Electronic Supplementary Information

Metal-free and site-selective α-C(sp³)–H oxidation of thioethers to access thioester derivatives

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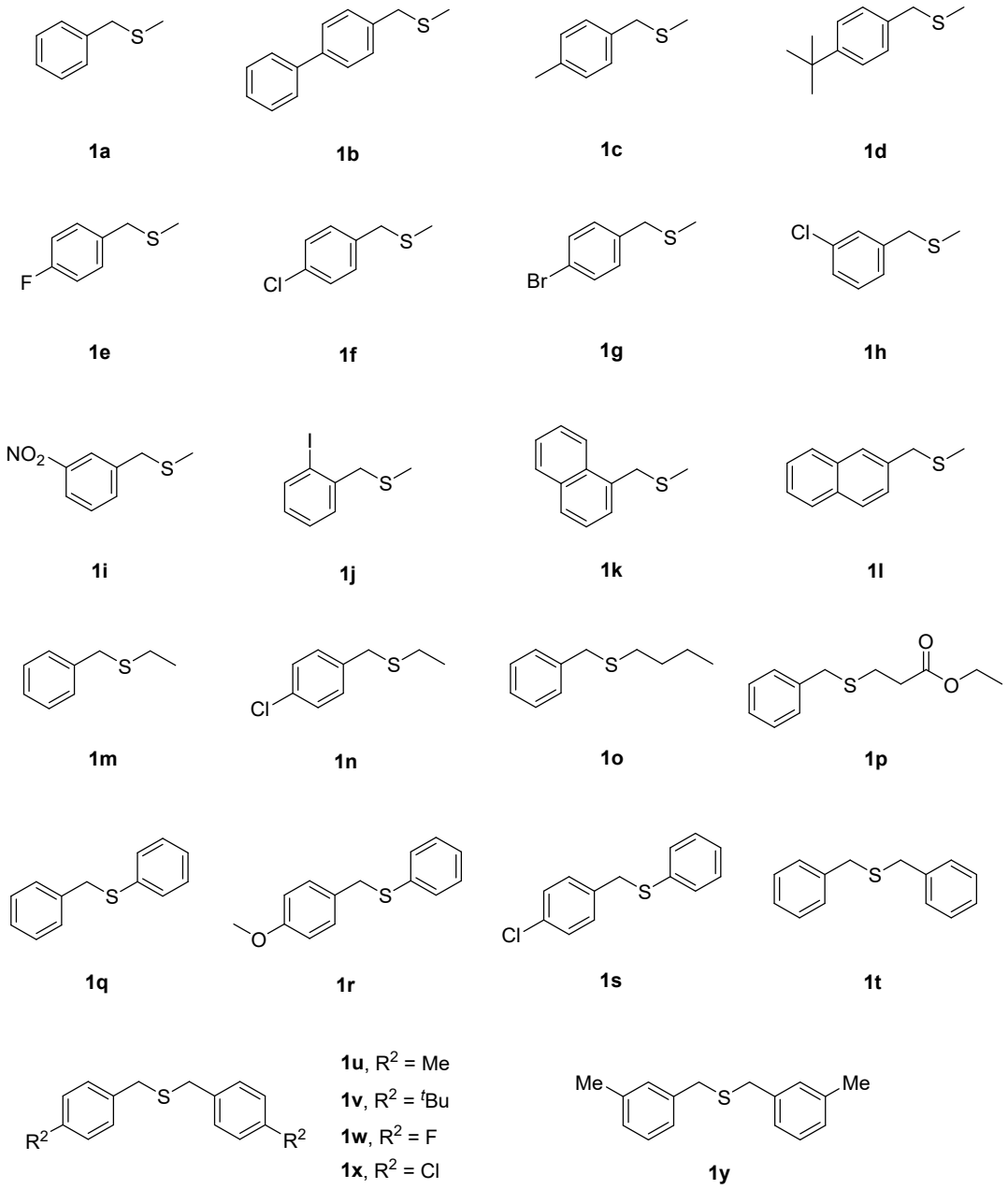
I. General Information

All the solvents and commercially available reagents were purchased and used directly. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light. Column chromatography was performed on EMD Silica Gel 60 (200–300 Mesh) using a forced flow of 0.5–1.0 bar. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE III–300 or 400 spectrometer. ^{1}H NMR data was reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data was reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). EI mass analysis was obtained using Shimadzu GCMS-QP2010plus. HRMS analysis was obtained using Agilent 6200 Accurate-Mass TOF LC/MS system with Electrospray Ionization (ESI). Melting points were measured by an X4-A microscopic melting point apparatus.

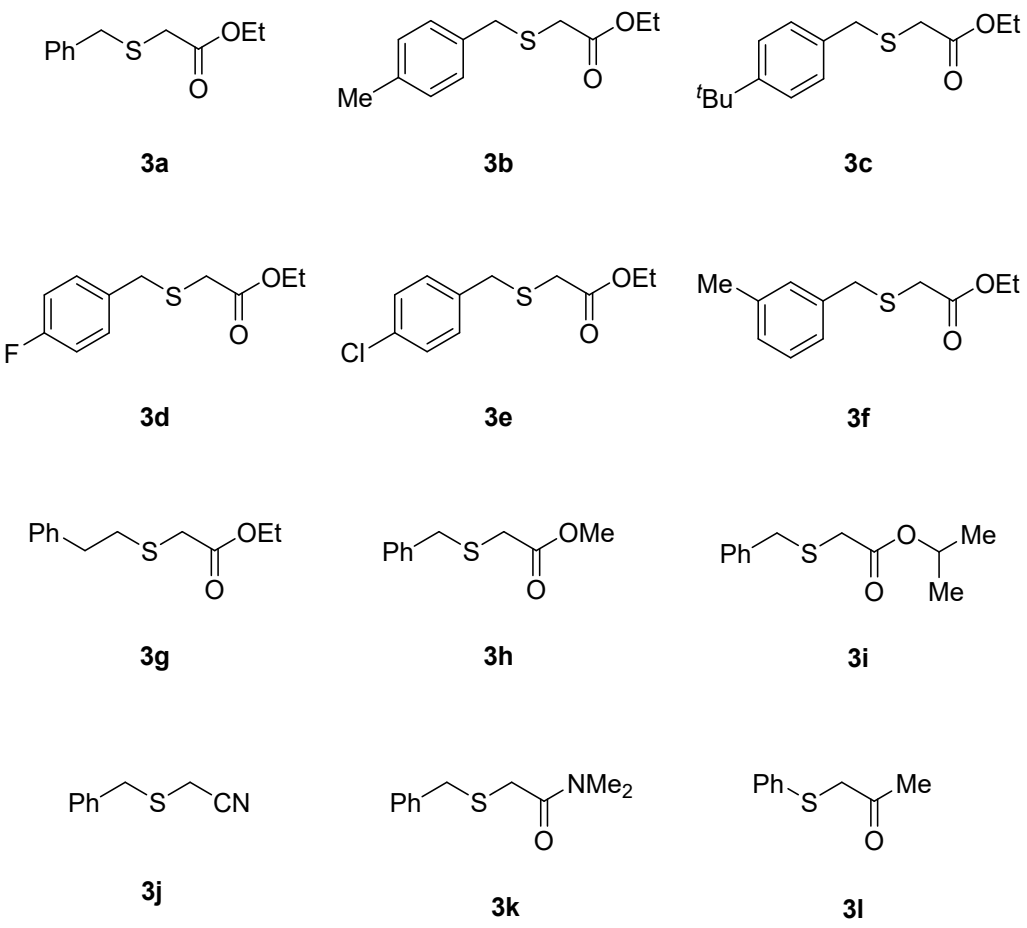
II. Experimental Section

1. Starting materials:



Scheme S1. Thioethers

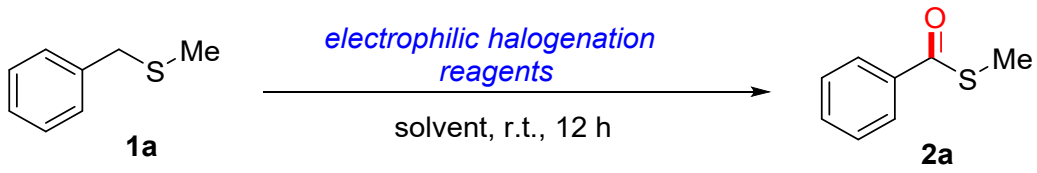
Thioethers (**1a-y**) were purchased from Energy-chemical, BLDpharm, Chemieliva, Chemhere, Adamas-beta®, TCI, J&K@ or Sigma-Aldrich.



Scheme S2. Thioether ester, nitrile, amide, and ketone derivatives

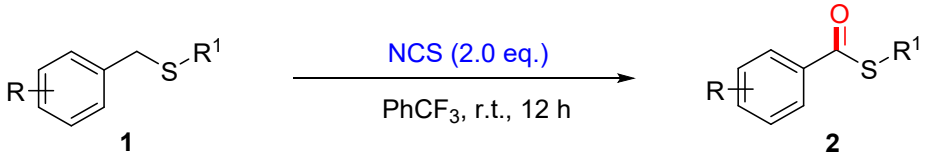
Thioether ester, nitrile, amide, and ketone derivatives (**3a-l**) were purchased from Chemieliva, Enamine, Adamas-beta®, TCI, J&K@ or Sigma-Aldrich.

2. Optimization of the reaction conditions for the product 2a

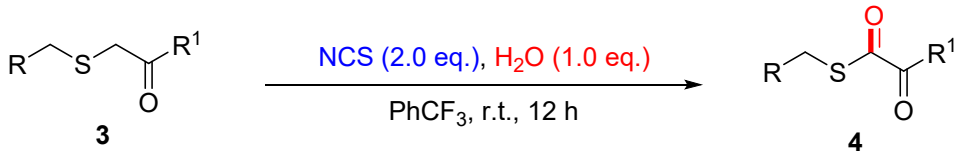


A 30 mL Schlenk tube was charged with benzyl methyl sulfide **1a** (0.2 mmol), solvent (2.0 mL) and electrophilic halogenation reagents (0.4 ~ 0.6 mmol). The tube was sealed and the reaction was then stirred vigorously at room temperature for 12 h. The reaction mixture was then concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to yield the desired product **2a**.

3. General procedure for the scope study

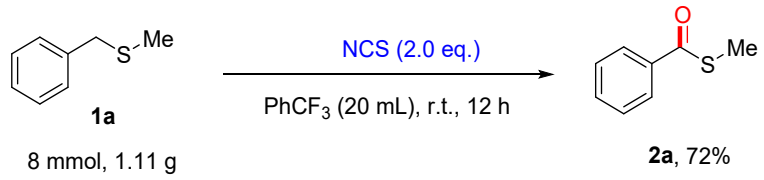


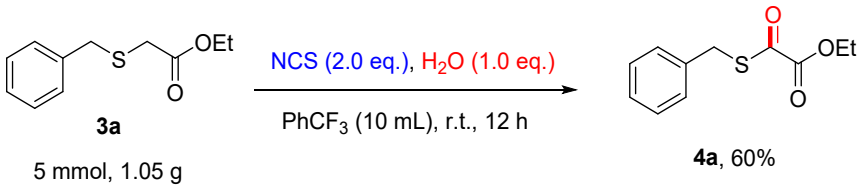
A 30 mL Schlenk tube was charged with thioesters **1** (0.2 mmol, 27.6 mg), $PhCF_3$ (2.0 mL) and NCS (0.4 mmol, 53.4 mg). The tube was sealed and the reaction was then stirred vigorously at room temperature for 12 h. The reaction mixture was then concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to yield the desired products **2**. *Caution! To prevent unpredictable variations in yields, the $PhCF_3$ used in this study was sourced from Adamas-beta®.*



A 30 mL Schlenk tube was charged with oxalate thioethers **3** (0.2 mmol), $PhCF_3$ (2.0 mL), NCS (0.4 mmol, 53.4 mg) and H_2O (0.2 mmol, 3.6 μL). The tube was sealed and the reaction was then stirred vigorously at room temperature for 12 h. The reaction mixture was then concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to yield the desired products **4**.

4. The gram-scale reaction

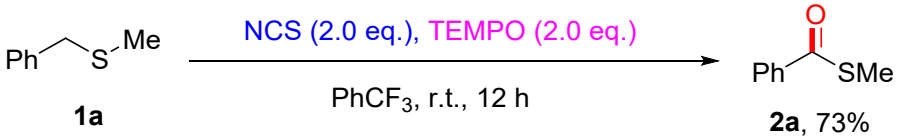




A 150 mL Schlenk tube was charged with benzyl methyl sulfide **1a** (8 mmol, 1.11 g), $PhCF_3$ (20.0 mL) and NCS (16 mmol, 2.14 g). The tube was sealed and the reaction was then stirred vigorously at room temperature for 12 h. After cooling to room temperature, the reaction mixture was then concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to yield the desired product **2a** (0.88 g, 72%).

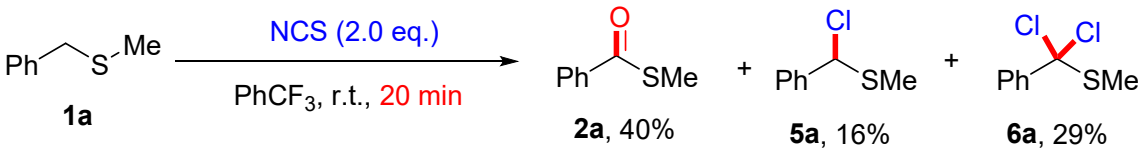
A 150 mL Schlenk tube was charged with ethyl 2-(benzylthio)acetate **3a** (5 mmol, 1.05 g), $PhCF_3$ (10.0 mL), NCS (16 mmol, 2.14 g) and H_2O (5 mmol, 90 μL). The tube was sealed and the reaction was then stirred vigorously at room temperature for 12 h. The reaction mixture was then concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to yield the desired product **4a** (0.67 g, 60%).

5. Mechanistic studies



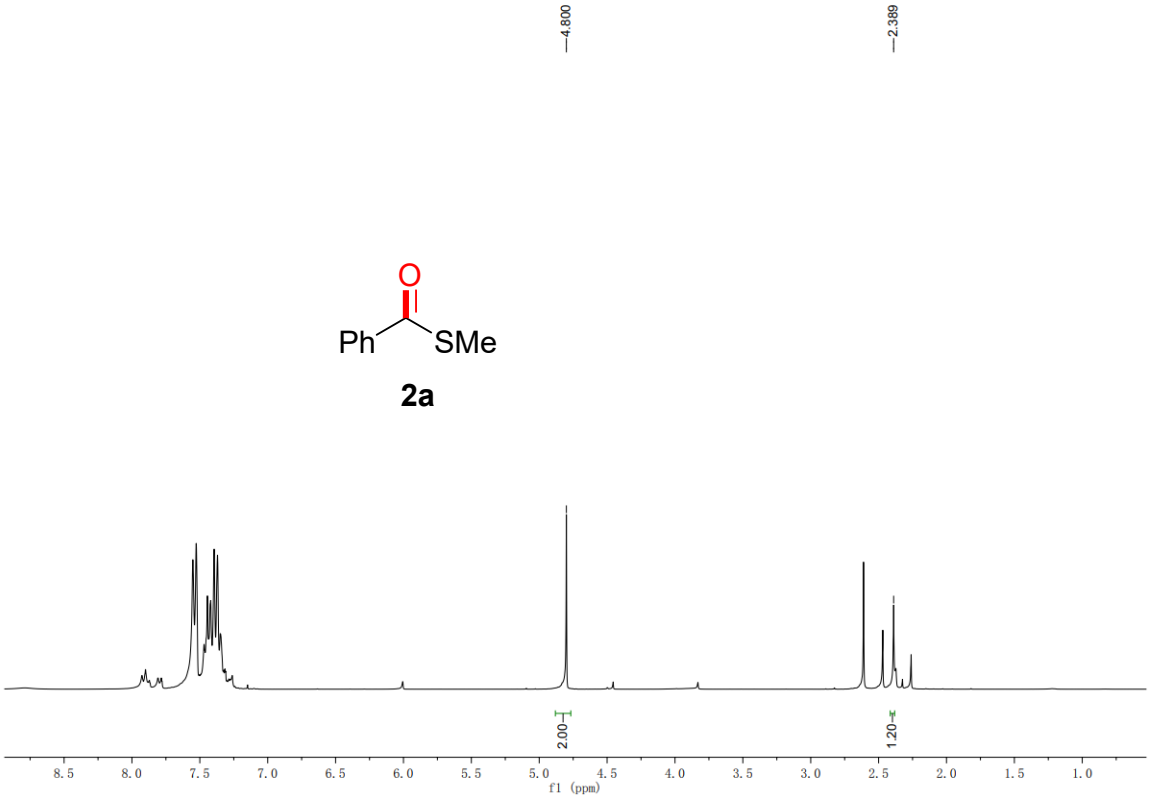
A 30 mL Schlenk tube was charged with benzyl methyl sulfide **1a** (0.2 mmol, 27.6 mg), $PhCF_3$ (2.0 mL), NCS (0.4 mmol, 53.4 mg) and TEMPO (0.4 mmol, 62.5 mg). The tube was sealed and the reaction was then stirred vigorously at room temperature for 12 h. After that, the reaction mixture was concentrated *in vacuo*. The residue was purified by flash

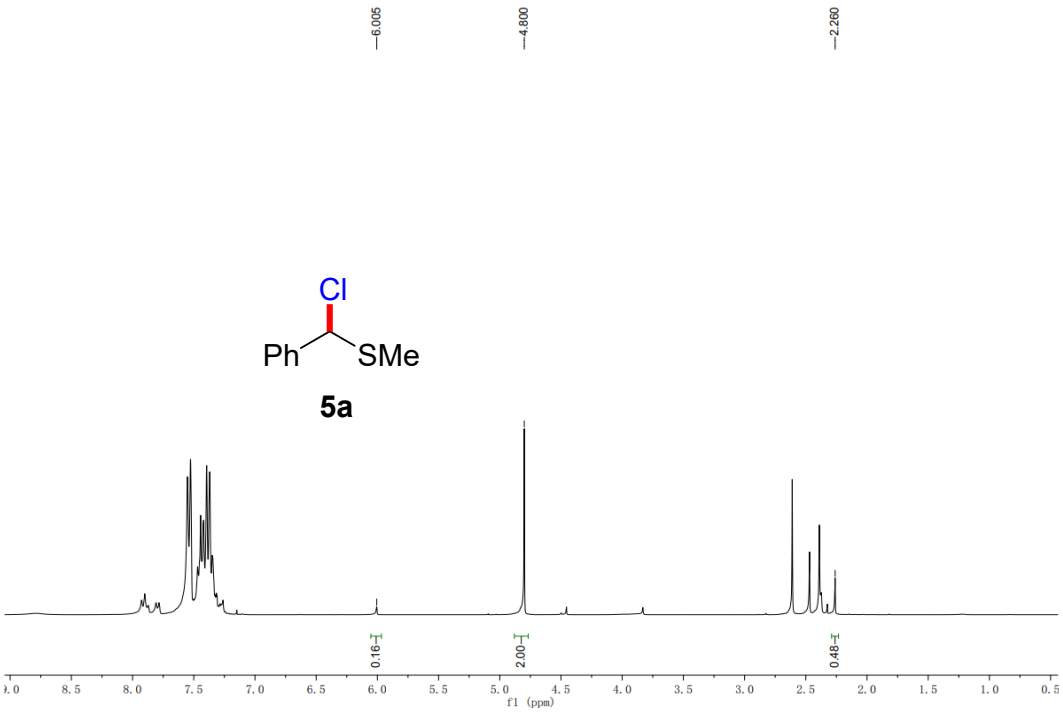
chromatography on silica gel to yield the desired product **2a** (22.2 mg, 73%).



A 30 mL Schlenk tube was charged with benzyl methyl sulfide **1a** (0.2 mmol, 27.6 mg), $PhCF_3$ (2.0 mL) and NCS (0.4 mmol, 53.4 mg). The tube was sealed and the reaction was then stirred vigorously at room temperature for 20 min. After that, the reaction mixture was concentrated *in vacuo*, and the crude product was analyzed by ^1H NMR in $CDCl_3$ and GCMS in MeCN. Yields and conversions are based on **1a**, determined by crude ^1H NMR using dibromomethane as the internal standard.

