Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Pd-Catalyzed Cycloisomerization/Nucleophilic Addition/Reduction: An Efficient Method for the Synthesis of Spiro-pseudoindoxyls Containing *N*, *N*′-Ketal

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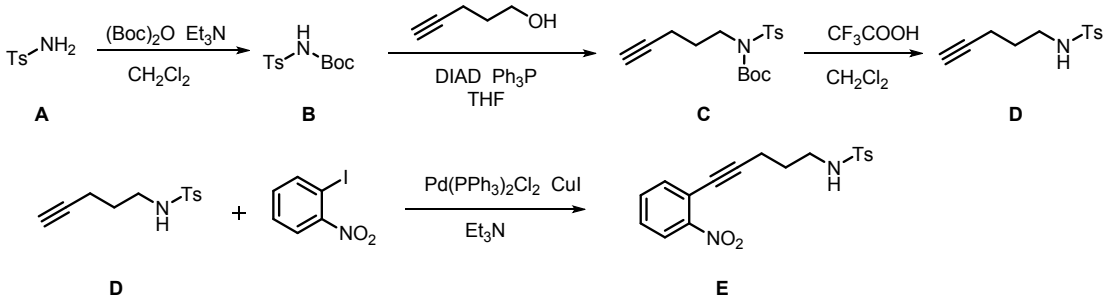
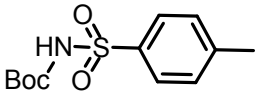
Detailed Synthetic Procedure

General Information: All reagents were used as received. 1,2-Dichloroethane (DCE) was distilled on phosphorus pentoxide; toluene and dioxane were dried by metallic sodium. N,N-dimethylformamide (DMF) was distilled from calcium hydride; CF_3CH_2OH and HFIP were purchased from purchased from duodian-chem Co. Ltd. $Pd(OAc)_2$ and tmphen were purchased from Boka Chem. Co. Ltd; PPh_3 was purchased from Sigma-Aldrich Co. LLC.; ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 400 Ultrashield NMR spectrometers. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 binocular microscope melting point apparatus (Beijing Tech Instruments Co.) and are uncorrected.

General procedure for the synthesis of the starting material E (4-methyl-N-(5-(2-nitrophenyl)pent-4-yn-1-yl)benzenesulfonamide)



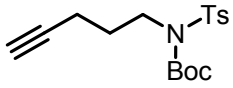
The synthetic route of substrates B (*tert*-butyl tosylcarbamate)[1]



A solution of Boc_2O (7.0 g, 32.1 mmol) in dichloromethane (10 mL) was added dropwise at room temperature to a solution of triethylamine (3.3 g, 32.1 mmol), DMAP (0.39 g, 3.21

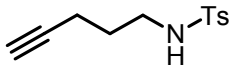
mmol) and p-toluenesulfonamide (5.0 g, 29.2 mmol) in dichloromethane (100 mL). The colorless reaction mixture was stirred at room temperature for 5 h. After completion the solvent was removed under vacuum, the residue was diluted with ethyl acetate (100 mL) and 1N HCl (80 mL). An organic layer was washed with water, brine and then dried over $MgSO_4$ and concentrated on a rotary evaporator to give a white solid. Crystallization from hot hexane (50 mL) gave **B**. White solid, yield 7.32 g, 93%. Mp 121–122 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.3 Hz, 2H), 7.57 (br, 1H), 7.35 (d, J = 8.3 Hz, 2H), 2.47 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 144.8, 135.9, 129.5, 128.2, 84.1, 27.9, 21.7.

The synthetic route of substrates C (*tert*-butyl pent-4-yn-1-yl(tosyl)carbamate)[2]



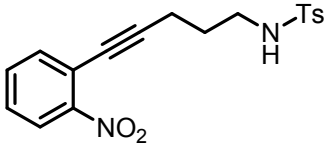
Under argon, a solution of N-(t-butoxycarbonyl)-N-p-toluenesulfonamide (2.5 g, 9.2 mmol), triphenylphosphine (2.9 g, 11.06 mmol) and pent-4-yn-1-ol (0.93 g, 11.06 mmol) in dry THF was chilled to 0 °C. Diisopropyl azodicarboxylate (2.24 g, 11.06 mmol) was then added dropwise. Then the reaction mixture was stirred at room temperature for 10 h. Concentrated in vacuo and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to give tert-butyl pent-4-yn-1-yl(tosyl)carbamate **C** 2.44 g, yield 79%. Mp 90–91 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 3.94 (t, J = 7.1Hz ,2H), 2.46 (s, 3H), 2.31 (td, J = 7.1, 2.5 Hz, 2H), 2.06 – 1.97 (m, 3H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 144.2, 137.3, 129.3, 127.9, 84.3, 83.1, 69.0, 46.3, 28.9, 27.9, 21.6, 16.0.

The synthetic route of substrates D (4-methyl-N-(5-(2-nitrophenyl)pent-4-yn-1-yl)benzenesulfonamide)



Trifluoroacetc acid (8.0 g, 72.3 mmol) was added dropwise to the solution of *t*-butyl pent-4-yn-1-yl(tosyl)carbamate (2.44 g, 7.23 mmol) in DCM at room temperature. The reaction mixture was stirred for 3 h and then added a saturated aqueous $NaHCO_3$ solution until the pH of water phase was 8~9. The crude product was extracted with DCM and the combined organic layer was dried over anhydrous Na_2SO_4, concentrated in vacuo to give **D** in 95% yield as a white solid. Mp 59–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.02–4.93 (m, 2H), 4.91 (t, J = 6.4 Hz, 1H), 3.07 (q, J = 6.8 Hz, 2H), 2.43 (s, 3H), 2.23 (dt, J = 6.8 Hz, 2.8 Hz, 2H), 1.95 (t, J = 2.8 Hz, 1H), 1.75–1.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 136.9, 129.7, 127.1, 82.9, 69.5, 42.1, 28.1, 22.0, 15.7.

The synthetic route of substrates E (4-methyl-N-(5-(2-nitrophenyl)pent-4-yn-1-yl)benzenesulfonamide)[3]

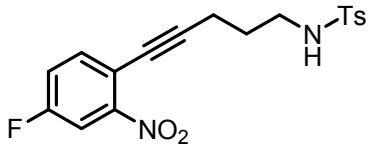


To a three-necked flask were added $Pd(PPh_3)_2Cl_2$ (141 mg, 0.201 mmol), CuI (38 mg, 0.201 mmol), 2-nitroiodobenzene (1.0 g, 4.02 mmol), Et_3N (2.03 g, 20.1 mmol) and THF. After degassing with argon and four evacuation/backfill-cycles with argon, **D** (1.14 g, 4.82 mmol) in tetrahydrofuran was added dropwise. The reaction mixture was stirred at room temperature. When the reaction was complete as monitored by TLC, H_2O was added to the resulting mixture. After separation of the organic layer, the water layer

was extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1) to give **E** 1.27 g as a yellow oil, yield 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.56 – 7.53 (m, 2H), 7.42 (ddd, J = 8.7, 5.5, 3.5 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 4.80 (t, J = 6.2 Hz, 1H), 3.17 (q, J = 6.6 Hz, 2H), 2.55 (t, J = 6.7 Hz, 2H), 2.41 (s, 3H), 1.82 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 143.4, 136.8, 134.9, 132.9, 129.7, 128.3, 127.1, 124.4, 118.8, 97.5, 76.9, 42.1, 28.1, 21.5, 17.0. HRMS (ESI) calcd for $C_{18}H_{19}N_2O_4S$ $(M+H)^+$ 359.1066, found 359.1056.

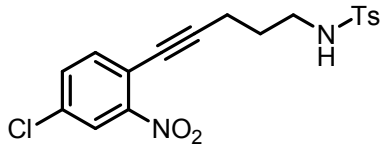
Similarly, the synthesis other substrate please refer to the procedure of **E**

N-(5-(4-fluoro-2-nitrophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide



pale brown oil, yield 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 2H), 7.68 (dd, J = 8.2, 2.5 Hz, 1H), 7.53 (dd, J = 8.6, 5.5 Hz, 1H), 7.30 – 7.24 (m, 3H), 5.38 (t, J = 6.2 Hz, 1H), 3.12 (q, J = 6.5 Hz, 2H), 2.50 (t, J = 6.8 Hz, 2H), 2.37 (s, 3H), 1.79 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 159.5, 150.3 (J = 9.0 Hz), 143.4, 136.8, 136.5 (J = 8.0 Hz), 129.7, 127.1, 120.6 (J = 21.0 Hz), 115.2 (J = 3.0 Hz), 112.2 (J = 27.0 Hz), 97.4, 76.0, 42.0, 28.0, 21.5, 16.9. HRMS (ESI) calcd for $C_{18}H_{18}FN_2O_4S$ $(M+H)^+$ 377.0971, found 377.0968.

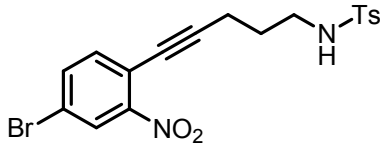
N-(5-(4-chloro-2-nitrophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide



pale yellow powder, yield 90%. Mp 92–93 ºC. ^{1}H NMR (400 MHz, CDCl3) δ 8.00 (s, 1H), 7.78 (d, J

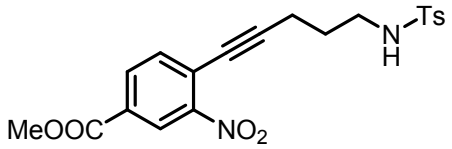
= 8.2 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 4.99 (t, *J* = 5.2 Hz, 1H), 3.16 (q, *J* = 6.6 Hz, 2H), 2.55 (t, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 1.83 (p, *J* = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 143.5, 136.8, 135.7, 134.0, 133.0, 129.8, 127.1, 124.7, 117.4, 98.6, 76.3, 42.0, 28.0, 21.5, 17.1. HRMS (ESI) calcd for $C_{18}H_{18}ClN_2O_4S$ $(M+H)^+$ 393.0676, found 393.0677.

N-(5-(4-bromo-2-nitrophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide



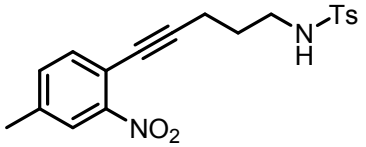
pale yellow oil, yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 4.88 (t, *J* = 6.3 Hz, 1H), 3.16 (q, *J* = 6.7 Hz, 2H), 2.55 (t, *J* = 6.7 Hz, 2H), 2.43 (s, 3H), 1.83 (p, *J* = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 143.5, 136.8, 135.9, 135.8, 129.8, 127.6, 127.1, 121.4, 117.8, 98.8, 76.4, 42.0, 28.0, 21.6, 17.1. HRMS (ESI) calcd for $C_{18}H_{18}BrN_2O_4S$ $(M+H)^+$ 437.0171, found 437.0163.

methyl 4-(5-(4-methylphenylsulfonamido)pent-1-yn-1-yl)-3-nitrobenzoate



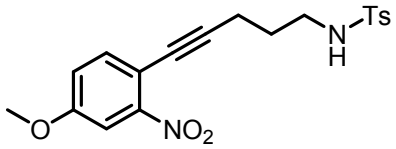
pale brown oil, yield 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 5.40 (t, *J* = 6.0 Hz, 1H), 3.94 (s, 3H), 3.12 (q, *J* = 6.7 Hz, 2H), 2.55 (t, *J* = 6.7 Hz, 2H), 2.37 (s, 3H), 1.82 (p, *J* = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 149.7, 143.4, 136.8, 135.1, 133.0, 129.9, 129.7, 127.1, 125.5, 123.0, 101.4, 76.7, 52.9, 42.0, 28.0, 21.5, 17.2. HRMS (ESI) calcd for $C_{20}H_{21}N_2O_6S$ $(M+H)^+$ 417.1120, found 417.1117.

4-methyl-N-(5-(4-methyl-2-nitrophenyl)pent-4-yn-1-yl)benzenesulfonamide



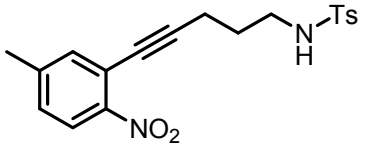
reddish brown oil, yield 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 3H), 7.43 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 5.00 (t, J = 5.8 Hz, 1H), 3.17 (q, J = 6.6 Hz, 2H), 2.53 (t, J = 6.7 Hz, 2H), 2.43 (s, 3H), 2.41 (s, 3H), 1.82 (p, J = 6.6 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 143.4, 139.1, 136.8, 134.5, 133.7, 129.7, 127.1, 124.8, 115.9, 96.1, 77.1, 42.1, 28.1, 21.5, 21.2, 17.0. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_4S$ $(M+H)^+$ 373.1222, found 373.1221.

N-(5-(4-methoxy-2-nitrophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide



pale brown oil, yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 2H), 7.47 (s, 1H), 7.43 (d, J = 8.6 Hz, 1H), 7.28 (d, J = 7.7 Hz, 2H), 7.07 (d, J = 8.4 Hz, 1H), 5.28 (s, 1H), 3.86 (s, 3H), 3.14 (q, J = 6.2 Hz, 2H), 2.50 (t, J = 6.2 Hz, 2H), 2.39 (s, 3H), 1.79 (p, J = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 150.6, 143.4, 136.9, 135.7, 129.7, 127.1, 119.7, 111.0, 109.2, 95.2, 76.8, 56.0, 42.1, 28.1, 21.5, 17.0. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_5S$ $(M+H)^+$ 389.1171, found 389.1173.

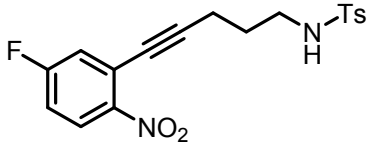
4-methyl-N-(5-(5-methyl-2-nitrophenyl)pent-4-yn-1-yl)benzenesulfonamide



yellow oil, yield 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 7.5 Hz, 2H), 7.34 (s, 1H), 7.28 (d, J = 7.4 Hz, 2H), 7.19 (d, J = 8.0 Hz, 1H), 5.13 (s, 1H), 3.16 (q, J = 6.2 Hz, 2H), 2.53 (t, J = 6.2 Hz, 2H), 2.39 (s, 6H), 1.81 (p, J = 6.2 Hz, 2H). ^{13}C

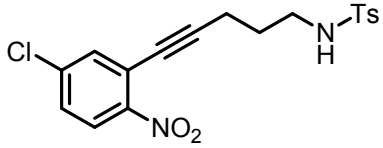
NMR (100 MHz, $CDCl_3$) δ 147.5, 144.1, 143.4, 136.8, 135.2, 129.7, 129.0, 127.1, 124.7, 118.9, 96.8, 77.4, 42.1, 28.1, 21.5, 21.2, 17.0. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_4S$ $(M+H)^+$ 373.1222, found 373.1209.

N-(5-(5-fluoro-2-nitrophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide



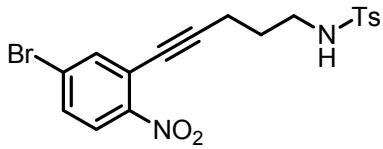
brown oil, yield 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 9.0, 5.1 Hz, 1H), 7.78 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.20 (dd, J = 8.5, 2.4 Hz, 1H), 7.14 – 7.06 (m, 1H), 5.25 (t, J = 5.9 Hz, 1H), 3.14 (q, J = 6.5 Hz, 2H), 2.55 (t, J = 6.7 Hz, 2H), 2.40 (s, 3H), 1.82 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 163.0, 146.0, 143.5, 136.7, 129.8, 127.3 (J = 10.0 Hz), 127.1, 121.8 (J = 11.0 Hz), 121.4 (J = 25.0 Hz), 115.7 (J = 23.0 Hz), 99.2, 76.3, 42.0, 27.9, 21.5, 17.0. HRMS (ESI) calcd for $C_{18}H_{18}FN_2O_4S$ $(M+H)^+$ 377.0971, found 377.0968.

N-(5-(5-chloro-2-nitrophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide



brown oil, yield 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 2.2 Hz, 1H), 7.26 (dd, J = 8.8, 2.2 Hz, 1H), 7.19 (d, J = 7.8 Hz, 2H), 5.30 (t, J = 6.3 Hz, 1H), 3.03 (q, J = 6.6 Hz, 2H), 2.44 (t, J = 6.8 Hz, 2H), 2.29 (s, 3H), 1.72 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 143.4, 139.2, 136.8, 134.4, 129.7, 128.4, 127.1, 125.9, 120.6, 99.3, 76.1, 42.0, 28.0, 21.5, 17.0. HRMS (ESI) calcd for $C_{18}H_{18}ClN_2O_4S$ $(M+H)^+$ 393.0676, found 393.0679.

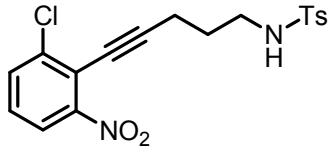
N-(5-(5-bromo-2-nitrophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide



yellow oil, yield 88%. ^{1}H NMR (400 MHz,

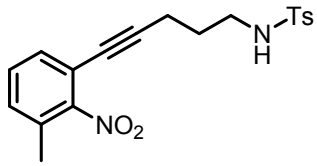
$CDCl_3$) δ 7.86 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 1.9 Hz, 1H), 7.52 (dd, J = 8.8, 2.0 Hz, 1H), 7.28 (d, J = 7.9 Hz, 2H), 5.33 (t, J = 6.1 Hz, 1H), 3.12 (q, J = 6.5 Hz, 2H), 2.53 (t, J = 6.8 Hz, 2H), 2.38 (s, 3H), 1.81 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 143.5, 137.4, 136.8, 131.4, 129.8, 127.6, 127.1, 125.9, 120.7, 99.3, 76.0, 42.0, 28.0, 21.5, 17.0. HRMS (ESI) calcd for $C_{18}H_{18}BrN_2O_4S$ $(M+H)^+$ 437.0171, found 437.0163.

N-(5-(2-chloro-6-nitrophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide



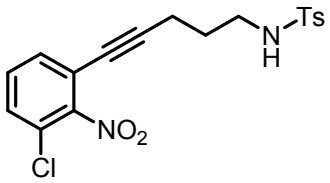
colourless oil, yield 45%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.1 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.28 (d, J = 8.1 Hz, 2H), 5.25 (t, J = 5.3 Hz, 1H), 3.17 (q, J = 6.6 Hz, 2H), 2.59 (t, J = 6.7 Hz, 2H), 2.39 (s, 3H), 1.84 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 142.4, 137.5, 135.8, 132.4, 128.7, 127.0, 126.1, 121.5, 117.4, 102.9, 72.6, 41.0, 26.9, 20.5, 16.2. HRMS (ESI) calcd for $C_{18}H_{18}ClN_2O_4S$ $(M+H)^+$ 393.0676, found 393.0665.

4-methyl-N-(5-(3-methyl-2-nitrophenyl)pent-4-yn-1-yl)benzenesulfonamide



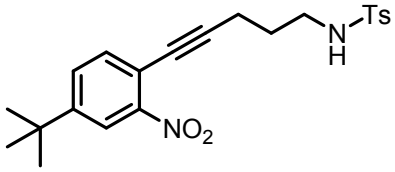
brown oil, yield 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.6 Hz, 2H), 7.27 – 7.20 (m, 4H), 7.17 – 7.12 (m, 1H), 5.14 (t, J = 5.3 Hz, 1H), 3.02 (q, J = 5.9 Hz, 2H), 2.41 – 2.32 (m, 5H), 2.25 (s, 3H), 1.68 (p, J = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 143.4, 136.9, 130.7, 130.7, 129.9, 129.8, 127.1, 116.6, 95.4, 75.2, 42.0, 28.1, 21.5, 17.4, 16.7. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_4S$ $(M+H)^+$ 373.1222, found 373.1215.

N-(5-(3-chloro-2-nitrophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide



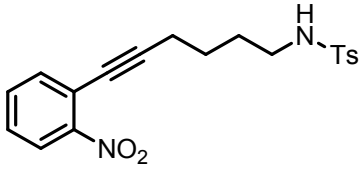
brown oil, yield 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H), 7.42 – 7.26 (m, 5H), 5.24 (t, J = 5.6 Hz, 1H), 3.05 (q, J = 6.7 Hz, 2H), 2.44 (t, J = 6.9 Hz, 2H), 2.40 (s, 3H), 1.75 (p, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 143.5, 136.8, 131.5, 130.7, 129.8, 129.7, 127.1, 124.9, 118.5, 97.4, 74.0, 41.9, 28.0, 21.5, 16.7. HRMS (ESI) calcd for $C_{18}H_{18}ClN_2O_4S$ $(M+H)^+$ 393.0676, found 393.0675.

N-(5-(4-(tert-butyl)-2-nitrophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide



brown oil, yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.78 (d, J = 7.9 Hz, 2H), 7.55 (d, J = 8.2 Hz, 1H), 7.46 (d, J = 8.2 Hz, 1H), 7.27 (d, J = 8.1 Hz, 2H), 5.27 (t, J = 6.0 Hz, 1H), 3.14 (q, J = 6.4 Hz, 2H), 2.51 (t, J = 6.7 Hz, 2H), 2.38 (s, 3H), 1.80 (p, J = 6.6 Hz, 2H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 149.7, 143.4, 136.8, 134.5, 130.1, 129.7, 127.1, 121.3, 116.0, 96.2, 77.1, 42.1, 35.1, 30.9, 28.1, 21.5, 17.0. HRMS (ESI) calcd for $C_{22}H_{27}N_2O_4S$ $(M+H)^+$ 415.1692, found 415.1684.

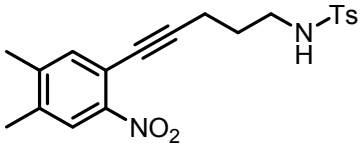
4-methyl-N-(6-(2-nitrophenyl)hex-5-yn-1-yl)benzenesulfonamide



yellow oil, yield 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.40 (ddd, J = 8.5, 6.7, 2.2 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 5.15 (t, J = 6.1 Hz, 1H), 2.99 (q, J = 6.3 Hz, 2H), 2.44 (t, J =

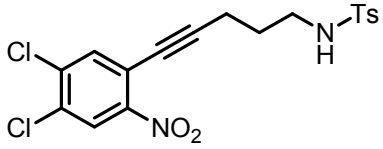
6.5 Hz, 2H), 2.39 (s, 3H), 1.77 – 1.58 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 143.4, 136.8, 134.8, 132.8, 129.7, 128.1, 127.1, 124.4, 119.0, 98.4, 76.5, 42.7, 28.4, 25.1, 21.5, 19.2. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_4S$ $(M+H)^+$ 373.1222, found 373.1213.

N-(5-(4,5-dimethyl-2-nitrophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide



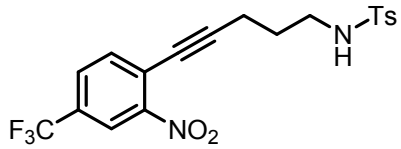
brown oil, yield 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 3H), 7.29 – 7.23 (m, 3H), 5.33 (t, J = 5.9 Hz, 1H), 3.14 (q, J = 6.4 Hz, 2H), 2.50 (t, J = 6.7 Hz, 2H), 2.37 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 1.80 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 143.3, 143.0, 137.7, 136.9, 135.5, 129.7, 127.1, 125.3, 116.2, 95.9, 77.4, 42.1, 28.1, 21.5, 19.6, 19.6, 17.0. HRMS (ESI) calcd for $C_{20}H_{23}N_2O_4S$ $(M+H)^+$ 387.1379, found 387.1379.

N-(5-(4,5-dichloro-2-nitrophenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide



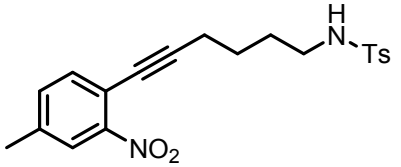
yellow oil, yield 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.72 (d, J = 7.1 Hz, 2H), 7.56 (s, 1H), 7.23 (d, J = 6.8 Hz, 2H), 5.30 (s, 1H), 3.06 (q, J = 6.4 Hz, 2H), 2.48 (t, J = 6.4 Hz, 2H), 2.34 (s, 3H), 1.76 (p, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 143.5, 137.8, 136.8, 135.8, 132.4, 129.7, 127.1, 126.4, 118.6, 100.1, 75.4, 41.9, 27.9, 21.5, 17.1. HRMS (ESI) calcd for $C_{18}H_{17}Cl_2N_2O_4S$ $(M+H)^+$ 427.0286, found 427.0282.

4-methyl-N-(5-(2-nitro-4-(trifluoromethyl)phenyl)pent-4-yn-1-yl)benzenesulfonamide



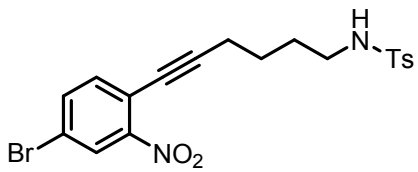
brown oil, yield 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.73 (d, J = 8.1 Hz, 3H), 7.65 (d, J = 8.2 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 5.18 (t, J = 6.2 Hz, 1H), 3.10 (q, J = 6.5 Hz, 2H), 2.54 (t, J = 6.8 Hz, 2H), 2.36 (s, 3H), 1.80 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 143.5, 136.8, 135.7, 130.2 (J = 34.3 Hz), 129.7, 129.2 (J = 3.3 Hz), 127.1, 122.7 (J = 271.0 Hz), 122.6, 121.8 (J = 3.9 Hz), 101.2, 76.2, 42.0, 27.9, 21.5, 17.1. HRMS (ESI) calcd for $C_{19}H_{18}F_3N_2O_4S$ $(M+H)^+$ 427.0939, found 427.3771.

4-methyl-N-(6-(4-methyl-2-nitrophenyl)hex-5-yn-1-yl)benzenesulfonamide



yellow oil, yield 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 3H), 7.42 (d, J = 7.9 Hz, 1H), 7.34 – 7.25 (m, 3H), 5.16 (t, J = 5.6 Hz, 1H), 2.98 (q, J = 6.4 Hz, 2H), 2.46 – 2.36 (m, 8H), 1.73 – 1.57 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 143.3, 138.9, 136.9, 134.5, 133.6, 129.7, 127.1, 124.7, 116.1, 97.2, 76.5, 42.7, 28.4, 25.2, 21.5, 21.1, 19.2. HRMS (ESI) calcd for $C_{20}H_{23}N_2O_4S$ $(M+H)^+$ 387.1379, found 387.1375.

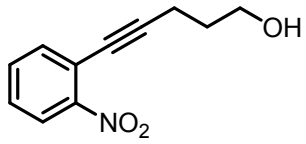
N-(6-(4-bromo-2-nitrophenyl)hex-5-yn-1-yl)-4-methylbenzenesulfonamide



yellow oil, yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.76 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.2 Hz, 1H), 7.41 (d, J = 8.3 Hz, 1H),

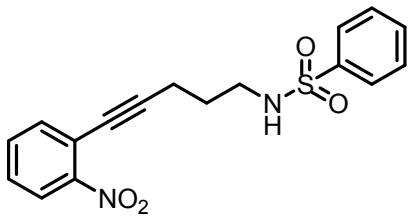
7.29 (d, J = 8.0 Hz, 2H), 5.13 (t, J = 6.0 Hz, 1H), 2.98 (q, J = 6.1 Hz, 2H), 2.48 – 2.37 (m, 5H), 1.72 – 1.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 143.4, 136.8, 135.9, 135.8, 129.7, 127.4, 127.1, 121.2, 118.0, 99.9, 75.9, 42.6, 28.5, 25.0, 21.5, 19.3. HRMS (ESI) calcd for $C_{19}H_{20}BrN_2O_4S$ $(M+H)^+$ 451.0327, found 451.0323.

5-(2-nitrophenyl)pent-4-yn-1-ol



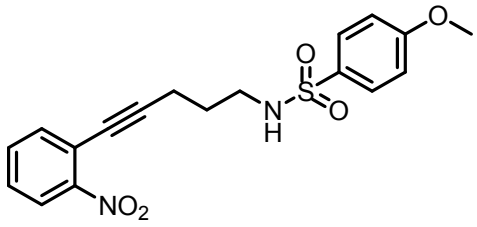
brown oil, yield 59%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.2 Hz, 1H), 7.56 (t, J = 7.0 Hz, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.43 – 7.37 (t, J = 7.0 Hz,1H), 3.84 (t, J = 6.1 Hz, 2H), 2.62 (t, J = 6.9 Hz, 2H), 2.32 (br, 1H), 1.89 (p, J = 6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 135.0, 132.9, 128.2, 124.6, 119.2, 98.7, 76.5, 61.4, 31.1, 16.54. ESI-MS: m/z 206.4 (100%, $[M+H]^+$).

N-(5-(2-nitrophenyl)pent-4-yn-1-yl)benzenesulfonamide



brown oil, yield 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 7.8 Hz, 2H), 7.57 – 7.45 (m, 5H), 7.40 (dt, J = 8.4, 4.3 Hz, 1H), 5.34 (s, 1H), 3.16 (q, J = 6.2 Hz, 2H), 2.52 (t, J = 6.6 Hz, 2H), 1.81 (p, J = 6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 139.8, 134.9, 132.9, 132.7, 129.2, 128.3, 127.1, 124.5, 118.8, 97.4, 77.0, 42.1, 28.1, 17.0. HRMS (ESI) calcd for $C_{17}H_{17}N_2O_4S$ $(M+H)^+$ 345.0909, found 345.0909.

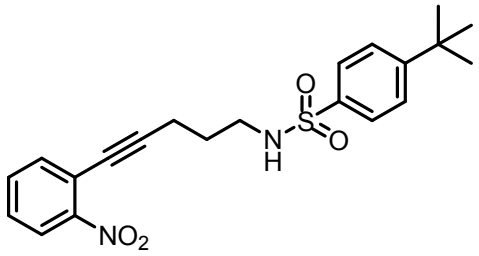
4-methoxy-N-(5-(2-nitrophenyl)pent-4-yn-1-yl)benzenesulfonamide



yellow oil, yield 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.2 Hz, 1H), 7.82

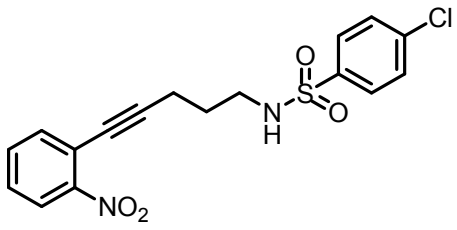
(d, J = 8.8 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.39 (dt, J = 8.6, 4.4 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 5.23 (t, J = 6.2 Hz, 1H), 3.81 (s, 3H), 3.13 (q, J = 6.5 Hz, 2H), 2.51 (t, J = 6.7 Hz, 2H), 1.80 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 149.8, 134.8, 132.8, 131.3, 129.2, 128.2, 124.5, 118.8, 114.3, 97.4, 77.0, 55.6, 42.0, 28.0, 17.0. HRMS (ESI) calcd for $C_{18}H_{19}N_2O_5S$ $(M+H)^+$ 375.1015, found 375.1016.

4-(tert-butyl)-N-(5-(2-nitrophenyl)pent-4-yn-1-yl)benzenesulfonamide



yellow oil, yield 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.52 – 7.44 (m, 4H), 7.39 – 7.32 (m, 1H), 5.50 (t, J = 6.1 Hz, 1H), 3.13 (q, J = 6.5 Hz, 2H), 2.50 (t, J = 6.8 Hz, 2H), 1.80 (p, J = 6.7 Hz, 2H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 149.8, 136.9, 134.8, 132.8, 128.2, 127.0, 126.1, 124.4, 118.8, 97.5, 76.9, 42.1, 35.0, 31.0, 28.2, 17.0. HRMS (ESI) calcd for $C_{21}H_{25}N_2O_4S$ $(M+H)^+$ 401.1535, found 401.1531.

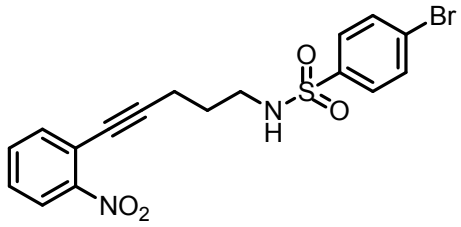
4**-chloro-N-(5-(2-nitrophenyl)pent-4-yn-1-yl)benzenesulfonamide**



white powder, yield 96%. Mp 88–89 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 8.6 Hz, 2H), 7.58 – 7.53 (m, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.46 – 7.40 (m, 1H), 5.10 (t, J = 5.7 Hz, 1H), 3.21 (q, J = 6.6 Hz, 2H), 2.57 (t, J = 6.7 Hz, 2H), 1.85 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 139.1, 138.4, 134.7, 132.9, 129.4, 128.6, 128.3, 124.6, 118.8, 97.1, 77.3, 42.1, 28.0, 17.0. HRMS (ESI) calcd for $C_{17}H_{16}ClN_2O_4S$ $(M+H)^+$ 379.0519,

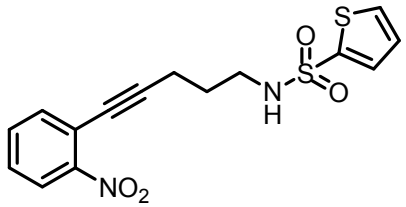
found 379.0522.

4-bromo-N-(5-(2-nitrophenyl)pent-4-yn-1-yl)benzenesulfonamide



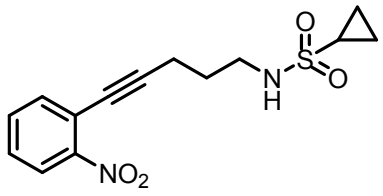
white powder, yield 95%. Mp 76–77 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.47 – 7.38 (m, 1H), 5.18 (t, *J* = 6.1 Hz, 1H), 3.19 (q, *J* = 6.5 Hz, 2H), 2.55 (t, *J* = 6.6 Hz, 2H), 1.83 (p, *J* = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 149.8, 138.9, 134.8, 132.9, 132.4, 128.7, 128.3, 127.6, 124.6, 118.8, 97.1, 77.2, 42.1, 28.0, 17.0. HRMS (ESI) calcd for $C_{17}H_{16}BrN_2O_4S$ $(M+H)^+$ 423.0014, found 423.0015.

N-(5-(2-nitrophenyl)pent-4-yn-1-yl)thiophene-2-sulfonamide



browm oil, yield 94%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.92 (d, *J* = 8.2 Hz, 1H), 7.61 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.54 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.37 (ddd, *J* = 8.6, 6.0, 3.0 Hz, 1H), 7.03 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.40 (t, *J* = 6.0 Hz, 1H), 3.22 (q, *J* = 6.5 Hz, 2H), 2.52 (t, *J* = 6.8 Hz, 2H), 1.82 (p, *J* = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 149.8, 140.7, 134.9, 132.9, 132.2, 132.0, 128.3, 127.6, 124.5, 118.8, 97.4, 77.1, 42.4, 28.0, 17.1. HRMS (ESI) calcd for $C_{15}H_{15}N_2O_4S_2$ $(M+H)^+$ 351.0473, found 351.0470.

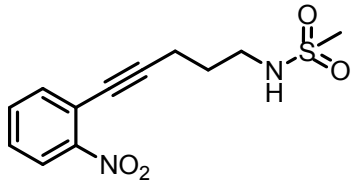
N-(5-(2-nitrophenyl)pent-4-yn-1-yl)cyclopropanesulfonamide



browm oil, yield 82%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.90 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.45 (m,

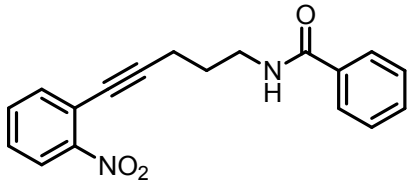
2H), 7.36 (t, J = 7.9 Hz, 1H), 5.10 (t, J = 5.2 Hz, 1H), 3.32 (q, J = 6.3 Hz, 2H), 2.55 (t, J = 6.7 Hz, 2H), 2.47 (ddd, J = 12.6, 8.1, 4.9 Hz, 1H), 1.86 (p, J = 6.6 Hz, 2H), 1.15 – 1.07 (m, 2H), 1.00 – 0.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 134.8, 132.9, 128.3, 124.4, 118.7, 97.5, 76.9, 42.2, 29.8, 28.7, 17.0, 5.3. HRMS (ESI) calcd for $C_{14}H_{17}N_2O_4S$ $(M+H)^+$ 309.0909, found 309.0907.

N-(5-(2-nitrophenyl)pent-4-yn-1-yl)methanesulfonamide



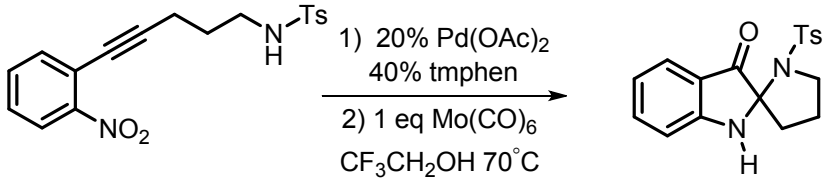
browm oil, yield 37%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.43 (t, J = 7.5 Hz, 1H), 4.90 (t, J = 5.6 Hz, 1H), 3.38 (q, J = 6.6 Hz, 2H), 3.02 (s, 3H), 2.62 (t, J = 6.6 Hz, 2H), 1.92 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 134.8, 132.9, 128.3, 124.5, 118.8, 97.2, 77.2, 42.1, 40.1, 28.4, 17.0. HRMS (ESI) calcd for $C_{12}H_{18}N_3O_4S$ $(M+NH_4)^+$ 300.1018, found 300.1020.

N-(5-(2-nitrophenyl)pent-4-yn-1-yl)benzamide



browm oil, yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.2 Hz, 2H), 7.57 – 7.49 (m, 2H), 7.47 – 7.32 (m, 4H), 6.84 (t, J = 6.1 Hz, 1H), 3.65 (q, J = 6.5 Hz, 2H), 2.59 (t, J = 6.8 Hz, 2H), 1.98 (p, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 149.9, 134.8, 134.5, 132.8, 131.4, 128.5, 128.2, 127.0, 124.5, 118.9, 98.1, 77.0, 39.3, 27.7, 17.5. HRMS (ESI) calcd for $C_{18}H_{17}N_2O_3$ $(M+H)^+$ 309.1239, found 309.1239.

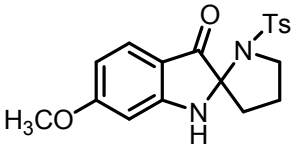
General procedure for spiro-pseudoindoxyl from *o*-alkynylnitrobenzene[4,5]



1a **2a**

In a 10 mL Schlenk tube, under a argon atmosphere, was added *o*-alkynylnitrobenzene (50 mg, 0.14 mmol) followed by $Pd(OAc)_2$ (6.26 mg, 0.028 mmol), tetramethylphenanthroline (13 mg, 0.056 mmol), $Mo(CO)_6$ (37 mg. 0.14 mmol) in 2.0 mL of TFE. The Schlenk tube was sealed and heated at 70 °C for either 24 h. The reaction mixture was then cooled down to room temperature and filtered through a pad of celite. The filtrate was then evaporated and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 3:1) to give **2a** as a yellow powder, yield 84%. Mp 201–202 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.9 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 6.88 (t, J = 7.5 Hz, 1H), 6.79 (d, J = 7.7 Hz, 1H), 4.97 (s, 1H), 3.65 (t, J = 8.1 Hz, 1H), 3.33 (dd, J = 15.9, 7.9 Hz, 1H), 2.42 (s, 3H), 2.30 – 1.89 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 158.4, 143.6, 137.7, 136.3, 129.4, 128.0, 124.9, 120.0, 119.8, 112.3, 83.2, 48.4, 39.9, 23.7, 21.6. HRMS (ESI) calcd for $C_{18}H_{19}N_2O_3S$ $(M+H)^+$ 343.1116, found 343.1116.

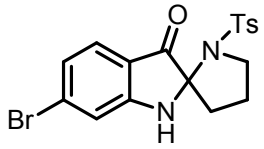
6-methoxy-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 83%. Mp 173–174 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 6.39 (d, J = 8.6 Hz, 1H), 6.20 (s, 1H), 5.56 (s, 1H), 3.70 (s, 3H), 3.69 – 3.62 (m, 1H), 3.22 (dd, J = 16.2, 8.2 Hz, 1H), 2.42 (s, 3H),

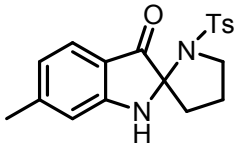
2.30 – 2.08 (m, 3H), 2.00 – 1.91 (m, 1H).^{13}C NMR (100 MHz, CDCl3) δ 196.3, 168.1, 161.0, 143.6, 136.2, 129.4, 128.1, 126.2, 113.0, 109.1, 95.1, 84.0, 55.6, 48.4, 39.9, 23.6, 21.6. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_4S$ $(M+H)^+$ 373.1222, found 373.1222.

6-bromo-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



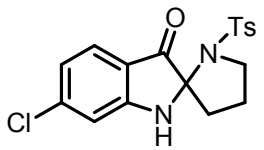
yellow powder, yield 74%. Mp 184–185 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (s, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 6.99 (s, 1H), 6.93 (d, J = 8.1 Hz, 1H), 5.76 (s, 1H), 3.42 – 3.36 (m, 1H), 3.32 – 3.25 (m, 1H), 2.41 (s, 3H), 2.08 – 1.96 (m, 3H), 1.90 – 1.80 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.3, 159.9, 143.7, 136.8, 132.2, 130.0, 127.9, 126.4, 121.5, 118.1, 114.6, 83.2, 48.6, 39.0, 23.7, 21.5. HRMS (ESI) calcd for $C_{18}H_{18}BrN_2O_3S$ $(M+H)^+$ 421.0222, found 421.0213.

6-methyl-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 84%. Mp 166–167 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 (d, J = 8.1 Hz, 2H), 7.52 (s, 1H), 7.41 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 7.8 Hz, 1H), 6.63 (s, 1H), 6.61 (s, 1H), 3.41 – 3.36 (m, 1H), 3.30 (dd, J = 16.0 Hz, 8.0 Hz, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 2.06 – 1.99 (m, 3H), 1.84 – 1.78 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.3, 160.0, 149.0, 143.5, 137.1, 129.8, 128.0, 124.5, 120.1, 116.9, 112.2, 83.3, 48.7, 39.2, 23.6, 22.5, 21.5. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_3S$ $(M+H)^+$ 357.1273, found 357.1273.

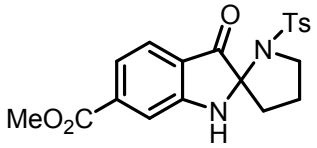
6-chloro-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 81%. Mp 185–186 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (s, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.50

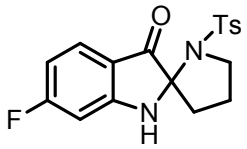
(d, J = 8.2 Hz, 1H), 7.42 (d, J = 8.1 Hz, 2H), 6.83 (s, 1H), 6.80 (d, J = 8.2 Hz, 1H), 3.41 – 3.35 (m, 1H), 3.32 – 3.25 (m, 1H), 2.41 (s, 3H), 2.08 – 1.96 (m, 3H), 1.90 – 1.82 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.7, 159.4, 143.2, 142.3, 136.4, 129.5, 127.4, 125.9, 118.2, 117.3, 111.1, 82.8, 48.1, 38.5, 23.2, 21.0. HRMS (ESI) calcd for $C_{18}H_{18}ClN_2O_3S$ $(M+H)^+$ 377.0727, found 377.0722.

methyl 3-oxo-1'-tosylspiro[indoline-2,2'-pyrrolidine]-6-carboxylate



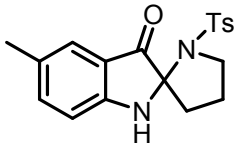
yellow powder, yield 46%. Mp 170–171 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 3H), 7.49 (d, J = 7.7 Hz, 1H), 7.43 (s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 5.16 (s, 1H), 3.91 (s, 3H), 3.61 (t, J = 7.7 Hz, 1H), 3.32 (dd, J = 15.8, 8.2 Hz, 1H), 2.40 (s, 3H), 2.30 – 2.01 (m, 3H), 1.98 – 1.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 166.4, 157.7, 143.8, 138.0, 136.2, 129.5, 127.9, 124.8, 122.9, 120.5, 113.4, 83.5, 52.6, 48.4, 39.9, 23.7, 21.5. HRMS (ESI) calcd for $C_{20}H_{21}N_2O_5S$ $(M+H)^+$ 401.1171, found 401.1174.

6-fluoro-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



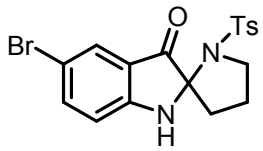
pale yellow powder, yield 70%. Mp 200–201 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.8 Hz, 2H), 7.67 – 7.60 (m, 1H), 7.30 (d, J = 7.8 Hz, 2H), 6.56 (t, J = 8.7 Hz, 1H), 6.43 (d, J = 9.2 Hz, 1H), 5.27 (s, 1H), 3.65 (t, J = 6.5 Hz, 1H), 3.29 (dd, J = 15.8, 8.2 Hz, 1H), 2.43 (s, 3H), 2.30 – 1.91 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 170.9, 168.3, 159.9 (J = 14 Hz), 143.8, 136.2, 129.5, 127.9, 116.4, 108.1 (J = 24 Hz), 98.9 (J = 26 Hz), 83.7, 48.41, 39.9, 23.6, 21.5. HRMS (ESI) calcd for $C_{18}H_{18}FN_2O_3S$ $(M+H)^+$ 361.1022, found 361.1024.

5-methyl-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



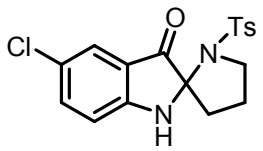
yellow powder, yield 64%. Mp 195–196 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.9 Hz, 2H), 7.45 (s, 1H), 7.34 – 7.25 (m, 3H), 6.74 (d, J = 8.2 Hz, 1H), 4.82 (s, 1H), 3.64 (t, J = 6.9 Hz, 1H), 3.32 (dd, J = 15.7, 8.6 Hz, 1H), 2.42 (s, 3H), 2.30 (s, 3H), 2.28 – 2.19 (m, 1H), 2.18 – 2.00 (m, 2H), 1.96 – 1.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 156.7, 143.5, 139.0, 136.4, 129.4, 129.4, 128.0, 124.4, 120.3, 112.4, 83.7, 48.4, 40.0, 23.7, 21.6, 20.6. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_3S$ $(M+H)^+$ 357.1273, found 357.1273.

5-bromo-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 67%. Mp 187–188 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.65 (m, 3H), 7.48 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 6.66 (d, J = 7.7 Hz, 1H), 5.31 (s, 1H), 3.65 (t, J = 8.0 Hz, 1H), 3.26 (dd, J = 16.0, 8.0 Hz, 1H), 2.43 (s, 3H), 2.29 – 1.87 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 156.9, 143.8, 140.1, 136.1, 129.5, 127.9, 127.3, 121.3, 114.0, 111.8, 83.7, 48.3, 39.9, 23.7, 21.6. HRMS (ESI) calcd for $C_{18}H_{18}BrN_2O_3S$ $(M+H)^+$ 421.0222, found 421.0218.

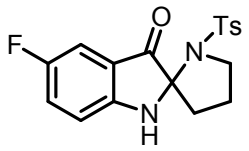
5-chloro-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 71%. Mp 183–184 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.5 Hz, 2H), 7.59 (s, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.30 (d, J = 7.5 Hz, 2H), 6.73 (d, J = 8.5 Hz, 1H), 5.19 (s, 1H), 3.66 (t, J = 7.6 Hz, 1H), 3.28 (dd, J = 15.6, 7.7 Hz, 1H), 2.43 (s, 3H), 2.30 – 1.89 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 156.6, 143.8, 137.5, 136.1, 129.5, 127.9, 124.9,

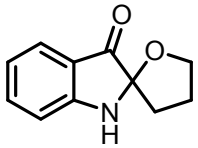
124.2, 120.8, 113.6, 83.8, 48.3, 39.9, 23.7, 21.6. HRMS (ESI) calcd for $C_{18}H_{18}ClN_2O_3S$ $(M+H)^+$ 377.0727, found 377.0724.

5-fluoro-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



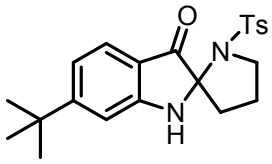
yellow powder, yield 58%. Mp 185–186 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2H), 7.37 – 7.21 (m, 4H), 6.80 (d, J = 6.0 Hz, 1H), 4.94 (s, 1H), 3.67 (t, J = 7.1 Hz, 1H), 3.32 (dd, J = 15.6, 8.1 Hz, 1H), 2.45 (s, 3H), 2.32 – 1.92 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 157.0 (J = 239.0 Hz), 154.9, 143.8, 136.1, 129.5, 127.9, 125.4 (J = 25.1 Hz), 120.5 (J = 7.3 Hz), 113.7 (J = 7.3 Hz), 110.0 (J = 22.8 Hz), 84.3, 48.4, 40.1, 23.8, 21.6. HRMS (ESI) calcd for $C_{18}H_{18}FN_2O_3S$ $(M+H)^+$ 361.1022, found 361.1020.

4,5-dihydro-3H-spiro[furan-2,2'-indolin]-3'-one



yellow oil. yield 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 6.83 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 8.1 Hz, 1H), 4.92 (s, 1H), 4.19 – 4.06 (m, 2H), 2.36 – 2.23 (m, 2H), 2.17 – 1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 159.8, 137.9, 125.1, 119.7, 119.1, 112.2, 95.1, 69.3, 34.1, 25.8. HRMS (ESI) calcd for $C_{11}H_{12}NO_2$ $(M+H)^+$ 190.0868, found 190.0863.

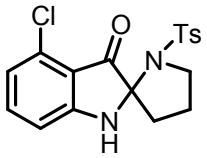
6-(tert-butyl)-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 48%. Mp 179–180 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.2 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 6.95 (d, J = 8.2 Hz, 1H), 6.81 (s, 1H), 4.96 (s, 1H), 3.65 (td, J = 8.2, 2.8 Hz, 1H), 3.29 (dd, J = 15.7, 8.8 Hz,

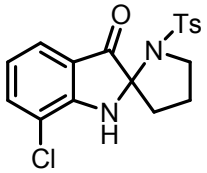
1H), 2.42 (s, 3H), 2.30 – 2.20 (m, 1H), 2.18 – 2.01 (m, 2H), 1.98 – 1.86 (m, 1H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 162.3, 158.9, 143.5, 136.3, 129.4, 128.0, 124.4, 118.2, 117.7, 109.1, 83.7, 48.4, 40.1, 35.7, 31.0, 23.7, 21.6. HRMS (ESI) calcd for $C_{22}H_{27}N_2O_3S$ $(M+H)^+$ 399.1742, found 399.1742.

4-chloro-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



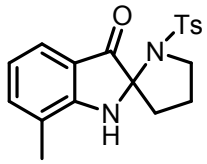
yellow powder, yield 45%. Mp 200–201 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 8.3 Hz, 1H), 7.25 (d, J = 7.3 Hz, 2H), 6.76 (d, J = 7.5 Hz, 1H), 6.65 (d, J = 8.1 Hz, 1H), 5.17 (s, 1H), 3.66 (t, J = 8.0 Hz, 1H), 3.27 (dd, J = 15.7, 7.5 Hz, 1H), 2.40 (s, 3H), 2.29 – 1.89 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 159.6, 143.8, 137.8, 135.9, 132.6, 129.5, 128.0, 120.6, 116.6, 110.5, 83.4, 48.4, 39.9, 23.5, 21.6. HRMS (ESI) calcd for $C_{18}H_{18}ClN_2O_3S$ $(M+H)^+$ 377.0727, found 377.0725.

7-chloro-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 27%. Mp 178–179 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.5 Hz, 2H), 7.54 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 7.4 Hz, 1H), 7.25 (d, J = 7.3 Hz, 2H), 6.80 (t, J = 7.5 Hz, 1H), 5.06 (s, 1H), 3.56 (t, J = 7.8 Hz, 1H), 3.41 (dd, J = 15.2, 7.6 Hz, 1H), 2.38 (s, 3H), 2.30 – 1.87 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 154.5, 143.7, 136.4, 136.3, 129.5, 127.9, 123.4, 121.4, 120.2, 117.3, 83.2, 48.5, 39.8, 23.7, 21.6. HRMS (ESI) calcd for $C_{18}H_{18}ClN_2O_3S$ $(M+H)^+$ 377.0727, found 377.0727.

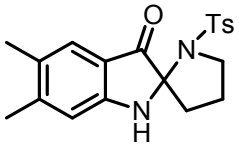
7-methyl-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 38%. Mp 178–179 ºC. ^{1}H NMR (400

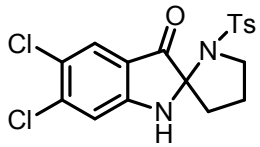
MHz, $CDCl_3$) δ 7.72 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 7.5 Hz, 1H), 7.31 (d, J = 7.1 Hz, 1H), 7.27 (d, J = 7.6 Hz, 2H), 6.82 (t, J = 7.2 Hz, 1H), 4.74 (s, 1H), 3.65 (t, J = 7.6 Hz, 1H), 3.40 (dd, J = 15.7, 7.9 Hz, 1H), 2.42 (s, 3H), 2.34 – 1.88 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 157.6, 143.5, 137.8, 136.5, 129.4, 128.0, 122.3, 121.3, 119.9, 119.6, 83.3, 48.6, 40.1, 23.6, 21.6, 15.8. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_3S$ $(M+H)^+$ 357.1273, found 357.1275.

5,6-dimethyl-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



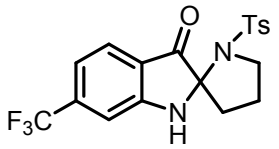
yellow powder, yield 48%. Mp 171–172 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.8 Hz, 2H), 7.38 (s, 1H), 7.25 (d, J = 7.8 Hz, 2H), 6.60 (s, 1H), 4.81 (s, 1H), 3.60 (t, J = 7.7 Hz, 1H), 3.28 (dd, J = 15.5, 7.6 Hz, 1H), 2.39 (s, 3H), 2.24 (s, 3H), 2.18 (s, 3H), 2.14 – 1.80 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 157.5, 148.6, 143.5, 136.4, 129.4, 128.8, 128.0, 124.7, 118.2, 113.4, 83.7, 48.4, 40.0, 23.7, 21.6, 21.3, 19.3. HRMS (ESI) calcd for $C_{20}H_{23}N_2O_3S$ $(M+H)^+$ 371.1429, found 371.1427.

5,6-dichloro-1'-tosylspiro[indoline-2,2'-pyrrolidin]-3-one



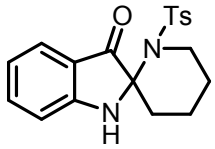
yellow powder, yield 53%. Mp 188–189 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 3H), 7.31 (d, J = 8.0 Hz, 2H), 6.93 (s, 1H), 5.20 (s, 1H), 3.64 (t, J = 7.7 Hz, 1H), 3.27 (dd, J = 16.0, 7.9 Hz, 1H), 2.44 (s, 3H), 2.30 – 1.90 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 156.2, 144.0, 141.9, 135.9, 129.6, 127.9, 125.9, 123.7, 119.4, 113.8, 83.8, 48.3, 39.9, 23.7, 21.6. HRMS (ESI) calcd for $C_{18}H_{17}Cl_2N_2O_3S$ $(M+H)^+$ 411.0337, found 411.0324.

1'-tosyl-6-(trifluoromethyl)spiro[indoline-2,2'-pyrrolidin]-3-one



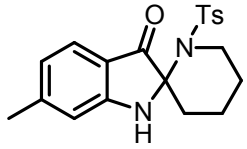
yellow powder, yield 60%. Mp 185–186 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, J = 8.0 Hz, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 7.8 Hz, 1H), 7.05 (s, 1H), 5.34 (s, 1H), 3.68 (t, J = 8.0 Hz, 1H), 3.33 (dd, J = 15.7, 8.4 Hz, 1H), 2.46 (s, 3H), 2.34 – 1.94 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 157.5, 144.0, 138.5 (J = 32.3 Hz), 136.0, 129.6, 127.9, 125.5, 123.5 (J = 272.0 Hz), 122.0, 116.1, 109.2, 83.6, 48.3, 39.9, 23.8, 21.6. HRMS (ESI) calcd for $C_{19}H_{18}F_3N_2O_3S$ $(M+H)^+$ 411.0990, found 411.0985.

1'-tosylspiro[indoline-2,2'-piperidin]-3-one



yellow powder, yield 59%. Mp 135–136 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.2 Hz, 2H), 7.74 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 6.6 Hz, 1H), 7.29 (d, J = 7.2 Hz, 2H), 6.92 (t, J = 7.0 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 5.39 (s, 1H), 3.45 (d, J = 11.5 Hz, 1H), 3.18 (t, J = 10.8 Hz, 1H), 2.44 (s, 3H), 2.01 – 1.50 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 157.1, 143.7, 137.0, 135.8, 129.3, 128.4, 125.2, 120.3, 119.8, 112.8, 76.7, 44.5, 36.1, 24.3, 21.6, 19.9. HRMS (ESI) calcd for $C_{19}H_{21}N_2O_3S$ $(M+H)^+$ 357.1273, found 357.1267.

