

SUPPORTING INFORMATION

Nickel-Catalyzed Cross-Coupling of *N*-Acyl Benzotriazoles with Oxiranes and Oxetanes for the Synthesis of β -Haloethyl and γ -Halopropyl Esters

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Table of Contents

1. General Information	S3
2. Synthesis of Starting Materials	S3
2.1 Preparation of <i>N</i> -acyl benzotriazoles	S3
2.2 Preparation of <i>N</i> -acyl amides 1a-S1-5	S5
3. General Procedure for the Ni-Catalyzed Coupling Reactions	S7
4. Characterization Data for the Products	S7
5. References	S20
6. Copies of NMR Spectra	S22

1. General Information

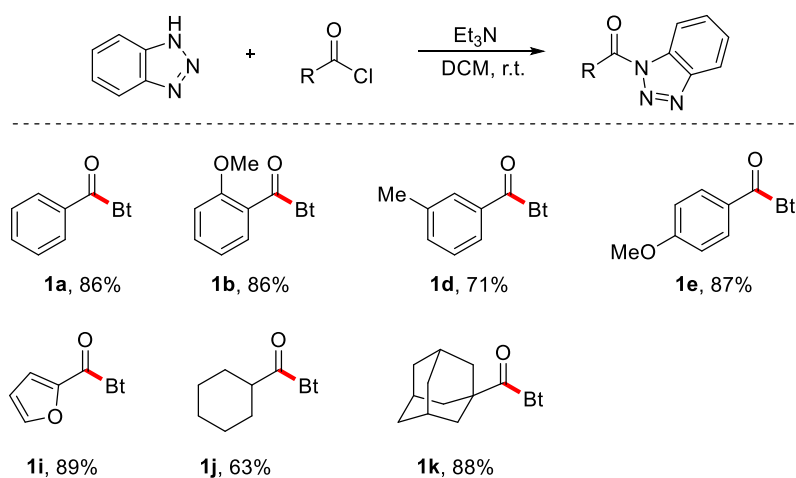
All the Ni-catalyzed reactions were set up using standard Schlenk techniques and carried out under N₂ atmosphere with super-dry solvents. All chemicals were obtained from commercial sources and used as received without further purification. The super-dry solvents (dioxane, toluene, THF, DMF, DMSO, etc) for catalytic reactions were purchased from Adamas stored in sure-seal bottles with molecular sieves as the desiccants.

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 glass plates. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 365 nm) and/or iodine. The products were isolated by flash column chromatography on silica gel (300–400 mesh).

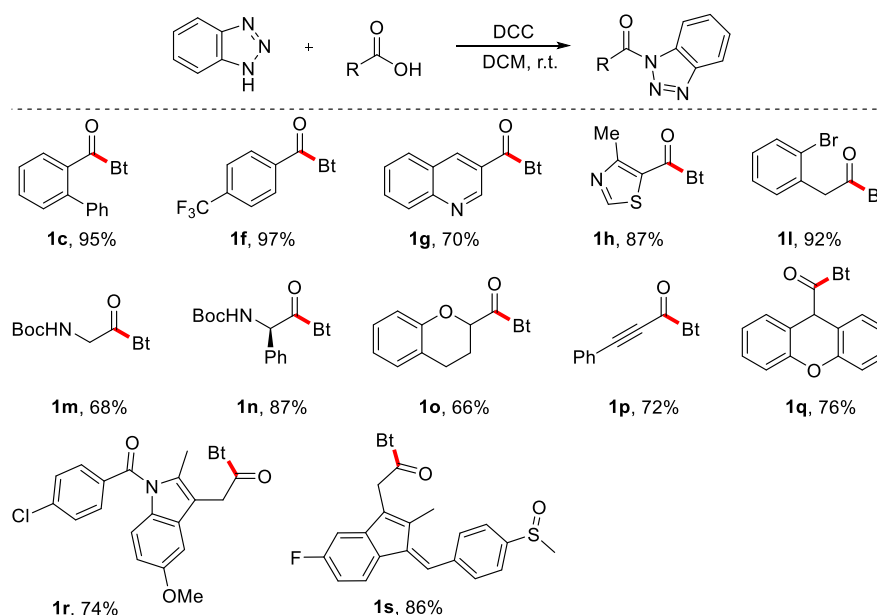
NMR spectra were recorded on a *Bruker AVANCE NEO* 400MHz/500MHz spectrometer at 25 °C in CDCl₃ or DMSO. Data are reported as following: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Chemical shifts (ppm) are given relative to solvent: reference for CDCl₃ was 7.26 ppm (¹H NMR) and 77.0 ppm (¹³C NMR); references for *d*₆-DMSO were 2.50 ppm (¹H NMR) and 40.0 ppm (¹³C NMR). High-resolution mass spectrometry (HRMS) was measured on an *Agilent 1290-6545XT* mass spectrometer.

2. Synthesis of Starting Materials

2.1 Preparation of *N*-acyl benzotriazoles

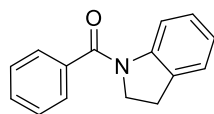


General Procedure A:¹ To a solution of benzotriazole (5.0 g, 42.0 mmol) and Et₃N (7.8 mL, 54.5 mmol) in anhydrous DCM (50 mL) was added the corresponding acyl chloride (50.4 mmol) dissolving in DCM (30 mL) at 0 °C under nitrogen. After stirring for 2 h, the reaction mixture was washed sequentially with 10% aq. HCl (3 × 20 mL), saturated aqueous NaHCO₃ (20 mL) and brine (20 mL) before drying over anhydrous Na₂SO₄. After removing of the solvent by rotoevaporation, the crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate). The compounds **1a**, **1b**, **1d**, **1e**, **1i**, **1j**, **1k**, **1a-S₁**, **1a-S₂** and **1a-S₃** were prepared by this procedure.



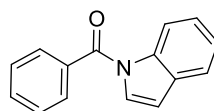
General Procedure B:² To a solution of benzotriazole (2.0 g, 16.8 mmol) and carboxylic acid (1.2 mmol) in DCM (30 mL) was added 1, 3-dicyclohexylcarbodiimide (5.2 g, 25.2 mmol). The mixture was then stirred at room temperature for 10 h. The precipitate was removed by filtration and the residue was concentrated in vacuo. The crude reaction mixture was then purified by flash column chromatography (Petroleum Ether/Ethyl Acetate) to afford the corresponding *N*-acyl benzotriazoles. The compounds **1c**, **1f**, **1g**, **1h**, **1l**, **1m**, **1n**, **1o**, **1p**, **1q**, **1r** and **1s** were prepared by this procedure.

2.2 Preparation of N-acyl amides 1a-S₁₋₅



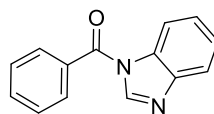
1-Benzoylindoline (1a-S₁)³

The compound was synthesized according to the General Procedure A on 8.39 mmol scale and purified by flash column chromatography (Petroleum ether/Ethyl acetate = 2/1) as white solid (1.56 g, 83%). ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.52 (m, 2H), 7.48 – 7.41 (m, 3H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.02 (s, 1H), 4.07 (s, 2H), 3.11 (t, *J* = 8.3 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 167.9, 142.6, 136.9, 132.3, 130.2, 128.5, 127.1, 127.0, 124.8, 123.8, 117.1, 50.5, 28.0.



1H-Indol-1-ylphenylmethanone (1a-S₂)³

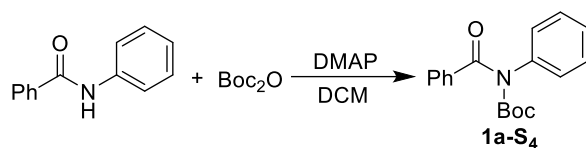
The compound was synthesized according to the General Procedure A on 8.54 mmol scale and purified by flash column chromatography (Petroleum ether/Ethyl acetate = 30/1) as white solid (1.49 g, 78%). ¹H NMR (400 MHz, CDCl₃) δ 8.45 (d, *J* = 8.2 Hz, 1H), 7.76 – 7.73 (m, 2H), 7.65 – 7.59 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.37 – 7.29 (m, 2H), 6.63 (d, *J* = 3.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 168.6, 136.0, 134.5, 131.8, 130.7, 129.1, 128.5, 127.5, 124.8, 123.9, 120.8, 116.3, 108.5.



1H-Benzimidazol-1-ylphenylmethanone (1a-S₃)³

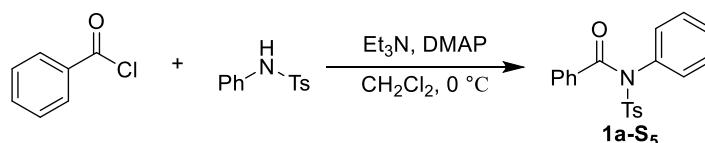
The compound was synthesized according to the General Procedure A on 8.46 mmol scale and purified by flash column chromatography (Petroleum ether/Ethyl acetate = 30/1) as white solid (1.20 g, 64%). ¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 1H), 8.22 – 8.18 (m, 1H), 7.87 – 7.84 (m, 1H), 7.83 – 7.79 (m, 2H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.49 – 7.41 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 143.9, 143.1, 133.1, 132.8, 132.1, 129.5, 129.0, 125.7, 125.2, 120.4, 115.4.

***tert*-Butyl benzoyl(phenyl)carbamate (**1a-S₄**)⁴**



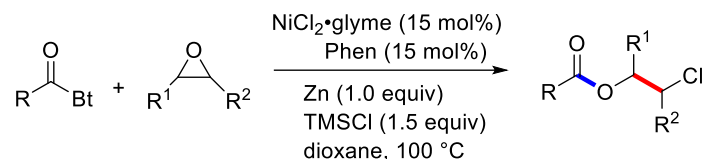
An oven-dried round-bottomed flask was charged with *N*-phenylbenzamide (5.0 mmol, 1.0 equiv), DMAP (0.6 g, 1 equiv) and CH₂Cl₂ (10 mL). Boc₂O (1.1 g, 1.0 equiv) was added in one portion and the reaction mixture was allowed to stir at room temperature for 15 h. After the indicated time, the reaction mixture was quenched by with NaHCO₃, extracted with EtOAc (3× 20 mL), washed with H₂O. The organic layers were combined, dried, and concentrated. The desired product **1a-S₄** was purified by flash column chromatography (Petroleum ether/Ethyl acetate = 10/1) as white solid (1.3 g, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.67 (m, 2H), 7.55 – 7.49 (m, 1H), 7.47 – 7.40 (m, 4H), 7.37 – 7.24 (m, 3H), 1.23 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 153.2, 139.0, 136.8, 131.6, 129.1, 128.2, 128.0, 127.8, 127.7, 83.3, 27.3.

***N*-Phenyl-*N*-tosylbenzamide (**1a-S₅**)⁵**



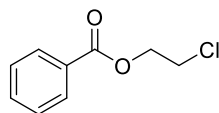
A solution of the *N*-phenyl tosylamide (1.24 g, 5.0 mmol), DMAP (0.5 mmol) and Et₃N (1.5 mL, 10 mmol) in CH₂Cl₂ (10 mL) was added slowly to benzoyl chloride (0.7 g, 5.0 mmol) in CH₂Cl₂ (10 mL) at 0 °C. The reaction mixture was stirred at room temperature for 2 h before washing with 5% HCl, brine and H₂O. The organic layer was dried over Na₂SO₄, filtered and evaporated under reduced pressure to give crude product, which was purified by column chromatography (Petroleum ether/Ethyl acetate = 10/1) to afford **1a-S₅** as white solid (1.7 g, 97%). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.38 Hz, 2H), 7.47 (d, *J* = 7.21 Hz, 2H), 7.37 – 7.28 (m, 6H), 7.25 – 7.15 (m, 4H), 2.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.9, 144.8, 137.3, 136.6, 135.1, 133.5, 131.7, 130.3, 129.5, 129.39, 129.38, 129.19, 129.17, 129.0, 128.9, 127.9, 127.2, 125.1, 121.5, 21.6.

3. General Procedure for the Ni-Catalyzed Coupling Reactions



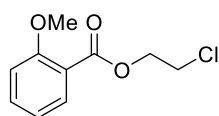
To an oven-dried Schlenk tube was sequentially charged with $\text{NiCl}_2\cdot\text{glyme}$ (6.6 mg, 0.03 mmol), Phen (5.4 mg, 0.03 mmol), zinc powder (13.1 mg, 0.2 mmol), *N*-acyl benzotriazole (0.2 mmol) under N_2 . Then the Schlenk tube was capped with a rubber septum before connecting to Schlenk line. After three vacuum and backfill cycles, dioxane (2 mL) was added with an injector. Then oxirane (0.4 mmol) and TMSCl (38.0 μL , 0.3 mmol) were added through microsyringes. The perimeter of the septum was carefully sealed with parafilm. Then the mixture was allowed for stirring at 100 $^\circ\text{C}$ metal sand bath for than 12 h. After the reaction mixture was cooled to room temperature, the solvent is removed by a rotary evaporator. The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate).

4. Characterization Data for the Products



2-Chloroethyl benzoate (3a)⁶

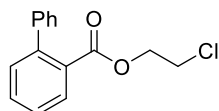
The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 15/1) as yellow oil (32.7 mg, 88%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.08 – 8.06 (m, 2H), 7.58 – 7.55 (m, 1H), 7.46 – 7.42 (m, 2H), 4.57 – 4.54 (m, 2H), 3.82 – 3.79 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.0, 133.1, 129.6, 129.5, 128.3, 64.3, 41.6.



2-Chloroethyl 2-methoxybenzoate (3b)⁷

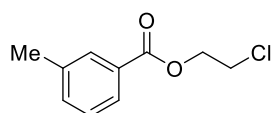
The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 25/1) as yellow oil (31.1 mg, 72%). $^1\text{H NMR}$ (600 MHz, CDCl_3)

δ 7.79 (d, $J = 7.77$ Hz, 1H), 7.42 (t, $J = 8.03$ Hz, 1H), 6.92 (d, $J = 8.30$ Hz, 2H), 4.48 (s, 2H), 3.84 (s, 3H), 3.74 (d, $J = 5.77$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 165.2, 159.2, 133.6, 131.5, 119.9, 119.1, 111.9, 64.0, 55.7, 41.5.



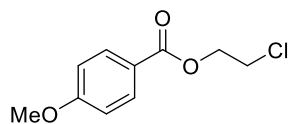
2-Chloroethyl [1,1'-biphenyl]-2-carboxylate (3c)⁸

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 20/1) as colorless oil (29.7 mg, 57%). ^1H NMR (400 MHz, CDCl_3) δ 7.88 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.56 (td, $J = 7.6, 1.4$ Hz, 1H), 7.46 – 7.36 (m, 5H), 7.34 – 7.30 (m, 2H), 4.29 (t, $J = 5.9$ Hz, 2H), 3.39 (t, $J = 5.9$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.8, 142.6, 141.2, 131.4, 130.6, 130.1, 129.8, 128.2, 127.9, 127.1, 127.0, 64.2, 40.8.



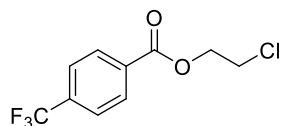
2-Chloroethyl 3-methylbenzoate (3d)⁷

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 20/1) as yellow oil (24.6 mg, 65%). ^1H NMR (600 MHz, CDCl_3) δ 7.99 – 7.80 (m, 1H), 7.48 – 7.27 (m, 1H), 4.53 (s, 2H), 3.78 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 165.9, 137.9, 133.7, 129.9, 129.3, 128.1, 126.6, 64.1, 41.5, 20.9.



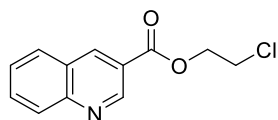
Benzoic acid, 4-methoxy-, 2-chloroethyl ester (3e)⁹

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 25/1) as colorless oil (25.5 mg, 59%). ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.9$ Hz, 2H), 6.89 (d, $J = 8.9$ Hz, 2H), 4.50 (t, $J = 6.3, 5.2$ Hz, 2H), 3.82 (s, 3H), 3.77 (t, $J = 6.3, 5.2$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.7, 163.5, 131.6, 121.8, 113.5, 64.0, 55.5, 41.7.



2-Chloroethyl-4-(trifluoromethyl)benzoate (3f)⁷

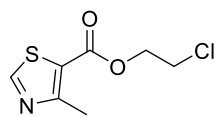
The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 15/1) as colorless oil (33.4 mg, 66%). **¹H NMR** (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.13 Hz, 2H), 7.68 (d, *J* = 8.23 Hz, 2H), 4.65 – 4.27 (m, 2H), 3.87 – 3.61 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 164.8, 134.5 (q, *J* = 32.65 Hz), 132.8 (d, *J* = 1.38 Hz), 130.0, 125.3 (q, *J* = 3.76 Hz), 122.2, 64.8, 41.4. **¹⁹F NMR** (376 MHz, CDCl₃) δ -63.29.



2-Chloroethyl quinoline-3-carboxylate (3g)

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 15/1) as colorless oil (22.3 mg, 47%). **¹H NMR** (400 MHz, CDCl₃) δ 9.44 (d, *J* = 2.0 Hz, 1H), 8.84 (d, *J* = 1.9 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.84 – 7.80 (m, 1H), 7.62 (dd, *J* = 11.2, 3.9 Hz, 1H), 4.67 – 4.64 (m, 2H), 3.88 – 3.85 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 164.9, 149.9, 138.9, 132.0, 129.4, 129.1, 127.5, 126.7, 122.4, 64.8, 41.5.

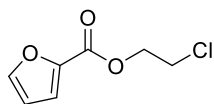
HRMS (ESI⁺) m/z: [M+Na]⁺ Calcd for C₁₂H₁₀ClNNaO₂, 258.0298; found: 258.0295.



2-Chloroethyl-4-methylthiazole-5-carboxylate (3h)

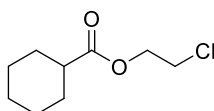
The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 30/1) as white solid (35.8 mg, 85%). **¹H NMR** (400 MHz, CDCl₃) δ 8.80 (s, 1H), 4.55 – 4.52 (m, 2H), 3.80 – 3.77 (m, 2H), 2.78 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 161.3, 161.0, 155.6, 121.3, 64.4, 41.3, 17.2.

HRMS (ESI⁺) m/z: [M+H]⁺ Calcd for C₇H₉ClNO₂S, 227.9862; Found: 227.9860.



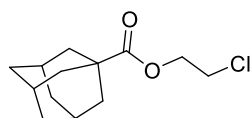
2-Chloroethyl furan-2-carboxylate (3i)⁷

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 10/1) as yellow oil (24.8 mg, 71%). ¹H NMR (600 MHz, CDCl₃) δ 7.79 (s, 1H), 7.41 (s, 1H), 6.71 (s, 1H), 4.80 – 4.41 (m, 2H), 3.98 (d, *J* = 4.86 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 157.9, 146.5, 143.8, 118.4, 111.8, 64.1, 41.3.



2-Chloroethyl cyclohexanecarboxylate (3j)⁶

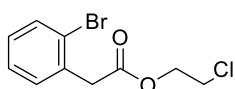
The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 13/1) as colorless oil (30.0 mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ 4.26 – 4.21 (m, 2H), 3.62 – 3.57 (m, 2H), 2.31 – 2.24 (m, 1H), 1.88 – 1.81 (m, 2H), 1.73 – 1.64 (m, 2H), 1.43 – 1.32 (m, 2H), 1.27 – 1.11 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 175.4, 63.5, 42.7, 41.6, 28.7, 25.5, 25.1.



2-Chloroethyl (3r,5r,7r)-adamantane-1-carboxylate (3k)

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 20/1) as colorless oil (39.0 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ 4.67 – 4.64 (m, 2H), 4.04 – 4.02 (m, 2H), 2.39 (d, *J* = 8.7 Hz, 3H), 2.26 (dd, *J* = 9.5, 2.7 Hz, 6H), 2.11 – 2.02 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 176.8, 63.3, 41.6, 40.5, 38.5, 36.2, 27.7.

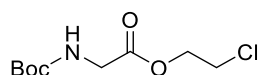
HRMS (ESI⁺) *m/z*: [M+Na]⁺ Calcd for C₁₃H₁₉ClNaO₂, 265.0971; Found: 265.0964.



2-Chloroethyl 2-bromobenzoate (3l)¹⁰

The crude product was purified by flash column chromatography (Petroleum

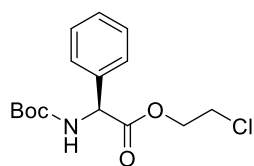
Ether/Ethyl Acetate = 20/1) as yellow oil (24.4 mg, 44%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.58 (d, $J = 8.1$ Hz, 1H), 7.32 – 7.26 (m, 2H), 7.19 – 7.13 (m, 1H), 4.41 – 4.36 (m, 2H), 3.84 (s, 2H), 3.71 – 3.65 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 170.0, 133.7, 132.6, 131.4, 128.9, 127.5, 124.8, 64.3, 41.3, 41.2.



2-Chloroethyl (*tert*-butoxycarbonyl) glycinate (**3m**)

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 15/1) as yellow oil (29.4 mg, 62%). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 5.43 – 5.31 (m, 1H), 4.26 (t, $J = 5.8$ Hz, 2H), 3.82 – 3.73 (m, 2H), 3.57 (t, $J = 5.7$ Hz, 1H), 1.31 (s, 9H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 169.9, 155.6, 79.5, 64.3, 41.9, 41.0, 27.9.

HRMS (ESI⁺) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_9\text{H}_{16}\text{ClNNaO}_4$, 260.0666; Found: 260.0670.



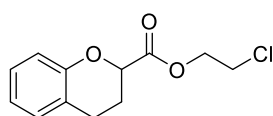
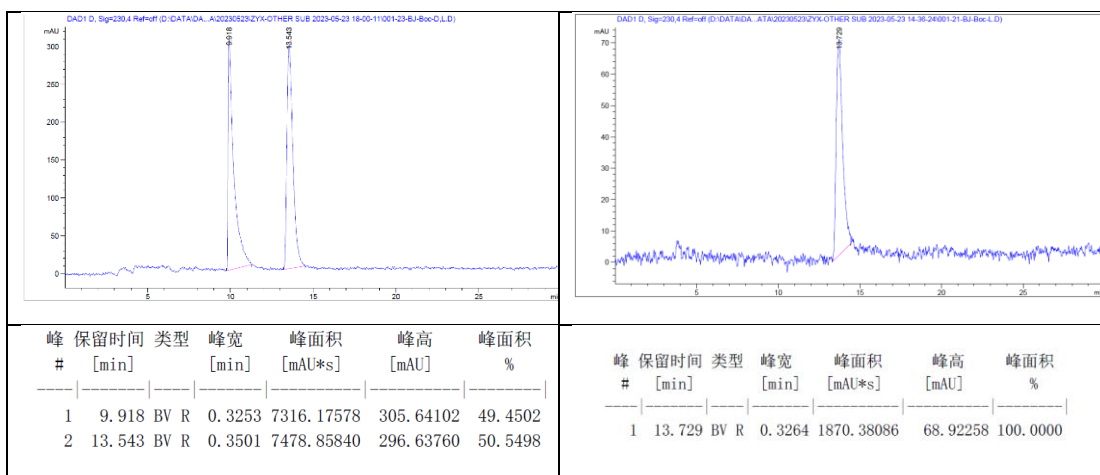
2-Chloroethyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-2-phenylacetate (**3n**)

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 10/1) as colorless solid (43.3 mg, 69%, >99% ee). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.23 (m, 5H), 5.72 – 5.60 (m, 1H), 5.35 – 5.29 (m, 1H), 4.36 – 4.23 (m, 2H), 3.56 – 3.51 (m, 2H), 1.40 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 170.3, 154.3, 135.8, 128.4, 128.0, 126.7, 79.6, 64.4, 57.1, 40.5, 27.7.

HRMS (ESI⁺) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{20}\text{ClNNaO}_4$, 336.0979; Found: 336.0978.

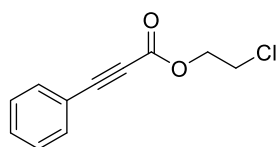
HPLC (Chiralpak AD-H column, hexane/^{*i*}PrOH = 85/15, flow rate 1.0 mL min⁻¹, $\lambda = 230$ nm): $t_1 = 9.9$ min, $t_2 = 13.5$ min.

Racemate 3n	Chiral 3n
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2-Chloroethyl chromane-2-carboxylate (3o)¹¹

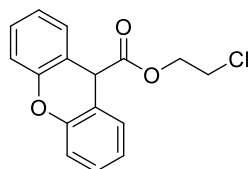
The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 10/1) as yellow oil (37.6 mg, 78%). ¹H NMR (400 MHz, CDCl₃) δ 7.18 – 7.10 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.97 – 6.85 (m, 2H), 4.79 (dd, *J* = 7.3, 3.7 Hz, 1H), 4.51 – 4.37 (m, 2H), 3.70 (t, *J* = 5.6 Hz, 2H), 2.92 – 2.73 (m, 2H), 2.36 – 2.17 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 170.3, 153.1, 129.2, 127.4, 121.0, 120.7, 116.6, 73.2, 64.4, 41.2, 24.3, 22.9.



2-Chloroethyl 3-phenylpropiolate (3p)

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 15/1) as yellow oil (14.2 mg, 33%). ¹H NMR (600 MHz, CDCl₃) δ 7.59 – 7.56 (m, 2H), 7.48 – 7.41 (m, 1H), 7.39 – 7.32 (m, 2H), 4.49 – 4.39 (m, 2H), 3.76 – 3.68 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 153.4, 132.9, 130.8, 128.5, 119.1, 87.2, 79.9, 65.1, 40.9.

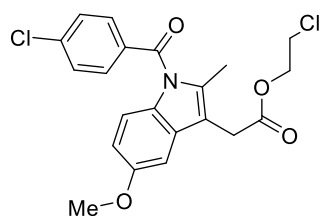
HRMS (ESI⁺) *m/z*: [M+Na]⁺ Calcd for C₁₁H₉ClNaO₂, 231.0189; Found: 231.0183.



2-Chloroethyl 9H-xanthene-9-carboxylate (3q)

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 20/1) as colorless oil (45.6 mg, 80%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.31 (m, 4H), 7.26 – 7.11 (m, 2H), 7.10 (td, $J = 7.5, 1.2$ Hz, 2H), 5.07 (s, 1H), 4.32 – 4.29 (m, 2H), 3.58 (dd, $J = 6.1, 5.4$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.3, 151.1, 129.0, 128.9, 123.2, 117.8, 116.8, 64.5, 44.9, 41.1.

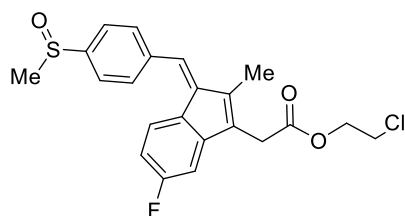
HRMS (ESI⁺) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{13}\text{ClNaO}_3$, 311.0451; Found: 311.0453.



2-Chloroethyl 1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-acetate (3r)

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 15/1) as yellow oil (23.6 mg, 47%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.6$ Hz, 3H), 7.33 (d, $J = 8.6$ Hz, 2H), 7.08 (d, $J = 8.7$ Hz, 1H), 6.99 (d, $J = 2.4$ Hz, 1H), 6.75 (dd, $J = 8.7, 2.4$ Hz, 1H), 4.51 – 4.46 (m, 2H), 4.44 – 4.39 (m, 2H), 3.80 (s, 3H), 3.68 (s, 2H), 2.33 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.4, 168.4, 156.2, 146.5, 139.6, 137.2, 133.9, 131.4, 130.9, 130.8, 130.6, 129.3, 126.6, 120.4, 115.1, 114.6, 112.1, 111.1, 101.4, 55.9, 31.7, 13.8.

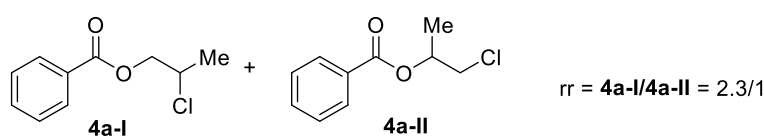
HRMS (ESI⁺) (m/z): $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{19}\text{Cl}_2\text{NNaO}_4$, 442.0589; Found: 442.0583.



2-Chloroethyl-2-(2,5-dimethyl-1-(4-(methylsulfinyl)benzylidene)-1H-inden-3-yl)acetate (3s)

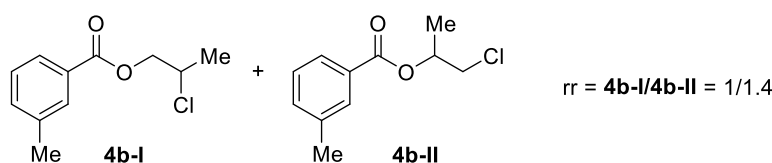
The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 35/1) as brownness oil (55.2 mg, 69%). ¹H NMR (600 MHz, CDCl₃) δ 7.81 – 7.75 (m, 1H), 7.74 – 7.67 (m, 2H), 7.64 – 7.61 (m, 1H), 7.24 – 7.15 (m, 1H), 7.15 – 7.07 (m, 1H), 3.63 (s, 1H), 3.57 (s, 1H), 2.92 – 2.87 (m, 3H), 2.83 (s, 3H), 2.27 (d, *J* = 17.57 Hz, 3H), 2.20 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 174.6, 164.1, 162.5, 146.6, 144.8, 141.7, 139.8, 138.4, 131.5, 130.3, 129.4, 128.2, 123.9, 123.7, 123.6, 111.9, 110.7, 106.2, 106.1, 43.5, 31.4, 10.5.

HRMS (ESI⁺) (m/z): [M+Na]⁺ Calcd for C₂₂H₂₀ClFNaO₃S, 441.0703; Found: 441.0698.



2-chloropropyl benzoate (4a-I) and 1-chloropropan-2-yl benzoate (4a-II)¹²

The crude product (obtained as two inseparable regioisomers) was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 30/1) as colorless oil (23.9 mg, 60%). ¹H NMR (400 MHz, CDCl₃) δ 8.18 – 7.92 (m, 2H), 7.63 – 7.54 (m, 1H), 7.49 – 7.42 (m, 2H), 5.43 – 5.30 (m, 0.5H), 4.43 (d, *J* = 5.97 Hz, 1H), 4.39 – 4.24 (m, 0.5H), 3.78 – 3.59 (m, 1H), 1.61 (d, *J* = 6.58 Hz, 2H), 1.47 (d, *J* = 6.37 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 166.1, 165.8, 133.2, 133.1, 129.7, 129.6, 128.4, 128.3, 70.2, 68.9, 54.0, 47.0, 29.7, 21.6, 17.7.

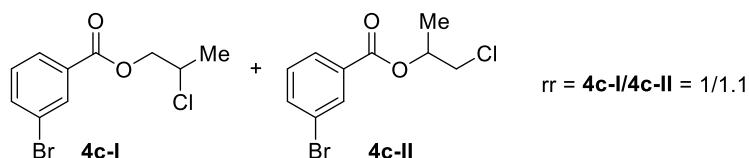


2-chloropropyl 3-methylbenzoate (4b-I) and 1-chloropropan-2-yl 3-methylbenzoate (4b-II)

The crude products (obtained as two inseparable regioisomers) were purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 20/1) as yellow oil (24.5 mg, 57%). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (t, *J* = 5.6 Hz, 2H), 7.38 – 7.31 (2H), 5.38 – 5.33 (m, 0.5H), 4.51 – 4.47 (m, 1H), 4.43 – 4.1 (m, 0.5H), 3.71 (d, *J* = 5.0 Hz, 1H), 2.41 (s, 3H), 1.60 (d, *J* = 6.6 Hz, 1H), 1.48 (d, *J* = 6.4 Hz, 2H). ¹³C NMR (101 MHz,

CDCl₃) δ 166.2, 165.9, 138.2, 138.2, 134.0, 133.9, 130.2, 130.2, 129.9, 129.5, 128.3, 128.3, 126.9, 126.8, 77.2, 70.1, 68.9, 54.1, 47.0, 21.6, 21.3, 17.7.

