

Supporting Information

Sodium trifluoromethanesulfinate-mediated photocatalytic aerobic oxidative esterification of aromatic aldehydes and alcohols

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Table of Contents

1. General information	P2
2. Investigations of the reaction conditions	P3
3. General Experimental procedures	P7
4. Investigations on the reaction mechanism	P8
5. Characterization data of the products	P14
6. References	P28
7. NMR spectra of products 3a-3al	P30

1. General information

A. Materials and general procedures

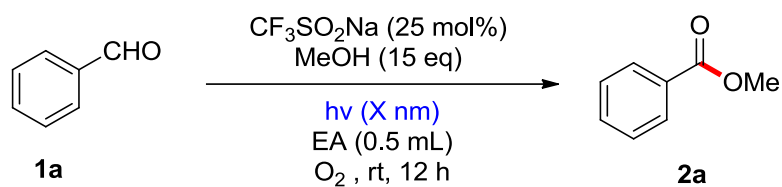
All reagents and solvents were purchased from commercial suppliers Adamas, Bide, TCI, J&K Chemical, Energy Chemical and Meryer, and they were directly used without further purification. $\text{CF}_3\text{SO}_2\text{Na}$ (purity $\geq 99\%$) was purchased from Shandong xiya reagents, PhSO_2Na (purity $\geq 99\%$) and EtSO_2Na (purity $\geq 99\%$) were purchased from Bide. All reactions were conducted in oven-dried reaction vessel under O_2 atmosphere (purity $\geq 99.99\%$) unless otherwise mentioned.

B. Analytical methods

Gas chromatographic-mass spectrometric (GC-MS) analysis was acquired on a JEOL JMS-Q1050GC system equipped with a flame-ionization detector. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL ECS-400 or JNM-ECA 600 spectrometers. Chemical shifts were reported in parts per million (ppm), ^1H NMR chemical shifts were internally referenced to tetramethylsilane (TMS) (^1H NMR: TMS references at 0.00 ppm) and residual proton signals of solvents (^1H NMR: CDCl_3 at 7.26 ppm, and $\text{DMSO}-d_6$ at 2.50 ppm), and ^{13}C NMR chemical shifts were internally referenced to carbon signals of solvents (^{13}C NMR: CDCl_3 at 77.16 ppm, $\text{DMSO}-d_6$ at 39.52 ppm). Coupling constants (J) were reported in Hz with the following splitting abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, and br = broad. High resolution mass spectroscopic data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Chromatographic purification of products was accomplished by column chromatography on silica gel (Qingdao Haiyang, 200-300 mesh).

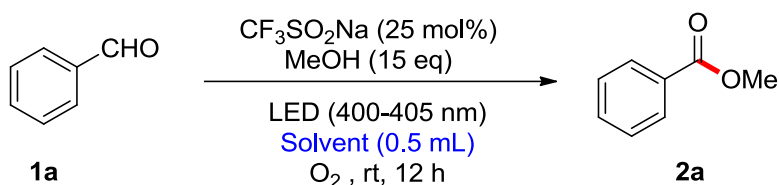
2. Investigations of the reaction conditions

Table S1 Different light sources for the esterification reaction^a



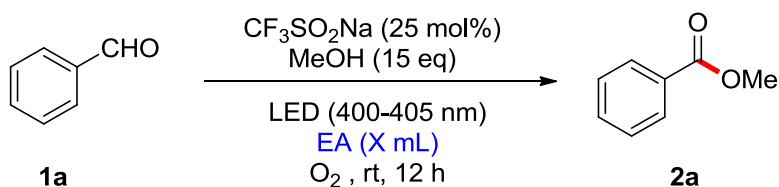
Entry	Light source (X nm)	Yield (%) ^b
1	400	84
2	dark	nr
3	360	46
4	380	73
5	420	np
6	450	np
7	White light	trace

^aReaction conditions: **1a** (0.2 mmol), $\text{CF}_3\text{SO}_2\text{Na}$ (25 mol%), MeOH (15 eq), ethyl acetate (EA) (0.5 mL) under O_2 atmosphere and 3 W light irradiation at room temperature for 12 h. The yields were determined by ^1H NMR using *p*-nitrotoluene as the internal standard

Table S2 Different solvents for the esterification reaction^a

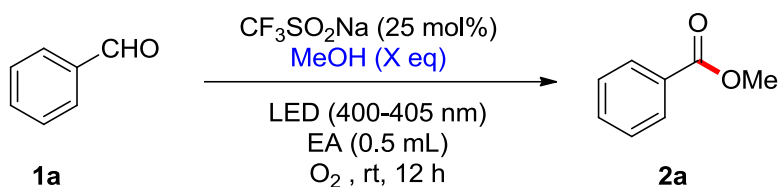
Entry	Solvent	Yield (%) ^b
1	EA	84
2	MeCN	59
3	CH_2Cl_2	74
4	THF	76
5	DCE	73
6	Acetone	np
7	Dioxane	np
8	DMF	nr
9	DMSO	nr

^aReaction conditions: **1a** (0.2 mmol), $\text{CF}_3\text{SO}_2\text{Na}$ (25 mol%), MeOH (15 eq), solvent (0.5 mL) under O_2 atmosphere and 3 W light irradiation at room temperature for 12 h. The yields were determined by ^1H NMR using *p*-nitrotoluene as the internal standard.

Table S3 Different solvent dosages for the esterification reaction^a

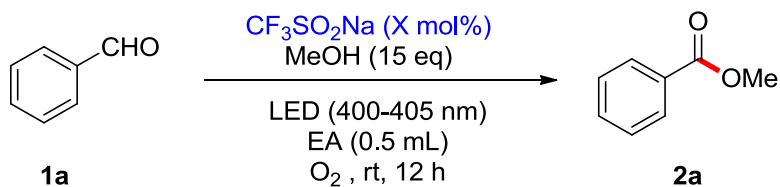
Entry	Solvent dosage (X mL)	Yield (%) ^b
1	0.25	78
2	0.5	84
3	0.75	79
4	1.0	72

^aReaction conditions: **1a** (0.2 mmol), $\text{CF}_3\text{SO}_2\text{Na}$ (25 mol%), MeOH (15 eq), EA (X mL) under O_2 atmosphere and 3 W light irradiation at room temperature for 12 h. The yields were determined by ^1H NMR using *p*-nitrotoluene as the internal standard

Table S4 Different methanol dosages for the esterification reaction^a

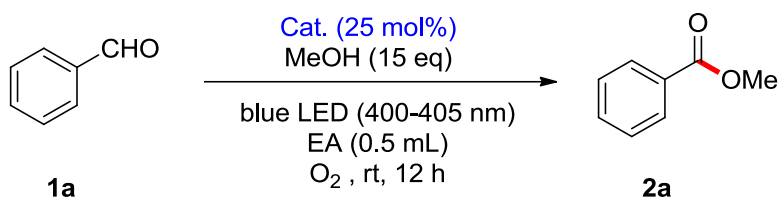
Entry	MeOH dosage (X eq)	Yield (%) ^b
1	9	59
2	12	75
3	15	84
4	18	76
5	21	77
6	24	57

^aReaction conditions: **1a** (0.2 mmol), $\text{CF}_3\text{SO}_2\text{Na}$ (25 mol%), MeOH (X eq), EA (0.5 mL) under O_2 atmosphere and 3 W light irradiation at room temperature for 12 h. The yields were determined by ^1H NMR using *p*-nitrotoluene as the internal standard

Table S5 Different $\text{CF}_3\text{SO}_2\text{Na}$ loadings for the esterification reaction^a

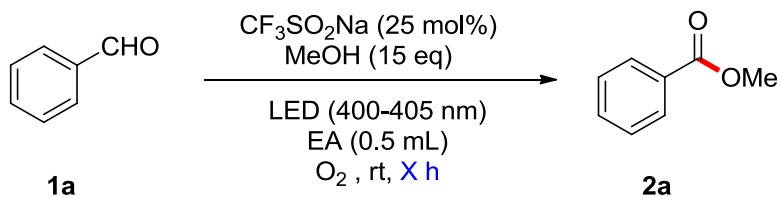
Entry	$\text{CF}_3\text{SO}_2\text{Na}$ loading (X mol %)	Yield (%) ^b
1	5	23
2	10	36
3	25	84
4	50	76
5	75	53
6	100	37

^aReaction conditions: **1a** (0.2 mmol), $\text{CF}_3\text{SO}_2\text{Na}$ (X mol%), MeOH (15 eq), EA (0.5 mL) under O_2 atmosphere and 3 W light irradiation at room temperature for 12 h. The yields were determined by ^1H NMR using *p*-nitrotoluene as the internal standard.

Table S6 Different catalyst for the esterification reaction^a

Entry	Cat. (25 mol %)	Yield (%) ^b
1	MeSO ₂ Na	nr
2	CF ₃ SO ₃ Na	nr
3	PhSO ₂ Na	np
4	EtSO ₂ Na	np
5	CF ₃ SOC1	np

^aReaction conditions: **1a** (0.2 mmol), CF₃SO₂Na (25 mol%), MeOH (15 eq), EA (0.5 mL) under O₂ atmosphere and 3 W light irradiation at room temperature for 12 h. The yields were determined by ¹H NMR using *p*-nitrotoluene as the internal standard.

Table S7 Different reaction time for the esterification reaction^a

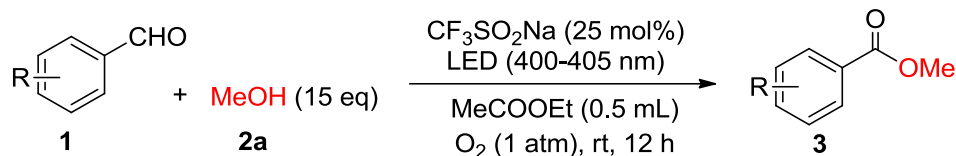
Entry	Reaction time (X h)	Yield (%) ^b
1	4	64
2	8	79
3	12	84
4	24	85

^aReaction conditions: **1a** (0.2 mmol), Cat. (25 mol%), MeOH (15 eq), EA (0.5 mL) under O₂ atmosphere and 3 W light irradiation at room temperature. The yields were determined by ¹H NMR using *p*-nitrotoluene as the internal standard.

3. General experimental procedures

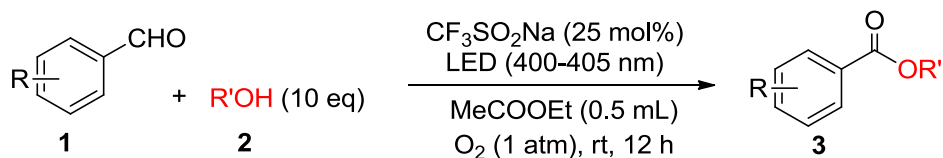
3.1 Experimental procedures

General procedure A



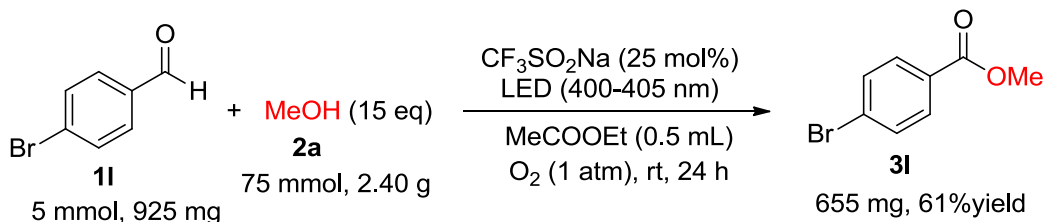
Aromatic aldehyde (0.2 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (25 mol%), MeOH (120 μ L, 15 equiv) and ethyl acetate (0.5 mL) were added to an oven-dried reaction tube equipped with magnetic stirring bar, and the reaction tube was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere (1 atm). After the reaction was completed, solution was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1-1:2) to give the corresponding ester.

General procedure B



Aromatic aldehyde (0.2 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (25 mol%), R'OH (2.0 mmol, 10 equiv) and ethyl acetate (0.5 mL) were added to an oven-dried reaction tube equipped with magnetic stirring bar, and the reaction tube was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere (1 atm). After the reaction was completed, solution was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give the corresponding ester.

3.2 Scale-up reaction for the oxidative esterification



4-Bromobenzaldehyde (5.0 mmol, 925 mg, 1.0 equiv), sodium trifluoromethanesulfinate

(25 mol%, 195 mg), MeOH (75 mmol, 2.4 g, 15 equiv) and ethyl acetate (12.5 mL) were added to an oven-dried reaction vessel (50 mL) equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 24 h under O₂ atmosphere (1 atm). After the reaction was completed, the resulting solution was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give product **3I** in 61% yield.

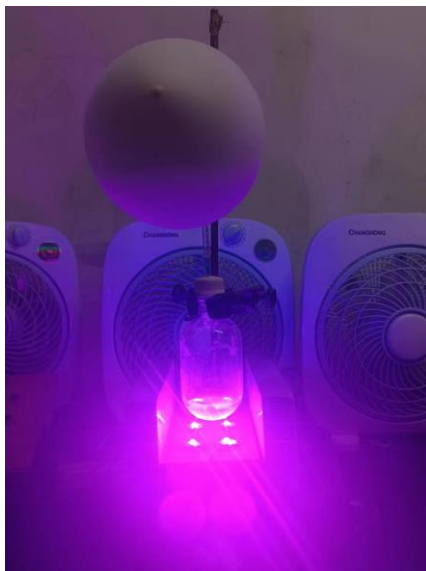


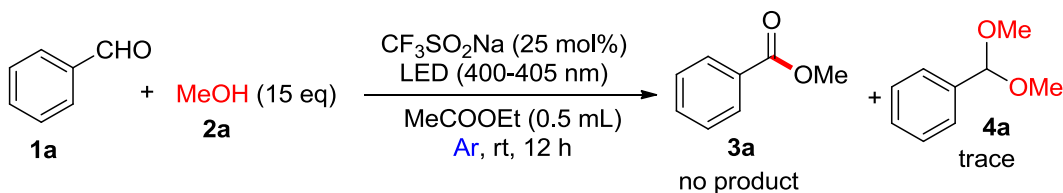
Figure S1 Scale-up reaction for the esterification of 4-bromobenzaldehyde and MeOH

4. Investigations on the reaction mechanism

4.1 Control experiments

In order to explore the possible mechanism of the present transformation, some control experiments were conducted as follows.

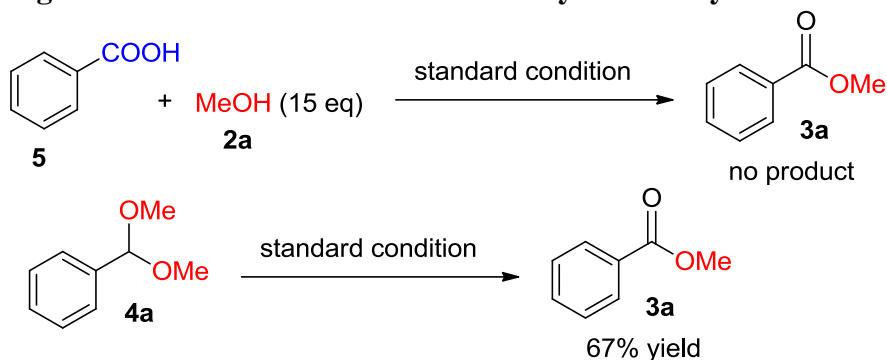
4.1.1 Investigation of atmosphere



Benzaldehyde (**1a**, 0.2 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (25 mol%), MeOH (3.0 mmol, 15 equiv) and ethyl acetate (0.5 mL) were added to an oven-dried reaction tube equipped with magnetic stirring bar, and the reaction tube was irradiated

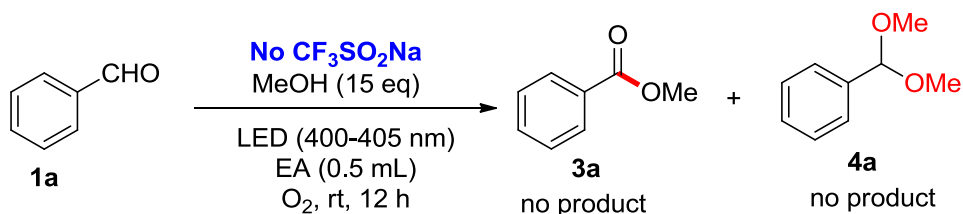
with 3 W LED (400-405 nm) for 12 h under Ar atmosphere. GCMS showed that only trace amount of (dimethoxymethyl)benzene (**4a**) was found without **3a** appearing.

4.1.2 Investigations on benzoic acid and benzaldehyde dimethyl acetal instead of **1a**



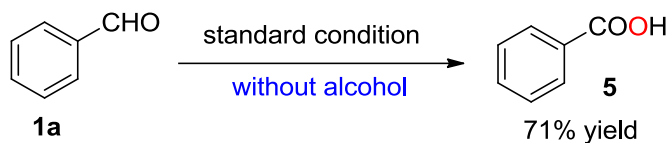
Benzoic acid (**5**, 0.2 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (25 mol%), MeOH (3.0 mmol, 15 equiv) and ethyl acetate (0.5 mL) were added to an oven-dried reaction tube equipped with magnetic stirring bar, and the reaction tube was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere. GCMS showed that no **3a** was found. When benzaldehyde dimethyl acetal (**4a**) was used as the reactant, 60% yield of **3a** was obtained, which showed that benzaldehyde dimethyl acetal (**4a**) maybe an intermediate in the reaction.

4.1.3 Control experiment of precatalyst CF₃SO₂Na



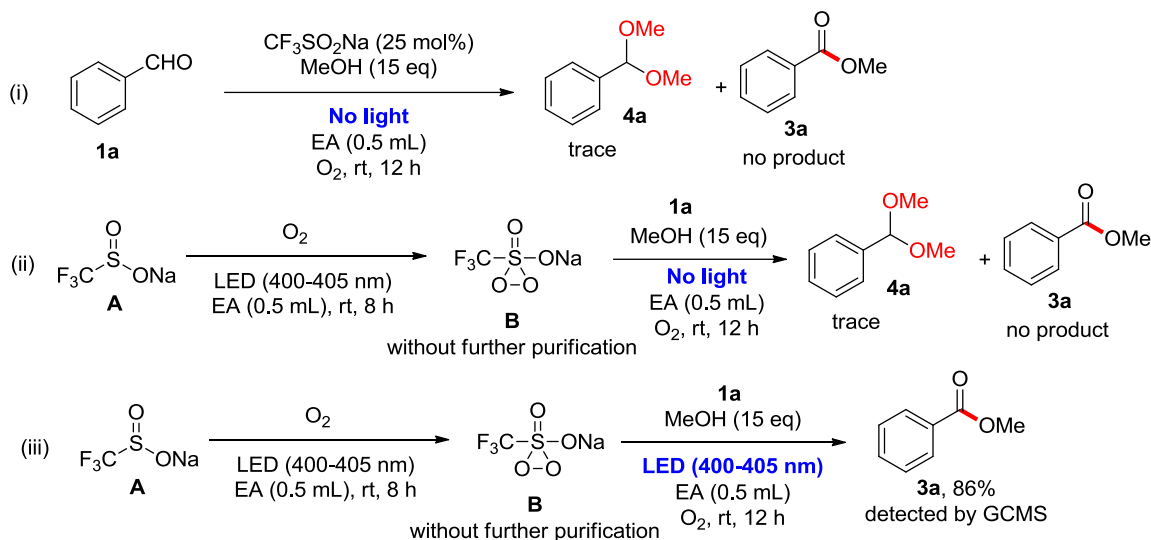
Benzaldehyde (**1a**, 0.2 mmol, 1.0 equiv), MeOH (3.0 mmol, 15 equiv) and ethyl acetate (0.5 mL) were added to an oven-dried reaction tube equipped with magnetic stirring bar, and the reaction tube was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere. GCMS showed that no **3a** and **4a** were found. The result indicated that precatalyst CF₃SO₂Na was indispensable in this transformation. The UV-vis absorption spectrum of CF₃SO₂Na and CF₃SO₄Na was recorded in our previous work.¹

4.1.4 Control experiment in the absence of alcohol



Benzaldehyde (**1a**, 0.2 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (25 mol%) and ethyl acetate (0.5 mL) were added to an oven-dried reaction tube equipped with magnetic stirring bar, and the reaction tube was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere. GCMS showed that benzoic acid (**5**) was obtained in 71% yield.

4.1.5 Other control experiments

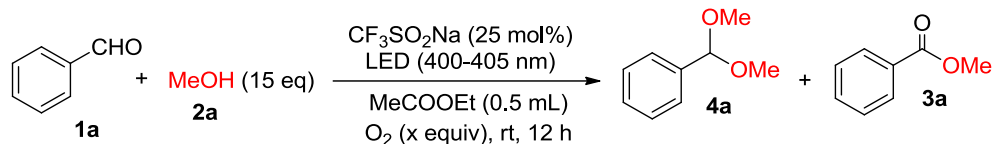


(i) Benzaldehyde (**1a**, 0.2 mmol, 1.0 equiv), MeOH (3.0 mmol, 15 equiv) sodium trifluoromethanesulfinate (25 mol%) and ethyl acetate (0.5 mL) were added to an oven-dried reaction tube equipped with magnetic stirring bar, and the reaction tube was stirred without light for 12 h under O₂ atmosphere. GCMS showed that only trace amount of **4a** was detected.

(ii) Sodium trifluoromethanesulfinate (0.05 mmol) and ethyl acetate (0.5 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 8 h under O₂ atmosphere. After the reaction was completed, the resulting solution was detected by ¹⁹F NMR spectrometer. The result showed that the CF₃SO₂Na (**A**) converted into pentacoordinate sulfide **B**. When benzaldehyde (**1a**, 0.2 mmol) was added to the above resulting solution, and the

solution was treated without light for another 12 h under O₂ atmosphere, GCMS showed that only trace amount of **4a** was detected. (iii) When the reaction system was irradiated with 3 W LED (400-405 nm) for another 12 h under O₂ atmosphere, 86% yield of **3a** was found. The result indicates light is essential for formation of **3a**.

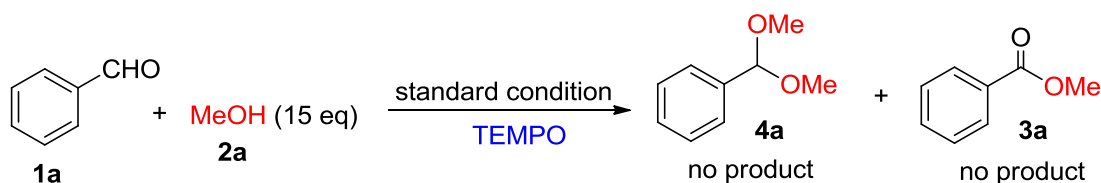
4.2 Investigation of oxygen dosage



O ₂ (equiv)	1	2	4	10	20	30	40
Yield of 4a	9%	23%	37%	40%	23%	10%	0
Yield of 3a	0%	0%	0%	0%	20%	41%	65%

Benzaldehyde (**1a**) (0.2 mmol, 1.0 equiv), MeOH (**2a**) (3.0 mmol, 15 equiv), sodium trifluoromethanesulfinate (25 mol%) and ethyl acetate (0.5 mL) were added to an oven-dried reaction tube equipped with magnetic stirring bar, and the reaction tube was irradiated with 3 W LED (400-405 nm) for 12 h with different O₂ dosage. Acetal (**4a**) gradually reduced and ester (**3a**) gradually increased with further increase of O₂ dosage. Note: Inject oxygen into the tube with a syringe after vacuumizing a reaction tube (Calculation method of the oxygen dosage: At first calculated the molar amount of oxygen, and then calculated the mass of oxygen. According to the density of oxygen (about 1.429 mg/mL under one atmosphere), the corresponding volume of oxygen under one atmosphere was calculated under one atmosphere. Finally, oxygen was extracted with a syringe under one atmosphere and injected into the tube.)

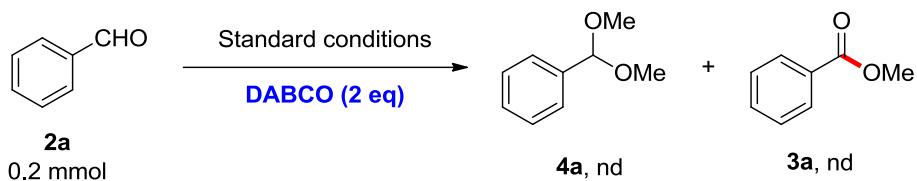
4.3 Radical quenching experiment



Benzaldehyde (**1a**, 0.2 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (25 mol%), MeOH (3.0 mmol, 15 equiv), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 3.0 equiv) and ethyl acetate (0.5 mL) were added to an oven-dried reaction vessel equipped with

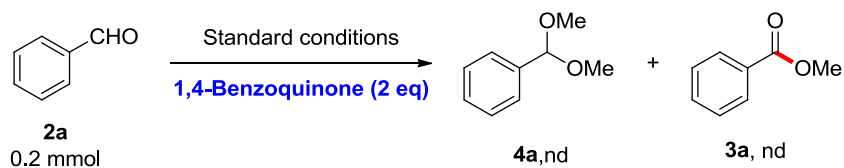
magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere. No desired product **3a** or intermediate **4a** was detected by TLC and GC-MS, indicating that the reaction was completely inhibited, and a radical progress was involved in this transformation.

4.4 Singlet oxygen inhibition experiment



Benzaldehyde (**1a**, 0.2 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (25 mol%), MeOH (120 μ L, 15 equiv), triethylenediamine (DABCO) (2.0 equiv) and ethyl acetate (0.5 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere. No desired product **3a** or intermediate **4a** was detected by TLC and GC-MS, DABCO as a singlet oxygen quencher successfully suppressed the reaction, indicating the presence of singlet oxygen species in the reaction.

4.5 Superoxide radical anion inhibition experiment



Benzaldehyde (**1a**, 0.2 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (25 mol%), MeOH (3.0 mmol, 15 equiv), 1,4-benzoquinone (2.0 equiv) and ethyl acetate (0.5 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere. No desired product **3a** or intermediate **4a** was detected by TLC and GC-MS, 1,4-benzoquinone as a superoxide radical anion inhibitor successfully suppressed the reaction, indicating the presence of superoxide radical anion species in the reaction.

4.6 The on/off experiments with LED (400-405 nm)

Benzaldehyde (**1a**) (0.2 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (25 mol%), MeOH (**2a**) (3.0 mmol, 15 equiv) and ethyl acetate (0.5 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated

with 3 W LED (400-405 nm) under O₂ atmosphere. The process of photocatalytic reaction with and without light was monitored by GC-MS (Figure S2).

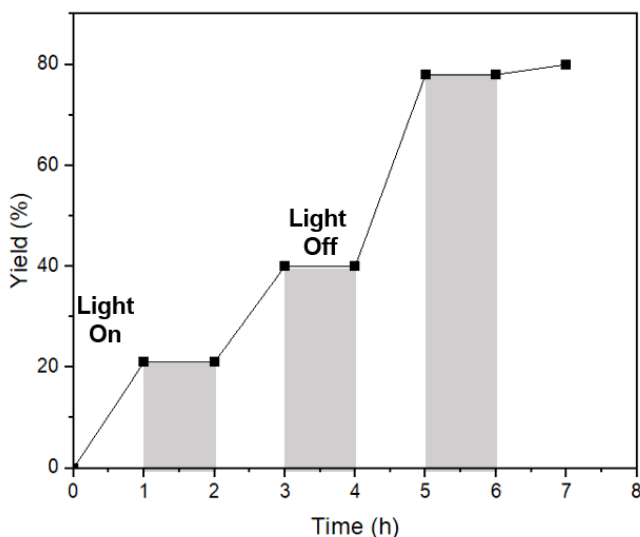
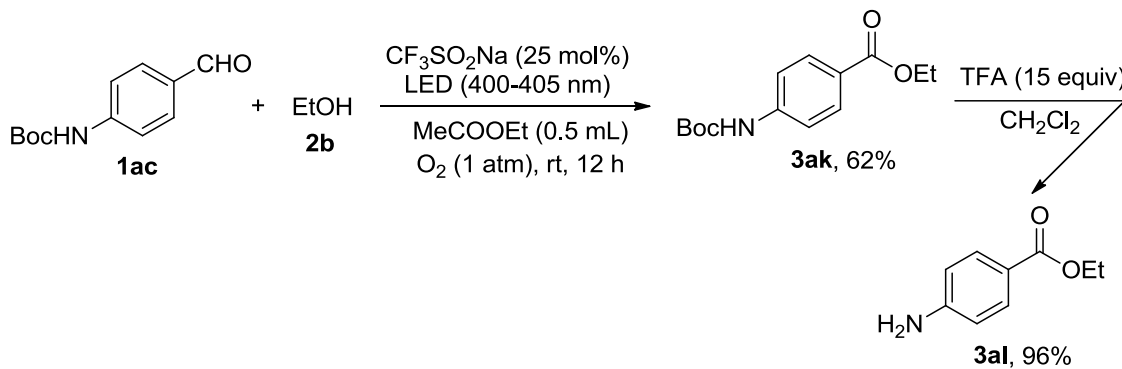


Figure S2 Time profile of the photocatalytic reaction with and without visible light using **1a** and **2a** as the substrates under the standard conditions.

4.7 Synthesis of benzocaine (**3al**)

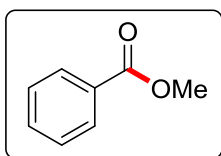


tert-Butyl (4-formylphenyl)carbamate (**1ac**) (0.2 mmol, 44.2 mg, 1.0 equiv), EtOH (3.0 mmol, 10 equiv) and ethyl acetate (0.5 mL) were added to an oven-dried reaction tube equipped with magnetic stirring bar, and the reaction tube was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3ak** as a white solid (32.9 mg, 62%).

Trifluoroacetic acid (141 mg, 2.0 mmol, 10 equiv) was added to a solution of ethyl 4-((*tert*-butoxycarbonyl) amino) benzoate (**3ak**) (0.124 mmol, 32.9 mg, 1.0 equiv) in

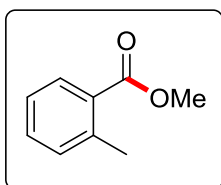
CH₂Cl₂ (0.1M) at 0 °C and stir for 2 h. The excess reagent and solvent were removed under reduced pressure, and the solution was extracted with dichloromethane (2×3 mL) after neutralizing with sat. NaHCO₃ solution. The organic phase was dried over anhydrous Na₂SO₄ and concentrated, and the residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 6:1) to give **3al** (19.6 mg) in 96% yield.

5. Characteriation data of products 3a-3aj



Benzoic acid methyl ester (3a):² Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3a** as a colorless oil (19.9 mg, 73%). ¹H and ¹³C NMR of **3a** is identical with the spectra of the known compound. ¹H NMR (400 MHz, chloroform-*d*) δ 8.05 - 8.02 (m, 2H), 7.56 - 7.49 (m, 1H), 7.45 - 7.39 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H). ¹³C NMR (100 MHz, chloroform-*d*) δ 167.19, 133.01, 130.23, 129.65, 128.45, 52.18.

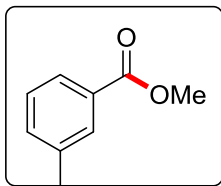
EI-MS of C₈H₈O₂ (**3a**): M⁺ m/z 136.



Methyl 2-methylbenzoate (3b):³ Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3b** as a colorless oil (18.9 mg, 63%). ¹H and ¹³C NMR of **3b** is identical with the spectra of the known compound.

¹H NMR (400 MHz, chloroform-*d*) δ 7.93 – 7.87 (m, 1H), 7.38 (td, J = 7.8, 1.6 Hz, 1H), 7.23 (m, 2H), 3.88 (s, 3H), 2.59 (s, 3H). ¹³C NMR (100 MHz, chloroform-*d*) δ 168.15, 140.28, 132.06, 131.78, 130.66, 129.61, 125.78, 51.88, 21.82.

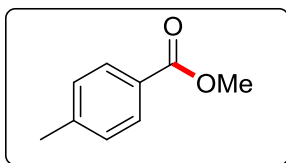
EI-MS of C₉H₁₀O₂ (**3b**): M⁺ m/z 150.



Methyl 3-methylbenzoate (3c):³ Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3c** as a white solid (21.3 mg, 71%). ¹H and ¹³C NMR of **3c** is identical with the spectra of the known compound.

¹H NMR (400 MHz, chloroform-*d*) δ 7.89 – 7.79 (m, 2H), 7.31 (dt, J = 15.0, 7.6 Hz, 2H), 3.89 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, chloroform-*d*) δ 167.21, 138.12, 133.55, 130.39, 130.15, 128.23, 126.75, 51.81, 21.12.

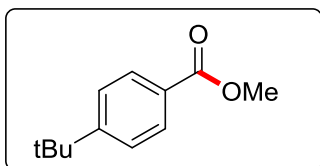
EI-MS of C₉H₁₀O₂ (**3c**): M⁺ m/z 150.0.



Methyl 4-methylbenzoate (3d):² Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3d** as a white solid (19.8 mg, 66%). ¹H and ¹³C NMR of **3d** is identical with the spectra of the known compound.

¹H NMR (400 MHz, chloroform-*d*) δ 7.94 – 7.90 (m, 2H), 7.24 – 7.19 (m, 2H), 3.88 (s, 3H), 2.39 (s, 3H). ¹³C NMR (100 MHz, chloroform-*d*) δ 168.16, 140.29, 132.06, 131.78, 130.66, 129.61, 125.79, 51.89, 21.83.

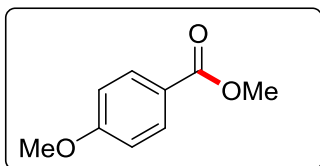
EI-MS of C₉H₁₀O₂ (**3d**): M⁺ m/z 150.0.



Methyl 4-(tert-butyl) benzoate (3e):⁴ Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3e** as a colorless oil (28.8 mg, 75%). ¹H and ¹³C NMR of **3e** is identical with the spectra of the known compound.

^1H NMR (400 MHz, chloroform-*d*) δ 7.96 (dd, $J = 8.5, 4.8$ Hz, 2H), 7.45 (dd, $J = 8.8, 4.7$ Hz, 2H), 3.89 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 167.27, 156.64, 129.53, 127.45, 125.44, 52.06, 35.16, 31.21.

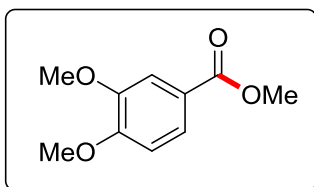
EI-MS of $\text{C}_{12}\text{H}_{16}\text{O}_2$ (**3e**): M^+ m/z 192.



Methyl 4-methoxybenzoate (3f):² Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3f** as a colorless oil (27.9 mg, 84%). ^1H and ^{13}C NMR of **3f** is identical with the spectra of the known compound.

^1H NMR (400 MHz, chloroform-*d*) δ 8.03–7.93 (m, 2H), 6.97 – 6.84 (m, 2H), 3.88 – 3.86 (m, 3H), 3.86–3.83 (m, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 166.97, 163.41, 131.68, 122.67, 113.68, 55.50, 51.97.

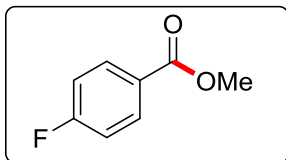
EI-MS of $\text{C}_9\text{H}_{10}\text{O}_3$ (**3f**): M^+ m/z 166.



Methyl 3,4-dimethoxybenzoate (3g):³ Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3g** as a white solid (29.8 mg, 76%). ^1H and ^{13}C NMR of **3g** is identical with the spectra of the known compound.

^1H NMR (400 MHz, chloroform-*d*) δ 7.67 (dt, $J = 8.5, 1.8$ Hz, 1H), 7.53 (t, $J = 1.8$ Hz, 1H), 6.87 (dd, $J = 8.4, 1.4$ Hz, 1H), 3.92 (t, $J = 1.6$ Hz, 6H), 3.88 (d, $J = 1.5$ Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 166.98, 153.01, 148.66, 123.66, 122.75, 111.99, 110.30, 56.09, 52.09.

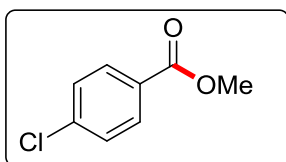
EI-MS of $\text{C}_{10}\text{H}_{12}\text{O}_4$ (**3g**): M^+ m/z 196.



