Supporting Information

(*Z*)-Tetrahydrothiophene and (*Z*)-Tetrahydrothiopyran Synthesis through Nucleophilic Substitution and Intramolecular Cycloaddition of Alkynyl Halide and $EtOCS_2K$

Xianglin Luo, Xiuwen Chen, Zhiyan Song, Junyi Liang, Chunshu Liao, Zhongzhi Zhu, Lu Chen, Yibiao Li*

School of Biotechnology & Health Sciences, Wuyi University, Jiangmen, Guangdong Province, 529090, P. R. China

E-mail: leeyib268@126.com

A. General methods

Unless otherwise noted, all commercial materials and solvents were used without further purification. ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz (or 600 Hz) and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 MHz (or 150 Hz) respectively, ^{1}H and ^{13}C NMR were referenced to $CDCl_3$ at δ 7.260 and 77.0 respectively. The different types of carbon in the structures have been identified by HSQC, HMBC and DEPT techniques. GC–MS was obtained using electron ionization. HRMS was carried out on a MAT 95XP (Thermo). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals. Commercial reagents were used without further purification.

C. General Procedure for the preparation of 1-(5-chloropent-1-ynyl) benzene

A mixture of iodobenzene (1 mmol), 5-chloropent-1-yne (1.2 mmol), $PdCl_2(PPh_3)_2$ (5 mol %), CuI (10 mol %), Et_3N (1 mL), and CH_3CN (2 mL) was added successively in a 20 mL Schlenk tube. After being stirred for 8 h at 30 °C, the solution was filtered by a small amount of silica gel. Then the residue was concentrated in vacuo and the crude was purified by flash chromatography with petroleum ether to afford the 1-(5-chloropent-1-ynyl) benzene as a white oil in 92 % yield.

D. General methods for the synthesis of (Z)- tetrahydrothiophenes

A 25 mL Schlenk tube was charged with 1-(5-chloropent-1-ynyl) benzene (89 mg, 0.5 mmol), $EtOCS_2K$ (160 mg, 1 mmol), DMF (2 mL) and H_2O (10 mmol) and magnetic stirring bar. The reaction was performed for 12 h at 80 °C. After the reaction finished, the reaction mixture was diluted with ethyl acetate and passed through Celite. After evaporation of the solvent the residue was adsorbed on silica gel and the crude product was purified by column chromatography using petroleum as eluent.

E. Synthesis of (Z)-2-benzylidenetetrahydrothio phene-2-oxide

A 25 mL Schlenk tube was charged with (Z)-2-benzylidenetetrahydrothiophene (88 mg, 0.5 mmol), m-CPBA (190 mg, 1.1mmol), CH_2Cl_2 (2 mL) and magnetic stirring bar under N_2 atmosphere condition. The reaction was performed for 48 h at room temperature. After the reaction finished, the solvent was removed under reduce pressure, and the residue was purified by column chromatography (ethyl acetate: petroleum ether = 1: 1, Rf = 0.51) to afford the pure product **4a**.

F. Characterization data for prepared compounds

(5-Chloropent-1-yn-1-yl)benzene (1a)[1]：Yellow liquid (78 mg, 88% yield); R_f = 0.59 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.33 – 7.26 (m, 3H), 3.73 (t, *J* = 6.4 Hz, 2H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.07 (pent, *J* = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.5, 128.2, 127.8, 123.5, 88.0, 81.5, 43.7, 31.4, 16.8.

1-(5-Chloropent-1-yn-1-yl)-2-methylbenzene (1b)：White liquid (70 mg, 73% yield); R_f =0.61 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.15 – 7.09 (m, 1H), 3.75 (t, *J* = 6.4 Hz, 2H), 2.67 (t, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 2.08 (pent, *J* = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.9, 131.8, 129.3, 127.7, 125.4, 123.3, 91.9, 80.4, 43.7, 31.5, 20.7, 17.0; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{14}Cl$, 193.0779, found: 193.0787.

1-(5-Chloropent-1-yn-1-yl)-3-methylbenzene (1c)：Yellow liquid (73 mg, 76% yield); R_f = 0.57 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 3H), 7.11 (d, *J* = 7.3 Hz, 1H), 3.73 (t, *J* = 6.4 Hz, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.33 (s, 3H), 2.08 – 2.02 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 132.1, 128.6, 128.6, 128.1, 123.3, 87.6, 81.6, 43.7, 31.4, 21.2, 16.8.

1-(5-Chloropent-1-yn-1-yl)-4-methylbenzene (1d)：White liquid (77 mg, 80% yield); R_f = 0.62 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 3.72 (t, *J* = 6.4 Hz, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 2.06 (pent, *J* = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 131.4, 129.0, 120.4, 87.2, 81.5, 43.8, 31.5, 21.4, 16.8.

4-(5-Chloropent-1-yn-1-yl)-1,2-dimethylbenzene (1e)：White liquid (92 mg, 89% yield); R_f = 0.64 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (s, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 3.72 (t, *J* = 6.4 Hz, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 2.25 (s, 3H), 2.23 (s, 3H), 2.04 (dd, *J* = 13.2, 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.6, 136.5, 132.6, 129.5, 128.9, 120.7, 86.9, 81.6, 43.8, 31.5, 19.7, 19.5, 16.8; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{13}H_{16}Cl$, 207.0935, found: 207.0946.

1-(*tert*-Butyl)-4-(5-chloropent-1-yn-1-yl)benzene (1f)：Yellow liquid (98 mg, 84% yield); R_f =0.61(petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (q, *J* = 8.6 Hz, 4H), 3.73 (d, *J* = 6.4 Hz, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.06 (pent, *J* = 6.6 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9, 131.2, 125.2, 120.5, 87.2, 81.5, 43.8, 34.7, 31.5, 31.1, 16.8; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{15}H_{20}Cl$, 235.1248, found: 235.1233.

1-(5-Chloropent-1-yn-1-yl)-4-methoxybenzene (1g)[2]： White liquid (78 mg, 75% yield); R_f = 0.59 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 2H), 6.87 – 6.76 (m, 2H), 3.79 (s, 3H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.59 (t, *J* = 6.8 Hz, 2H), 2.04 (pent, *J* = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 132.8, 115.6, 113.7, 86.4, 81.1, 55.1, 43.7, 31.4, 16.7.

1-(5-chloropent-1-yn-1-yl)-4-nitrobenzene: Yellow liquid (90 mg, 81% yield); R_f = 0.39(petroleum ether / ethyl acetate = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.10 (m, 2H), 7.52 – 7.47 (m, 2H), 3.70 (dd, *J* = 8.1, 4.5 Hz, 2H), 2.64 (t, *J* = 6.9 Hz, 2H), 2.10 – 2.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 132.2, 130.5, 123.4, 94.2, 80.0, 43.5, 30.9, 16.9.

1-(5-Chloropent-1-yn-1-yl)-4-fluorobenzene (1i): White liquid (75 mg, 77% yield); R_f = 0.63 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.02 – 6.95 (m, 2H), 3.71 (t, *J* = 6.3 Hz, 2H), 2.59 (t, *J* = 6.8 Hz, 2H), 2.05 (pent, *J* = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1 (d, J_{C-F} = 246.8 Hz), 133.4 (d, J_{C-F} = 8.3 Hz), 119.6 (d, J_{C-F} = 3.6 Hz), 115.4 (d, J_{C-F} = 21.9 Hz), 87.7, 80.4, 43.7, 31.3, 16.7.

1-Chloro-4-(5-chloropent-1-yn-1-yl)benzene (1j): White liquid (86 mg, 81% yield); R_f =0.59 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.30 (m, 2H), 7.28 – 7.24 (m, 2H), 3.71 (t, *J* = 6.3 Hz, 2H), 2.60 (t, *J* = 6.8 Hz, 2H), 2.05 (pent, *J* = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.7, 132.8, 128.5, 122.0, 89.1, 80.4, 43.7, 31.3, 16.8.

4-(5-Chloropent-1-yn-1-yl)benzonitrile (1k) [3]: Yellow liquid (84 mg, 83% yield); R_f = 0.55 (petroleum ether / ethyl acetate = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 3.69 (t, *J* = 6.3 Hz, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 2.06 (pent, *J* = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.1, 131.9, 128.5, 118.5, 111.0, 93.1, 80.2, 43.5, 31.0, 16.8.

1-(5-Chloropent-1-yn-1-yl)-4-(trifluoromethyl)benzene (1l): White liquid (92 mg, 75% yield); R_f = 0.61 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 3.72 (t, *J* = 6.3 Hz, 2H), 2.64 (t, *J* = 6.8 Hz, 2H), 2.11 – 2.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.8, 129.5 (q, J_{C-F} = 32.6 Hz), 127.4, 125.1 (q, J_{C-F} = 3.6 Hz), 123.9 (q, J_{C-F} = 270.4 Hz), 90.9, 80.3, 43.6, 31.2, 16.8.

4-(5-Chloropent-1-yn-1-yl)-1,1'-biphenyl (1m): Yellow liquid (100 mg, 79% yield); R_f = 0.53 (petroleum ether / ethyl acetate = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 5.2, 3.3 Hz, 2H),

7.60 – 7.56 (m, 2H), 7.55 – 7.51 (m, 2H), 7.49 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.42 – 7.37 (m, 1H), 3.77 (t, *J* = 6.4 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 2.15 – 2.08 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 140.2, 131.9, 128.7, 127.4, 126.9, 126.8, 122.4, 88.7, 81.3, 43.7, 31.4, 16.9; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{17}H_{16}Cl$, 255.0935, found: 255.0919.

2-(5-Chloropent-1-yn-1-yl)naphthalene (1n): Yellow liquid (97 mg, 85% yield); R_f = 0.61 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 – 8.31 (m, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.61 – 7.57 (m, 1H), 7.53 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 3.81 (t, *J* = 6.3 Hz, 2H), 2.79 (t, *J* = 6.8 Hz, 2H), 2.20 – 2.15 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.4, 133.1, 130.2, 128.2, 128.2, 126.6, 126.3, 126.1, 125.2, 121.2, 93.0, 79.5, 43.8, 31.5, 17.1.

2-(5-Chloropent-1-yn-1-yl)pyridine (1o)[4]: Yellow liquid (79 mg, 88% yield); R_f = 0.54 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.62 (ddd, *J* = 9.2, 5.4, 1.5 Hz, 1H), 7.44 – 7.33 (m, 1H), 7.25 – 7.15 (m, 1H), 3.74 – 3.69 (m, 2H), 2.66 – 2.61 (m, 2H), 2.07 (tt, *J* = 8.1, 3.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 143.4, 136.0, 126.8, 122.5, 88.6, 81.1, 43.6, 30.9, 16.6.

3-(5-Chloropent-1-yn-1-yl)pyridine (1p)[5]: Yellow liquid (70 mg, 79% yield); R_f = 0.56 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.51 (d, *J* = 4.1 Hz, 1H), 7.74 – 7.65 (m, 1H), 7.24 (dd, *J* = 7.8, 4.9 Hz, 1H), 3.73 (t, *J* = 6.3 Hz, 2H), 2.65 (t, *J* = 6.8 Hz, 2H), 2.10 – 2.07 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 148.1, 138.5, 122.9, 120.6, 91.7, 78.2, 43.6, 31.1, 16.8.

4-(5-Chloropent-1-yn-1-yl)pyridine (1q): Brown liquid (64 mg, 71% yield); R_f =0.57 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.4 Hz, 2H), 7.23 (d, *J* = 4.7 Hz, 2H), 3.68 (t, *J* = 6.3 Hz, 2H), 2.61 (t, *J* = 6.9 Hz, 2H), 2.04 (pent, *J* = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 131.7, 125.7, 93.5, 79.2, 43.5, 30.9, 16.8; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{11}ClN$, 180.0575, found: 180.0563.

5-(5-Chloropent-1-yn-1-yl)-2-methoxypyridine (1r)：White liquid (87 mg, 83% yield); R_f = 0.59 (petroleum ether / ethyl acetate = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 1.6 Hz, 1H), 7.57 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.68 (d, *J* = 8.6 Hz, 1H), 3.94 (s, 3H), 3.72 (t, *J* = 6.3 Hz, 2H), 2.62 (t, *J* =

6.8 Hz, 2H), 2.07 (dd, *J* = 13.1, 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 149.8, 141.2, 113.3, 110.5, 89.4, 78.1, 53.6, 43.7, 31.3, 16.8; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{13}ClNO$, 210.0680, found: 210.0668.

3-(5-Chloropent-1-yn-1-yl)-2-methoxypyridine (1s): Yellow liquid (86 mg, 82% yield); R_f = 0.62 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 4.5 Hz, 1H), 7.62 (d, *J* = 7.3 Hz, 1H), 6.82 (dd, *J* = 7.1, 5.2 Hz, 1H), 3.99 (s, 3H), 3.73 (t, *J* = 6.4 Hz, 2H), 2.66 (t, *J* = 6.8 Hz, 2H), 2.08 (dd, *J* = 13.1, 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 145.7, 141.6, 116.3, 107.6, 93.8, 76.2, 54.0, 43.7, 31.3, 17.2; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{13}ClNO$, 210.0680, found: 210.0667.

2-Bromo-5-(5-chloropent-1-yn-1-yl)pyridine (1t): Yellow solid (98 mg, 76% yield); R_f = 0.59 (petroleum ether / ethyl acetate = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.2 Hz, 1H), 7.49 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 3.68 – 3.65 (m, 2H), 2.60 (t, *J* = 6.9 Hz, 2H), 2.07 – 2.01 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 140.6, 140.4, 127.4, 119.9, 93.2, 43.5, 30.9, 16.8; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{10}ClNBr$, 257.9680, found: 257.9662.

3-Bromo-5-(5-chloropent-1-yn-1-yl)pyridine (1u)：Yellow liquid (91 mg, 71% yield); R_f =0.57 (petroleum ether / ethyl acetate = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.1 Hz, 1H), 8.51 (d, *J* = 1.4 Hz, 1H), 7.81 (t, *J* = 1.9 Hz, 1H), 3.68 (t, *J* = 6.3 Hz, 2H), 2.62 (t, *J* = 6.9 Hz, 2H), 2.04 (dd, *J* = 13.1, 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 149.3, 140.8, 122.0, 119.9, 93.3, 76.9, 43.5, 30.9, 16.8; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{10}ClNBr$, 257.9680, found: 257.9661.

2-Chloro-5-(5-chloropent-1-yn-1-yl)pyridine (1v): Yellow liquid (80 mg, 75% yield); R_f = 0.61 (petroleum ether / ethyl acetate = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.1 Hz, 1H), 7.62 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 3.70 (d, *J* = 6.3 Hz, 2H), 2.63 (t, *J* = 6.9 Hz, 2H), 2.05 (dd, *J* = 13.1, 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 149.8, 141.0, 123.7, 119.5, 93.0, 77.0, 43.5, 31.0, 16.8; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{10}Cl_2N$, 214.0185, found: 214.0172.

6-(5-Chloropent-1-yn-1-yl)quinoline (1w): Yellow liquid (93 mg, 81% yield); R_f = 0.54 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 – 8.80 (m, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.85 (s, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.38 (ddd, *J* = 8.2, 4.0, 1.5 Hz, 1H), 3.73 (t, *J* = 6.3 Hz, 2H), 2.65 (t, *J* = 6.8 Hz, 2H), 2.07 (dd, *J* = 13.1, 6.6 Hz, 2H); ^{13}C NMR (125

MHz, $CDCl_3$) δ 150.6, 147.3, 135.6, 132.3, 130.8, 129.3, 127.9, 121.8, 121.6, 89.5, 81.1, 43.7, 31.3, 16.9; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{14}H_{13}ClN$, 230.0731, found: 230.0715.

2-(5-Chloropent-1-yn-1-yl)thiophene (1x) [3]: Yellow liquid (79 mg, 86% yield); R_f = 0.49 (petroleum ether); ^1H NMR (500 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 5.2, 1.1 Hz, 1H), 7.14 (d, *J* = 3.6 Hz, 1H), 6.95 (dd, *J* = 5.2, 3.6 Hz, 1H), 3.70 (t, *J* = 6.3 Hz, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 2.05 (dd, *J* = 13.2, 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.3, 126.8, 126.28, 123.6, 92.1, 74.6, 43.7, 31.2, 17.1.

5-(5-Chloropent-1-yn-1-yl)-1-methyl-1H-pyrazole (1y): Yellow liquid (76 mg, 84% yield); R_f = 0.59 (petroleum ether / ethyl acetate = 5:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 1H), 6.33 (s, 1H), 3.89 (s, 3H), 3.69 (t, *J* = 6.3 Hz, 2H), 2.67 (t, *J* = 6.8 Hz, 2H), 2.06 (dd, *J* = 13.1, 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 125.6, 109.5, 95.9, 70.1, 43.5, 37.1, 31.0, 16.9; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_9H_{12}ClN_2$, 183.0684, found: 183.0673.

5-(6-Chlorohex-1-yn-1-yl)-1-methyl-1H-pyrazole (1z): Yellow liquid (85 mg, 87% yield); R_f = 0.64 (petroleum ether / ethyl acetate = 5:1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 1.9 Hz, 1H), 6.31 (d, *J* = 1.9 Hz, 1H), 3.88 (s, 3H), 3.59 (t, *J* = 6.5 Hz, 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 1.96 – 1.91 (m, 2H), 1.82 – 1.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 125. 8, 109.4, 97.0, 69.8, 44.3, 37.1, 31.5, 25.5, 18.8; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{14}ClN_2$, 197.0840, found: 197.0828.

3-(6-Chlorohex-1-yn-1-yl)pyridine (1aa): Yellow liquid (83 mg, 86% yield); R_f = 0.62 (petroleum ether / ethyl acetate = 5:1); ^1H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 1.3 Hz, 1H), 8.47 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.65 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.20 (ddd, *J* = 7.8, 4.9, 0.6 Hz, 1H), 3.59 (t, *J* = 6.5 Hz, 2H), 2.46 (t, *J* = 7.0 Hz, 2H), 1.96 – 1.90 (m, 2H), 1.78 – 1.72 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 148.0, 138.4, 122.9, 120.8, 92.9, 77.9, 44.4, 31.5, 25.6, 18.7; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{13}ClN$, 194.0731, found: 194.0719.

(Z)-2-benzylidenetetrahydrothiophene (3a)：yellow liquid (84 mg, 95% yield); R_f = 0.58 (petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.0 Hz, 1H), 6.57 (s, 1H), 3.25 (t, *J* = 6.2 Hz, 2H), 2.89 (t, *J* = 6.6 Hz, 2H), 2.14 – 2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 137.7, 128.1, 127.5, 125.5, 116.9, 40.1, 35.5, 28.2; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{13}S$, 177.0732, found: 177.0725.

(Z)-2-(2-methylbenzylidene)tetrahydrothiophene (3b)：yellow liquid (85 mg, 89% yield); R_f = 0.53 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.18 (dd, *J* = 15.8, 8.0 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.52 (s, 1H), 3.11 (t, *J* = 6.4 Hz, 2H), 2.81 (t, *J* = 6.6 Hz, 2H), 2.28 (s, 3H), 2.04 – 2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 136.7, 135.4, 129.9, 127.0, 126.0, 125.6, 114.6, 39.6, 34.8, 28.5, 20.0; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{15}S$, 191.0889, found: 191.0883.

(Z)-2-(3-methylbenzylidene)tetrahydrothiophene (3c)[6]：yellow liquid (72 mg, 76% yield); R_f = 0.47 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 6.3 Hz, 3H), 6.96 (d, *J* = 6.6 Hz, 1H), 6.44 (s, 1H), 3.16 (t, *J* = 6.4 Hz, 2H), 2.80 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 2.01 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 137.7, 128.3, 128.1, 126.5, 124. 7, 117.0, 40.1, 35.5, 28.3, 21.5.

(Z)-2-(4-methylbenzylidene)tetrahydrothiophene (3d)：yellow liquid (65 mg, 68% yield); R_f = 0.59 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.10 (m, 2H), 6.44 (s, 1H), 3.16 (t, *J* = 6.4 Hz, 2H), 2.80 (t, *J* = 6.8 Hz, 2H), 2.32 (s, 3H), 2.01 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 135.3, 135.0, 128.9, 127.5, 116.9, 40.0, 35.5, 28.4, 21.1; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{15}S$, 191.0889, found: 191.0879.

(Z)-2-(3,4-dimethylbenzylidene)tetrahydrothiophene (3e)：yellow solid (79 mg, 77% yield); R_f = 0.41(petroleum ether); mp 70.5-71.0℃；^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.41 (s, 1H), 3.14 (t, *J* = 6.6 Hz, 2H), 2.77 (td, *J* = 6.8, 1.6 Hz, 2H), 2.24 (s, 3H), 2.22 (s, 3H), 1.98 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.6, 136.1, 135.3, 133.9, 129.4, 128.8, 124.9, 116.8, 39.9, 35.4, 28.3, 19.8, 19.4; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{13}H_{17}S$, 205.1045, found: 205.1038.

(Z)-2-(3-(tert-butyl)benzylidene)tetrahydrothiophene (3f)：yellow liquid (85 mg, 73% yield); R_f = 0.55(petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 4H), 6.45 (s, 1H), 3.15 (t, *J* = 6.4 Hz, 2H), 2.79 (t, *J* = 6.8 Hz, 2H), 2.00 (p, *J* = 6.6 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 142.0, 134.9, 127.3, 125.1, 116.7, 40.0, 35.4, 34.4, 31.3, 28.3; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{15}H_{21}S$, 233.1358, found: 233.1347.

(Z)-2-(4-methoxybenzylidene)tetrahydrothiophene (3g)：dark brown liquid (85 mg, 83% yield); R_f = 0.62 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.42 (s, 1H), 3.78 (s, 3H), 3.16 (t, *J* = 6.4 Hz, 2H), 2.78 (t, *J* = 6.8 Hz, 2H), 2.00 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 140.4, 130.6, 128.7, 116.4, 113.7, 55.2, 39.9, 35.4, 28.3; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{15}OS$, 207.0838, found: 207.0830.

(Z)-4-((dihydrothiophen-2(3H)-ylidene)methyl)aniline (3h)：dark brown liquid (79 mg, 83% yield); R_f = 0.42 (petroleum ether / ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 6.63 (t, *J* = 8.4 Hz, 2H), 6.34 (s, 1H), 3.51 (s, 2H), 3.14 (q, *J* = 6.4 Hz, 2H), 2.76 (t, *J* = 6.8 Hz, 2H), 1.98 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 138.7, 128.6, 128.5, 116.8, 114.9, 39.8, 35.3, 28.3；ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{14}NS$, 192.0841, found: 192.0835.

(Z)-2-(4-fluorobenzylidene)tetrahydrothiophene (3i)：yellow liquid (86 mg, 89% yield); R_f = 0.58 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.43 (s, 1H), 3.17 (t, *J* = 6.4 Hz, 2H), 2.79 (t, *J* = 6.9 Hz, 2H), 2.02 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ160.8 (d, J_{C-F} = 244 Hz), 142. 7, 133.9 (d, J_{C-F} = 3 Hz), 129.0 (d, J_{C-F} = 8 Hz), 115.8, 115.0 (d, J_{C-F} = 21 Hz), 40.0, 35.5, 28.3; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{12}FS$, 195.0638, found: 195.0632.

(Z)-2-(4-chlorobenzylidene)tetrahydrothiophene (3j)：yellow liquid (90 mg, 86% yield); R_f = 0.44 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 6.40 (s, 1H), 3.16 (t, *J* = 6.4 Hz, 2H), 2.78 (td, *J* = 6.9, 1.2 Hz, 2H), 2.00 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 136.2, 130.9, 128.7, 128.3, 115.7, 40.2, 35.6, 28.3; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{12}SCl$, 211.0343, found: 211.0333.

(Z)-2-(4-isocyanobenzylidene)tetrahydrothiophene (3k)：yellow solid (85 mg, 85% yield); R_f = 0.49 (petroleum ether/ethyl acetate = 10:1); mp 103.2-105.7℃；^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 6.47 (d, *J* = 9.6 Hz, 1H), 3.24 (t, *J* = 6.4 Hz, 2H), 2.87 (td, *J* = 7.2, 1.8 Hz, 2H), 2.07 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.9, 142.2, 132.1, 127.8, 119.4, 115.6, 108.2, 40.7, 36.1, 28.3; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{12}NS$, 202.0685, found:202.0679.

(Z)-2-(4-(trifluoromethyl)benzylidene)tetrahydrothiophene (3l)：white liquid (106 mg, 87% yield); R_f = 0.49 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 6.49 (s, 1H), 3.21 (t, *J* = 6.4 Hz, 2H), 2.84 (t, *J* = 6.8 Hz, 2H), 2.04 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 141.3, 127.6 (q, J_{C-F}=3.2 Hz, 1C), 127.0, 125.7, 125.1 (q, J_{C-F}=3.8 Hz), 115.7, 40.5, 35.8, 28.3; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{12}SF_3$, 245.0606, found: 245.0594.

2-([1,1'-biphenyl]-4-ylmethylene)tetrahydrothiophene (3m)：yellow liquid (91 mg, 72% yield); R_f = 0.51 (petroleum ether / ethyl acetate =20:1); mp 75.1-78.9℃；^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 4H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.23 (m, 1H), 6.44 (s, 1H), 3.07 (t, *J* = 6.4 Hz, 2H), 2.71 (m, 2H), 1.89 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.3, 140.6, 137.8, 136.7, 128.5, 127.8, 126.8, 126.6, 126.6, 116.3, 40.1, 35.5, 28.1; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{17}H_{17}S$, 253.1045, found: 253.1032.

(Z)-tetrahydro-2-((naphthalen-3-yl) methylene) thiophene (3n)：yelow liquid (72 mg, 64% yield); R_f = 0.52 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 5.8 Hz, 2H), 7.45 (s, 1H), 7.06 (s, 1H), 3.13 (t, *J* = 6.4 Hz, 2H), 2.92 (t, *J* = 6.8 Hz, 2H), 2.09 (dd, *J* = 13.8, 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 135.0, 133.7, 131.3, 128.5, 126.7, 125.8, 125.6, 125.4, 125.2, 124.0, 113. 5, 39.5, 34.7, 28.7; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{15}H_{15}S$, 227.0889, found: 227.0880.

(Z)-2-(dihydrothiophen-2(3H)-ylidene)-1-phenylethan-1-one (3o): yelow liquid (95 mg, 93% yield); R_f = 0.48 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.90 (m, 2H), 7.50 – 7.46 (m, 1H), 7.45 – 7.39 (m, 2H), 7.19 (t, *J* = 1.3 Hz, 1H), 3.08 (t, *J* = 6.5 Hz, 2H), 2.92 (td, *J* = 6.9, 1.3 Hz, 2H), 2.06 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.8, 171.5, 138.3, 131.8, 128.3 (2C), 127.7 (2C), 110.4, 40.0, 35.3, 27.6. ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{13}OS$, 205.0682, found: 205.0681.

3-(Z)-2-benzylidenetetrahydro-2H-thiopyran (3p) yelow liquid (71 mg, 75% yield); R_f = 0.58 (petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 3H), 6.82 (s, 1H), 2.85 – 2.81 (m, 2H), 2.80 – 2.76 (m, 2H), 2.07 – 1.99 (m, 2H), 1.73 – 1.66 (m, 2H) ;

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.7, 136.2, 128.8 (2C), 128.1 (2C), 126.4, 117.8, , 30.6, 29.8, 26.5, 26.3. ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{12}H_{15}S$, 191.0889, found: 191.0888.

(Z)-2-((dihydrothiophen-2(3H)-ylidene)methyl)pyridine (3r)：yellow solid (69 mg, 78% yield); R_f = 0.57 (petroleum ether / ethyl acetate = 10:1); mp 57.4-61.4℃；^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 4.8 Hz, 1H), 7.63 – 7.52 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.98 (dd, *J* = 7.2, 6.0 Hz, 1H), 6.57 (s, 1H), 3.09 (t, *J* = 6.4 Hz, 2H), 2.87 (t, *J* = 6.8 Hz, 2H), 2.04 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 150.1, 148.4, 135.8, 122.5, 119.4, 115.3, 39.8, 35.2, 28.2; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{12}NS$, 178.0685, found: 178.0679.

(Z)-3-((dihydrothiophen-2(3H)-ylidene)methyl)pyridine (3s)：yellow brown liquid (73 mg, 82% yield); R_f = 0.42 (petroleum ether / ethyl acetate =5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.58 (d, *J* = 1.8 Hz, 1H), 8.35 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.26 (dd, *J* = 8.4, 4.8 Hz, 1H), 6.42 (s, 1H), 3.21 (t, *J* = 6.4 Hz, 2H), 2.84 (td, *J* = 6.9, 1.5 Hz, 2H), 2.04 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.2, 146.5, 145.9, 133.5, 133.5, 123.0, 112.9, 40.2, 35.8, 28.2; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{12}NS$, 178.0685, found: 178.0681.

(Z)-4-((dihydrothiophen-2(3H)-ylidene)methyl)pyridine (3t)：dark brown liquid (79 mg, 89% yield); R_f = 0.41 (petroleum ether / ethyl acetate =5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.4 Hz, 2H), 7.33 – 7.25 (m, 2H), 6.40 (s, 1H), 3.25 (t, *J* = 6.4 Hz, 2H), 2.87 (t, *J* = 6.9 Hz, 2H), 2.07 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 149.5, 144.9, 121.9, 114.6, 40.7, 36.2, 28.2; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{12}NS$, 178.0685, found: 178.0679.

(Z)-5-((dihydrothiophen-2(3H)-ylidene)methyl)-2-methoxypyridine (3u): yellow liquid (86 mg, 83% yield); R_f = 0.47 (petroleum ether / ethyl acetate =5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 1.7 Hz, 1H), 7.73 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 6.36 (s, 1H), 3.93 (s, 3H), 3.19 (t, *J* = 6.4 Hz, 2H), 2.80 (t, *J* = 6.8 Hz, 2H), 2.07 – 1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 146.1, 142.7, 137.2, 127.2, 113.0, 110.1, 53.4, 40.0, 35.6, 28.4; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{14}NOS$, 208.0791, found: 208.0781.

4-((Z)-(dihydrothiophen-2(3H)-ylidene)methyl)-2-methoxypyridine (3v)：yellow solid (97 mg, 94% yield); R_f = 0.51 (petroleum ether / ethyl acetate =5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 4.8 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 6.90 (dd, *J* = 7.2, 5.6 Hz, 1H), 6.66 (s, 1H), 3.95 (s, 3H), 3.17 (t, *J* = 6.4 Hz, 2H), 2.85 (t, *J* = 7.0 Hz, 2H), 2.02 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 145.5, 143.3, 134.9, 121.2, 116.5, 109.6, 53.3, 40.2, 35.4, 28.2; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{14}NOS$, 208.0791, found: 208.0782.

(Z)-2-bromo-5-((dihydrothiophen-2(3H)-ylidene)methyl)pyridine (3w): yellow solid (107 mg, 84% yield); R_f = 0.48 (petroleum ether / ethyl acetate =5:1); mp 58.9-62.0℃；^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.0 Hz, 1H), 7.66 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 6.35 (s, 1H), 3.23 (t, *J* = 6.4 Hz, 2H), 2.83 (t, *J* = 6.8 Hz, 2H), 2.06 (p, *J* = 6.6 Hz, 2H)；^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 147.9, 137.8, 136.1, 132.9, 127.3, 111.8, 40.4, 36.0, 28.3; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{11}NSBr$, 255.9790, found: 255.9782.

(Z)-3-bromo-5-((dihydrothiophen-2(3H)-ylidene)methyl)pyridine (3x)：dark brown liquid (102 mg, 80% yield); R_f = 0.47 (petroleum ether / ethyl acetate =5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.41 (d, *J* = 1.6 Hz, 1H), 7.94 (s, 1H), 6.35 (s, 1H), 3.24 (t, *J* = 6.4 Hz, 2H), 2.86 (t, *J* = 6.8 Hz, 2H), 2.07 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 147.3, 146.8, 135.9, 135.3, 120.5, 111.7, 40.5, 36.0, 28.3; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{11}NSBr$, 255.9790, found: 255.9783.

(Z)-2-chloro-5-((dihydrothiophen-2(3H)-ylidene)methyl)pyridine (3y)：yellow liquid (98 mg, 93% yield); R_f = 0.46 (petroleum ether / ethyl acetate =5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.4 Hz, 1H), 7.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.26 (t, *J* =8.4 Hz, 1H), 6.37 (s, 1H), 3.22 (t, *J* = 6.4 Hz, 2H), 2.84 (t, *J* = 6.8 Hz, 2H), 2.06 (p, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 147.6, 147.4, 136.3, 132.6, 123.5, 111.8, 40.3, 35.9, 28.3; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{11}NSCl$, 212.0295, found: 212.0289.

7-((Z)-(dihydrothiophen-2(3H)-ylidene) methyl) quinoline (3z): brown liquid (98 mg, 86% yield); R_f = 0.58 (petroleum ether/ ethyl acetate = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 2.0 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 1.2 Hz, 1H), 7.77 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.37 (dd, *J* = 8.4, 4.4 Hz, 1H), 6.64 (s, 1H), 3.26 (t, *J* = 6.4 Hz, 2H), 2.91 (t, *J* = 6.8 Hz, 2H), 2.10

(p, J = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 146.7, 145.5, 136.1, 135.9, 130.5, 129.0, 128.4, 125.1, 121.2, 116.3, 40.4, 35.7, 28.3; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{14}H_{14}NS$, 228.0841, found: 228.0828.

2-((Z)-(dihydrothiophen-2(3H)-ylidene) methyl) thiophene (3aa)：yellow brown liquid (80 mg, 88% yield); R_f = 0.45 (petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (d, J =4.8 Hz, 1H), 7.00 (dd, J = 5.0, 3.6 Hz, 1H), 6.98 (d, J = 3.1 Hz, 1H), 6.69 (s, 1H), 3.22 (t, J = 6.4 Hz, 2H), 2.81 – 2.78 (m, 2H), 2.06 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.1, 142.1, 127.0, 124.4, 123.4, 110.4, 39.2, 36.1, 29.1; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_9H_{11}S_2$, 183.0297, found: 183.0289.

4-((Z)-(dihydrothiophen-2(3H)-ylidene) methyl)-1-methyl-1H-pyrazole (3ab)：yelow liquid (81 mg, 90% yield); R_f = 0.62 (petroleum ether/ ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 6.48 (s, 1H), 6.33 (s, 1H), 3.81 (s, 3H), 3.18 (t, J = 6.4 Hz, 2H), 2.83 (t, J = 6.8 Hz, 2H), 2.09 (p, J = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 139.7, 138.0, 104.3, 103.1, 39.3, 36.2, 35.3, 28.9; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_9H_{13}N_2S$, 181.0794, found: 181.0787.

5-((Z)-(tetrahydrothiopyran-2-ylidene) methyl)-1-methyl-1H-pyrazole (33ac)：yelow liquid (85 mg, 88% yield); R_f = 0.47 (petroleum ether/ ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 6.62 (s, 1H), 6.23 (s, 1H), 3.82 (s, 3H), 2.80 – 2.73 (m, 2H), 2.65 – 2.58 (m, 2H), 1.97 (dt, J = 11.9, 6.1 Hz, 2H), 1.83 – 1.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.0, 137.7, 111.7, 106.7, 36.4, 36.1, 28.8, 25.4, 25.3; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{10}H_{15}N_2S$, 195.0950, found: 195.0944.

3-((Z)-(tetrahydrothiopyran-2-ylidene) methyl) pyridine (3ad)：yelow liquid (83 mg, 87% yield); R_f = 0.55 (petroleum ether/ ethyl acetate = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.40 (d, J = 3.6 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.23 (dd, J = 7.7, 4.9 Hz, 1H), 6.39 (s, 1H), 2.75 – 2.70 (m, 2H), 2.65 – 2.58 (m, 2H), 2.01 – 1.94 (m, 2H), 1.77 (dt, J = 12.0, 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 147.0, 138.3, 135.7, 132.6, 122.6, 122.5, 36.9, 29.4, 25.9, 25.9; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{14}NS$, 192.0841, found: 192.0835.

O-ethyl S-(5-phenylpent-4-yn-1-yl) carbonodithioate (5)：yellow liquid (57 mg, 64% yield); R_f = 0.41 (petroleum ethe); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.34 – 7.27 (m, 3H), 4.69 (q, *J* = 7.1 Hz, 2H), 3.33 (t, *J* = 7.3 Hz, 2H), 2.58 (t, *J* = 6.9 Hz, 2H), 2.04 (p, *J* = 7.0 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.6, 131.5, 128.2, 127.7, 123.6, 88.5, 81.6, 69.9, 34.7, 27.5, 18.6, 13.8; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{14}H_{17}S_2O$, 265.0715, found: 265.0701.

(Z)-2-benzylidenetetrahydrothiophene (3a-d)：white liquid (81 mg, 92% yield); R_f = 0.62 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.49 (s, 0.1H), 3.20 (t, *J* = 6.4 Hz, 2H), 2.83 (t, *J* = 6.8 Hz, 2H), 2.06 – 2.02 (m, 2H). GC-MS (EI, 70 eV) m/z: 191, 162, 147, 115.

(Z)-2-benzylidenetetrahydrothiophene 2-oxide (4a)：white solid (85 mg, 82% yield); R_f = 0.41 (petroleum ether/ ethyl acetate = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 8.4 Hz, 3H), 6.83 (s, 1H), 3.13 (t, *J* = 7.1 Hz, 2H), 2.90 (t, *J* = 6.8 Hz, 2H), 2.23 – 2.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 132.8, 132.5, 129.6, 129.3, 128.3, 53.0, 31.4, 19.6; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{13}SO_2$, 209.0631, found: 209.0620.

(Z)-2-([1,1'-biphenyl]-4-ylmethylene)tetrahydrothiophene 1,1-dioxide (4b)：white solid (125 mg, 88% yield); R_f = 0.48 (petroleum ether/ ethyl acetate = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.63 – 7.58 (m, 4H), 7.43 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.85 (s, 1H), 3.17 (t, *J* = 7.1 Hz, 2H), 2.92 (td, *J* = 6.9, 2.0 Hz, 2H), 2.23 (dd, *J* = 14.0, 7.0 Hz, 2H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 140.1, 137.5, 132.4, 131.4, 130.3, 128.7, 127.6, 127.0, 126.9, 53.0, 31.5, 19.7; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{17}H_{17}S_2O_2$, 285.0944, found: 285.0938.

(Z)-2-(thiophen-2-ylmethylene)tetrahydrothiophene 1,1-dioxide (4c): white solid (92 mg, 86% yield); R_f = 0.58 (petroleum ether/ ethyl acetate = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 3.6 Hz, 1H), 7.43 (d, *J* = 5.0 Hz, 1H), 7.07 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.87 (s, 1H), 3.21 (t, *J* = 7.2 Hz, 2H), 2.92 (td, *J* = 6.8, 2.0 Hz, 2H), 2.26 (dd, *J* = 14.0, 6.8 Hz, 2H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.8, 134.6, 131.8, 129.4, 128.2, 123.8, 53.1, 31.4, 19.9; ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_9H_{11}S_2O_2$, 215.0195, found: 215.0190.

References:

1. A. Elhage, A. E. Lanterna, J. C. Scaiano, *ACS Sustainable Chem. Eng.,* **2018**, *6*, 1717-1722.

2. W. Liu, L. Li, C.-J. Li, *Nat. Commun.,* **2015**, *6*, 6526-6531.

3. A. Fuerstner, C. Mathes, C. W. Lehmann, *Chem. Eur. J.,* **2001**, *7*, 5299-5317.

4. M. Corpet, C. Gosmini, *Chem. Commun.,* **2012**, *48*, 11561-11563.

5. D. Gelman, S. L. Buchwald, *Angew. Chem. Int. Ed.,* **2003**, *42*, 5993-5996.

6. J.-H. Li, Q. Huang, S.-Y. Wang and S.-J. Ji, *Org. Lett.*, **2018**, *20*, 4704-4708.

G: Crystal Structure of 3e

The solid states structure of **3e** was confirmed by single crystal X-ray diffraction as shown in Figure 1. Suitable colorless plate crystals were obtained by slow concentration of a DCM/Petroleum ether solution of **3e**.

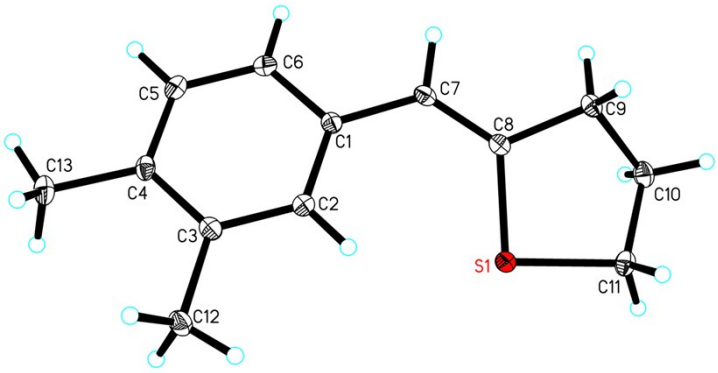


Figure 1. ORTEP Structure of 3e (*CCDC 1881760*)

Crystal Data for $C_{13}H_{16}S$ (M =204.32 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 12.8311(9) Å, b = 7.0802(5) Å, c = 12.0660(8) Å, β = 90.396(7)°, V = 1096.13(13) Å^3, Z = 4, T = 100.00(10) K, μ(MoKα) = 0.252 mm^{-1}, *Dcalc* = 1.238 g/cm^3, 7903 reflections measured (6.35° ≤ 2Θ ≤ 59.262°), 2619 unique (R_{int} = 0.0362, R_{sigma} = 0.0452) which were used in all calculations. The final R_1 was 0.0432 (I > 2σ(I)) and wR_2 was 0.1086 (all data).

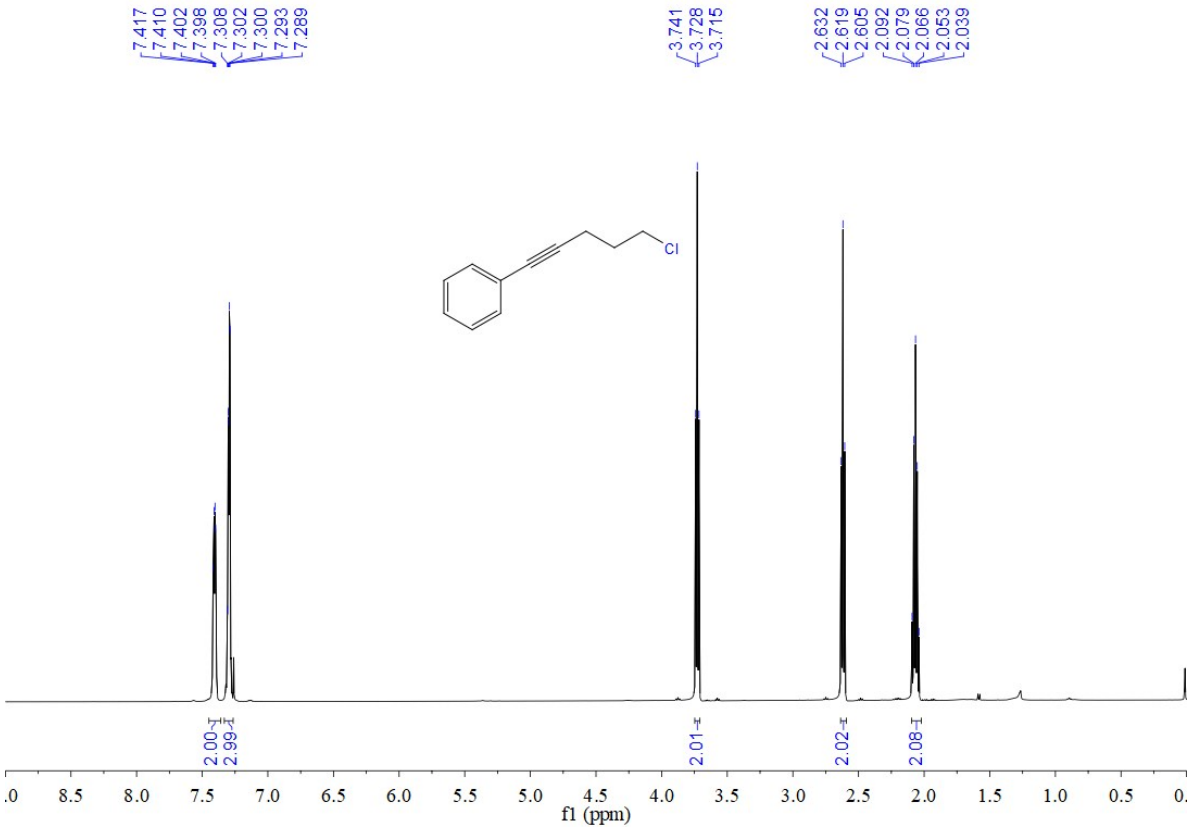
Table 1 Crystal data and structure refinement for HLJ1027.

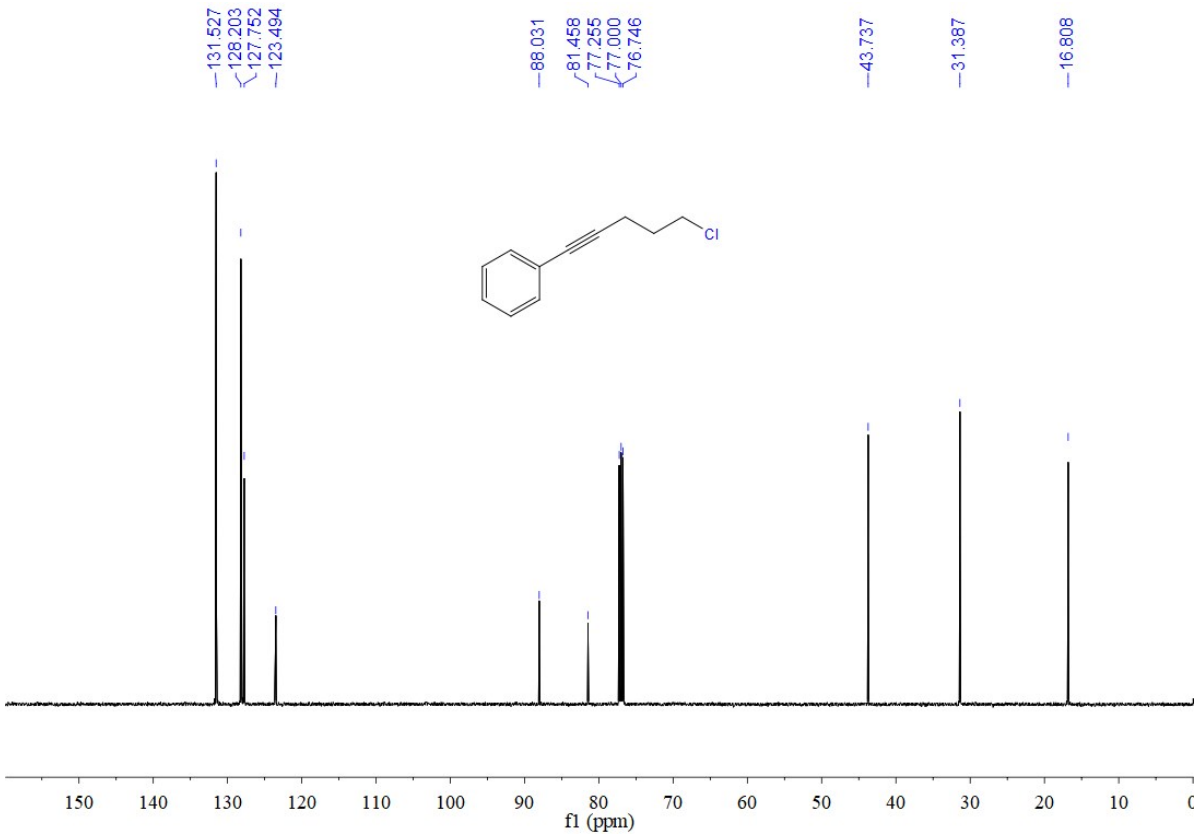
Identification code	HLJ1027
Empirical formula	$C_{13}H_{16}S$
Formula weight	204.32
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.8311(9)
b/Å	7.0802(5)
c/Å	12.0660(8)

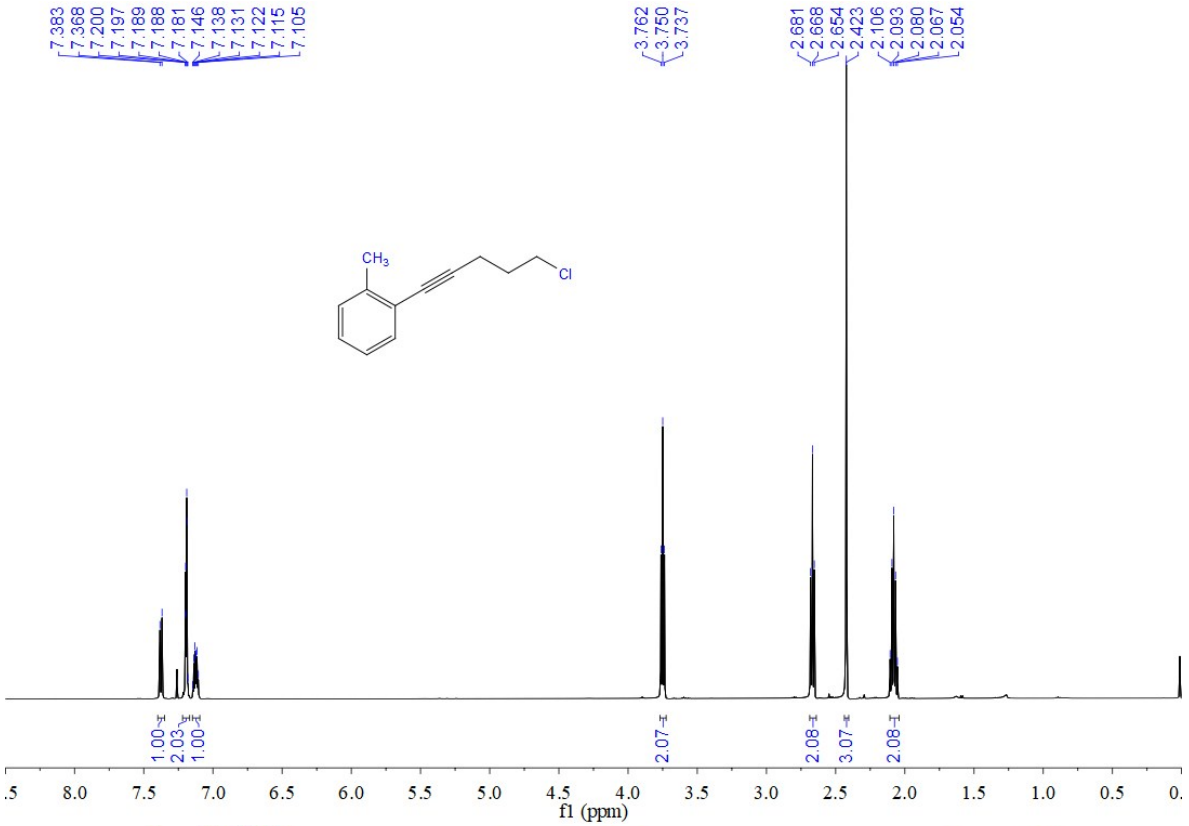
α/°	90
β/°	90.396(7)
γ/°	90
Volume/Å^3	1096.13(13)
Z	4
ρ_{calc}g/cm^3	1.238
μ/mm^{-1}	0.252
F(000)	440.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.35 to 59.262
Index ranges	-17 ≤ h ≤ 17, -8 ≤ k ≤ 8, -15 ≤ l ≤ 16
Reflections collected	7903
Independent reflections	2619 [R_{int} = 0.0362, R_{sigma} = 0.0452]
Data/restraints/parameters	2619/0/129
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0432, wR_2 = 0.1006
Final R indexes [all data]	R_1 = 0.0528, wR_2 = 0.1086
Largest diff. peak/hole / e Å^{-3}	0.30/-0.37

Crystallographic data for 3e (*CCDC* 1881760) are available as CIF files free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

