Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.




# Supporting Information

## Visible Light-Induced Selective Aerobic Oxidative Transposition of Vinyl Halides Using a Tetrahalogenoferrate (III) Complex Catalyst

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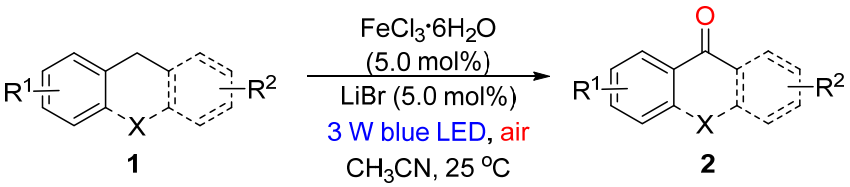
## 1. General information

Column chromatography was carried out with *silica gel* 60 (particle size 0.040–0.063 mm, 230–400 mesh) and commercially available solvents. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with *silica gel* 60 F254 with visualization by a UV lamp (254 or 360 nm).

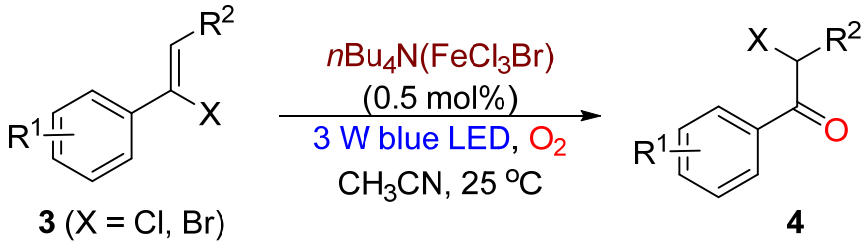
$^{1}$H and $^{13}$C NMR spectra were recorded at 300 and 75 MHz at 25 $^{o}$C with a 300 MHz instrument. Chemical shifts are reported in parts per million (ppm), using the residual solvent signal as an internal standard: $CDCl_3$ ($^{1}$H NMR: $\delta$ 7.26, singlet; $^{13}$C NMR: $\delta$ 77.0, triplet). Multiplicities were given as: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *quintet*, *m* (multiplets), *dd* (doublet of doublets), *dt* (doublet of triplets), and *br* (broad). Coupling constants (*J*) were recorded in Hertz (Hz). The number of proton atoms (*n*) for a given resonance was indicated by *n*H. The number of carbon atoms (*n*) for a given resonance was indicated by *n*C. HRMS was reported in units of mass of charge ratio (m/z). Mass samples were dissolved in DCM and MeOH (HPLC grade) unless otherwise stated. Electrochemical measurements were carried out by cyclic voltammetry (CV). The cyclic voltammetry was performed with an Autolab potentiostat by Echochemie under nitrogen atmosphere in a one-compartment electrolysis cell consisting of a platinum wire working electrode, a platinum wire counter electrode, and a quasi Ag/AgCl reference electrode. Cyclic voltammograms were monitored at scan rates of either 100 $mV \bullet s^{-1}$ or 50 $mV \bullet s^{-1}$ and recorded in distilled acetonitrile. The concentration of the complex was maintained at 0.5 mM or less and each solution contained 0.1 M of tetrabutylammonium hexafluorophosphate (TBAP) as the electrolyte.

## 2. General experimental procedure for the synthesis of 2



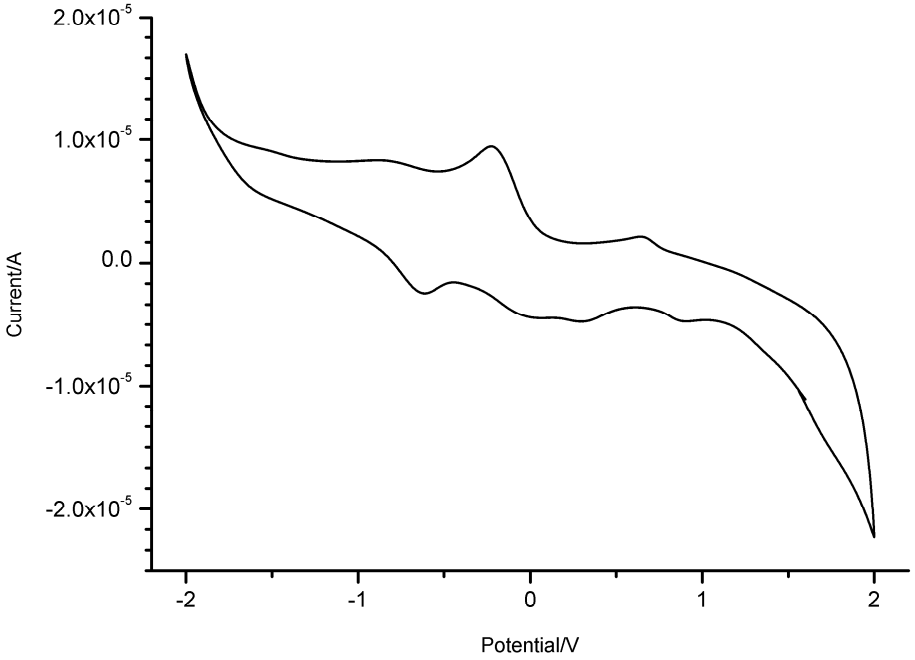

To a stirred solution of $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol, 0.05 equiv) and LiBr (0.87 mg, 0.01 mmol, 0.05 equiv) in 2.0 mL of MeCN (HPLC grade) was added compound **1** (0.2 mmol, 1.0 equiv). Then the reaction mixture was stirred at 25 °C under an ambient atmosphere (the temperature was maintained in an incubator) and irradiated by a 3 W blue LED (λ = 450–455 nm). The reaction was monitored by TLC or GC analysis. Upon complete consumption of **1**, the solvent was removed *in vacuo*. The reaction mixture was purified by flash chromatography on *silica gel*, followed by gradient elution with petroleum ether to petroleum ether/ethyl acetate (100/1 ratio), then concentrated the solvent *in vacuo* to afford products **2a-r**.

### 3. General experimental procedure for the synthesis of 4




$FeCl_3 \cdot 6H_2O$ (0.27 mg, 0.001 mmol, 0.005 equiv) and TBAB (0.32 mg, 0.001 mmol, 0.005 equiv) were added in 2.0 mL of MeCN (HPLC grade) and the reaction mixture was stirred for 10 minutes at 25 $^{o}$C (the temperature was maintained in an incubator) under an ambient atmosphere with an oxygen balloon. To the stirred solution, compound **3** was then added and irradiated by a 3 W blue LED (λ = 450–455 nm). The reaction was monitored by TLC or GC analysis. Upon complete consumption of **3**, the solvent was removed *in vacuo*. The reaction mixture was purified by flash chromatography on *silica gel*, followed by gradient elution with petroleum ether to petroleum ether/ethyl acetate (100/1 ratio), then concentrated the solvent *in vacuo* to afford products **4a-v** and **5**.

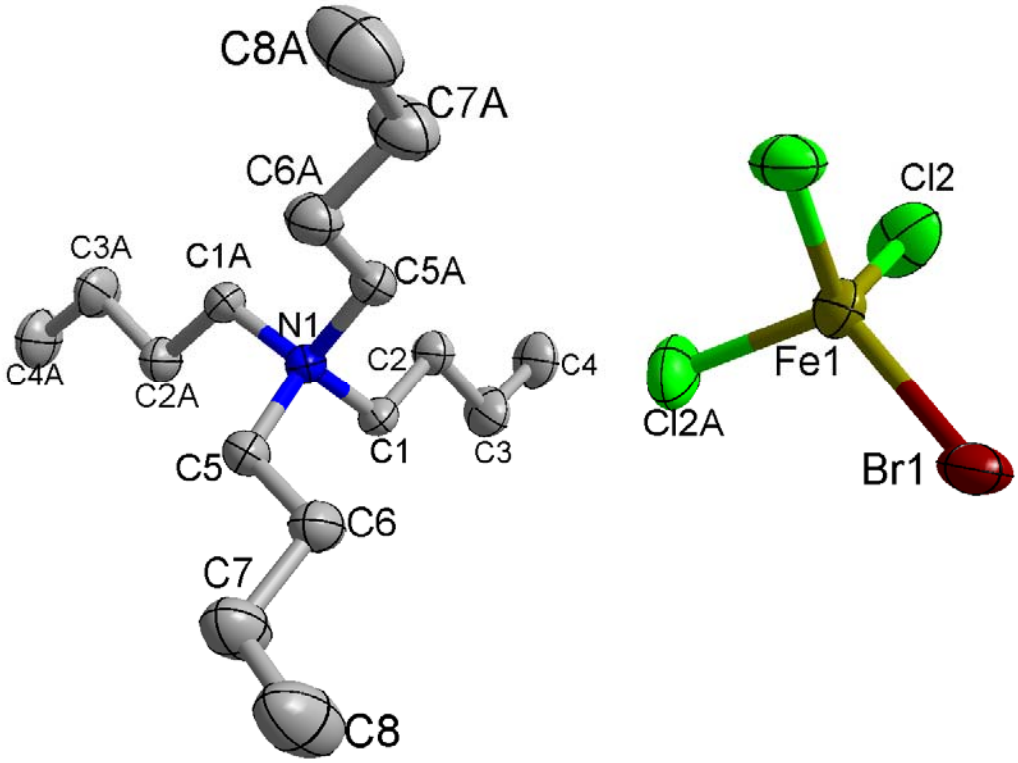
## 4. The measurement of redox potentials TBA($FeCl_3Br$)




$E_{1/2(red1)}$ = −0.295 V, $E_{1/2(ox1)}$ = −0.642 V. $E_{1/2(ox1)}/E_{1/2(red1)}$ are half-wave potentials of the first oxidation/reduction measured in $CH_3CN$ versus SCE

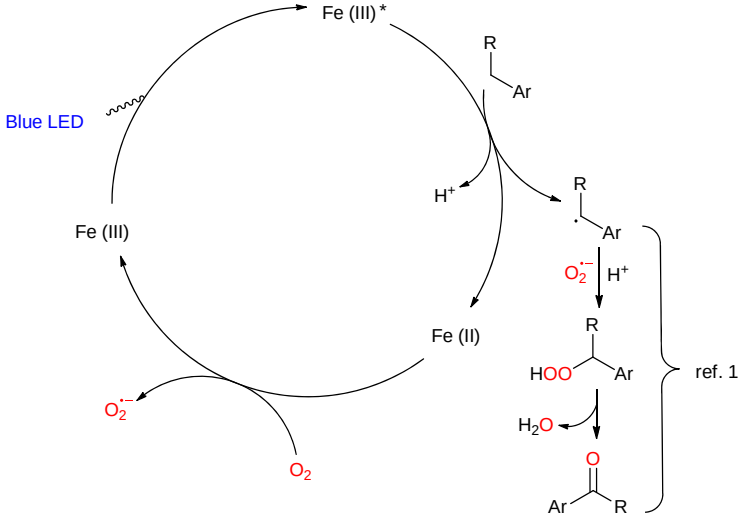
## 5. X-Ray crystallography of TBA($FeCl_3Br$)

TBA($FeCl_3Br$): CCDC 1525407



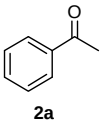

**Displacement ellipsoids are drawn at the 30% probability level. (Solvent: ethyl acetate)**

## 6. Proposed mechanism for oxygenation of benzylic $sp^3$ C−H



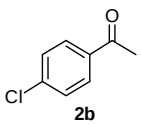

1. H. Yi, C. Bian, X. Hu, L. Niu, A. Lei, *Chem. Commun.,* 2015, **51**, 14046.

## 7. Characterization data



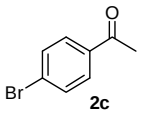
**2a**

Colorless oil; 93% yield (from **1a**, 22.3 mg); 92% yield (from **1s**, 22.1 mg) $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.04–7.88 (m, 2H), 7.54 (ddd, *J* = 6.5, 3.8, 1.2 Hz, 1H), 7.43 (dd, *J* = 10.3, 4.6 Hz, 2H), 2.58 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 198.1, 136.9, 133.0, 128.5, 128.2, 26.5.



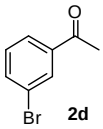
**2b**

Colorless oil; 71% yield (21.9 mg); 1H NMR (300 MHz, CDCl3) δ 7.94–7.79 (m, 2H), 7.48–7.32 (m, 2H), 2.57 (d, J = 1.3 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl3) δ 196.8, 139.4, 135.3, 129.6, 128.8, 26.5.



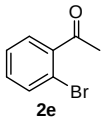
**2c**

White soild; 67% yiled (26.7 mg); $^{1}$H NMR (300 MHz, CDCl3) δ 7.87–7.71 (m, 2H), 7.63–7.49 (m, 2H), 2.55 (s, 3H); $^{13}$C NMR (75 MHz, CDCl3) δ 196.9, 135.7, 131.8, 129.7, 128.2, 26.4.



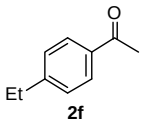
**2d**

Colorless oil; 78% yield (31.0 mg); $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.07 (t, *J* = 1.7 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.72–7.64 (m, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 2.58 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 196.6, 138.7, 135.9, 131.3, 130.2, 126.8, 122.9, 26.6.



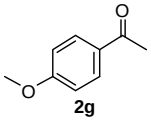
**2e**

Colorless oil; 72% yield (28.7 mg); $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.33–7.27 (m, 1H), 2.62 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 201.2, 141.2, 133.7, 131.7, 128.8, 127.3, 118.7, 30.2.



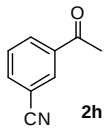
**2f**

Colorless oil; 68% yield (20.2 mg); $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 2.76 (q, *J* = 7.6 Hz, 2H), 2.63 (s, 3H), 1.31 (t, *J* = 7.6 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 197.9, 150.1, 134.9, 128.5, 128.1, 28.9, 26.6, 15.2.



**2g**

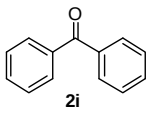
Pale yellow oil; 74% yield (22.2 mg); $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.8 Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 196.8, 163.5, 130.6, 130.3, 113.7, 55.5, 26.3.



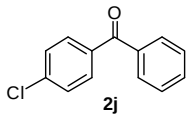
**2h**

Colorless oil; 35% yield (10.2 mg); $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.17 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 2.63 (s, 3H); $^{13}$C NMR

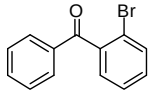
(75 MHz, $CDCl_3$) δ 195.8, 137.6, 135.9, 132.2, 131.9, 129.6, 117.9, 113.0, 26.5.


**2i**

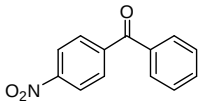
White solid; 76% yield (27.7 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.91–7.73 (m, 4H), 7.64–7.53 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 196.5, 137.4, 132.3, 129.9, 128.1.


**2j**

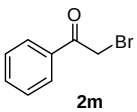
White solid; 79% yield (34.2 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.87–7.70 (m, 4H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.48 (dd, *J* = 12.1, 7.9 Hz, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 195.5, 138.9, 137.2, 135.8, 132.6, 131.4, 129.9, 128.6, 128.4.


**2k**

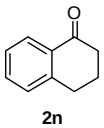
White solid; 90% yield (47.0 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.85–7.78 (m, 2H), 7.66 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.62–7.56 (m, 1H), 7.47 (dd, *J* = 10.6, 4.6 Hz, 2H), 7.41 (dd, *J* = 6.6, 1.9 Hz, 1H), 7.36 (td, *J* = 7.9, 1.9 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 195.9, 140.6, 136.1, 133.7, 133.2, 131.1, 130.2, 129.0, 128.6, 127.2, 119.5.


**2l**

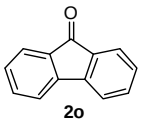
White solid; 54% yield (24.5mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.40 – 8.28 (m, 2H), 7.99 – 7.89 (m, 2H), 7.80 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.66 (ddd, *J* = 7.4, 4.0, 1.2 Hz, 1H), 7.52 (dd, *J* = 10.5, 4.6 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 194.8, 149.8, 142.8, 136.2, 133.5, 130.7, 130.1, 128.7, 123.5.


**2m**

White solid; 81% yield (from **1m**, 32.2 mg); 83% yield (from **3a**, 33.0 mg) $^1$H NMR (300 MHz, $CDCl_3$) δ 8.02–7.94 (m, 2H), 7.65–7.56 (m, 1H), 7.48 (dd, *J* = 10.4, 4.7 Hz, 2H), 4.46 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 191.2, 133.9, 128.9, 128.8, 30.9.

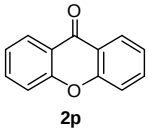

**2n**

Colorless oil; 72% yield (21.0 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.28 (dd, *J* = 18.9, 7.9 Hz, 2H), 2.96 (t, *J* = 6.0 Hz, 2H), 2.65 (t, *J* = 6.5 Hz, 2H), 2.28–1.98 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 198.4, 144.5, 133.4, 132.6, 128.8, 127.2, 126.6, 39.2, 29.7, 23.3.



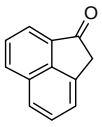
**2o**

White solid; 88% yield (31.7 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.3 Hz, 2H), 7.54–7.43 (m, 4H), 7.33–7.25 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 193.9, 144.4, 134.7, 134.1, 129.0, 124.3, 120.3.



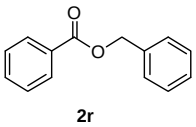
**2p**

White solid; 99% yield (37.6 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.9 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 177.2, 156.1, 134.8, 126.7, 123.9, 121.7, 117.9.



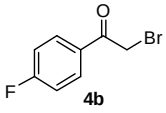
**2q**

White solid; 52% yield (17.5 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 7.0 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 6.8 Hz, 1H), 3.82 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 203.0, 142.9, 134.9, 134.6, 131.5, 130.9, 128.3, 128.0, 123.9, 121.4, 121.0, 42.0.



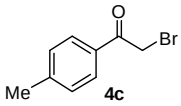
**2r**

White solid; 86% yield (36.5 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 6.9 Hz, 1H), 7.42 (dd, *J* = 12.9, 8.8 Hz, 7H), 5.39 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 166.4, 136.0, 133.0, 130.0, 129.7, 128.6, 128.3, 128.2, 128.1, 66.6.



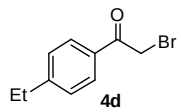
**4b**

White solid; 82% yield (35.6 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.08–7.97 (m, 2H), 7.22–7.11 (m, 2H), 4.41 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 189.8, 167.8, 164.4, 131.8, 131.7, 130.3, 130.2, 116.2, 116.0, 30.4.



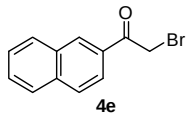
**4c**

White solid; 83% yield (35.3 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.43 (s, 2H), 2.43 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 191.0, 145.0, 131.4, 129.5, 129.0, 30.9, 21.8.



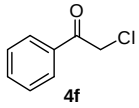
**4d**

White solid; 86% yield (39.1 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.44 (s, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 191.0, 151.1, 131.6, 129.2, 128.4, 31.0, 29.0, 15.1.



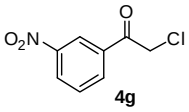
**4e**

White solid; 76% yield (37.9 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.99 (dd, *J* = 14.5, 8.3 Hz, 2H), 7.94–7.84 (m, 2H), 7.70–7.49 (m,2H), 4.58 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 191.2, 135.8, 132.3, 131.2, 130.9, 129.6, 129.0, 128.8, 127.8, 127.0, 124.1, 31.0.



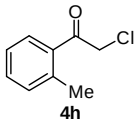
**4f**

White solid; 80% yield (24.7 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 4.72 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 191.0, 134.2, 134.0, 128.9, 128.5, 46.0.



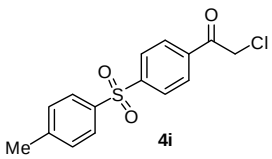
**4g**

White solid; 72% yield (28.7mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.79 (t, *J* = 1.9 Hz, 1H), 8.48 (ddd, *J* = 8.2, 2.1, 0.9 Hz, 1H), 8.39–8.24 (m, 1H), 7.74 (t, *J* = 8.0 Hz, 1H), 4.73 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 189.3, 148.5, 135.3, 134.1, 130.3 128.2, 123.5, 45.4.



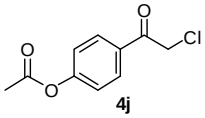
**4h**

White solid; 73% yield (24.6 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.0 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 2H), 4.64 (s, 2H), 2.53 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 194.2, 139.5, 134.5, 132.4, 128.6, 125.8, 47.9, 21.4.



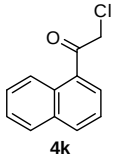
**4i**

Colorless oil; 54% yield (36.5 mg); 1H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.65 (s, 2H), 2.46 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 189.8, 153.6, 146.0, 132.8, 132.0, 130.4, 130.0, 128.5, 122.9, 45.7, 21.8.



**4j**

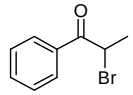
White solid; 87% yield (37.0 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 4.69 (s, 2H), 2.33 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 189.9, 168.7, 154.9, 131.7, 130.2, 122.1, 45.8, 21.1.



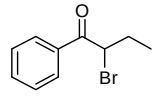
**4k**

White solid; 74% yield (30.3 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.89 (t, *J* = 7.4 Hz, 2H), 7.69–7.47 (m, 3H), 4.78 (s, 2H);

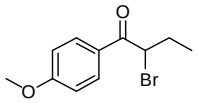
$^{13}$C NMR (75 MHz, $CDCl_3$) δ 194.4, 134.0, 133.9, 132.4, 130.4, 128.6, 128.5, 128.2, 126.8, 125.5, 124.2, 48.0.


**4l**

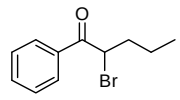
Pale yellow oil; 74% yield (36.2 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 6.9 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 5.45–5.18 (m, 1H), 1.91 (d, *J* = 6.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 193.3, 134.0, 133.6, 128.9, 128.7, 41.4, 20.1


**4m**

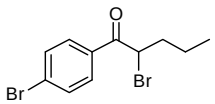
Pale yellow oil; 85% yield (38.6 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.0 Hz, 2H), 5.08 (dd, *J* = 9.3, 4.3 Hz, 1H), 2.36–2.05 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 193.2, 134.5, 133.6, 128.8, 128.7, 49.0, 26.9, 12.1.


**4m**

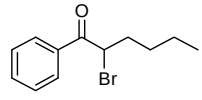
White solid; 81% yield (41.6 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 5.04 (t, *J* = 6.8 Hz, 1H), 3.87 (s, 3H), 2.33–1.99 (m, 2H), 1.07 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 191.8, 163.9, 131.2, 127.2, 113.9, 55.5, 49.0, 27.0, 12.2.


**4o**

Pale yellow oil; 90% yield (43.2 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 5.16 (t, *J* = 6.9 Hz, 1H), 2.25–2.04 (m, 2H), 1.69–1.34 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 193.3, 134.4, 133.6, 128.8, 128.7, 47.0, 35.4, 20.7, 13.6.

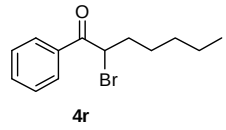

**4p**

Pale yellow oil; 86% yield (49.0 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 5.07 (t, *J* = 7.0 Hz, 1H), 2.23 – 2.01 (m, 2H), 1.49 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 192.2, 133.1, 132.1, 130.3, 128.9, 46.8, 35.2, 20.7, 13.6.


**4q**

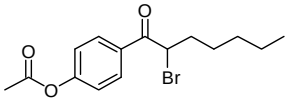
Pale yellow oil; 88% yield (45.0 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.1 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 2H), 5.14 (t, *J* = 6.8 Hz,

1H), 2.29 – 2.05 (m, 2H), 1.56 – 1.30 (m, 4H), 0.93 (d, $J$ = 5.7 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 193.3, 134.4, 133.6, 128.8, 128.7, 47.2, 33.2, 29.6, 22.2, 13.9.



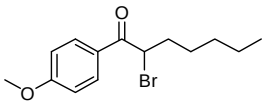
**4r**

Pale yellow oil; 79% yield (42.7 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, $J$ = 7.6 Hz, 2H), 7.60 (t, $J$ = 7.1 Hz, 1H), 7.49 (t, $J$ = 7.4 Hz, 2H), 5.14 (t, $J$ = 7.0 Hz, 1H), 2.29–2.01 (m, 2H), 1.60–1.29 (m, 6H), 0.89 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 193.3, 134.4, 133.6, 128.8, 128.7, 47.2, 33.4, 31.2, 27.2, 22.4, 13.9.



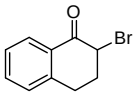
**4s**

Pale yellow oil; 82% yield (42.7 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, $J$ = 8.3 Hz, 2H), 7.21 (d, $J$ = 8.3 Hz, 2H), 5.09 (t, $J$ = 7.1 Hz, 1H), 2.32 (s, 3H), 2.25–2.04 (m, 2H), 1.55–1.39 (m, 2H), 1.34 (s, 4H), 0.89 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 192.0, 168.7, 154.6, 132.0, 130.5, 121.9, 47.1, 33.4, 31.2, 27.1, 22.4, 21.1, 13.9.



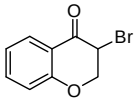
**4t**

Pale yellow oil; 86% yield (51.5 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, $J$ = 7.6 Hz, 2H), 6.95 (d, $J$ = 8.4 Hz, 2H), 5.10 (t, $J$ = 7.0 Hz, 1H), 3.87 (s, 3H), 2.12 (tt, $J$ = 22.1, 10.9 Hz, 2H), 1.47 (dd, $J$ = 18.7, 10.0 Hz, 2H), 1.33 (s, 4H), 0.88 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 191.9, 163.9, 131.2, 127.3, 113.9, 55.5, 47.2, 33.6, 31.3, 27.2, 22.4, 13.9.



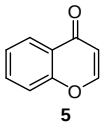
**4u**

Pale yellow oil; 58% yield (26.3 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, $J$ = 7.8 Hz, 1H), 7.49 (t, $J$ = 7.4 Hz, 1H), 7.32 (t, $J$ = 7.5 Hz, 1H), 7.25 (d, $J$ = 8.6 Hz, 1H), 4.70 (s, 1H), 3.41–3.19 (m, 1H), 2.89 (d, $J$ = 17.1 Hz, 1H), 2.63–2.22 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 190.5, 143.0, 134.1, 129.9, 128.7, 128.6, 127.1, 50.4, 31.9, 26.1.



**4v**

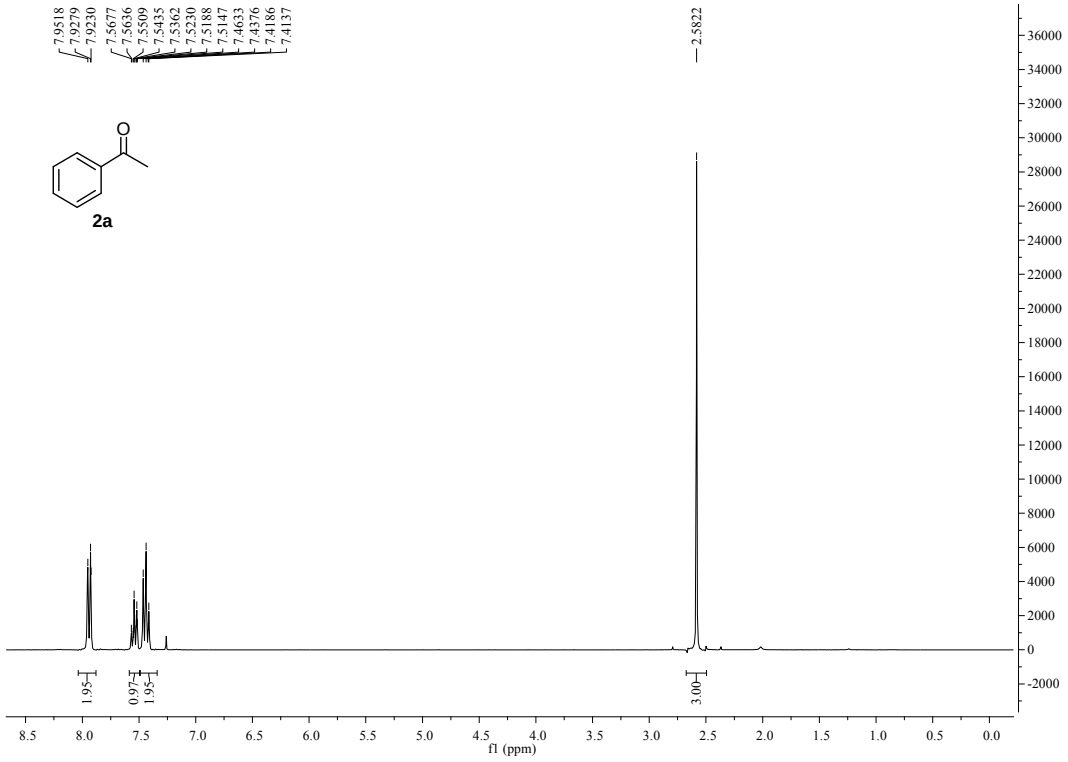
Pale yellow oil; 33% yield (15.0 mg); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, $J$ = 7.9 Hz, 1H), 7.54 (t, $J$ = 7.7 Hz, 1H), 7.07 (dd, $J$ = 19.8, 8.1 Hz, 2H), 4.78 – 4.38 (m, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 185.2, 160.6, 136.7, 128.2, 122.3, 118.7, 117.9, 71.2, 45.3.