(a) NMR analysis of the crude product

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Ph
SMe
0.16
2.00
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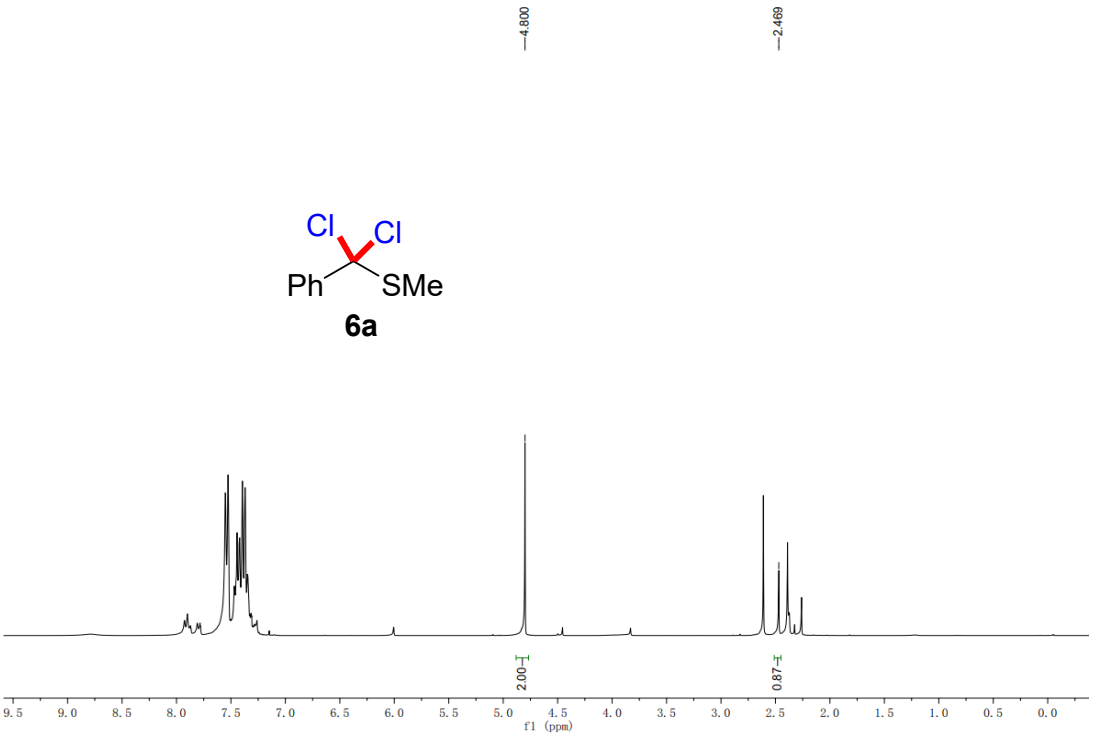
f1 (ppm)

5a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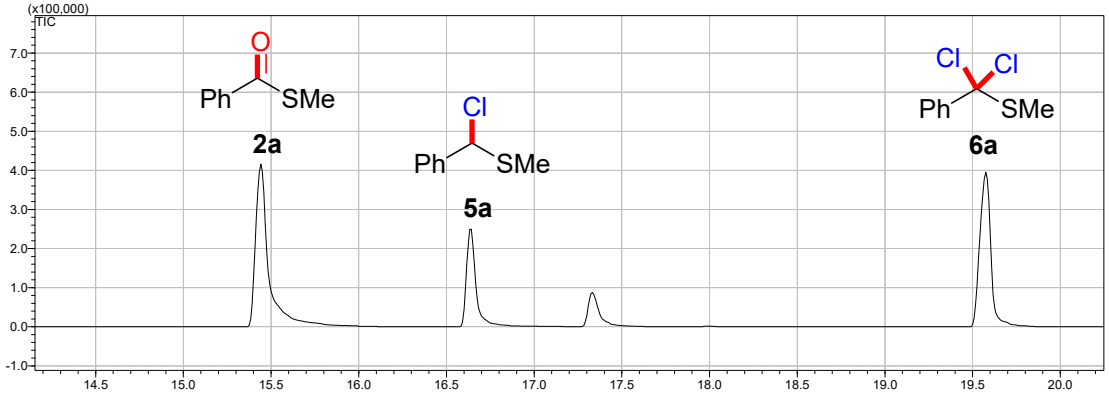
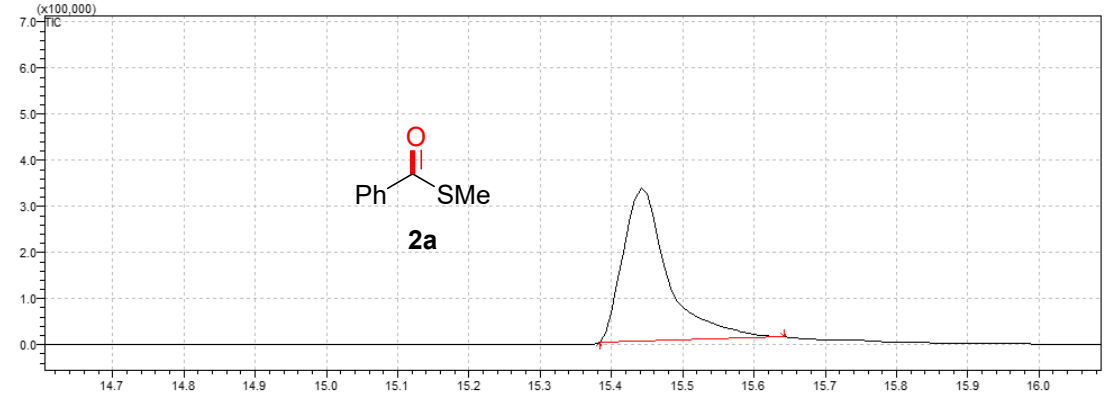
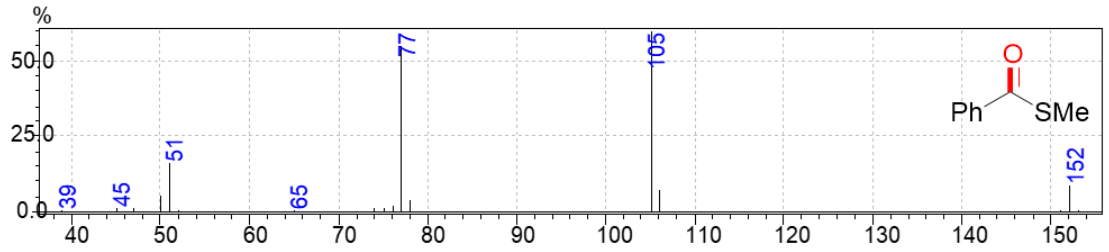
Cl
Ph
SMe
2.00
0.87
f1 (ppm)

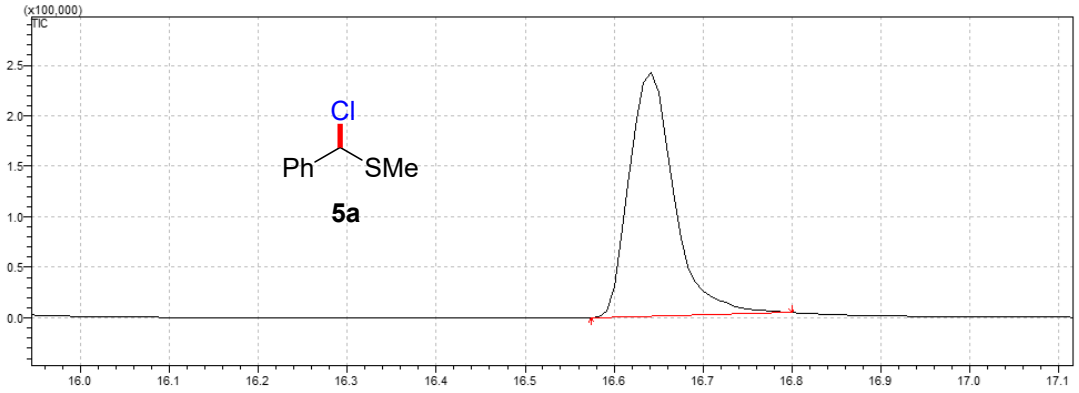
6a

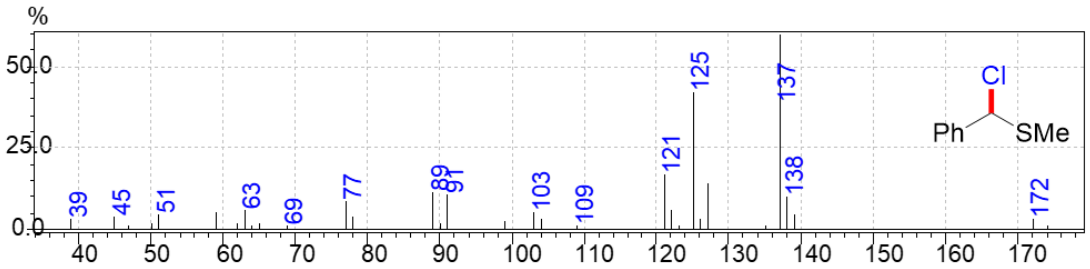
(b) GC-MS analysis of the crude product








(x100,000)
TIC
Cl
Ph
SMe
5a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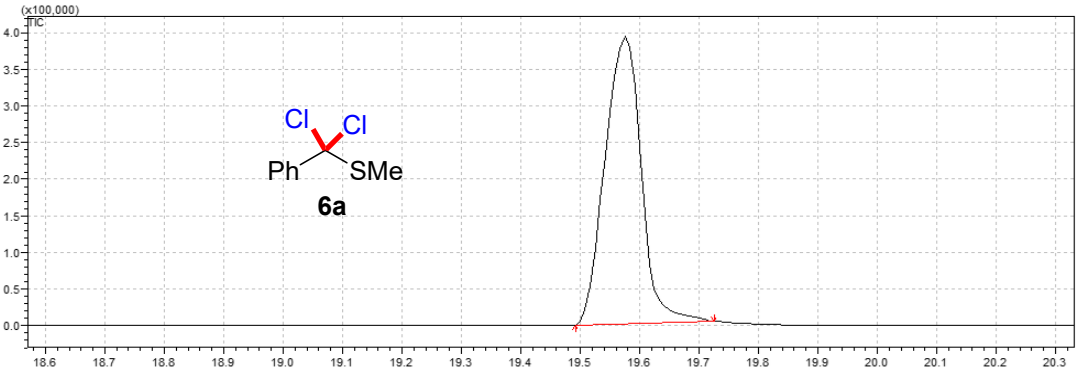
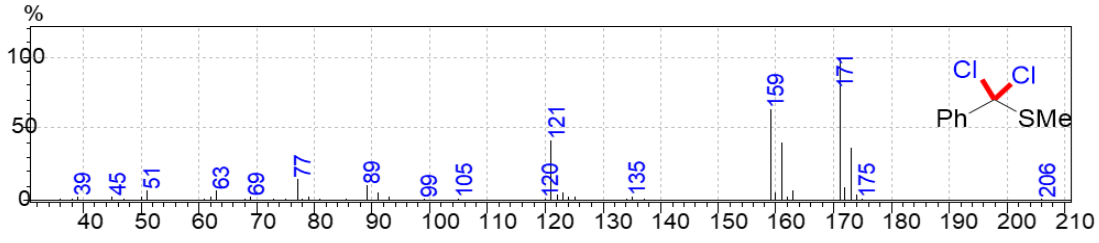
138
172
Cl
Ph
SMe


(x100,000)
TIC
Cl
Cl
Ph
SMe
6a


%
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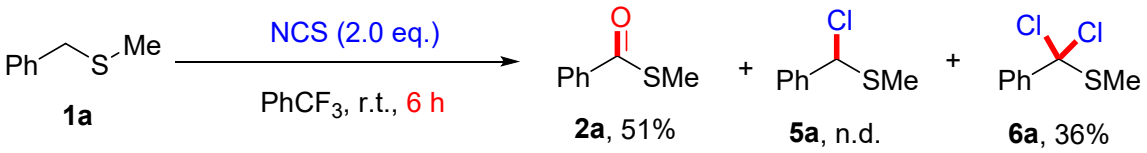
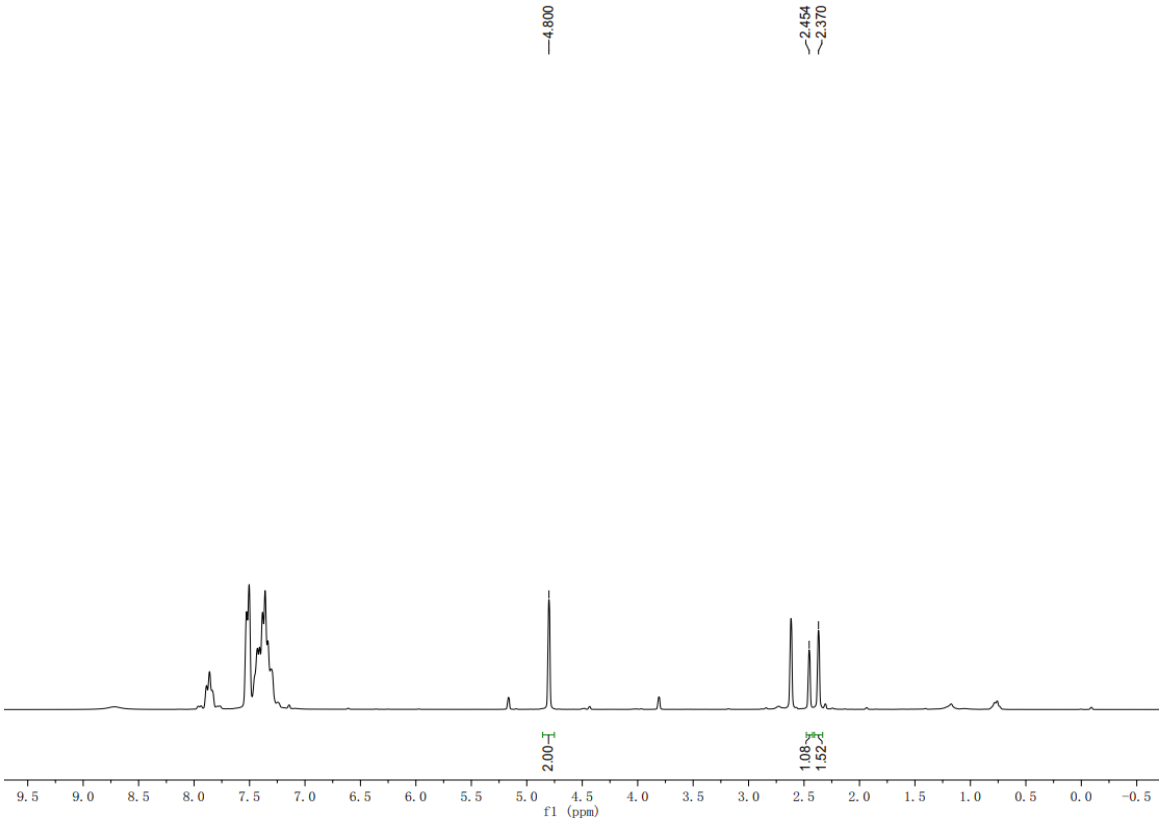
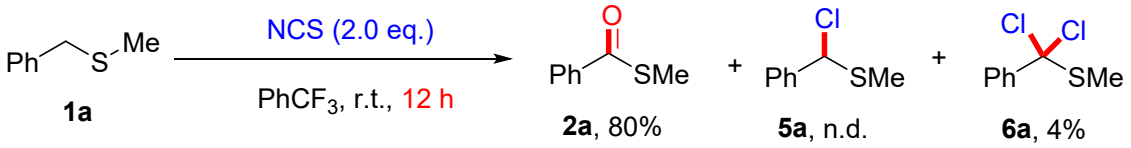
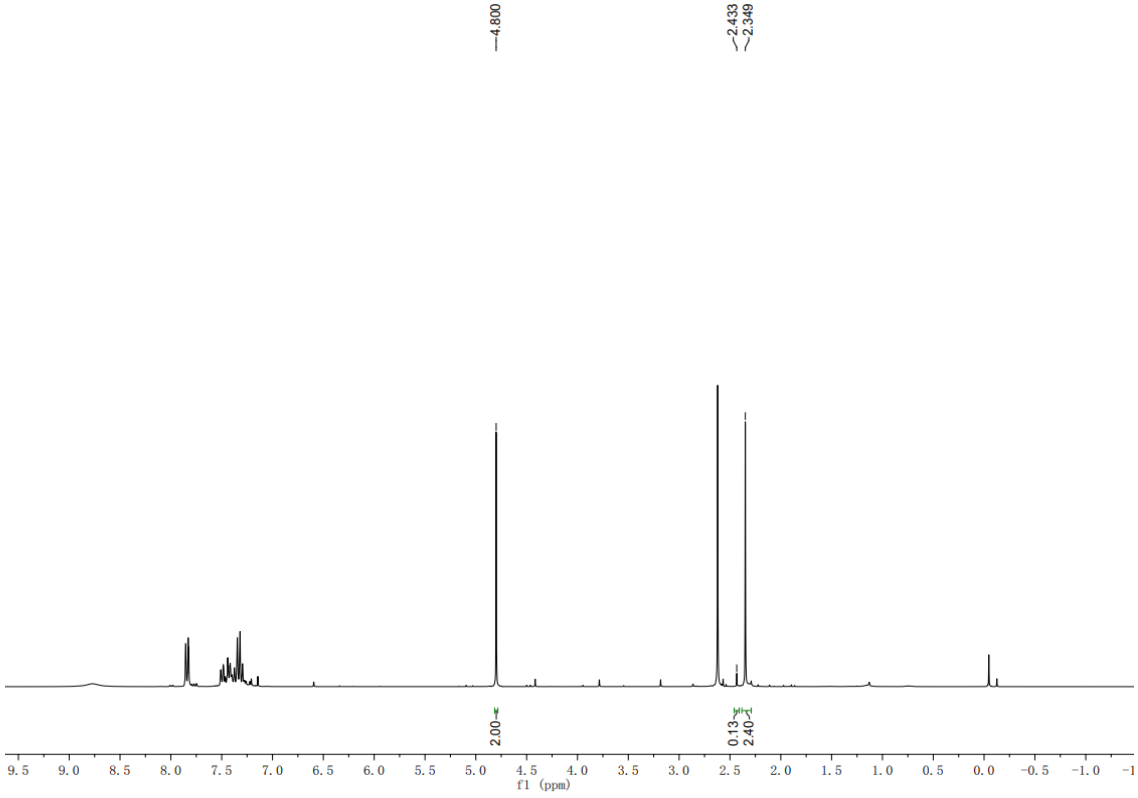


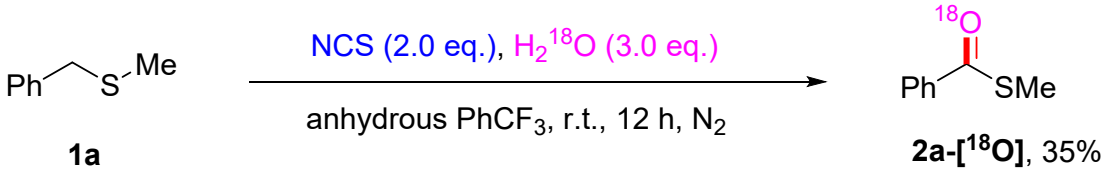
A 30 mL Schlenk tube was charged with benzyl methyl sulfide **1a** (0.2 mmol, 27.6 mg), $PhCF_3$ (2.0 mL) and NCS (0.4 mmol, 53.4 mg). The tube was sealed and the reaction was then stirred vigorously at room temperature for 6 h. After that, the reaction mixture was concentrated *in vacuo*, and the crude product was analyzed by ^1H NMR in $CDCl_3$. Yields and conversions are based on **1a**, determined by crude ^1H NMR using dibromomethane as the internal standard.



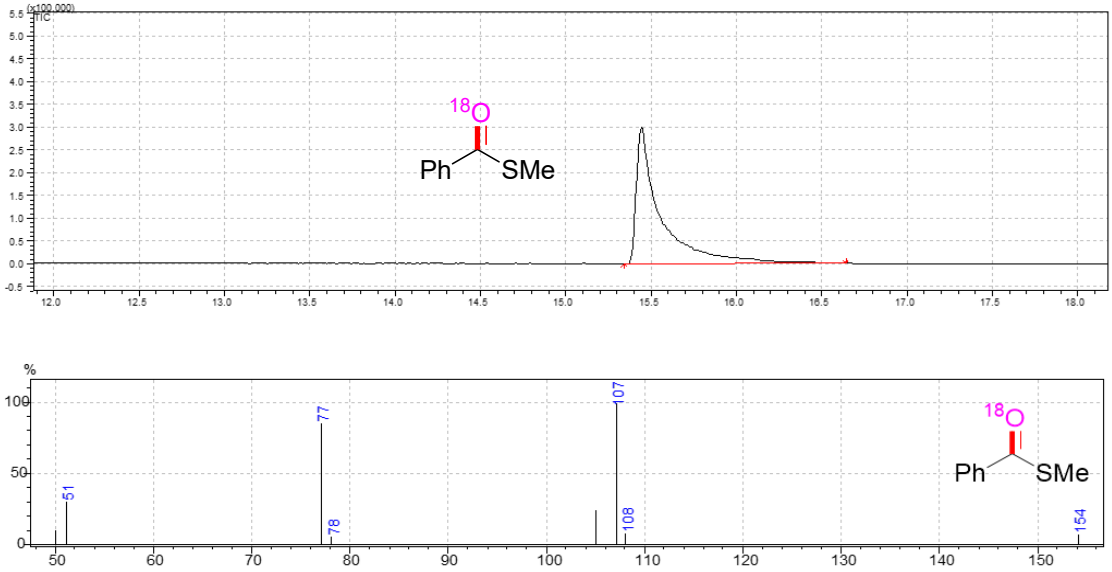


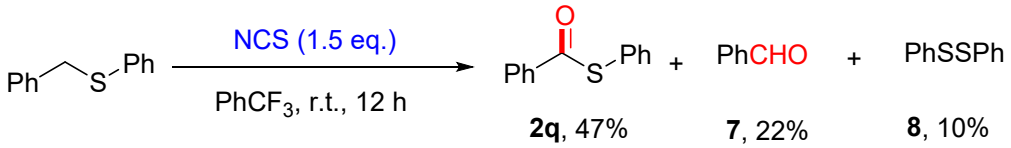
A 30 mL Schlenk tube was charged with benzyl methyl sulfide **1a** (0.2 mmol, 27.6 mg), $PhCF_3$ (2.0 mL) and NCS (0.4 mmol, 53.4 mg). The tube was sealed and the reaction was then stirred vigorously at room temperature for 12 h. After that, the reaction mixture was concentrated *in vacuo*, and the crude product was analyzed by ^1H NMR in $CDCl_3$. Yields and conversions are based on **1a**, determined by crude ^1H NMR using dibromomethane as the internal standard.





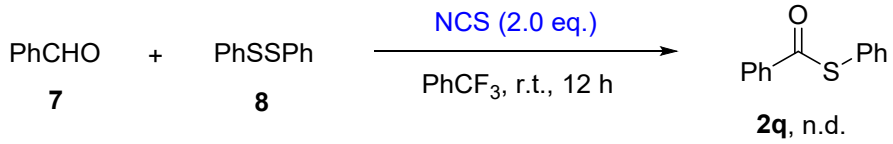
A 30 mL Schlenk tube was charged with benzyl methyl sulfide **1a** (0.2 mmol, 27.6 mg), anhydrous $PhCF_3$ (2.0 mL), NCS (0.4 mmol, 53.4 mg) and $H_2{}^{18}O$ (0.6 mmol, 10.8 μL) under N_2 atmosphere. The tube was sealed and the reaction was then stirred vigorously at room temperature for 12 h. The reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **2a-[^{18}O]** (10.8 mg, 35%). In addition, product **2a-[^{18}O]** was confirmed by GC-MS.





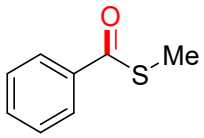
A 30 mL Schlenk tube was charged with benzyl methyl sulfide (0.2 mmol, 40.0 mg), $PhCF_3$ (2.0 mL), and NCS (0.3 mmol, 40.11 mg). The tube was sealed and the reaction was then stirred vigorously under the protection of nitrogen at room temperature for 12 h. The

reaction mixture was then concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to yield *S*-phenyl benzothioate **2q** (20.1 mg, 47%), benzaldehyde (4.7 mg, 22%) and diphenyl disulfide (4.4 mg, 10%).



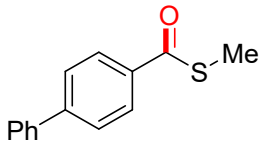
A 30 mL Schlenk tube was charged with benzaldehyde **7** (0.2 mmol), $PhCF_3$ (2.0 mL), diphenyl disulfide (0.1 mmol) and NCS (0.4 mmol). The tube was sealed and the reaction was then stirred vigorously under the protection of nitrogen at room temperature for 12 h. Monitor the reaction system through TLC, no desired product **2q** was detected. After that, the reaction mixture was concentrated *in vacuo*, and no product **2q** was found in GC-MS.

6. Data of compounds



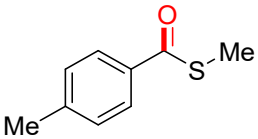
2a

Colorless oil, 24.3 mg, yield: 80% (known compound[1]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J = 7.5 Hz, 2H), 7.42 (t, J = 6.6 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.51, 137.07, 133.30, 128.63, 127.15, 11.76.



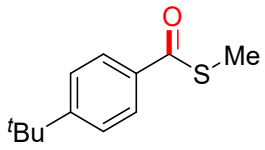
2b

Colorless oil, 36.5 mg, yield: 80% (known compound[1]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H), 7.70 – 7.61 (m, 4H), 7.51 – 7.40 (m, 3H), 2.51 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.90, 144.95, 138.74, 134.71, 127.91, 127.20, 126.64, 126.20, 126.18, 10.69.



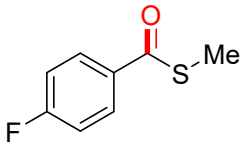
2c

Colorless oil, 25.2 mg, yield: 76% (known compound[1]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.12, 144.12, 134.57, 129.27, 127.21, 21.68, 11.66.



