Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2014

Electronic Supplementary Information

Rhodium(III)-Catalyzed Oxidative Coupling of *N*-Sulfonyl 2-Aminobenzaldehydes with Oxygenated Allylic Olefins through C-H Activation

Tingting Yang,[b,c] Tao Zhang,[b] Shangdong Yang,[c] Shanshan Chen [*a] and Xingwei Li [*b]

[a] *School of Natural Sciences, Anhui Agricultural University, Hefei 230036, China.*
[b]*Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.*
[c]*College of Chemistry and chemical engineering, Lanzhou University, Lanzhou 730000, China*

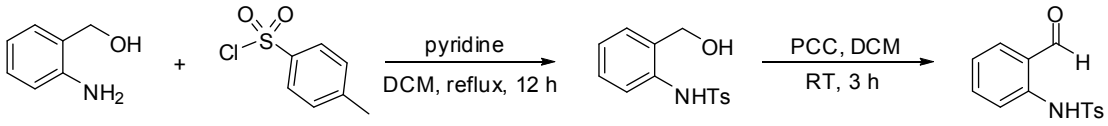
xwli@dicp.ac.cn

Table of Contents

I. General Considerations

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All reactions were carried out using Schlenk techniques or in an argon-filled glovebox. NMR Spectra were recorded on a Bruker 400 MHz or 500 MHz NMR spectrometer in the solvents indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy. HRMS data were obtained on a Thermo Scientific LTQ Orbirap Discovery spectrometer (Bremen, Germany). Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE).

II. General procedure of preparation of starting materials



Synthesis of *N*-(2-(hydroxymethyl)phenyl)-4-methylbenzenesulfonamide[1]

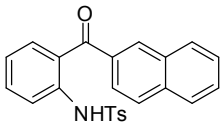
2-Aminobenzylalcohol (1.23 g, 0.010 mol) was dissolved in dichloromethane (10 mL), and pyridine (1 mL, 0.013 mol) was added to the solution. Then TsCl (2.29 g, 0.012 mol) was added and the solution was refluxed for 12 h. The solution was allowed to cool to room temperature and washed with hydrochloric acid (20 mL, 1 mol/L), brine (3 x 10 mL), and dried over Na_2SO_4. After removal of the solvent, the residue was crystallized from CH_2Cl_2/toluene to give *N*-Ts 2-aminobenzylic alcohol (2.4 g, 86% yield).

Synthesis of *N*-(2-formylphenyl)-4-methylbenzenesulfonamide.

A suspension of PCC (2.6 g, 12 mmol) in dry CH_2Cl_2 (40 ml) and benzylalcohol (2.1 g, 8.0 mmol) in the same solvent (80 mL) was stirred at room temperature for 3 h. The raw product was crystallized from $CHCl_3$/EtOH (1:5, 24 mL) to yield **1a** white solid (1.6 g, 5.8 mmol, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.77 (s, 1H), 9.82 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.59 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.16 (td, *J* = 7.6, 0.9 Hz, 1H), 2.36 (s, 3H). Characterization data of the compound agree with those in literature reports.[2]

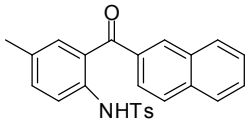
III. Preparation and Characterization of the Products 3.

N-Sulfonyl 2-aminobenzaldehyde (0.2 mmol), 7-oxabenzonorbornadienes (0.24 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), Ag_2CO_3 (0.4 mmol) and KPF_6 (0.4 mmol) were charged into a pressure tube, to which was added DCE (2 mL) under argon. The reaction mixture was stirred at 100 °C for 16 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE to afford the naphthylation product.



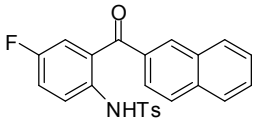
Compound **3aa**, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.91 – 7.80 (m, 4H), 7.67 (s, 1H), 7.63 (t, *J* = 7.4 Hz, 2H), 7.55 (dd, *J* = 19.0, 8.2 Hz, 4H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 143.7, 138.5, 135.7, 135.2, 134.6, 133.5, 132.6, 132.1, 131.8, 129.4, 129.3, 128.7, 128.1, 127.8, 127.4, 127.2, 127.0, 125.2, 124.1, 123.8, 21.0. HRMS: $[M + Na]^+$ calculated for $C_{24}H_{19}NNaO_3S$: 424.0978, found 424.0978.



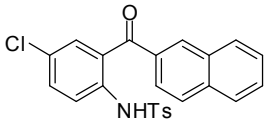
Compound **3ba**, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.83 (dd, *J* = 12.7, 8.4 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.65 – 7.55 (m, 4H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.37 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.18 (d, *J* = 1.2 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 2.27 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 143.6, 135.63, 135.56, 135.2, 134.5, 134.1, 134.0, 132.6, 132.1, 131.8, 129.38, 129.36, 128.7, 128.2, 128.1, 127.8, 127.2, 127.0, 125.2, 125.0, 20.9, 20.8. HRMS: $[M + H]^+$ calculated for $C_{25}H_{22}NO_3S$: 416.1315, found 416.1314.



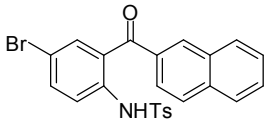
Compound **3ca**, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.88 – 7.81 (m, 3H), 7.67 – 7.63 (m, 1H), 7.61 – 7.57 (m, 3H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.09 (dd, *J* = 8.4, 2.9 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 2H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2(d, *J* = 1.7 Hz), 158.7(d, *J* = 245.9 Hz), 143.8, 135.4, 135.2, 133.9(d, *J* = 3.1 Hz), 133.5, 132.4, 131.7, 130.2(d, *J* = 6.2 Hz), 129.4 (d, *J* = 5.4 Hz), 129.0, 128.3, 128.0, 127.9, 127.8, 127.23, 127.16, 124.9, 120.3 (d, *J* = 22.2 Hz), 118.3 (d, *J* = 23.8 Hz), 20.8. HRMS: $[M + H]^+$ calculated for $C_{24}H_{19}FNO_3S$: 420.1064, found 420.1061.



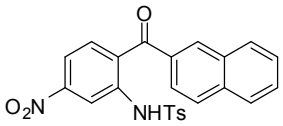
Compound **3da**, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.93 – 7.83 (m, 3H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.54 – 7.48 (m, 3H), 7.39 (d, *J* = 2.4 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 2H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 143.9, 136.8, 135.42, 135,38, 133.8, 133.3, 132.3, 131.8, 131.7,129.7, 129.51, 129.48, 129.1, 129.0, 128.4, 127.8, 127.21, 127.17, 126.1, 124.9, 21.0. HRMS: $[M + H]^+$ calculated for $C_{24}H_{19}ClNO_3S$: 436.0769, found 436.0771.



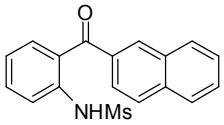
Compound **3ea**, 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.92 – 7.83 (m, 3H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.68 – 7.63 (m, 3H), 7.61 – 7.56 (m, 2H), 7.52 (dd, *J* = 10.3, 5.2 Hz, 3H), 6.92 (d, *J* = 8.1 Hz, 2H), 1.89 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 144.0, 137.4, 136.2, 135.42, 135.39, 134.6, 133.8, 132.3, 131.8, 129.52, 129.49, 129.3, 129.0, 128.4, 127.9, 127.2, 126.1, 124.9, 117.1, 21.0. One carbon is not visible because of overlapping. HRMS: $[M + H]^+$ calculated for $C_{24}H_{19}BrNO_3S$: 480.0264, found 480.0269.



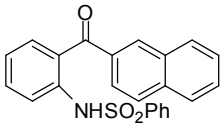
Compound **3fa**, 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.63 (d, *J* = 2.1 Hz, 1H), 7.94 (ddd, *J* = 19.1, 8.5, 2.9 Hz, 3H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.71 – 7.57 (m, 7H), 6.97 (d, *J* = 8.1 Hz, 2H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 150.0, 144.5, 139.6, 135.6, 135.2, 133.5, 133.1, 132.7, 131.8, 131.4, 129.8, 129.5, 129.4, 128.7, 127.9, 127.4, 127.3, 124.7, 118.3, 118.0, 21.0. HRMS: $[M + H]^+$ calculated for $C_{24}H_{19}N_2O_5S$: 447.1009, found 447.1007.



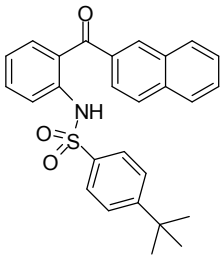
Compound **3ga**, 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.16 (s, 1H), 7.93 (dd, *J* = 12.1, 8.6 Hz, 3H), 7.86 – 7.79 (m, 2H), 7.69 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.65 – 7.55 (m, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 3.09 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 140.0, 135.25, 135.23, 134.5, 134.2, 132.1, 131.6, 129.4, 128.7, 128.5, 127.9, 127.1, 125.4, 123.9, 122.7, 119.6, 40.2. HRMS: $[M + H]^+$ calculated for $C_{18}H_{16}NO_3S$: 326.0845, found 326.0848.



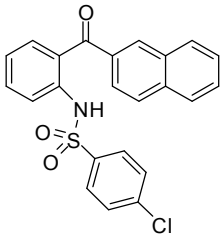
Compound **3ha**, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.90 – 7.80 (m, 4H), 7.70 (d, *J* = 8.1 Hz, 3H), 7.64 – 7.53 (m, 4H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.19 (dd, *J* = 9.8, 6.1 Hz, 3H), 7.13 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 138.9, 138.7, 135.2, 134.8, 133.7, 133.0, 132.8, 131.83, 131.81, 129.3, 128.9, 128.6, 128.2, 127.8, 127.2, 127.0, 126.7, 125.2, 123.7, 123.2. HRMS: $[M + H]^+$ calculated for $C_{23}H_{18}NO_3S$: 388.1002, found 388.1005.



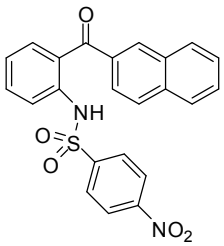
Compound **3ia**, 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.90 – 7.83 (m, 5H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.58 (ddd, *J* = 15.3, 12.5, 4.4 Hz, 4H), 7.48 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 1.07 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 156.6, 139.2, 136.2, 135.2, 134.9, 133.8, 133.3, 131.9, 131.6, 129.4, 128.6, 128.2, 127.8, 126.99, 126.95, 126.0, 125.9, 125.3, 123.3, 122.9, 34.9, 30.8. HRMS: $[M + Na]^+$ calculated for $C_{27}H_{25}NNaO_3S$: 466.1447, found 466.1443.



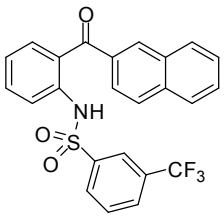
Compound **3ja**, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.91 – 7.81 (m, 4H), 7.74 (s, 1H), 7.65 – 7.55 (m, 6H), 7.48 – 7.45 (m, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 139.5, 138.2, 137.2, 135.3, 134.5, 133.7, 133.0, 131.86, 131.85, 129.5, 129.1, 128.8, 128.7, 128.4, 127.8, 127.2, 127.1, 125.1, 124.1, 123.8. HRMS: $[M + H]^+$ calculated for $C_{23}H_{17}ClNO_3S$: 422.0612, found 422.0616.



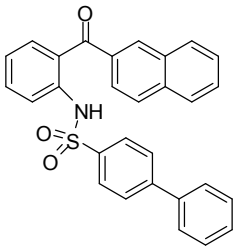
Compound **3ka**, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.84 (dt, *J* = 8.8, 7.3 Hz, 5H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.68 (s, 1H), 7.65 – 7.54 (m, 4H), 7.49 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 149.8, 144.4, 137.3, 135.3, 134.1, 133.8, 132.7, 132.0, 131.7, 129.15, 129.13, 128.55, 128.49, 127.9, 127.5, 127.4, 124.8, 124.7, 124.3, 124.0. HRMS: $[M + Na]^+$ calculated for $C_{23}H_{16}N_2NaO_5S$: 455.0672, found 455.0677.



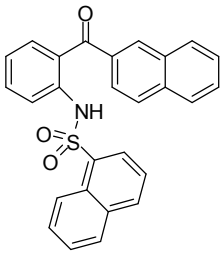
Compound **3la**, 80% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.93 – 7.90 (m, 2H), 7.89 – 7.84 (m, 3H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.67 (s, 1H), 7.65 – 7.56 (m, 4H), 7.48 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.20 (td, *J* = 7.7, 1.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 139.1(d, *J* = 254.1 Hz), 135.4, 134.5, 133.9, 133.0, 131.8, 131.4(d, *J* = 33.5 Hz), 131.1 (d, *J* = 3.5 Hz), 130.4, 129.7, 129.4, 129.34, 129.32 (d, *J* = 6.7 Hz), 129.31, 128.8, 128.4, 127.8, 127.1 (d, *J* = 7.0 Hz), 125.1, 124.4, 124.3, 123.9, 122.9 (q, *J* = 271.5 Hz). HRMS: $[M + Na]^+$ calculated for $C_{24}H_{16}F_3NNaO_3S$: 478.0695, found 478.0695.



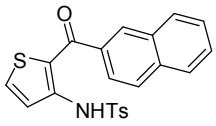
Compound **3ma**, 49% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.89 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.73 – 7.71 (m, 3H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.53 (m, 4H), 7.44 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.30 – 7.26 (m, 2H), 7.17 – 7.12 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.2, 145.6, 138.6, 137.3, 135.2, 134.6, 133.6, 132.9, 131.81, 131.78, 129.3, 128.8, 128.6, 128.24, 128.22, 127.8, 127.74, 127.68, 127.4, 127.3, 127.0, 126.9, 125.2, 124.2, 123.9. One carbon is not visible because of overlapping. HRMS: $[M + H]^+$ calculated for $C_{29}H_{22}NO_3S$: 464.1315, found 464.1322.



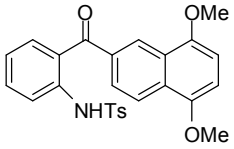
Compound **3na**, 49% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.54 (dd, *J* = 8.7, 0.7 Hz, 1H), 8.18 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.81 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.73 (dd, *J* = 8.4, 5.1 Hz, 2H), 7.69 – 7.66 (m, 1H), 7.61 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.54 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.39 – 7.33 (m, 4H), 7.25 – 7.22 (m, 2H), 7.09 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 7.00 (td, *J* = 7.6, 1.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.9, 138.4, 135.2, 134.6, 134.4, 133.9, 133.6, 133.3, 132.5, 131.7, 130.3, 129.3, 128.6, 128.5, 128.4, 128.0, 127.7, 127.6, 126.9, 126.8, 126.6, 125.0, 124.1, 123.8, 123.3, 122.6. One carbon is not visible because of overlapping. HRMS: $[M + H]^+$ calculated for $C_{27}H_{20}NO_3S$: 438.1158, found 438.1161.



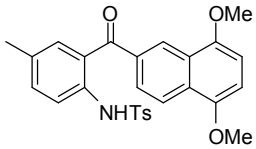
Compound **3oa**, 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (s, 1H), 8.27 (s, 1H), 7.88 (t, *J* = 9.8 Hz, 3H), 7.80 (t, *J* = 7.3 Hz, 3H), 7.61 – 7.50 (m, 4H), 7.24 (d, *J* = 7.9 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 145.5, 144.2, 136.6, 136.4, 135.0, 134.4, 132.1, 129.8, 129.5, 129.2, 128.6, 128.3, 127.8, 127.1, 127.0, 124.5, 120.8, 118.5, 21.5. HRMS: $[M + H]^+$ calculated for $C_{22}H_{18}NO_3S_2$: 408.0723, found 408.0721.



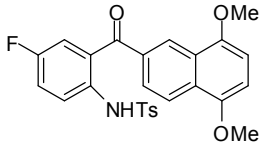
Compound **3ab**, 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 1.4 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.42 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 3H), 3.95 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 150.2, 149.1, 143.6, 138.6, 134.2, 133.4, 132.8, 129.4, 127.9, 127.7, 127.1, 126.2, 125.2, 124.7, 124.3, 123.9, 122.1, 106.3, 104.9, 104.1, 55.8, 55.6, 20.9. HRMS: $[M + H]^+$ calculated for $C_{26}H_{24}NO_5S$: 462.1370, found 462.1367.



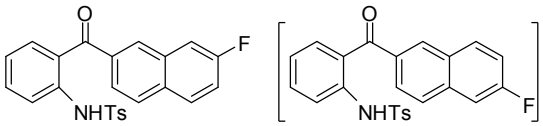
Compound **3bb**, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 8.03 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.53 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.17 (s, 1H), 6.85 (d, *J* = 8.4 Hz, 3H), 6.77 (d, *J* = 8.4 Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H), 2.26 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 150.2, 149.1, 143.6, 135.7, 135.4, 134.1, 134.04, 134.02, 132.9, 129.4, 128.3, 127.9, 127.1, 126.2, 125.2, 125.0, 124.7, 122.0, 106.4, 104.2, 55.9, 55.7, 20.9, 20.8. HRMS: $[M + H]^+$ calculated for $C_{27}H_{26}NO_5S$: 476.1526, found 476.1533.



Compound **3cb**, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 1.3 Hz, 1H), 7.83 (dd, *J* = 9.0, 4.9 Hz, 1H), 7.56 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.26 (m, 1H), 7.07 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.82 (dt, *J* = 19.2, 8.4 Hz, 4H), 3.99 (s, 3H), 3.97 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4 (d, *J* = 1.7 Hz), 158.8(d, *J* = 245.8 Hz), 150.2, 149.1, 143.8, 135.0, 134.0 (d, *J* = 2.9 Hz), 133.1, 130.5 (d, *J* = 6.4 Hz), 129.4, 128.05, 127,98 (d, *J* = 7.8 Hz), 127.1, 126.5, 124.9, 124.6, 122.4, 120.2 (d, *J* = 22.2 Hz), 118.5 (d, *J* = 23.8 Hz), 106.7, 104.2, 55.9, 55.6, 20.8. HRMS: $[M + H]^+$ calculated for $C_{26}H_{23}FNO_5S$: 480.1275, found 480.1285.



Compound(**3ac:3ac`=1:0.9)**, 81% yield.

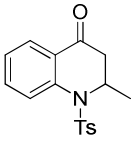
Compound **3ac**: ^{1}H NMR (400 MHz, $CDCl_3$) δ selected signals 9.77 (s, 1H), 1.97 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 197.6, 112.3(d, J = 20.6 Hz), 111.2(d, J = 20.1 Hz), 21.06.

Compound **3s`**: ^{1}H NMR (400 MHz, $CDCl_3$) δ selected signals 9.84 (s, 1H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 117.5(d, J = 25.3 Hz), 119.0(d, J = 25.2 Hz), 21.08.

HRMS: $[M + H]^+$ calculated for $C_{24}H_{19}FNO_3S$: 420.1064, found 420.1059.

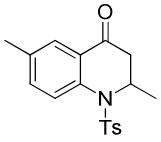
IV. Preparation and Characterization of Products 6 and 8.

N-Sulfonyl 2-aminobenzaldehyde (0.2 mmol), allyl carbonates (0.6 mmol), Cp*Rh$(OAc)_2$ (2.5 mol%), and PivOCs (0.3 mol) were charged into the sealed tube, to which was added DCE (2 mL) under argon. The reaction mixture was stirred at 100 °C for 18 h. After cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE to afford compounds.



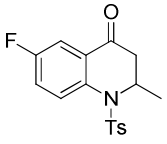
Compound **6a**, 85% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 14.4, 8.0 Hz, 2H), 7.59 (t, J = 7.8 Hz, 1H), 7.52 (d, J = 8.1 Hz, 2H), 7.27 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 4.90 (p, J = 6.5 Hz, 1H), 2.45 – 2.33 (m, 4H), 2.24 (d, J = 17.7 Hz, 1H), 1.28 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 144.4, 139.7, 136.7, 134.9, 130.0, 127.1, 126.9, 126.3, 125.6, 125.5, 51.9, 42.0, 21.5, 19.6. HRMS (ESI) calcd for $C_{17}H_{18}NO_3S$ $[M+H]^+$ 316.1007; found 316.1003.



Compound **6b**, 72% yield

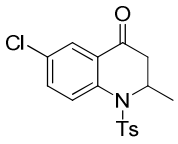
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 1.5 Hz, 1H), 7.50 (d, J = 8.3 Hz, 2H), 7.41 (dd, J = 8.4, 1.8 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 4.92 – 4.82 (m, 1H), 2.41 – 2.31 (m, 7H), 2.23 – 2.16 (m, 1H), 1.27 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 144.3, 137.2, 136.7, 135.8, 135.7, 130.0, 127.1, 126.9, 126.4, 125.3, 51.8, 41.9, 21.5, 20.7, 19.6. HRMS (ESI) calcd for $C_{18}H_{20}NO_3S$ $[M+H]^+$ 330.1164; found 330.1162.



Compound **6c**, 75% yield

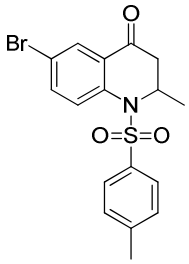
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 9.1, 4.6 Hz, 1H), 7.58 (dd, J = 8.3, 3.0 Hz, 1H), 7.50 (d, J = 8.1 Hz, 2H), 7.36 – 7.28 (m, 1H), 7.23 (d, J = 8.1 Hz, 2H), 4.88 (m, 1H), 2.42 – 2.29 (m, 4H), 2.23 (d, J = 17.8 Hz, 1H), 1.27 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 160.3 (d, J = 246.7 Hz), 144.6, 136.3, 135.7 (d, J = 7.0 Hz), 130.1, 128.9 (d, J = 7.4

Hz), 127.0 (d, *J* = 6.4 Hz), 126.9, 122.1 (d, *J* = 23.1 Hz), 112.8 (d, *J* = 23.3 Hz), 51.8, 41.5, 21.5, 19.5. HRMS (ESI) calcd for $C_{17}H_{17}FNO_3S$ $[M+H]^+$ 334.0913; found 334.0907.



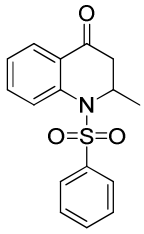
Compound **6d**, 61% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.58 – 7.48 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 4.95 – 4.82 (m, 1H), 2.42 – 2.31 (m, 4H), 2.25 (dd, *J* = 17.8, 1.6 Hz, 1H), 1.28 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 144.7, 138.1, 136.4, 134.7, 131.7, 130.1, 127.8, 126.9, 126.7, 126.3, 51.9, 41.7, 21.5, 19.5. HRMS (ESI) calcd for $C_{17}H_{17}ClNO_3S$ $[M+H]^+$ 350.0618; found 350.0608.



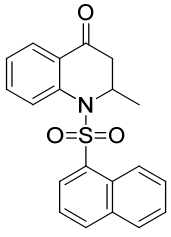
Compound **6e**, 68% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.4 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.74 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.94 (qd, *J* = 6.9, 3.5 Hz, 1H), 2.44 (s, 3H), 2.39 (dd, *J* = 17.9, 5.7 Hz, 1H), 2.30 (dd, *J* = 17.8, 1.7 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 144.7, 138.6, 137.6, 136.2, 130.1, 129.8, 127.9, 126.8, 126.4, 119.3, 51.8, 41.6, 21.5, 19.4. HRMS (ESI) calcd for $C_{17}H_{17}BrNO_3S$ $[M+H]^+$ 394.0113; found 394.0111.



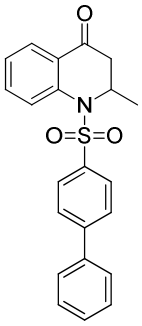
Compound **6f**, 74% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.68 – 7.63 (m, 2H), 7.63 – 7.53 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.25 (m, 1H), 4.96 – 4.86 (m, 1H), 2.38 (dd, *J* = 17.8, 5.8 Hz, 1H), 2.25 (dd, *J* = 17.8, 1.6 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 139.6, 139.5, 134.9, 133.4, 129.4, 127.1, 126.8, 126.2, 125.7, 125.5, 51.9, 42.0, 19.6. HRMS (ESI) calcd for $C_{16}H_{16}NO_3S$ $[M+H]^+$ 302.0851; found 302.0848.



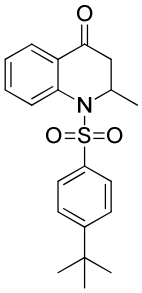
Compound **6g**, 78% yield

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.83 (m, 3H), 7.61 (ddd, *J* = 8.4, 7.4, 1.7 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.48 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 7.32 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H), 7.29 – 7.23 (m, 1H), 4.88 – 4.79 (m, 1H), 2.14 (dd, *J* = 17.6, 1.9 Hz, 1H), 2.07 (dd, *J* = 17.6, 5.6 Hz, 1H), 1.33 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0, 139.9, 135.0, 134.9, 134.8, 134.3, 130.3, 129.0, 128.3, 128.1, 127.2, 127.1, 125.8, 125.4, 125.3, 124.3, 124.2, 51.8, 42.2, 19.4. HRMS (ESI) calcd for $C_{20}H_{18}NO_3S$ $[M+H]^+$ 352.1007; found 352.1025.



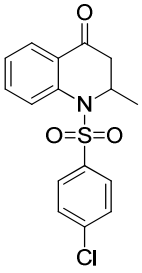
Compound **6h**, 77% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.57 (m, 3H), 7.57 – 7.50 (m, 2H), 7.41 (ddd, *J* = 10.9, 9.8, 5.6 Hz, 3H), 7.28 (dd, *J* = 13.1, 5.3 Hz, 1H), 5.01 – 4.91 (m, 1H), 2.50 (dd, *J* = 17.7, 5.8 Hz, 1H), 2.29 (dd, *J* = 17.7, 1.4 Hz, 1H), 1.31 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 146.3, 139.6, 138.7, 138.1, 134.9, 129.0, 128.7, 127.9, 127.4, 127.4, 127.2, 126.1, 125.6, 125.4, 52.0, 42.1, 19.5. HRMS (ESI) calcd for $C_{22}H_{20}NO_3S$ $[M+H]^+$ 378.1164; found 378.1172.



Compound **6i**, 57% yield

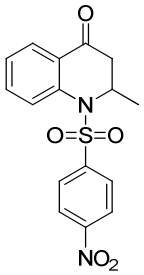
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 17.5, 8.1 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 3H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 4.91 (p, *J* = 6.8 Hz, 1H), 2.42 (dd, *J* = 17.7, 5.8 Hz, 1H), 2.26 (d, *J* = 17.6 Hz, 1H), 1.29 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 157.4, 139.7, 136.6, 134.9, 127.1, 126.8, 126.4, 126.0, 125.4, 125.3, 51.9, 42.1, 35.2, 31.0, 19.5. HRMS (ESI) calcd for $C_{20}H_{24}NO_3S$ $[M+H]^+$ 358.1477; found 358.1481.



Compound **6j**, 80% yield

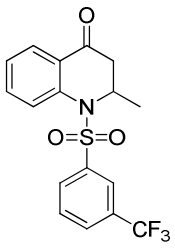
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.87 (dd, *J* = 8.3, 0.7 Hz, 1H),

7.63 – 7.56 (m, 3H), 7.42 – 7.37 (m, 2H), 7.29 (td, *J* = 7.8, 1.0 Hz, 1H), 4.95 – 4.87 (m, 1H), 2.45 (dd, *J* = 17.8, 5.8 Hz, 1H), 2.30 (dd, *J* = 17.7, 1.6 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.8, 140.0, 139.2, 138.1, 135.0, 129.7, 128.3, 127.3, 126.0, 125.9, 125.5, 52.1, 42.1, 19.54. HRMS (ESI) calcd for $C_{16}H_{15}ClNO_3S$ $[M+H]^+$ 336.0461; found 336.0455.



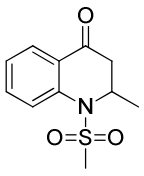
Compound **6k**, 60% yield

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.25 (m, 2H), 7.95 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.90 – 7.82 (m, 3H), 7.64 (ddd, *J* = 8.4, 7.4, 1.7 Hz, 1H), 7.34 (td, *J* = 7.7, 1.0 Hz, 1H), 5.02 – 4.95 (m, 1H), 2.45 (dd, *J* = 17.8, 5.8 Hz, 1H), 2.35 (dd, *J* = 17.8, 1.7 Hz, 1H), 1.32 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.3, 150.3, 145.1, 138.7, 135.2, 128.2, 127.6, 126.4, 125.9, 125.6, 124.6, 52.5, 42.3, 19.6. HRMS (ESI) calcd for $C_{16}H_{15}N_2O_5S$ $[M+H]^+$ 347.0702; found 347.0703.