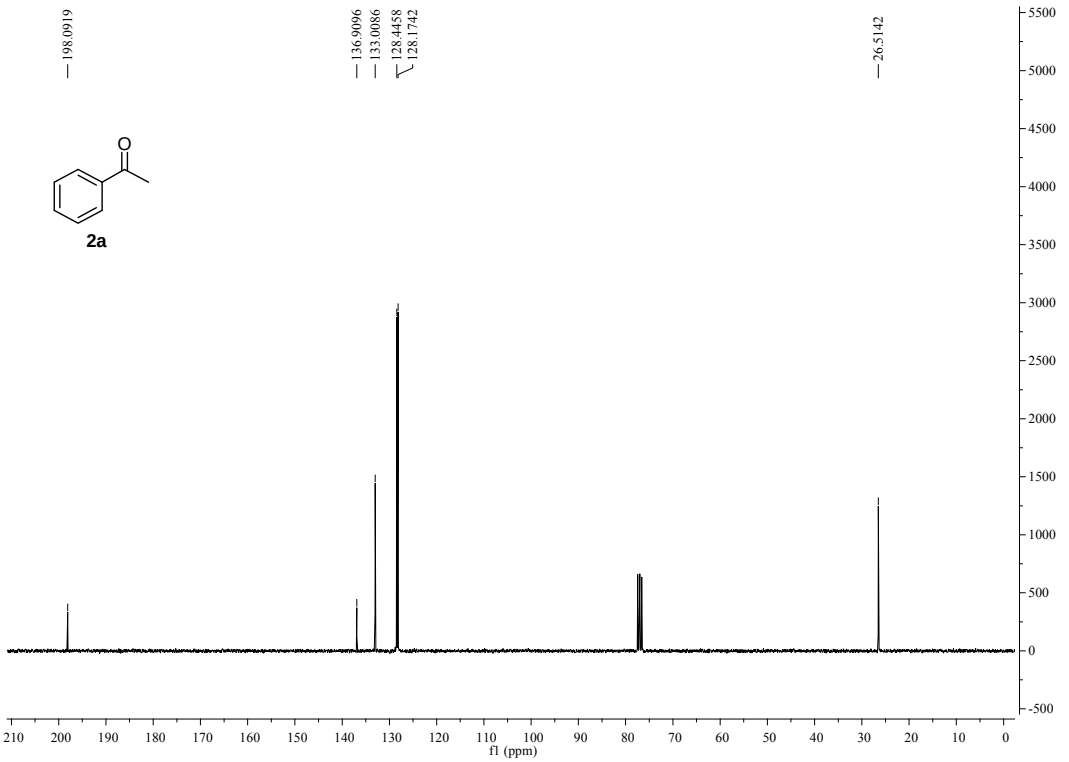


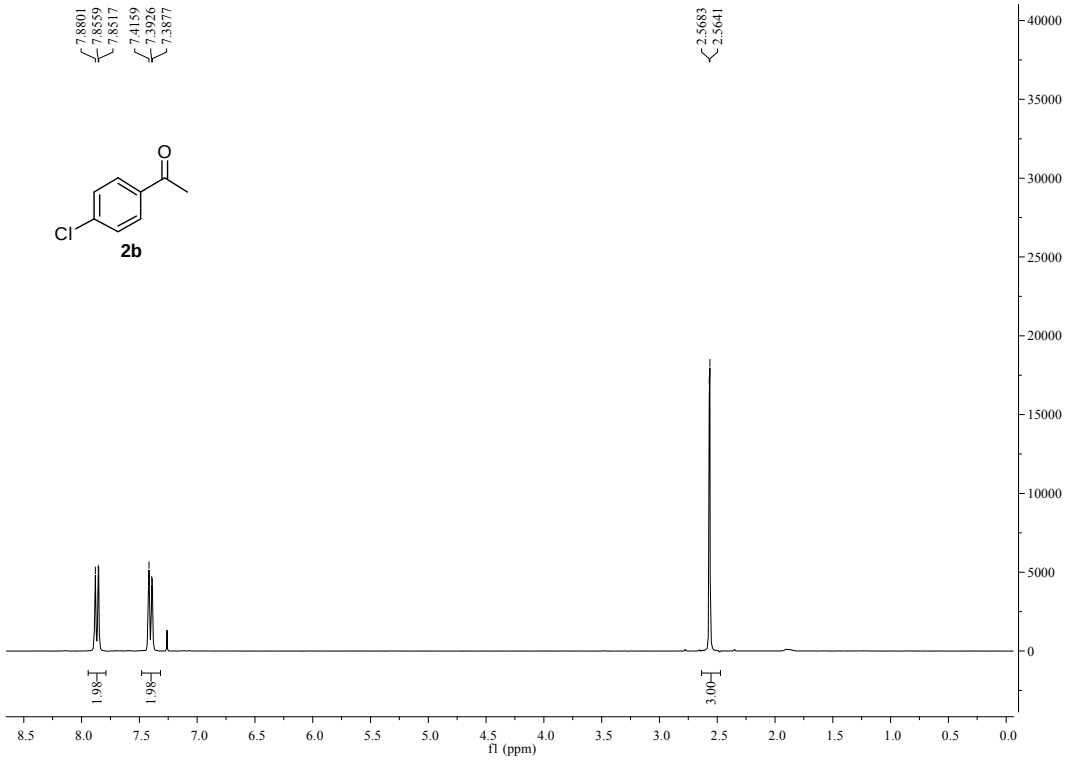
**5**

White solid; 45% yield (13.2 mg); $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 5.7 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.41 (dd, *J* = 18.0, 8.8 Hz, 2H), 6.33 (d, *J* = 5.6 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 177.6, 156.4, 155.3, 133.7, 125.7, 125.2, 124.8, 118.1, 112.9.

## 8. NMR spectra

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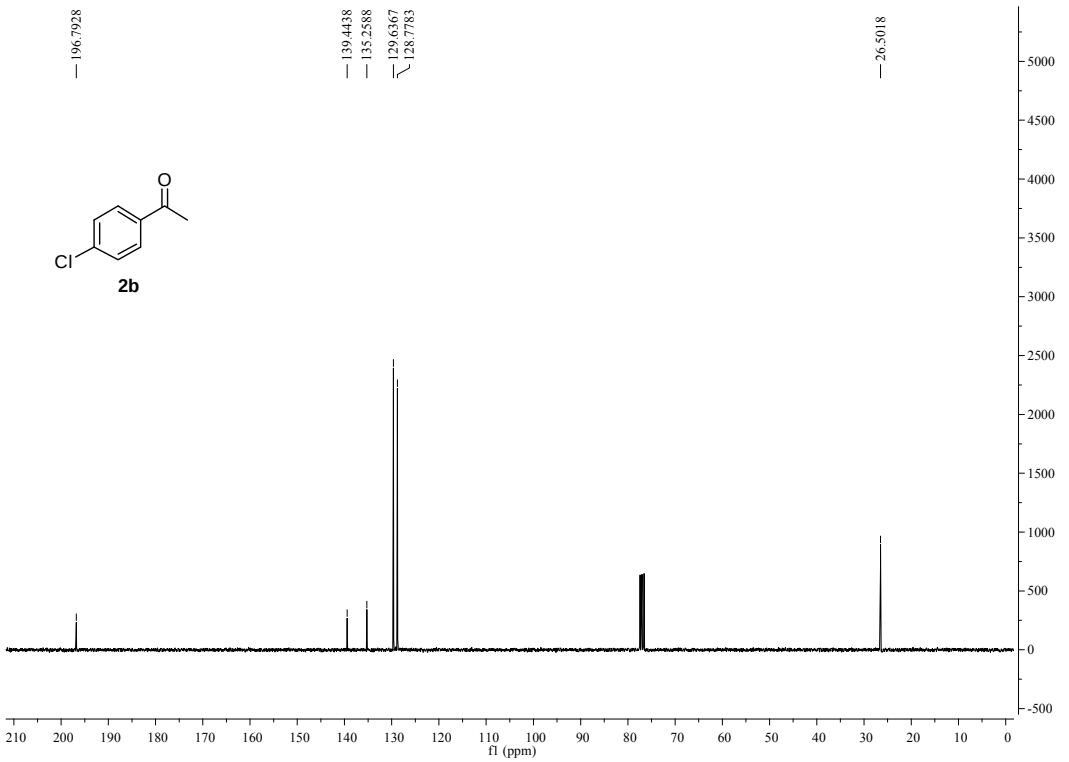
3.00
f1 (ppm)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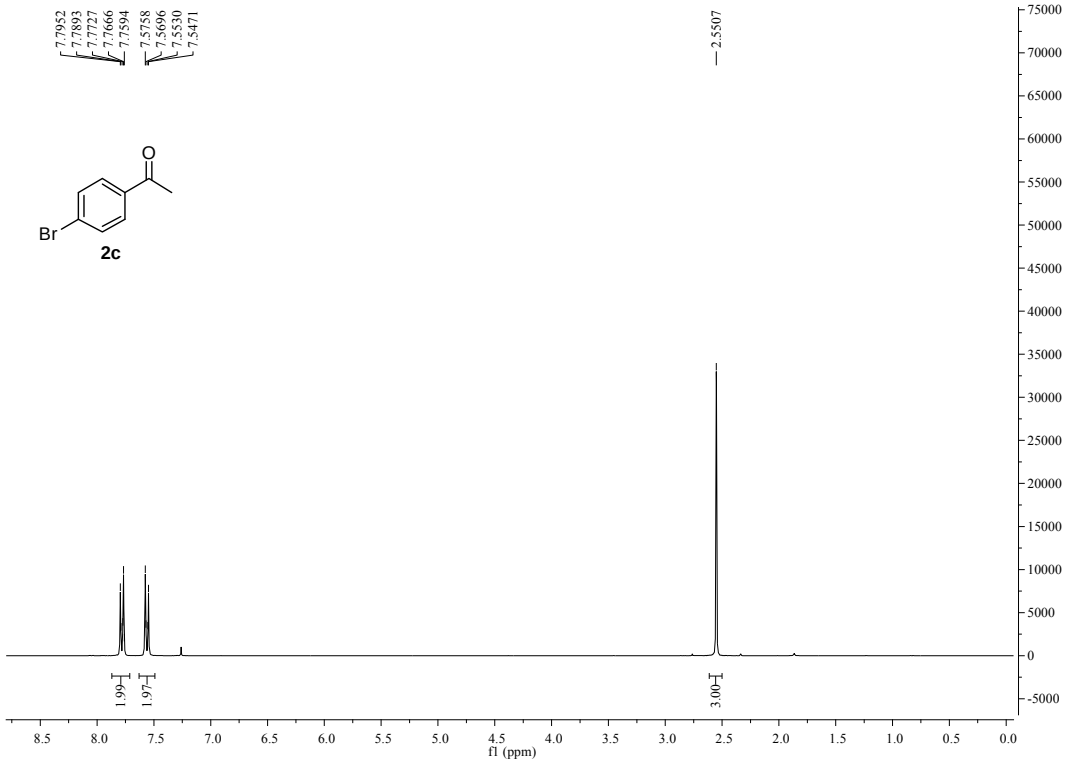
O
Cl
2b
f1 (ppm)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2c
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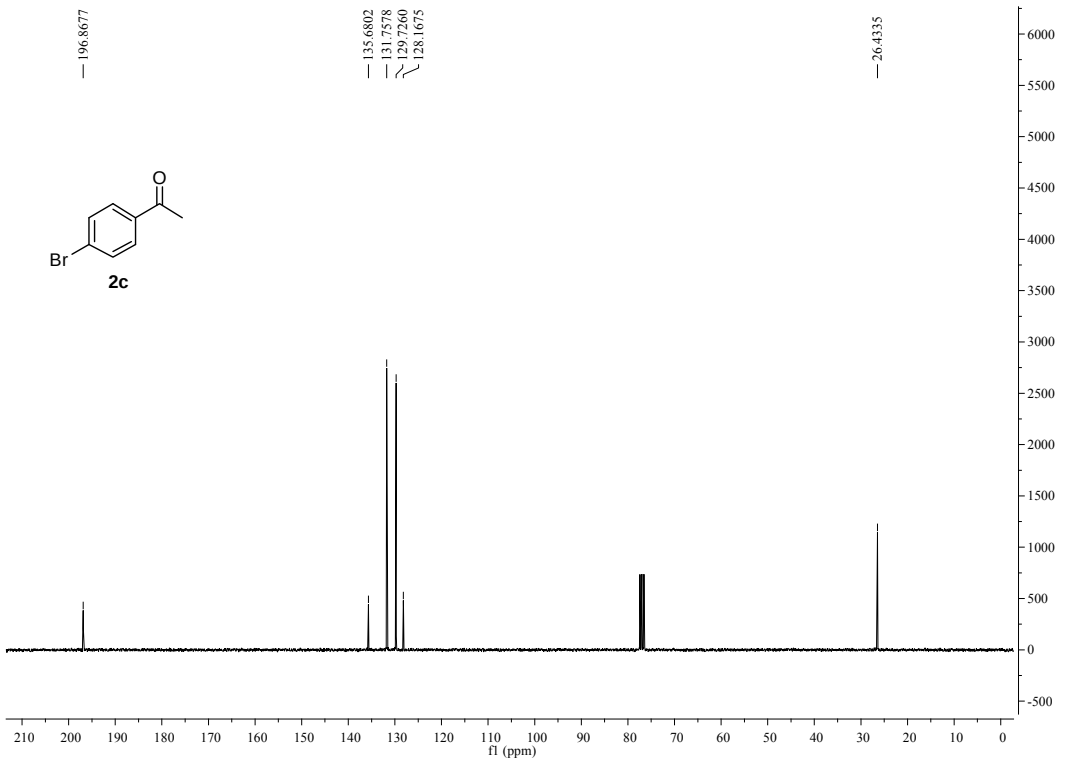
3.00
f1 (ppm)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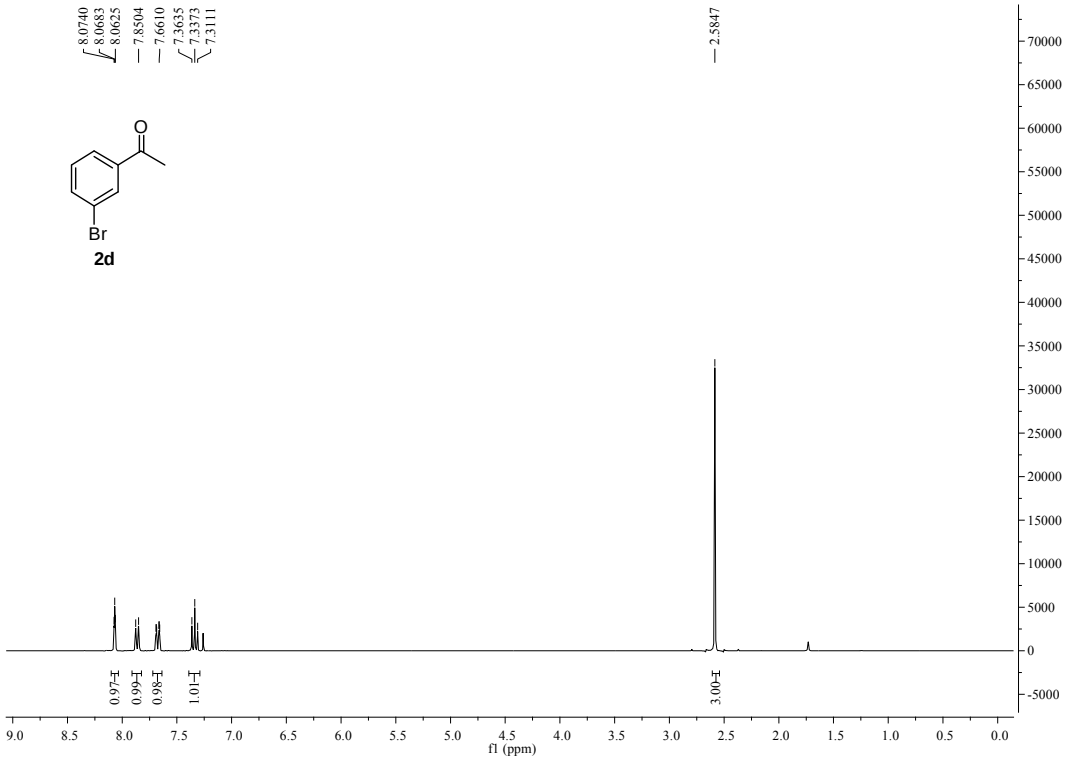
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3.00
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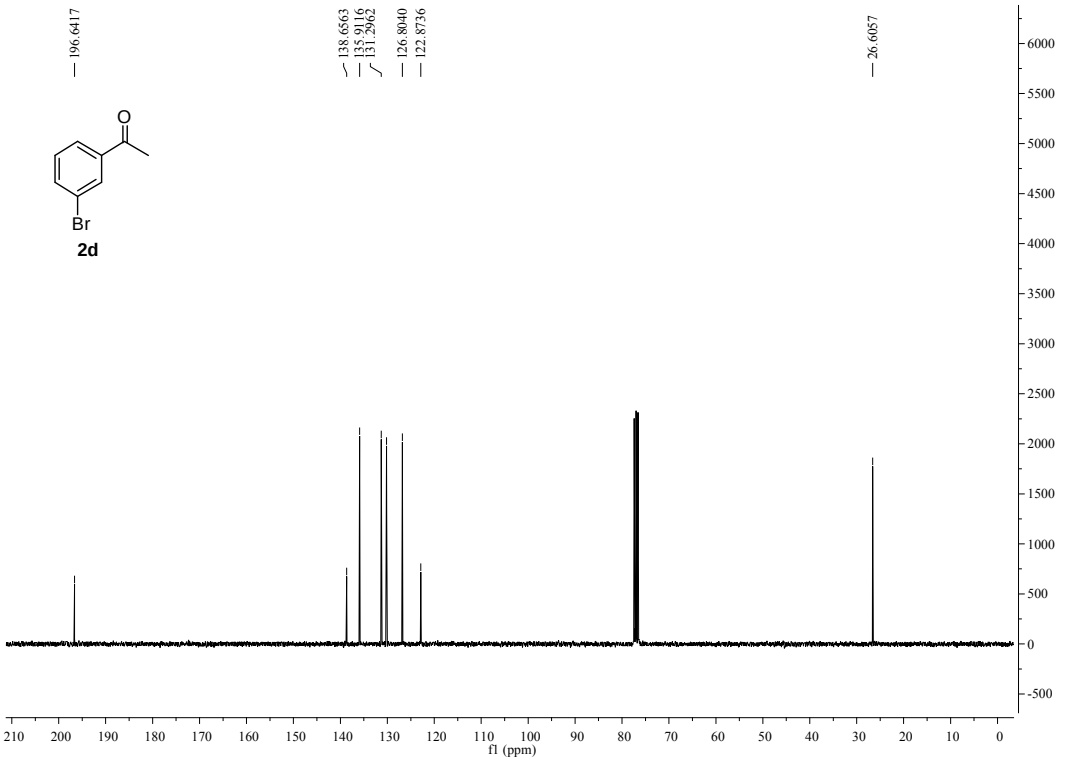
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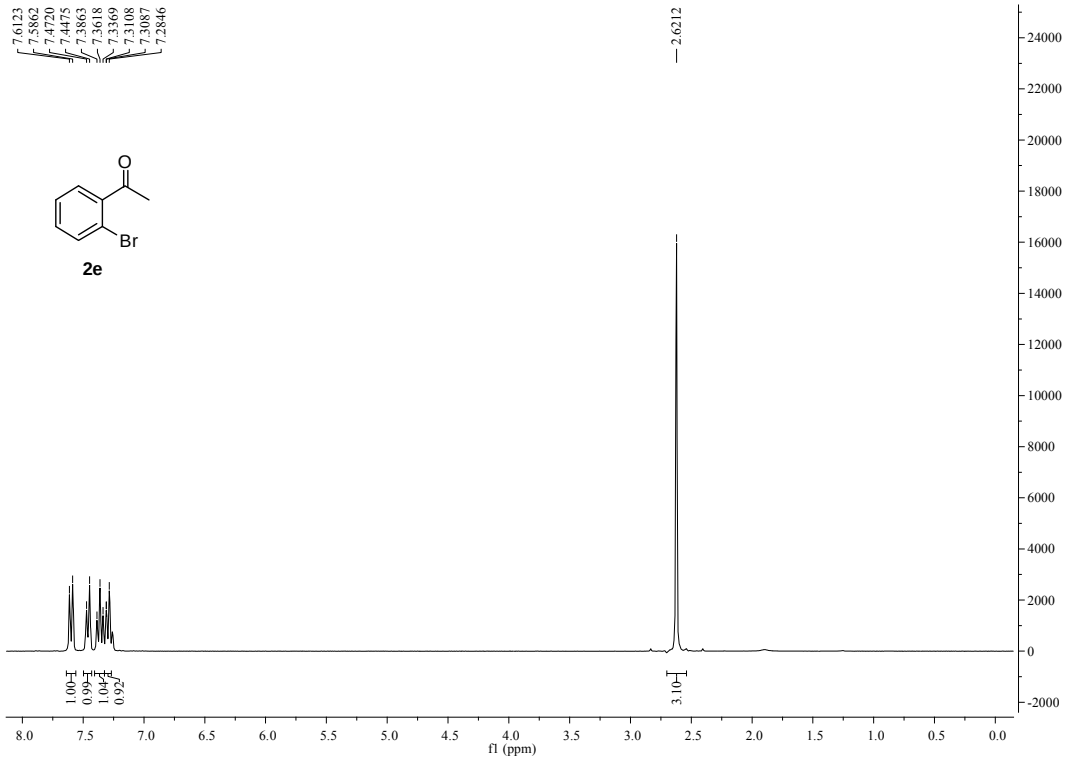
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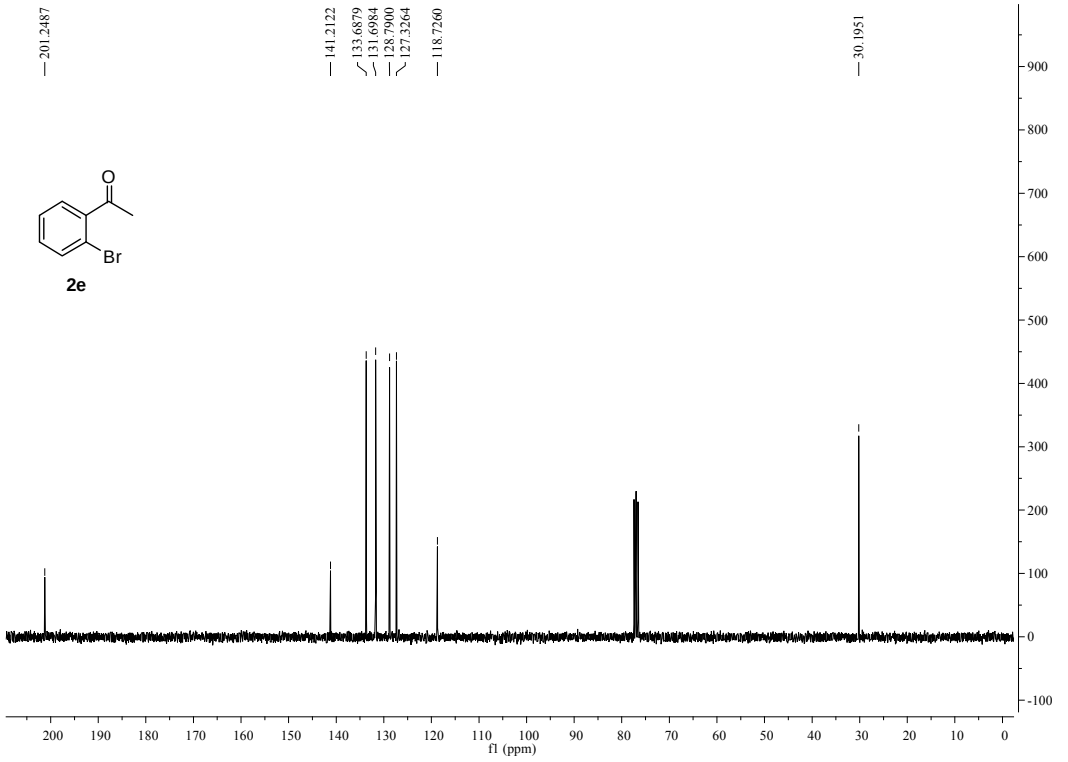
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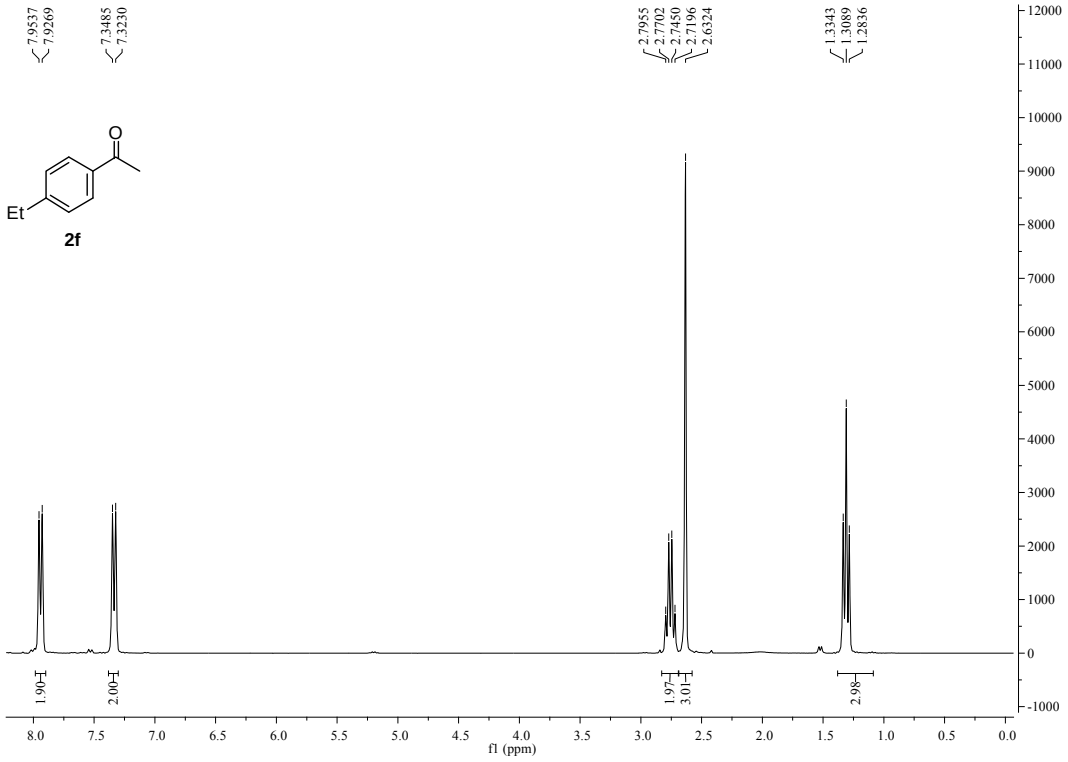
f1 (ppm)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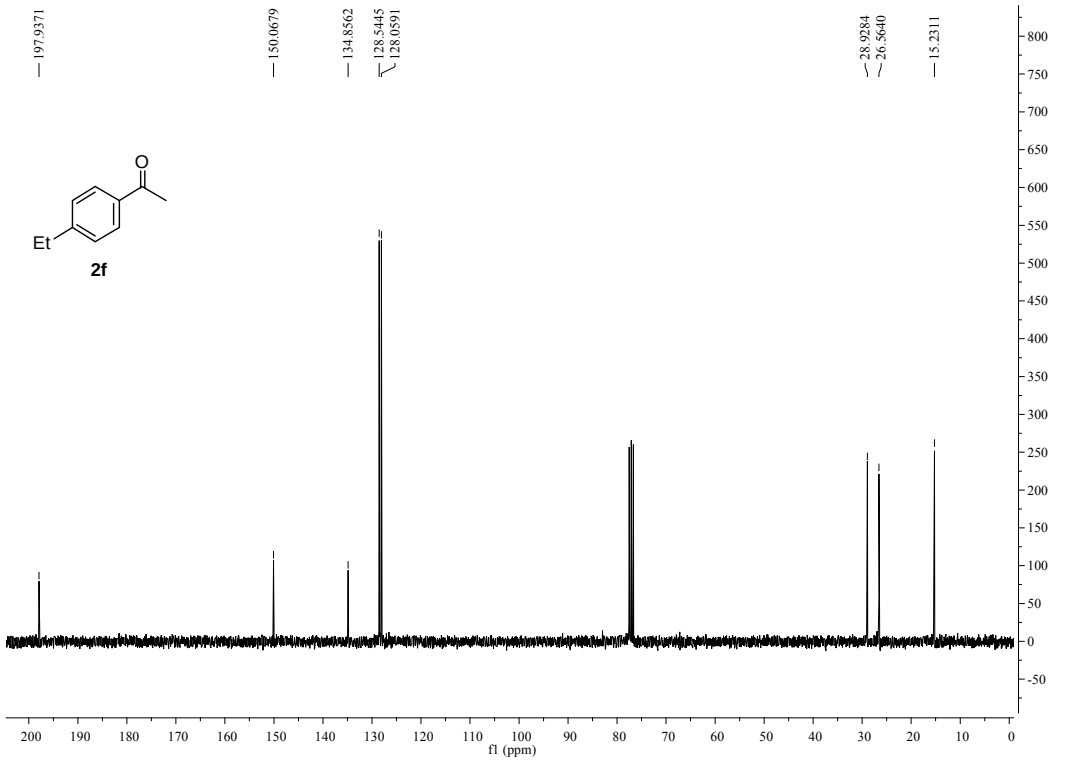
O
Et
2f
1.90
2.00
1.97
3.01
2.98
f1 (ppm)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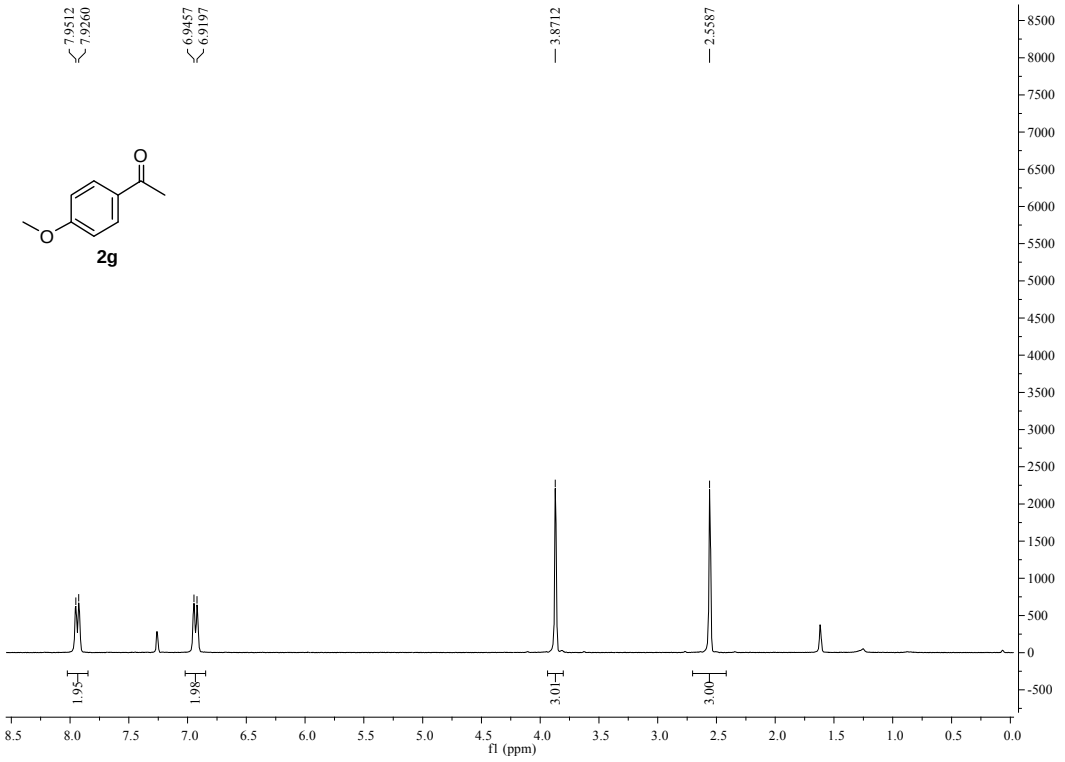
128.5445
128.0591
28.9284
26.5640
15.2211
O
Et
2f
f1 (ppm)