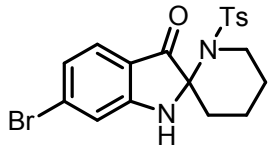
6-methyl-1'-tosylspiro[indoline-2,2'-piperidin]-3-one



yellow powder, yield 59%. Mp 186–187 ºC. ^{1}H NMR (400 MHz, CD_3OD-$CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 7.9 Hz, 2H), 6.69 (d, J = 7.9 Hz, 1H), 6.63 (s, 1H), 3.42 (d, J = 11.6 Hz, 1H), 3.04 (t, J = 10.7 Hz, 1H), 2.43 (s, 3H), 2.36 (s, 3H), 1.94 – 1.78 (m, 3H), 1.67 – 1.50 (m, 3H). ^{13}C NMR (100 MHz, CD_3OD-$CDCl_3$) δ 198.8, 158.4, 149.1, 143.9, 135.4, 129.2, 128.4, 124.7, 121.0, 117.2, 112.5, 77.0, 44.6, 36.2, 24.3, 22.3,

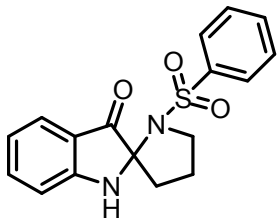
21.3, 19.6. HRMS (ESI) calcd for $C_{20}H_{23}N_2O_3S$ $(M+H)^+$ 371.1429, found 371.1432.

6-bromo-1'-tosylspiro[indoline-2,2'-piperidin]-3-one



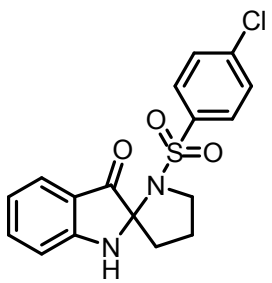
yellow powder, yield 63%. Mp 200–201 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 1H), 7.40 (d, J = 8.1 Hz, 2H), 6.99 – 6.92 (m, 2H), 3.34 – 3.29 (m, 1H), 2.84 (t, J = 11.4 Hz, 1H), 2.40 (s, 3H), 1.80 – 1.37 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.3, 158.2, 143.6, 135.2, 130.9, 129.3, 128.0, 126.2, 121.0, 117.9, 114.2, 76.4, 44.4, 35.8, 23.9, 21.0, 18.8. HRMS (ESI) calcd for $C_{19}H_{20}BrN_2O_3S$ $(M+H)^+$ 435.0378, found 435.0365.

1'-(phenylsulfonyl)spiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 73%. Mp 189–190 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.5 Hz, 2H), 7.66 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 7.3 Hz, 1H), 7.54 – 7.44 (m, 3H), 6.89 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 5.12 (s, 1H), 3.67 (td, J = 8.3, 3.1 Hz, 1H), 3.36 (dd, J = 15.7, 8.7 Hz, 1H), 2.33 – 2.23 (m, 1H), 2.22 – 2.04 (m, 2H), 1.96 (ddd, J = 11.9, 6.1, 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 158.4, 139.3, 137.7, 132.8, 128.8, 127.9, 124.9, 119.9, 119.8, 112.3, 83.3, 48.5, 39.8, 23.7. HRMS (ESI) calcd for $C_{17}H_{17}N_2O_3S$ $(M+H)^+$ 329.0960, found 329.0954.

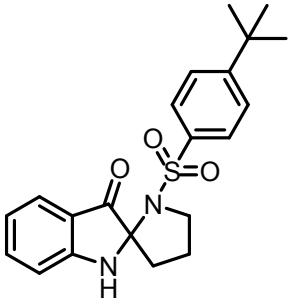
1'-((4-chlorophenyl)sulfonyl)spiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 78%. Mp 182–183 ºC. ^{1}H NMR (400 MHz, $CDCl_3$-CD_3OD) δ 7.81 (d, J = 7.9 Hz, 2H), 7.62 (d, J = 7.5 Hz, 1H), 7.54 – 7.45 (m, 3H), 6.86 (t, J = 7.5 Hz, 1H), 6.82

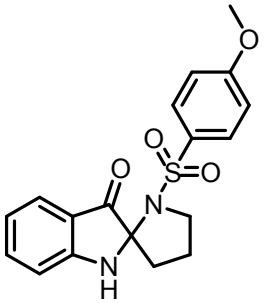
(d, J = 8.1 Hz, 1H), 3.56 (t, J = 7.2 Hz, 1H), 3.42 (dd, J = 15.4, 7.9 Hz, 1H), 2.30 – 2.05 (m, 3H), 2.00 – 1.89 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$-CD_3OD) δ 199.9, 159.1, 139.3, 138.0, 137.8, 129.3, 129.0, 124.8, 119.3, 119.2, 112.1, 83.2, 48.5, 39.3, 23.5. HRMS (ESI) calcd for $C_{17}H_{15}ClN_2O_3S$ $(M+H)^+$ 363.0570, found 363.0561.

1'-((4-(tert-butyl)phenyl)sulfonyl)spiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 83%. Mp 175–176 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 7.6 Hz, 1H), 6.87 (t, J = 7.4 Hz, 1H), 6.80 (d, J = 8.1 Hz, 1H), 5.05 (s, 1H), 3.65 (td, J = 8.3, 3.0 Hz, 1H), 3.34 (dd, J = 15.8, 8.7 Hz, 1H), 2.32 – 2.03 (m, 3H), 1.94 (ddd, J = 11.9, 6.0, 3.1 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$-CD_3OD) δ 200.3, 159.2, 156.6, 138.0, 136.1, 127.7, 126.0, 125.8, 124.8, 119.1, 112.1, 83.2, 48.3, 39.3, 35.0, 30.9, 23.6. HRMS (ESI) calcd for $C_{21}H_{25}N_2O_3S$ $(M+H)^+$ 385.1586, found 385.1588.

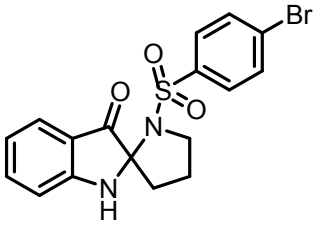
1'-((4-methoxyphenyl)sulfonyl)spiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 68%. Mp 167–168 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.8 (d, J = 8.9 Hz, 2H), 7.64 (d, J = 7.7 Hz, 1H), 7.50 – 7.43 (m, 1H), 6.95 (d, J = 8.9 Hz, 2H), 6.87 (t, J = 7.4 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H), 5.08 (s, 1H), 3.87 (s, 3H), 3.63 (td, J = 8.3, 3.2 Hz, 1H), 3.30 (td, J = 8.8, 7.0 Hz, 1H), 2.31 – 2.21 (m, 1H), 2.19 – 2.02 (m, 2H), 1.94 (ddd, J = 12.1, 6.2, 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$-CD_3OD) δ 200.3, 163.1, 159.1, 137.9, 130.7, 130.0, 124.7, 119.2, 119.1, 113.9,

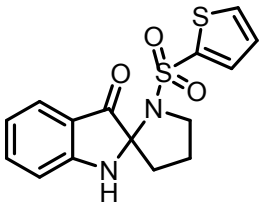
112.1, 83.2, 55.5, 48.3, 39.4, 23.5. HRMS (ESI) calcd for $C_{18}H_{19}N_2O_4S$ $(M+H)^+$ 359.1066, found 359.1064.

1'-((4-bromophenyl)sulfonyl)spiro[indoline-2,2'-pyrrolidin]-3-one



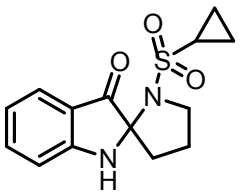
yellow powder, yield 82%. Mp 172–173 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 2H), 7.67 – 7.61 (m, 3H), 7.50 (t, J = 7.7 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 4.91 (s, 1H), 3.65 (td, J = 8.4, 3.0 Hz, 1H), 3.34 (dd, J = 15.7, 8.6 Hz, 1H), 2.32 – 1.91 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$-CD_3OD) δ 200.0, 159.2, 138.3, 138.1, 132.0, 129.4, 127.8, 124.8, 119.3, 119.1, 112.1, 83.2, 48.5, 39.2, 23.5. HRMS (ESI) calcd for $C_{17}H_{16}BrN_2O_3S$ $(M+H)^+$ 407.0065, found 407.0066.

1'-(thiophen-2-ylsulfonyl)spiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 79%. Mp 184–185 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.7 Hz, 1H), 7.62 (d, J = 3.0 Hz, 1H), 7.58 (d, J = 4.8 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.89 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 8.1 Hz, 1H), 4.88 (s, 1H), 3.69 (td, J = 8.5, 2.9 Hz, 1H), 3.53 (dd, J = 15.8, 8.7 Hz, 1H), 2.37 – 1.93 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.5, 159.4, 139.8, 137.5, 133.5, 133.0, 127.4, 124.2, 118.7, 118.2, 112.0, 82.6, 48.5, 38.4, 23.1. HRMS (ESI) calcd for $C_{15}H_{15}N_2O_3S_2$ $(M+H)^+$ 335.0524, found 335.0511.

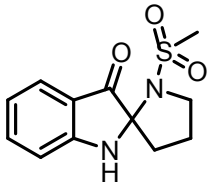
1'-(cyclopropylsulfonyl)spiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 81%. Mp 192–193 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.7 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H),

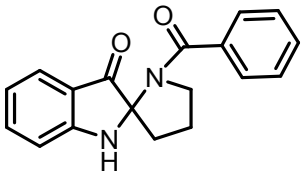
6.88 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 8.2 Hz, 1H), 5.10 (s, 1H), 3.76 (td, J = 8.1, 1.9 Hz, 1H), 3.62 (dd, J = 15.5, 7.7 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.39 – 2.29 (m, 1H), 2.27 – 2.01 (m, 3H), 1.23 – 1.16 (m, 1H), 1.14 – 1.02 (m, 2H), 0.96 – 0.87 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 199.5, 159.6, 137.9, 124.6, 119.0, 118.4, 112.4, 82.8, 49.2, 39.4, 29.7, 23.8, 5.0, 4.8. HRMS (ESI) calcd for $C_{14}H_{17}N_2O_3S$ $(M+H)^+$ 293.0960, found 293.0960.

1'-(methylsulfonyl)spiro[indoline-2,2'-pyrrolidin]-3-one



yellow powder, yield 87%. Mp 191–192 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70 (s, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 6.76 (t, J = 7.4 Hz, 1H), 3.64 – 3.56 (m, 1H), 3.43 (dd, J = 15.5, 8.9 Hz, 1H), 2.99 (s, 3H), 2.18 – 2.01 (m, 3H), 1.94 – 1.86 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.8, 159.3, 137.4, 124.1, 118.6, 118.0, 112.1, 82.2, 48.5, 39.0, 38.9, 23.1. HRMS (ESI) calcd for $C_{14}H_{15}N_2O_3S$ $(M+H)^+$ 267.0803, found 267.0795.

1'-benzoylspiro[indoline-2,2'-pyrrolidin]-3-one



yellow oil, yield 37%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 7.0 Hz, 2H), 7.47 – 7.33 (m, 4H), 6.87 (t, J = 7.3 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 4.88 (s, 1H), 3.71 (t, J = 5.8 Hz, 2H), 2.34 – 2.18 (m, 2H), 2.04 – 1.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 168.8, 158.2, 136.9, 135.6, 130.4, 128.2, 127.4, 124.6, 120.9, 119.7, 112.4, 82.0, 50.7, 37.3, 24.2. HRMS (ESI) calcd for $C_{18}H_{17}N_2O_2$ $(M+H)^+$ 293.1290, found 293.1285.

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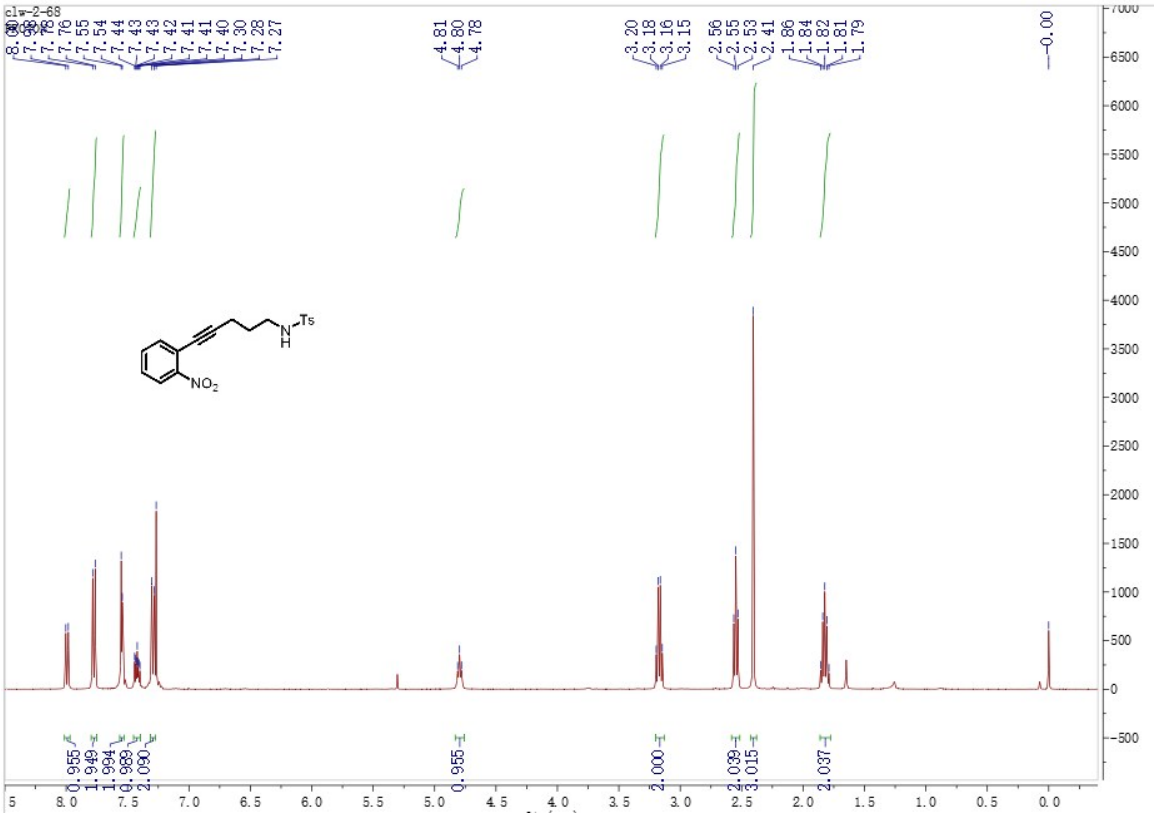
(4) Jana, N.; Zhou, F.; Driver, T. G. *J. Am. Chem. Soc*. **2015**, *137*, 6738.

