Supplementary Information for

Electrochemical S-H and O-H Insertion Reactions from Thiols or Salicylic Acids with Diazo Esters

Zhiqin He,[a] Wei Zhao,[a] Yufeng Li,[a] Yang Yu,[c] Fei Huang*[,a,b]

[a]School of Food Science and Pharmaceutical Engineering, Nanjing Normal University, Nanjing, 210023, P. R. China
[b]School of Pharmaceutical Sciences, Nanjing Tech University, Nanjing, 211816, P. R. China
[c]School of Environmental Science and Engineering, Nanjing Tech University, Nanjing, 211816, P. R. China
Email: huangfei0208@yeah.net

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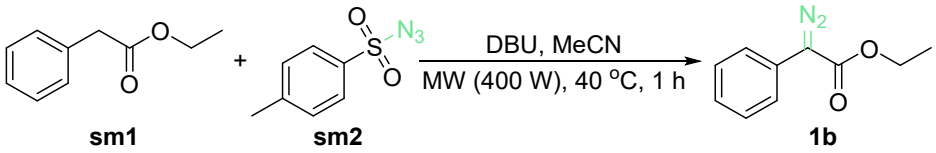
1. General information

The solvents were dried and distilled prior to use by the literature methods. Analytical TLC plates, Sigma-Aldrich silica gel 60F200 were viewed by UV light (254 nm). Column chromatographic purifications were performed on SDZF silica gel 160. The instrument for electrolysis was IKA ElectraSyn 2.0 and both cathode and anode electrodes were graphite electrodes (52 mm × 8 mm × 2 mm). ^{1}H and ^{13}C NMR spectra were obtained on a Bruker NMR spectrometer at 400 MHz and 100 MHz, respectively, and referenced internally based on the residual solvent signal. The data reporting for ^{1}H NMR spectra is as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant in hertz, and number of protons. The data reporting for ^{13}C spectra is given as chemical shift (δ, ppm). High-resolution mass spectra (HRMS) were measured on a Waters GC-TOF CA156 mass spectrometer. X-ray Crystallographic analysis was achieved by the Shanghai institute of Organic Chemistry, Chinese Academy of Sciences. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Compounds **3a**,[1] **3b**,[1] **3c**,[1] **3d**,[2] **3e**,[2] **3g**,[3] **3h**,[4] **3i**,[1] **3j**,[1] **3k**,[5] **3l**,[5] **3m**,[1] **3n**,[2] **3o**,[1] **3p**,[2] **3q**,[6] **3w**,[7] **3y**,[8] **3z1**,[9] **5a**,[6] and 5**f**[10] are known and their spectroscopic feature is in good agreement with that reported in the literature.

2. Experimental procedures

2.1 Preparation of α-diazoesters[1]

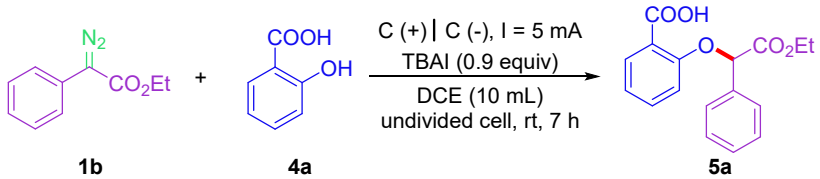


A typical procedure for the synthesis of α-diazoesters 1 - *Synthesis of **1b**:* DBU (2.24 mL, 15 mmol) was added slowly to a stirred solution of ethyl 2-phenylacetate (**sm1a**, 1.41 mL, 10.0 mmol) and tosylazide (**sm2**, 2.42 mL, 11.0 mmol) in the CH_3CN (20 mL) at 0 °C. After that, it was placed in microwave reactor that was heated to 40 °C (400 W, monitored by IR temperature sensor) and maintained at this temperature for 30 min. After cooling to room temperature, the

reaction mixture was quenched with saturated aqueous solution of NH_4Cl (5 mL), extracted with DCM (3 × 30 mL), washed with brine (3 × 30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the product. The residue was purified by flash chromatography (petroleum ether (60-90 °C)/AcOEt, 10:1) to afford the corresponding ethyl-2-diazo-2-phenylacetate **1b** as a yellow oil (1.65 g, 87%).

2.2 Screening the optimum reaction conditions for the synthesis of 5a

Table S1. Screening of reaction conditions.[a]



1b **4a** **5a**

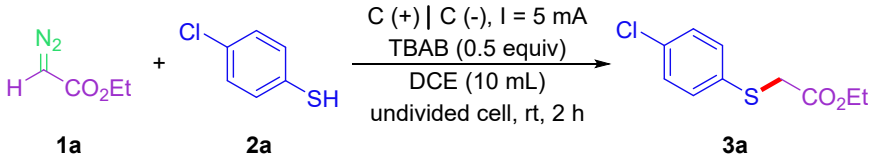
Entry	Variation from the standard conditions	Yield[b] (%)
1	none	**80**
2	DCM instead of DCE	51
3	MeCN instead of DCE	40
4	C (+) | Ni (-) instead of C (+) | C (-)	49
5	C (+) | Pt (-) instead of C (+) | C (-)	37
6	3 mA instead of 5 mA	60
7	7 mA instead of 5 mA	36
8[c]	TBAB instead of TBAI	20
9	$^{n}Bu_4NBF_4$ instead of TBAI	23
10	0.6 mmol **4a**	34
11	1.2 mmol **4a**	64
12	No electric current	33

[a]Reaction Conditions: **1b** (0.3 mmol), **4a** (0.9 mmol), TBAI (0.27 mmol) in DCE (10 mL), graphite electrodes (52 mm × 8 mm × 2 mm) as anode and cathode, constant current = 5 mA, undivided cell, room temperature, 7 h. [b]Isolated yield.

Among a set of representative solvents (Table S1,† entry 1-3), DCE performed better. On replacing the graphite cathode with a Ni cathode or a Pt cathode, the yields decreased strongly (Table S1,† entries 4 and 5). Decreasing the operating current to 3 mA or increasing the operating current to 7 mA delivered the product **5a** in low yield (Table S1,† entries 6 and 7). Other electrolytes, such as TBAB or $^{n}Bu_4NBF_4$ gave a worse performance than TBAI (Table S1,† entries 8 and 9). The ratio of **4a:1b** was

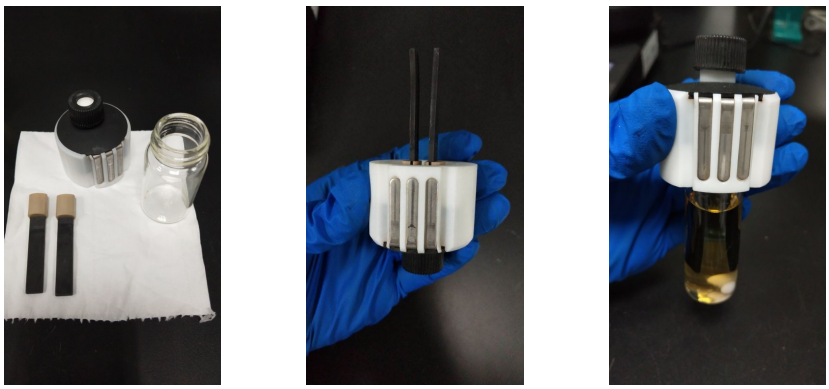
also evaluated, 1:2 and 1:4 gave inferior results (Table S1,† entries 10 and 11). At last, it was observed that this conversion reduced sharply without current, suggesting that electricity was critical for this reaction (Table S1,† entry 12).

2.3 General procedure for S-H insertion of thiols



A typical procedure for the synthesis of S-H insertion products of thiols (3) - *Synthesis of ethyl 2-((4-chlorophenyl)thio)acetate (**3a**):* An ElectraSyn vial (12 mL) with a stir bar was charged with TBAB (80.6 mg, 0.25 mmol), ethyl 2-diazoacetate (**1a**) (57.1 mg, 0.5 mmol) and 4-chlorobenzenethiol (**2a**) (144.6 mg, 1.0 mmol) and DCE (10 mL). [Liquid compounds were added after the addition of DCE. The order of the addition does not affect the result] The ElectraSyn vial cap equipped with graphite electrodes was inserted into the mixture. Then, the reacton mixture was electrolyzed under a constant current of 5 mA until complete consumption of the starting material as judged by TLC. After the reaction, the ElectraSyn vial cap was removed and the combined organic phase was concentrated under reduced pressure. The resultant mixture was subject to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/ethyl acetate = 10:1, v/v) to afford **3a** as a colorless oil (86.5 mg, 75%).

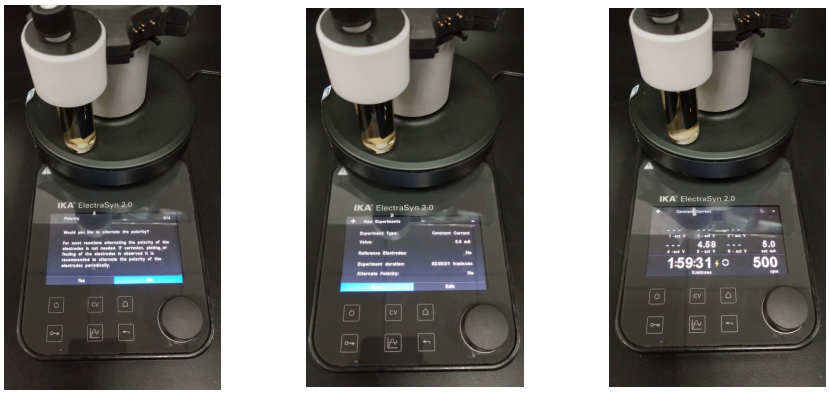
Graphical guide for electrochemical S-H insertion:



Left: graphite electrodes, ElectraSyn 2.0 cap and ElectraSyn 2.0 vial (12 mL). Middle: ElectraSyn 2.0 cap equipped with graphite electrodes. Right: the cap was screwed into the vial and the electrodes were submerged into the solution.

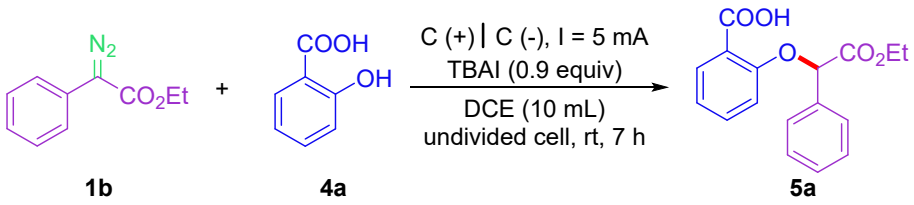
Left: select New experiments. Middle: select Constant Current. Right: adjust the current value.

Left: select Time. Middle: define the “time. Right: indicate the “mmol“ of the substrate.



Left: no alternate polarity. Middle: select the “start“. Right: start the reaction on the ElectraSyn 2.0 with a stirring speed of 500 rpm.

2.4 General procedure for O-H insertion of salicylic acids

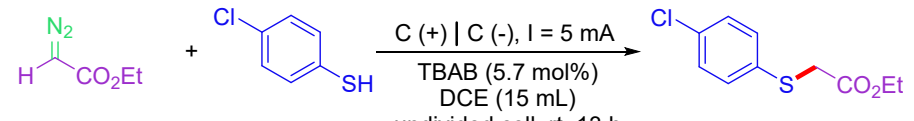


1b **4a** **5a**

A typical procedure for the synthesis of O-H insertion products of salicylic acids (5) - *Synthesis of (R)-2-(2-ethoxy-2-oxo-1-phenylethoxy)benzoic acid (**5a**):* An ElectraSyn vial (12 mL) with a stir bar was charged with TBAI (99.7 mg, 0.27 mmol), ethyl 2-diazo-2-phenylacetate (**1b**) (57.1 mg, 0.3 mmol) and salicylic acid (**4a**) (124.3 mg, 0.9 mmol) and DCE (10 mL). [Liquid compounds were added after the addition of DCE. The order of the addition does not affect the result]. The ElectraSyn vial cap equipped with graphite electrodes were inserted into the mixture. Then, the mixture was electrolyzed under a constant current of 5 mA until complete consumption of the starting material as judged by TLC. After the reaction, the the ElectraSyn vial cap was removed and the combined organic phase was concentrated under reduced pressure. The resultant mixture was subject to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/ethyl acetate = 10:1, v/v) to afford **5a** as a colorless oil (72.1 mg, 80%).

2.5 A gram-scale experiment

1 gram-scale experiment for the synthesis of 3a



1a, 8.8 mmol
1.00 g

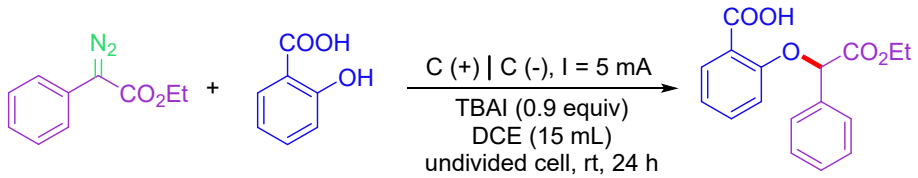
2a, 13.2 mmol
1.90 g

3a, 82%
1.67 g

An ElectraSyn vial (20 mL) with a stir bar was charged with TBAB (161.2 mg, 0.5 mmol), ethyl 2-diazoacetate (**1a**) (1.00 g, 8.8 mmol) and 4-chlorobenzenethiol (**2a**) (1.90 g, 13.2 mmol) and DCE (15 mL). [Liquid compounds were added after the addition of DCE. The order of the addition does not affect the result]. The ElectraSyn vial cap equipped with graphite electrodes were inserted into the mixture. Then, the reacton mixture was electrolyzed under a constant current of 5 mA until complete

consumption of the starting material as judged by TLC. After the reaction, the ElectraSyn vial cap was removed and the combined organic phase was concentrated under reduced pressure. The resultant mixture was subject to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/ethyl acetate = 10:1, v/v) to afford **3a** as a colorless oil (1.67 g, 82%).

1 gram-scale experiment for the synthesis of 5a



1b, 5.3 mmol
1.01 g

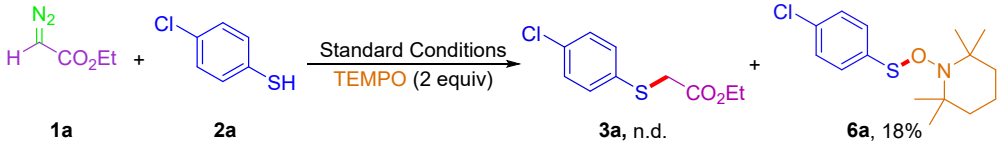
4a, 10.6 mmol
1.46 g

5a, 79%
1.25 g

An ElectraSyn vial (20 mL) with a stir bar was charged with TBAI (0.89 g, 2.4 mmol), ethyl 2-diazo-2-phenylacetate (**1b**) (1.01 g, 5.3 mmol) and salicylic acid (**4a**) (1.46 mg, 10.6 mmol) and DCE (15 mL). [Liquid compounds were added after the addition of DCE. The order of the addition does not affect the result]. The ElectraSyn vial cap equipped with anode (graphite) and cathode (graphite) were inserted into the mixture. Then, the mixture was electrolyzed under a constant current of 5 mA until complete consumption of the starting material as judged by TLC for 24 hours. After completion of the reaction, the ElectraSyn vial cap was removed and the combined organic phase was concentrated under reduced pressure. The resultant mixture was subject to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/ethyl acetate = 10:1, v/v) to afford **5a** as a colorless oil (1.25 g, 79%).

2.6 Mechanism research

Radical-trapping experiment with TEMPO

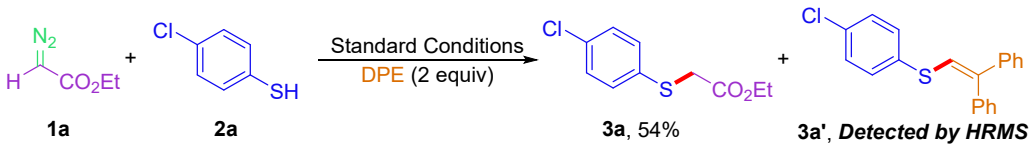


1a **2a** **3a**, n.d. **6a**, 18%

An ElectraSyn vial (12 mL) with a stir bar was charged with TBAB (80.6 mg, 0.25 mmol), ethyl 2-diazoacetate (**1a**) (57.1 mg, 0.5 mmol), 4-chlorobenzenethiol (**2a**)

(144.6 mg, 1.0 mmol), TEMPO (156.3 mg, 1.0 mmol) and DCE (10 mL). [Liquid compounds were added after the addition of DCE. The order of the addition does not affect the result]. The ElectraSyn vial cap equipped with graphite electrodes were inserted into the mixture. Then, the reacton mixture was electrolyzed under a constant current of 5 mA until complete consumption of the starting material as judged by TLC. After the reaction, the ElectraSyn vial cap was removed and the combined organic phase was concentrated under reduced pressure. There, **3a** was not detected by TLC and HRMS. The resultant mixture was subject to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/ethyl acetate = 10:1, v/v) to afford **6a** as a colorless oil (27.0 mg, 18%).

Radical-trapping experiment with DPE



1a **2a** **3a**, 54% **3a'**, ***Detected by HRMS***

An ElectraSyn vial (12 mL) with a stir bar was charged with TBAB (80.6 mg, 0.25 mmol), ethyl 2-diazoacetate (**1a**) (57.1 mg, 0.5 mmol), 4-chlorobenzenethiol (**2a**) (144.6 mg, 1.0 mmol), DPE (180.3 mg, 1.0 mmol) and DCE (10 mL). [Liquid compounds were added after the addition of DCE. The order of the addition does not affect the result]. The ElectraSyn vial cap equipped with graphite electrodes were inserted into the mixture. Then, the reacton mixture was electrolyzed under a constant current of 5 mA until complete consumption of the starting material as judged by TLC. After the reaction, the ElectraSyn vial cap was removed and the combined organic phase was concentrated under reduced pressure. The resultant mixture was subject to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/ethyl acetate = 10:1, v/v) to afford **3a** as a colorless oil (62.3 mg, 54%). And the radical intermediated **3a′** was trapped by DPE were detected by HRMS (**Figure S1**).

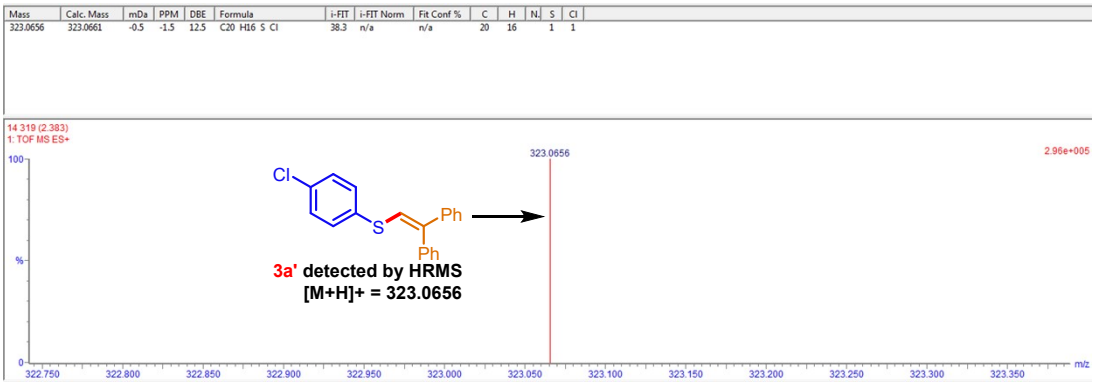
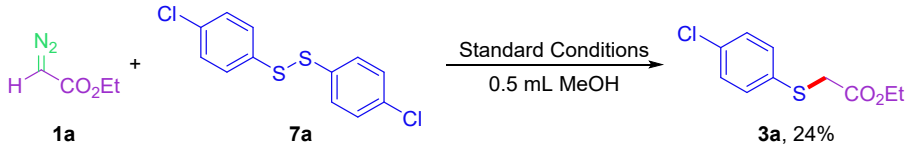


Figure S1. HRMS analysis of the formation of product **3a′**.

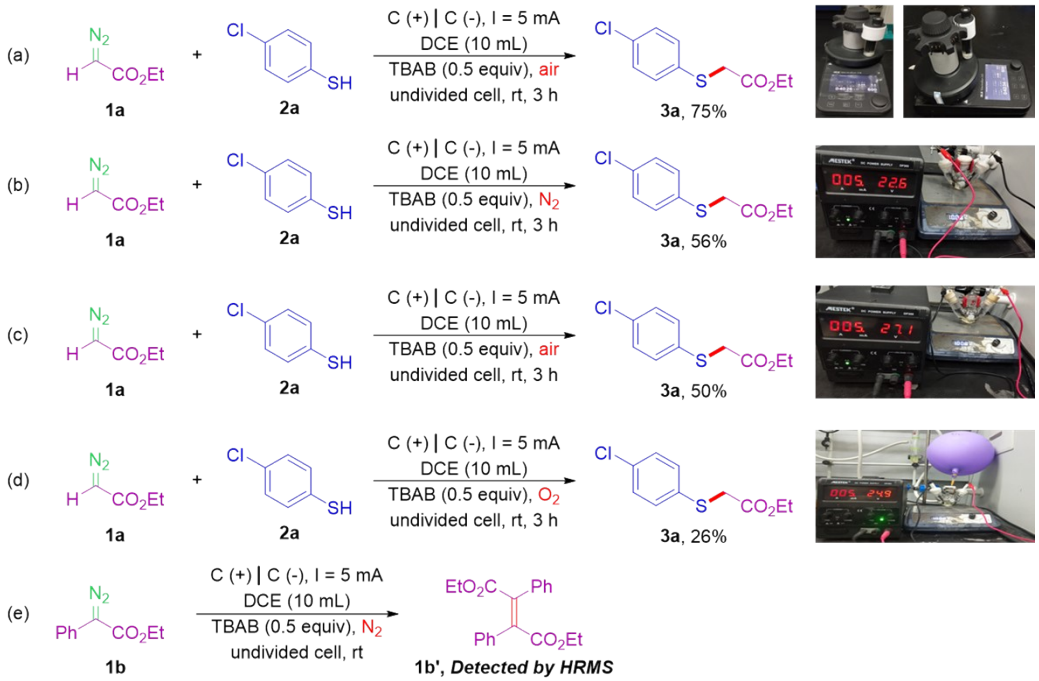
The experiment starting from disulfide 7a



1a **7a** **3a**, 24%

An ElectraSyn vial (12 mL) with a stir bar was charged with TBAB (80.6 mg, 0.25 mmol), 1,2-bis(4-chlorophenyl)disulfane (**7a**) (287.3 mg, 1.0 mmol), ethyl 2-diazoacetate (**1a**) (57.1 mg, 0.5 mmol), MeOH (0.5 mL) and DCE (10 mL). [Liquid compounds were added after the addition of DCE. The order of the addition does not affect the result]. The ElectraSyn vial cap equipped with graphite electrodes were inserted into the mixture. Then, the reacton mixture was electrolyzed under a constant current of 5 mA until complete consumption of the starting material as judged by TLC. After the reaction, the ElectraSyn vial cap was removed and the combined organic phase was concentrated under reduced pressure. The resultant mixture was subject to purification by column chromatography on silica gel (eluent: petroleum ether (60-90 ^{o}C)/ethyl acetate = 10:1, v/v) to afford **3a** as a colorless oil (28 mg, 24%).

The gas protection experiments



The gas protection test cannot be conducted for IKA ElectraSyn 2.0 in our laboratory (eqn (a)), thus we use the dual display potentiostat (DP-305) (made in China) for this control experiments. In an oven-dried undivided three-necked cell (25 mL) equipped with a stir bar, TBAB (80.6 mg, 0.25 mmol) and 4-chlorobenzenethiol (**2a**) (144.6 mg, 1.0 mmol) were combined and added. The cell was equipped with carbon cloth (60 mm × 6 mm) as the anode and cathode and then charged with nitrogen. Under the protection of N_2, DCE (10 mL) and ethyl 2-diazoacetate (**1a**) (57.1 mg, 0.5 mmol) was injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzsd at a constant current of 5.0 mA at room temperature for 3.0 h. After the reaction, the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/ethyl acetate = 10:1, v/v) to afford **3a** as a colorless oil (64.0 mg, 56%) (eqn (b)).

In an oven-dried undivided three-necked cell (25 mL) equipped with a stir bar, TBAB (80.6 mg, 0.25 mmol), 4-chlorobenzenethiol (**2a**) (144.6 mg, 1.0 mmol), DCE (10 mL) and ethyl 2-diazoacetate (**1a**) (57.1 mg, 0.5 mmol) were combined and added. The cell was equipped with carbon cloth (60 mm × 6 mm) as the anode and cathode. The reaction mixture was stirred and electrolyzsd at a constant current of 5.0 mA at room temperature for 3.0 h. After the reaction, the pure product was obtained by flash

column chromatography on silica gel (eluent: petroleum ether (60-90 °C)/ethyl acetate = 10:1, v/v) to afford **3a** as a colorless oil (57.0 mg, 50%) (eqn (c)).

In an oven-dried undivided three-necked cell (25 mL) equipped with a stir bar, TBAB (80.6 mg, 0.25 mmol) and 4-chlorobenzenethiol (**2a**) (144.6 mg, 1.0 mmol) were combined and added. The cell was equipped with carbon cloth (60 mm × 6 mm) as the anode and cathode and then charged with oxygen. Under the protection of O_2, DCE (10 mL) and ethyl 2-diazoacetate (**1a**) (57.1 mg, 0.5 mmol) was injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzsd at a constant current of 5.0 mA at room temperature for 3.0 h. After the reaction, the pure product was obtained by flash column chromatography on silica gel. (eluent: petroleum ether (60-90 °C)/ethyl acetate = 10:1, v/v) to afford **3a** as a colorless oil (30.0 mg, 26%) (eqn (d)).

In an oven-dried undivided three-necked cell (25 mL) equipped with a stir bar, TBAB (80.6 mg, 0.25 mmol) was added. The cell was equipped with carbon cloth (60 mm × 6 mm) as the anode and cathode and then charged with nitrogen. Under the protection of N_2, DCE (10 mL) and ethyl 2-diazo-2-phenylacetate (**1b**) (95.1 mg, 0.5 mmol) was injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzsd at a constant current of 5.0 mA at room temperature (eqn (e)). And we found the formation of **1b'** (the dimerization of **1b**) detected by HRMS (**Figure S2**).

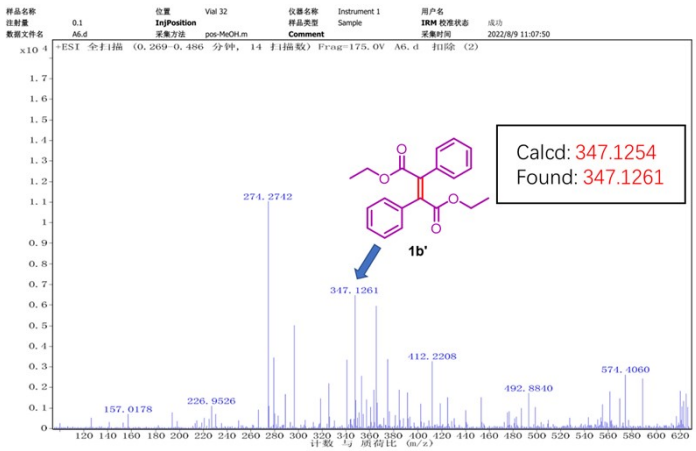


Figure S2. HRMS analysis of the formation of product **1b'**.

2.7 CV experiments

Cyclic voltammetry was performed in a three electrode cell under air at room temperature. The working electrode was a 3 mm glassy carbon electrode while the counter electrode was a platinum mesh. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. The solvent (DCE = 10 mL) containing TBAB (0.1 mmol) and $^{n}Bu_4NBF_4$ (0.1 mmol) were poured into thr electrochemical cell in cyclic voltammetry experiments. The scan rate was 0.1 V/s, ranging from 0.0 V to 3.8 V. The peak potentials *vs*. Ag/AgCl for used. An obvious oxidation peak of TEMPO was observed at 2.70 V. The oxidation peak of 4-chlorobenzenethiol **2a** could also observed at 2.50 V. So, **2a** was oxidized preferentially at the anode than TEMPO in this system, which indicated that the feasibility of TEMPO as a free radical trapping agent. A reduction peak of 4,4′-dichlorodiphenyl disulfide **7a** was observed at -1.58 V under the reaction solvent system. Therefore, the **7a** may involve in reduction processes in the catalytic cycle.

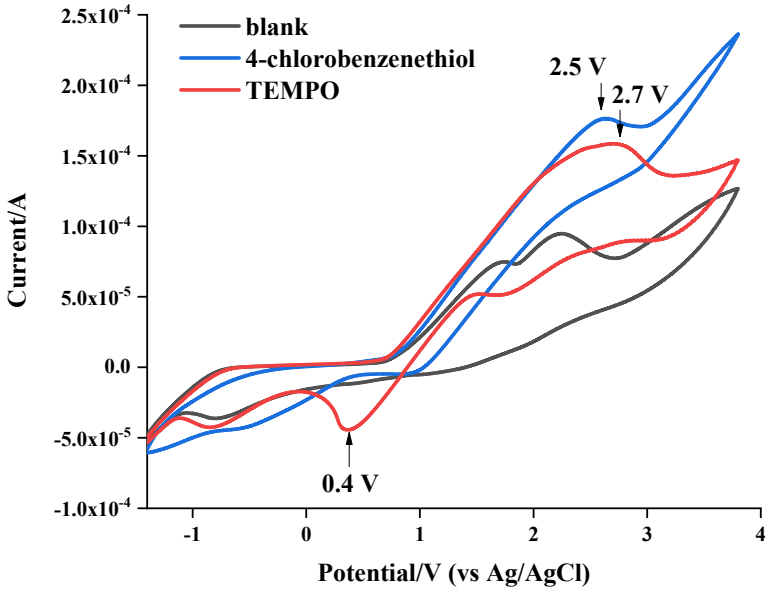


Figure S3. Cyclic voltammograms of related compounds (0.1 mmol) in DCE with $^{n}Bu_4NBF_4$ (0.01 M) and TBAB (0.01 M) at a scan rate of v = 100 mV/s.

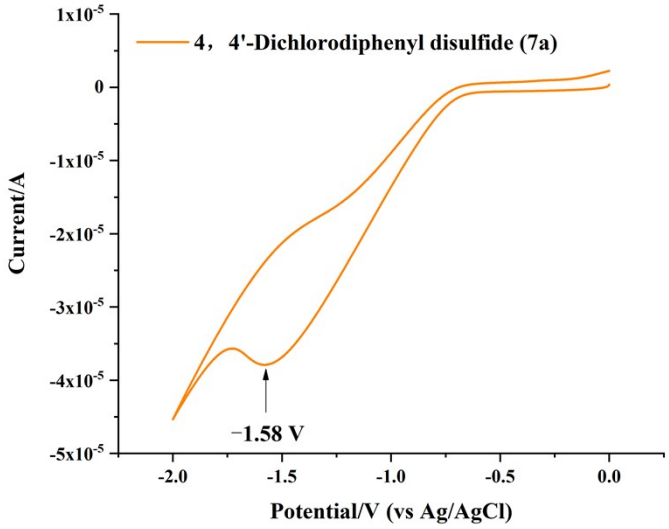
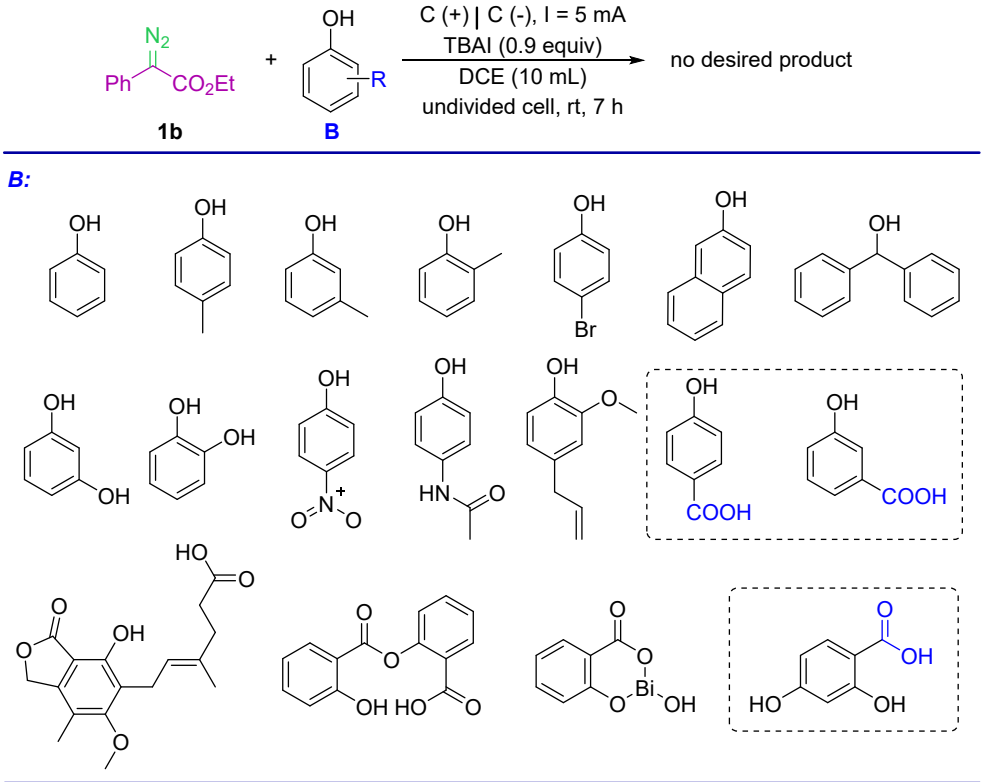


Figure S4. Cyclic voltammetry of **7a** (0.1 mmol) in DCE with TBAB (0.01 M) at a scan rate of v = 100 mV/s.

2.8 Failed experiments

Table S2. Different substituent groups on the benzene ring of phenol.[a]



[a] Conditions: **1b** (0.3 mmol), **B** (0.9 mmol), TBAI (0.27 mmol) in DCE (10 mL), graphite electrodes (52 mm × 8 mm × 2 mm) as anode and cathode, constant current = 5 mA, undivided cell, room temperature, 7 h, isolated yield.

