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Supporting Information for:

Practical In-situ-generation of Phosphinite Ligands for Palladium-catalyzed Carbonylation of (Hetero)aryl Bromides Forming Esters

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Abstract: An effective method for alkoxycarbonylation of (hetero)aryl bromides is developed in the presence of *in-situ*-generated phosphinite ligands $^tBu_2POR$ (R = ^nBu, ^nPr, Et or Me). For this purpose commercially available $^tBu_2PCl$ was used as the pre-ligand in the presence of different alcohols. Under optimal conditions, structurally diverse aryl bromides were transformed to the corresponding ester in good yields. For the first time cross coupling reactions with two alcohols – one generating the ligand, the other used as substrate - were developed. Through this method, ligand optimization can be performed in a more efficient manner and the desired products could be obtained with good yields and selectivity. A stable dimeric palladium(II) complex $[Pd(4\text{-}MeOC_6H_4)(Br)(\mathbf{L2})]_2$ was obtained *via* oxidative addition of 4-bromoanisole to $Pd(0)(\mathbf{L2})_2$ (**L2** = $^tBu_2PO^nBu$), which was generated *in-situ*.

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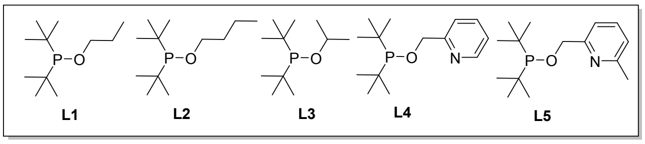
General Considerations

All chemicals were purchased from Sigma-Aldrich, Strem, Acros, TCI or Alfa Aesar and used as received unless stated otherwise. Alcohols and solvents (Anhydrous and under inert atmosphere) were collected from the solvent purification system and used under standard schlenk technique. Liquid bases were distilled under reduced pressure and stored under argon. NMR spectra were recorded on Bruker Avance 300 and Bruker ARX 400 spectrometers. Chemical shifts (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H NMR) and 77.00 ppm (^{13}C NMR); references for C_6D_6 were 7.15 ppm (^{1}H NMR) and 127.9 ppm (^{13}C NMR) Multiplets were assigned as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet) dd (doublet of doublet), m (multiplet) and br. s (broad singlet). Unless otherwise stated, yields refer to isolated yields, estimated to be >95% pure according to ^{1}H-NMR spectroscopy or GC. GC-yields were calculated using n-hexadecane as internal standard. All measurements were carried out at room temperature unless otherwise stated. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). Gas chromatography analysis was performed on an Agilent HP-7890A instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using argon as carrier gas. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck). Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by direct methods (SHELXS-97) [1] and refined by full-matrix least-squares procedures on F^2 (SHELXL-2014) [2].

Experimental Sections

1. Synthesis and characterization of phosphinite ligands.

1.1 General procedure for synthesis of **L1** – **L3**


L1 **L2** **L3** **L4** **L5**

The procedure to synthesize **L1** and **L2** is according to the literature [3]. More specifically, sodium (276.0 mg, 12 mmol) was added into n-propanol or n-butanol (20 mL) in a 100 mL Schlenk tube under an atmosphere of argon. The mixture was kept stirring until sodium completely dissolved in alcohol. The solvent was removed under high vacuum to afford white solid. Diethyl ether (30 mL) and ^{t}Bu$_2$PCl (1.52 mL, 8 mmol) were then added into the suspension at room temperature. The reaction mixture was stirred for 16 h and degassed water (20 mL) was added. The organic phase was separated and dried over Na_2SO_4 under argon. By a cannula, the solution was filtered under argon through a Celite pad and diethyl ether was removed under vacuum. A colorless, clear and pyrophoric liquid was obtained in the yield of 96% (1.58 g, **L1**) and 83% (1.36 g, **L2**), respectively.

As for **L3**, due to the bulky steric hindrance, after addition of sodium into i-propanol, the reaction mixture should be heated to reflux for at least 4 h. Moreover, the reaction of sodium isopropoxide with ^{t}Bu$_2$PCl in diethyl ether should be heated to reflux as well. The other procedure is similar to the one for synthesis of **L1** and **L2**. The yield of **L3** is 84% (1.38 g).

1.2 General procedure for synthesis of **L4** and **L5**

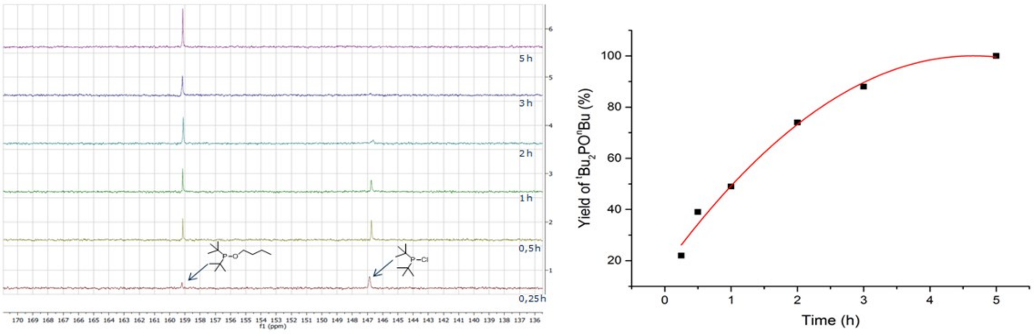
The procedure to synthesize **L4** and **L5** is according to the literature [4]: To a THF (30 mL) solution of (pyridine-2-yl)methanol or (3-methylpyridine-2-yl)methanol (6.7 mmol) was added n-BuLi (2.5 mol/L, 2.7 mL) at – 78 °C. Then ^{t}Bu$_2$PCl (1.27 mL, 6.7 mmol) was added into the mixture dropwise at -78 °C. After finishing adding, the reaction mixture was allowed to be stirred overnight from -78 °C to room temperature. Subsequently, THF was removed under reduced pressure, and diethyl ether was added to precipitate LiCl. After filtration and removal of solvents, **L4** and **L5** was obtained in the yields of 70% (1.20 g, yellow oil, **L4**) and 90% (1.62 g, pale yellow oil, **L5**), respectively.

1.3 Characterization of **L1**–**L5**

L1: ^{1}H NMR (300MHz, C_6D_6, ppm): δ 0.82 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.12 (d, $J^3_{H,P}$ = 12.0 Hz, 9H, C(CH_3)$_3$), 1.52 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH$_2$), 3.64 (q', $|J^3_{H,H} + J^3_{H,P}|$ = 18.0 Hz, 2H, OCH$_2$); ^{31}P{^{1}H } NMR (121.5 MHz, C_6D_6, ppm): δ 159.8 (s)
L2: ^{1}H NMR (300MHz, C_6D_6, ppm): δ 0.83 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.12 (d, $J^3_{H,P}$ = 12.0 Hz, 9H, C(CH_3)$_3$), 1.30 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH$_2$), 1.50 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH$_2$), 3.70 (q', $|J^3_{H,H} + J^3_{H,P}|$ = 18.0 Hz, 2H, OCH$_2$); ^{31}P{^{1}H } NMR (121.5 MHz, C_6D_6, ppm): δ 159.8 (s)
L3: ^{1}H NMR (300MHz, C_6D_6, ppm): δ 1.12 (d, $J^3_{H,P}$ = 12.0 Hz, 9H, C(CH_3)$_3$), 1.14 (d, $J^3_{H,H}$ = 6.0 Hz, 6H, OCH(CH_3)$_3$), 1.52 (m, 1H, OCH(CH$_3$)$_3$); ^{31}P{^{1}H } NMR (121.5 MHz, C_6D_6, ppm): δ 152.0 (s)
L4: ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 1.14 (d, $J^3_{H,P}$ = 12.0 Hz, 9H, C(CH_3)$_3$), 4.94 (br, 2H, CH_2), 7.15 – 8.55 (m, 4H, C$_5$$H_4$N); ^{31}P{^{1}H } NMR (121.5 MHz, C_6D_6, ppm): δ 165.5 (s)
L5: ^{1}H NMR (300MHz, $CDCl_3$, ppm): δ 1.06 (d, $J^3_{H,P}$ = 12.0 Hz, 9H, C(CH_3)$_3$), 2.45 (s, 3H, ArCH_3), 4.84 (br, 2H, CH_2), 6.93 – 7.54 (m, 3H, C$_5$$H_3$N); ^{31}P{^{1}H } NMR (121.5 MHz, C_6D_6, ppm): δ 165.3 (s)

2. The *in situ* ^{31}P{^{1}H} NMR spectra of the transformation from ^{t}Bu$_2$PCl to ^{t}Bu$_2$PO^{n}Bu or ^{t}Bu$_2$PO^{i}Pr

In order to clarify the transformation from ^{t}Bu$_2$PCl to ^{t}Bu$_2$PO^{n}Bu, ^{31}P{^{1}H} NMR spectroscopy was used to monitor this procedure. Similar to the loading of alcohol and base in catalytic reaction, 0.03 mmol ^{t}Bu$_2$PCl was added into 2 mL butanol in the presence of 0.45 mL DBU. The sample was monitored after 0.25 h, 0.5 h, 1 h, 2 h, 3 h and 5 h. According to the in situ ^{31}P{^{1}H} NMR spectra, after 5 h could ^{t}Bu$_2$PCl transform to phosphinite completely (Figure S1).



(a) (b)

Fig. S1 The ^{31}P{^{1}H} NMR spectra of the transformation from ^{t}Bu$_2$PCl to ^{t}Bu$_2$PO^{n}Bu (**a**); the relation between yield of ^{t}Bu$_2$PO^{n}Bu (%) with time (h) (**b**).

The reaction of $^{t}Bu_2PCl$ with $^{t}Bu_2PO^{i}Pr$ underwent in the presence of DBU at 80 °C for 24 h. Subsequently, $^{31}P\{^{1}H\}$ NMR spectroscopy was used to test the mixture. Although the reaction temperature was elevated and reaction time was extended, the yield of $^{t}Bu_2PO^{i}Pr$ was only 57% according to the spectrum (Figure S2). The bulky steric hindrance of isopropanol may lead to this problem.

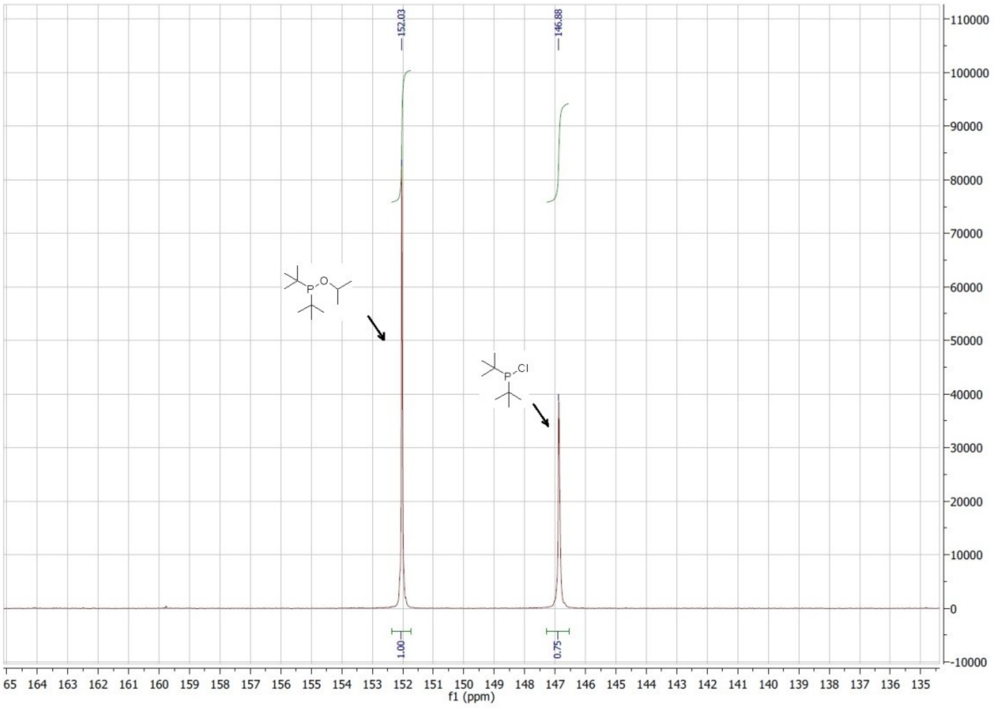
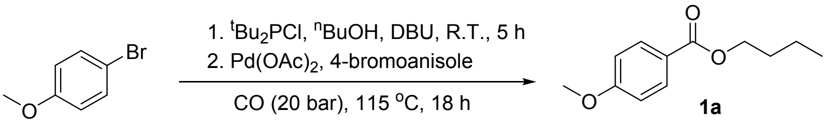


Fig. S2 The $^{31}P\{^{1}H\}$ NMR spectra of the transformation from $^{t}Bu_2PCl$ to $^{t}Bu_2PO^{i}Pr$

3. Detailed Optimization Conditions

3.1 **Table S1**. Butoxycarbonylation of 4-bromoanisole through in situ protocol. [a]



1a

Standard conditions

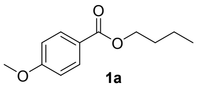
Entry	Variation from standard conditions	Conversion of substrate (%) [b]	Yield of **1a** (%) [b]
1	none	100	98
2	$^{t}BuPCl_2$ instead of $^{t}Bu_2PCl$	29	28
3	PCl_3 instead of $^{t}Bu_2PCl$	0	0
4	Ph_2PCl instead of $^{t}Bu_2PCl$	8	7
5	NEt_3 instead of DBU	83	78
6	TMEDA instead of DBU	51	48
7	$^{t}BuOK$ instead of DBU	0	0
8	Pre-reaction underwent for 3 h	87	85
9	5 bar CO instead of 20 bar CO	93	90
10	4-chloroanisole instead of 4-bromoanisole	15	0

[a] Standard reaction conditions: 1. $^{t}Bu_2PCl$ (0.03 mmol), n-butanol (2 mL), DBU (3 mmol), R.T., 5 h; 2. $Pd(OAc)_2$ (0.01 mmol), 4-bromoanisole (2 mmol), CO (20 bar), 115 °C, 18 h. [b] determined by GC, n-hexadecane as internal standard.

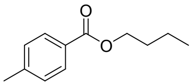
The in-situ-generated phosphinite ligand showed excellent reactivity in palladium-catalyzed butoxycarbonylation reaction (entry 1). In contrast, phosphonites (entry 2) and phosphites (entry 3) which could be generated in situ [4] led to very poor conversion. Meanwhile, when Ph_2PCl replaced $^{t}Bu_2PCl$ as pre-ligand, the reaction can hardly occur (Entry 4). Weaker or stronger base, shorter pre-reaction time and lower pressure of CO would influence the reaction in different extent (Entry 5 - 9). We also explored the possibility for alkoxycarbonylation of aryl chloride with the in situ protocol. However, the conversion of substrate was only 15% while no desirable product was detected (Entry 10).

4. General procedure for alkoxycarbonylation of (hetero)aryl bromides through *in-situ* protocol

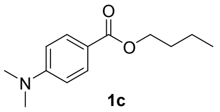
A 10 mL Schlenk tube was charged with $^{t}Bu_2PCl$ (5.4 mg, 0.03 mmol), alcohol (2 mL) and DBU (0.45 mL 3 mmol) under an argon atmosphere. The mixture was then stirred at room temperature for 5 h. Subsequently, the solution was transferred to a vial (12 mL reaction volume) which was charged with $Pd(AcO)_2$ (2.2 mg, 0.01 mmol) and equipped with a septum, a small cannula and a stirring bar. After addition of corresponding aryl bromide (2 mmol), the vials were placed in an alloy plate which was transferred to a 300 mL autoclave (4560 series from Parr Instruments®) under an argon atmosphere. The autoclave was flushed three times with CO and then pressurized to 20 bar CO. The reaction was kept stirring at 115 °C for 18 h. After cooling down to room temperature, CO was released carefully. Hexadecane (452.0 mg, 2 mmol), the internal standard, was injected into reaction vials and the mixture was stirred for 10 min. The sample was analyzed by GC to determine the conversion and yield. Pure product could be obtained by column chromatography on silica gel (general eluent: hexane/ethylacetate = 9:1).


1a

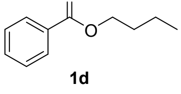
Isolated yield: 0.41 g, 98%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 0.99 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.49 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.76 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 3.87 (s, 3H, OCH_3) , 4.31 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 6.92 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 8.02 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.8 (CH_3), 19.3 (CH_2), 30.7 (CH_2), 55.4 (OCH_3), 64.5 (OCH_2), 113.6 (C_{Ar}), 123.0 (C_{Ar}), 131.5 (C_{Ar}), 163.2 (C_{Ar}), 166.4 (C=O).
MS (EI) calculated for $C_{12}H_{16}O_3$: 208.1; found: 208.1


1b

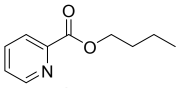
Isolated yield: 0.33 g, 86%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 0.88 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.38 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.65 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 2.03 (s, 3H, Ar-CH_3) , 4.21 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.12 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 7.84 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.8 (CH_3), 19.3 (CH_2), 21.6 (CH_2), 30.8 (Ar-CH_3), 64.6 (OCH_2), 127.8 (C_{Ar}), 129.3 (C_{Ar}), 129.6 (C_{Ar}), 143.4 (C_{Ar}), 166.7 (C=O).
MS (EI) calculated for $C_{12}H_{16}O_2$: 192.1; found: 192.1


1c

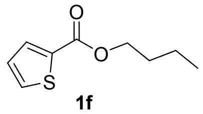
Isolated yield: 0.38 g, 86%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.00 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.50 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.75 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 3.05 (br, 6H, $N(CH_3)_2$) , 4.29 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 6.68 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 7.94 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.8 (CH_3), 19.4 (CH_2), 31.0 (CH_2), 40.2 ($N(CH_3)_2$), 64.1 (OCH_2), 111.0 (C_{Ar}), 117.8 (C_{Ar}), 131.2 (C_{Ar}), 153.0 (C_{Ar}), 167.0 (C=O).
MS (EI) calculated for $C_{13}H_{19}NO_2$: 221.1; found: 221.1


1d

Isolated yield: 0.30 g, 84%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 0.89 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.38 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.64 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 4.23 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.33 (m, 2H, Ar), 7.45 (m, 1H, Ar), 7.96 (m, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.8 (CH_3), 19.3 (CH_2), 30.8 (CH_2), 64.8 (OCH_2), 128.3 (C_{Ar}), 129.5 (C_{Ar}), 130.5 (C_{Ar}), 132.8 (C_{Ar}), 166.7 (C=O).
MS (EI) calculated for $C_{11}H_{14}O_2$: 178.1; found: 178.1


1e

Isolated yield: 0.33 g, 92%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 0.89 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.40 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.73 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 4.35 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.40 (m, 1H, Ar), 7.76 (m, 1H, Ar), 8.05 (m, 1H, Ar), 8.69 (m, 1H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 12.7 (CH_3), 18.1 (CH_2), 29.7 (CH_2), 64.7 (OCH_2), 124.0 (C_{Ar}), 125.8 (C_{Ar}), 136.0 (C_{Ar}), 147.2 (C_{Ar}), 148.8 (C_{Ar}), 164.2 (C=O).
MS (EI) calculated for $C_{10}H_{13}NO_2$: 179.1; found: 179.1



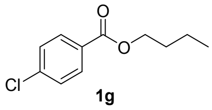
1f

Isolated yield: 0.32 g, 87%. Colorless oil.

^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 0.89 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.38 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.65 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 4.22 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.01 (m, 1H, Ar), 7.46 (m, 1H, Ar), 7.72 (m, 1H, Ar);

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.8 (CH_3), 19.2 (CH_2), 30.8 (CH_2), 65.0 (OCH_2), 127.7 (C_{Ar}), 132.2 (C_{Ar}), 133.2 (C_{Ar}), 134.1 (C_{Ar}), 162.4 (C=O).

MS (EI) calculated for $C_9H_{12}O_2S$: 184.1; found: 184.1



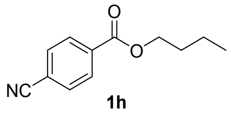
1g

Isolated yield: 0.35 g, 83%. Colorless oil.

^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 0.90 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.38 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.67 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 4.24 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.32 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 7.88 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.8 (CH_3), 19.3 (CH_2), 30.8 (CH_2), 65.1 (OCH_2), 128.6 (C_{Ar}), 129.0 (C_{Ar}), 131.0 (C_{Ar}), 139.2 (C_{Ar}), 165.8 (C=O).

MS (EI) calculated for $C_{11}H_{13}ClO_2$: 212.1; found: 212.1



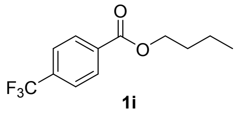
1h

Isolated yield: 0.34 g, 83%. White crystals.

^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 0.92 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.40 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.70 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 4.29 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.68 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 8.07 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.8 (CH_3), 19.2 (CH_2), 30.7 (CH_2), 65.7 (OCH_2), 116.3 (C_{Ar}), 118.1 (C≡N), 130.1 (C_{Ar}), 132.2 (C_{Ar}), 134.3 (C_{Ar}), 165.0 (C=O).

MS (EI) calculated for $C_{12}H_{13}NO_2$: 203.1; found: 203.1



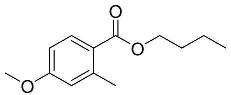
1i

Isolated yield: 0.38 g, 78%. Colorless oil.

^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 0.88 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.38 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.66 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 4.25 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.59 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 8.04 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.7 (CH_3), 19.2 (CH_2), 30.7 (CH_2), 65.4 (OCH_2), 123.4 ($J^1_{C,F}$ = 234.0 Hz, CF_3), 125.3 (C_{Ar}), 130.0 (C_{Ar}), 133.9 ($J^3_{C,F}$ = 27.0 Hz, C_{Ar}), 134.7 ($J^2_{C,F}$ = 32.2 Hz, C_{Ar}), 165.4 (C=O).

MS (EI) calculated for $C_{12}H_{13}F_3O_2$: 246.1; found: 246.1



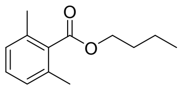
1j

Isolated yield: 0.36 g, 80%. Colorless oil.

^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.02 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.52 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.78 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 2.65 (s, 3H, Ar-CH_3), 3.88 (s, 3H, OCH_3), 4.31 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 6.78 (m, 2H, Ar), 7.98 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar);

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.8 (CH_3), 19.4 (CH_2), 22.4 (Ar-CH_3), 30.9 (CH_2), 55.3 (OCH_3), 64.3 (OCH_2), 110.9 (C_{Ar}), 116.9 (C_{Ar}), 122.1 (C_{Ar}), 132.9 (C_{Ar}), 143.0 (C_{Ar}), 162.2 (C_{Ar}), 167.2 (C=O).

MS (EI) calculated for $C_{13}H_{18}O_3$: 222.1; found: 222.1

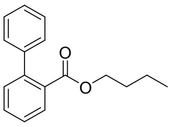


1k

Isolated yield: 0.30 g, 74%. Colorless oil.