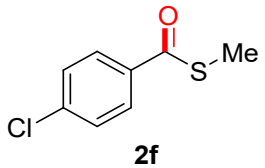
2d

Colorless oil, 29.0 mg, yield: 70% (known compound[1]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 2.47 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.06, 157.05, 134.49, 127.06, 125.57, 35.16, 31.11, 11.65.



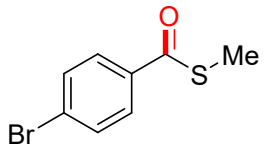
2e

Colorless oil, 24.8 mg, yield: 73% (known compound[2]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.94 (m, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.00, 165.88 (d, *J* = 254.7 Hz), 133.42 (d, *J* = 3.0 Hz), 129.67 (d, *J* = 9.3 Hz), 115.76 (d, *J* = 22.1 Hz), 11.82.



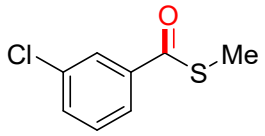
2f

Colorless oil, 29.8 mg, yield: 80% (known compound[1]).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 2.48 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.27, 139.66, 135.37, 128.93, 128.49, 11.81.



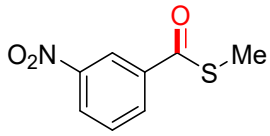
2g

Colorless oil, 39.0 mg, yield: 85% (known compound[1]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 2H), 7.64 – 7.55 (m, 2H), 2.48 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.49, 135.80, 131.92, 128.61, 128.33, 11.82.



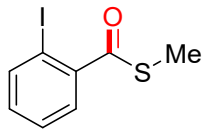
2h

Colorless oil, 34.2 mg, yield: 92% (known compound[3]).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (t, *J* = 1.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.29 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.30, 138.55, 134.91, 133.20, 129.95, 127.19, 125.29, 11.90.



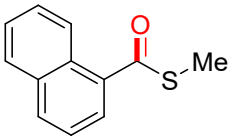
2i

Colorless oil, 37.0 mg, yield: 94% (known compound[4]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 – 8.74 (m, 1H), 8.43 – 8.38 (m, 1H), 8.29 – 8.23 (m, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.40, 148.36, 138.27, 132.65, 129.92, 127.48, 122.10, 12.03.



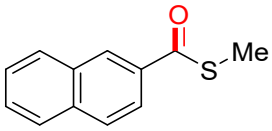
2j

Colorless oil, 33.4 mg, yield: 60%.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.61 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.19 – 7.12 (m, 1H), 2.51 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.64, 142.74, 140.84, 132.32, 128.80, 128.00, 91.30, 12.80. HRMS (ESI, *m/z*): calcd. for C_8H_8IOS $[M+H]^+$: 278.9335, found: 278.9342.



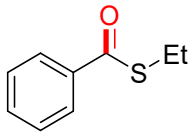
2k

Colorless oil, 33.2 mg, yield: 82% (known compound[3]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 – 8.39 (m, 1H), 7.96 – 7.88 (m, 2H), 7.80 – 7.76 (m, 1H), 7.53 – 7.43 (m, 2H), 7.41 (d, *J* = 7.4 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.76, 134.52, 132.70, 131.71, 128.12, 127.26, 126.87, 126.50, 125.57, 124.22, 123.43, 11.66.



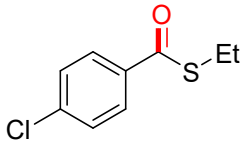
2l

Colorless oil, 33.5 mg, yield: 83% (known compound[4]).^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.03 – 7.94 (m, 2H), 7.90 – 7.83 (m, 2H), 7.62 – 7.51 (m, 2H), 2.54 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.39, 135.75, 134.37, 132.48, 129.59, 128.50, 128.48, 128.44, 127.83, 126.92, 123.15, 11.90.



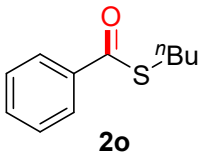
2m

Colorless oil, 28.2 mg, yield: 85% (known compound[4]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.91 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.08 (q, *J* = 7.4 Hz, 2H), 1.36 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.17, 137.23, 133.27, 128.60, 127.18, 23.47, 14.81.



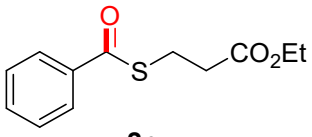
2n

Colorless oil, 35.2 mg, yield: 88% (known compound[5]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.46 – 7.39 (m, 2H), 3.08 (q, *J* = 7.4 Hz, 2H), 1.35 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.97, 139.61, 135.55, 128.89, 128.53, 23.62, 14.74.



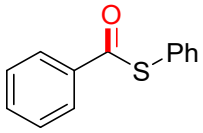
2o

Colorless oil, 27.2 mg, yield: 70% (known compound[6]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 – 7.85 (m, 2H), 7.50 – 7.44 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 3.00 (t, *J* = 7.3 Hz, 2H), 1.57 (q, *J* = 7.5 Hz, 2H), 1.42 – 1.34 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.15, 137.31, 133.19, 128.56, 127.18, 31.64, 28.76, 22.07, 13.63.



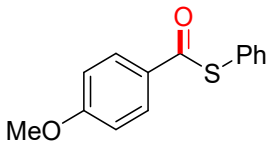
2p

Colorless oil, 33.8 mg, yield: 71% (known compound[7]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.61 – 7.54 (m, 1H), 7.50 – 7.39 (m, 2H), 4.17 (q, J = 7.1 Hz, 2H), 3.32 (t, J = 7.0 Hz, 2H), 2.73 (t, J = 7.0 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.56, 171.75, 136.84, 133.50, 128.64, 127.24, 60.81, 34.51, 24.06, 14.22.



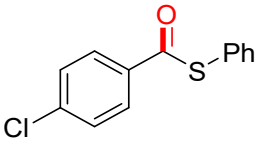
2q

Colorless oil, 35.6 mg, yield: 83% (known compound[8]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.54 – 7.49 (m, 1H), 7.46 – 7.34 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.16, 136.70, 135.13, 133.69, 129.55, 129.28, 128.79, 127.52, 127.41.



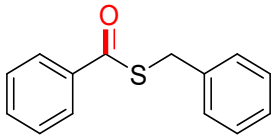
2r

Colorless oil, 37.6 mg, yield: 77% (known compound[8]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (dd, J = 8.2, 1.4 Hz, 2H), 7.55 – 7.47 (m, 1H), 7.42 – 7.30 (m, 4H), 6.90 (d, J = 8.7 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.07, 160.83, 136.70, 136.66, 133.59, 128.75, 127.48, 117.93, 115.01, 55.41.



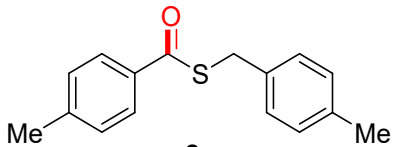
2s

Colorless oil, 37.7 mg, yield: 76% (known compound[8]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 2H), 7.65 – 7.60 (m, 1H), 7.53 – 7.47 (m, 2H), 7.44 (brs, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.67, 136.38, 136.33, 136.02, 133.89, 129.53, 128.84, 127.54, 125.86.



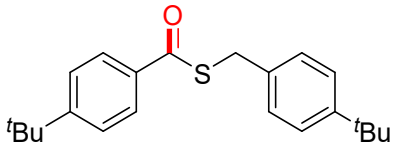
2t

Colorless oil, 41.0 mg, yield: 90% (known compound[1]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 7.4 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.38 – 7.17 (m, 7H), 4.25 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.27, 136.44, 135.75, 132.42, 127.95, 127.62, 127.60, 126.30, 126.27, 32.30.



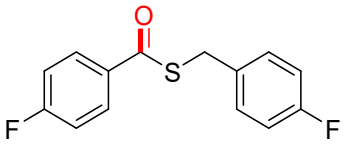
2u

Colorless oil, 45.0 mg, yield: 88%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.24 (dd, J = 12.0, 8.2 Hz, 4H), 7.11 (d, J = 7.9 Hz, 2H), 4.27 (s, 2H), 2.39 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.08, 144.29, 137.02, 134.55, 134.34, 129.36, 129.30, 128.91, 127.39, 33.04, 21.72, 21.16. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{17}OS$ $[M+H]^+$: 257.0995, found: 257.1000.



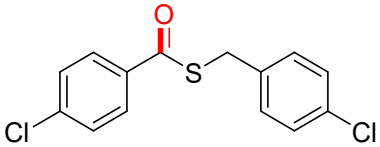
2v

White solid, 56.5 mg, yield: 83%. m.p. = 54 ~ 55 °C.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.28 (m, 4H), 4.29 (s, 2H), 1.31 (d, *J* = 7.8 Hz, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.07, 157.24, 150.23, 134.49, 134.27, 128.68, 127.24, 125.59, 35.19, 34.52, 32.90, 31.35, 31.10. HRMS (ESI, *m/z*): calcd. for $C_{22}H_{29}OS$ $[M+H]^+$: 341.1934, found: 341.1933.



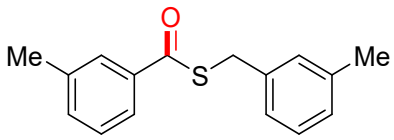
2w

Colorless oil, 42.2 mg, yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.37 – 7.32 (m, 2H), 7.15 – 7.09 (m, 2H), 7.03 – 6.97 (m, 2H), 4.28 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.69, 166.01 (d, *J* = 255.3 Hz), 162.08 (d, *J* = 246.1 Hz), 133.22 (d, *J* = 3.3 Hz), 133.04 (d, *J* = 3.1 Hz), 130.61 (d, *J* = 8.1 Hz), 129.88 (d, *J* = 9.4 Hz), 115.85 (d, *J* = 22.4 Hz), 115.56 (d, *J* = 21.8 Hz), 32.68. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{10}F_2NaOS$ $[M+Na]^+$: 287.0313, found: 287.0313.



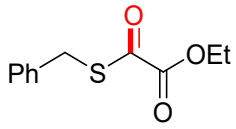
2x

Colorless oil, 51.0 mg, yield: 86% (known compound[9]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.43 – 7.38 (m, 2H), 7.32 – 7.25 (m, 4H), 4.26 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.87, 140.02, 135.93, 134.97, 133.30, 130.35, 129.02, 128.84, 128.67, 32.75.



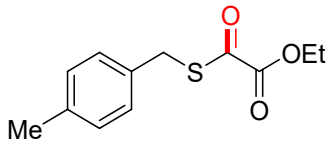
2y

Colorless oil, 42.0 mg, yield: 82%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 6.4 Hz, 2H), 7.39 – 7.29 (m, 2H), 7.19 (d, J = 6.9 Hz, 3H), 7.06 (d, J = 6.8 Hz, 1H), 4.28 (s, 2H), 2.39 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.53, 138.53, 138.38, 137.42, 136.86, 134.23, 129.71, 128.59, 128.54, 128.14, 127.82, 126.04, 124.55, 33.32, 21.40, 21.34. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{17}OS$ $[M+H]^+$: 257.0995, found:257.0998.



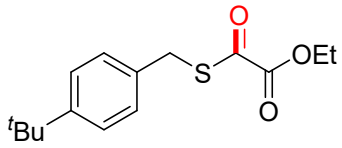
4a

Colorless oil, 31.4 mg, yield: 70% (known compound[10]). 1H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 5H), 4.36 (q, J = 7.2 Hz, 2H), 4.20 (s, 2H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.06, 158.95, 136.05, 129.05, 128.80, 127.74, 63.66, 33.71, 13.99.



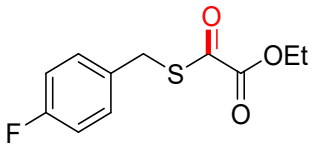
4b

Colorless oil, 36.2 mg, yield: 76%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, J = 7.5 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 4.36 (q, J = 6.8 Hz, 2H), 4.18 (s, 2H), 2.33 (s, 3H), 1.38 (t, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.14, 158.99, 137.53, 132.94, 129.47, 128.94, 63.60, 33.50, 21.15, 13.98. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{15}O_3S$ $[M+H]^+$: 239.0736, found: 239.0736.



4c

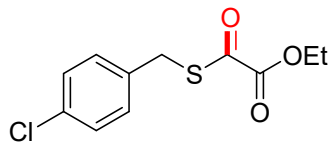
Colorless oil, 44.8 mg, yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 4.19 (s, 2H), 1.38 (t, J = 7.1 Hz, 3H), 1.30 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.15, 158.99, 150.76, 132.89, 128.73, 125.74, 63.61, 34.56, 33.37, 31.31, 13.99. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{20}NaO_3S$ $[M+Na]^+$: 303.1025, found: 303.1024.



4d

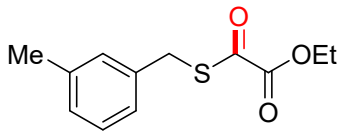
Colorless oil, 37.8 mg, yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (t, J = 6.9 Hz, 2H), 6.91 (t, J = 8.6 Hz, 2H), 4.29 (q, J = 7.1 Hz, 2H), 4.09 (s, 2H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.96, 162.24 (d, J = 246.6 Hz), 158.87, 131.97, 130.71 (d, J

= 8.2 Hz), 115.66 (d, J = 21.7 Hz), 63.69, 32.92, 13.95. HRMS (ESI, *m/z*): calcd. for $C_{11}H_{11}FNaO_3S$ $[M+Na]^+$: 265.0305, found: 265.0300.



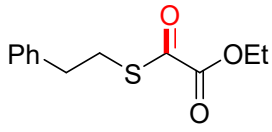
4e

White solid, 42.3 mg, yield: 82%. m.p. = 48 ~ 49 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (brs, 4H), 4.37 (q, J = 7.1 Hz, 2H), 4.16 (s, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.90, 158.83, 134.72, 133.62, 130.39, 128.92, 63.74, 32.97, 13.96. HRMS (ESI, *m/z*): calcd. for $C_{11}H_{11}ClNaO_3S$ $[M+Na]^+$: 281.0010, found: 281.0010.



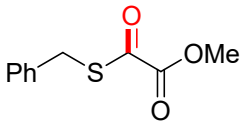
4f

Colorless oil, 35.7 mg, yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (t, J = 7.4 Hz, 1H), 7.16 – 7.05 (m, 3H), 4.36 (q, J = 7.2 Hz, 2H), 4.17 (s, 2H), 2.33 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.07, 158.97, 138.54, 135.89, 129.73, 128.68, 128.51, 126.05, 63.61, 33.68, 21.33, 13.97. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{15}O_3S$ $[M+H]^+$: 239.0736, found: 239.0734.



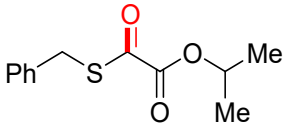
4g

Colorless oil, 40.5 mg, yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 6.8 Hz, 2H), 7.24 (t, J = 5.4 Hz, 3H), 4.37 (q, J = 7.1 Hz, 2H), 3.27 – 3.17 (m, 2H), 2.97 – 2.86 (m, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.61, 159.05, 139.38, 128.67, 128.59, 126.79, 63.58, 35.05, 30.74, 14.00. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{15}O_3S$ $[M+H]^+$: 239.0736, found: 239.0732.



4h

Colorless oil, 29.8 mg, yield: 71% (known compound[11]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 5H), 4.22 (s, 2H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.65, 159.42, 135.92, 129.03, 128.81, 127.78, 53.88, 33.74.



4i

Colorless oil, 32.0 mg, yield: 67%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 5H), 5.22 – 5.08 (m, 1H), 4.19 (s, 2H), 1.35 (d, J = 6.3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.38, 158.46, 136.16, 129.06, 128.79, 127.71, 72.21, 33.70, 21.55. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{15}O_3S$ $[M+H]^+$: 239.0736, found: 239.0736.

III. References and notes:

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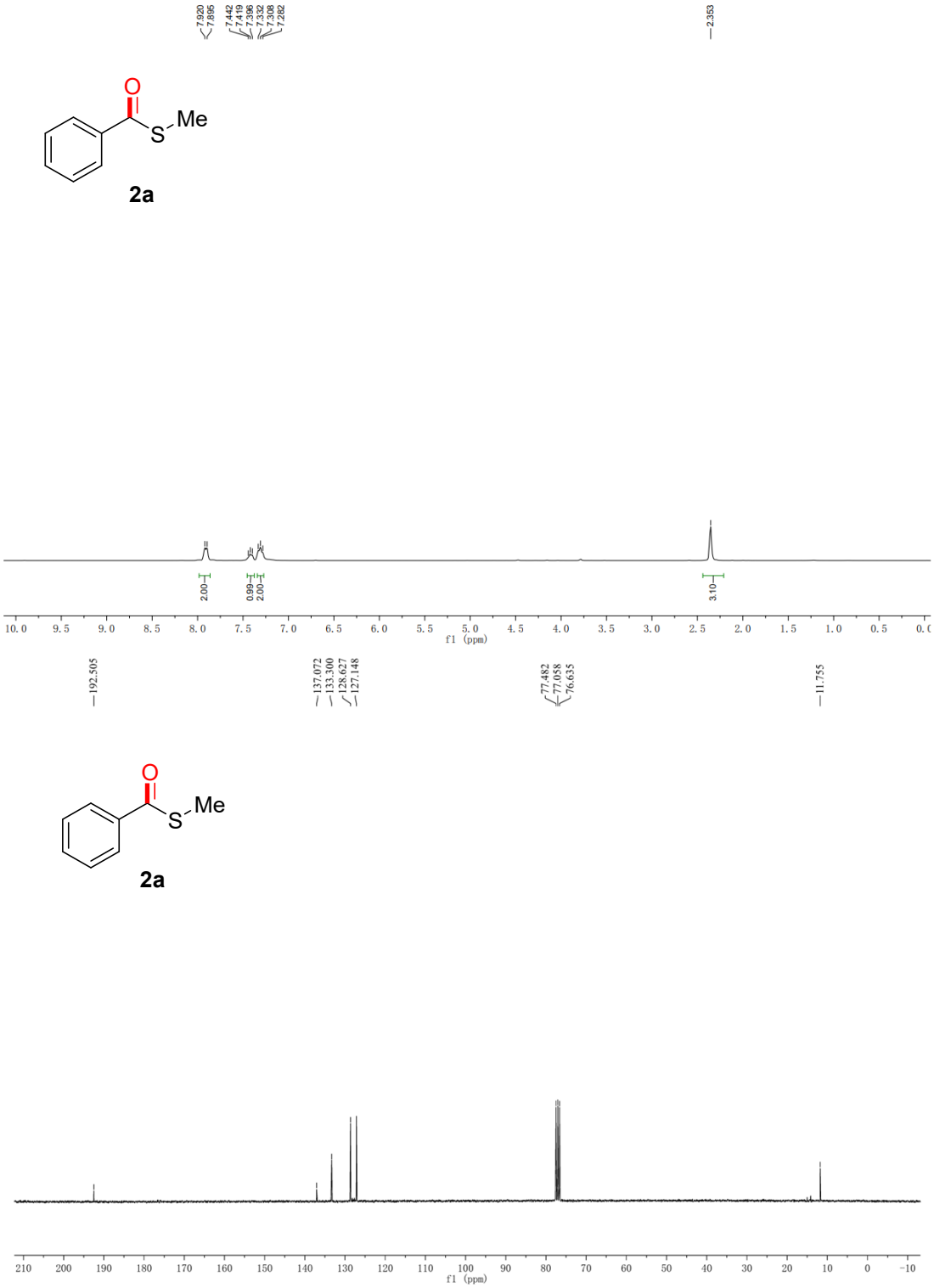
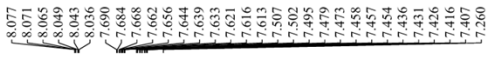
(11) C. Jouen, M. C. Lasne, J.C. Pommelet. Synthesis of α-fluorinated-α,α-difunctionalized sulfides and sulfones. *Tetrahedron Lett.* **1996**, *37*, 2413-2416.

