A practical synthesis of benzothiophenes via visible-light-promoted cyclization of disulfides and alkynes

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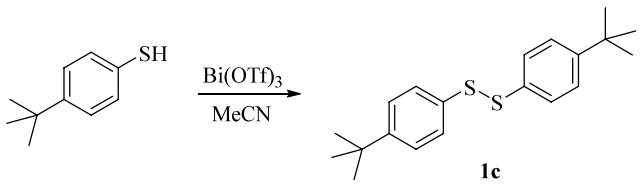
Supporting Information

1. General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 spectrometer. Chemical shifts of protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26). Chemical shifts of carbon are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0). Peaks are labeled as single (s), broad singlet (br), doublet (d), triplet (t), double doublet (dd), doublet of triplets (dt), multiplet (m). Melting points were measured on a WRS-2A melting point apparatus and are uncorrected. All products were further characterized by HRMS (high resolution mass spectra). Copies of their ^{1}H NMR and ^{13}C NMR spectra were provided. GC spectra were taken on an Agilent-6890A instrument. THF was dried and redistilled according to standard methods.

2. General Procedures

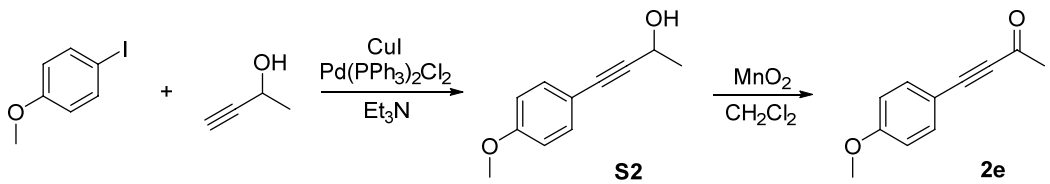
Preparation of aryl disulfides 1c, 1e, 1i, 1l, 1m [1]



1c

To a 25 mL round-bottom flask was added 4-(*tert*-butyl)benzenethiol (0.5 g, 3 mmol), $Bi(OTf)_3$ (10 mg, 0.015 mmol) and MeCN (10 mL). The reaction mixture was stirred at room temperature for 4 hours. Then the solvent was removed and the crude product was purified by column chromatography on silica gel (petroleum ether) to give the product **1c** (0.92 g, 92 %).

Preparation of alkynes (2e, 2f, 2g, 2j, 2k)

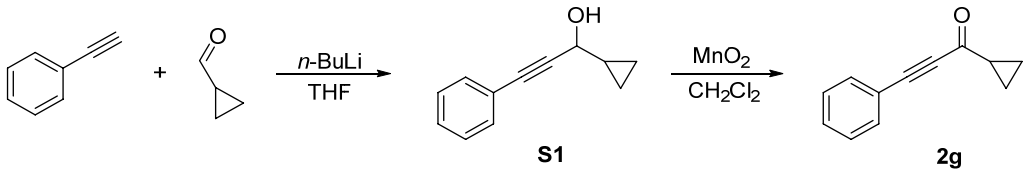


S2 **2e**

Compound **S2** was synthesized according to a known procedure.[2] To a round bottom flask was

added $Pd(PPh_3)_2Cl_2$ (35 mg, 0.05 mmol) and CuI (19 mg, 0.1 mmol). The flask was purged with N_2 for 5 minutes. Et_3N (30 mL) was added *via* cannula under N_2 atmosphere. 1-Iodo-4-methoxybenzene (1.07 g, 5 mmol) was added, and then but-3-yn-2-ol (0.39 g, 5.5 mmol) was added. The reaction mixture was stirred at room temperature until the reaction was completed. The crude mixture was filtered and the solid residue was washed with Et_3N. The combined organics were concentrated under reduced pressure. The residue was purified by column chromatography over silica gel (petroleum ether/ethyl acetate = 4/1) to give the product **S2** (0.8 g, 91%).

Compound **2e** was synthesized according to a known procedure.[3] To a solution of aryl propargyl alcohols **S2** (0.8 g, 4.5 mmol) in CH_2Cl_2 (20 mL) was added MnO_2 (3.95 g, 45 mmol) at room temperature. The resulting mixture was stirred overnight. Then the solid was filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel (petroleum ether/ethyl acetate = 20/1) to give the product **4e** (0.7 g, 89%).

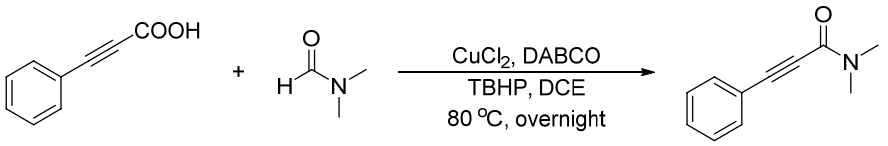


S1 **2g**

Compound **S1** was synthesized according to a known procedure.[4] To a solution of acetylene (1.02 g, 10 mmol) in anhydrous THF (20 mL) was added *n*-BuLi (10 mmol, 2.4 M in hexane) at 0 ℃ under an Argon atmosphere. The resulting solution was stirred at that temperature for 1 h. Then cyclopropanecarbaldehyde (0.35 g, 5 mmol) in anhydrous THF (15 mL) was added by a syringe. The reaction mixture was stirred for 12 h at room temperature. The mixture was then quenched by adding saturated aqueous NH_4Cl (20 mL) and extracted with diethyl ether (20 mL × 2). The combined organic layer was dried over $MgSO_4$ and concentrated under vacuum to give the crude product, which was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1) to give the product **S1** (0.75g, 87%).

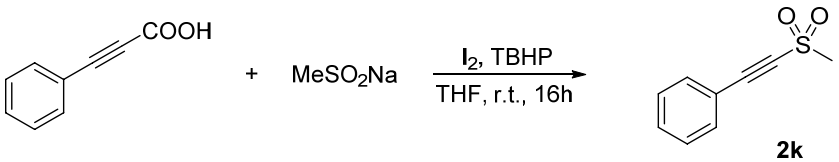
Compound **2g** was synthesized according to a known procedure.[3] To a solution of aryl propargyl alcohols **S1** (0.75g, 4.4 mmol) in CH_2Cl_2 (20 mL) was added MnO_2 (3.79 g, 44

mmol) at room temperature. The resulting mixture was stirred overnight. Then the solid was filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel (petroleum ether/ethyl acetate = 20/1) to give the product **2g** (0.64g, 86%).



2j

Compound **2j** was synthesized according to a known procedure.[5] To a solution of 3-phenylpropiolic acid (0.44 g, 3 mmol), $CuCl_2$ (20.2 mg, 0.15 mmol) and DABCO (33.7 mg, 0.3 mmol) in DCE (10 mL) was added DMF (3.29 g, 45 mol) and TBHP (70% in water, 6 mmol). The flask was filled with argon, and the mixture was stirred at 80 ℃ (oil bath temperature) until the complete consumption of the starting material as monitored by TLC. Then the mixture was washed with brine. The aqueous phase was extracted with ethyl acetate. The combined organic layer was dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography over silica gel (petroleum ether/ethyl acetate = 1/1) to give the product **2j** (0.21 g, 40%).

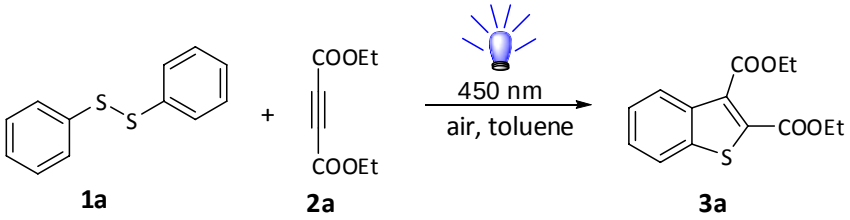


2k

Compound **2k** was synthesized according to a known procedure.[6] To a solution of 3-phenylpropiolic acid (0.73 g, 5 mmol), sodium methylsulfonate (1.03 g, 10 mmol) and iodine (0.64 g, 2.5 mmol) in THF (30 mL) was added TBHP (70% in water ,15 mmol). The resulting mixture was stirred at room temperature for 24 h. The reaction mixture was quenched by the addition of saturated aqueous $Na_2S_2O_3$ (30 mL). The reaction mixture was extracted with EtOAc (3 × 40 mL). The combined organic layer was washed with H_2O (50 mL) and brine (50 mL), and dried over $MgSO_4$. The organic layer was filtered and concentrated under vacuum. The residue was purified by column chromatography over silica

gel (petroleum ether/ethyl acetate = 15/1) to give the product **2k** (0.15g, 17%).

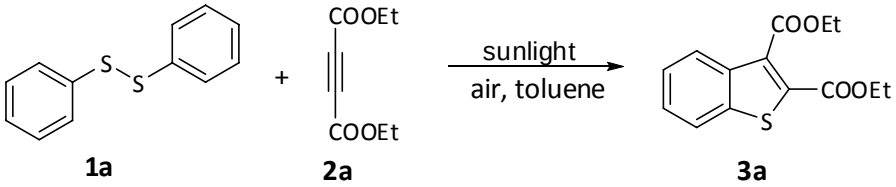
Preparation of the benzothiophene 3a



1a **2a** **3a**

To a 20 mL glass tube with a stir bar was charged disulfides **1a** (43.7 mg, 0.2 mmol), alkynes **2a** (85.1 mg, 0.5 mmol) and toluene (2 mL). The solution was stirred at room temperature with the irradiation of a 12 W blue LED for 24 h. The solvent was removed under vacuum. The residue was purified by column chromatography over silica gel (petroleum ether/ethyl acetate = 25/1) to give the product **3a** (75 mg, 68%).

Preparation of the benzothiophene 3a under sunlight irradiation



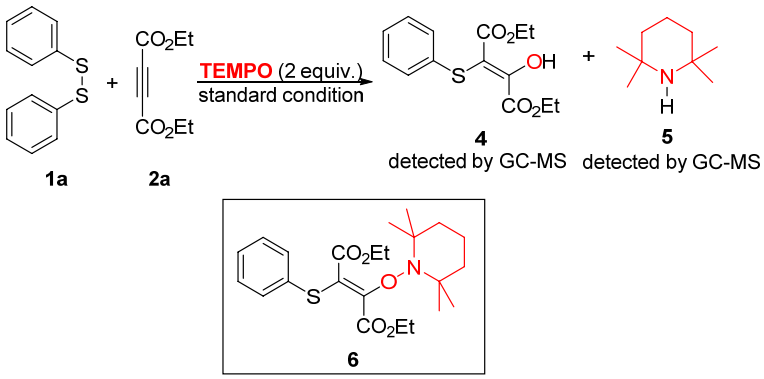
1a **2a** **3a**

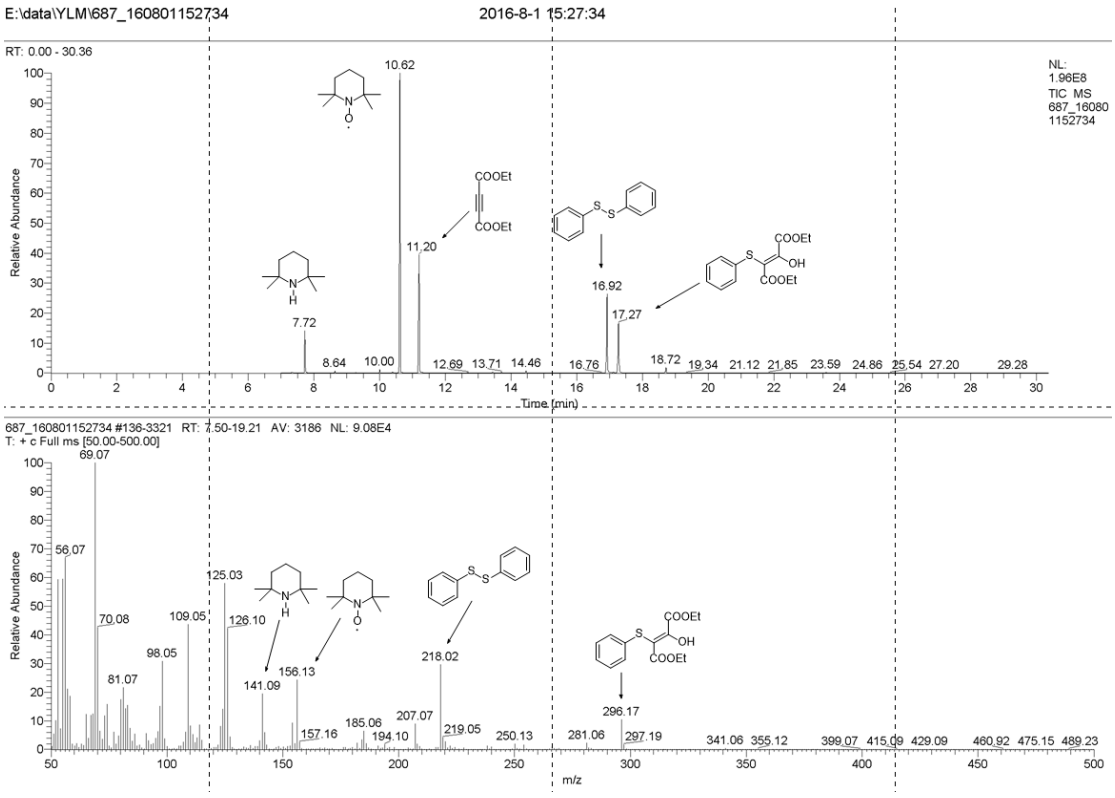
To a 20 mL glass tube was charged disulfides **1a** (43.7 mg, 0.2 mmol), alkynes **2a** (85.1 mg, 0.5 mmol) and toluene (2 mL). The solution was irradiated under sun-light for 27 h (9 h per day for 3 days, from 9:00 to 18:00 each day). The solvent was removed under vacuum. The residue was purified by column chromatography over silica gel (petroleum ether/ethyl acetate = 25/1) to give the product **3a** (66 mg, 60%) as a white solid. (2016/08/07 – 2016/08/09. Guangzhou, Guangdong province, China. temperature: 26 ℃ - 36 ℃)

3. Experiments of Reaction Mechanism

Radical trapping experiment

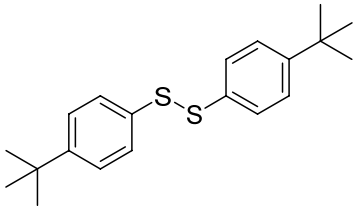
To a 20 mL glass tube with a stir bar was charged **1a** (43.7 mg, 0.2 mmol), **2a** (85.1 mg, 0.5 mmol), TEMPO (62.5mg, 0.4 mmol) and toluene (2 mL). The solution was stirred at room temperature with the irradiation of a 12 W blue LED lamp. After 24 h, the reaction mixture was detected by GC-MS.





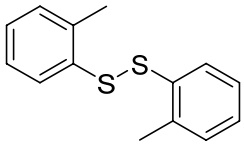
4. Characterization Data

1,2-Bis(4-(*tert*-butyl)phenyl)disulfane (1c)



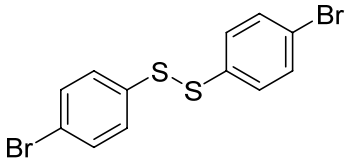
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.41 (m, 4H), 7.33–7.29 (m, 4H), 1.29 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.6, 134.1, 127.9, 126.1, 34.6, 31.3. Analytical data matches literature data.[7]

1,2-Di-*o*-tolyldisulfane (1e)



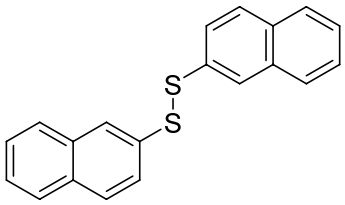
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.49 (m, 2H), 7.17–7.09 (m, 6H), 2.42 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.6, 135.5, 130.3, 128.9, 127.4, 126.7, 20.0. Analytical data matches literature data.[7]

1,2-Bis(4-bromophenyl)disulfane (1i)



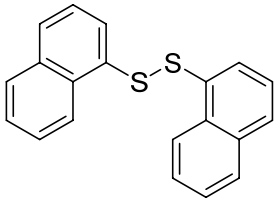
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.39 (m, 4H), 7.35–7.30 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 135.8, 132.2, 129.5, 121.6. Analytical data matches literature data.[7]

1,2-Di(naphthalen-2-yl)disulfane (1l)



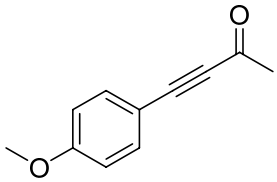
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 1.5 Hz, 1H), 7.79–7.74 (m, 2H), 7.72–7.70 (m, 1H), 7.61 (dd, J = 8.7, 1.9 Hz, 1H), 7.47–7.39 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 134.3, 133.5, 132.6, 129.0, 127.8, 127.5, 126.8, 126.7, 126.3, 125.7. Analytical data matches literature data.[8]

1,2-Di(naphthalen-1-yl)disulfane (1m).



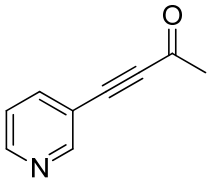
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36–8.30 (m, 2H), 7.86–7.80 (m, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.61 (dd, J = 7.2, 1.1 Hz, 2H), 7.51–7.45 (m, 4H), 7.30–7.28 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 134.2, 133.6, 132.9, 130.4, 129.3, 128.6, 126.7, 126.4, 125.5, 125.2. Analytical data matches literature data.[8]

4-(4-Methoxyphenyl)but-3-yn-2-one (2e)



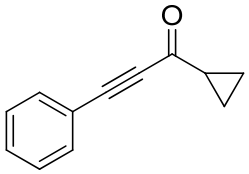
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.50 (m, 2H), 6.91–6.87 (m, 2H), 3.84 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 184.5, 161.7, 135.1, 114.4, 111.8, 91.5, 88.3, 55.4, 32.6. HRMS (ESI): calculated for $C_{11}H_{11}O_2$ $(M+H)^+$: 175.0754, found: 175.0753.

4-(Pyridin-3-yl)but-3-yn-2-one (2f)



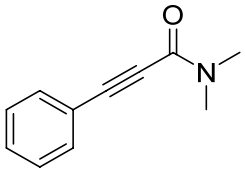
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (dd, J = 2.0, 0.8 Hz, 1H), 8.66 (dd, J = 4.9, 1.9 Hz, 1H), 7.86 (dt, J = 7.9, 1.9 Hz, 1H), 7.34 (ddd, J = 7.9, 4.9, 0.8 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.9, 153.3, 150.7, 139.8, 123.2, 117.3, 90.7, 86.1, 32.6. HRMS (ESI): calculated for C_9H_8NO $(M+H)^+$: 146.0600, found: 146.0593.

1-Cyclopropyl-3-phenylprop-2-yn-1-one (2g)



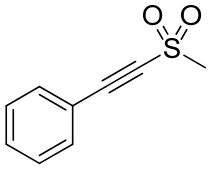
Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58–7.53 (m, 2H), 7.47–7.42 (m, 1H), 7.3 (m, 2H), 2.19–2.13 (m, 1H), 1.35–1.29 (m, 2H), 1.11–1.06 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 188.2, 132.9, 130.6, 128.6, 120.06, 90.4, 86.2, 24.6, 11.1. HRMS (ESI): calculated for $C_{12}H_{11}O$ $(M+H)^+$: 171.0804, found: 171.0800.

***N,N*-dimethyl-3-phenylpropiolamide (2j)**



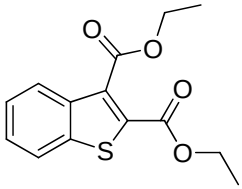
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.52 (m, 2H), 7.42–7.33 (m, 3H), 3.29 (s, 3H), 3.03 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.6, 132.3, 129.9, 128.5, 120.7, 90.2, 81.6, 38.3, 34.2. Analytical data matches literature data.[5]

((Methylsulfonyl)ethynyl)benzene (2k)



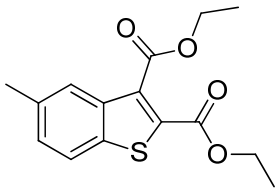
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.57 (m, 2H), 7.55–7.50 (m, 1H), 7.45–7.39 (m, 2H), 3.30 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 132.9, 131.7, 128.8, 117.6, 91.5, 84.6, 46.9. Analytical data matches literature data.[6]

Diethyl benzo[b]thiophene-2,3-dicarboxylate (3a)



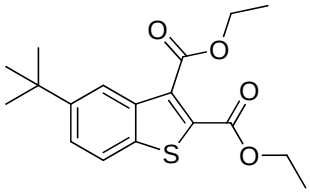
White solid, M.p. 68–70 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95–7.92 (m, 1H), 7.86–7.83 (m, 1H), 7.51–7.43 (m, 2H), 4.50 (q, J = 7.1 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.46–1.38 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.4, 161.8, 140.3, 136.9, 133.6, 133.2, 127.3, 125.5, 124.4, 122.5, 62.1, 61.9, 14.1. **HRMS** (ESI): calculated for $C_{14}H_{15}O_4S$ $(M+H)^+$: 279.0686, found: 279.0673.

Diethyl 5-methylbenzo[b]thiophene-2,3-dicarboxylate (3b).



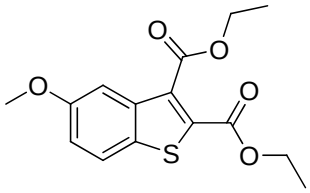
Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.4 Hz, 1H), 4.50 (q, J = 7.1 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 2.47 (s, 3H), 1.45–1.37 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.7, 161.8, 137.7, 137.2, 135.6, 133.4, 133.0, 129.3, 124.0, 122.1, 62.0, 61.9, 21.4, 14.1. **HRMS** (ESI): calculated for $C_{15}H_{17}O_4S$ $(M+H)^+$: 293.0842, found: 293.0830.

Diethyl 5-(*tert*-butyl)benzo[b]thiophene-2,3-dicarboxylate (3c)



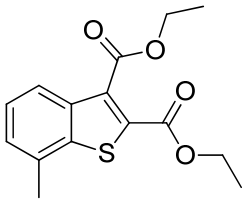
Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.88 (d, J = 1.8 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.57 (dd, J = 8.6, 1.8 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.47–1.36 (m, 15H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.7, 161.9, 149.0, 137.8, 137.0, 133.5, 133.4, 126.1, 122.0, 120.1, 62.0, 61.8, 34.9, 31.4, 14.19, 14.15. **HRMS** (ESI): calculated for $C_{18}H_{23}O_4S$ $(M+H)^+$: 335.1312, found: 335.1296.

Diethyl 5-methoxybenzo[b]thiophene-2,3-dicarboxylate (3d)



White solid. M.p. 58–60 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.9 Hz, 1H), 7.39 (d, J = 2.4 Hz, 1H), 7.15 (dd, J = 8.9, 2.4 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 4.42 (q, J = 7.1 Hz, 2H), 1.47–1.39 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.5, 161.9, 158.4, 138.0, 135.0, 132.9, 132.3, 123.2, 118.6, 105.4, 62.0, 61.8, 55.5, 14.13, 14.12. **HRMS** (ESI): calculated for $C_{15}H_{17}O_5S$ $(M+H)^+$: 309.0791, found: 309.0797.

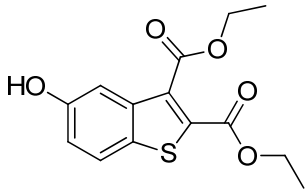
Diethyl 7-methylbenzo[b]thiophene-2,3-dicarboxylate (3e)



White solid. M.p. 72–73 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.1 Hz, 1H), 7.40–7.36 (m, 1H), 7.27 (d, J = 8.1 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 2.56 (s, 3H), 1.45–1.38 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 164.6, 161.9, 140.7, 136.8,

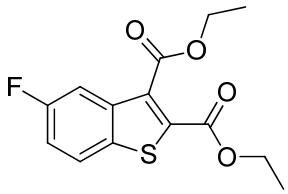
134.2, 132.8, 132.1, 127.4, 126.1, 122.1, 62.0, 61.9, 20.0, 14.2. **HRMS** (ESI): calculated for $C_{15}H_{17}O_4S$ $(M+H)^+$: 293.0842, found: 293.0831.

Diethyl 5-hydroxybenzo[b]thiophene-2,3-dicarboxylate (3f)



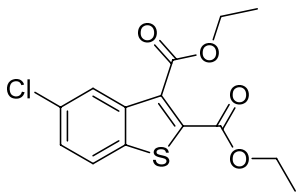
White solid. M.p. 101–103 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.8 Hz, 1H), 7.40 (d, J = 2.2 Hz, 1H), 7.07 (dd, J = 8.8, 2.2 Hz, 1H), 6.42 (br, 1H), 4.48–4.37 (m, 4H), 1.42–1.37 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.0, 162.0, 154.6, 138.1, 135.3, 132.6, 131.7, 123.4, 118.2, 108.7, 62.23, 62.16, 14.12, 14.05. **HRMS** (ESI): calculated for $C_{14}H_{15}O_5S$ $(M+H)^+$: 295.0635, found: 295.0623.

Diethyl 5-fluorobenzo[b]thiophene-2,3-dicarboxylate (3g)



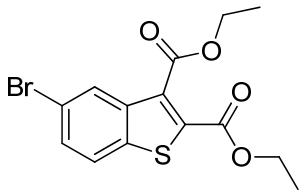
White solid. M.p. 103–104 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 8.9, 4.7 Hz, 1H), 7.67 (dd, J = 9.4, 2.5 Hz, 1H), 7.28–7.22 (m, 1H), 4.49 (q, J = 7.1 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.46–1.38 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.8, 162.5, 161.6, 160.1, 138.0, 137.9, 136.8, 135.5, 132.1, 132.0, 123.9, 123.8, 116.7, 116.4, 110.2, 109.9, 62.3, 62.0, 14.1. **HRMS** (ESI): calculated for $C_{14}H_{14}FO_4S$ $(M+H)^+$: 297.0591, found: 297.0583.

Diethyl 5-chlorobenzo[b]thiophene-2,3-dicarboxylate (3h)



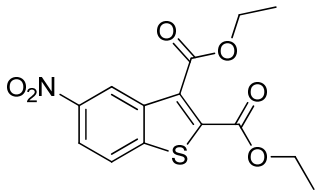
White solid. M.p. 66–68 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, J = 2.0 Hz, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.44 (dd, J = 8.7, 2.0 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.45–1.38 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.7, 161.5, 138.1, 137.9, 136.2, 132.1, 131.9, 127.9, 124.1, 123.5, 62.3, 62.1, 14.1. **HRMS** (ESI): calculated for $C_{14}H_{14}ClO_4S$ $(M+H)^+$: 313.0296, found: 313.0285.

Diethyl 5-bromobenzo[b]thiophene-2,3-dicarboxylate (3i)



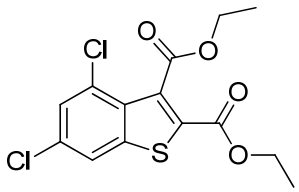
White solid. M.p. 84–85 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12 (dd, J = 1.9, 0.4 Hz, 1H), 7.69 (dd, J = 8.7, 0.4 Hz, 1H), 7.56 (dd, J = 8.7, 1.9 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 1.45–1.38 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.7, 161.4, 138.6, 138.3, 135.8, 131.8, 130.4, 127.2, 123.8, 119.8, 62.3, 62.1, 14.1. **HRMS** (ESI): calculated for $C_{14}H_{14}BrO_4S$ $(M+H)^+$: 356.9791, found: 356.9783.

Diethyl 5-nitrobenzo[b]thiophene-2,3-dicarboxylate (3j)



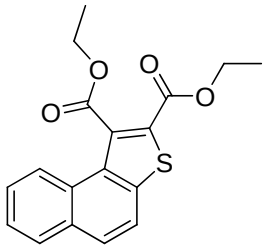
Pale yellow solid. M.p. 58–59 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.90 (d, J = 2.2 Hz, 1H), 8.33 (dd, J = 9.0, 2.2 Hz, 1H), 7.99 (d, J = 9.0 Hz, 1H), 4.54 (q, J = 7.1 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 1.48–1.40 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.0, 161.0, 146.4, 145.1, 138.90, 136.8, 133.0, 123.4, 121.3, 120.6, 62.7, 62.5, 14.1. **HRMS** (ESI): calculated for $C_{14}H_{14}NO_6S$ $(M+H)^+$: 324.0237, found: 324.0241.

Diethyl 4,6-dichlorobenzo[b]thiophene-2,3-dicarboxylate (3k)



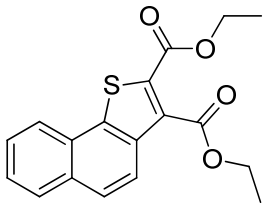
White solid. M.p. 83–84 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74 (d, J = 1.8 Hz, 1H), 7.43 (d, J = 1.8 Hz, 1H), 4.50 (q, J = 7.2 Hz, 2H), 4.40 (q, J = 7.2 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H), 1.39 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.0, 160.8, 143.1, 134.2, 133.7, 132.4, 132.3, 130.4, 127.1, 121.0, 62.5, 62.4, 14.1, 13.9. **HRMS** (ESI): calculated for $C_{14}H_{13}Cl_2O_4S$ $(M+H)^+$: 346.9906, found: 346.9905.