For O-H insertion, we have tried different phenols with diazo compounds for the construction of C-O bonds. However, no obvious target product was produced. As shown in the Table S2, 4-hydroxybenzoic acid, 3-hydroxybenzoic acid and 2,4-dihydroxybenzoic acid all contain carboxyl group, but the envisaged products were not generated. Therefore, we speculated that it may be related to hydrogen bond and the damage of this system to the electrode.[11]

2.9 NMR experiments

No obvious target product was produced when the substrate contained carboxylic acids, such as 4-hydroxybenzoic acid **4d** and 3-hydroxybenzoic acid **4e**. Therefore, it cannot be ruled out whether acidity can promote the reaction. Based on the above results and the literature proceedings,[12] we speculate that hydrogen bond plays a vital role in this conversion. Then, hydrogen bond was further studied through NMR in $(CD_3)_2SO$. Comparing the chemical shifts of hydrogen in hydroxyl group in Fig S5, obvious hydrogen bond was observed for 2-hydroxybenzoic acid (13.8921>10.2144>9.7373), which agreed with our previously proposed hydrogen-bond interaction.

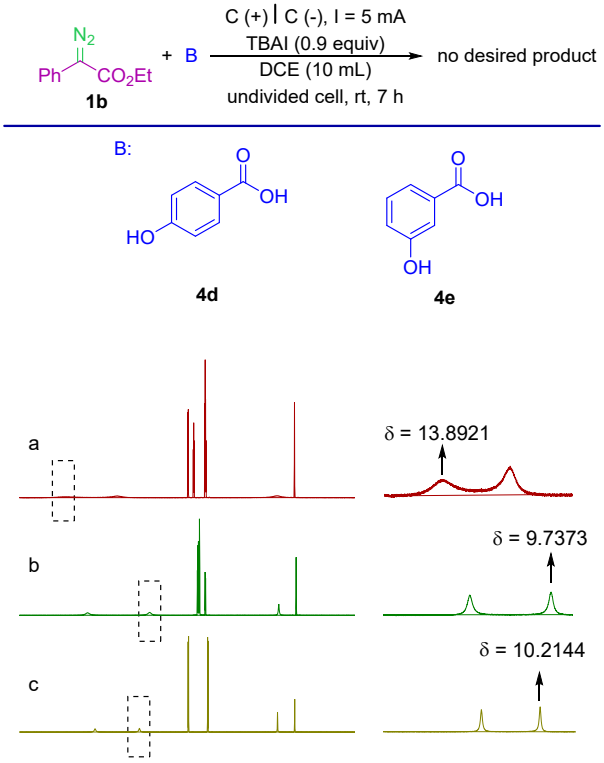
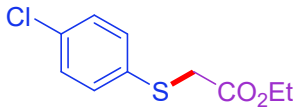
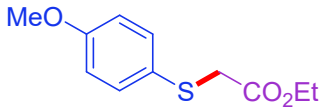


Figure S5. ^{1}H NMR spectra of the benzoic acid signals in $(CD_3)_2SO$. (a) 2-hydroxybenzoic acid, (b) 3-hydroxybenzoic acid, (c) 4-hydroxybenzoic acid.

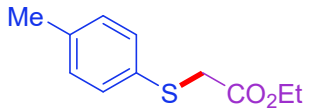
3. Characterization data for products



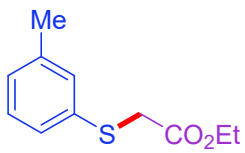
Ethyl 2-((4-chlorophenyl)thio)acetate (3a): 86.5 mg, 75% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.60 (s, 2H), 1.22 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.6, 133.6, 133.3, 131.6, 129.3, 61.8, 37.0, 14.2. The analytical data are consistent with literature.[1]



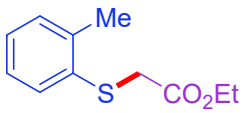
Ethyl 2-((4-methoxyphenyl)thio)acetate (3b): 84.9 mg, 75% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 3.50 (s, 2H), 1.21 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.1, 159.8, 134.4, 125.1, 114.8, 61.5, 55.5, 38.8, 14.2. The analytical data are consistent with literature.[1]



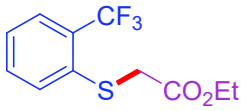
Ethyl 2-(p-tolylthio)acetate (3c): 73.6 mg, 70% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.58 (s, 2H), 2.32 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 169.9, 137.4, 131.2, 131.0, 129.9, 61.6, 37.5, 21.2, 14.2. The analytical data are consistent with literature.[1]



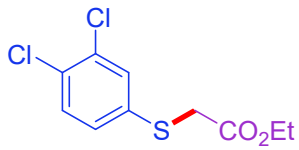
Ethyl 2-(m-tolylthio)acetate (3d): 67.3 mg, 64% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 3H), 7.03 (d, J = 7.0 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.62 (s, 2H), 2.32 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.8, 138.8, 134.8, 130.6, 128.9, 127.8, 127.0, 61.5, 36.7, 21.3, 14.1. The analytical data are consistent with literature.[2]



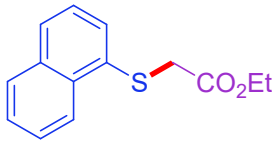
Ethyl 2-(o-tolylthio)acetate (3e): 76.8 mg, 73% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 1H), 7.20 – 7.09 (m, 3H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.61 (s, 2H), 2.42 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.8, 138.5, 134.3, 130.4, 129.7, 127.0, 126.7, 61.7, 36.1, 20.5, 14.2. The analytical data are consistent with literature.[2]



Ethyl 2-((2-(trifluoromethyl)phenyl)thio)acetate (3f): 80.6 mg, 61% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.2, 134.5, 132.7, 132.3, 130.7 (q, *J* = 30.2 Hz), 127.1, 127.0 (q, *J* = 5.7 Hz), 123.8 (q, *J* = 273.7 Hz), 61.8, 37.1, 14.1. HRMS (EI) calcd for $C_{11}H_{12}F_3O_2S$ $[M+H]^+$ 265.0505, found 265.0513.

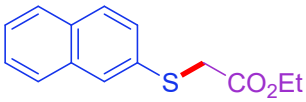


Ethyl 2-((3,4-dichlorophenyl)thio)acetate (3g): 120.6 mg, 91% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 2.2 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.22 (dd, *J* = 8.4, 2.2 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.2, 135.4, 133.1, 131.3, 130.8, 129.0, 100.1, 62.0, 36.5, 14.2. The analytical data are consistent with literature.[3]

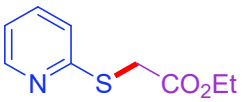


Ethyl 2-(naphthalen-1-ylthio)acetate (3h): 103.5 mg, 84% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.71 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.62 – 7.49 (m, 2H), 7.42 (dd, *J* = 8.1, 7.3 Hz, 1H), 4.09 (q, *J* = 7.1 Hz,

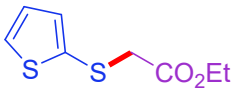
2H), 3.66 (s, 2H), 1.14 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.8, 134.1, 133.4, 131.9, 130.7, 128.8, 126.9, 126.5, 125.7, 125.2, 61.6, 37.4, 14.1. The analytical data are consistent with literature.[4]



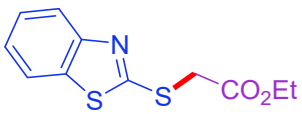
Ethyl 2-(naphthalen-2-ylthio)acetate (3i): 80.1 mg, 65% yield, colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.78 (m, 3H), 7.52 – 7.42 (m, 3H), 4.17 (q, J = 7.1 Hz, 2H), 3.74 (s, 2H), 1.21 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.7, 133.7, 132.4, 132.1, 128.6, 128.2, 127.7, 127.6, 127.3, 126.6, 126.1, 61.6, 36.7, 14.1. The analytical data are consistent with literature.[1]



Ethyl 2-(pyridin-2-ylthio)acetate (3j): 94.7 mg, 96% yield, colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (ddd, J = 4.9, 1.7, 0.9 Hz, 1H), 7.45 (ddd, J = 8.0, 7.5, 1.8 Hz, 1H), 7.19 (dt, J = 8.1, 0.9 Hz, 1H), 6.95 (ddd, J = 7.3, 4.9, 1.0 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.94 (s, 2H), 1.22 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.8, 157.0, 149.3, 136.1, 122.0, 119.8, 61.5, 32.3, 14.1. The analytical data are consistent with literature.[1]

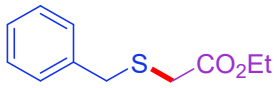


Ethyl 2-(thiophen-2-ylthio)acetate (3k): 70.0 mg, 69% yield, colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 5.4, 1.2 Hz, 1H), 7.20 (dd, J = 3.6, 1.2 Hz, 1H), 6.97 (dd, J = 5.4, 3.6 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.48 (s, 2H), 1.24 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.5, 135.2, 132.5, 130.6, 127.7, 61.6, 41.1, 14.2. The analytical data are consistent with literature.[5]

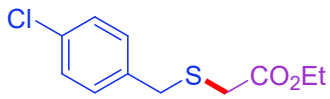


Ethyl 2-(benzo[*d*]thiazol-2-ylthio)acetate (3l): 100.0 mg, 79% yield, colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.1 Hz, 1H), 7.75 (dd, J = 8.0, 0.5 Hz, 1H), 7.41 (t, J = 7.7 Hz, 1H),

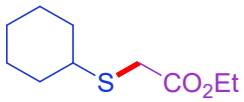
7.30 (t, J = 7.6 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 4.17 (s, 2H), 1.29 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 168.4, 164.9, 153.0, 135.6, 126.2, 124.6, 121.8, 121.2, 62.2, 35.3, 14.3. The analytical data are consistent with literature.[5]



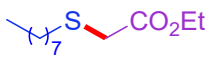
Ethyl 2-(benzylthio)acetate (3m): 65.2 mg, 62% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 7.27 – 7.21 (m, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.82 (s, 2H), 3.05 (s, 2H), 1.28 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.5, 137.3, 129.3, 128.6, 127.4, 61.4, 36.4, 32.3, 14.3. The analytical data are consistent with literature.[1]



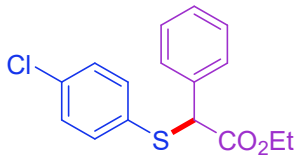
(4-chlorobenzyl)(2-(ethylperoxy)-2λ²-ethyl)sulfane (3n): 74.6 mg, 61% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 0.8 Hz, 4H), 4.17 (q, J = 7.1 Hz, 2H), 3.79 (s, 2H), 3.04 (s, 2H), 1.28 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.4, 135.9, 133.2, 130.6, 128.8, 61.5, 35.7, 32.3, 14.3. The analytical data are consistent with literature.[2]



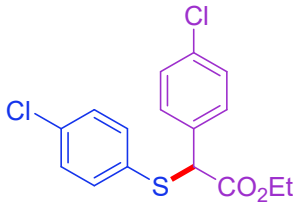
Ethyl 2-(cyclohexylthio)acetate (3o): 40.5 mg, 40% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 (q, J = 7.2 Hz, 2H), 3.24 (s, 2H), 2.92 – 2.68 (m, 1H), 2.04 – 1.93 (m, 2H), 1.80 – 1.71 (m, 2H), 1.48 – 1.06 (m, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 171.1, 61.4, 44.1, 33.2, 32.2, 26.1, 25.9, 14.3. The analytical data are consistent with literature.[1]



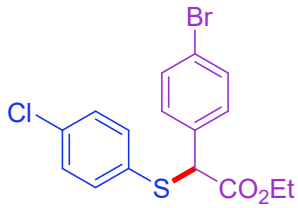
Ethyl 2-(octylthio)acetate (3p): 70.9 mg, 61% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 (q, J = 7.1 Hz, 2H), 3.19 (s, 2H), 2.67 – 2.57 (m, 2H), 1.63 – 1.53 (m, 2H), 1.40 – 1.32 (m, 2H), 1.30 – 1.23 (m, 11H), 0.87 (t, J = 6.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8, 61.4, 33.9, 32.8, 31.9, 29.4, 29.3, 29.1, 28.9, 22.8, 14.3, 14.2. The analytical data are consistent with literature.[2]



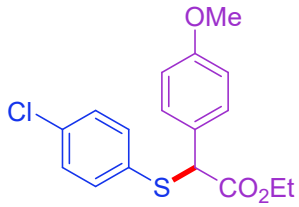
Ethyl (S)-2-((4-chlorophenyl)thio)-2-phenylacetate (3q): 98.2 mg, 64% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.36 – 7.32 (m, 1H), 7.31 (m, 3H), 7.28 (m, 1H), 7.25 – 7.20 (m, 2H), 4.86 (s, 1H), 4.21 – 4.07 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.3, 135.5, 134.5, 134.4, 132.2, 129.2, 128.9, 128.7, 128.6, 62.0, 56.6, 14.1. The analytical data are consistent with literature.[6]



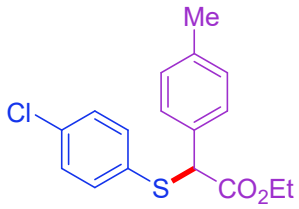
Ethyl (S)-2-(4-chlorophenyl)-2-((4-chlorophenyl)thio)acetate (3r): 117.7 mg, 69% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.30 (m, 2H), 7.27 (t, *J* = 3.5 Hz, 2H), 7.24 (dd, *J* = 8.6, 2.1 Hz, 2H), 4.80 (s, 1H), 4.18 – 4.09 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.9, 134.8, 134.7, 134.5, 134.1, 131.7, 130.0, 129.3, 129.0, 62.2, 55.9, 14.1. HRMS (EI) calcd for $C_{16}NH_{18}Cl_2O_2S$ $[M+NH_4]^+$ 358.0430, found 358.0430.



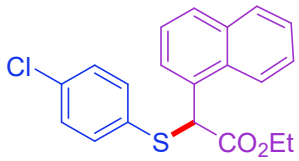
Ethyl (S)-2-(4-bromophenyl)-2-((4-chlorophenyl)thio)acetate (3s): 129.2 mg, 67% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.8, 2.2 Hz, 2H), 7.28 (dd, *J* = 8.6, 2.1 Hz, 4H), 7.23 (dd, *J* = 8.7, 2.1 Hz, 2H), 4.79 (s, 1H), 4.19 – 4.08 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.8, 134.8, 134.6, 132.0, 131.6, 130.3, 129.3, 122.7, 62.1, 56.0, 14.1. HRMS (EI) calcd for $C_{16}H_{15}BrClO_2S$ $[M+H]^+$ 384.9659, found 384.9654.



Ethyl (S)-2-((4-chlorophenyl)thio)-2-(4-methoxyphenyl)acetate (3t): 52.2 mg, 31% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* =8.7, 2.5 Hz, 2H), 7.29 (dd, *J* = 8.8, 2.2 Hz, 2H), 7.23 (dd, *J* = 8.8, 2.2 Hz, 2H), 6.87 – 6.83 (m, 2H), 4.83 (s, 1H), 4.17 – 4.07 (m, 2H), 3.79 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.4, 159.7, 134.3, 134.2, 132.4, 129.8, 129.2, 127.3, 114.2, 61.9, 55.9, 55.4, 14.1. HRMS (EI) calcd for $C_{17}H_{17}ClO_3SNa$ $[M+Na]^+$ 359.0479, found 359.0479.

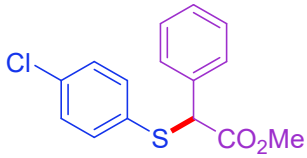


Ethyl (S)-2-((4-chlorophenyl)thio)-2-(p-tolyl)acetate (3u): 83.4 mg, 52% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3, 4H), 7.23 (dd, *J* = 8.8, 2.3 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 4.84 (s, 1H), 4.12 (m, 2H), 2.33 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.4, 138.4, 134.3, 134.1, 132.5, 132.4, 129.6, 129.2, 128.5, 61.9, 56.3, 21.3, 14.1. HRMS (EI) calcd for $C_{17}H_{17}ClO_2SNa$ $[M+Na]^+$ 343.0530, found 343.0532.

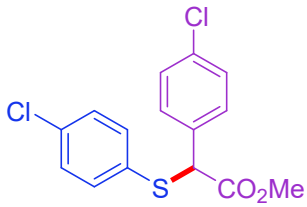


Ethyl (S)-2-((4-chlorophenyl)thio)-2-(naphthalen-1-yl)acetate (3v): 35.7 mg, 20% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.58 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.30 (dd, *J* = 8.9, 2.3 Hz, 2H), 7.21 (dd, *J* = 8.9, 2.3 Hz, 2H), 5.62 (s, 1H), 4.24 – 4.06 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 134.4, 134.3, 134.1, 132.6, 131.1, 131.0, 129.3, 129.2, 129.1, 127.0, 126.9, 126.1,

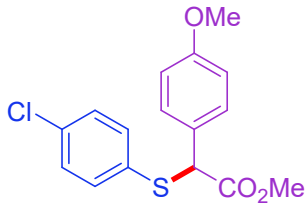
125.5, 123.2, 62.2, 53.3, 14.2. HRMS (EI) calcd for $C_{20}H_{17}ClO_2SNa$ $[M+Na]^+$ 379.0530, found 379.0525.



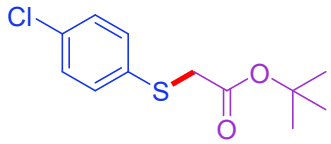
Methyl (S)-2-((4-chlorophenyl)thio)-2-phenylacetate (3w): 103.9 mg, 71% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.34 – 7.27 (m, 5H), 7.23 (dd, *J* = 8.8, 2.2 Hz, 2H), 4.88 (s, 1H), 3.69 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 135.4, 134.5, 134.4, 132.1, 129.2, 128.9, 128.6, 128.5, 56.5, 52.9. The analytical data are consistent with literature.[7]



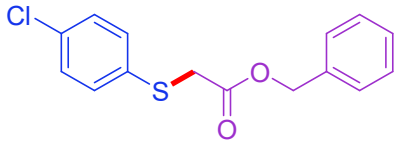
Methyl (S)-2-(4-chlorophenyl)-2-((4-chlorophenyl)thio)acetate (3x): 99.8 mg, 61% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.6, 2.1 Hz, 2H), 7.30 (dd, *J* = 8.7, 2.6 Hz, 2H), 7.27 (dd, *J* = 8.7, 2.5 Hz, 2H), 7.24 (dd, *J* = 8.6, 2.1 Hz, 2H), 4.82 (s, 1H), 3.69 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.3, 134.9, 134.7, 134.5, 134.0, 131.5, 130.0, 129.4, 129.0, 55.8, 53.0. HRMS (EI) calcd for $C_{15}H_{13}Cl_2O_2S$ $[M+H]^+$ 327.0008, found 327.0024.



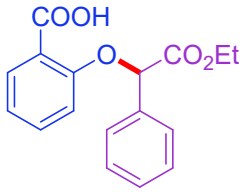
Methyl (S)-2-((4-chlorophenyl)thio)-2-(4-methoxyphenyl)acetate (3y): 90.38 mg, 56% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 9.2, 2.5 Hz, 2H), 7.35 (dd, *J* = 8.7, 2.2 Hz, 2H), 7.32 – 7.27 (m, 2H), 6.92 (dd, *J* = 9.3, 2.6 Hz, 2H), 4.91 (s, 1H), 3.87 (s, 3H), 3.75 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.0, 159.8, 134.5, 134.4, 132.2, 129.8, 129.3, 127.3, 114.3, 55.9, 55.4, 52.9. The analytical data are consistent with literature.[8]



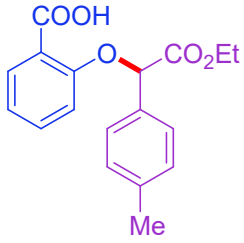
Tert-butyl 2-((4-chlorophenyl)thio)acetate (3z1): 81.5 mg, 63% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 8.9, 2.3 Hz, 2H), 7.25 (dd, *J* = 8.9, 2.3 Hz, 2H), 3.52 (s, 2H), 1.40 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.6, 133.9, 132.9, 131.3, 129.2, 82.2, 37.9, 28.0. The analytical data are consistent with literature.[9]



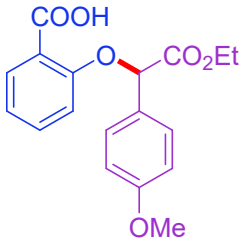
Benzyl 2-((4-chlorophenyl)thio)acetate (3z2): 93.69 mg, 64% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 3H), 7.29 (dd, *J* = 9.0, 2.4 Hz, 3H), 7.28 – 7.25 (m, 1H), 7.22 (dd, *J* = 8.9, 2.3 Hz, 2H), 5.13 (s, 2H), 3.64 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.4, 135.3, 133.4, 133.3, 131.8, 129.3, 128.7, 128.6, 128.5, 67.5, 37.0. HRMS (EI) calcd for $C_{15}H_{14}ClO_2S$ $[M+H]^+$ 293.0398, found 293.0406.



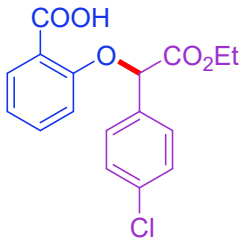
(R)-2-(2-Ethoxy-2-oxo-1-phenylethoxy)benzoic acid (5a): 72.1 mg, 80% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.00 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.59 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.51 – 7.41 (m, 4H), 7.00 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.91 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 6.15 (s, 1H), 4.24 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.4, 168.4, 161.9, 136.4, 133.6, 130.4, 129.6, 129.0, 127.7, 119.5, 117.7, 111.9, 75.3, 62.1, 14.1. The analytical data are consistent with literature.[6]



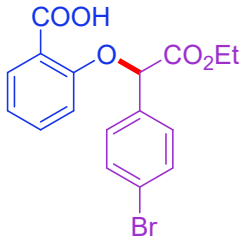
(R)-2-(2-Ethoxy-2-oxo-1-(p-tolyl)ethoxy)benzoic acid (5b): 62.3 mg, 65% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.98 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.99 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.90 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 6.11 (s, 1H), 4.30 – 4.15 (m, 2H), 2.39 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.5, 168.6, 161.9, 139.7, 136.3, 130.7, 130.5, 129.7, 127.8, 119.5, 117.7, 112.0, 75.2, 62.0, 21.4, 14.1. HRMS (EI) calcd for $C_{18}H_{18}O_5Na$ $[M+Na]^+$ 337.1046, found 337.1045.



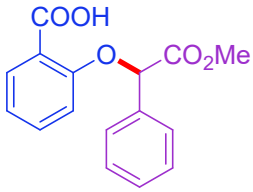
(R)-2-(2-Ethoxy-1-(4-methoxyphenyl)-2-oxoethoxy)benzoic acid (5c): 21.8 mg, 22% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.46 (m, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.89 (t, *J* = 7.1 Hz, 1H), 6.08 (s, 1H), 4.30 – 4.16 (m, 2H), 3.83 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.5, 168.7, 161.9, 160.6, 136.3, 130.5, 129.3, 125.7, 119.5, 117.7, 114.5, 112.0, 75.0, 62.0, 55.5, 14.2. HRMS (EI) calcd for $C_{18}H_{18}O_6Na$ $[M+Na]^+$ 353.0996, found 353.0999.



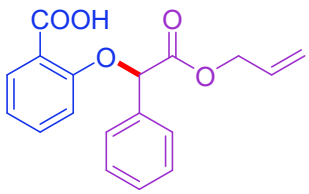
(R)-2-(1-(4-Chlorophenyl)-2-ethoxy-2-oxoethoxy)benzoic acid (5d): 47.2 mg, 47% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.96 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.11 (s, 1H), 4.23 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.2, 168.1, 162.0, 136.5, 135.7, 132.1, 130.3, 129.3, 129.1, 119.6, 117.8, 111.7, 74.5, 62.3, 14.1. HRMS (EI) calcd for $C_{17}H_{15}ClO_5Na$ $[M+Na]^+$ 357.0500, found 357.0503.



(R)-2-(1-(4-Bromophenyl)-2-ethoxy-2-oxoethoxy)benzoic acid (5e): 83.0 mg, 73% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.96 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.57 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.92 (ddd, *J* = 8.1, 7.2, 1.0 Hz, 1H), 6.10 (s, 1H), 4.32 – 4.16 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.2, 168.0, 162.0, 136.6, 132.7, 132.3, 130.3, 129.4, 123.9, 119.6, 117.9, 111.7, 74.6, 62.3, 14.1. HRMS (EI) calcd for $C_{17}H_{15}BrO_5Na$ $[M+Na]^+$ 400.9995, found 400.9992.

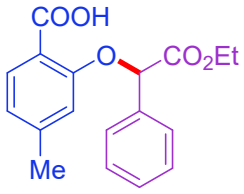


(R)-2-(2-Methoxy-2-oxo-1-phenylethoxy)benzoic acid (5f): 39.5 mg, 46% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.00 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.58 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.51 – 7.43 (m, 4H), 7.00 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.91 (ddd, *J* = 8.1, 7.3, 1.0 Hz, 1H), 6.18 (s, 1H), 3.77 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.4, 168.9, 162.0, 136.4, 133.5, 130.4, 129.7, 129.1, 127.8, 119.5, 117.8, 111.8, 75.1, 53.0. The analytical data are consistent with literature.[10]

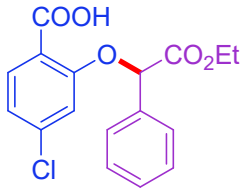


(R)-2-(2-(Allyloxy)-2-oxo-1-phenylethoxy)benzoic acid (5g): 23.4 mg, 25% yield, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 7.99 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.58 (dd, *J* = 7.3, 2.3 Hz, 2H), 7.49 (ddd, *J* = 8.8, 7.4, 1.8 Hz, 1H), 7.44 (m, 3H), 7.00 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.91 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 6.19 (s, 1H), 5.85 (ddt, *J* = 17.2, 10.6, 5.6 Hz, 1H), 5.23 (ddd, *J* =

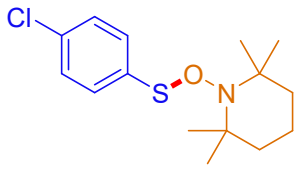
17.1, 2.9, 1.5 Hz, 1H), 5.20 (ddd, J = 10.1, 2.4, 1.4 Hz, 1H), 4.76 – 4.50 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.4, 168.2, 162.0, 136.5, 133.5, 131.3, 130.4, 129.7, 129.1, 127.8, 119.5, 118.8, 117.8, 111.9, 75.2, 66.4. HRMS (EI) calcd for $C_{18}H_{16}O_5Na$ $[M+Na]^+$ 335.0890, found 335.0890.



(R)-2-(2-Ethoxy-2-oxo-1-phenylethoxy)-4-methylbenzoic acid (5h): 33.9 mg, 36% yield, colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.57 (dd, J = 7.3, 2.1 Hz, 2H), 7.47 – 7.40 (m, 3H), 6.80 (s, 1H), 6.72 (dd, J = 8.1, 1.0 Hz, 1H), 6.12 (s, 1H), 4.29 – 4.16 (m, 2H), 2.35 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.4, 168.6, 162.0, 147.9, 133.8, 130.2, 129.5, 129.0, 127.8, 120.8, 117.9, 109.3, 75.1, 62.1, 22.1, 14.1. HRMS (EI) calcd for $C_{18}H_{18}O_5Na$ $[M+Na]^+$ 337.1046, found 337.1045.



(R)-4-Chloro-2-(2-ethoxy-2-oxo-1-phenylethoxy)benzoic acid (5i): 30.1 mg, 30% yield, colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.90 (d, J = 8.6 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.46 – 7.37 (m, 3H), 7.02 (d, J = 2.0 Hz, 1H), 6.89 (dd, J = 8.6, 2.0 Hz, 1H), 6.13 (s, 1H), 4.30 – 4.15 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.9, 168.3, 162.5, 142.3, 133.4, 131.5, 129.7, 129.1, 127.8, 120.3, 118.0, 110.6, 75.5, 62.2, 14.1. HRMS (EI) calcd for $C_{17}H_{16}ClO_5$ $[M+H]^+$ 335.0681, found 335.0682.



1-(((4-Chlorophenyl)thio)oxy)-2,2,6,6-tetramethylpiperidine (6a): 27.0 mg, 18% yield, colorless oil, ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.44 – 7.37 (m, 2H), 1.65 (s, 6H),

1.57 – 1.35 (m, 9H), 0.90 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 149.0, 135.8, 128.9, 127.6, 61.6, 59.1, 43.6, 41.5, 35.5, 32.9, 28.9, 28.0, 17.3. HRMS (EI) calcd for $C_{15}H_{23}ClNOS$ $[M+H]^+$ 300.1183, found 300.1186.

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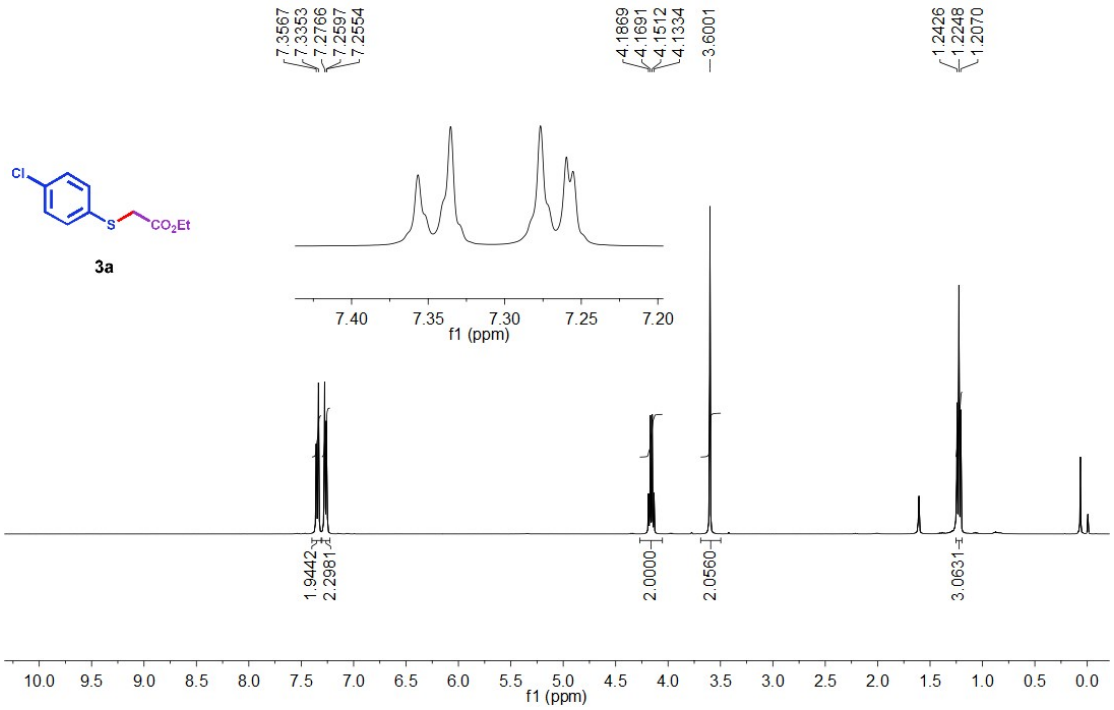
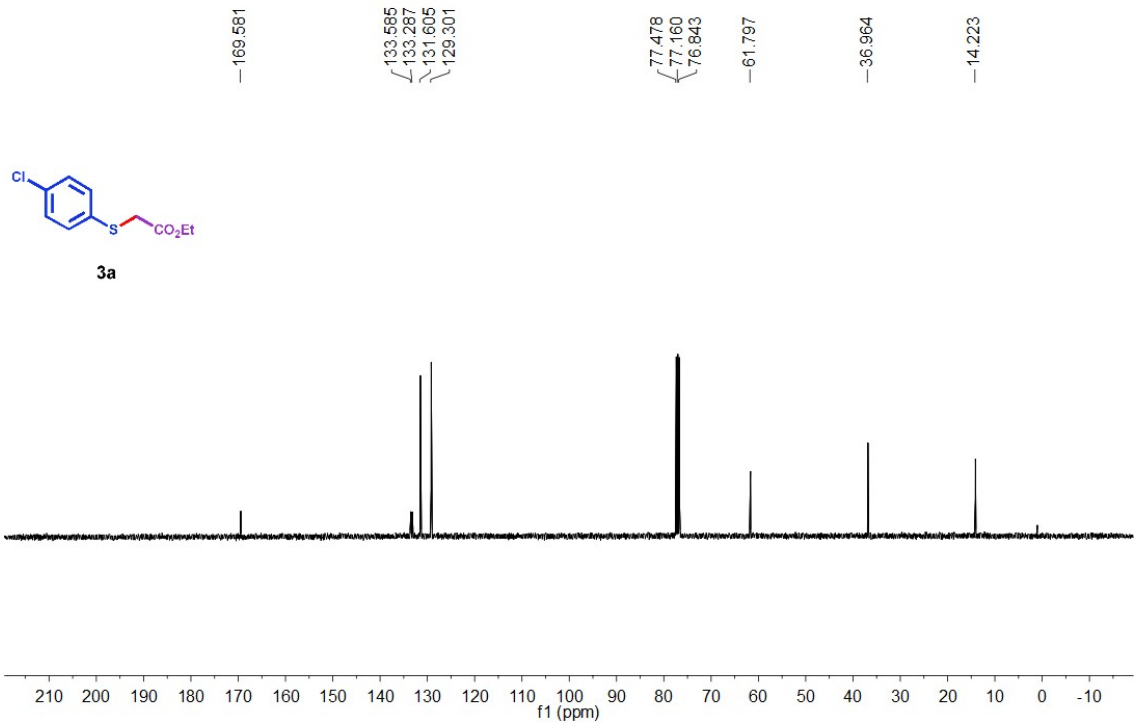
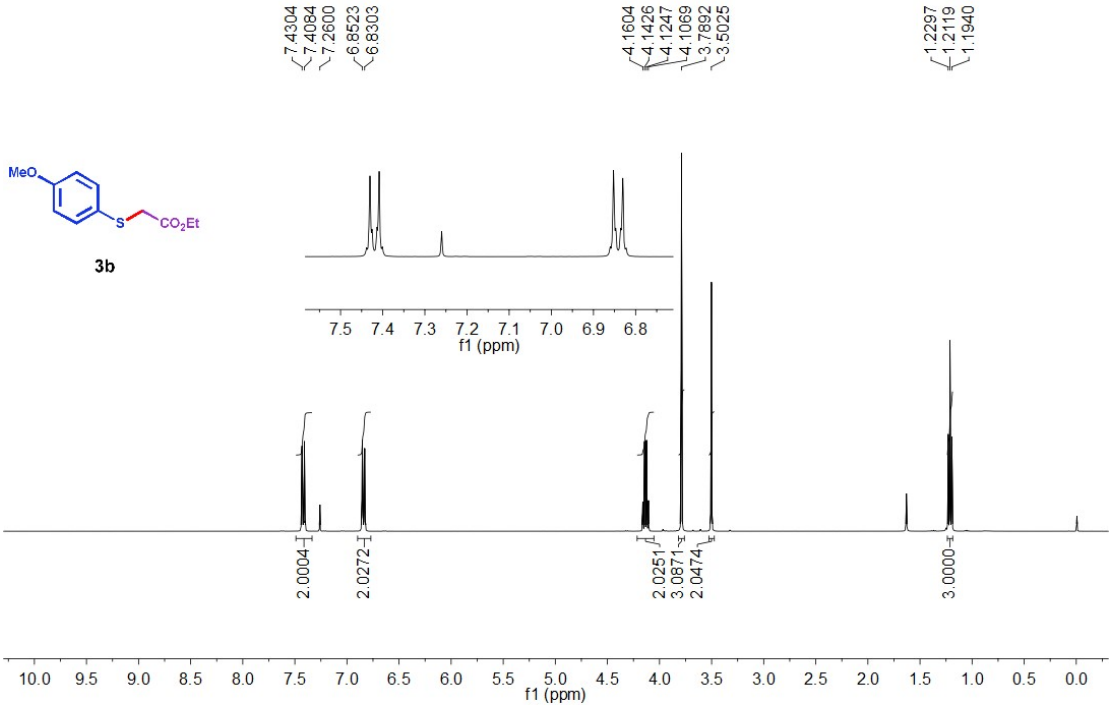
5. Copies of NMR spectra