(5) Zhou, F.; Wang, D. S.; Driver, T. G. *Adv.Synth. Catal*. **2015**, *357*, 3463.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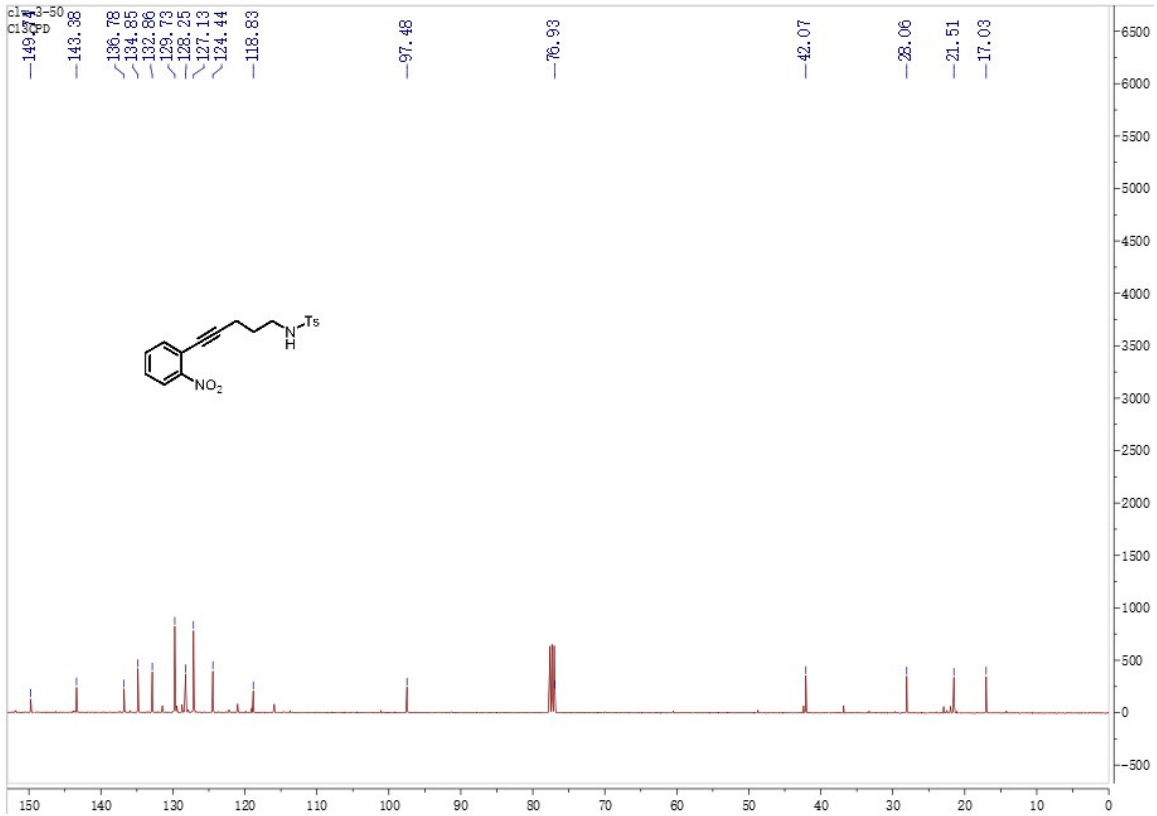
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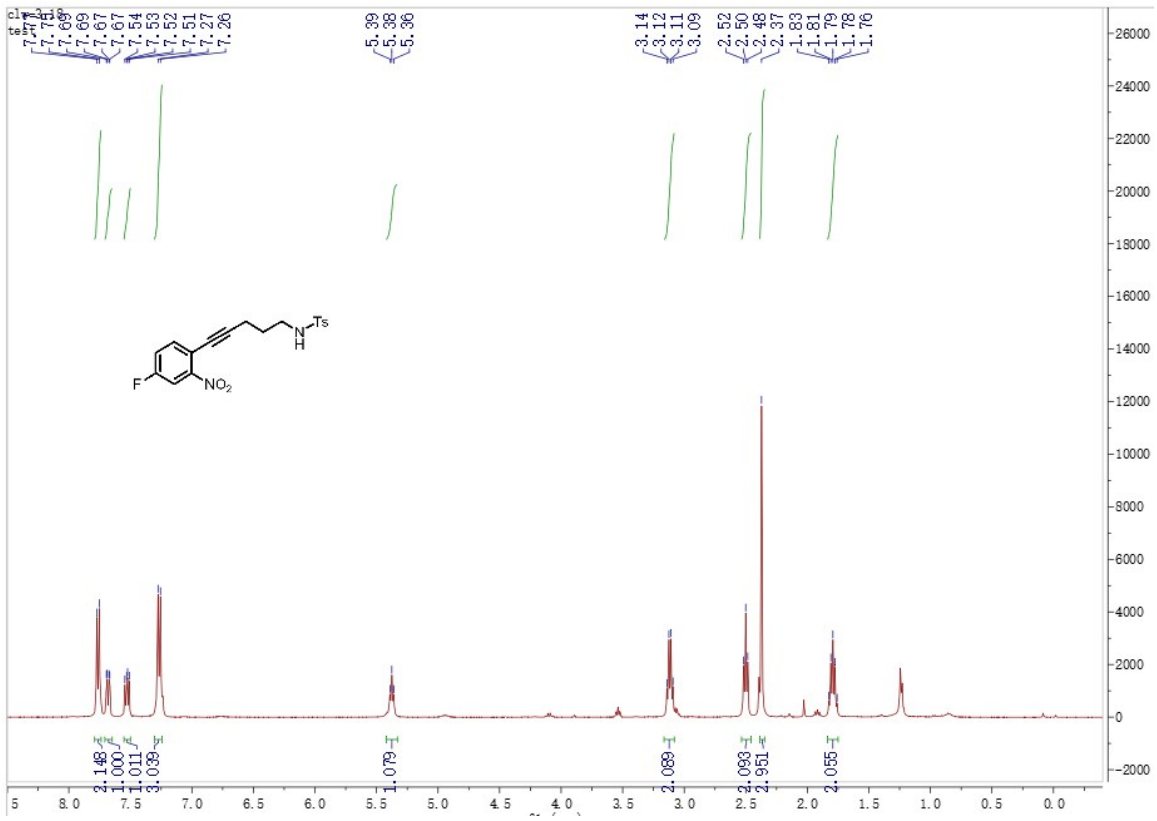
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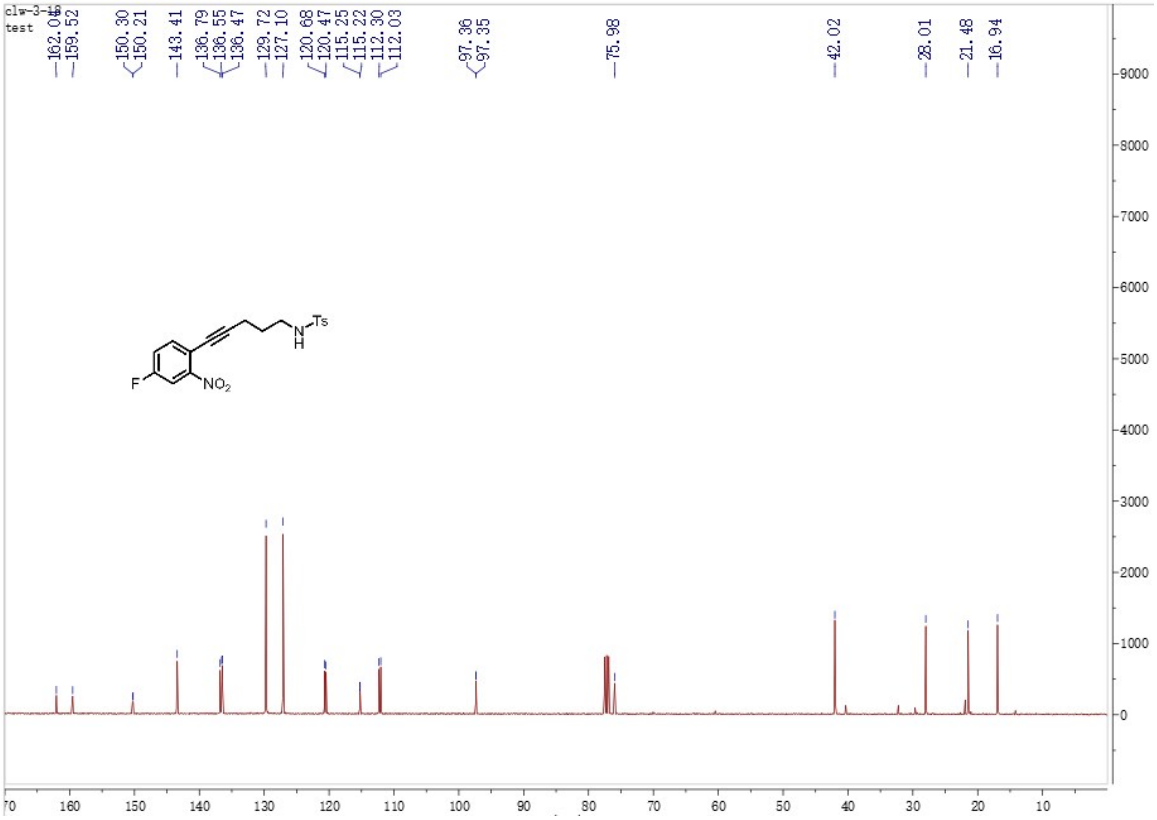
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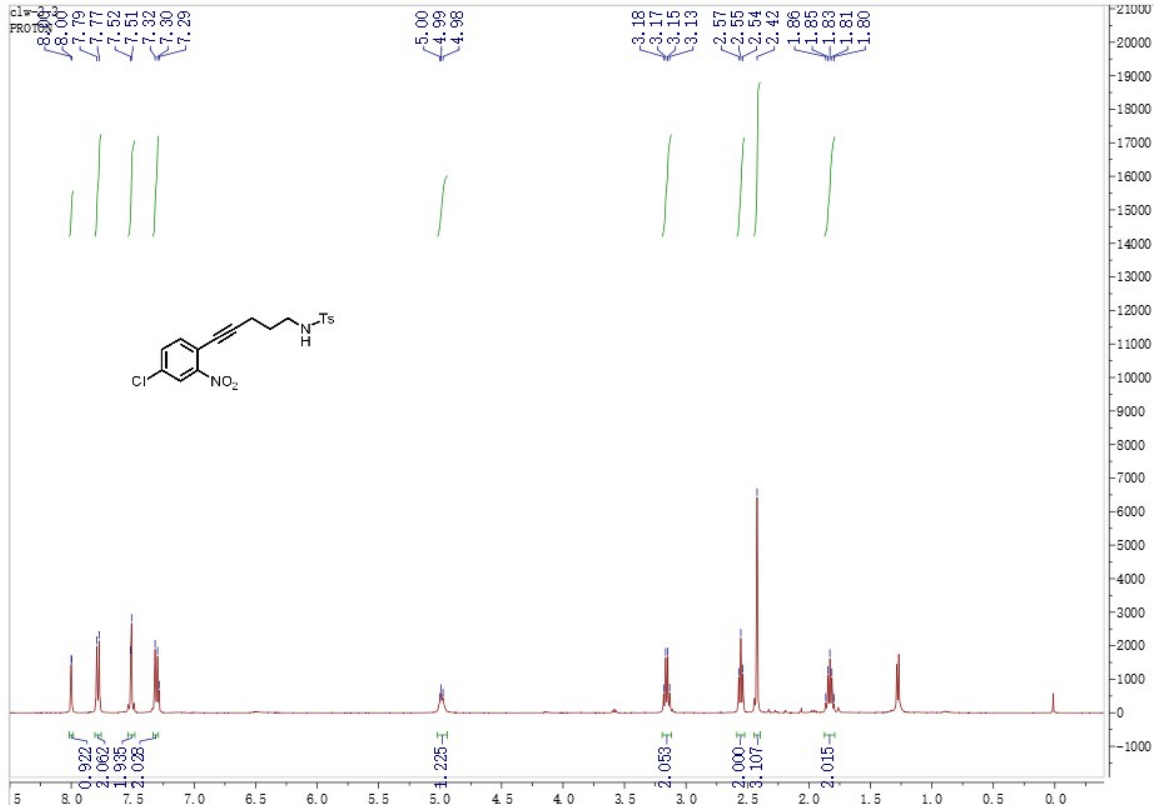
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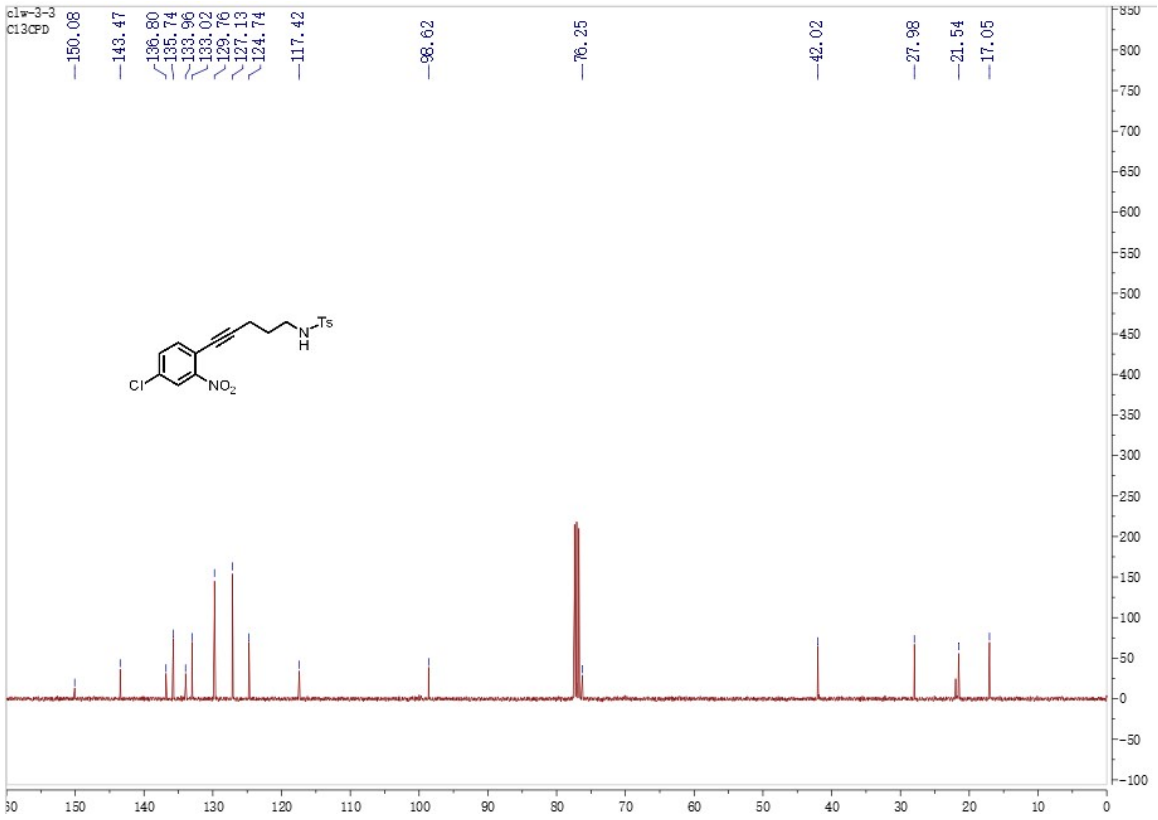
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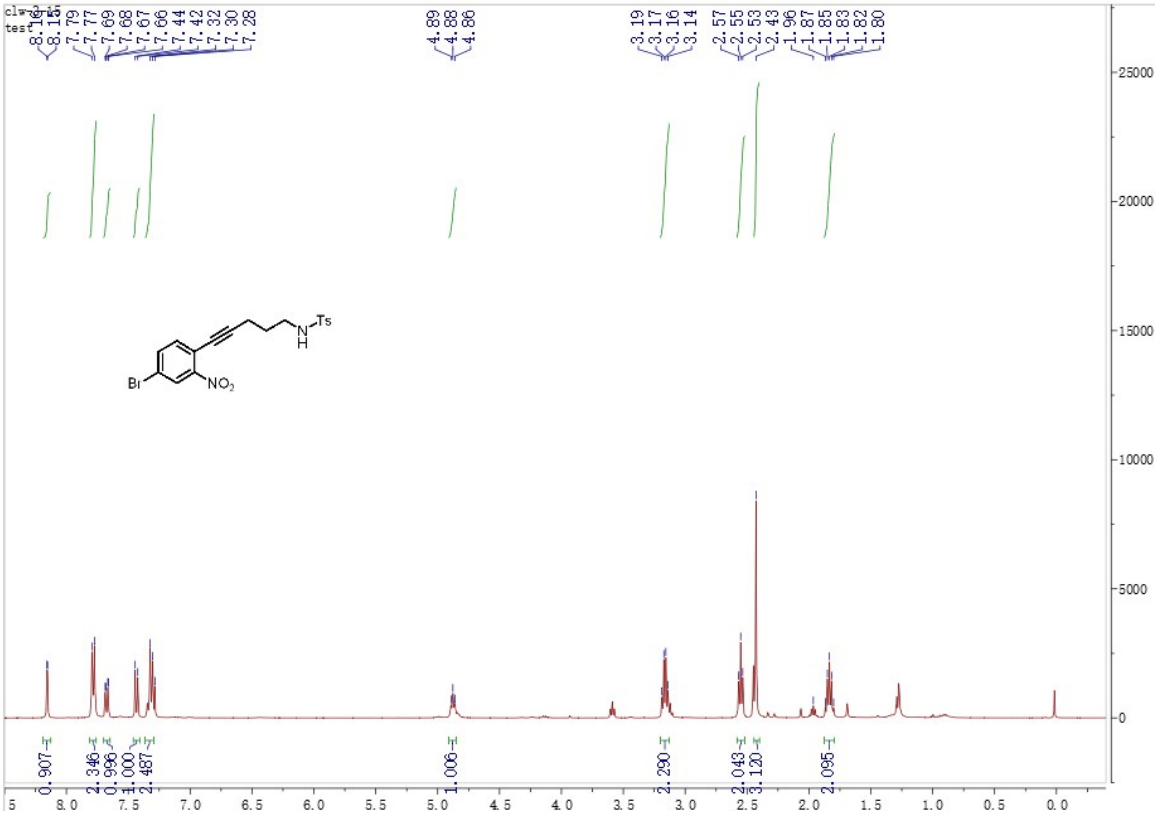
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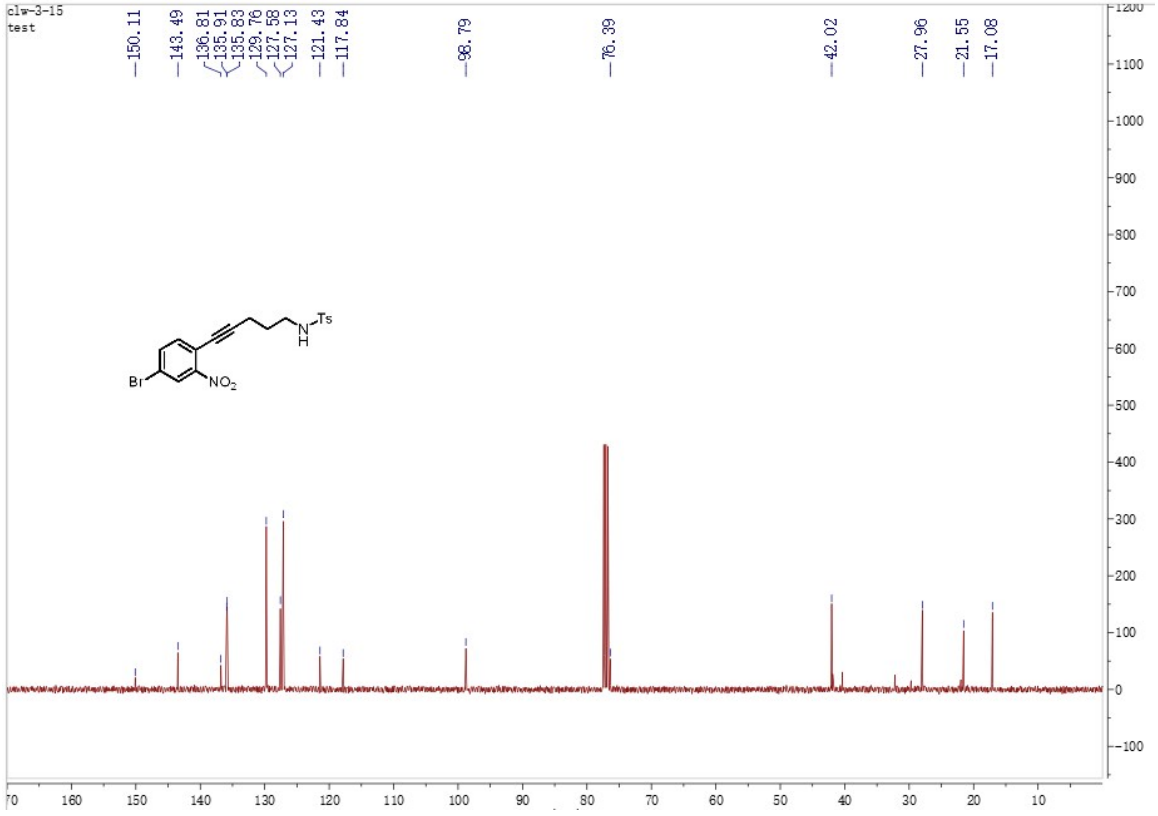
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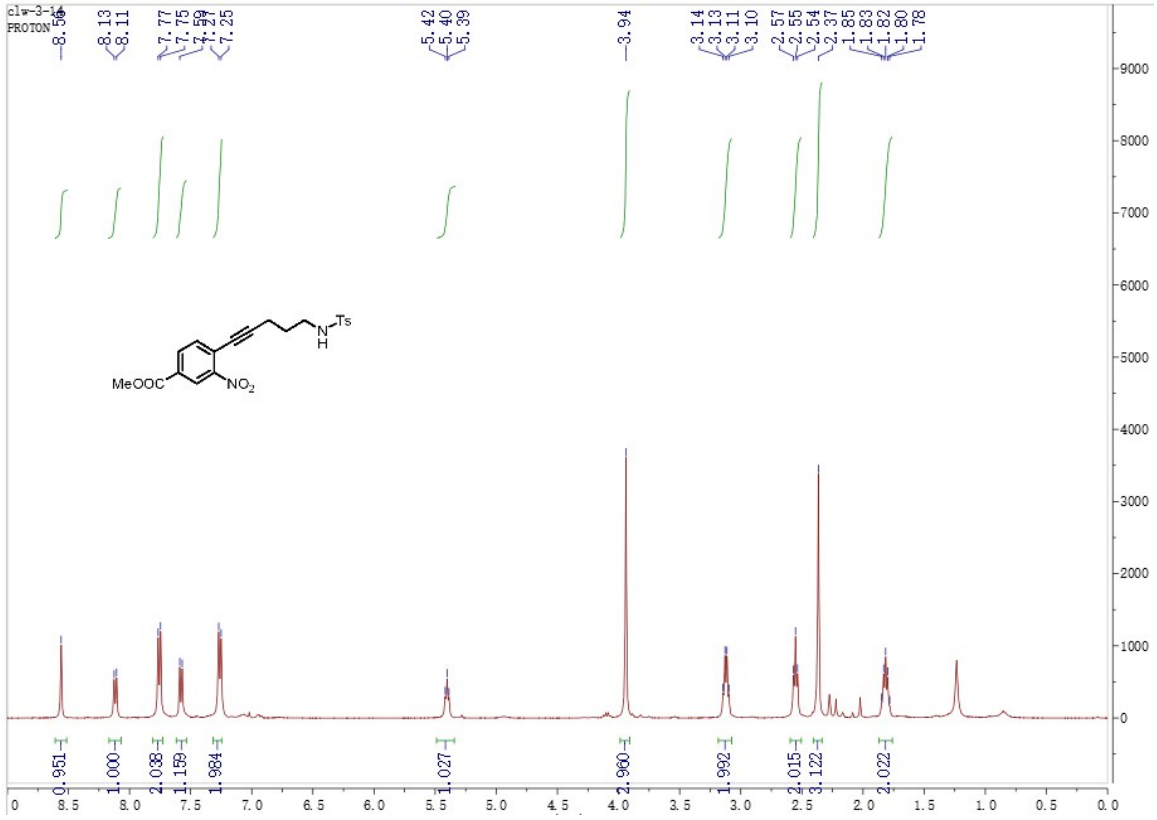
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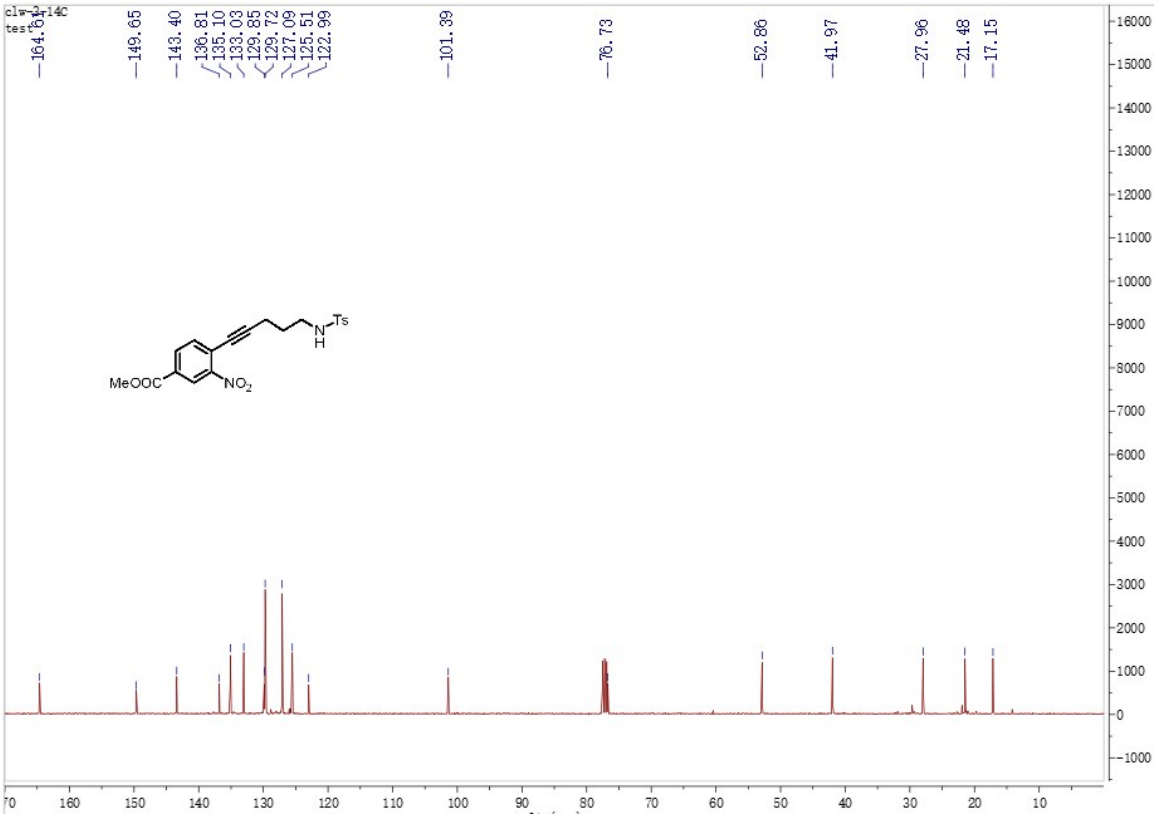
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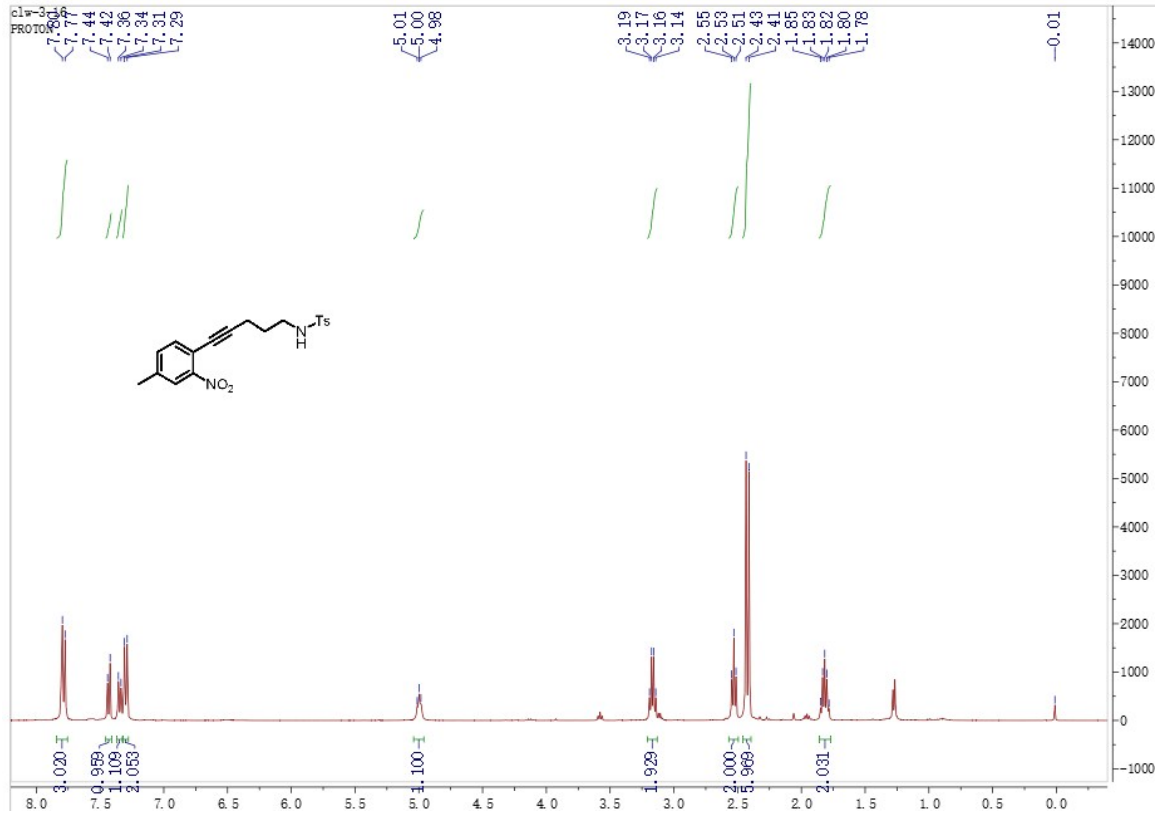
MeOOC
NO2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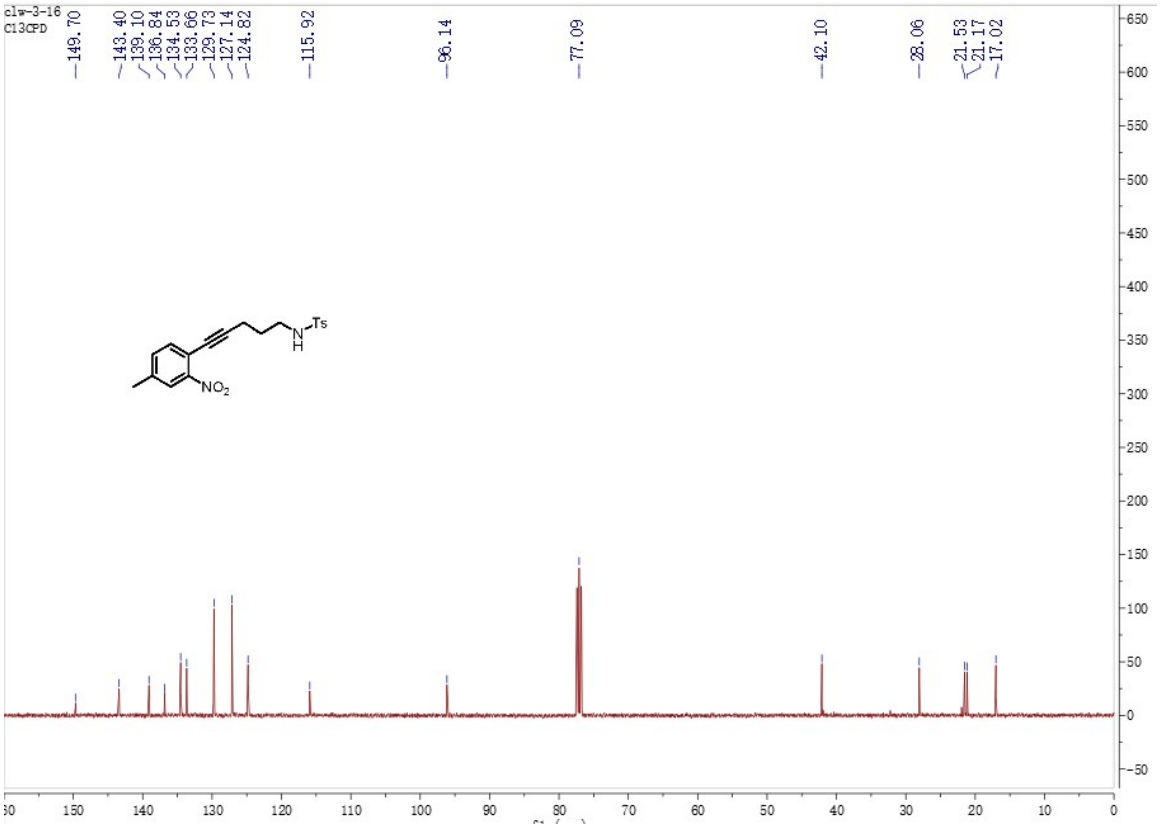
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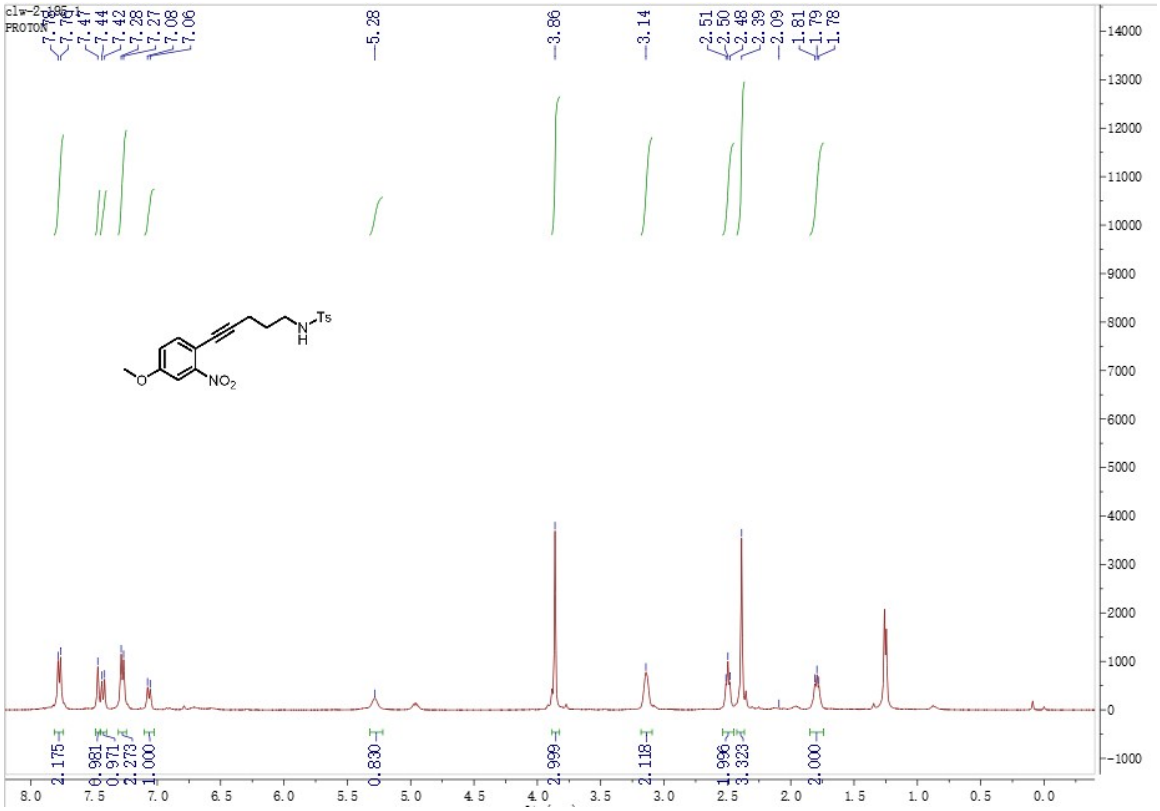
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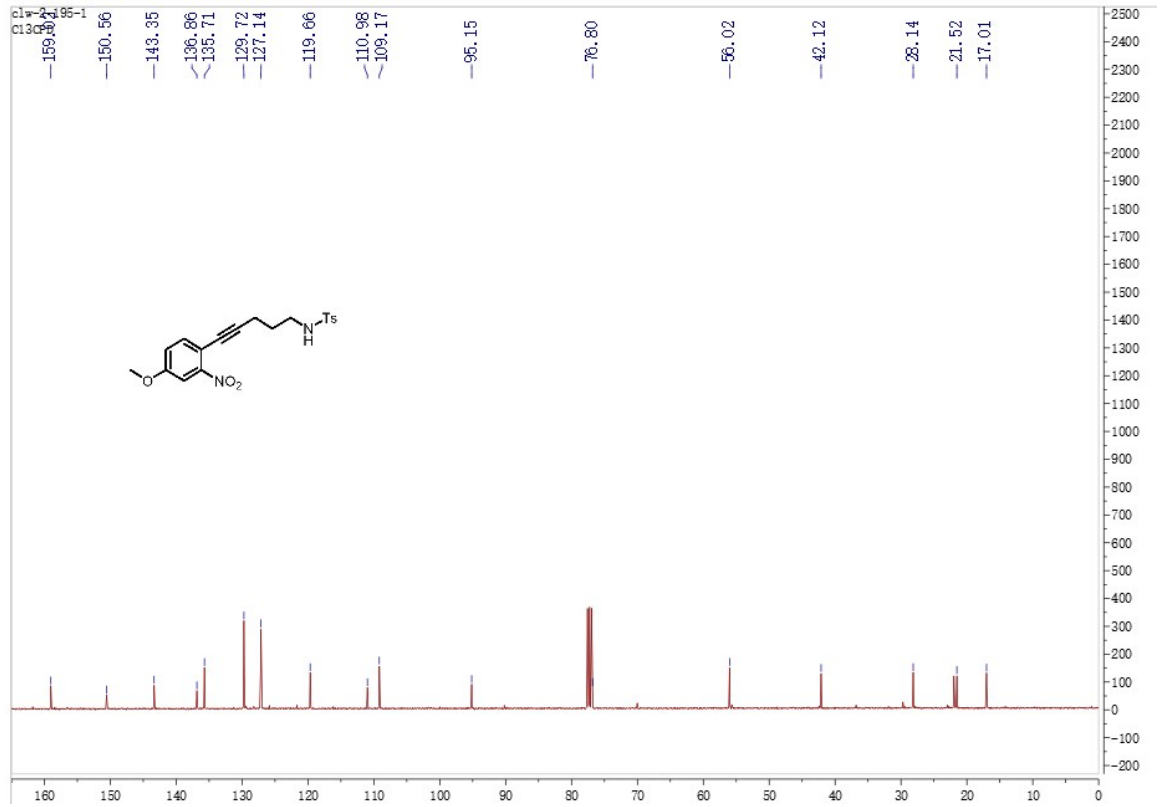
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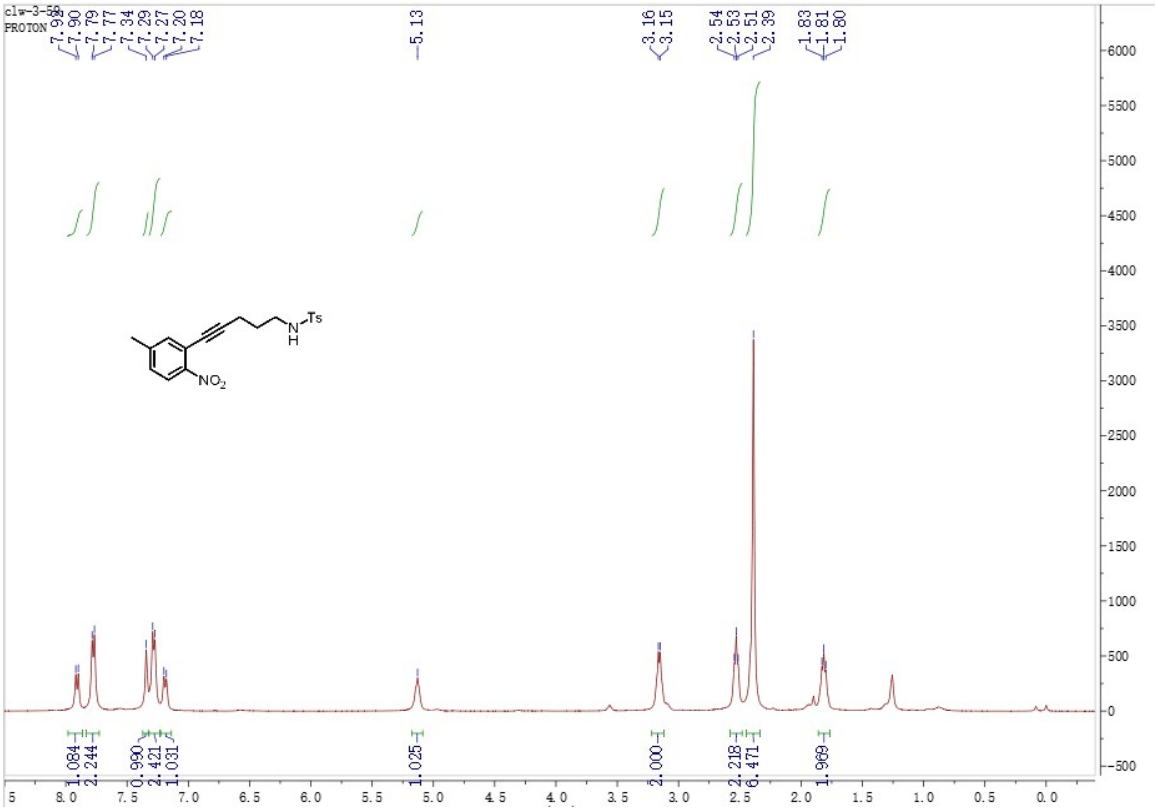
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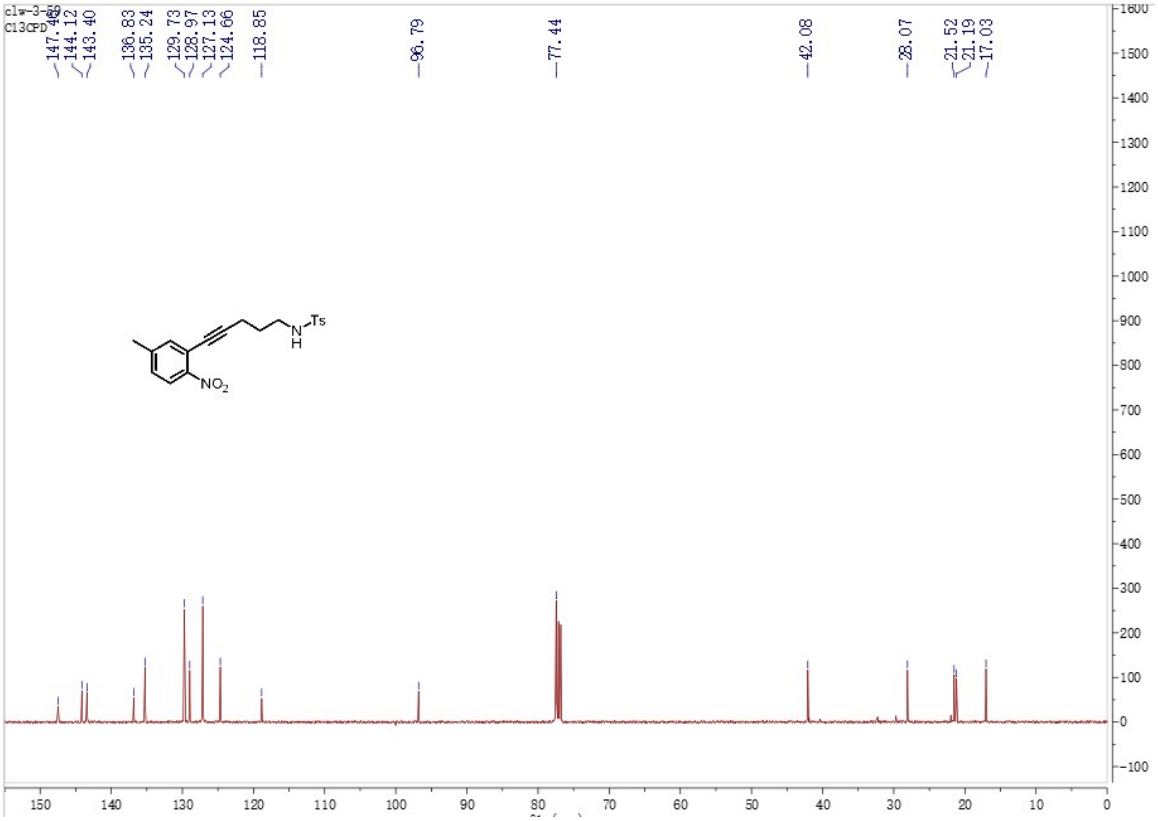
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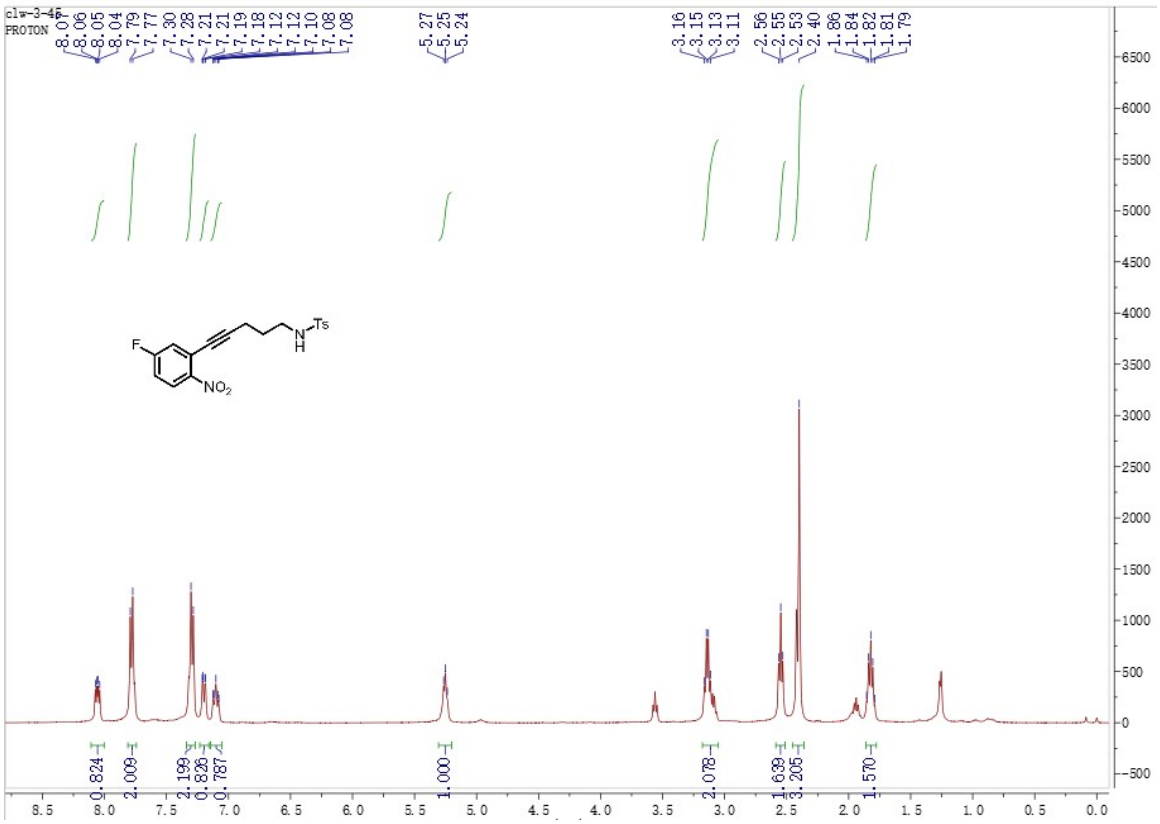
NO2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F
NO2
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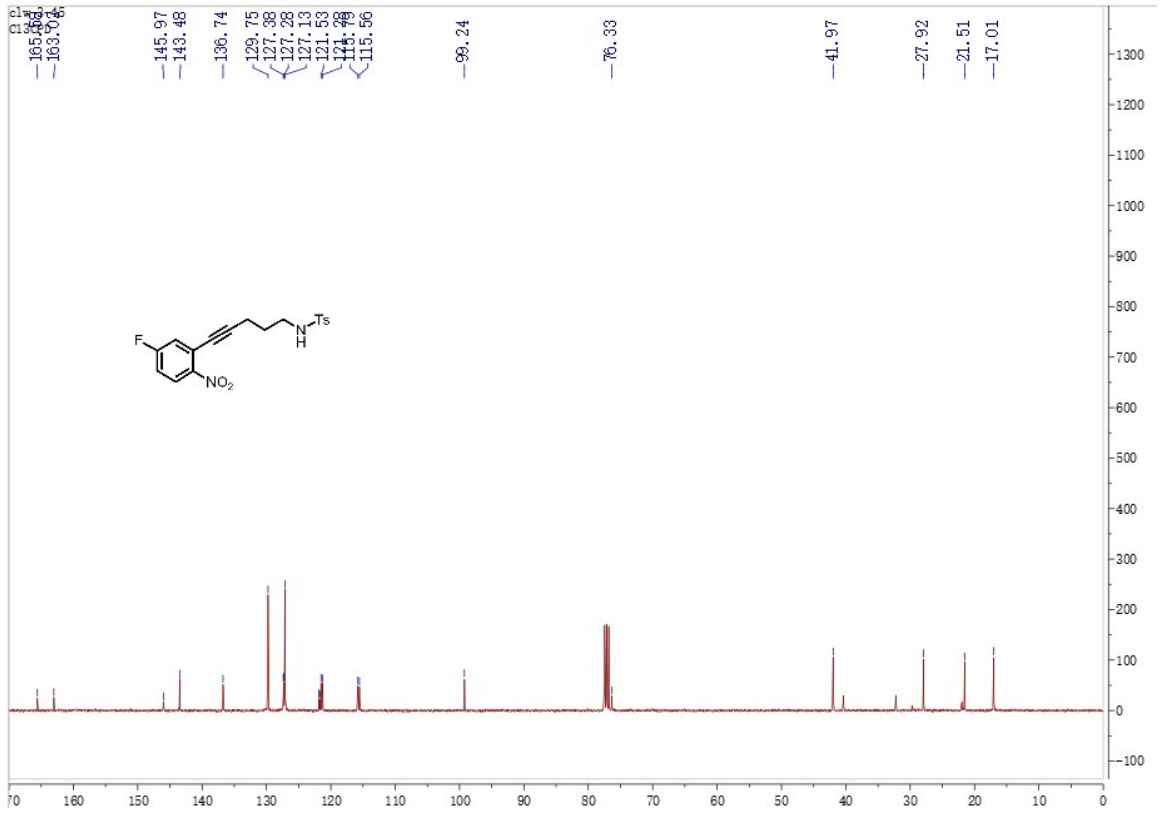
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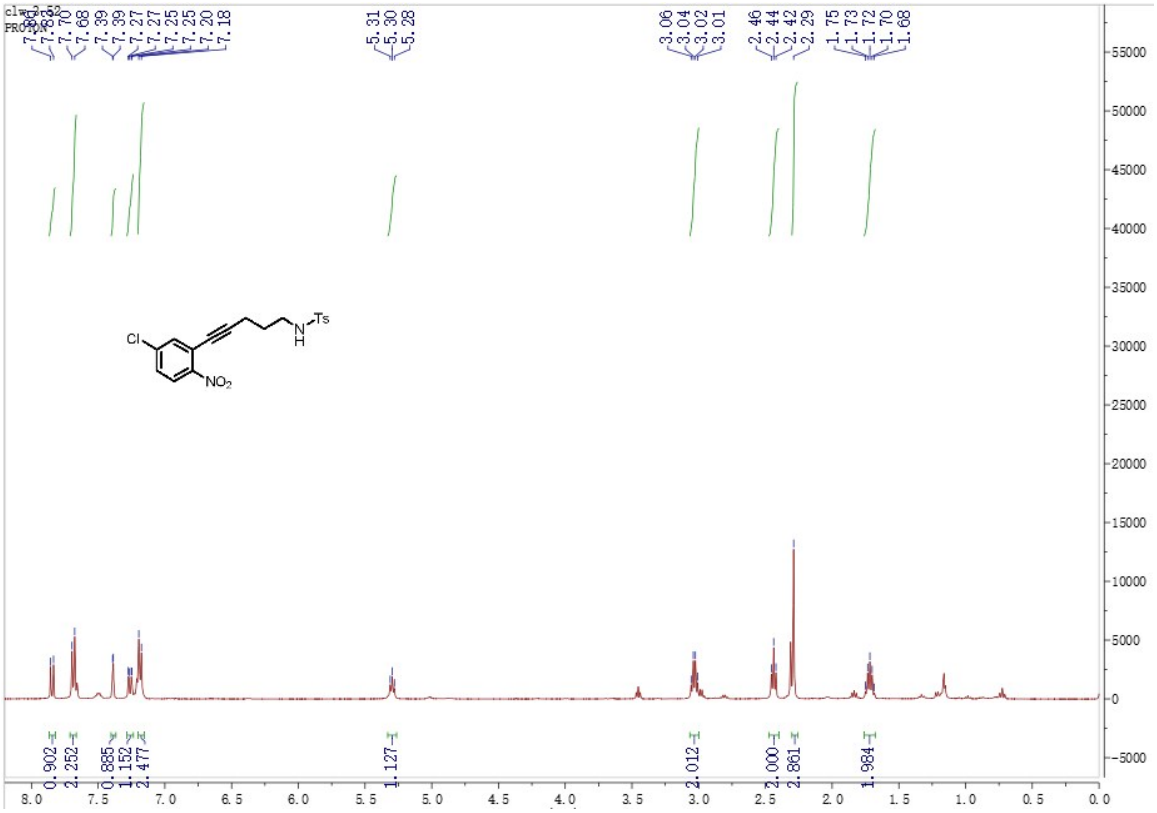
Ts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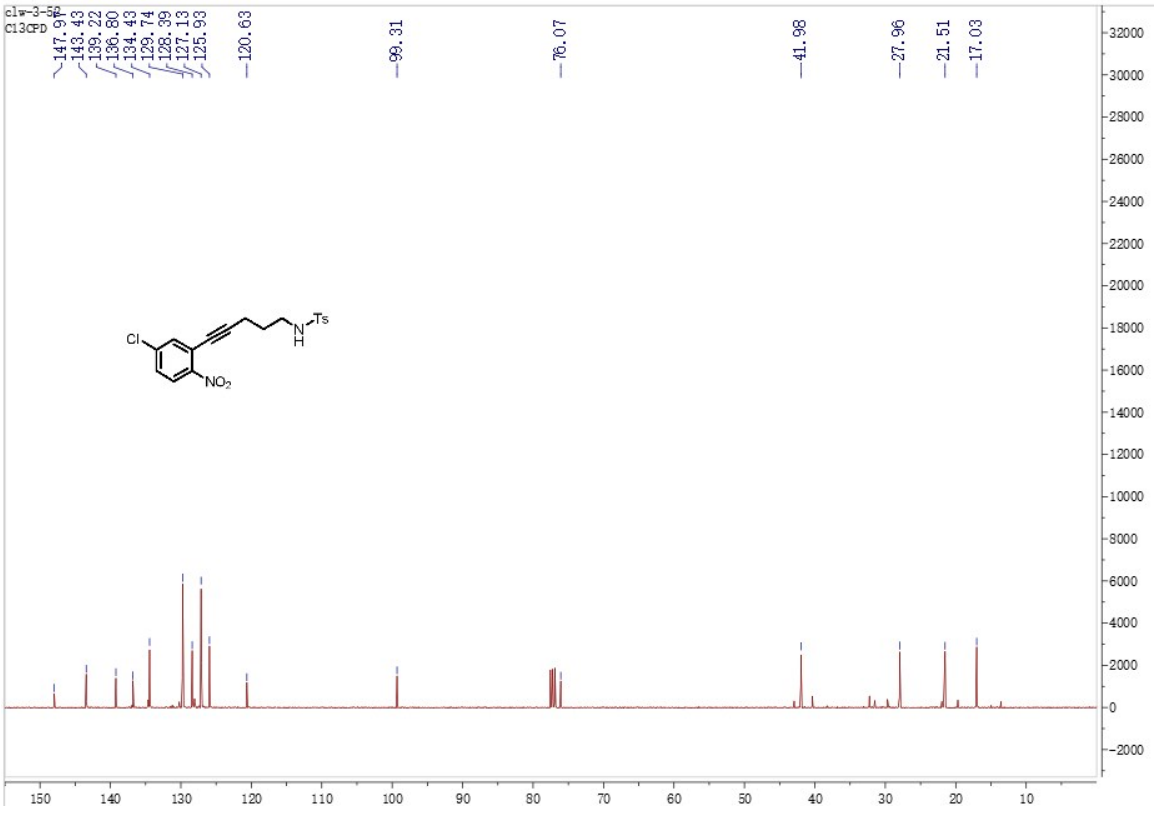
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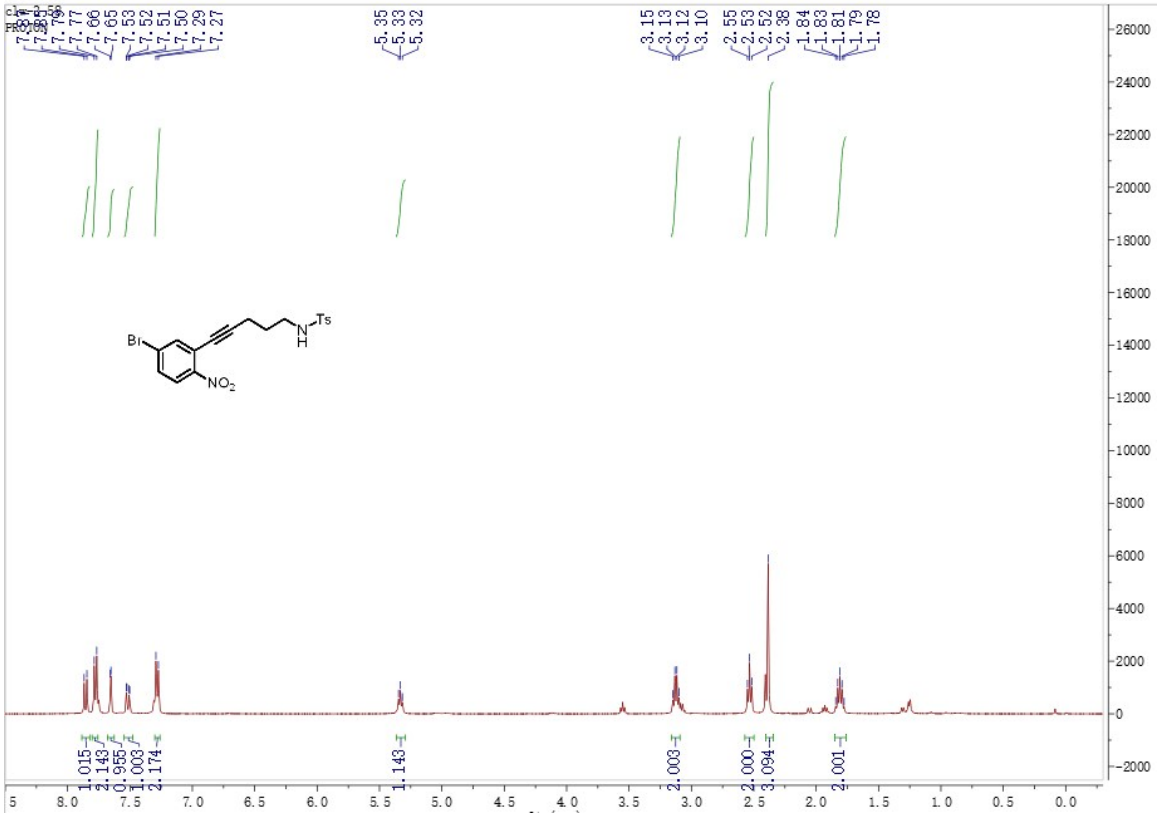
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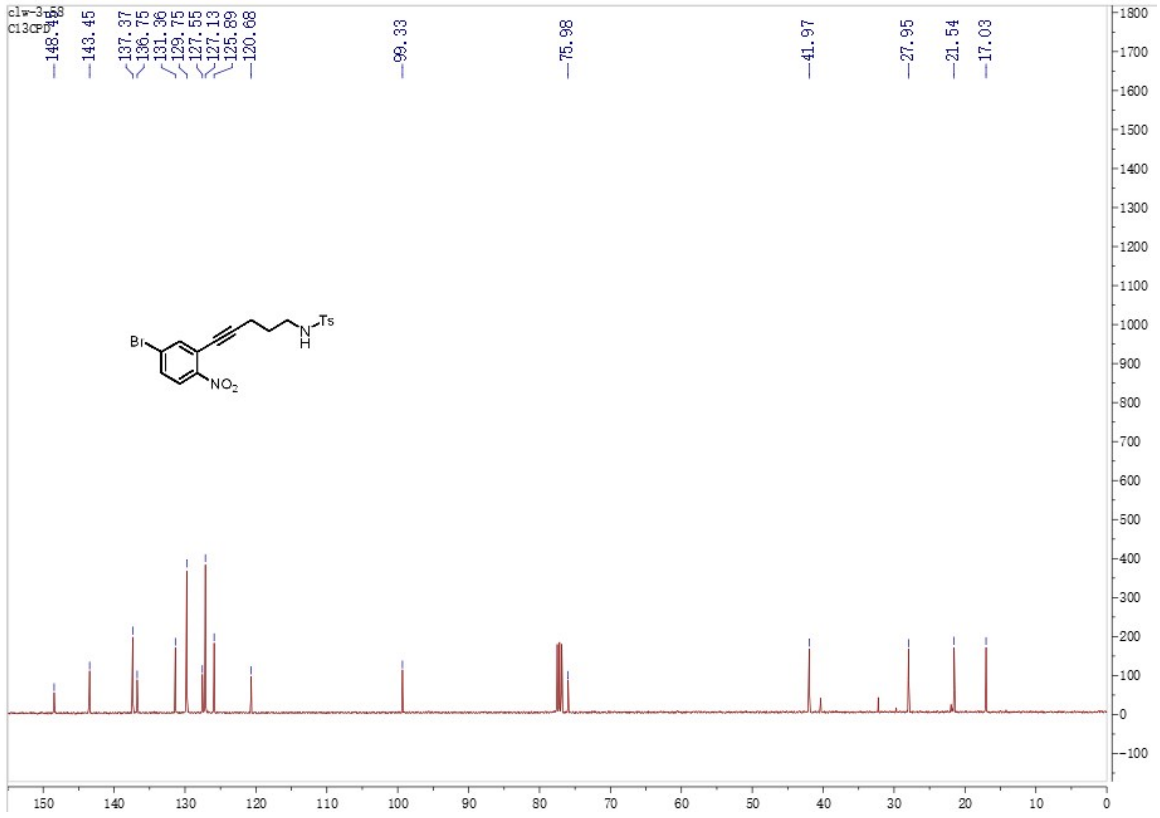
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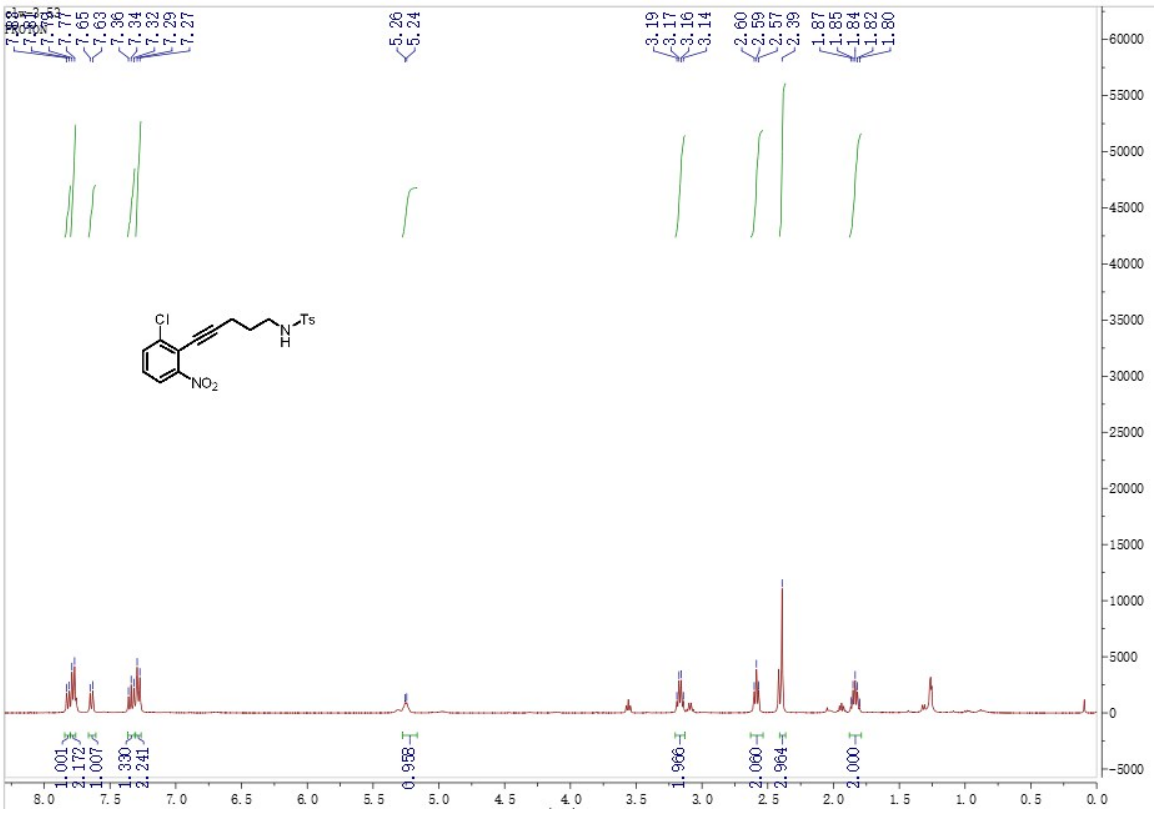
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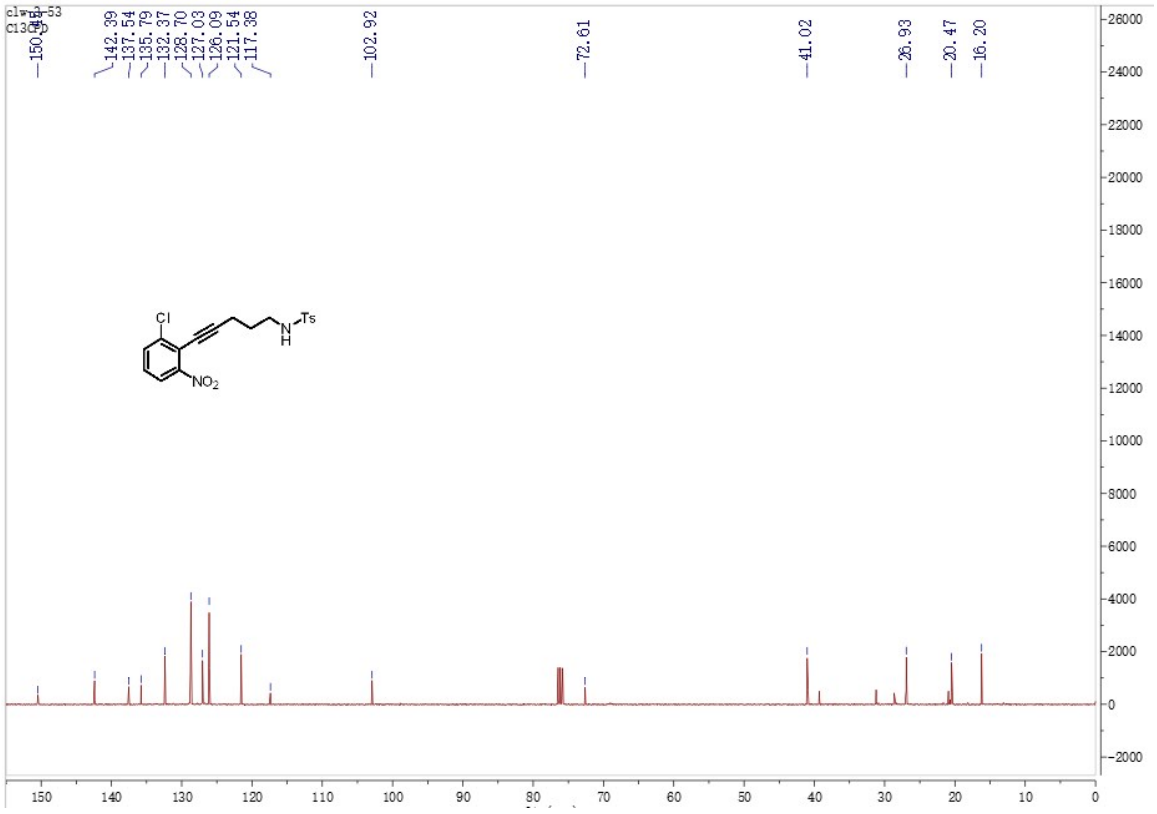
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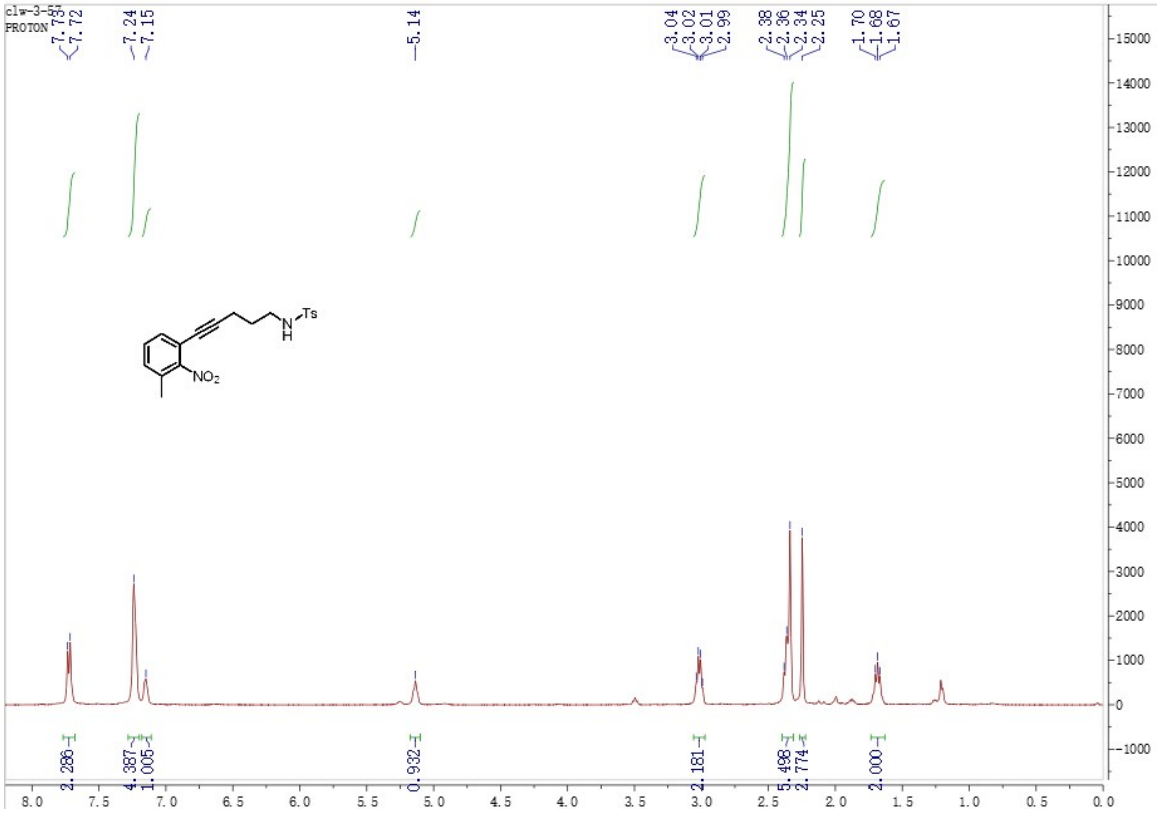
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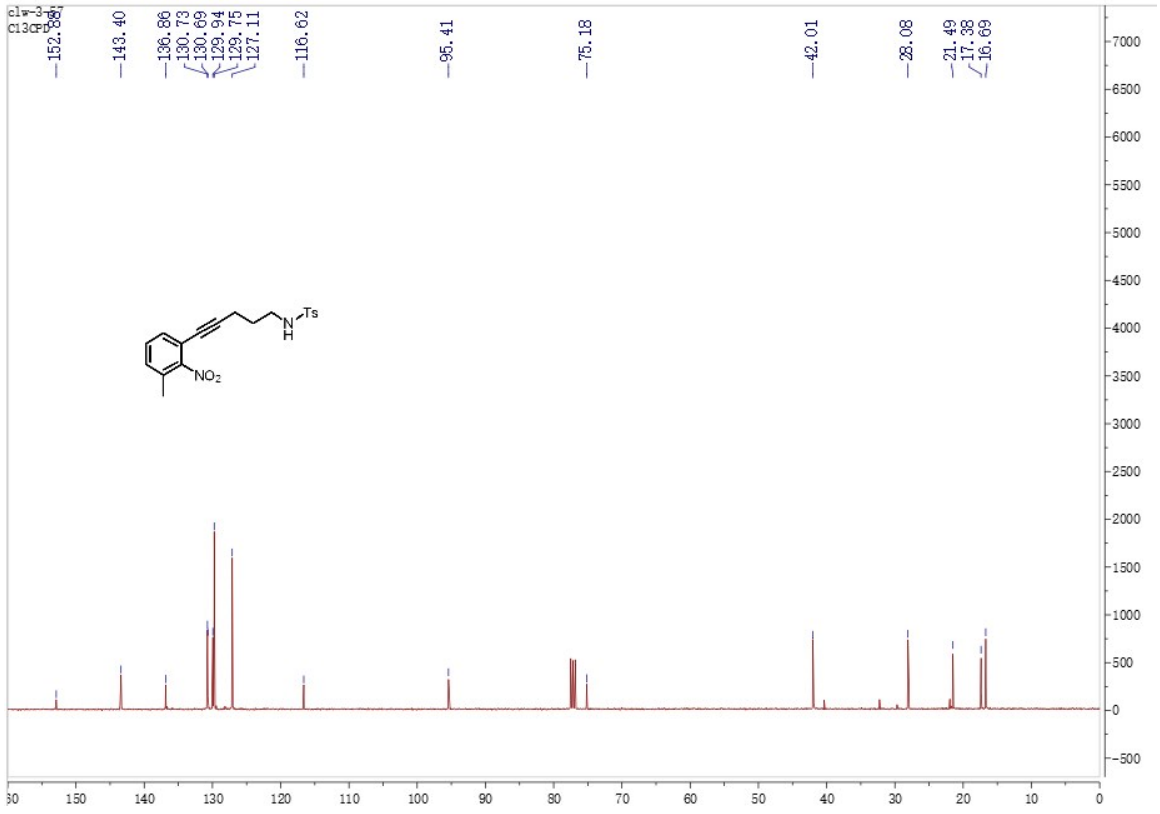
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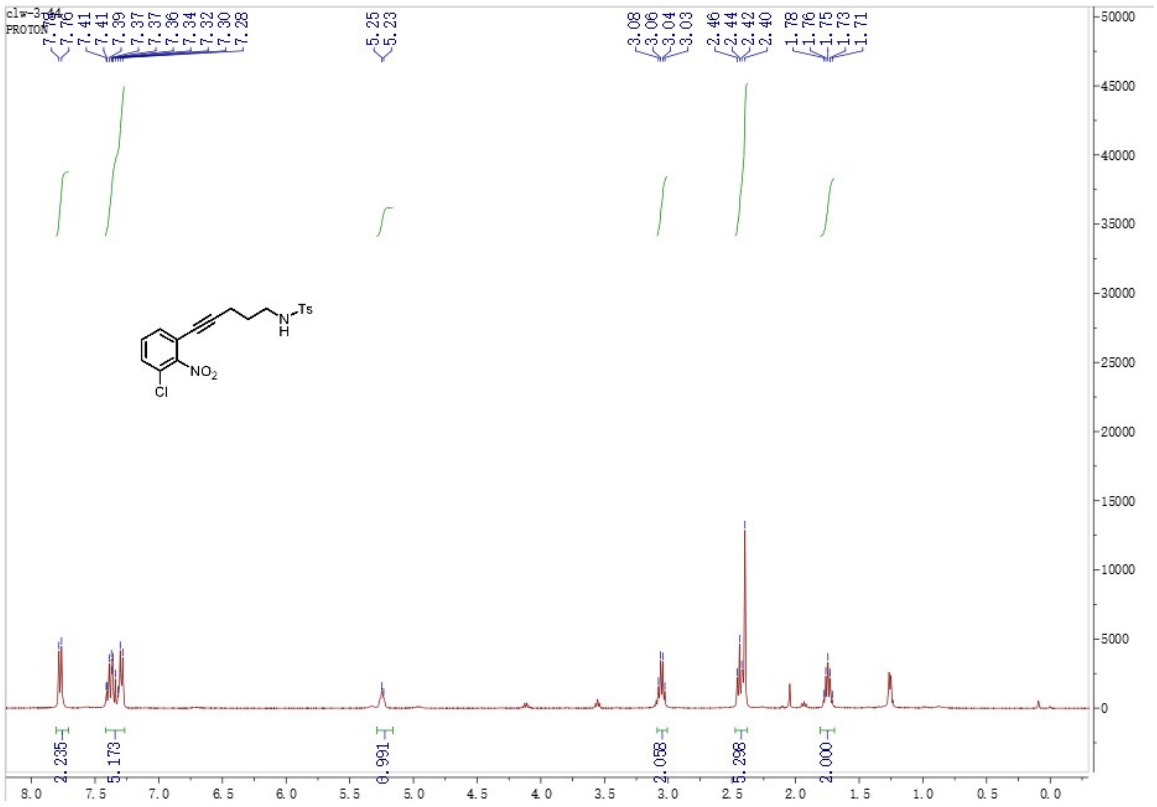
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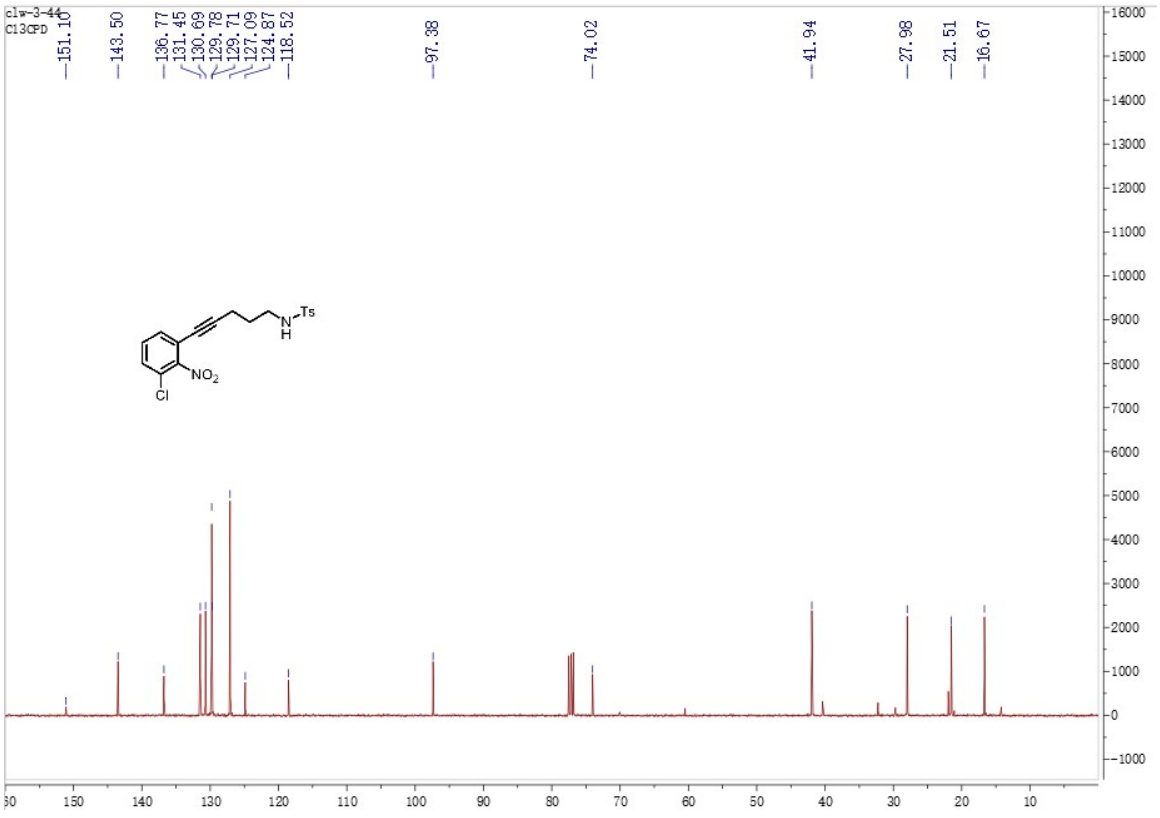
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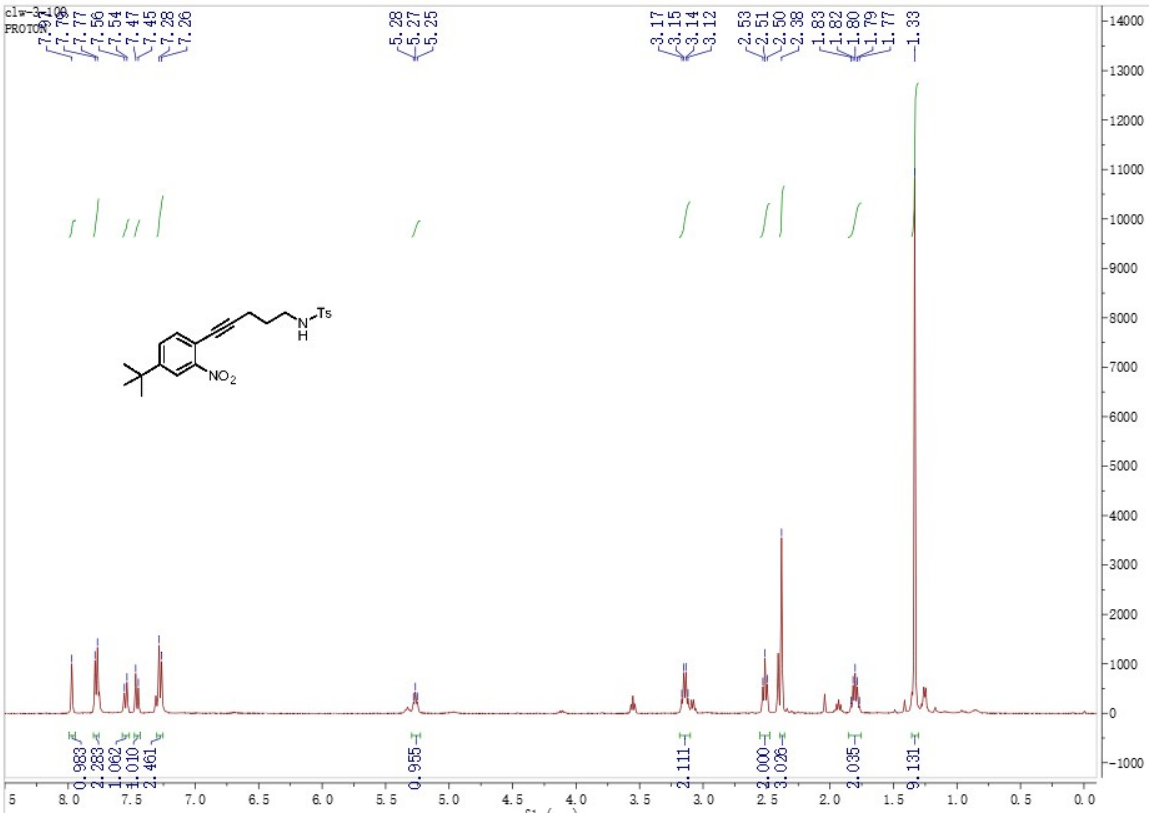
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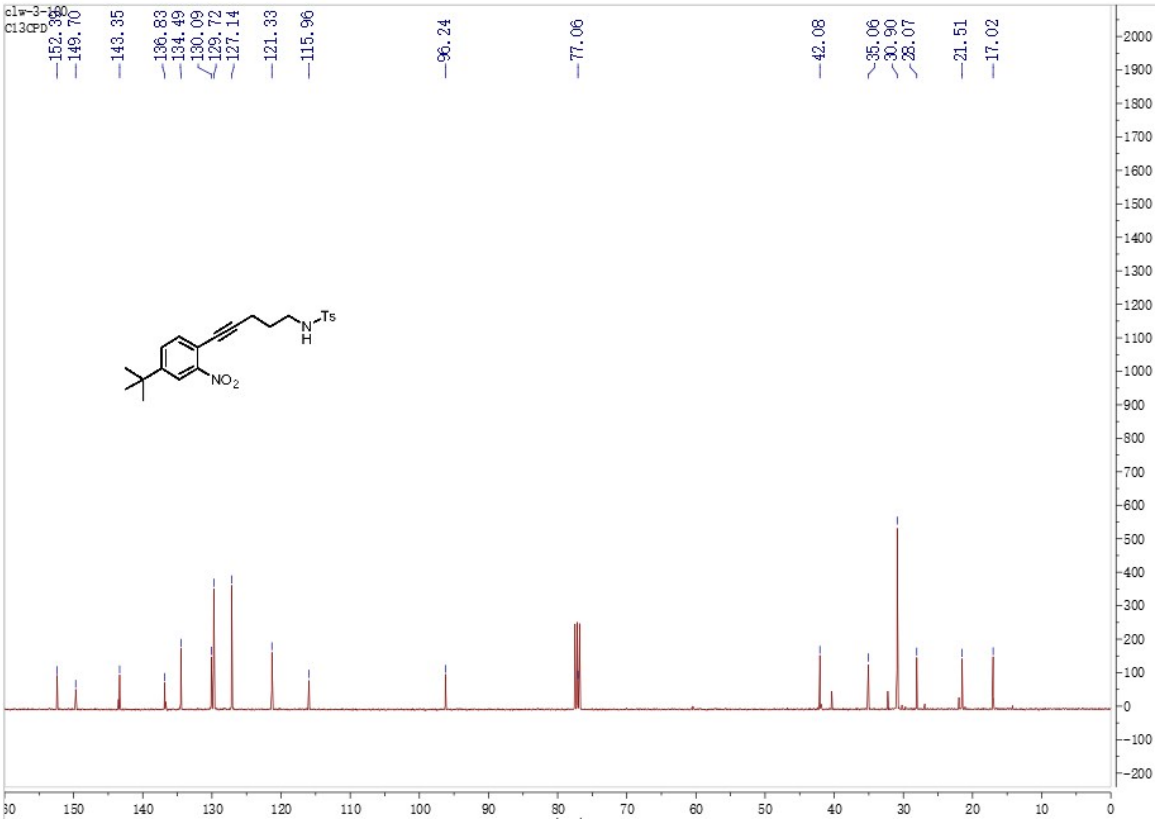
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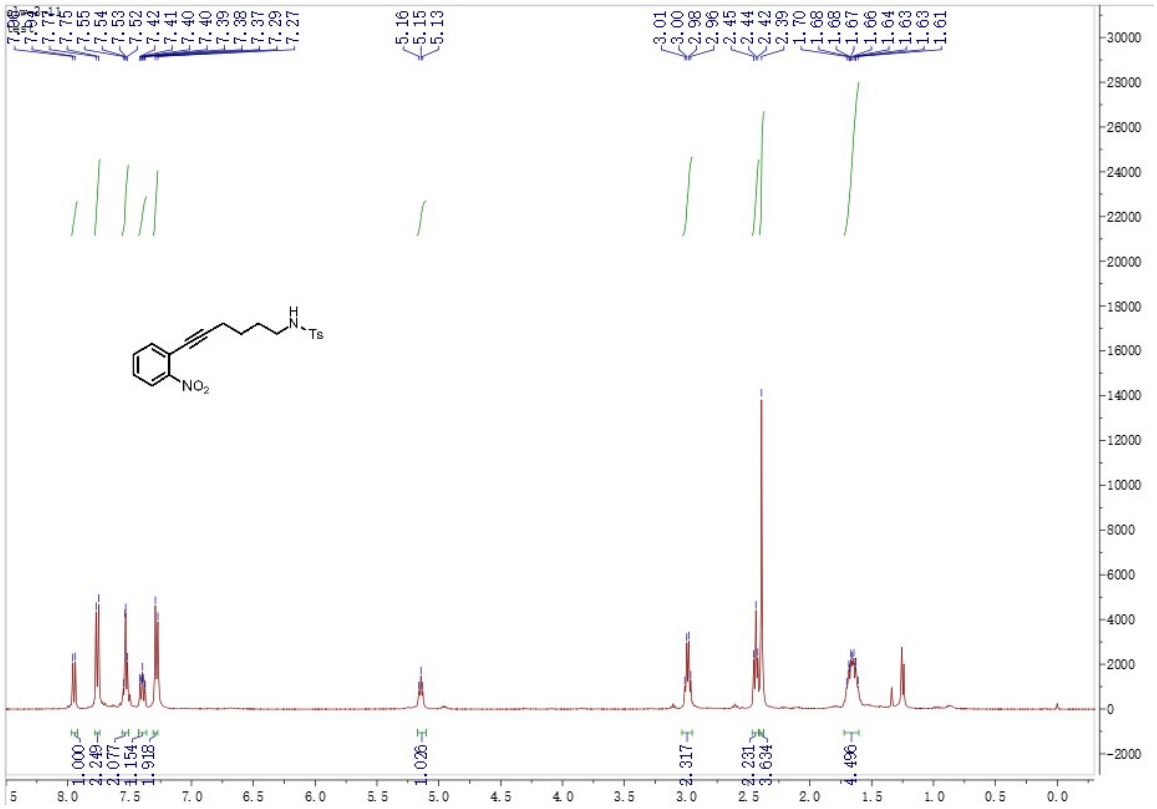
NO2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1.63
1.63
1.61
Ts
NO2
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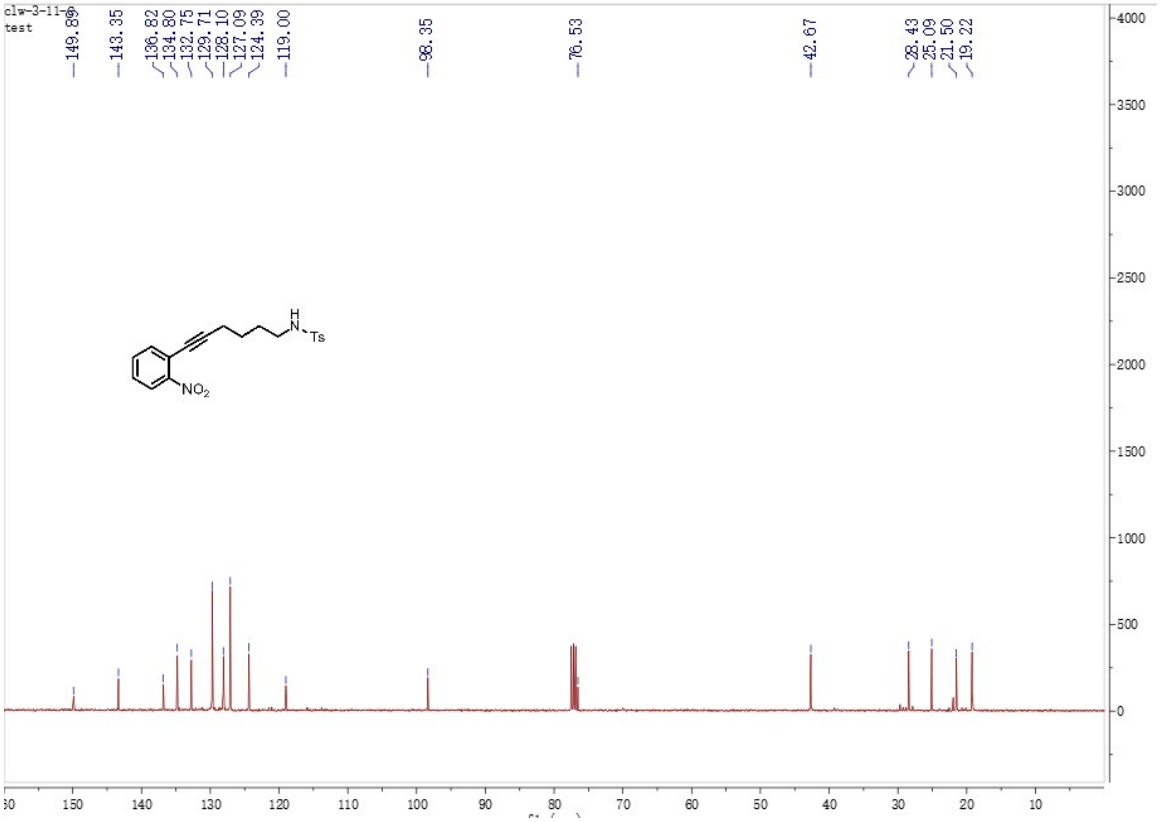
2.249
2.077
1.154
1.918
1.026
2.317
2.231
3.634
4.496


clw-3-11-c
test
149.89
143.35
136.82
134.80
132.75
129.71
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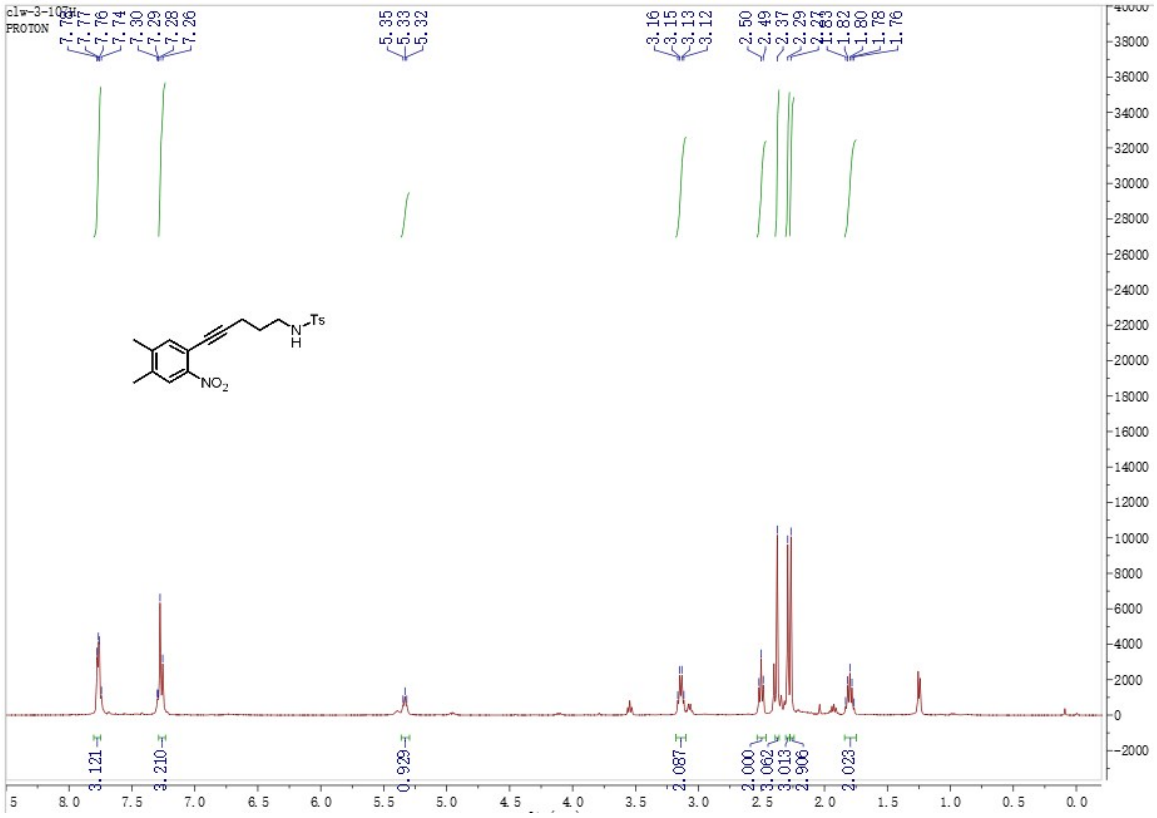
98.35
76.53
42.67
28.43
25.09
21.50
19.22
Ts
NO2


PROTON
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7.77
7.76
7.74
7.30
7.29
7.28
7.26
5.35
5.33
5.32
3.16
3.15
3.13
3.12
2.50
2.49
2.37
2.29
1.83
1.82
1.80
1.78
1.76
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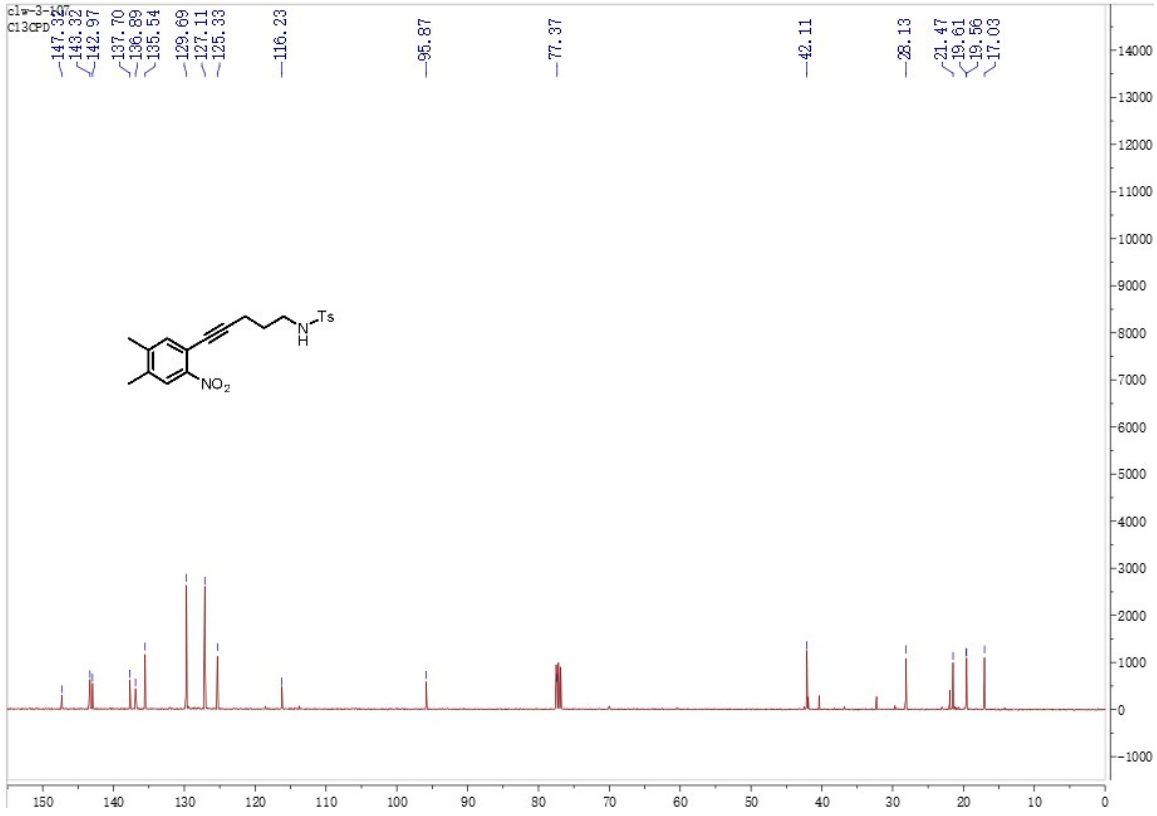
N
H
NO2
3.121
3.210
0.929
2.087
2.000
3.062
3.013
2.906
2.023