IV. ^{1}H and ^{13}C NMR

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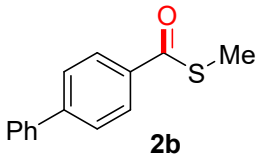
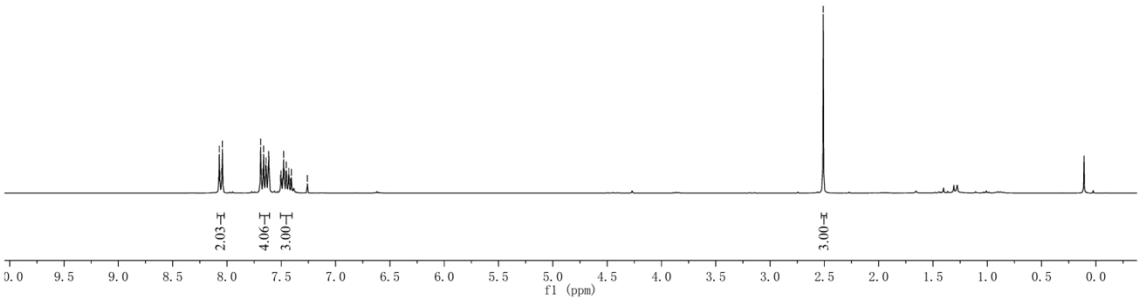
8.065
8.049
8.043
8.036
7.690
7.684
7.668
7.662
7.656
7.644
7.639
7.633
7.621
7.616
7.613
7.507
7.502
7.495
7.479
7.473
7.458
7.457
7.454
7.436
7.431
7.426
7.416
7.407
7.260
2.510


O
S
Me
Ph

2b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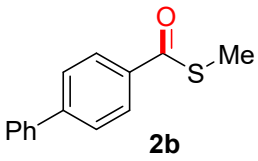
4.06
3.00
3.00
f1 (ppm)


190.897

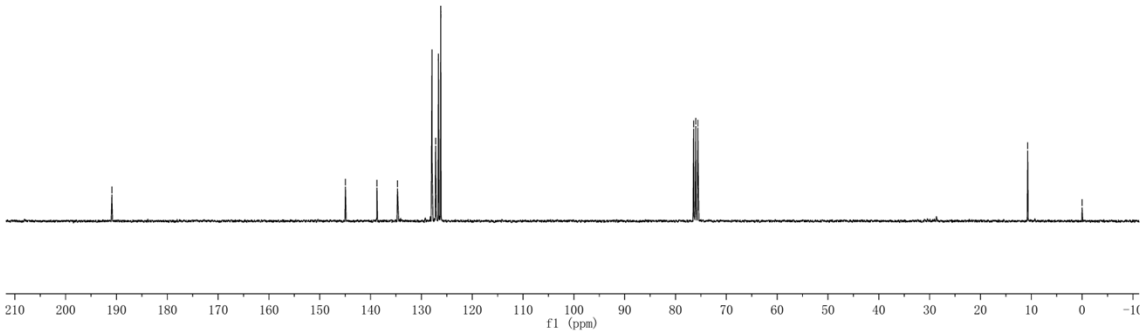
144.953
138.742
134.706
127.913
127.203
126.636
126.196
126.184


76.432
76.009
75.585


10.693
0.000


O
S
Me
Ph

2b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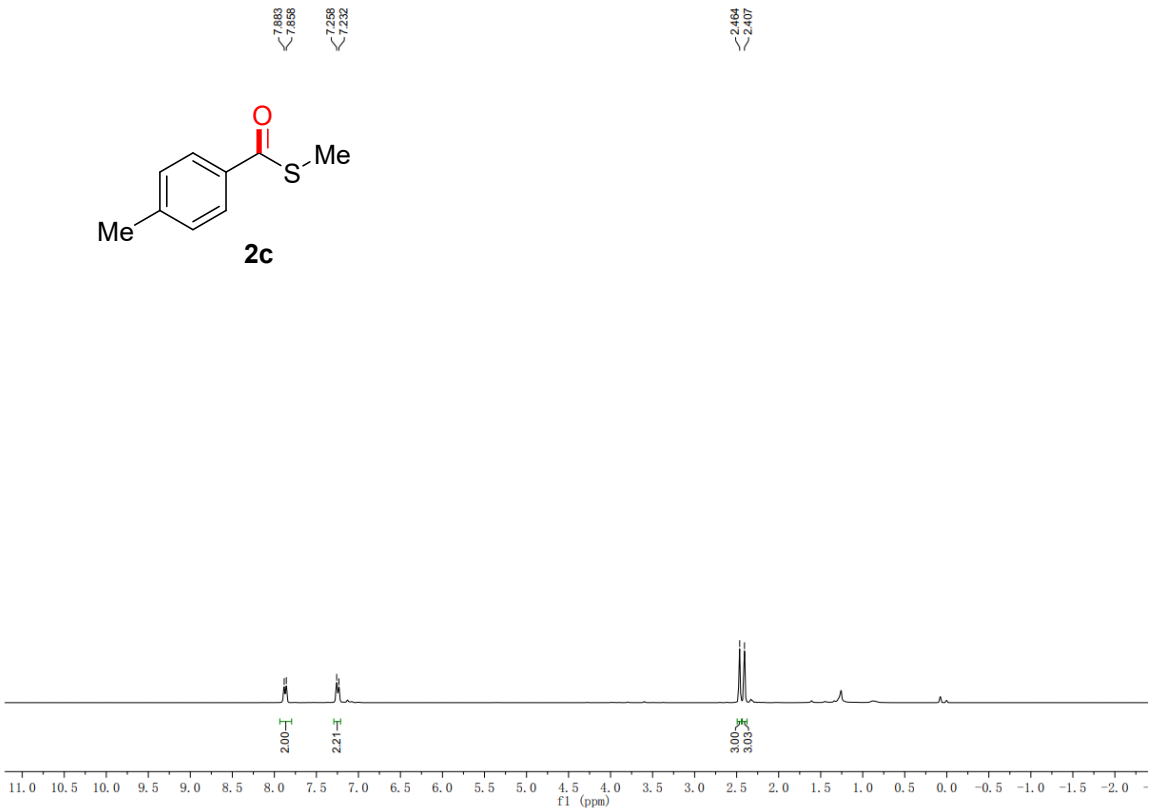
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7.258
7.232
2.464
2.407
O
S
Me
Me
2c
2.00
2.21
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3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)
192.116
144.116
134.570
129.273
127.207
77.465
77.042
76.619
21.684
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O
S
Me
Me
2c
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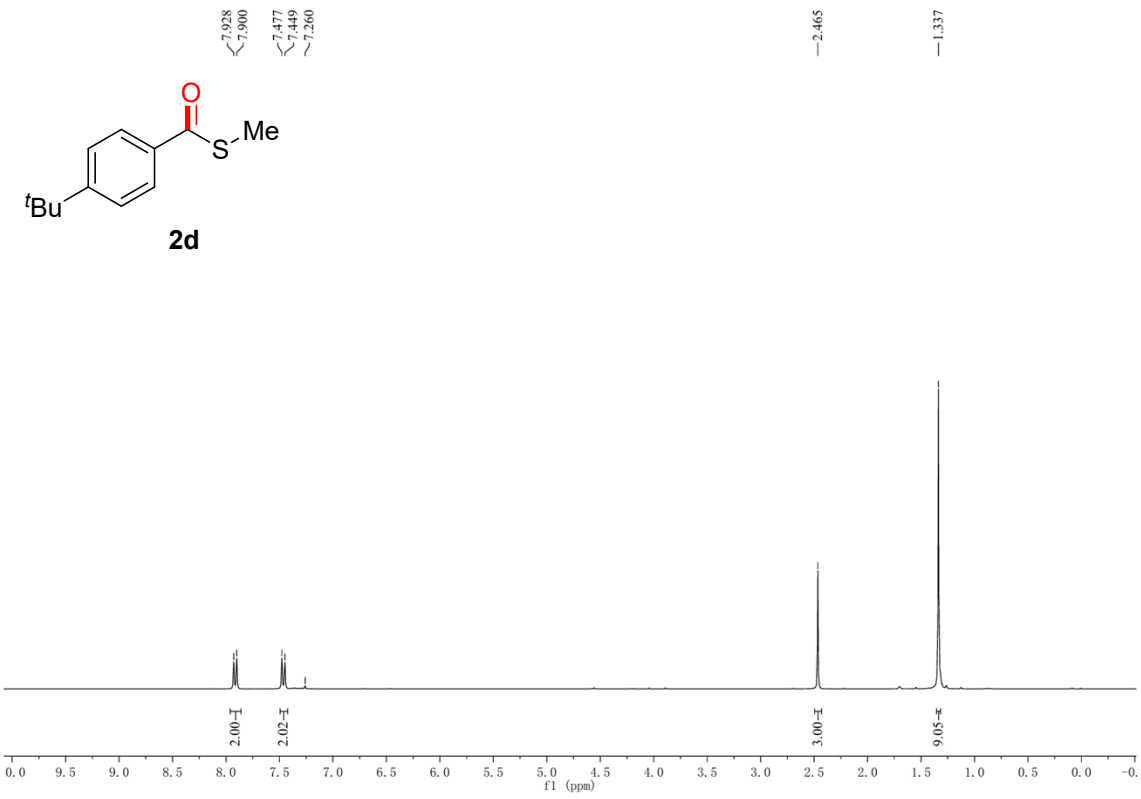
f1 (ppm)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S
Me
tBu
2d
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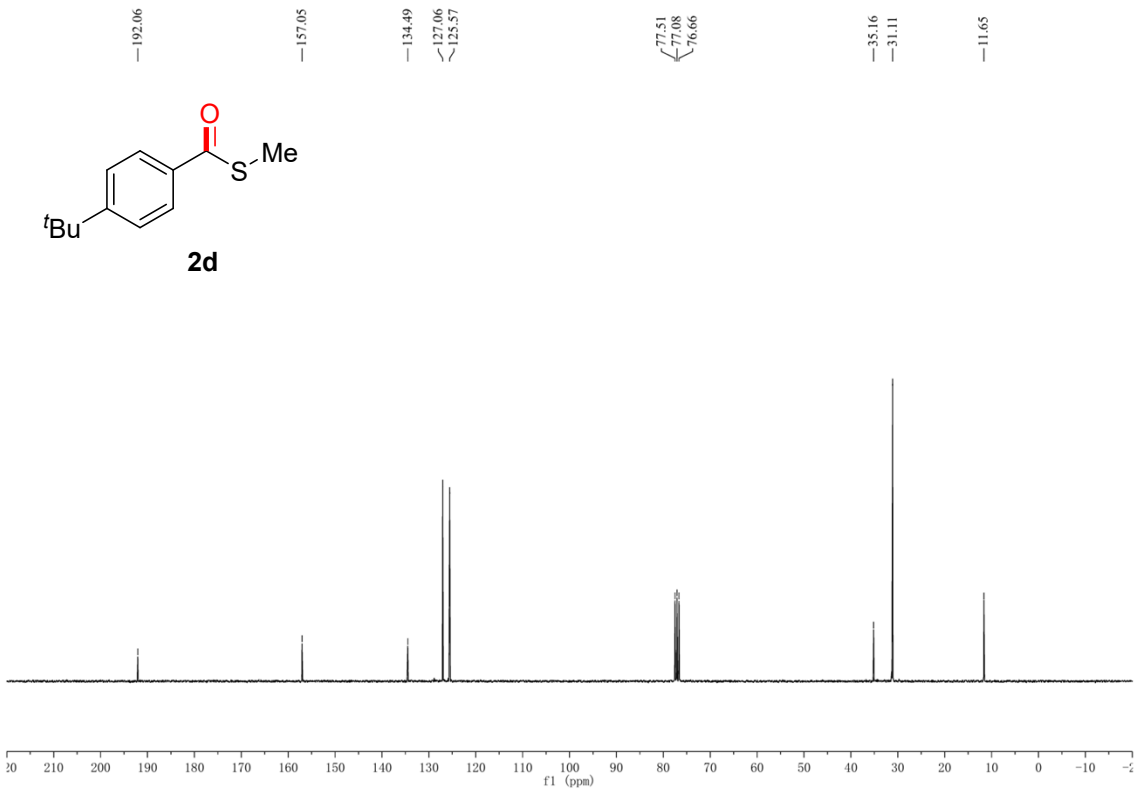
2.02
3.00
9.05
f1 (ppm)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134.49
127.06
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76.66
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31.11
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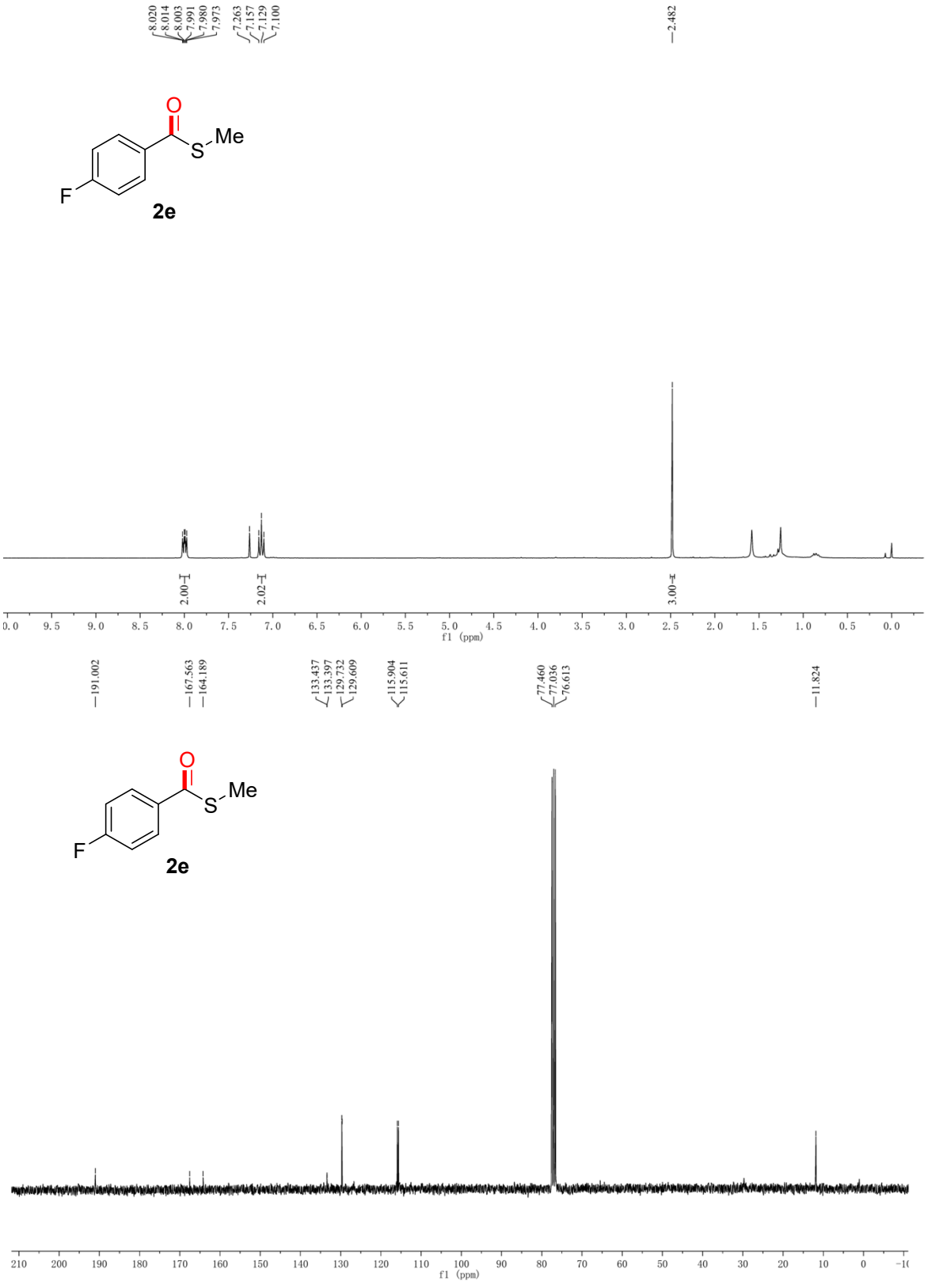
O
S
Me
tBu
2d
f1 (ppm)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7.157
7.129
7.100
2.482
O
S
Me
F
2e
2.00
2.02
3.00
f1 (ppm)
191.002
167.563
164.189
133.437
133.397
129.732
129.609
115.904
115.611
77.460
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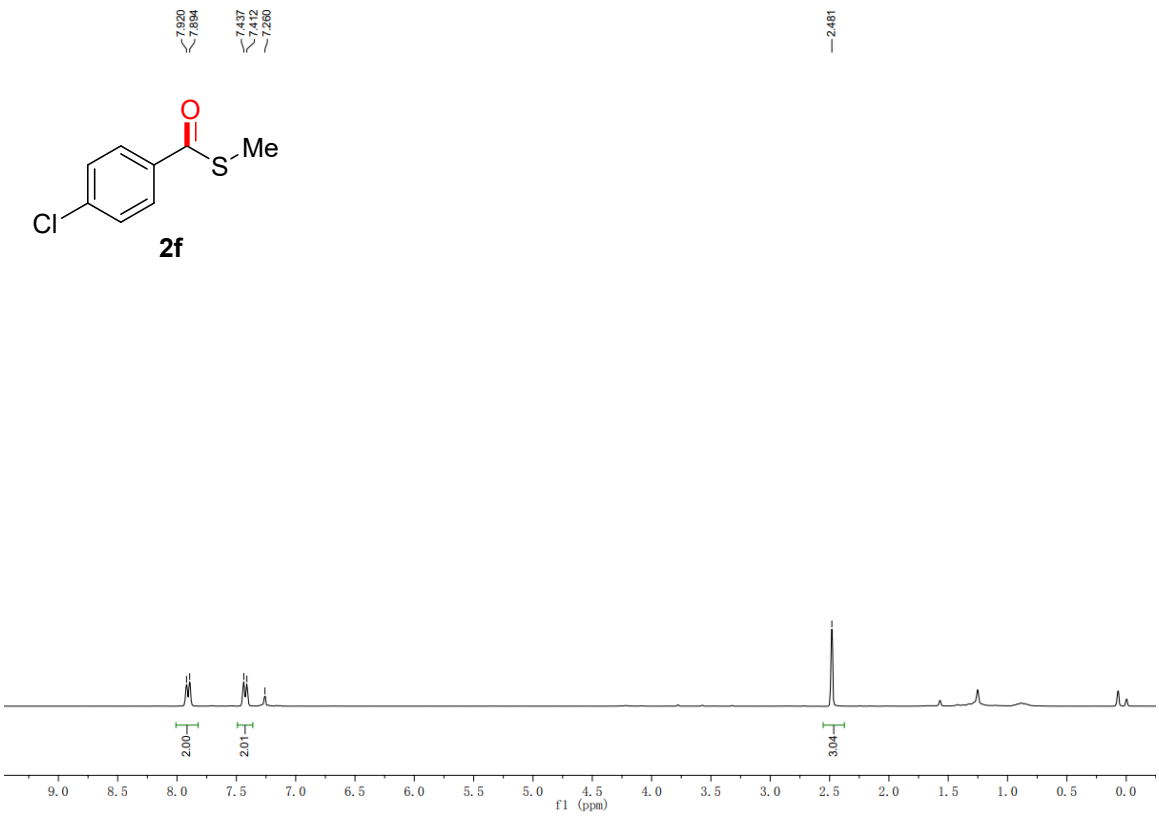
76.613
11.824
O
S
Me
F
2e
f1 (ppm)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O
S
Me
Cl
2f
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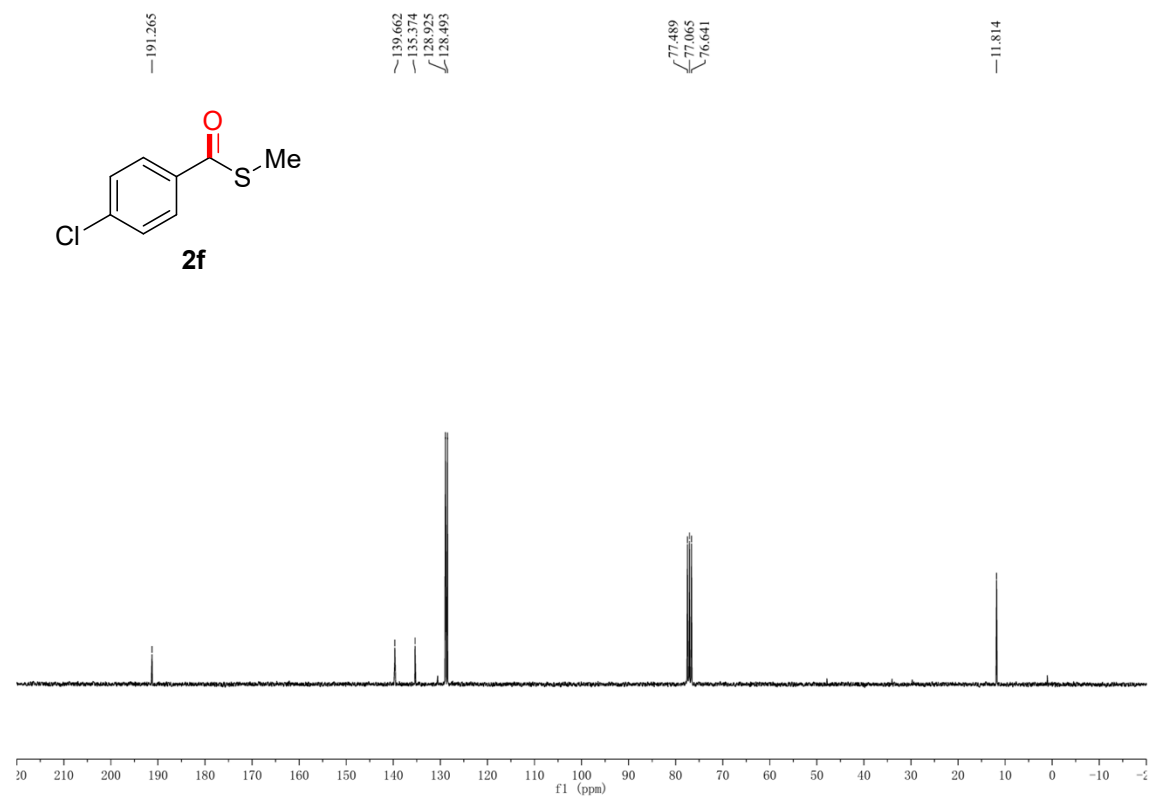
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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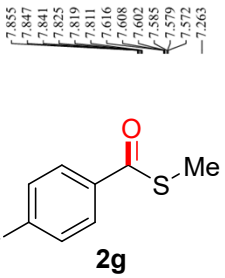
S
Me
Cl
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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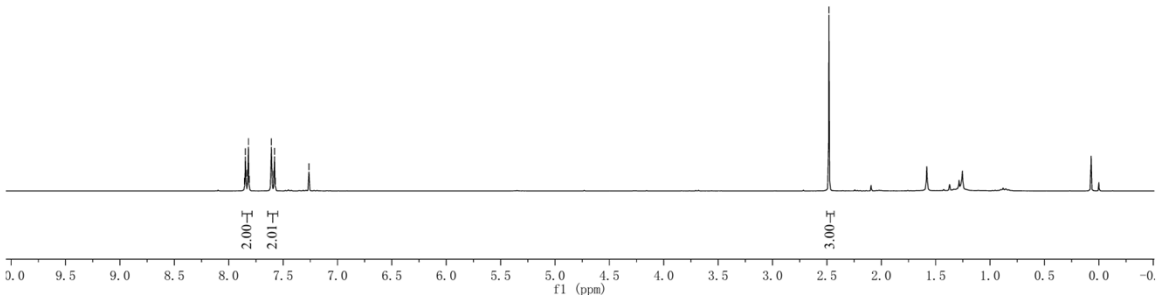
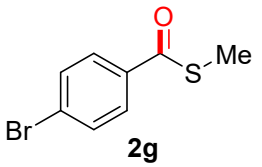
7.263
2.482
O
S
Me
Br

2g


2.00
2.01
3.00
f1 (ppm)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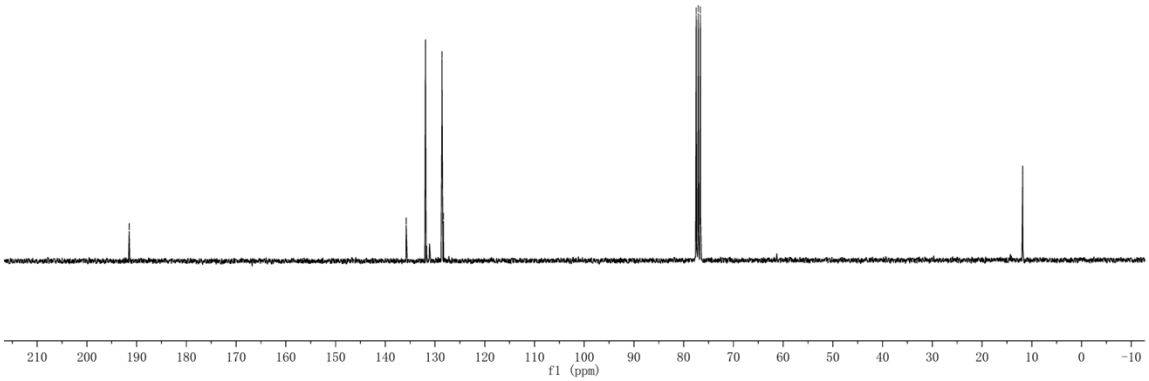
O
S
Me
Br

2g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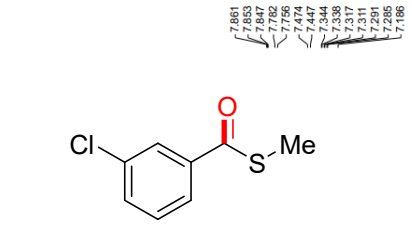
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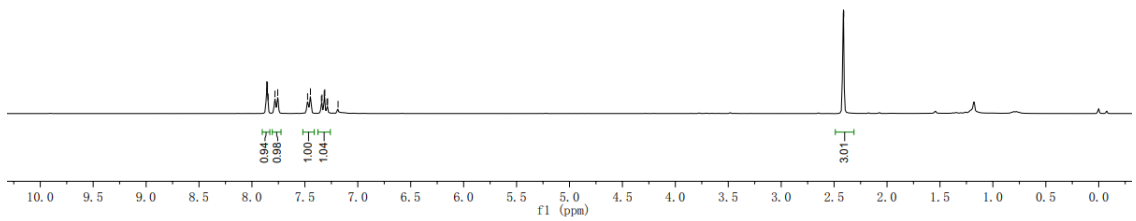
7.285
7.186
2.409
Cl
O
S
Me