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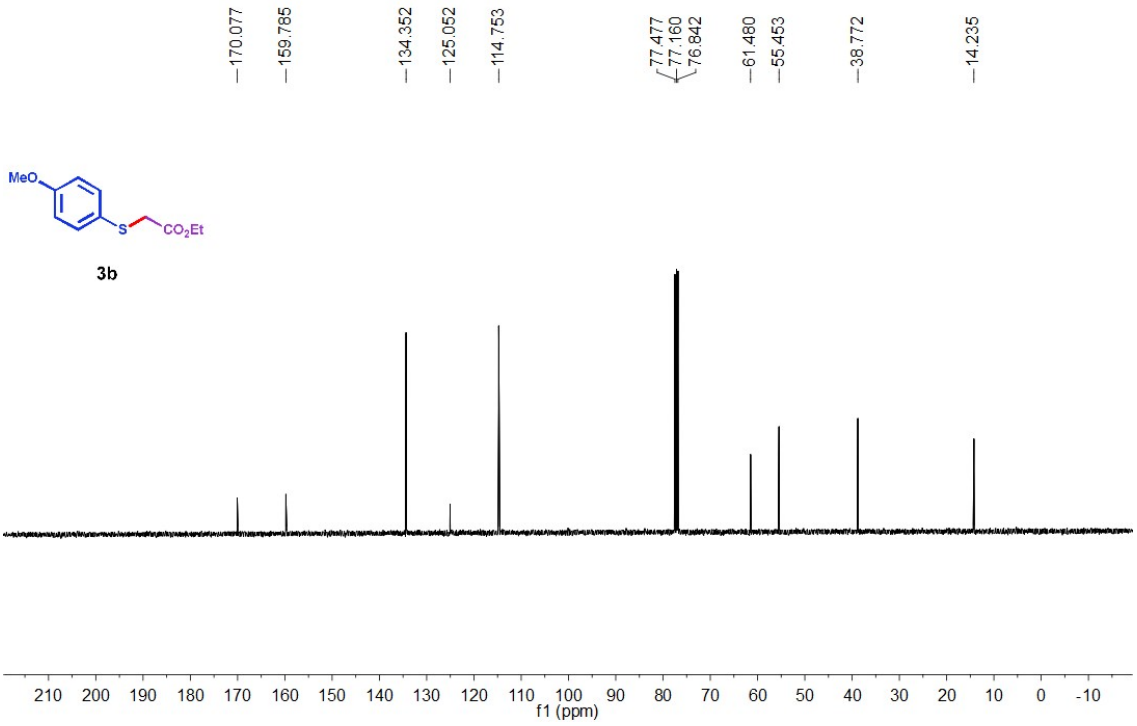
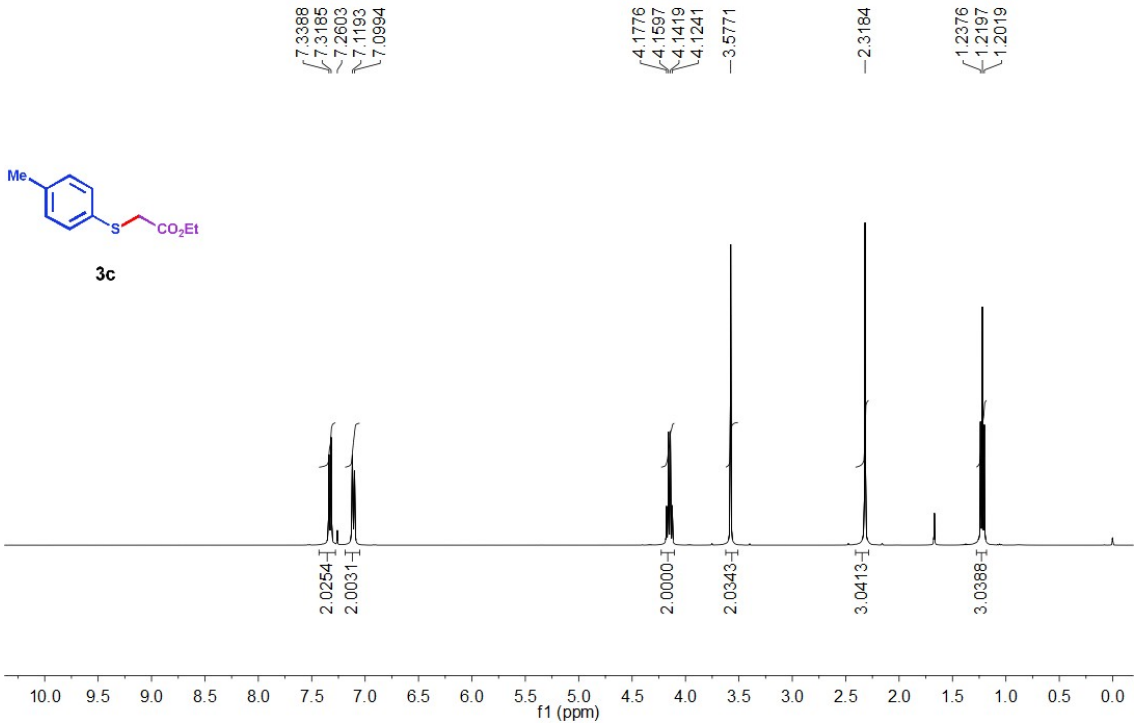
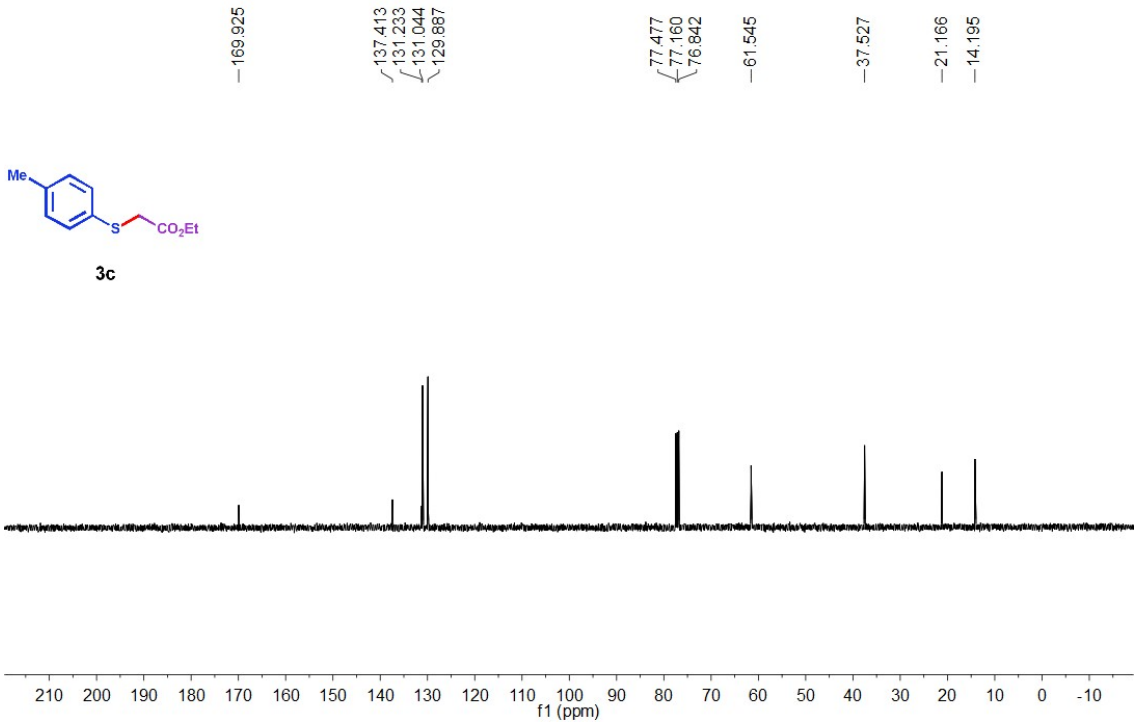
2.0474
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

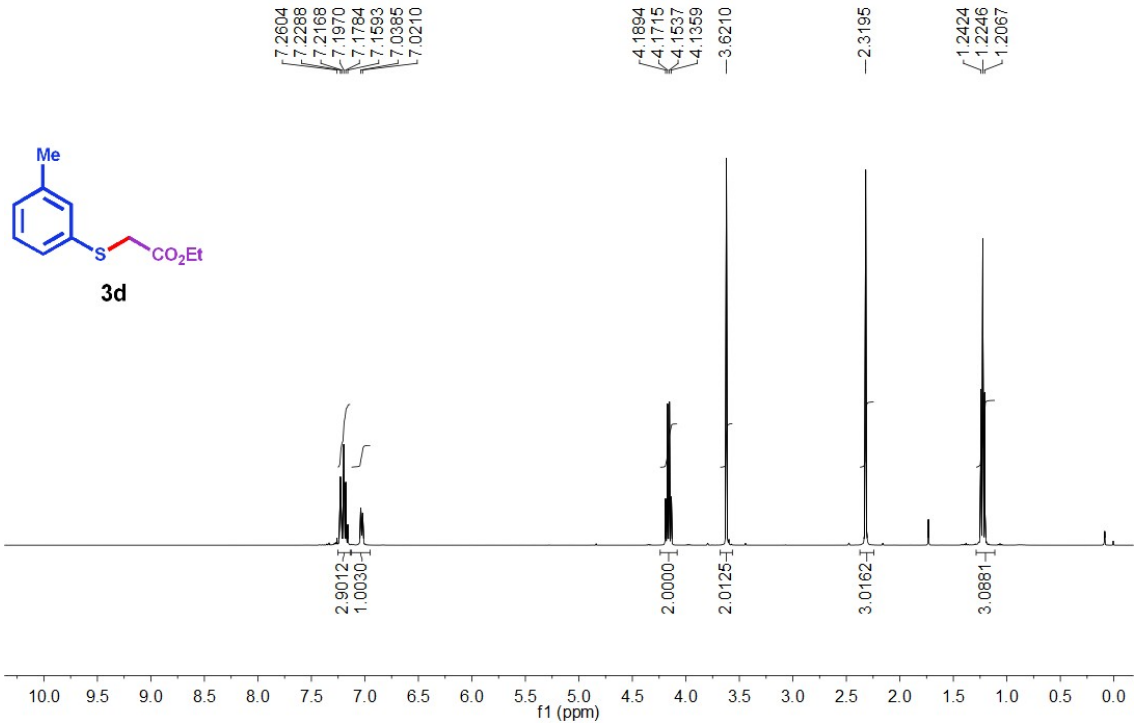

170.077
159.785
134.352
125.052
114.753
77.477
77.160
76.842
61.480
55.453
38.772
14.235
MeO
S
CO2Et
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

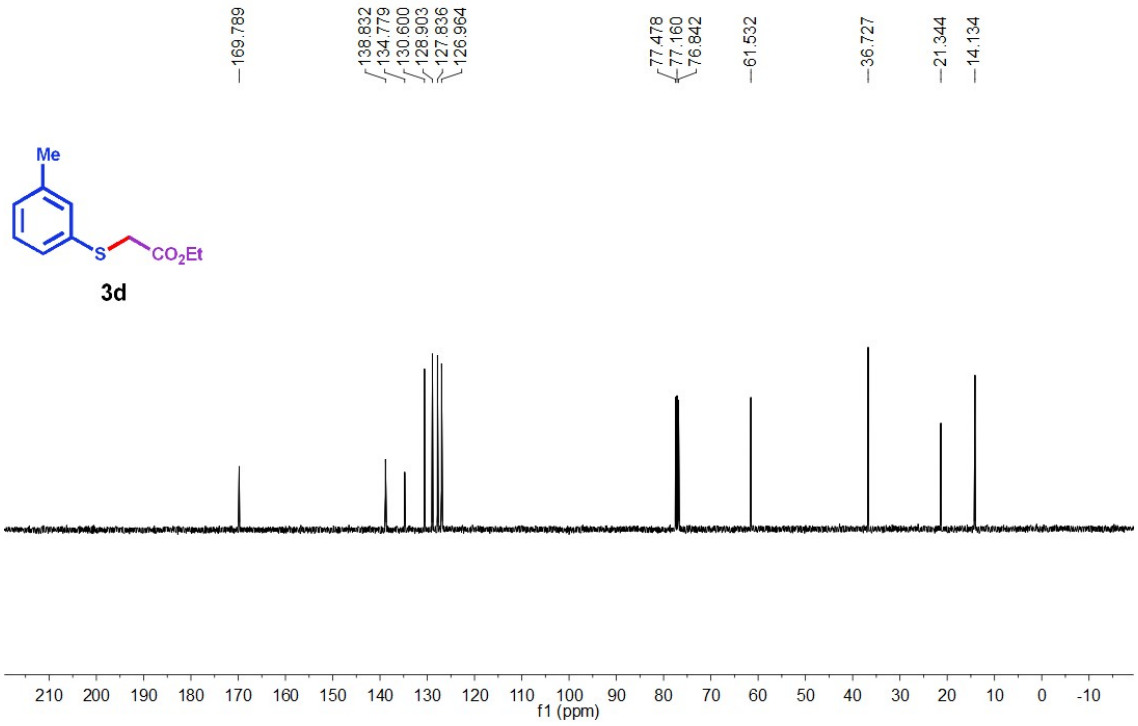

7.3388
7.3185
7.2603
7.1193
7.0994
4.1776
4.1597
4.1419
4.1241
3.5771
2.3184
1.2376
1.2197
1.2019
Me
S
CO2Et
2.0254
2.0031
2.0000
2.0343
3.0413
3.0388
f1 (ppm)

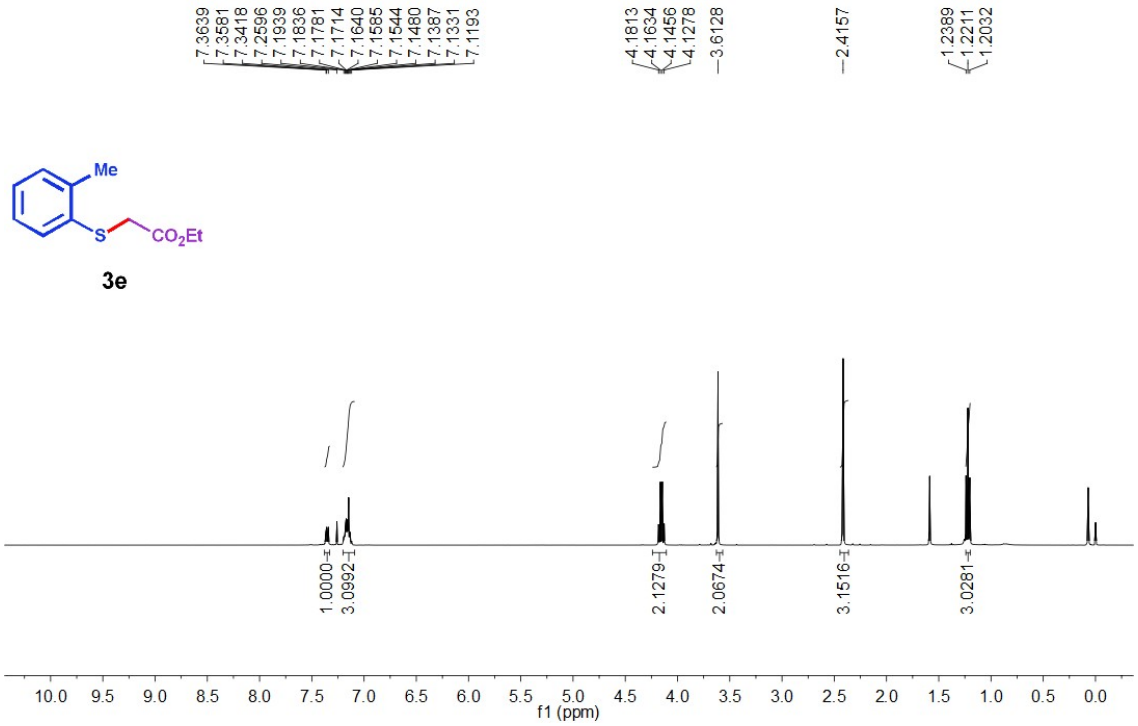
3c


169.925
137.413
131.233
131.044
129.887
77.477
77.160
76.842
61.545
37.527
21.166
14.195
Me
S
CO2Et
f1 (ppm)

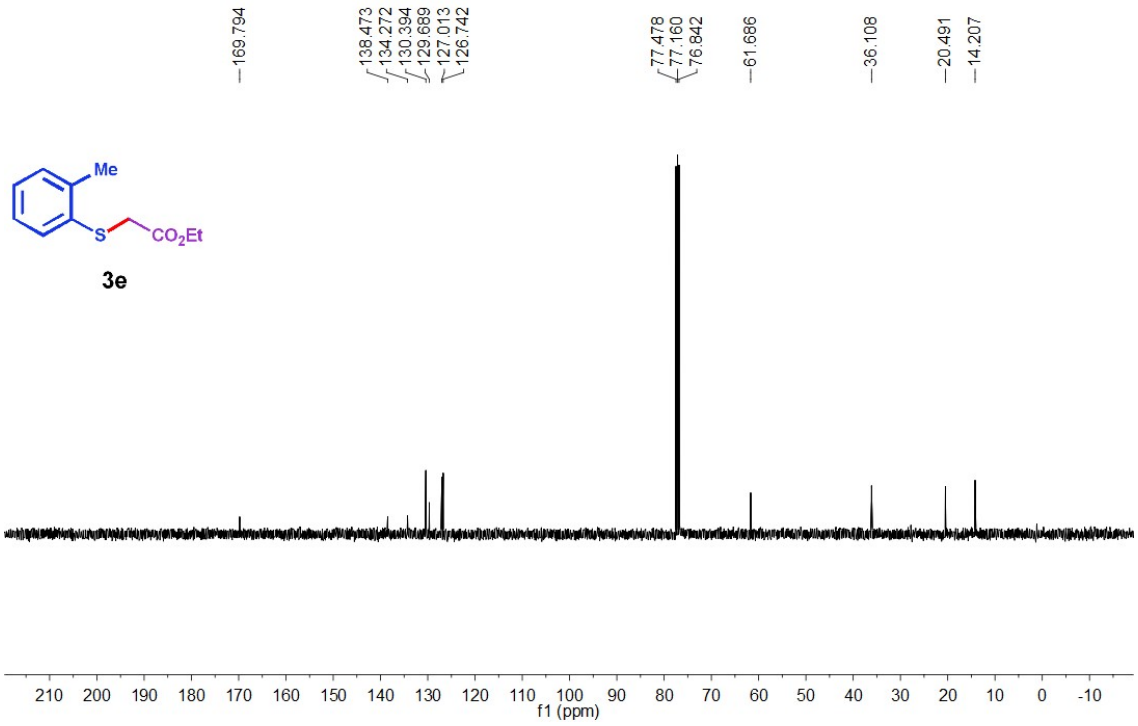
3c


7.2604
7.2288
7.2168
7.1970
7.1784
7.1593
7.0385
7.0210
4.1894
4.1715
4.1537
4.1359
3.6210
2.3195
1.2424
1.2246
1.2067
Me
S
CO2Et
3d
2.9012
1.0030
2.0000
2.0125
3.0162
3.0881
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

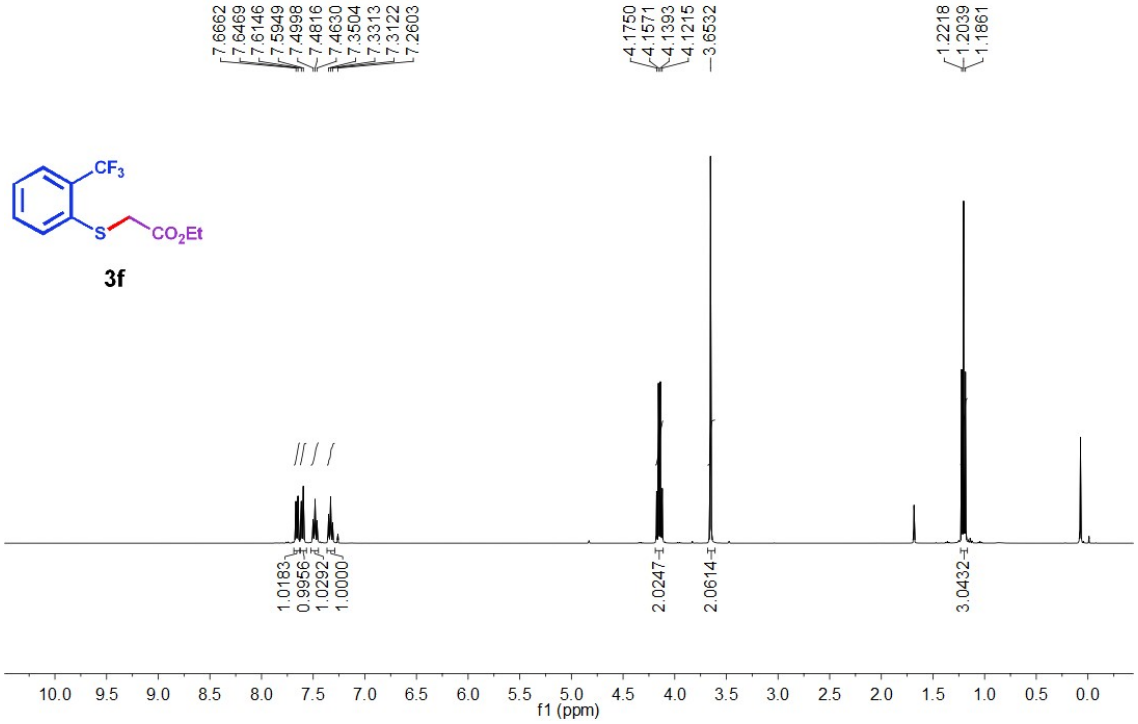

169.789
138.832
134.779
130.600
128.903
127.836
126.964
77.478
77.160
76.842
61.532
36.727
21.344
14.134
Me
S
CO2Et
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

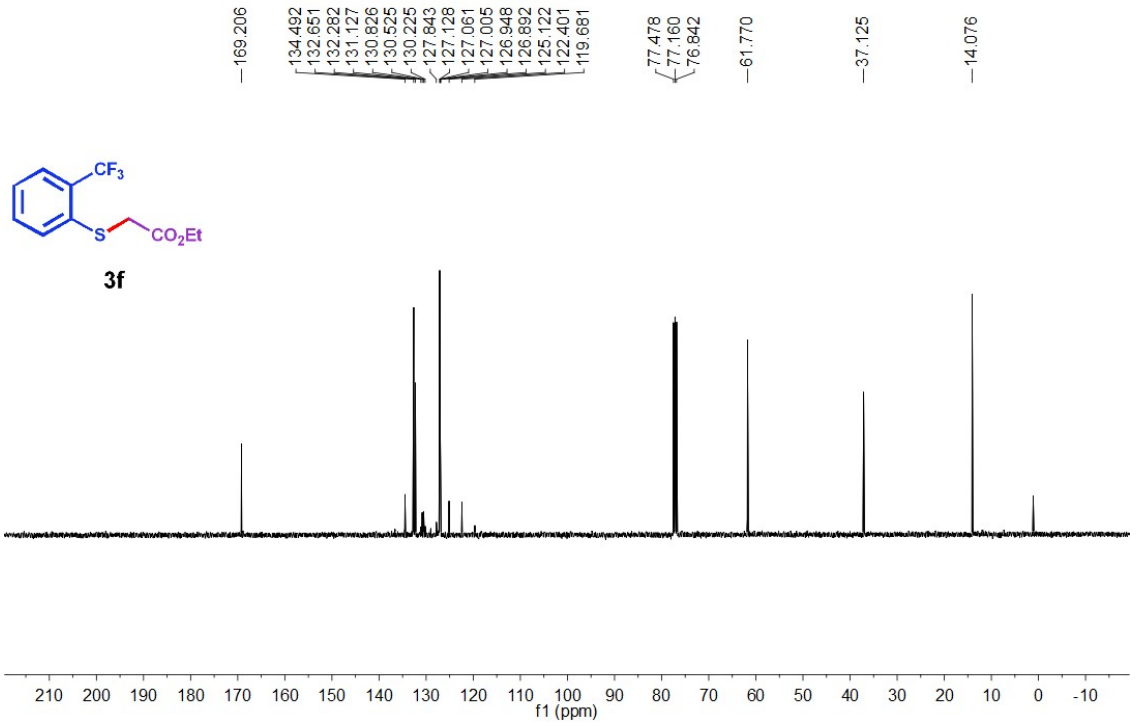

7.3639
7.3581
7.3418
7.2596
7.1939
7.1836
7.1781
7.1714
7.1640
7.1585
7.1544
7.1480
7.1387
7.1331
7.1193
4.1813
4.1634
4.1456
4.1278
3.6128
2.4157
1.2389
1.2211
1.2032
Me
S
CO2Et
1.0000
3.0992
2.1279
2.0674
3.1516
3.0281
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

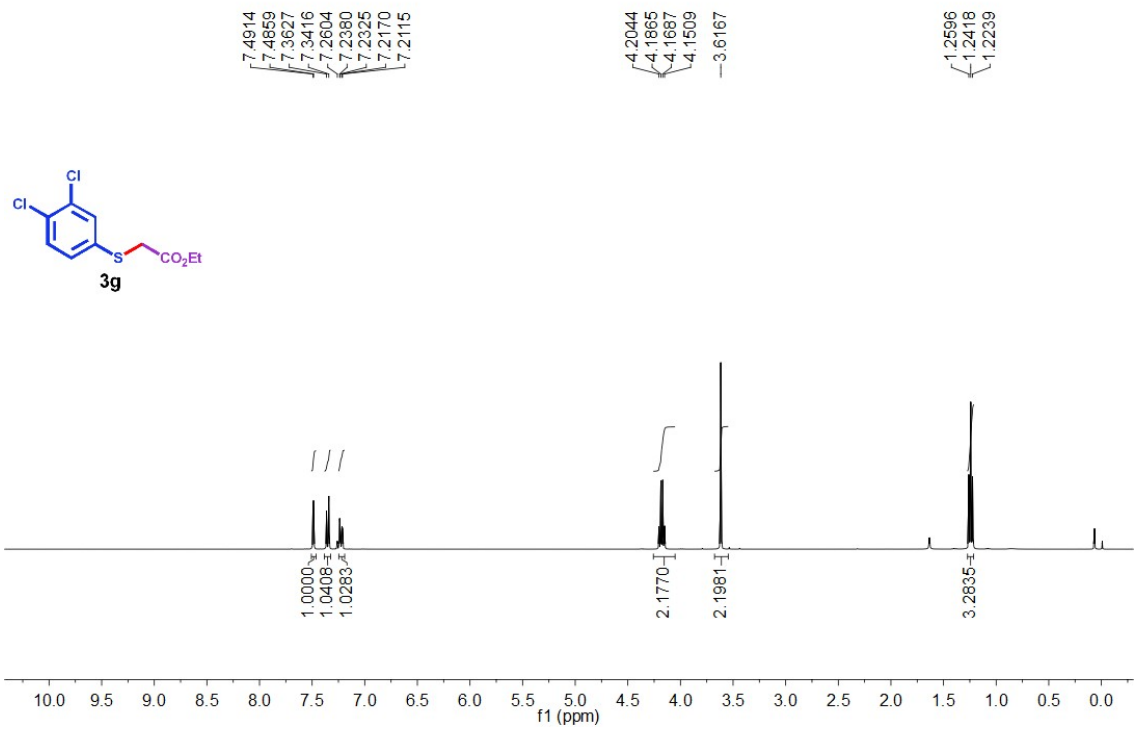
3e

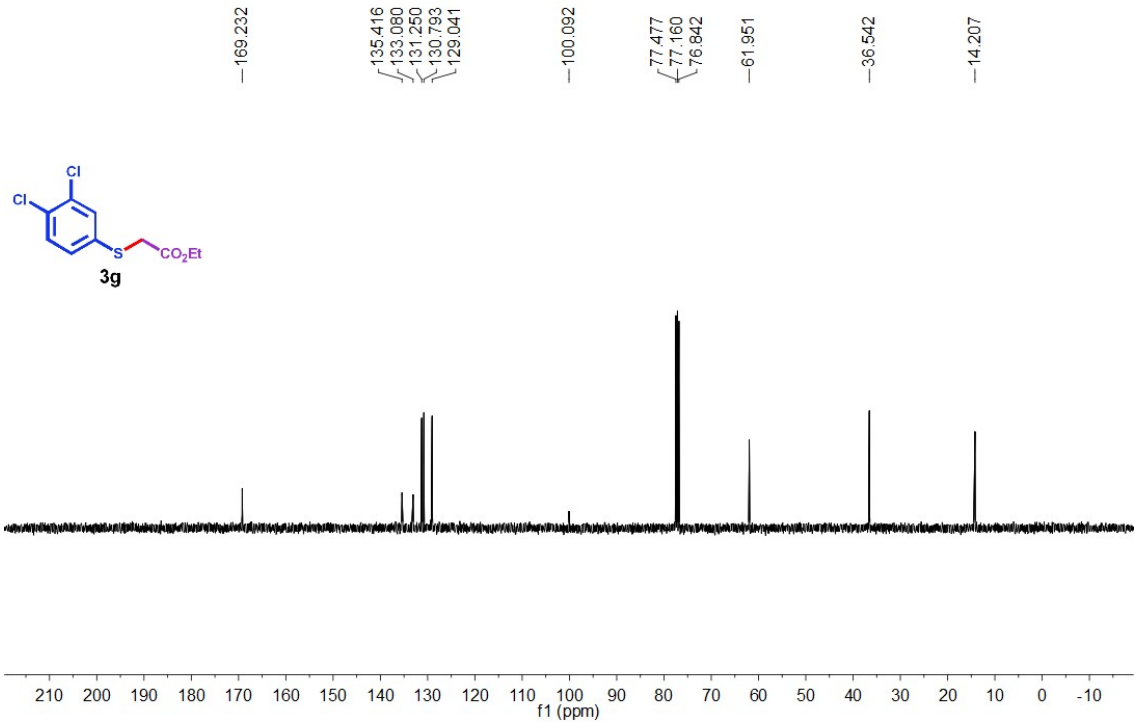

169.794
138.473
134.272
130.394
129.689
127.013
126.742
77.478
77.160
76.842
61.686
36.108
20.491
14.207
Me
S
CO2Et
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