Diethyl naphtho[2,1-b]thiophene-1,2-dicarboxylate (3l)



White solid. M.p. 129–130 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.20–8.15 (m, 1H), 7.96–7.92 (m, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.63–7.54 (m, 2H), 4.65 (q, J = 7.1 Hz, 2H), 4.42 (q, J = 7.1 Hz, 2H), 1.50 (t, J = 7.1 Hz, 3H), 1.42 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.6, 161.6, 140.8, 135.8, 131.7, 131.6, 129.9, 129.2, 129.1, 127.5, 126.1, 122.9, 120.2, 62.6, 61.9, 14.2, 14.0. **HRMS** (ESI): calculated for $C_{18}H_{17}O_4S$ $(M+H)^+$: 329.0842, found: 329.0840.

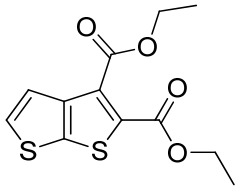
Diethyl naphtho[1,2-b]thiophene-2,3-dicarboxylate (3m)



Red solid, M.p. 87–88 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7.8 Hz, 1H), 7.28 (dd, J = 7.8, 0.8 Hz, 1H), 7.21–7.12 (m, 2H), 7.01 (dd, J = 7.4, 1.1 Hz, 1H), 6.85 (dd, J = 7.4, 1.1 Hz, 1H), 4.42 (q, J = 7.2 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 1.37 (dt, J = 18.1, 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.3, 161.8, 136.6, 135.5, 130.8, 129.8, 129.63, 129.61,

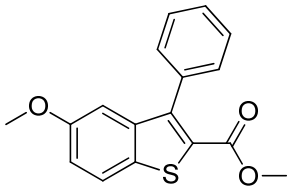
127.1, 126.7, 124.43, 124.38, 123.1, 120.1, 62.5, 62.0, 14.00, 13.95. **HRMS** (ESI): calculated for $C_{18}H_{17}O_4S$ $(M+H)^+$: 329.0842, found: 329.0826.

Diethyl thieno[2,3-b]thiophene-2,3-dicarboxylate (3n)



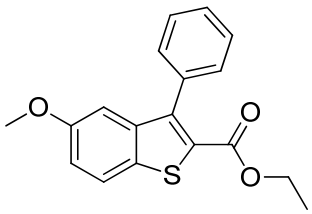
Light brown liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (d, J = 5.3 Hz, 1H), 7.34 (d, J = 5.3 Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 1.40 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.8, 161.1, 145.4, 140.7, 136.5, 129.9, 129.7, 120.5, 61.90, 61.85, 14.2, 14.1. **HRMS** (ESI): calculated for $C_{12}H_{13}O_4S_2$ $(M+H)^+$: 285.0250, found: 285.0237.

Methyl 5-methoxy-3-phenylbenzo[b]thiophene-2-carboxylate (4b)



Colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.8 Hz, 1H), 7.51–7.43 (m, 3H), 7.40 (d, J = 7.8 Hz, 2H), 7.13 (dd, J = 8.8, 2.2 Hz, 1H), 6.93 (d, J = 2.1 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 163.0, 157.9, 143.8, 141.1, 134.7, 133.1, 129.6, 129.0, 128.2, 128.1, 123.3, 118.3, 106.4, 55.5, 52.2. **HRMS** (ESI): calculated for $C_{17}H_{15}O_3S$ $(M+H)^+$: 299.0736, found: 299.0736.

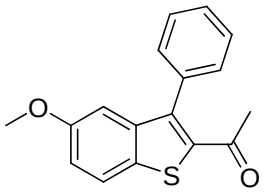
Ethyl 5-methoxy-3-phenylbenzo[b]thiophene-2-carboxylate (4c)



Colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.8 Hz, 1H), 7.51–7.43 (m, 3H), 7.41–7.36 (m, 2H), 7.12 (dd, J = 8.8, 2.5 Hz, 1H), 6.92 (d, J = 2.5 Hz, 1H), 4.21 (q, J = 7.1

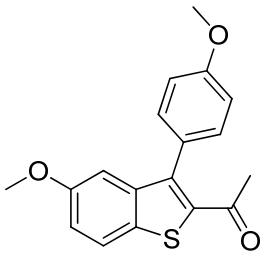
Hz, 2H), 3.73 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.6, 157.9, 143.3, 141.2, 135.0, 133.1, 129.9, 129.6, 128.1, 128.0, 123.2, 118.1, 106.5, 61.2, 55.5, 13.9. HRMS (ESI, m/z): calculated for $[M+H]^+$: 295.0635, found: 295.0623. **HRMS** (ESI): calculated for $C_{18}H_{17}O_3S$ $(M+H)^+$: 313.0893, found: 313.0889. Analytical data matches literature data.[9]

1-(5-Methoxy-3-phenylbenzo[b]thiophen-2-yl)ethan-1-one (4d)



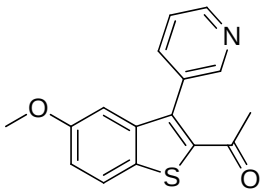
Pale yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.8 Hz, 1H), 7.56–7.49 (m, 3H), 7.40–7.38 (m, 2H), 7.12 (dd, J = 8.8, 2.5 Hz, 1H), 6.80 (d, J = 2.5 Hz, 1H), 3.72 (s, 3H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.6, 157.9, 142.0, 141.8, 141.6, 135.3, 133.4, 129.7, 128.9, 128.7, 123.4, 118.4, 106.8, 55.5, 29.6. **HRMS** (ESI): calculated for $C_{17}H_{15}O_2S$ $(M+H)^+$: 283.0787, found: 283.0781.

1-(5-Methoxy-3-(4-methoxyphenyl)benzo[b]thiophen-2-yl)ethan-1-one (4e)



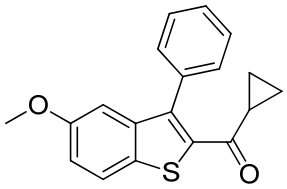
White solid. M.p. 133–135 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.8 Hz, 1H), 7.33–7.29 (m, 2H), 7.12 (dd, J = 8.8, 2.5 Hz, 1H), 7.09–7.04 (m, 2H), 6.84 (d, J = 2.5 Hz, 1H), 3.91 (s, 3H), 3.74 (s, 3H), 2.10 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 193.8, 160.0, 157.9, 142.2, 141.8, 141.6, 133.4, 130.9, 127.2, 123.4, 118.4, 114.4, 106.8, 55.5, 55.4, 29.7. **HRMS** (ESI): calculated for $C_{18}H_{17}O_3S$ $(M+H)^+$: 313.0893, found: 313.0883.

1-(5-Methoxy-3-(pyridin-3-yl)benzo[b]thiophen-2-yl)ethan-1-one (4f)



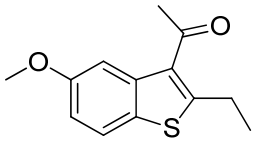
Pale yellow solid. M.p. 57–59 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.76 (dd, J = 4.9, 2.2 Hz, 1H), 8.66 (dd, J = 2.2, 0.8 Hz, 1H), 7.79–7.73 (m, 2H), 7.50 (ddd, J = 8.0, 4.9, 0.8 Hz, 1H), 7.16 (dd, J = 8.0, 2.5 Hz, 1H), 6.77 (d, J = 2.5 Hz, 1H), 3.74 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 192.4, 158.2, 150.2, 149.8, 141.6, 141.5, 137.25, 137.23. 133.2, 131.4, 123.6, 123.5, 118.9, 106.1, 55.6, 30.1. **HRMS** (ESI): calculated for $C_{16}H_{14}NO_2S$ $(M+H)^+$: 284.0740, found: 284.0727.

Cyclopropyl(5-methoxy-3-phenylbenzo[b]thiophen-2-yl)methanone (4g)



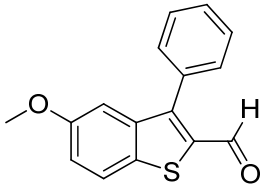
Pale yellow solid. M.p. 93–94 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.8 Hz, 1H), 7.54–7.44 (m, 5H), 7.11 (dd, J = 8.8, 2.5 Hz, 1H), 6.93 (d, J = 2.5 Hz, 1H), 3.74 (s, 3H), 1.83–1.77 (m, 1H), 1.18–1.12 (m, 2H), 0.72–0.67 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.4, 157.9, 141.8, 141.7, 140.8, 135.3, 133.3, 130.1, 128.7, 128.5, 123.4, 118.0, 106.7, 55.5, 20.8, 12.7. **HRMS** (ESI): calculated for $C_{19}H_{17}O_2S$ $(M+H)^+$: 309.0944, found: 309.0936.

1-(3-Ethyl-5-methoxybenzo[b]thiophen-2-yl)ethanone (4h)



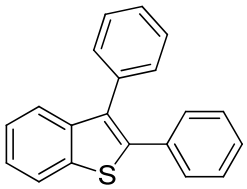
White solid. M.p. 65–66 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64–7.59 (m, 2H), 6.97 (dd, J = 8.7, 2.6 Hz, 1H), 3.87 (s, 3H), 3.17 (q, J = 7.5 Hz, 2H), 2.65 (s, 3H), 1.41 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.3, 158.2, 157.4, 139.5, 132.3, 129.7, 122.4, 114.3, 106.5, 55.6, 31.7, 24.3, 16.0. **HRMS** (ESI): calculated for $C_{13}H_{15}O_2S$ $(M+H)^+$: 235.0787, found: 235.0779.

5-Methoxy-3-phenylbenzo[b]thiophene-2-carbaldehyde (4i)



Yellow solid. M.p. 105–106 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.81–7.76 (m, 1H), 7.58–7.50 (m, 5H), 7.20–7.14 (m, 2H), 3.79 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 185.9, 158.2, 147.1, 140.4, 140.1, 134.7, 132.6, 130.4, 129.0, 128.9, 124.0, 119.4, 106.5, 55.6. **HRMS** (ESI): calculated for $C_{16}H_{13}O_2S$ $(M+H)^+$: 269.0631, found: 269.0626.

2,3-Diphenylbenzo[b]thiophene (4j)



White solid. M.p. 113–114 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.87–7.83 (m, 1H), 7.60–7.55 (m, 1H), 7.41–7.28 (m, 9H), 7.24–7.19 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.0, 139.6, 138.9, 135.6, 134.3, 133.3, 130.5, 129.7, 128.7, 128.8, 127.7, 127.4, 124.6, 124.5, 123.4, 122.1. **HRMS** (ESI): calculated for $C_{20}H_{15}S$ $(M+H)^+$: 287.0934, found: 287.0929.

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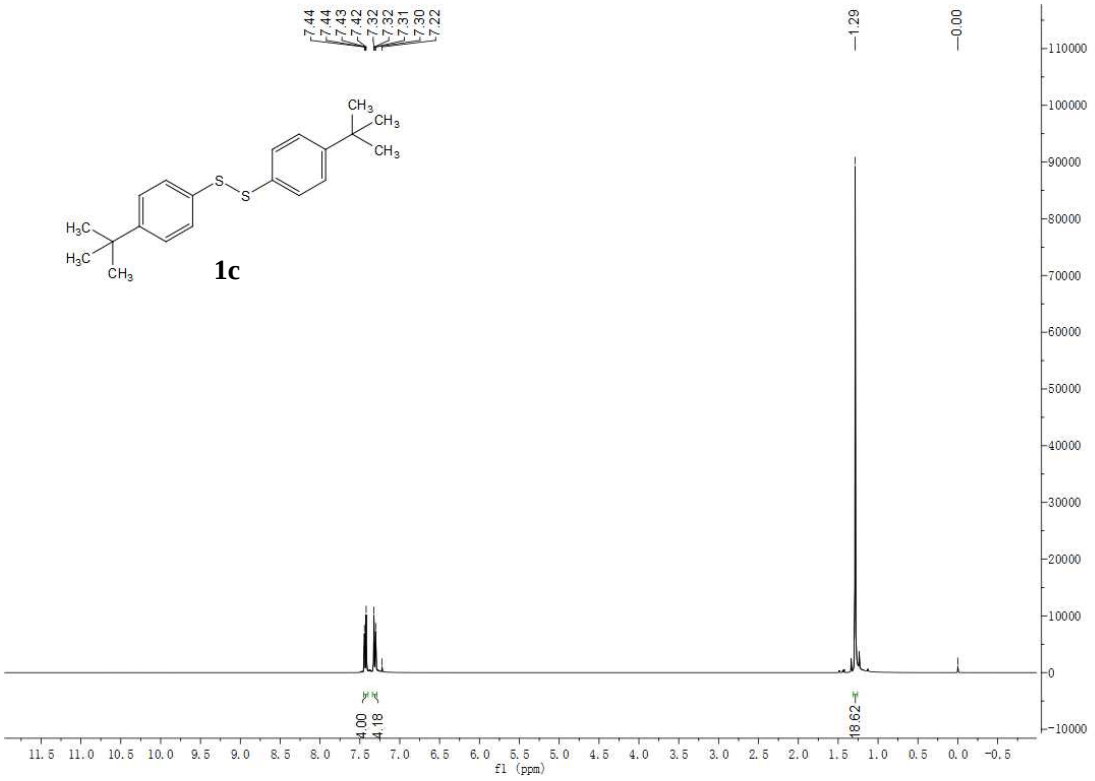
5. NMR Spectra



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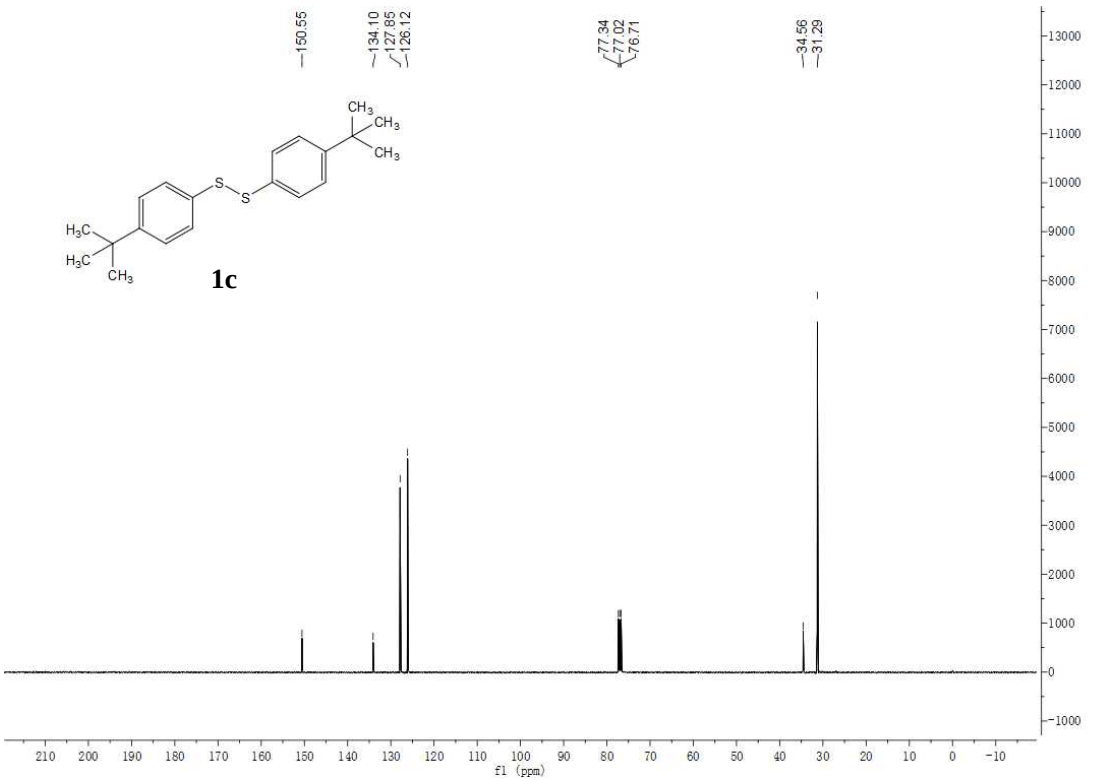

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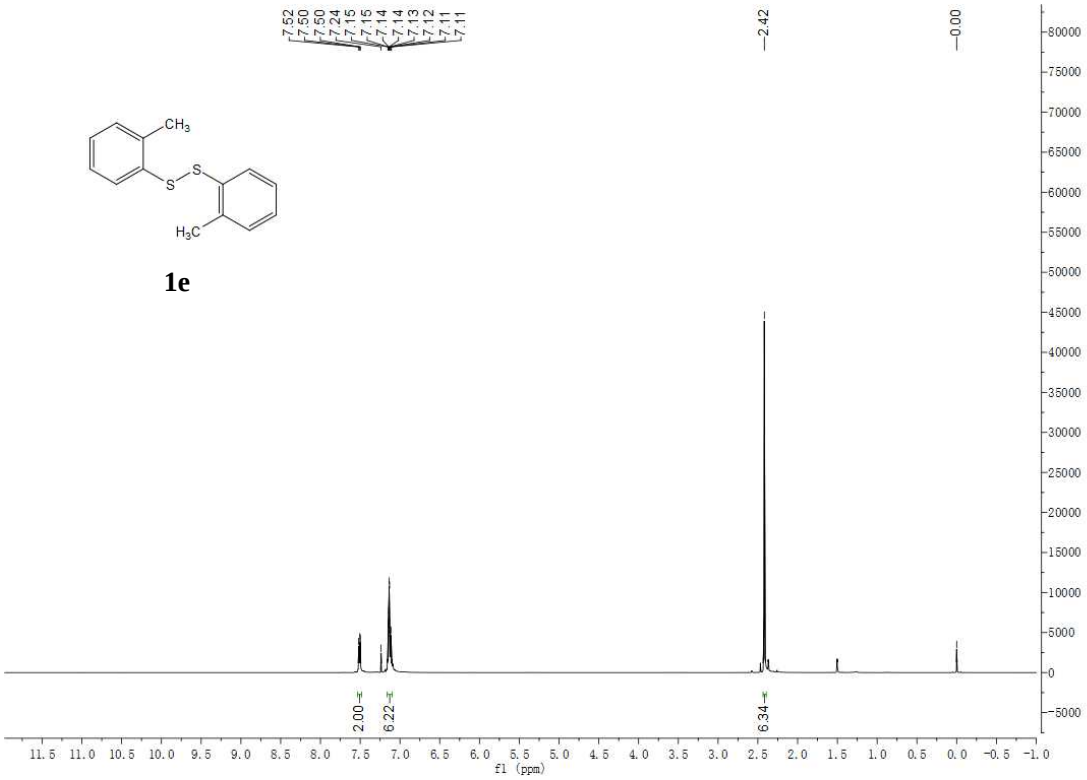
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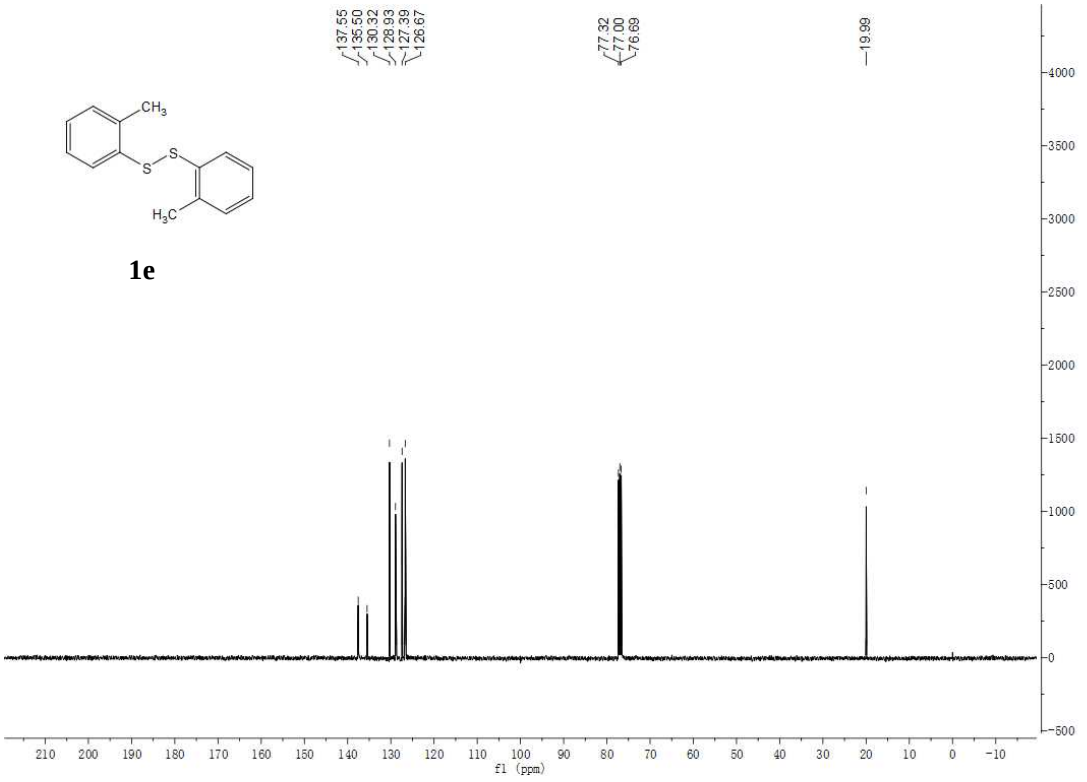
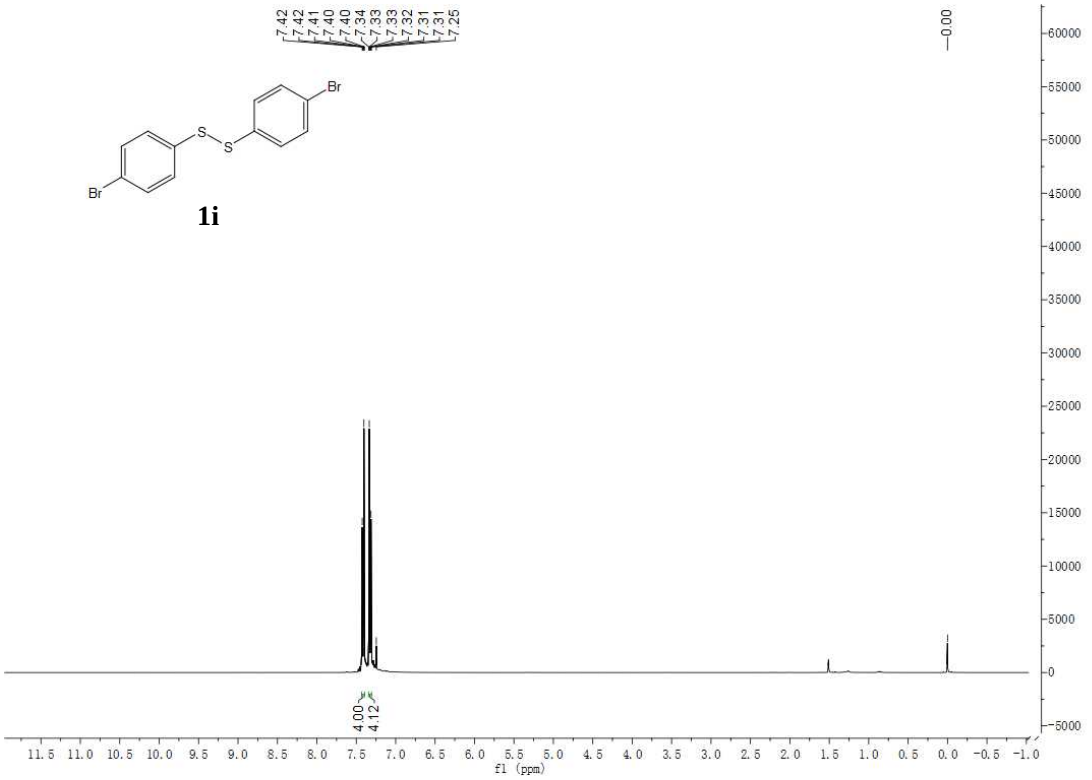
7.50
7.50
7.24
7.15
7.15
7.14
7.14
7.13
7.12
7.11
7.11
2.42
0.00
CH3
S
S
H3C
2.00
6.22
6.34
f1 (ppm)

1e


137.55
135.50
130.32
128.93
127.39
126.67
77.32
77.00
76.69
19.99
CH3
S
S
H3C
f1 (ppm)

1e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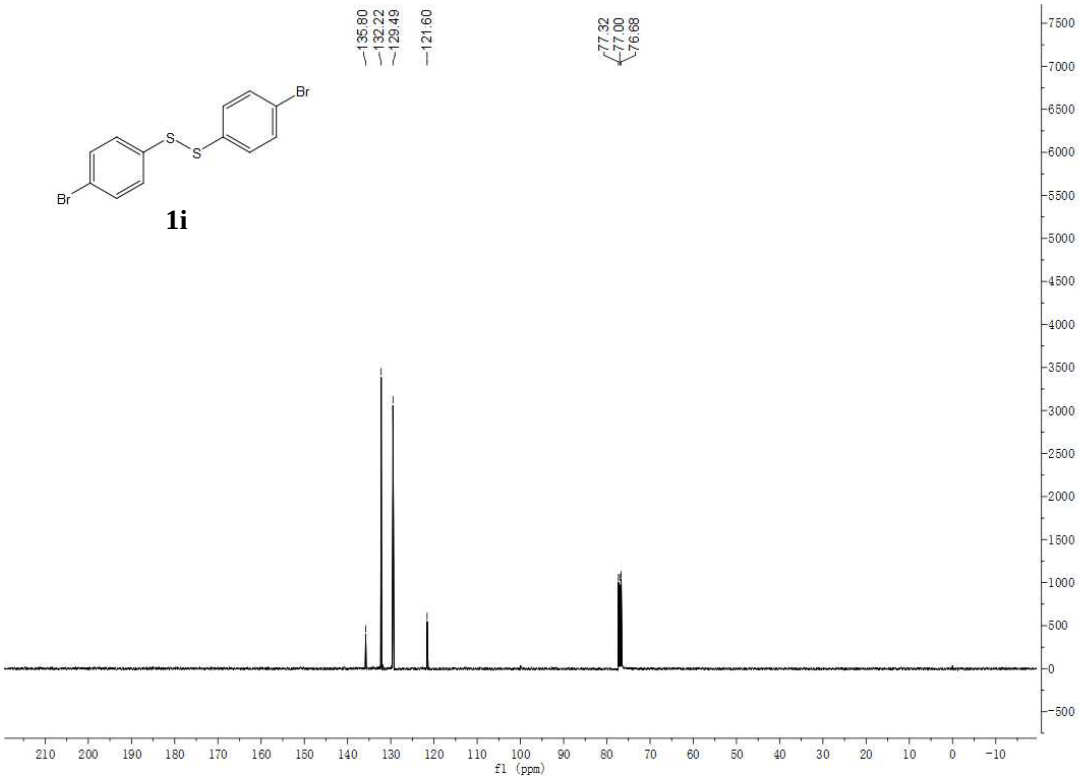
7.42
7.41
7.40
7.40
7.34
7.33
7.33
7.32
7.31
7.31
7.25
0.00
Br
S
S
Br
4.00
4.12
f1 (ppm)

1i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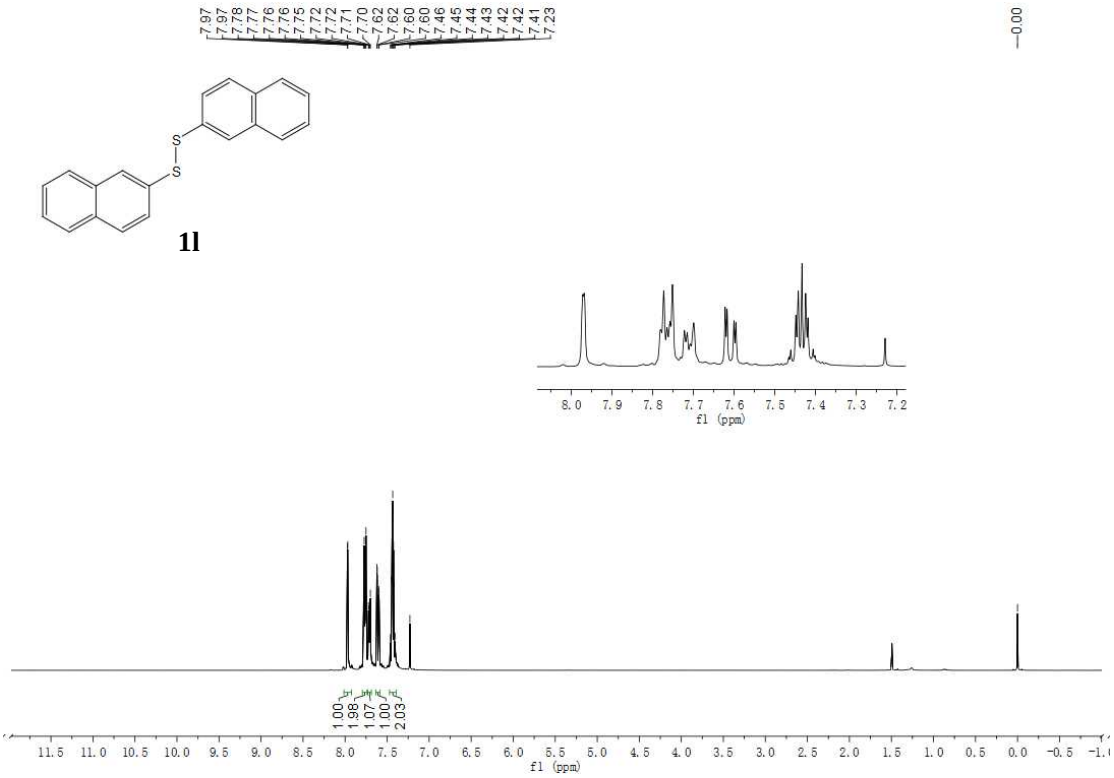
77.00
76.68
Br
S
S
Br
f1 (ppm)