C13CPD
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136.89
135.54
129.69
127.11
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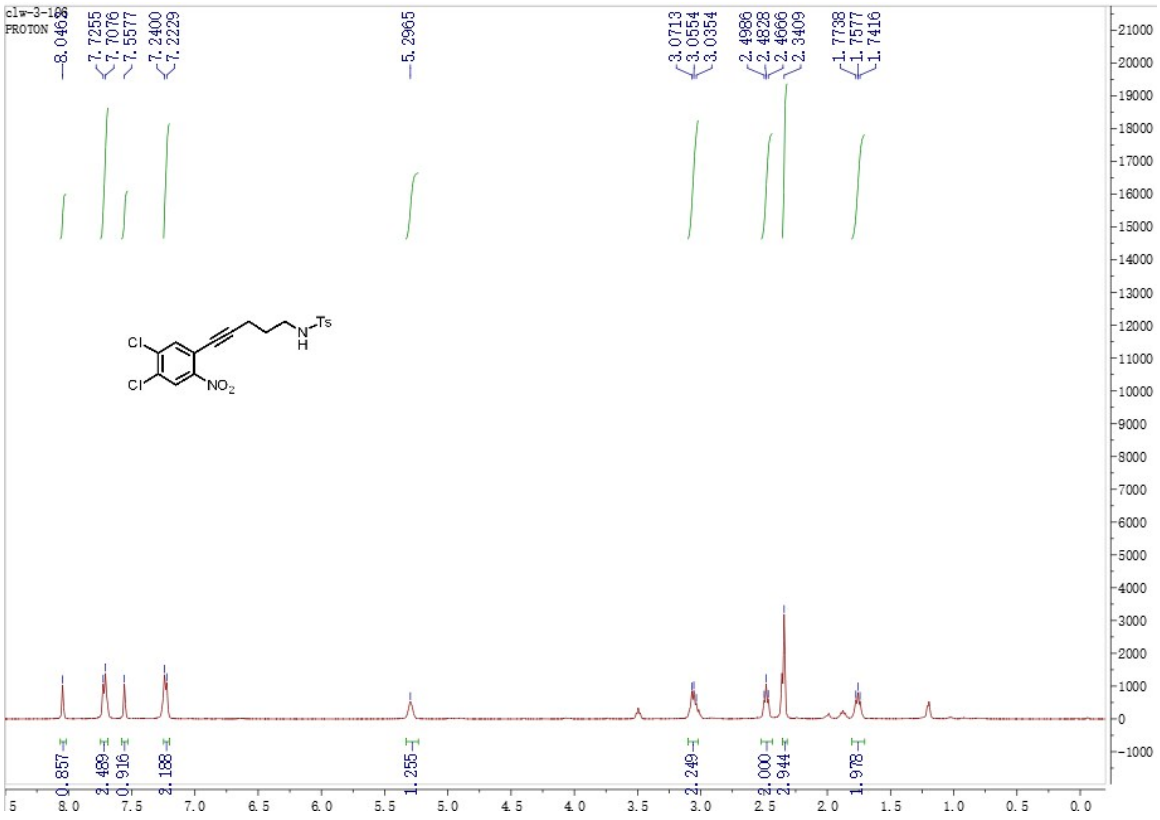
77.37
42.11
28.13
21.47
19.61
19.56
17.03
Ts
N
H
NO2


clw-3-166
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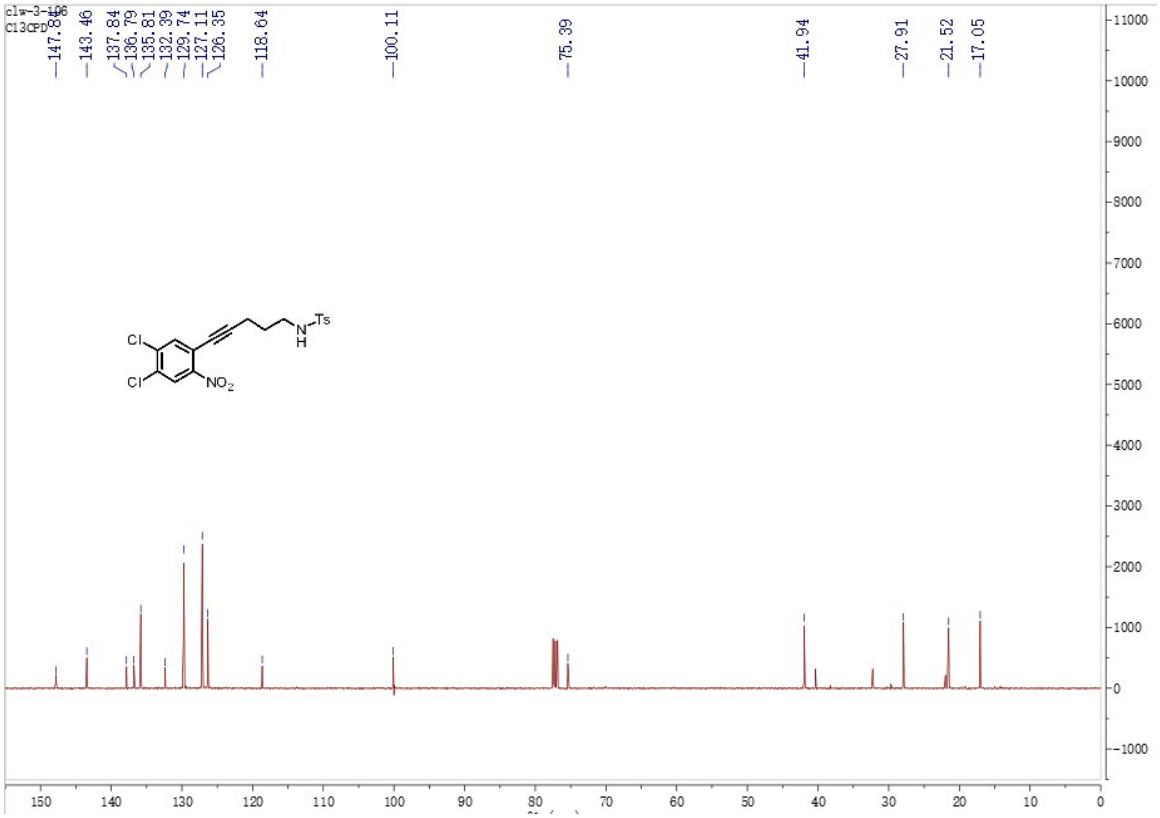
7.7255
7.7076
7.5577
7.2400
7.2229
5.2965
3.0713
3.0554
3.0354
2.4986
2.4828
2.4666
2.3409
1.7738
1.7577
1.7416
Cl
Cl
NO2
N
H
Ts
0.857
2.489
0.916
2.188
1.255
2.249
2.000
2.944
1.978


clw-3-166
C13CPD
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143.46
137.84
136.79
135.81
132.39
129.74
127.11
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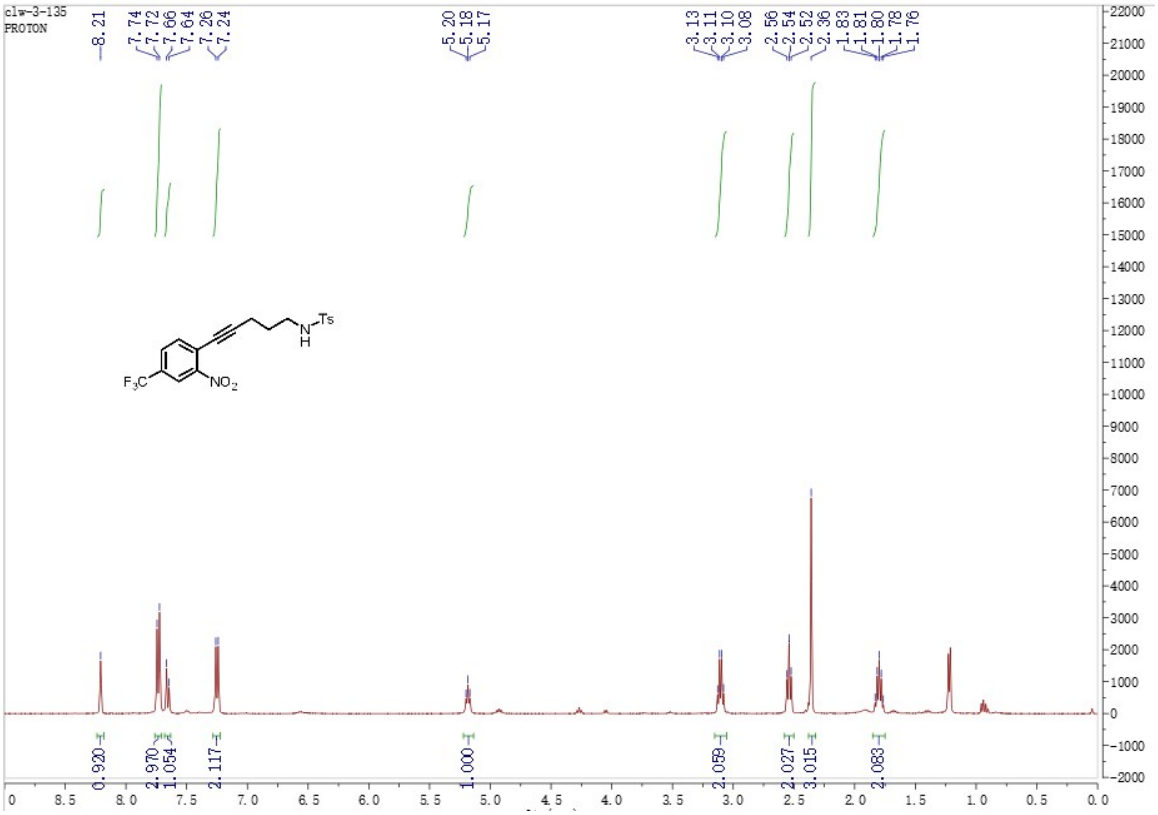
100.11
75.39
41.94
27.91
21.52
17.05
Cl
Cl
NO2
N
H
Ts


clw-3-135
PROTON
8.21
7.74
7.72
7.66
7.64
7.26
7.24
5.20
5.18
5.17
3.13
3.11
3.10
3.08
2.56
2.54
2.52
2.36
1.83
1.81
1.80
1.78
1.76
Ts
N
H
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NO2
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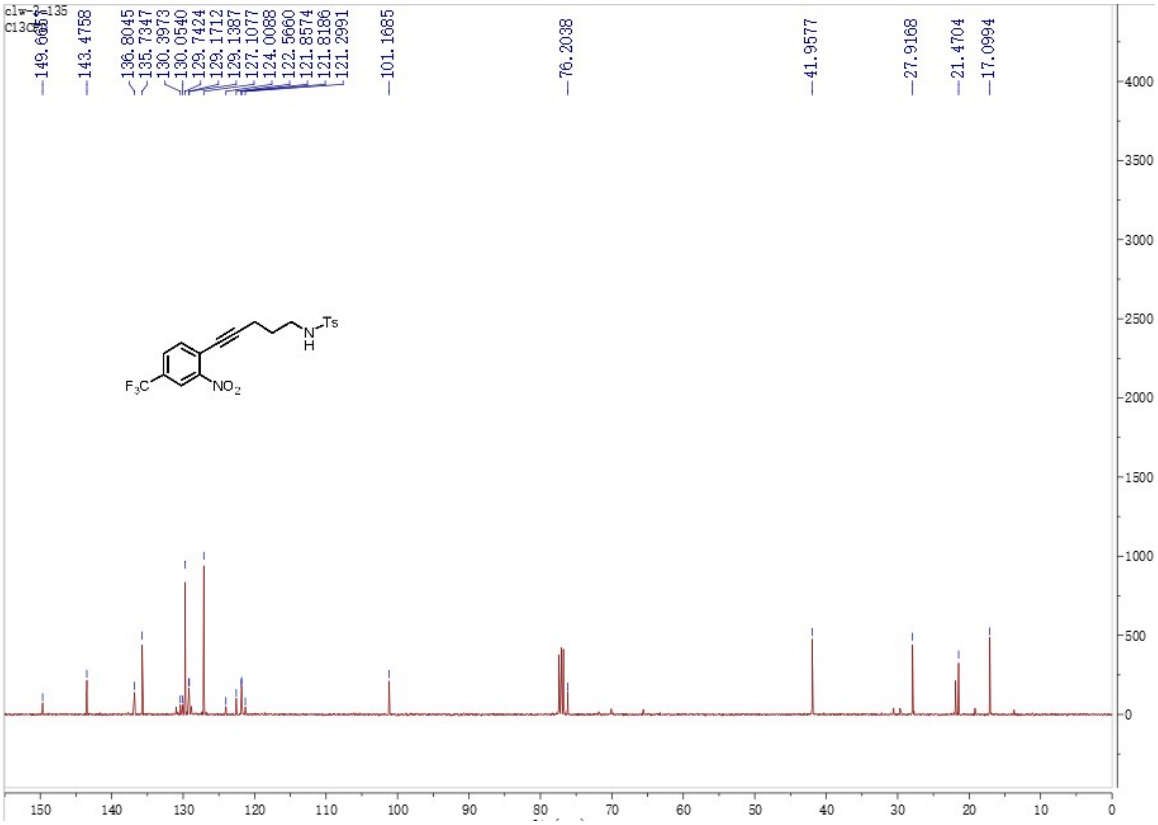
1.054
2.117
1.000
2.059
2.027
3.015
2.083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135.7347
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130.0540
129.7424
129.1712
129.1387
127.1077
124.0088
122.5660
121.8574
121.8186
121.2991
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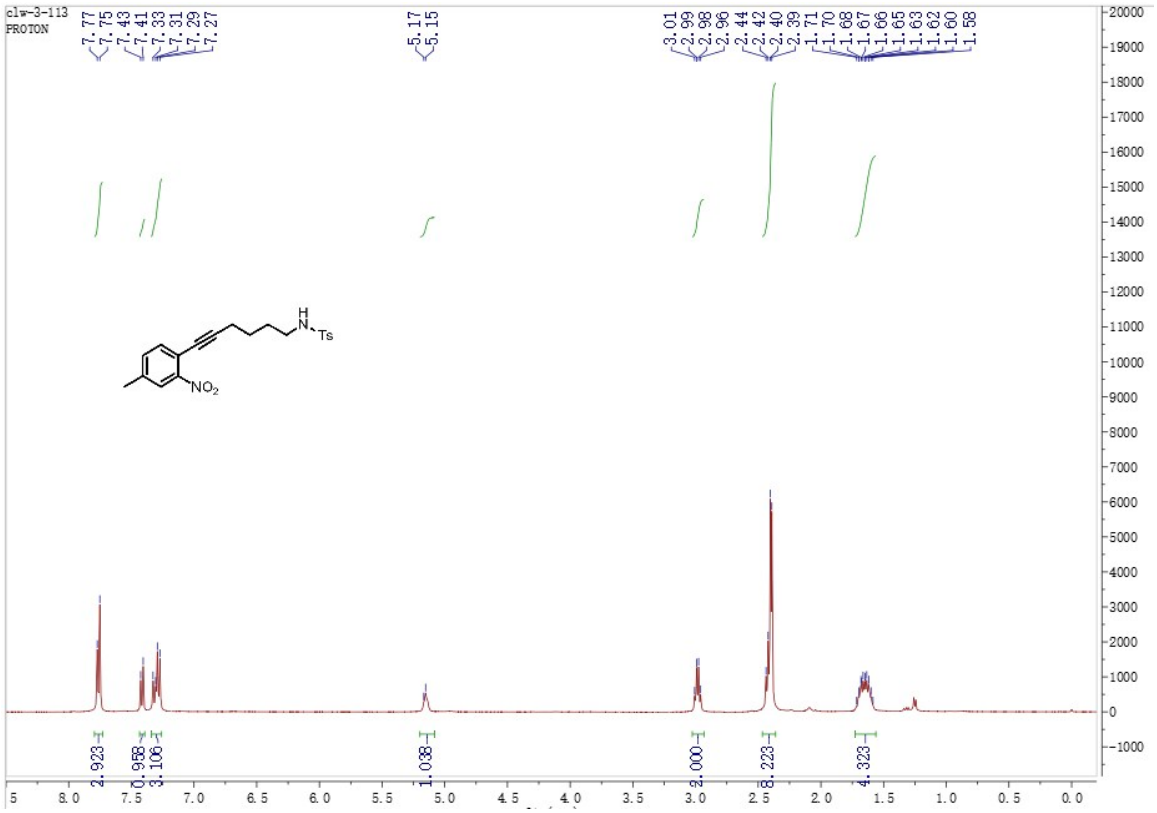
41.9577
27.9168
21.4704
17.0994
Ts
N
H
F3C
NO2


clw-3-113
PROTON
7.77
7.75
7.43
7.41
7.33
7.31
7.29
7.27
5.17
5.15
3.01
2.99
2.98
2.96
2.44
2.42
2.40
2.39
1.71
1.70
1.68
1.67
1.66
1.65
1.63
1.62
1.60
1.58
Ts
NO2
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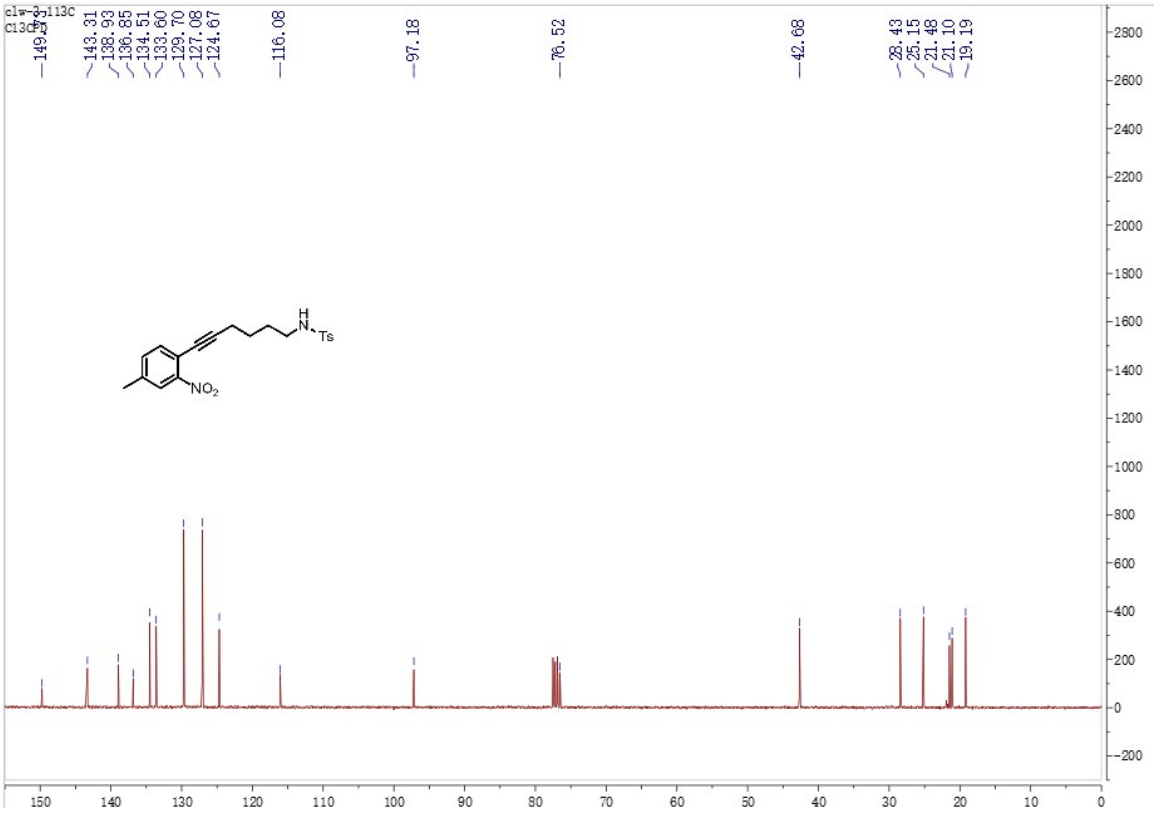
0.958
3.100
1.088
2.000
8.223
4.323


clw-3-113C
149.23
143.31
138.93
136.85
134.51
133.60
129.70
127.08
124.67
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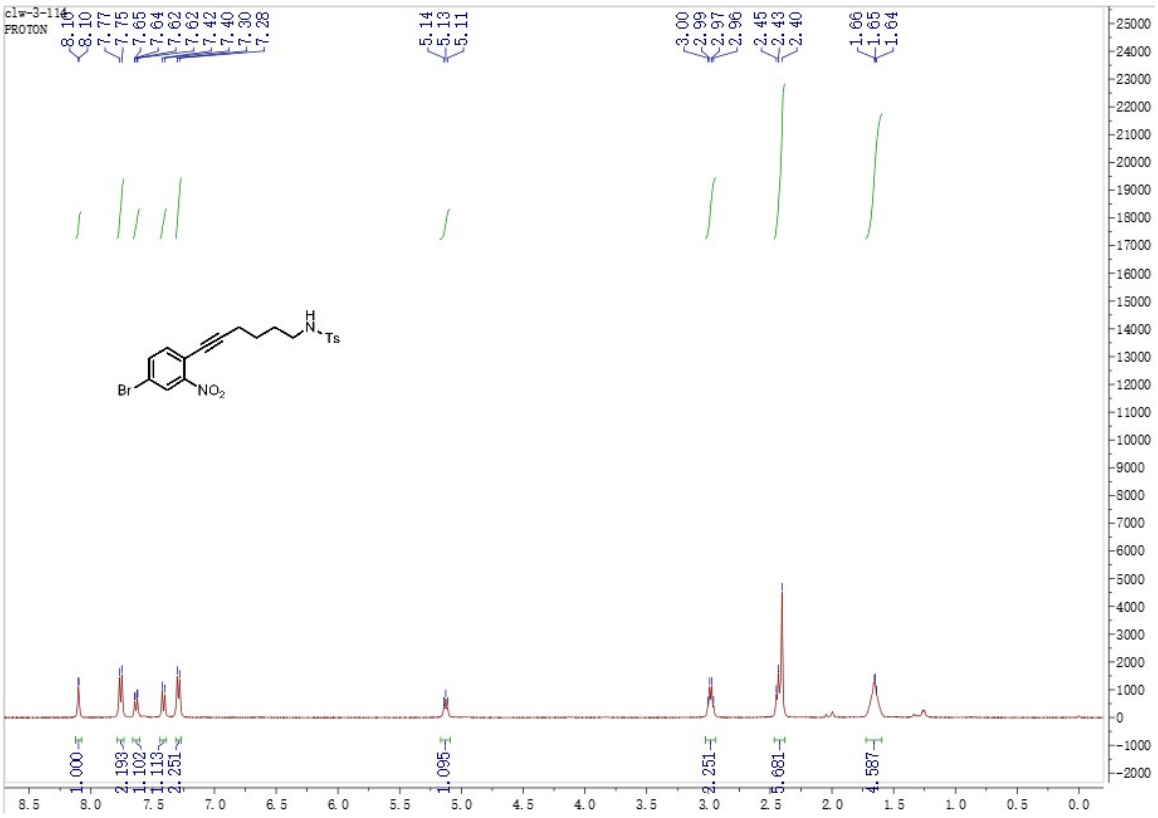
97.18
76.52
42.68
28.43
25.15
21.48
21.10
19.19
Ts
NO2


clw-3-114
PROTON
8.10
7.77
7.75
7.65
7.64
7.62
7.62
7.42
7.40
7.30
7.28
5.14
5.13
5.11
3.00
2.99
2.97
2.96
2.45
2.43
2.40
1.66
1.65
1.64
Ts
Br
NO2
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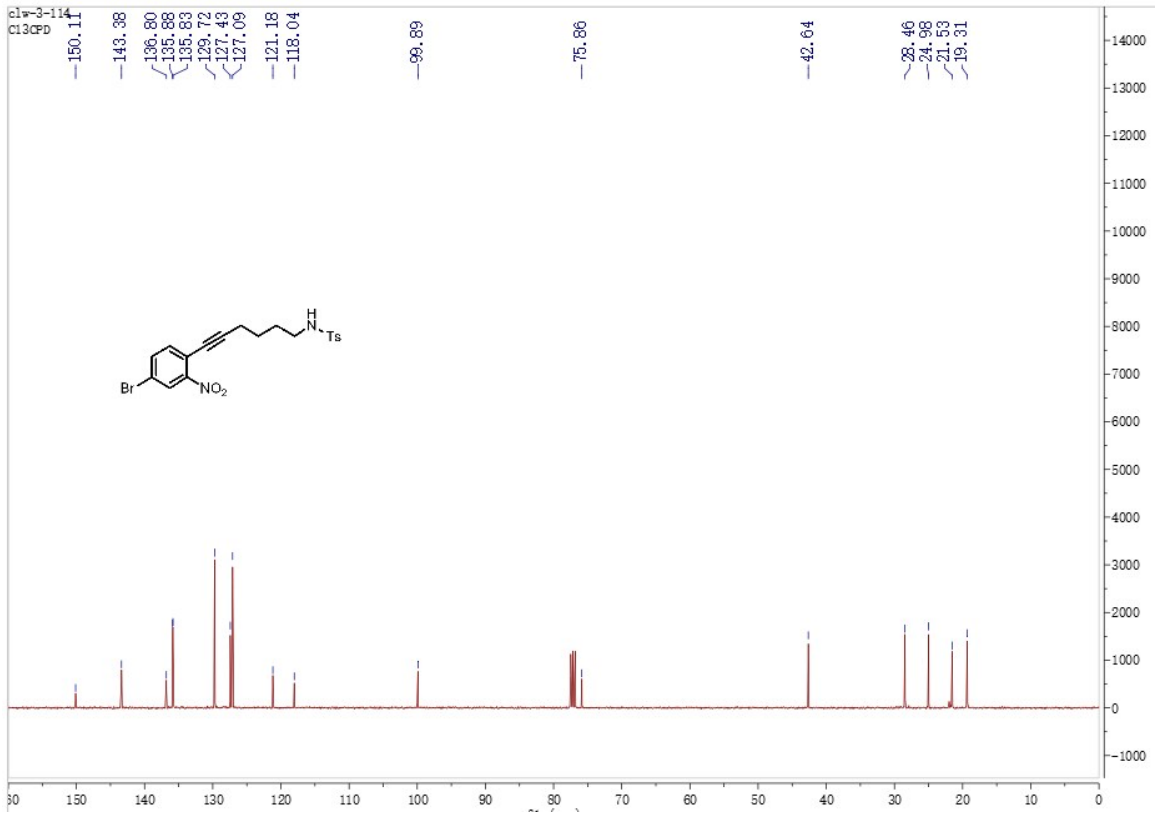
1.102
1.113
2.251
1.095
2.251
5.681
4.587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136.80
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135.83
129.72
127.43
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99.89
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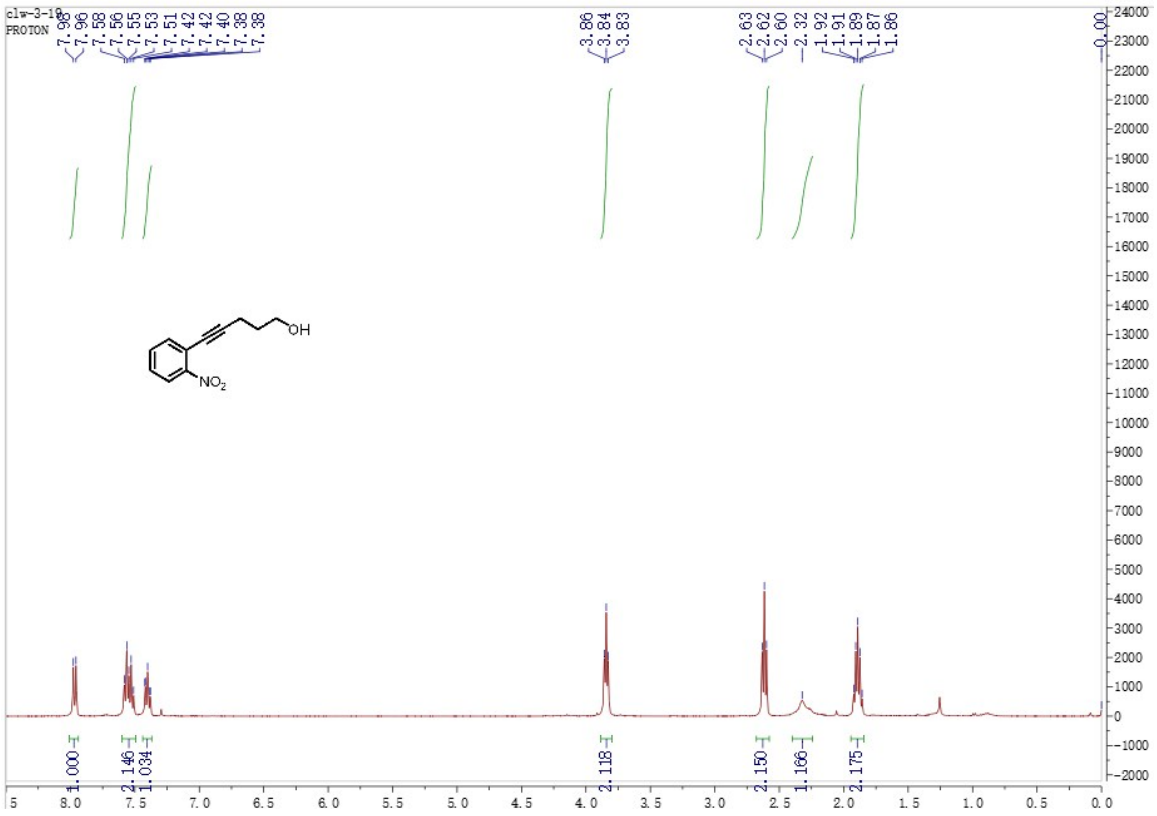
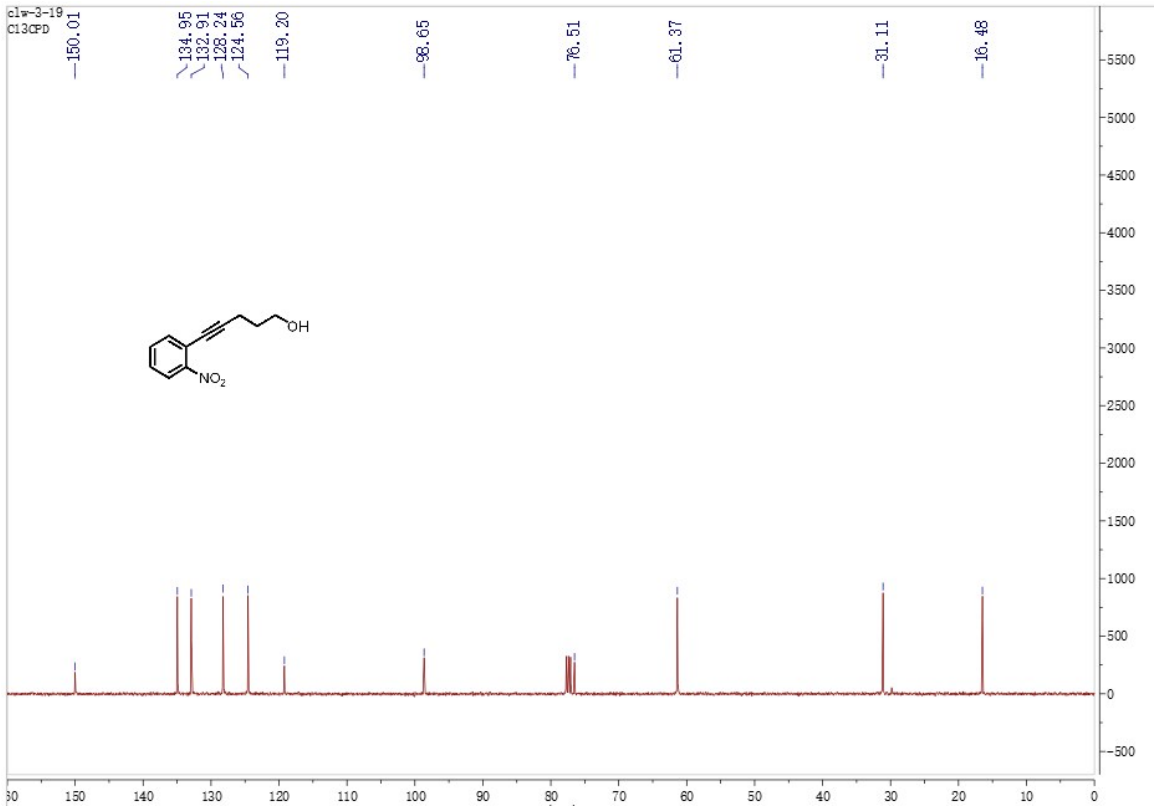
42.64
28.46
24.98
21.53
19.31
Ts
Br
NO2


clw-3-19
PROTON
7.98
7.96
7.58
7.56
7.55
7.53
7.51
7.42
7.40
7.38
7.38
3.86
3.84
3.83
2.63
2.62
2.60
2.32
1.92
1.91
1.89
1.87
1.86
0.00
OH
NO2
1.000
2.146
1.034
2.118
2.150
1.166
2.175


clw-3-19
C13CPD
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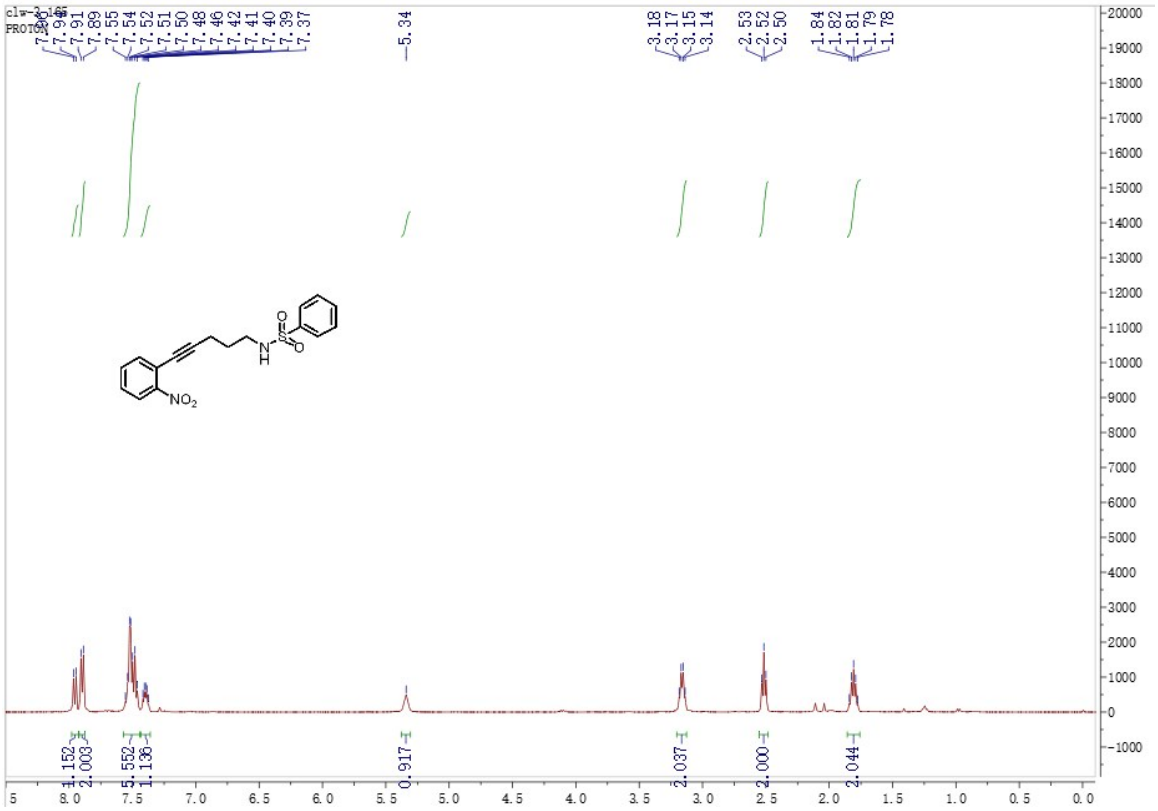
124.56
119.20
98.65
76.51
61.37
31.11
16.48
OH
NO2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7.89
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7.54
7.52
7.51
7.50
7.48
7.46
7.42
7.41
7.40
7.39
7.37
5.34
3.18
3.17
3.15
3.14
2.53
2.52
2.50
1.84
1.82
1.81
1.79
1.78
O
S
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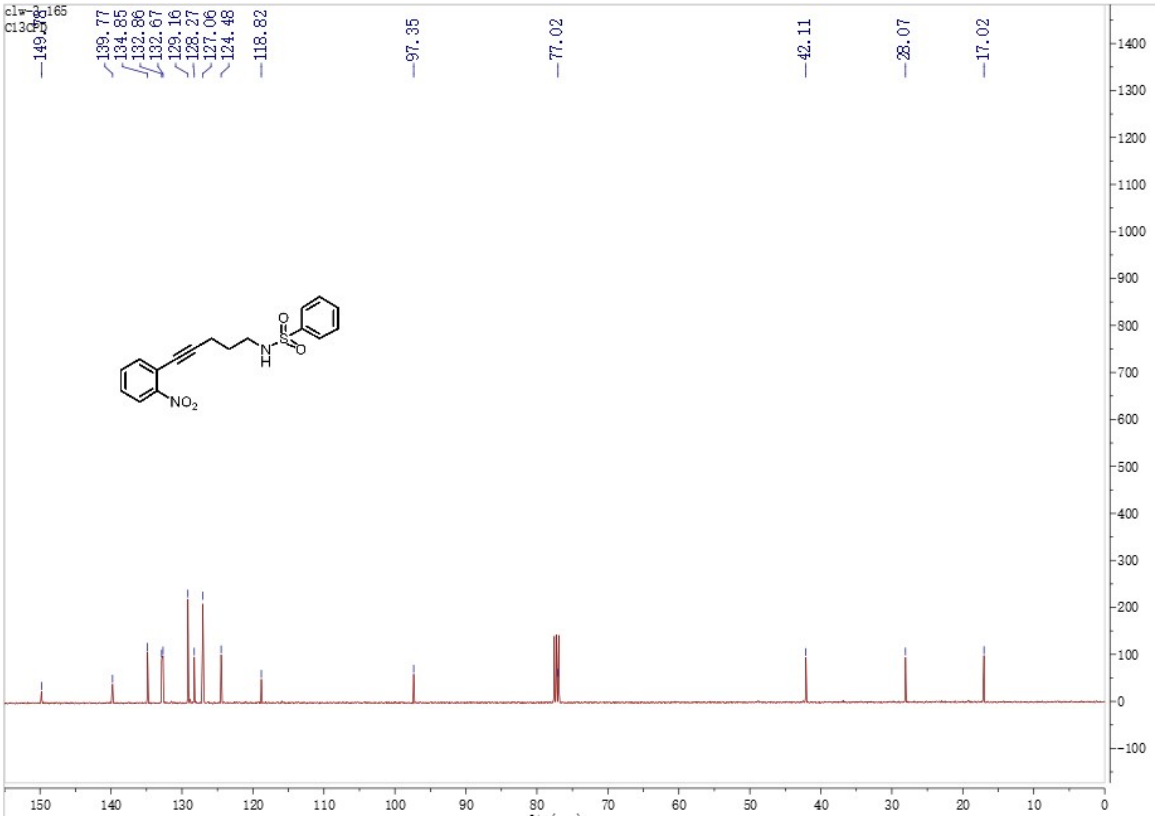
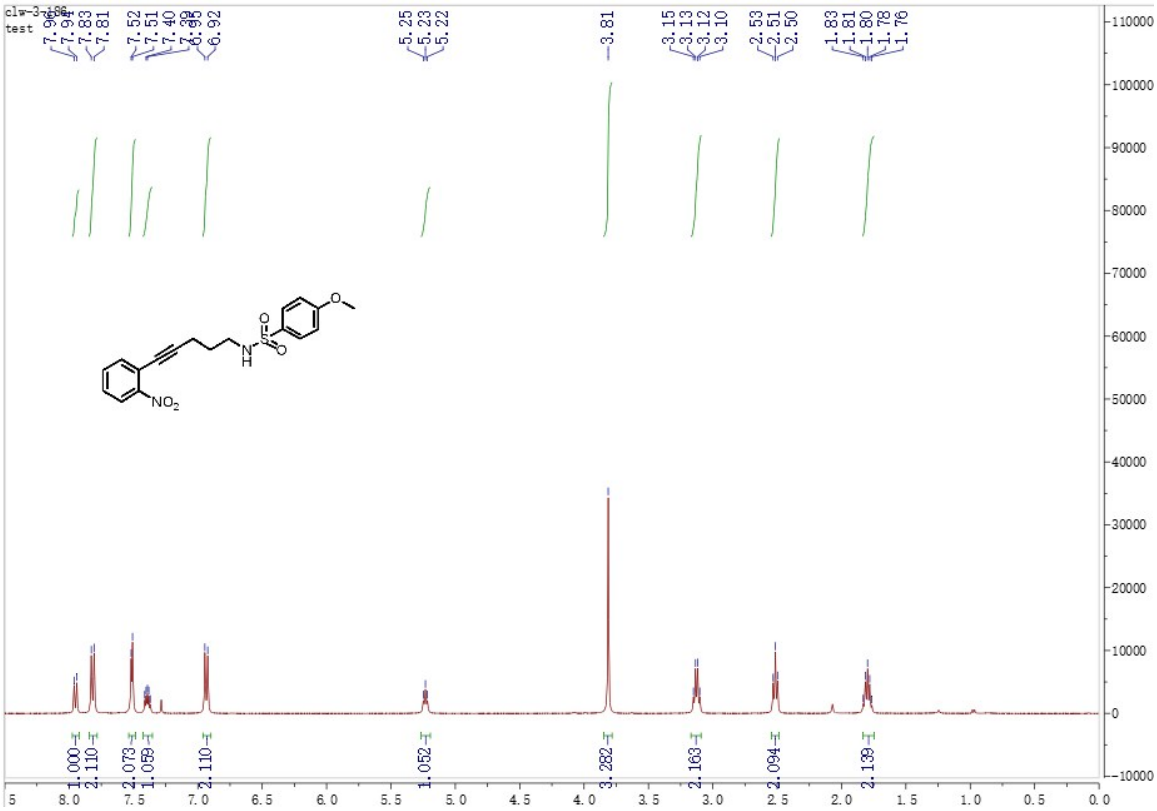
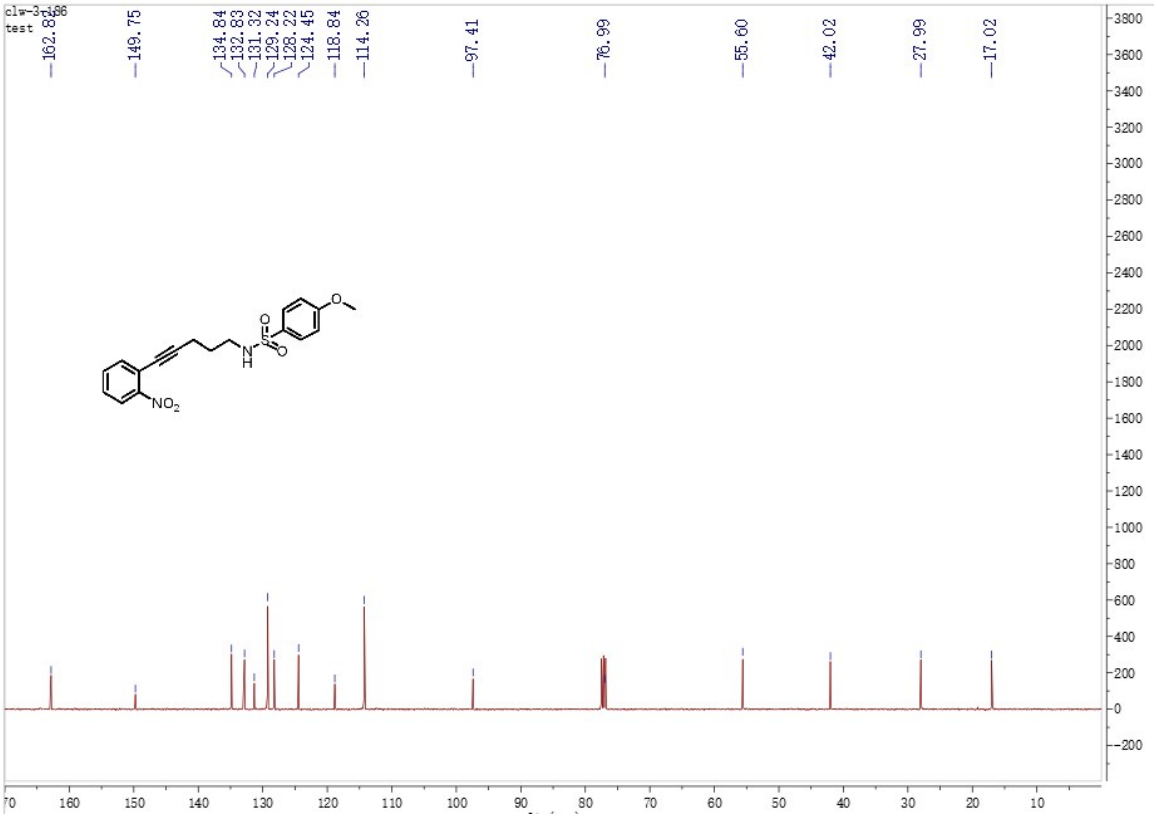
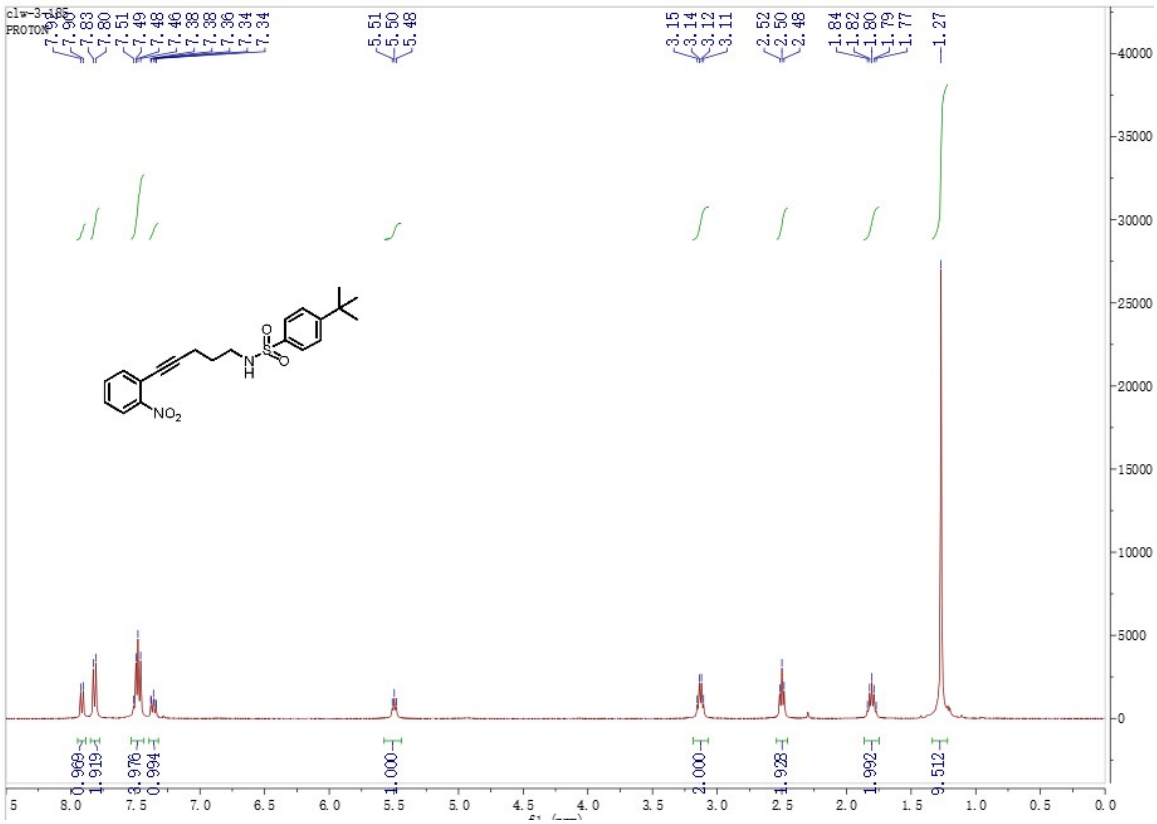
1.136
0.917
2.037
2.000
2.044


