Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

– Supporting Information–

Visible Light Induced Deoxygenation of Sulfoxides with Isopropanol

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1. General information

All reagents were of analytical grade and obtained from commercial suppliers and used without further purification (except **a22**). ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE III HD 400 at 400 MHz and 100 MHz respectively, using $CDCl_3$ or DMSO-d6 as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. GC-MS were performed on Thermo Trace DSQ. Column chromatography was performed using silica gel (200−300 mesh). A 25 W LED light source was assembled from 430−440 nm 2835 LED beads with a peak wavelength of 435 nm without the use of any filter (Planck ShenZhen Opto-Electronic Technology Co.,Ltd).

2. Preparation of starting material

The sulfoxide 1-methyl-3-(methylsulfinyl)benzene (**a22**) was synthetized according to the previously reported procedure. [2] Its NMR data is in entire agreement with previous descriptions. [18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.39 – 7.33 (m, 2H), 7.24 (m, 1H), 2.66 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 139.6, 131.8, 129.1, 123.7, 120.6, 43.9, 21.4.

3. Experimental setup

4. Typical procedure for the deoxygenation of sulfoxides

To a quarts test-tube (25 mL) were added AQ (10.4 mg, 0.05 mmol), TEAF (dihydrate, 4.6 mg, 0.025 mmol), sulfoxide **a** (0.5 mmol) and 2 mL of mixed solvent (sulfolane /*i*-PrOH = 3:1). The reaction mixture was stirred at room temperature under the irradiation at 430−440 nm (25 W LED, distance = 8−10 cm, cooling by air) for 12 h. After this, the reaction was quenched by the addition of 10 mL of water, and the aqueous solution was extracted with CH_2Cl_2 (3 × 10 mL). The combined extract was dried with anhydrous $MgSO_4$ and evaporated under vacuum. The residue was purified by a silica gel packed flash chromatography column to afford the desired sulfide **b**.

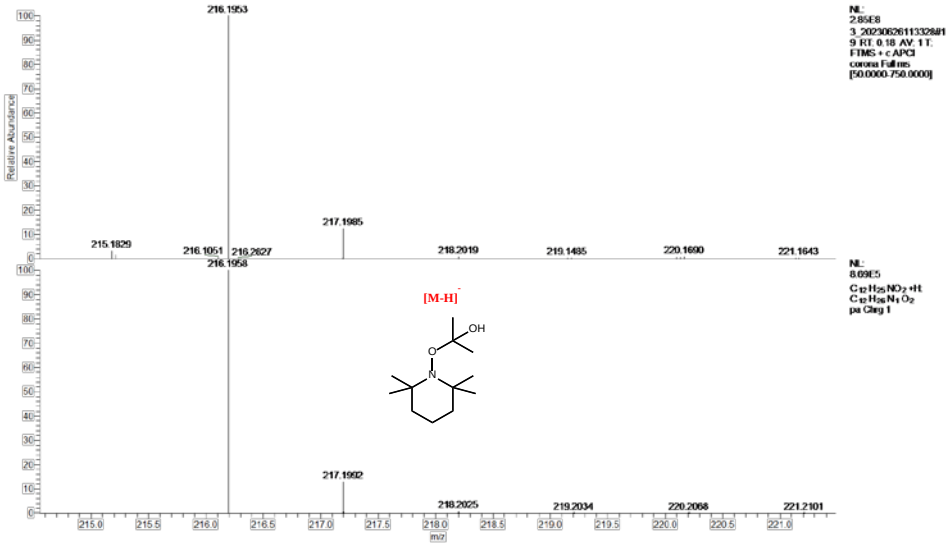
5. Gram scale synthesis

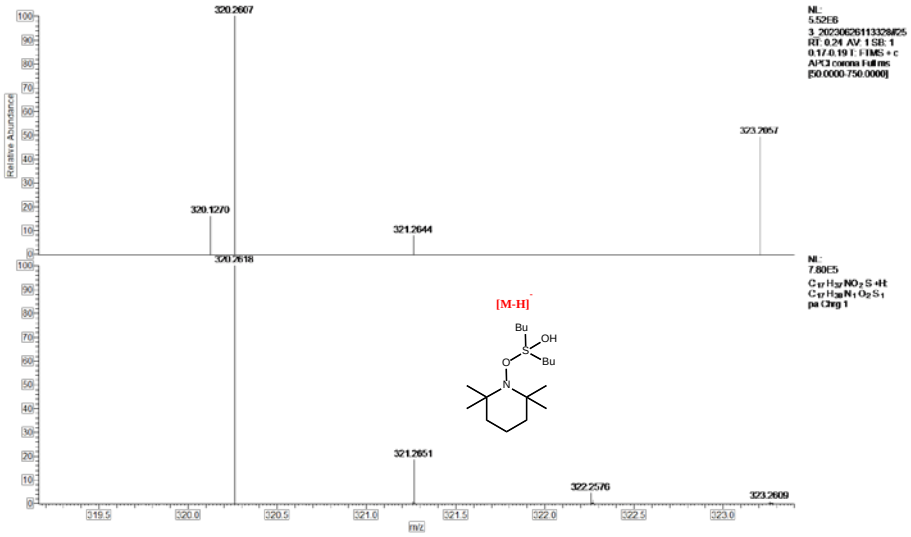
To a quarts test-tube (50 mL) were added AQ (104.1 mg, 0.5 mmol), TEAF (dihydrate, 46.3 mg, 0.25 mmol), di-n-octyl sulfoxide (**a2**) (1.37 g, 5 mmol) and 20 mL of mixed solvent (sulfolane /i-PrOH = 3:1). The reaction mixture was stirred at room temperature under the irradiation at 430-440 nm (25 W LED × 3, distance = 8 cm, cooling by air) for 12 h. After that, the reaction mixture was transferred to a separating funnel and diluted with CH_2Cl_2 (100 mL). The organic phase was washed three times with water, dried over $MgSO_4$ and concentrated. The crude product was purified by a silica gel packed flash chromatography column with pure hexane as the eluent to give **b2** (1.05 g, 81% yield).

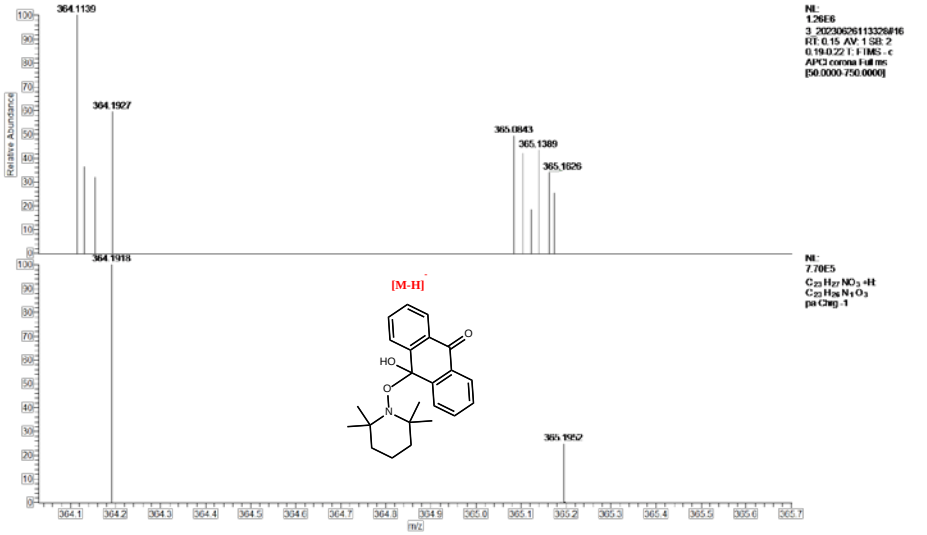
6. Mechanistic Studies

6.1 Radical trapping experiments

The trapping products of radical intermediate were detected by HRMS (thermo fisher Q Exactive, using APCI in negative ion mode)



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364.1918
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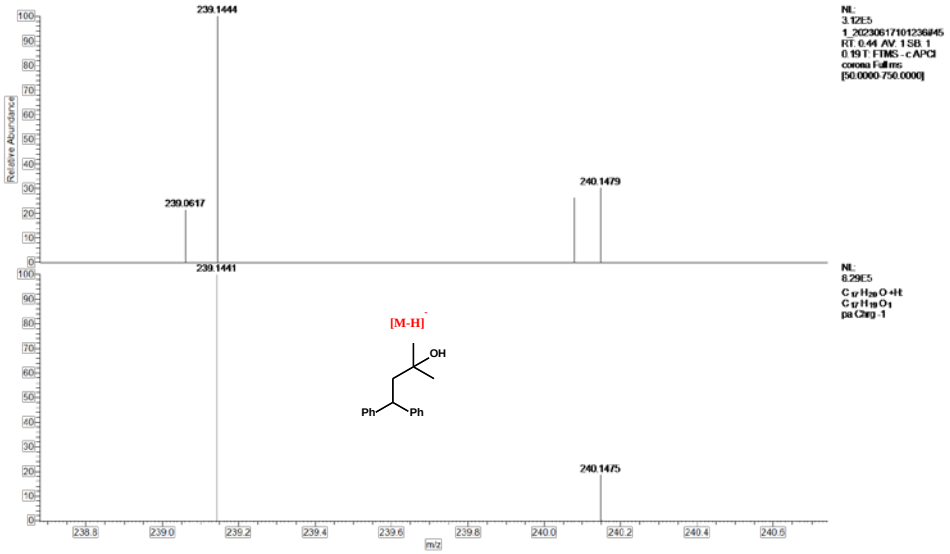
N
O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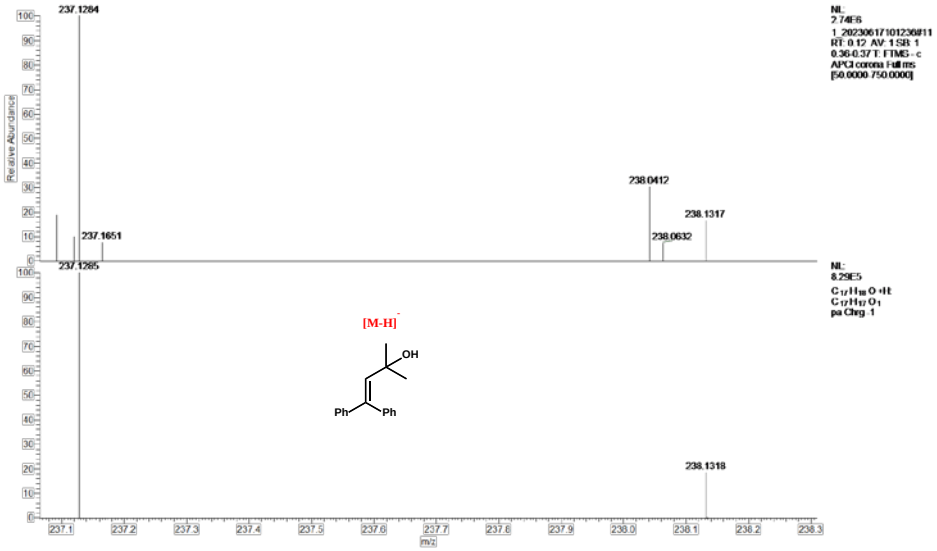
Ph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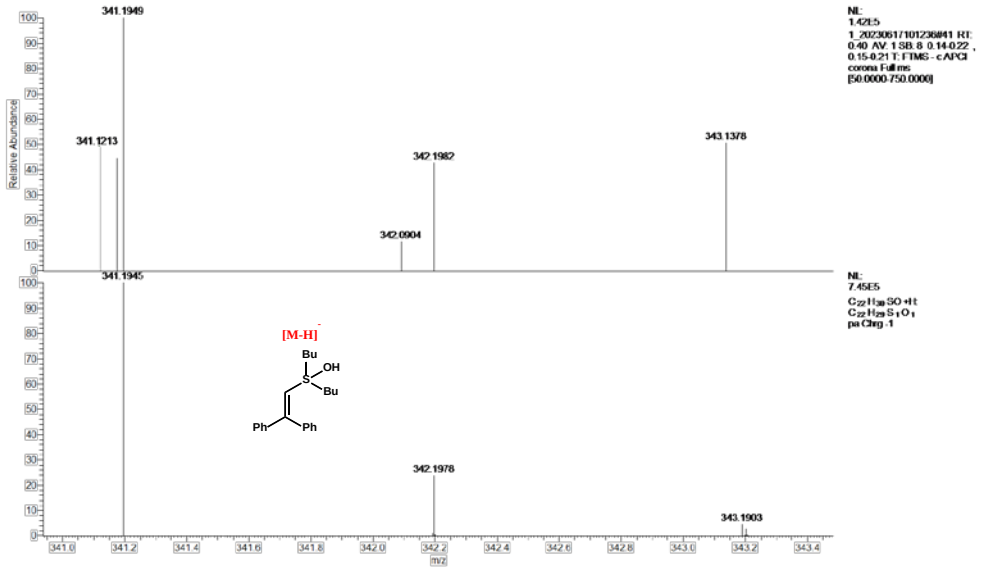
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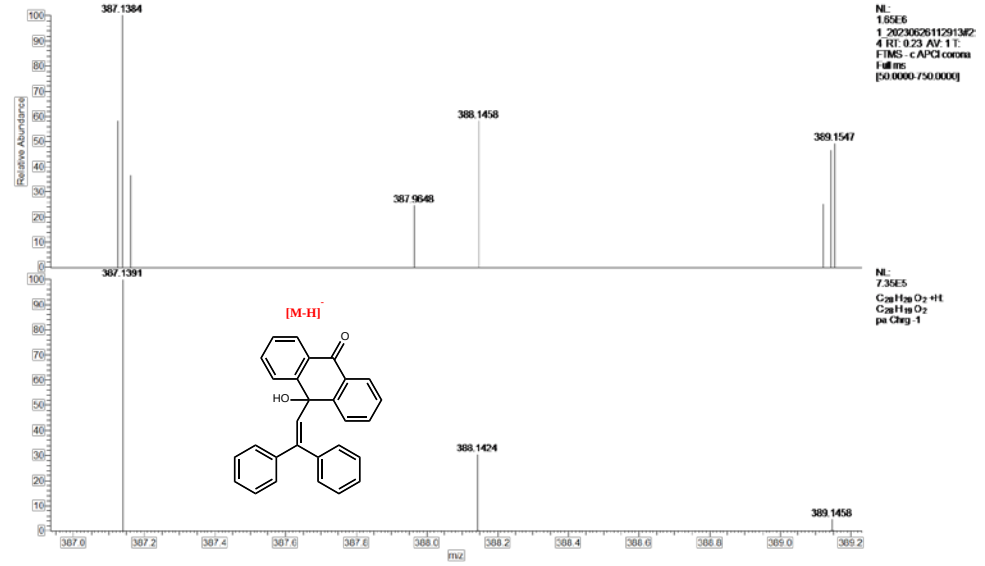
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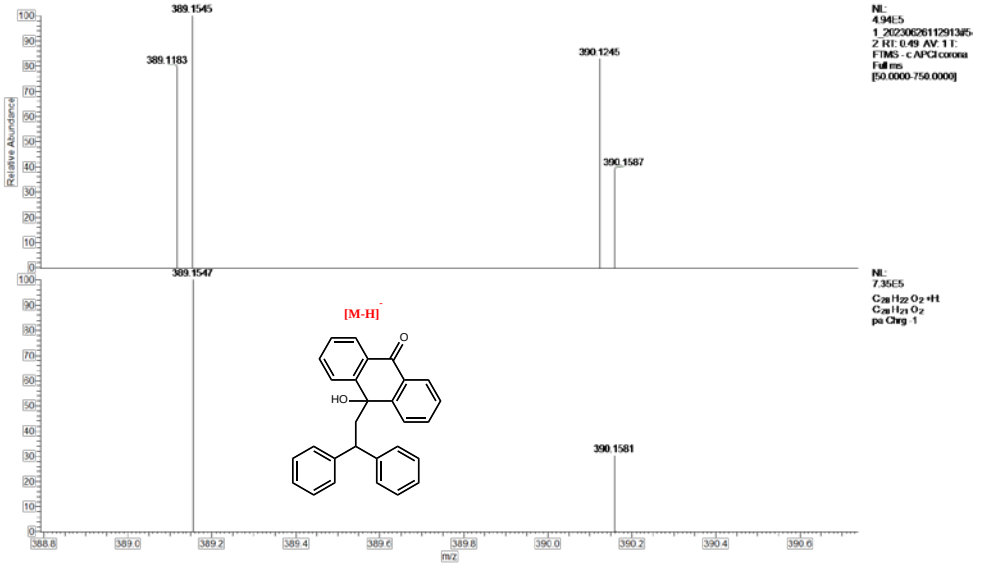
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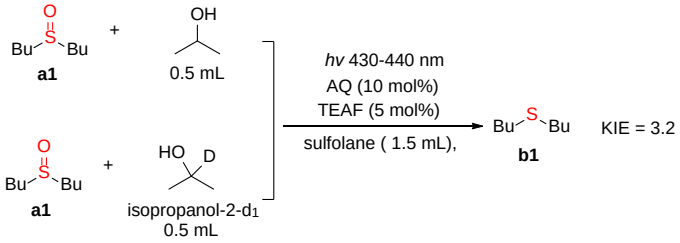
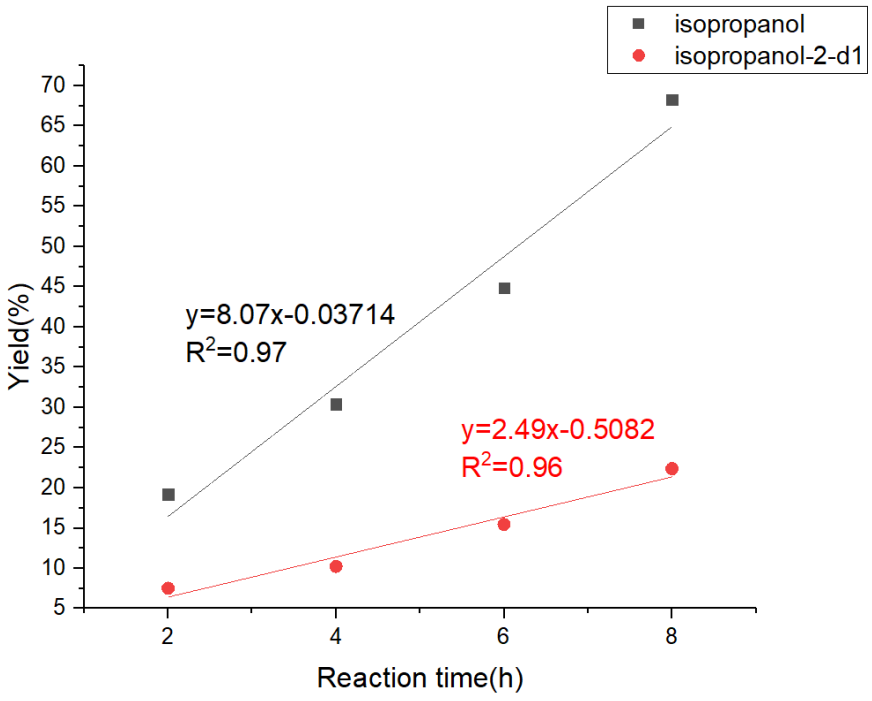
6.2 Parallel KIE experiments

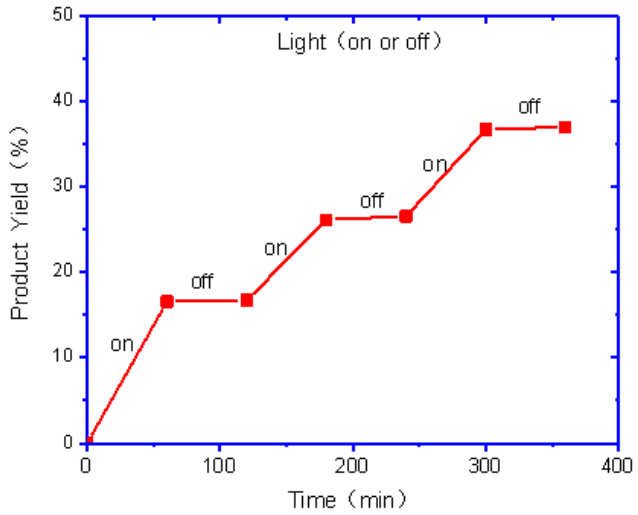


To a quarts test-tube (25 mL) were added AQ (10.4 mg, 0.05 mmol), TEAF (dihydrate, 4.6 mg, 0.025 mmol), sulfoxide **a** (0.5 mmol), isopropanol or isopropanol-2-d1 (0.5 mL) and sulfolane (1.5 mL). The reaction mixture was stirred at room temperature under the irradiation at 430−440 nm (25 W LED, distance = 8−10 cm, cooling by air) for indicated time. Then, the reaction was quenched by the addition of 10 mL of water, and the aqueous solution was extracted with CH_2Cl_2 (3 × 10 mL). The combined extract was dried with anhydrous $MgSO_4$. After filtration and evaporation, the obtained crude mixture was analyzed by GC/MS using *n*-dodecane as an internal standard.

	Time（h）	2	4	6	8
Yield	isopropanol	19.21	30.43	44.86	68.25
	isopropanol-2-d1	7.52	10.23	15.46	22.38

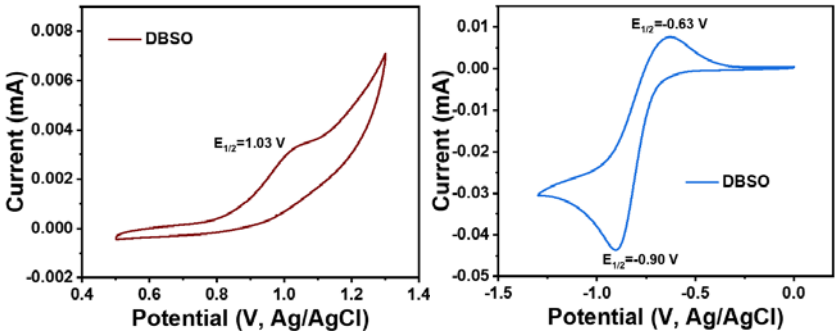


6.3 Light on/off experiments

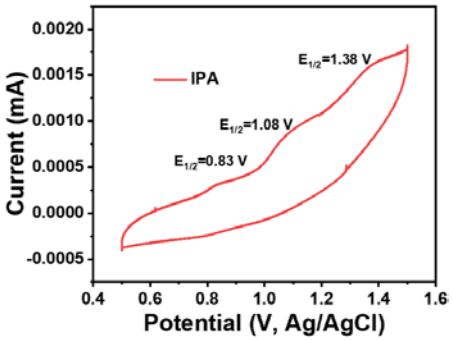


6.4 Cyclic voltammetry experiments

Cyclic voltammetry (CV) experiments of isopropanol and dibutyl sulfoxide were recorded on a Bio-Logic VMP-300 multi-channel electrochemical workstation using the three-electrode cell with a rate of 20 mV s^{-1} in CH_3CN solution (*N*,*N*,*N*-tributylbutan-1-aminium hexafluorophosphate, 0.1mol mL^{-1}) and bubbling with nitrogen for two minutes. In which glassy carbon electrode (GCE) was used as a working electrode, Ag/AgCl and KCl (sat.) worked as the reference electrode, and platinum disk as the counter electrode.

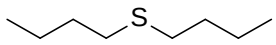


(a) CV curves of dibutyl sulfoxide (DBSO)



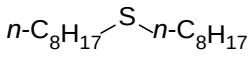
(b) CV curves of isopropanol

7. Analytic data of the obtained compounds



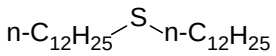
dibutyl sulfide (b1) [1]

Yield: 60.7 mg, 83% (99% GC yield); colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (t, *J* = 7.4 Hz, 2H), 1.59 (p, *J* = 7.4 Hz, 2H), 1.43 (h, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 31.8, 22.0, 13.7.