1i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7.77
7.76
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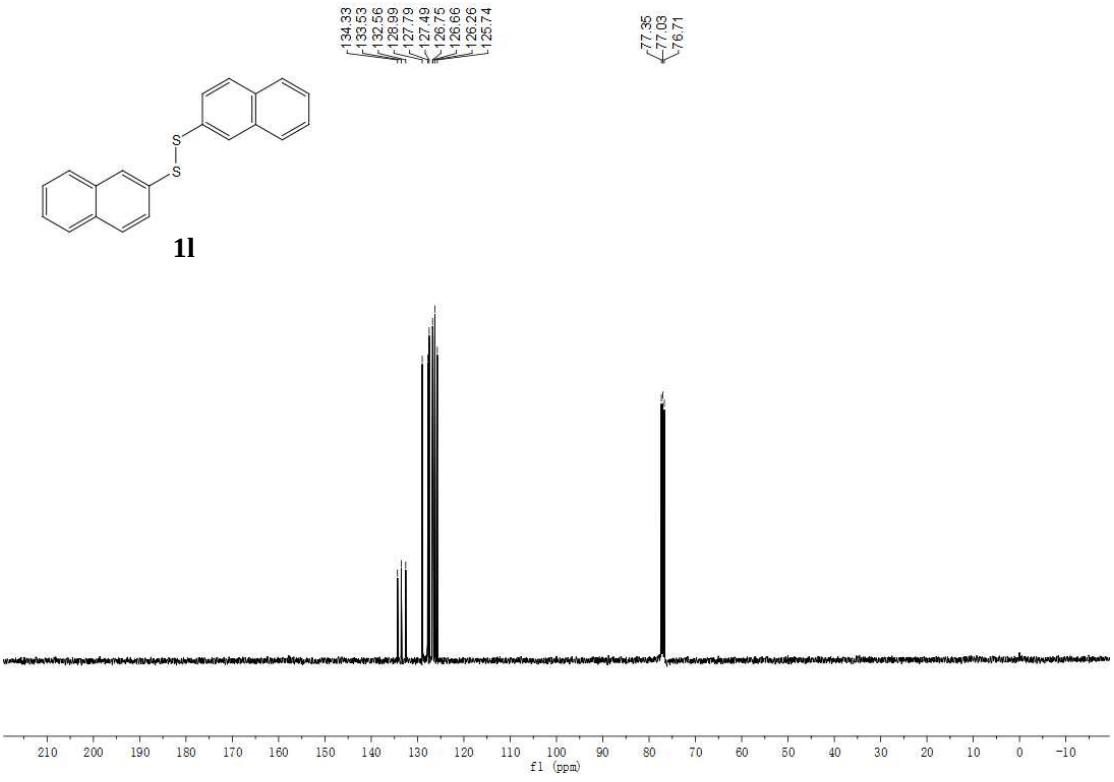
7.75
7.72
7.72
7.71
7.70
7.62
7.62
7.60
7.60
7.46
7.45
7.44
7.43
7.42
7.42
7.41
7.23
0.00
S
S
1l
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
1.00
1.98
1.07
1.00
2.03
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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126.26
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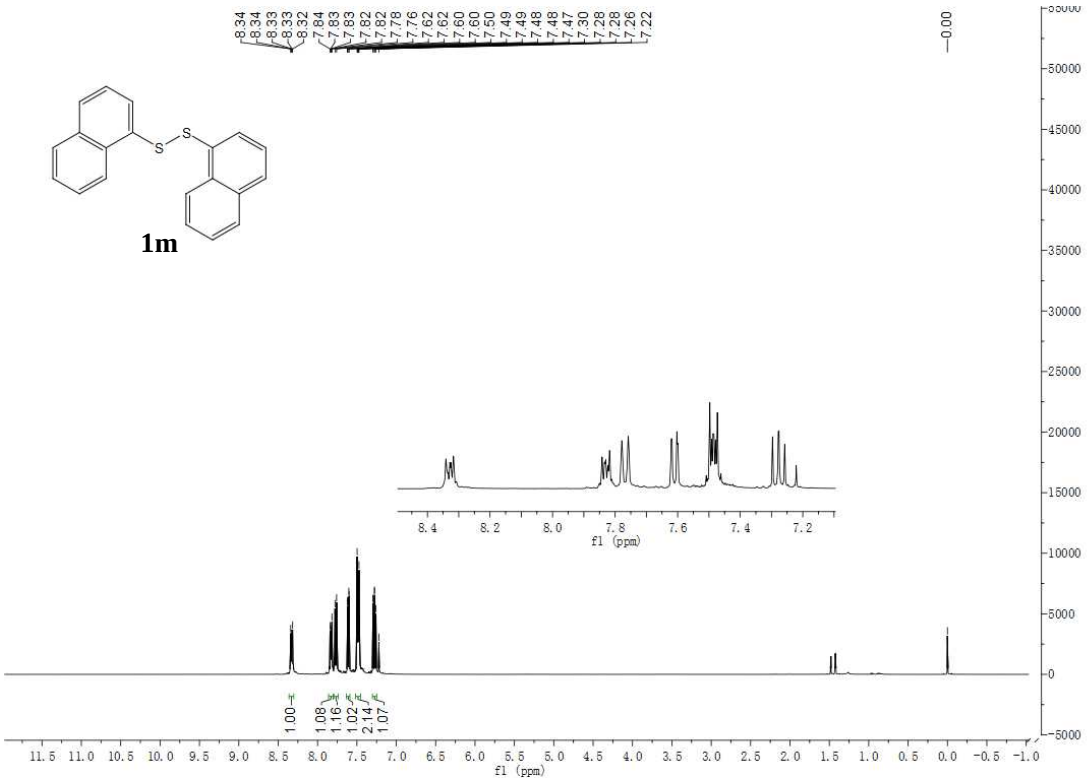
76.71
S
S
1l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.33
8.33
8.32
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7.83
7.83
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7.82
7.78
7.76
7.62
7.62
7.60
7.60
7.50
7.49
7.49
7.48
7.48
7.47
7.30
7.28
7.28
7.26
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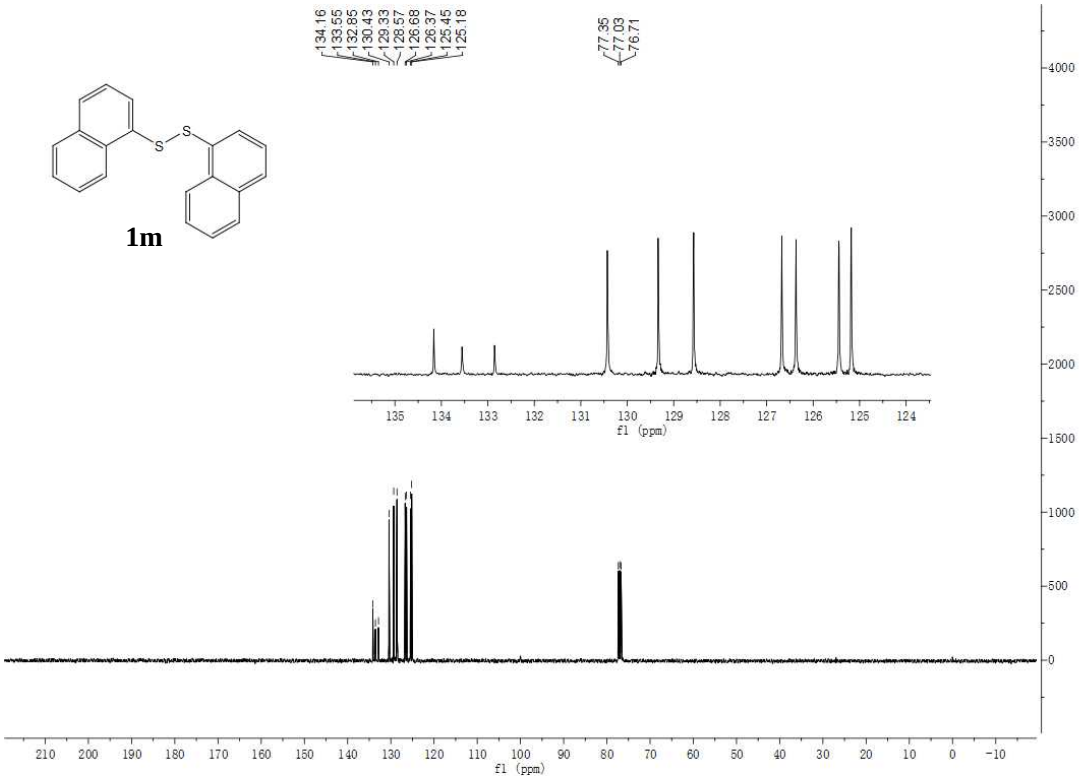
0.00
1m
1.00
1.08
1.16
1.02
2.14
1.07
f1 (ppm)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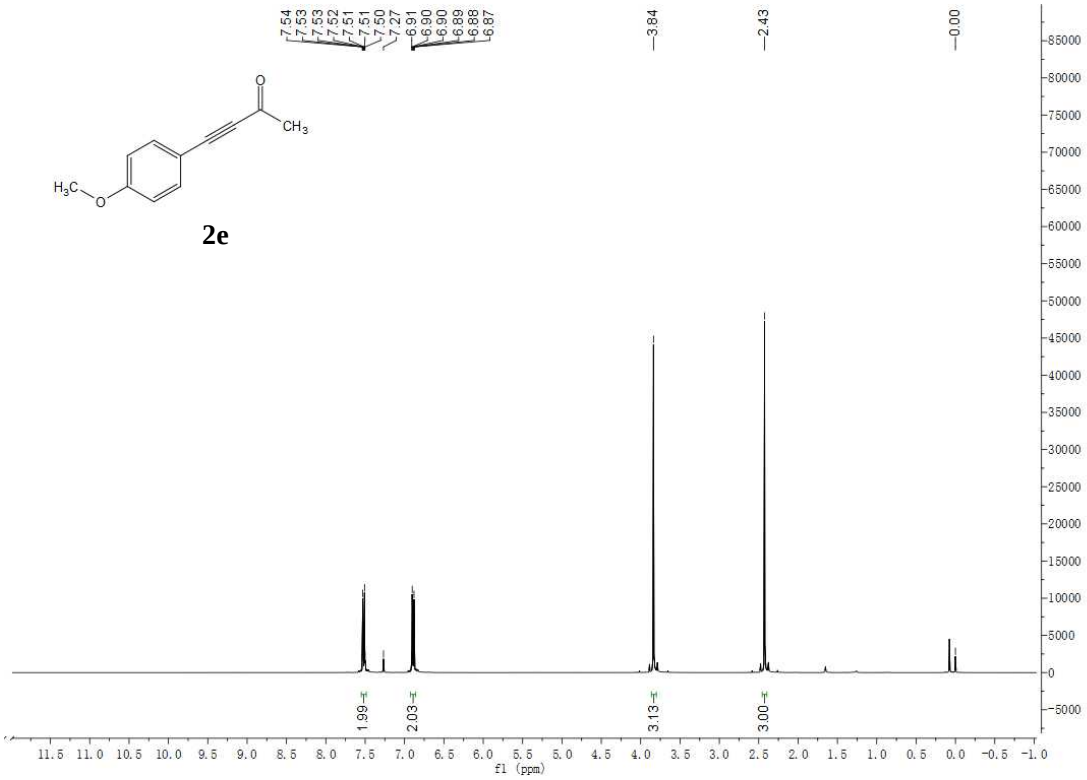
126.37
125.45
125.18
77.35
77.03
76.71
1m
f1 (ppm)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7.53
7.53
7.52
7.51
7.51
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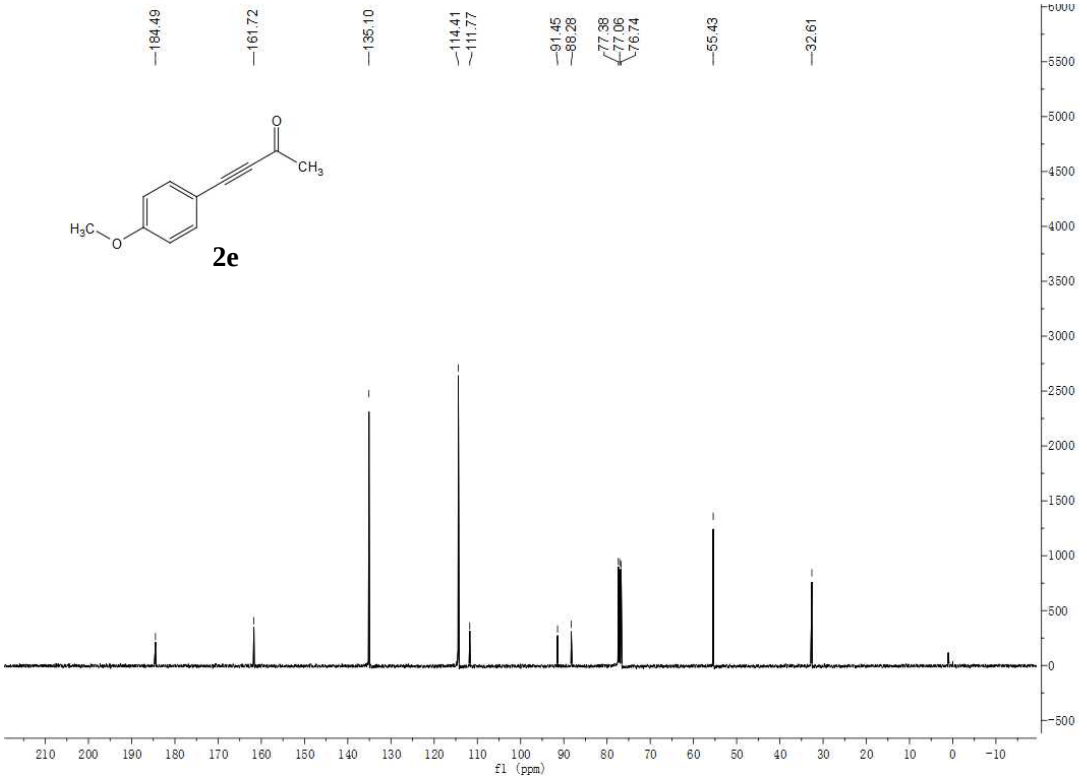
7.27
6.91
6.90
6.90
6.89
6.88
6.87
3.84
2.43
0.00
O
CH3
H3C
O
1.99
2.03
3.13
3.00
f1 (ppm)

2e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161.72
135.10
114.41
111.77
91.45
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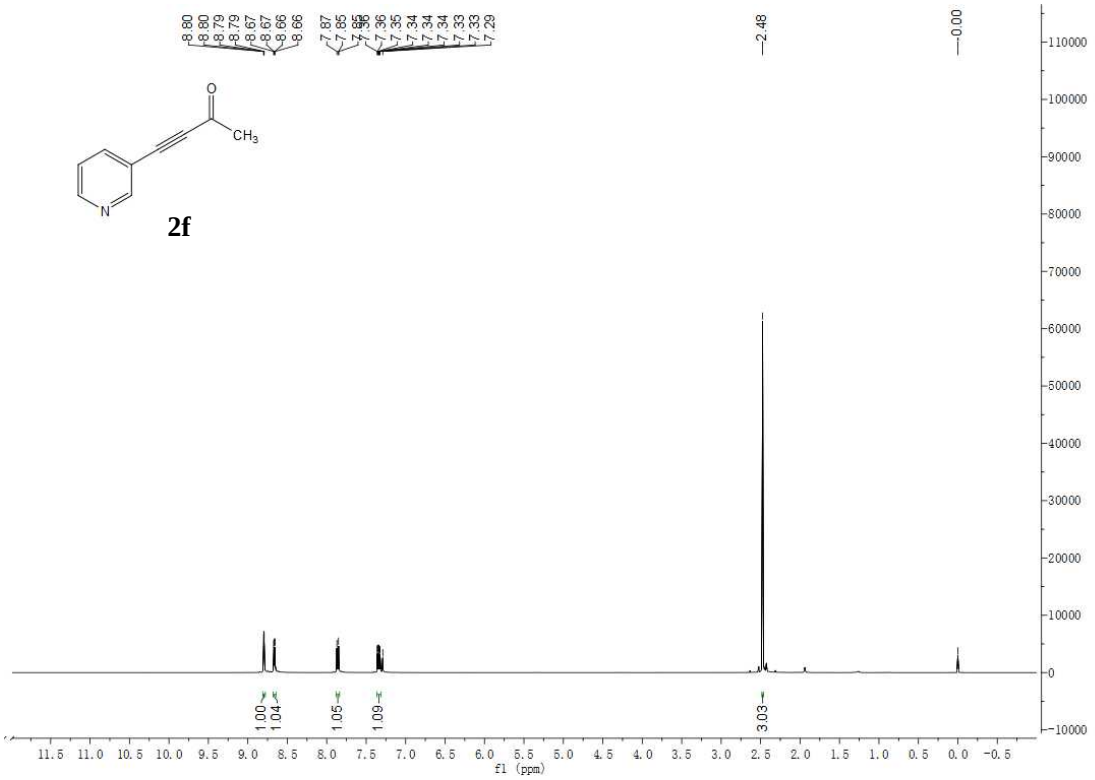
77.38
77.06
76.74
55.43
32.61
O
CH3
H3C
O
f1 (ppm)

2e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8.80
8.79
8.79
8.67
8.67
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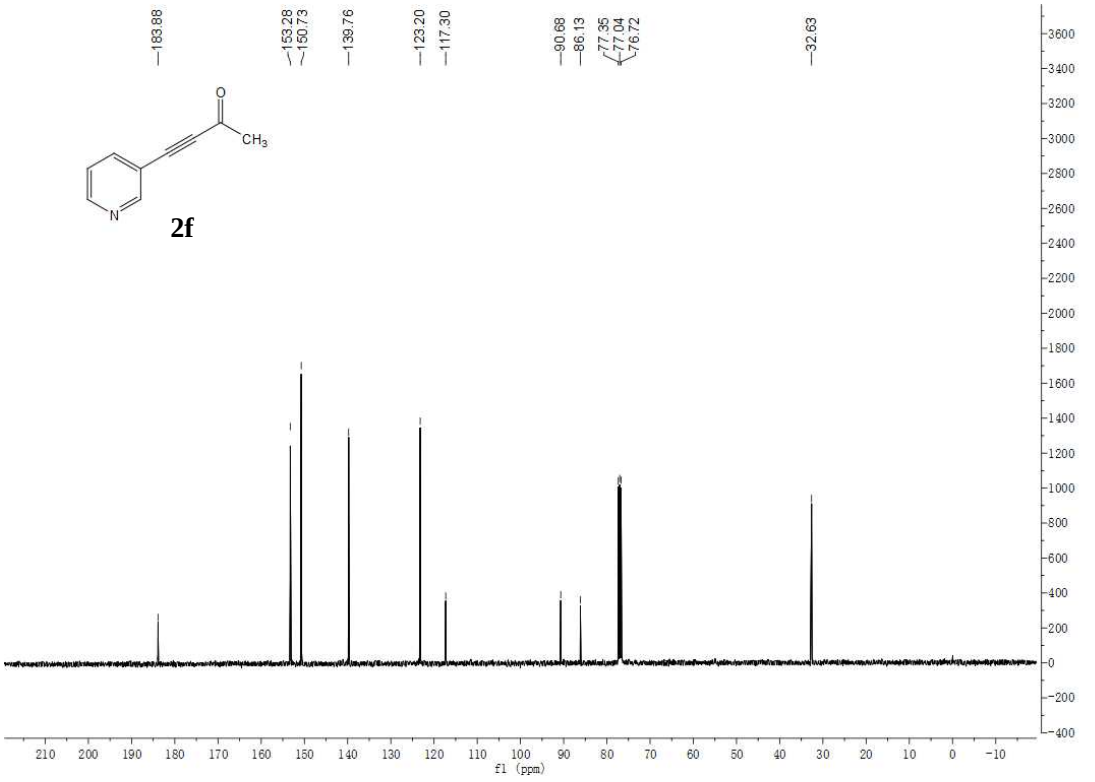
8.66
7.87
7.85
7.36
7.35
7.34
7.34
7.33
7.33
7.29
2.48
0.00
O
CH3
N
2f
1.00
1.04
1.05
1.09
3.03
f1 (ppm)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86.13
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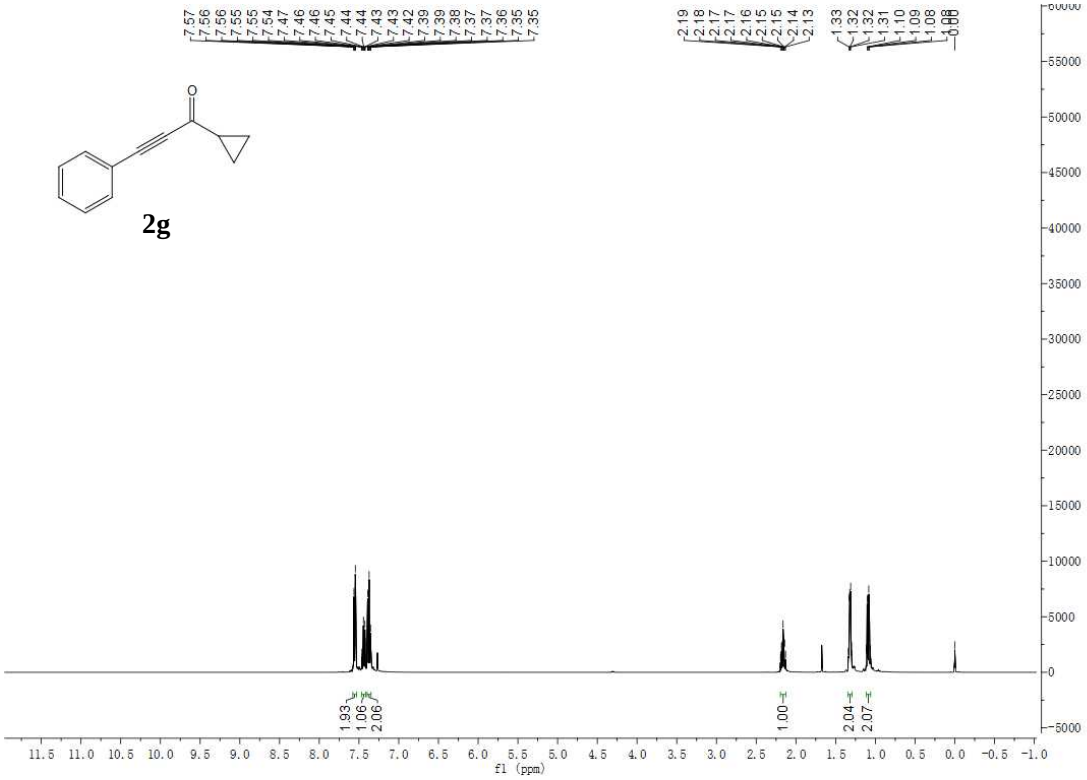
77.04
76.72
32.63
O
CH3
N
2f
f1 (ppm)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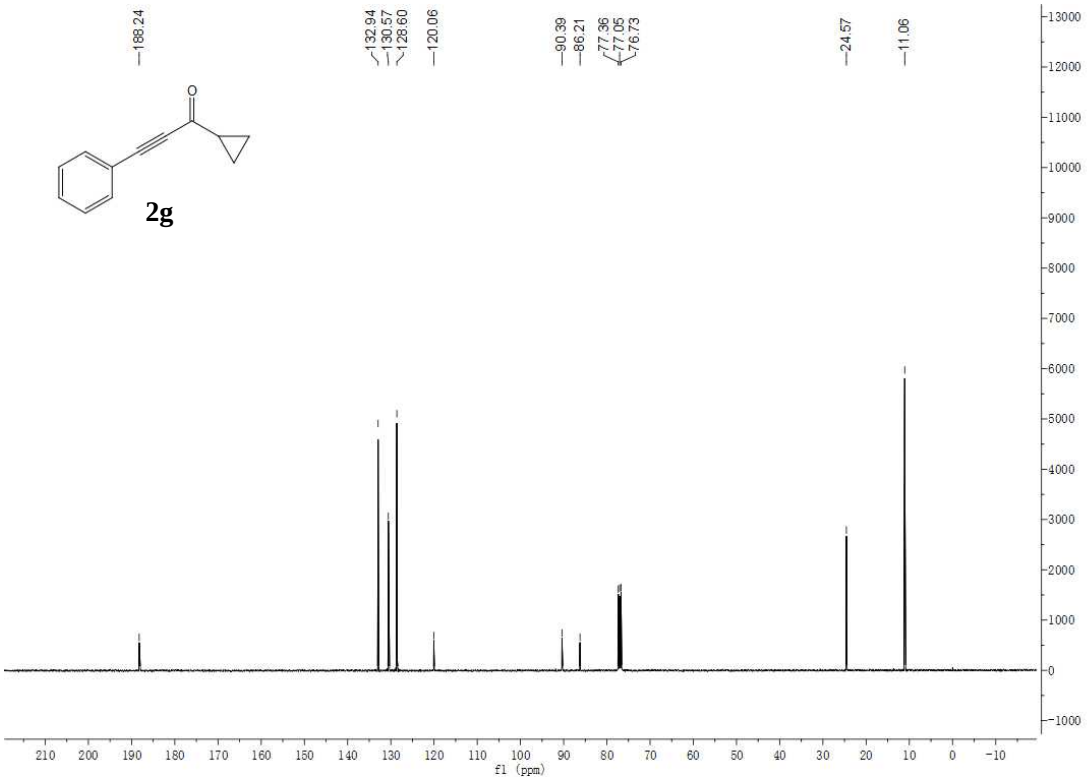
7.56
7.56
7.55
7.55
7.54
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.39
7.39
7.38
7.37
7.37
7.36
7.35
7.35
2.19
2.18
2.17
2.17
2.16
2.15
2.15
2.14
2.13
1.33
1.32
1.32
1.31
1.10
1.09
1.08
0.00
O
2g
1.93
1.06
2.06
1.00
2.04
2.07
f1 (ppm)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86.21
77.36
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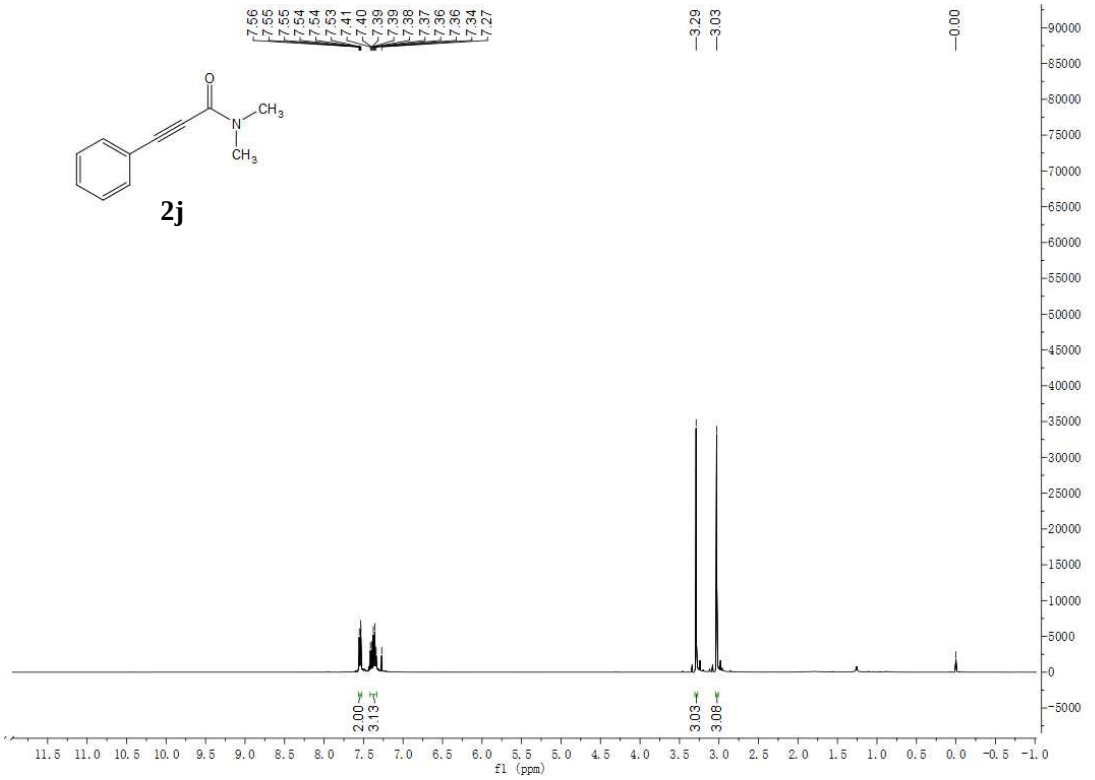
76.73
24.57
11.06
O
2g
f1 (ppm)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7.39
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7.36
7.36
7.34
7.27
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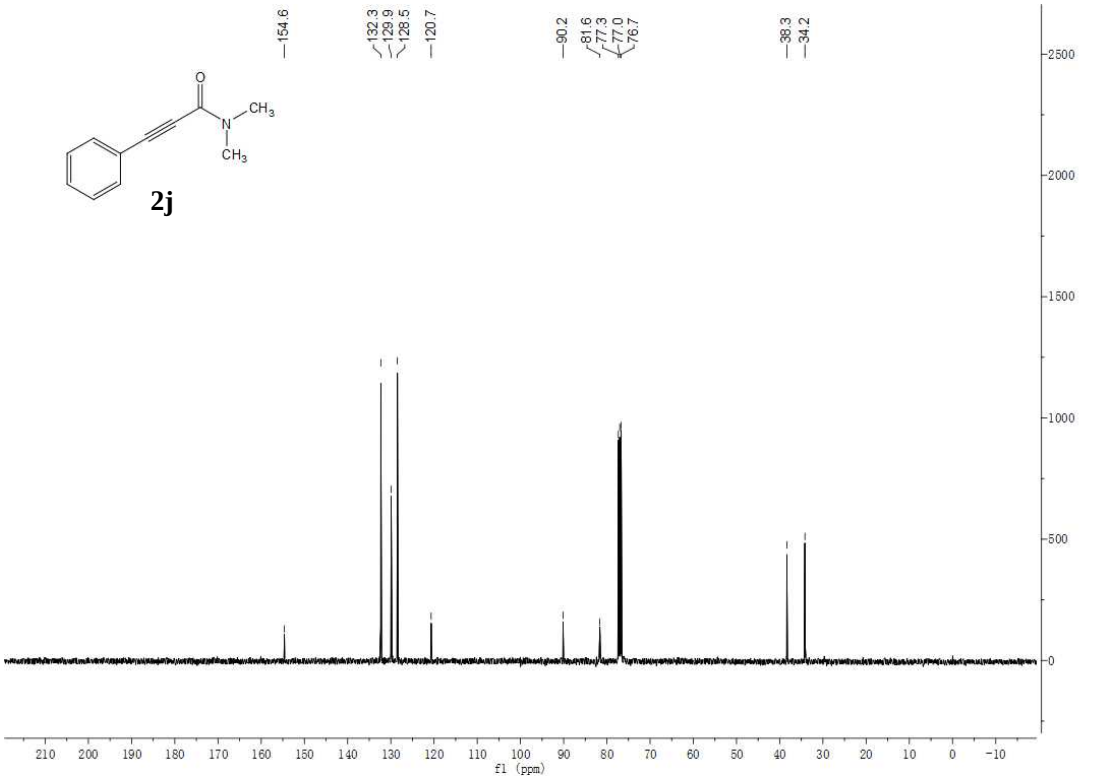
N
CH3
CH3
2j
2.00
3.13
3.03
3.08
f1 (ppm)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77.3
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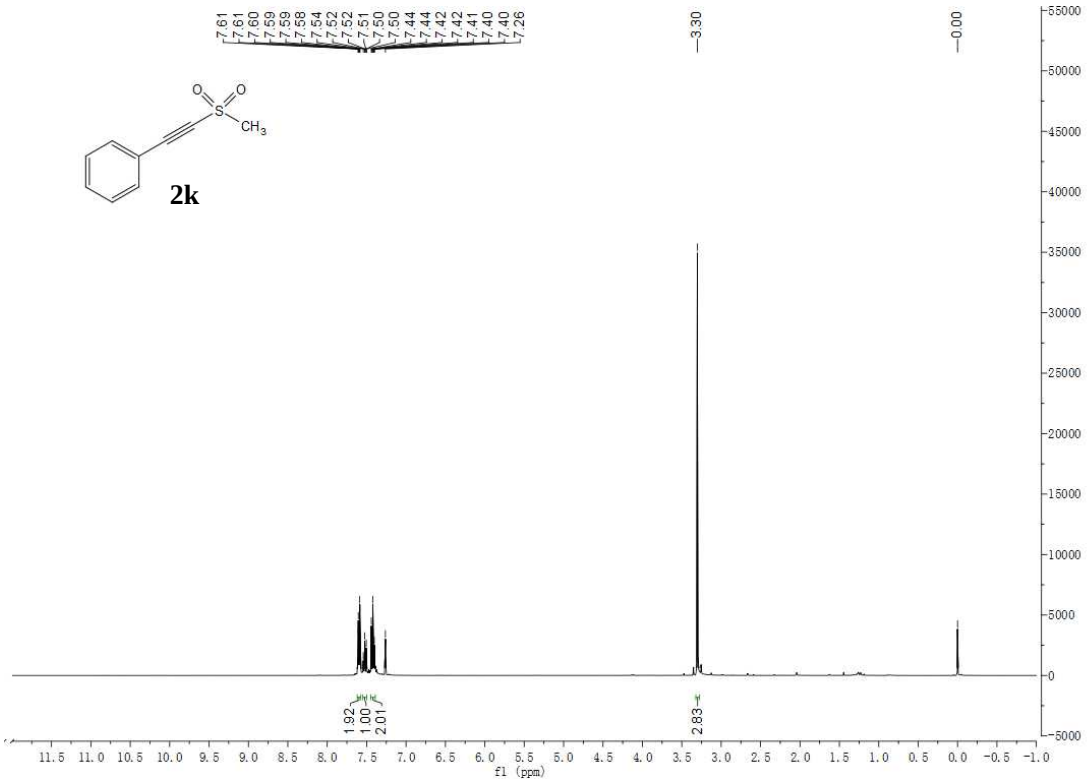
38.3
34.2
O
N
CH3
CH3
2j
f1 (ppm)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7.61
7.60
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7.59
7.58
7.54
7.52
7.52
7.51
7.50
7.50
7.44
7.44
7.42
7.42
7.41
7.40
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7.26
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1.92
1.00
2.01
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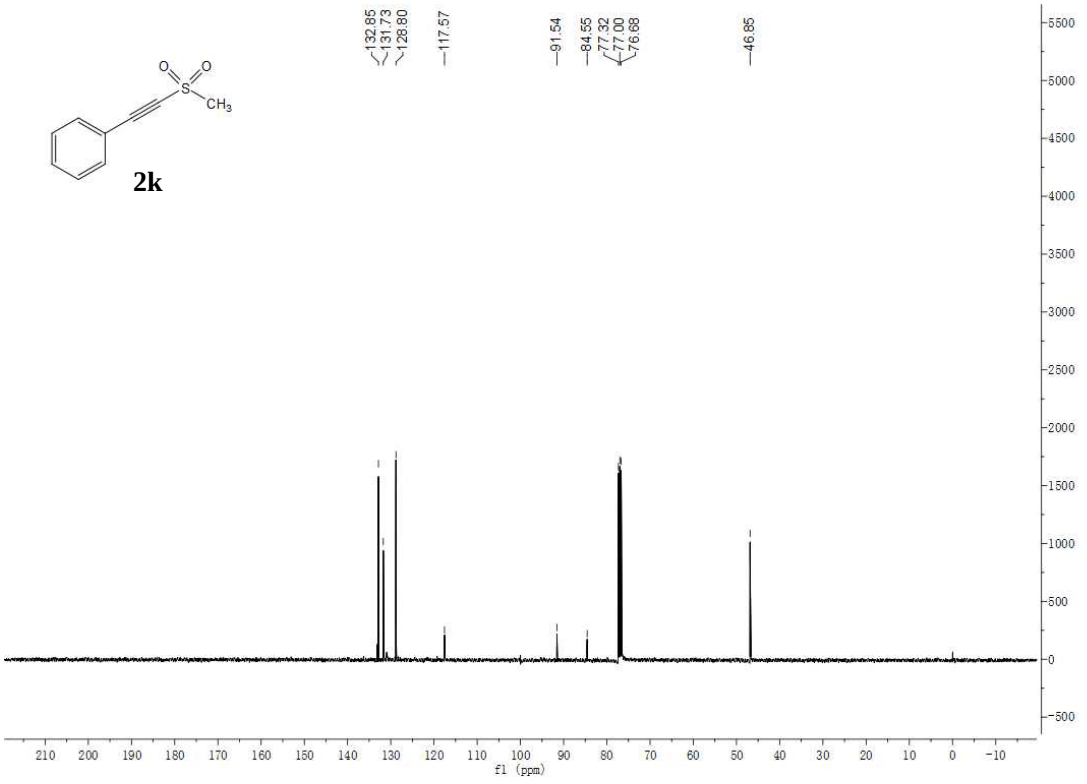
f1 (ppm)