149.21
139.77
134.85
132.86
132.67
129.16
128.27
127.06
124.48
118.82
97.35
77.02
42.11
28.07
17.02
O
S
O
N
H
NO2


clw-3-186
test
7.96
7.94
7.83
7.81
7.52
7.51
7.40
6.95
6.92
5.25
5.23
5.22
3.81
3.15
3.13
3.12
3.10
2.53
2.51
2.50
1.83
1.81
1.80
1.78
1.76
1.000
2.110
2.073
1.059
2.110
1.052
3.282
2.163
2.094
2.139
O
O
S
N
H
O
NO2


clw-3-186
test
162.82
149.75
134.84
132.83
131.32
129.24
128.22
124.45
118.84
114.26
97.41
76.99
55.60
42.02
27.99
17.02
O
O
S
N
H
O
NO2


clw-3-185
PROTON
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7.83
7.80
7.51
7.49
7.48
7.46
7.38
7.36
7.34
5.51
5.50
5.48
3.15
3.14
3.12
3.11
2.52
2.50
2.48
1.84
1.82
1.80
1.79
1.77
1.27
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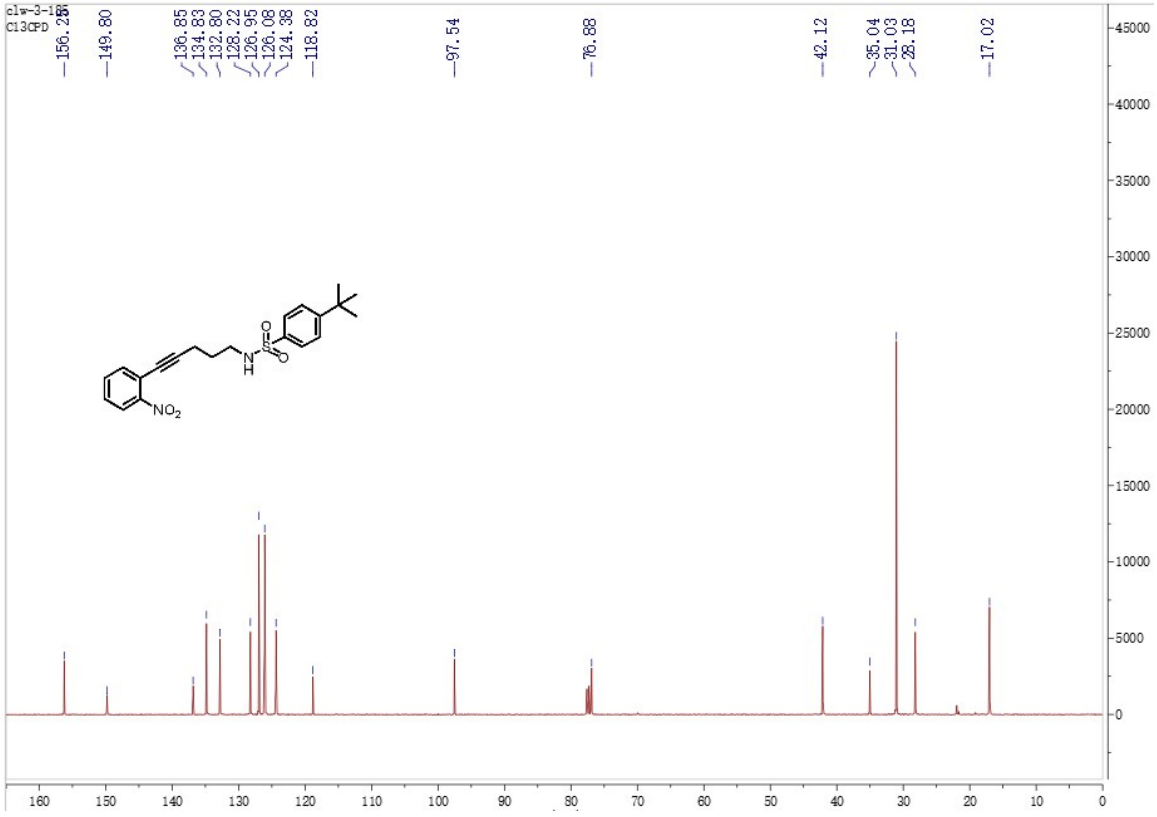
1.919
3.976
0.994
1.000
2.000
1.928
1.992
9.512
NO2


clw-3-185
C13CPD
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134.83
132.80
128.22
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76.88
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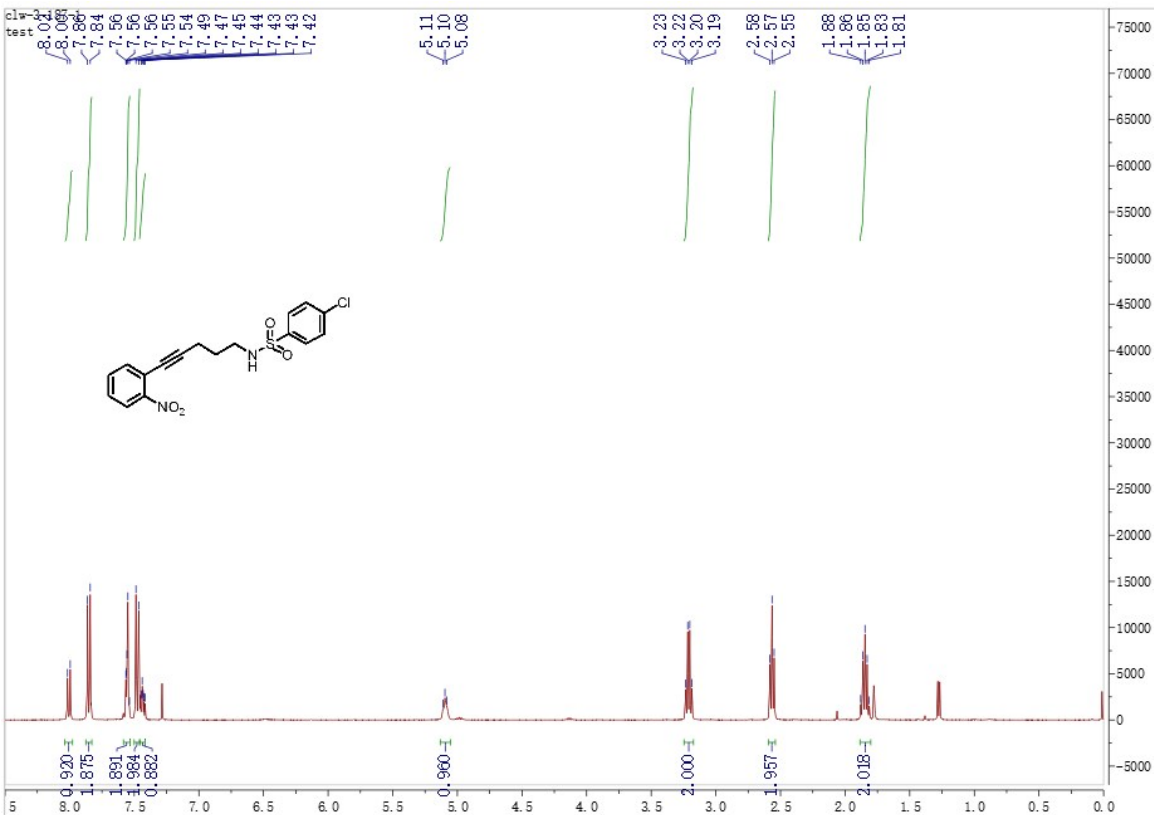
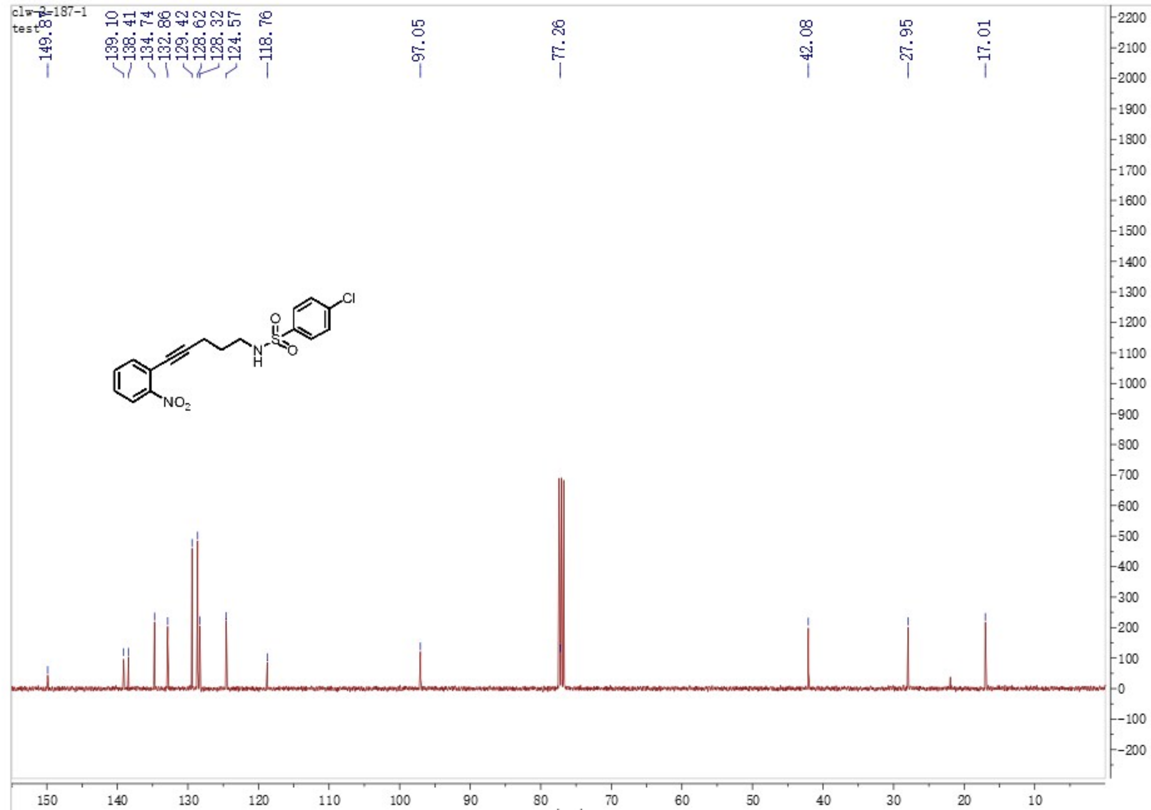
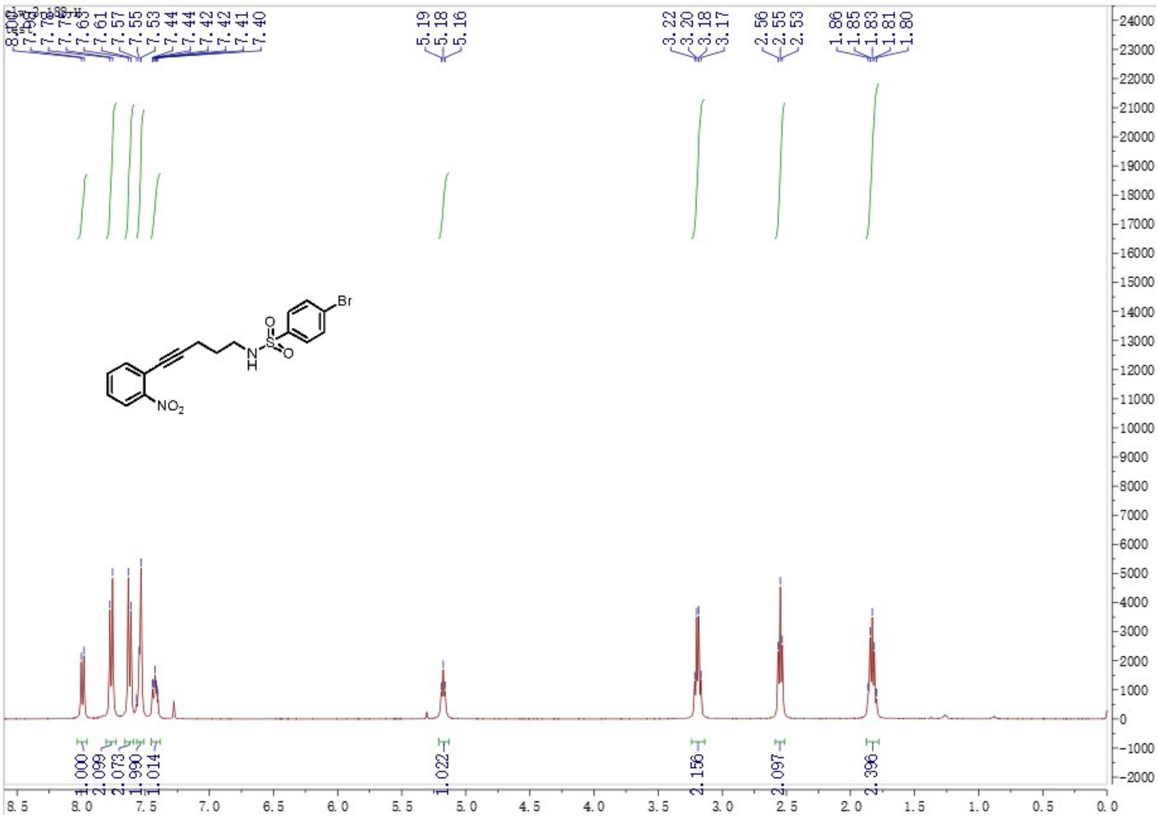
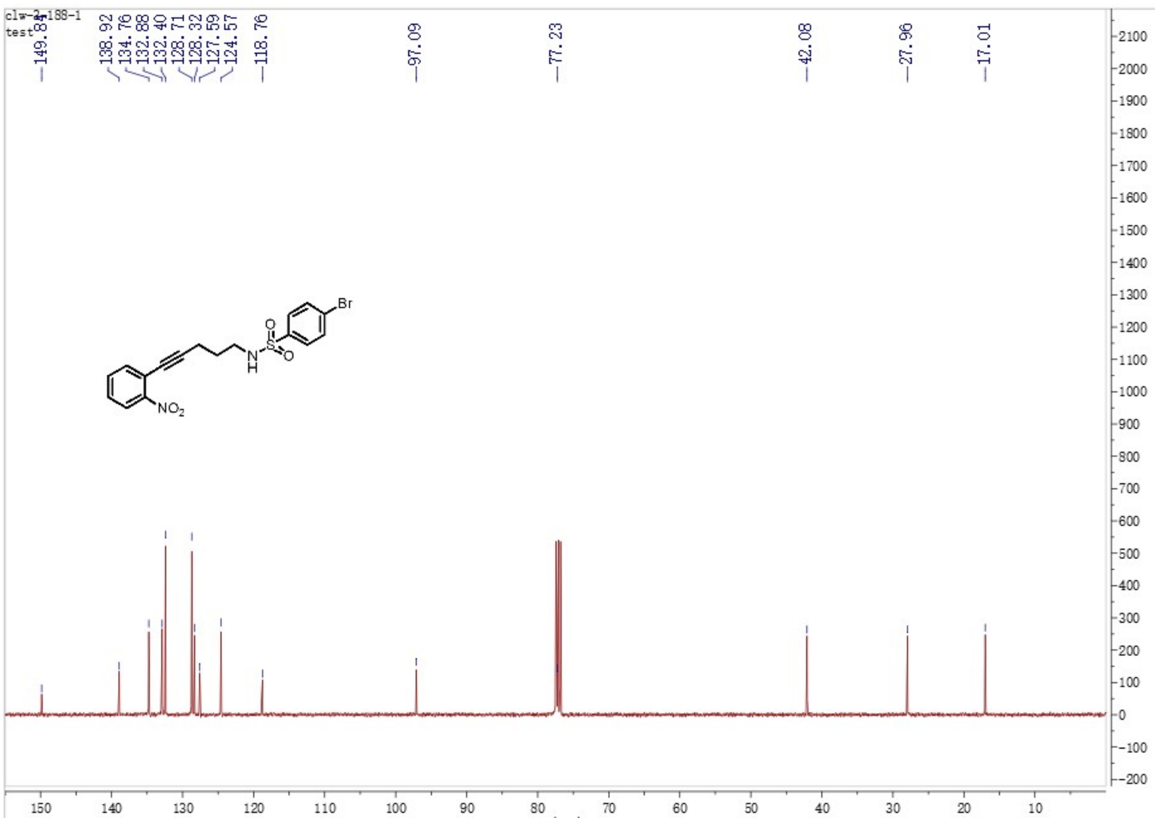
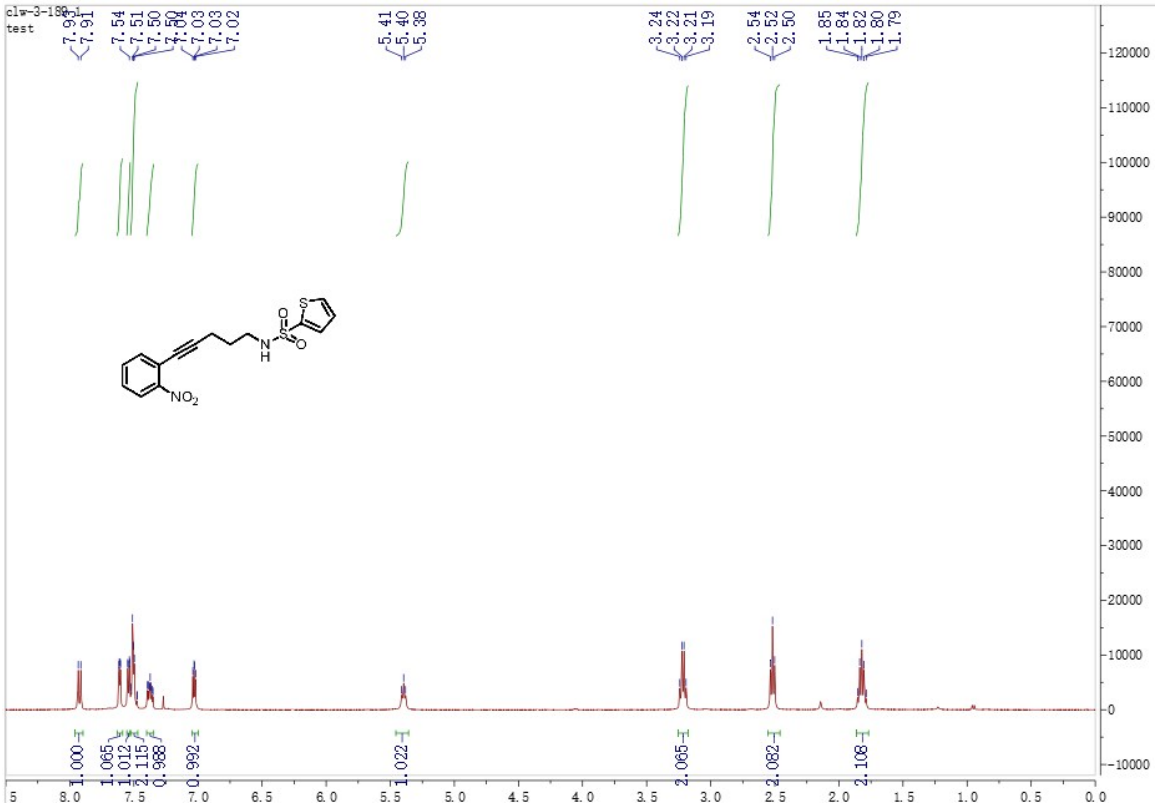
35.04
31.03
28.18
17.02
NO2

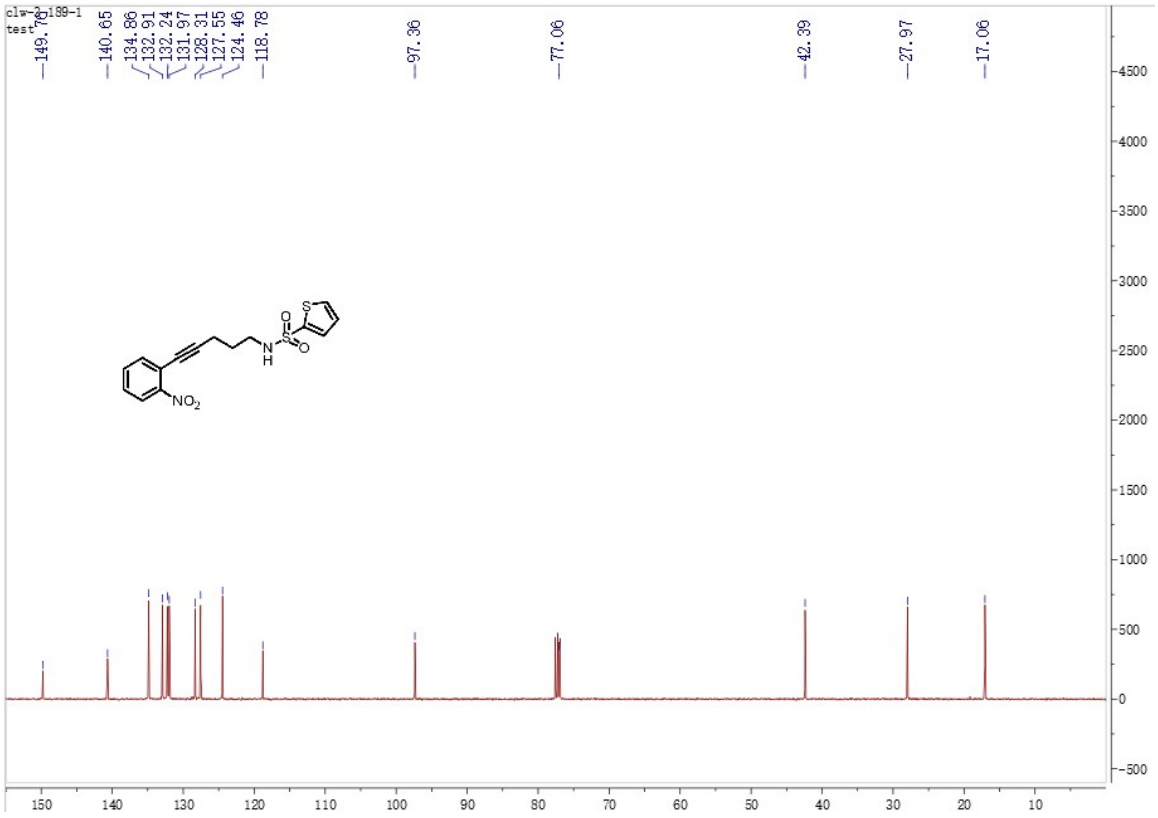









clw-3-189-1
test
7.91
7.91
7.54
7.51
7.50
7.50
7.04
7.03
7.03
7.02
5.41
5.40
5.38
3.24
3.22
3.21
3.19
2.54
2.52
2.50
1.85
1.84
1.82
1.80
1.79
1.000
1.065
1.012
2.115
0.988
0.992
1.022
2.065
2.082
2.108


clw-3-189-1
test
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134.86
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131.97
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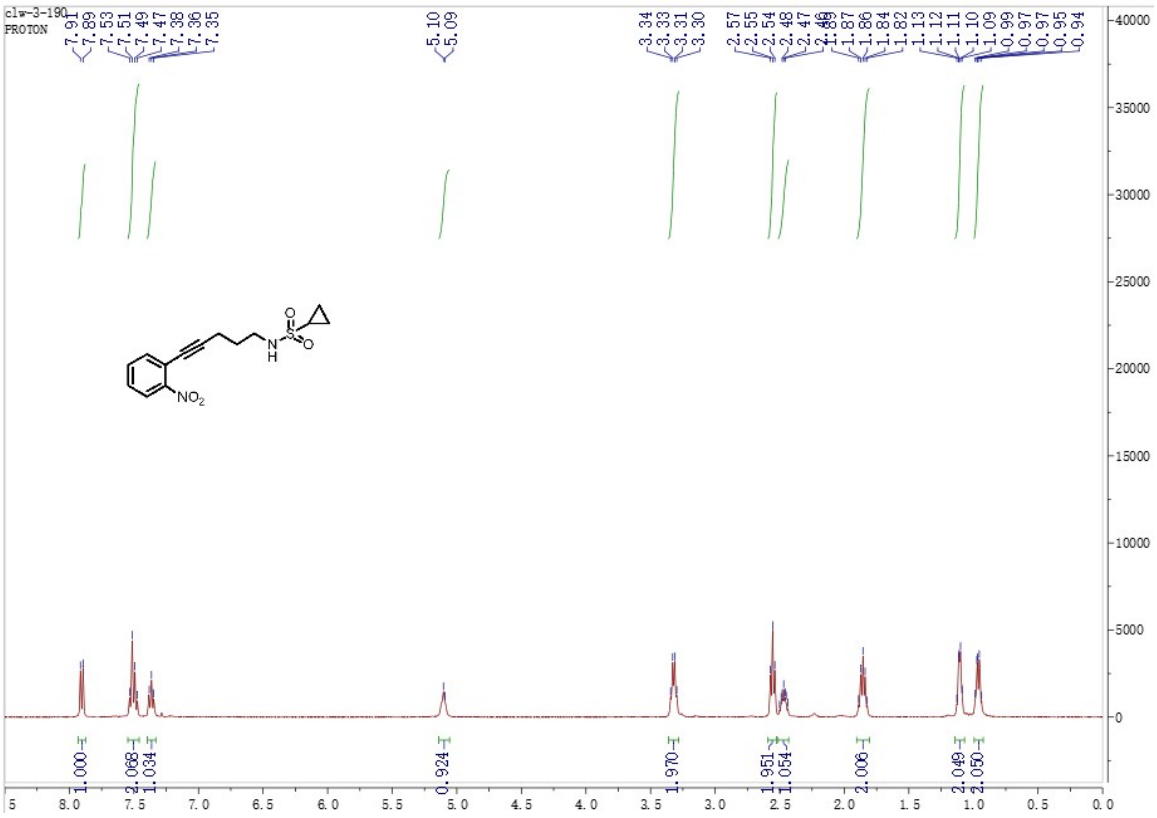
124.46
118.78
97.36
77.06
42.39
27.97
17.06


clw-3-190
PROTON
7.91
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7.53
7.51
7.49
7.47
7.38
7.36
7.35
5.10
5.09
3.34
3.33
3.31
3.30
2.57
2.55
2.54
2.48
2.47
1.87
1.86
1.84
1.82
1.13
1.12
1.11
1.10
1.09
0.99
0.97
0.97
0.95
0.94
1.000
2.068
1.034
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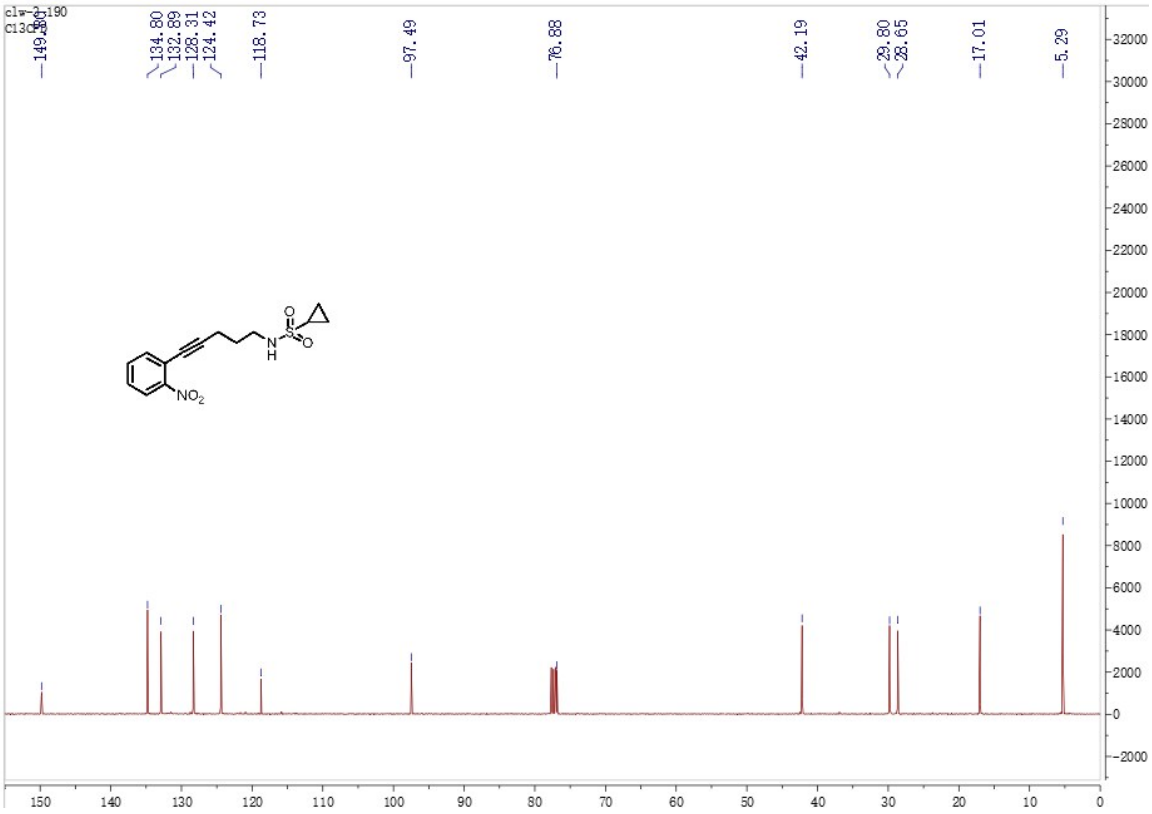
1.970
1.951
1.054
2.006
2.049
2.050
O
S
O
N
H
NO2


clw-2-190
C13CPD
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124.42
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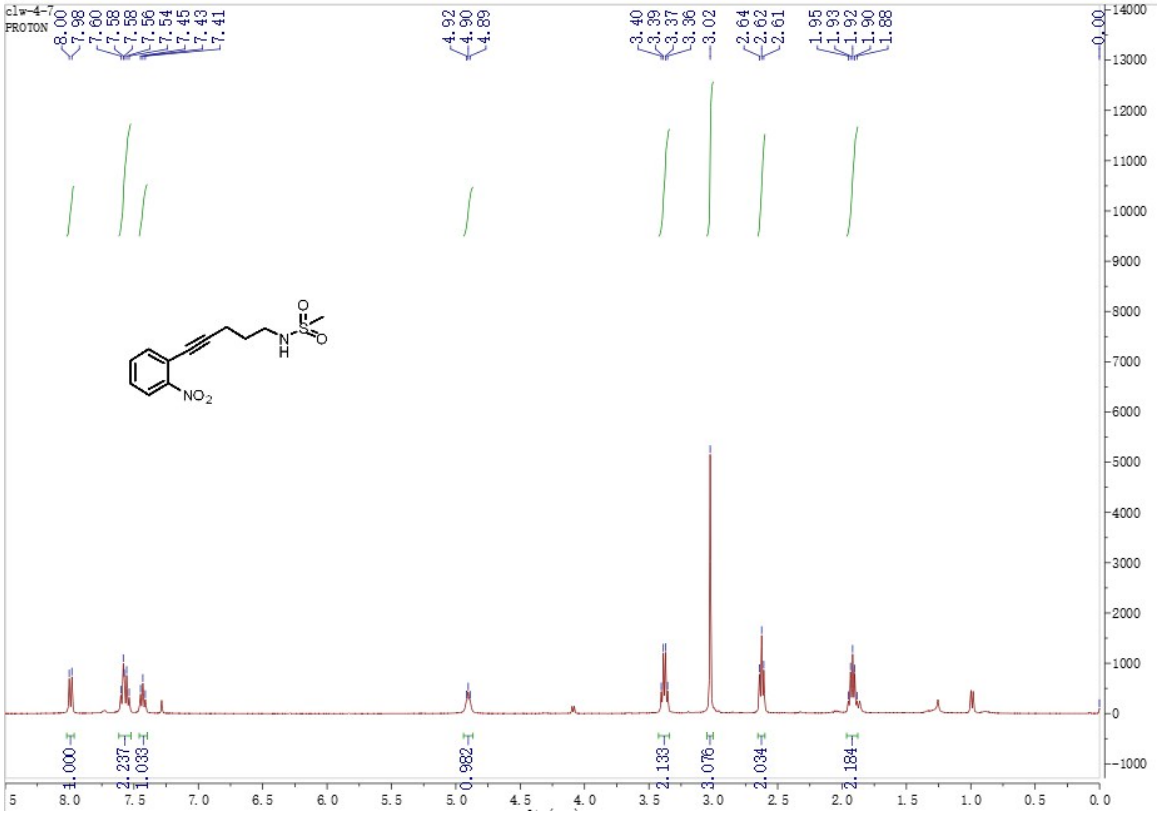
76.88
42.19
29.80
28.65
17.01
5.29
O
S
O
N
H
NO2


clw-4-7
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7.58
7.58
7.56
7.54
7.45
7.43
7.41
4.92
4.90
4.89
3.40
3.39
3.37
3.36
3.02
2.64
2.62
2.61
1.95
1.93
1.92
1.90
1.88
0.00
1.000
2.237
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0.982
2.133
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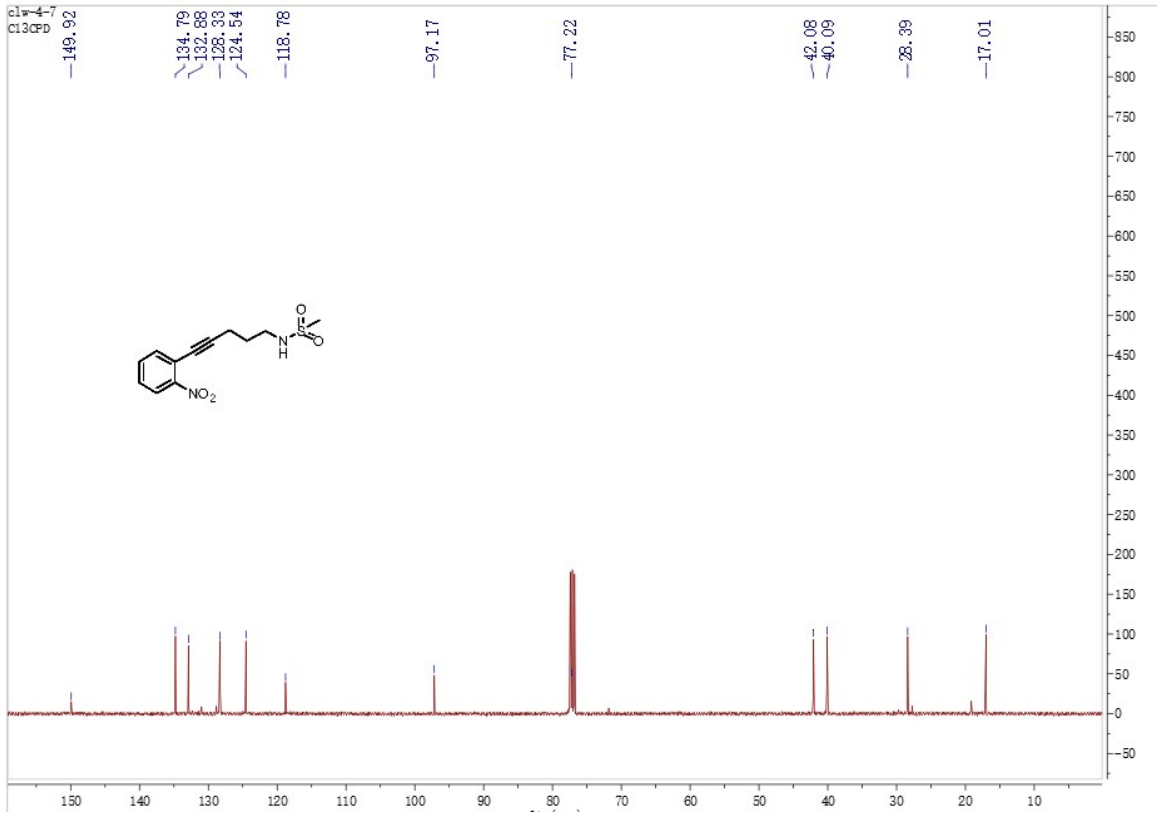
2.034
2.184
NO2


clw-4-7
C13CPD
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124.54
118.78
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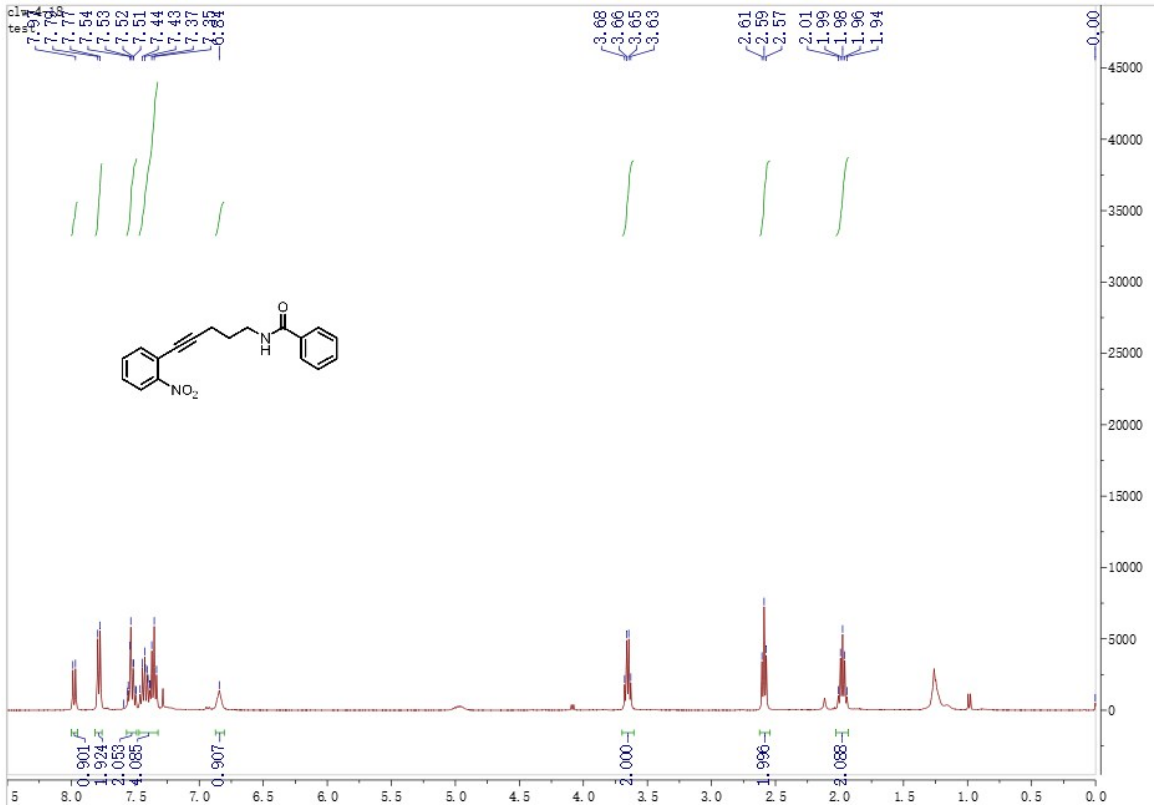
77.22
42.08
40.09
28.39
17.01
NO2


clw-4-18
test
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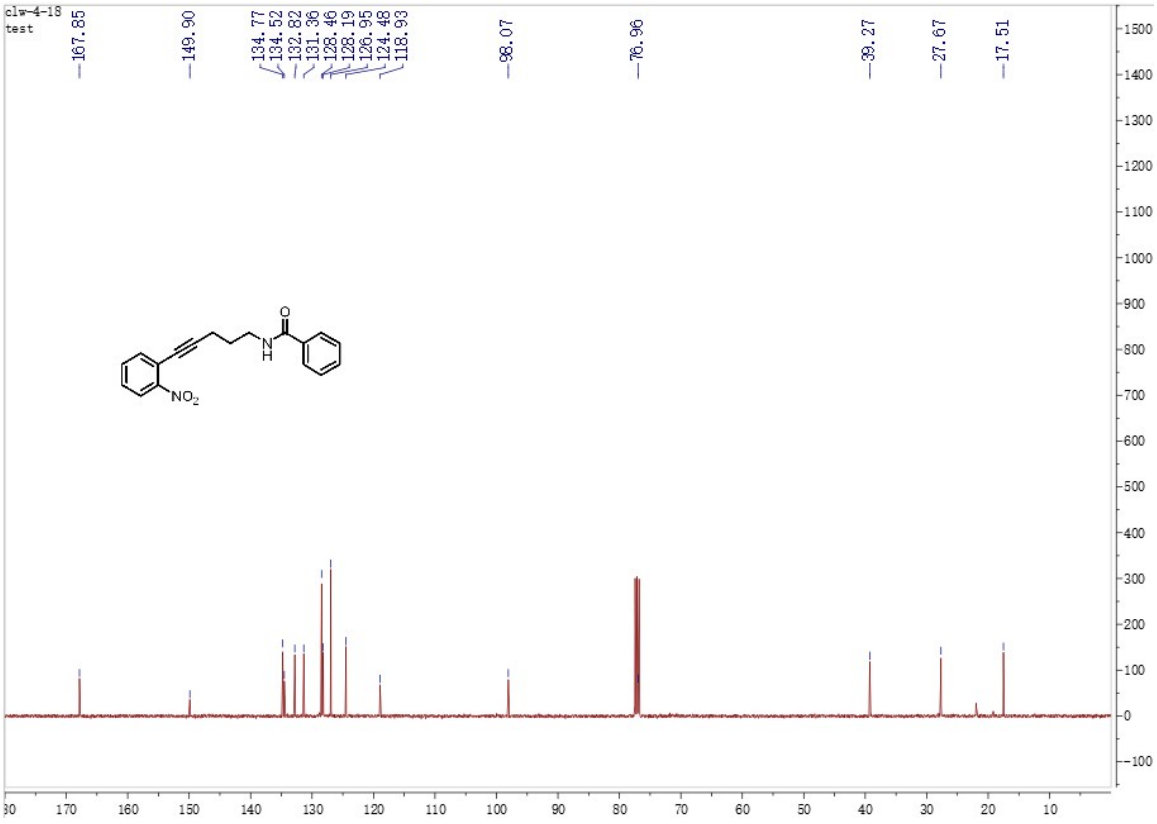
7.54
7.53
7.52
7.51
7.44
7.43
7.37
7.35
3.68
3.66
3.65
3.63
2.61
2.59
2.57
2.01
1.99
1.98
1.96
1.94
0.00
0.901
1.924
2.053
4.085
0.907
2.000
1.966
2.088
NO2


clw-4-18
test
167.85
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134.52
132.82
131.36
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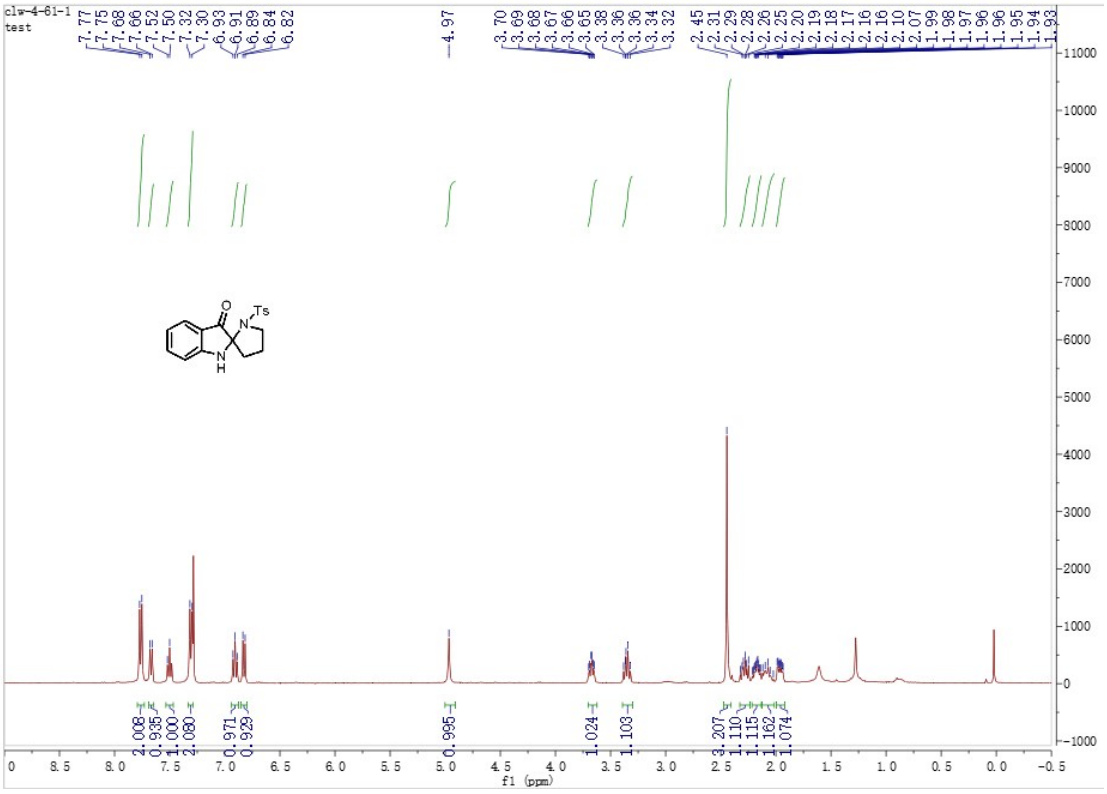
128.19
126.95
124.48
118.93
98.07
76.96
39.27
27.67
17.51
NO2


clw-4-61-1
test
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7.75
7.68
7.66
7.52
7.50
7.32
7.30
6.93
6.91
6.89
6.84
6.82
4.97
3.70
3.69
3.68
3.67
3.66
3.65
3.38
3.36
3.36
3.34
3.32
2.45
2.31
2.29
2.28
2.26
2.25
2.20
2.19
2.18
2.17
2.16
2.16
2.10
2.07
1.99
1.98
1.97
1.96
1.96
1.95
1.94
1.93
Ts
2.008
0.935
1.000
2.080
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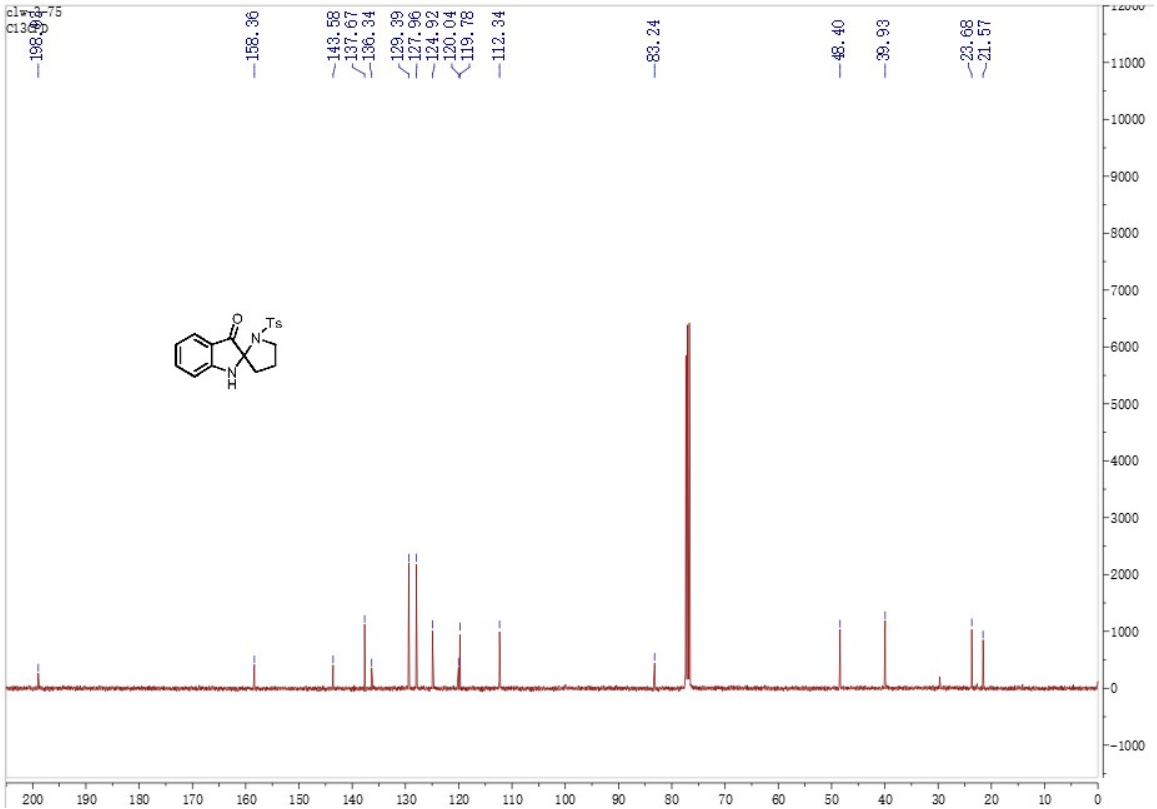
0.995
1.024
1.103
3.207
1.110
1.115
1.162
1.074
f1 (ppm)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124.92
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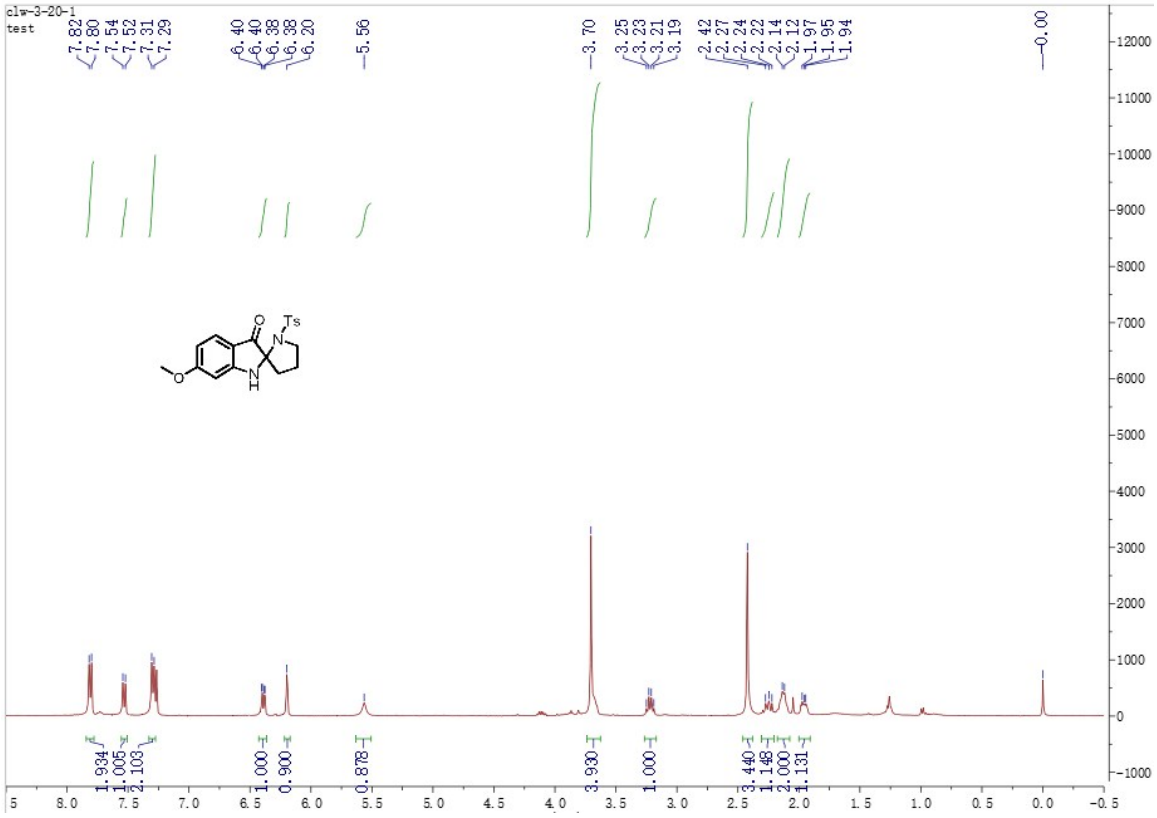
48.40
39.93
23.68
21.57
Ts