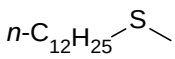
dioctyl sulfide (b2) [2]

Yield: 117.6 mg, 91%; colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (t, *J* = 7.6 Hz, 4H), 1.58 (m, 4H), 1.45 – 1.18 (m, 20H), 0.87 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 32.2, 31.8, 29.8, 29.2, 29.0, 22.7, 14.1.



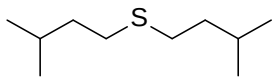
didodecyl sulfide (b3) [3]

Yield: 148.3 mg, 80%; colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (t, *J* = 8.5 Hz, 4H), 1.57 (t, *J* = 7.8 Hz, 4H), 1.38 (d, *J* = 7.3 Hz, 4H), 1.26 (m, 32H), 0.88 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 32.2, 31.9, 29.8, 29.7, 29.6, 29.4, 29.3, 29.0, 22.7, 14.1.



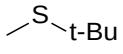
dodecyl methyl sulfide (b4) [1]

Yield: 94.1 mg, 87%; colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (t, *J* = 7.4 Hz, 2H), 2.10 (s, 3H), 1.60 (p, *J* = 7.3 Hz, 2H), 1.38 (t, *J* = 7.3 Hz, 2H), 1.27 (m, 16H), 0.89 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 34.3, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.2, 29.1, 28.8, 22.6, 15.4, 14.0.



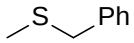
diisopentyl sulfide (b5) [4]

Yield: 75.0 mg, 86% (95% GC yield); colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (t, 4H), 1.74 – 1.62 (m, 2H), 1.47 (q, *J* = 7.3 Hz, 4H), 0.91 (d, *J* = 7.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 38.7, 30.1, 27.5, 22.3.



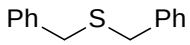
tert-butyl methyl sulfide (b6) [5]

Yield: 31.3 mg, 26% (84% GC yield); colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 40.7, 30.2, 11.4.



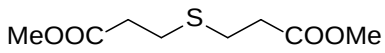
benzyl methyl sulfide (b7) [6]

Yield: 55.3 mg, 80%; colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 3.5 Hz, 4H), 7.25 – 7.21 (m, 1H), 3.66 (s, 2H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 128.9, 128.5, 127.0, 38.4, 15.0.



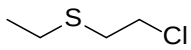
dibenzyl sulfide (b8) [1]

Yield: 49.3 mg, 46%; white solid; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.19 (m, 10H), 3.60 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 129.0, 128.5, 127.0, 35.6.



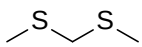
dimethyl 3,3'-thiodipropionate (b9) [7]

Yield: 95.9 mg, 92%; colorless oil; hexane/ethyl acetate = 5:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 6H), 2.81 (t, *J* = 6.5 Hz, 4H), 2.63 (t, *J* = 7.7 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 51.8, 34.5, 27.0.



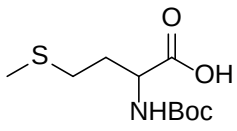
2-chloroethyl ethyl sulfide (b10) [8]

Yield: 49.9 mg, 80% (99% GC yield); colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (t, 2H), 2.87 (t, *J* = 8.2 Hz, 2H), 2.60 (q, *J* = 10.4, 9.0 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 43.1, 33.8, 26.3, 14.9.



bis(methylthio)methane (b11) [1]

Yield: 32.5 mg, 60% (95% GC yield); colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (s, 2H), 2.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 40.1, 14.3.

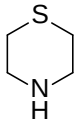


(*tert*-butoxycarbonyl)methionine (b12) [9]

Yield: 93.3 mg, 80%; white solid; hexane/ethyl acetate = 2:1, with 2% AcOH; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47 (d, *J* = 6.4 Hz, 1H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.34 – 1.84 (m, 5H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.4, 156.1, 78.5, 52.8, 30.8, 30.3, 28.6, 15.0.

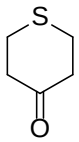
tetrahydrothiophene (b13) [1]

Yield: 25.6 mg, 58% (98% GC yield); colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (t, 4H), 2.09 – 1.80 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 31.7, 31.0.



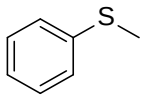
thiomorpholine (b14) [10]

Yield: 43.9 mg, 85%; colorless oil; hexane/ethyl acetate = 10:1, with 5% Et_3N; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.11 (q, *J* = 3.6, 2.9 Hz, 4H), 2.60 (t, *J* = 4.6 Hz, 4H), 1.87 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 47.8, 28.2.



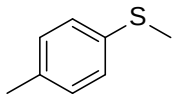
tetrahydro-4H-thiopyran-4-one (b15) [11]

Yield: 54.0 mg, 93%; colorless oil; hexane/ethyl acetate = 10:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96 (t, *J* = 6.0 Hz, 1H), 2.69 (t, *J* = 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.3, 44.0, 30.0.



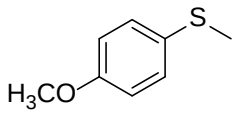
methyl phenyl sulfide (16) [1]

Yield: 55.9 mg, 90%; colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 7.18 (t, *J* = 6.5 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 128.8, 126.7, 125.0, 15.9.



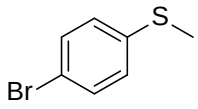
methyl p-tolyl sulfide (17) [1]

Yield: 61.5 mg, 89%; colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 2.45 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.1, 134.8, 129.7, 127.3, 21.0, 16.5.



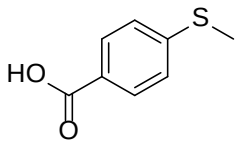
4-methoxyphenyl methyl sulfide (b18) [1]

Yield: 64.0 mg, 83%; colorless oil; hexane/ethyl acetate = 10:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 130.1, 128.7, 114.6, 55.3, 18.0.



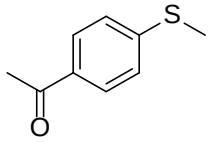
4-bromophenyl methyl sulfide (b19) [1]

Yield: 86.3 mg, 85%; white solid; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 131.8, 128.1, 118.6, 15.9.



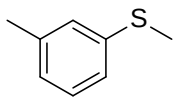
4-(methylthio)benzoic acid (b20) [12]

Yield: 73.2 mg, 87%; white solid, hexane/ethyl acetate = 5:1, with 5% AcOH; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.88 (s, 1H), 7.87 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.5, 145.3, 130.2, 127.1, 125.3, 14.4.



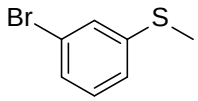
1-(4-(methylthio)phenyl)ethan-1-one (b21) [1]

Yield: 75.6 mg, 91%; white solid; hexane/ethyl acetate = 10:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 2.58 (s,3H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 145.8, 133.4, 128.7, 124.9, 26.4, 14.7



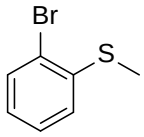
methyl(m-tolyl)sulfane (b22) [19]

Yield: 59.4 mg, 86%; colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.6 Hz, 1H), 7.15 – 7.07 (m, 2H), 6.99 (d, *J* = 7.5 Hz, 1H), 2.51 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.2, 128.7, 127.4, 126.0, 123.7, 21.4, 15.9.



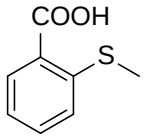
(3-bromophenyl)(methyl)sulfane (b23) [19]

Yield: 83.3 mg, 82%; colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 2.0 Hz, 1H), 7.28 (m, 1H), 7.22 – 7.11 (m, 2H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 130.1, 128.8, 128.0, 125.0, 122.9, 15.7.



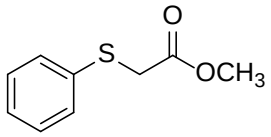
2-bromophenyl methyl sulfide (b24) [1]

Yield: 77.2 mg, 76%; colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.32 (td, *J* = 7.6, 1.3 Hz, 1H), 7.16 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.03 (td, *J* = 7.6, 1.5 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 132.6, 127.7, 125.6, 125.4, 121.7, 15.7.



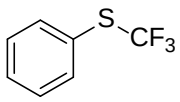
2-(methylthio)benzoic acid (b25) [2]

Yield: 58.9 mg, 70%; white solid; hexane/ethyl acetate = 5:1, with 5% AcOH; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.01 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.9, 143.0, 133.0, 131.4, 127.7, 125.0, 123.9, 15.2.



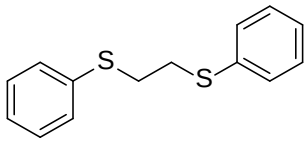
methyl 2-(phenylthio)acetate (b26) [2]

Yield: 72.0 mg, 79%; colorless oil; hexane/ethyl acetate = 10:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.21 (m, 1H), 3.74 (s, 3H), 3.68 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 134.9, 129.9, 129.0, 127.0, 52.5, 36.5.



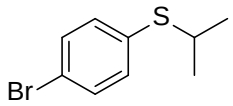
phenyl trifluoromethyl sulfide (b27) [12]

Yield: 24.9 mg, 28%; colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.1 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 130.8, 129.7 (q, *J* = 306.6 Hz), 129.5, 124.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -42.76.



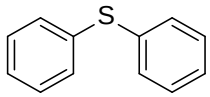
1,2-bis(phenylthio)ethane (b28) [14]

Yield: 114.6 mg, 93%; white solid; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 8H), 7.27 – 7.22 (m, 2H), 3.12 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 130.0, 129.0, 126.5, 33.3.



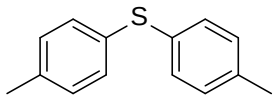
4-bromophenyl isopropyl sulfide (b29) [13]

Yield: 92.4 mg, 80%; colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 3.37 (hept, *J* = 6.6 Hz, 1H), 1.31 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.3, 131.8, 38.3, 23.0.



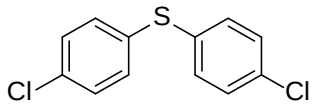
diphenyl sulfide (b30) [1]

Yield: 76.4 mg, 82%; colorless oil; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 131.1, 129.2, 127.1.



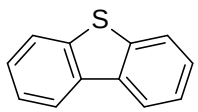
di-p-tolyl sulfide (b31) [1]

Yield: 80.4 mg, 75%; white solid; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 4H), 2.37 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 132.7, 131.1, 129.9, 21.1.



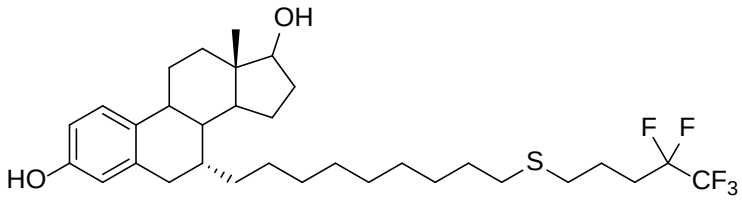
bis(4-chlorophenyl) sulfide (b32) [1]

Yield: 111.0 mg, 87%; white solid; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.9, 133.4, 132.3, 129.4.



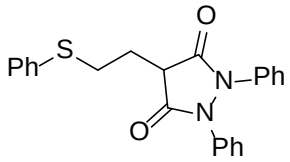
dibenzo[b,d]thiophene (b33) [15]

Yield: 82.0 mg, 89%; white solid; pure hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dt, *J* = 7.3, 3.6 Hz, 2H), 7.89 (dt, *J* = 7.2, 3.6 Hz, 2H), 7.55 – 7.44 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 135.5, 126.7, 124.3, 122.8, 121.5.



fulvestran sulfide [16]

Yield: 162.5 mg, 55%; white solid; hexane/ethyl acetate = 3:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.4 Hz, 1H), 6.65 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.57 (d, *J* = 2.7 Hz, 1H), 3.78 (t, *J* = 8.5 Hz, 1H), 2.88 (dd, *J* = 16.9, 5.5 Hz, 1H), 2.73 (d, *J* = 16.8 Hz, 1H), 2.61 (t, *J* = 7.0 Hz, 2H), 2.52 (t, *J* = 7.4 Hz, 2H), 2.42 – 2.27 (m, 2H), 2.26 – 2.10 (m, 3H), 1.91 (m, 3H), 1.76 (m, 1H), 1.69 – 1.55 (m, 4H), 1.53 – 1.42 (m, 2H), 1.38 (m, 4H), 1.35 – 1.25 (m, 10H), 1.23 – 1.15 (m, 2H), 1.05 (m, 1H), 0.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 137.1, 131.7, 127.0, 118.9 (qt, J_{CF}^{1} = 285.0 Hz, J_{CF}^{2} = 36.1 Hz) 116.2, 115.6 (qt, J_{CF}^{1} = 251.8 Hz, J_{CF}^{2} = 37.6 Hz) 112.9, 82.1, 46.5, 43.4, 42.0, 38.1, 36.9, 34.6, 33.2, 32.0, 31.3, 30.5, 30.0, 29.7, 29.6 (t, J_{CF} = 22 Hz), 29.5, 29.2, 28.9, 28.2, 27.3, 25.6, 22.7, 20.4, 11.1. ^{19}F NMR (377 MHz, $CDCl_3$) δ -85.40, -117.90



sulfinpyrazone sulfide [17]

Yield: 288.4 mg, 75%; white solid; hexane/ethyl acetate = 1:5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (q, *J* = 9.1 Hz, 12H), 7.16 (q, *J* = 7.8 Hz, 3H), 3.66 – 3.57 (m, 1H), 3.20 (t, *J* = 8.5 Hz, 2H), 2.35 (q, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 135.8, 134.8, 129.9, 129.1, 129.0, 126.9, 126.6, 122.7, 44.5, 30.4, 27.1.

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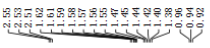
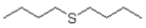
9. Copies of NMR spectra





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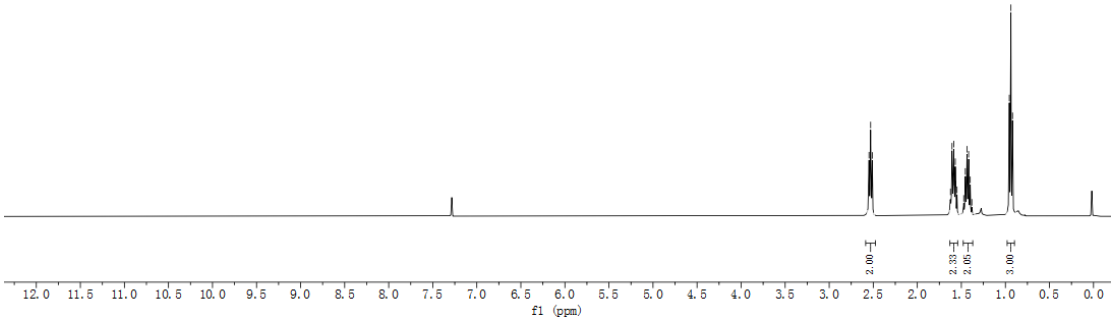

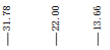

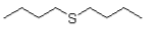

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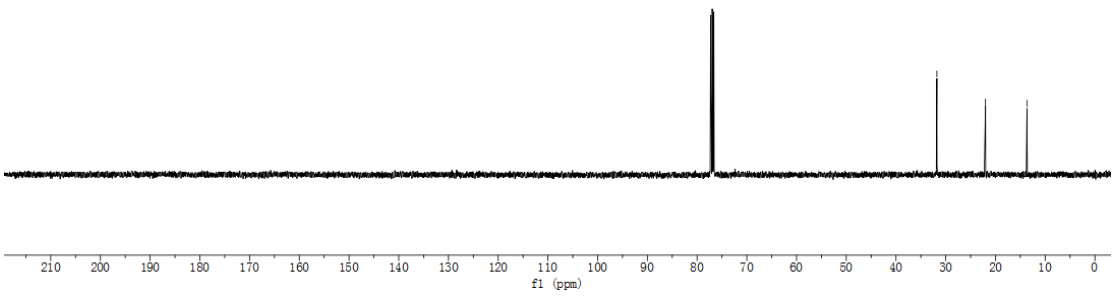

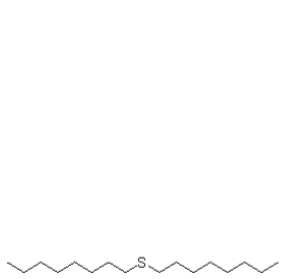

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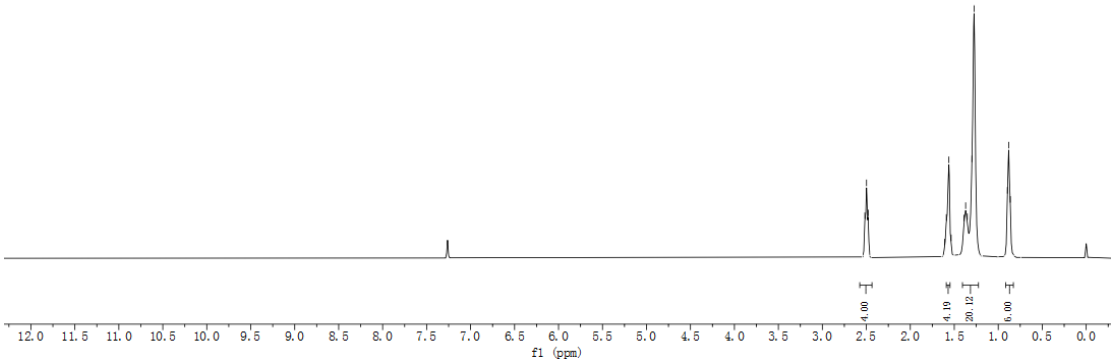

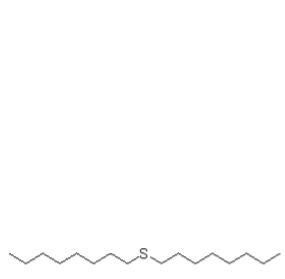

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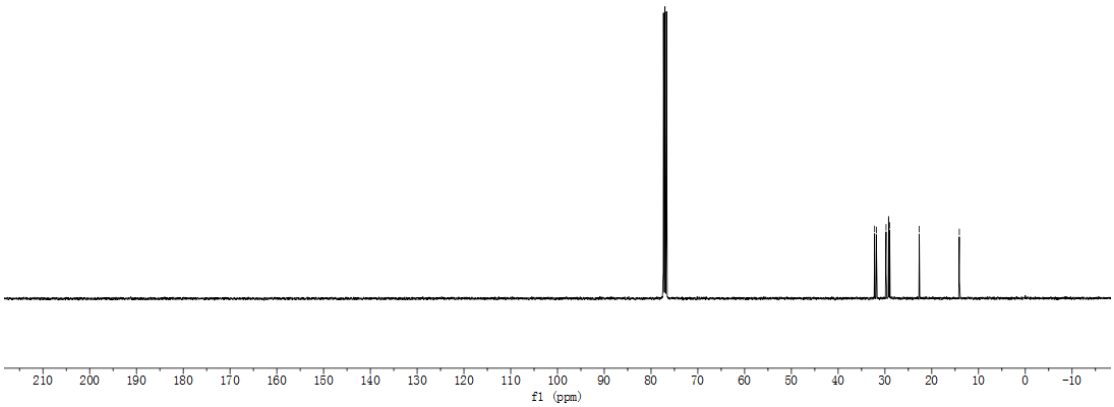

