Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Conversion of Esters to Thioesters under Mild Conditions

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Supporting Information

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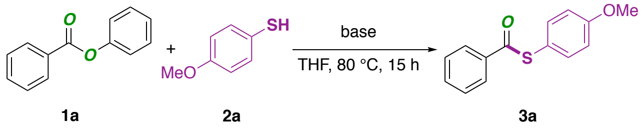
General Information

All starting materials reported in the manuscript have been prepared according to the method reported previously.[1-15] Spectroscopic data matched literature values. All experiments were performed using standard Schlenk techniques under argon atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ^{1}H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at 400 (^{1}H NMR) and 100 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.26 and 77.16 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (J) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent 7890A GC System and Agilent 7000B inert XL EI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 220 °C, then hold at 220 °C for 15 min (splitless mode of injection, total run time of 22.0 min). Infrared spectrum was measured on a Thermo Scientific Nicolet^{TM} iS^{TM} 50 Spectrometer. HRMS data were recorded on Agilent 6530 Accurate-Mass Q-TOF LCMS spectrometer by ESI in positive mode. Melting point was recorded on INESA (SGWX-4B) equipment without corrected. All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Information. ^{1}H NMR, ^{13}C NMR and HRMS data are reported for all new compounds.

Table SI-1. Summary of Optimization Studies[a]



entry	catalyst	solvent	temp	yield (%)
1	-	THF	80 °C	<2
2	Na_2CO_3	THF	80 °C	75
3	K_2CO_3	THF	80 °C	71
4	Cs_2CO_3	THF	80 °C	<2
5	K_3PO_4	THF	80 °C	73
6	NaOAc	THF	80 °C	19
7	KOAc	THF	80 °C	92
8	KF	THF	80 °C	40
9	KOAc	dioxane	80 °C	74
10	KOAc	toluene	80 °C	10
11	KOAc	THF	60 °C	62
12	KOAc	THF	25 °C	3
13[b]	KOAc	THF	80 °C	81
14[c]	KOAc	THF	80 °C	78

[a]Conditions: **1a** (1.0 equiv), **2a** (3.0 equiv), base (4.5 equiv), THF, 80 °C, 15 h. [b]**2a** (2.0 equiv), base (3.0 equiv). [c]**2a** (1.5 equiv), base (2.0 equiv).

Experimental Procedures for the Synthesis of Ester and Products

General Procedure for Ester Synthesis. A previously published procedure was followed.[5] An oven-dried flask (25 mL) equipped with a stir bar was charged with phenol (5.0 mmol, 1.0 equiv), dimethylaminopyridine (typically, 0.025 mmol, 0.005 equiv), triethylamine (typically, 6.0 mmol, 1.2 equiv), and dichloromethane (typically, 10 mL), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Acyl chloride (typically, 5.0 mmol, 1.0 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 °C, and the reaction mixture was stirred 12 h at room temperature. After the indicated time, the reaction mixture was diluted with ethyl acetate (30 mL), washed with 1 M HCl (20 mL), H_2O (20 mL), brine (20 mL). Then the organic layer was dried by Na_2SO_4, filtrated and concentrated. Unless stated otherwise, the crude product was purified by recrystallization (toluene) to give analytically pure product.

General Procedure for Metal-Free Thioesterification of Ester. An oven-dried vial equipped with a stir bar was charged with ester (neat, 0.10 mmol, 1.0 equiv), thiophenol (typically, 0.30 mmol, 3.0 equiv) and KOAc (typically, 0.45 mmol, 4.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. THF (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 80 °C, and stirred for the indicated time at 80 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. Purification by chromatography on silica gel (hexane/dichloromethane) afforded the title products.

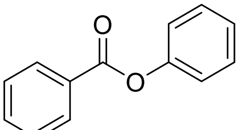
Representative Procedure for Metal-Free Thioesterification of Ester. An oven-dried vial equipped with a stir bar was charged with phenyl benzoate (neat, 19.8 mg, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (typically, 42.1 mg, 0.30 mmol, 3.0 equiv) and KOAc (typically, 44.1 mg, 0.45 mmol, 4.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. THF (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 80 °C, and stirred for the indicated time at 80 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. Purification by chromatography on silica gel (hexane/dichloromethane) afforded the title product. Yield 92% (22.5 mg). White solid. Characterization data are included in the section below.

General Procedure for Pd-Catalyzed Suzuki-Miyaura Reaction. An oven-dried vial equipped with a stir bar was charged with ester (neat, 1 mmol, 1.0 equiv), arylboronic acid (typically, 1.5 mmol, 1.5 equiv), $Pd_2(dba)_3$ (typically, 0.02 mmol, 2 mol%), ligand (typically, 0.06 mmol, 6 mol%) and K_3PO_4 (typically, 2 mmol, 2.0 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (0.2 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 100 °C, and stirred for 15 h at 100 °C. After the indicated time, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. Purification by chromatography on silica gel (hexane/dichloromethane) afforded the title products.

General Procedure for Ni-Catalyzed Decarbonylation of Thioester. An oven-dried vial equipped with a stir bar was charged with thioester (neat, 0.10 mmol, 1.0 equiv), $Ni_2(dppp)Cl_2$ (typically, 0.01 mmol, 10 mol%) and Na_2CO_3 (typically, 0.15 mmol, 1.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (0.2 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for 15 h at 160 °C. After the indicated time, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. Purification by chromatography on silica gel (hexane/dichloromethane) afforded the title products.

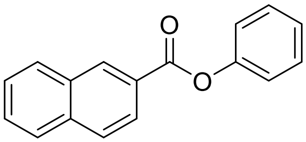
Characterization Data of Starting Materials

Note: All starting materials have been prepared according to the previously published procedure.[1-15]



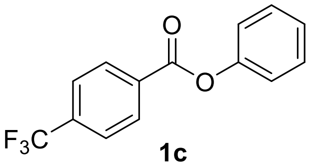
1a

Phenyl benzoate (1a).[1] Yield: 90% (0.891 g). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.31-8.14 (d, *J* = 8.0 Hz, 2 H), 7.69-7.60 (t, *J* = 9.2 Hz, 1 H), 7.57-7.49 (t, *J* = 9.5 Hz, 2 H), 7.49-7.39 (t, *J* = 9.5 Hz, 2 H), 7.33-7.20 (m, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 165.34, 151.10, 133.73, 130.32, 129.72, 129.64, 128.71, 126.03, 121.86.



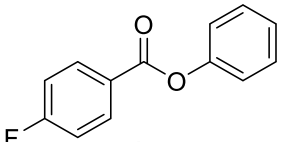
1b

Phenyl 2-naphthoate (1b).[1] Yield: 92% (1.141 g). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.82 (s, 1 H), 8.27-8.15 (dd, *J* = 2.0, 1.7 Hz, 1 H), 8.06-7.90 (m, 3 H), 7.70-7.53 (m, 2 H), 7.53-7.40 (m, 2 H), 7.38-7.27 (m, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 165.49, 151.17, 135.93, 132.62, 132.05, 129.66, 129.61, 128.75, 128.52, 127.96, 126.96, 126.88, 126.05, 125.59, 121.91.



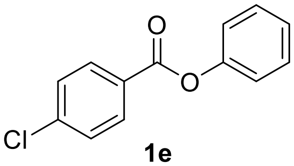
1c

Phenyl 4-(trifluoromethyl)benzoate (1c).[1] Yield: 65% (0.865 g). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.33 (d, *J* = 8.2 Hz, 2 H), 7.79 (d, *J* = 8.2 Hz, 2 H), 7.52-7.40 (t, *J* = 7.7 Hz, 2 H), 7.35-7.28 (t, *J* = 7.4 Hz, 1 H), 7.27-7.19 (d, *J* = 8.2 Hz, 2 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.15, 150.80, 135.16 (q, J^2 = 32.8 Hz), 132.97, 130.72, 129.77, 126.38, 125.77 (d, J^3 = 4.2 Hz), 123.71 (d, J^1 = 273.0 Hz), 121.69. **^{19}F (376 MHz, CDCl$_3$)** δ -63.12.



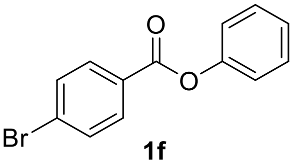
1d

4-Fluoro-benzoic acid phenyl ester (1d).[1] Yield: 87% (0.940 g). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.35-8.12 (m, 2 H), 7.50-7.40 (t, *J* = 7.6 Hz, 2 H), 7.33-7.27 (t, *J* = 7.4 Hz, 1 H), 7.25-7.10 (m, 4 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.28 (d, J^1 = 255.1 Hz), 164.37, 150.94, 132.93 (d, J^3 = 9.4 Hz), 129.67, 126.13, 125.92 (d, J^4 = 2.9 Hz), 121.80, 115.93 (d, J^2 = 22.2 Hz). **^{19}F (376 MHz, CDCl$_3$)** δ -104.43.



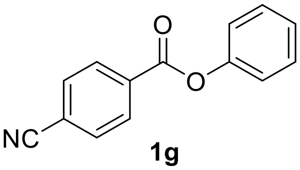
1e

Phenyl-4-chloro benzoate (1e).[2] Yield: 90% (1.047 g). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.15 (d, *J* = 8.5 Hz, 2 H), 7.50 (d, *J* = 8.7 Hz, 2 H), 7.47-7.41 (t, *J* = 7.9 Hz, 2 H), 7.33-7.27 (t, *J* = 7.4 Hz, 1 H), 7.22 (d, *J* = 8.6 Hz, 2 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.46, 150.89, 140.24, 131.67, 129.67, 129.07, 128.14, 126.17, 121.74.



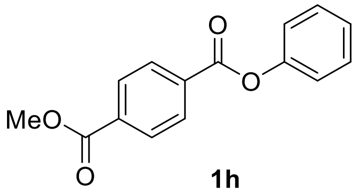
1f

Phenyl-(4-bromo) benzoate (1f).[3] Yield: 92% (1.270 g). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.07 (d, *J* = 8.6 Hz, 2 H), 7.66 (d, *J* = 8.6 Hz, 2 H), 7.49-7.39 (t, *J* = 8.7 Hz, 2 H), 7.33-7.27 (t, *J* = 7.4 Hz, 1 H), 7.22 (d, *J* = 8.3 Hz, 2 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.62, 150.87, 132.07, 131.78, 129.68, 128.96, 128.59, 126.19, 121.73.



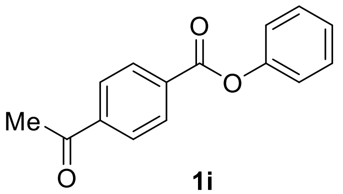
1g

Phenyl-(4-cyano) benzoate (1g).[3] Yield: 89% (0.993 g). Yellow solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.31 (d, *J* = 8.4 Hz, 2 H), 7.82 (d, *J* = 8.5 Hz, 2 H), 7.50-7.40 (t, *J* = 7.6 Hz, 2 H), 7.36-7.28 (t, *J* = 7.4 Hz, 1 H), 7.22 (d, *J* = 7.6 Hz, 2 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 163.70, 150.63, 133.51, 132.51, 130.75, 129.77, 126.47, 121.54, 117.98, 117.09.



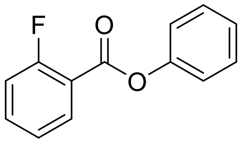
1h

Phenyl-(4-methylester) terephalate (1h).[2] Yield: 93% (1.191 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 8.7 Hz, 2 H), 8.17 (d, *J* = 8.6 Hz, 2 H), 7.53-7.38 (t, *J* = 7.5 Hz, 2 H), 7.33-7.27 (t, *J* = 7.4 Hz, 1 H), 7.23 (d, *J* = 7.2 Hz, 2 H), 3.97 (s, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.32, 164.53, 150.87, 134.60, 133.47, 130.27, 129.85, 129.71, 126.27, 121.71, 52.67.



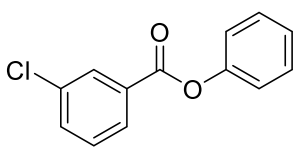
1i

Phenyl 4-acethylbenzoate (1i).[2] Yield: 86% (1.033 g). Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.29 (d, *J* = 8.8 Hz, 2 H), 8.07 (d, *J* = 8.7 Hz, 2 H), 7.49-7.39 (t, *J* = 7.5 Hz, 2 H), 7.33-7.27 (t, *J* = 7.4 Hz, 1 H), 7.23 (m, 2 H), 2.67 (s, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.59, 164.44, 150.83, 140.79, 133.41, 130.52, 129.69, 128.47, 126.26, 121.68, 27.05.



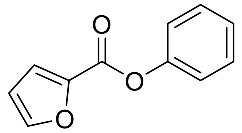
1j

Phenyl 2-fluorobenzoate (1j).[3] Yield: 90% (0.972 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.17-8.03 (t, *J* = 7.5 Hz, 1 H), 7.61-7.52 (m, 1 H), 7.46-7.37 (t, *J* = 7.8 Hz, 2 H), 7.30-7.14 (m, 5 H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.40 (d, J^1 = 260 Hz), 162.88 (d, J^5 = 4.2 Hz), 150.73, 135.32 (d, J^4 = 9.3 Hz), 132.62, 129.61, 126.15, 124.24 (d, J^6 = 3.8 Hz), 121.77, 118.21 (d, J^3 = 9.4 Hz), 117.31 (d, J^2 = 22.0 Hz). **^{19}F (376 MHz, $CDCl_3$)** δ -108.14.



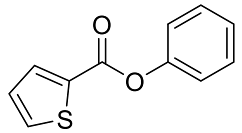
1k

Phenyl 3-chlorobenzoate (1k).[4] Yield: 90% (1.047 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.20 (s, 1 H), 8.10 (d, *J* = 8.8 Hz, 1 H), 7.62 (d, *J* = 9 Hz, 1 H), 7.51-7.39 (m, 3 H), 7.33-7.27 (t, *J* = 7.5 Hz, 1 H), 7.22 (d, *J* = 8.4 Hz, 2 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.12, 150.83, 134.88, 133.74, 131.45, 130.31, 130.03, 129.70, 128.41, 126.25, 121.70.



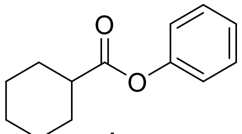
1l

Phenyl furan-2-carboxylate (1l).[1] Yield: 85% (0.799 g). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.67 (dd, *J* = 1.8, 0.9 Hz, 1 H), 7.47-7.36 (m, 3 H), 7.33-7.19 (m, 3 H), 6.59 (dd, *J* = 3.5, 1.8 Hz, 1 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 157.02, 150.27, 147.24, 144.07, 129.61, 126.16, 121.69, 119.53, 112.28.



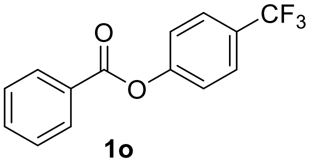
1m

Phenyl thiophene-2-carboxylate (1m).[2] Yield: 86% (0.877 g). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.95 (d, *J* = 4.8 Hz, 1 H), 7.62 (dd, *J* = 5.0, 1.3 Hz, 1 H), 7.43-7.36 (t, *J* = 7.9 Hz, 2 H), 7.30-7.16 (m, 3 H), 7.14 (dd, *J* = 5.0, 3.8 Hz, 1 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 160.70, 150.67, 134.79, 133.61, 133.00, 129.58, 128.14, 126.10, 121.76.



1n

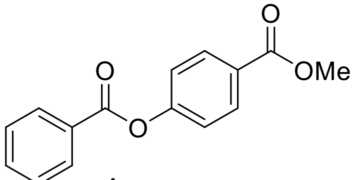
Phenyl cyclohexanecarboxylate (1n).[5] Yield: 92% (0.939 g). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.43-7.32 (m, 2 H), 7.25-7.18 (t, *J* = 7.4 Hz, 1 H), 7.11-7.01 (m, 2 H), 2.69-2.46 (m, 1 H), 2.07 (dd, *J* = 13.5, 3.3 Hz, 2 H), 1.93-1.74 (m, 2 H), 1.75-1.49 (m, 3 H), 1.48-1.18 (m, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 174.72, 151.01, 129.48, 125.73, 121.69, 43.32, 29.07, 25.84, 25.48.



1o

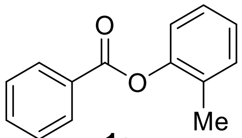
4-(Trifluoromethyl)phenyl benzoate (1o).[1] Yield: 65% (0.865 g). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.22 (d, *J* = 7.0 Hz, 2 H), 7.76-7.63 (m, 3 H), 7.59-7.49 (t, *J* = 7.7 Hz, 2 H), 7.36

(d, J = 8.4 Hz, 2 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.82, 153.62, 134.13, 130.41, 129.09, 128.85, 128.32 (d, J^2 = 32.8 Hz), 127.01 (q, J^3 = 3.7 Hz), 124.05 (d, J^1 = 271.9 Hz), 122.42. **^{19}F (376 MHz, CDCl$_3$)** δ -62.17.



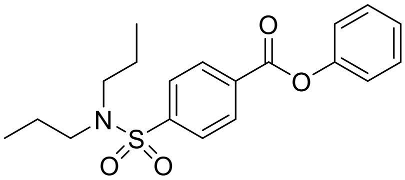
1p

Methyl 4-(benzoyloxy)benzoate (1p).[6] Yield: 93% (1.191 g). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.21 (d, J = 7.8 Hz, 2 H), 8.13 (d, J = 8.8 Hz, 2 H), 7.70-7.61 (t, J = 7.5 Hz, 1 H), 7.57-7.47 (t, J = 7.9 Hz, 2 H), 7.31 (d, J = 8.8 Hz, 2 H), 3.93 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.47, 164.77, 154.74, 134.02, 131.36, 130.37, 129.21, 128.80, 127.90, 121.90, 52.34.



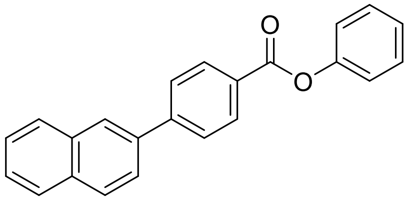
1q

2-Methylphenyl benzoate (1q).[2] Yield: 92% (0.976 g). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.31 (d, J = 7.0 Hz, 2 H), 7.75-7.63 (t, J = 8.1 Hz, 1 H), 7.62-7.49 (t, J = 7.8 Hz, 2 H), 7.40-7.17 (m, 4 H), 2.31 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.89, 149.61, 133.63, 131.23, 130.35, 130.20, 129.52, 128.66, 127.04, 126.14, 122.07, 16.28.



1r

Phenyl 4-(*N*, *N*-dipropylsulfamoyl)benzoate (1r).[7] Yield: 93% (1.679 g). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.32 (d, J = 8.7 Hz, 2 H), 7.95 (d, J = 8.4 Hz, 2 H), 7.50-7.40 (t, J = 7.4 Hz, 2 H), 7.34-7.27 (t, J = 7.4 Hz, 1 H), 7.22 (d, J = 8.7 Hz, 2 H), 3.27-2.96 (t, J = 7.6 Hz, 4 H), 1.64-1.49 (m, 4 H), 0.94-0.82 (t, J = 7.4 Hz, 6 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.00, 150.74, 144.99, 132.96, 130.91, 129.74, 127.28, 126.37, 121.61, 50.04, 22.05, 11.28.

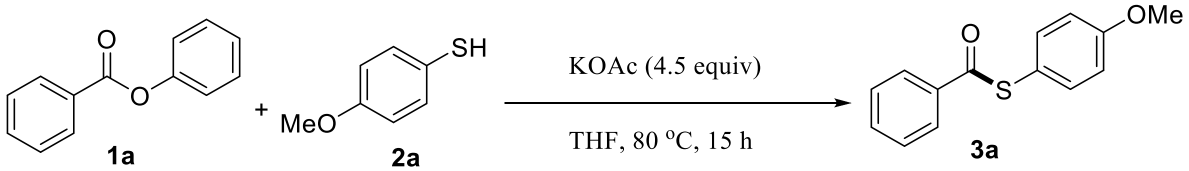


1s

Phenyl 4-(naphthalen-2-yl)benzoate (1s).[8] Yield: 81% (0.263 g). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.32 (d, *J* = 8.5 Hz, 2 H), 8.13 (s, 1 H), 8.01-7.83 (m, 5 H), 7.80 (dd, *J* = 8.5, 1.9 Hz, 1 H), 7.66-7.49 (m, 2 H), 7.51-7.39 (m, 2 H), 7.34-7.16 (m, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 165.27, 151.15, 146.39, 137.29, 133.70, 133.20, 130.94, 129.67, 128.91, 128.53, 128.45, 127.85, 127.63, 126.75, 126.69, 126.62, 126.06, 125.35, 121.91.

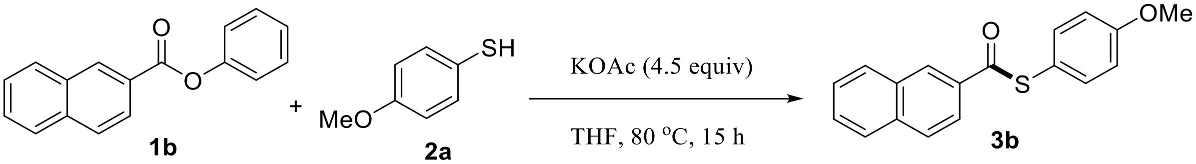
Characterization Data of Desired Products

S-(4-Methoxyphenyl) benzothioate (3a, Figure 2)[9]



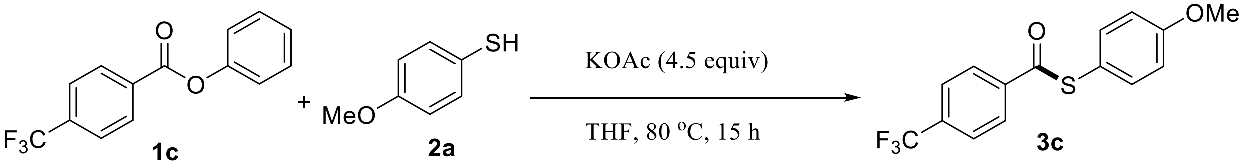
According to the general procedure, the reaction of phenyl benzoate (**1a**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 92% yield (22.5 mg). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.03 (d, *J* = 8.3 Hz, 2 H), 7.68-7.55 (t, *J* = 7.4 Hz, 1 H), 7.52-7.45 (t, *J* = 7.7 Hz, 2 H), 7.42 (d, *J* = 8.8 Hz, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 3.85 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 191.25, 160.93, 136.79, 133.72, 128.86, 127.60, 118.01, 115.11, 55.53.

S-(4-Methoxyphenyl) naphthalene-2-carbothioate (3b, Figure 2)



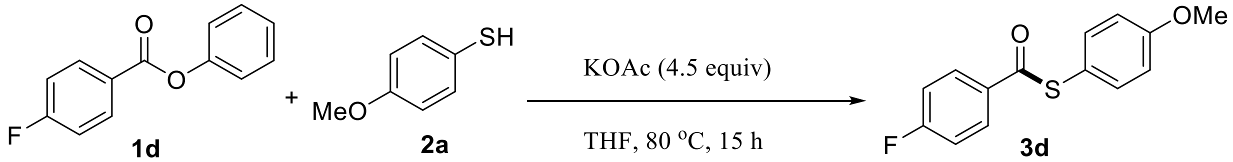
According to the general procedure, the reaction of phenyl 2-naphthoate (**1b**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 98% yield (28.8 mg). *New compound.* White solid. **Mp** = 135-137 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.61 (s, 1 H), 8.08-7.96 (t, *J* = 8.3 Hz, 2 H), 7.96-7.85 (t, *J* = 7.8 Hz, 2 H), 7.70-7.54 (m, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 191.17, 160.97, 136.84, 136.01, 134.11, 132.63, 129.76, 129.09, 128.76, 128.73, 128.00, 127.12, 123.45, 118.11, 115.15, 55.55. **IR:** 2967, 2923, 2847, 1655, 1595, 1574, 1498, 1459, 1295, 1245, 1172, 1120, 1021, 963, 903, 867, 830, 812, 755, 687, 650, 549 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{18}H_{15}O_2S$ (M^+ + H) 295.0793, found 295.0758.

S-(4-Methoxyphenyl) 4-(trifluoromethyl)benzothioate (3c, Figure 2)[10]



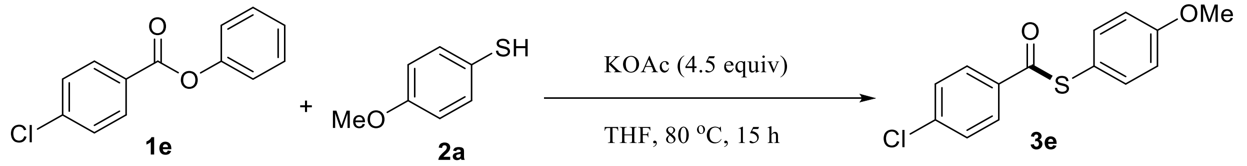
According to the general procedure, the reaction of phenyl 4-(trifluoromethyl)benzoate (**1c**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 93% yield (29.0 mg). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.12 (d, *J* = 8.1 Hz, 2 H), 7.75 (d, *J* = 8.9 Hz, 2 H), 7.42 (d, *J* = 8.8 Hz, 2 H), 7.01 (d, *J* = 8.8Hz, 2 H), 3.86 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 190.49, 161.19, 139.61, 136.69, 134.98 (d, J^2 = 32.7 Hz), 127.94, 125.96 (d, J^3 = 3.7 Hz), 123.66 (d, J^1 = 273.1 Hz), 117.17, 115.27, 55.55. **^{19}F (376 MHz, CDCl$_3$)** δ -63.11.

S-(4-Methoxyphenyl) 4-fluorobenzothioate (3d, Figure 2)[9]



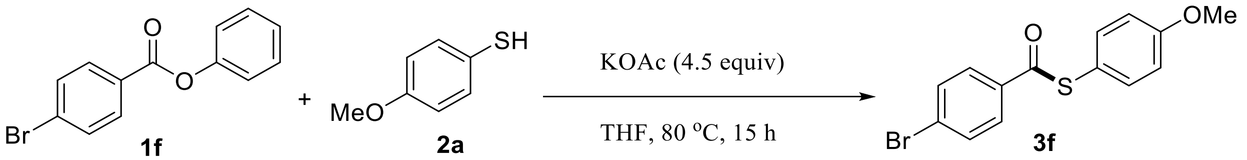
According to the general procedure, the reaction of 4-fluoro-benzoic acid phenyl ester (**1d**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 96% yield (25.2 mg). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.05 (dd, *J* = 8.9, 5.3 Hz, 2 H), 7.41 (d, *J* = 8.8 Hz, 2 H), 7.21-7.10 (t, *J* = 8.6 Hz, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 3.85 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 189.79, 166.18 (d, J^1 = 255.1 Hz), 161.02, 136.79, 133.12 (d, J^4 = 2.9 Hz), 130.17 (d, J^3 = 9.4 Hz), 117.71, 116.02 (d, J^2 = 22.4 Hz), 115.16, 55.53. **^{19}F (376 MHz, CDCl$_3$)** δ -104.34.

S-(4-Methoxyphenyl) 4-chlorobenzothioate (3e, Figure 2)[11]



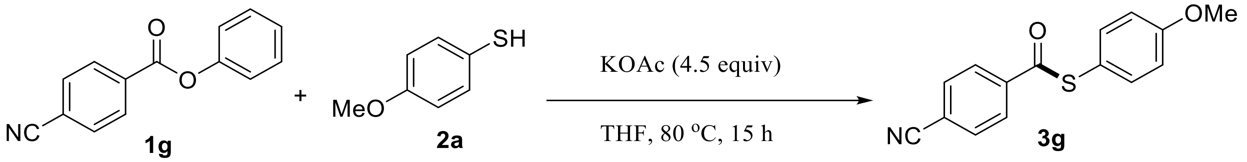
According to the general procedure, the reaction of phenyl-4-chloro benzoate (**1e**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 97% yield (27.0 mg). White solid. **<u>^{1}H NMR (400 MHz, CDCl$_3$)</u>** δ 7.96 (d, *J* = 8.6 Hz, 2 H), 7.46 (d, *J* = 8.6 Hz, 2 H), 7.41 (d, *J* = 8.8 Hz, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 3.85 (s, 3 H). **<u>^{13}C NMR (100 MHz, CDCl$_3$)</u>** δ 190.16, 161.07, 140.12, 136.76, 135.14, 129.19, 128.96, 117.56, 115.19, 55.55.

S-(4-Methoxyphenyl) 4-bromobenzothioate (3f, Figure 2)[11]



According to the general procedure, the reaction of phenyl-(4-bromo) benzoate (**1f**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 96% yield (30.9 mg). White solid. **<u>^{1}H NMR (400 MHz, CDCl$_3$)</u>** δ 7.88 (d, *J* = 8.6 Hz, 2 H), 7.62 (d, *J* = 8.6 Hz, 2 H), 7.40 (d, *J* = 8.8 Hz, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 3.85 (s, 3 H). **<u>^{13}C NMR (100 MHz, CDCl$_3$)</u>** δ 190.35, 161.07, 136.75, 135.57, 132.17, 129.05, 128.78, 117.50, 115.19, 55.54.

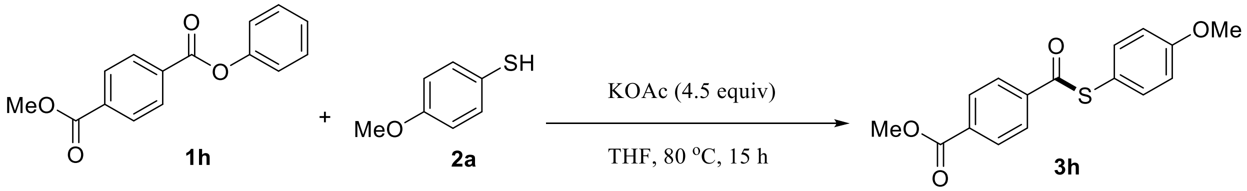
S-(4-Methoxyphenyl) 4-cyanobenzothioate (3g, Figure 2)



According to the general procedure, the reaction of phenyl-(4-cyano) benzoate (**1g**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in

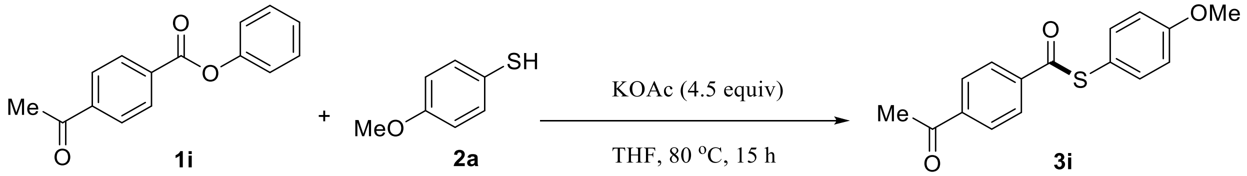
THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 64% yield (17.2 mg). *New compound.* Yellow solid. **Mp** = 128-130 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.11 (d, *J* = 8.6 Hz, 2 H), 7.79 (d, *J* = 8.5 Hz, 2 H), 7.41 (d, *J* = 8.8 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 3.86 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 190.21, 161.29, 139.98, 136.65, 132.76, 128.04, 117.97, 116.94, 116.79, 115.34, 55.58. **IR:** 2962, 2920, 2847, 2229, 1665, 1592, 1577, 1498, 1446, 1410, 1295, 1248, 1201, 1170, 1110, 1031, 906, 864, 828, 797, 770, 643, 551 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{15}H_{12}NO_2S$ (M$^+$ + H) 270.0589, found 295.0556.

Methyl 4-(((4-methoxyphenyl)thio)carbonyl)benzoate (3h, Figure 2)



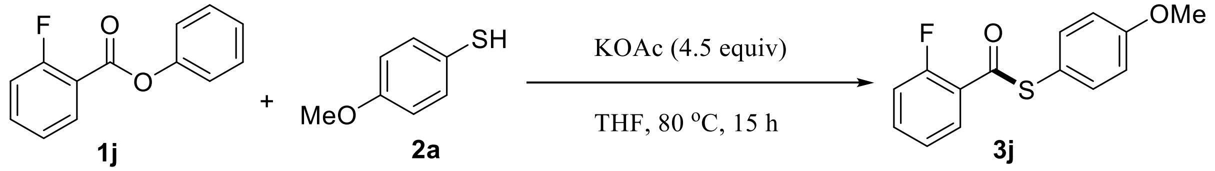
According to the general procedure, the reaction of phenyl-(4-methylester) terephalate (**1h**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 98% yield (29.6 mg). *New compound.* White solid. **Mp** = 117-119 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.14 (d, *J* = 8.7 Hz, 2 H), 8.07 (d, *J* = 8.7 Hz, 2 H), 7.42 (d, *J* = 9.0 Hz, 2 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 3.96 (s, 3 H), 3.86 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 190.84, 166.27, 161.12, 140.14, 136.70, 134.47, 130.10, 127.52, 117.44, 115.23, 55.55, 52.68. **IR:** 2962, 2920, 2847, 1725, 1668, 1597, 1498, 1438, 1404, 1277, 1256, 1206, 1172, 1107, 1021, 903, 864, 820, 797, 773, 695, 640, 585 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{16}H_{15}O_4S$ (M$^+$ + H) 303.0691, found 303.0659.

S-(4-Methoxyphenyl) 4-acetylbenzothioate (3i, Figure 2)



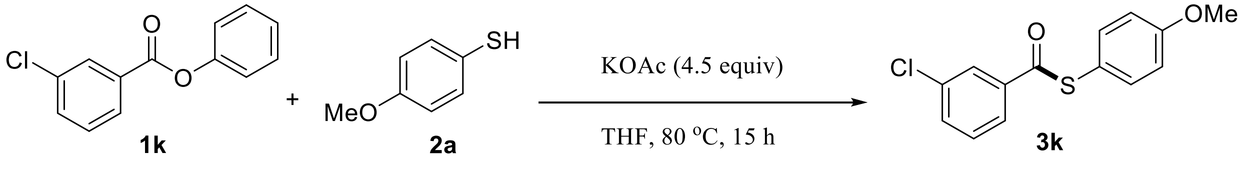
According to the general procedure, the reaction of phenyl 4-acethylbenzoate (**1i**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 91% yield (26.0 mg). *New compound.* White solid. **Mp** = 146-148 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.10 (d, *J* = 8.8 Hz, 2 H), 8.05 (d, *J* = 8.6 Hz, 2 H), 7.42 (d, *J* = 8.9 Hz, 2 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 3.86 (s, 3 H), 2.66 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 197.50, 190.80, 161.13, 140.70, 140.10, 136.69, 128.75, 127.81, 117.39, 115.25, 55.56, 27.05. **IR:** 2962, 2923, 2850, 1686, 1668, 1657, 1595, 1574, 1496, 1404, 1357, 1295, 1256, 1206, 1175, 1081, 1023, 911, 833, 820, 797, 747, 734, 643, 580 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{16}H_{15}O_3S$ (M$^+$ + H) 287.0742, found 287.0709.

S-(4-Methoxyphenyl) 2-fluorobenzothioate (3j, Figure 2)



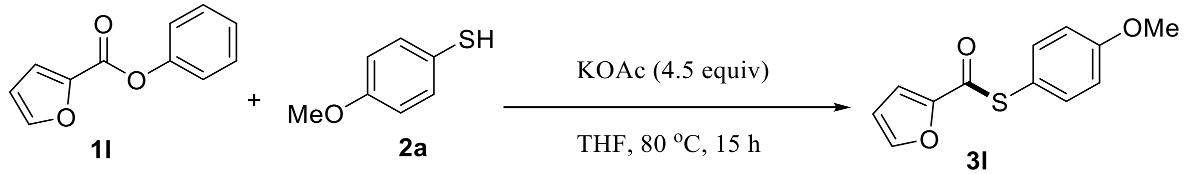
According to the general procedure, the reaction of phenyl 2-fluorobenzoate (**1j**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 79% yield (20.7 mg). *New compound.* White solid. **Mp** = 54-56 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.96-7.84 (t, *J* = 7.5 Hz, 1 H), 7.60-7.48 (m, 1 H), 7.43 (d, *J* = 8.8 Hz, 2 H), 7.32-7.10 (m, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 3.85 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 188.34 (d, J^5 = 5.3 Hz), 161.05, 160.67 (d, J^1 = 256.4 Hz) 134.66 (d, J^4 = 8.7 Hz), 130.04, 125.32 (d, J^3 = 11.7 Hz), 124.45 (d, J^7 = 3.6 Hz), 118.03 (d, J^6 = 4.4 Hz), 117.09 (d, J^2 = 22.4 Hz), 115.13, 55.54. **^{19}F (376 MHz, CDCl$_3$)** δ -109.74. **IR:** 2974, 2928, 2839, 1678, 1587, 1569, 1490, 1480, 1451, 1433, 1292, 1250, 1230, 1196, 1183, 1177, 1026, 906, 830, 799, 773, 737, 677, 643, 580 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{14}H_{12}FO_2S$ (M$^+$ + H) 263.0542, found 263.0513.

S-(4-Methoxyphenyl) 3-chlorobenzothioate (3k, Figure 2)



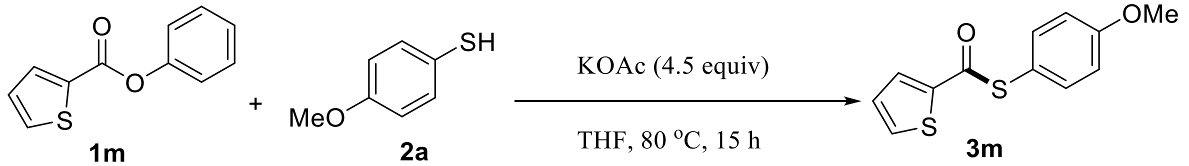
According to the general procedure, the reaction of phenyl 3-chlorobenzoate (**1k**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 84% yield (23.4 mg). *New compound.* White solid. **Mp** = 79-81 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.98 (s, 1 H), 7.91 (d, *J* = 7.8 Hz, 1 H), 7.57 (d, *J* = 9.1 Hz, 1 H), 7.48-7.36 (m, 3 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 3.85 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 190.15, 161.10, 138.32, 136.72, 135.13, 133.59, 130.17, 127.59, 125.70, 117.39, 115.21, 55.54. **IR:** 2964, 2928, 2934, 1683, 1657, 1595, 1566, 1493, 1454, 1423, 1292, 1245, 1185, 1170, 1023, 945, 903, 823, 799, 731, 690, 564 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{14}H_{12}ClO_2S$ (M^+ + H) 279.0247, found 279.0216.

S-(4-Methoxyphenyl) furan-2-carbothioate (3l, Figure 2)



According to the general procedure, the reaction of phenyl furan-2-carboxylate (**1l**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 95% yield (22.2 mg). *New compound.* White solid. **Mp** = 68-70°C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.62 (s, 1 H), 7.41 (d, *J* = 8.8 Hz, 2 H), 7.25 (d, *J* = 2.8 Hz, 1 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 6.57 (dd, *J* = 3.6, 1.7 Hz, 1 H), 3.85 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 179.79, 161.04, 150.60, 146.53, 136.89, 116.77, 116.25, 115.13, 112.52, 55.52. **IR:** 3123, 2922, 2845, 1650, 1593, 1575, 1492, 1457, 1381, 1295, 1248, 1175, 1149, 1104, 1074, 1016, 948, 885, 847, 822, 799, 772, 593, 575 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{12}H_{11}O_3S$ (M^+ + H) 235.0429, found 235.0407.