Methyl 4-fluorobenzoate (3h):² Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3h** as a colorless oil (24.4 mg, 79%). ¹H and ¹³C NMR of **3h** is identical with the spectra of the known compound.

¹H NMR (400 MHz, chloroform-*d*) δ 8.04–8.00 (m, 2H), 7.10 – 7.05 (m, 2H), 3.88 (d, J = 2.7 Hz, 3H). ¹³C NMR (100 MHz, chloroform-*d*) δ 167.07, 166.20, 164.55, 132.23, 132.14, 126.47, 126.44, 115.68, 115.46, 52.25. ¹⁹F NMR (400 MHz, chloroform-*d*) δ -105.73.

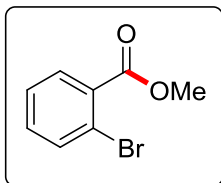
EI-MS of C₈H₇FO₂ (**3h**): M⁺ m/z 154.



Methyl 4-chlorobenzoate (3i):² Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3i** as a white solid (31.7 mg, 93%). ¹H and ¹³C NMR of **3i** is identical with the spectra of the known compound.

¹H NMR (400 MHz, chloroform-*d*) δ 8.08 – 7.83 (m, 2H), 7.48 – 7.29 (m, 2H), 3.89 (s, 3H). ¹³C NMR (100 MHz, chloroform-*d*) δ 166.32, 139.46, 131.07, 128.80, 128.66, 52.37.

EI-MS of C₈H₇ClO₂ (**3i**): M⁺ m/z 170.

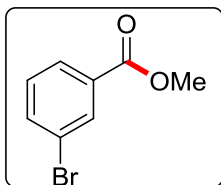


Methyl 2-bromobenzoate (3j):⁵ Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3j** as a white solid (35.7 mg, 83%). ¹H and ¹³C NMR of **3j** is identical with the spectra of the known compound.

¹H NMR (400 MHz, chloroform-*d*) δ 7.78 (td, J = 7.3, 2.2 Hz, 1H), 7.68 – 7.59 (m, 1H),

7.41 – 7.28 (m, 2H), 3.92 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 166.73, 134.44, 132.68, 132.21, 131.40, 127.25, 121.75, 52.58.

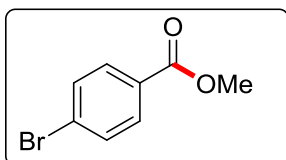
EI-MS of $\text{C}_8\text{H}_7\text{BrO}_2$ (**3j**): M^+ m/z 214, 216.



Methyl 3-bromobenzoate (3k):³ Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3k** as a white solid (34.0 mg, 79%). ^1H and ^{13}C NMR of **3k** is identical with the spectra of the known compound.

^1H NMR (400 MHz, chloroform-*d*) δ 8.19 (d, $J = 31.6$ Hz, 1H), 8.04 – 7.87 (m, 1H), 7.69 (d, $J = 25.9$ Hz, 1H), 7.44 – 7.11 (m, 1H), 4.23–3.56 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.90, 136.00 (d, $J = 6.5$ Hz), 132.73 (d, $J = 6.1$ Hz), 132.16, 130.11, 128.28 (d, $J = 6.7$ Hz), 122.54, 52.58.

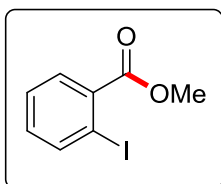
EI-MS of $\text{C}_8\text{H}_7\text{BrO}_2$ (**3k**): M^+ m/z 214, 216.



Methyl 4-bromobenzoate (3l):² Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3l** as a white solid (32.3 mg, 75%). ^1H and ^{13}C NMR of **3l** is identical with the spectra of the known compound.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.76 (m, 1H), 7.69 – 7.61 (m, 1H), 7.39 – 7.26 (m, 1H), 3.92 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.73, 134.44, 132.68, 132.21, 131.40, 127.25, 121.75, 52.58.

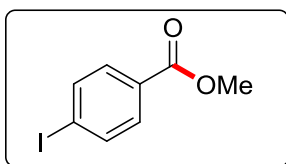
EI-MS of $\text{C}_8\text{H}_7\text{BrO}_2$ (**3l**): M^+ m/z 214, 216.



Methyl 2-iodobenzoate (3m):⁵ Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3m** as a white solid (44.0 mg, 84%). ¹H and ¹³C NMR of **3m** is identical with the spectra of the known compound.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.94 (m, 1H), 7.83 – 7.73 (m, 1H), 7.42 – 7.34 (m, 1H), 7.19 – 7.09 (m, 1H), 3.91 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 167.05, 141.41, 135.14, 132.77, 131.04, 128.00, 94.20, 52.61.

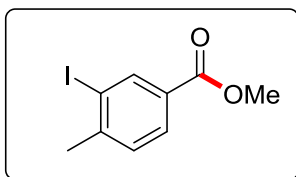
EI-MS of C₈H₇IO₂ (**3m**): M⁺ m/z 262.



Methyl 4-iodobenzoate (3n):⁵ Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3n** as a white solid (45.1 mg, 86%). ¹H and ¹³C NMR of **3n** is identical with the spectra of the known compound.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.76 (m, 2H), 7.73 (t, J = 6.2 Hz, 2H), 3.89 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.70, 137.81, 131.13, 129.69, 100.84, 52.40.

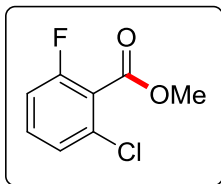
EI-MS of C₈H₇IO₂ (**3n**): M⁺ m/z 262.



Methyl 3-iodo-4-methylbenzoate (3o):⁶ Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3o** as a white solid (34.2 mg, 62%). ¹H and ¹³C NMR of **3o** is identical with the spectra of the known compound.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.65 – 8.27 (m, 1H), 8.12 – 7.66 (m, 1H), 7.28 (dt, J = 13.4, 6.7 Hz, 1H), 4.14 – 3.42 (m, 3H), 2.84 – 1.96 (m, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 165.69, 146.89, 140.11, 129.61, 129.38, 100.58, 52.33, 28.45

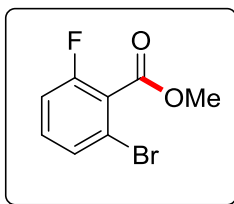
EI-MS of C₉H₉IO₂ (**3o**): M⁺ m/z 276.



Methyl 2-chloro-6-fluorobenzoate (3p):⁷ Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3p** as a white solid (20.4 mg, 54%). ¹H and ¹³C NMR of **3p** is identical with the spectra of the known compound.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.69 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.62 (dd, *J* = 8.2, 6.6 Hz, 1H), 3.92 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 165.30, 160.33, 157.86, 133.74, 131.66, 131.60, 126.21, 126.17, 117.56, 117.32, 114.89, 114.68, 52.38. ¹⁹F NMR (400 MHz, Chloroform-*d*) δ -105.92.

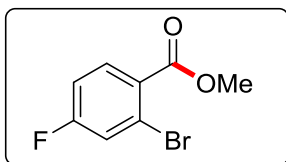
EI-MS of C₈H₆ClFO₂ (**3p**): M⁺ *m/z* 188.



Methyl 2-bromo-6-fluorobenzoate (3q):⁷ Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3q** as a light yellow solid (28.0 mg, 60%). ¹H and ¹³C NMR of **3q** is identical with the spectra of the known compound.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.39 (dd, *J* = 8.3, 2.5 Hz, 1H), 7.06 (ddd, *J* = 8.8, 7.6, 2.6 Hz, 1H), 3.91 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 165.64, 165.20, 162.64, 133.52, 133.43, 128.03, 128.00, 123.27, 123.18, 122.11, 121.86, 114.73, 114.52, 52.62. ¹⁹F NMR (400 MHz, Chloroform-*d*) δ -105.66.

EI-MS of C₈H₆BrFO₂ (**3q**): M⁺ *m/z* 232, 234.

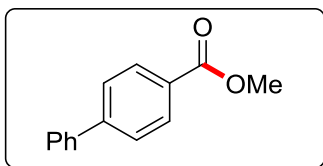


Methyl 2-bromo-4-fluorobenzoate (3r):⁷ Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum

ether/ethyl acetate = 9:1) to give **3r** as a white solid (27.5 mg, 59%). ^1H and ^{13}C NMR of **3r** is identical with the spectra of the known compound.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, $J = 8.9, 6.1$ Hz, 1H), 7.39 (dd, $J = 8.4, 2.5$ Hz, 1H), 7.12 – 7.02 (m, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.64, 165.20, 162.64, 133.52, 133.43, 128.03, 128.00, 123.27, 123.18, 122.11, 121.86, 114.73, 114.52, 52.62. ^{19}F (400 MHz, Chloroform-*d*) δ -105.69.

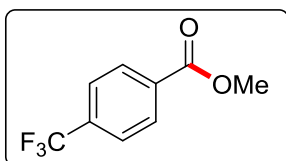
EI-MS of $\text{C}_8\text{H}_6\text{BrFO}_2$ (**3r**): M^+ m/z 232, 234.



Methyl [1,1'-biphenyl]-4-carboxylate (3s):⁸ Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3s** as a white solid (36.5 mg, 86%). ^1H and ^{13}C NMR of **3s** is identical with the spectra of the known compound.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.06 (m, 2H), 7.72 – 7.58 (m, 4H), 7.46 (m, 2H), 7.42 – 7.36 (m, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.12, 145.73, 140.10, 130.21, 129.04, 128.94, 128.25, 127.39, 127.16, 52.25.

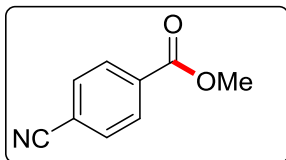
EI-MS of $\text{C}_{14}\text{H}_{12}\text{O}_2$ (**3s**): M^+ m/z 212.



Methyl 4-(trifluoromethyl)benzoate (3t):² Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3t** as a white solid (31.0 mg, 76%). ^1H and ^{13}C NMR of **3t** is identical with the spectra of the known compound.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.24 (m, 2H), 8.21 – 8.17 (m, 2H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.26, 150.64, 135.58, 130.79, 123.62, 52.90. ^{19}F NMR (400 MHz, Chloroform-*d*) δ -62.91.

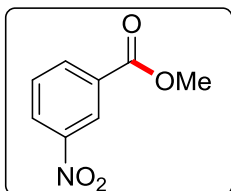
EI-MS of $\text{C}_9\text{H}_7\text{F}_3\text{O}_2$ (**3t**): M^+ m/z 204.



Methyl 4-cyanobenzoate (3u):² Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3u** as a white solid (28.0 mg, 59%). ¹H and ¹³C NMR of **3u** is identical with the spectra of the known compound.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 8.08 (m, 2H), 7.80 – 7.69 (m, 2H), 3.94 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 165.53, 134.01, 132.32, 130.19, 118.07, 116.48, 52.83.

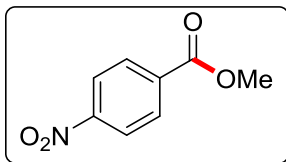
EI-MS of C₉H₇NO₂ (**3u**): M⁺ m/z 161.



Methyl 3-nitrobenzoate (3v):³ Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3v** as a white solid (24.3 mg, 67%). ¹H and ¹³C NMR of **3v** is identical with the spectra of the known compound.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.88 (d, J = 21.5 Hz, 1H), 8.52 – 8.24 (m, 2H), 7.79 – 7.53 (m, 1H), 4.00 (d, J = 22.5 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 165.11, 148.37, 135.41 (d, J = 4.7 Hz), 131.97, 129.78 (d, J = 4.5 Hz), 127.53 (d, J = 4.7 Hz), 124.73 (d, J = 4.8 Hz), 52.93.

EI-MS of C₈H₇NO₂ (**3v**): M⁺ m/z 181.

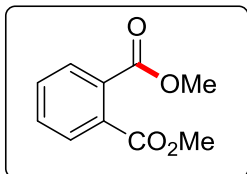


Methyl 4-nitrobenzoate (3w):² Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3w** as a white solid (32.6 mg, 90%). ¹H and ¹³C NMR of **3w** is identical with

the spectra of the known compound.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, $J = 2.0$ Hz, 1H), 8.26 (d, $J = 2.2$ Hz, 1H), 8.20 (d, $J = 2.1$ Hz, 1H), 8.18 (d, $J = 2.0$ Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.26, 150.64, 135.58, 130.79, 123.62, 52.90.

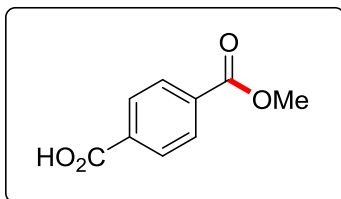
EI-MS of $\text{C}_8\text{H}_7\text{NO}_2$ (**3w**): M^+ m/z 181.



Dimethyl phthalate (3x):⁵ Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3x** as a white solid (33.0 mg, 85%). ^1H and ^{13}C NMR of **3x** is identical with the spectra of the known compound.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.64 (m, 2H), 2H), 3.97 – 3.66 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.11, 132.01, 131.18, 128.94, 52.68.

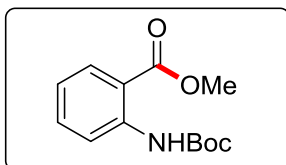
EI-MS of $\text{C}_{10}\text{H}_{10}\text{O}_4$ (**3x**): M^+ m/z 194.



4-(Methoxycarbonyl) benzoic acid (3y):⁹ Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 1:2) to give **3y** as a white solid (26.3 mg, 73%). ^1H and ^{13}C NMR of **3y** is identical with the spectra of the known compound.

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.01 (d, $J = 3.9$ Hz, 4H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 167.09, 166.15, 135.35, 133.68, 130.10, 129.86, 52.96.

EI-MS of $\text{C}_9\text{H}_8\text{O}_4$ (**3y**): M^+ m/z 180.

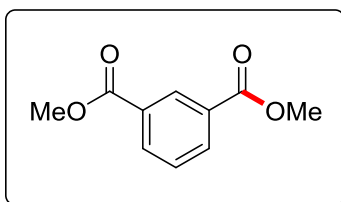


Methyl 4-borinobenzoate (3z):¹⁰ Prepared according to general procedure A. The

reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 1:2) to give **3z** as a white solid (31.7 mg, 63%). ^1H and ^{13}C NMR of **3z** is identical with the spectra of the known compound.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.42 (dd, $J = 8.6, 1.2$ Hz, 1H), 7.96 (dd, $J = 8.1, 1.7$ Hz, 1H), 7.48 (ddd, $J = 8.8, 7.2, 1.7$ Hz, 1H), 6.96 (ddd, $J = 8.2, 7.3, 1.2$ Hz, 1H), 3.88 (s, 3H), 1.51 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.64, 152.95, 142.40, 134.58, 130.93, 121.16, 118.81, 114.32, 80.55, 52.25, 28.38.

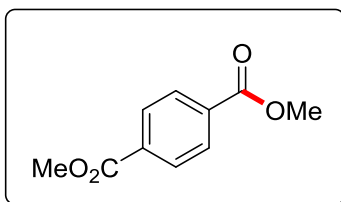
EI-MS of $\text{C}_{13}\text{H}_{17}\text{NO}_4$ (**3z**): M^+ m/z 251.



Methyl 3-nitrobenzoate (3aa):⁵ Prepared according to general procedure A. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3aa** as a white solid (29.9 mg, 77%). ^1H and ^{13}C NMR of **3aa** is identical with the spectra of the known compound.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.66 (q, $J = 2.1$ Hz, 1H), 8.25 – 8.13 (m, 2H), 7.59 – 7.44 (m, 1H), 3.92 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.32, 133.89, 130.79, 130.65, 128.72, 52.45.

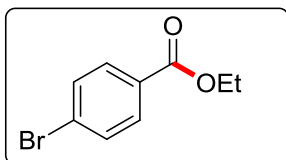
EI-MS of $\text{C}_{10}\text{H}_{10}\text{O}_4$ (**3aa**): M^+ m/z 194.



Dimethyl terephthalate (3ab):³ Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3ab** as a white solid (24.3 mg, 67%). ^1H and ^{13}C NMR of **3ab** is identical with the spectra of the known compound.

^1H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 4H), 3.93 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.38, 133.98, 129.64, 52.54.

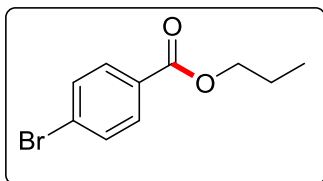
EI-MS of $\text{C}_{10}\text{H}_{10}\text{O}_4$ (**3ab**): M^+ m/z 194.



Ethyl 4-bromobenzoate (3ac):⁴ Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3ac** as a Colorless oil (33.9 mg, 74%). ¹H and ¹³C NMR of **3ac** is identical with the spectra of the known compound.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.72 (m, 2H), 7.73 – 7.44 (m, 2H), 4.36 (q, *J* = 6.7 Hz, 2H), 1.38 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 165.99, 131.74, 131.18, 129.47, 127.99, 61.33, 14.38.

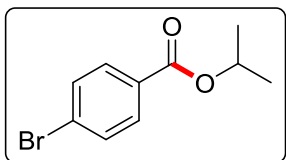
EI-MS of C₉H₉BrO₂ (**3ac**): M⁺ *m/z* 228, 230.



Propyl 4-bromobenzoate (3ad):⁴ Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3ad** as a Colorless oil (19.9 mg, 41%). ¹H and ¹³C NMR of **3ad** is identical with the spectra of the known compound.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 4.26 (t, *J* = 6.7 Hz, 2H), 1.77 (h, *J* = 7.1 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.04, 131.75, 131.18, 129.48, 127.99, 66.89, 22.14, 10.59.

EI-MS of C₁₀H₁₁BrO₂ (**3ad**): M⁺ *m/z* 242, 244.

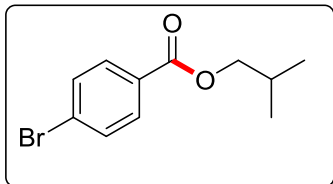


Isopropyl 4-bromobenzoate (3ae):⁴ Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3ae** as a Colorless oil (30.6 mg, 63%). ¹H and ¹³C NMR of **3ae** is identical with the spectra of the known compound.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.34 – 7.68 (m, 2H), 7.65 – 7.45 (m, 2H), 5.31 –

5.15 (m, 1H), 1.35 (dd, $J = 6.4, 1.0$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform- d) δ 165.47, 131.68, 131.17, 129.88, 127.85, 68.85, 22.00.

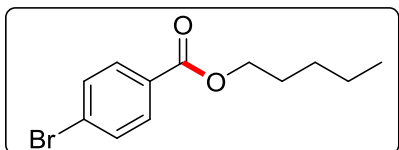
EI-MS of $\text{C}_{10}\text{H}_{11}\text{BrO}_2$ (**3ae**): M^+ m/z 242, 244.



Isobutyl 4-bromobenzoate (3af):⁴ Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3af** as a white solid (33.4 mg, 65%). ^1H and ^{13}C NMR of **3af** is identical with the spectra of the known compound.

^1H NMR (400 MHz, Chloroform- d) δ 7.90 (d, $J = 8.5$ Hz, 2H), 7.57 (d, $J = 8.3$ Hz, 2H), 4.09 (d, $J = 6.5$ Hz, 2H), 2.07 (dt, $J = 13.3, 6.6$ Hz, 1H), 1.01 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, Chloroform- d) δ 166.00, 131.77, 131.17, 129.49, 128.01, 71.34, 27.95, 19.26

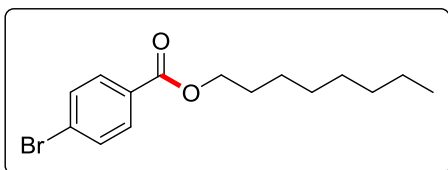
EI-MS of $\text{C}_{11}\text{H}_{13}\text{BrO}_2$ (**3af**): M^+ m/z 256, 258



Pentyl 4-bromobenzoate (3ag):¹¹ Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3ag** as a colorless oil (32.0 mg, 59%). ^1H and ^{13}C NMR of **3ag** is identical with the spectra of the known compound.

^1H NMR (400 MHz, Chloroform- d) δ 7.92 – 7.85 (m, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 4.31 (t, $J = 6.7$ Hz, 2H), 1.76 (p, $J = 7.0$ Hz, 2H), 1.45 – 1.36 (m, 4H), 0.93 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform- d) δ 165.88, 131.39 (d, $J = 59.7$ Hz), 129.72, 127.85, 65.38, 28.45, 28.21, 22.30, 13.82.

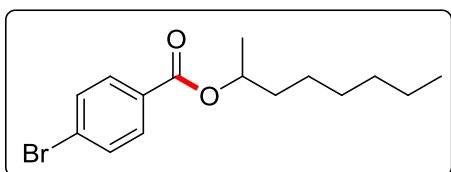
EI-MS of $\text{C}_{12}\text{H}_{15}\text{BrO}_2$ (**3ag**): M^+ m/z 270, 272.



Octyl 4-bromobenzoate (3ah):¹² Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3ah** as a white solid (37.0 mg, 59%). ¹H and ¹³C NMR of **3ah** is identical with the spectra of the known compound.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.85 (m, 2H), 7.58 – 7.52 (m, 2H), 4.30 (t, *J* = 6.7 Hz, 2H), 1.83 – 1.69 (m, 2H), 1.50 – 1.38 (m, 2H), 1.38 – 1.23 (m, 8H), 0.95 – 0.79 (m, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 165.82, 131.68, 131.09, 129.73, 127.83, 65.38, 31.77, 29.22, 29.14, 28.77, 26.04, 22.58, 13.94.

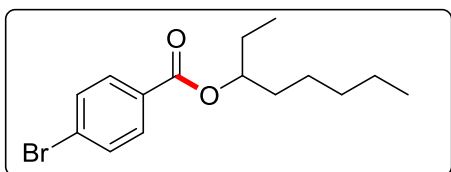
HR-ESIMS: calculated for C₁₅H₂₂BrO₂ [M+H]⁺ *m/z* 313.0798; found 313.0794



Octan-2-yl 4-bromobenzoate (3ai):¹² Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3ai** as a white solid (23.2 mg, 37%). ¹H and ¹³C NMR of **3ai** is identical with the spectra of the known compound.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 5.14 (h, *J* = 6.2 Hz, 1H), 1.81 – 1.52 (m, 2H), 1.40 – 1.22 (m, 11H), 0.87 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 165.40, 131.63, 131.07, 130.13, 127.70, 72.16, 36.10, 31.72, 29.12, 25.36, 22.52, 19.97, 13.90.

HR-ESIMS: calculated for C₁₅H₂₂BrO₂ [M+H]⁺ *m/z* 313.0798; found 313.0797

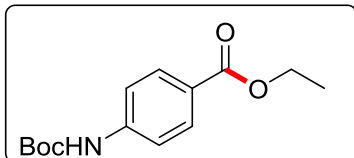


Octan-3-yl 4-bromobenzoate (3aj): Prepared according to general procedure B. The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) to give **3aj** as a white solid (23.2 mg, 37%). ¹H and ¹³C NMR of **3aj** is identical with the spectra of the known compound.

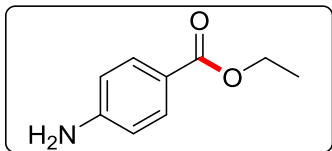
¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 8.7, 3.4 Hz, 2H), 7.54 (dd, *J* = 8.6, 3.2 Hz, 2H), 5.12 (m, 1H), 1.64 (dtt, *J* = 51.1, 9.5, 4.7 Hz, 2H), 1.49 – 1.16 (m, 11H), 0.97 –

0.68 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.51, 131.67, 131.14, 129.92, 127.82, 72.21, 36.09, 31.80, 29.22, 25.47, 22.65, 20.10, 14.13.

HR-ESIMS: calculated for $\text{C}_{15}\text{H}_{22}\text{BrO}_2$ $[\text{M}+\text{H}]^+$ m/z 313.0798; found 313.0793



Ethyl 4-((tert-butoxycarbonyl) amino) benzoate (3ak):¹³ ^1H and ^{13}C NMR of **3ak** is identical with the spectra of the known compound. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, $J = 8.8$ Hz, 2H), 7.42 (d, $J = 8.8$ Hz, 2H), 6.73 (s, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 1.51 (s, 9H), 1.37 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.39, 152.31, 142.72, 130.93, 124.80, 117.40, 81.26, 60.84, 28.36, 14.45.



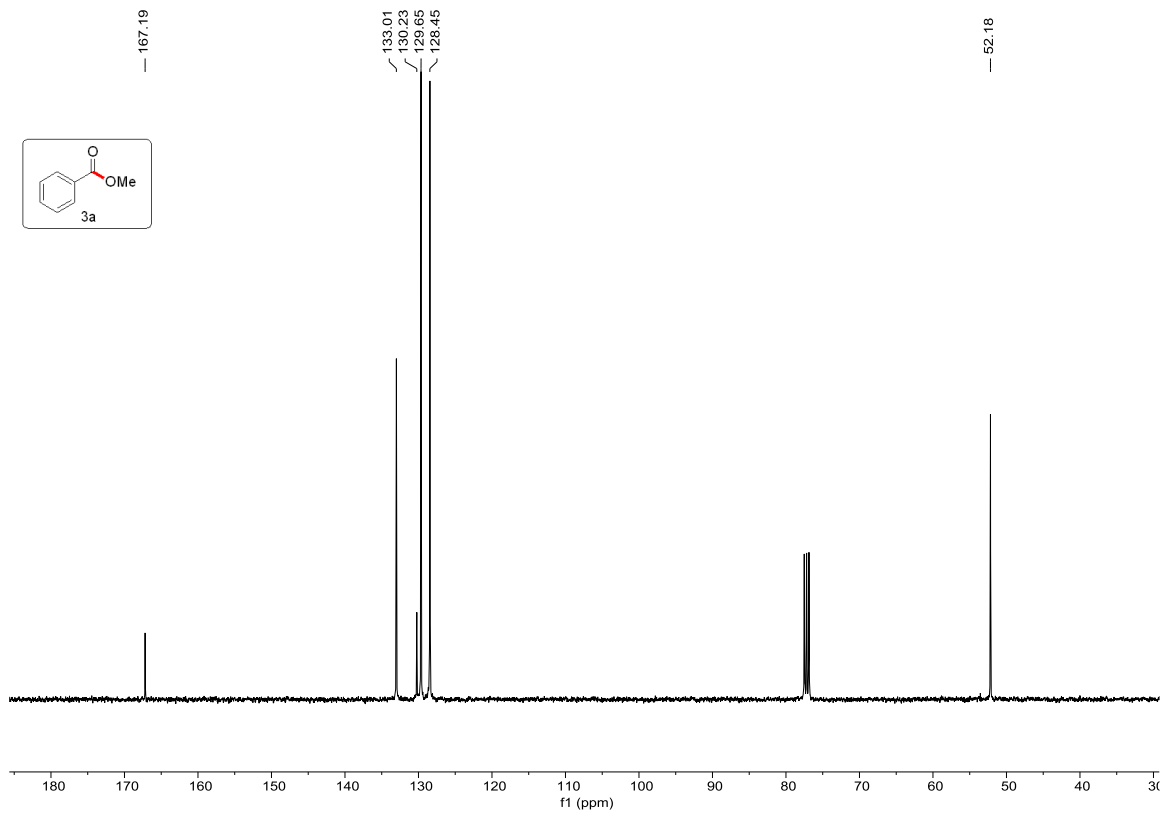
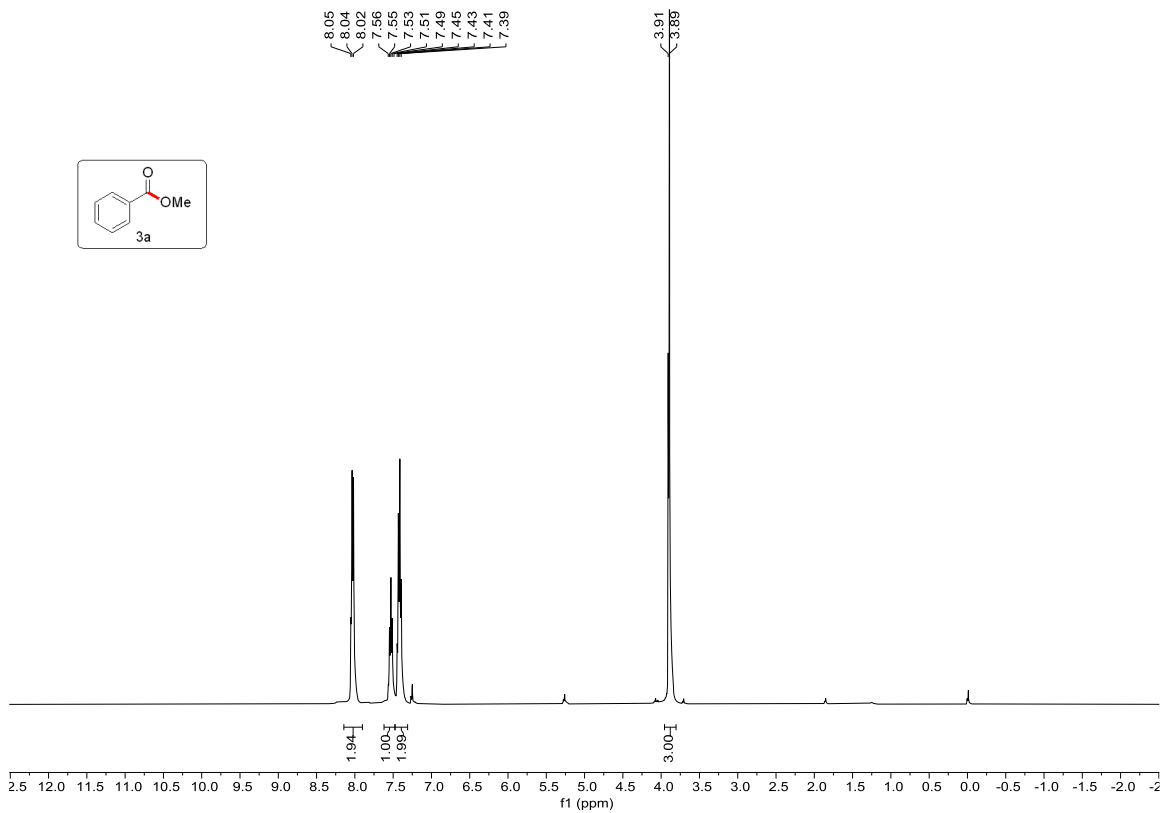
Ethyl 4-aminobenzoate (3al):¹³ ^1H and ^{13}C NMR of **3al** is identical with the spectra of the known compound. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.81 (m, 2H), 6.64 – 6.58 (m, 2H), 4.30 (q, $J = 7.1$ Hz, 2H), 4.07 (s, 2H), 1.34 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.87, 150.97, 131.64, 120.04, 113.85, 60.41, 14.51.