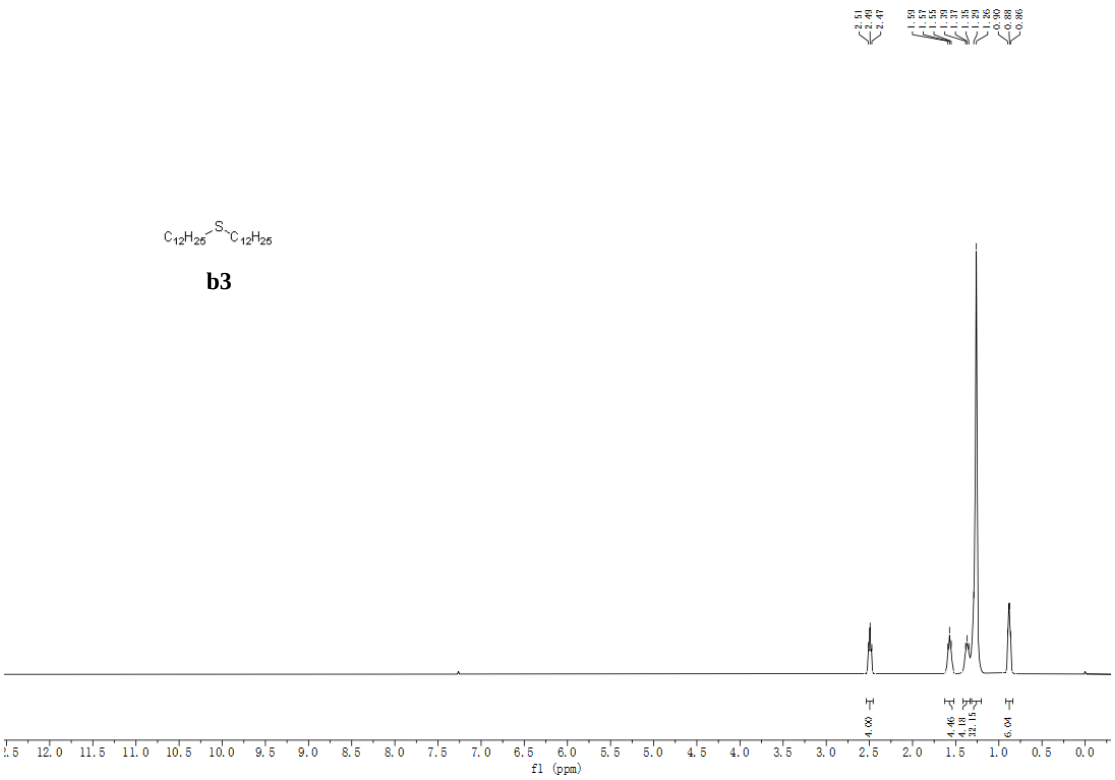
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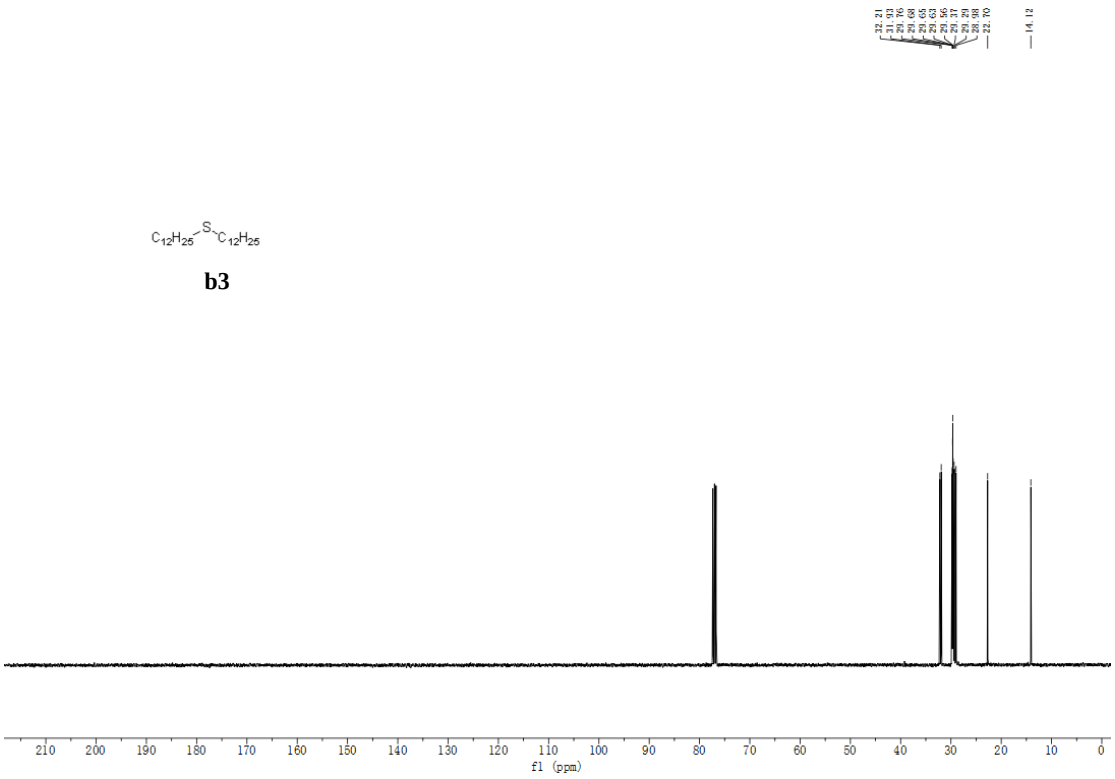
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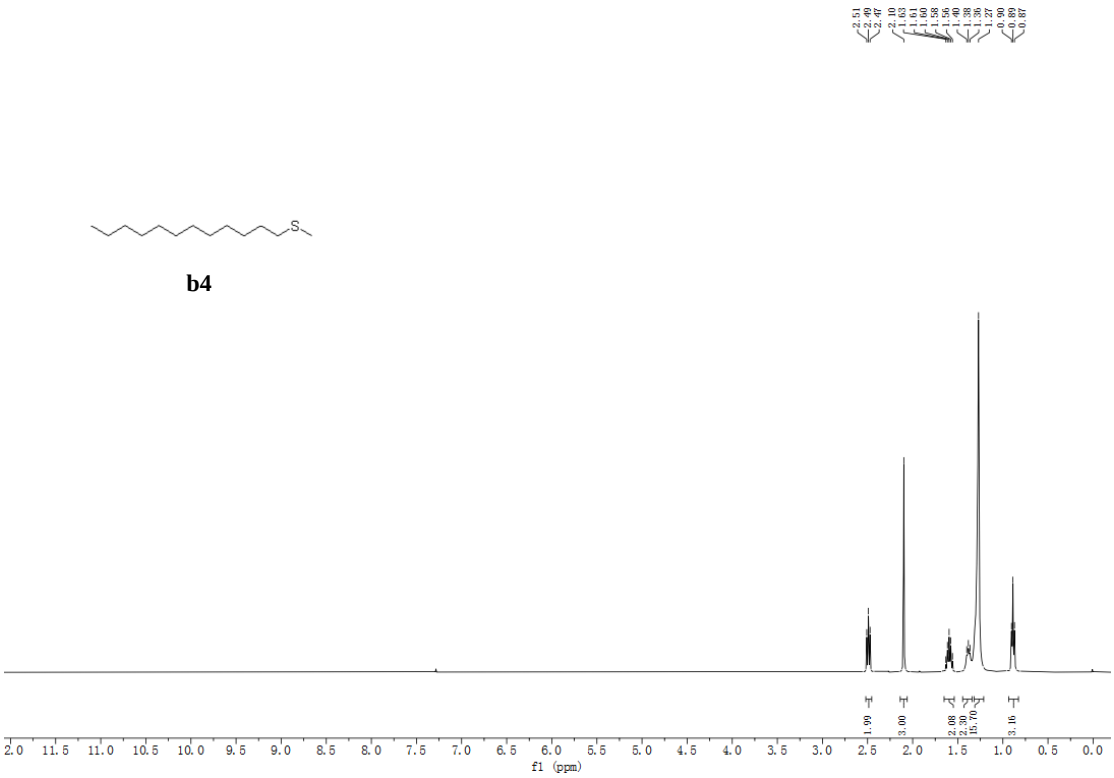
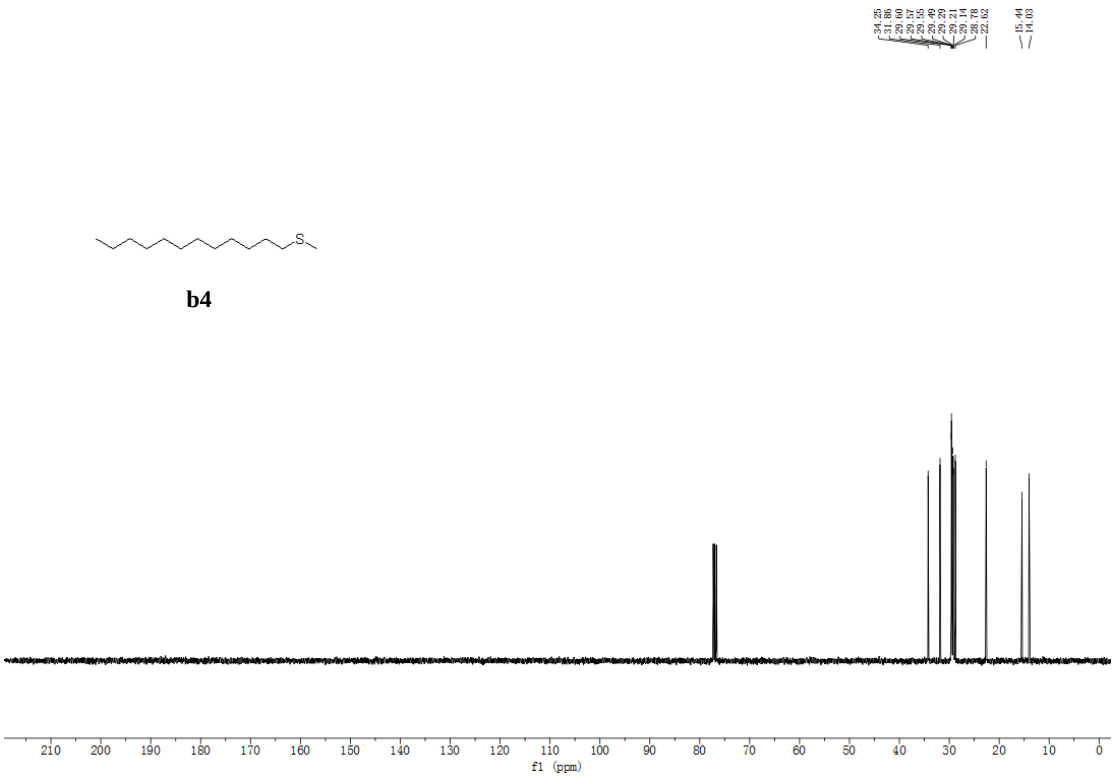
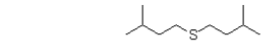
b3
f1 (ppm)


2.51
2.49
2.47
2.10
1.63
1.61
1.60
1.58
1.56
1.40
1.38
1.36
1.27
0.90
0.89
0.87
S
1.99
3.00
2.08
2.30
15.70
3.16
f1 (ppm)

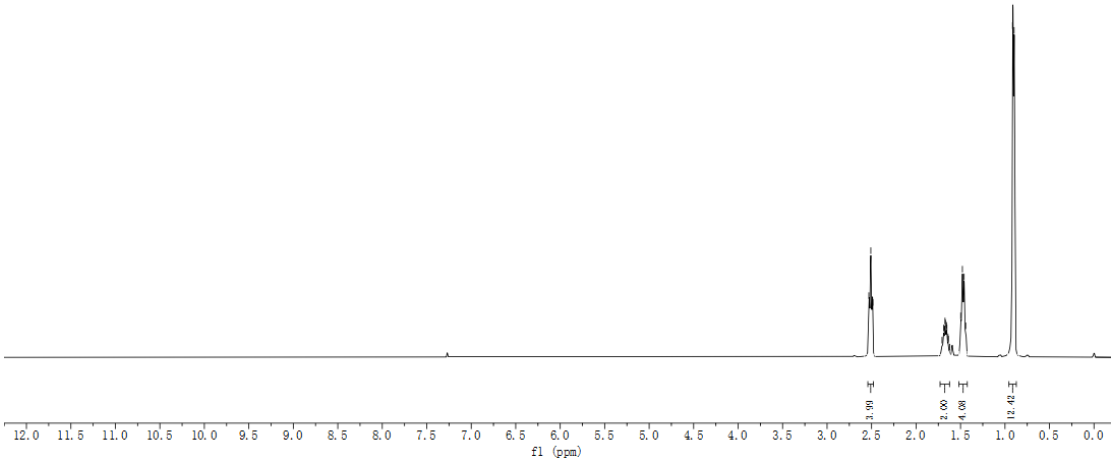
b4

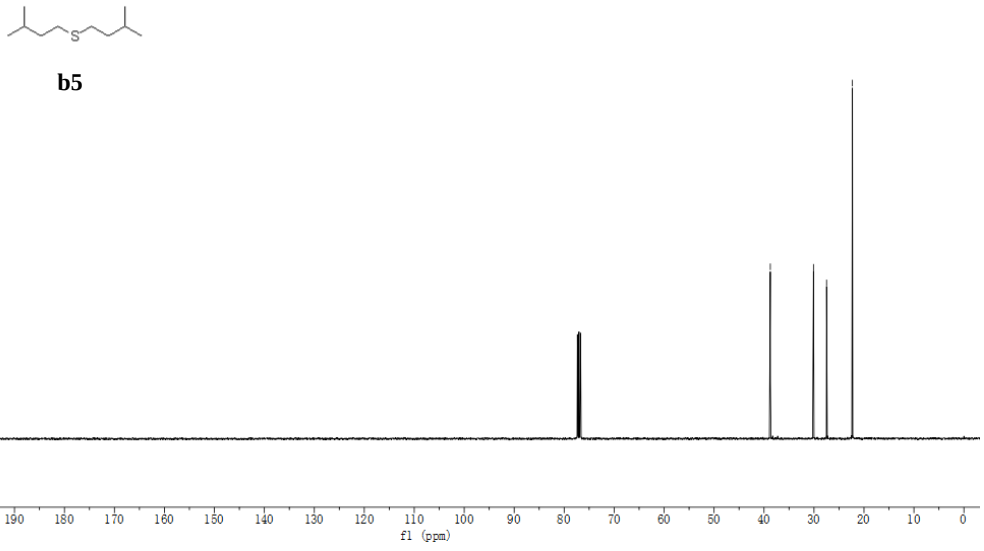

34.25
31.86
29.60
29.57
29.55
29.49
29.29
29.21
29.14
28.78
22.62
15.44
14.03
S
f1 (ppm)

b4

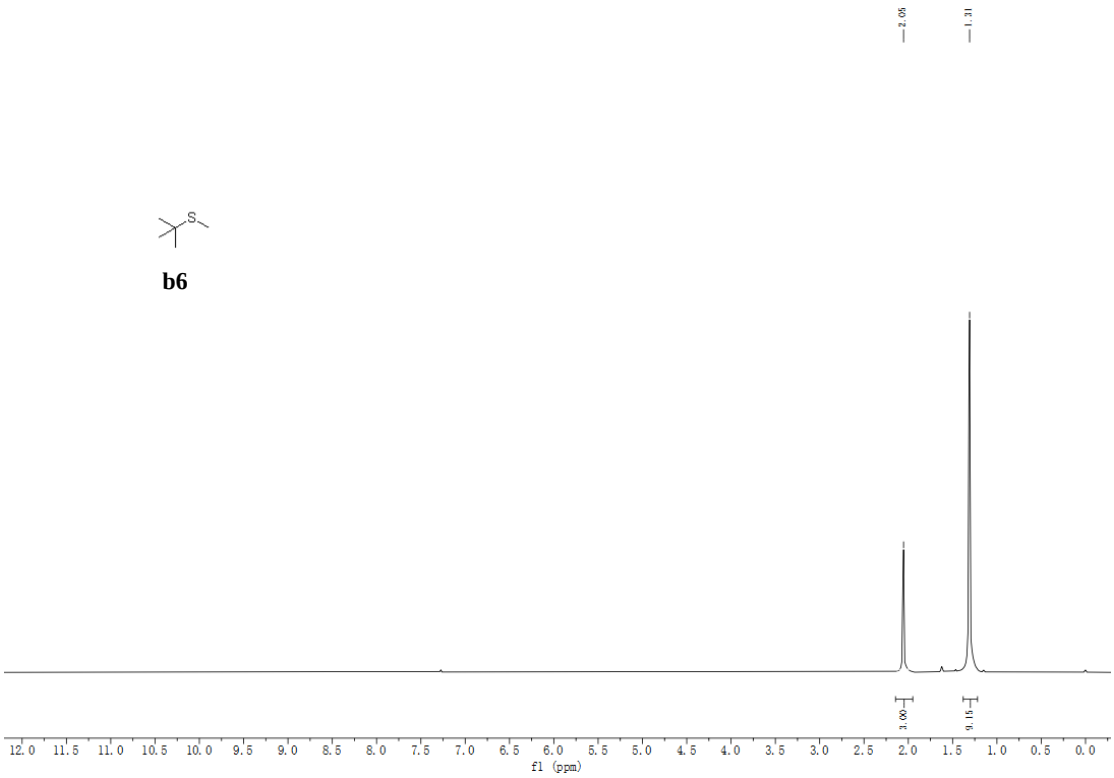


b5

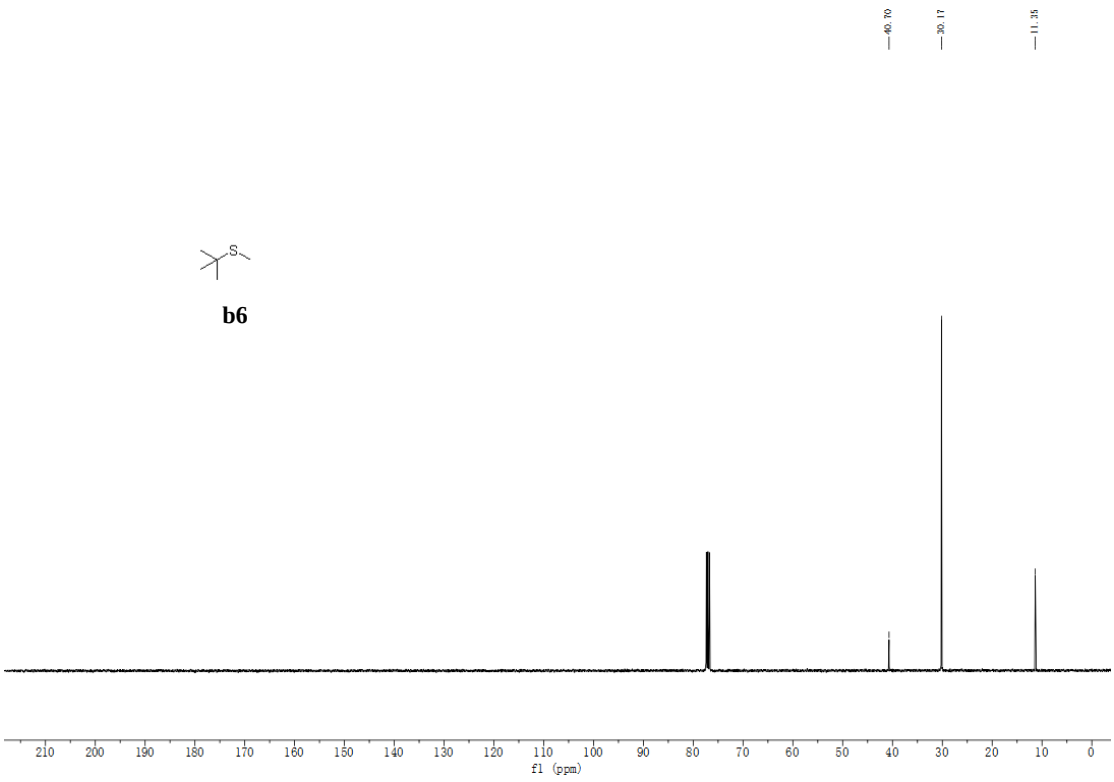




b5


2.66
1.31
S
3.00
9.15
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
f1 (ppm)

b6


40.70
30.17
11.35
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

b6

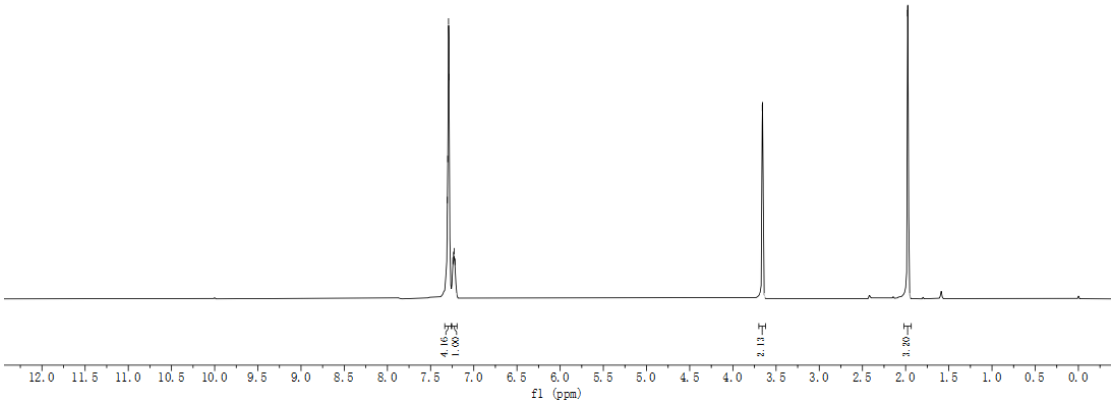

7.31
7.30
7.29
7.28
7.24
7.24
7.23
7.22

3.66

1.98


S

b7


4.16
1.00
2.13
3.20
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
f1 (ppm)

138.31

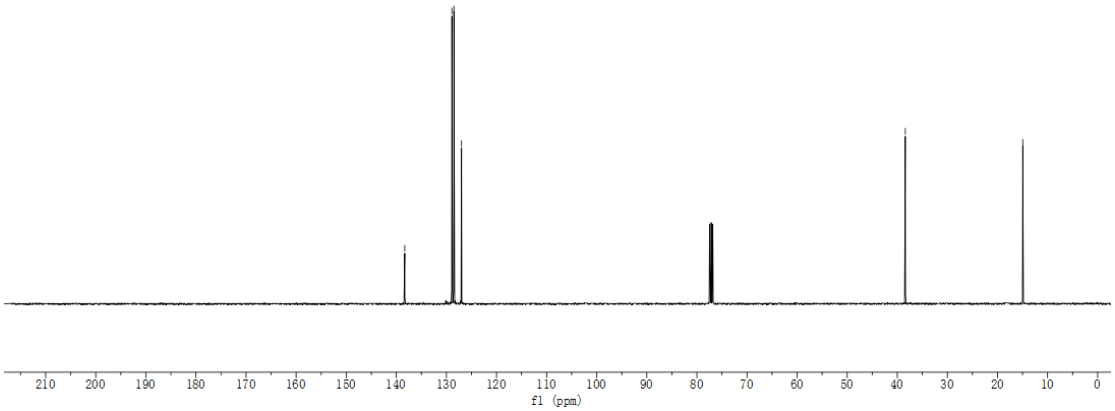

128.91
128.50
126.99

38.39

14.95

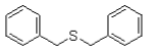

S

b7

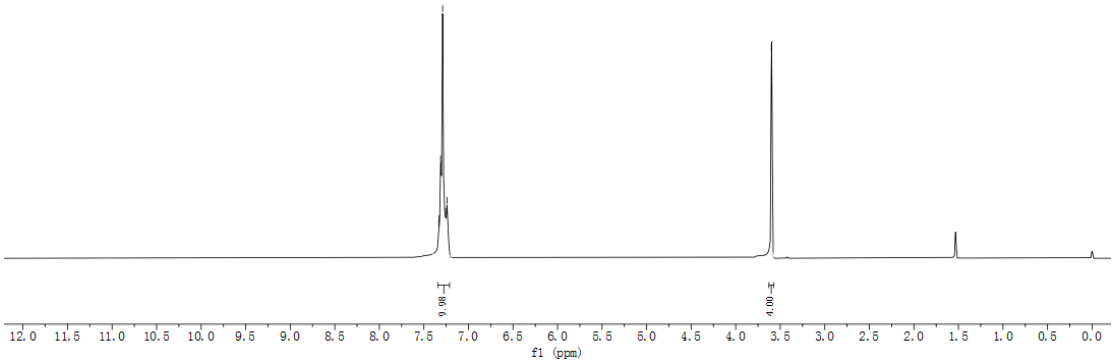

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.33
7.33
7.31
7.29
7.26
7.24