7.9512
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6.9457
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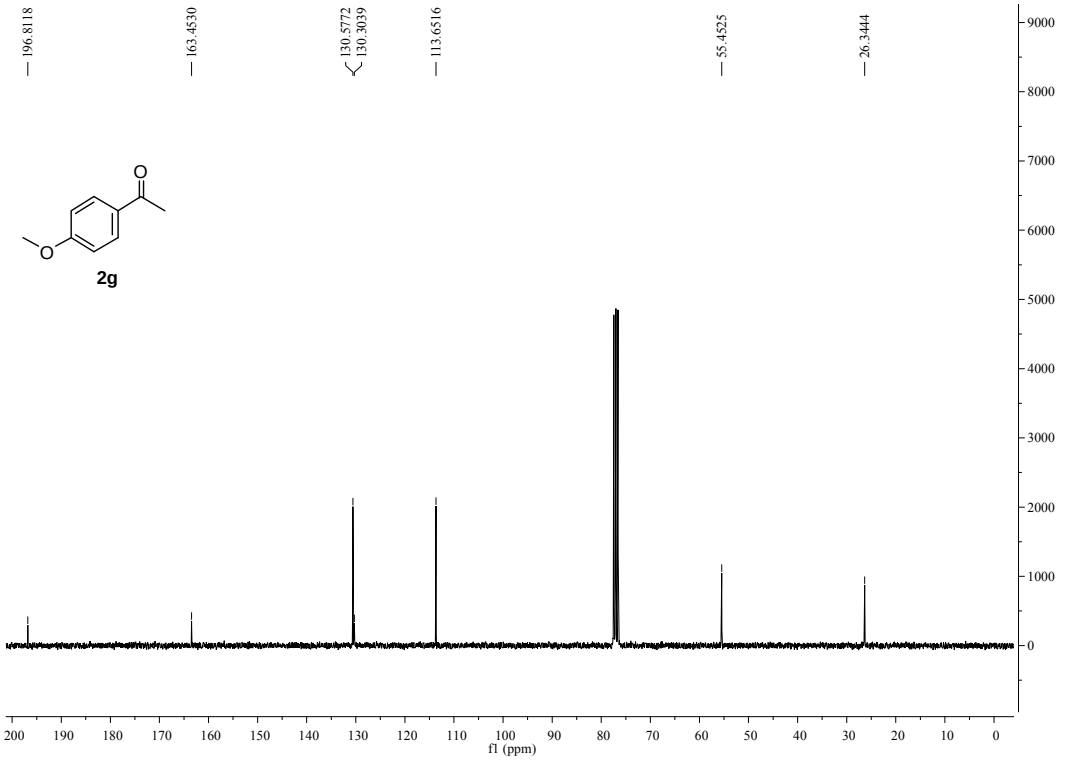
3.8712
2.5587
1.95
1.98
3.01
3.00
f1 (ppm)

2g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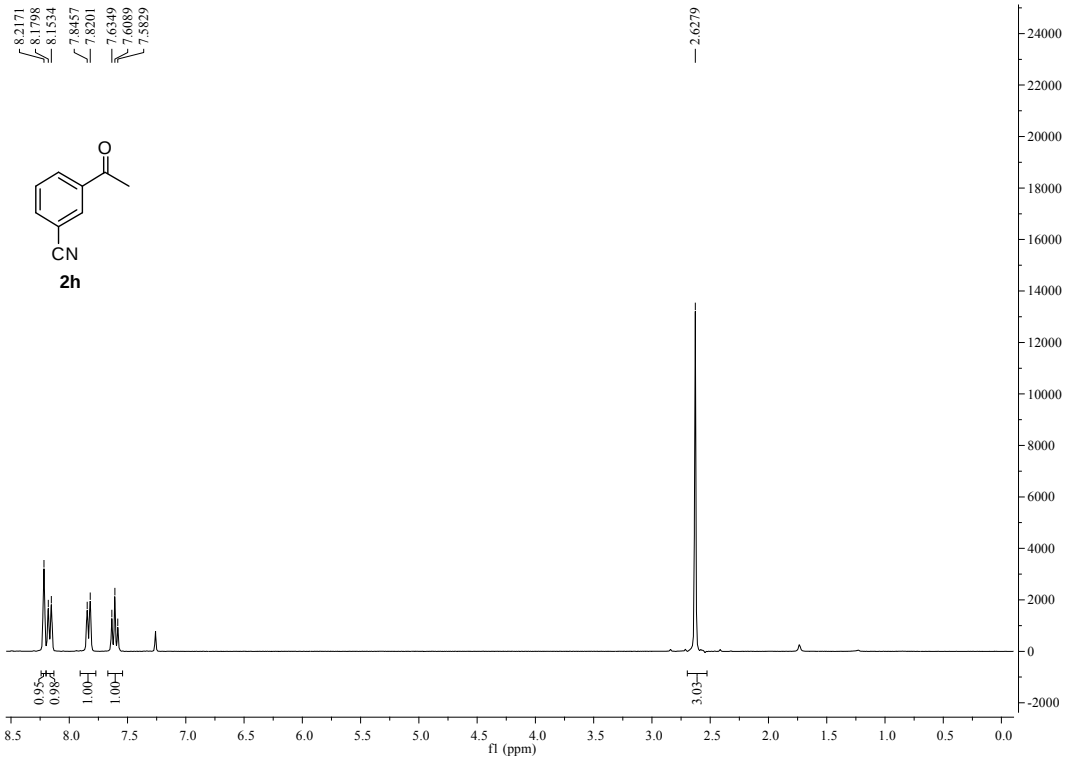
130.3039
113.6516
55.4525
26.3444
f1 (ppm)

2g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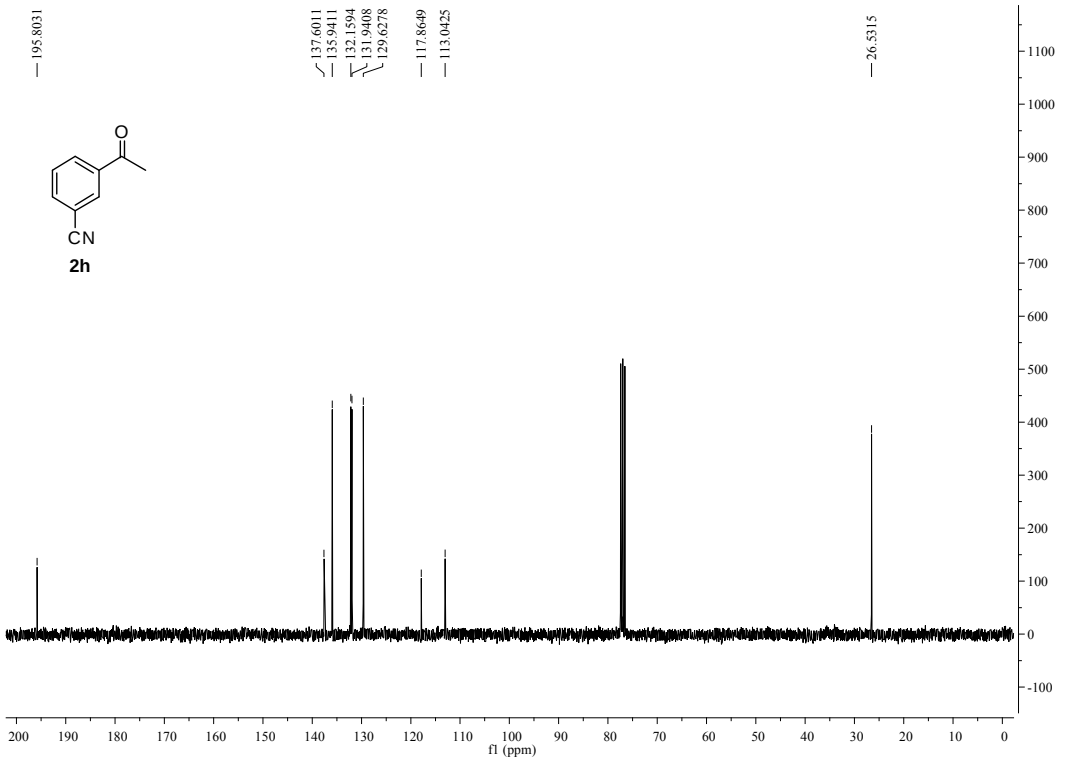
8.1798
8.1534
7.8457
7.8201
7.6349
7.6089
7.5829
2.6279
O
CN
2h
0.95
0.98
1.00
1.00
3.03
f1 (ppm)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117.8649
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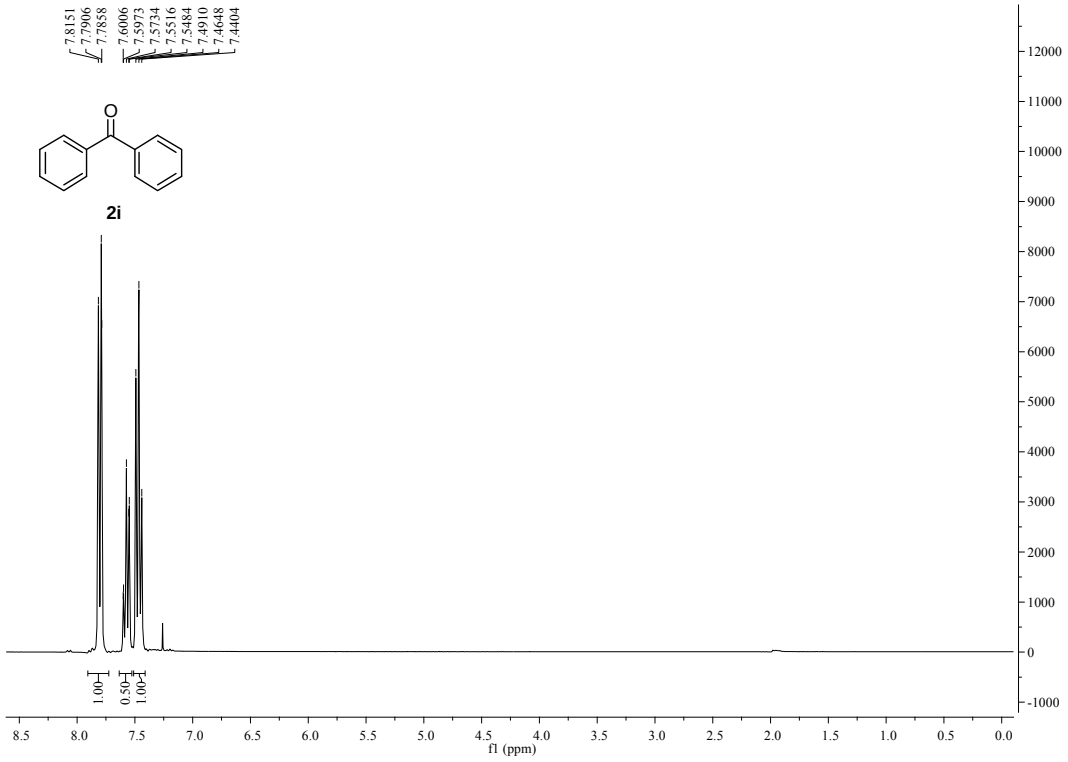
26.5315
O
CN
2h
f1 (ppm)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7.5973
7.5734
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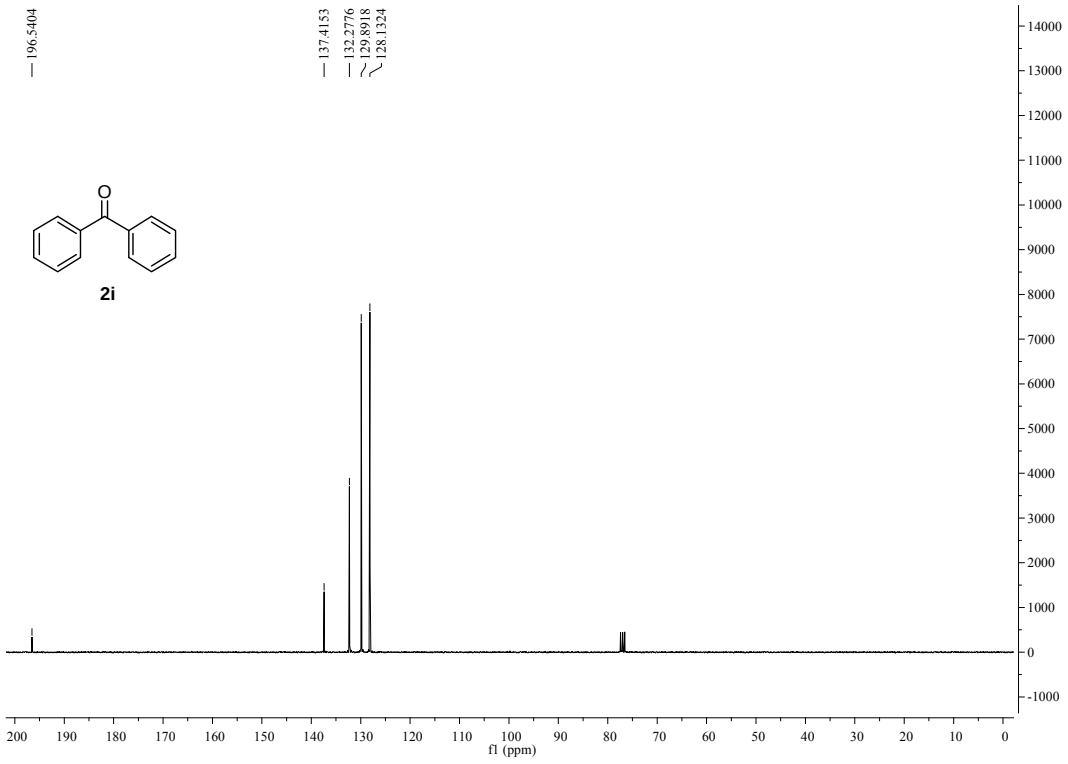
7.4910
7.4648
7.4404
O
2i
1.00
0.50
1.00
f1 (ppm)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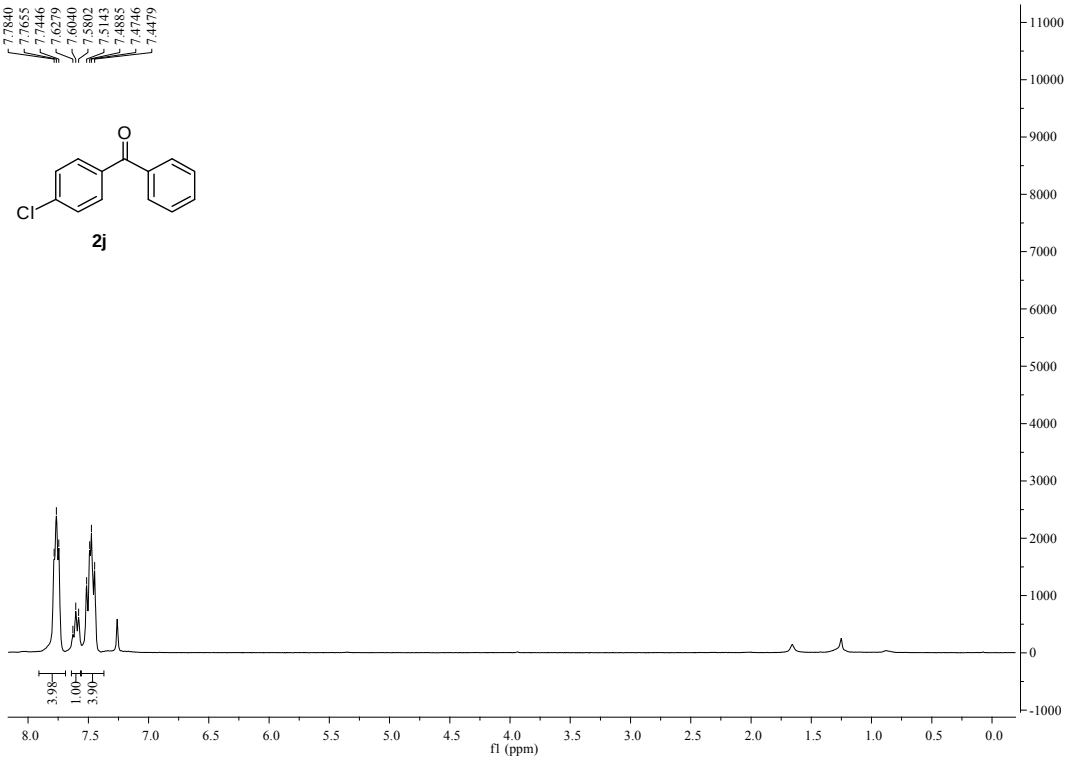
2i
f1 (ppm)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7.6040
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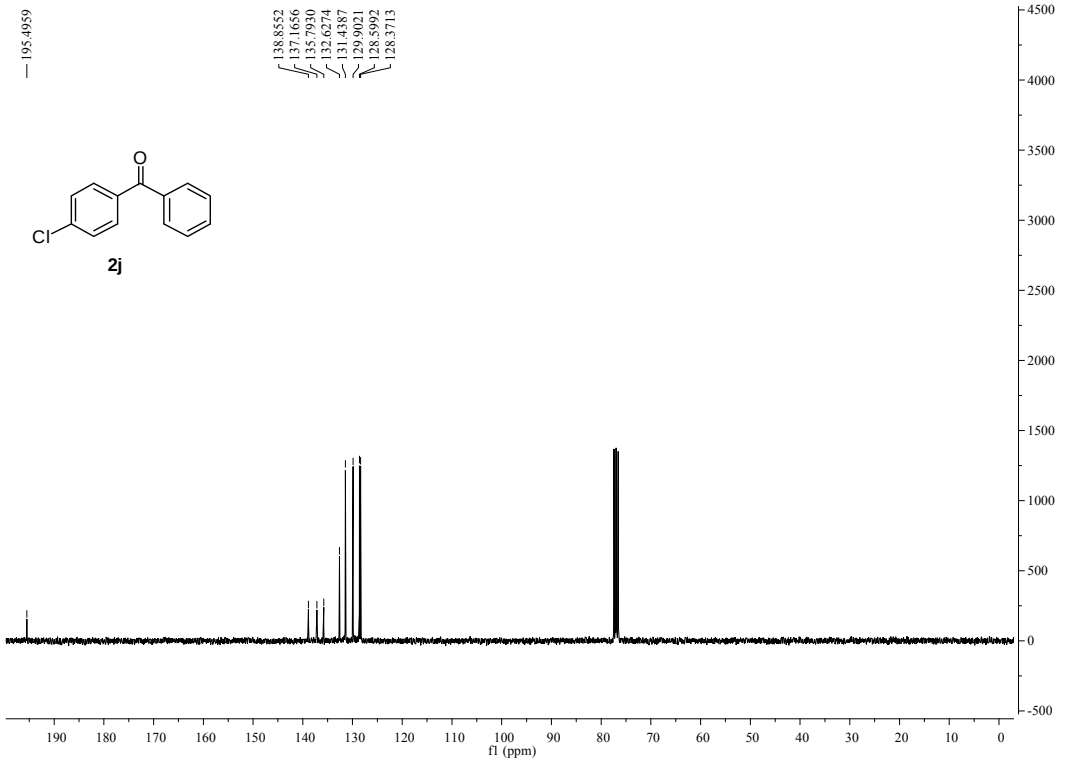
7.5143
7.4885
7.4746
7.4479
O
Cl
2j
3.98
1.00
3.90
f1 (ppm)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128.3713
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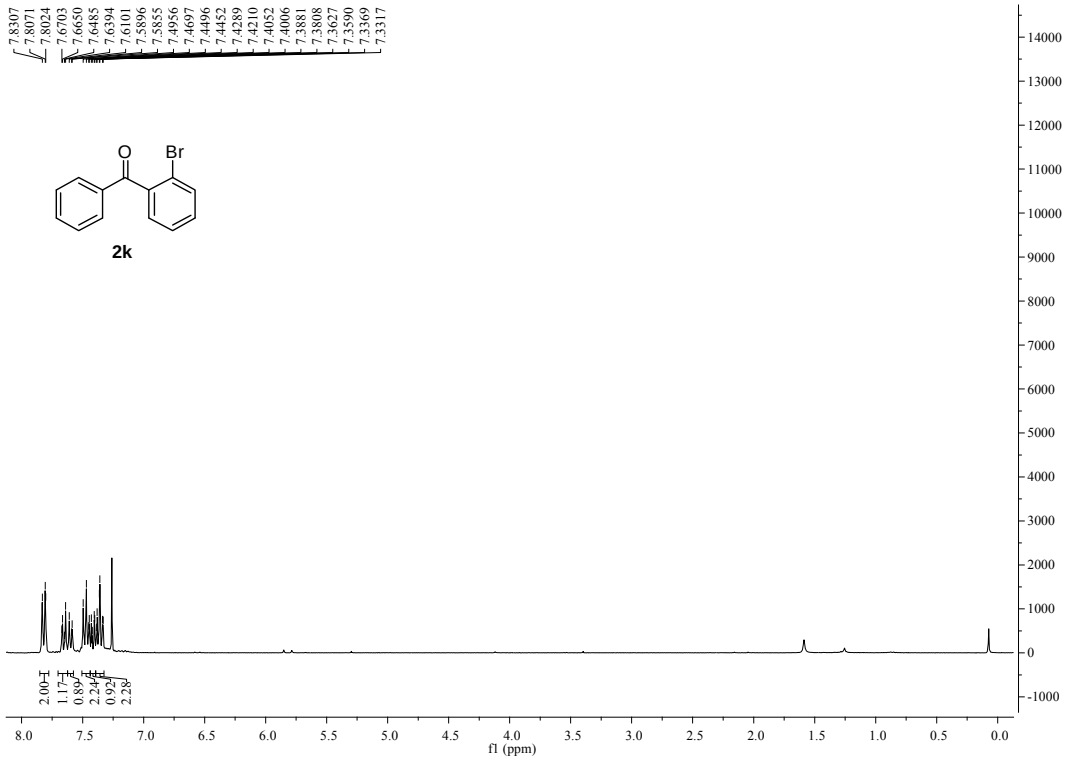
Cl
2j
f1 (ppm)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7.5896
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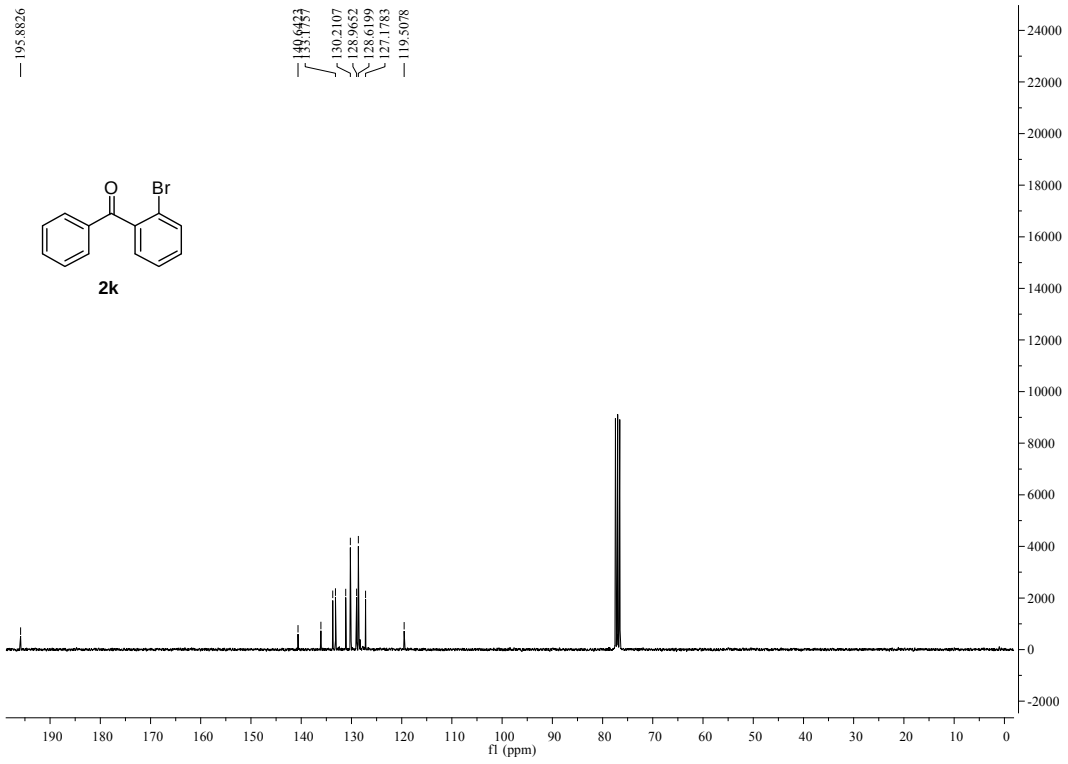
7.4956
7.4697
7.4496
7.4452
7.4289
7.4210
7.4052
7.4006
7.3881
7.3808
7.3627
7.3590
7.3369
7.3317
O
Br
2k
2.00
1.17
0.89
2.24
0.92
2.29
fl (ppm)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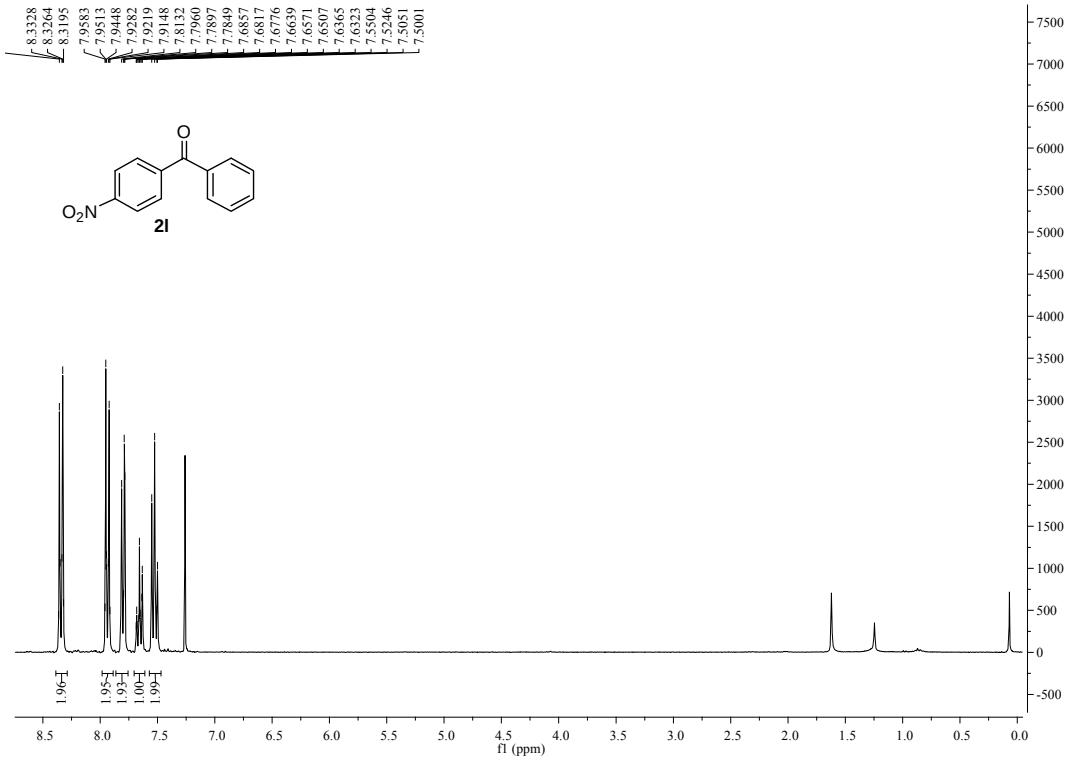
130.2107
128.9652
128.6199
127.1783
119.5078
O
Br
2k
fl (ppm)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8.3264
8.3195
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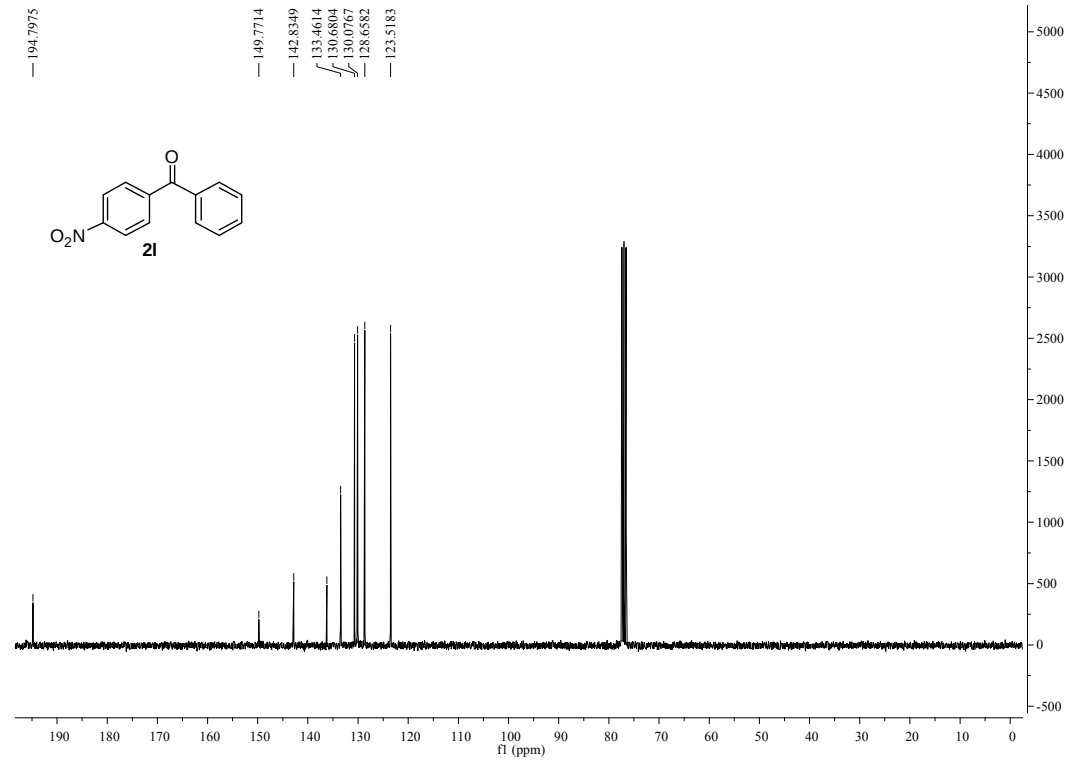
7.9513
7.9448
7.9282
7.9219
7.9148
7.8132
7.7960
7.7897
7.7849
7.6857
7.6817
7.6776
7.6639
7.6571
7.6507
7.6365
7.6323
7.5504
7.5246
7.5051
7.5001
O
O2N
2l
1.96
1.95
1.93
1.00
1.99
f1 (ppm)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130.0767
128.6582
123.5183
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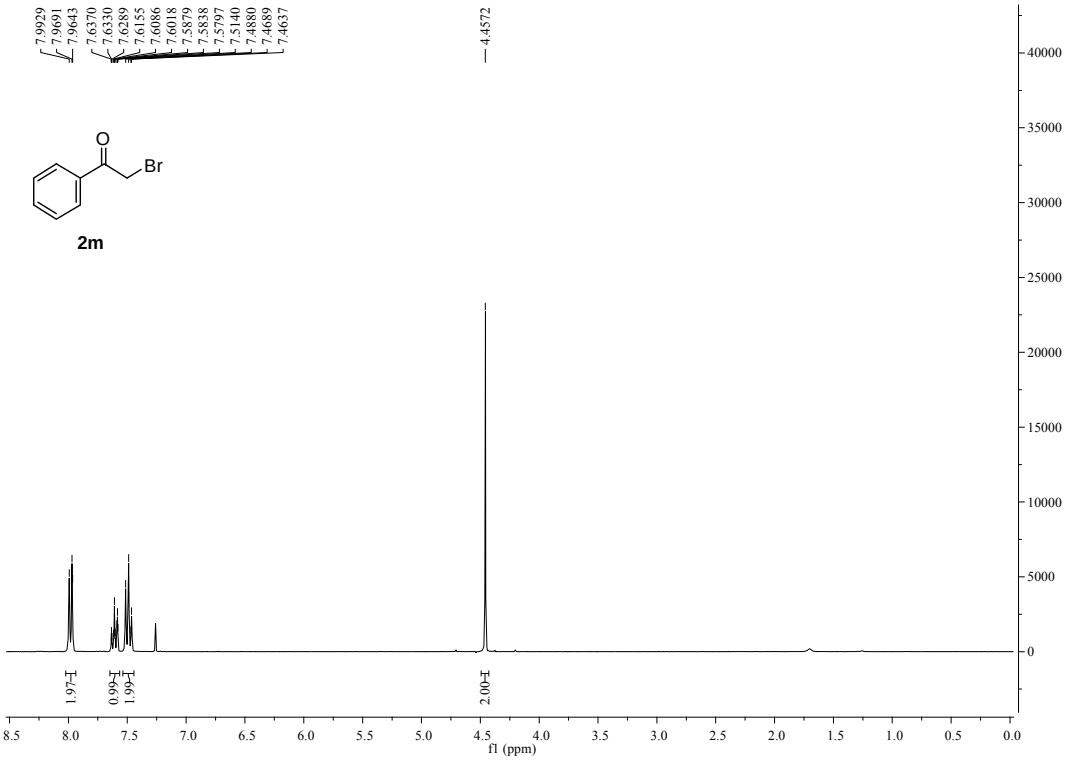
O2N
2l
f1 (ppm)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7.6330
7.6289
7.6155
7.6086
7.6018
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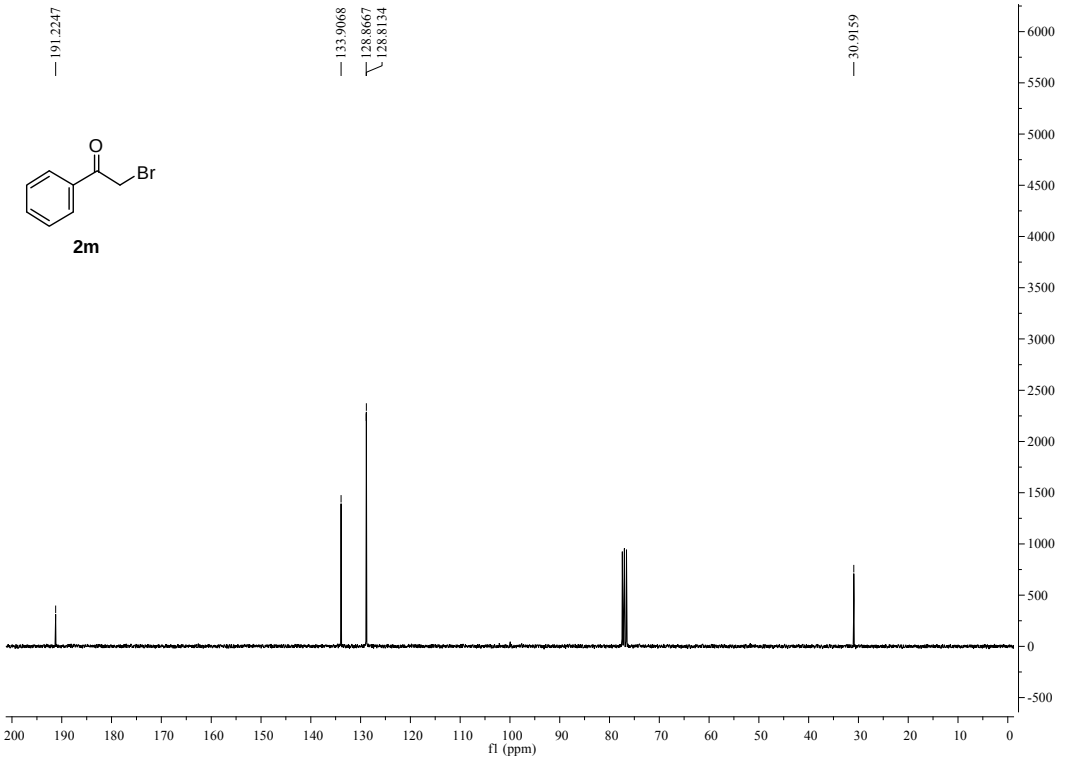
7.5838
7.5797
7.5140
7.4880
7.4689
7.4637
4.4572
O
Br
2m
1.97
0.99
1.99
2.00
f1 (ppm)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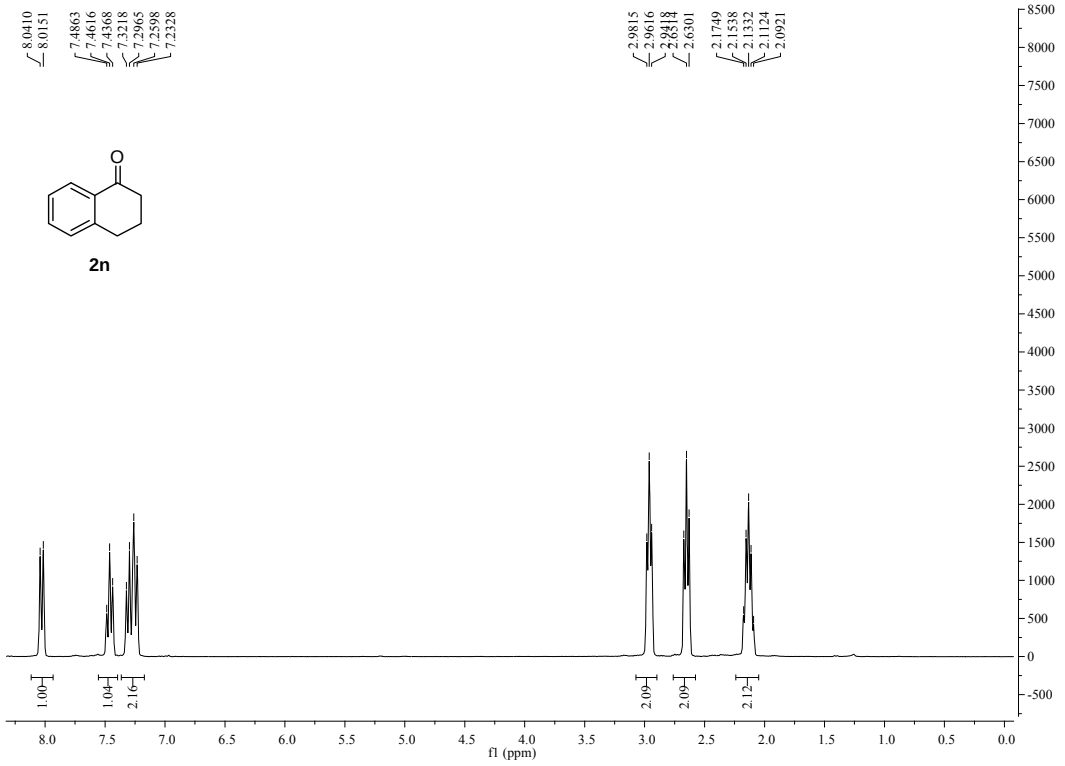
128.8134
30.9159
O
Br
2m
f1 (ppm)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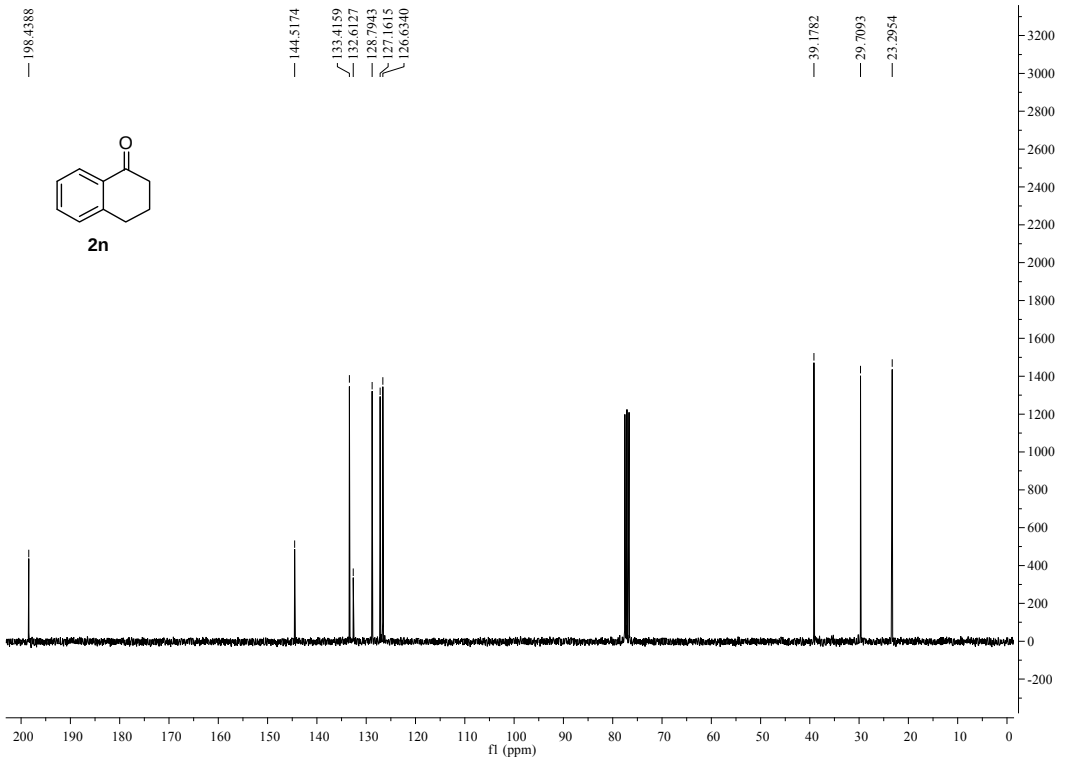
7.4863
7.4616
7.4368
7.3218
7.2965
7.2598
7.2328
2.9815
2.9616
2.9418
2.6314
2.6301
2.1749
2.1538
2.1332
2.1124
2.0921
O
2n
1.00
1.04
2.16
2.09
2.09
2.12
f1 (ppm)