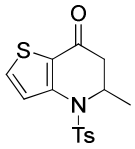
Compound **6l**, 73% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.81 (t, *J* = 9.0 Hz, 2H), 7.68 – 7.62 (m, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 5.01 – 4.91 (m, 1H), 2.41 (dd, *J* = 17.9, 5.6 Hz, 1H), 2.32 (dd, *J* = 17.9, 1.7 Hz, 1H), 1.31 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 140.7, 138.9, 135.1, 132.1 (q, *J* = 33.6), 130.2, 130.0 (q, *J* = 3.4), 129.9, 127.4, 126.3, 126.1, 125.7, 124.1 (q, *J* = 3.8), 122.8 (q, *J* = 270.5), 52.3, 42.1, 19.6. HRMS (ESI) calcd for $C_{17}H_{15}F_3NO_3S$ $[M+H]^+$ 370.0725; found 370.0756.



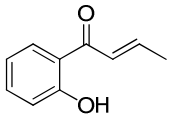
Compound **6m**, 80% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.54 (m, 1H), 7.29 – 7.22 (m, 1H), 5.08 – 4.97 (m, 1H), 3.17 – 3.05 (m, 4H), 2.62 (dd, *J* = 17.5, 1.6 Hz, 1H), 1.34 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 139.7, 135.3, 127.8, 124.8, 124.5, 123.1, 51.9, 43.8, 40.6, 18.9. HRMS (ESI) calcd for $C_{11}H_{14}NO_3S$ $[M+H]^+$ 240.0694; found 240.0696.



Compound **6n**, 60% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 5.4 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 5.4 Hz, 1H), 7.29 – 7.24 (m, 2H), 4.94 – 4.75 (m, 1H), 2.43 – 2.32 (m, 4H), 2.43 – 2.33 (m, 4H), 2.21 (dd, *J* = 17.1, 1.7 Hz, 1H), 2.21 (dd, *J* = 17.1, 1.7 Hz, 1H), 1.36 (d, *J* = 6.9 Hz, 3H), 1.36 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.73, 144.74, 144.40, 136.29, 134.38, 130.13, 129.73, 126.61, 124.56, 54.10, 41.39, 21.53, 18.99. HRMS (ESI) calcd for $C_{15}H_{16}NO_3S_2$ $[M+H]^+$ 322.0572; found 322.0574.

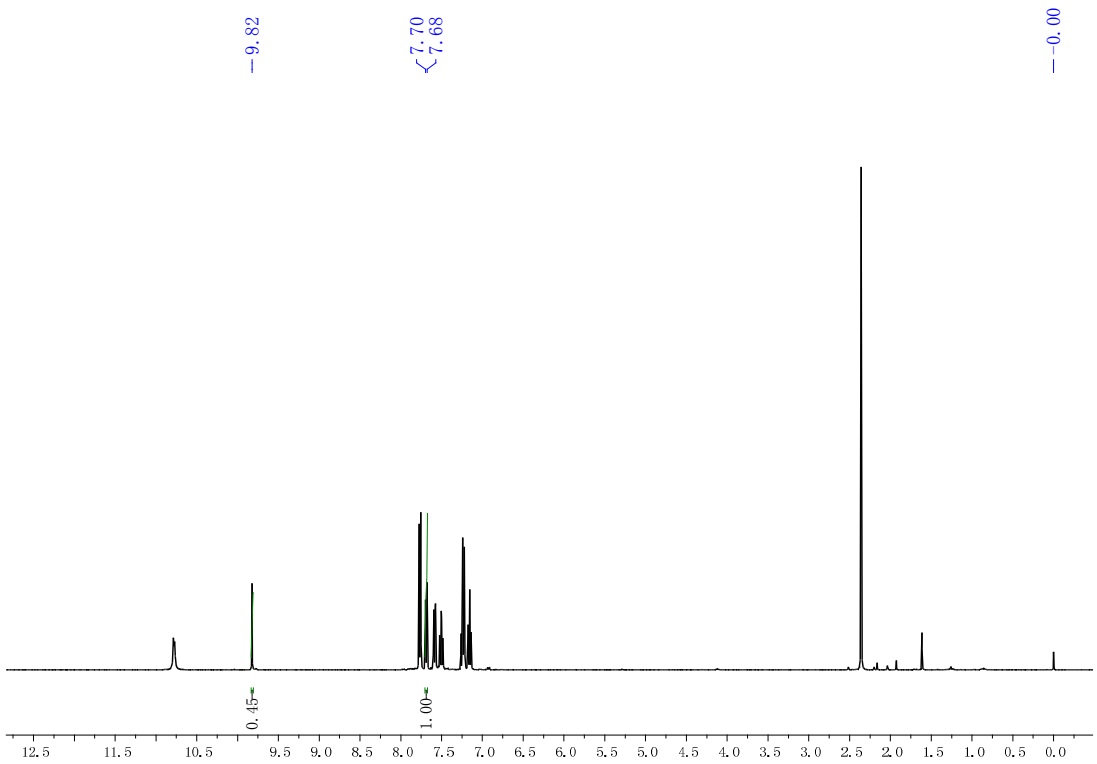


Compound **8**, 53% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.70 (s, 1H), 7.79 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.25 – 7.15 (m, 1H), 7.01 (ddd, *J* = 11.7, 9.4, 1.3 Hz, 2H), 6.92 – 6.85 (m, 1H), 2.02 (dd, *J* = 6.8, 1.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.98, 163.54, 145.81, 136.14, 129.79, 125.50, 119.48, 118.69, 118.45, 18.64. HRMS (ESI) calcd for $C_{10}H_{11}O_2$ $[M+H]^+$ 163.0759; found 163.0752.

V. Deuterium-Labeling Experiment

An equimolar mixture of **1a** and **1a-*d*$_1$** (0.4 mmol in total), 7-oxabenzonorbornadienes (0.24 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), biphenyl (HPLC internal standard, 0.15 mmol), Ag_2CO_3 (0.4 mmol) and KPF_6 (0.4 mmol) were charged into a pressure tube, to which was added DCE (2 mL) under argon. The reaction mixture was stirred at 100 ^{o}C for 2 h. After quenched at 0 ^{o}C, the conversion was determined using HPLC to be 24%. The solvent was then removed under reduced pressure and the residue was purified by silica gel chromatography using EA/PE to give the recovered starting aldehydes. ^{1}H NMR analysis of the level of deuteration of the recovered aldehydes (55% C-D and 45% C-H) gave k_H/k_D = 1.9.



	C-H	C-D
t = 0	1	1
conversion	-kx	-x
t = 1h	1-kx	1-x

(1-x)/(1-kx) = 0.57/0.43 = 1.222

(kx+x)/2 = 0.24

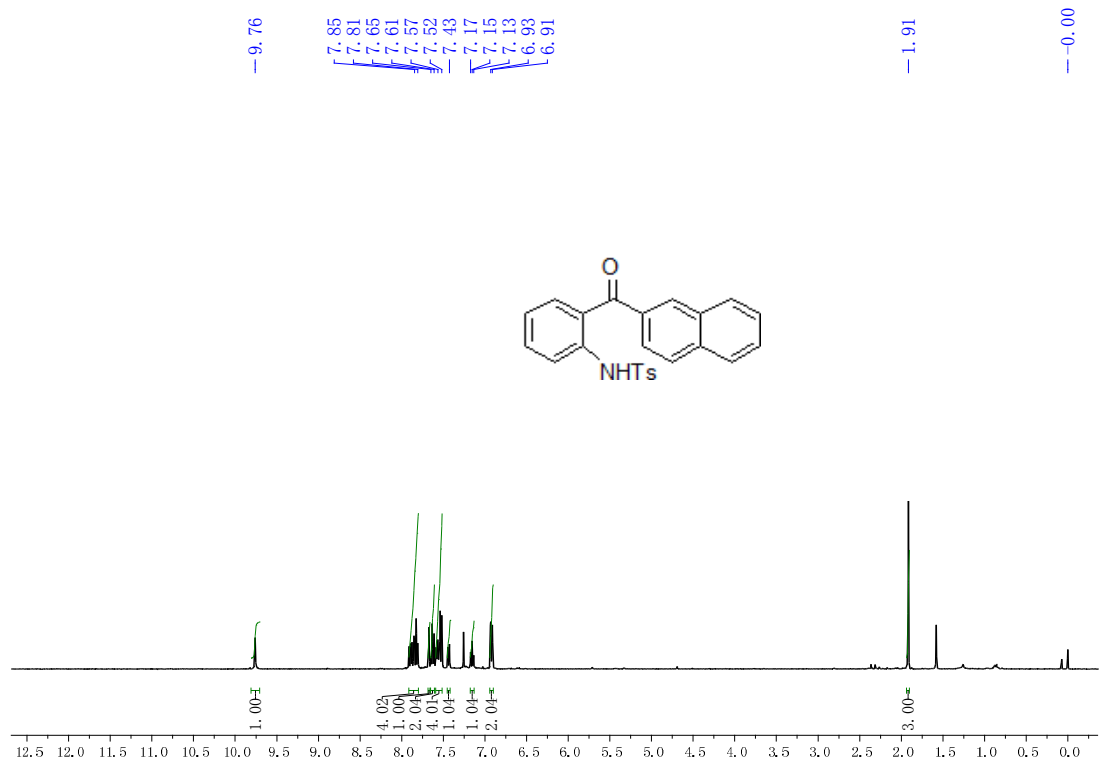
k = KIE = 1.9

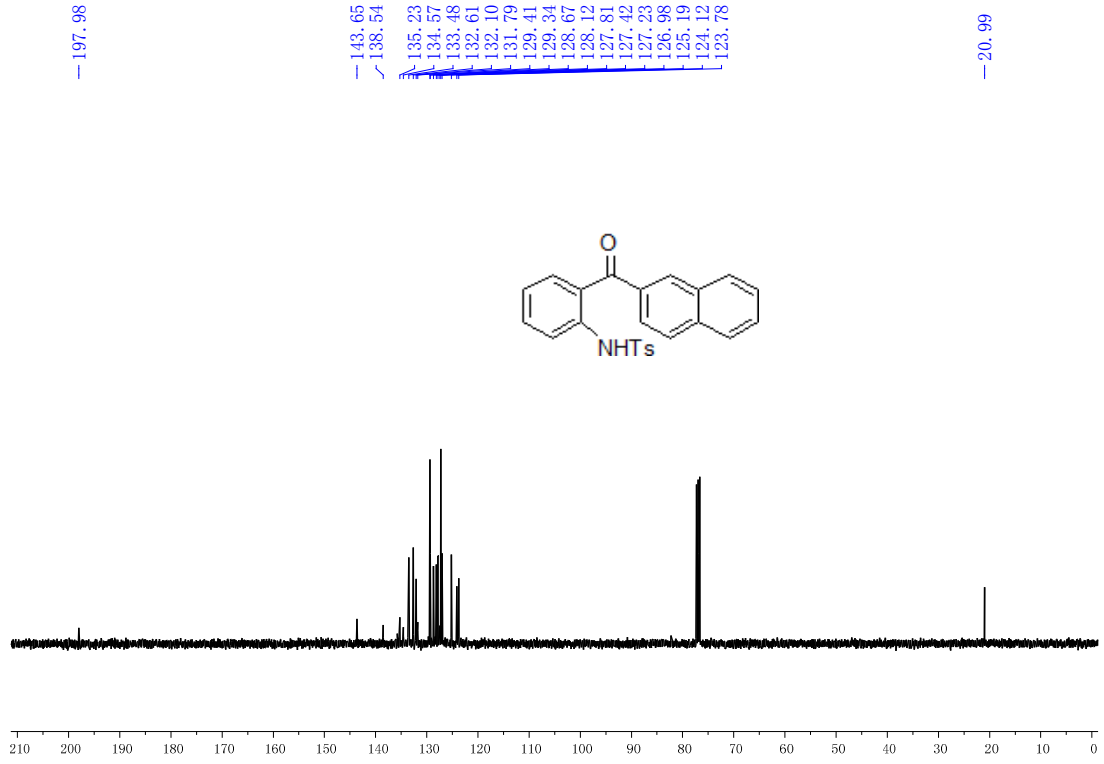
References:

1 F. Jiang, Z. Wu and W. Zhang, *Tetrahedron*, 2011, **67**, 1501.

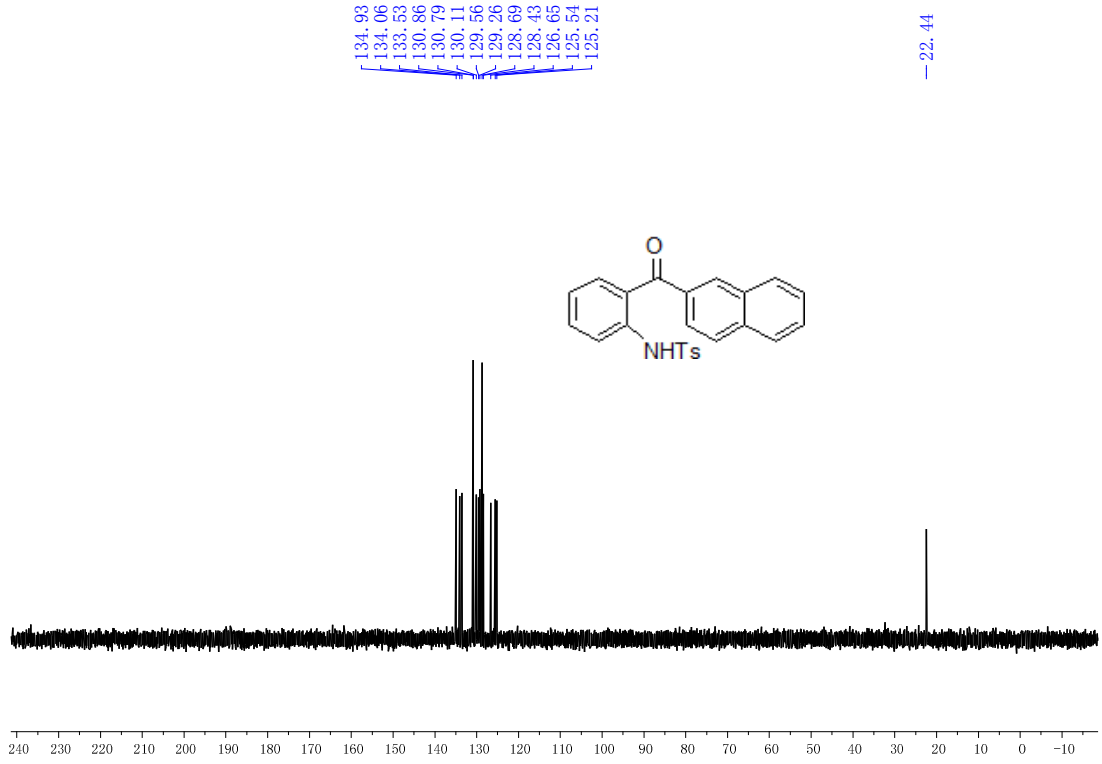
2 M. a. Hechavarría Fonseca, E. Eibler, M. Zabel and B. König, *Tetrahedron: Asymmetry*, 2003, **14**, 1989.

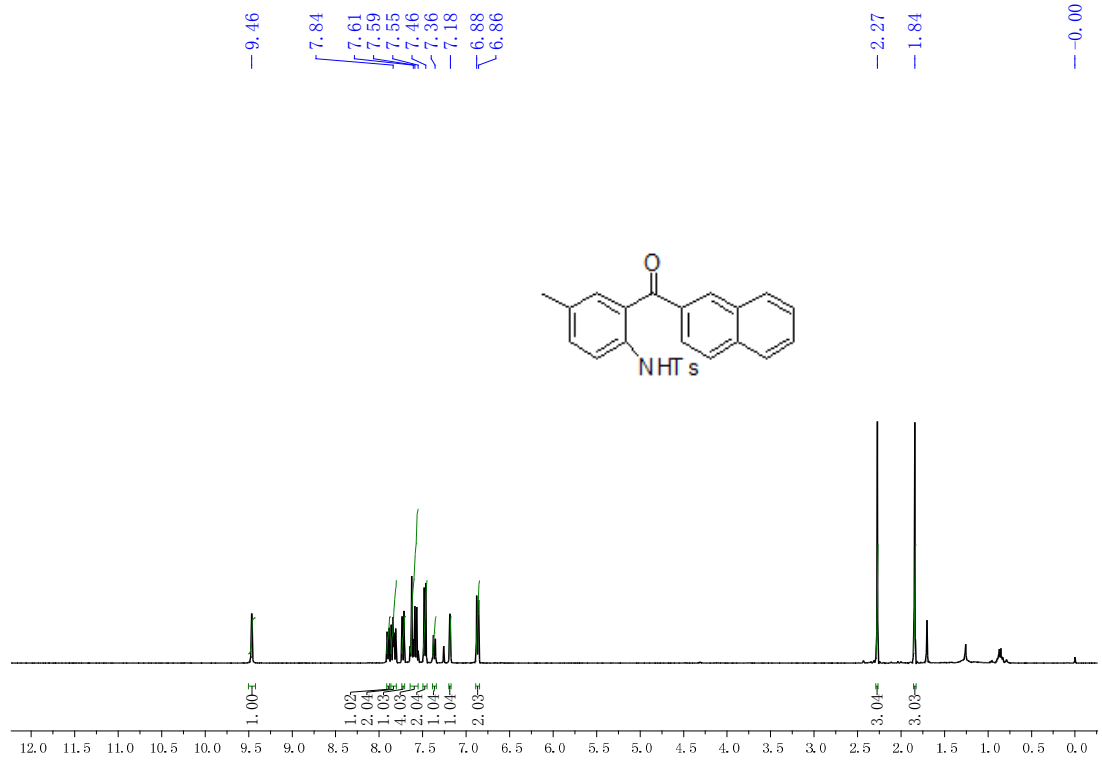
VI. NMR Spectra of Products

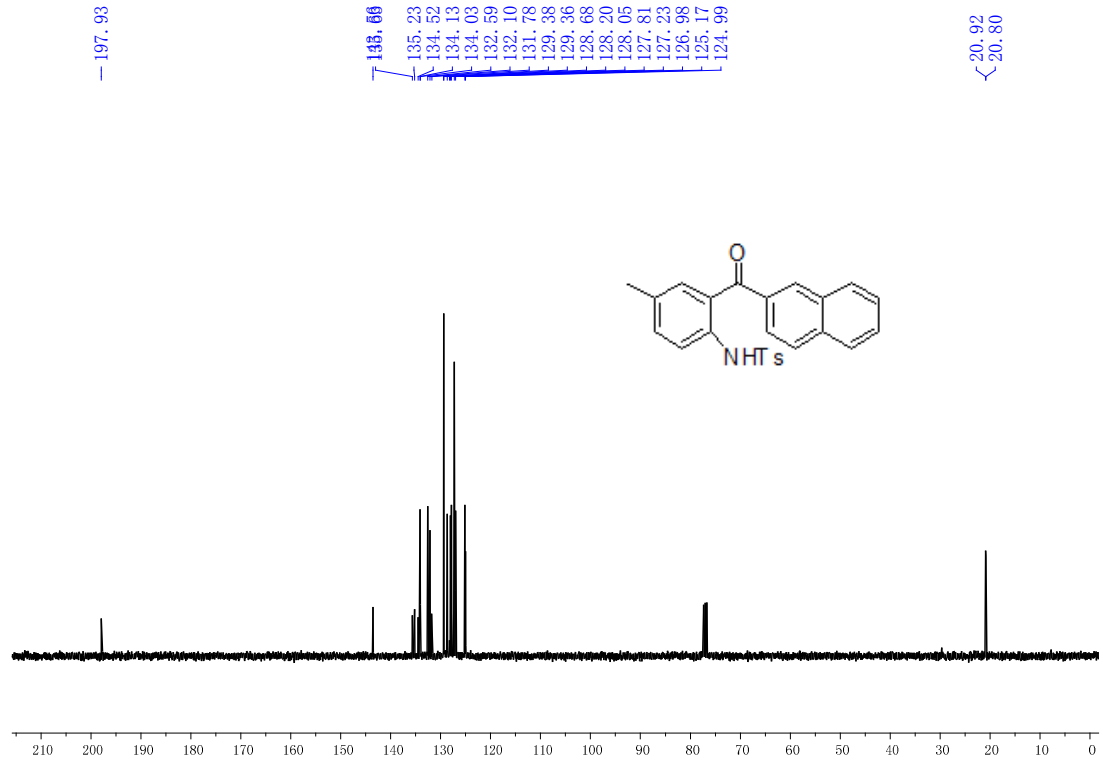


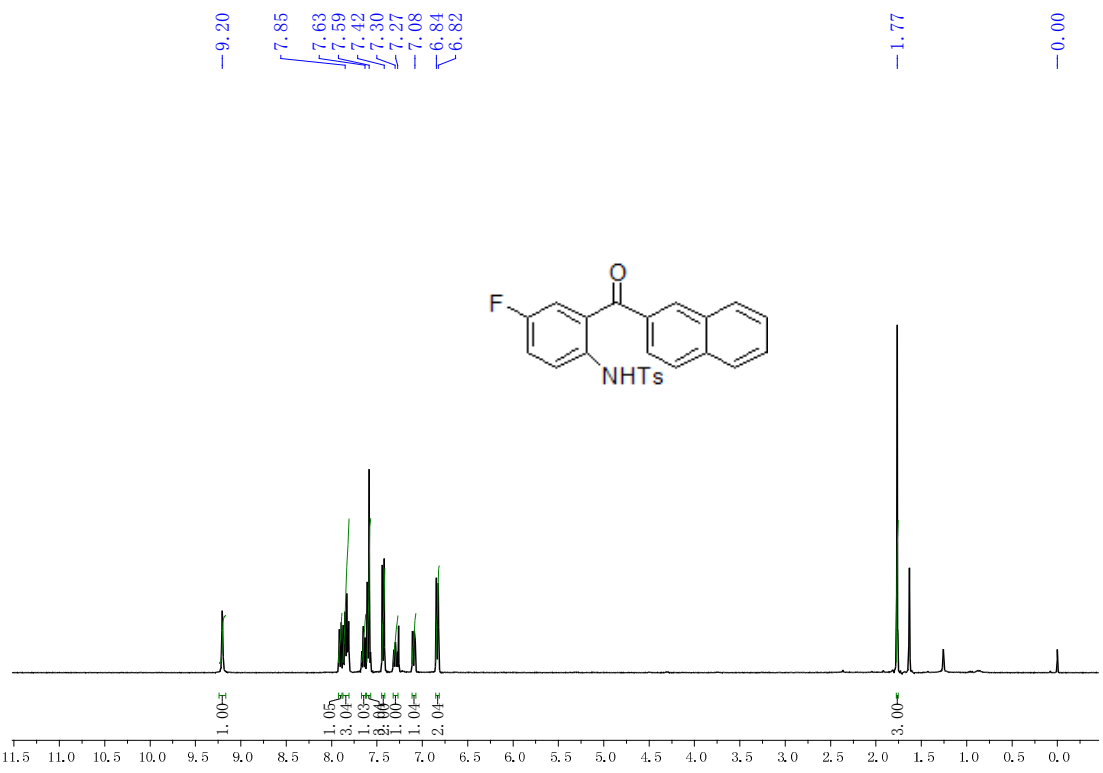


DEPT-135

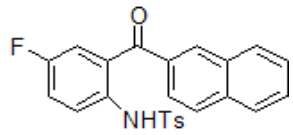

134.93
134.06
133.53
130.86
130.79
130.11
129.56
129.26
128.69
128.43
126.65
125.54
125.21
22.44
O
NHTs
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

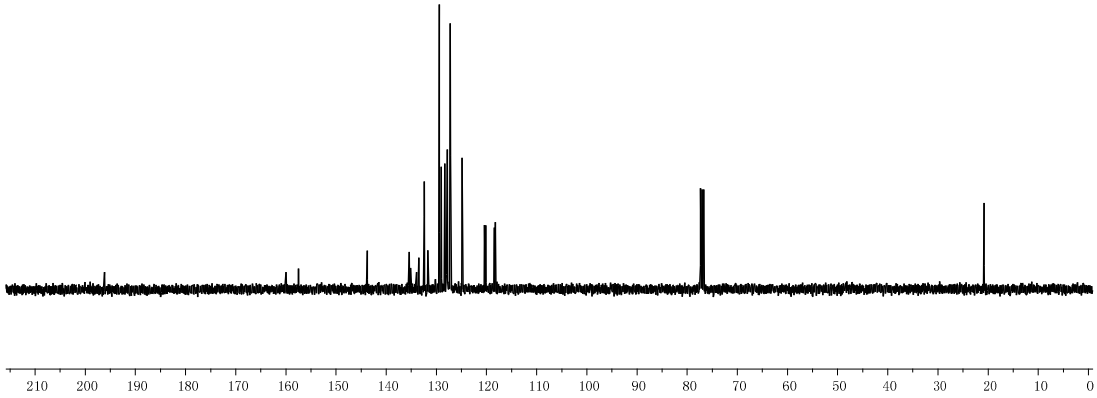

9.46
7.84
7.61
7.59
7.55
7.46
7.36
7.18
6.88
6.86
2.27
1.84
0.00
O
NHTs
1.00
1.02
2.04
1.03
4.03
2.04
1.04
1.04
2.03
3.04
3.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


197.93
135.23
134.52
134.13
134.03
132.59
132.10
131.78
129.38
129.36
128.68
128.20
128.05
127.81
127.23
126.98
125.17
124.99
20.92
20.80
O
NHTs
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

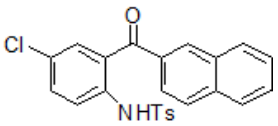

9.20
7.85
7.63
7.59
7.42
7.30
7.27
7.08
6.84
6.82
1.77
0.00
O
F
NHTs
1.00
1.05
3.04
1.03
2.00
1.00
1.04
2.04
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

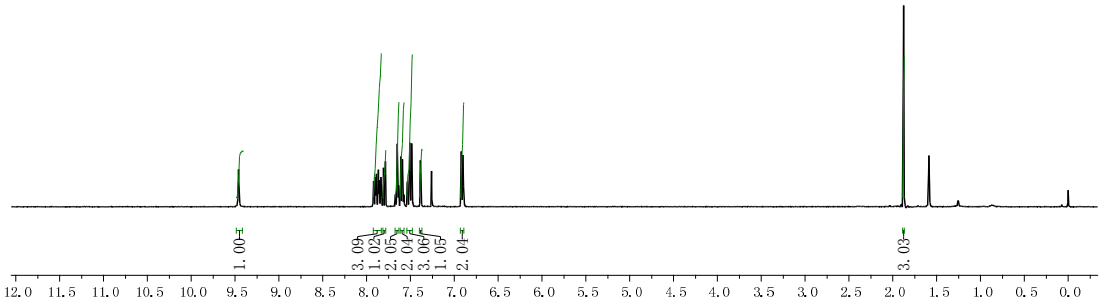
196.1949
196.1776
159.9484
157.4895
143.7920
131.6748
129.4086
127.8749
124.8652
120.3818
120.1600
118.4639
118.2260
20.8223