3.60

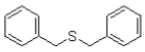


b8

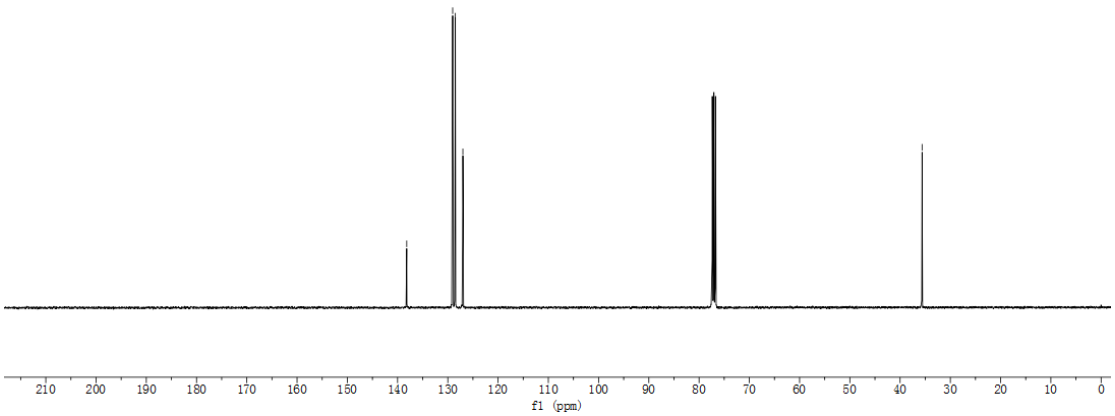

9.98
4.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

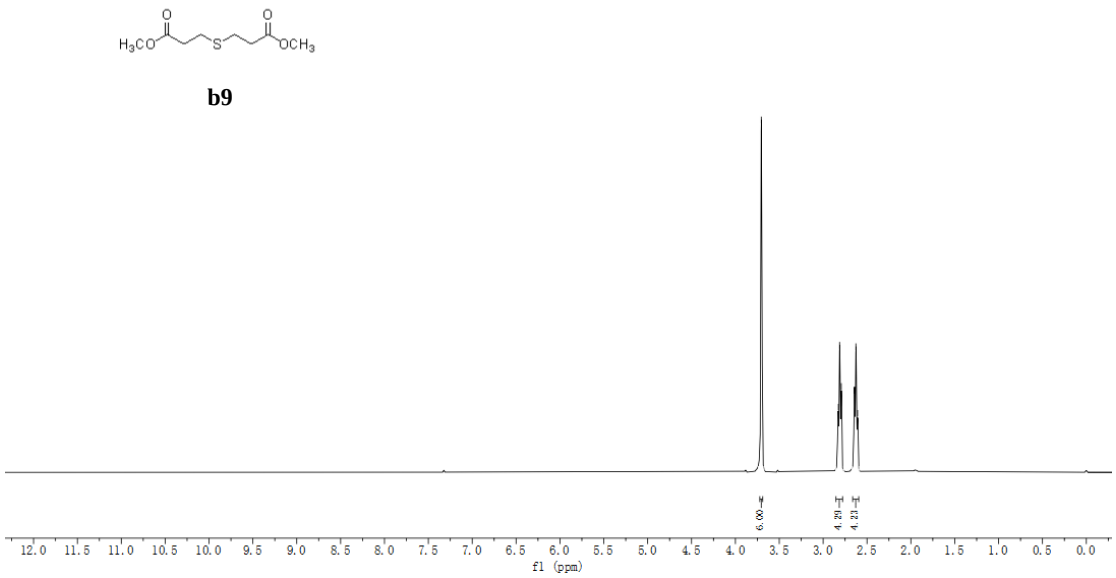

138.17
129.03
128.50
127.00

35.62

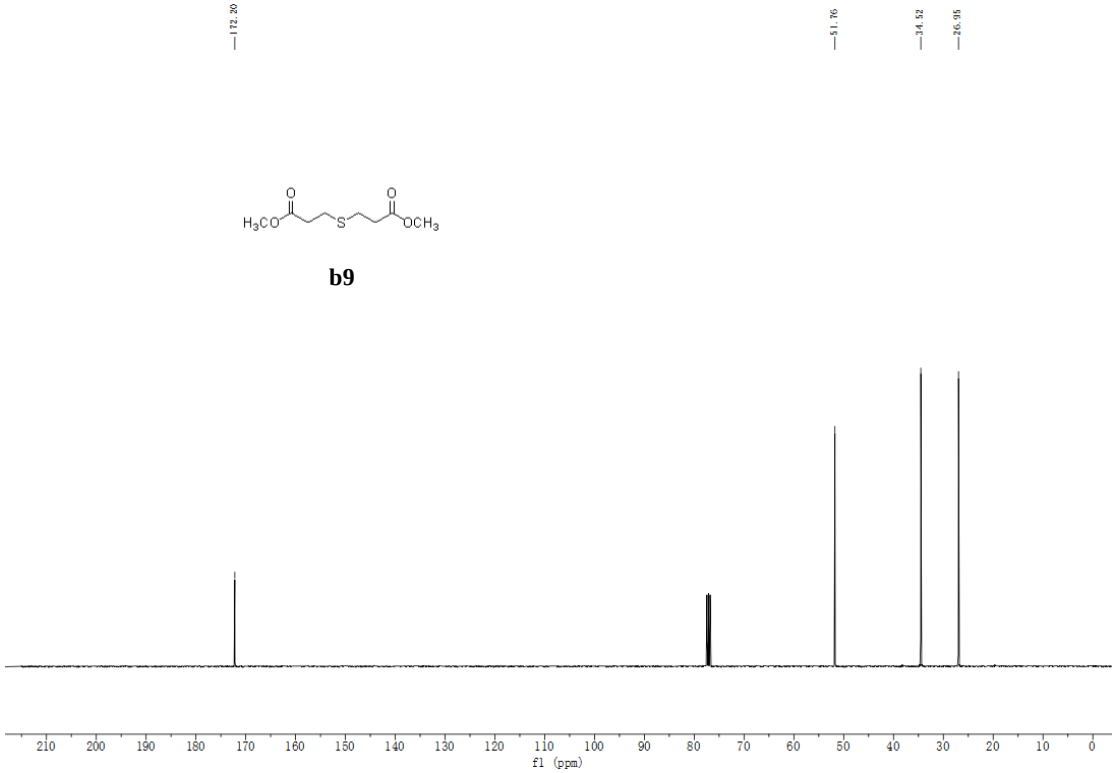


b8

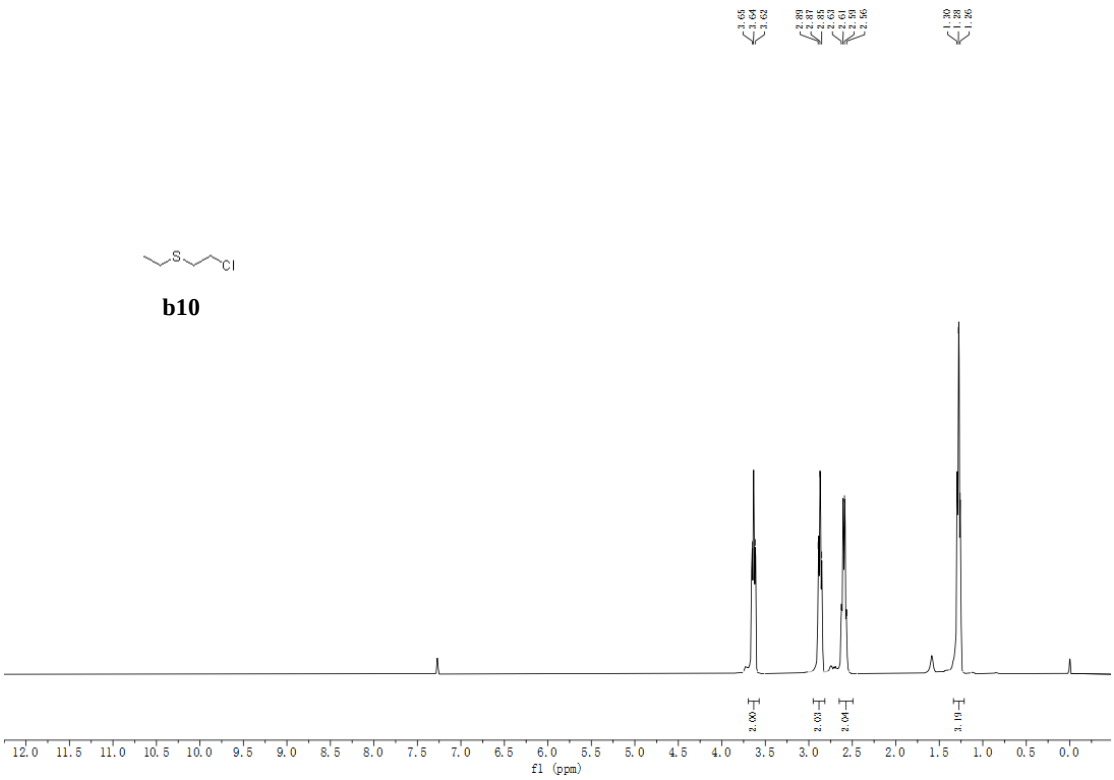

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


3.71
2.83
2.81
2.79
2.66
2.63
2.61
6.00
4.29
4.23
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
f1 (ppm)

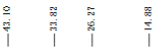
b9


172.20
51.76
34.52
26.95
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

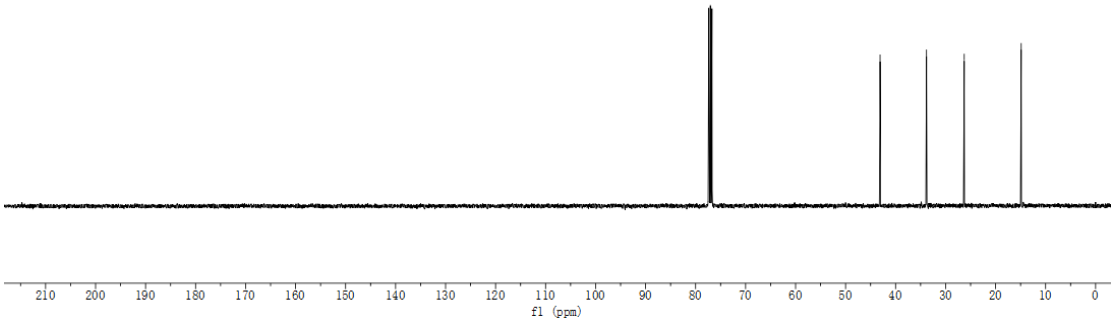
b9

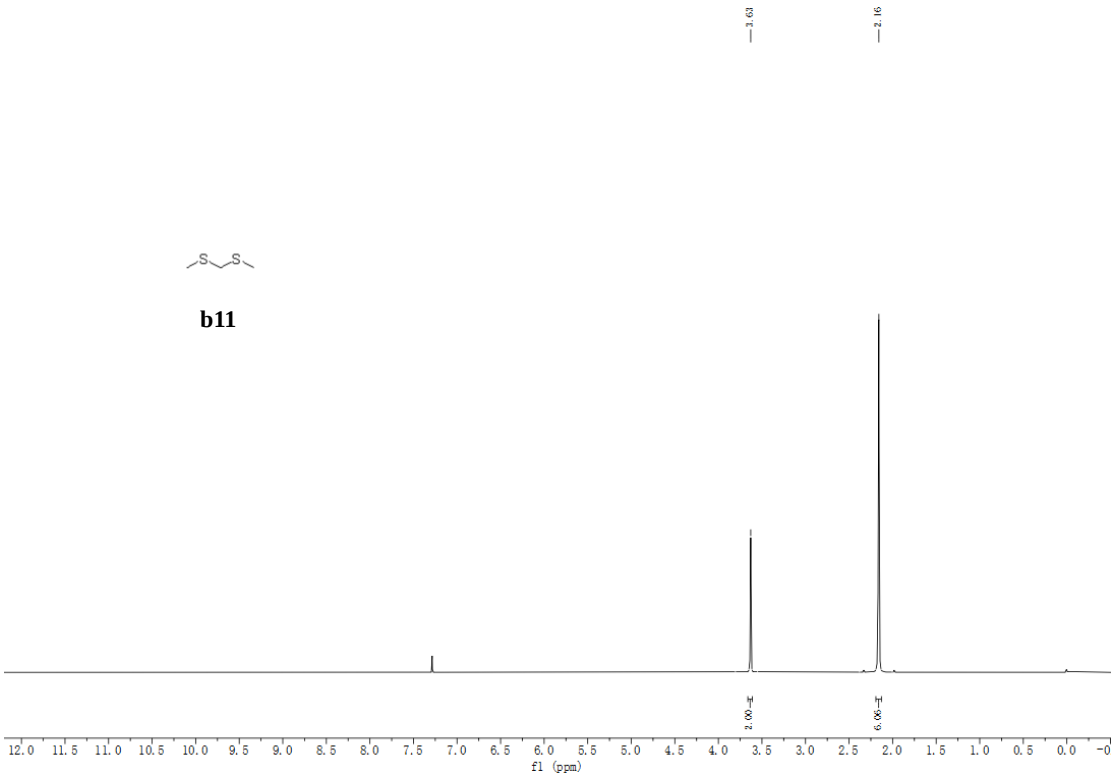

2.65
2.64
2.62
2.89
2.87
2.85
2.63
2.61
2.59
2.56
1.30
1.28
1.26
2.00
2.03
2.04
3.19
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

b10

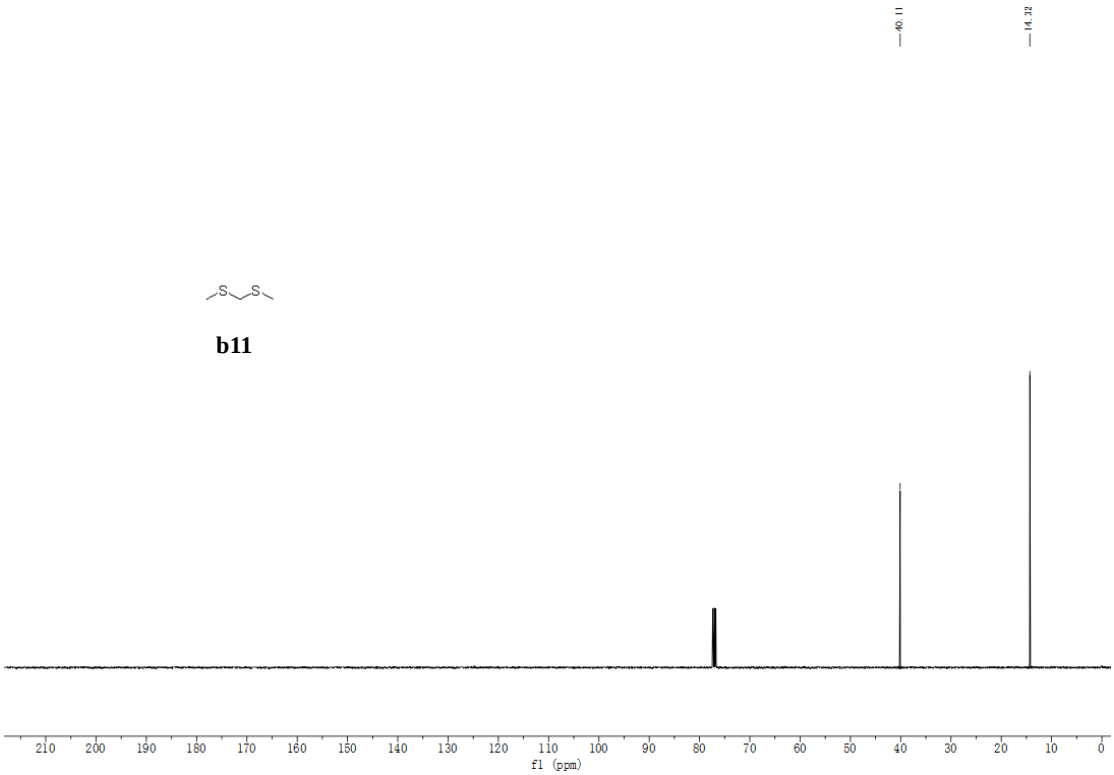

43.10
33.82
26.27
14.88

b10

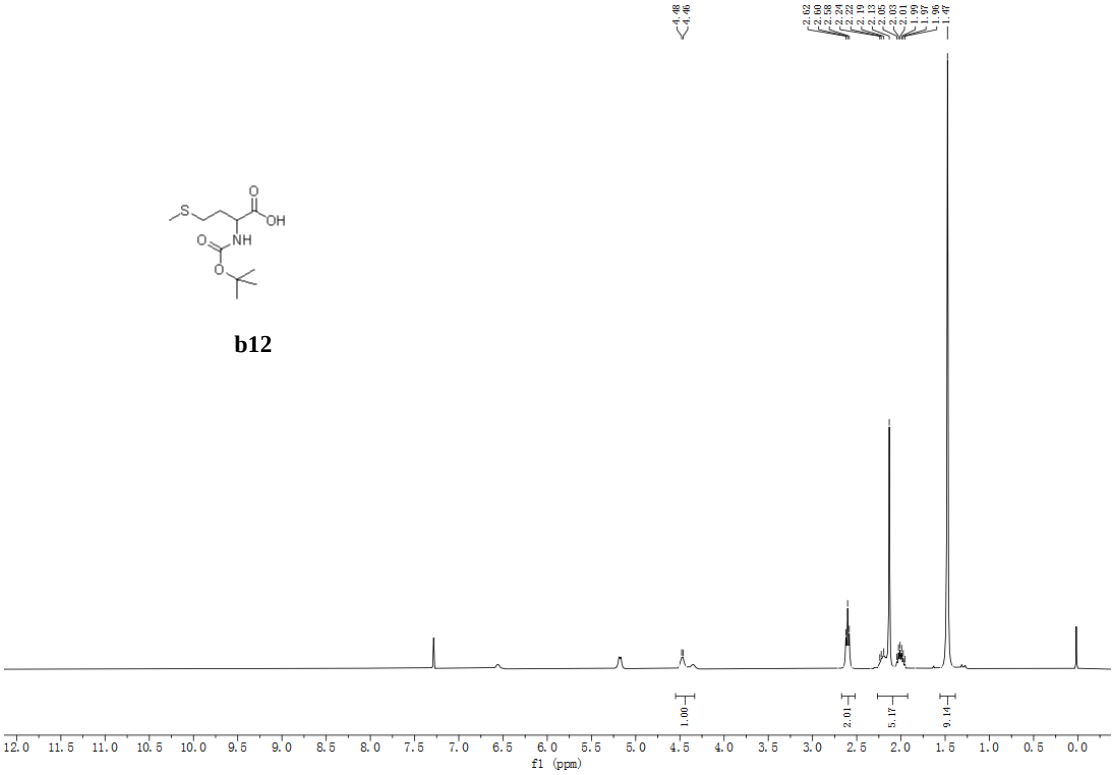

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


3.63
2.16
2.00
6.06
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
f1 (ppm)

b11

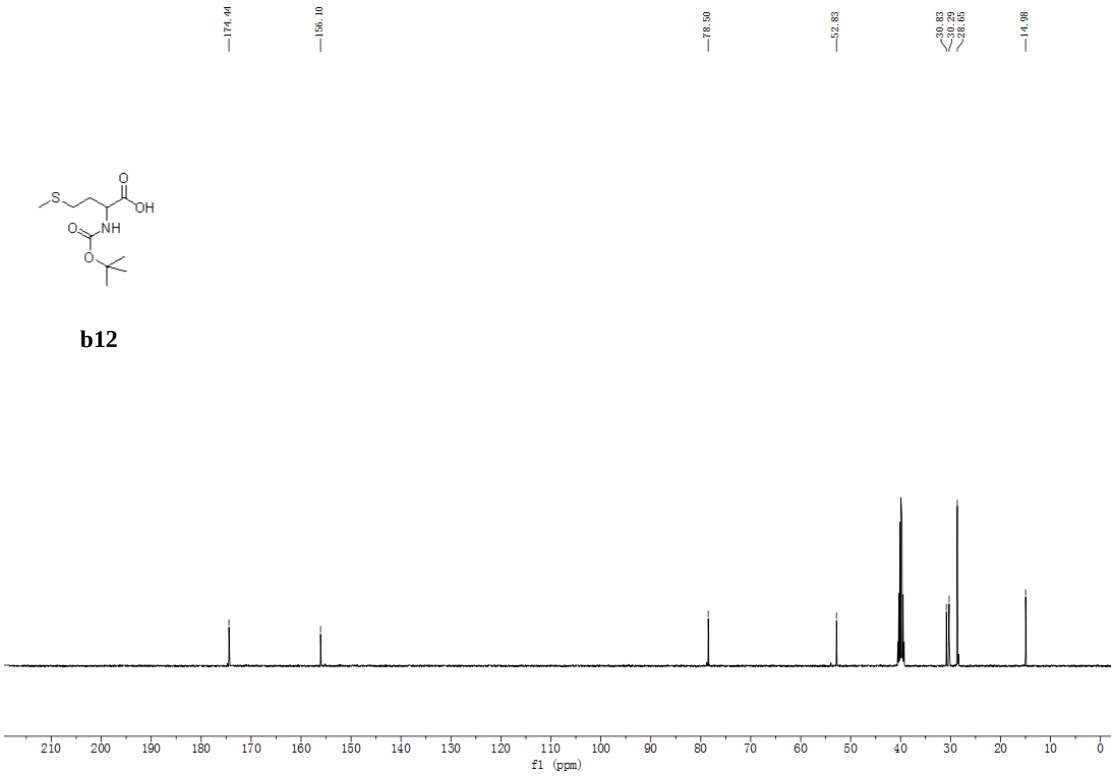

40.11
14.32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

b11


4.48
4.46
2.62
2.60
2.58
2.24
2.22
2.19
2.15
2.13
2.05
2.03
2.01
1.99
1.97
1.96
1.47
1.00
2.01
5.17
9.14
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
f1 (ppm)

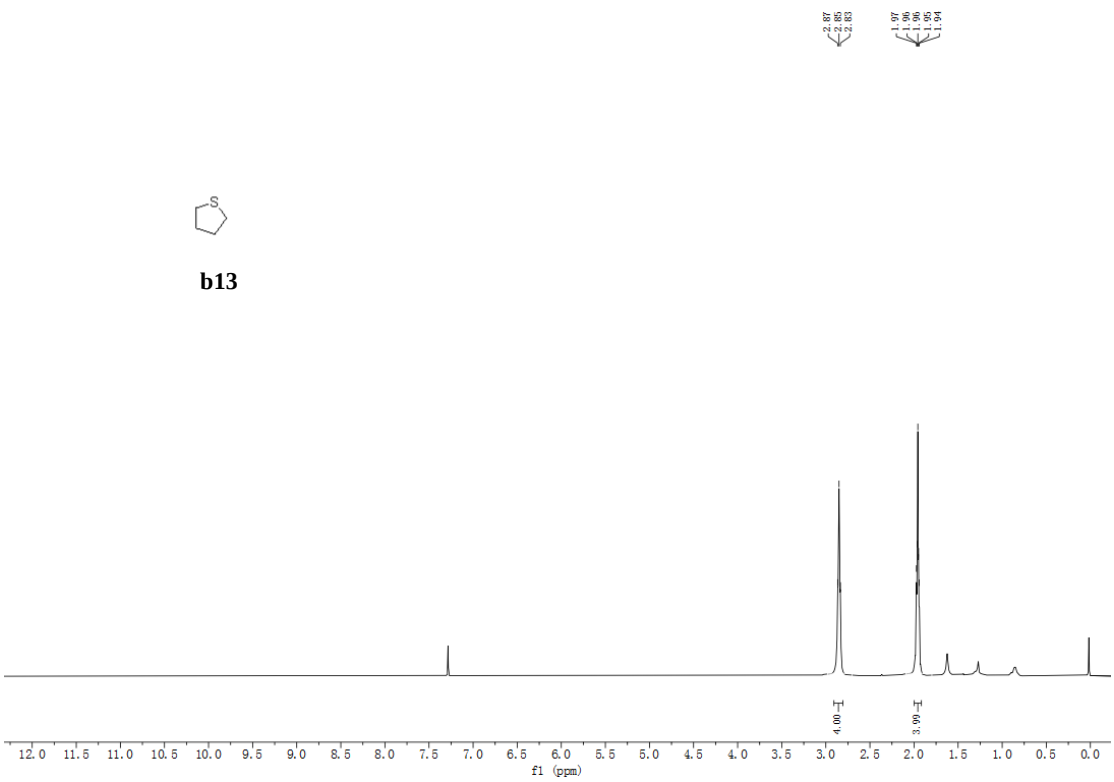
S
O
OH
NH
O
O

b12

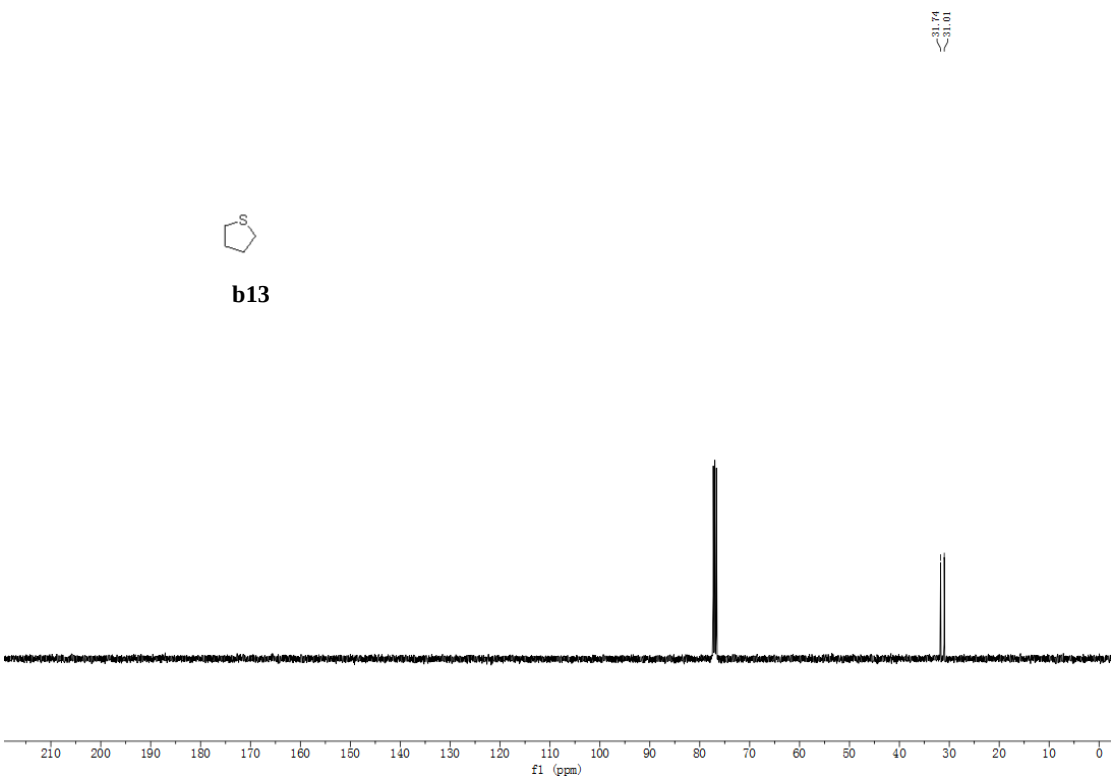

174.44
156.10
78.50
52.83
30.83
30.29
28.65
14.98
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S
O
OH
NH
O
O