H: ^{1}H NMR and ^{13}C NMR spectra for products



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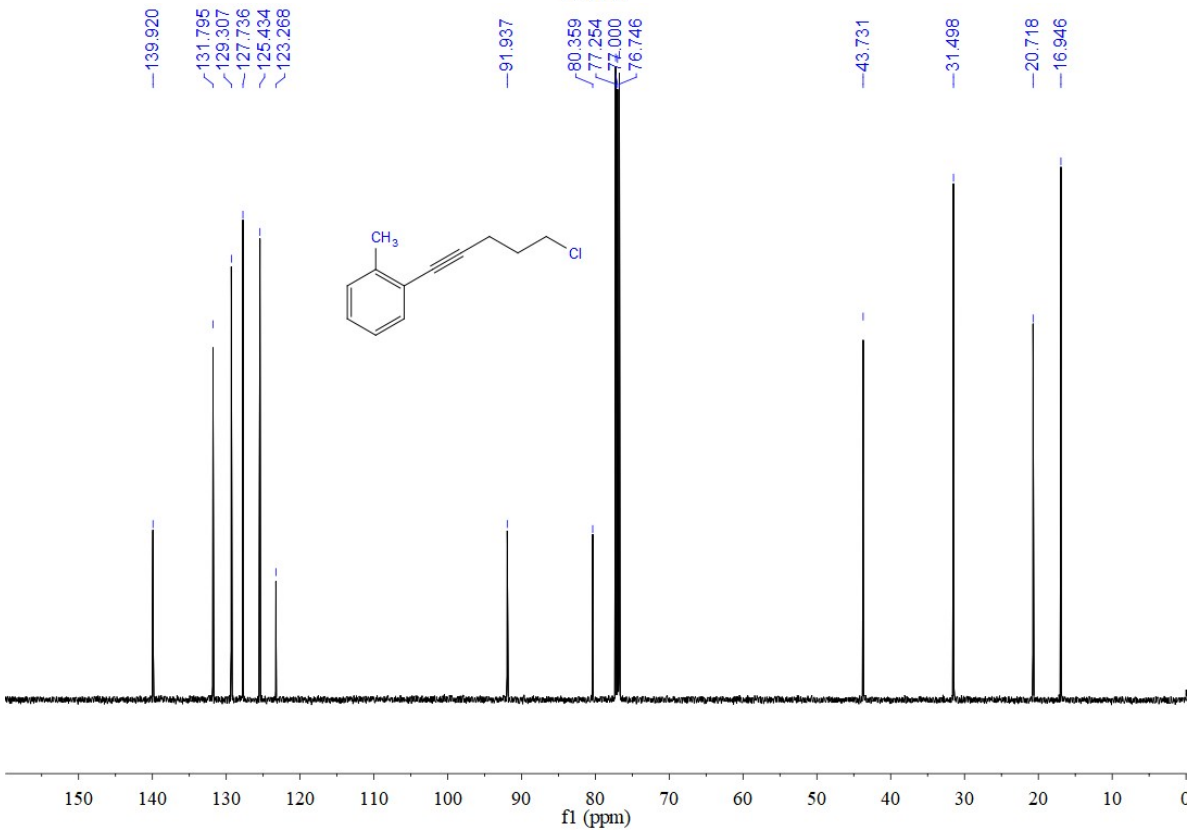
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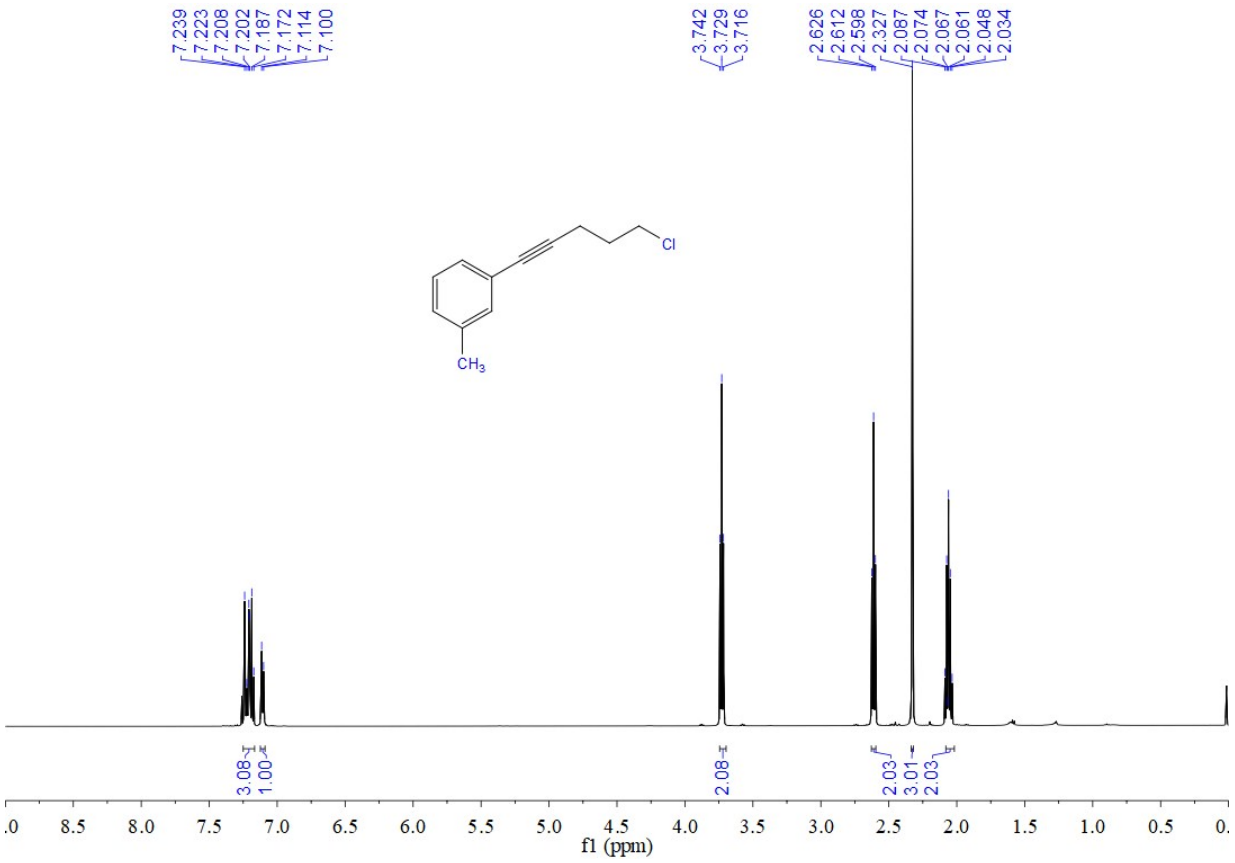
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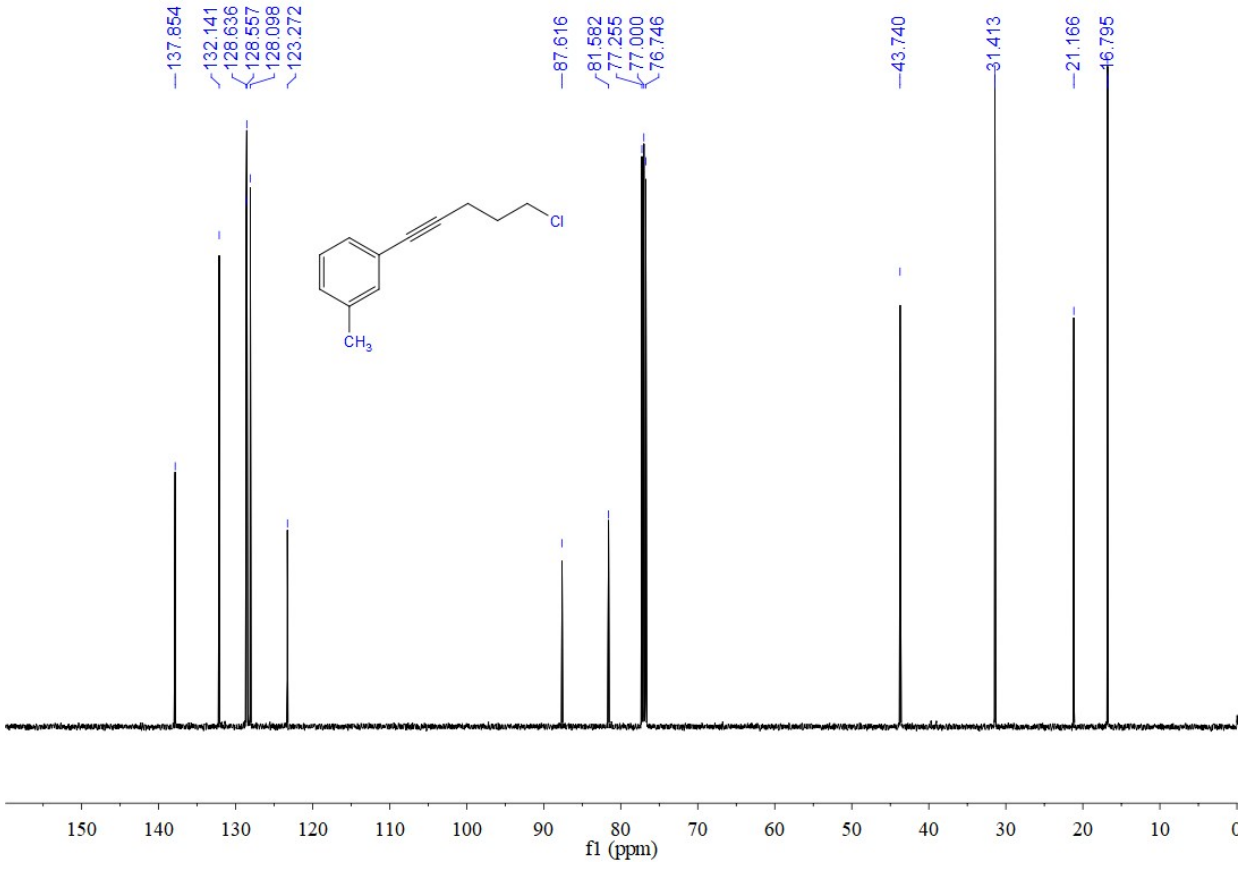
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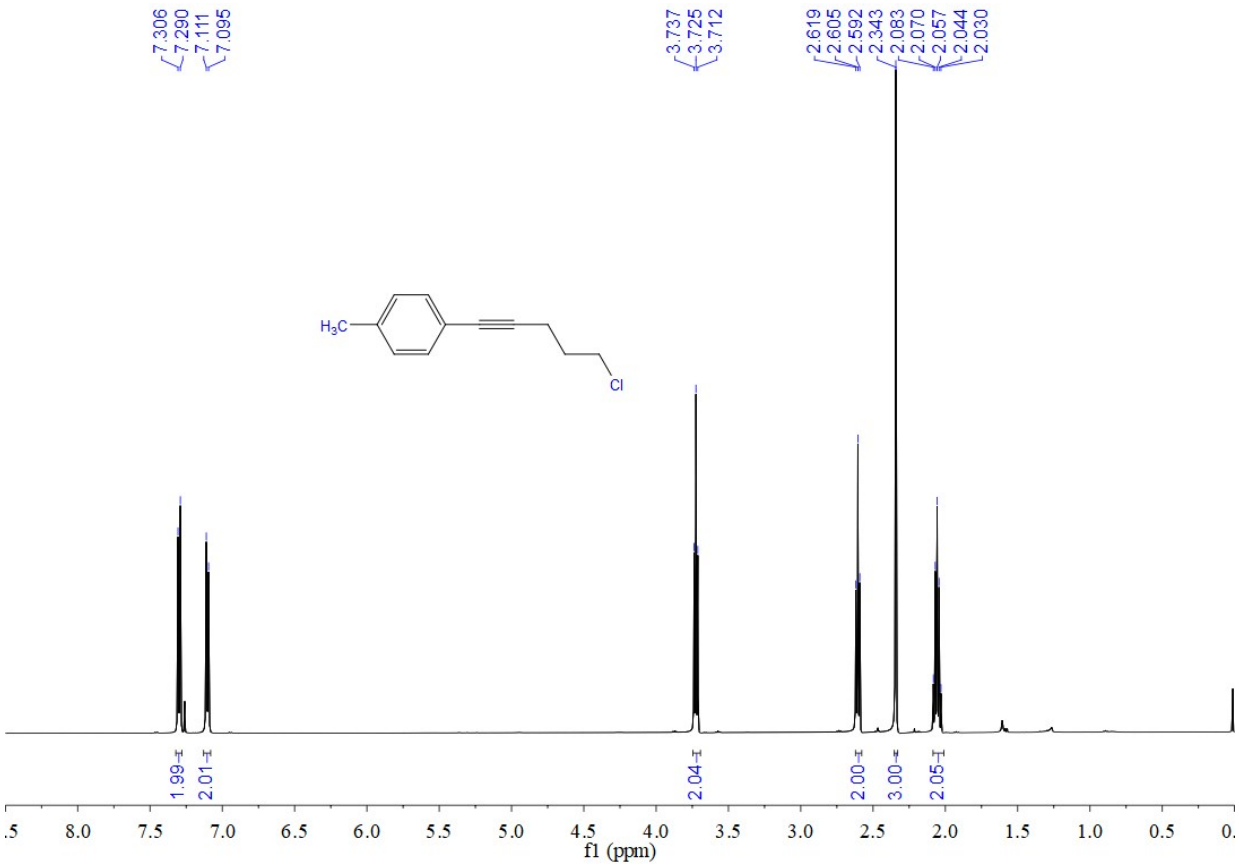
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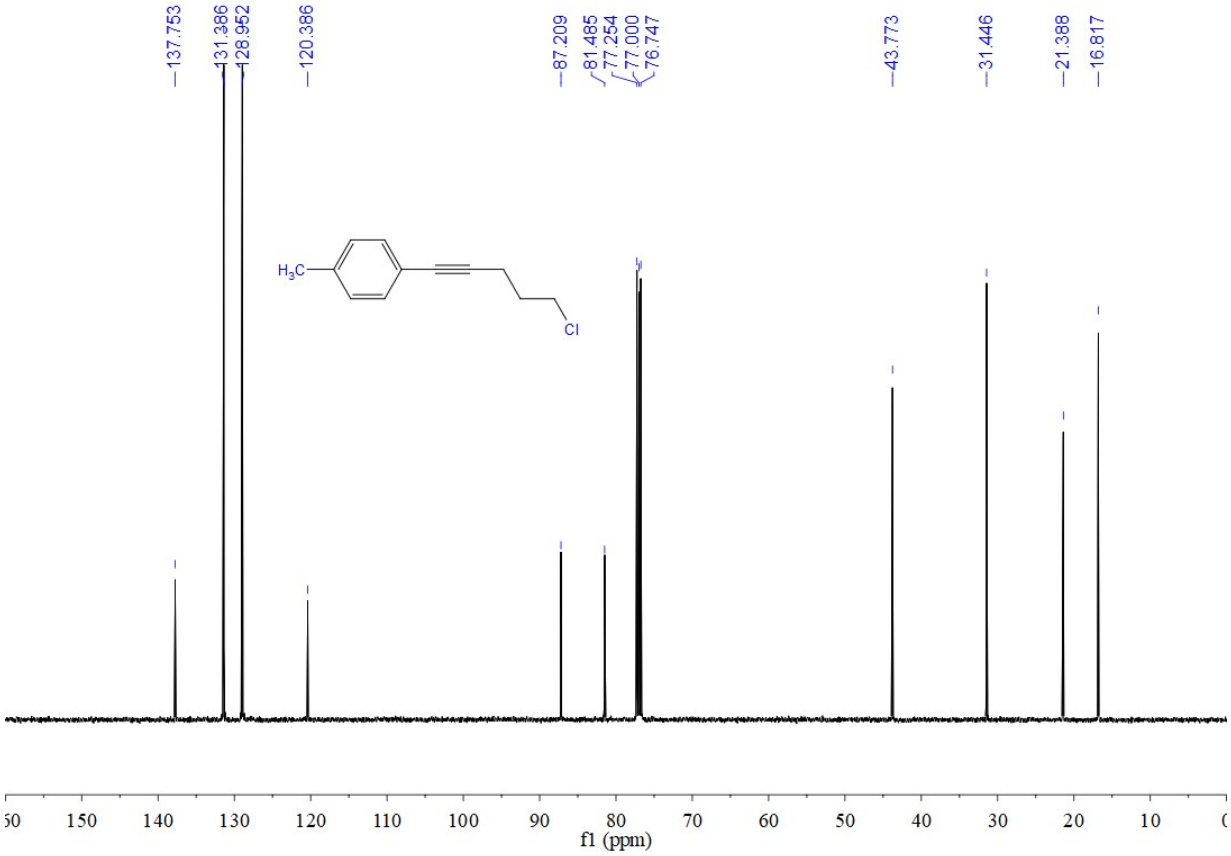
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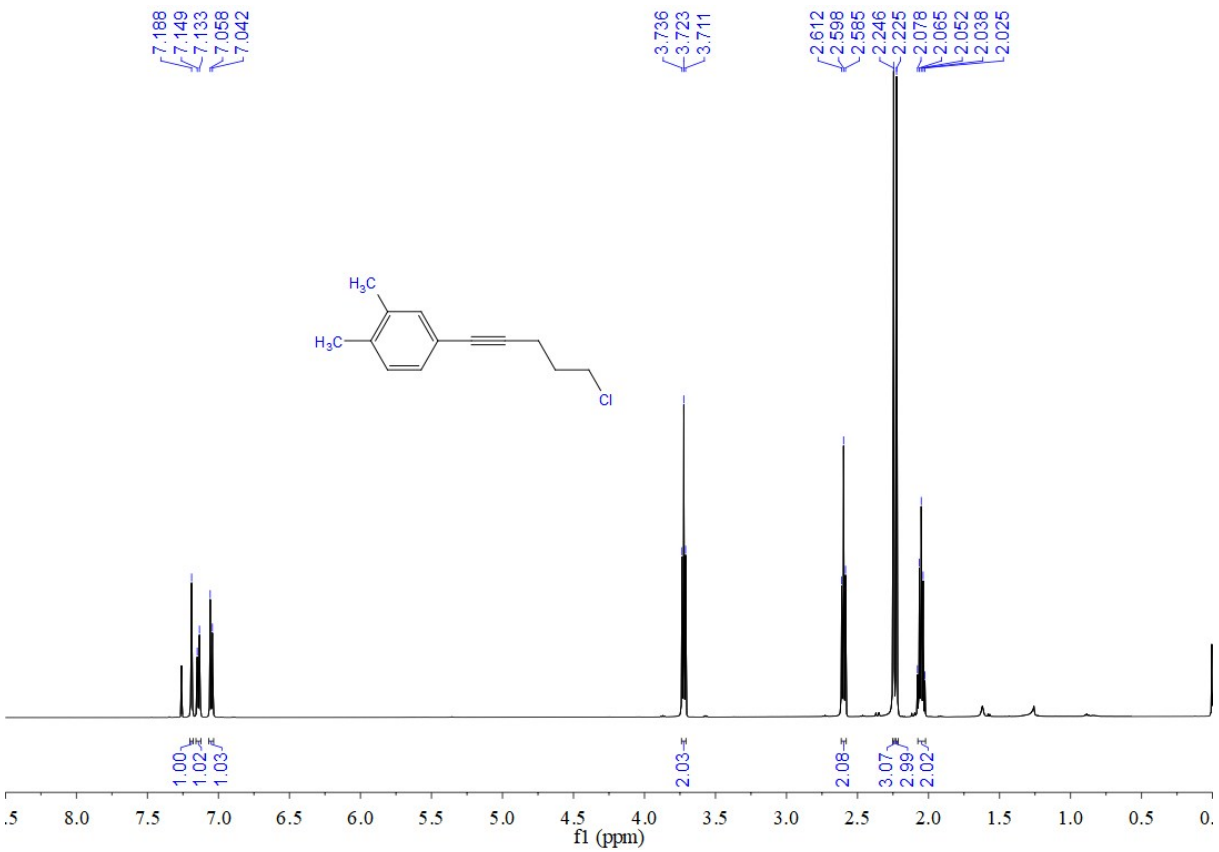
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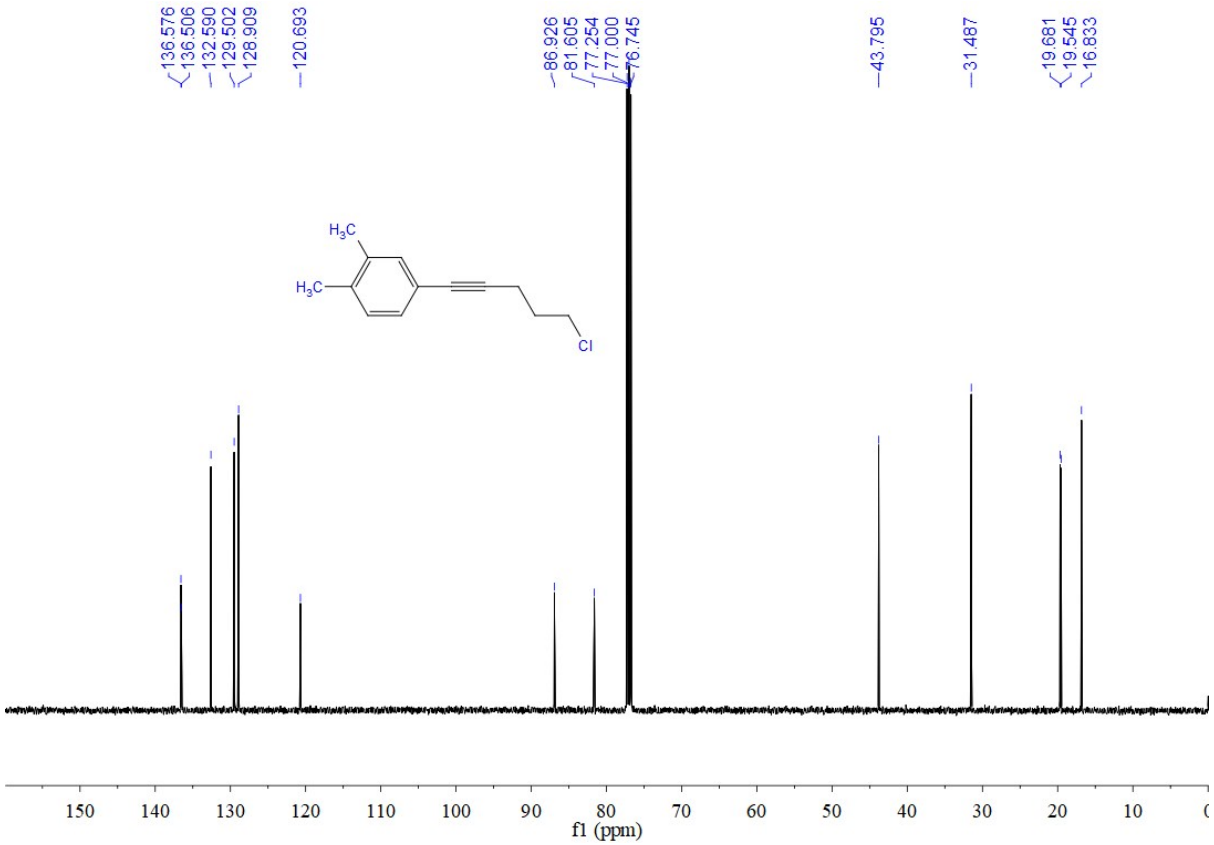
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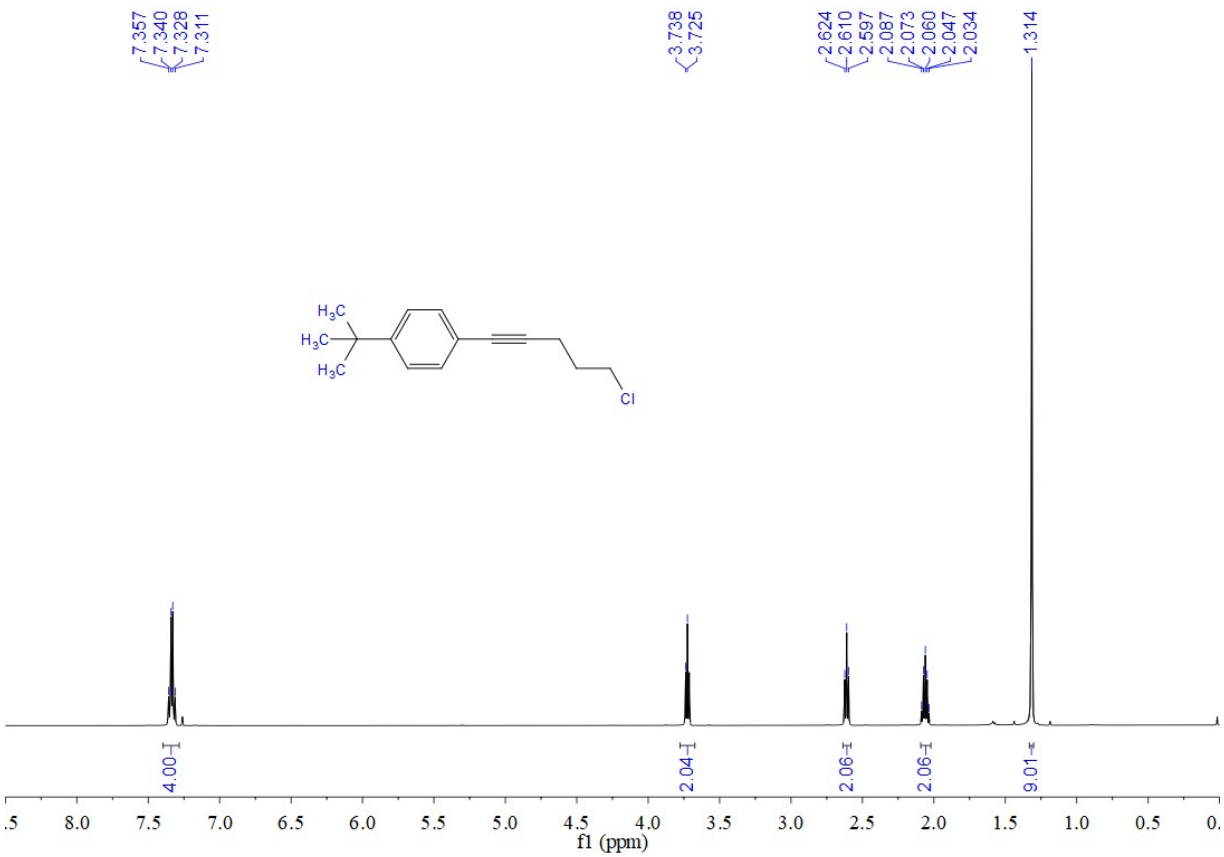
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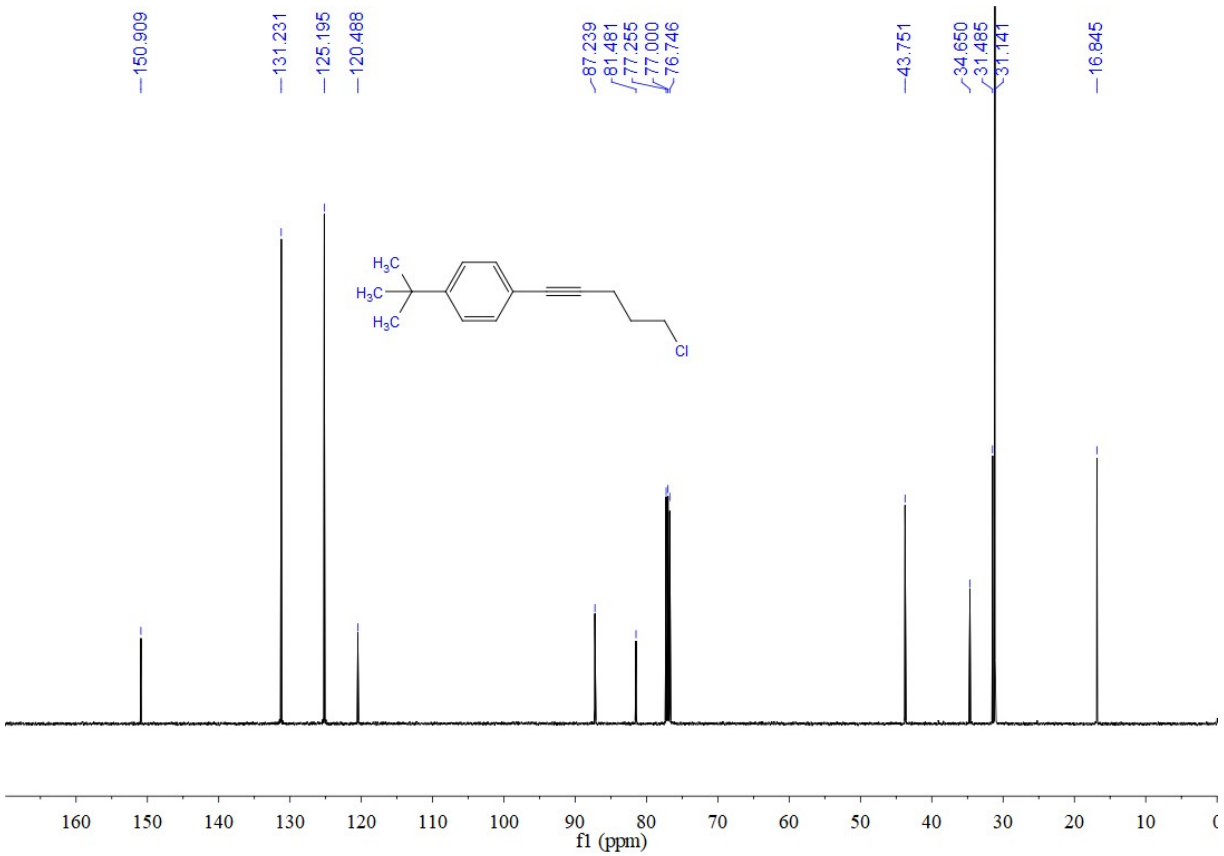
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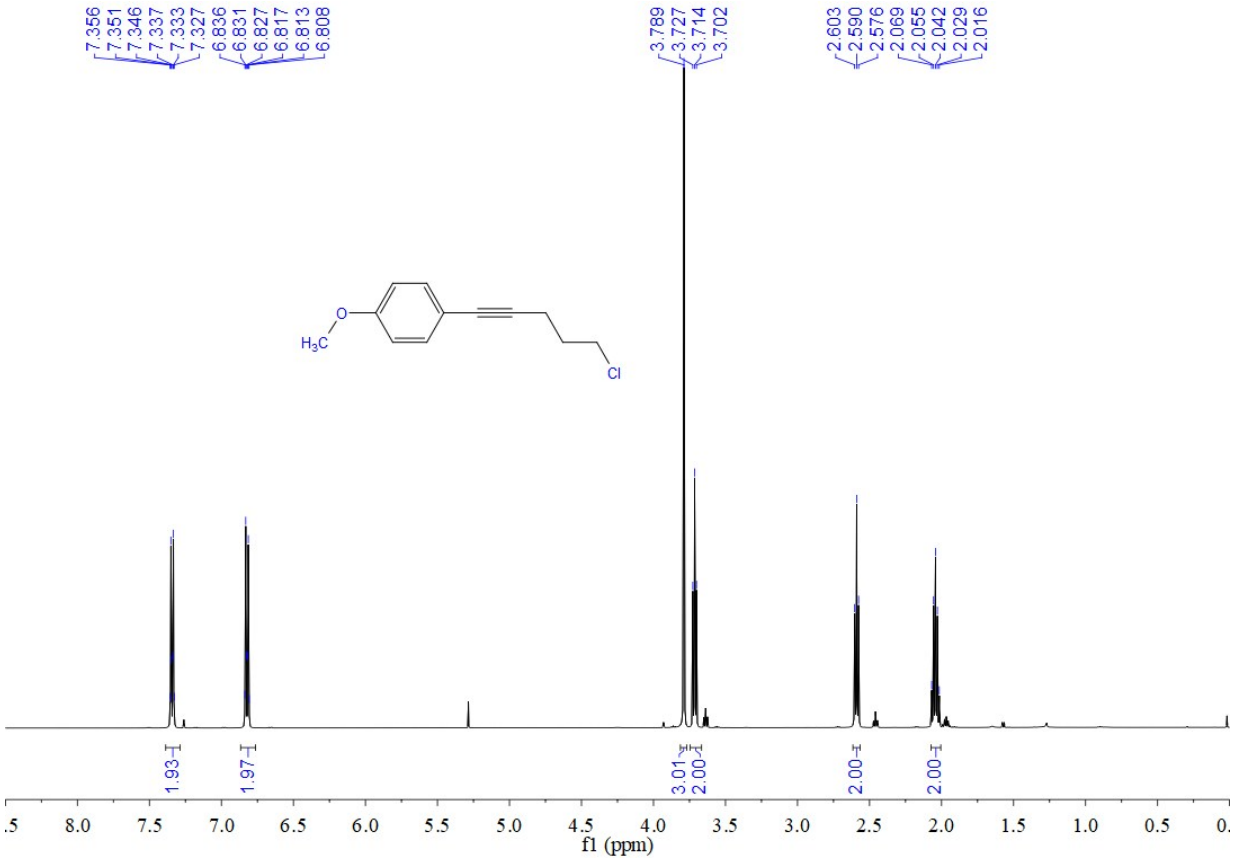
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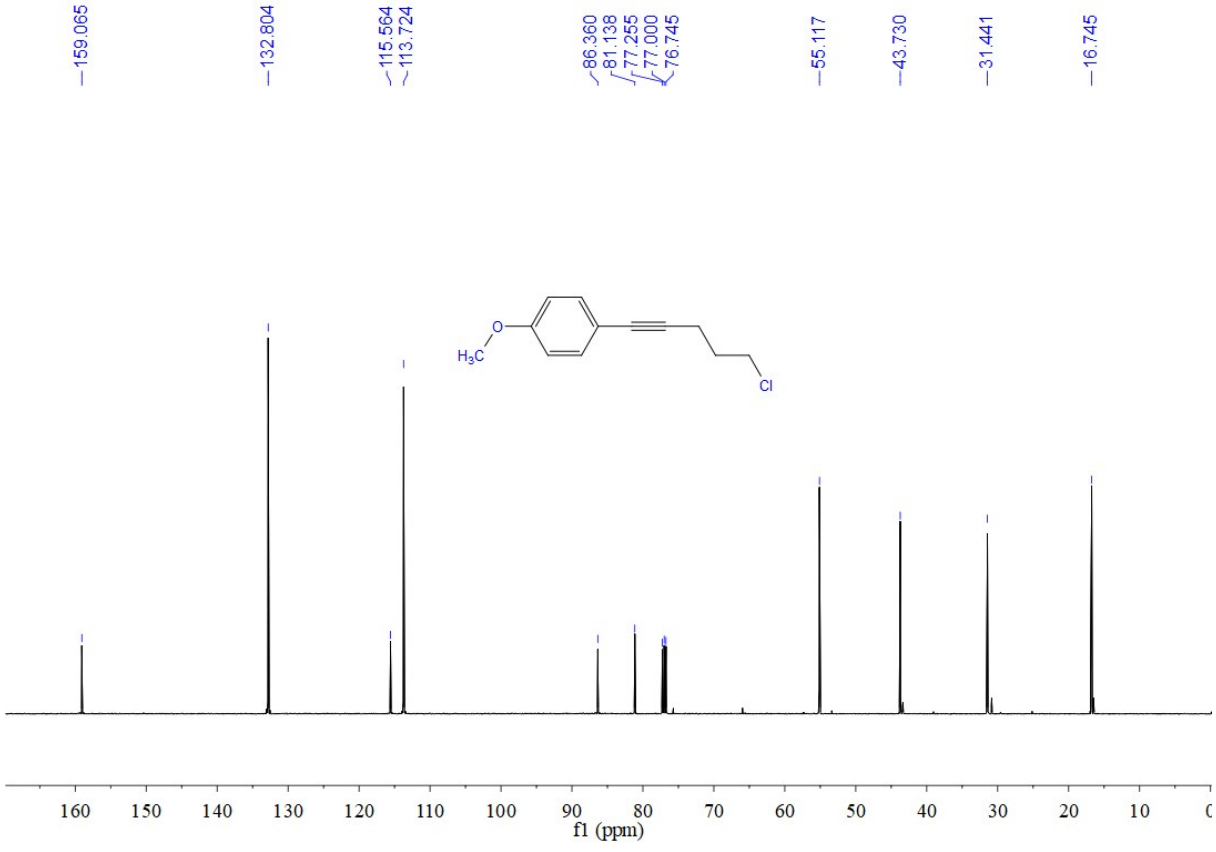
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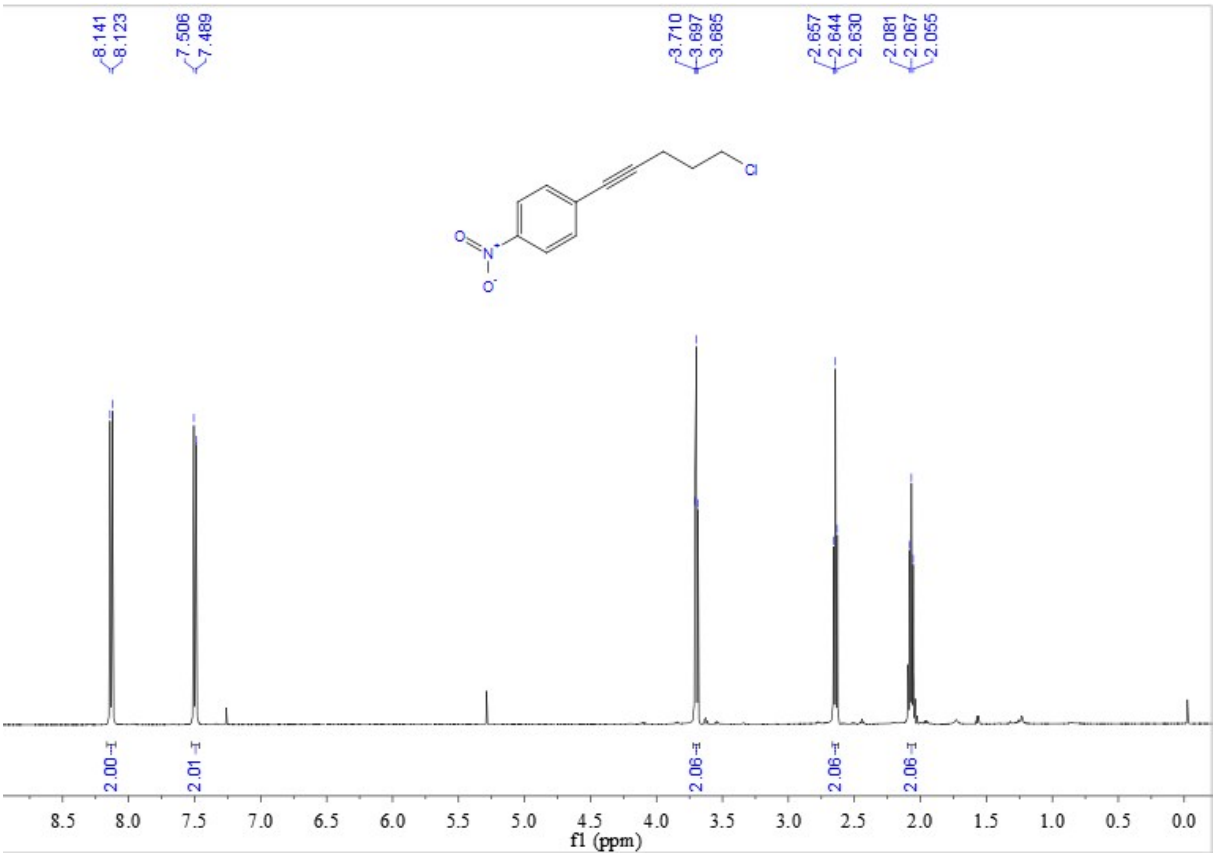
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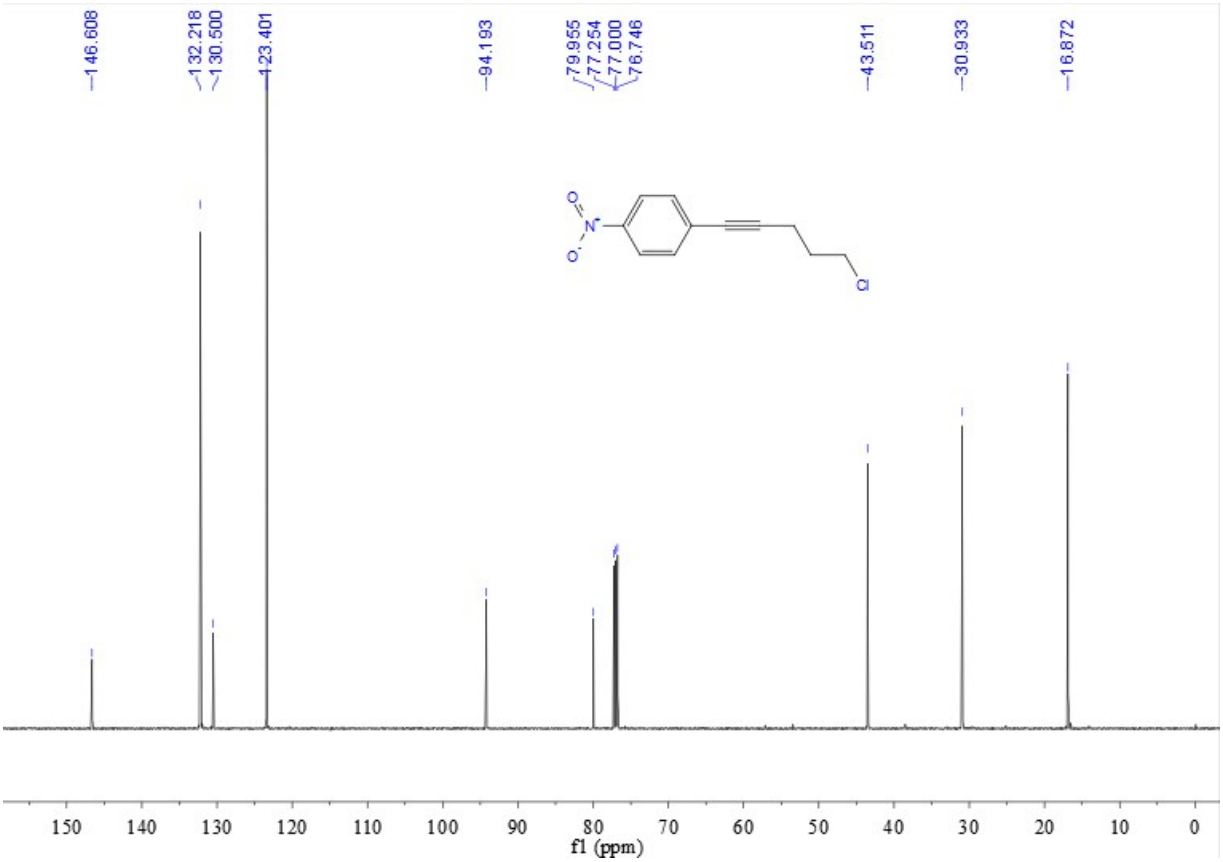
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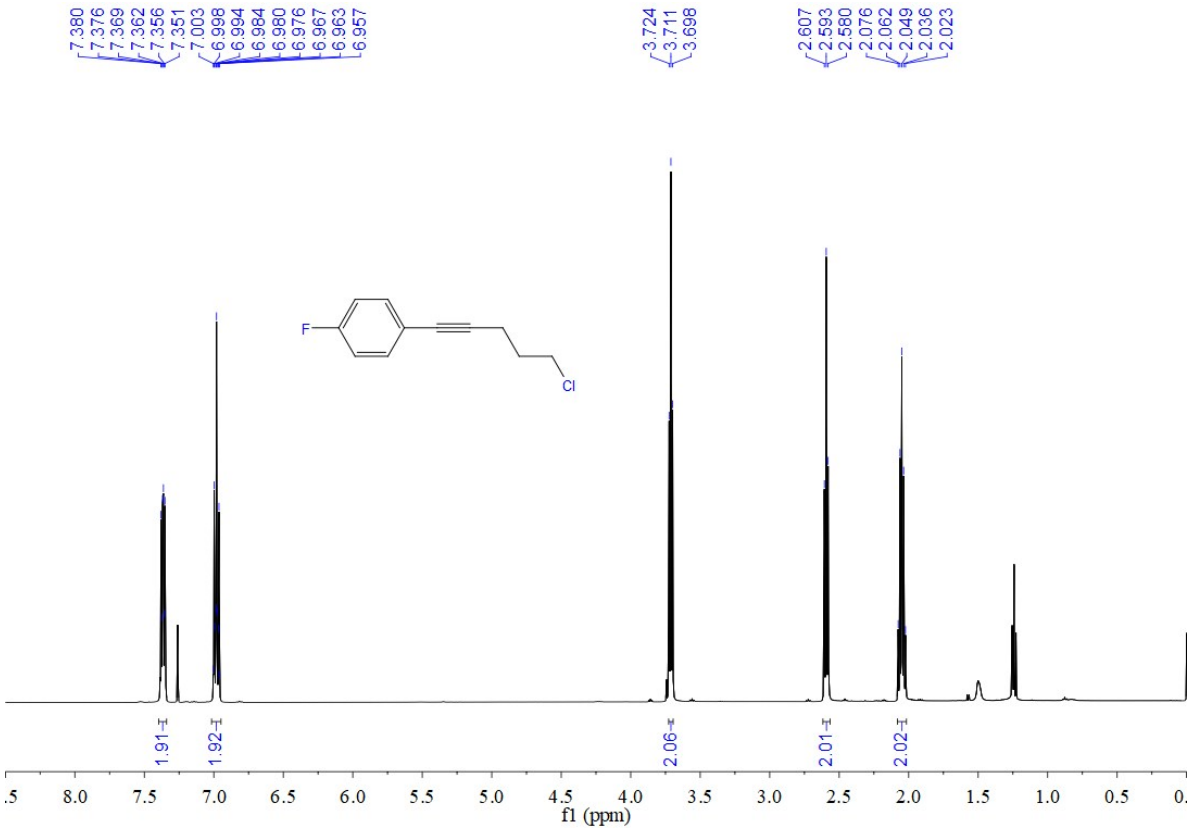
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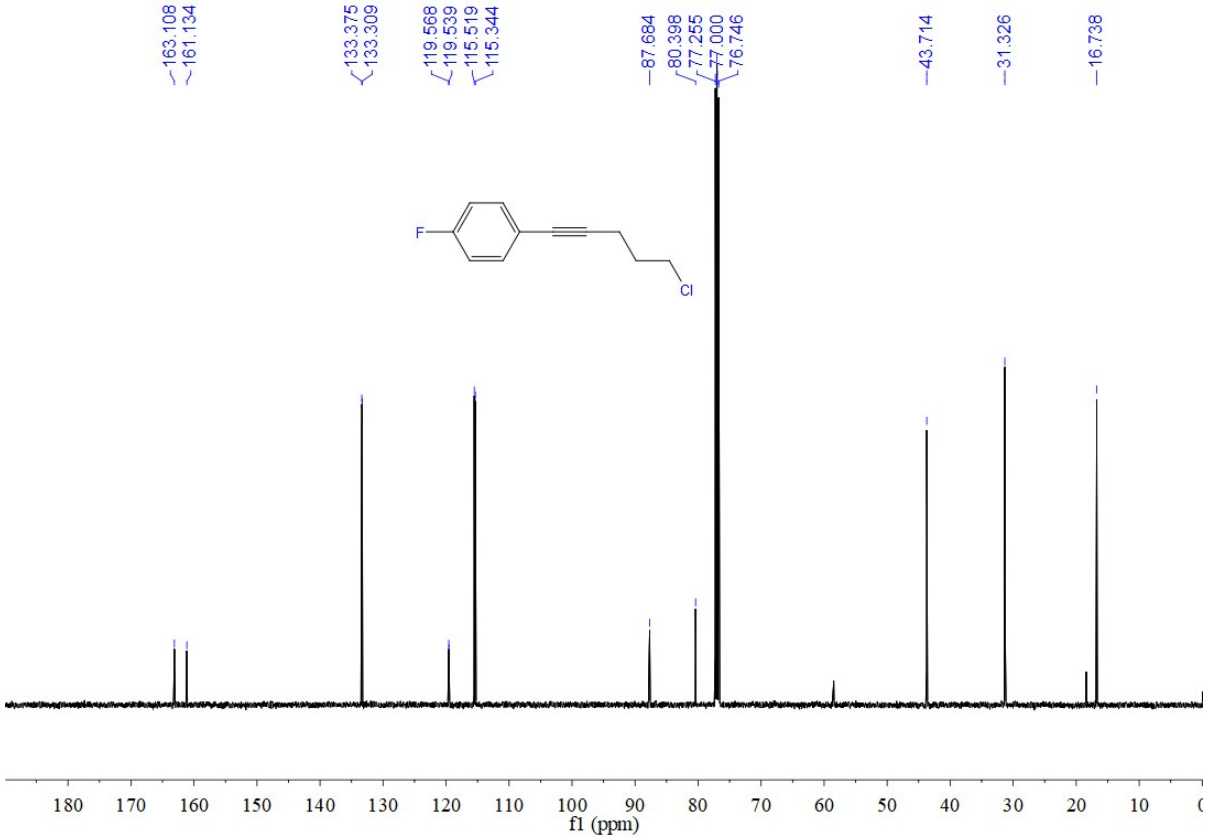
2.01
2.02
f1 (ppm)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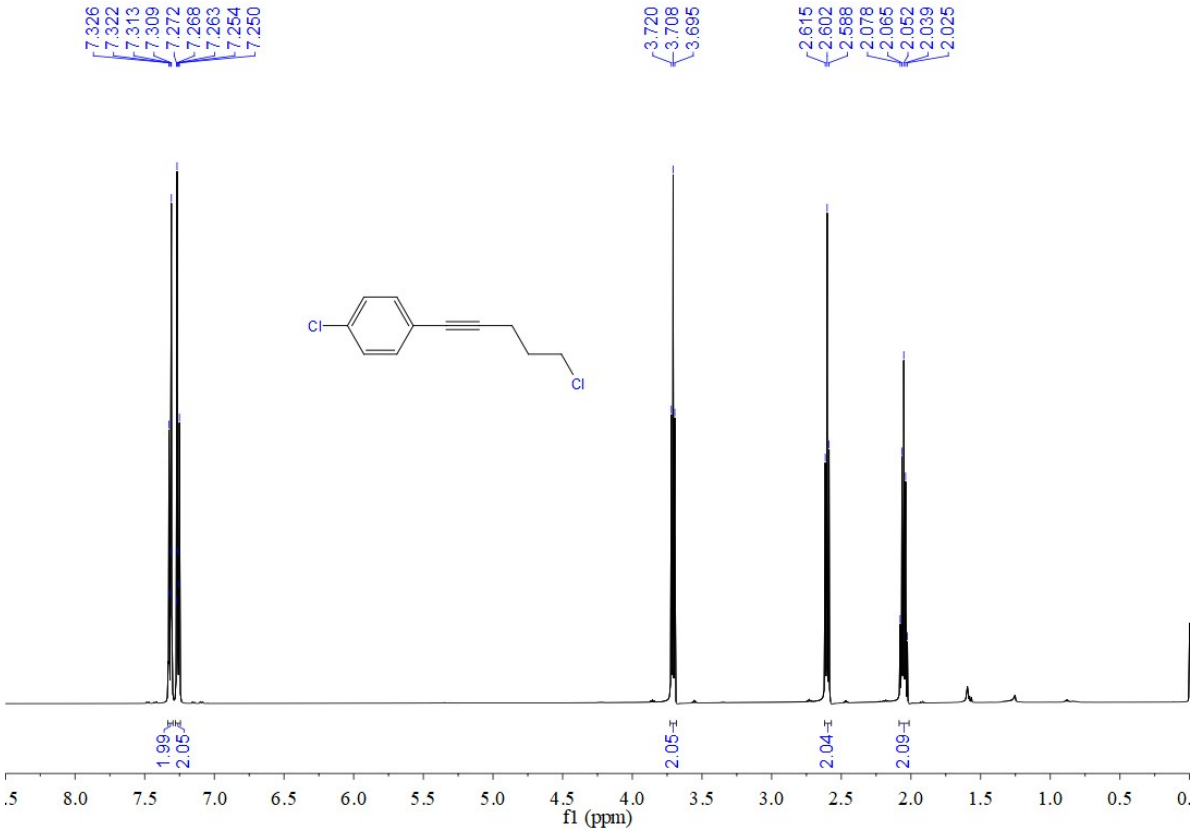
161.134
133.375
133.309
119.568
119.539
115.519
115.344
87.684
80.398
77.255
77.000
76.746
43.714
31.326
16.738
F
Cl
f1 (ppm)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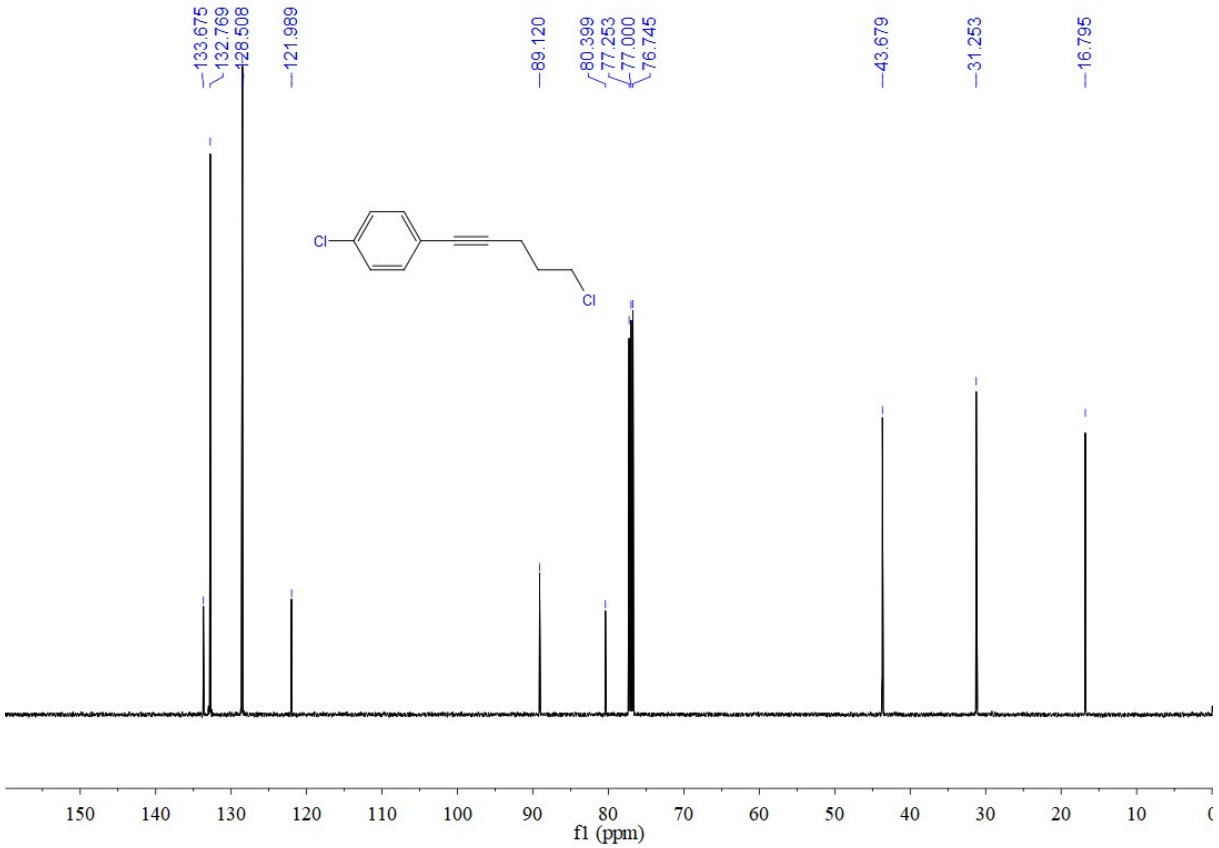
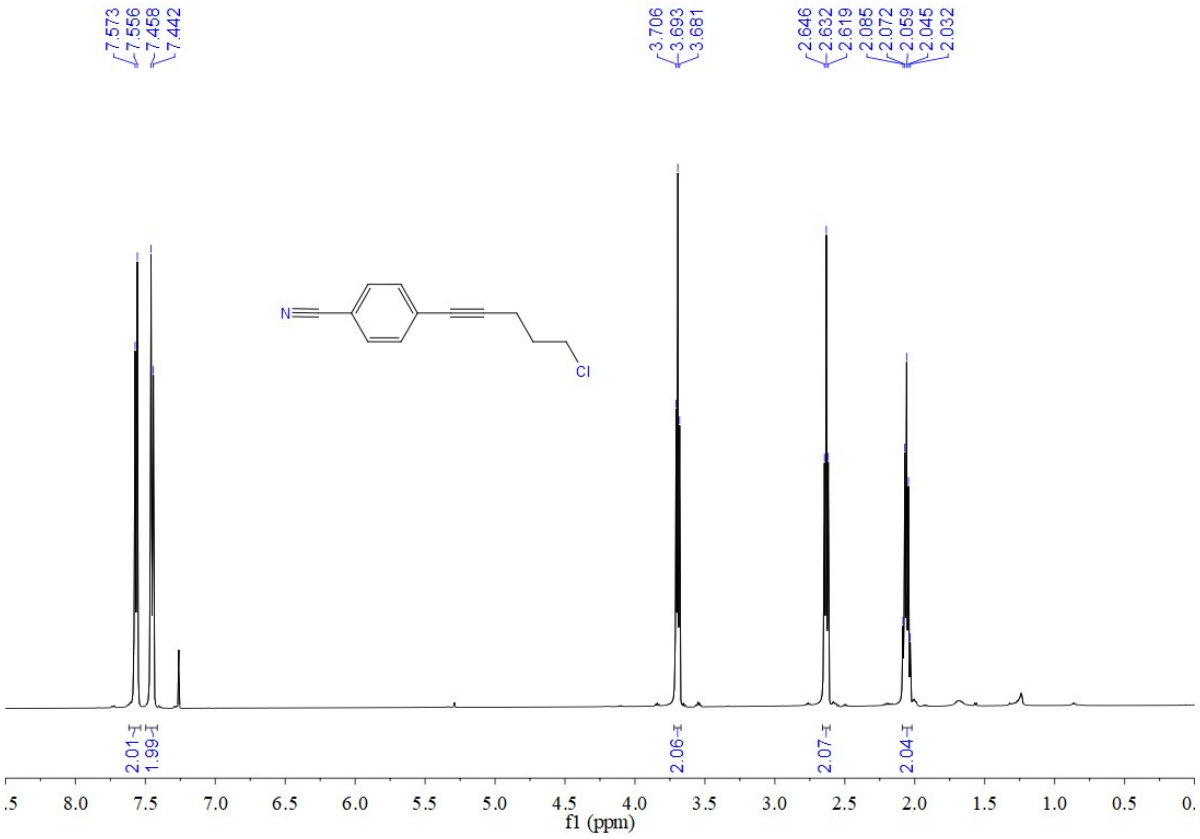
7.322
7.313
7.309
7.272
7.268
7.263
7.254
7.250
3.720
3.708
3.695
2.615
2.602
2.588
2.078
2.065
2.052
2.039
2.025
Cl
Cl
1.99
2.05
2.05
2.04
2.09
f1 (ppm)