2h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3.01
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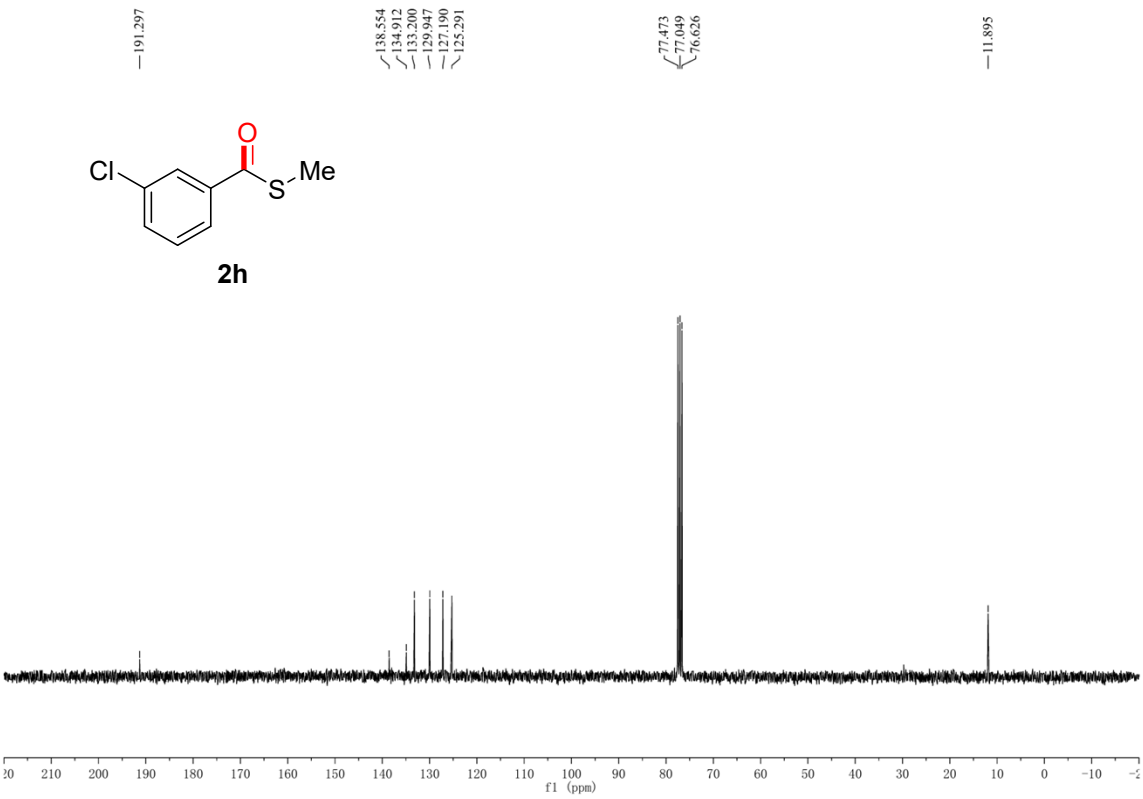
f1 (ppm)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125.291
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77.049
76.626
11.895
Cl
O
S
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

2h


8.770
8.764
8.758
8.426
8.423
8.419
8.416
8.399
8.396
8.392
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7.260
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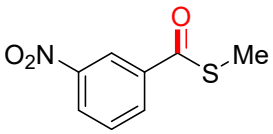
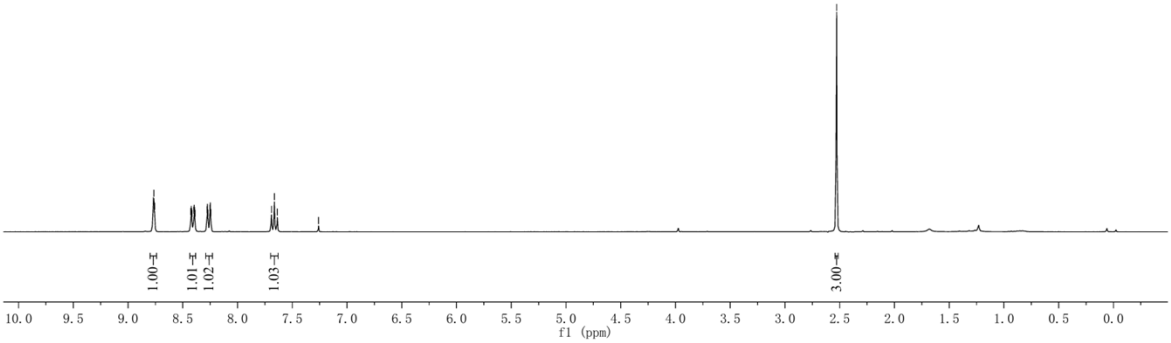

O
O2N
S
Me

2i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7.5
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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122.097
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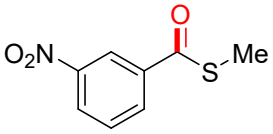
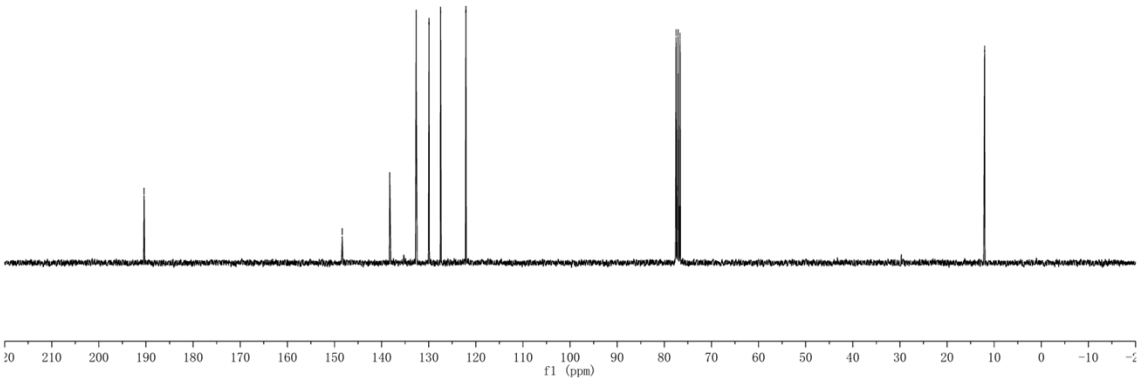
77.079
76.656
12.025


O
O2N
S
Me

2i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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.958
7.955
7.932
7.929
7.622
7.617
7.597
7.591
7.433
7.430
7.408
7.405
7.383
7.379
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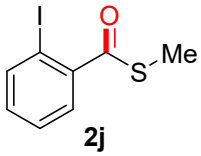
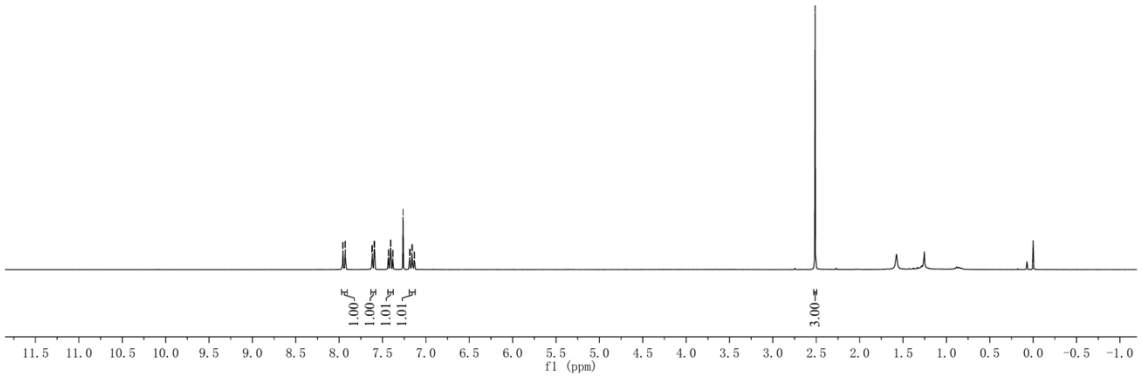
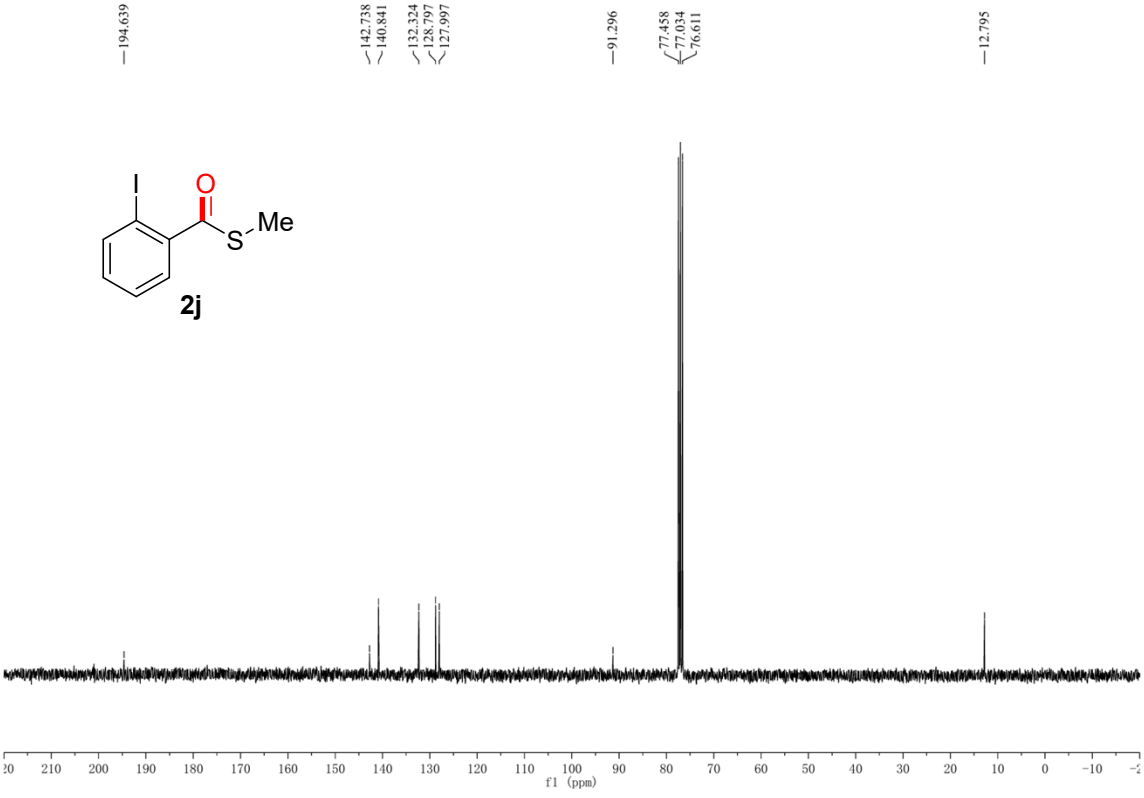
7.130
2.513


I
O
S
Me

2j


1.00
1.00
1.01
1.01
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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132.324
128.797
127.997
91.296
77.458
77.034
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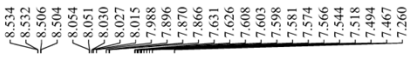
I
O
S
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2j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8.051
8.030
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7.896
7.870
7.866
7.631
7.626
7.608
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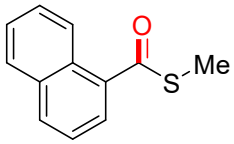
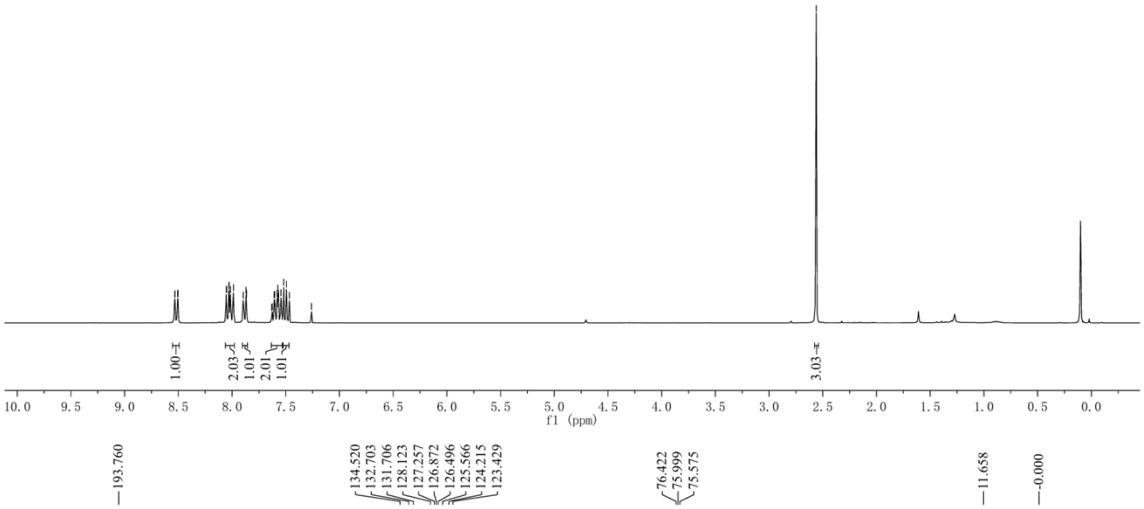
7.518
7.494
7.467
7.260
2.561


O
S
Me

2k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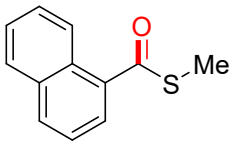
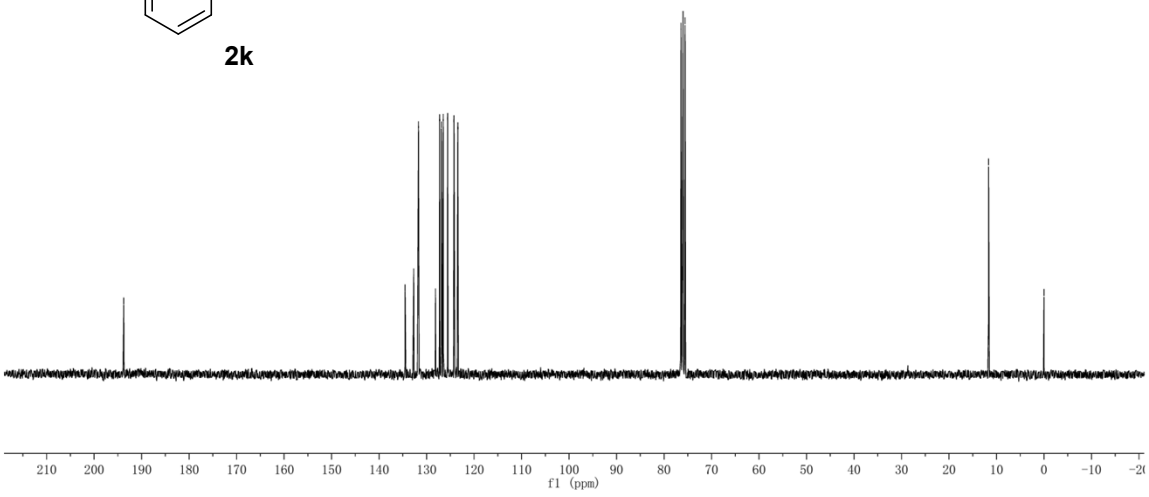
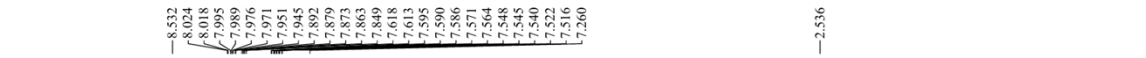
2.03
1.01
2.01
1.01
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

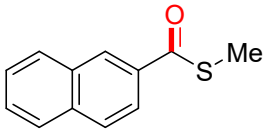
193.760
134.520
132.703
131.706
128.123
127.257
126.872
126.496
125.566
124.215
123.429
76.422
75.999
75.575
11.658
0.000


O
S
Me

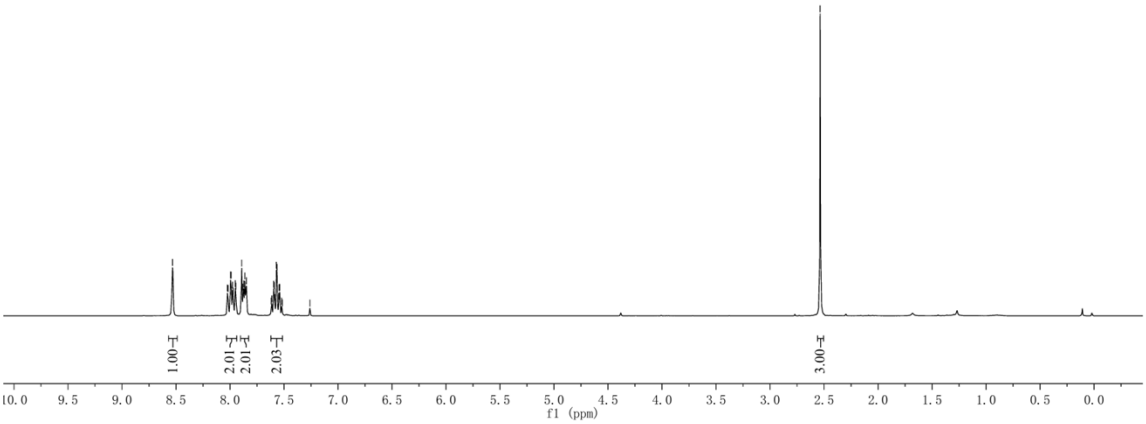
2k


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)

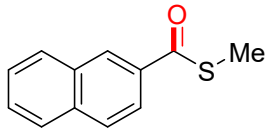

8.532
8.024
8.018
7.995
7.989
7.976
7.971
7.951
7.945
7.892
7.879
7.873
7.863
7.849
7.618
7.613
7.595
7.590
7.586
7.571
7.564
7.548
7.545
7.540
7.522
7.516
7.260
2.536


O
S
Me

2l

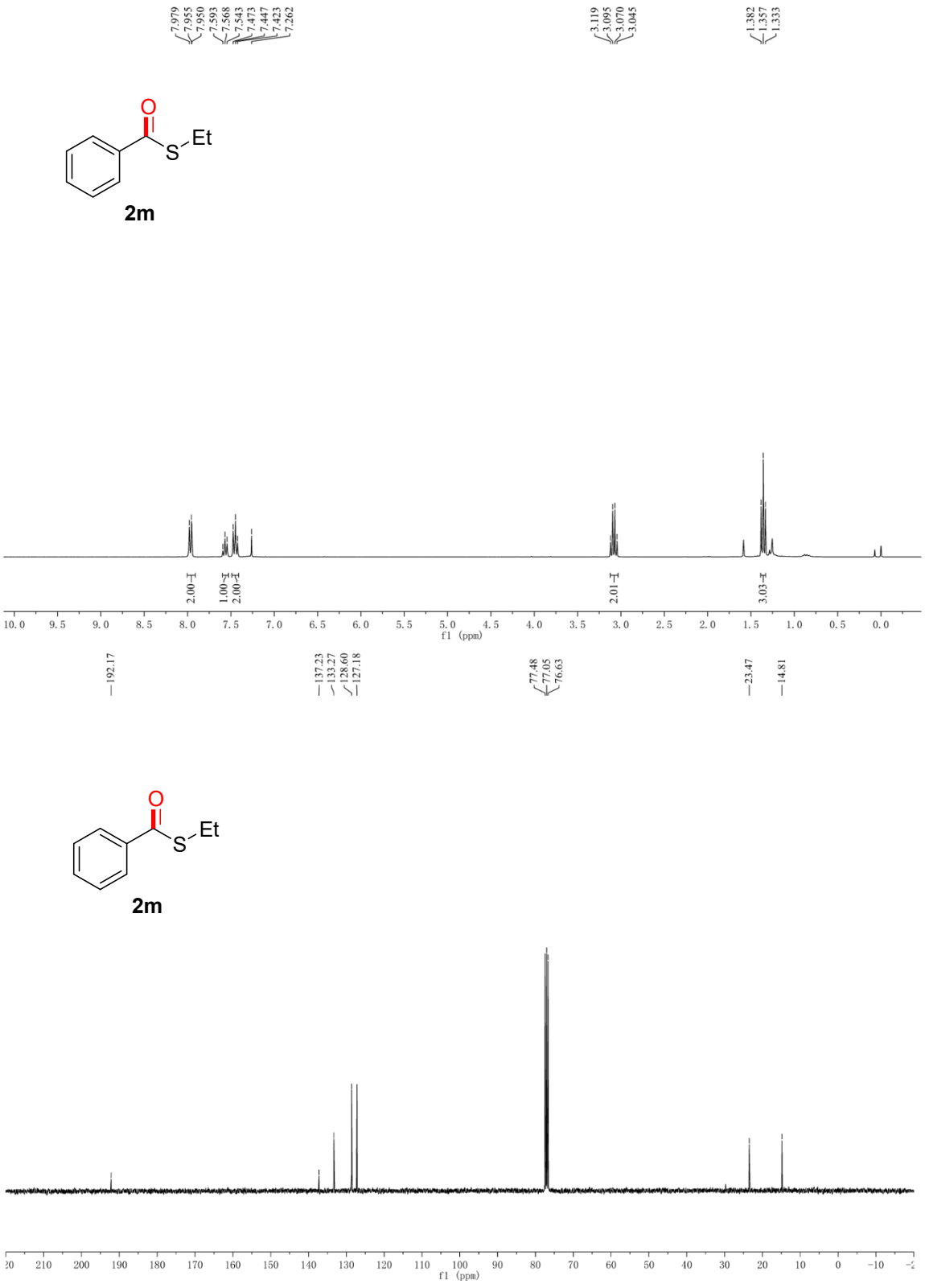

1.00
2.01
2.01
2.03
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


192.389
135.745
134.373
132.477
129.585
128.502
128.480
128.438
127.830
126.924
123.153
77.529
77.106
76.682
11.898


