
4.203
4.167
2.418
2.302
2.195
2.176
2.157
1.547
1.531
1.520
1.513
1.302
1.267
1.206
0.884
0.868
0.851
O
S
O
CN
1.95
2.00
1.05
1.04
0.99
1.00
1.98
3.09
3.00
1.99
2.02
6.48
3.32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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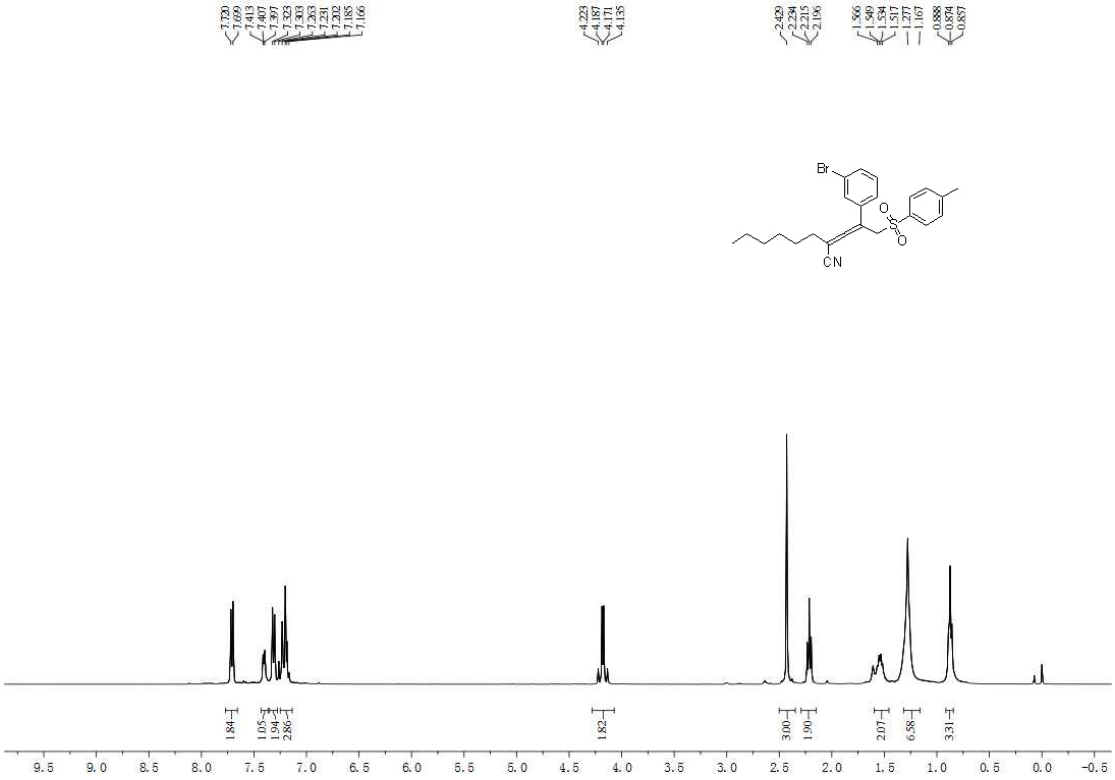
135.04
131.26
129.96
129.63
128.74
128.45
127.40
123.98
113.83
102.09
86.42
77.32
77.00
76.68
57.16
31.59
31.31
28.39
27.46
22.48
21.60
21.34
13.95
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Product 4l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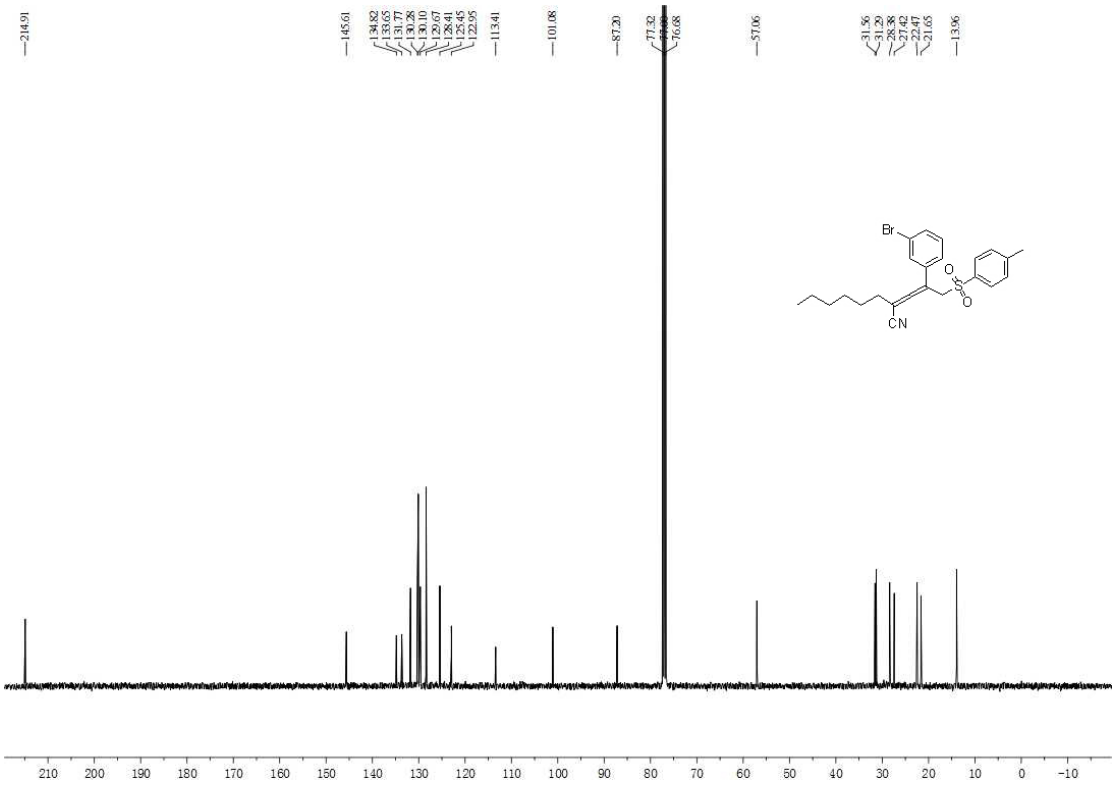
7.397
7.323
7.303
7.203
7.201
7.232
7.185
7.166
4.223
4.187
4.171
4.135
2.429
2.234
2.215
2.196
1.566
1.549
1.534
1.517
1.277
1.167
0.888
0.874
0.857
Br
O
S
O
CN
1.84
1.05
1.94
2.86
1.82
3.00
1.90
2.07
6.58
3.31
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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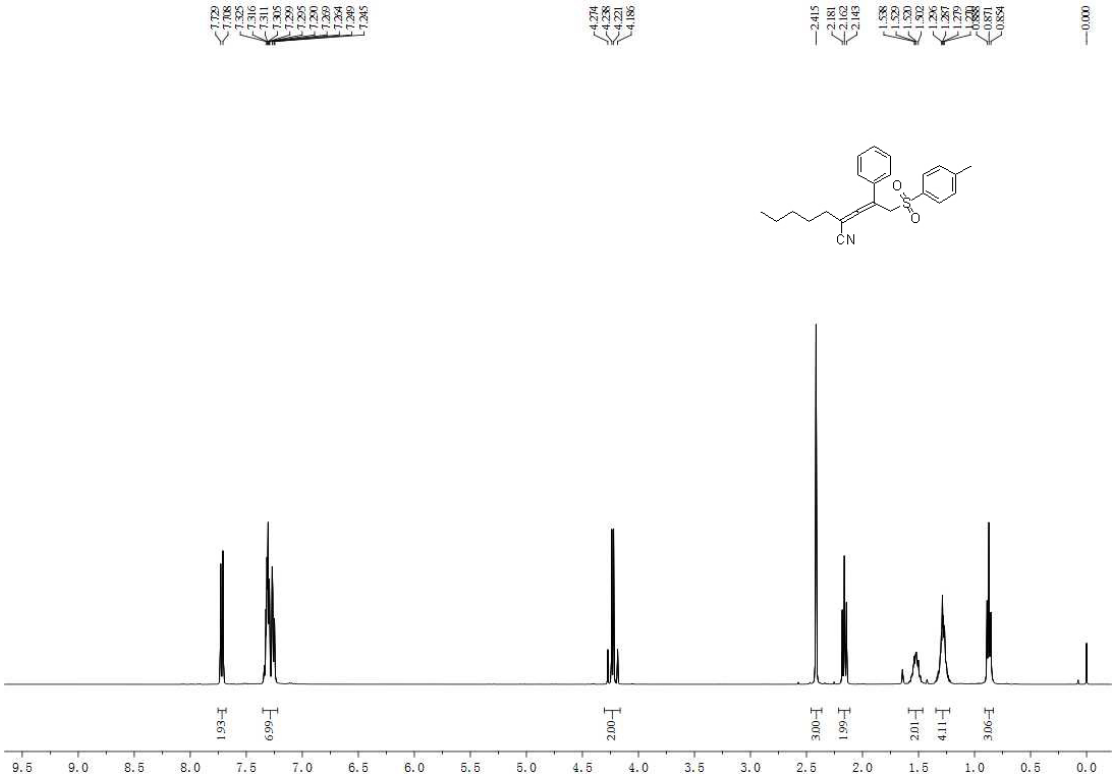
134.82
133.65
131.77
130.28
130.10
128.67
128.41
125.45
122.95
113.41
101.08
87.20
77.32
76.68
57.06
31.56
31.29
28.38
27.42
22.47
21.65
13.96
Br
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Product 4m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7.708
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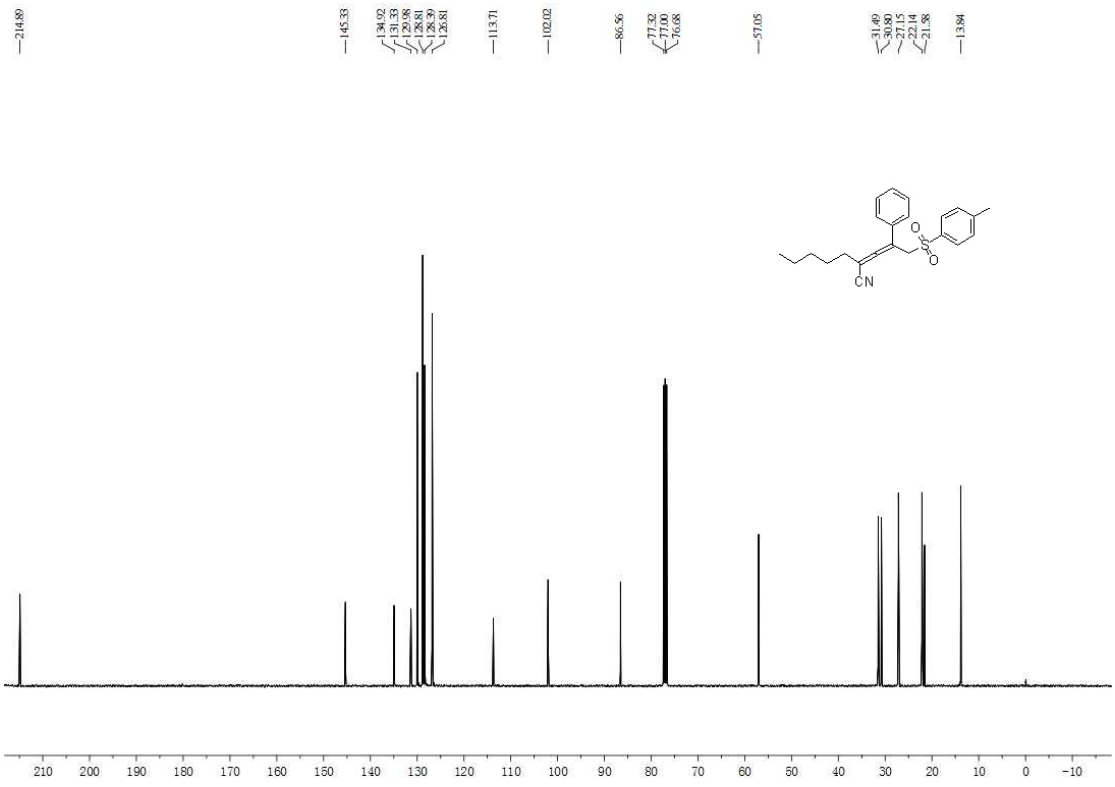
7.311
7.305
7.299
7.295
7.290
7.289
7.264
7.249
7.245
4.274
4.258
4.221
4.186
2.415
2.181