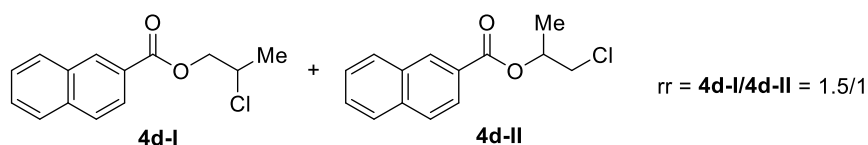
HRMS (ESI⁺) (m/z): [M+Na]⁺ Calcd for C₁₁H₁₃ClNaO₂, 235.0502; Found: 235.0496.



2-Chloropropyl 3-bromobenzoate (4c-I) and 1-Chloropropan-2-yl 3-bromobenzoate (4c-II)

The crude products (obtained as two inseparable regioisomers) were purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 25/1) as yellow oil (28.5 mg, 51%). **¹H NMR** (400 MHz, CDCl₃) δ 8.20 – 8.15 (m, 1H), 8.03 – 7.96 (m, 1H), 7.74 – 7.66 (m, 1H), 7.36 – 7.31 (m, 1H), 5.41 – 5.30 (m, 0.5H), 4.43 (d, *J* = 5.97 Hz, 1H), 4.36 – 4.27 (m, 0.5H), 3.73 – 3.69 (m, 1H), 1.62 – 1.57 (d, *J* = 6.62 Hz, 1H), 1.49 – 1.42 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 164.7, 164.4, 136.2, 136.1, 132.7, 132.6, 131.9, 131.6, 130.0, 129.9, 128.3, 128.2, 122.5, 122.4, 70.7, 69.3, 53.8, 46.8, 21.6, 17.7.

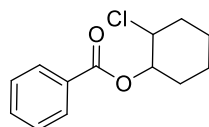
HRMS (ESI⁺) (m/z): [M+Na]⁺ Calcd for C₁₀H₁₀BrClNaO₂, 298.9450; Found: 298.9445.



2-Chloropropyl 2-naphthoate (4d-I) and 1-Chloropropan-2-yl 2-naphthoate (4d-II)

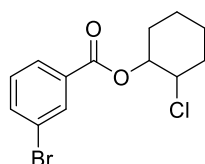
The crude product (obtained as two inseparable regioisomers) were purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 25/1) as yellow oil (24.9 mg, 50%). **¹H NMR** (400 MHz, CDCl₃) δ 8.64 (d, *J* = 4.74 Hz, 1H), 8.11 – 8.05 (m, 1H), 7.97 (d, *J* = 7.99 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.63 – 7.52 (m, 2H), 5.49 – 5.36 (m, 0.5H), 4.50 (d, *J* = 6.01 Hz, 1H), 4.38 (m, 0.5H), 3.77 (d, *J* = 5.04 Hz, 1H), 1.65 (d, *J* = 6.64 Hz, 2H), 1.53 (d, *J* = 6.34 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.2, 165.9, 135.7, 135.6, 132.4, 131.3, 131.2, 129.4, 129.3, 128.4, 128.3, 128.2, 128.1, 127.74, 127.73, 127.2, 126.8, 126.7, 126.6, 70.3, 69.0, 54.1, 47.0, 31.4, 30.2, 29.7, 21.6, 17.7.

HRMS (ESI⁺) (m/z): [M+Na]⁺ Calcd for C₁₄H₁₃ClNaO₂, 271.0502; Found: 271.0496.



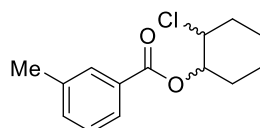
2-Chlorocyclohexyl benzoate (4e)⁶

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 30/1) as yellow oil (27.6 mg, 58%). ¹H NMR (400 MHz, CDCl₃) δ 8.10 – 7.85 (m, 2H), 7.56 – 7.48 (m, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 5.08 – 5.00 (m, 1H), 4.03 – 3.96 (m, 1H), 2.31 – 2.14 (m, 2H), 1.82 – 1.63 (m, 3H), 1.53 – 1.39 (m, 2H), 1.39 – 1.27 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 165.3, 132.7, 129.9, 129.4, 128.1, 76.0, 60.3, 34.4, 30.3, 24.1, 22.9.



2-Chlorocyclohexyl 3-bromobenzoate (4f)¹³

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 20/1) as colorless oil (31.2 mg, 49%). ¹H NMR (400 MHz, CDCl₃) δ 8.20 (t, *J* = 3.37 Hz, 1H), 8.02 – 7.99 (m, 1H), 7.71 – 7.65 (m, 1H), 7.33 (t, *J* = 7.89 Hz, 1H), 5.12 – 4.99 (m, 1H), 4.09 – 3.98 (m, 1H), 2.36 – 2.20 (m, 2H), 1.88 – 1.73 (m, 3H), 1.58 – 1.46 (m, 2H), 1.44 – 1.35 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 164.1, 135.8, 132.4, 132.0, 129.8, 128.2, 122.3, 76.8, 60.4, 34.7, 30.6, 24.4, 23.1.

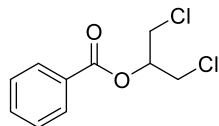


2-chlorocyclohexyl 3-methylbenzoate (4g)

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 30/1) as yellow oil (38.1 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 6.44 Hz, 2H), 7.38 – 7.28 (m, 2H), 5.11 – 4.98 (m, 1H), 4.08 – 3.97 (m, 1H), 2.39 (s, 3H), 2.33 – 2.18 (m, 2H), 1.83 – 1.71 (m,

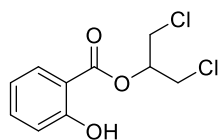
3H), 1.60 – 1.28 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.6, 137.9, 133.6, 130.0, 128.1, 126.7, 76.0, 60.4, 34.5, 30.4, 24.2, 23.0, 21.1, 14.2.

HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{17}\text{ClNaO}_2$, 275.0815; Found: 275.0810.



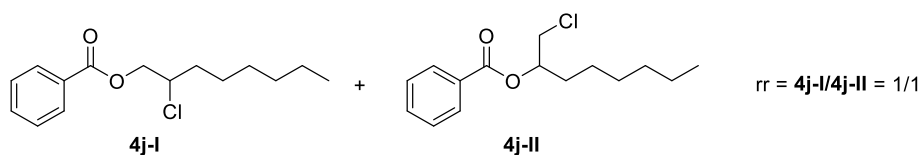
2-Propanol, 1,3-dichloro-, 2-benzoate (4h)¹⁴

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 20/1) as yellow oil (33.2 mg, 71%). ^1H NMR (400 MHz, CDCl_3) δ 8.10 – 8.06 (m, 2H), 7.62 – 7.58 (m, 1H), 7.56 – 7.45 (m, 2H), 5.43 (p, $J = 5.1$ Hz, 1H), 3.90 (d, $J = 5.1$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.3, 133.6, 129.9, 129.1, 128.5, 72.0, 42.4.



1,3-Dichloropropan-2-yl 2-hydroxybenzoate (4i)¹⁵

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 25/1) as colorless oil (31.2 mg, 62%). ^1H NMR (400 MHz, CDCl_3) δ 10.42 (s, 1H), 7.92 – 7.84 (dd, $J = 8.0, 1.8$ Hz, 1H), 7.58 – 7.43 (m, 1H), 7.04 – 6.97 (d, $J = 9.4$ Hz, 1H), 6.96 – 6.85 (m, 1H), 5.50 – 5.43 (m, 1H), 3.91 – 3.85 (d, $J = 5.2$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 161.9, 136.5, 130.1, 119.5, 117.7, 111.5, 72.4, 42.2.

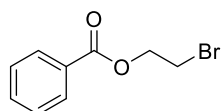


2-Chlorooctyl benzoate (4j-II) and 1-chlorooctan-2-yl benzoate (4j-II)

The crude products (obtained as two inseparable regioisomers) were purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 30/1) as colorless oil (41.0 mg, 76%). ^1H NMR (400 MHz, CDCl_3) δ 8.09 – 8.00 (m, 2H), 7.56 – 7.49 (m, 1H),

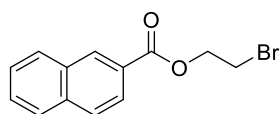
7.42 (t, $J = 7.6$ Hz, 2H), 5.32 – 5.21 (m, 0.5H), 4.52 – 4.27 (m, 1.5H), 4.23 – 4.13 (m, 0.5H), 3.78 – 3.65 (m, 0.5H), 1.92 – 1.70 (m, 2H), 1.64 – 1.16 (m, 8H), 0.95 – 0.83 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.7, 132.9, 132.8, 129.5, 128.2, 128.1, 73.2, 67.8, 59.1, 45.6, 34.5, 31.4, 31.3, 28.8, 28.5, 25.8, 24.8, 22.3, 13.8.

HRMS (ESI⁺) m/z: $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{21}\text{ClNaO}_2$, 291.1128; Found: 291.1122.



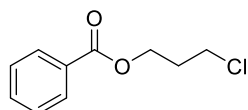
2-Bromoethyl benzoate (4k)¹⁶

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 15/1) as a yellow oil (24.1 mg, 52%). ^1H NMR (400 MHz, CDCl_3) δ 8.09 (dd, $J = 8.2, 1.1$ Hz, 2H), 7.60 – 7.56 (m, 1H), 7.46 (t, $J = 7.7$ Hz, 2H), 4.62 (t, $J = 6.1$ Hz, 2H), 3.64 (t, $J = 6.1$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.0, 133.2, 129.7, 129.5, 128.4, 64.1, 28.8.



2-Bromoethyl 2-naphthoate (4l)¹⁷

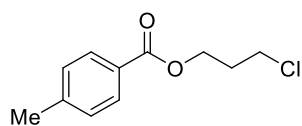
The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 25/1) as colorless oil (41.0 mg, 73%). ^1H NMR (400 MHz, CDCl_3) δ 8.64 (s, 1H), 8.08 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.97 (d, $J = 8.2$ Hz, 1H), 7.91 – 7.87 (m, 2H), 7.63 – 7.53 (m, 2H), 4.69 (t, $J = 6.1$ Hz, 2H), 3.70 (t, $J = 6.1$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.2, 135.6, 132.4, 131.3, 129.4, 128.4, 128.2, 127.7, 126.8, 126.7, 125.1, 64.3, 28.8.



1-Propanol, 3-chloro-, 1-benzoate (4m)¹⁸

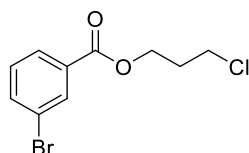
The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 30/1) as colorless oil (15.1 mg, 38%). ^1H NMR (500 MHz, CDCl_3) δ 8.05 – 7.98 (m, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 4.48 (t,

$J = 6.1$ Hz, 2H), 3.70 (t, $J = 6.4$ Hz, 2H), 2.24 (p, $J = 6.2$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.3, 133.0, 130.0, 129.5, 128.4, 61.6, 41.2, 31.7.



Benzoic acid, 4-methyl 3-chloropropyl ester (4n)¹⁹

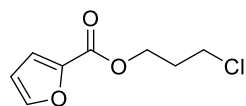
The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 40/1) as colorless oil (13.4 mg, 31%). ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.0$ Hz, 2H), 4.45 (t, $J = 6.0$ Hz, 2H), 3.69 (t, $J = 6.4$ Hz, 2H), 2.40 (s, 3H), 2.22 (p, $J = 6.3$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.4, 143.7, 129.5, 129.0, 127.2, 61.4, 41.3, 31.7, 21.6.



3-Chloropropyl-3-bromo-benzoate (4o)

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 30/1) as colorless oil (10.7 mg, 19%). ^1H NMR (500 MHz, CDCl_3) δ 8.14 (s, 1H), 7.95 (d, $J = 7.8$ Hz, 1H), 7.69 – 7.66 (m, 1H), 7.31 (t, $J = 7.9$ Hz, 1H), 4.47 (t, $J = 6.0$ Hz, 2H), 3.68 (t, $J = 6.4$ Hz, 2H), 2.23 (p, $J = 6.2$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 164.9, 135.9, 132.5, 131.9, 129.9, 128.1, 122.4, 62.1, 41.1, 31.5.

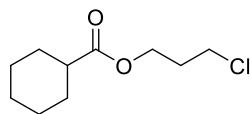
HRMS (ESI⁺) (m/z): $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{10}\text{H}_{10}\text{BrClNaO}_2$, 298.9450; Found: 298.9445.



3-Chloropropyl 2-furancarboxylate (4p)²⁰

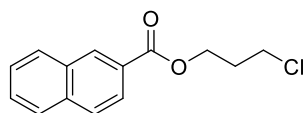
The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 30/1) as colorless oil (14.5 mg, 39%). ^1H NMR (500 MHz, CDCl_3) δ 7.56 (d, $J = 1.0$ Hz, 1H), 7.16 (dd, $J = 3.5, 0.9$ Hz, 1H), 6.49 (dd, $J = 3.5, 1.7$

Hz, 1H), 4.43 (t, $J = 6.1$ Hz, 2H), 3.65 (t, $J = 6.4$ Hz, 2H), 2.19 (p, $J = 6.3$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 158.43, 146.36, 144.36, 118.03, 111.80, 61.51, 41.03, 31.56.



3-Chloropropyl cyclohexanecarboxylate (4q)²¹

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 30/1) as colorless oil (16.1 mg, 39%). ^1H NMR (500 MHz, CDCl_3) δ 4.18 (t, $J = 6.1$ Hz, 2H), 3.58 (t, $J = 6.5$ Hz, 2H), 2.27 – 2.25 (m, 1H), 2.06 (p, $J = 6.3$ Hz, 2H), 1.87 (dd, $J = 13.2, 3.8$ Hz, 2H), 1.75 – 1.69 (m, 2H), 1.64 – 1.59 (m, 1H), 1.45 – 1.36 (m, 2H), 1.30 – 1.15 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 175.9, 60.7, 43.1, 41.2, 31.6, 28.9, 25.6, 25.3.



3-Chloropropyl-2-naphthalenecarboxylate (4r)

The crude product was purified by flash column chromatography (Petroleum Ether/Ethyl Acetate = 30/1) as a colorless oil (21.1 mg, 42%). ^1H NMR (500 MHz, CDCl_3) δ 8.60 (d, $J = 1.6$ Hz, 1H), 8.06 (dd, $J = 8.5, 1.7$ Hz, 1H), 7.96 (d, $J = 8.6$ Hz, 1H), 7.89 (d, $J = 8.7$ Hz, 2H), 7.64 – 7.48 (m, 2H), 4.55 (t, $J = 6.0$ Hz, 2H), 3.75 (t, $J = 6.4$ Hz, 2H), 2.29 (p, $J = 6.2$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.5, 135.5, 132.4, 131.0, 129.3, 128.3, 128.2, 127.7, 127.2, 126.7, 125.1, 61.8, 41.3, 31.8.

HRMS (ESI⁺) (m/z): $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{13}\text{ClNaO}_2$, 271.0502; Found: 271.0496.

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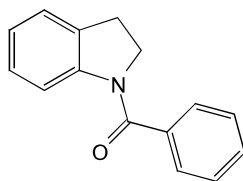
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6. Copies of NMR Spectra

7.56
7.54
7.54
7.48
7.46
7.44
7.42
7.42
7.22
7.20
7.02

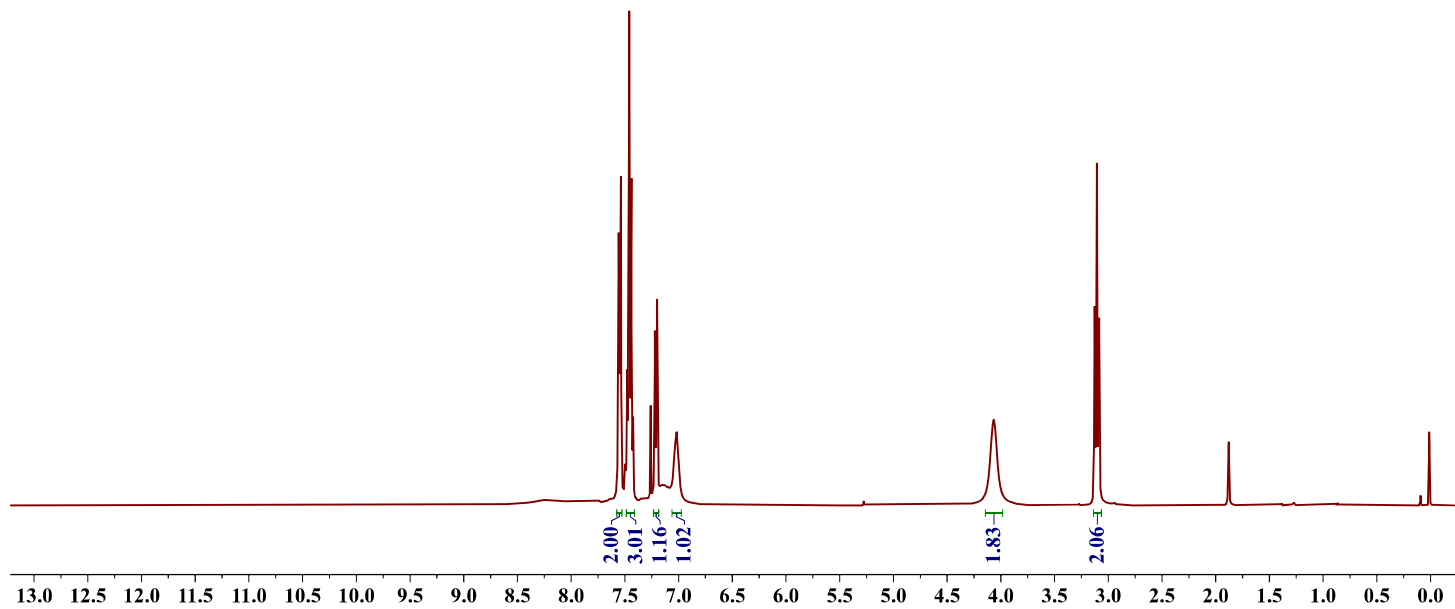
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1a-S₁

¹H NMR (400 MHz, CDCl₃)



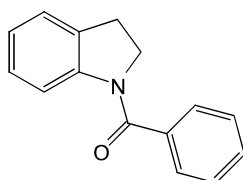
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123.83

77.32
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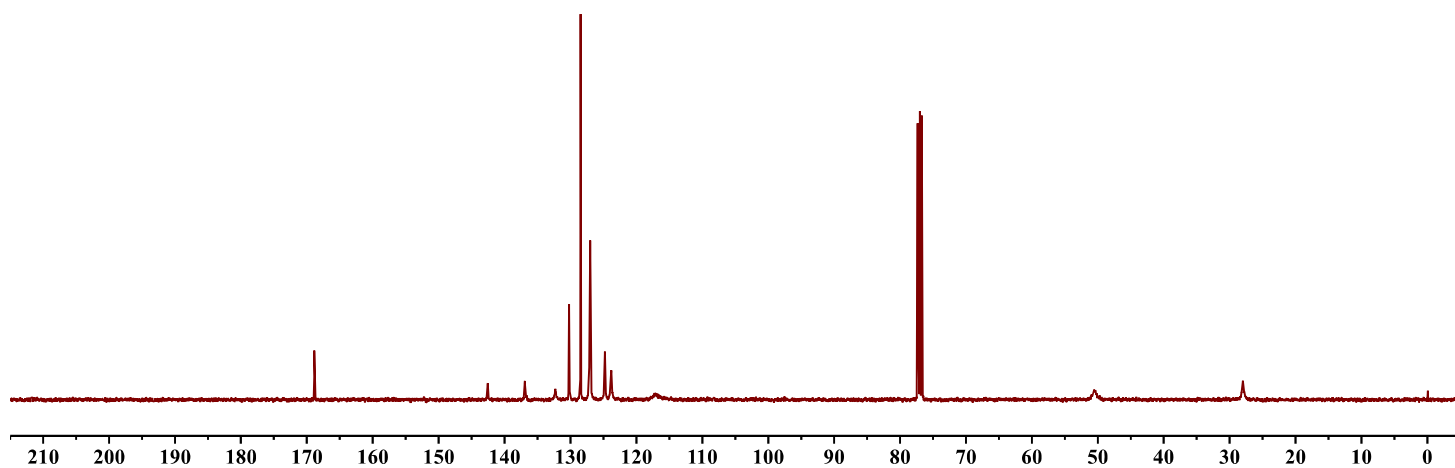
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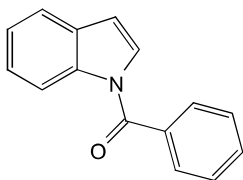


1a-S₁

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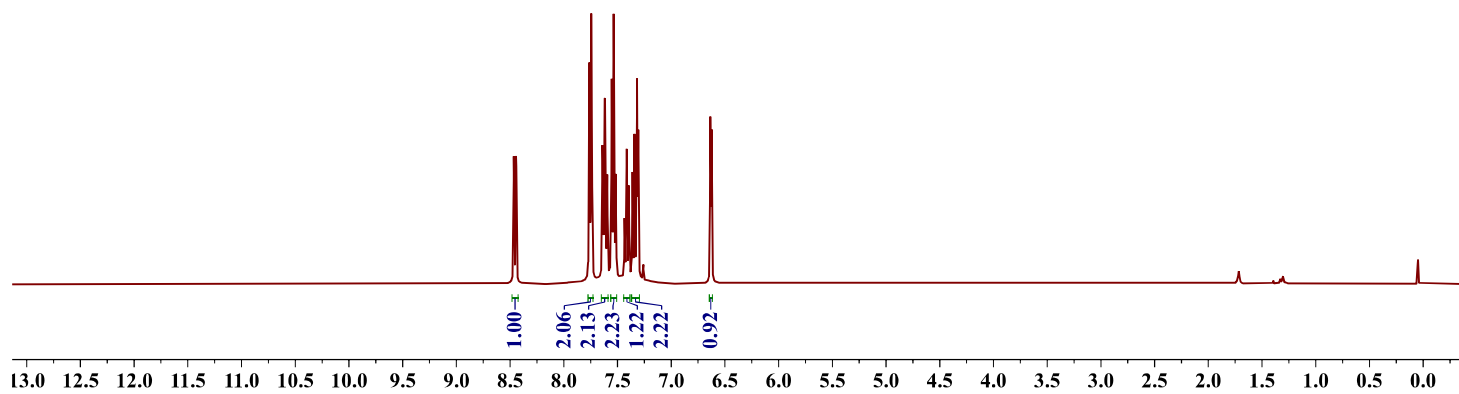


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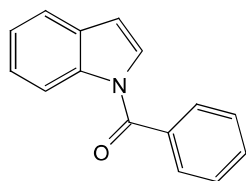


1a-S₂

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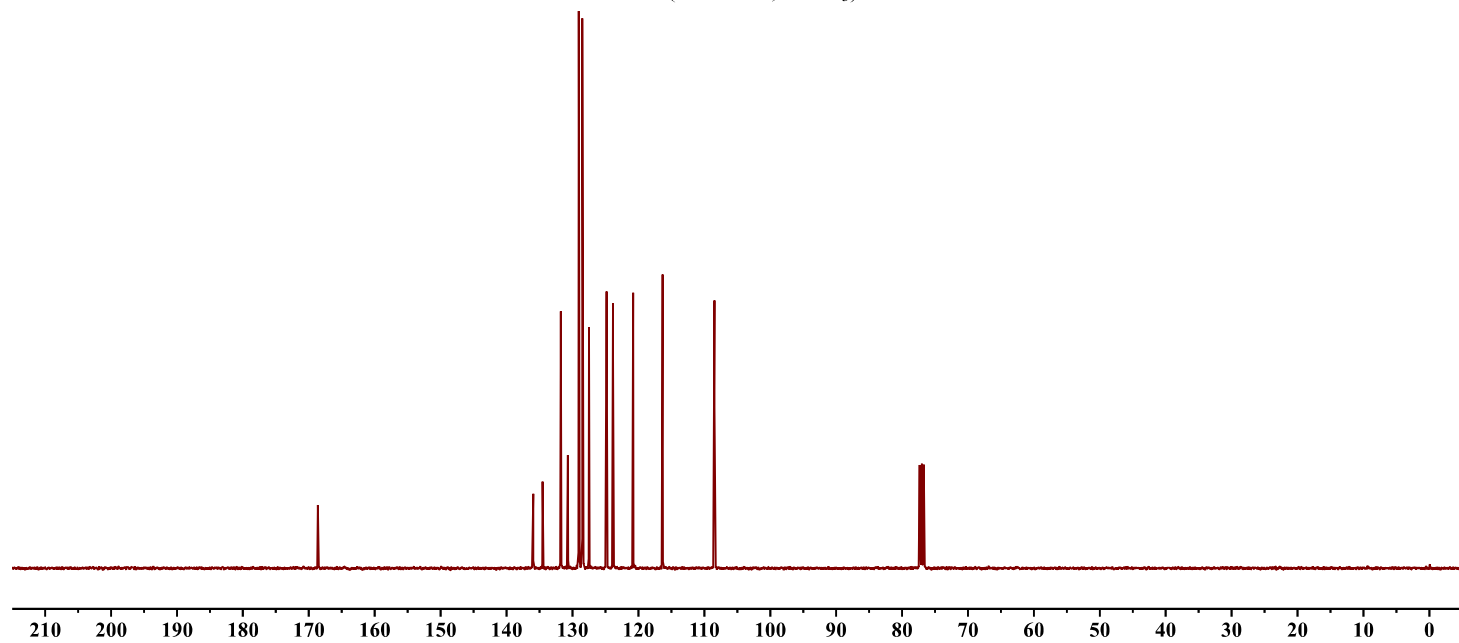


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108.47
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77.00
76.68

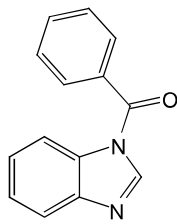


1a-S₂

¹³C NMR (101 MHz, CDCl₃)

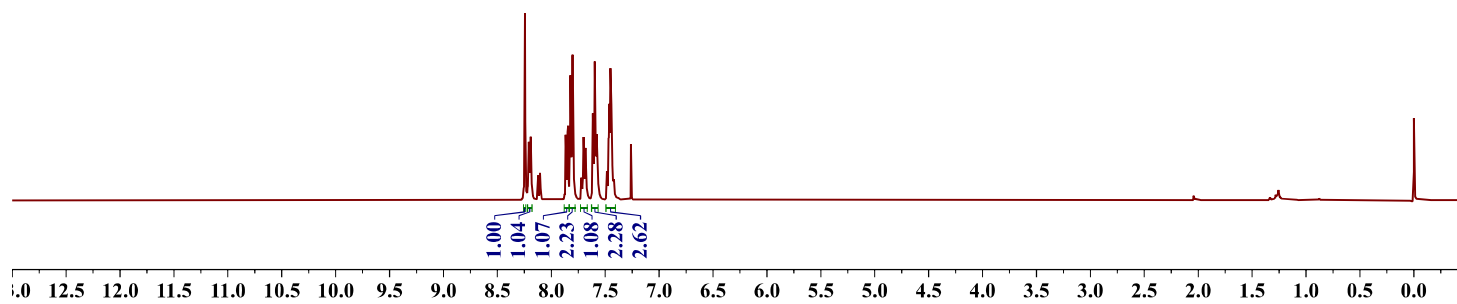


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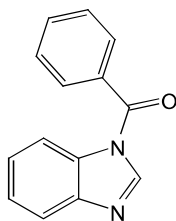


1a-S₃

¹H NMR (400 MHz, CDCl₃)