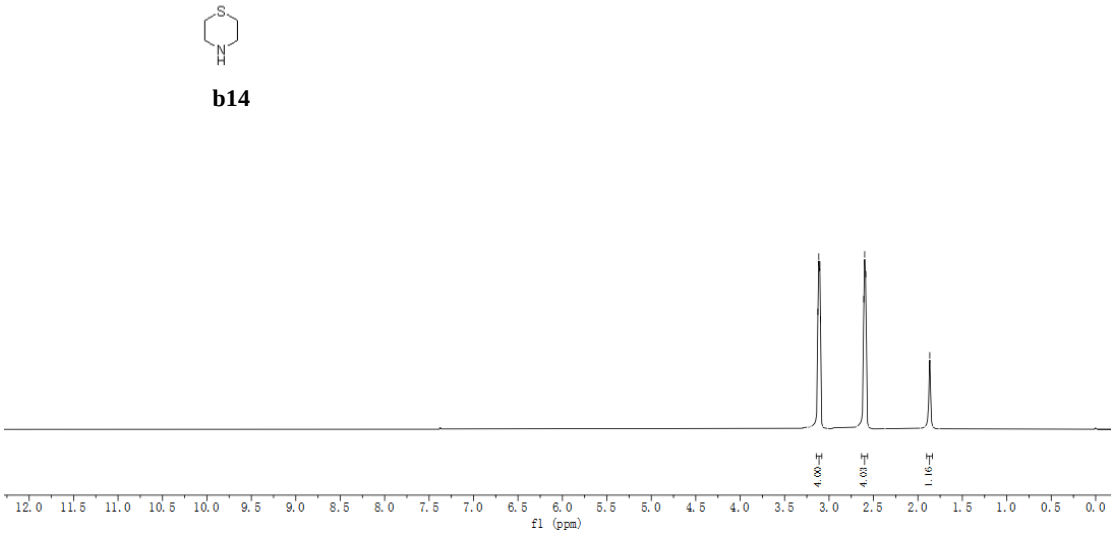
b12


2.87
2.85
2.83
1.97
1.96
1.96
1.95
1.94
4.00
3.99
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
f1 (ppm)

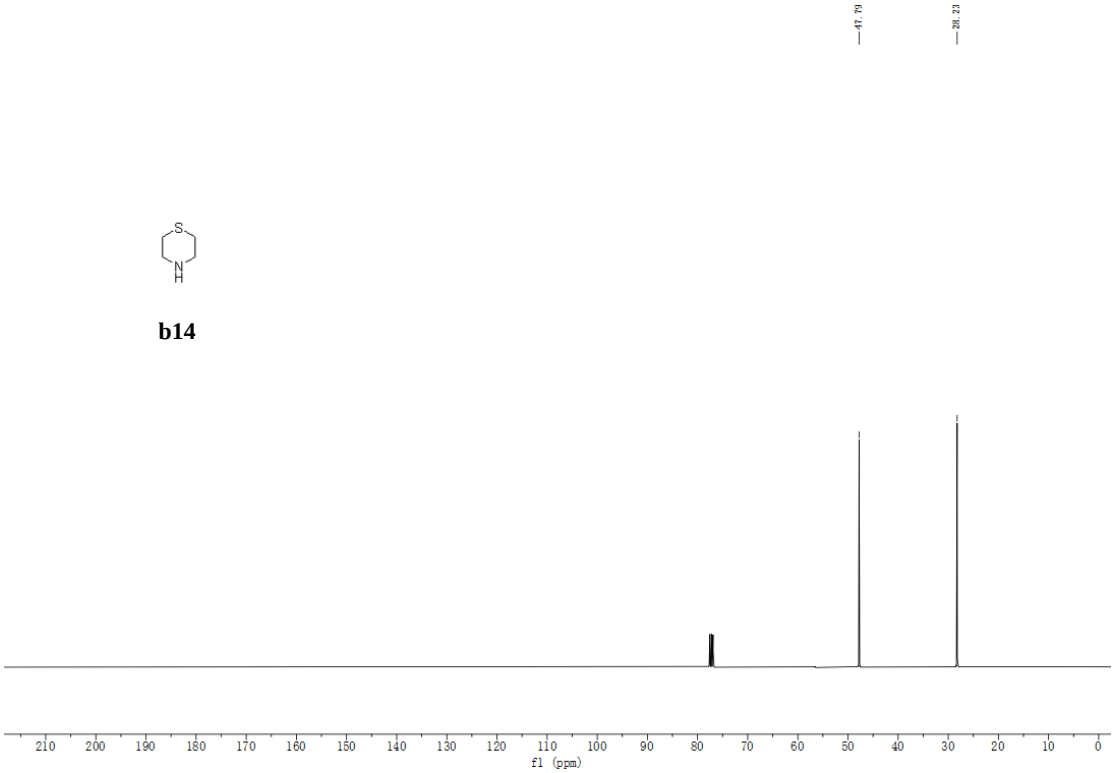
b13


31.74
31.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

b13

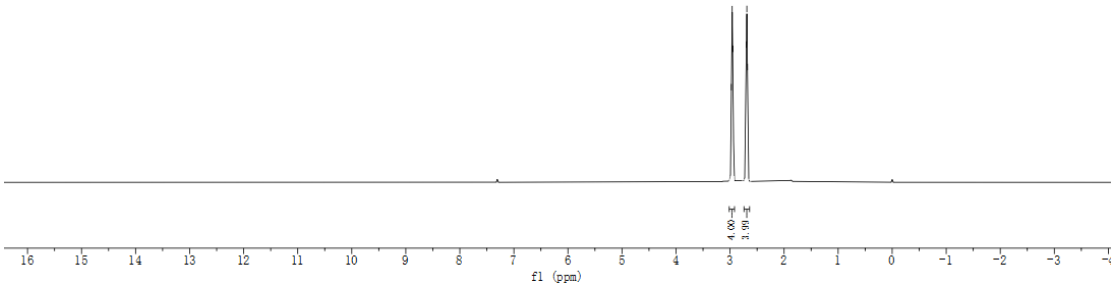

3.13
3.12
3.10
3.10
2.61
2.60
2.59
1.87
4.00
4.03
1.16
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

b14

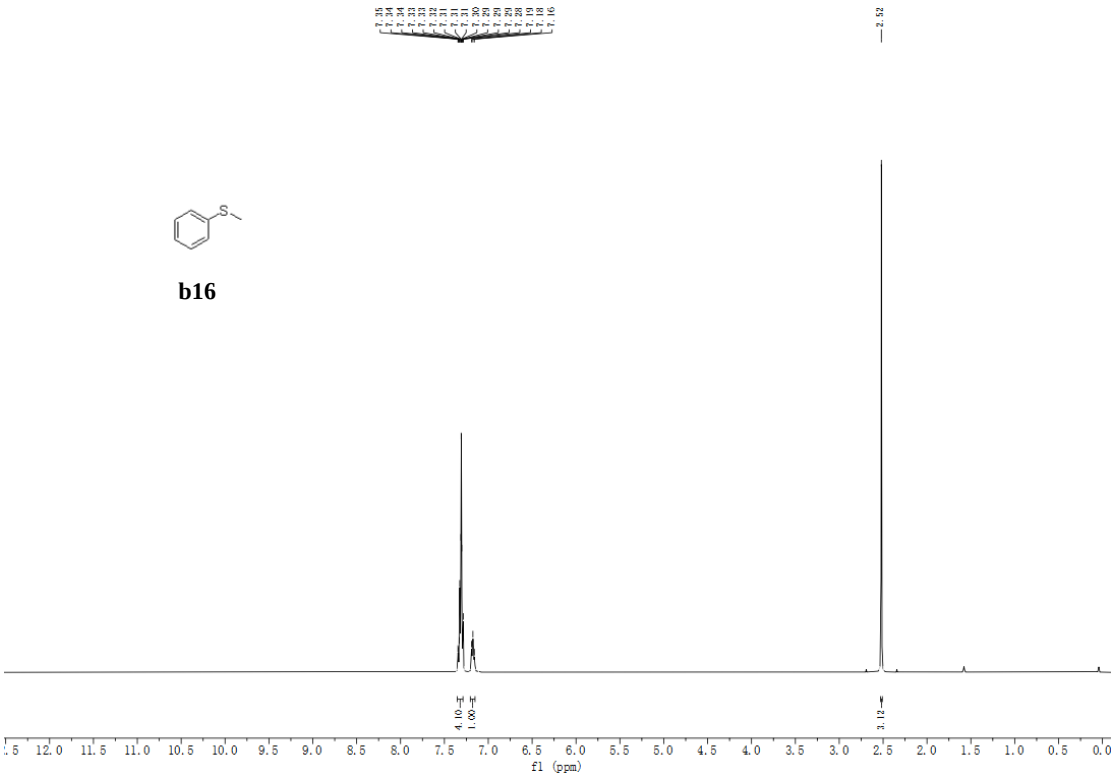

47.79
28.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

b14

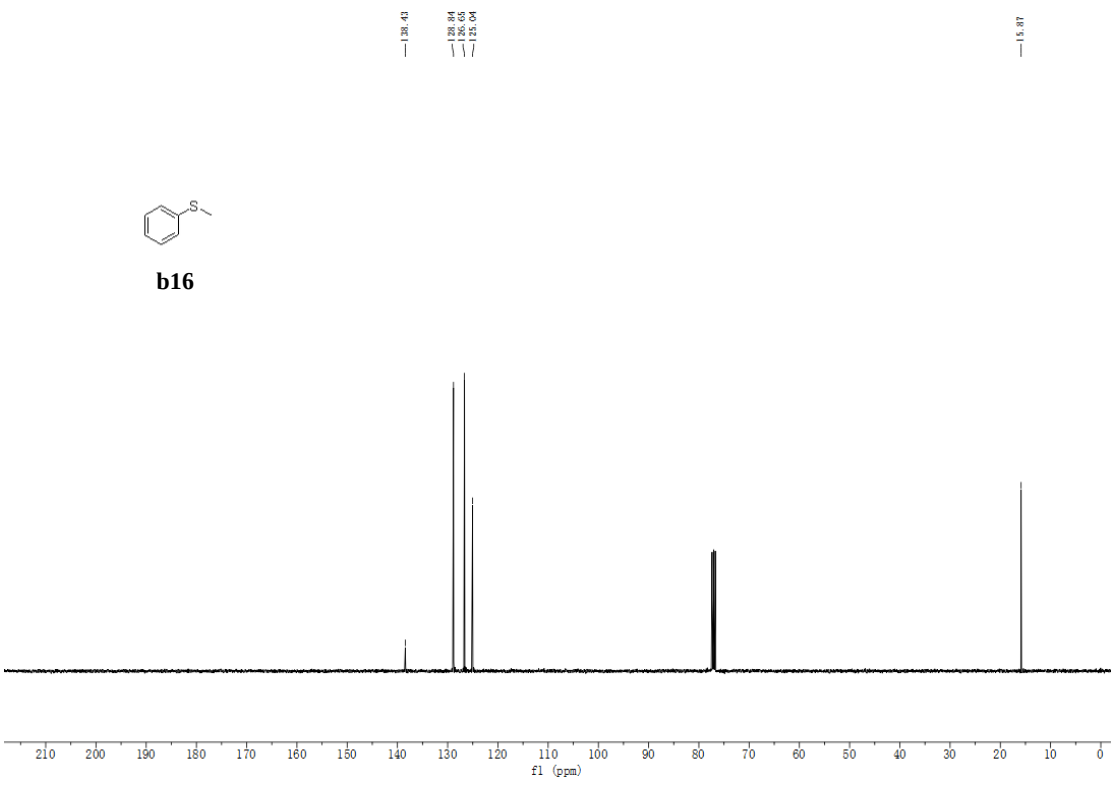
b15



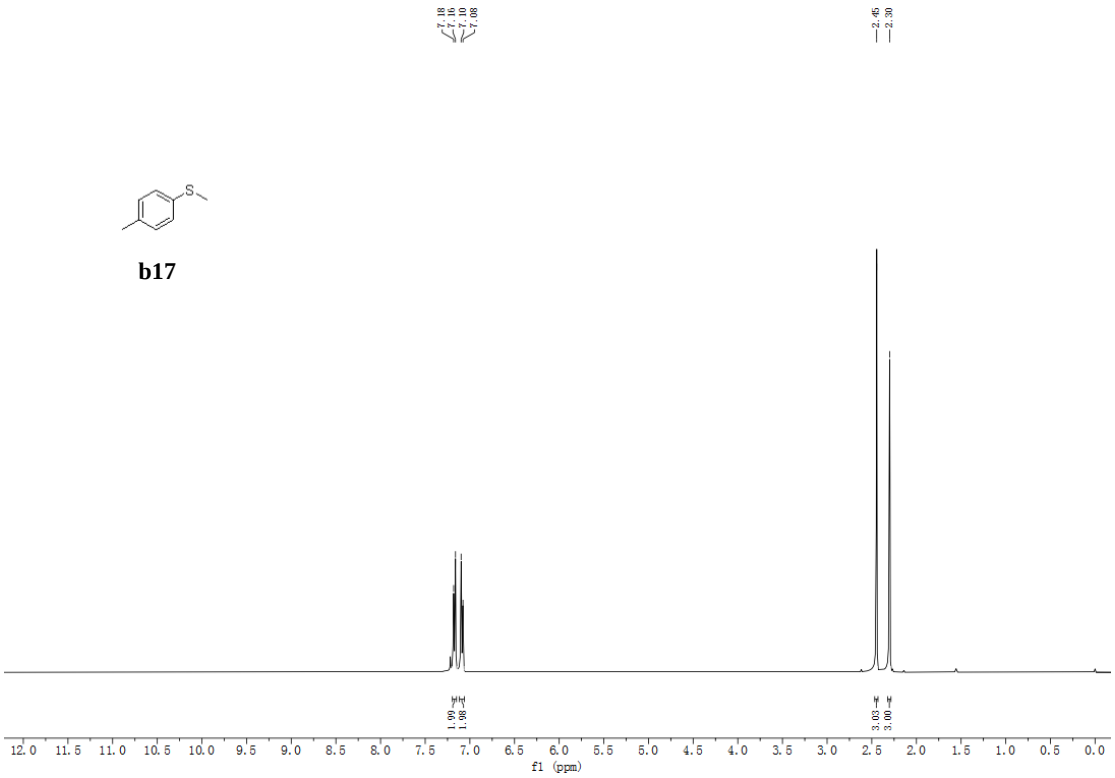
b15


7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.19
7.18
7.16
2.52
4.10
1.00
3.12
f1 (ppm)

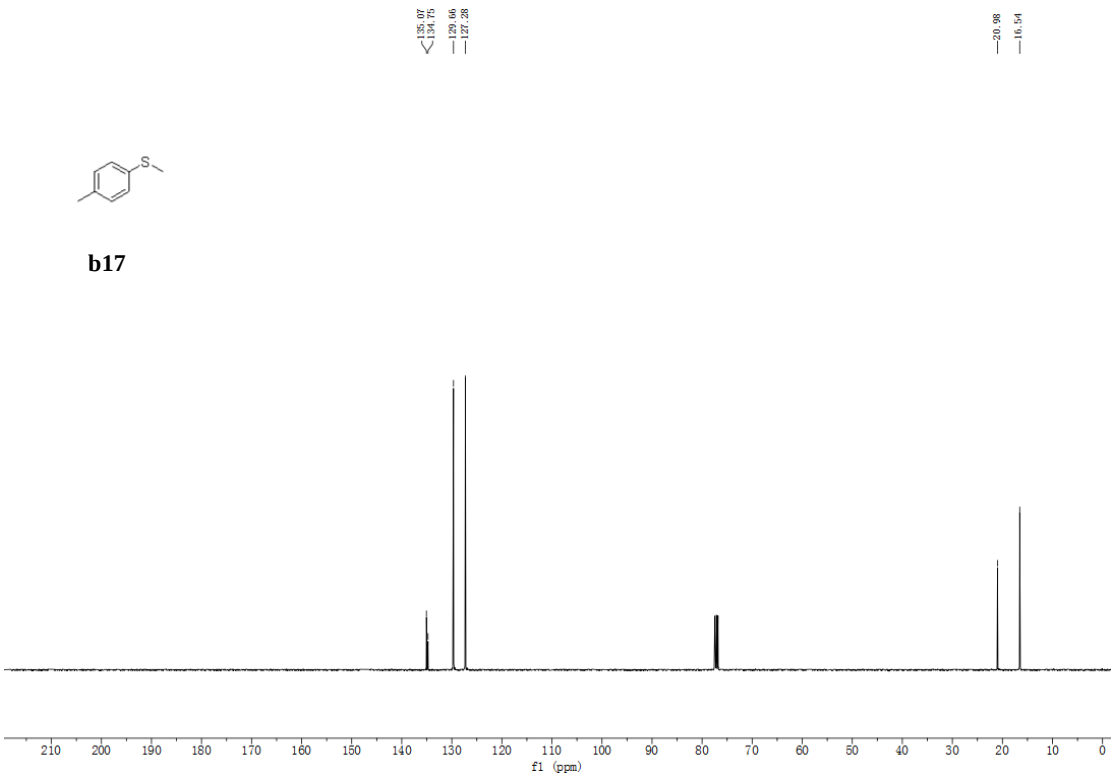
b16


138.43
128.84
126.65
125.04
15.87
f1 (ppm)

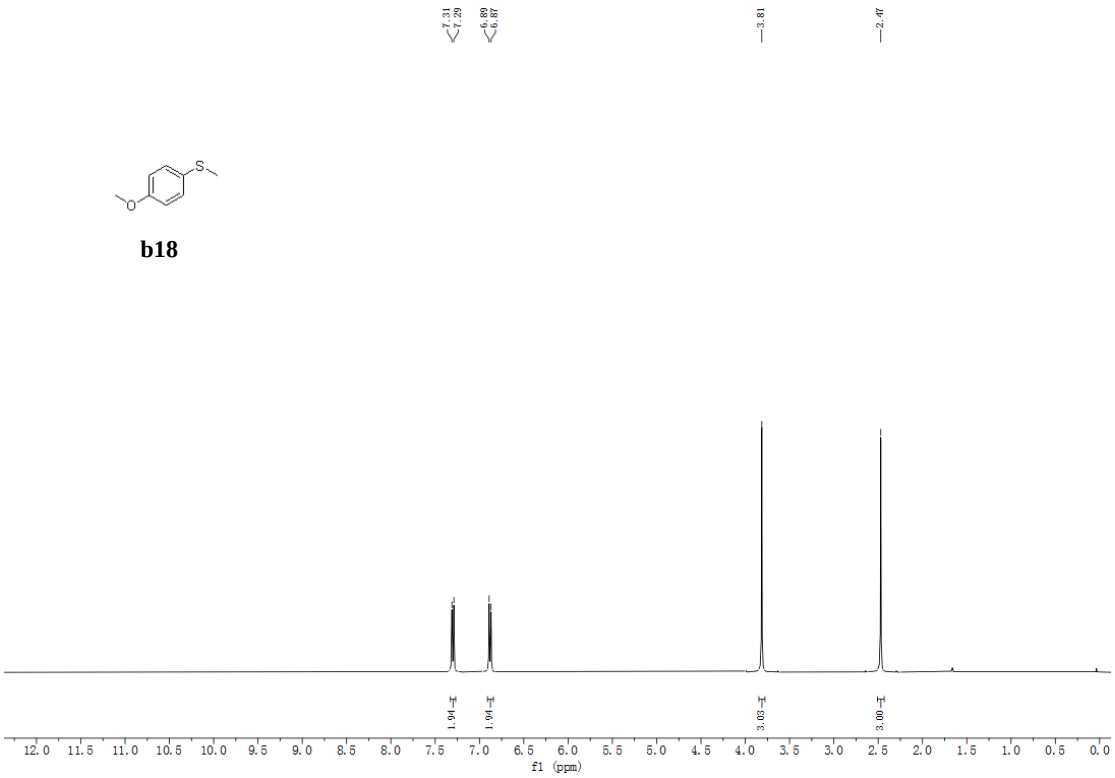
b16


7.18
7.16
7.10
7.08
2.45
2.30
1.99
1.98
3.03
3.00
f1 (ppm)

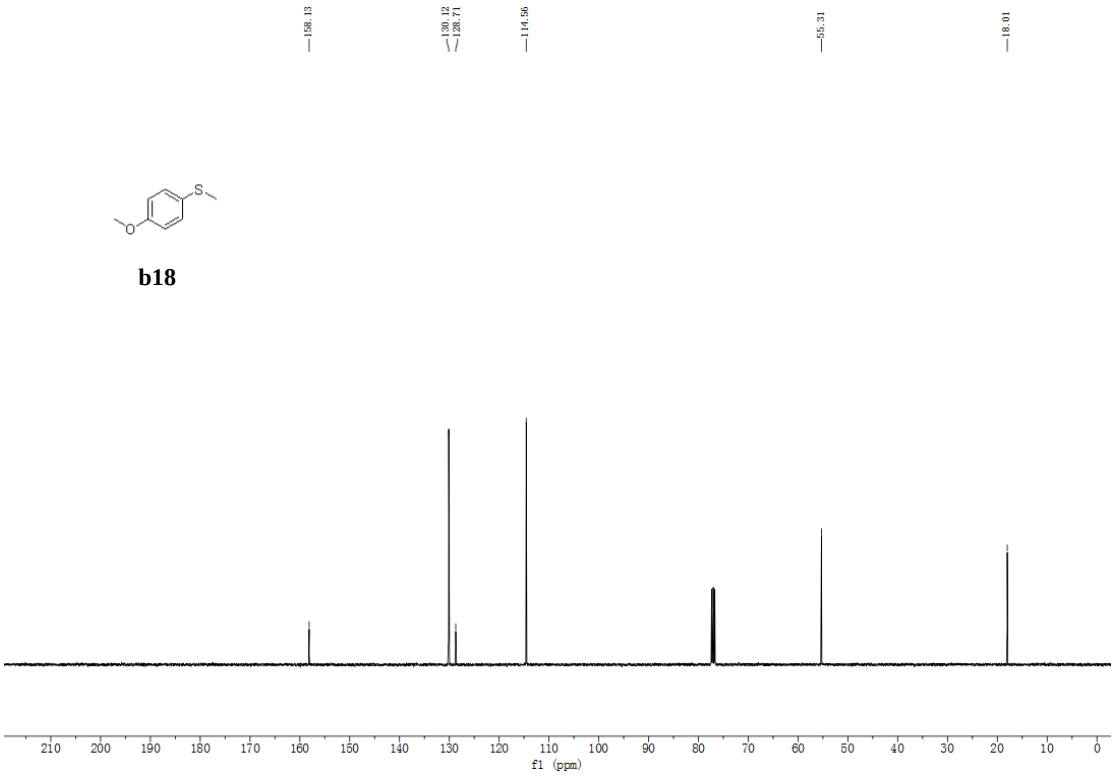
b17


135.07
134.75
129.66
127.28
20.98
16.54
f1 (ppm)