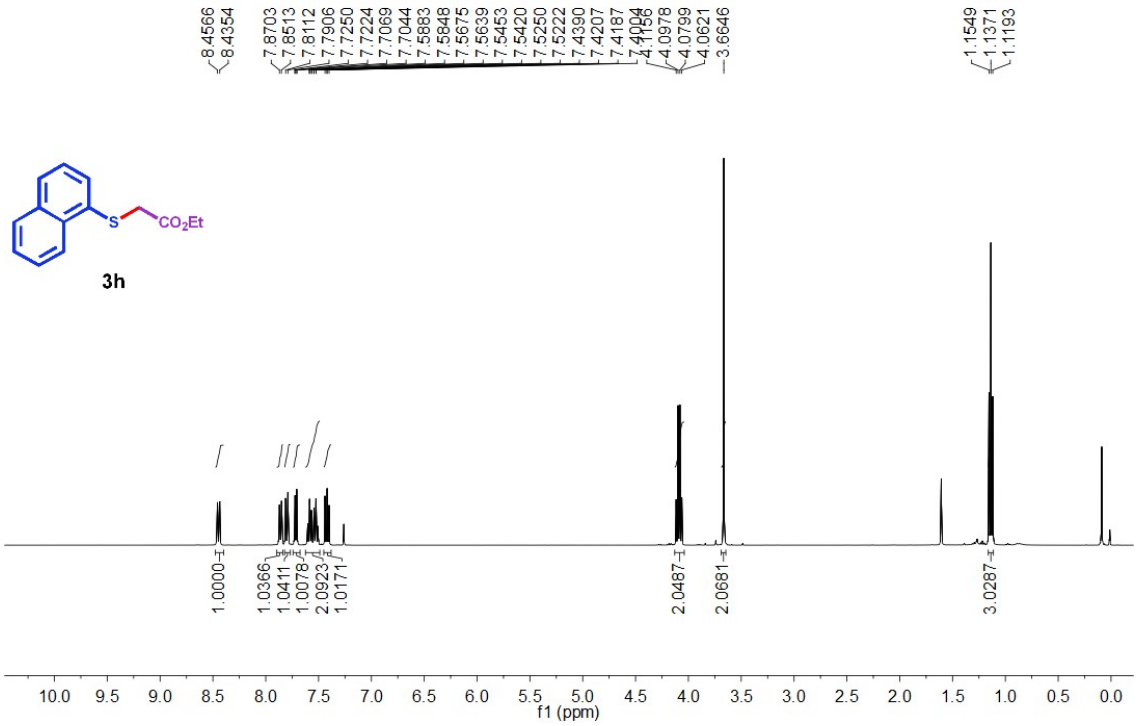
3e

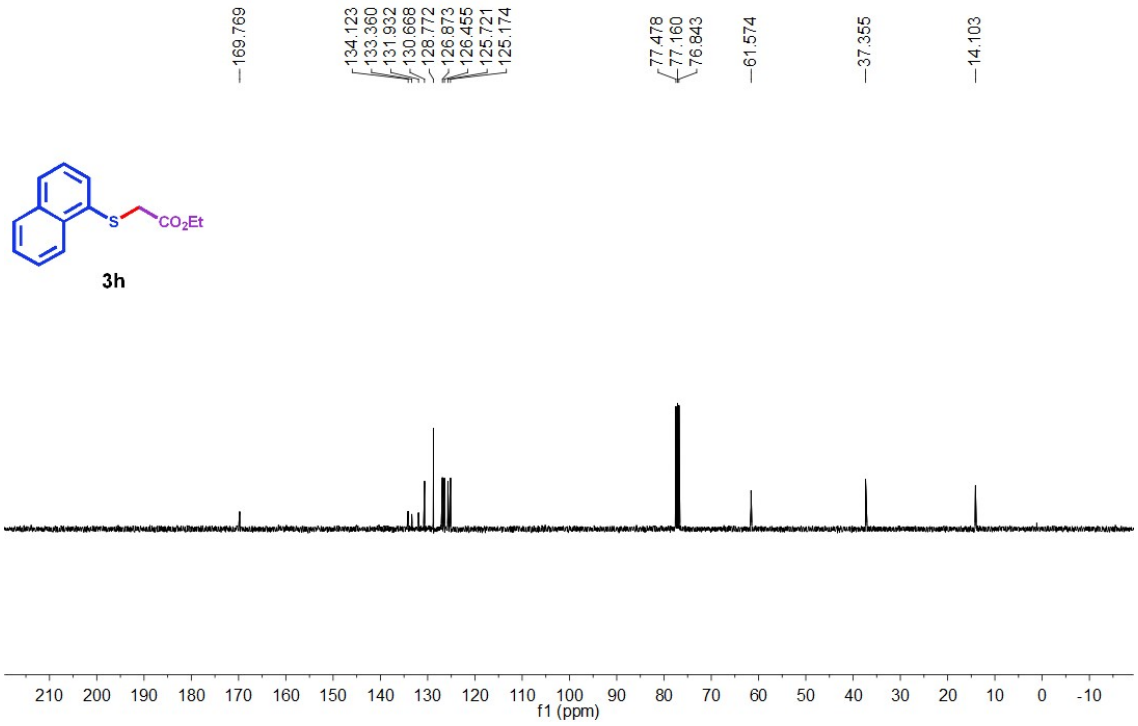

7.6662
7.6469
7.6146
7.5949
7.4998
7.4816
7.4630
7.3504
7.3313
7.3122
7.2603
4.1750
4.1571
4.1393
4.1215
3.6532
1.2218
1.2039
1.1661
CF3
S
CO2Et
3f
1.0183
0.9956
1.0292
1.0000
2.0247
2.0614
3.0432
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

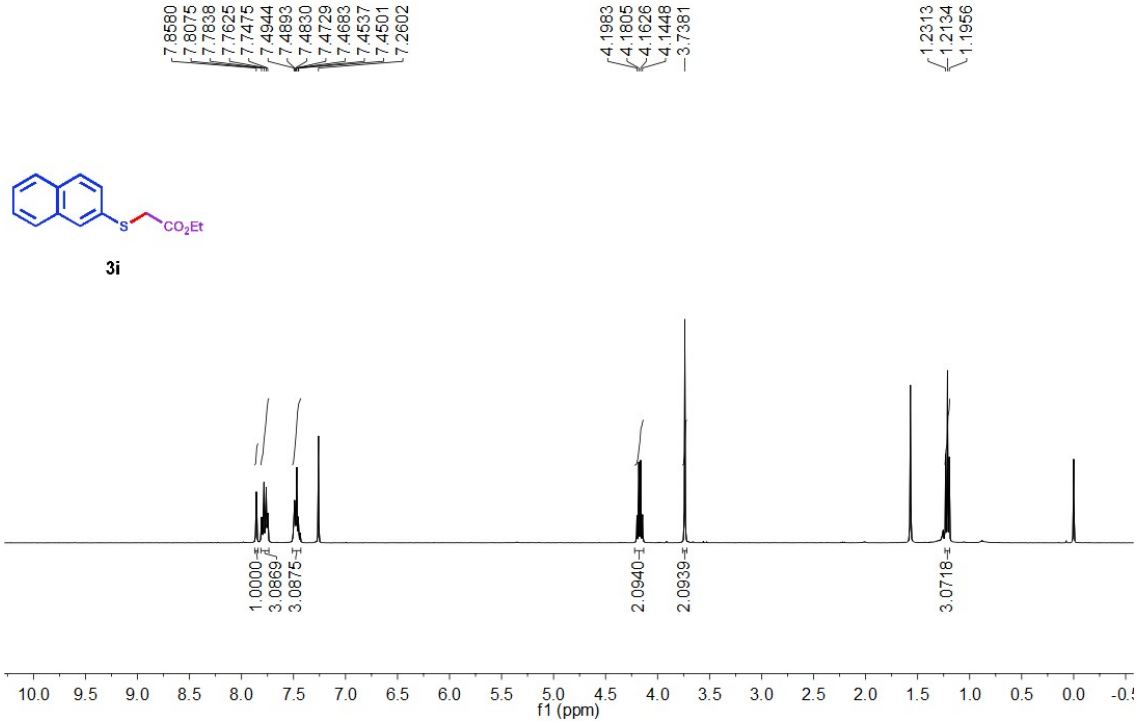

169.206
134.492
132.651
132.282
131.127
130.826
130.525
130.225
127.843
127.128
127.061
127.005
126.948
126.892
125.122
122.401
119.681
77.478
77.160
76.842
61.770
37.125
14.076
CF3
S
CO2Et
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

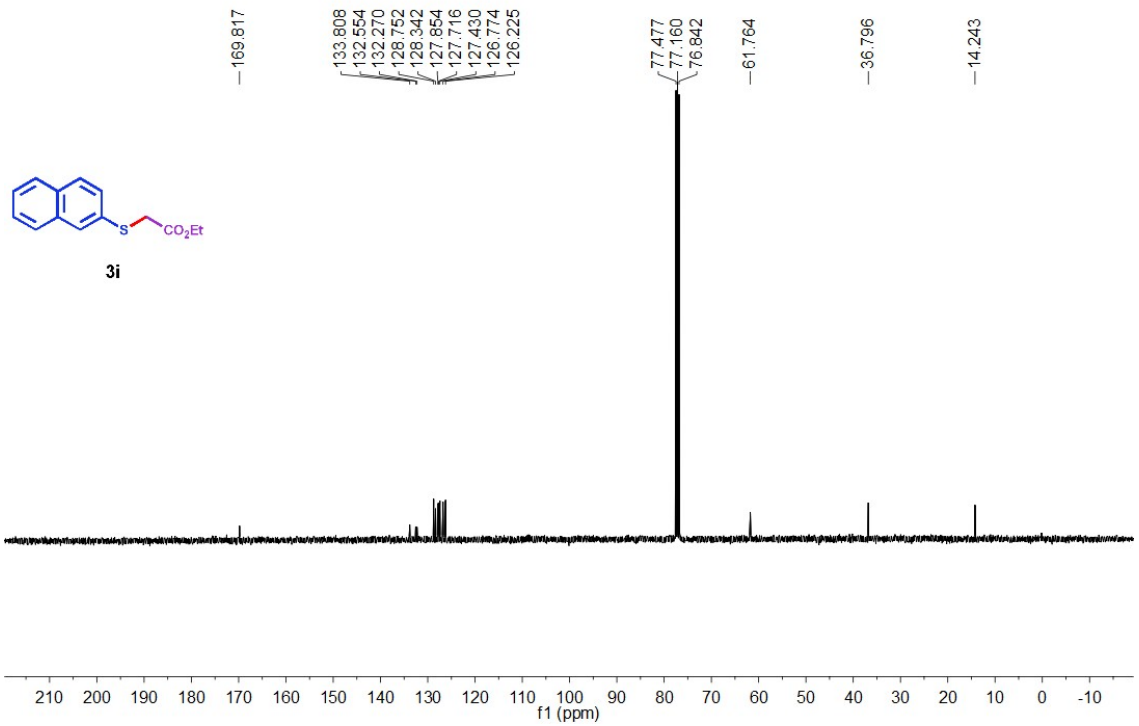

7.4914
7.4859
7.3627
7.3416
7.2604
7.2380
7.2325
7.2170
7.2115
4.2044
4.1865
4.1687
4.1509
3.6167
1.2596
1.2418
1.2239
Cl
Cl
S
CO2Et
3g
1.0000
1.0408
1.0283
2.1770
2.1981
3.2835
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

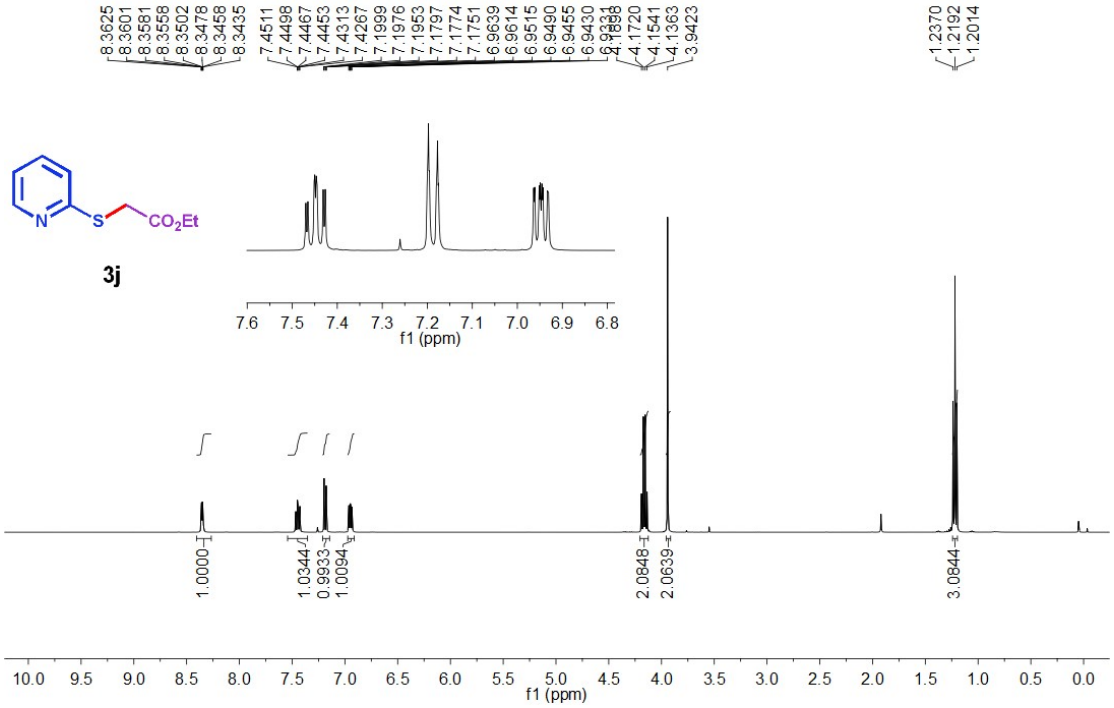

169.232
135.416
133.080
131.250
130.793
129.041
100.092
77.477
77.160
76.842
61.951
36.542
14.207
Cl
Cl
S
CO2Et
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

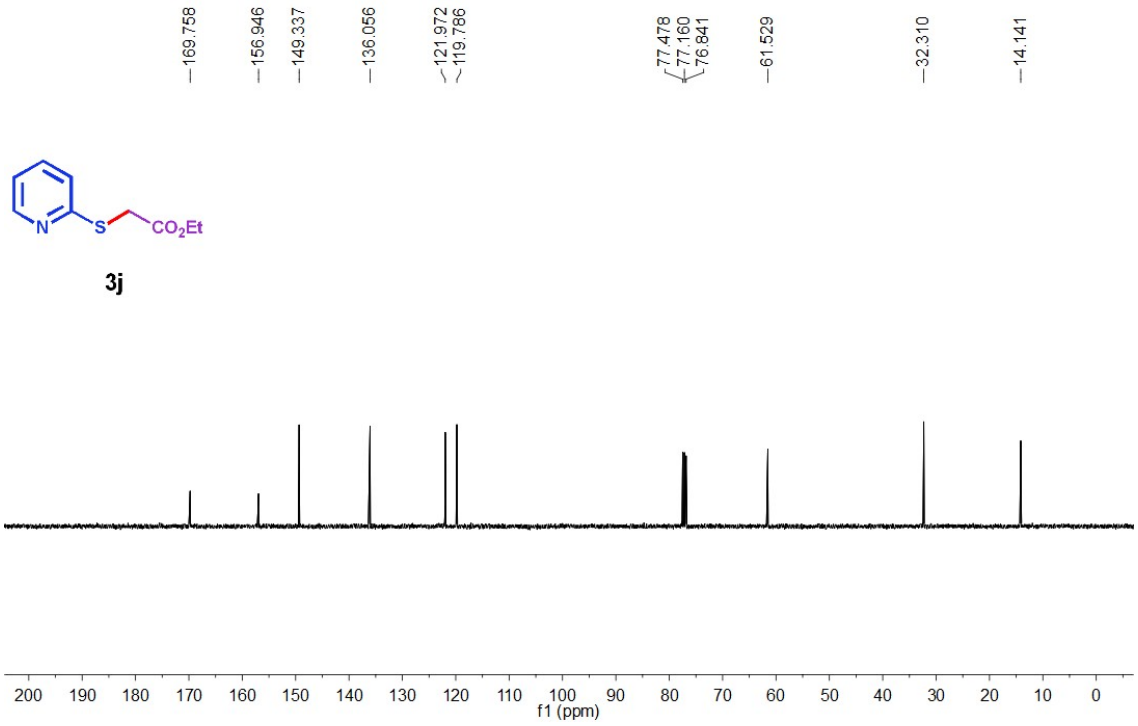

8.4566
8.4354
7.8703
7.8513
7.8112
7.7906
7.7250
7.7224
7.7069
7.7044
7.5883
7.5848
7.5675
7.5639
7.5453
7.5420
7.5250
7.5222
7.4390
7.4207
7.4187
4.0978
4.0799
4.0621
3.6646
1.1549
1.1371
1.1193
S
CO2Et
3h
1.0000
1.0366
1.0411
1.0078
2.0923
1.0171
2.0487
2.0681
3.0287
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

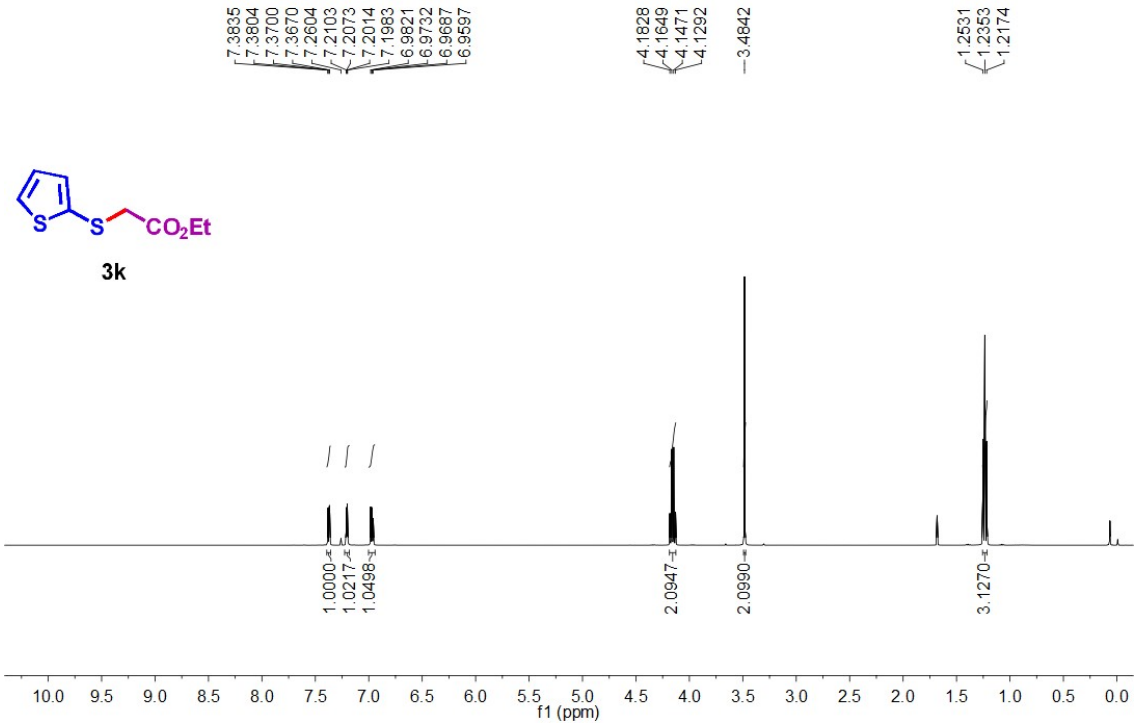

169.769
134.123
133.360
131.932
130.668
128.772
126.873
126.455
125.721
125.174
77.478
77.160
76.843
61.574
37.355
14.103
S
CO2Et
3h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

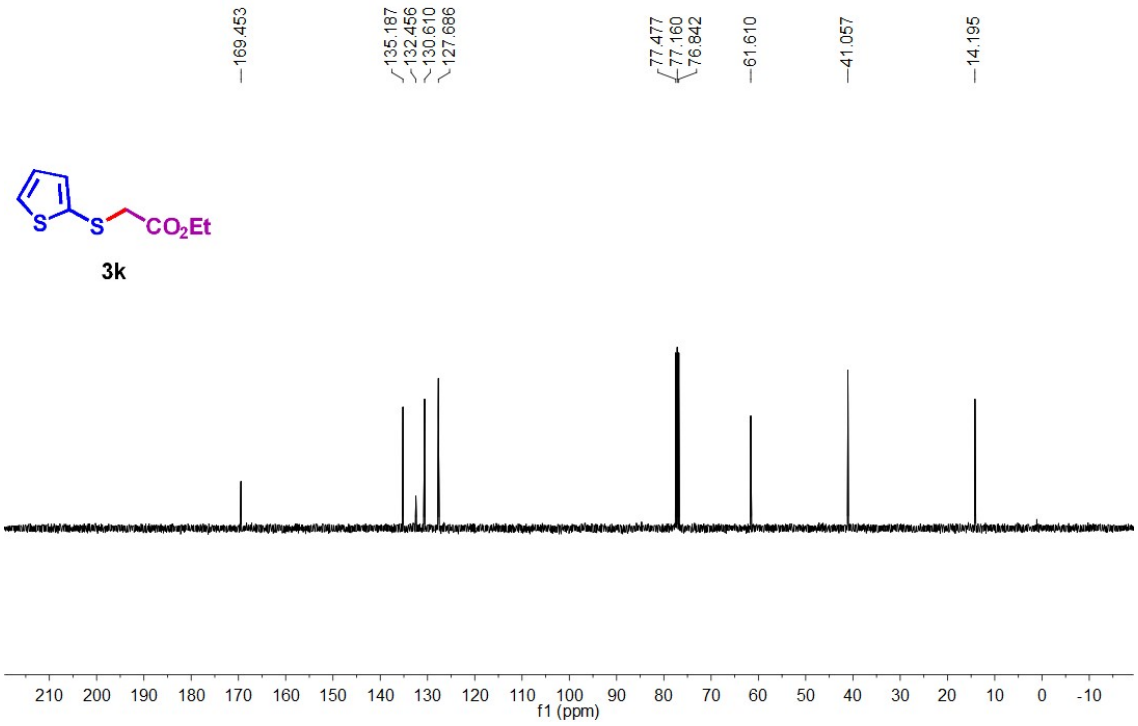

7.8580
7.8075
7.7838
7.7625
7.7475
7.4944
7.4893
7.4830
7.4729
7.4683
7.4537
7.4501
7.2602
4.1983
4.1805
4.1626
4.1448
3.7381
1.2313
1.2134
1.1956
CO2Et
3i
1.0000
3.0869
3.0875
2.0940
2.0939
3.0718
f1 (ppm)

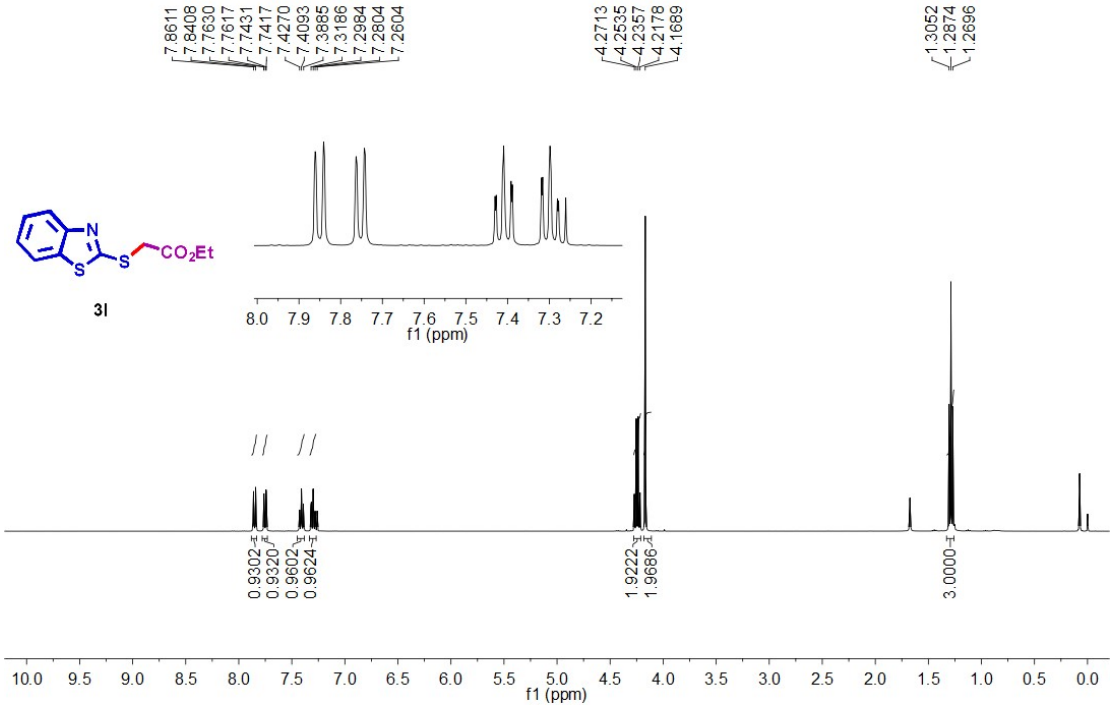

169.817
133.808
132.554
132.270
128.752
128.342
127.854
127.716
127.430
126.774
126.225
77.477
77.160
76.842
61.764
36.796
14.243
CO2Et
3i
f1 (ppm)

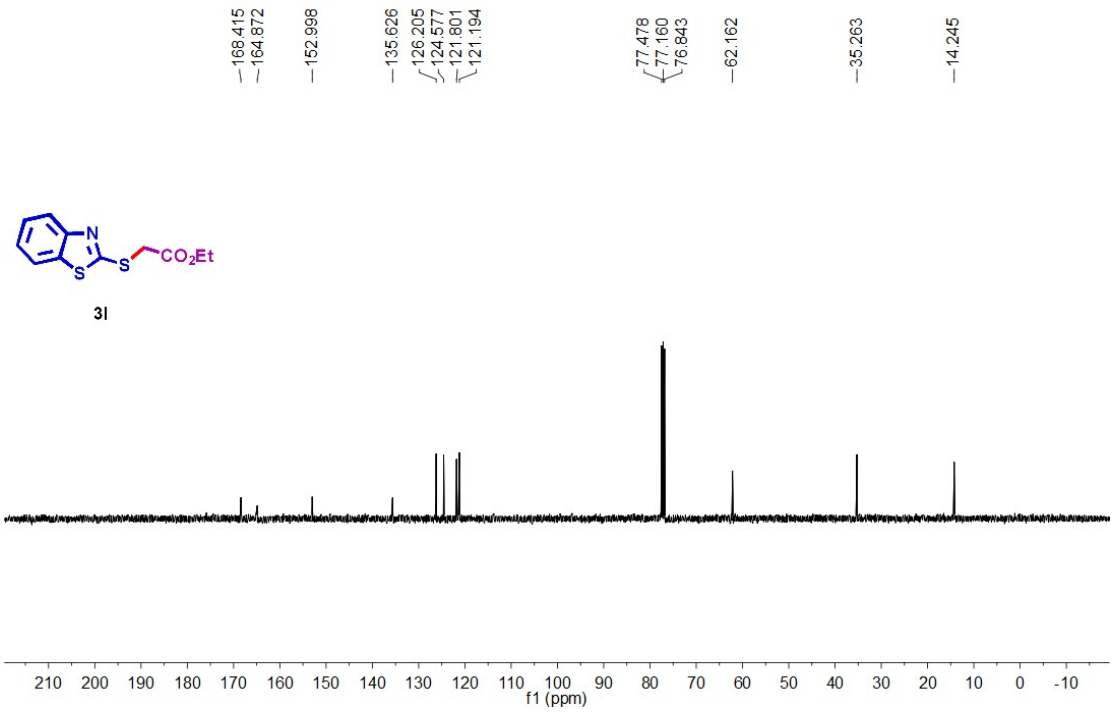

8.3625
8.3601
8.3581
8.3558
8.3502
8.3478
8.3458
8.3435
7.4511
7.4498
7.4467
7.4453
7.4313
7.4267
7.1999
7.1976
7.1953
7.1797
7.1774
7.1751
6.9639
6.9614
6.9515
6.9490
6.9455
6.9430
4.1720
4.1541
4.1363
3.9423
1.2370
1.2192
1.2014
N
S
CO2Et
3j
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.0000
1.0344
0.9933
1.0094
2.0848
2.0639
3.0844
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

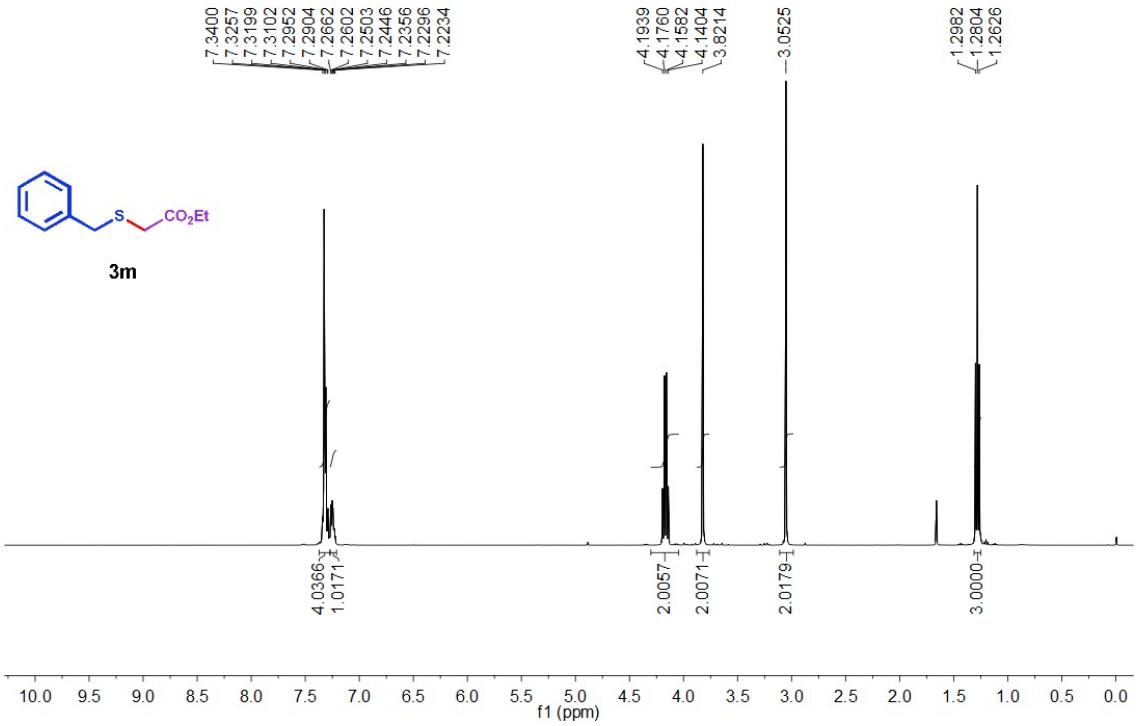

169.758
156.946
149.337
136.056
121.972
119.786
77.478
77.160
76.841
61.529
32.310
14.141
N
S
CO2Et
3j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.3835
7.3804
7.3700
7.3670
7.2604
7.2103
7.2073
7.2014
7.1983
6.9821
6.9732
6.9687
6.9597
4.1828
4.1649
4.1471
4.1292
3.4842
1.2531
1.2353
1.2174
CO2Et
3k
1.0000
1.0217
1.0498
2.0947
2.0990
3.1270
f1 (ppm)


169.453
135.187
132.456
130.610
127.686
77.477
77.160
76.842
61.610
41.057
14.195
CO2Et
3k
f1 (ppm)

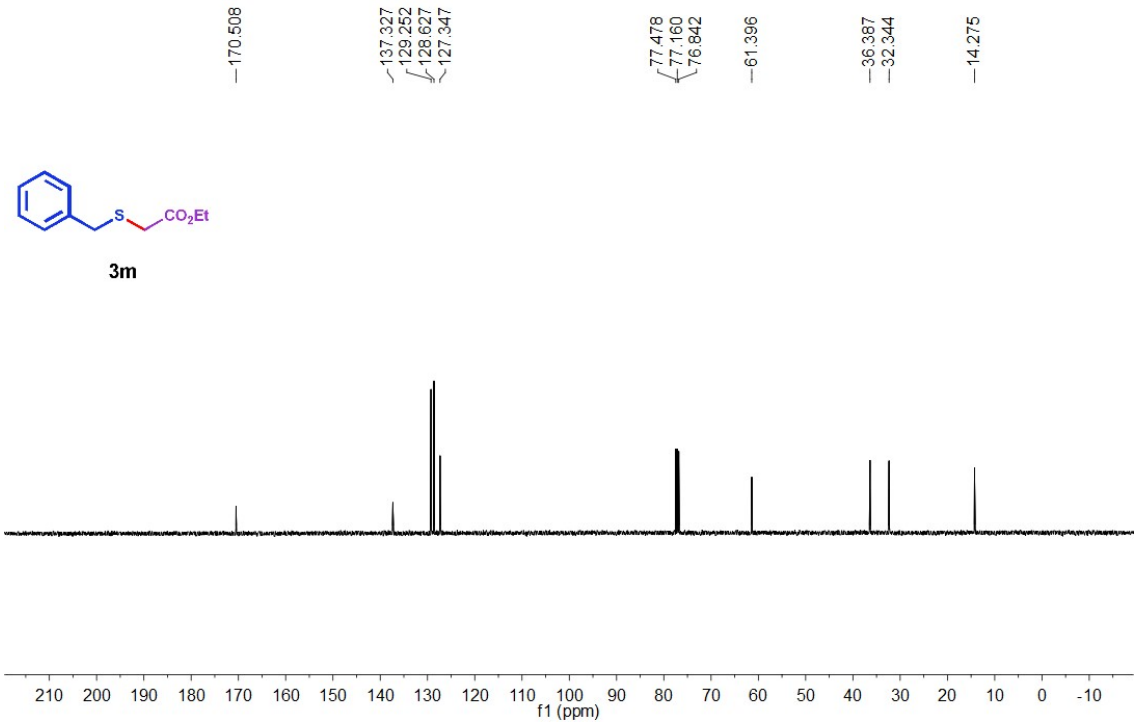

7.8611
7.8408
7.7630
7.7617
7.7431
7.7417
7.4270
7.4093
7.3885
7.3186
7.2984
7.2804
7.2604
4.2713
4.2535
4.2357
4.2178
4.1689
1.3052
1.2874
1.2696
CO2Et
3l
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
0.9302
0.9320
0.9602
0.9624
1.9222
1.9686
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.415
164.872
152.998
135.626
126.205
124.577
121.801
121.194
77.478
77.160
76.843
62.162
35.263
14.245
CO2Et
3l
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)


7.3400
7.3257
7.3199
7.3102
7.2952
7.2904
7.2662
7.2602
7.2503
7.2446
7.2356
7.2296
7.2234
4.1939
4.1760
4.1582
4.1404
3.8214
3.0525
1.2982
1.2804
1.2626
4.0366
1.0171
2.0057
2.0071
2.0179
3.0000
f1 (ppm)