clw-3-20-1
test
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7.80
7.54
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6.40
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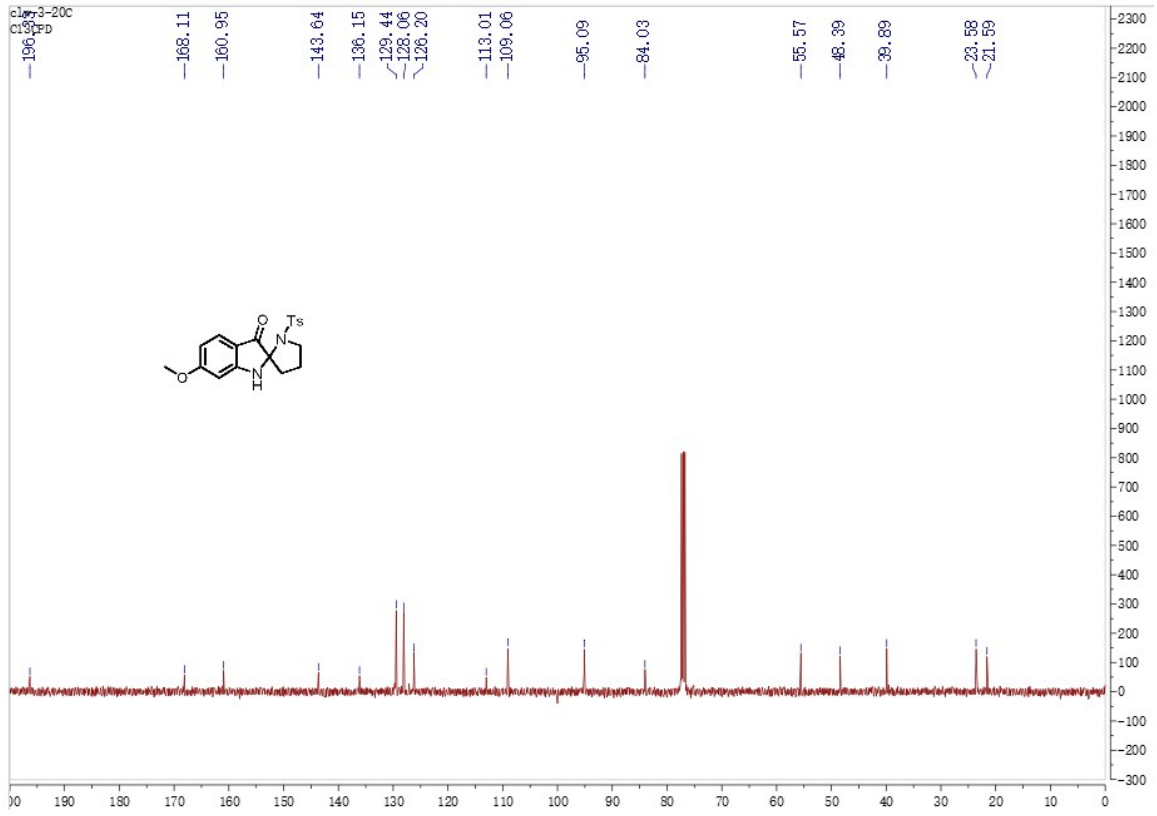
6.38
6.20
5.56
3.70
3.25
3.23
3.21
3.19
2.42
2.27
2.24
2.22
2.14
2.12
1.97
1.95
1.94
0.00
Ts
O
N
H
O
1.934
1.005
2.103
1.000
0.900
0.878
3.930
1.000
3.440
1.148
2.000
1.131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C13CPD
196.93
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143.64
136.15
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128.06
126.20
113.01
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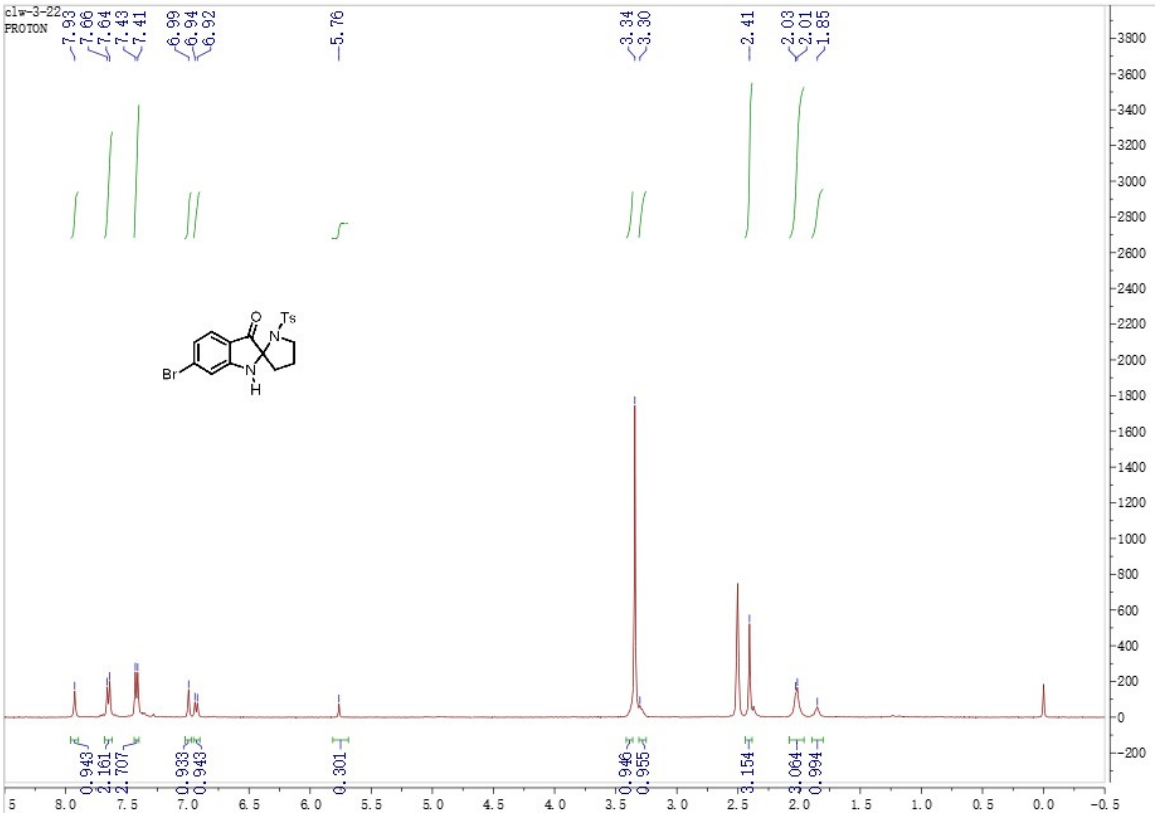
95.09
84.03
55.57
48.39
39.89
23.58
21.59
Ts
O
N
H
O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PROTON
7.93
7.66
7.64
7.43
7.41
6.99
6.94
6.92
5.76
3.34
3.30
2.41
2.03
2.01
1.85
Ts
N
O
Br
H
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2.707
0.933
0.943
0.301
0.946
0.955
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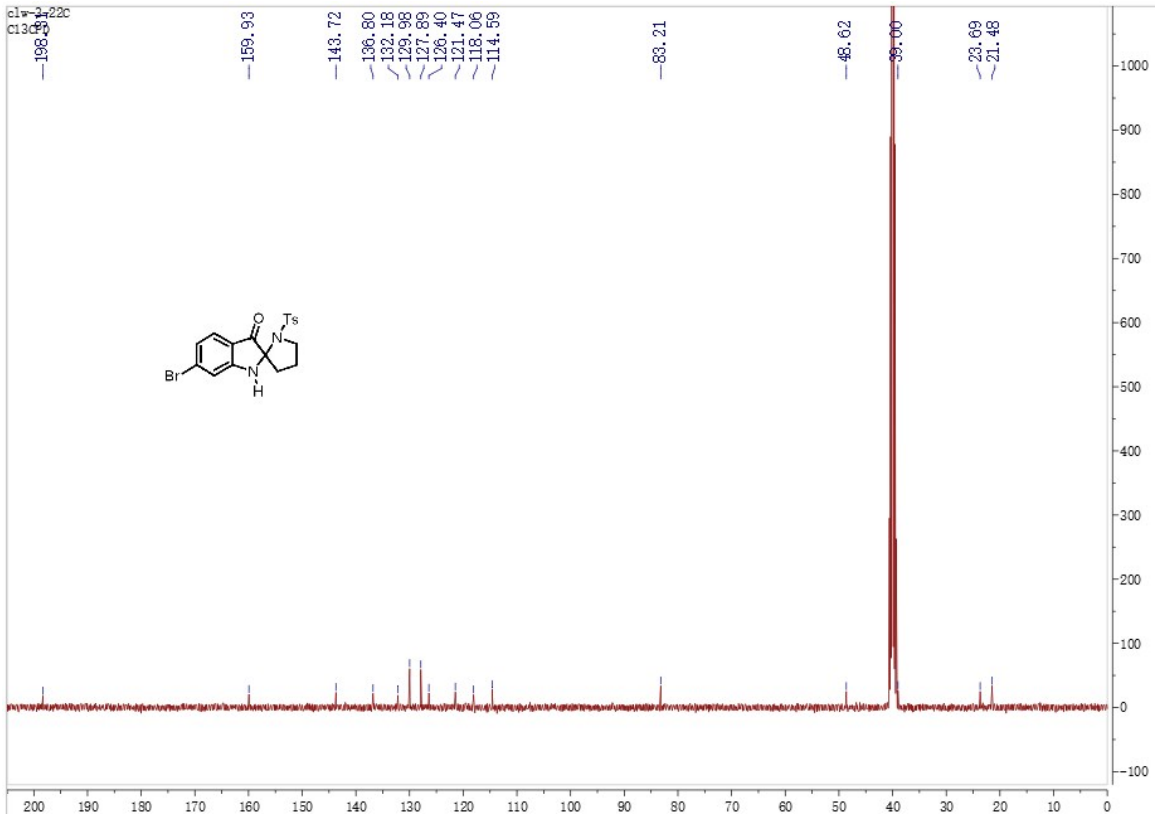
3.064
0.994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114.59
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39.00
23.69
21.48
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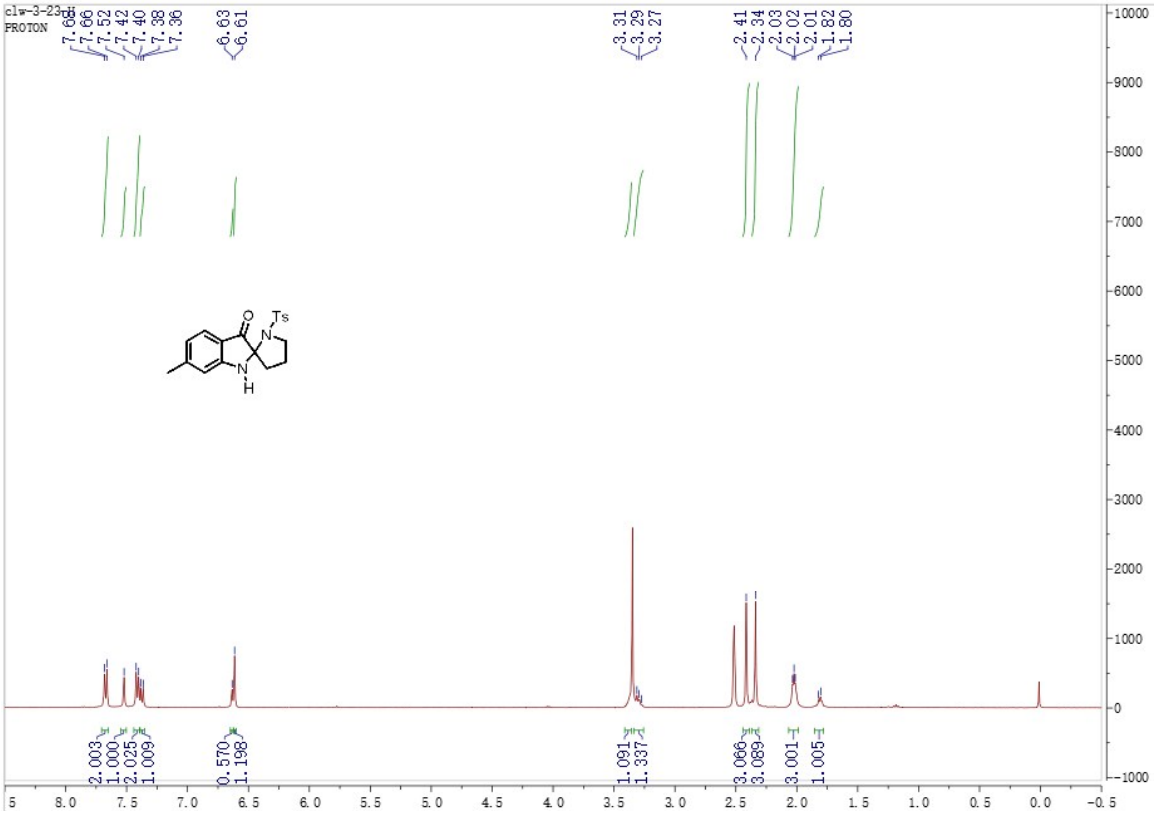
N
O
Br
H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7.42
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7.38
7.36
6.63
6.61
3.31
3.29
3.27
2.41
2.34
2.03
2.02
2.01
1.82
1.80
Ts
N
O
H
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2.025
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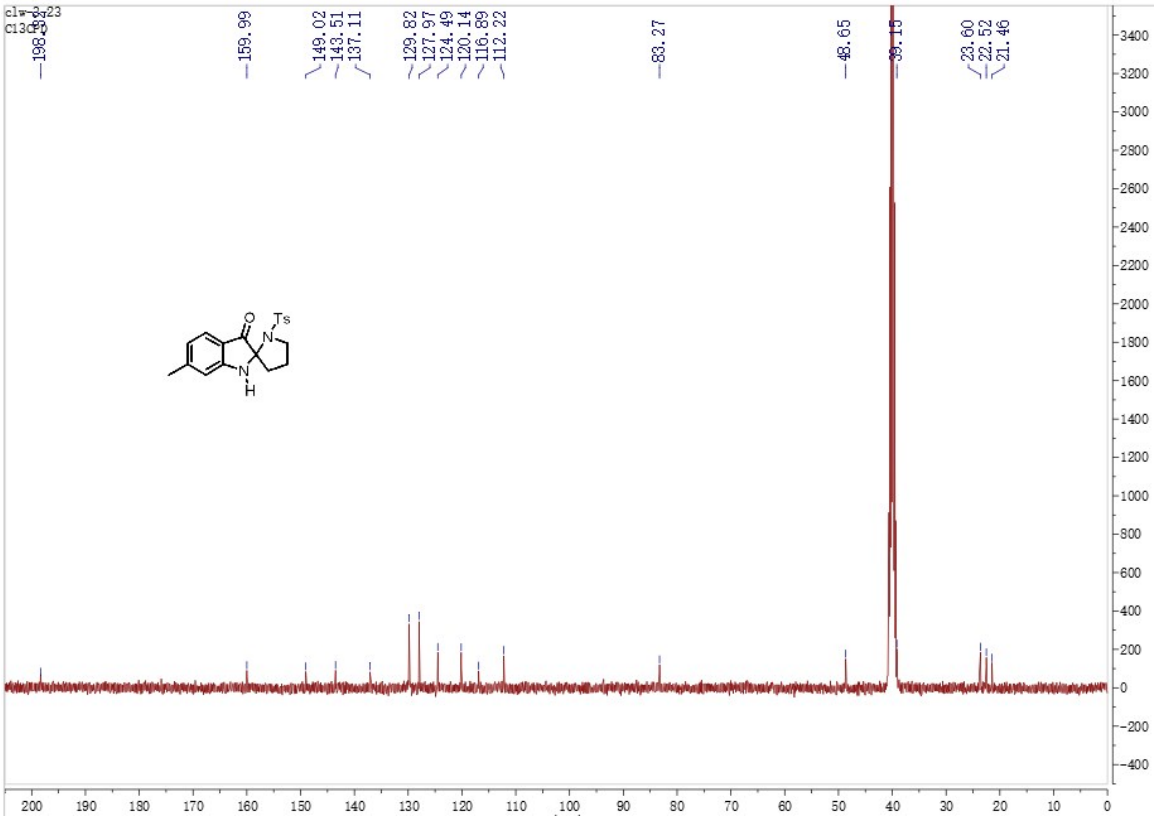
1.091
1.337
3.066
3.089
3.001
1.005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112.22
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48.65
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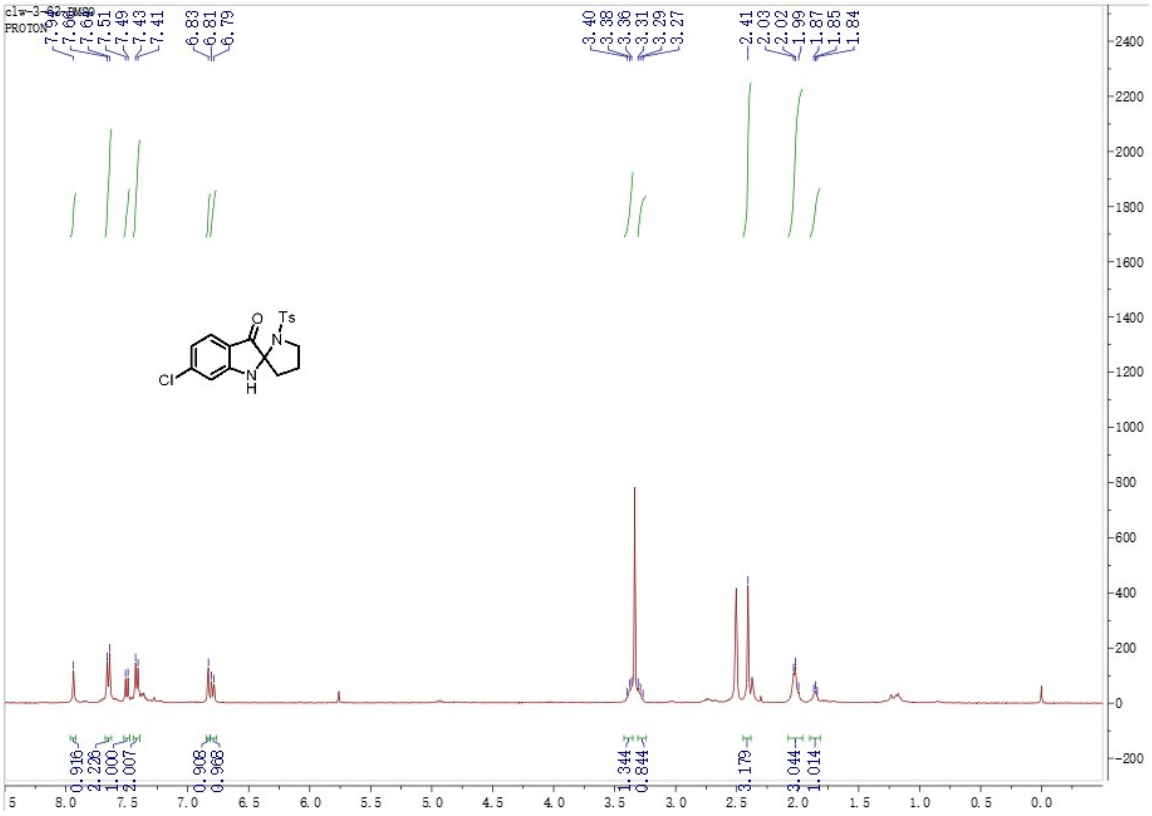
23.60
22.52
21.46
Ts
N
O
H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7.61
7.51
7.49
7.43
7.41
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6.81
6.79
3.40
3.38
3.36
3.31
3.29
3.27
2.41
2.03
2.02
1.99
1.87
1.85
1.84
Ts
O
N
Cl
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0.968
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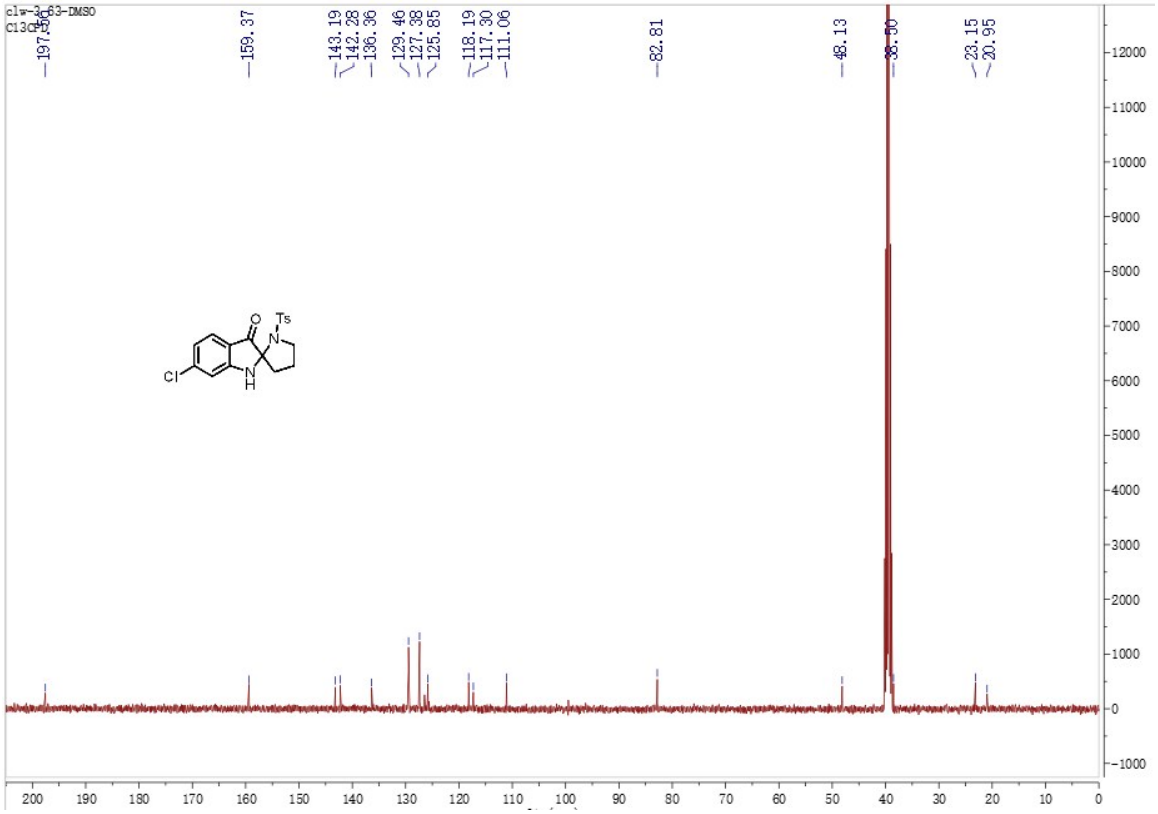
0.844
3.179
3.044
1.014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129.46
127.38
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111.06
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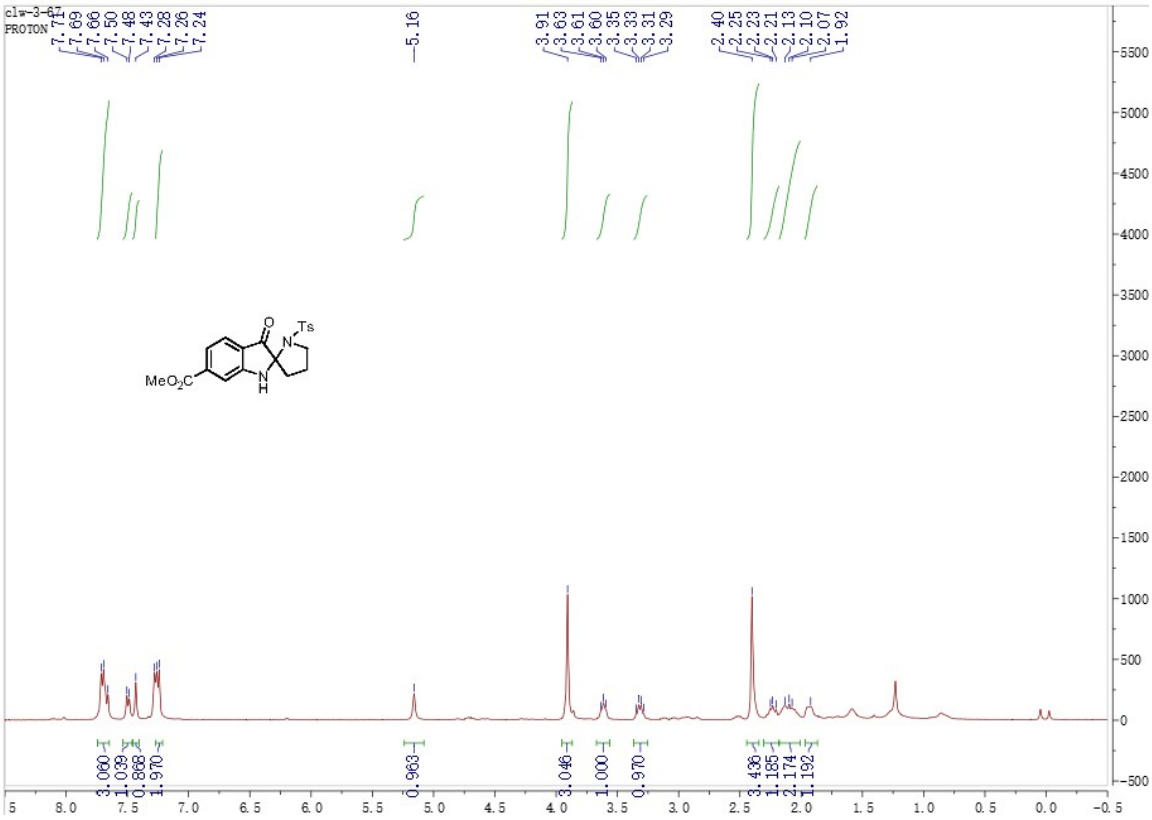
48.13
38.50
23.15
20.95
Ts
O
N
Cl
H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7.69
7.66
7.50
7.48
7.43
7.28
7.26
7.24
5.16
3.91
3.63
3.61
3.60
3.35
3.33
3.31
3.29
2.40
2.25
2.23
2.21
2.13
2.10
2.07
1.92
3.060
1.039
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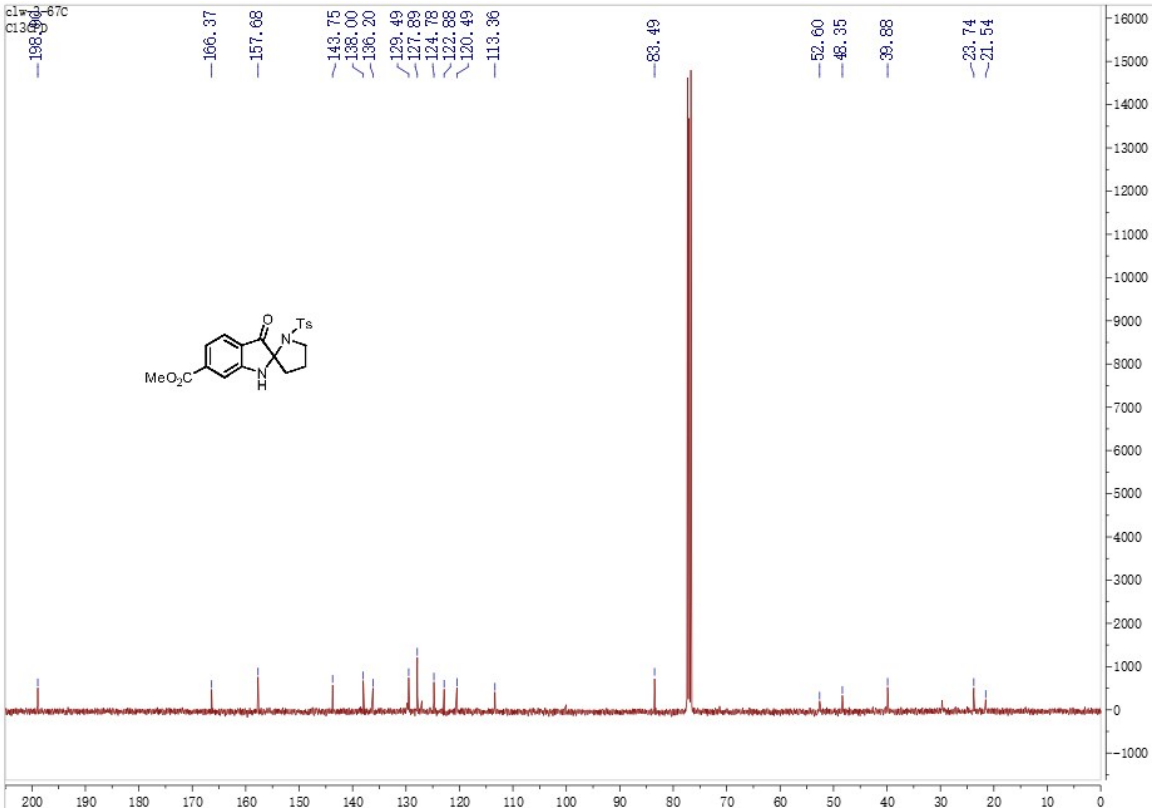
0.963
3.046
1.000
0.970
3.436
1.185
2.174
1.192
Ts
MeO2C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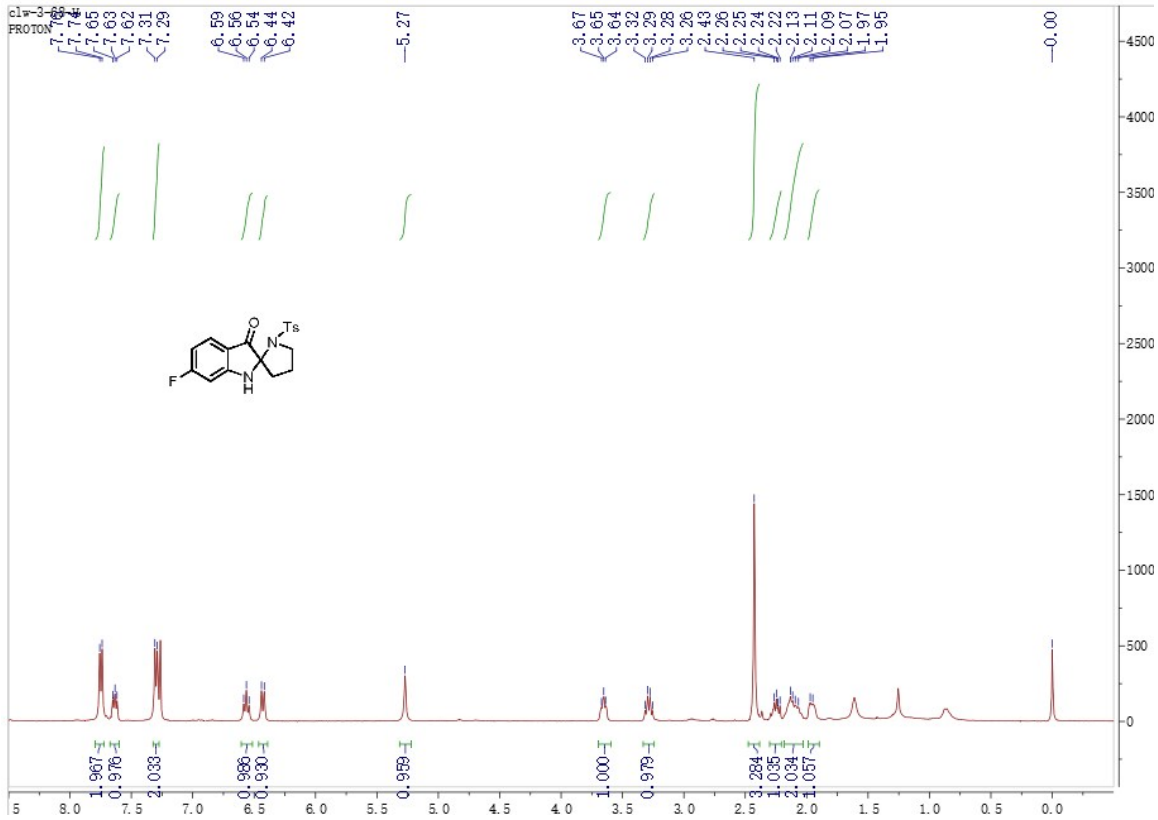
113.36
83.49
52.60
48.35
39.88
23.74
21.54
Ts
MeO2C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6.59
6.56
6.54
6.44
6.42
5.27
3.67
3.65
3.64
3.32
3.29
3.28
3.26
2.43
2.26
2.25
2.24
2.22
2.13
2.11
2.09
2.07
1.97
1.95
0.00
Ts
N
O
F
H
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0.979
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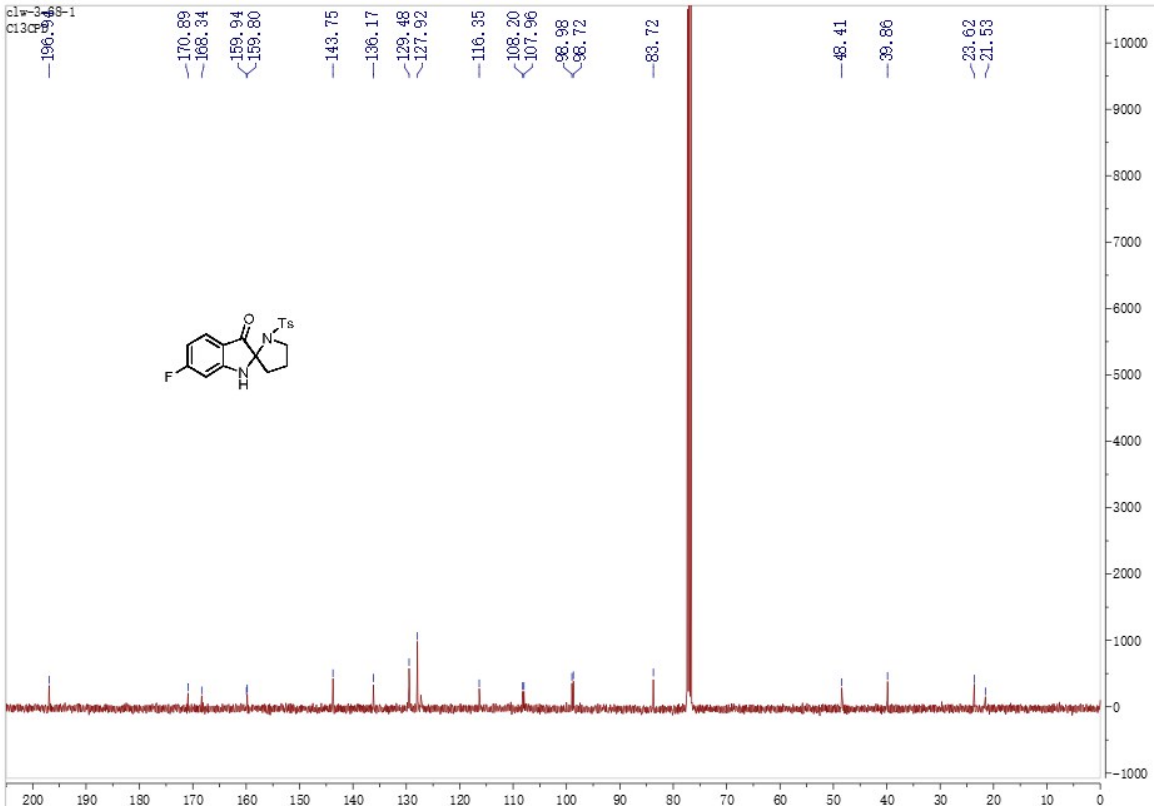
1.057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127.92
116.35
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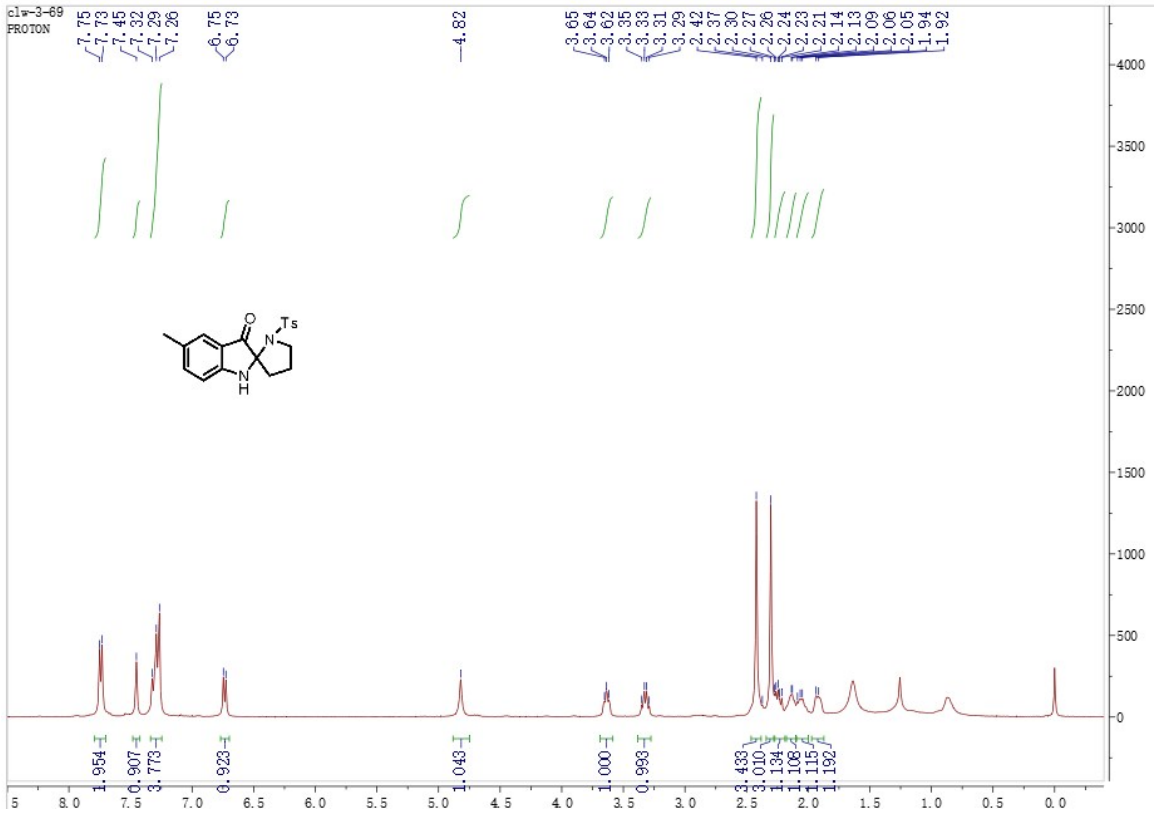
98.72
83.72
48.41
39.86
23.62
21.53
Ts
N
O
F
H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7.73
7.45
7.32
7.29
7.26
6.75
6.73
4.82
3.65
3.64
3.62
3.35
3.33
3.31
3.29
2.42
2.37
2.30
2.27
2.26
2.24
2.23
2.21
2.14
2.13
2.09
2.06
2.05
1.94
1.92
Ts
N
H
O
1.954
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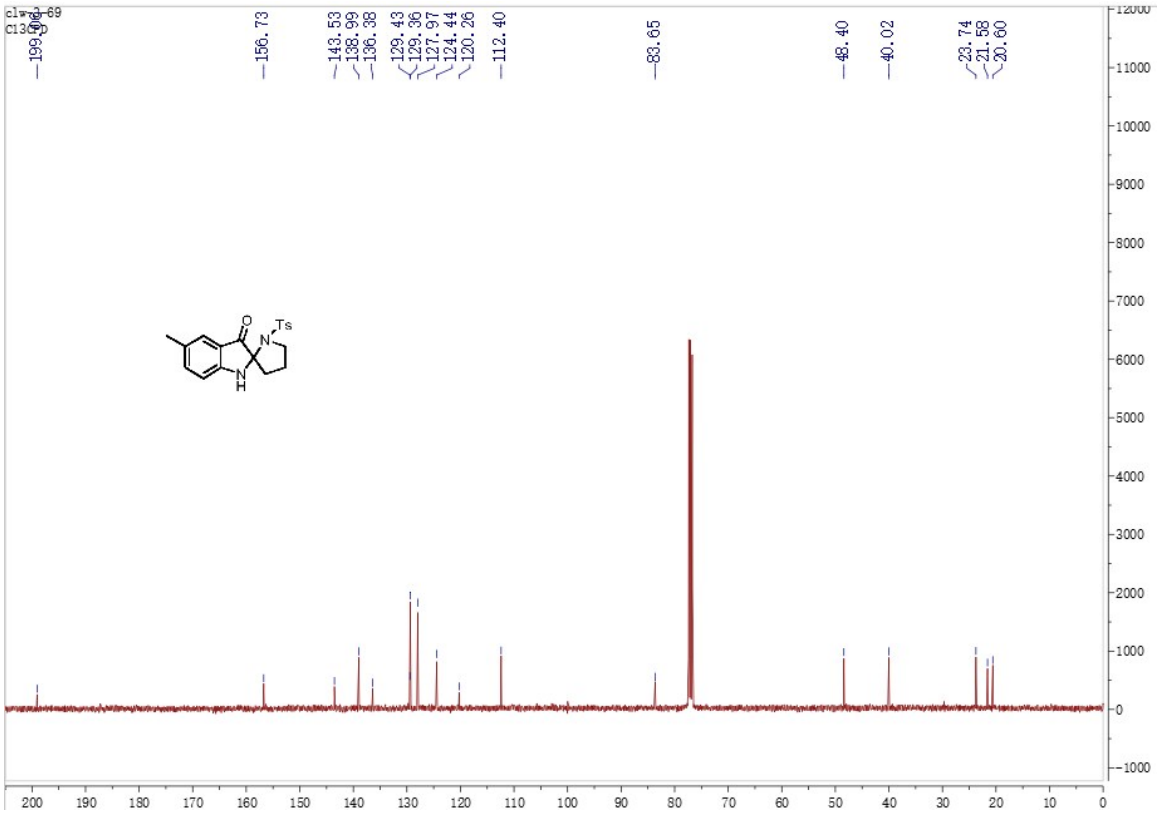
1.108
1.115
1.192


clw-3-69
C13CPD
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129.36
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112.40
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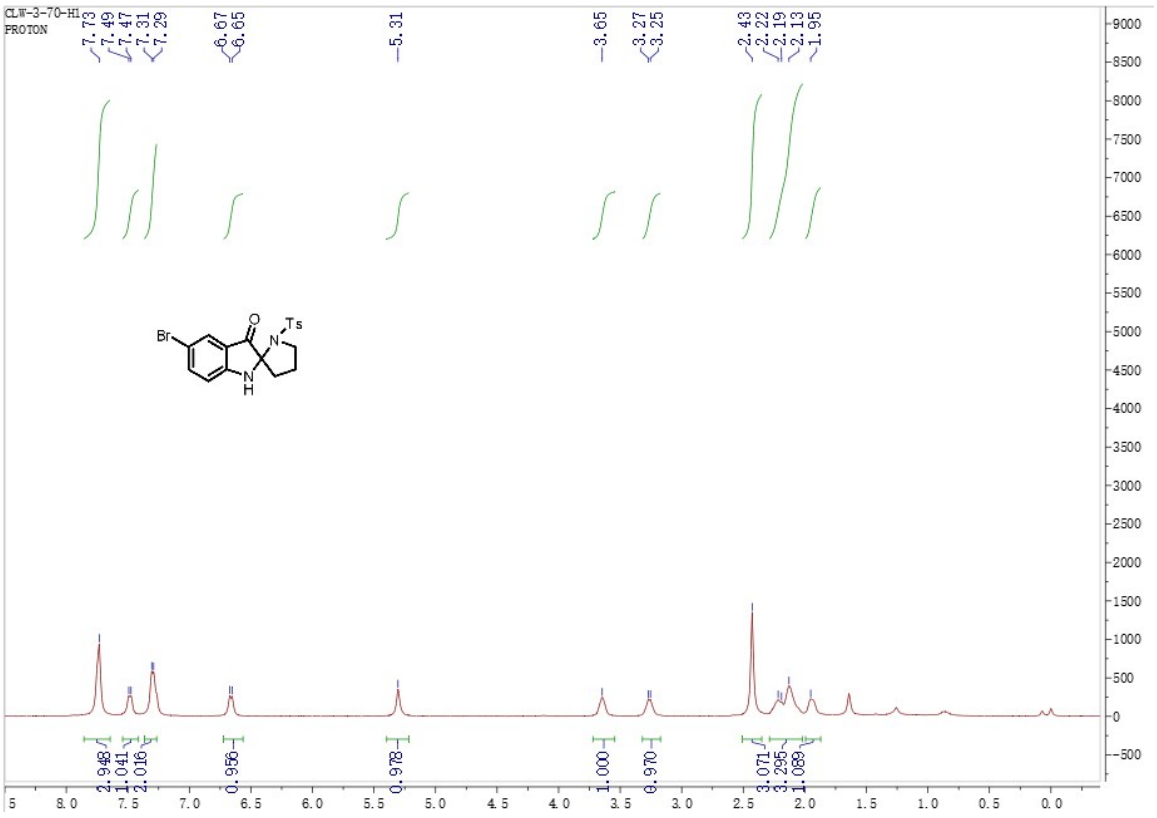
48.40
40.02
23.74
21.58
20.60
Ts
N
H
O


CLW-3-70-H1
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7.47
7.31
7.29
6.67
6.65
5.31
3.65
3.27
3.25
2.43
2.22
2.19
2.13
1.95
Br
O
N
Ts
H
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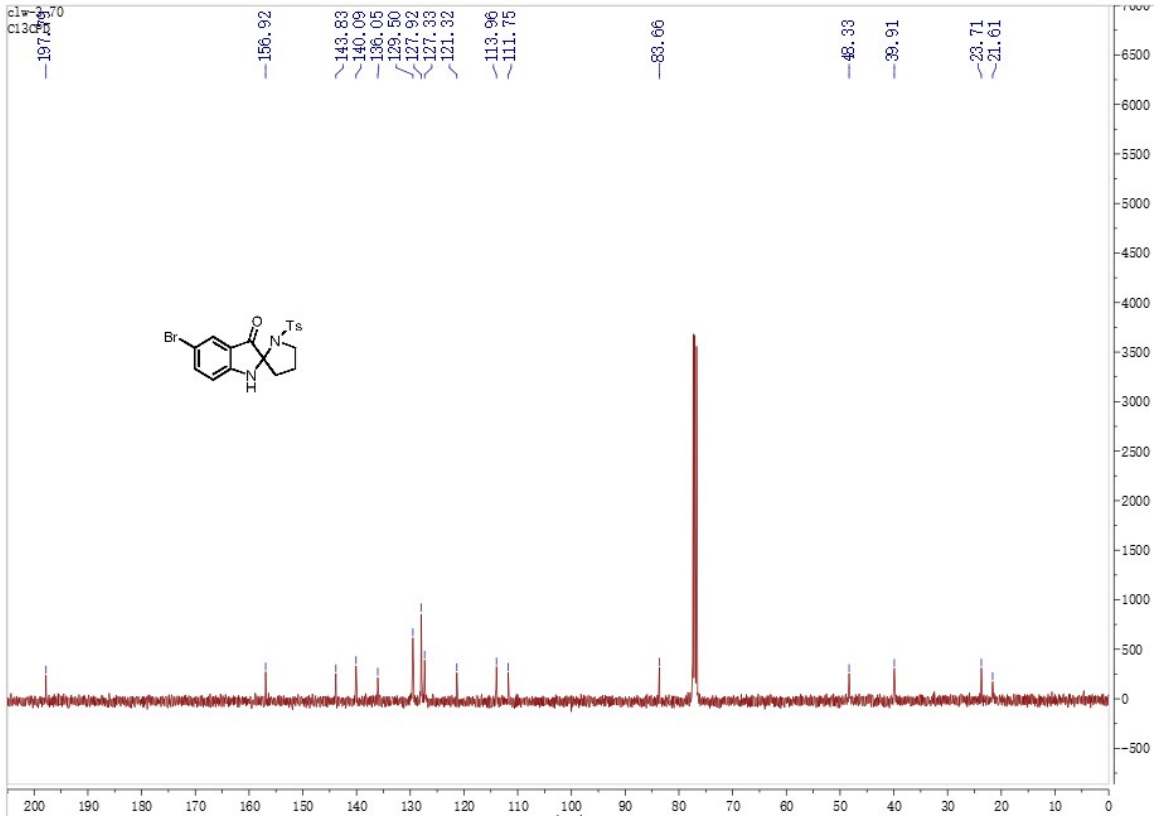
1.000
0.970
3.071
3.295
1.089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140.09
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129.50
127.92
127.33
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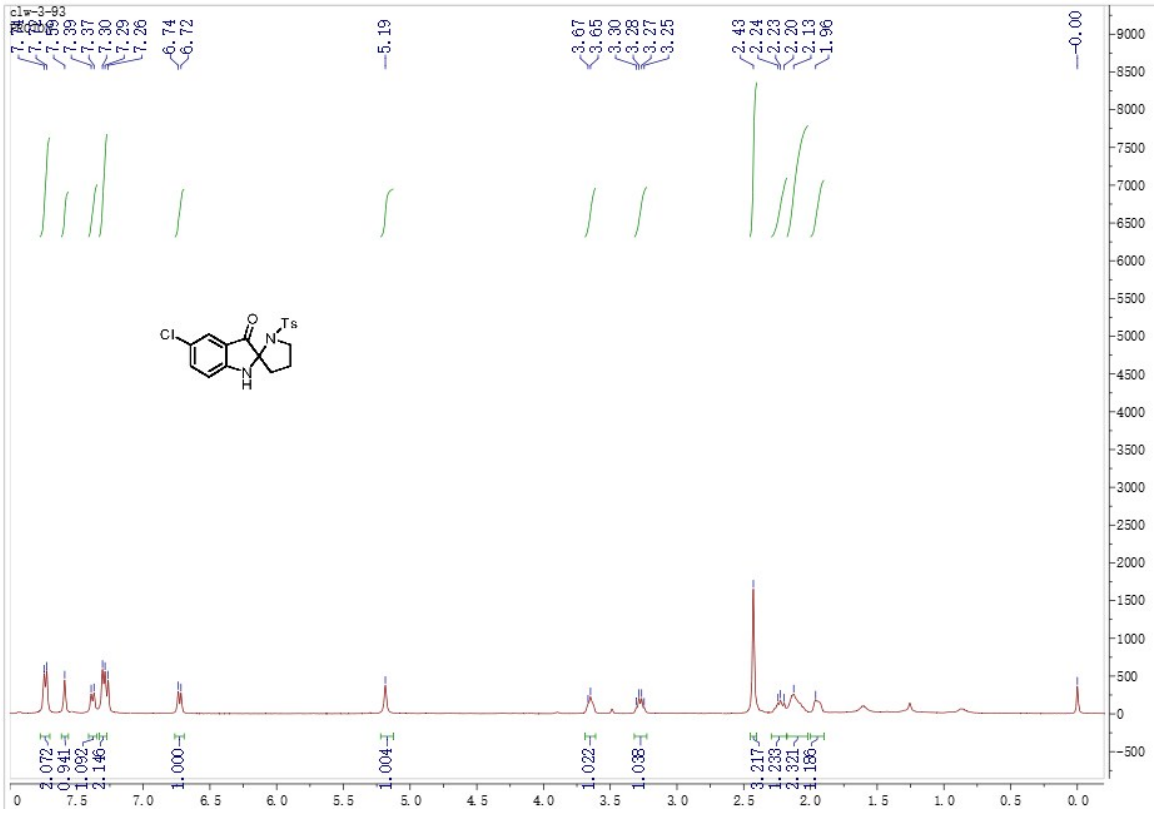
111.75
83.66
48.33
39.91
23.71
21.61
Br
O
N
Ts
H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7.56
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7.29
7.26
6.74
6.72
5.19
3.67
3.65
3.30
3.28
3.27
3.25
2.43
2.24
2.23
2.20
2.13
1.96
0.00
Cl
O
N
Ts
H
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2.146
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1.004
1.022
1.038
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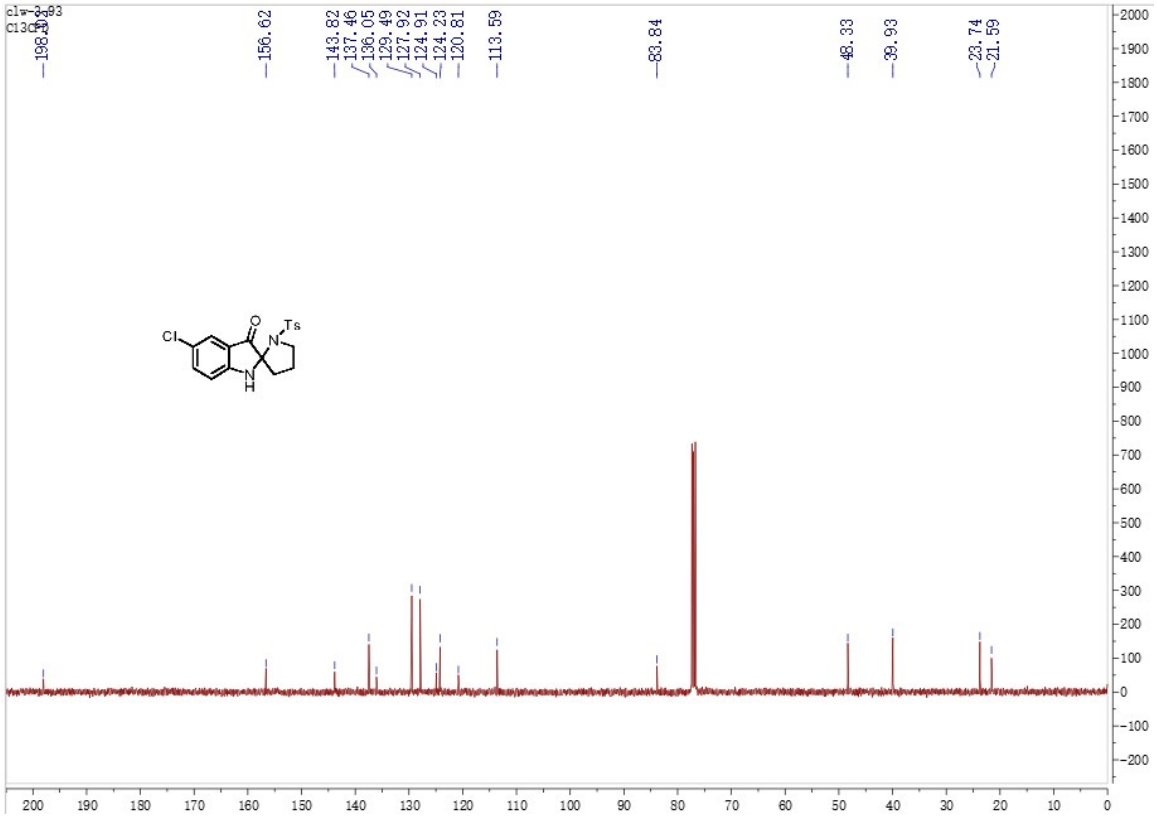
1.186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113.59
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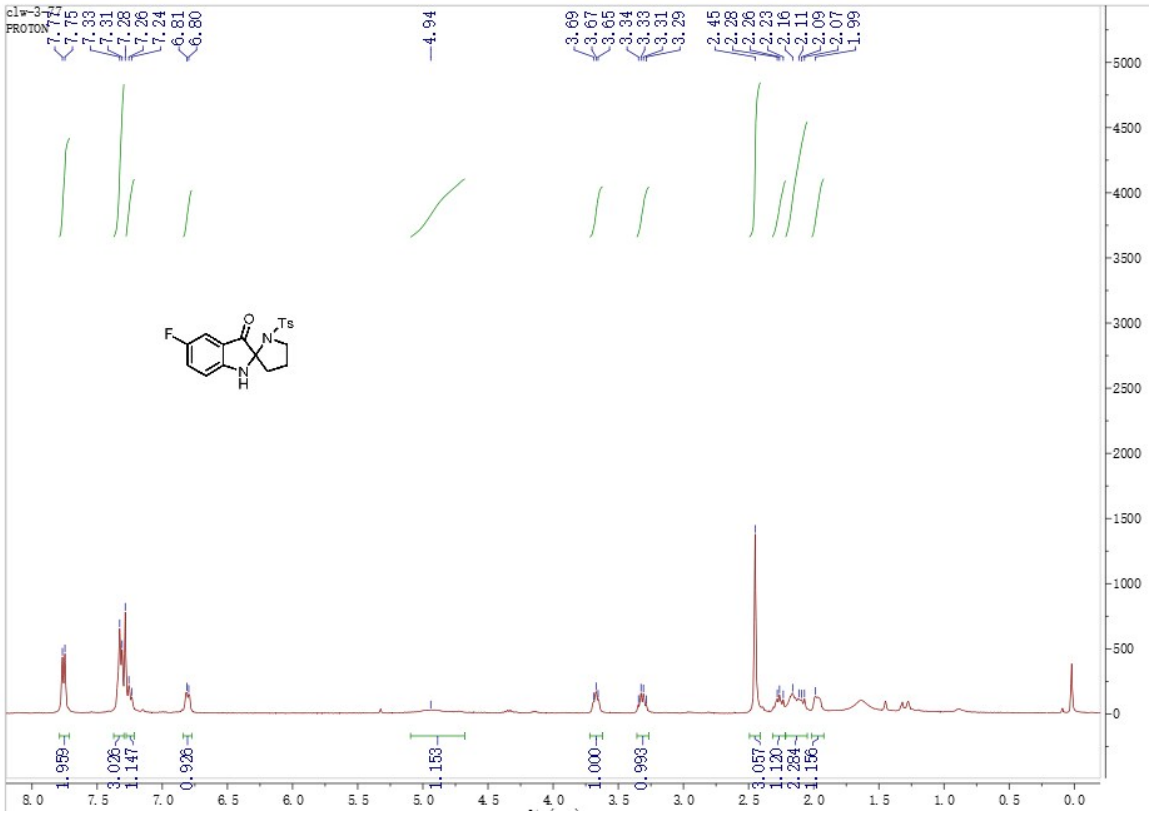
23.74
21.59
Cl
O
N
Ts
H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6.80
4.94
3.69
3.67
3.65
3.34
3.33
3.31
3.29
2.45
2.28
2.26
2.23
2.16
2.11
2.09
2.07
1.99
F
O
N
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1.000
0.993
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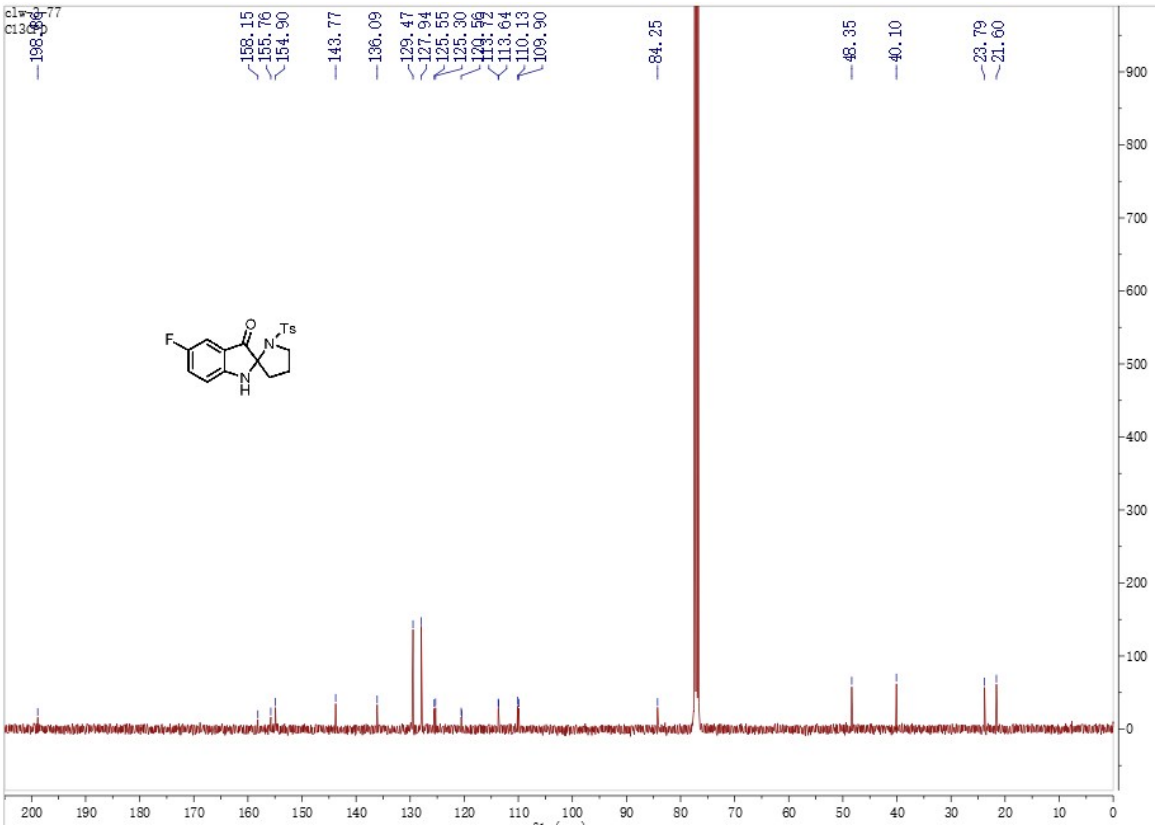
1.120
2.284
1.156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129.47
127.94
125.55
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110.13
109.90
84.25
48.35
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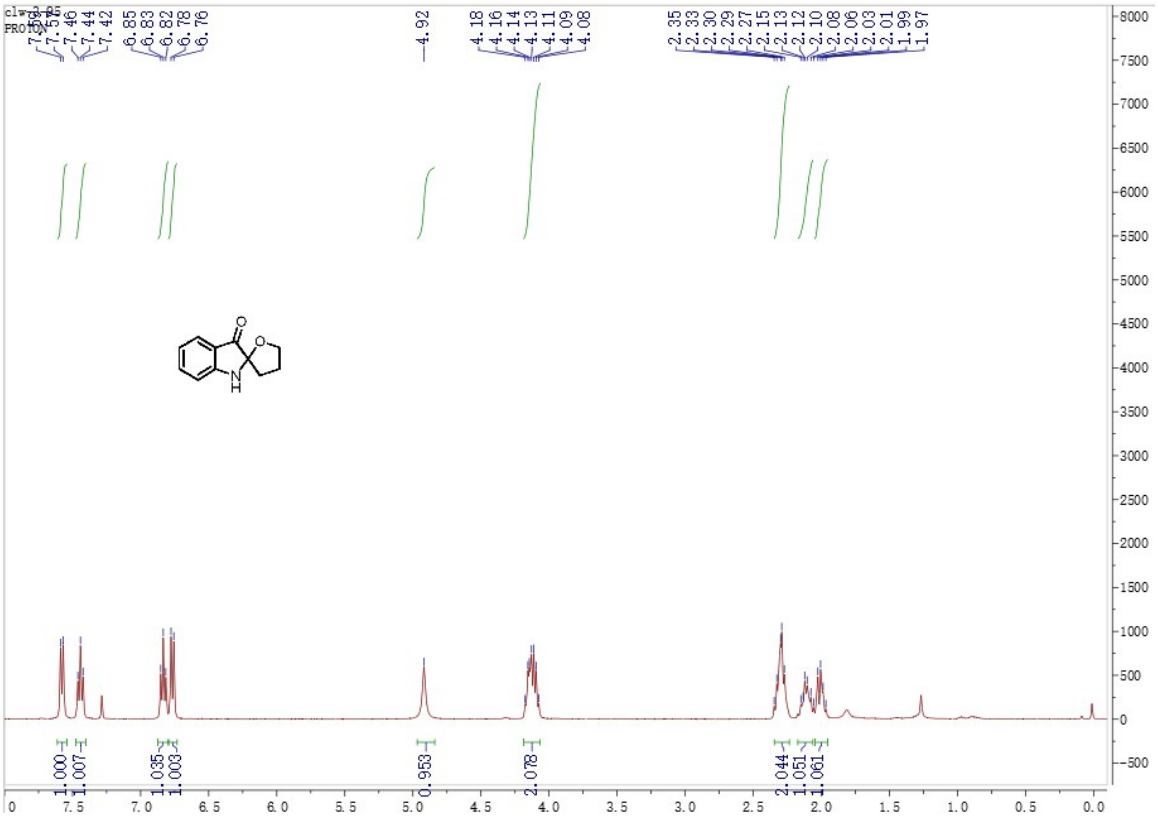
23.79
21.60
F
O
N
Ts
H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7.44
7.42
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6.83
6.82
6.78
6.76
4.92
4.18
4.16
4.14
4.13
4.11
4.09
4.08
2.35
2.33
2.30
2.29
2.27
2.15
2.13
2.12
2.10
2.08
2.06
2.03
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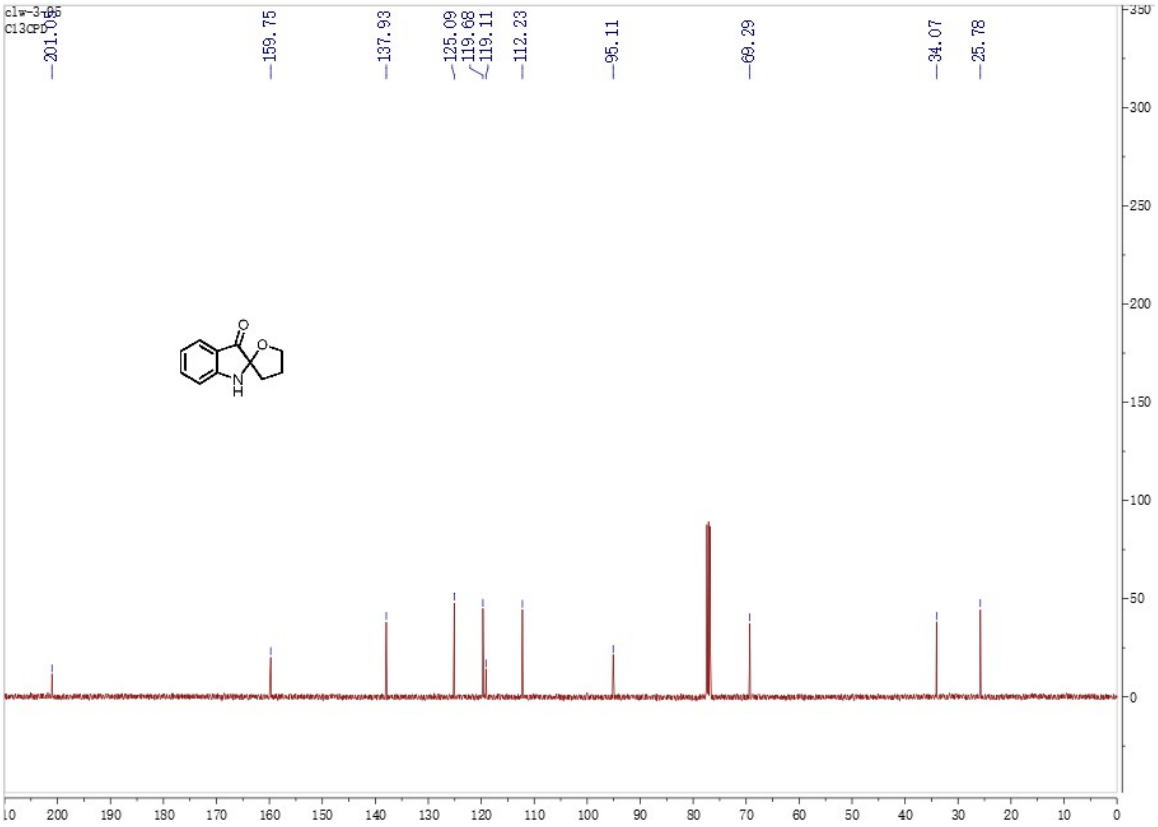
1.061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69.29
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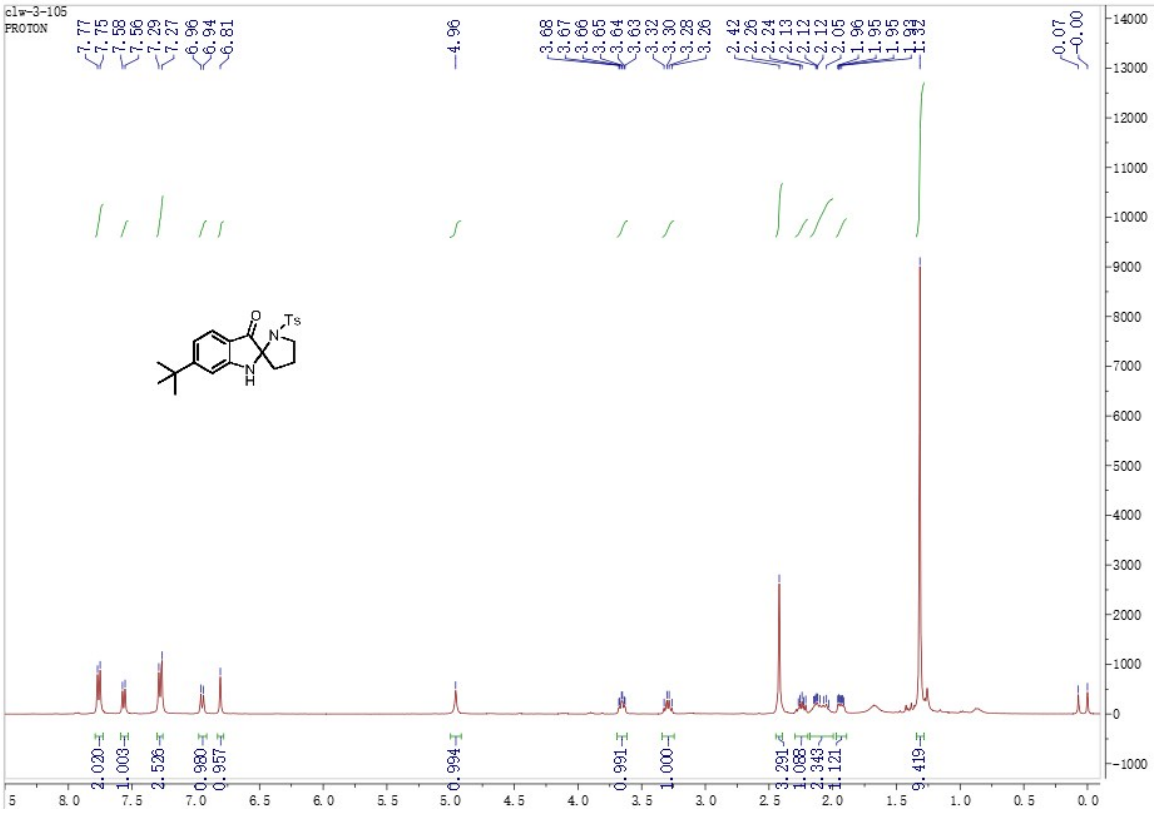
25.78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7.29
7.27
6.96
6.94
6.81
4.96
3.68
3.67
3.66
3.65
3.64
3.63
3.32
3.30
3.28
3.26
2.42
2.26
2.24
2.13
2.12
2.12
2.05
1.96
1.95
1.93
1.92
0.07
0.00
Ts
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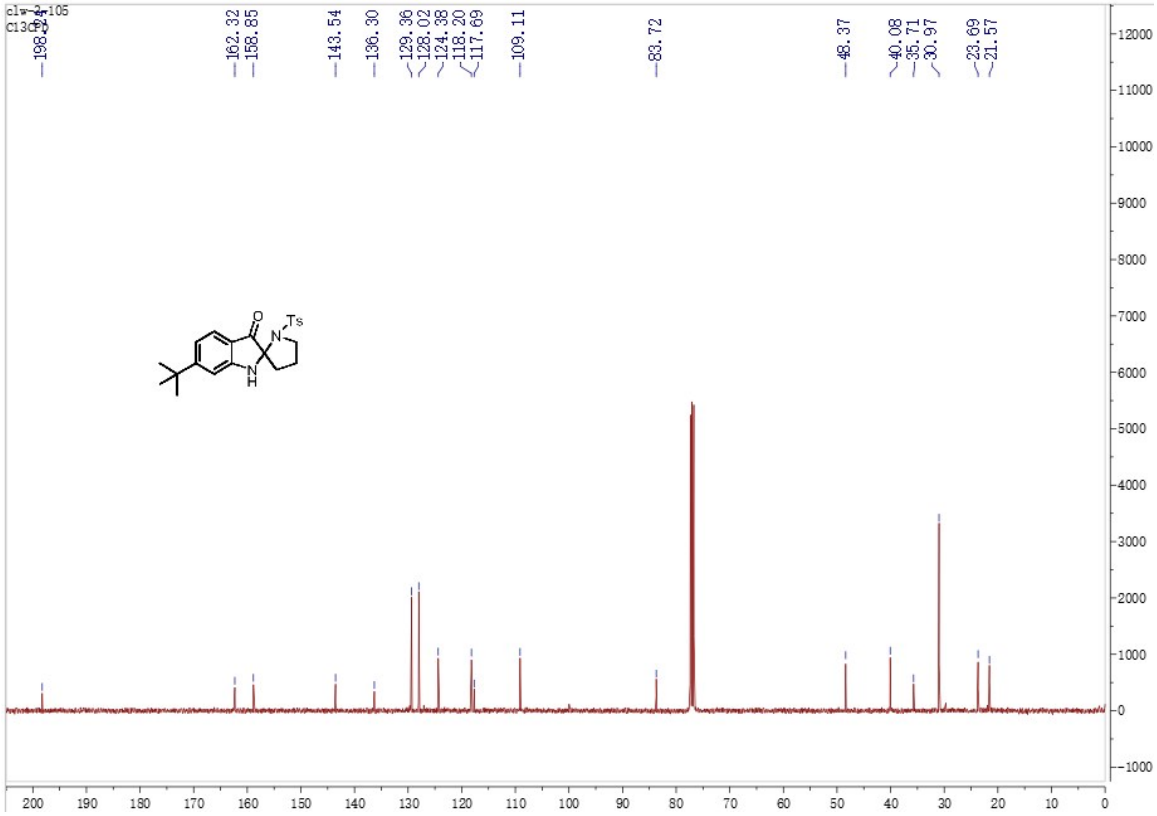
9.419