198.4388
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126.6340
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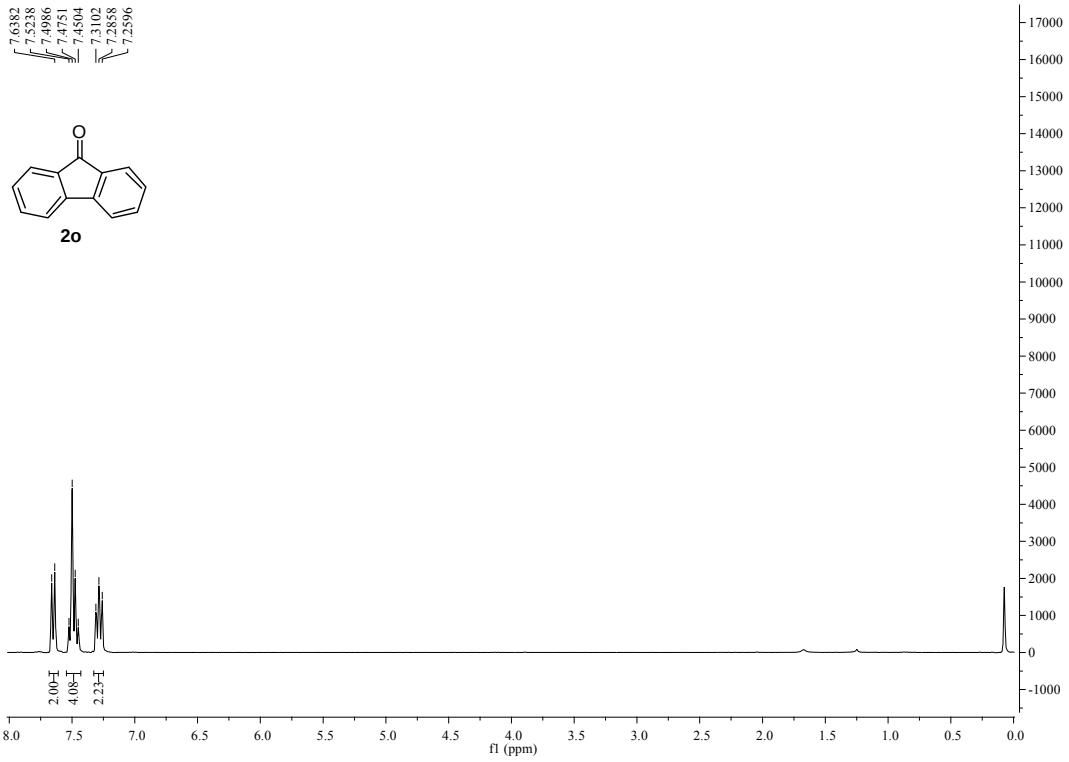
2n
f1 (ppm)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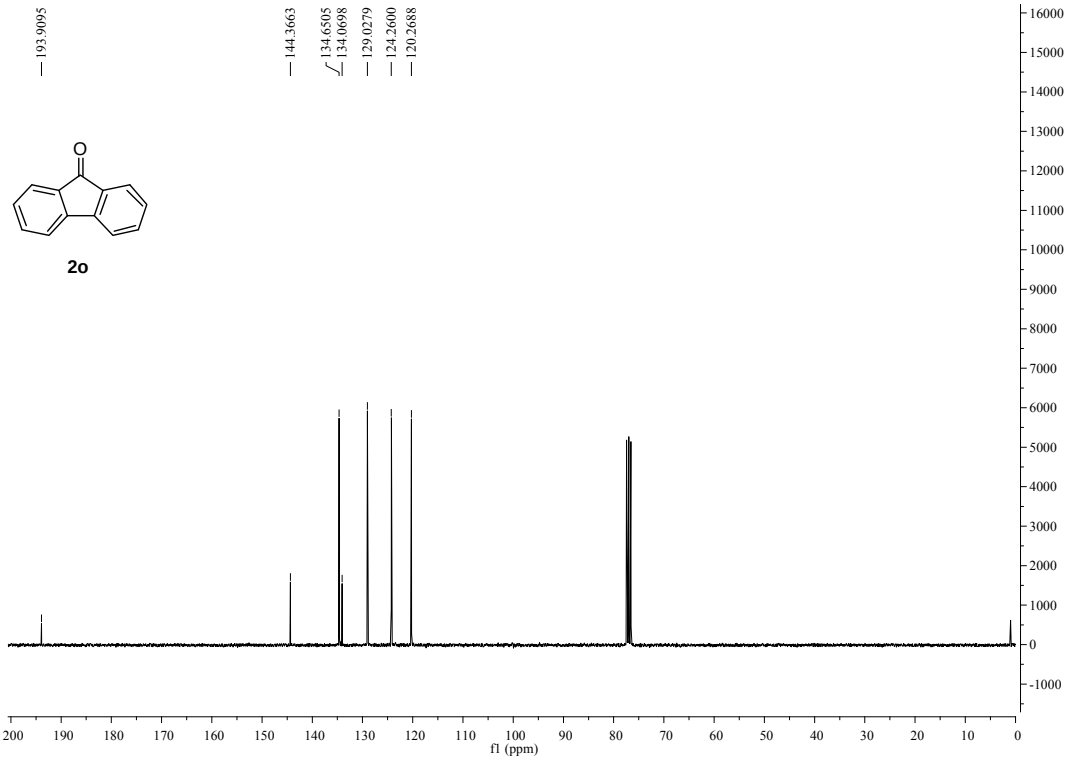
7.4986
7.4751
7.4504
7.3102
7.2858
7.2596
O
2o
2.00
4.08
2.23
fl (ppm)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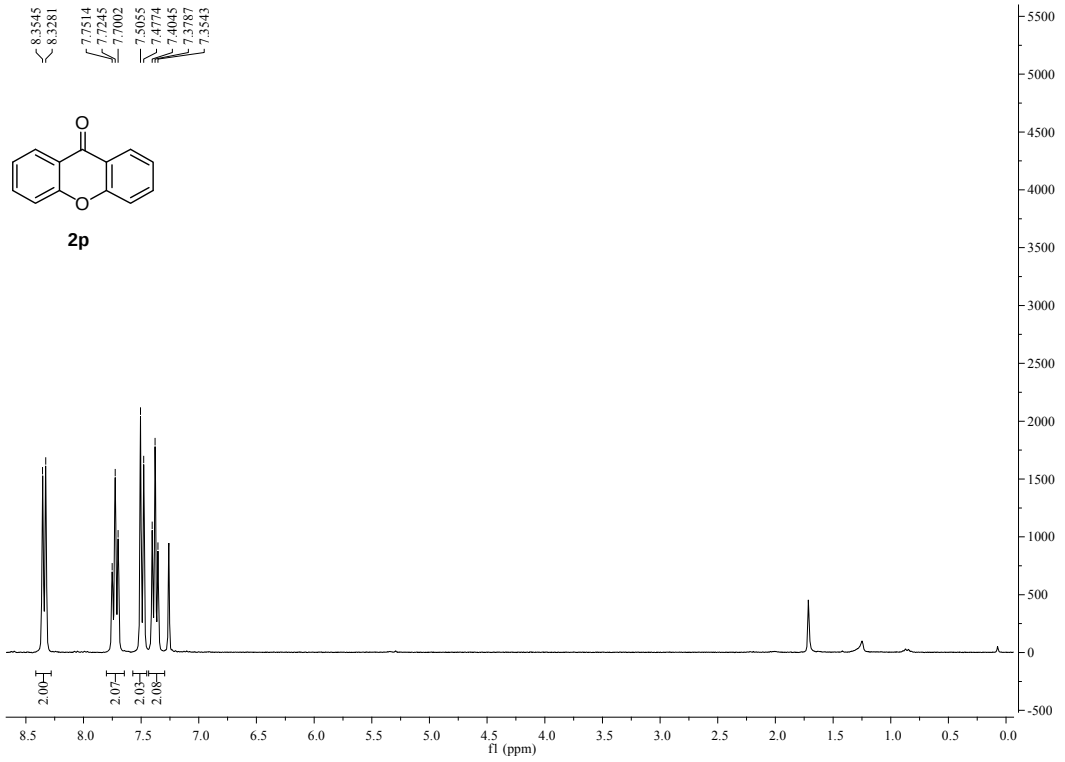
129.0279
124.2600
120.2688
O
2o
fl (ppm)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7.7514
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7.7002
7.5055
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O
O
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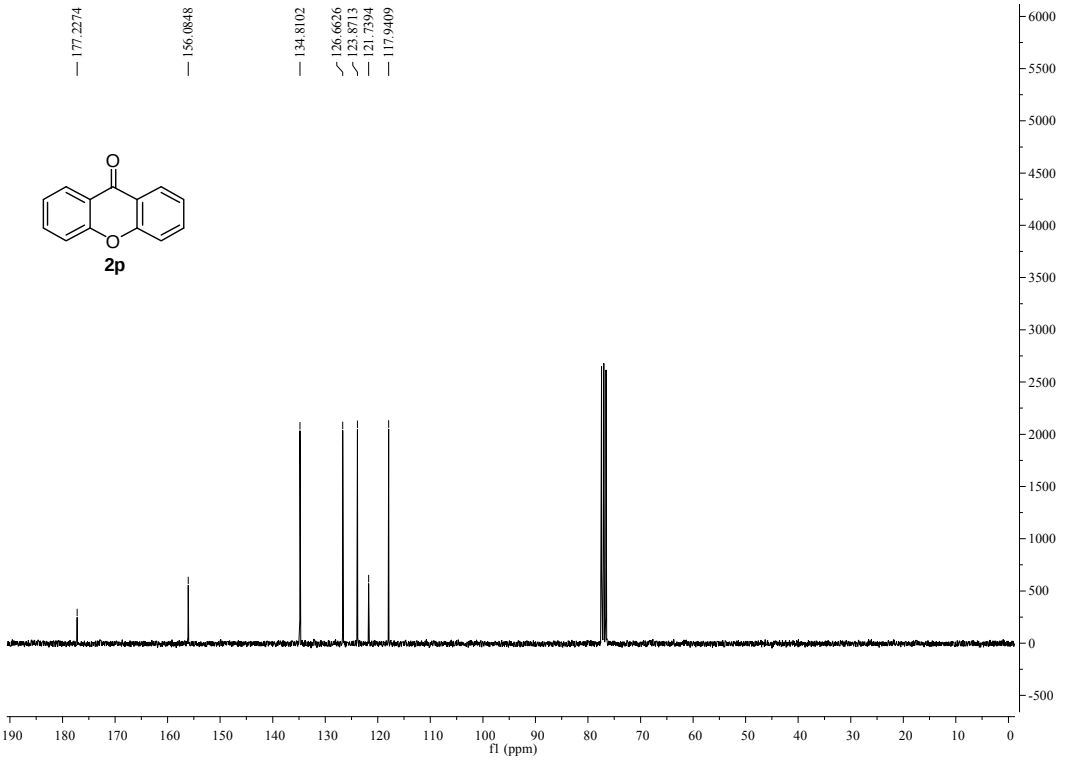
2.08
f1 (ppm)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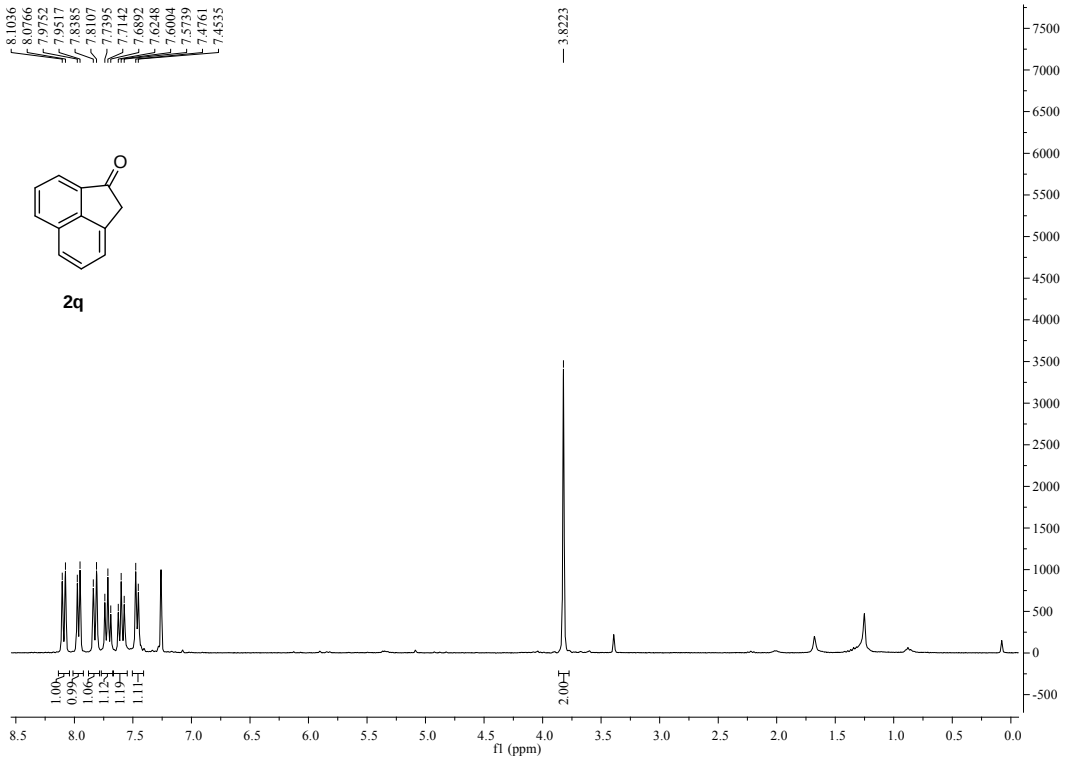
O
O
2p
f1 (ppm)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7.6892
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7.6004
7.5739
7.4761
7.4535
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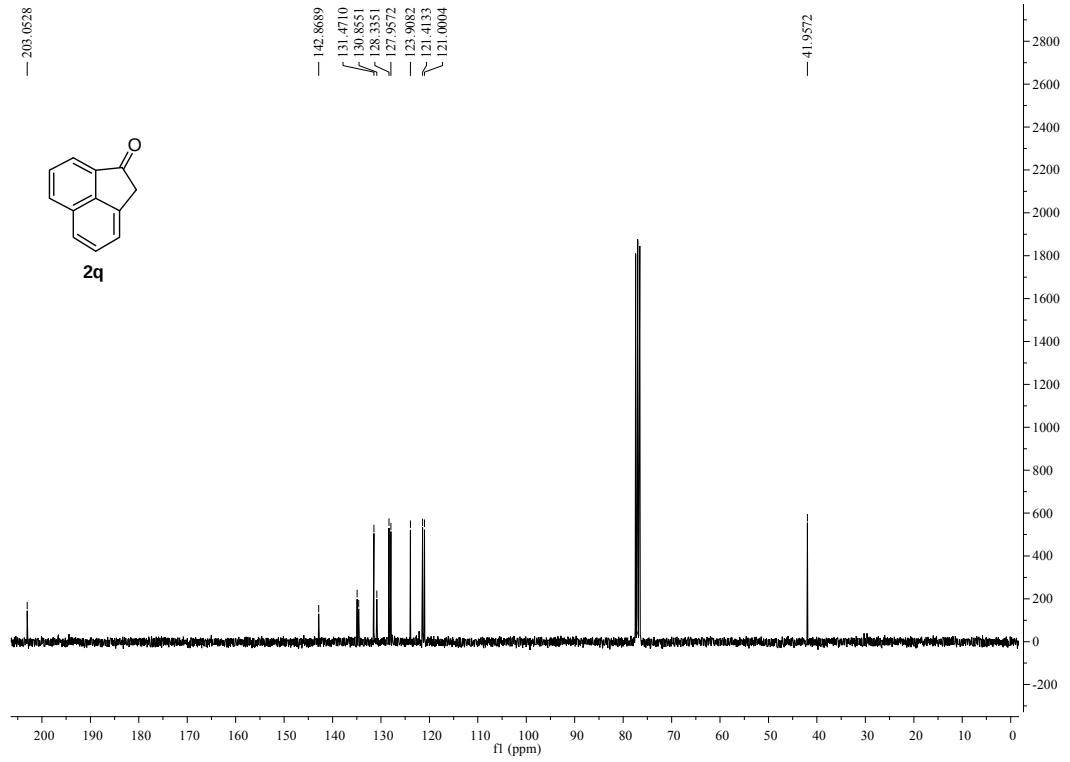
1.06
1.12
1.19
1.11
2.00
f1 (ppm)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121.0004
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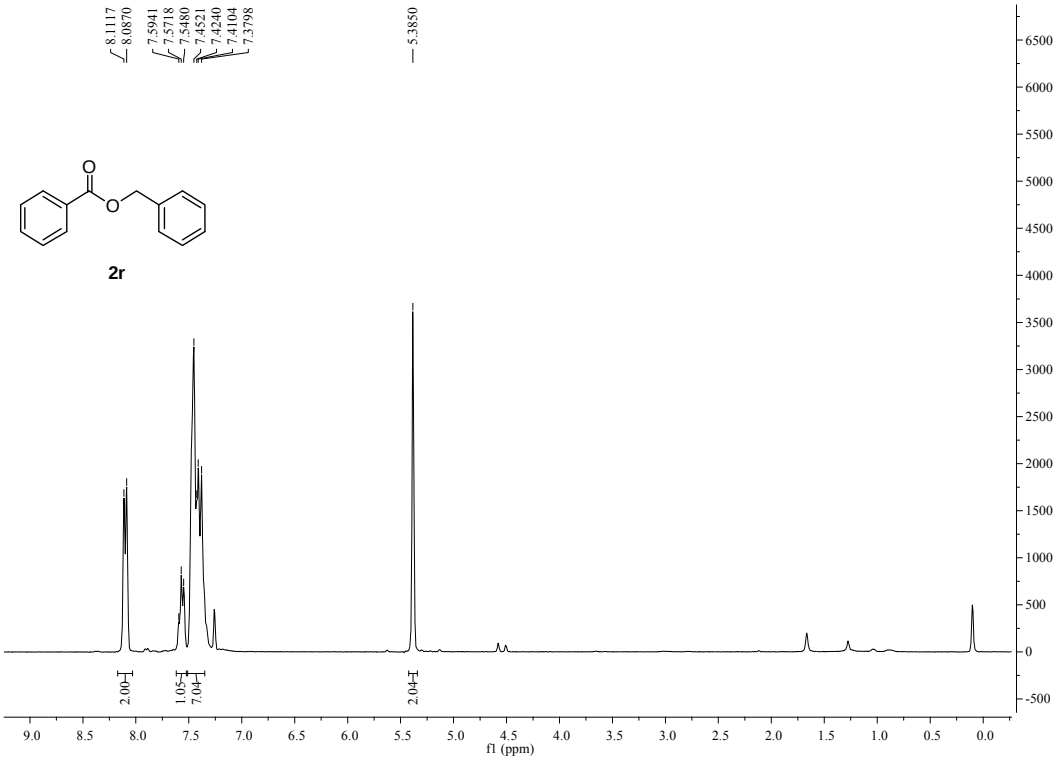
2q
f1 (ppm)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7.5718
7.5480
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5.3850
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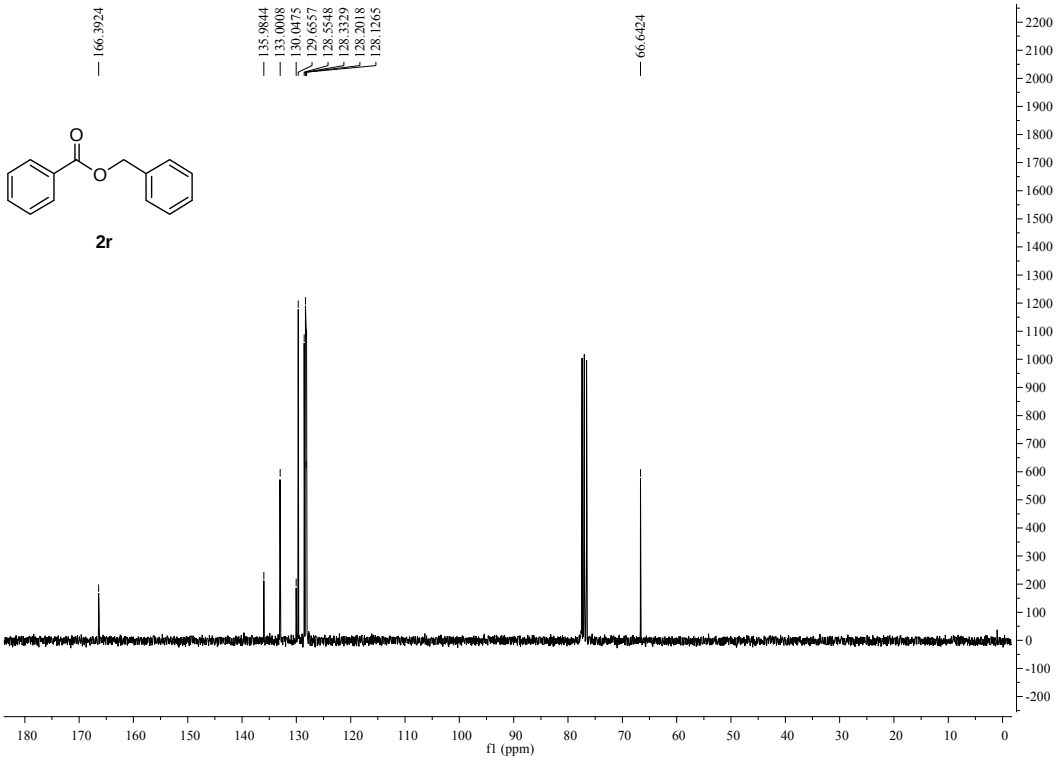
f1 (ppm)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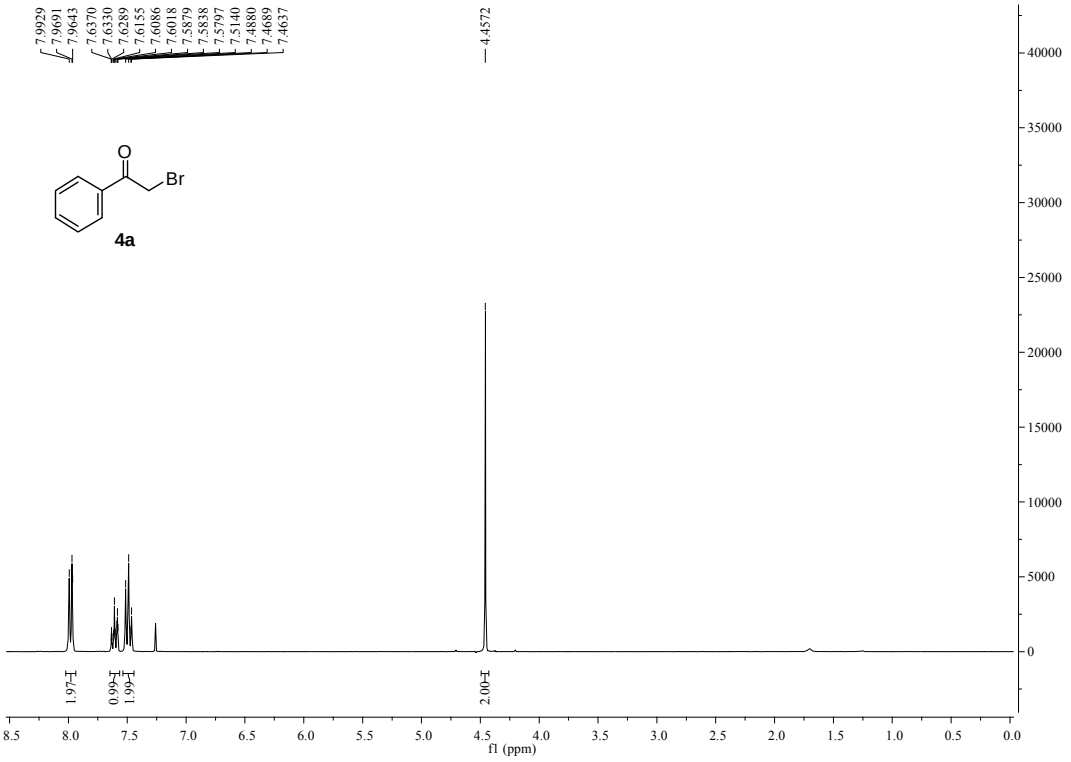
2r
f1 (ppm)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7.5838
7.5797
7.5140
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7.4637
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Br
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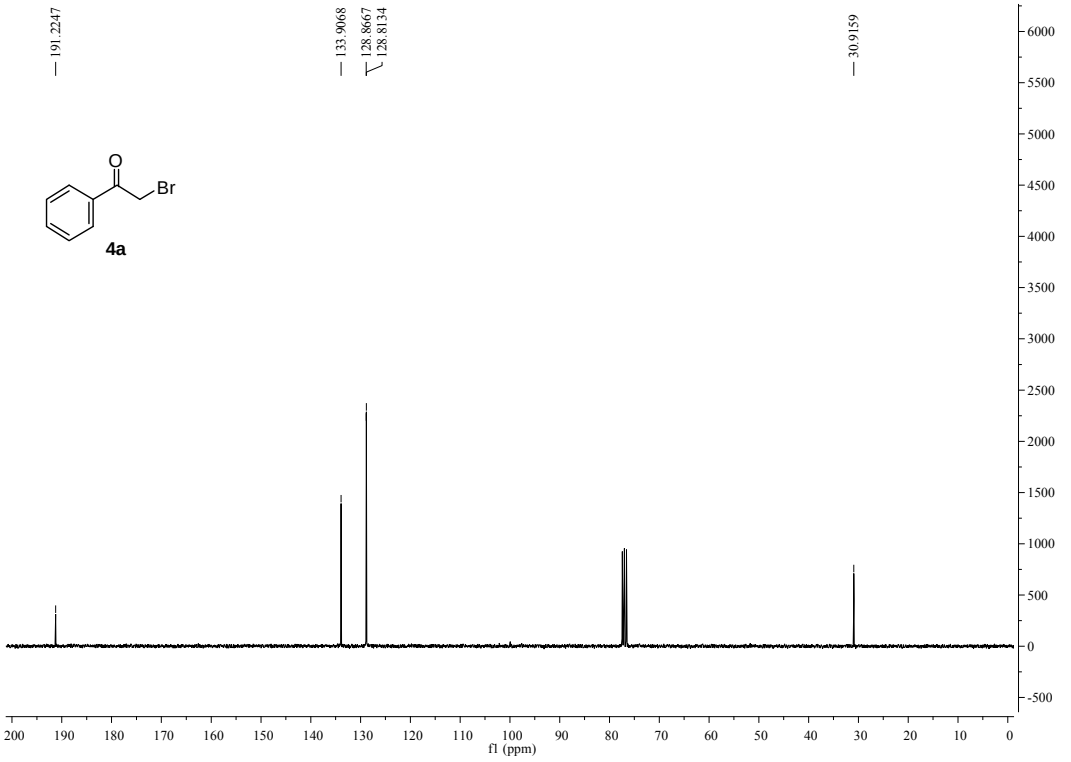
2.00
f1 (ppm)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Br
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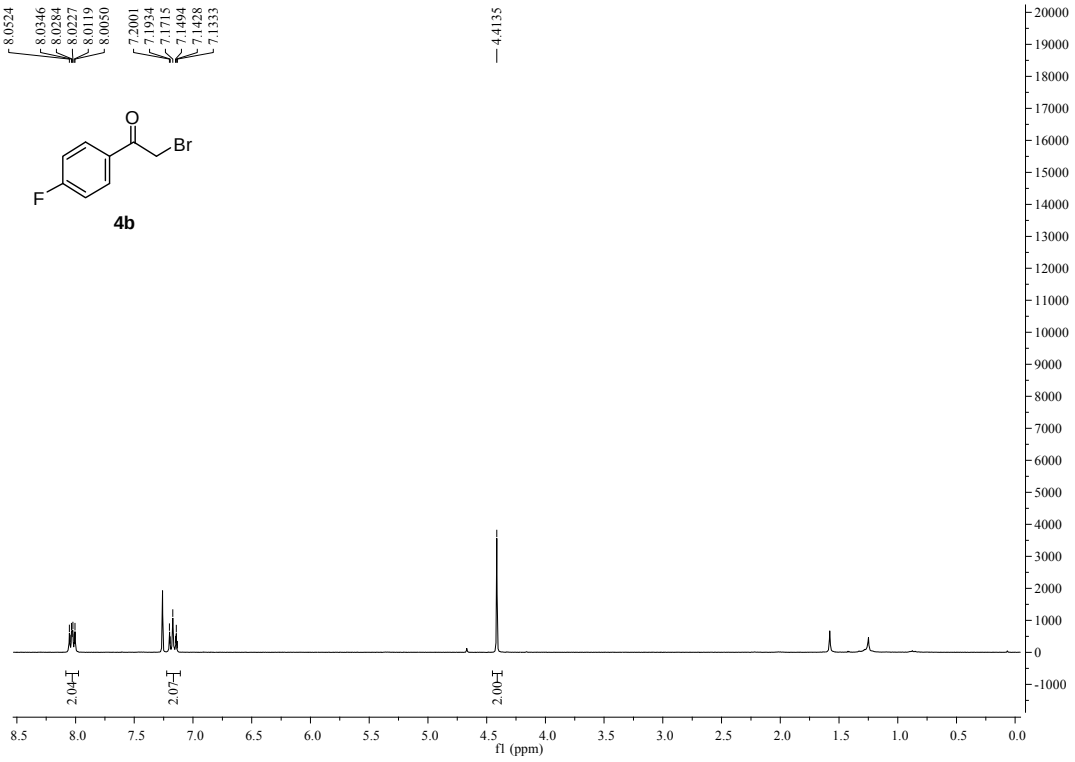
f1 (ppm)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8.0119
8.0050
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7.1934
7.1715