133.675
132.769
128.508
121.989
89.120
80.399
77.253
77.000
76.745
43.679
31.253
16.795
Cl
Cl
f1 (ppm)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7.556
7.458
7.442
3.706
3.693
3.681
2.646
2.632
2.619
2.085
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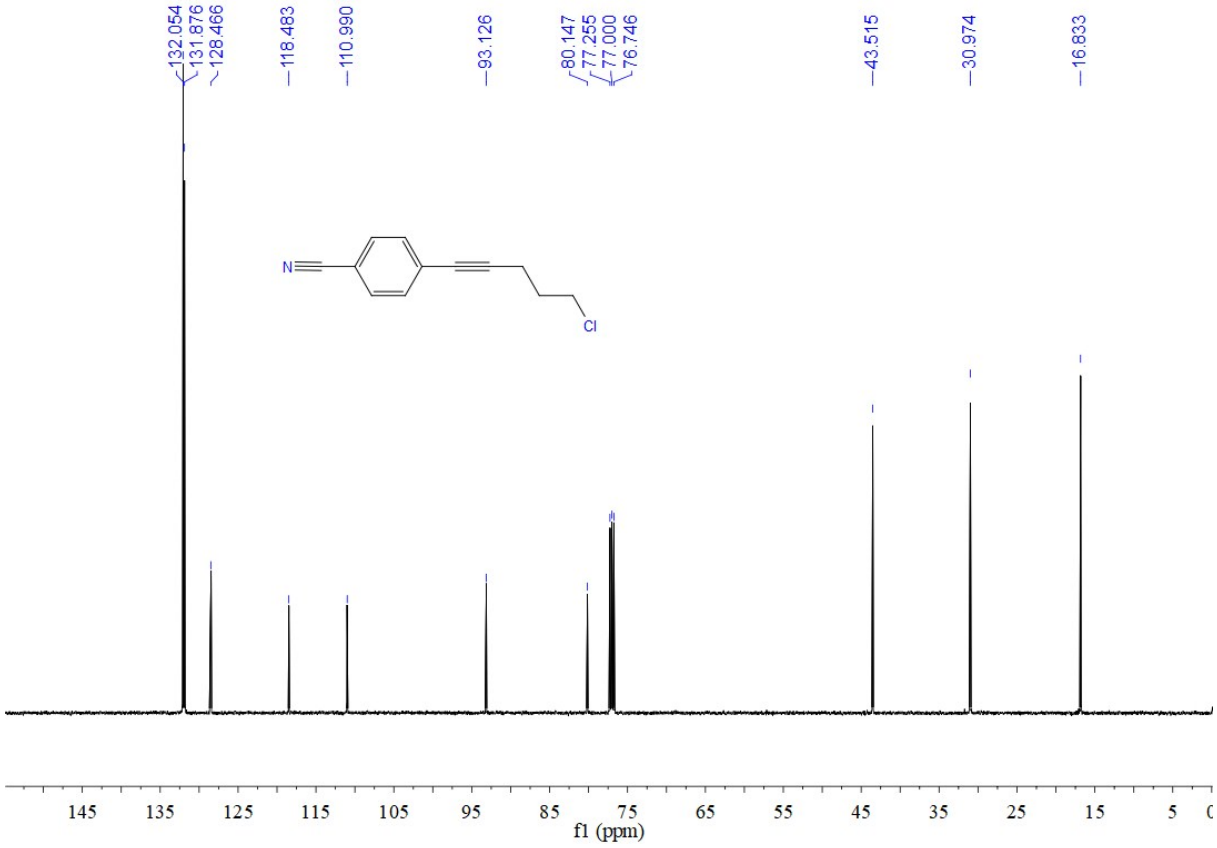
2.059
2.045
2.032
N
Cl
2.01
1.99
2.06
2.07
2.04
f1 (ppm)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131.876
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77.255
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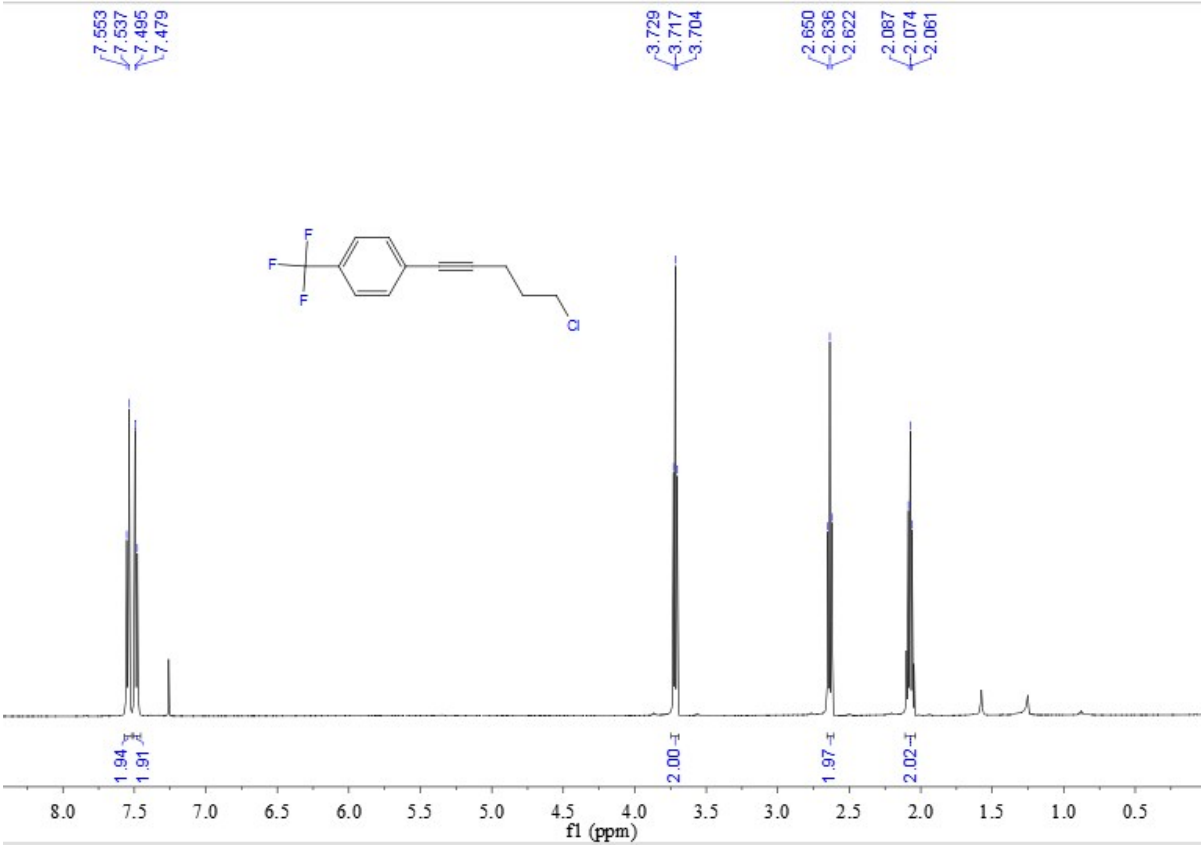
Cl
f1 (ppm)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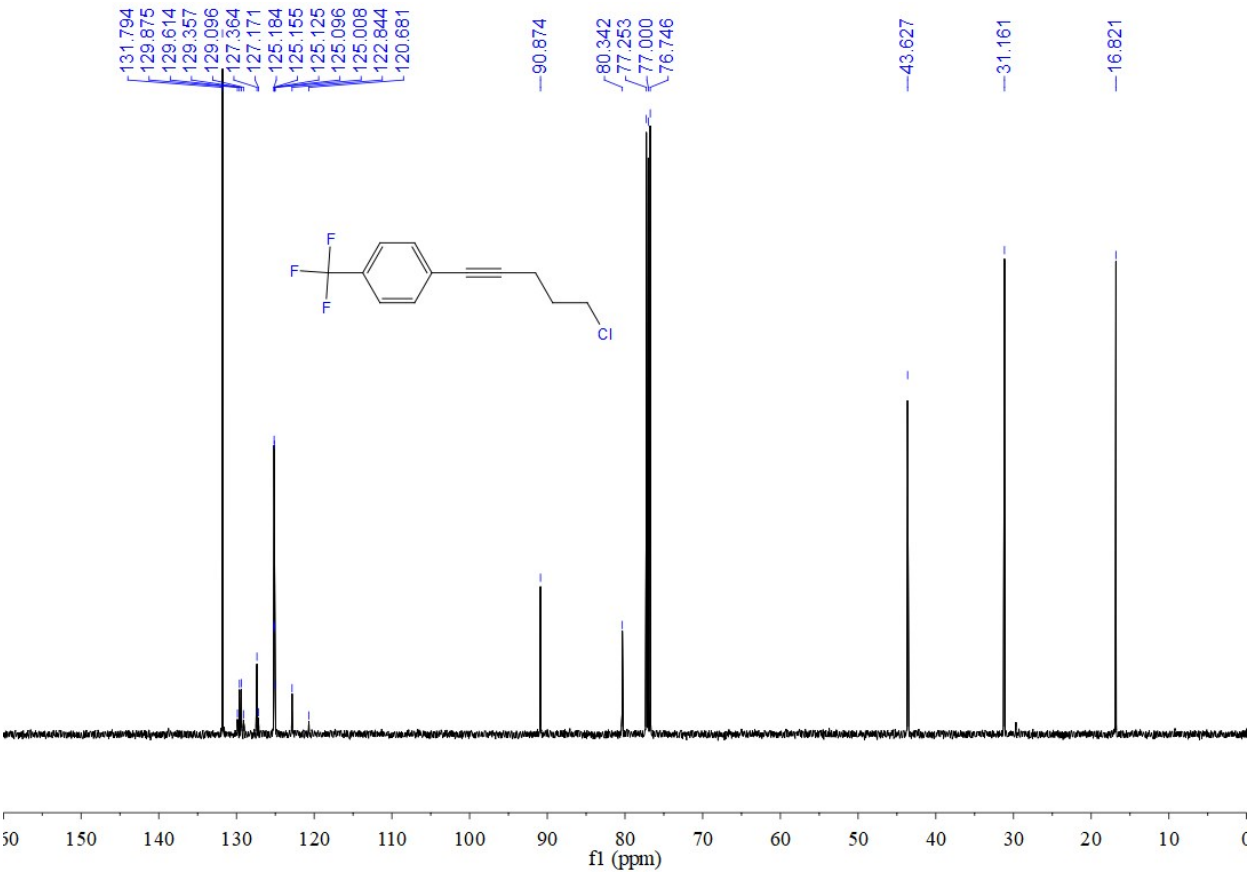
7.537
7.495
7.479
3.729
3.717
3.704
2.650
2.636
2.622
2.087
2.074
2.061
F
F
F
Cl
1.94
1.91
2.00
1.97
2.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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129.875
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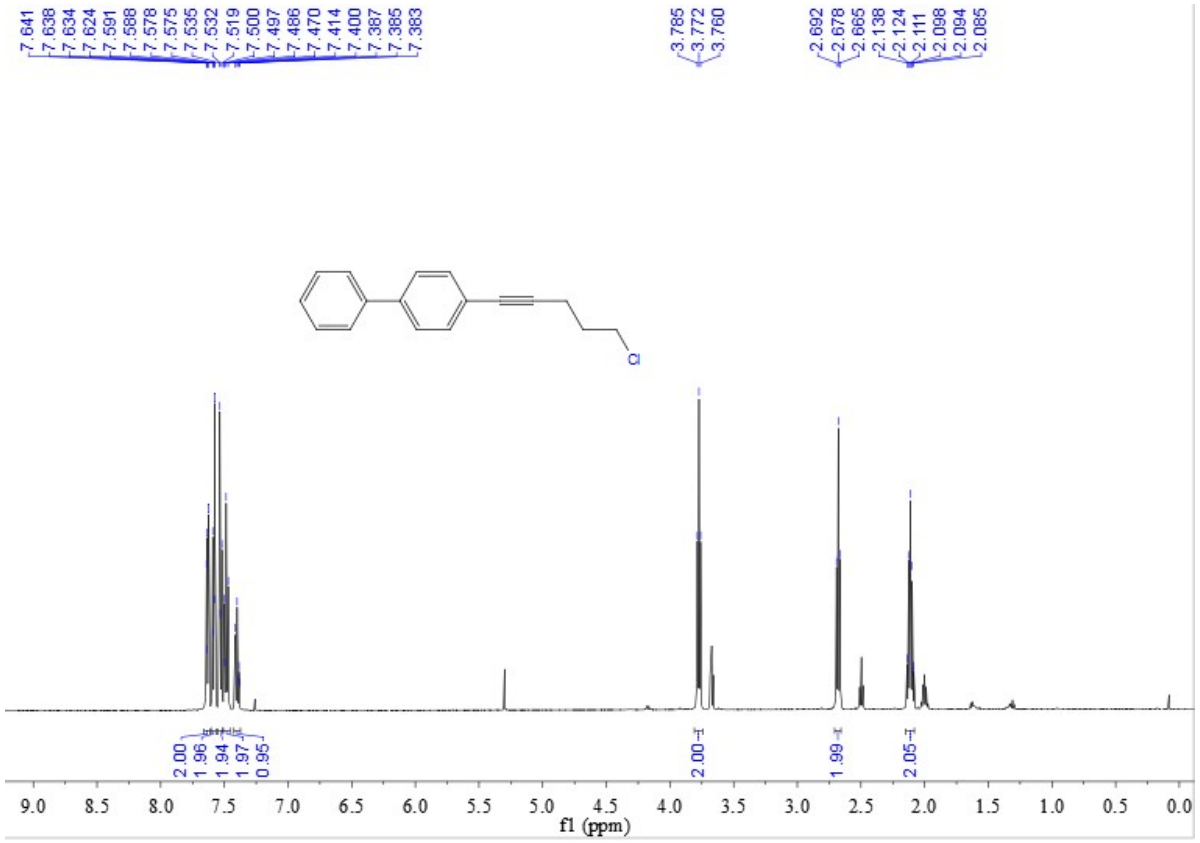
127.171
125.184
125.155
125.125
125.096
125.008
122.844
120.681
90.874
80.342
77.253
77.000
76.746
43.627
31.161
16.821
F
F
F
Cl
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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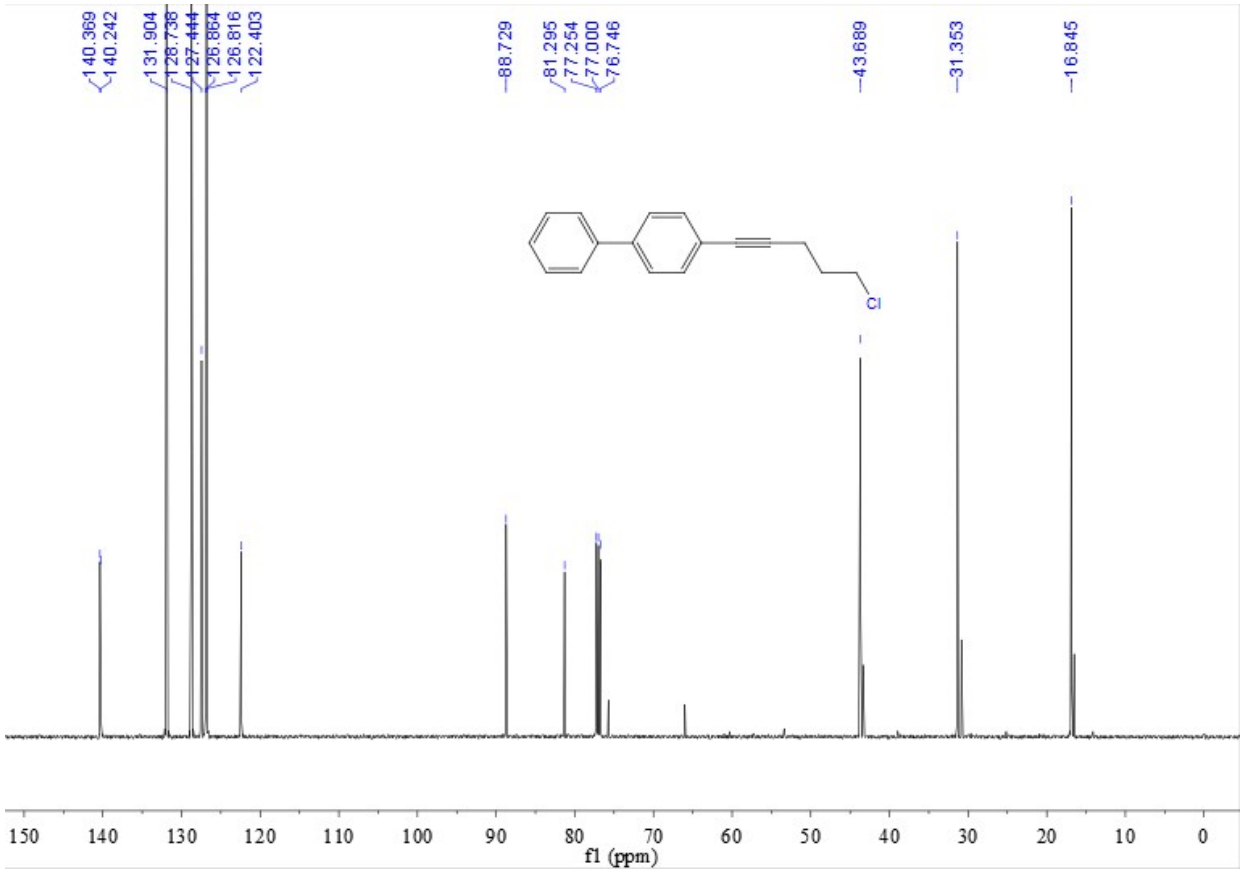
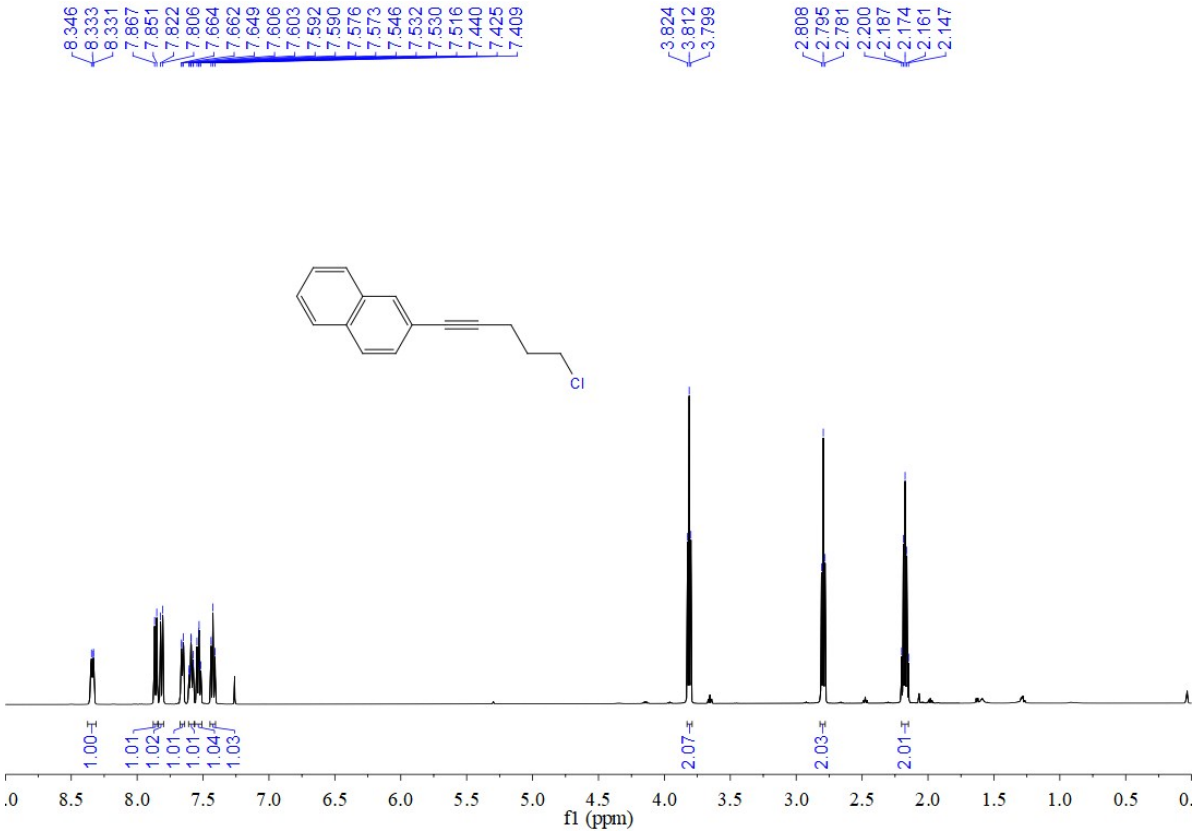
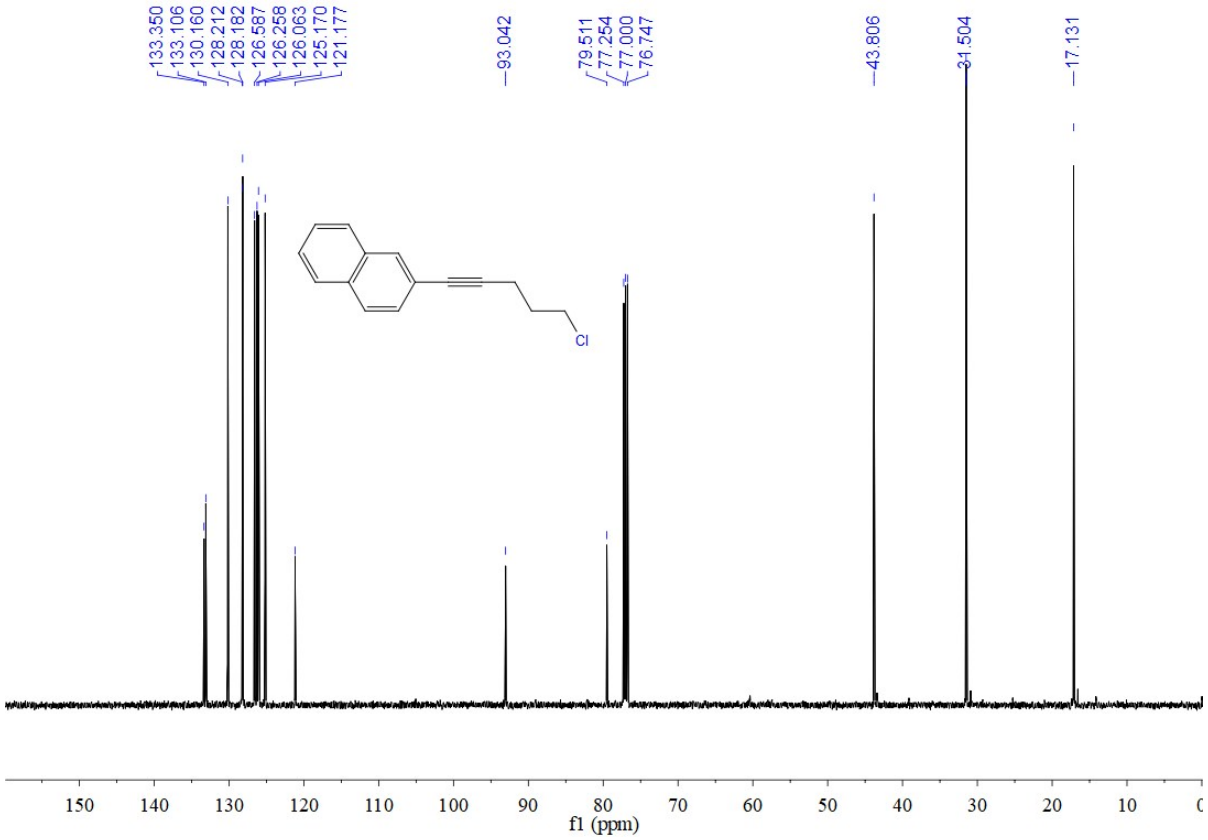
7.634
7.624
7.591
7.588
7.578
7.575
7.535
7.532
7.519
7.500
7.497
7.486
7.470
7.414
7.400
7.387
7.385
7.383
3.785
3.772
3.760
2.692
2.678
2.665
2.138
2.124
2.111
2.098
2.094
2.085
Cl
2.00
1.96
1.94
1.97
0.95
2.00
1.99
2.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.369
140.242
131.904
128.736
127.444
126.864
126.816
122.403
88.729
81.295
77.254
77.000
76.746
43.689
31.353
16.845
Cl
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.346
8.333
8.331
7.867
7.851
7.822
7.806
7.664
7.662
7.649
7.606
7.603
7.592
7.590
7.576
7.573
7.546
7.532
7.530
7.516
7.440
7.425
7.409
3.824
3.812
3.799
2.808
2.795
2.781
2.200
2.187
2.174
2.161
2.147
Cl
1.00
1.01
1.02
1.01
1.01
1.04
1.03
2.07
2.03
2.01
f1 (ppm)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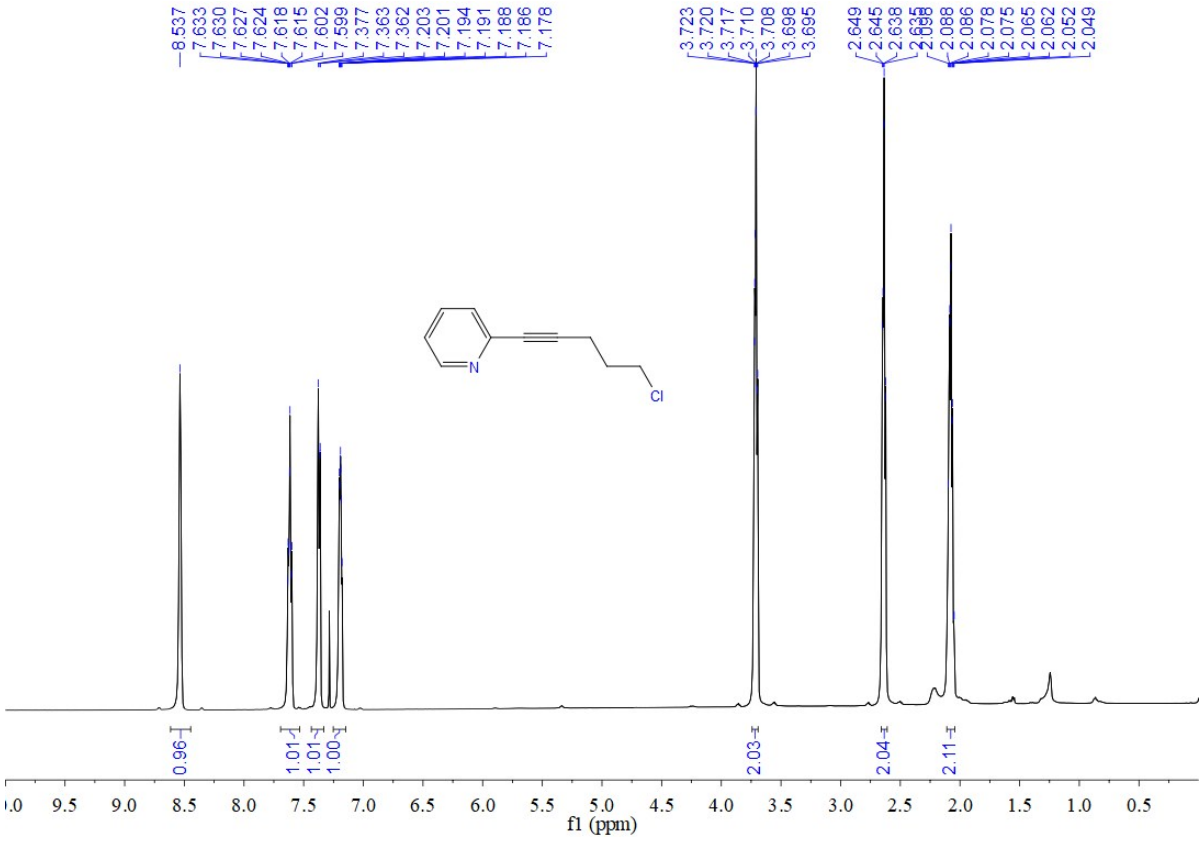
133.106
130.160
128.212
128.182
126.587
126.258
126.063
125.170
121.177
93.042
79.511
77.254
77.000
76.747
43.806
31.504
17.131
Cl
f1 (ppm)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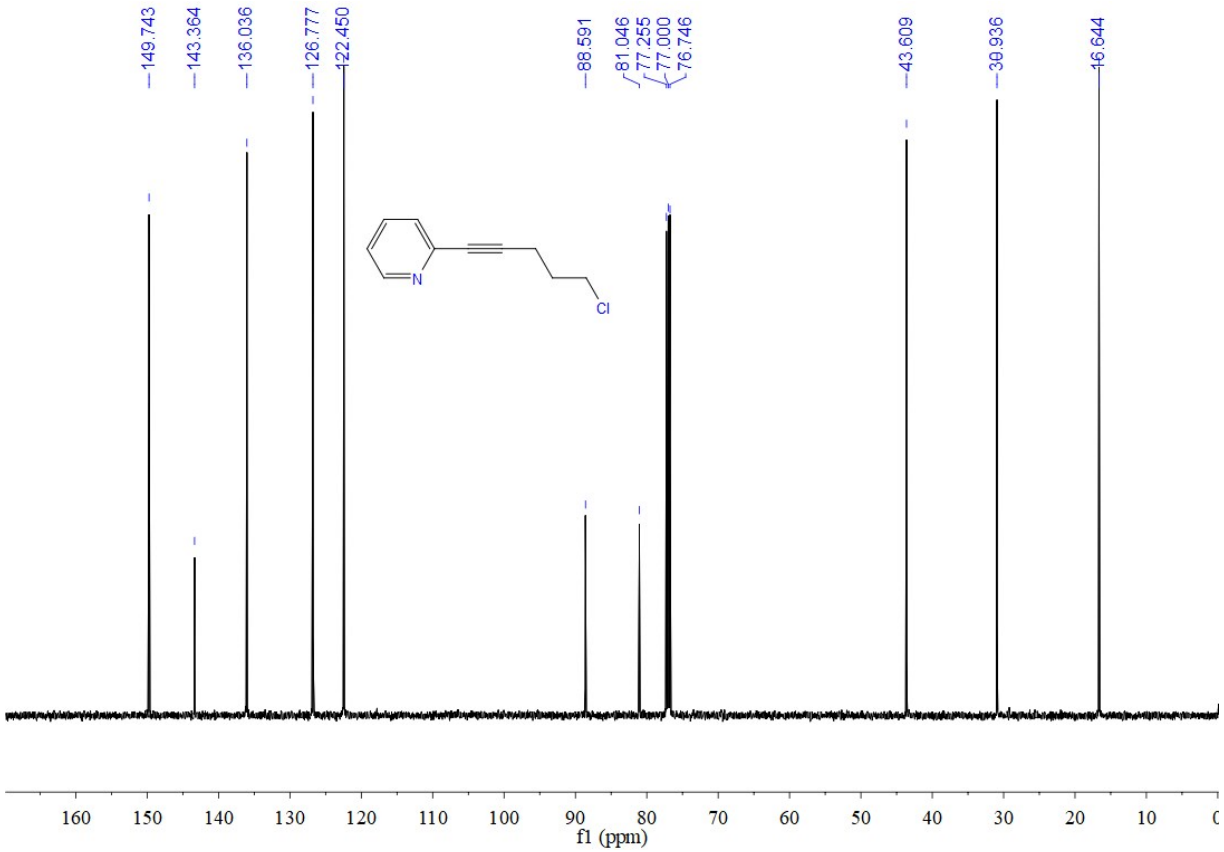
7.633
7.630
7.627
7.624
7.618
7.615
7.602
7.599
7.377
7.363
7.362
7.203
7.201
7.194
7.191
7.188
7.186
7.178
3.723
3.720
3.717
3.710
3.708
3.698
3.695
2.649
2.645
2.638
2.088
2.086
2.078
2.075
2.065
2.062
2.052
2.049
0.96
1.01
1.01
1.00
2.03
2.04
2.11
N
Cl
f1 (ppm)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81.046
77.255
77.000
76.746
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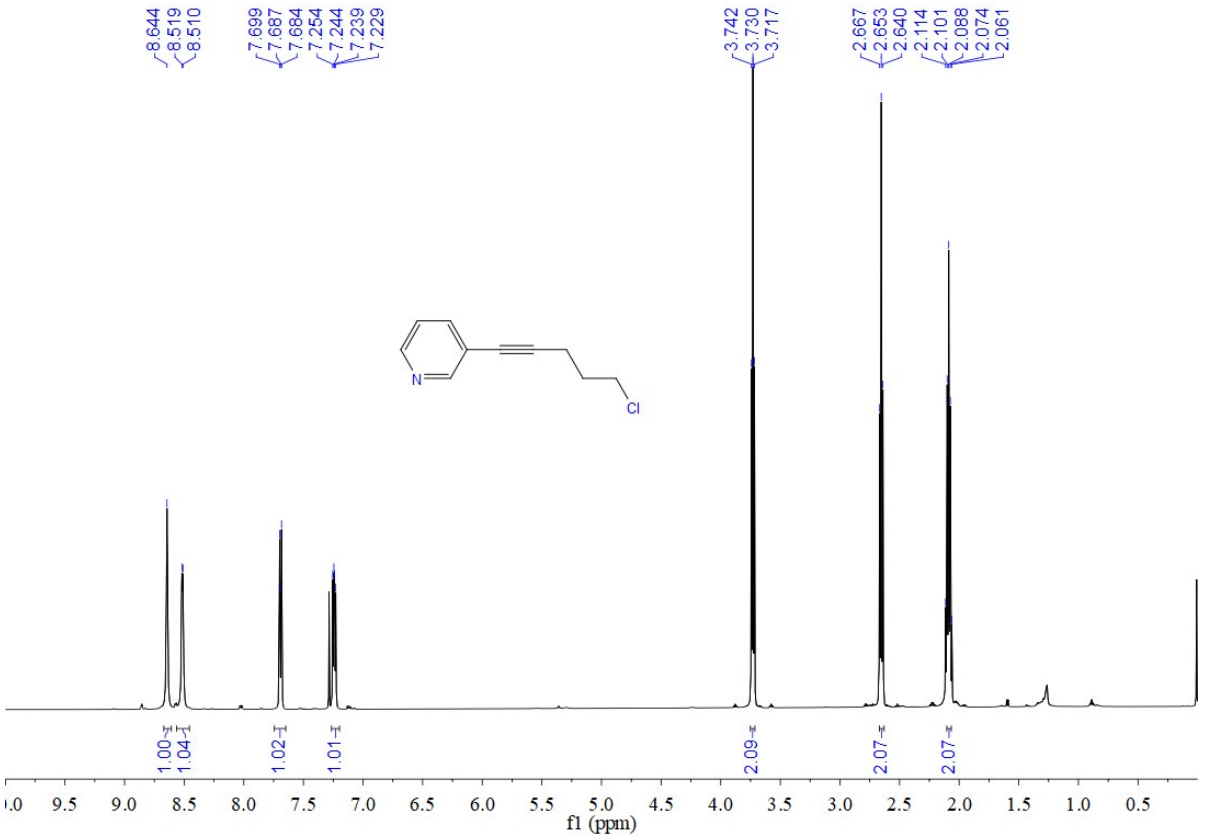
30.936
16.644
N
Cl
f1 (ppm)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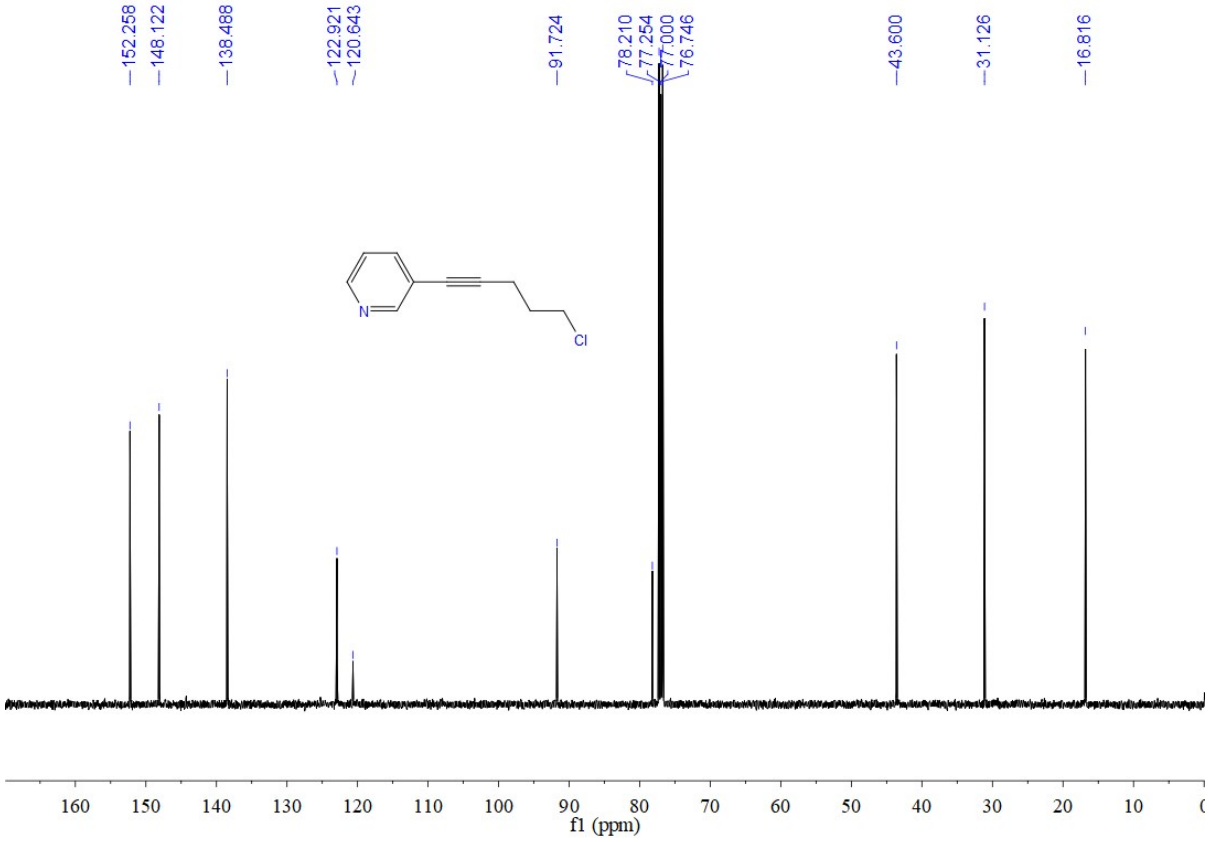
8.519
8.510
7.699
7.687
7.684
7.254
7.244
7.239
7.229
3.742
3.730
3.717
2.667
2.653
2.640
2.114
2.101
2.088
2.074
2.061
N
Cl
1.00
1.04
1.02
1.01
2.09
2.07
2.07
f1 (ppm)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138.488
122.921
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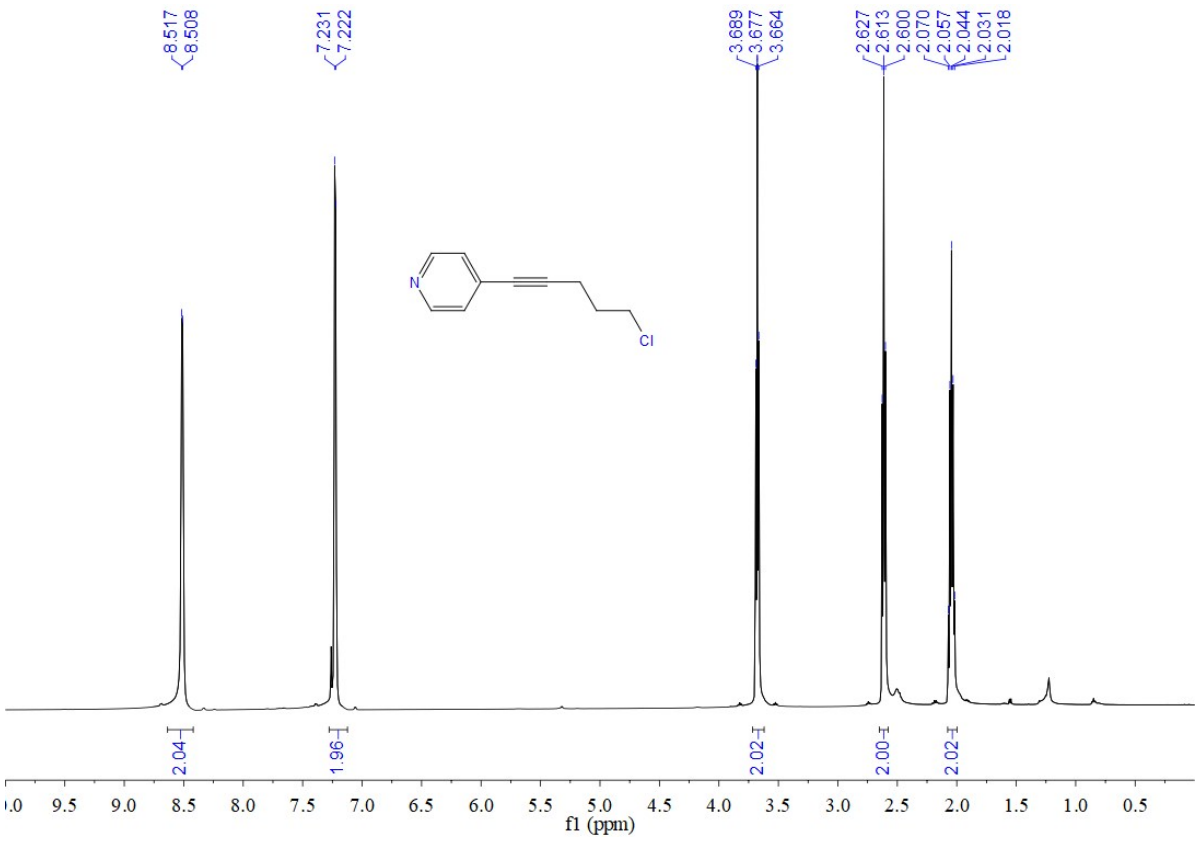
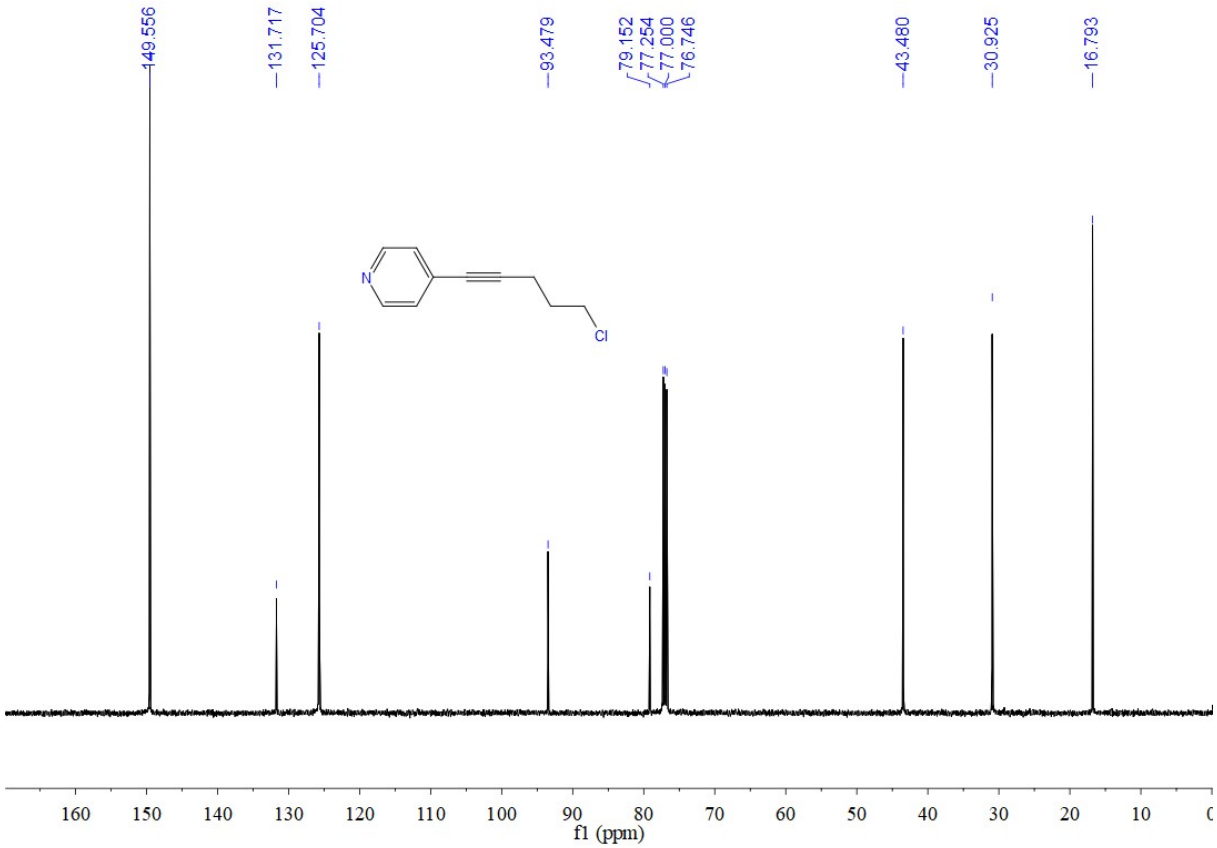
91.724
78.210
77.254
77.000
76.746
43.600
31.126
16.816
N
Cl
f1 (ppm)


8.517
8.508
7.231
7.222
3.689
3.677
3.664
2.627
2.613
2.600
2.070
2.057
2.044
2.031
2.018
N
Cl
2.04
1.96
2.02
2.00
2.02
f1 (ppm)


149.556
131.717
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79.152
77.254
77.000
76.746
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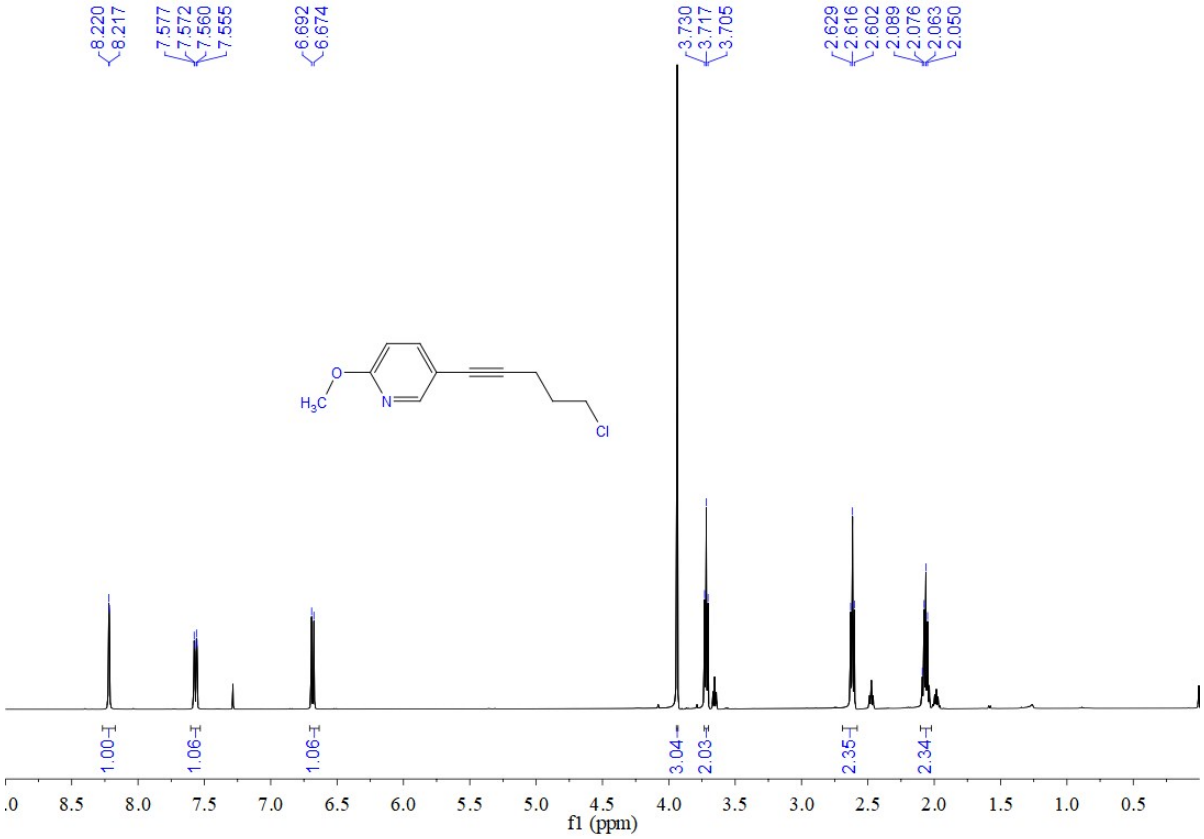
N
Cl
f1 (ppm)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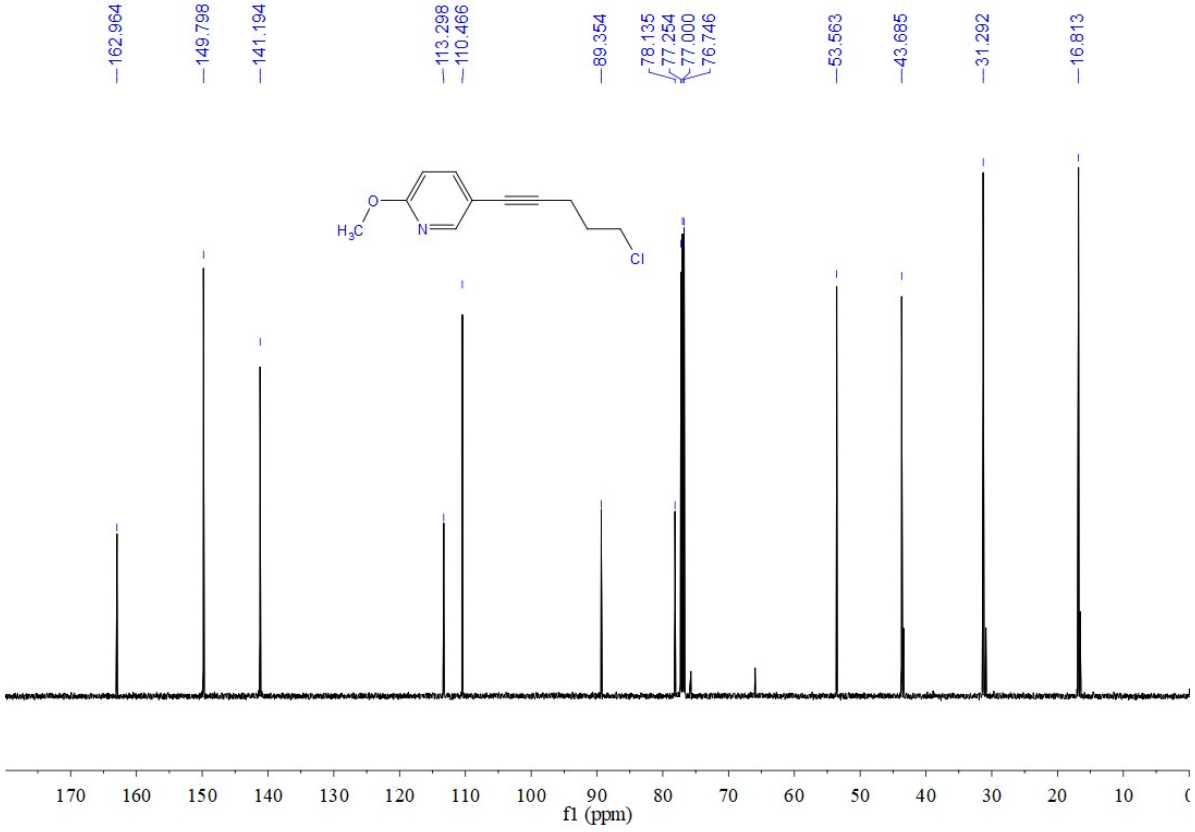
8.217
7.577
7.572
7.560
7.555
6.692
6.674
3.730
3.717
3.705
2.629
2.616
2.602
2.089
2.076
2.063
2.050
1.00
1.06
1.06
3.04
2.03
2.35
2.34
f1 (ppm)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78.135
77.254
77.000
76.746
53.563
43.685
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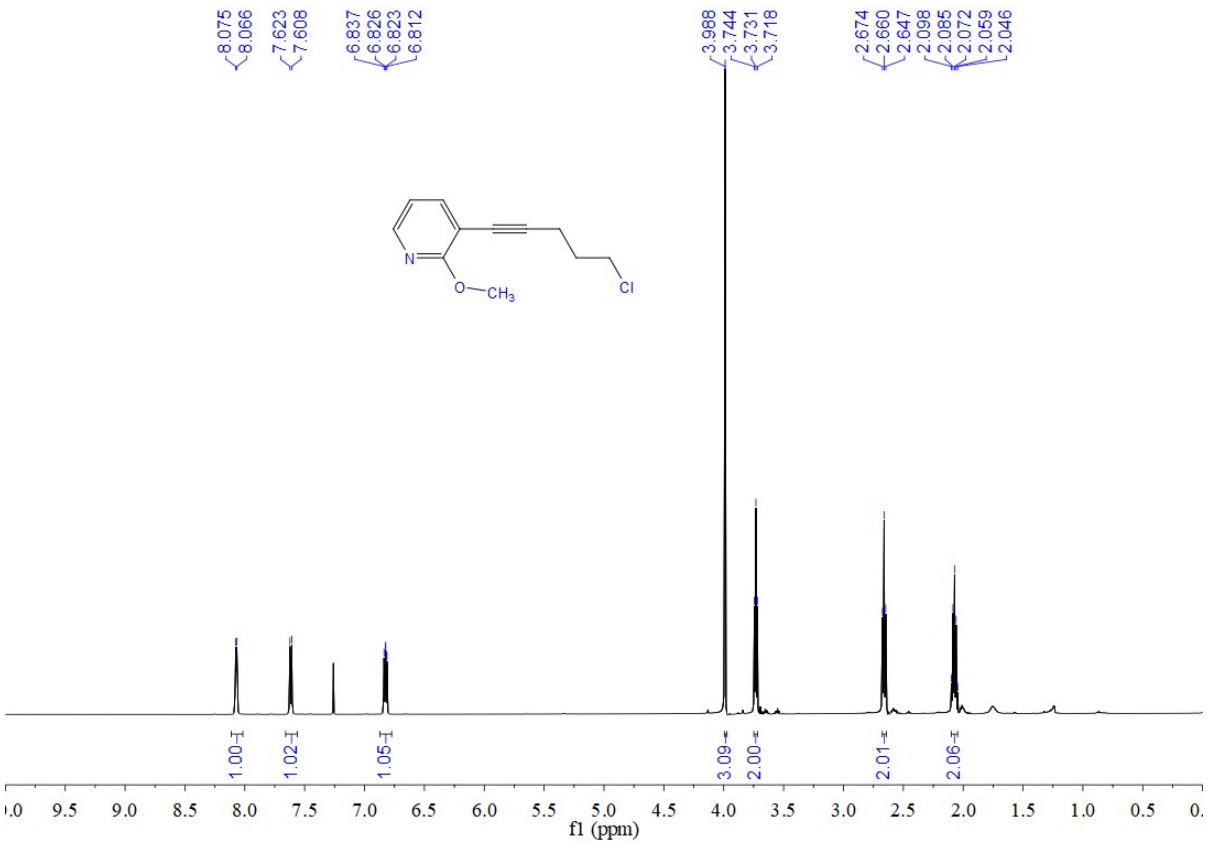
16.813
f1 (ppm)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8.066
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7.608
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6.823
6.812
3.988
3.744
3.731
3.718
2.674
2.660
2.647
2.098
2.085
2.072
2.059
2.046
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O
CH3
Cl
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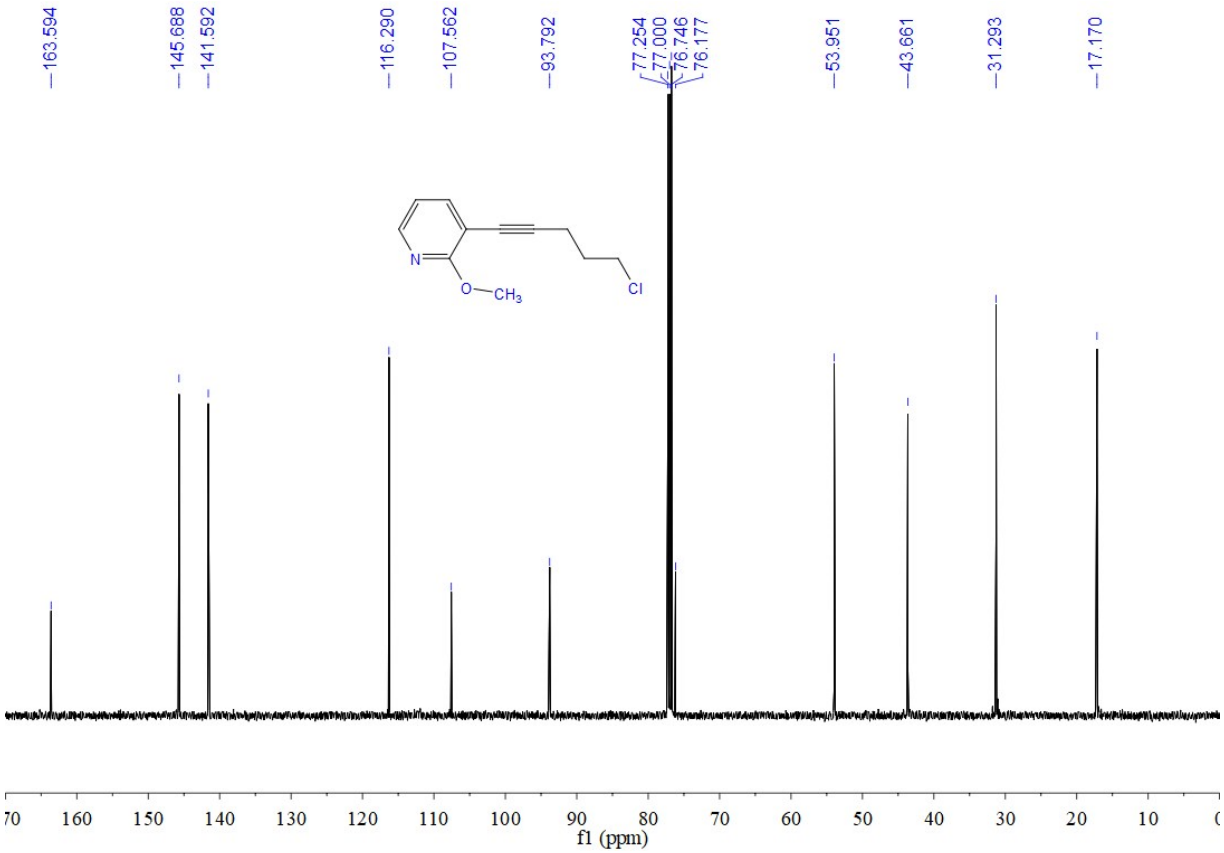
1.02
1.05
3.09
2.00
2.01
2.06
f1 (ppm)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93.792
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77.000
76.746
76.177
53.951
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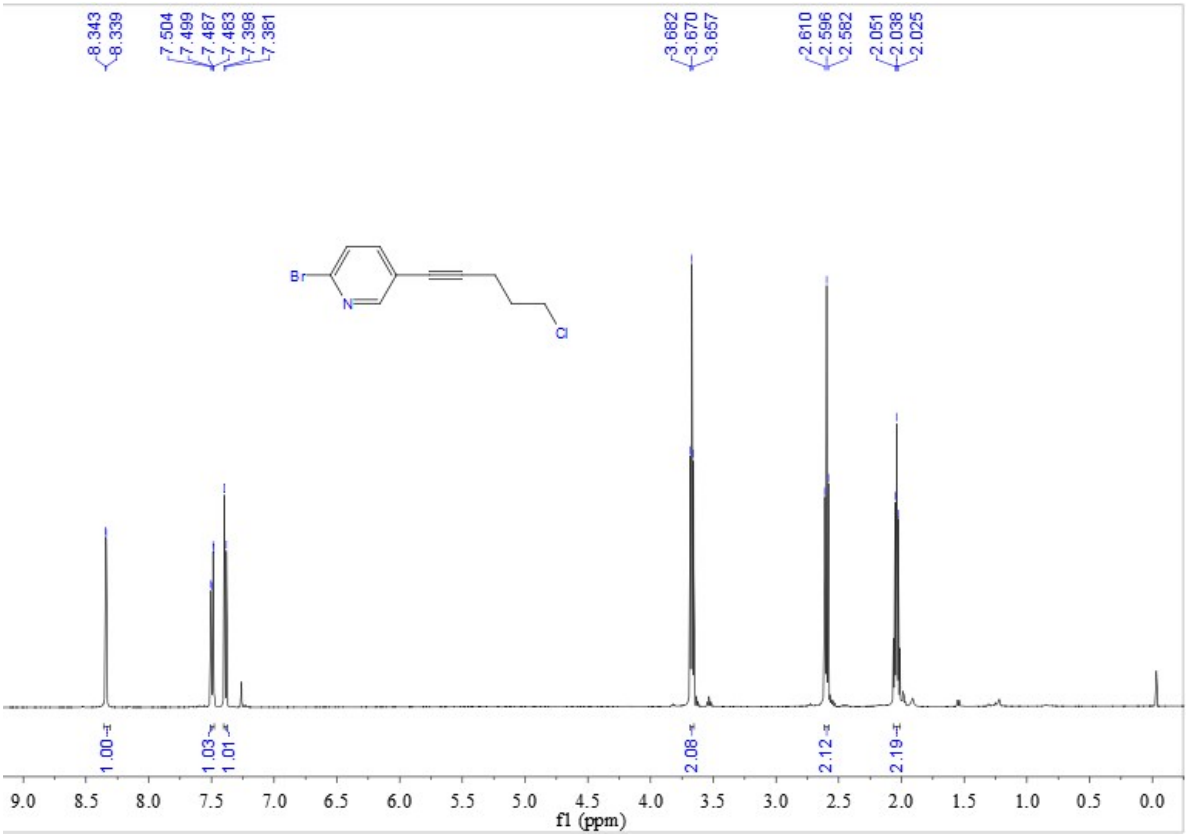
17.170
N
O
CH3
Cl
f1 (ppm)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7.398
7.381
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3.657
2.610
2.596
2.582
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2.025
Br
N
Cl
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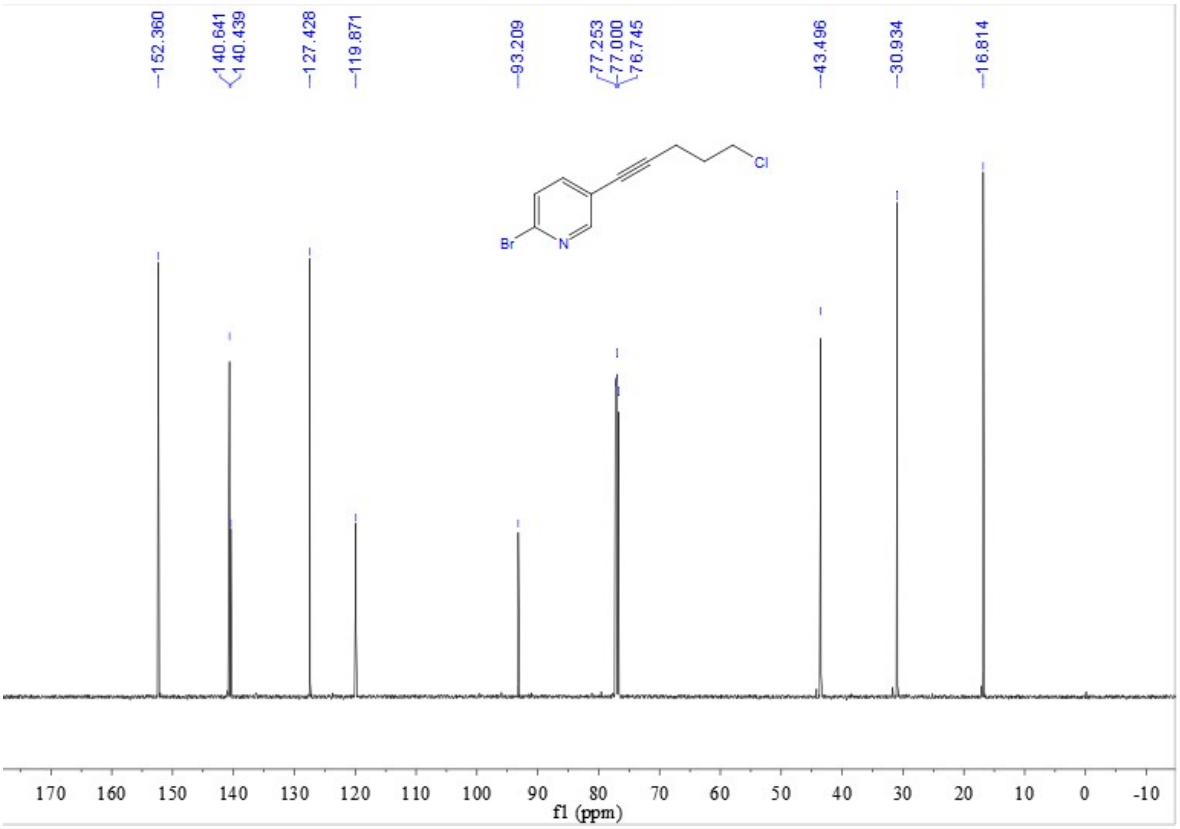
1.01
2.08
2.12
2.19
f1 (ppm)