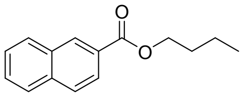
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.03 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.52 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.80 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 2.39 (s, 6H, Ar-CH_3), 4.40 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.09 (d, $J^3_{H,H}$ = 6.0 Hz, 1H, Ar), 7.24 (m, 2H, Ar);

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.7 (CH_3), 19.3 (CH_2), 19.7 (Ar-CH_3), 30.7 (CH_2), 64.9 (OCH_2), 127.6 (C_{Ar}), 129.2 (C_{Ar}), 134.3 (C_{Ar}), 134.8 (C_{Ar}), 170.2 (C=O).
MS (EI) calculated for $C_{13}H_{18}O_2$: 206.1; found: 206.1



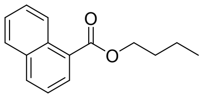
1l

Isolated yield: 0.30 g, 67%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 0.87 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.16 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.40 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 4.11 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.27 – 7.49 (m, 7H, Ar), 7.58 (m, 1H, Ar), 7.90 (m, 1H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.7 (CH_3), 19.0 (CH_2), 30.3 (CH_2), 64.9 (OCH_2), 127.2 (C_{Ar}), 128.1 (C_{Ar}), 128.4 (C_{Ar}), 129.8 (C_{Ar}), 130.7 (C_{Ar}), 131.1 (C_{Ar}), 131.4 (C_{Ar}), 141.6 (C_{Ar}), 142.4 (C_{Ar}), 169.1 (C=O).
MS (EI) calculated for $C_{17}H_{18}O_2$: 254.1; found: 254.1



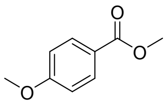
1m

Isolated yield: 0.41 g, 90%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 0.92 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.44 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.72 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 4.30 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.46 (m, 2H, Ar), 7.78 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar), 7.78 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar), 7.86 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar), 7.98 (dd, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar), 8.52 (s, 1H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.9 (CH_3), 19.4 (CH_2), 30.9 (CH_2), 65.0 (OCH_2), 125.3 (C_{Ar}), 126.6 (C_{Ar}), 127.8 (C_{Ar}), 128.1 (C_{Ar}), 128.2 (C_{Ar}), 129.4 (C_{Ar}), 131.0 (C_{Ar}), 132.5 (C_{Ar}), 135.5 (C_{Ar}), 166.9 (C=O).
MS (EI) calculated for $C_{15}H_{16}O_2$: 228.1; found: 228.1



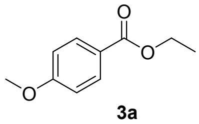
1n

Isolated yield: 0.39 g, 86%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 0.91 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.42 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 1.72 (quintet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 4.33 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.36 – 7.54 (m, 3H, Ar), 7.78 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar), 7.90 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar), 8.08 (dd, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar), 8.84 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.9 (CH_3), 19.4 (CH_2), 30.9 (CH_2), 65.0 (OCH_2), 124.5 (C_{Ar}), 125.9 (C_{Ar}), 126.2 (C_{Ar}), 127.6 (C_{Ar}), 127.7 (C_{Ar}), 128.6 (C_{Ar}), 130.1 (C_{Ar}), 131.4 (C_{Ar}), 133.2 (C_{Ar}), 133.9 (C_{Ar}), 167.7 (C=O).
MS (EI) calculated for $C_{15}H_{16}O_2$: 228.1; found: 228.1



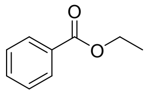
2a

Isolated yield: 0.29 g, 87%. White crystals.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 3.79 (s, 3H, Ar-OCH_3), 3.81 (s, 3H, C(O)OCH_3), 6.84 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 7.92 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 51.9 (Ar-OCH_3), 55.4 [C(O)OCH_3], 113.6 (C_{Ar}), 122.6 (C_{Ar}), 131.6 (C_{Ar}), 163.3 (C_{Ar}), 166.9 (C=O).
MS (EI) calculated for $C_9H_{10}O_3$: 166.1; found: 166.1



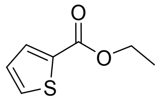
3a

Isolated yield: 0.33 g, 92%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.42 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 3.89 (s, 3H, OCH_3), 4.38 (q, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 6.95 (d, $J^3_{H,H}$ = 6.0 Hz, 2H, Ar), 8.04 (d, $J^3_{H,H}$ = 6.0 Hz, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 14.4 (CH_3), 55.4 (OCH_3), 60.6 (OCH_2), 113.5 (C_{Ar}), 122.9 (C_{Ar}), 131.5 (C_{Ar}), 163.2 (C_{Ar}), 166.4 (C=O).
MS (EI) calculated for $C_{10}H_{12}O_3$: 180.1; found: 180.1



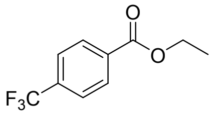
3b

Isolated yield: 0.28 g, 94%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.44 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, C*H*$_3$), 4.42 (q, $J^3_{H,H}$ = 6.0 Hz, 2H, OC*H*$_2$), 7.47 (m, 2H, Ar), 7.59 (m, 1H, Ar), 8.10 (m, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 14.4 (*C*H$_3$), 61.0 (O*C*H$_2$), 128.3 (*C*$_{Ar}$), 129.5 (*C*$_{Ar}$), 130.5 (*C*$_{Ar}$), 132.8 (*C*$_{Ar}$), 166.6 (*C*=O).
MS (EI) calculated for $C_9H_{10}O_2$: 150.1; found: 150.1



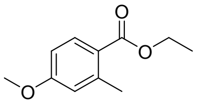
3c

Isolated yield: 0.25 g, 80%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.41 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, C*H*$_3$), 4.38 (q, $J^3_{H,H}$ = 6.0 Hz, 2H, OC*H*$_2$), 7.12 (m, 1H, Ar), 7.58 (m, 1H, Ar), 7.83 (m, 1H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 14.4 (*C*H$_3$), 61.1 (O*C*H$_2$), 127.7 (*C*$_{Ar}$), 132.2 (*C*$_{Ar}$), 133.3 (*C*$_{Ar}$), 134.1 (*C*$_{Ar}$), 162.3 (*C*=O).
MS (EI) calculated for $C_7H_8O_2S$: 156.0; found: 156.0



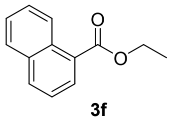
3d

Isolated yield: 0.31 g, 72%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.46 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, C*H*$_3$), 4.46 (q, $J^3_{H,H}$ = 6.0 Hz, 2H, OC*H*$_2$), 7.74 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 8.20 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 14.2 (*C*H$_3$), 61.5 (O*C*H$_2$), 123.4 ($J^1_{C,F}$ = 234.0 Hz, *C*F$_3$), 125.3 (*C*$_{Ar}$), 130.0 (*C*$_{Ar}$), 133.9 ($J^3_{C,F}$ = 28.5 Hz, *C*$_{Ar}$), 134.7 ($J^2_{C,F}$ = 32.2 Hz, *C*$_{Ar}$), 165.4 (*C*=O).
MS (EI) calculated for $C_{10}H_9F_3O_2$: 218.1; found: 218.1



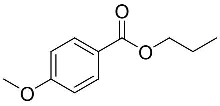
3e

Isolated yield: 0.33 g, 84%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.42 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, C*H*$_3$), 2.65 (s, 3H, Ar-C*H*$_3$), 3.87 (s, 3H, OC*H*$_3$), 4.36 (q, $J^3_{H,H}$ = 6.0 Hz, 2H, OC*H*$_2$), 6.77 – 6.80 (m, 2H, Ar), 7.98 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 14.4 (*C*H$_3$), 22.4 (Ar-*C*H$_3$), 55.3 (O*C*H$_3$), 60.3 (O*C*H$_2$), 110.9 (*C*$_{Ar}$), 116.9 (*C*$_{Ar}$), 122.1 (*C*$_{Ar}$), 132.9 (*C*$_{Ar}$), 143.0 (*C*$_{Ar}$), 162.2 (*C*$_{Ar}$), 167.2 (*C*=O).
MS (EI) calculated for $C_{11}H_{14}O_3$: 194.1; found: 194.1



3f

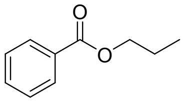
Isolated yield: 0.36 g, 90%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.52 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, C*H*$_3$), 4.54 (q, $J^3_{H,H}$ = 6.0 Hz, 2H, C*H*$_2$), 7.52 – 7.70 (m, 3H, Ar), 7.94 (d, $J^3_{H,H}$ = 6.0 Hz, 1H, Ar), 8.06 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar), 8.25 (d, $J^3_{H,H}$ = 6.0 Hz, 1H, Ar), 8.98 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 14.4 (*C*H$_3$), 61.1 (O*C*H$_2$), 124.5 (*C*$_{Ar}$), 125.9 (*C*$_{Ar}$), 126.2 (*C*$_{Ar}$), 127.5 (*C*$_{Ar}$), 127.7 (*C*$_{Ar}$), 128.6 (*C*$_{Ar}$), 130.1 (*C*$_{Ar}$), 131.4 (*C*$_{Ar}$), 133.2 (*C*$_{Ar}$), 133.9 (*C*$_{Ar}$), 167.7 (*C*=O).
MS (EI) calculated for $C_{13}H_{12}O_2$: 200.1; found: 200.1



4a

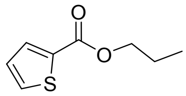
Isolated yield: 0.34 g, 87%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.04 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, C*H*$_3$), 1.80 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, C*H*$_2$), 3.87 (s, 3H, OC*H*$_3$) , 4.27 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OC*H*$_2$), 6.94 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 8.02 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 10.6 (CH_3), 22.2 (CH_2), 55.4 (OCH_3), 66.2 (OCH_2), 113.6 (C_{Ar}), 123.0 (C_{Ar}), 131.5 (C_{Ar}), 163.2 (C_{Ar}), 166.4 (C=O).
MS (EI) calculated for $C_{11}H_{14}O_3$: 194.1; found: 194.1
Scale-up experiment: A 50 mL Schlenk tube was charged with $^tBu_2PCl$ (54.0 mg, 0.3 mmol), n-propanol (10 mL) and DBU (4.5 mL, 30 mmol) under an argon atmosphere. The mixture was then stirred at room temperature for 5 h. Subsequently, the solution was transferred to a 25 mL autoclave which was charged with $Pd(AcO)_2$ (22.0 mg, 0.1 mmol) and equipped with a stirring bar. After addition of 4-bromoanisole (3.7 g, 20 mmol), the autoclave was flushed three times with CO and then pressurized to 20 bar CO. The reaction was kept stirring at 115 °C for 18 h. After cooling down to room temperature, CO was released carefully. 3.7 g Pure product was obtained by column chromatography on silica gel (general eluent: hexane/ethylacetate = 9:1), isolated yield is 96%.



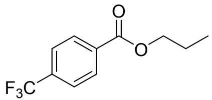
4b

Isolated yield: 0.27 g, 83%. Colorless oil.
^1H NMR (300MHz, $CDCl_3$, ppm): δ 0.95 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.71 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 4.20 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.30 – 7.49 (m, 3H, Ar), 7.95 - 7.98 (m, 2H, Ar);
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 10.6 (CH_3), 22.1 (CH_2), 66.5 (OCH_2), 128.3 (C_{Ar}), 129.5 (C_{Ar}), 130.5 (C_{Ar}), 132.8 (C_{Ar}), 166.7 (C=O).
MS (EI) calculated for $C_{10}H_{12}O_2$: 164.1; found: 164.1



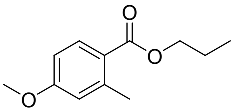
4c

Isolated yield: 0.28 g, 82%. Yellow oil.
^1H NMR (300MHz, $CDCl_3$, ppm): δ 1.06 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.82 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 4.30 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.14 (m, 1H, Ar), 7.58 (m, 1H, Ar), 7.84 (m, 1H, Ar);
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 10.5 (CH_3), 22.1 (CH_2), 66.7 (OCH_2), 127.7 (C_{Ar}), 132.2 (C_{Ar}), 133.2 (C_{Ar}), 134.1 (C_{Ar}), 162.4 (C=O).
MS (EI) calculated for $C_8H_{10}O_2S$: 170.0; found: 170.0



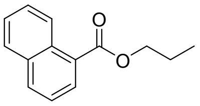
4d

Isolated yield: 0.35 g, 76%. Colorless oil.
^1H NMR (300MHz, $CDCl_3$, ppm): δ 1.08 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.86 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 4.36 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 7.74 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 8.20 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 10.4 (CH_3), 22.0 (CH_2), 67.1 (OCH_2), 123.4 ($J^1_{C,F}$ = 234.0 Hz, CF_3), 125.3 (C_{Ar}), 130.0 (C_{Ar}), 133.9 ($J^3_{C,F}$ = 27.0 Hz, C_{Ar}), 134.7 ($J^2_{C,F}$ = 32.2 Hz, C_{Ar}), 165.4 (C=O).
MS (EI) calculated for $C_{11}H_{11}F_3O_2$: 232.1; found: 232.1



4e

Isolated yield: 0.36 g, 87%. Colorless oil.
^1H NMR (300MHz, $CDCl_3$, ppm): δ 1.07 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.82 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 2.65 (s, 3H, Ar-CH_3), 3.88 (s, 3H, OCH_3), 4.27 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OCH_2), 6.78 (m, 2H, Ar), 8.00 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar);
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 10.7 (CH_3), 22.2 (CH_2), 22.4 (Ar-CH_3), 55.3 (OCH_3), 66.1 (OCH_2), 110.9 (C_{Ar}), 116.9 (C_{Ar}), 122.1 (C_{Ar}), 132.9 (C_{Ar}), 143.0 (C_{Ar}), 162.2 (C_{Ar}), 167.2 (C=O).
MS (EI) calculated for $C_{12}H_{16}O_3$: 208.1; found: 208.1



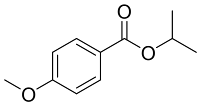
4f

Isolated yield: 0.38 g, 90%. Pale yellow oil.

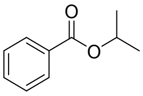
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.14 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, C*H$_3$*), 1.92 (sextet, $J^3_{H,H}$ = 6.0 Hz, 2H, C*H$_2$*), 4.45 (t, $J^3_{H,H}$ = 6.0 Hz, 2H, OC*H$_2$*), 7.53 – 7.70 (m, 3H, Ar), 7.94 (d, $J^3_{H,H}$ = 6.0 Hz, 1H, Ar), 8.07 (d, $J^3_{H,H}$ = 6.0 Hz, 1H, Ar), 8.26 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar), 9.00 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 10.7 (*C*H$_3$), 22.2 (*C*H$_2$), 66.7 (O*C*H$_2$), 124.5 (*C*$_{Ar}$), 125.9 (*C*$_{Ar}$), 126.2 (*C*$_{Ar}$), 127.6 (*C*$_{Ar}$), 127.7 (*C*$_{Ar}$), 128.6 (*C*$_{Ar}$), 130.1 (*C*$_{Ar}$), 131.4 (*C*$_{Ar}$), 133.2 (*C*$_{Ar}$), 133.9 (*C*$_{Ar}$), 167.7 (*C*=O).
MS (EI) calculated for $C_{14}H_{14}O_2$: 214.1; found: 214.1

5. General procedure for alkoxycarbonylation of (hetero)aryl bromides through cross-*in-situ* protocol

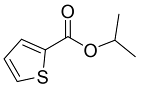
A 10 mL Schlenk tube was charged with ^{t}Bu$_2$PCl (5.4 mg, 0.03 mmol), n-propanol (10 µL) and DBU (0.45 mL 3 mmol) under an argon atmosphere. The mixture was then stirred at room temperature for 5 h. Subsequently, the mixture was transferred to a vial (12 mL reaction volume) which was charged with Pd(AcO)$_2$ (2.2 mg, 0.01 mmol), alcohol (2 mL) or 1,4-dioxane solution of alcohol (4 mmol alcohol solved in 1.6 mL 1,4-dioxane) and equipped with a septum, a small cannula and a stirring bar. After addition of corresponding aryl bromide (2 mmol), the vials were placed in an alloy plate which was transferred to a 300 mL autoclave (4560 series from Parr Instruments®) under an argon atmosphere. The autoclave was flushed three times with CO and then pressurized to 20 bar CO. The reaction was kept stirring at 115 °C for 18 h. After cooling down to room temperature, CO was released carefully. Hexadecane (452.0 mg, 2 mmol), the internal standard, was injected into reaction vials and the mixture was stirred for 10 min. The sample was analyzed by GC to determine the conversion and yield. Pure product could be obtained by column chromatography on silica gel (general eluent: hexane/ethylacetate = 9:1).


5a

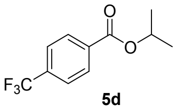
Isolated yield: 0.33 g, 85%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.40 (d, $J^3_{H,H}$ = 6.0 Hz, 3H, C*H$_3$*), 3.89 (s, 3H, OC*H$_3$*) , 5.27 (sep, $J^3_{H,H}$ = 6.0 Hz, H, OC*H*), 6.95 (d, $J^3_{H,H}$ = 6.0 Hz, 2H, Ar), 8.04 (d, $J^3_{H,H}$ = 6.0 Hz, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 22.0 (*C*H$_3$), 55.4 (O*C*H$_3$), 67.9 (O*C*H), 113.5 (*C*$_{Ar}$), 123.4 (*C*$_{Ar}$), 131.5 (*C*$_{Ar}$), 163.2 (*C*$_{Ar}$), 165.9 (*C*=O).
MS (EI) calculated for $C_{11}H_{14}O_3$: 194.1; found: 194.1


5b

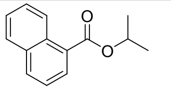
Isolated yield: 0.27 g, 83%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.28 (d, $J^3_{H,H}$ = 6.0 Hz, 3H, C*H$_3$*), 5.17 (sep, $J^3_{H,H}$ = 6.0 Hz, 1H, OC*H*), 7.32 – 7.48 (m, 3H, Ar), 7.94 - 7.98 (m, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 21.2 (*C*H$_3$), 68.3 (O*C*H), 128.3 (*C*$_{Ar}$), 129.5 (*C*$_{Ar}$), 130.9 (*C*$_{Ar}$), 132.7 (*C*$_{Ar}$), 166.1 (*C*=O).
MS (EI) calculated for $C_{10}H_{12}O_2$: 164.1; found: 164.1


5c

Isolated yield: 0.29 g, 86%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.40 (d, $J^3_{H,H}$ = 6.0 Hz, 3H, C*H$_3$*), 5.26 (sep, $J^3_{H,H}$ = 6.0 Hz, 1H, OC*H*), 7.12 (m, 1H, Ar), 7.57 (m, 1H, Ar), 7.82 (m, 1H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 21.9 (*C*H$_3$), 68.8 (O*C*H), 127.6 (*C*$_{Ar}$), 132.2 (*C*$_{Ar}$), 133.1 (*C*$_{Ar}$), 134.7 (*C*$_{Ar}$), 161.8 (*C*=O).
MS (EI) calculated for $C_8H_{10}O_2S$: 170.0; found: 170.0


5d

Isolated yield: 0.33 g, 72%. Colorless oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.31 (d, $J^3_{H,H}$ = 6.0 Hz, 3H, C*H$_3$*), 5.20 (sep, $J^3_{H,H}$ = 6.0 Hz, 1H, OC*H*), 7.62 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 8.07 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 21.9 (*C*H$_3$), 69.2 (O*C*H$_2$), 120.1 ($J^1_{C,F}$ = 271.5 Hz, *C*F$_3$), 125.3 (*C*$_{Ar}$), 129.9 (*C*$_{Ar}$), 134.1 (*C*$_{Ar}$), 134.2 ($J^2_{C,F}$ = 32.2 Hz, *C*$_{Ar}$), 164.8 (*C*=O).
MS (EI) calculated for $C_{11}H_{11}F_3O_2$: 232.1; found: 232.1



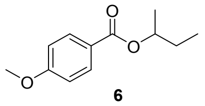
5e

Isolated yield: 0.36 g, 83%. Colorless oil.

^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.30 (d, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 5.25 (sep, $J^3_{H,H}$ = 6.0 Hz, 1H, OCH), 7.30 – 7.49 (m, 3H, Ar), 7.70 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar), 7.82 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar), 8.02 (dd, $J^3_{H,H}$ = 6.0 Hz, 1H, Ar), 8.80 (d, $J^3_{H,H}$ = 6.0 Hz, 1H, Ar);

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 22.1 (CH$_3$), 66.7 (OCH), 124.6 (C_{Ar}), 125.9 (C_{Ar}), 126.2 (C_{Ar}), 127.7 (C_{Ar}), 128.0 (C_{Ar}), 128.6 (C_{Ar}), 130.0 (C_{Ar}), 131.4 (C_{Ar}), 133.1 (C_{Ar}), 133.9 (C_{Ar}), 167.7 (C=O).

MS (EI) calculated for $C_{14}H_{14}O_2$: 214.1; found: 214.1



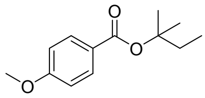
6

Isolated yield: 0.35 g, 84%. Colorless oil.

^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.01 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.36 (d, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1.74 (m, 2H, CH_2), 3.90 (s, 3H, OCH_3), 5.11 (sextet, $J^3_{H,H}$ = 6.0 Hz, H, OCH), 6.96 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 8.04 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 9.8 (CH$_3$), 19.6 (CH$_3$), 29.0 (CH$_2$), 55.4 (OCH$_3$), 72.4 (OCH), 113.5 (C_{Ar}), 123.4 (C_{Ar}), 131.5 (C_{Ar}), 163.2 (C_{Ar}), 166.0 (C=O).

MS (EI) calculated for $C_{12}H_{16}O_3$: 208.1; found: 208.1



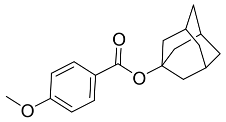
7

Isolated yield: 0.31 g, 70%. Colorless oil.

^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.01 (t, $J^3_{H,H}$ = 6.0 Hz, 3H, CH_3), 1,60 (s, 6H, C(CH_3)$_2$), 1.95 (q, $J^3_{H,H}$ = 6.0 Hz, 2H, CH_2), 3.88 (s, 3H, OCH_3), 6.94 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 8.00 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 8.4 (CH$_3$), 25.7 (CH$_3$), 33.0 (CH$_2$), 55.4 (OCH$_3$), 82.9 (OC(CH$_3$)$_2$CH$_2$), 113.4 (C_{Ar}), 124.5 (C_{Ar}), 131.4 (C_{Ar}), 163.0 (C_{Ar}), 165.5 (C=O).

MS (EI) calculated for $C_{13}H_{19}O_3$: 222.1; found: 222.1



8

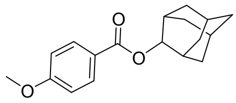
A 10 mL Schlenk tube was charged with ^{t}Bu$_2$PCl (5.4 mg, 0.03 mmol), n-propanol (10 µL) and DBU (0.45 mL 3 mmol) under an argon atmosphere. The mixture was then stirred at room temperature for 5 h. Subsequently, the mixture was transferred to a vial (12 mL reaction volume) which was charged with Pd(AcO)$_2$ (2.2 mg, 0.01 mmol), 1-adamantanol (0.3 g, 2.0 mmol) 1,4-dioxane (1.6 mL) and equipped with a septum, a small cannula and a stirring bar. After addition of 4-bromoanisole (0.6 g, 3.0 mmol), the vials were placed in an alloy plate which was transferred to a 300 mL autoclave (4560 series from Parr Instruments®) under an argon atmosphere. The autoclave was flushed three times with CO and then pressurized to 20 bar CO. The reaction was kept stirring at 125 °C for 20 h. After cooling down to room temperature, CO was released carefully. Pure product could be obtained by column chromatography on silica gel (general eluent: hexane/ethylacetate = 9:1).

Isolated yield: 0.32 g, 60%. Colorless solid.

^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.64 (br, 6H, Ad), 2.15 (m, 9H, Ad), 3.78 (s, 3H, OCH_3), 6.82 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 7.86 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 30.9 (C_{Ad}), 36.3 (C_{Ad}), 41.5 (C_{Ad}), 55.4 (OCH$_3$), 80.6 (OC_{Ad}), 113.4 (C_{Ar}), 124.6 (C_{Ar}), 131.4 (C_{Ar}), 162.9 (C_{Ar}), 165.3 (C=O).

HSMS calculated for $C_{18}H_{22}O_3$: 286.1569; found: 286.1573



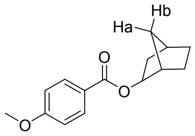
9

Synthesis method is similar to the one of **8**.

Isolated yield: 0.46 g, 81%. Colorless oil.

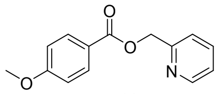
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.51 (br, 1H, Ad), 1.56 (br, 1H, Ad), 1.68 (br, 2H, Ad), 1.78 (br, 5H, Ad), 2.04 (br, 3H, Ad), 2.09 (br, 1H, Ad), 3.75 (s, 3H, OCH_3), 5.07 (br, 1H, OAd), 6.84 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 7.96 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 27.1 (C_{Ad}), 27.4 (C_{Ad}), 32.1 (C_{Ad}), 36.4 (C_{Ad}), 37.4 (C_{Ad}), 55.4 (O*C*H$_3$), 77.0 (OC_{Ad}), 113.5 (C_{Ar}), 123.6 (C_{Ar}), 131.5 (C_{Ar}), 163.2 (C_{Ar}), 165.5 (*C*=O).
HSMS calculated for $C_{18}H_{22}O_3$: 286.1569; found: 286.1561



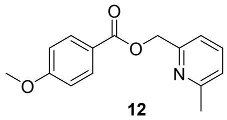
10

Synthesis method is similar to the one of **8**.
Isolated yield: 0.46 g, 93%. Colorless solid.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 1.18-1.30 (m, 3H, Norbornyl), 1.52 - 1.71 (m, 4H, Norbornyl), 1.86 (ddd, 1H, $J^2_{H,H}$ = 15 Hz, $J^3_{H,H}$ = 9 Hz, $J^3_{H,H}$ = 3 Hz, *Ha* or *Hb*), 2.38 - 2.49 (m, 2H, Norbornyl), 3.90 (s, 3H, OC*H$_3$*), 4.87 (br, 1H, OC*H*), 6.94 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 8.02 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 24.3 ($C_{norbornyl}$), 28.2 ($C_{norbornyl}$), 35.5 ($C_{norbornyl}$), 39.7 ($C_{norbornyl}$), 41.6 ($C_{norbornyl}$), 55.4 (O*C*H$_3$), 77.8 (O$C_{norbornyl}$), 113.5 (C_{Ar}), 123.4 (C_{Ar}), 131.5 (C_{Ar}), 163.2 (C_{Ar}), 166.0 (*C*=O).
HSMS calculated for $C_{15}H_{18}O_3$: 246.1256; found: 246.1248.