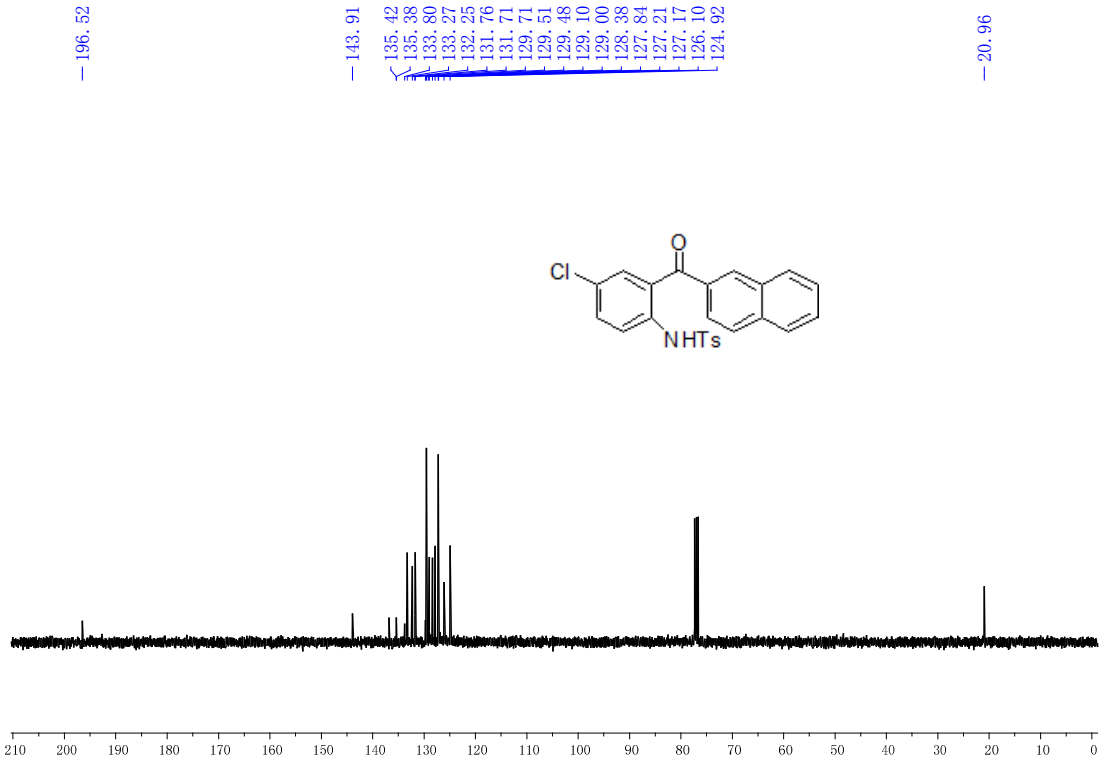


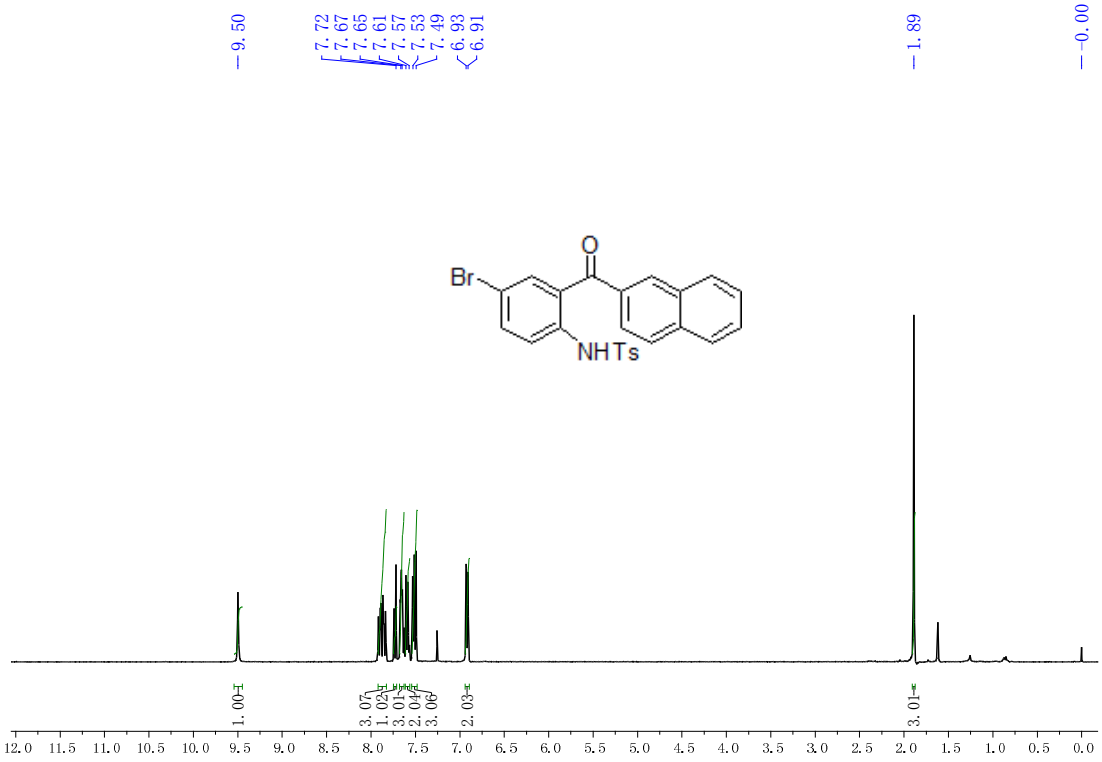


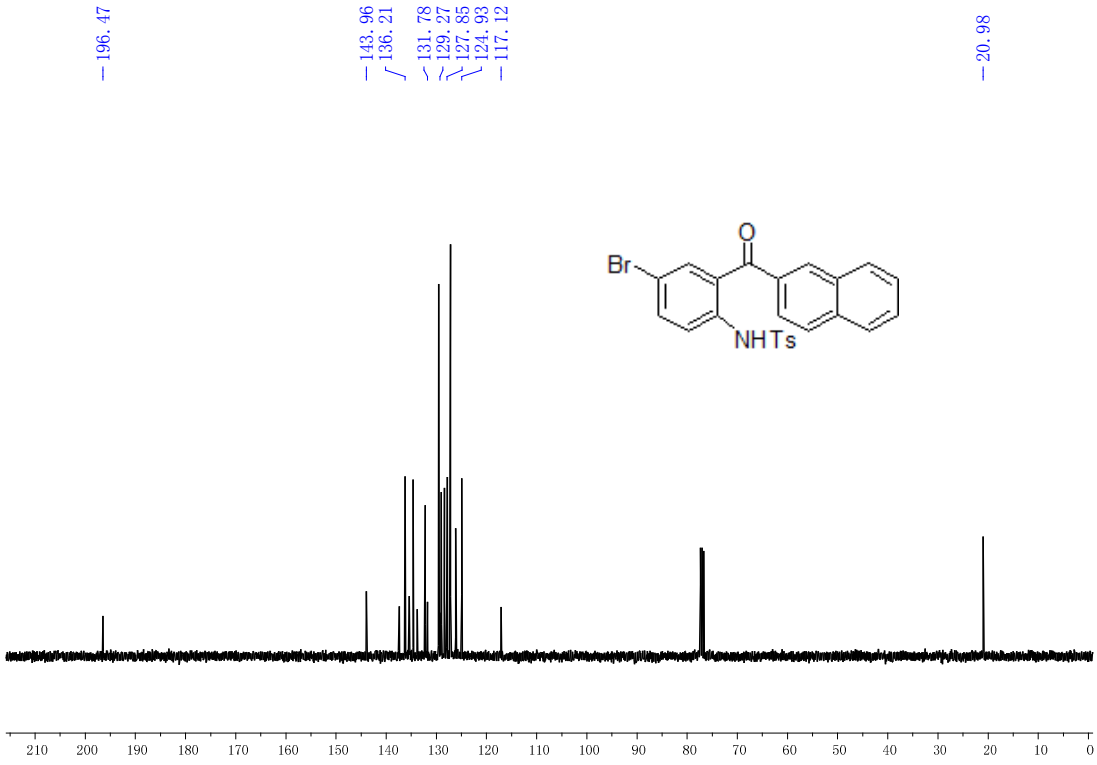
9.46
7.89
7.67
7.61
7.54
7.51
7.38
6.92
6.90
1.88
0.00

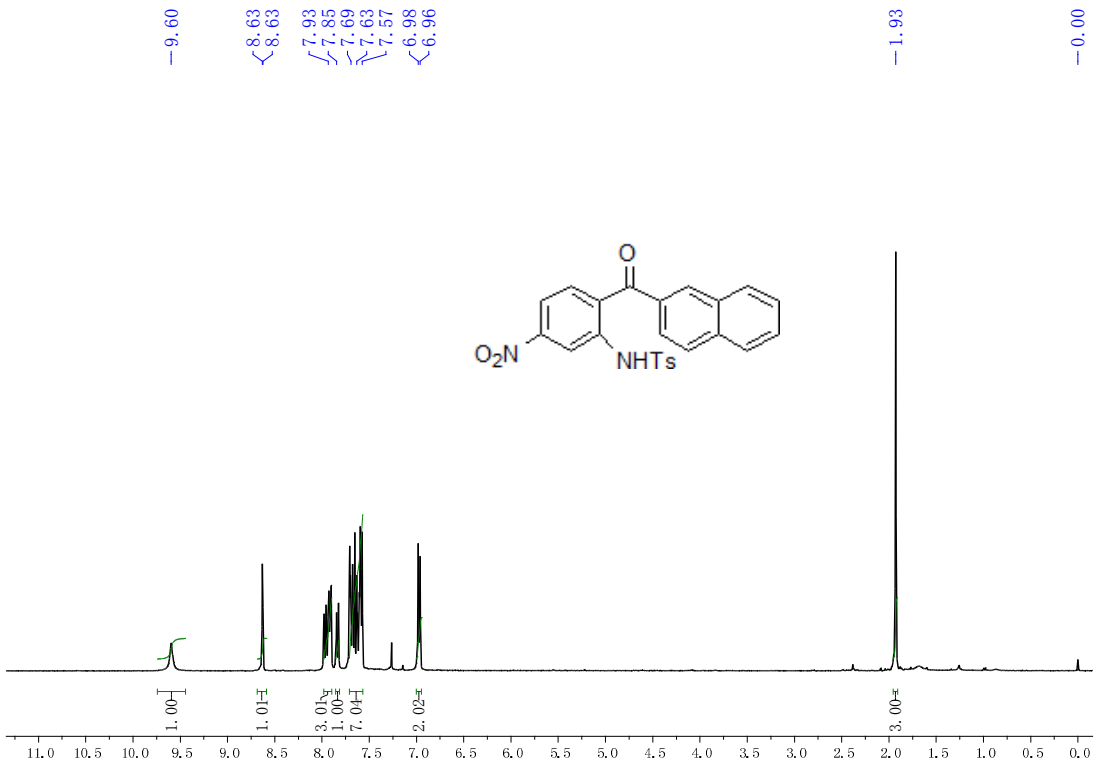


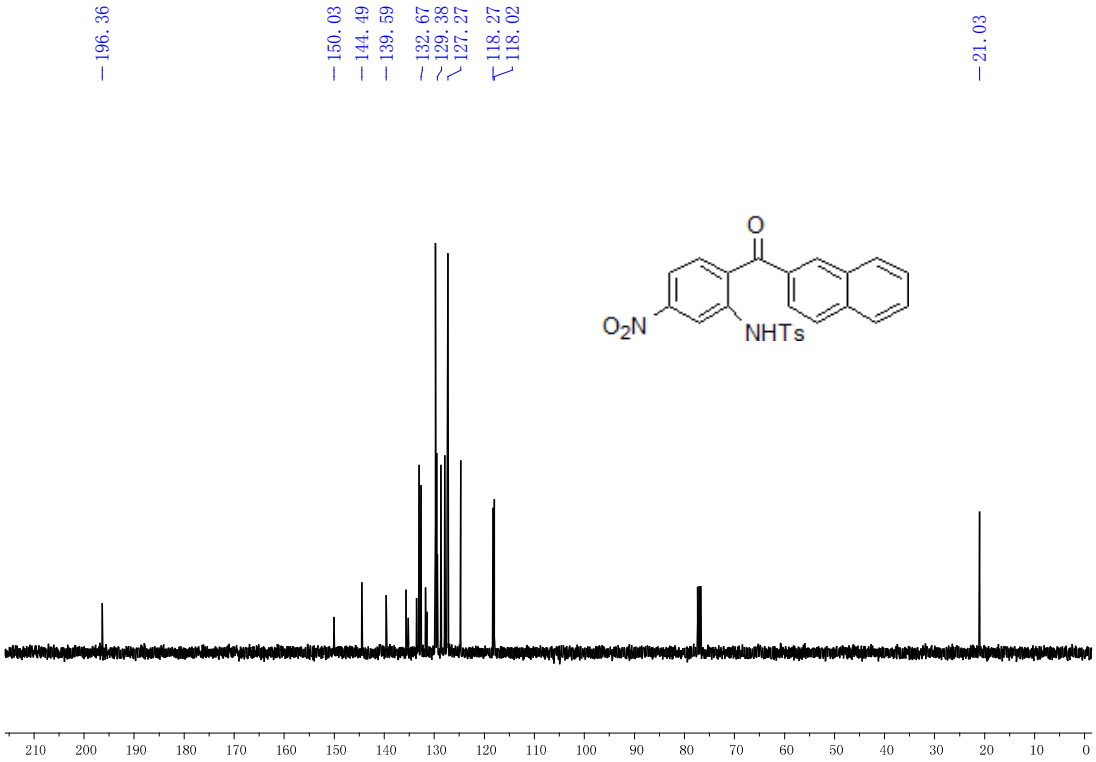


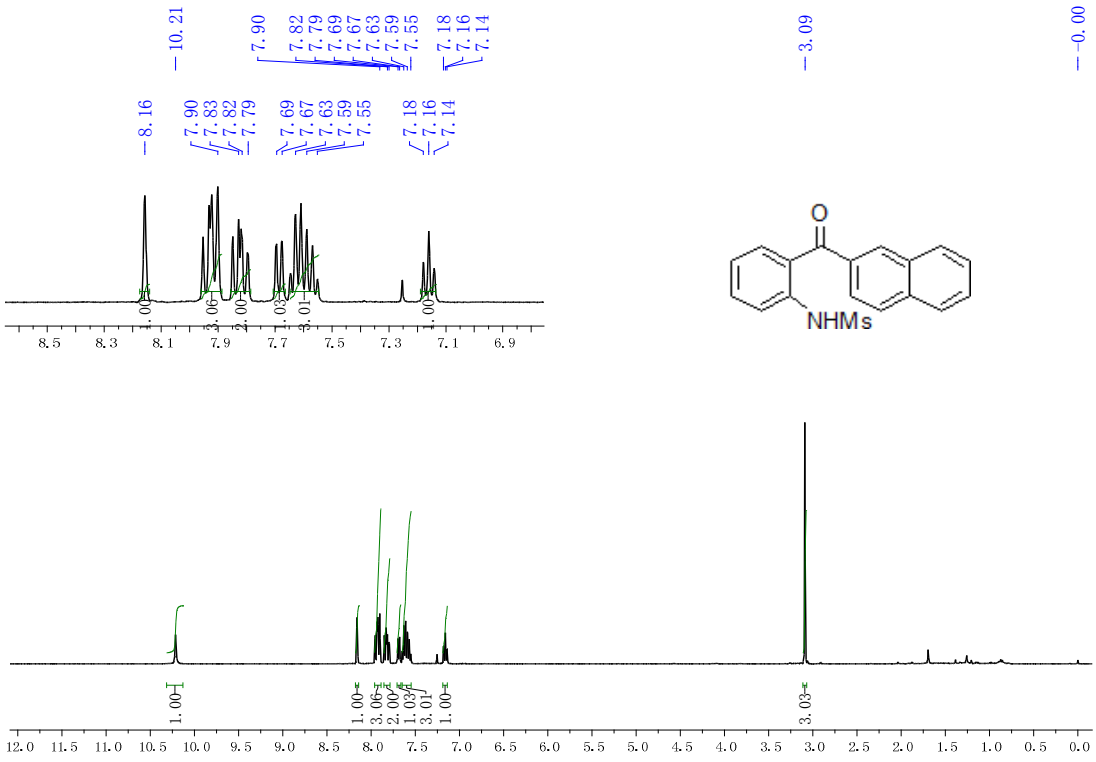

196.52
143.91
135.42
135.38
133.80
133.27
132.25
131.76
131.71
129.71
129.51
129.48
129.10
129.00
128.38
127.84
127.21
127.17
126.10
124.92
20.96
O
Cl
NHTs
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

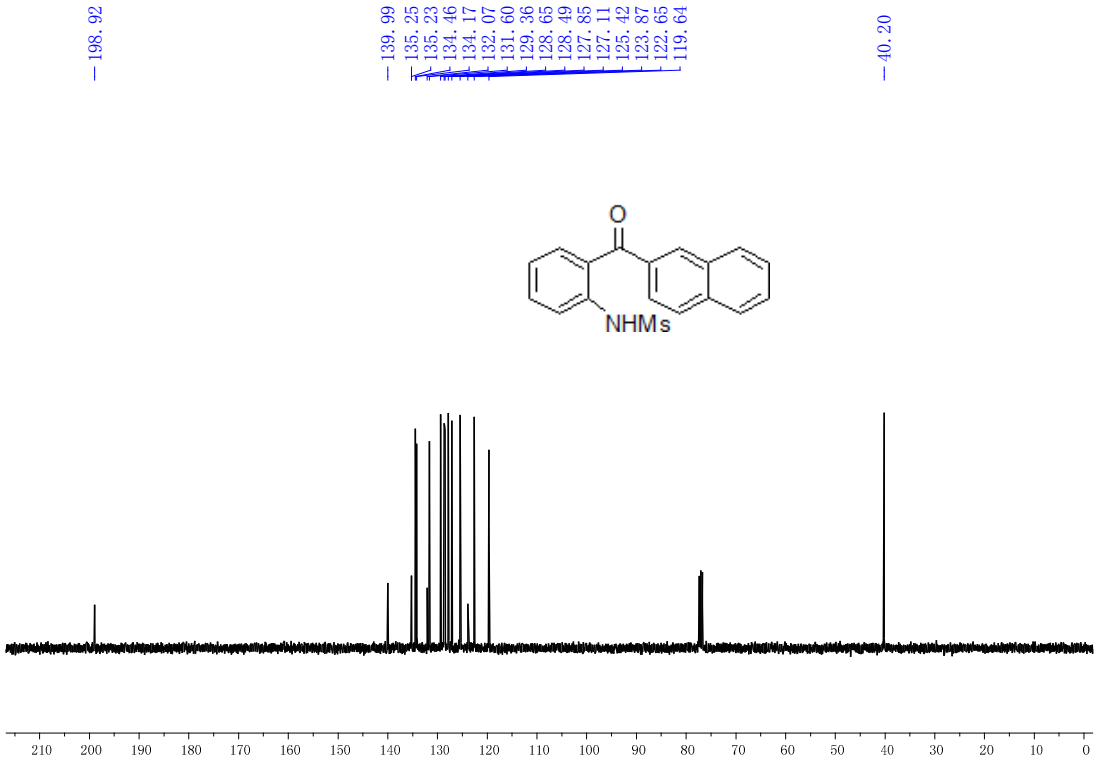

9.50
7.72
7.67
7.65
7.61
7.57
7.53
7.49
6.93
6.91
1.89
0.00
O
Br
NHTs
1.00
3.07
1.02
3.01
2.04
3.06
2.03
3.01
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

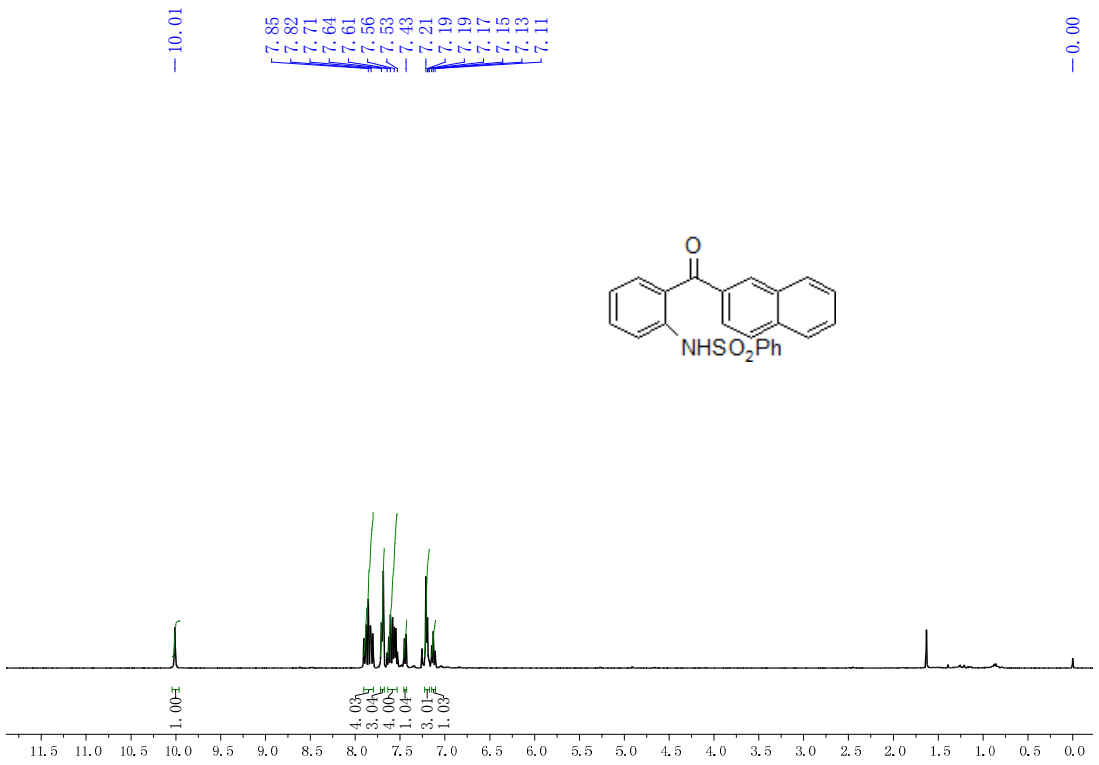

196.47
143.96
136.21
131.78
129.27
127.85
124.93
117.12
20.98
Br
O
NHTs
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

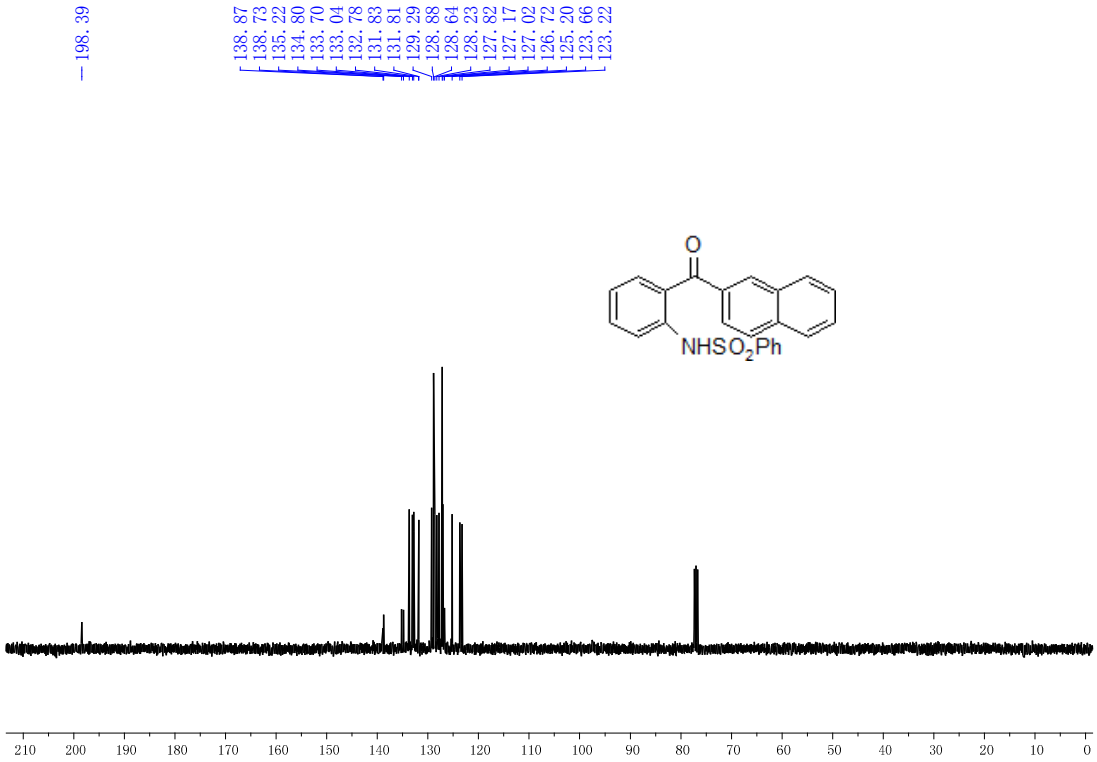

9.60
8.63
8.63
7.93
7.85
7.69
7.63
7.57
6.98
6.96
1.93
0.00
O
O2N
NHTs
1.00
1.01
3.01
1.00
7.04
2.02
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

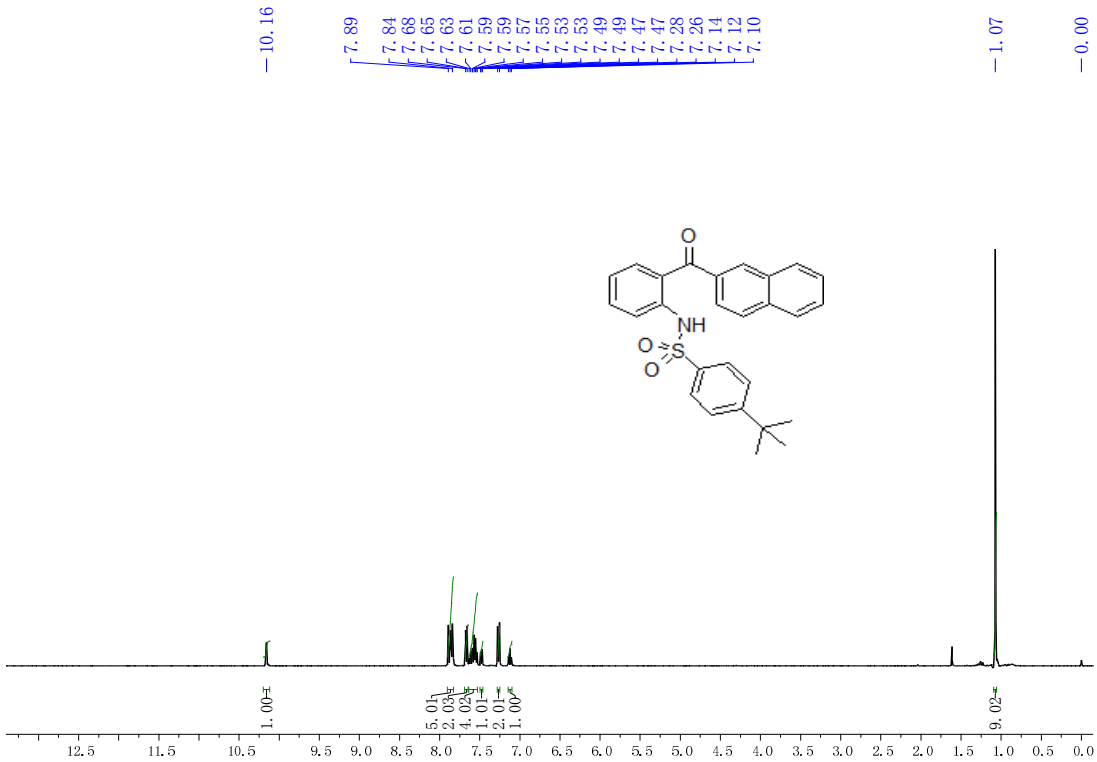

196.36
150.03
144.49
139.59
132.67
129.38
127.27
118.27
118.02
21.03
O
O2N
NHTs

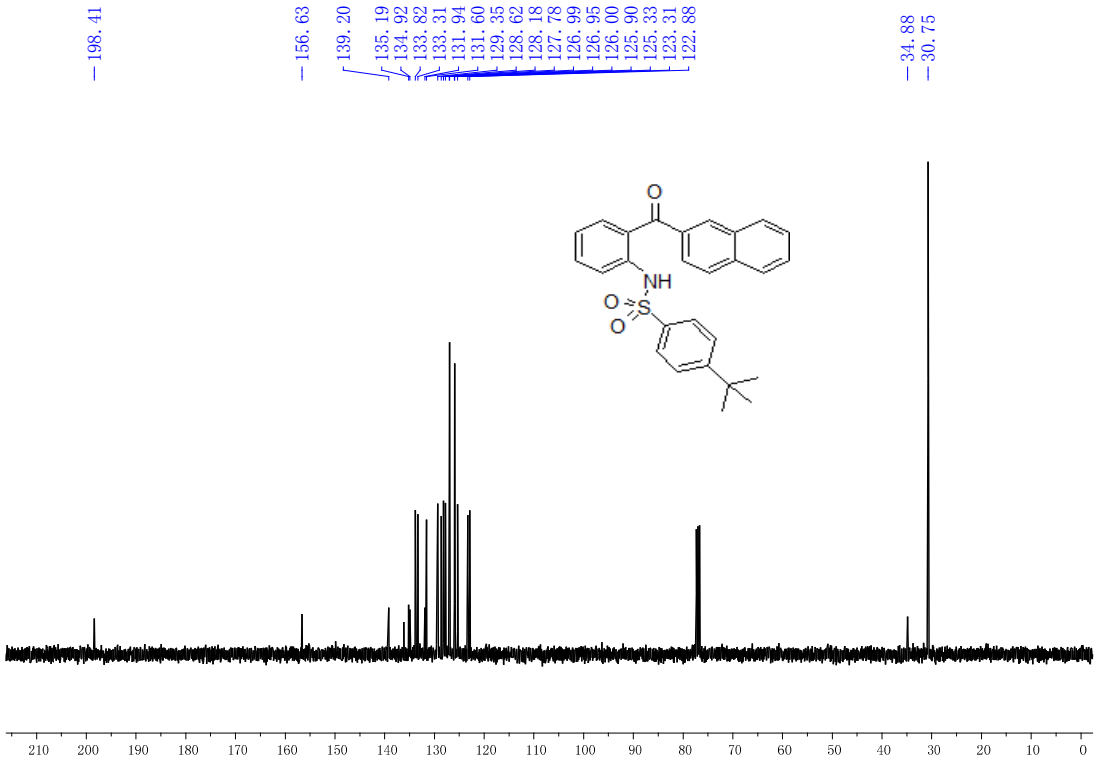

10.21
7.90
7.82
7.79
7.69
7.67
7.63
7.59
7.55
7.18
7.16
7.14
3.09
0.00
8.16
O
NHMs