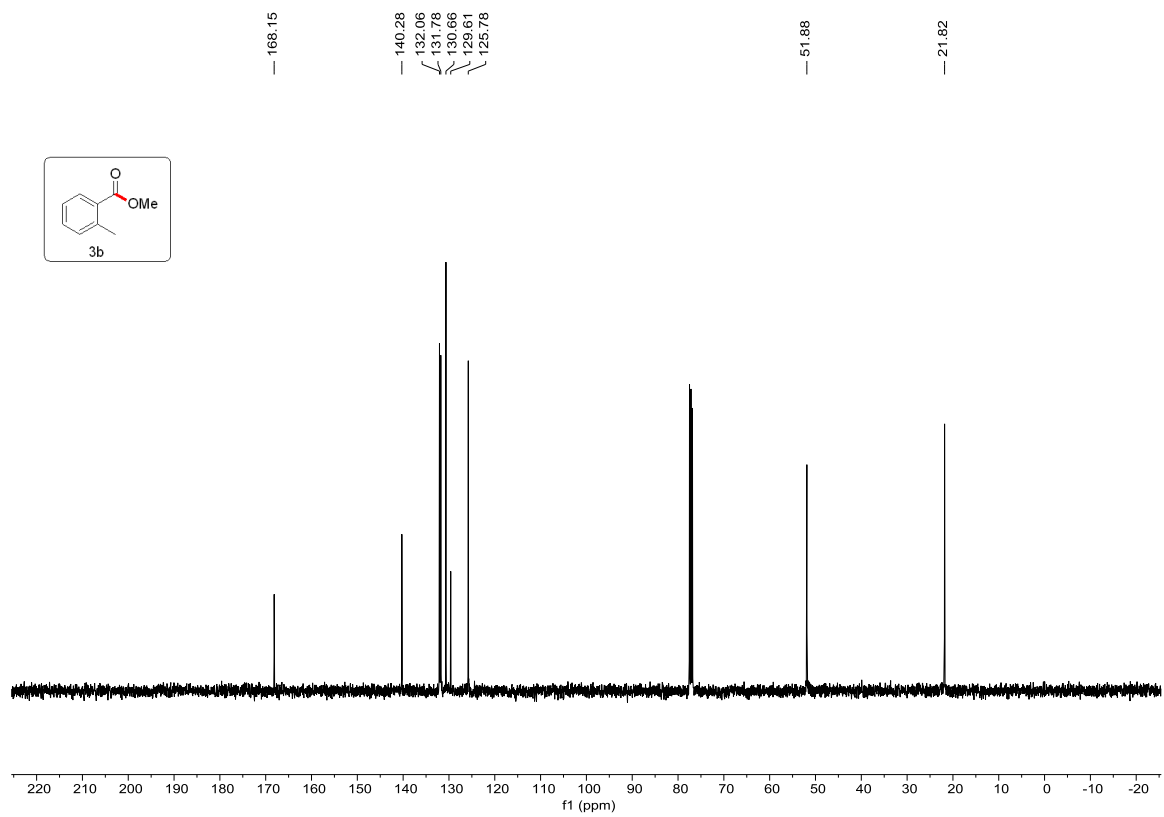
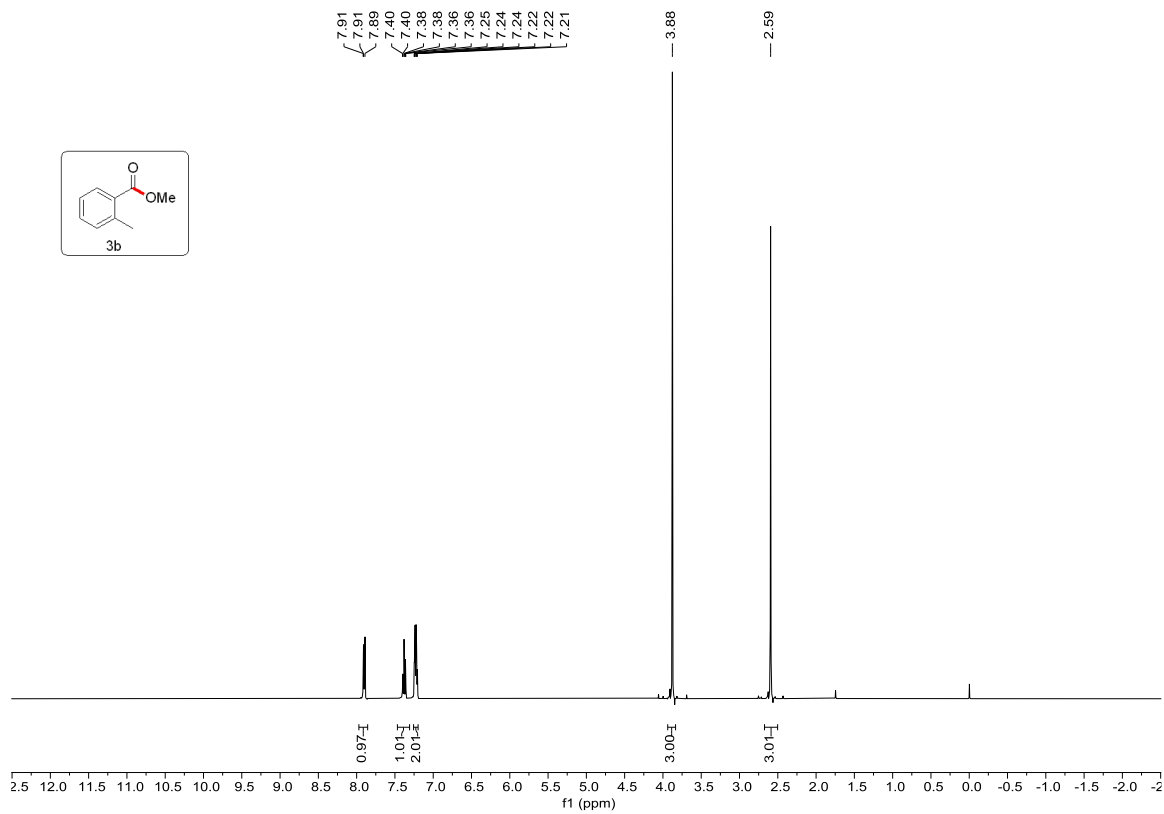
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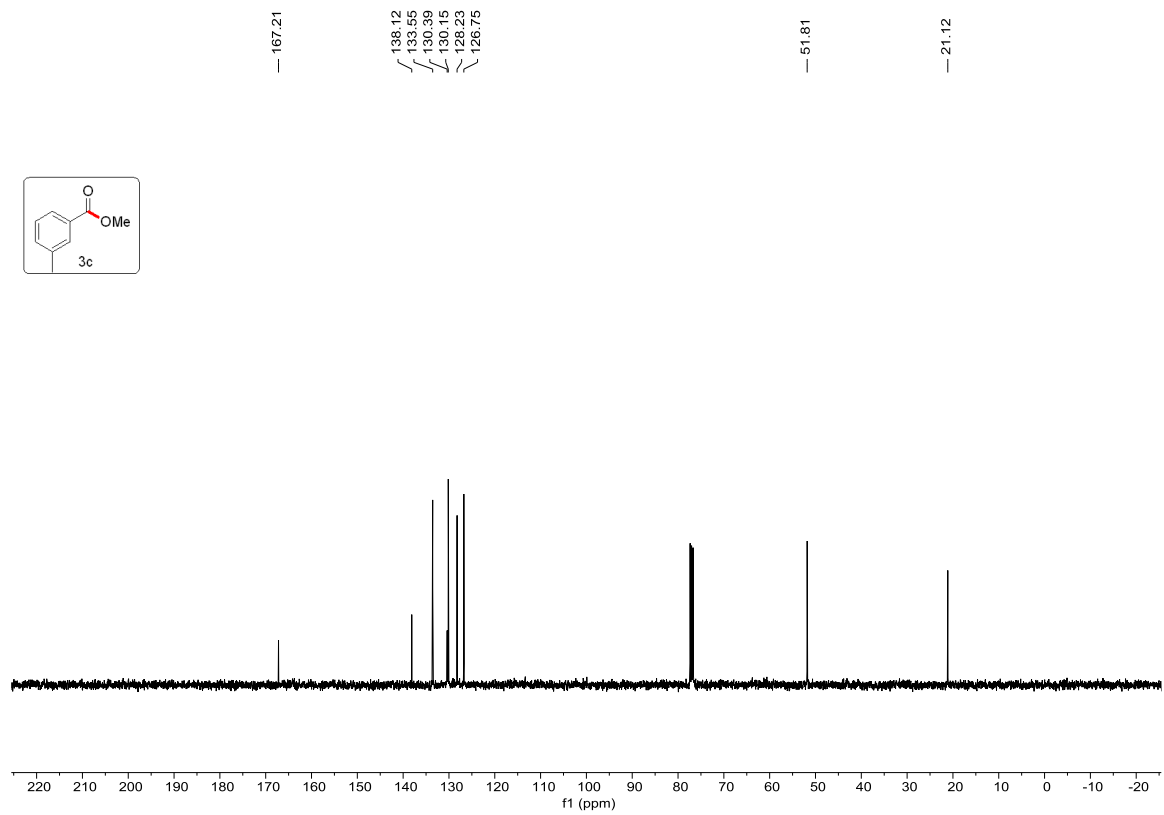
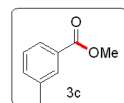
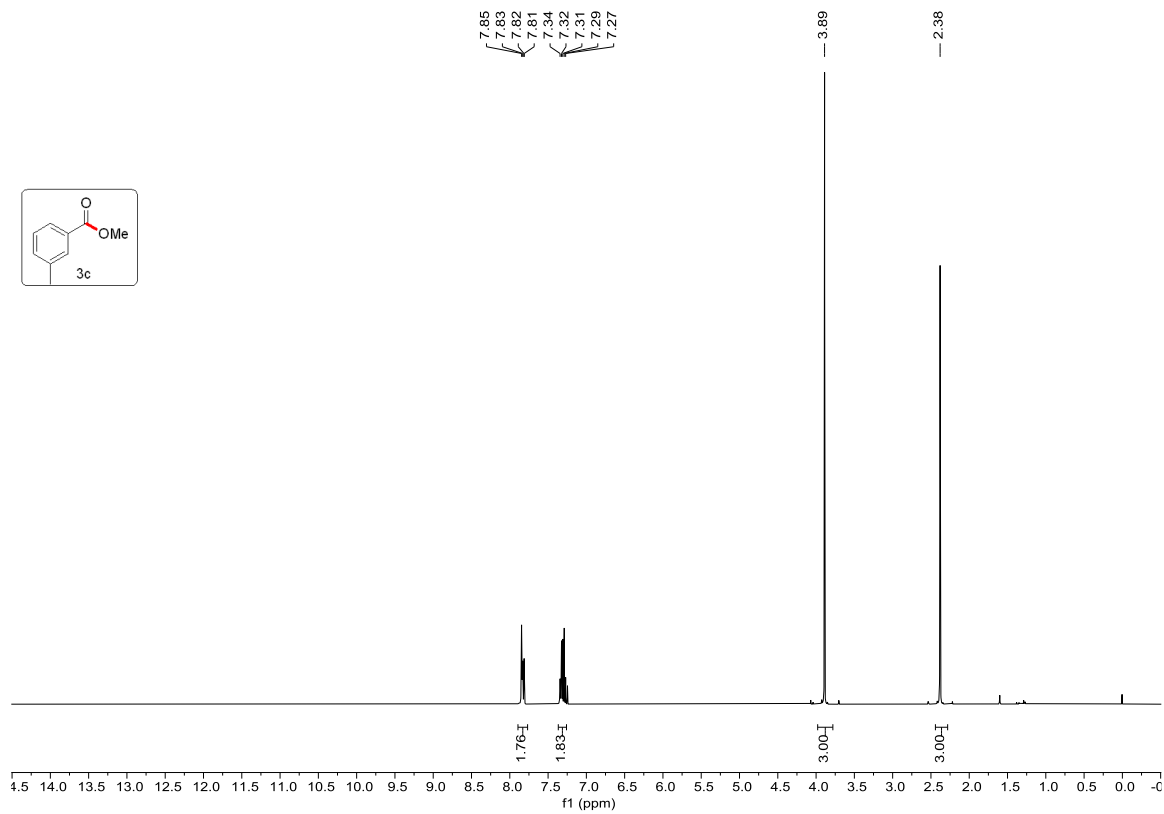
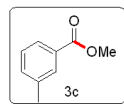
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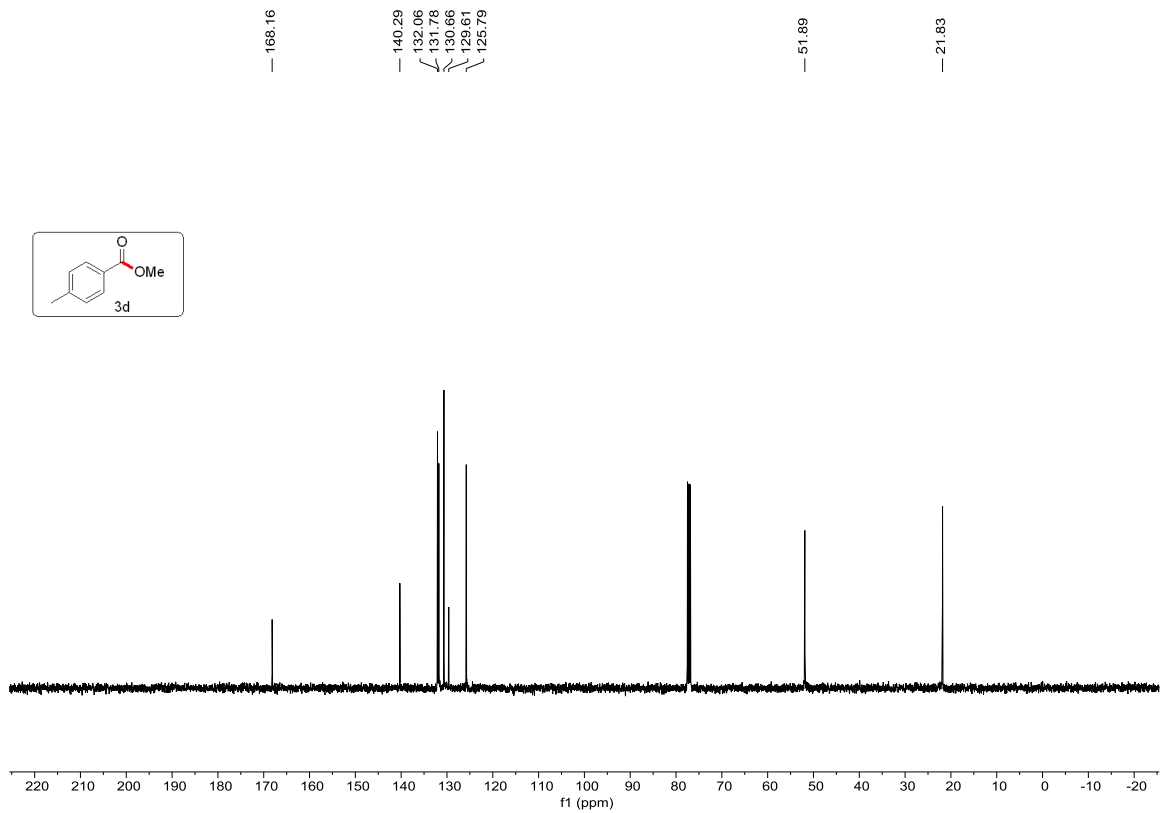
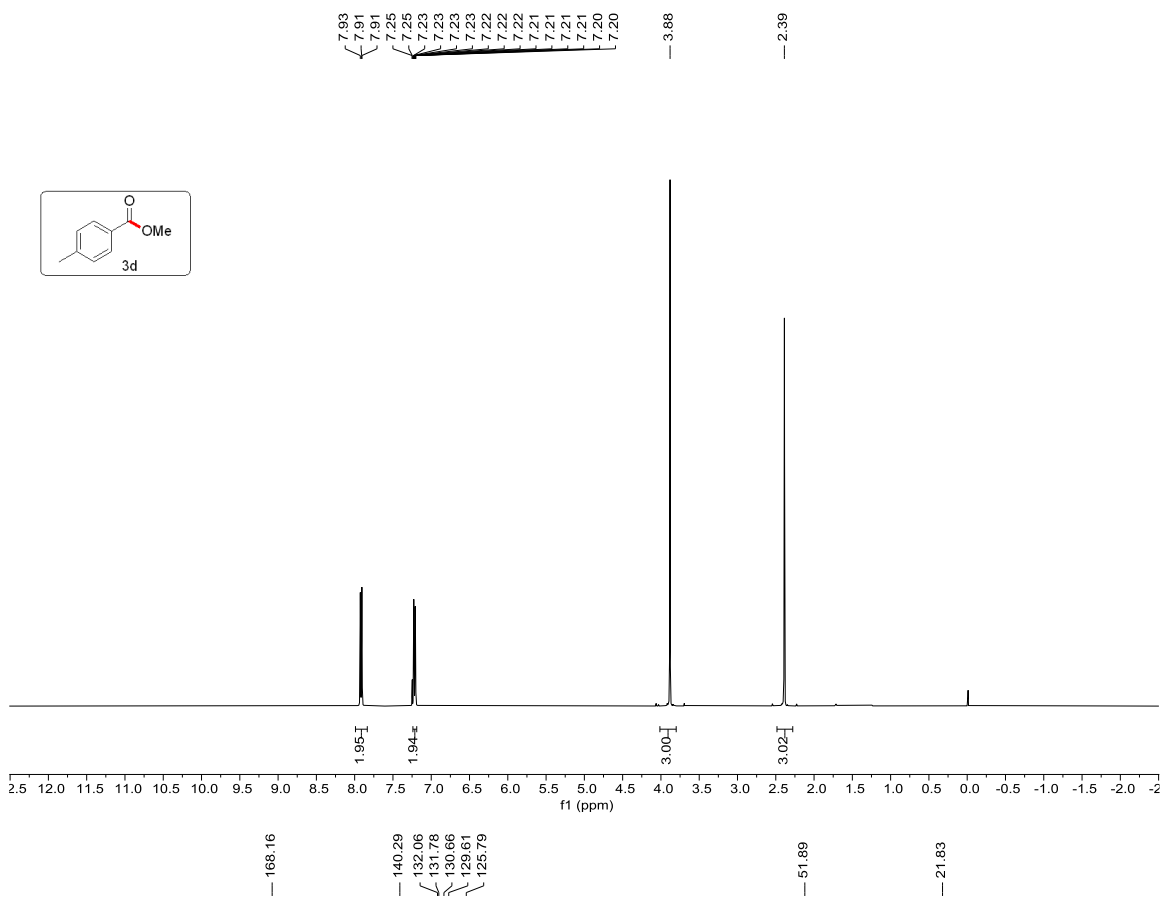
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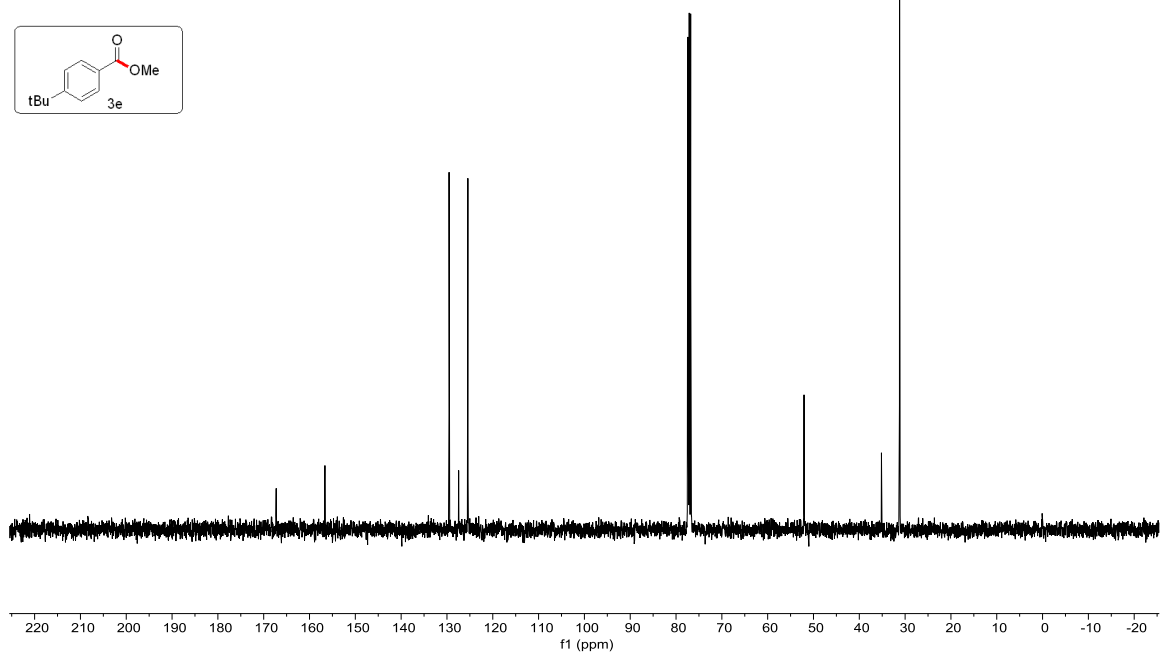
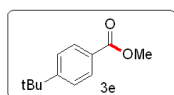
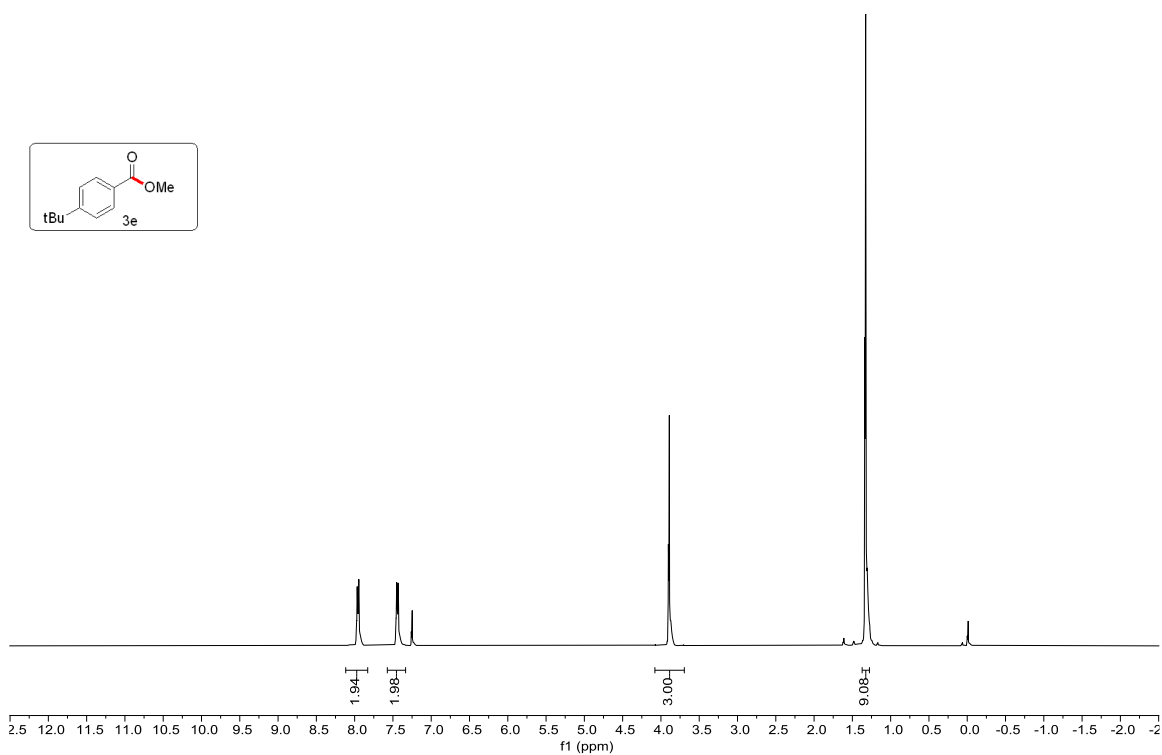
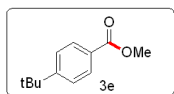
7. NMR Spectra of products 3a-3al

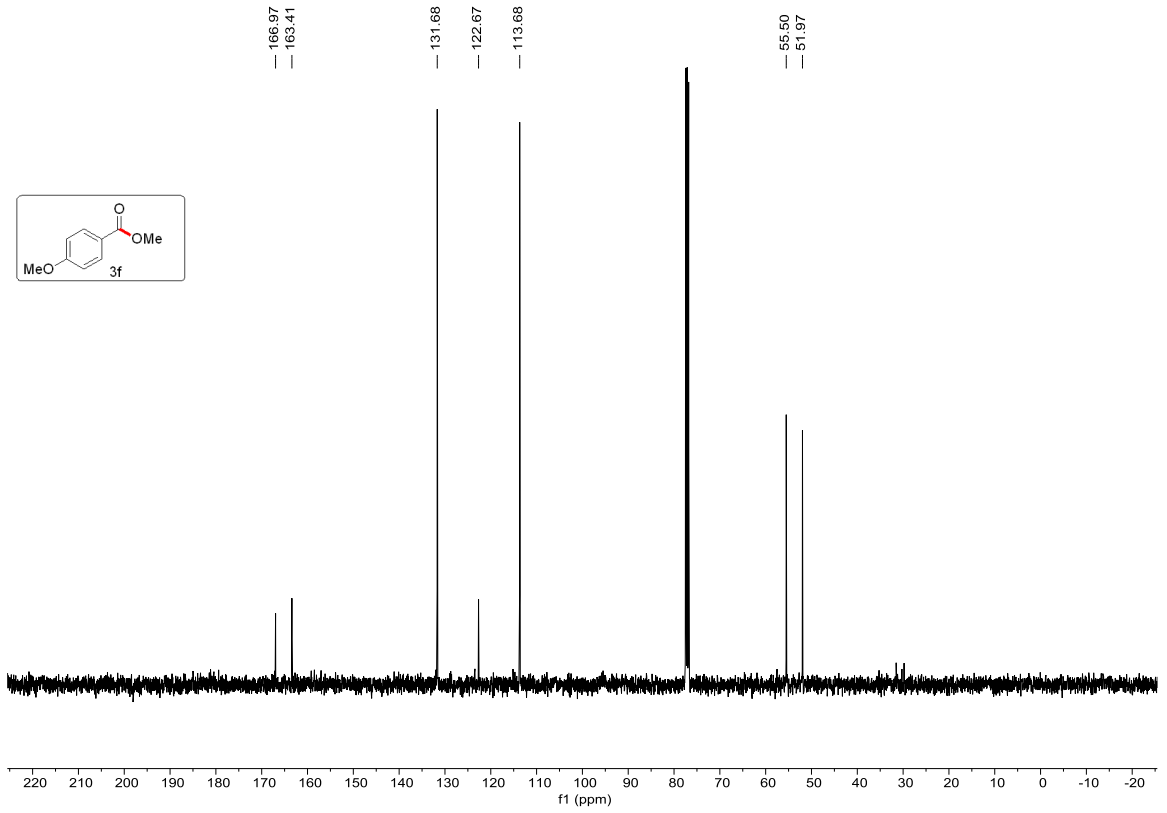
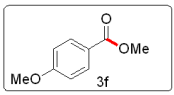
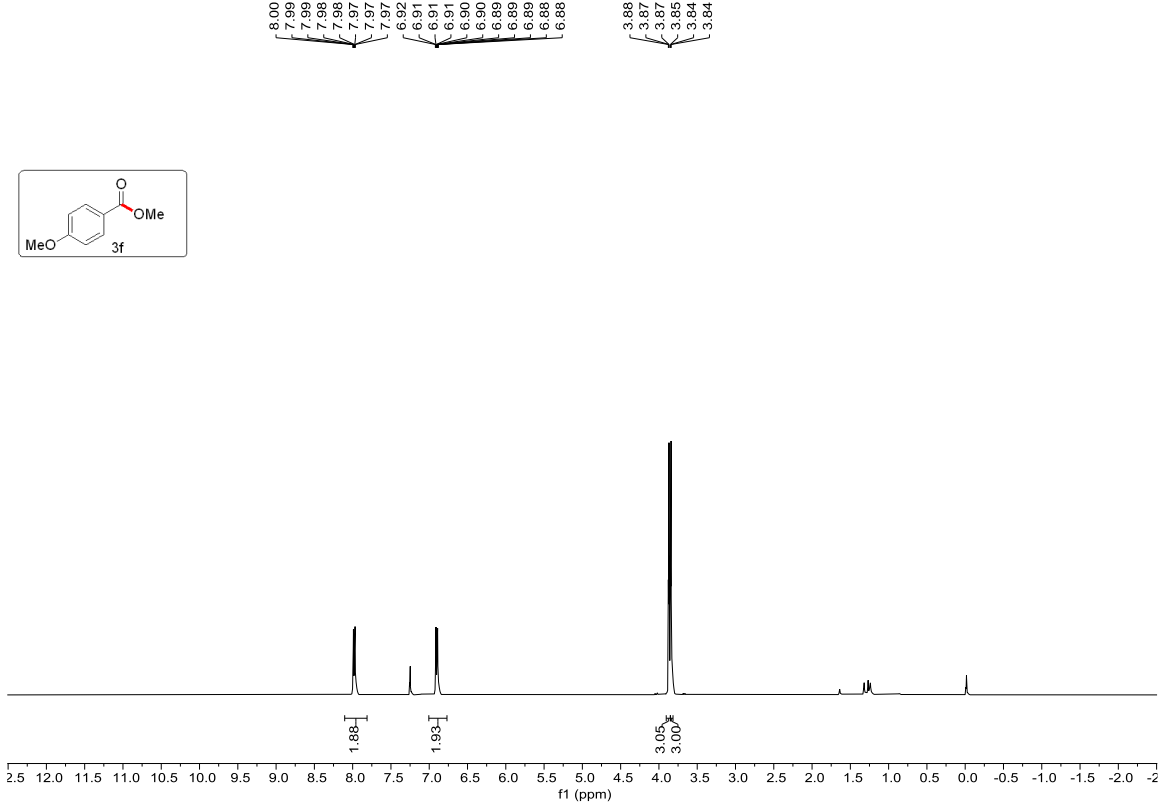
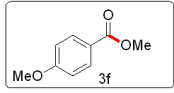


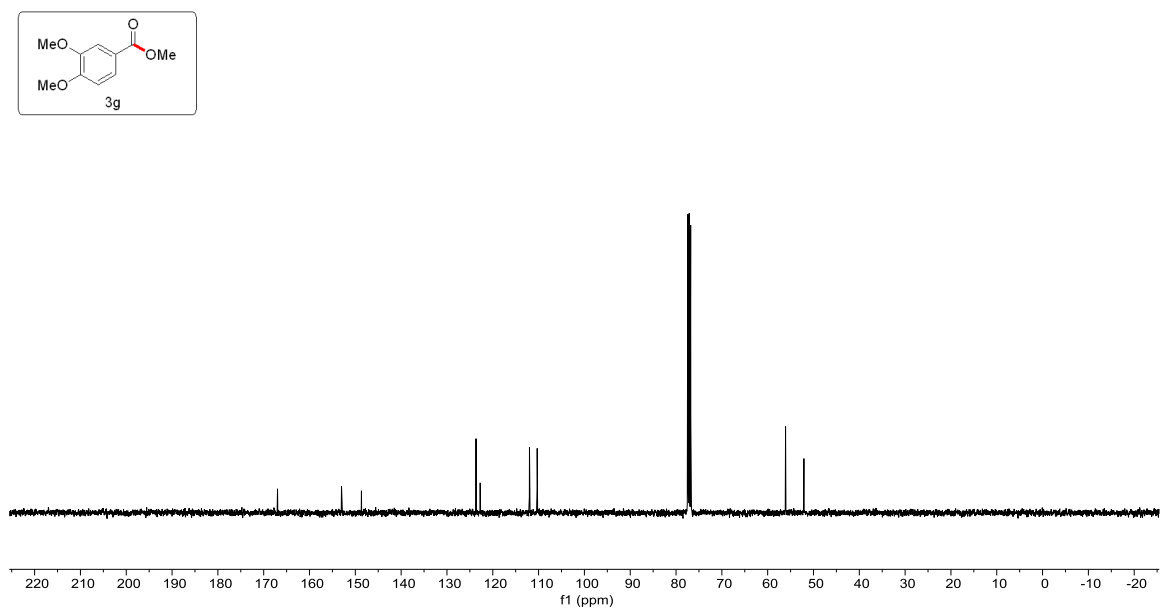
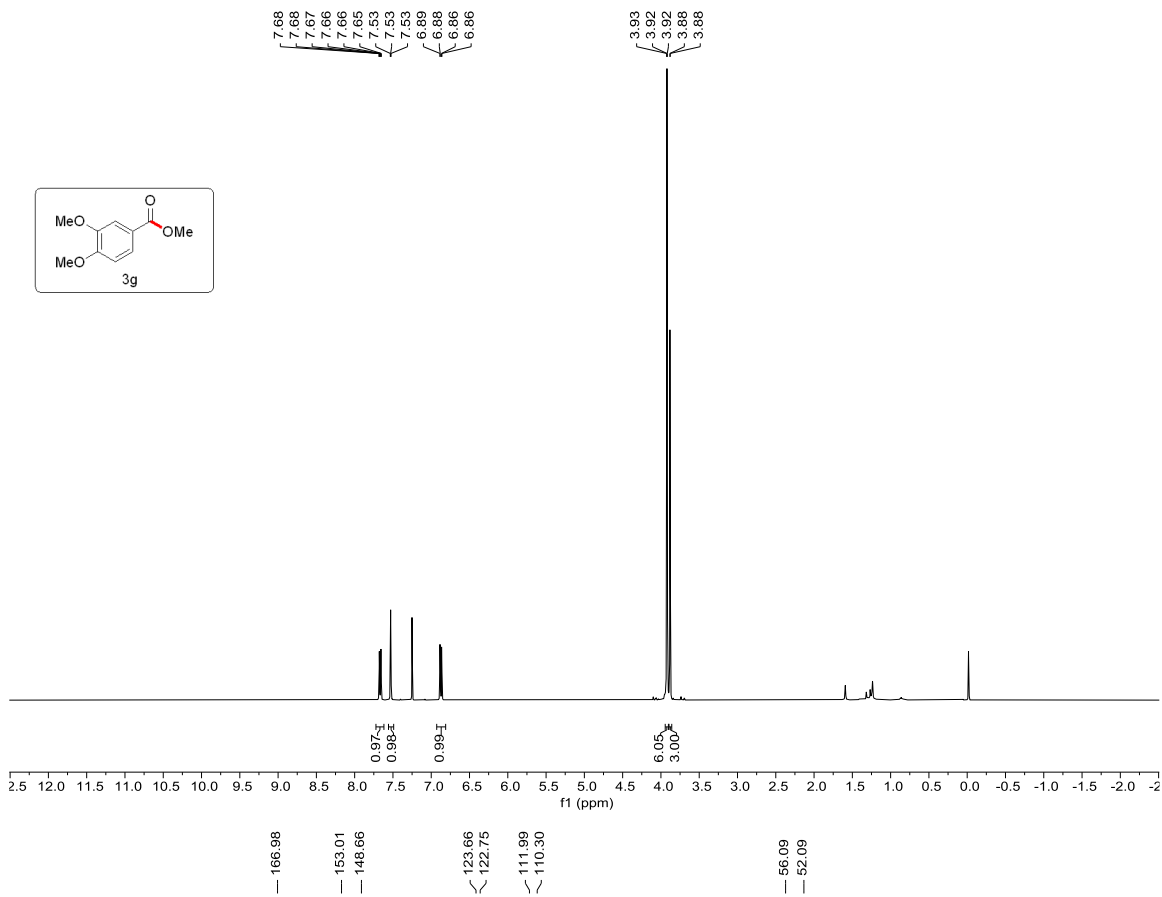


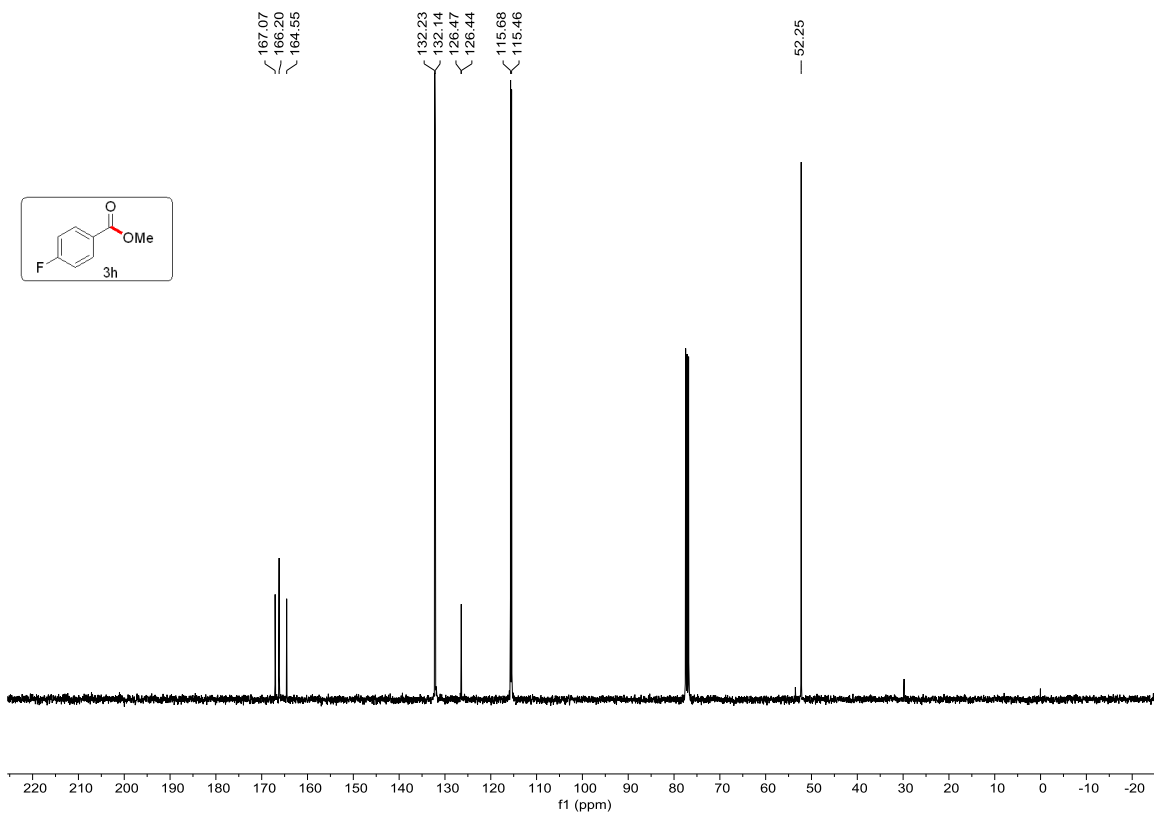
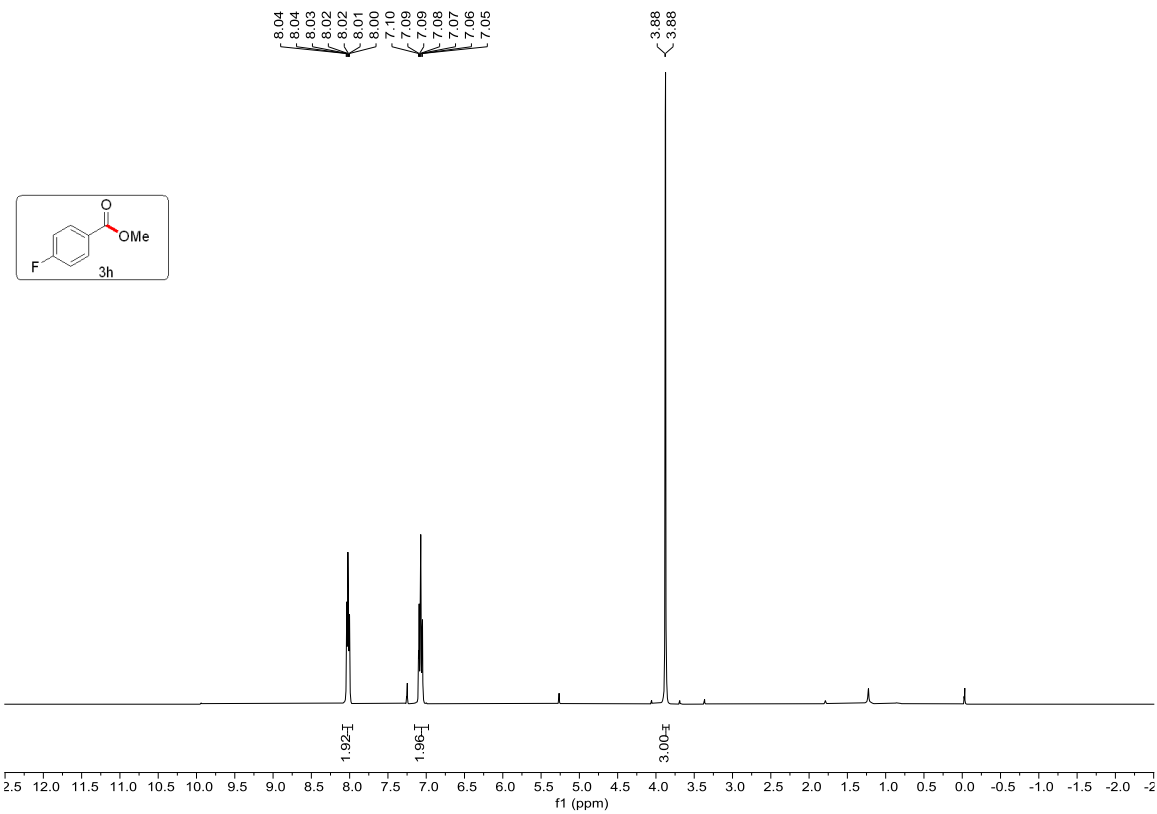