clw-2-105
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129.36
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117.69
109.11
83.72
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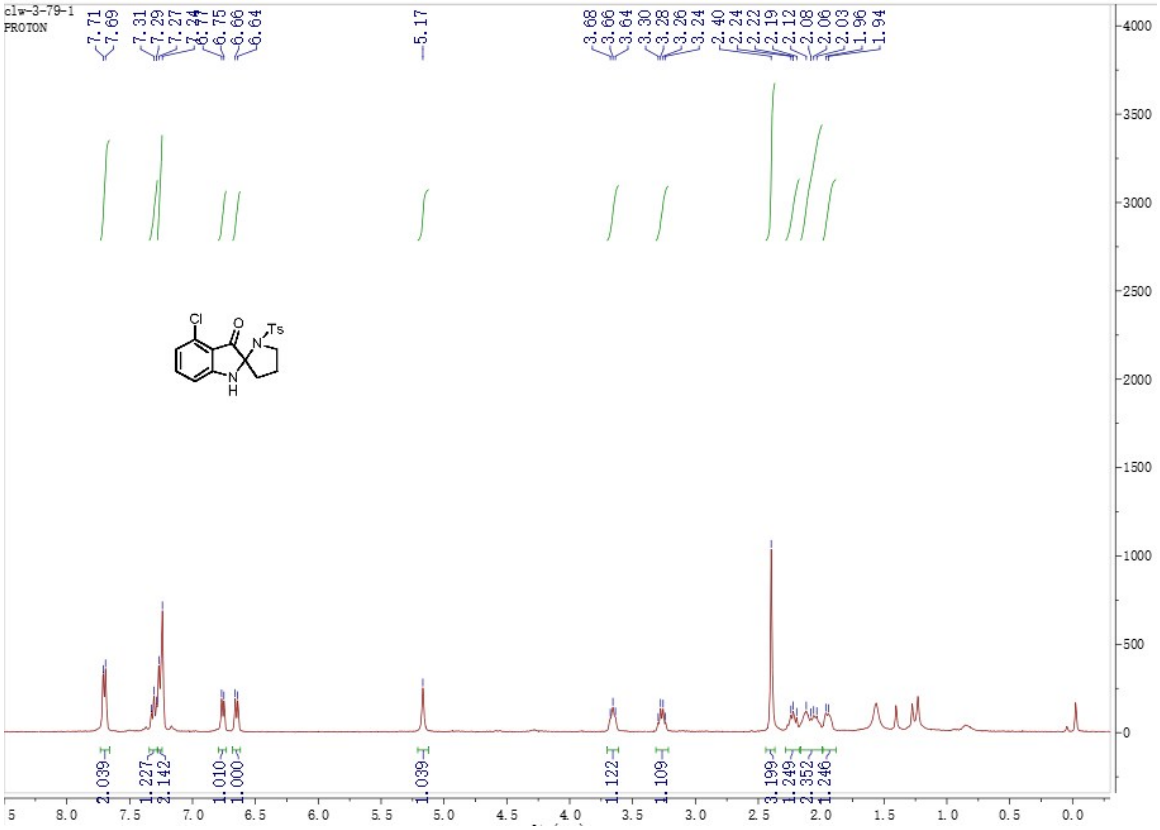
35.71
30.97
23.69
21.57
Ts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7.27
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6.66
6.64
5.17
3.68
3.66
3.64
3.30
3.28
3.26
3.24
2.40
2.24
2.22
2.19
2.12
2.08
2.06
2.03
1.96
1.94
Cl
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N
Ts
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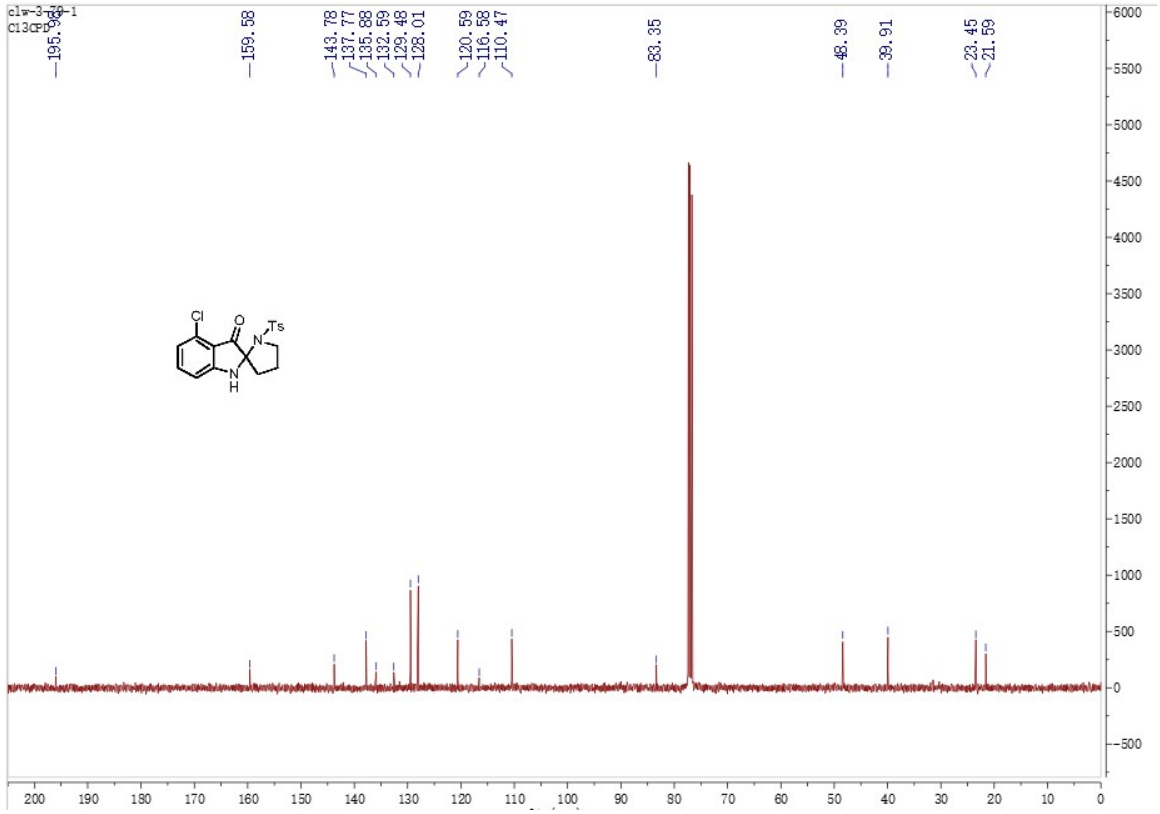
1.246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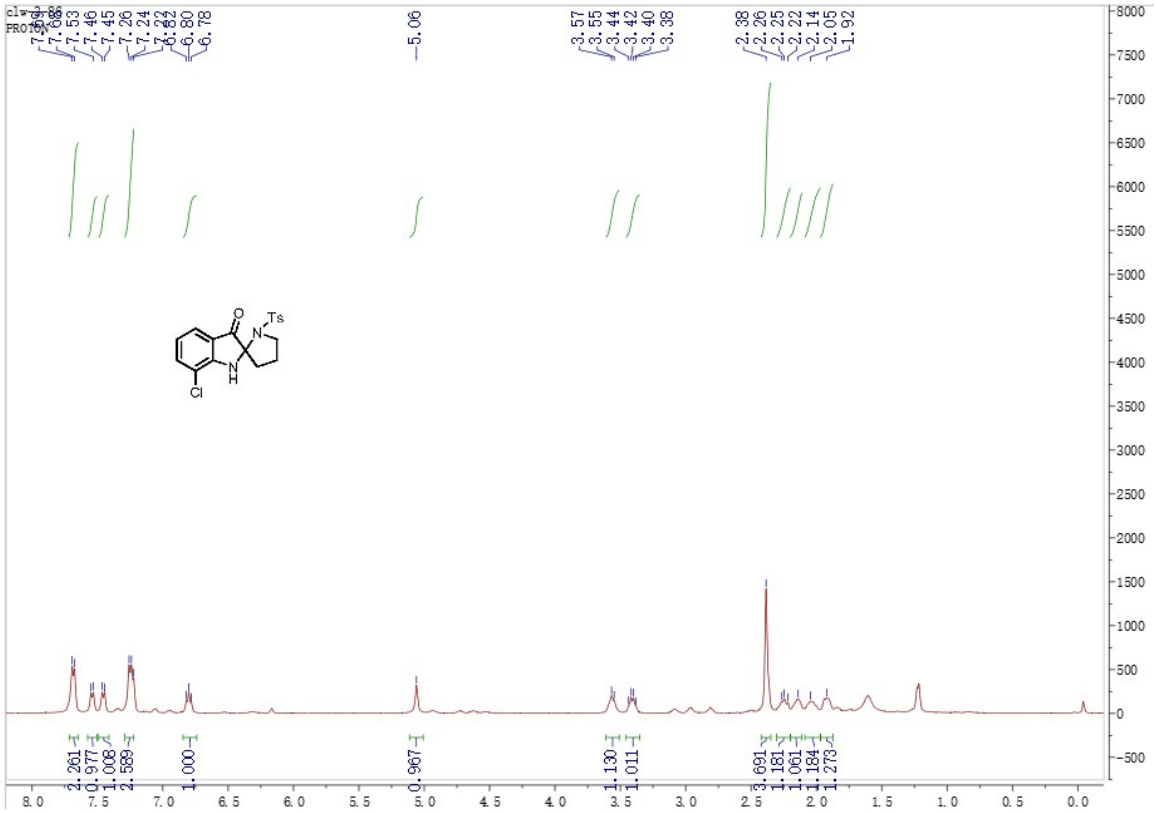
110.47
83.35
48.39
39.91
23.45
21.59
Cl
O
N
Ts
H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2.38
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2.25
2.22
2.14
2.05
1.92
Ts
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N
H
Cl
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1.011
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1.181
1.061
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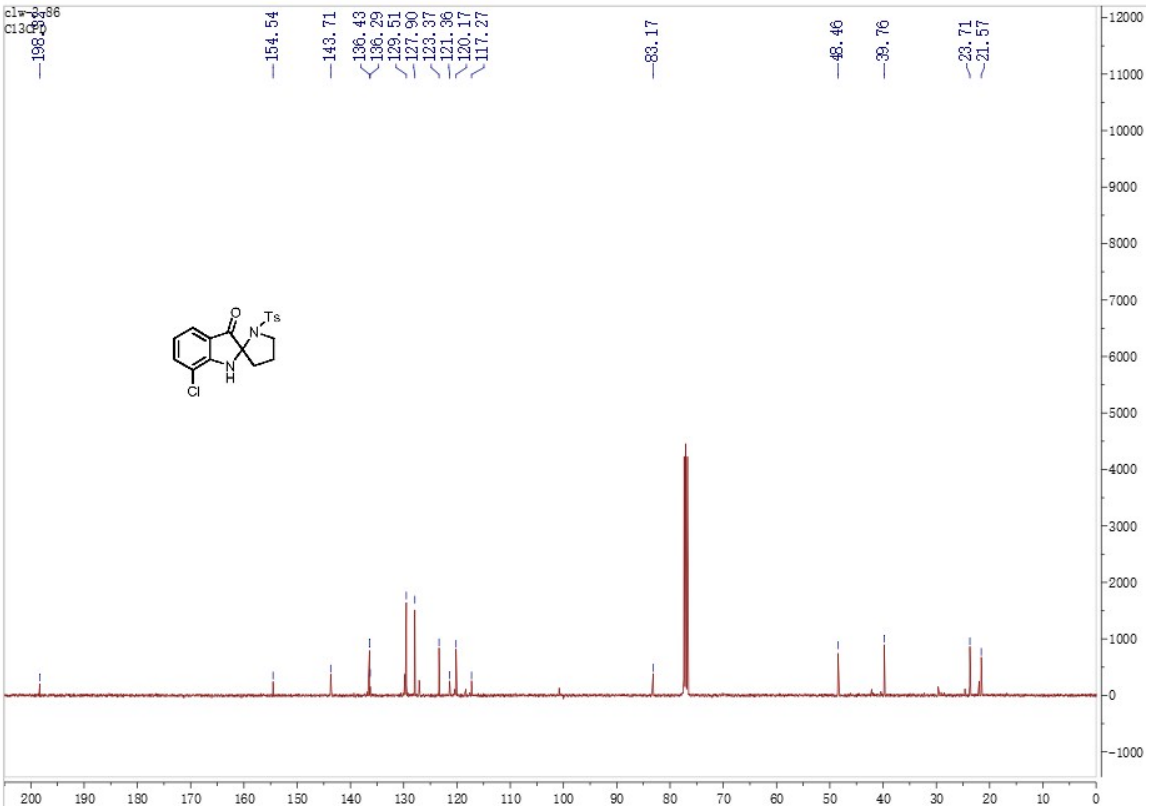
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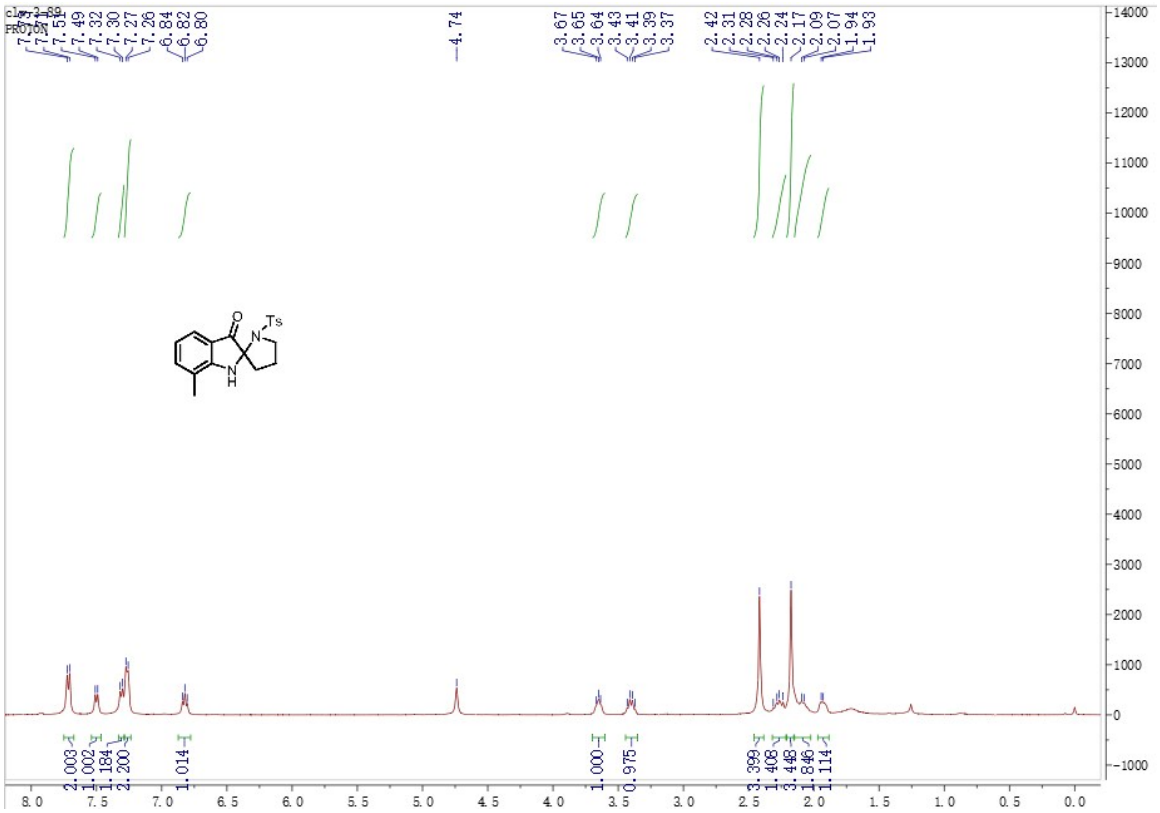
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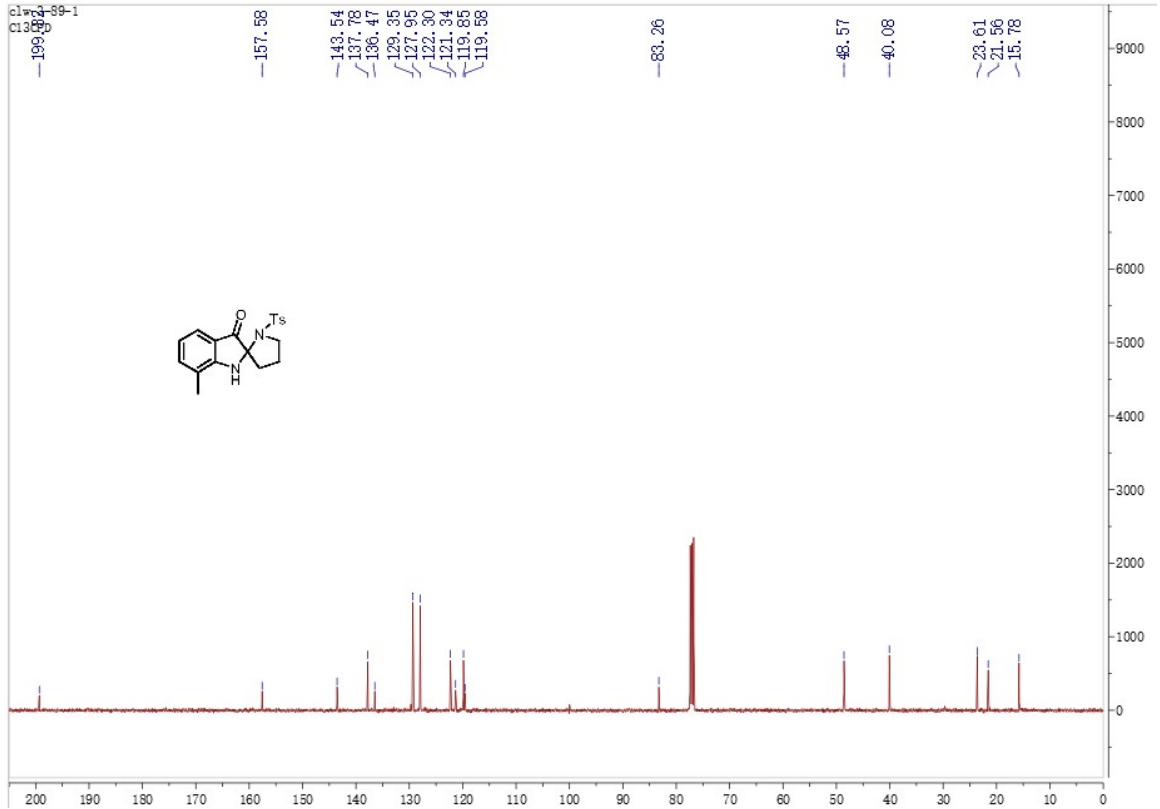
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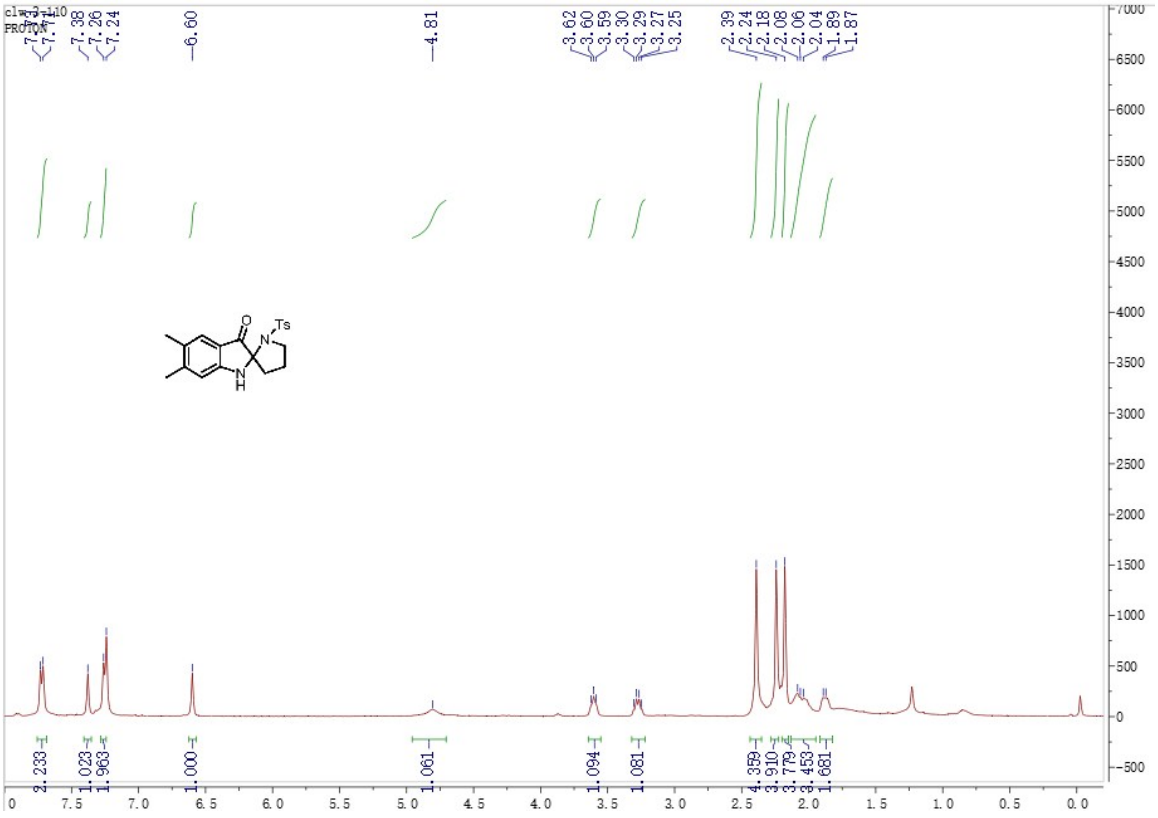
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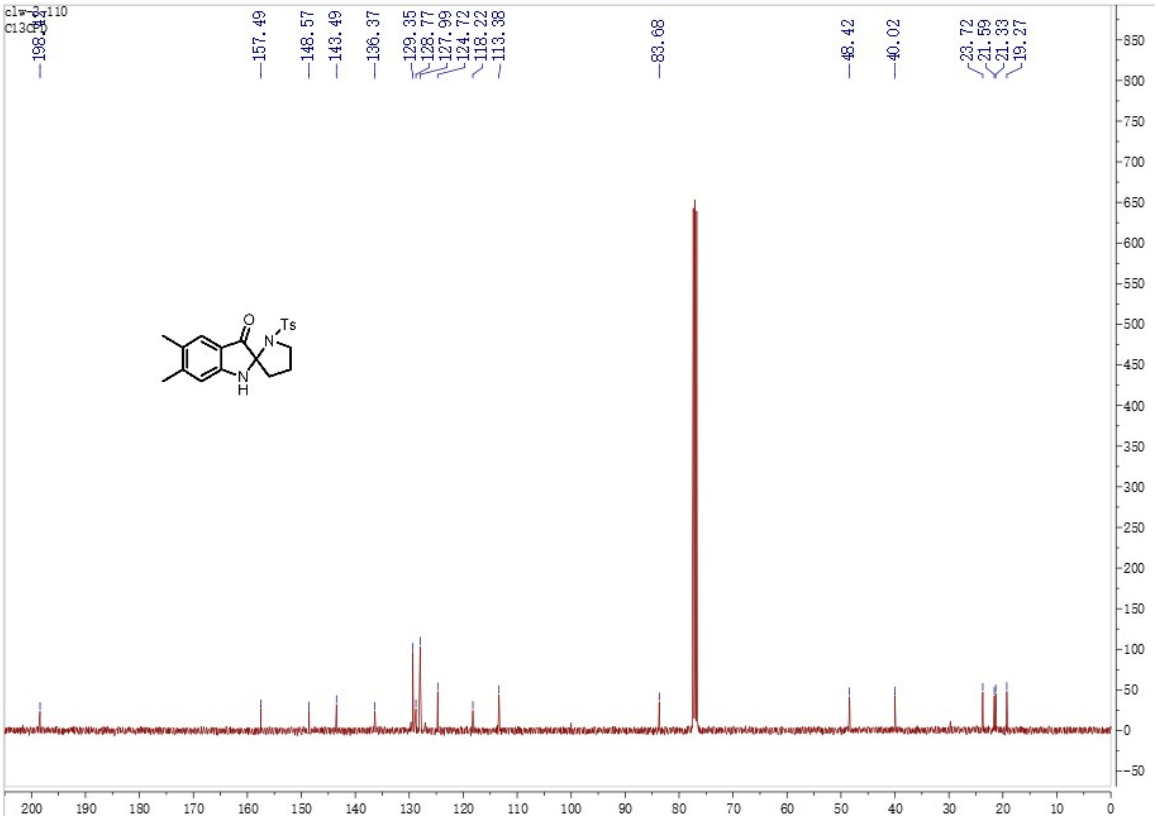
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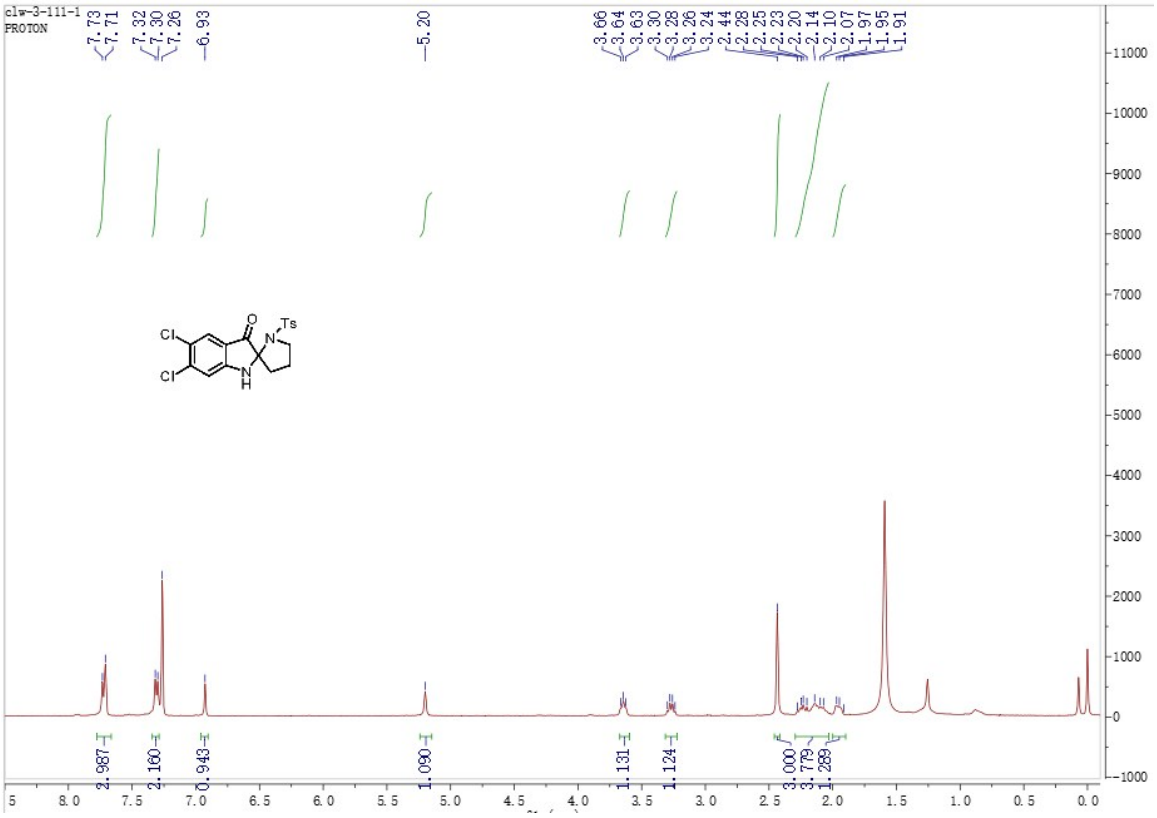
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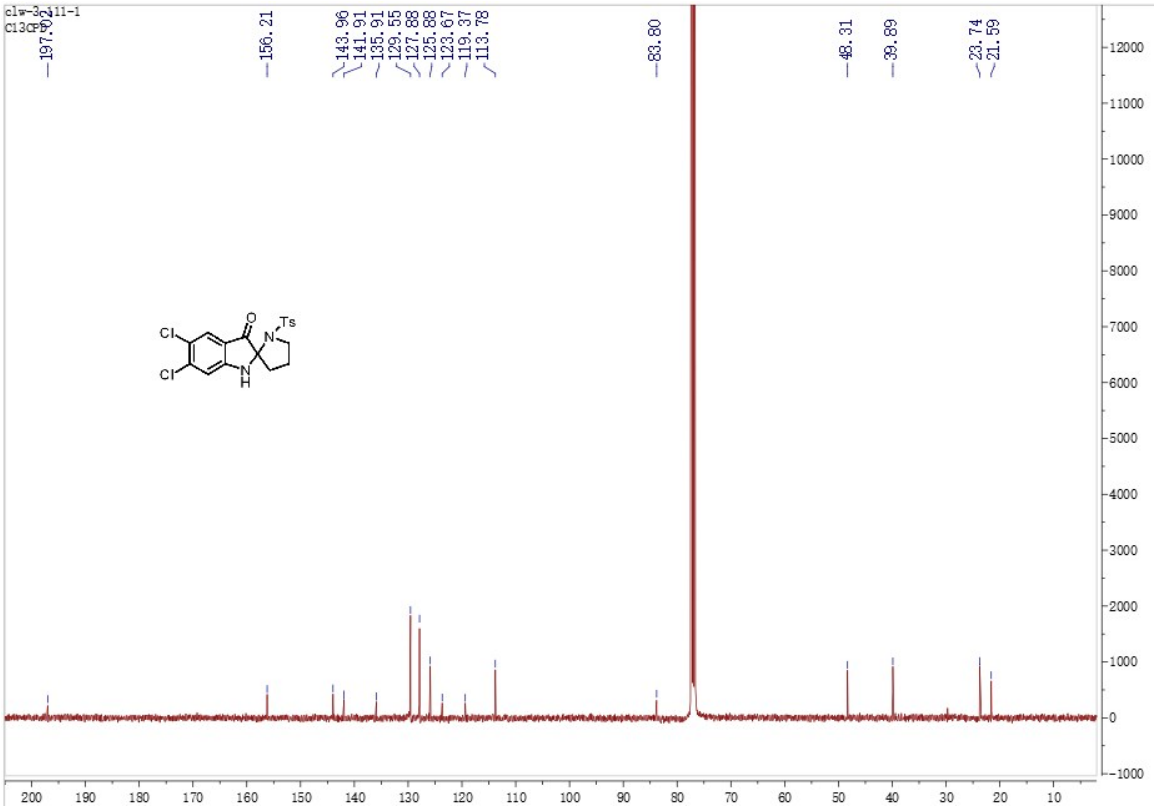
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Cl
O
N
Ts
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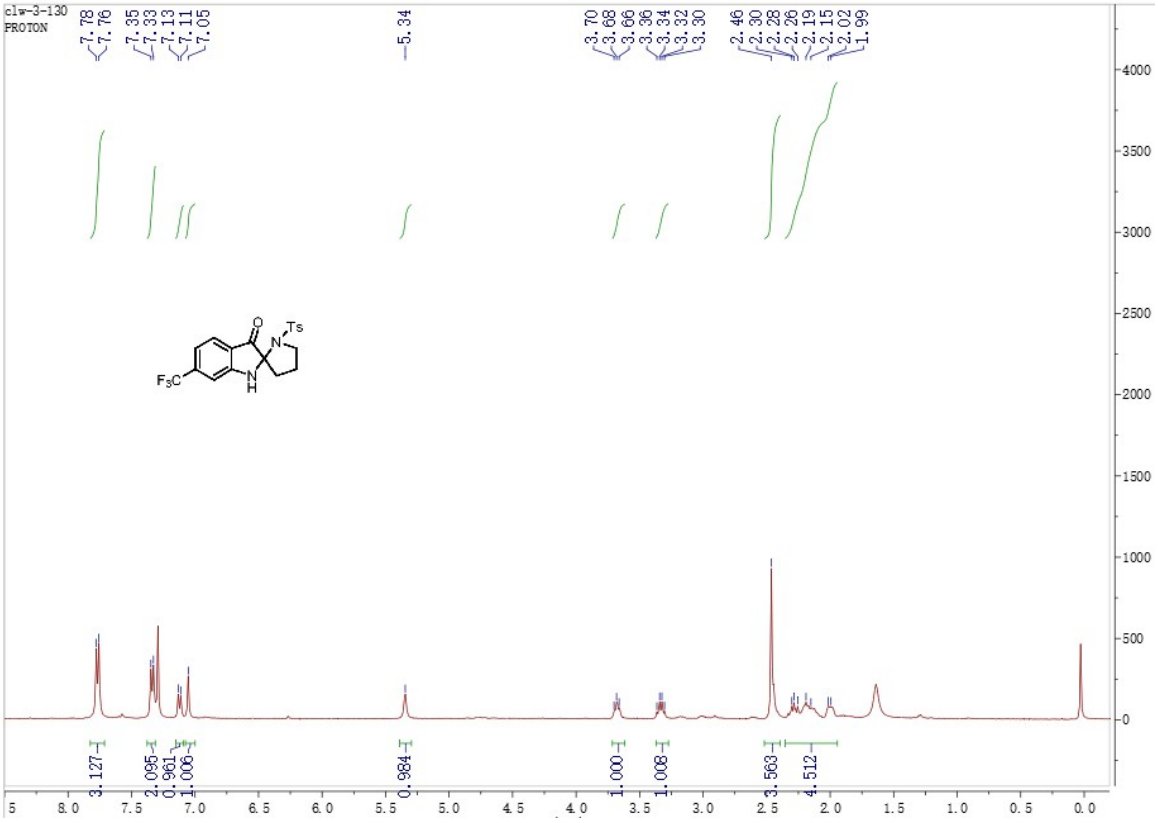
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3.34
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2.30
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2.02
1.99
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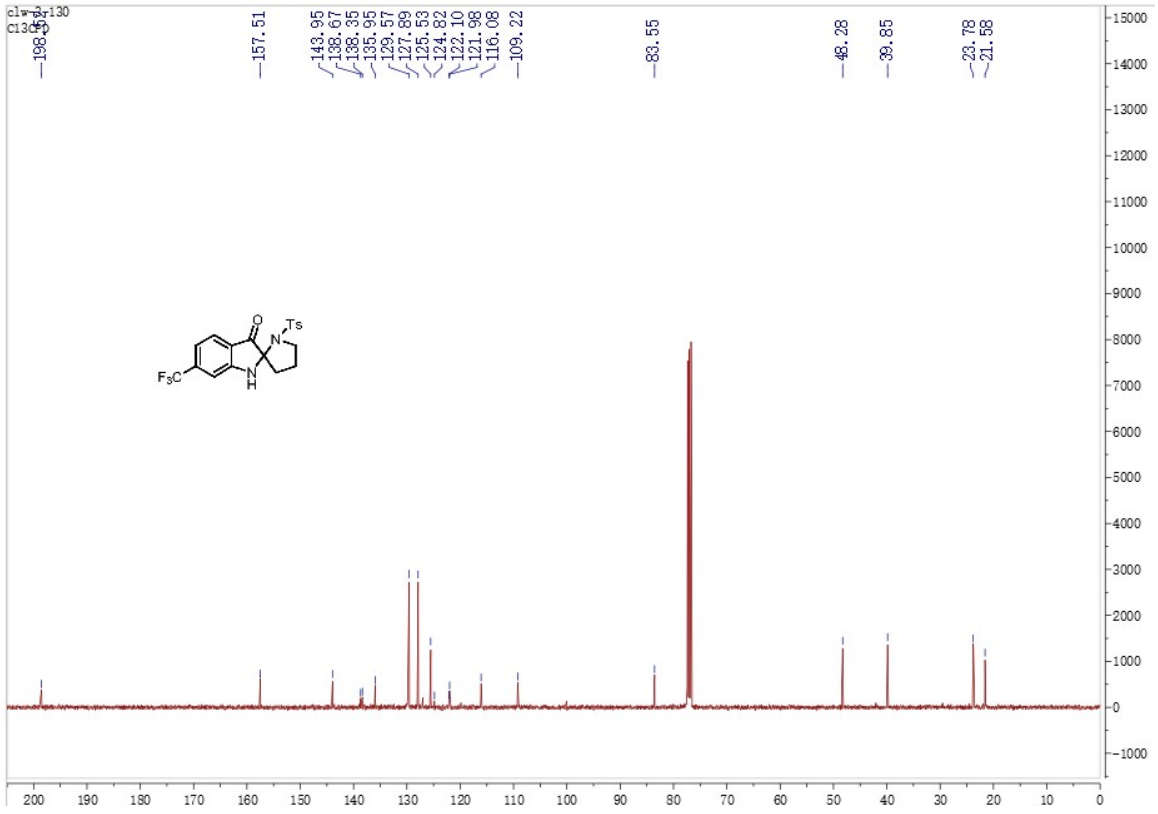
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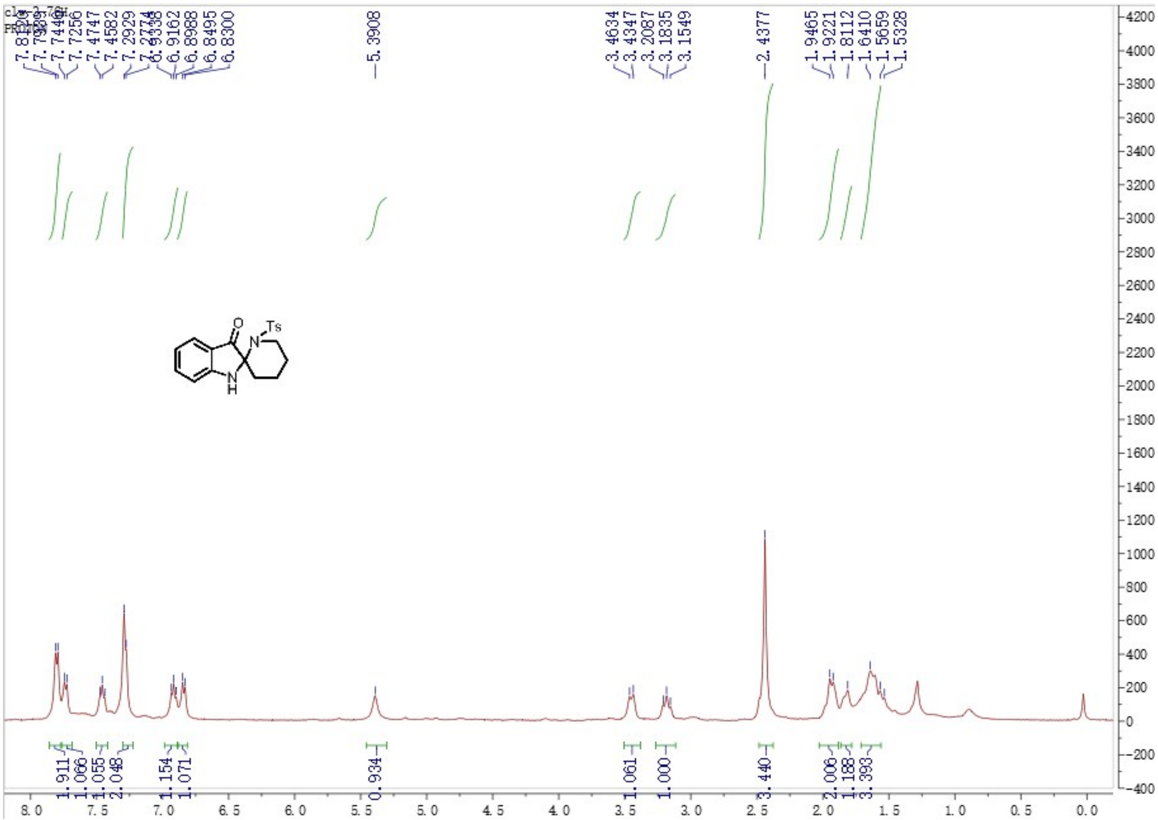

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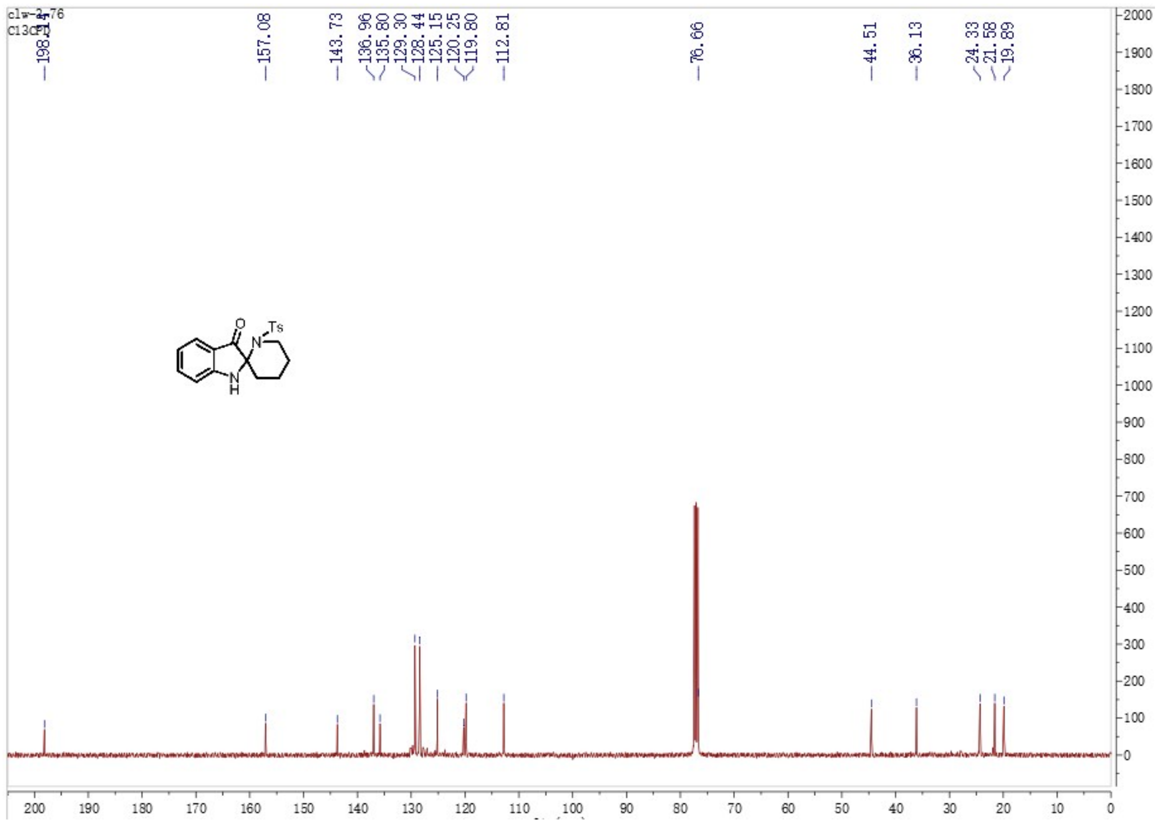

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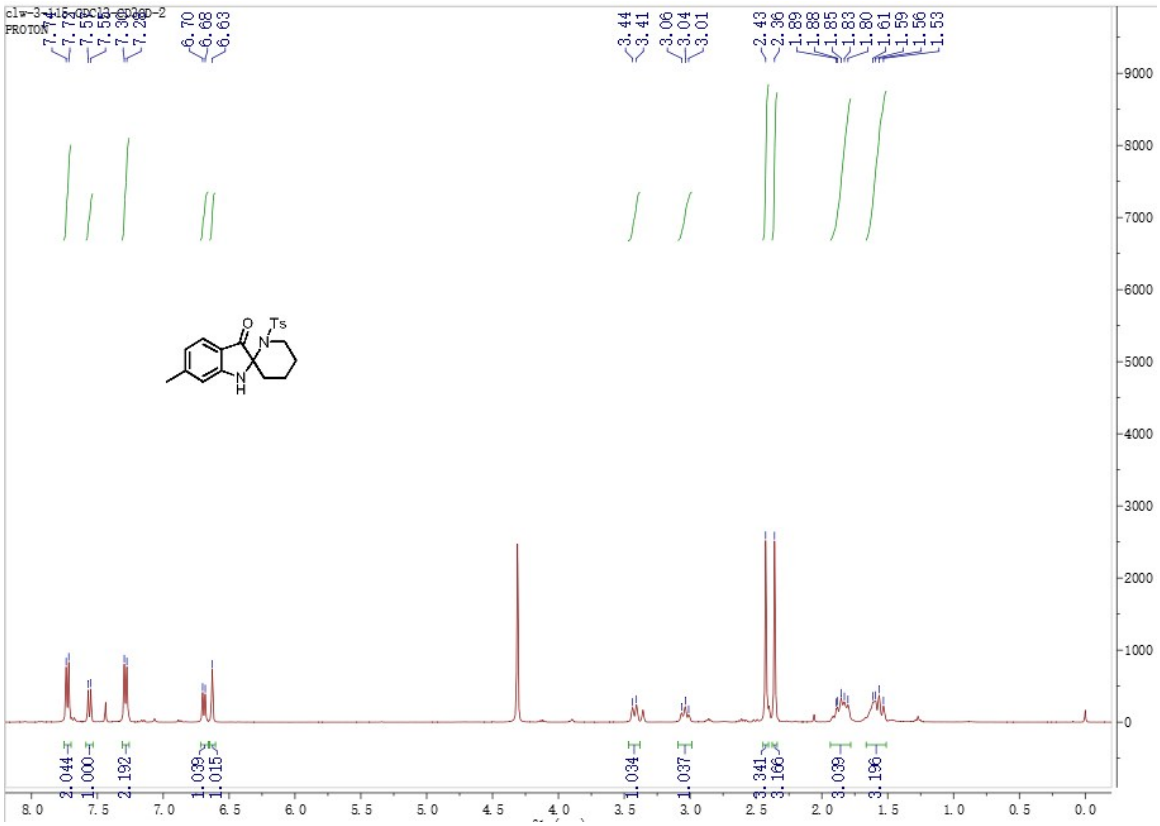
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3.04
3.01
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1.85
1.83
1.80
1.61
1.59
1.56
1.53
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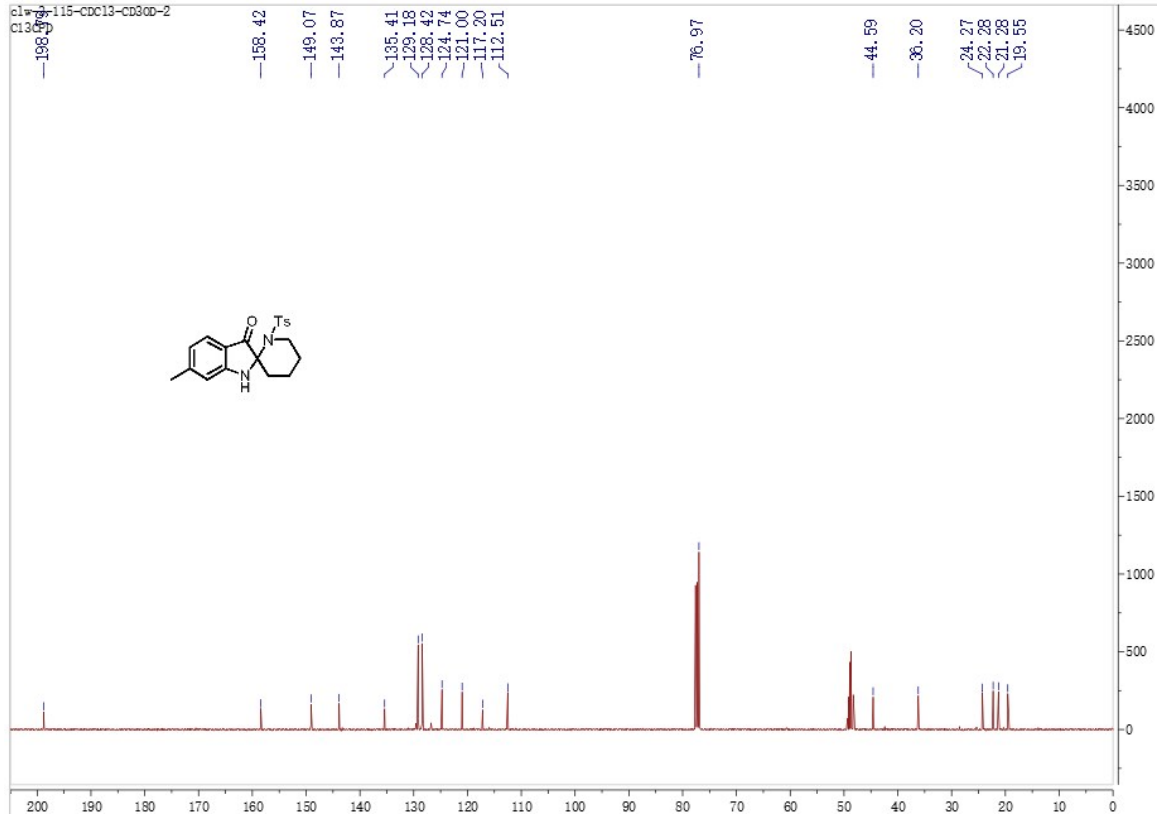
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21.28
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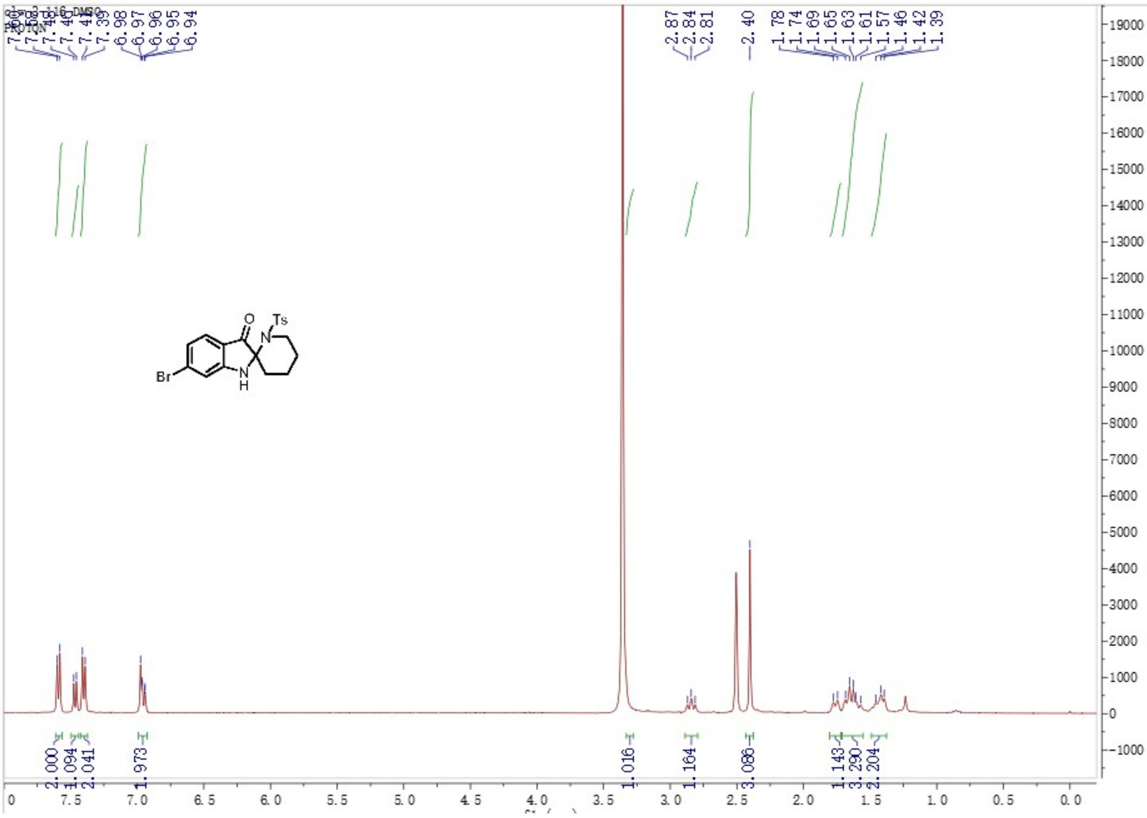