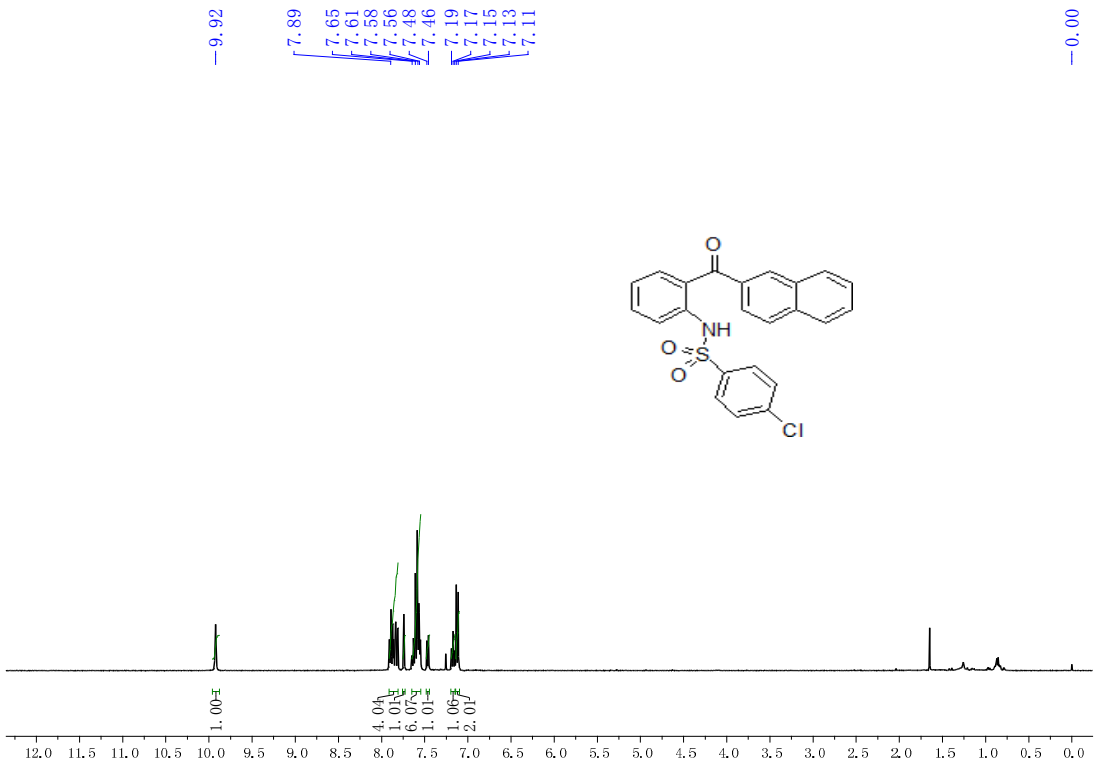

198.92
139.99
135.25
135.23
134.46
134.17
132.07
131.60
129.36
128.65
128.49
127.85
127.11
125.42
123.87
122.65
119.64
40.20
O
NHMs
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

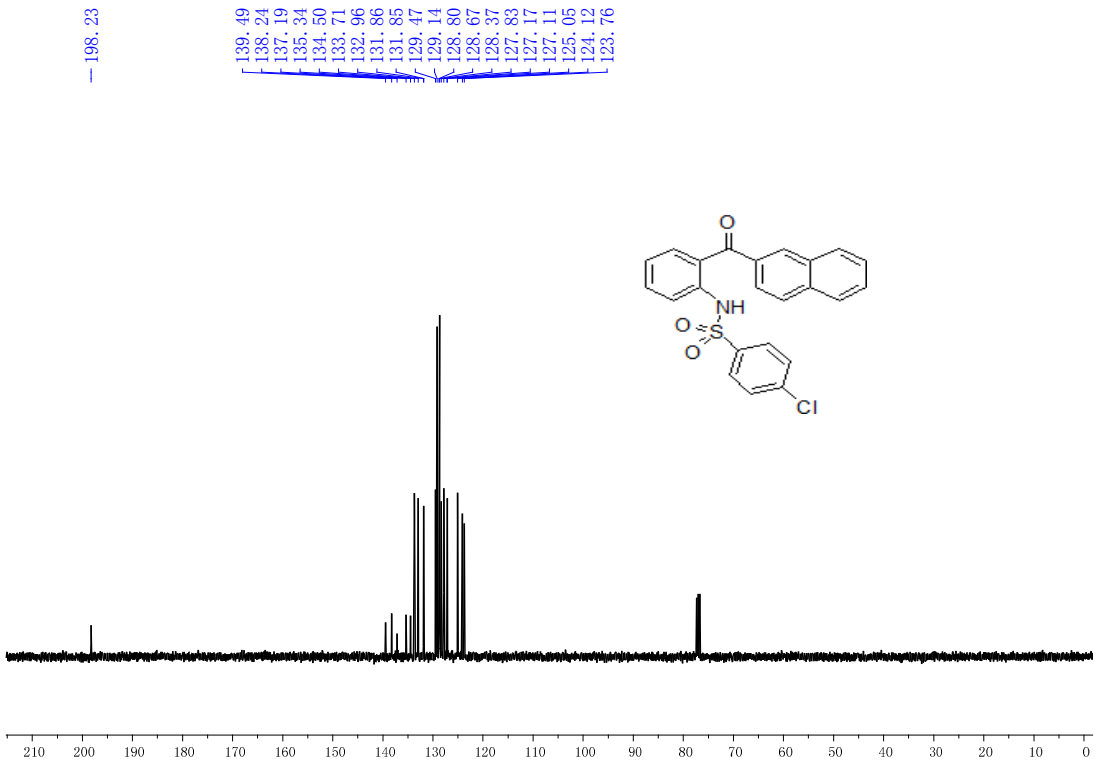

10.01
7.85
7.82
7.71
7.64
7.61
7.56
7.53
7.43
7.21
7.19
7.19
7.17
7.15
7.13
7.11
0.00
O
NHSO2Ph
1.00
4.03
3.04
4.00
1.04
3.01
1.03
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

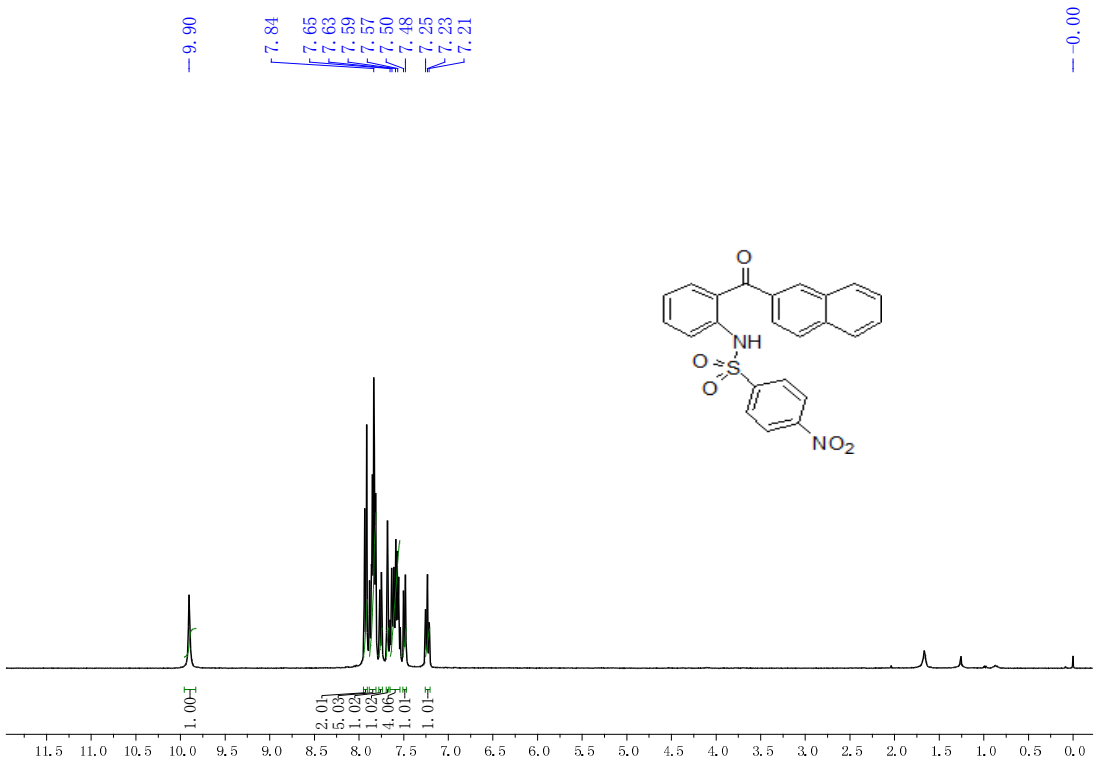

198.39
138.87
138.73
135.22
134.80
133.70
133.04
132.78
131.83
131.81
129.29
128.88
128.64
128.23
127.82
127.17
127.02
126.72
125.20
123.66
123.22
O
NHSO2Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

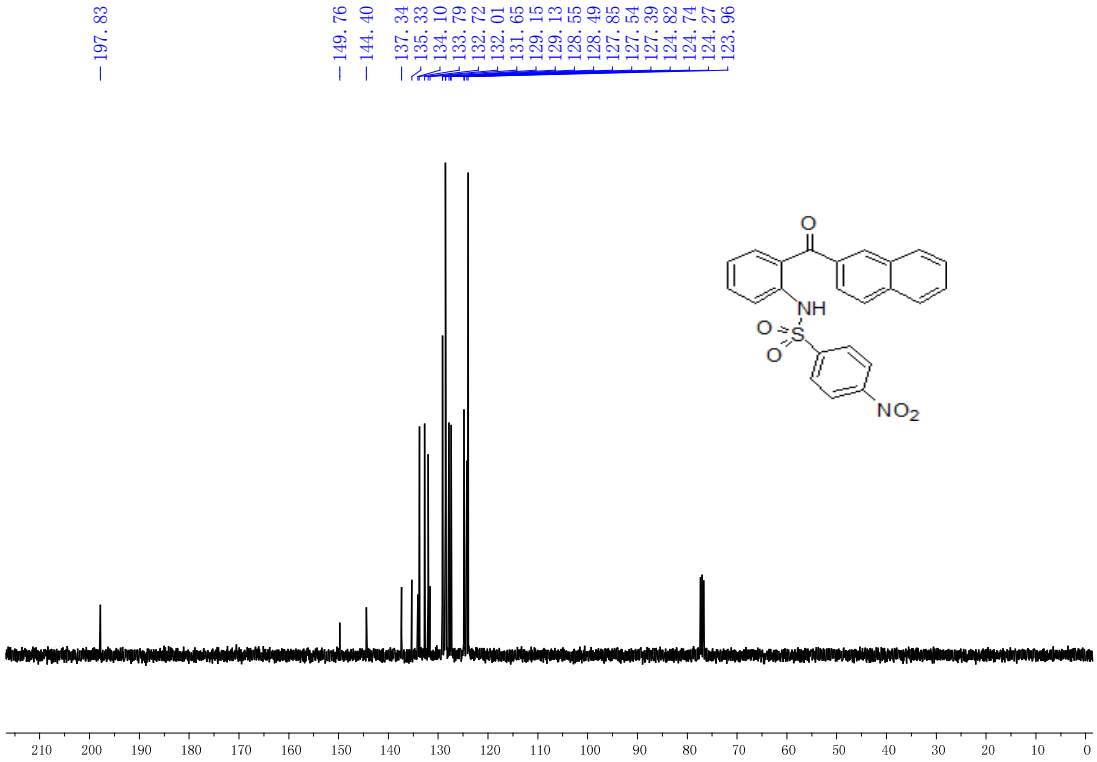

10.16
7.89
7.84
7.68
7.65
7.63
7.61
7.59
7.59
7.57
7.55
7.53
7.53
7.49
7.49
7.47
7.47
7.28
7.26
7.14
7.12
7.10
1.07
0.00
O
NH
O
S
O
1.00
5.01
2.03
4.02
1.01
2.01
1.00
9.02
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

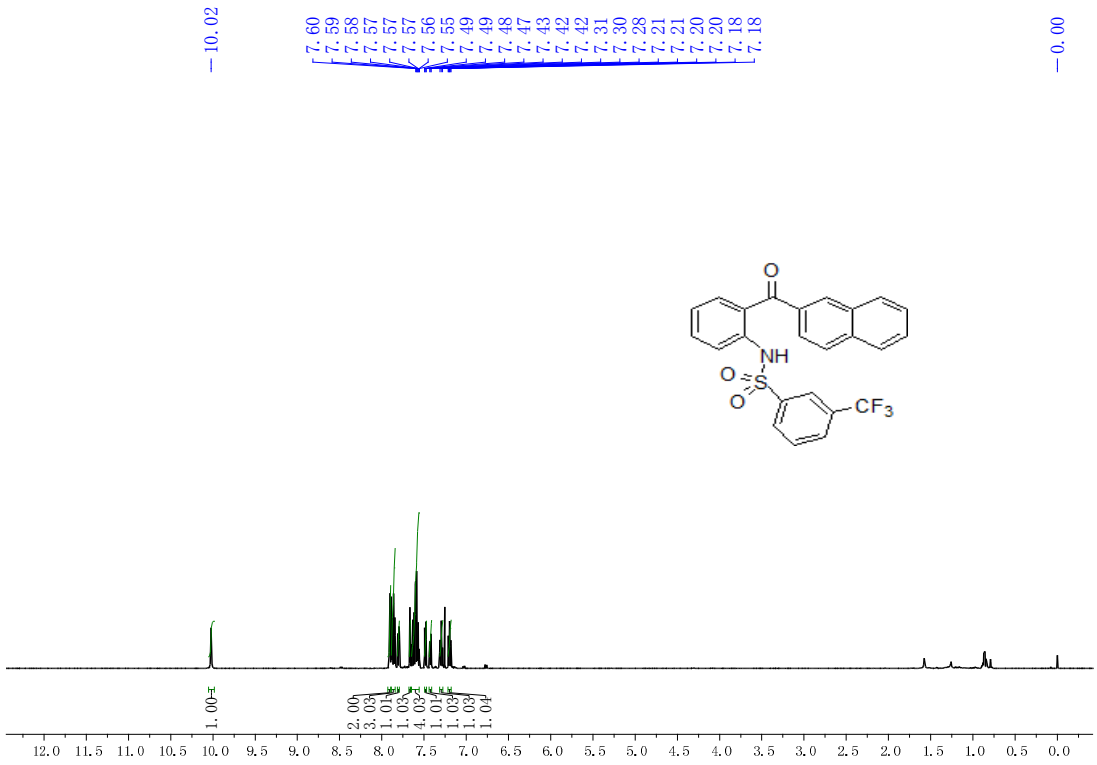

198.41
156.63
139.20
135.19
134.92
133.82
133.31
131.94
131.60
129.35
128.62
128.18
127.78
126.99
126.95
126.00
125.90
125.33
123.31
122.88
34.88
30.75
O
NH
O
S
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

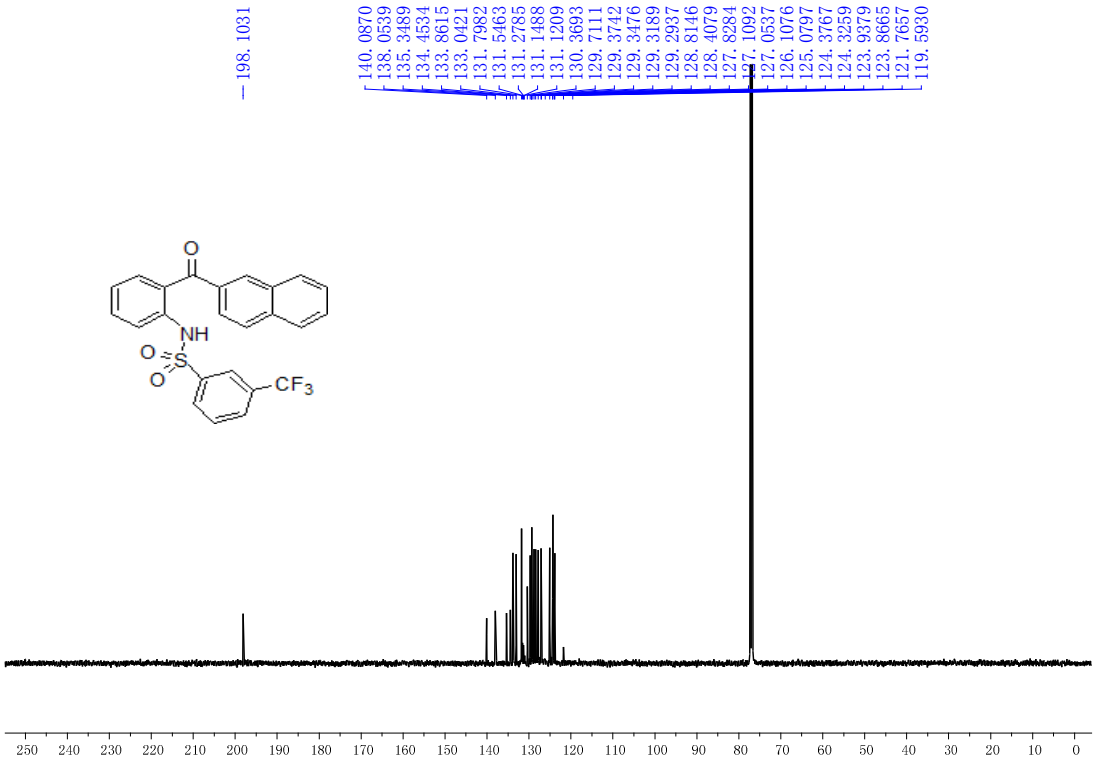

9.92
7.89
7.65
7.61
7.58
7.56
7.48
7.46
7.19
7.17
7.15
7.13
7.11
0.00
O
NH
O
S
O
Cl
1.00
4.04
1.01
6.07
1.01
1.06
2.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

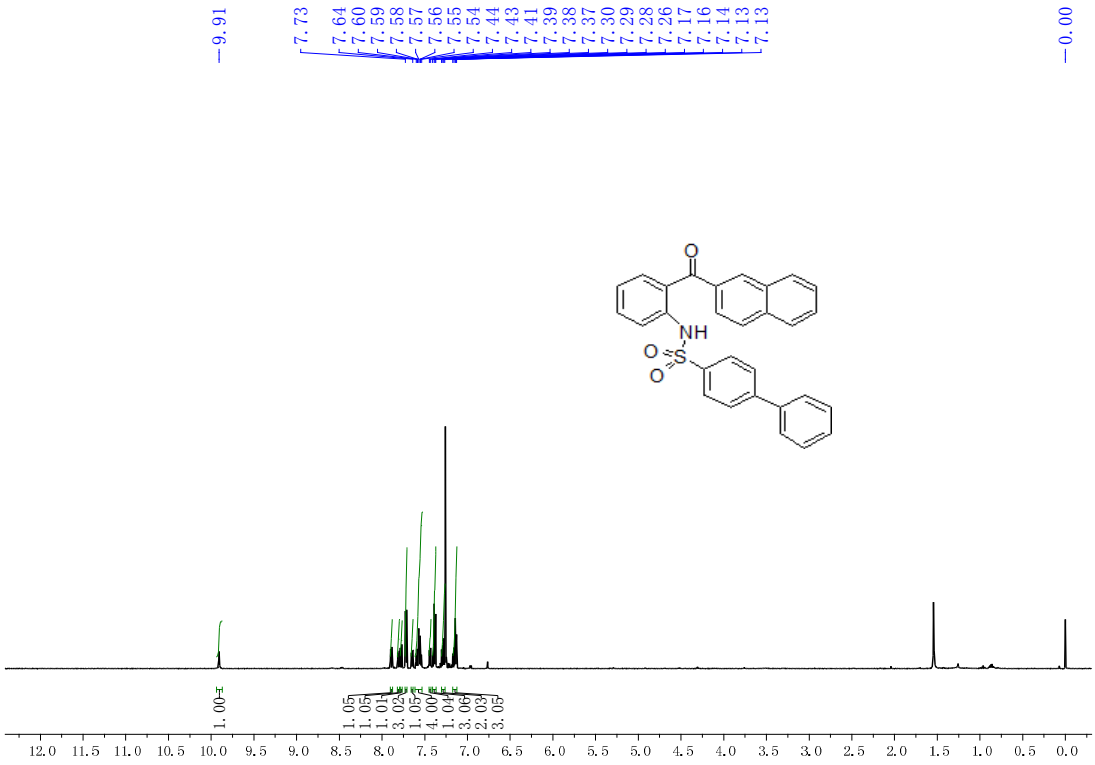

198.23
139.49
138.24
137.19
135.34
134.50
133.71
132.96
131.86
131.85
129.47
129.14
128.80
128.67
128.37
127.83
127.17
127.11
125.05
124.12
123.76
O
NH
O
S
O
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

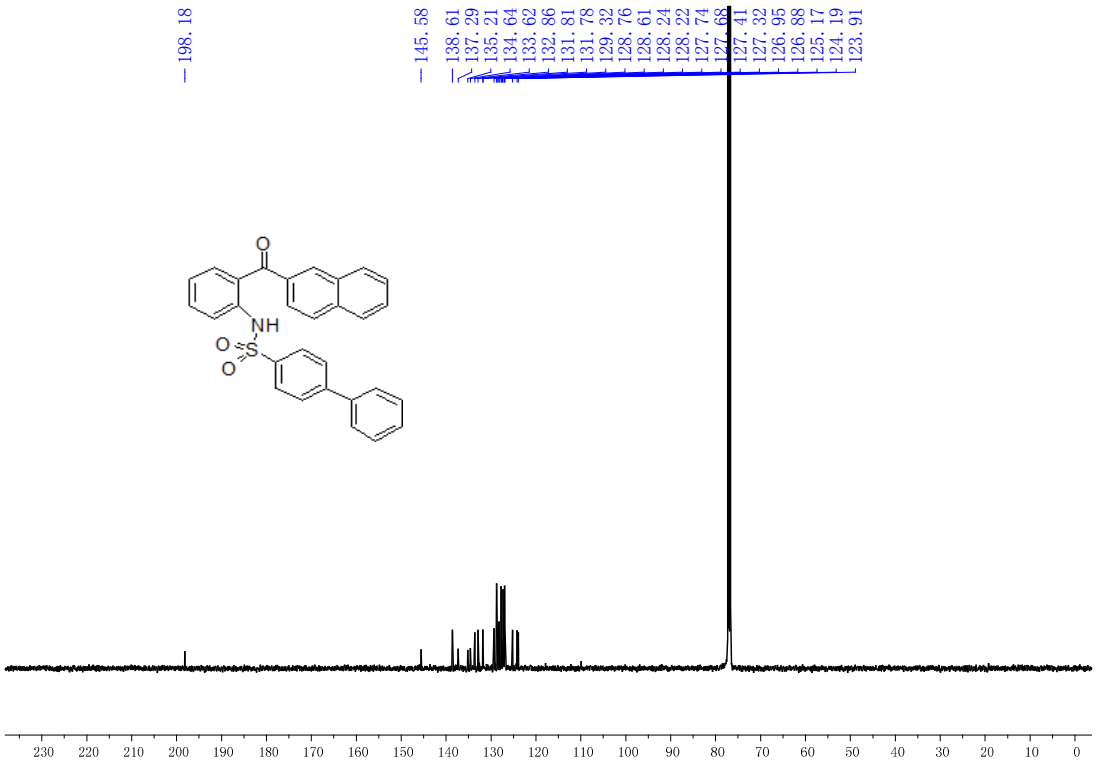

9.90
7.84
7.65
7.63
7.59
7.57
7.50
7.48
7.25
7.23
7.21
0.00
O
NH
O
S
O
NO2
1.00
2.01
5.03
1.02
1.02
4.06
1.01
1.01
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

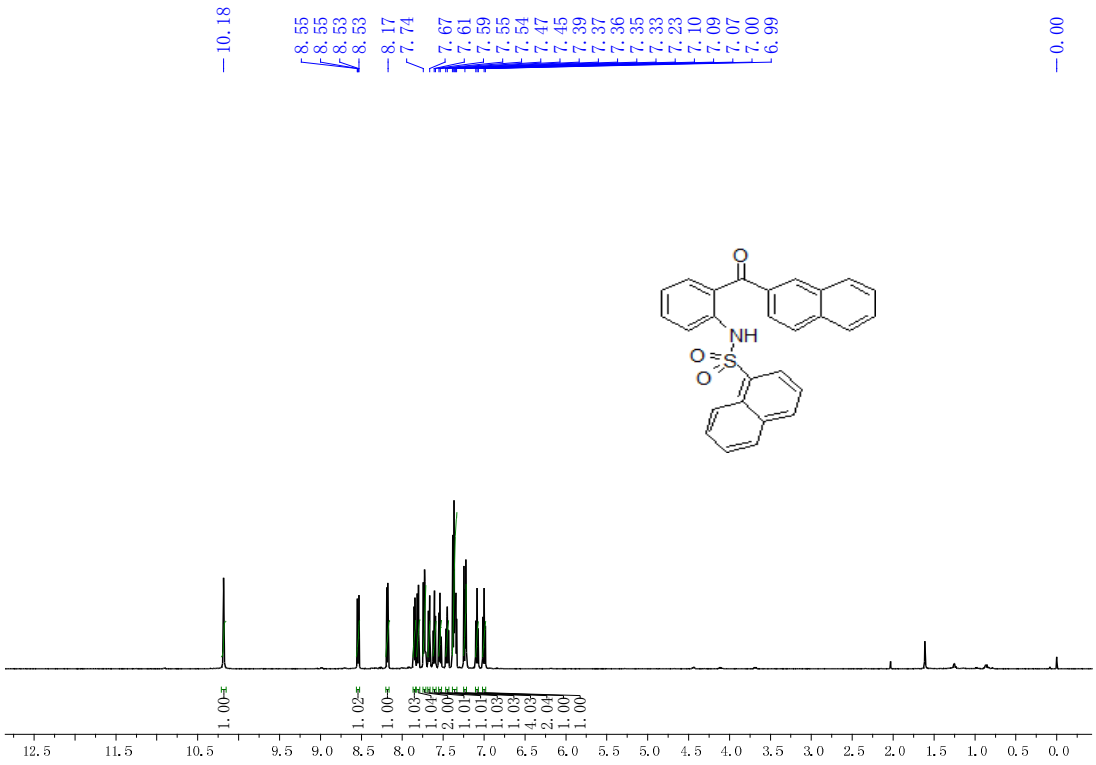

197.83
149.76
144.40
137.34
135.33
134.10
133.79
132.72
132.01
131.65
129.15
129.13
128.55
128.49
127.85
127.54
127.39
124.82
124.74
124.27
123.96
O
NH
O
S
O
NO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

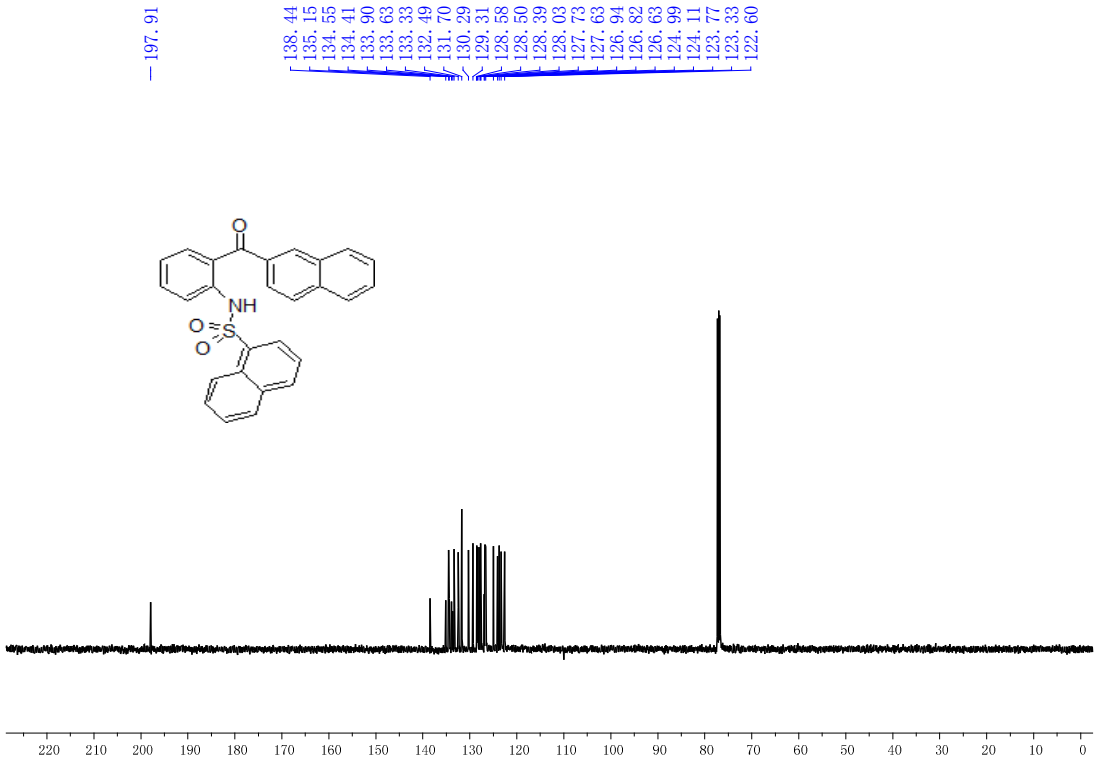

10.02
7.60
7.59
7.58
7.57
7.57
7.57
7.57
7.56
7.55
7.49
7.49
7.48
7.47
7.43
7.42
7.42
7.31
7.30
7.28
7.21
7.21
7.20
7.20
7.18
7.18
0.00
O
NH
O
S
O
CF3
1.00
2.00
3.03
1.01
1.03
4.03
1.01
1.03
1.03
1.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