2k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76.68
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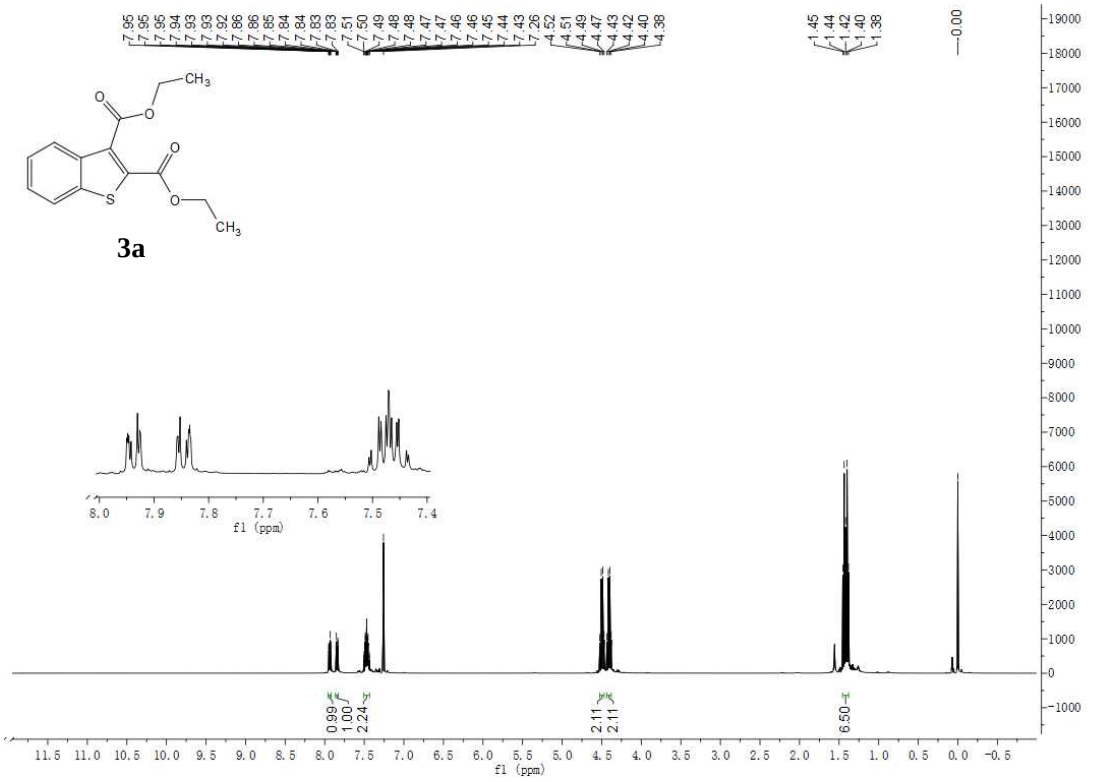
f1 (ppm)

2k



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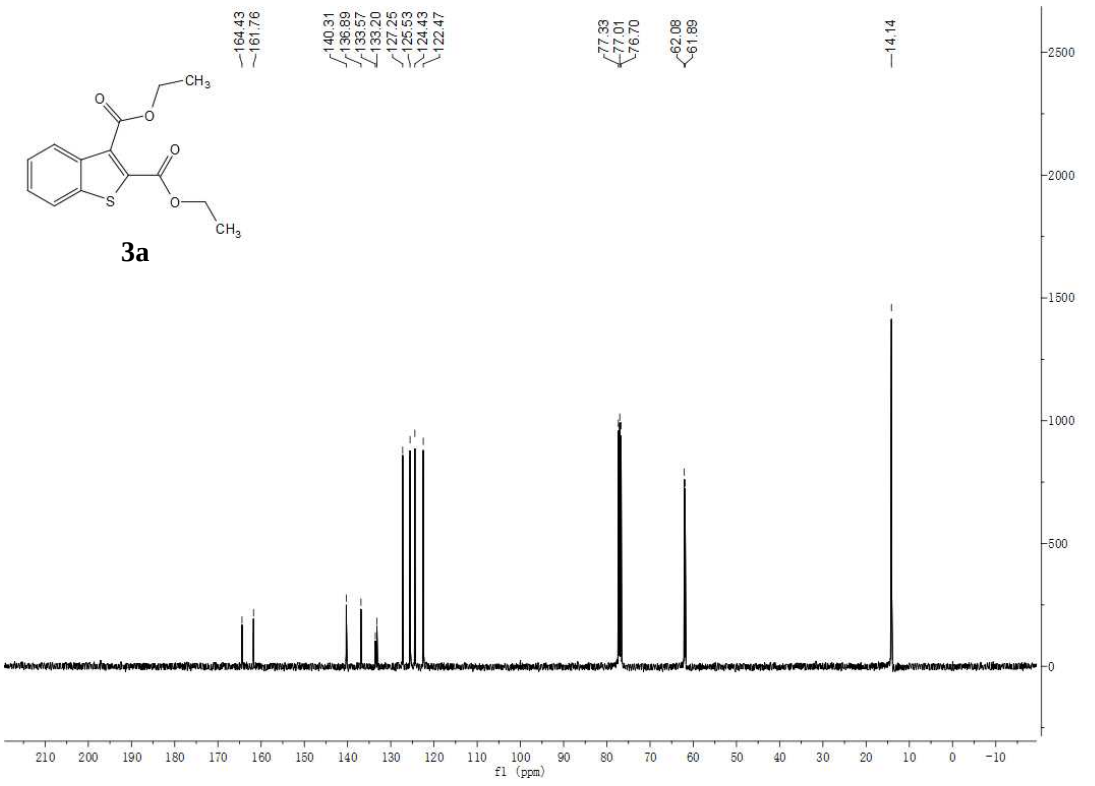
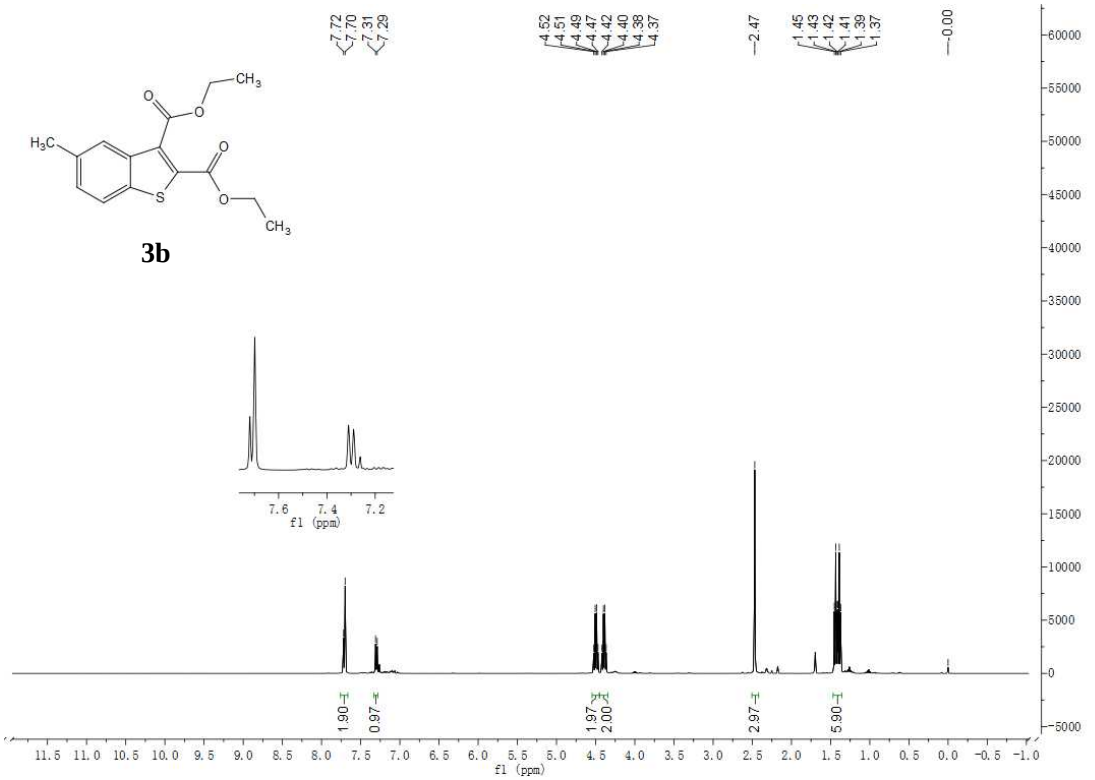


3a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4.47
4.42
4.40
4.38
4.37
2.47
1.45
1.43
1.42
1.41
1.39
1.37
0.00
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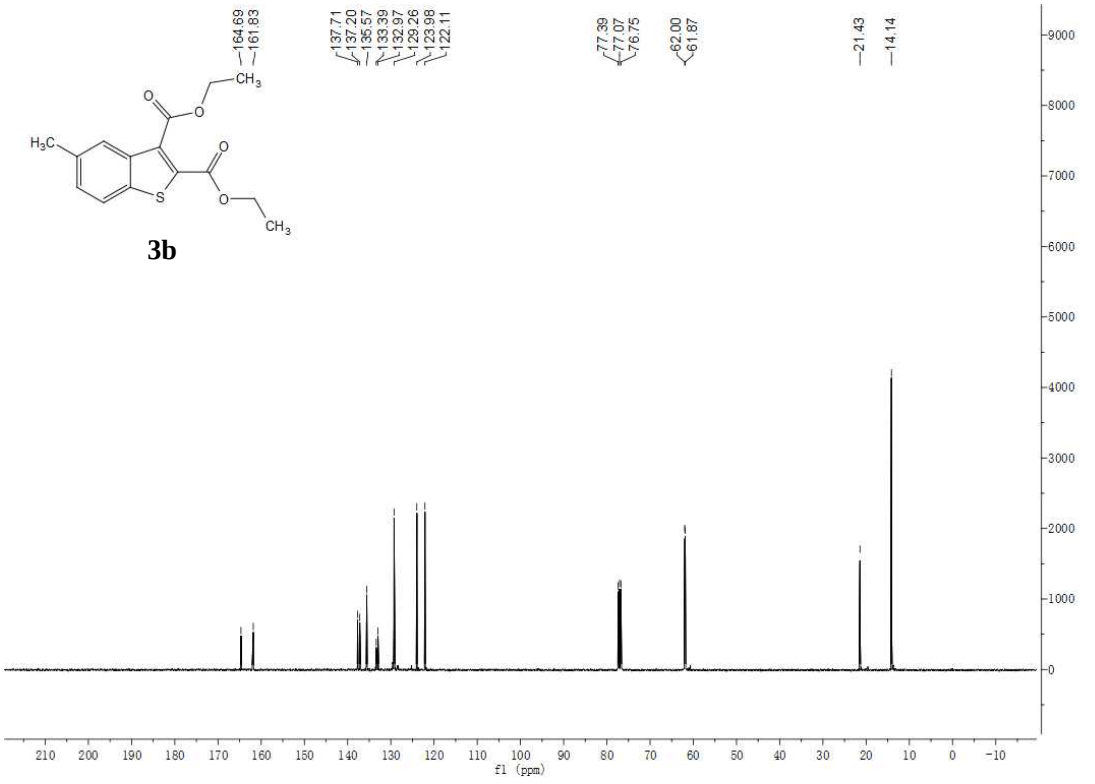
1.97
2.00
2.97
5.90
f1 (ppm)

3b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137.20
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133.39
132.97
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123.98
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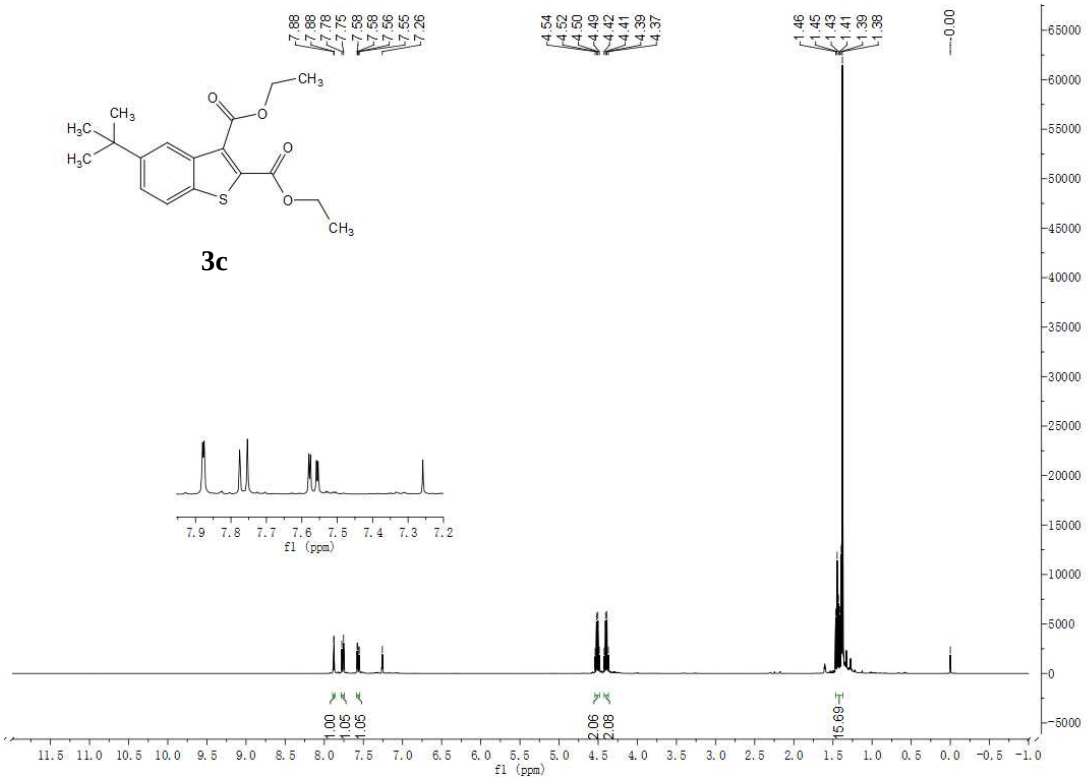
14.14
f1 (ppm)

3b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7.58
7.56
7.55
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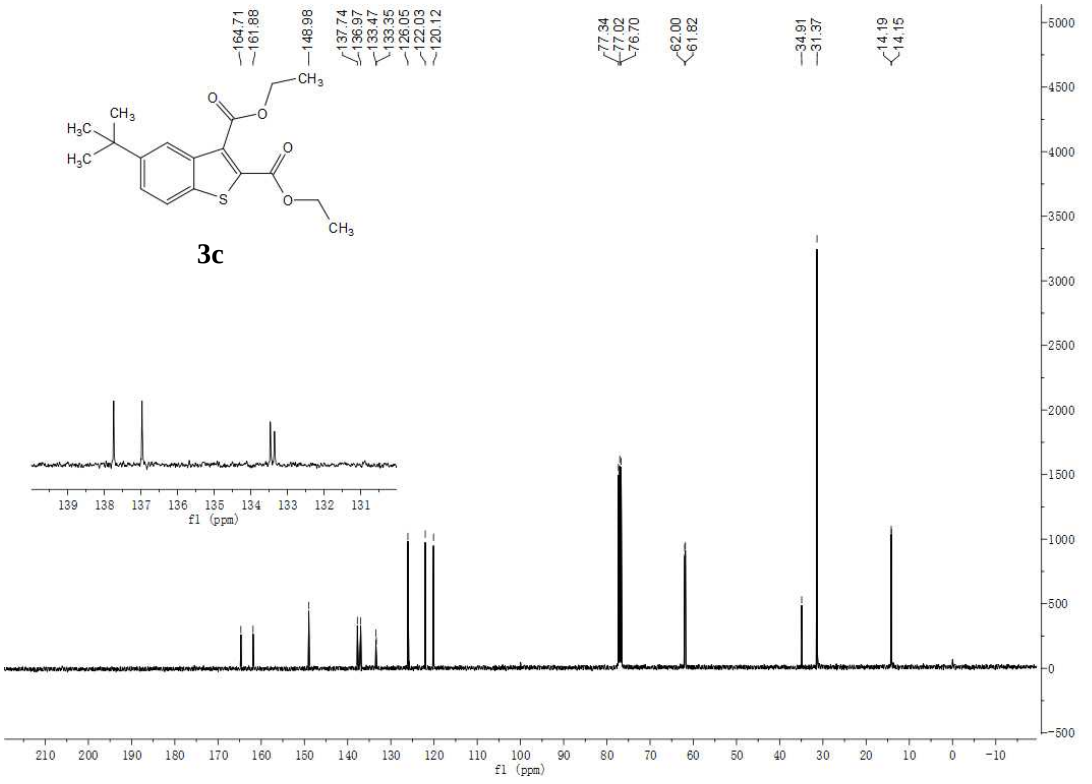
4.52
4.50
4.49
4.42
4.41
4.39
4.37
1.46
1.45
1.43
1.41
1.39
1.38
0.00
CH3
H3C
H3C
O
O
O
O
S
CH3
3c
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
1.00
1.05
1.05
2.06
2.08
15.69
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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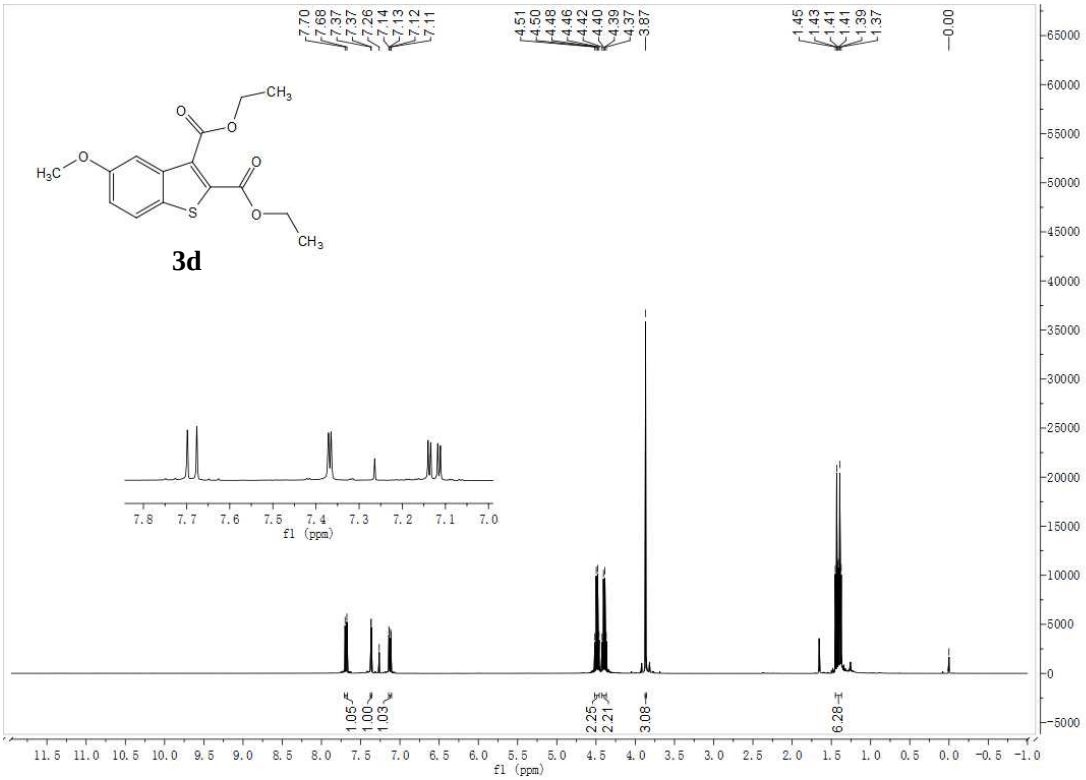
133.47
133.35
126.05
122.03
120.12
77.34
77.02
76.70
62.00
61.82
34.91
31.37
14.19
14.15
CH3
H3C
H3C
O
O
O
O
S
CH3
3c
139 138 137 136 135 134 133 132 131
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.12
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4.50
4.48
4.46
4.42
4.40
4.39
4.37
3.87
1.45
1.43
1.41
1.41
1.39
1.37
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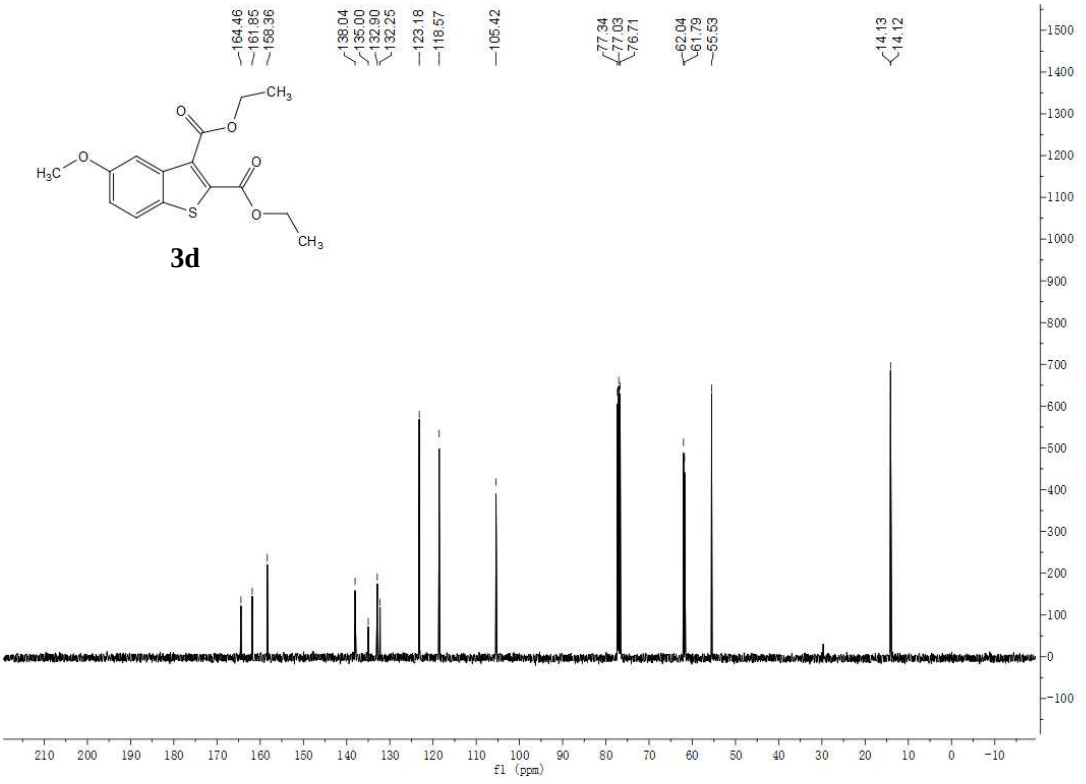
1.05
1.00
1.03
2.25
2.21
3.08
6.28
f1 (ppm)