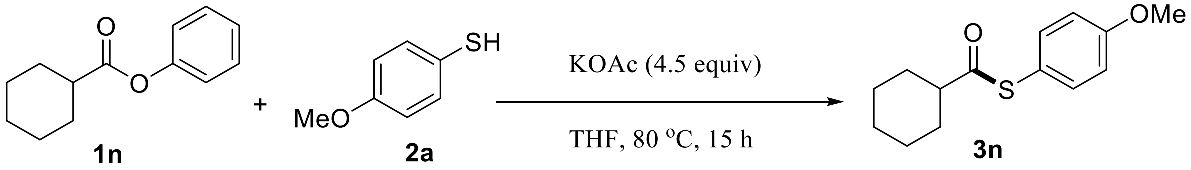
S-(4-Methoxyphenyl) thiophene-2-carbothioate (3m, Figure 2)[12]



According to the general procedure, the reaction of phenyl thiophene-2-carboxylate (**1m**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 98% yield (24.5 mg). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.90 (d, *J* = 5.0

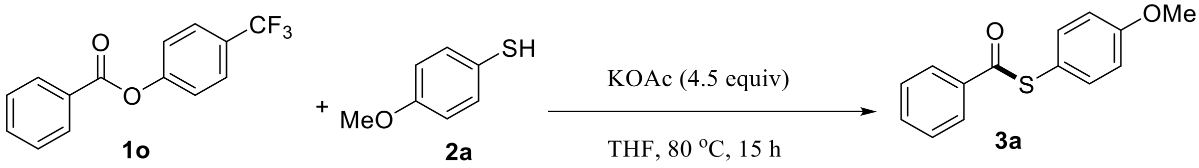
Hz, 1 H), 7.66 (d, *J* = 3.8 Hz, 1 H), 7.43 (d, *J* = 8.8 Hz, 2 H), 7.15 (dd, *J* = 5.0, 3.8 Hz, 1 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 3.85 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 183.15, 161.04, 141.55, 136.82, 133.20, 131.61, 128.12, 117.60, 115.09, 55.54.

S-(4-Methoxyphenyl) cyclohexanecarbothioate (3n, Figure 2)[13]



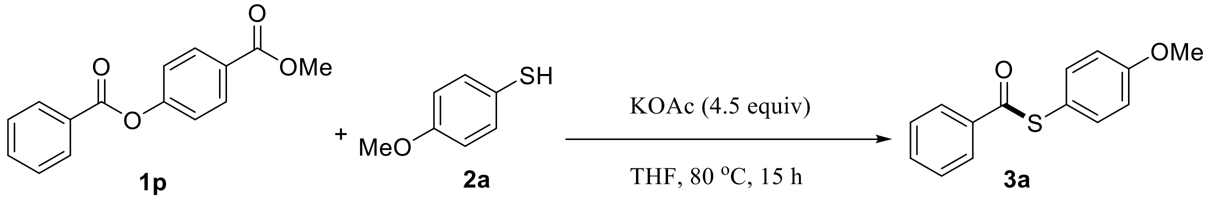
According to the general procedure, the reaction of phenyl cyclohexanecarboxylate (**1n**, 0.10 mmol, 1.0 equiv), 2-thiophenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 59% yield (14.8 mg). *New compound.* Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.30 (d, *J* = 8.8 Hz, 2 H), 6.93 (d, *J* = 8.8 Hz, 2 H), 3.82 (s, 3 H), 2.65-2.53 (m, 1 H), 1.99 (dd, *J* = 11.3, 1.5 Hz, 2 H), 1.85-1.76 (m, 2 H), 1.71-1.61 (m, 1 H), 1.55-1.45 (m, 2 H), 1.39-1.14 (m, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 201.97, 160.62, 136.32, 118.75, 114.92, 55.49, 52.41, 29.67, 25.74, 25.64.

S-(4-Methoxyphenyl) benzothioate (1o, Figure 2)[9]



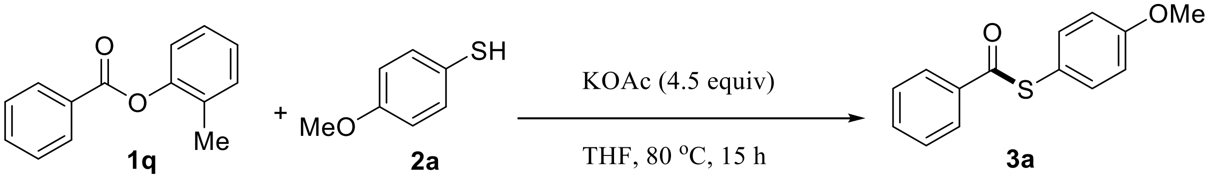
According to the general procedure, the reaction of 4-(trifluoromethyl)phenyl benzoate (**1o**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 98% yield (23.9 mg).

***S*-(4-Methoxyphenyl) benzothioate (1p, Figure 2)[9]**



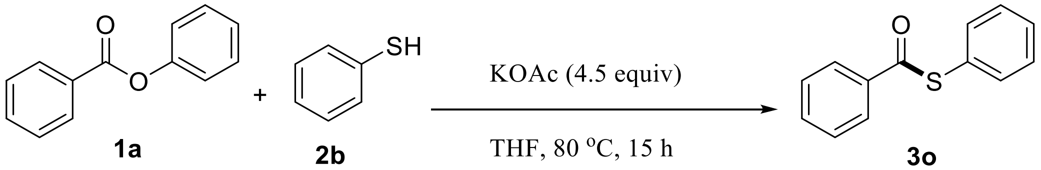
According to the general procedure, the reaction of methyl 4-(benzoyloxy)benzoate (**1p**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 98% yield (23.9 mg).

***S*-(4-Methoxyphenyl) benzothioate (1q, Figure 2)[9]**



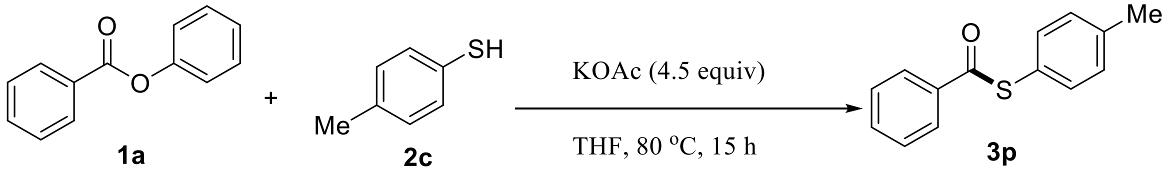
According to the general procedure, the reaction of 2-methylphenyl benzoate (**1q**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 37% yield (9.0 mg).

***S*-Phenyl benzothioate (3o, Figure 2)[14]**



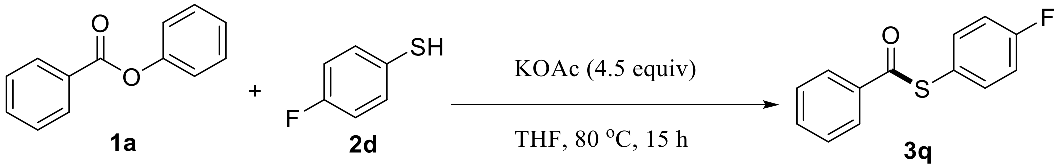
According to the general procedure, the reaction of phenyl benzoate (**1a**, 0.10 mmol, 1.0 equiv), benzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 80% yield (17.1 mg). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.11-7.96 (m, 2 H), 7.66-7.57 (t, *J* = 7.4 Hz, 1 H), 7.57-7.40 (m, 7 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 190.29, 136.77, 135.24, 133.80, 129.67, 129.39, 128.89, 127.62, 127.48.

***S*-(*p*-Tolyl) benzothioate (3p, Figure 2)**[14]



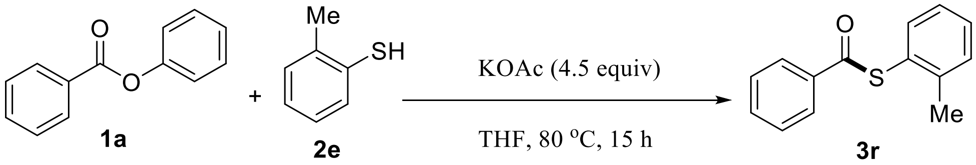
According to the general procedure, the reaction of phenyl benzoate (**1a**, 0.10 mmol, 1.0 equiv), 4-methylbenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 76% yield (17.3 mg). White solid. **<u>^{1}H NMR (400 MHz, CDCl$_3$)</u>** δ 8.04 (d, *J* = 7.2 Hz, 2 H), 7.65-7.56 (t, *J* = 7.4 Hz, 1 H), 7.54-7.45 (t, *J* = 7.7 Hz, 2 H), 7.42 (d, *J* = 8.2 Hz, 2 H), 7.29 (d, *J* = 7.7 Hz, 2 H), 2.42 (s, 3 H). **<u>^{13}C NMR (100 MHz, CDCl$_3$)</u>** δ 190.71, 139.93, 136.82, 135.15, 133.70, 130.24, 128.84, 127.59, 123.88, 21.49.

***S*-(4-Fluorophenyl) benzothioate (3q, Figure 2)**[14]



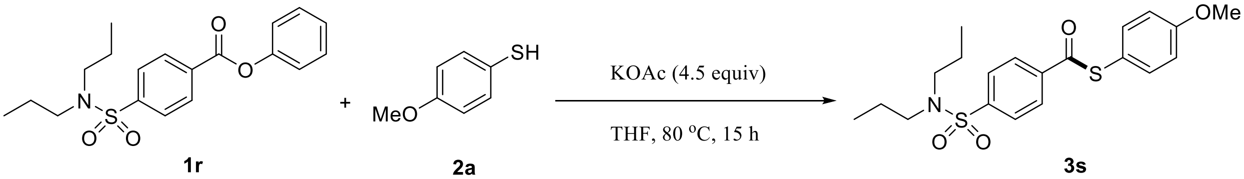
According to the general procedure, the reaction of phenyl benzoate (**1a**, 0.10 mmol, 1.0 equiv), 4-fluorobenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 94% yield (21.8 mg). White solid. **<u>^{1}H NMR (400 MHz, CDCl$_3$)</u>** δ 8.02 (d, *J* = 7.1 Hz, 2 H), 7.67-7.57 (t, *J* = 7.4 Hz, 1 H), 7.54-7.43 (m, 4 H), 7.22-7.11 (t, *J* = 8.7 Hz, 2 H). **<u>^{13}C NMR (100 MHz, CDCl$_3$)</u>** δ 190.29, 163.79 (d, J^1 = 250.0 Hz), 137.30 (d, J^3 = 8.6 Hz), 136.54, 133.96, 128.95, 127.64, 122.75 (d, J^4 = 3.5 Hz), 116.69 (d, J^2 = 22.3 Hz). **^{19}F (376 MHz, CDCl$_3$)** δ -110.03.

S-(o-Tolyl) benzothioate (3r, Figure 2)[14]



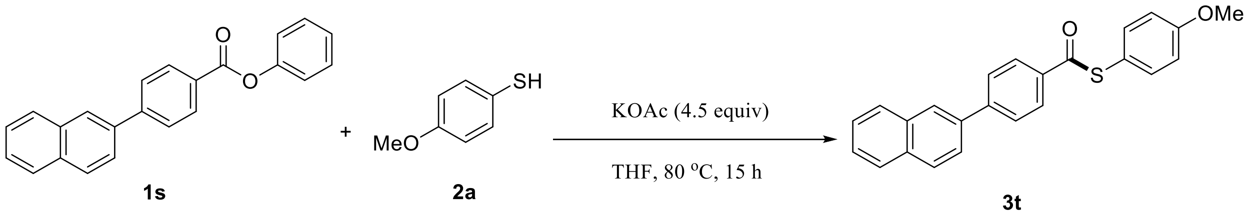
According to the general procedure, the reaction of phenyl benzoate (**1a**, 0.10 mmol, 1.0 equiv), 2-methylbenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 51% yield (11.6 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 8.6 Hz, 2 H), 7.66-7.58 (t, *J* = 7.4 Hz, 1 H), 7.55-7.44 (m, 3 H), 7.43-7.33 (m, 2 H), 7.32-7.22 (m, 1H), 2.41(s, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 189.81, 142.80, 136.93, 136.55, 133.71, 130.97, 130.37, 128.87, 127.68, 126.93, 126.81, 20.95.

S-(4-Methoxyphenyl) 4-(*N*, *N*-dipropylsulfamoyl)benzothioate (3s, Figure 3)[15]



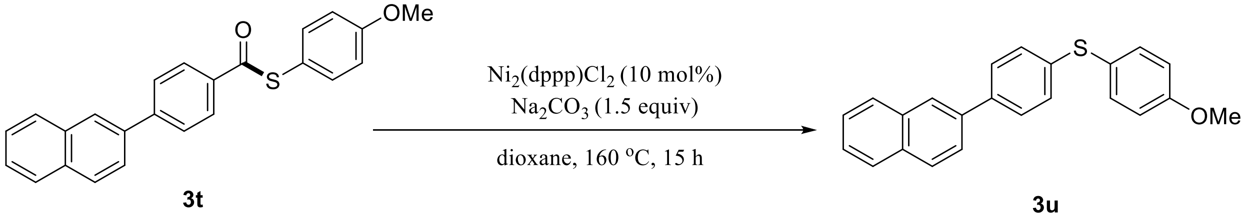
According to the general procedure, the reaction of phenyl 4-(*N*, *N*-dipropylsulfamoyl)benzoate (**1r**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 98% yield (39.9 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12 (d, *J* = 8.5 Hz, 2 H), 7.91 (d, *J* = 8.5 Hz, 2 H), 7.41 (d, *J* = 8.3 Hz, 2 H), 7.00 (d, *J* = 8.1 Hz, 2 H), 3.85 (s, 3 H), 3.20-3.01 (t, *J* = 7.6 Hz, 4 H), 1.68-1.47 (m, 4 H), 0.88 (t, *J* = 7.4 Hz, 6 H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.33, 161.19, 144.78, 139.56, 136.65, 128.15, 127.49, 117.08, 115.27, 55.55, 50.10, 22.10, 11.29.

S-(4-Methoxyphenyl) 4-(naphthalen-2-yl)benzothioate (3t, Figure 3)



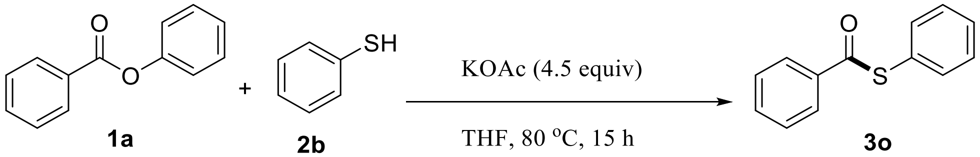
According to the general procedure, the reaction of phenyl 4-(naphthalen-2-yl)benzoate (**1s**, 0.10 mmol, 1.0 equiv), 4-methoxybenzenethiol (0.30 mmol, 3.0 equiv) and KOAc (0.45 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C, afforded after work-up and chromatography the title compound in 91% yield (33.7 mg). *New compound*. White solid. **Mp** = 150-152 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.15 (d, *J* = 8.5 Hz, 2 H), 8.11 (s, 1 H), 8.01-7.86 (m, 3 H), 7.83 (d, *J* = 8.4 Hz, 2 H), 7.77 (dd, *J* = 8.5, 1.9 Hz, 1 H), 7.54 (t, *J* = 5.4 Hz, 2 H), 7.46 (d, *J* = 8.8 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 3.86 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 190.71, 160.93, 146.34, 137.15, 136.80, 135.49, 133.67, 133.18, 128.89, 128.52, 128.22, 127.83, 127.70, 126.73, 126.68, 126.55, 125.26, 118.02, 115.12, 55.51. **IR:** 2953, 2837, 1670, 1597, 1498, 1462, 1290, 1248, 1217, 1175, 1026, 903, 859, 817, 750, 648 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{24}H_{19}O_2S$ ($M^+ + H$) 371.1106, found 371.1072.

2-(4-(4-Methoxyphenoxy)phenyl)naphthalene (3u, Figure 3)



According to the general procedure, the reaction of S-(4-methoxyphenyl) 4-(naphthalen-2-yl)benzothioate (**3t**, 0.10 mmol), Na_2CO_3 (0.15 mmol) and $Ni_2(dppp)Cl_2$ (10 mol%) in dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 92% yield (30.0 mg). *New compound*. White solid. **Mp** = 126-128 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.00 (s, 1 H), 7.93-7.79 (m, 3 H), 7.70 (dd, *J* = 8.5, 1.9 Hz, 1 H), 7.60 (d, *J* = 8.5 Hz, 2 H), 7.56-7.43 (m, 4 H), 7.28 (d, *J* = 8.5 Hz, 2 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 3.84 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 160.07, 138.77, 138.08, 137.91, 135.60, 133.79, 132.73, 128.74, 128.62, 128.29, 128.00, 127.78, 126.48, 126.10, 125.62, 125.41, 124.32, 115.21, 55.53. **IR:** 2964, 2839, 1587, 1490, 1284, 1245, 1177, 1089, 1031, 1010, 807, 739 cm^{-1}. **HRMS (ESI)** m/z calcd for $C_{23}H_{19}OS$ ($M^+ + H$) 343.1157, found 343.1111.

Easy-to-handle large scale synthesis of *S*-phenyl benzothioate (3o, Figure 3)[14]



According to the general procedure, the reaction of phenyl benzoate (**1a**, 1.0 g, 5.0 mmol), benzenethiol (15.0 mmol, 3.0 equiv) and KOAc (22.5 mmol, 4.5 equiv) in THF (0.20 M) for 15 h at 80 °C. The reaction mixture was concentrated in vacuum and the residue was washed with 50 mL EtOAc. After removal of EtOAc, the crude product was purified by recrystallization (n-hexane) to give analytically pure product in 83 % yield (0.90 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11-7.96 (m, 2 H), 7.66-7.57 (t, *J* = 7.4 Hz, 1 H), 7.57-7.40 (m, 7 H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.29, 136.77, 135.24, 133.80, 129.67, 129.39, 128.89, 127.62, 127.48.

Computational Methods

Computational Methods. All of the calculations were performed using Gaussian 09 suite of programs. All of the geometry optimizations were performed at the B3LYP/6-311++G(d,p**)** level of theory in the gas phase. Extensive studies have showed that this level is accurate in predicting properties and resonance energies of carboxylic acid derivatives (*J. Org. Chem.* **2012**, *77*, 5492, *J. Am. Chem. Soc.* **2018**, *140*, 727, and references cited therein). This method was further verified by obtaining good correlations between the calculated structures and the X-ray structure in the series. All conformations within 3 kcal/mol from the lowest energy conformer were explored (*J. Am. Chem. Soc.* **1996**, *118*, 8658). The absence of imaginary frequencies was used to characterize the structures as minima on the potential energy surface. All of the optimized geometries were verified as minima (no imaginary frequencies). Electronic and thermal energies were calculated for all structures. Energetic parameters were calculated under standard conditions (298.15 K and 1 atm). For geometry optimizations, we employed the X-ray structure of 4-bromophenyl benzoate as the starting geometry and performed full optimization (*Acta Crystallogr. Sect. E* **2008**, *64*, 771). *S*-Phenyl thiobenzoate and phenyl benzoate isomerization barrier was determined by ester bond rotation. COSNAR method was used for determination of resonance energies (*J. Am. Chem. Soc.* **1993**, *115*, 6951). Optimized ester conformations were used as starting geometries for isodesmic calculations for the ether, keto, and hydrocarbon derivatives. Structural representations were generated using CYLview software (Legault, C. Y. CYLview version 1.0 BETA, University of Sherbrooke). All other representations were generated using GaussView (GaussView, 5, Dennington, R.; Keith, T.; Millam, J. Semichem Inc., Shawnee Mission, KS, 2009).

Full Reference for Gaussian 09

Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Table SI-2. Total Energies for Optimized Structures of Ester, Ether, Ketone and Hydrocarbon Calculated using B3LYP/6-311++G(d,p)[a]

		$-E_T$ (ester) [au]	$-E_T$ (ether) [au]	$-E_T$ (ketone) [au]	$-E_T$(hydrocarbon) [au]	ΔE_T [au]	ΔE_T [kJ/mol]	ΔE_T [kcal/mol]
$PhCO_2Ph$	Ester	652.0392767	577.9759668	616.1048198	542.0672189	0.025709	67.5	16.1
PhCOSPh	Thioester	975.0023299	900.9549019	616.1048198	542.0694308	0.012039	31.6	7.6

[a] *J. Am. Chem. Soc.* **1993**, *115*, 6951.

Rotational profile of thioester PhCOSPh

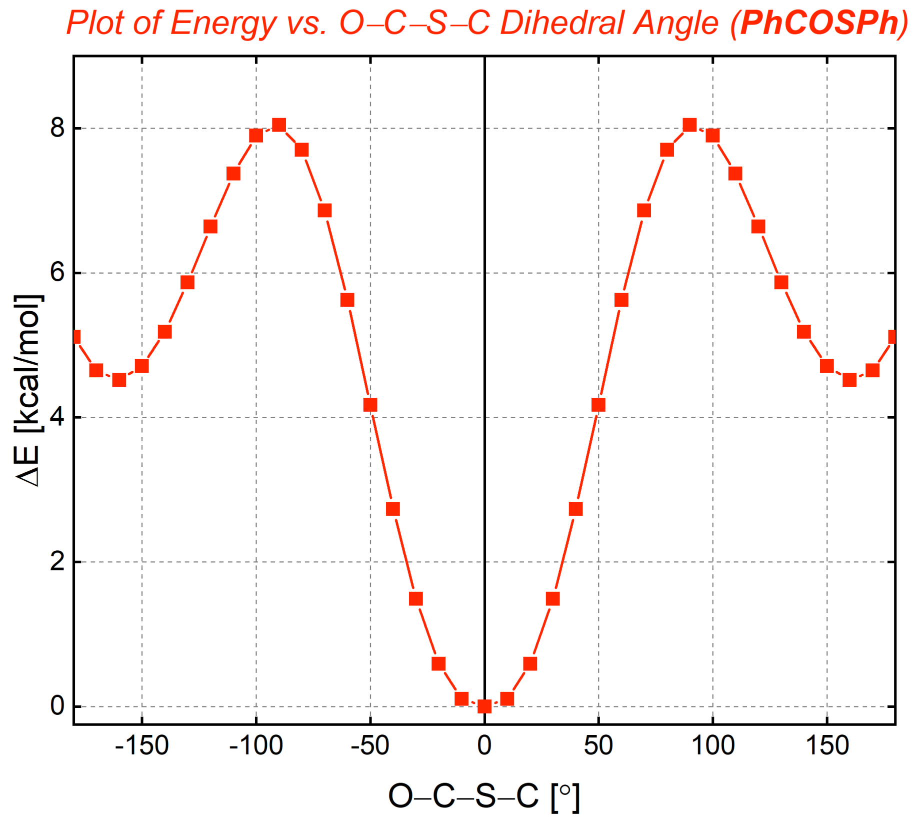


Chart SI-1. Correlation of ΔE [kcal/mol] to O–C–S–C [°] in PhCOSPh.

Rotational profile of ester $PhCO_2Ph$

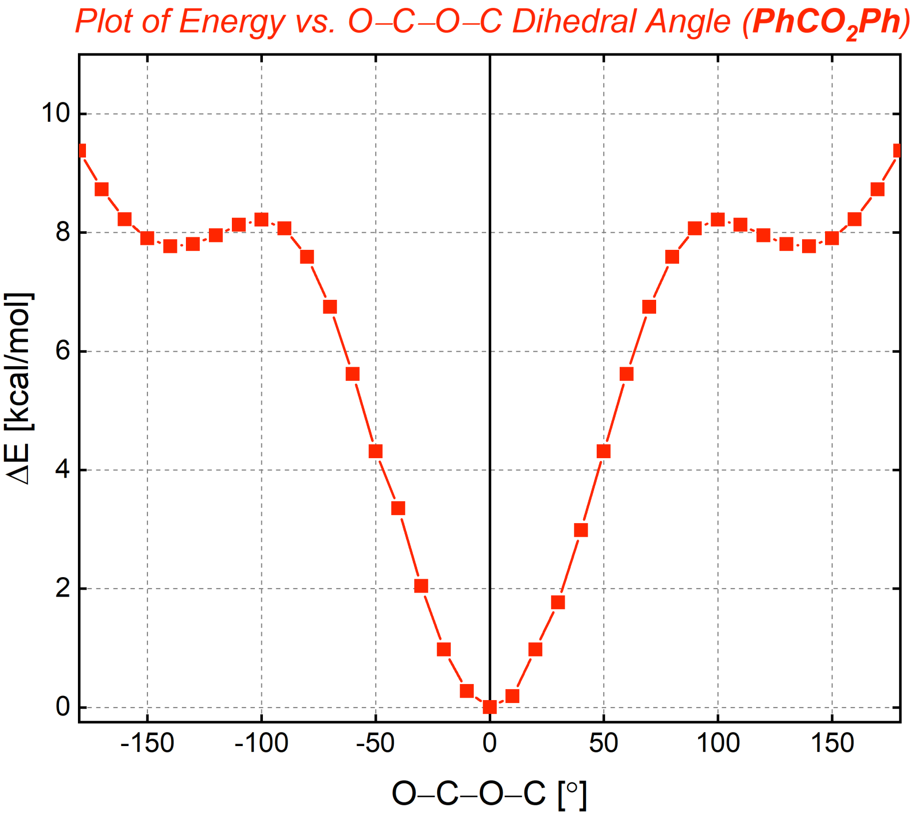


Chart SI-2. Correlation of ΔE [kcal/mol] to O–C–O–C [°] in $PhCO_2Ph$.

Cartesian Coordinates with Zero-Point Energies and Thermal Corrections

PhCO$_2$Ph

Energy: -652.039277 au

Sum of electronic and thermal Energies: -651.832704 au

Geometry:

O	-0.42596400	0.45855000	0.14428000
O	0.03426000	-1.64508800	-0.56902100
C	-1.80958900	0.25944400	0.08846600
C	-2.43658400	-0.65455700	0.92772200
H	-1.84802600	-1.27514300	1.59089500
C	-3.82500300	-0.75969100	0.89084500
H	-4.32254900	-1.47197900	1.53899200
C	-4.57269900	0.04306000	0.02960400
C	-3.92687900	0.95646400	-0.80137400
H	-4.50157300	1.58457800	-1.47232600
C	-2.53761300	1.06761200	-0.77564700
H	-2.01563200	1.77149600	-1.41242600
C	0.41714500	-0.56508300	-0.19953900
C	1.84543700	-0.16611900	-0.06223300
C	2.23286000	1.09766500	0.39935900
H	1.47715000	1.82303100	0.66959800
C	3.58444000	1.41188300	0.50904200
H	3.88251100	2.39044700	0.86760500
C	4.55278200	0.47137200	0.15876200
H	5.60479200	0.71974400	0.24477200
C	4.16935500	-0.78859300	-0.30224600
H	4.92154800	-1.51991600	-0.57475600
C	2.82059800	-1.10782800	-0.41194400
H	2.50270500	-2.08041500	-0.76663700
H	-5.65279100	-0.04332300	0.00730900

PhCOSPh

Energy: -975.002330 au

Sum of electronic and thermal Energies: -974.798351 au

Geometry:

O	-0.04633100	1.46634700	0.11249500
C	2.07780400	-0.47455400	-0.04523800
C	2.73668400	-0.37030500	1.18137100
H	2.23041900	-0.66882500	2.09122000
C	4.03978000	0.12051000	1.22697700
H	4.54910400	0.20344600	2.18041500
C	4.68487600	0.50437200	0.05247400
C	4.02577300	0.39667600	-1.17111000
H	4.52428000	0.69491500	-2.08646300
C	2.72302200	-0.09400800	-1.22355300
H	2.20644400	-0.17953500	-2.17170200
C	-0.56925100	0.38455300	0.02657800
C	-2.05242400	0.18742900	0.01742800
C	-2.66006700	-1.07296700	-0.03018900
H	-2.05713200	-1.97227400	-0.06010900
C	-4.04764900	-1.18107800	-0.03495600
H	-4.51067900	-2.16036600	-0.07066700
C	-4.83882800	-0.03380100	0.00690800
H	-5.91959300	-0.12078500	0.00279200
C	-4.23927700	1.22518700	0.05481000
H	-4.85251900	2.11847900	0.08758100
C	-2.85380600	1.33662200	0.06080300
H	-2.37126700	2.30521500	0.09868300
H	5.69894300	0.88595700	0.09049700
S	0.41955200	-1.15055100	-0.11225200

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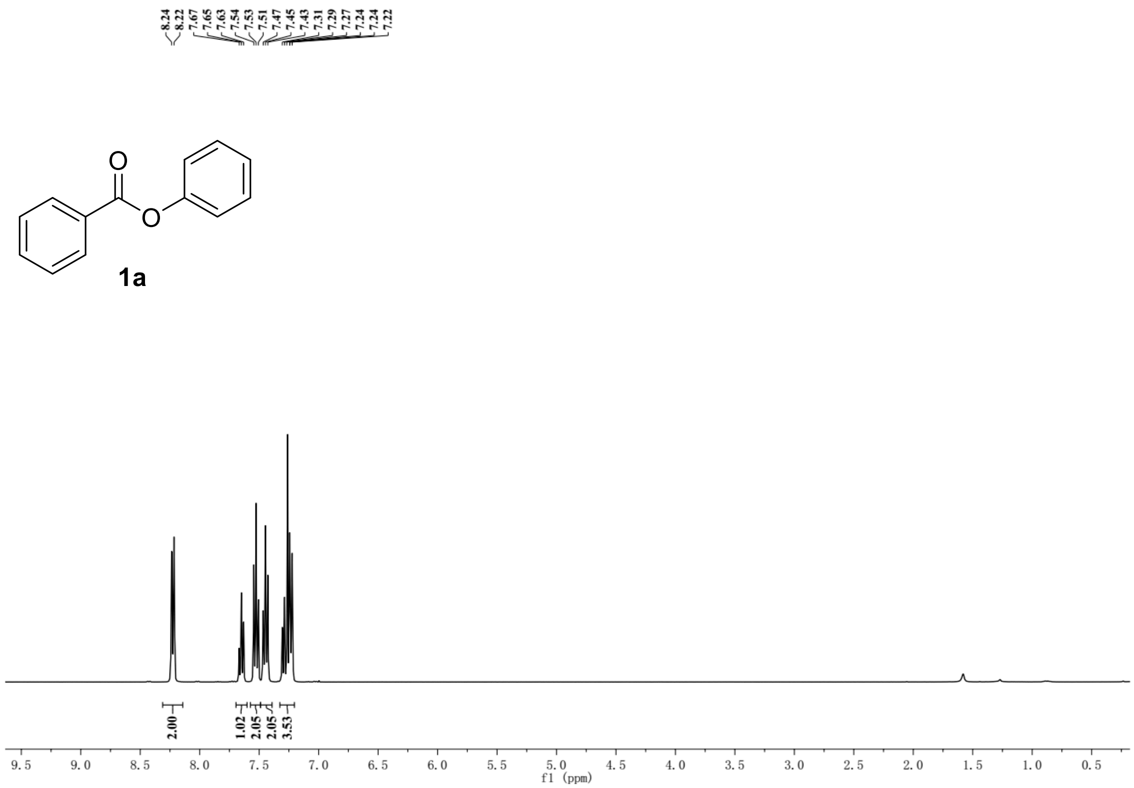
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8.22
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7.65
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7.27
7.24
7.24
7.22
2.00
1.02
2.05
2.05
3.53
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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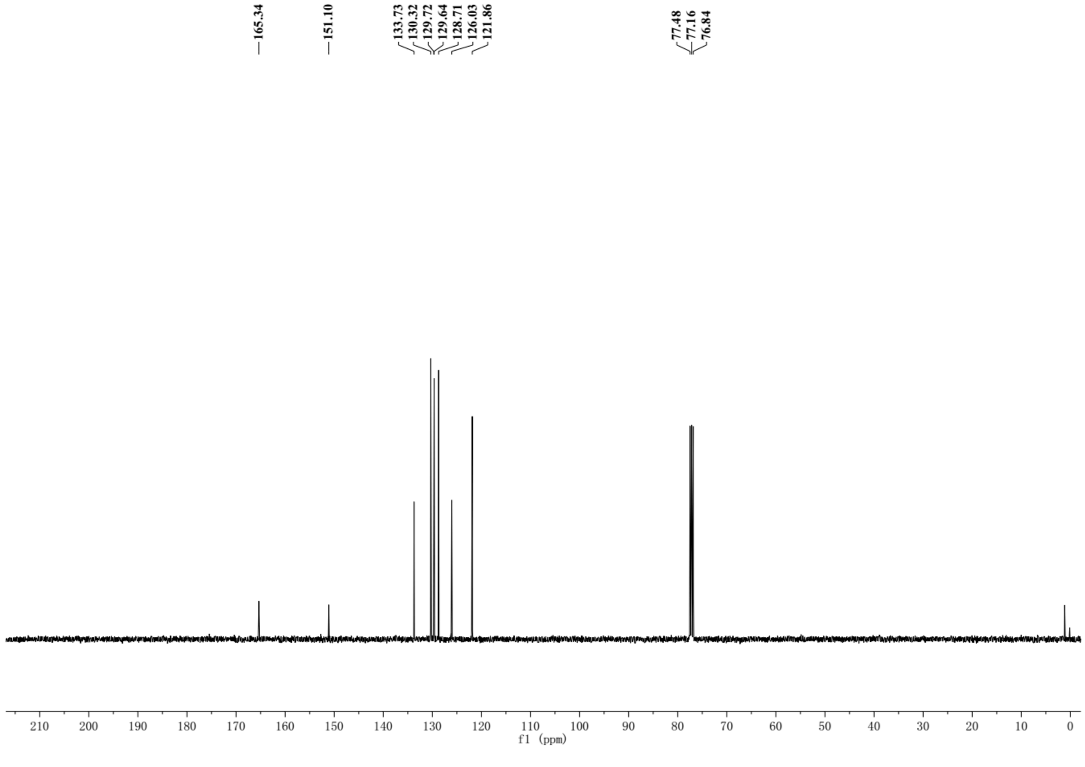
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

1a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129.72
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77.48
77.16
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200
190
180
170
160
150
140
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110
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90
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50
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10
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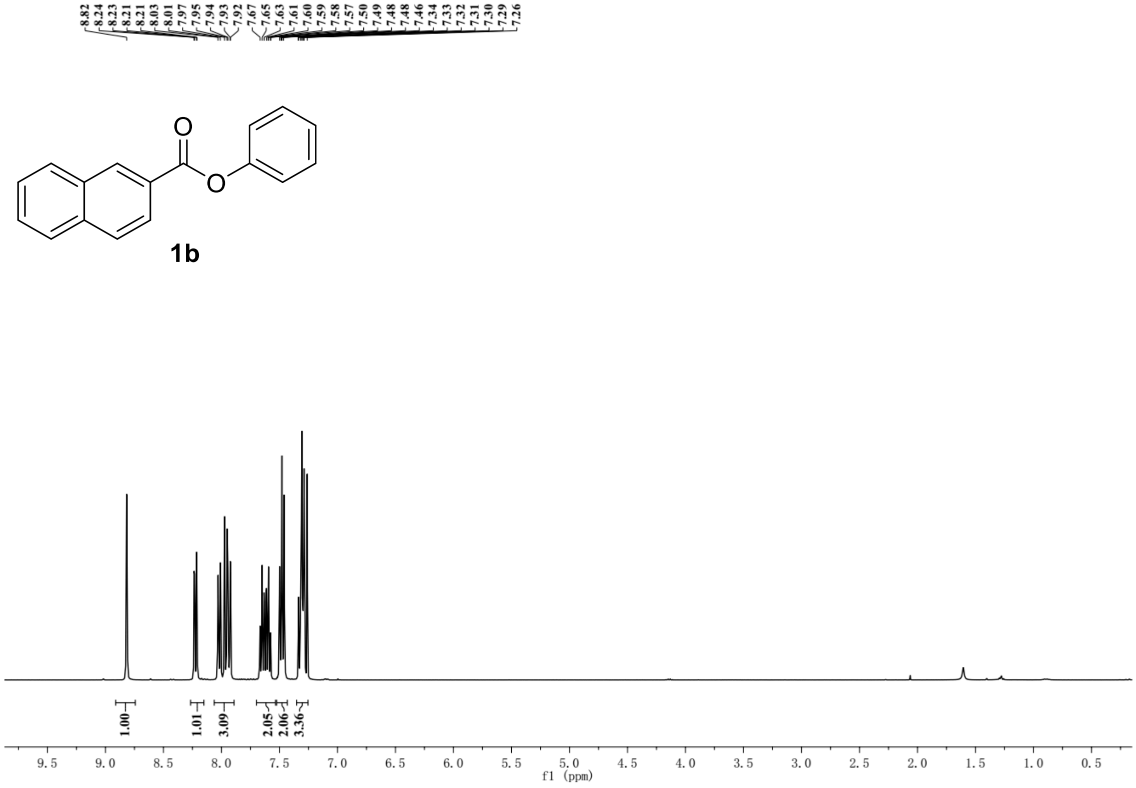
f1 (ppm)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8.03
8.01
7.97
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7.94
7.93
7.92
7.67
7.65
7.63
7.61
7.60
7.59
7.58
7.57
7.50
7.49
7.48
7.48
7.46
7.34
7.33
7.32
7.31
7.30
7.29
7.26
O
O
1.00
1.01
3.09
2.05
2.06
3.36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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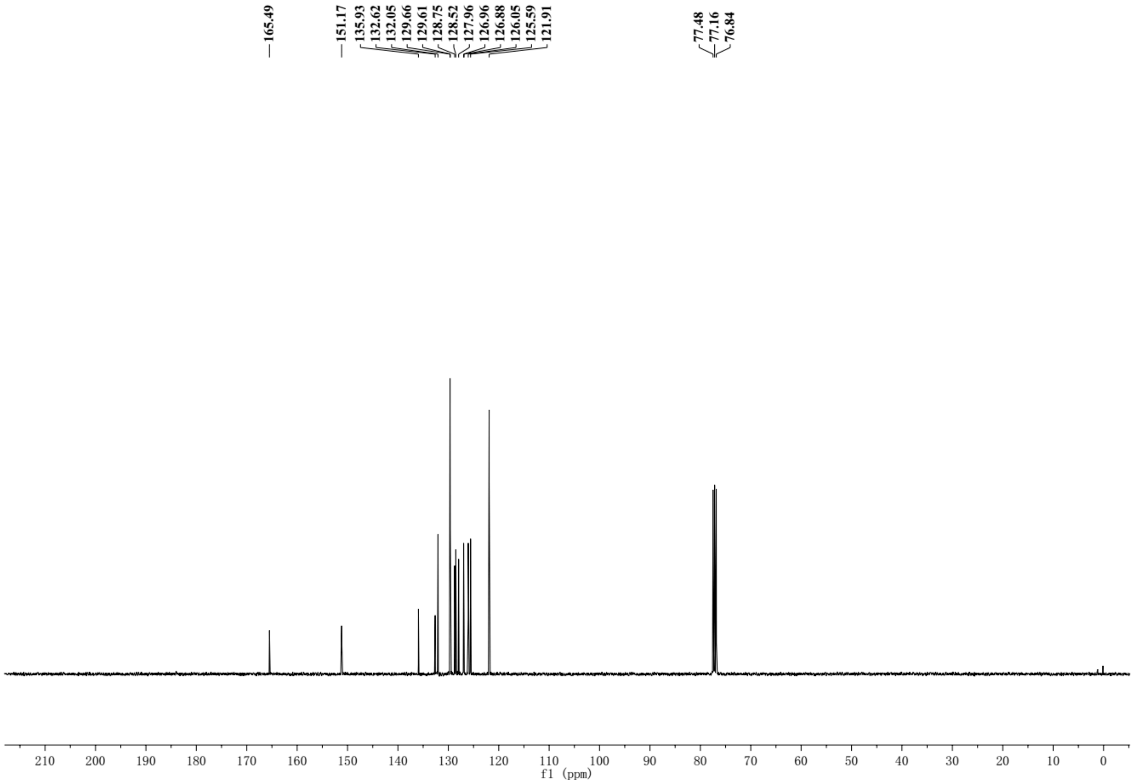
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