2.162
2.143
1.538
1.529
1.520
1.502
1.296
1.287
1.279
0.888
0.880
0.871
0.854
0.000
O
S
O
CN
1.93
6.99
2.00
3.00
1.99
2.01
4.11
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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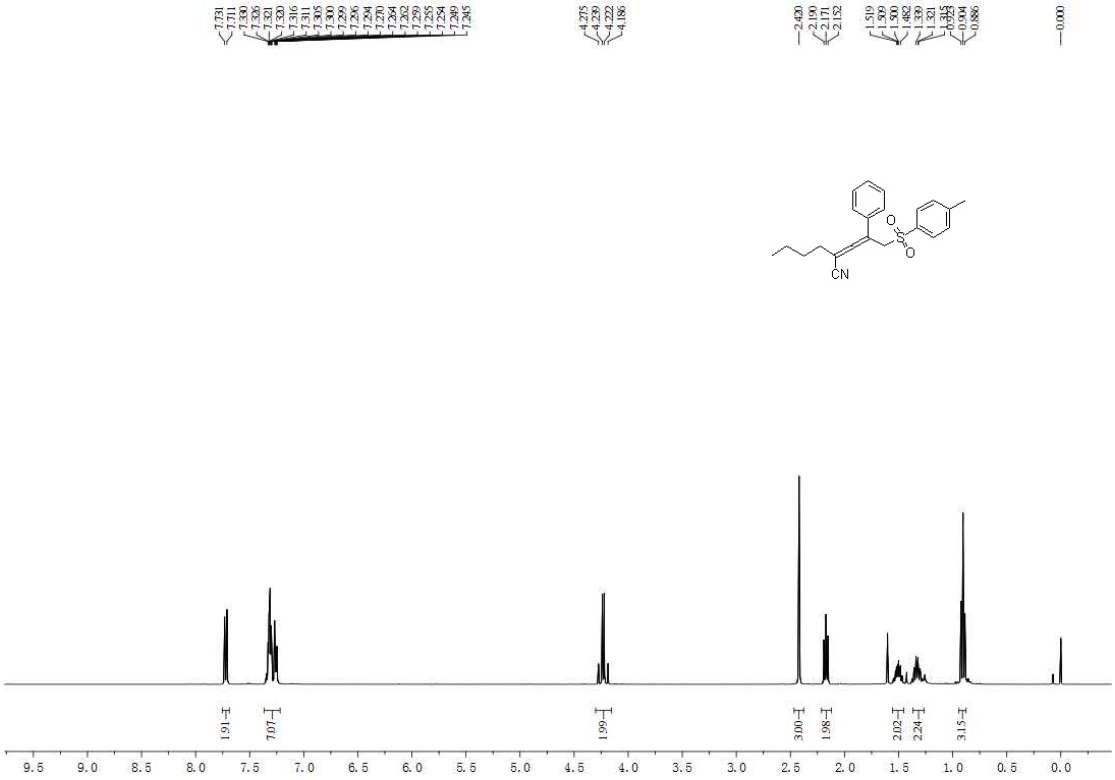
129.98
128.81
128.39
126.81
113.71
102.02
86.56
77.32
77.00
76.68
57.05
31.49
30.80
27.15
22.14
21.58
13.84
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Product 4n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7.321
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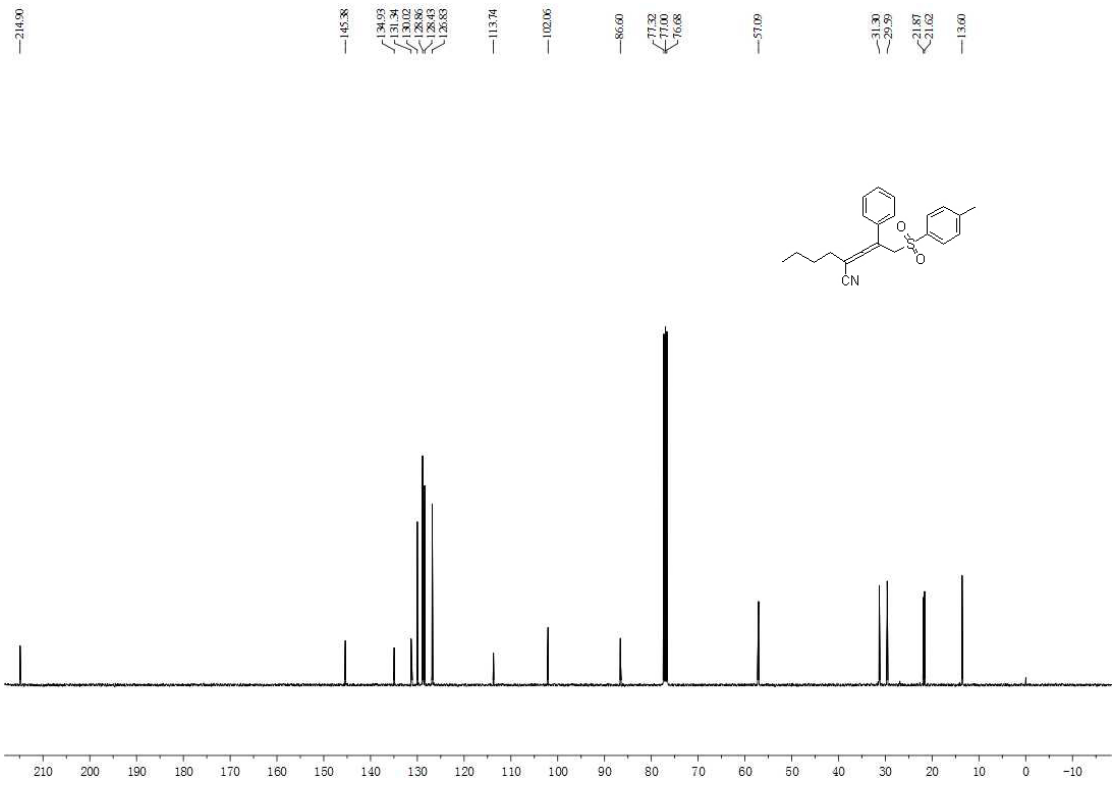
7.311
7.305
7.300
7.299
7.296
7.294
7.270
7.264
7.262
7.259
7.255
7.254
7.249
7.245
4.275
4.239
4.222
4.186
2.400
2.190
2.171
2.152
1.519
1.509
1.500
1.482
1.339
1.321
0.945
0.904
0.886
0.000
O
S
O
CN
1.91
7.07
1.99
3.00
1.98
2.02
2.24
3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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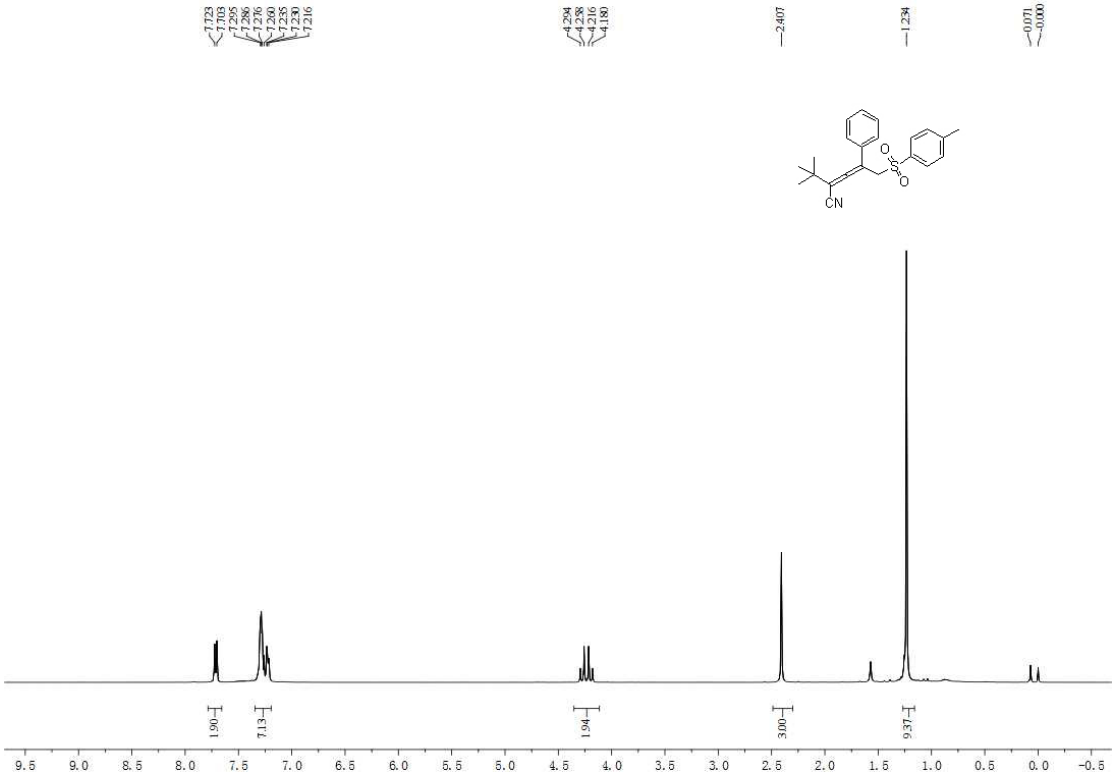
134.93
131.34
131.02
128.86
128.43
126.83
113.74
102.06
86.60
77.32
77.00
76.68
57.09
31.30
29.59
21.87
21.62
13.60
CN
O
S
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Product 4o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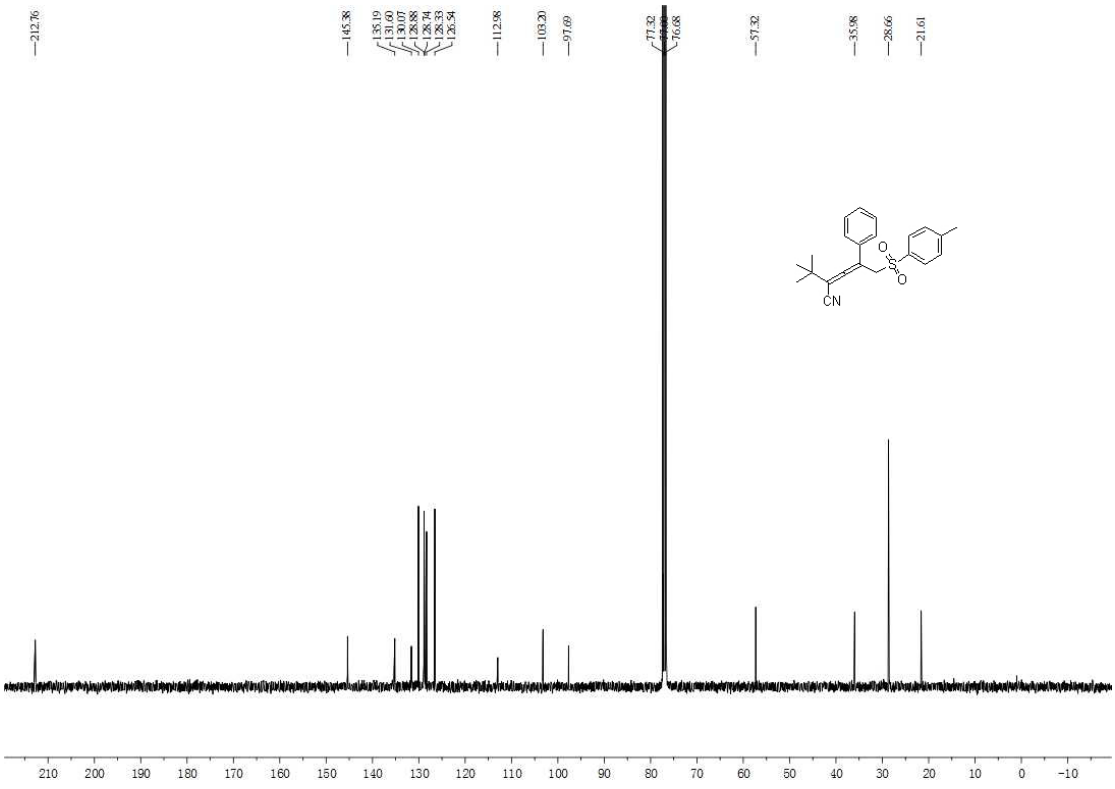
7.295
7.286
7.276
7.260
7.235
7.229
7.216
4.294
4.238
4.216
4.180
2.407
1.234
0.071
-0.000
CN
O
S
O
1.90
7.13
1.94
3.00
9.37
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