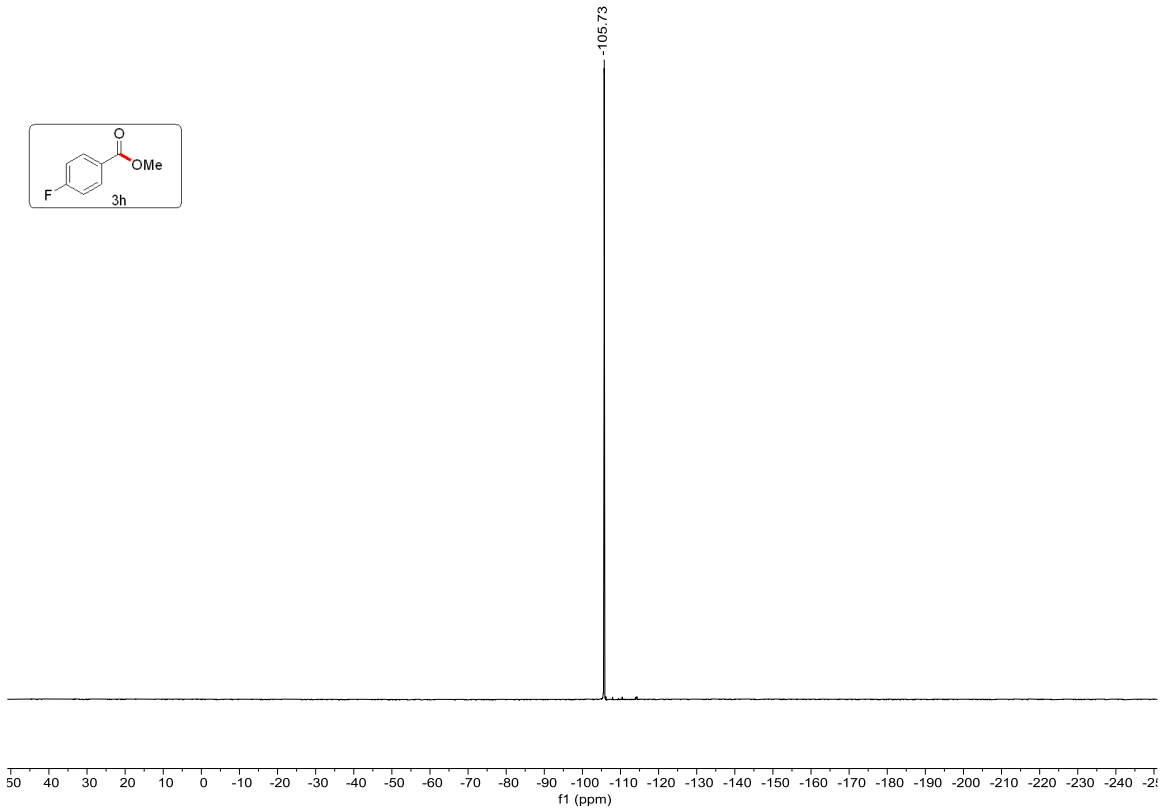
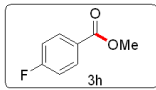






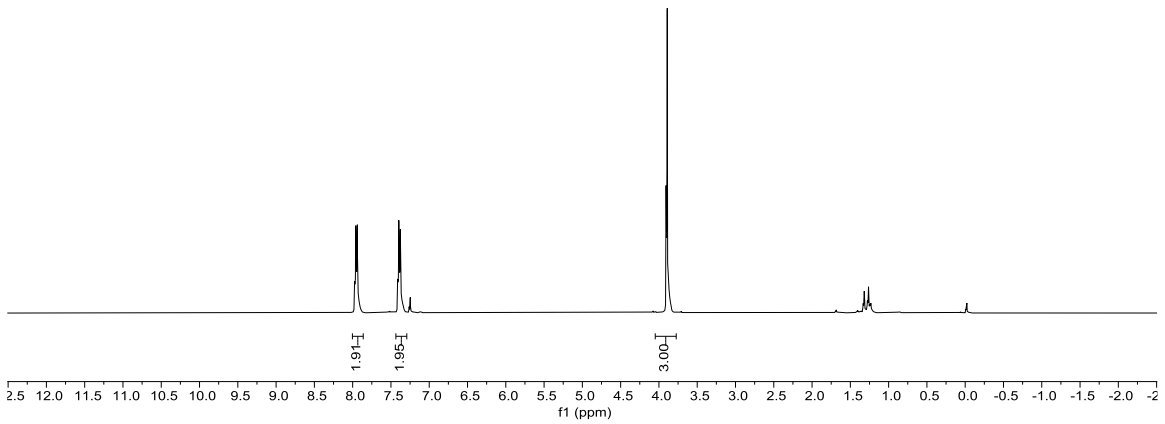
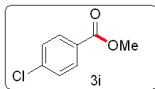


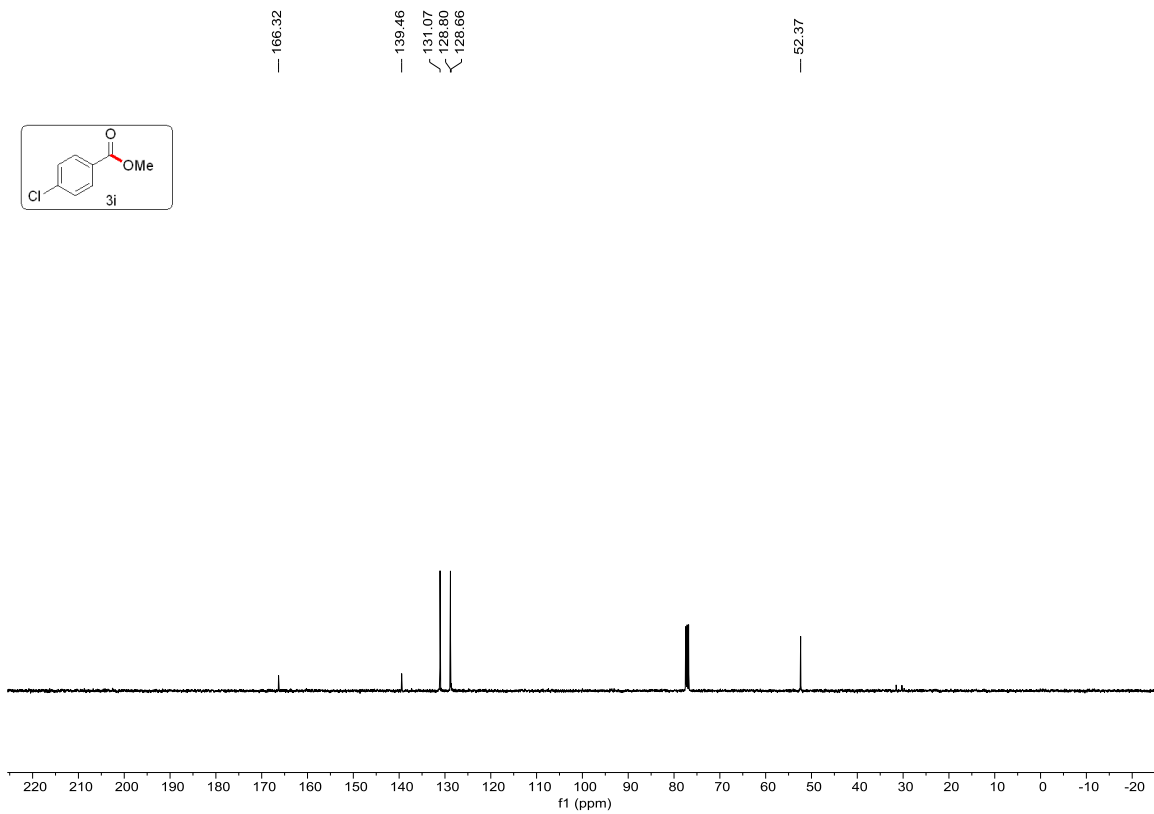
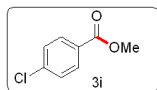




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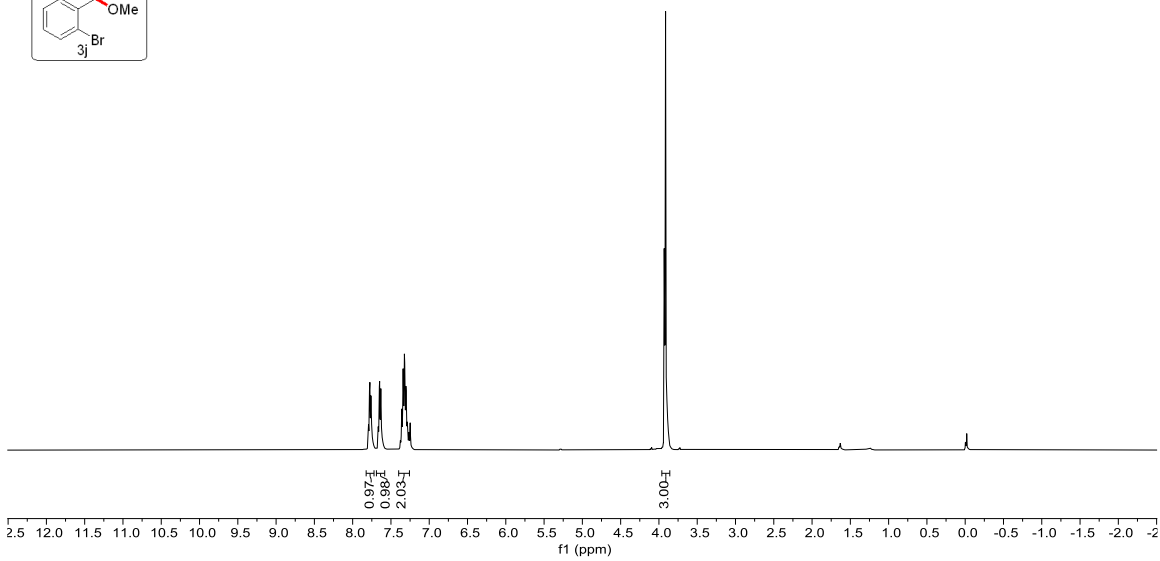
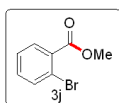
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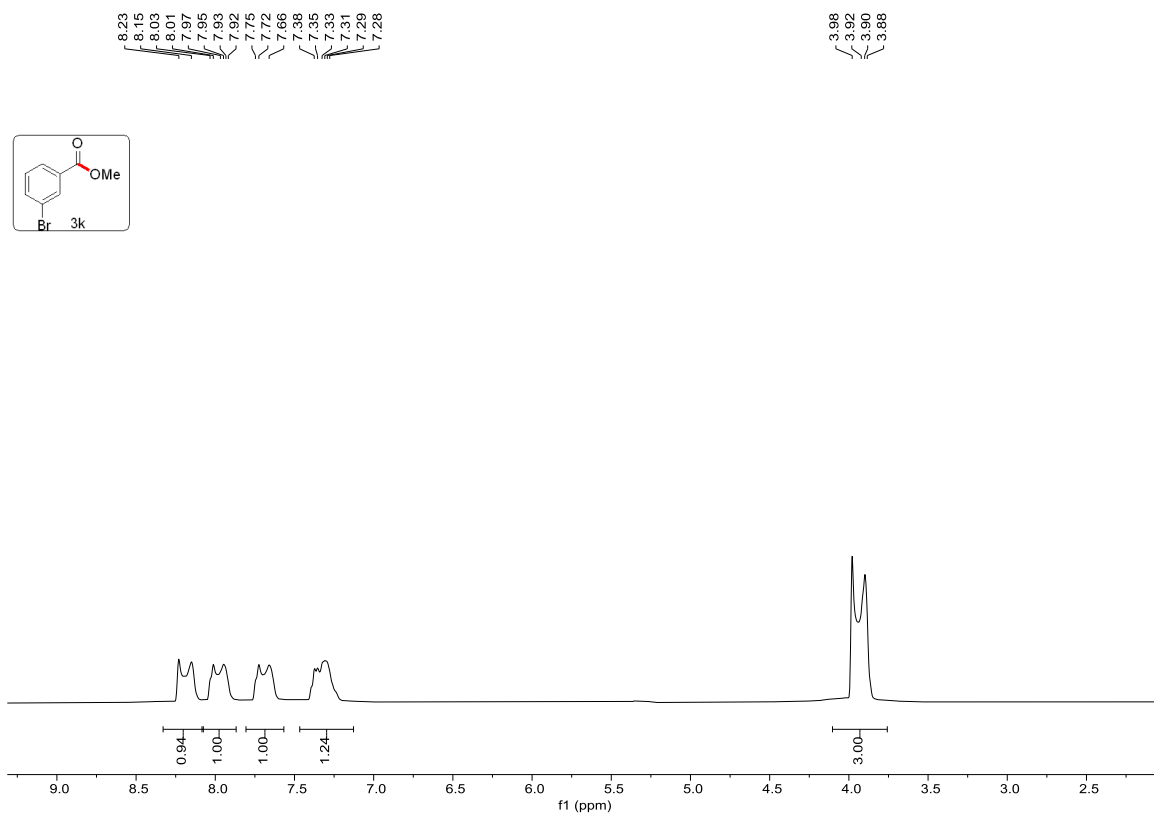
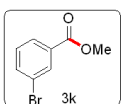
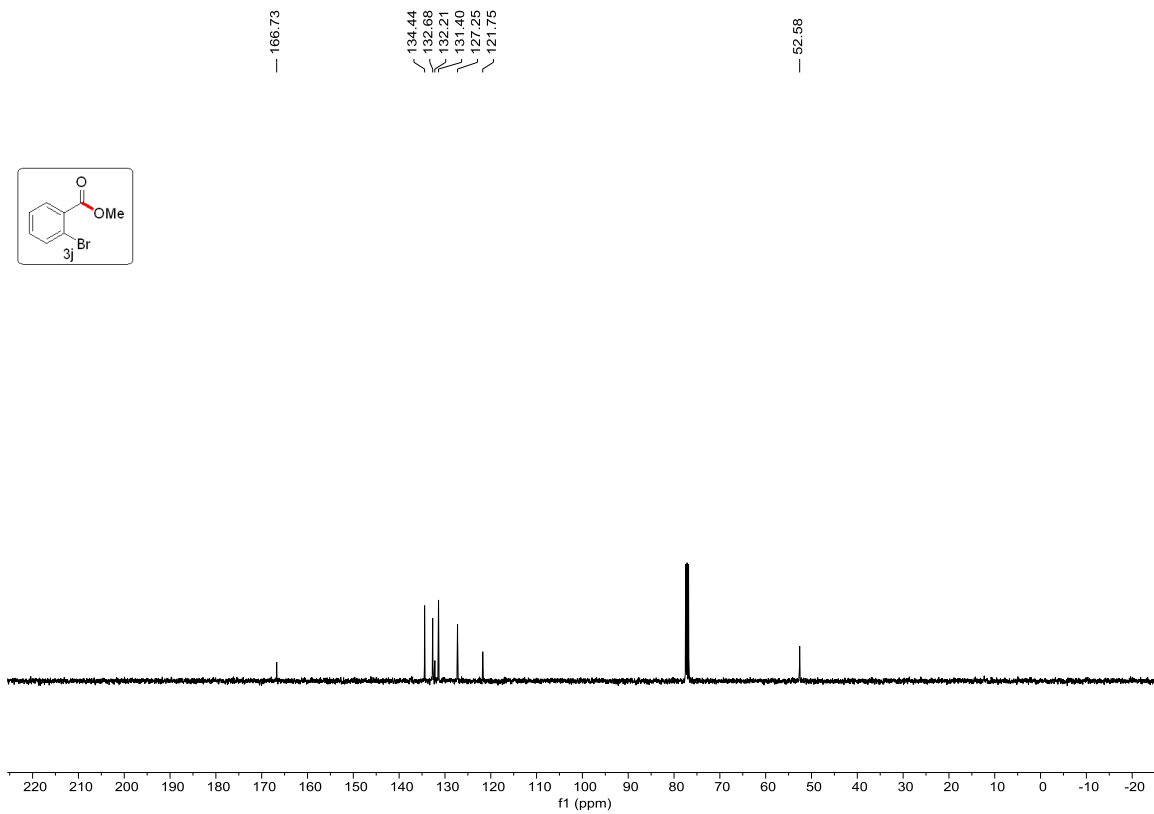
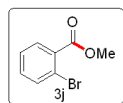


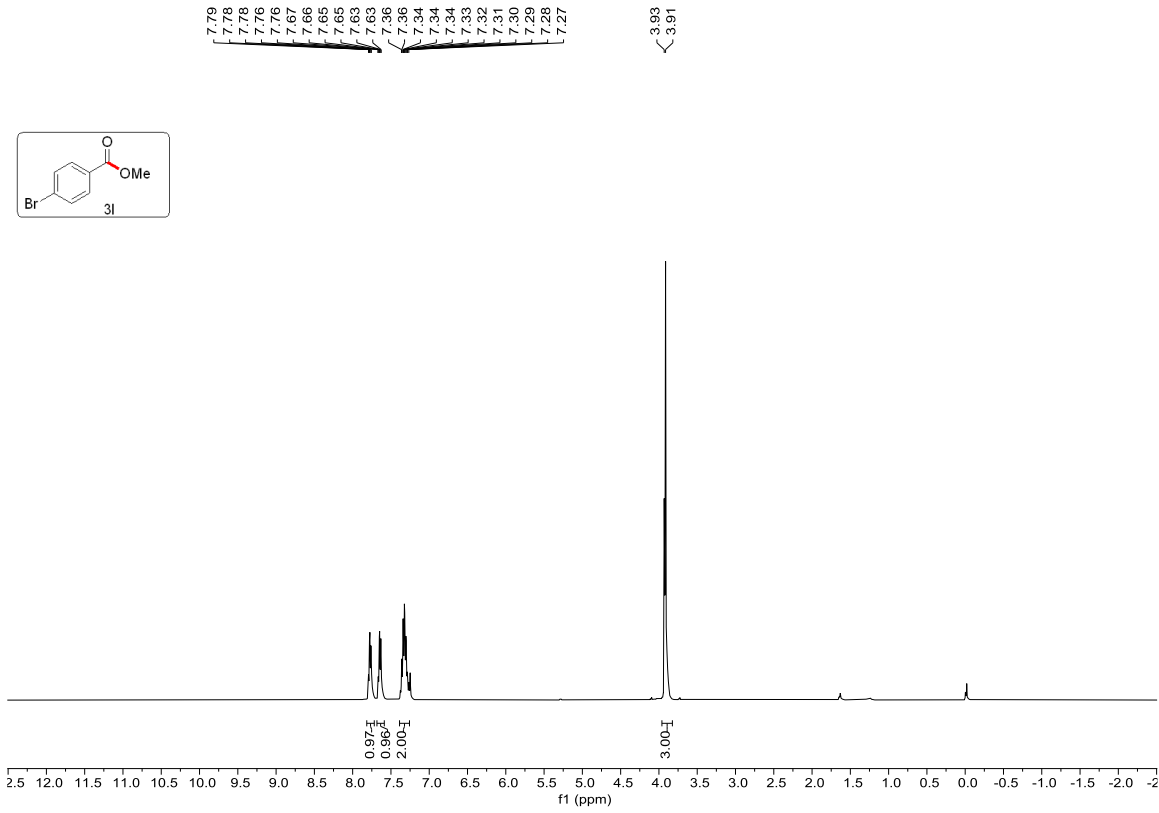
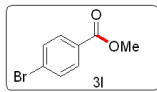
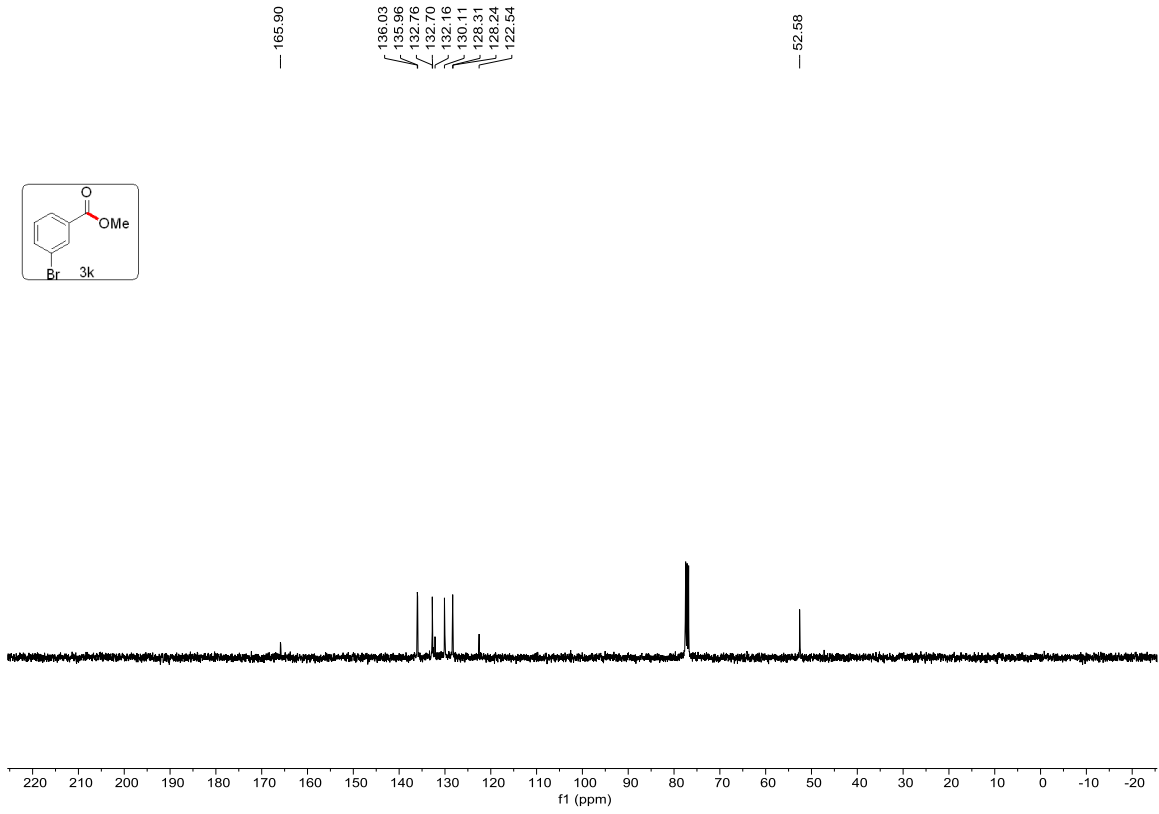
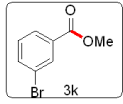


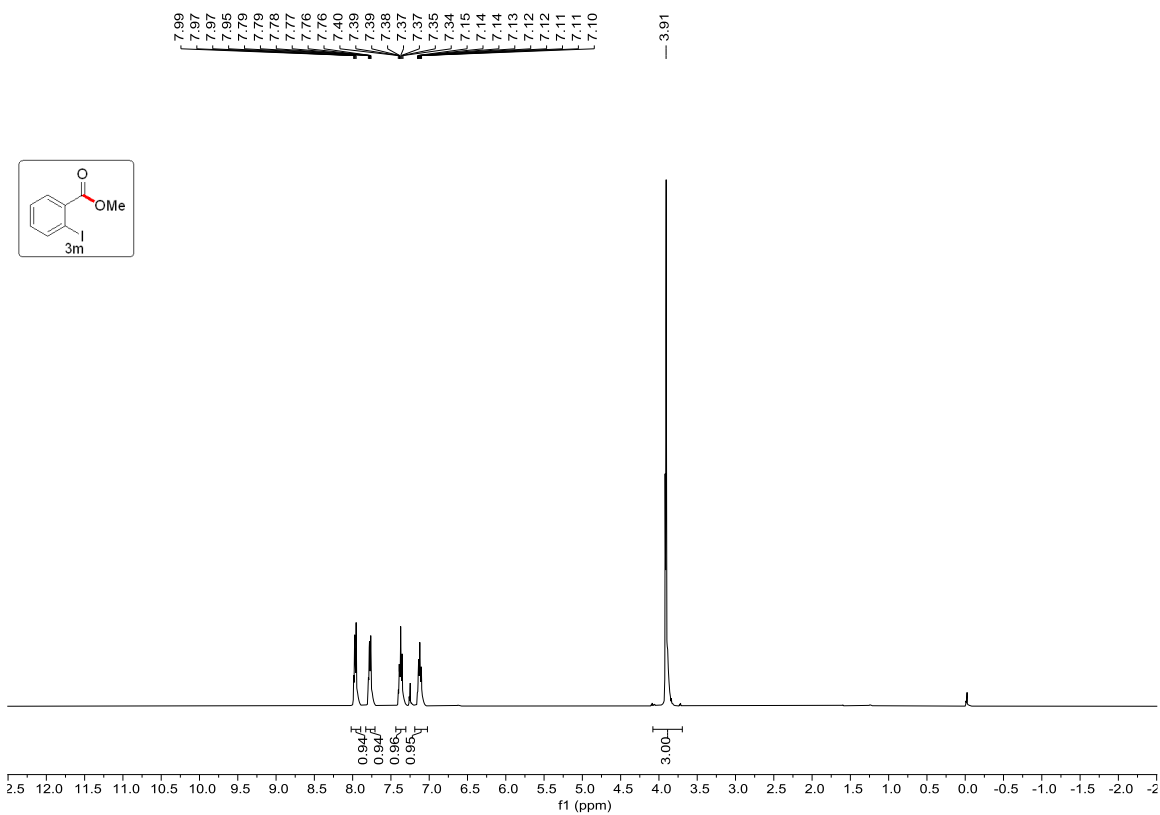
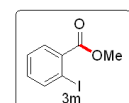
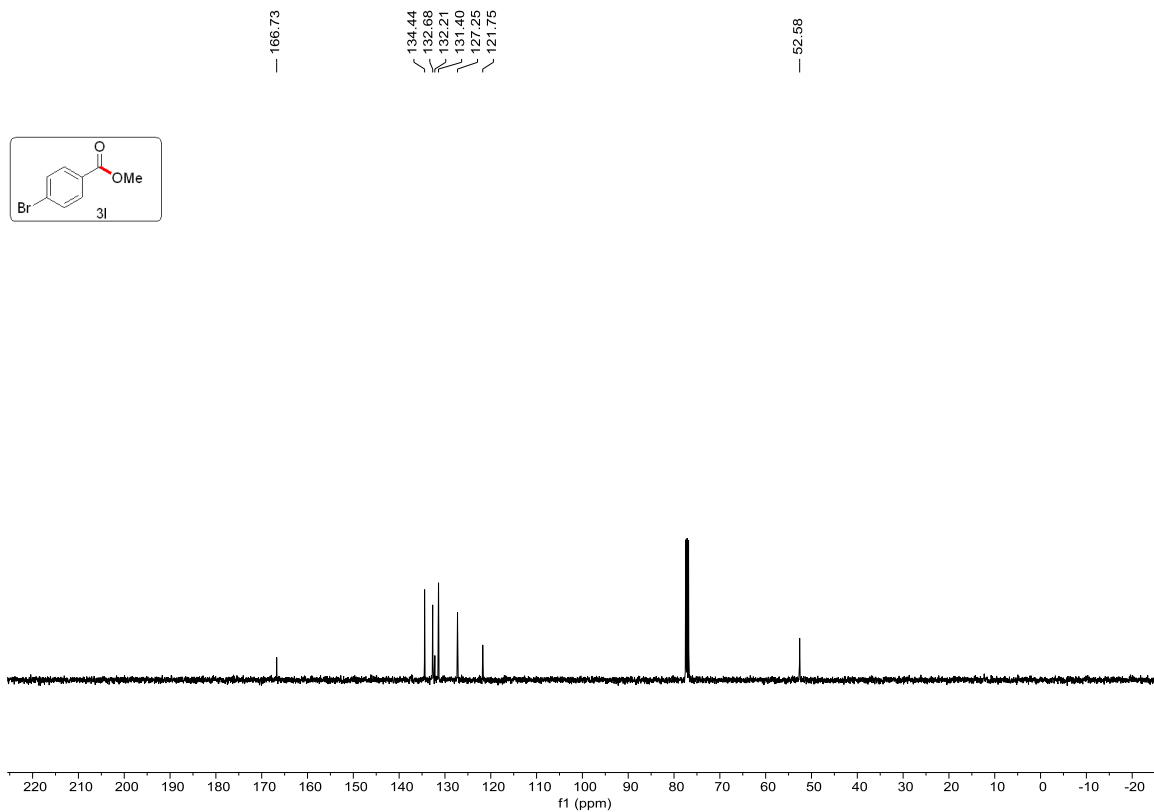
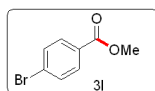
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7.29
7.28
7.27

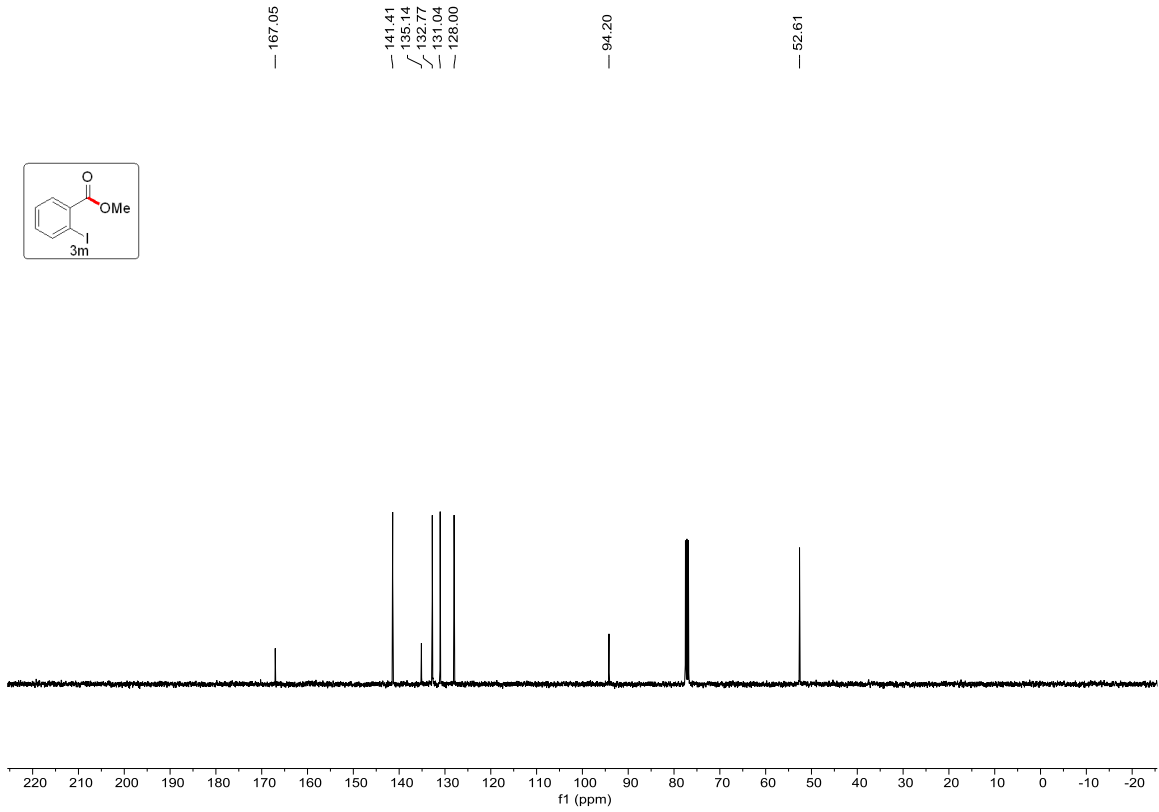
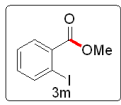
3.93
3.91





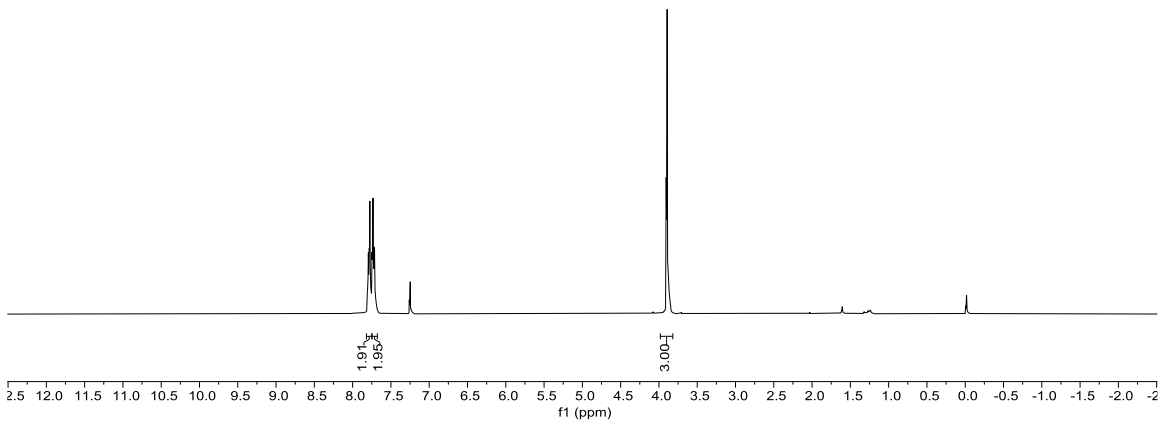
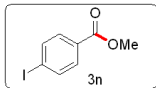


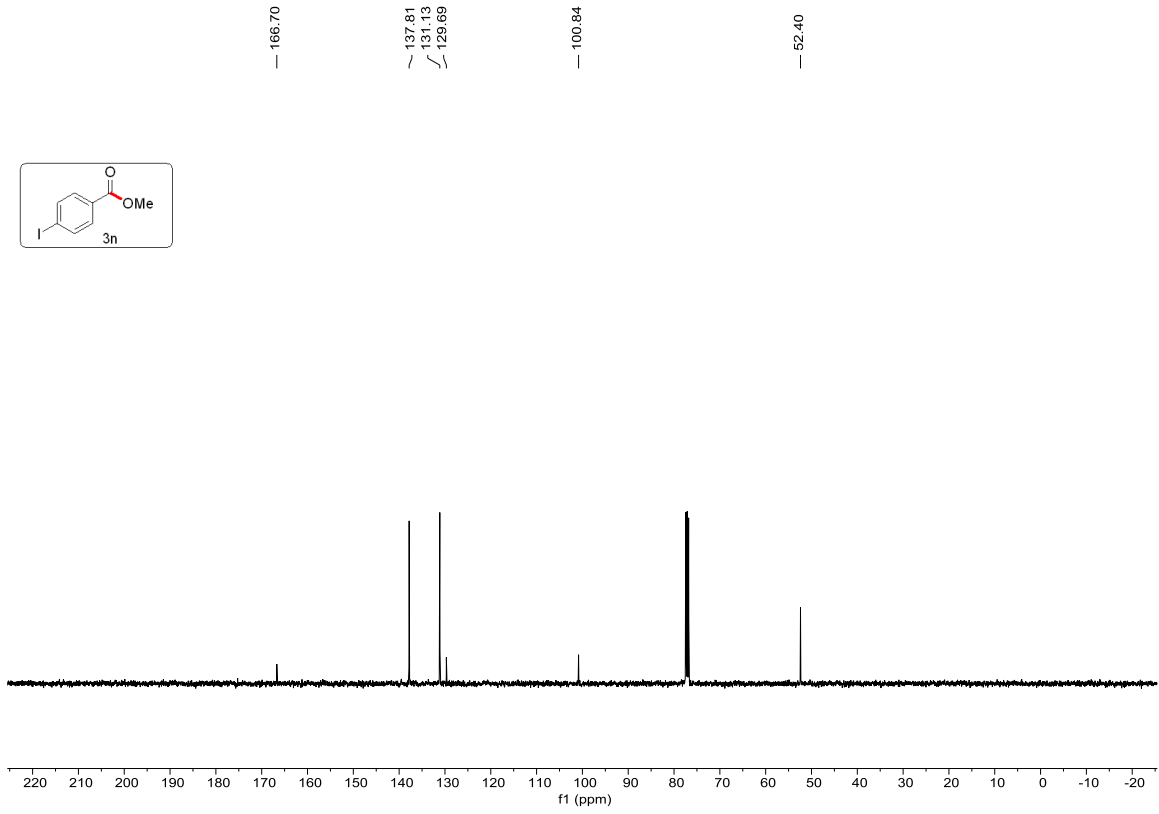
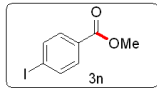