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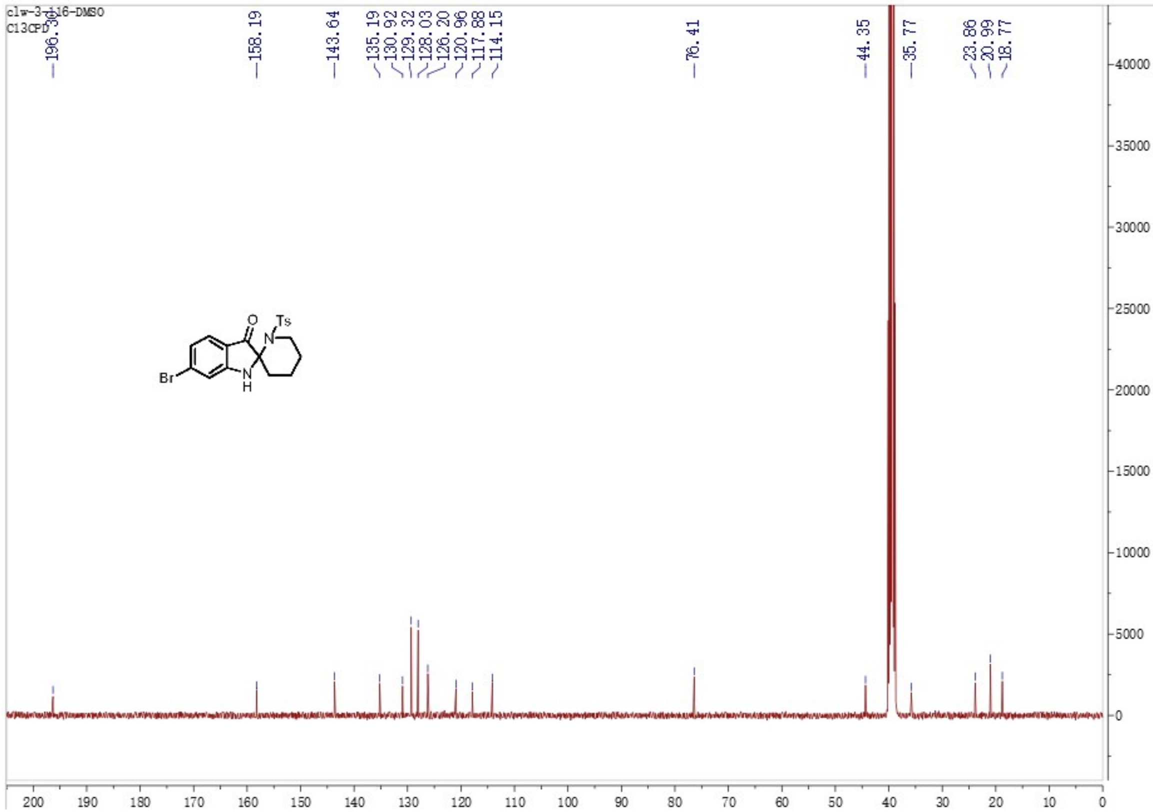

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N
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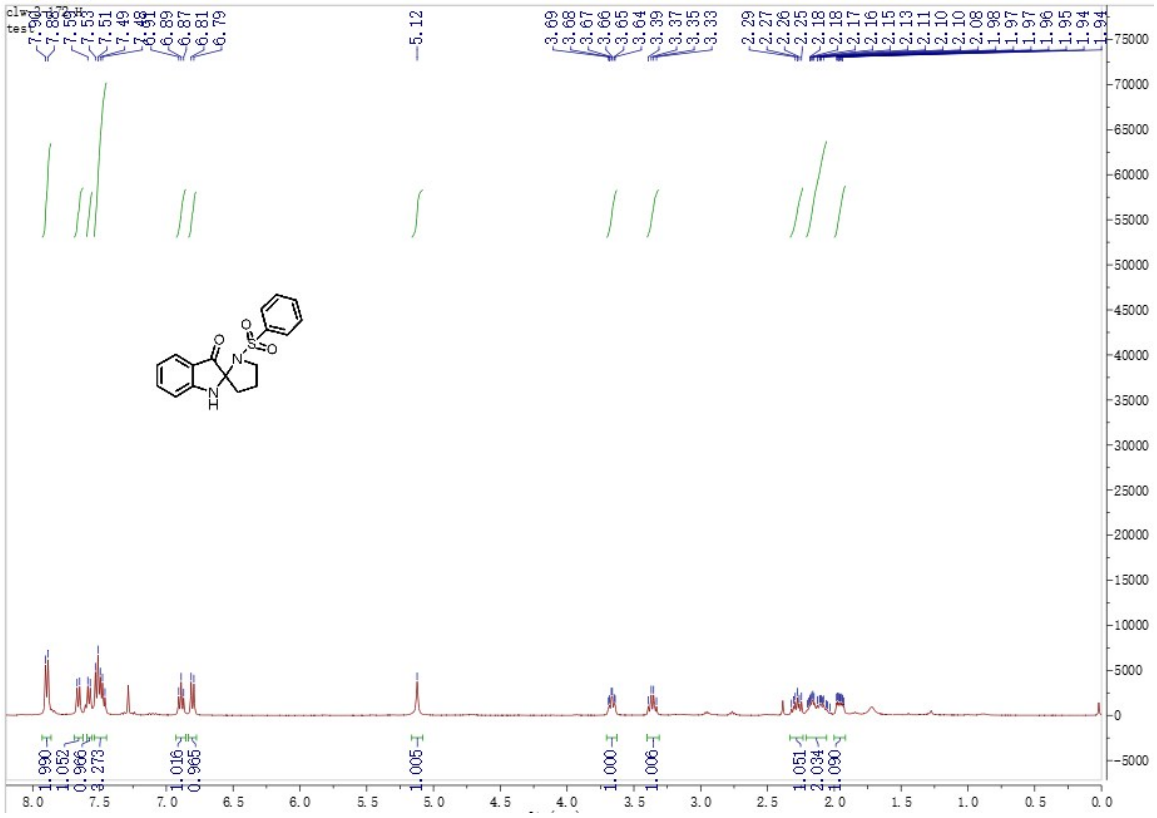

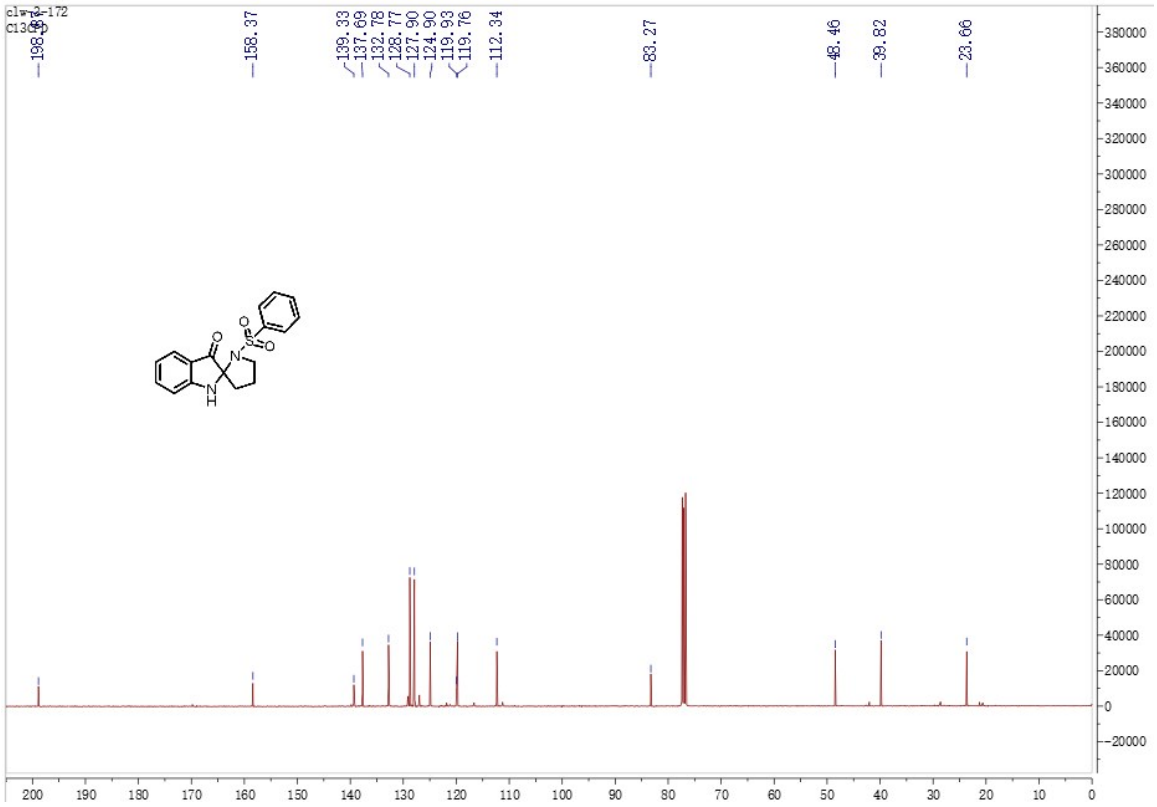

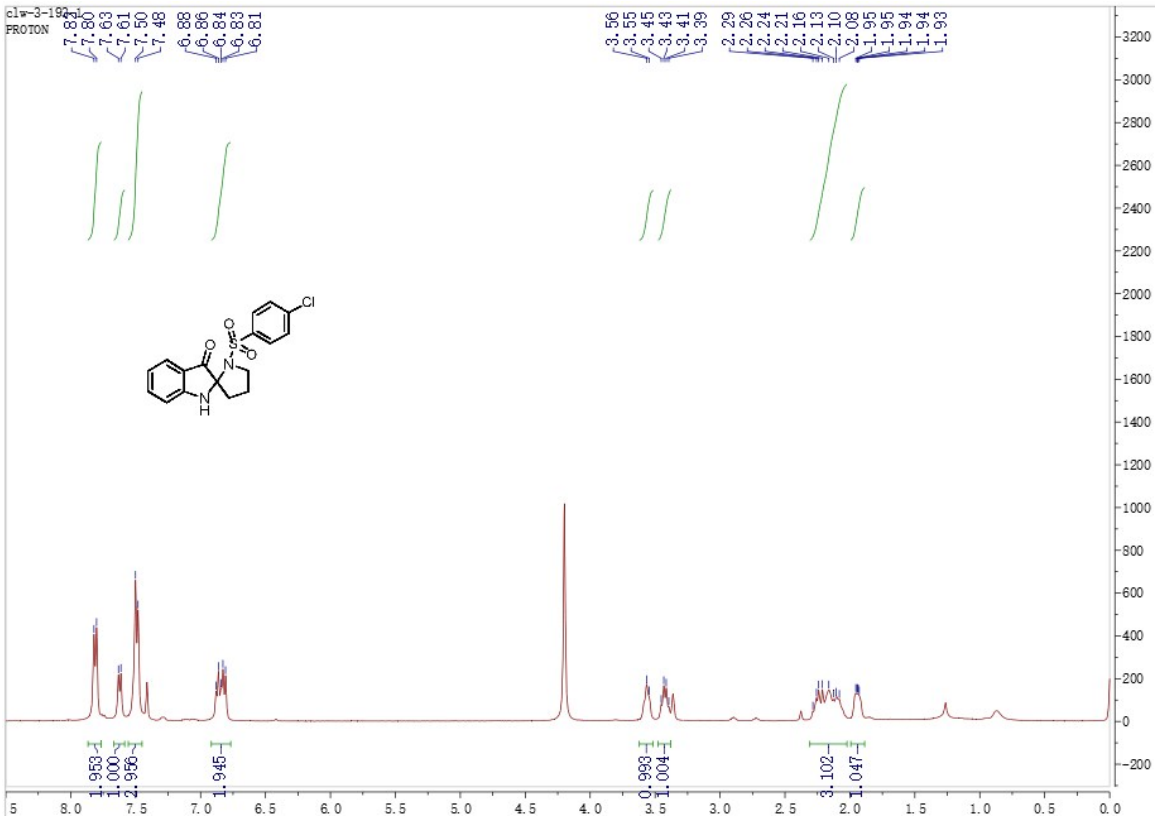
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2.10
2.08
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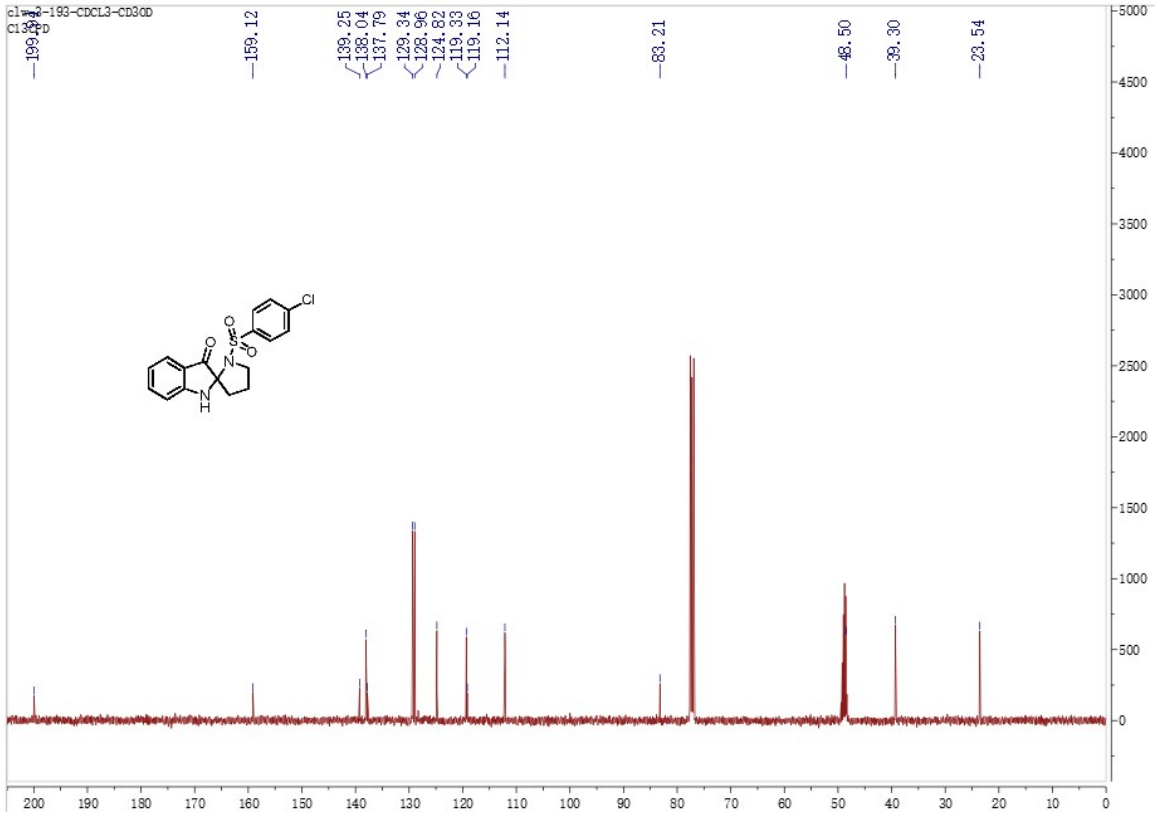
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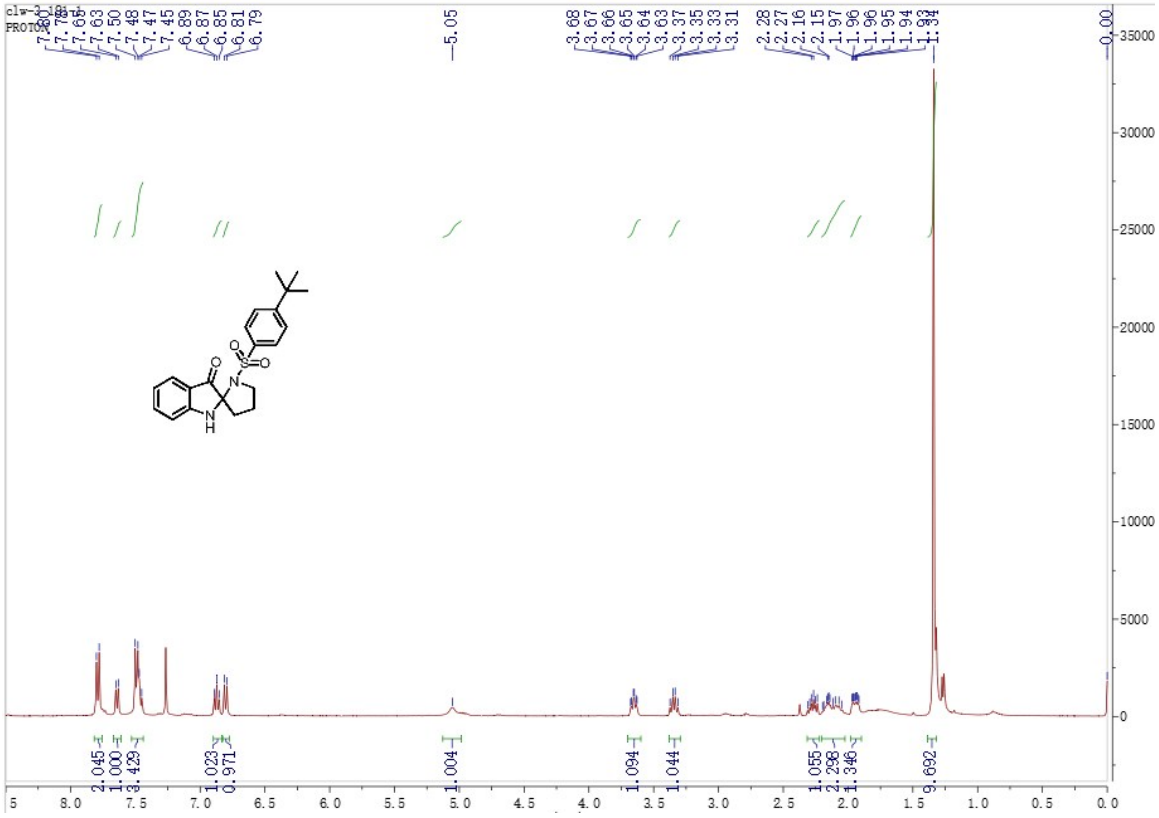
S
O
O
H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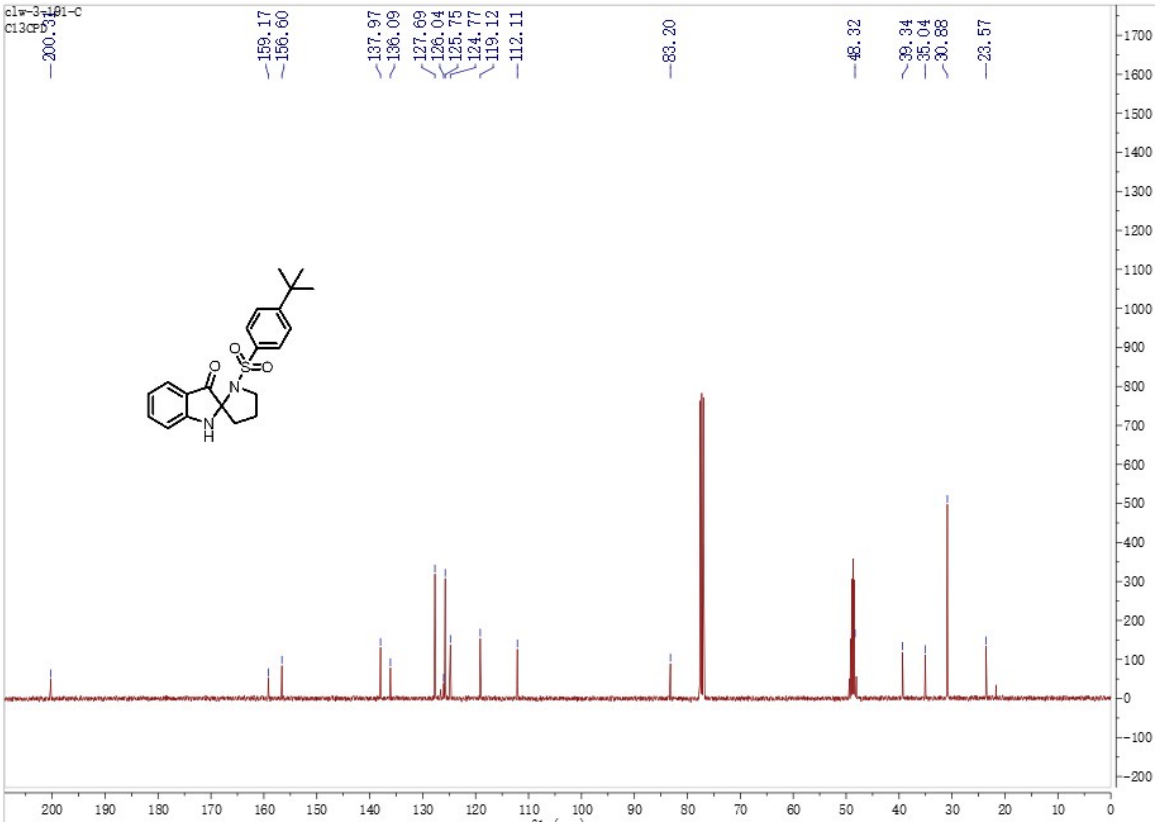
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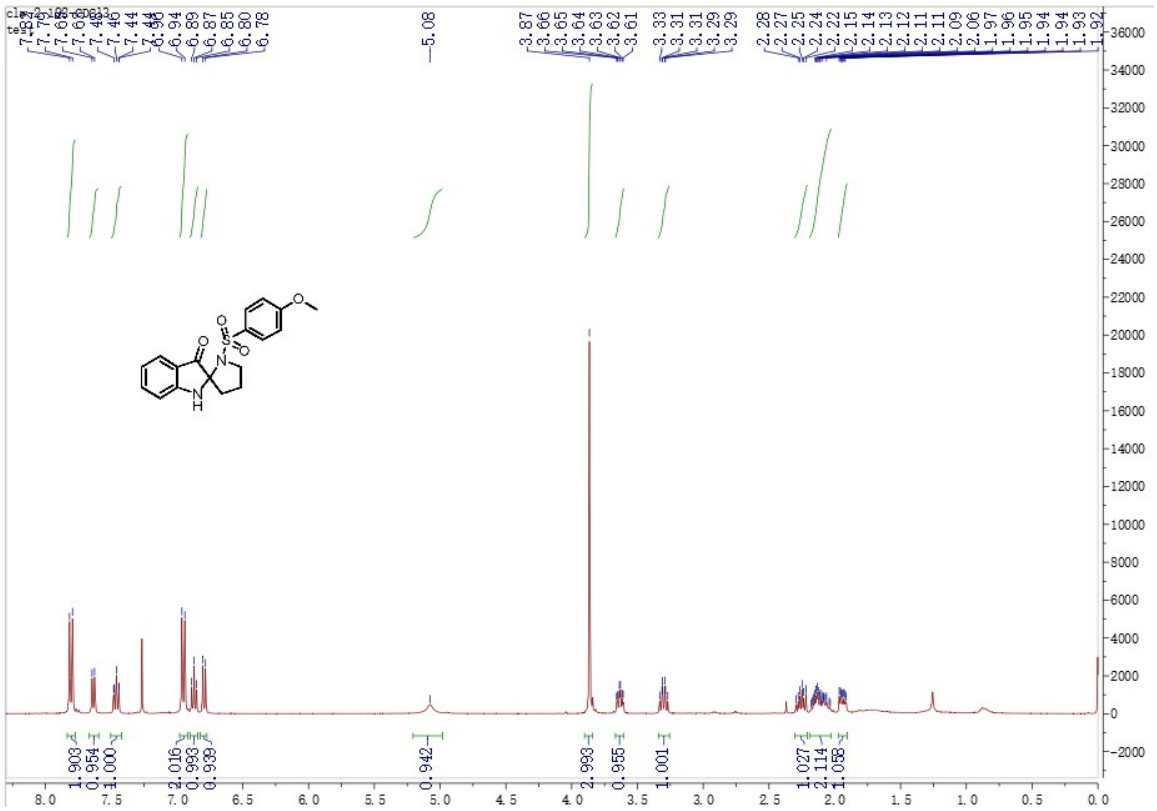
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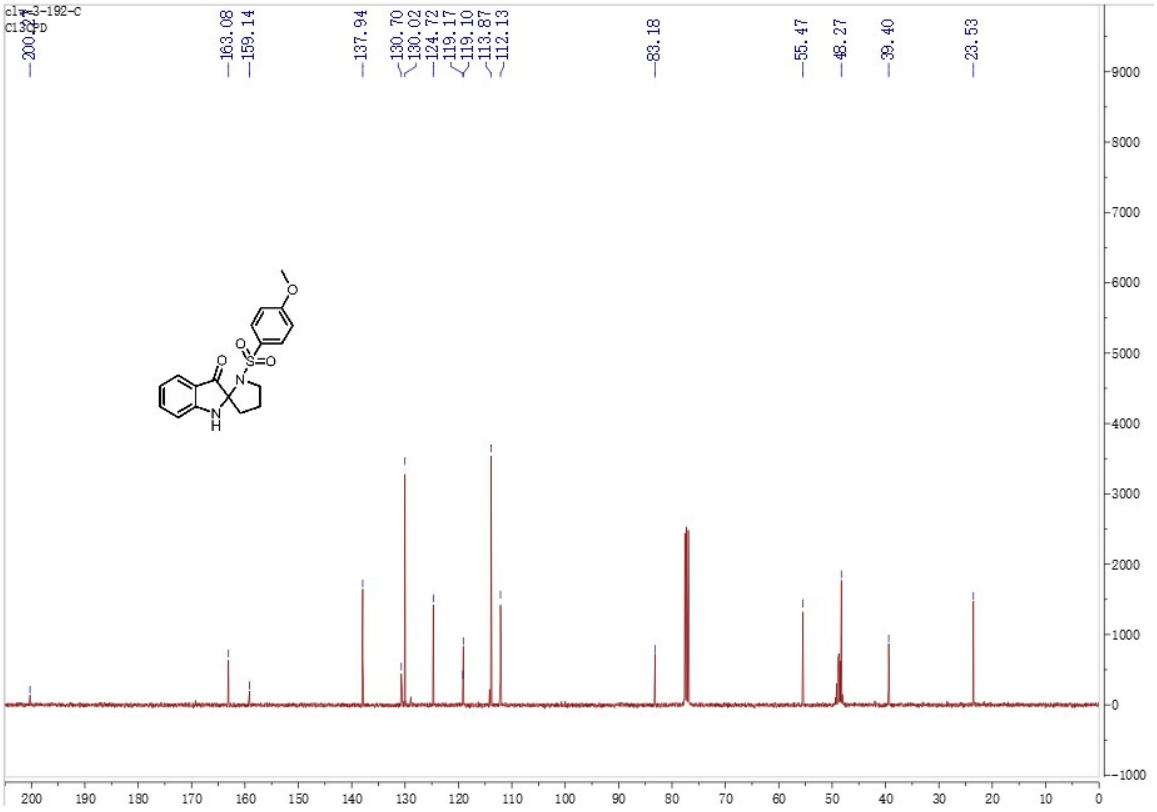
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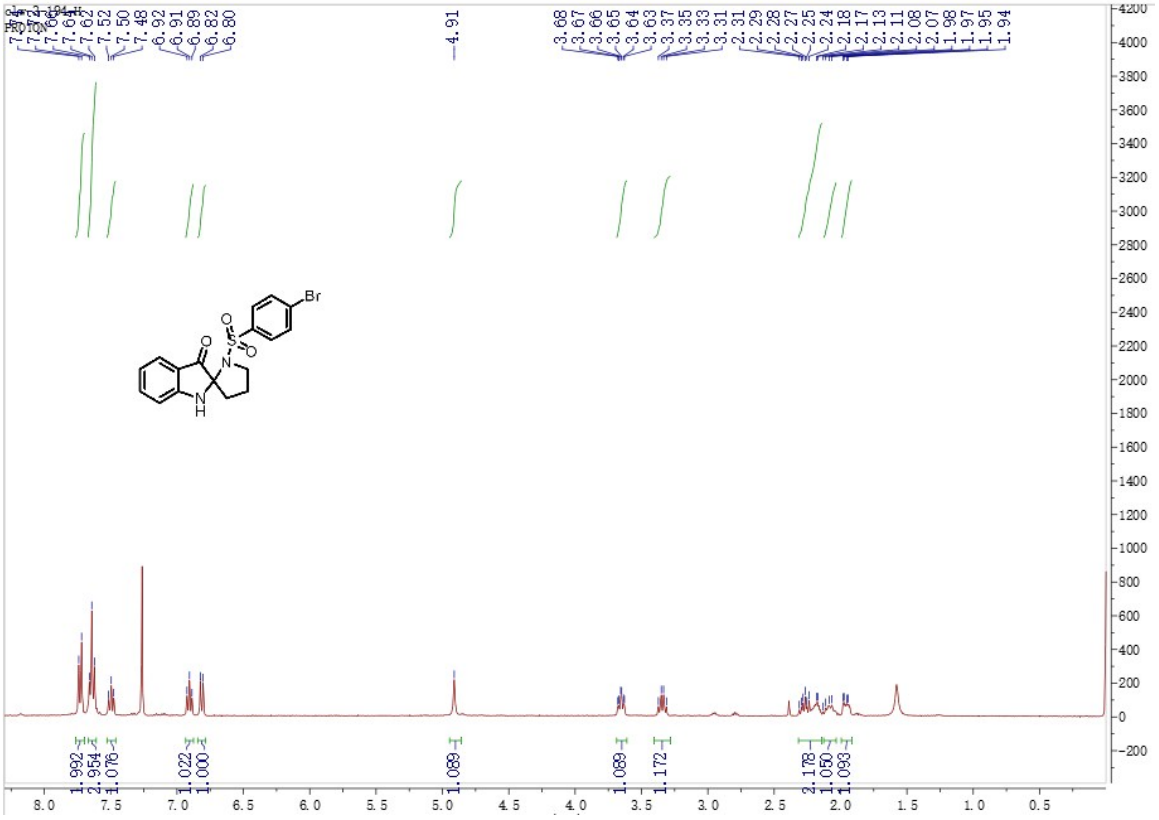
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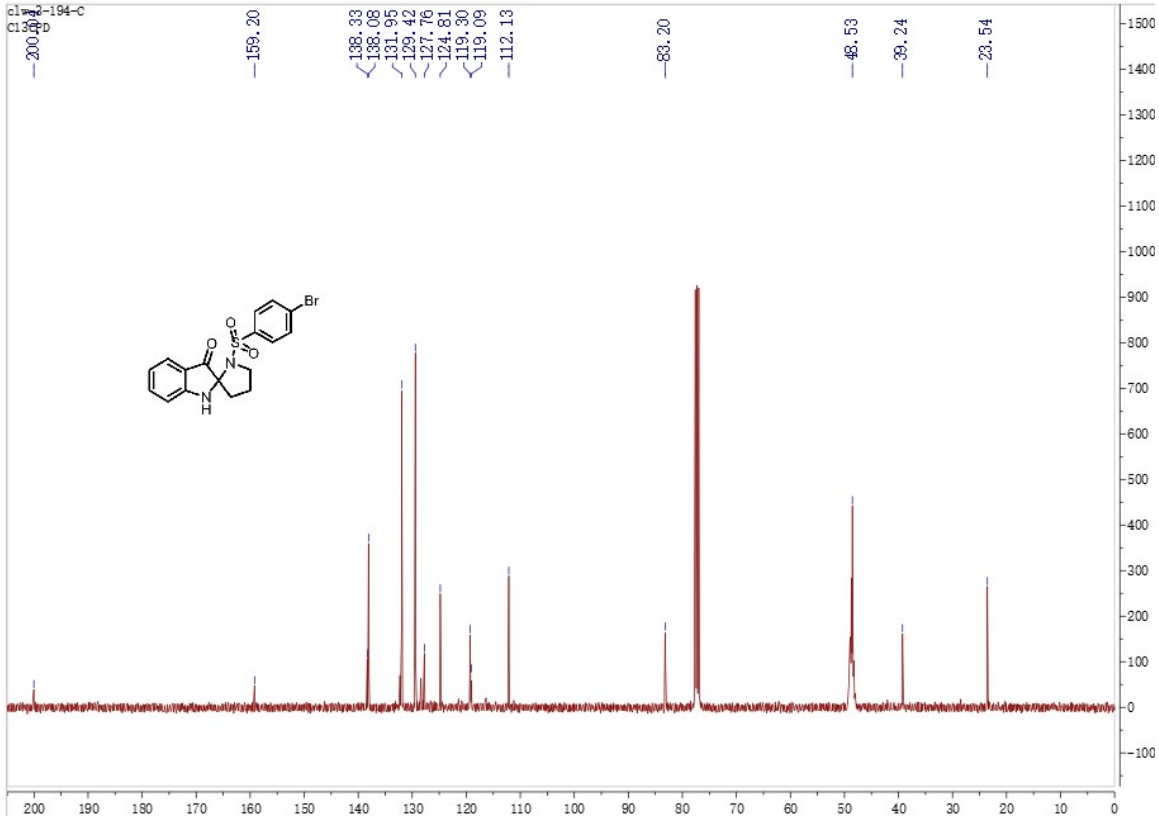
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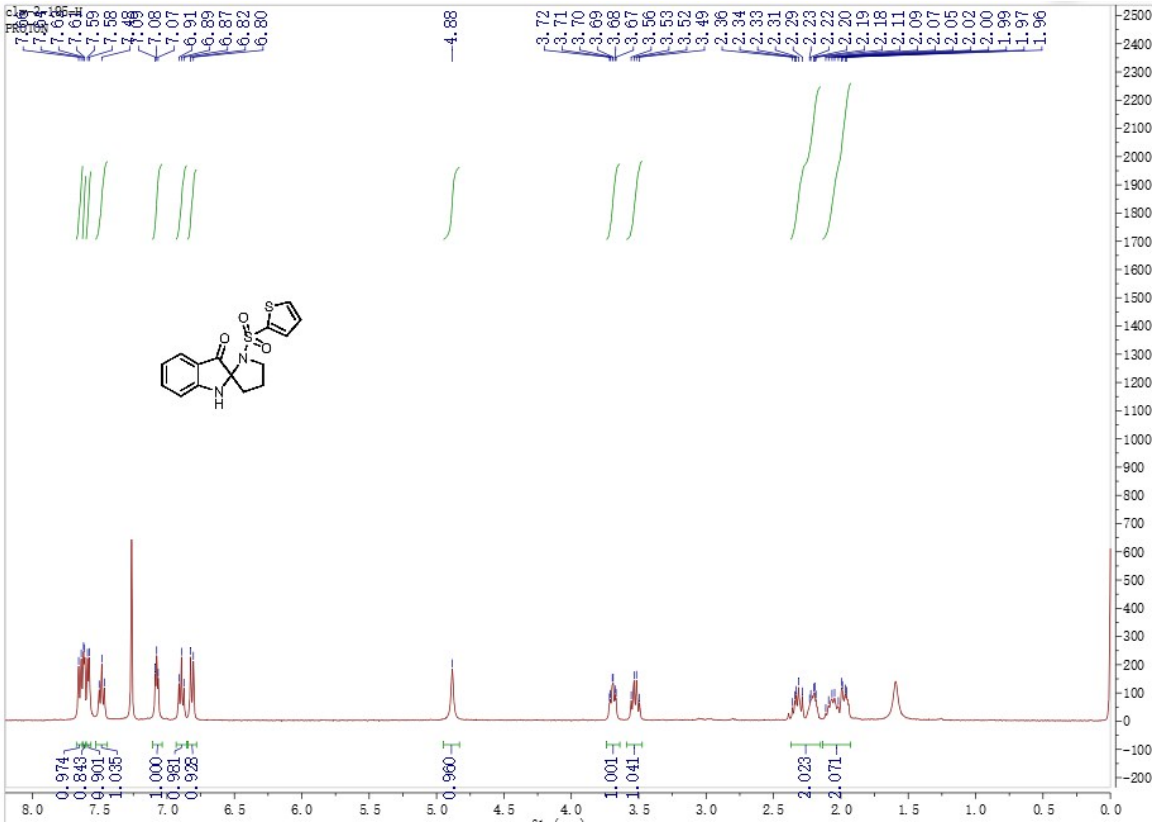
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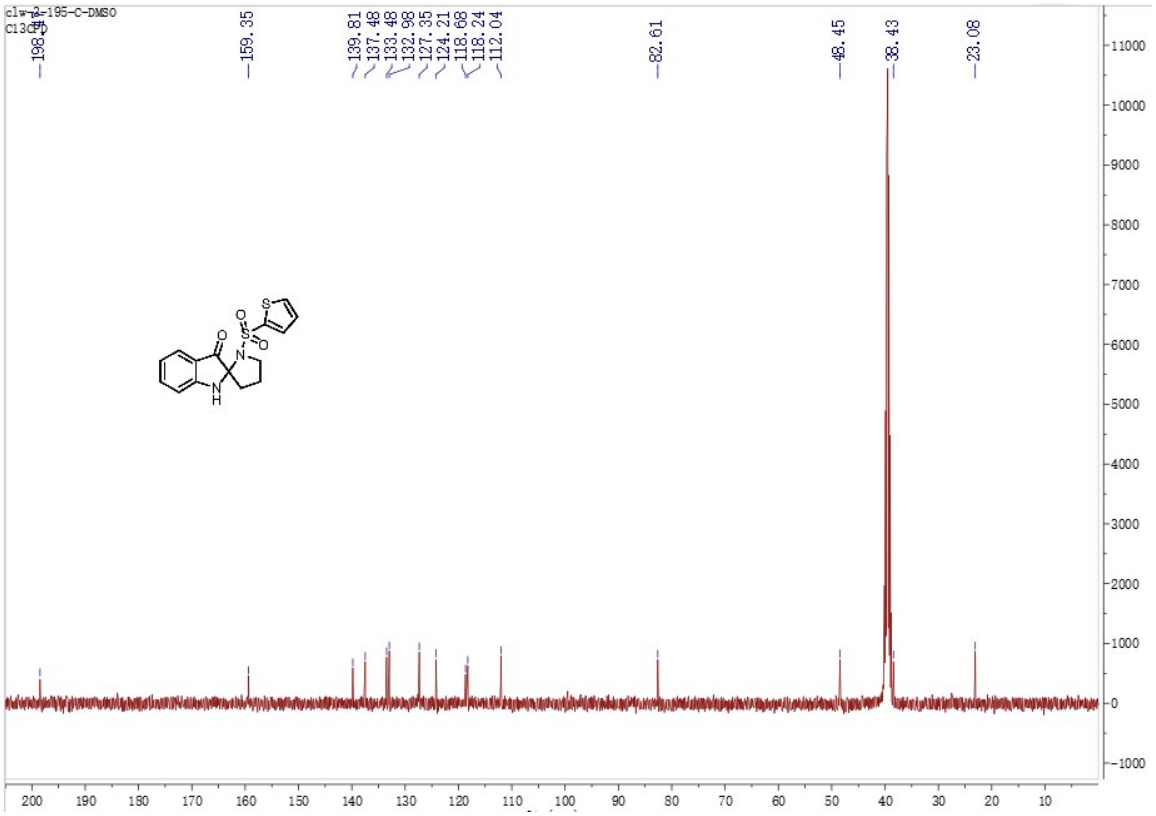
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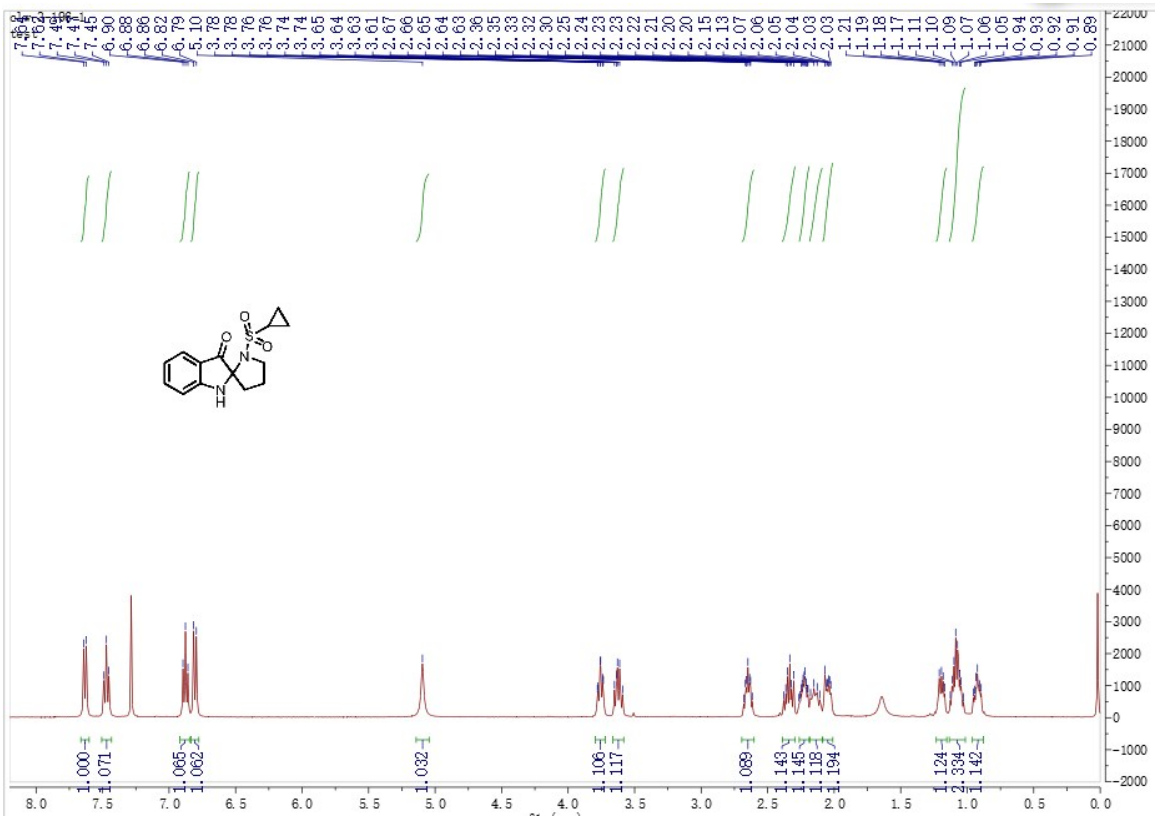

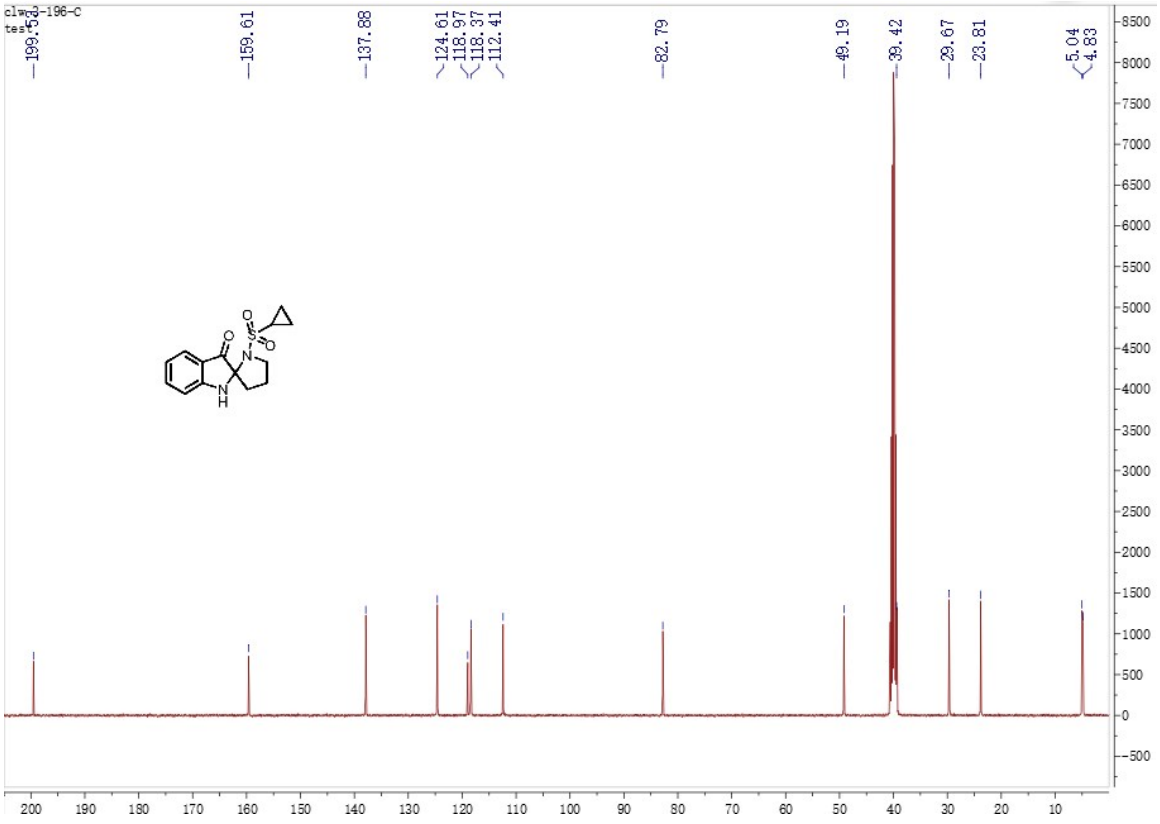

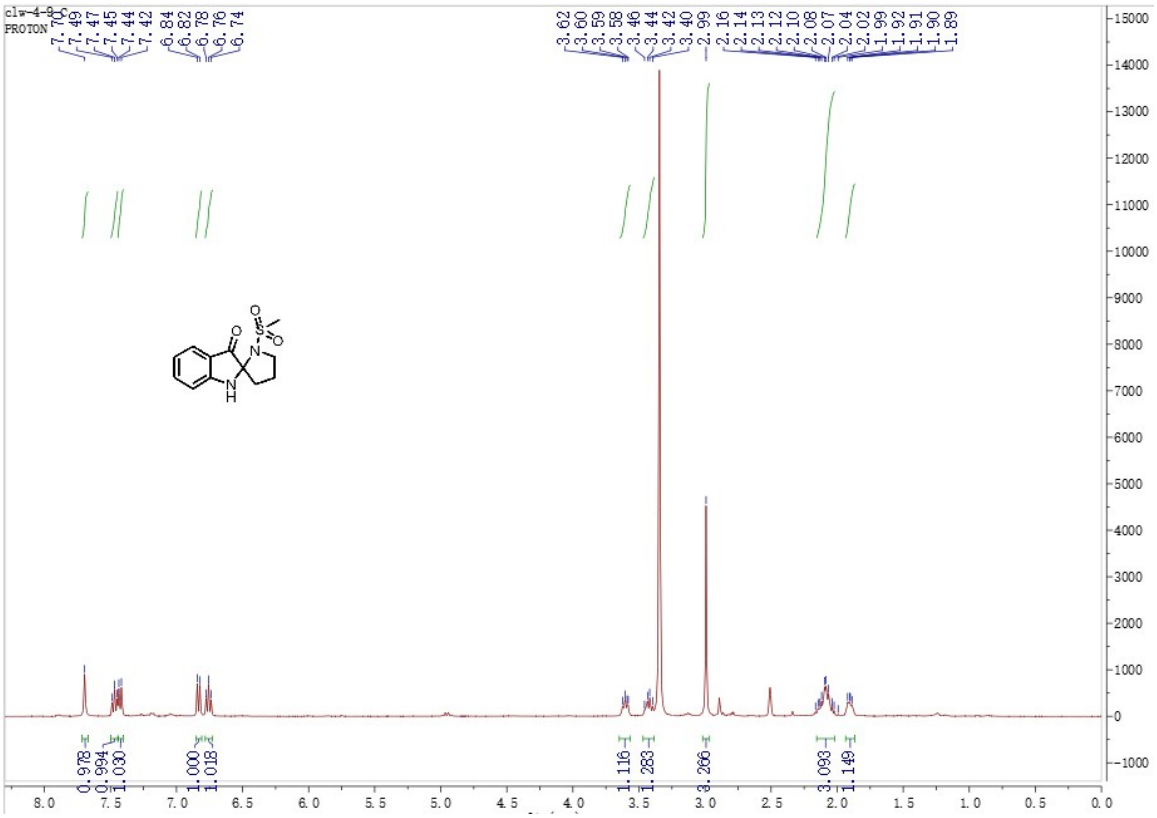
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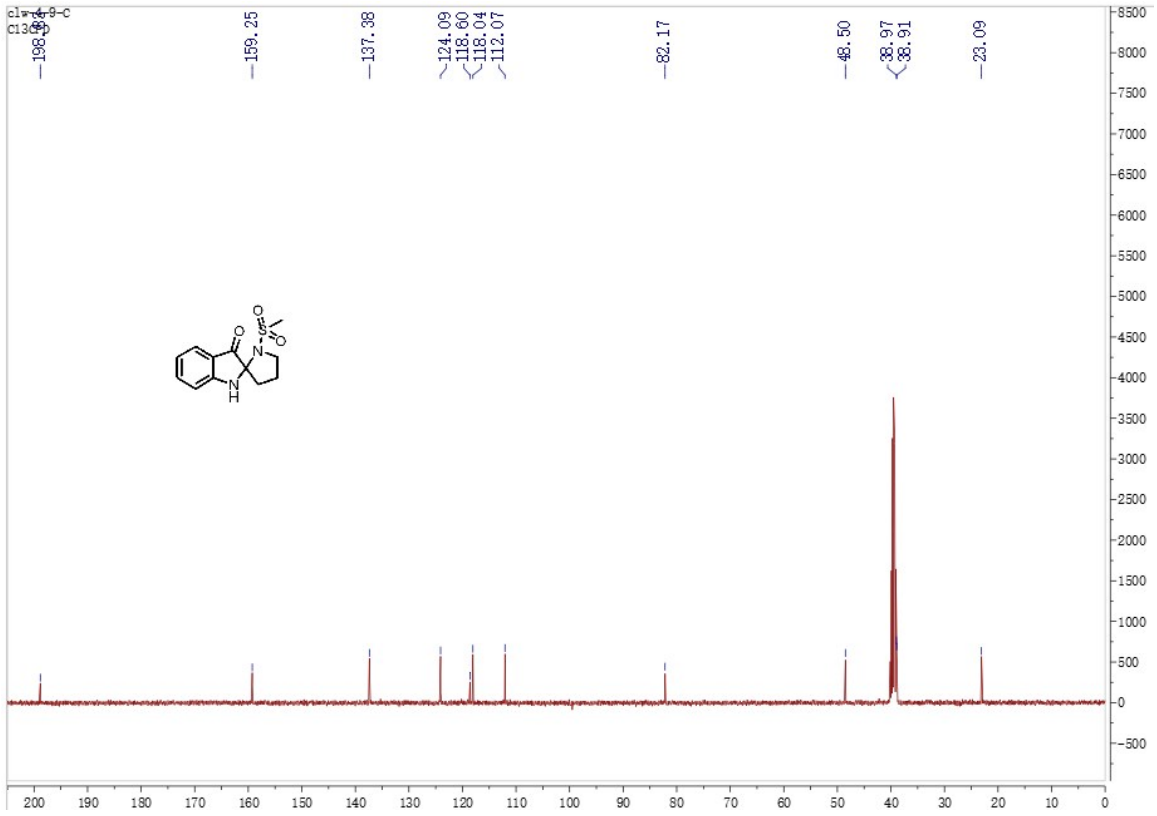
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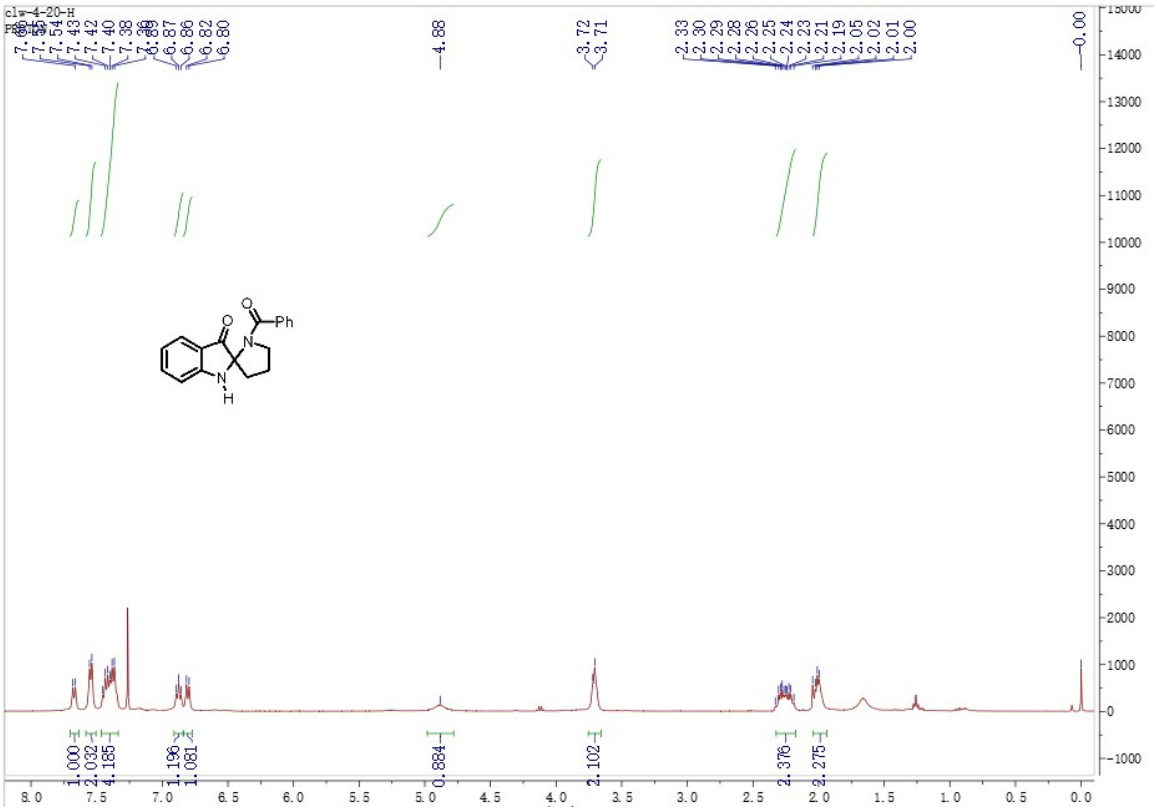
23.09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7.56
7.54
7.43
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7.38
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6.86
6.82
6.80
4.88
3.72
3.71
2.33
2.30
2.29
2.28
2.26
2.25
2.24
2.23
2.21
2.19
2.05
2.02
2.01
2.00
0.00
Ph
O
N
H
1.000
2.032
4.185
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1.081
0.884
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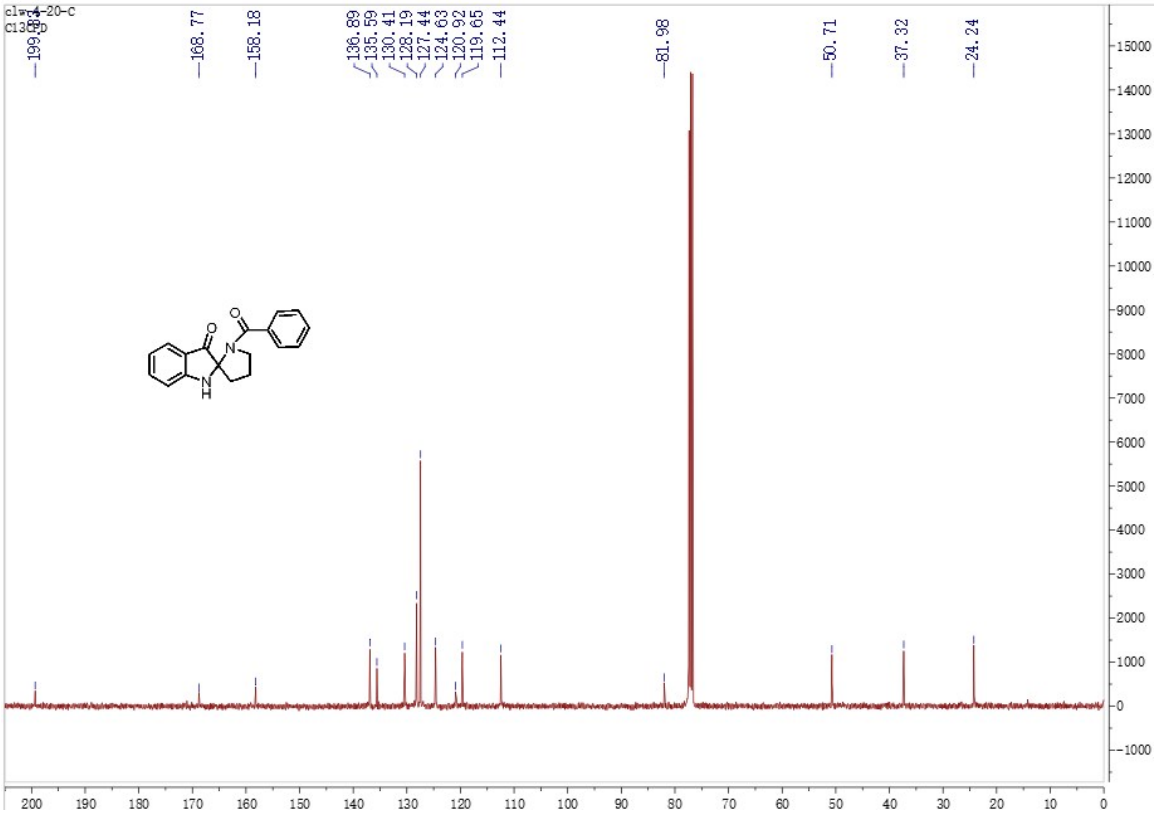
2.376
2.275


clw-4-20-C
199.84
168.77
158.18
136.89
135.59
130.41
128.19
127.44
124.63
120.92
119.65
112.44
81.98
50.71
37.32
24.24
O
N
H