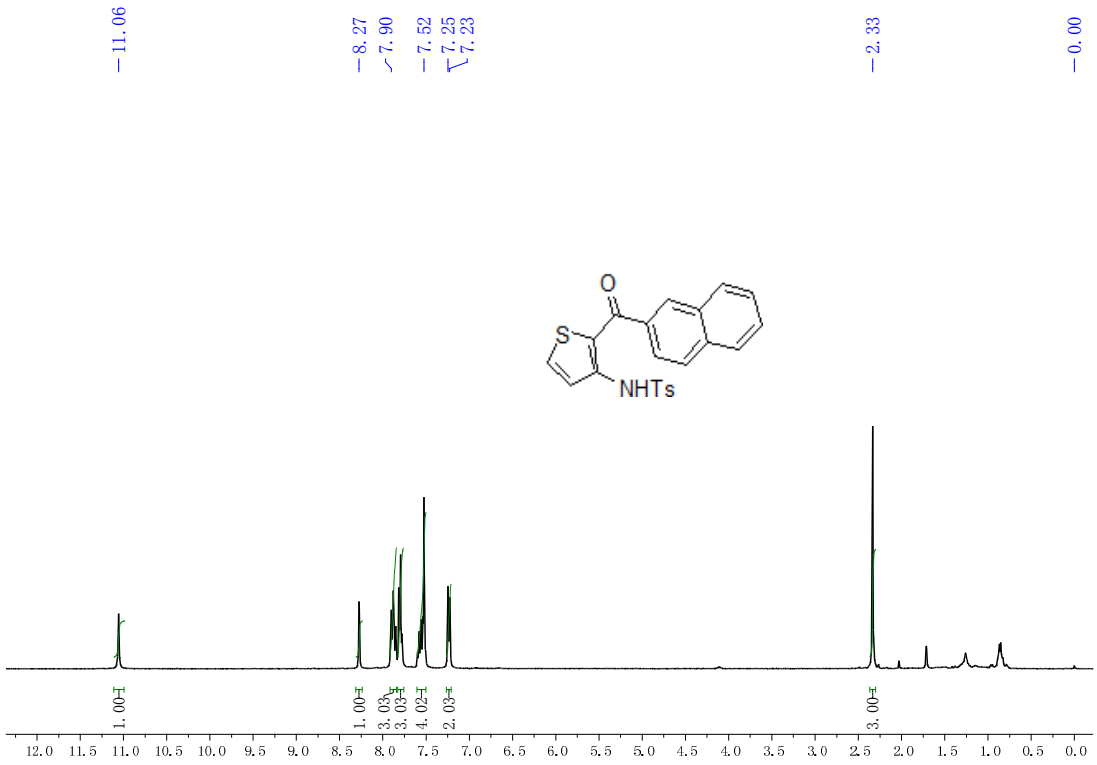

198.1031
140.0870
138.0539
135.3489
134.4534
133.8615
133.0421
131.7982
131.5463
131.2785
131.1488
131.1209
130.3693
129.7111
129.3742
129.3476
129.3189
129.2937
128.8146
128.4079
127.8284
127.1092
127.0537
126.1076
125.0797
124.3767
124.3259
123.9379
123.8665
121.7657
119.5930
O
NH
O
S
O
CF3
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

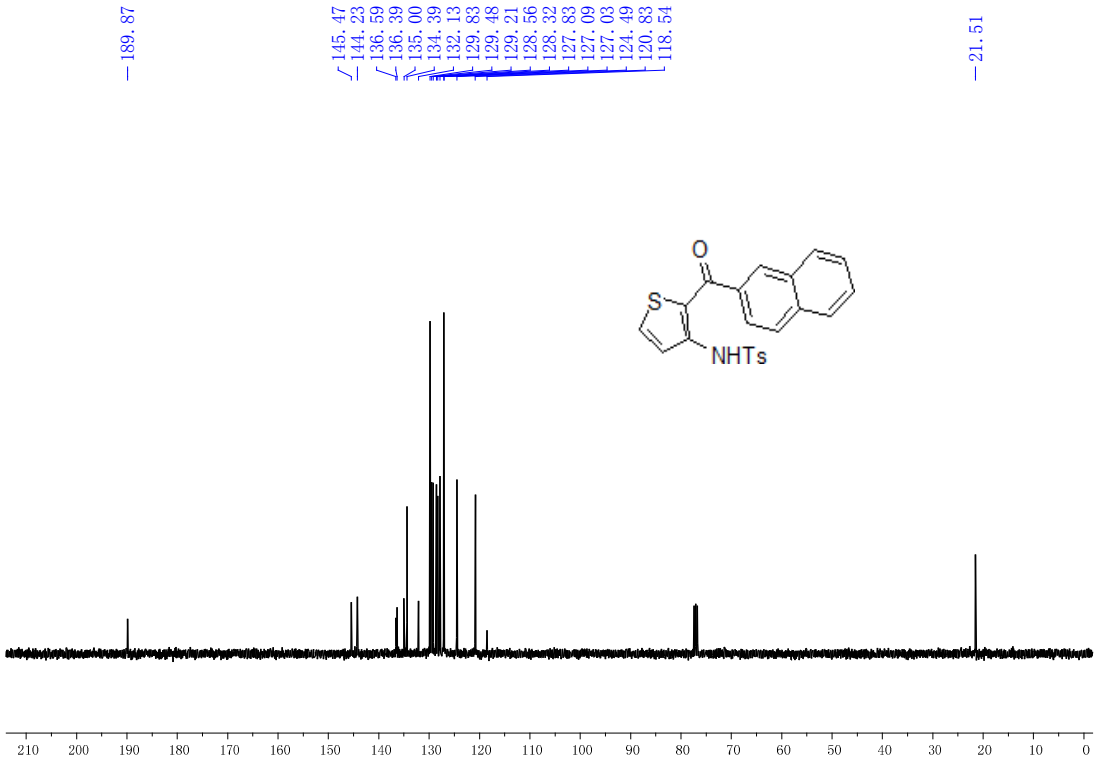

9.91
7.73
7.64
7.60
7.59
7.58
7.57
7.56
7.55
7.54
7.44
7.43
7.41
7.39
7.38
7.37
7.30
7.29
7.28
7.26
7.17
7.16
7.14
7.13
7.13
0.00
O
NH
O
S
O
1.00
1.05
1.05
1.01
3.02
1.05
4.00
1.04
3.06
2.03
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

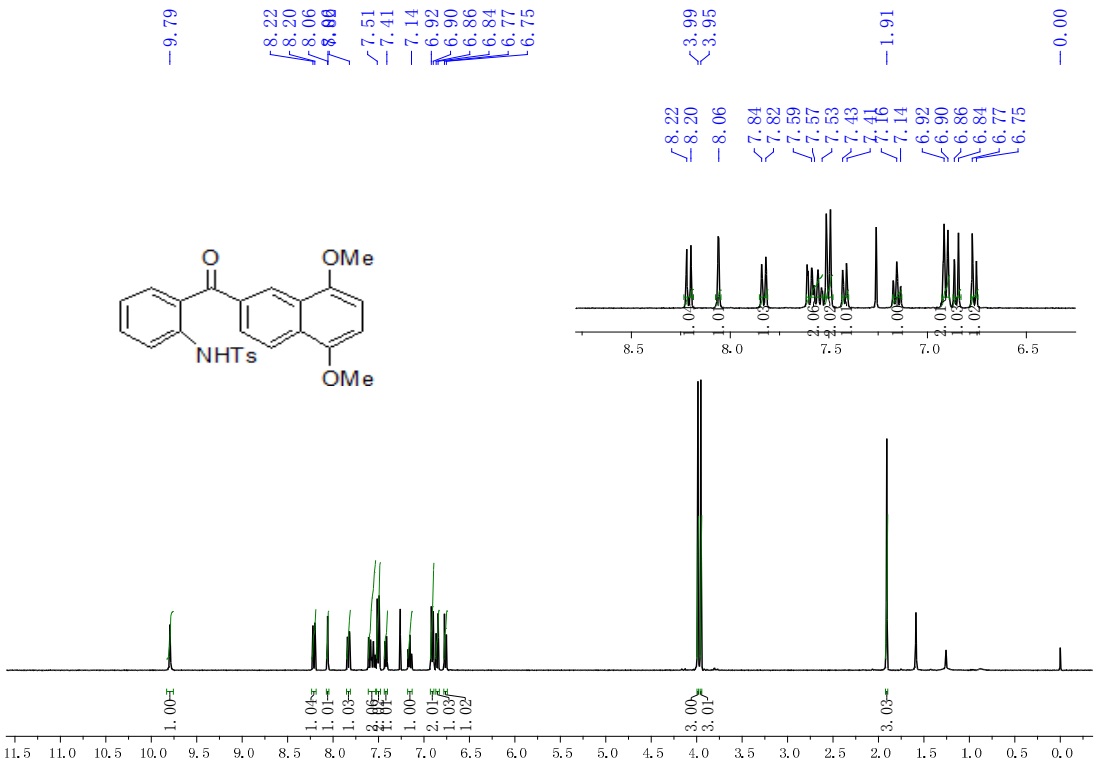

198.18
145.58
138.61
137.29
135.21
134.64
133.62
132.86
131.81
131.78
129.32
128.76
128.61
128.24
128.22
127.74
127.68
127.41
127.32
126.95
126.88
125.17
124.19
123.91
O
NH
O
S
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


10.18
8.55
8.55
8.53
8.53
8.17
7.74
7.67
7.61
7.59
7.55
7.54
7.47
7.45
7.39
7.37
7.36
7.35
7.33
7.23
7.10
7.09
7.07
7.00
6.99
0.00
O
NH
O
S
O
1.00
1.02
1.00
1.03
1.04
2.00
1.01
1.01
1.03
1.03
4.03
2.04
1.00
1.00
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

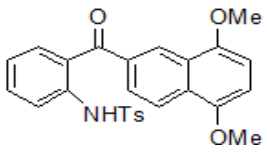

197.91
138.44
135.15
134.55
134.41
133.90
133.63
133.33
132.49
131.70
130.29
129.31
128.58
128.50
128.39
128.03
127.73
127.63
126.94
126.82
126.63
124.99
124.11
123.77
123.33
122.60
O
NH
O
S
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

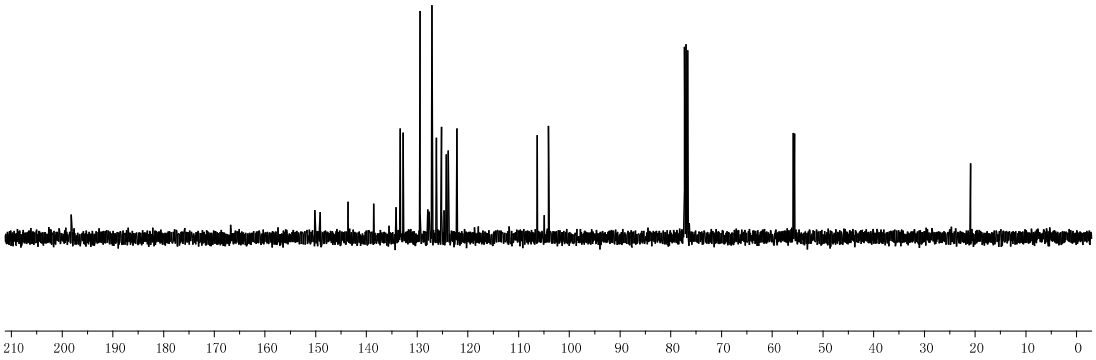

11.06
8.27
7.90
7.52
7.25
7.23
2.33
0.00
O
S
NHTs
1.00
1.00
3.03
3.03
4.02
2.03
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


189.87
145.47
144.23
136.59
136.39
135.00
134.39
132.13
129.83
129.48
129.21
128.56
128.32
127.83
127.09
127.03
124.49
120.83
118.54
21.51
O
S
NHTs

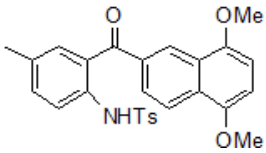

9.79
8.22
8.20
8.06
7.51
7.41
7.14
6.92
6.90
6.86
6.84
6.77
6.75
3.99
3.95
1.91
0.00
O
OMe
NHTs
OMe

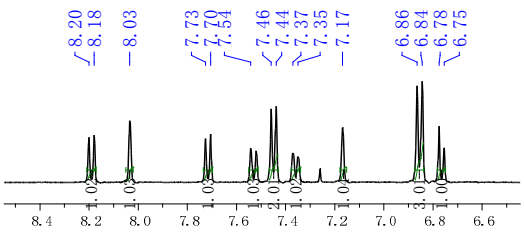
198.21
150.18
149.13
143.63
138.57
133.36
127.12
125.21
124.28
122.14
106.34
104.94
104.09
55.84
55.60
20.92

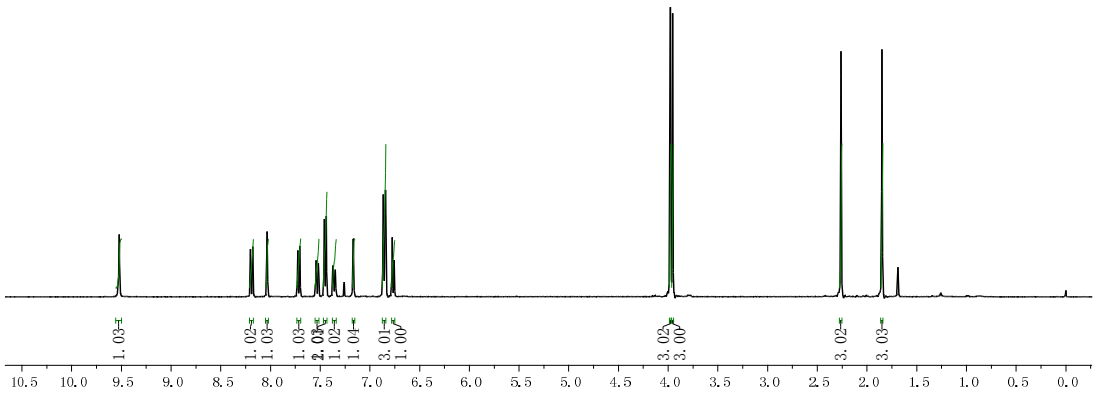


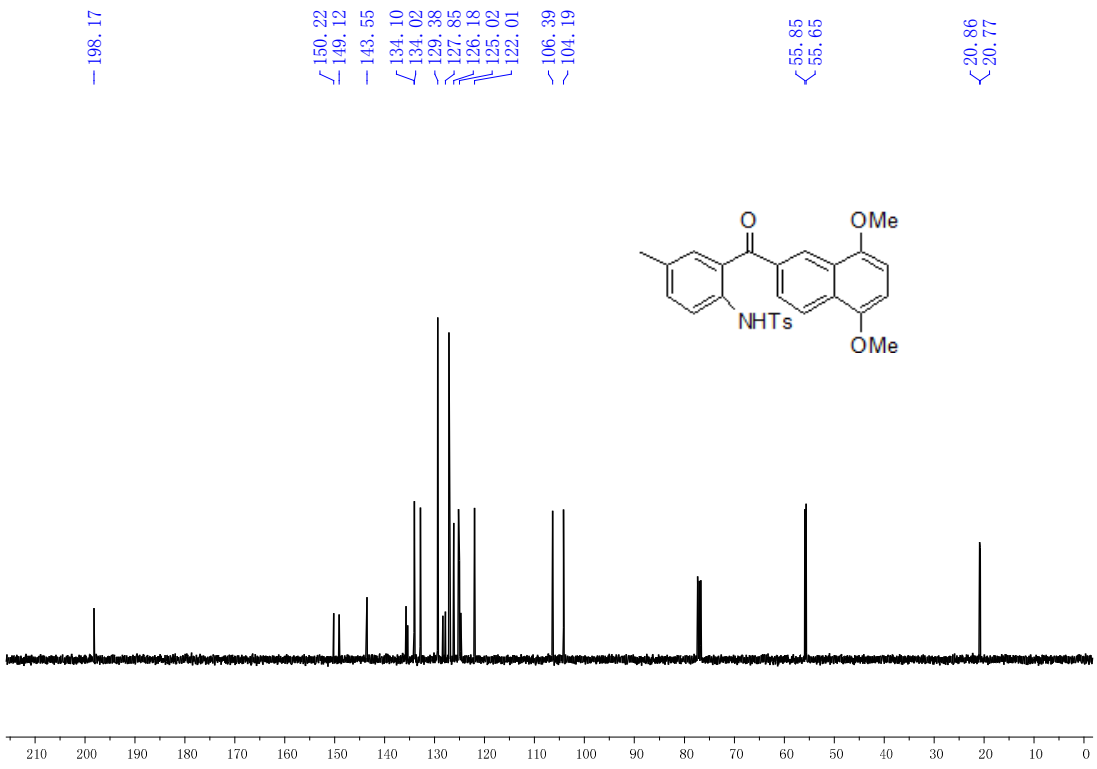


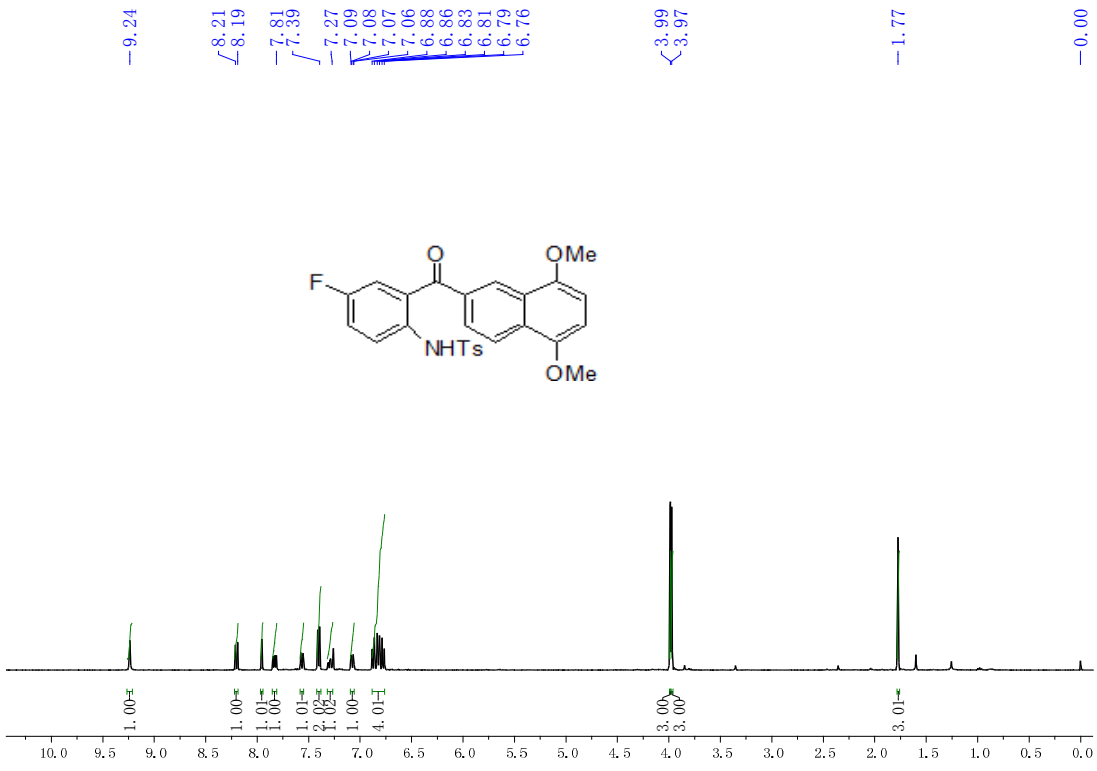
9.52
8.20
8.18
8.03
7.70
7.44
7.17
6.86
6.84
6.78
6.75
3.98
3.96
2.26
1.85
0.00



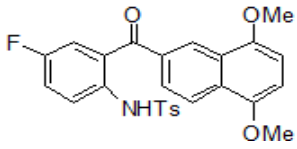


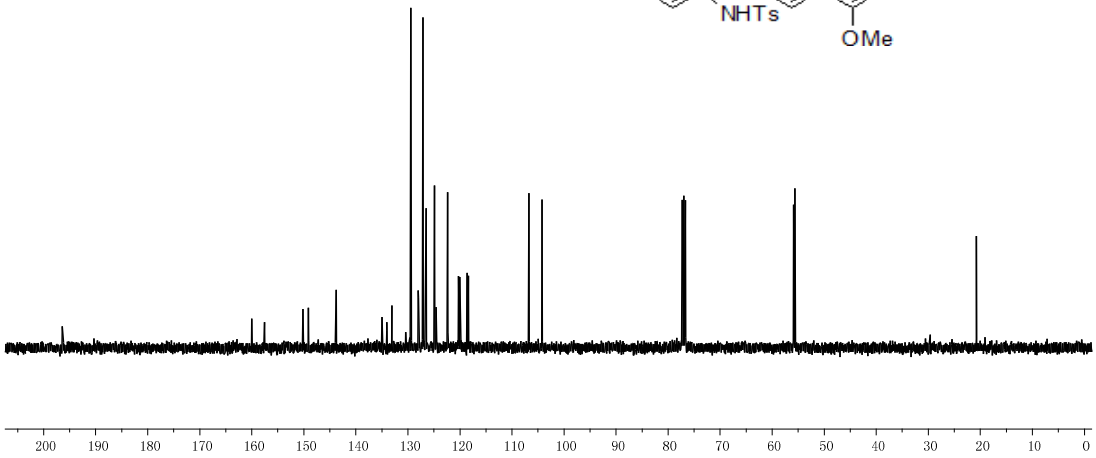



198.17
150.22
149.12
143.55
134.10
134.02
129.38
127.85
126.18
125.02
122.01
106.39
104.19
55.85
55.65
20.86
20.77
O
OMe
NHTs
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

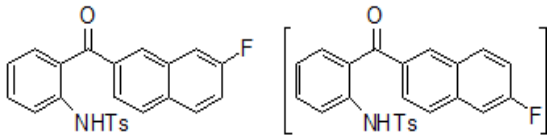

9.24
8.21
8.19
7.81
7.39
7.27
7.09
7.08
7.07
7.06
6.88
6.86
6.83
6.81
6.79
6.76
3.99
3.97
1.77
0.00
O
OMe
F
NHTs
OMe
1.00
1.00
1.01
1.00
1.01
2.02
1.00
4.01
3.00
3.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

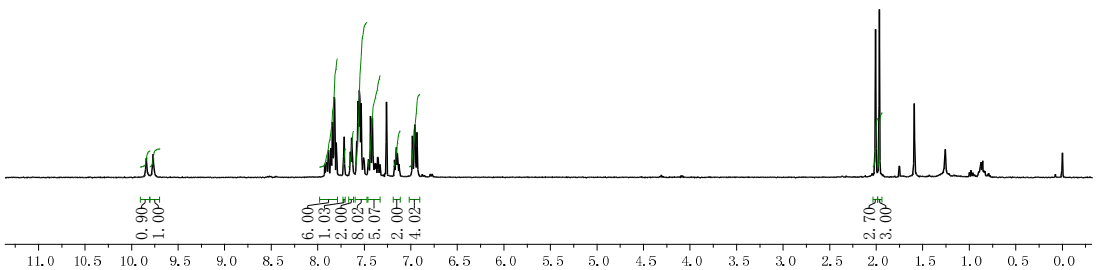
196.45
196.43
160.00
157.55
149.09
129.43
128.02
127.11
124.88
122.35
120.05
118.39
106.74
104.22
55.85
55.60
20.75



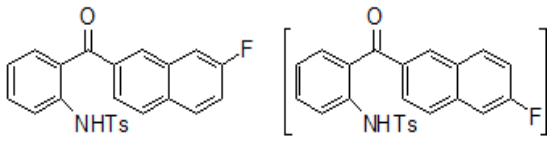


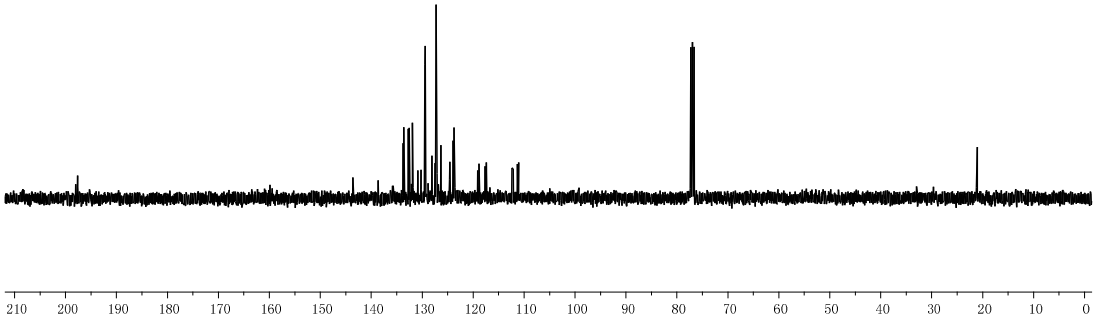
9.84
9.77
7.55
7.43
7.41
7.39
7.38
7.38
7.37
7.36
7.35
7.34
7.33
7.17
7.16
7.16
7.16
7.14
7.14
7.13
6.98
6.96
6.95
6.93
2.01
1.97
0.00



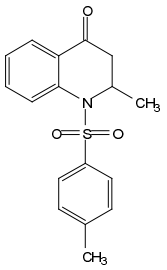


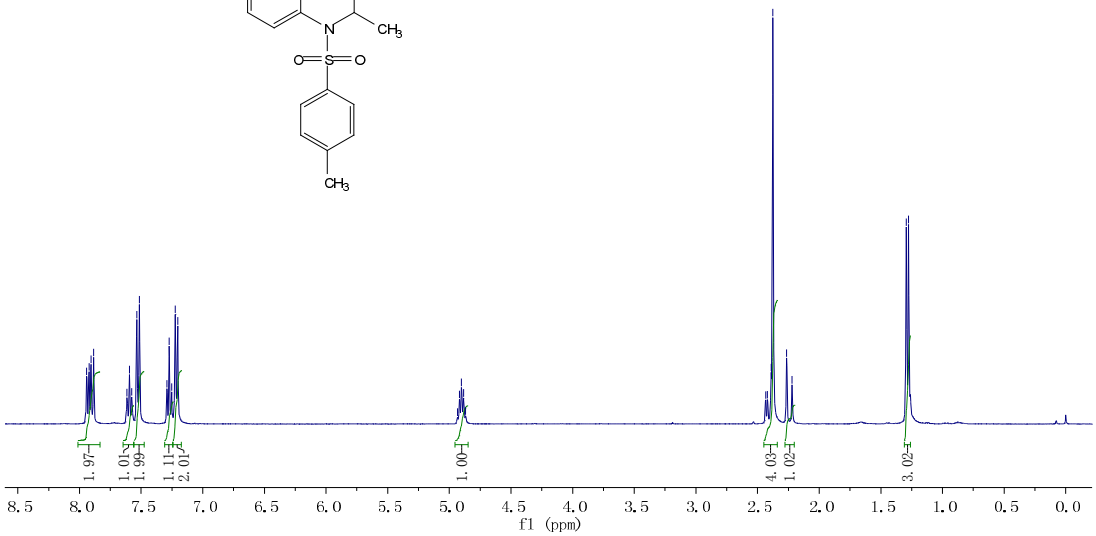
197.98
197.62
143.66
143.61
132.54
130.31
128.10
124.62
123.67
117.41
112.36
112.15
111.30
111.09
21.08
21.06