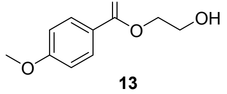
11

Isolated yield: 0.40 g, 83%. White powder.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 3.90 (s, 3H, OC*H$_3$*), 5.50 (s, 2H, OC*H$_2$*), 6.98 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 7.28 (m, 1H, Ar), 7.48 (d, $J^3_{H,H}$ = 9.0 Hz, 1H, Ar), 7.75 (m, 1H, Ar), 8.12 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 8.65 (m, 1H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 55.4 (O*C*H$_3$), 66.9 (O*C*H$_2$), 113.7 (C_{Ar}), 121.7 (C_{Ar}), 122.2 (C_{Ar}), 122.8 (C_{Ar}), 131.8 (C_{Ar}), 136.8 (C_{Ar}), 149.4 (C_{Ar}), 156.3 (C_{Ar}), 163.6 (C_{Ar}), 166.0 (*C*=O).
MS (EI) calculated for $C_{14}H_{13}NO_3$: 243.1; found: 243.1



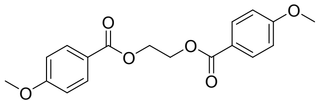
12

Isolated yield: 0.42 g, 81%. White powder.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 2.62 (s, 3H, Ar-C*H$_3$*), 3.90 (s, 3H, OC*H$_3$*), 5.47 (s, 2H, OC*H$_2$*), 6.97 (d, $J^3_{H,H}$ = 6.0 Hz, 2H, Ar), 7.14 (d, $J^3_{H,H}$ = 6.0 Hz, 1H, Ar), 7.30 (m, 1H, Ar), 7.64 (t, $J^3_{H,H}$ = 6.0 Hz, 1H, Ar), 8.12 (d, $J^3_{H,H}$ = 6.0 Hz, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 24.4 (Ar-*C*H$_3$), 55.5 (O*C*H$_3$), 67.0 (O*C*H$_2$), 113.7 (C_{Ar}), 118.6 (C_{Ar}), 122.3 (C_{Ar}), 122.4 (C_{Ar}), 131.9 (C_{Ar}), 137.1 (C_{Ar}), 155.6 (C_{Ar}), 158.1 (C_{Ar}), 163.6 (C_{Ar}), 166.0 (*C*=O).
MS (EI) calculated for $C_{15}H_{15}NO_3$: 257.1; found: 257.1



13

Isolated yield: 0.30 g, 76%. Pale yellow oil.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 3.35 (s, 1H, O*H*), 3.80 (s, 3H, OC*H$_3$*), 3.90 (m, 2H, C*H$_2$*OH), 4.38 (m, 2H, OC*H$_2$*), 6.86 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar), 7.98 (d, $J^3_{H,H}$ = 9.0 Hz, 2H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 55.4 (O*C*H$_3$), 61.0 (*C*H$_2$OH), 66.3 (O*C*H$_2$), 113.6 (C_{Ar}), 122.2 (C_{Ar}), 131.7 (C_{Ar}), 163.5 (C_{Ar}), 166.8 (*C*=O).
MS (EI) calculated for $C_{10}H_{12}O_4$: 196.1; found: 196.1



14

Isolated yield: 0.17 g, 52%. White crystals.
^{1}H NMR (300MHz, CDCl$_3$, ppm): δ 3.78 (s, 6H, OC*H$_3$*), 4,54 (s, 4H, OC*H$_2$*C*H$_2$*O), 6.84 (d, $J^3_{H,H}$ = 6.0 Hz, 4H, Ar), 7.94 (d, $J^3_{H,H}$ = 6.0 Hz, 4H, Ar);
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 55.5 (O*C*H$_3$), 62.6 (O*C*H$_2$*C*H$_2$O), 113.7 (C_{Ar}), 122.3 (C_{Ar}), 131.8 (C_{Ar}), 163.5 (C_{Ar}), 166.1 (*C*=O).
MS (EI) calculated for $C_{18}H_{18}O_6$: 330.1; found: 330.1

5. Synthetic Procedure for Pd(0)(**L2**)$_2$, [Pd(4-MeOC$_6$H$_4$)(Br)(**L2**)]$_2$ (**15**)and detailed crystal data

5.1 Synthesis of Pd(0)(**L2**)$_2$

A 25 mL Schlenk tube was charged with ^{t}Bu$_2$PCl (0.22 g, 1.02 mmol), ^{n}BuOH (10 mL) and DBU (0.69 mL 4.6 mmol) under an argon atmosphere. The mixture was then stirred at room temperature for 5 h. After removal of volatile material under vacuum, the colorless oil (^{t}Bu$_2$PO^{n}Bu, **L2**) was transferred to another 25 mL Schlenk tube which was charged with 5 mL heptane solution of Pd(Allyl)(Cp) (0.11 g, 0.5 mmol). The mixture was kept stirring at room temperature for 24 h. During this period, the color of mixture turned pale yellow from dark red. After that the solvent was removed under vacuum and residue was washed with cold pentane (3 mL × 3). As a result, the Pd(**L2**)$_2$ was obtained as yellow oil. Yield: 82%, 0.22 g. ^{1}H NMR (300MHz, C$_6$D$_6$, ppm): δ 0.88 (t, $J^3_{H,H}$ = 6.0 Hz, 6H, C*H$_3$*), 1.36 (m, 36H, C(C*H$_3$)$_3$*), 1.58 (m, 4H, C*H$_2$*), 1.67 (m, 4H, C*H$_2$*), 4.20 (m, 4H, OC*H$_2$*); ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$, ppm): δ 164.9; ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 14.0 (*C*H$_3$), 19.4 (*C*H$_2$), 28.5 (C(*C*H$_3$)$_3$), 29.6 (*C*(CH$_3$)$_3$), 37.4 (*C*H$_2$), 74.2 (O*C*H$_2$).

5.2 Synthesis of [Pd(4-MeOC$_6$H$_4$)(Br)(**L2**)]$_2$ (**15**)

A 25 mL Schlenk tube was charged with 5 mL Toluene solution of Pd(**L2**)$_2$ (0.22 g, 0.4 mmol) under an argon atmosphere. 4-Bromoanisole (0.30 g, 1.6 mmol) was added into mixture with string. The mixture was then stirred at 70 ^{o}C for 2 h. After removal of solvent, the residue was washed by heptane (3 mL × 3) and re-crystallized in 2 mL toluene. The solution was placed at 0 ^{o}C. Pale yellow crystals of complex **15** were obtained from this toluene solution at 0 ^{o}C. Yield: 52%, 0.11 g.
^{1}H NMR (300MHz, C$_6$D$_6$, ppm): δ 0.65 (t, $J^3_{H,H}$ = 6.0 Hz, 6H, C*H$_3$*), 0.96 (br, 8H, C*H$_2$*), 1.33 and 1.38 (s, 36H, C(C*H$_3$)$_3$*), 2.94 (br, 4H, OC*H$_2$*), 3.32 (s, 6H, OC*H$_3$*), 6.62 (m, 4H, Ar), 7.52 (br, 4H, Ar); ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$, ppm): δ 156.7; ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm): δ 13.7 (*C*H$_3$), 18.8 (*C*H$_2$), 29.2 (C(*C*H$_3$)$_3$), 29.3 (C(*C*H$_3$)$_3$), 42.2 (*C*(CH$_3$)$_3$), 54.5 (O*C*H$_3$), 59.3 (O*C*H$_2$), 113.1 (C$_{Ar}$), 137.4 (C$_{Ar}$), 157.1 (C$_{Ar}$). Anal. Calcd for $C_{39}H_{68}Br_2O_4P_2Pd_2$ (1020.10 g mol^{-1}): C, 44.59; H, 6.70. Found: C, 44.68; H, 6.80.

5.3 X-ray crystal structure analysis of complex **15**

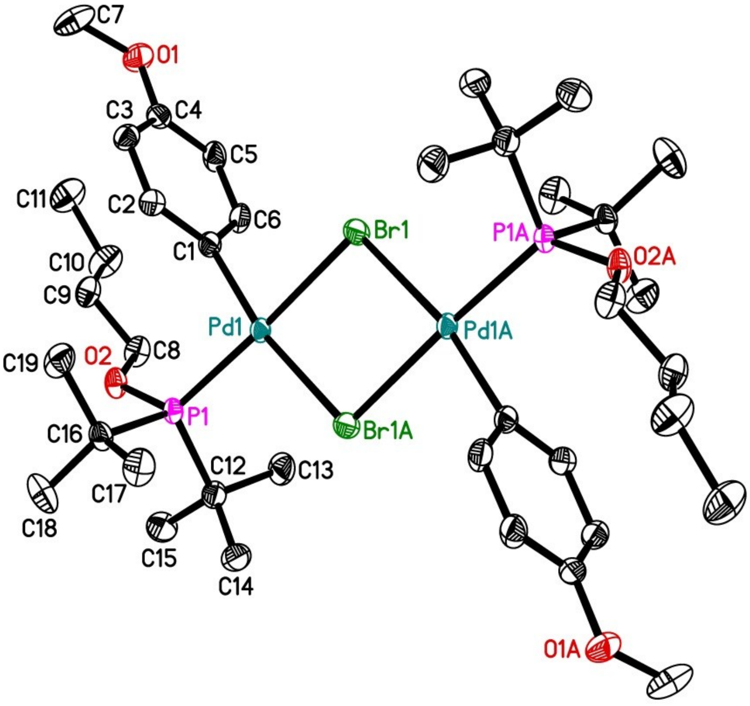


Figure S3. Molecular structure of **15**. Displacement ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity. The asymmetric unit contains half of the molecule; the remaining part is generated by the following symmetry operator: -x+1, -y+1, -z+2.

Table S2. Selected X-ray crystallographic data

formula	$C_{38}H_{68}Br_2O_4P_2Pd_2$
M_z	1023.48
crystal system	Monoclinic
space group	$P2_1/n$
a [Å]	14.0608(4)
b [Å]	8.2017(3)
c [Å]	19.8933(6)
α [^{o}]	90.00
β [^{o}]	108.3254(5)
γ [^{o}]	90.00
V [Å^3]	2177.80(12)
T [K]	150(2)
Z	2
μ[mm^{-1}]	2.769
total reflns	24082
unique reflns	5790
R_{int}	0.0200
R_1[I>2σ(I)]	0.0181
wR(F^2) [I>2σ(I)]	0.0431
R_1(all data)	0.0215
wR(F^2)(all data)	0.0445
GOF on F^2	1.042
no. of refined params	225

Table S3. Selected bond lengths (Å) and angles (^{o}) for **15**

Pd1-C1	2.0062(14)	P1-Pd1-Br1A	98.815(10)
Pd1-P1	2.2611(4)	Br1-Pd1-Br1A	83.380(6)
Pd1-Br1	2.53224(19)	C1-Pd1-P1	92.34(4)
Pd1-Br1A	2.57555(19)	Pd1-Br-Pd1A	96.619(6)
C1-Pd1-Br1	85.45(4)	C8-O2-P1-Pd1	55.36(12)

5.4 Catalytic procedure of butoxycarbonylation of 4-bromoanisole with complex **15** as catalyst.

A 10 mL Schlenk tube was charged with **15** (15.3 mg, 0.015 mmol) and n-butanol (2 mL) under an argon atmosphere. Subsequently, the mixture was transferred to a vial (12 mL reaction volume) which was charged with DBU (0.45 mL 3 mmol), 4-bromoanisole (0.37 mg, 2 mmol) and equipped with a septum, a small cannula and a stirring bar. The vial was placed in an alloy plate which was transferred to a 300 mL autoclave (4560 series from Parr Instruments®) under an argon atmosphere. The autoclave was flushed three times with CO and then pressurized to 20 bar CO. The reaction was kept stirring at 115 ^{o}C for 18 h. After cooling down to room temperature, CO was released carefully. Pure product could be obtained by column chromatography on silica gel (eluent: hexane/ethylacetate = 9:1). Yield: 85%, 0.35 g.

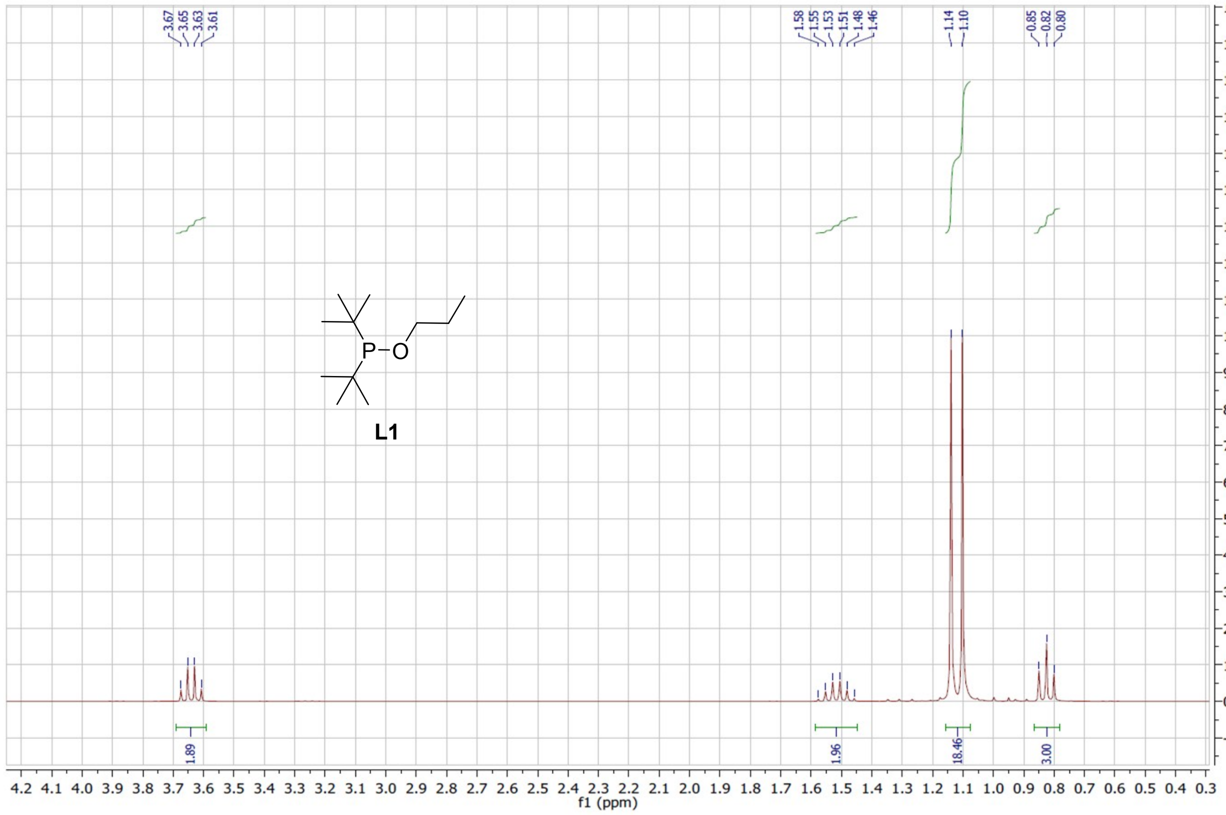
5.5 **Table S4.** ^{1}H NMR chemical shifts of butoxy protons in complex **15** and Pd(**L2**)$_2$

Complex	δH(CH3), ppm	δH(γ-CH2), ppm	δH(β-CH2), ppm	δH(α-CH2), ppm
15 [a]	0.65	0.96	0.96	2.94
Pd(0)(**L2**)$_2$ [a]	0.88	1.58	1.67	4.20

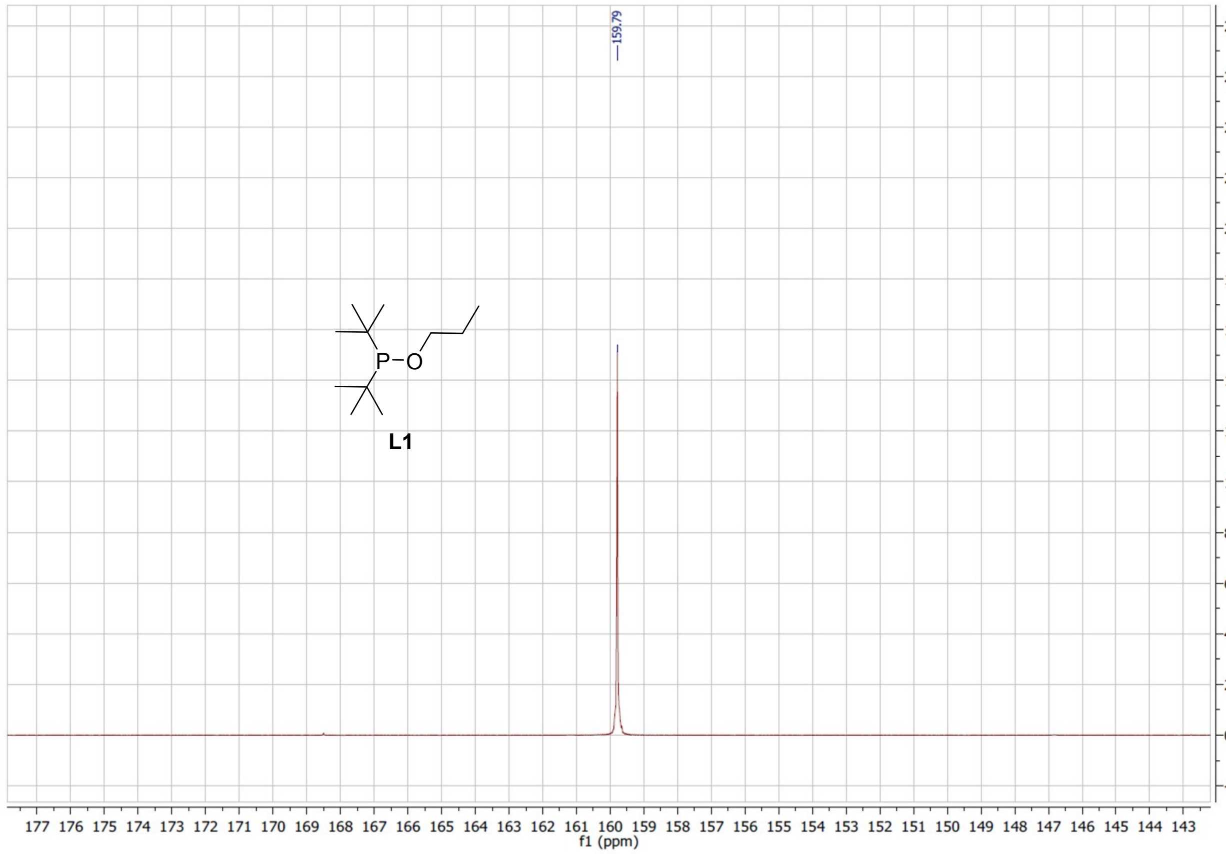
[a] ^{1}H NMR spectra were recorded in C_6D_6.

NMR spectra

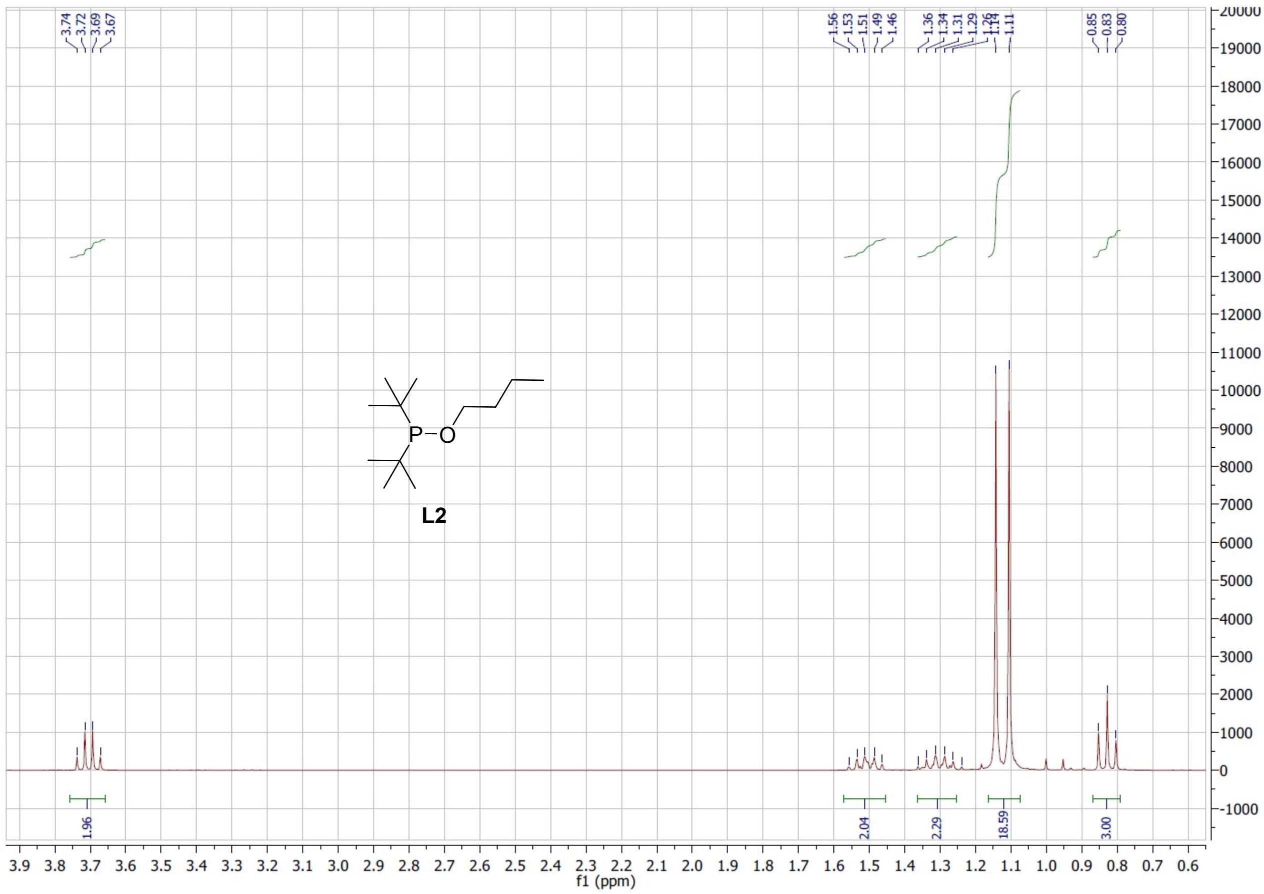
^{1}H NMR (300MHz, C_6D_6, ppm)



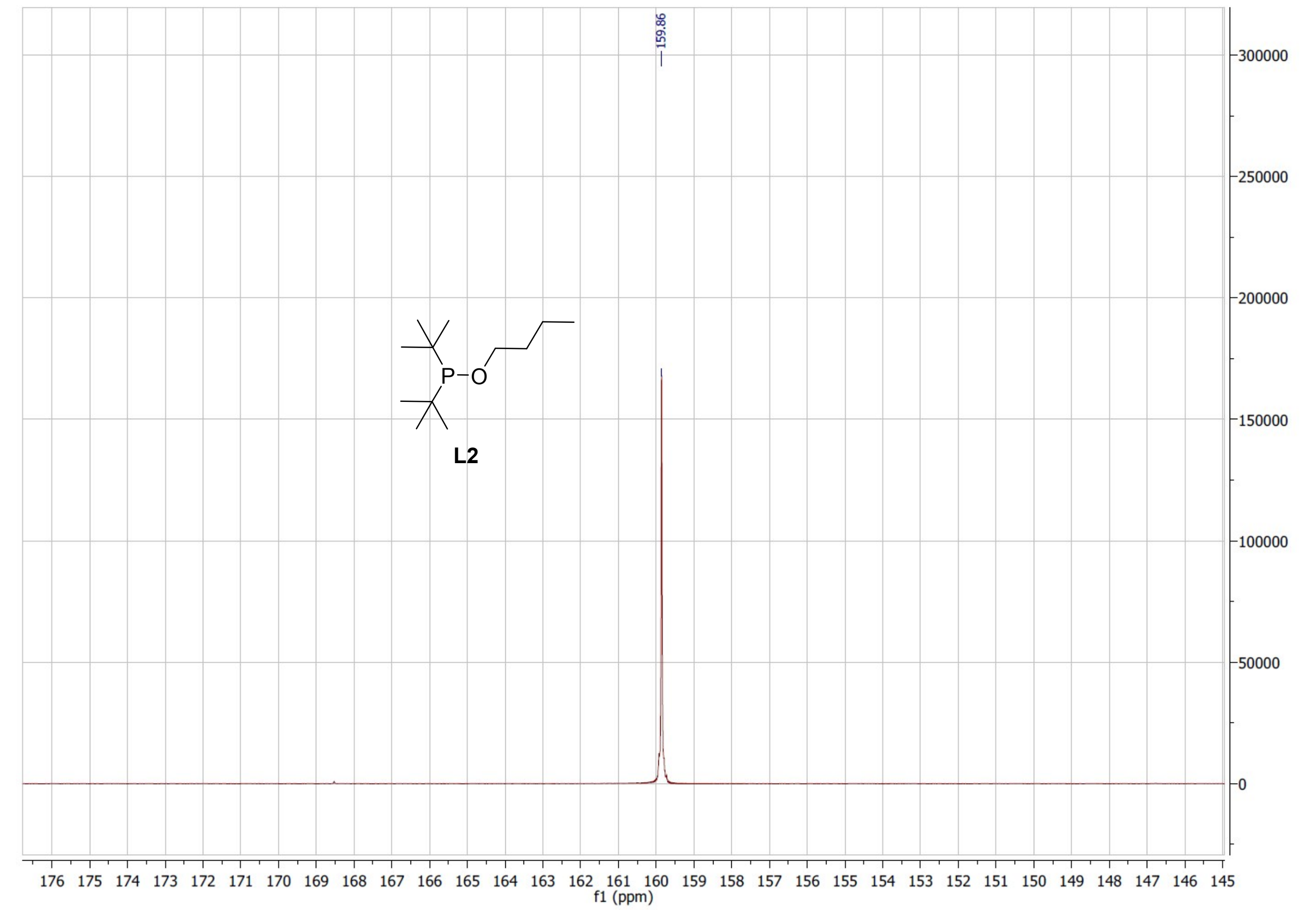
^{31}P{^{1}H } NMR (121.5 MHz, C_6D_6, ppm)