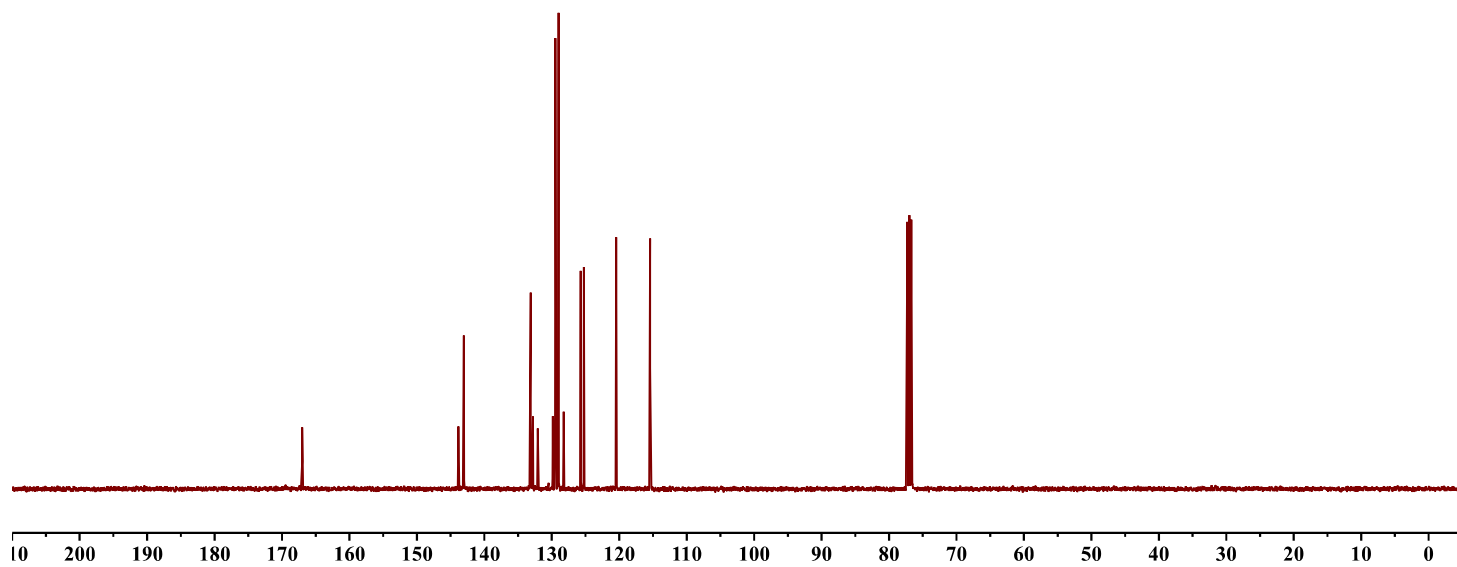


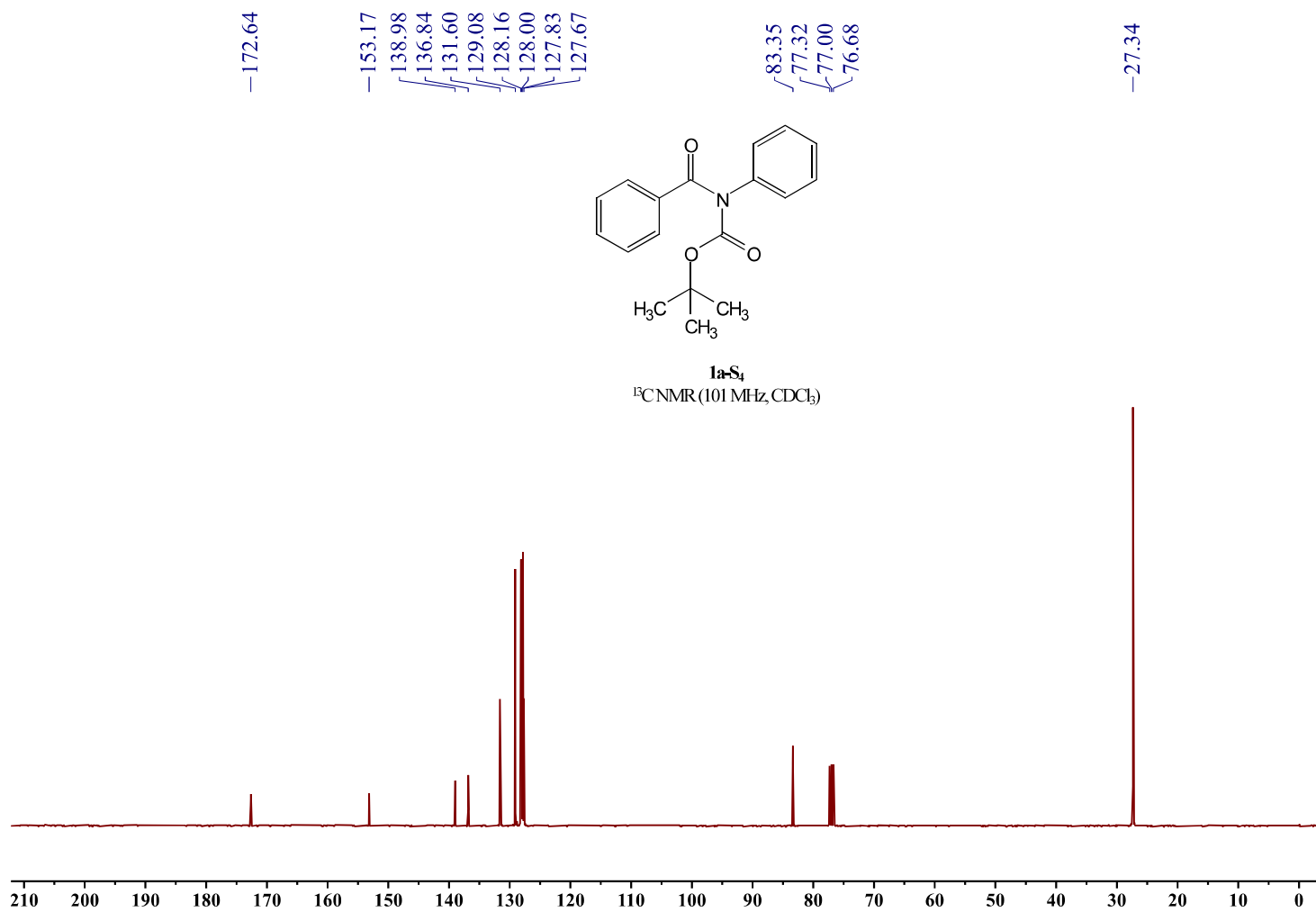
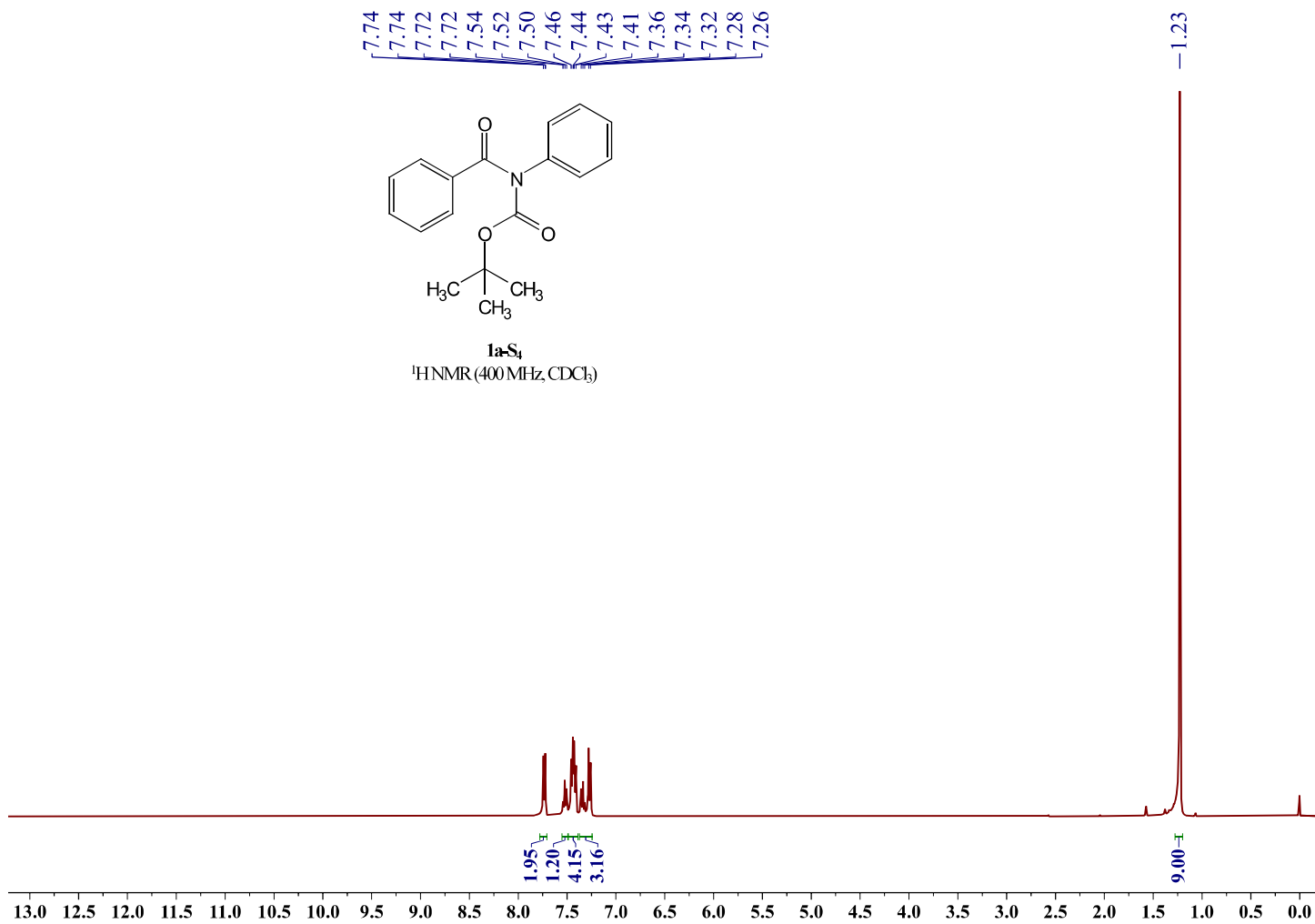
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132.06
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77.00



1a-S₃

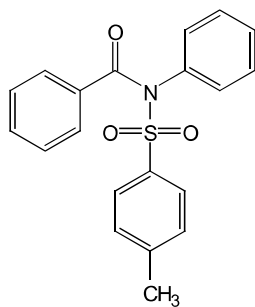
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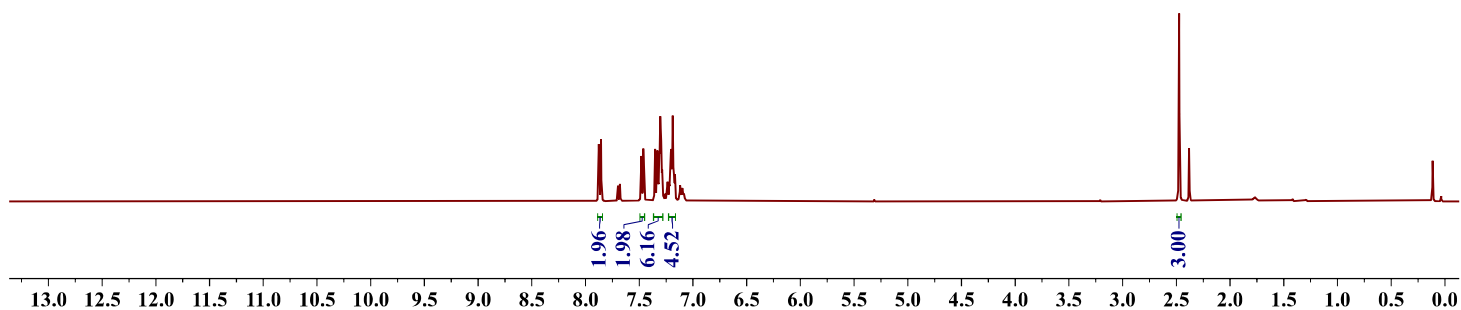


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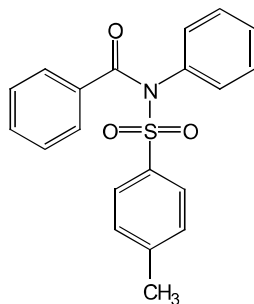


1a-S₅
¹H NMR (400 MHz, CDCl₃)

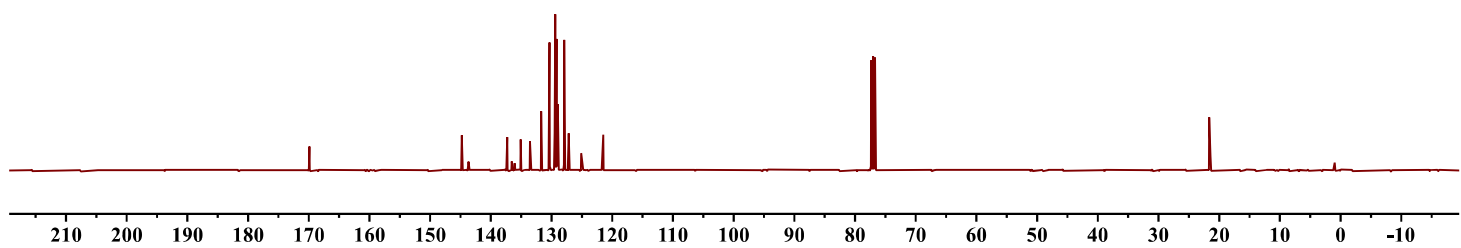


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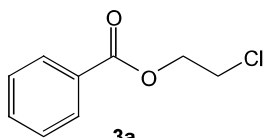
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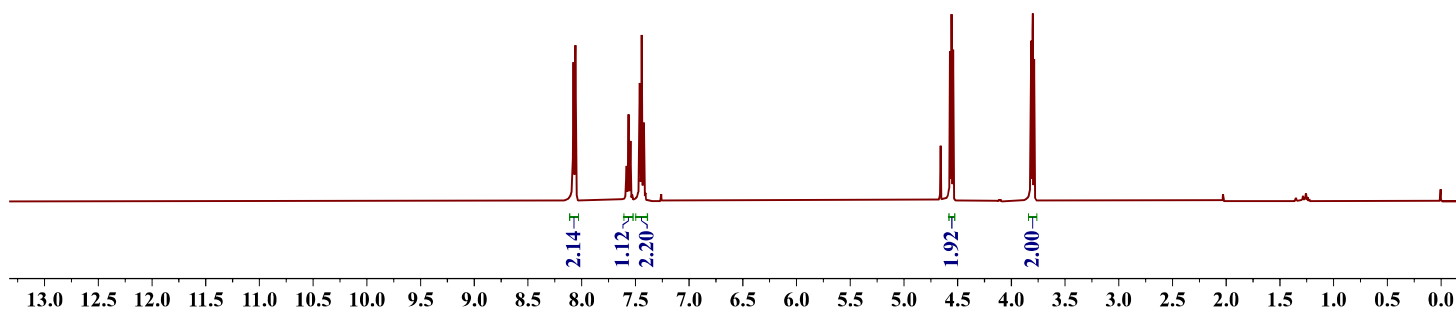
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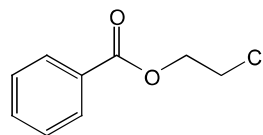
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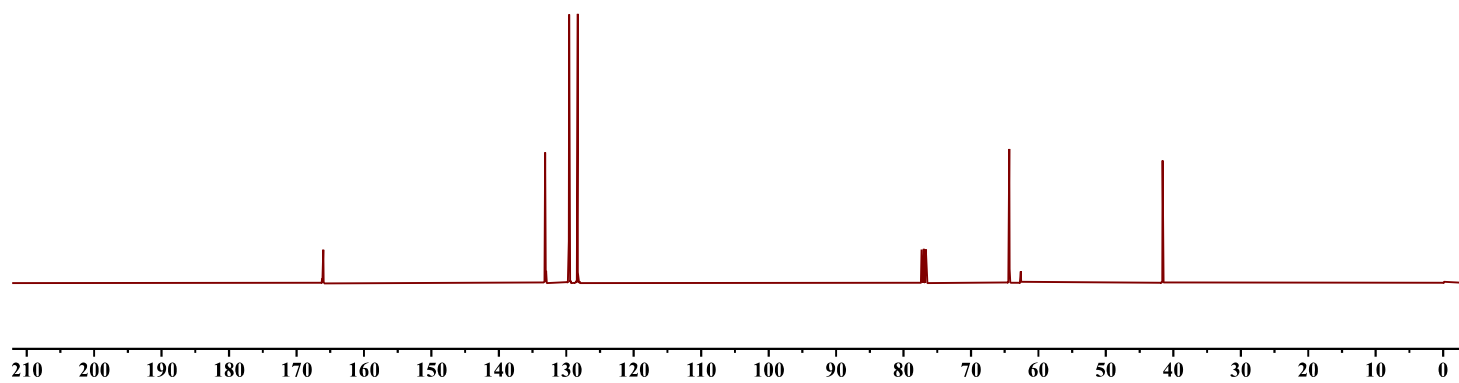
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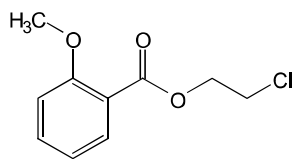
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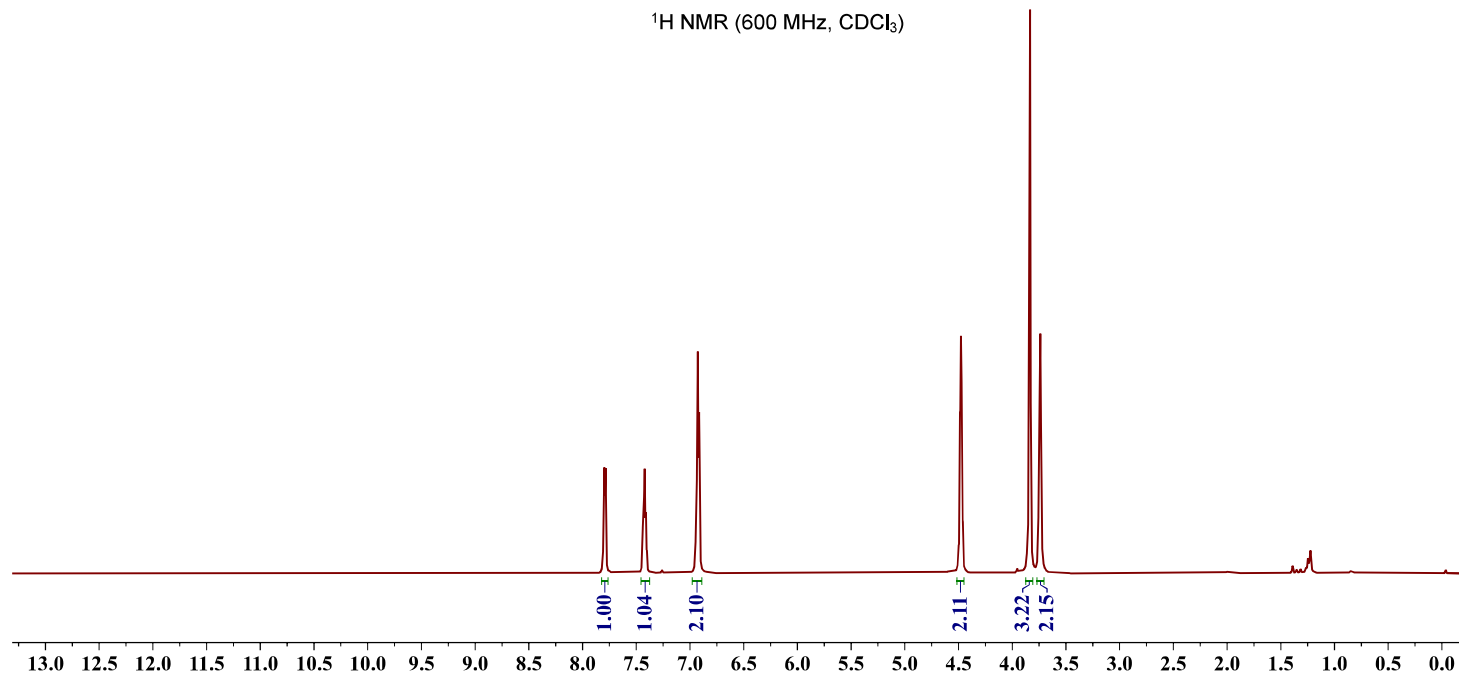


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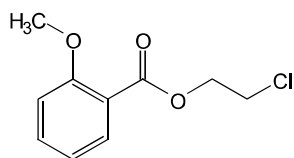


3b

¹H NMR (600 MHz, CDCl₃)

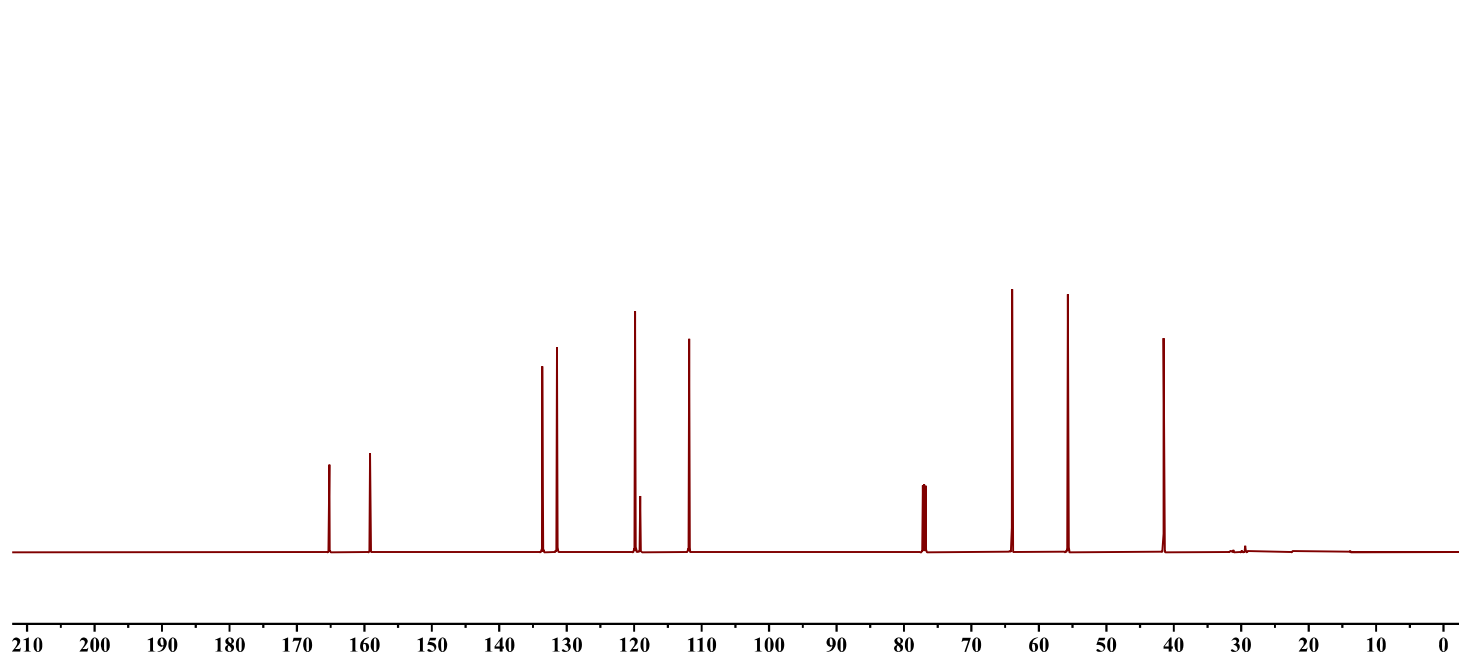


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63.97
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41.50

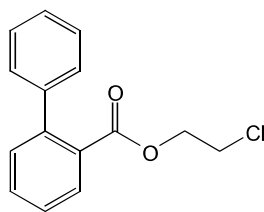


3b

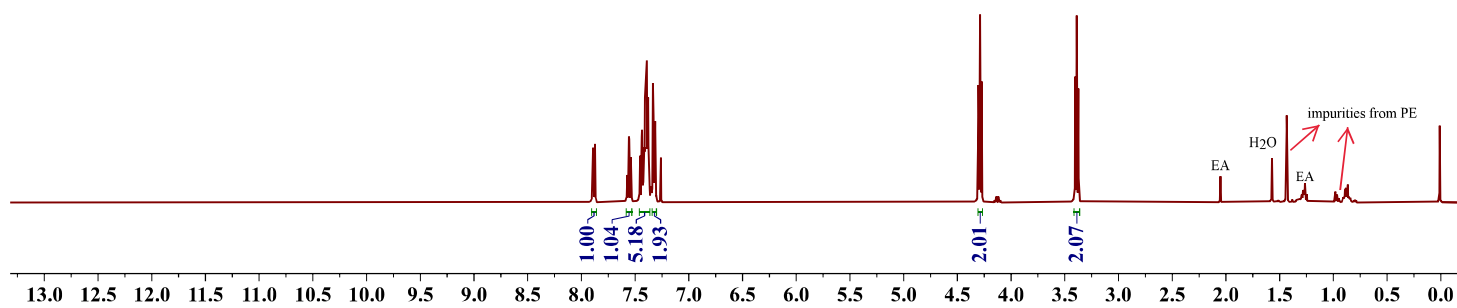
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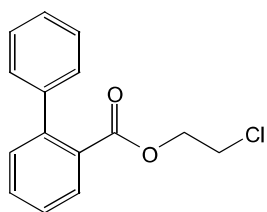
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3.37



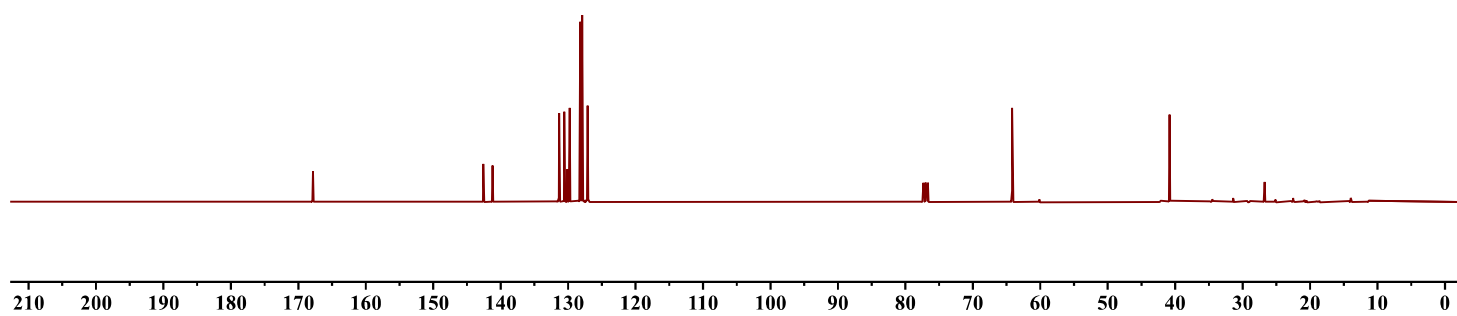
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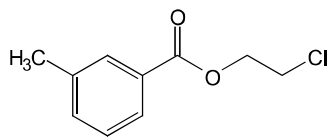
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-64.16
-40.82



3c
¹³C NMR (101 MHz, CDCl₃)

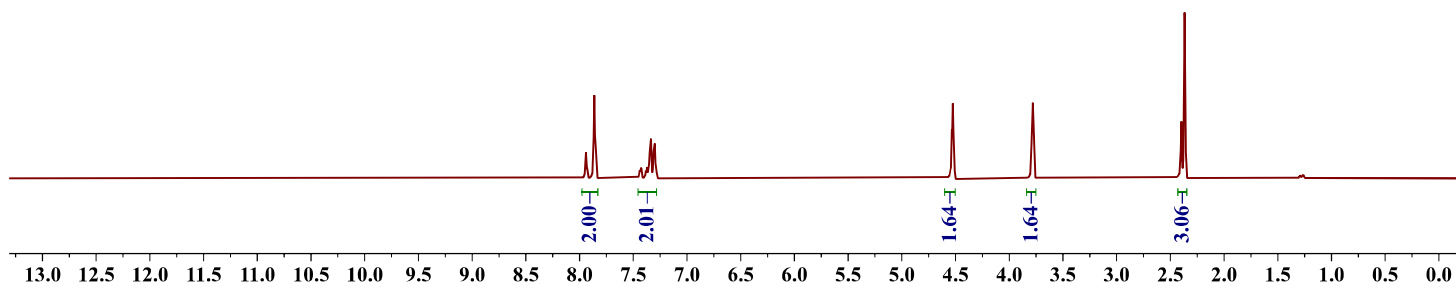


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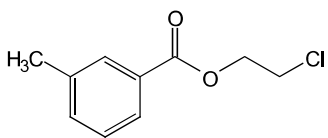


3d

¹H NMR (600 MHz, CDCl₃)

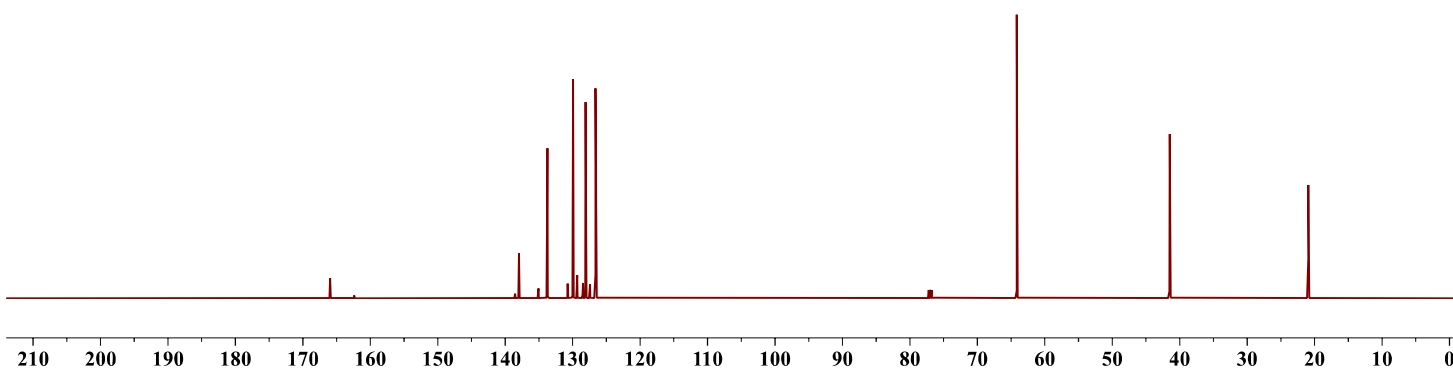


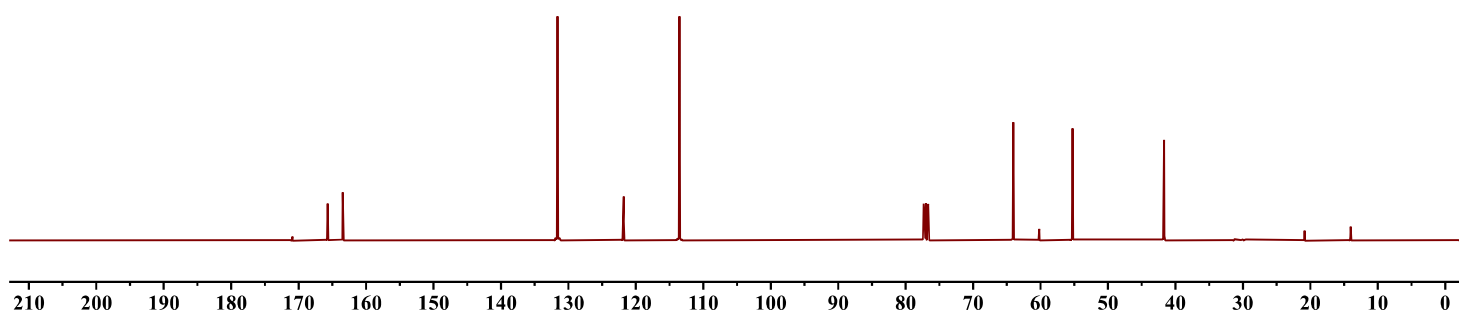
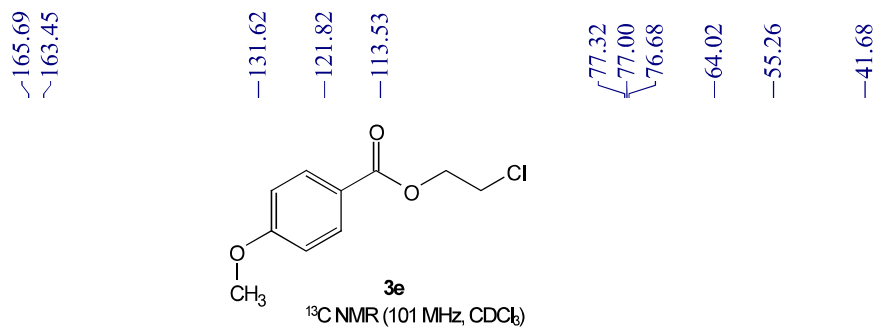
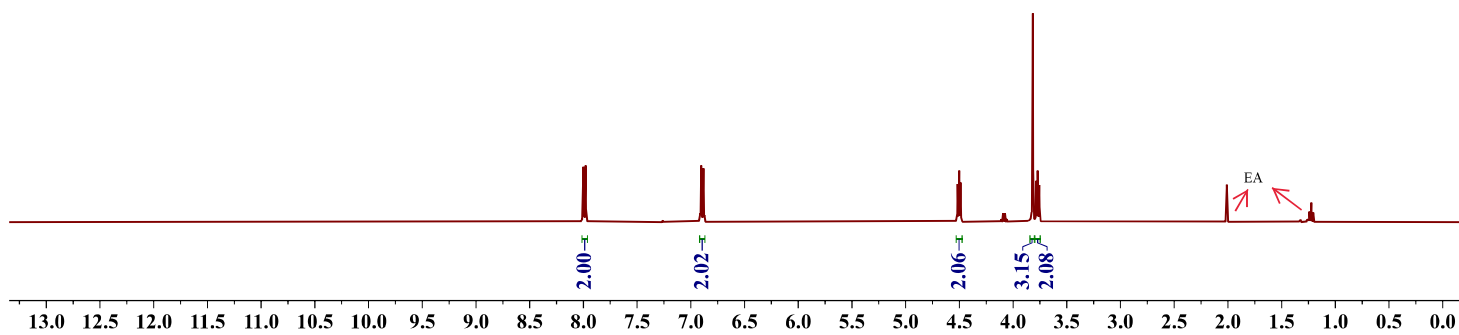
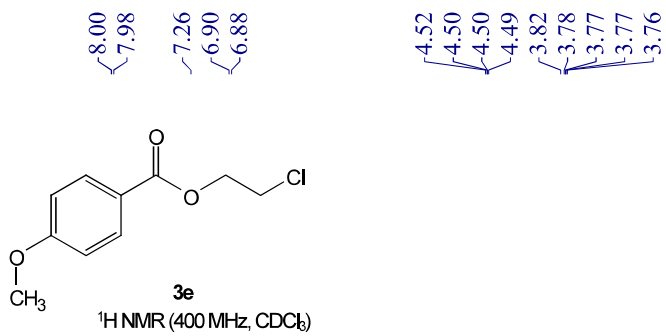
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-20.94