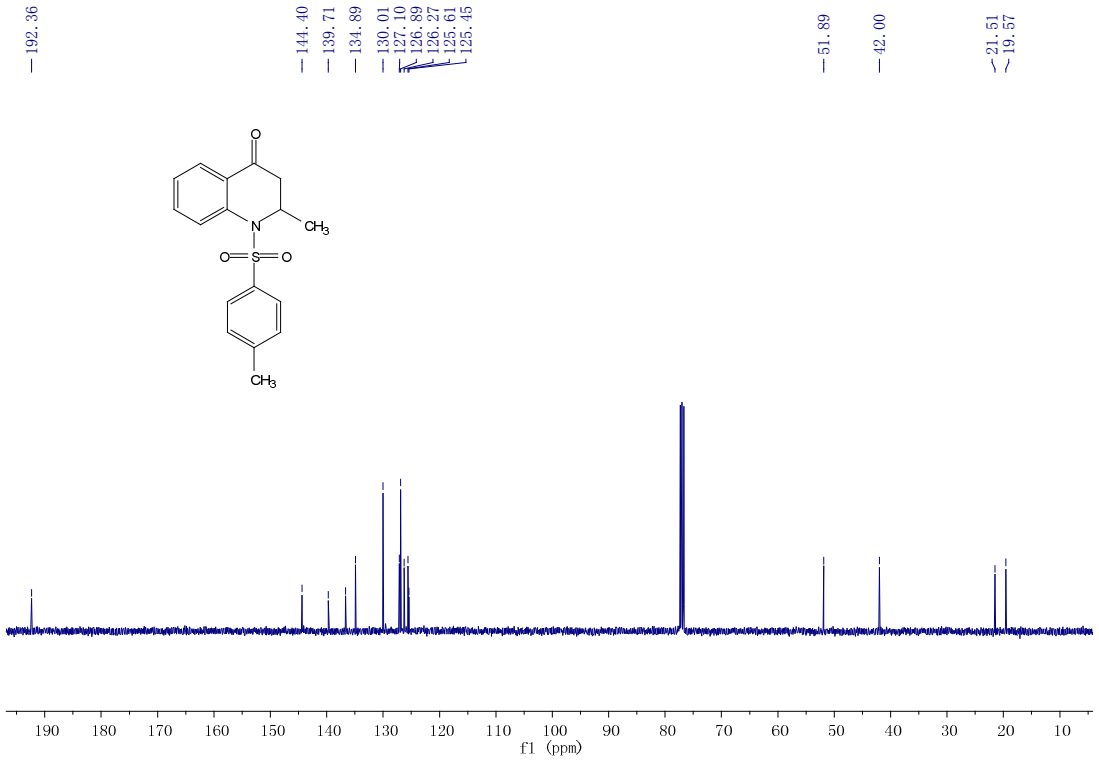


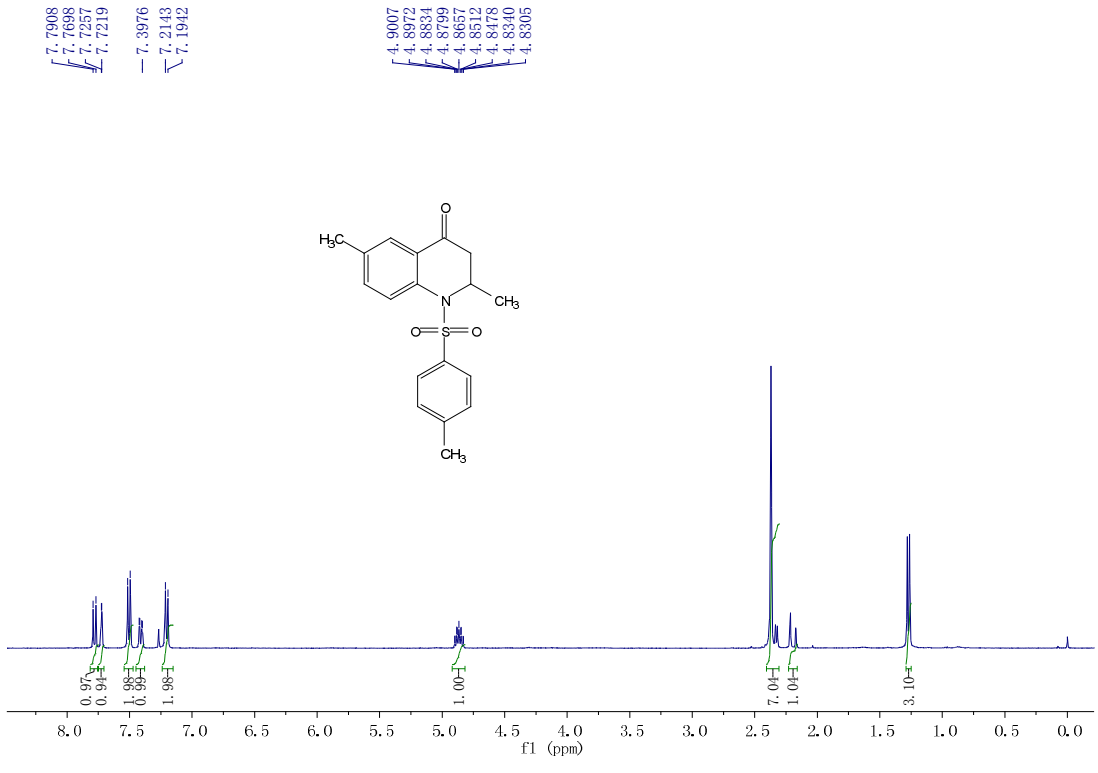


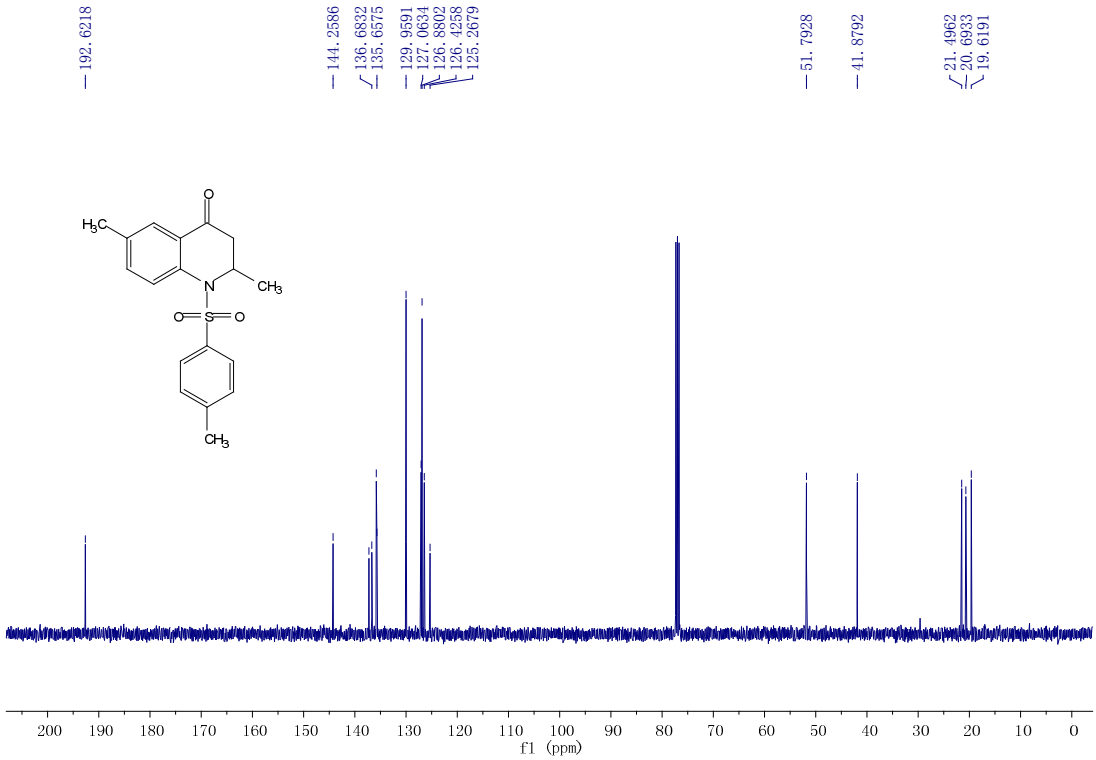
7.94
7.92
7.91
7.89
7.58
7.51
7.29
7.27
7.25
7.22
7.20
4.93
4.92
4.90
4.88
4.87
2.43
2.42
2.39
2.38
2.26
2.22
1.29
1.28

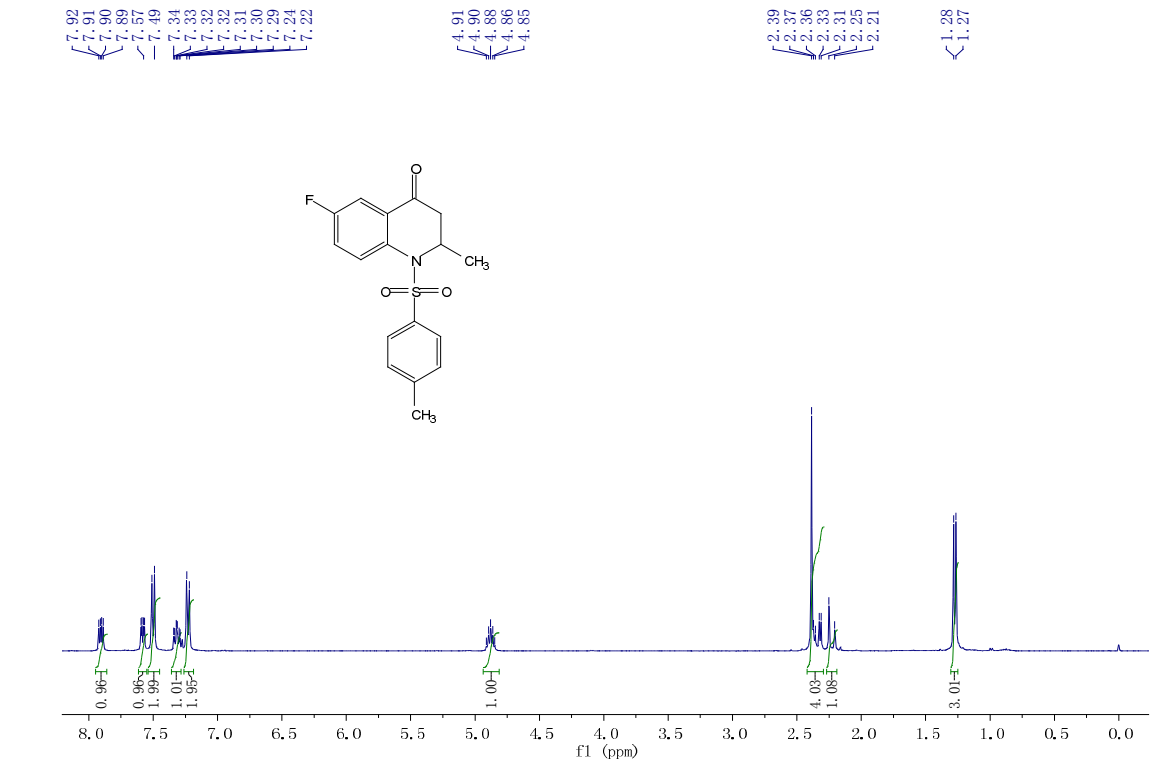


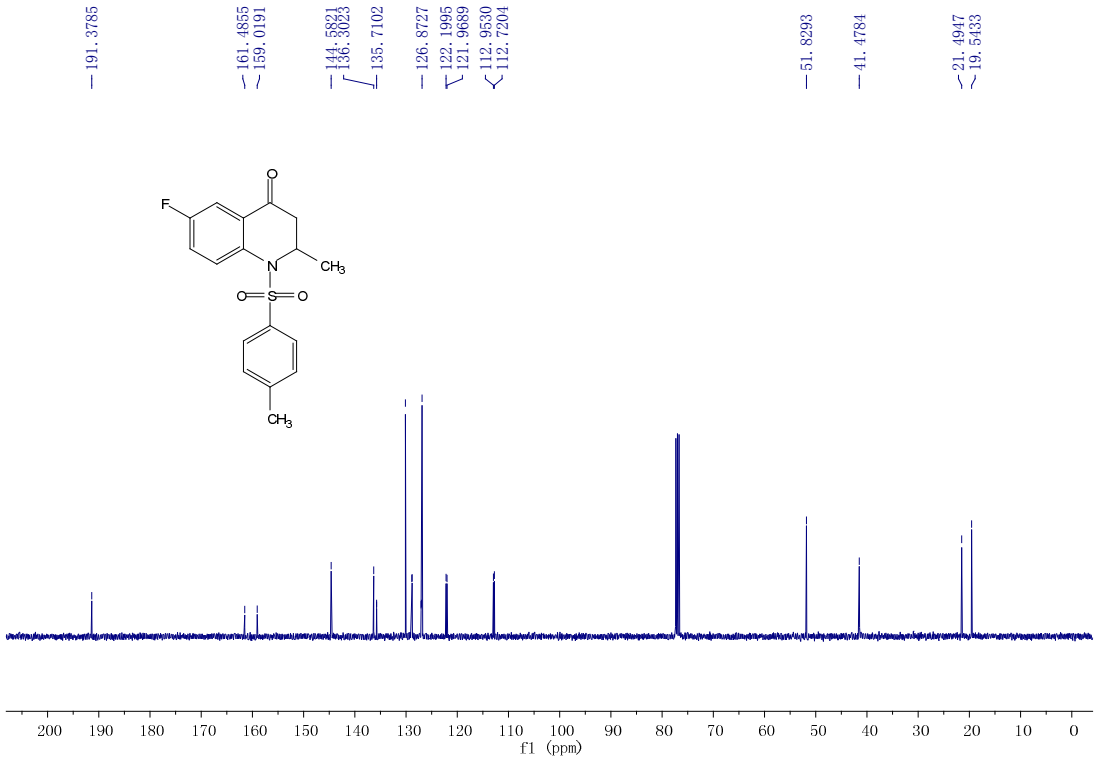


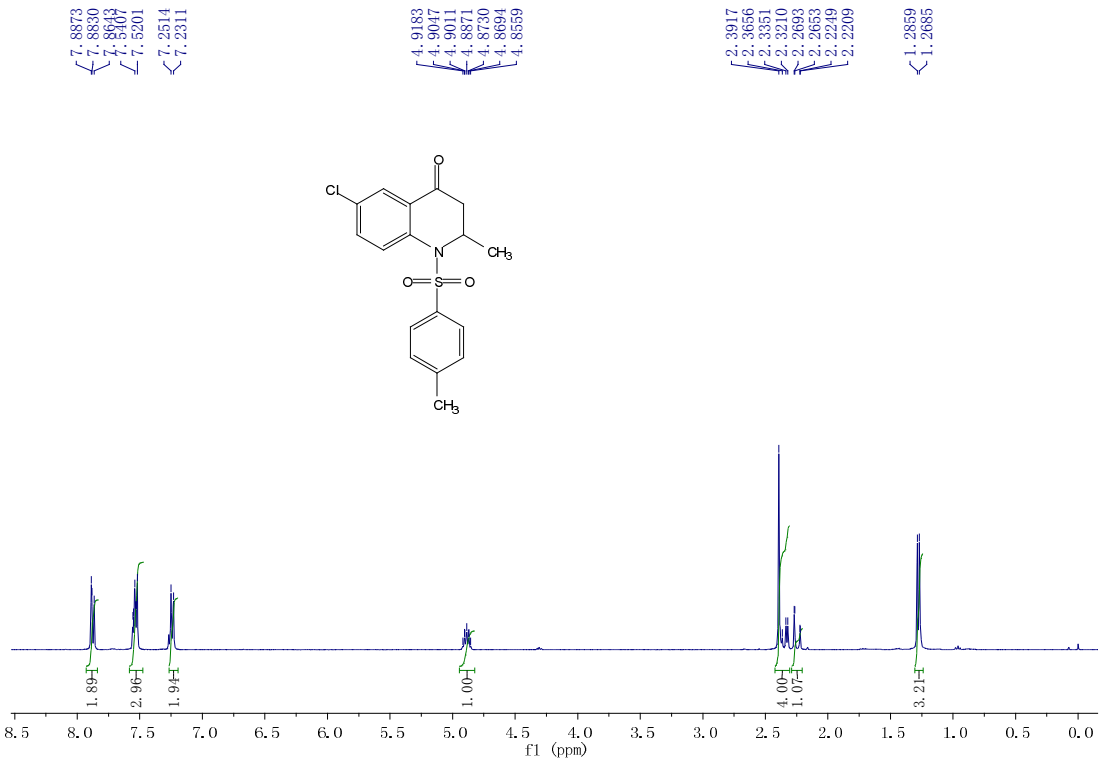

192.36
144.40
139.71
134.89
130.01
127.10
126.89
126.27
125.61
125.45
51.89
42.00
21.51
19.57
O
N
CH3
O=S=O
CH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

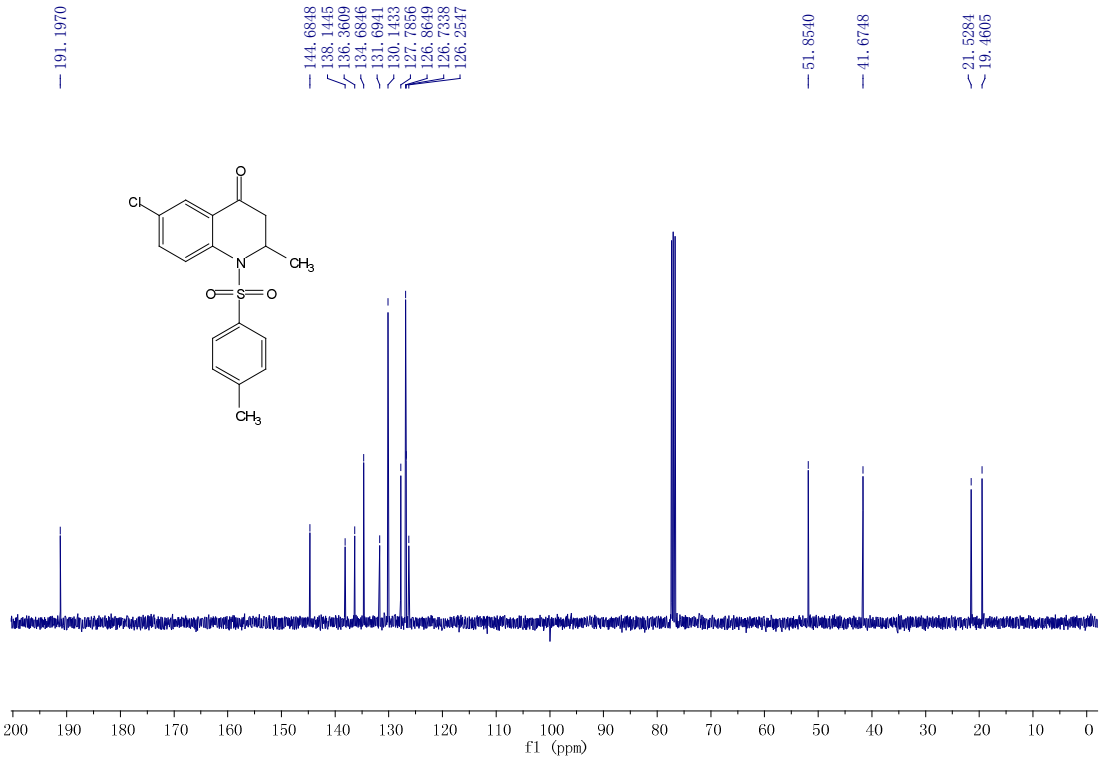

7.7908
7.7698
7.7257
7.7219
7.3976
7.2143
7.1942
4.9007
4.8972
4.8834
4.8799
4.8657
4.8512
4.8478
4.8340
4.8305
H3C
O
N
CH3
O=S=O
CH3
0.97
0.94
1.98
0.99
1.98
1.00
7.04
1.04
3.10
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

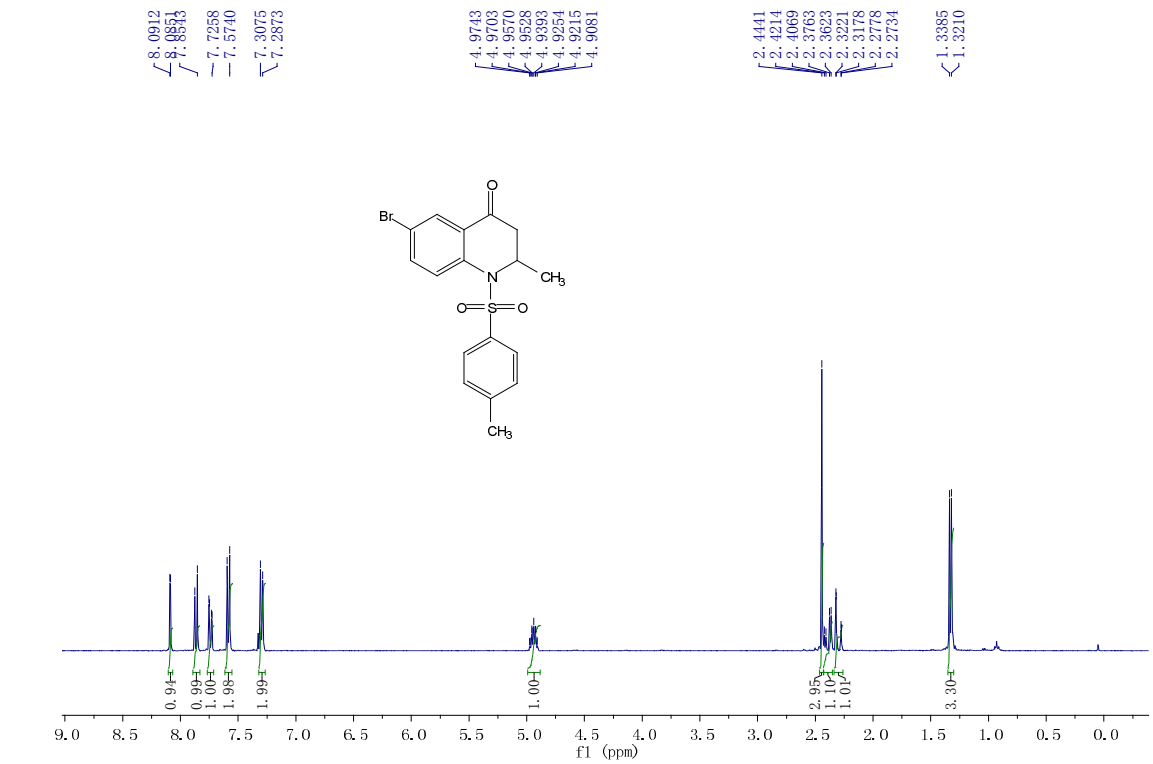

192.6218
144.2586
136.6832
135.6575
129.9591
127.0634
126.8802
126.4258
125.2679
51.7928
41.8792
21.4962
20.6933
19.6191
H3C
O
N
CH3
O=S=O
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

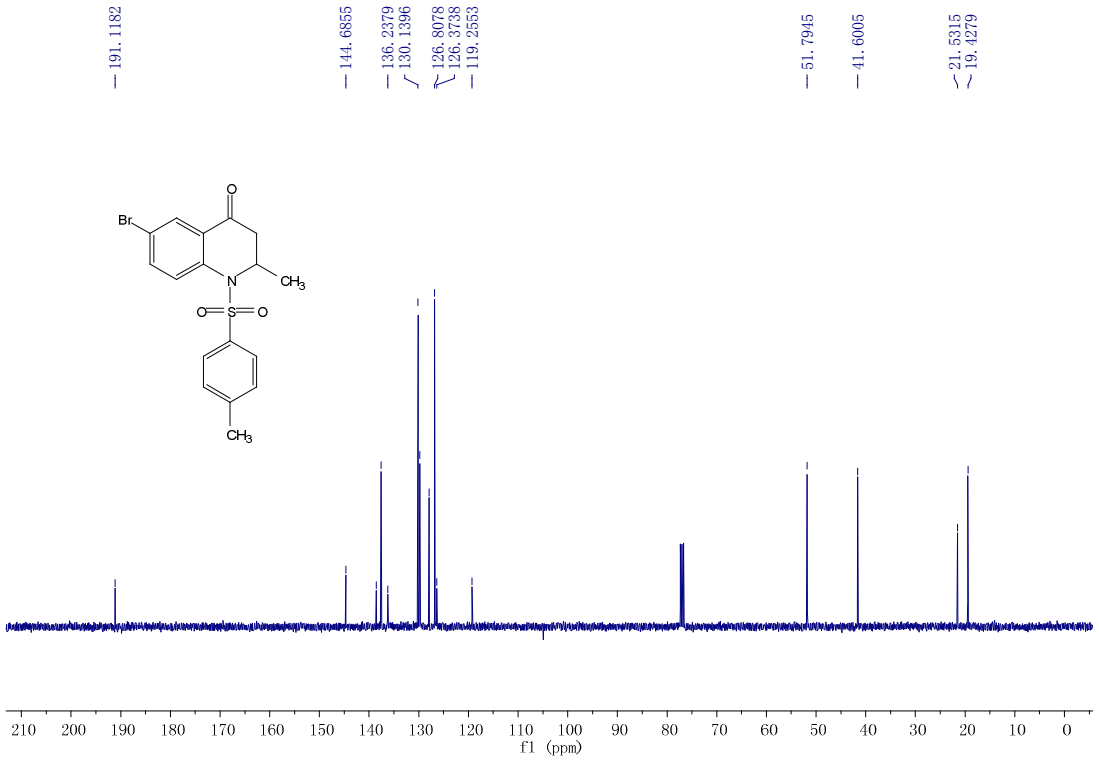

7.92
7.91
7.90
7.89
7.57
7.49
7.34
7.33
7.32
7.32
7.31
7.30
7.29
7.24
7.22
4.91
4.90
4.88
4.86
4.85
2.39
2.37
2.36
2.33
2.31
2.25
2.21
1.28
1.27
F
O
N
CH3
O=S=O
CH3
0.96
0.96
1.99
1.01
1.95
1.00
4.03
1.08
3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

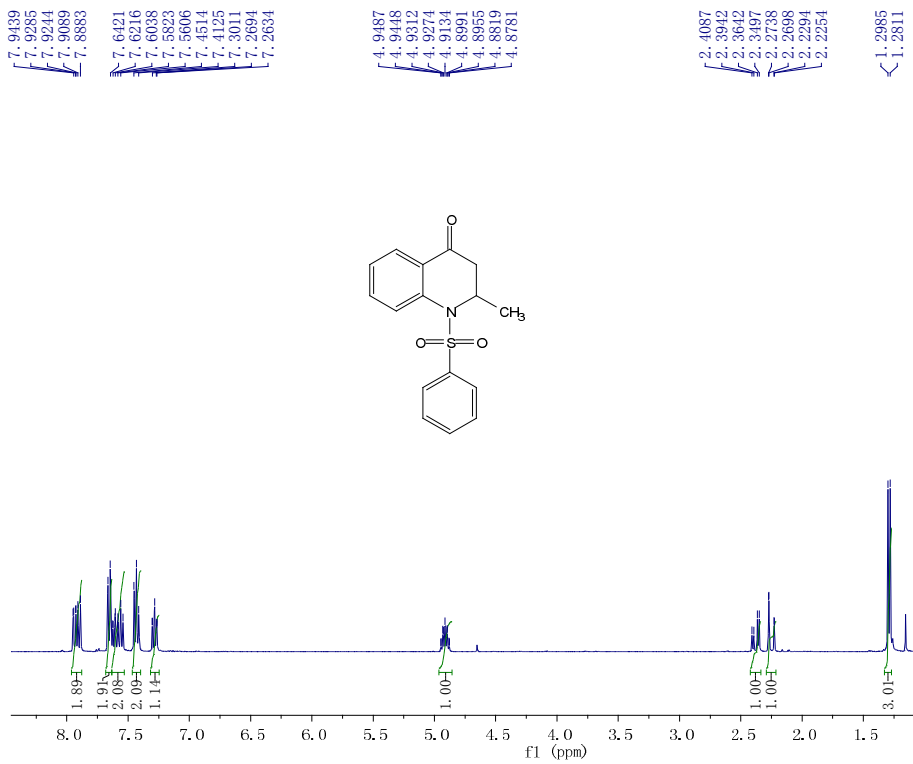

191.3785
161.4855
159.0191
144.5821
136.3023
135.7102
126.8727
122.1995
121.9689
112.9530
112.7204
51.8293
41.4784
21.4947
19.5433
O
F
N
CH3
O
S
O
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