1b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132.05
129.66
129.61
128.75
128.52
127.96
126.96
126.88
126.05
125.59
121.91
77.48
77.16
76.84
210
200
190
180
170
160
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130
120
110
100
90
80
70
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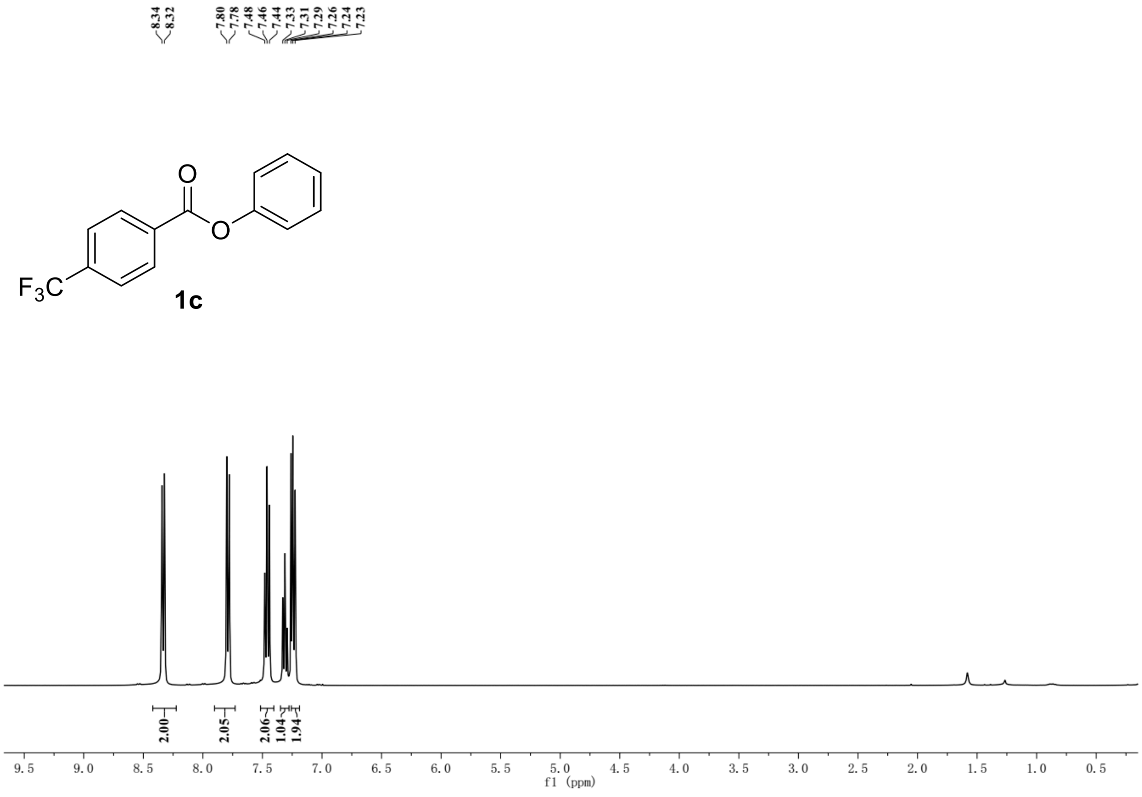
50
40
30
20
10
0
f1 (ppm)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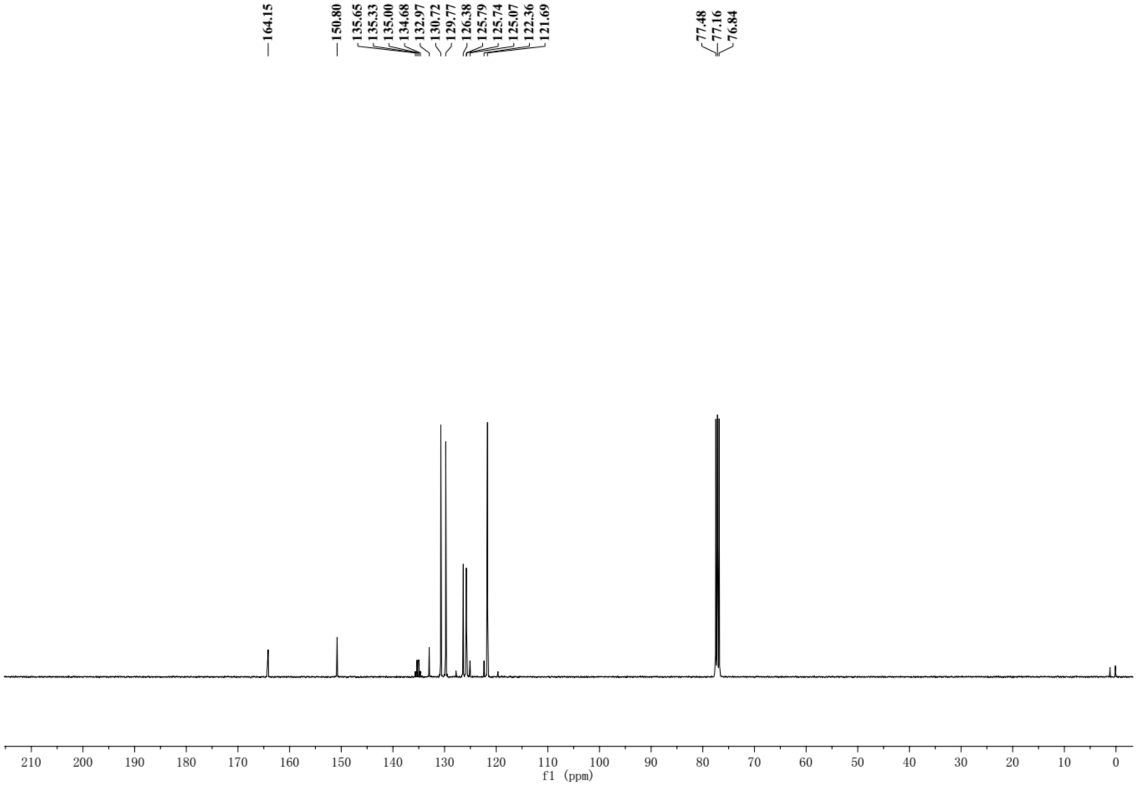
7.46
7.44
7.33
7.31
7.29
7.26
7.24
7.23
O
O
F3C
2.00
2.05
2.06
1.04
1.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

1c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125.74
125.07
122.36
121.69
77.48
77.16
76.84
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1c

-63.12
F3C
O
O
20
10
0
-10
-20
-30
-40
-50
-60
-70
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-100
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-120
-130
-140
-150
-160
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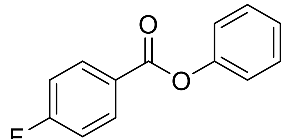
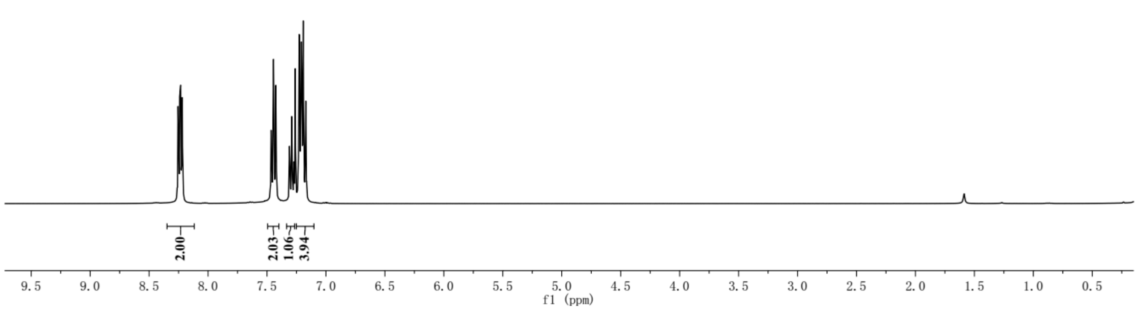
-190
-200
-210
f1 (ppm)


O
O
F

1d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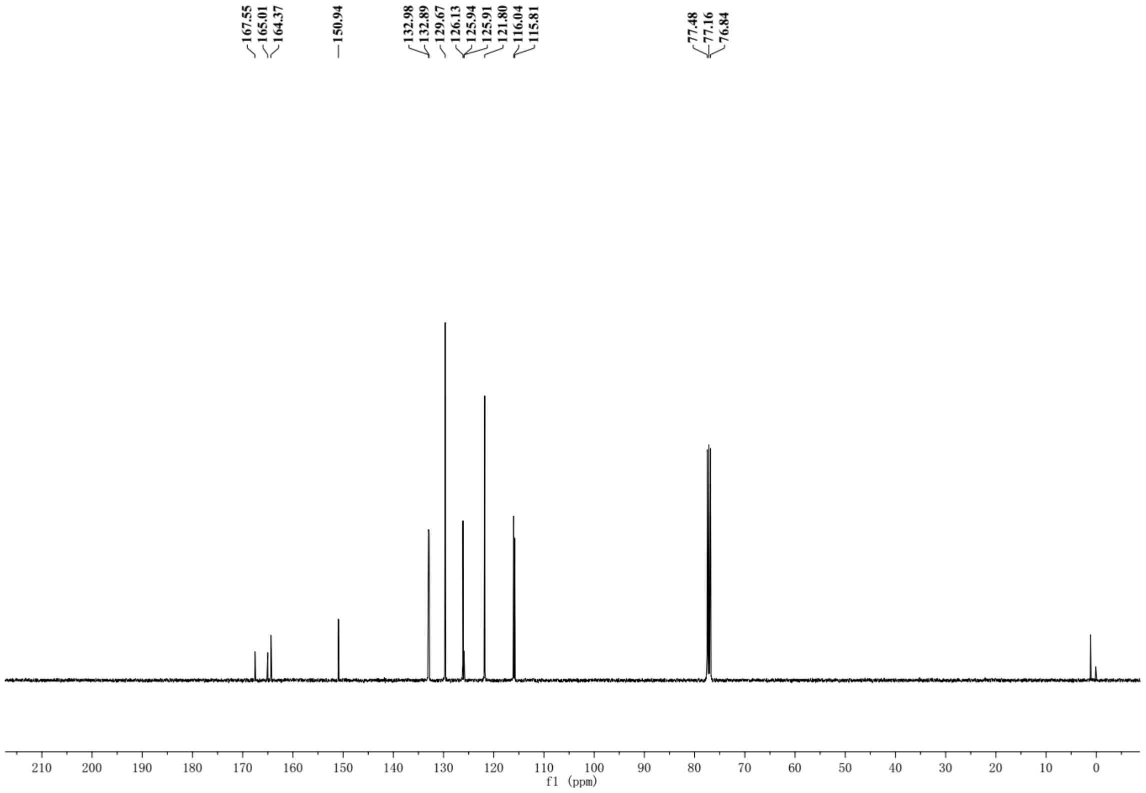
7.26
7.23
7.21
7.19
7.17
2.00
2.03
1.06
3.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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125.94
125.91
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77.48
77.16
76.84
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200
190
180
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130
120
110
100
90
80
70
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50
40
30
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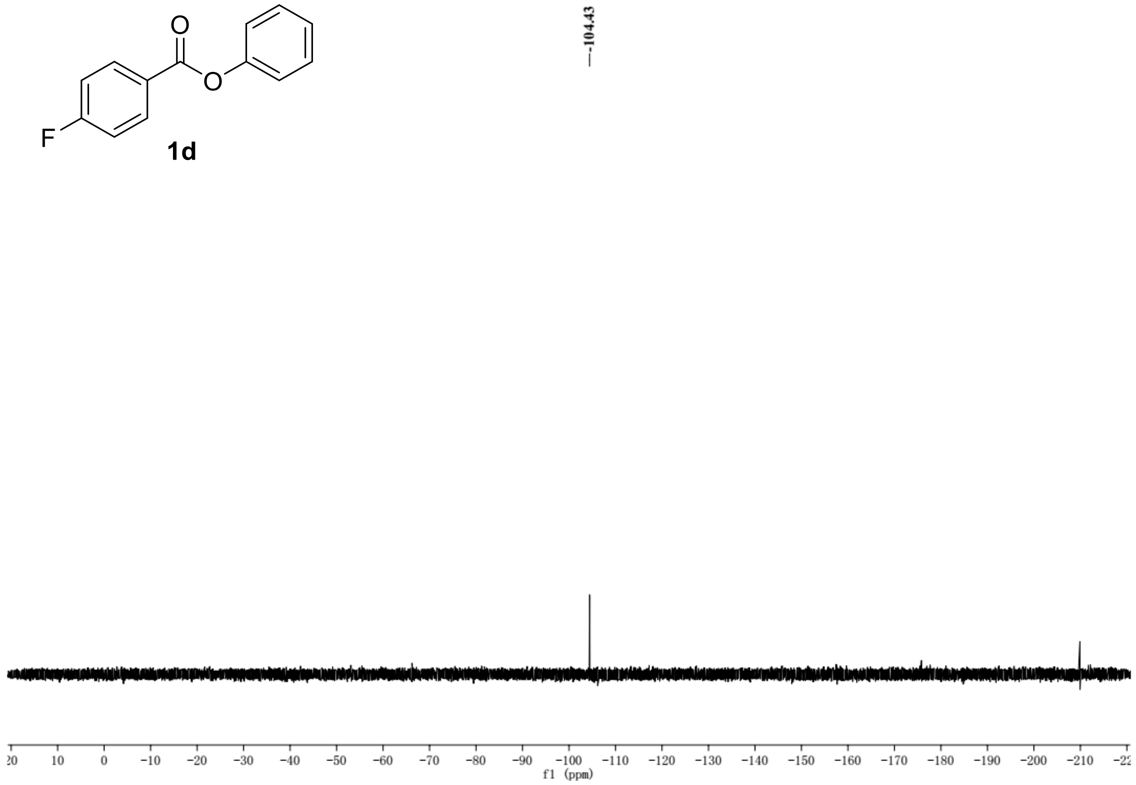
10
0
f1 (ppm)


1d
O
O
F
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20
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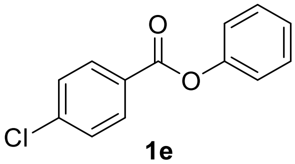
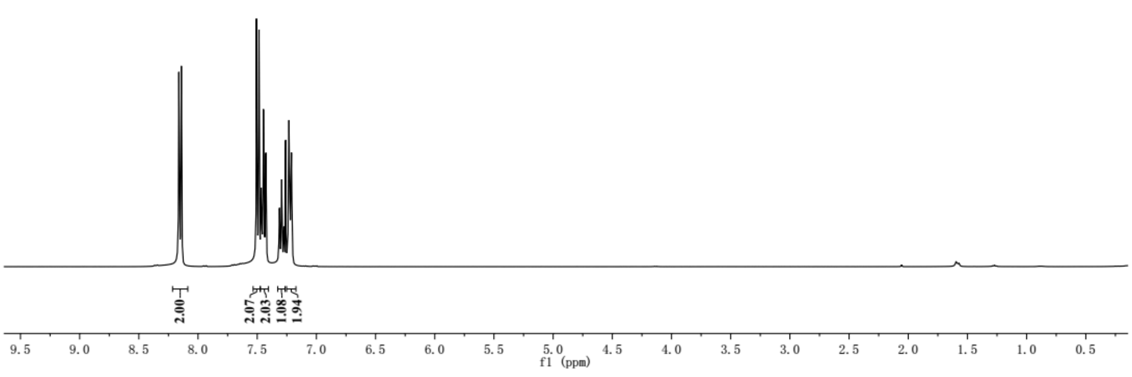
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)


O
O
Cl

1e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7.31
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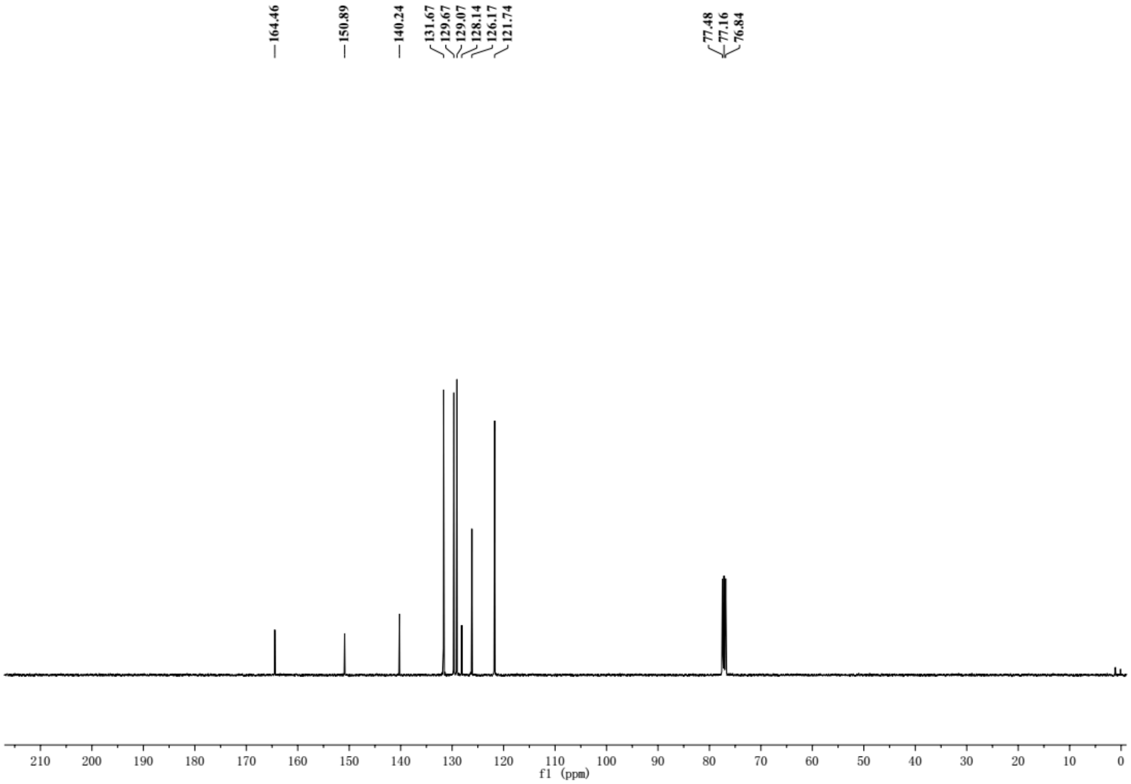
7.27
7.26
7.23
7.21
2.00
2.07
2.03
1.08
1.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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126.17
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77.48
77.16
76.84
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200
190
180
170
160
150
140
130
120
110
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90
80
70
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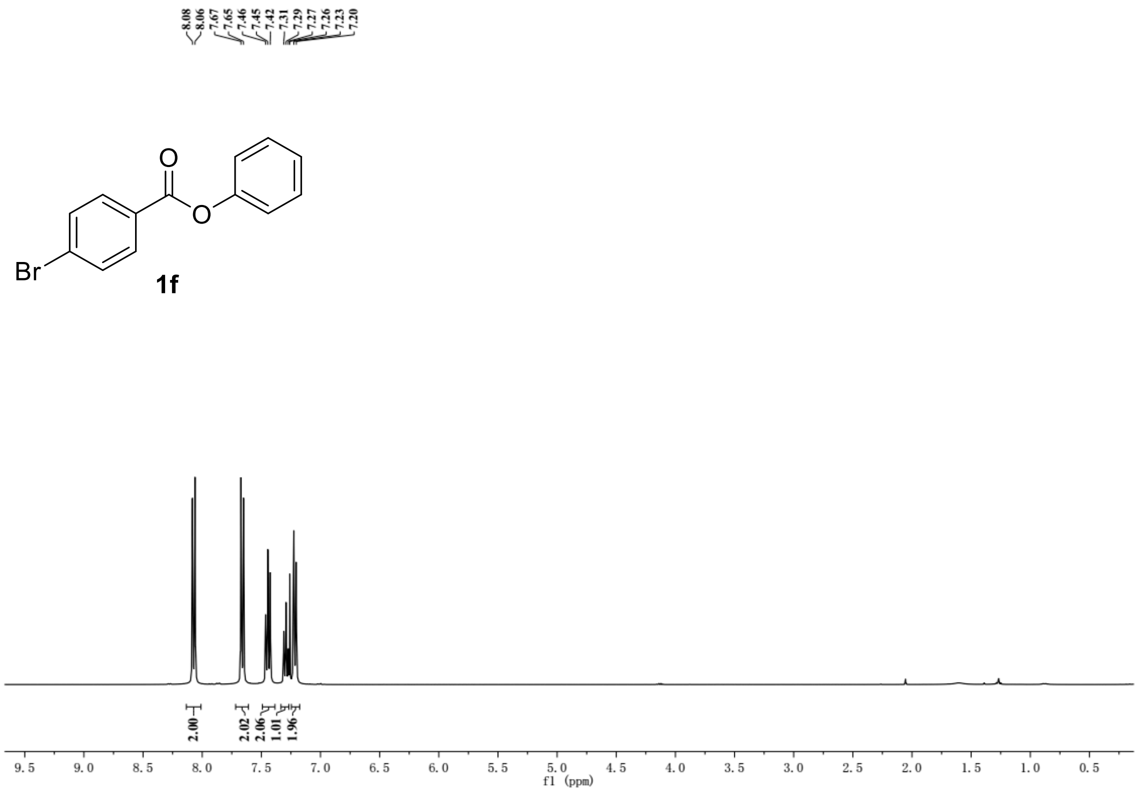
50
40
30
20
10
0
f1 (ppm)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8.06
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7.45
7.42
7.31
7.29
7.27
7.26
7.23
7.20
O
O
Br
2.00
2.02
2.06
1.01
1.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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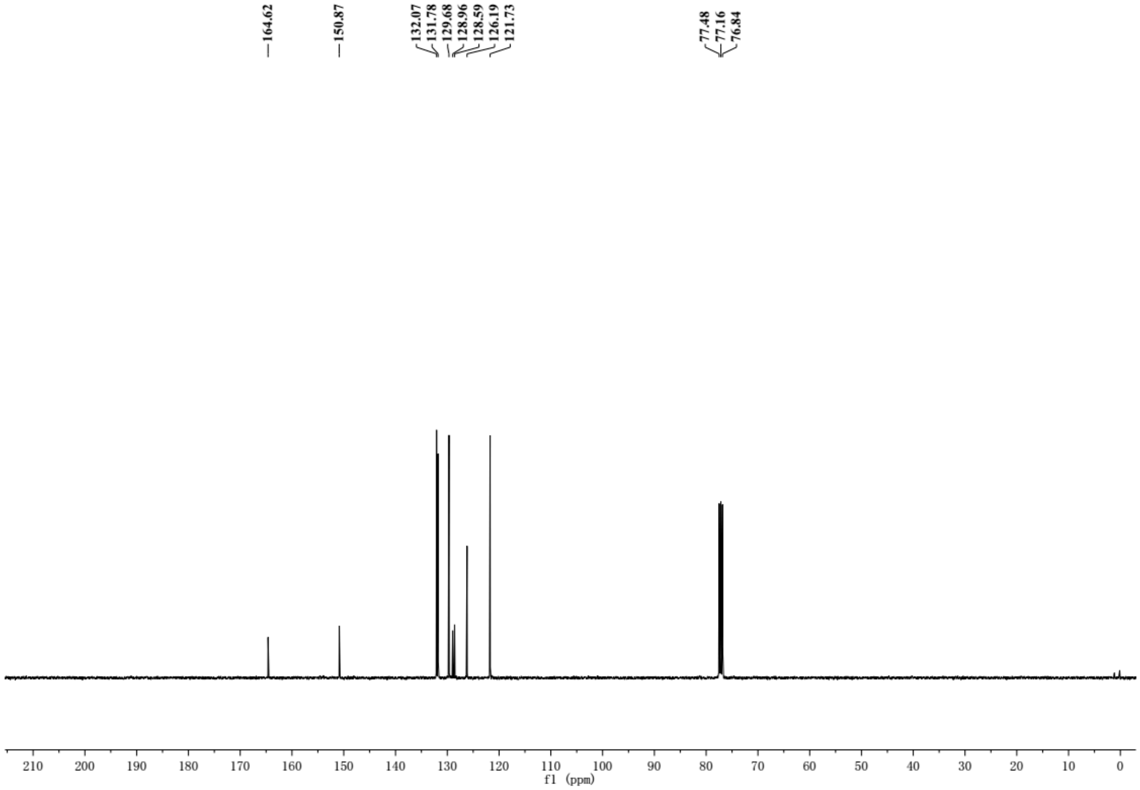
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

1f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128.59
126.19
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77.48
77.16
76.84
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200
190
180
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160
150
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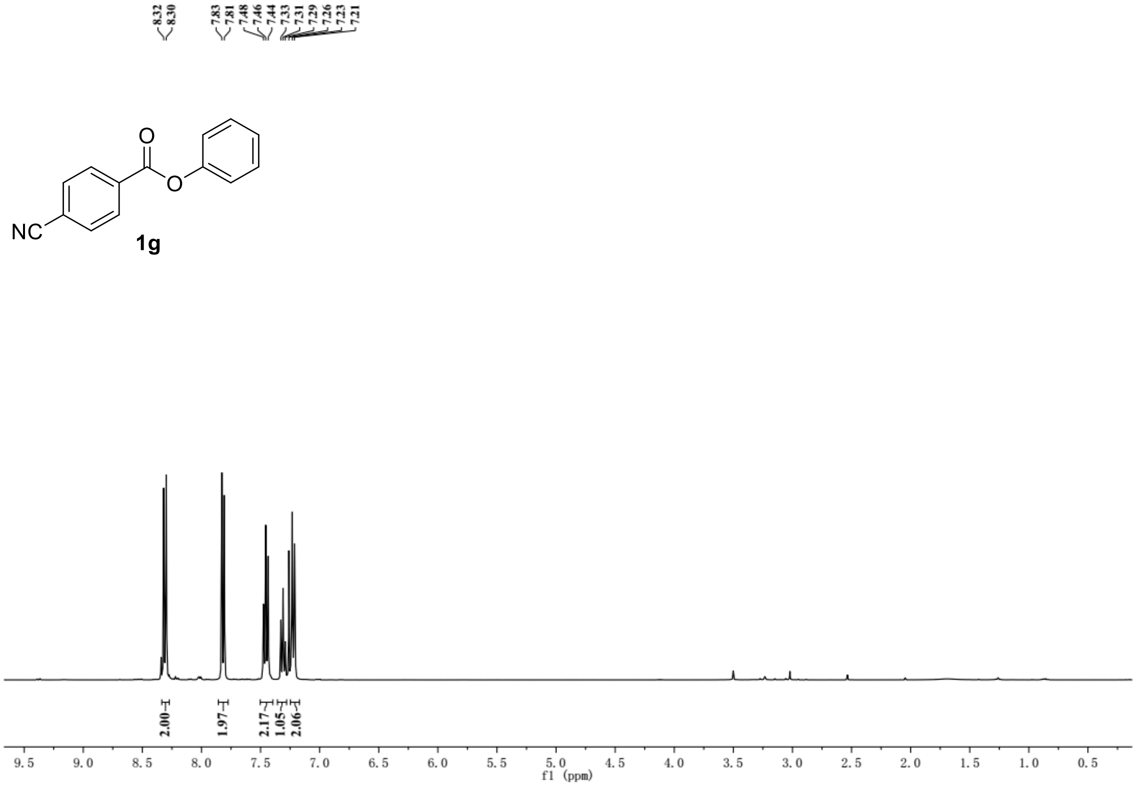
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.33
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7.29
7.26
7.23
7.21
O
O
NC
2.00
1.97
2.17
1.05
2.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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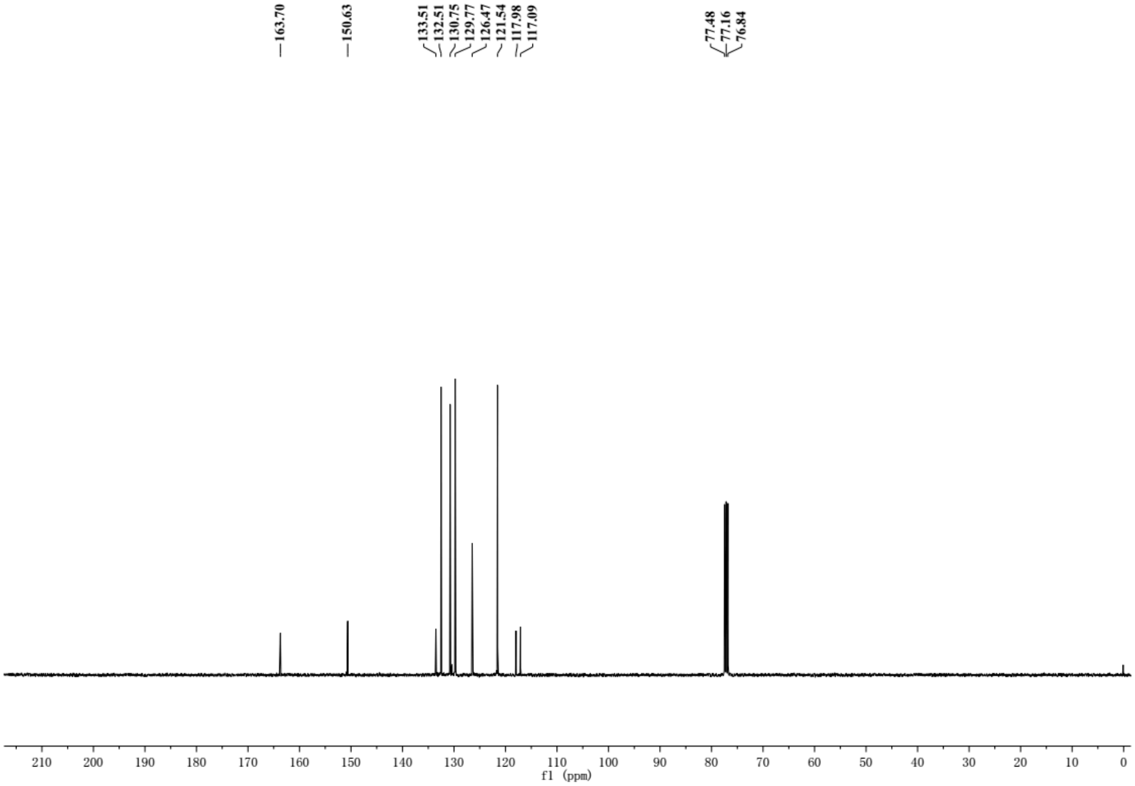
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