3d

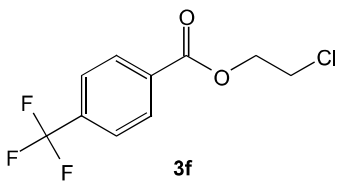
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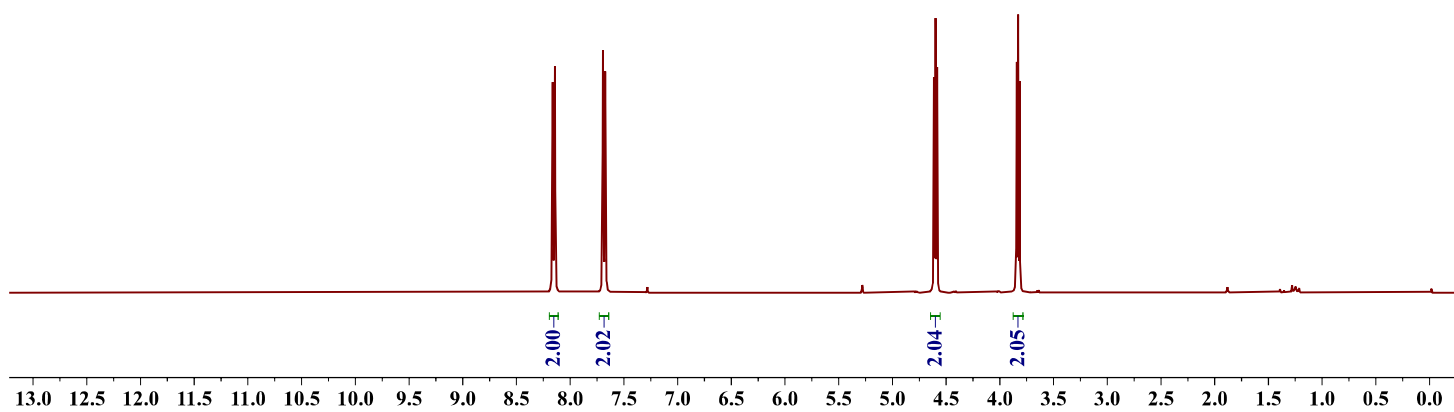


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3.83
3.82



¹H NMR (400 MHz, CDCl₃)



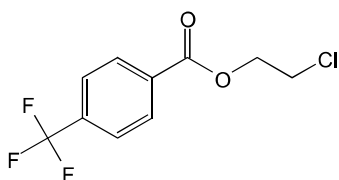
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125.39
125.35
125.31
125.28
124.86
122.15

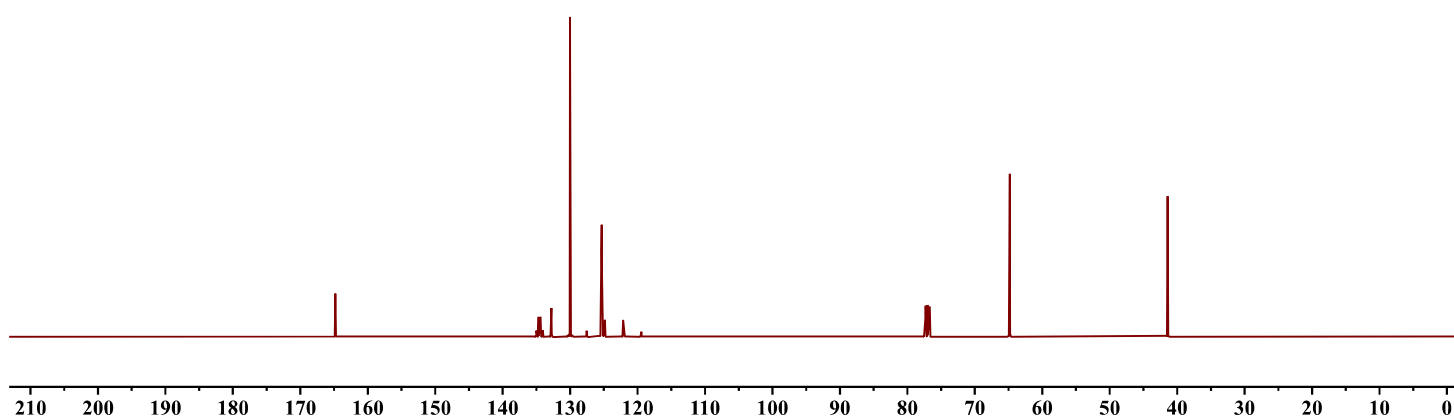
77.32
77.00
76.68

64.81

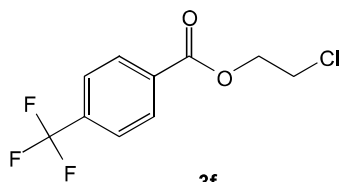
41.42



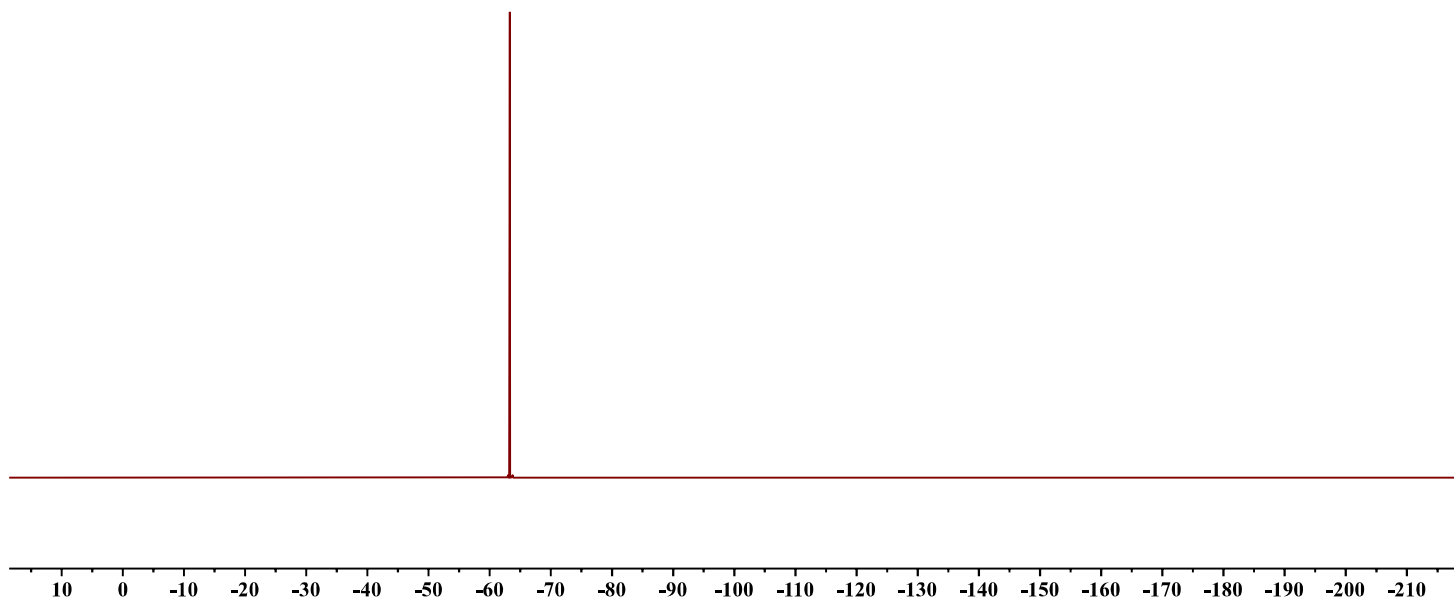
¹³C NMR (101 MHz, CDCl₃)



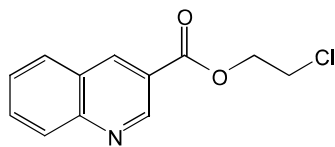
--63.29



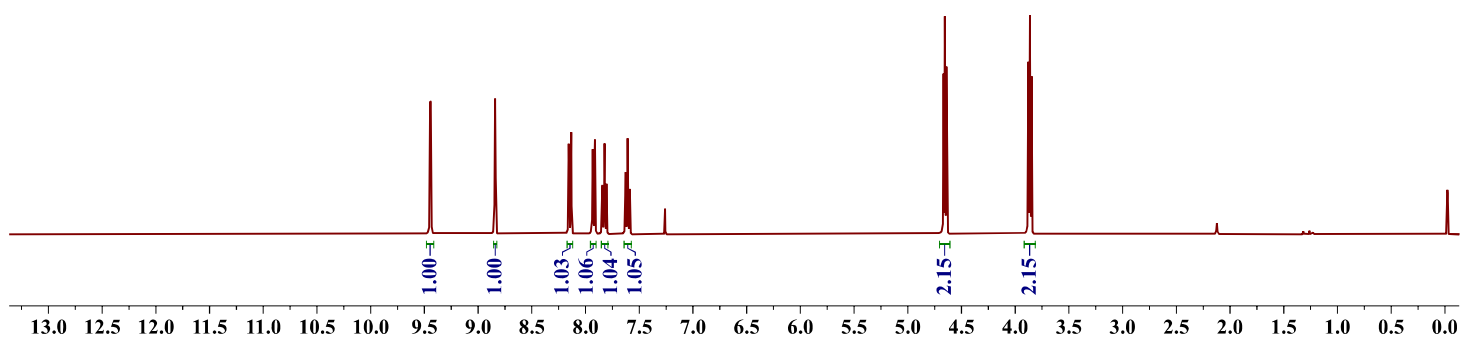
¹⁹F NMR (376 MHz, CDCl₃)



9.45
9.44
8.84
8.84
8.16
8.13
7.93
7.91
7.84
7.84
7.83
7.82
7.81
7.80
7.63
7.63
7.61
7.61
7.60
7.59
7.59
7.26
7.26
4.67
4.65
4.64
3.88
3.86
3.85



¹H NMR (400 MHz, CDCl₃)



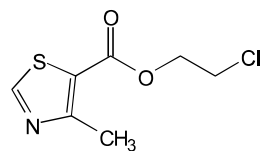
161.34
161.01
155.63

121.33

77.32
77.00
76.68

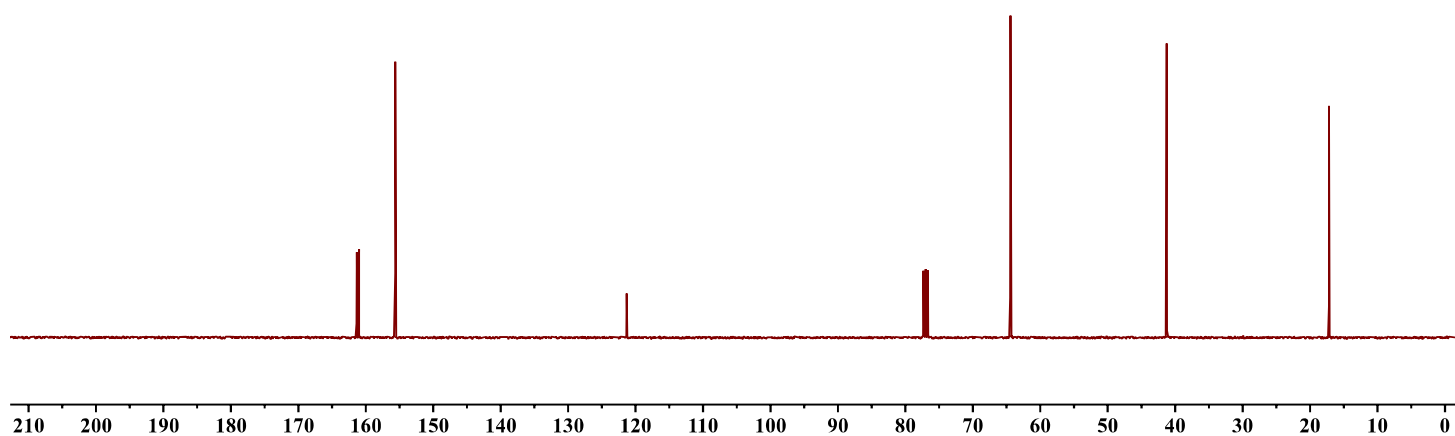
41.26

17.20



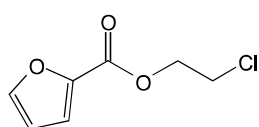
3h

¹³C NMR (101 MHz, CDCl₃)



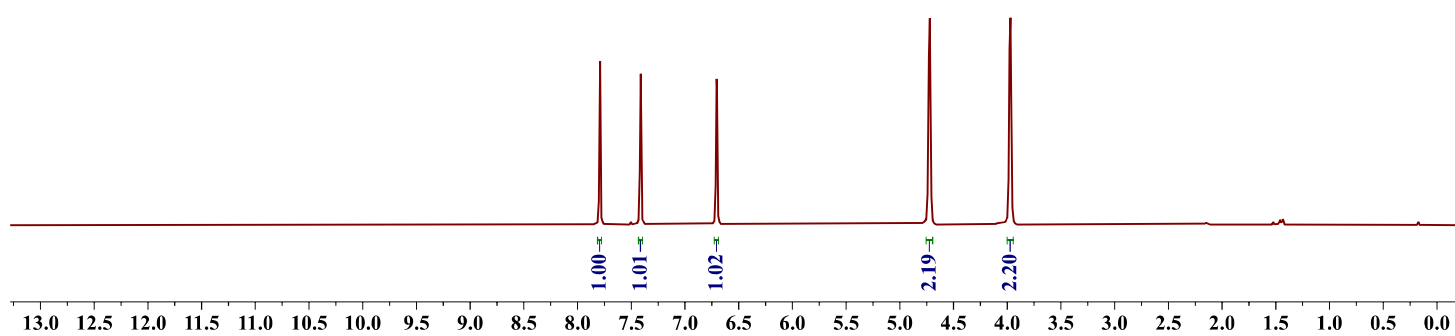
7.79
7.41
7.26
6.71

4.73
4.72
4.71
3.98
3.97
3.96

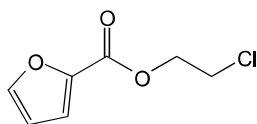


3i

¹H NMR (600 MHz, CDCl₃)

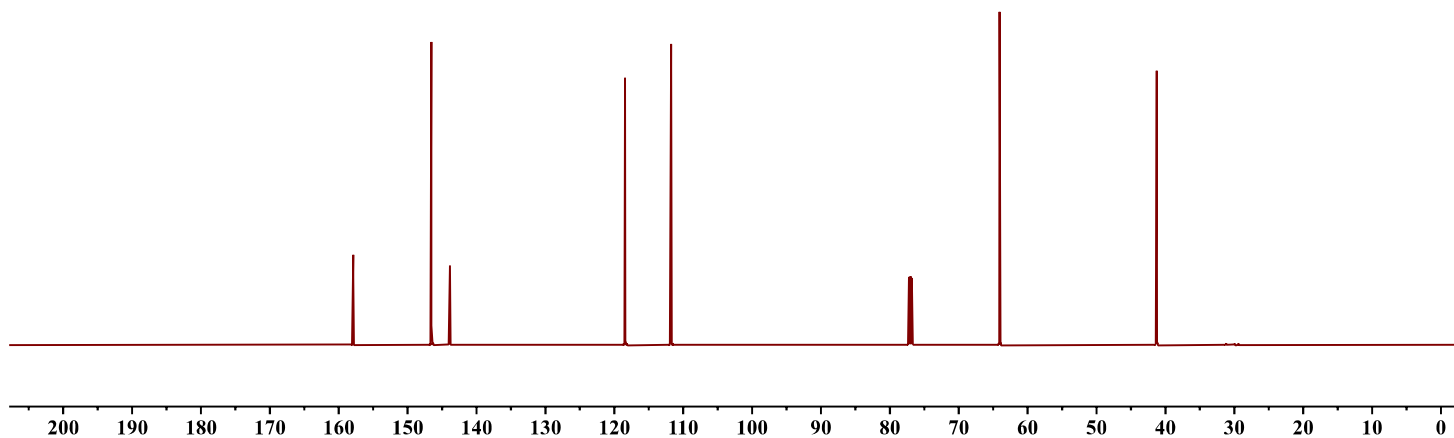


-157.91
-146.55
-143.84
-118.43
-111.76
77.21
77.00
76.79
-64.06
-41.28

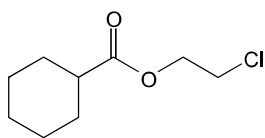


3i

¹³C NMR (151 MHz, CDCl₃)

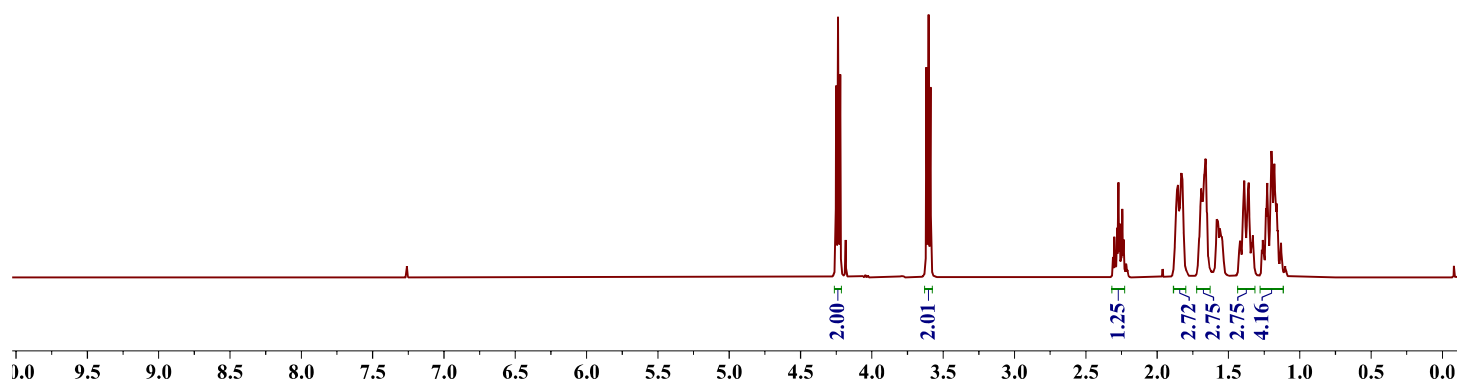


7.26
4.25
4.24
4.22
3.62
3.60
3.59
2.31
2.30
2.29
2.28
2.27
2.26
2.25
2.24
2.24
1.86
1.85
1.83
1.82
1.69
1.68
1.67
1.66
1.42
1.39
1.36
1.34
1.33
1.27
1.26
1.24
1.23
1.22
1.20
1.18
1.16
1.14
1.13
1.12



3j

¹H NMR (400 MHz, CDCl₃)



—181.89
—175.44

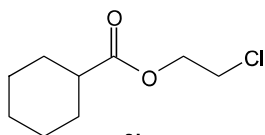
77.32
77.00
76.68

—63.47

42.74
41.55

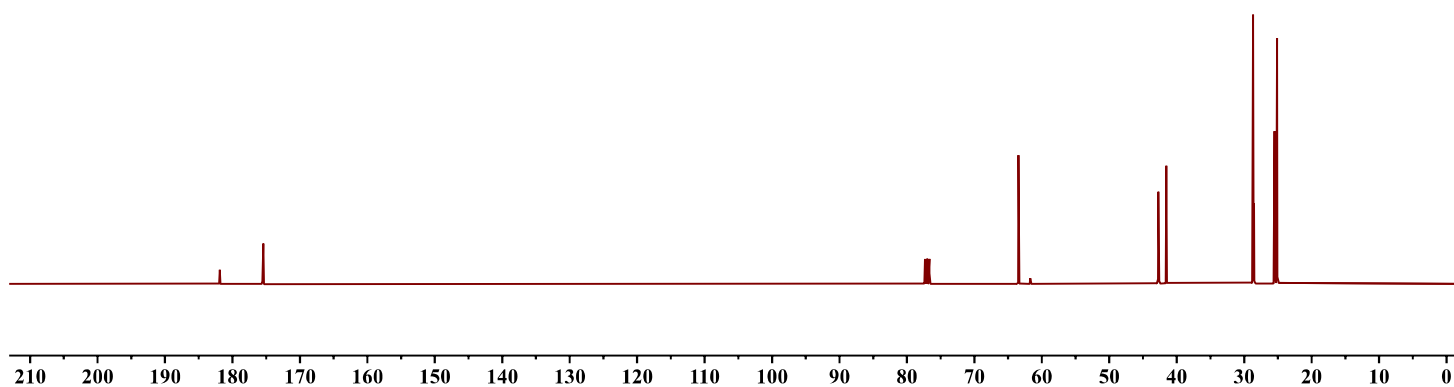
28.70
28.54

25.48
25.13



3j

¹³C NMR (101 MHz, CDCl₃)



—7.26

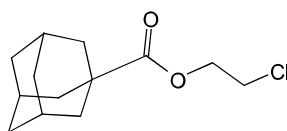
4.31
4.30
4.28

3.68
3.67
3.66

2.04
2.02
2.01

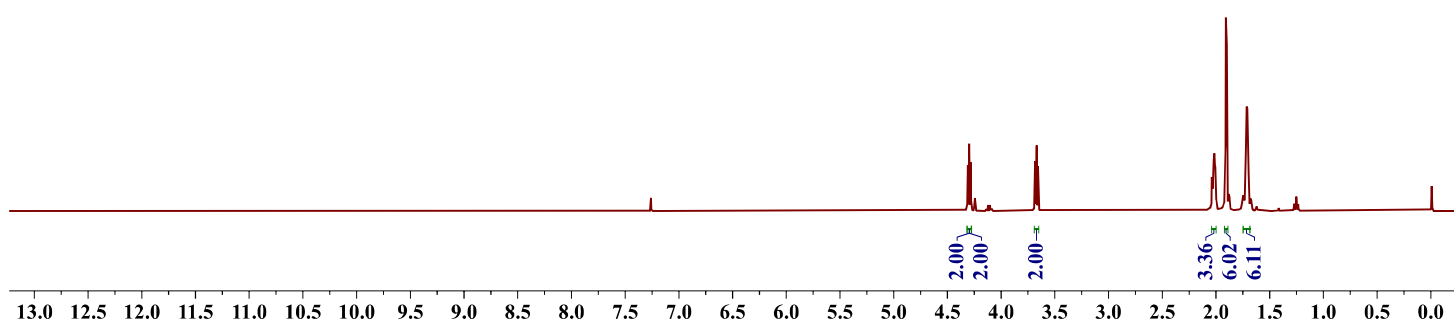
1.91
1.90
1.75

1.72
1.71
1.68



3k

¹H NMR (400 MHz, CDCl₃)

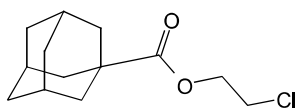


-176.83

77.32
77.00
76.68

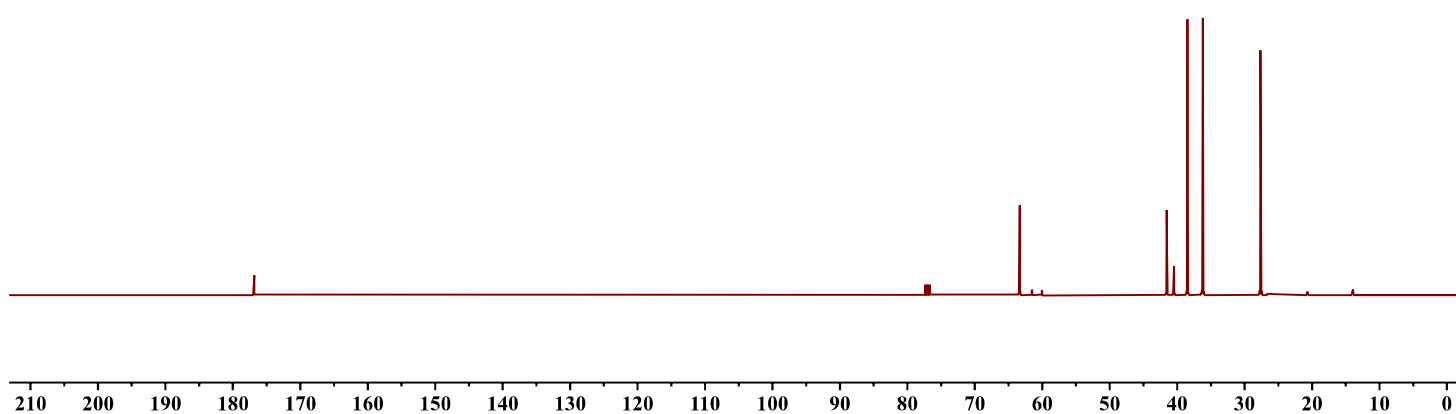
-63.34

41.56
40.48
38.48
36.20
-27.66



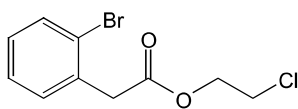
3k

¹³C NMR (101 MHz, CDCl₃)



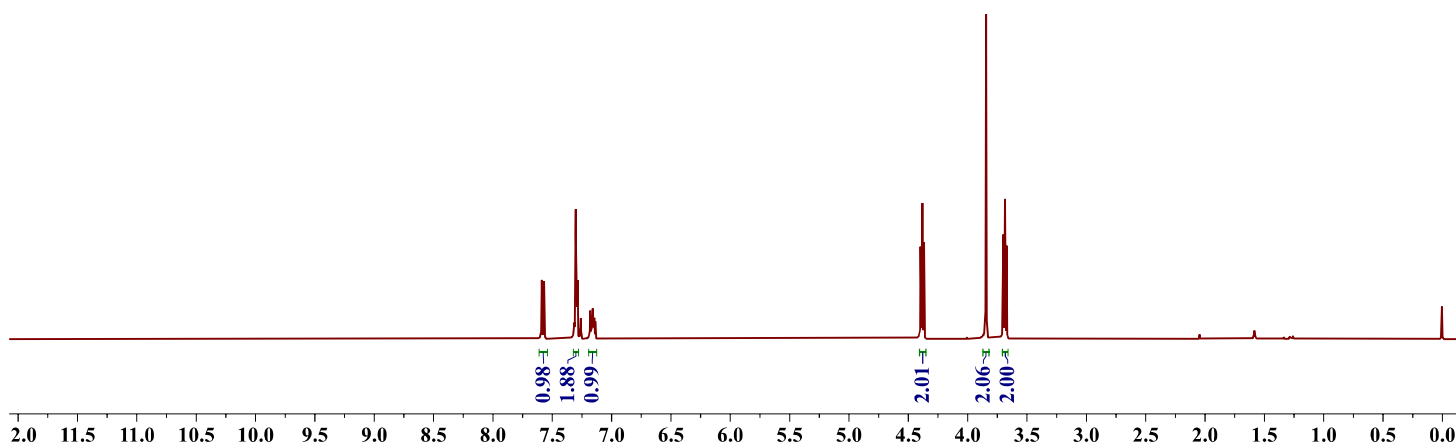
7.59
7.57
7.30
7.30
7.29
7.29
7.26
7.18
7.17
7.17
7.16
7.15
7.14
7.14

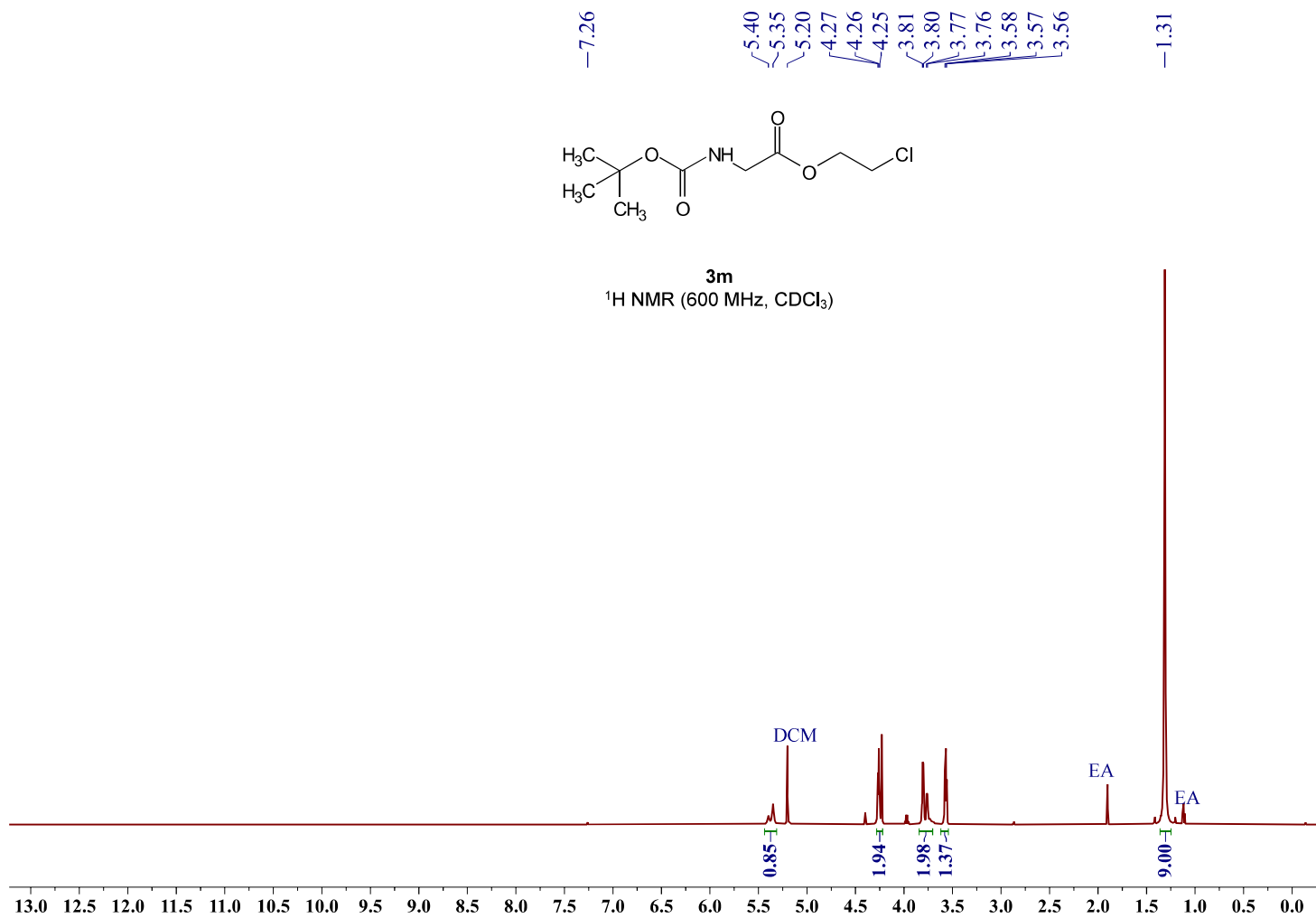
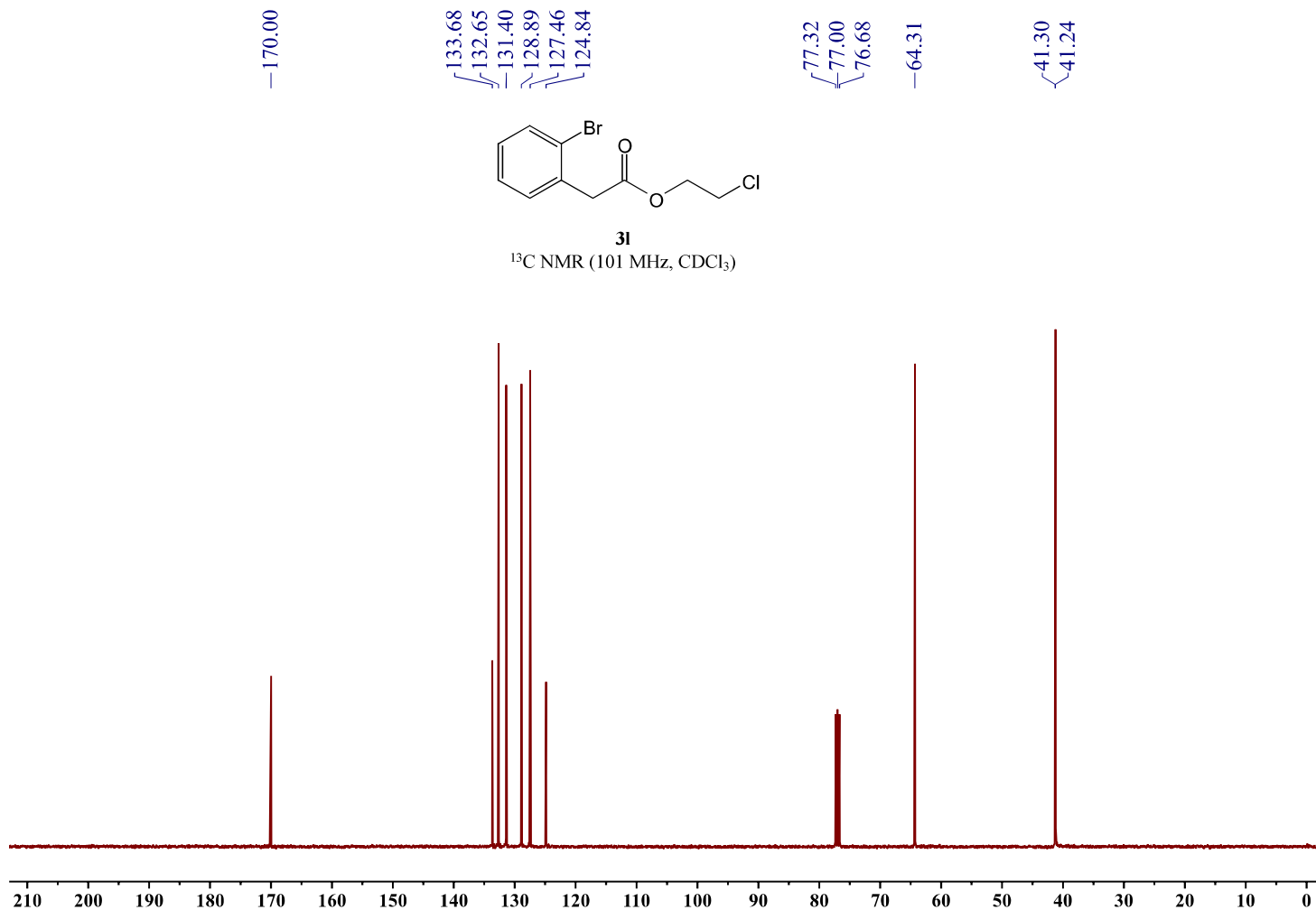
4.40
4.38
4.37
3.84
3.70
3.69
3.67