^{1}H NMR (300MHz, C_6D_6, ppm)

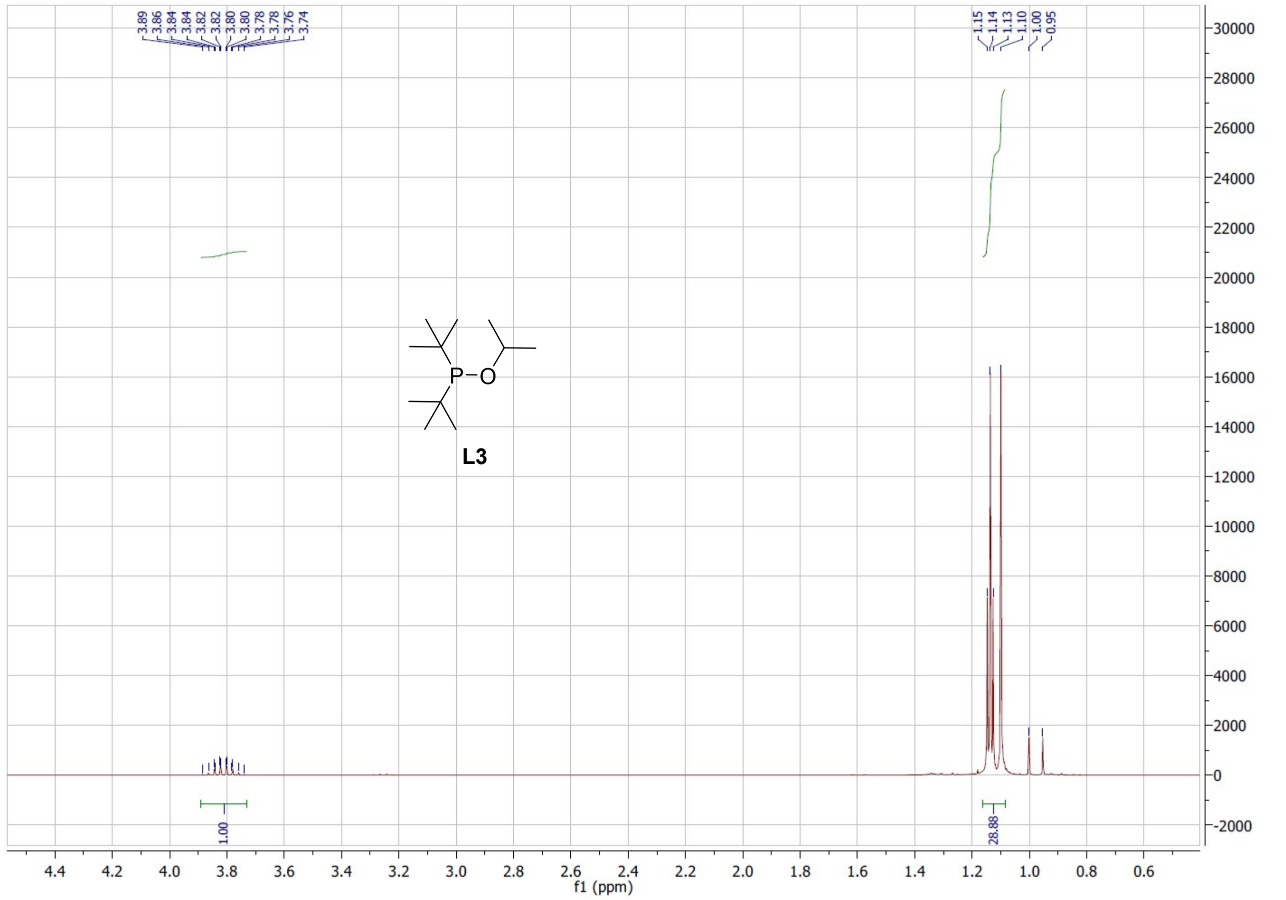


$^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6, ppm)



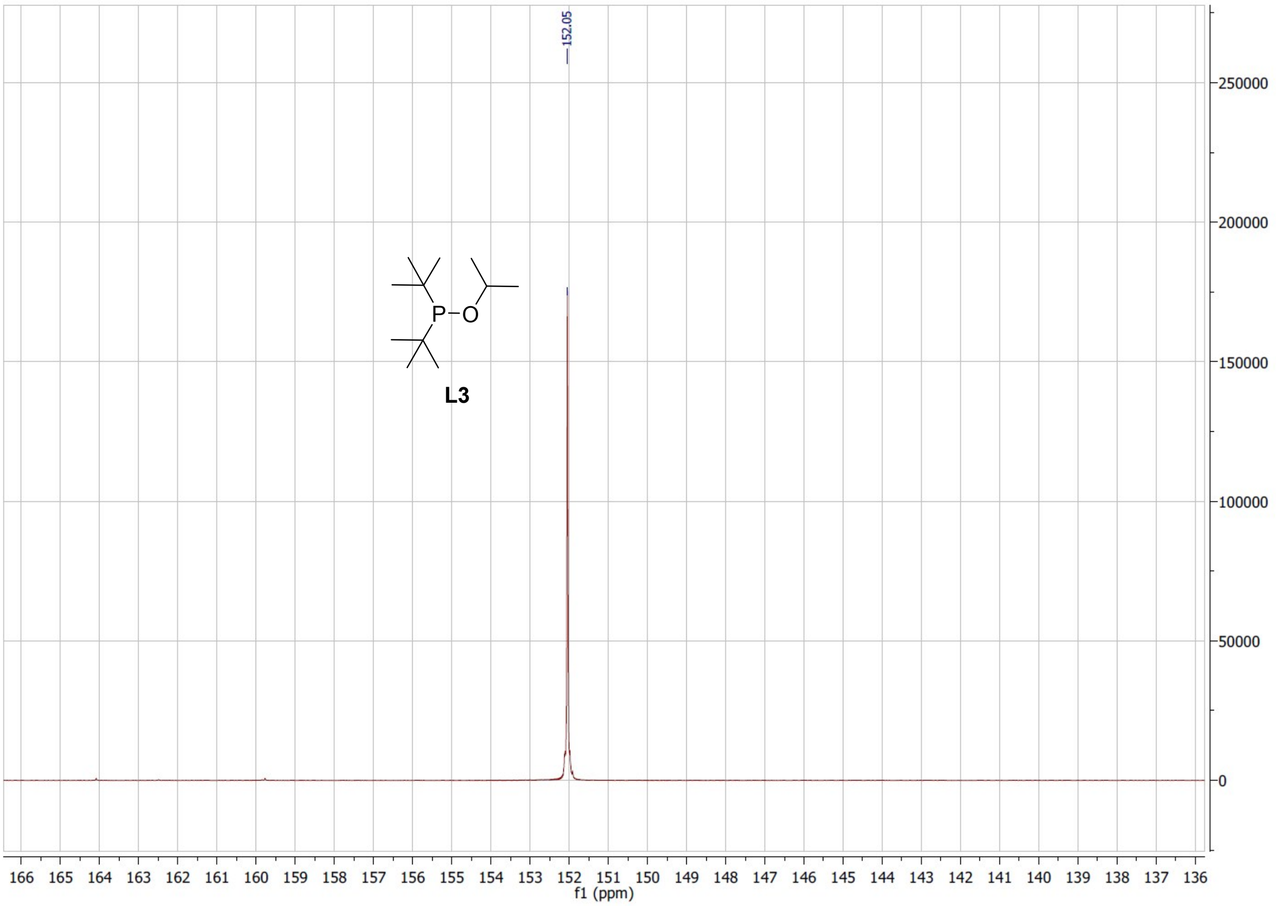
L2

^{1}H NMR (300MHz, C_6D_6, ppm)

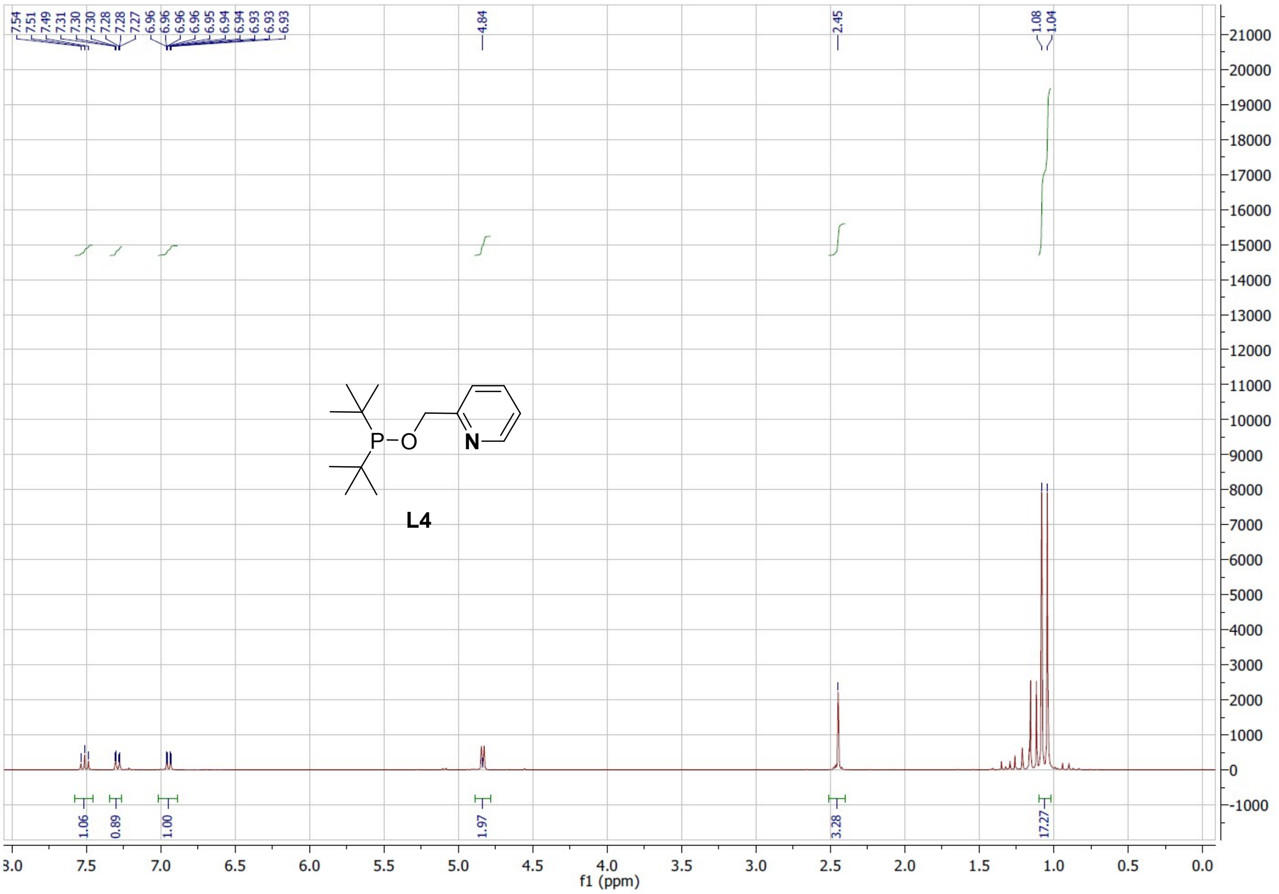


L3

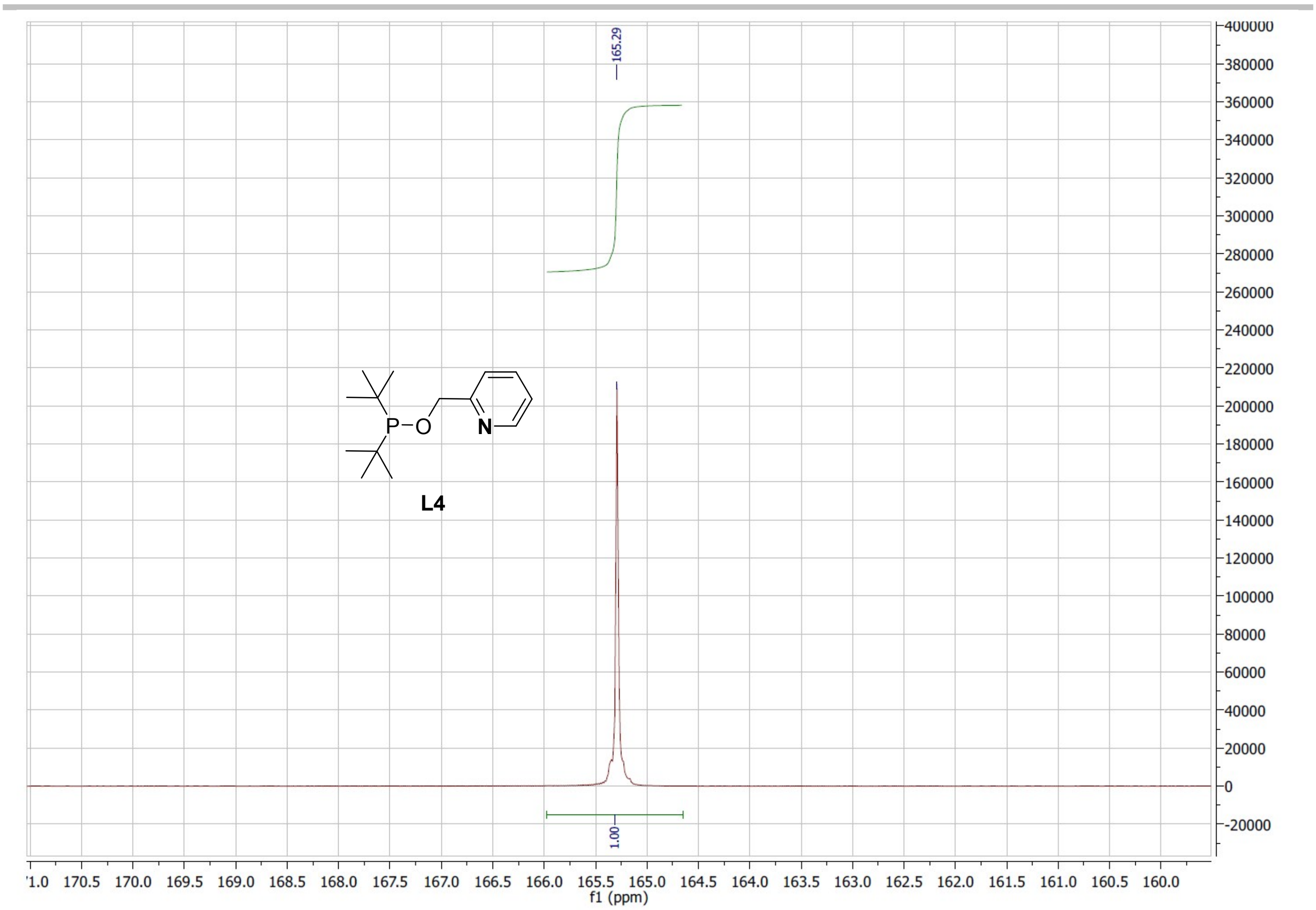
^{31}P{^{1}H } NMR (121.5 MHz, C_6D_6, ppm)



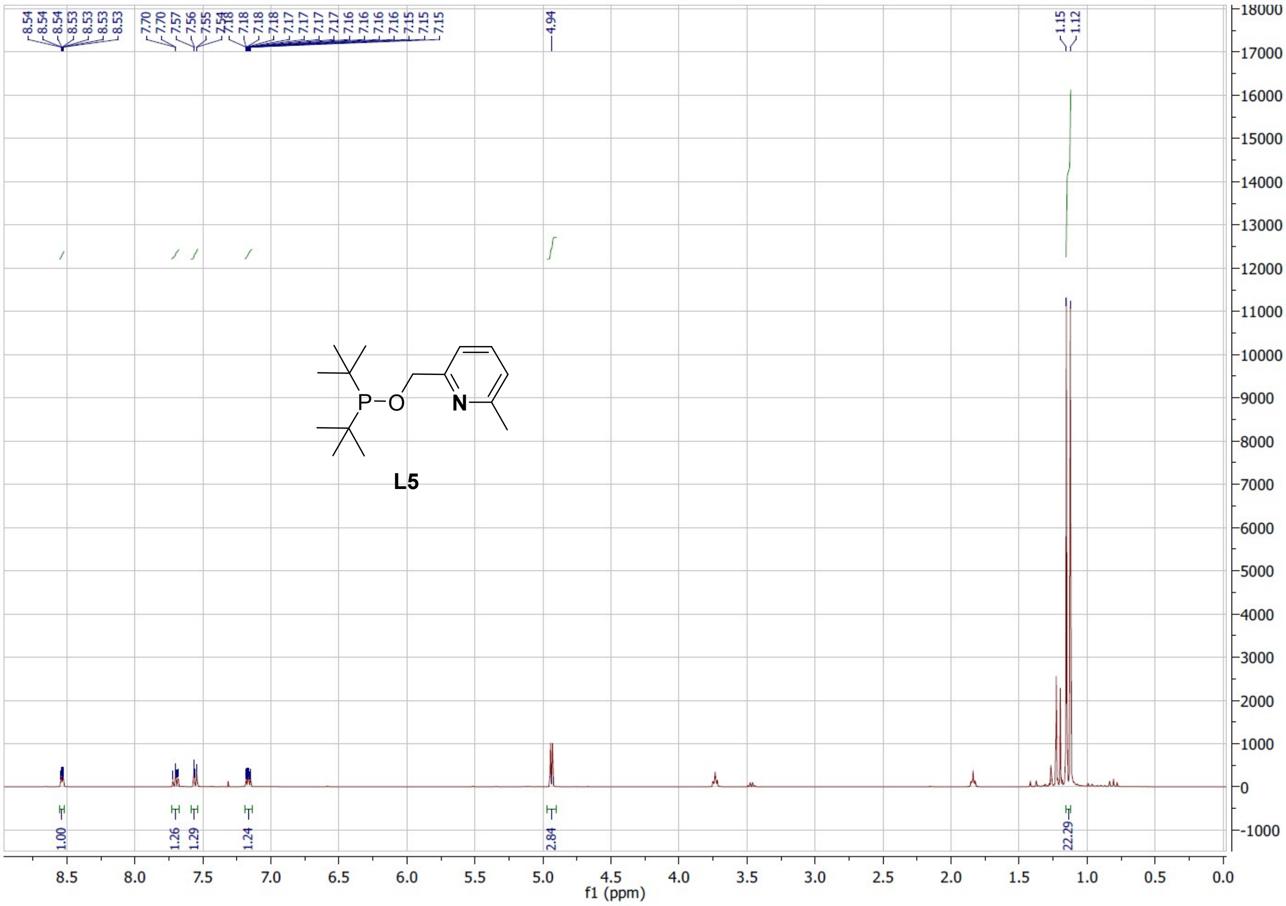
^{1}H NMR (300MHz, C_6D_6, ppm)



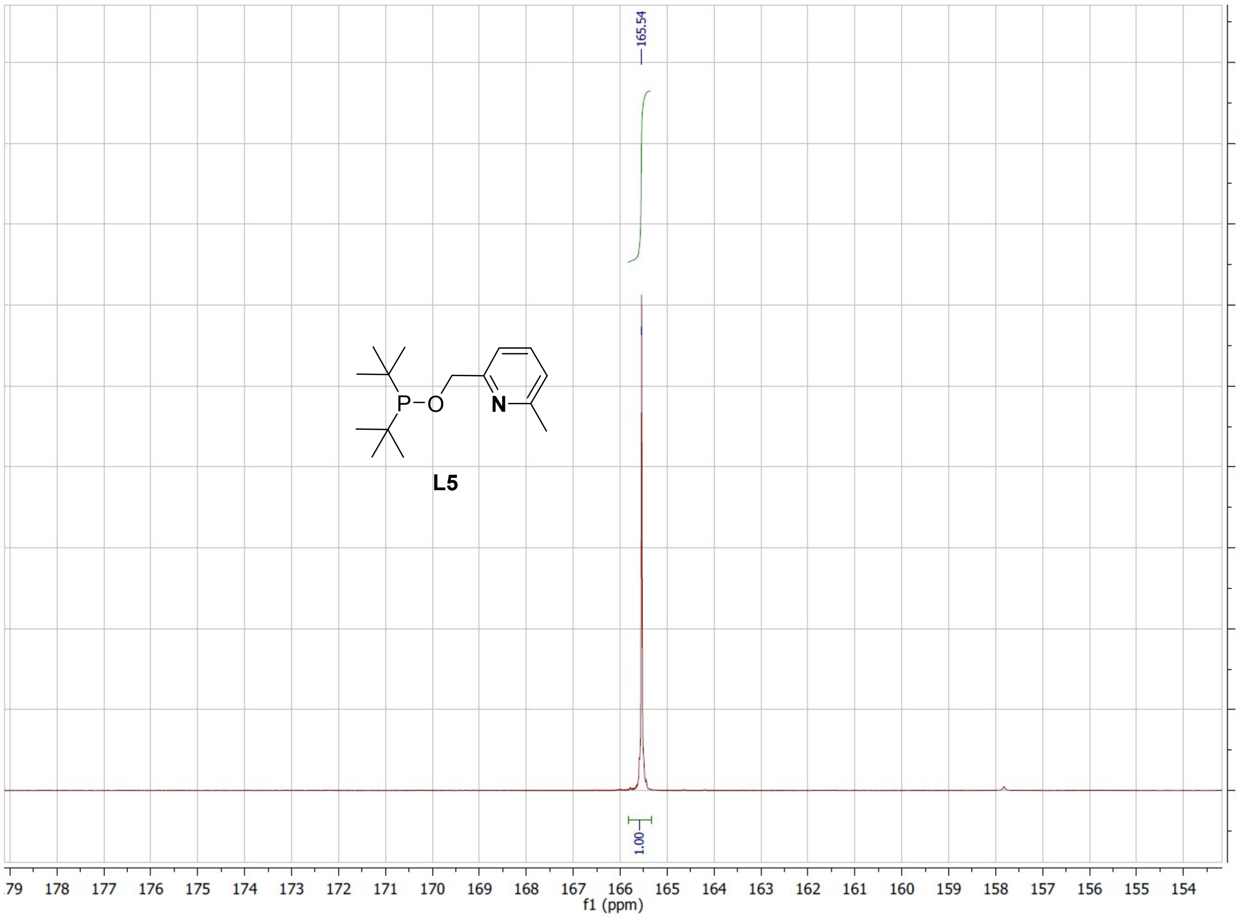
^{31}P{^{1}H } NMR (121.5 MHz, C_6D_6, ppm)



^{1}H NMR (300MHz, C_6D_6, ppm)