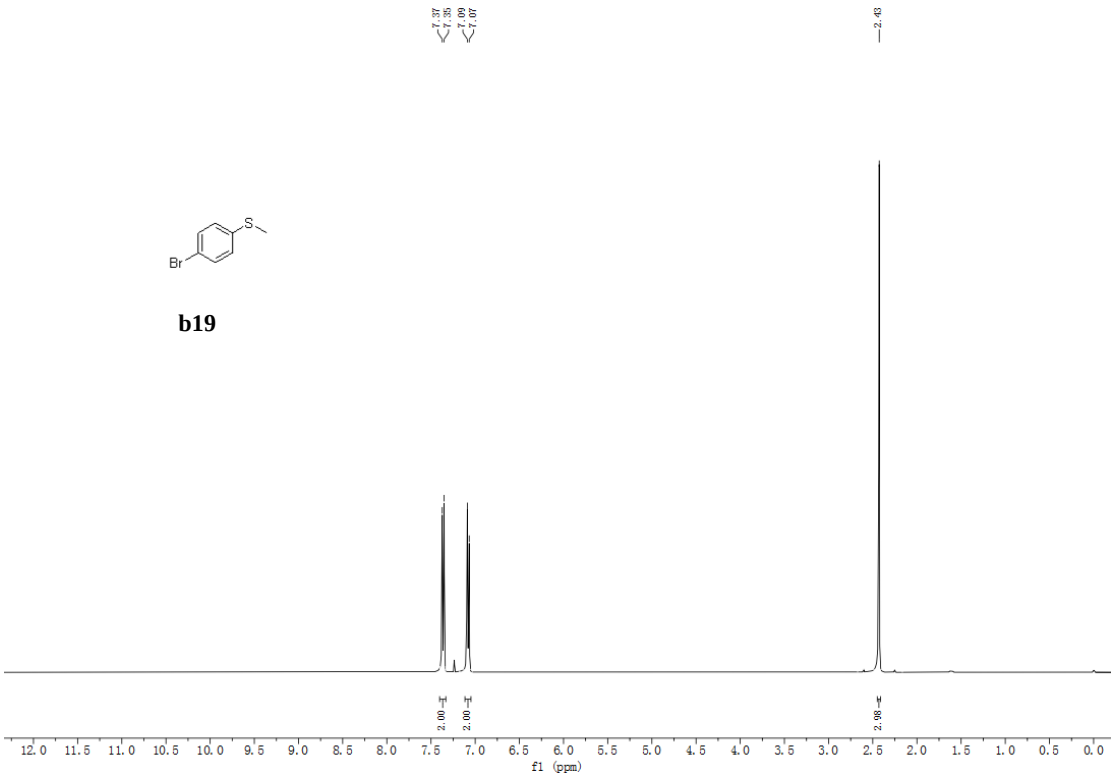
b17


7.31
7.29
6.89
6.87
3.81
2.47
1.94
1.94
3.03
3.00
f1 (ppm)

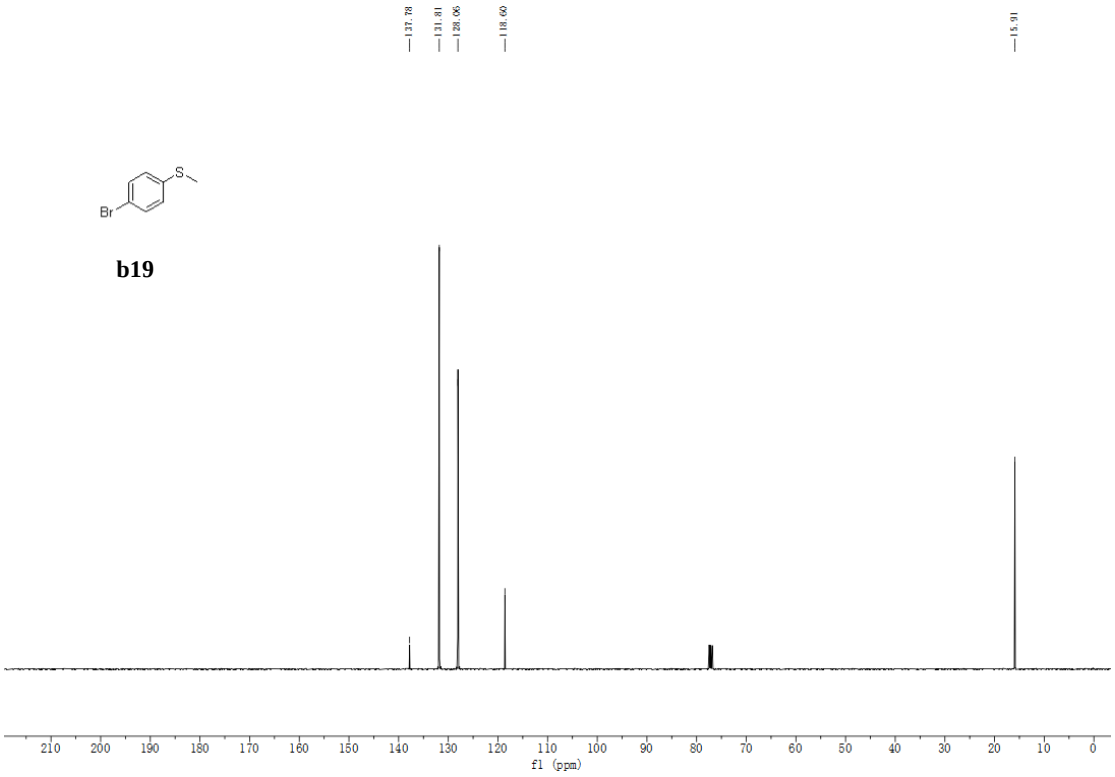
b18


158.13
130.12
128.71
114.56
55.31
18.01
f1 (ppm)

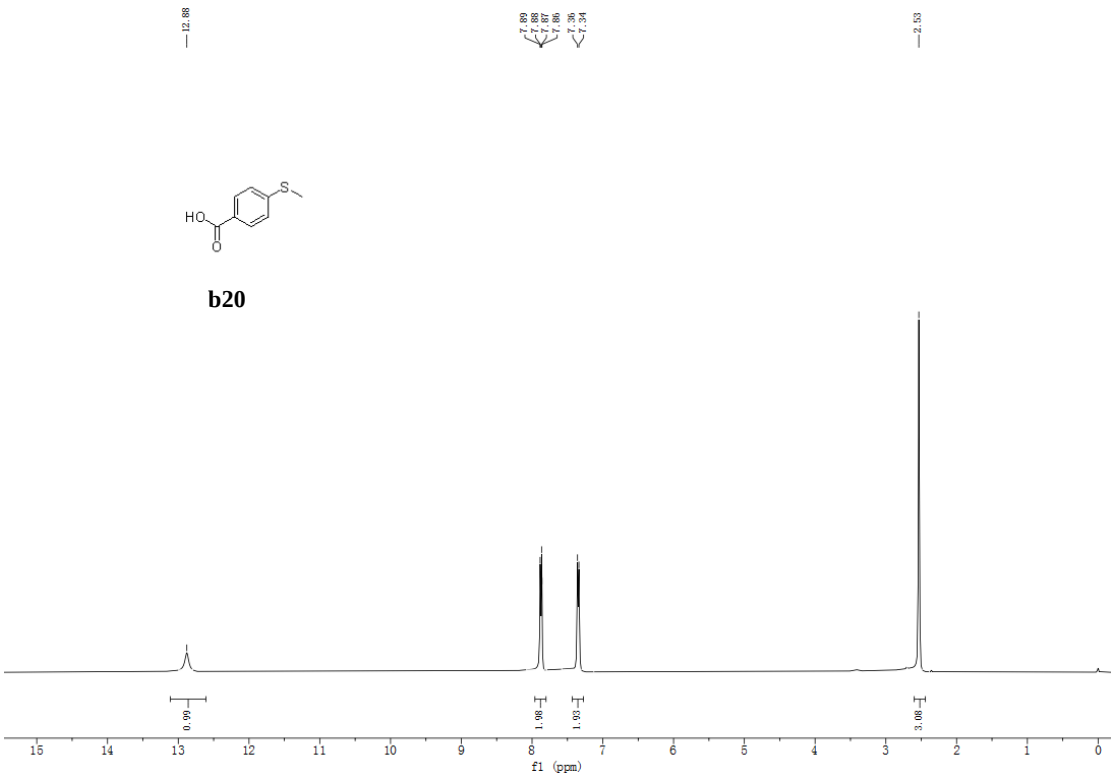
b18


7.37
7.35
7.09
7.07
2.43
Br
S
2.00
2.00
2.98
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
f1 (ppm)

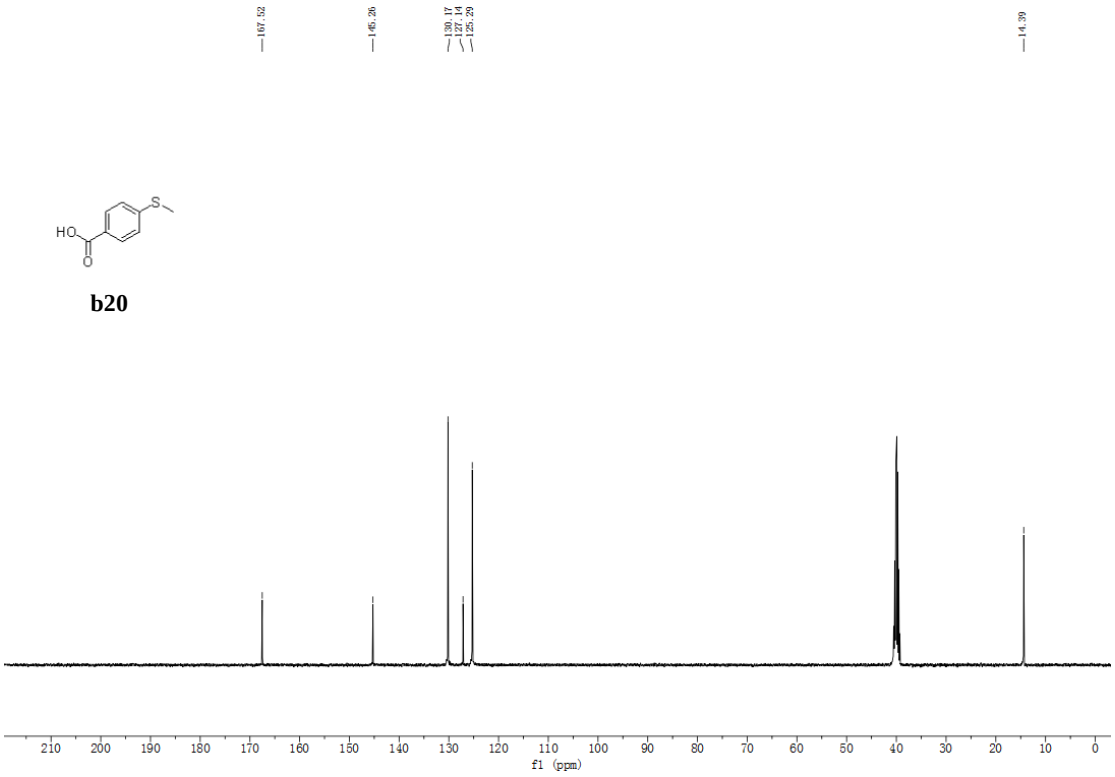
b19


137.78
131.81
128.06
118.60
15.91
Br
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

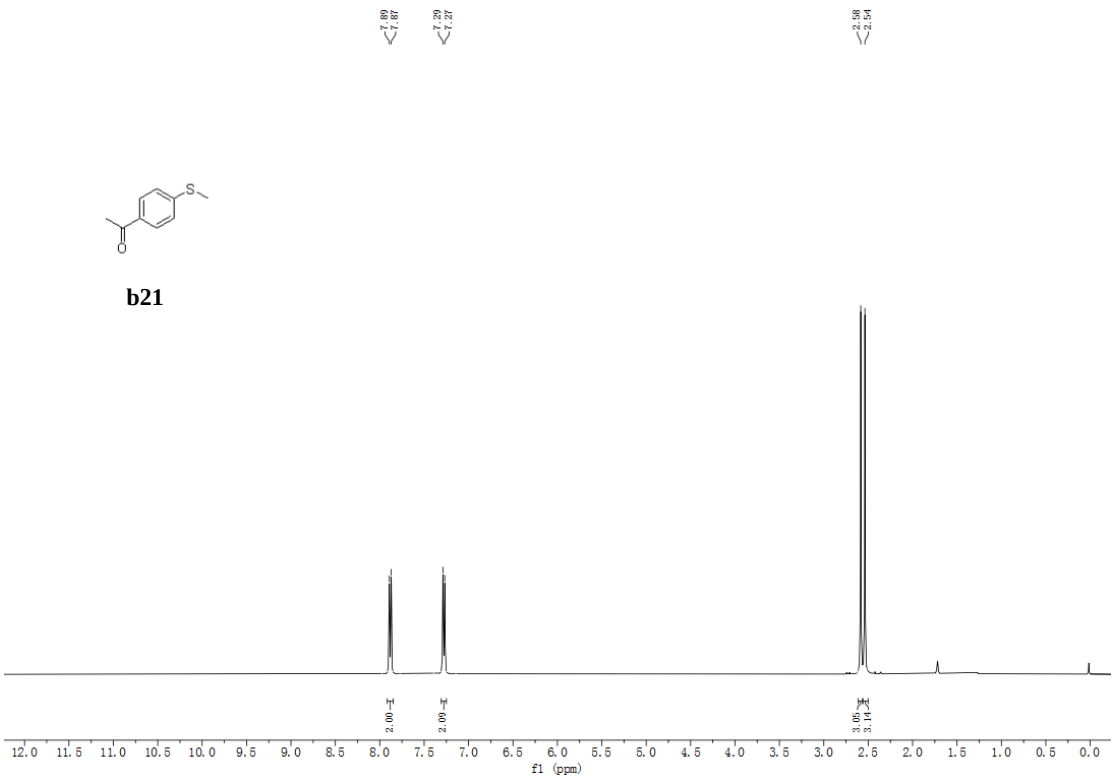
b19


12.88
7.89
7.88
7.87
7.86
7.35
7.34
2.53
HO
O
S
0.99
1.98
1.93
3.08
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

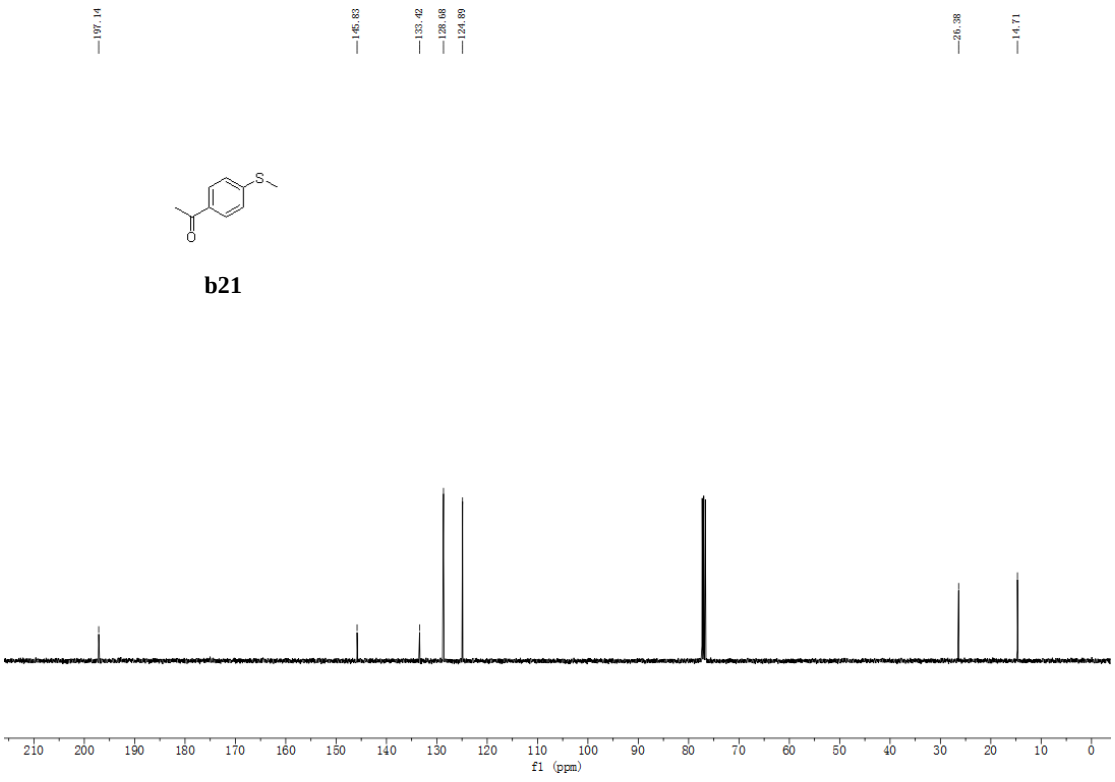
b20


167.52
145.26
130.17
127.14
125.29
14.39
HO
O
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

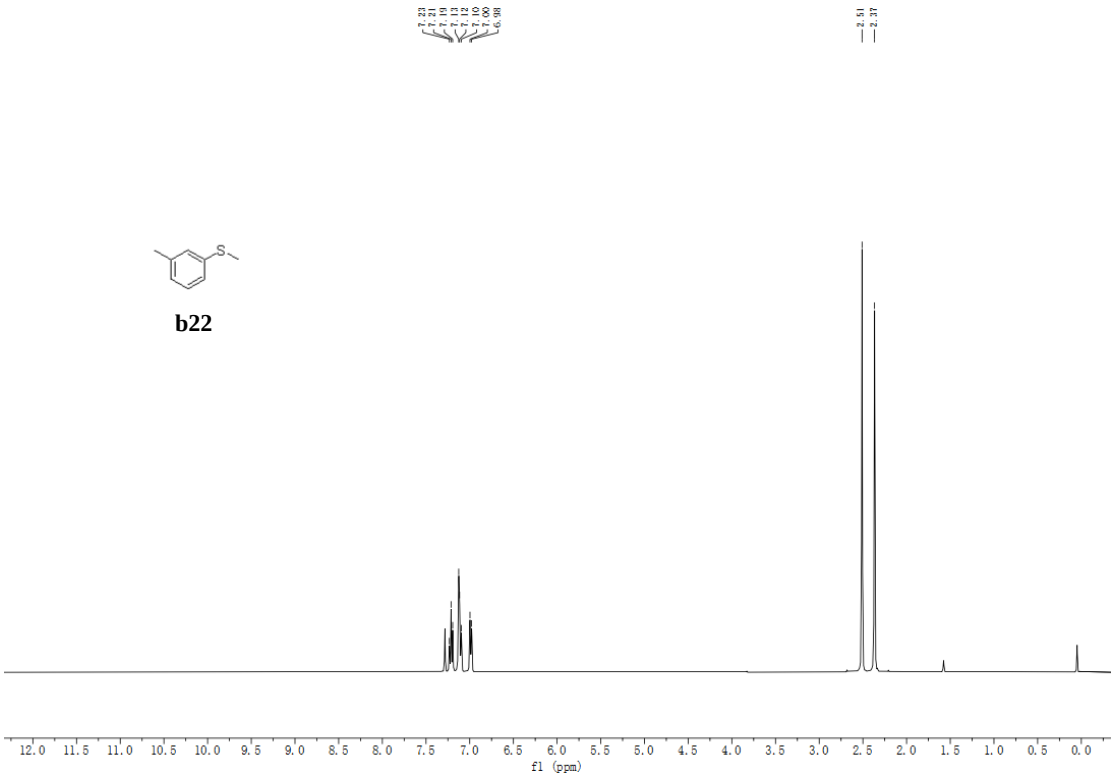
b20

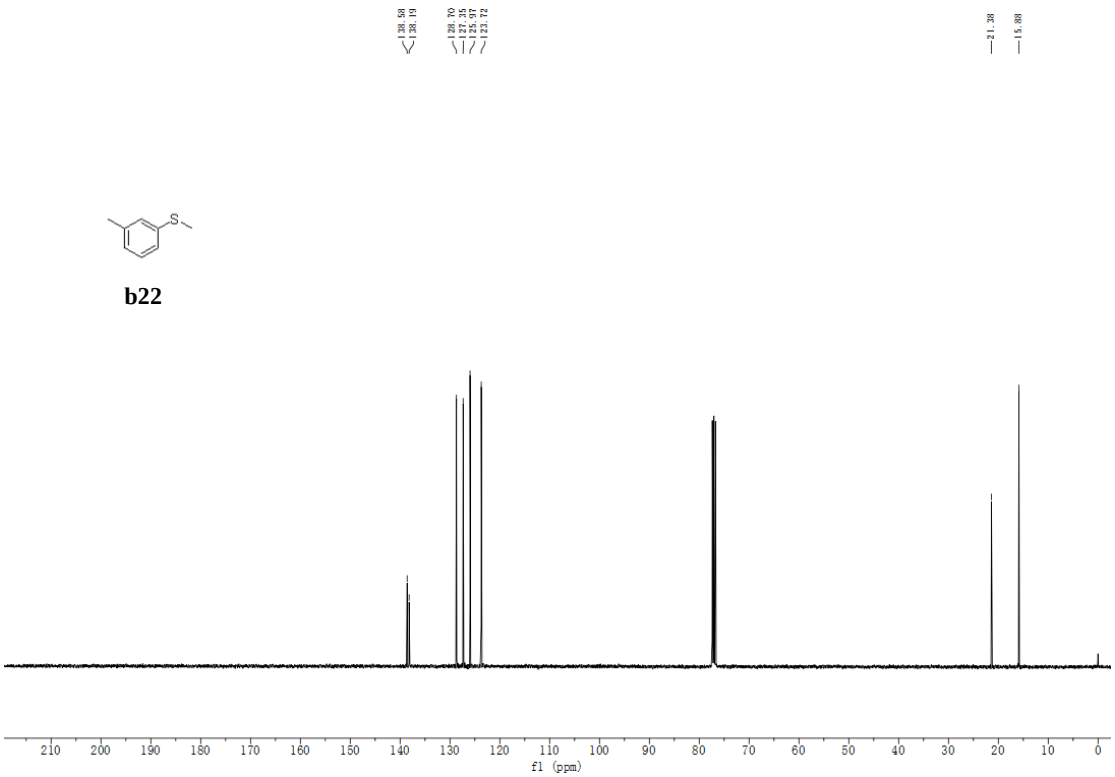

7.89
7.87
7.29
7.27
2.58
2.54
2.00
2.09
3.05
3.14
f1 (ppm)

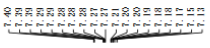
b21

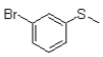

197.14
145.83
133.42
128.68
124.89
26.38
14.71
f1 (ppm)

b21

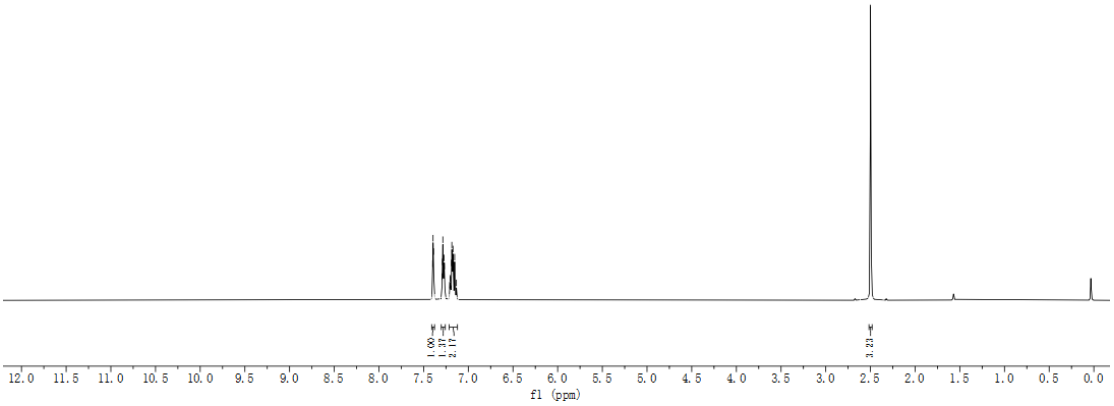

7.23
7.21
7.19
7.13
7.12
7.10
7.00
6.98
2.51
2.37
S
b22
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