212.76
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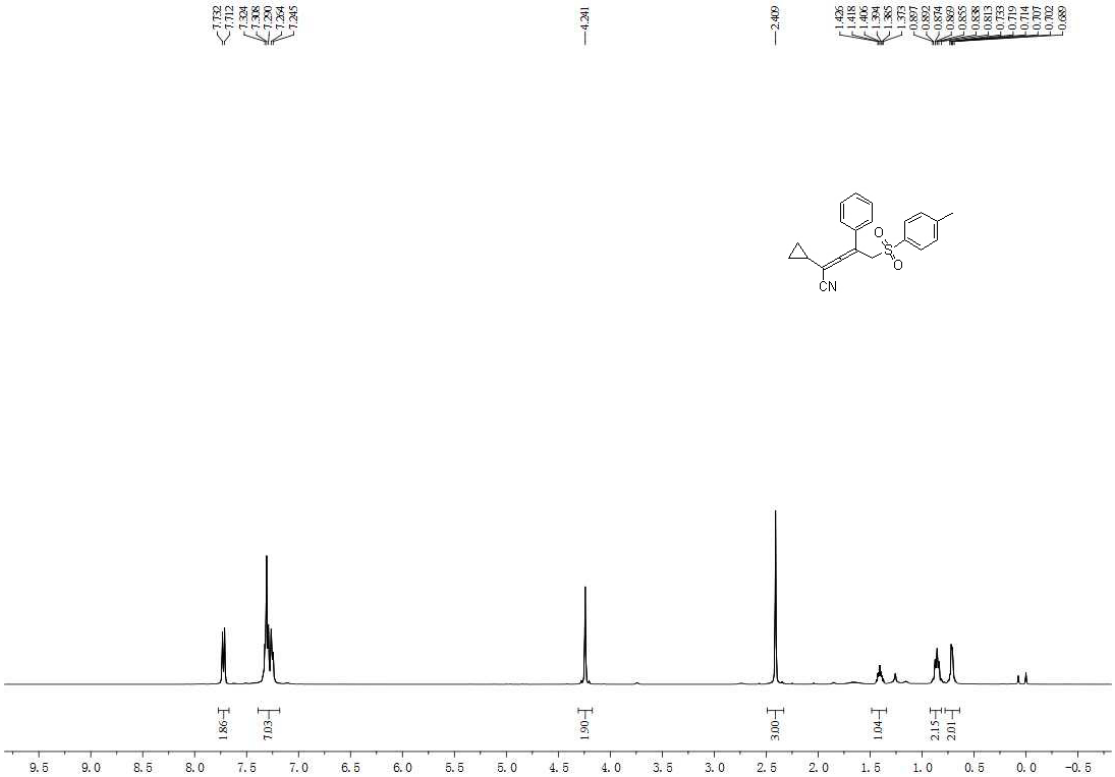
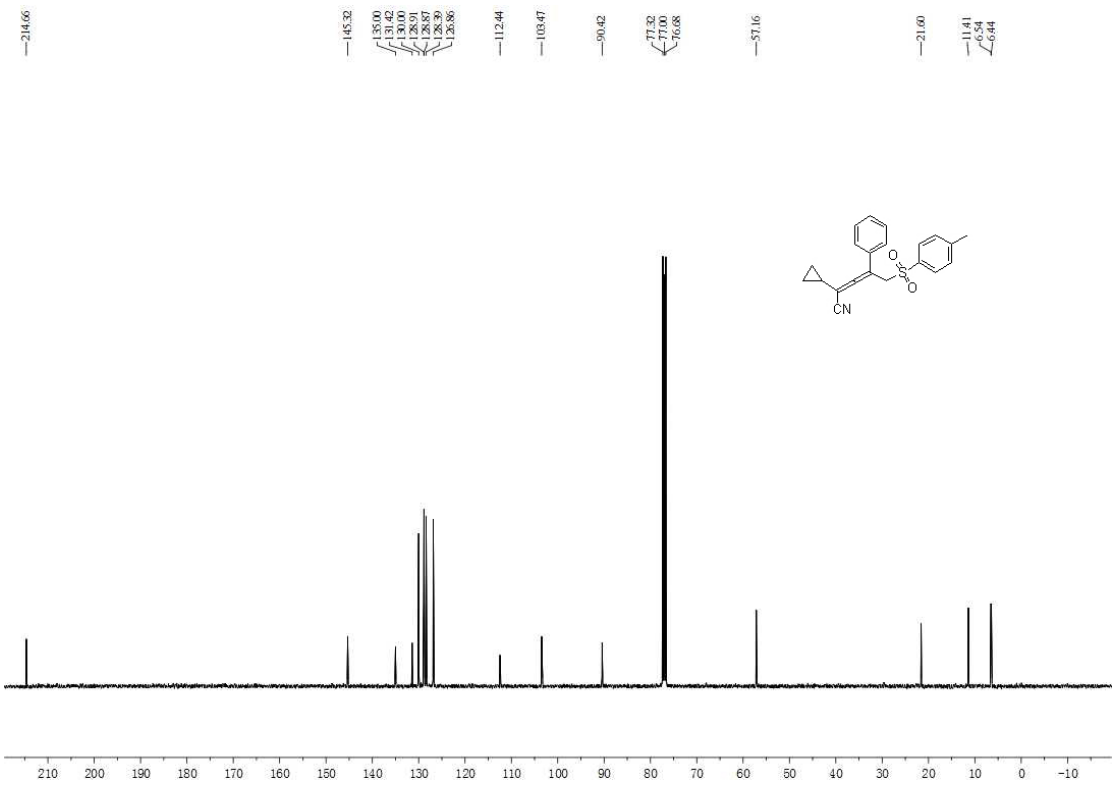
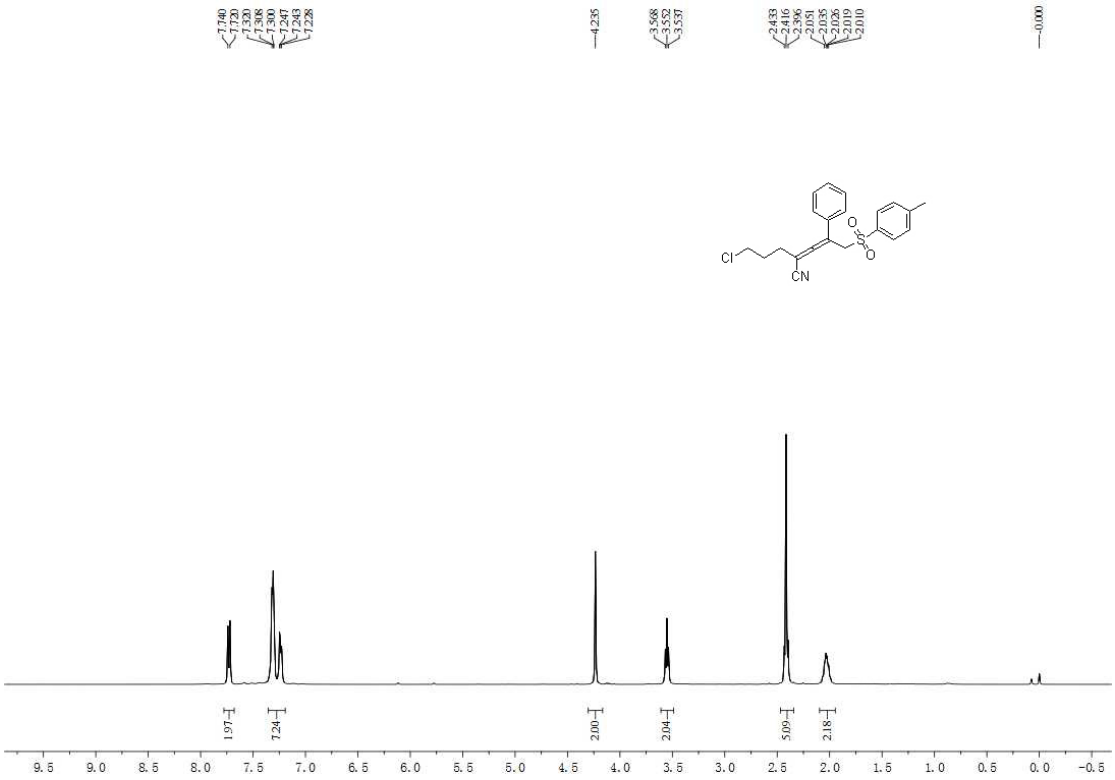
135.19
131.60
130.07
128.88
128.74
128.33
126.54
112.98
103.20
97.69
77.32
77.00
76.68
57.32
35.98
28.66
21.61
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