152.360
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77.253
77.000
76.745
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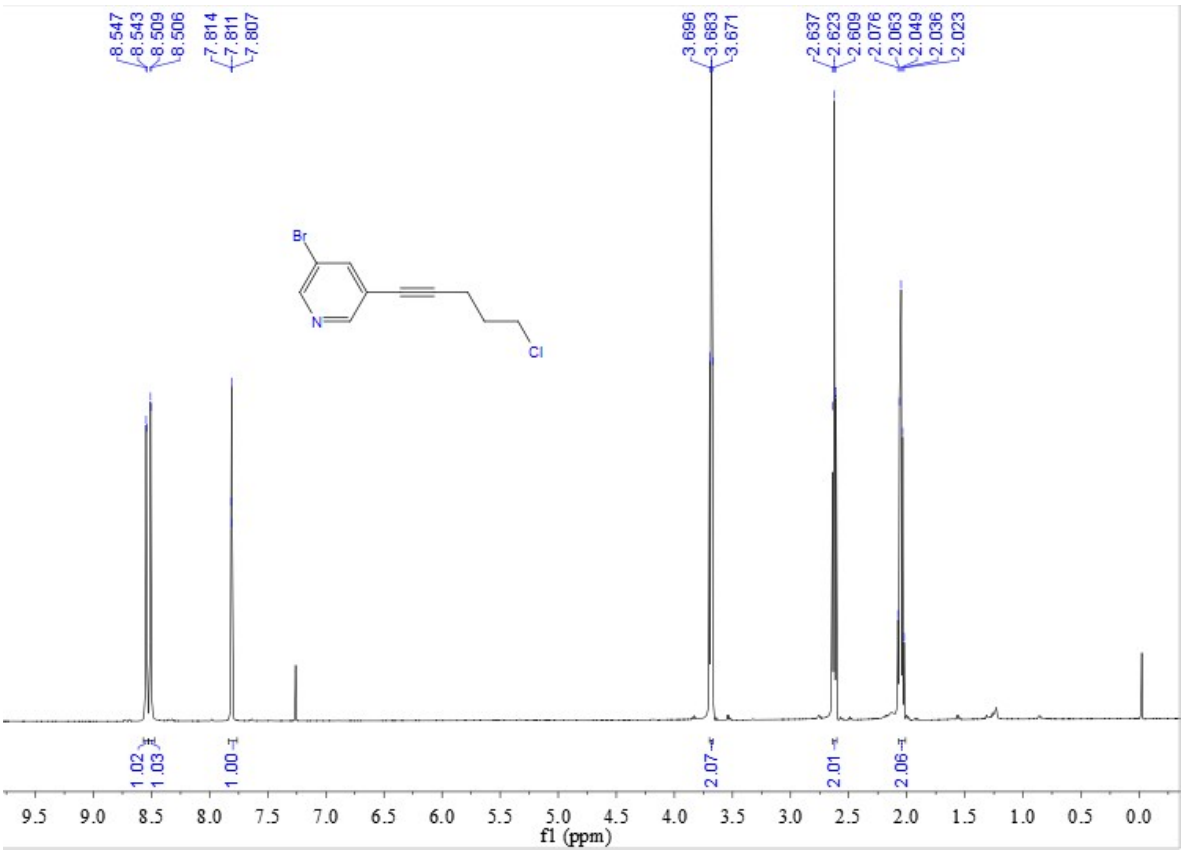
16.814
Br
N
Cl
f1 (ppm)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7.814
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7.807
3.696
3.683
3.671
2.637
2.623
2.609
2.076
2.063
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2.036
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Br
N
Cl
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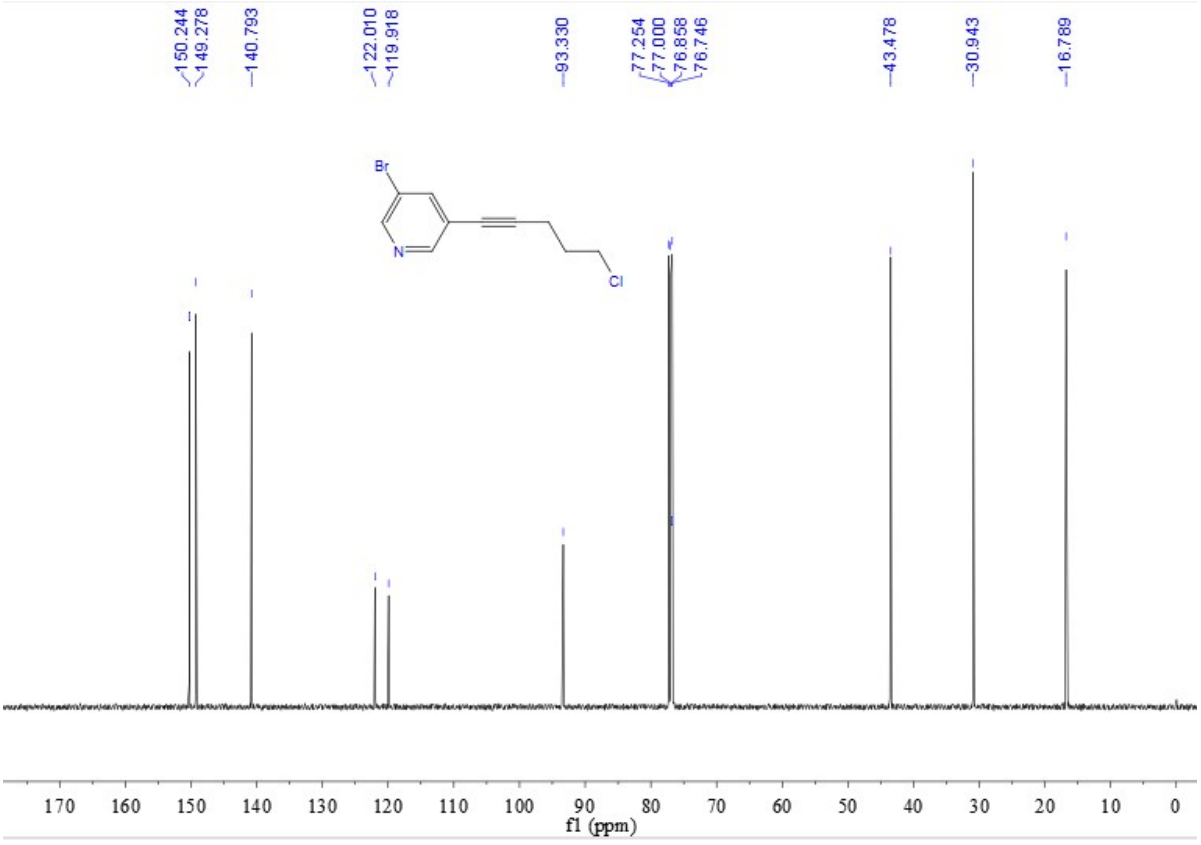
1.03
1.00
2.07
2.01
2.06
f1 (ppm)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77.000
76.858
76.746
43.478
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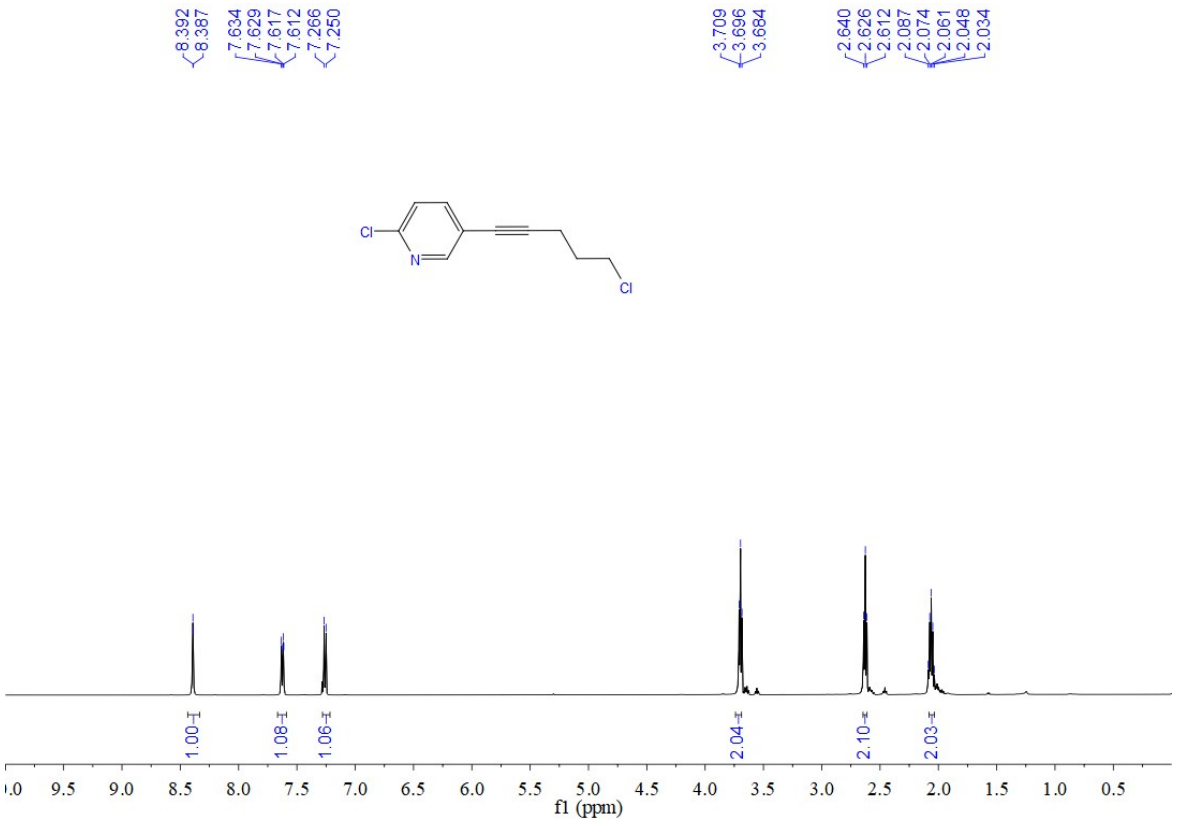
16.789
Br
N
Cl
f1 (ppm)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7.617
7.612
7.266
7.250
3.709
3.696
3.684
2.640
2.626
2.612
2.087
2.074
2.061
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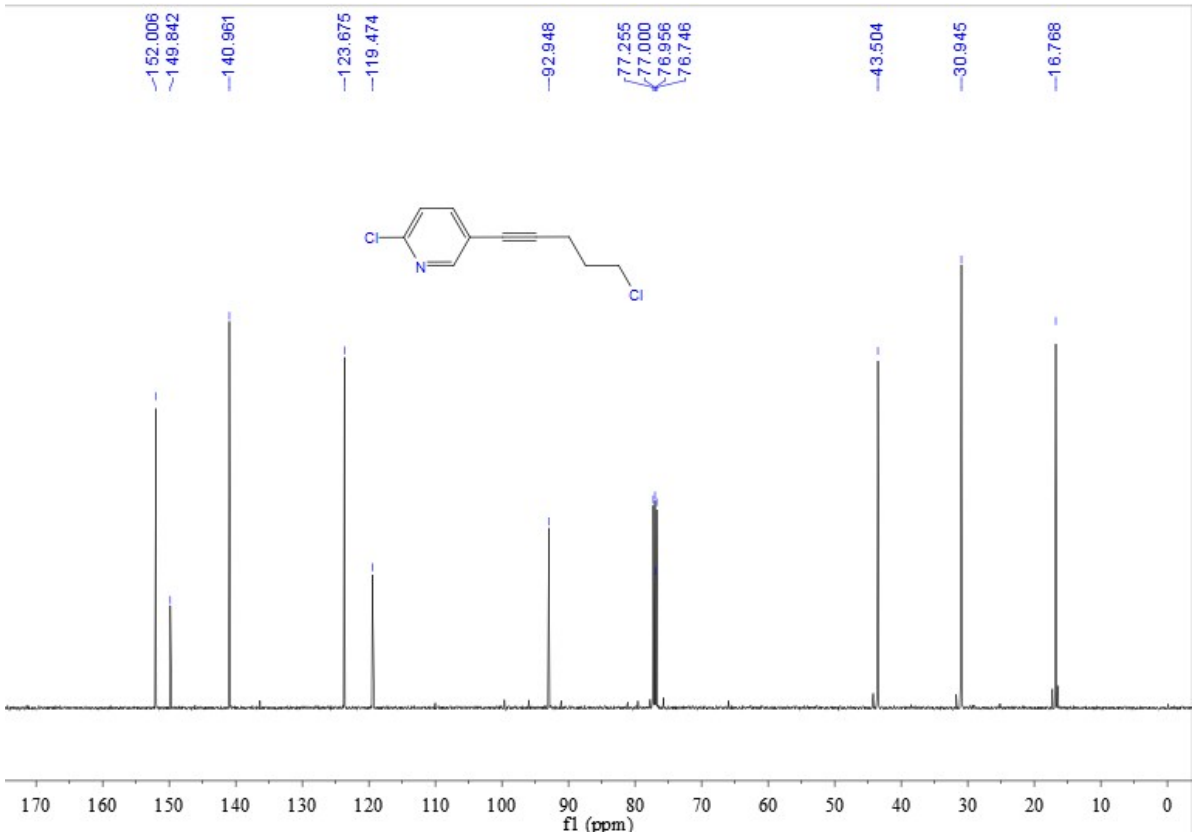
2.034
Cl
N
Cl
1.00
1.08
1.06
2.04
2.10
2.03
f1 (ppm)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77.000
76.956
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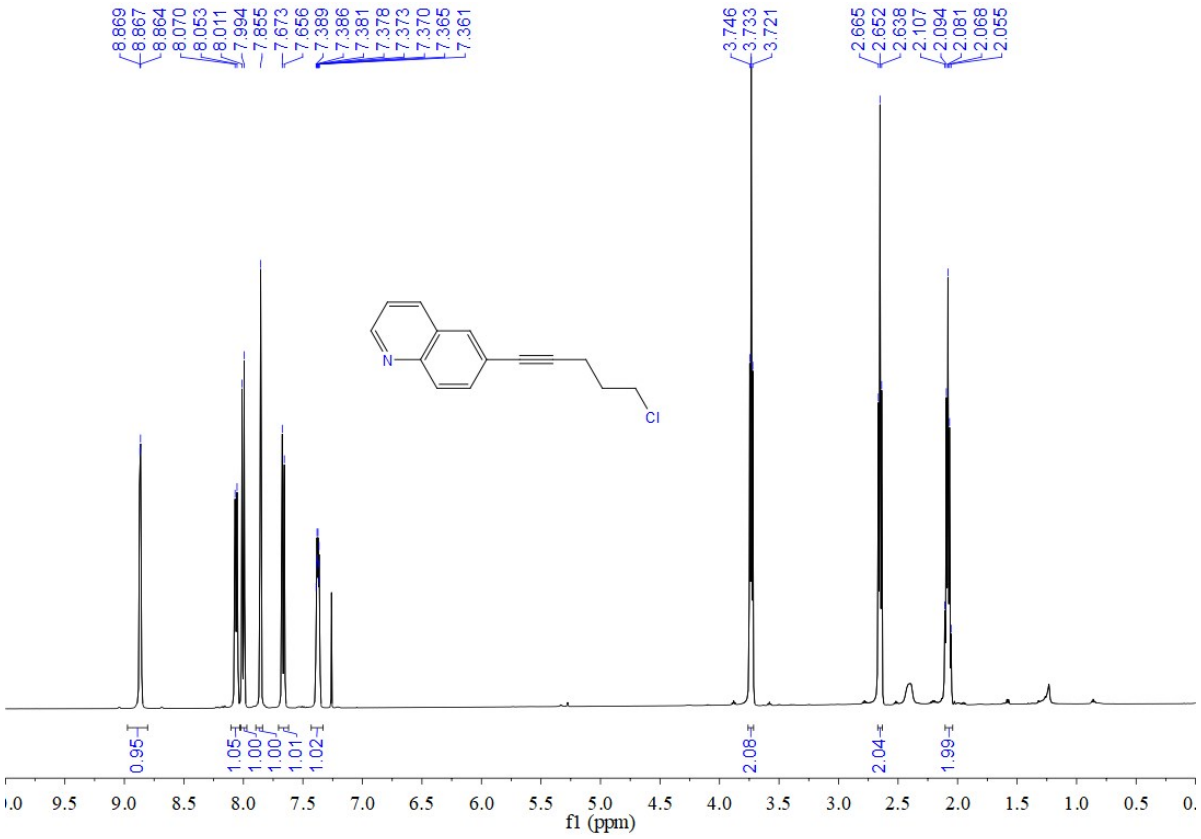
N
Cl
f1 (ppm)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8.070
8.053
8.011
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7.855
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7.386
7.381
7.378
7.373
7.370
7.365
7.361
3.746
3.733
3.721
2.665
2.652
2.638
2.107
2.094
2.081
2.068
2.055
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1.00
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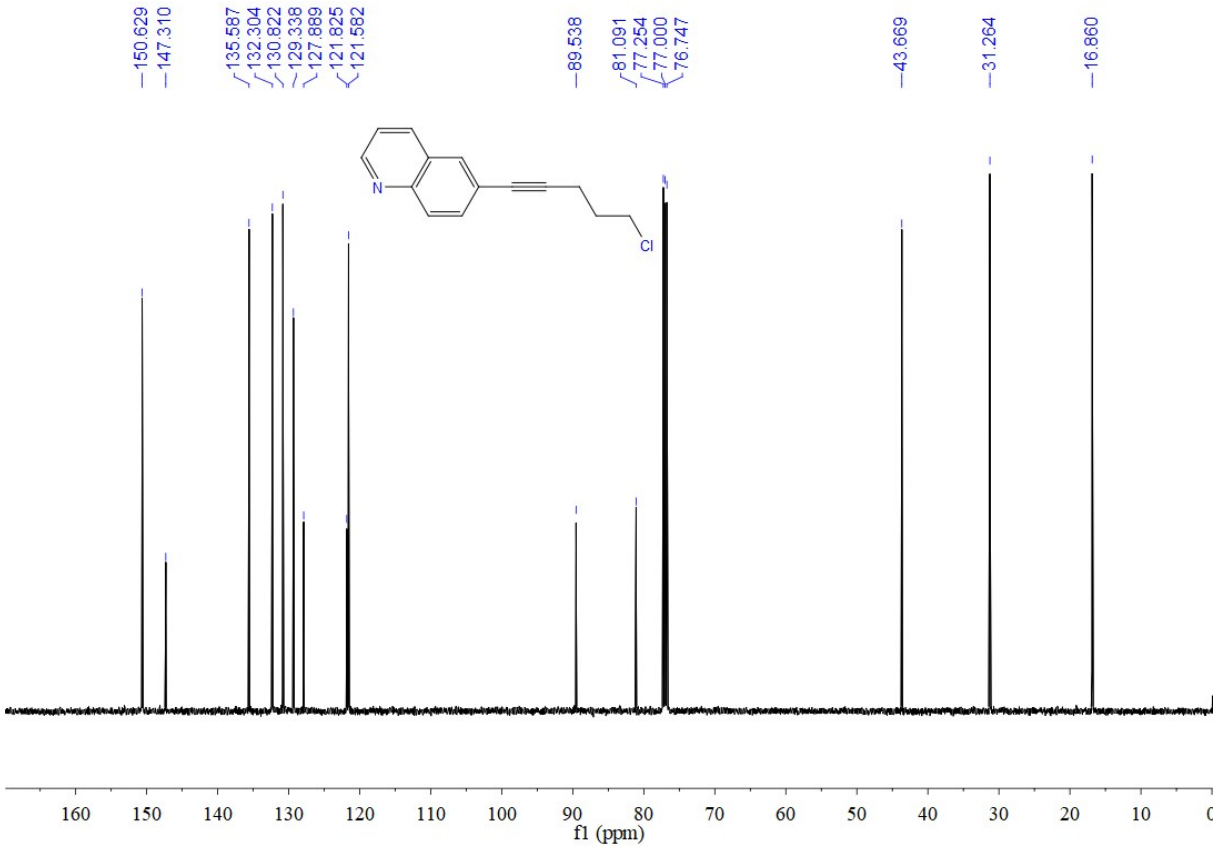
1.02
2.08
2.04
1.99
f1 (ppm)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121.825
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31.264
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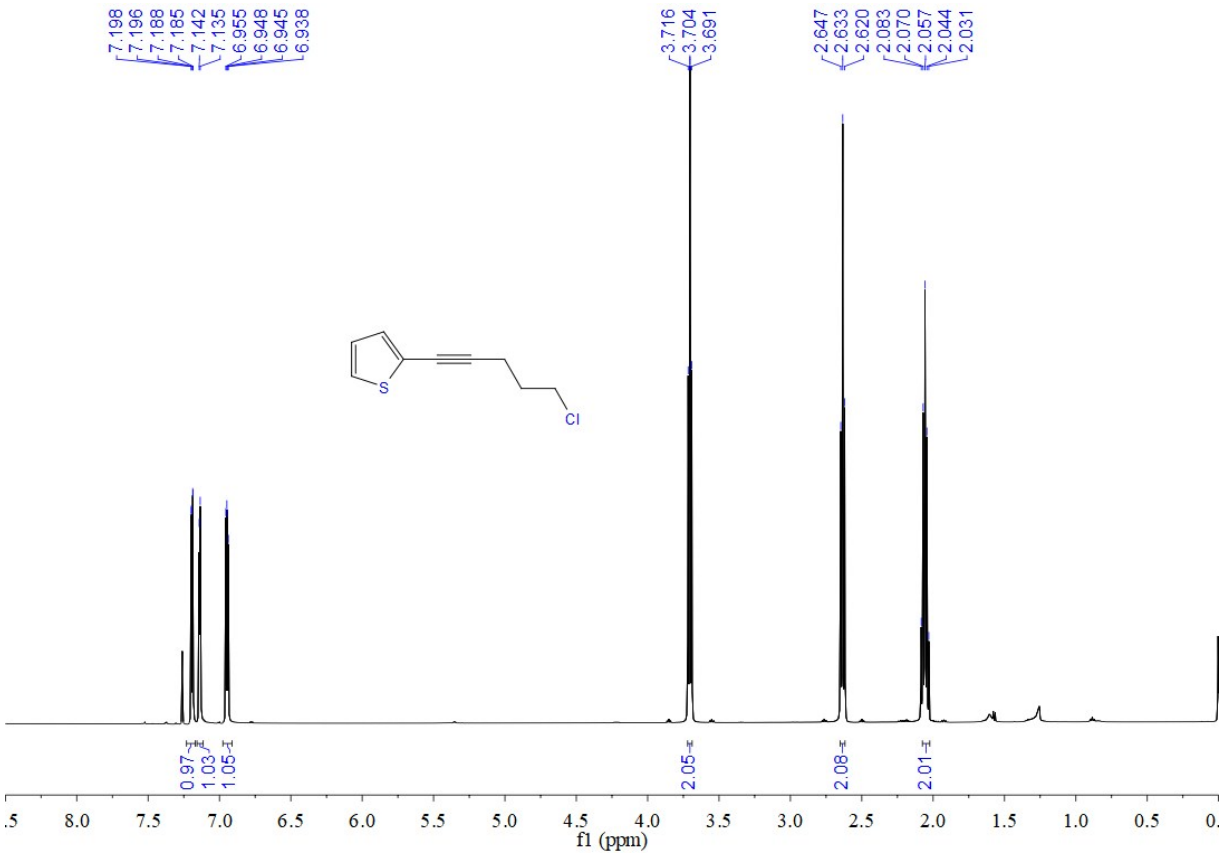
Cl
f1 (ppm)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6.948
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6.938
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3.704
3.691
2.647
2.633
2.620
2.083
2.070
2.057
2.044
2.031
S
Cl
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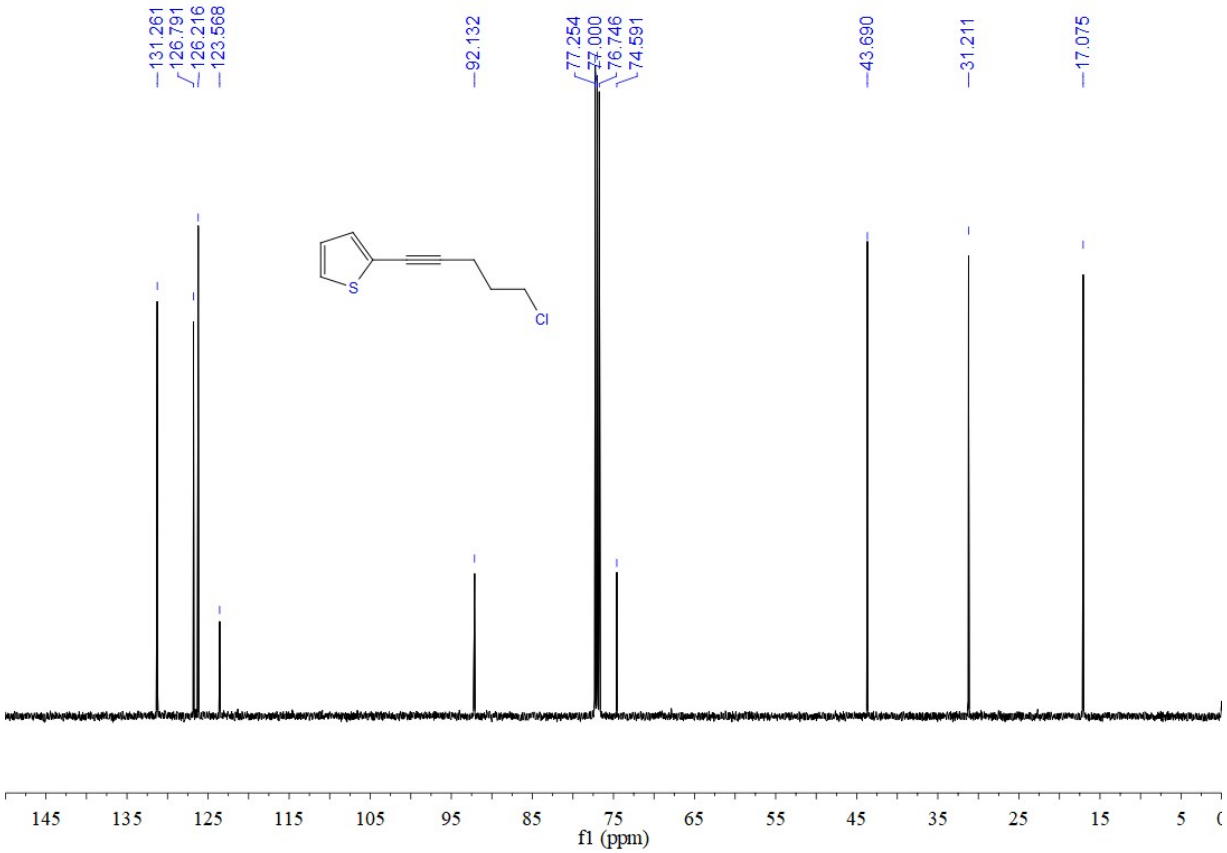
1.03
1.05
2.05
2.08
2.01
f1 (ppm)


131.261
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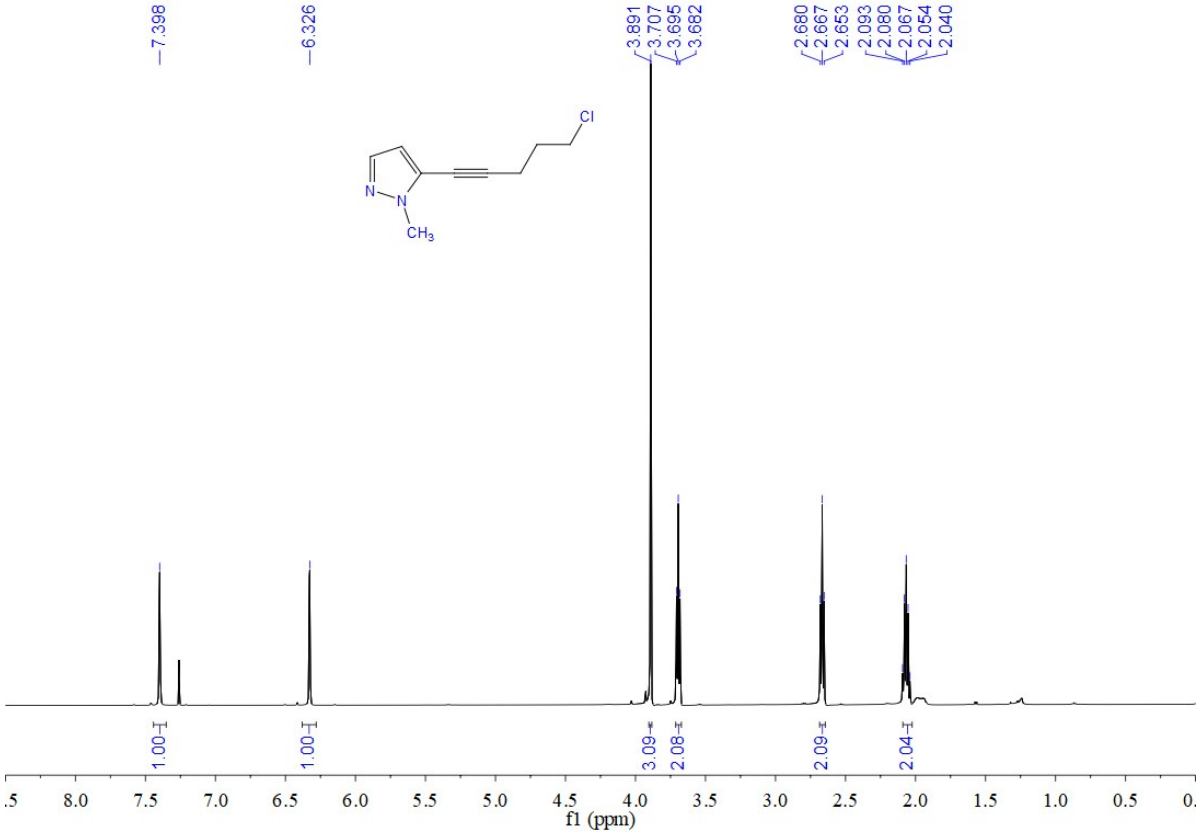
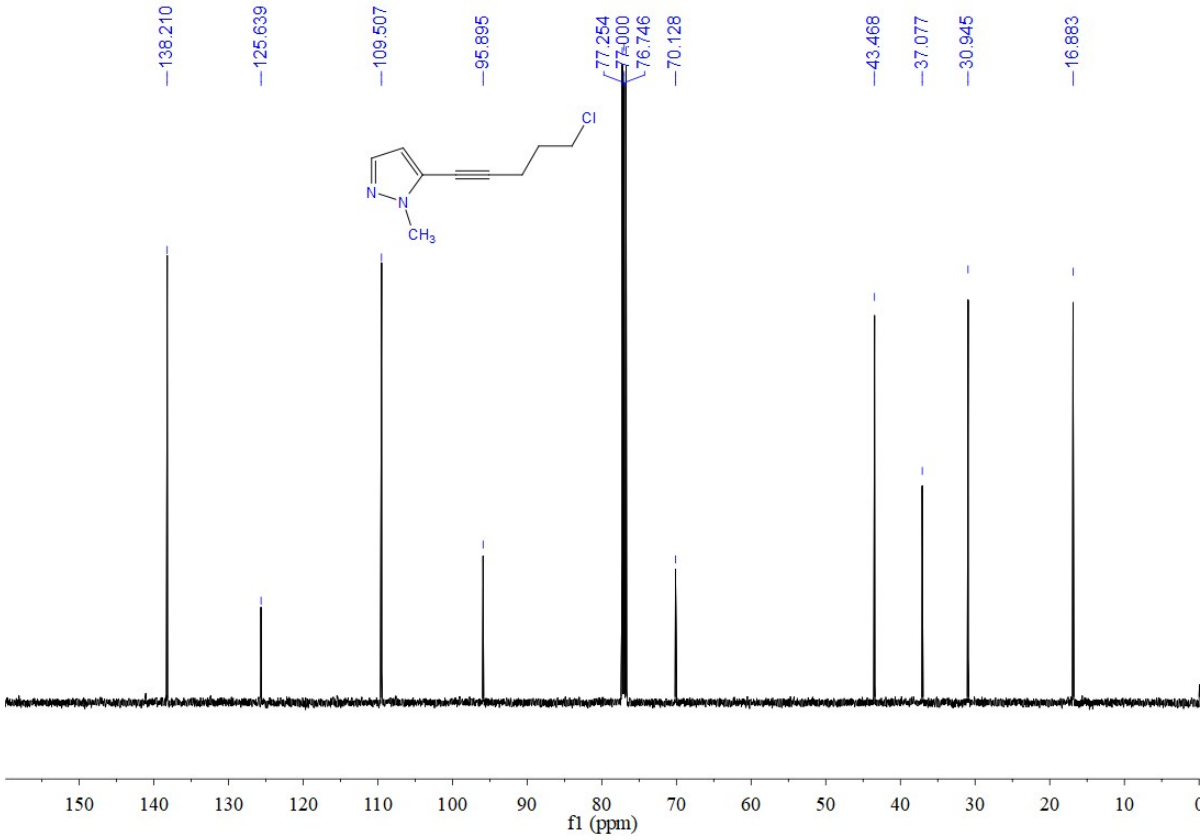
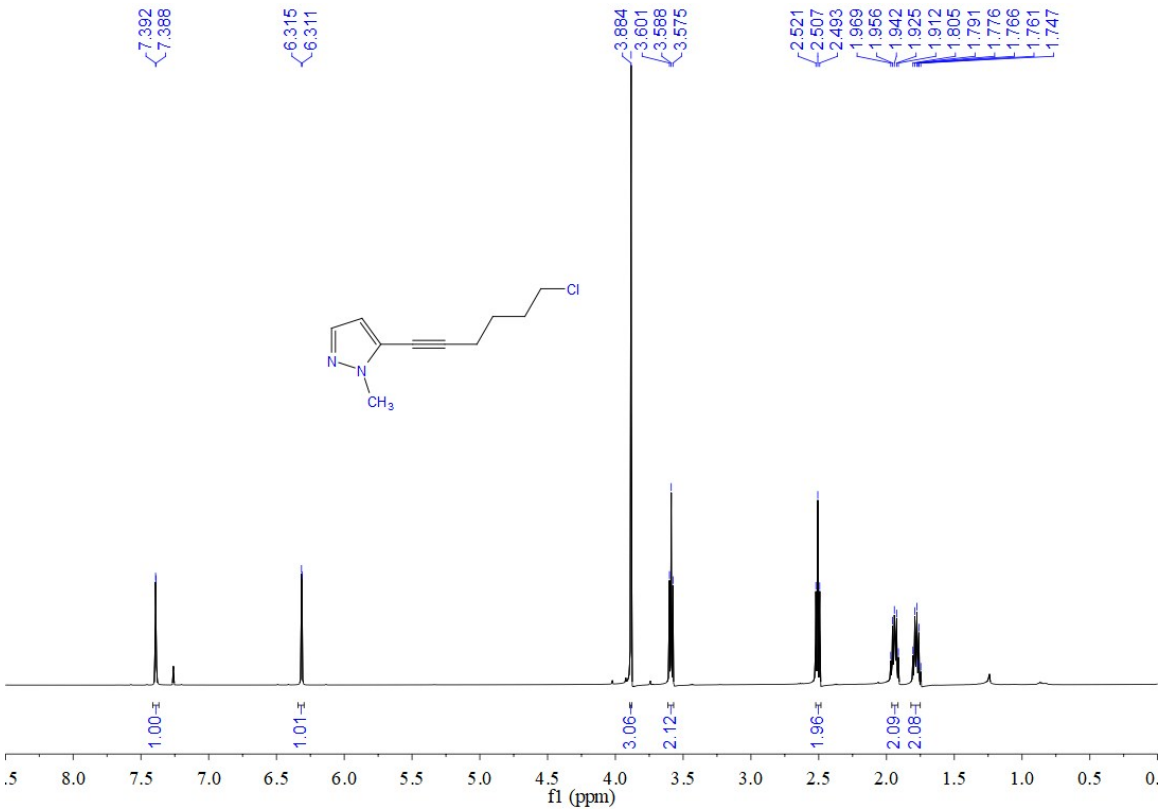
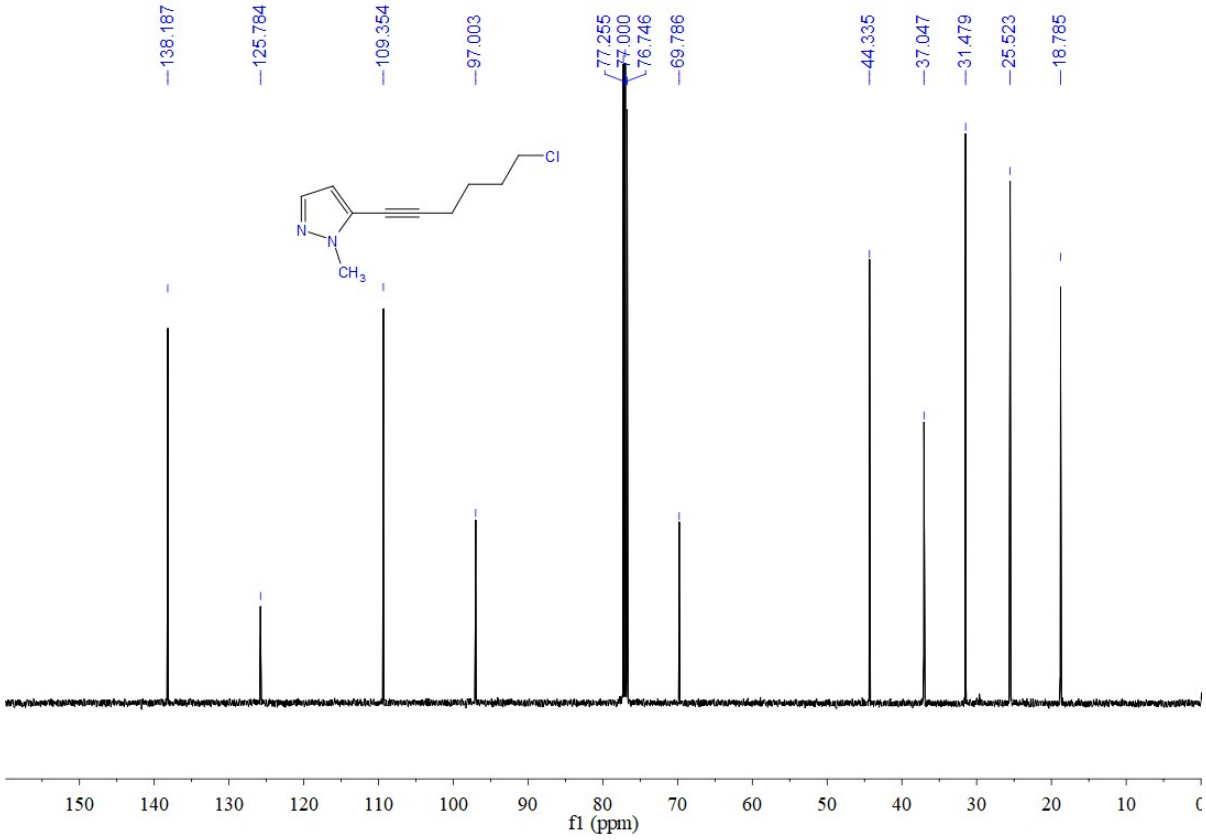
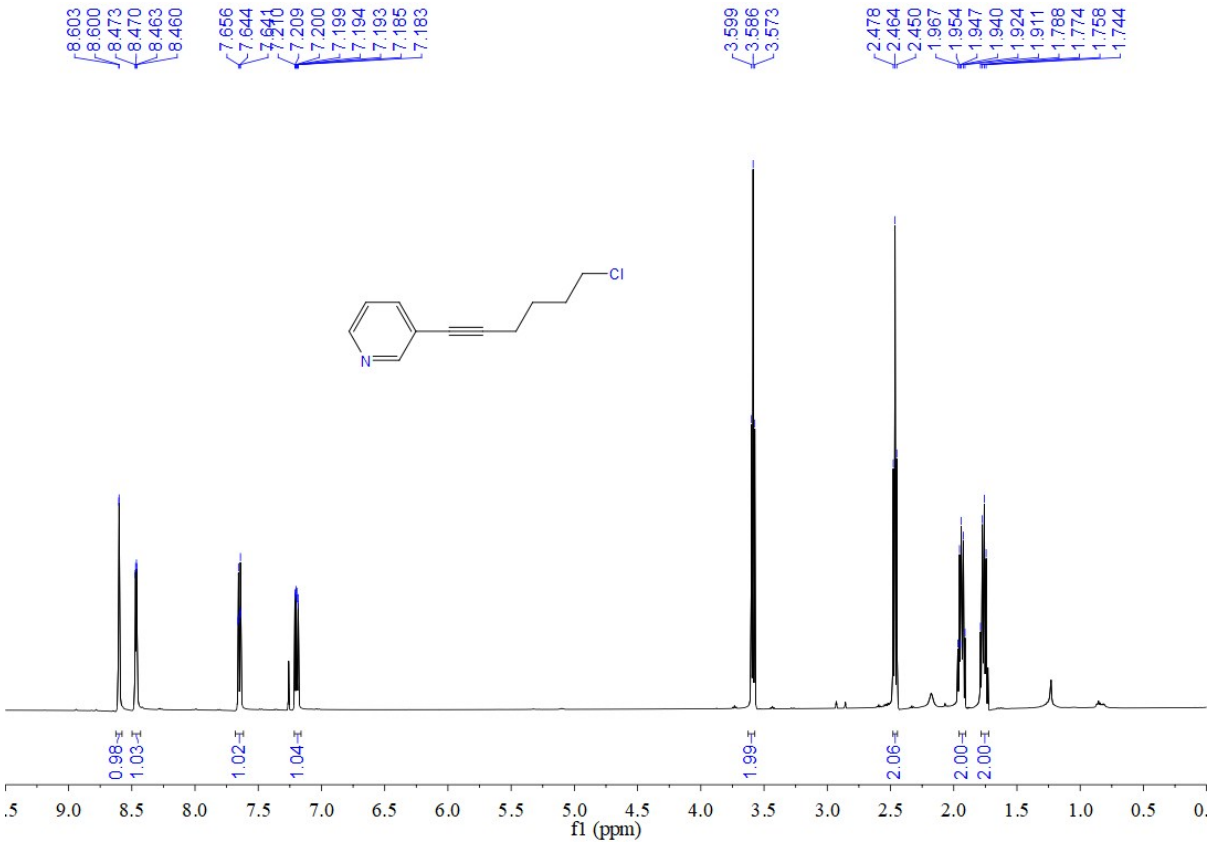
126.216
123.568
92.132
77.254
77.000
76.746
74.591
43.690
31.211
17.075
S
Cl
f1 (ppm)

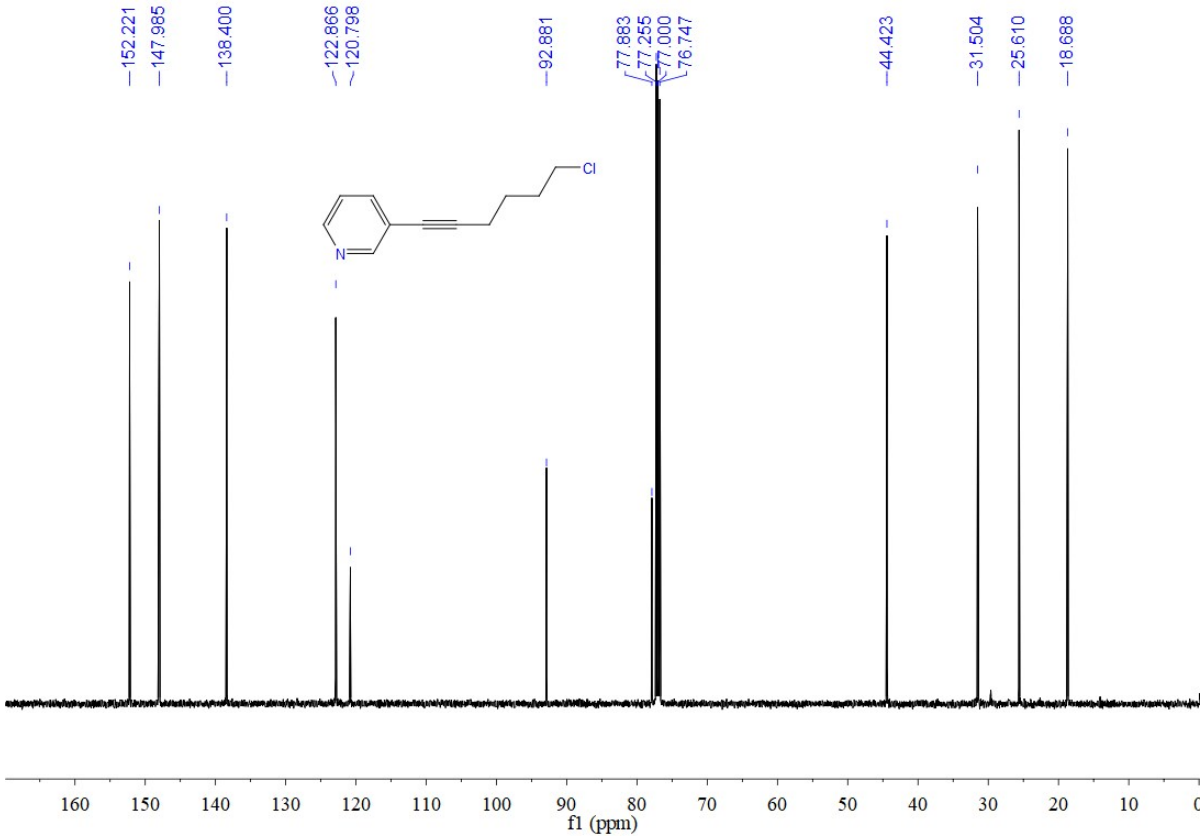

7.398
6.326
3.891
3.707
3.695
3.682
2.680
2.667
2.653
2.093
2.080
2.067
2.054
2.040
Cl
N
N
CH3
1.00
1.00
3.09
2.08
2.09
2.04
f1 (ppm)


138.210
125.639
109.507
95.895
77.254
77.000
76.746
70.128
43.468
37.077
30.945
16.883
Cl
N
N
CH3
f1 (ppm)

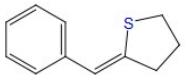

7.392
7.388
6.315
6.311
3.884
3.601
3.588
3.575
2.521
2.507
2.493
1.969
1.956
1.942
1.925
1.912
1.805
1.791
1.776
1.766
1.761
1.747
Cl
N
N
CH3
1.00
1.01
3.06
2.12
1.96
2.09
2.08
f1 (ppm)

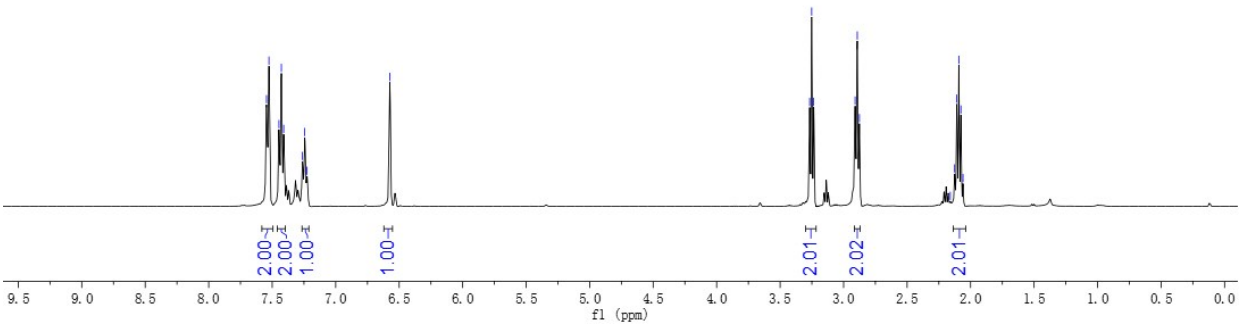

138.187
125.784
109.354
97.003
77.255
77.000
76.746
69.786
44.335
37.047
31.479
25.523
18.785
Cl
N
N
CH3
f1 (ppm)


8.603
8.600
8.473
8.470
8.463
8.460
7.656
7.644
7.641
7.210
7.209
7.200
7.199
7.194
7.193
7.185
7.183
3.599
3.586
3.573
2.478
2.464
2.450
1.967
1.954
1.947
1.940
1.924
1.911
1.788
1.774
1.758
1.744
Cl
N
0.98
1.03
1.02
1.04
1.99
2.06
2.00
2.00
f1 (ppm)

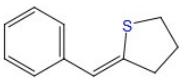

152.221
147.985
138.400
122.866
120.798
92.881
77.883
77.255
77.000
76.747
44.423
31.504
25.610
18.688
Cl
N
f1 (ppm)

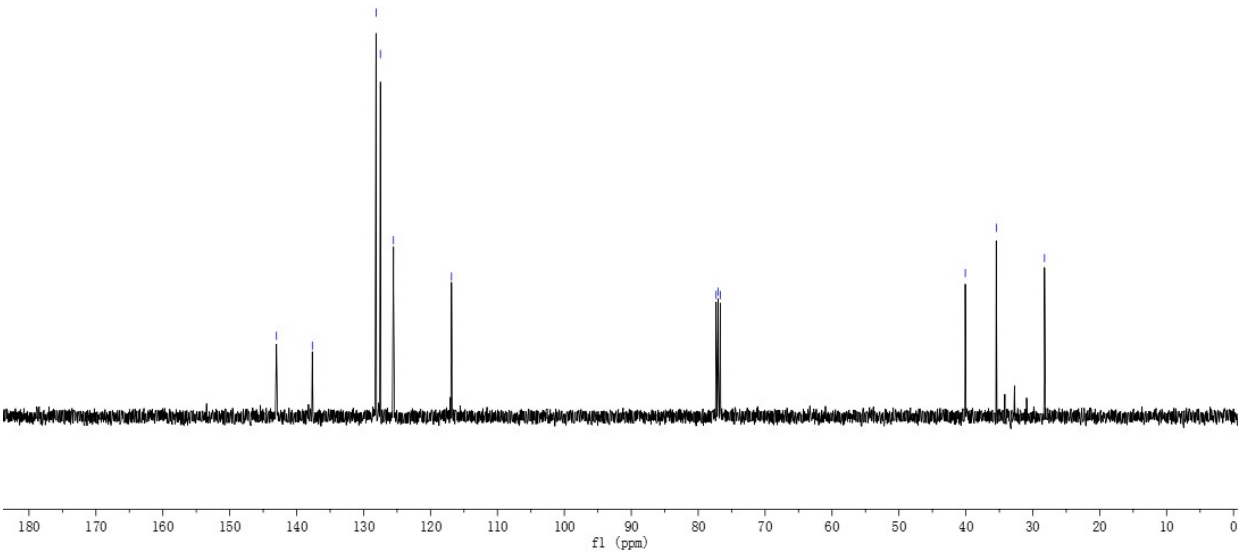

7.545
7.526
7.447
7.428
7.409
7.261
7.244
7.226
6.574
3.267
3.252
3.236
2.909
2.893
2.876
2.160
2.126
2.109
2.093
2.076
2.060