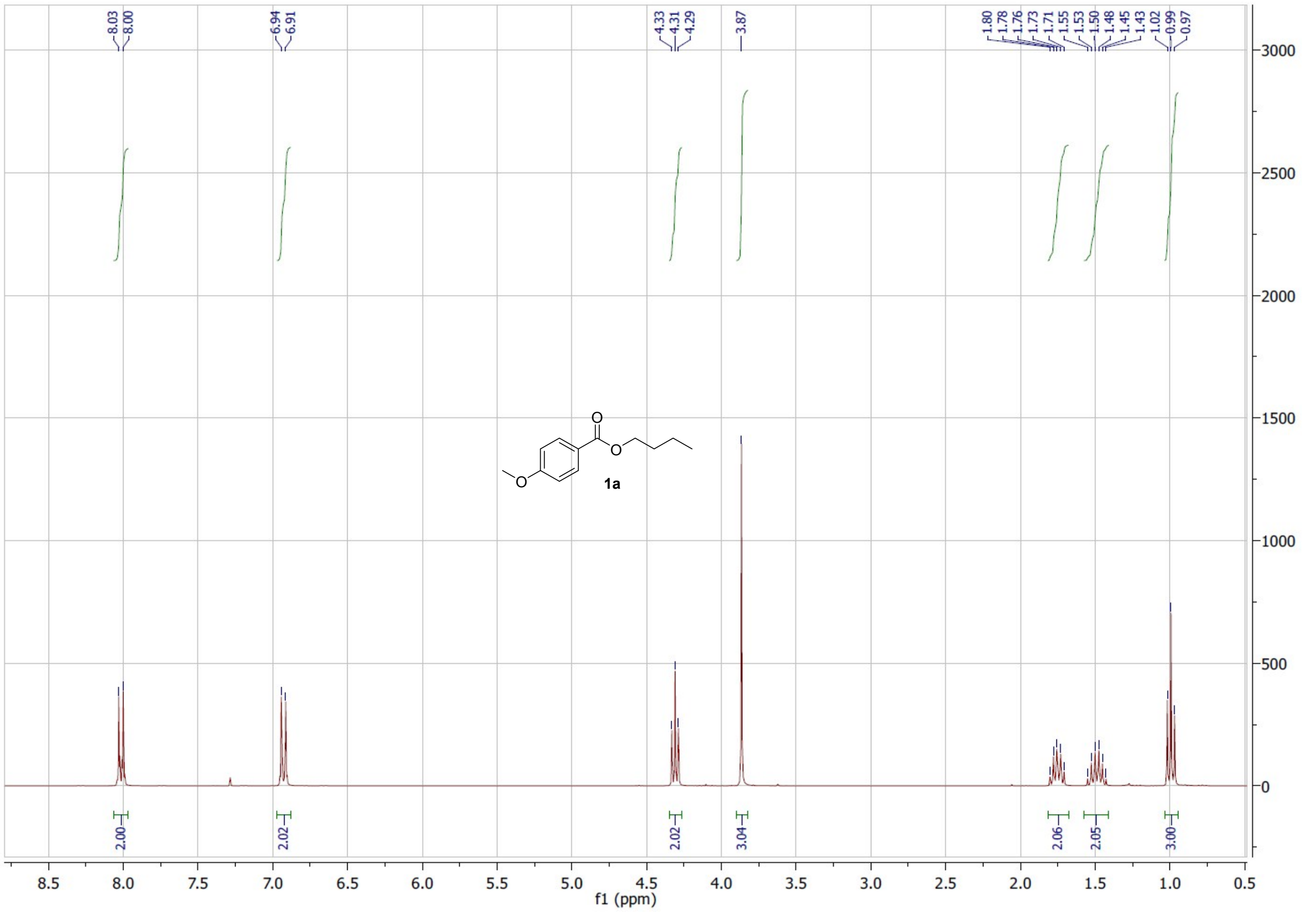


^{31}P{^{1}H } NMR (121.5 MHz, C_6D_6, ppm)



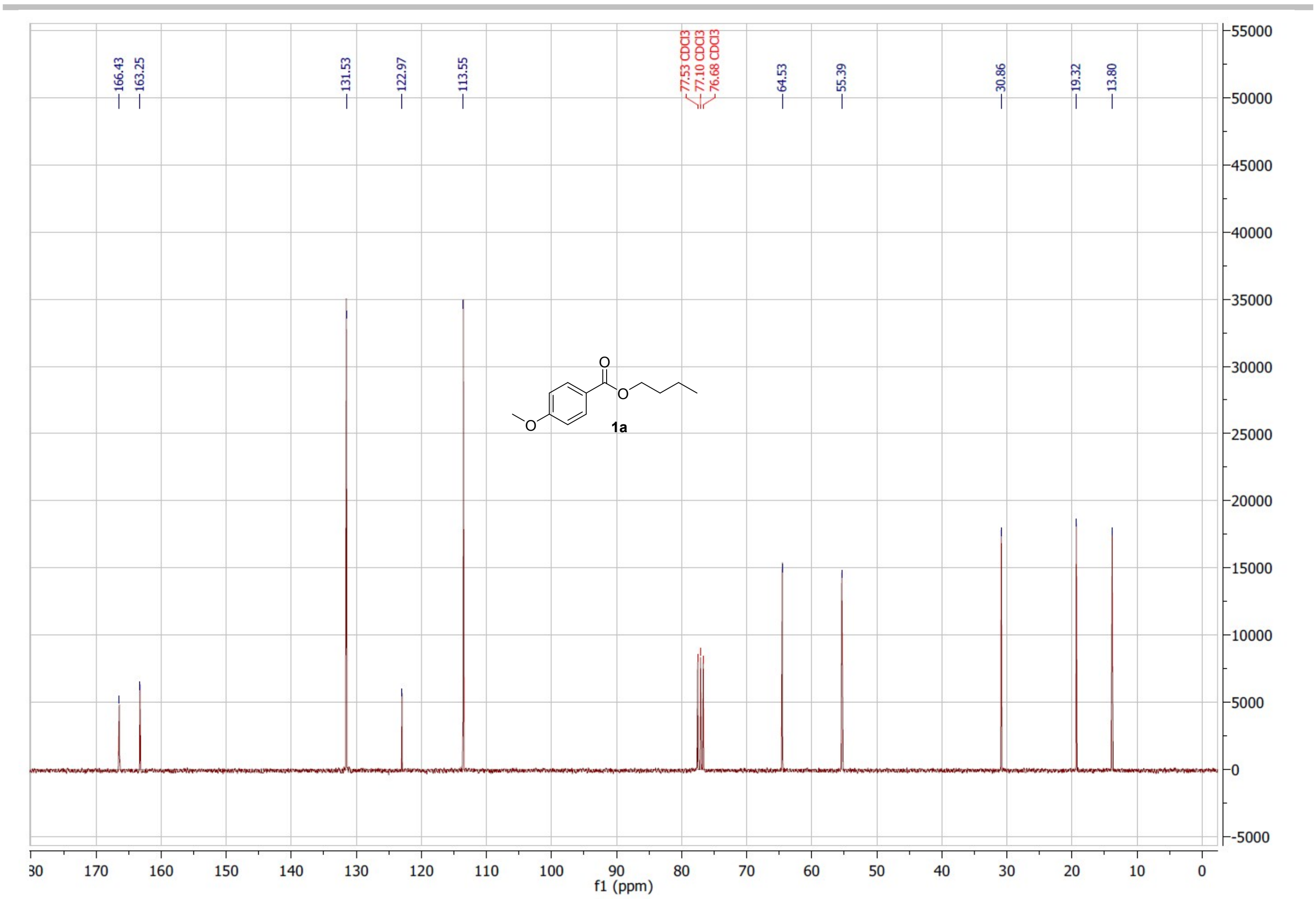
L5

^{1}H NMR (300MHz, CDCl$_3$, ppm)

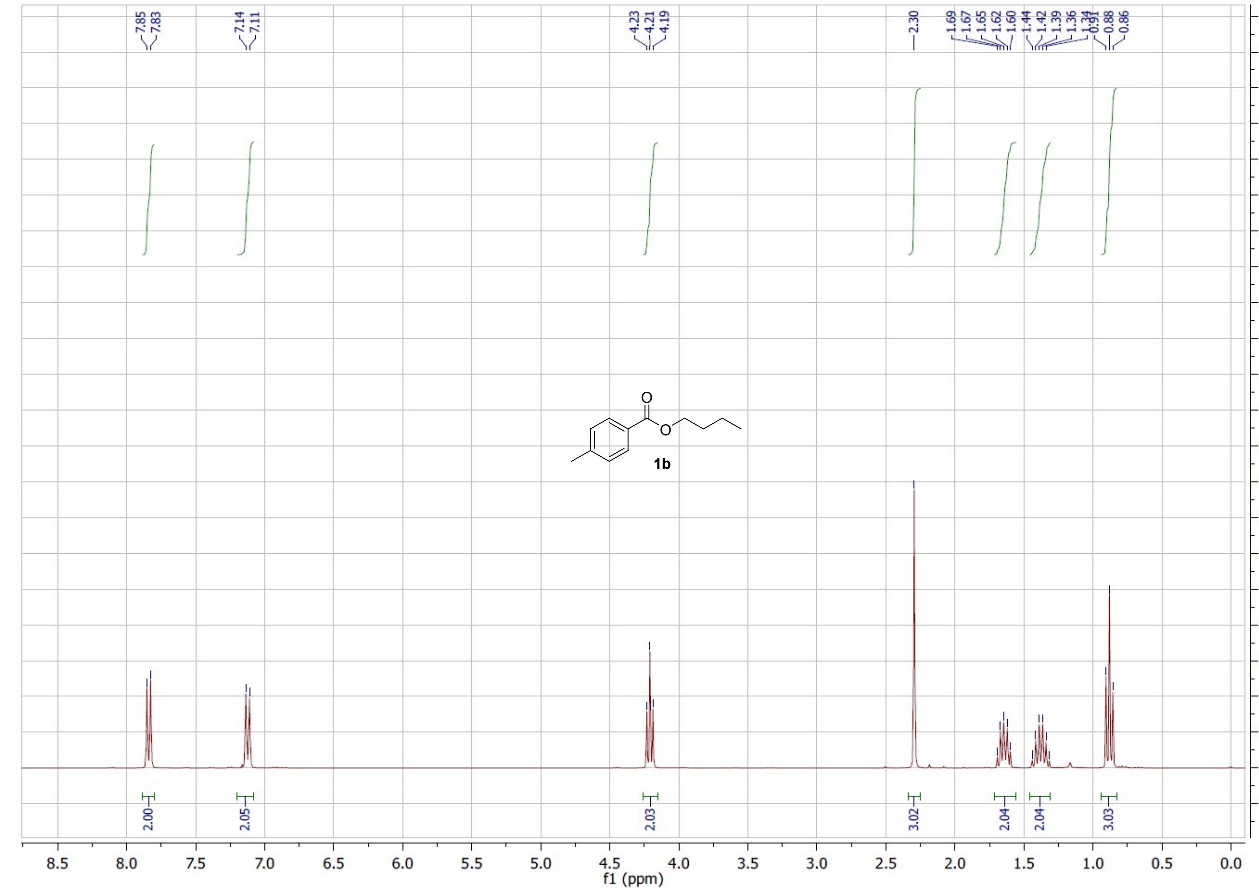


1a

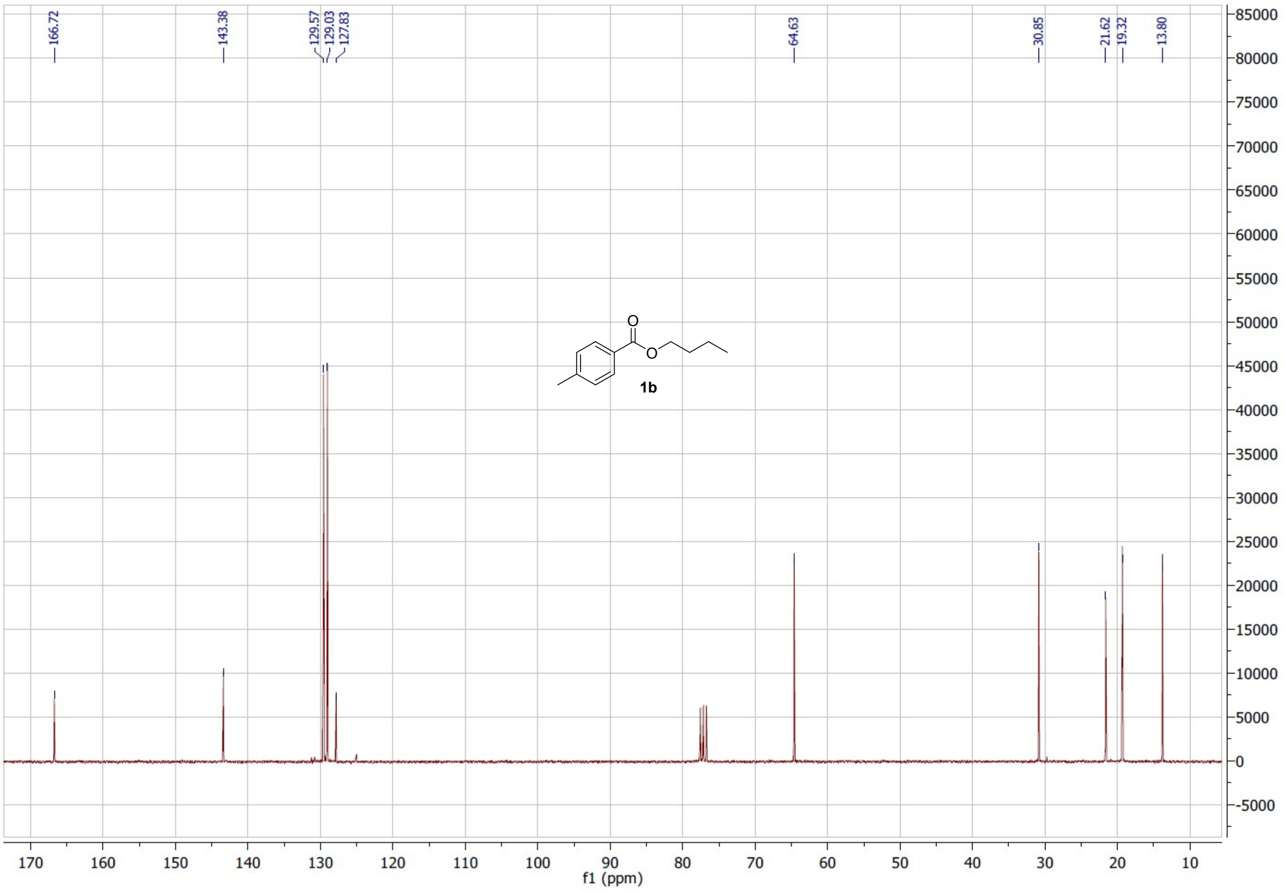
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm)



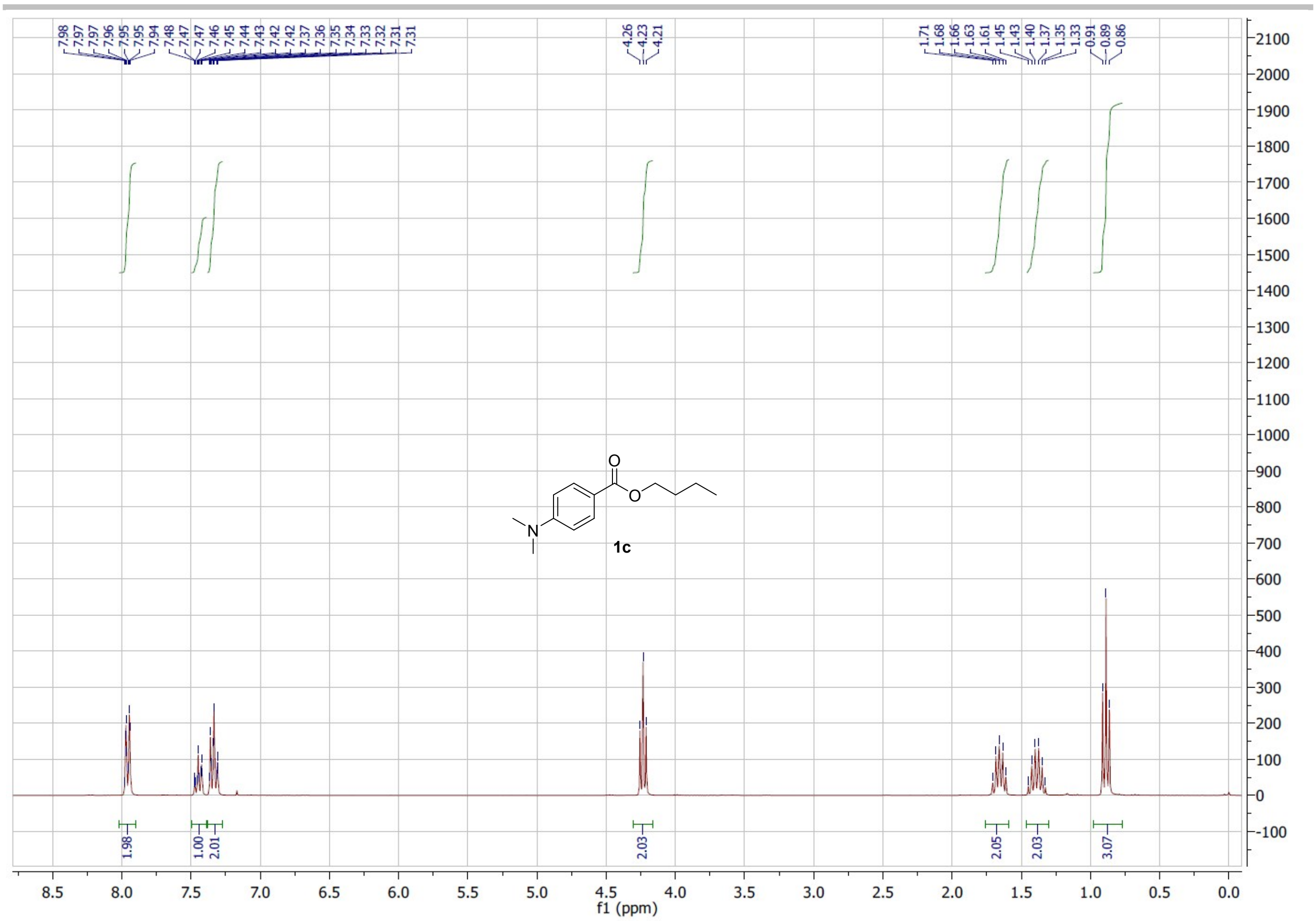
^{1}H NMR (300MHz, CDCl$_3$, ppm)



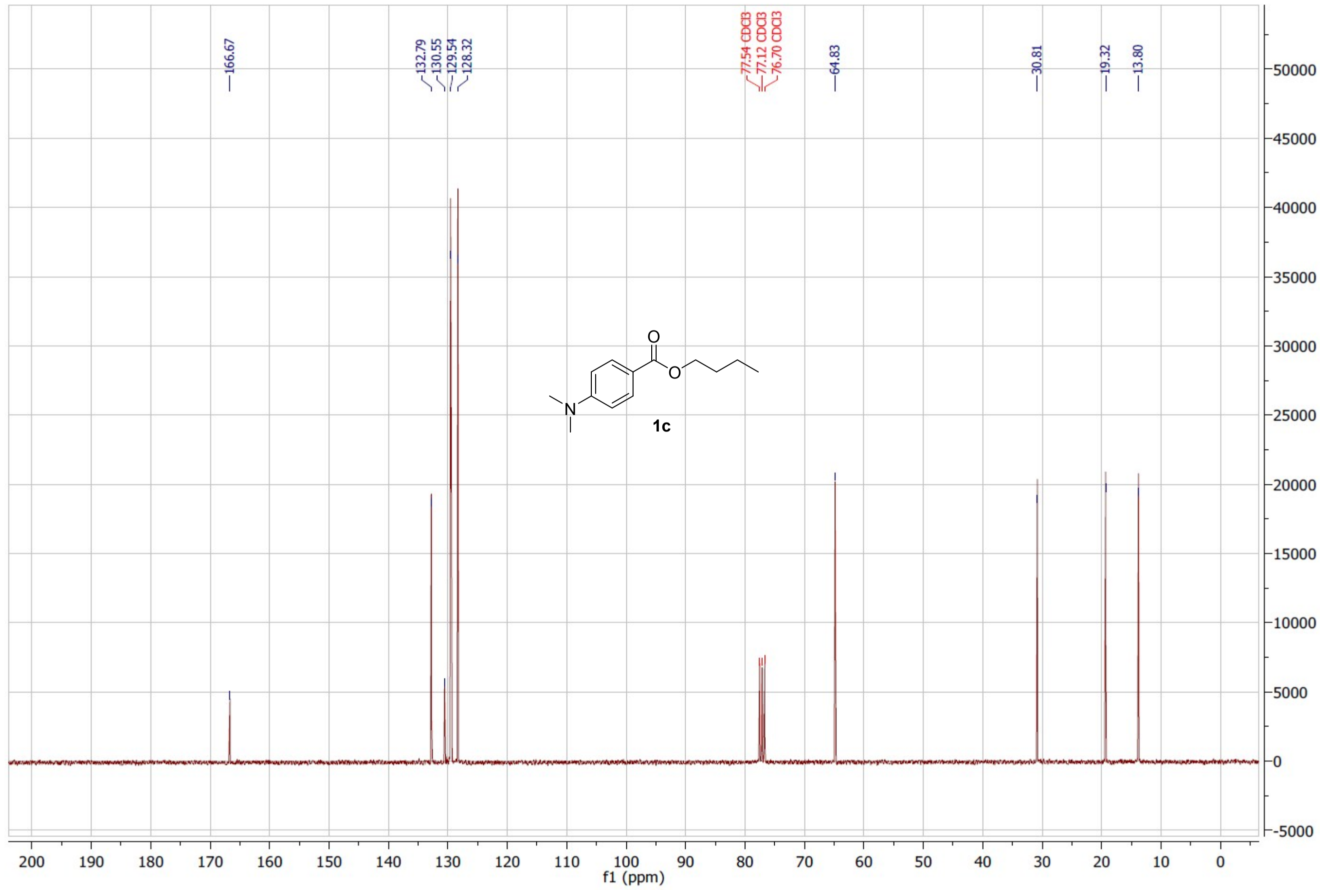
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm)



^{1}H NMR (300MHz, $CDCl_3$, ppm)



$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm)



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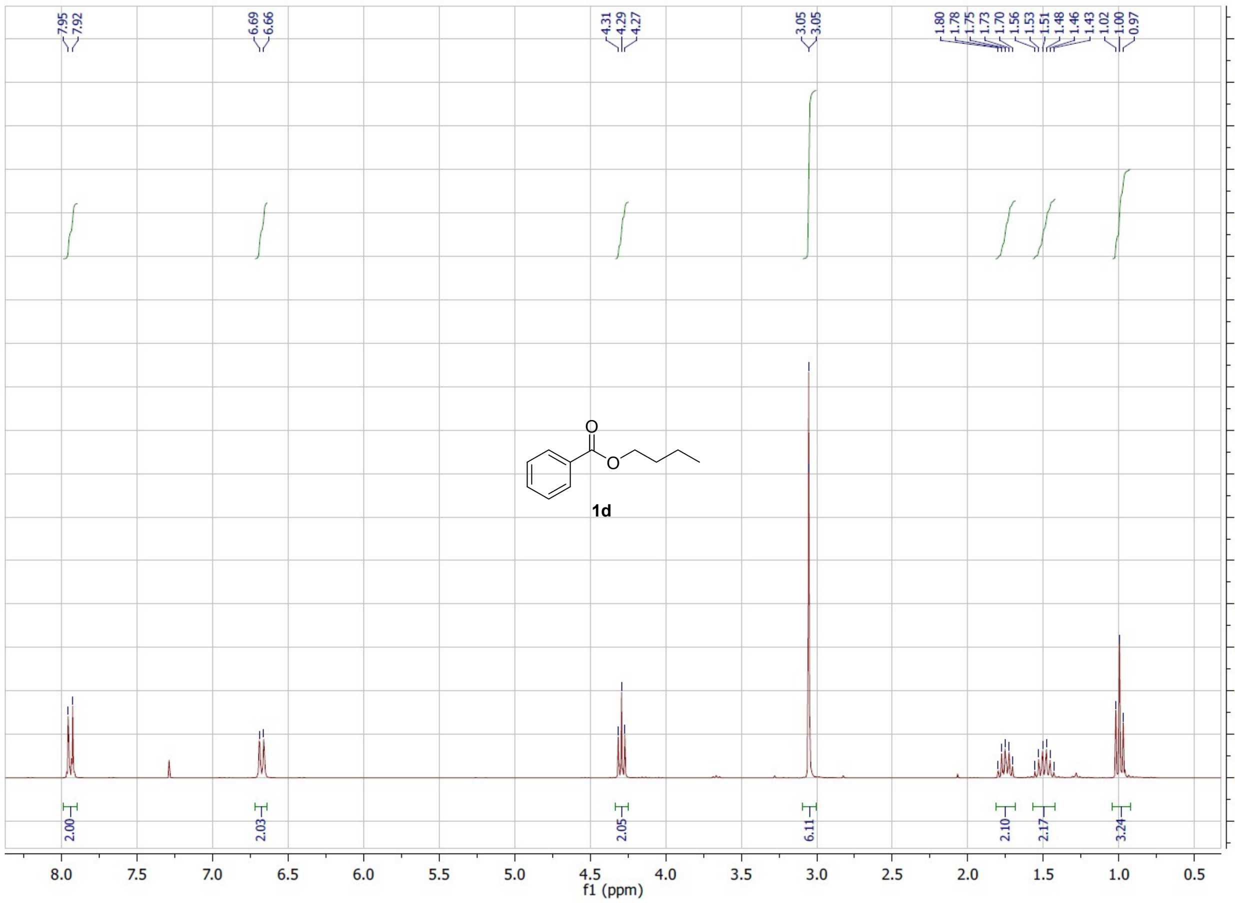