1g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117.09
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77.16
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210
200
190
180
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160
150
140
130
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110
100
90
80
70
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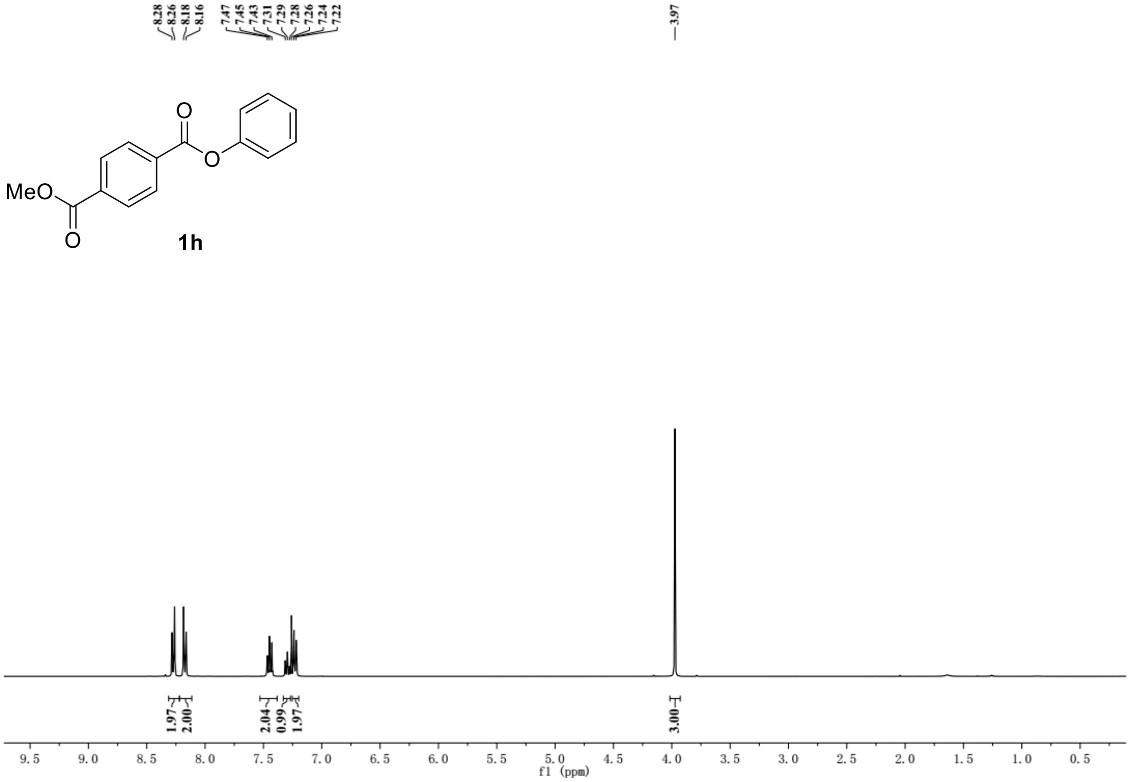
50
40
30
20
10
0
f1 (ppm)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7.31
7.29
7.28
7.26
7.24
7.22
3.97
MeO
O
O
O
1h
1.97
2.00
2.04
0.99
1.97
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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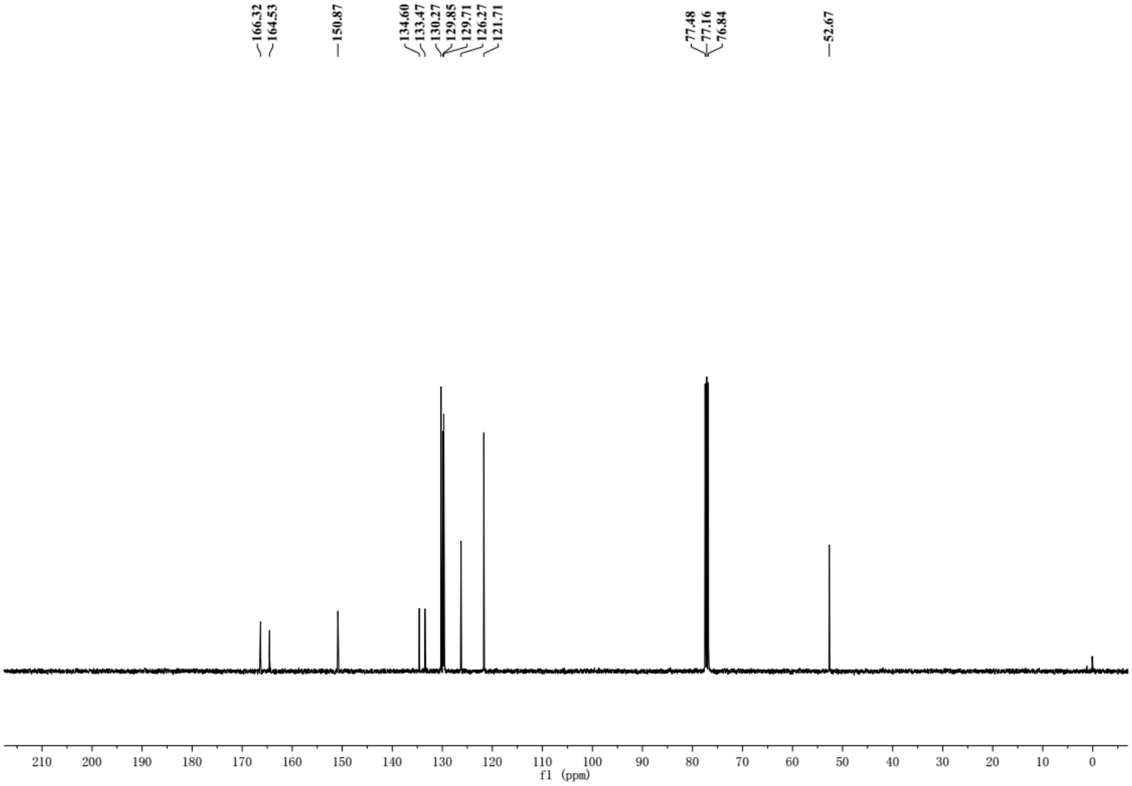
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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76.84
52.67
210
200
190
180
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90
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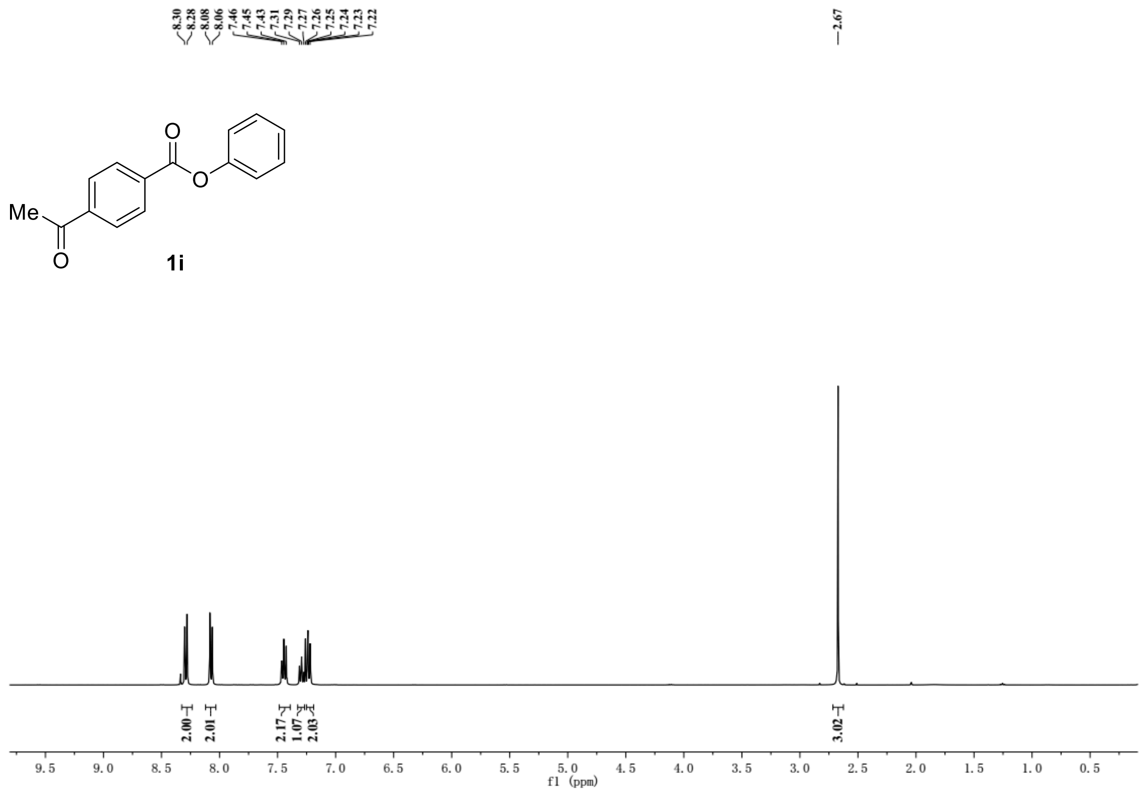
50
40
30
20
10
0
f1 (ppm)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7.43
7.31
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7.27
7.26
7.25
7.24
7.23
7.22
2.67
Me
O
O
O
1i
2.00
2.01
2.17
1.07
2.03
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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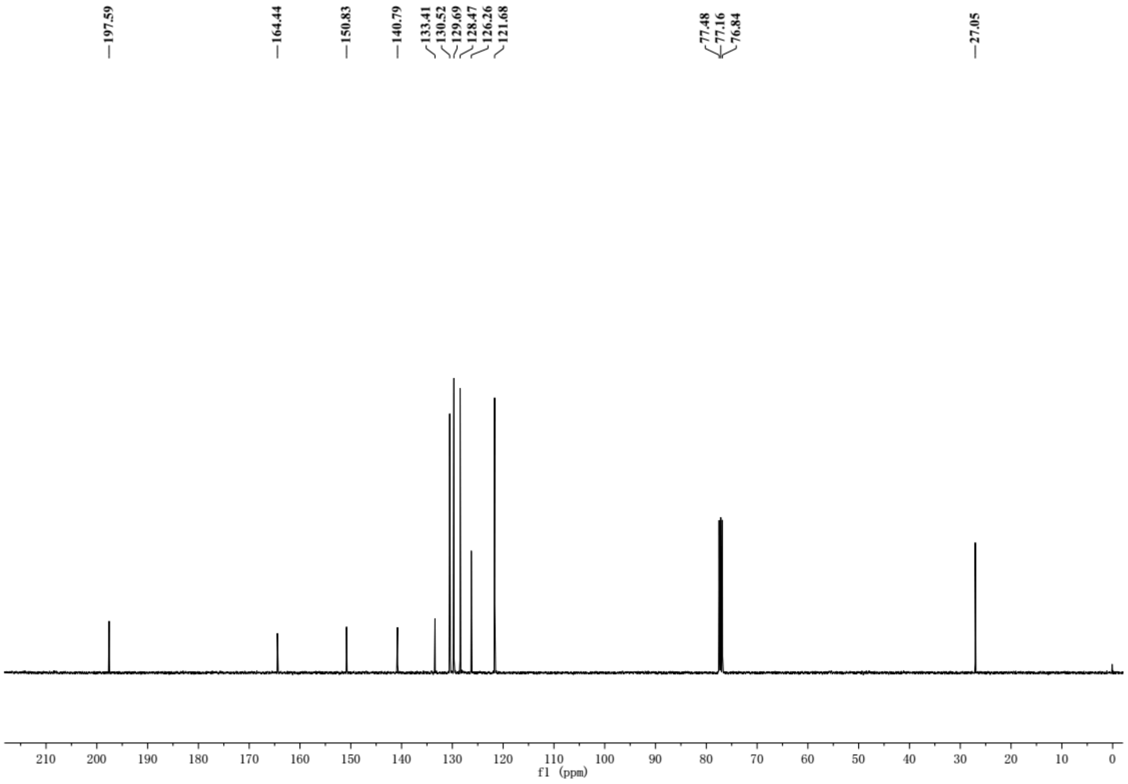
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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76.84
27.05
210
200
190
180
170
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130
120
110
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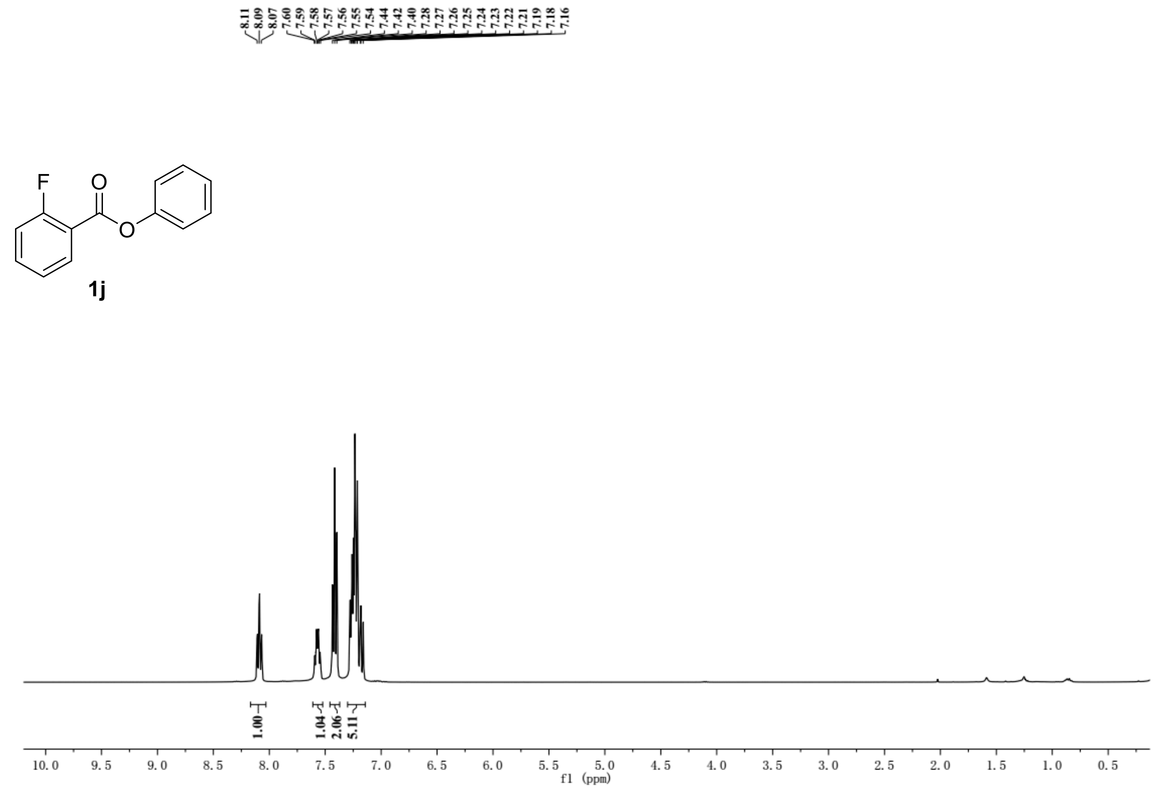
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.19
7.18
7.16
F
O
O
1j
1.00
1.04
2.06
5.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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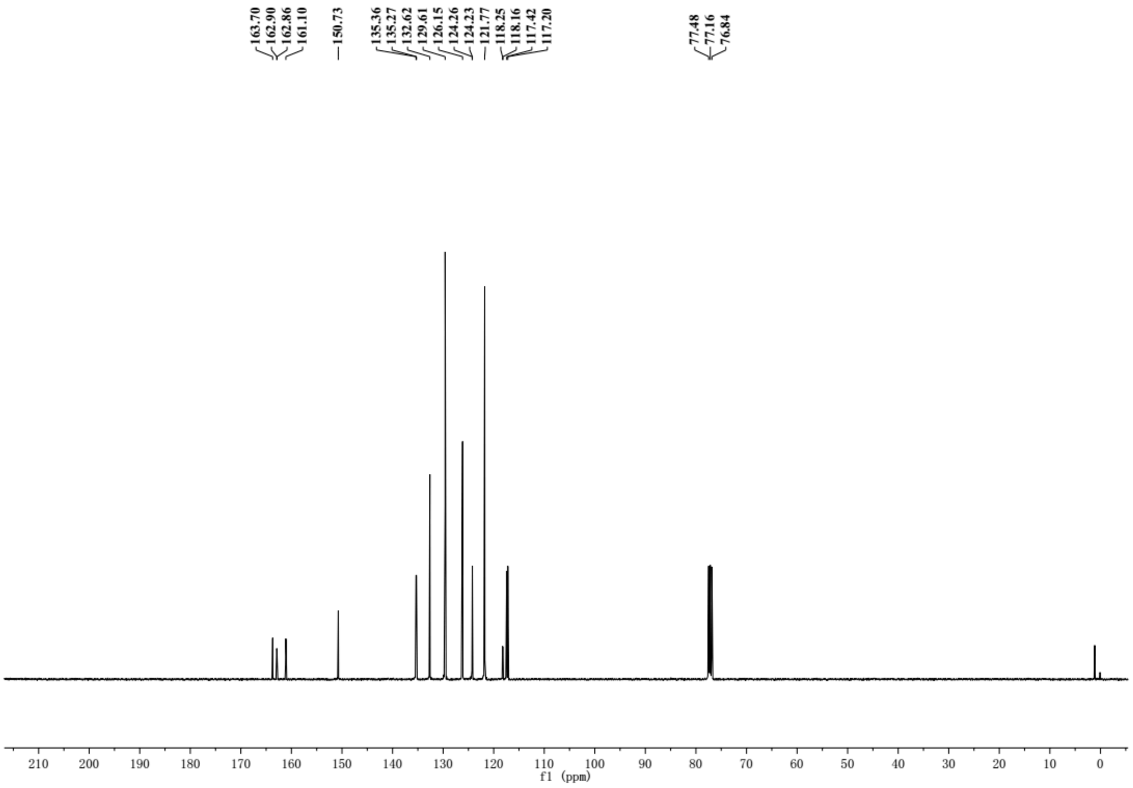
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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124.26
124.23
121.77
118.25
118.16
117.42
117.20
77.48
77.16
76.84
210
200
190
180
170
160
150
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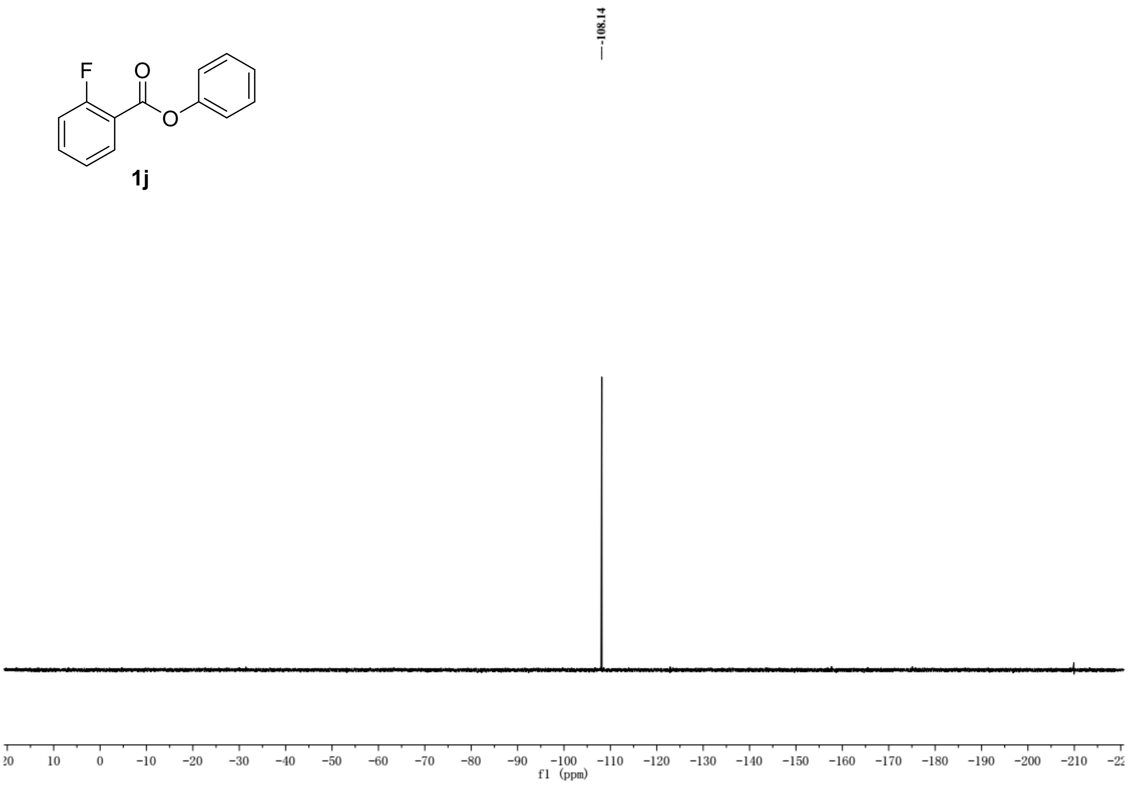
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
O
O
1j
-108.14
20
10
0
-10
-20
-30
-40
-50
-60
-70
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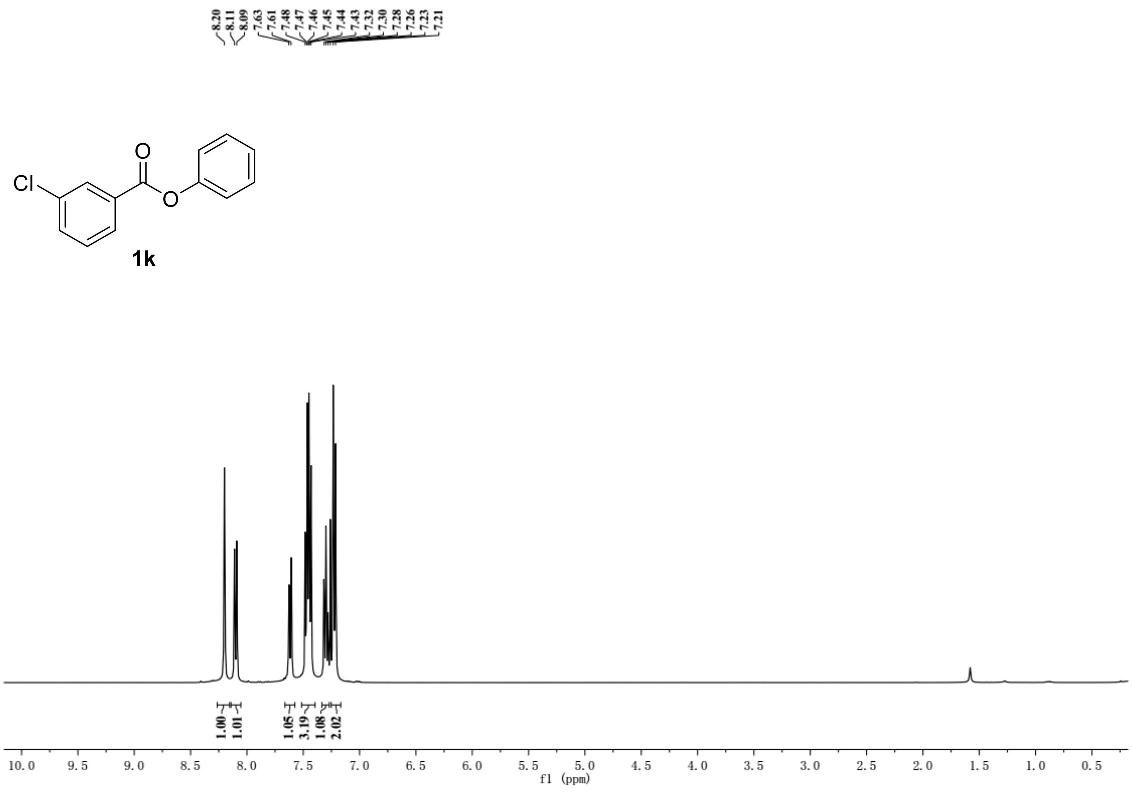
-200
-210
-22
f1 (ppm)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7.30
7.28
7.26
7.23
7.21
Cl
O
O
1k
1.00
1.01
1.05
3.19
1.08
2.02
10.0
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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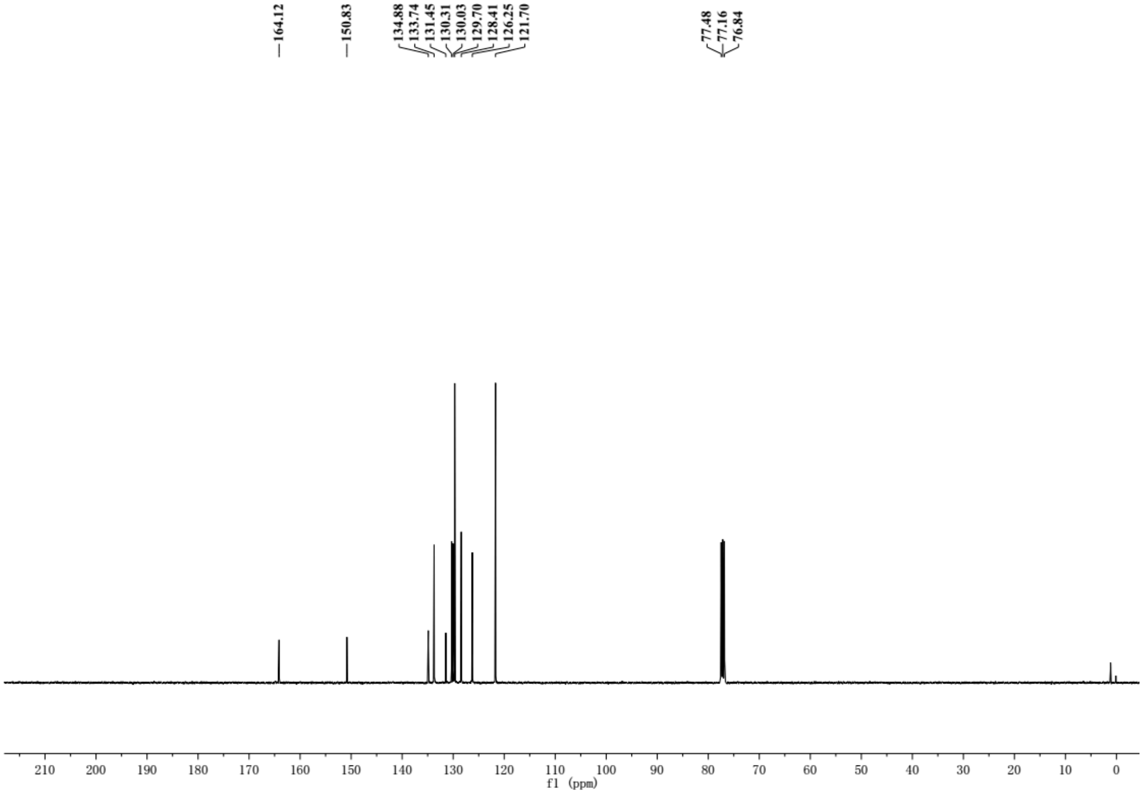
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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121.70
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76.84
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200
190
180
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130
120
110
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90
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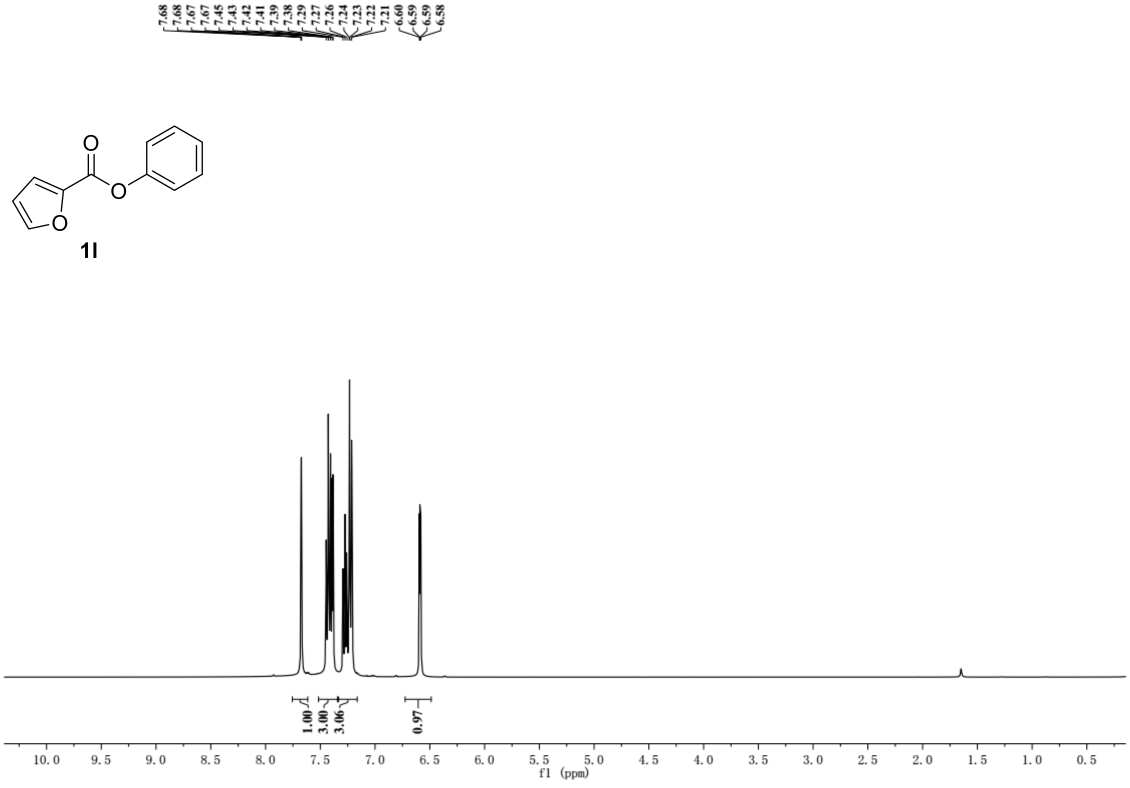
50
40
30
20
10
0
f1 (ppm)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7.26
7.24
7.23
7.22
7.21
6.60
6.59
6.59
6.58
O
O
O
1.00
3.00
3.06
0.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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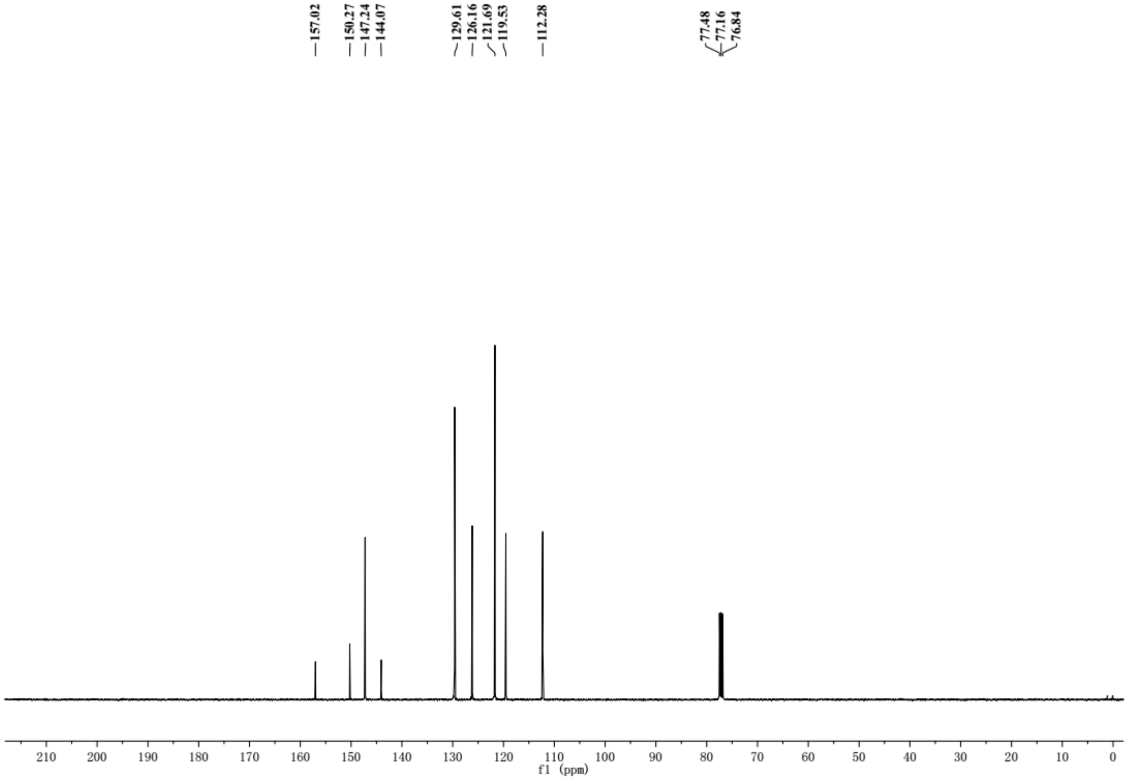
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

1l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77.48
77.16
76.84
210
200
190
180
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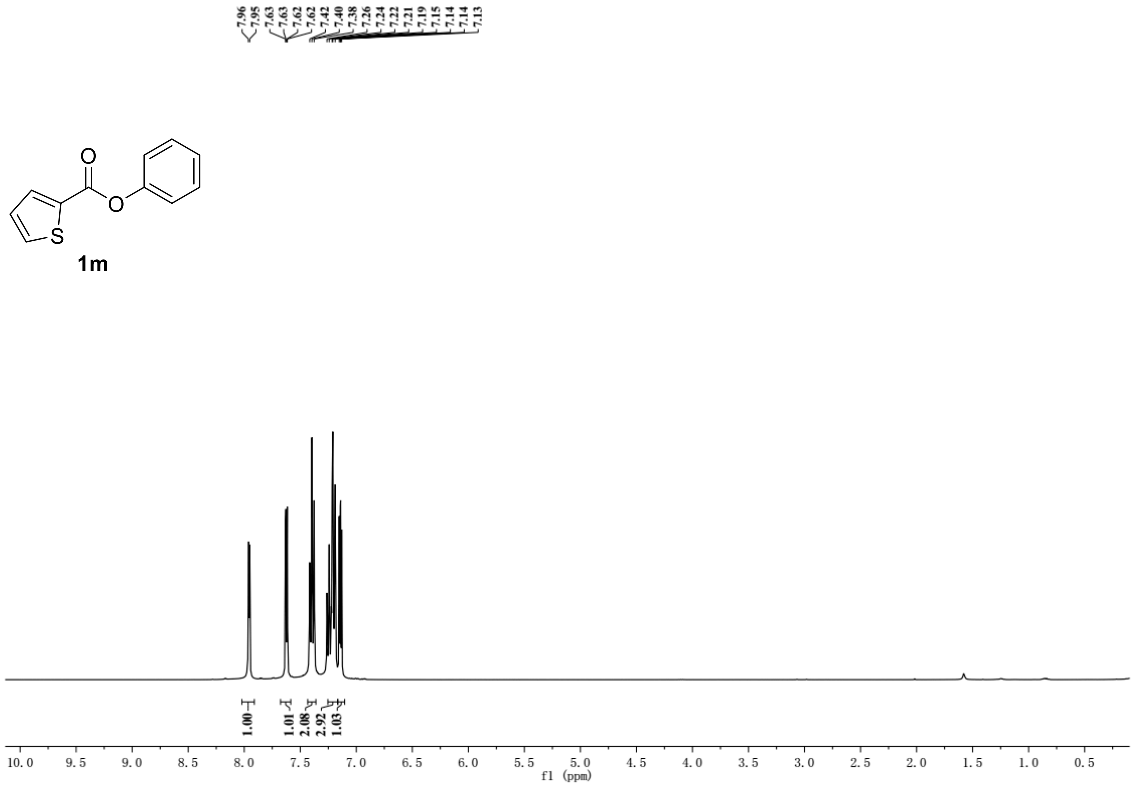
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.21
7.19
7.15
7.14
7.14
7.13
O
O
S
1m
1.00
1.01
2.08
2.92
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9.0
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8.0
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7.0
6.5
6.0
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2.5
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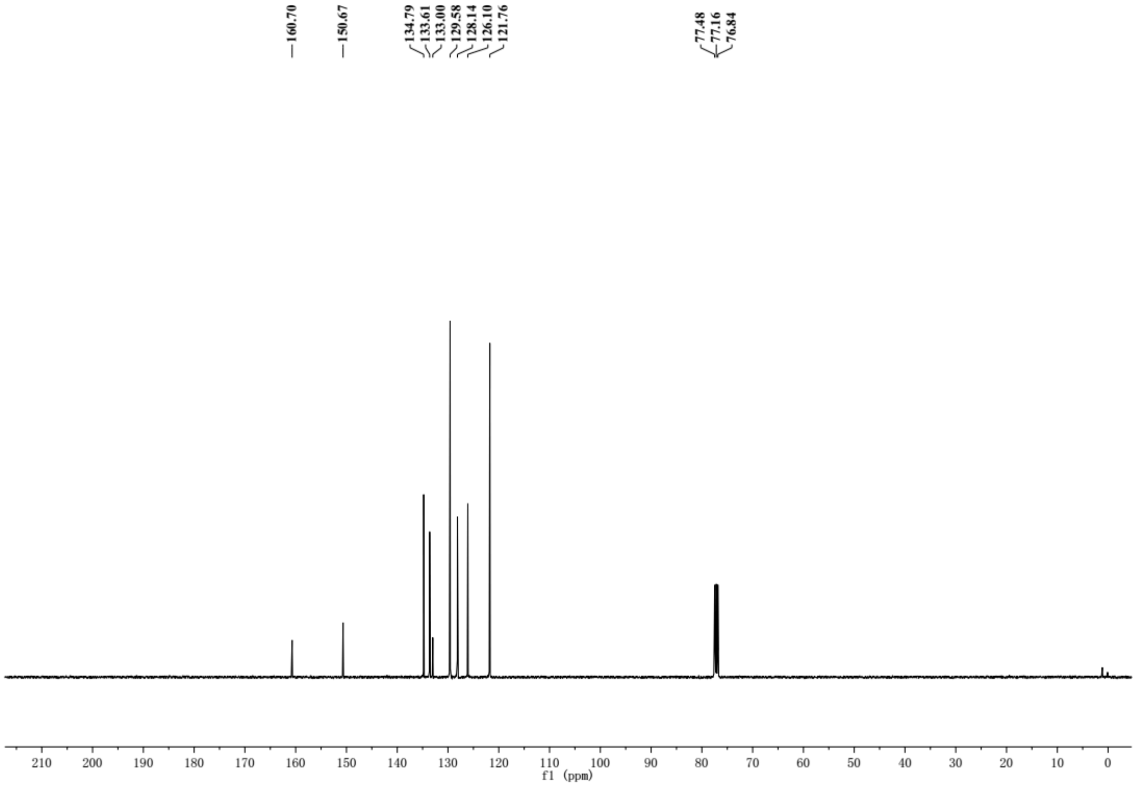
1.5
1.0
0.5
f1 (ppm)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76.84
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200
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180
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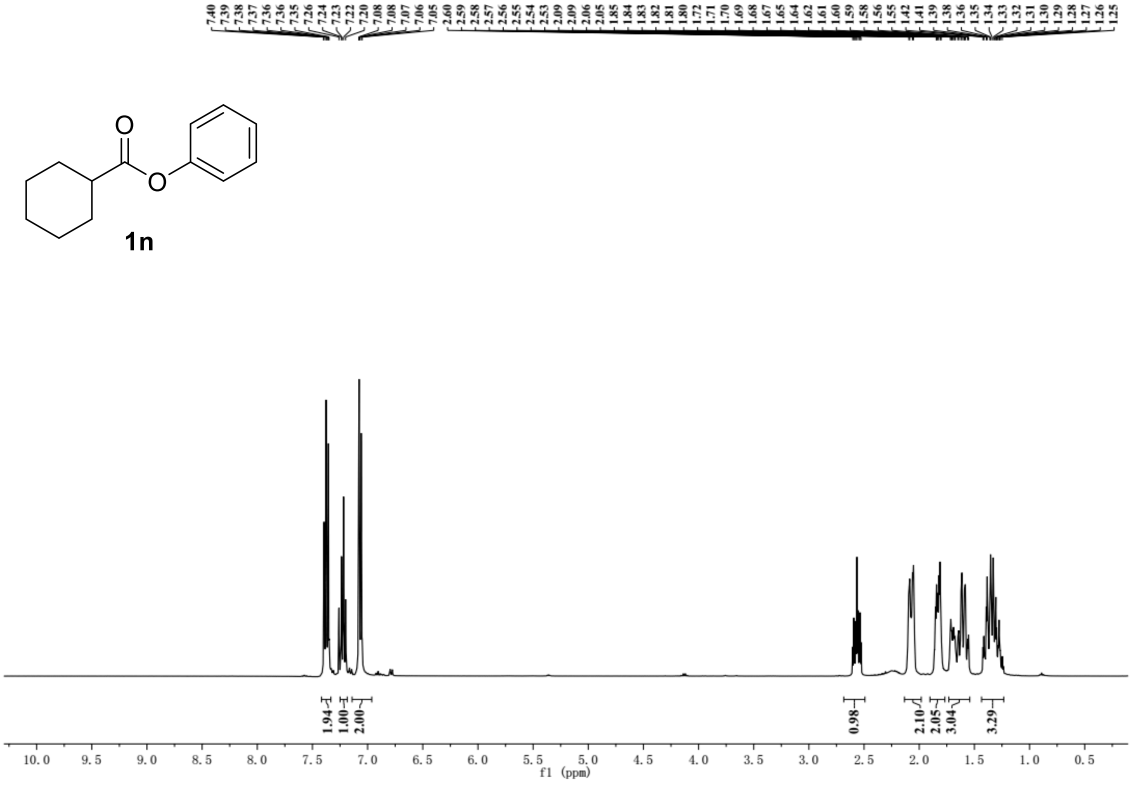
f1 (ppm)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7.06
7.05
2.60
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2.58
2.57
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2.55
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2.53
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2.09
2.06
2.05
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1.84
1.83
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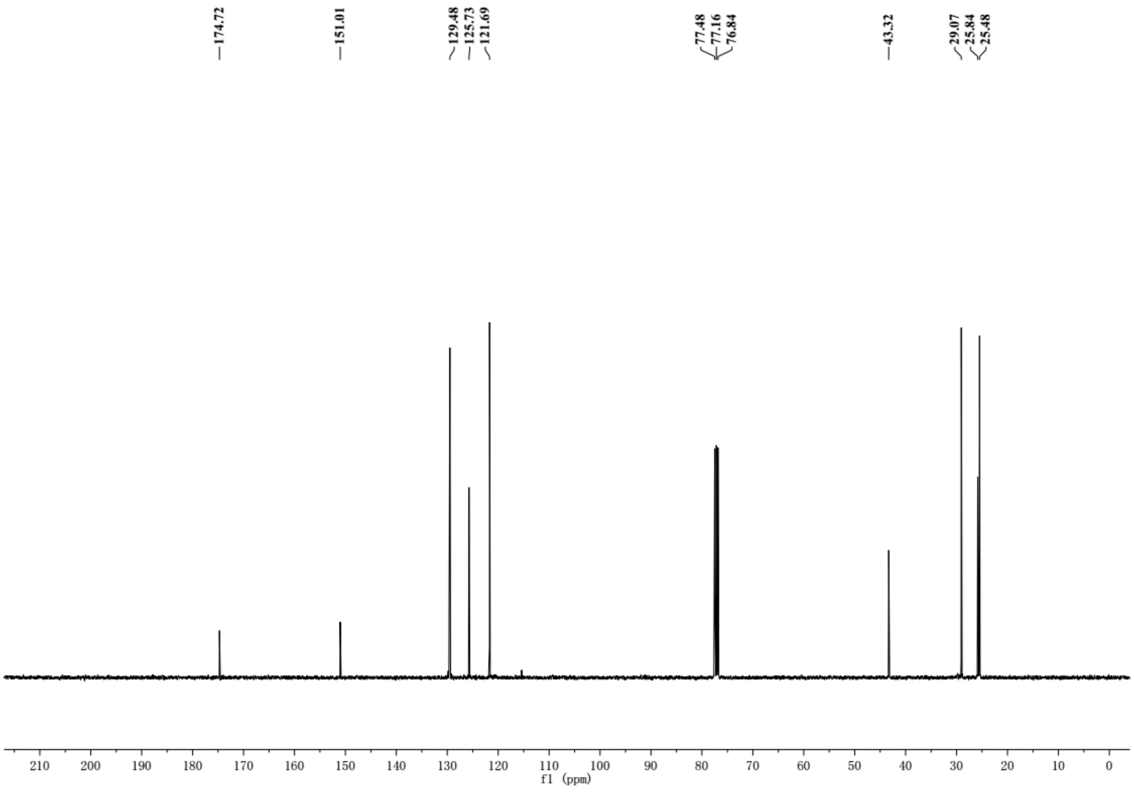
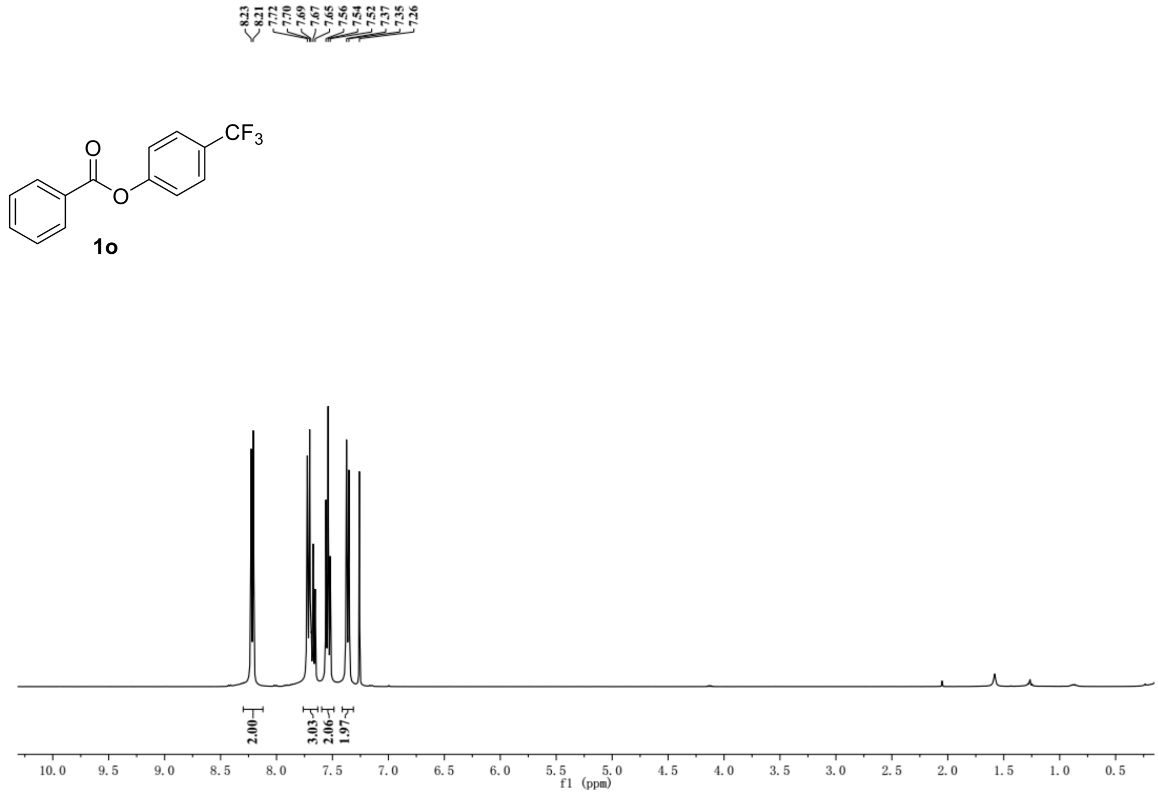
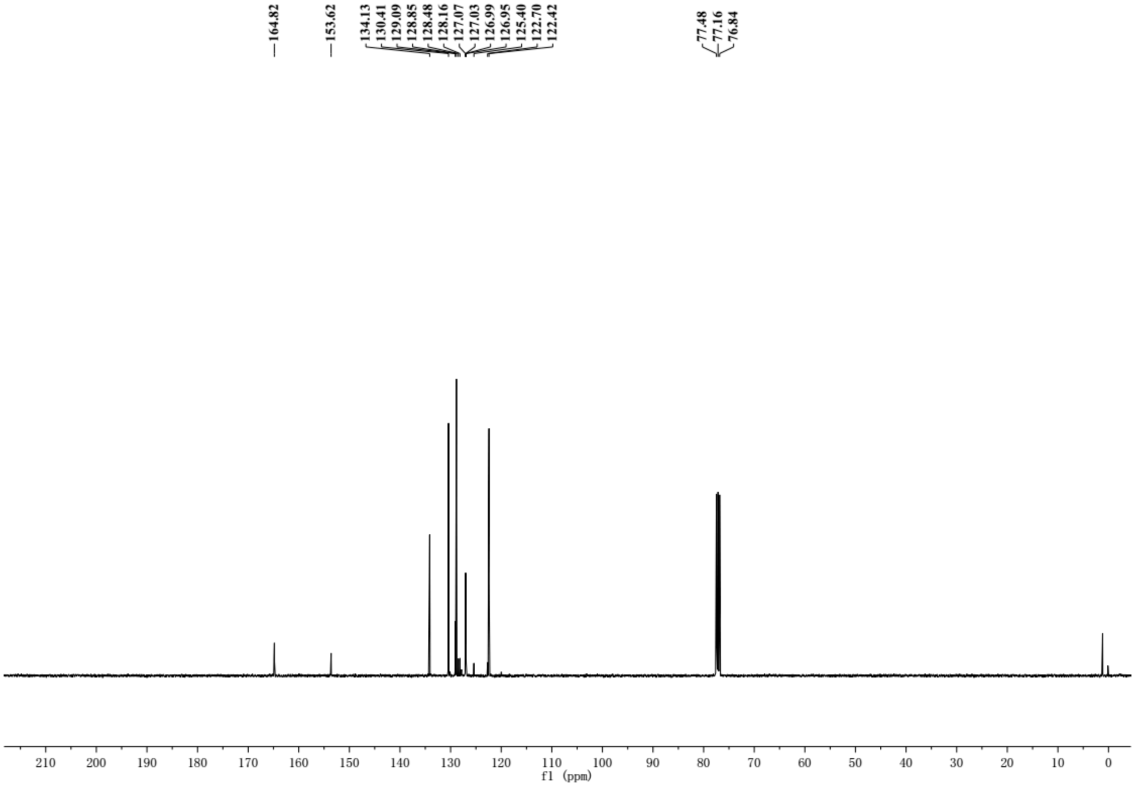
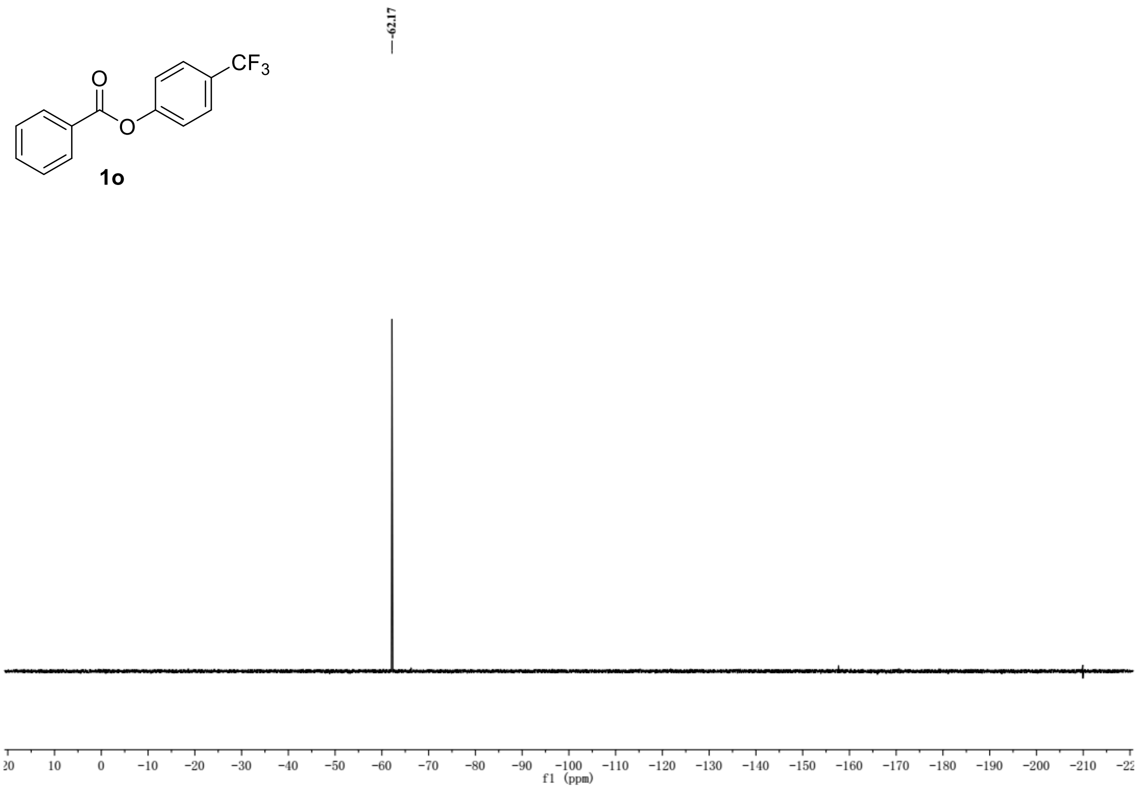
1.80
1.72
1.71
1.70
1.69
1.68
1.67
1.65
1.64
1.62
1.61
1.60
1.59
1.58
1.56
1.55
1.42
1.41
1.39
1.38
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.29
1.28
1.27
1.26
1.25
O
O
1n
1.94
1.00
2.00
0.98
2.10
2.05
3.04
3.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