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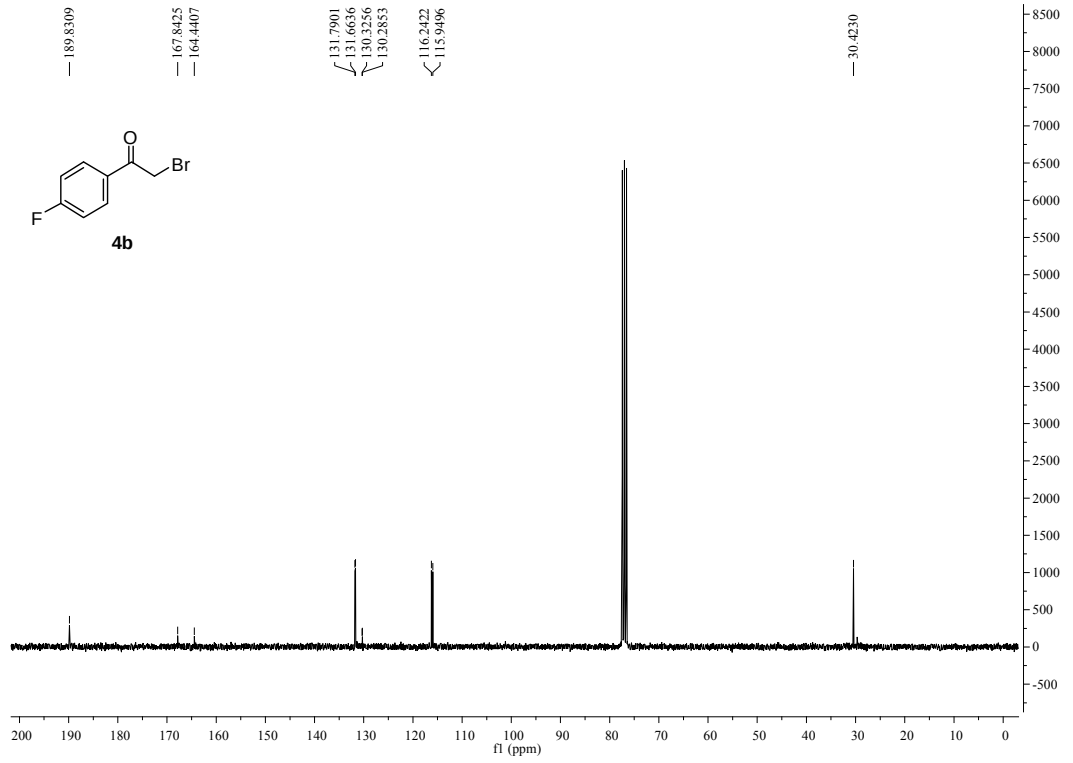
7.1333
4.4135
O
Br
F
4b
2.04
2.07
2.00
f1 (ppm)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164.4407
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130.2853
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115.9496
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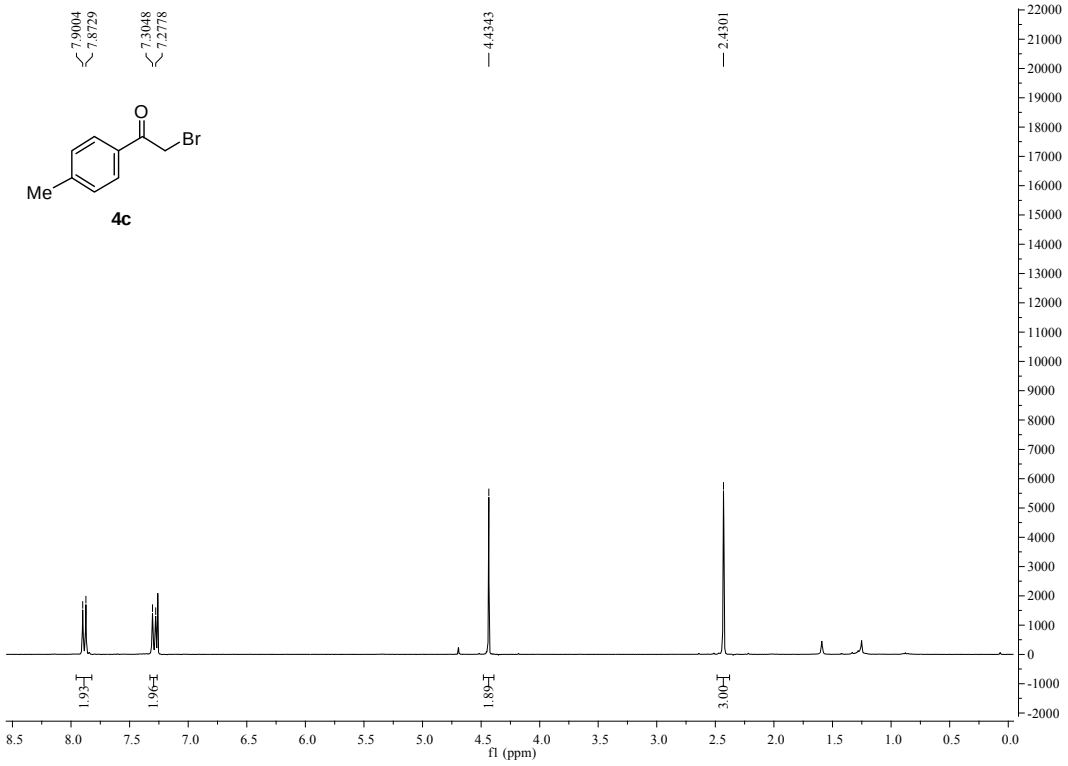
O
Br
F
4b
f1 (ppm)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Br
Me
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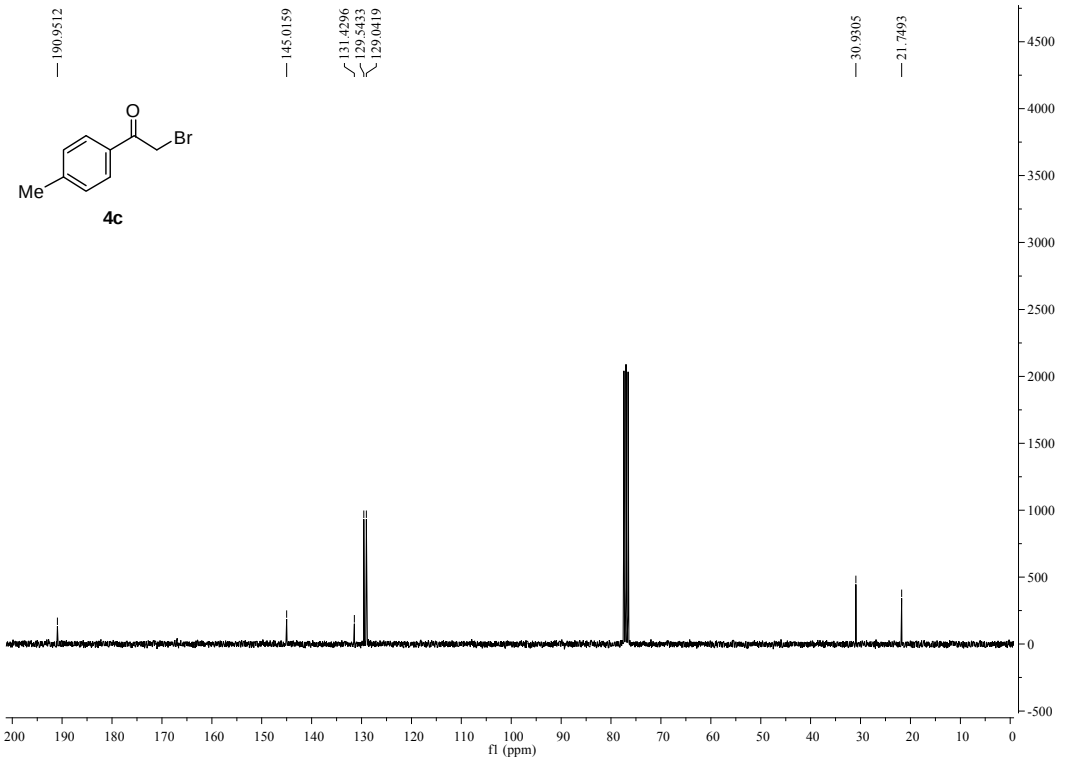
3.00
f1 (ppm)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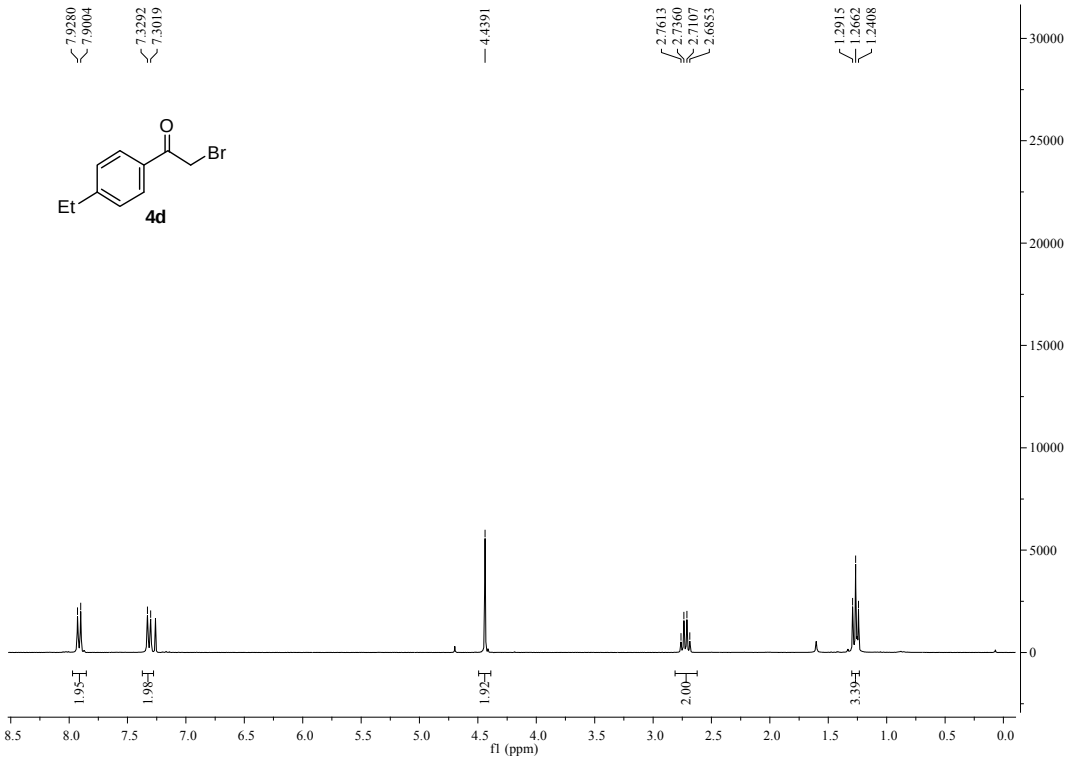
Me
4c
f1 (ppm)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2.6853
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O
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Et
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1.92
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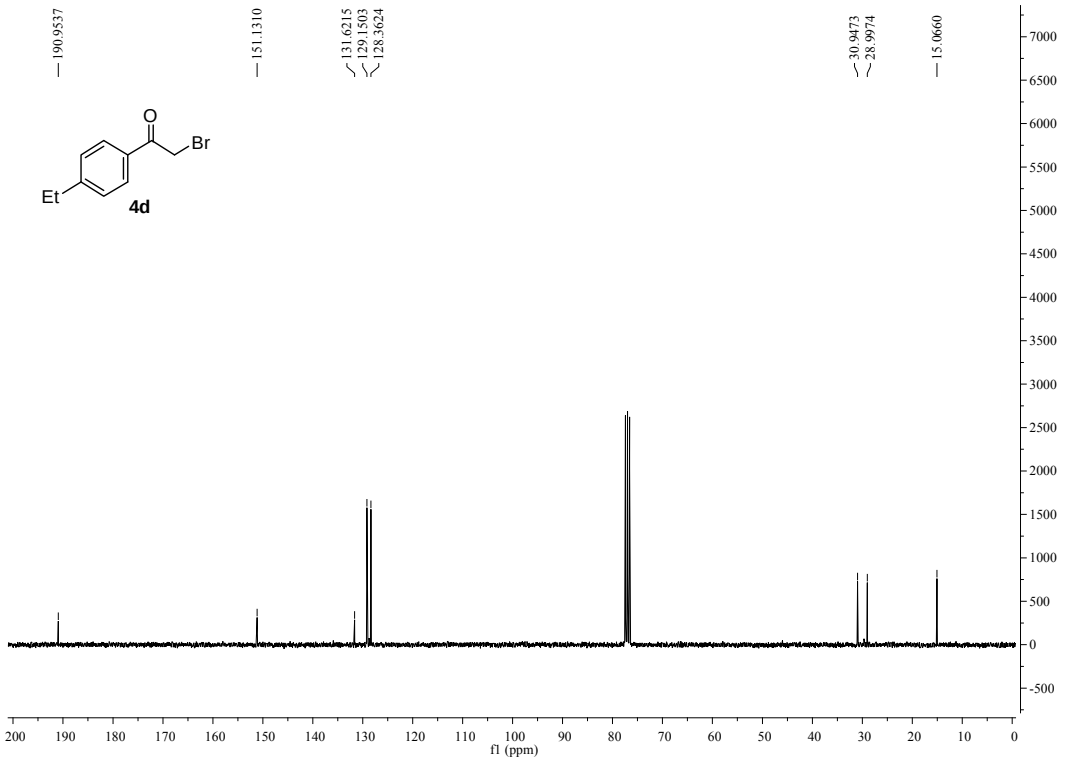
3.39
fl (ppm)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28.9974
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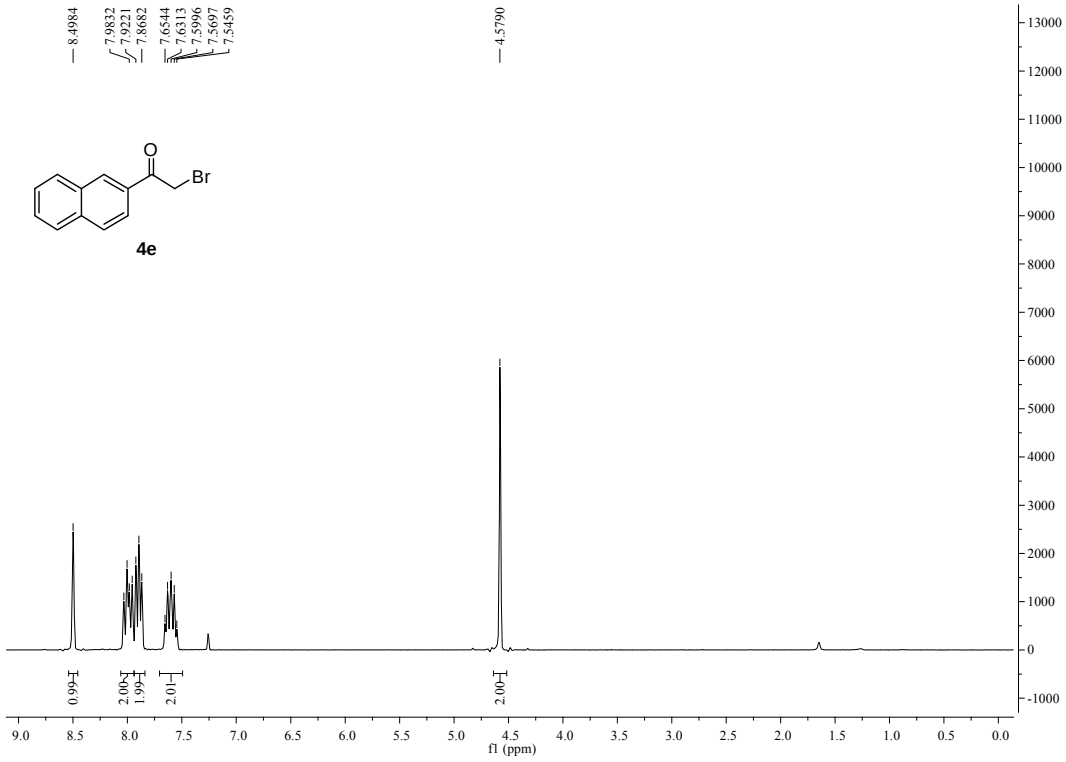
Br
Et
4d
fl (ppm)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4.5790
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Br
4e
0.99
2.00
1.99
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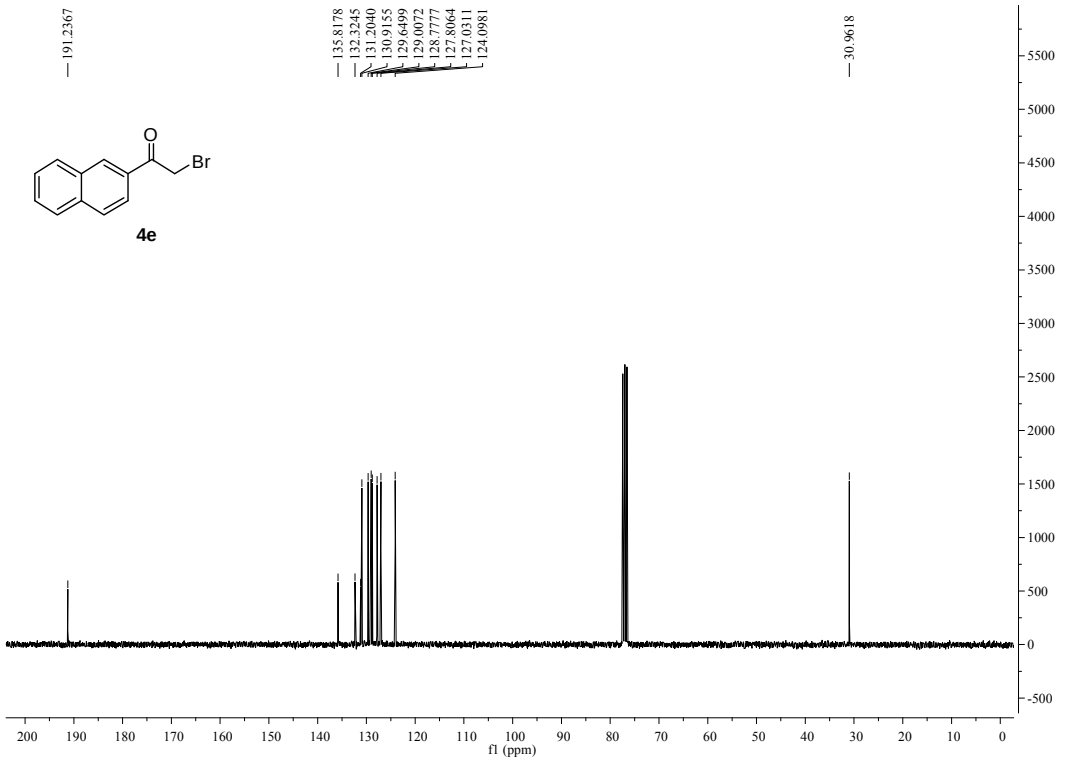
2.00
f1 (ppm)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30.9618
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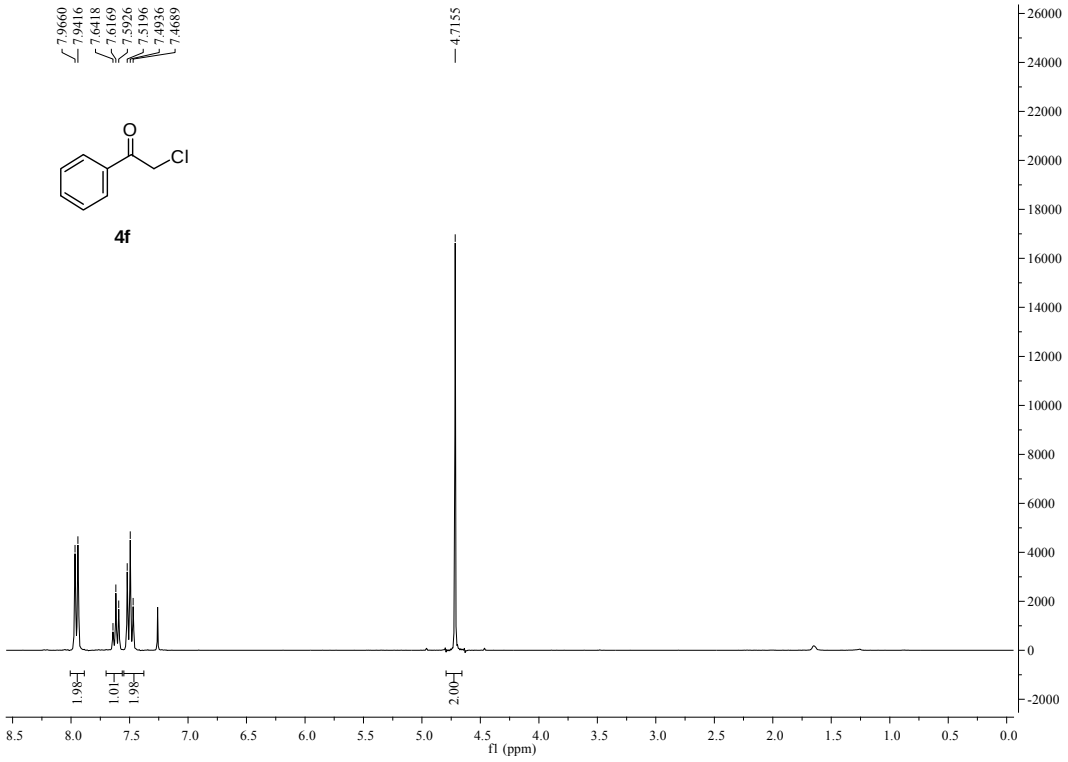
Br
4e
f1 (ppm)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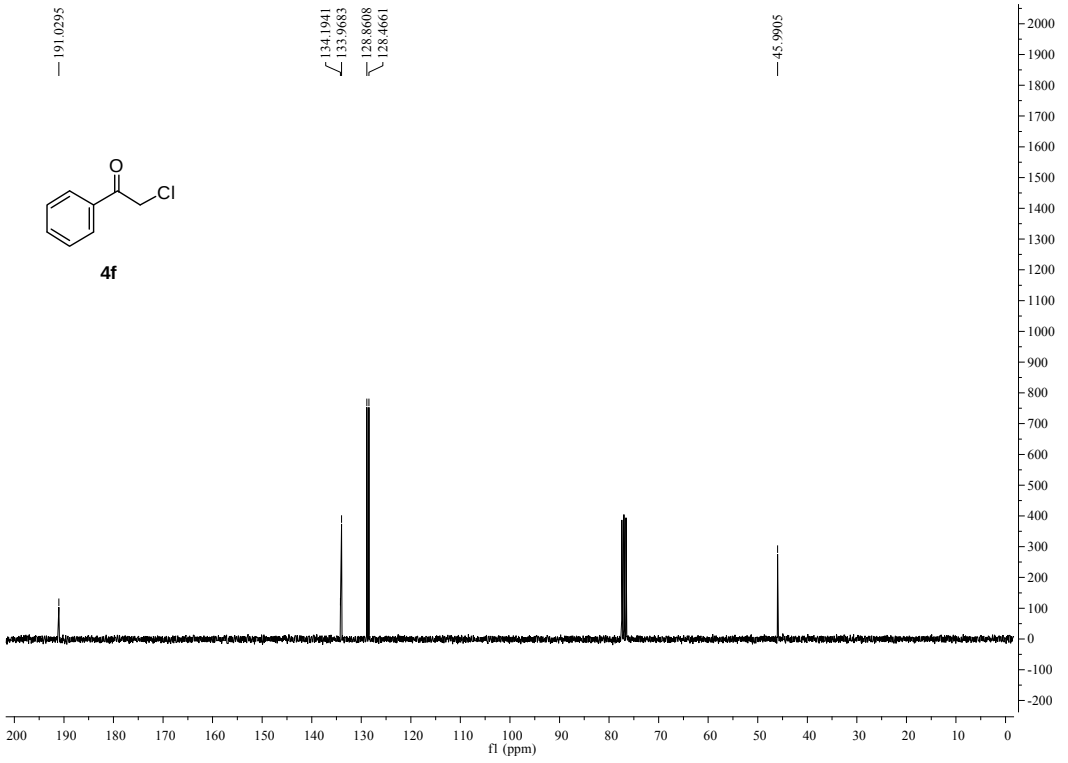
1.01
1.98
2.00
f1 (ppm)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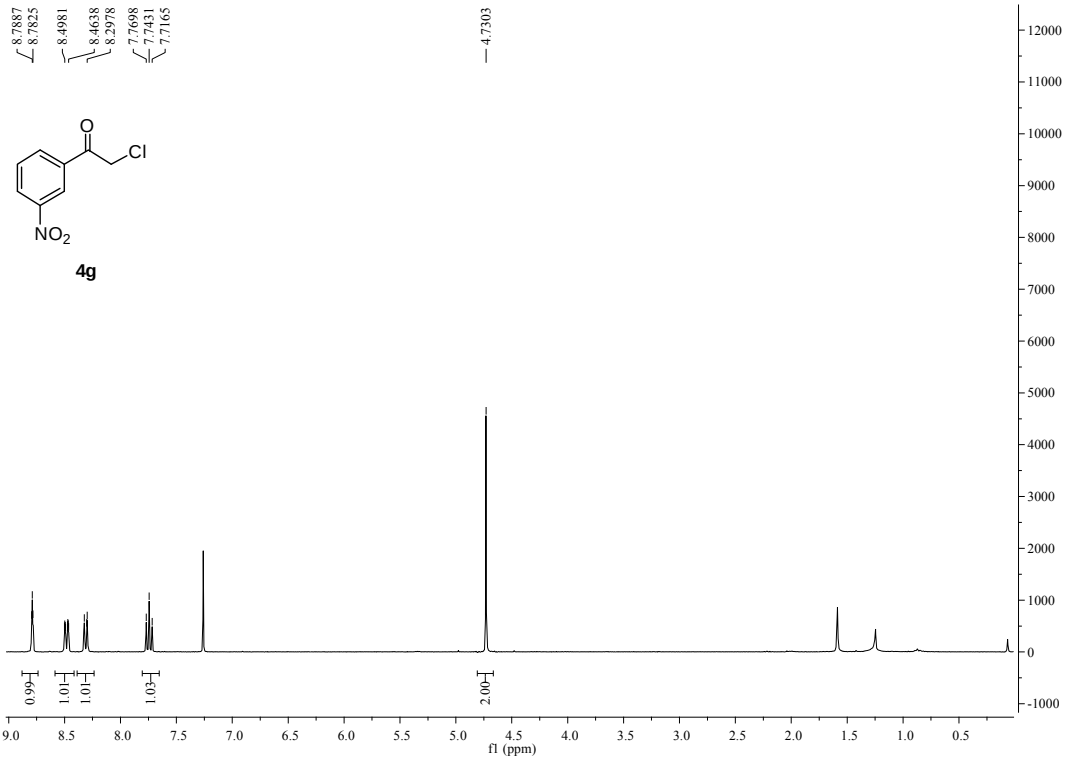
4f
f1 (ppm)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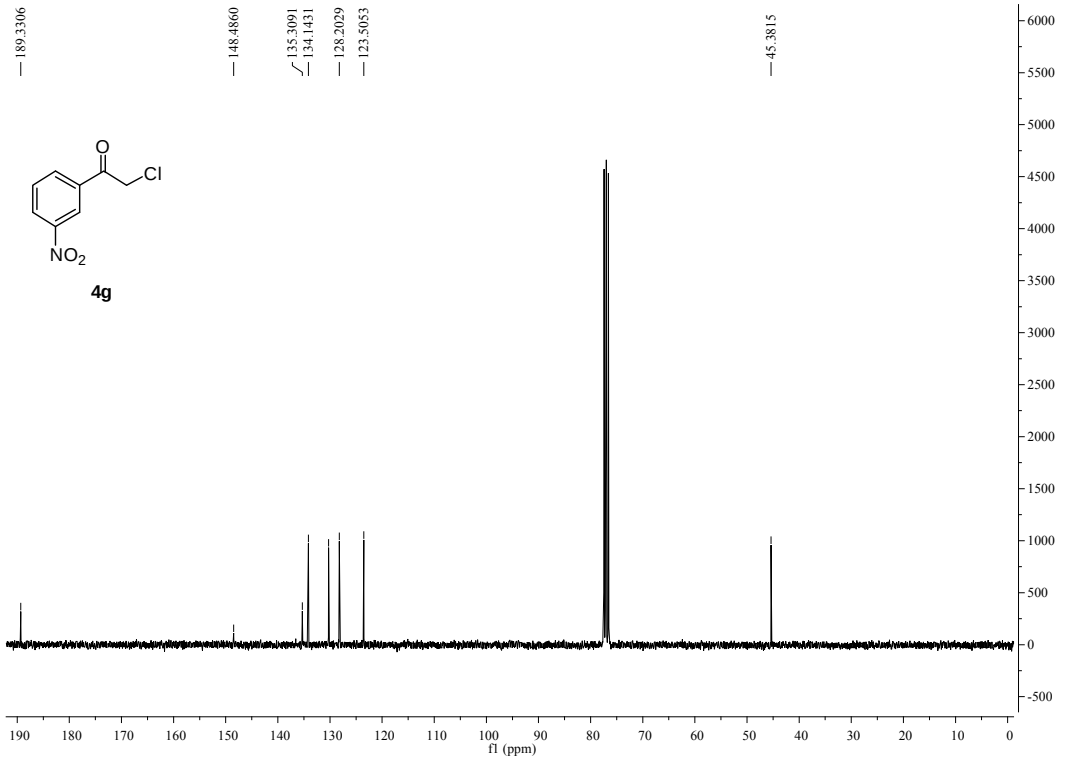
8.4638
8.2978
7.7698
7.7431
7.7165
4.7303
O
Cl
NO2
4g
0.99
1.01
1.01
1.03
2.00
fl (ppm)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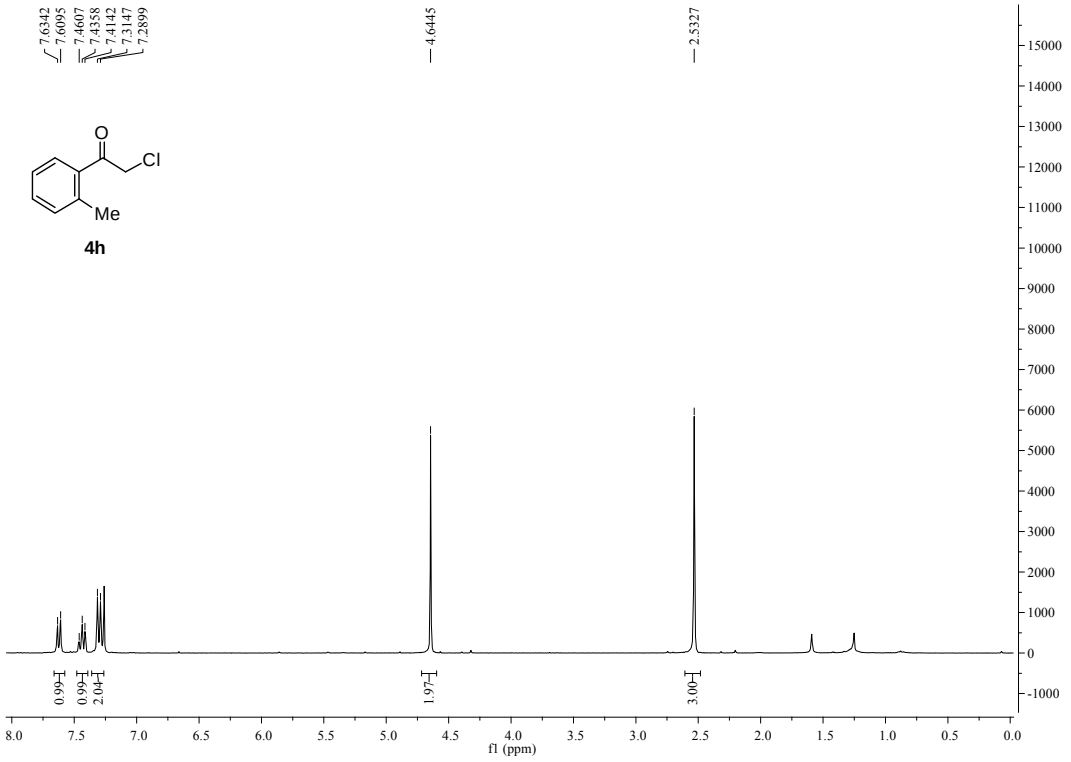
135.3091
134.1431
128.2029
123.5053
45.3815
O
Cl
NO2
4g
fl (ppm)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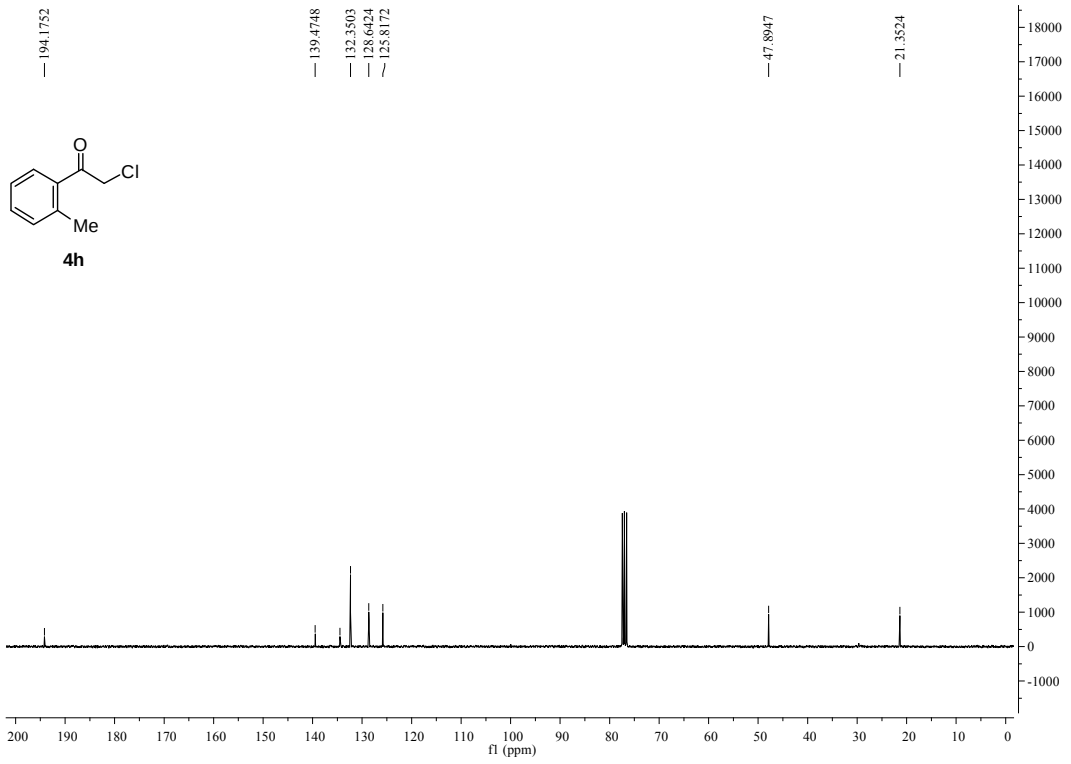