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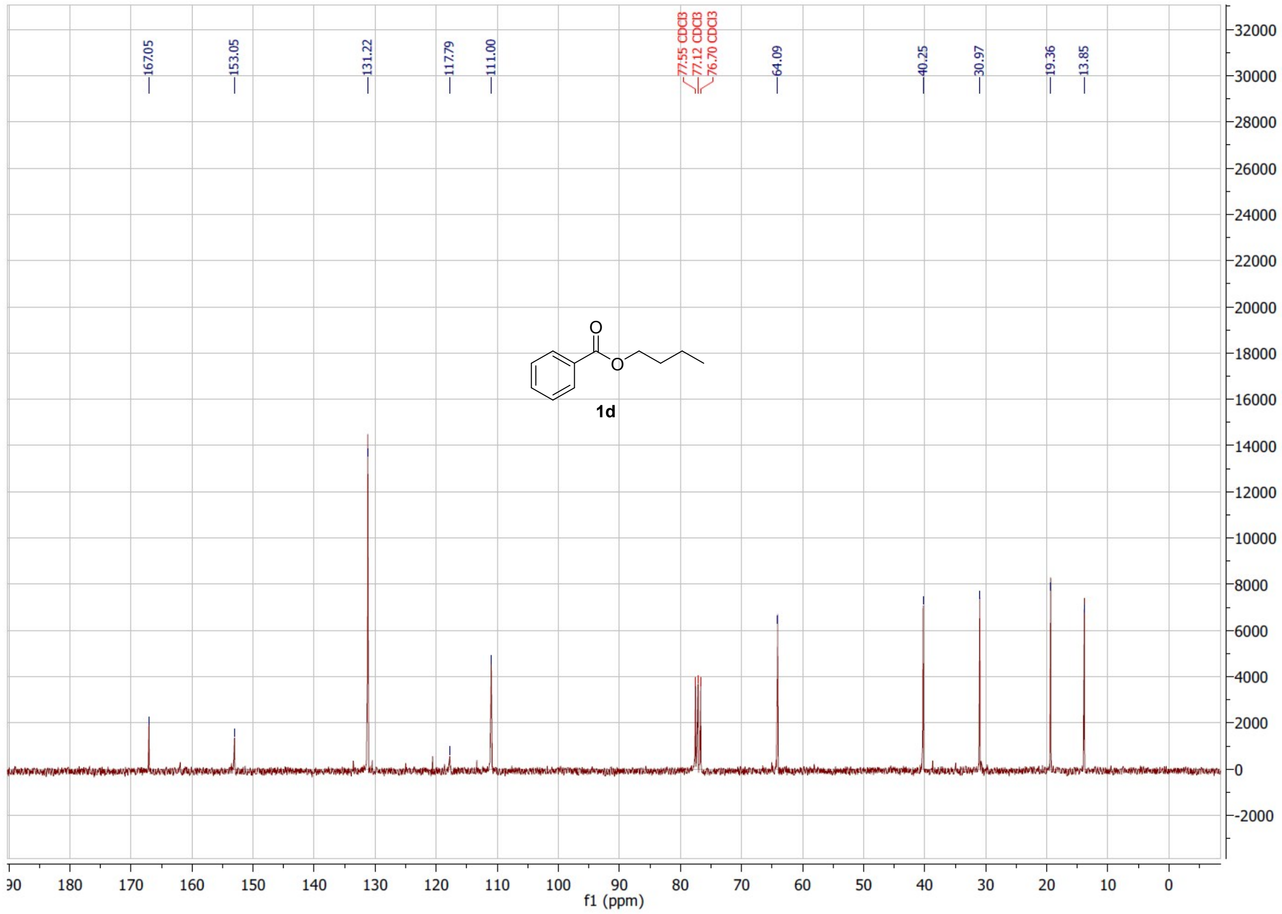

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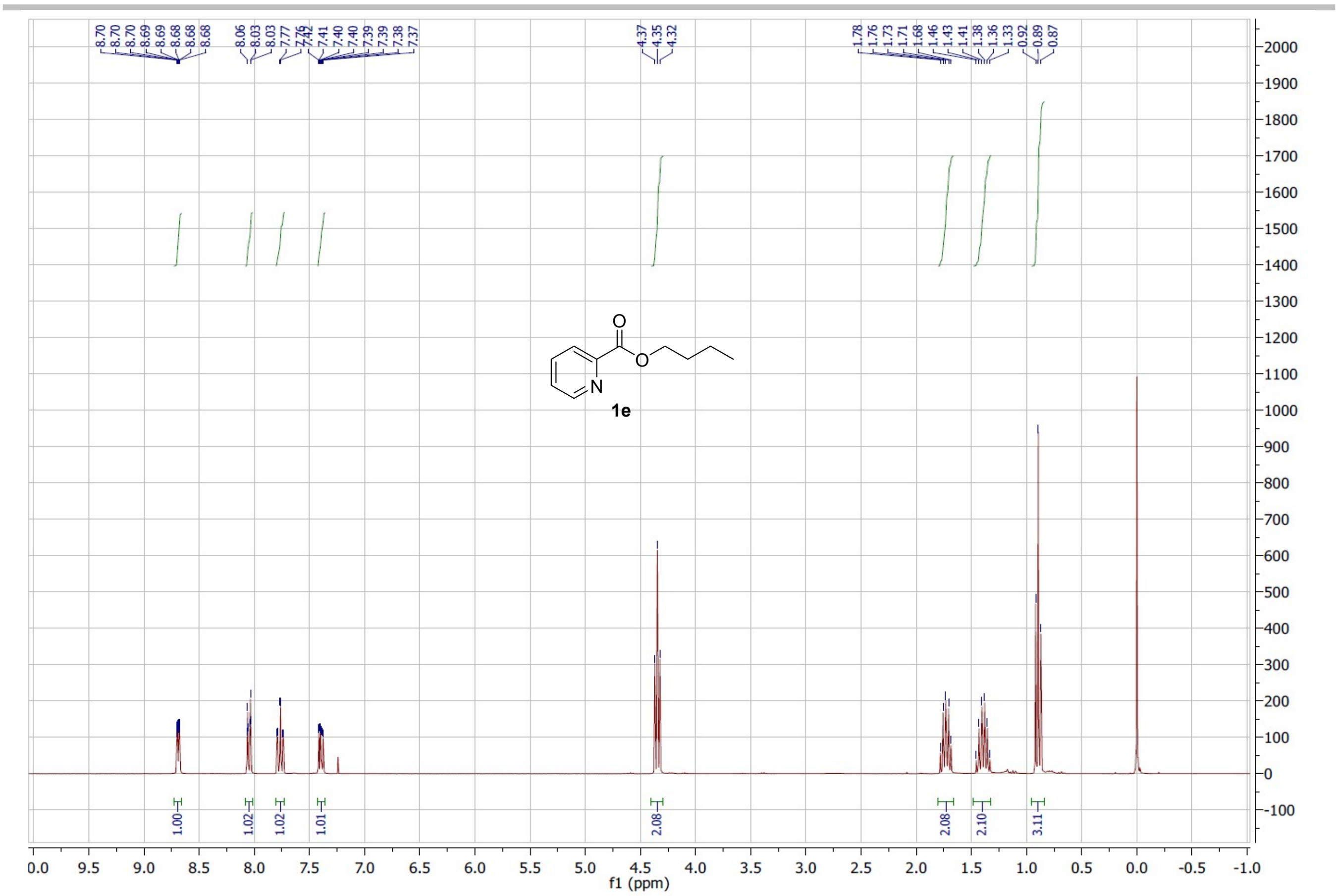

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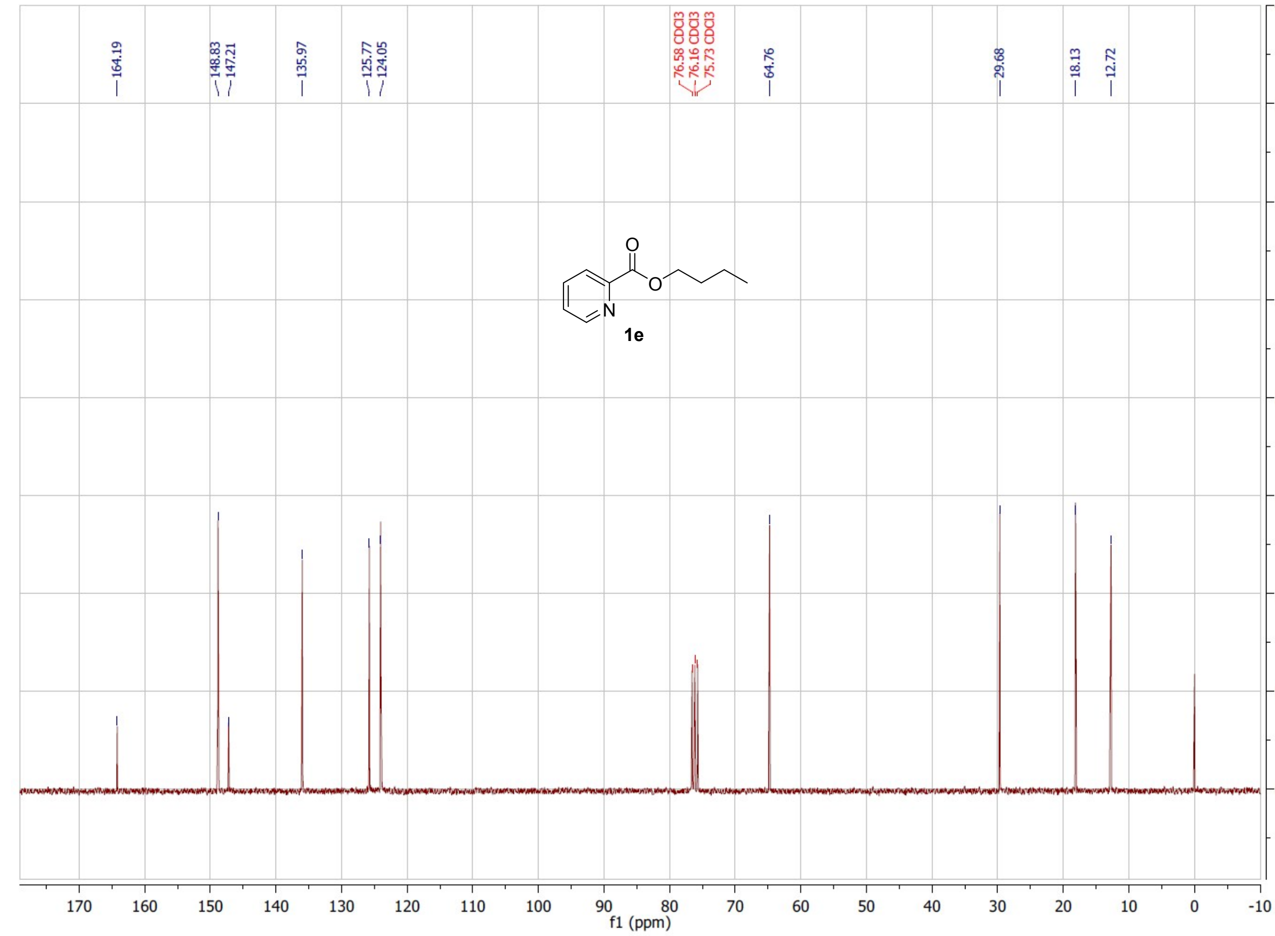
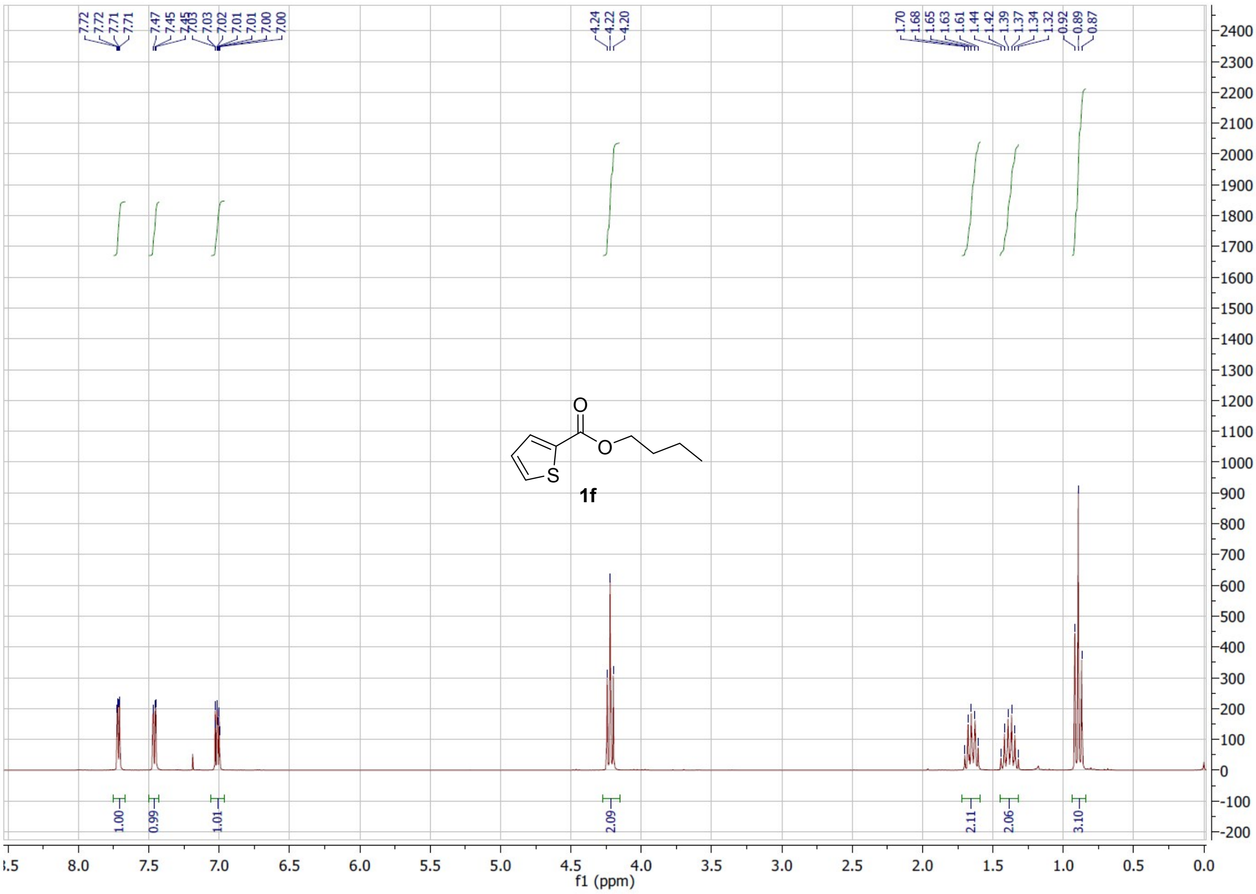
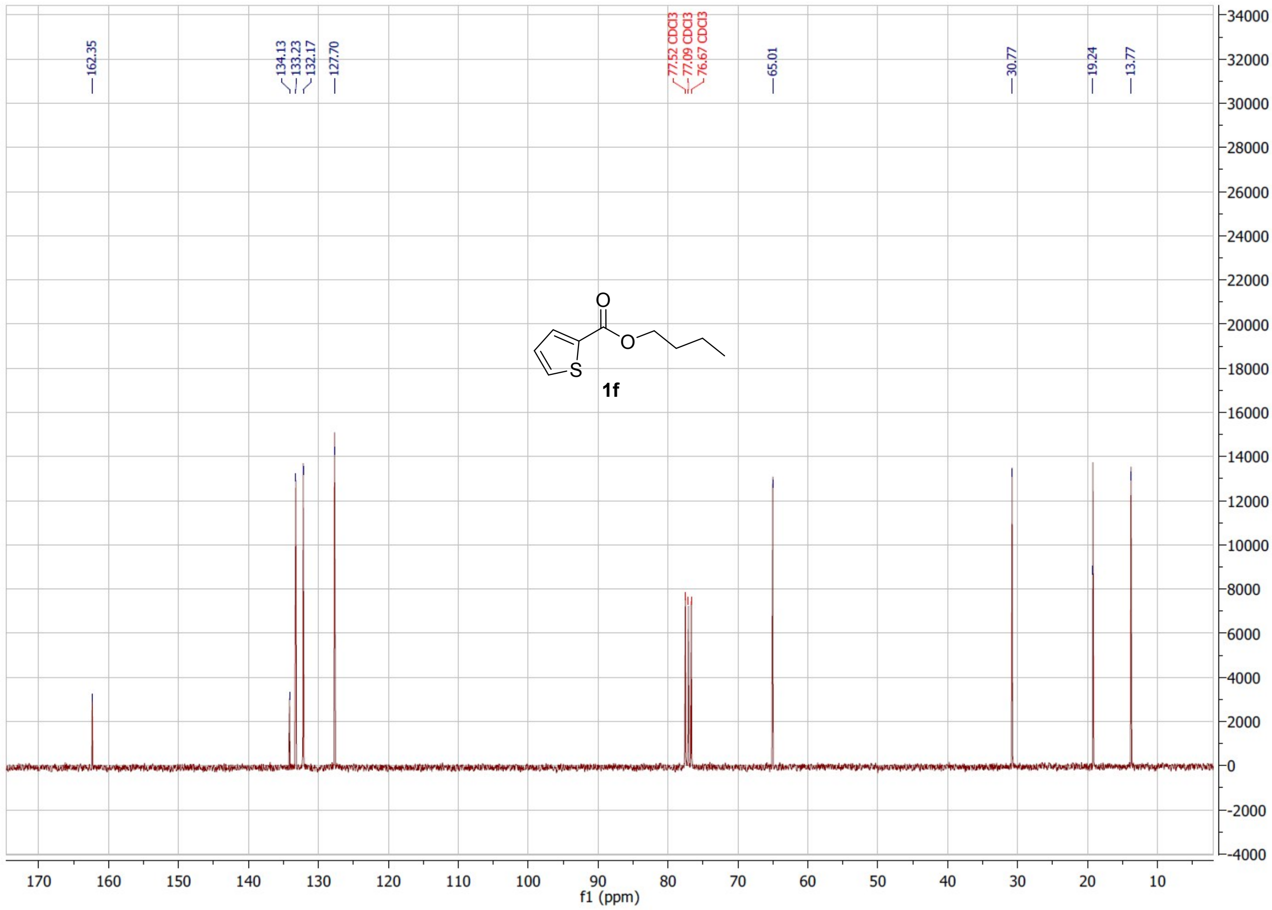


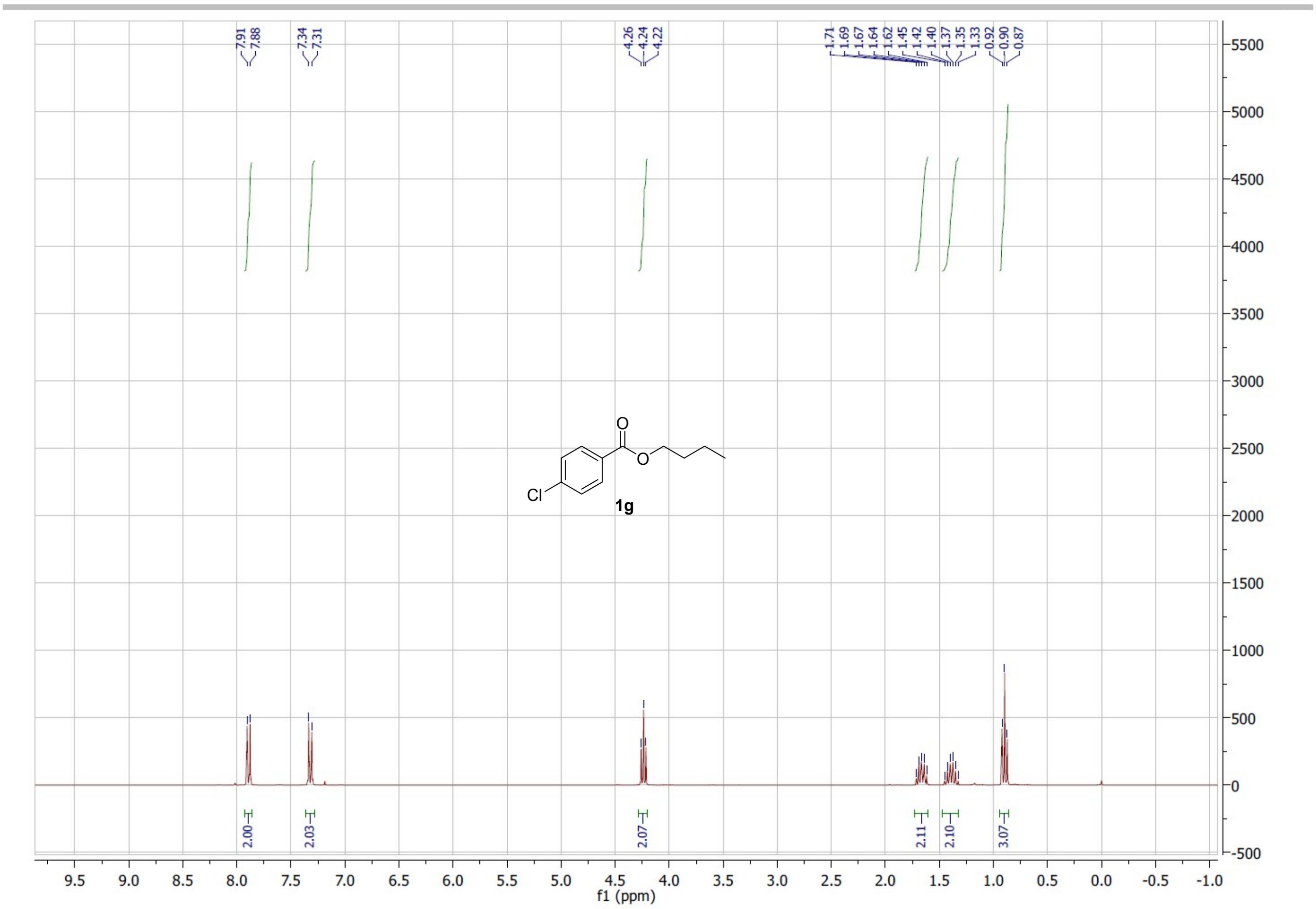
^1H NMR (300MHz, $CDCl_3$, ppm)



¹³C{¹H} NMR (75 MHz, CDCl$_3$, ppm)



¹H NMR (300MHz, CDCl$_3$, ppm)



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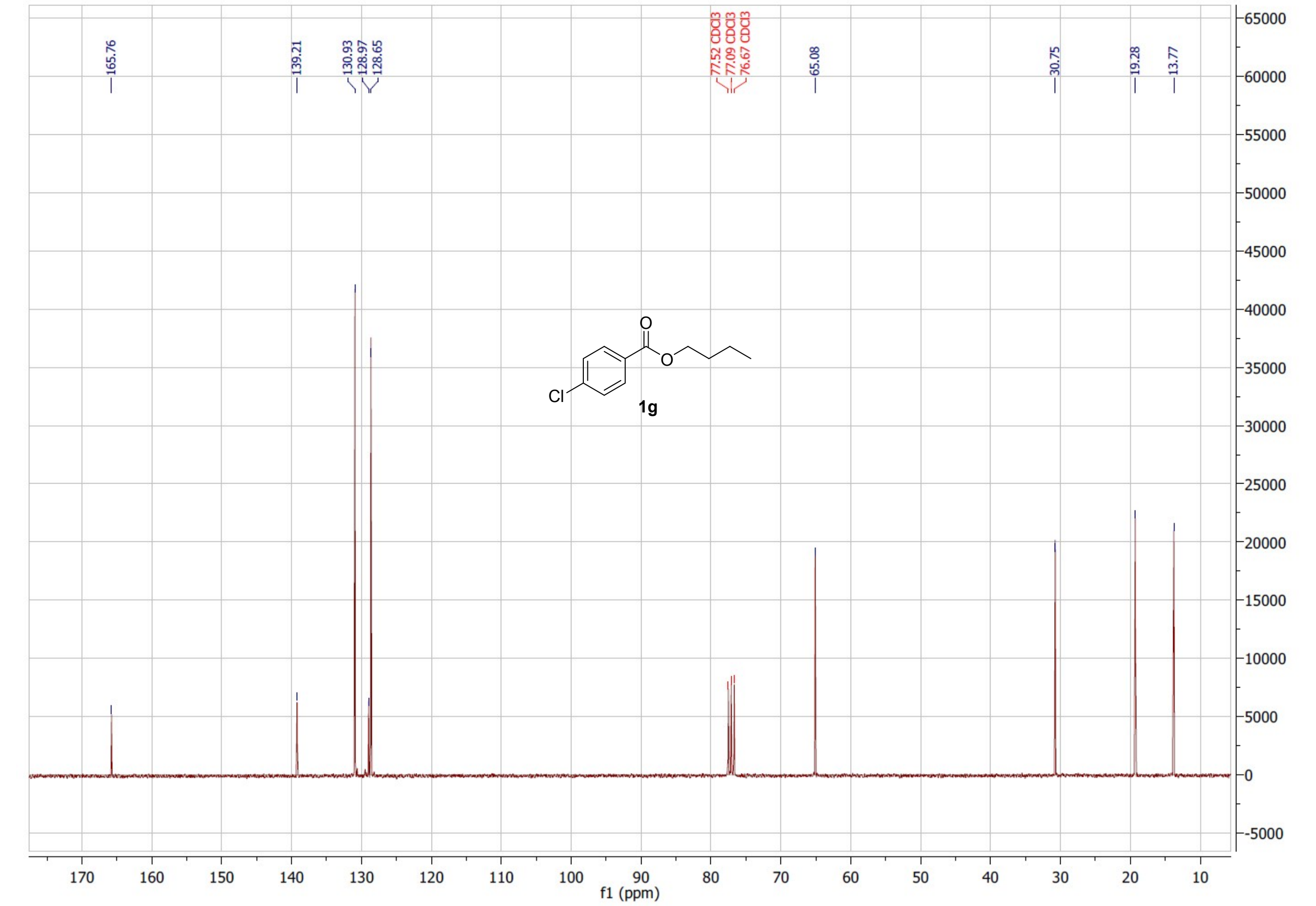