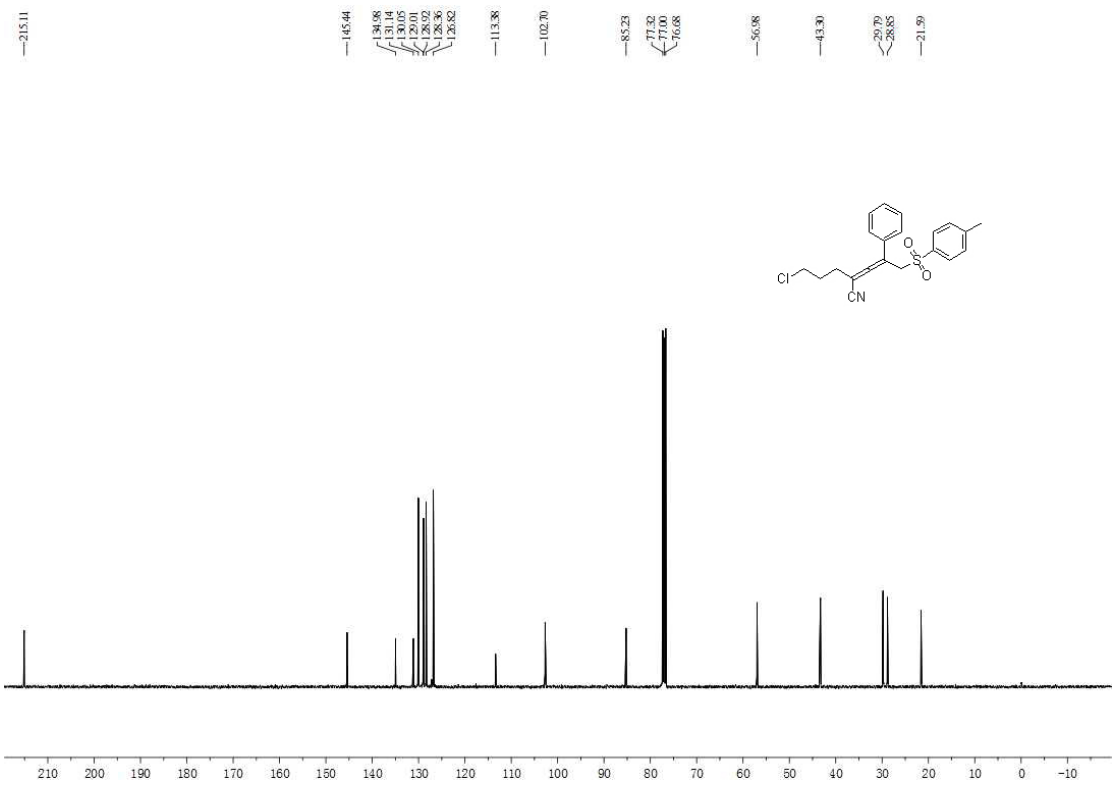
Product 4p


7.732
7.712
7.324
7.308
7.290
7.264
7.245
4.291
2.489
1.426
1.418
1.406
1.394
1.385
1.373
0.897
0.893
0.874
0.869
0.855
0.838
0.813
0.733
0.719
0.714
0.707
0.702
0.689
O
S
O
CN
1.86
7.03
1.90
3.00
1.04
2.15
2.01
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

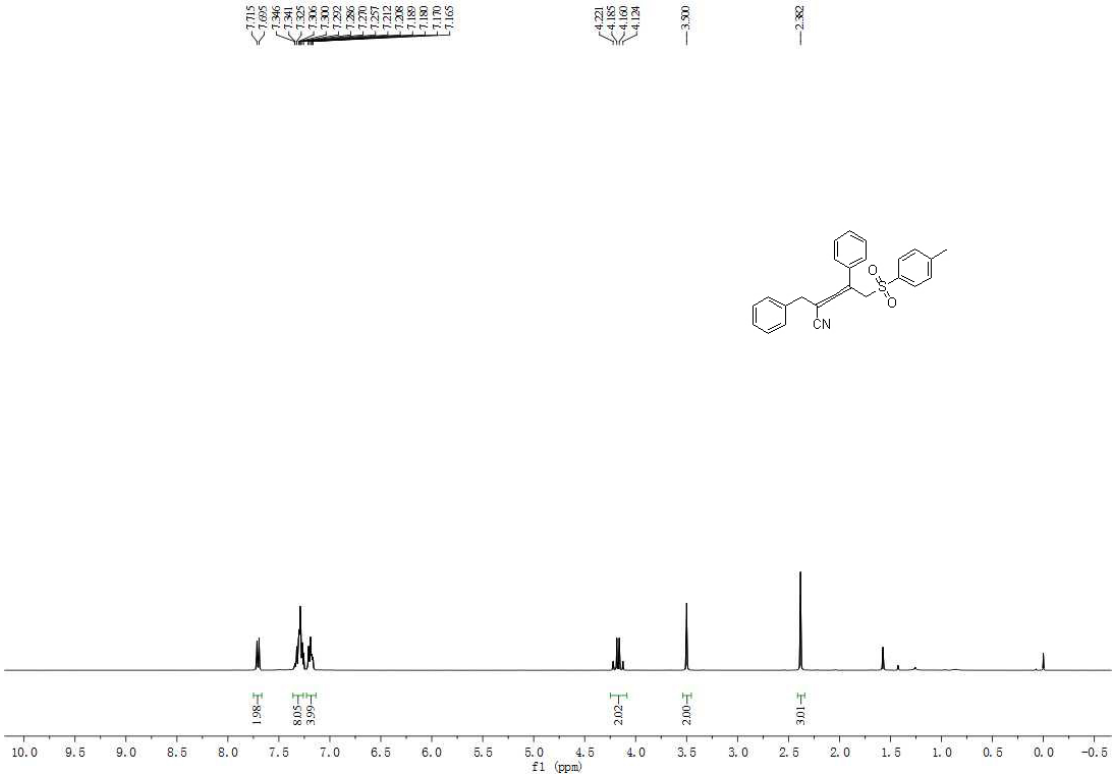

214.66
145.32
135.00
131.42
130.00
128.91
128.87
128.39
126.95
112.44
103.47
90.42
77.32
77.00
76.68
57.16
21.60
11.41
6.54
6.44
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

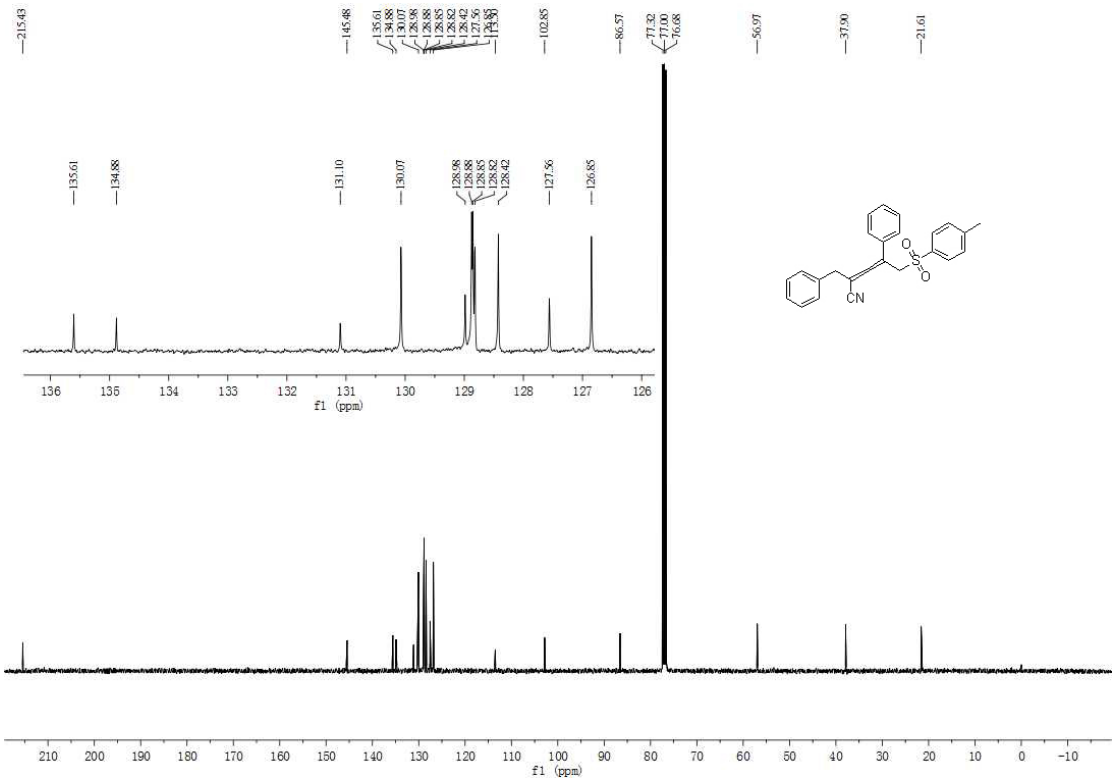
Product 4q


7.740
7.720
7.320
7.308
7.300
7.247
7.243
7.228
4.235
3.568
3.552
3.537
2.433
2.416
2.396
2.051
2.035
2.026
2.019
2.010
0.000
Cl
O
S
O
CN
1.97
7.24
2.00
2.04
5.09
2.18
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