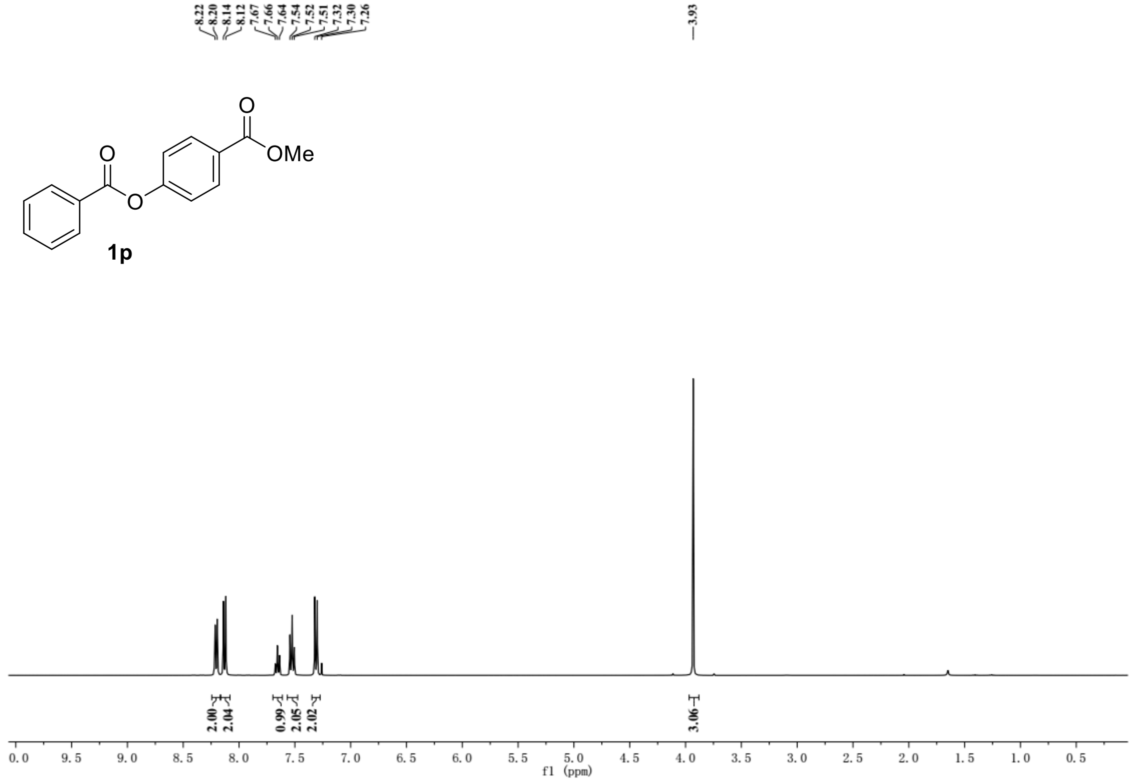

174.72
151.01
129.48
125.73
121.69
77.48
77.16
76.84
43.32
29.07
25.84
25.48
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.23
8.21
7.72
7.70
7.69
7.67
7.65
7.56
7.54
7.52
7.37
7.35
7.26
CF3
O
O
2.00
3.03
2.06
1.97
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
f1 (ppm)

1o

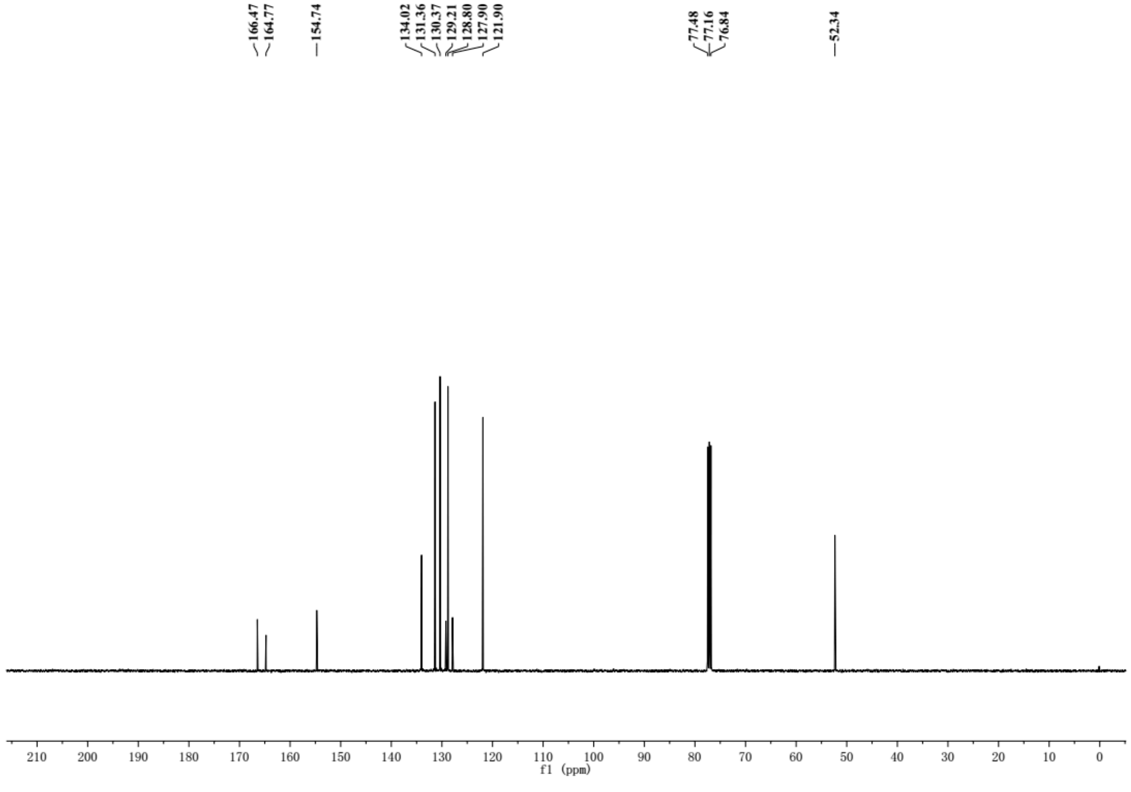

164.82
153.62
134.13
130.41
129.09
128.85
128.48
128.16
127.07
127.03
126.99
126.95
125.40
122.70
122.42
77.48
77.16
76.84
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CF3
O
O
1o
-62.17
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

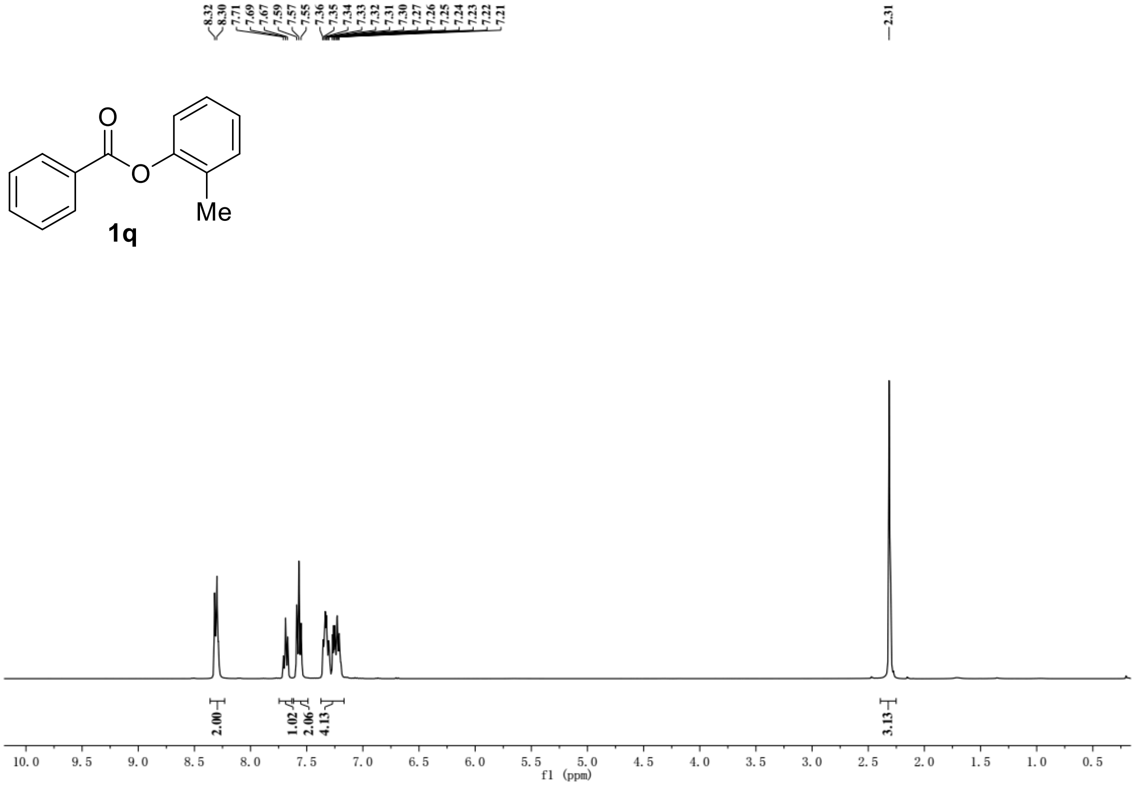


1p

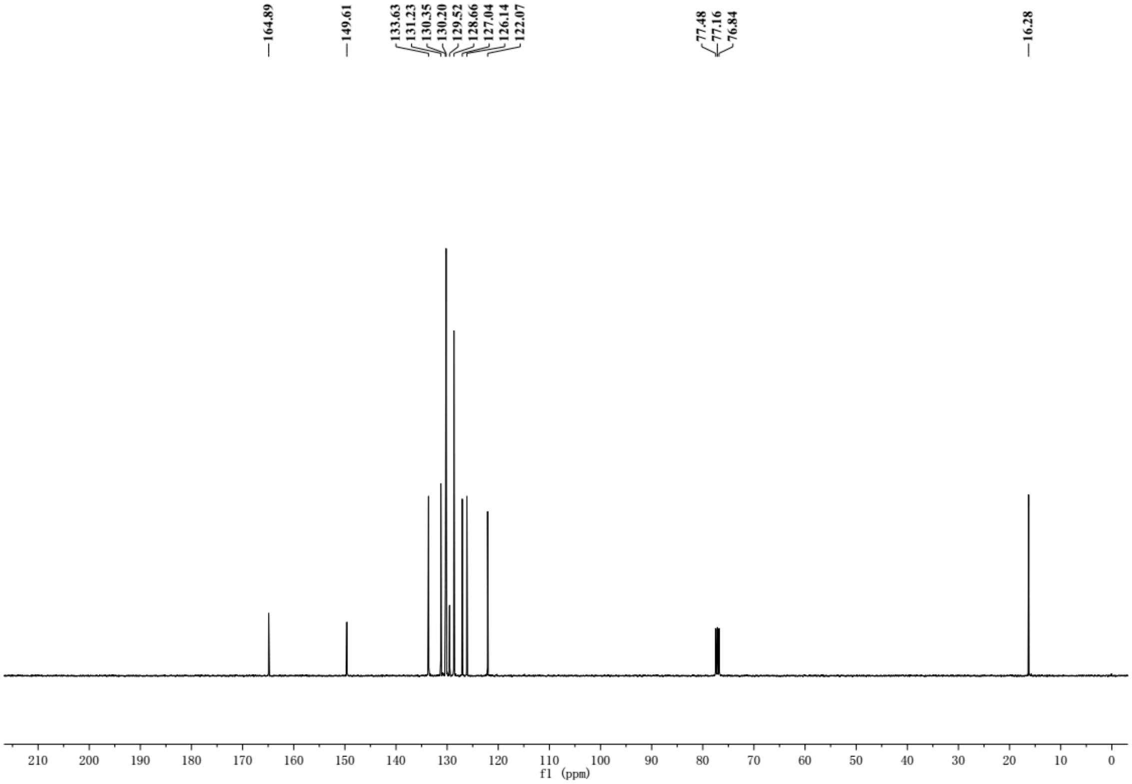
8.22
8.20
8.14
8.12
7.67
7.66
7.64
7.54
7.52
7.51
7.32
7.30
7.26
3.93
OMe
O
2.00
2.04
0.99
2.05
2.02
3.06
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

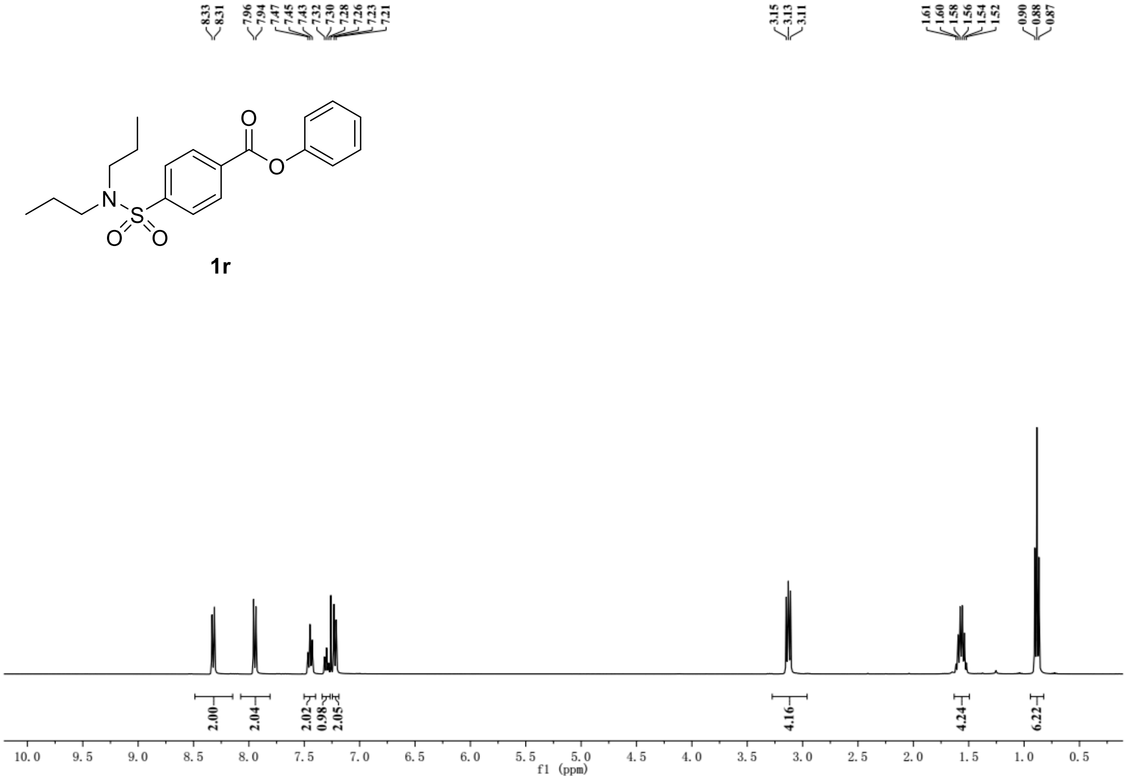


166.47
164.77
154.74
134.02
131.36
130.37
129.21
128.80
127.90
121.90
77.48
77.16
76.84
52.34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

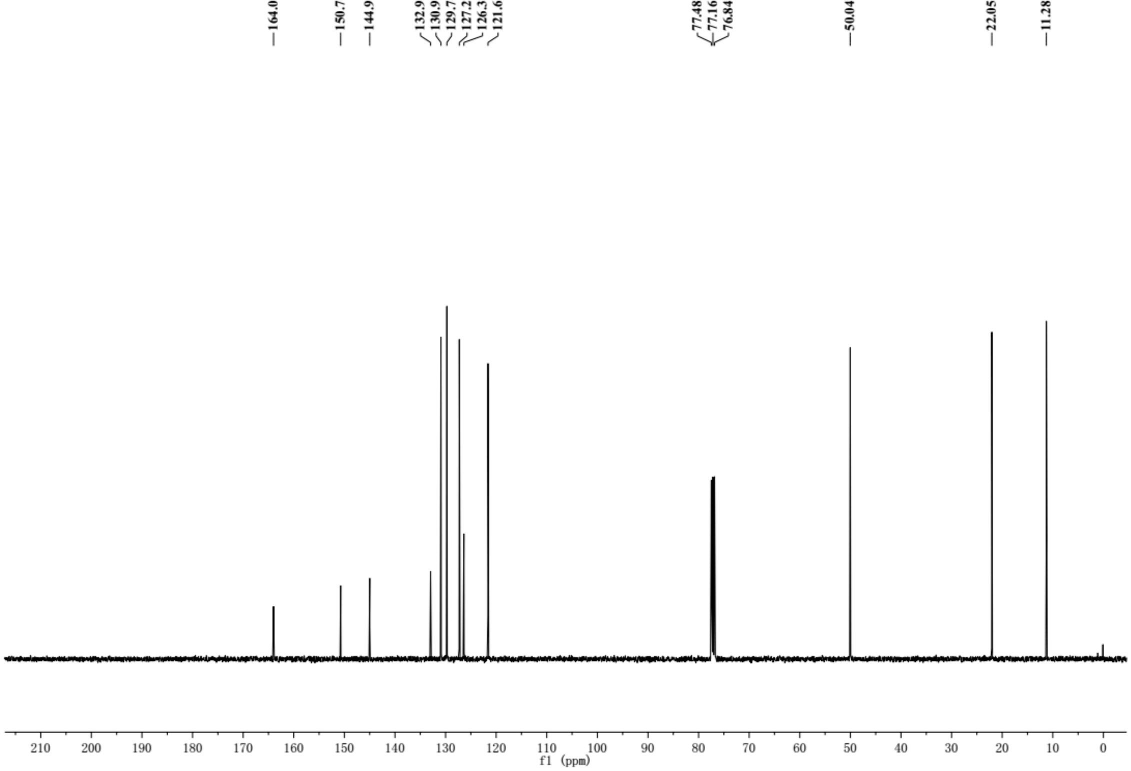

8.32
8.30
7.71
7.69
7.67
7.59
7.57
7.55
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.27
7.26
7.25
7.24
7.23
7.22
7.21
2.31
O
O
Me
2.00
1.02
2.06
4.13
3.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

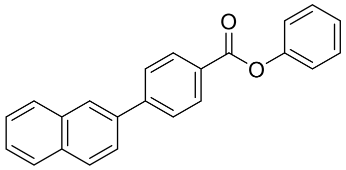
1q


164.89
149.61
133.63
131.23
130.35
130.20
129.52
128.66
127.04
126.14
122.07
77.48
77.16
76.84
16.28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

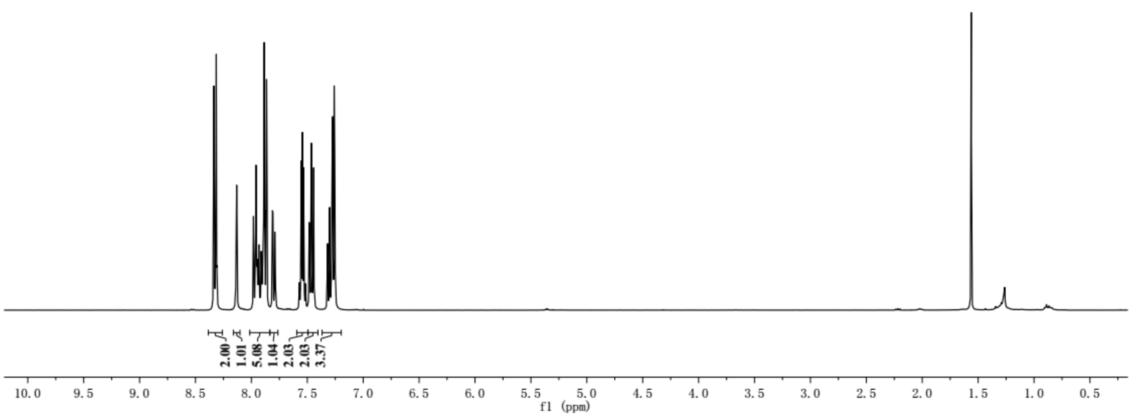

8.33
8.31
7.96
7.94
7.47
7.45
7.43
7.32
7.30
7.28
7.26
7.23
7.21
3.15
3.13
3.11
1.61
1.60
1.58
1.56
1.54
1.52
0.90
0.88
0.87
O
O
N
S
O
O
2.00
2.04
2.02
0.98
2.05
4.16
4.24
6.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

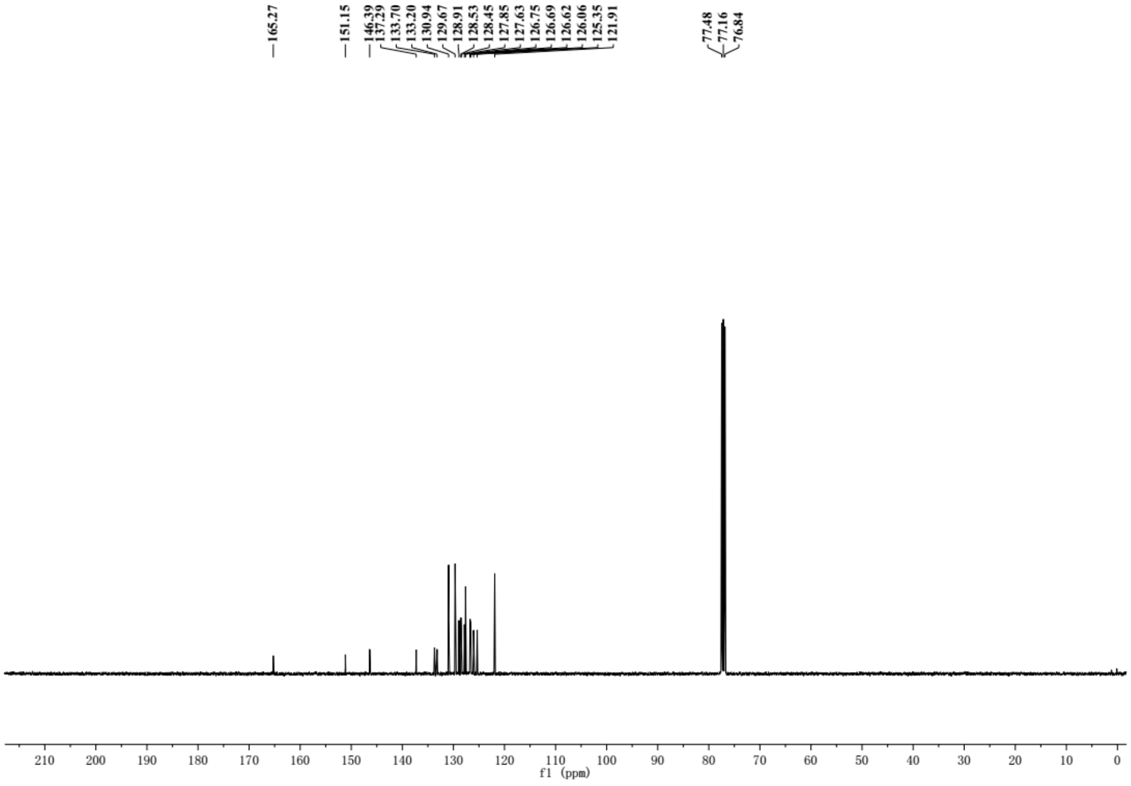
1r

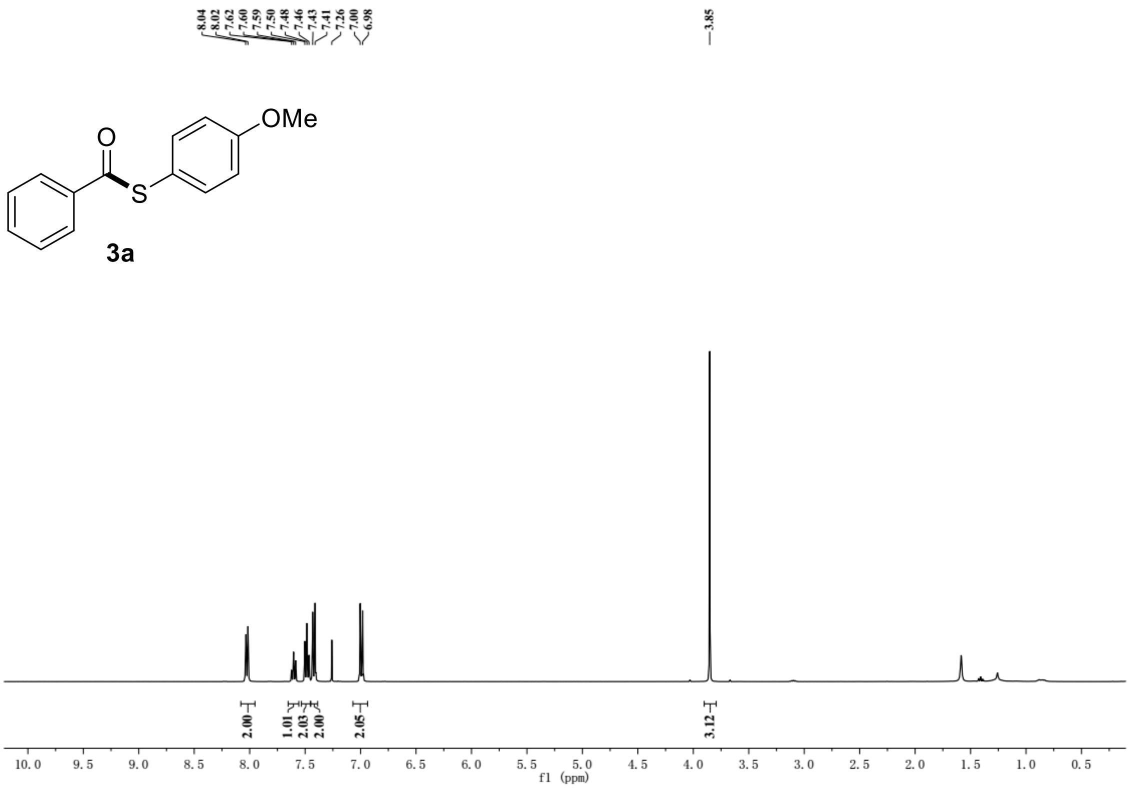

164.00
150.74
144.99
132.96
130.91
129.74
127.28
126.37
121.61
77.48
77.16
76.84
50.04
22.05
11.28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

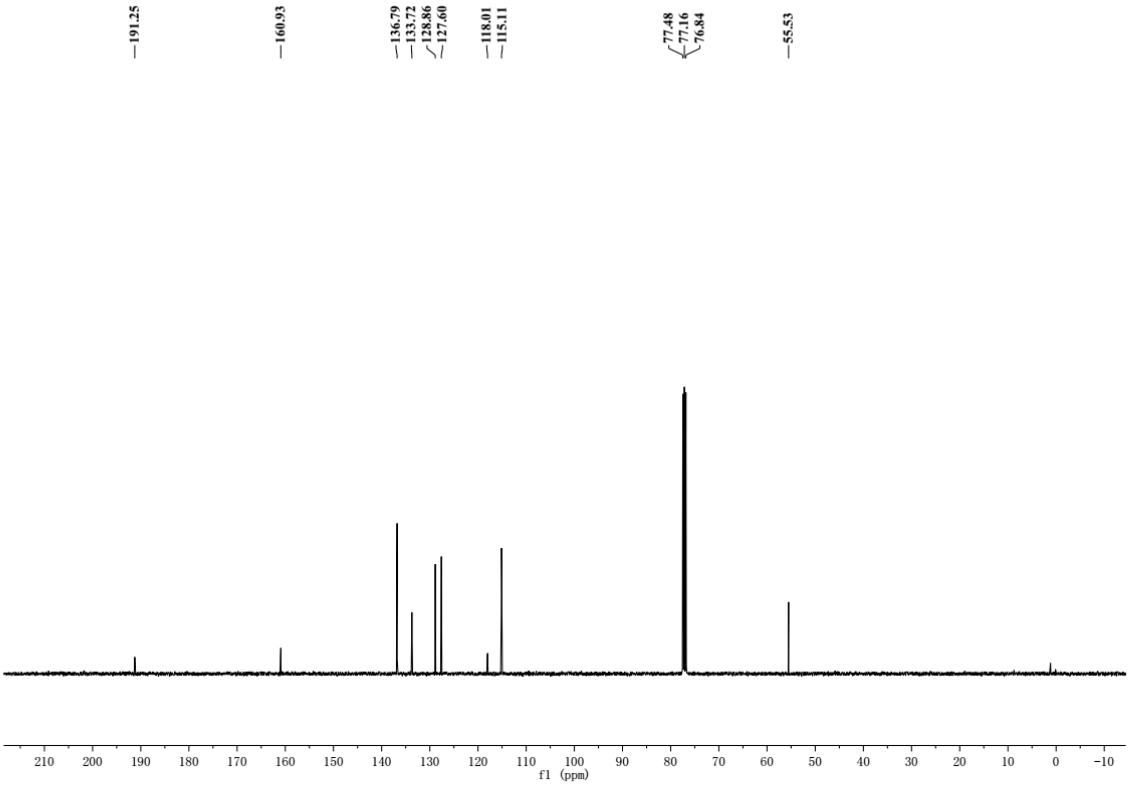


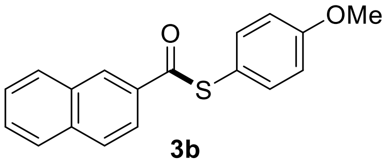
1s


8.34
8.31
8.13
7.98
7.96
7.95
7.94
7.93
7.91
7.90
7.89
7.88
7.87
7.86
7.81
7.81
7.79
7.79
7.57
7.56
7.55
7.54
7.53
7.52
7.48
7.47
7.46
7.45
7.44
7.32
7.30
7.28
7.27
7.26
7.25
2.00
1.01
5.08
1.04
2.03
2.03
3.37
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
f1 (ppm)

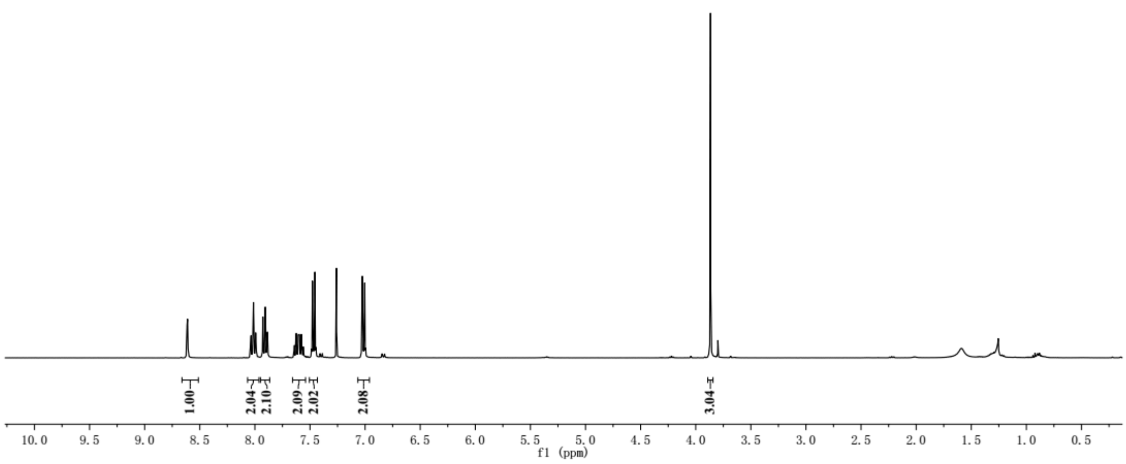

165.27
151.15
146.39
137.29
133.70
133.20
130.94
129.67
128.91
128.53
128.45
127.85
127.63
126.75
126.69
126.62
126.06
125.35
121.91
77.48
77.16
76.84
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

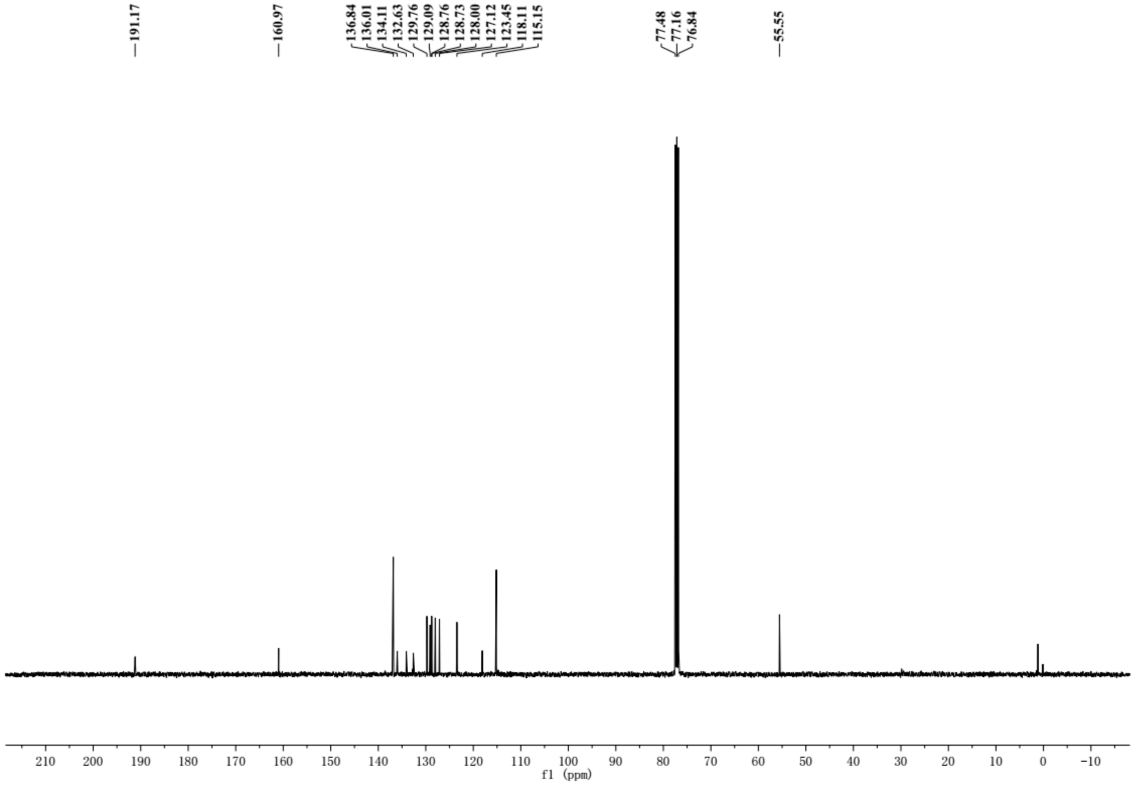

8.04
8.02
7.62
7.60
7.59
7.50
7.48
7.46
7.43
7.41
7.26
7.00
6.98
3.85
OMe
O
S
3a
2.00
1.01
2.03
2.00
2.05
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

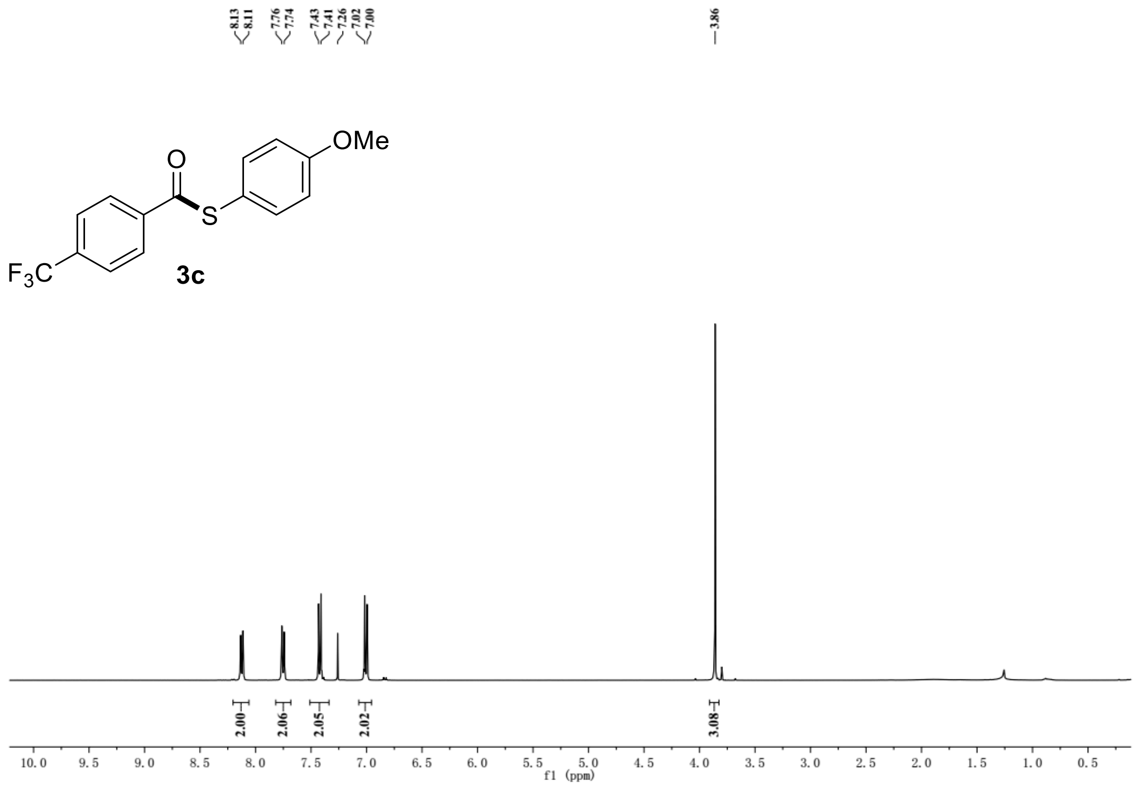

191.25
160.93
136.79
133.72
128.86
127.60
118.01
115.11
77.48
77.16
76.84
55.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