3d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132.25
123.18
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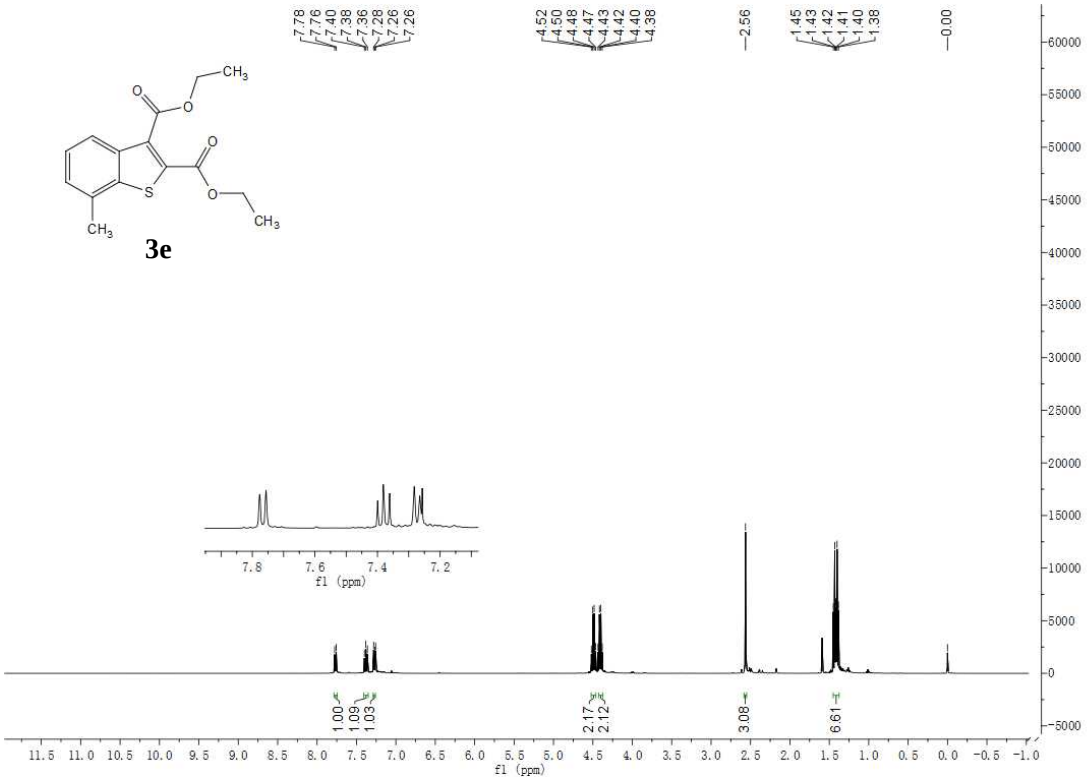
77.03
76.71
62.04
61.79
55.53
14.13
14.12
f1 (ppm)

3d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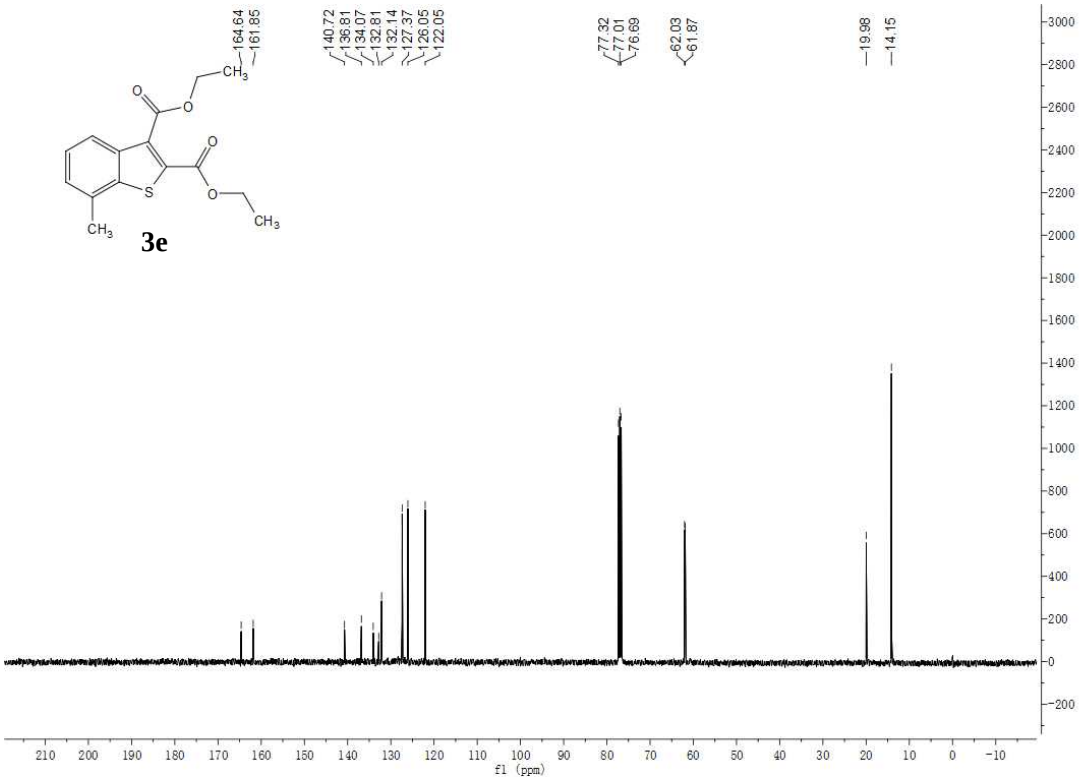
7.36
7.28
7.26
7.26
4.52
4.50
4.48
4.47
4.43
4.42
4.40
4.38
2.56
1.45
1.43
1.42
1.41
1.40
1.38
0.00
1.00
1.09
1.03
2.17
2.12
3.08
6.61
f1 (ppm)

3e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122.05
77.32
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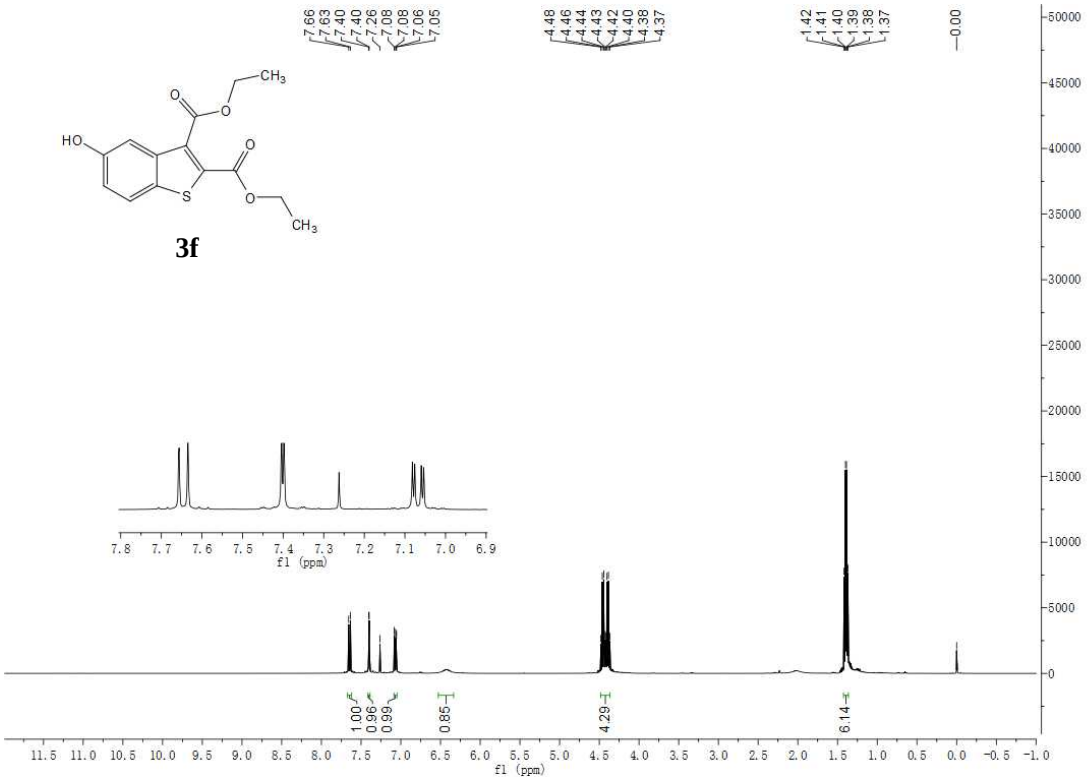
76.69
62.03
61.87
19.98
14.15
f1 (ppm)

3e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7.08
7.08
7.06
7.05
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4.46
4.44
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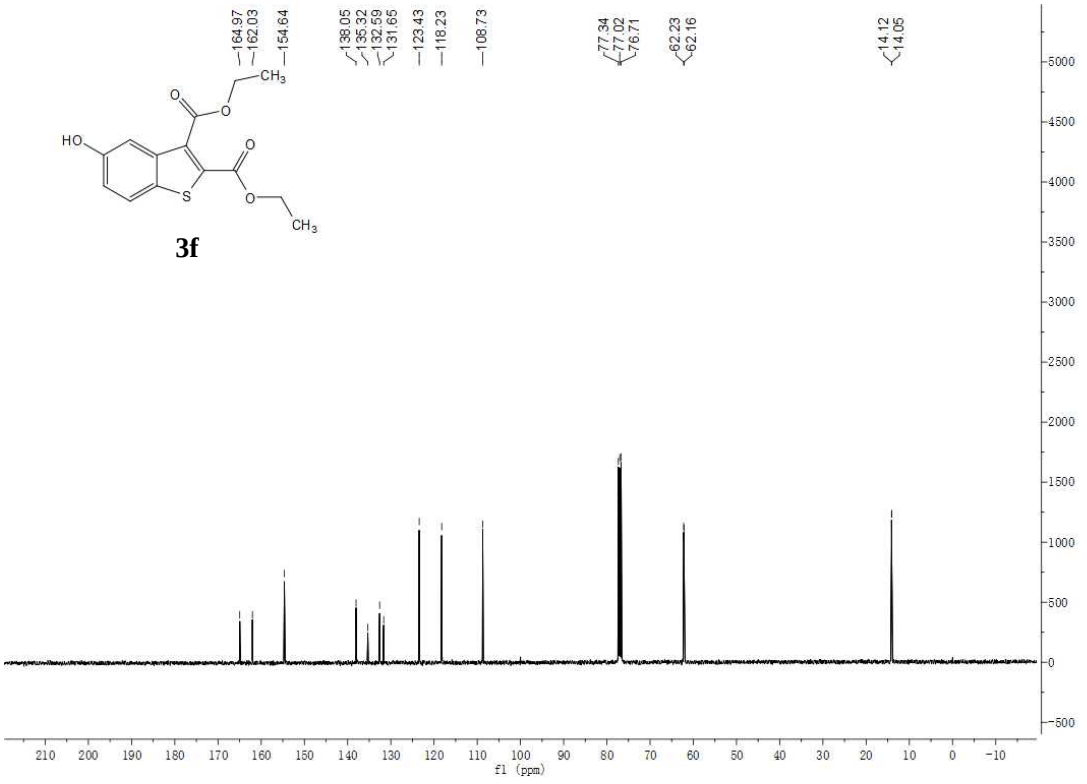
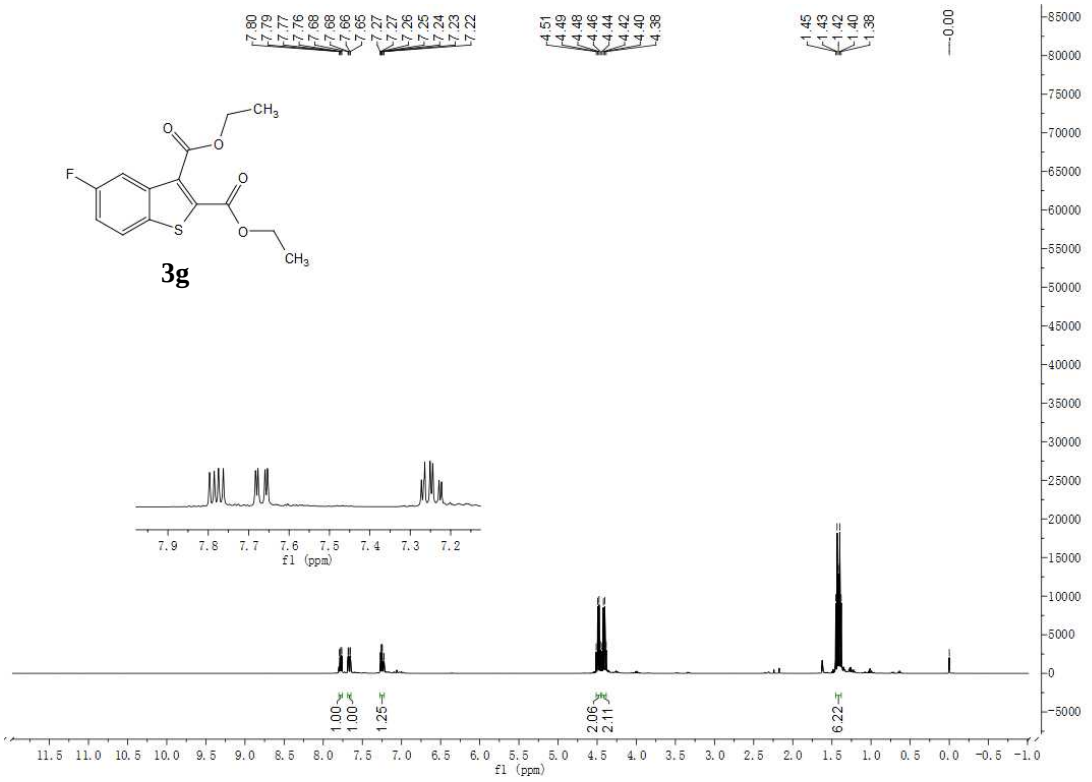
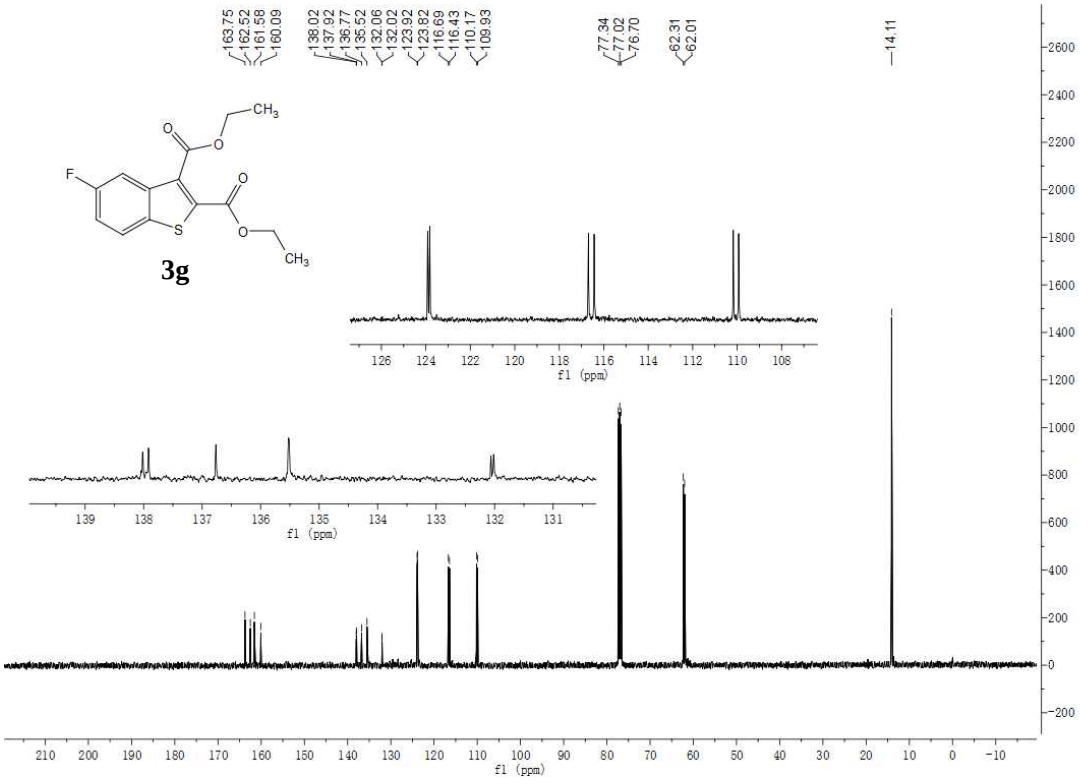
4.42
4.40
4.38
4.37
1.42
1.41
1.40
1.39
1.38
1.37
0.00
HO
O
O
O
O
S
CH3
CH3
1.00
0.96
0.99
0.85
4.29
6.14
f1 (ppm)

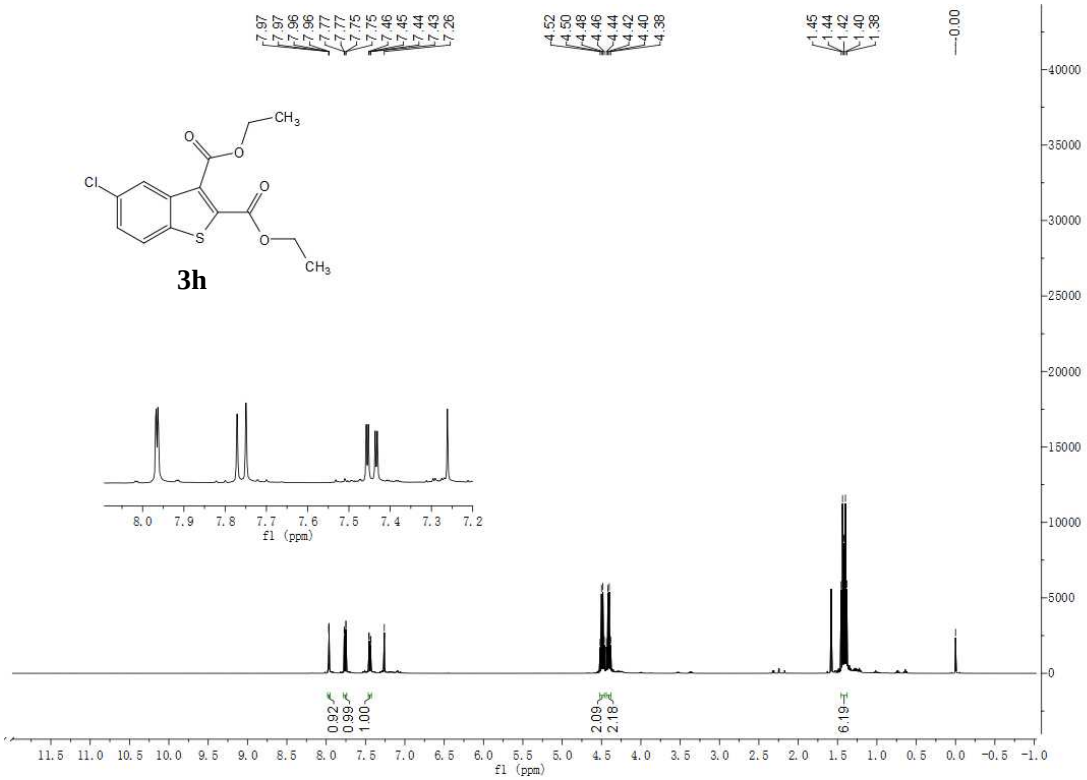
3f

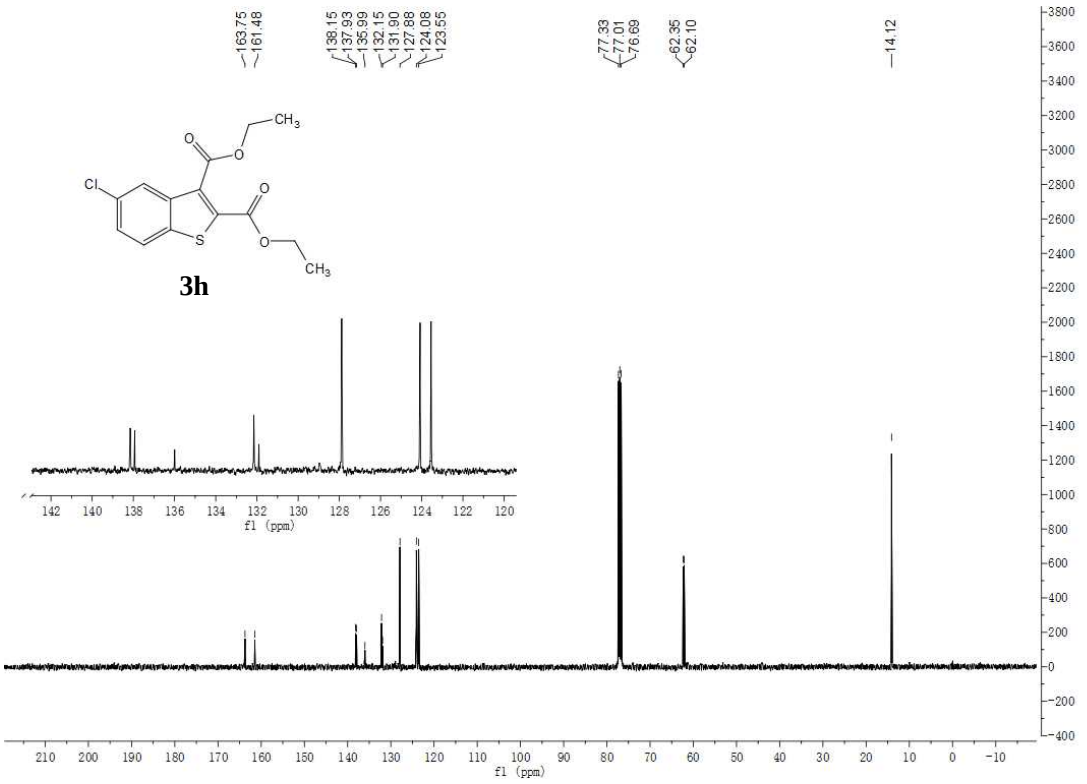

164.97
162.03
154.64
138.05
135.32
132.59
131.65
123.43
118.23
108.73
77.34
77.02
76.71
62.23
62.16
14.12
14.05
HO
O
O
O
O
S
CH3
CH3
f1 (ppm)

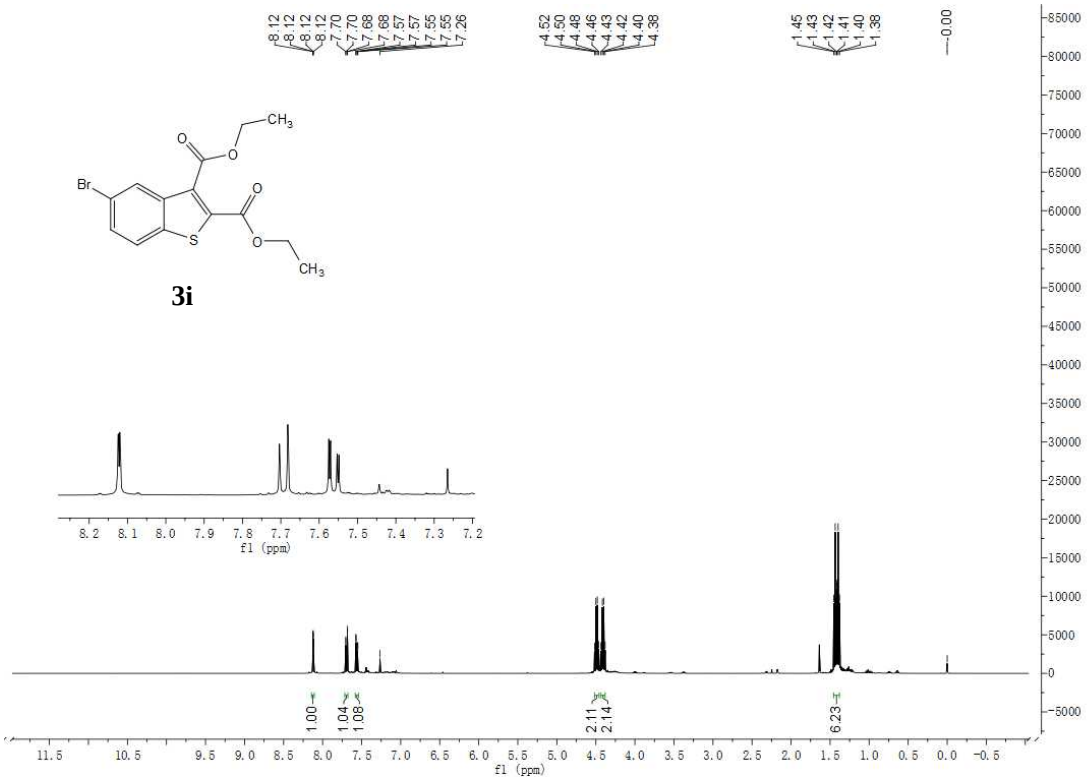
3f


7.80
7.79
7.77
7.76
7.68
7.68
7.66
7.65
7.27
7.26
7.25
7.24
7.23
7.22
4.51
4.49
4.48
4.46
4.44
4.42
4.40
4.38
1.45
1.43
1.42
1.40
1.38
0.00
F
O
O
O
O
S
CH3
CH3
3g
1.00
1.00
1.25
2.06
2.11
6.22
f1 (ppm)