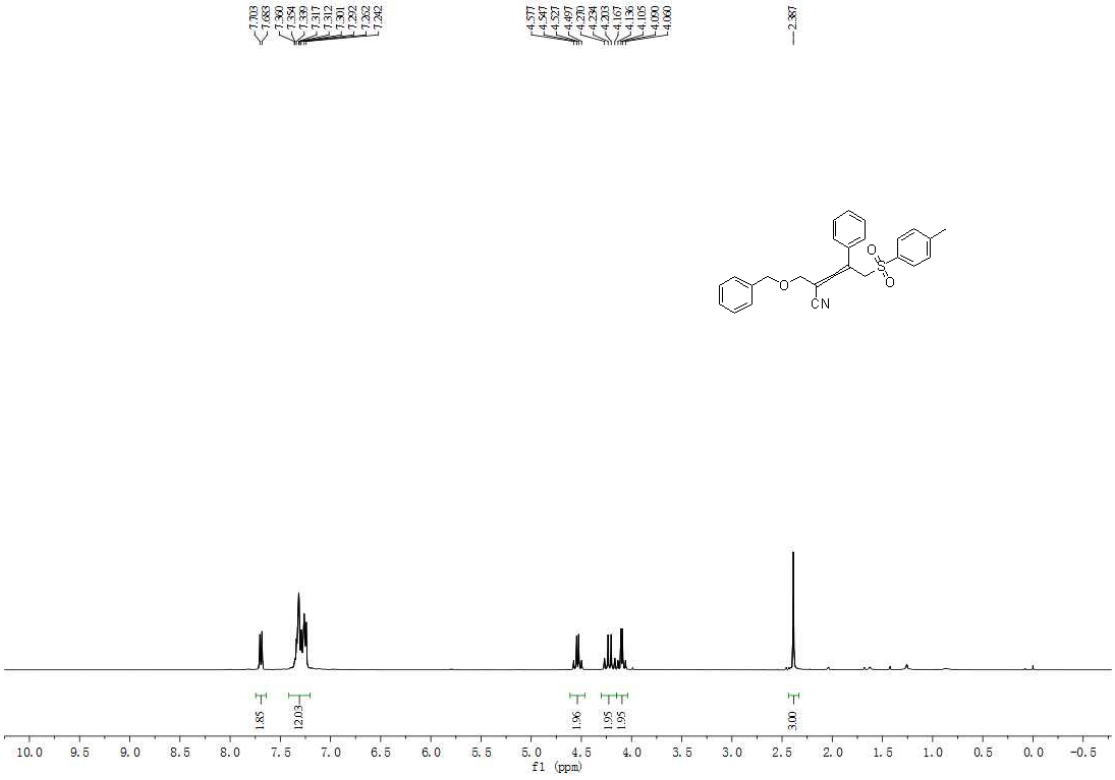

215.11
145.44
134.98
131.14
130.05
129.01
128.92
128.36
126.82
113.38
102.70
85.23
77.32
77.00
76.68
56.98
43.30
29.79
28.85
21.59
Cl
CN
O
S
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

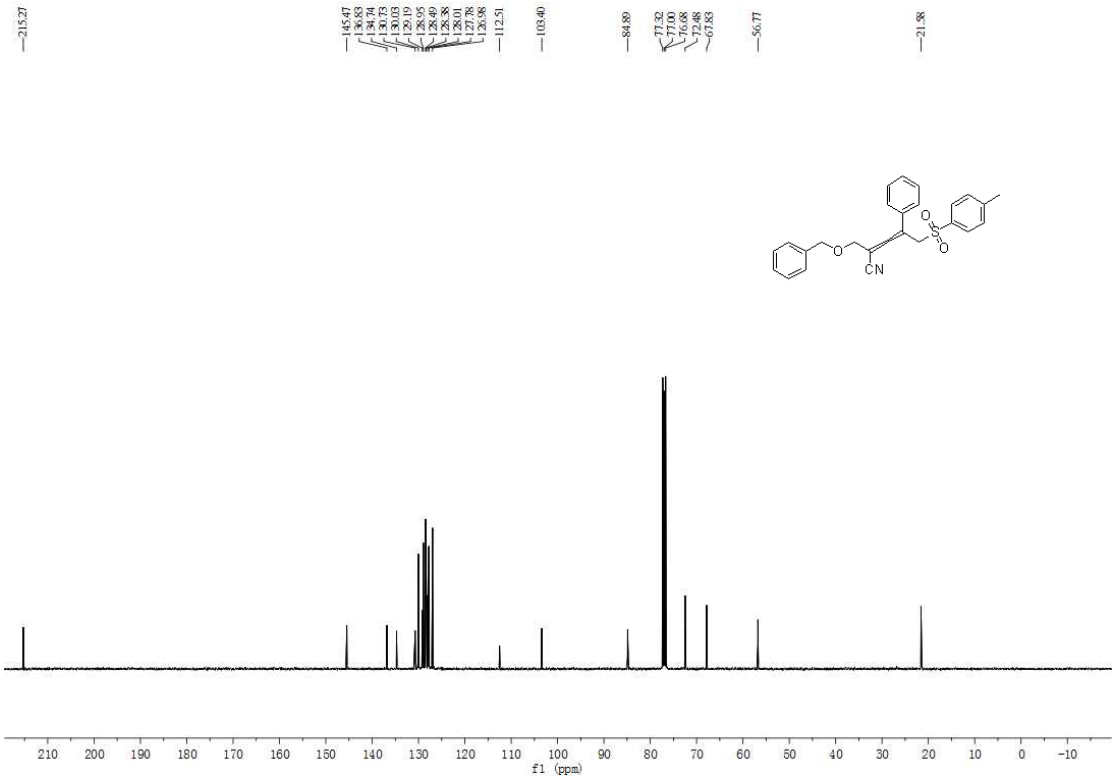
Product 4r


7.715
7.695
7.346
7.341
7.325
7.306
7.300
7.292
7.286
7.270
7.257
7.212
7.208
7.189
7.180
7.170
7.165
4.221
4.185
4.160
4.124
3.500
2.382
CN
O
S
O
1.98
8.05
3.99
2.02
2.00
3.01
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)

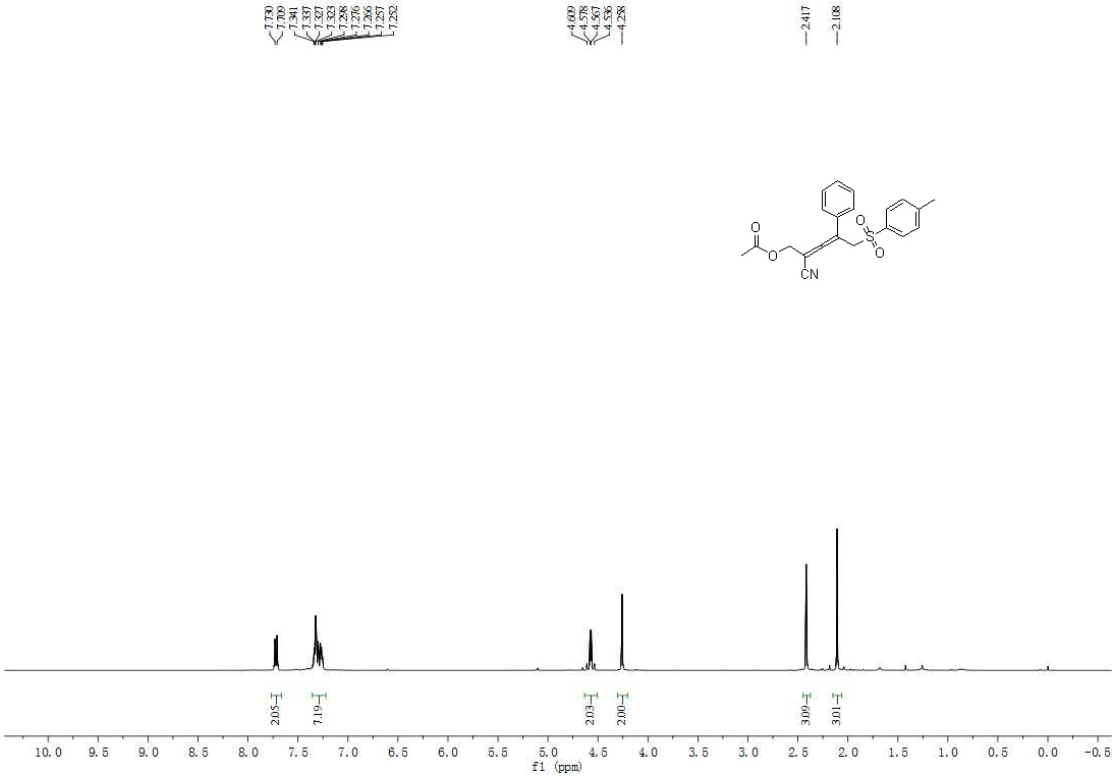

215.43
145.48
135.61
134.88
130.07
128.98
128.88
128.85
128.82
128.42
127.56
126.85
102.85
86.57
77.32
77.00
76.68
56.97
37.90
21.61
131.10
f1 (ppm)
CN

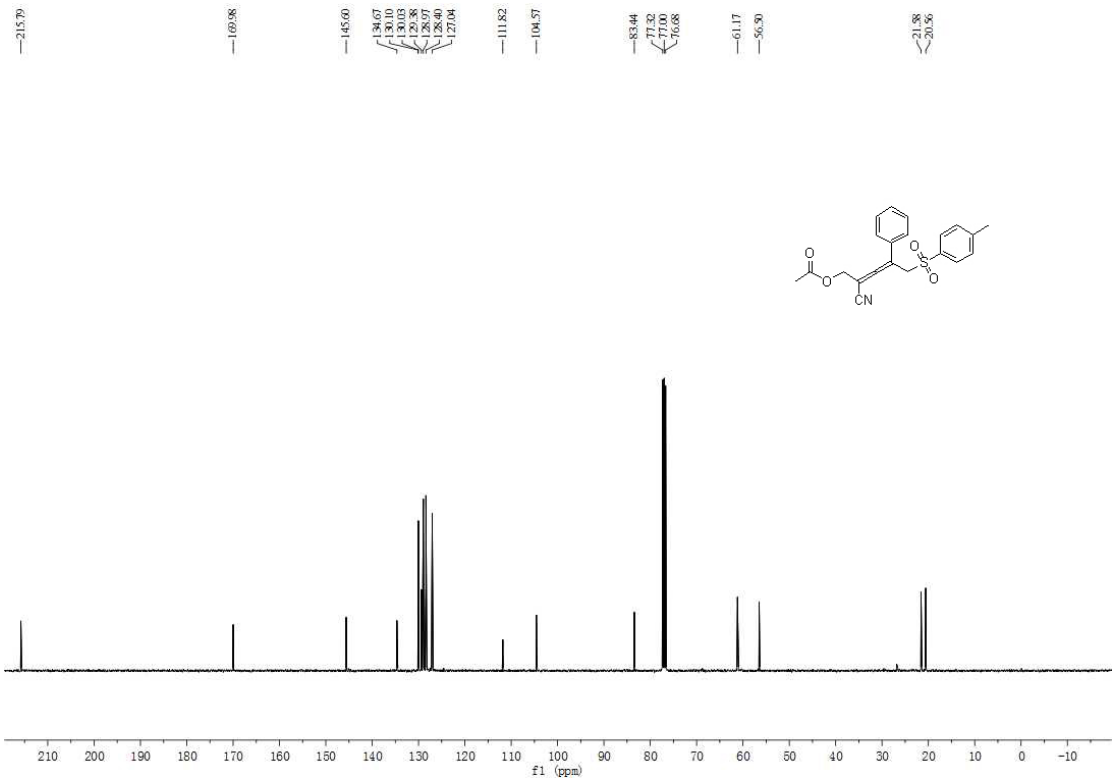
Product 4s


7.703
7.683
7.360
7.354
7.339
7.317
7.312
7.301
7.292
7.283
7.242
4.577
4.547
4.527
4.497
4.270
4.234
4.203
4.157
4.136
4.105
4.000
4.000
2.387
1.85
12.03
1.96
1.95
1.95
3.00
f1 (ppm)
CN