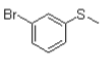

138.58
138.19
129.70
127.35
125.97
123.72
21.38
15.88
S
b22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



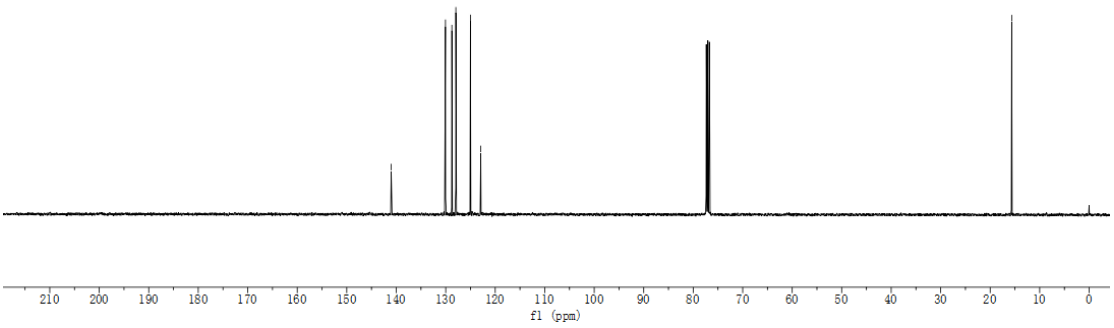


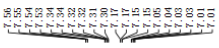
b23


1.00
1.37
2.17
3.23
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
f1 (ppm)



b23


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

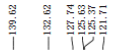

7.56
7.55
7.54
7.53
7.34
7.34
7.32
7.32
7.31
7.30
7.17
7.17
7.15
7.15
7.05
7.04
7.03
7.03
7.01
7.01

2.50


Br
S

b24

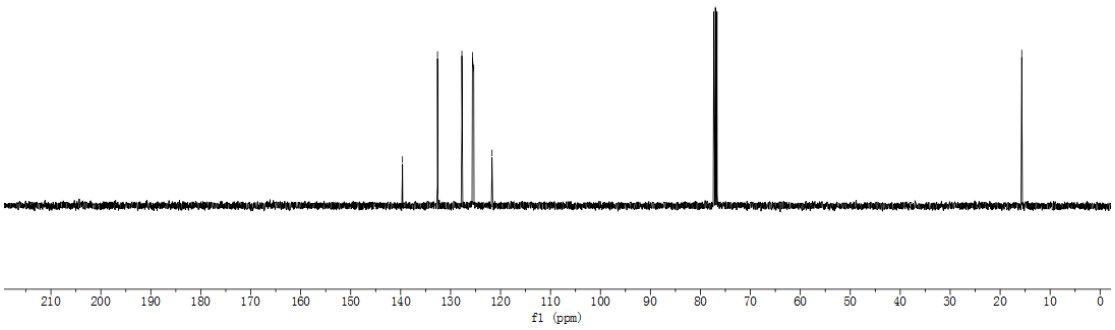
1.00
1.03
1.02
1.01
3.15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

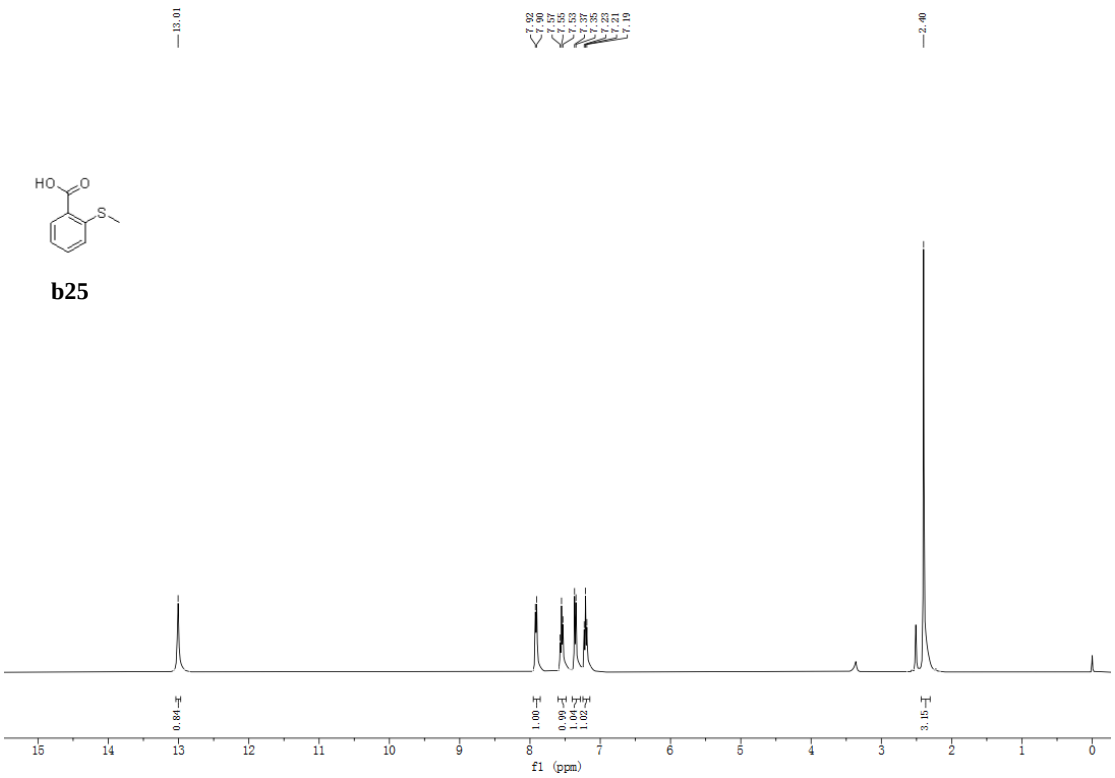

139.62
132.62
127.74
125.63
125.37
121.71

15.68

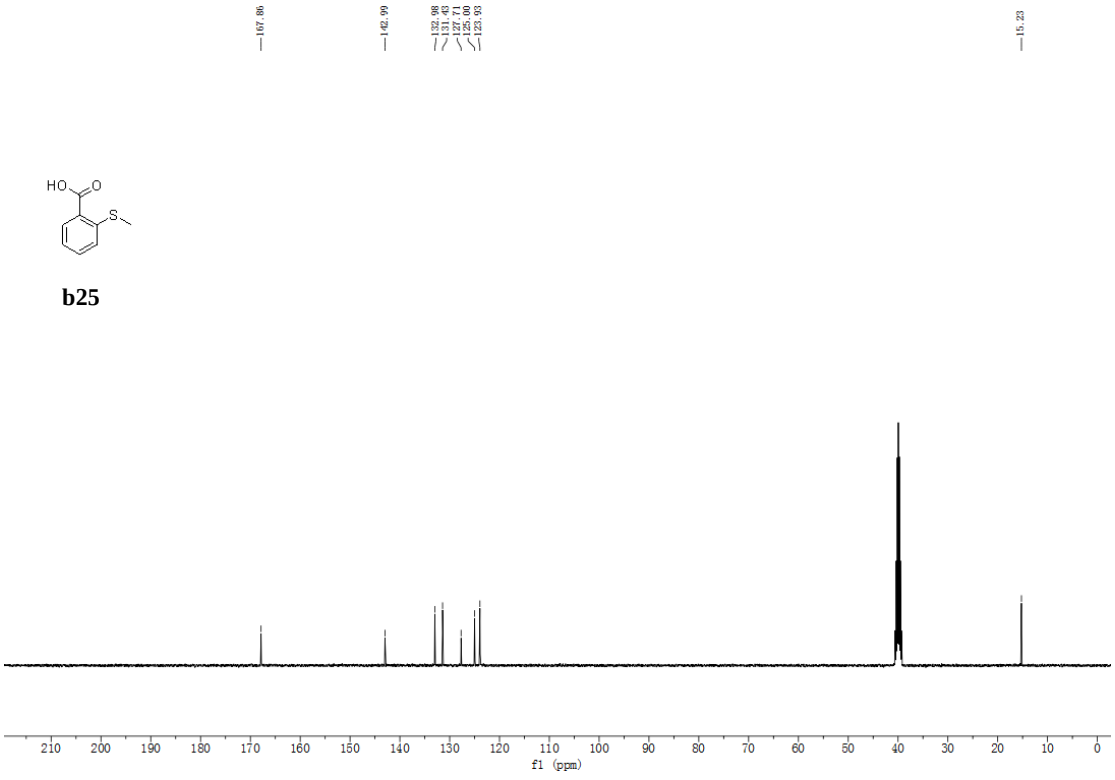

Br
S

b24

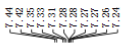

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

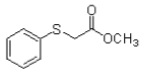

13.01
7.92
7.90
7.57
7.55
7.53
7.37
7.35
7.23
7.21
7.19
2.40
HO
O
S
0.84
1.00
0.99
1.04
1.02
3.15
f1 (ppm)

b25

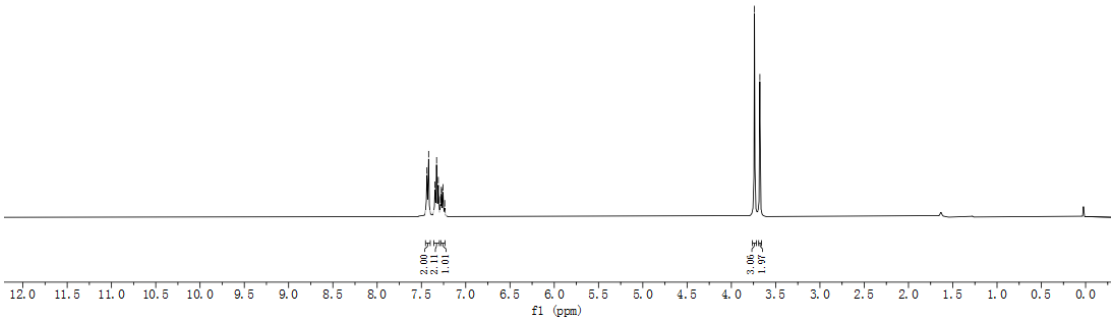

167.86
142.99
132.98
131.43
127.71
125.90
123.93
15.23
HO
O
S
f1 (ppm)

b25

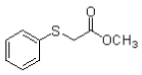

7.44
7.42
7.35
7.33
7.31
7.28
7.27
7.27
7.26
7.24
3.74
3.68


S
O
OCH3

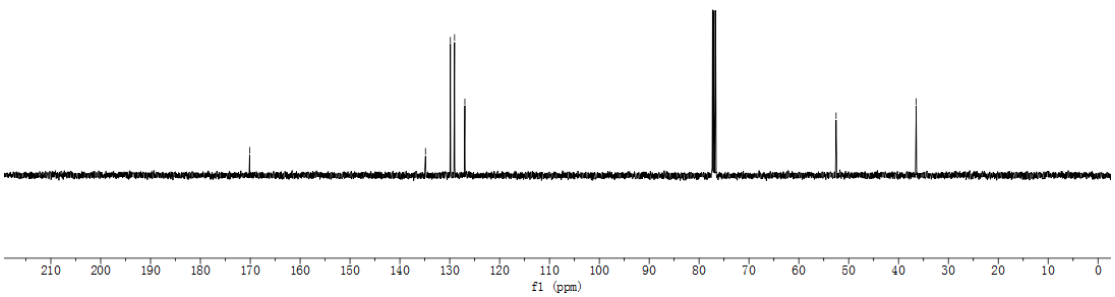
b26

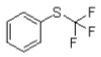

2.00
2.11
1.01
3.06
1.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.13
134.87
129.87
129.04
126.97
52.53
36.46

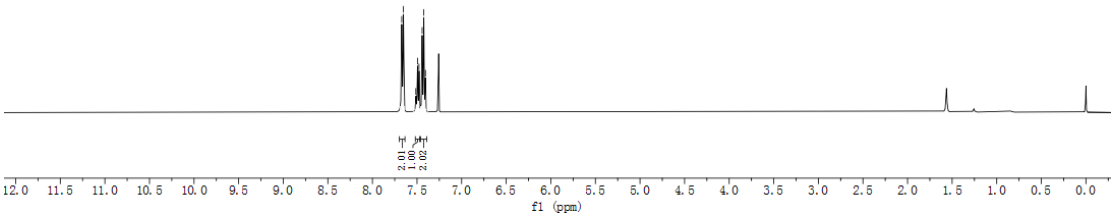

S
O
OCH3

b26

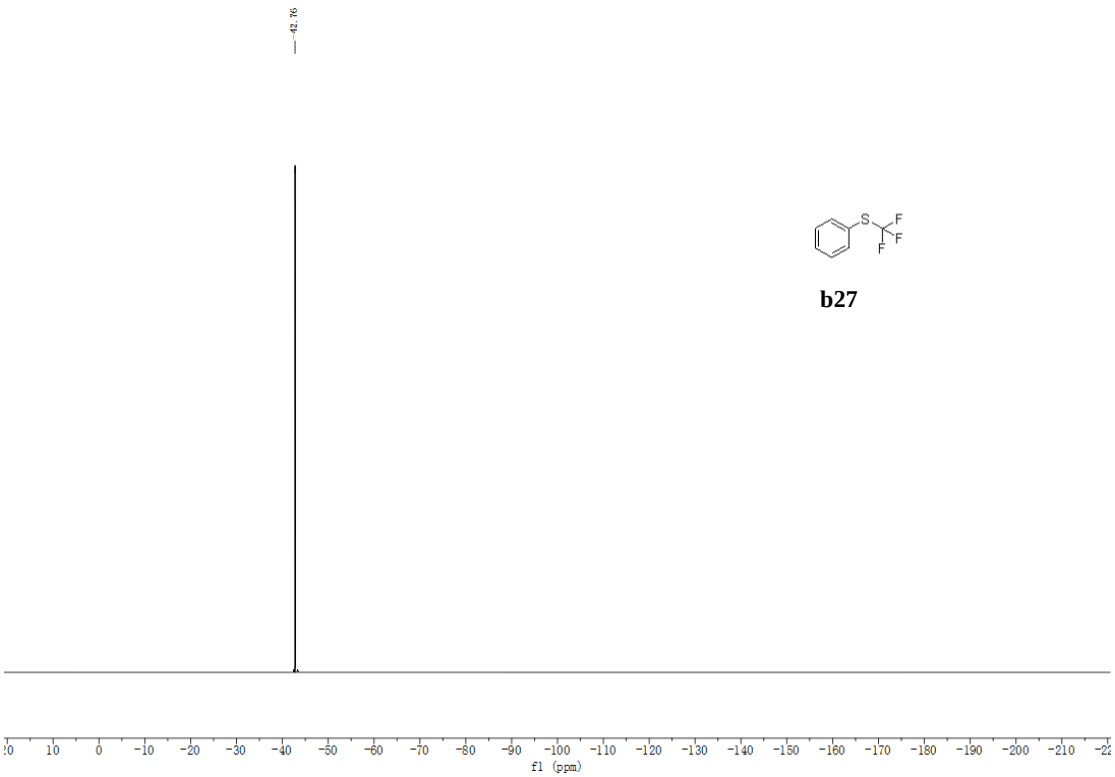

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



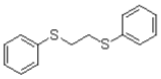
b27



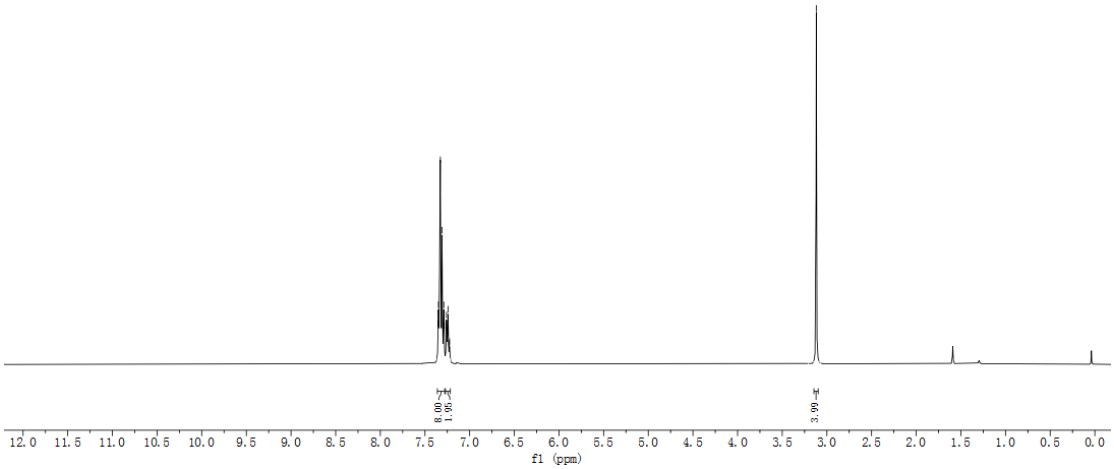
b27

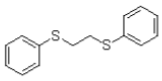

-42.76
S
F
F
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

b27



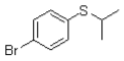
b28


7.35
7.35
7.33
7.33
7.31
7.29
7.28
7.26
7.26
7.25
7.25
7.24
7.23
7.23
7.22
3.12
8.00
1.90
3.99
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
f1 (ppm)

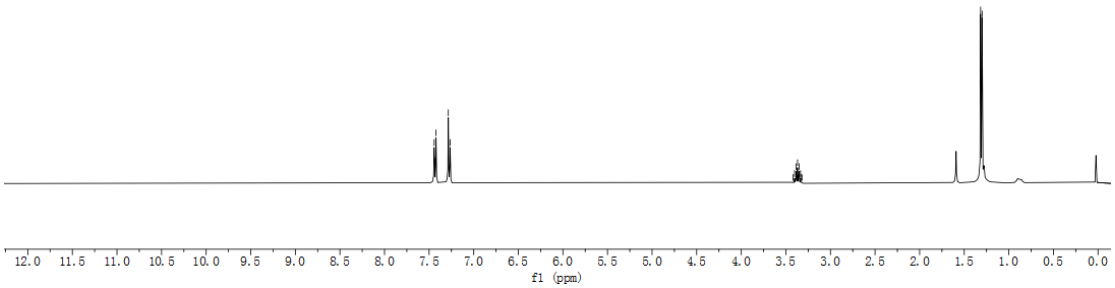


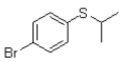
b28

134.98
130.00
129.01
126.54
33.33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