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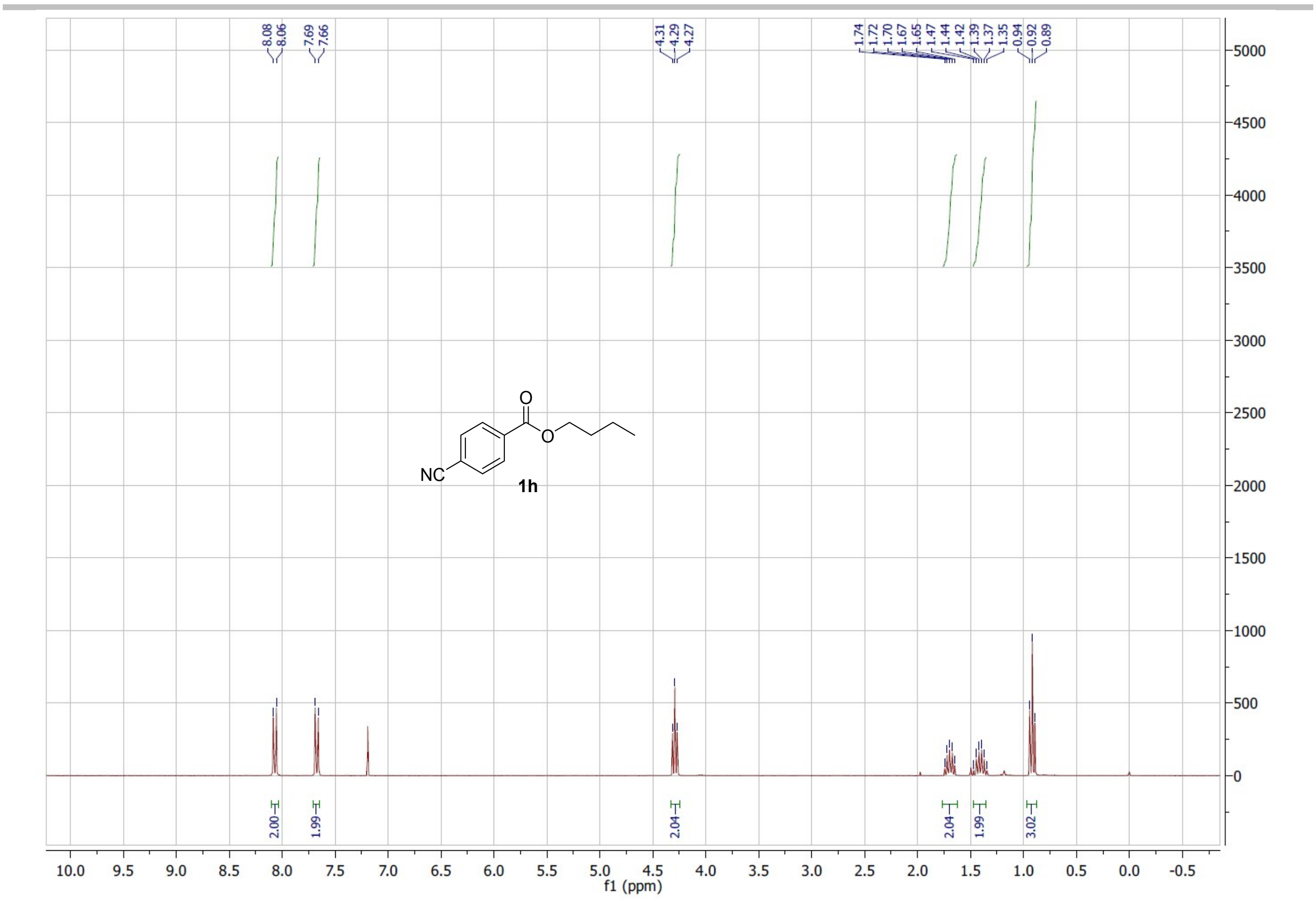

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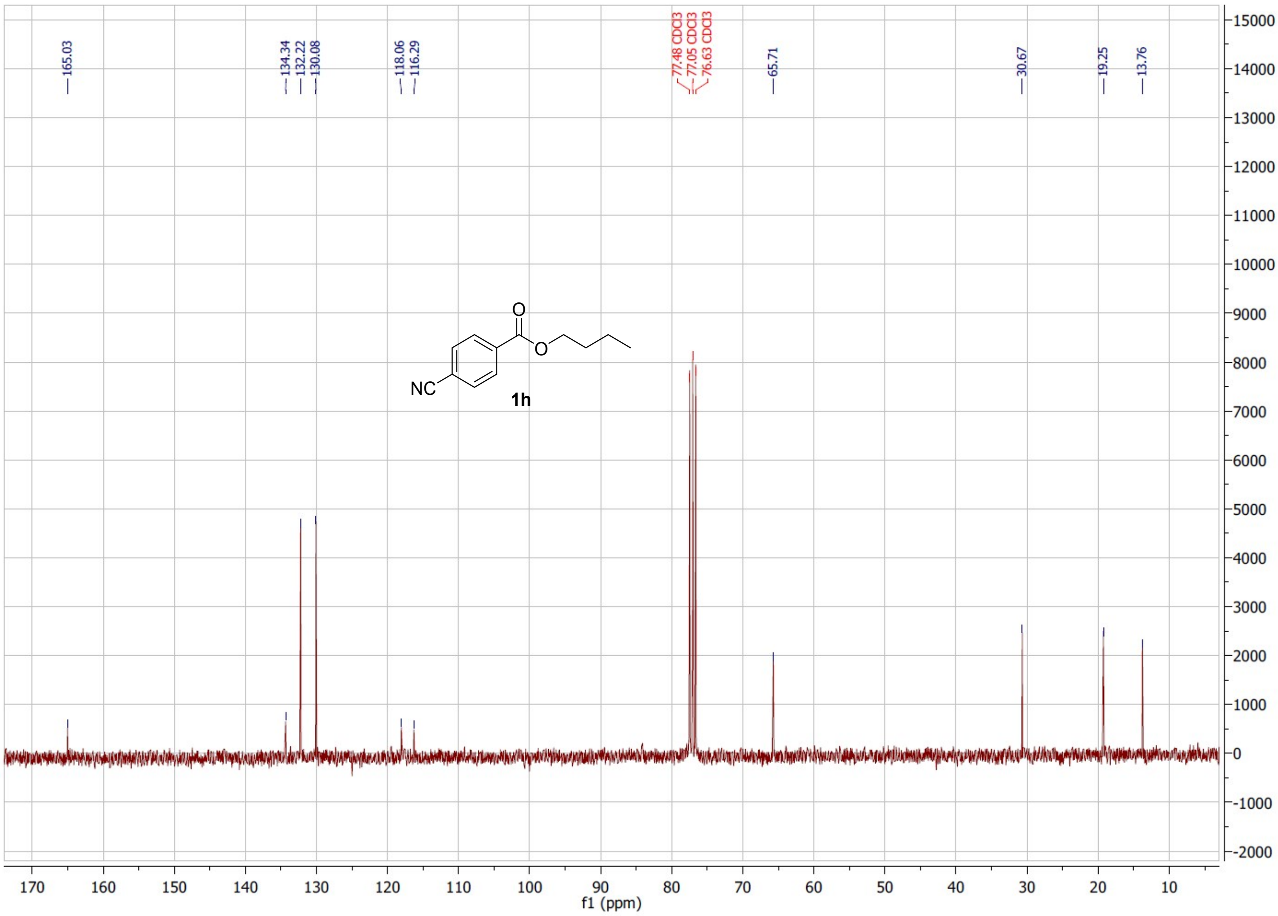

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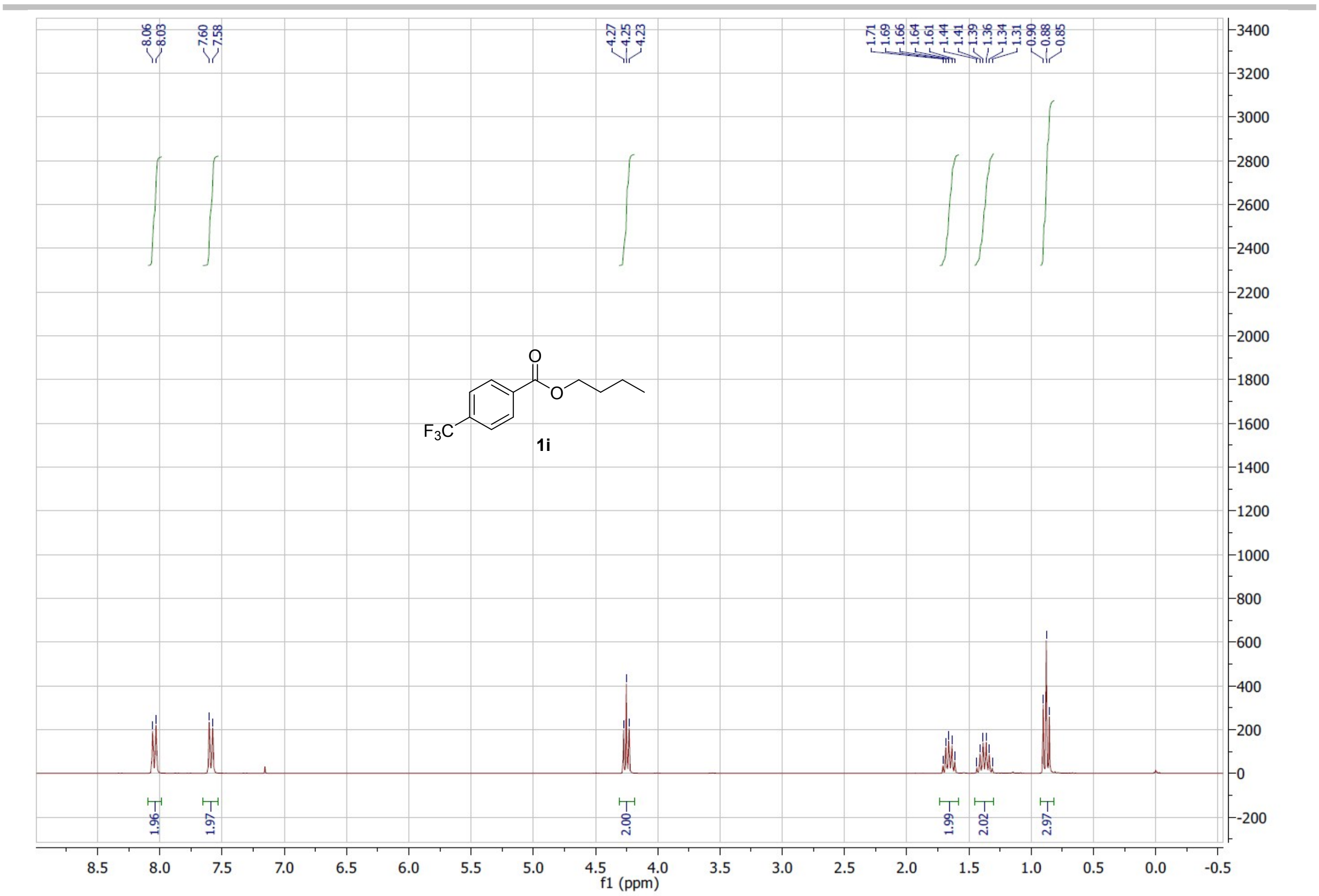

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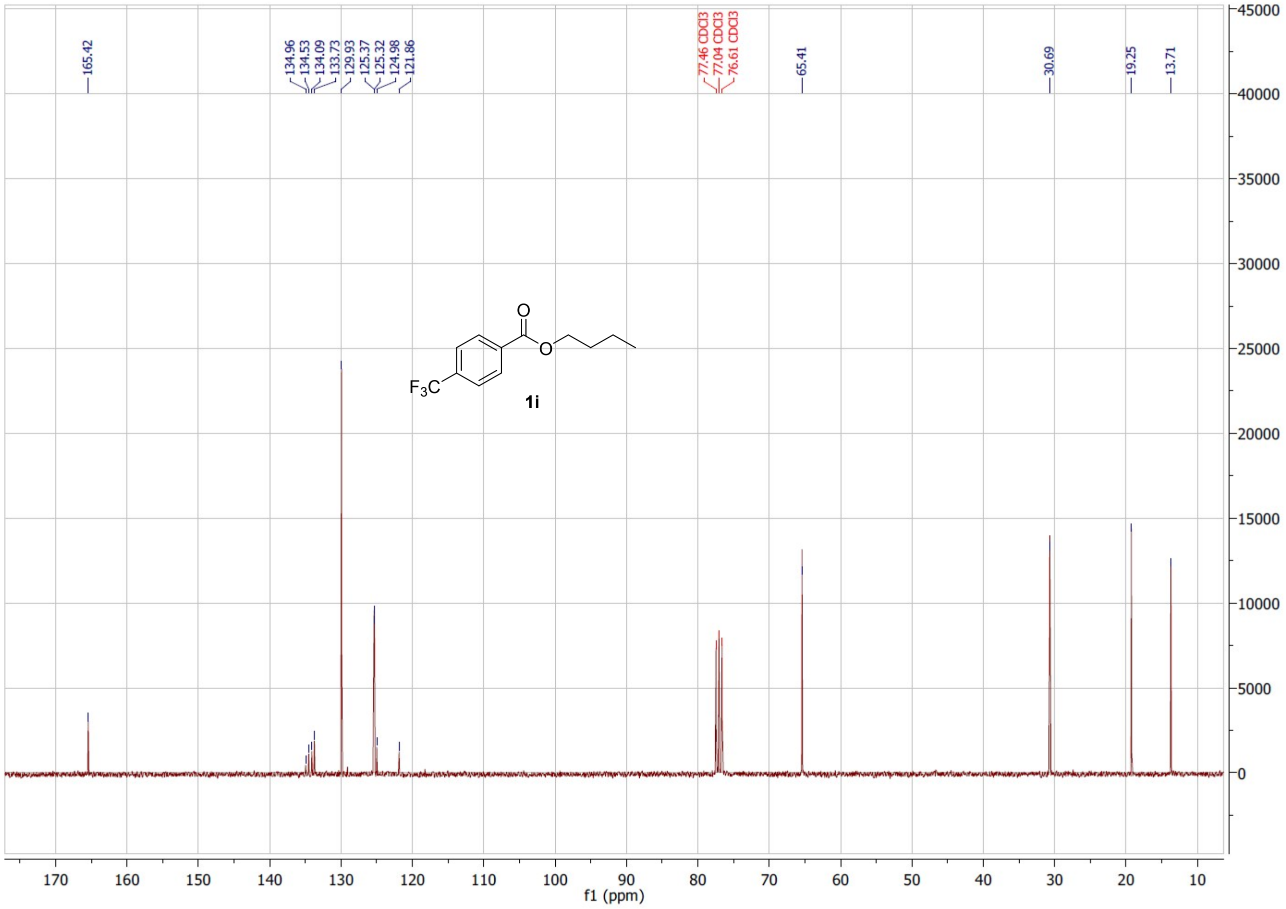

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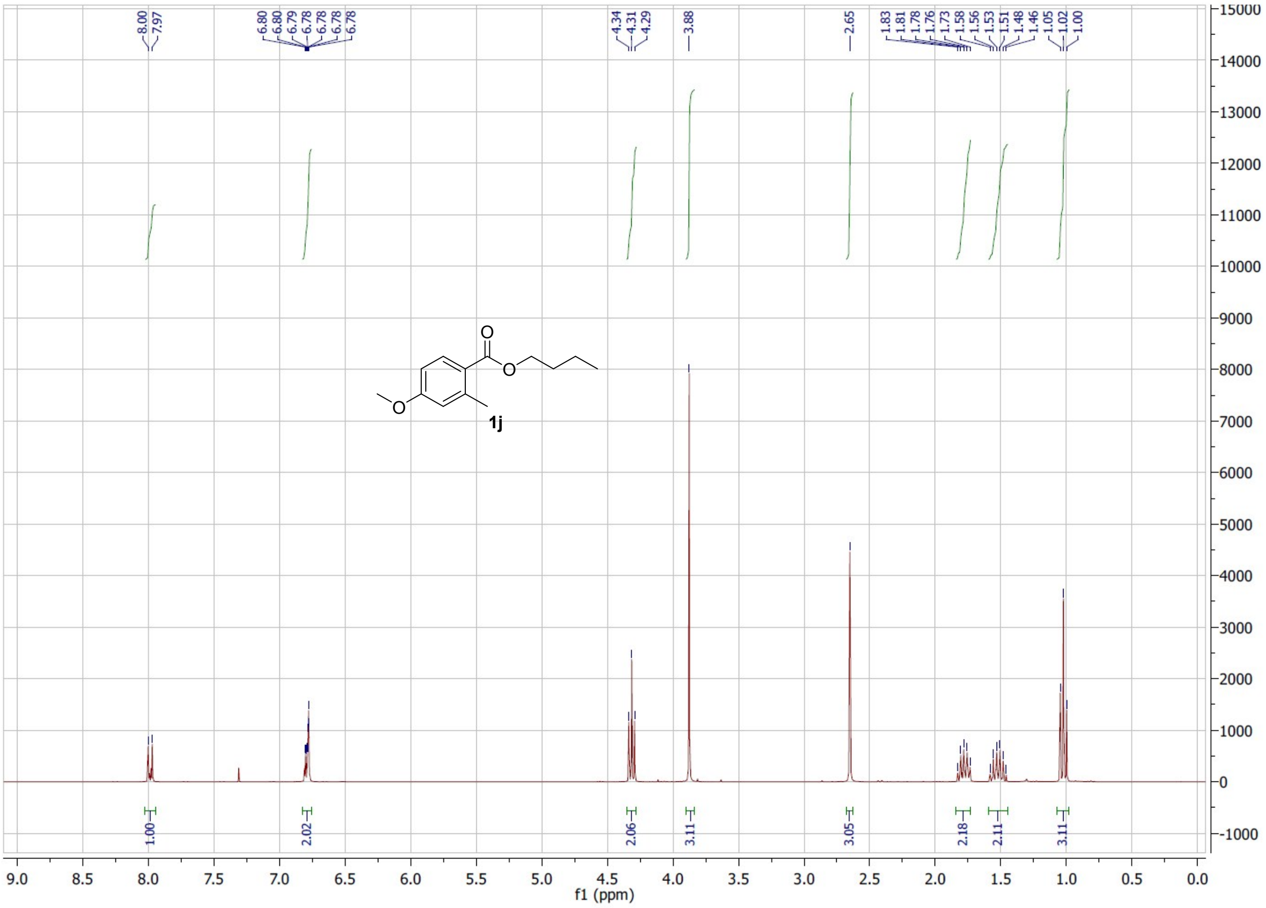

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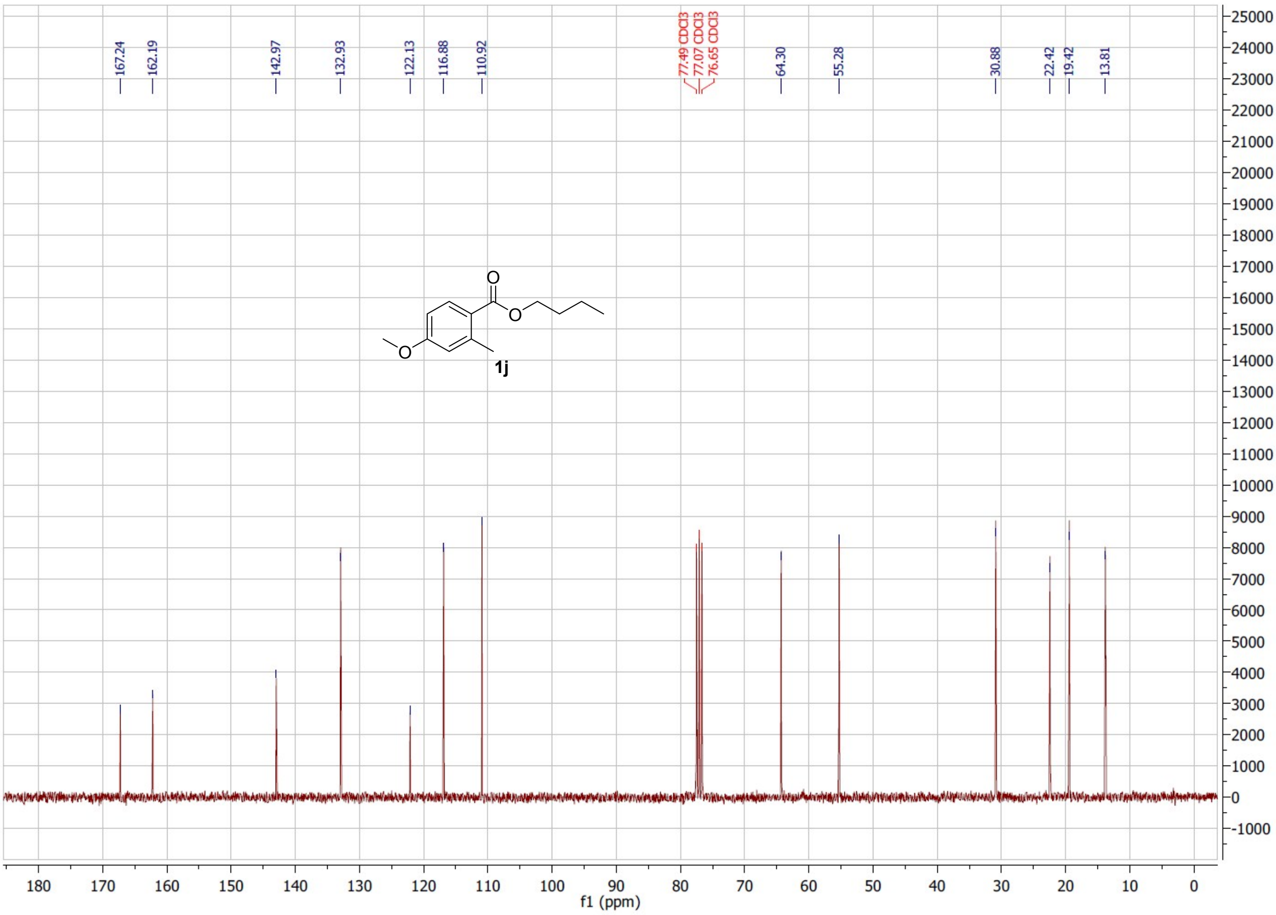