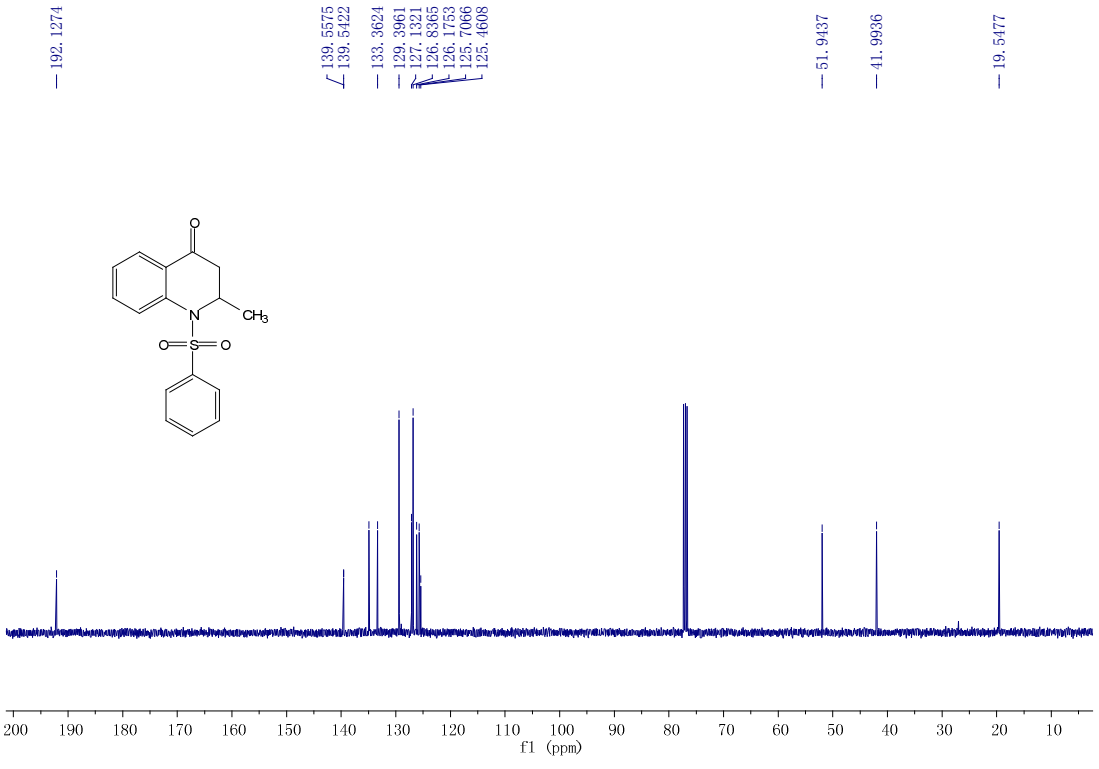

7.8873
7.8830
7.8643
7.5407
7.5201
7.2514
7.2311
4.9183
4.9047
4.9011
4.8871
4.8730
4.8694
4.8559
2.3917
2.3656
2.3351
2.3210
2.2093
2.2653
2.2249
2.2209
1.2859
1.2685
Cl
O
N
CH3
O=S=O
CH3
1.89
2.96
1.94
1.00
4.00
1.07
3.21
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

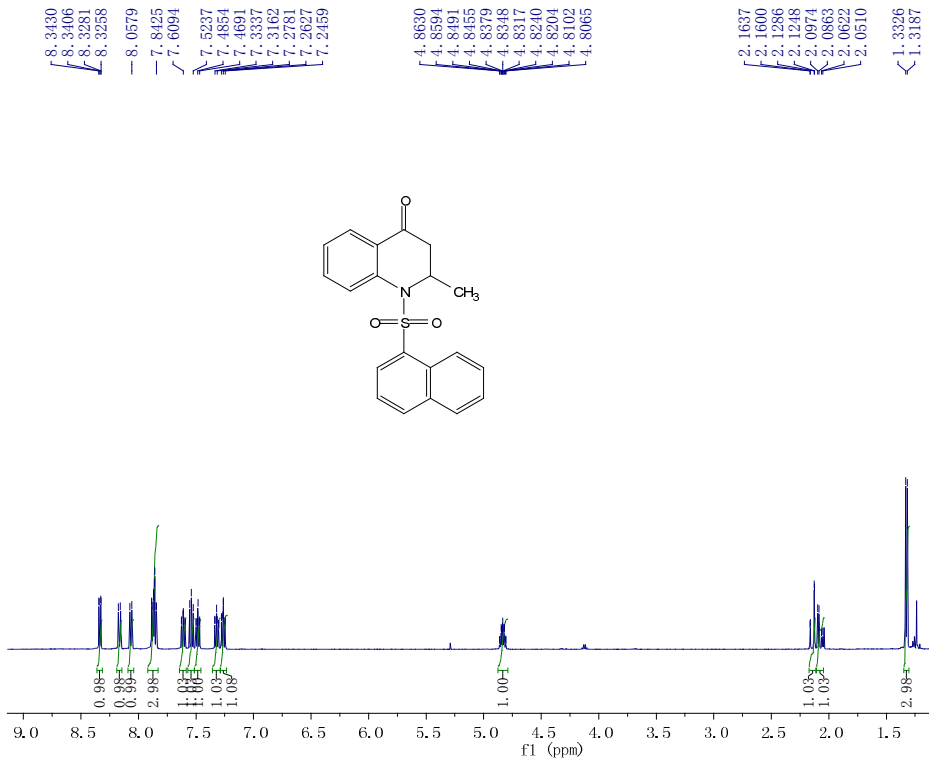

191.1970
144.6848
138.1445
136.3609
134.6846
131.6941
130.1433
127.7856
126.8649
126.7338
126.2547
51.8540
41.6748
21.5284
19.4605
Cl
O
N
CH3
O=S=O
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

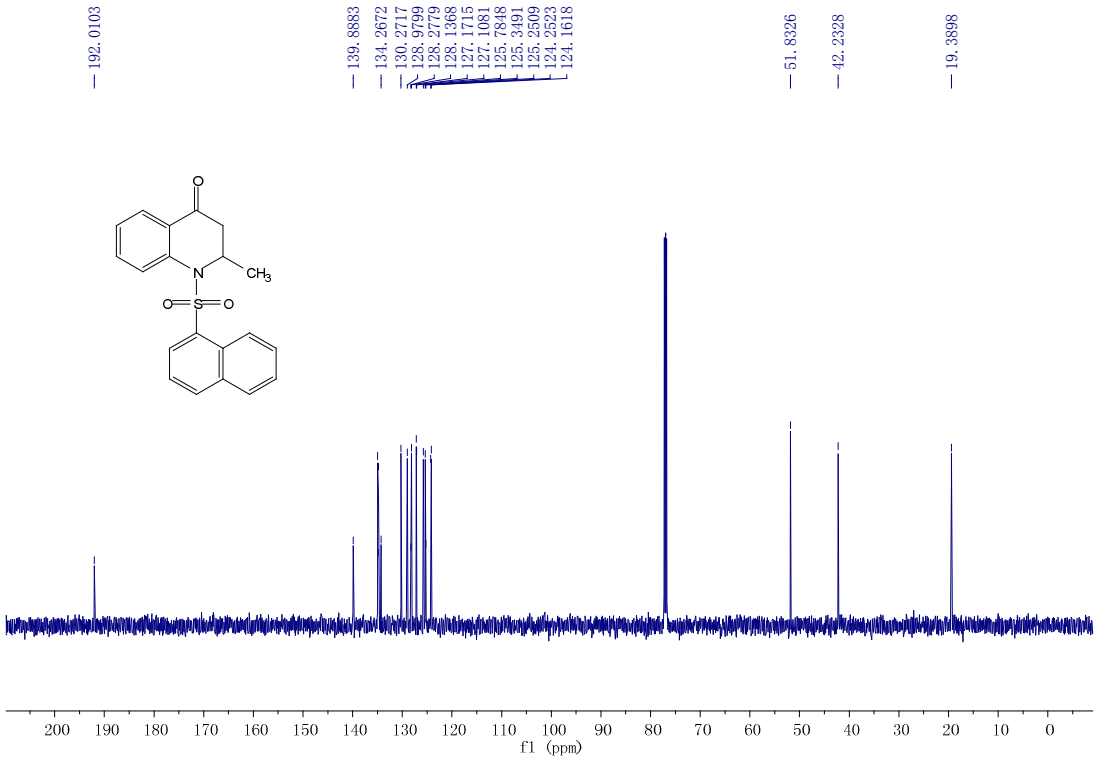

8.0912
8.0851
7.8543
7.7258
7.5740
7.3075
7.2873
4.9743
4.9703
4.9570
4.9528
4.9393
4.9254
4.9215
4.9081
2.4441
2.4214
2.4069
2.3763
2.3623
2.3221
2.3178
2.2778
2.2734
1.3385
1.3210
Br
O
N
S
O
O
CH3
CH3
0.94
0.99
1.00
1.98
1.99
1.00
2.95
1.10
1.01
3.30
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

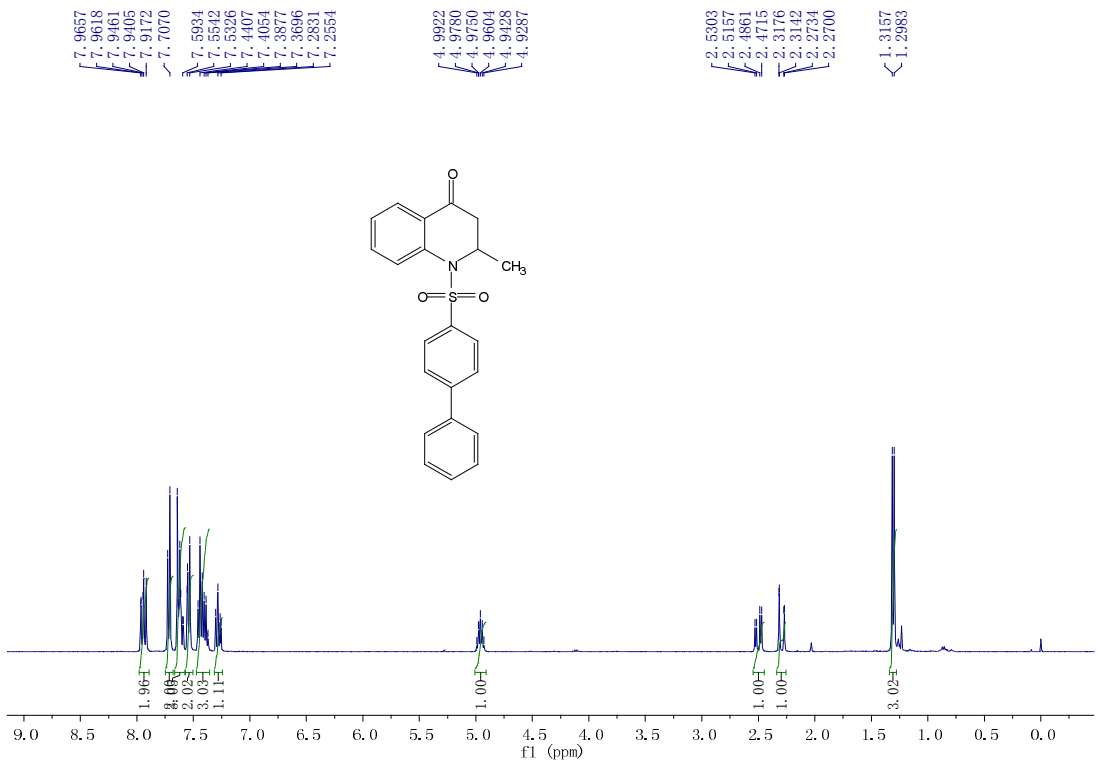

191.1182
144.6855
136.2379
130.1396
126.8078
126.3738
119.2553
51.7945
41.6005
21.5315
19.4279
Br
O
N
S
O
O
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

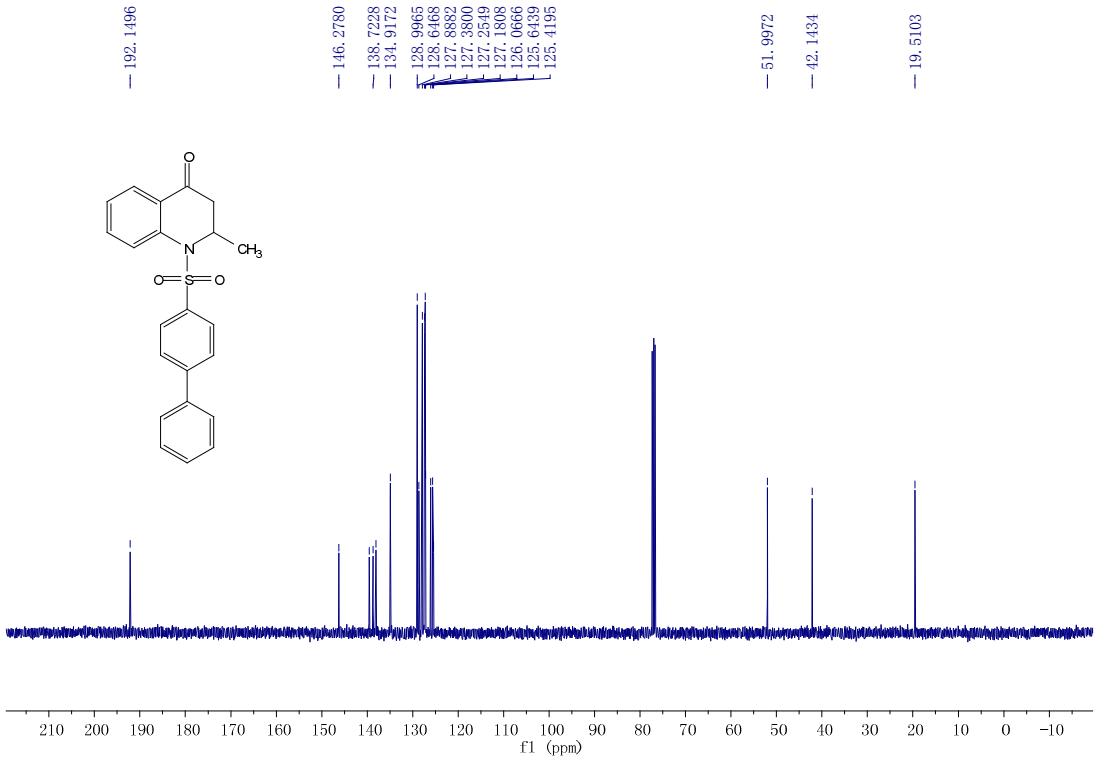

7.9439
7.9285
7.9244
7.9089
7.8883
7.6421
7.6216
7.6038
7.5823
7.5606
7.4514
7.4125
7.3011
7.2694
7.2634
4.9487
4.9448
4.9312
4.9274
4.9134
4.8991
4.8955
4.8819
4.8781
2.4087
2.3942
2.3642
2.3497
2.2738
2.2698
2.2294
2.2254
1.2985
1.2811
O
N
CH3
O=S=O
1.89
1.91
2.08
2.09
1.14
1.00
1.00
1.00
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

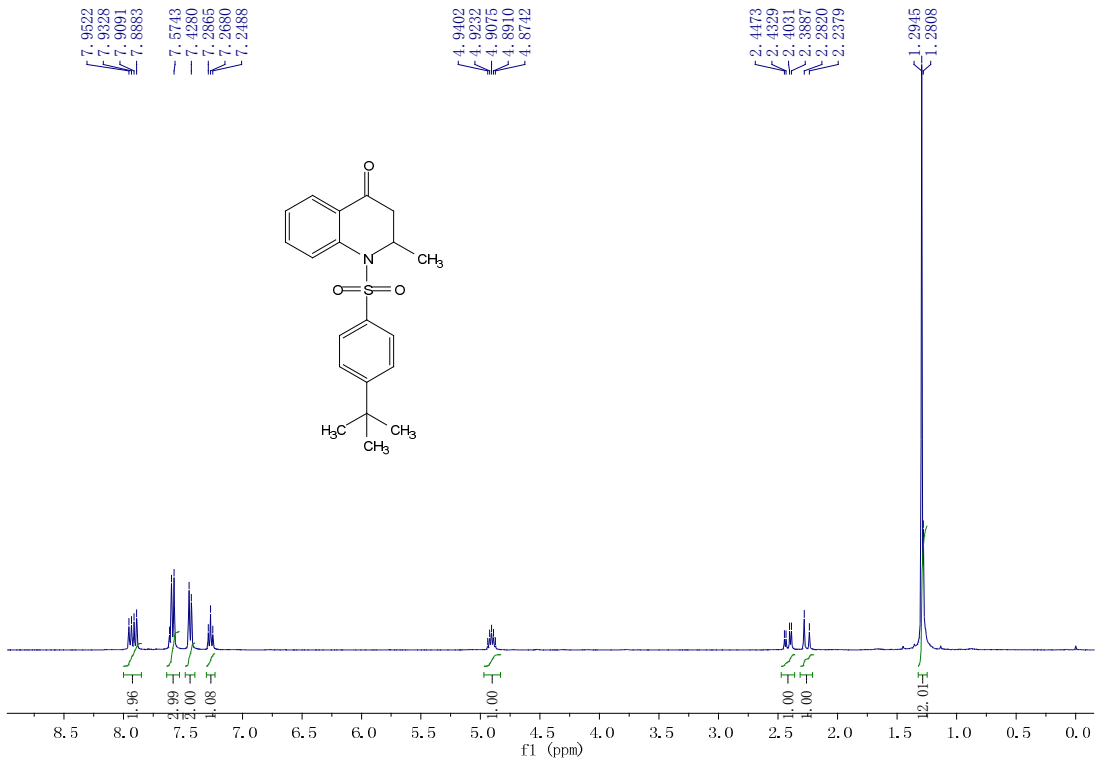

192.1274
139.5575
139.5422
133.3624
129.3961
127.1321
126.8365
126.1753
125.7066
125.4608
51.9437
41.9936
19.5477
O
N
CH3
O=S=O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

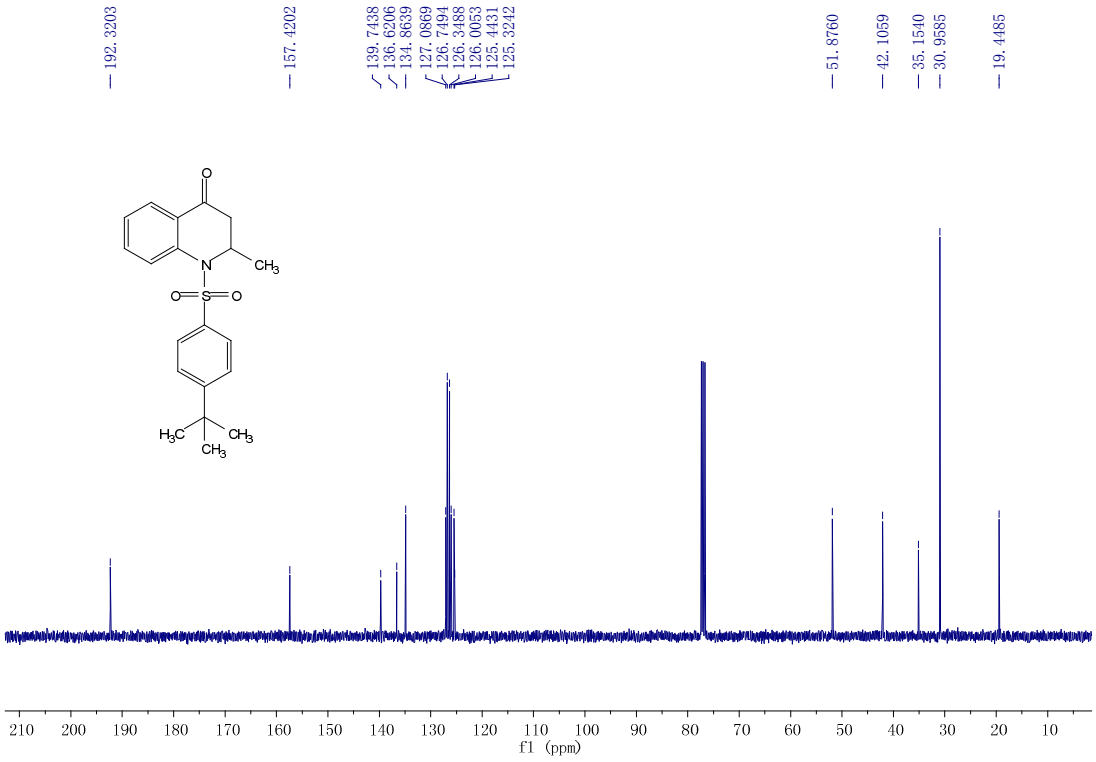

8.3430
8.3406
8.3281
8.3258
8.0579
7.8425
7.6094
7.5237
7.4854
7.4691
7.3337
7.3162
7.2781
7.2627
7.2459
4.8630
4.8594
4.8491
4.8455
4.8379
4.8348
4.8317
4.8240
4.8204
4.8102
4.8065
2.1637
2.1600
2.1286
2.1248
2.0974
2.0863
2.0622
2.0510
1.3326
1.3187
O
N
CH3
O=S=O
0.98
0.98
0.99
2.98
1.03
1.00
1.03
1.08
1.00
1.03
1.03
2.98
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

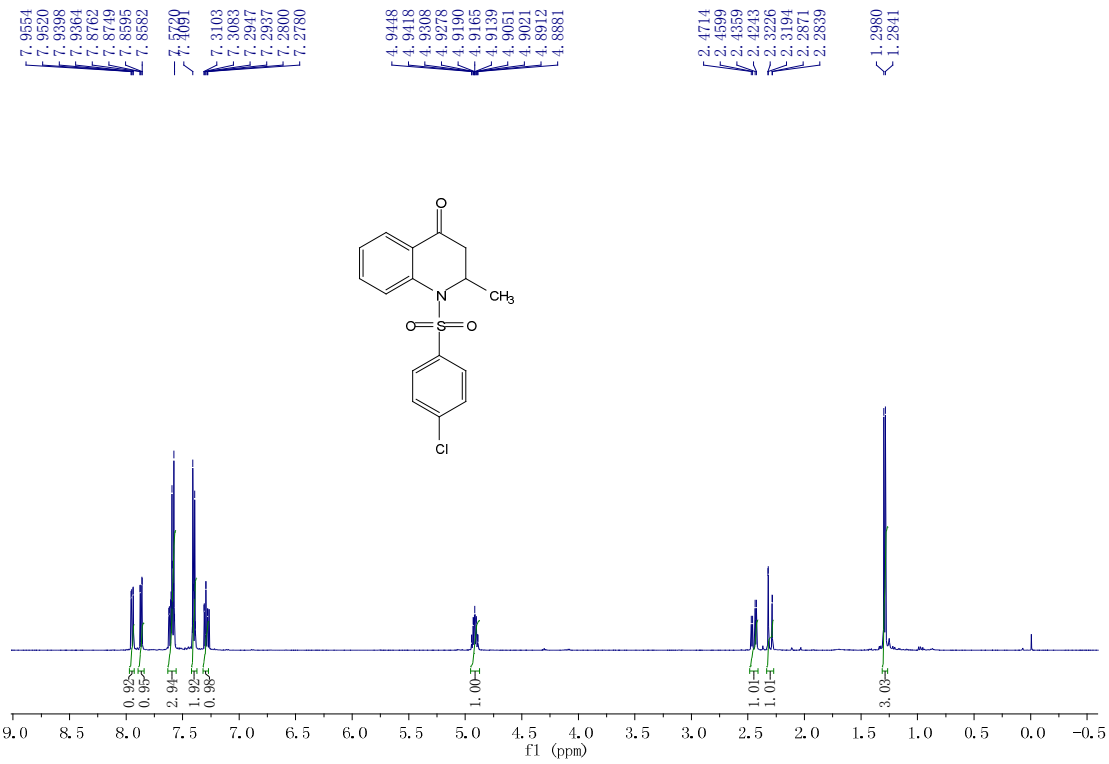

192.0103
139.8883
134.2672
130.2717
128.9799
128.2779
128.1368
127.1715
127.1081
125.7848
125.3491
125.2509
124.2523
124.1618
51.8326
42.2328
19.3898
O
N
CH3
O=S=O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

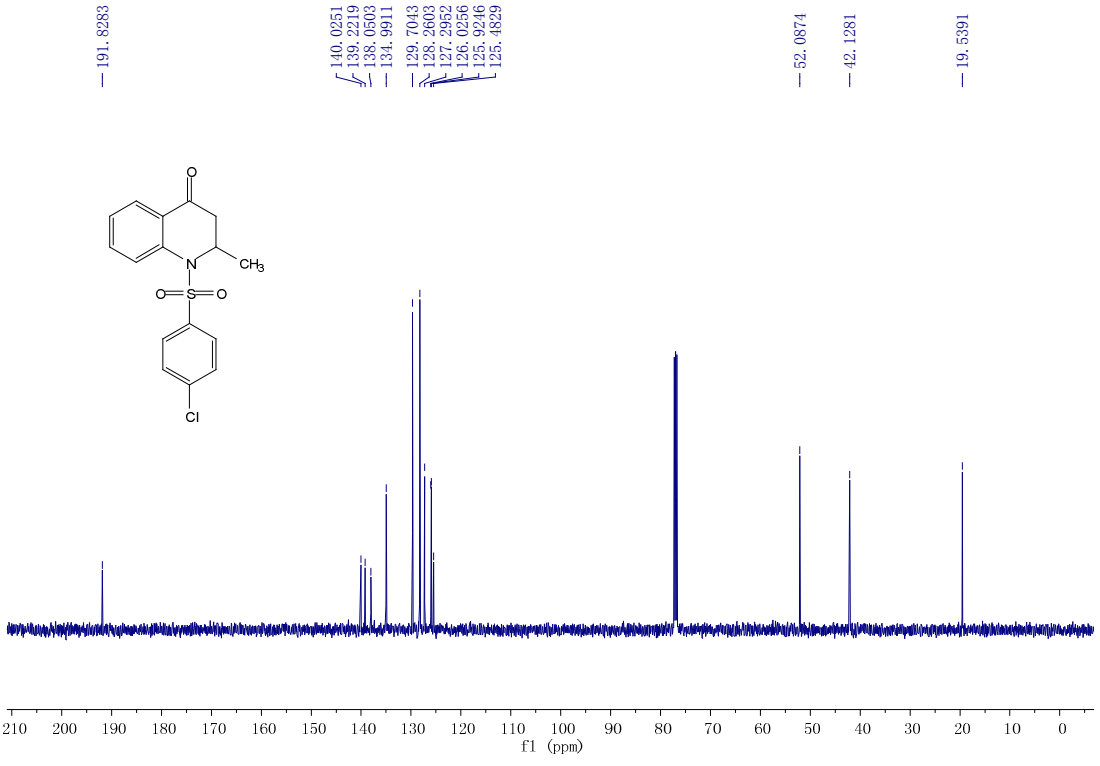

7.9657
7.9618
7.9461
7.9405
7.9172
7.7070
7.5934
7.5542
7.5326
7.4407
7.4054
7.3877
7.3696
7.2831
7.2554
4.9922
4.9780
4.9750
4.9604
4.9428
4.9287
2.5303
2.5157
2.4861
2.4715
2.3176
2.3142
2.2734
2.2700
1.3157
1.2983
O
N
CH3
O=S=O
1.96
4.06
2.02
3.03
1.11
1.00
1.00
1.00
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

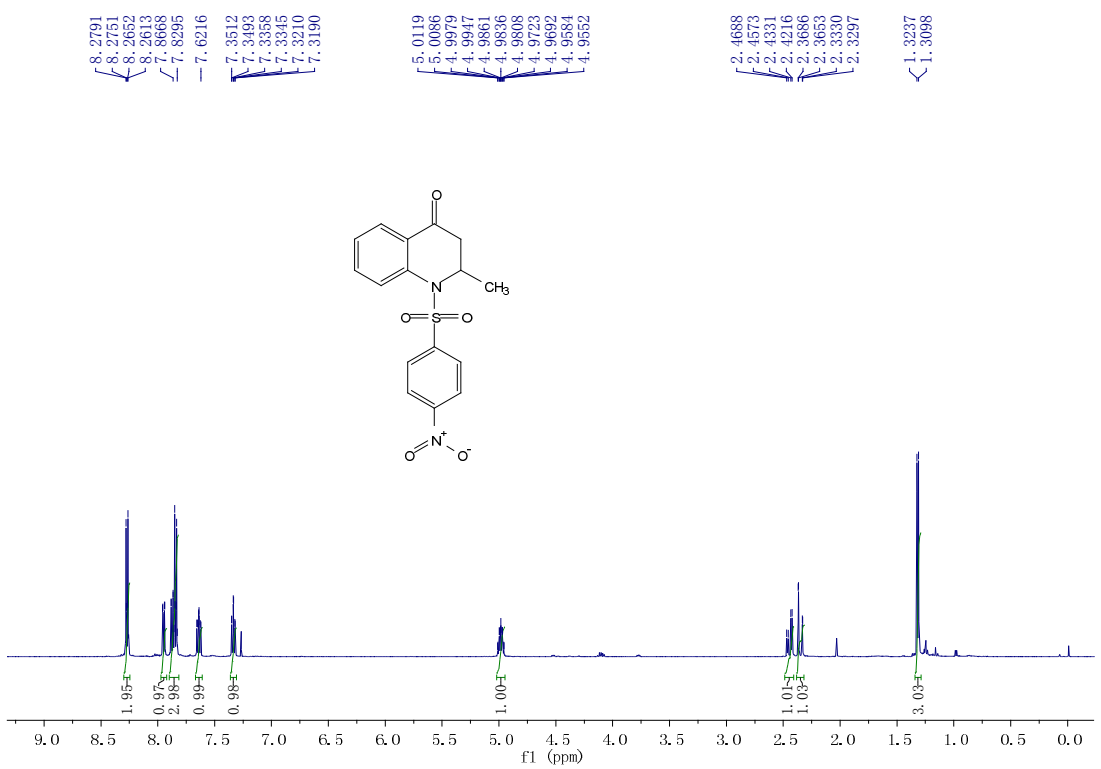

192.1496
146.2780
138.7228
134.9172
128.9965
128.6468
127.8882
127.3800
127.2549
127.1808
126.0666
125.6439
125.4195
51.9972
42.1434
19.5103
O
N
CH3
O=S=O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