O
S
OMe

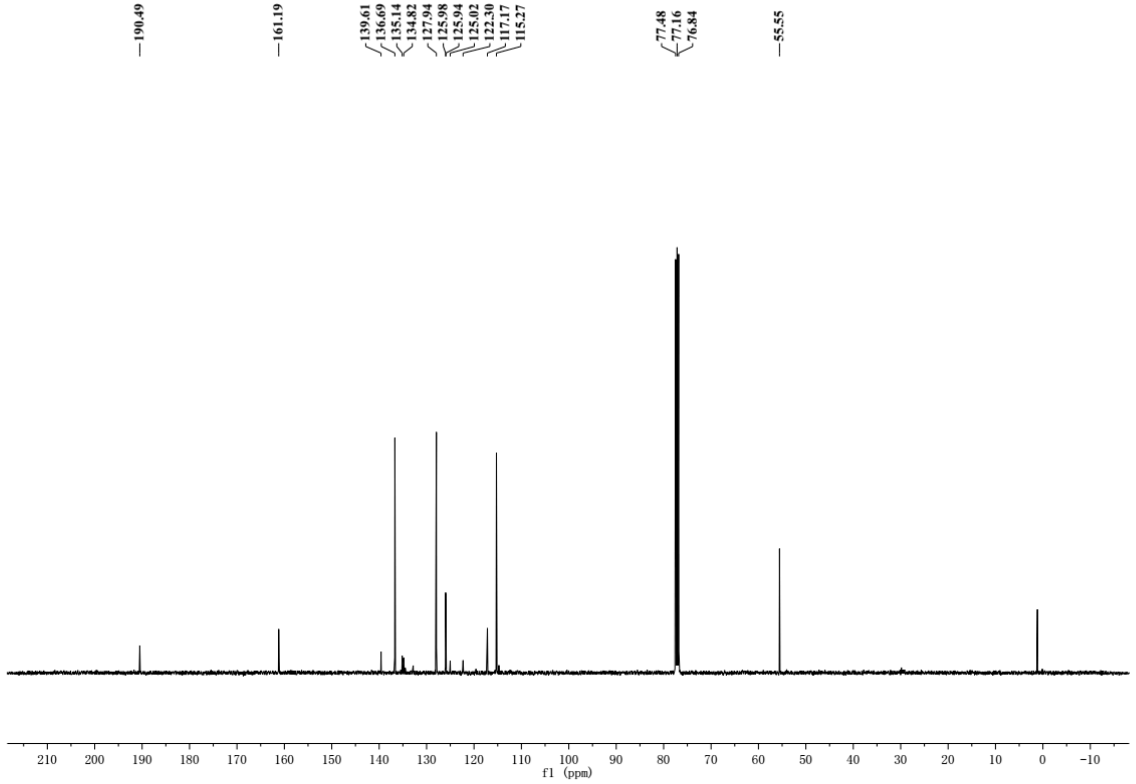
3b

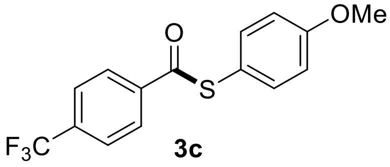

8.61
8.03
8.01
7.99
7.93
7.91
7.89
7.64
7.63
7.62
7.61
7.60
7.59
7.58
7.56
7.48
7.46
7.26
7.03
7.00
3.87
1.00
2.04
2.10
2.09
2.02
2.08
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


191.17
160.97
136.84
136.01
134.11
132.63
129.76
129.09
128.76
128.73
128.00
127.12
123.45
118.11
115.15
77.48
77.16
76.84
55.55
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)

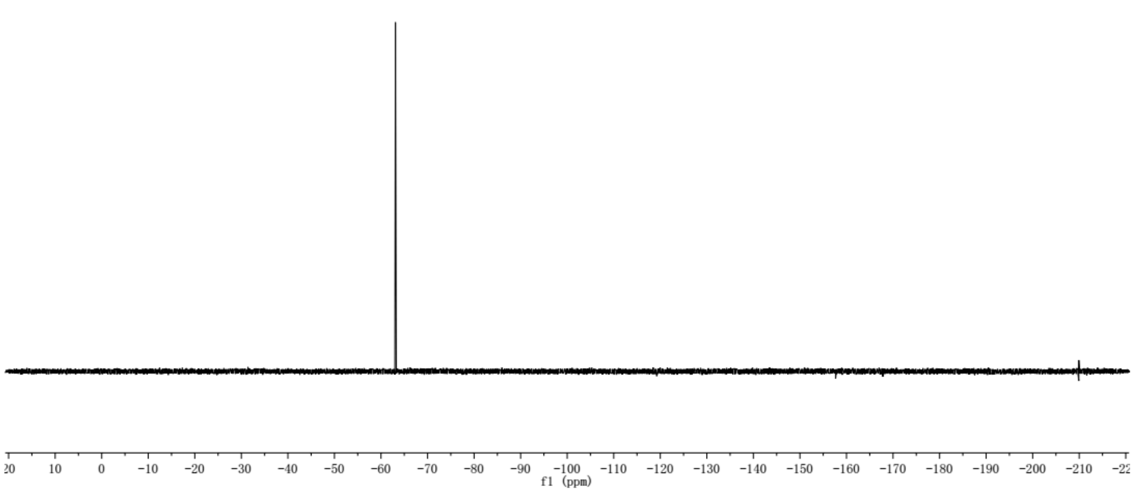

8.13
8.11
7.76
7.74
7.43
7.41
7.26
7.02
7.00
3.86
O
S
OMe
F_3C
2.00
2.06
2.05
2.02
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

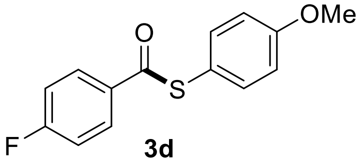
3c


190.49
161.19
139.61
136.69
135.14
134.82
127.94
125.98
125.94
125.02
122.30
117.17
115.27
77.48
77.16
76.84
55.55
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)

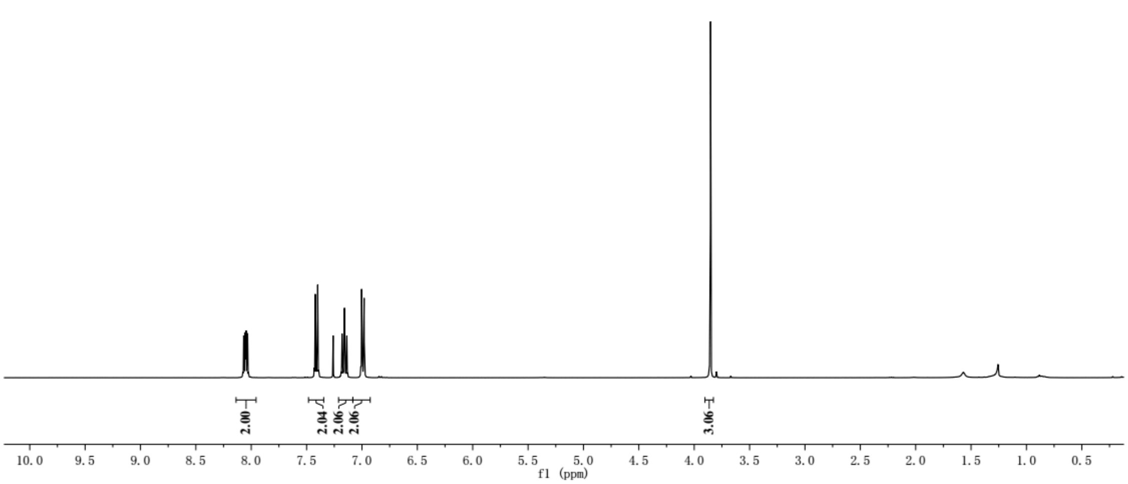

O
S
OMe
F_3C

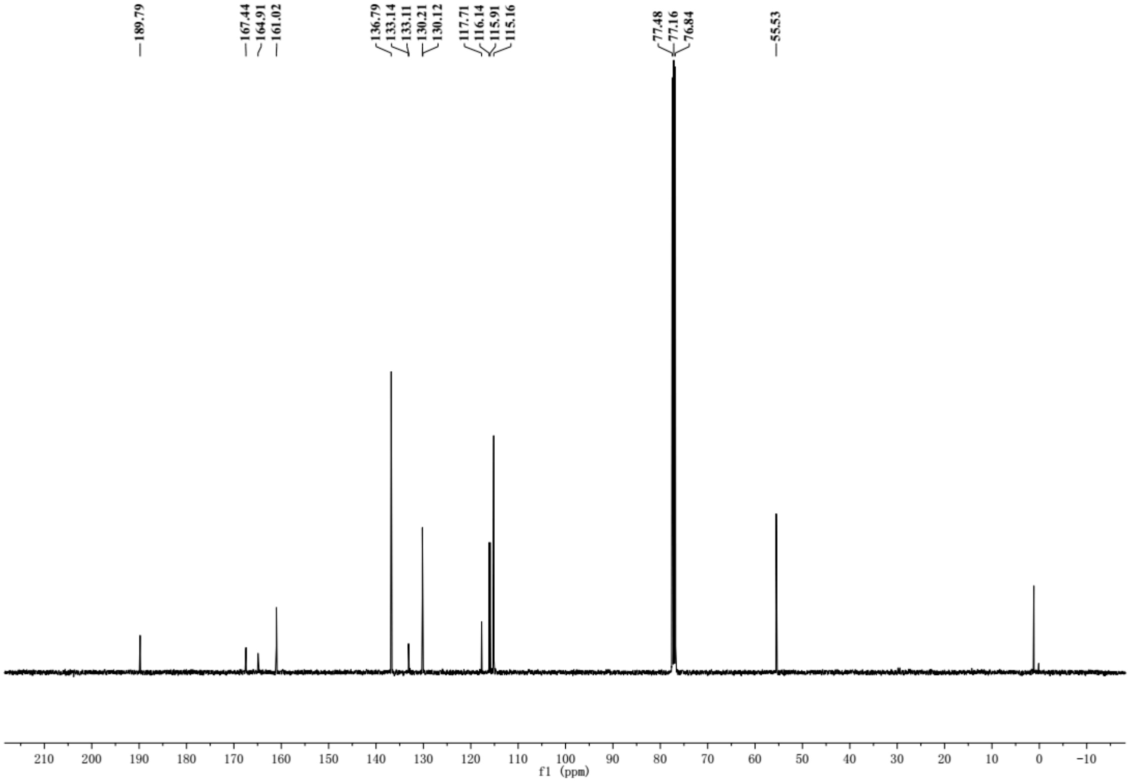
3c


—63.11
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−22
f1 (ppm)


O
S
OMe
F

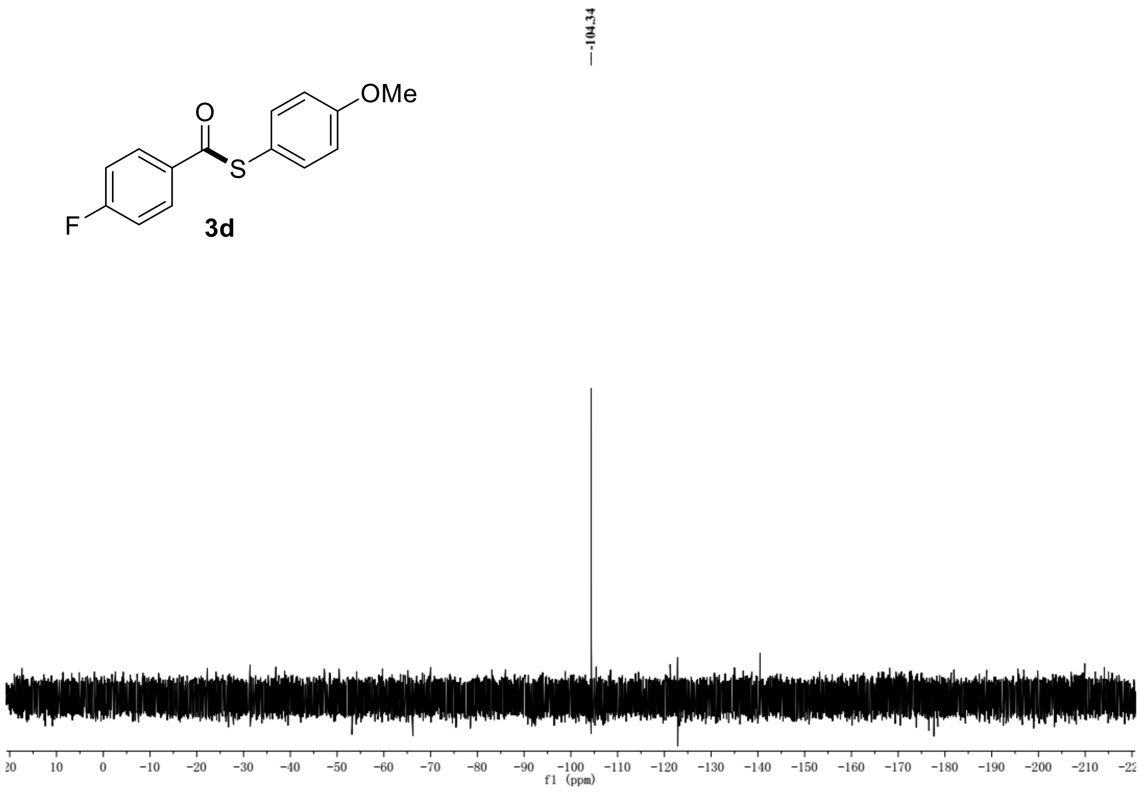
3d

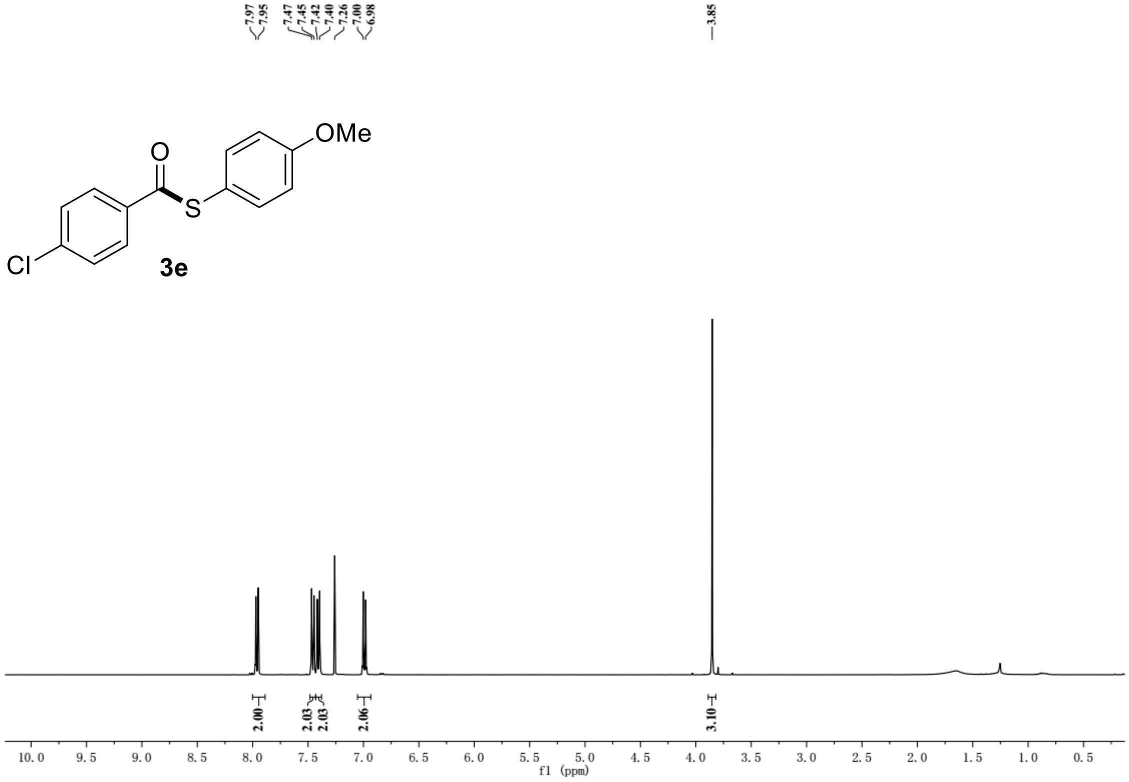

8.07
8.05
8.05
8.03
7.42
7.40
7.26
7.18
7.16
7.14
7.00
6.98
3.85
2.00
2.04
2.06
2.06
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

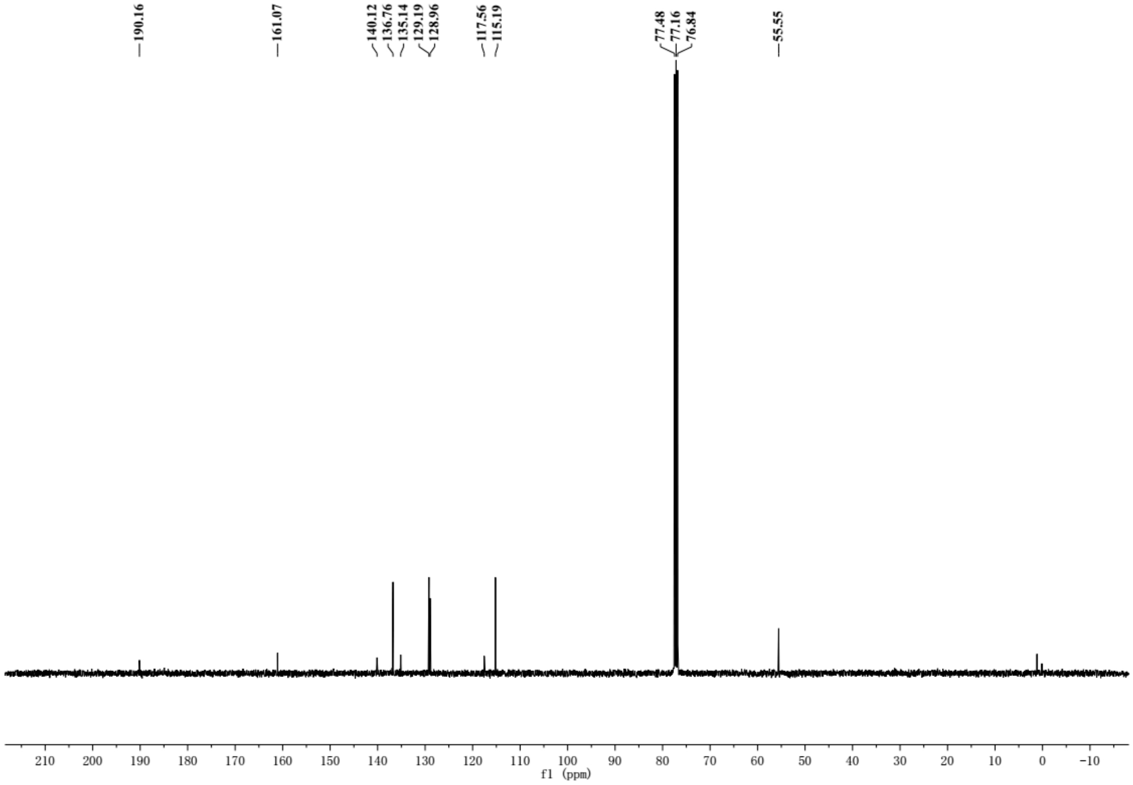

189.79
167.44
164.91
161.02
136.79
133.14
133.11
130.21
130.12
117.71
116.14
115.91
115.16
77.48
77.16
76.84
55.53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

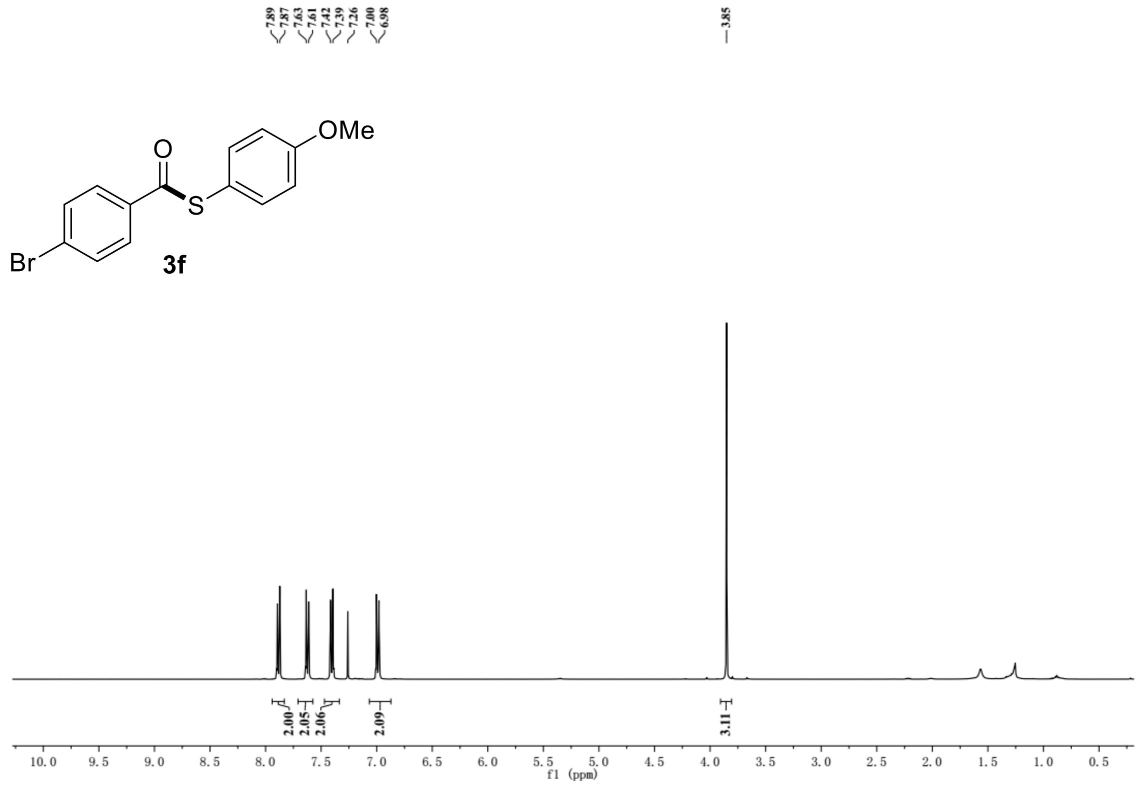
O
S
OMe
F

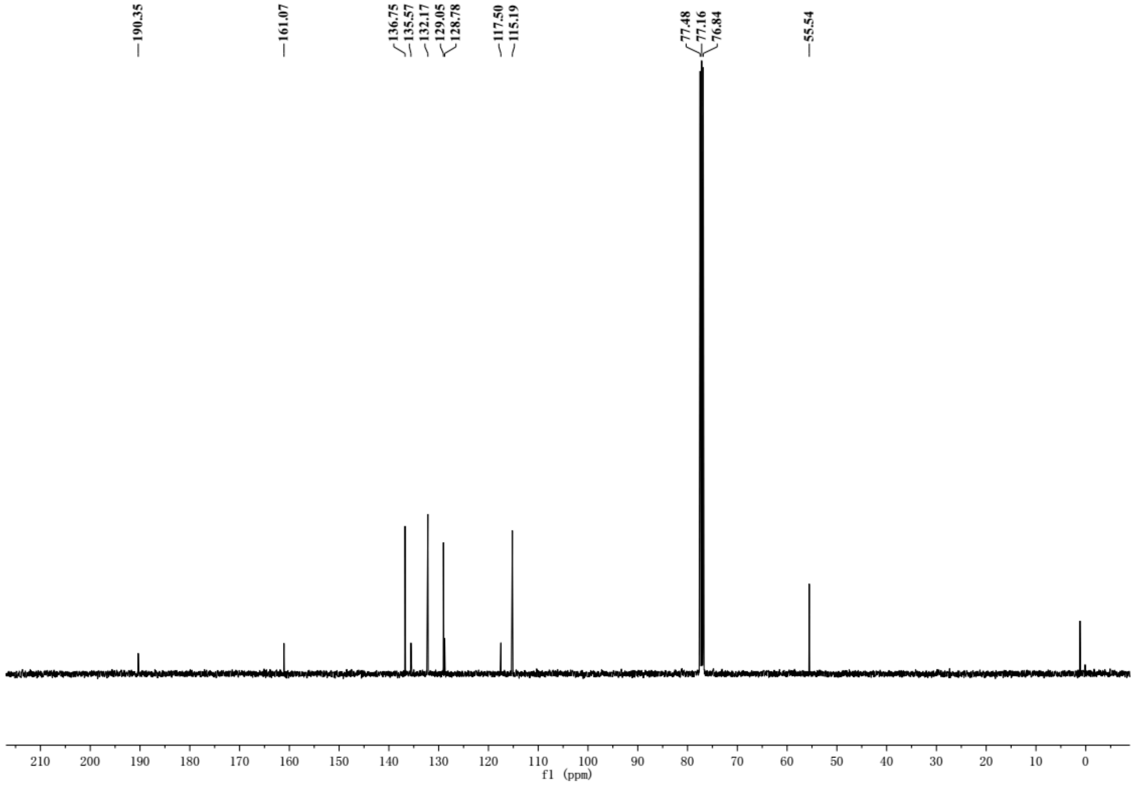
3d

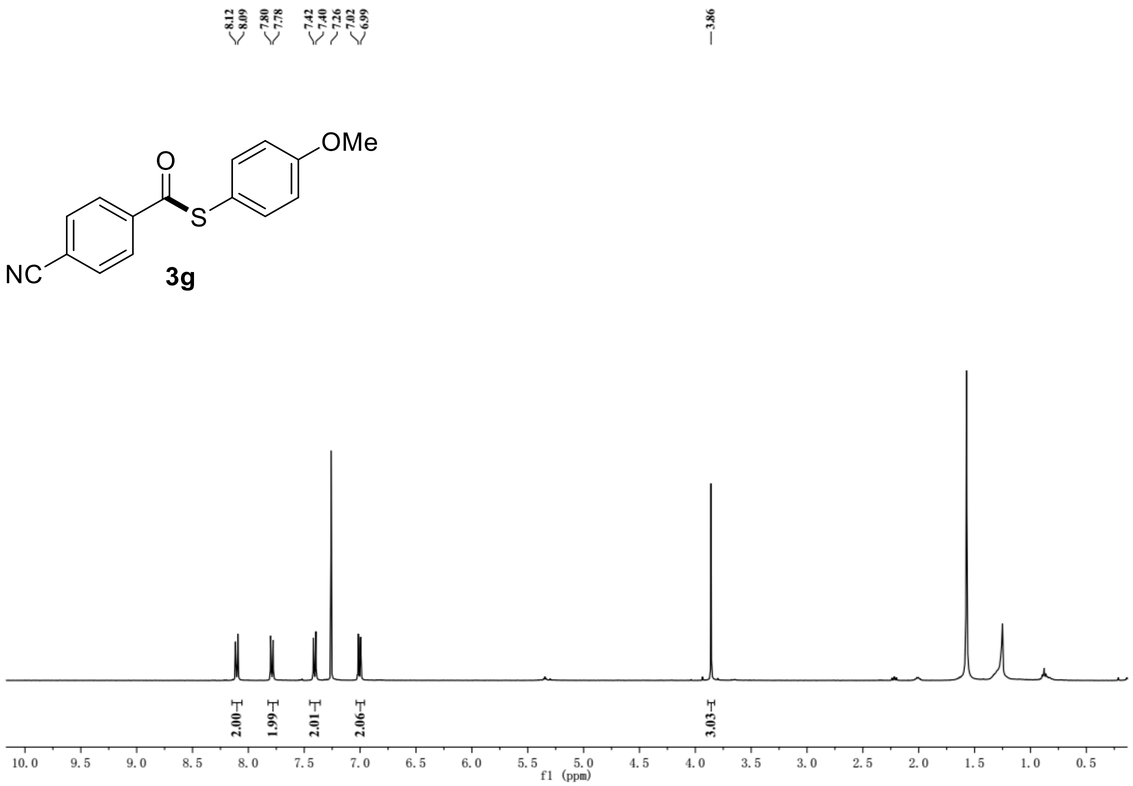

-104.34
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)


3e
7.97
7.95
7.47
7.45
7.42
7.40
7.26
7.00
6.98
3.85
OMe
O
S
Cl
2.00
2.03
2.03
2.06
3.10
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
f1 (ppm)


190.16
161.07
140.12
136.76
135.14
129.19
128.96
117.56
115.19
77.48
77.16
76.84
55.55
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)


7.89
7.87
7.63
7.61
7.42
7.39
7.26
7.00
6.98
3.85
OMe
O
S
Br
3f
2.00
2.05
2.06
2.09
3.11
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
f1 (ppm)