O
S
Me

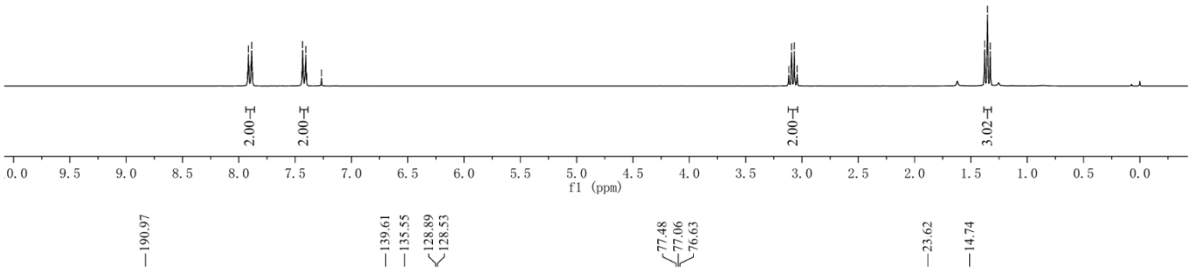
2l

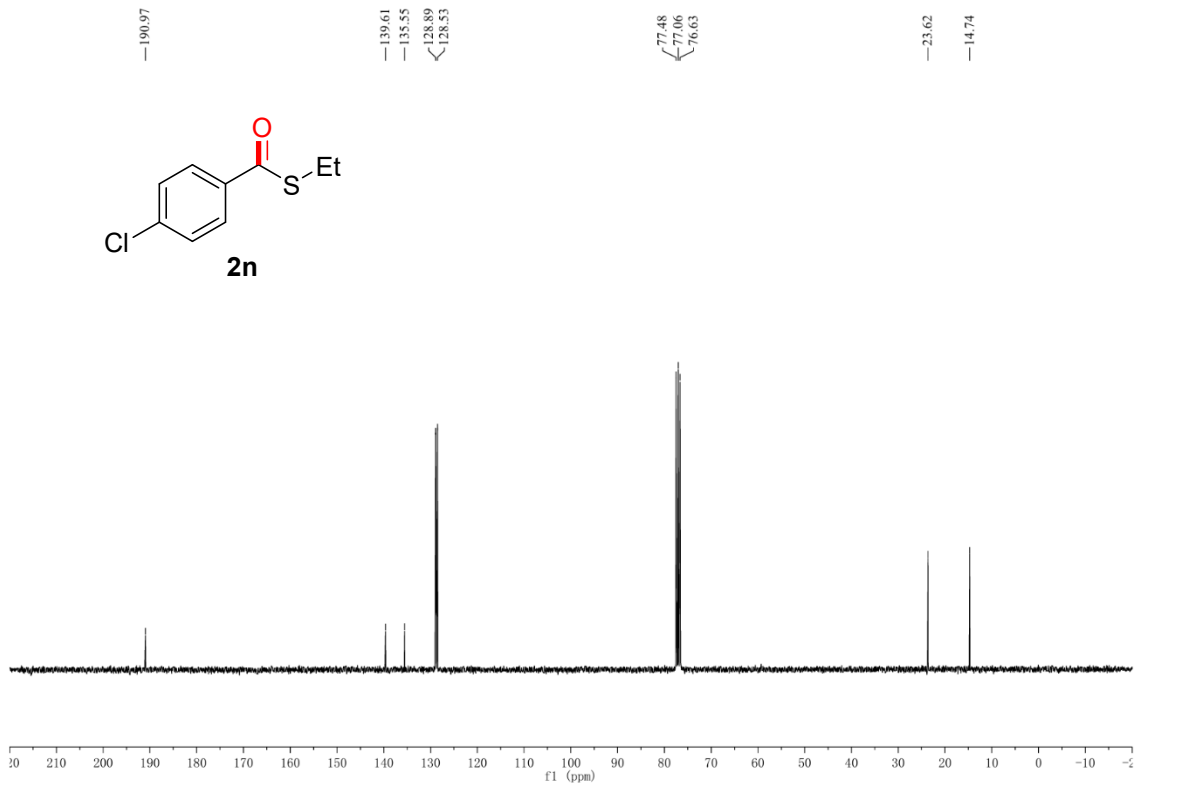
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.979
7.955
7.950
7.593
7.568
7.543
7.473
7.447
7.423
7.262
3.119
3.095
3.070
3.045
1.382
1.357
1.333
O
S
Et
2m
2.00
1.00
2.00
2.01
3.03
f1 (ppm)
192.17
137.23
133.27
128.60
127.18
77.48
77.05
76.63
23.47
14.81
O
S
Et
2m
f1 (ppm)


7.922
7.915
7.908
7.892
7.886
7.878
7.441
7.434
7.427
7.411
7.405
7.397
7.266
3.117
3.093
3.068
3.043
1.378
1.353
1.328
O
S
Et
Cl

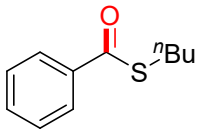
2n


2.00
2.00
2.00
3.02
f1 (ppm)

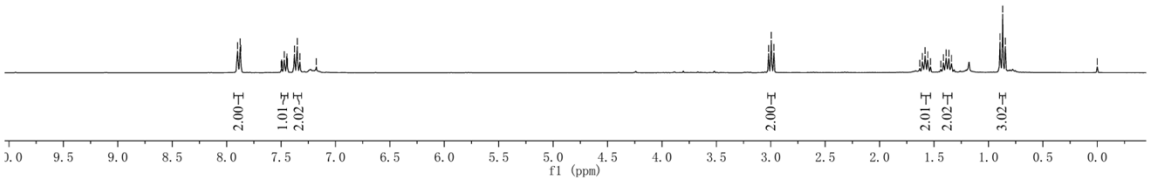

190.97
139.61
135.55
128.89
128.53
77.48
77.06
76.63
23.62
14.74
O
S
Et
Cl
f1 (ppm)

2n

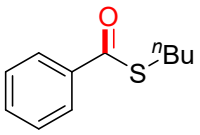

7.899
7.876
7.871
7.498
7.494
7.490
7.470
7.449
7.445
7.442
7.377
7.351
7.327
7.176
3.020
2.996
2.971
1.631
1.607
1.582
1.557
1.532
1.438
1.414
1.389
1.363
1.339
0.894
0.870
0.845
0.000


O
S
nBu

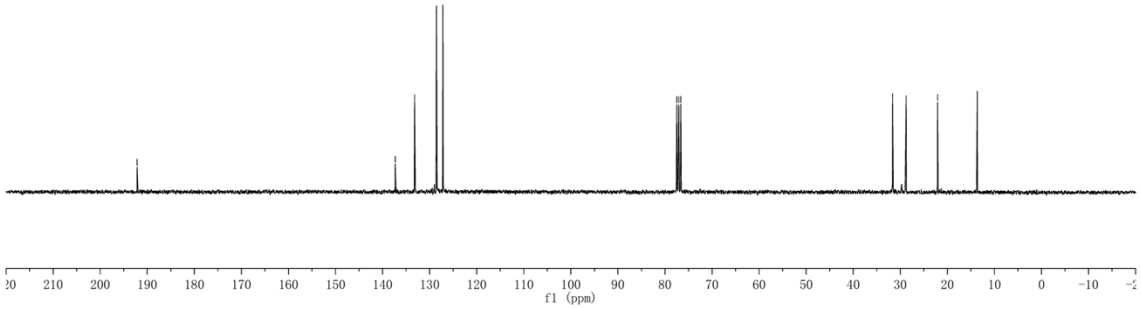
2o


2.00
1.01
2.02
2.00
2.01
2.02
3.02
f1 (ppm)

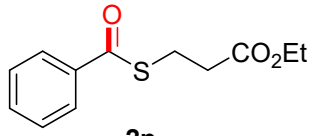

192.149
137.312
133.192
128.555
127.182
77.484
77.061
76.638
31.641
28.756
22.071
13.631


O
S
nBu

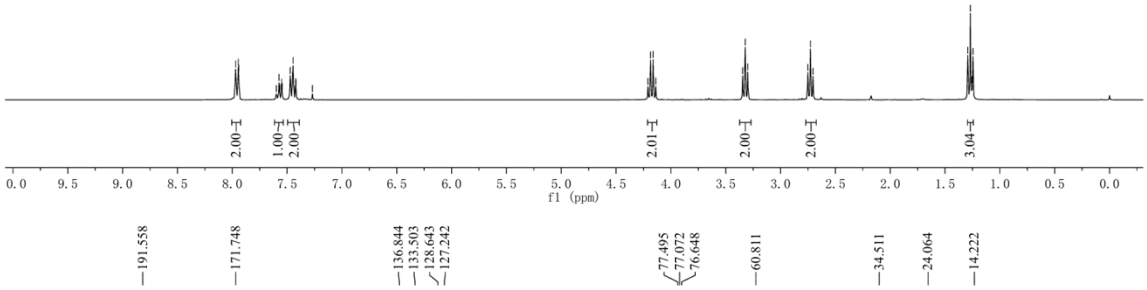
2o


f1 (ppm)

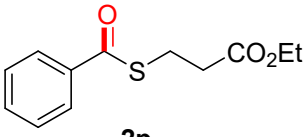

7.969
7.945
7.941
7.598
7.574
7.567
7.554
7.549
7.545
7.472
7.467
7.451
7.446
7.427
7.422
7.419
7.269
4.210
4.186
4.162
4.138
3.346
3.322
3.299
2.751
2.728
2.704
1.293
1.269
1.255
1.245


O
S
CO2Et

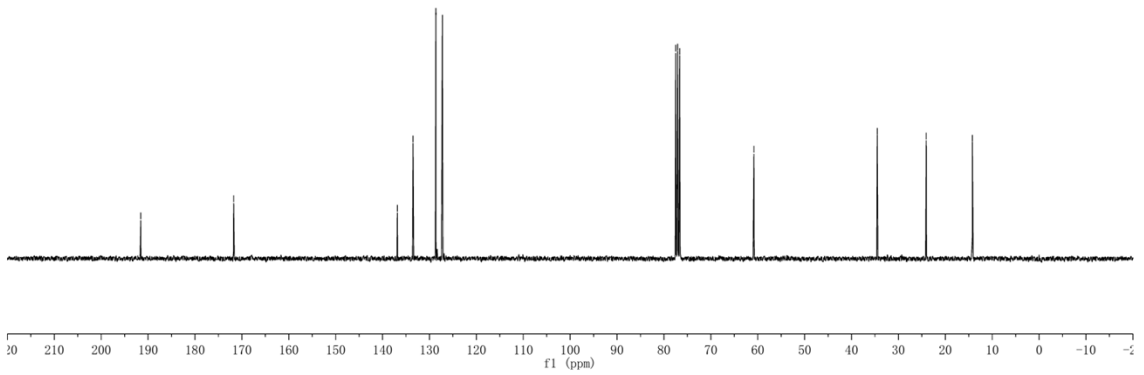
2p

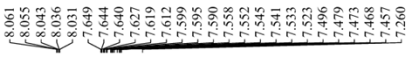

2.00
1.00
2.00
2.01
2.00
2.00
3.04
f1 (ppm)

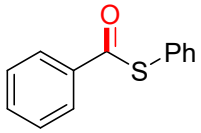
191.558
171.748
136.844
133.503
128.643
127.242
77.495
77.072
76.648
60.811
34.511
24.064
14.222


O
S
CO2Et

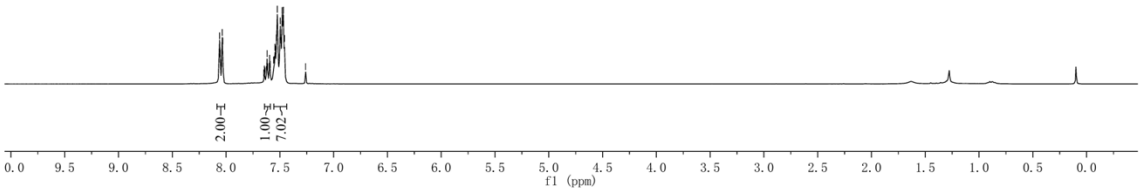
2p

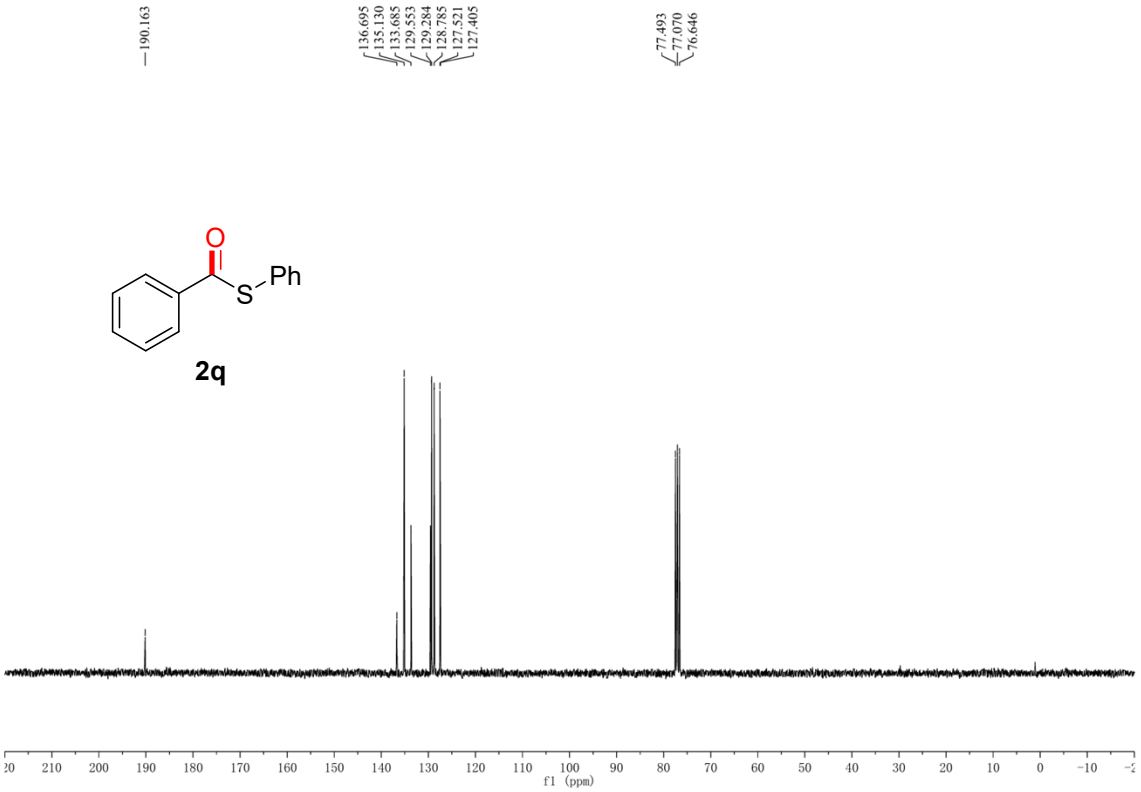

f1 (ppm)


8.061
8.055
8.043
8.036
8.031
7.649
7.644
7.640
7.627
7.619
7.612
7.599
7.595
7.590
7.558
7.552
7.545
7.541
7.533
7.523
7.496
7.479
7.473
7.468
7.457
7.260

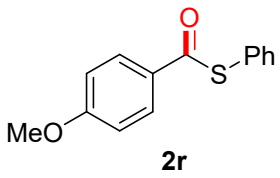

O
S
Ph

2q

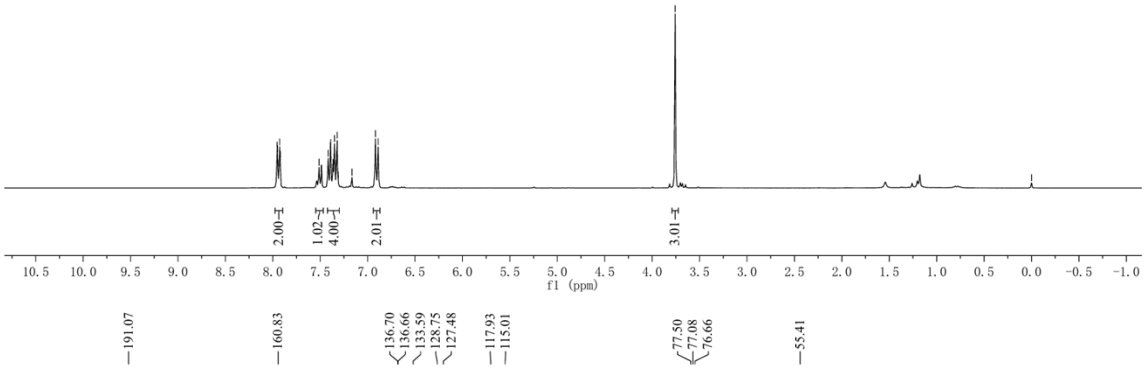

2.00
1.00
7.02
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.163
136.695
135.130
133.685
129.553
129.284
128.785
127.521
127.405
77.493
77.070
76.646
O
S
Ph
2q
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)

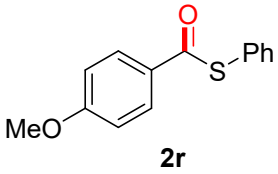

7.95
7.95
7.95
7.93
7.92
7.51
7.49
7.49
7.48
7.42
7.39
7.39
7.37
7.37
7.36
7.35
7.34
7.33
7.33
7.32
7.31
7.17
6.92
6.89
3.76
0.00


O
S
Ph
MeO

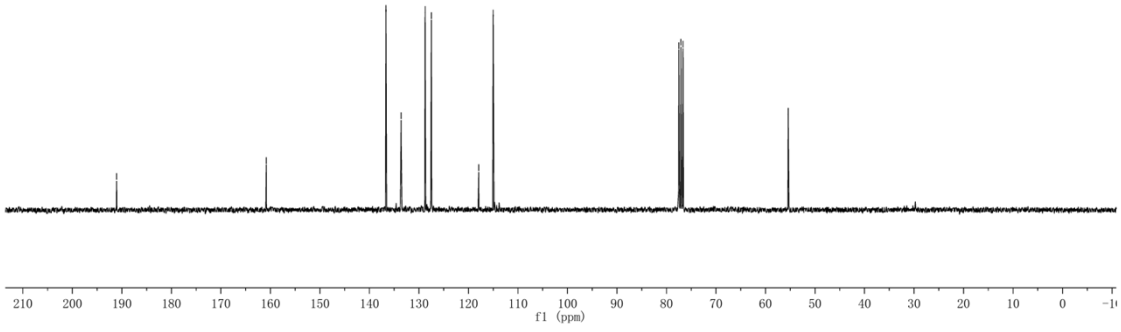
2r

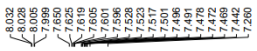

2.00
1.02
4.00
2.01
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

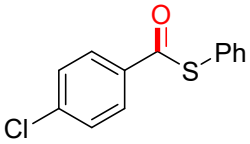
191.07
160.83
136.70
136.66
133.59
128.75
127.48
117.93
115.01
77.50
77.08
76.66
55.41


O
S
Ph
MeO

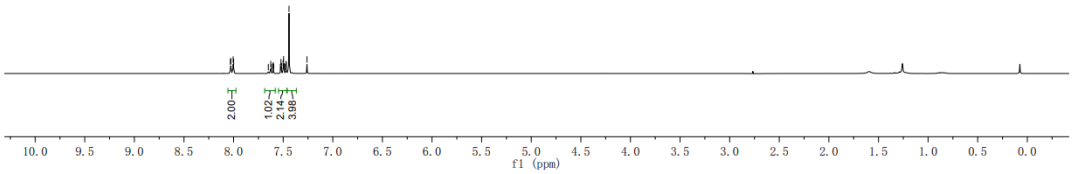
2r

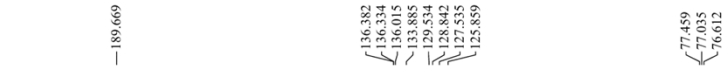

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

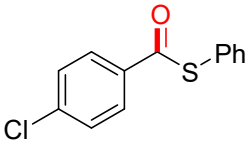

8.032
8.028
8.005
7.999
7.650
7.625
7.618
7.605
7.601
7.596
7.528
7.523
7.517
7.501
7.496
7.491
7.478
7.472
7.469
7.462
7.260


O
S
Ph
Cl

2s


2.00
1.02
2.14
3.88
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)

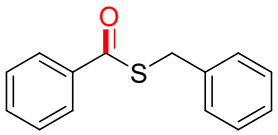

189.669
136.382
136.334
136.015
133.885
129.534
128.842
127.535
125.859
77.459
77.035
76.612


O
S
Ph
Cl

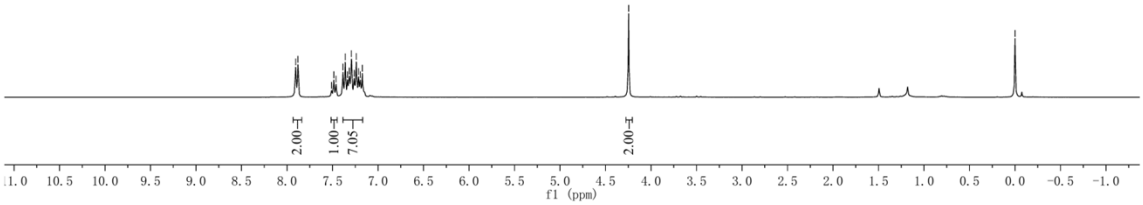
2s

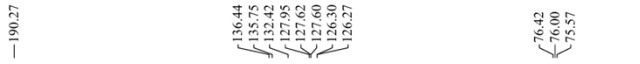
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

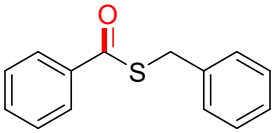

7.90
7.88
7.51
7.49
7.46
7.39
7.36
7.33
7.32
7.29
7.26
7.24
7.21
7.19
7.17
4.25
0.00