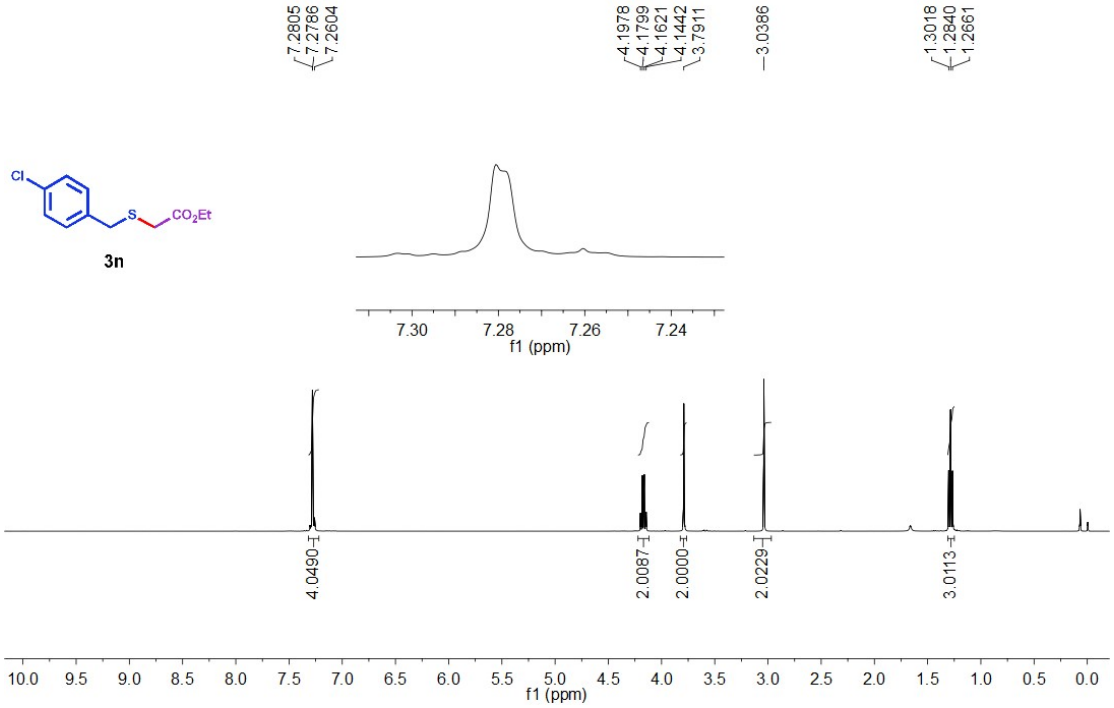
S
CO2Et

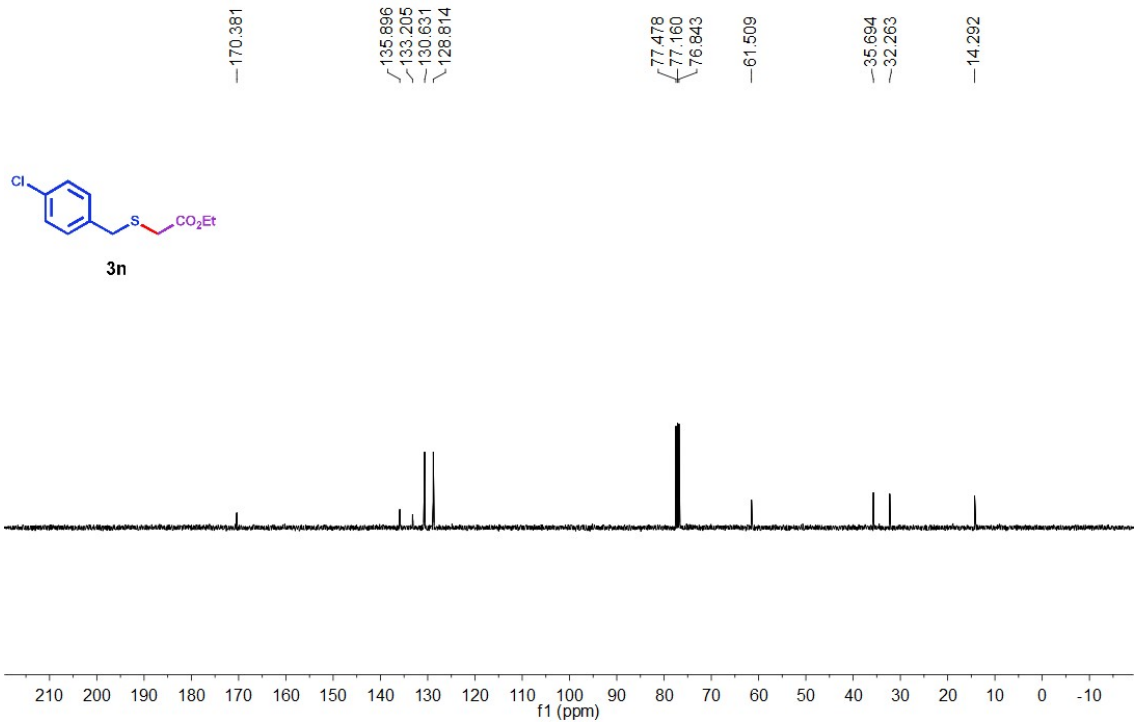
3m

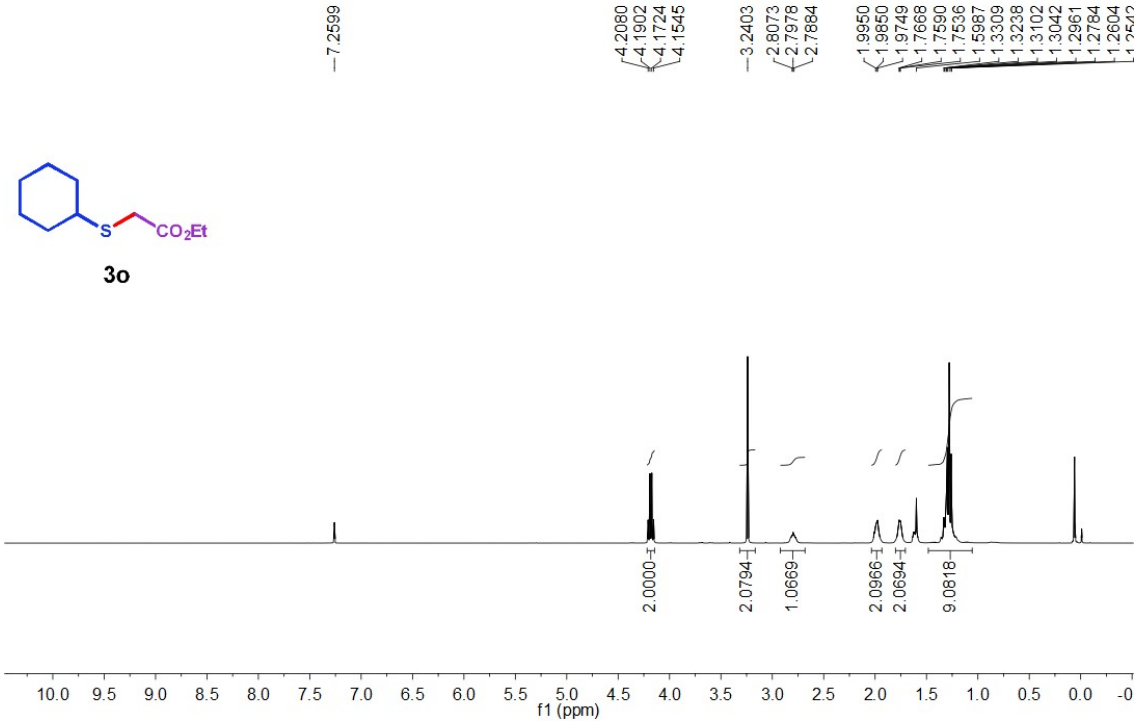

170.508
137.327
129.252
128.627
127.347
77.478
77.160
76.842
61.396
36.387
32.344
14.275
f1 (ppm)

S
CO2Et

3m


7.2805
7.2786
7.2604
4.1978
4.1799
4.1621
4.1442
3.7911
3.0386
1.3018
1.2840
1.2661
Cl
S
CO2Et
3n
7.30
7.28
7.26
7.24
f1 (ppm)
4.0490
2.0087
2.0000
2.0229
3.0113
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.381
135.896
133.205
130.631
128.814
77.478
77.160
76.843
61.509
35.694
32.263
14.292
Cl
S
CO2Et
3n
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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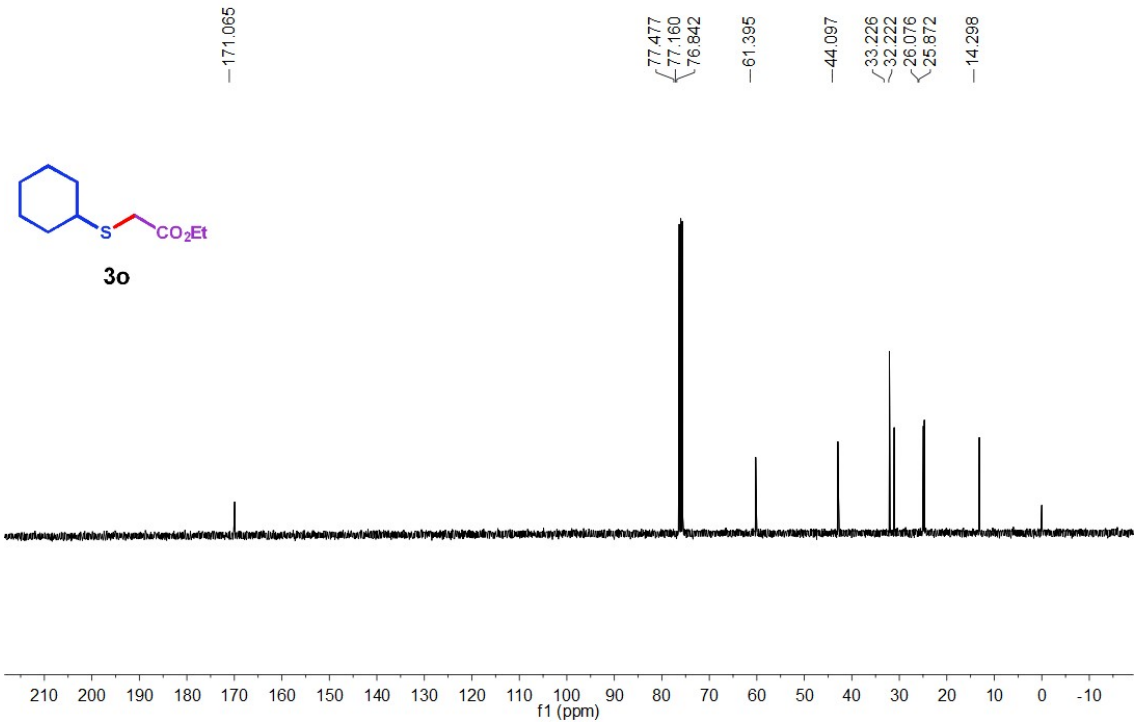
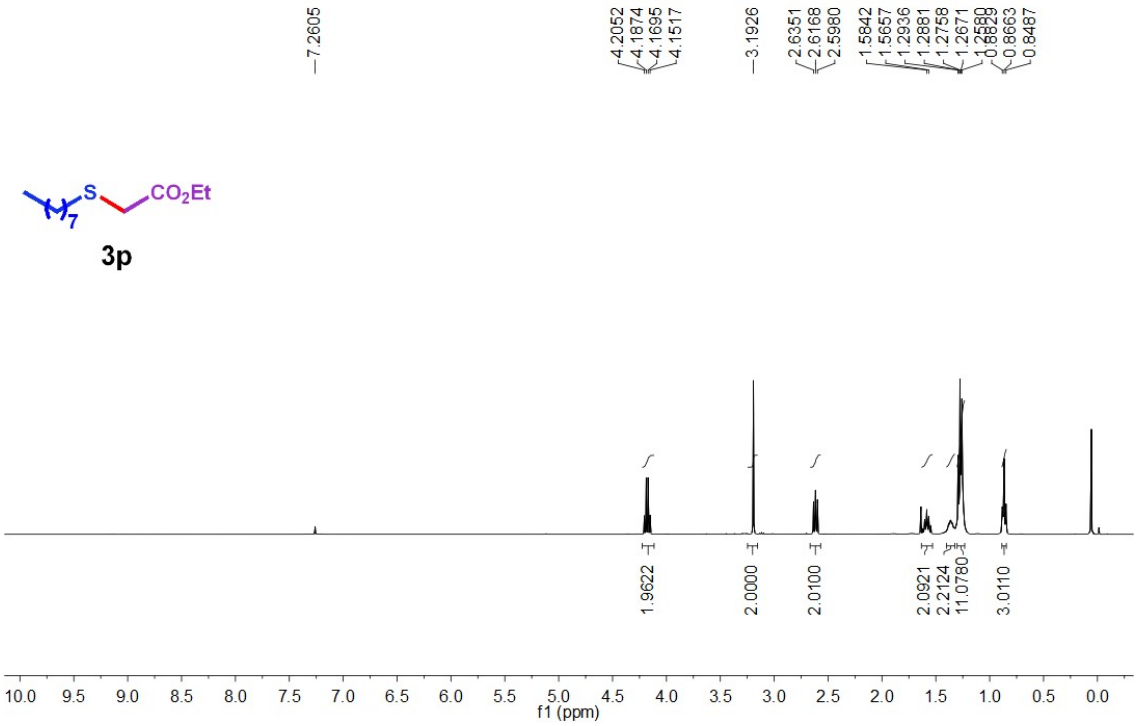
4.2080
4.1902
4.1724
4.1545
3.2403
2.8073
2.7978
2.7884
1.9950
1.9850
1.9749
1.7668
1.7590
1.7536
1.5987
1.3309
1.3238
1.3102
1.3042
1.2961
1.2784
1.2604
S
CO2Et
2.0000
2.0794
1.0669
2.0966
2.0694
9.0818
f1 (ppm)

3o


171.065
77.477
77.160
76.842
61.395
44.097
33.226
32.222
26.076
25.872
14.298
S
CO2Et
f1 (ppm)

3o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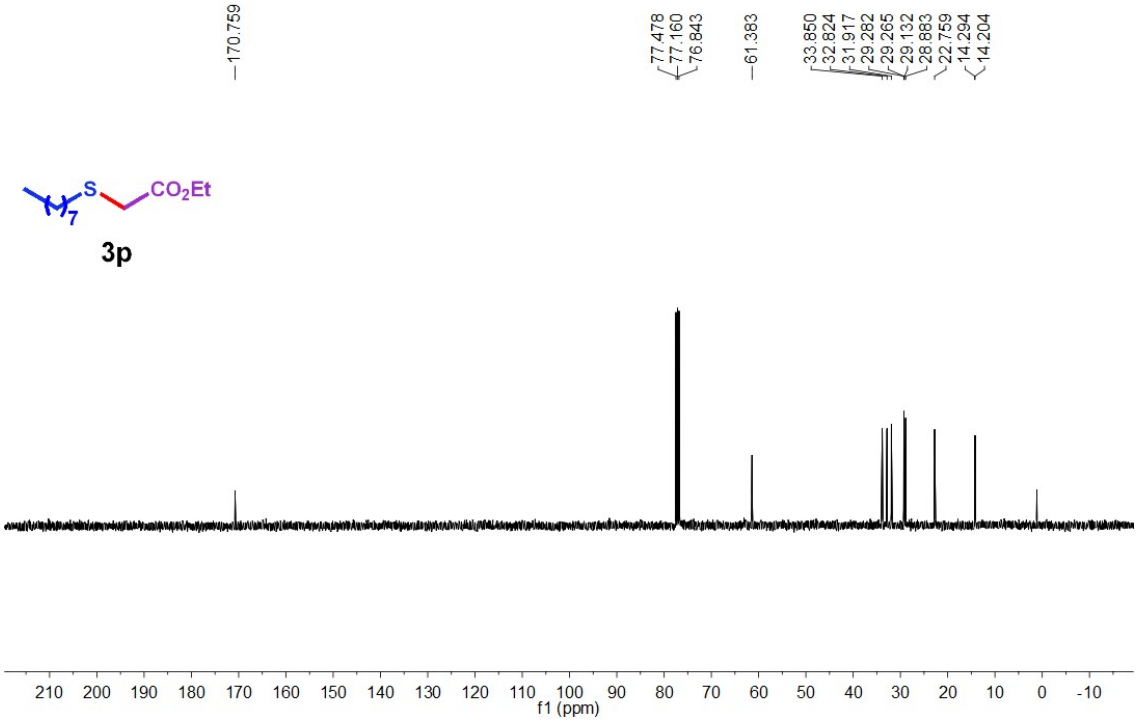
4.2052
4.1874
4.1695
4.1517
3.1926
2.6351
2.6168
2.5980
1.5842
1.5657
1.2936
1.2881
1.2758
1.2671
0.8663
0.8487
CO2Et
3p
1.9622
2.0000
2.0100
2.0921
2.2124
11.0780
3.0110
f1 (ppm)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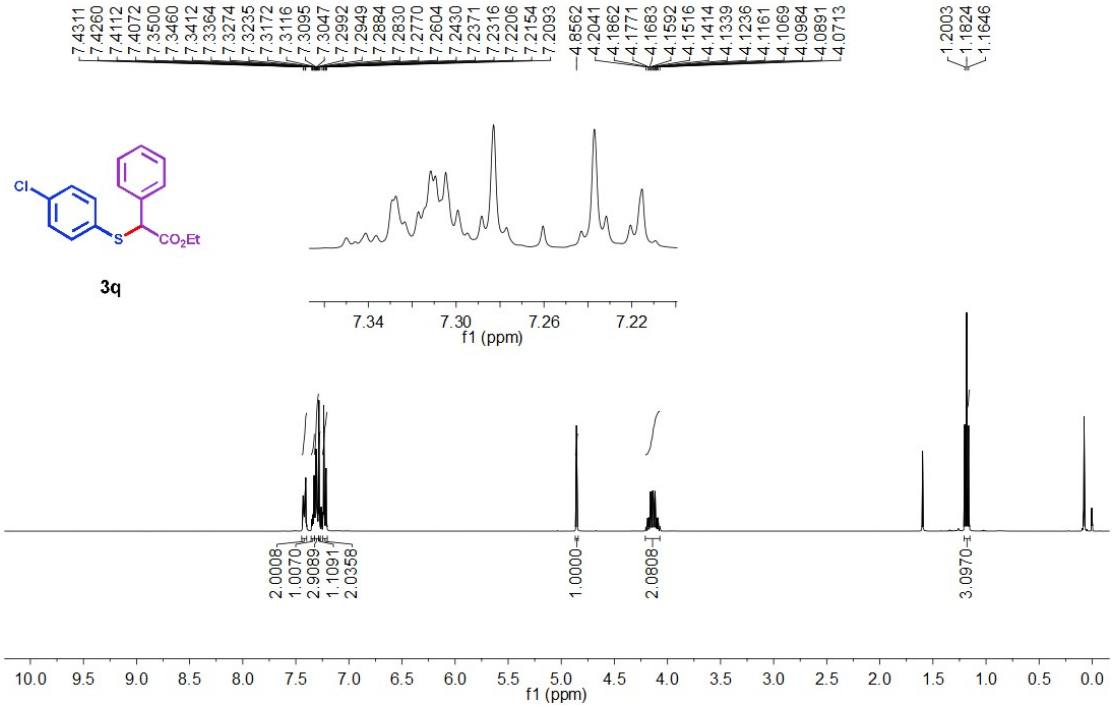
77.478
77.160
76.843
61.383
33.850
32.824
31.917
29.282
29.265
29.132
28.883
22.759
14.294
14.204
CO2Et
3p
f1 (ppm)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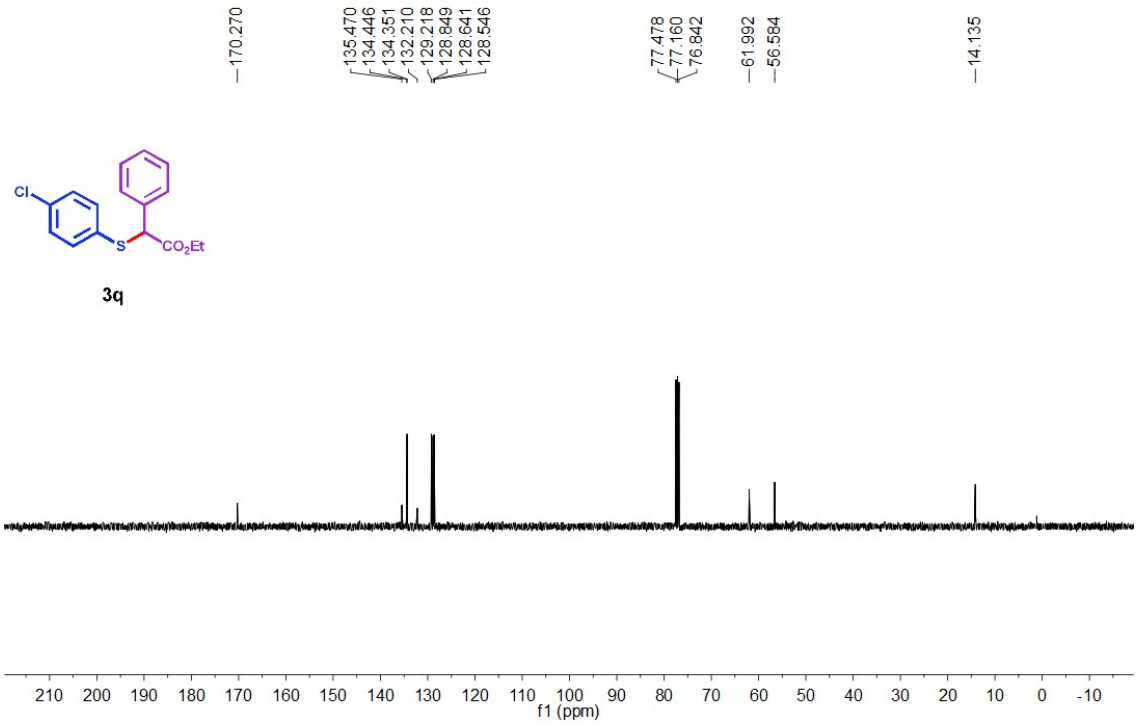
7.4260
7.4112
7.4072
7.3500
7.3460
7.3412
7.3364
7.3274
7.3235
7.3172
7.3116
7.3095
7.3047
7.2992
7.2949
7.2884
7.2830
7.2770
7.2604
7.2430
7.2371
7.2316
7.2206
7.2154
7.2093
4.8562
4.2041
4.1862
4.1771
4.1683
4.1592
4.1516
4.1414
4.1339
4.1236
4.1161
4.1069
4.0984
4.0891
4.0713
1.2003
1.1824
1.1646
Cl
S
CO2Et
3q
7.34
7.30
7.26
7.22
f1 (ppm)
2.0008
1.0070
2.9089
1.1091
2.0358
1.0000
2.0808
3.0970
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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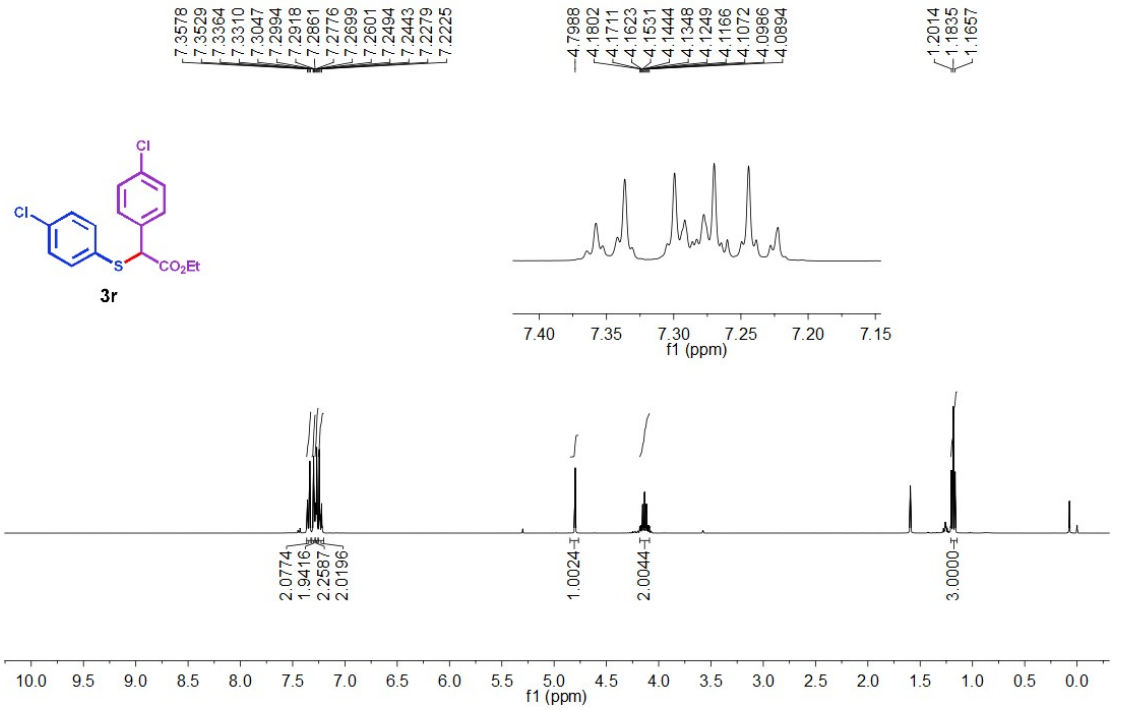
134.446
134.351
132.210
129.218
128.849
128.641
128.546
77.478
77.160
76.842
61.992
56.584
14.135
Cl
S
CO2Et
3q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.3364
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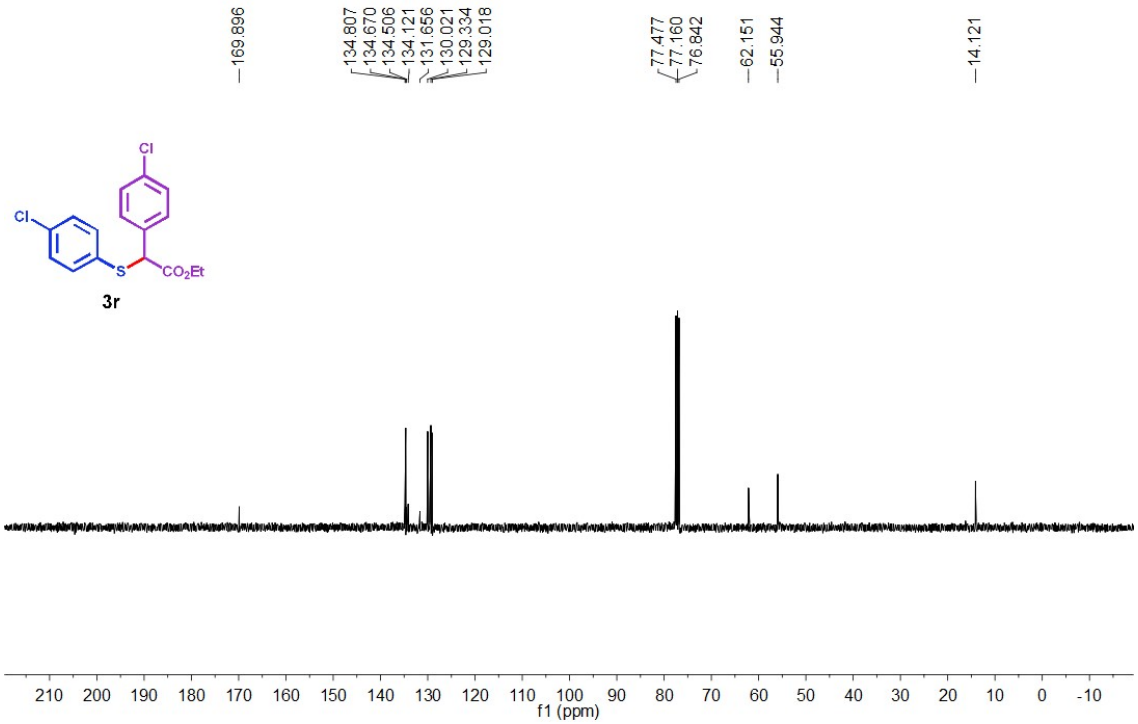
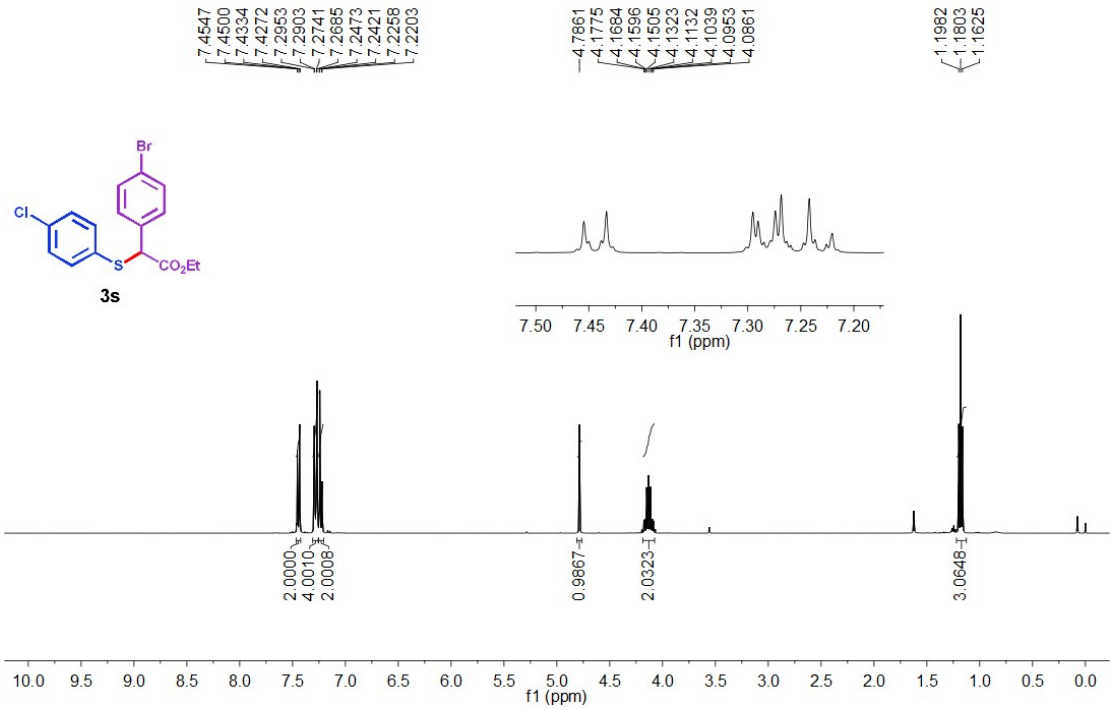
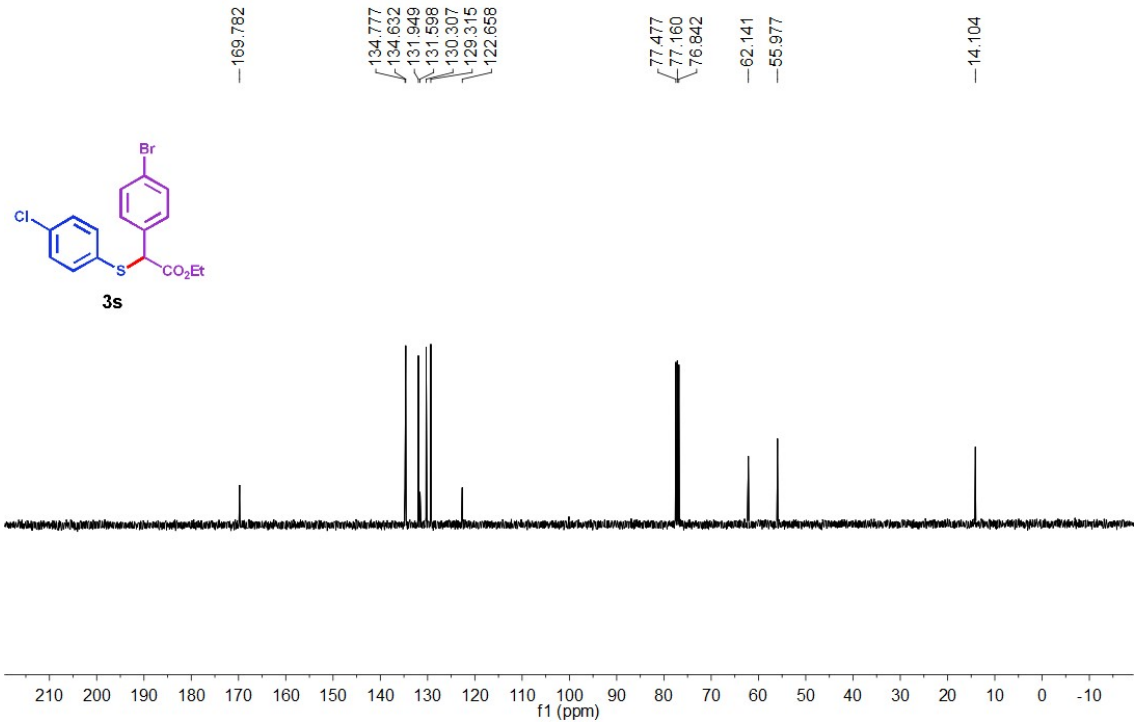
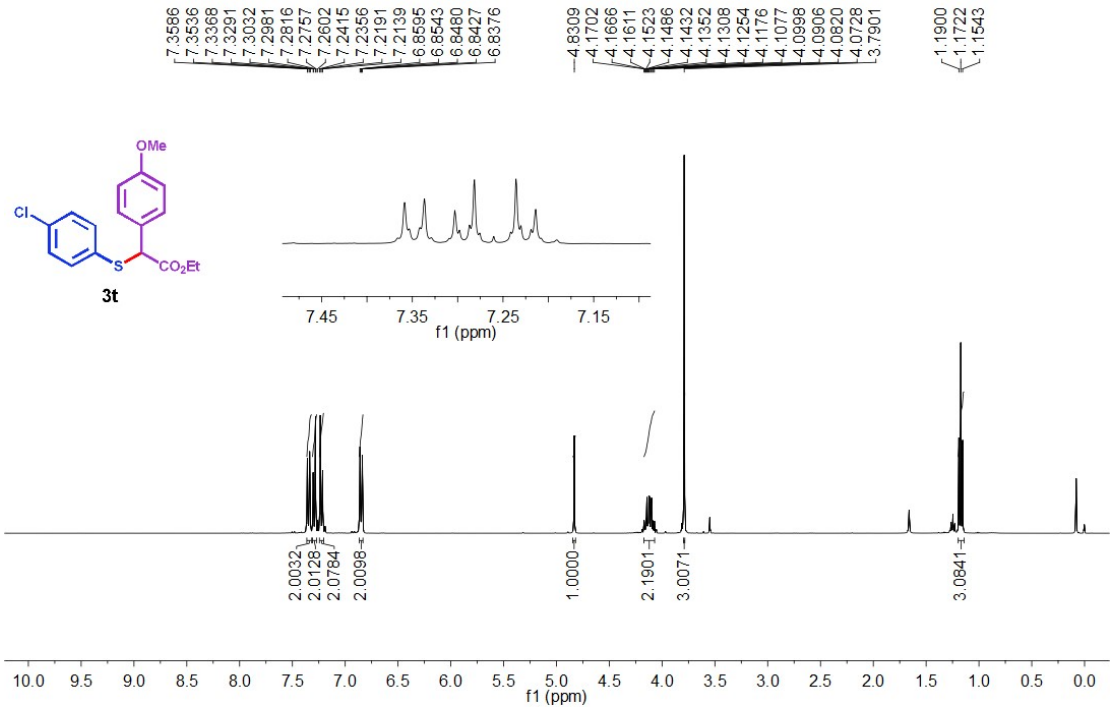
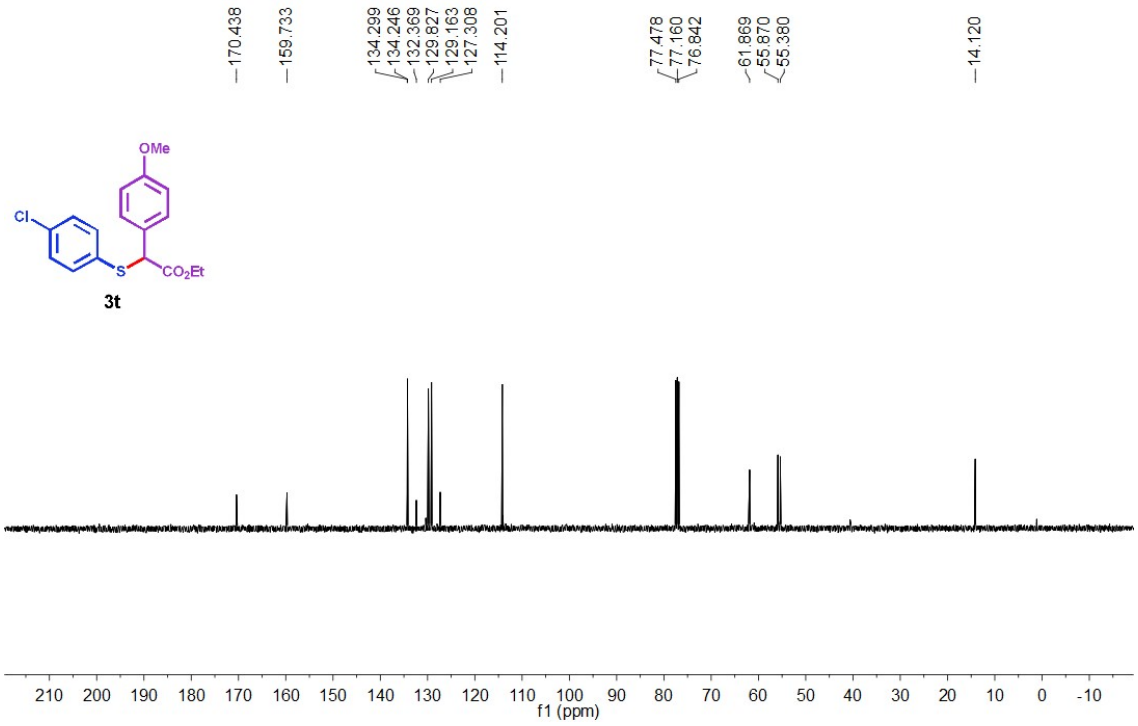
7.3047
7.2994
7.2918
7.2861
7.2776
7.2699
7.2601
7.2494
7.2443
7.2279
7.2225
4.7988
4.1802
4.1711
4.1623
4.1531
4.1444
4.1348
4.1249
4.1166
4.1072
4.0986
4.0894
1.2014
1.1835
1.1657
Cl
Cl
S
CO2Et
3r
7.40
7.35
7.30
7.25
7.20
7.15
f1 (ppm)
2.0774
1.9416
2.2587
2.0196
1.0024
2.0044
3.0000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