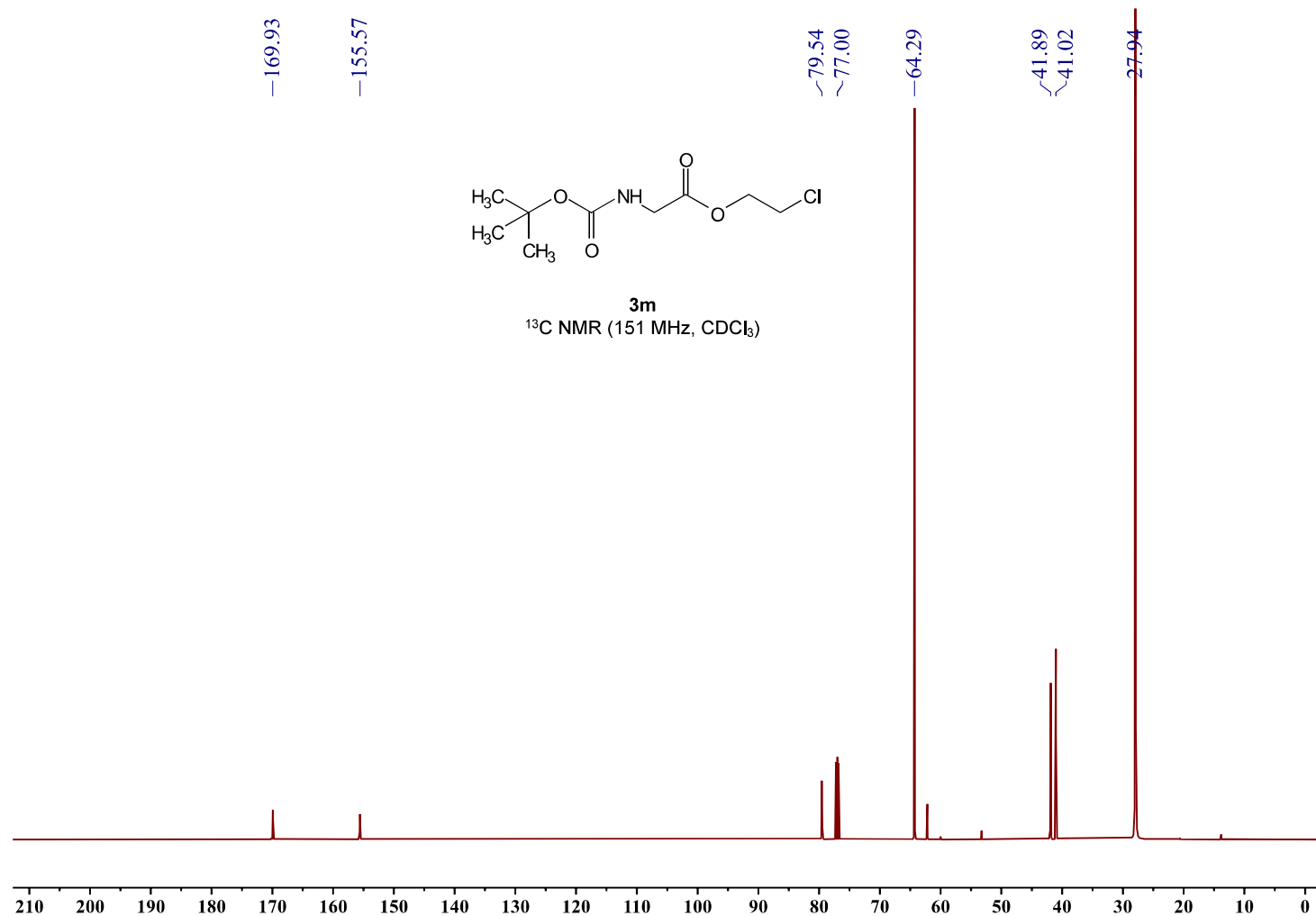


3l

¹H NMR (400 MHz, CDCl₃)

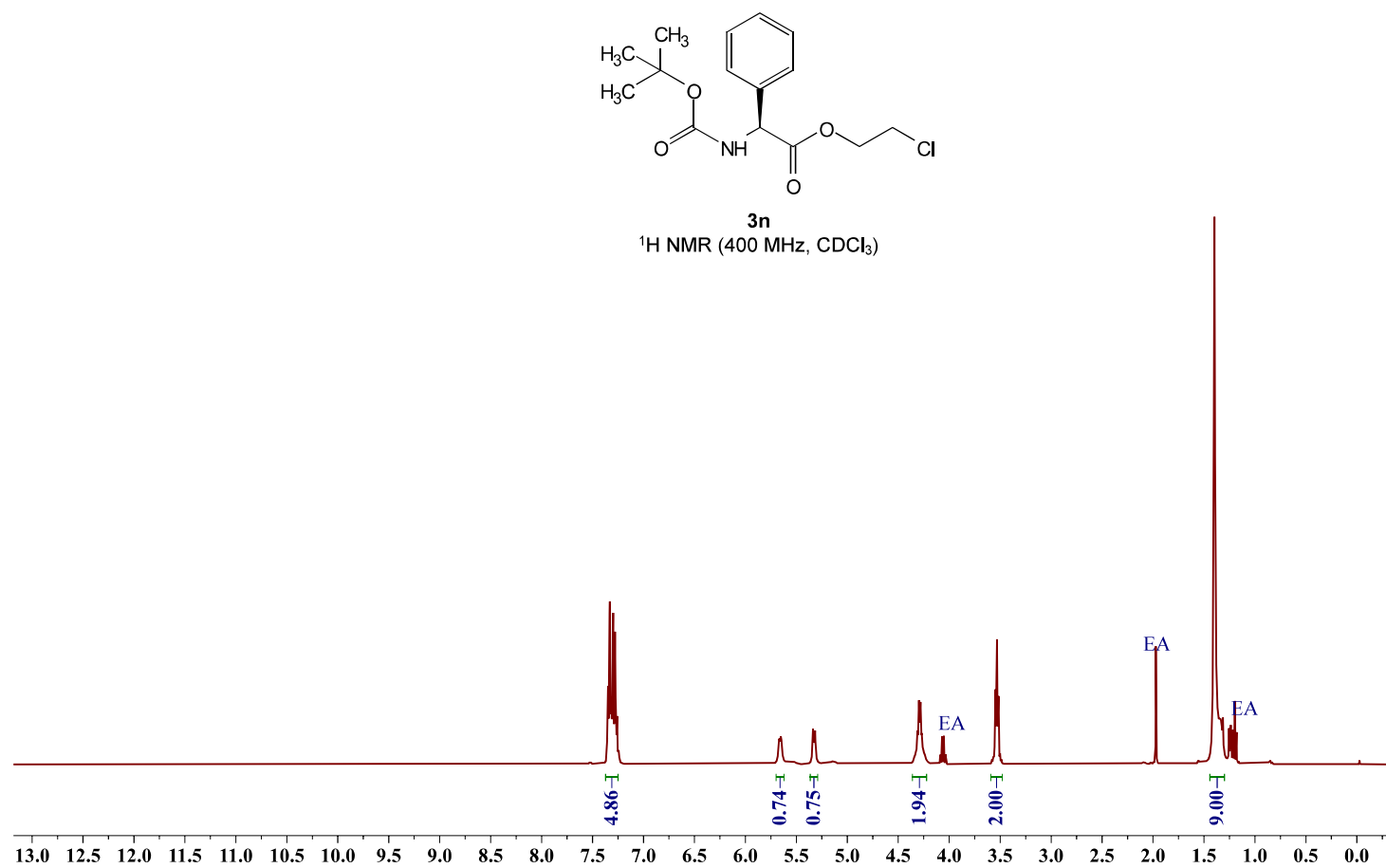




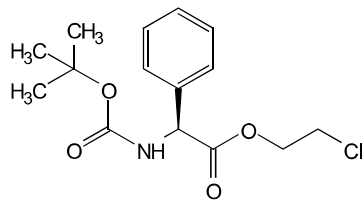


^1H NMR (400 MHz, CDCl_3) spectrum of **3n** showing chemical shifts (ppm):

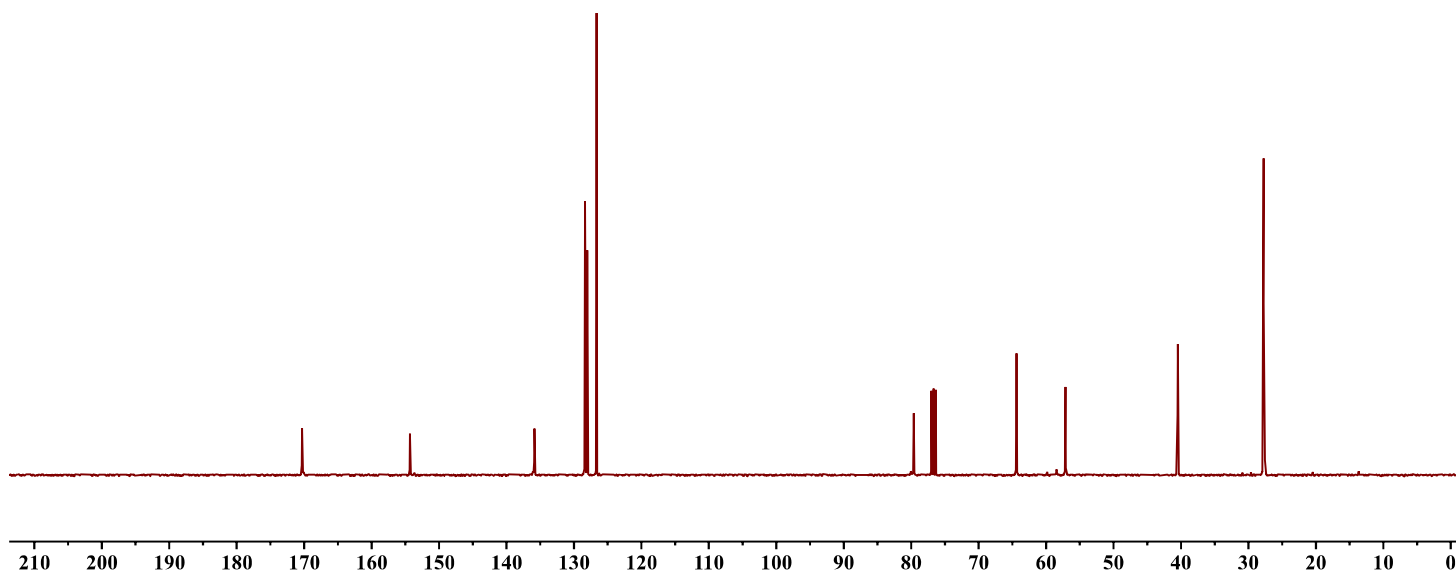
- 7.35
- 7.35
- 7.34
- 7.33
- 7.32
- 7.31
- 7.30
- 7.29
- 7.28
- 7.26
- 5.67
- 5.65
- 5.34
- 5.32
- 4.34
- 4.33
- 4.31
- 4.30
- 4.28
- 4.27
- 4.25
- 4.24
- 3.55
- 3.55
- 3.54
- 3.53
- 3.52
- 3.52
- 1.97
- 1.40



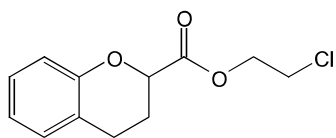
-170.31
 -154.30
 135.85
 128.37
 128.01
 126.66
 -79.61
 -77.00
 -64.37
 -57.13
 -40.48
 -27.75



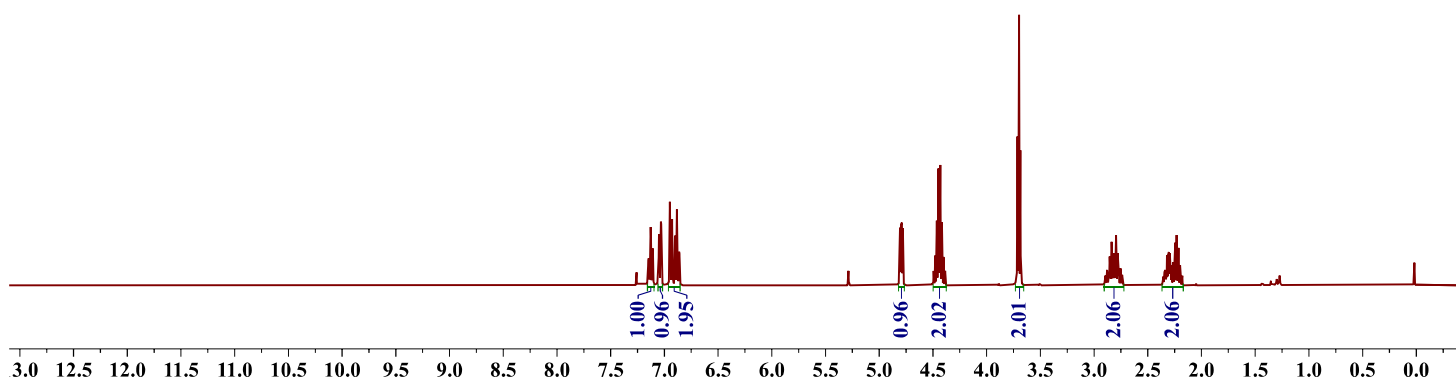
3n
¹³C NMR (101 MHz, CDCl₃)



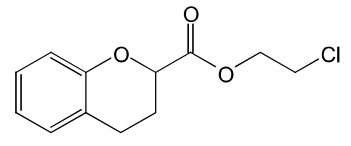
7.15
 7.13
 7.13
 7.11
 7.11
 7.05
 7.03
 6.95
 6.95
 6.93
 6.93
 6.90
 6.90
 6.88
 6.88
 6.86
 6.86
 4.81
 4.80
 4.79
 4.78
 4.48
 4.46
 4.45
 4.44
 4.43
 4.43
 4.42
 4.40
 3.71
 3.70
 3.69
 2.85
 2.84
 2.82
 2.81
 2.80
 2.78
 2.32
 2.31
 2.31
 2.30
 2.30
 2.29
 2.25
 2.25
 2.23
 2.23
 2.21



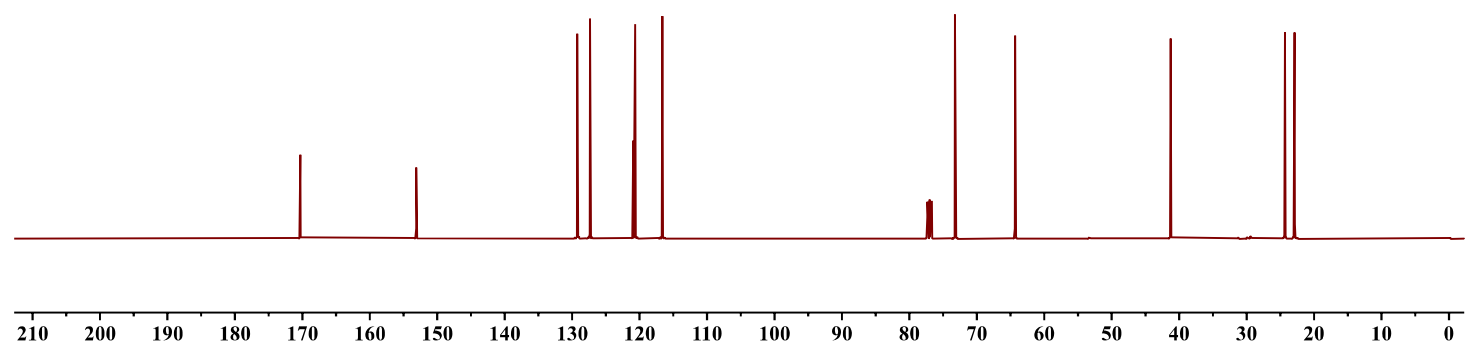
3o
¹H NMR (400 MHz, CDCl₃)



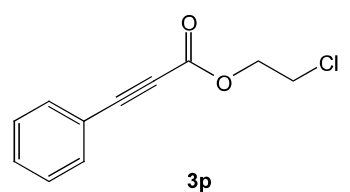
-170.31
 -153.09
 129.25
 127.36
 120.95
 120.67
 116.63
 77.32
 77.00
 76.68
 73.22
 64.35
 -41.25
 24.33
 22.89



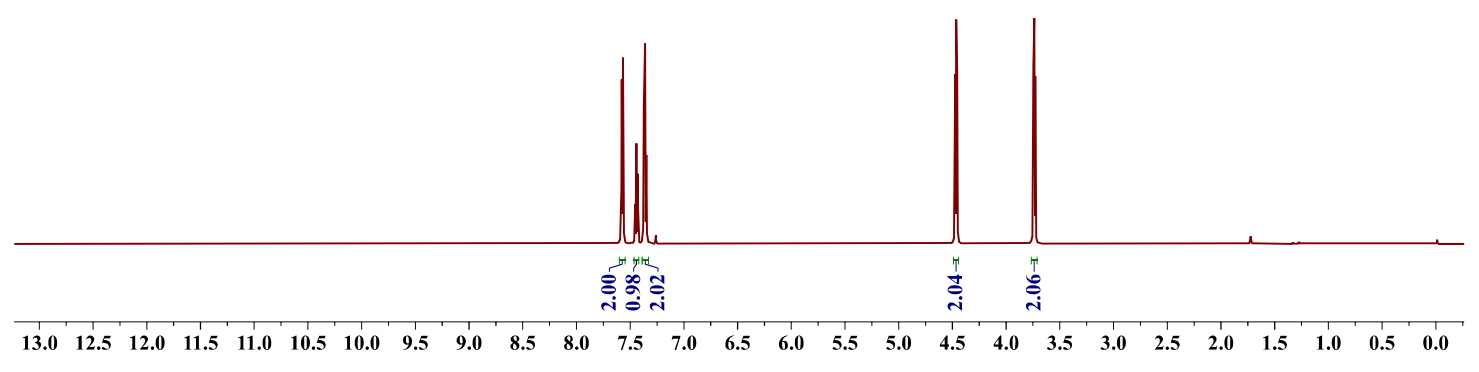
3o
¹³C NMR (101 MHz, CDCl₃)



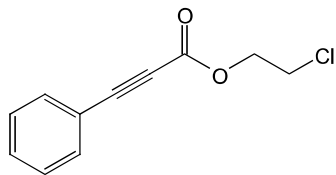
7.58
 7.57
 7.56
 7.46
 7.45
 7.45
 7.45
 7.44
 7.44
 7.43
 7.43
 7.43
 7.37
 7.37
 7.36
 7.36
 7.36
 7.35
 7.26
 4.47
 4.46
 4.45
 3.75
 3.74
 3.73



3p
¹H NMR (600 MHz, CDCl₃)

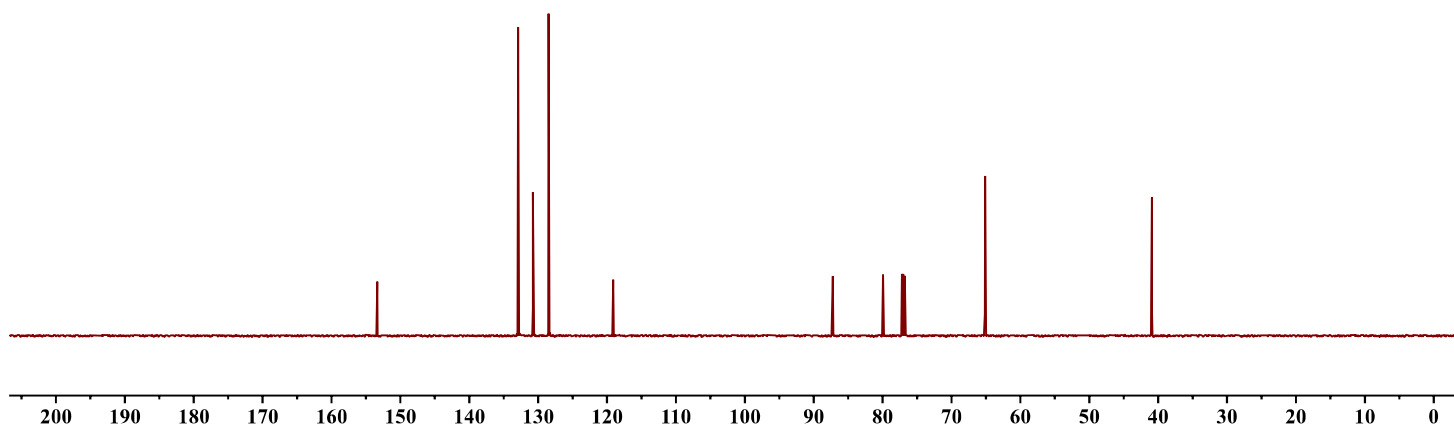


—153.35
 /132.92
 —130.76
 \128.49
 —119.12
 /87.22
 /79.93
 \77.00
 —65.13
 —40.92

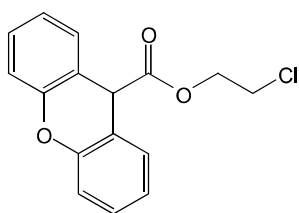


3p

¹³C NMR (151 MHz, CDCl₃)

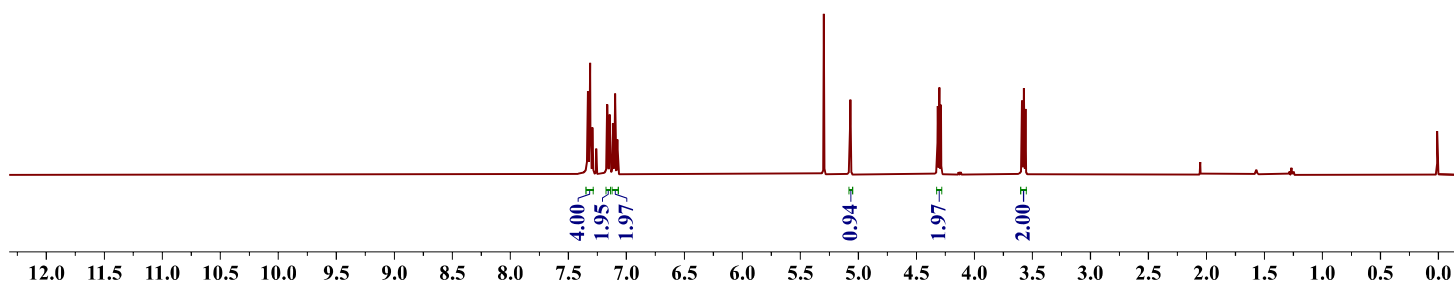


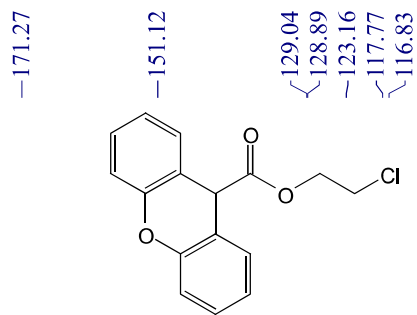
7.34
 7.33
 7.33
 7.31
 7.31
 7.29
 7.29
 7.26
 7.17
 7.15
 7.12
 7.11
 7.10
 7.09
 7.08
 7.08
 5.30
 5.07
 4.32
 4.30
 4.30
 4.30
 4.29
 3.59
 3.58
 3.57
 3.56



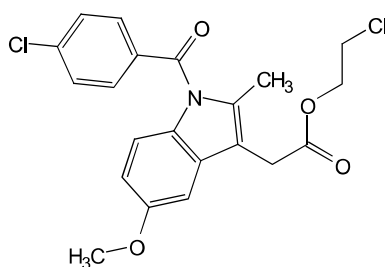
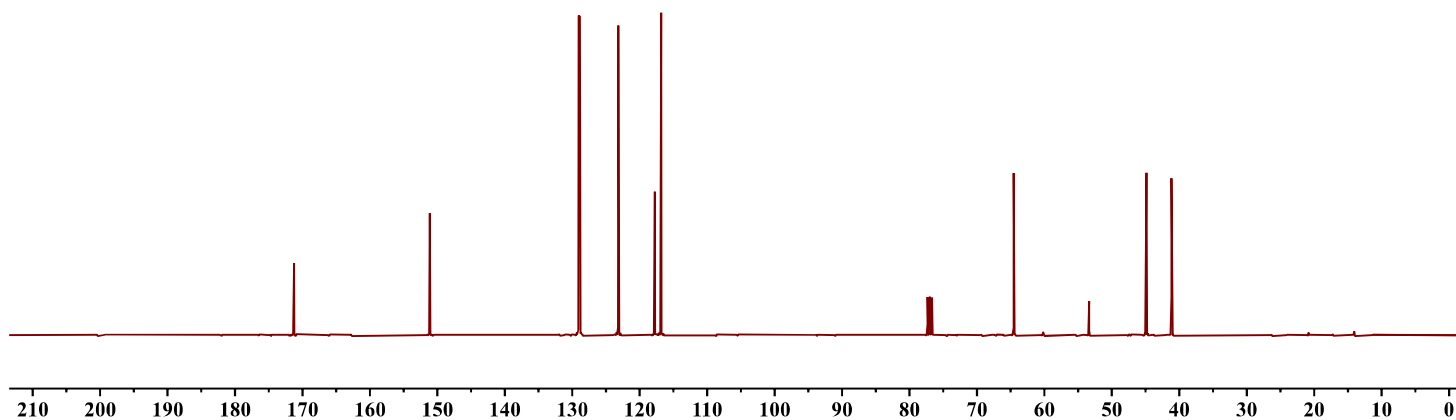
3q

¹H NMR (400 MHz, CDCl₃)

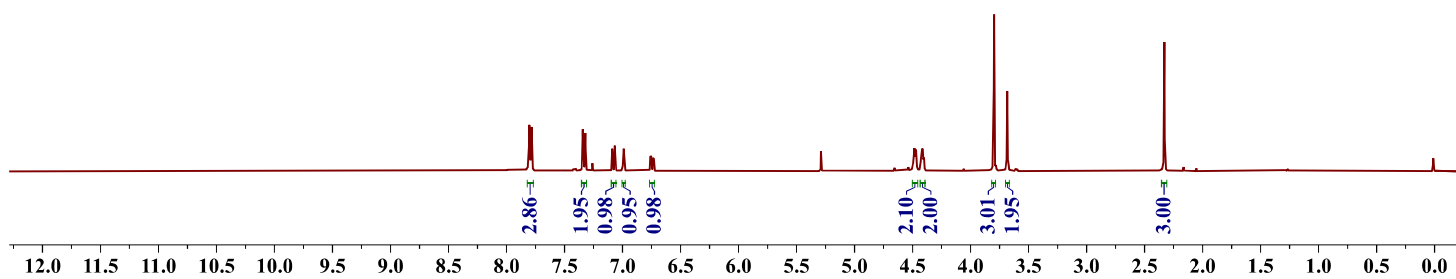




3q
 ^{13}C NMR (101 MHz, CDCl_3)



3r
 ^1H NMR (400 MHz, CDCl_3)



169.20
168.27

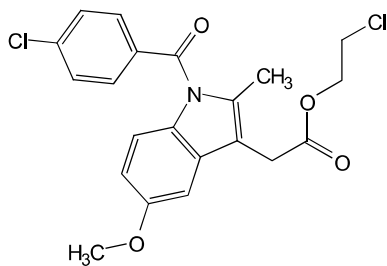
156.08
146.33
139.40
137.02
133.70
131.23
130.78
130.61
130.42
129.14
126.39
120.25
114.97
114.49
111.95
110.93
101.28

77.32
77.00
76.68

55.70

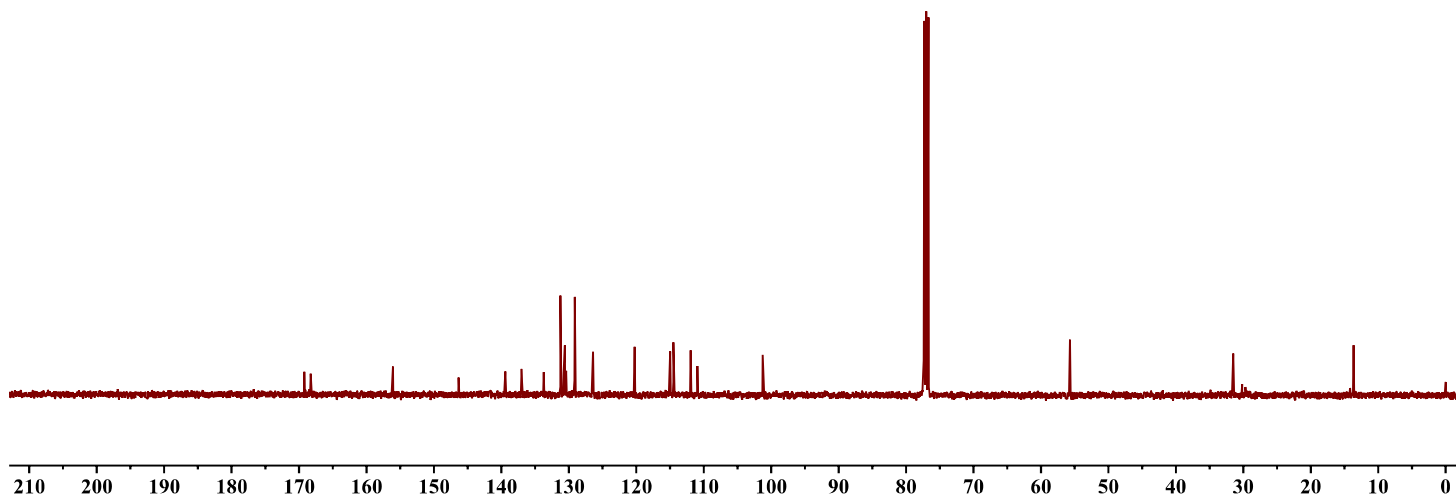
31.50

13.64



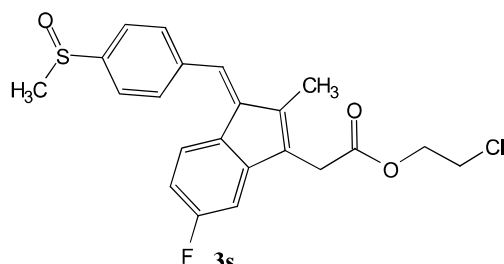
3r

¹³C NMR (101 MHz, CDCl₃)