O
S

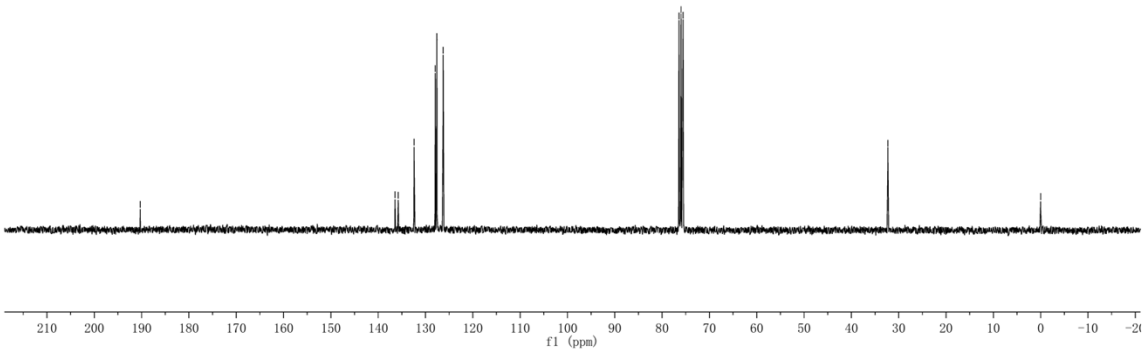
2t

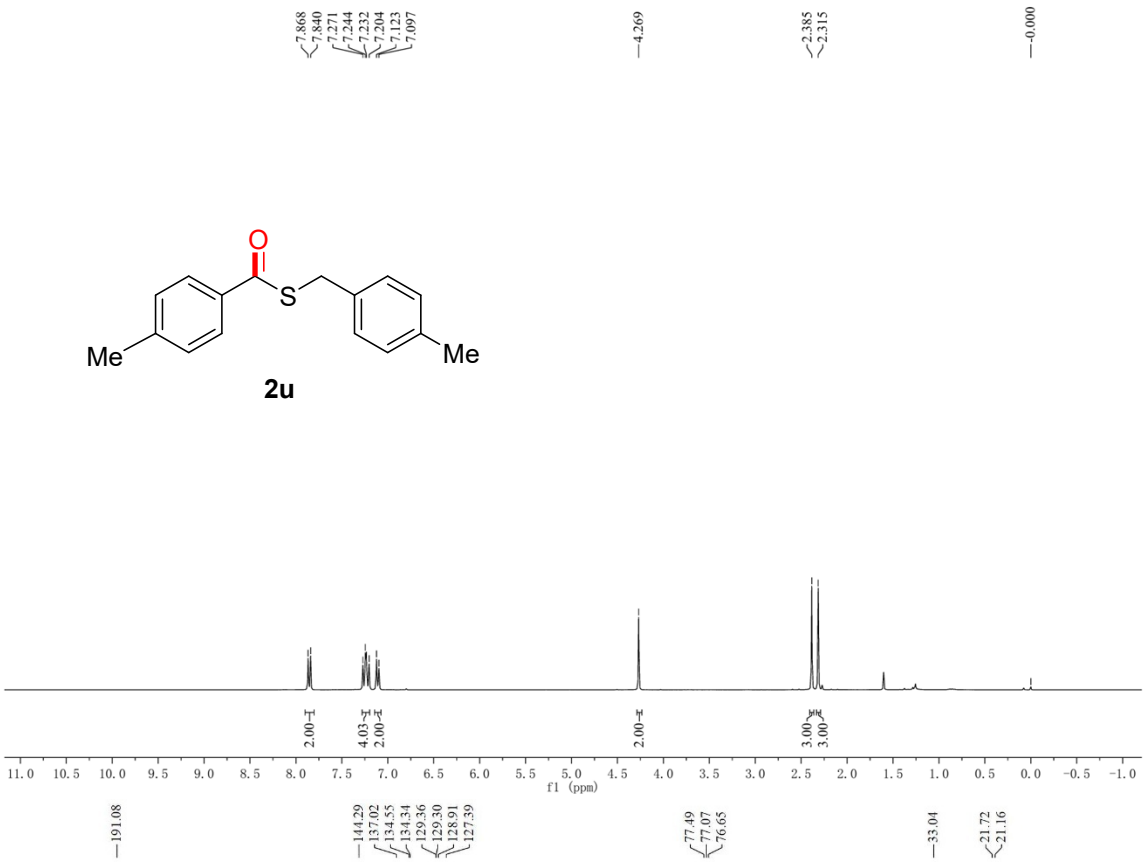

2.00
1.00
7.05
2.00
f1 (ppm)

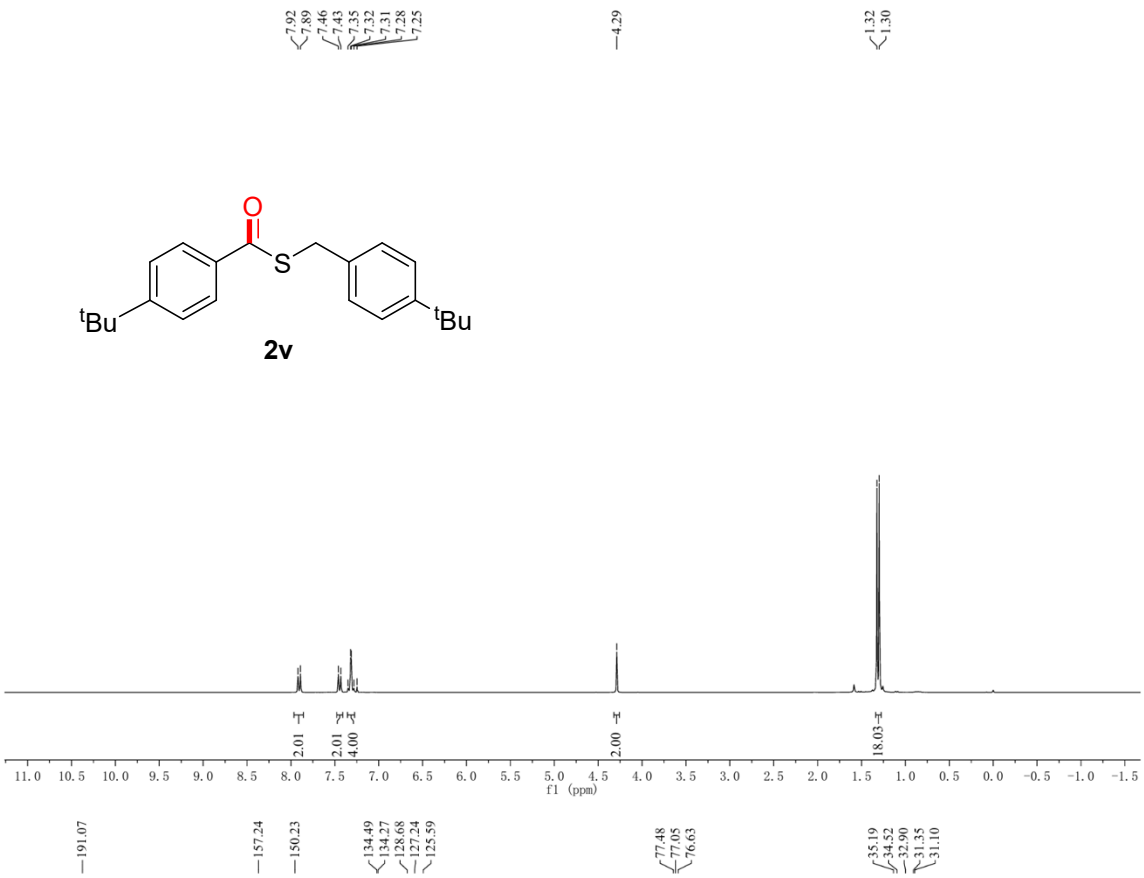

190.27
136.44
135.75
132.42
127.95
127.62
127.60
126.30
126.27
76.42
76.00
75.57
32.30
0.00


O
S

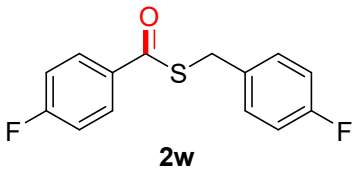
2t


f1 (ppm)

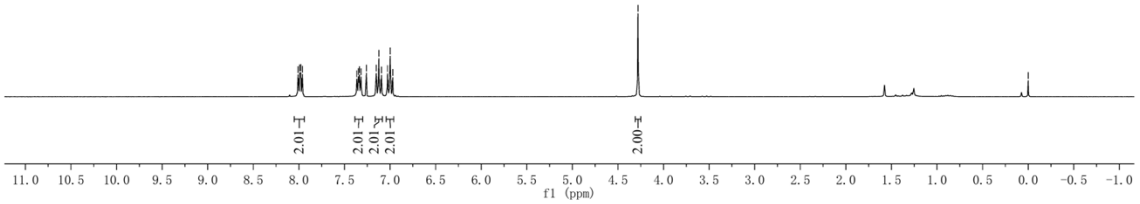

7.868
7.840
7.271
7.244
7.232
7.204
7.123
7.097
4.269
2.385
2.315
0.000
O
S
Me
Me
2u
2.00
4.03
2.00
2.00
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
191.08
144.29
137.02
134.55
134.34
129.36
129.30
128.91
127.39
77.49
77.07
76.65
33.04
21.72
21.16
O
S
Me
Me
2u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.92
7.89
7.46
7.43
7.35
7.32
7.31
7.28
7.25
4.29
1.32
1.30
O
S
tBu
tBu
2v
2.01
2.01
4.00
2.00
18.03
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 −1.5
f1 (ppm)
191.07
157.24
150.23
134.49
134.27
128.68
127.24
125.59
77.48
77.05
76.63
35.19
34.52
32.90
31.35
31.10
O
S
tBu
tBu
2v
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

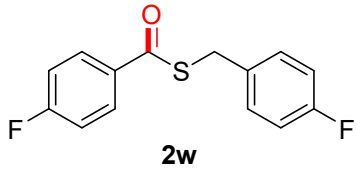

8.009
8.002
7.991
7.979
7.968
7.961
7.365
7.347
7.337
7.319
7.260
7.152
7.145
7.123
7.101
7.094
7.028
7.021
6.999
6.977
6.970
4.280
0.000


O
S
F
F

2w


2.01
2.01
2.01
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

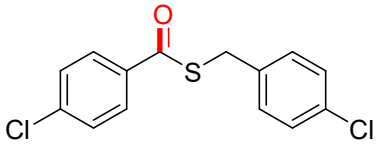

189.69
167.71
164.32
163.71
160.45
133.25
133.02
130.66
130.55
129.94
129.82
116.00
115.70
115.42
77.47
77.04
76.62
32.68


O
S
F
F

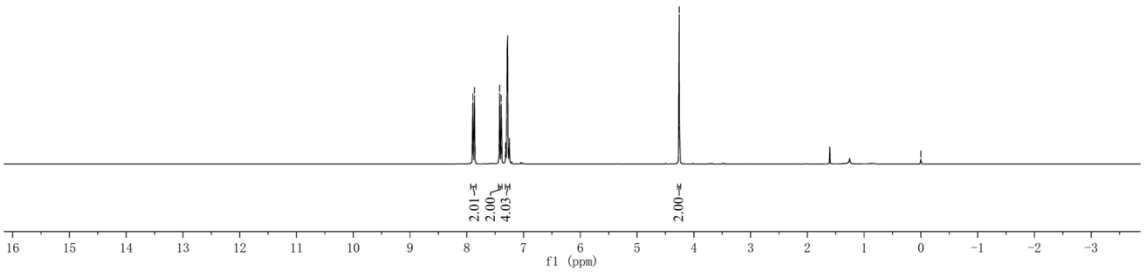
2w

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

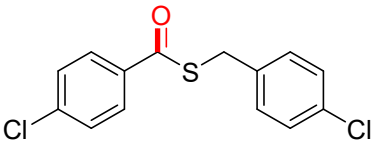

7.902
7.894
7.888
7.872
7.865
7.856
7.429
7.421
7.415
7.399
7.392
7.384
7.316
7.306
7.288
7.278
7.260
7.250
4.258
0.000


O
S
Cl
Cl

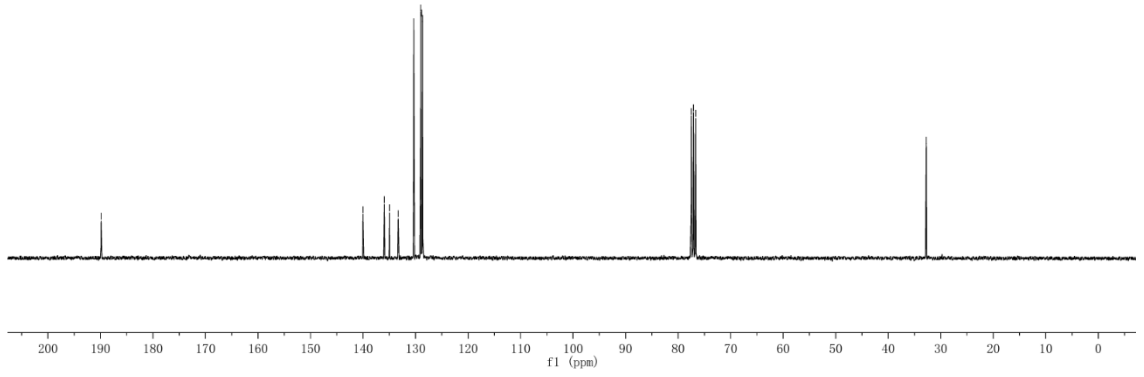
2x


2.01
2.00
4.03
2.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

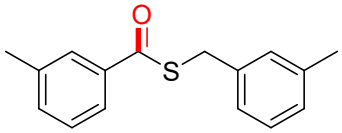

189.87
140.02
135.93
134.97
133.30
130.35
129.02
128.84
128.67
77.50
77.07
76.65
32.75


O
S
Cl
Cl

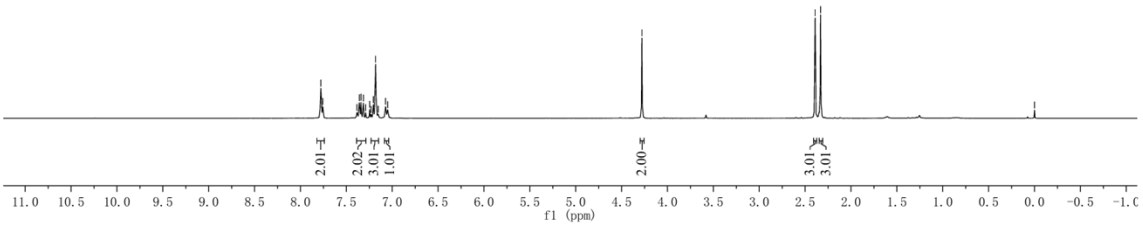
2x


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

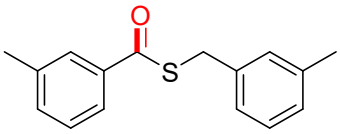

7.78
7.76
7.38
7.36
7.34
7.31
7.29
7.25
7.23
7.21
7.18
7.15
7.07
7.05
4.28
2.39
2.33
0.00


O
S

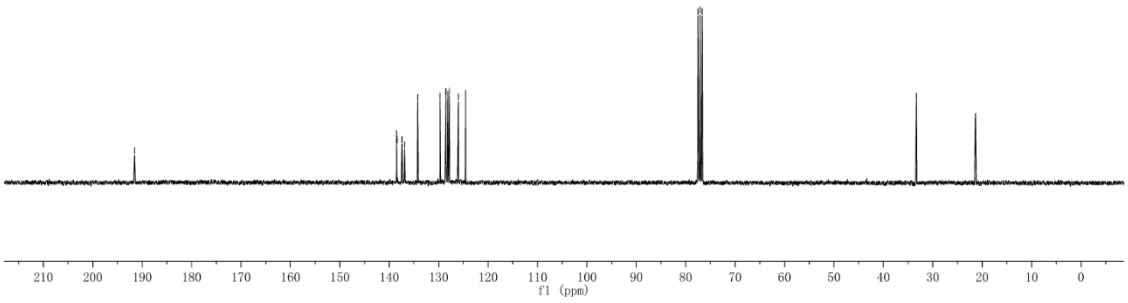
2y

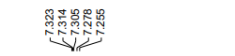

2.01
2.02
3.01
1.01
2.00
3.01
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

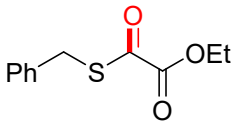

191.53
138.53
138.38
137.42
136.86
134.23
129.71
128.59
128.54
128.14
127.82
126.04
124.55
77.50
77.08
76.66
33.32
21.40
21.34


O
S

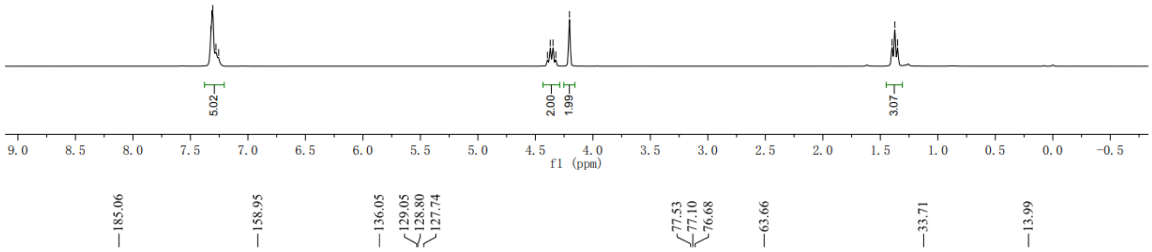
2y


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

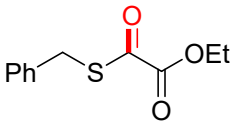

7.323
7.314
7.305
7.278
7.255
4.395
4.371
4.347
4.323
4.204
1.398
1.374
1.350


O
Ph
S
OEt
O

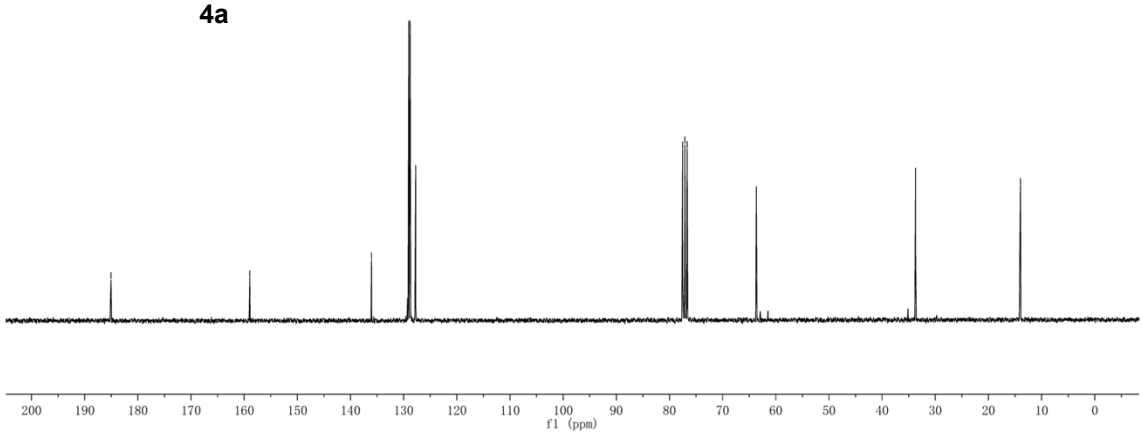
4a

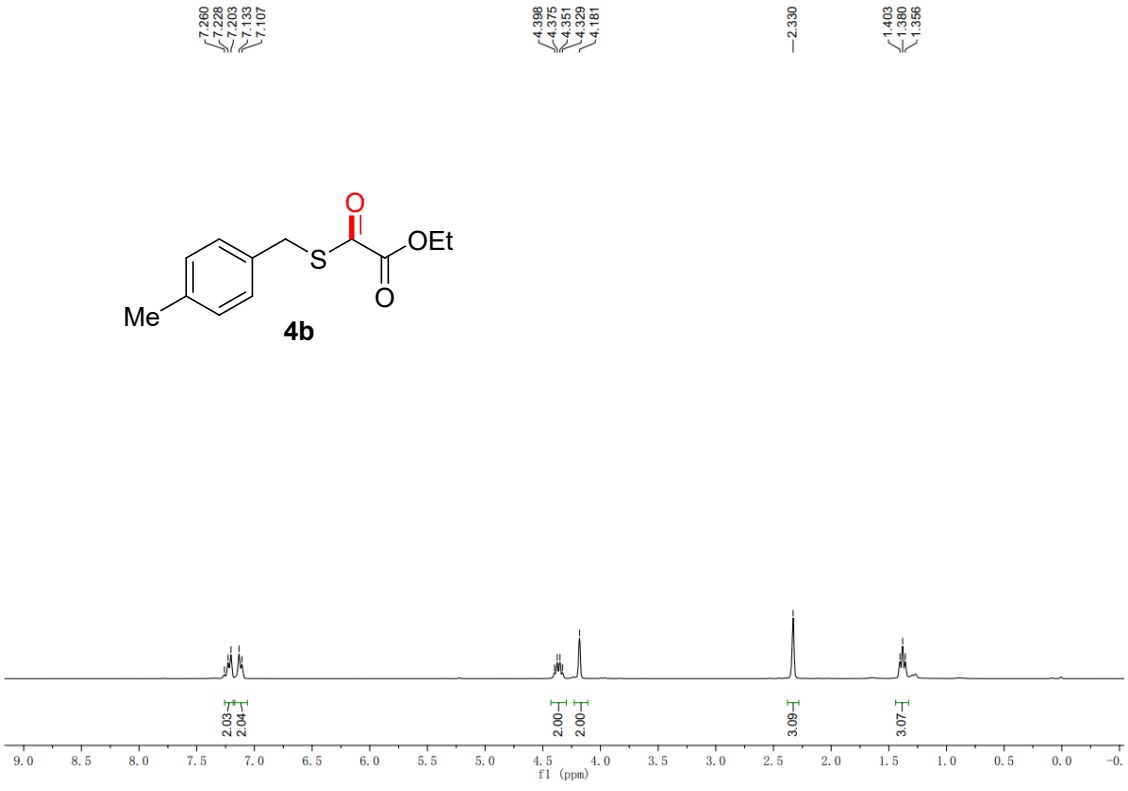

5.02
2.00
1.99
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

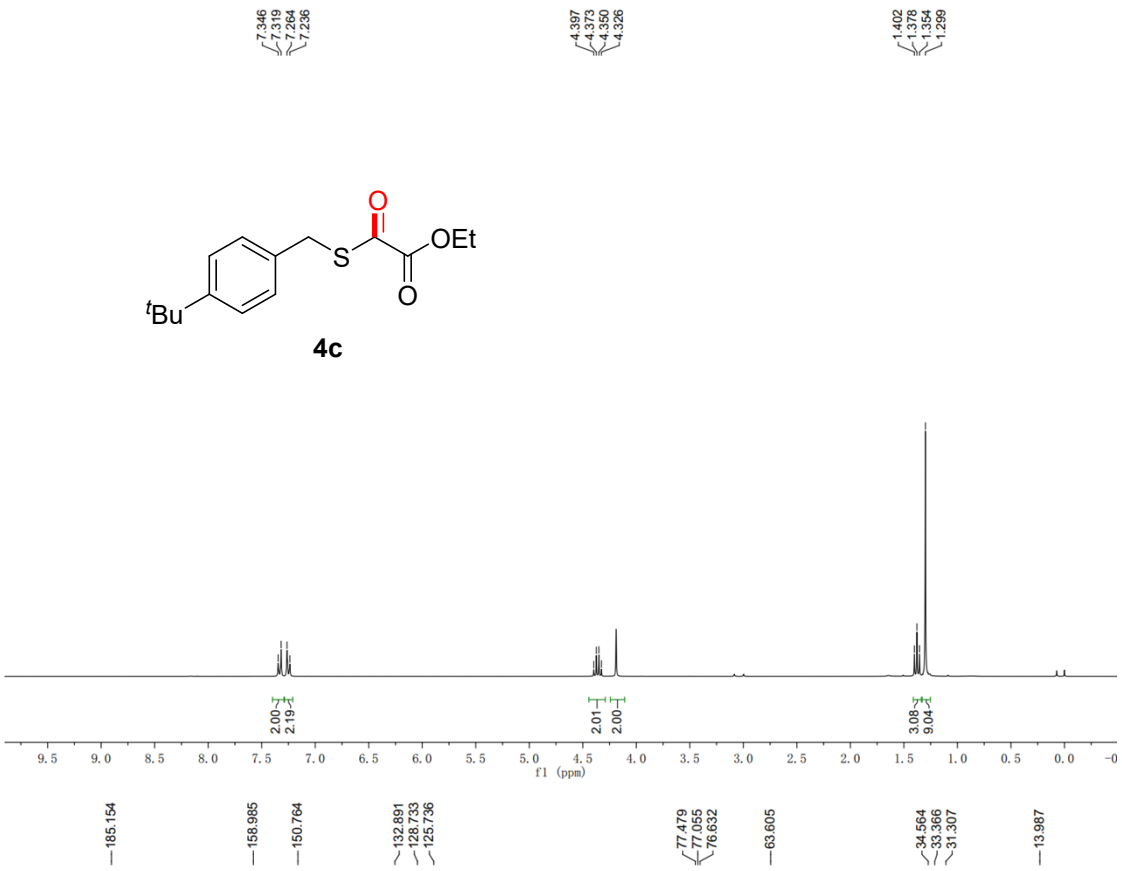
185.06
158.95
136.05
129.05
128.80
127.74
77.53
77.10
76.68
63.66
33.71
13.99