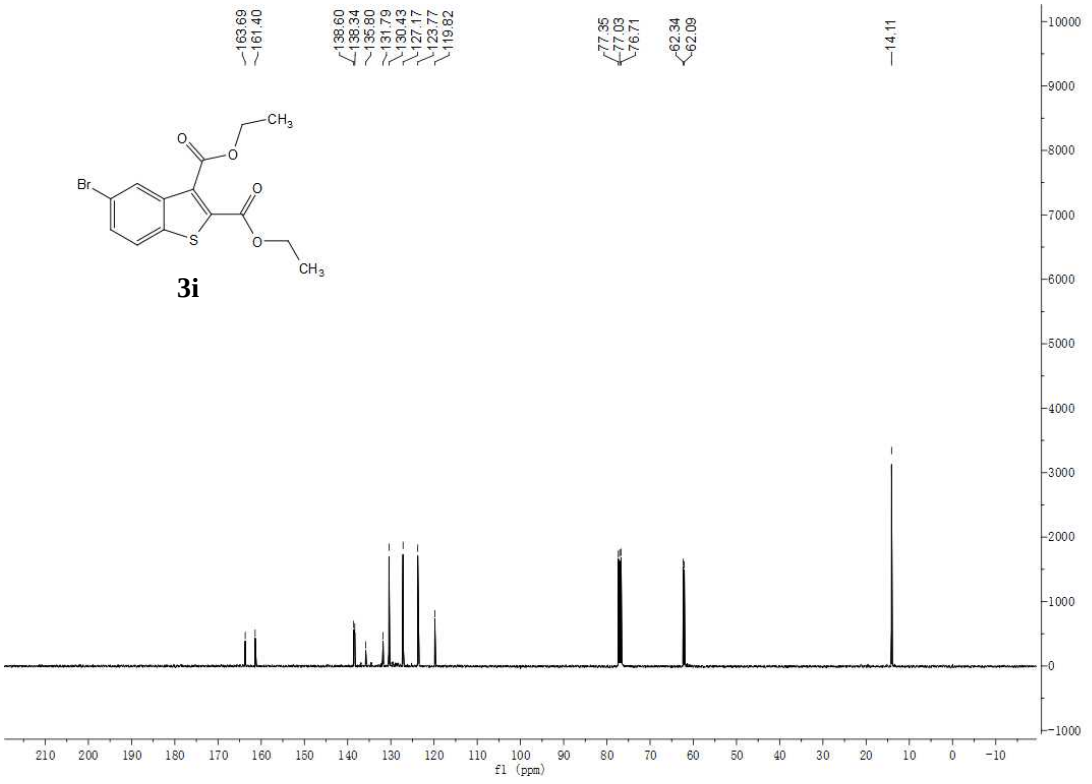

163.75
162.52
161.58
160.09
138.02
137.92
136.77
135.52
132.06
132.02
123.92
123.82
116.69
116.43
110.17
109.93
77.34
77.02
76.70
62.31
62.01
14.11
F
O
O
O
O
S
CH3
CH3
3g
f1 (ppm)


7.97
7.96
7.77
7.75
7.46
7.45
7.44
7.43
7.26
4.52
4.50
4.48
4.46
4.44
4.42
4.40
4.38
1.45
1.44
1.42
1.40
1.38
0.00
Cl
O
O
O
O
S
CH3
CH3
3h
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
0.92
0.99
1.00
2.09
2.18
6.19
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 -0.5 -1.0
f1 (ppm)

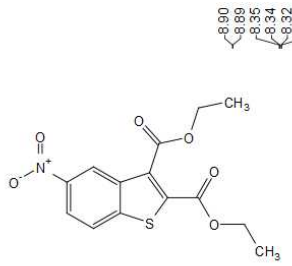

163.75
161.48
138.15
137.93
135.99
132.15
131.90
127.88
124.08
123.55
77.33
77.01
76.69
62.35
62.10
14.12
Cl
O
O
O
O
S
CH3
CH3
3h
142 140 138 136 134 132 130 128 126 124 122 120
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.12
8.12
8.12
8.12
7.70
7.70
7.68
7.68
7.57
7.57
7.55
7.55
7.26
4.52
4.50
4.48
4.46
4.43
4.42
4.40
4.38
1.45
1.43
1.42
1.41
1.40
1.38
0.00
Br
O
O
O
O
S
CH3
CH3
1.00
1.04
1.08
2.11
2.14
6.23
f1 (ppm)

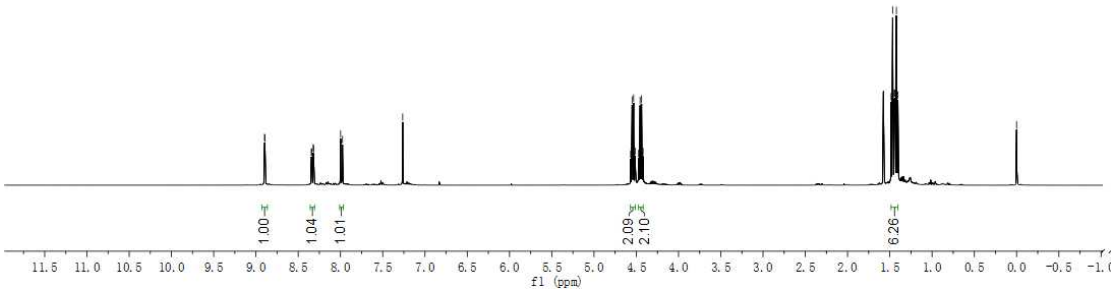
3i

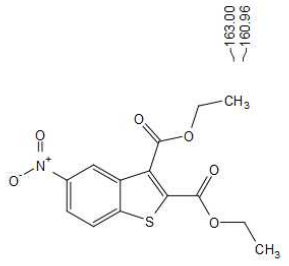

163.69
161.40
138.60
138.34
135.80
131.79
130.43
127.17
123.77
119.82
77.35
77.03
76.71
62.34
62.09
14.11
Br
O
O
O
O
S
CH3
CH3
f1 (ppm)

3i

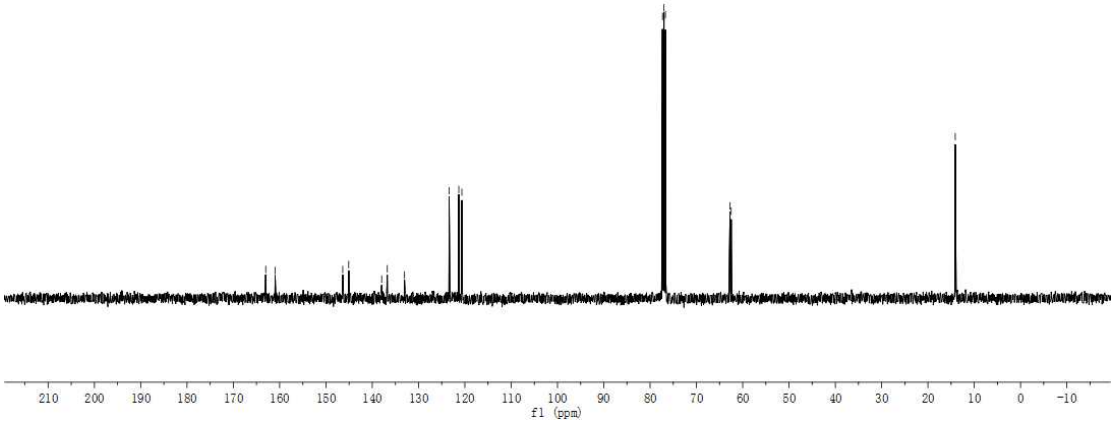


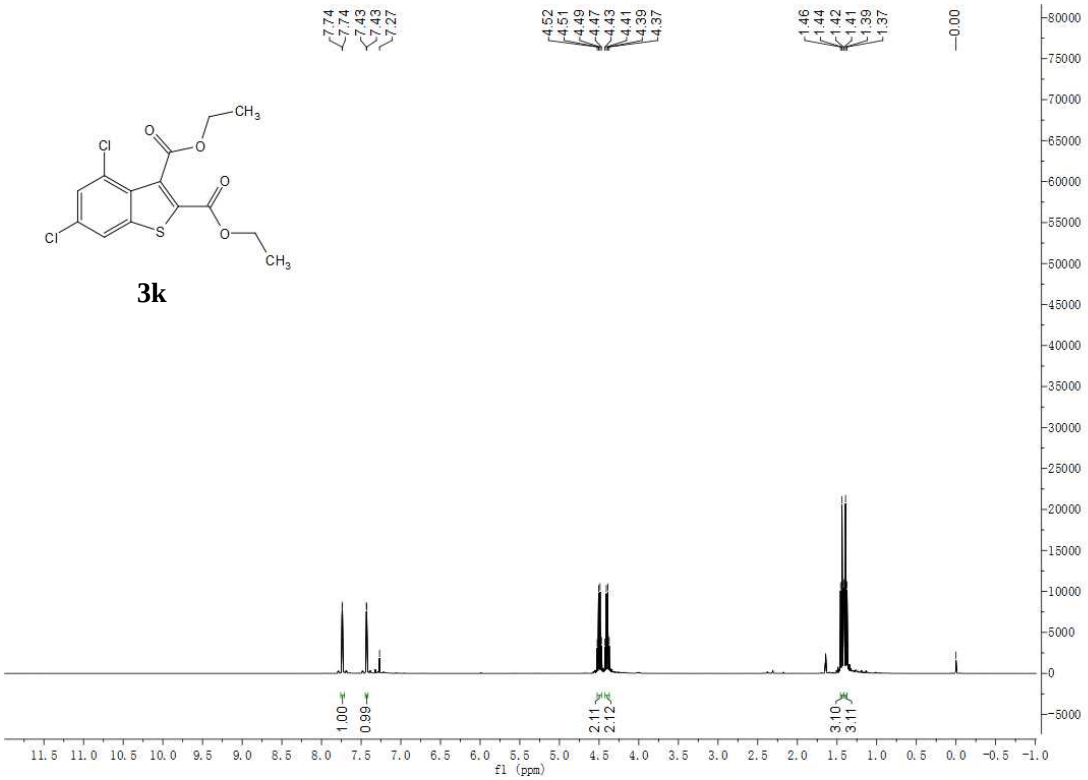
3j



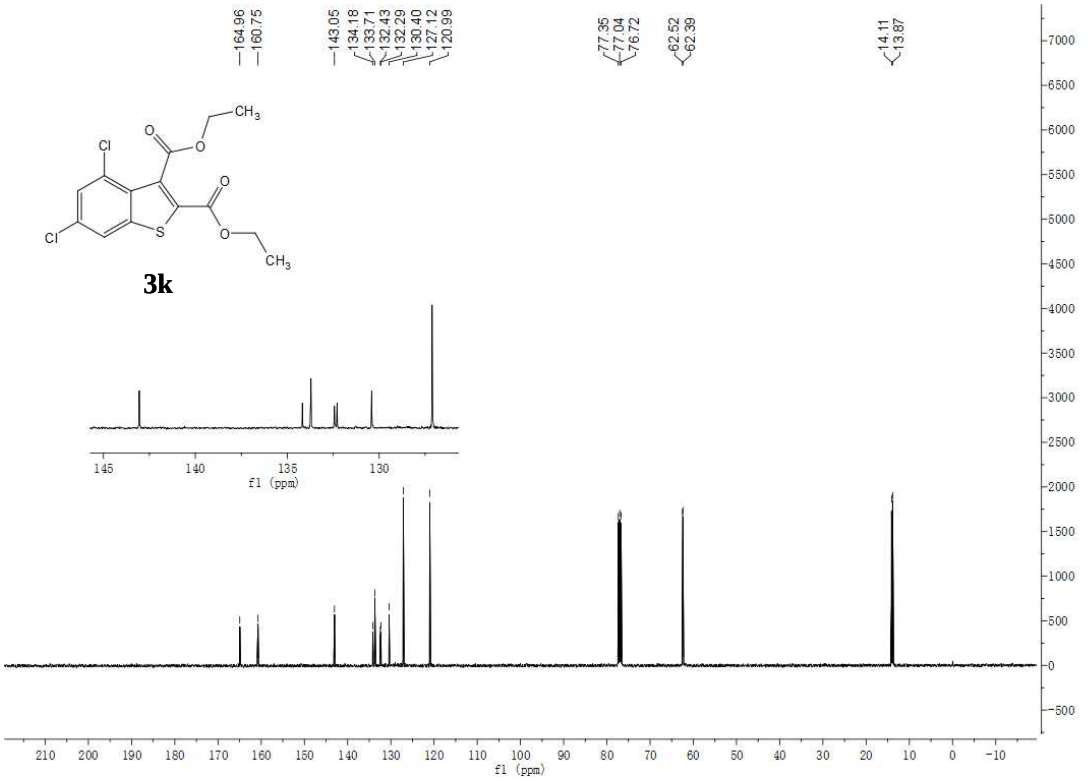


3j

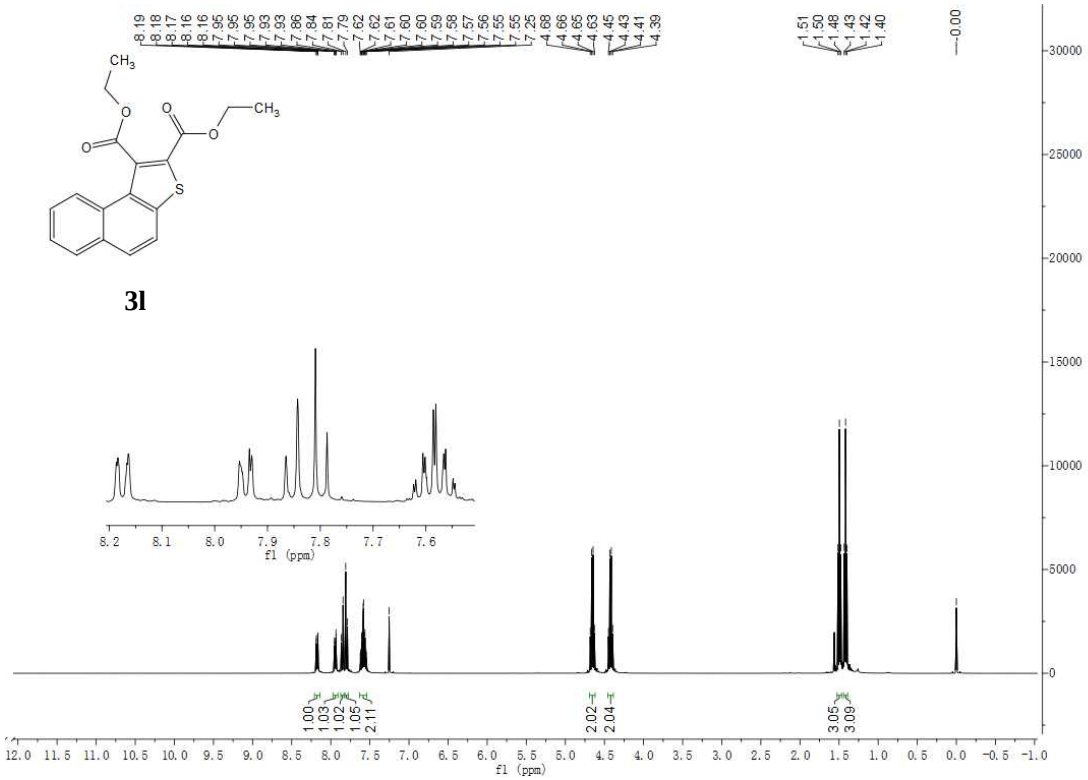



7.74
7.74
7.43
7.43
7.27
4.52
4.51
4.49
4.47
4.43
4.41
4.39
4.37
1.46
1.44
1.42
1.41
1.39
1.37
0.00
1.00
0.99
2.11
2.12
3.10
3.11
f1 (ppm)

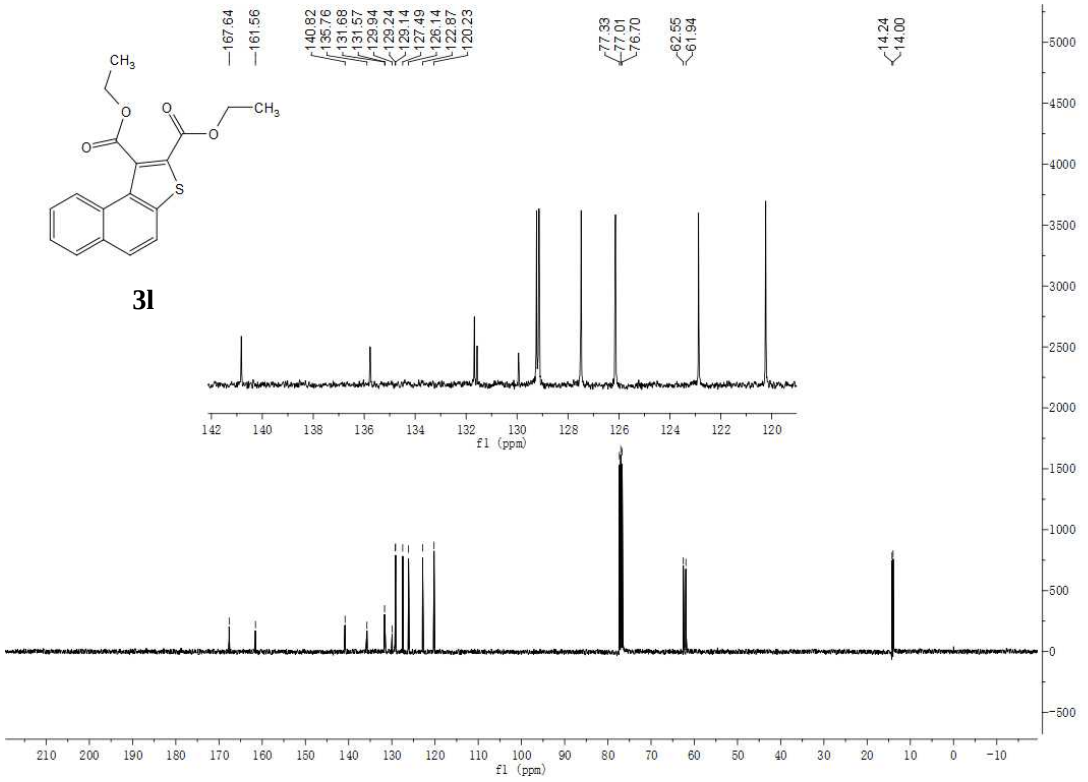
3k


164.96
160.75
143.05
134.18
133.71
132.43
132.29
130.40
127.12
120.99
77.35
77.04
76.72
62.52
62.39
14.11
13.87
f1 (ppm)