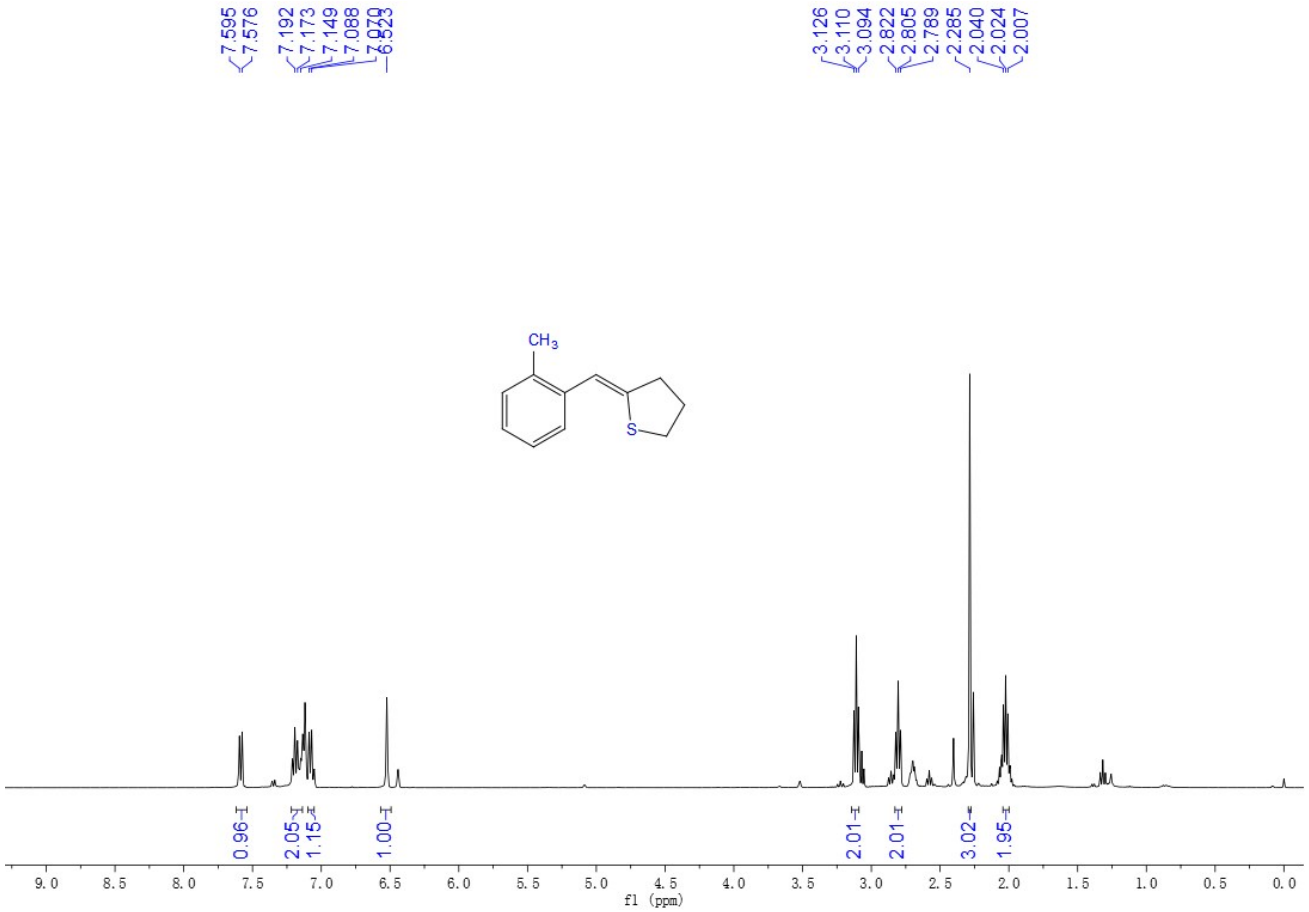

S

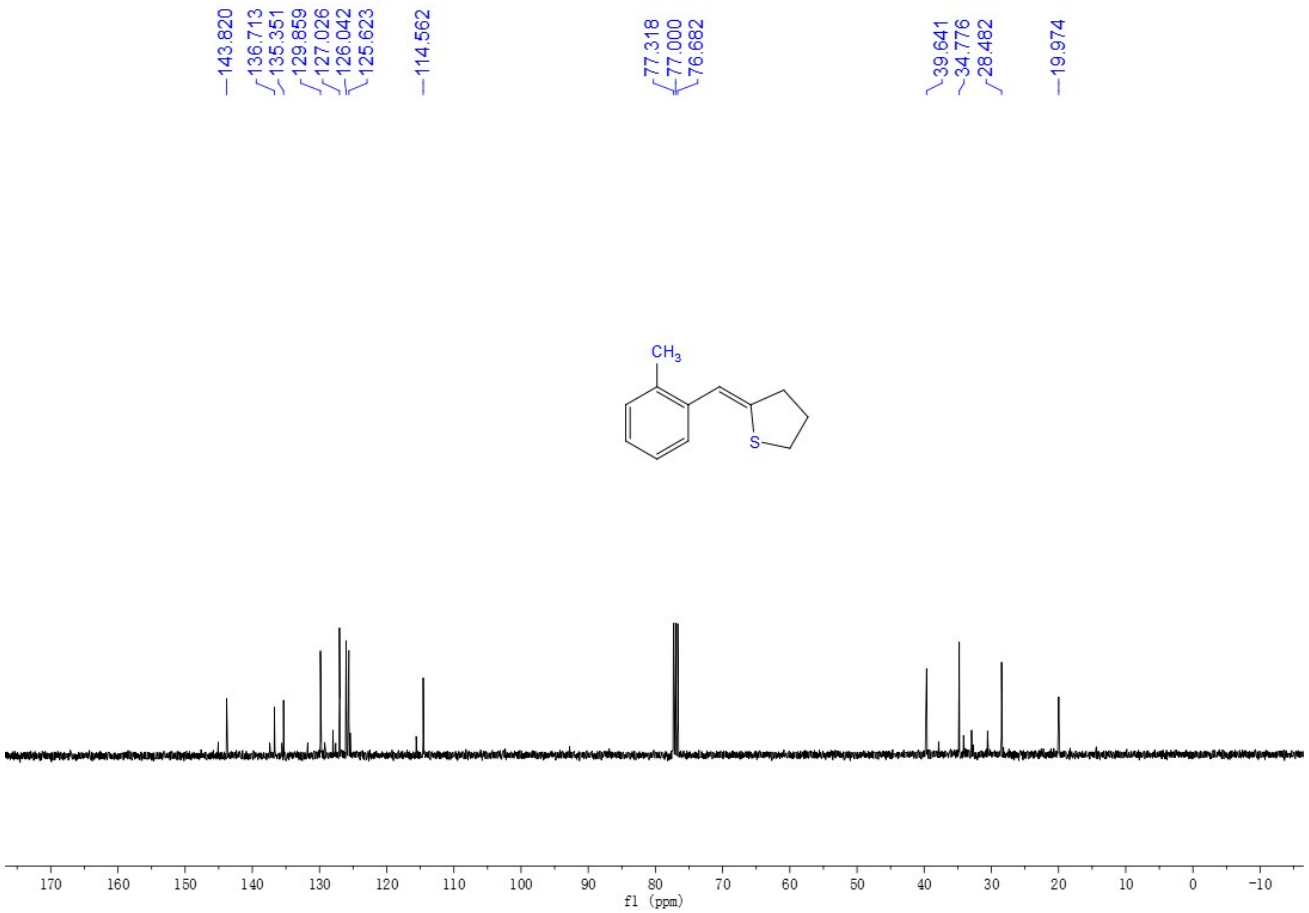

2.00
2.00
1.00
1.00
2.01
2.02
2.01
f1 (ppm)

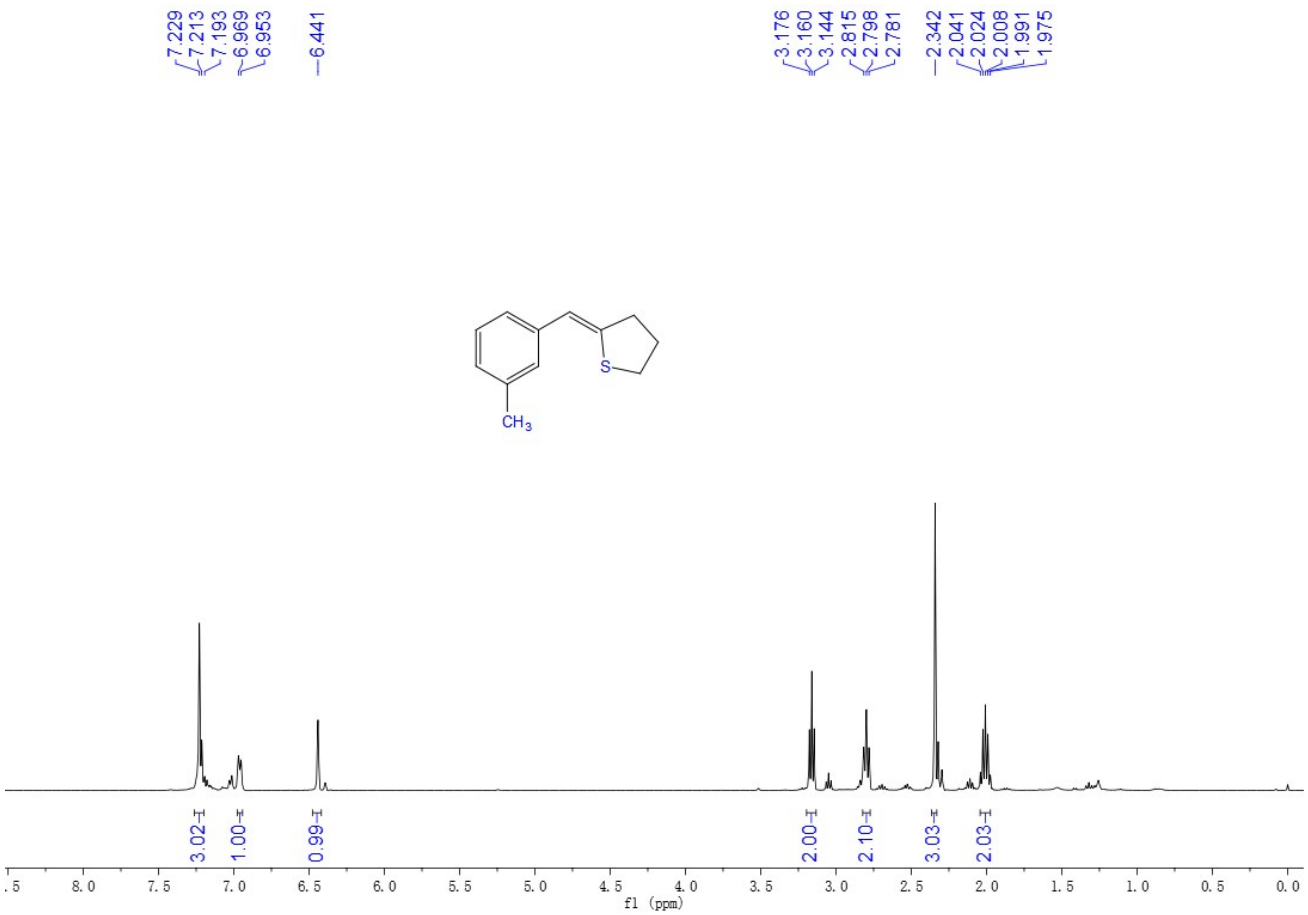

143.023
137.658
128.134
127.484
125.533
116.865
77.321
77.000
76.687
40.084
35.455
28.244

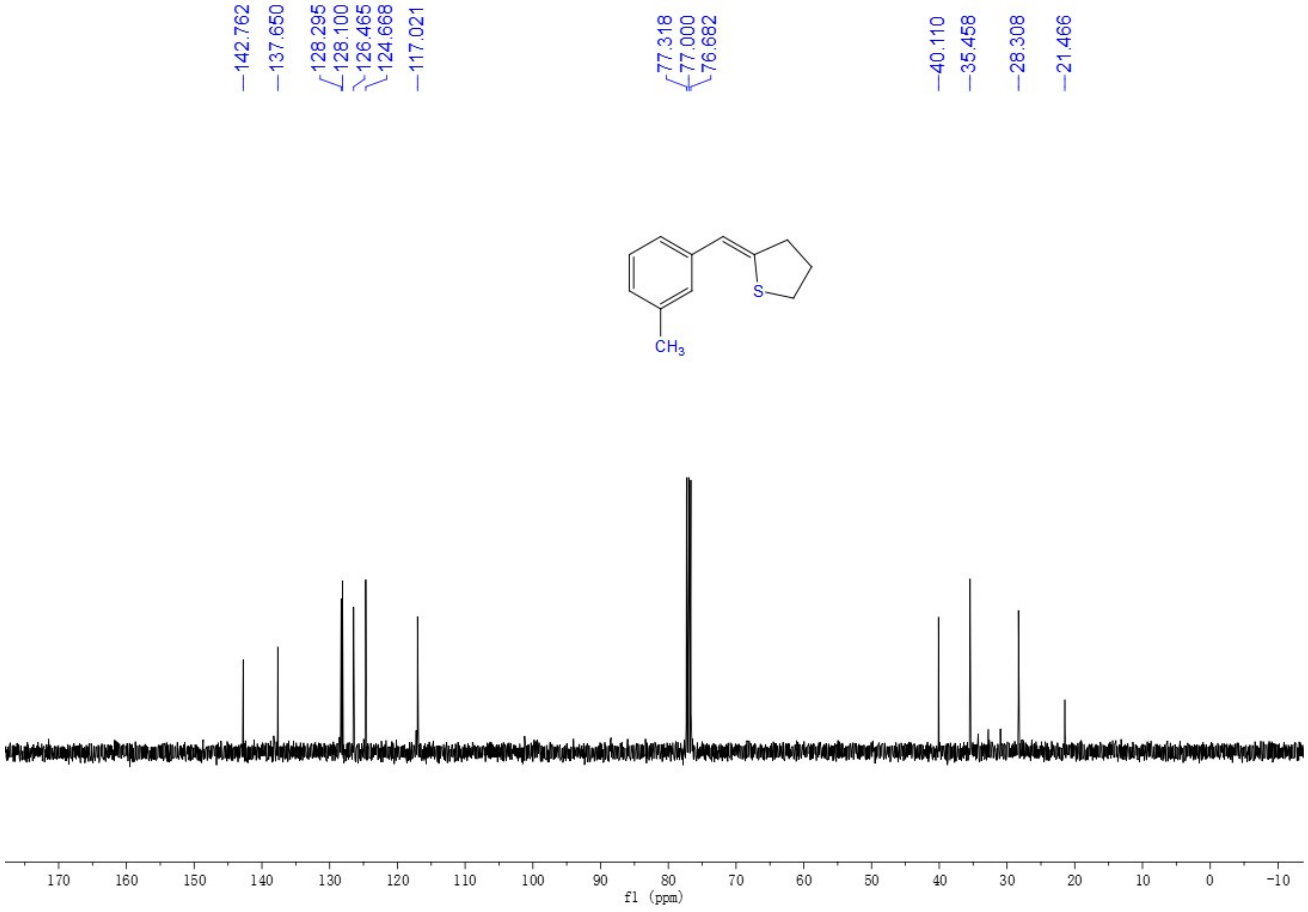

S

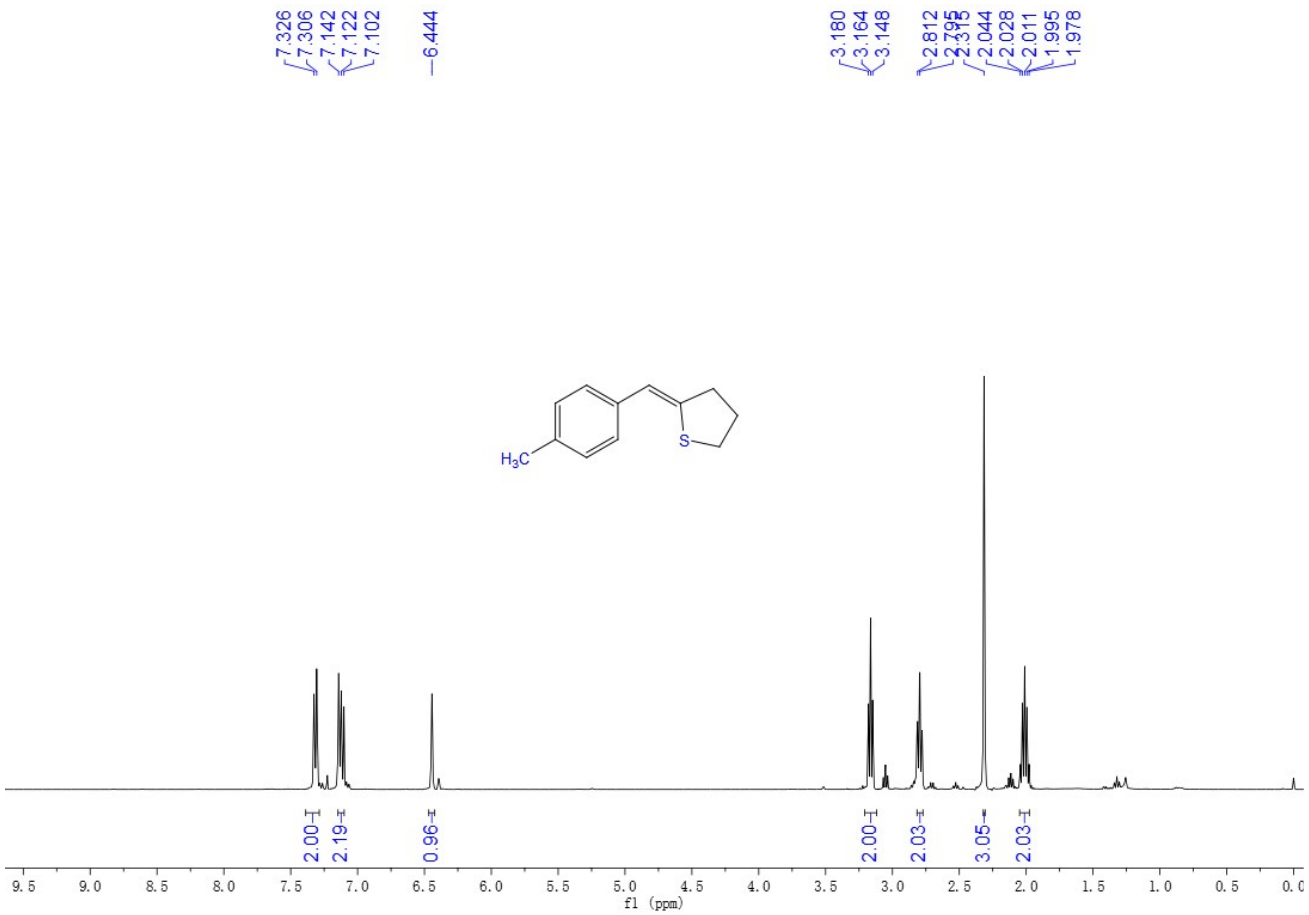

f1 (ppm)

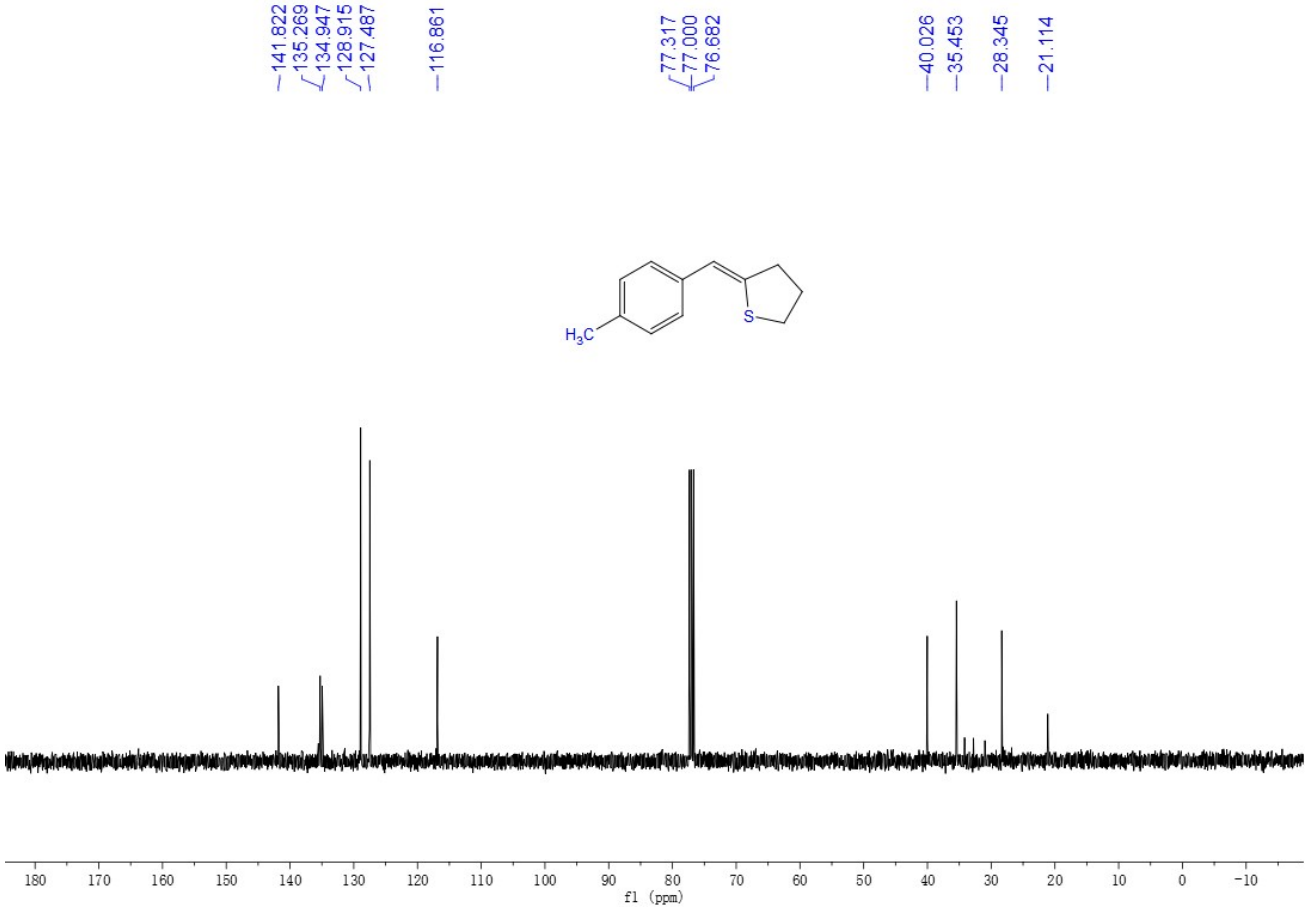

7.595
7.576
7.192
7.173
7.149
7.088
6.523
3.126
3.110
3.094
2.822
2.805
2.789
2.285
2.040
2.024
2.007
CH3
S
0.96
2.05
1.15
1.00
2.01
2.01
3.02
1.95
f1 (ppm)

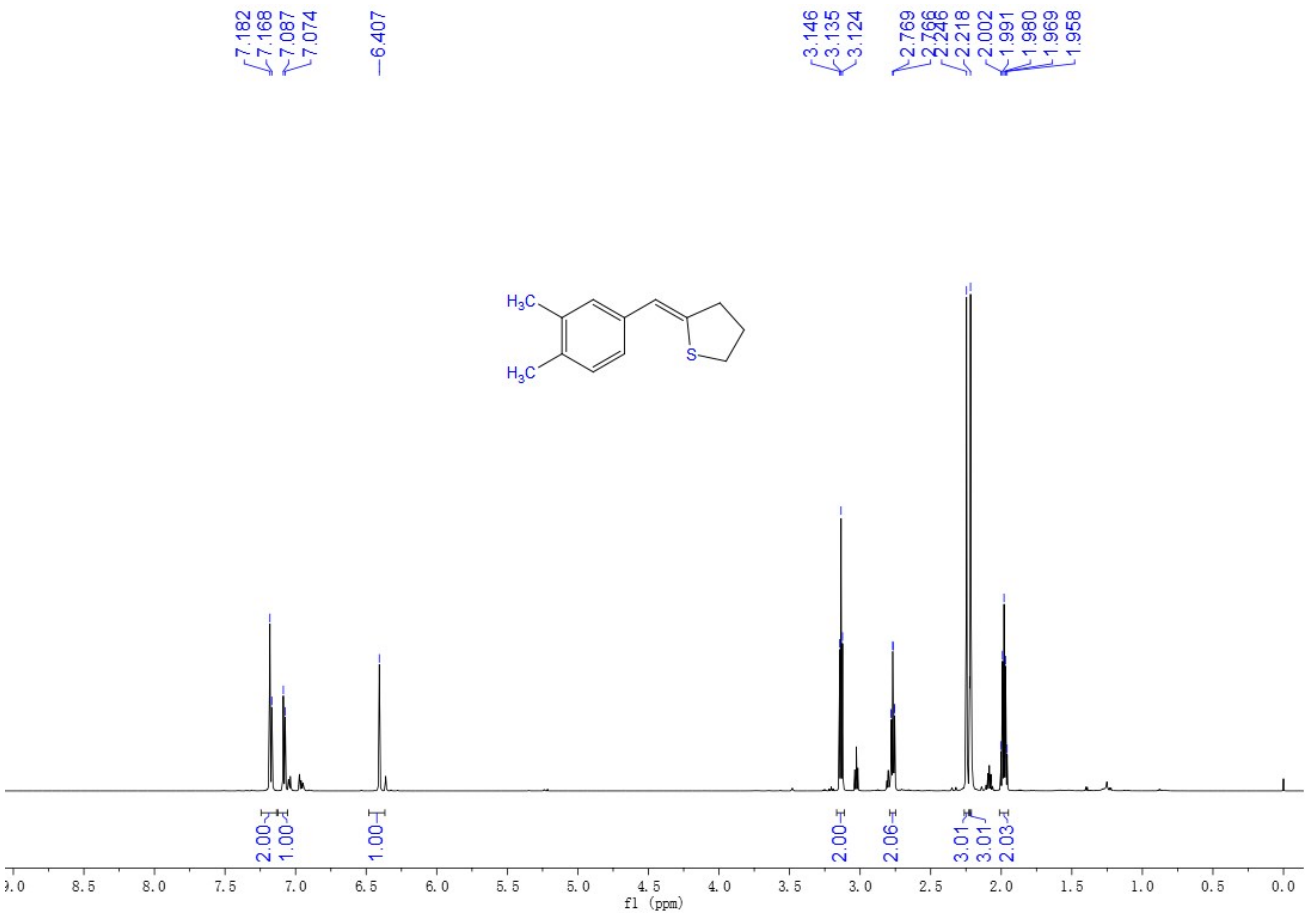

143.820
136.713
135.351
129.859
127.026
126.042
125.623
114.562
77.318
77.000
76.682
39.641
34.776
28.482
19.974
CH3
S
f1 (ppm)

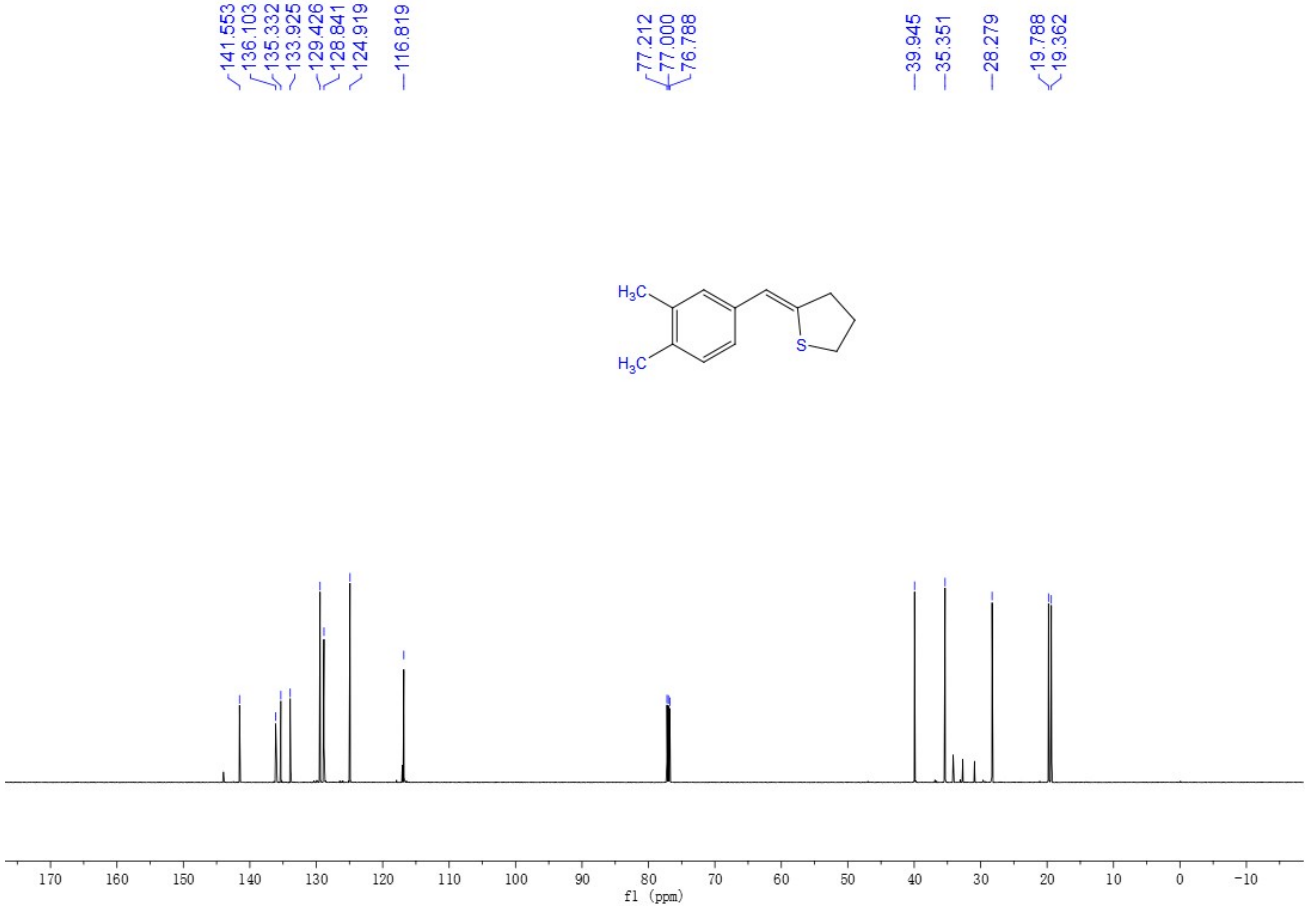

7.229
7.213
7.193
6.969
6.953
6.441
3.176
3.160
3.144
2.815
2.798
2.781
2.342
2.041
2.024
2.008
1.991
1.975
S
CH3
3.02
1.00
0.99
2.00
2.10
3.03
2.03
f1 (ppm)

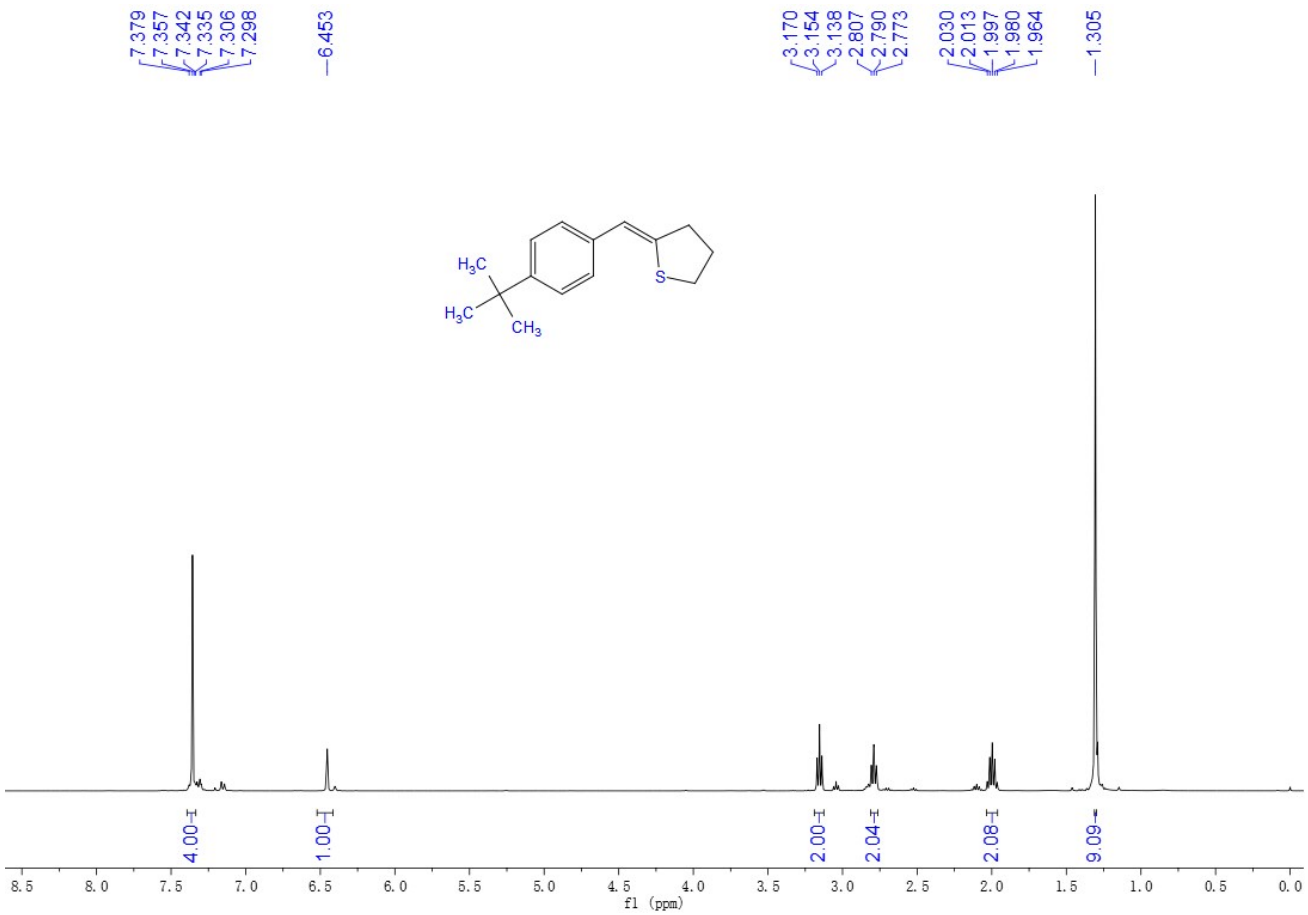

142.762
137.650
128.295
128.100
126.465
124.668
117.021
77.318
77.000
76.682
40.110
35.458
28.308
21.466
S
CH3
f1 (ppm)

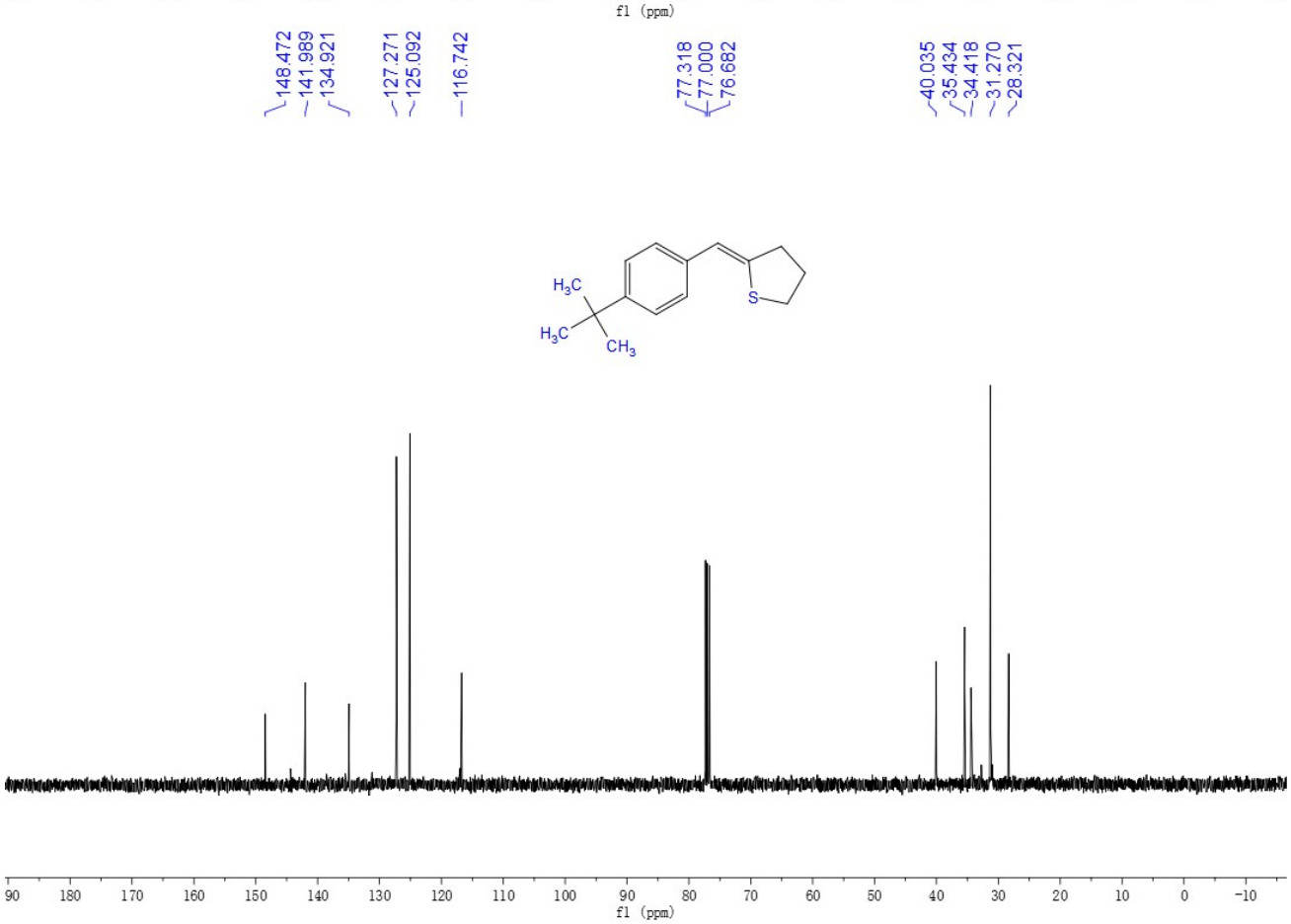

7.326
7.306
7.142
7.122
7.102
6.444
3.180
3.164
3.148
2.812
2.795
2.044
2.028
2.011
1.995
1.978
H3C
S
2.00
2.19
0.96
2.00
2.03
3.05
2.03
f1 (ppm)

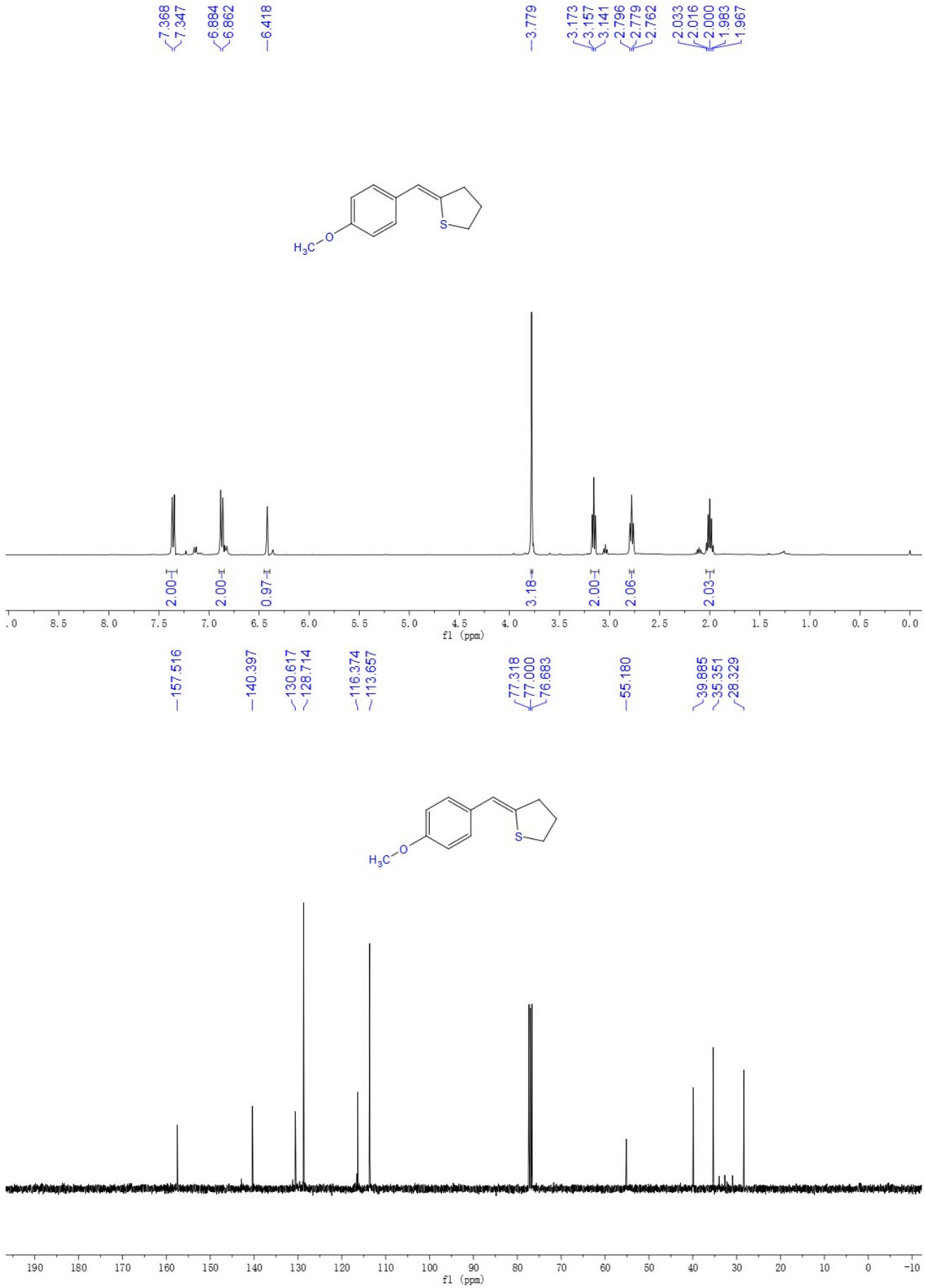

141.822
135.269
134.947
128.915
127.487
116.861
77.317
77.000
76.682
40.026
35.453
28.345
21.114
H3C
S
f1 (ppm)

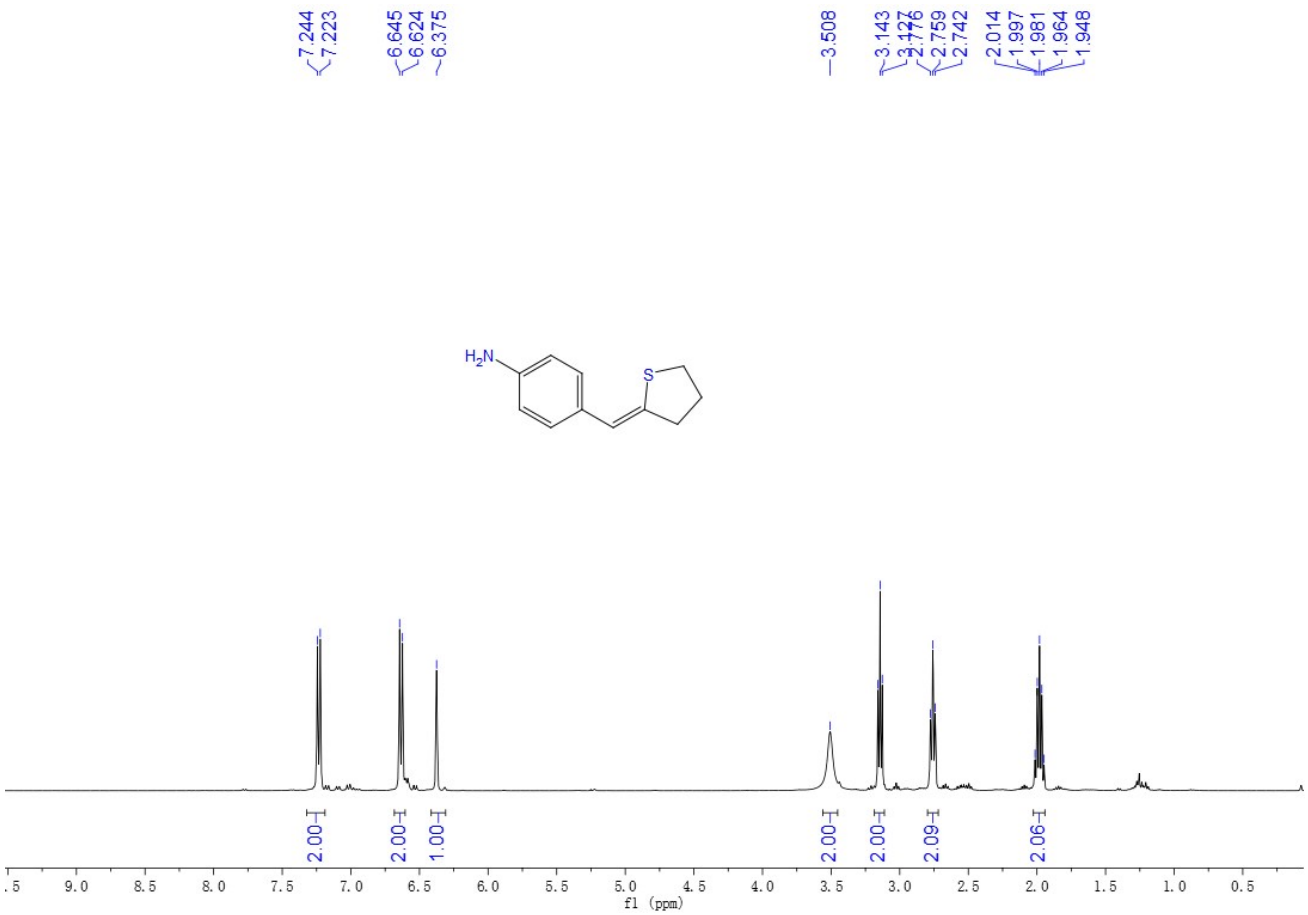

7.182
7.168
7.087
7.074
6.407
3.146
3.135
3.124
2.769
2.246
2.218
2.002
1.991
1.980
1.969
1.958
H3C
H3C
S
2.00
1.00
1.00
2.00
2.06
3.01
3.01
2.03
f1 (ppm)

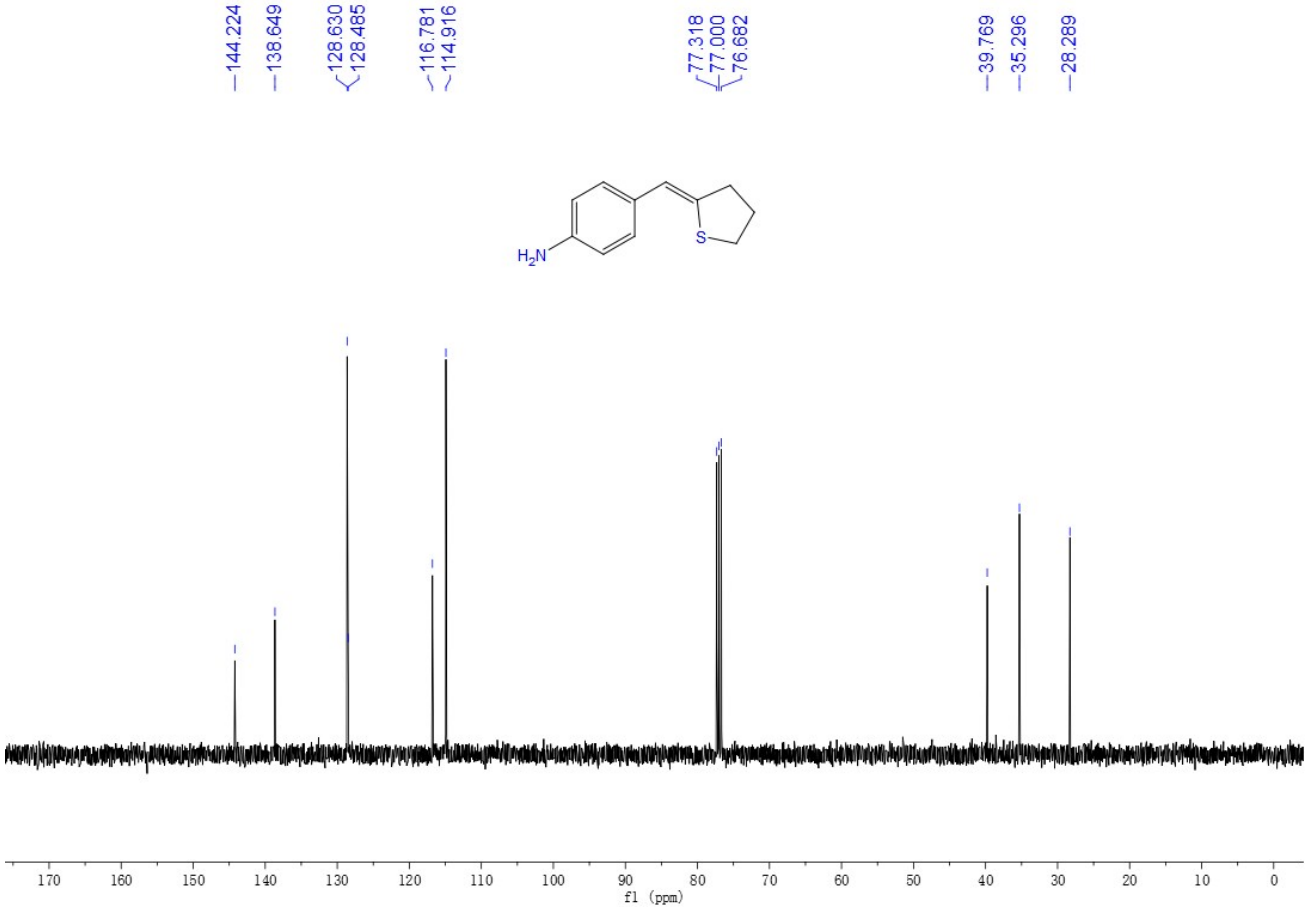

141.553
136.103
135.332
133.925
129.426
128.841
124.919
116.819
77.212
77.000
76.788
39.945
35.351
28.279
19.788
19.362
H3C
H3C
S
f1 (ppm)


7.379
7.357
7.342
7.335
7.306
7.298
6.453
3.170
3.154
3.138
2.807
2.790
2.773
2.030
2.013
1.997
1.980
1.964
1.305
H3C
H3C
CH3
S
4.00
1.00
2.00
2.04
2.08
9.09
f1 (ppm)


148.472
141.989
134.921
127.271
125.092
116.742
77.318
77.000
76.682
40.035
35.434
34.418
31.270
28.321
H3C
H3C
CH3
S
f1 (ppm)


7.368
7.347
6.884
6.862
6.418
3.779
3.173
3.157
3.141
2.796
2.779
2.762
2.033
2.016
2.000
1.983
1.967
H3C
O
S
2.00
2.00
0.97
3.18
2.00
2.06
2.03
f1 (ppm)
157.516
140.397
130.617
128.714
116.374
113.657
77.318
77.000
76.683
55.180
39.885
35.351
28.329
H3C
O
S
f1 (ppm)


7.244
7.223
6.645
6.624
6.375
3.508
3.143
3.127
2.776
2.759
2.742
2.014
1.997
1.981
1.964
1.948
H2N
S
2.00
2.00
1.00
2.00
2.00
2.09
2.06
f1 (ppm)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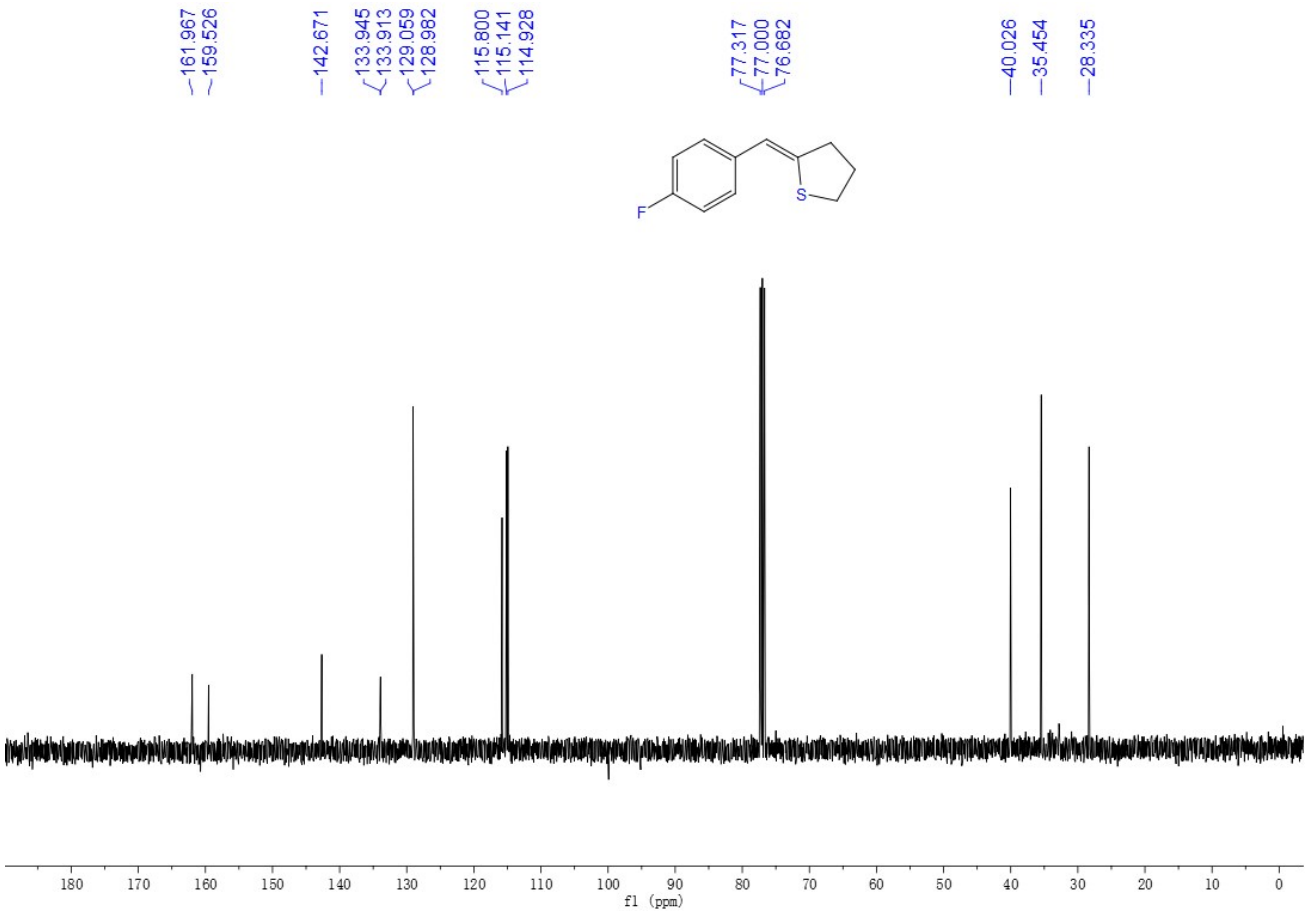
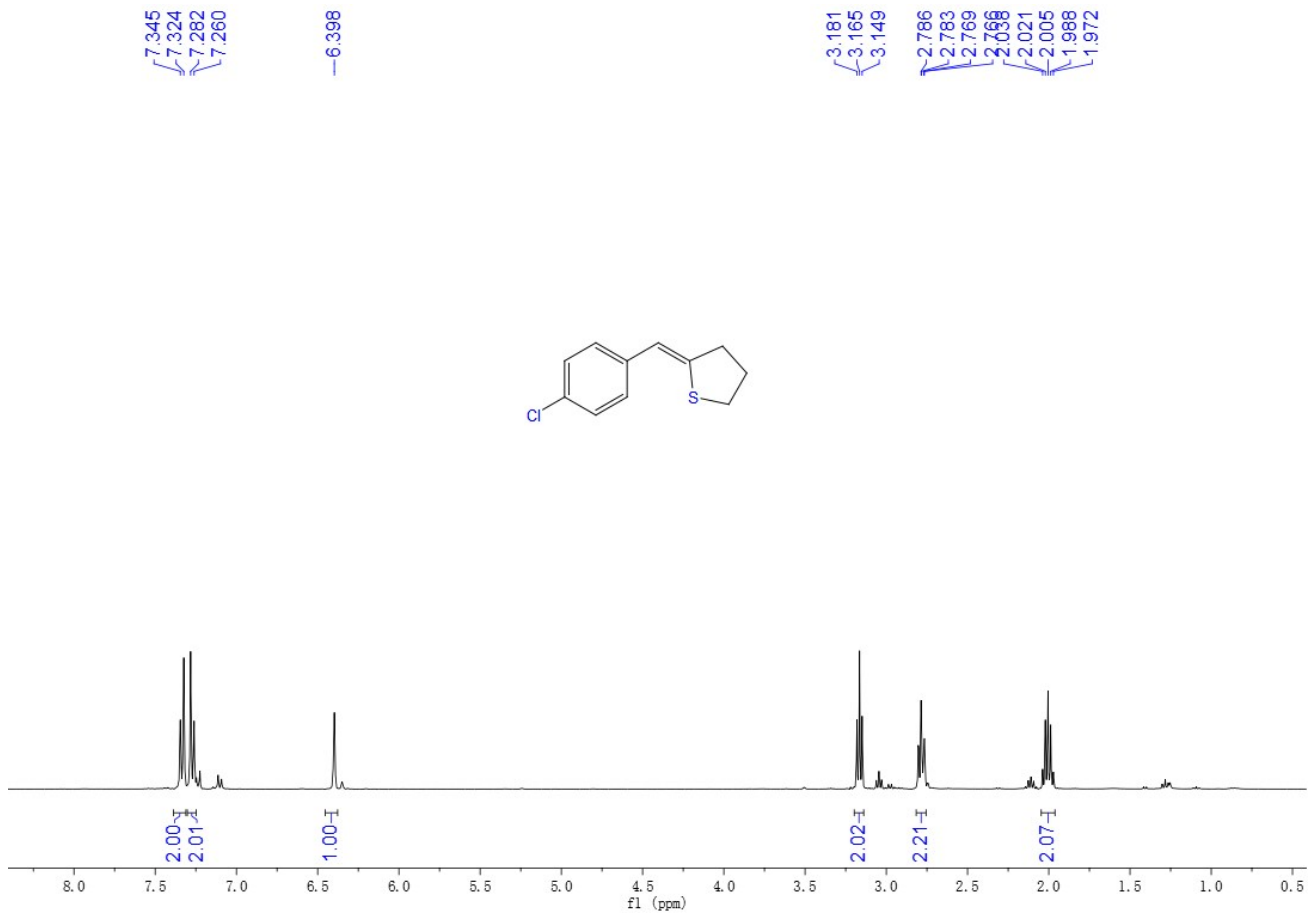
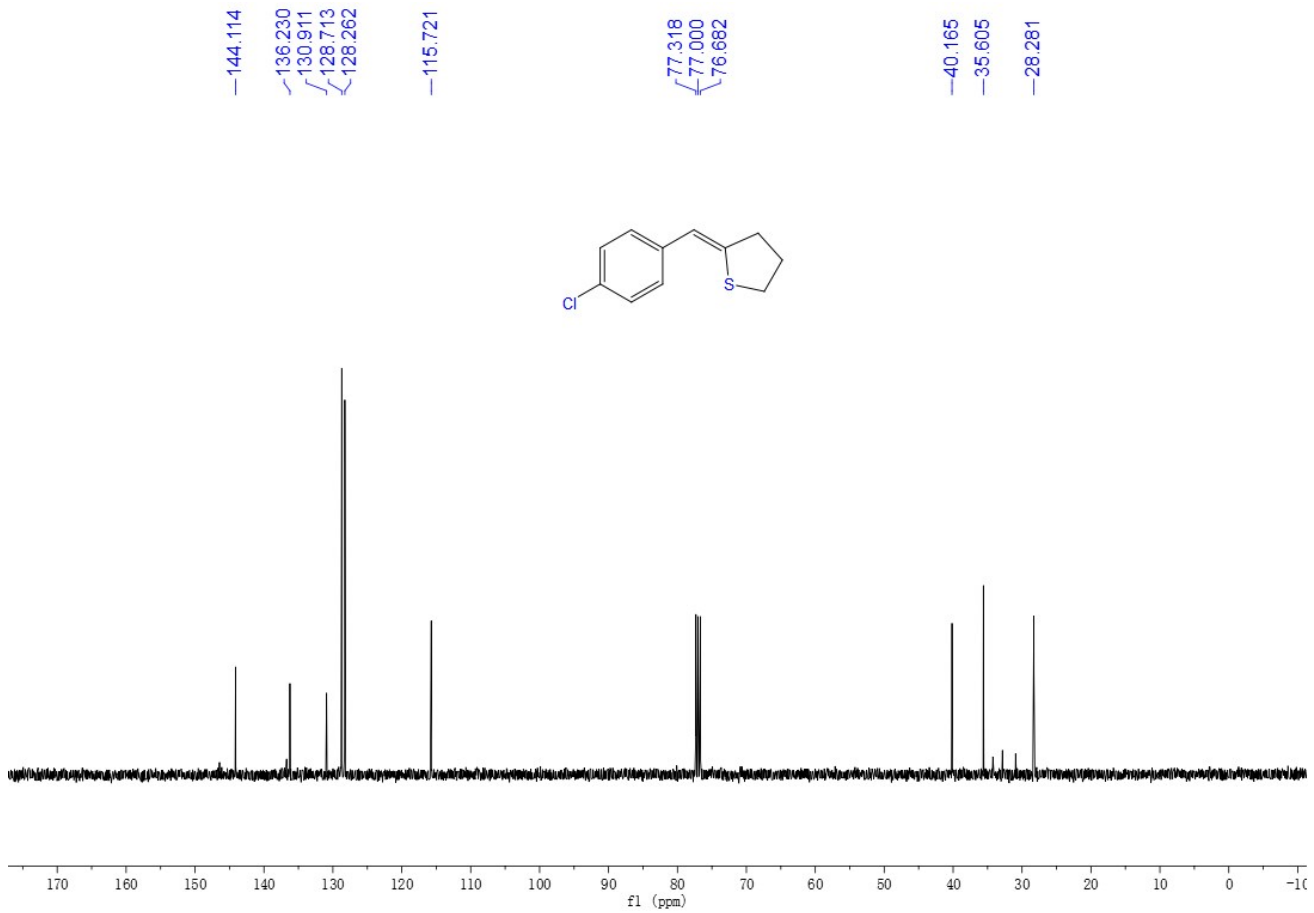
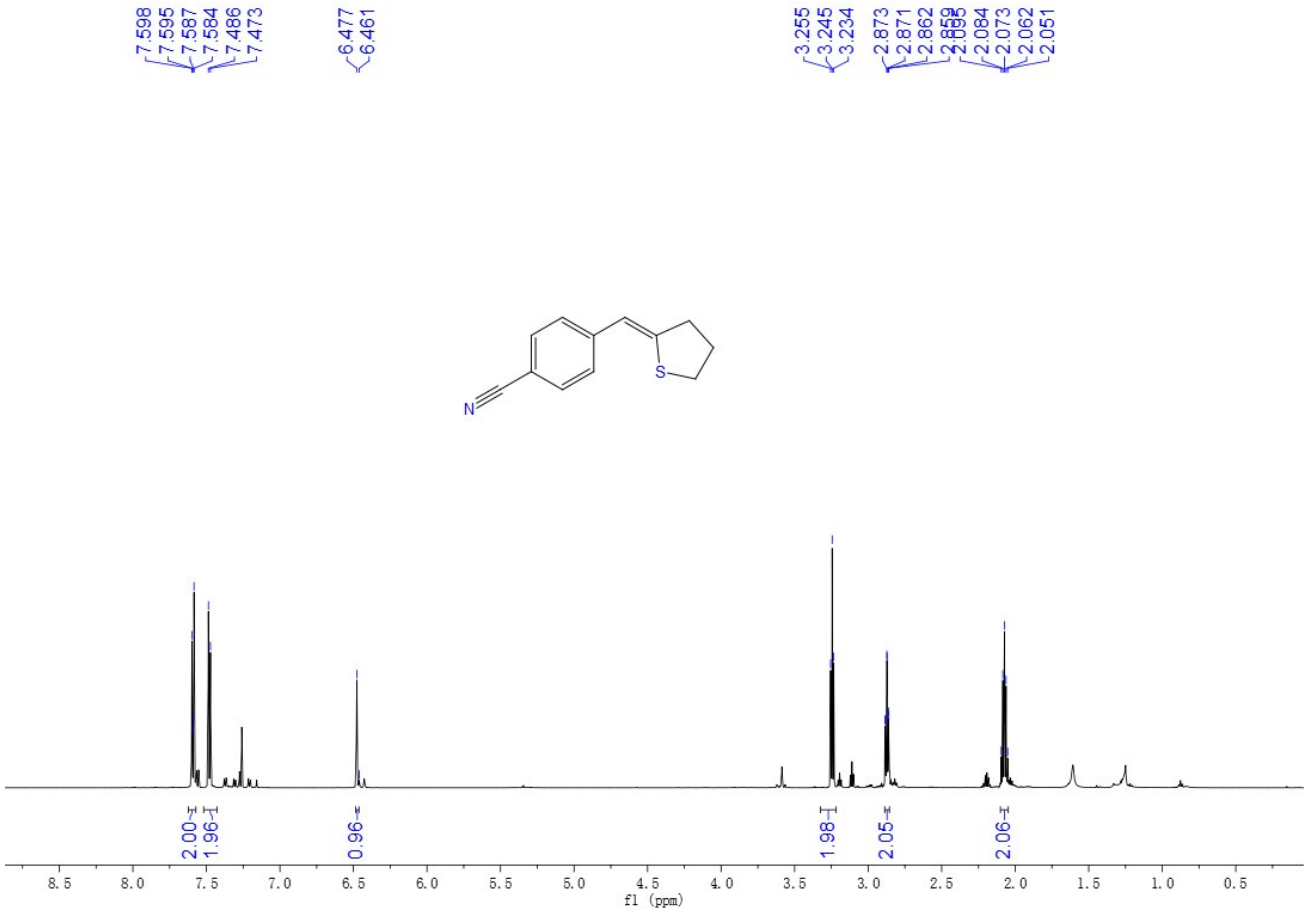
138.649
128.630
128.485
116.781
114.916
77.318
77.000
76.682
39.769
35.296
28.289
H2N
S
f1 (ppm)