7.4607
7.4358
7.4142
7.3147
7.2899
4.6445
2.5327
O
Cl
Me
4h
0.99
0.99
2.04
1.97
3.00
f1 (ppm)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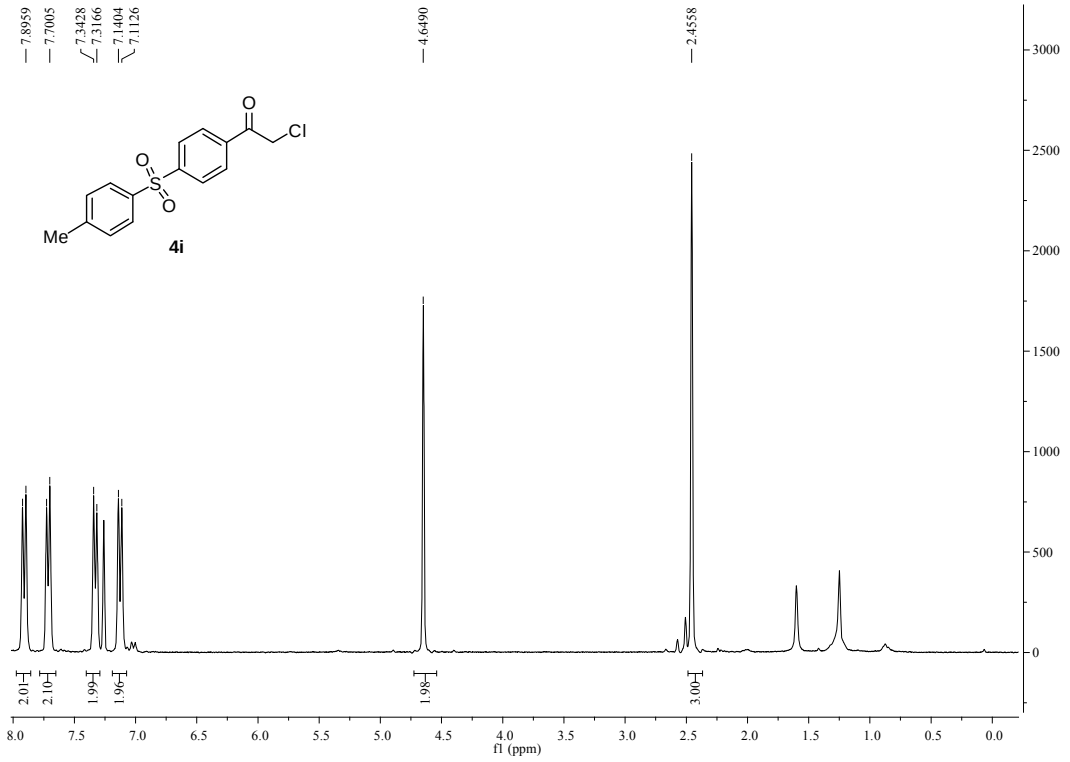
132.3503
128.6424
125.8172
47.8947
21.3524
O
Cl
Me
4h
f1 (ppm)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7.3428
7.3166
7.1404
7.1126
4.6490
2.4558
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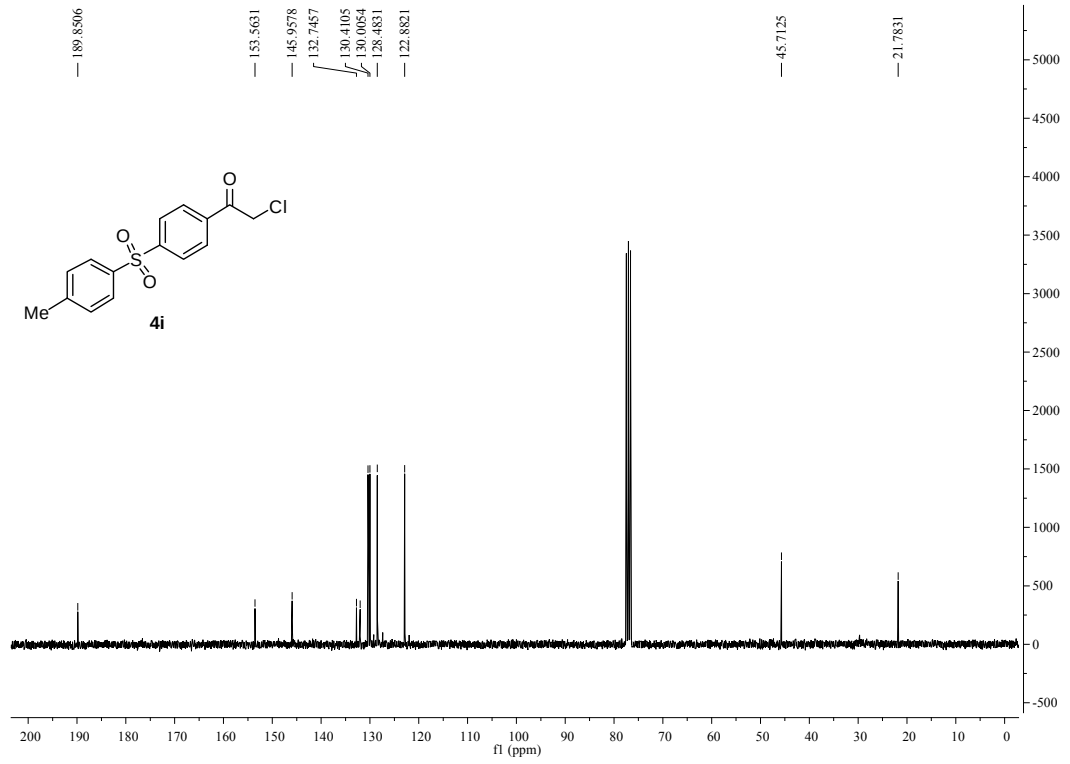
Cl
O
S
O
Me
4i
2.01
2.10
1.99
1.96
1.98
3.00
f1 (ppm)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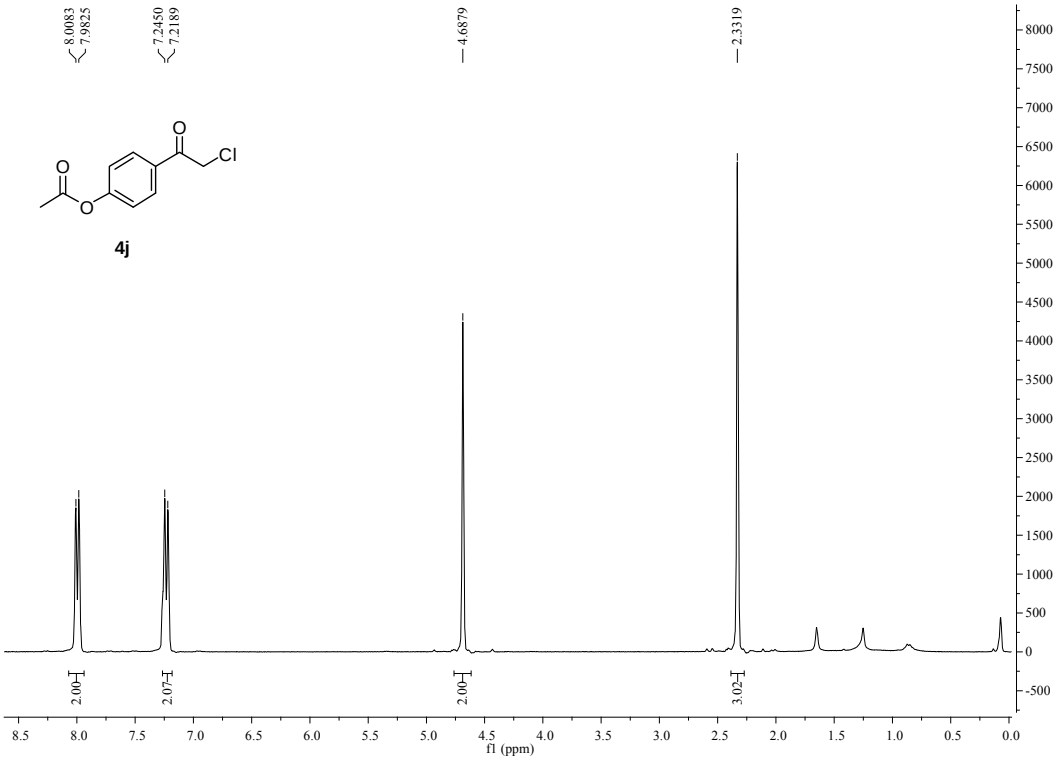
Cl
O
S
O
Me
4i
f1 (ppm)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7.2450
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4.6879
2.3319
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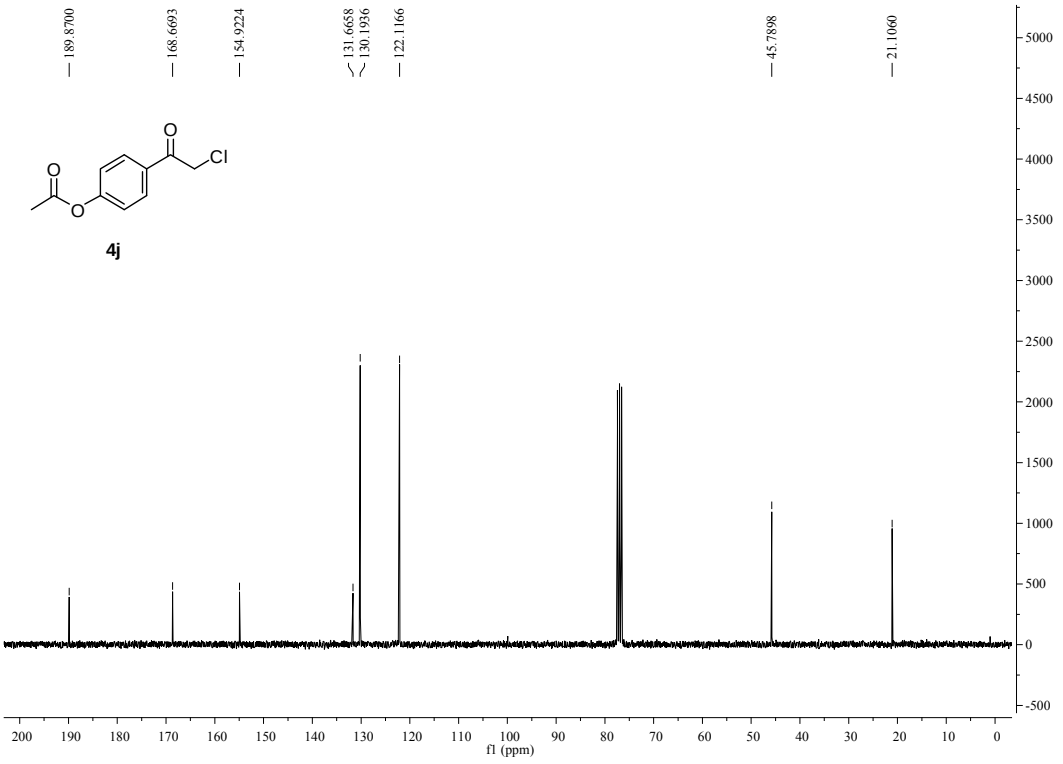
Cl
O
O
4j
2.00
2.07
2.00
3.02
f1 (ppm)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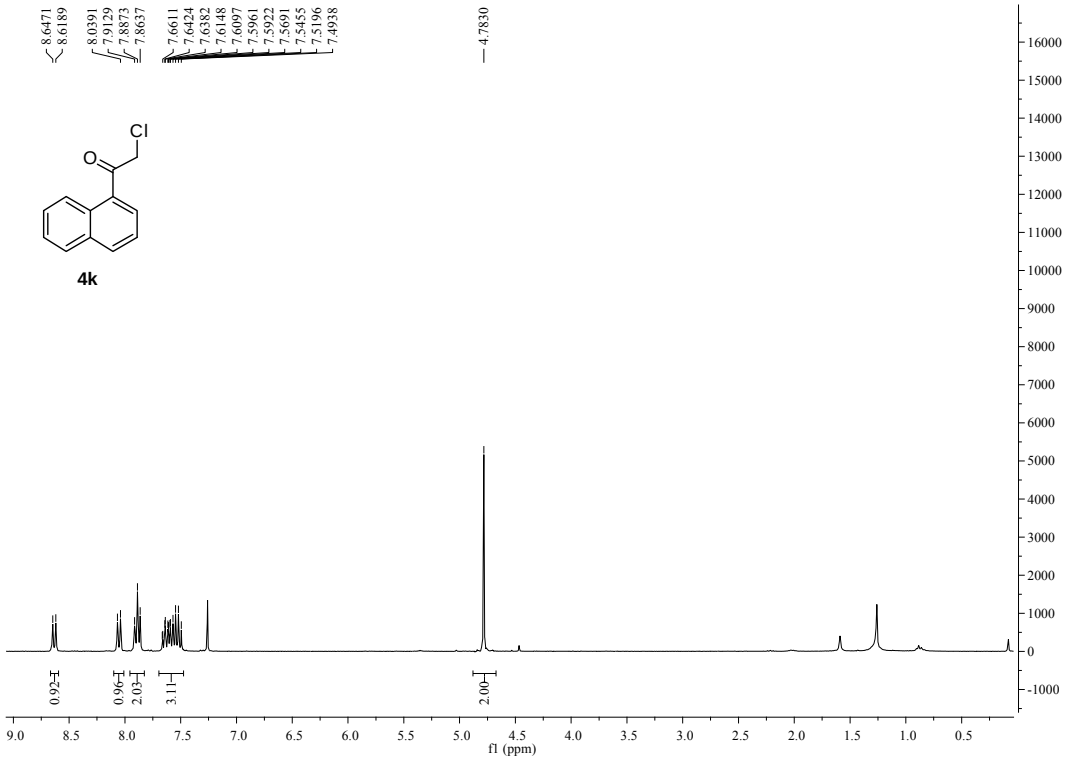
Cl
O
O
4j
f1 (ppm)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8.6189
8.0391
7.9129
7.8873
7.8637
7.6611
7.6424
7.6382
7.6148
7.6097
7.5961
7.5922
7.5691
7.5455
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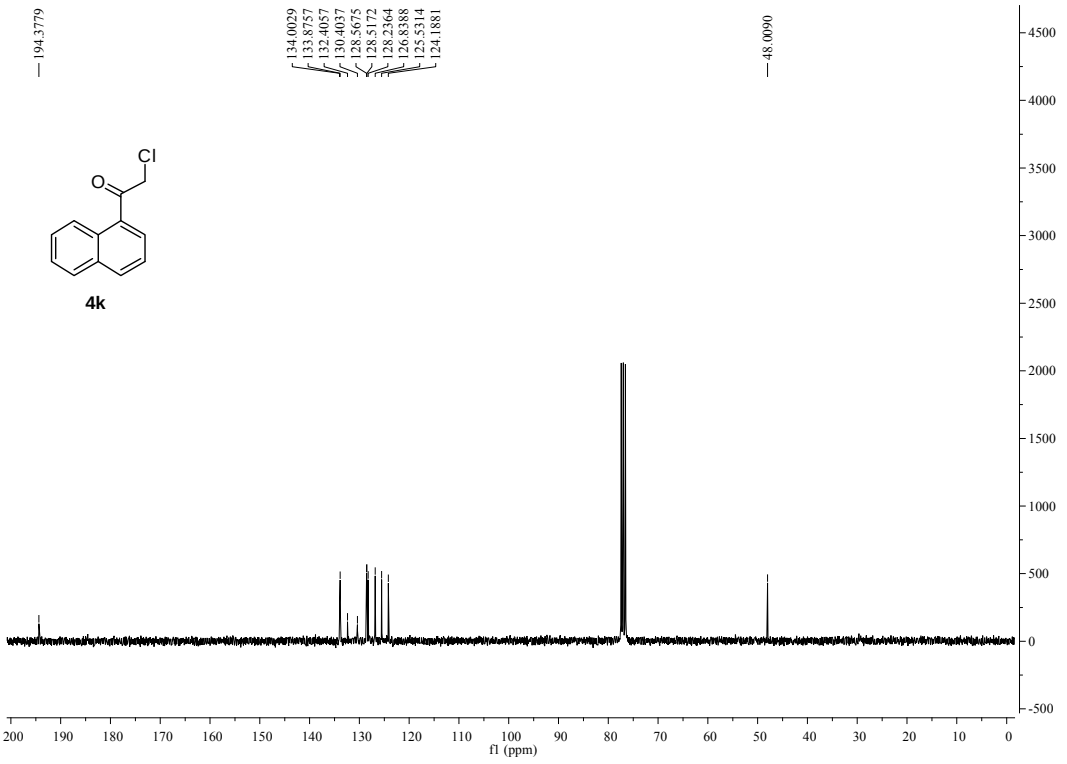
4.7830
Cl
O
4k
0.92
0.96
2.03
3.11
2.00
f1 (ppm)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132.4057
130.4037
128.5675
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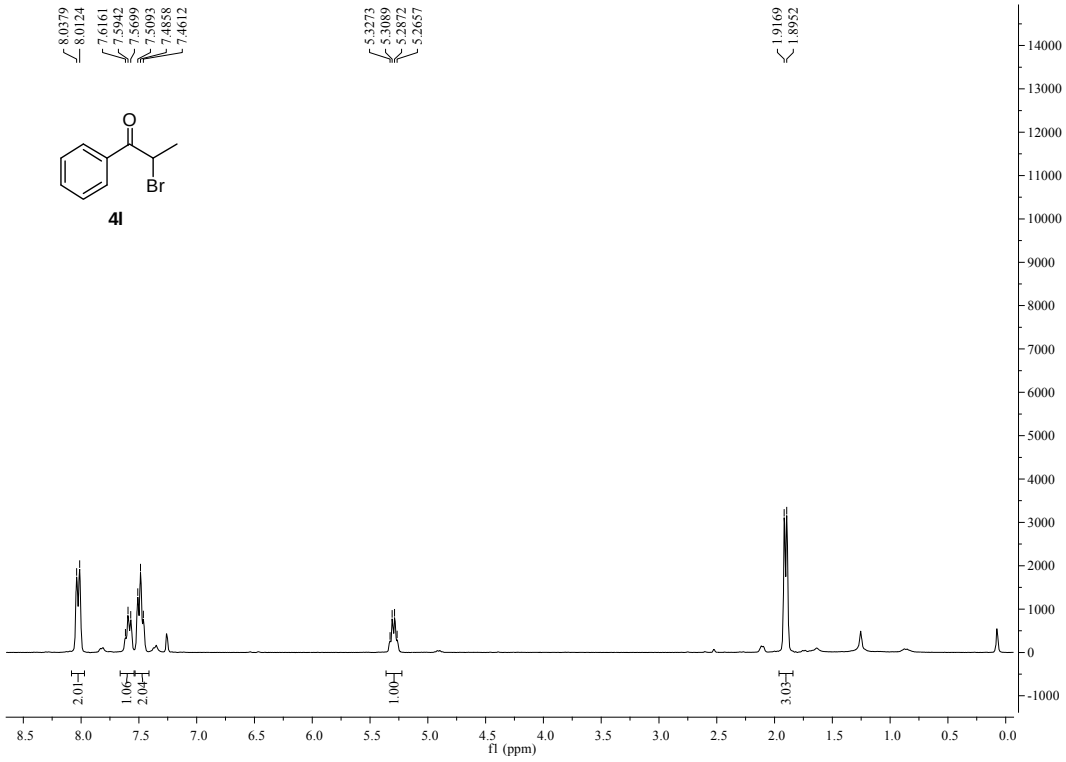
125.5314
124.1881
48.0090
Cl
O
4k
f1 (ppm)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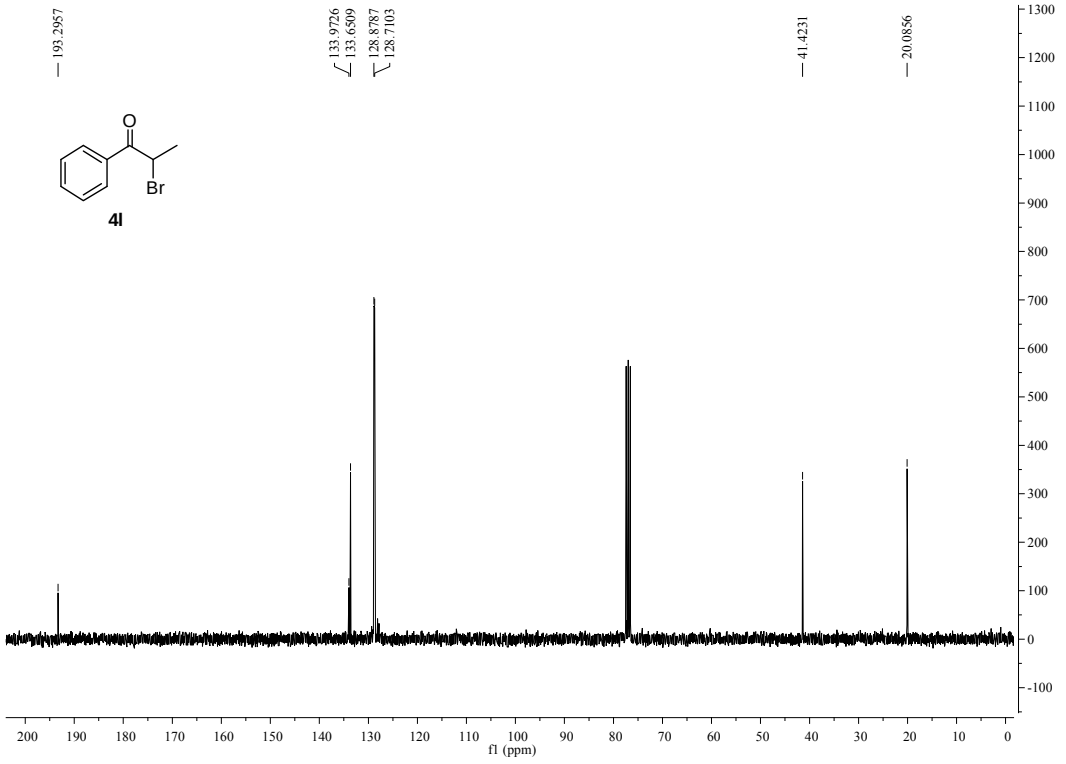
8.0124
7.6161
7.5942
7.5699
7.5093
7.4858
7.4612
5.3273
5.3089
5.2872
5.2657
1.9169
1.8952
O
Br
4l
2.01
1.06
2.04
1.00
3.03
f1 (ppm)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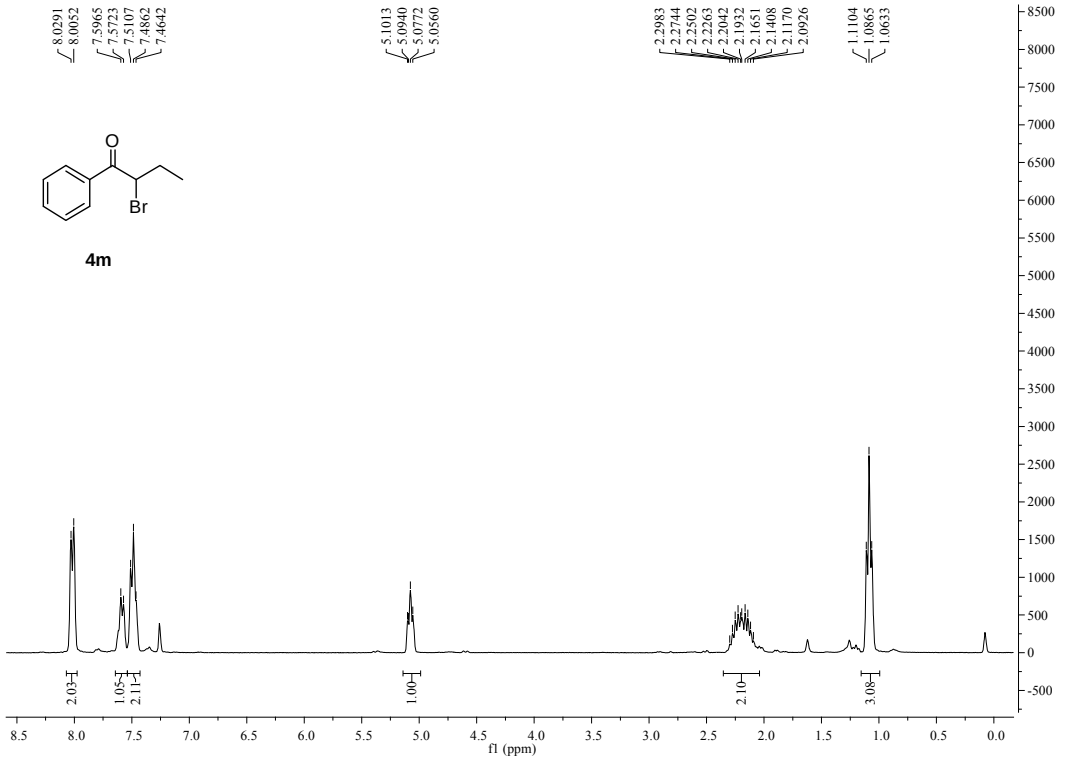
133.6509
128.8787
128.7103
41.4231
20.0856
O
Br
4l
f1 (ppm)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7.5107
7.4862
7.4642
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5.0940
5.0772
5.0560
2.2983
2.2744
2.2502
2.2263
2.2042
2.1932
2.1651
2.1408
2.1170
2.0926
1.1104
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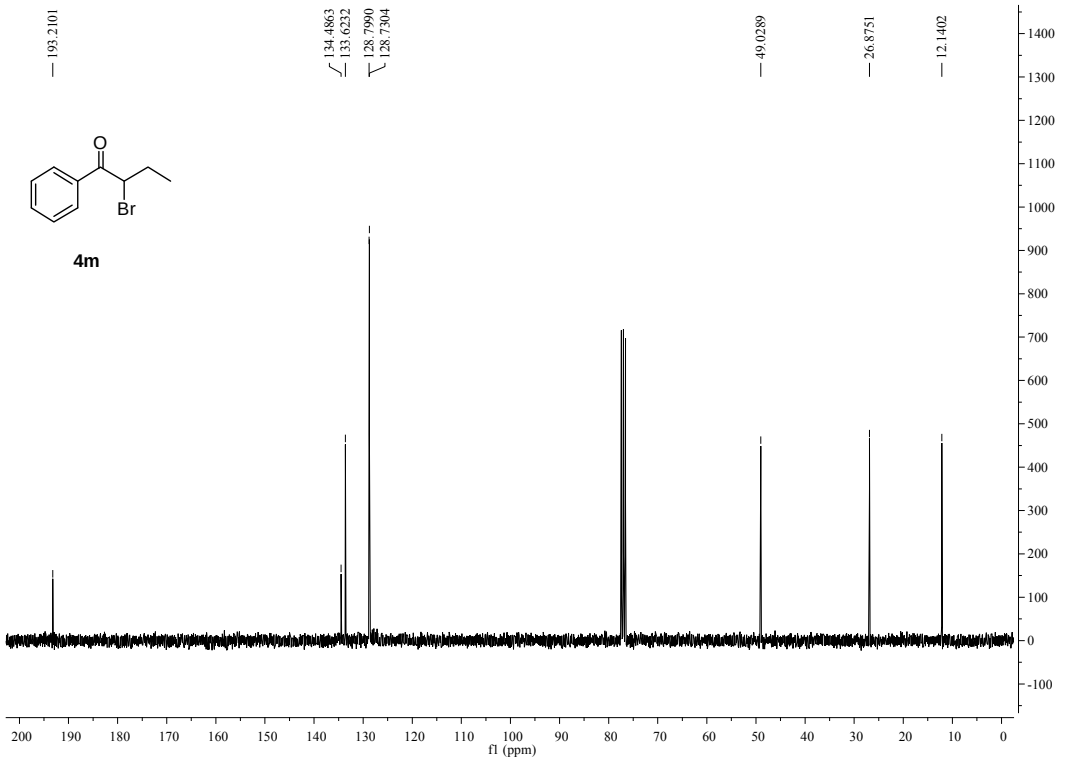
O
Br
4m
2.03
1.05
2.11
1.00
2.10
3.08