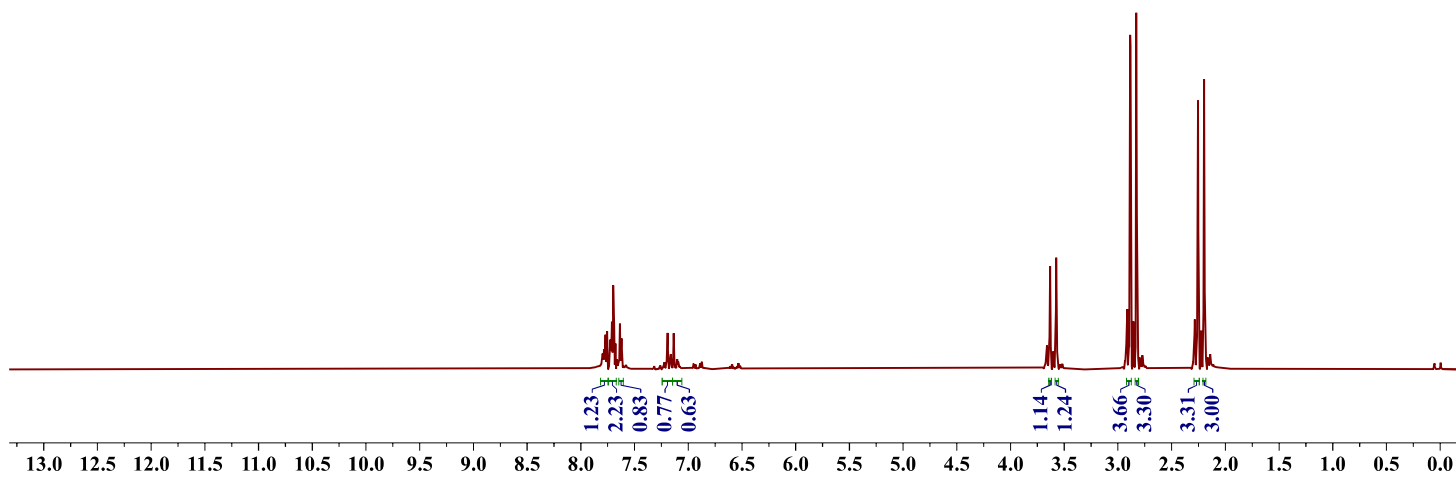
7.80
7.78
7.77
7.76
7.75
7.73
7.71
7.70
7.69
7.68
7.64
7.62
7.26
7.22
7.19
7.16
7.13
7.10
7.09

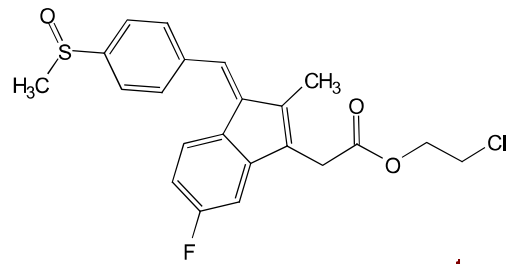
3.63
3.57
2.91
2.89
2.83
2.28
2.25
2.20



3s

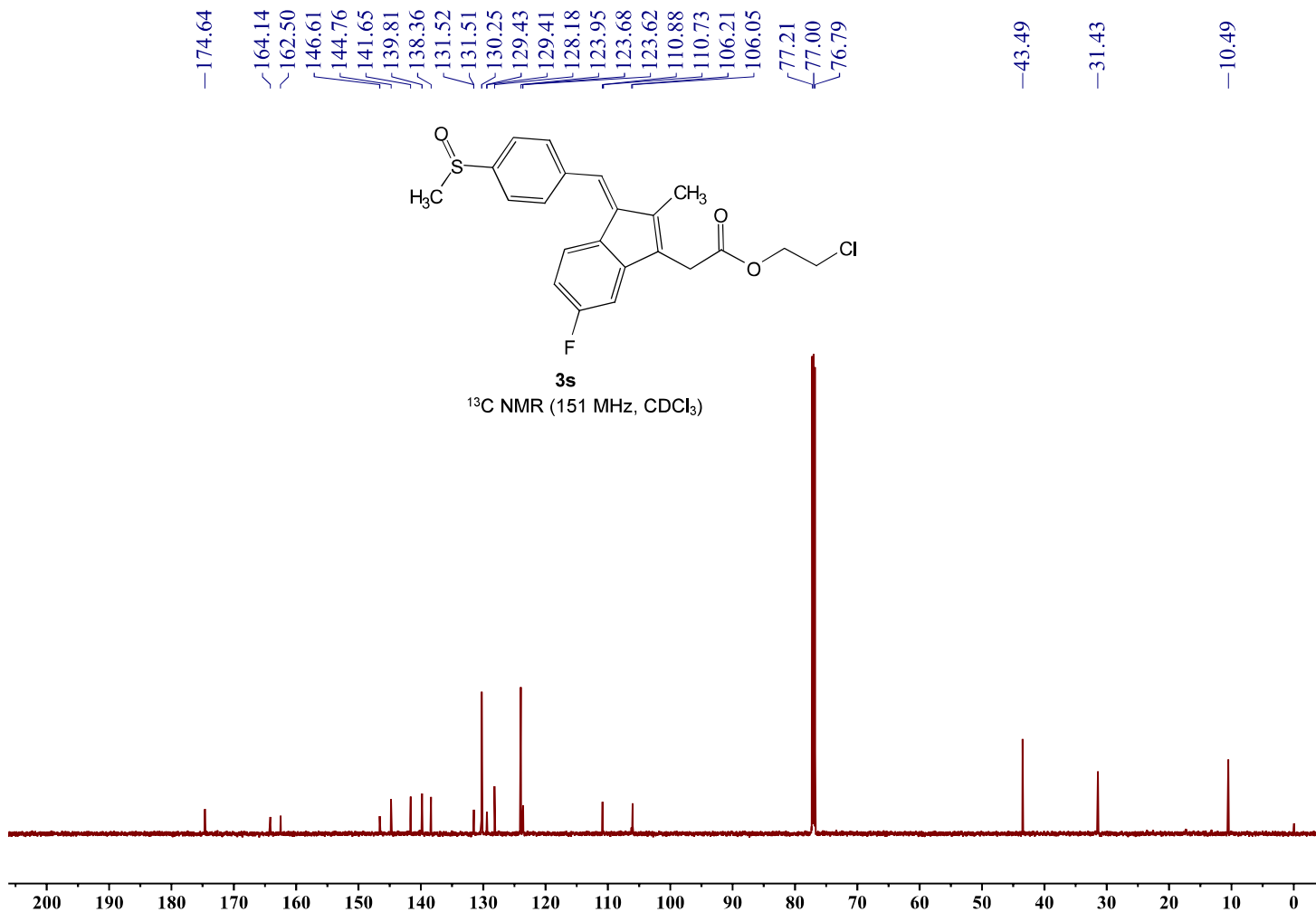
¹H NMR (600 MHz, CDCl₃)



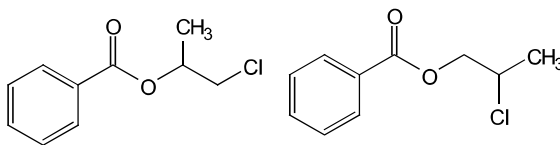


3s

¹³C NMR (151 MHz, CDCl₃)

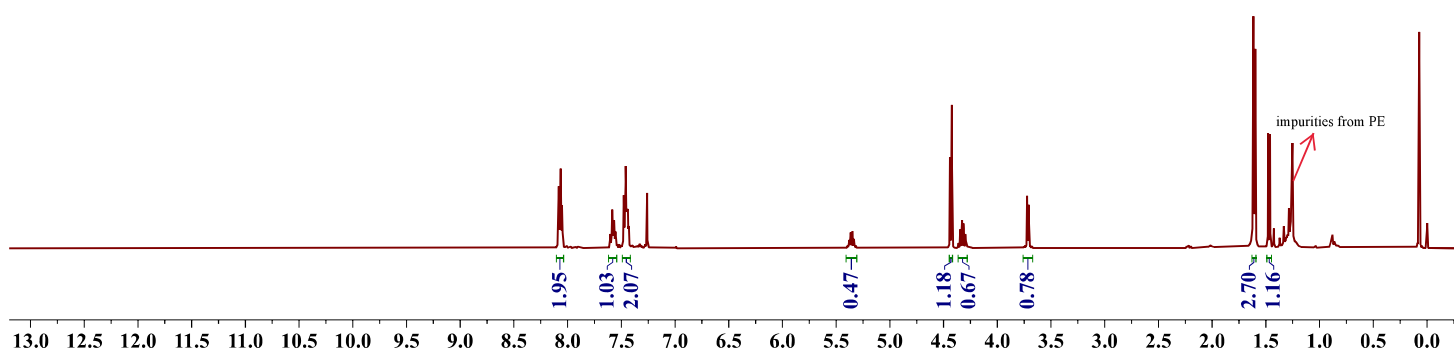


Chemical shift values (ppm): 8.08, 8.07, 8.06, 8.06, 8.05, 8.05, 7.60, 7.58, 7.57, 7.57, 7.57, 7.55, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.26, 5.39, 5.38, 5.36, 5.35, 5.34, 5.32, 4.44, 4.42, 4.36, 4.35, 4.33, 4.31, 4.30, 4.29, 4.28, 3.75, 3.74, 3.72, 3.71, 1.62, 1.60, 1.48, 1.46.



4a

¹H NMR (400 MHz, CDCl₃)



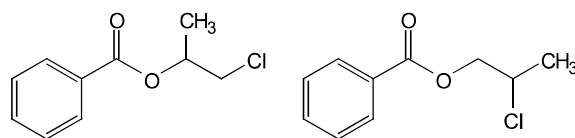
166.06
165.78

133.25
133.12
129.71
129.68
128.44
128.37

77.32
77.00
76.68
70.17
68.93

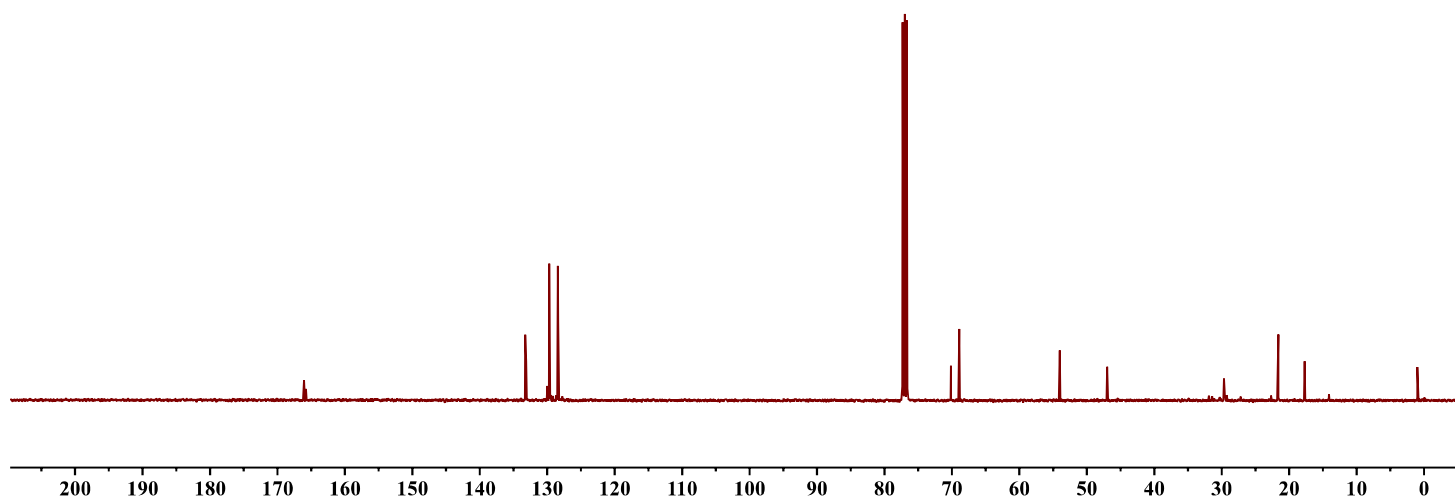
-54.02
-46.99

29.68
21.61
17.68

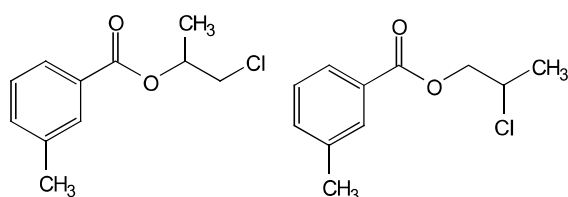


4a

¹³C NMR (101 MHz, CDCl₃)

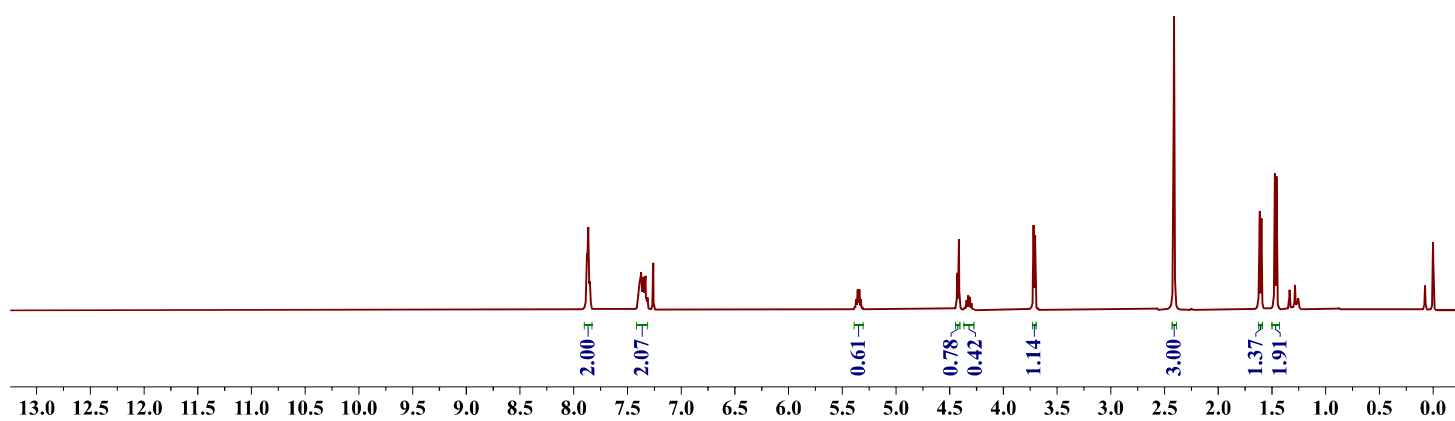


7.88
7.87
7.86
7.85
7.39
7.38
7.36
7.35
7.34
7.33
7.32
7.31
7.26
5.38
5.37
5.36
5.35
5.34
5.34
5.33
5.32
5.31
4.43
4.41
4.36
4.34
4.33
4.31
4.30
4.28
3.72
3.71
2.41



4b

¹H NMR (400 MHz, CDCl₃)

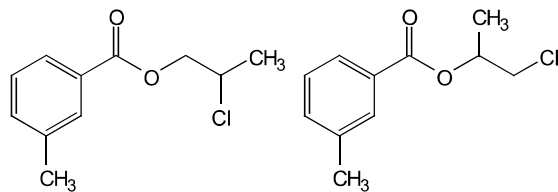


166.22
165.94
138.24
138.17
134.01
133.88
130.20
130.16
129.89
129.53
128.32
128.26
126.84
126.81

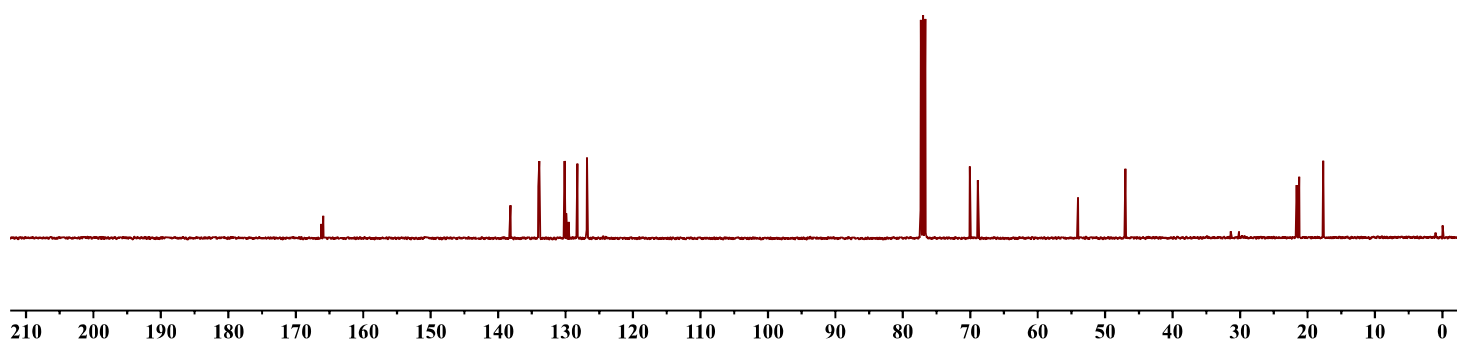
77.32
77.20
77.00
76.68
70.06
68.86

-54.05
-46.99

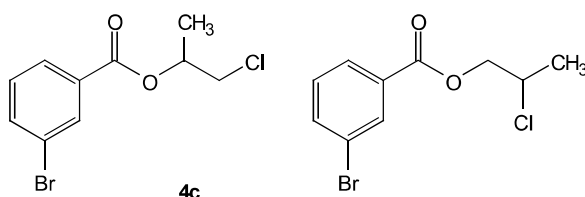
21.62
21.26
17.68



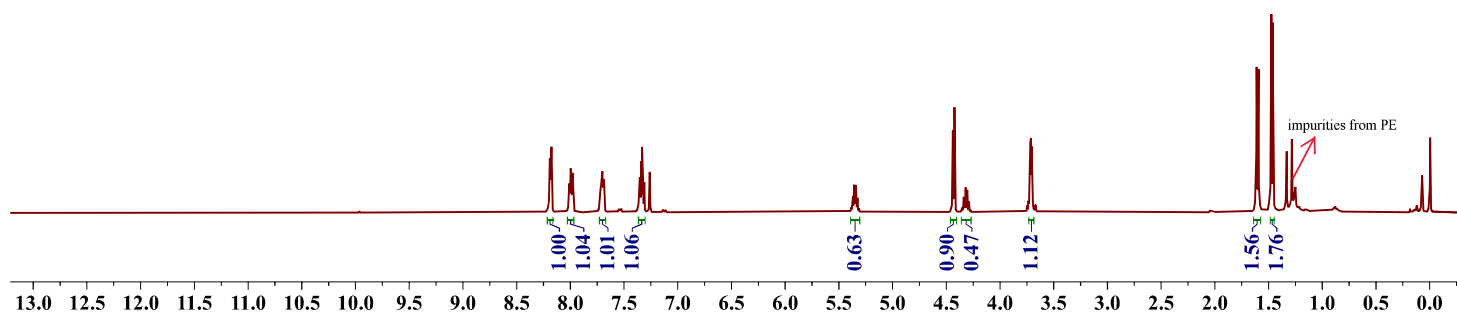
¹³C NMR (101 MHz, CDCl₃)



8.20
8.19
8.19
8.18
8.18
8.17
8.01
8.01
8.01
8.00
8.00
7.99
7.99
7.99
7.98
7.98
7.97
7.72
7.72
7.72
7.71
7.71
7.70
7.70
7.69
7.69
7.69
7.68
7.36
7.35
7.34
7.33
7.32
7.31
7.26
5.37
5.36
5.34
4.44
4.42
4.32
4.31
3.72
3.71
3.71
3.70
1.61
1.59
1.48
1.46



¹H NMR (400 MHz, CDCl₃)



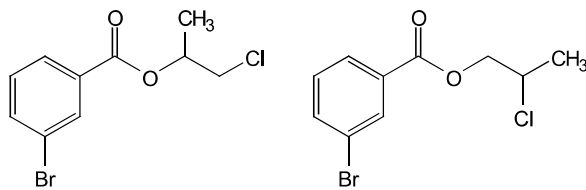
164.72
164.44

136.21
136.07
132.67
132.63
131.92
131.56
130.03
129.97
128.31
128.29
122.52
122.46

77.32
77.00
76.68
70.71
69.26

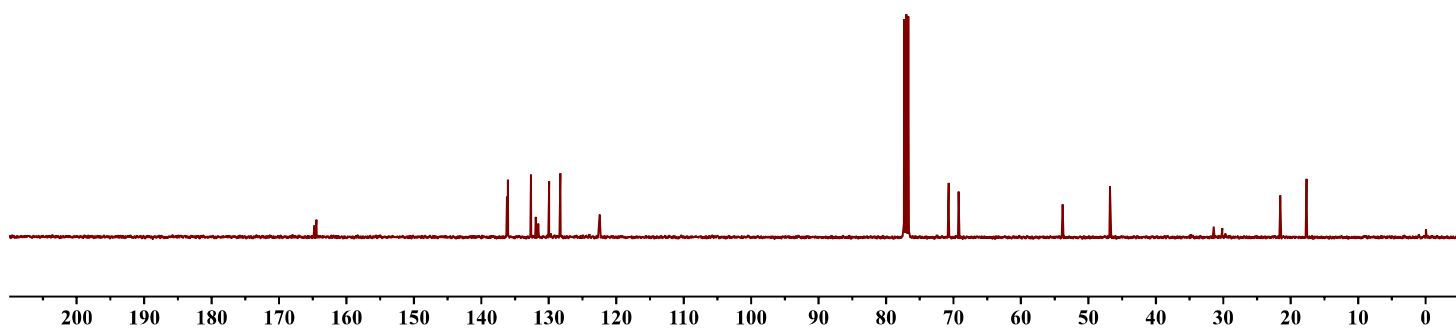
53.84
46.81

21.58
17.68

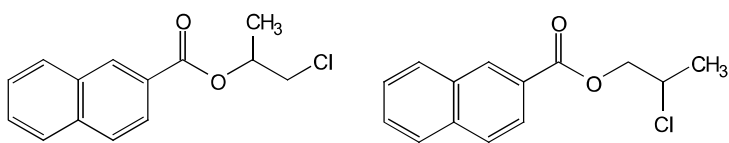


4c

^{13}C NMR (101 MHz, CDCl_3)

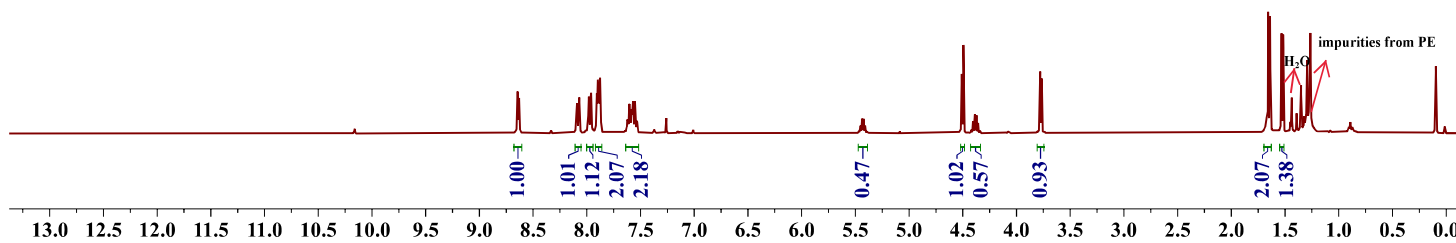


8.64
8.63
8.10
8.09
8.09
8.08
8.07
8.06
7.98
7.96
7.91
7.89
7.88
7.62
7.62
7.60
7.59
7.58
7.57
7.57
7.55
7.53
7.26
5.47
5.45
5.44
5.42
5.41
5.39
4.51
4.49
4.42
4.40
4.39
4.37
4.36
4.34
3.78
3.77
1.66
1.64
1.53
1.52



4d

^1H NMR (400 MHz, CDCl_3)

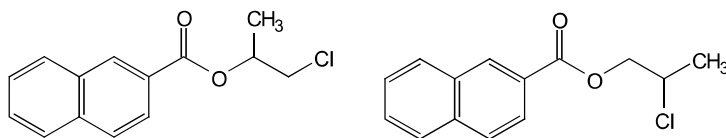


166.19
165.92
135.61
135.57
132.41
131.30
131.20
129.37
129.34
128.39
128.31
128.23
128.15
127.74
127.73
127.20
126.84
126.69
126.64

77.32
77.00
76.68
70.29
69.04

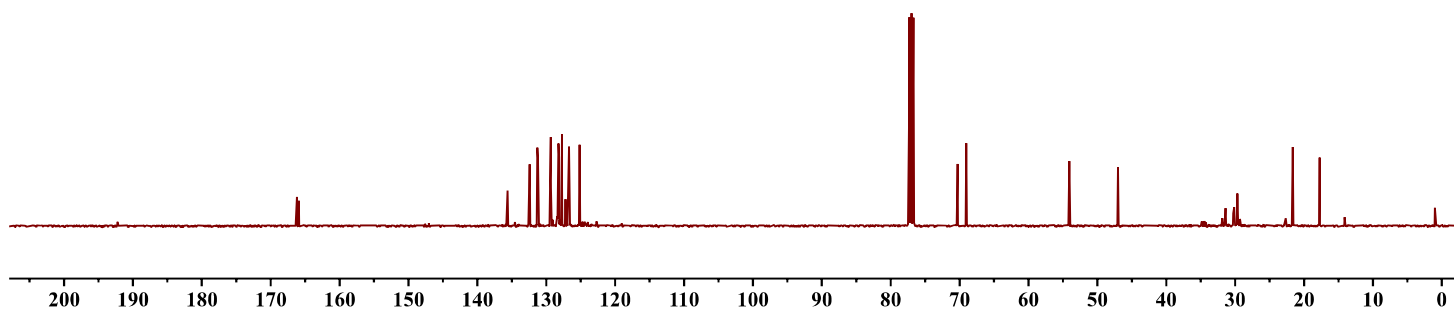
-54.08
-47.02

31.39
30.15
29.66
21.64
17.73

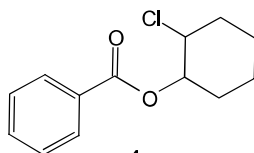


4d

^{13}C NMR (101 MHz, CDCl_3)

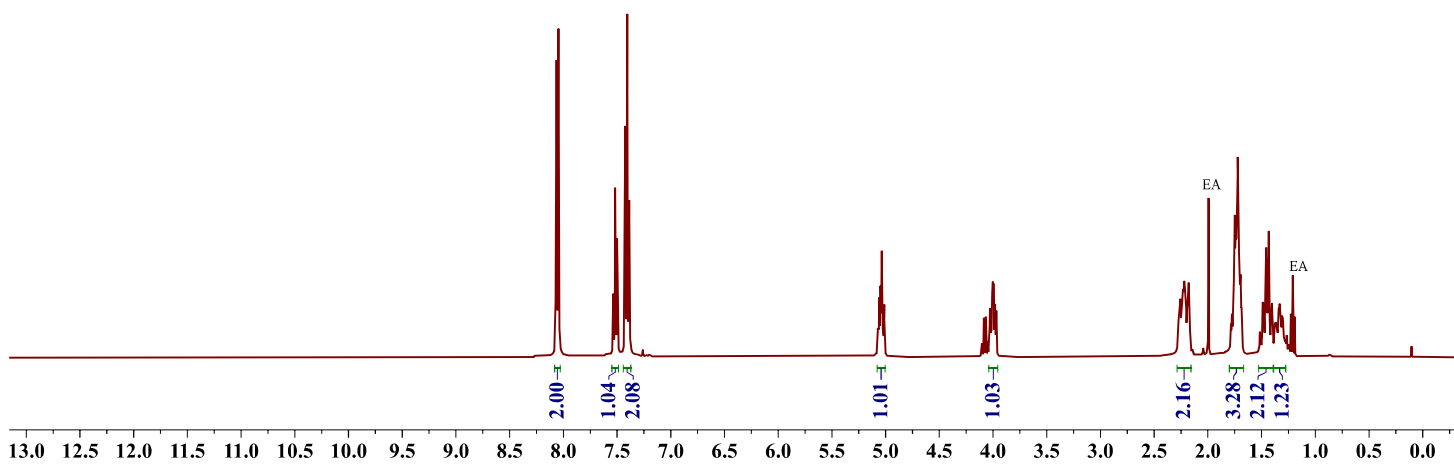


8.06
8.05
8.04
7.54
7.52
7.51
7.50
7.43
7.41
7.39
5.06
5.05
5.04
5.02
5.01
4.03
4.02
4.01
4.00
3.99
3.98
3.97
2.27
2.26
2.25
2.25
2.23
2.22
2.21
2.21
2.19
2.18
2.18
2.18
1.78
1.76
1.75
1.74
1.74
1.73
1.72
1.70
1.70
1.69
1.49
1.48
1.46
1.43
1.41
1.34
1.33



4e

^1H NMR (400 MHz, CDCl_3)



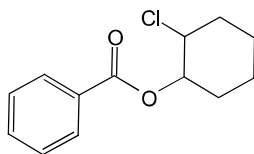
-165.31

132.74
129.97
129.39
128.09

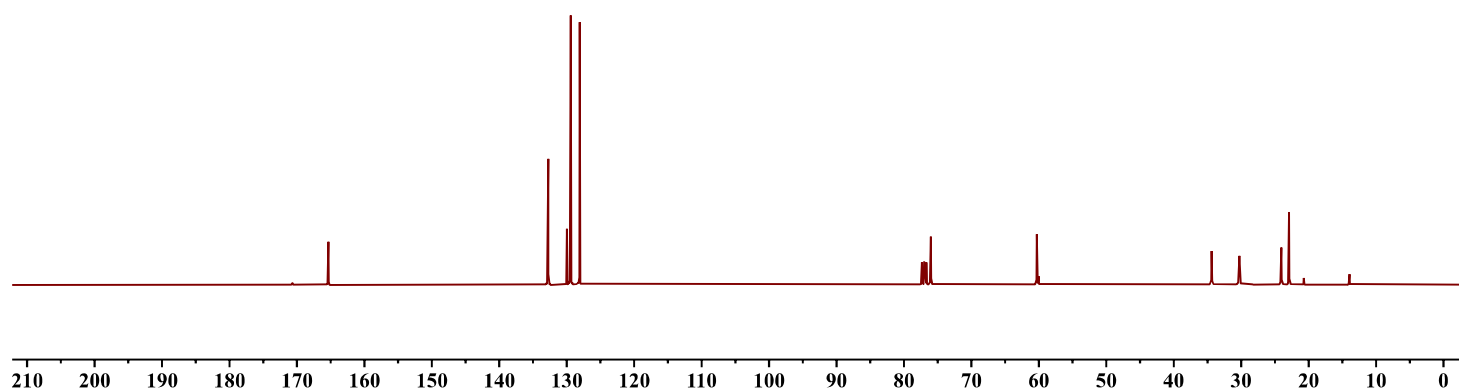
77.32
77.00
76.68
76.03

-60.30

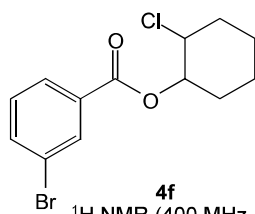
34.38
30.28
24.07
22.90



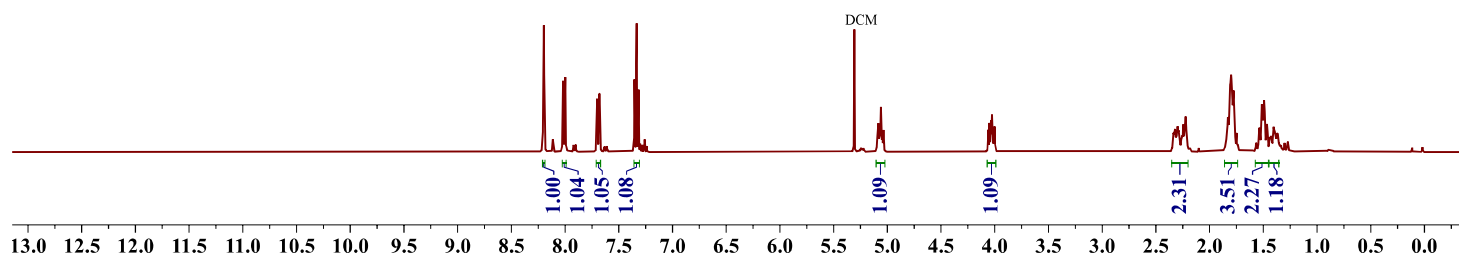
4e
¹³C NMR (101 MHz, CDCl₃)