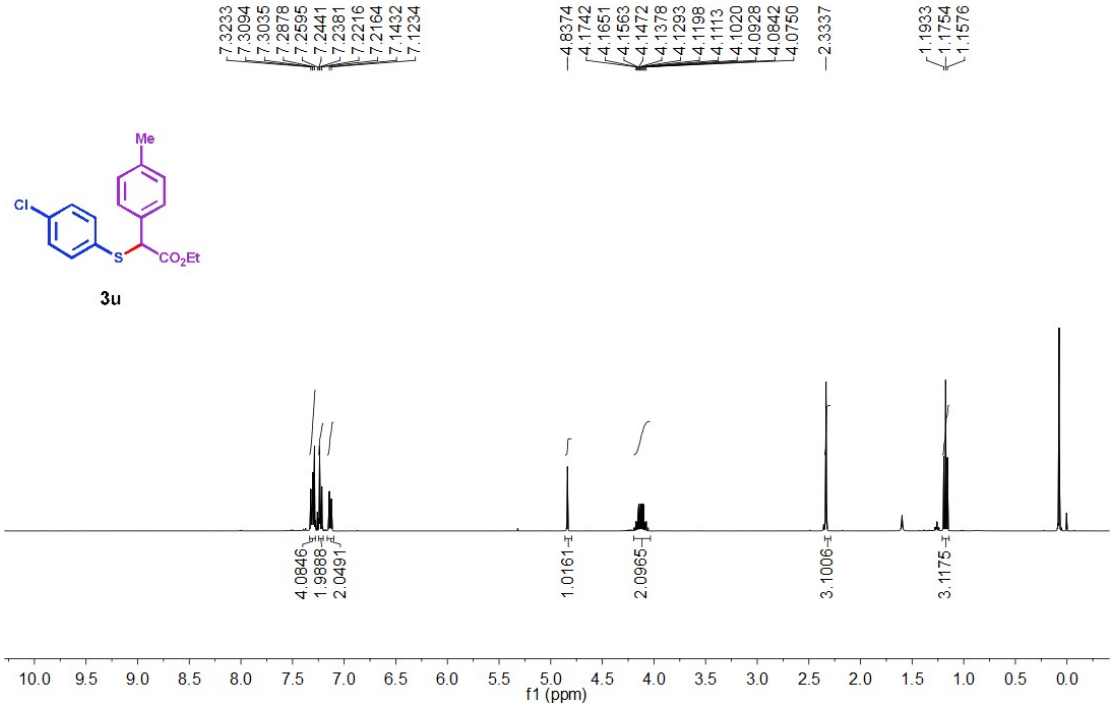

169.896
134.807
134.670
134.506
134.121
131.656
130.021
129.334
129.018
77.477
77.160
76.842
62.151
55.944
14.121
Cl
Cl
S
CO2Et
3r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

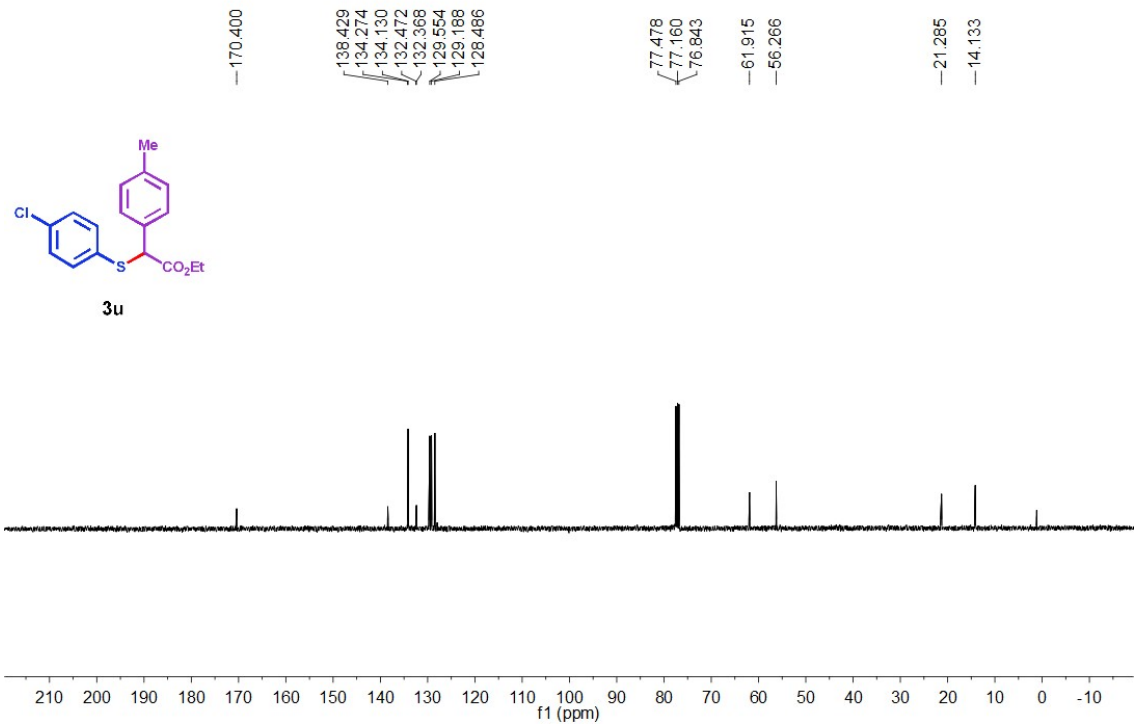

7.4547
7.4500
7.4334
7.4272
7.2953
7.2903
7.2741
7.2685
7.2473
7.2421
7.2258
7.2203
4.7861
4.1775
4.1684
4.1596
4.1505
4.1323
4.1132
4.1039
4.0953
4.0861
1.1982
1.1803
1.1625
Br
Cl
S
CO2Et
3s
7.50 7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
2.0000
4.0010
2.0008
0.9867
2.0323
3.0648
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.782
134.777
134.632
131.949
131.598
130.307
129.315
122.658
77.477
77.160
76.842
62.141
55.977
14.104
Br
Cl
S
CO2Et
3s
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)


7.3586
7.3536
7.3368
7.3291
7.3032
7.2981
7.2816
7.2757
7.2602
7.2415
7.2356
7.2191
7.2139
6.8595
6.8543
6.8480
6.8427
6.8376
4.8309
4.1702
4.1666
4.1611
4.1523
4.1486
4.1432
4.1352
4.1308
4.1254
4.1176
4.1077
4.0998
4.0906
4.0820
4.0728
3.7901
1.1900
1.1722
1.1543
OMe
Cl
S
CO2Et
3t
7.45
7.35
7.25
7.15
f1 (ppm)
2.0032
2.0128
2.0784
2.0098
1.0000
2.1901
3.0071
3.0841
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.438
159.733
134.299
134.246
132.369
129.827
129.163
127.308
114.201
77.478
77.160
76.842
61.869
55.870
55.380
14.120
OMe
Cl
S
CO2Et
3t
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)


7.3233
7.3094
7.3035
7.2878
7.2595
7.2441
7.2381
7.2216
7.2164
7.1432
7.1234
4.8374
4.1742
4.1651
4.1563
4.1472
4.1378
4.1293
4.1198
4.1113
4.1020
4.0928
4.0842
4.0750
2.3337
1.1933
1.1754
1.1576
Me
Cl
S
CO2Et
3u
4.0846
1.9888
2.0491
1.0161
2.0965
3.1006
3.1175
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.400
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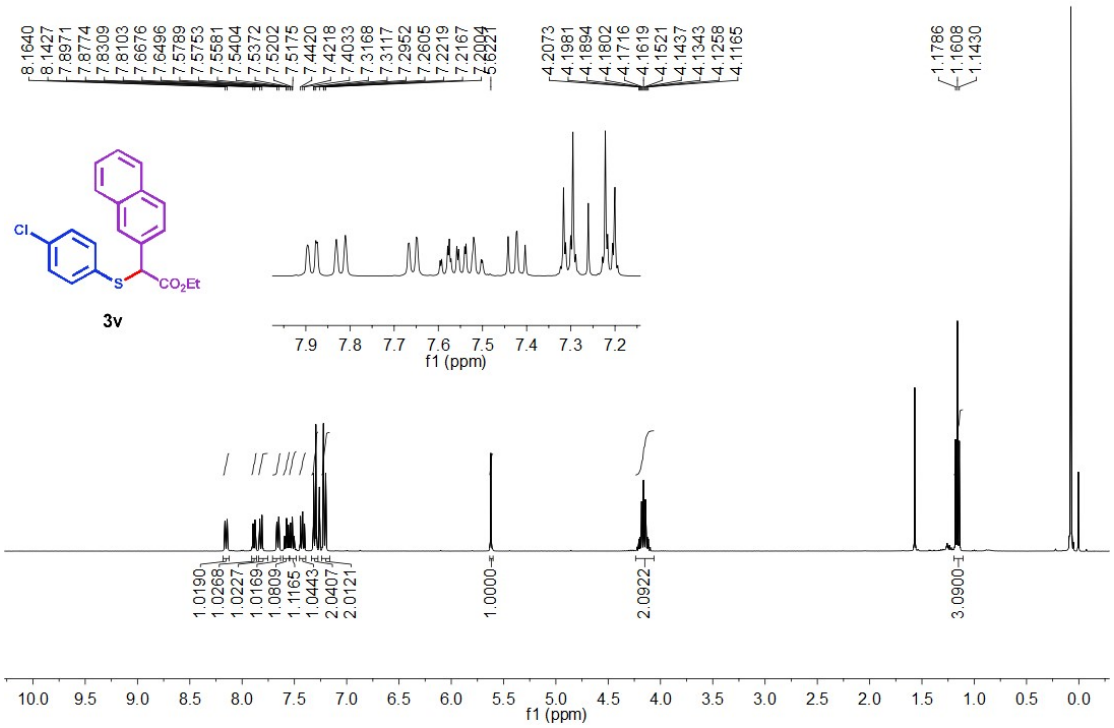
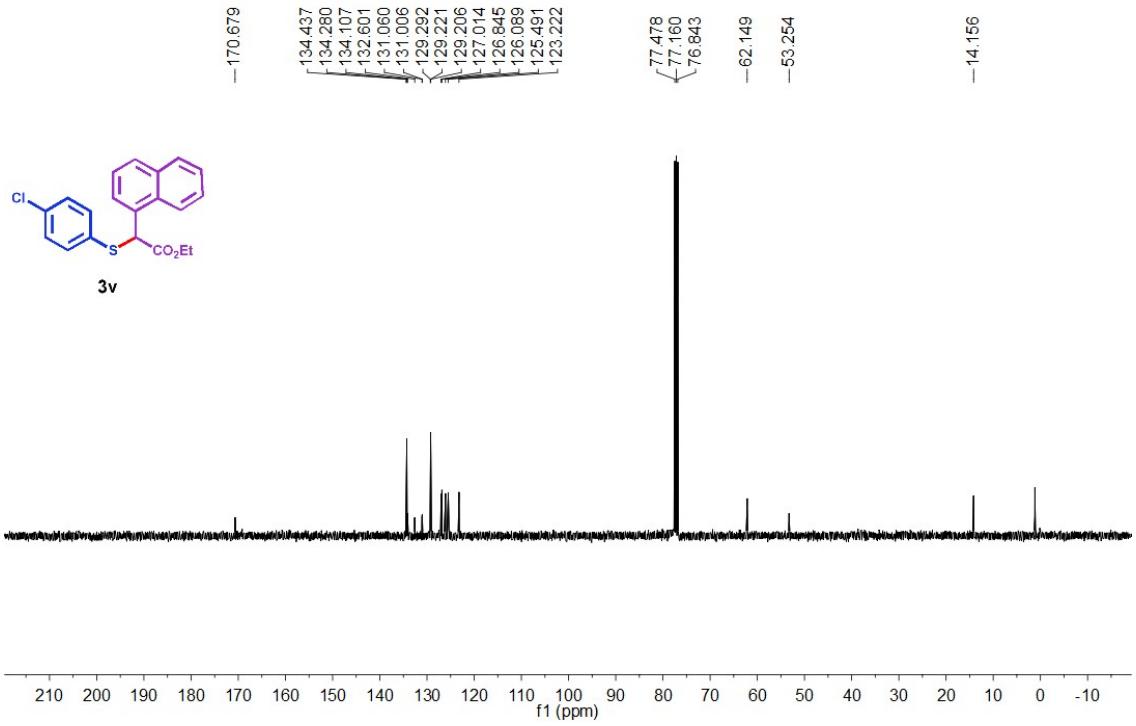
134.274
134.130
132.472
132.368
129.554
129.188
128.486
77.478
77.160
76.843
61.915
56.266
21.285
14.133
Me
Cl
S
CO2Et
3u
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.1640
8.1427
7.8971
7.8774
7.8309
7.8103
7.6676
7.6496
7.5789
7.5753
7.5581
7.5404
7.5372
7.5202
7.5175
7.4420
7.4218
7.4033
7.3168
7.3117
7.2952
7.2605
7.2219
7.2167
7.2004
5.6221
4.2073
4.1981
4.1894
4.1802
4.1716
4.1619
4.1521
4.1437
4.1343
4.1258
4.1165
1.1786
1.1608
1.1430
Cl
S
CO2Et
3v
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
1.0190
1.0268
1.0227
1.0169
1.0809
1.1165
1.0443
2.0407
2.0121
1.0000
2.0922
3.0900
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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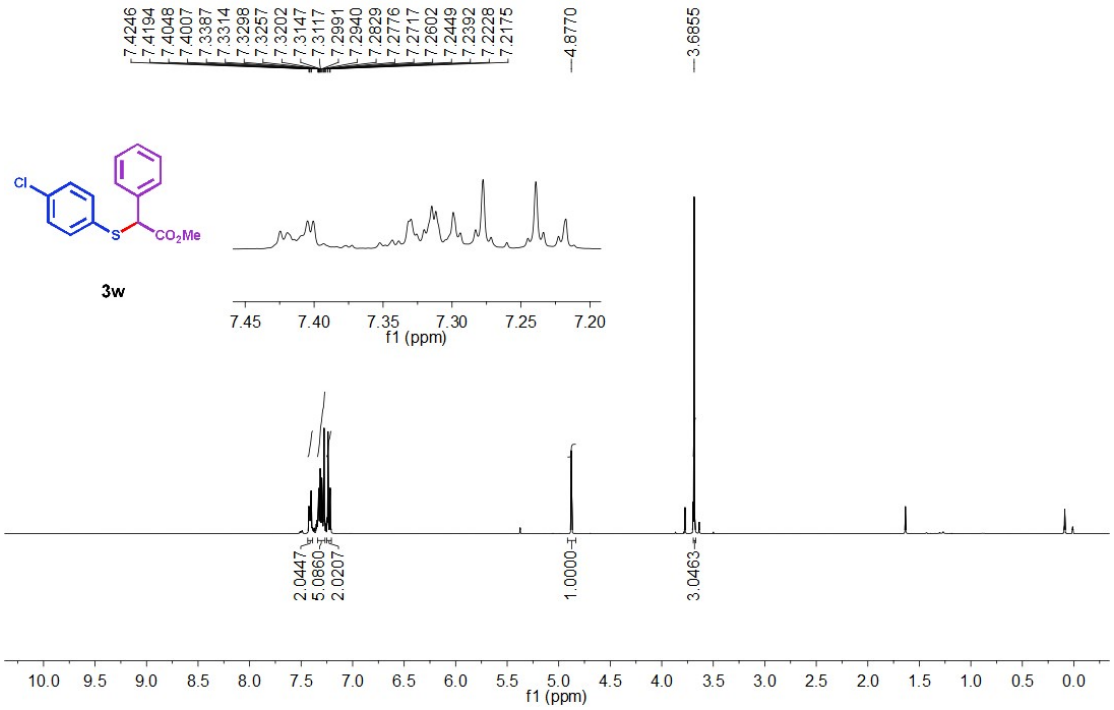
131.006
129.292
129.221
129.206
127.014
126.845
126.089
125.491
123.222
77.478
77.160
76.843
62.149
53.254
14.156
Cl
S
CO2Et
3v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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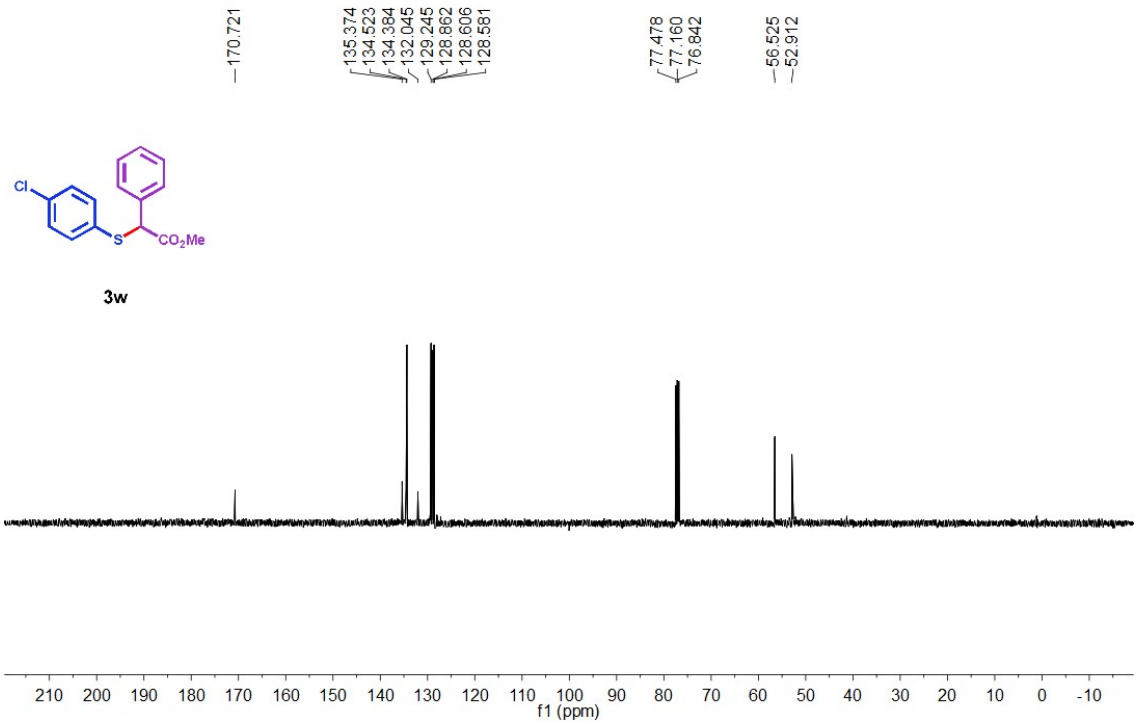
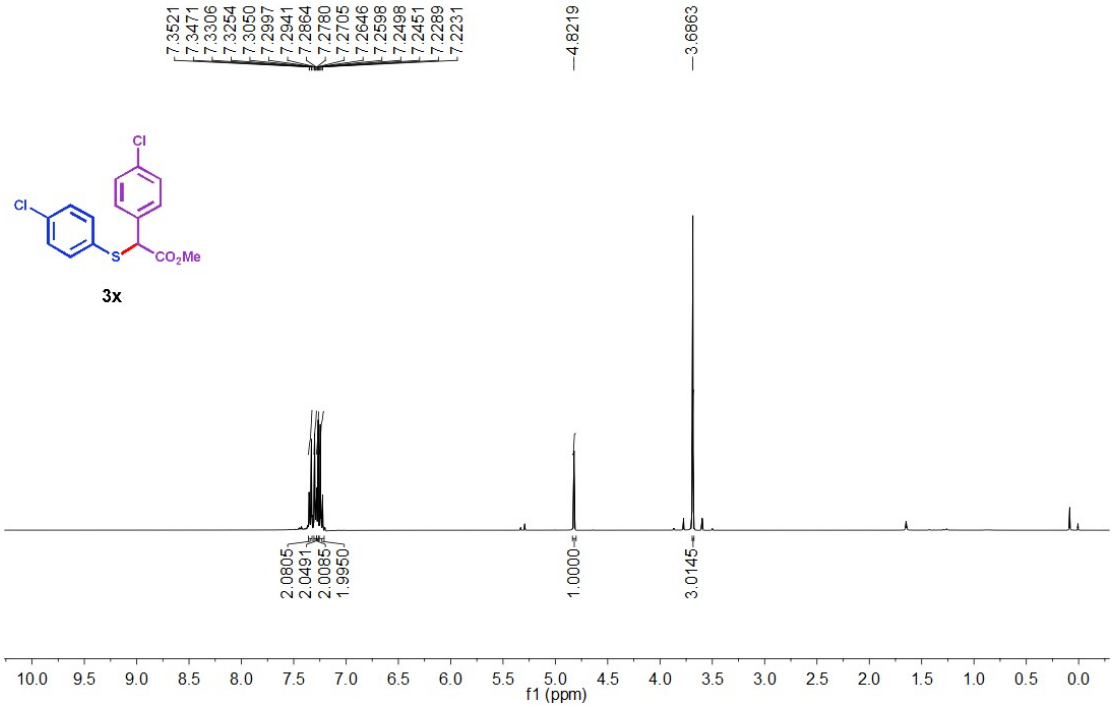
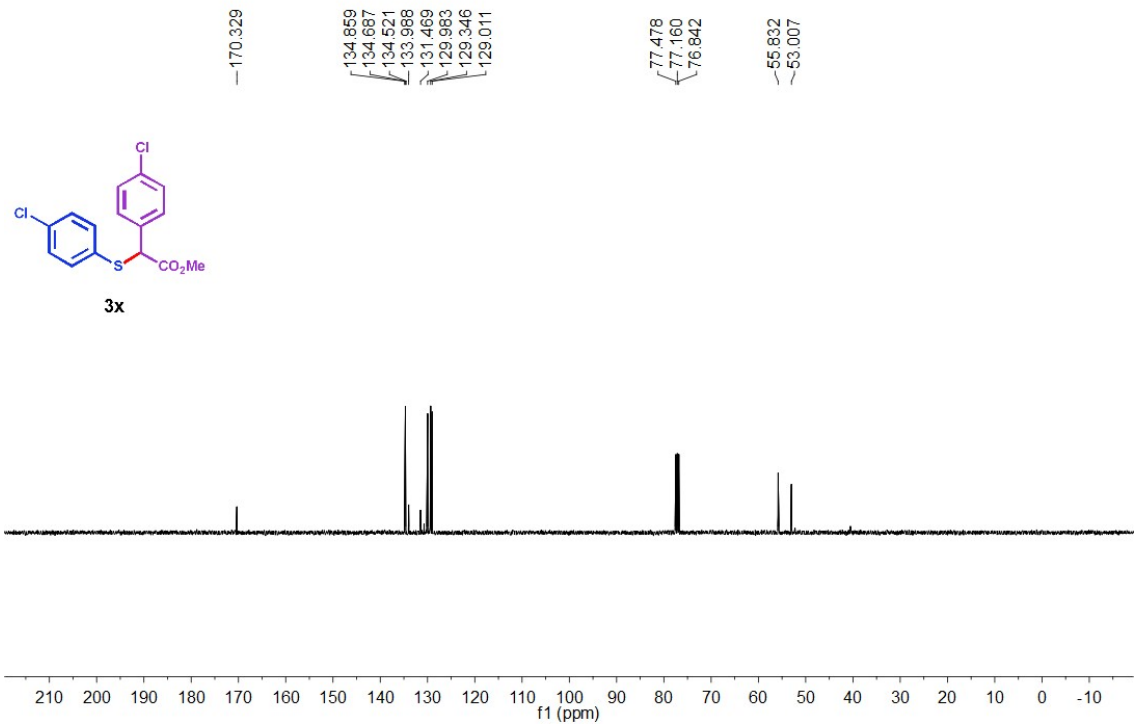
7.4194
7.4048
7.4007
7.3387
7.3314
7.3298
7.3257
7.3202
7.3147
7.3117
7.2991
7.2940
7.2829
7.2776
7.2717
7.2602
7.2449
7.2392
7.2228
7.2175
4.8770
3.6855
Cl
S
CO2Me
3w
7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
2.0447
5.0860
2.0207
1.0000
3.0463
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.721
135.374
134.523
134.384
132.045
129.245
128.862
128.606
128.581
77.478
77.160
76.842
56.525
52.912
Cl
S
CO2Me
3w
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)


7.3521
7.3471
7.3306
7.3254
7.3050
7.2997
7.2941
7.2864
7.2780
7.2705
7.2646
7.2598
7.2498
7.2451
7.2289
7.2231
4.8219
3.6863
Cl
Cl
S
CO2Me
2.0805
2.0491
2.0085
1.9950
1.0000
3.0145
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3x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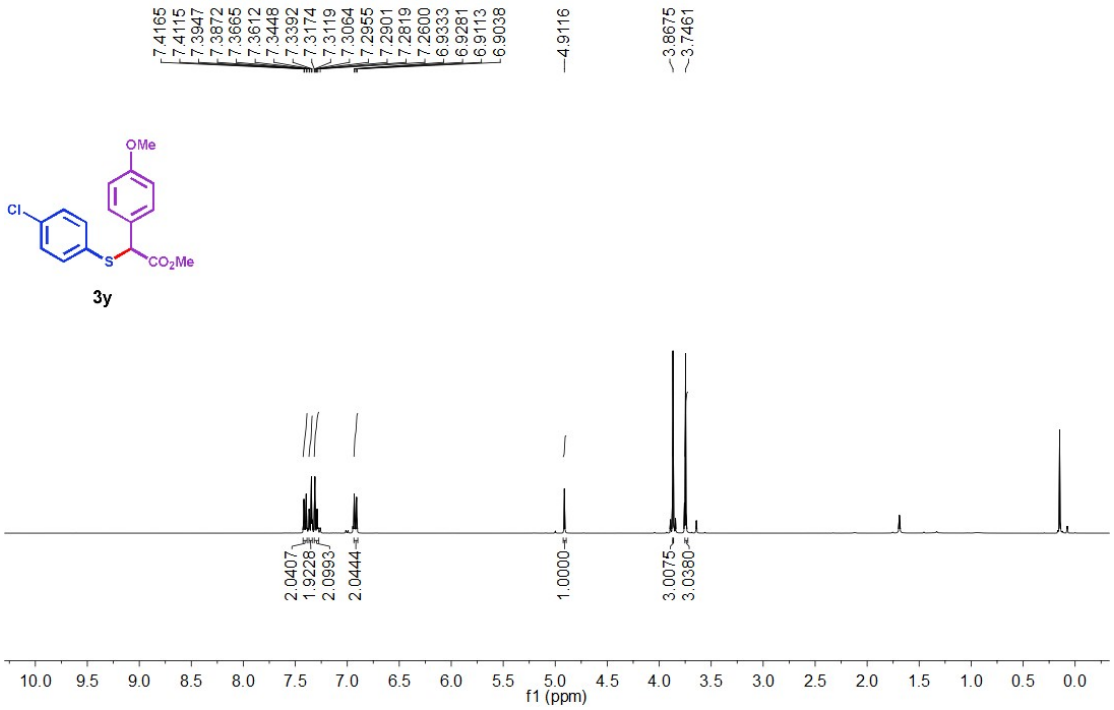
133.988
131.469
129.983
129.346
129.011
77.478
77.160
76.842
55.832
53.007
Cl
Cl
S
CO2Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3x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7.4115
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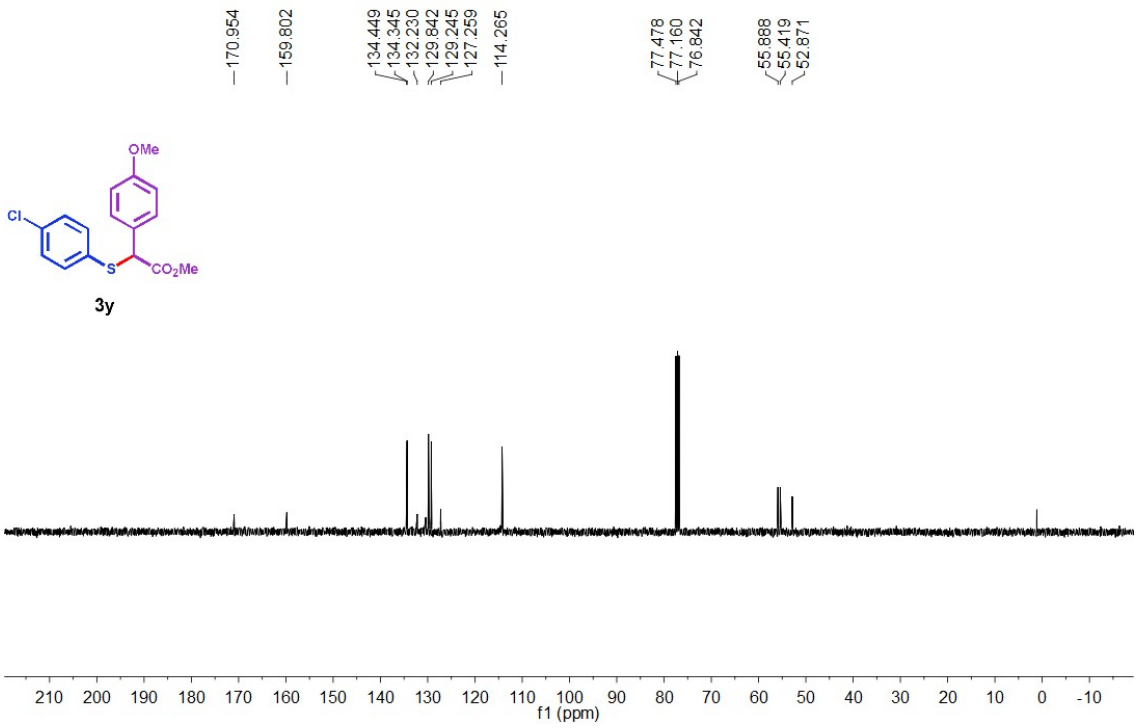
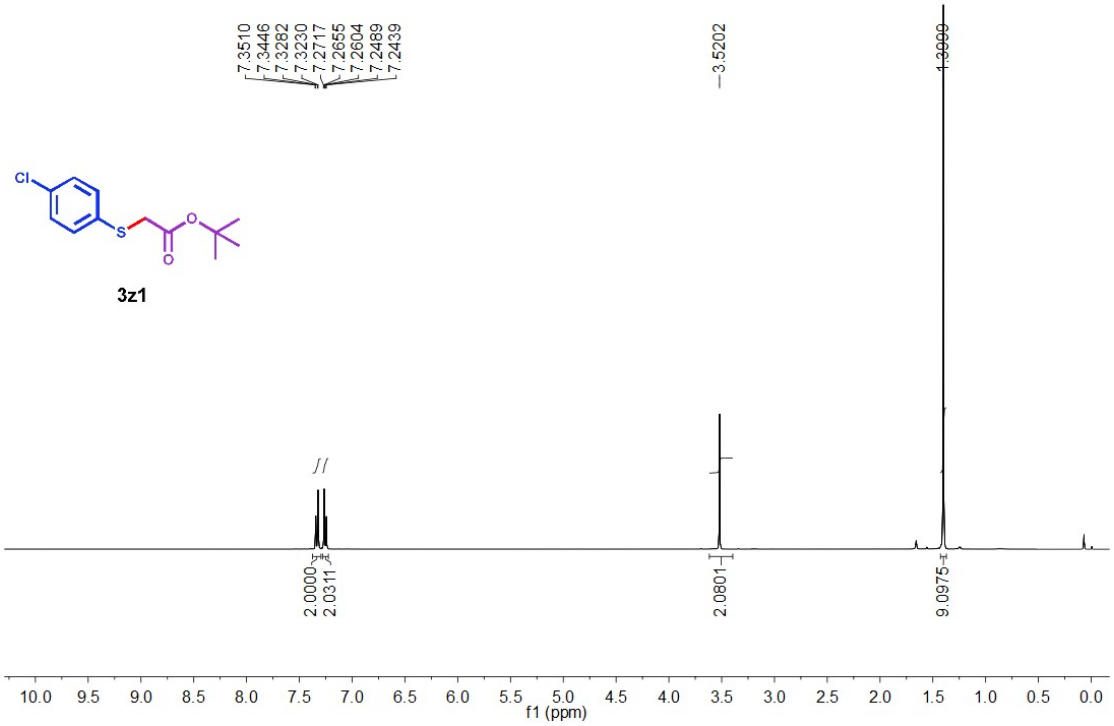
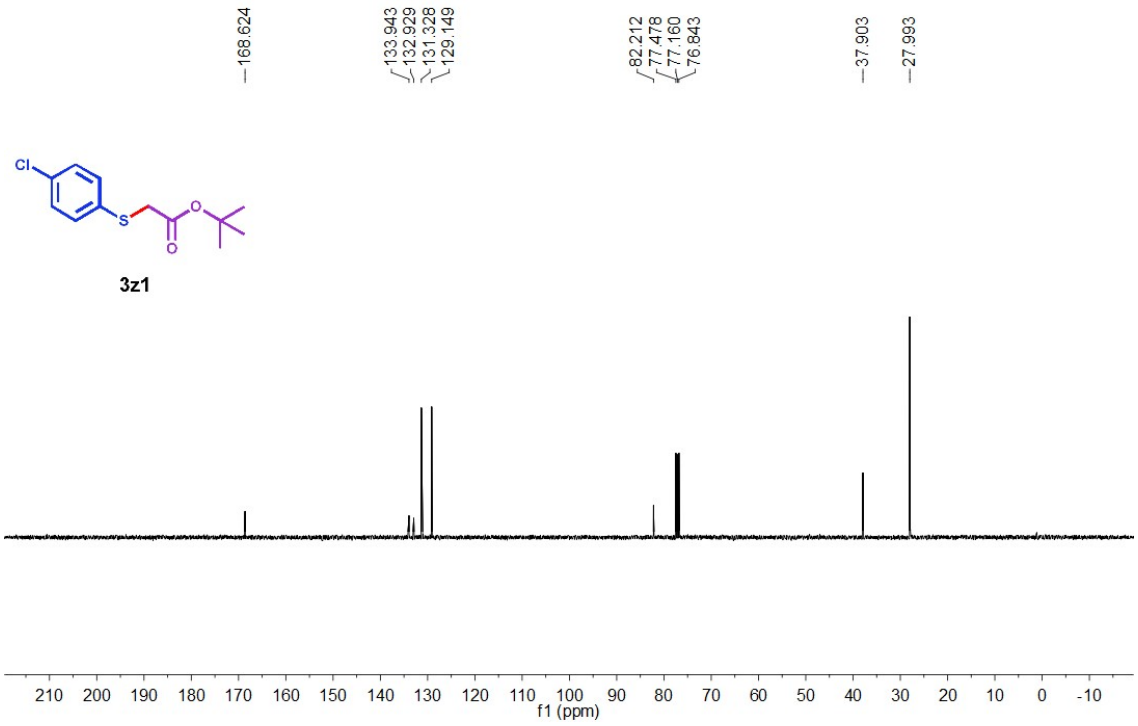
7.3872
7.3665
7.3612
7.3448
7.3392
7.3174
7.3119
7.3064
7.2955
7.2901
7.2819
7.2600
6.9333
6.9281
6.9113
6.9038
4.9116
3.8675
3.7461
OMe
Cl
S
CO2Me
3y
2.0407
1.9228
2.0993
2.0444
1.0000
3.0075
3.0380
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.954
159.802
134.449
134.345
132.230
129.842
129.245
127.259
114.265
77.478
77.160
76.842
55.888
55.419
52.871
OMe
Cl
S
CO2Me
3y
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)