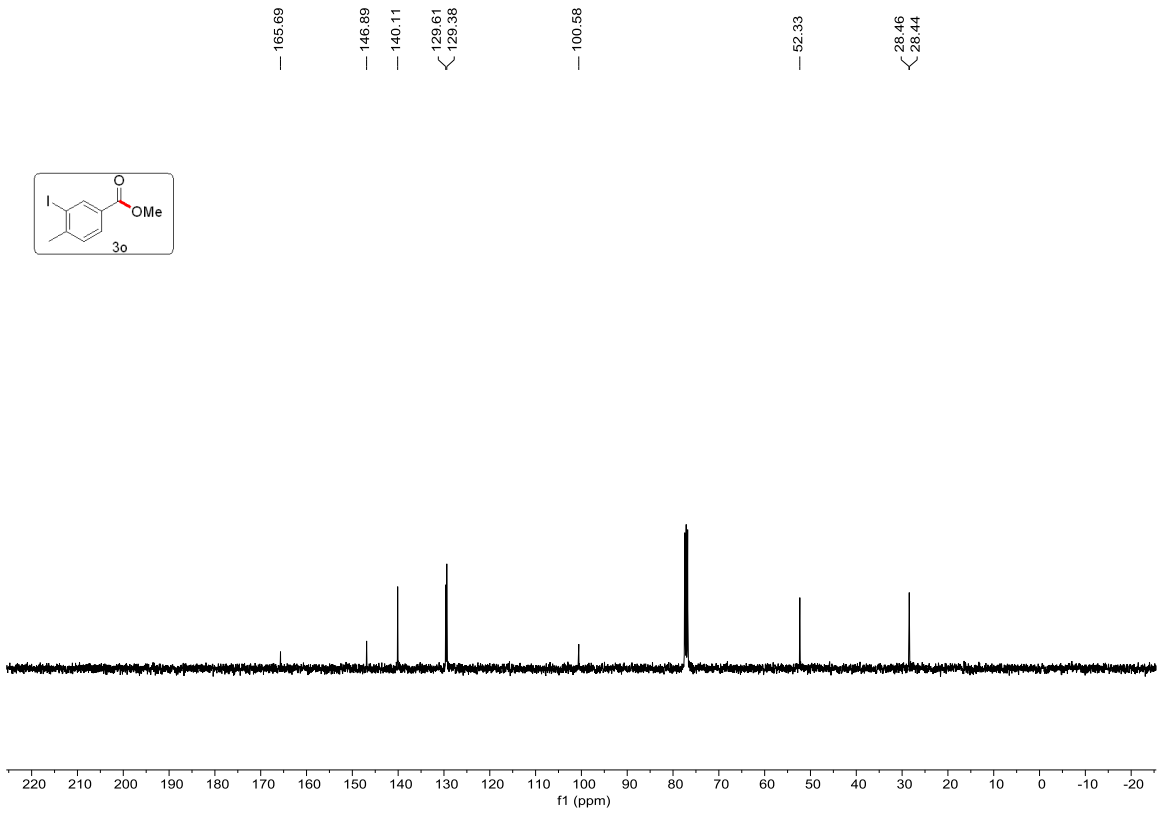
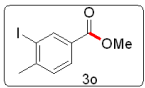
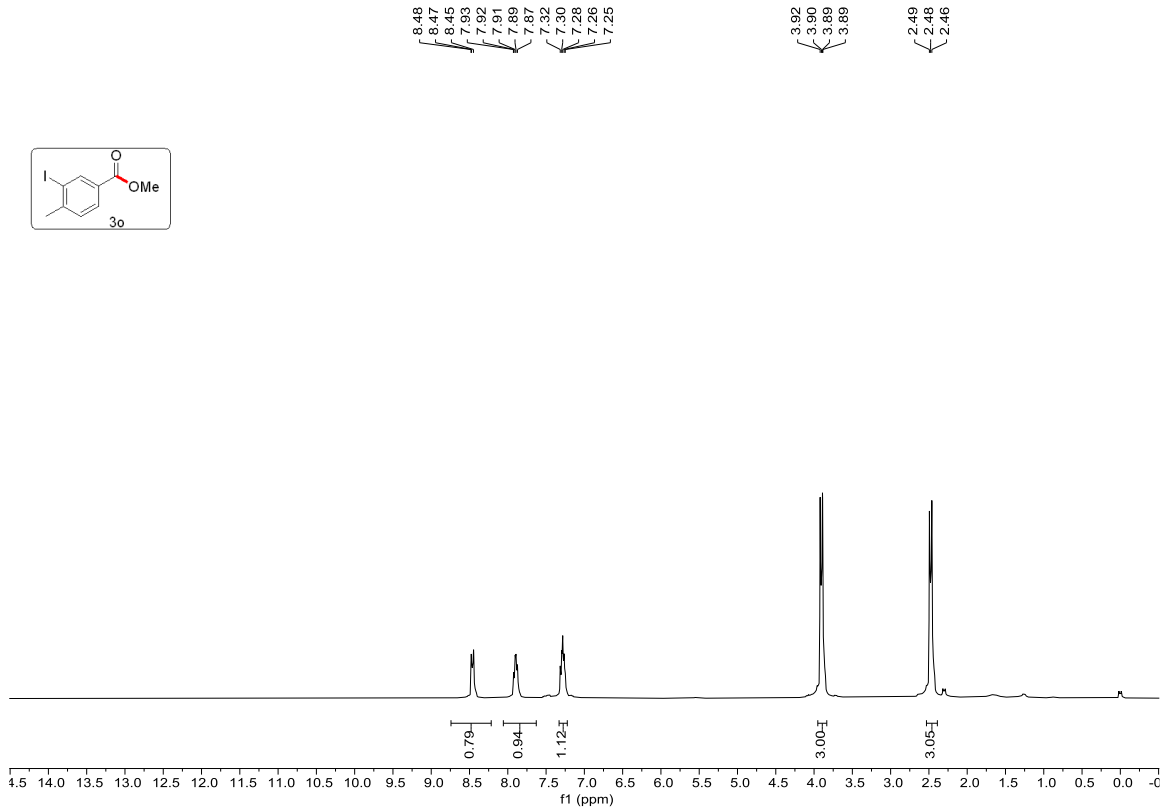
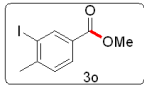


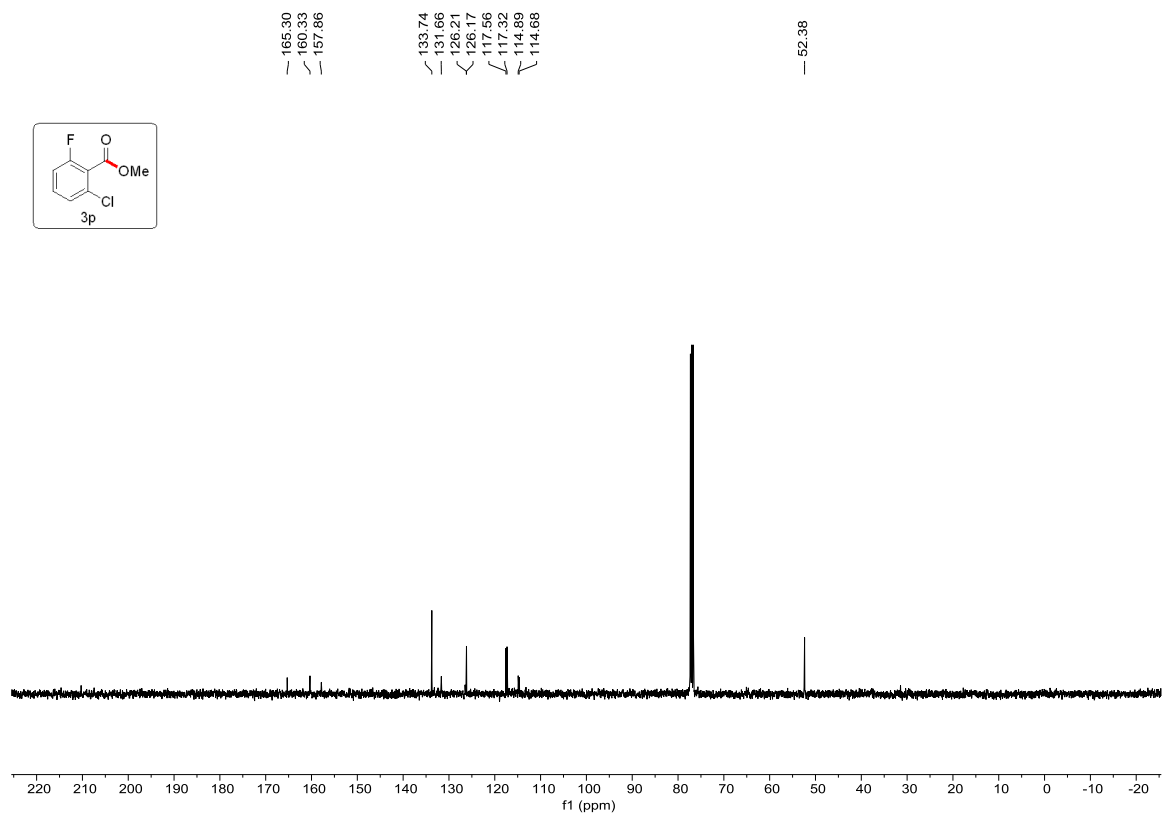
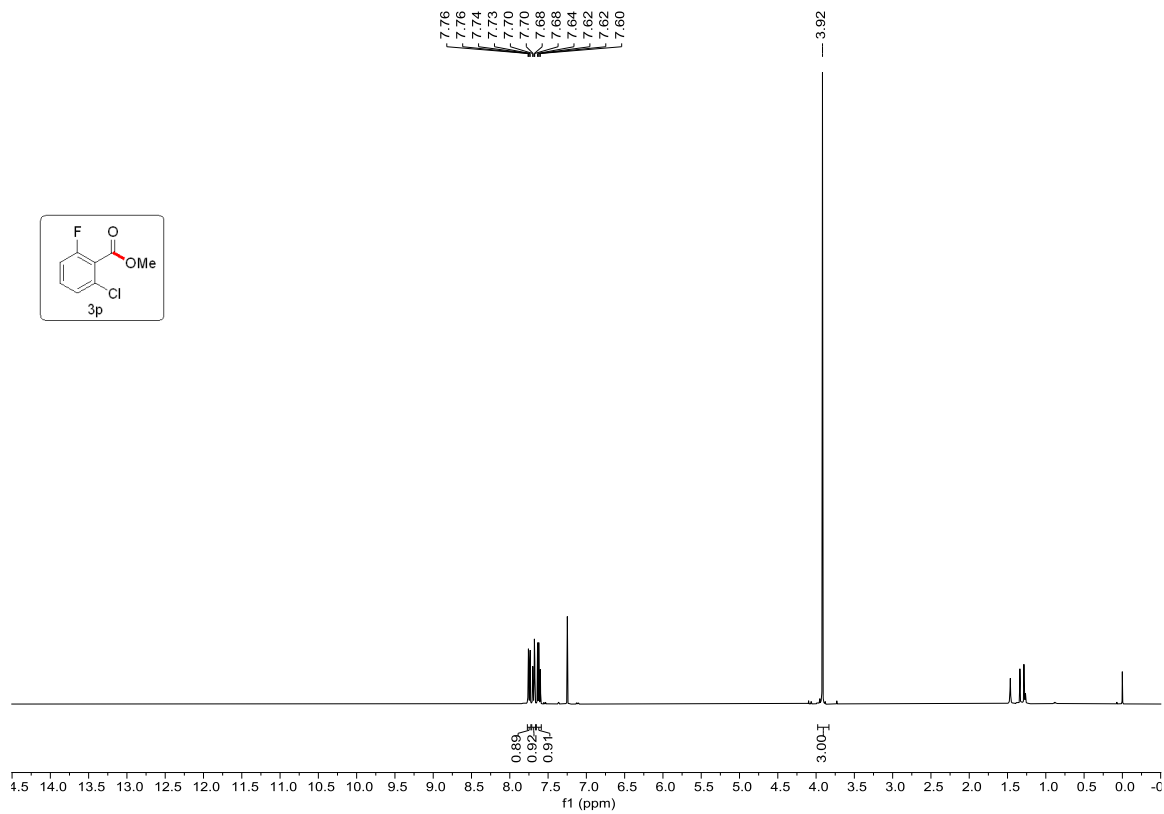
7.81
7.80
7.79
7.77
7.75
7.74
7.73
7.72

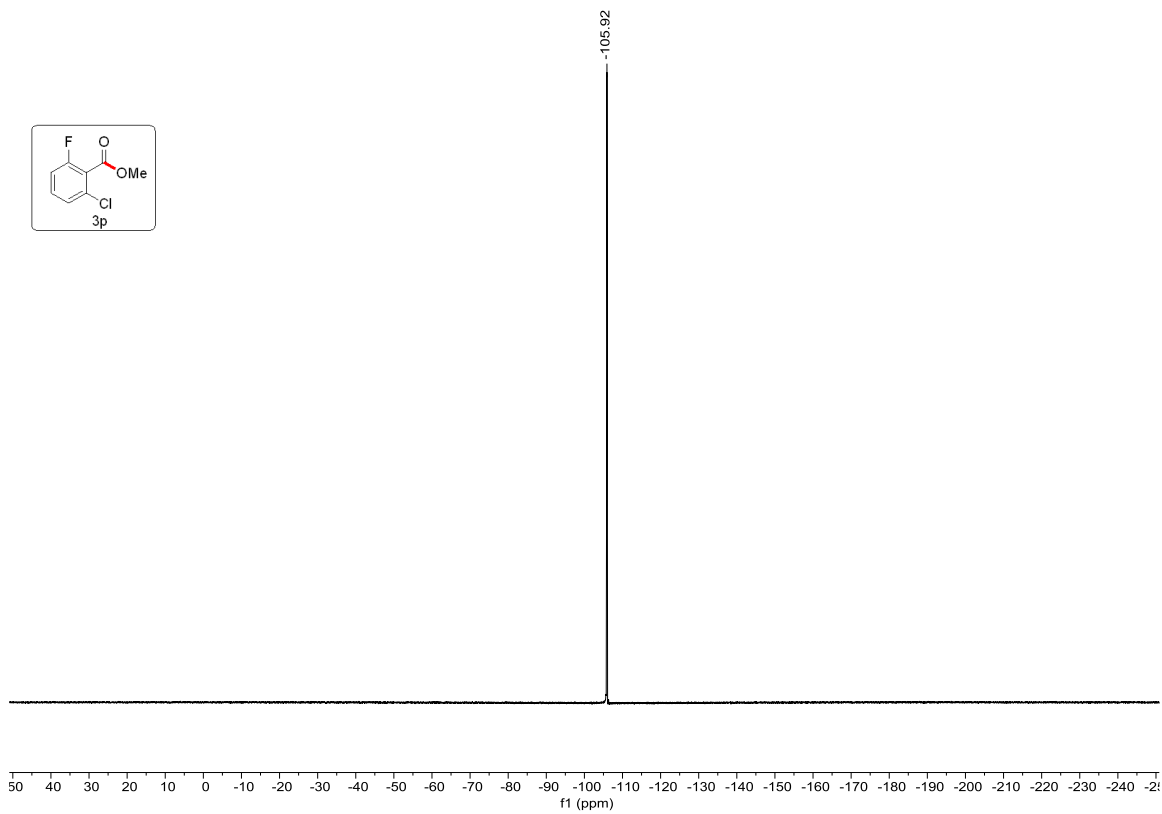
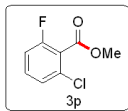
3.89

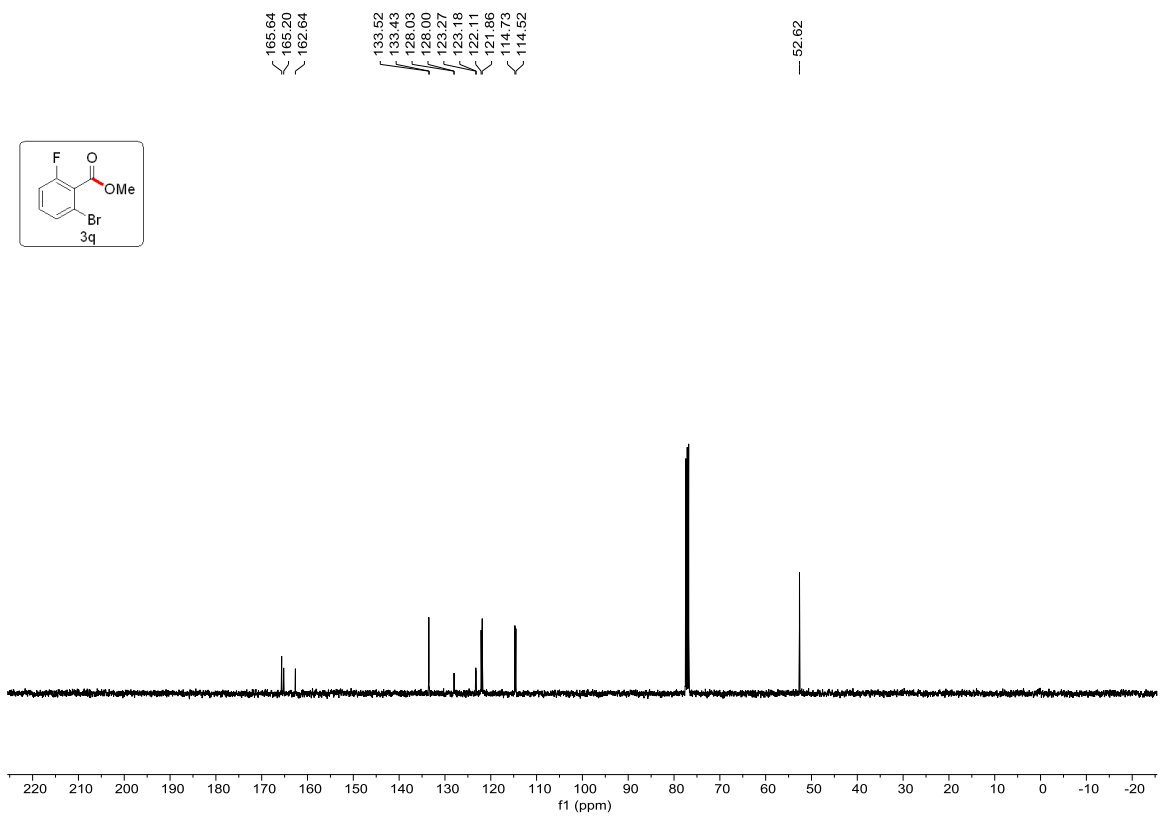
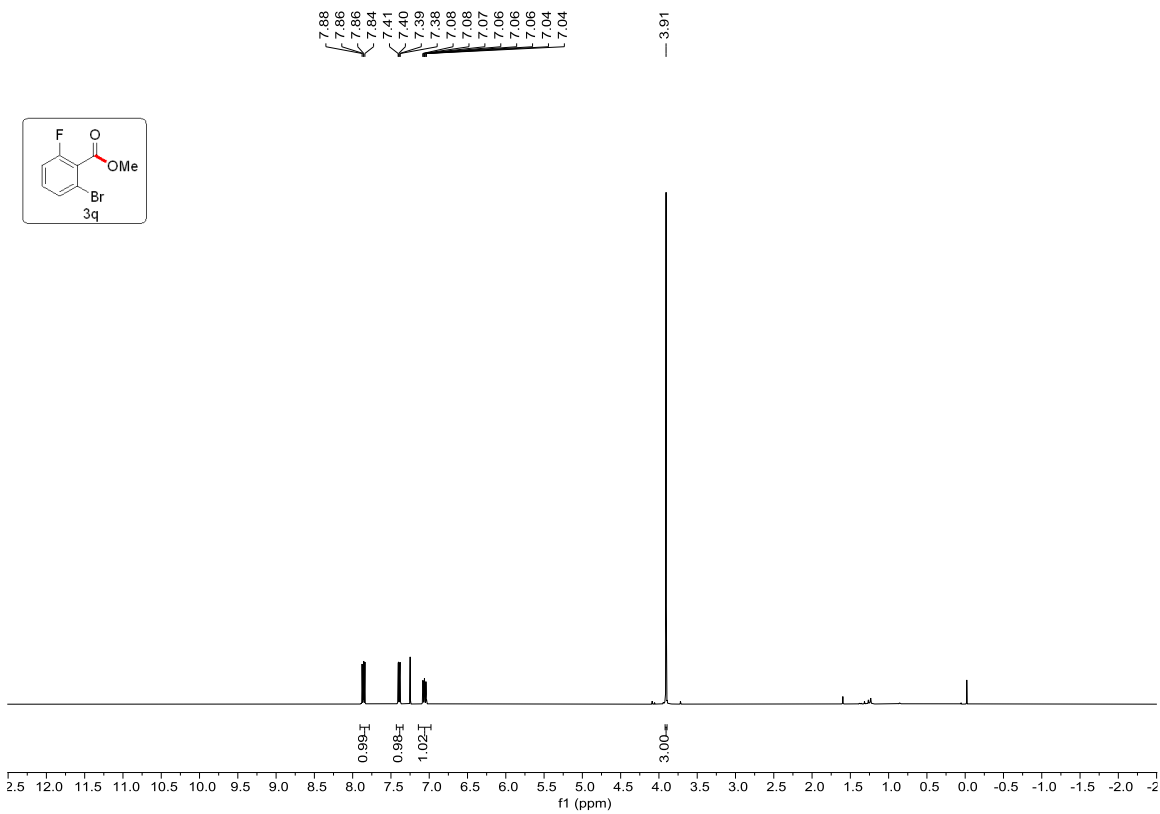


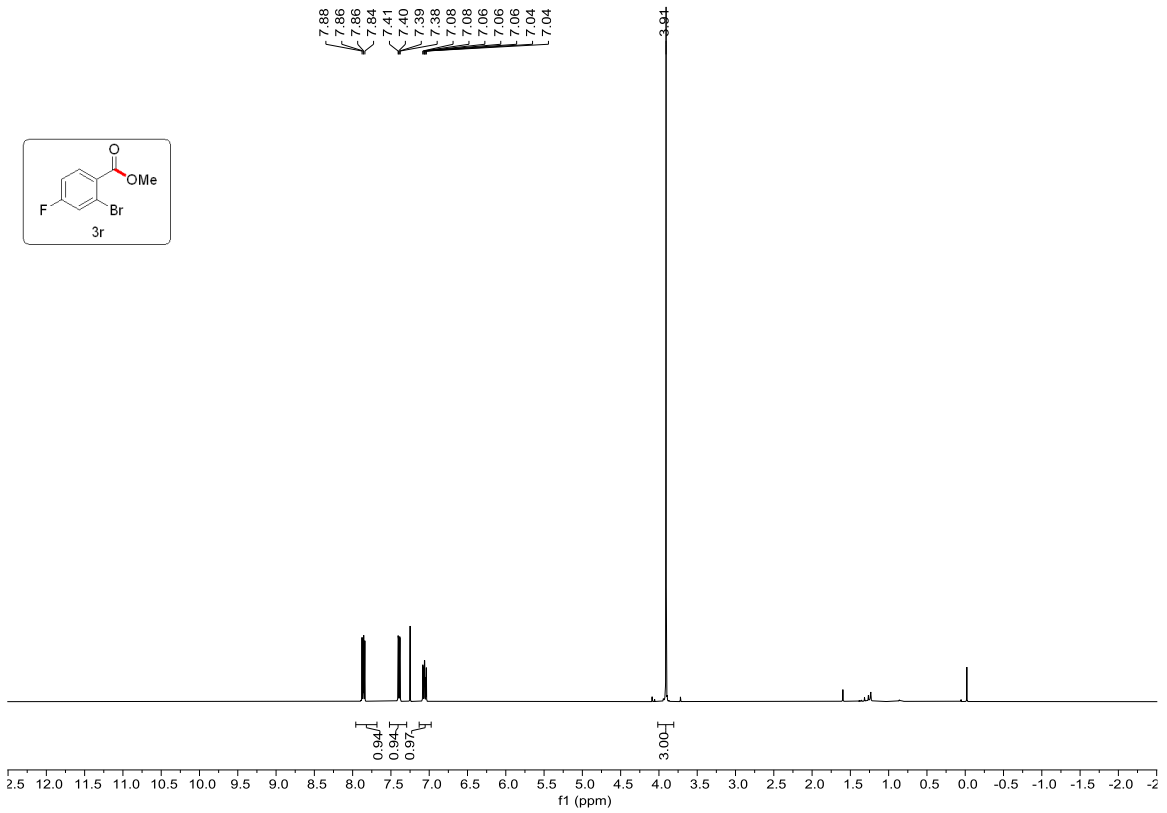
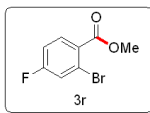
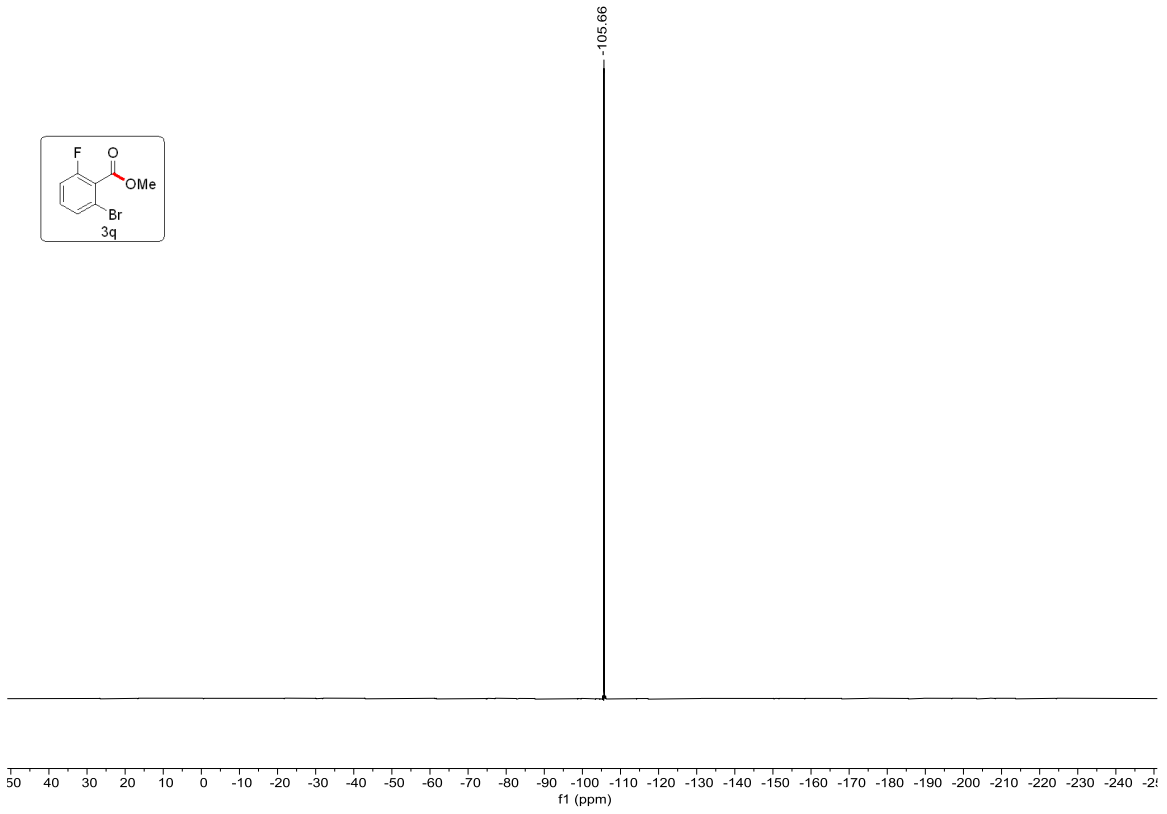
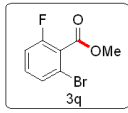


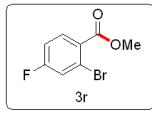






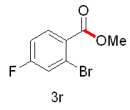
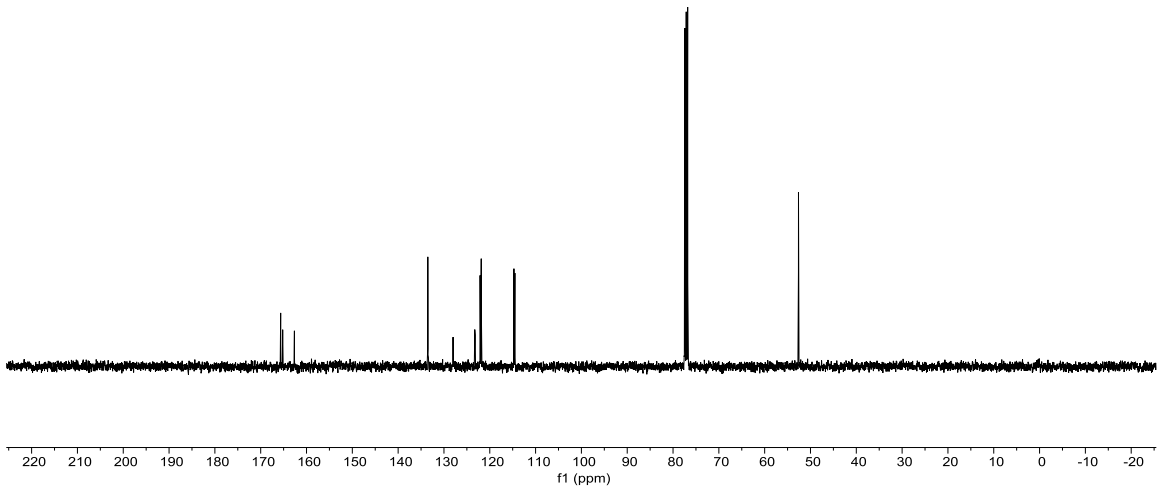




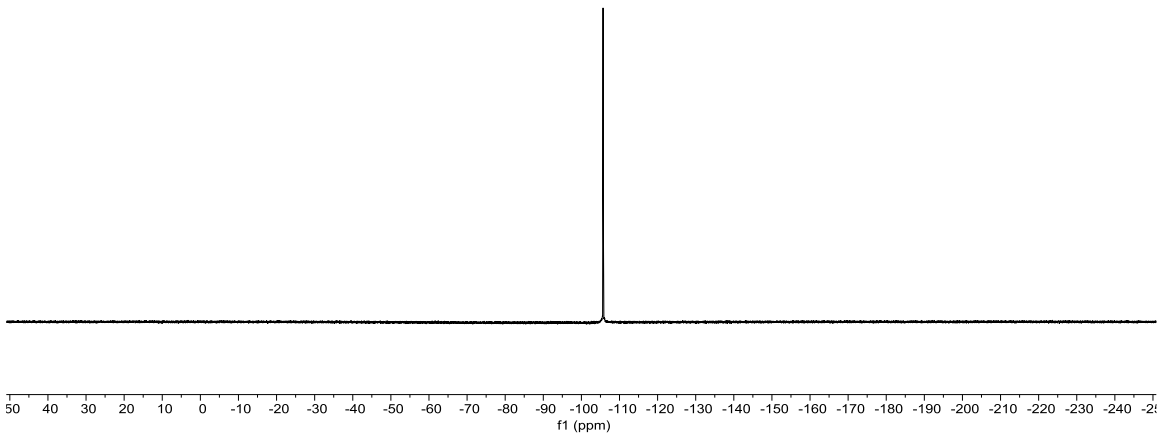


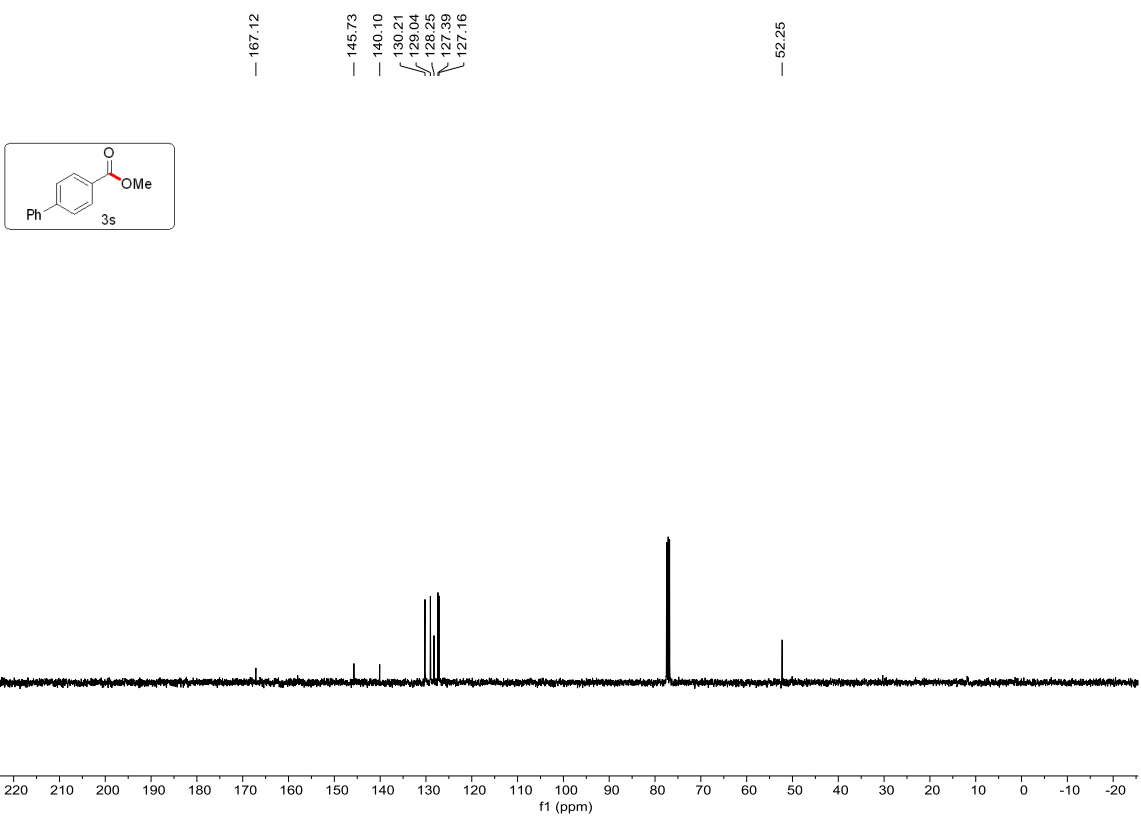
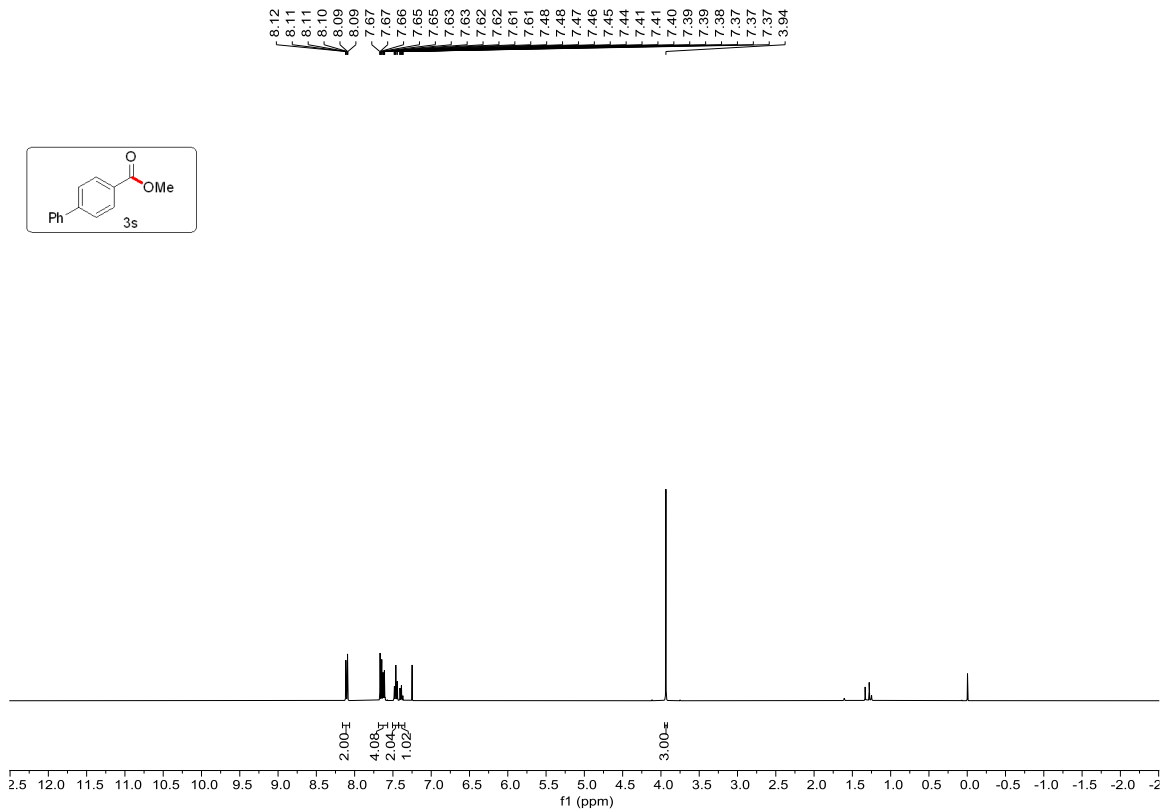
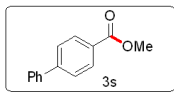
165.64
165.20
162.64
133.52
133.43
128.03
128.00
123.27
123.18
122.11
121.86
114.73
114.52