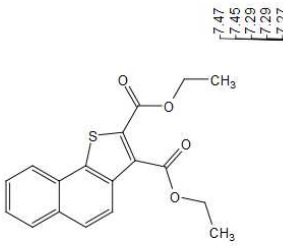
3k



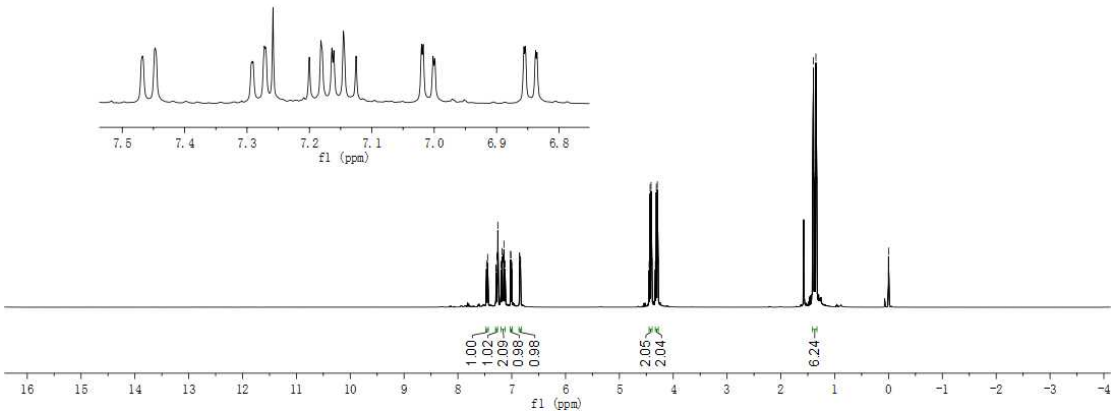
3l

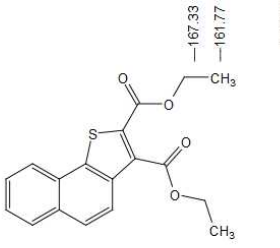


3l

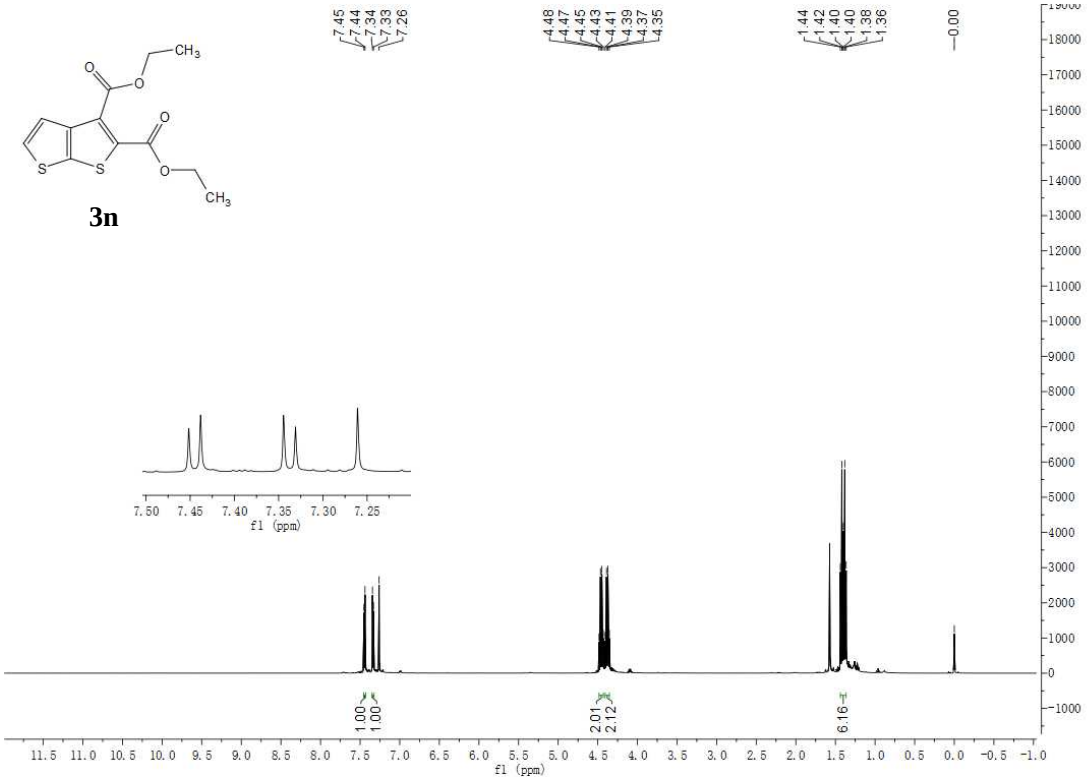


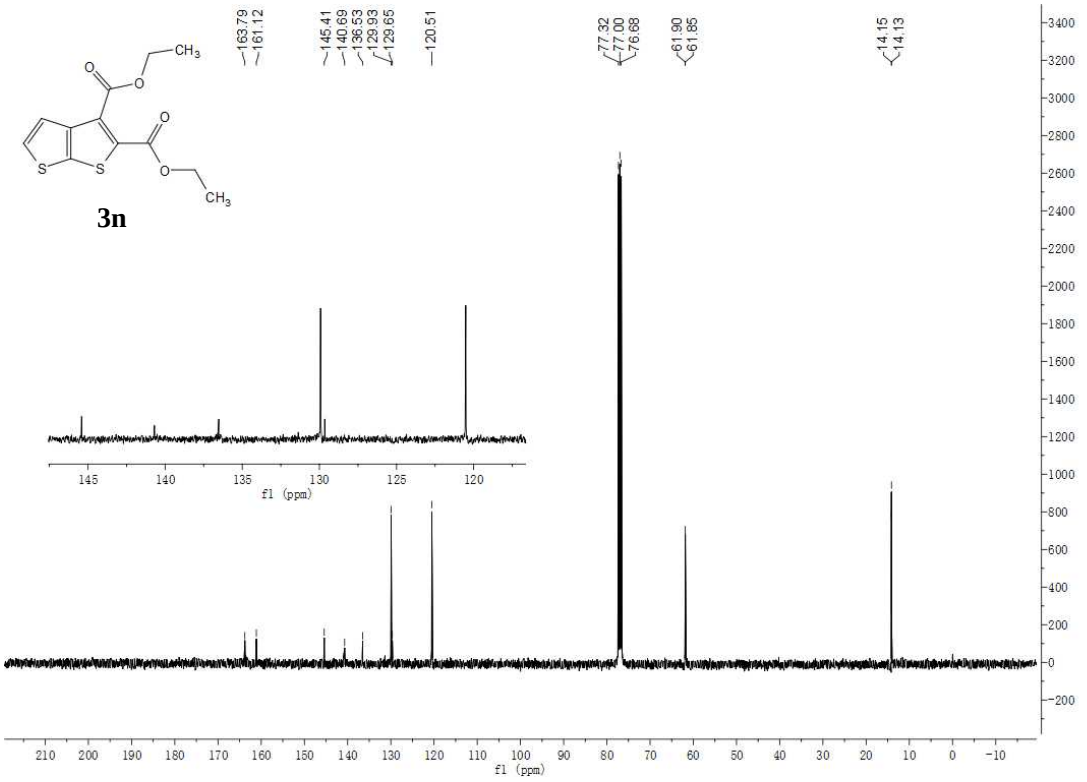
3m

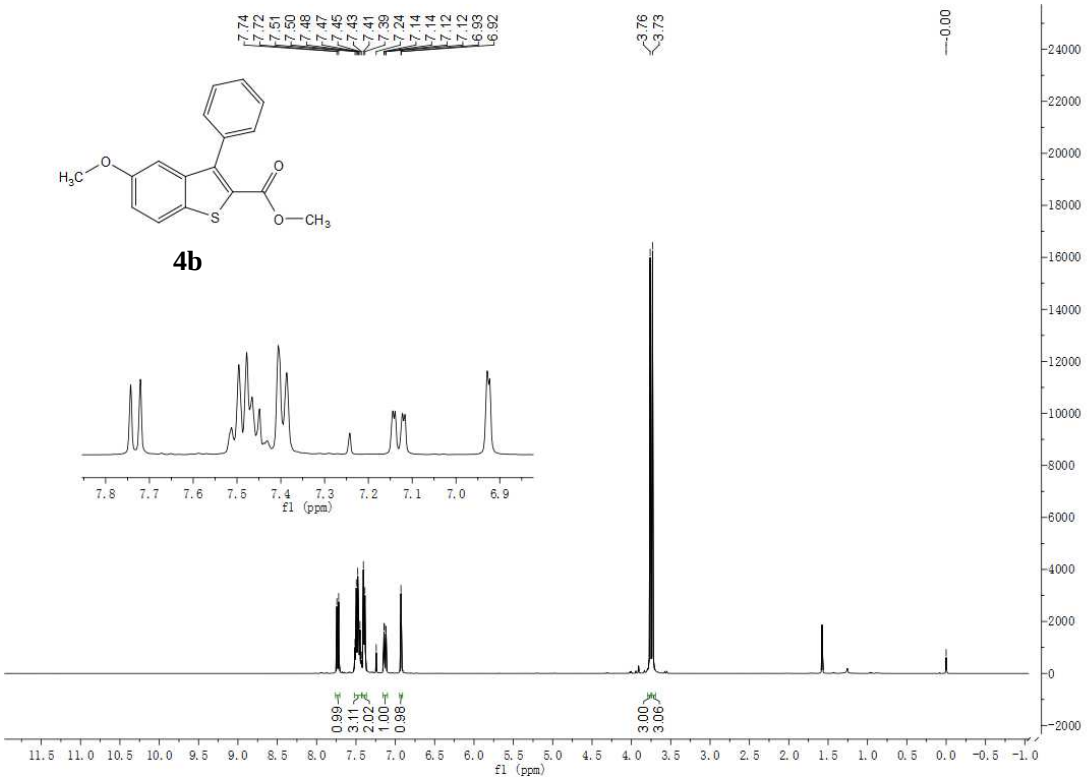


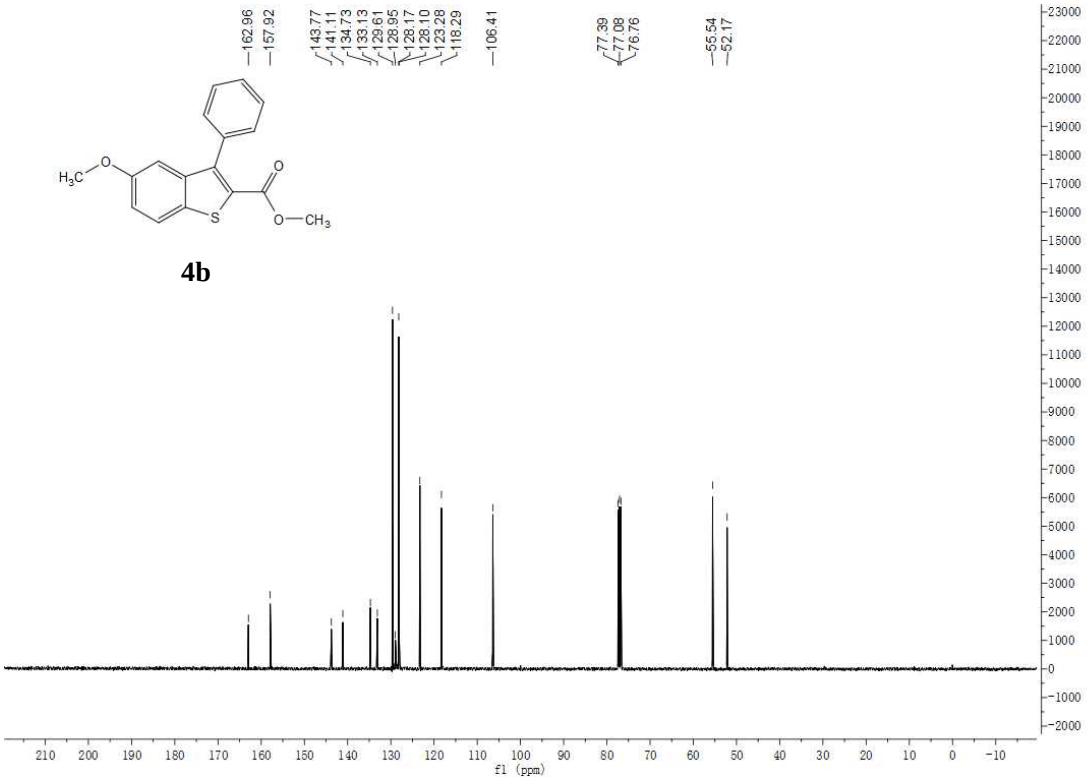


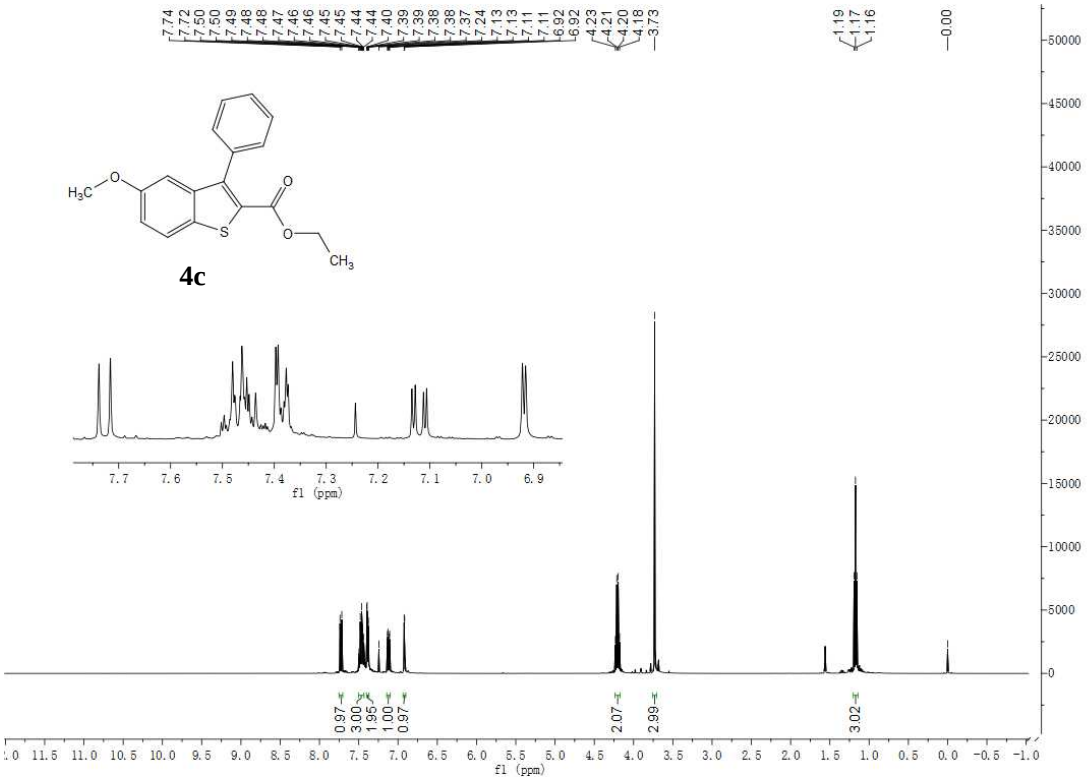
3m

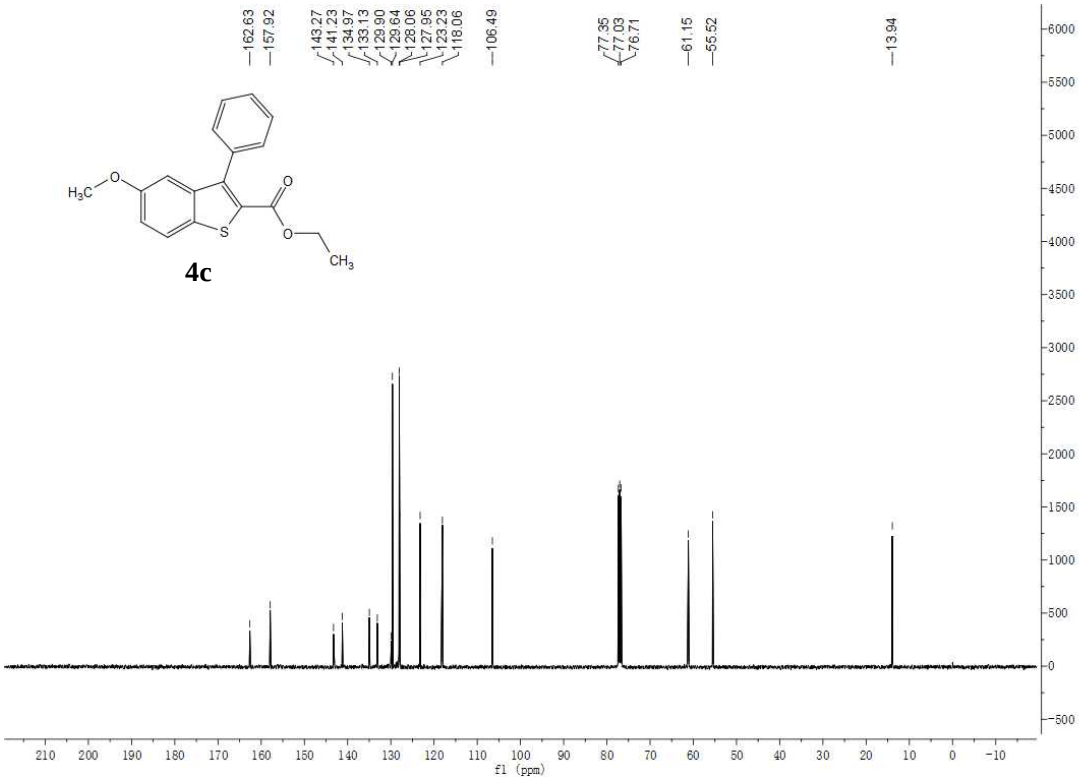

3n
7.45
7.44
7.34
7.33
7.26
4.48
4.47
4.45
4.43
4.41
4.39
4.37
4.35
1.44
1.42
1.40
1.40
1.38
1.36
0.00
1.00
1.00
2.01
2.12
6.16
f1 (ppm)

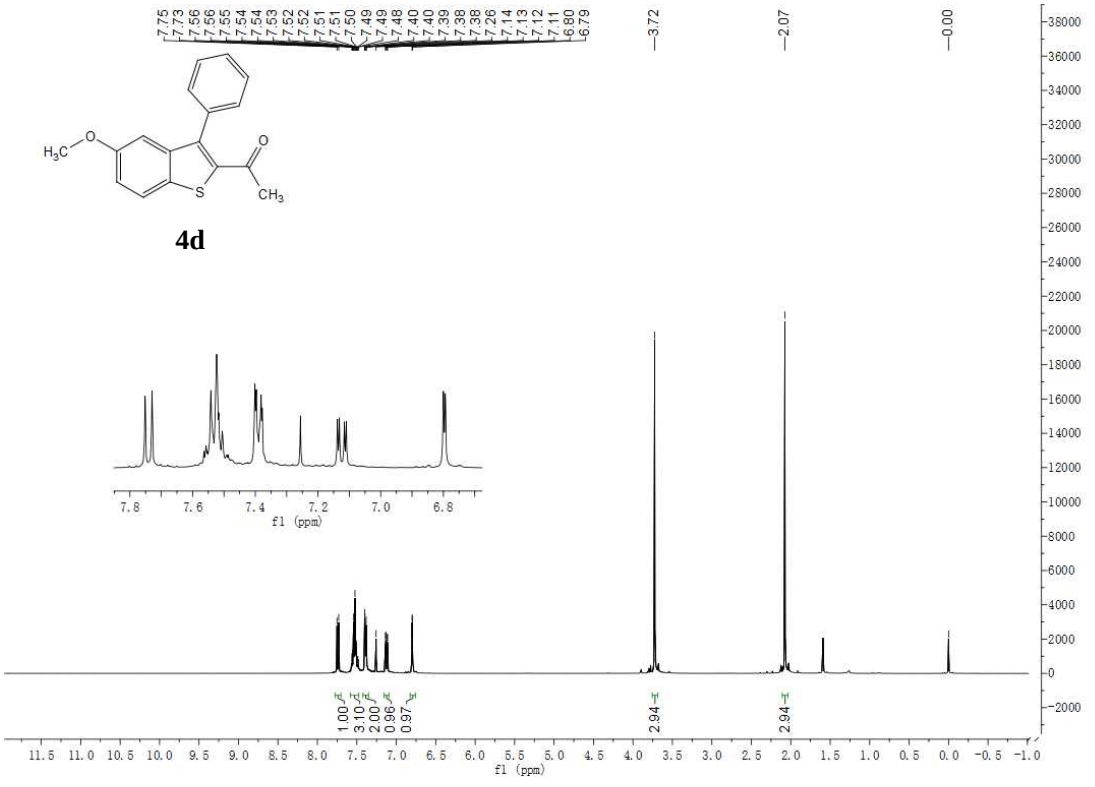

3n
163.79
161.12
145.41
140.69
136.53
129.93
129.65
120.51
77.32
77.00
76.68
61.90
61.85
14.15
14.13
f1 (ppm)


7.74
7.72
7.51
7.50
7.48
7.47
7.45
7.43
7.41
7.39
7.24
7.14
7.14
7.12
7.12
6.93
6.92
3.76
3.73
0.00
H3C
O
O
S
O—CH3
4b
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
0.99
3.11
2.02
1.00
0.98
3.00
3.06
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 -0.5 -1.0
f1 (ppm)

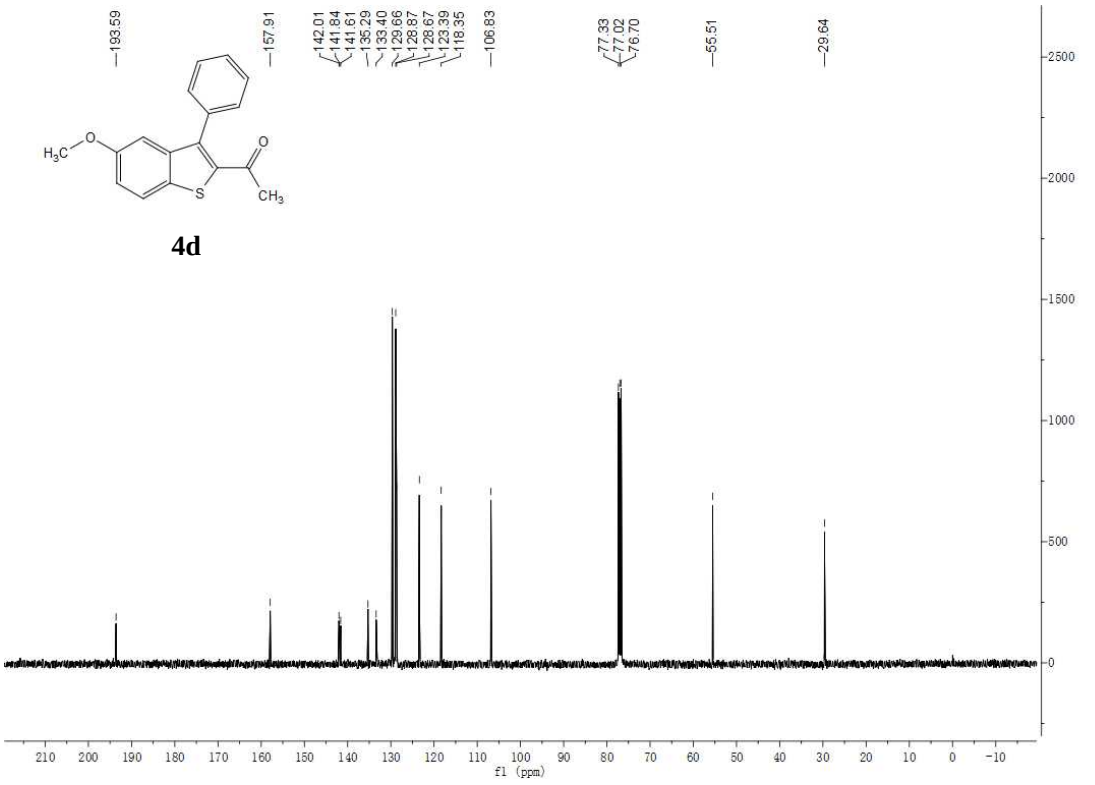

162.96
157.92
143.77
141.11
134.73
133.13
129.61
128.95
128.17
128.10
123.28
118.29
106.41
77.39
77.08
76.76
55.54
52.17
H3C
O
O
S
O—CH3
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

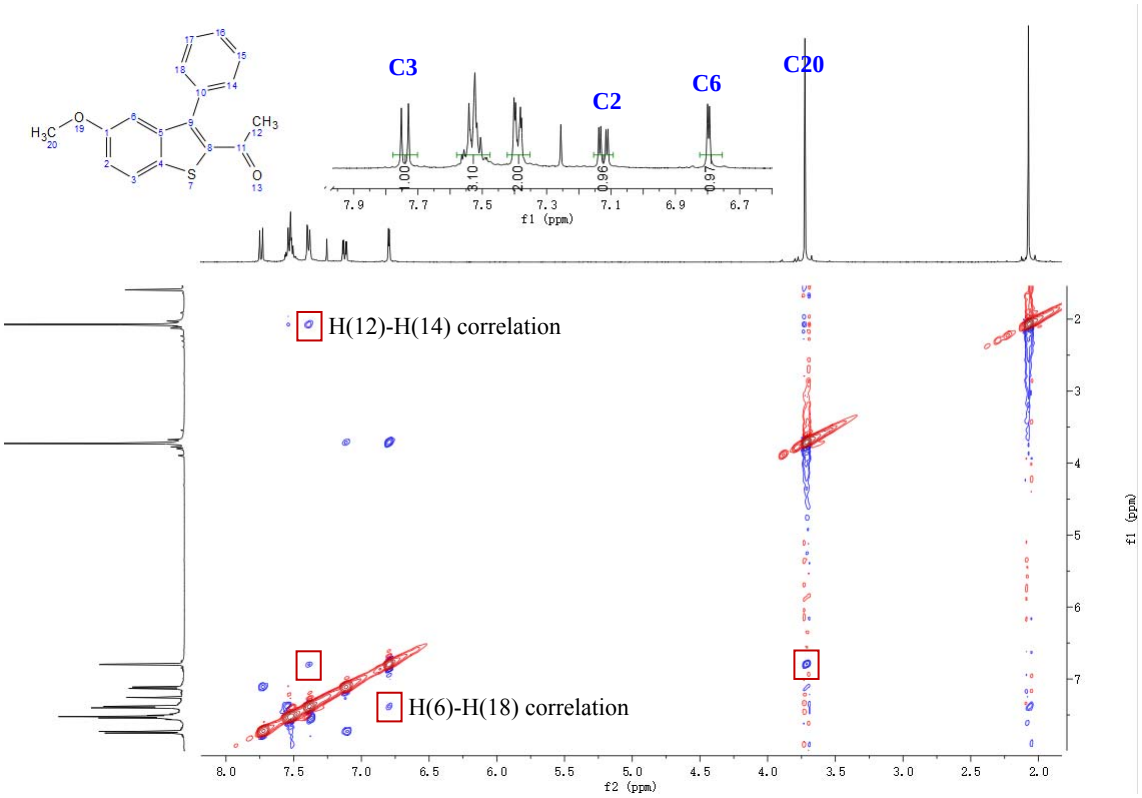

7.74
7.72
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.40
7.39
7.39
7.38
7.38
7.37
7.24
7.13
7.13
7.11
7.11
6.92
6.92
4.23
4.21
4.20
4.18
3.73
1.19
1.17
1.16
0.00
H3C
O
S
O
O
CH3
4c
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
0.97
3.00
1.95
1.00
0.97
2.07
2.99
3.02
f1 (ppm)

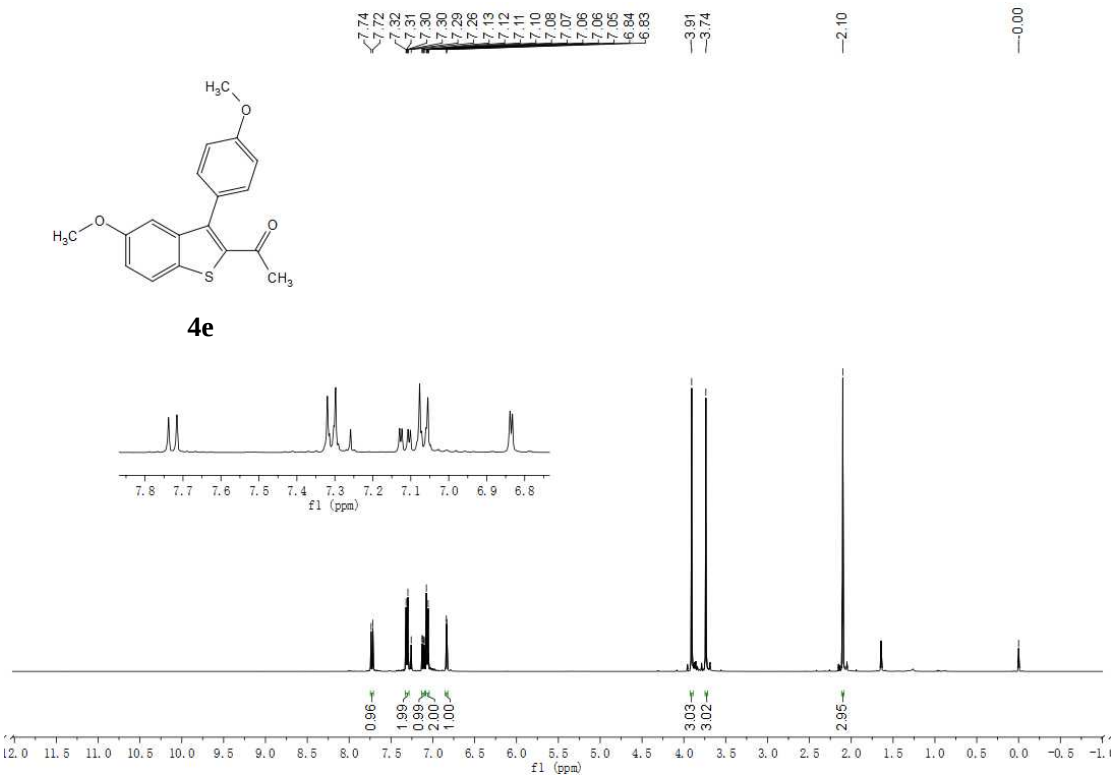

162.63
157.92
143.27
141.23
134.97
133.13
129.90
129.64
128.06
127.95
123.23
118.06
106.49
77.35
77.03
76.71
61.15
55.52
13.94
H3C
O
S
O
O
CH3
4c
f1 (ppm)


7.75
7.73
7.56
7.56
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.51
7.50
7.49
7.49
7.48
7.40
7.40
7.39
7.38
7.38
7.26
7.14
7.13
7.12
7.11
6.80
6.79
3.72
2.07
0.00
H3C
O
S
O
CH3
4d
7.8
7.6
7.4
7.2
7.0
6.8
f1 (ppm)
1.00
3.10
2.00
0.96
0.97
2.94
2.94
f1 (ppm)

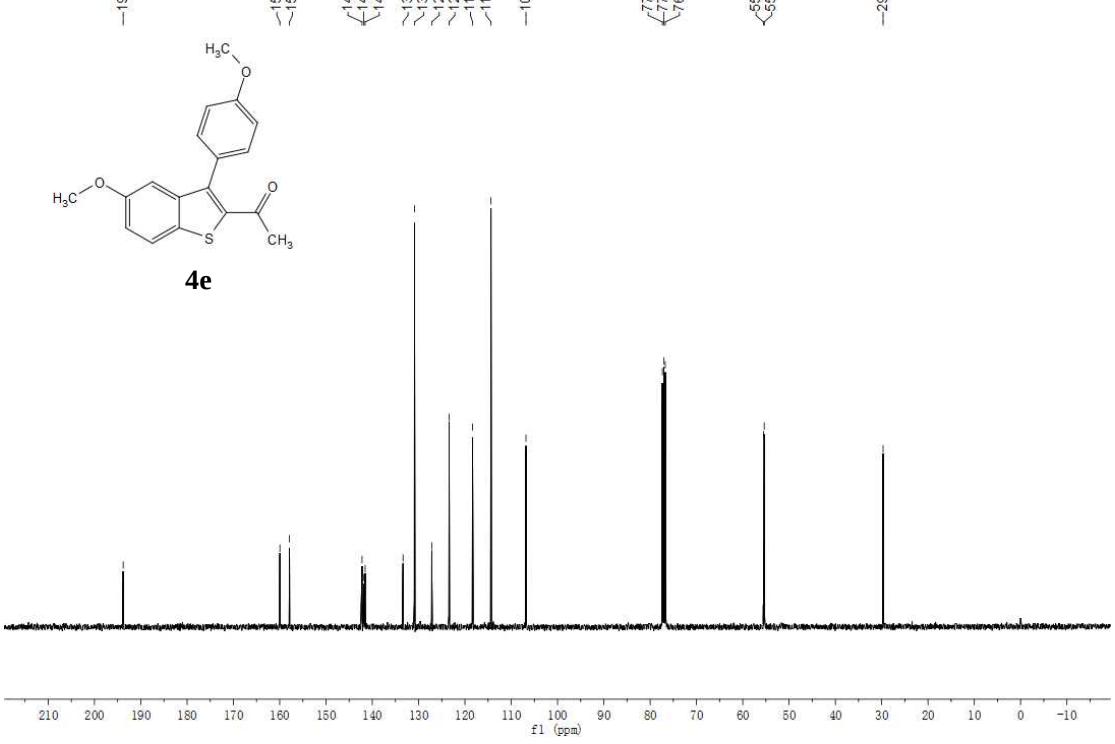
.


193.59
157.91
142.01
141.84
141.61
135.29
133.40
129.66
128.87
128.67
123.39
118.35
106.83
77.33
77.02
76.70
55.51
29.64
H3C
O
S
O
CH3
4d
f1 (ppm)

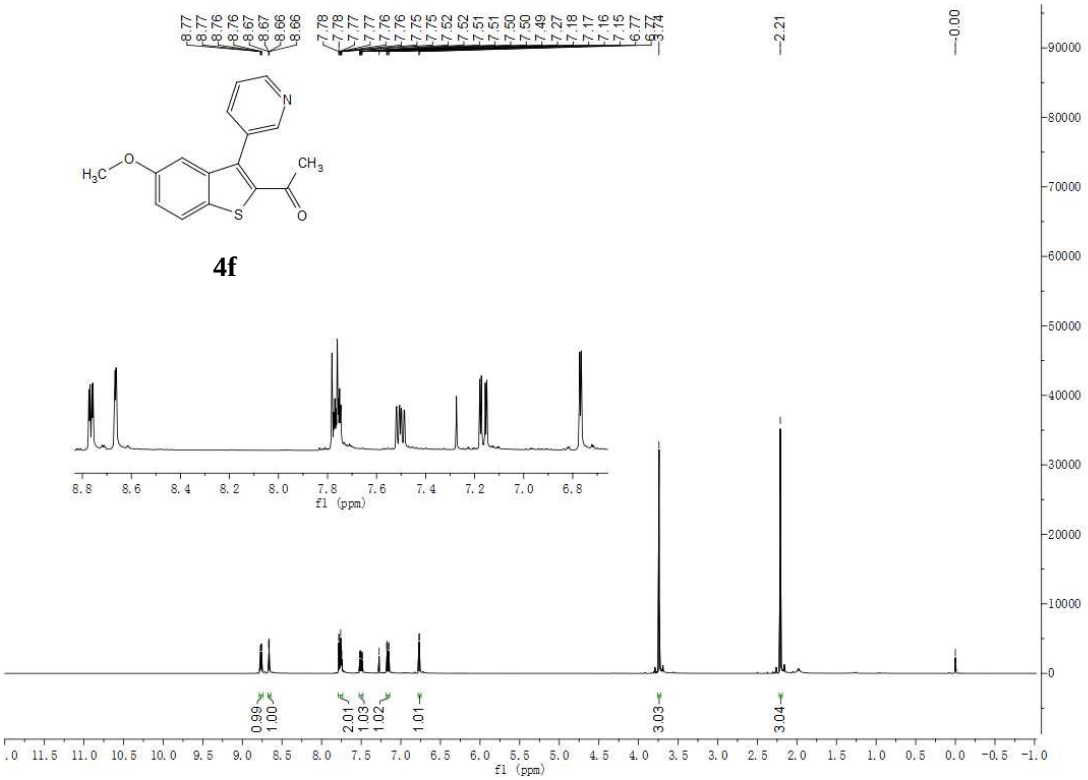

C3
C2
C6
C20
1.00
3.10
2.00
0.96
0.97
7.9
7.7
7.5
7.3
7.1
6.9
6.7
f1 (ppm)
H(12)-H(14) correlation
H(6)-H(18) correlation
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
f1 (ppm)


7.74
7.72
7.32
7.31
7.30
7.30
7.29
7.26
7.13
7.12
7.11
7.10
7.08
7.07
7.06
7.06
7.05
6.84
6.83
3.91
3.74
2.10
0.00
0.96
1.99
0.99
2.00
1.00
3.03
3.02
2.95
f1 (ppm)

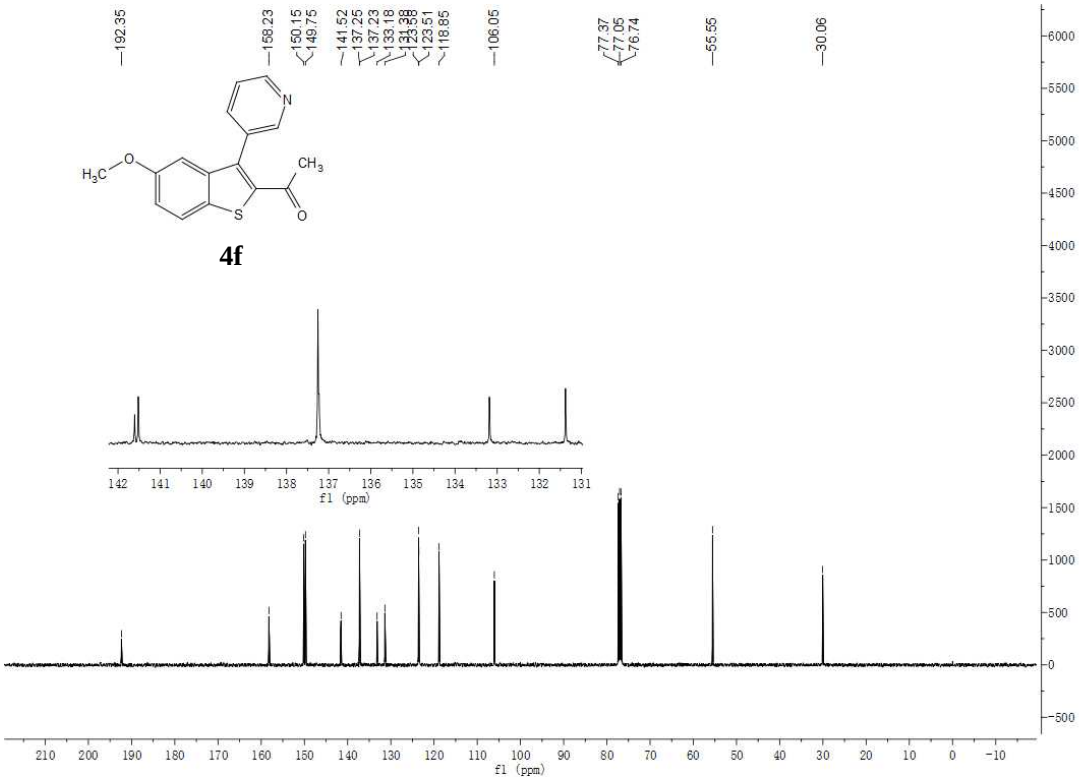
4e


193.80
159.95
157.89
142.21
141.81
141.55
133.36
130.89
127.17
123.41
118.35
114.37
106.81
77.36
77.05
76.73
55.53
55.36
29.70
f1 (ppm)