7.395
7.382
7.374
7.360
7.033
7.012
6.990
6.429
3.190
3.174
3.158
2.811
2.794
2.777
2.051
2.035
2.018
2.002
1.985
F
S
2.00
2.04
1.00
2.00
2.11
2.04
f1 (ppm)


161.967
159.526
142.671
133.945
133.913
129.059
128.982
115.800
115.141
114.928
77.317
77.000
76.682
40.026
35.454
28.335
F
S
f1 (ppm)


7.345
7.324
7.282
7.260
6.398
3.181
3.165
3.149
2.786
2.783
2.769
2.766
2.038
2.021
2.005
1.988
1.972
Cl
S
2.00
2.01
1.00
2.02
2.21
2.07
f1 (ppm)


144.114
136.230
130.911
128.713
128.262
115.721
77.318
77.000
76.682
40.165
35.605
28.281
Cl
S
f1 (ppm)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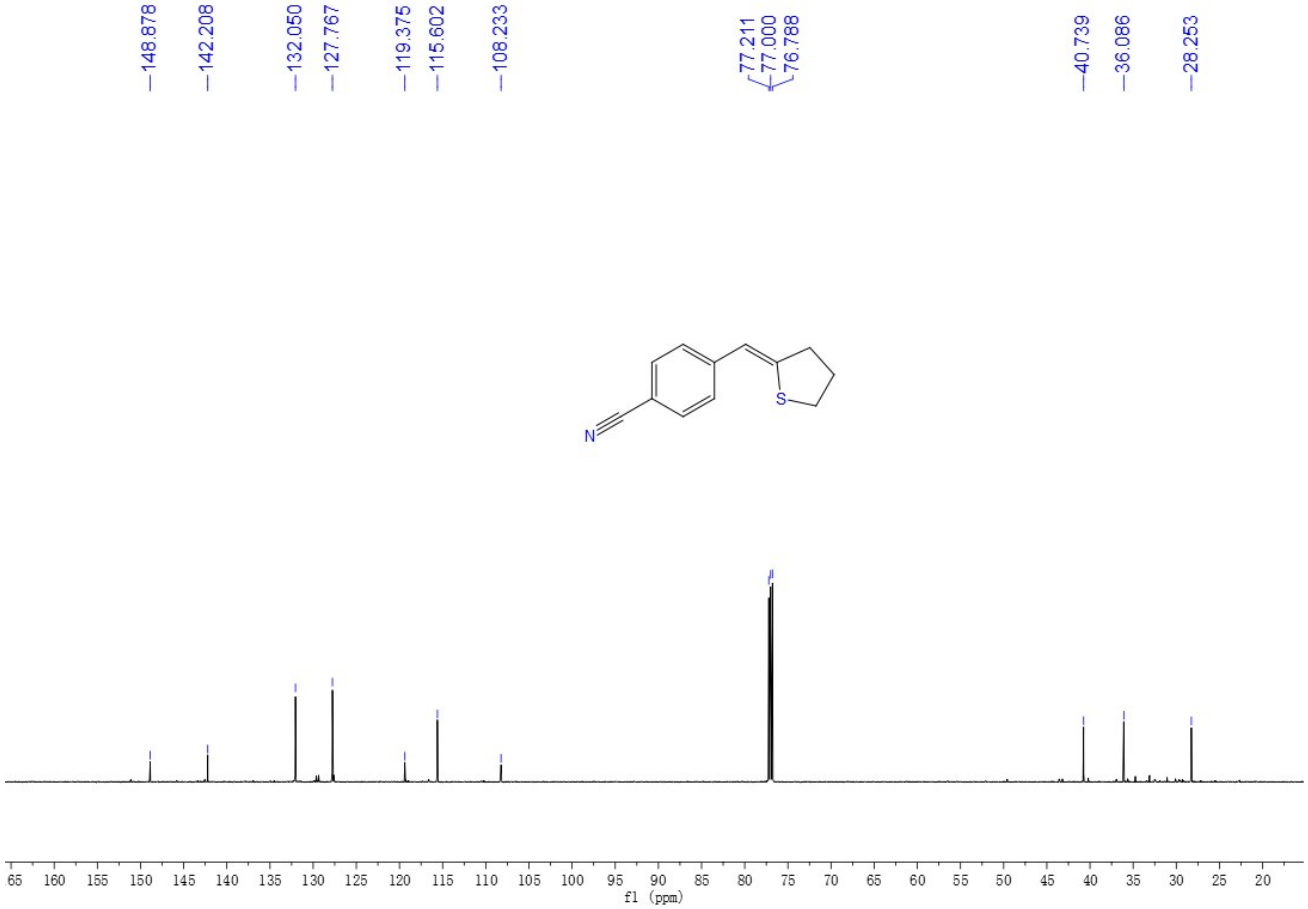
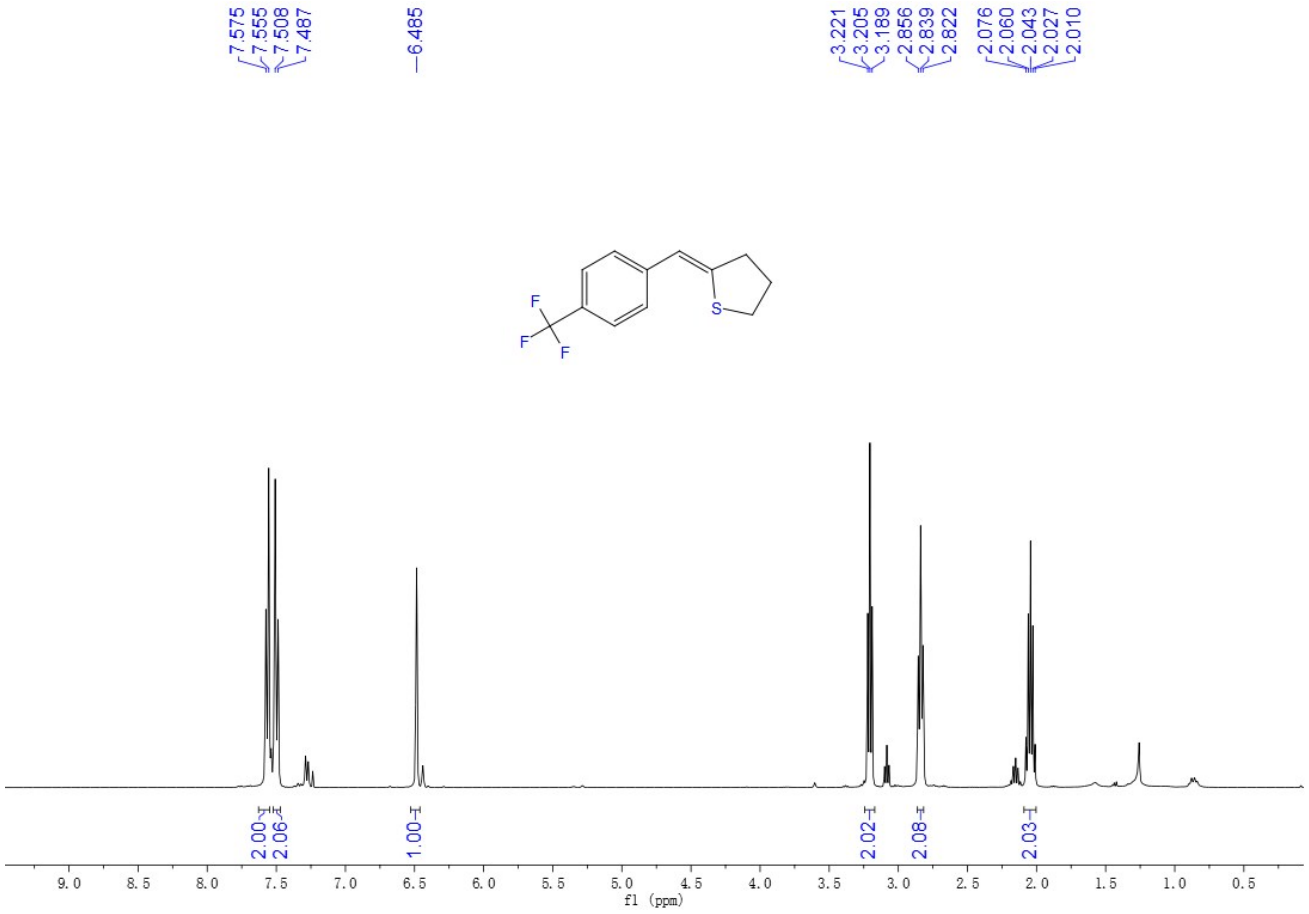
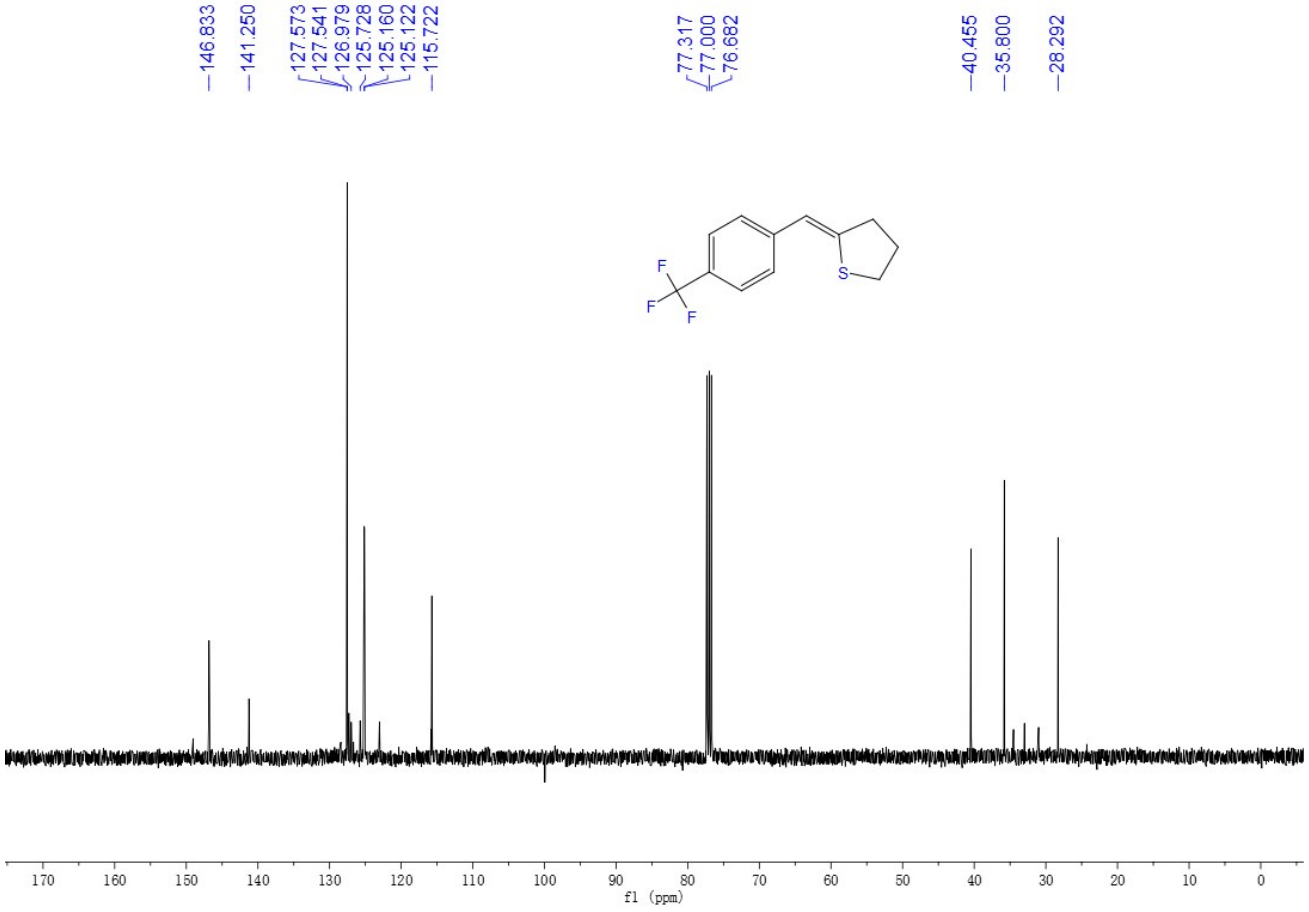
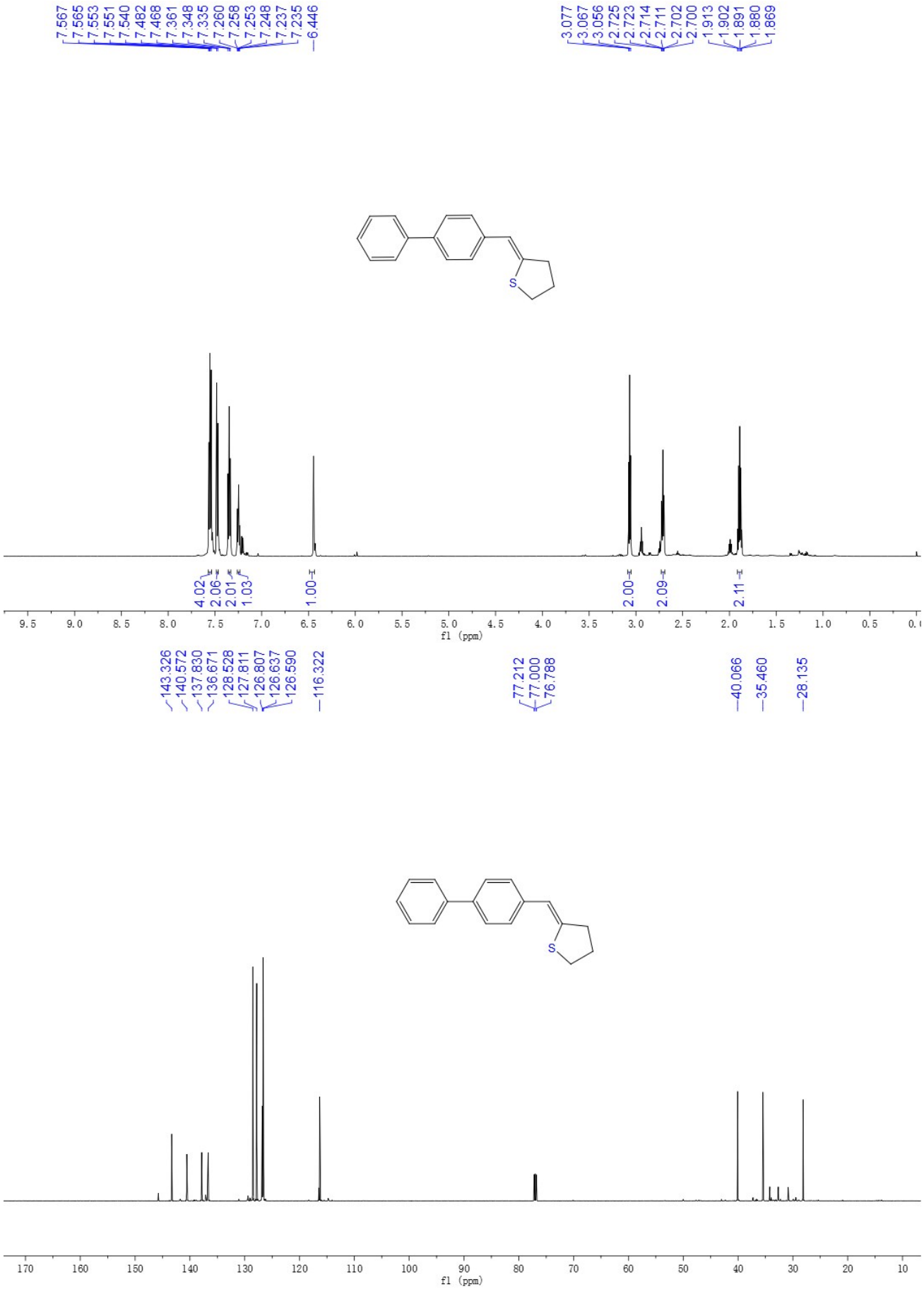
7.595
7.587
7.584
7.486
7.473
6.477
6.461
3.255
3.245
3.234
2.873
2.871
2.862
2.084
2.073
2.062
2.051
N
S
2.00
1.96
0.96
1.98
2.05
2.06
f1 (ppm)


148.878
142.208
132.050
127.767
119.375
115.602
108.233
77.211
77.000
76.788
40.739
36.086
28.253
N
S
f1 (ppm)


7.575
7.555
7.508
7.487
6.485
3.221
3.205
3.189
2.856
2.839
2.822
2.076
2.060
2.043
2.027
2.010
F
F
F
S
2.00
2.06
1.00
2.02
2.08
2.03
f1 (ppm)


146.833
141.250
127.573
127.541
126.979
125.728
125.160
125.122
115.722
77.317
77.000
76.682
40.455
35.800
28.292
F
F
F
S
f1 (ppm)


7.567
7.565
7.553
7.551
7.540
7.482
7.468
7.361
7.348
7.335
7.260
7.258
7.253
7.248
7.237
7.235
6.446
3.077
3.067
3.056
2.725
2.723
2.714
2.711
2.702
2.700
1.913
1.902
1.891
1.880
1.869
S
4.02
2.06
2.01
1.03
1.00
2.00
2.09
2.11
f1 (ppm)
143.326
140.572
137.830
136.671
128.528
127.811
126.807
126.637
126.590
116.322
77.212
77.000
76.788
40.066
35.460
28.135
S
f1 (ppm)


8.080
8.061
7.833
7.812
7.730
7.711
7.690
7.494
7.473
7.463
7.455
7.058
3.149
3.133
3.117
2.937
2.920
2.903
2.127
2.111
2.094
2.077
2.058
2.040
S
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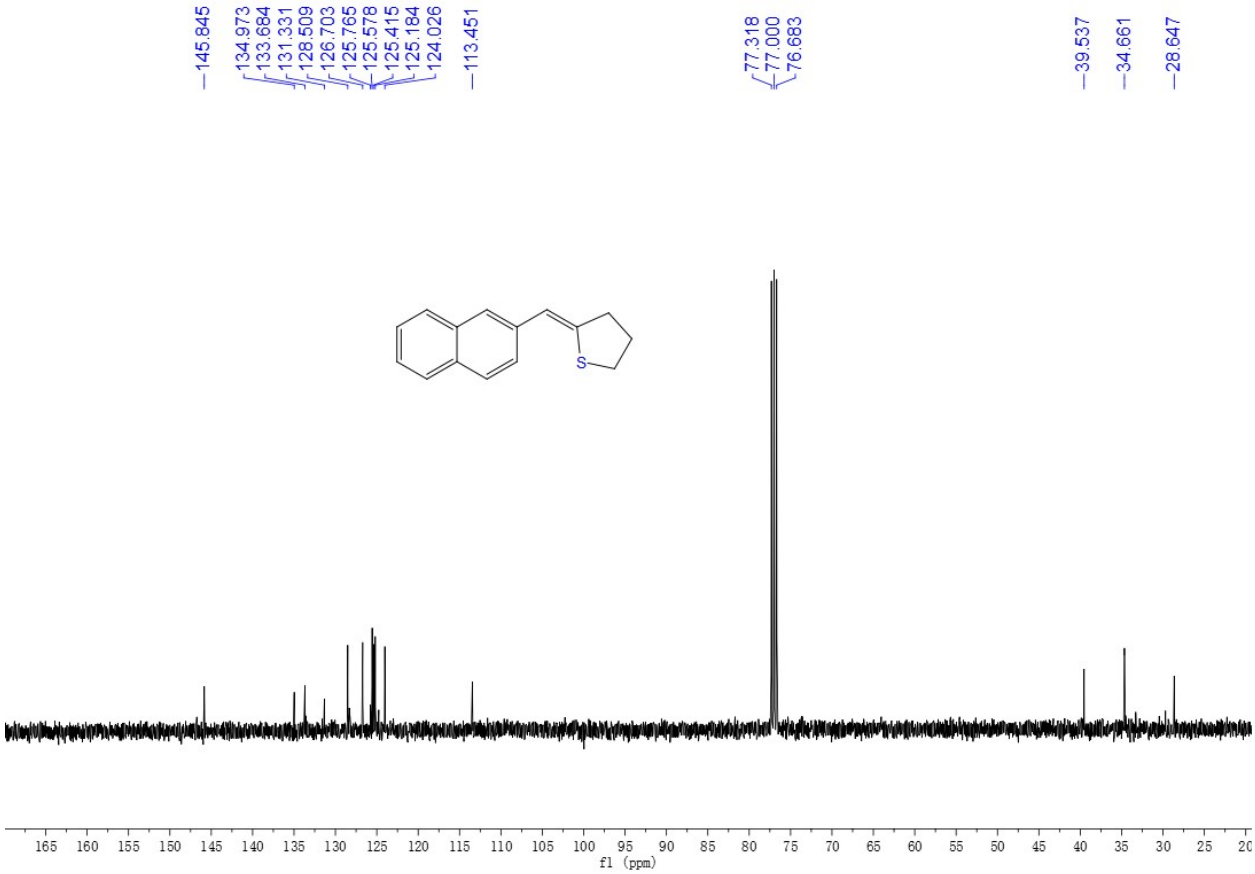
1.07
2.06
2.00
1.00
1.00
2.04
2.00
2.11
f1 (ppm)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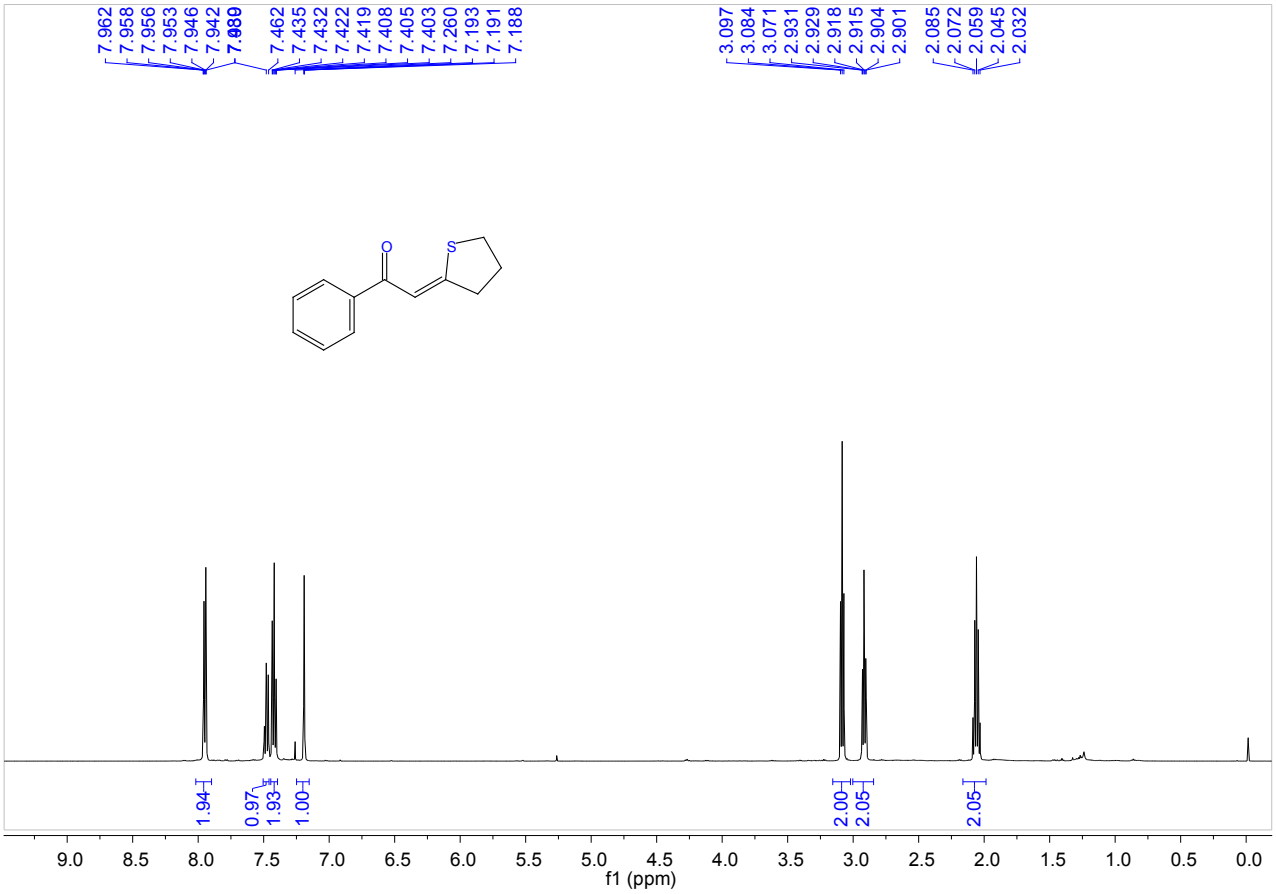
134.973
133.684
131.331
128.509
126.703
125.765
125.578
125.415
125.184
124.026
113.451
77.318
77.000
76.683
39.537
34.661
28.647
S
f1 (ppm)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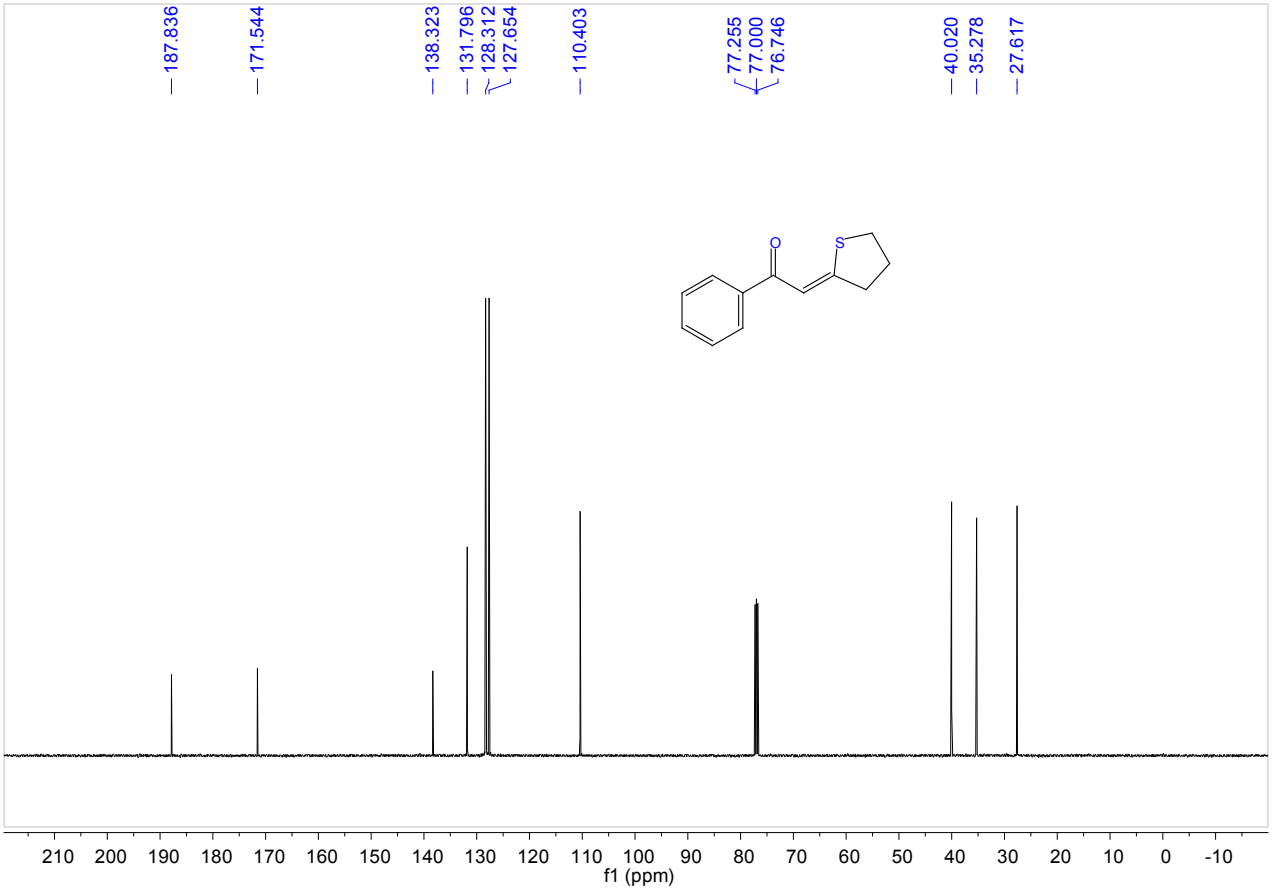
7.956
7.953
7.946
7.942
7.462
7.435
7.432
7.422
7.419
7.408
7.405
7.403
7.260
7.193
7.191
7.188
3.097
3.084
3.071
2.931
2.929
2.918
2.915
2.904
2.901
2.085
2.072
2.059
2.045
2.032
O
S
1.94
0.97
1.93
1.00
2.00
2.05
2.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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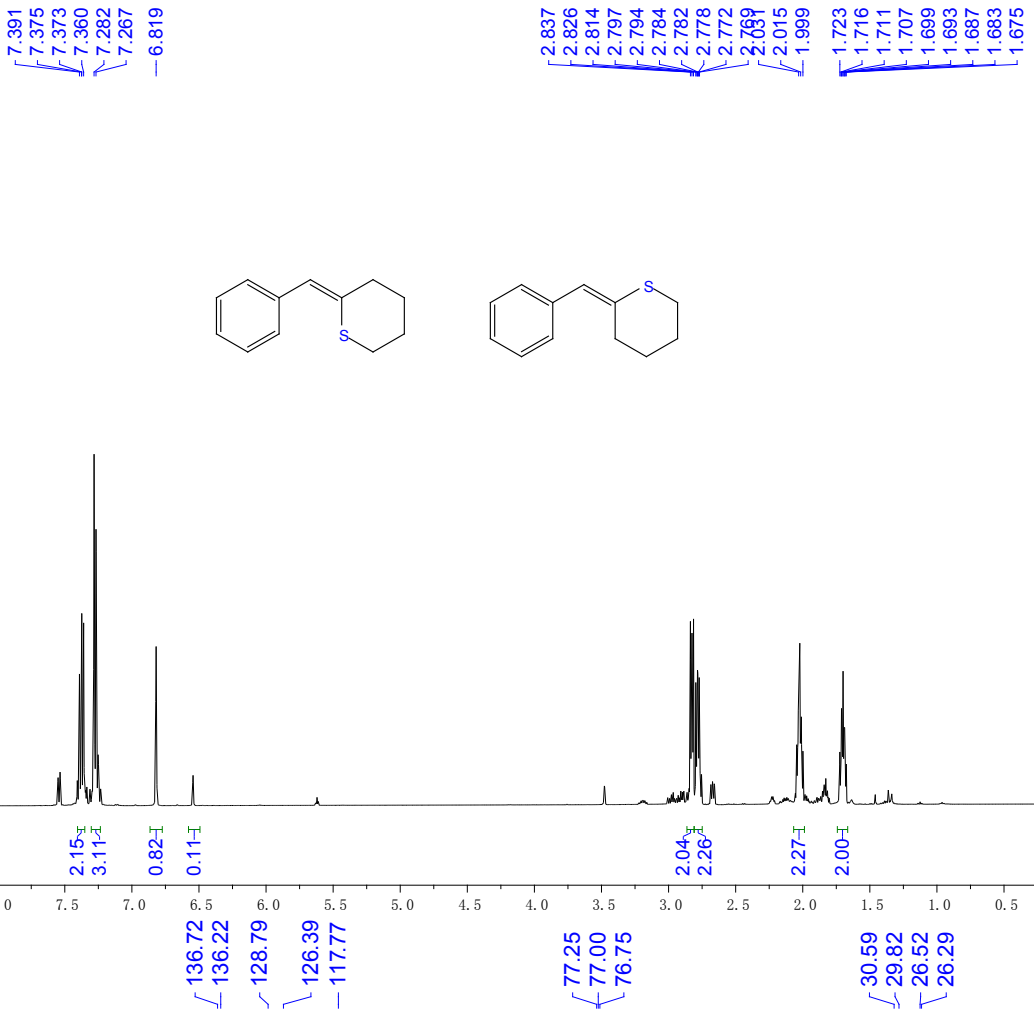
171.544
138.323
131.796
128.312
127.654
110.403
77.255
77.000
76.746
40.020
35.278
27.617
O
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.282
7.267
6.819
2.837
2.826
2.814
2.797
2.794
2.784
2.782
2.778
2.772
2.769
2.031
2.015
1.999
1.723
1.716
1.711
1.707
1.699
1.693
1.687
1.683
1.675
S
S
2.15
3.11
0.82
0.11
2.04
2.26
2.27
2.00
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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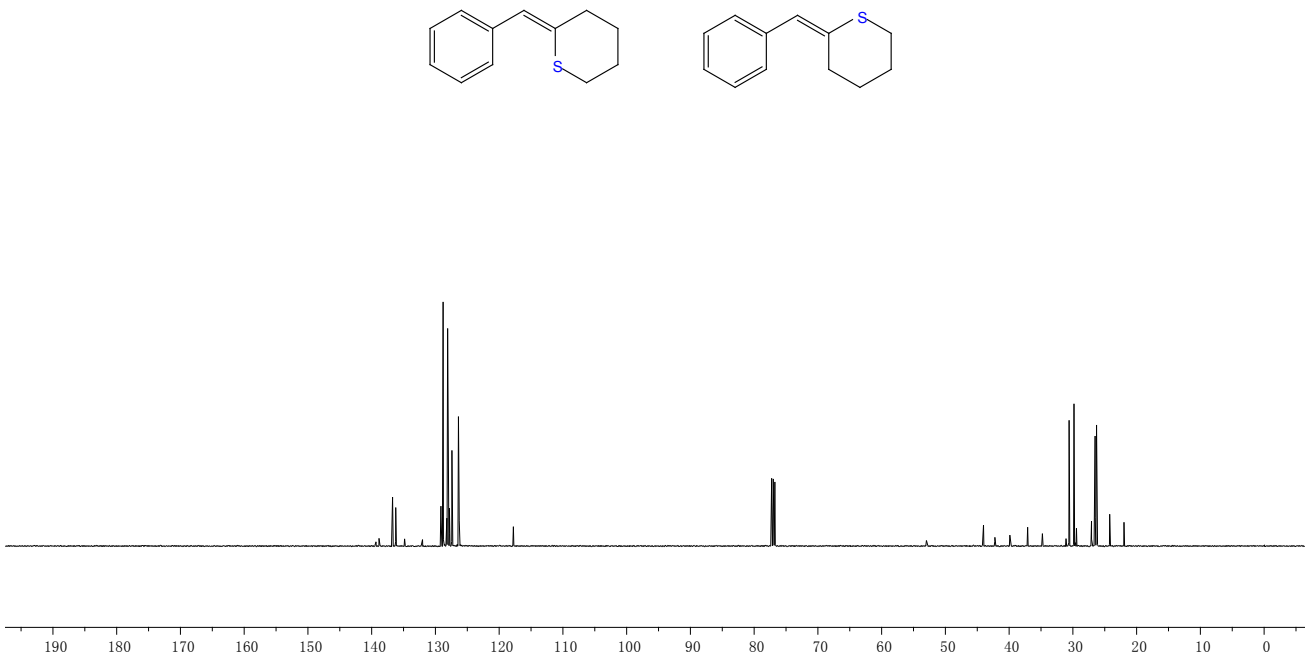
136.22
128.79
126.39
117.77
77.25
77.00
76.75
30.59
29.82
26.52
26.29


S
S
190
180
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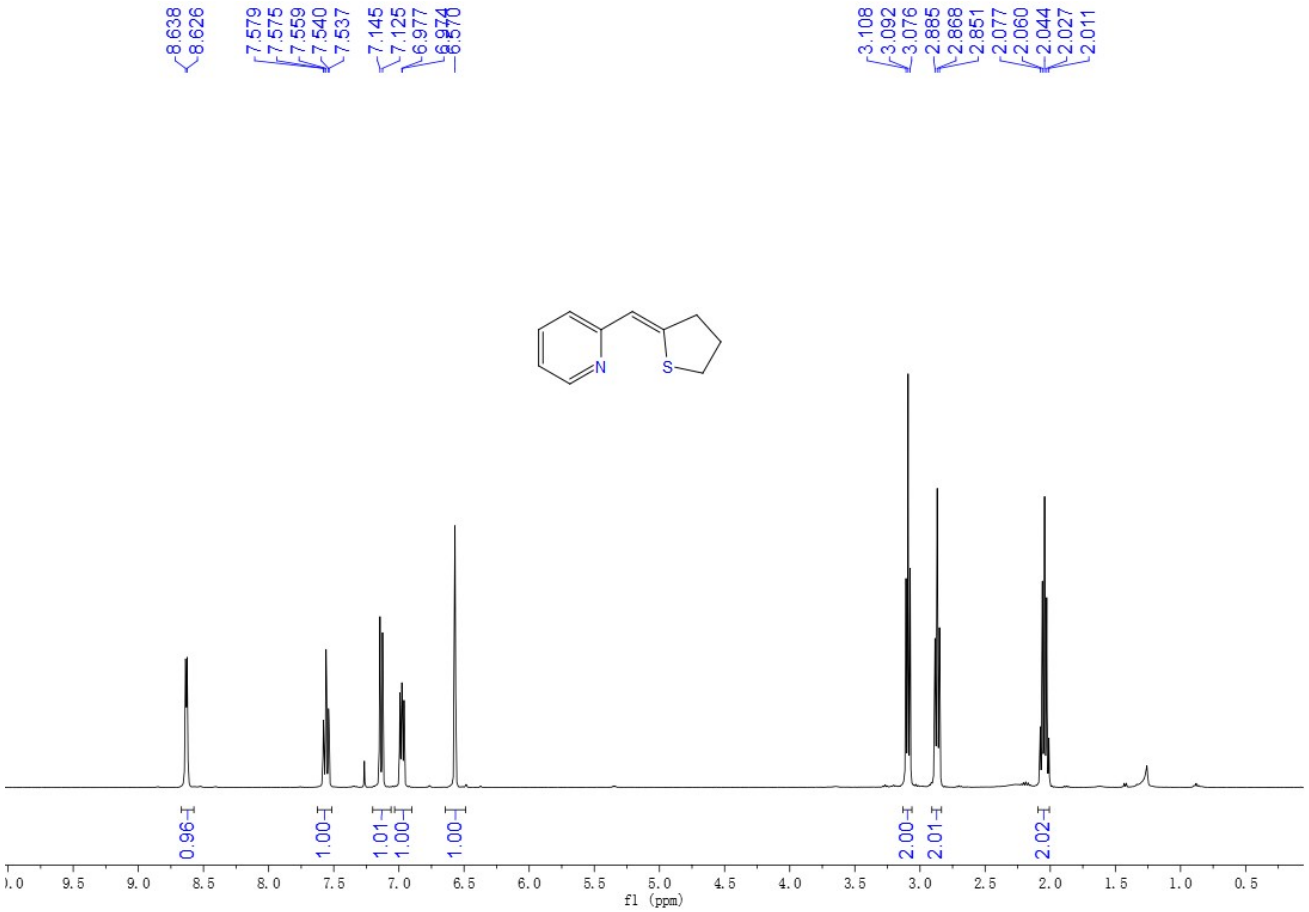
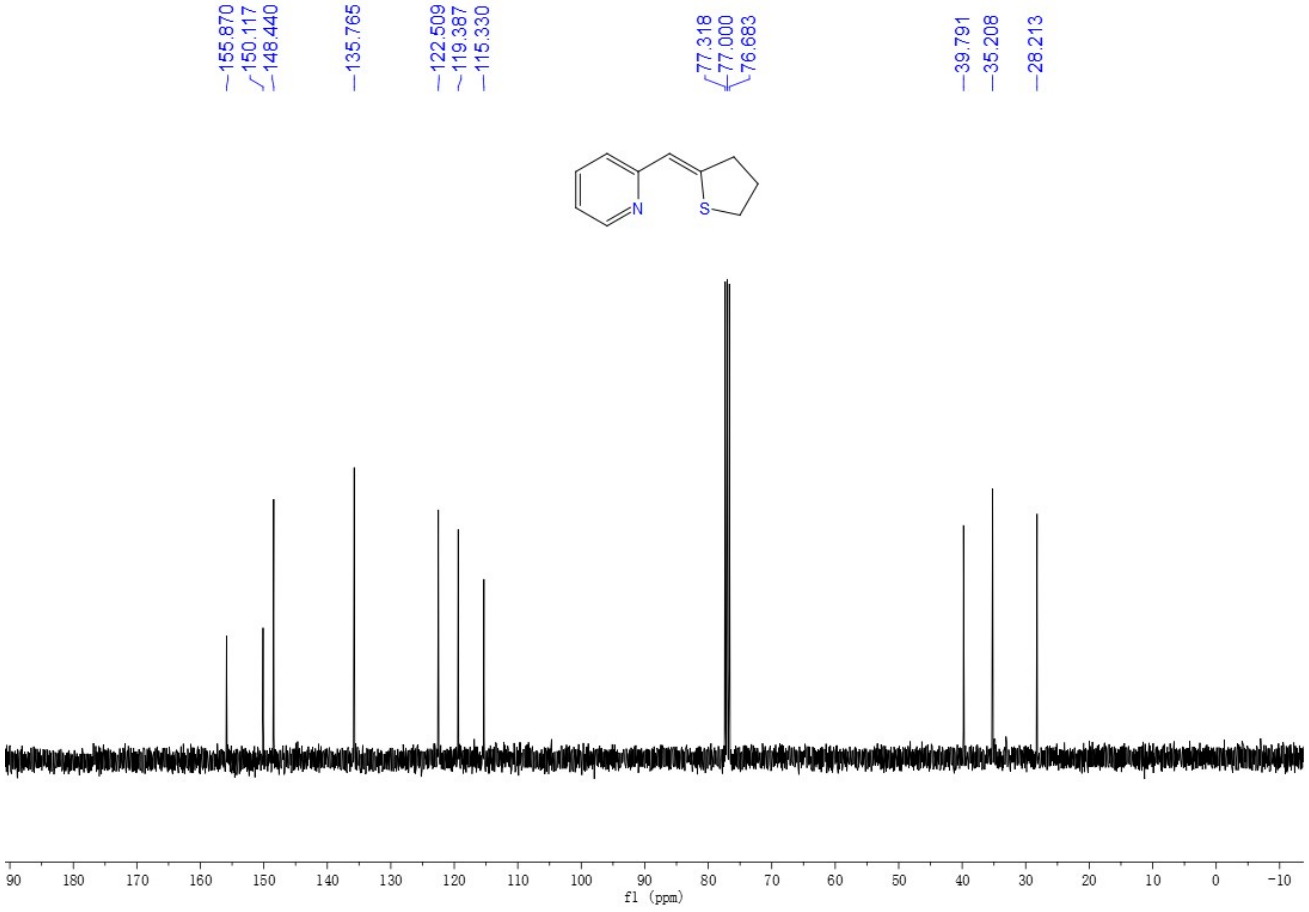
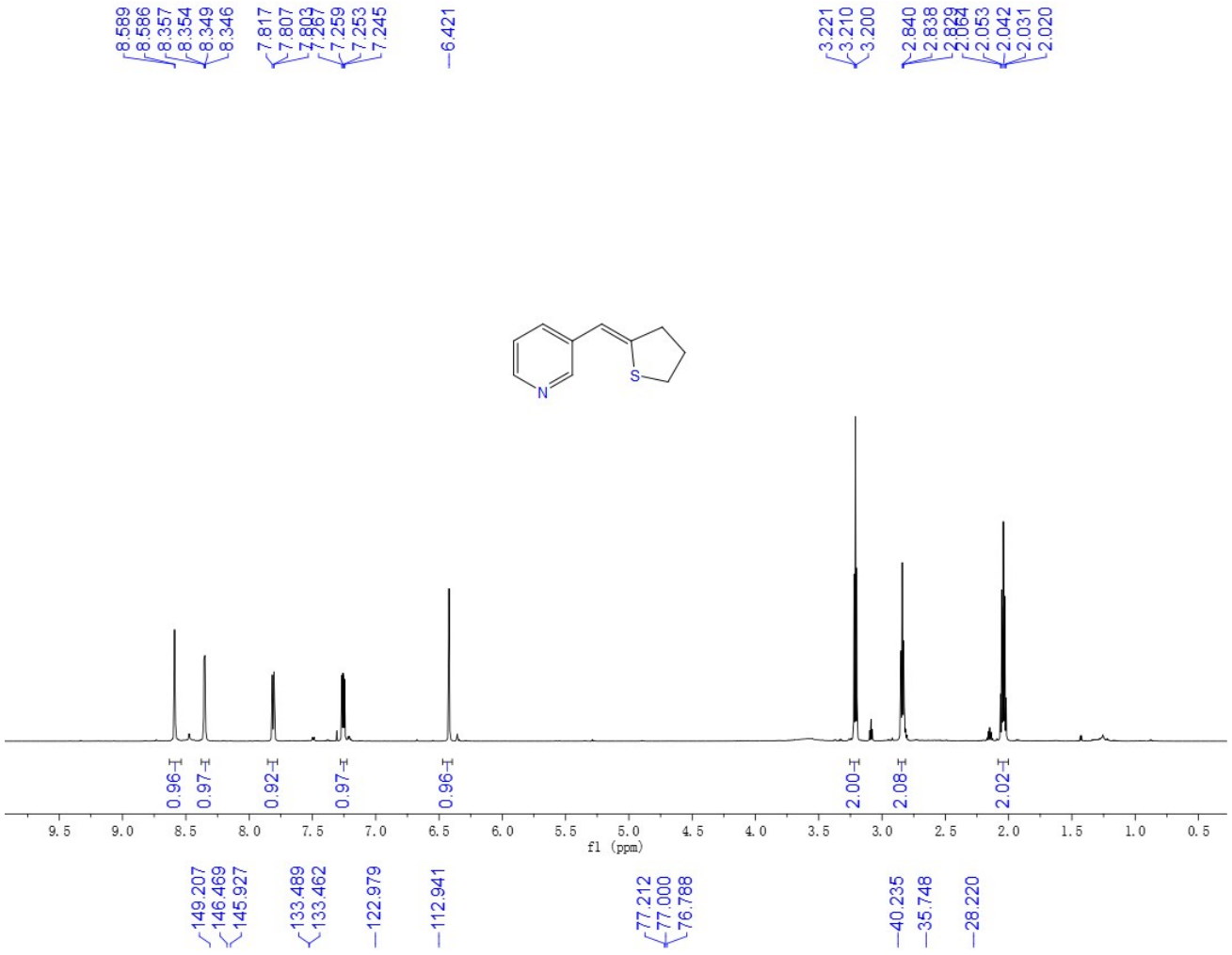
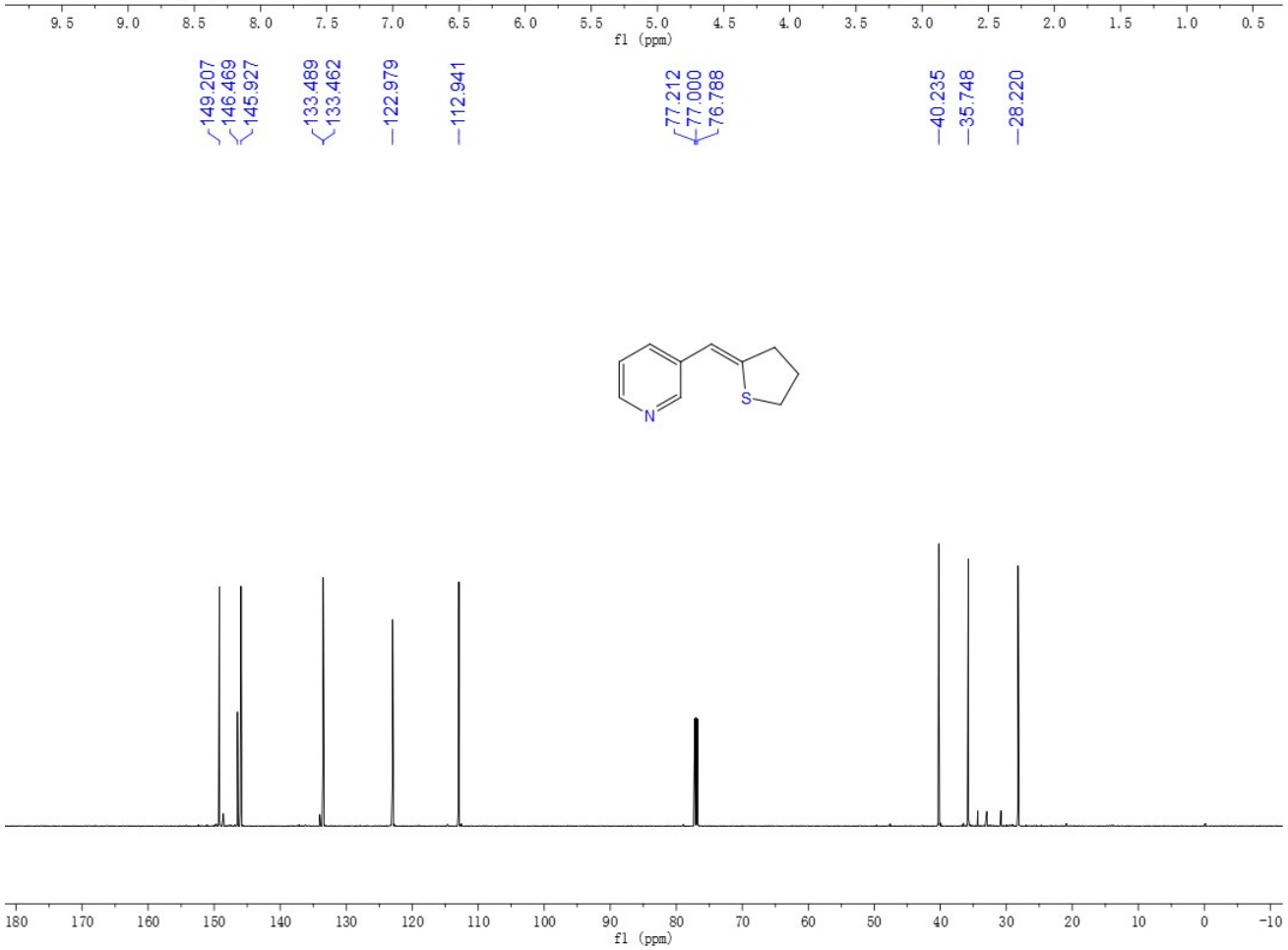
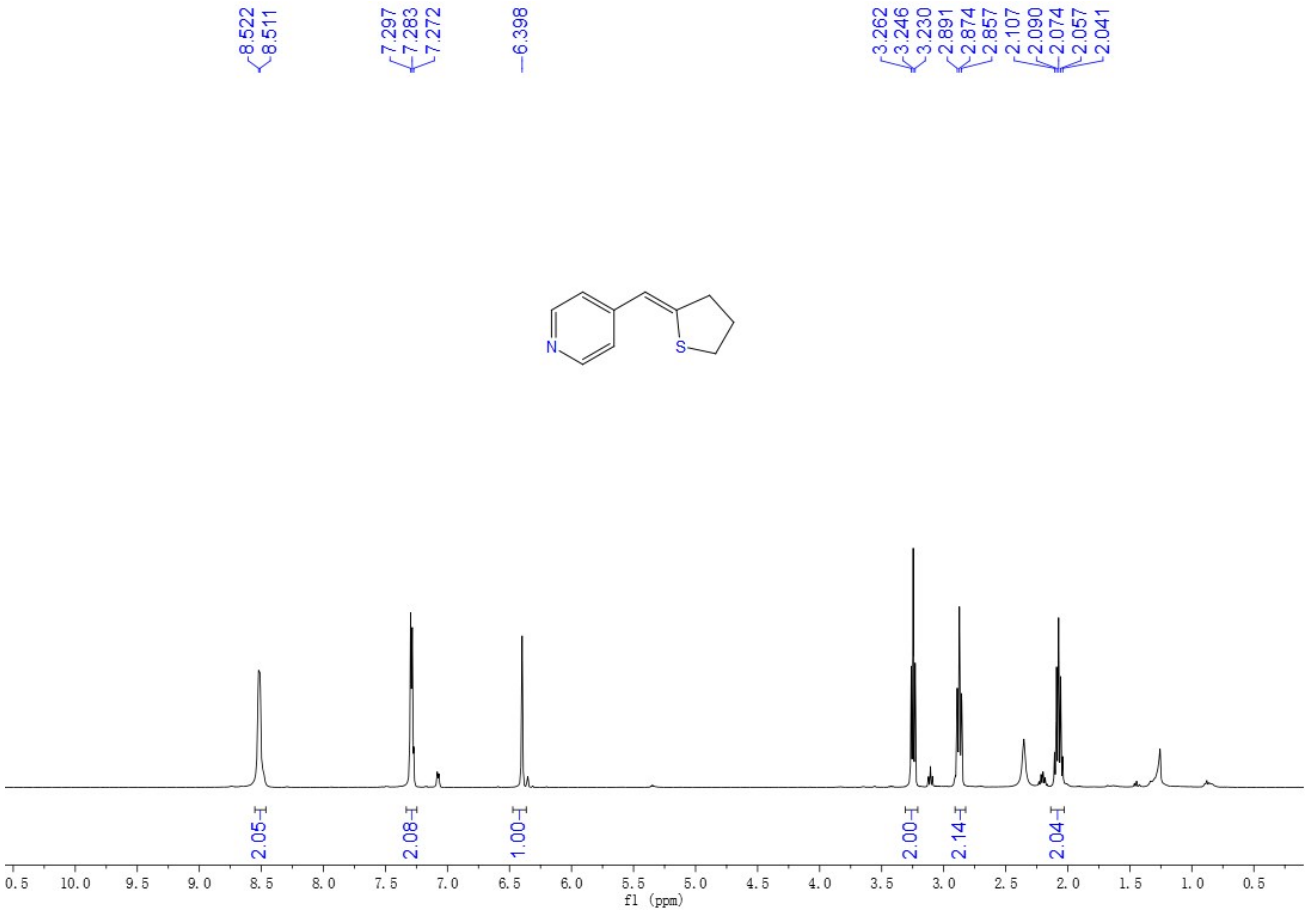
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.638
8.626
7.579
7.575
7.559
7.540
7.537
7.145
7.125
6.977
3.108
3.092
3.076
2.885
2.868
2.851
2.077
2.060
2.044
2.027
2.011
0.96
1.00
1.01
1.00
1.00
2.00
2.01
2.02
f1 (ppm)