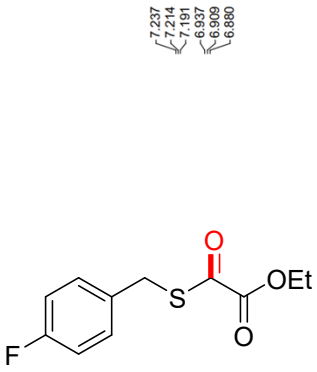

O
Ph
S
OEt
O

4a

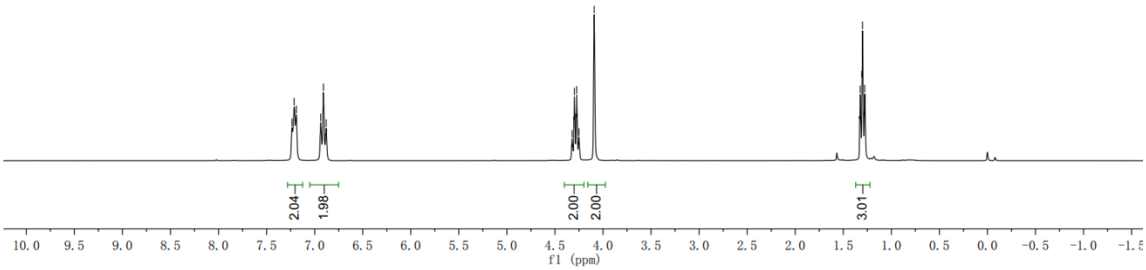

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260
7.228
7.203
7.133
7.107
4.398
4.375
4.351
4.329
4.181
2.330
1.403
1.380
1.356
O
OEt
S
O
Me
4b
2.03
2.04
2.00
2.00
3.09
3.07
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)
185.138
158.987
137.533
132.945
129.474
128.939
77.505
77.082
76.658
63.596
33.498
21.146
13.982
O
OEt
S
O
Me
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)

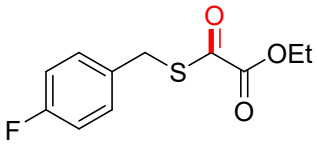

7.346
7.319
7.264
7.236
4.397
4.373
4.350
4.326
1.402
1.378
1.354
1.299
O
S
OEt
O
tBu
4c
2.00
2.19
2.01
2.00
3.08
9.04
f1 (ppm)
185.154
158.985
150.764
132.891
128.733
125.736
77.479
77.055
76.632
63.605
34.564
33.366
31.307
13.987
O
S
OEt
O
tBu
4c
f1 (ppm)


7.237
7.214
7.191
6.937
6.909
6.880
4.322
4.298
4.274
4.250
4.092
1.324
1.300
1.276
O
OEt
S
O
F

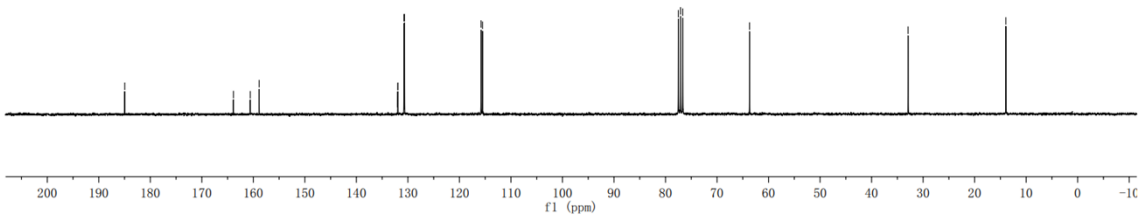
4d

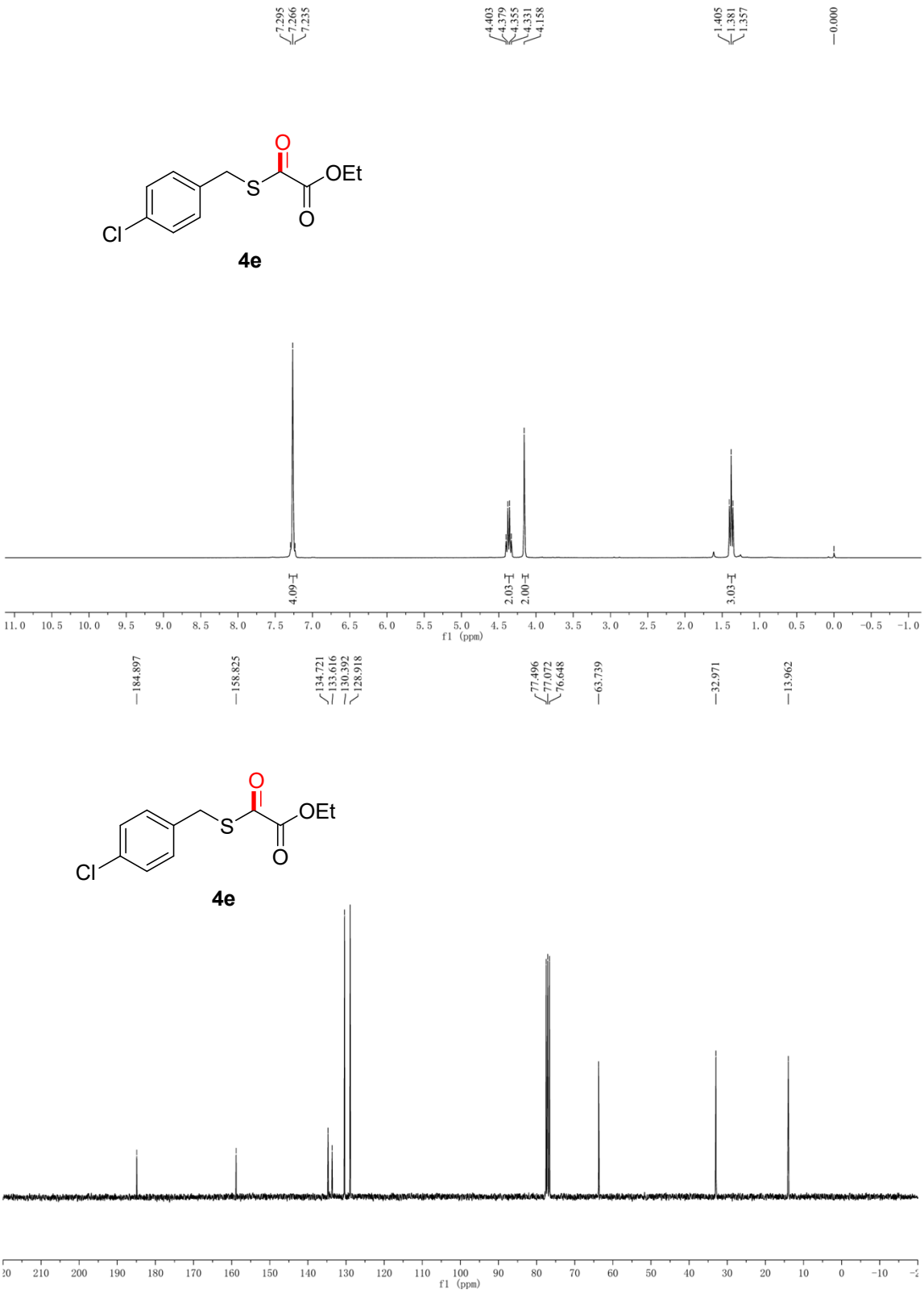

2.04
1.98
2.00
2.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

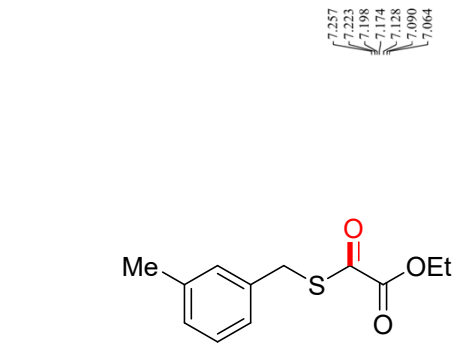

184.961
163.870
160.602
158.871
131.970
131.926
130.763
130.654
115.804
115.517
77.506
77.083
76.659
63.687
32.917
13.946


O
OEt
S
O
F

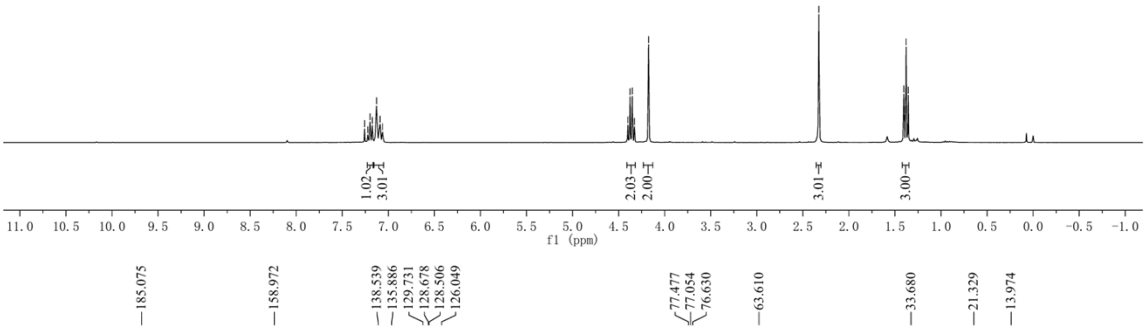
4d

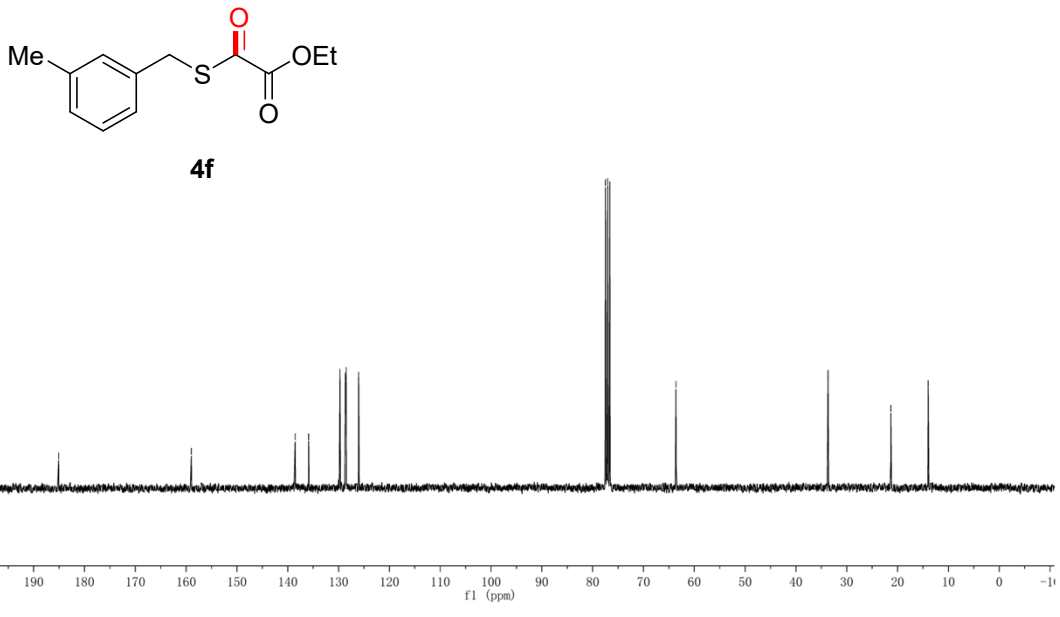

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.295
7.266
7.235
4.403
4.379
4.355
4.331
4.158
1.405
1.381
1.357
0.000
O
OEt
S
O
Cl
4e
4.09
2.03
2.00
3.03
f1 (ppm)
184.897
158.825
134.721
133.616
130.392
128.918
77.496
77.072
76.648
63.739
32.971
13.962
O
OEt
S
O
Cl
4e
f1 (ppm)

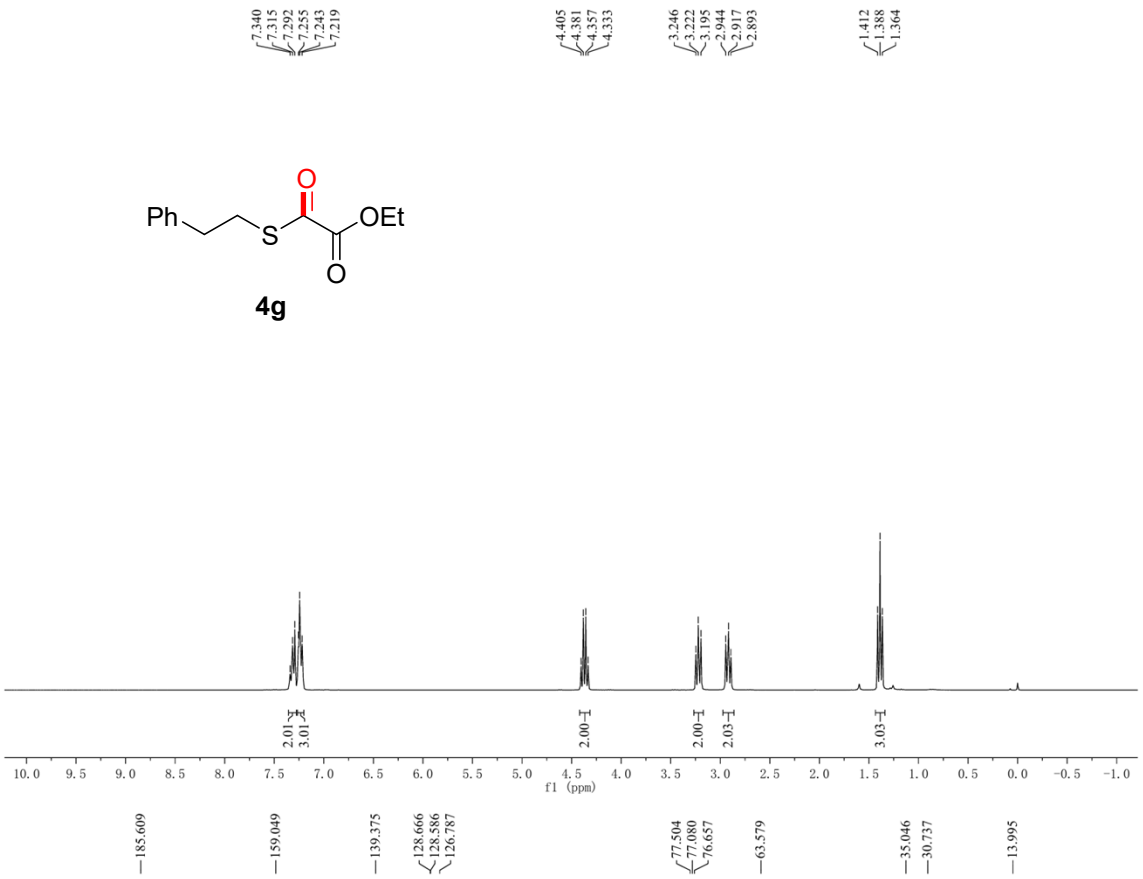


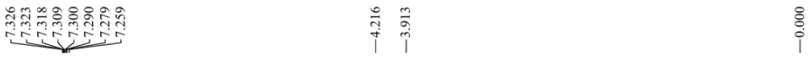
4f

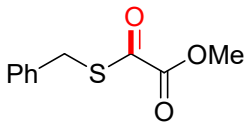




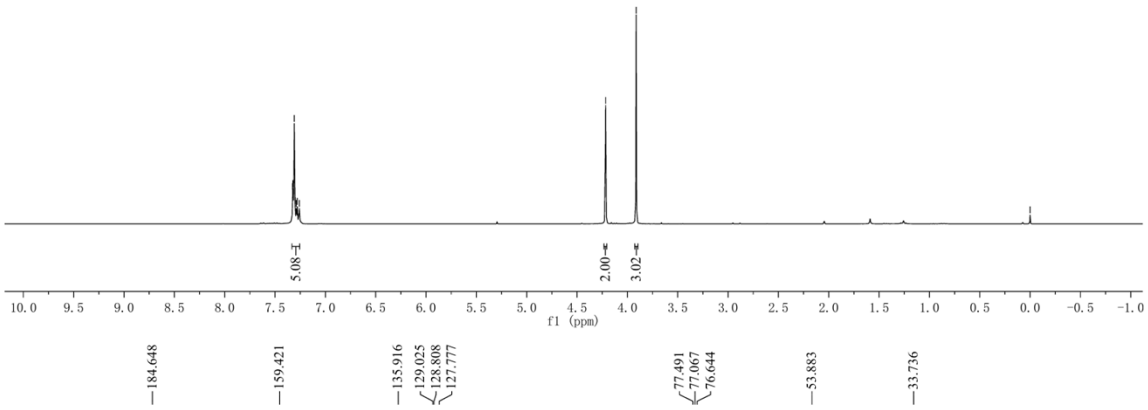
4f


7.340
7.315
7.292
7.255
7.243
7.219
4.405
4.381
4.357
4.333
3.246
3.222
3.195
2.944
2.917
2.893
1.412
1.388
1.364
Ph
S
O
OEt
O
4g
2.01
3.01
2.00
2.00
2.03
3.03
f1 (ppm)
185.609
159.049
139.375
128.666
128.586
126.787
77.504
77.080
76.657
63.579
35.046
30.737
13.995
Ph
S
O
OEt
O
4g
f1 (ppm)

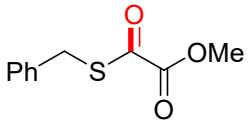

7.326
7.323
7.318
7.309
7.300
7.290
7.279
7.259
4.216
3.913
0.000


O
Ph
S
OMe
O

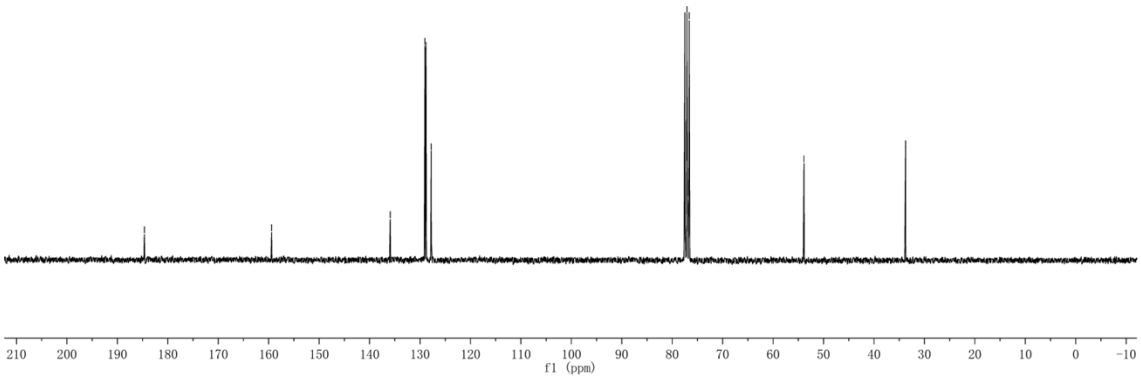
4h


5.08
2.00
3.02
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)

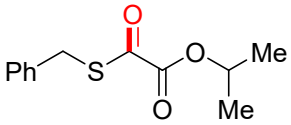
184.648
159.421
135.916
129.025
128.808
127.777
77.491
77.067
76.644
53.883
33.736


O
Ph
S
OMe
O

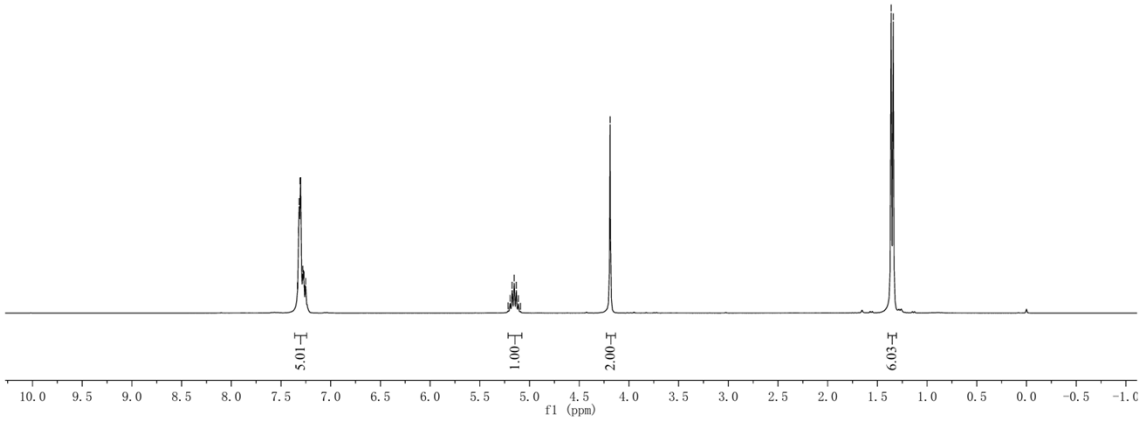
4h

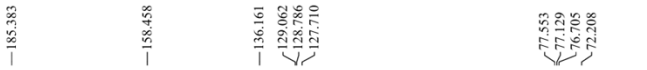

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

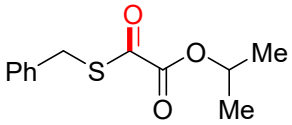

7.335
7.323
7.318
7.308
7.302
7.285
7.280
7.273
7.268
7.257
7.252
5.216
5.195
5.175
5.154
5.133
5.112
5.091
4.189
1.362
1.341


O
Ph
S
O
O
Me
Me

4i


5.01
1.00
2.00
6.03
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)


185.383
158.458
136.161
129.062
128.786
127.710
77.553
77.129
76.705
72.208
33.696
21.552


O
Ph
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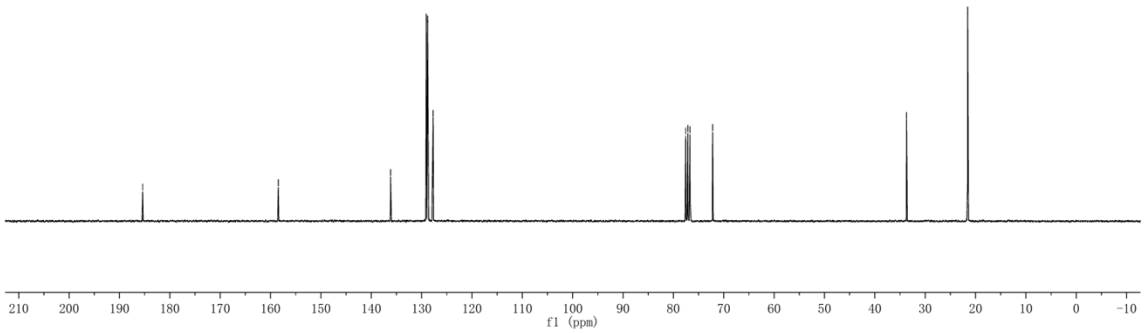
4i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f1 (ppm)