f1 (ppm)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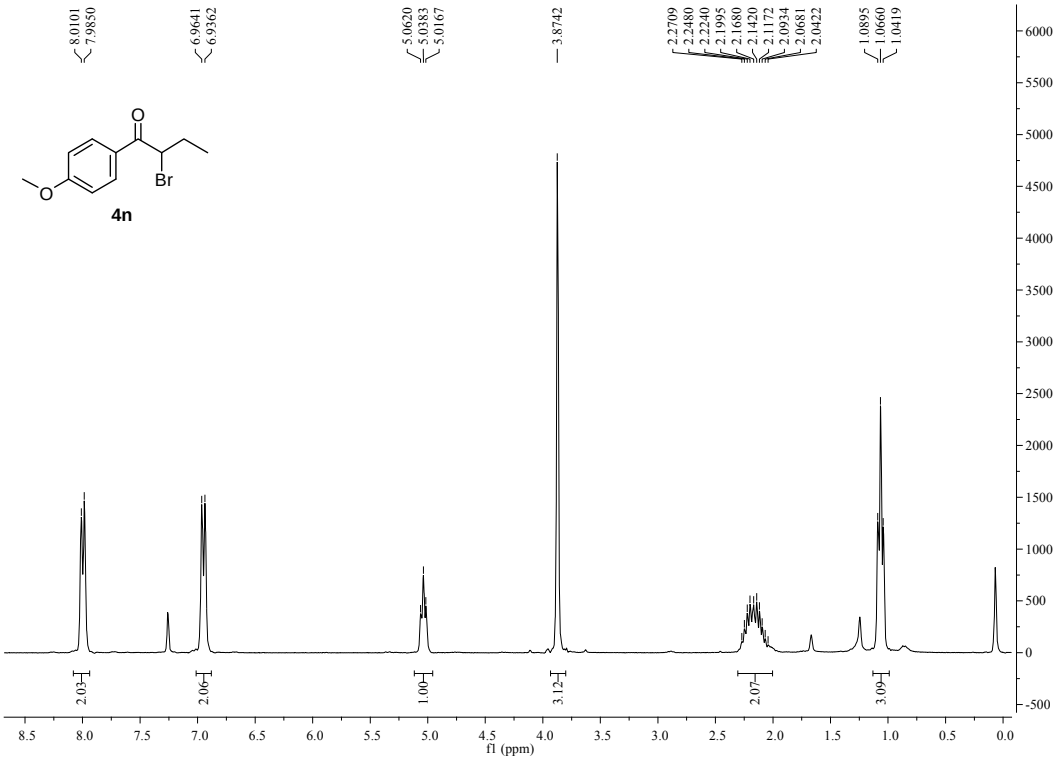
49.0289
26.8751
12.1402
O
Br
4m
f1 (ppm)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2.2709
2.2480
2.2240
2.1995
2.1680
2.1420
2.1172
2.0934
2.0681
2.0422
1.0895
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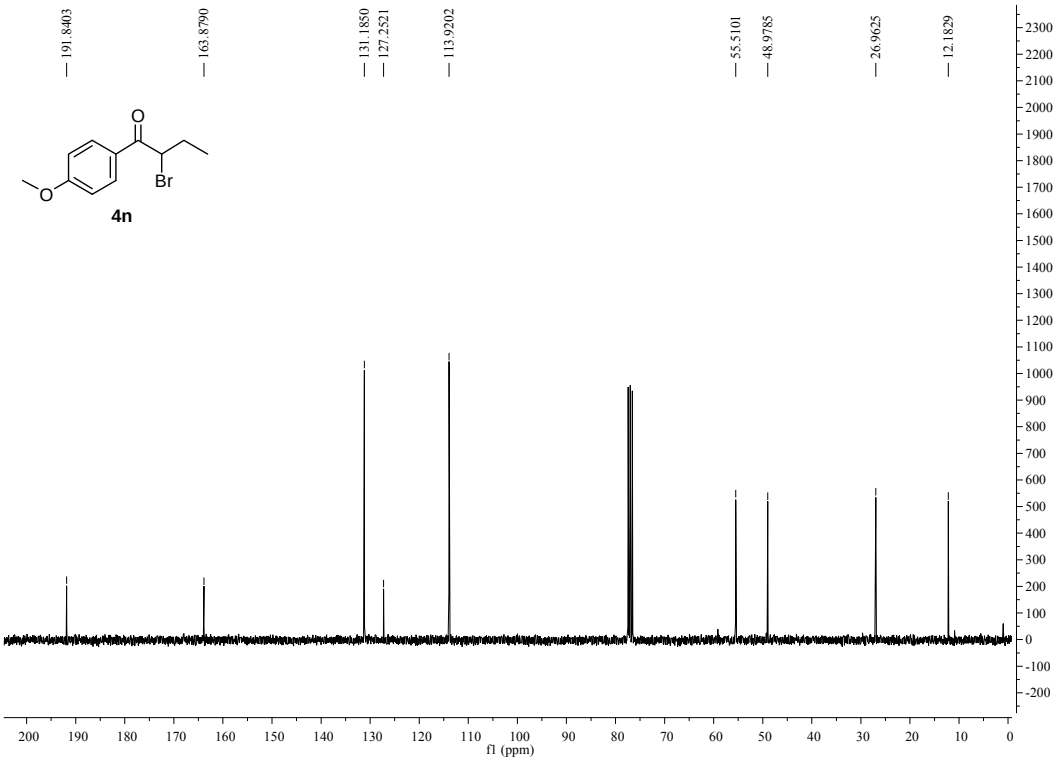
1.0419
O
Br
O
4n
2.03
2.06
1.00
3.12
2.07
3.09
f1 (ppm)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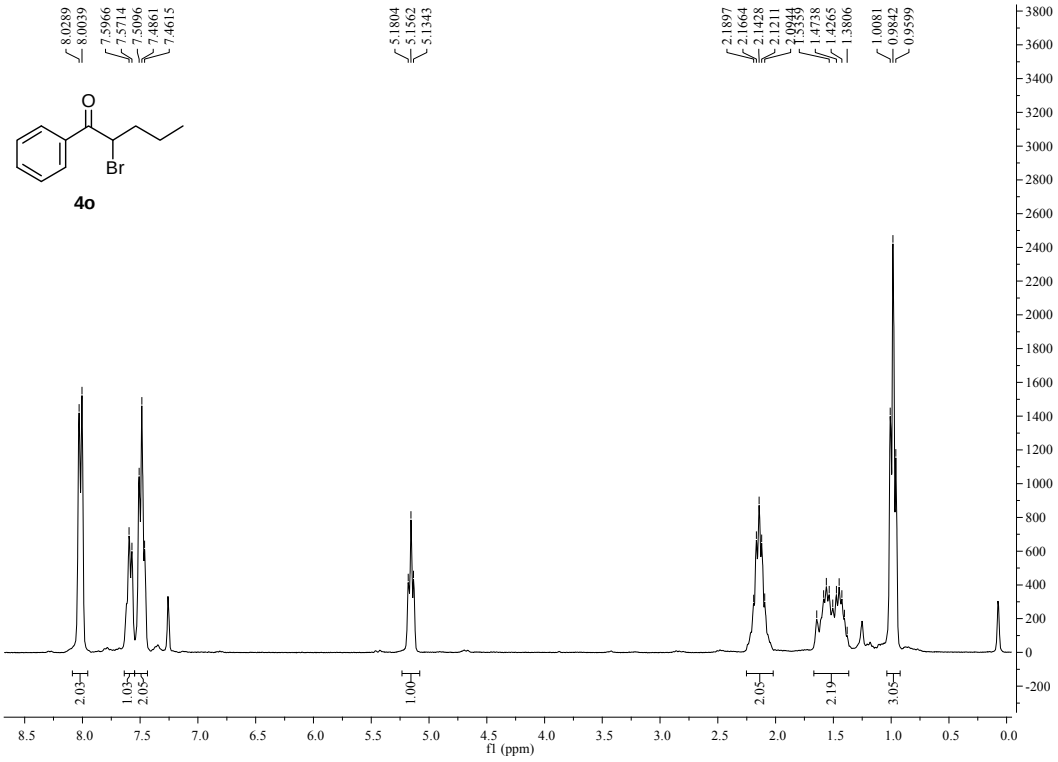
48.9785
26.9625
12.1829
O
Br
O
4n
f1 (ppm)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2.1897
2.1664
2.1428
2.1211
1.4738
1.4265
1.3806
1.0081
0.9842
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Br
4o
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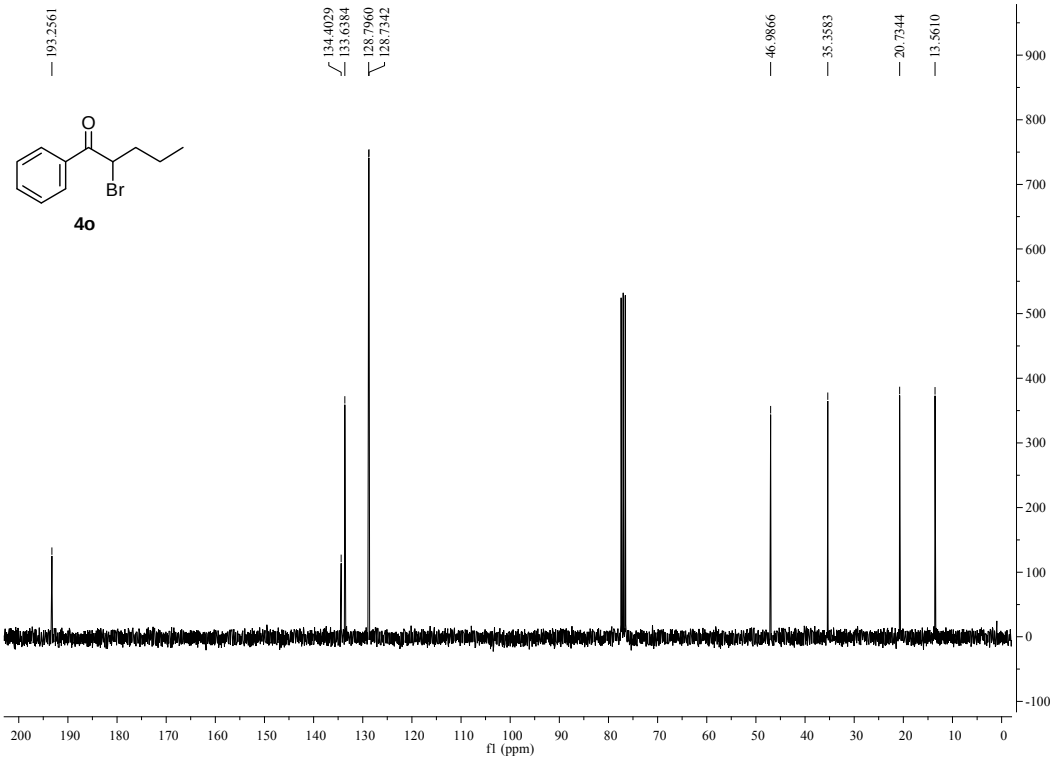
1.03
2.05
1.00
2.05
2.19
3.05
f1 (ppm)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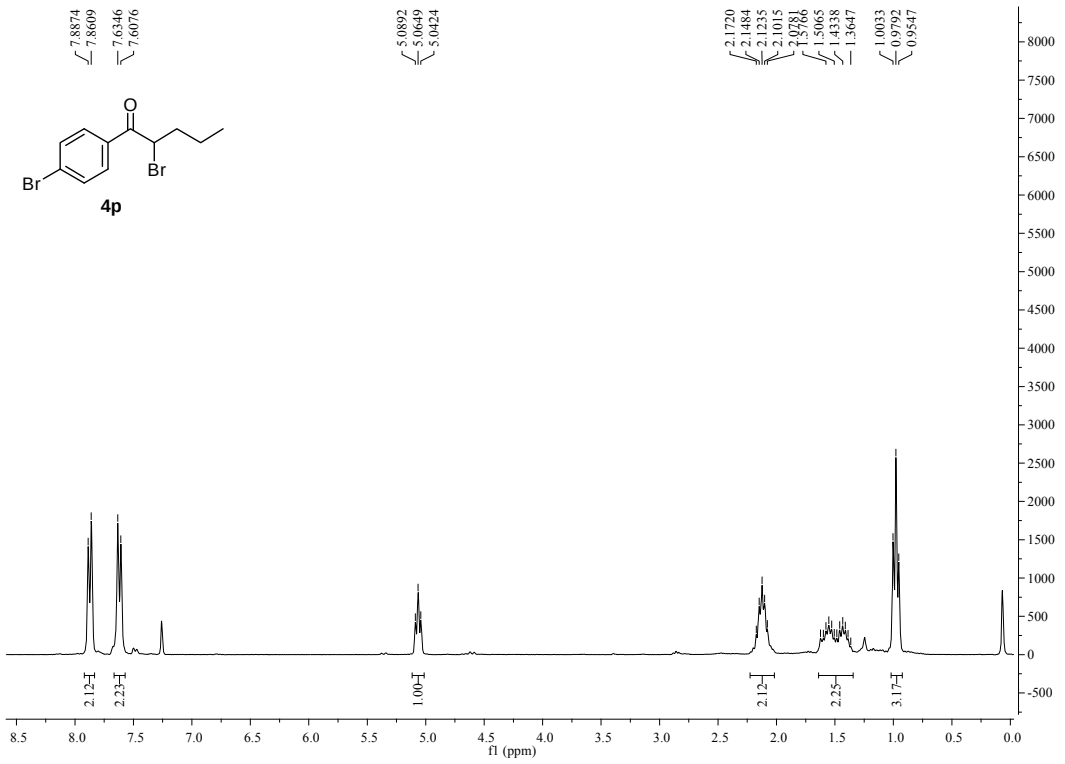
35.3583
20.7344
13.5610
O
Br
4o
f1 (ppm)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5.0424
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2.1015
1.5781
1.5066
1.4338
1.3647
1.0033
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Br
Br
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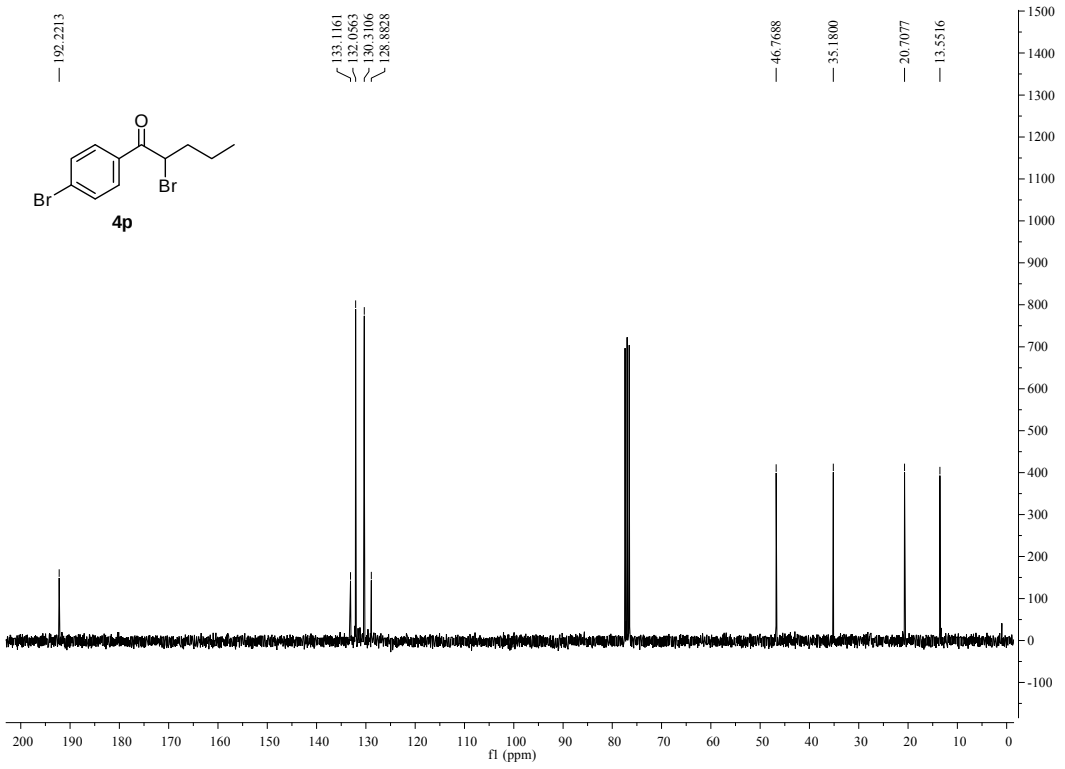
2.23
1.00
2.12
2.25
3.17
f1 (ppm)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20.7077
13.5516
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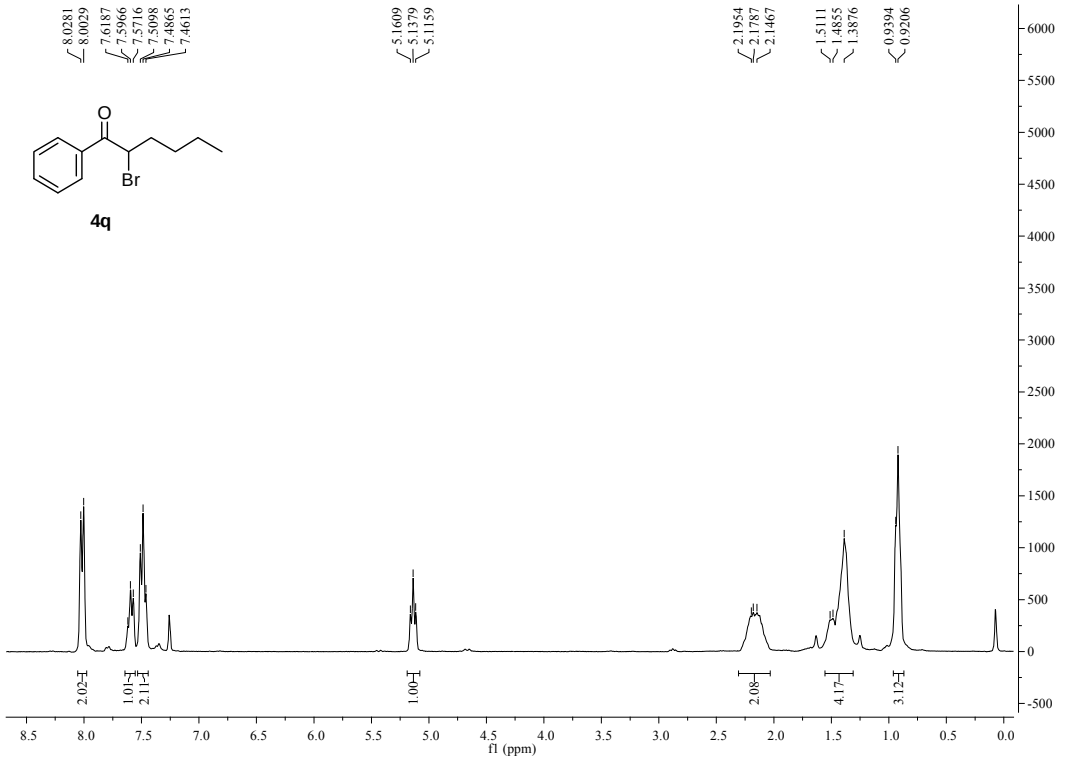
Br
Br
4p
f1 (ppm)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5.1159
2.1954
2.1787
2.1467
1.5111
1.4855
1.3876
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Br
4q
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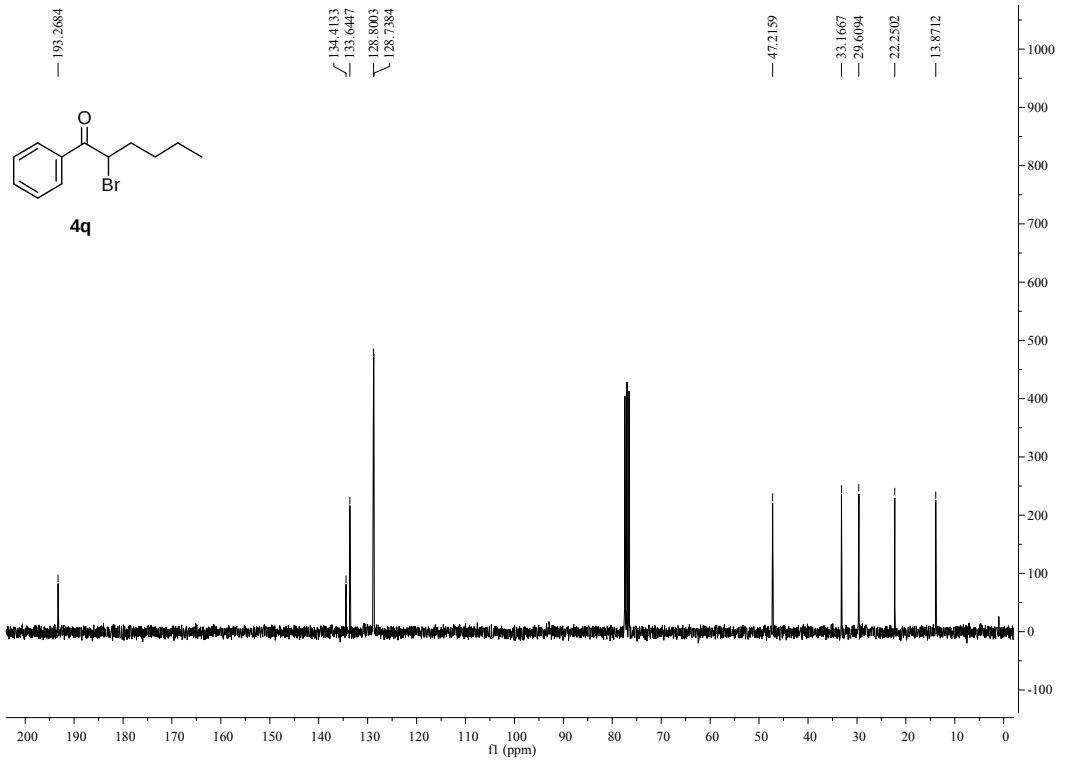
1.00
2.08
4.17
3.12
fl (ppm)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13.8712
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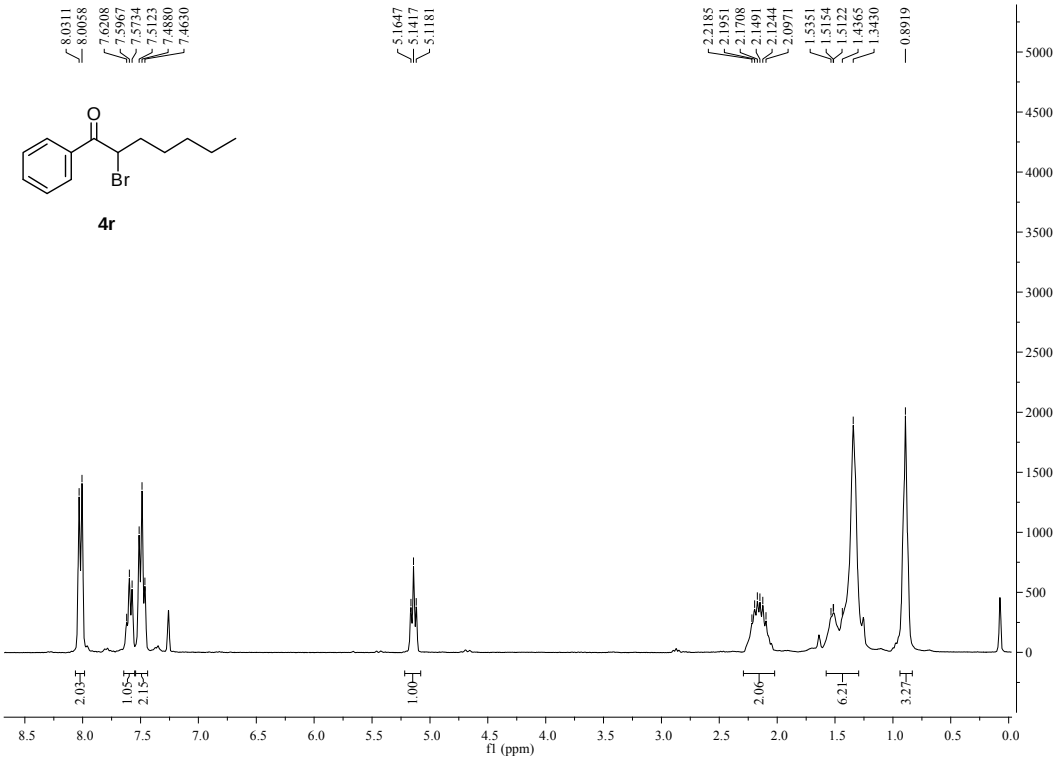
Br
4q
fl (ppm)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5.1647
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2.2185
2.1951
2.1708
2.1491
2.1244
2.0971
1.5351
1.5154
1.5122
1.4365
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Br
4r
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1.05