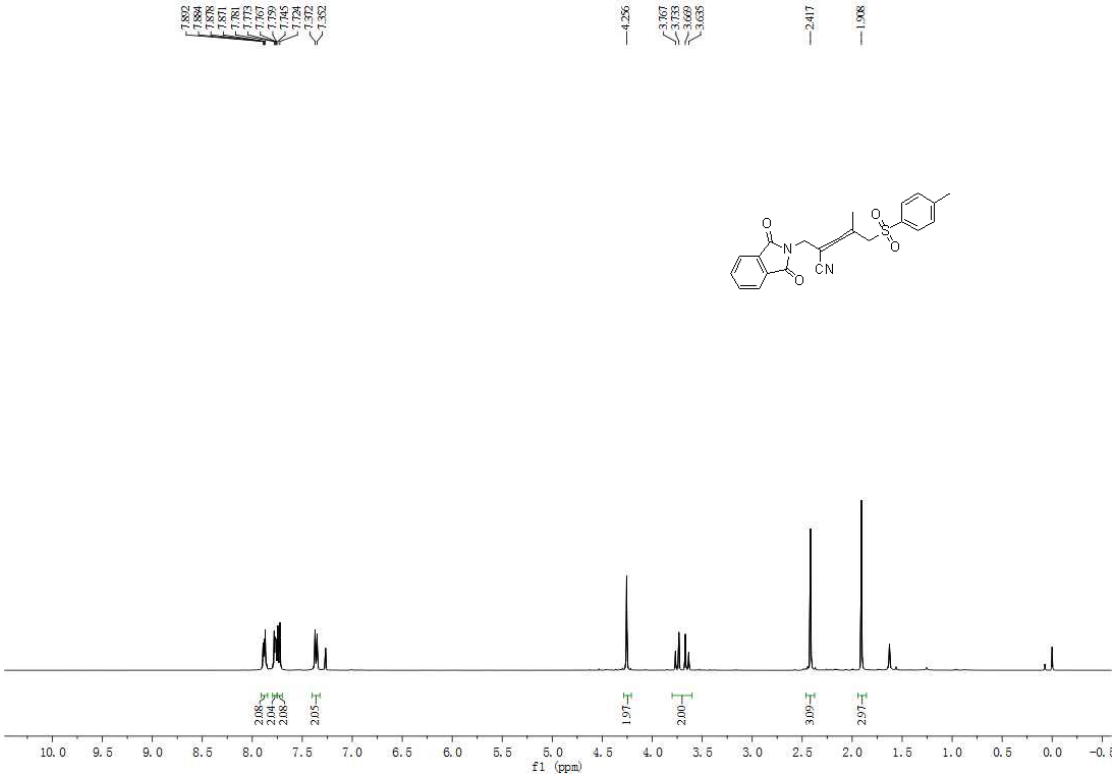

215.27
145.47
136.83
134.74
130.73
130.03
129.19
128.95
128.49
128.38
128.01
127.78
126.98
112.51
103.40
84.89
77.32
77.00
76.68
72.48
67.83
56.77
21.58
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

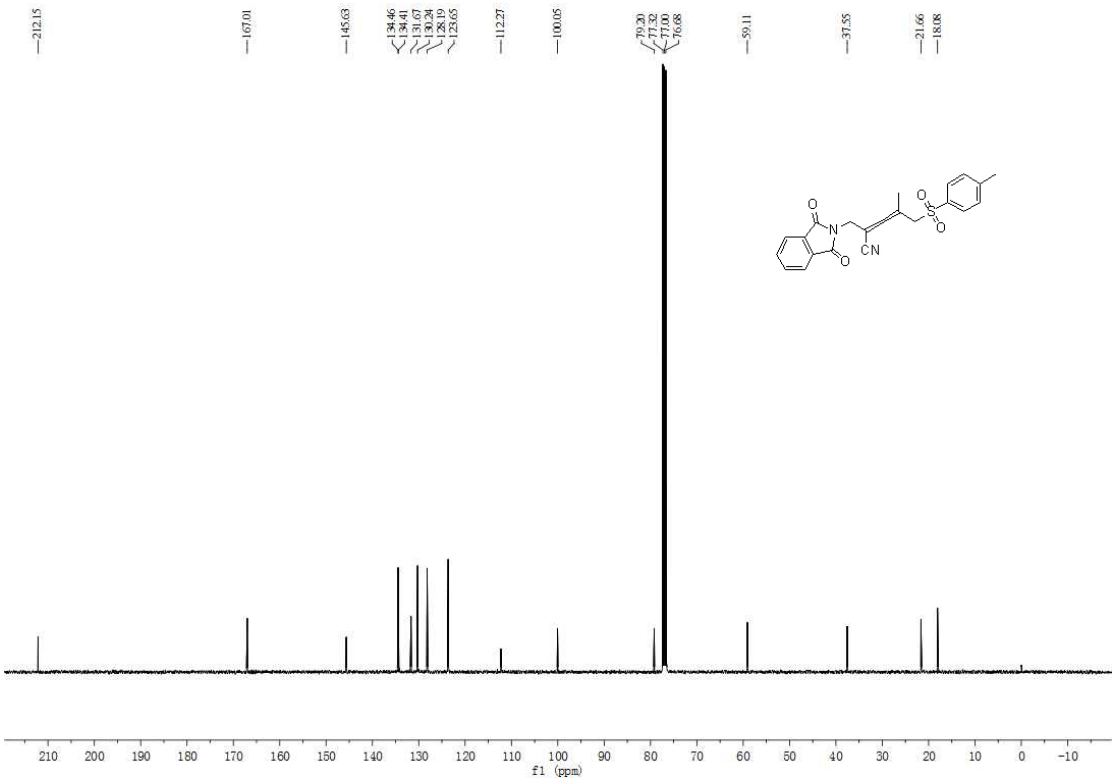
Product 4t


7.730
7.709
7.341
7.337
7.327
7.323
7.298
7.276
7.266
7.257
7.252
4.609
4.578
4.567
4.536
4.258
2.417
2.108
O
O
O
S
O
CN
2.05
7.19
2.03
2.00
3.09
3.01
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)

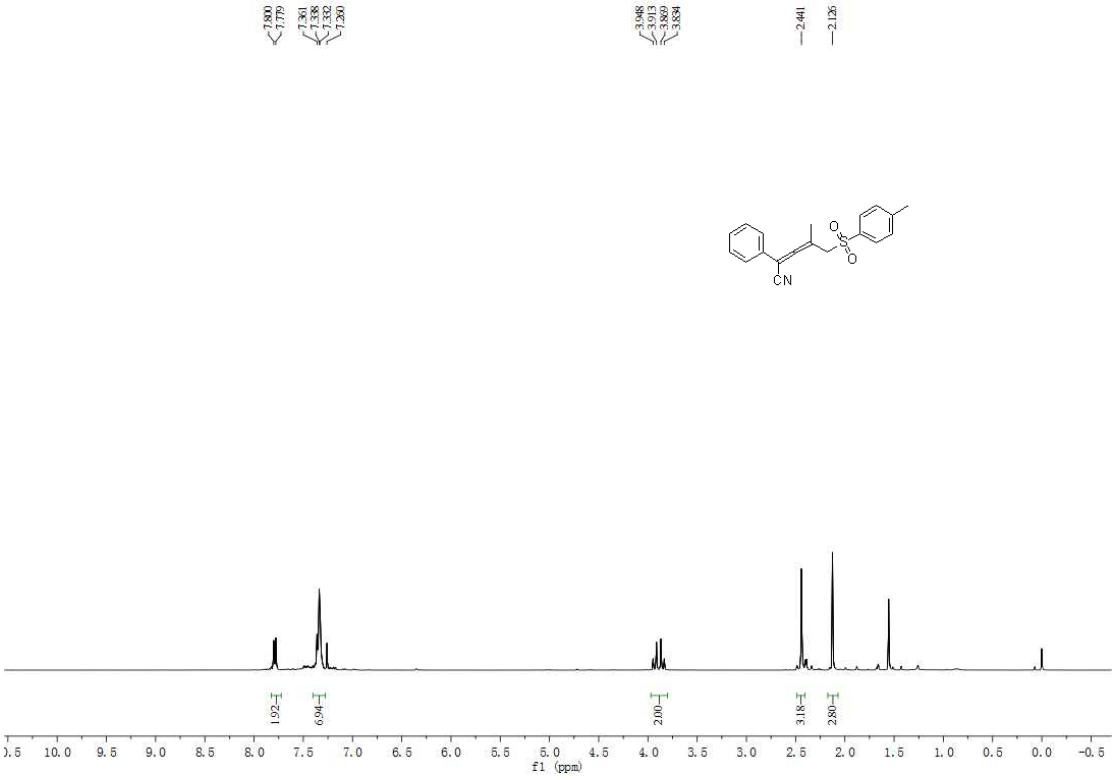

215.79
169.98
145.60
134.67
130.10
130.03
129.38
128.97
128.40
127.04
111.82
104.57
83.44
77.32
77.00
76.68
61.17
56.30
21.58
20.56
O
O
O
S
O
CN
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

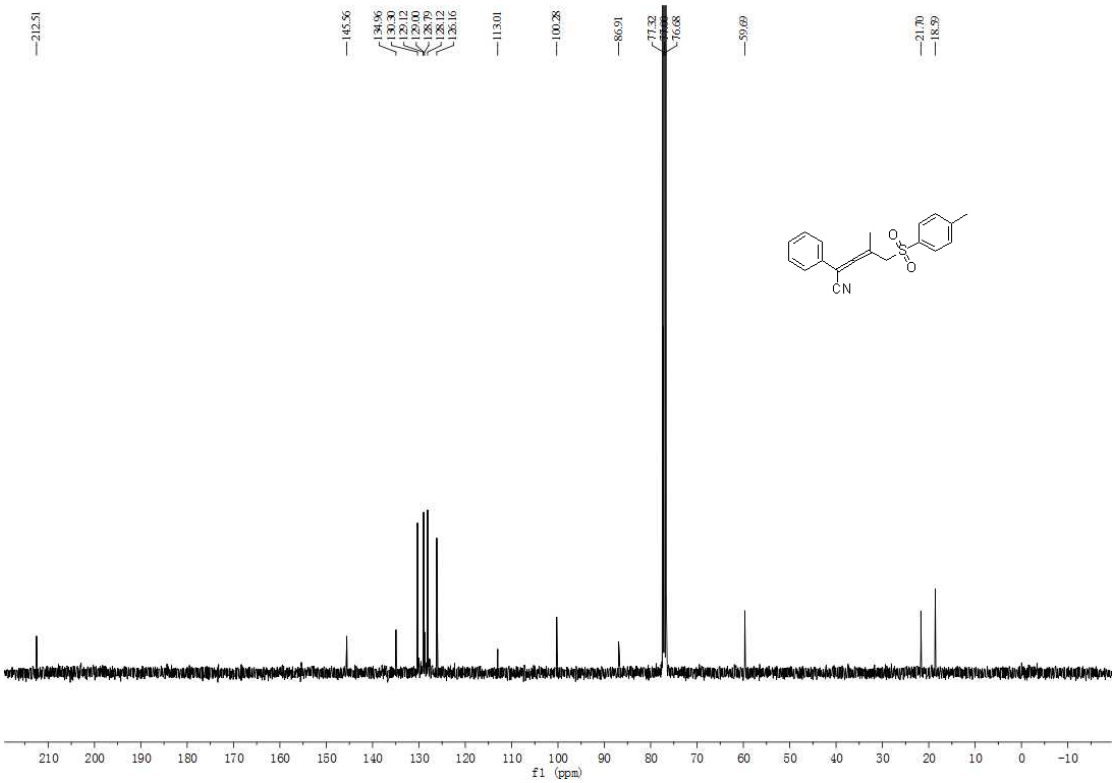
Product 4u


7.802
7.794
7.788
7.781
7.773
7.767
7.759
7.745
7.739
7.731
7.727
7.352
4.256
3.767
3.733
3.699
3.635
2.417
1.908
O
N
O
O
S
O
CN
2.08
2.04
2.08
2.05
1.97
2.00
3.09
2.97
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
f1 (ppm)