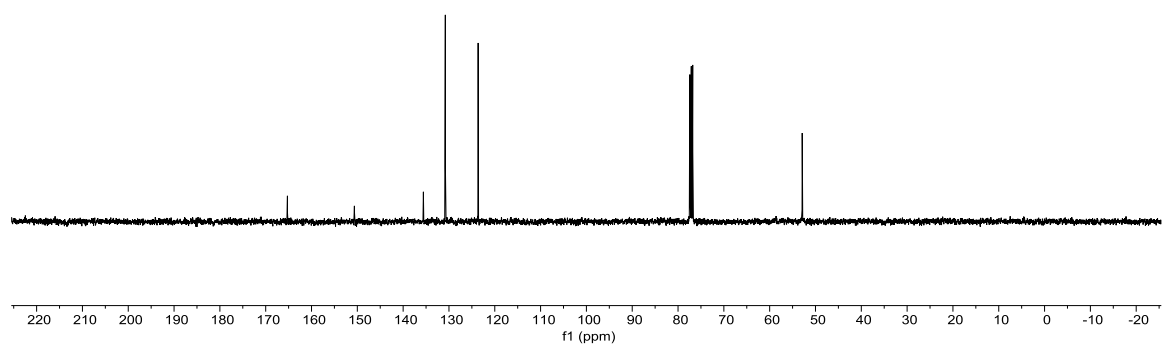
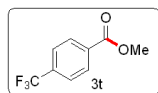
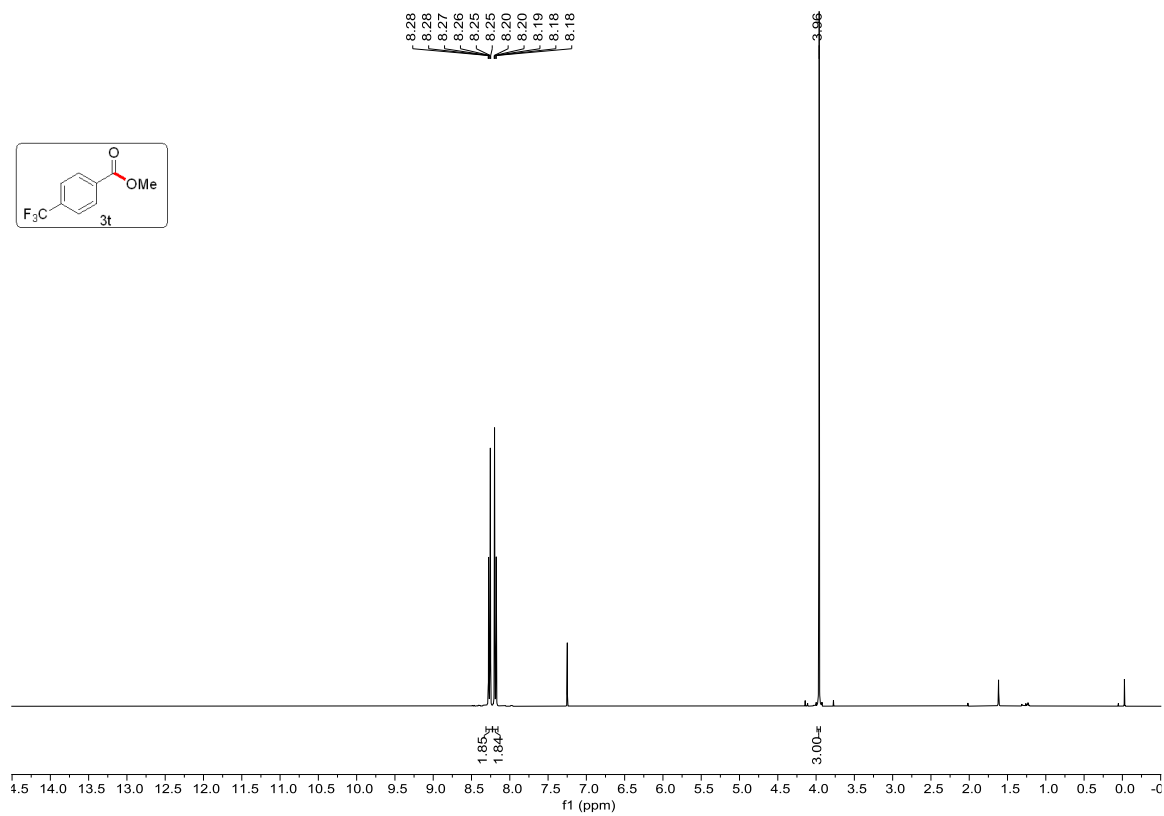
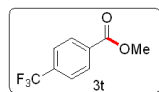
52.62

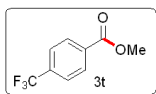


-105.69

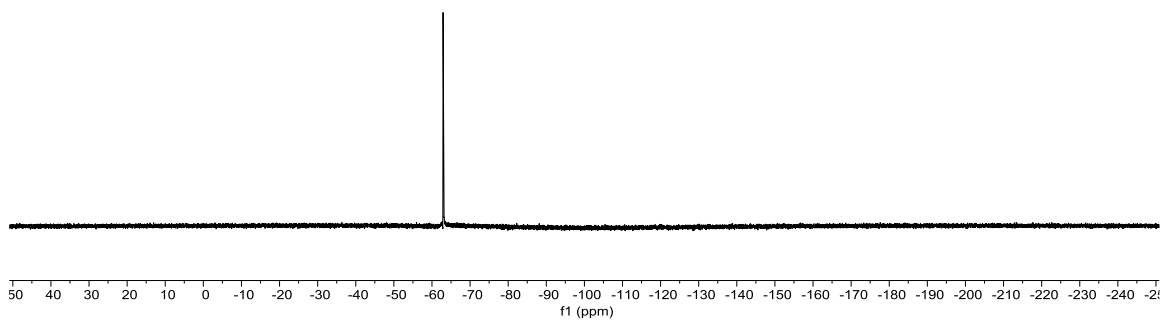


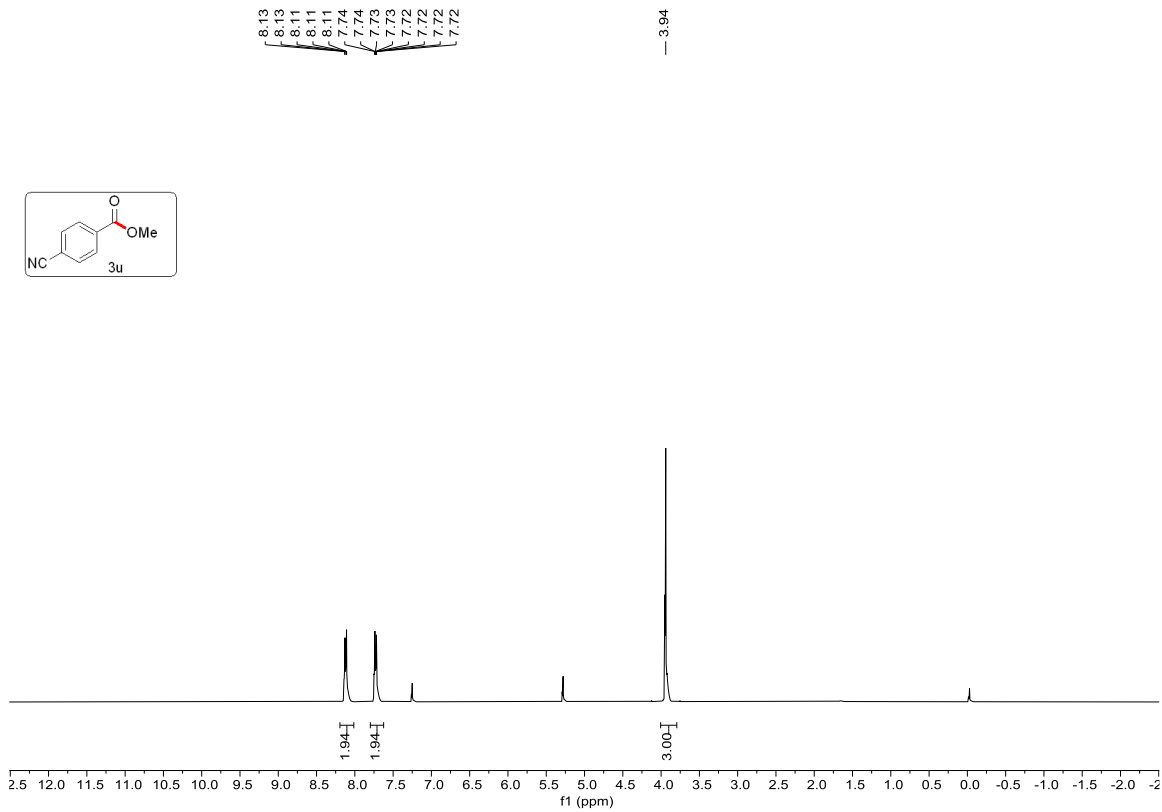
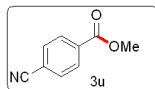




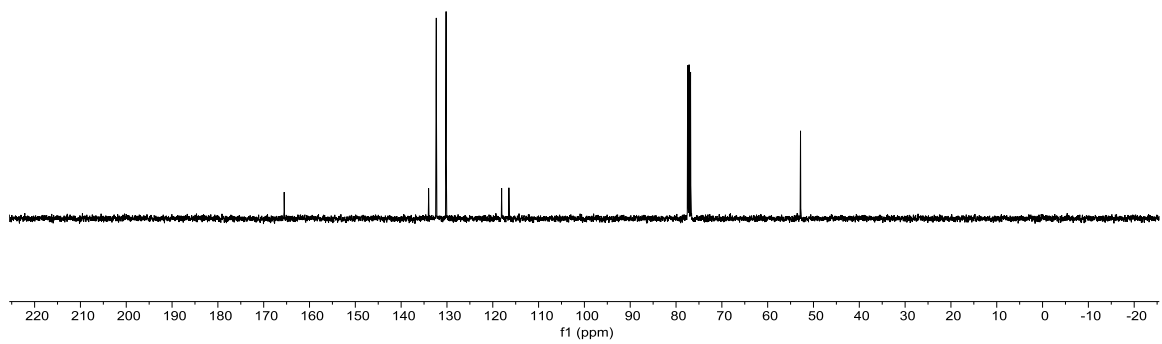
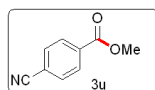


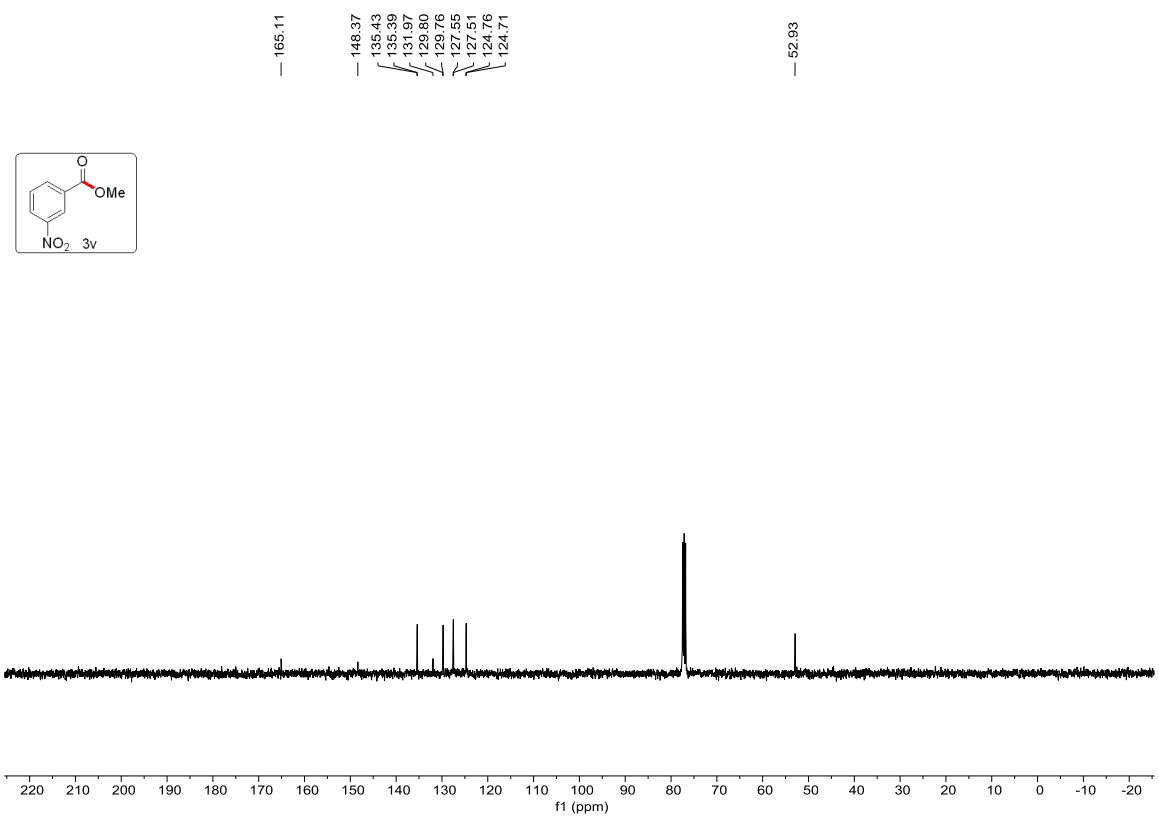
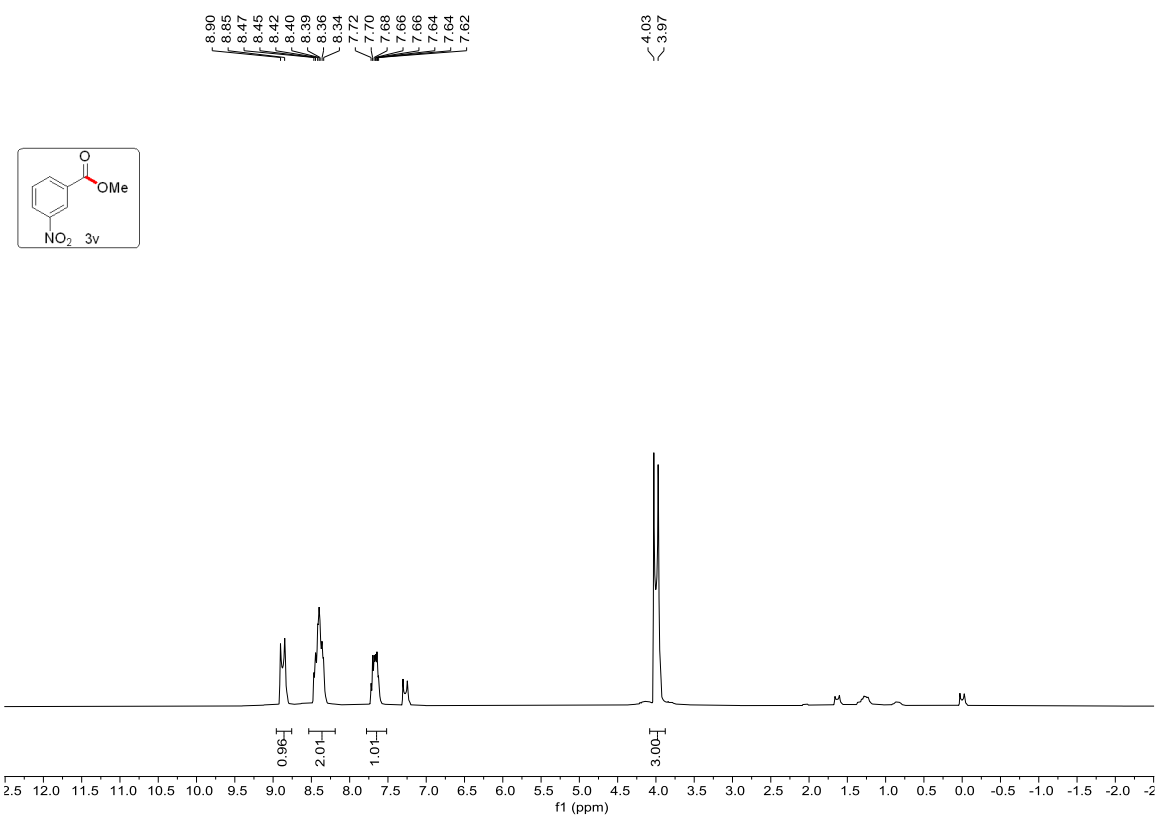
—62.91

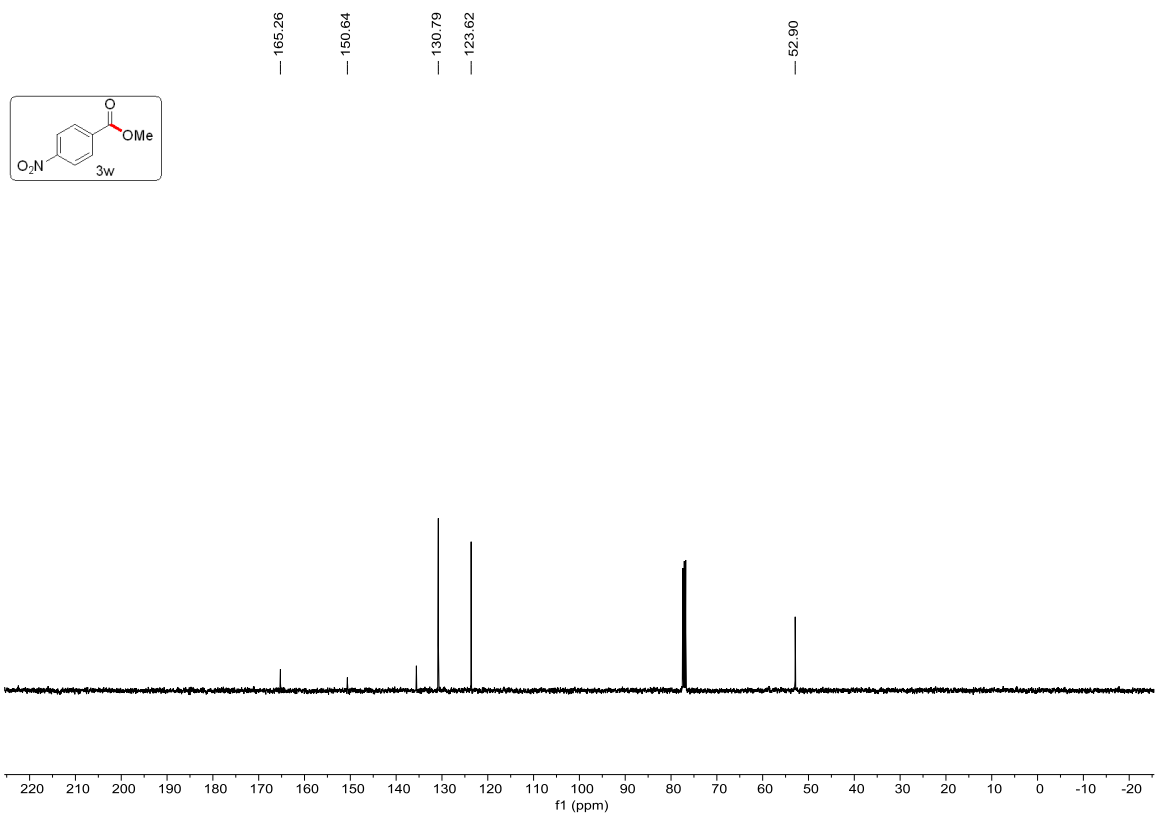
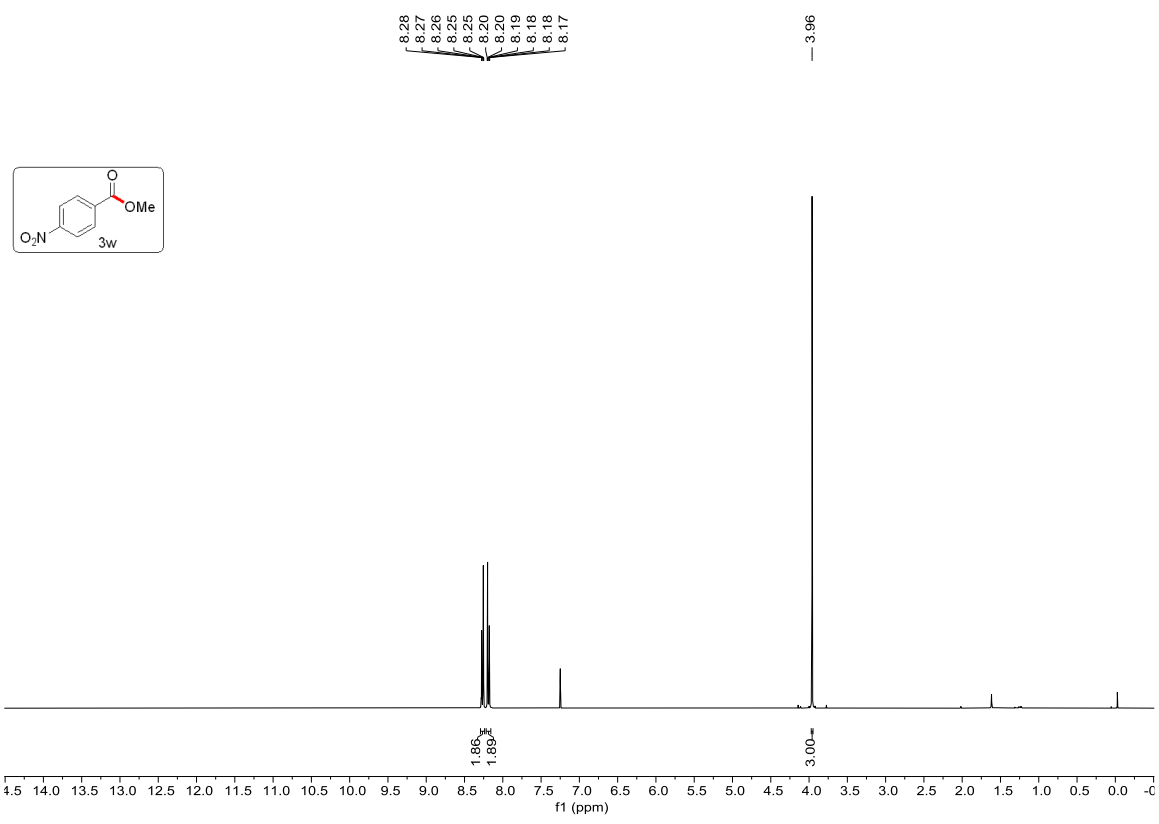


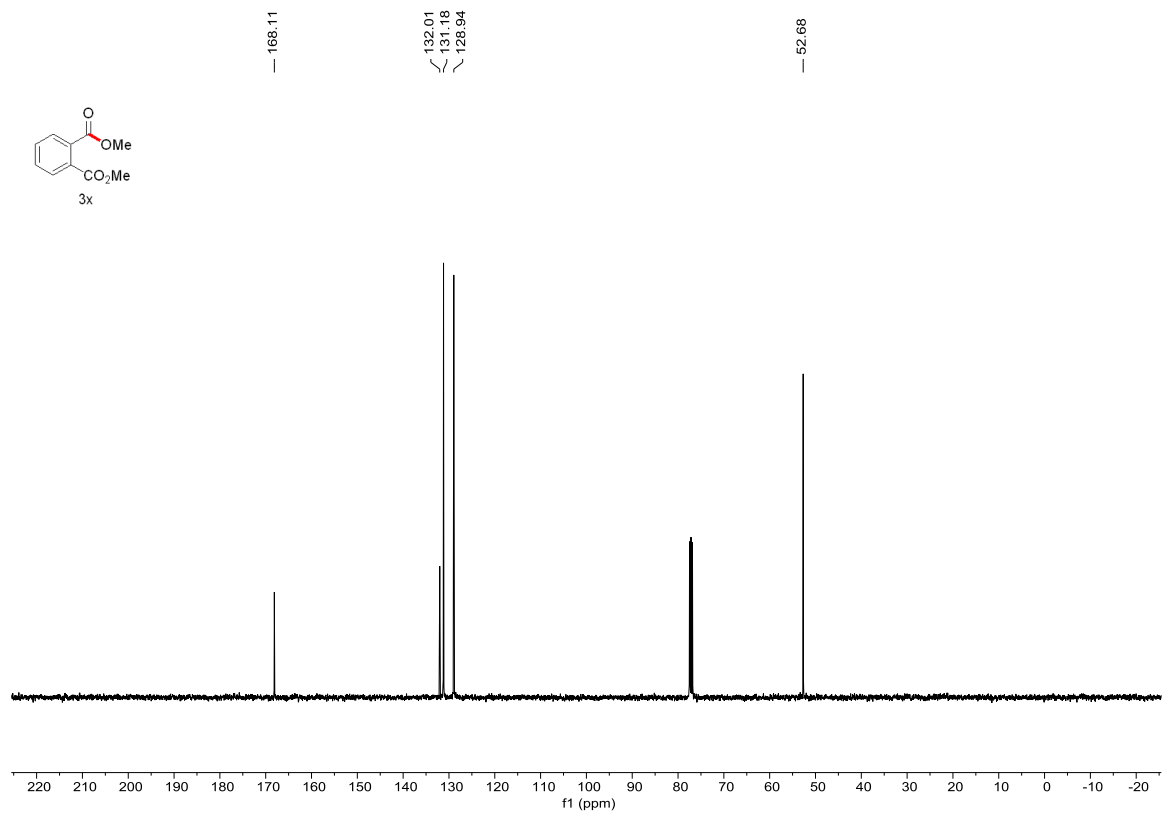
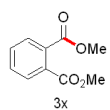
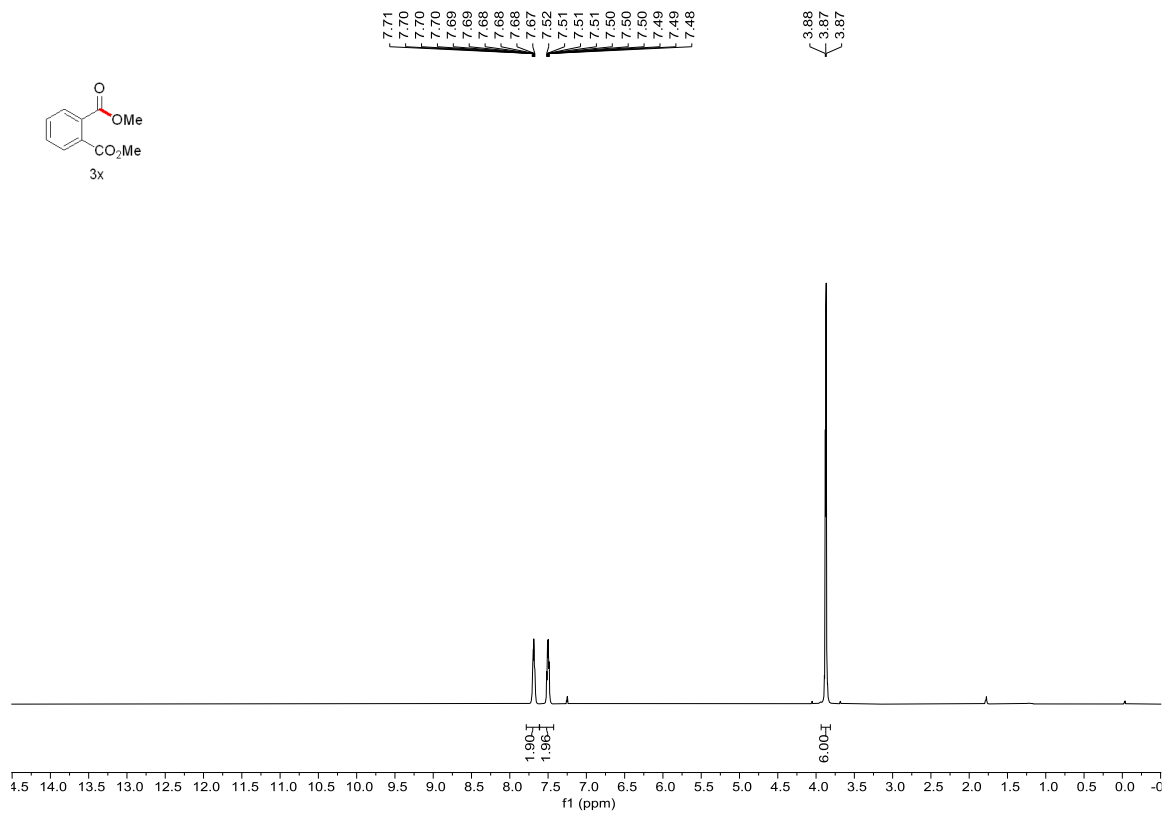
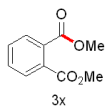


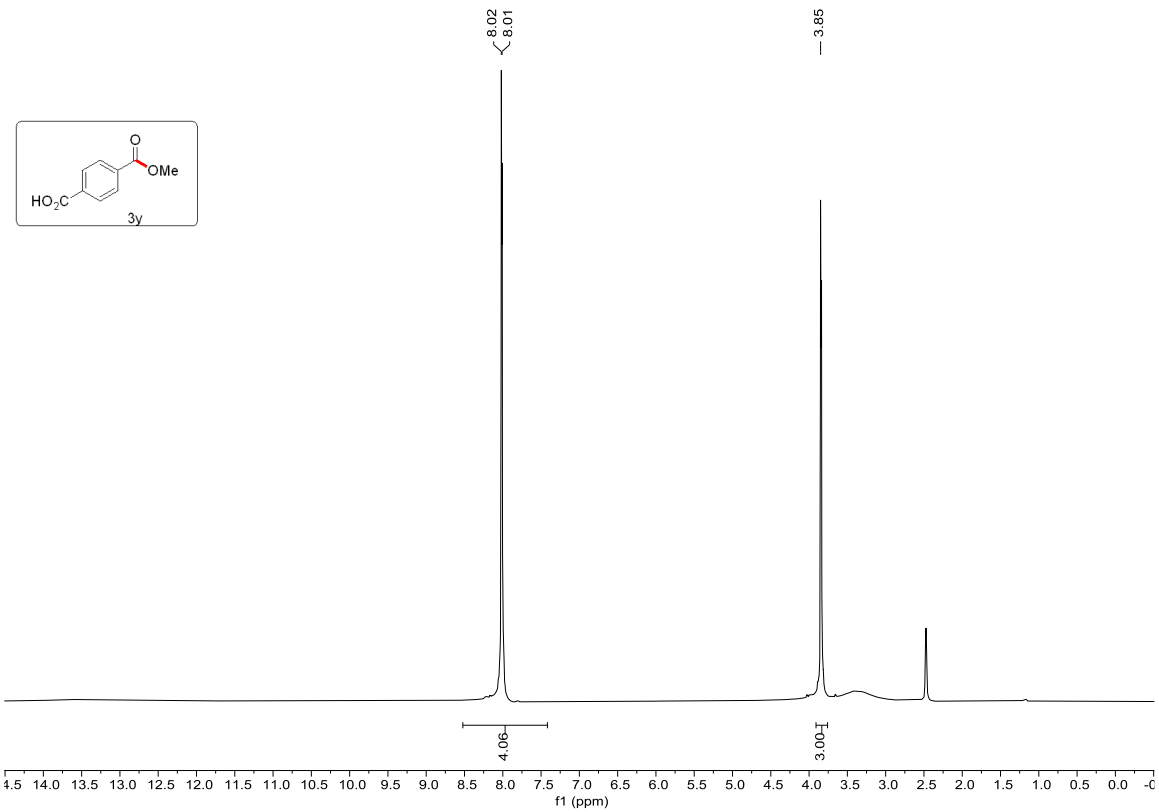
Chemical shifts (ppm): 165.53, 134.01, 132.32, 130.19, 118.07, 116.48, 52.83