2.15
1.00
2.06
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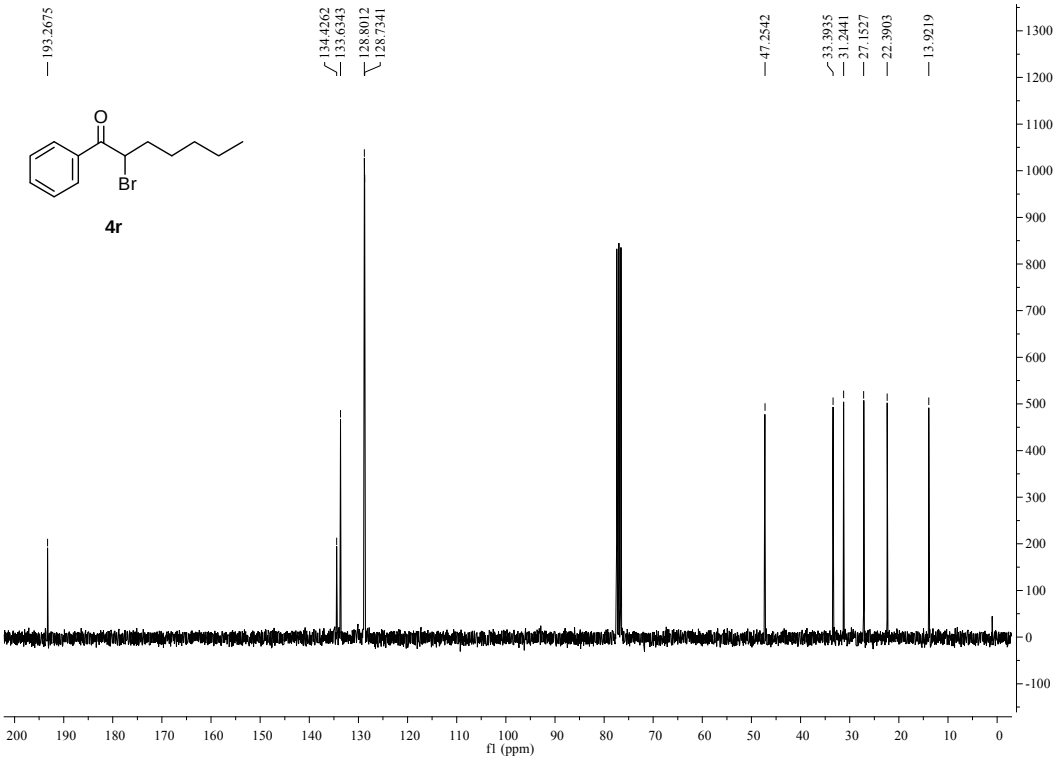
3.27
fl (ppm)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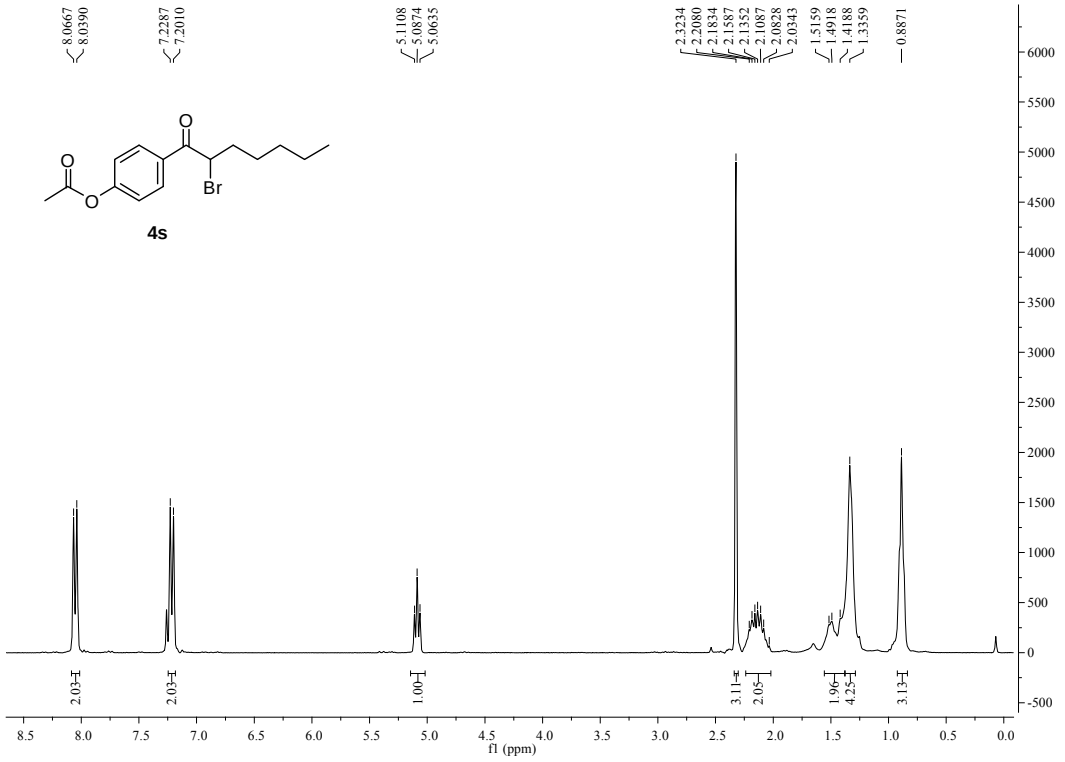
Br
4r
fl (ppm)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2.1352
2.1087
2.0828
2.0343
1.5159
1.4918
1.4188
1.3359
0.8871
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O
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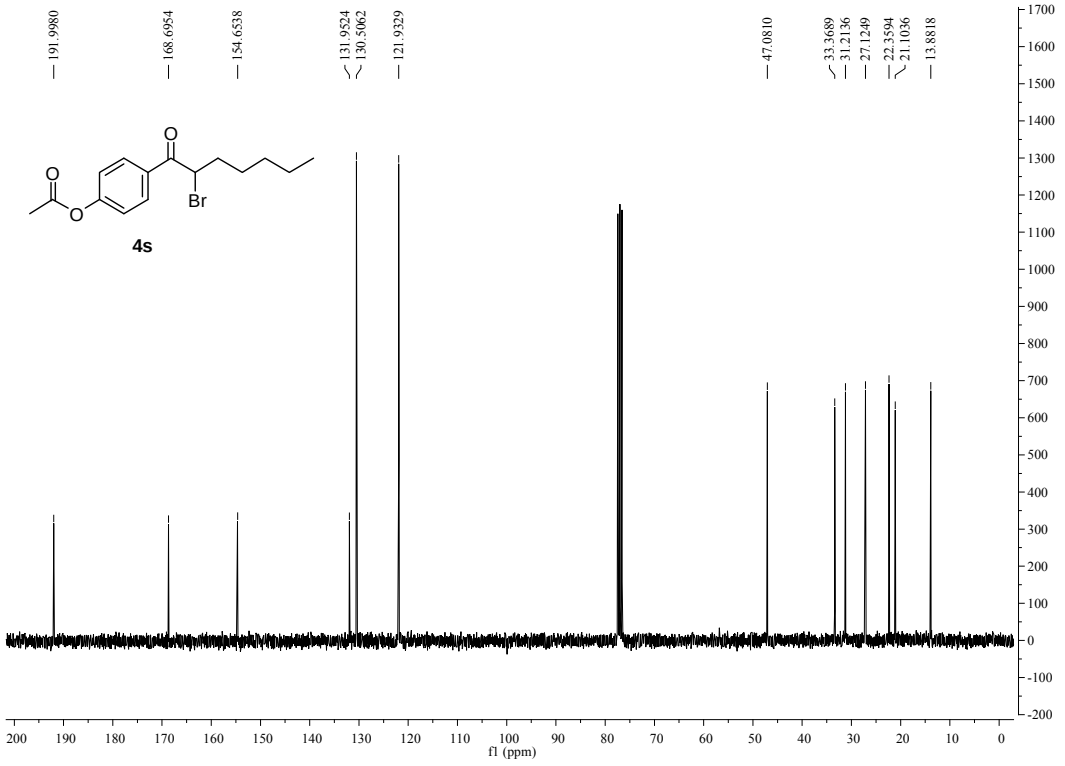
2.03
1.00
3.11
2.05
1.96
4.25
3.13
f1 (ppm)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22.3594
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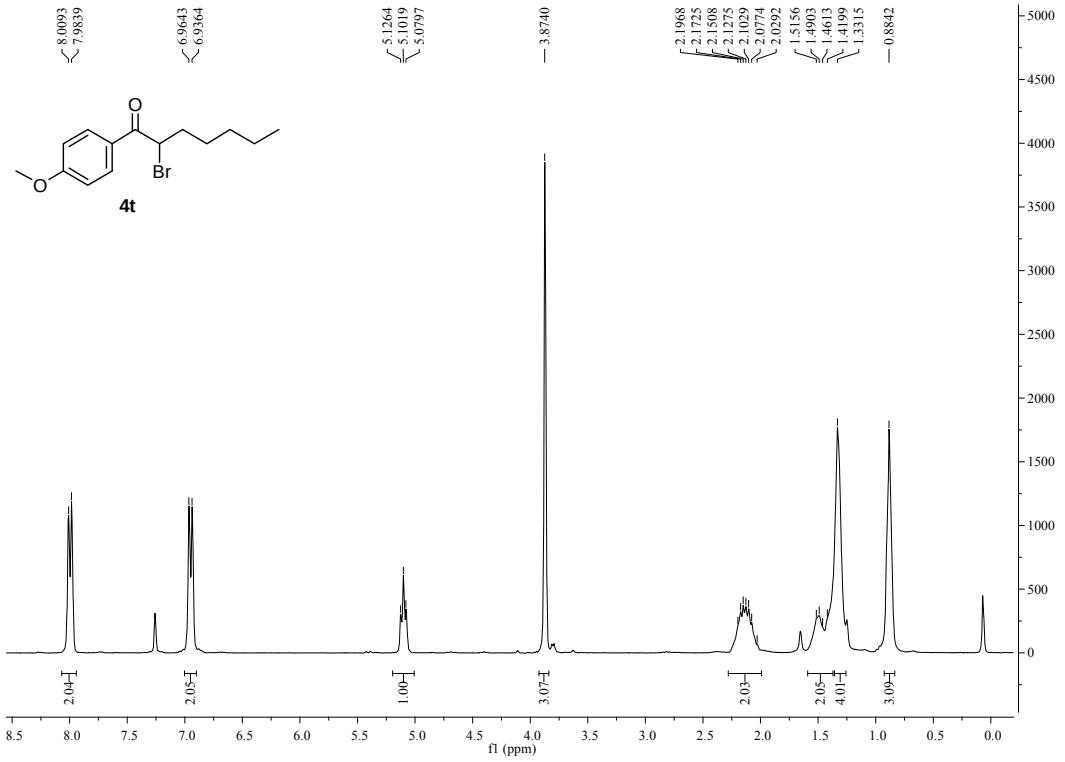
13.8818
O
O
Br
4s
f1 (ppm)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2.1029
2.0774
2.0292
1.5156
1.4903
1.4613
1.4199
1.3315
0.8842
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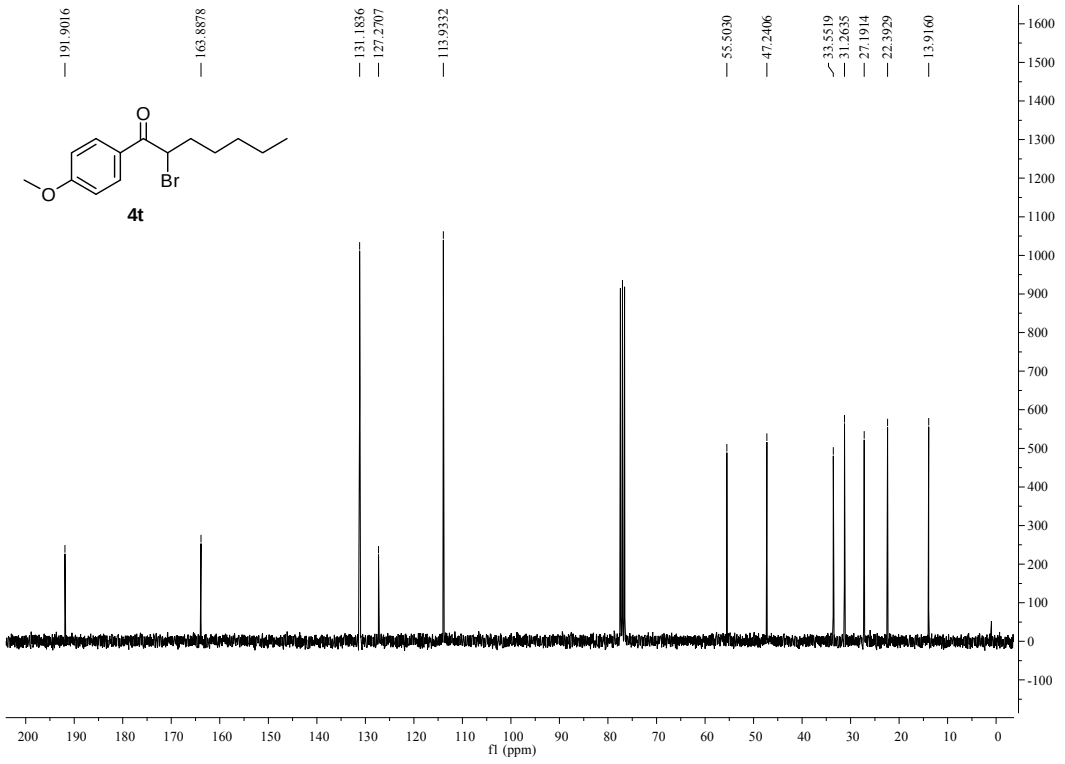
2.05
1.00
3.07
2.03
2.05
4.01
3.09
f1 (ppm)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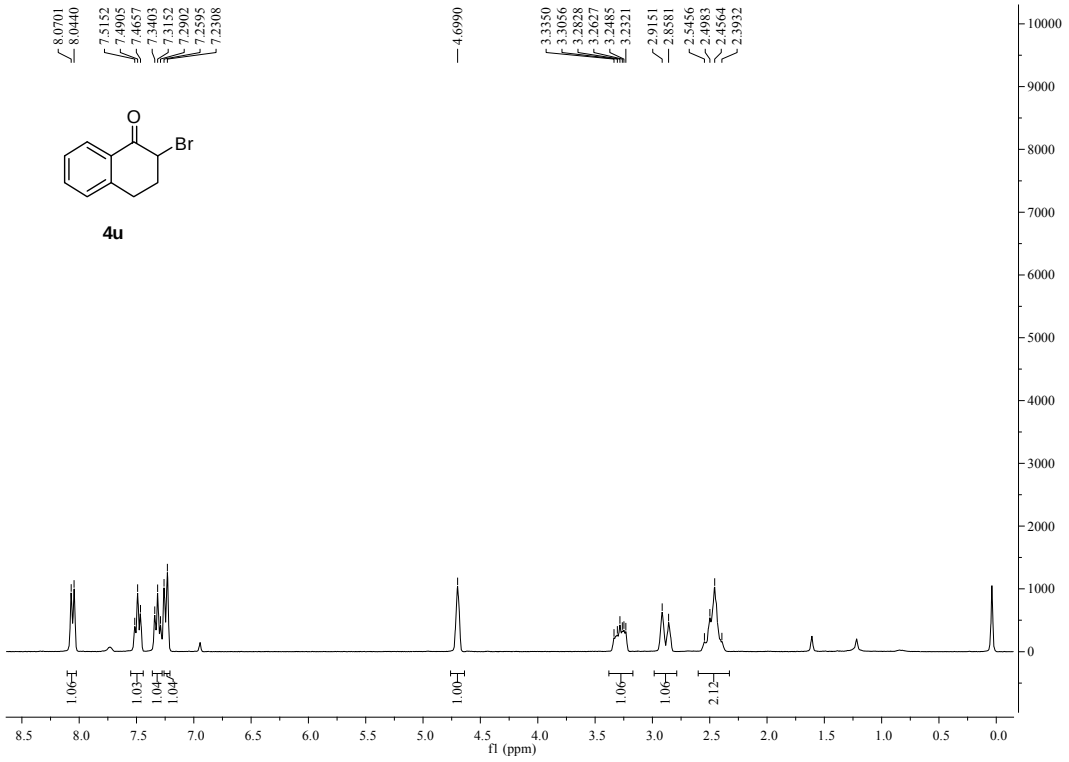
Br
O
4t
f1 (ppm)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3.3350
3.3056
3.2828
3.2627
3.2485
3.2321
2.9151
2.8581
2.5456
2.4983
2.4564
2.3932
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4u
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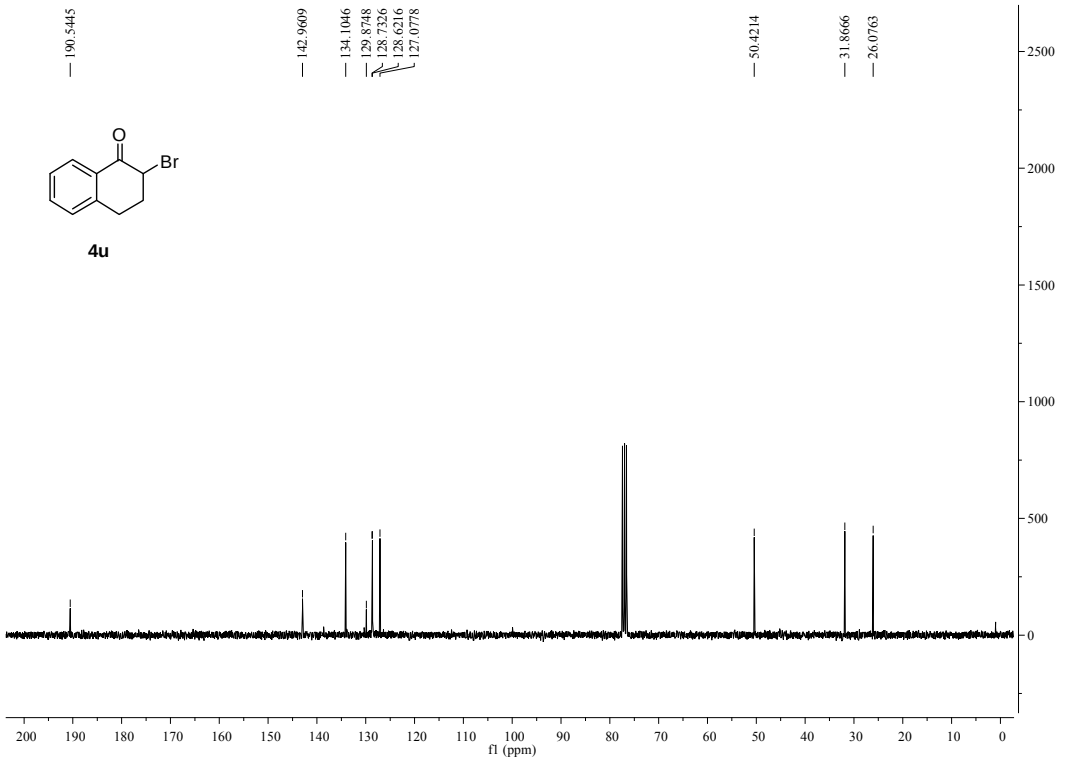
1.03
1.04
1.04
1.00
1.06
1.06
2.12
f1 (ppm)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26.0763
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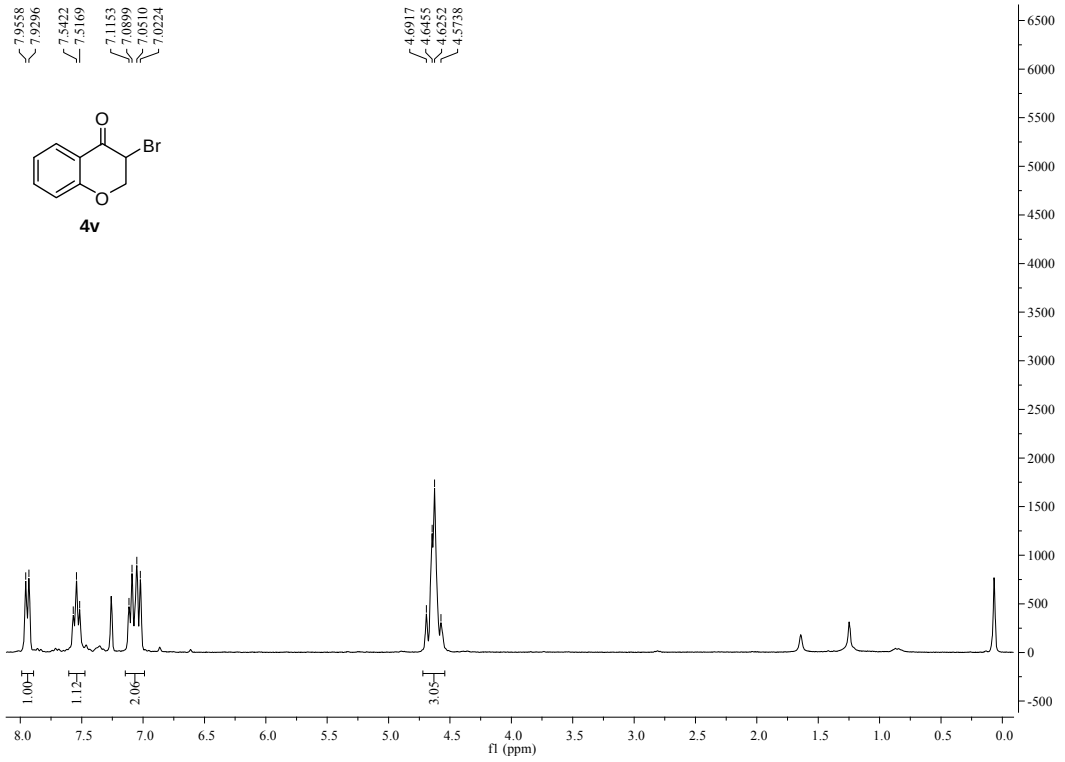
Br
4u
f1 (ppm)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7.0510
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4.5738
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Br
O
4v
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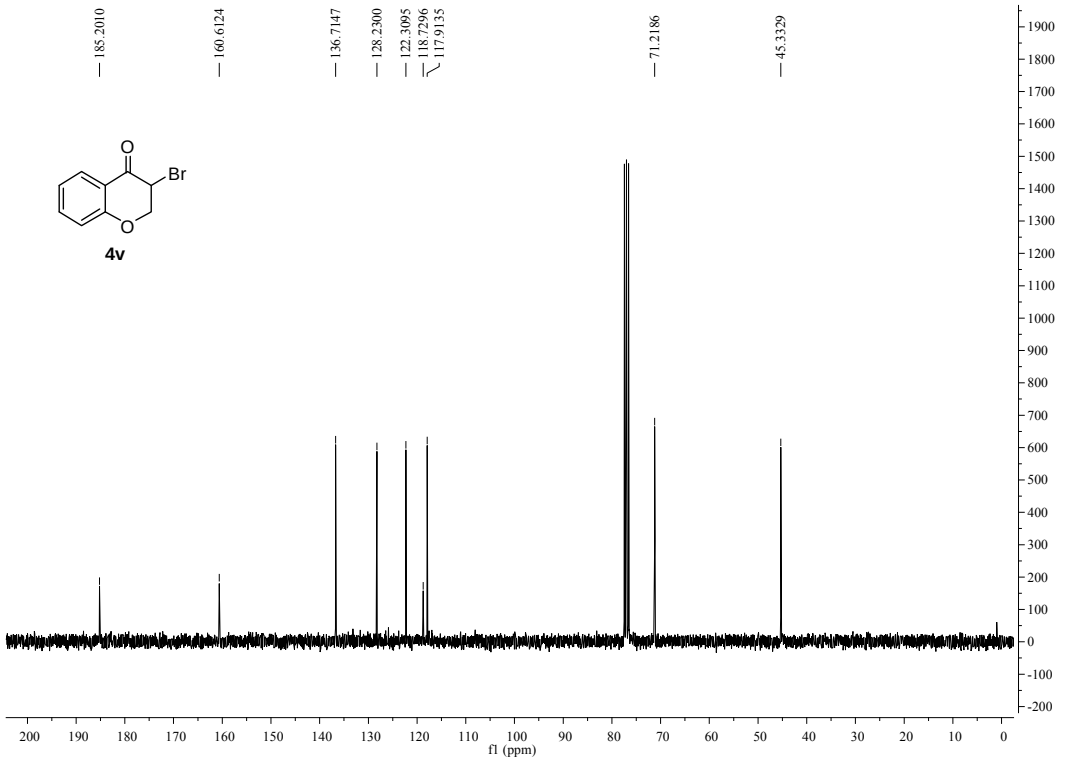
1.12
2.06
3.05
fl (ppm)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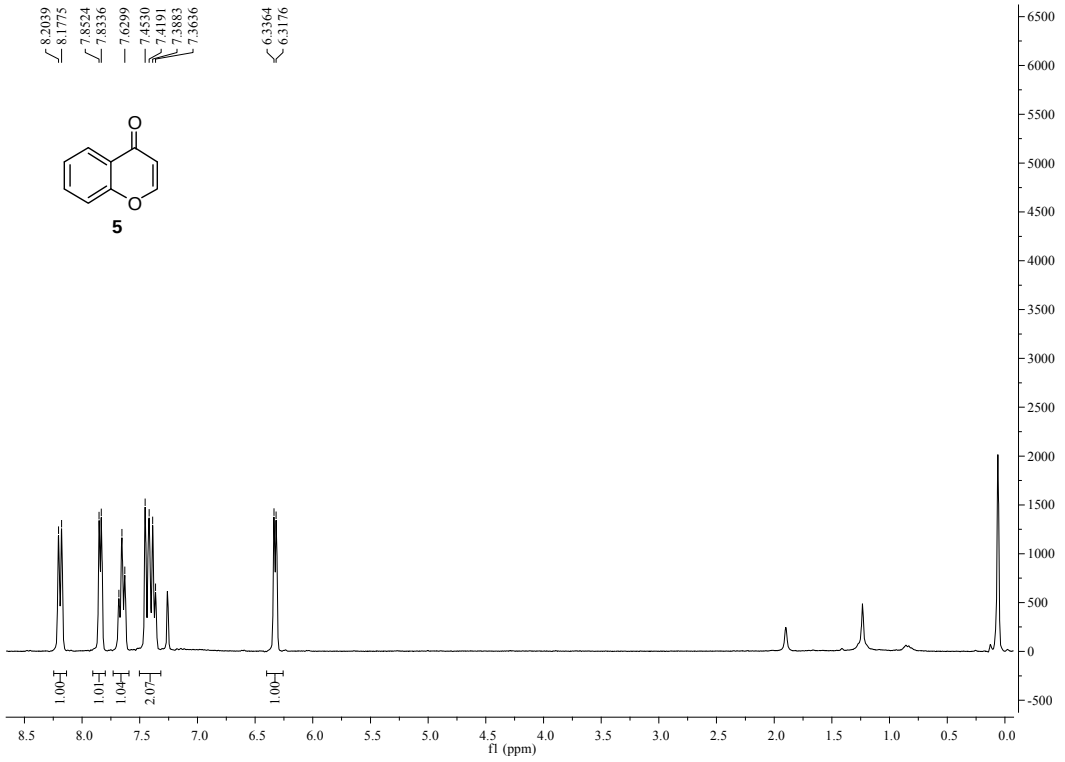
Br
O
4v
fl (ppm)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O
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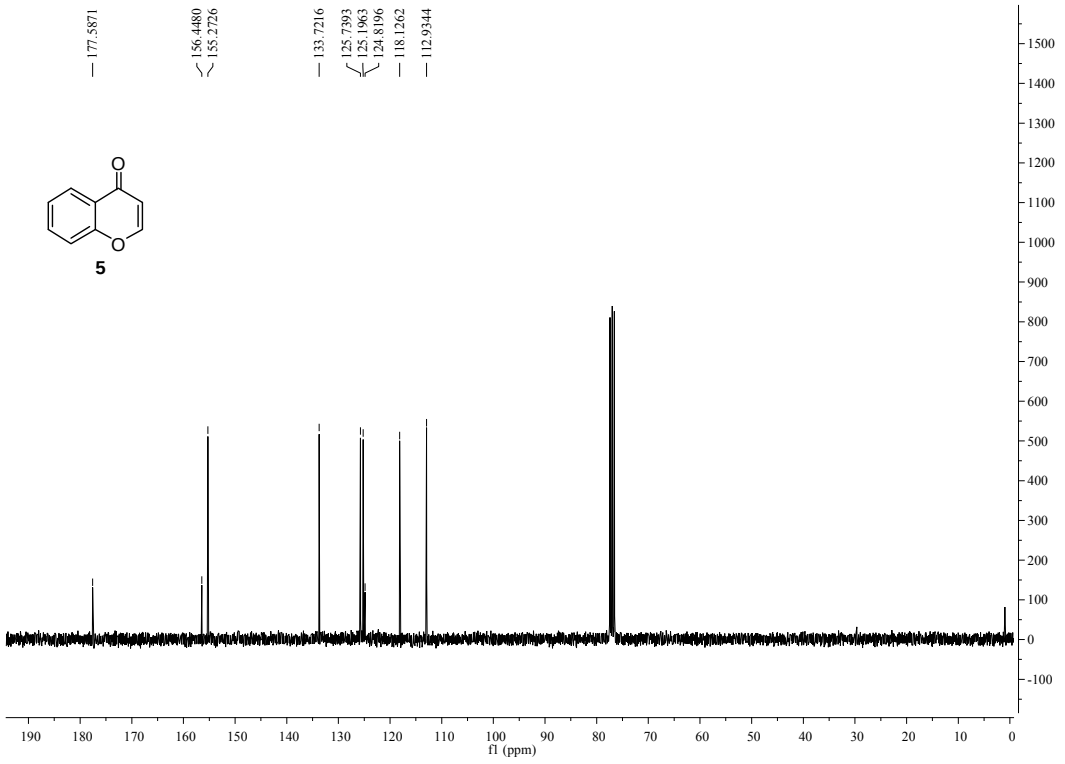
1.00
f1 (ppm)


177.5871
156.4480
155.2726
133.7216
125.7393
125.1963
124.8196
118.1262
112.9344
O
O
5
f1 (ppm)