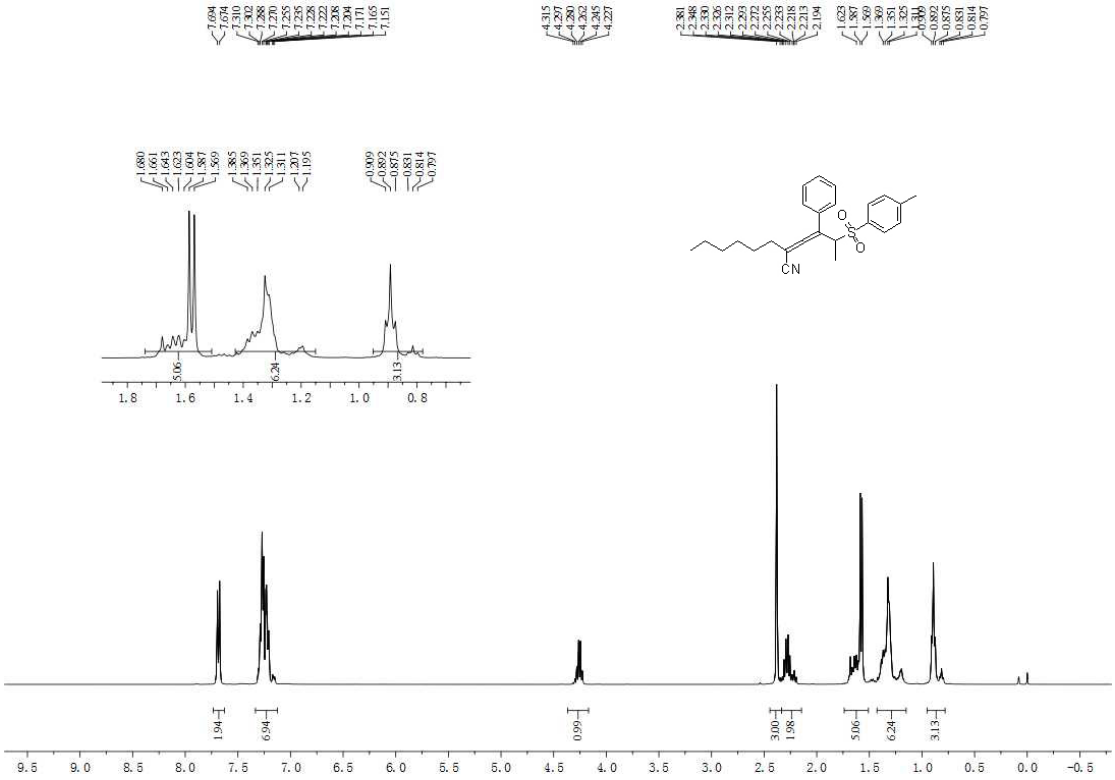

212.15
167.01
145.63
134.46
134.41
131.67
130.24
128.19
125.65
112.27
100.05
79.20
77.32
77.00
76.68
59.11
37.55
21.66
18.08
O
N
O
CN
O
S
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

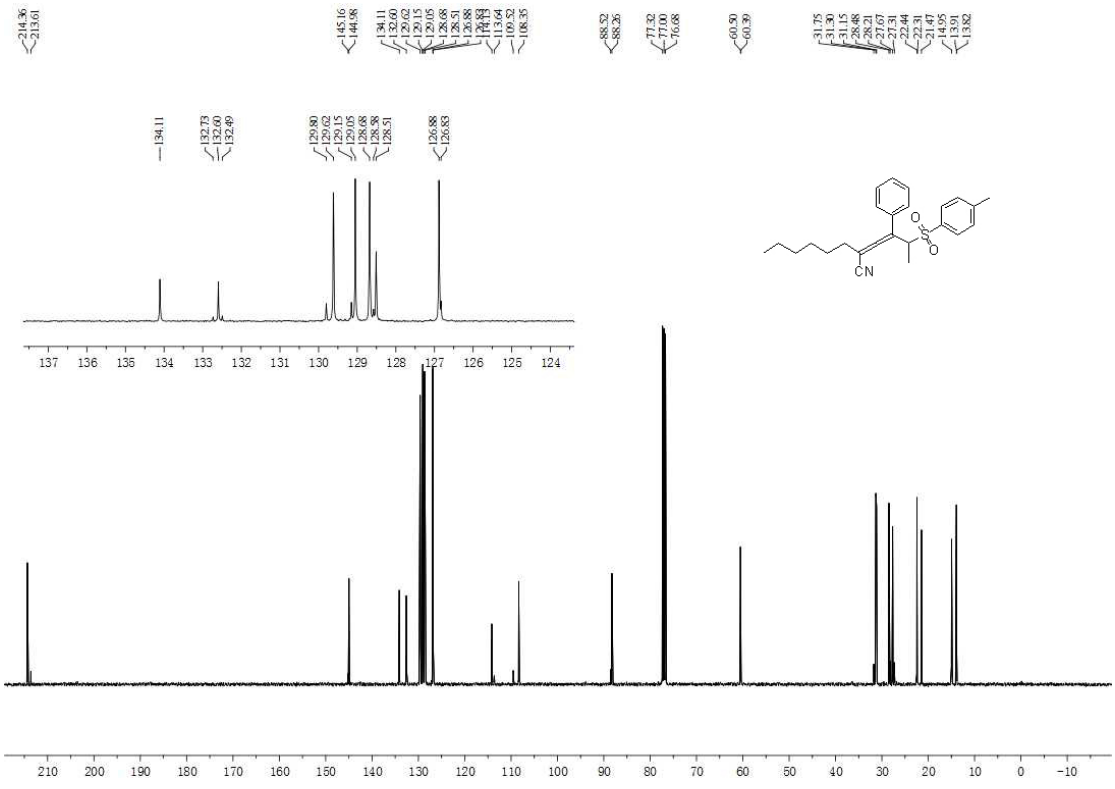
Product 4v


7.800
7.779
7.361
7.338
7.332
7.200
3.948
3.913
3.869
3.834
2.441
2.126
O
S
O
CN
1.92
6.94
2.00
3.18
2.80
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)