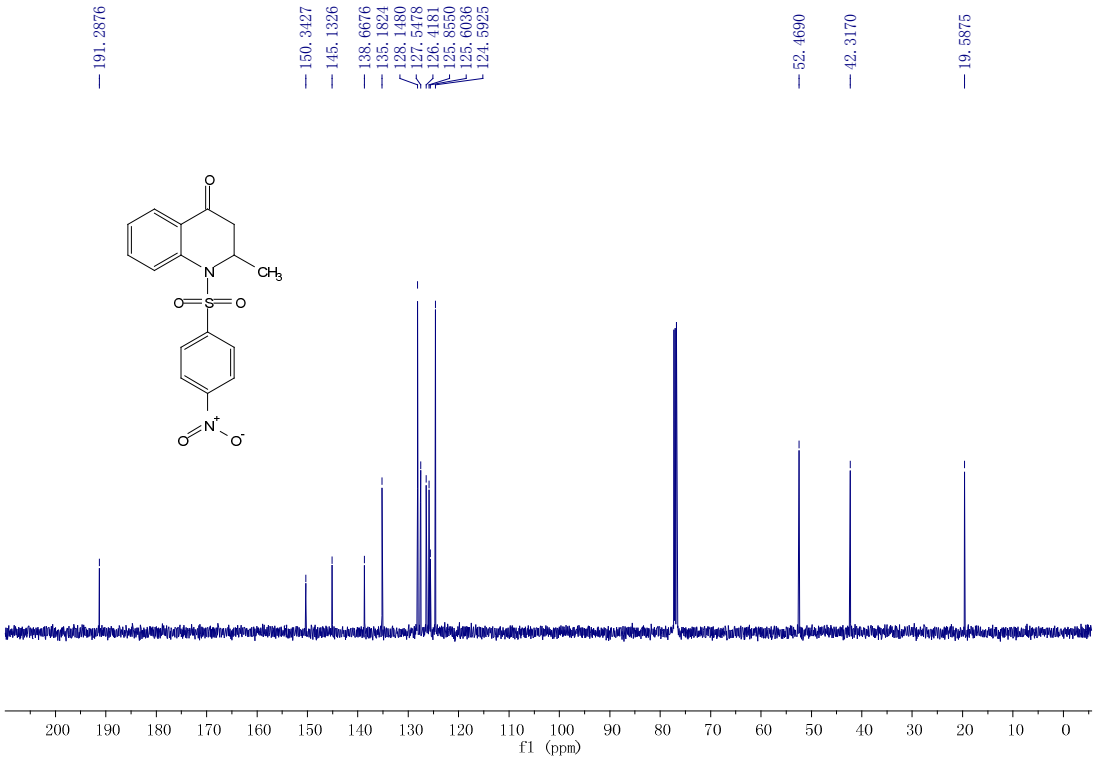

7.9522
7.9328
7.9091
7.8883
7.5743
7.4280
7.2865
7.2680
7.2488
4.9402
4.9232
4.9075
4.8910
4.8742
2.4473
2.4329
2.4031
2.3887
2.2820
2.2379
1.2945
1.2808
1.96
2.99
2.00
1.08
1.00
1.00
1.00
12.01
f1 (ppm)

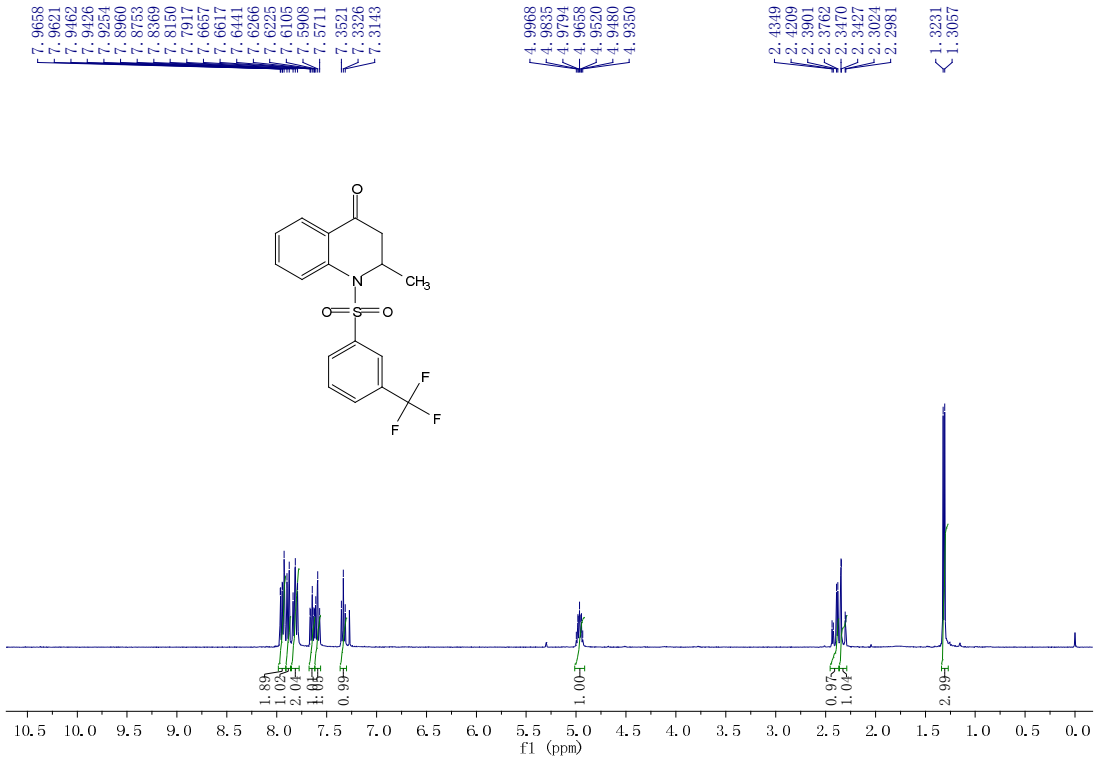

192.3203
157.4202
139.7438
136.6206
134.8639
127.0869
126.7494
126.3488
126.0053
125.4431
125.3242
51.8760
42.1059
35.1540
30.9585
19.4485
f1 (ppm)

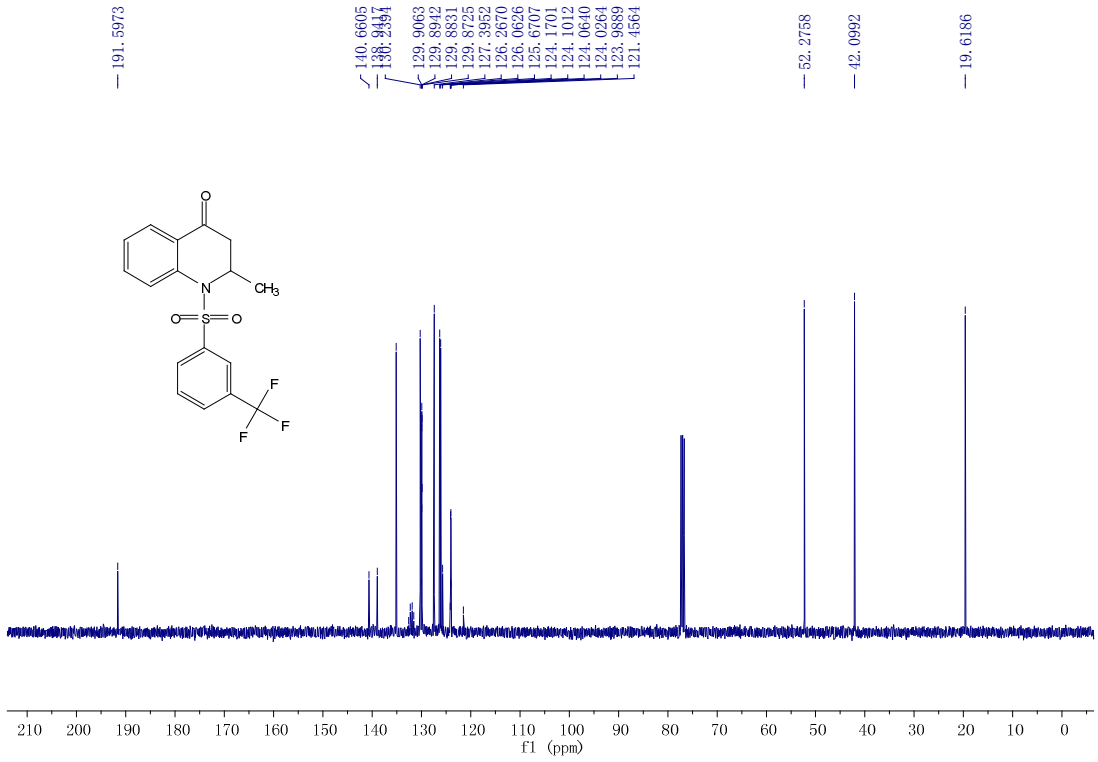

7.9554
7.9520
7.9398
7.9364
7.8762
7.8749
7.8595
7.8582
7.5730
7.4091
7.3103
7.3083
7.2947
7.2937
7.2800
7.2780
4.9448
4.9418
4.9308
4.9278
4.9190
4.9165
4.9139
4.9051
4.9021
4.8912
4.8881
2.4714
2.4599
2.4359
2.4243
2.3226
2.3194
2.2871
2.2839
1.2980
1.2841
O
N
CH3
O=S=O
Cl
0.92
0.95
2.94
1.92
0.98
1.00
1.01
1.01
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

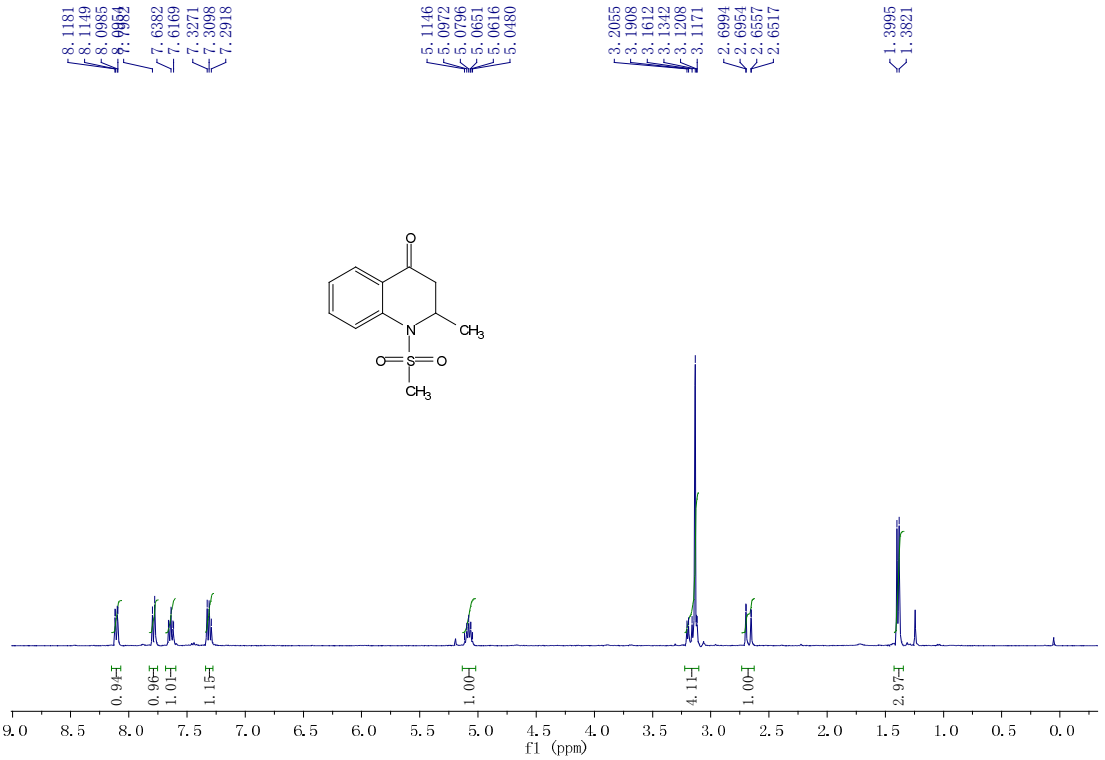

191.8283
140.0251
139.2219
138.0503
134.9911
129.7043
128.2603
127.2952
126.0256
125.9246
125.4829
52.0874
42.1281
19.5391
O
N
CH3
O=S=O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

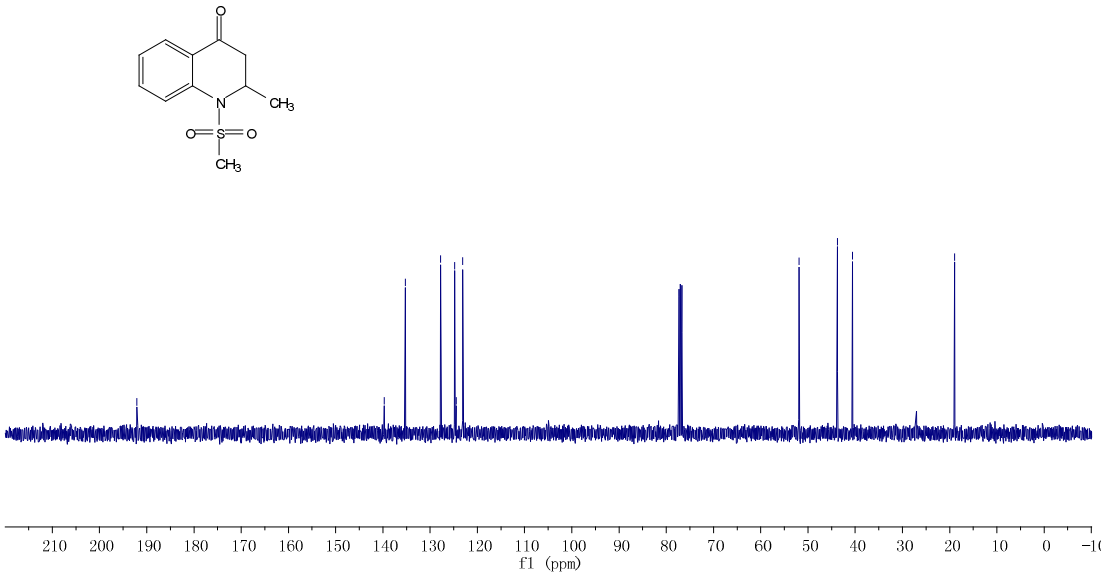

8.2791
8.2751
8.2652
8.2613
7.8668
7.8295
7.6216
7.3512
7.3493
7.3358
7.3345
7.3210
7.3190
5.0119
5.0086
4.9979
4.9947
4.9861
4.9836
4.9808
4.9723
4.9692
4.9584
4.9552
2.4688
2.4573
2.4331
2.4216
2.3686
2.3653
2.3330
2.3297
1.3237
1.3098
CH3
1.95
0.97
2.98
0.99
0.98
1.00
1.01
1.03
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

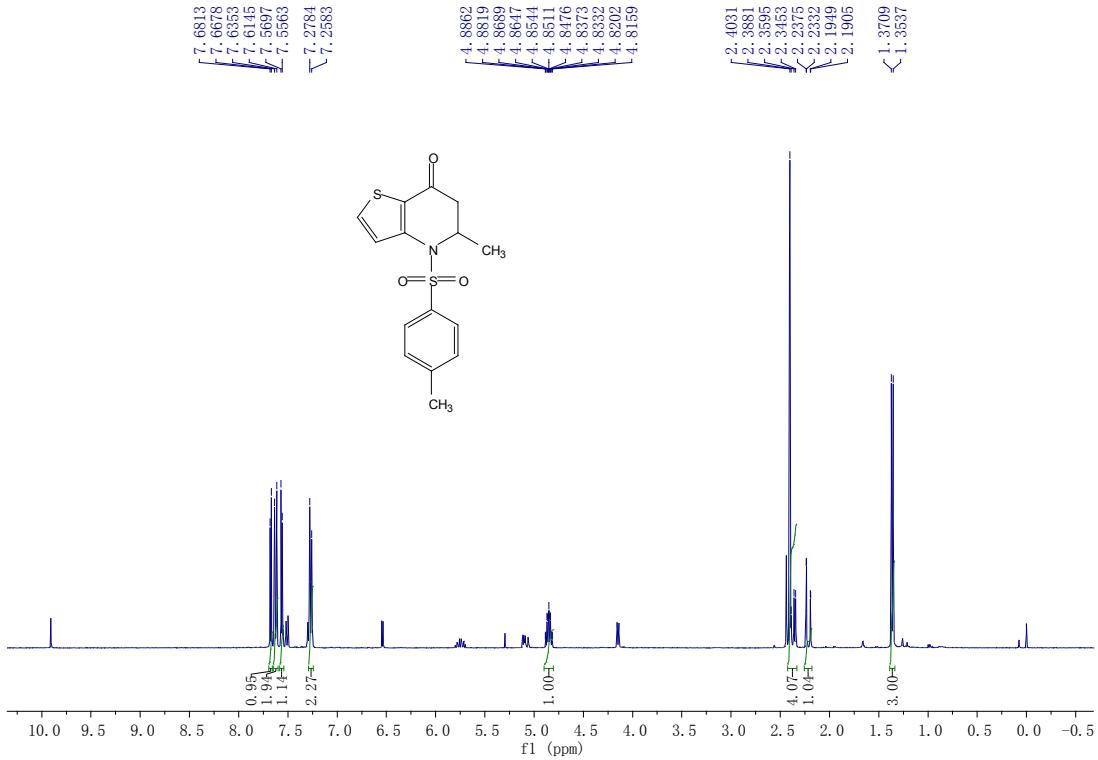

191.2876
150.3427
145.1326
138.6676
135.1824
128.1480
127.5478
126.4181
125.8550
125.6036
124.5925
52.4690
42.3170
19.5875
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

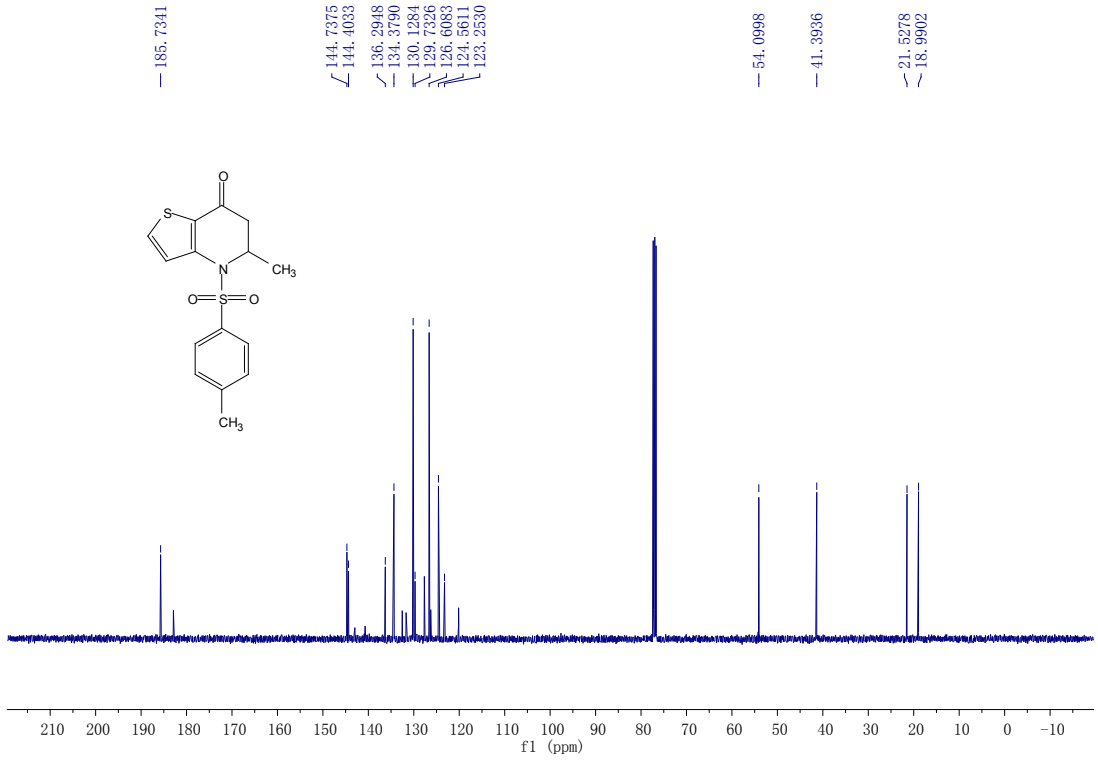

7.9658
7.9621
7.9462
7.9426
7.9254
7.8960
7.8753
7.8369
7.8150
7.7917
7.6657
7.6617
7.6441
7.6266
7.6225
7.6105
7.5908
7.5711
7.3521
7.3326
7.3143
4.9968
4.9835
4.9794
4.9658
4.9520
4.9480
4.9350
2.4349
2.4209
2.3901
2.3762
2.3470
2.3427
2.3024
2.2981
1.3231
1.3057
O
N
CH3
O=S=O
F
F
F
1.89
1.02
2.04
1.01
1.01
0.99
1.00
0.97
1.04
2.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

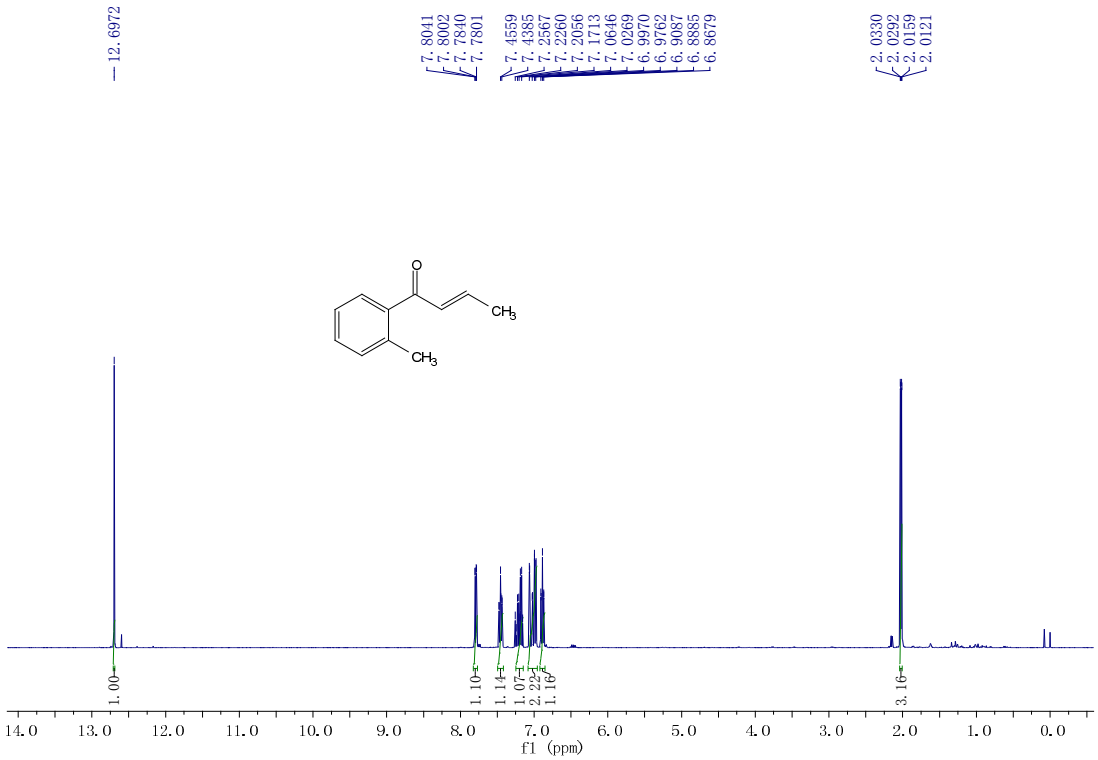

191.5973
140.6605
138.9447
138.2394
129.9063
129.8942
129.8831
129.8725
127.3952
126.2670
126.0626
125.6707
124.1701
124.1012
124.0640
124.0264
123.9889
121.4564
52.2758
42.0992
19.6186
O
N
CH3
O=S=O
F
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

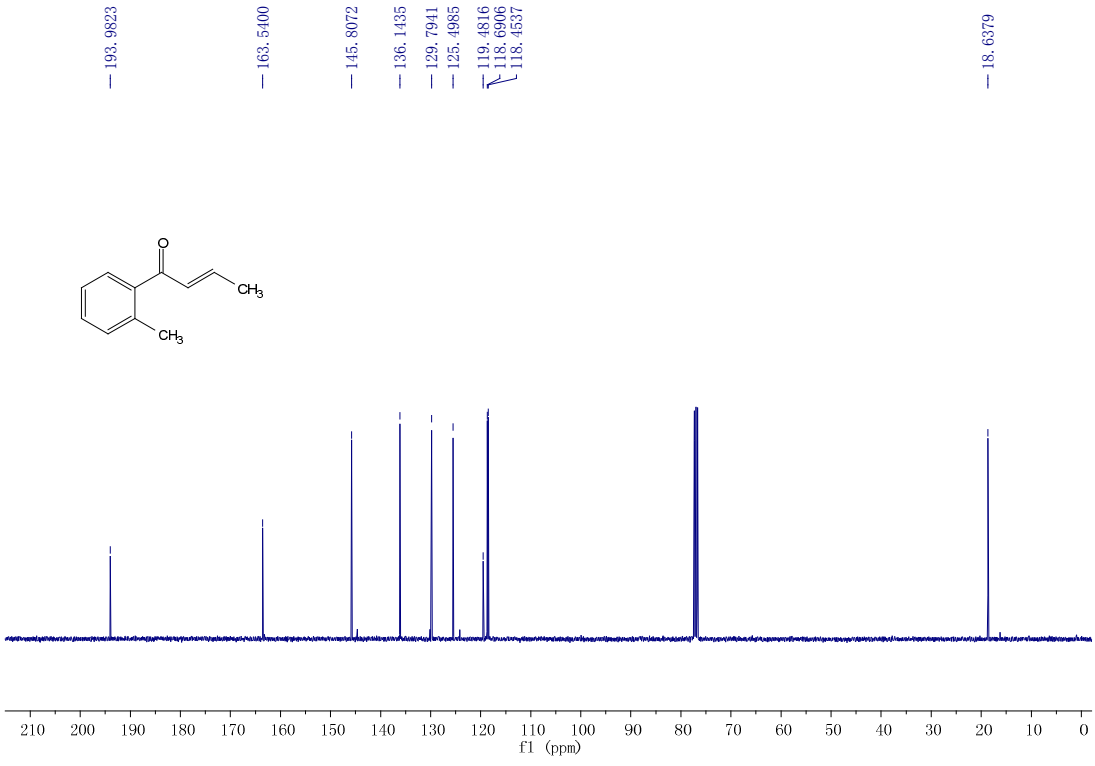

8.1181
8.1149
8.0985
7.6382
7.6169
7.3271
7.3098
7.2918
5.1146
5.0972
5.0796
5.0651
5.0616
5.0480
3.2055
3.1908
3.1612
3.1342
3.1208
3.1171
2.6994
2.6954
2.6557
2.6517
1.3995
1.3821
0.94
0.96
1.01
1.15
1.00
4.11
1.00
2.97
f1 (ppm)


192.1329
139.7423
135.2642
127.7627
124.8082
124.4954
123.1178
51.8916
43.7673
40.5725
18.9245
f1 (ppm)


7.6813
7.6678
7.6353
7.6145
7.5697
7.5563
7.2784
7.2583
4.8862
4.8819
4.8689
4.8647
4.8544
4.8511
4.8476
4.8373
4.8332
4.8202
4.8159
2.4031
2.3881
2.3595
2.3453
2.2375
2.2332
2.1949
2.1905
1.3709
1.3537
0.95
1.94
1.14
2.27
1.00
4.07
1.04
3.00
f1 (ppm)


185.7341
144.7375
144.4033
136.2948
134.3790
130.1284
129.7326
126.6083
124.5611
123.2530
54.0998
41.3936
21.5278
18.9902
f1 (ppm)


12.6972
7.8041
7.8002
7.7840
7.7801
7.4559
7.4385
7.2567
7.2260
7.2056
7.1713
7.0646
7.0269
6.9970
6.9762
6.9087
6.8885
6.8679
2.0330
2.0292
2.0159
2.0121
O
CH3
CH3
1.00
1.10
1.14
1.07
2.22
1.16
3.16
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


193.9823
163.5400
145.8072
136.1435
129.7941
125.4985
119.4816
118.6906
118.4537
18.6379
O
CH3
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)