155.870
150.117
148.440
135.765
122.509
119.387
115.330
77.318
77.000
76.683
39.791
35.208
28.213
f1 (ppm)


8.589
8.586
8.357
8.354
8.349
8.346
7.817
7.807
7.803
7.267
7.259
7.253
7.245
6.421
3.221
3.210
3.200
2.840
2.838
2.829
2.053
2.042
2.031
2.020
0.96
0.97
0.92
0.97
0.96
2.00
2.08
2.02
f1 (ppm)


149.207
146.469
145.927
133.489
133.462
122.979
112.941
77.212
77.000
76.788
40.235
35.748
28.220
f1 (ppm)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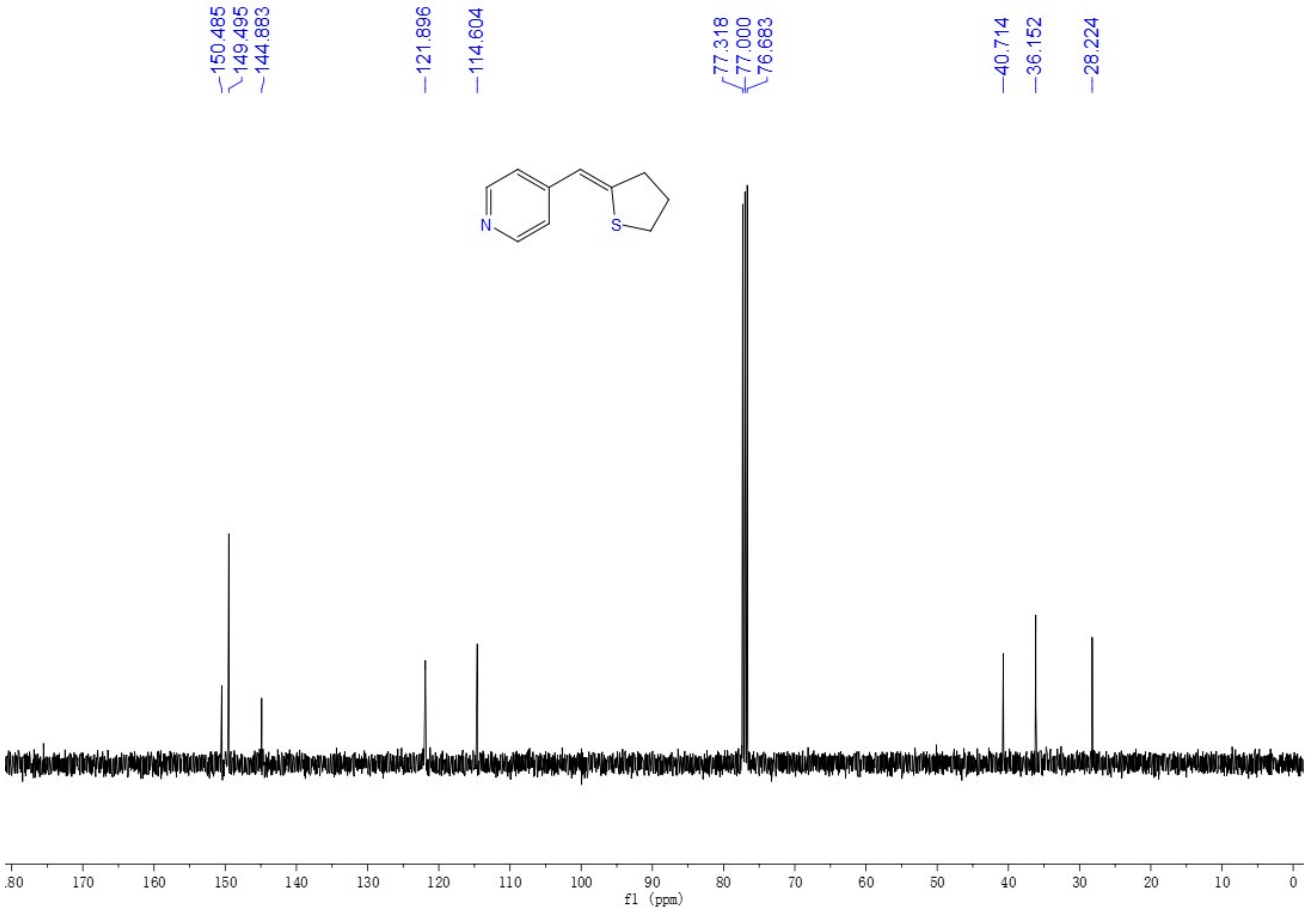
8.511
7.297
7.283
7.272
6.398
3.262
3.246
3.230
2.891
2.874
2.857
2.107
2.090
2.074
2.057
2.041
N
S
2.05
2.08
1.00
2.00
2.14
2.04
f1 (ppm)


150.485
149.495
144.883
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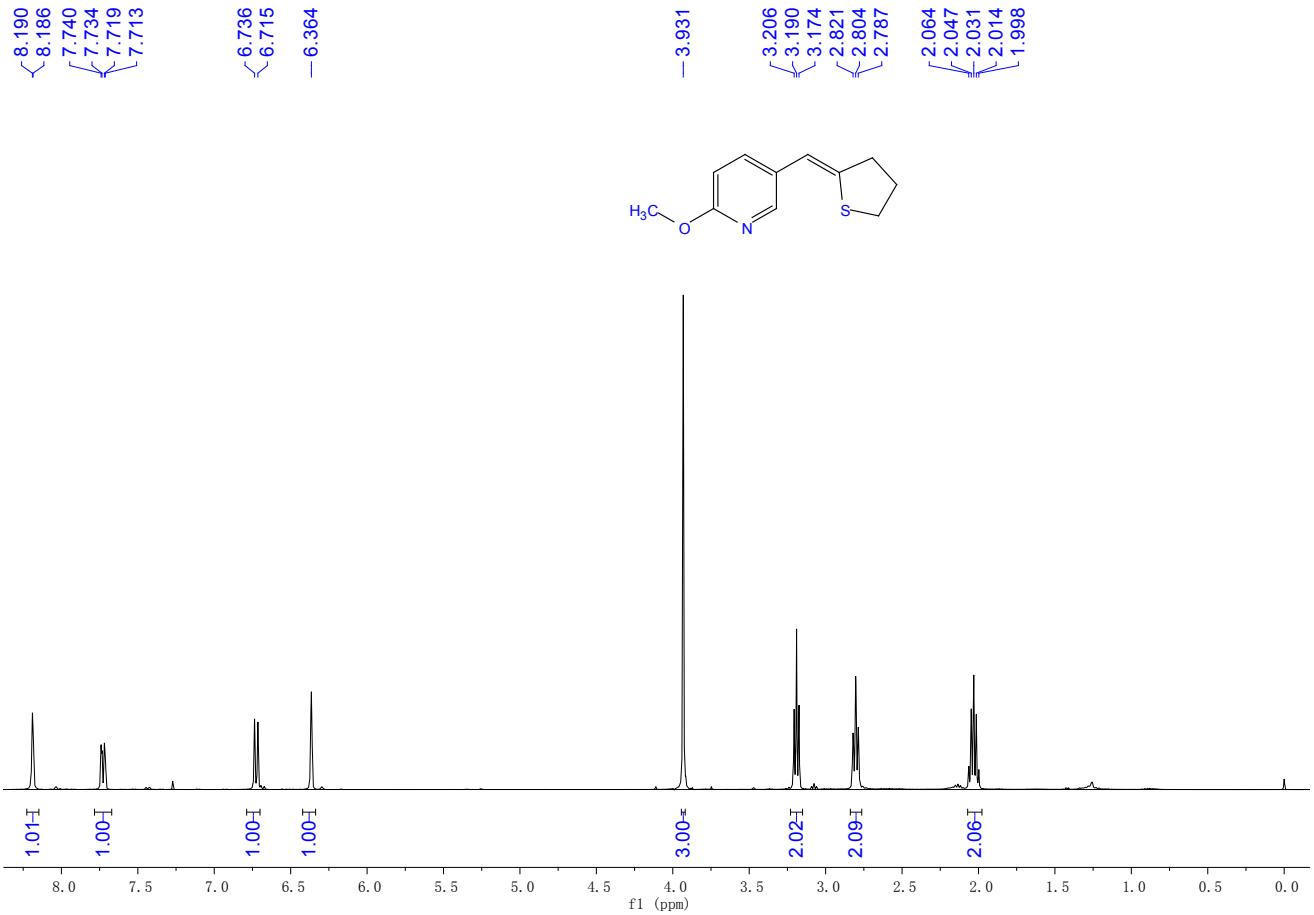
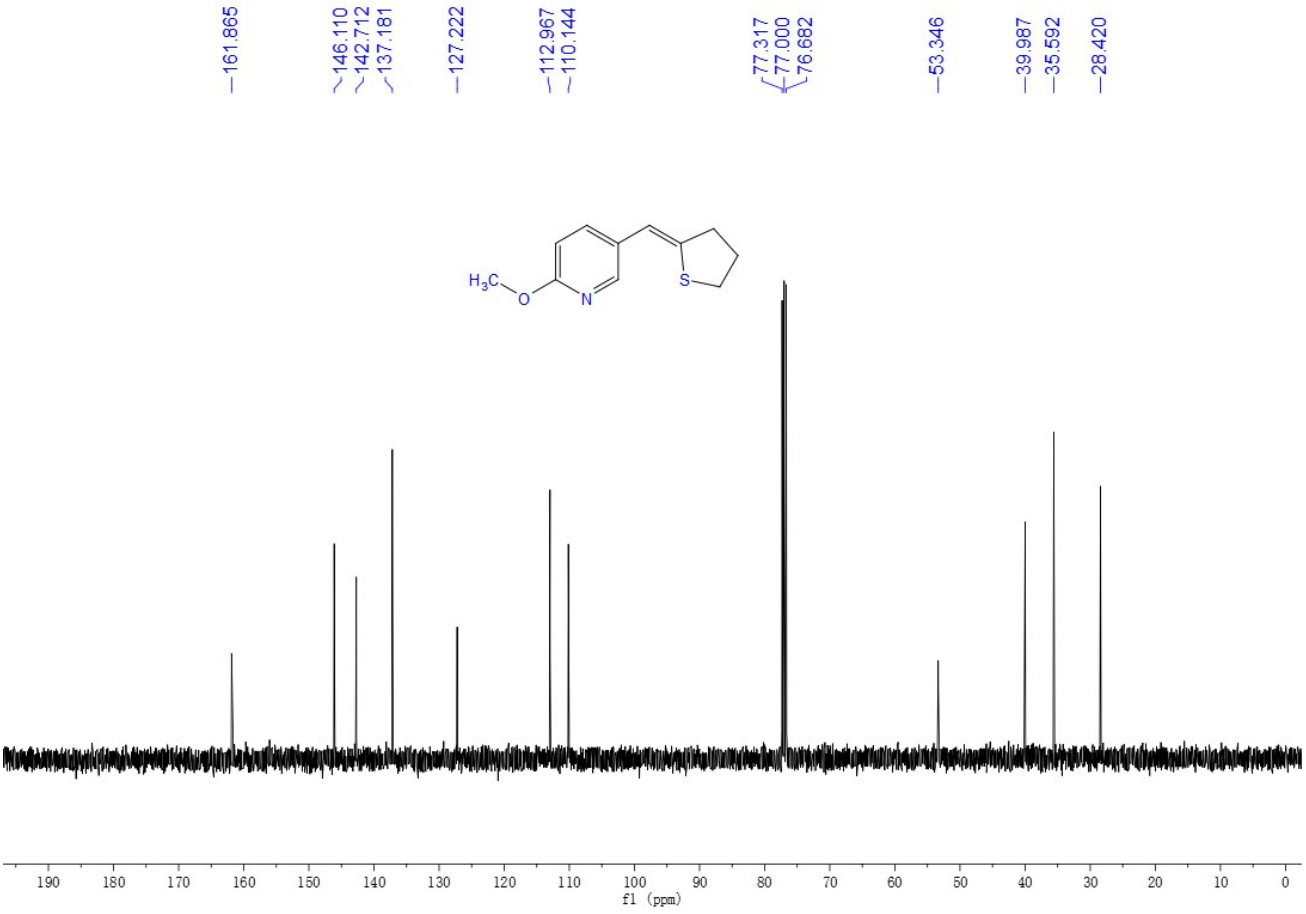
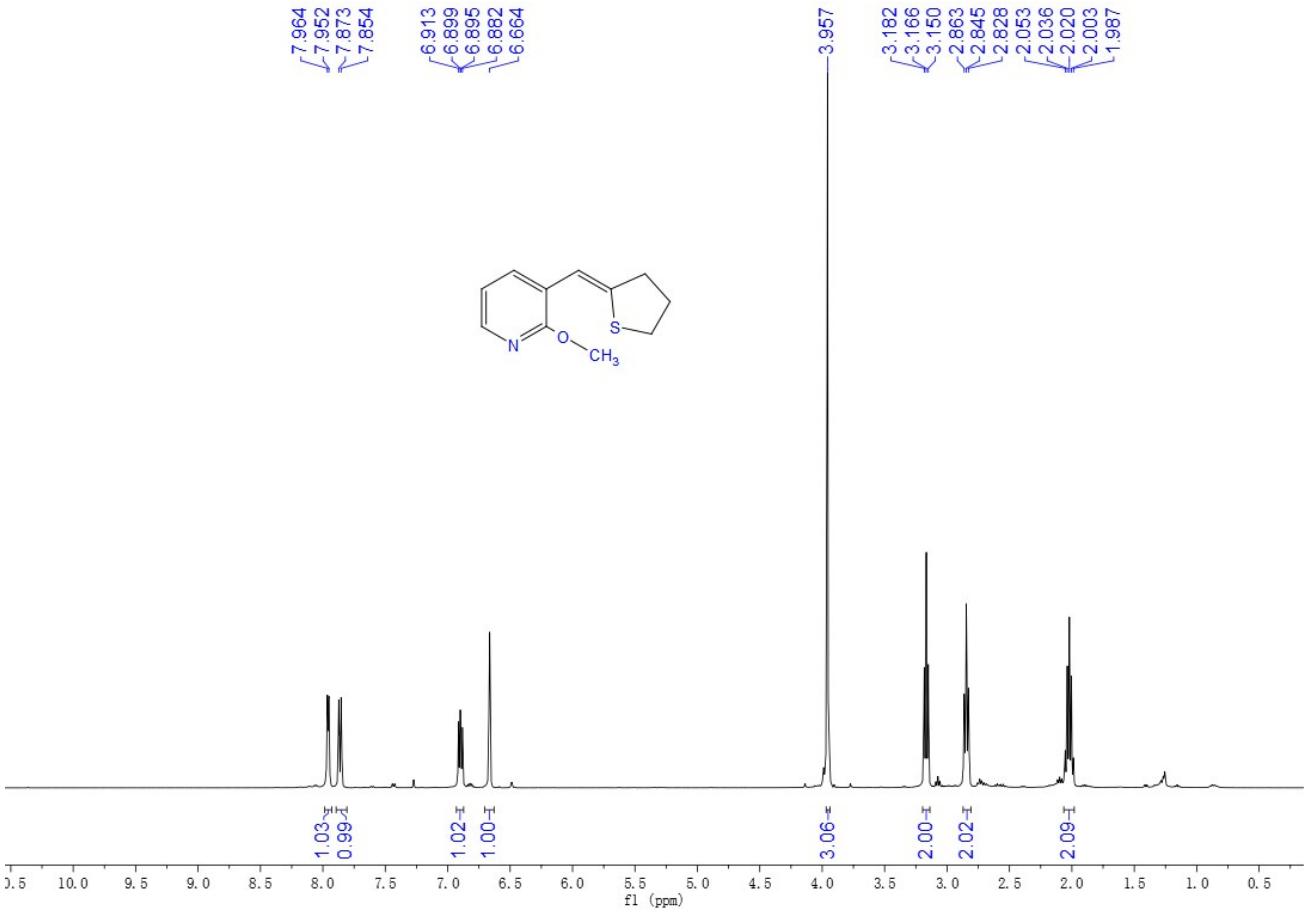
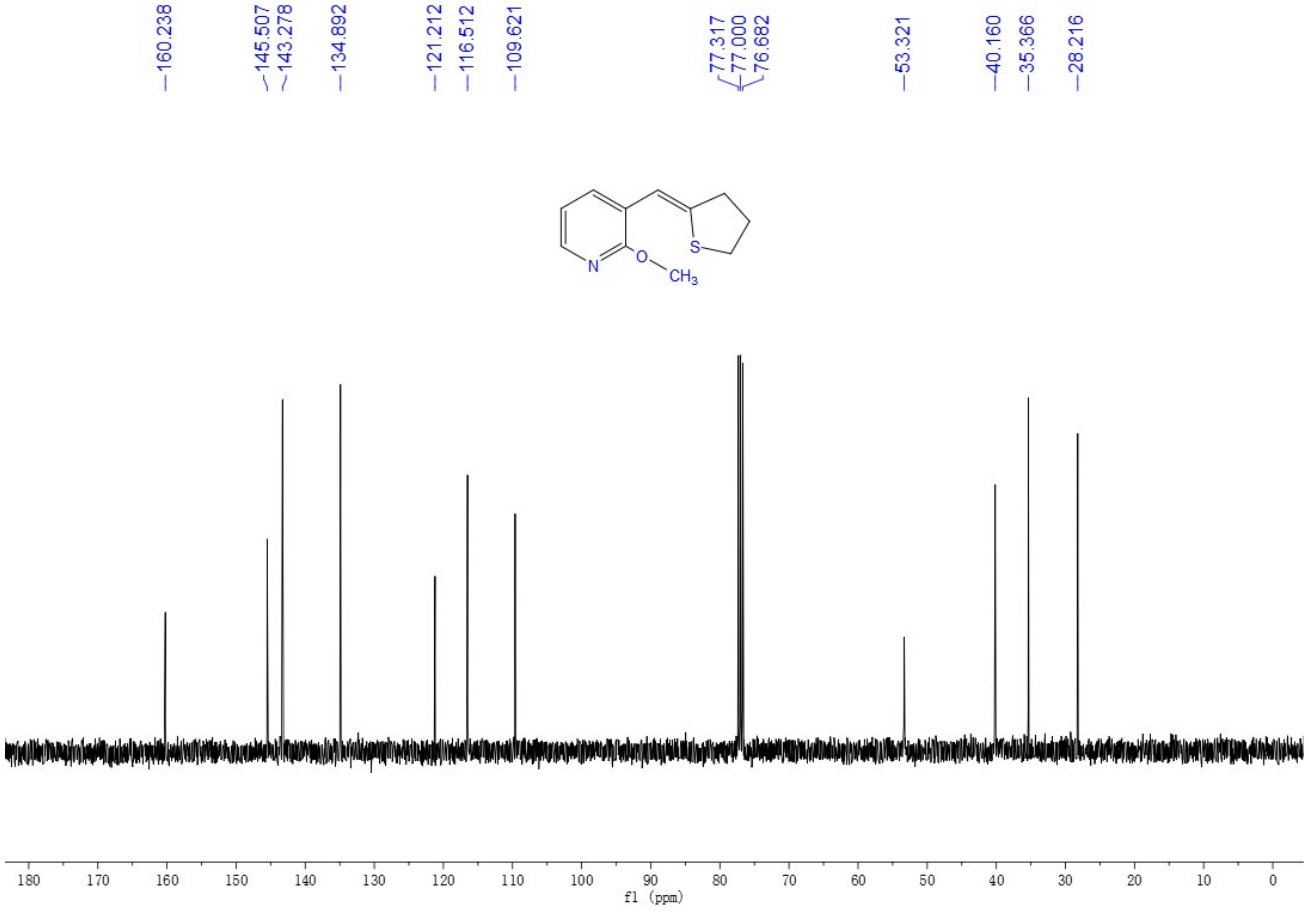
114.604
77.318
77.000
76.683
40.714
36.152
28.224
N
S
f1 (ppm)


8.190
8.186
7.740
7.734
7.719
7.713
6.736
6.715
6.364
3.931
3.206
3.190
3.174
2.821
2.804
2.787
2.064
2.047
2.031
2.014
1.998
H3C
O
N
S
1.01
1.00
1.00
1.00
3.00
2.02
2.09
2.06
f1 (ppm)


161.865
146.110
142.712
137.181
127.222
112.967
110.144
77.317
77.000
76.682
53.346
39.987
35.592
28.420
H3C
O
N
S
f1 (ppm)


7.964
7.952
7.873
7.854
6.913
6.899
6.895
6.882
6.664
3.957
3.182
3.166
3.150
2.863
2.845
2.828
2.053
2.036
2.020
2.003
1.987
1.03
0.99
1.02
1.00
3.06
2.00
2.02
2.09
f1 (ppm)


160.238
145.507
143.278
134.892
121.212
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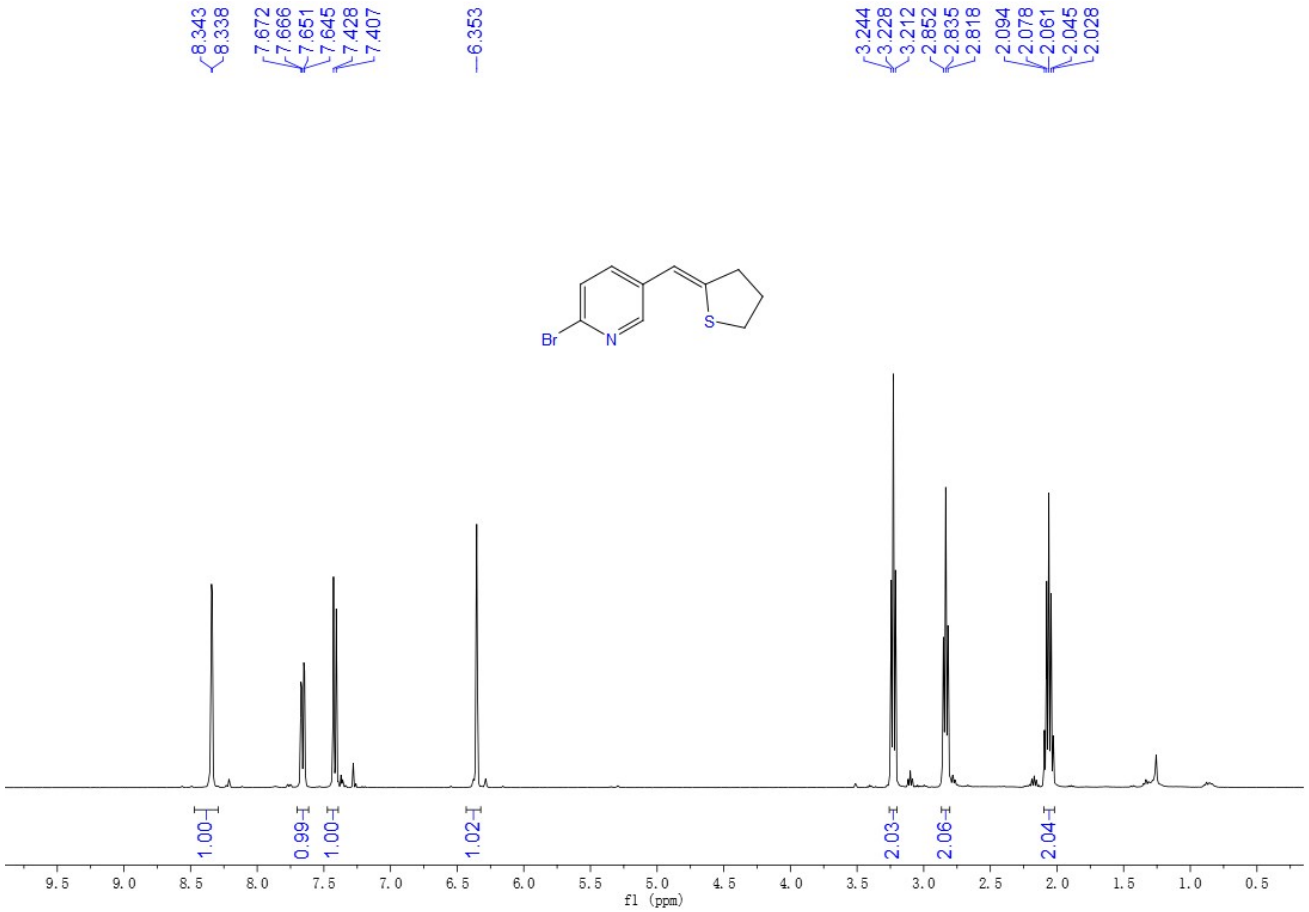
109.621
77.317
77.000
76.682
53.321
40.160
35.366
28.216
f1 (ppm)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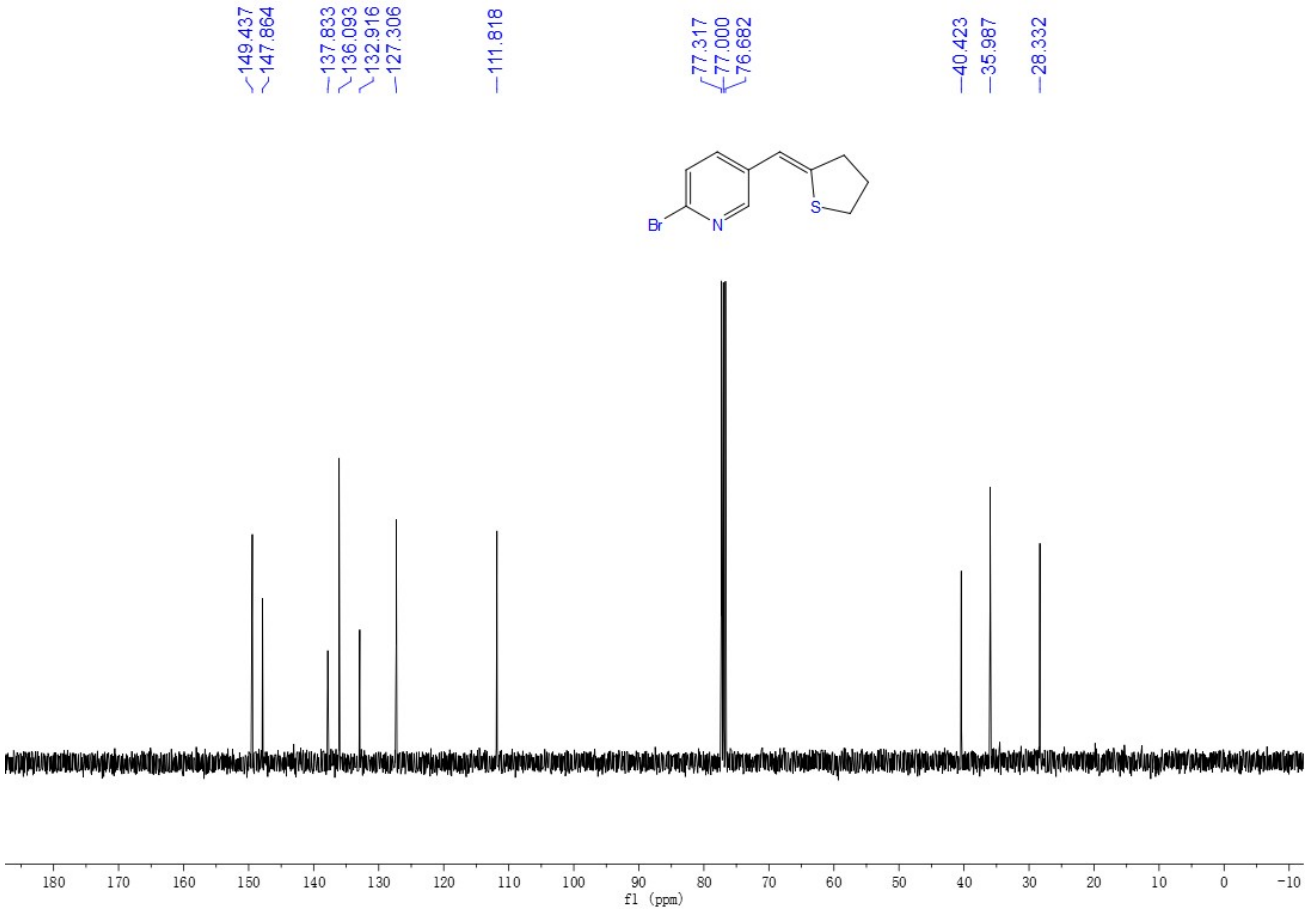
8.338
7.672
7.666
7.651
7.645
7.428
7.407
6.353
3.244
3.228
3.212
2.852
2.835
2.818
2.094
2.078
2.061
2.045
2.028
Br
N
S
1.00
0.99
1.00
1.02
2.03
2.06
2.04
f1 (ppm)


149.437
147.864
137.833
136.093
132.916
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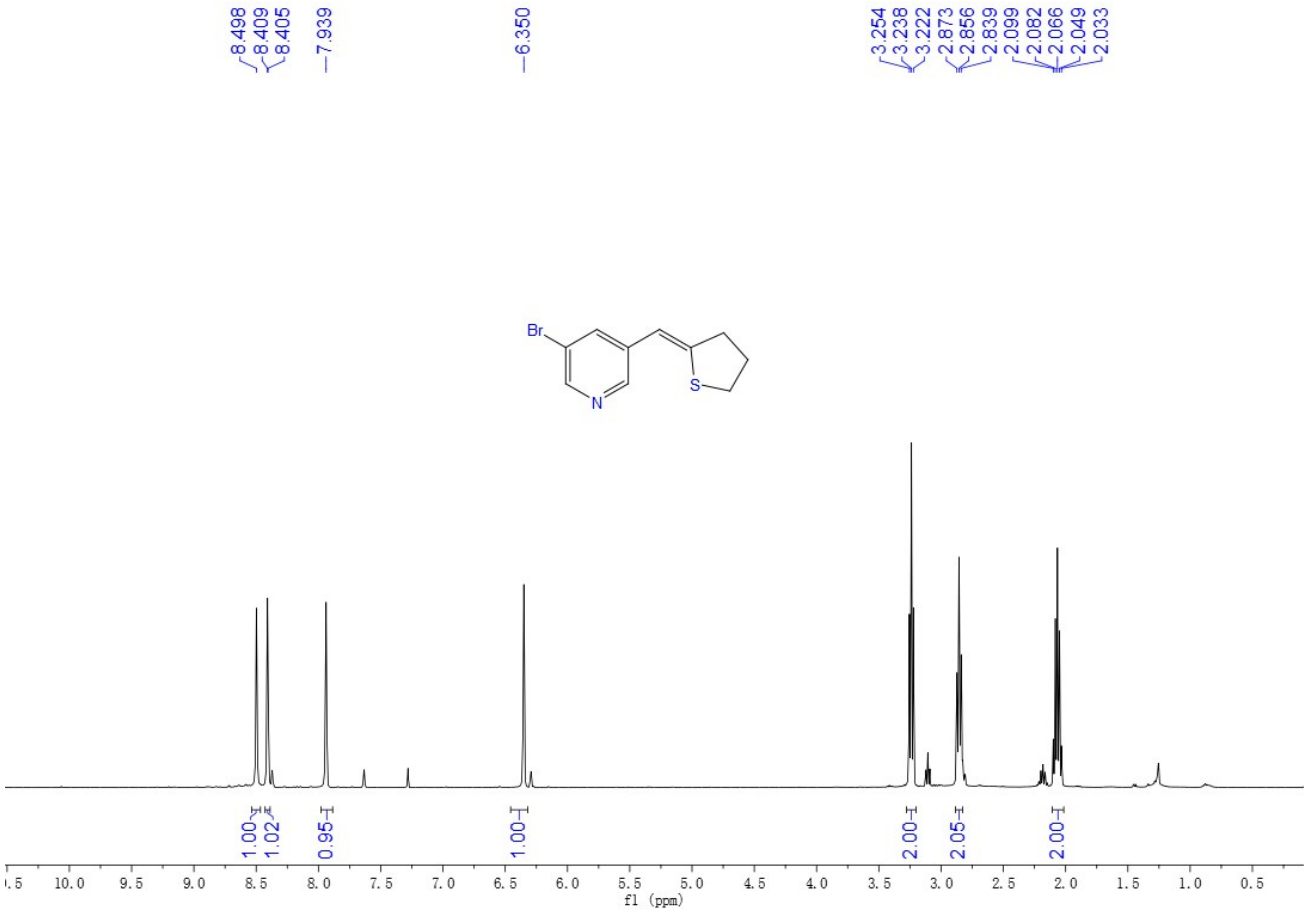
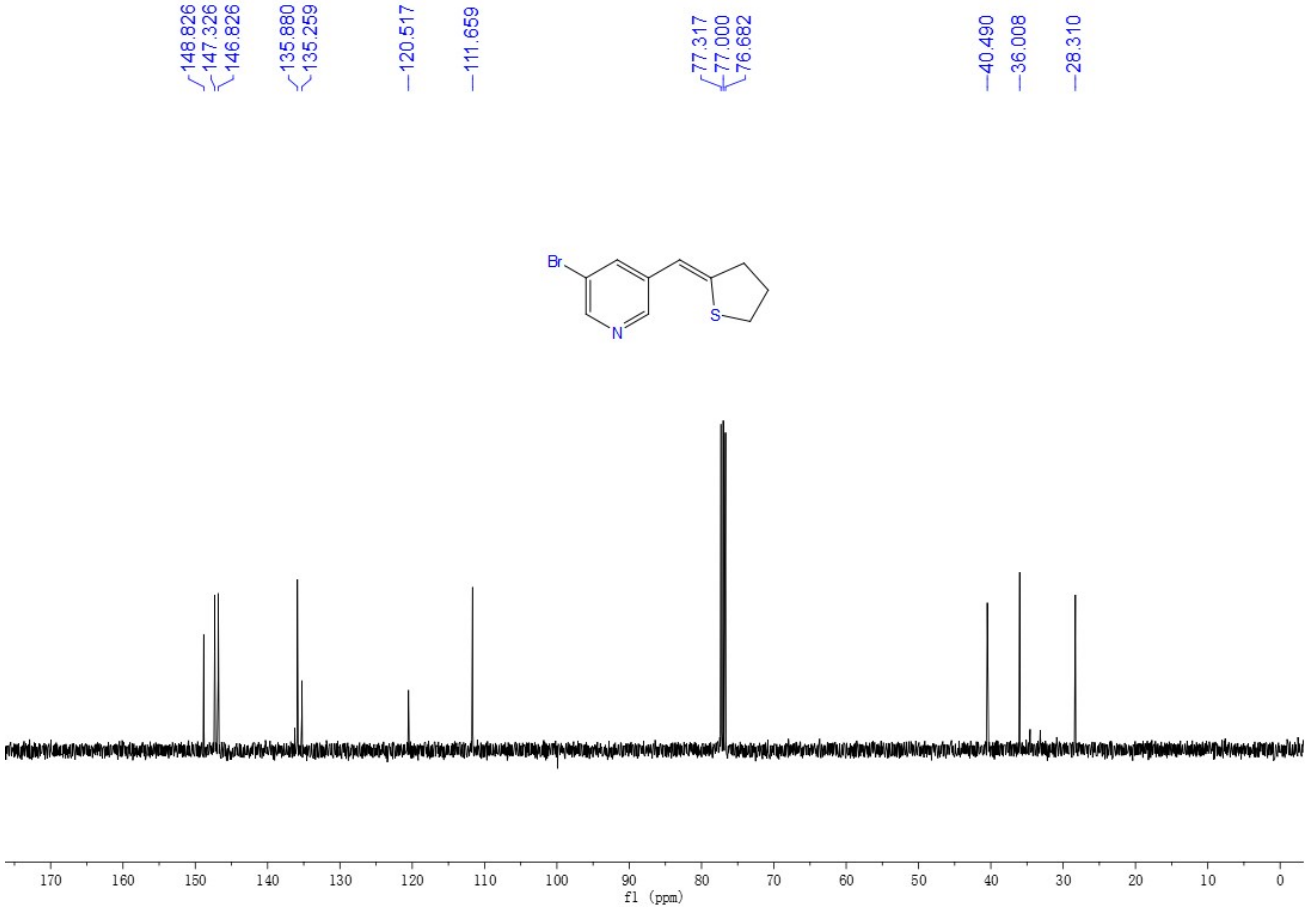
111.818
77.317
77.000
76.682
40.423
35.987
28.332
Br
N
S
f1 (ppm)


8.498
8.409
8.405
7.939
6.350
3.254
3.238
3.222
2.873
2.856
2.839
2.099
2.082
2.066
2.049
2.033
Br
N
S
1.00
1.02
0.95
1.00
2.00
2.05
2.00
f1 (ppm)


148.826
147.326
146.826
135.880
135.259
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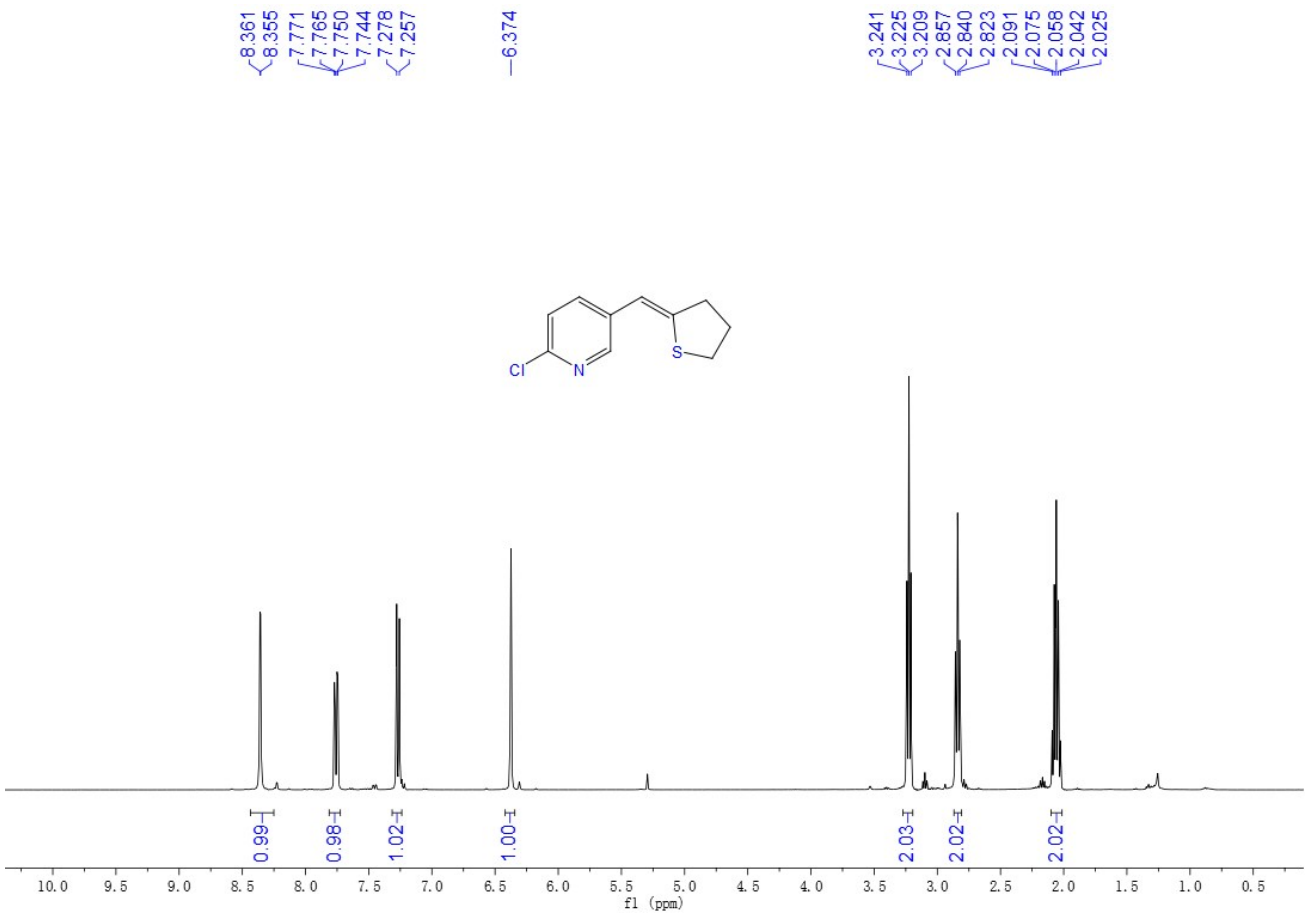
111.659
77.317
77.000
76.682
40.490
36.008
28.310
Br
N
S
f1 (ppm)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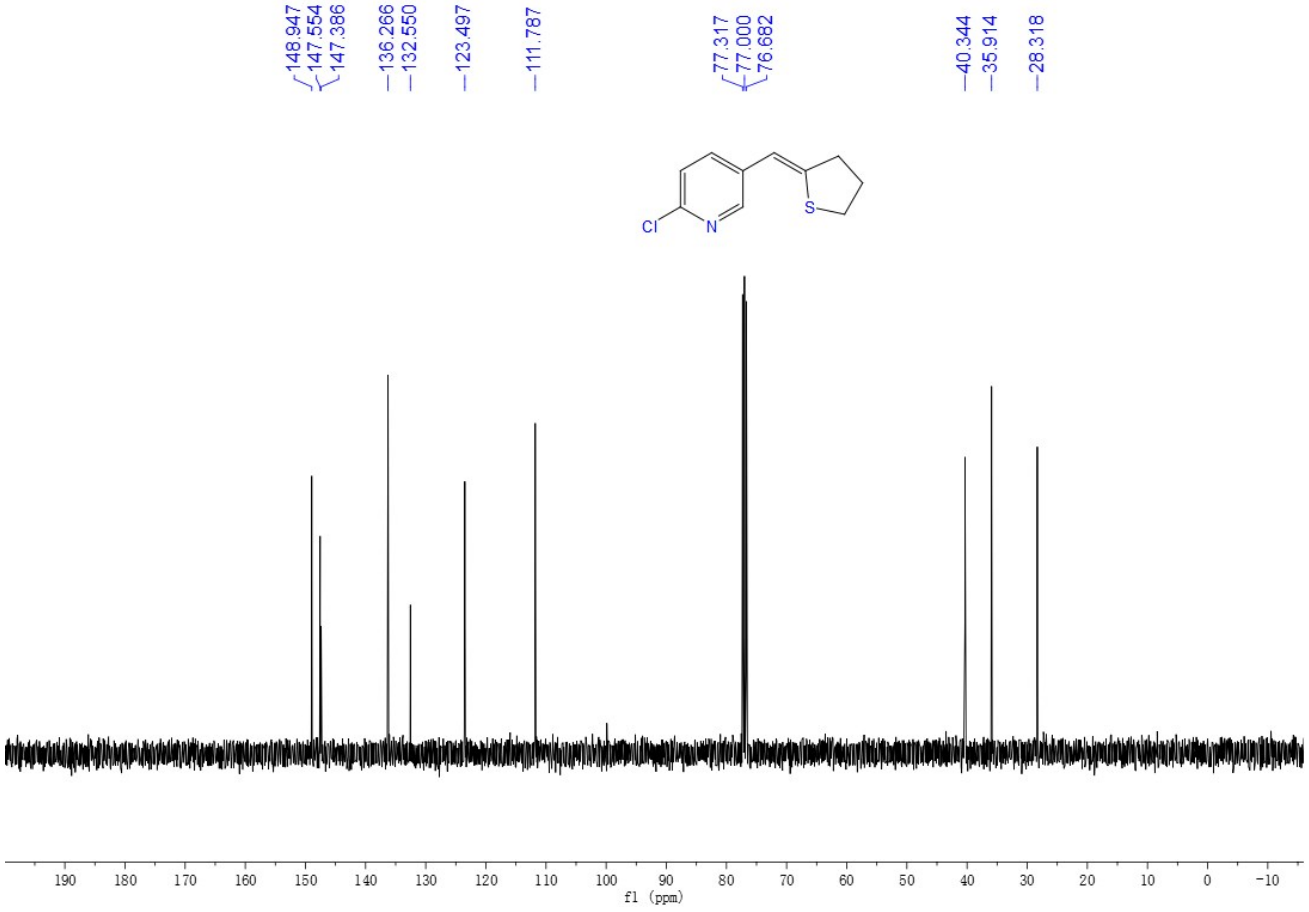
7.771
7.765
7.750
7.744
7.278
7.257
6.374
3.241
3.225
3.209
2.857
2.840
2.823
2.091
2.075
2.058
2.042
2.025
Cl
N
S
0.99
0.98
1.02
1.00
2.03
2.02
2.02
f1 (ppm)


148.947
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147.386
136.266
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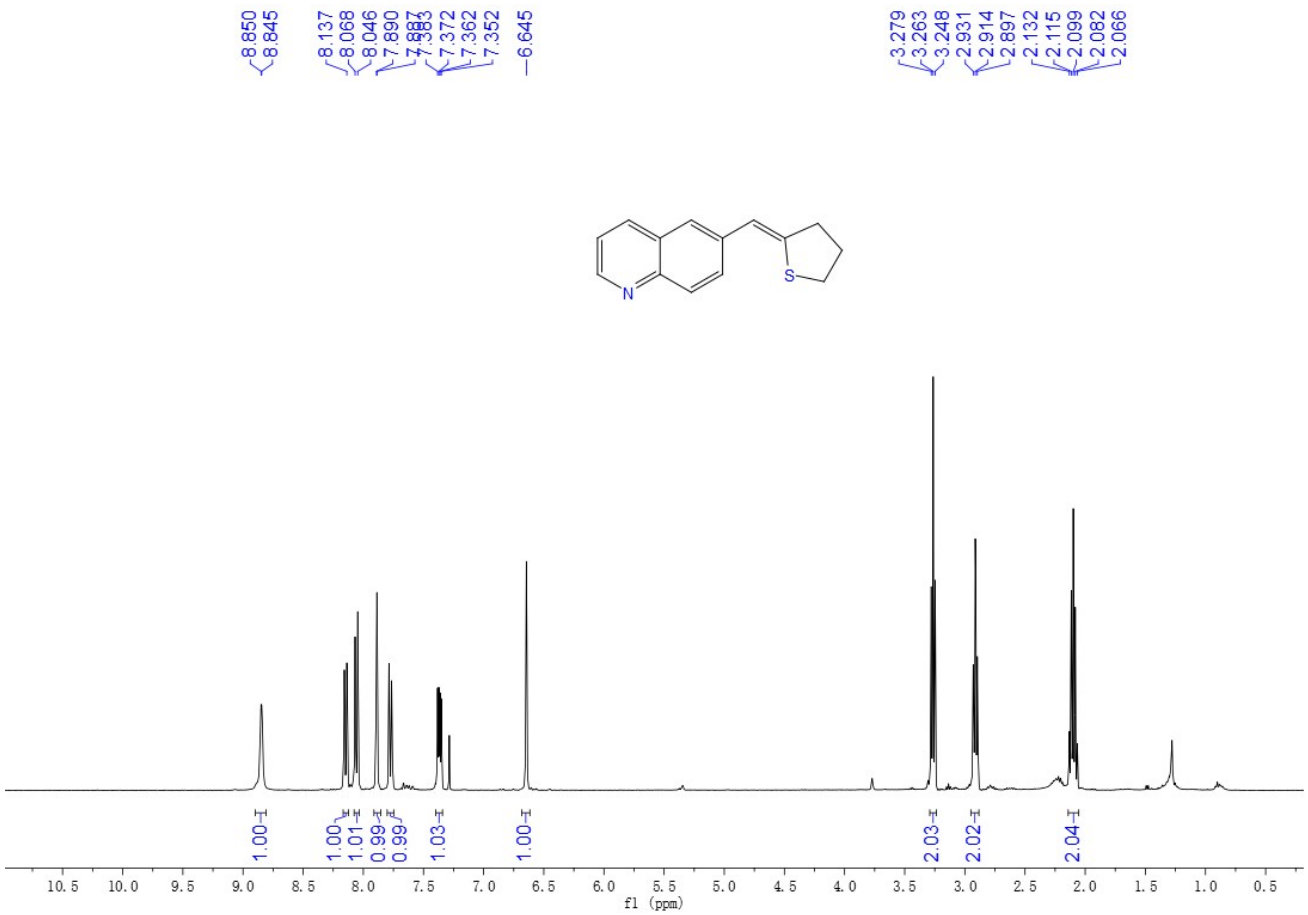
77.317
77.000
76.682
40.344
35.914
28.318
Cl
N
S
f1 (ppm)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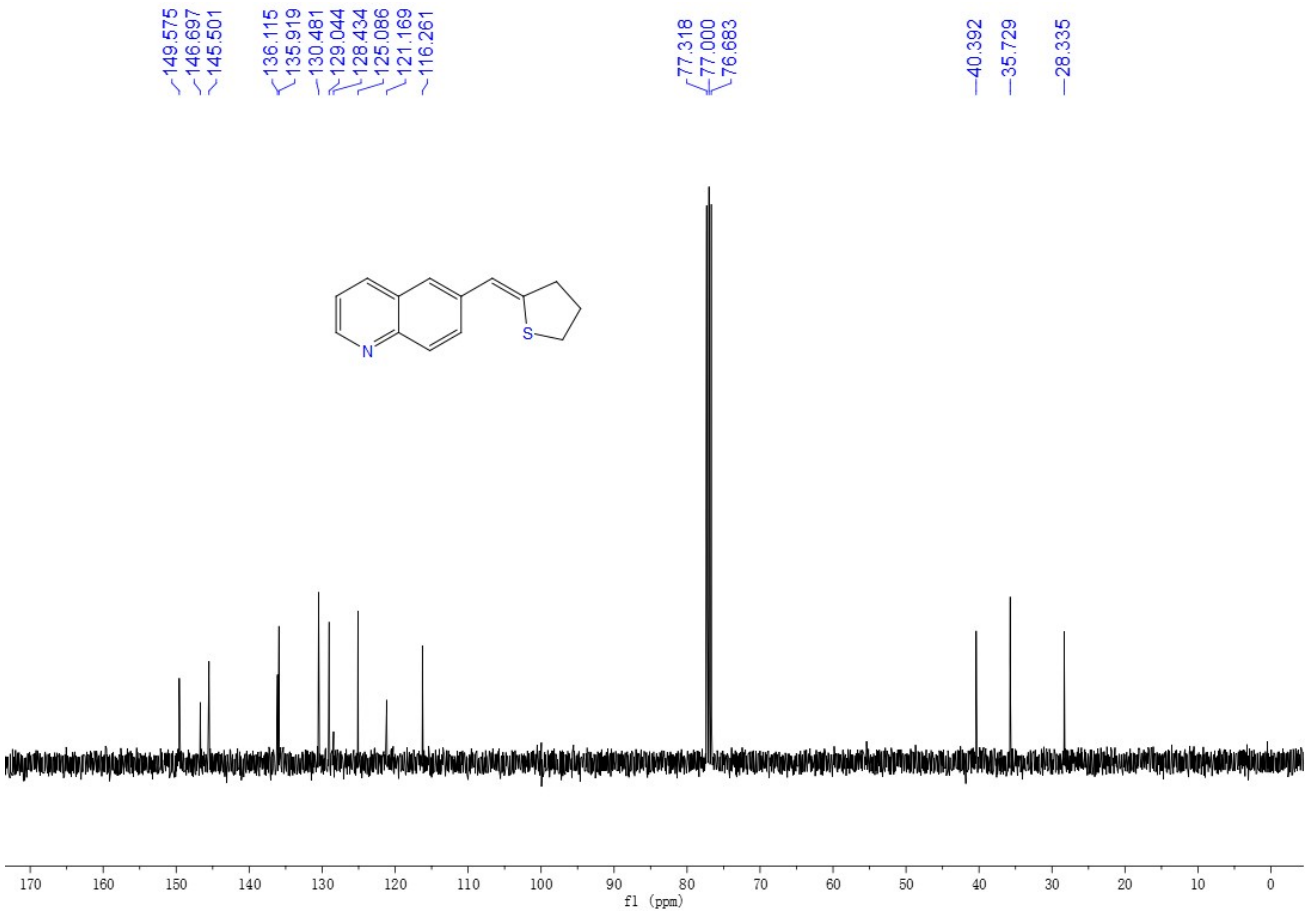
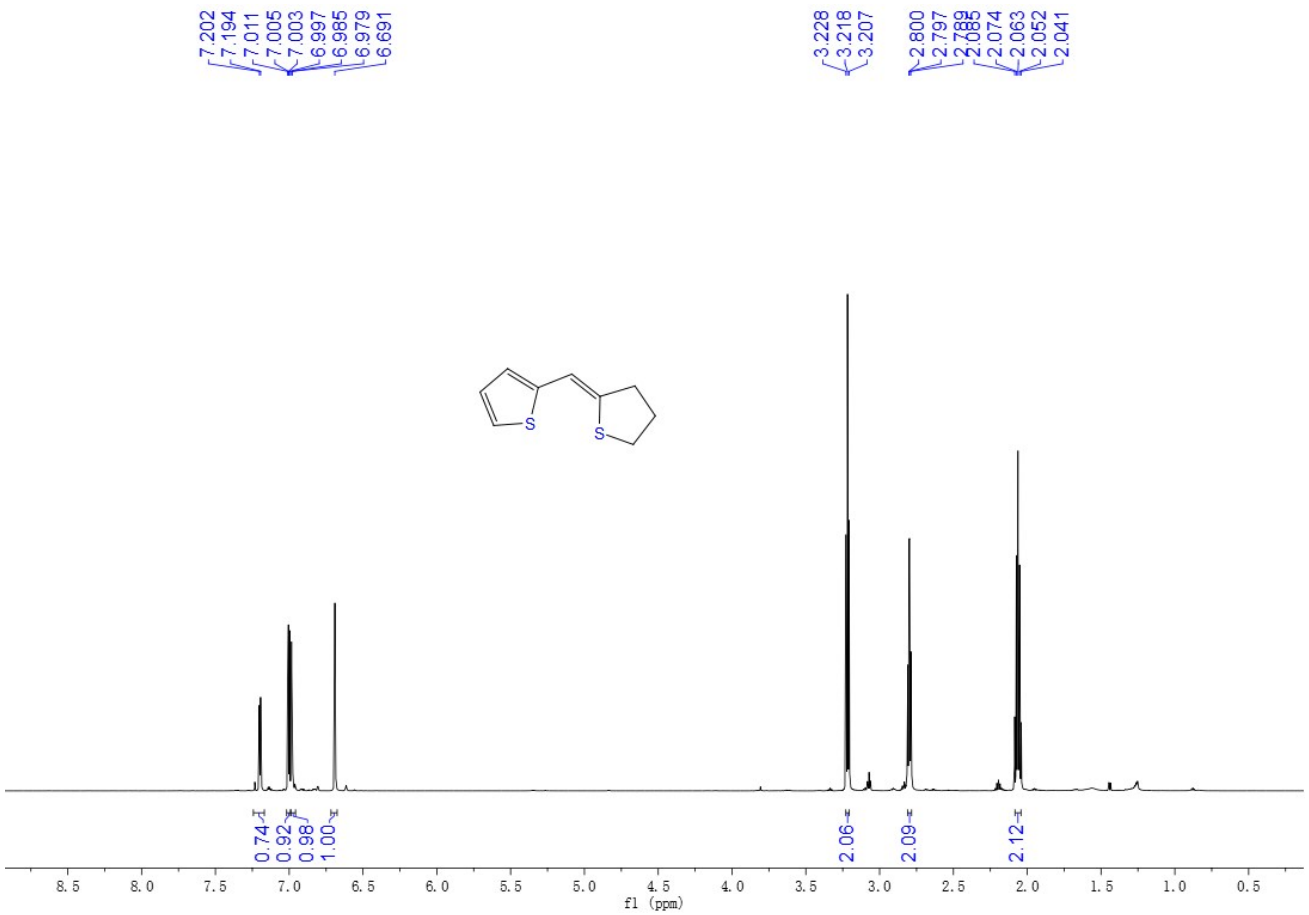
8.137
8.068
8.046
7.890
7.887
7.383
7.372
7.362
7.352
6.645
3.279
3.263
3.248
2.931
2.914
2.897
2.132
2.115
2.099
2.082
2.066
N
S
1.00
1.00
1.01
0.99
0.99
1.03
1.00
2.03
2.02
2.04
f1 (ppm)


149.575
146.697
145.501
136.115
135.919
130.481
129.044
128.434
125.086
121.169
116.261
77.318
77.000
76.683
40.392
35.729
28.335
N
S
f1 (ppm)