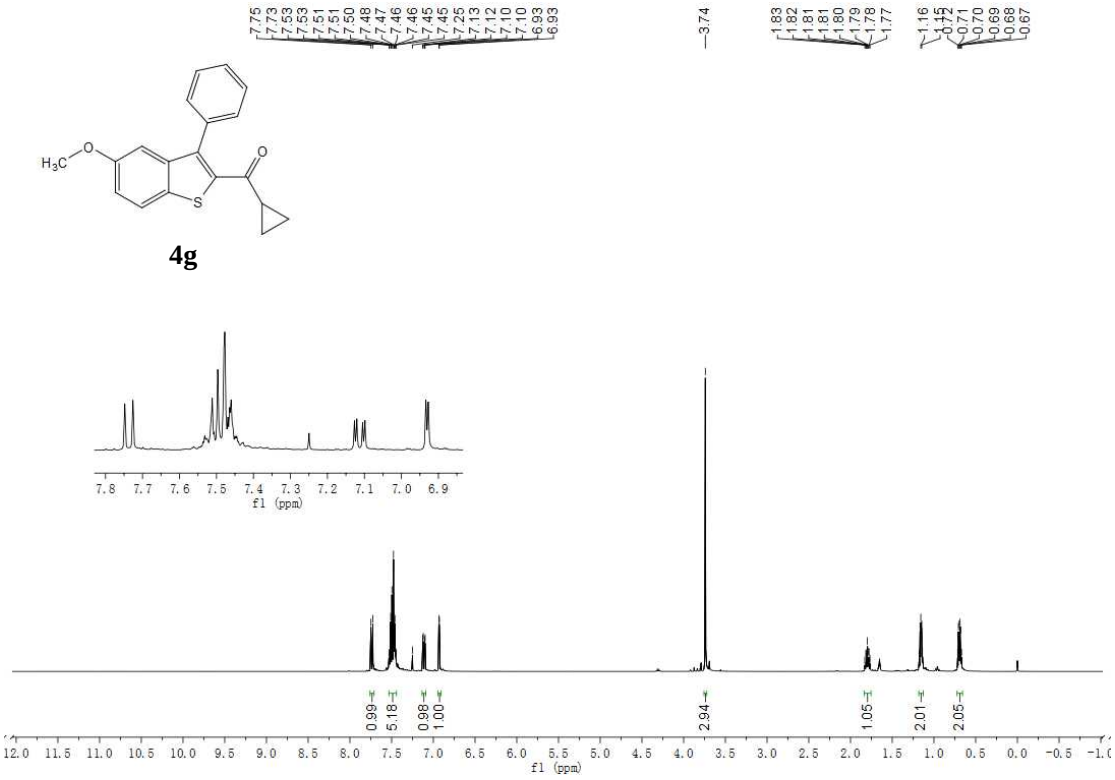
4e


8.77
8.77
8.76
8.76
8.67
8.67
8.66
8.66
7.78
7.78
7.77
7.77
7.76
7.76
7.75
7.75
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.27
7.18
7.17
7.16
7.15
6.77
6.77
3.74
2.21
0.00
N
O
H3C
CH3
S
O
f1 (ppm)
0.99
1.00
2.01
1.03
1.02
1.01
3.03
3.04
f1 (ppm)

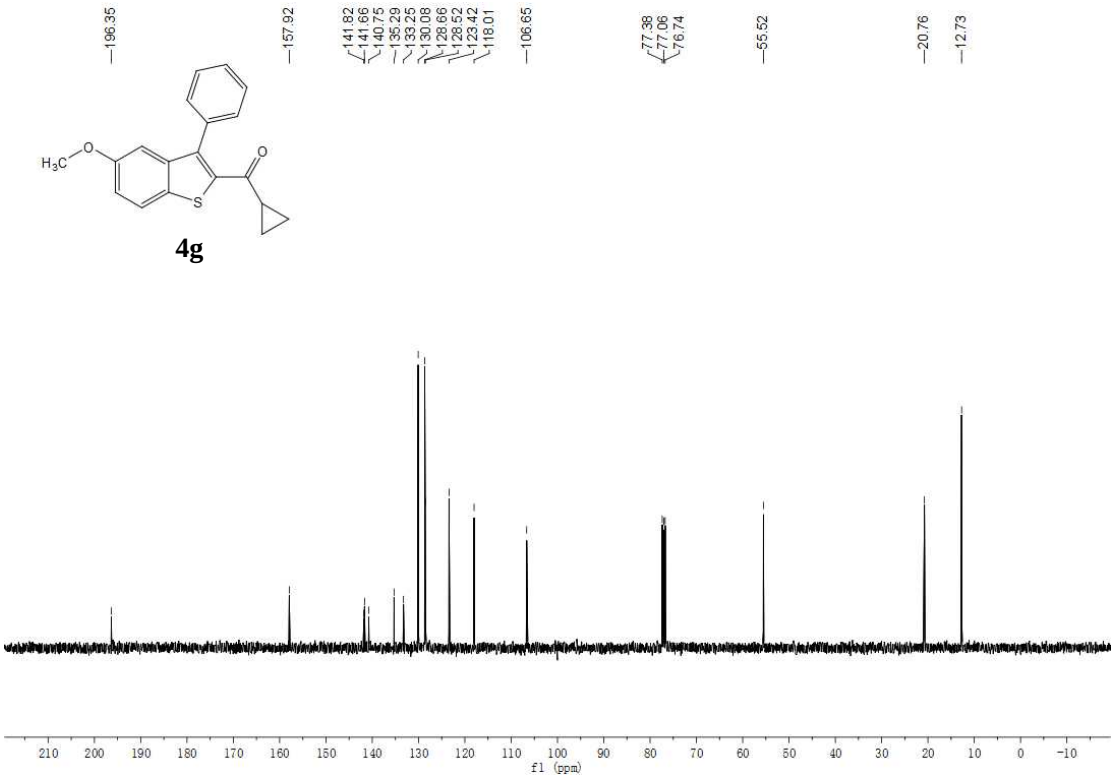
4f


192.35
158.23
150.15
149.75
141.52
137.25
137.23
133.18
131.38
123.58
123.51
118.85
106.05
77.37
77.05
76.74
55.55
30.06
N
O
H3C
CH3
S
O
f1 (ppm)
f1 (ppm)

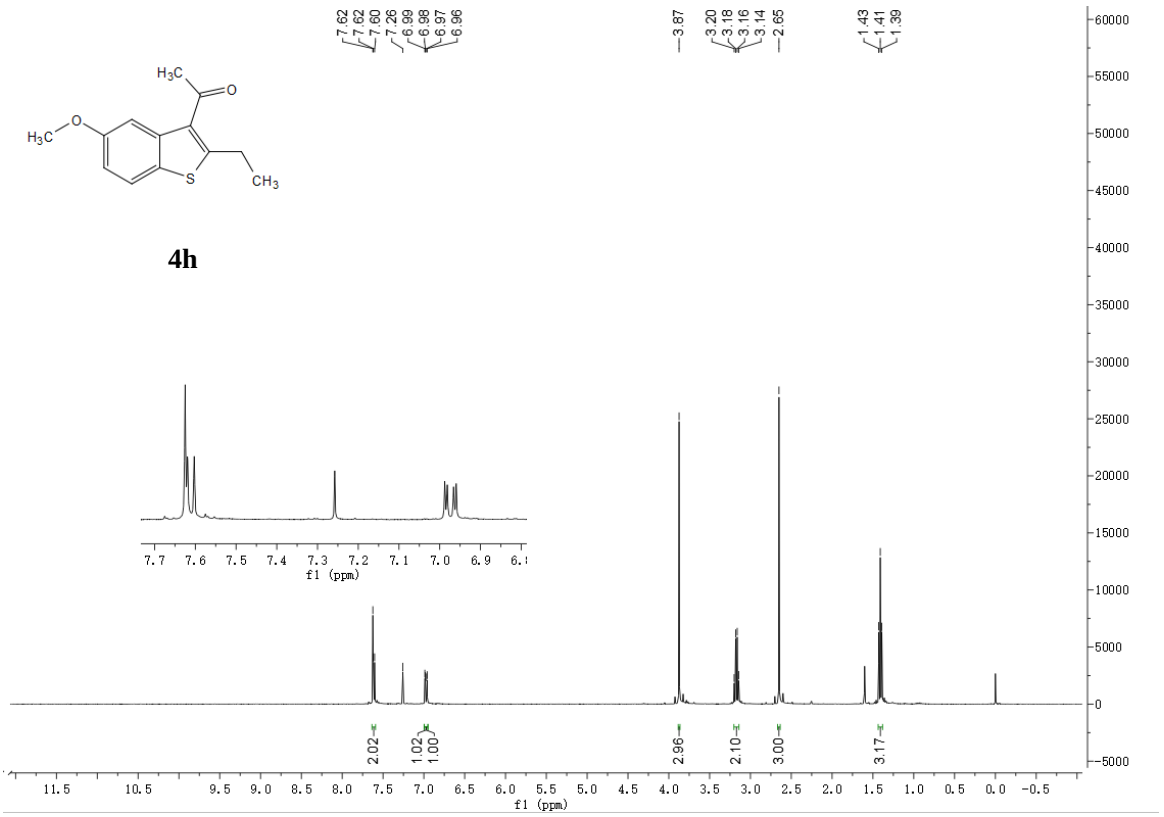
4f


7.75
7.73
7.53
7.51
7.50
7.48
7.47
7.46
7.46
7.45
7.45
7.25
7.13
7.12
7.10
6.93
6.93
3.74
1.83
1.82
1.81
1.81
1.80
1.79
1.78
1.77
1.16
1.15
0.71
0.70
0.69
0.68
0.67
H3C
O
O
S
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
0.99
5.18
0.98
1.00
2.94
1.05
2.01
2.05
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 -0.5
f1 (ppm)

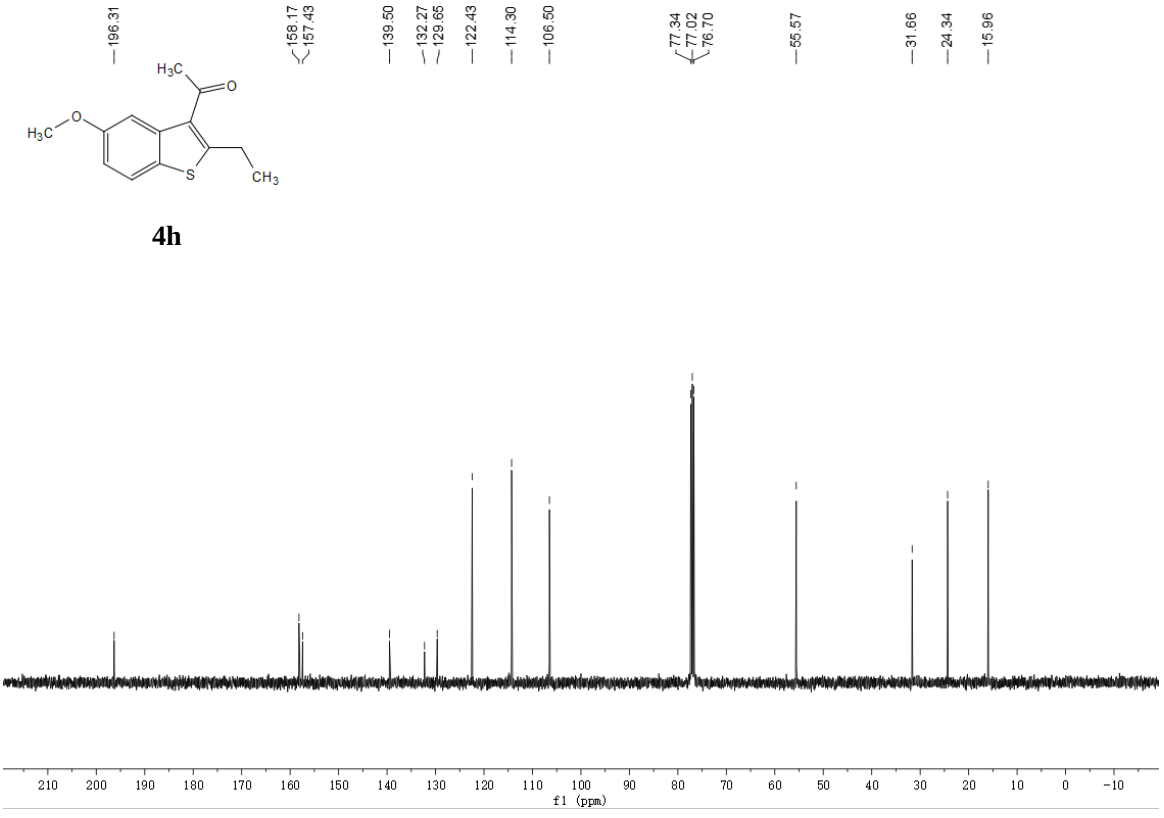
4g


196.35
157.92
141.82
141.66
140.75
135.29
133.25
130.08
128.66
128.52
123.42
118.01
106.65
77.38
77.06
76.74
55.52
20.76
12.73
H3C
O
O
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

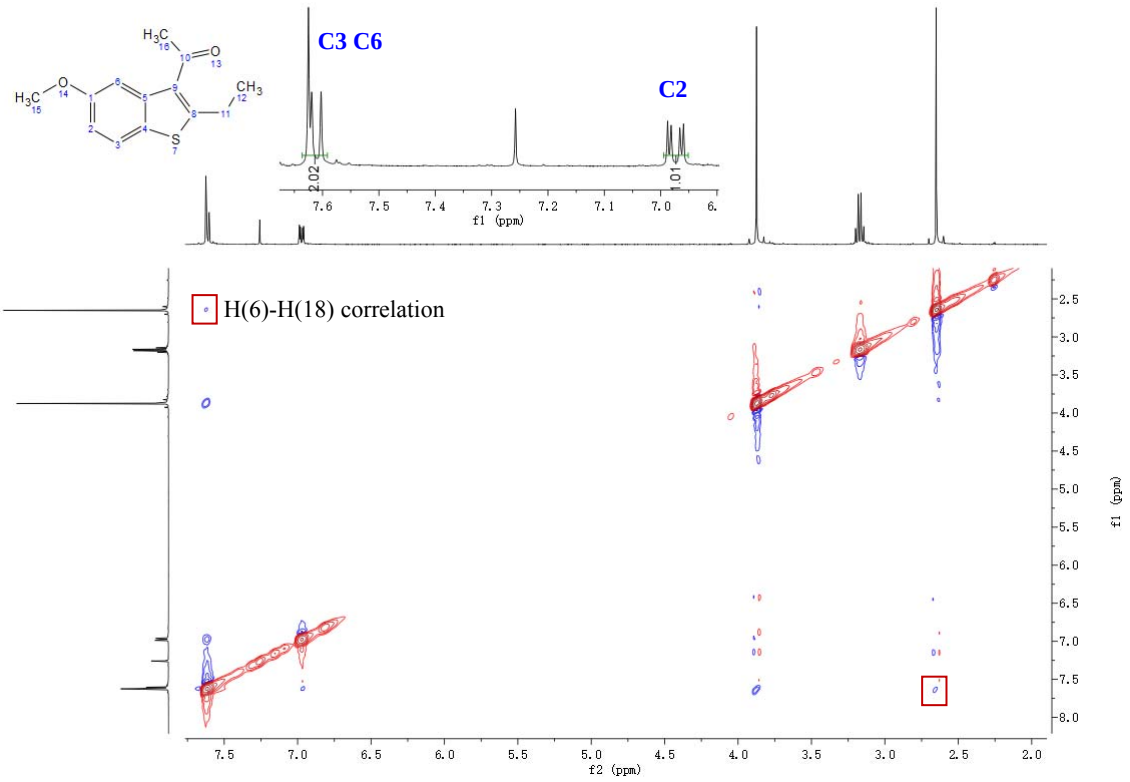
4g

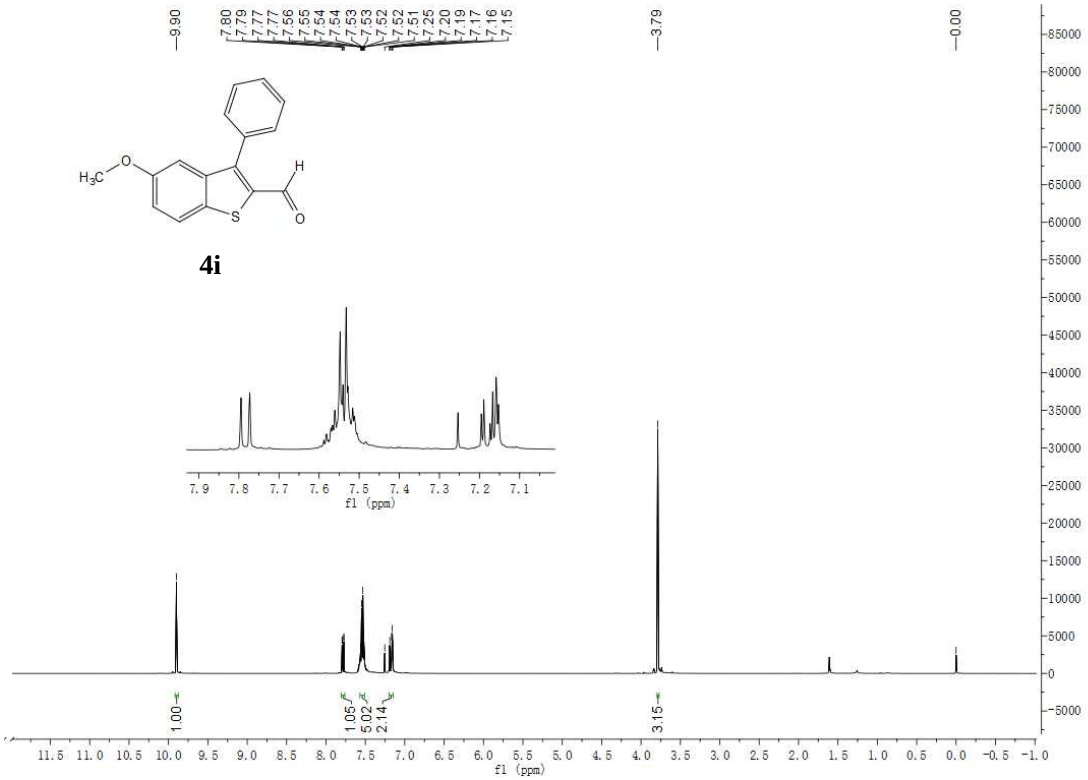

7.62
7.62
7.60
7.26
6.99
6.98
6.97
6.96
3.87
3.20
3.18
3.16
3.14
2.65
1.43
1.41
1.39
H3C
O
H3C
O
S
CH3
f1 (ppm)
2.02
1.02
1.00
2.96
2.10
3.00
3.17

4h

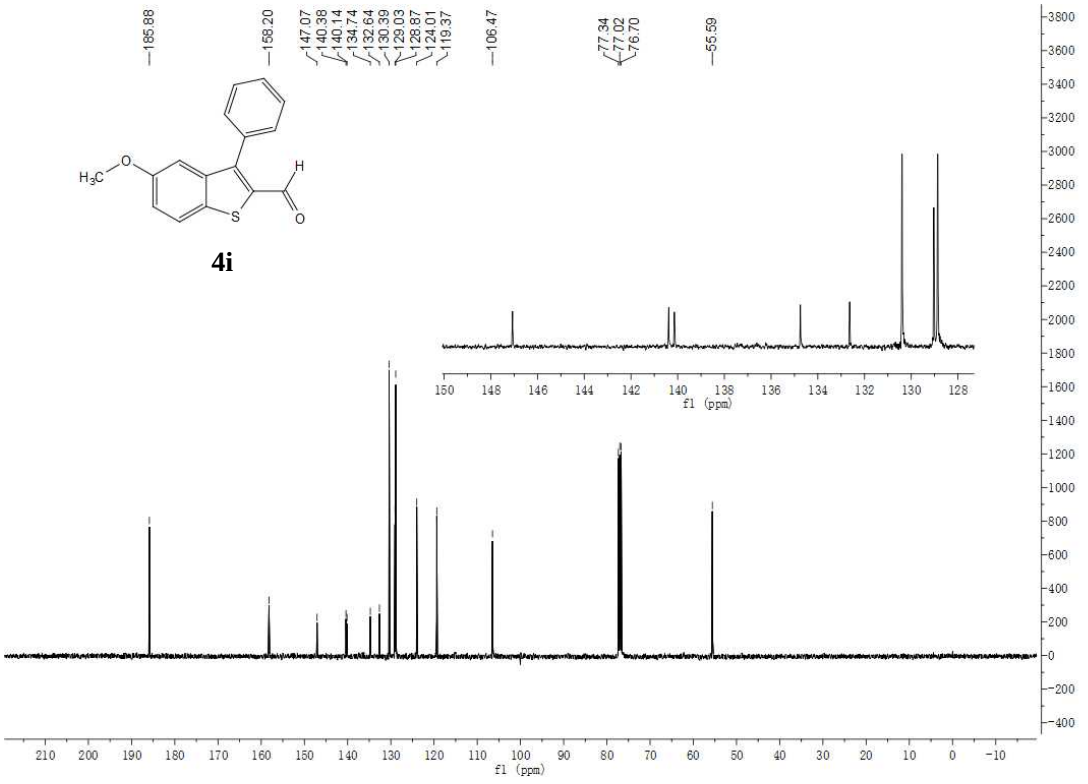

196.31
158.17
157.43
139.50
132.27
129.65
122.43
114.30
106.50
77.34
77.02
76.70
55.57
31.66
24.34
15.96
H3C
O
H3C
O
S
CH3
f1 (ppm)

4h

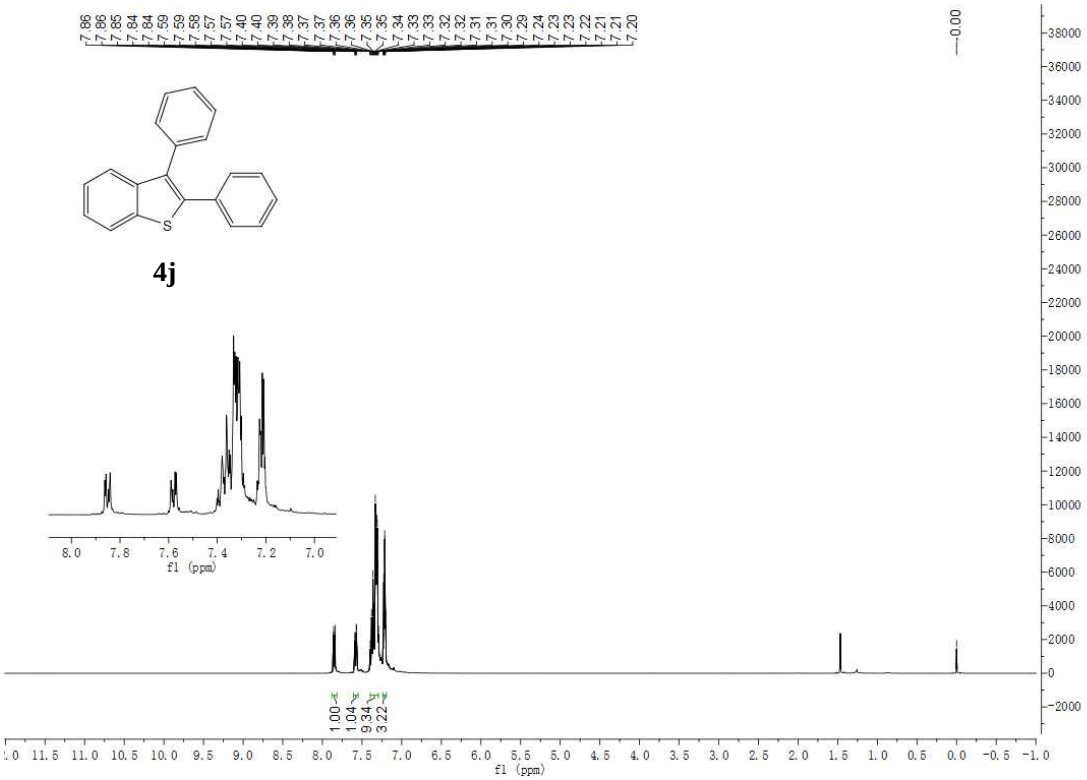

C3 C6
C2
2.02
1.01
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.
f1 (ppm)
H(6)-H(18) correlation
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f2 (ppm)
2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0
f1 (ppm)

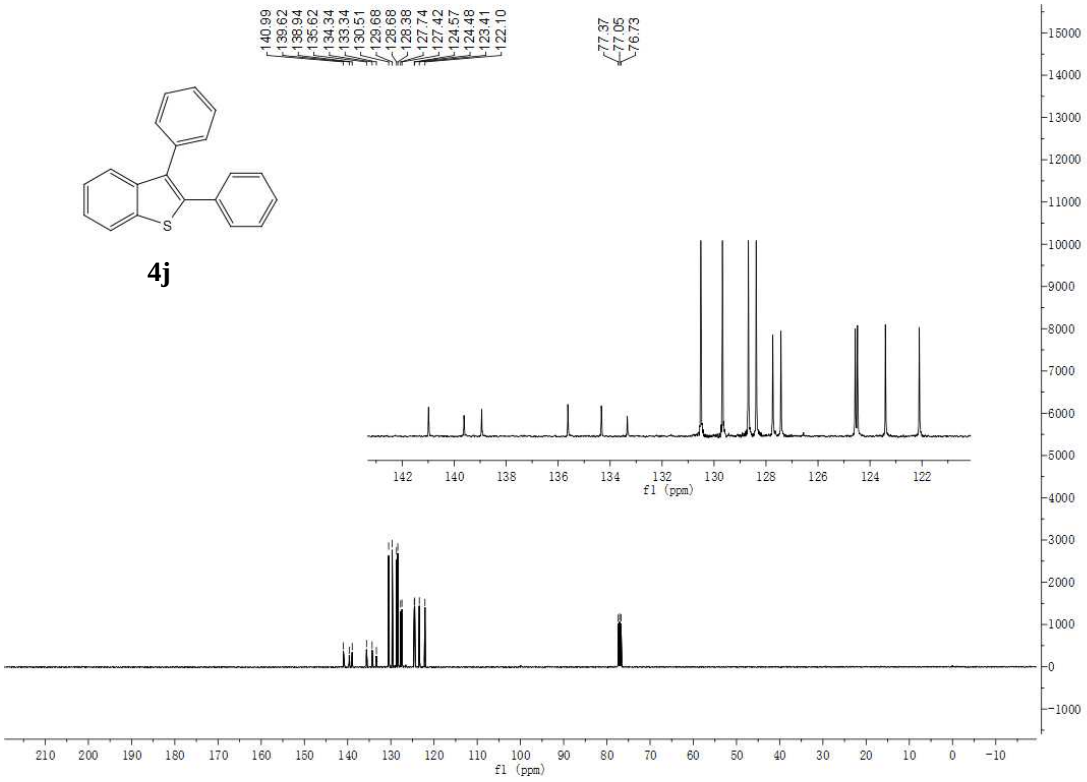

9.90
7.80
7.79
7.77
7.77
7.56
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.25
7.20
7.19
7.17
7.16
7.15
3.79
0.00
H3C
O
S
H
O
1.00
1.05
5.02
2.14
3.15
f1 (ppm)

4i


185.88
158.20
147.07
140.38
140.14
134.74
132.64
130.39
129.03
128.87
124.01
119.37
106.47
77.34
77.02
76.70
55.59
H3C
O
S
H
O
f1 (ppm)

4i


7.86
7.86
7.85
7.84
7.84
7.59
7.59
7.58
7.57
7.57
7.40
7.40
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.24
7.23
7.23
7.22
7.21
7.21
7.20
0.00
S
4j
8.0
7.8
7.6
7.4
7.2
7.0
f1 (ppm)
1.00
1.04
9.34
3.22
f1 (ppm)


140.99
139.62
138.94
135.62
134.34
133.34
130.51
129.68
128.68
128.38
127.74
127.42
124.57
124.48
123.41
122.10
77.37
77.05
76.73
S
4j
142
140
138
136
134
132
130
128
126
124
122
f1 (ppm)
f1 (ppm)