8.20
8.19
8.02
8.01
8.00
7.70
7.68
7.35
7.33
7.31
7.26
5.31
4.06
4.05
4.04
4.03
4.02
4.01
4.00
2.35
2.34
2.33
2.32
2.31
2.30
2.29
2.28
2.26
2.25
2.24
2.22
1.84
1.83
1.81
1.80
1.78
1.75
1.74
1.57
1.54
1.51
1.49
1.47
1.44
1.43
1.40
1.38
1.37



4f
¹H NMR (400 MHz, CDCl₃)



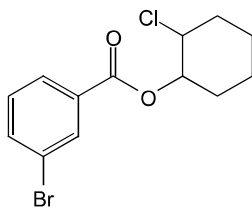
-164.13

135.77
132.43
132.00
129.81
128.15
122.28

77.32
77.00
76.77
76.68

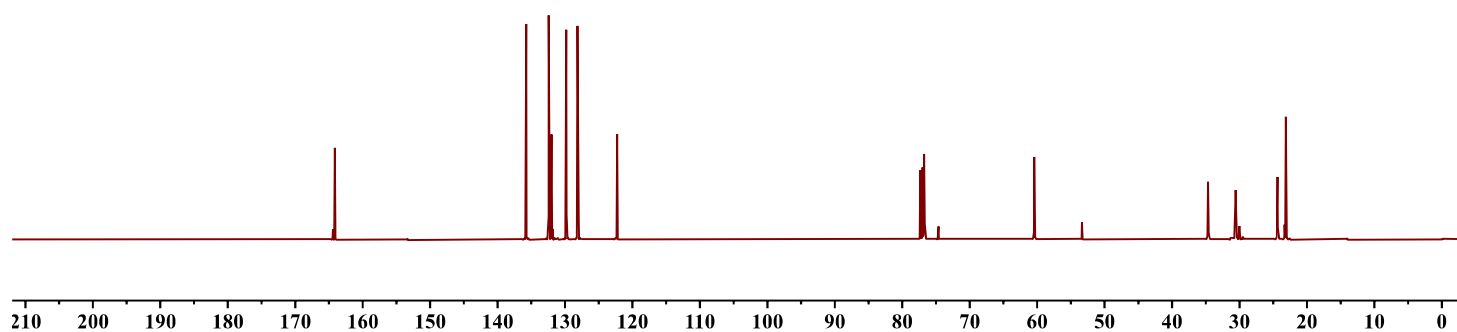
-60.42

34.65
30.57
24.35
23.12

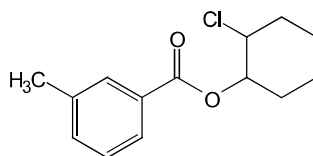


4f

¹³C NMR (101 MHz, CDCl₃)

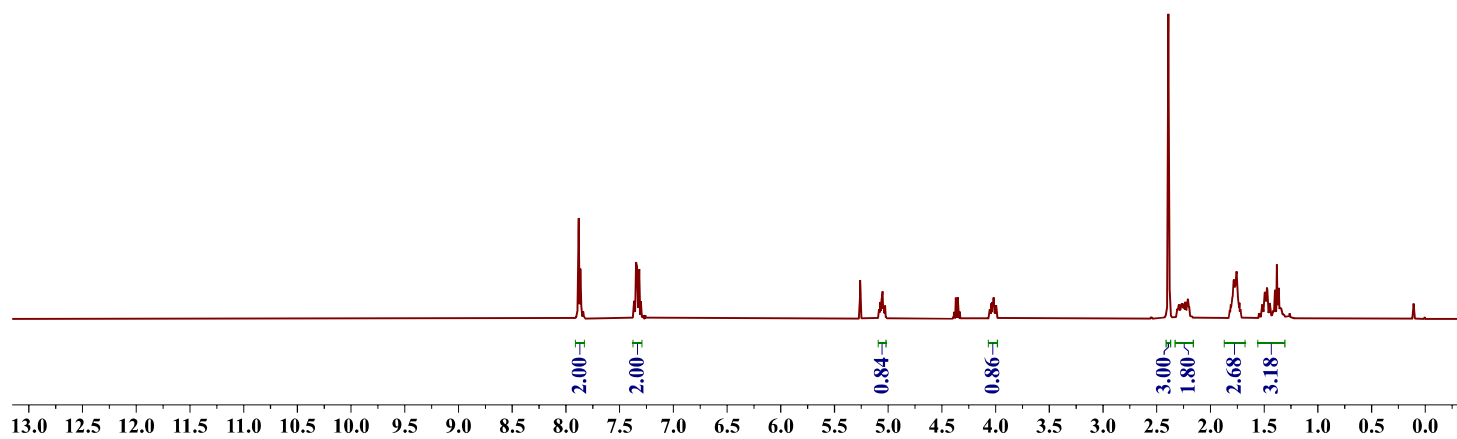


7.88
7.86
7.37
7.36
7.35
7.34
7.32
7.30
5.07
5.06
5.05
5.04
5.03
4.05
4.04
4.02
4.02
4.02
4.01
3.99
2.39
2.38
2.31
2.30
2.29
2.28
2.27
2.25
2.23
2.22
2.21
1.81
1.79
1.78
1.77
1.76
1.75
1.73
1.52
1.51
1.50
1.49
1.47
1.45
1.40
1.38
1.36
1.35
1.35
1.34



4g

¹H NMR (400 MHz, CDCl₃)



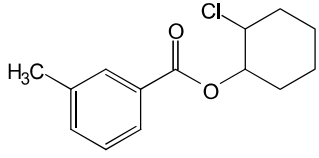
165.64

137.94
133.60
130.00
128.08
126.66

77.32
77.00
76.68
76.05

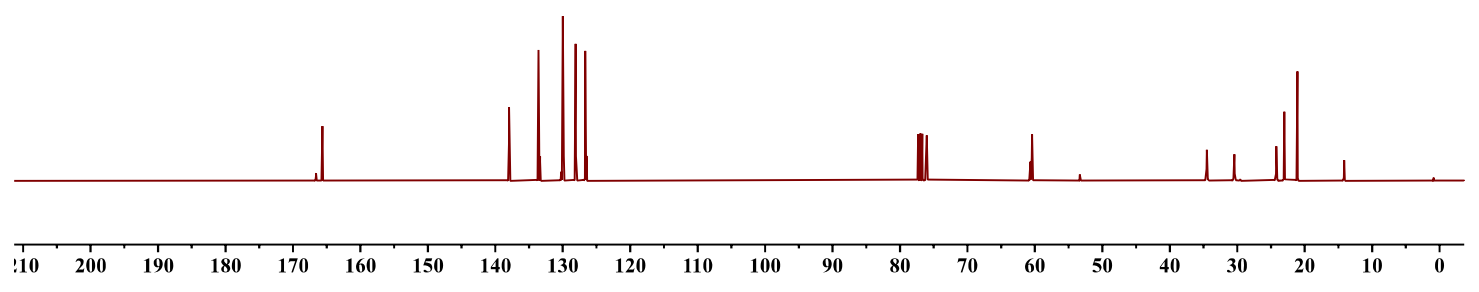
60.43

34.51
30.42
24.22
23.03
21.08
14.17

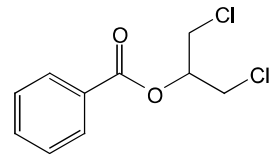


4g

¹³C NMR (101 MHz, CDCl₃)

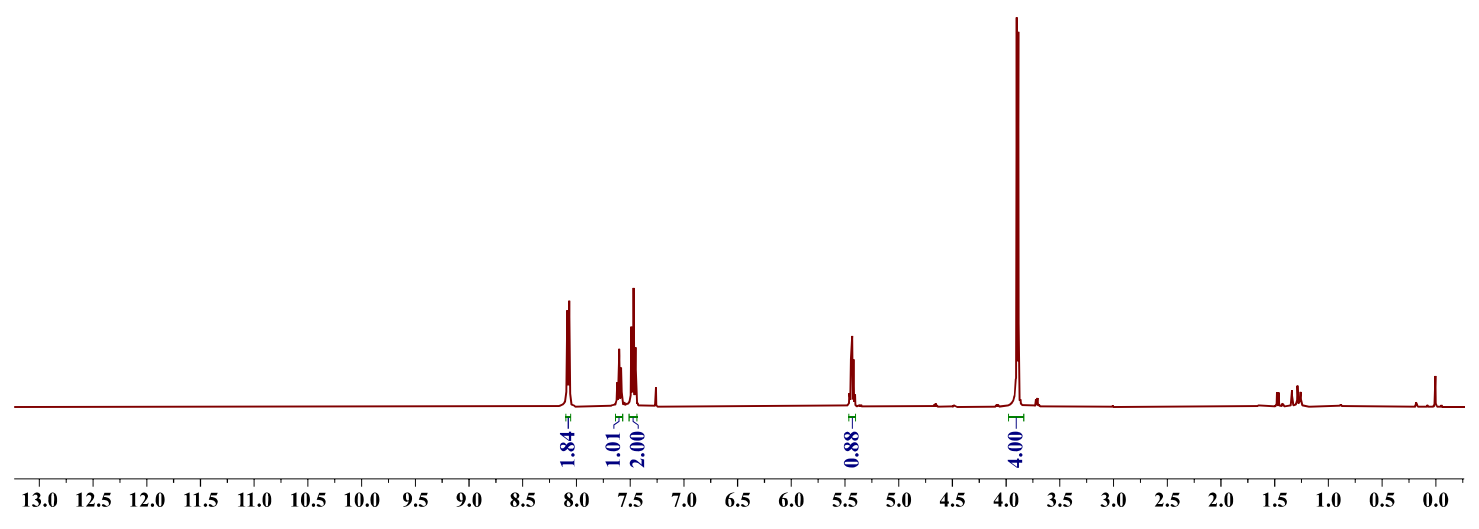


8.09
8.08
8.07
8.06
7.62
7.62
7.61
7.60
7.59
7.58
7.49
7.47
7.45
7.26
5.46
5.45
5.43
5.42
5.41
3.90
3.89



4h

¹H NMR (400 MHz, CDCl₃)

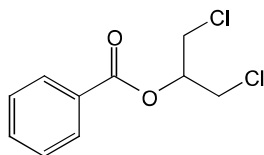


—165.33

133.58
129.87
128.50

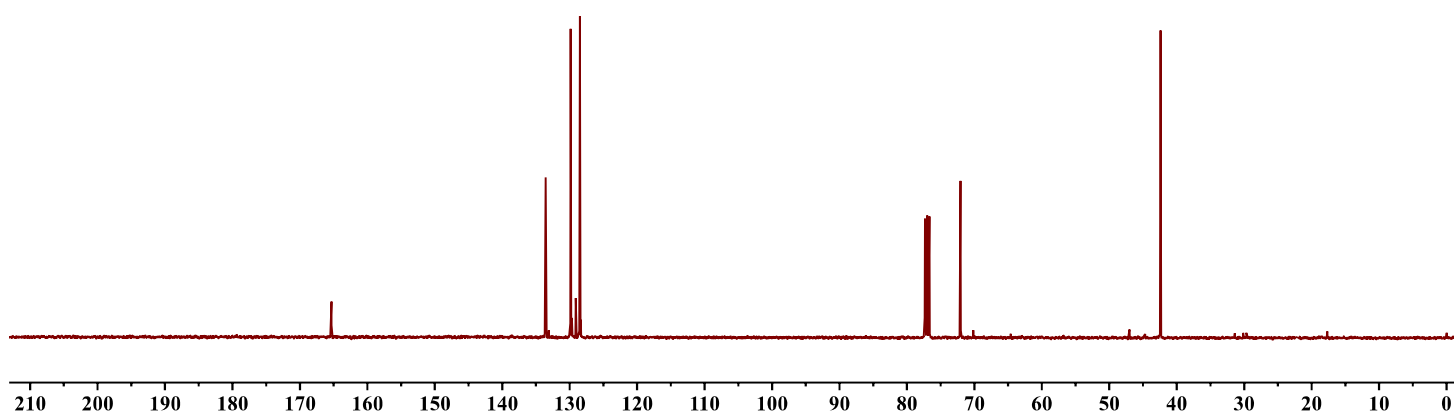
77.32
77.00
76.68
72.05

—42.42

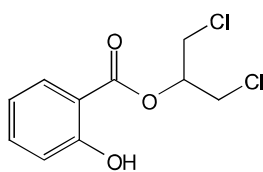


4h

¹³C NMR (101 MHz, CDCl₃)

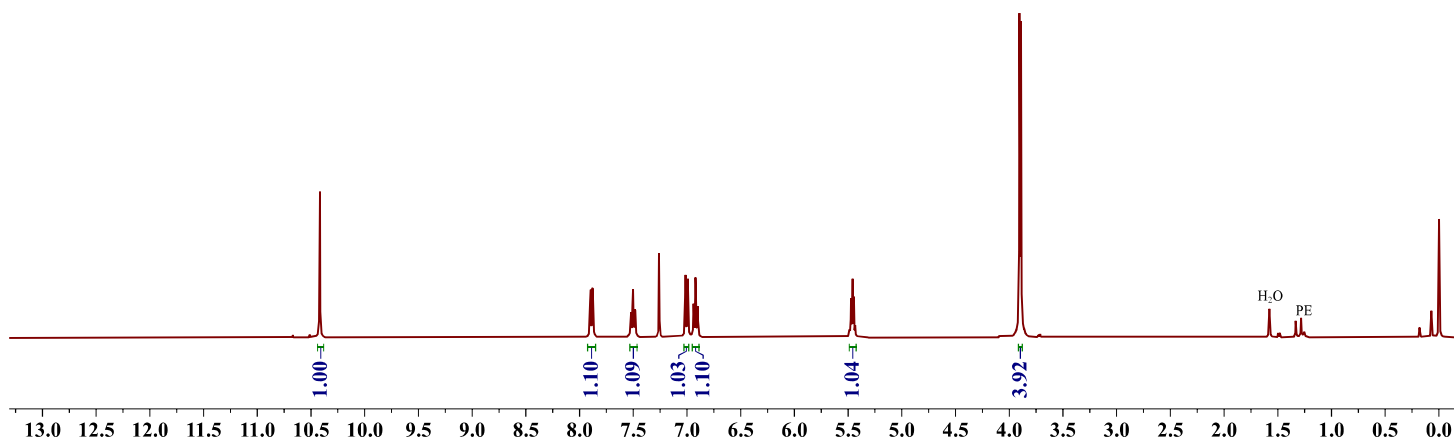


10.42
7.90
7.90
7.88
7.88
7.52
7.52
7.50
7.49
7.48
7.26
7.02
6.99
6.94
6.94
6.92
6.90
6.90
5.48
5.47
5.46
5.45
5.43
3.90
3.89



4i

¹H NMR (400 MHz, CDCl₃)



-168.83

-161.87

-136.47

-130.10

-119.46

-117.73

-111.53

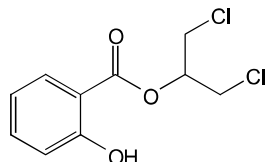
77.32

77.00

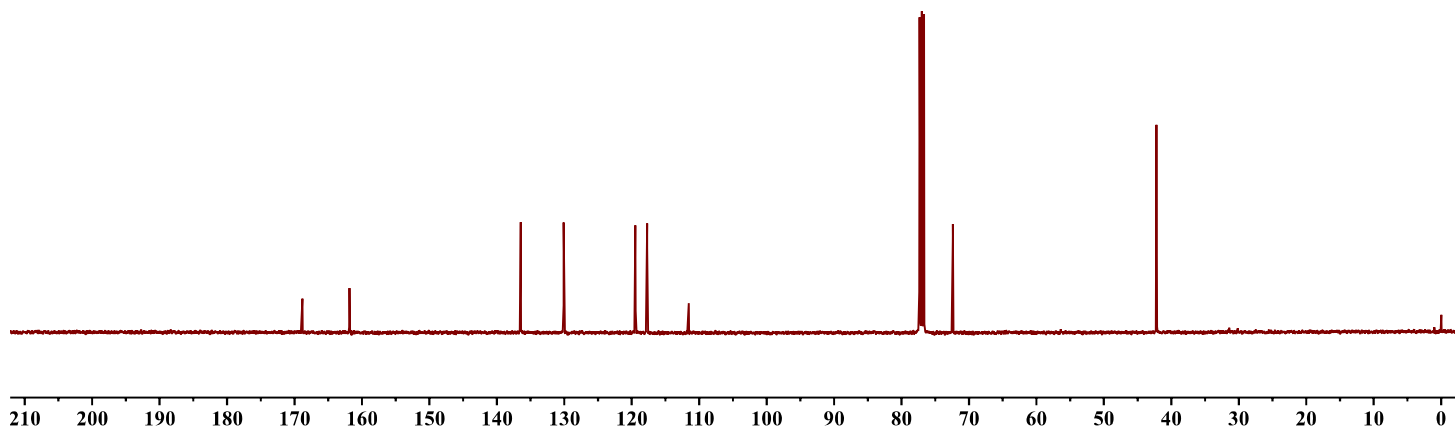
76.68

72.41

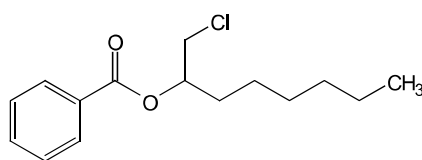
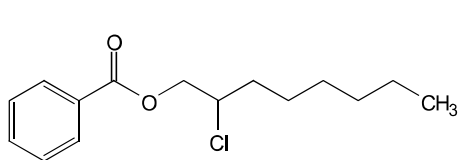
-42.19



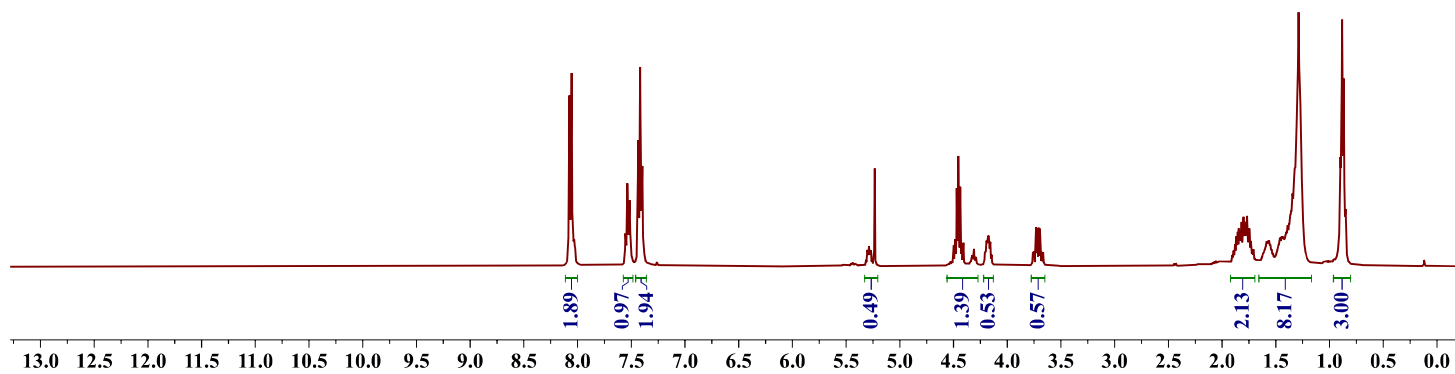
4i
¹³C NMR (101 MHz, CDCl₃)

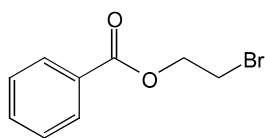
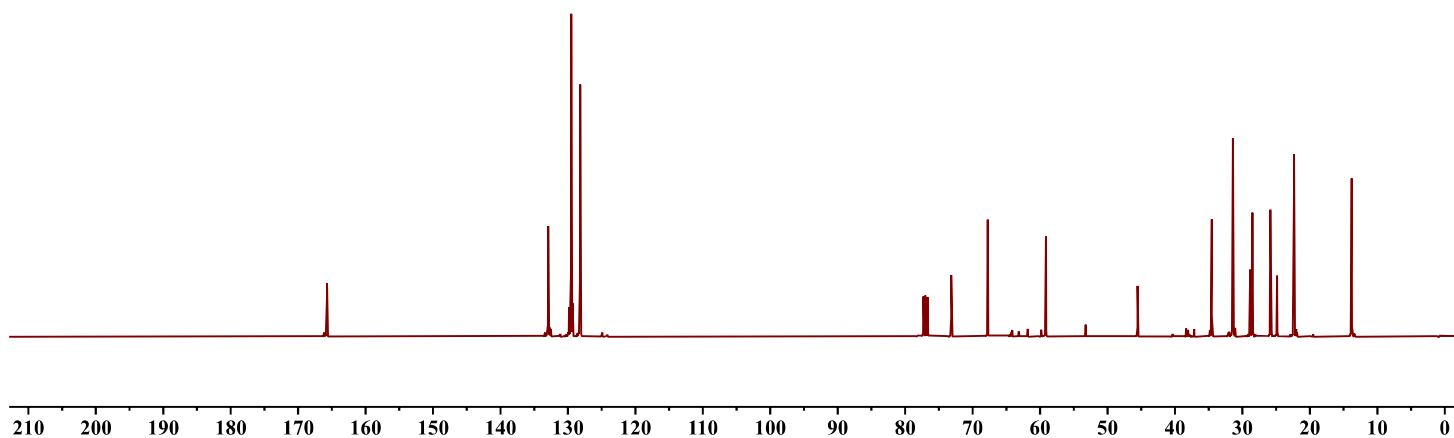
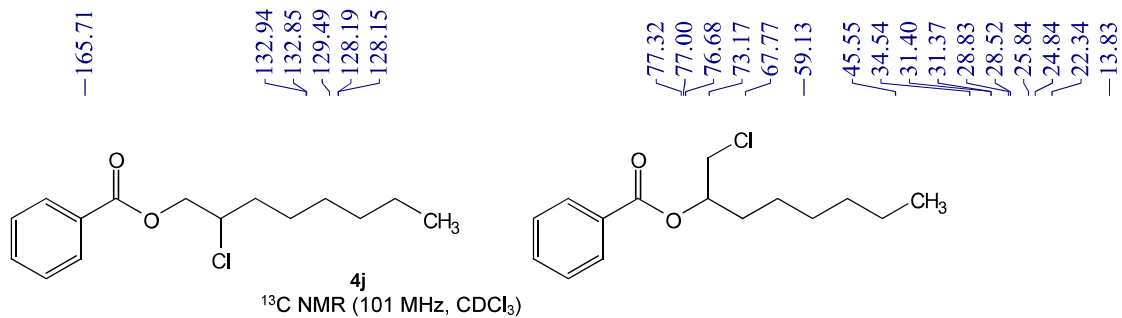


8.08
8.06
8.05
8.04
7.55
7.54
7.53
7.52
7.51
7.44
7.42
7.40
5.23
4.49
4.47
4.46
4.44
4.19
4.18
4.17
3.73
3.72
3.71
3.69
1.87
1.86
1.85
1.84
1.83
1.82
1.80
1.79
1.78
1.77
1.75
1.74
1.73
1.58
1.57
1.56
1.46
1.45
1.44
1.43
1.34
1.29
0.90
0.88
0.87
0.85

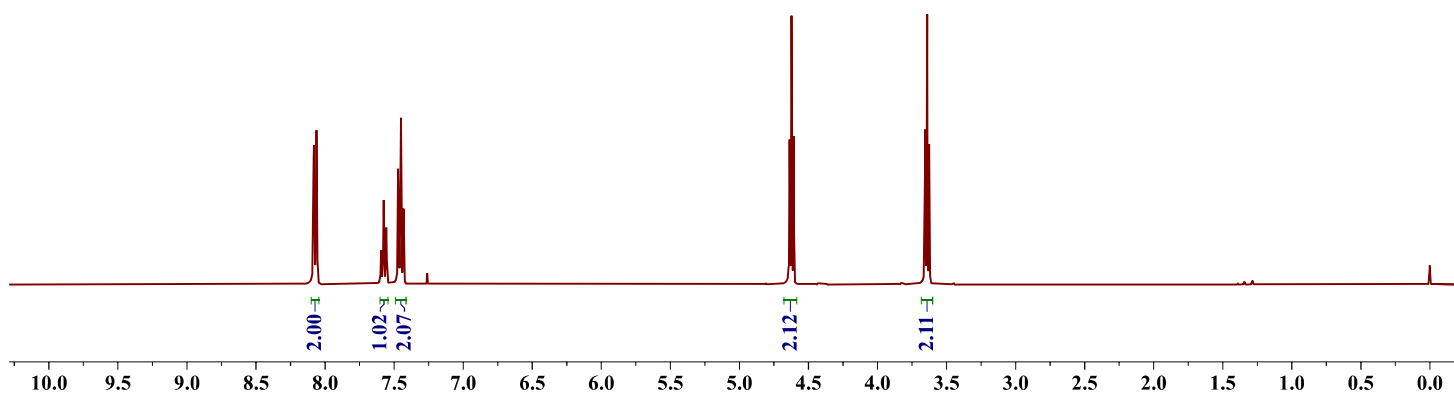


4j
¹H NMR (400 MHz, CDCl₃)





4k
¹H NMR (400 MHz, CDCl₃)



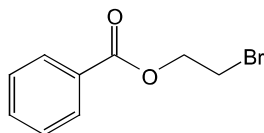
-165.97

133.20
129.66
128.38

77.32
77.00
76.68

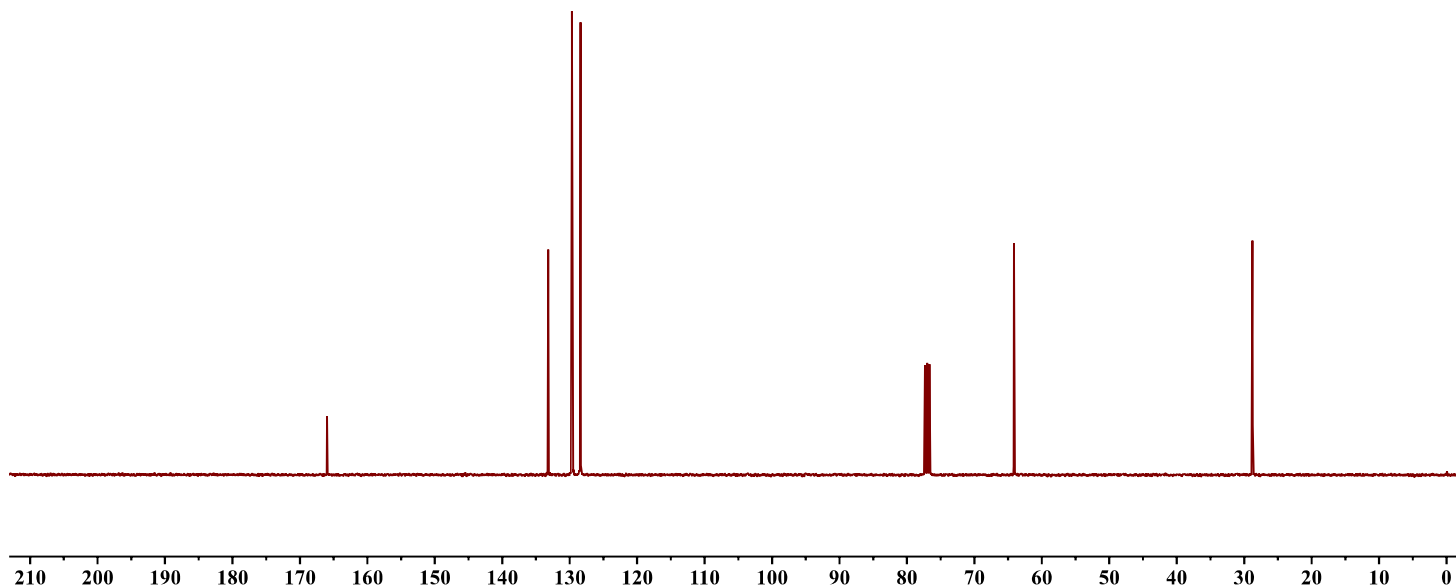
-64.13

-28.76

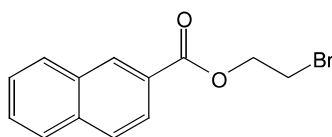


4k

¹³C NMR (101 MHz, CDCl₃)

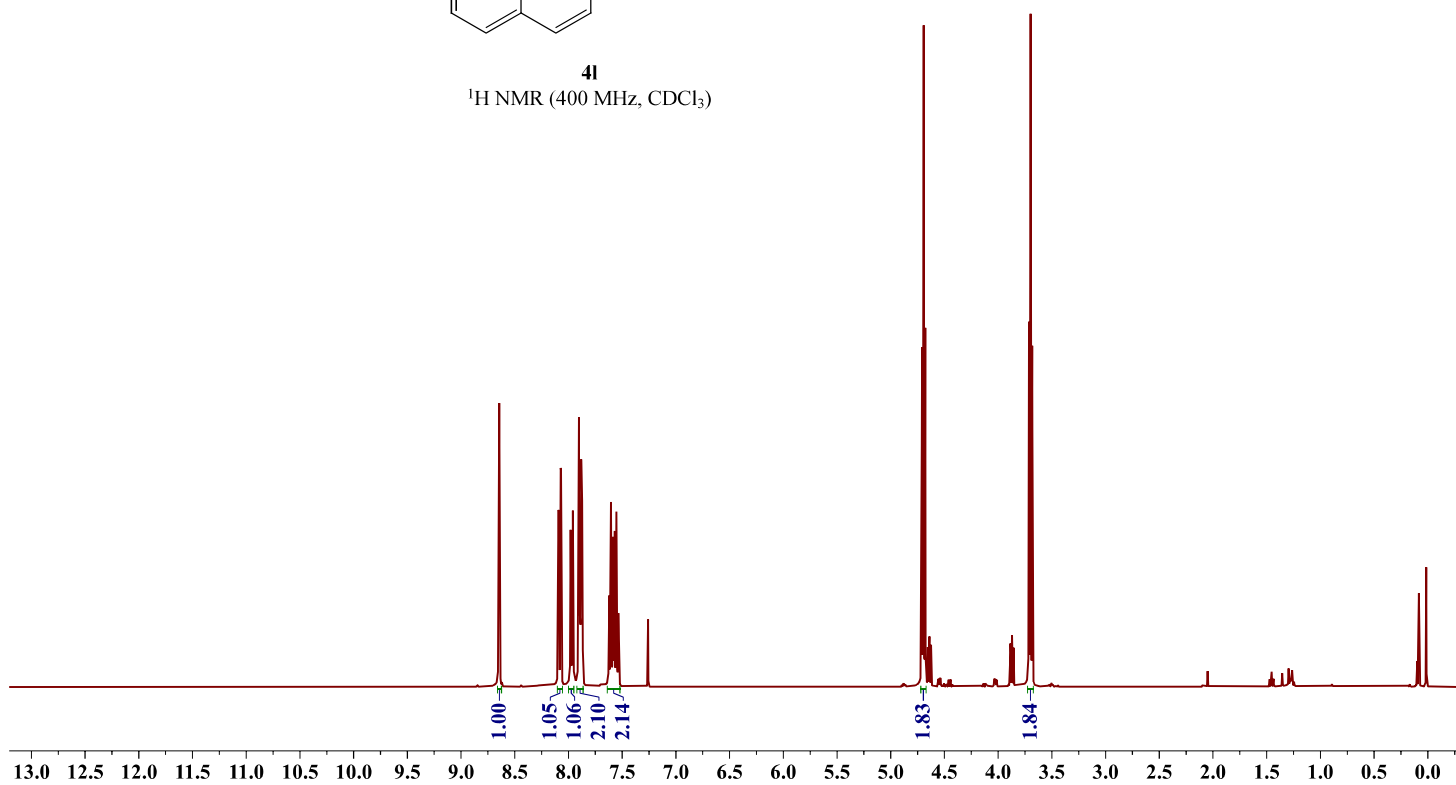


8.64
8.09
8.09
8.07
8.07
7.98
7.96
7.90
7.89
7.88
7.87
7.62
7.62
7.61
7.60
7.60
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.54
7.53
7.26
4.71
4.69
4.68
3.71
3.70
3.68