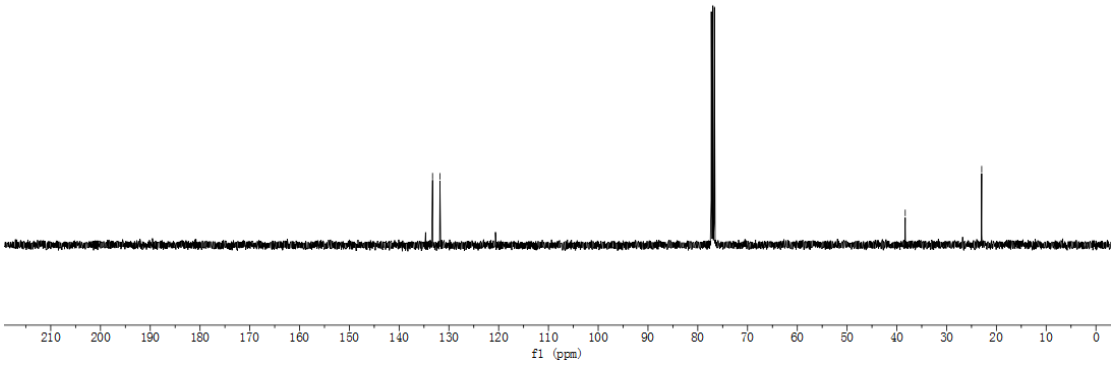


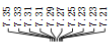
b29

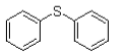




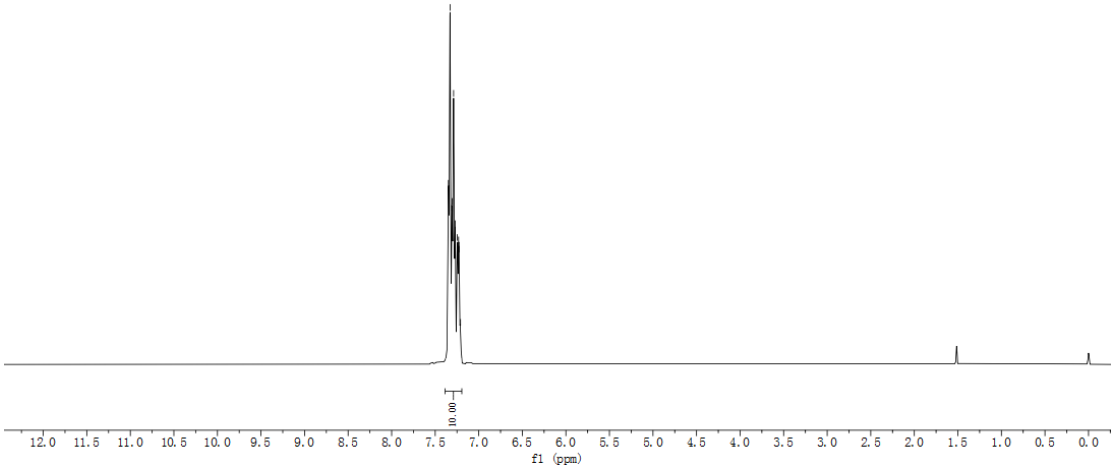
b29



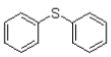

7.35
7.33
7.31
7.31
7.30
7.27
7.25
7.23
7.23
7.21



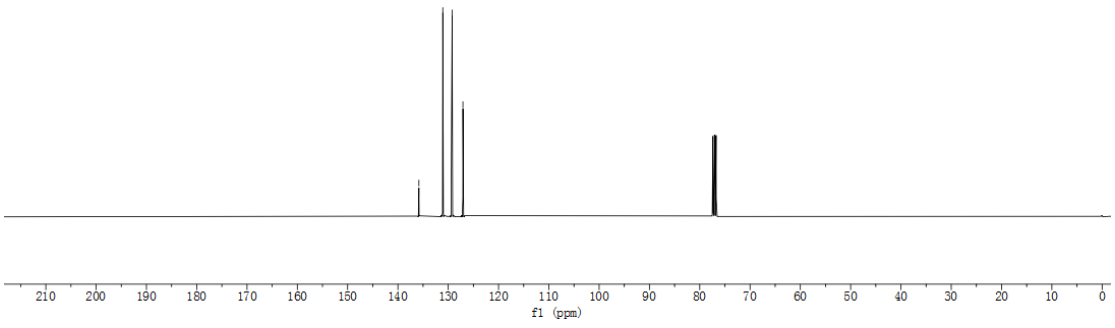
b30

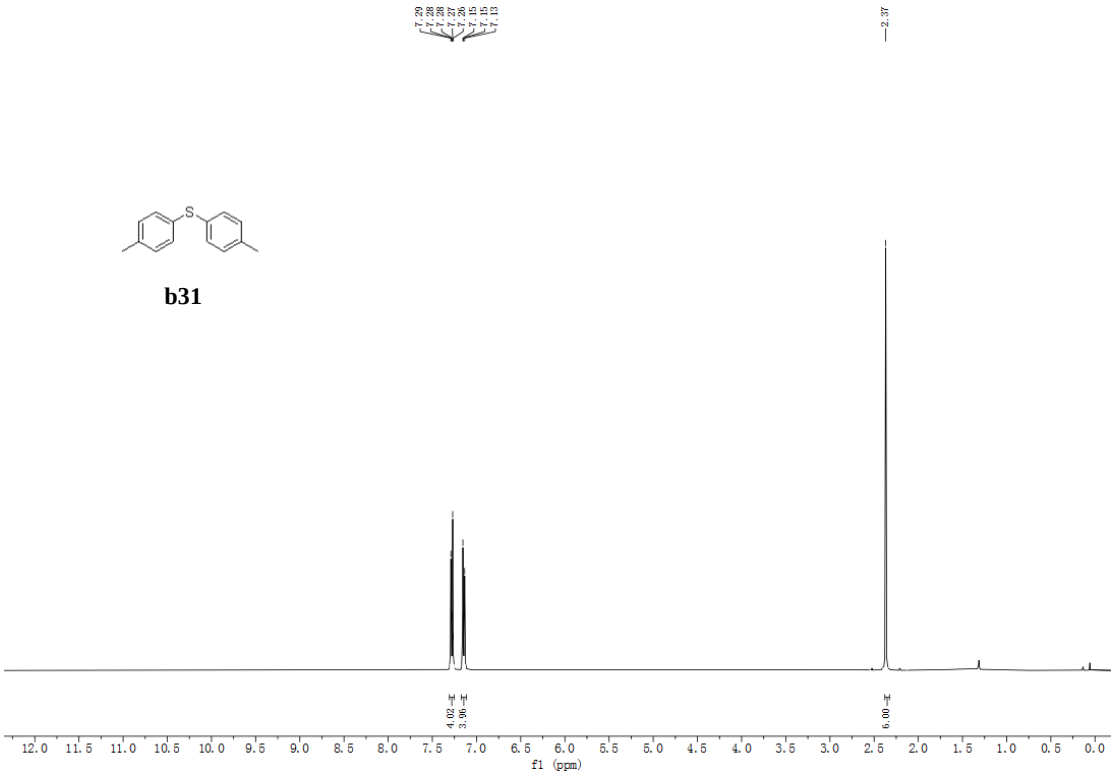

10.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


135.83
131.08
129.23
127.68

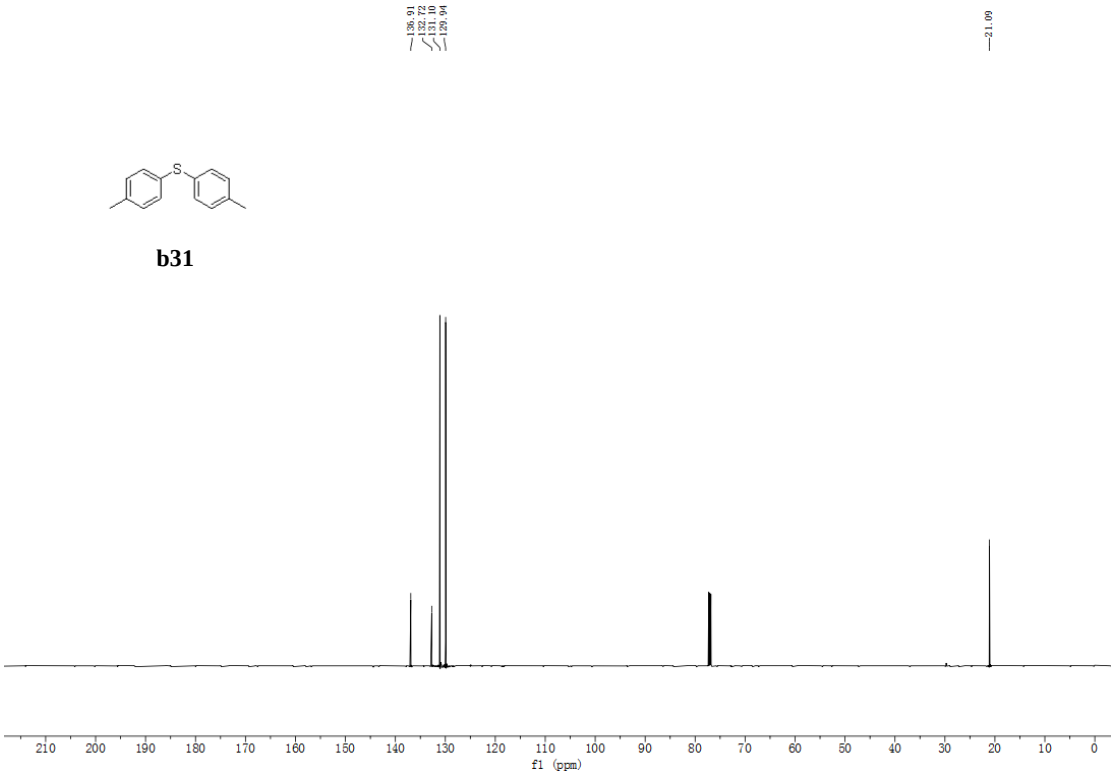


b30

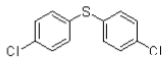

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.29
7.28
7.27
7.26
7.15
7.15
7.13
2.37
4.02
3.96
6.00
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
f1 (ppm)

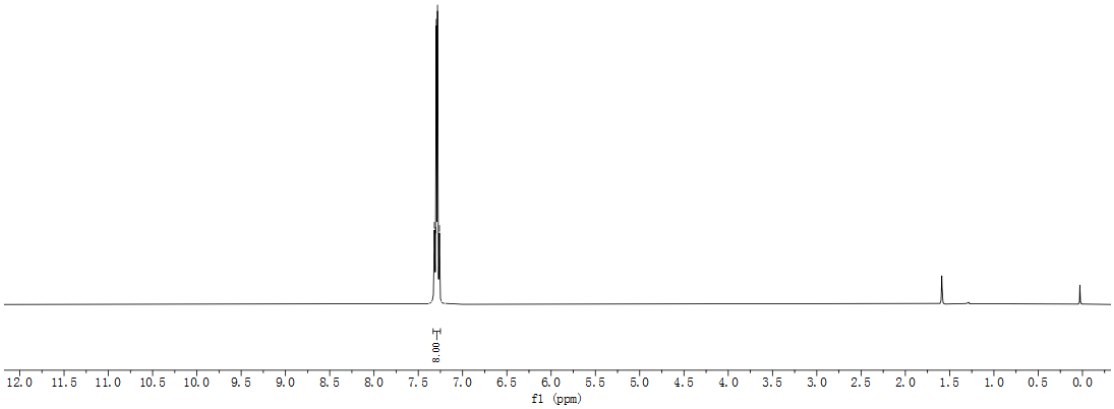
b31

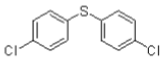

136.91
132.72
131.10
129.94
21.09
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

b31

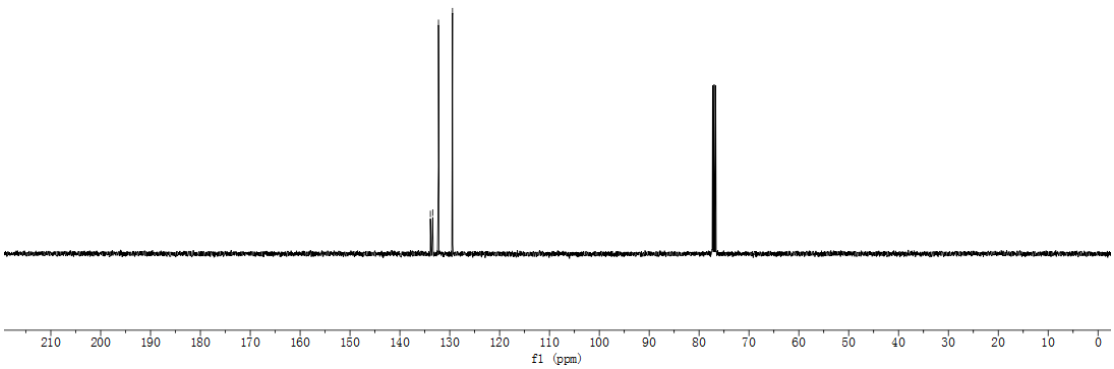


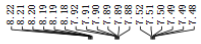
b32

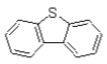




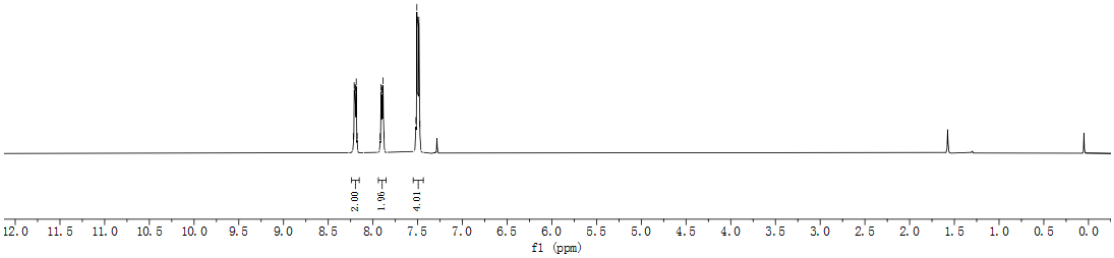
b32

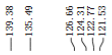


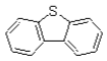

8.22
8.21
8.20
8.19
8.19
8.18
7.92
7.91
7.90
7.89
7.89
7.88
7.52
7.51
7.50
7.49
7.49
7.48



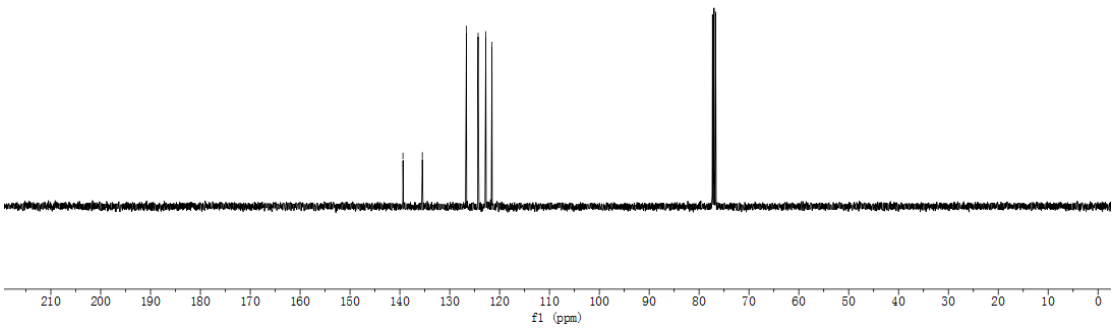
b33

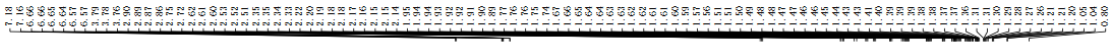

2.00
1.96
4.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

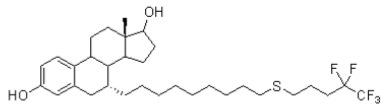

139.38
135.49
126.66
124.31
122.77
121.53

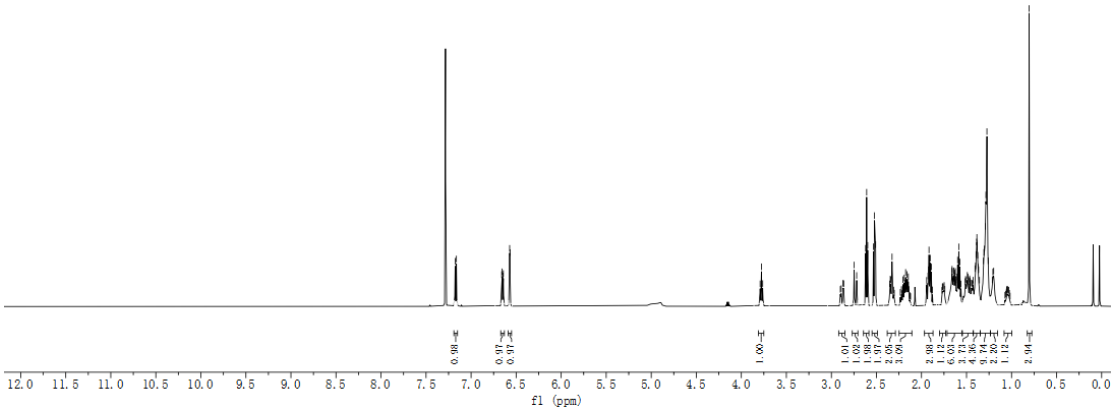


b33

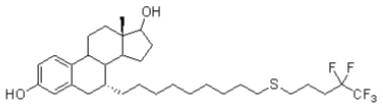

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

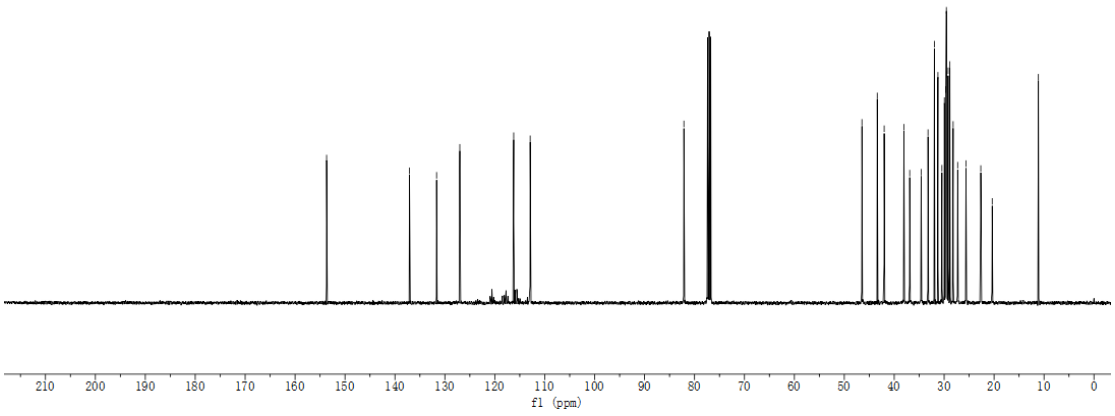


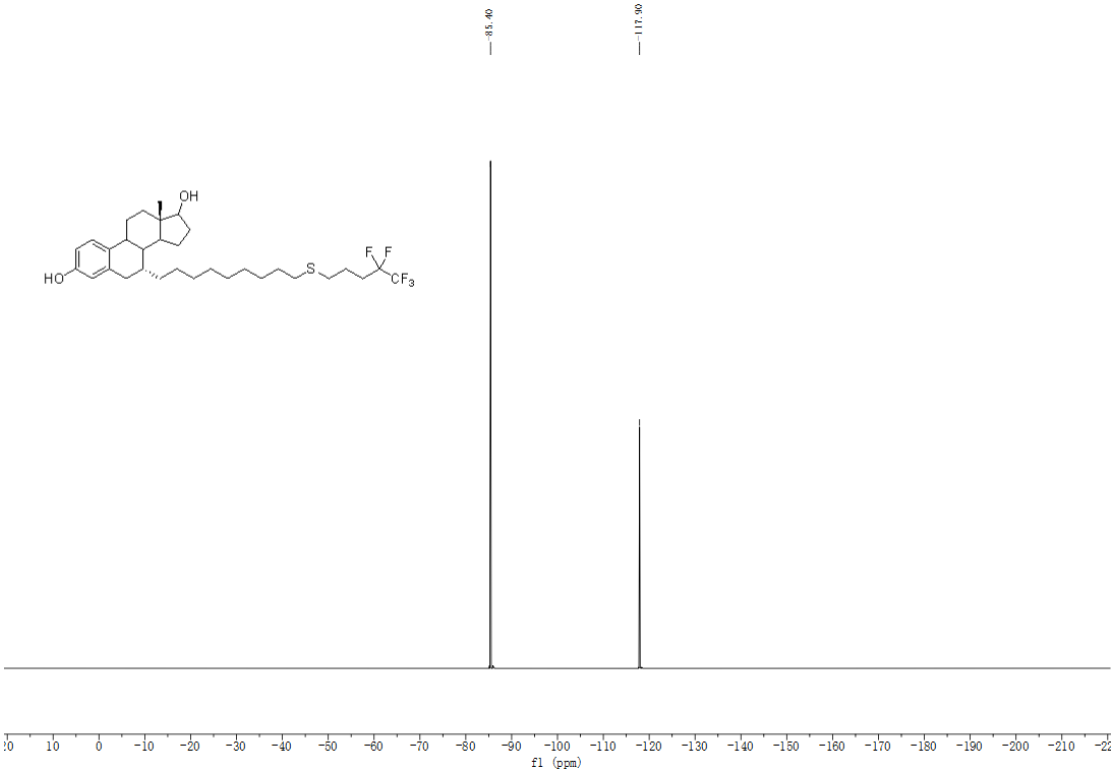

OH
HO
S
F
F
CF3

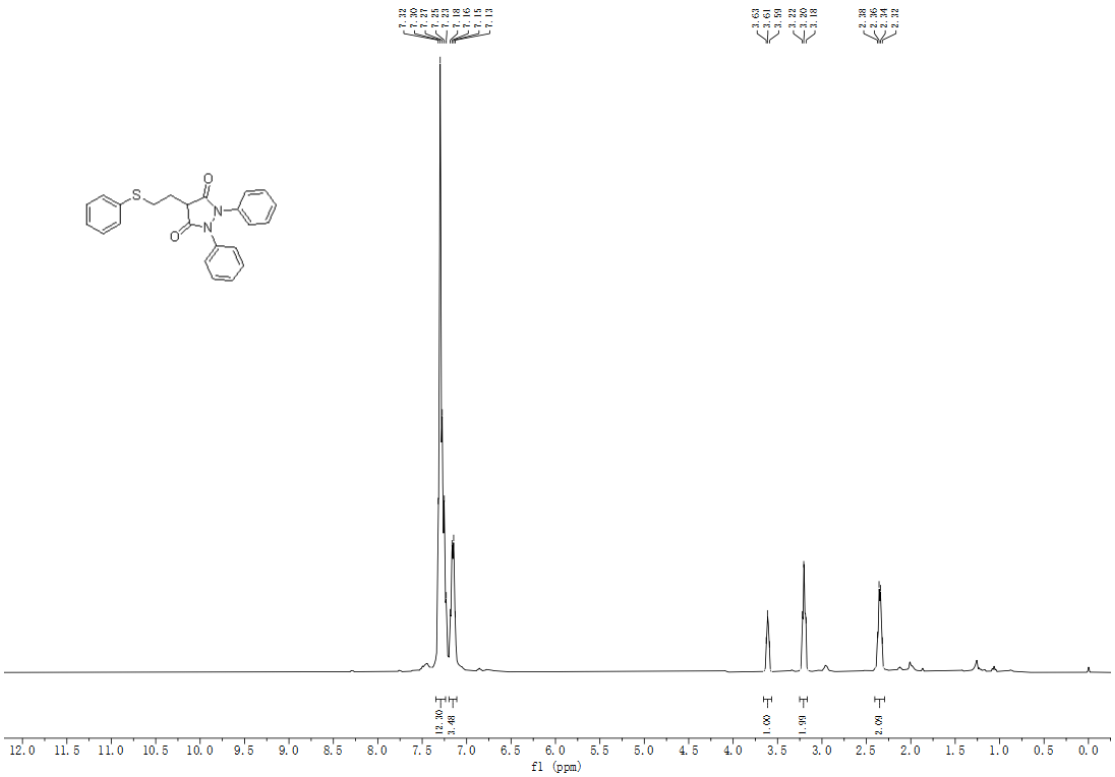

0.98
0.97
0.97
1.00
1.01
1.02
1.98
1.97
2.05
3.09
2.98
6.02
3.73
4.36
9.24
2.04
1.12
2.94
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

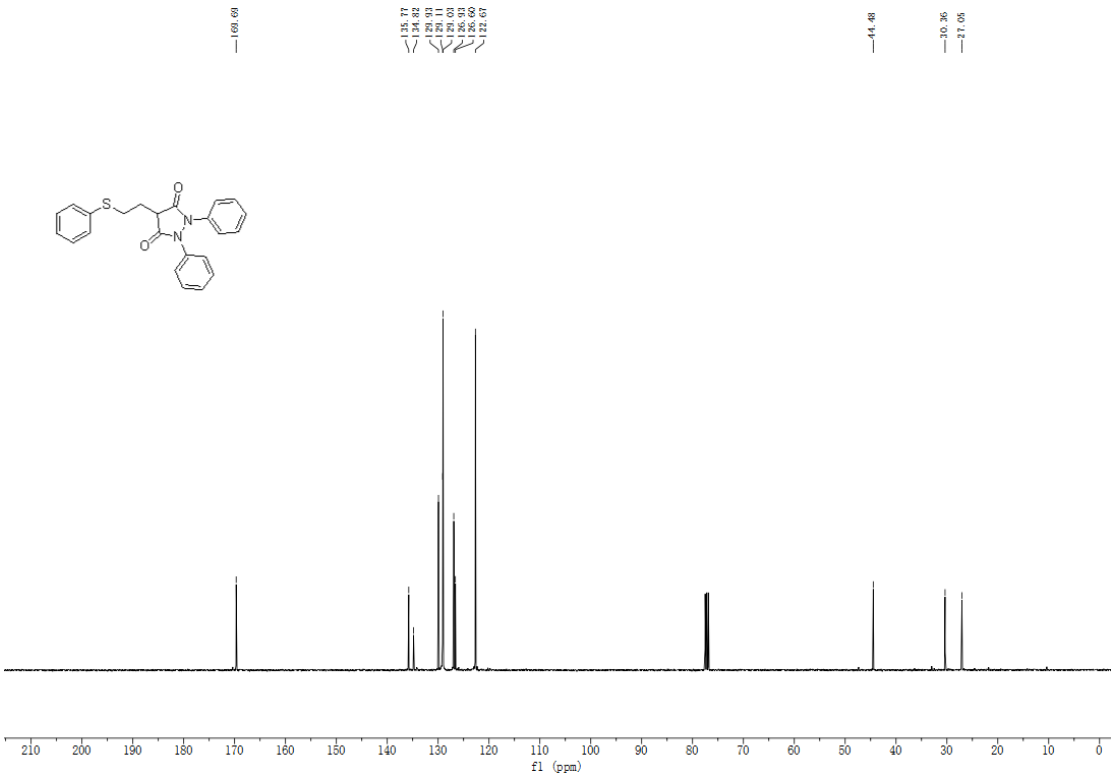

153.69
137.09
131.66
127.01
116.32
112.92
82.13
46.47
43.40
42.01
38.06
36.09
34.61
33.23
31.96
31.15
30.45
29.96
29.68
29.55
29.38
29.21
28.86
28.30
27.72
25.63
22.66
20.37
11.13


OH
HO
S
F
F
CF3


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


-85.40
-117.90
OH
HO
F F
S
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.32
7.30
7.27
7.25
7.21
7.18
7.16
7.15
7.13
7.11
3.63
3.61
3.59
2.22
2.20
2.18
2.38
2.36
2.34
2.32
12.30
3.46
1.00
1.99
2.09
f1 (ppm)


169.69
135.77
134.82
129.93
129.11
128.03
126.93
126.60
122.67
44.48
30.36
27.05
f1 (ppm)