7.3510
7.3446
7.3282
7.3230
7.2717
7.2655
7.2604
7.2489
7.2439
3.5202
1.3999
Cl
S
O
O
3z1
2.0000
2.0311
2.0801
9.0975
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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131.328
129.149
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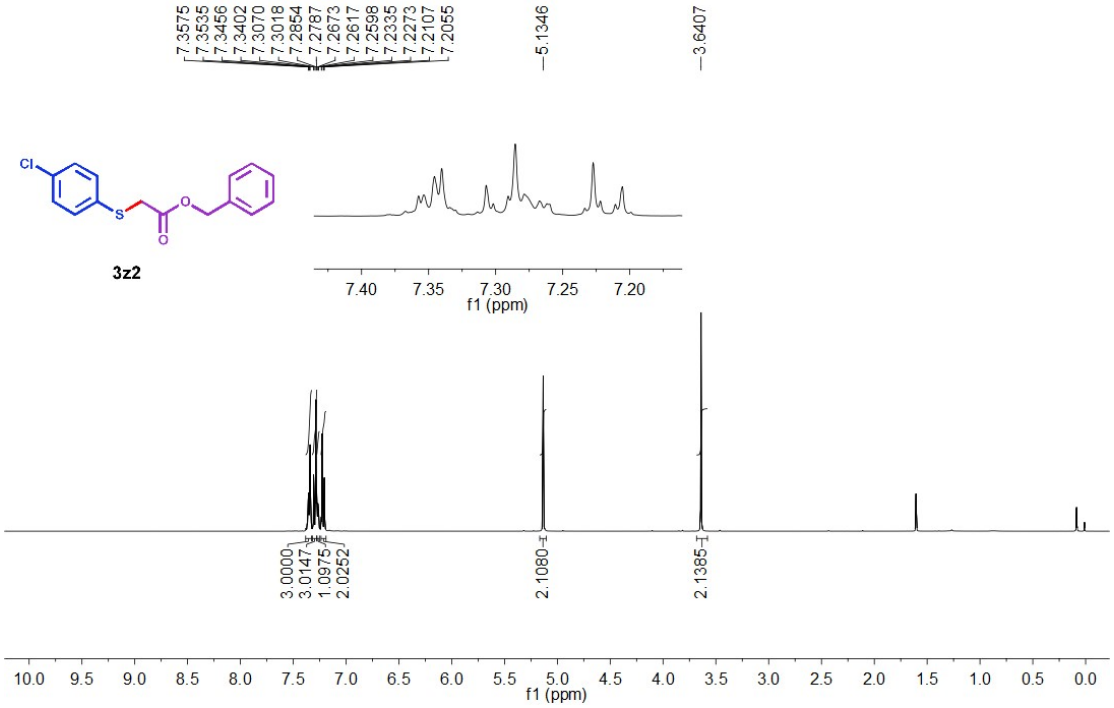
77.160
76.843
37.903
27.993
Cl
S
O
O
3z1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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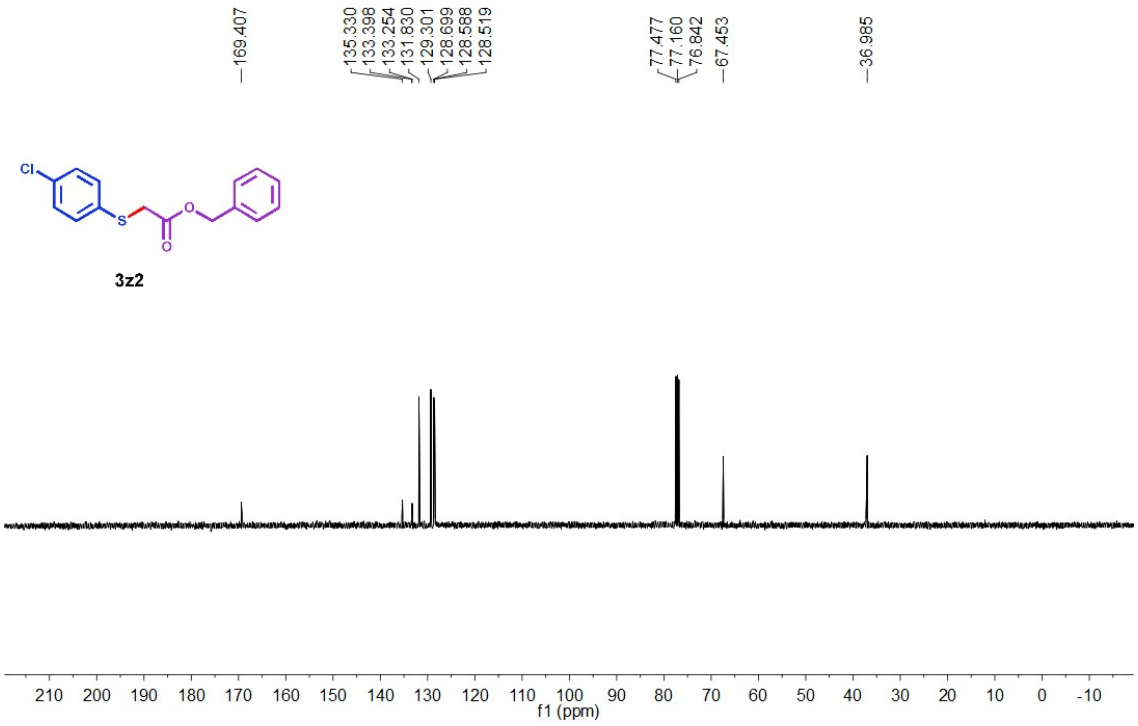
7.3402
7.3070
7.3018
7.2854
7.2787
7.2673
7.2617
7.2598
7.2335
7.2273
7.2107
7.2055
5.1346
3.6407
Cl
S
O
O
3z2
7.40
7.35
7.30
7.25
7.20
f1 (ppm)
3.0000
3.0147
1.0975
2.0252
2.1080
2.1385
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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133.398
133.254
131.830
129.301
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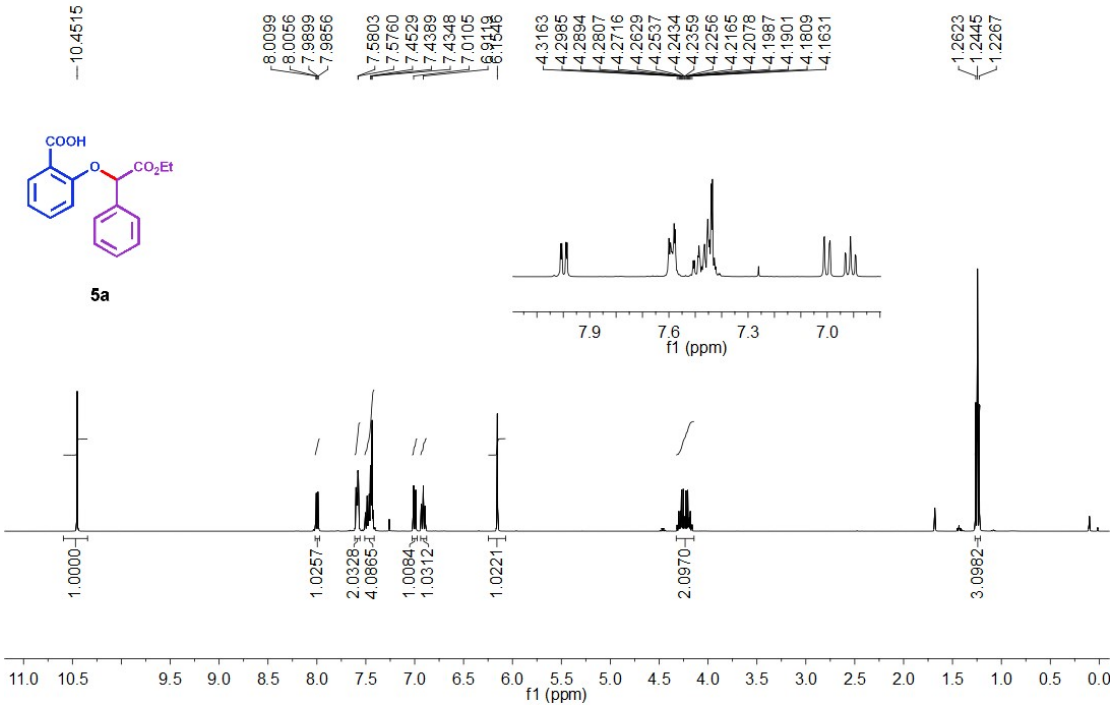
128.588
128.519
77.477
77.160
76.842
67.453
36.985
Cl
S
O
O
3z2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.0056
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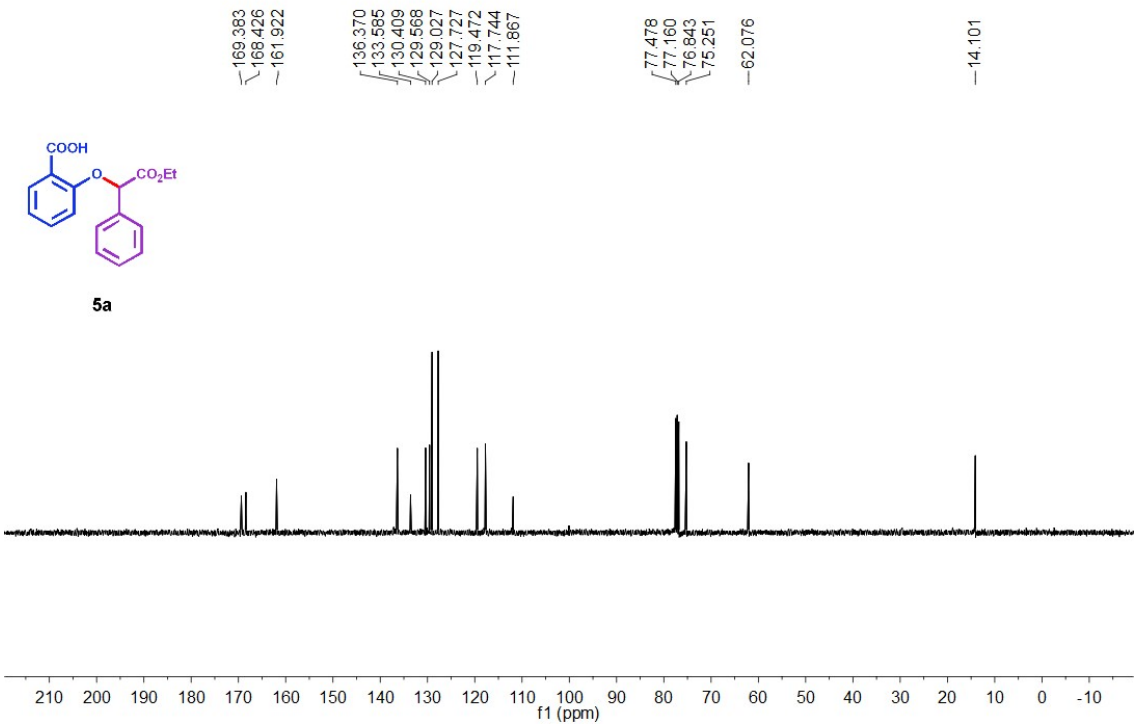
7.9856
7.5803
7.5760
7.4529
7.4389
7.4348
7.0105
6.9419
6.1546
4.3163
4.2985
4.2894
4.2807
4.2716
4.2629
4.2537
4.2434
4.2359
4.2256
4.2165
4.2078
4.1987
4.1901
4.1809
4.1631
1.2623
1.2445
1.2267
COOH
CO2Et
5a
7.9
7.6
7.3
7.0
f1 (ppm)
1.0000
1.0257
2.0328
4.0865
1.0084
1.0312
1.0221
2.0970
3.0982
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.568
129.027
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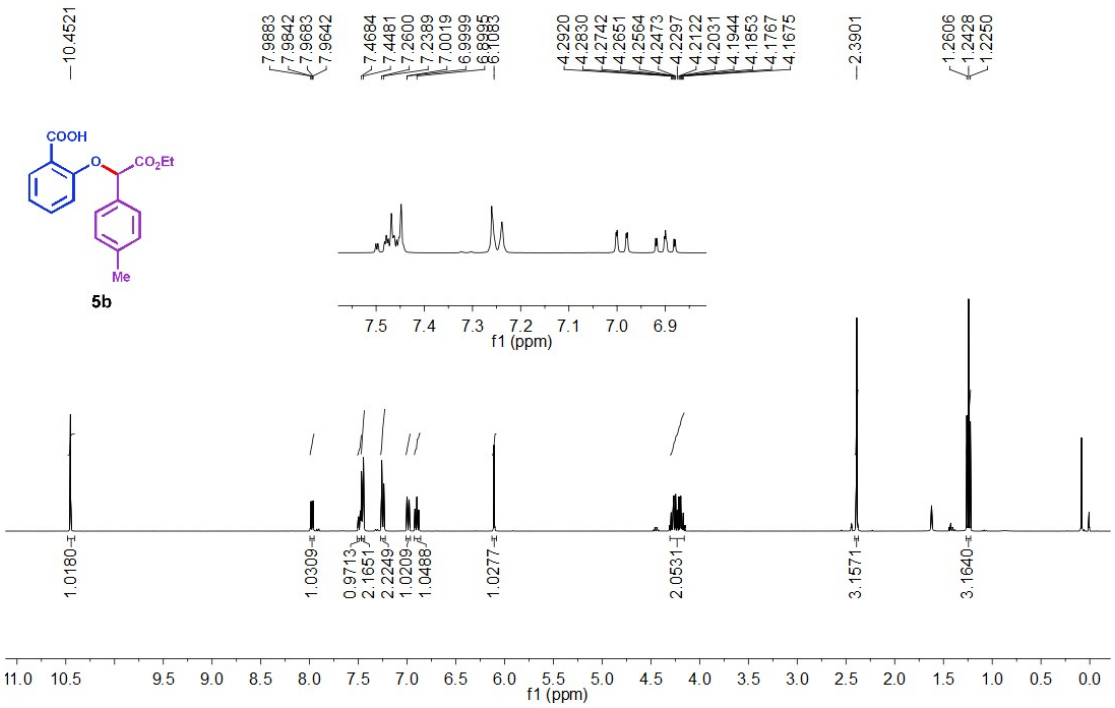
119.472
117.744
111.867
77.478
77.160
76.843
75.251
62.076
14.101
COOH
CO2Et
5a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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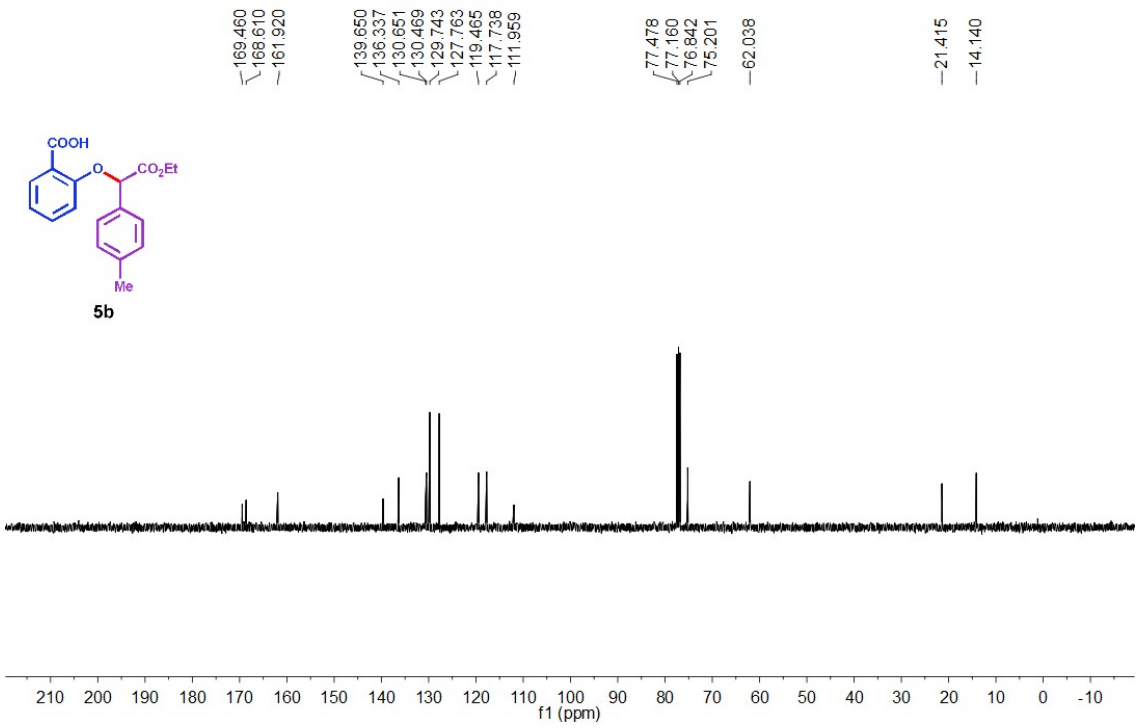
7.4481
7.2600
7.2389
7.0019
6.9999
6.8895
6.8083
4.2920
4.2830
4.2742
4.2651
4.2564
4.2473
4.2297
4.2122
4.2031
4.1944
4.1853
4.1767
4.1675
2.3901
1.2606
1.2428
1.2250
COOH
O
CO2Et
Me
5b
7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.0180
1.0309
0.9713
2.1651
2.2249
1.0209
1.0488
1.0277
2.0531
3.1571
3.1640
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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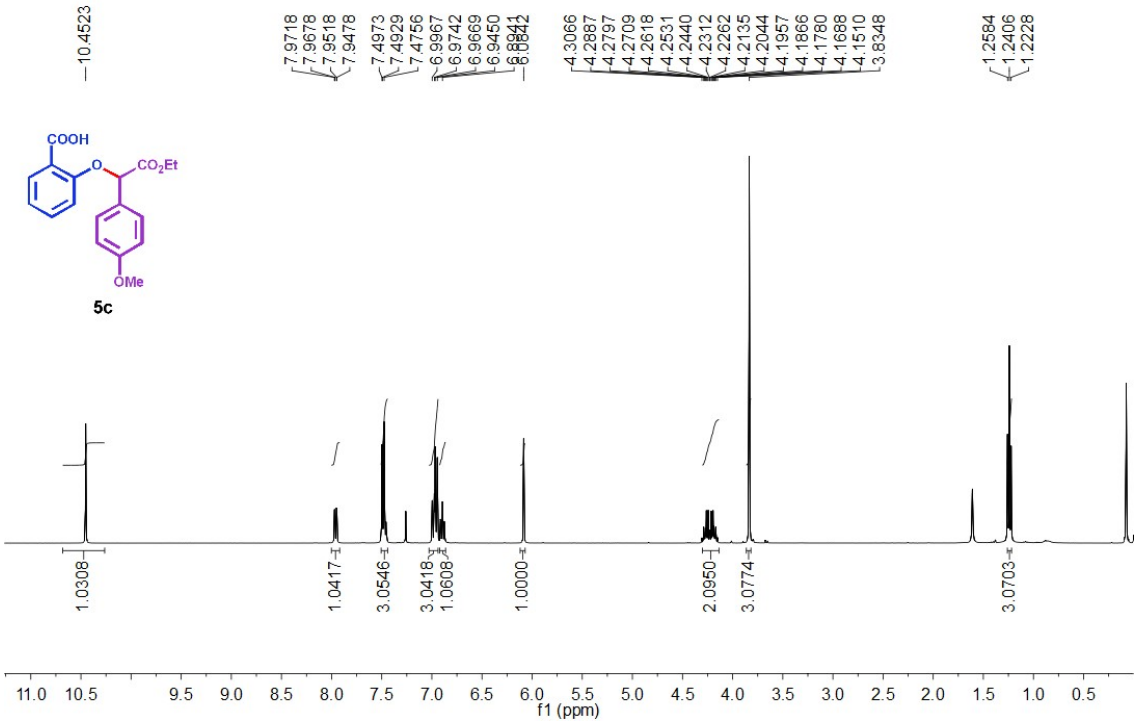
168.610
161.920
139.650
136.337
130.651
130.469
129.743
127.763
119.465
117.738
111.959
77.478
77.160
76.842
75.201
62.038
21.415
14.140
COOH
O
CO2Et
Me
5b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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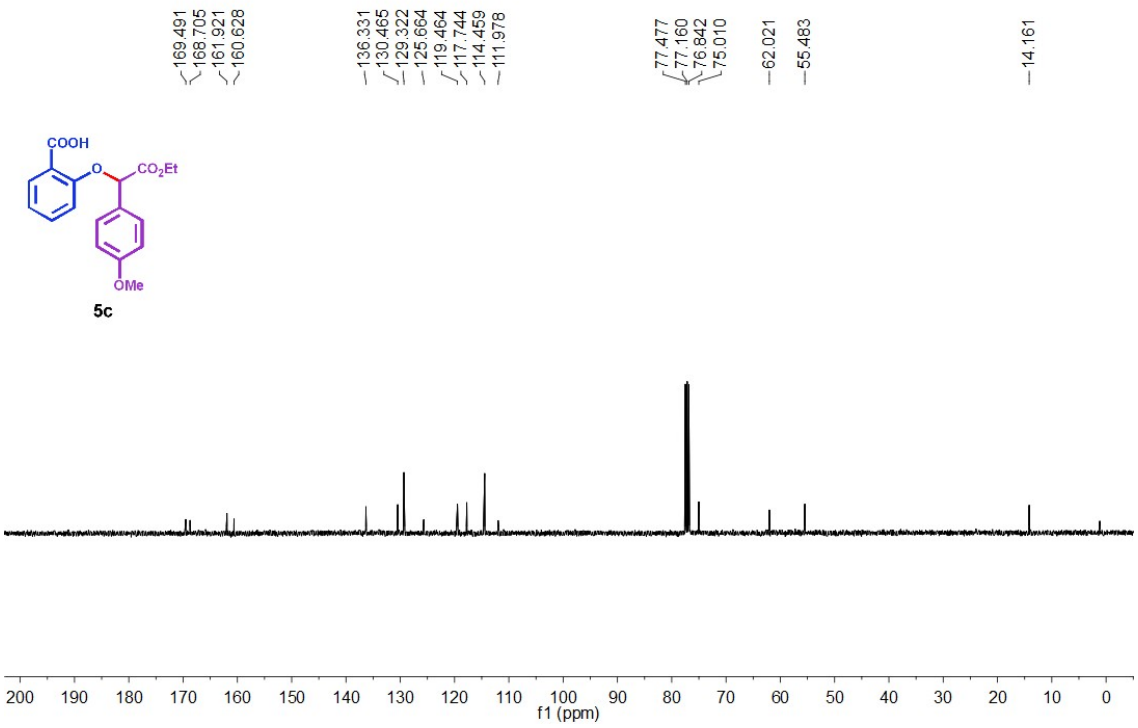
7.9678
7.9518
7.9478
7.4973
7.4929
7.4756
6.9967
6.9742
6.9669
6.9450
6.8941
6.8842
4.3066
4.2887
4.2797
4.2709
4.2618
4.2531
4.2440
4.2312
4.2262
4.2135
4.2044
4.1957
4.1866
4.1780
4.1688
4.1510
3.8348
1.2584
1.2406
1.2228
COOH
O
CO2Et
OMe
5c
1.0308
1.0417
3.0546
3.0418
1.0608
1.0000
2.0950
3.0774
3.0703
11.0 10.5 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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168.705
161.921
160.628
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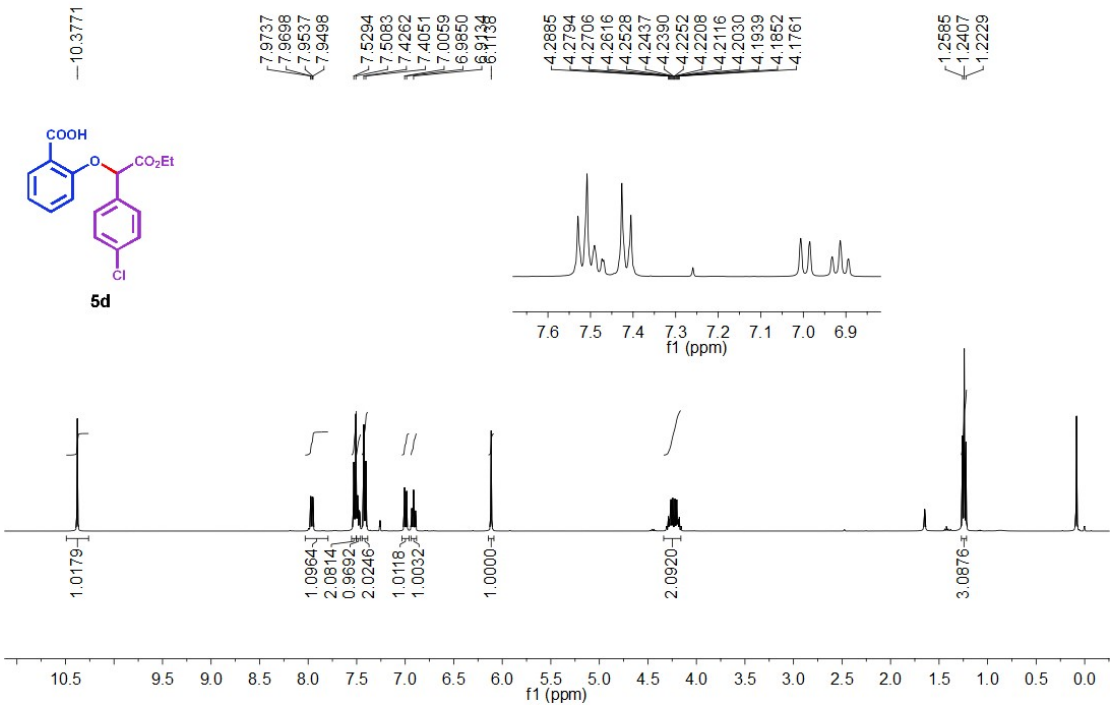
130.465
129.322
125.664
119.464
117.744
114.459
111.978
77.477
77.160
76.842
75.010
62.021
55.483
14.161
COOH
O
CO2Et
OMe
5c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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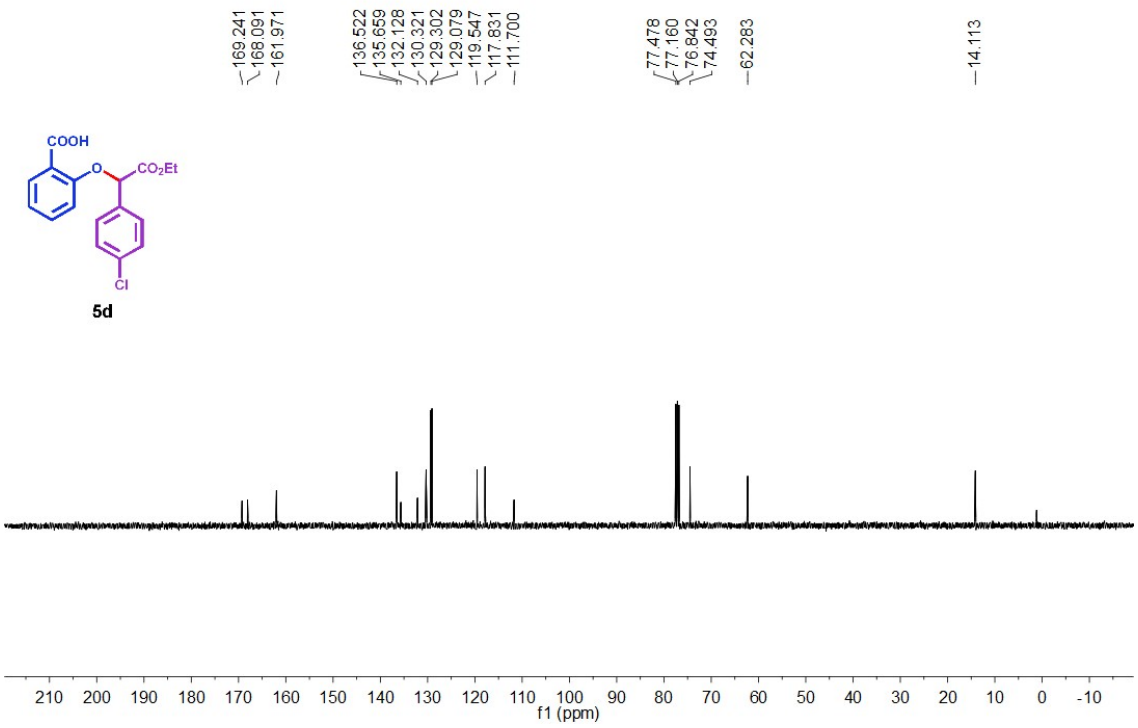
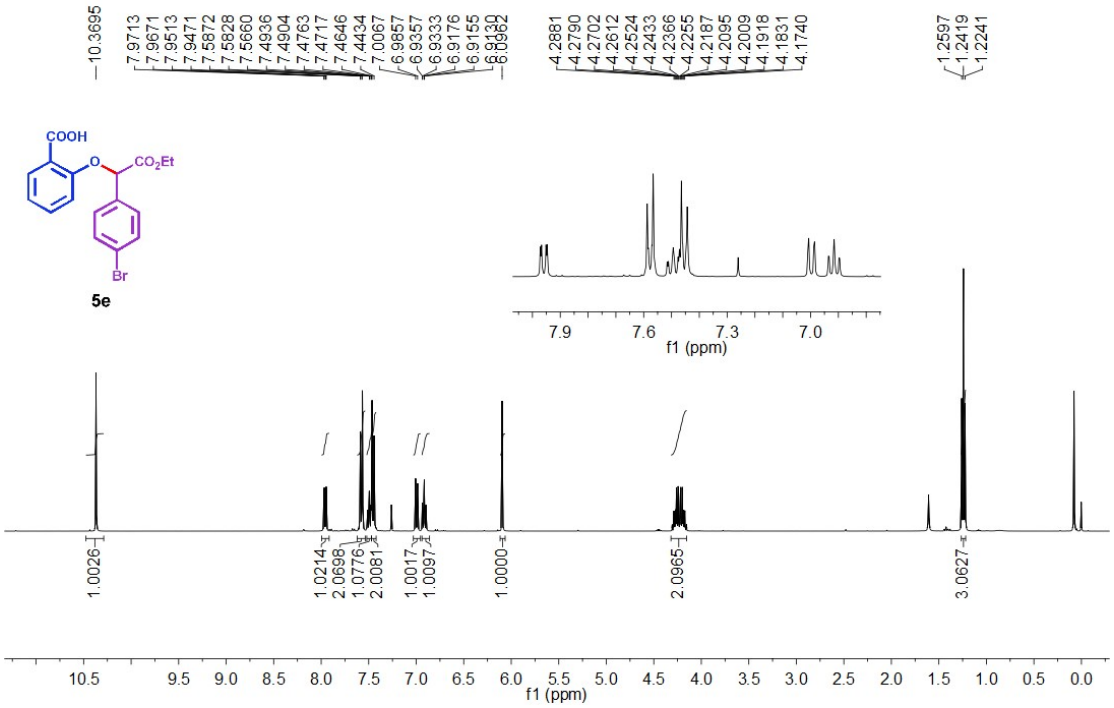
7.9737
7.9698
7.9537
7.9498
7.5294
7.5083
7.4262
7.4051
7.0059
6.9850
6.9134
6.9138
4.2885
4.2794
4.2706
4.2616
4.2528
4.2437
4.2390
4.2252
4.2208
4.2116
4.2030
4.1939
4.1852
4.1761
1.2585
1.2407
1.2229
COOH
O
CO2Et
Cl
5d
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.0179
1.0964
2.0814
0.9692
2.0246
1.0118
1.0032
1.0000
2.0920
3.0876
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.241
168.091
161.971
136.522
135.659
132.128
130.321
129.302
129.079
119.547
117.831
111.700
77.478
77.160
76.842
74.493
62.283
14.113
COOH
O
CO2Et
Cl
5d
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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7.9671
7.9513
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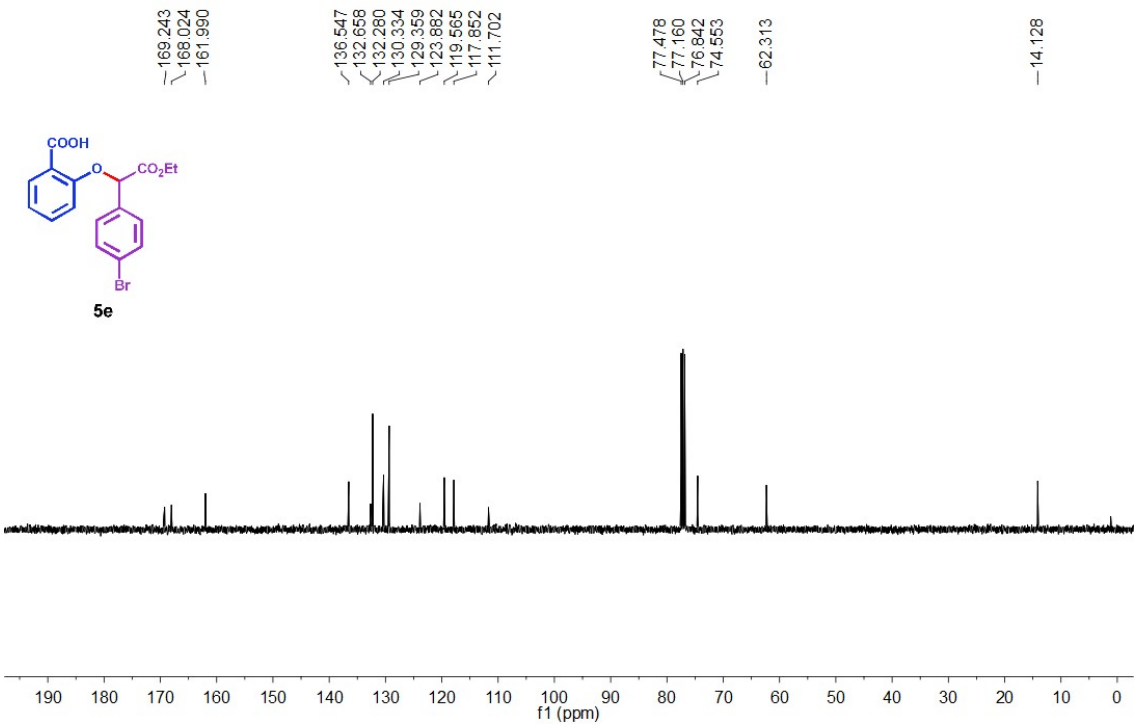