4l

¹H NMR (400 MHz, CDCl₃)



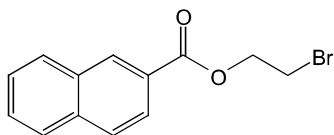
-166.17

135.60
132.39
131.32
129.36
128.38
128.22
127.73
126.77
126.68
125.13

77.32
77.00
76.68

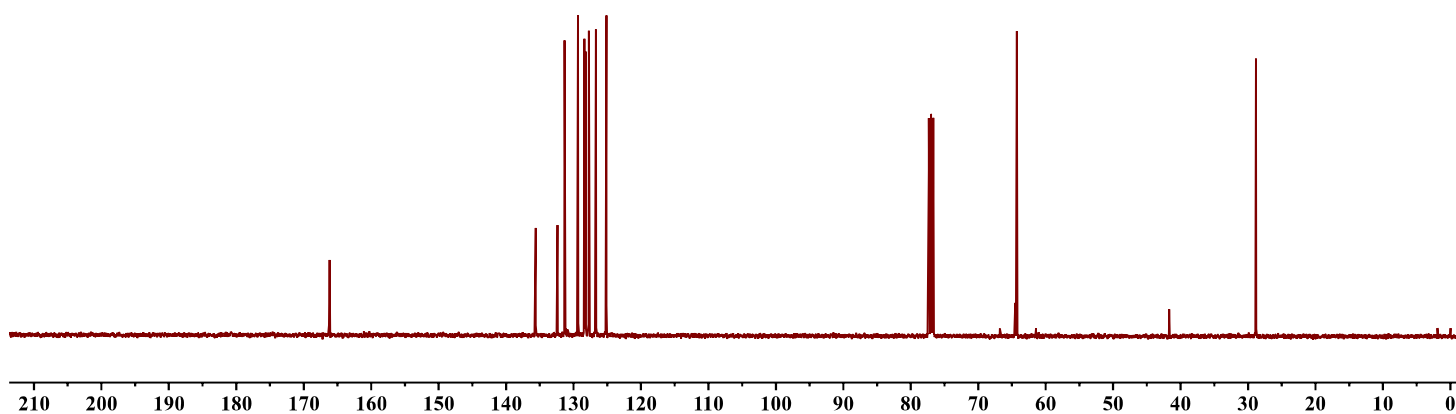
-64.28

-28.81



4l

¹³C NMR (101 MHz, CDCl₃)

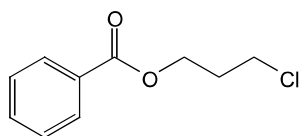


8.04
8.03
8.02
7.58
7.57
7.57
7.56
7.55
7.54
7.46
7.44
7.42

4.49
4.48
4.46

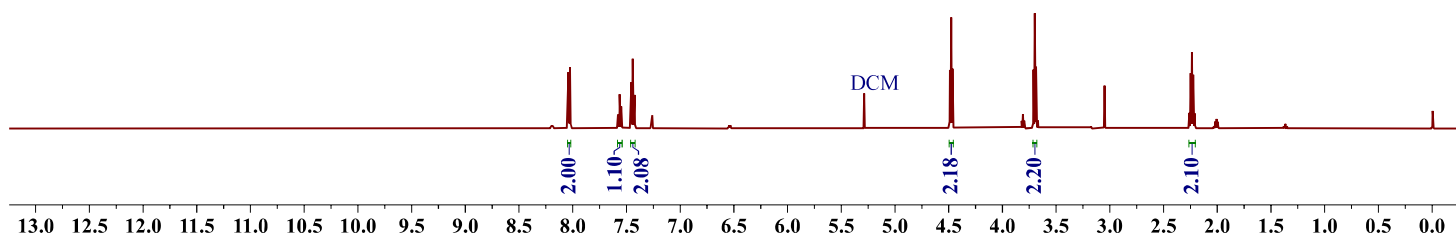
3.71
3.70
3.69

2.26
2.25
2.24
2.22
2.21



4m

¹H NMR (500 MHz, CDCl₃)



—166.35

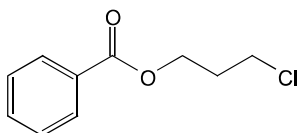
133.02
129.97
129.52
128.36

—77.00

—61.62

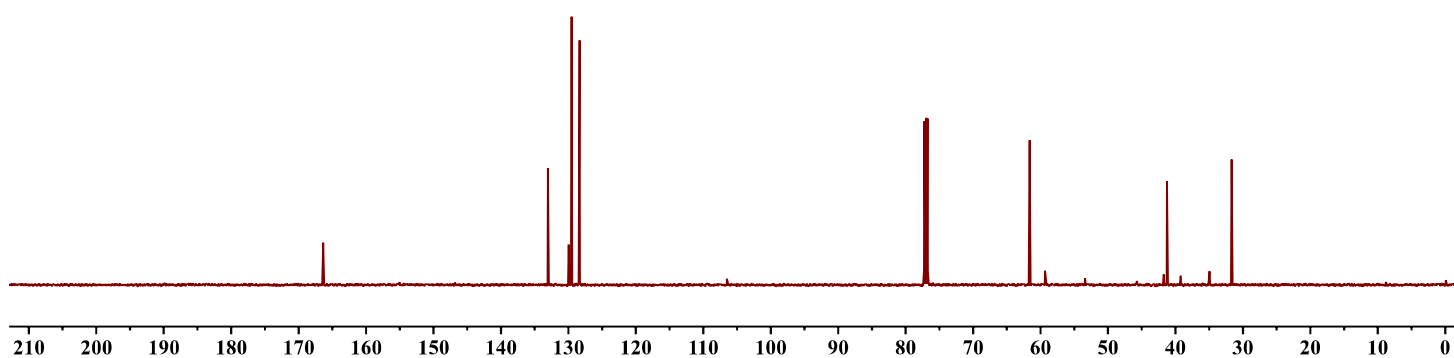
—41.24

—31.68



4m

¹³C NMR (126 MHz, CDCl₃)

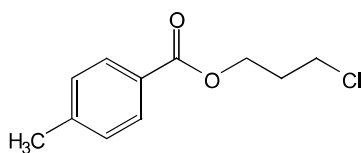


7.92
7.91
7.26
7.26
7.24
7.22

4.46
4.45
4.44

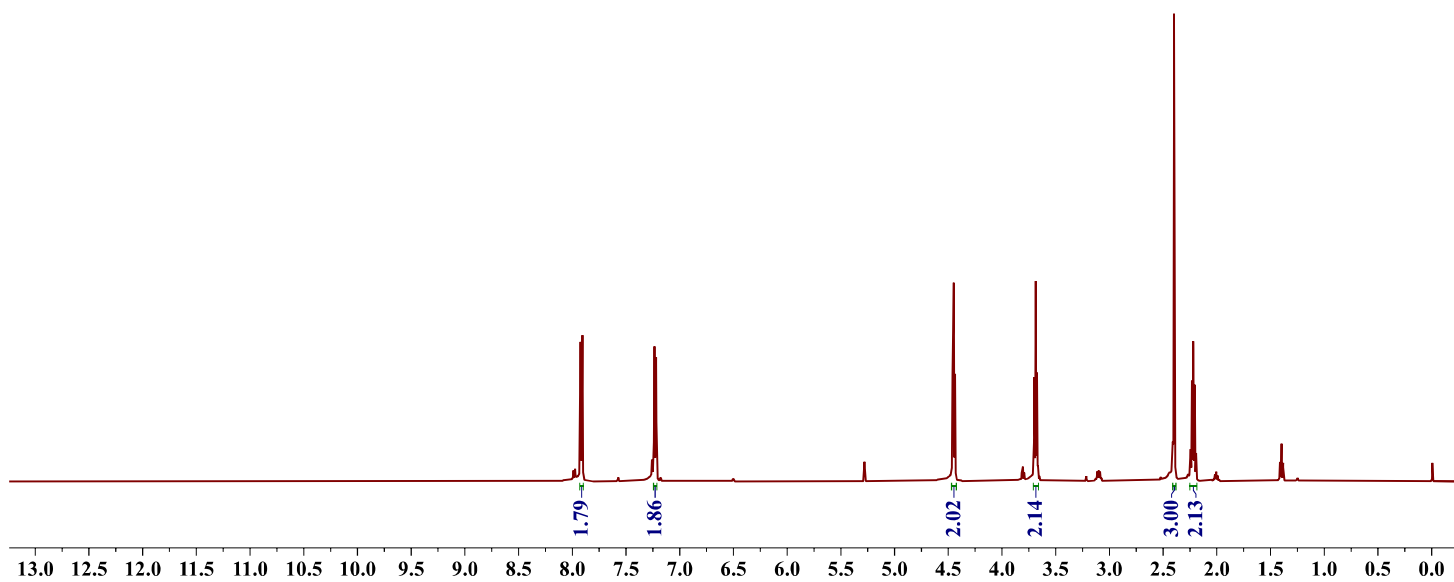
3.70
3.69
3.67

2.40
2.24
2.23
2.22
2.21
2.19

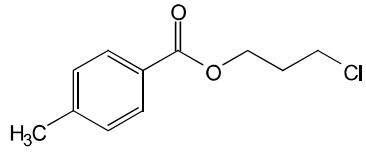


4n

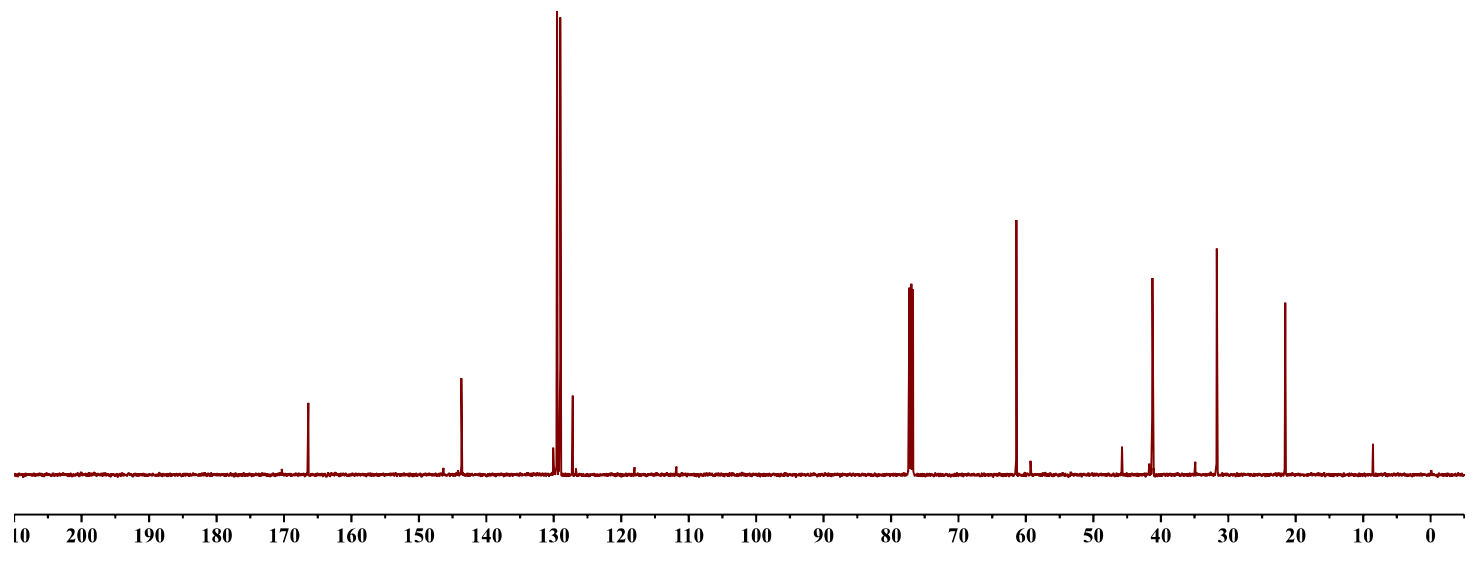
¹H NMR (500 MHz, CDCl₃)



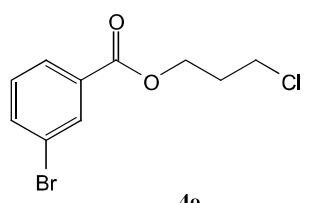
—166.39 —143.69 —129.51 —129.03 —127.20 —77.00 —61.40 —41.26 —31.70 —21.57



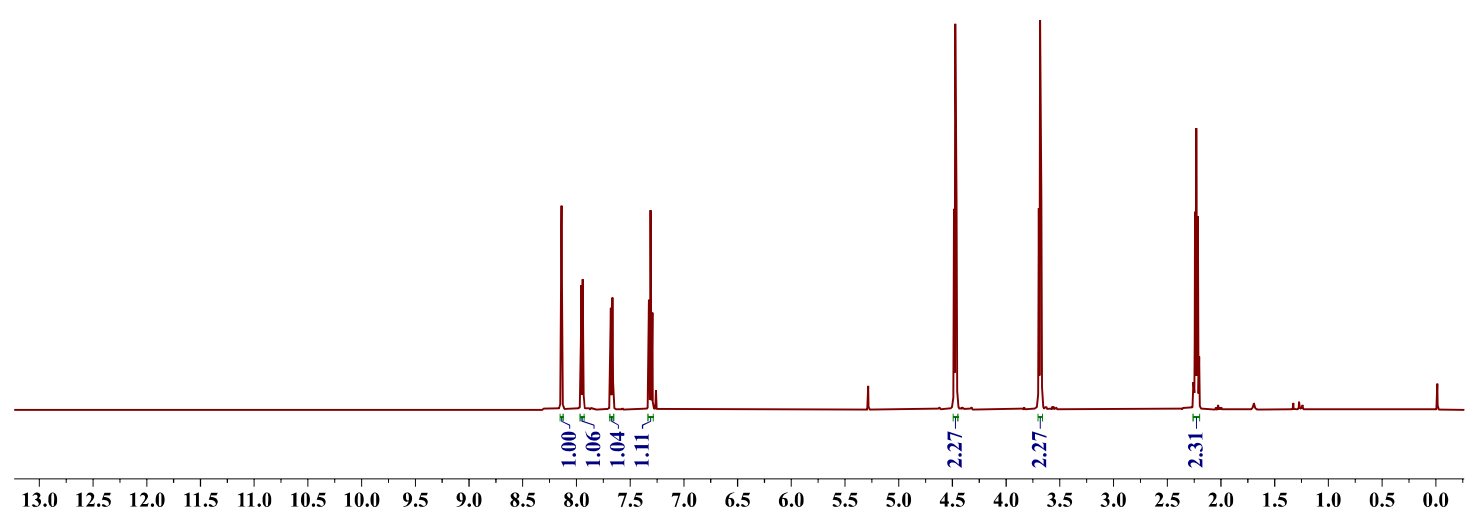
4n
¹³C NMR (126 MHz, CDCl₃)

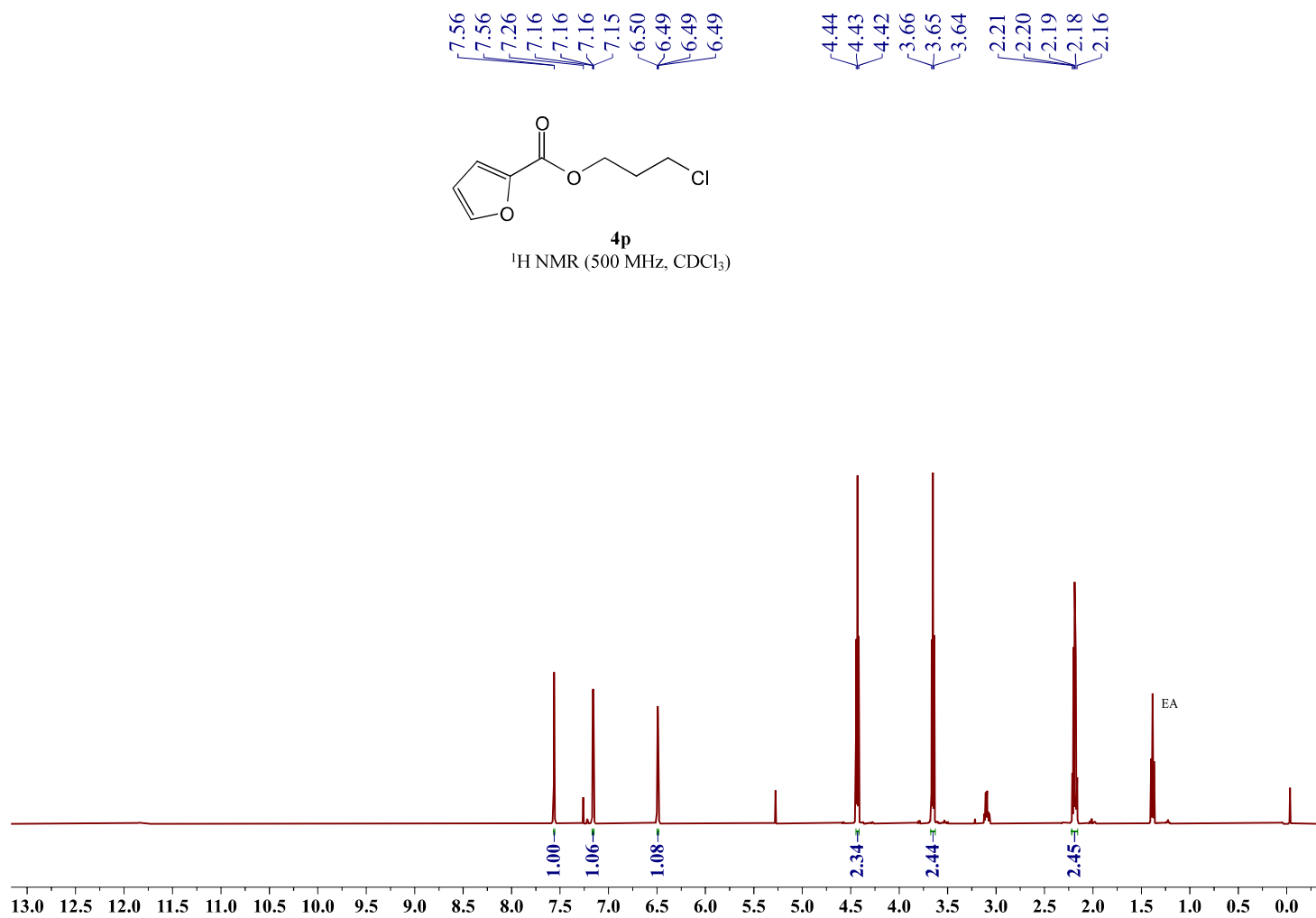
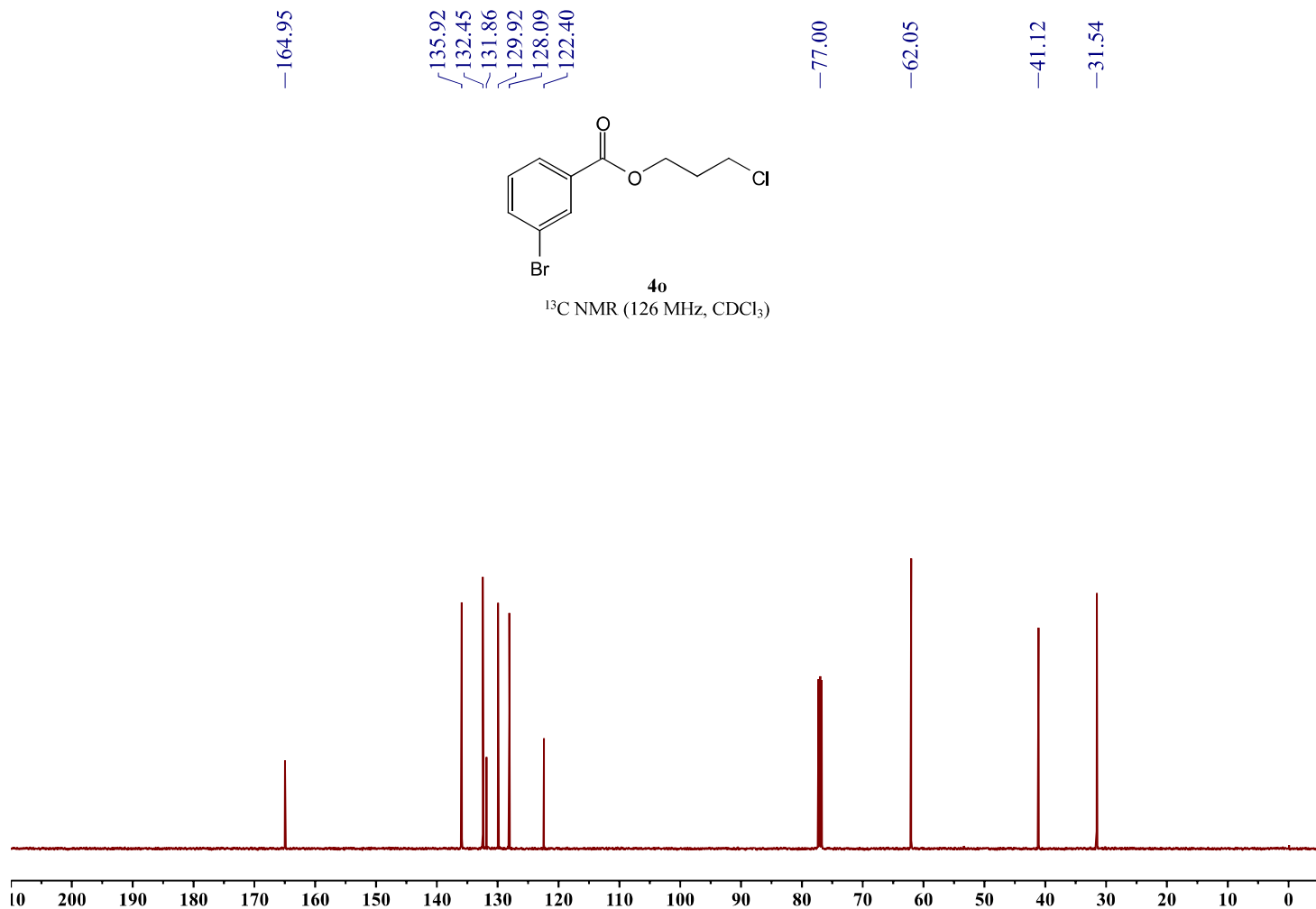


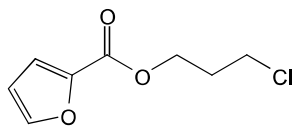
8.14 7.96 7.94 7.68 7.68 7.68 7.67 7.66 7.66 7.33 7.31 7.29 4.48 4.47 4.46 3.70 3.68 3.67 2.25 2.24 2.23 2.22 2.20



4o
¹H NMR (500 MHz, CDCl₃)



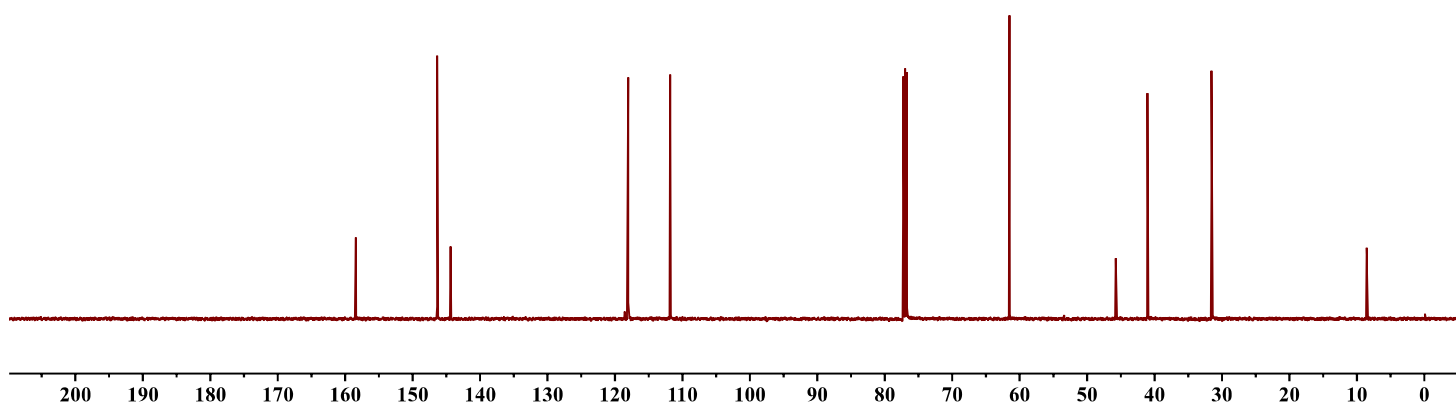




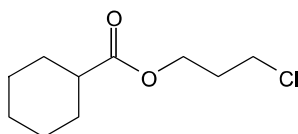
4p

^{13}C NMR (126 MHz, CDCl_3)

—158.43
~146.36
~144.36
—118.03
—111.80
—77.00
—61.51
—45.75
—41.03
—31.56
—8.53

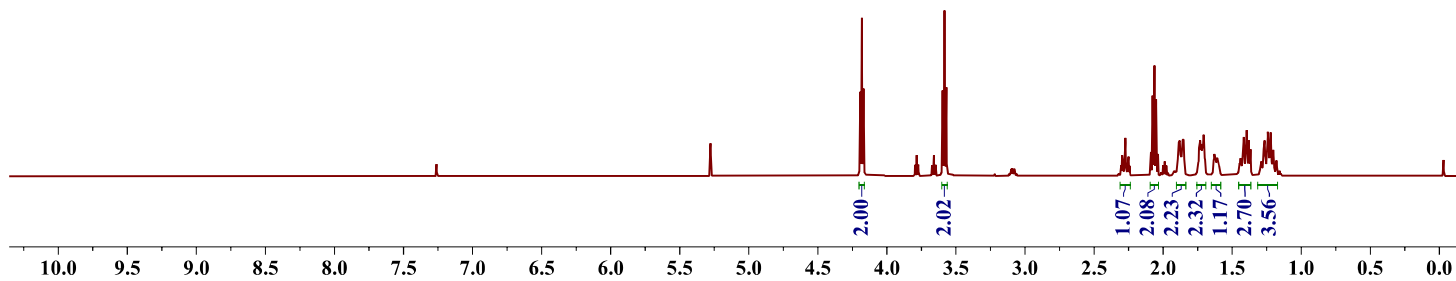


7.26
5.28
4.19
4.18
4.17
3.60
3.58
3.57
2.30
2.29
2.28
2.27
2.26
2.25
2.24
2.09
2.08
2.06
2.05
2.04
1.89
1.88
1.87
1.86
1.85
1.74
1.73
1.72
1.71
1.70
1.63
1.62
1.61
1.60
1.45
1.44
1.42
1.40
1.38
1.37
1.30
1.29
1.27
1.26
1.25
1.24
1.23
1.22
1.20
1.18



4q

^1H NMR (500 MHz, CDCl_3)

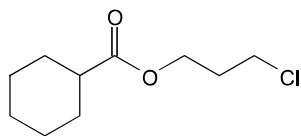


-175.86

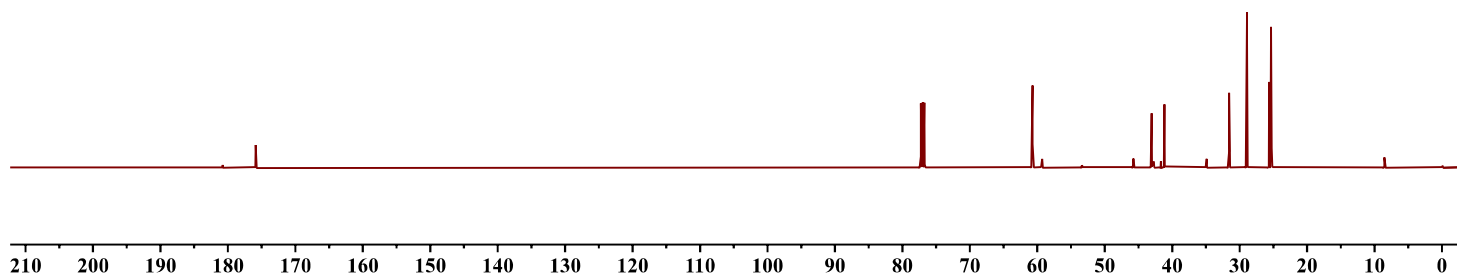
77.25
77.00
76.75

-60.72

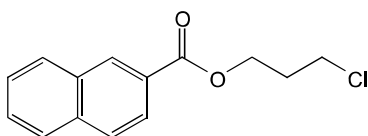
43.06
41.16
31.57
28.92
25.64
25.33



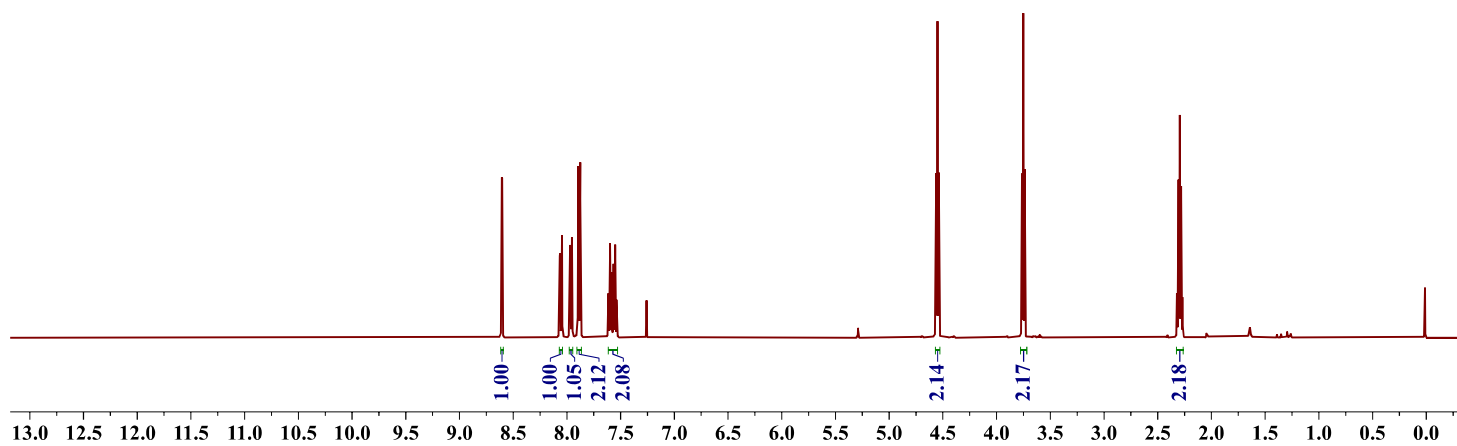
4q
¹³C NMR (126 MHz, CDCl₃)



8.61
8.60
8.07
8.06
8.05
8.05
7.97
7.95
7.89
7.88
7.62
7.61
7.60
7.59
7.58
7.57
7.57
7.55
7.54
7.54
7.26
4.56
4.55
4.54
3.76
3.75
3.74
2.32
2.31
2.29
2.28
2.27



4r
¹H NMR (500 MHz, CDCl₃)



-166.52

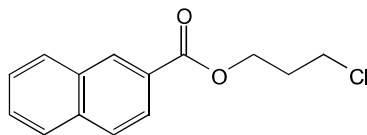
135.52
132.42
131.04
129.31
128.29
128.17
127.73
127.21
126.67
125.10

-77.00

-61.80

-41.32

-31.76



4r

¹³C NMR (126 MHz, CDCl₃)