190.35
161.07
136.75
135.57
132.17
129.05
128.78
117.50
115.19
77.48
77.16
76.84
55.54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.78
7.42
7.40
7.26
7.02
6.99
3.86
OMe
O
S
NC
3g
2.00
1.99
2.01
2.06
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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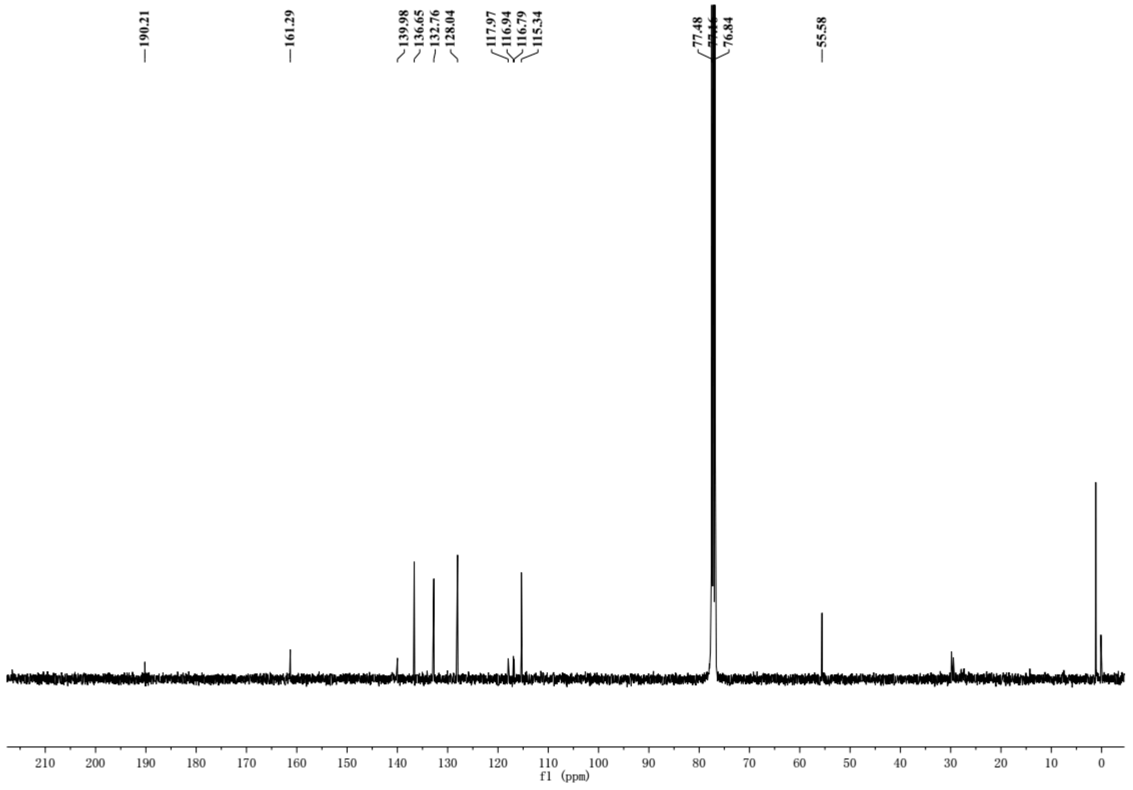
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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136.65
132.76
128.04
117.97
116.94
116.79
115.34
77.48
76.84
55.58
210
200
190
180
170
160
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140
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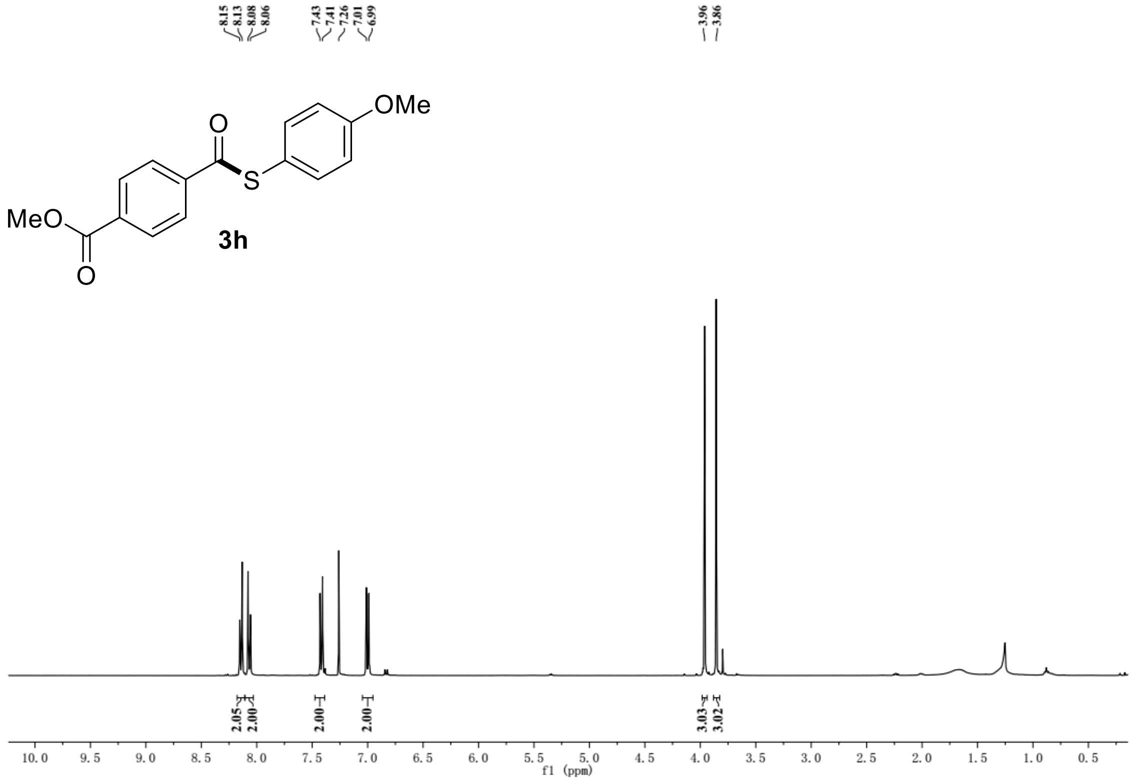
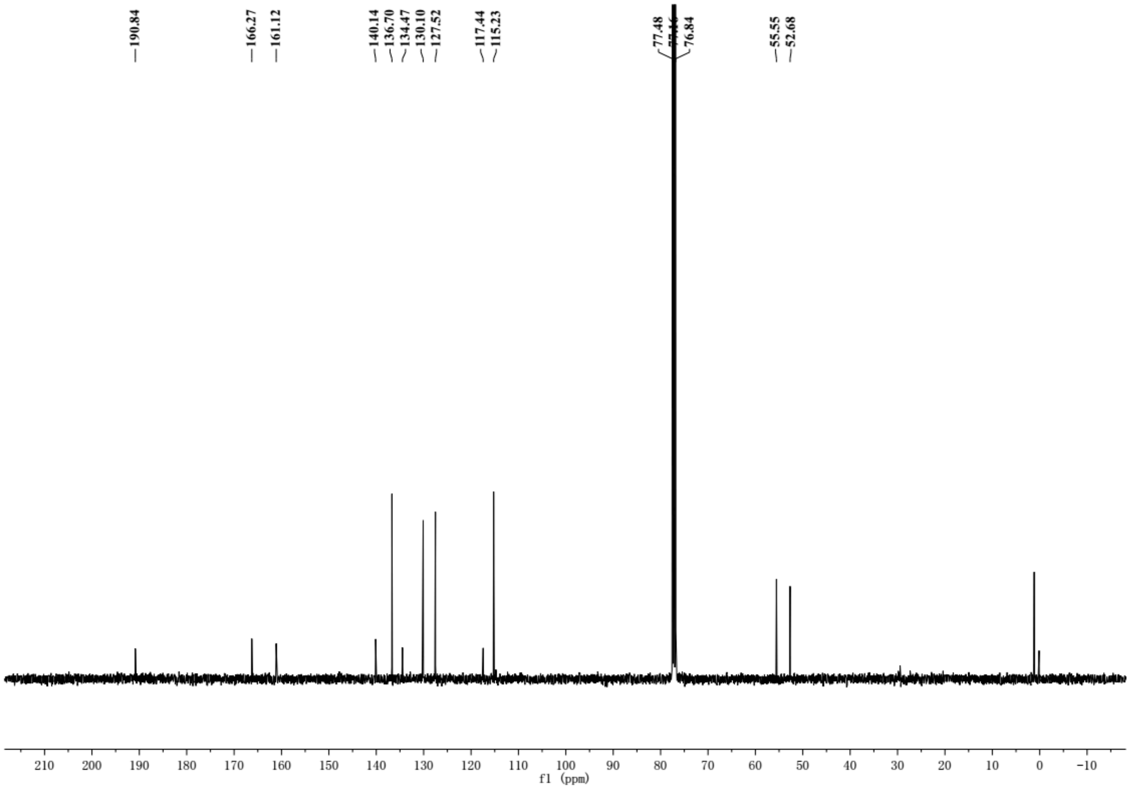
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.15
8.13
8.08
8.06
7.43
7.41
7.26
7.01
6.99
3.96
3.86
OMe
O
S
MeO
O
3h
2.05
2.00
2.00
2.00
3.03
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
f1 (ppm)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134.47
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127.52
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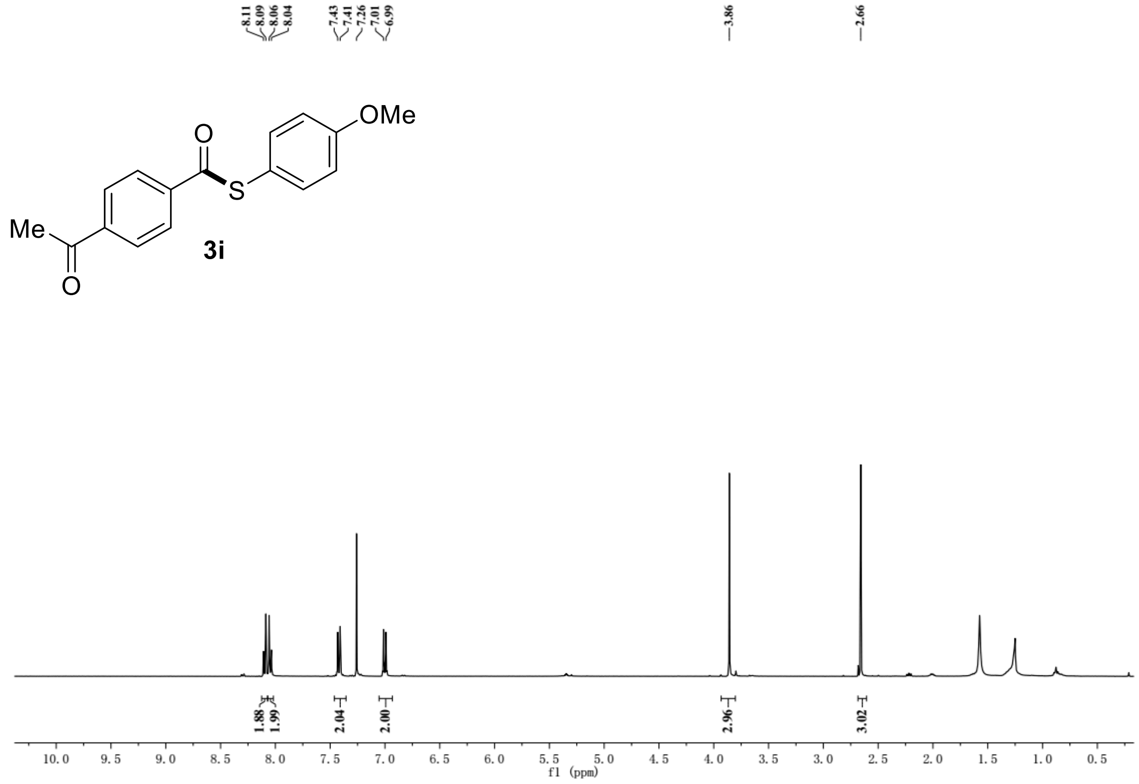
115.23
77.48
77.16
76.84
55.55
52.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.06
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7.26
7.01
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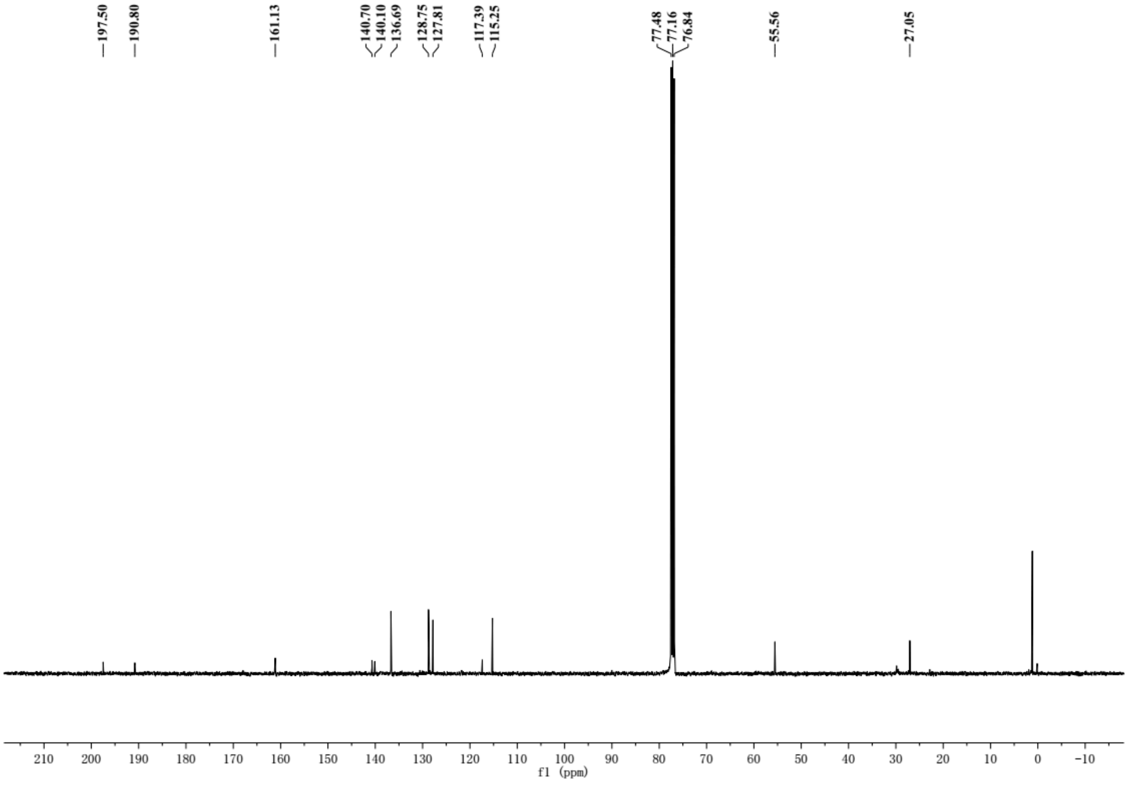
3.86
2.66
OMe
O
S
Me
O
3i
1.88
1.99
2.04
2.00
2.96
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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127.81
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77.48
77.16
76.84
55.56
27.05
210
200
190
180
170
160
150
140
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120
110
100
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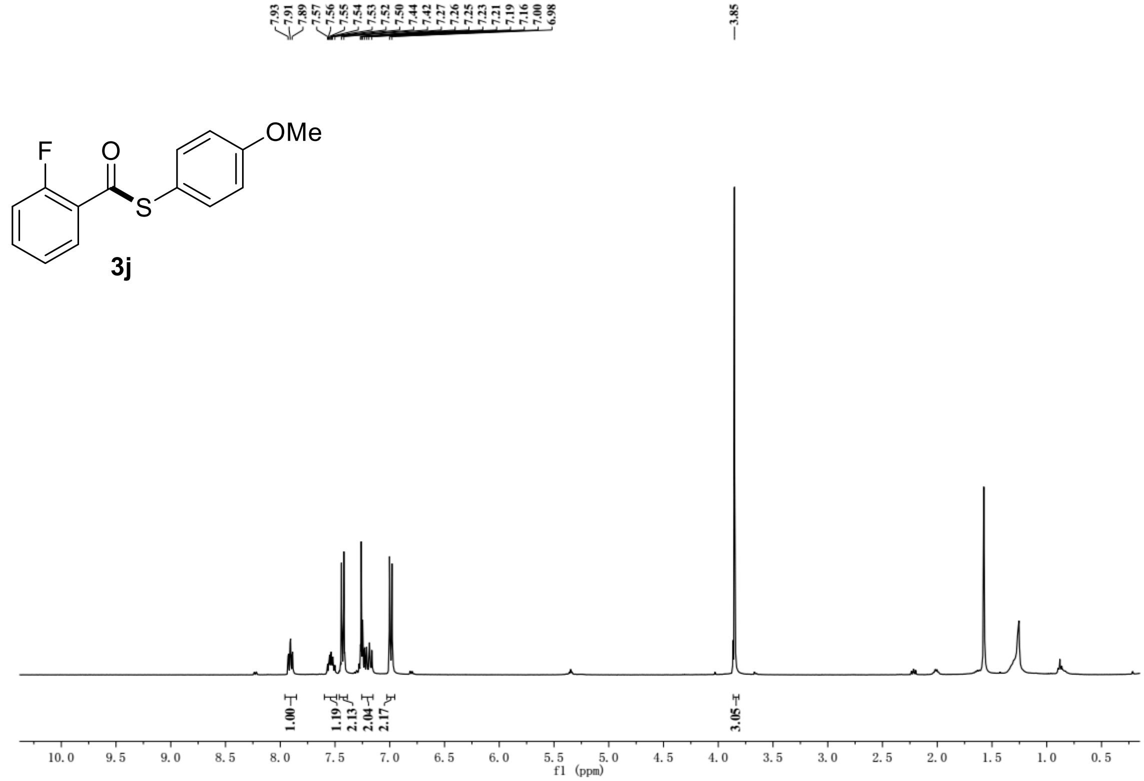
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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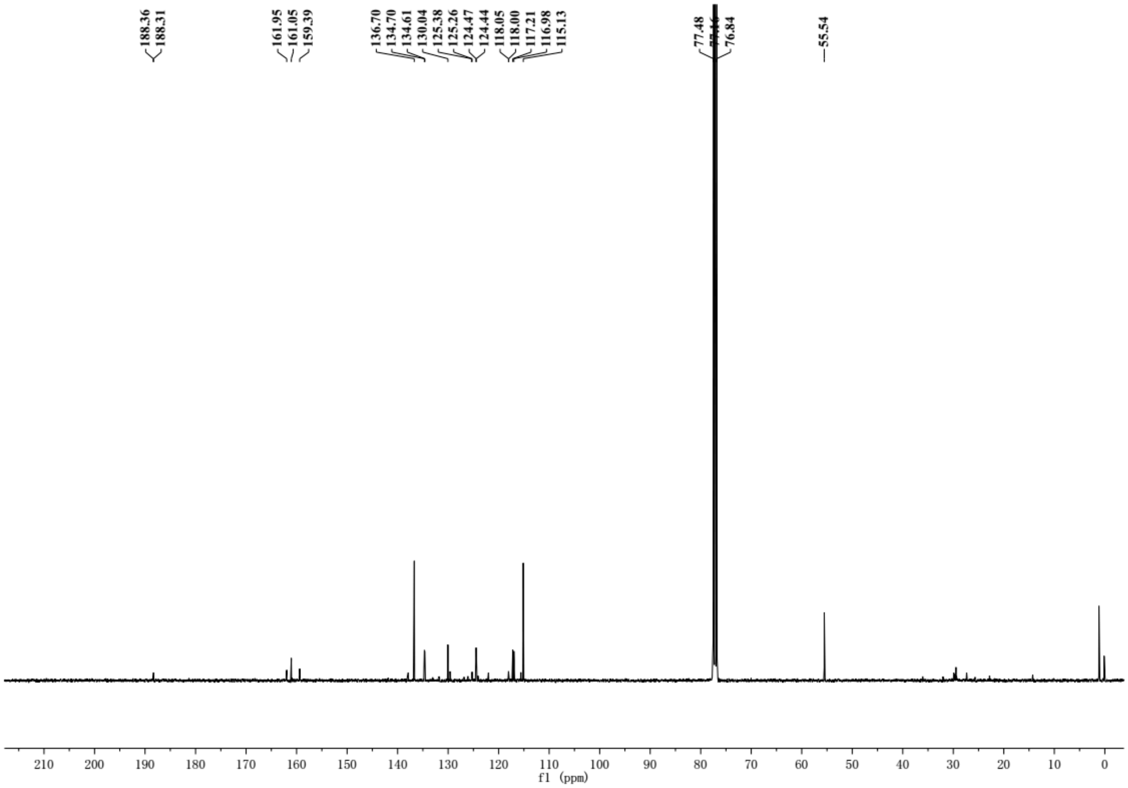
7.54
7.53
7.52
7.50
7.44
7.42
7.27
7.26
7.25
7.23
7.21
7.19
7.16
7.00
6.98
3.85
F
O
S
OMe
3j
1.00
1.19
2.13
2.04
2.17
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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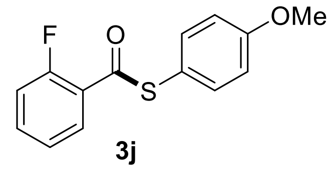
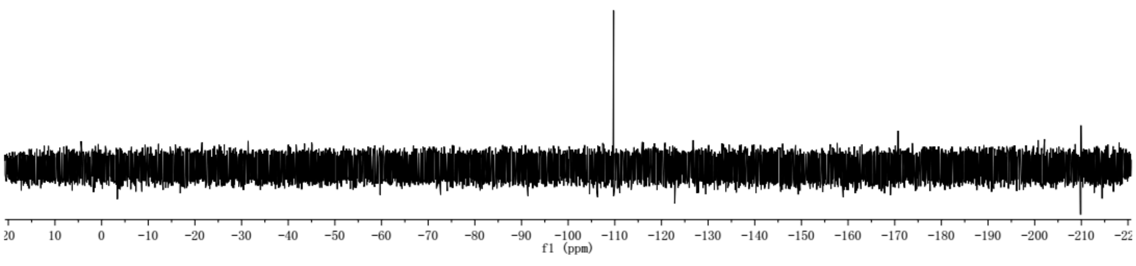
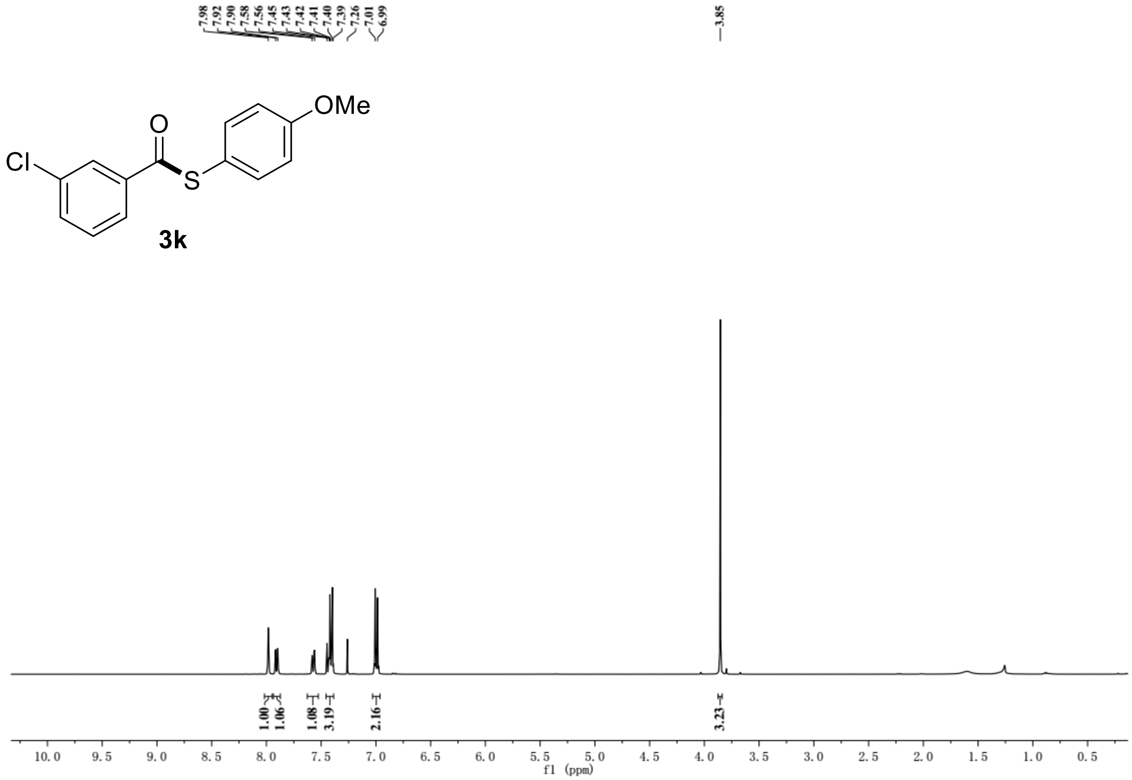
188.31
161.95
161.05
159.39
136.70
134.70
134.61
130.04
125.38
125.26
124.47
124.44
118.05
118.00
117.21
116.98
115.13
77.48
76.84
55.54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
O
S
OMe

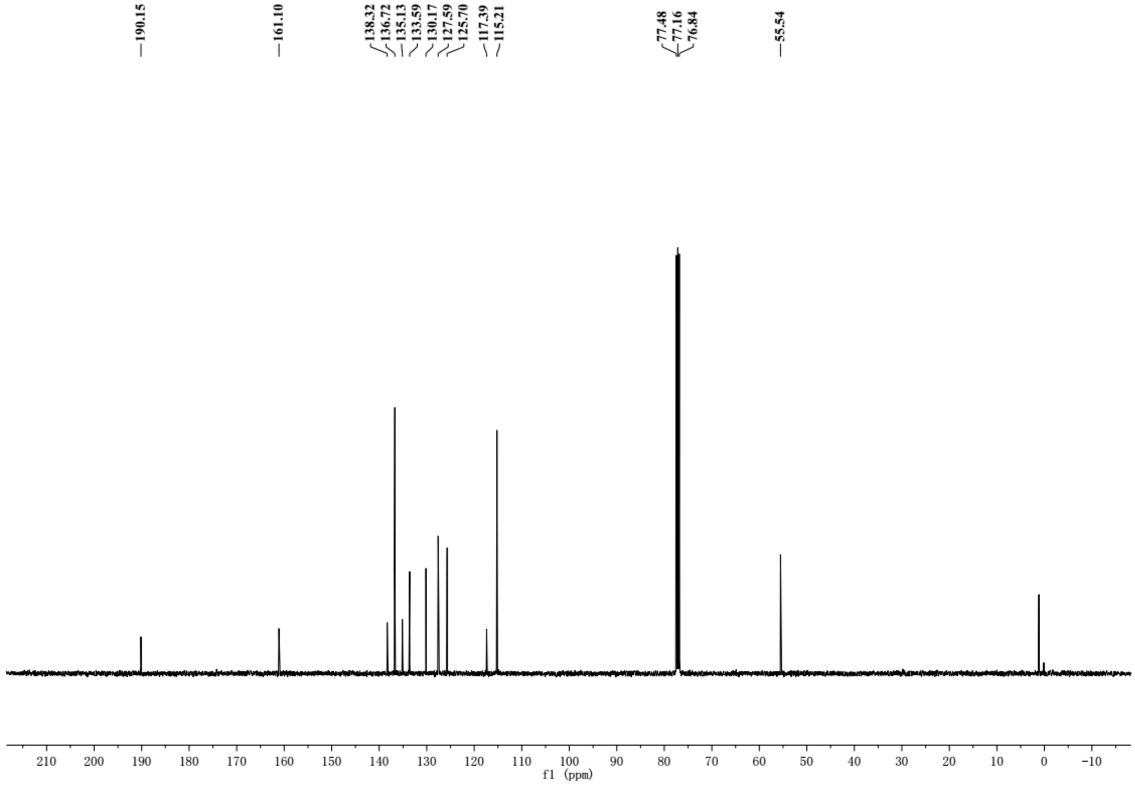
3j


-109.74
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−22
f1 (ppm)

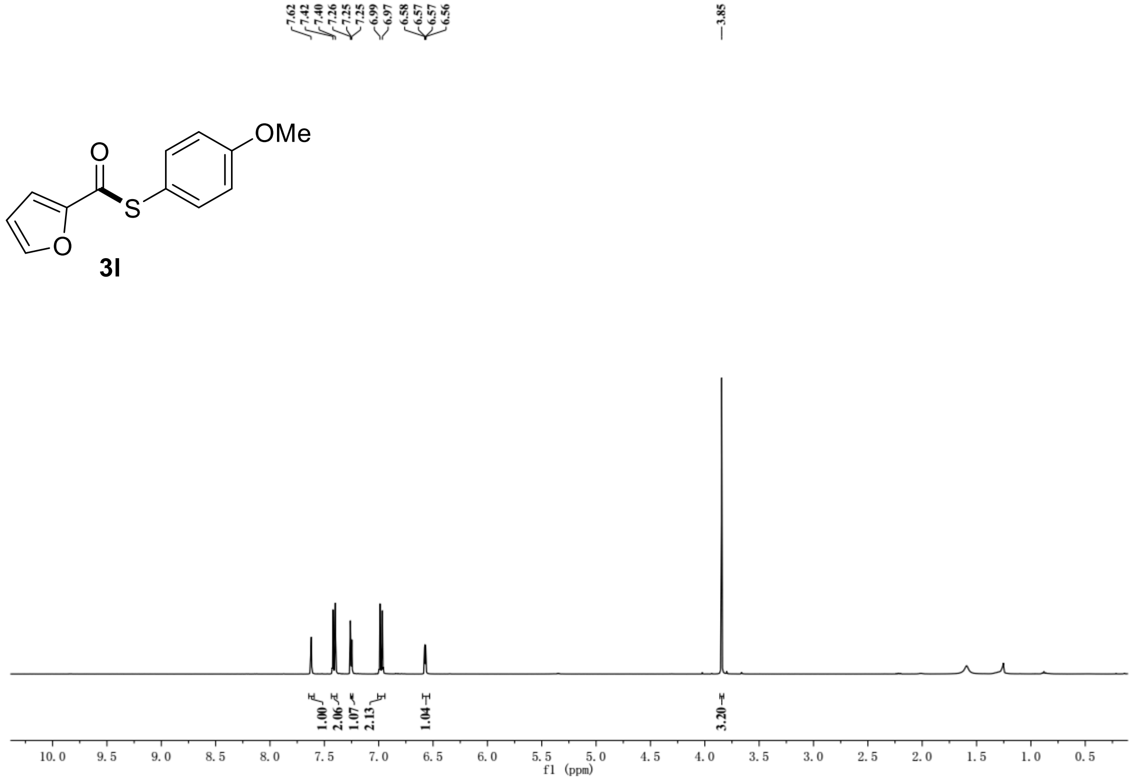


3k

OMe
O
Cl
S
7.98
7.92
7.90
7.58
7.56
7.45
7.43
7.42
7.41
7.40
7.39
7.26
7.01
6.99
3.85
1.00
1.06
1.08
3.19
2.16
3.23
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
f1 (ppm)



190.15
161.10
138.32
136.72
135.13
133.59
130.17
127.59
125.70
117.39
115.21
77.48
77.16
76.84
55.54
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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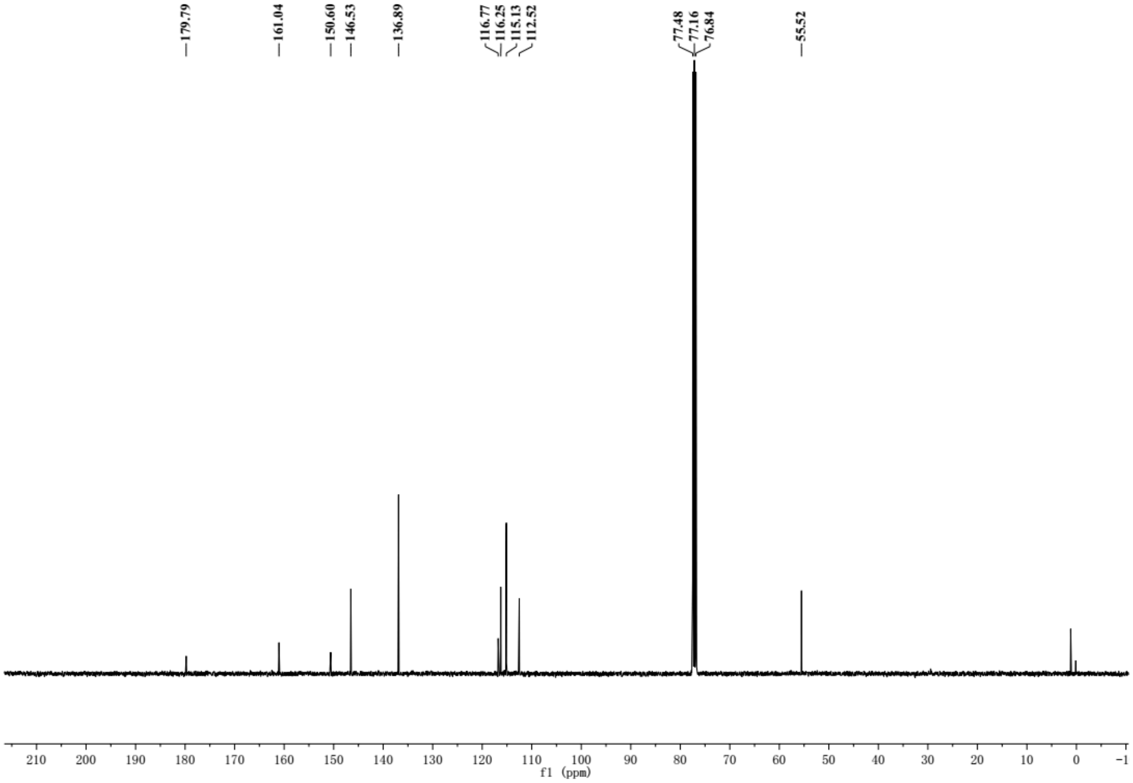
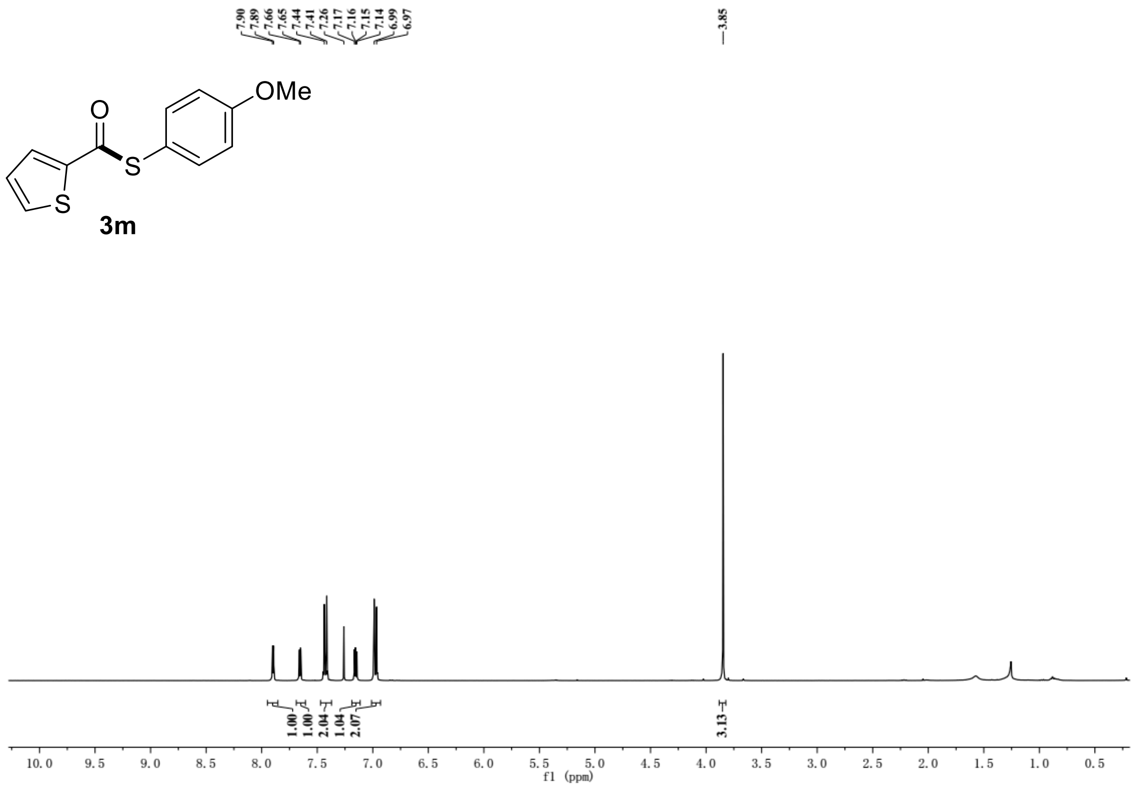
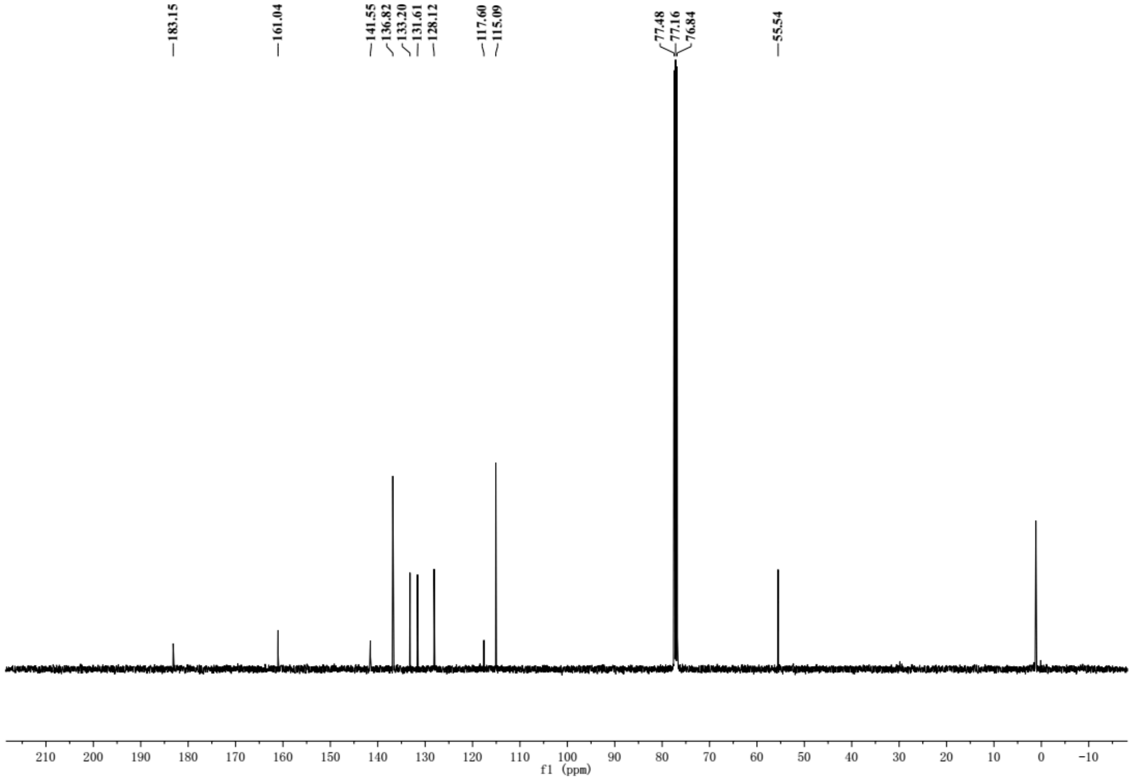
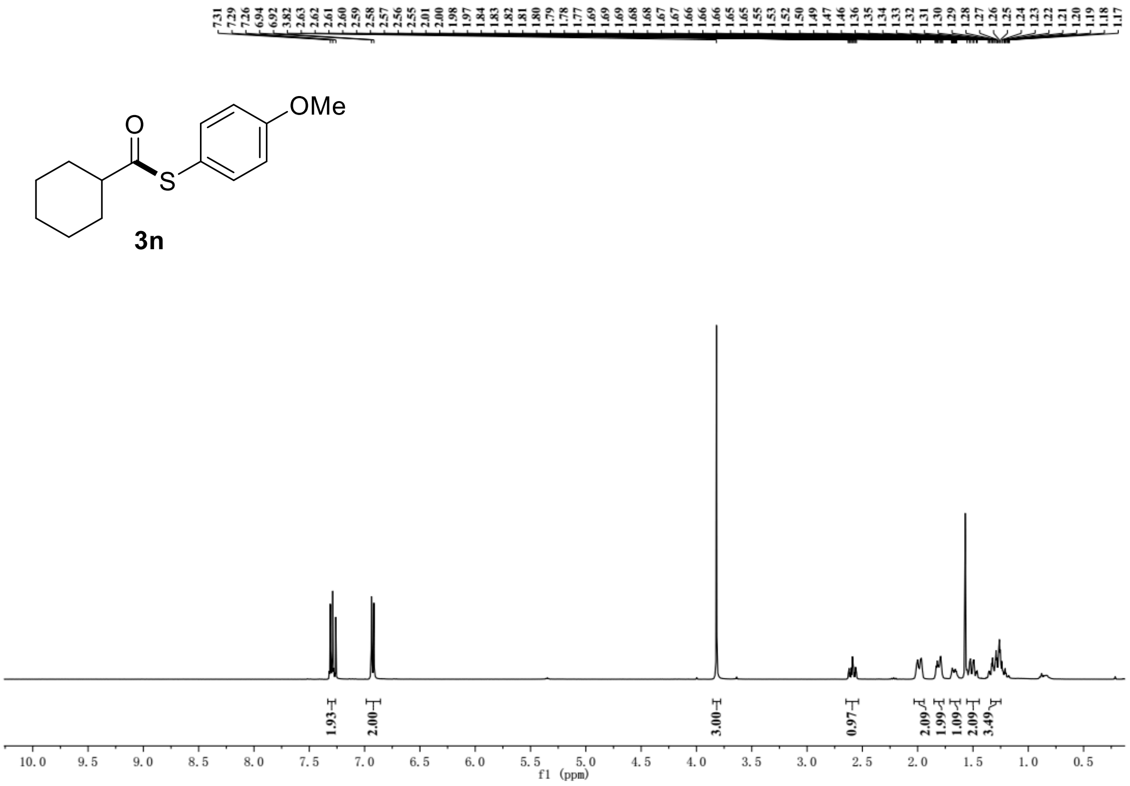
7.42
7.40
7.26
7.25
7.25
6.99
6.97
6.58
6.57
6.57
6.56
3.85
OMe
O
S
O
3l
1.00
2.06
1.07
2.13
1.04
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


179.79
161.04
150.60
146.53
136.89
116.77
116.25
115.13
112.52
77.48
77.16
76.84
55.52
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7.90
7.89
7.66
7.65
7.44
7.41
7.26
7.17
7.16
7.15
7.14
6.99
6.97
3.85
OMe
O
S
S
1.00
1.00
2.04
1.04
2.07
3.13
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
f1 (ppm)

3m


183.15
161.04
141.55
136.82
133.20
131.61
128.12
117.60
115.09
77.48
77.16
76.84
55.54
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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7.29
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3.82
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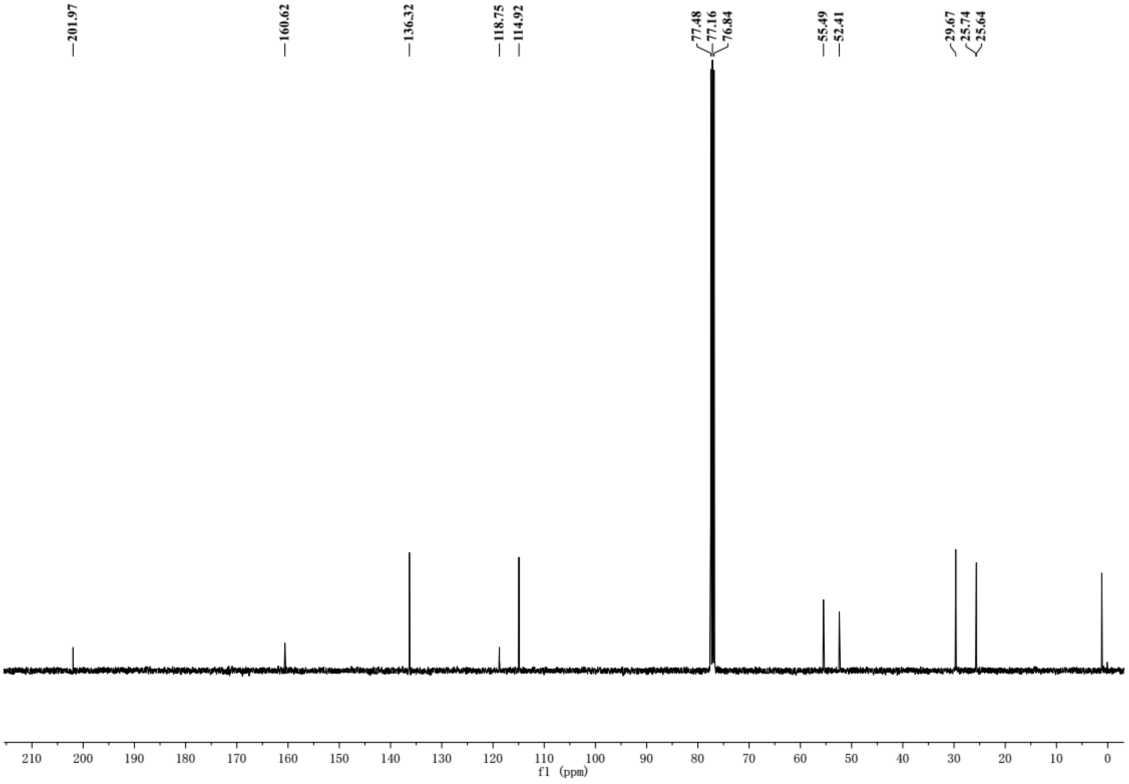
2.62
2.61
2.60
2.59
2.58
2.57
2.56
2.55
2.01
2.00
1.98
1.97
1.84
1.83
1.82
1.81
1.80
1.79
1.78
1.77
1.69
1.69
1.69
1.68
1.68
1.67
1.67
1.66
1.66
1.66
1.65
1.65
1.55
1.53
1.52
1.50
1.49
1.47
1.46
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.29
1.28
1.27
1.26
1.25
1.24
1.23
1.22
1.21
1.20
1.19
1.18
1.17
OMe
O
S
3n
1.93
2.00
3.00
0.97
2.09
1.99
1.09
2.09
3.49
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
f1 (ppm)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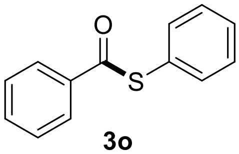
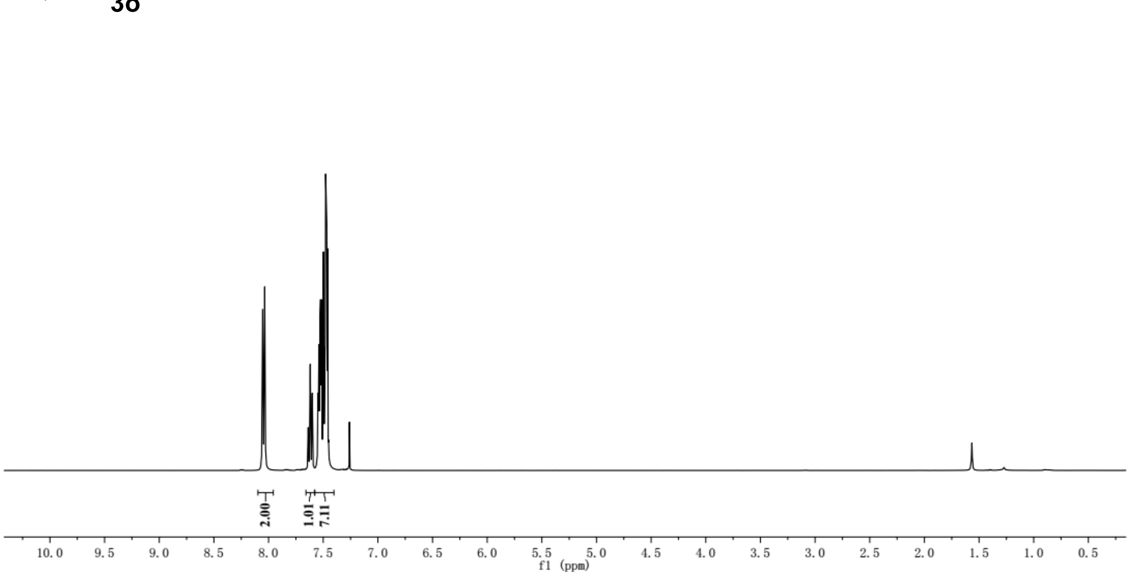
160.62
136.32
118.75
114.92
77.48
77.16
76.84
55.49
52.41
29.67
25.74
25.64
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
S