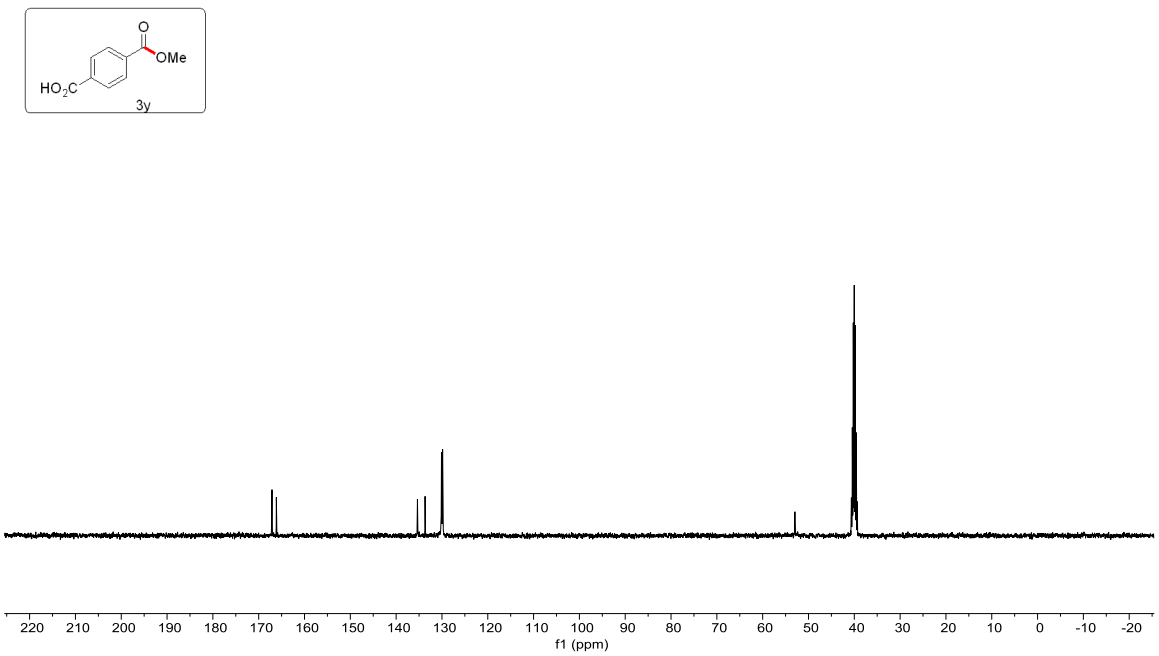


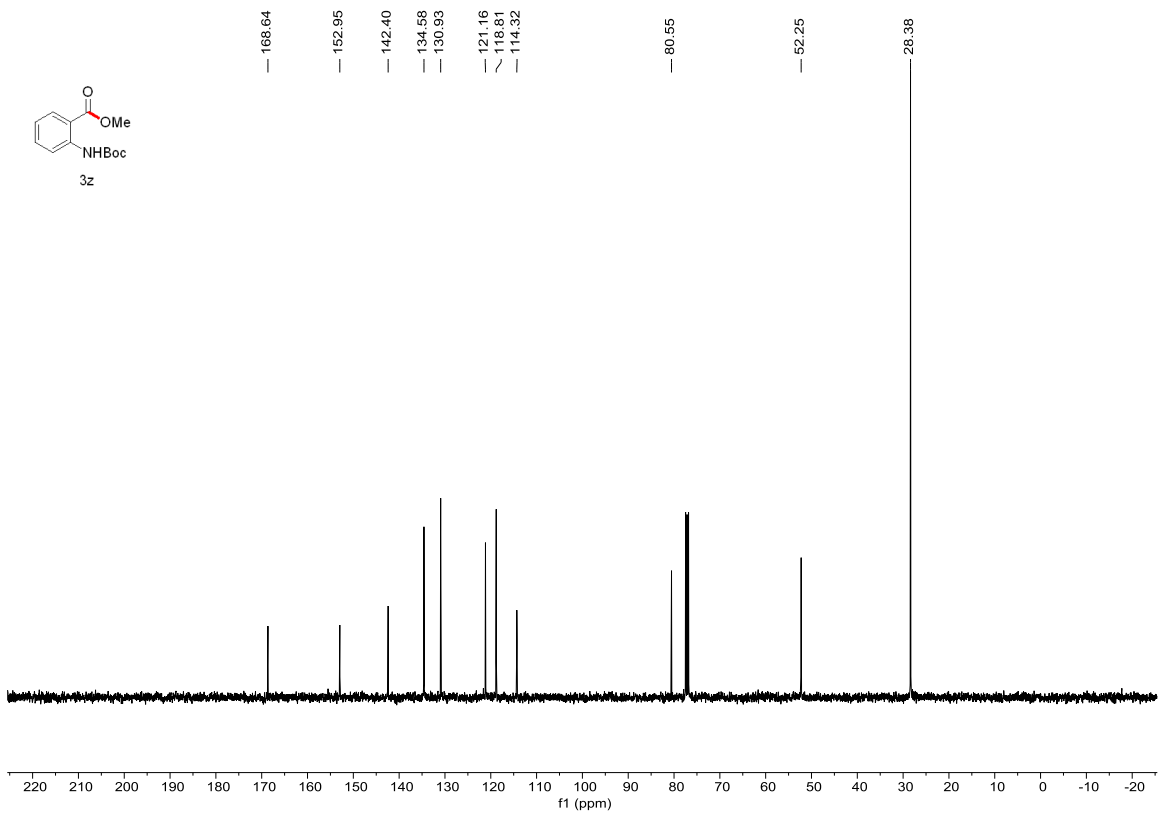
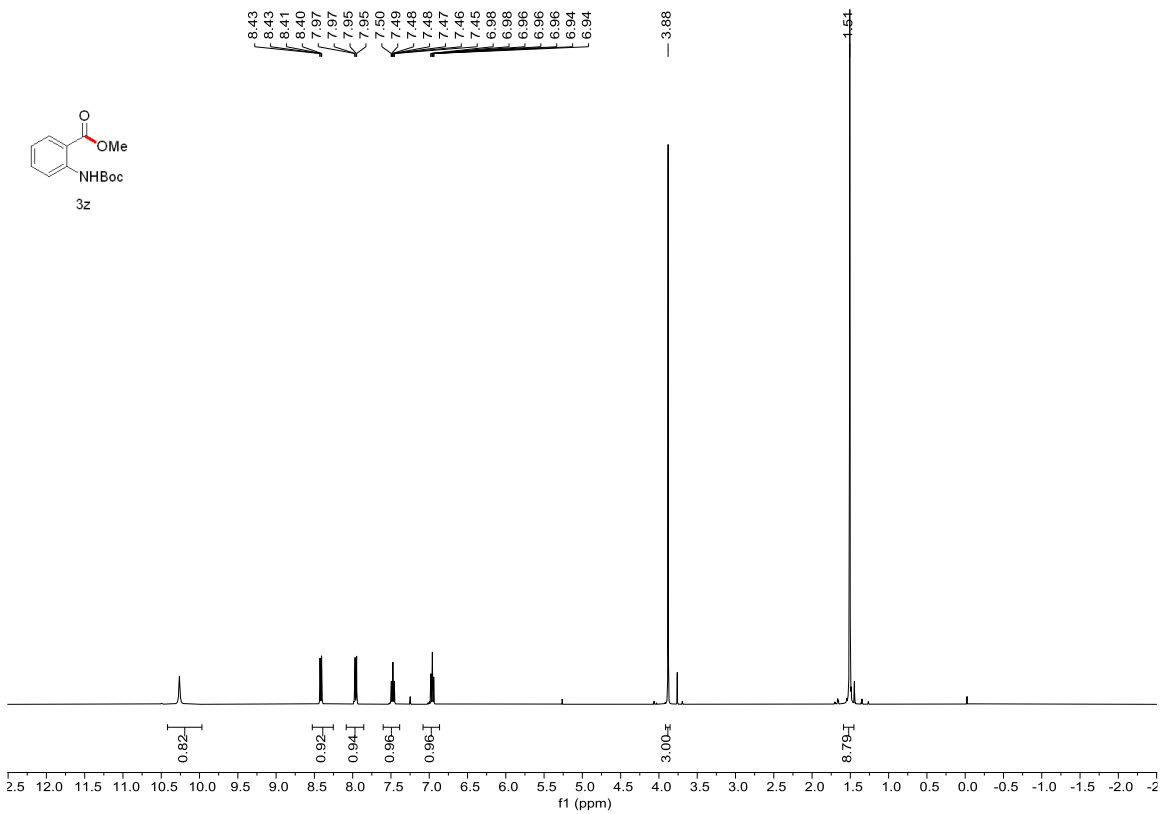


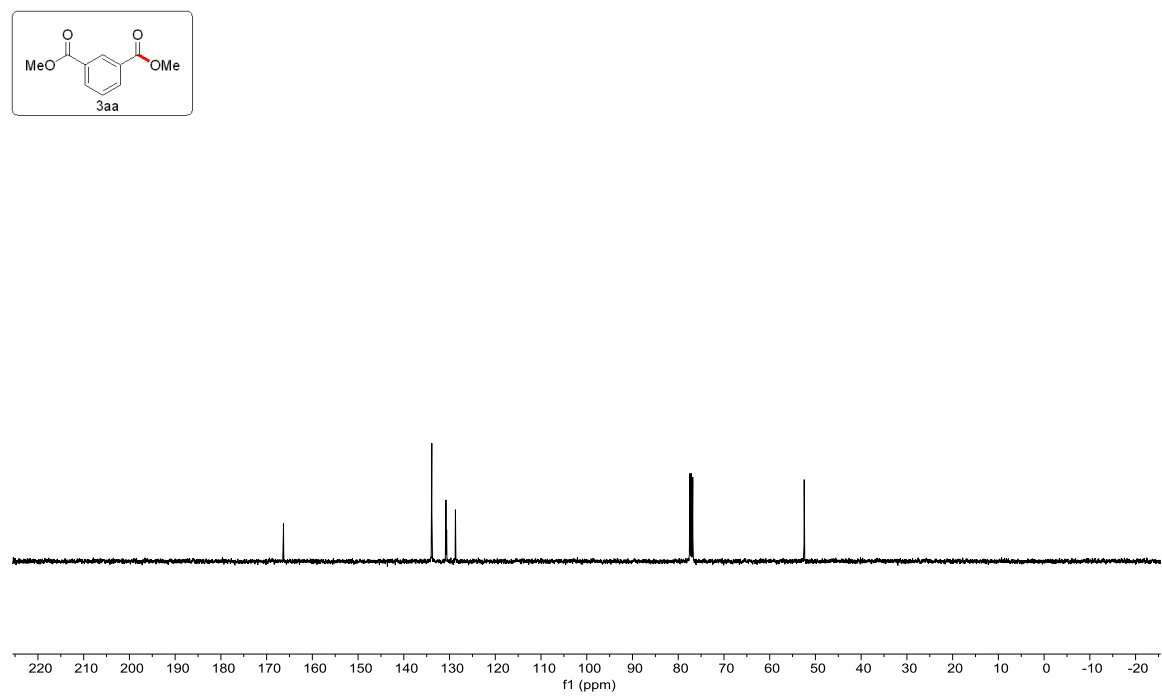
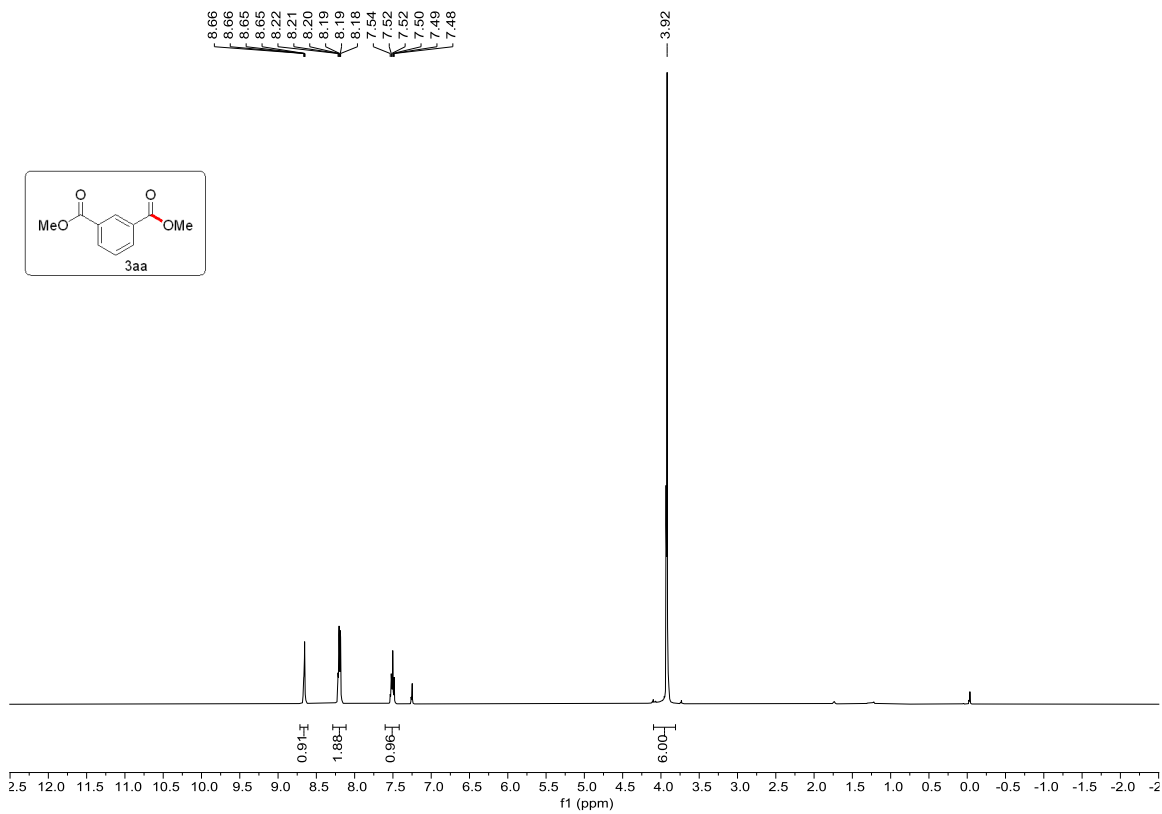
167.09
166.15

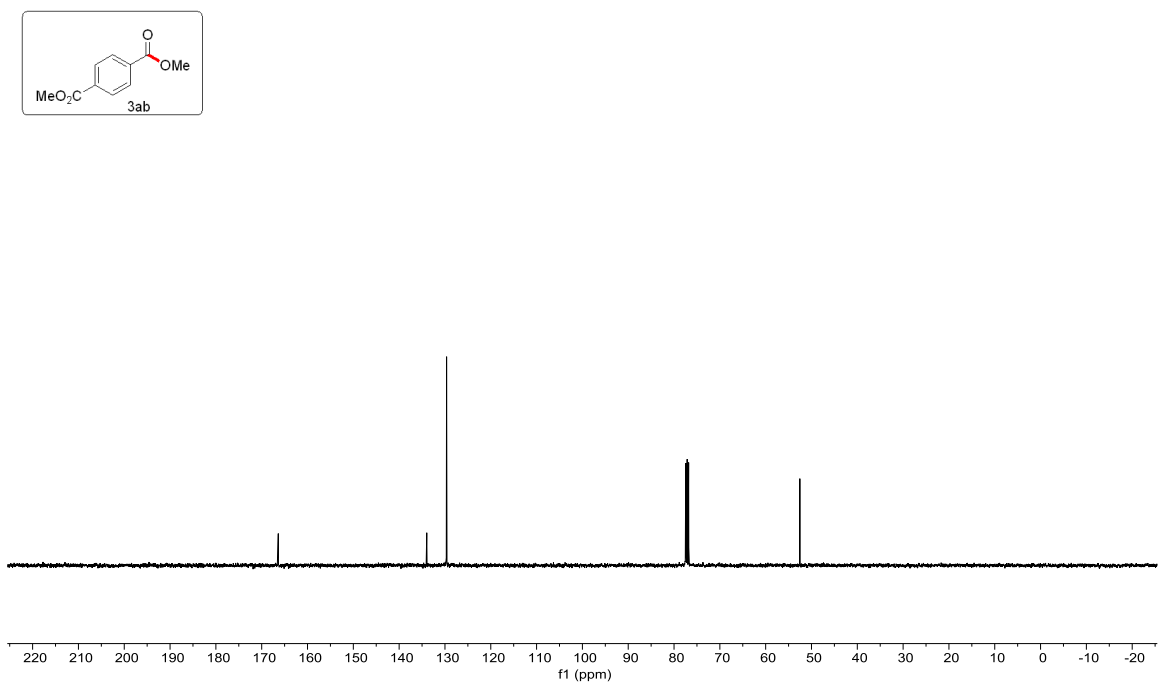
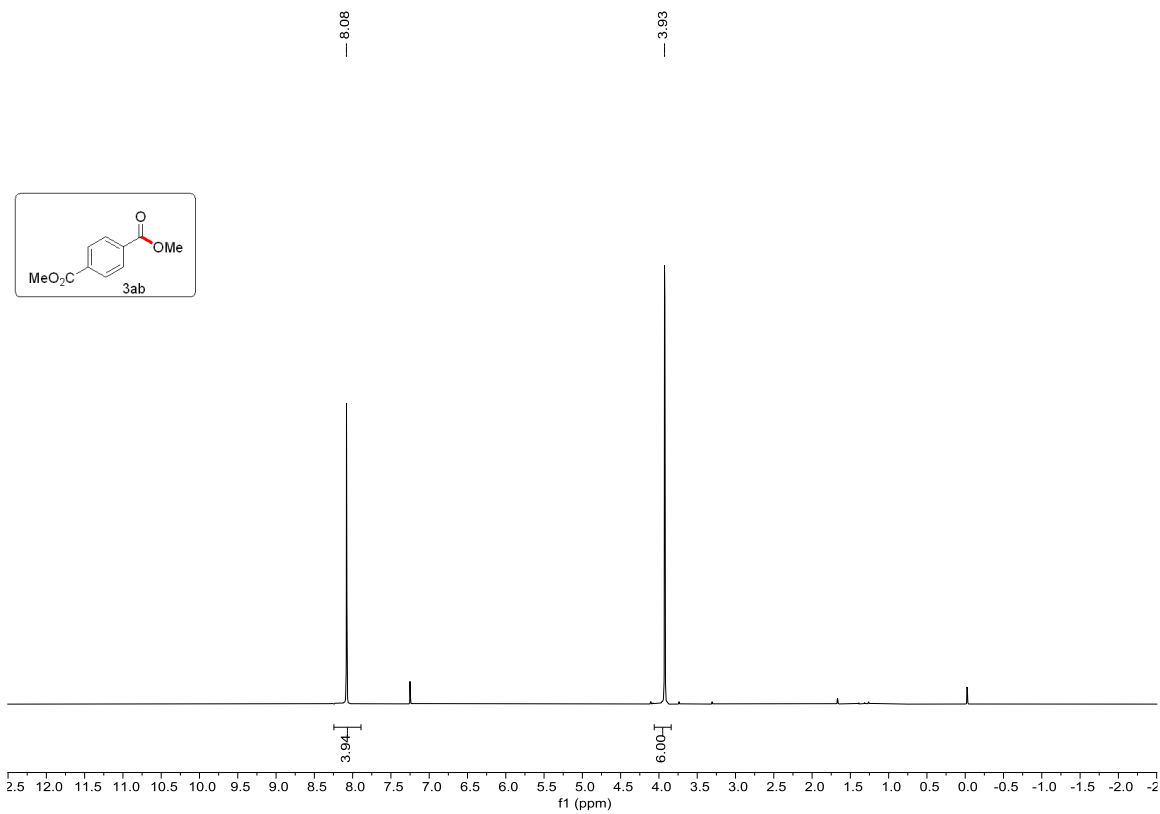
135.35
132.68
130.66
129.66

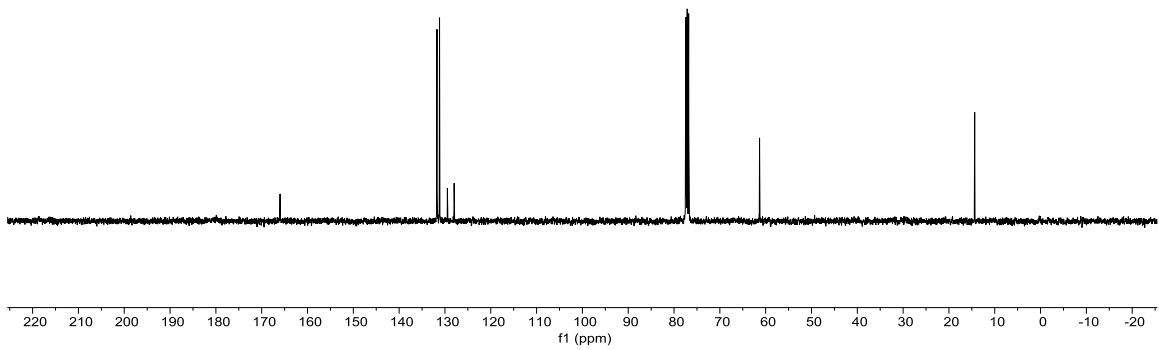
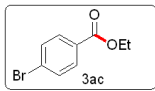
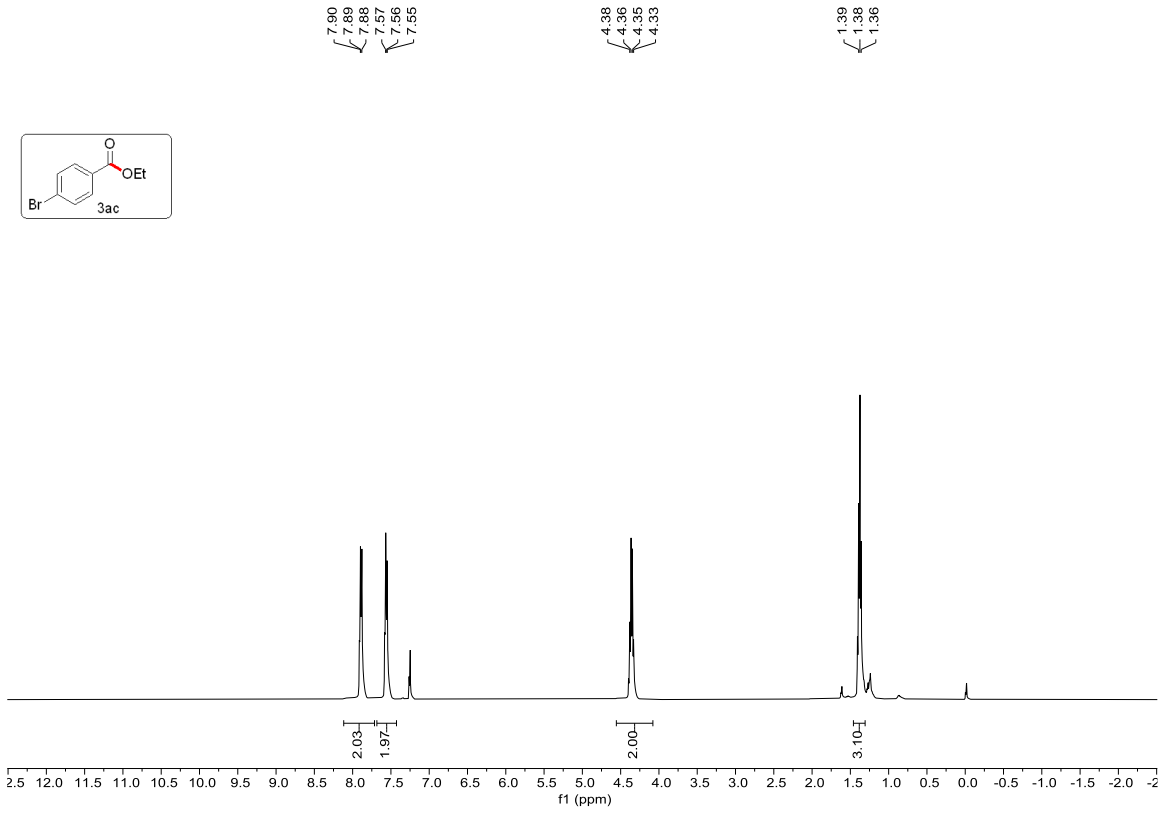
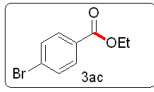
52.96

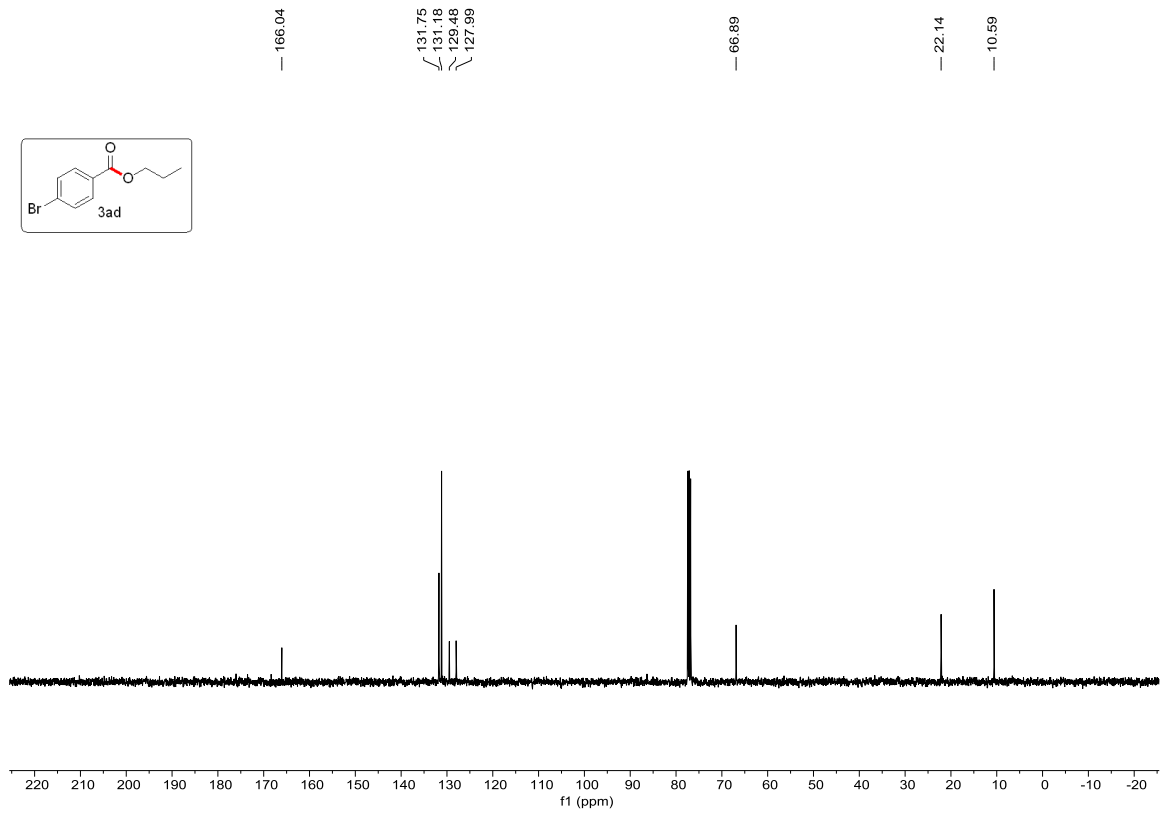
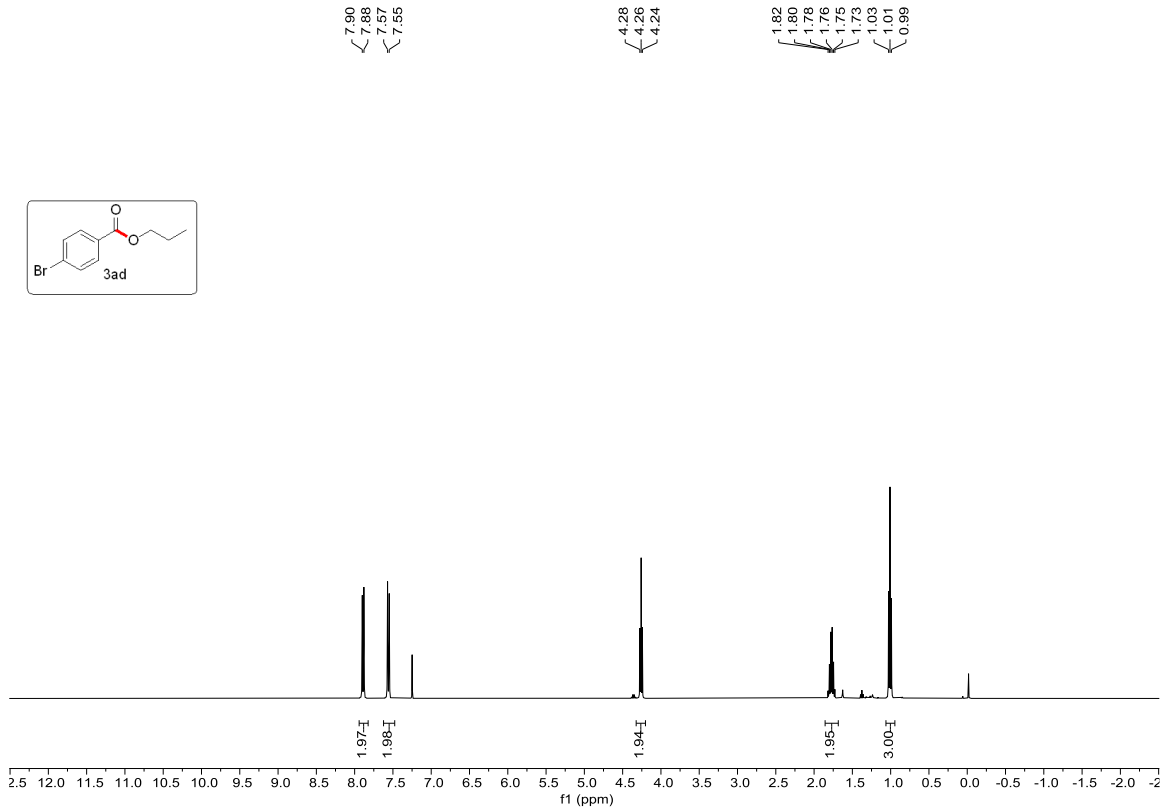
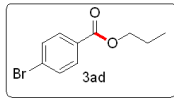


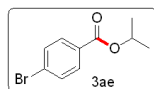
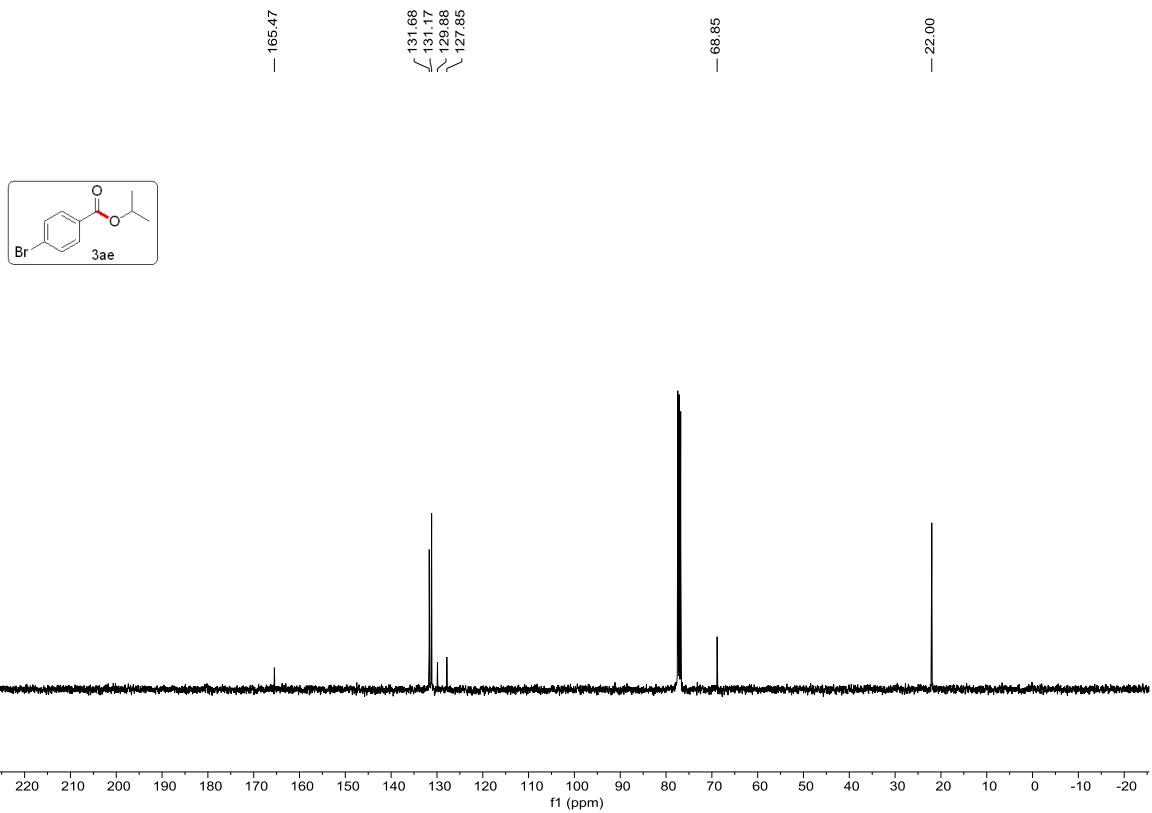
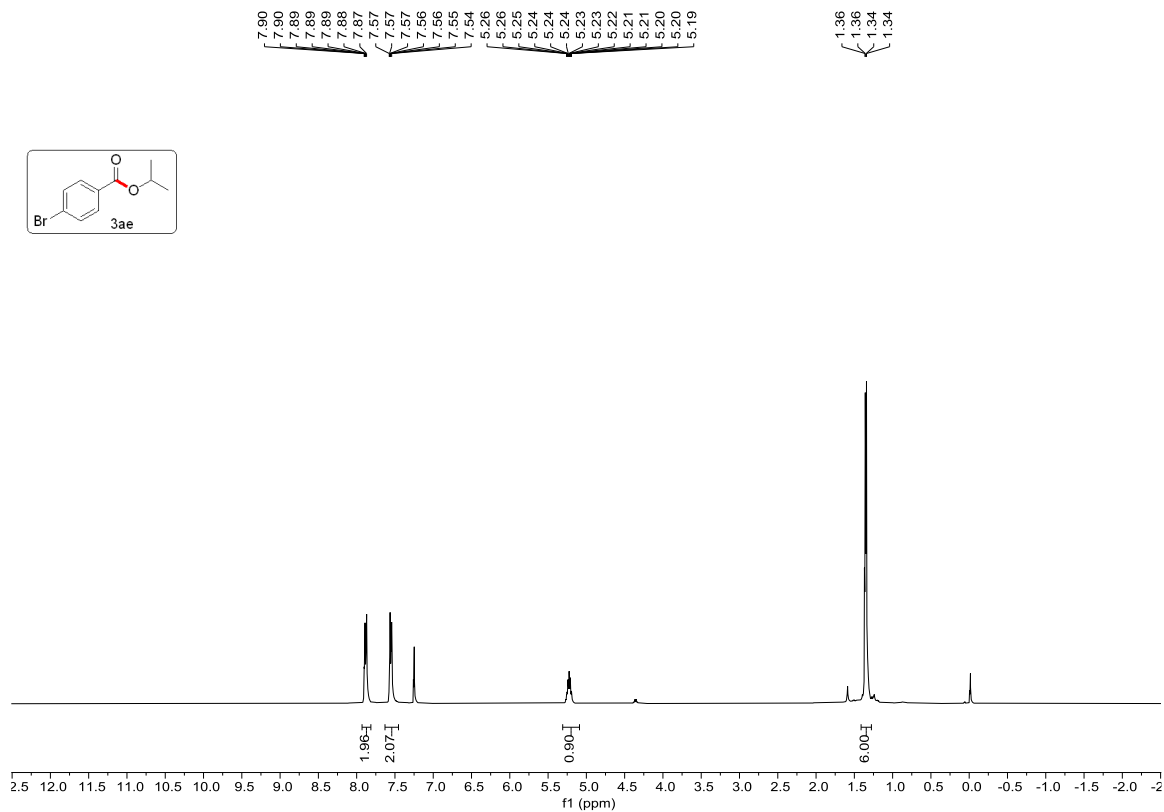
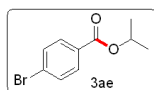