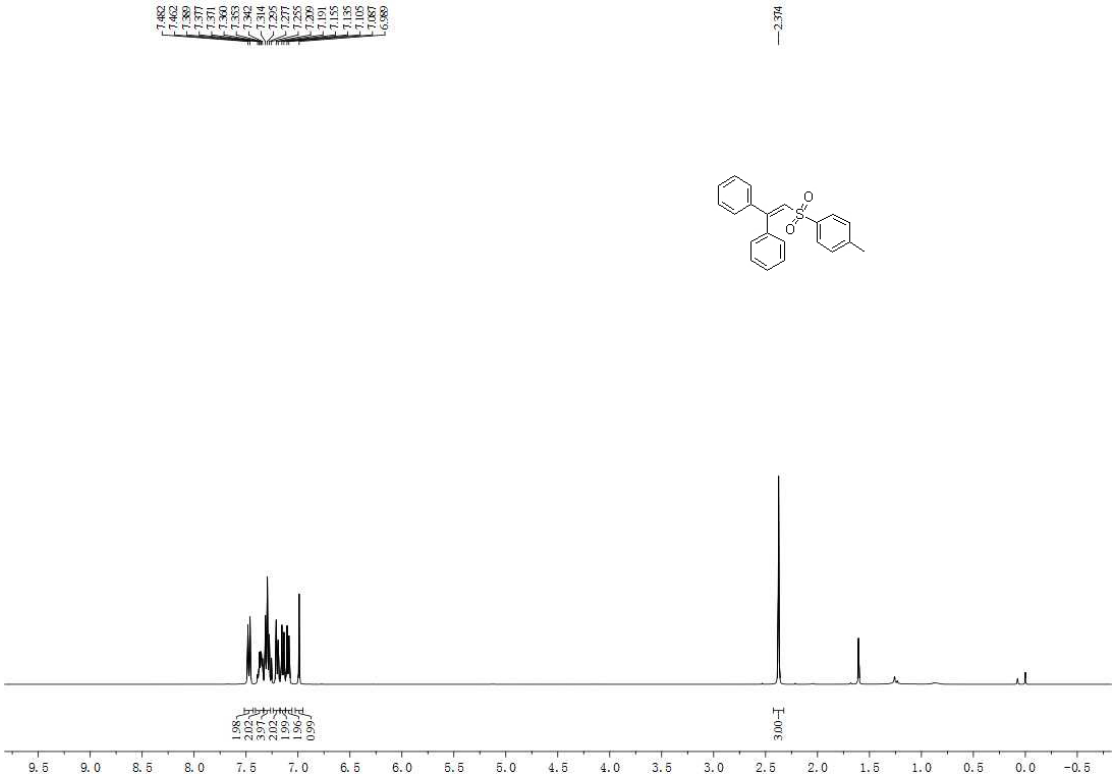


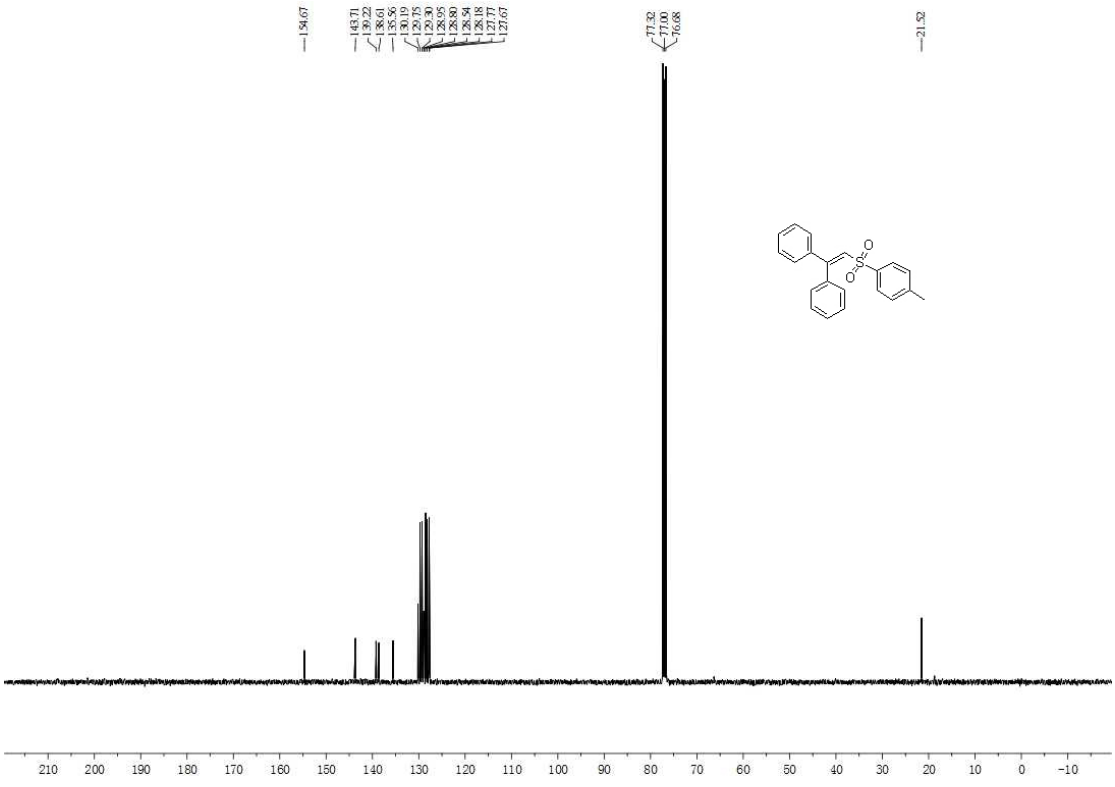
Product 4w



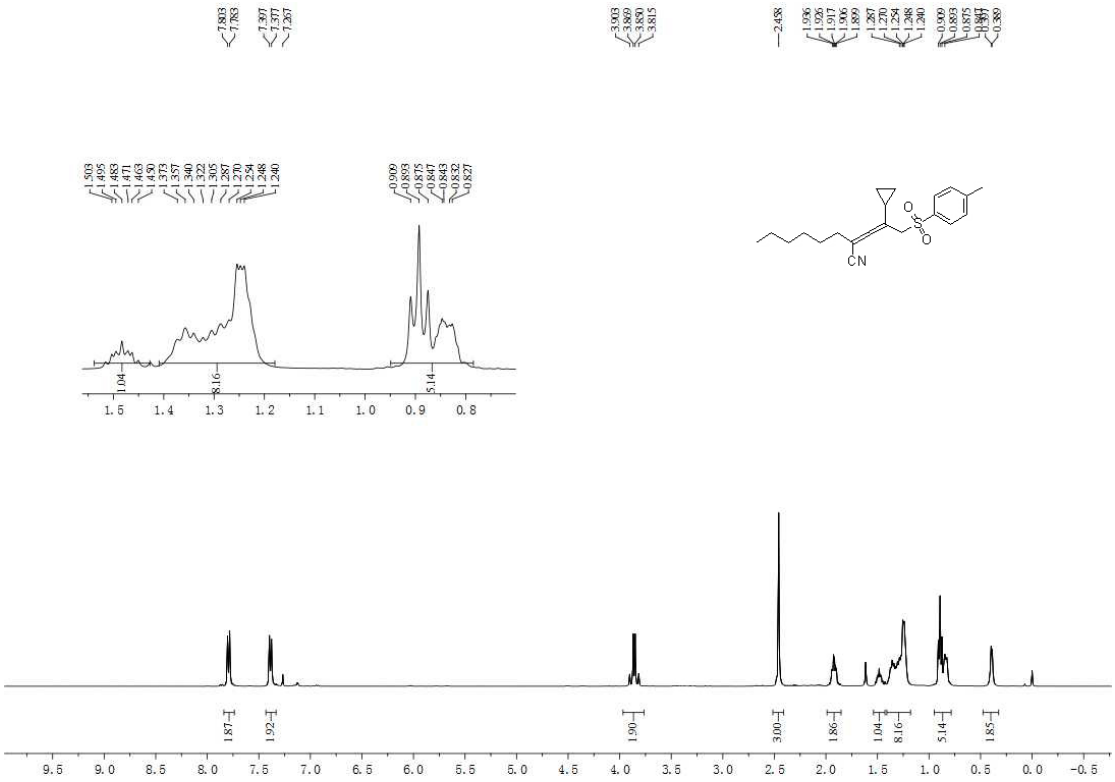


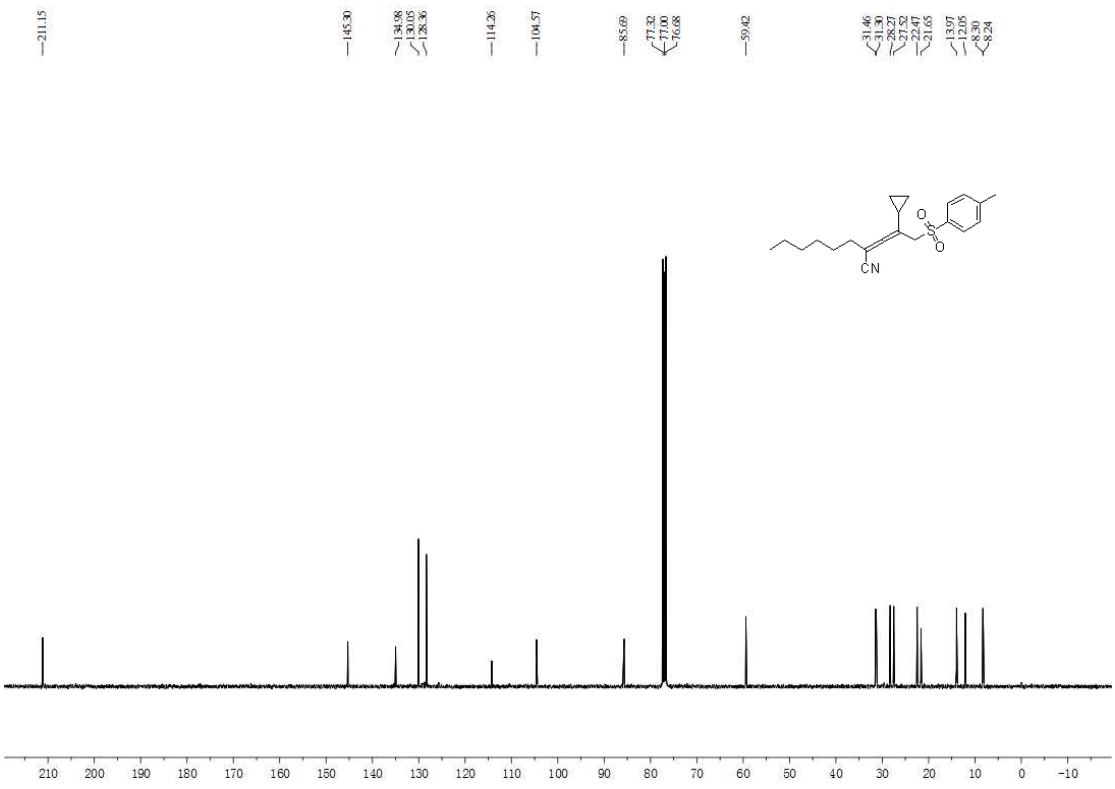
Product 5



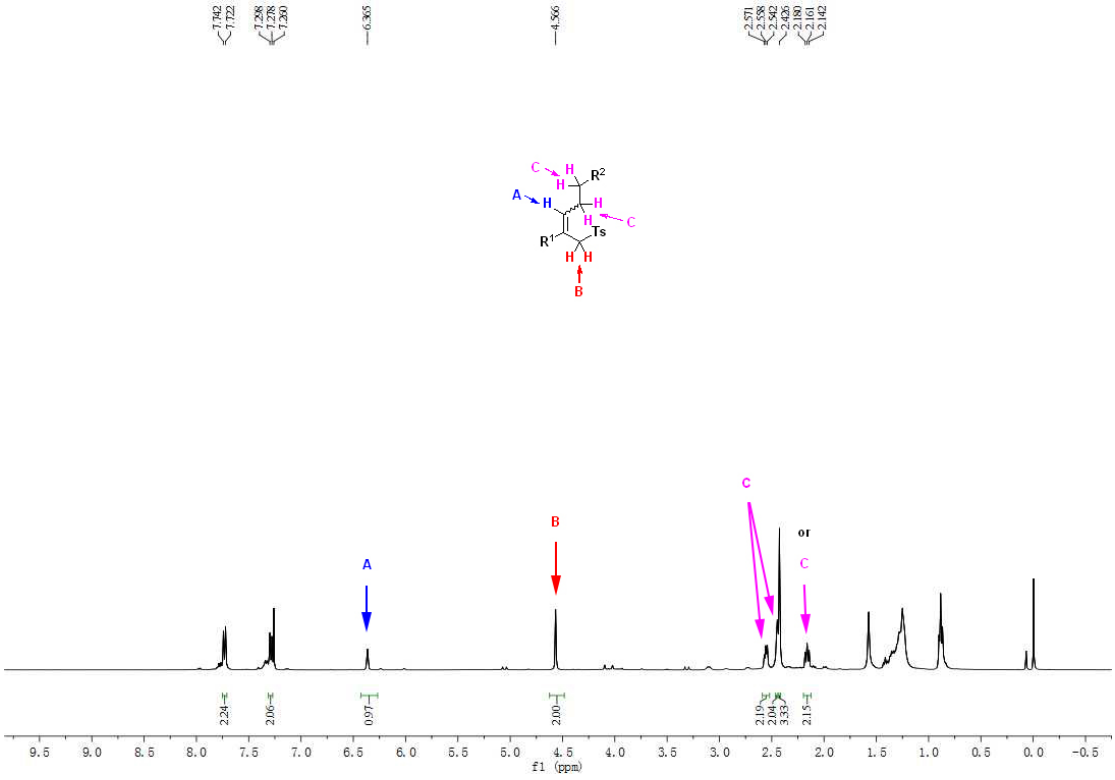


Product 4y




211.15
145.30
134.58
130.05
128.36
114.26
104.57
85.69
77.32
77.00
76.68
59.42
31.46
31.30
28.27
27.52
22.47
21.65
13.97
12.05
8.30
8.24
O
S
O
CN

Product 4y'


7.742
7.722
7.298
7.278
7.260
6.365
4.566
2.571
2.558
2.542
2.526
2.180
2.161
2.142
C
H
H
R2
A
H
H
H
C
R1
Ts
H
H
B
A
B
C
or
C
2.24
2.06
0.97
2.00
2.19
2.04
3.33
2.15
f1 (ppm)