3o


8.06
8.05
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8.03
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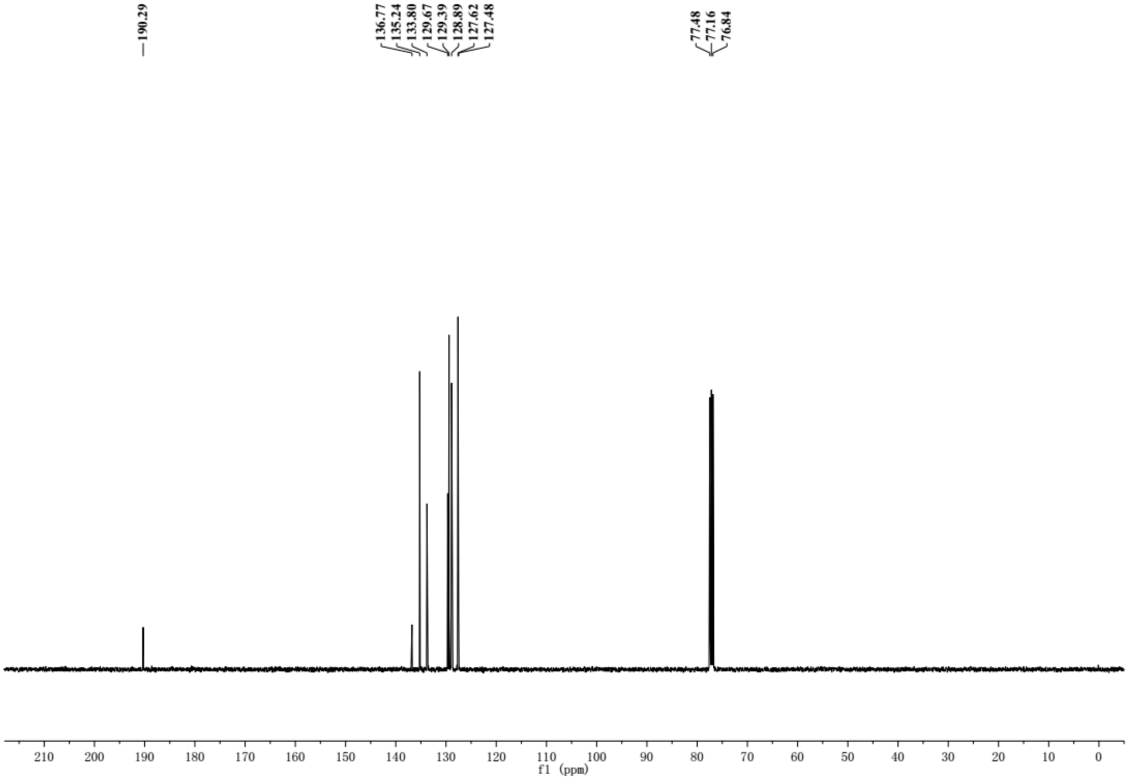
7.62
7.60
7.55
7.54
7.53
7.52
7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.26
2.00
1.01
7.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190.29
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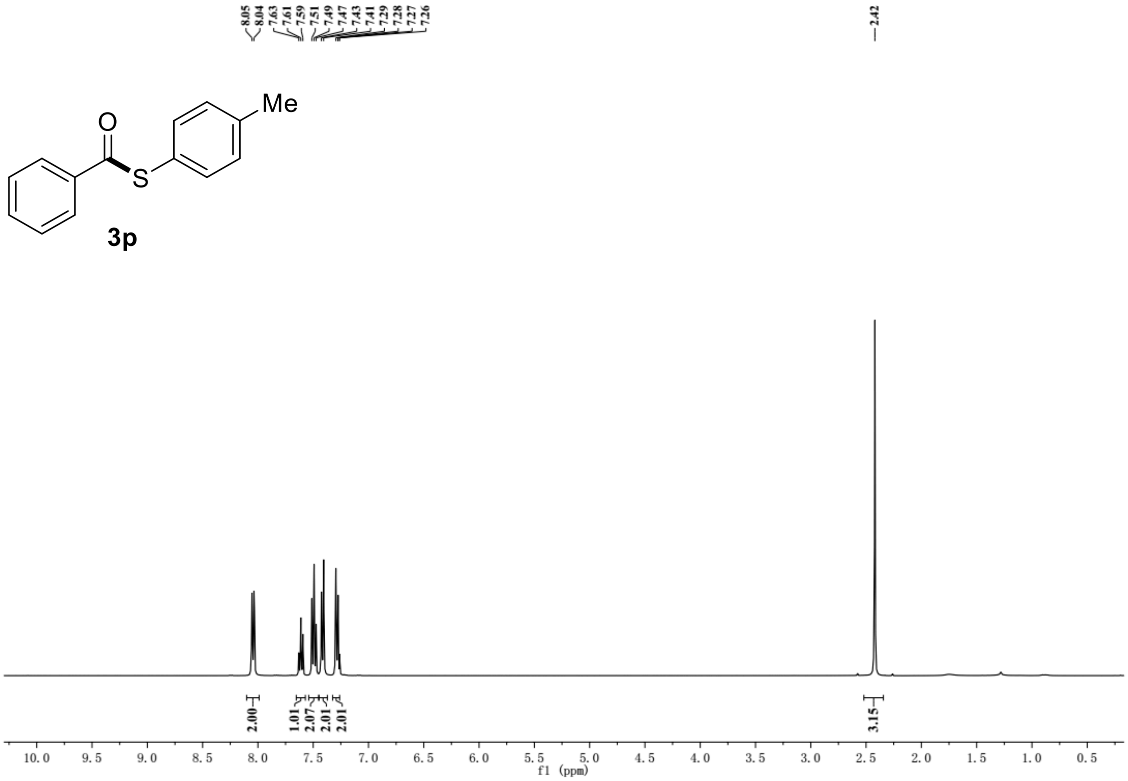
129.67
129.39
128.89
127.62
127.48
77.48
77.16
76.84
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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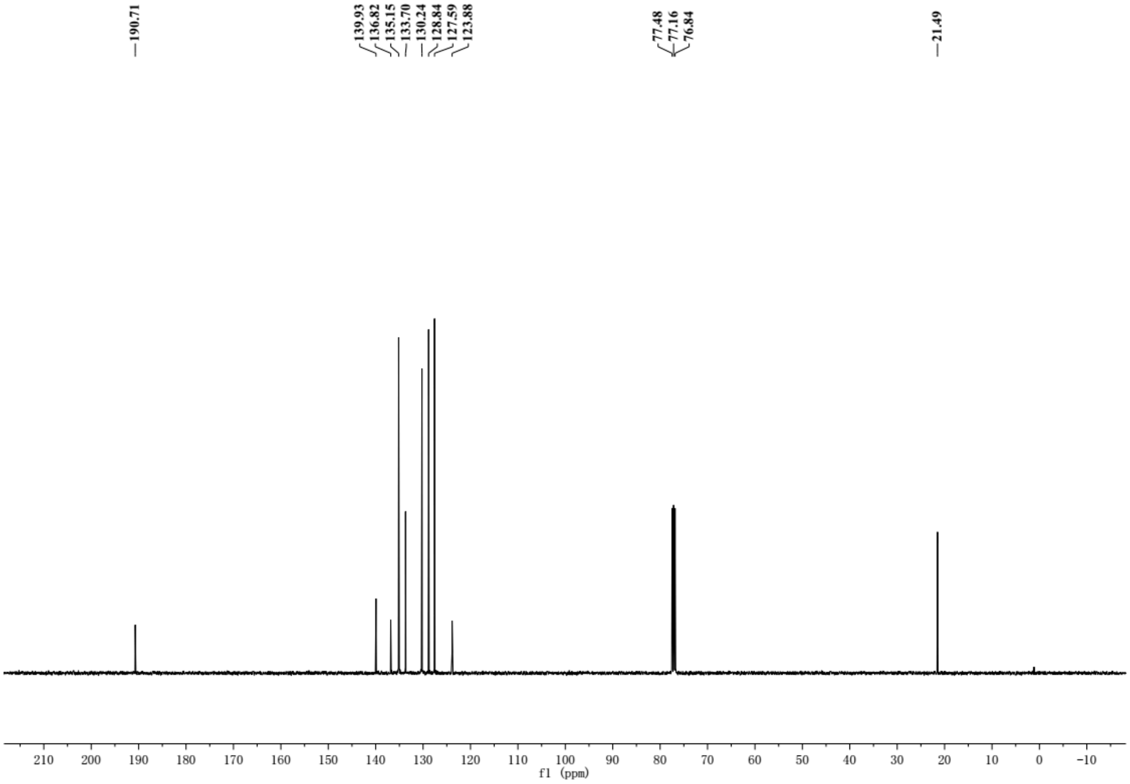
7.51
7.49
7.47
7.43
7.41
7.29
7.28
7.27
7.26
2.42
O
S
Me
3p
2.00
1.01
2.07
2.01
2.01
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


190.71
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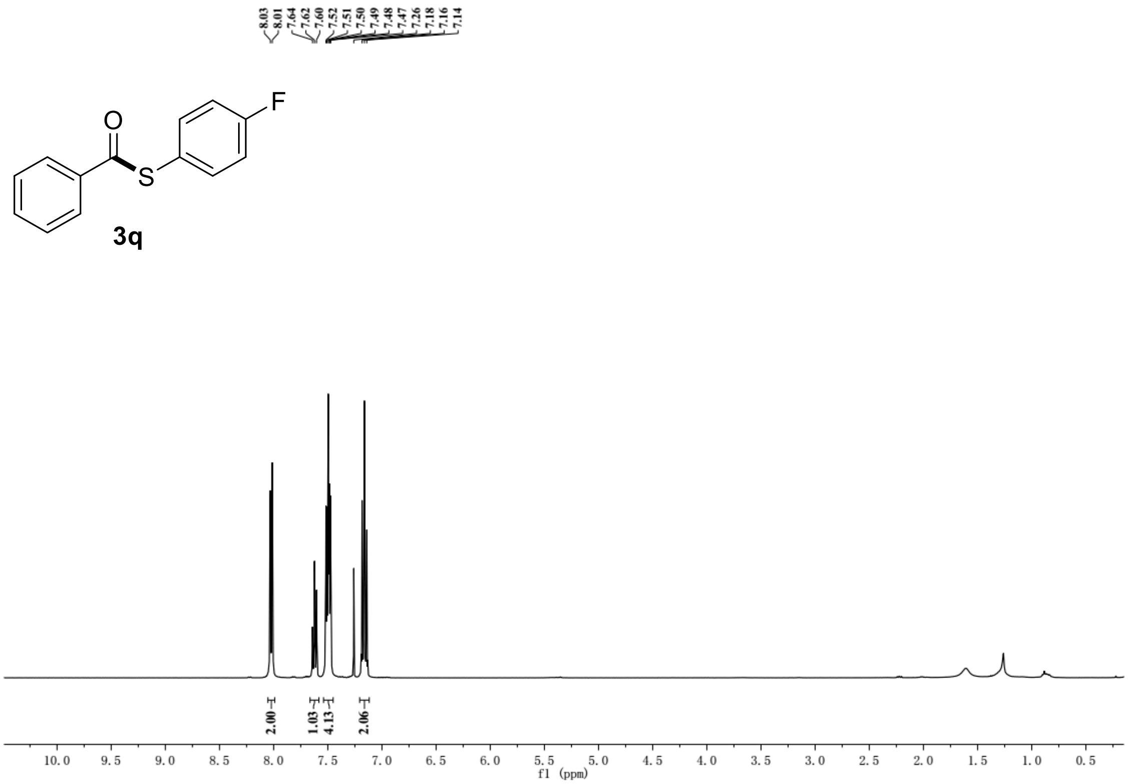
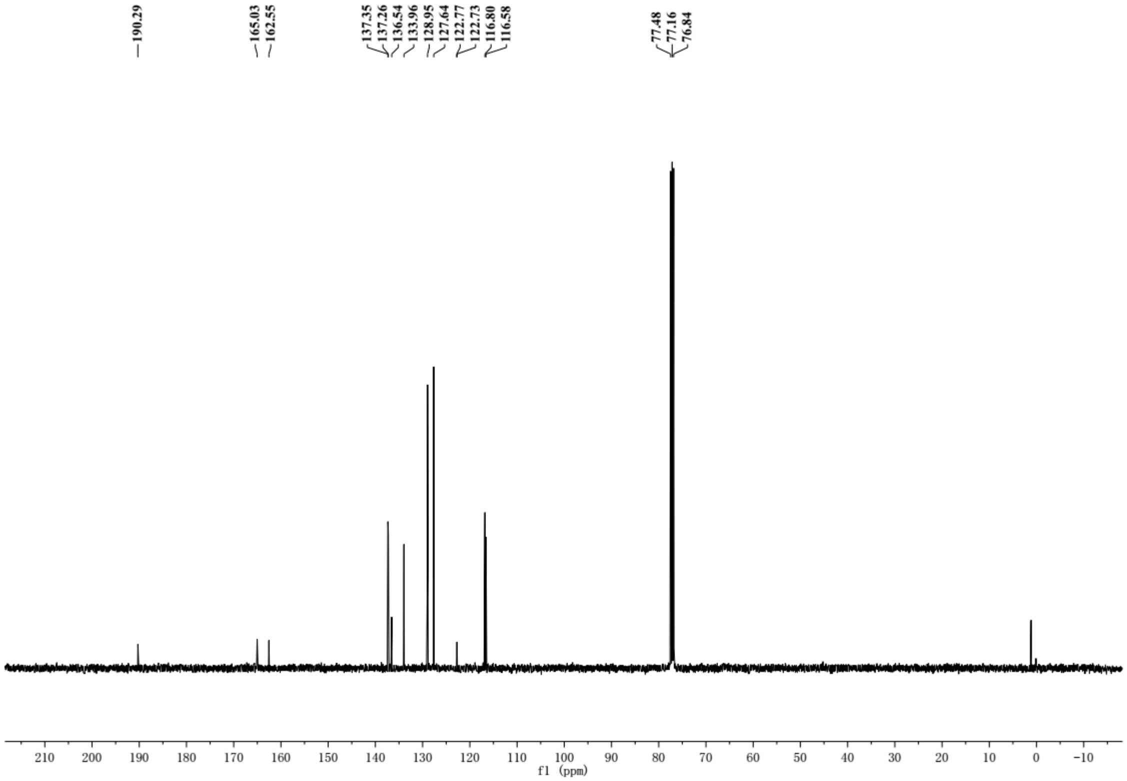
135.15
133.70
130.24
128.84
127.59
123.88
77.48
77.16
76.84
21.49
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3q

8.03
8.01
7.64
7.62
7.60
7.52
7.51
7.50
7.49
7.48
7.47
7.26
7.18
7.16
7.14
O
S
F
2.00
1.03
4.13
2.06
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
f1 (ppm)



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165.03
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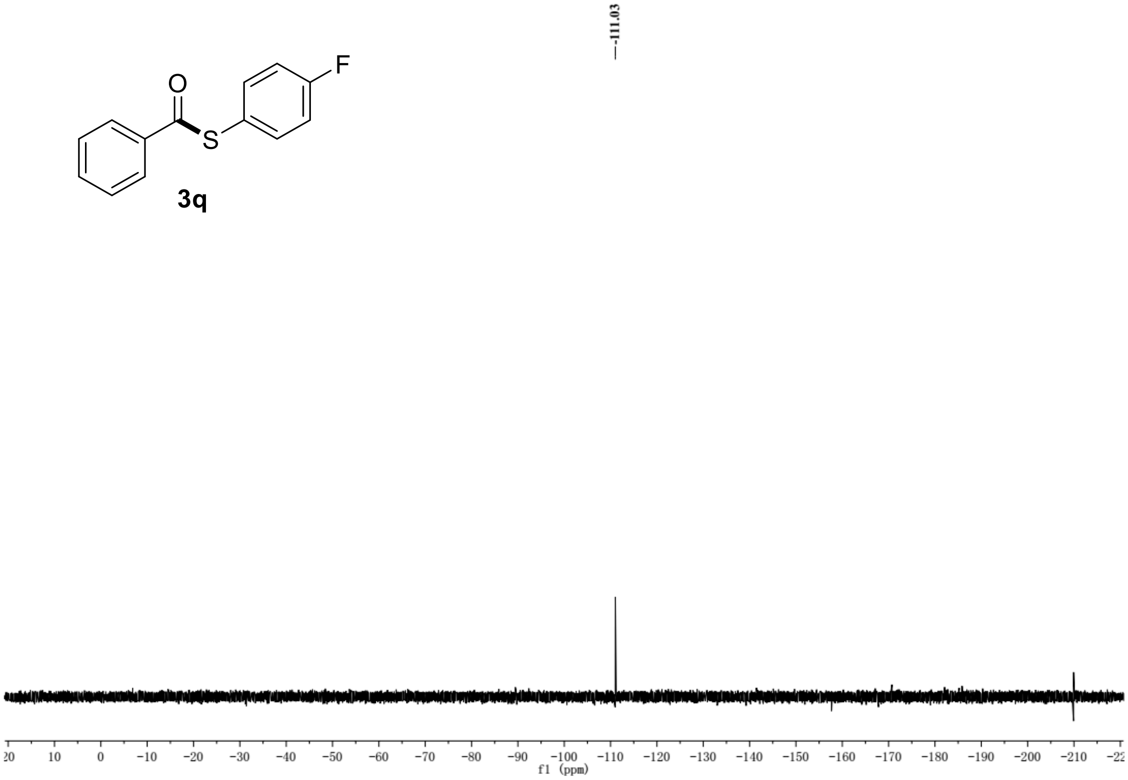
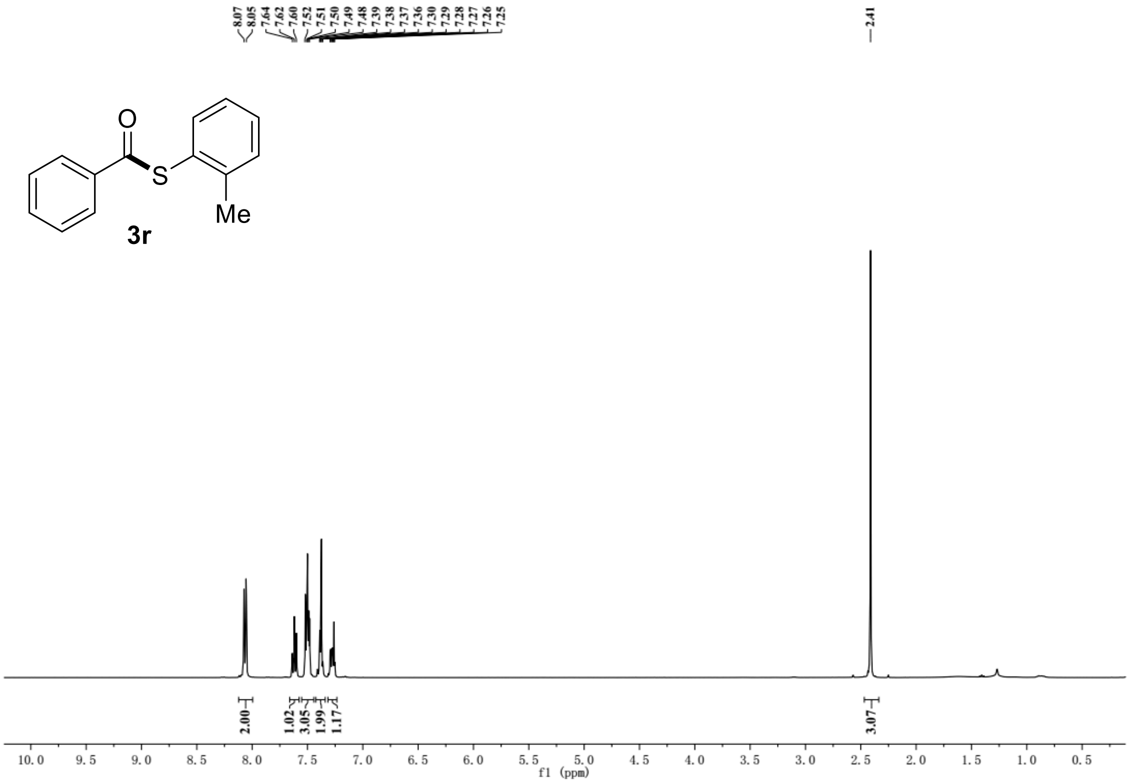
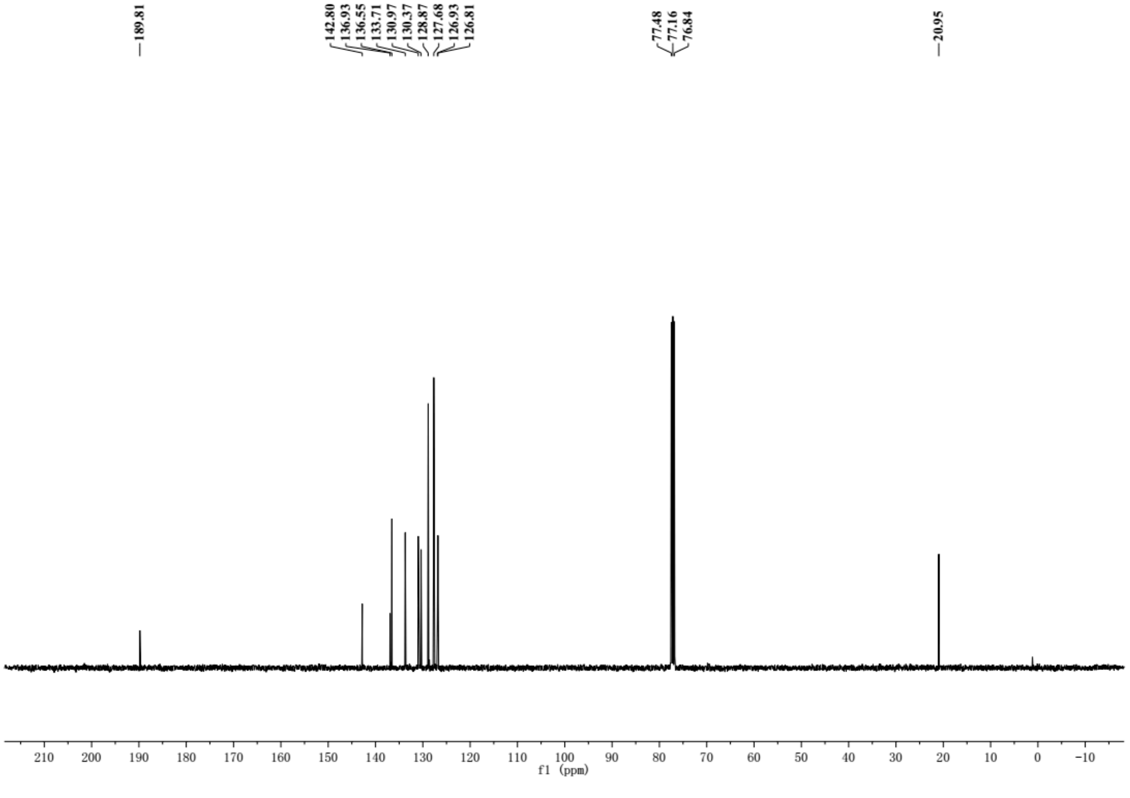
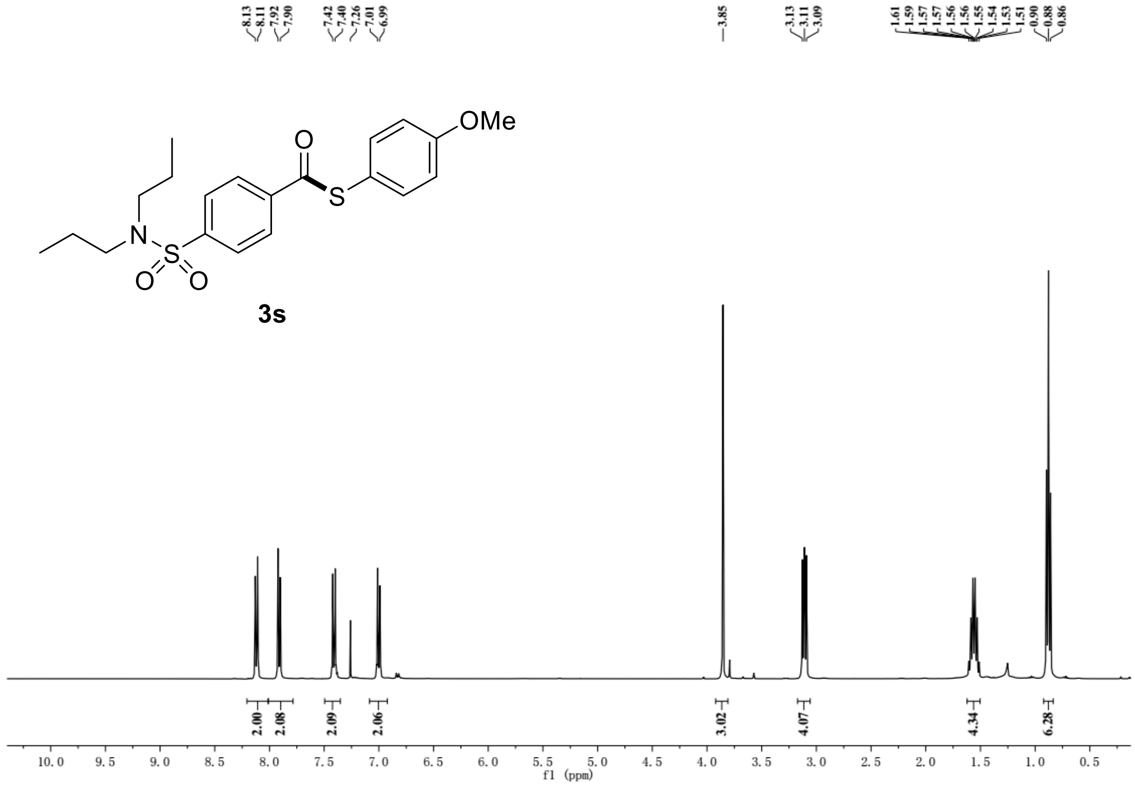
137.26
136.54
133.96
128.95
127.64
122.77
122.73
116.80
116.58
77.48
77.16
76.84
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


O
S
F
3q
-111.03
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−22
f1 (ppm)


8.07
8.05
7.64
7.62
7.60
7.52
7.51
7.50
7.49
7.48
7.39
7.38
7.37
7.36
7.30
7.29
7.28
7.27
7.26
7.25
2.41
O
S
Me
3r
2.00
1.02
3.05
1.99
1.17
3.07
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
f1 (ppm)


189.81
142.80
136.93
136.55
133.71
130.97
130.37
128.87
127.68
126.93
126.81
77.48
77.16
76.84
20.95
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)


8.13
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7.90
7.42
7.40
7.26
7.01
6.99
3.85
3.13
3.11
3.09
1.61
1.59
1.57
1.57
1.56
1.56
1.55
1.54
1.53
1.51
0.90
0.88
0.86
OMe
O
S
N
S
O
O
2.00
2.08
2.09
2.06
3.02
4.07
4.34
6.28
10.0
9.5
9.0
8.5
8.0
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7.0
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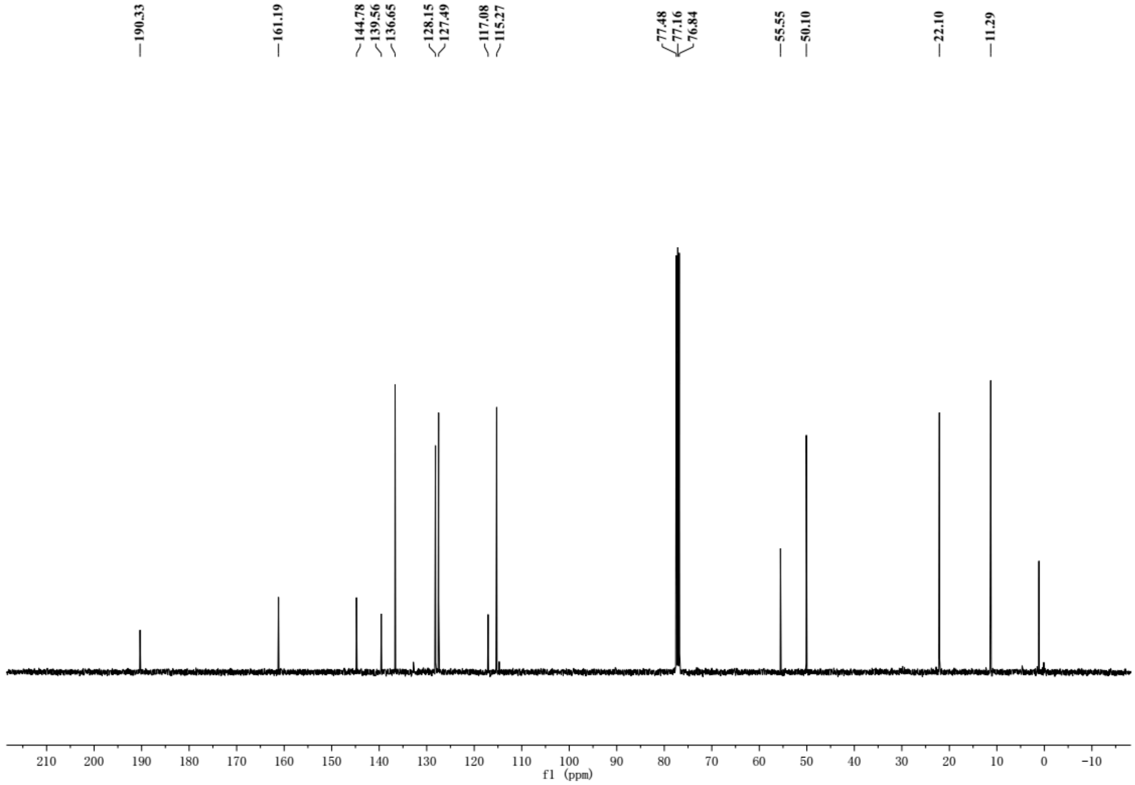
f1 (ppm)

3s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50.10
22.10
11.29
210
200
190
180
170
160
150
140
130
120
110
100
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30
20
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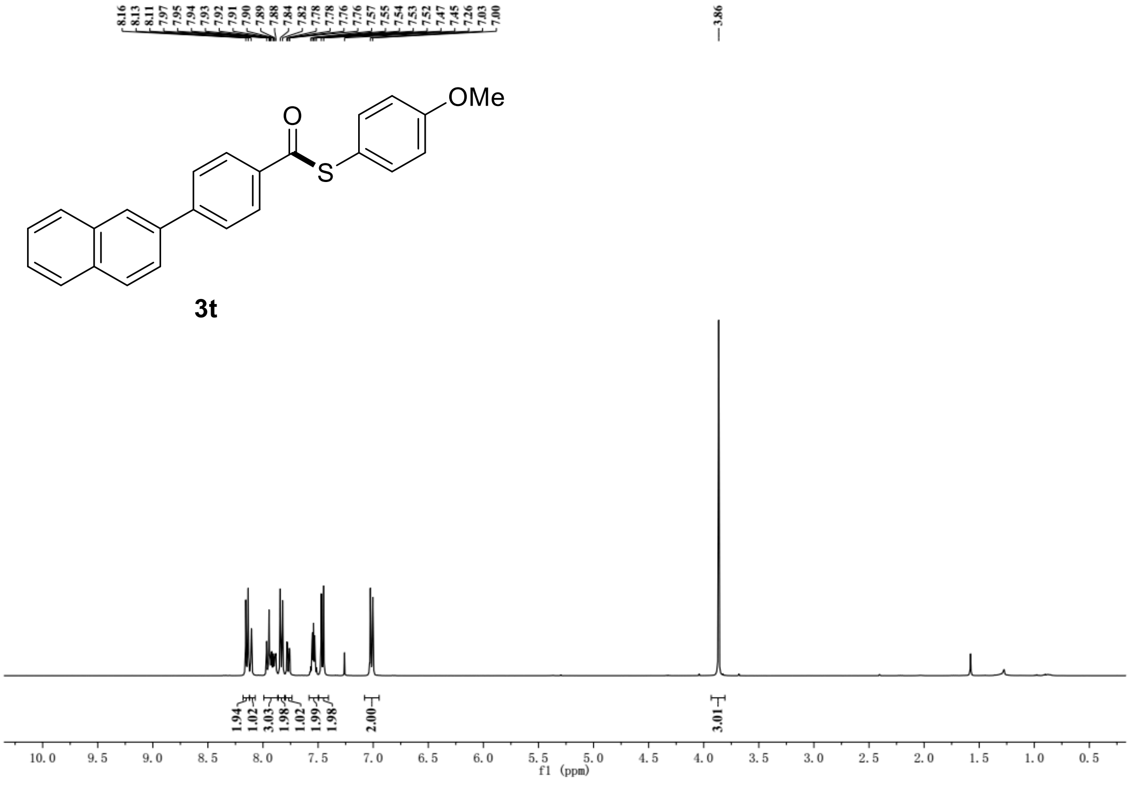
-10
f1 (ppm)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7.76
7.57
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7.54
7.53
7.52
7.47
7.45
7.26
7.03
7.00
3.86
OMe
O
S
3t
1.94
1.02
3.03
1.98
1.02
1.99
1.98
2.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
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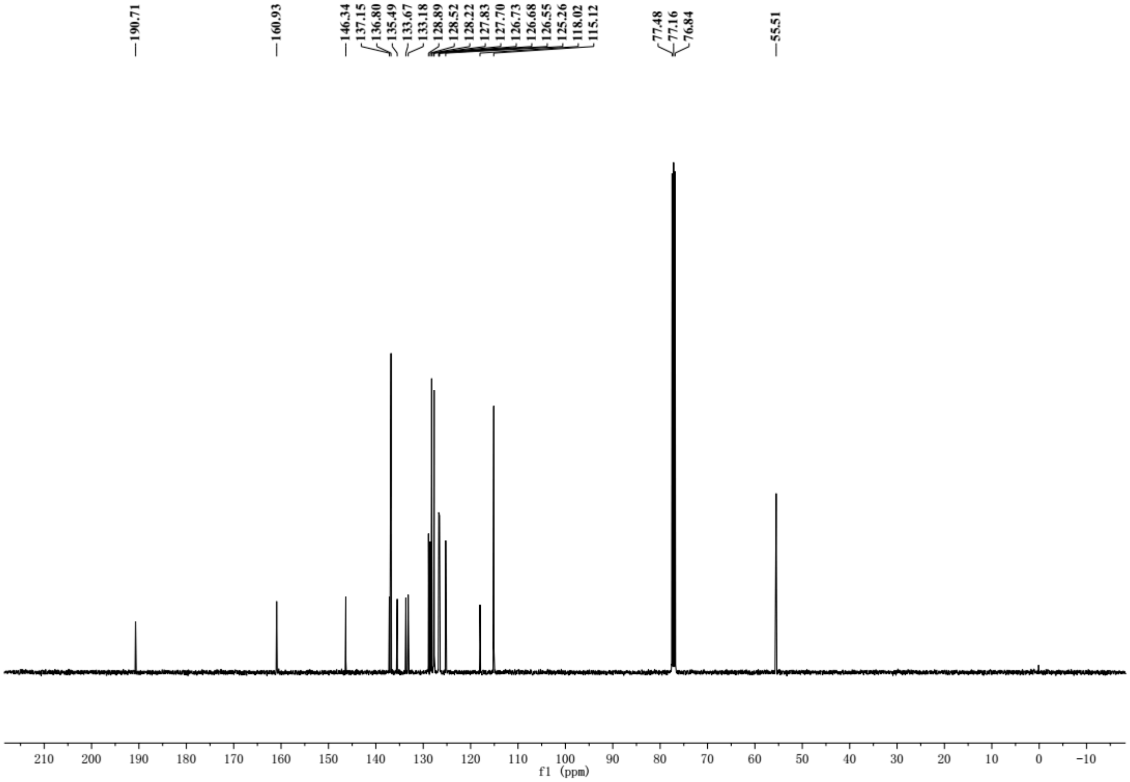
f1 (ppm)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127.70
126.73
126.68
126.55
125.26
118.02
115.12
77.48
77.16
76.84
55.51
210
200
190
180
170
160
150
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120
110
100
90
80
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50
40
30
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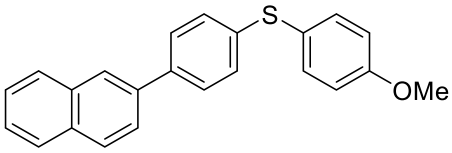
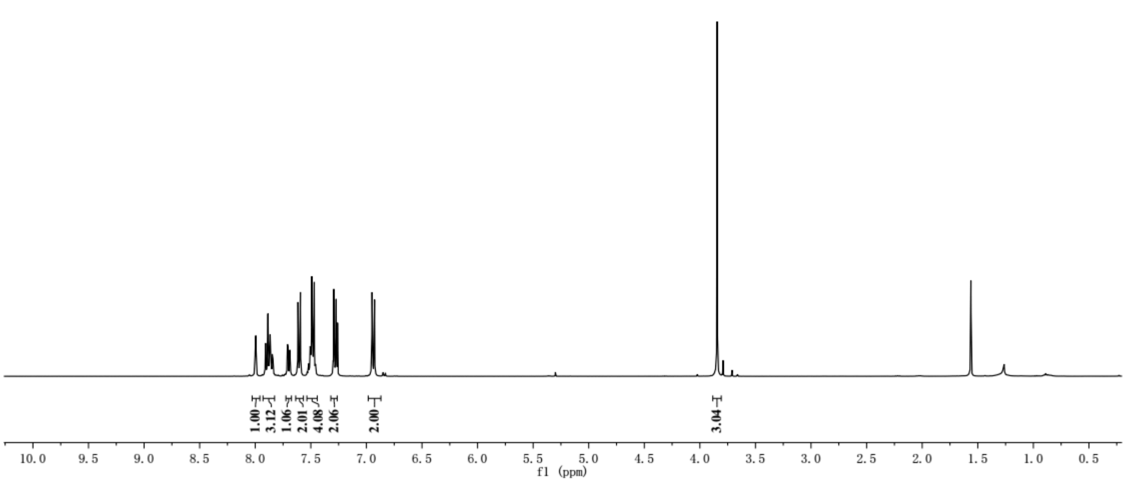
10
0
−10
f1 (ppm)


S
OMe

3u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7.59
7.53
7.52
7.52
7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.29
7.27
7.26
6.95
6.93
3.84
1.00
3.12
1.06
2.01
4.08
2.06
2.00
3.04
10.0
9.5
9.0
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8.0
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7.0
6.5
6.0
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4.0
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3.0
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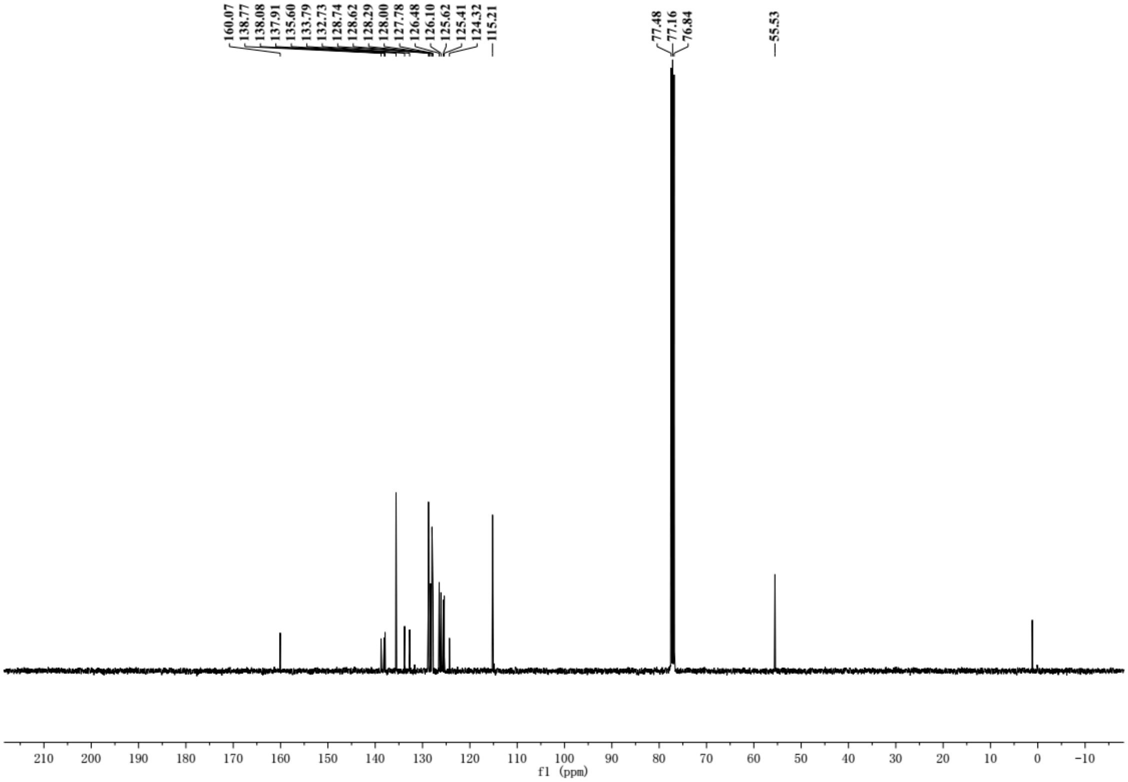
f1 (ppm)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126.10
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125.41
124.32
115.21
77.48
77.16
76.84
55.53
210
200
190
180
170
160
150
140
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120
110
100
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80
70
60
50
40
30
20
10
0
-10
f1 (ppm)