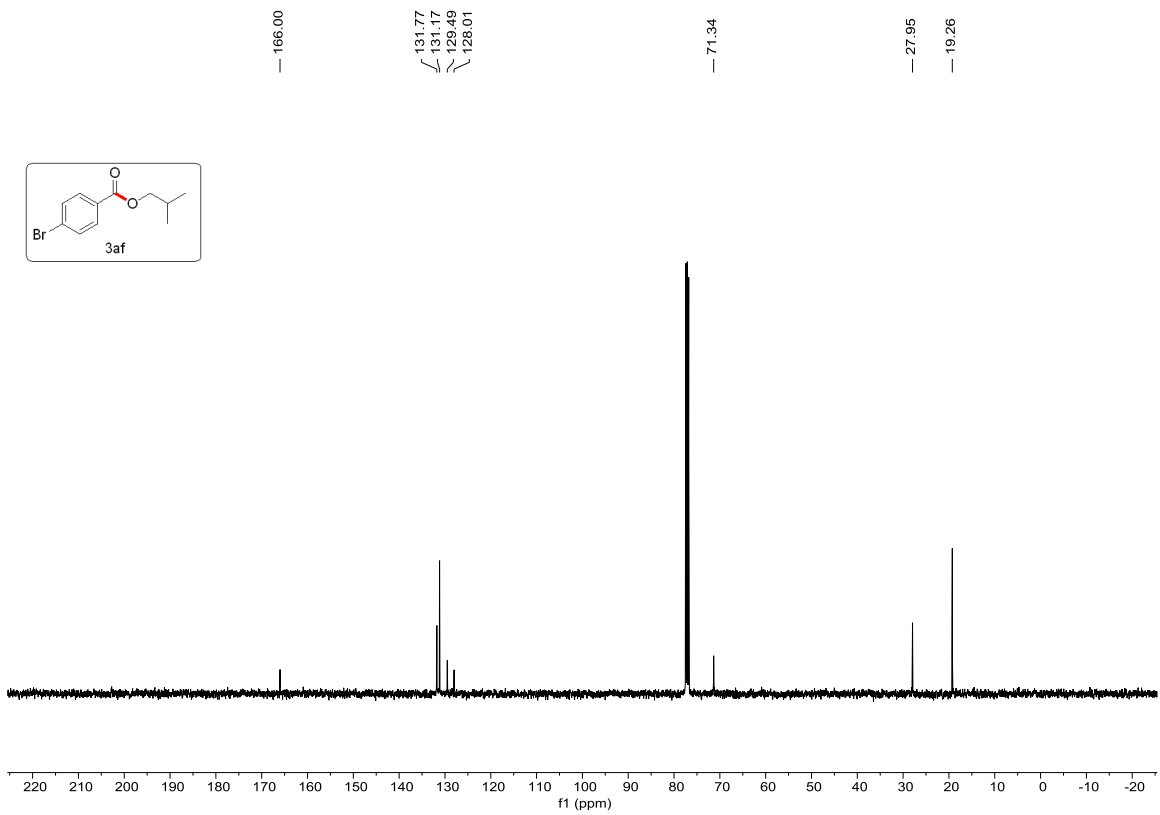
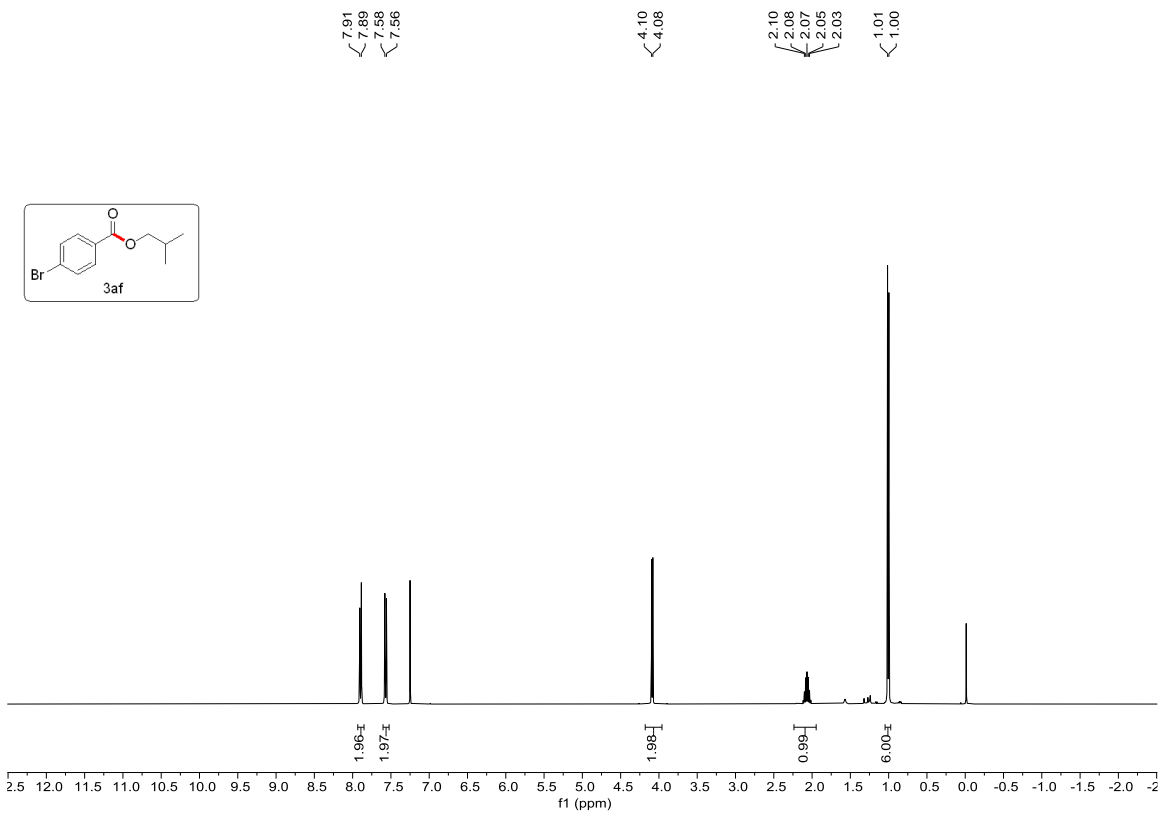


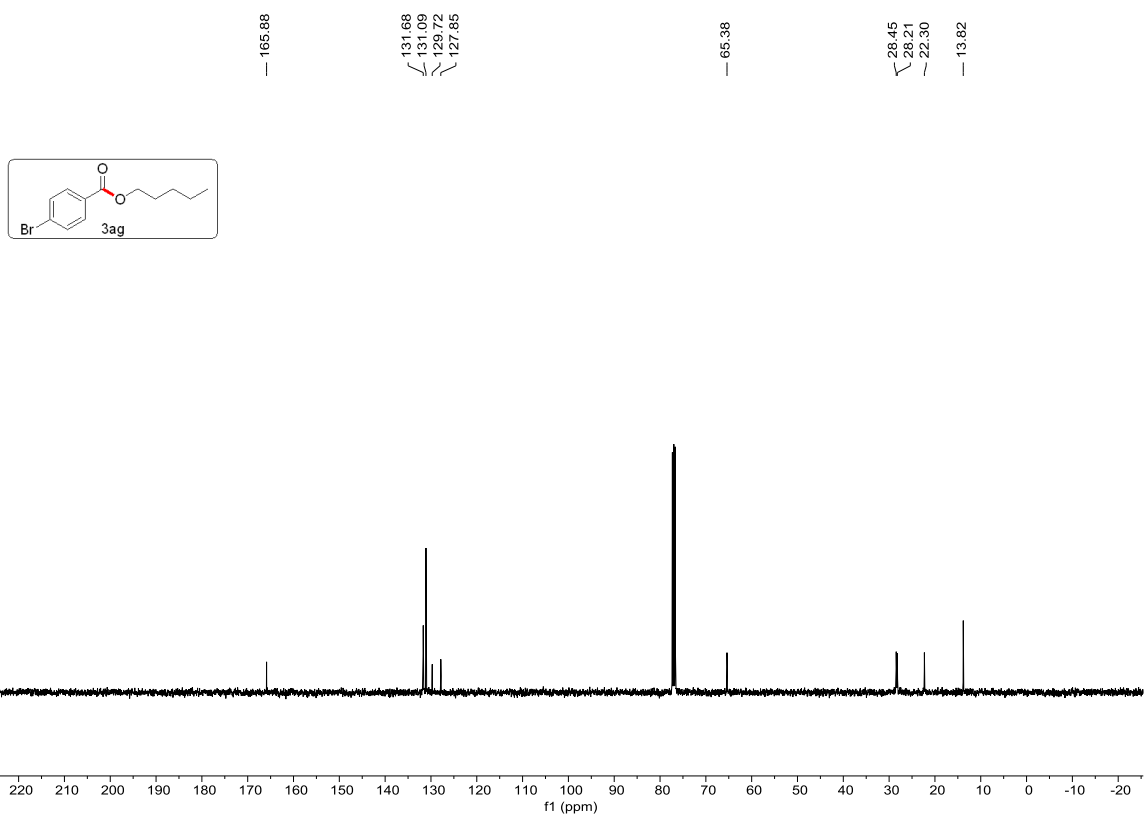
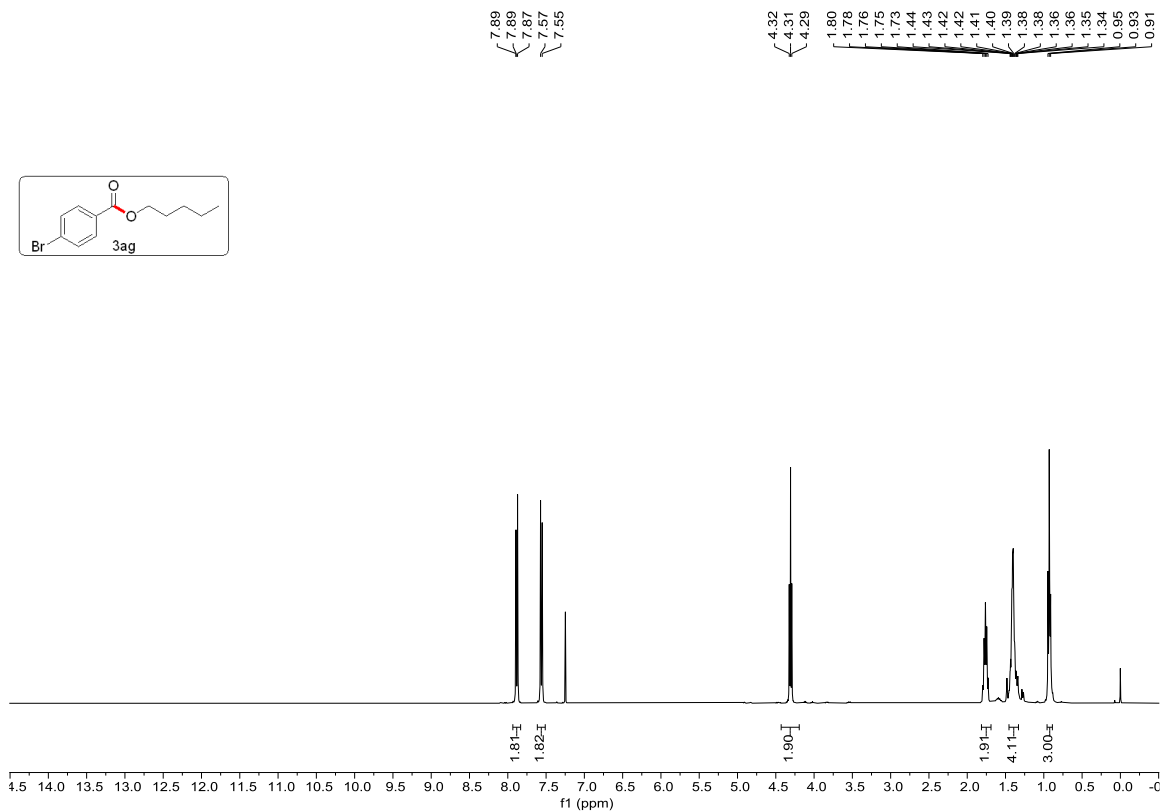
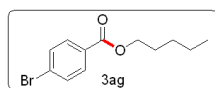


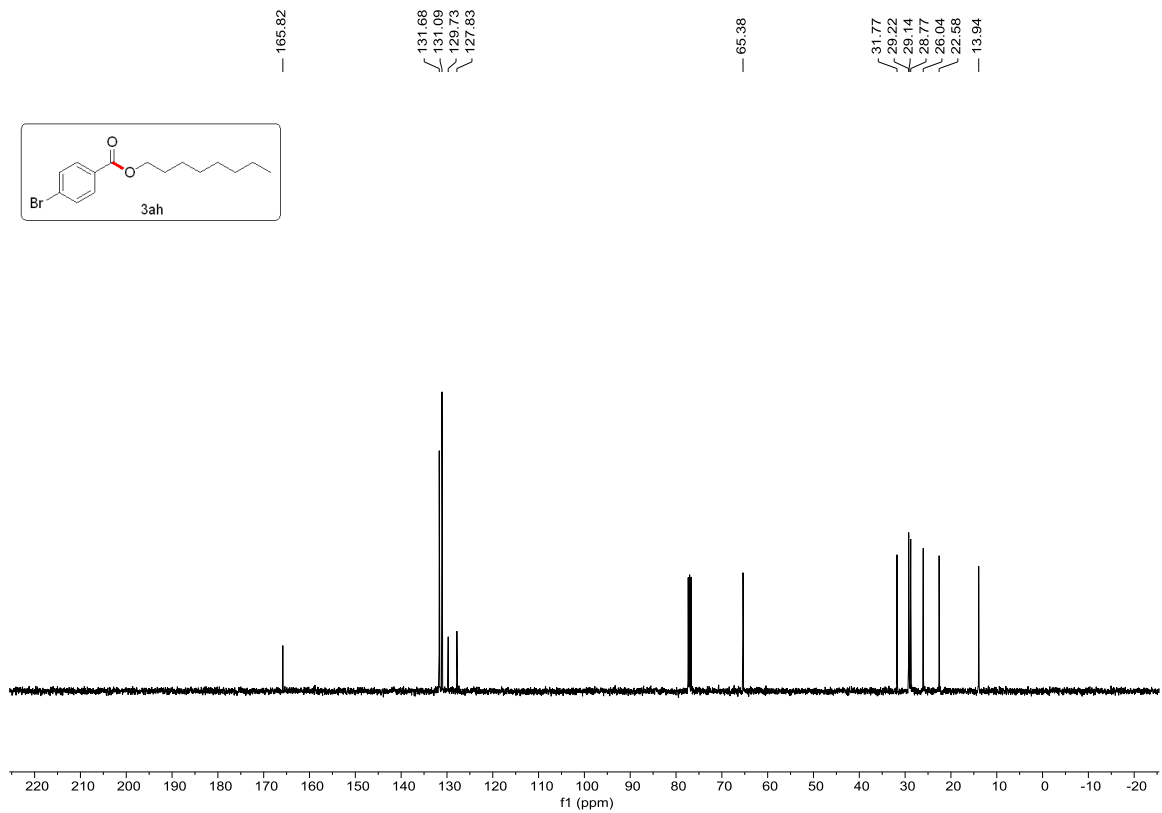
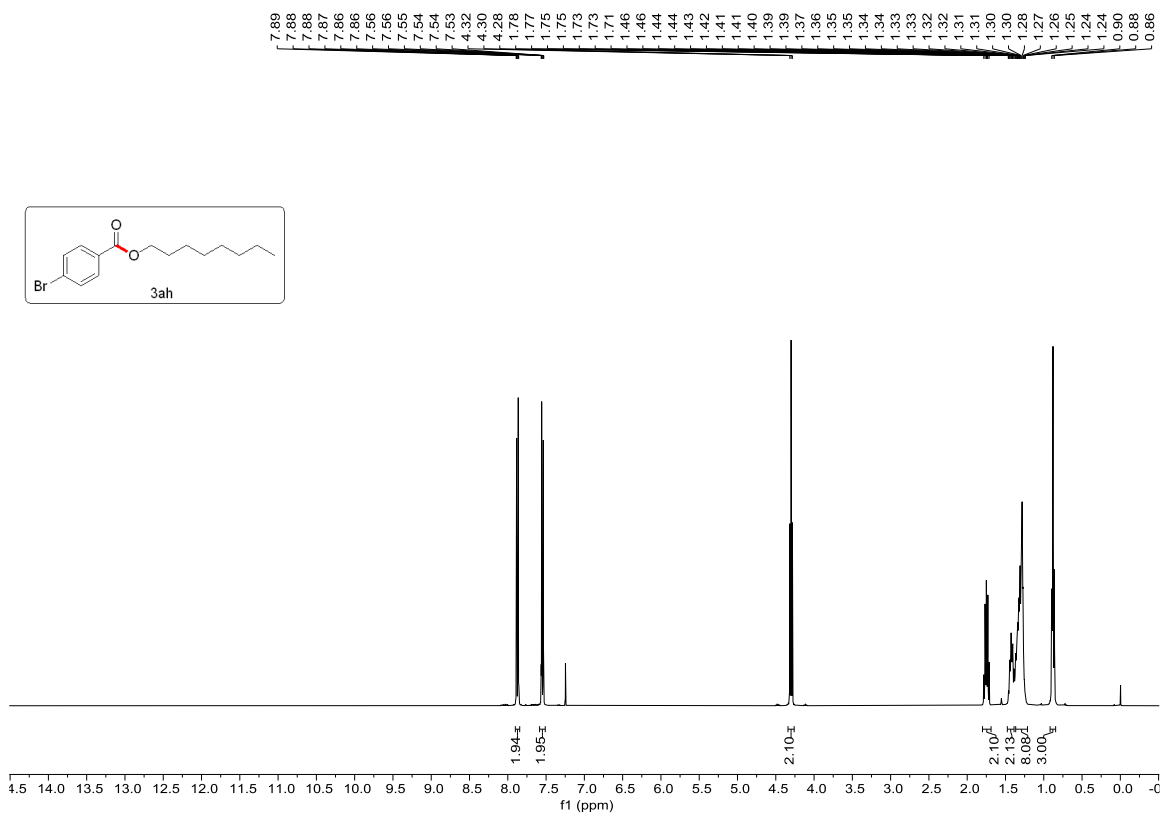


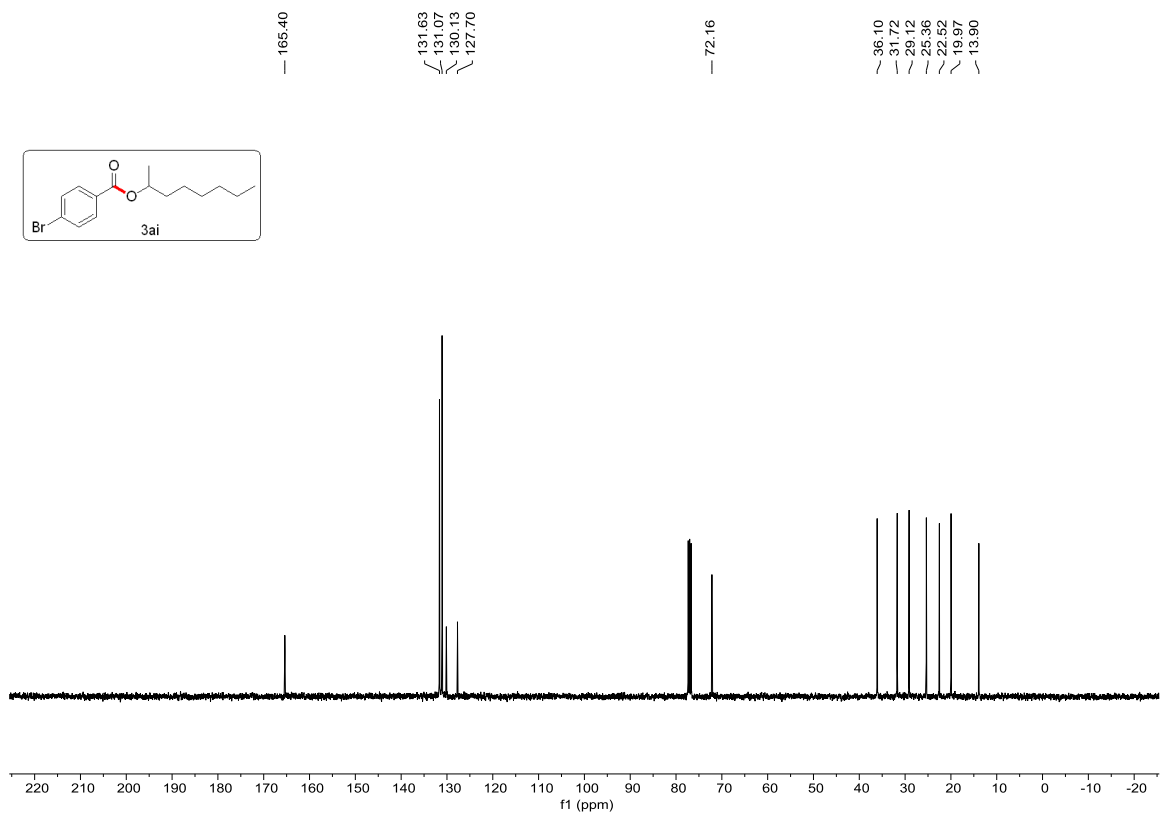
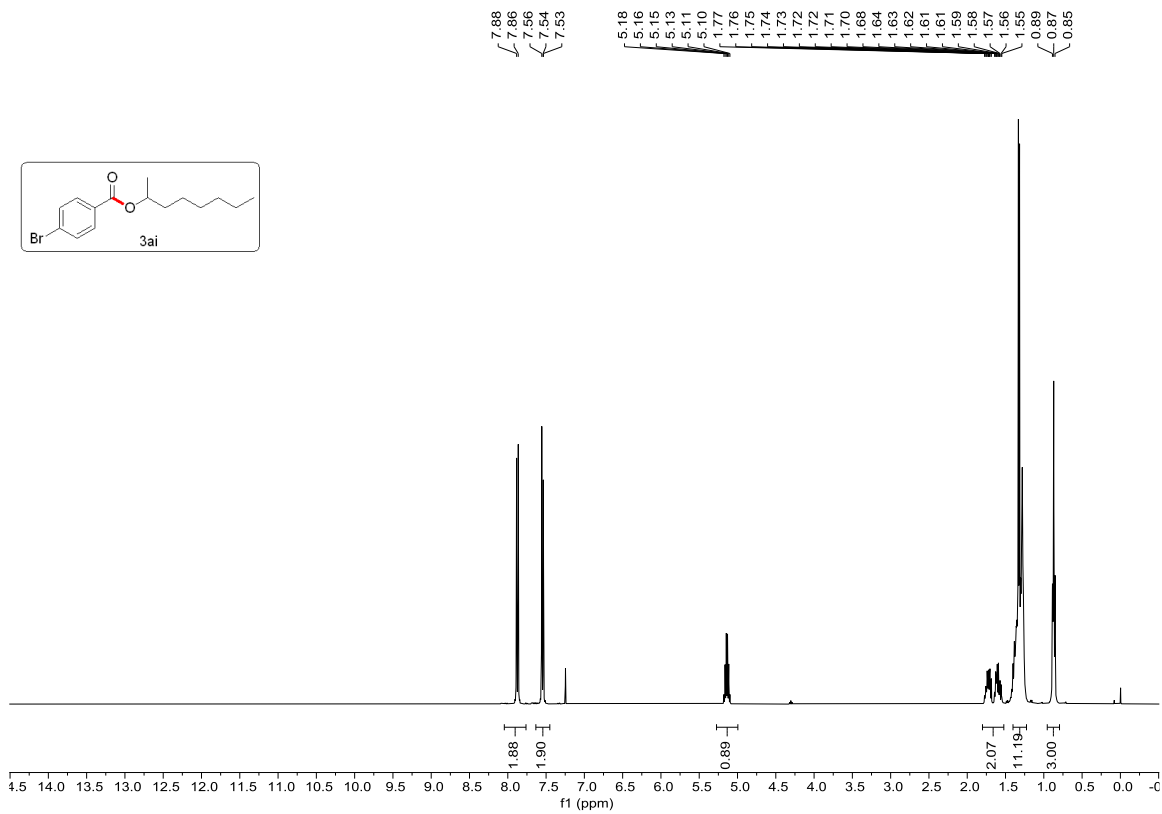


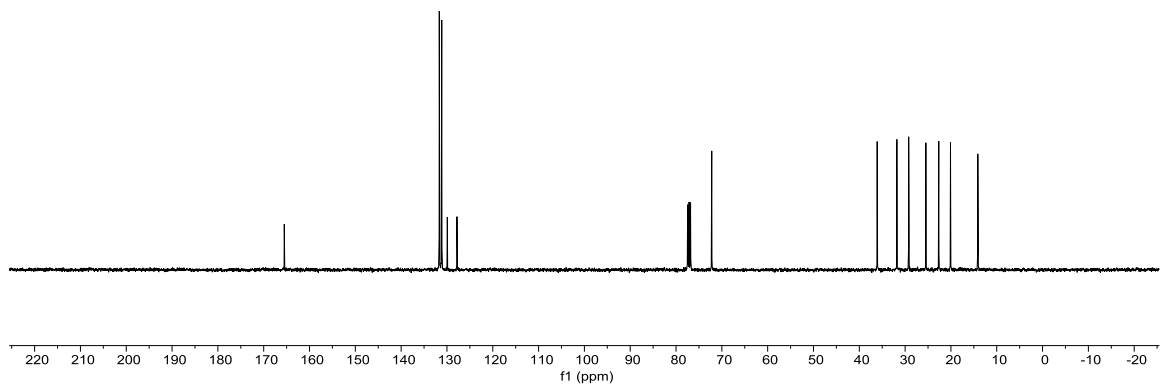
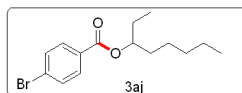
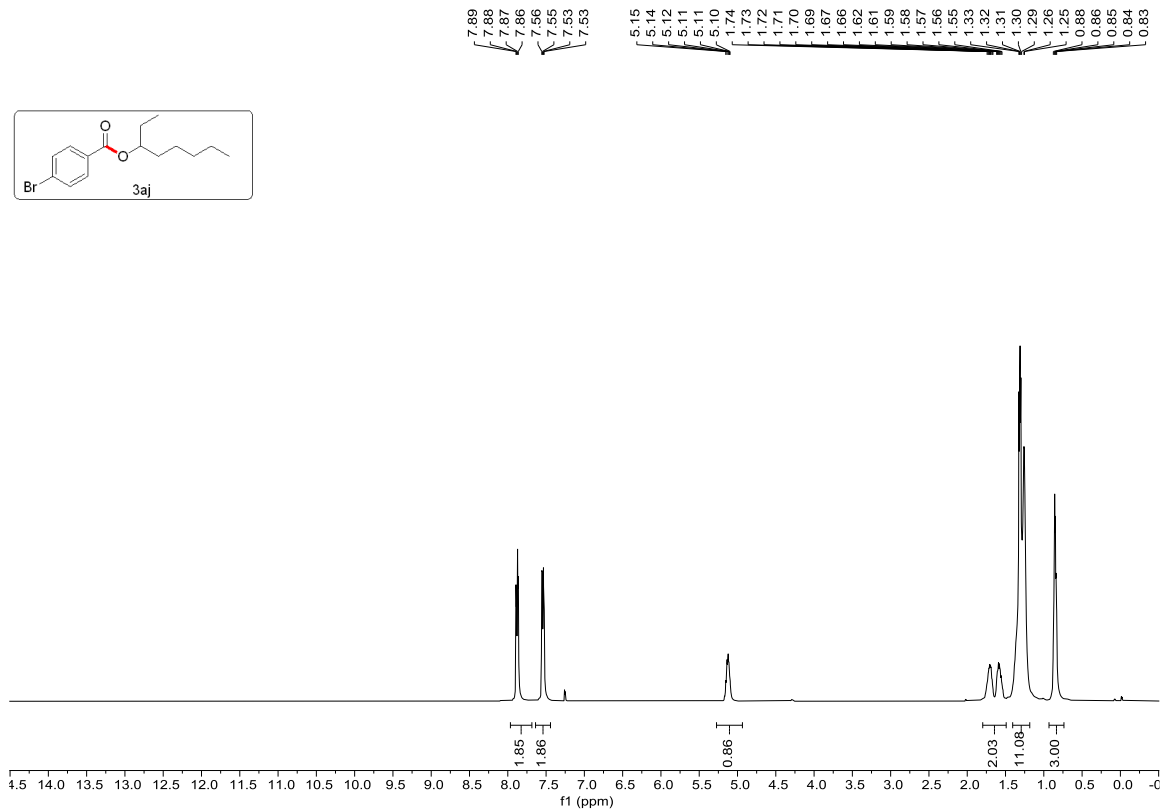
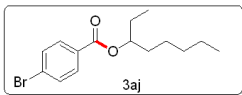


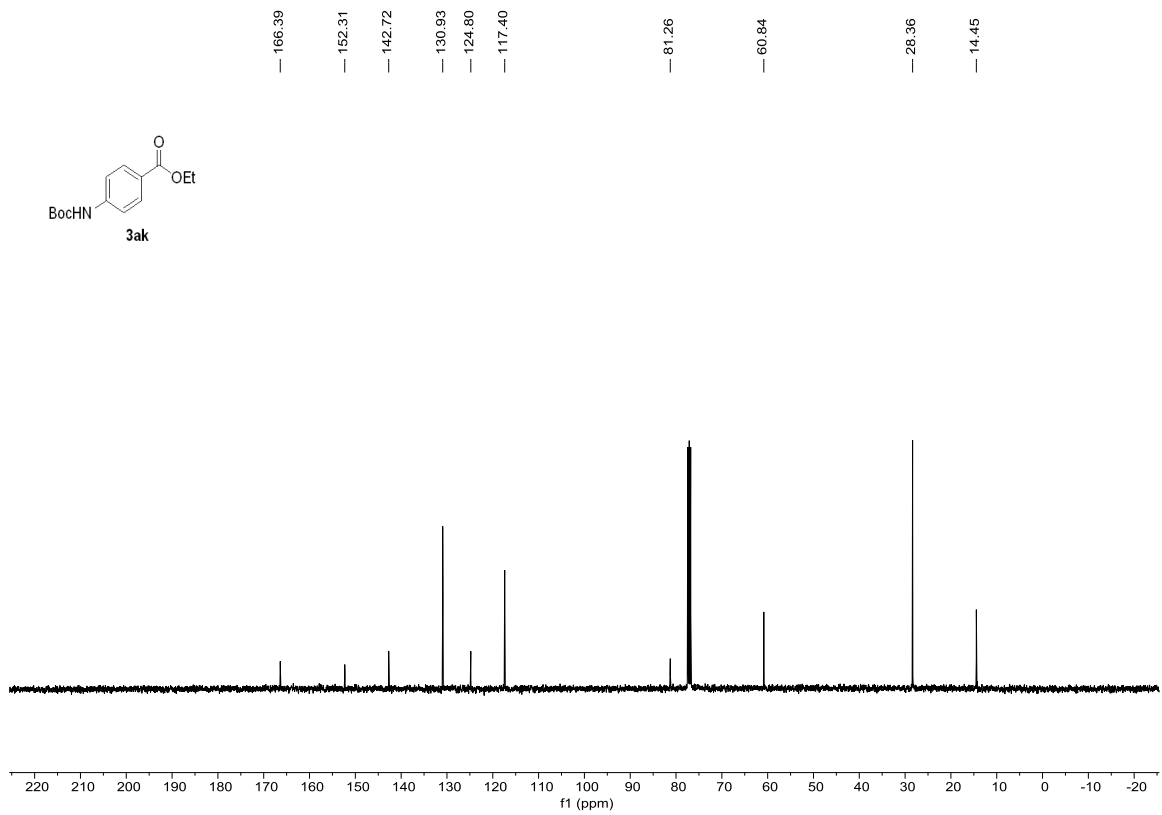
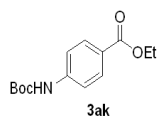
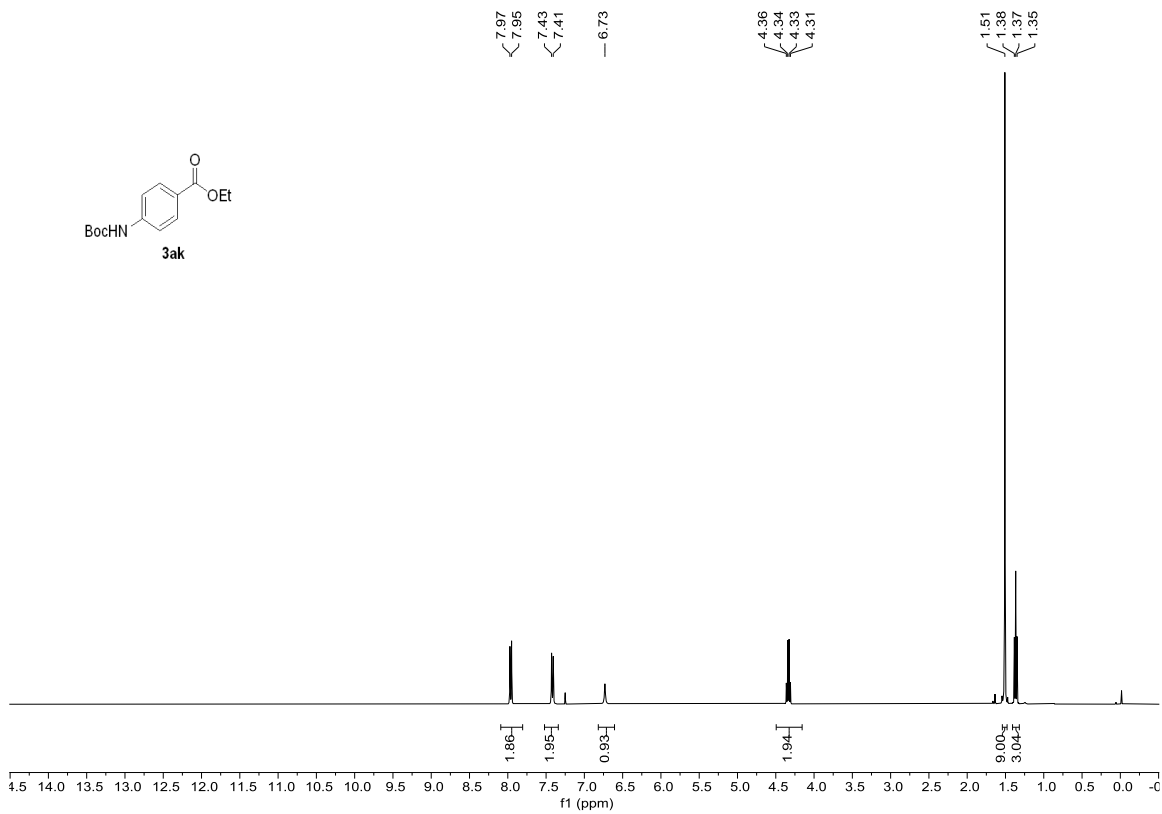
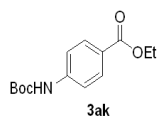


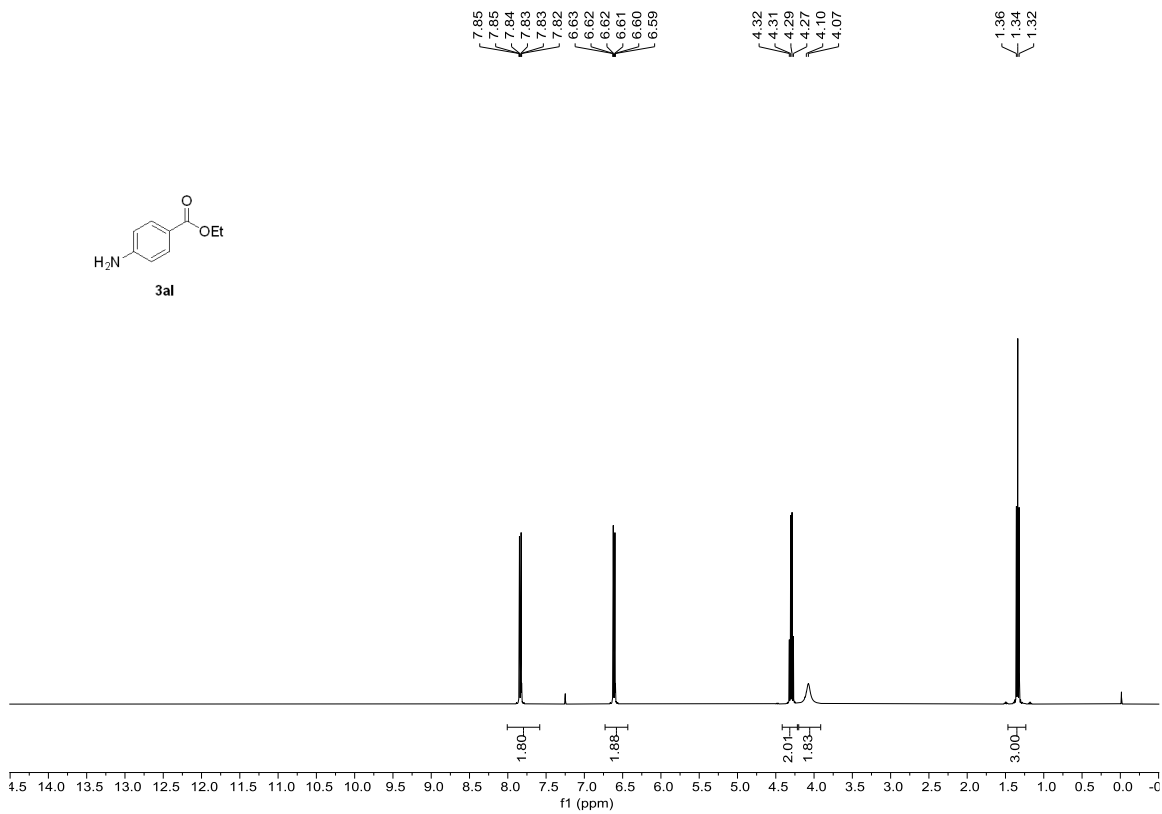
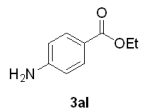












— 166.87
 — 150.97
 — 131.64
 — 120.04
 — 113.85
 — 60.41
 — 14.51