7.5828
7.5660
7.4936
7.4904
7.4763
7.4717
7.4646
7.4434
7.0067
6.9857
6.9357
6.9333
6.9176
6.9155
6.9130
6.8962
4.2881
4.2790
4.2702
4.2612
4.2524
4.2433
4.2366
4.2255
4.2187
4.2095
4.2009
4.1918
4.1831
4.1740
1.2597
1.2419
1.2241
COOH
O
CO2Et
Br
5e
7.9
7.6
7.3
7.0
f1 (ppm)
1.0026
1.0214
2.0698
1.0776
2.0081
1.0017
1.0097
1.0000
2.0965
3.0627
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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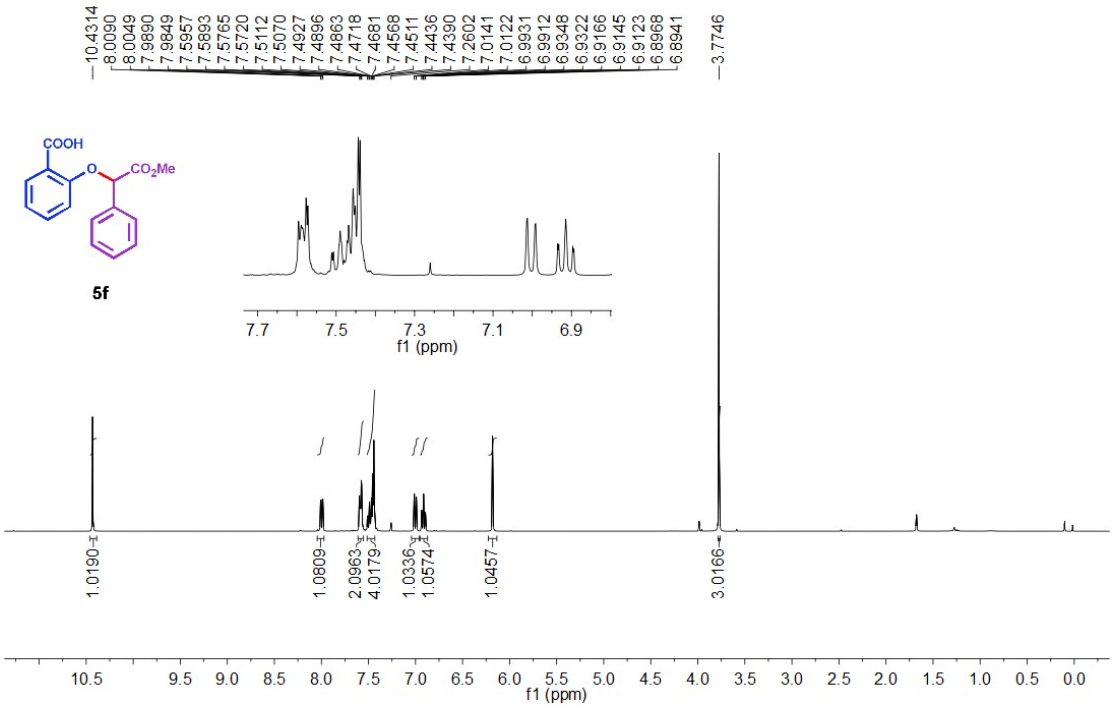
129.359
123.882
119.565
117.852
111.702
77.478
77.160
76.842
74.553
62.313
14.128
COOH
O
CO2Et
Br
5e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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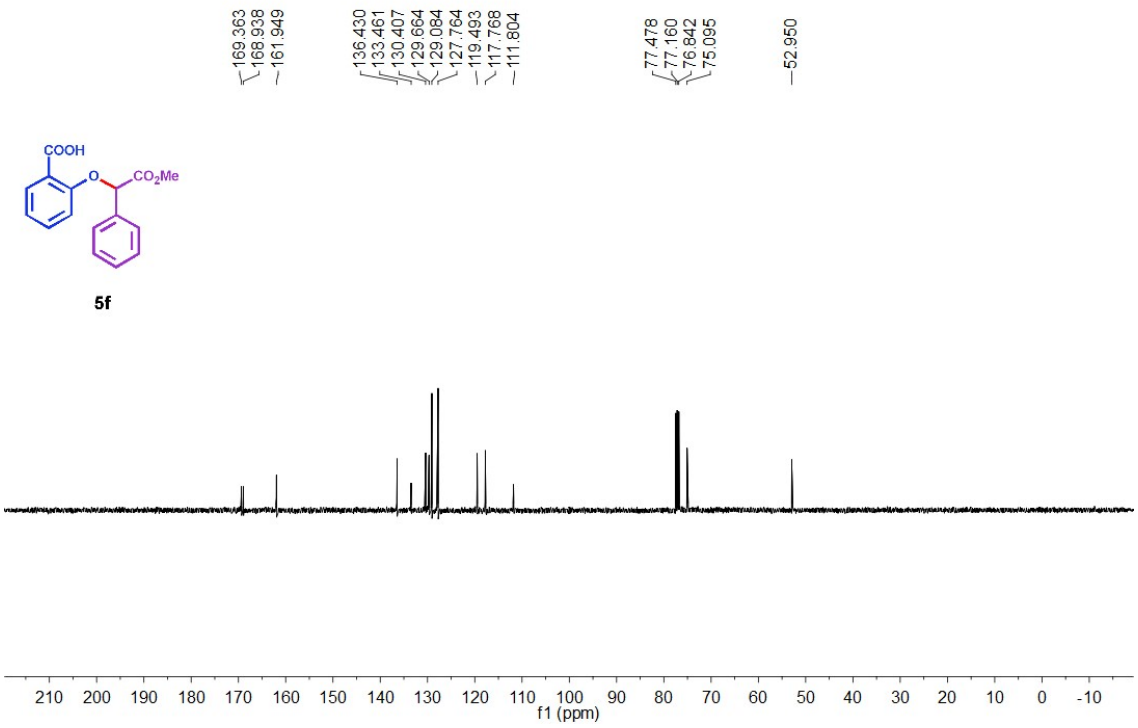
7.9849
7.5957
7.5893
7.5765
7.5720
7.5112
7.5070
7.4927
7.4896
7.4863
7.4718
7.4681
7.4568
7.4511
7.4436
7.4390
7.2602
7.0141
7.0122
6.9931
6.9912
6.9348
6.9322
6.9166
6.9145
6.9123
6.8968
6.8941
3.7746
COOH
CO2Me
5f
7.7
7.5
7.3
7.1
6.9
f1 (ppm)
1.0190
1.0809
2.0963
4.0179
1.0336
1.0574
1.0457
3.0166
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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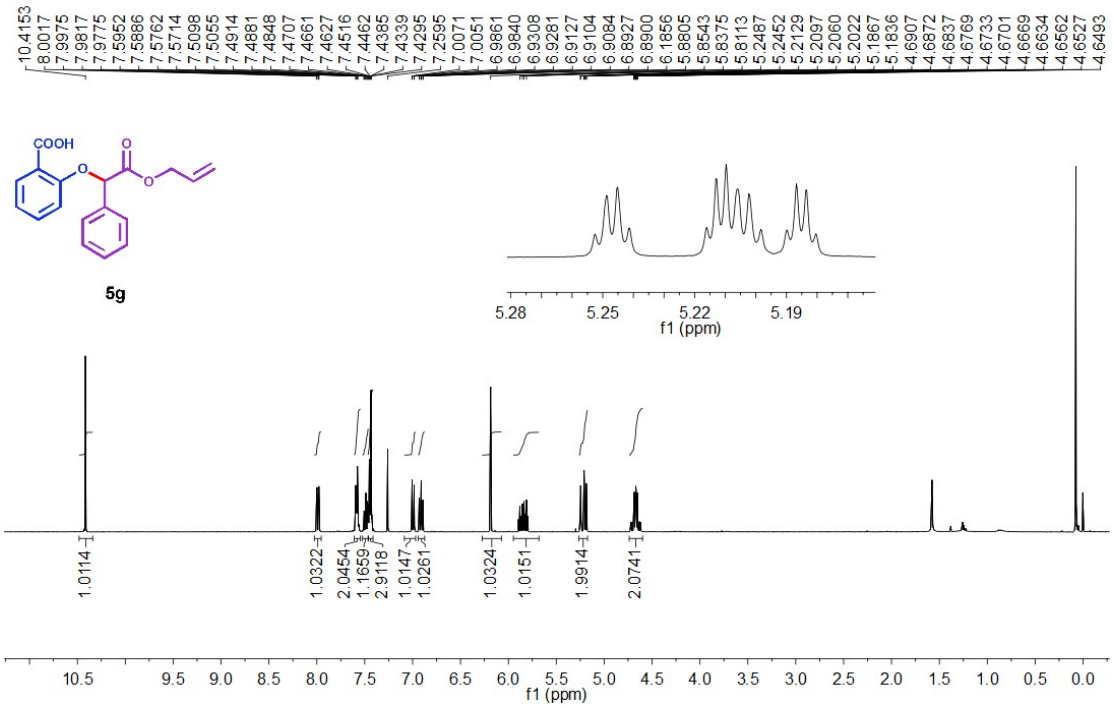
127.764
119.493
117.768
111.804
77.478
77.160
76.842
75.095
52.950
COOH
CO2Me
5f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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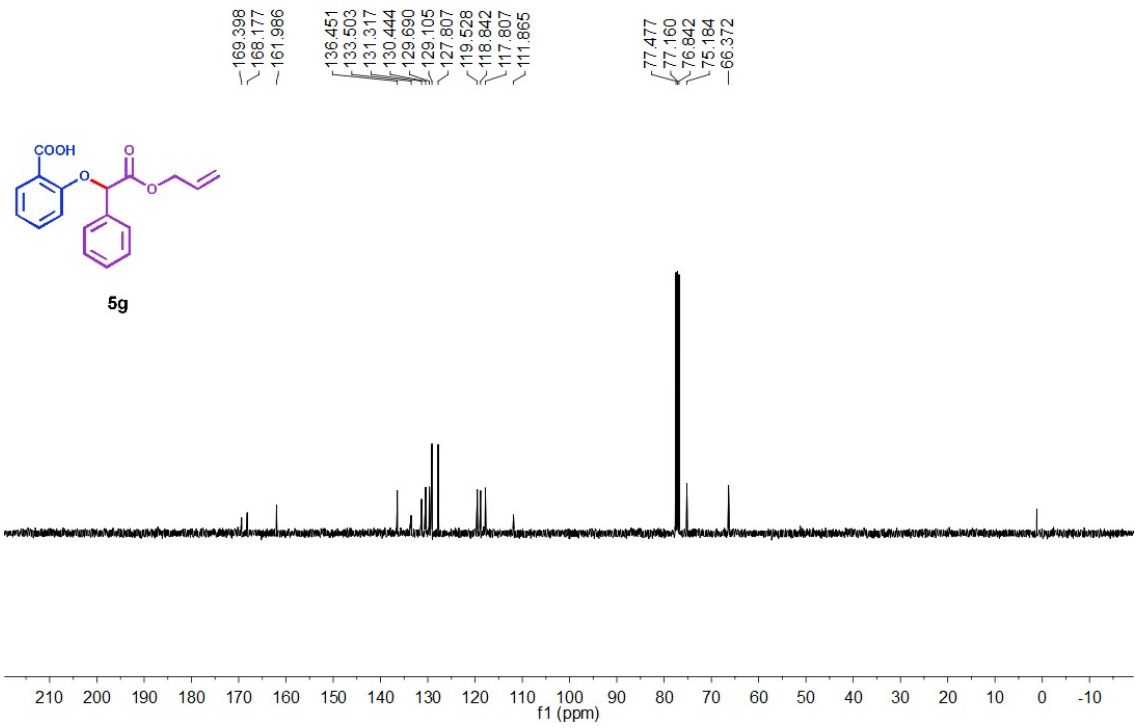
7.5055
7.4914
7.4881
7.4848
7.4707
7.4661
7.4627
7.4516
7.4462
7.4385
7.4339
7.4295
7.2595
7.0071
7.0051
6.9861
6.9840
6.9308
6.9281
6.9127
6.9104
6.9084
6.8927
6.8900
6.1856
5.8805
5.8543
5.8375
5.8113
5.2487
5.2452
5.2129
5.2097
5.2060
5.2022
5.1867
5.1836
4.6907
4.6872
4.6837
4.6769
4.6733
4.6701
4.6669
4.6634
4.6562
4.6527
4.6493
COOH
O
O
O
5g
5.28
5.25
5.22
5.19
f1 (ppm)
1.0114
1.0322
2.0454
1.1659
2.9118
1.0147
1.0261
1.0324
1.0151
1.9914
2.0741
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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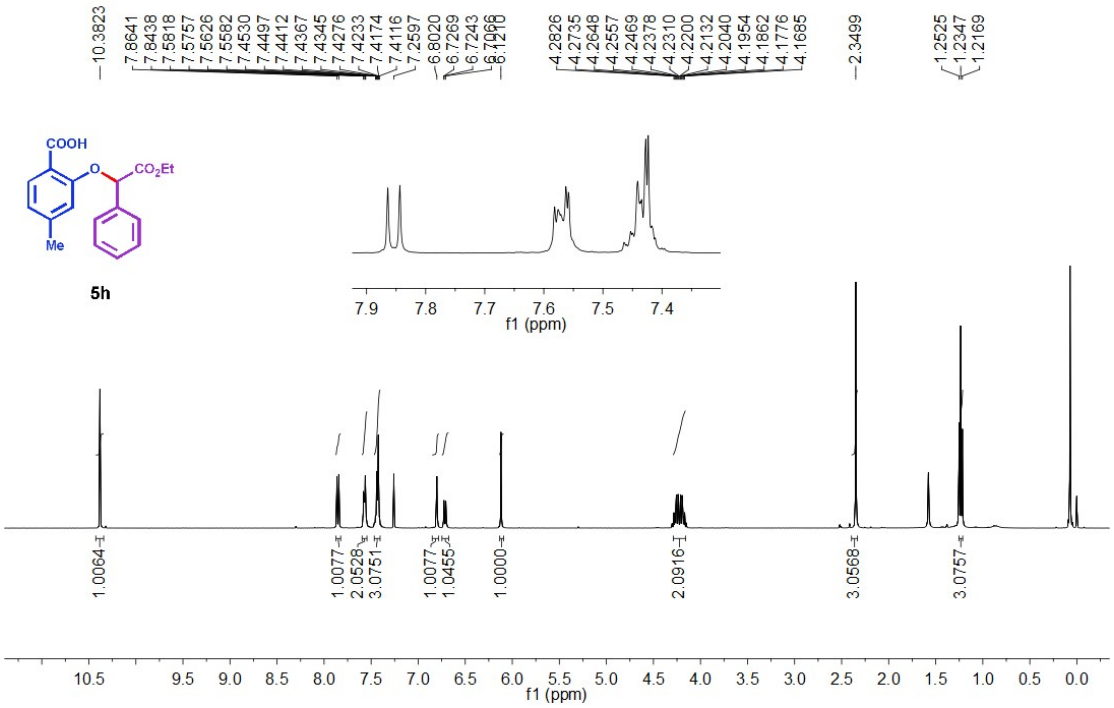
117.807
111.865
77.477
77.160
76.842
75.184
66.372
COOH
O
O
O
5g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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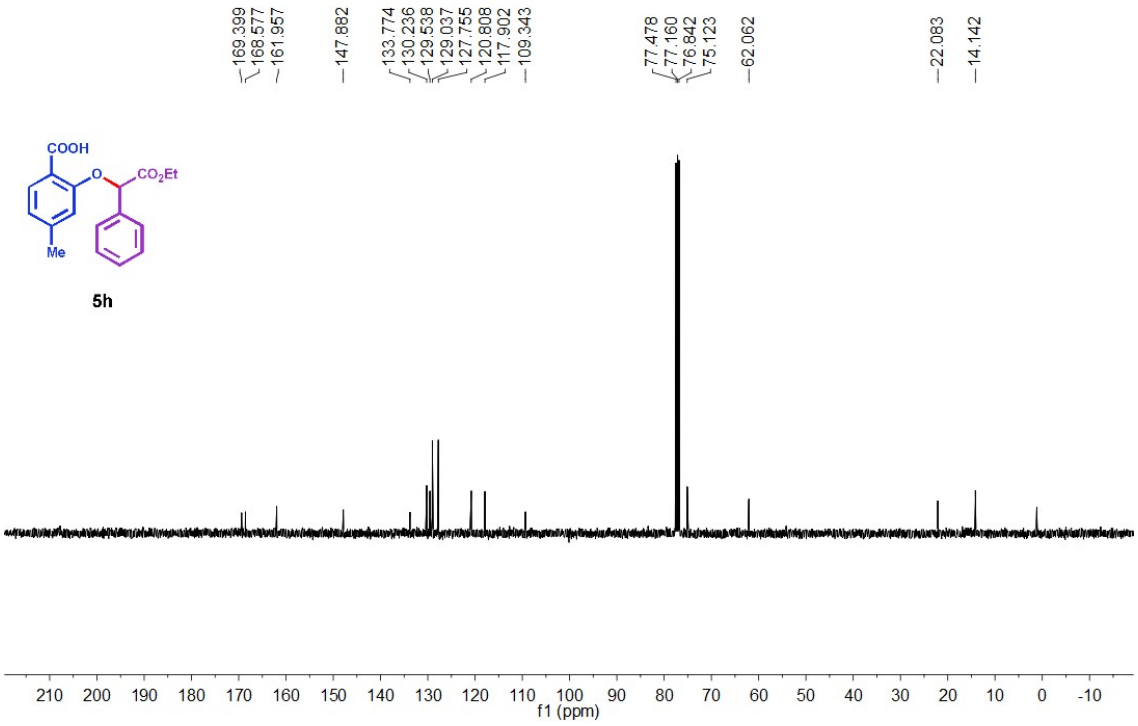
7.4412
7.4367
7.4345
7.4276
7.4233
7.4174
7.4116
7.2597
6.8020
6.7269
6.7243
6.7066
4.2826
4.2735
4.2648
4.2557
4.2469
4.2378
4.2310
4.2200
4.2132
4.2040
4.1954
4.1862
4.1776
4.1685
2.3499
1.2525
1.2347
1.2169
COOH
O
CO2Et
Me
5h
7.9 7.8 7.7 7.6 7.5 7.4
f1 (ppm)
1.0064
1.0077
2.0528
3.0751
1.0077
1.0455
1.0000
2.0916
3.0568
3.0757
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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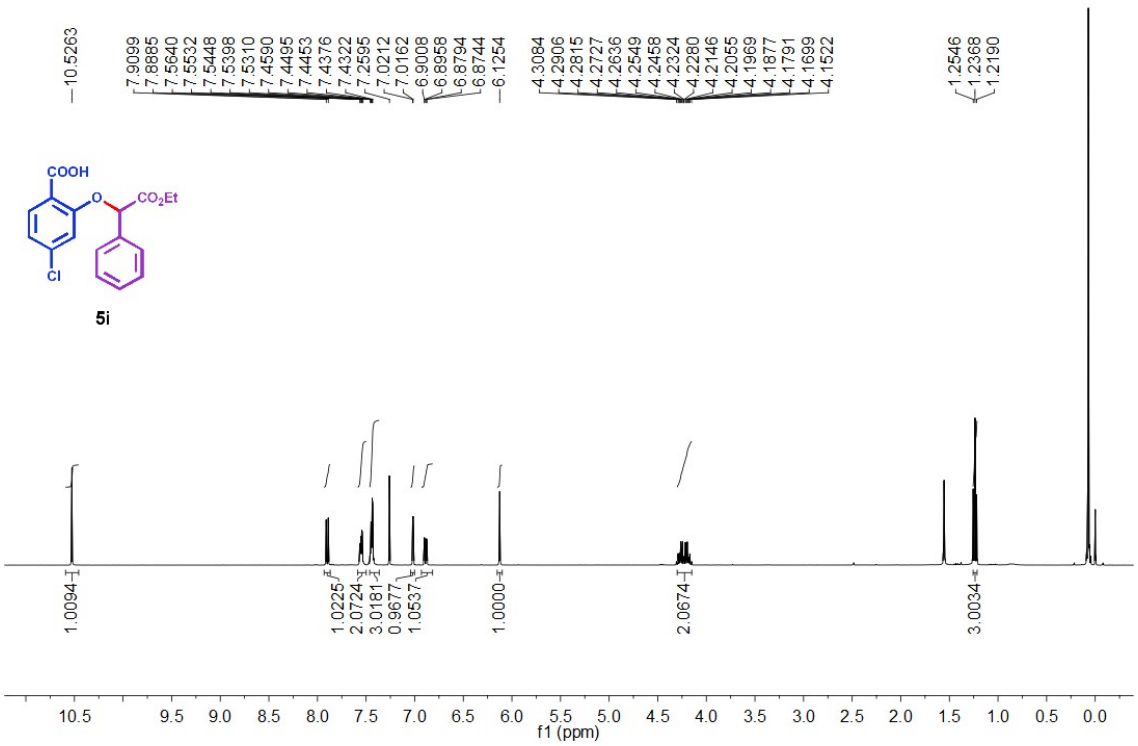
77.478
77.160
76.842
75.123
62.062
22.083
14.142
COOH
O
CO2Et
Me
5h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.5310
7.4590
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7.4453
7.4376
7.4322
7.2595
7.0212
7.0162
6.9008
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6.8794
6.8744
6.1254
4.3084
4.2906
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4.2727
4.2636
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4.2458
4.2324
4.2280
4.2146
4.2055
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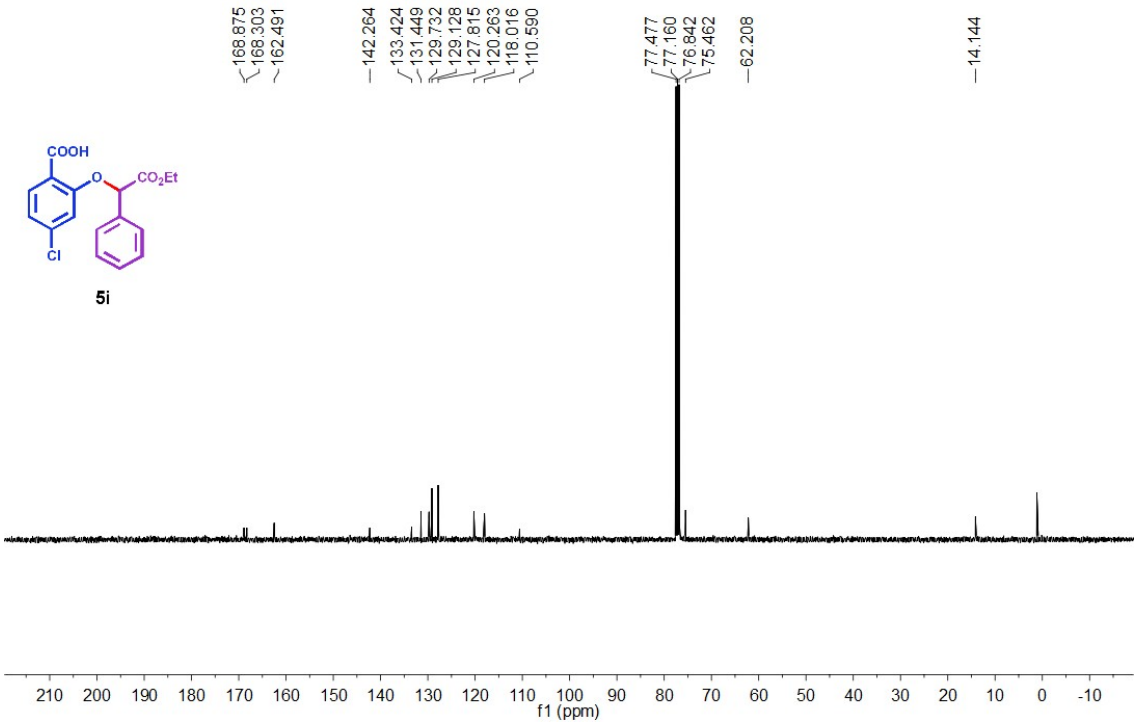
4.1877
4.1791
4.1699
4.1522
1.2546
1.2368
1.2190
COOH
O
CO2Et
Cl
5i
1.0094
1.0225
2.0724
3.0181
0.9677
1.0537
1.0000
2.0674
3.0034
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.875
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133.424
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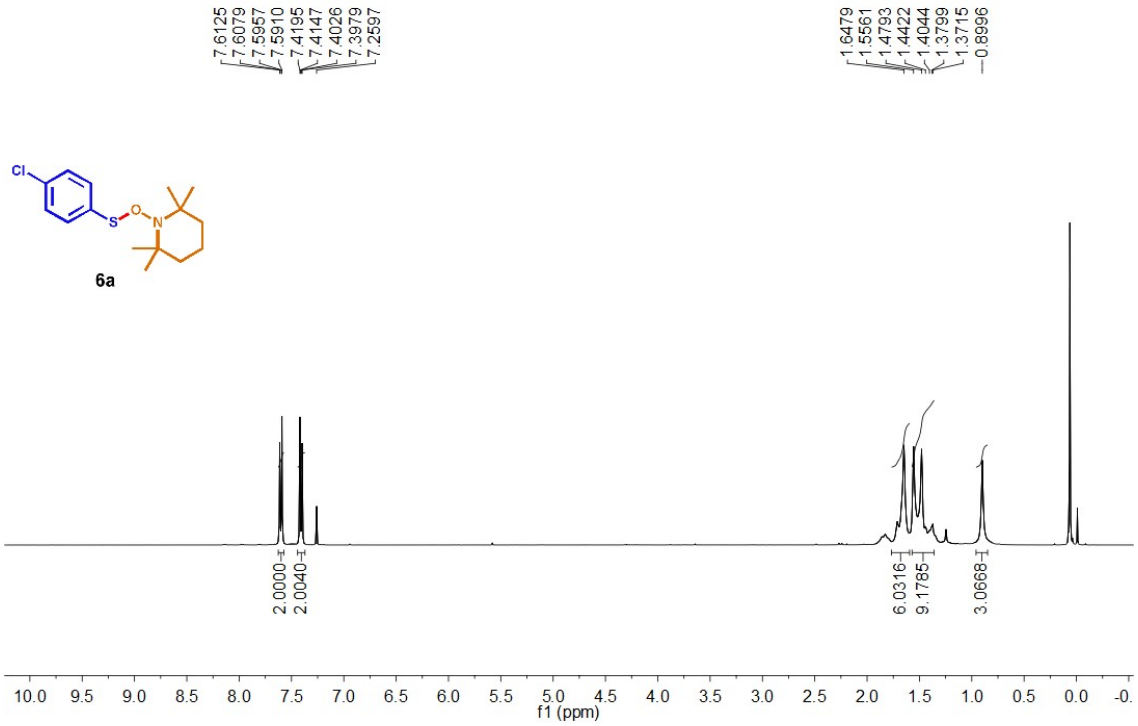
129.732
129.128
127.815
120.263
118.016
110.590
77.477
77.160
76.842
75.462
62.208
14.144
COOH
O
CO2Et
Cl
5i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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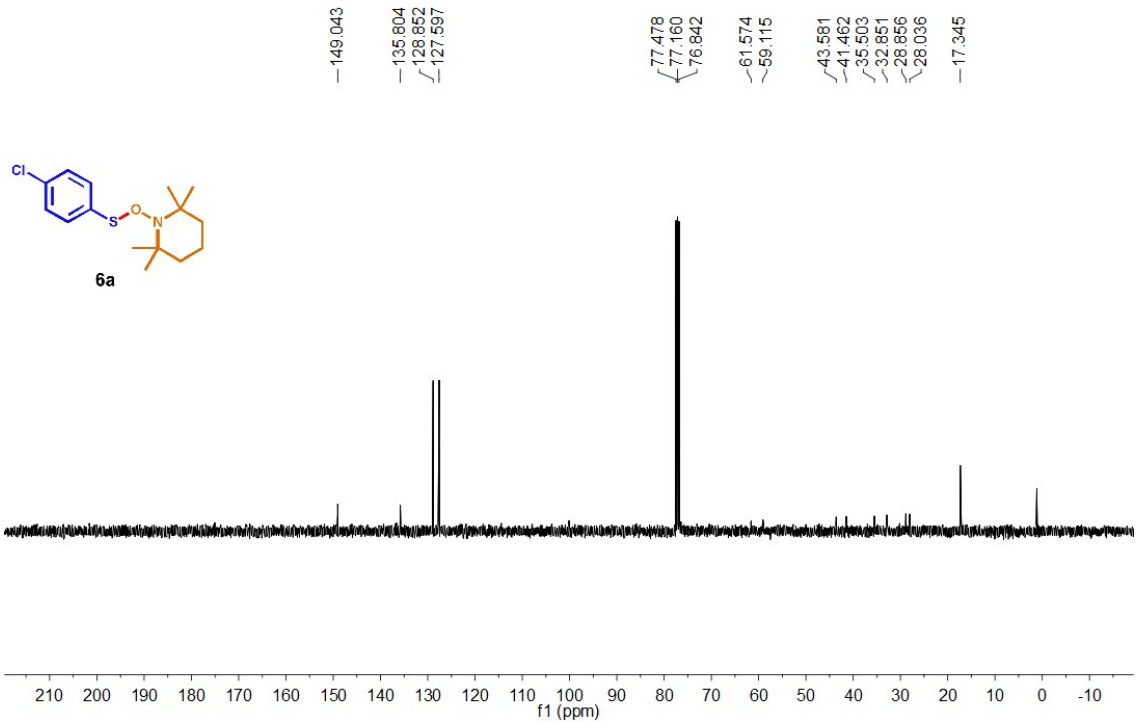
7.5957
7.5910
7.4195
7.4147
7.4026
7.3979
7.2597
1.6479
1.5561
1.4793
1.4422
1.4044
1.3799
1.3715
0.8996
Cl
S
O
N
6a
2.0000
2.0040
6.0316
9.1785
3.0668
f1 (ppm)


149.043
135.804
128.852
127.597
77.478
77.160
76.842
61.574
59.115
43.581
41.462
35.503
32.851
28.856
28.036
17.345
Cl
S
O
N
6a
f1 (ppm)