7.202
7.194
7.011
7.005
7.003
6.997
6.985
6.979
6.691
3.228
3.218
3.207
2.800
2.797
2.789
2.085
2.074
2.063
2.052
2.041
S
S
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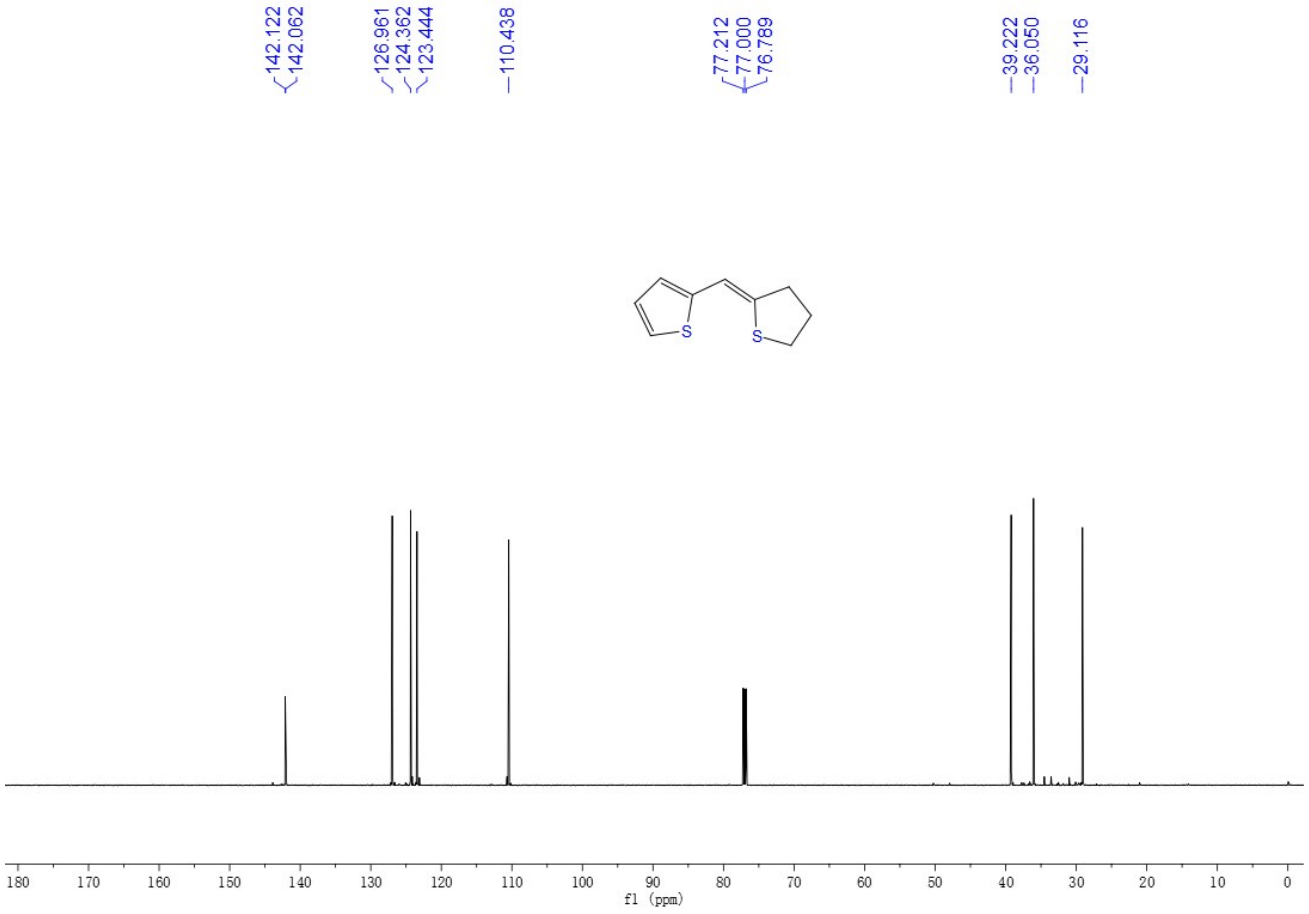
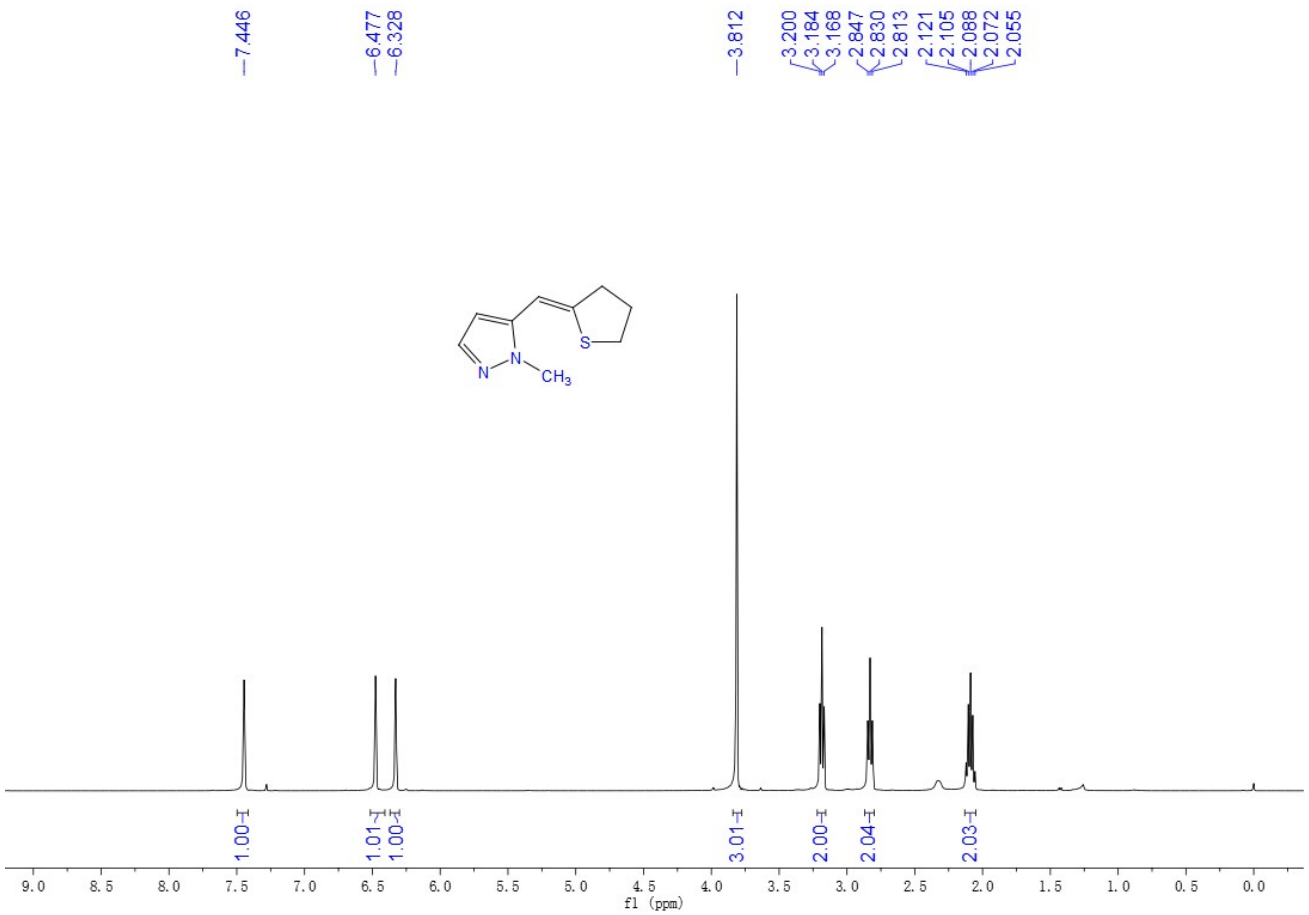
0.92
0.98
1.00
2.06
2.09
2.12
f1 (ppm)


142.122
142.062
126.961
124.362
123.444
110.438
77.212
77.000
76.789
39.222
36.050
29.116
S
S
f1 (ppm)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6.477
6.328
3.812
3.200
3.184
3.168
2.847
2.830
2.813
2.121
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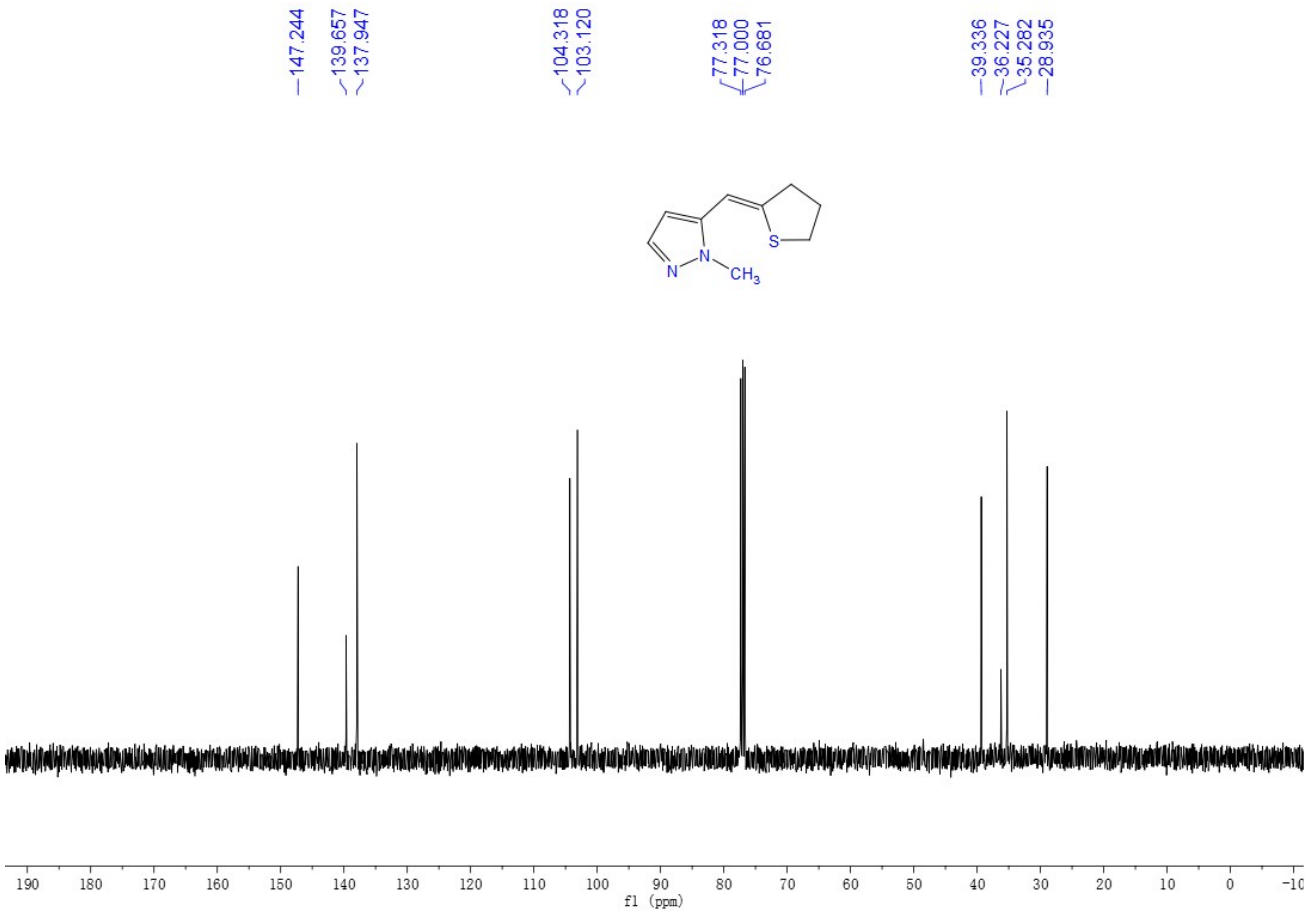
3.01
2.00
2.04
2.03
f1 (ppm)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137.947
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103.120
77.318
77.000
76.681
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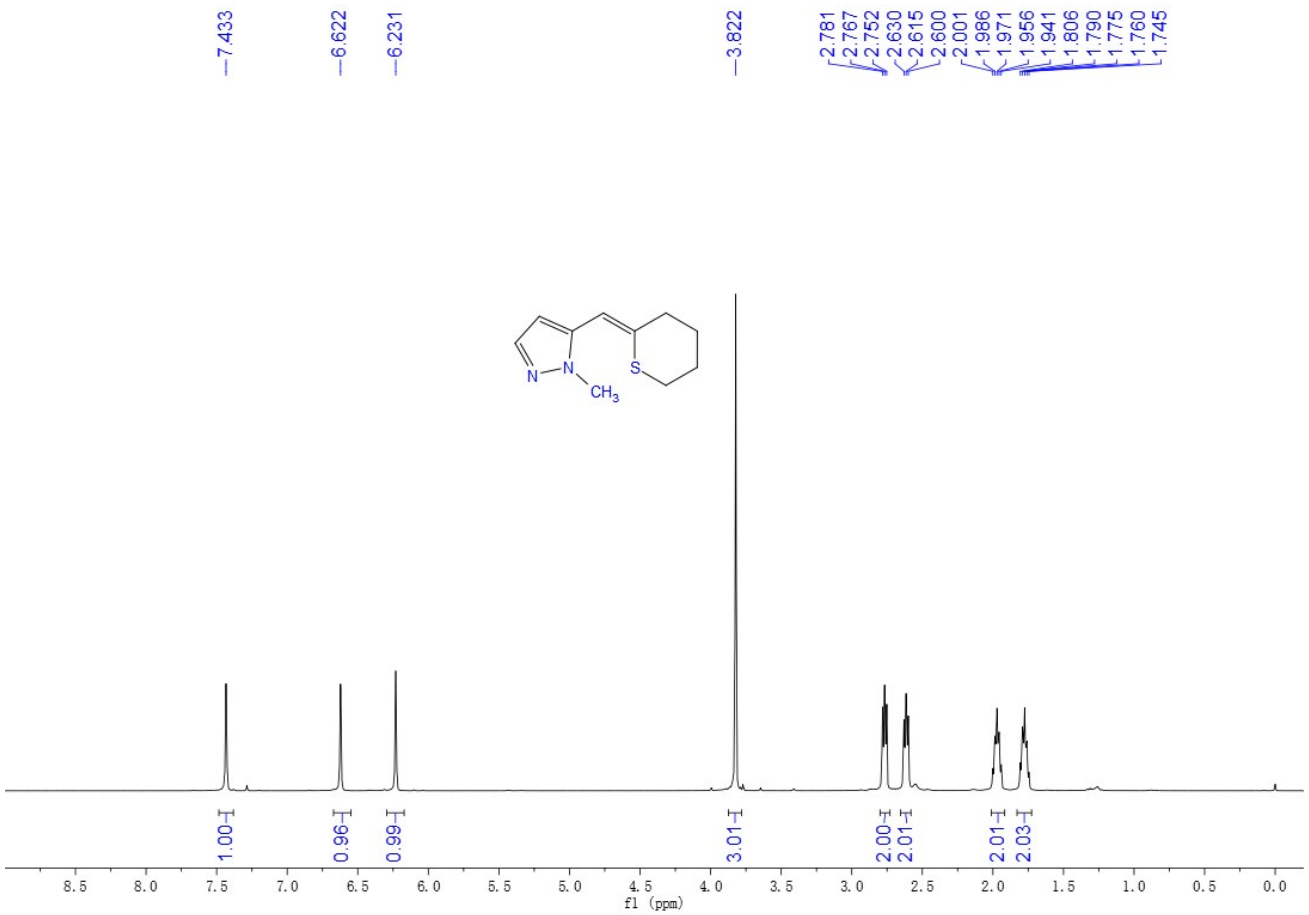
36.227
35.282
28.935
f1 (ppm)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6.231
3.822
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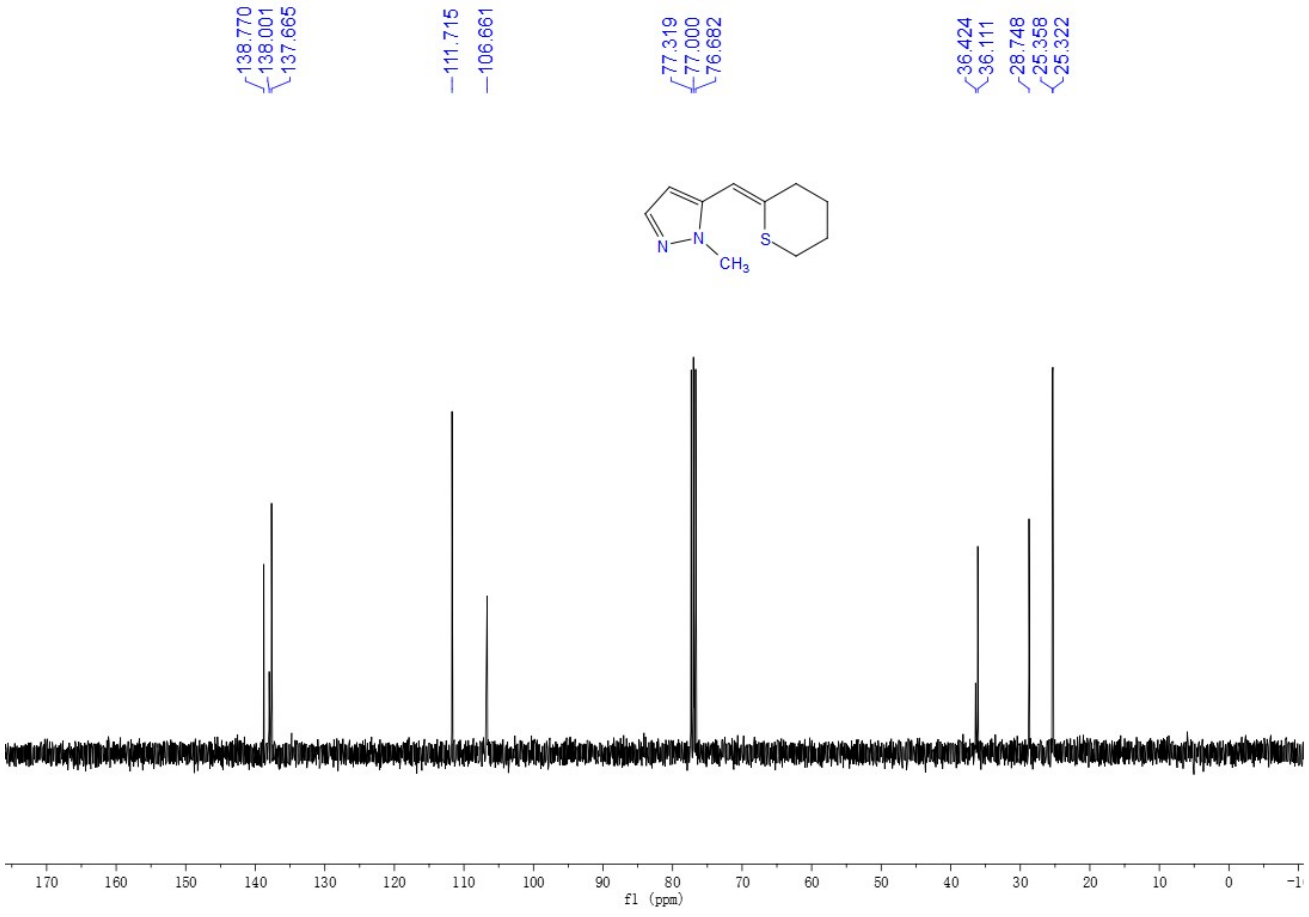
2.767
2.752
2.630
2.615
2.600
2.001
1.986
1.971
1.956
1.941
1.806
1.790
1.775
1.760
1.745
1.00
0.96
0.99
3.01
2.00
2.01
2.01
2.03
f1 (ppm)


138.770
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77.000
76.682
36.424
36.111
28.748
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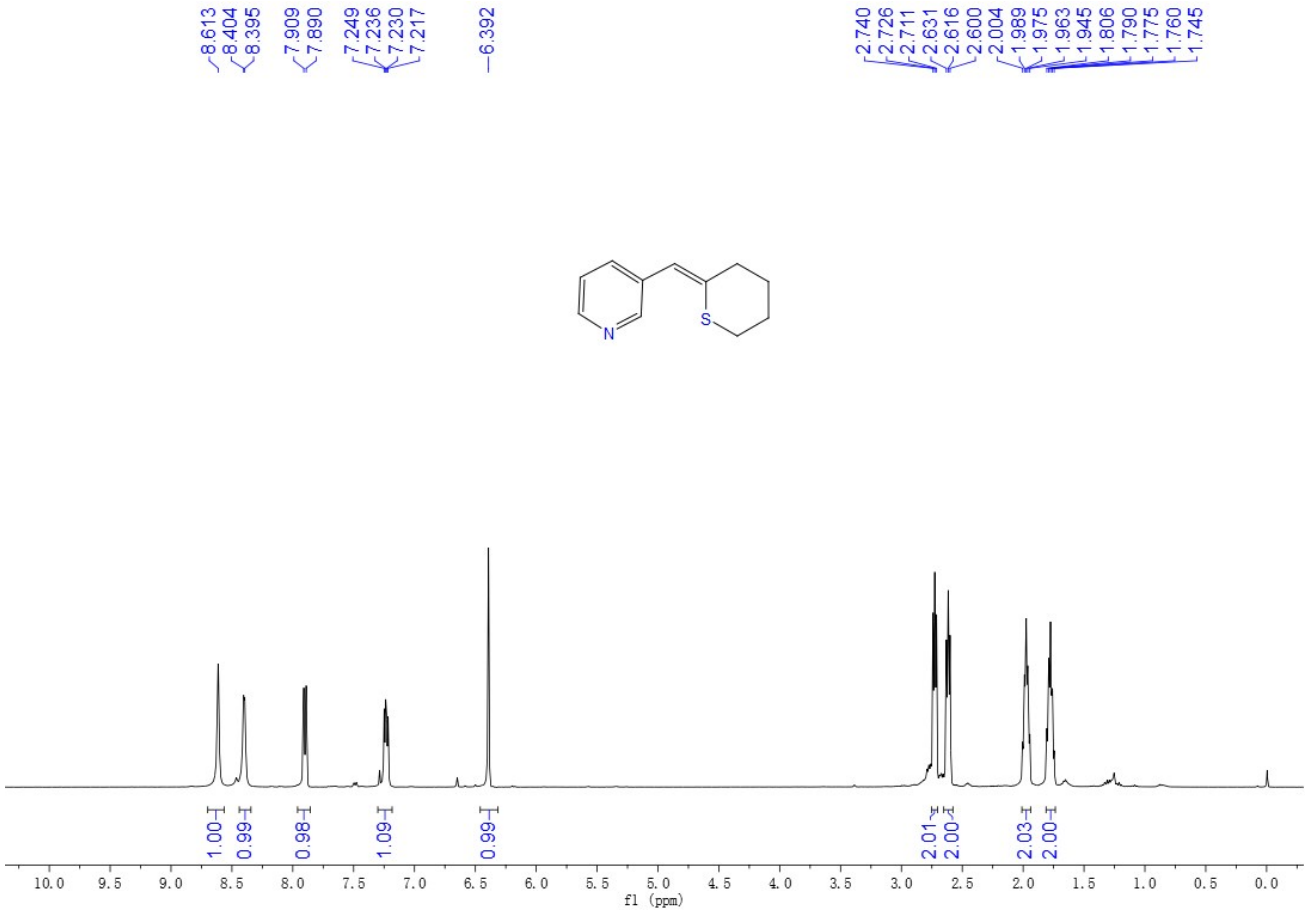
25.322
f1 (ppm)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7.909
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7.249
7.236
7.230
7.217
6.392
2.740
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2.711
2.631
2.616
2.600
2.004
1.989
1.975
1.963
1.945
1.806
1.790
1.775
1.760
1.745
N
S
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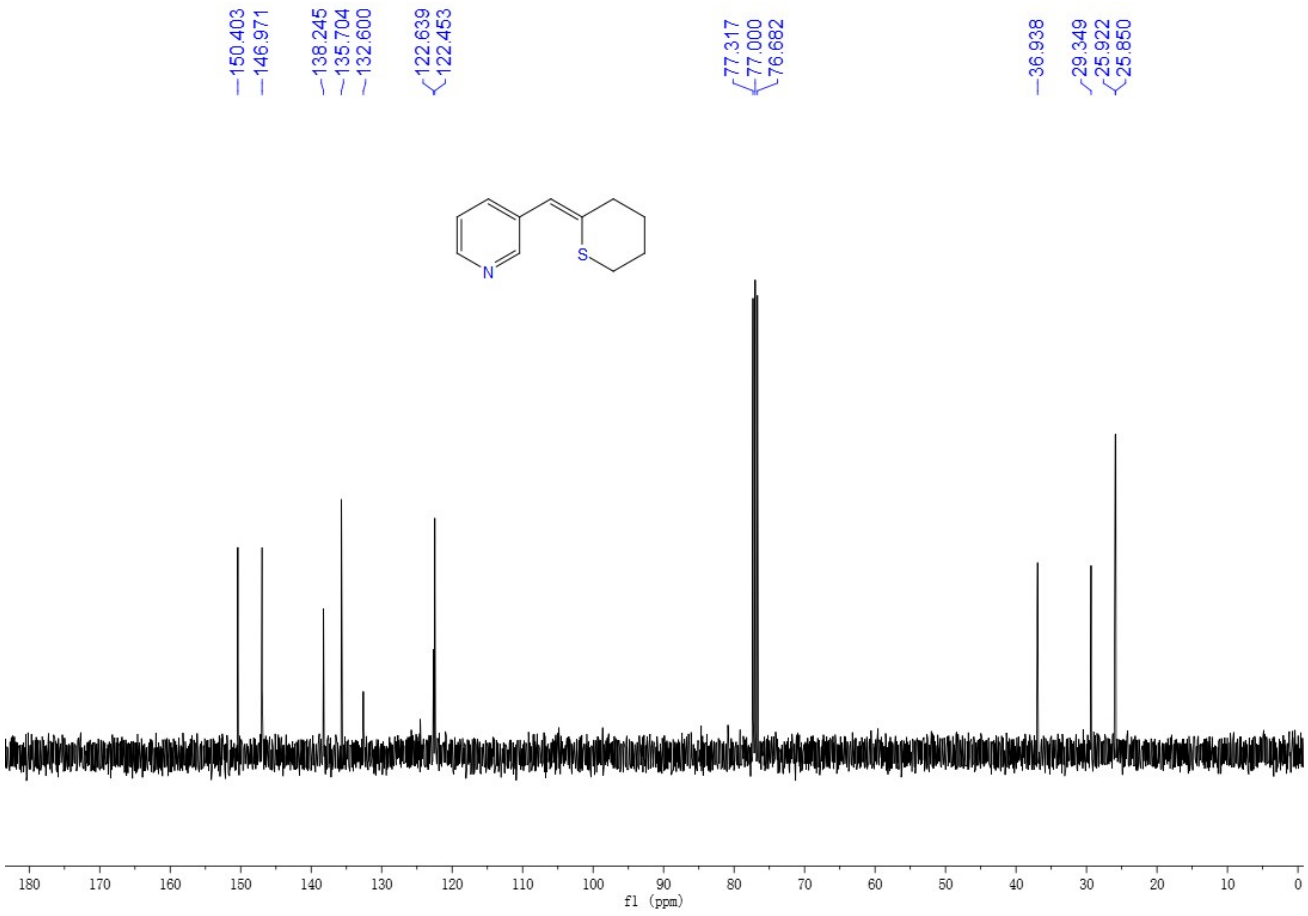
0.99
0.98
1.09
0.99
2.01
2.00
2.03
2.00
f1 (ppm)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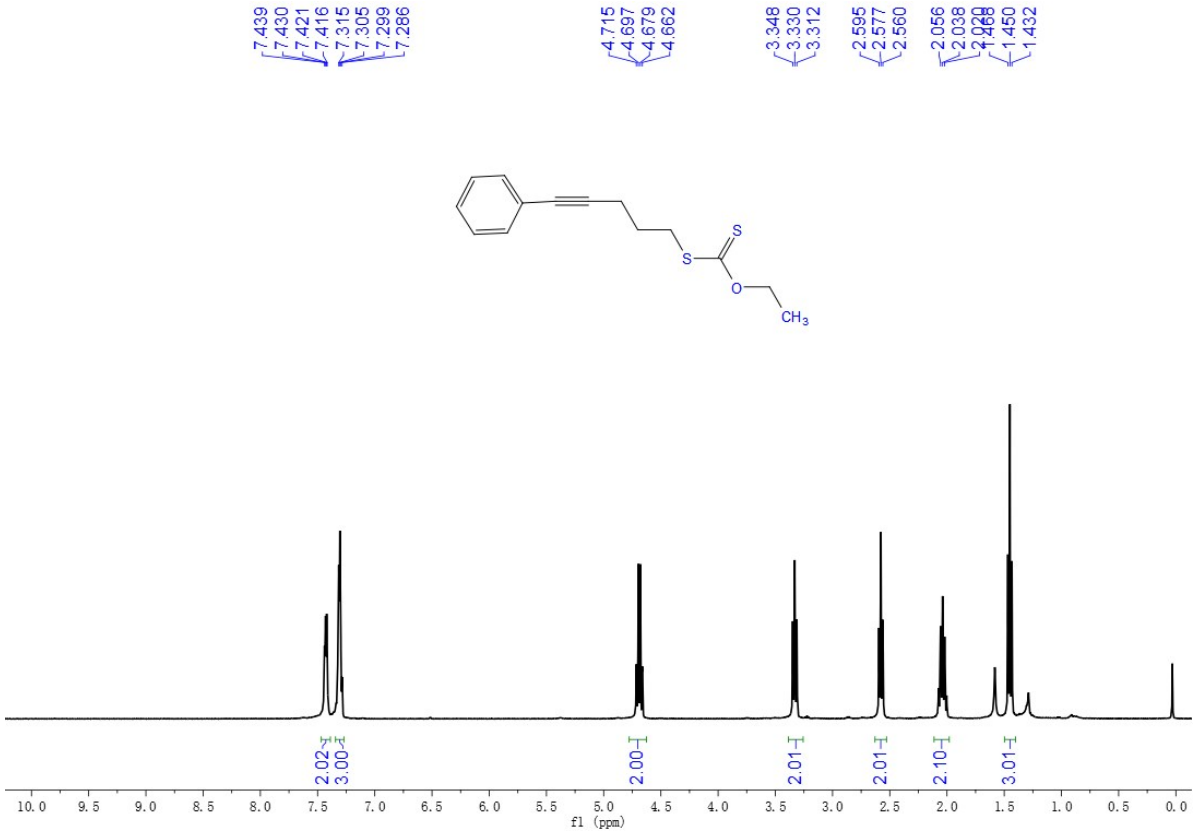
N
S
f1 (ppm)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7.299
7.286
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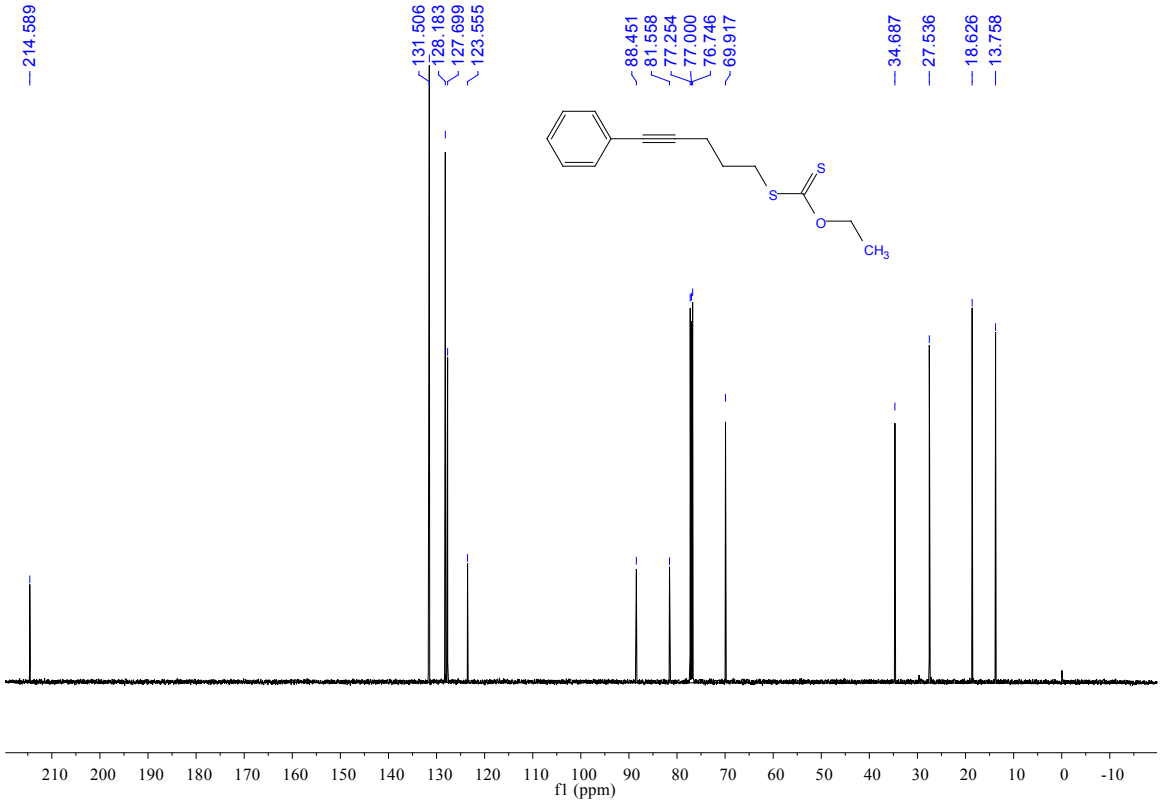
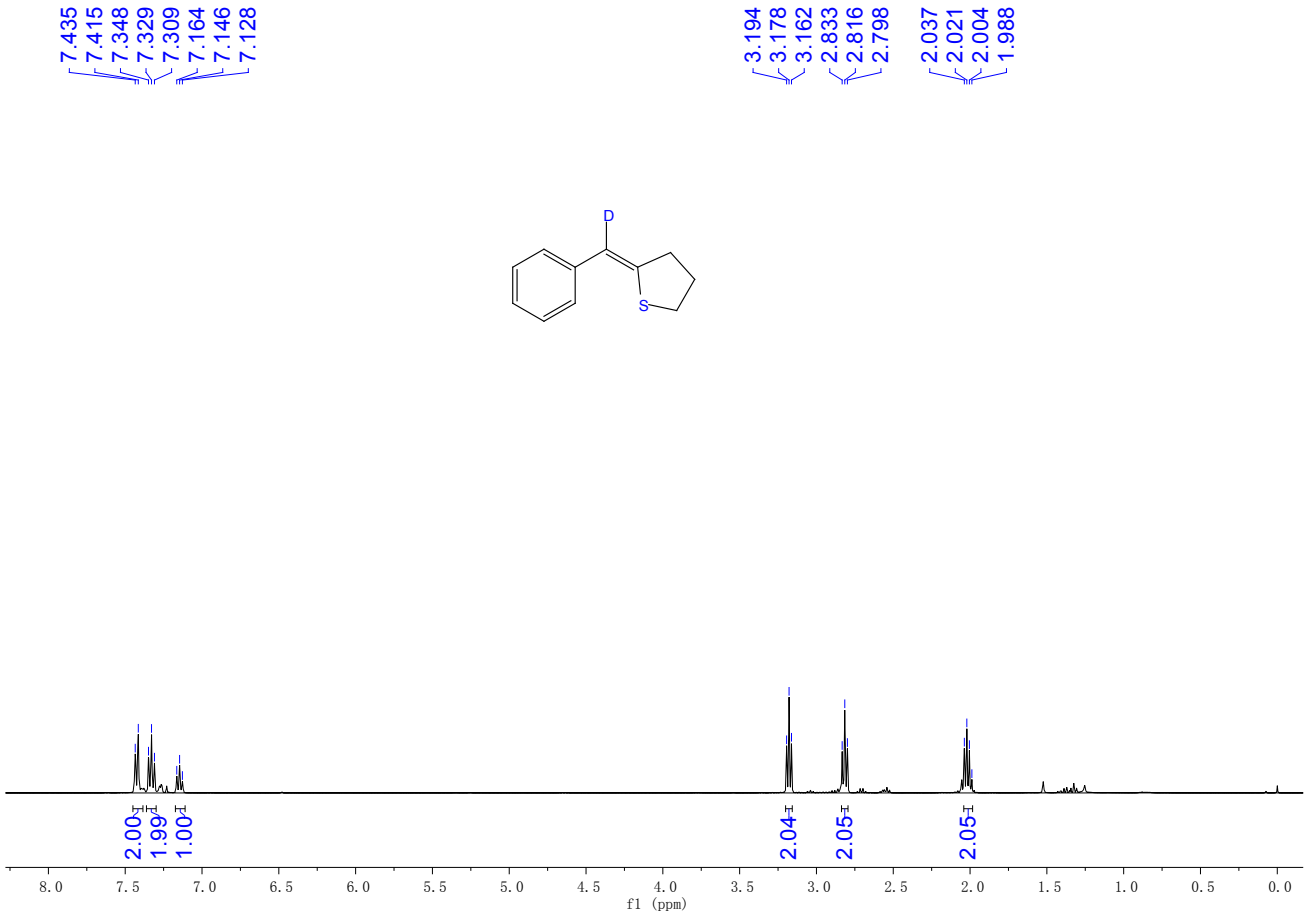
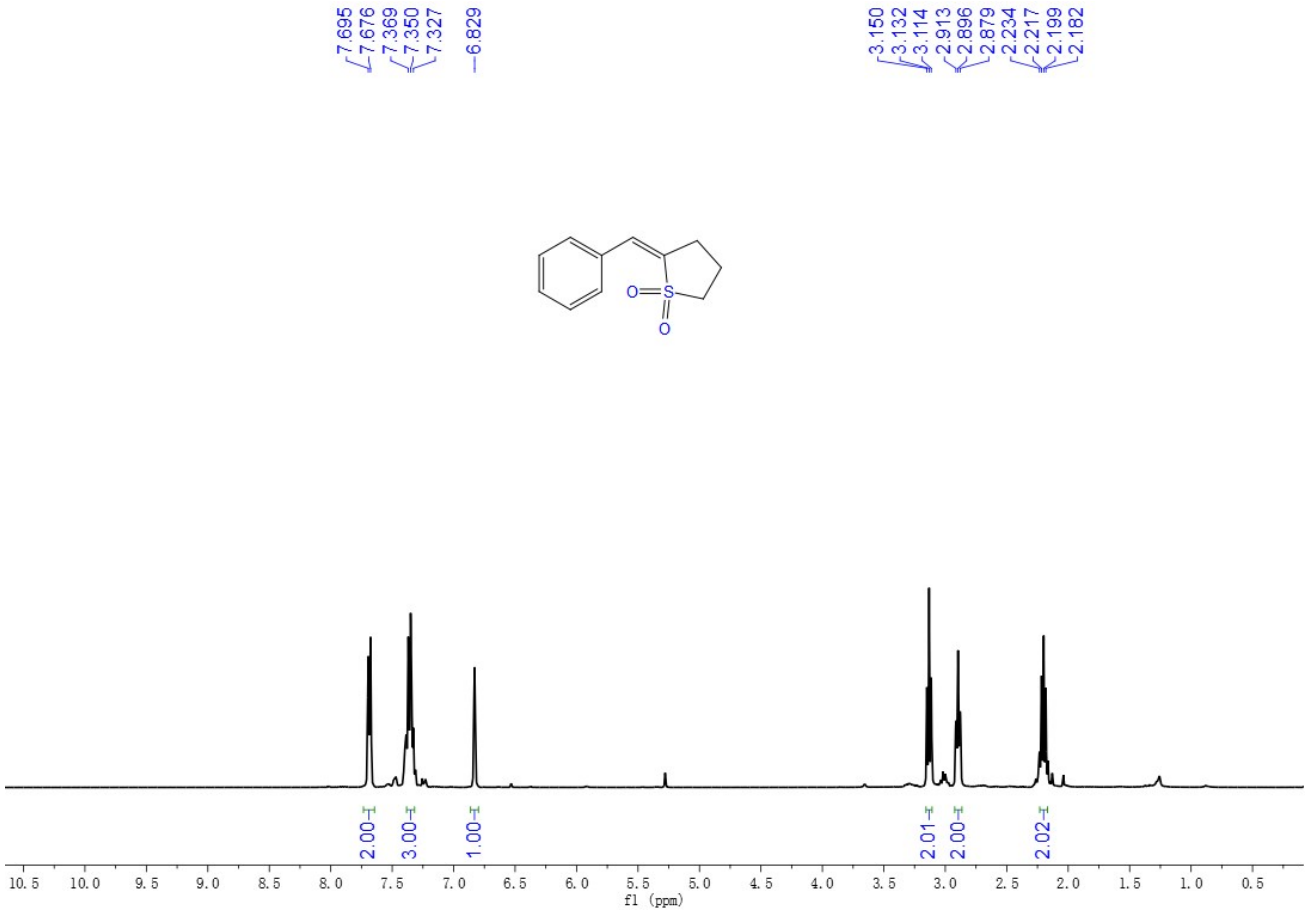
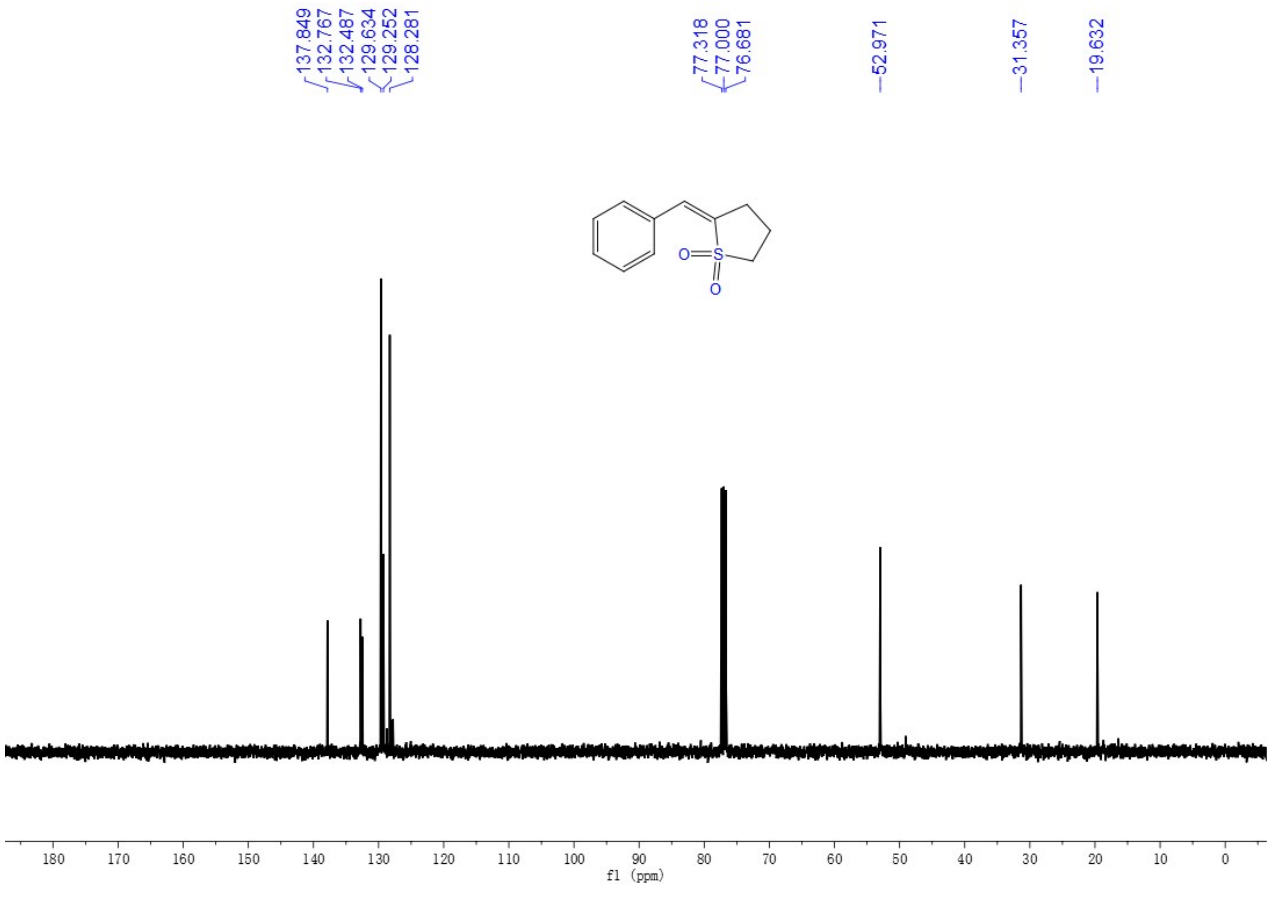
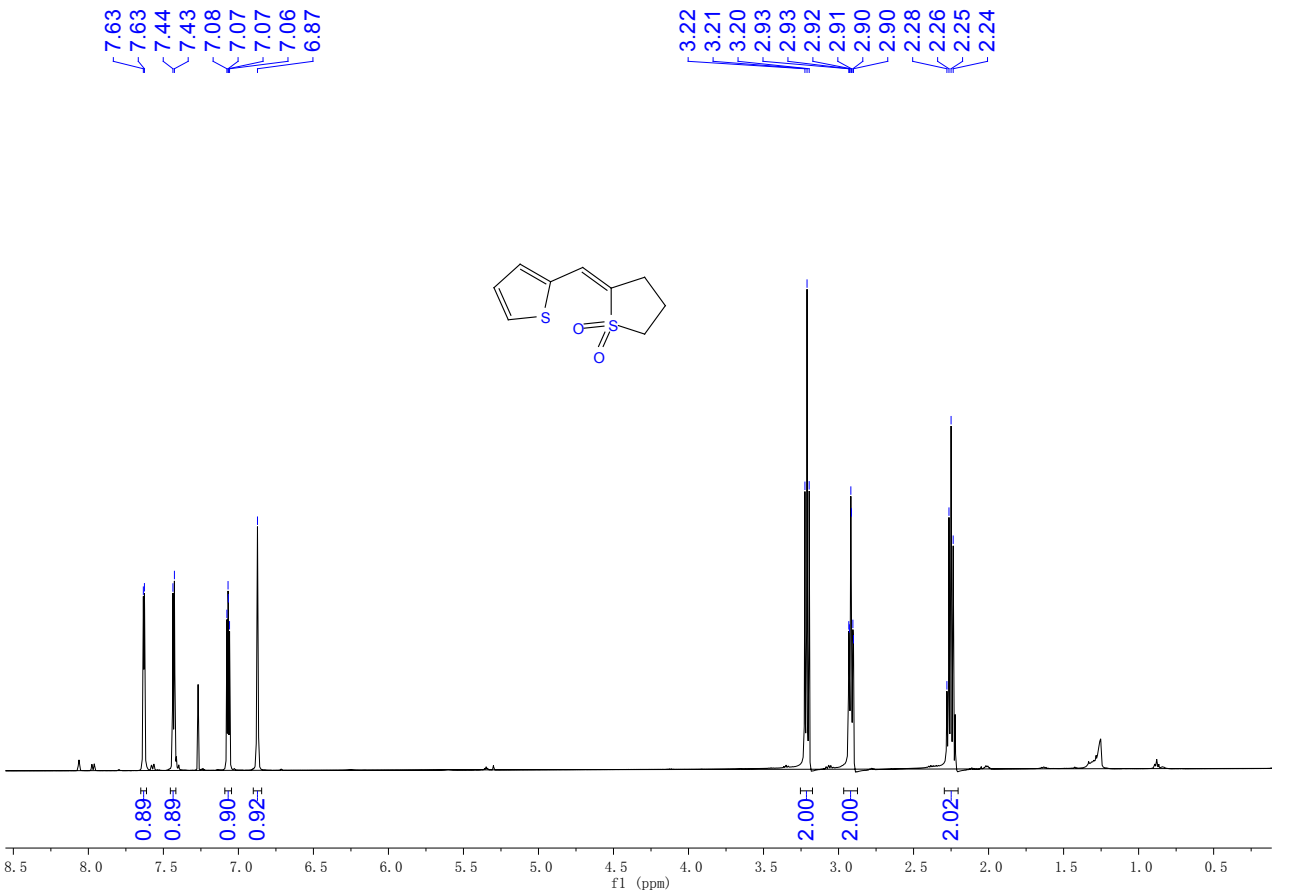
4.697
4.679
4.662
3.348
3.330
3.312
2.595
2.577
2.560
2.056
2.038
1.450
1.432
S
S
O
CH3
2.02
3.00
2.00
2.01
2.01
2.10
3.01
f1 (ppm)

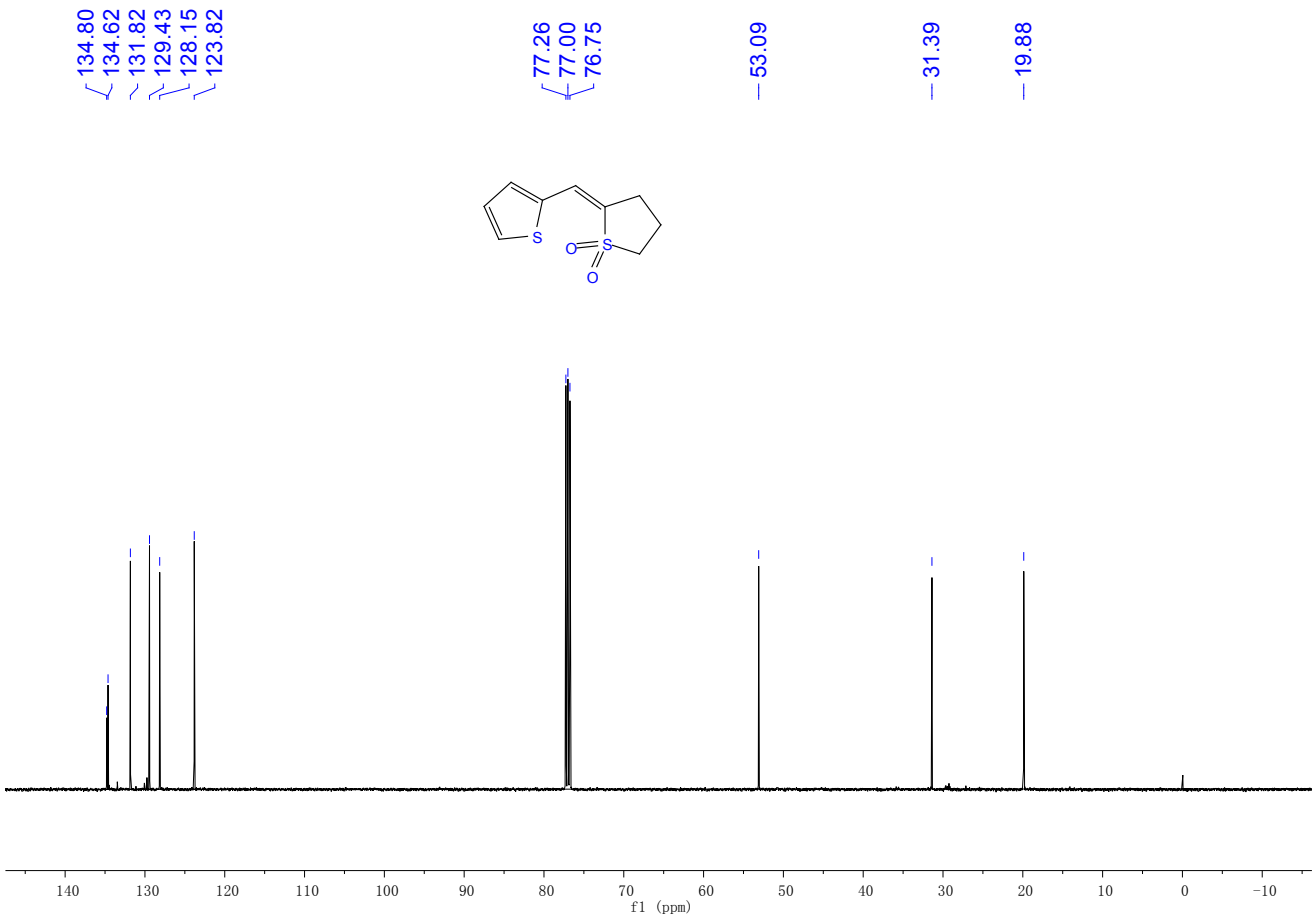

214.589
131.506
128.183
127.699
123.555
88.451
81.558
77.254
77.000
76.746
69.917
34.687
27.536
18.626
13.758
S
S
O
CH3
f1 (ppm)


7.435
7.415
7.348
7.329
7.309
7.164
7.146
7.128
3.194
3.178
3.162
2.833
2.816
2.798
2.037
2.021
2.004
1.988
D
S
2.00
1.99
1.00
2.04
2.05
2.05
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)


7.695
7.676
7.369
7.350
7.327
6.829
3.150
3.132
3.114
2.913
2.896
2.879
2.234
2.217
2.199
2.182
O=S
O
2.00
3.00
1.00
2.01
2.00
2.02
f1 (ppm)

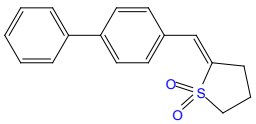

137.849
132.767
132.487
129.634
129.252
128.281
77.318
77.000
76.681
52.971
31.357
19.632
O=S
O
f1 (ppm)

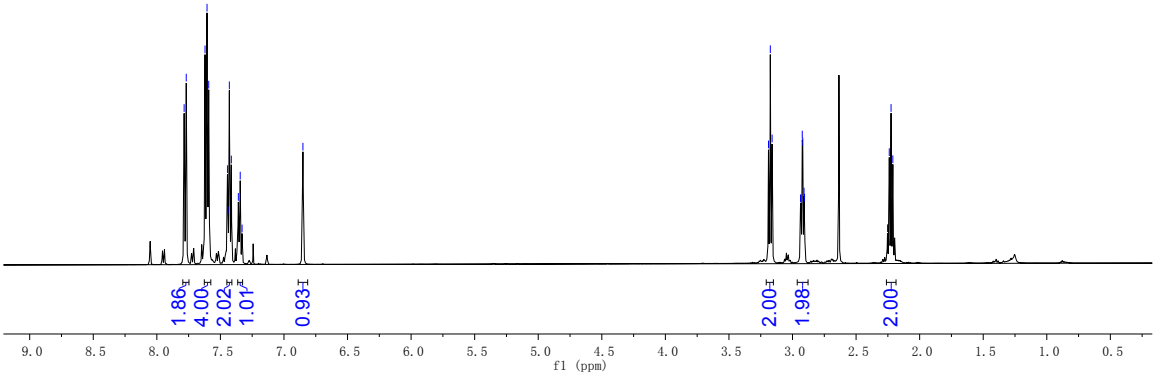

7.63
7.63
7.44
7.43
7.08
7.07
7.07
7.06
6.87
3.22
3.21
3.20
2.93
2.93
2.92
2.91
2.90
2.90
2.28
2.26
2.25
2.24
S
O
S
O
0.89
0.89
0.90
0.92
2.00
2.00
2.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


134.80
134.62
131.82
129.43
128.15
123.82
77.26
77.00
76.75
53.09
31.39
19.88
S
O
S
O
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.79
7.77
7.62
7.61
7.59
7.44
7.44
7.43
7.41
7.36
7.34
7.33
6.85


3.19
3.17
3.16
2.94
2.93
2.92
2.92
2.91
2.91
2.25
2.24
2.22
2.21

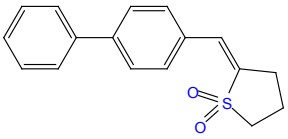

O
S
O

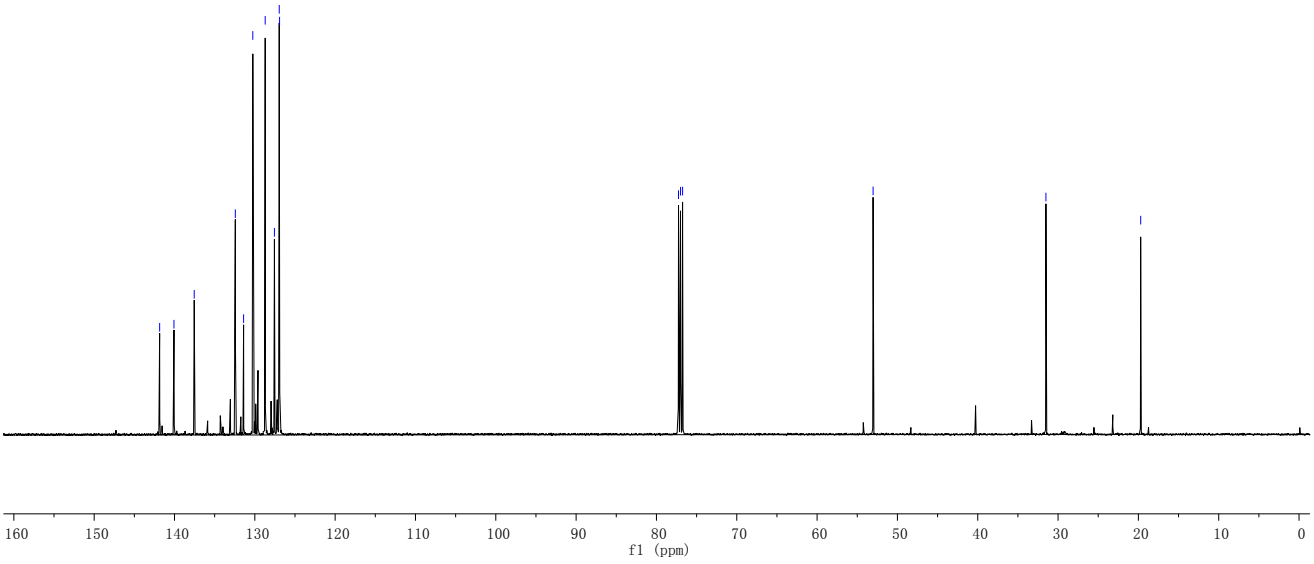

1.86
4.00
2.02
1.01
0.93
2.00
1.98
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


141.85
140.07
137.54
132.43
131.40
130.25
128.71
127.56
126.96
126.92


77.25
77.00
76.75


53.03
31.51
19.71


O
S
O


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)