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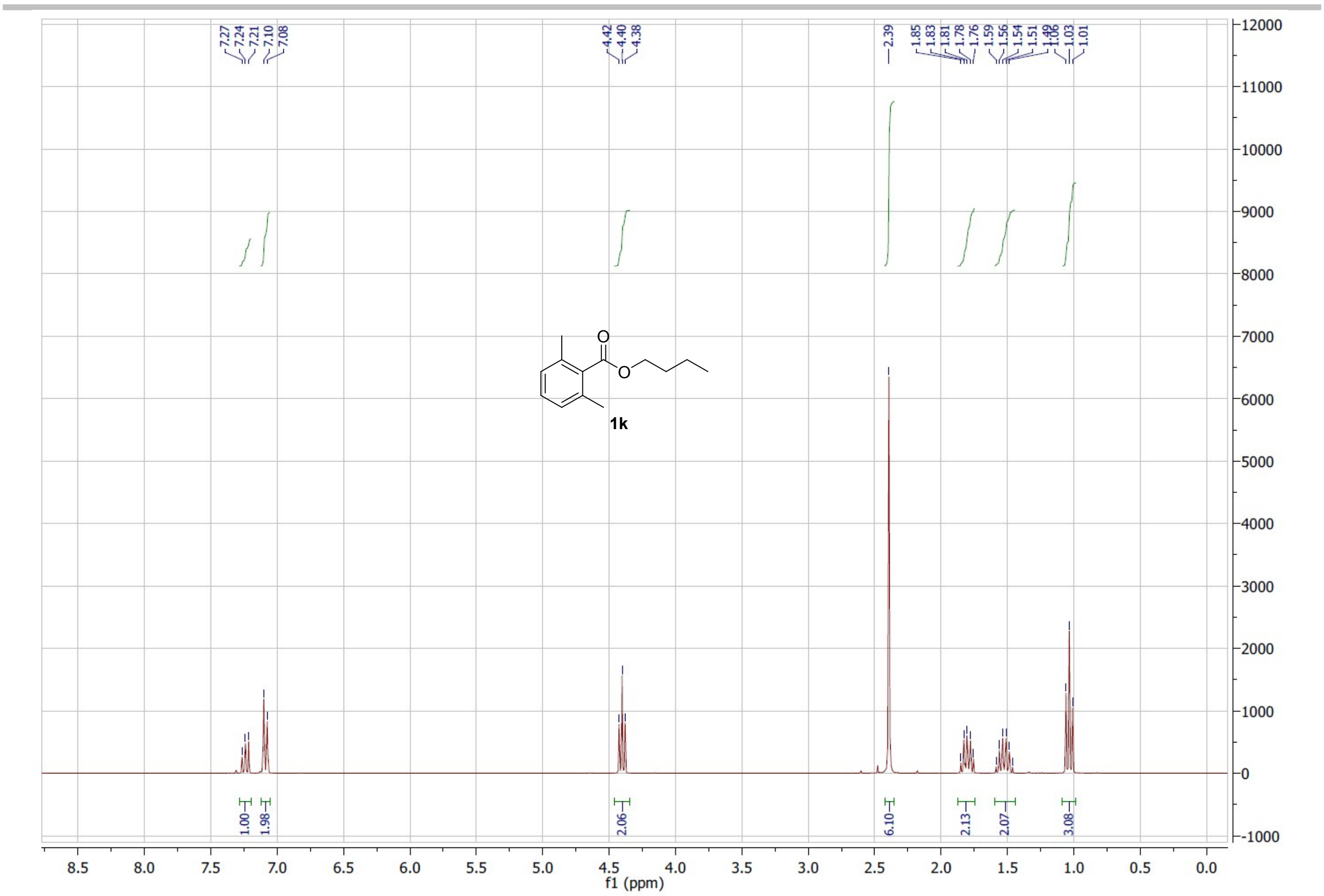

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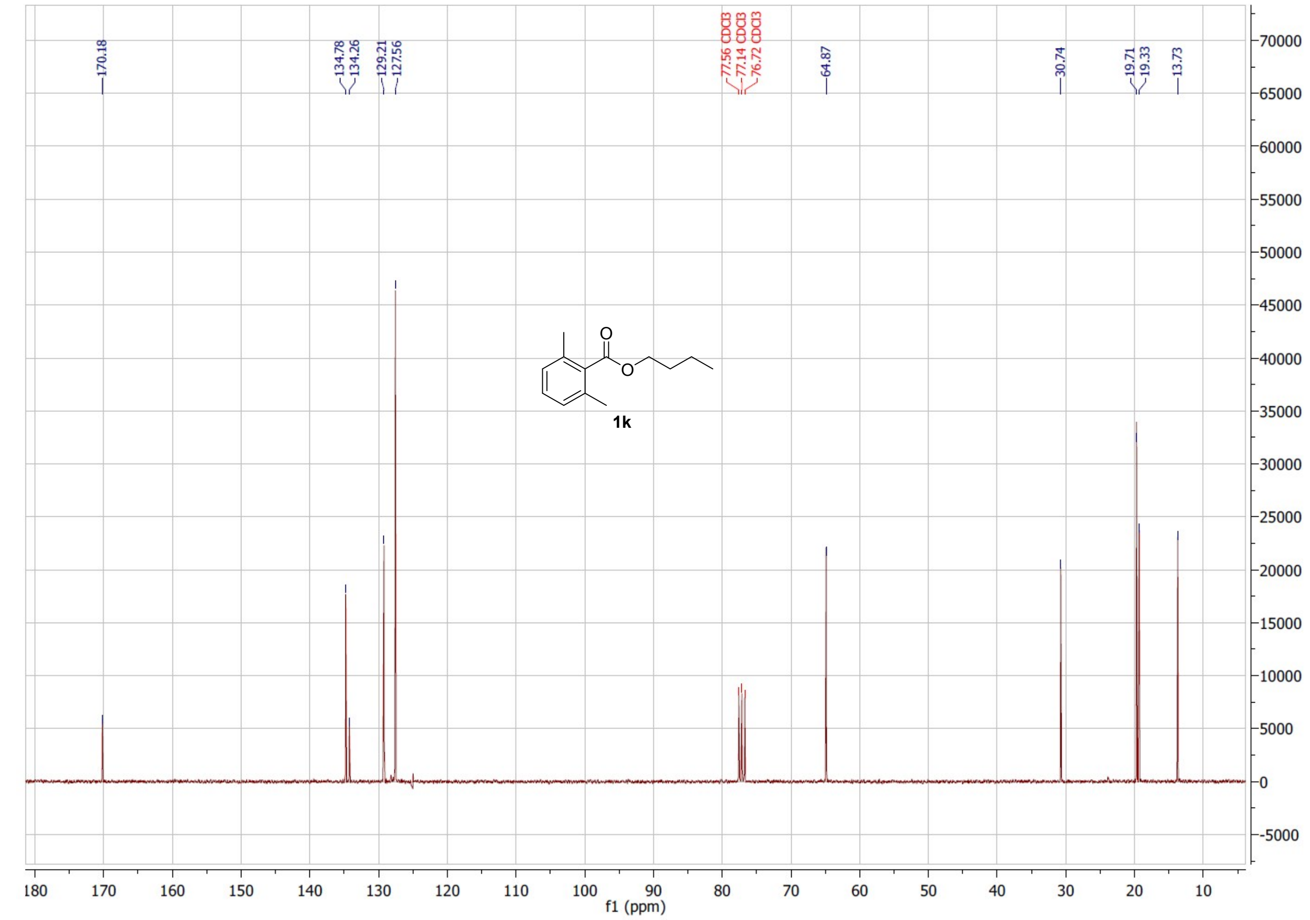

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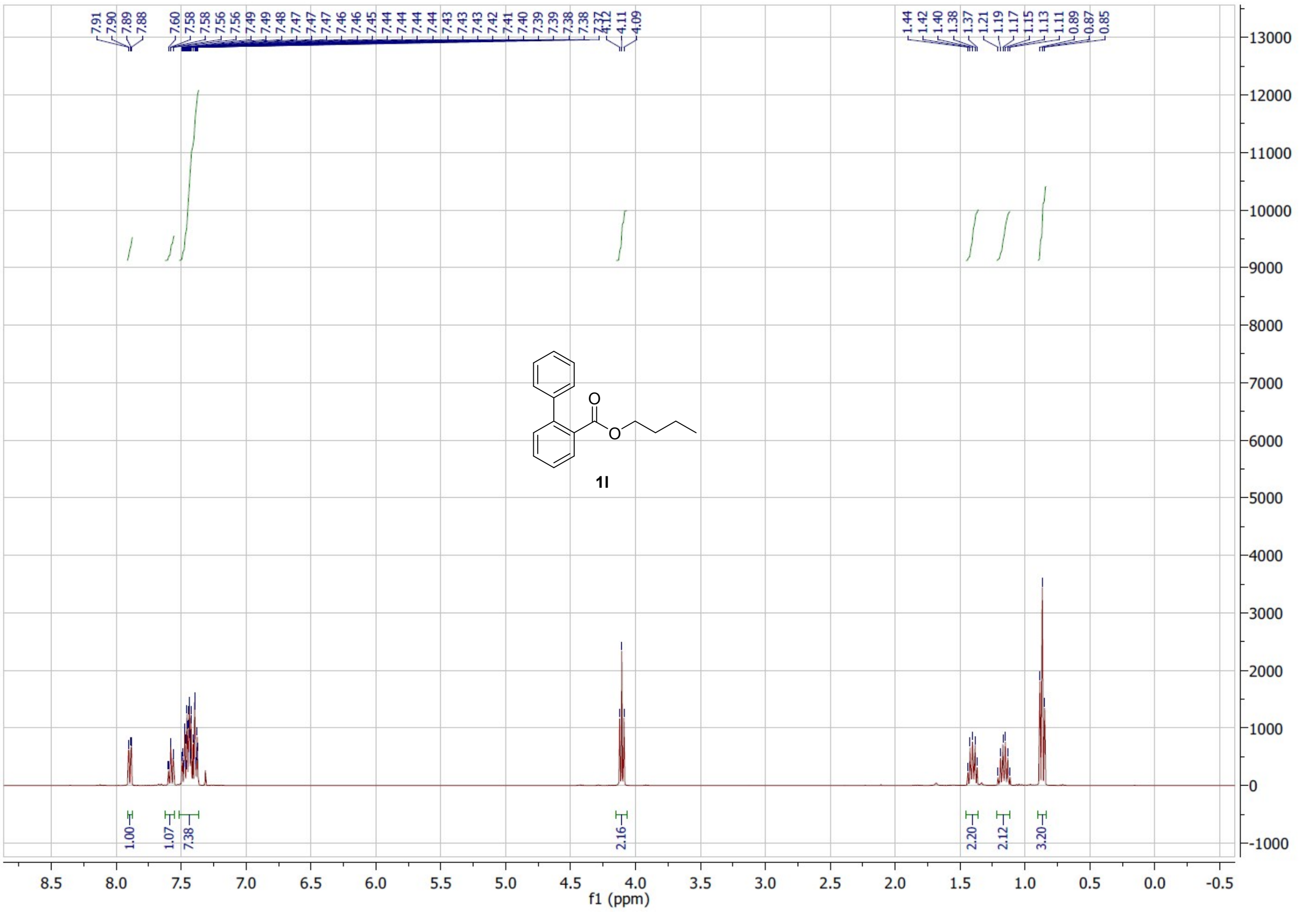

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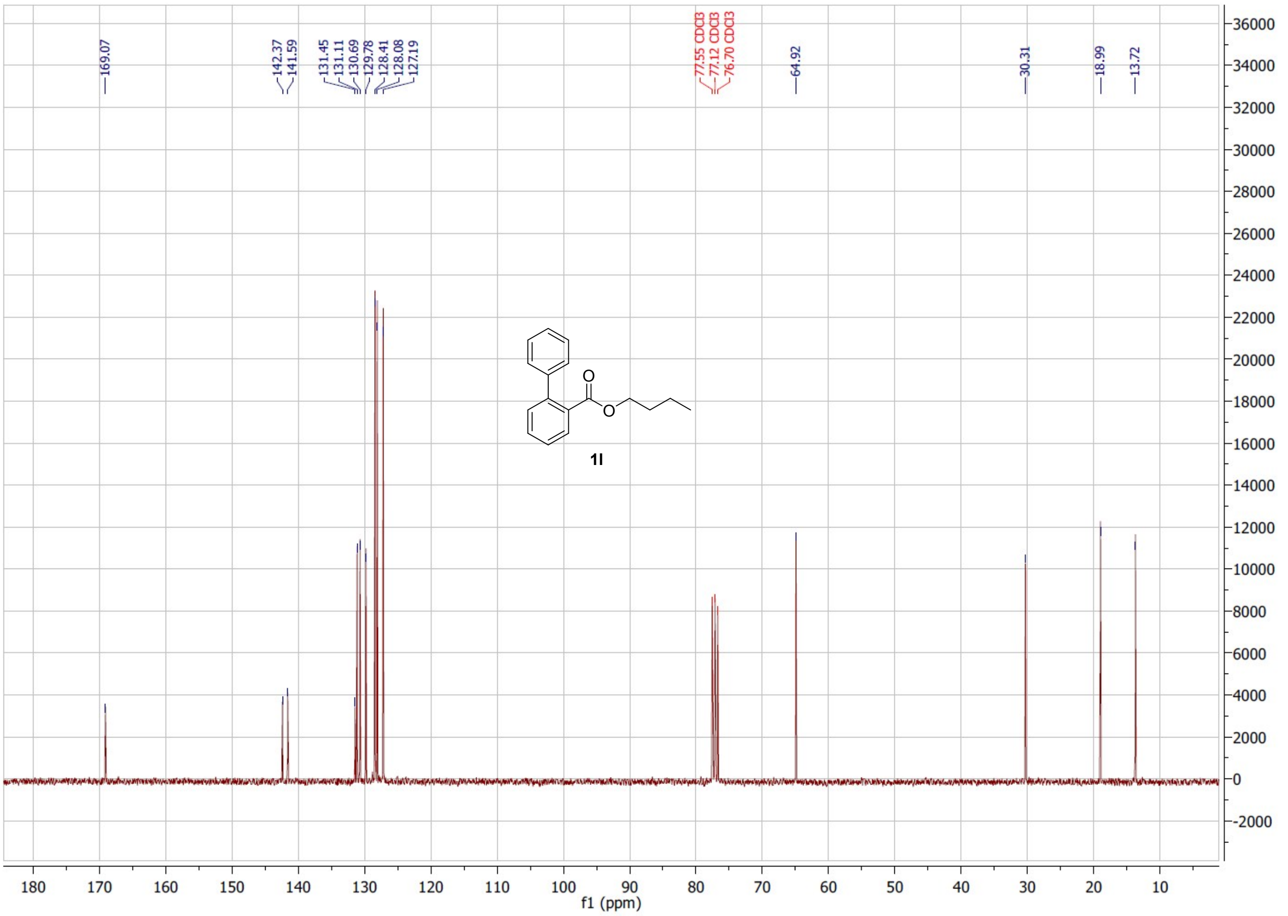

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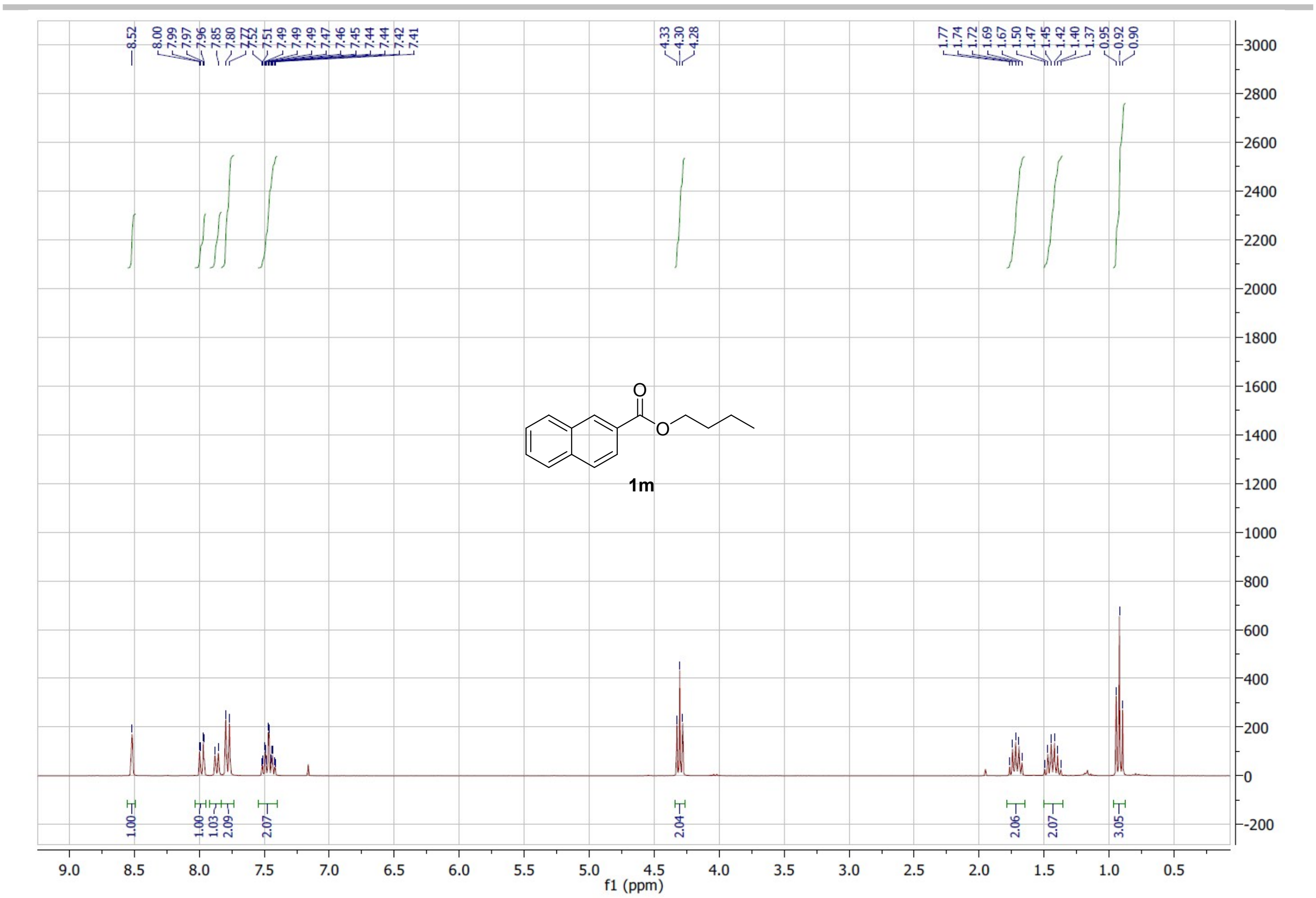

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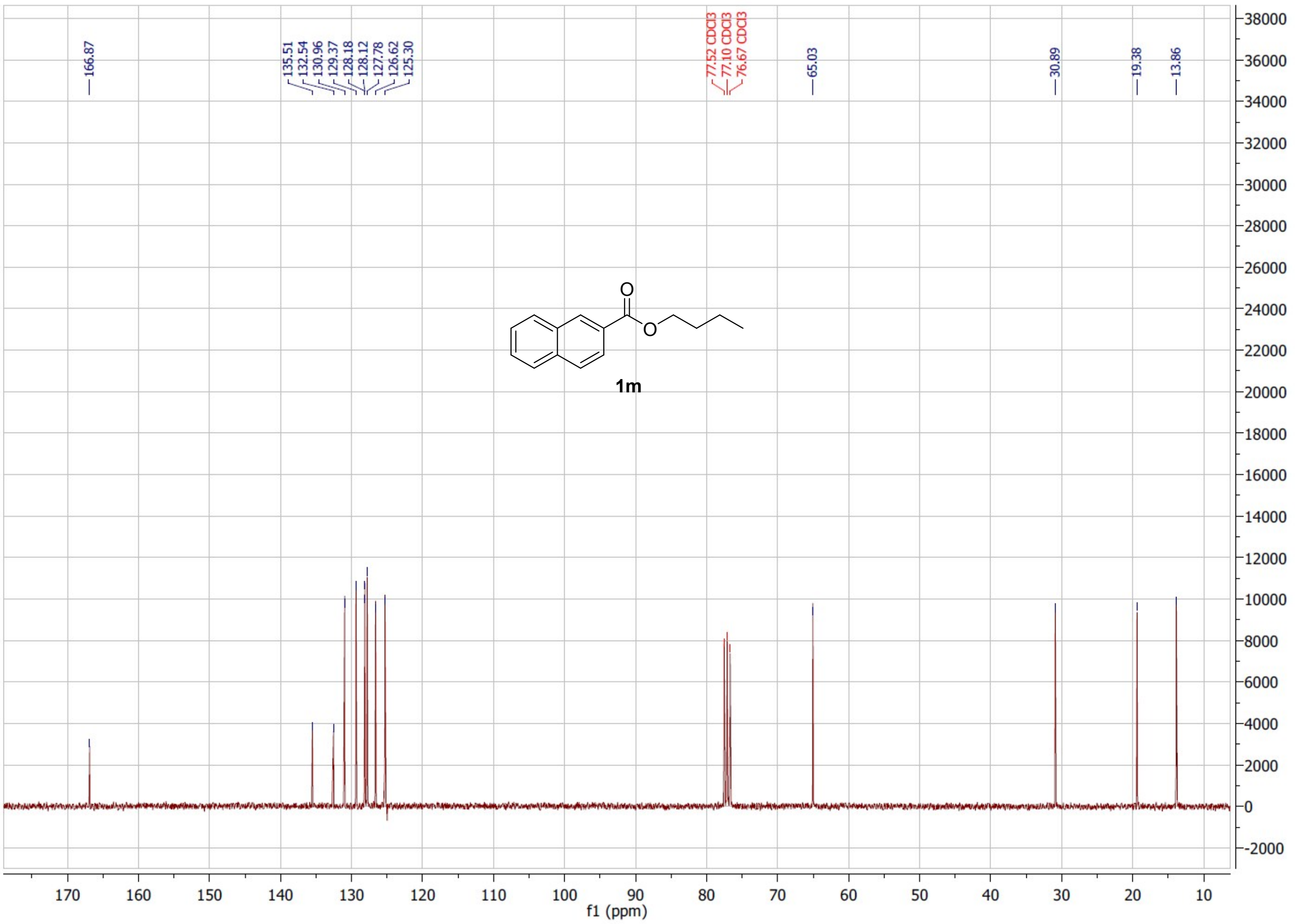

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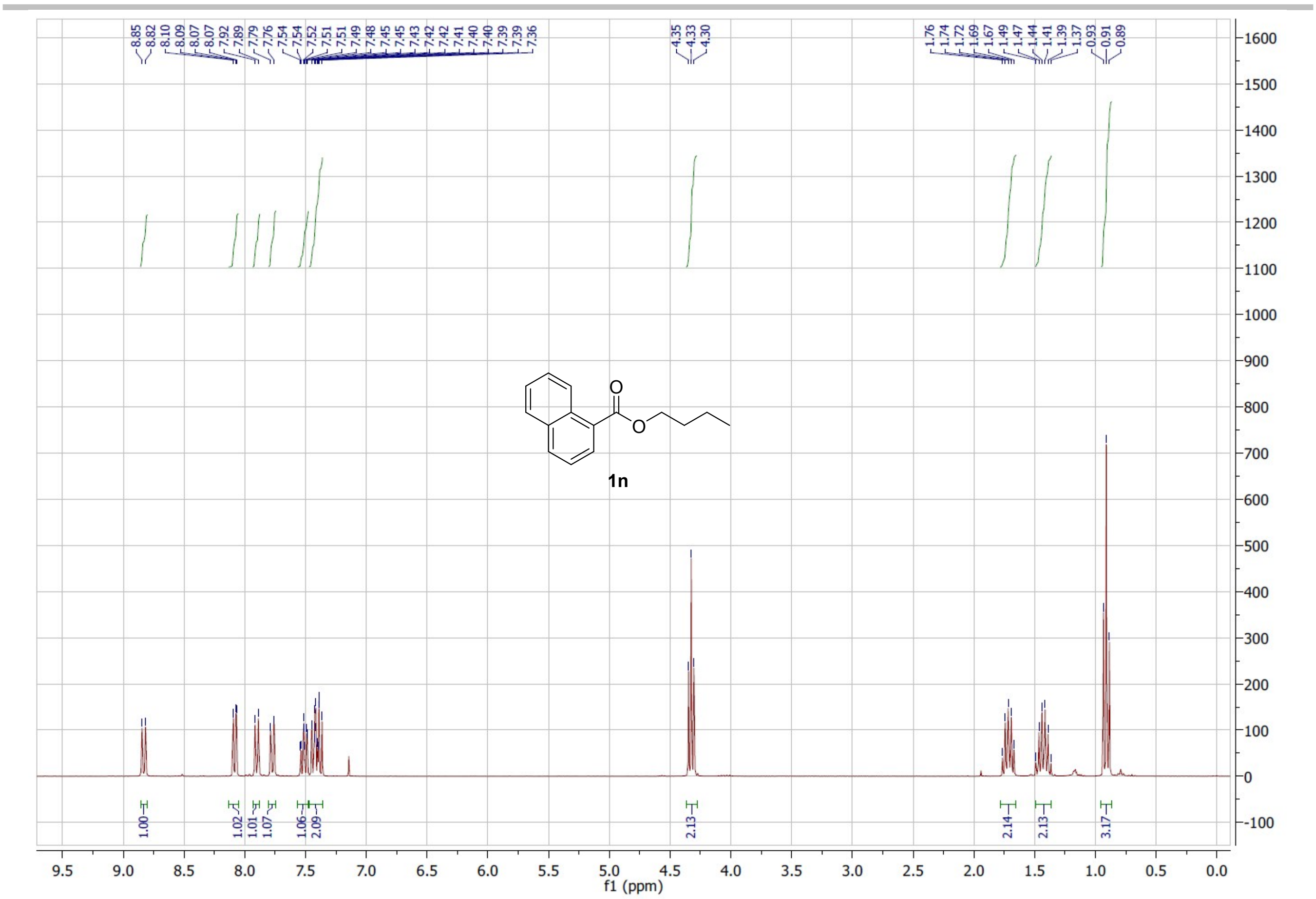

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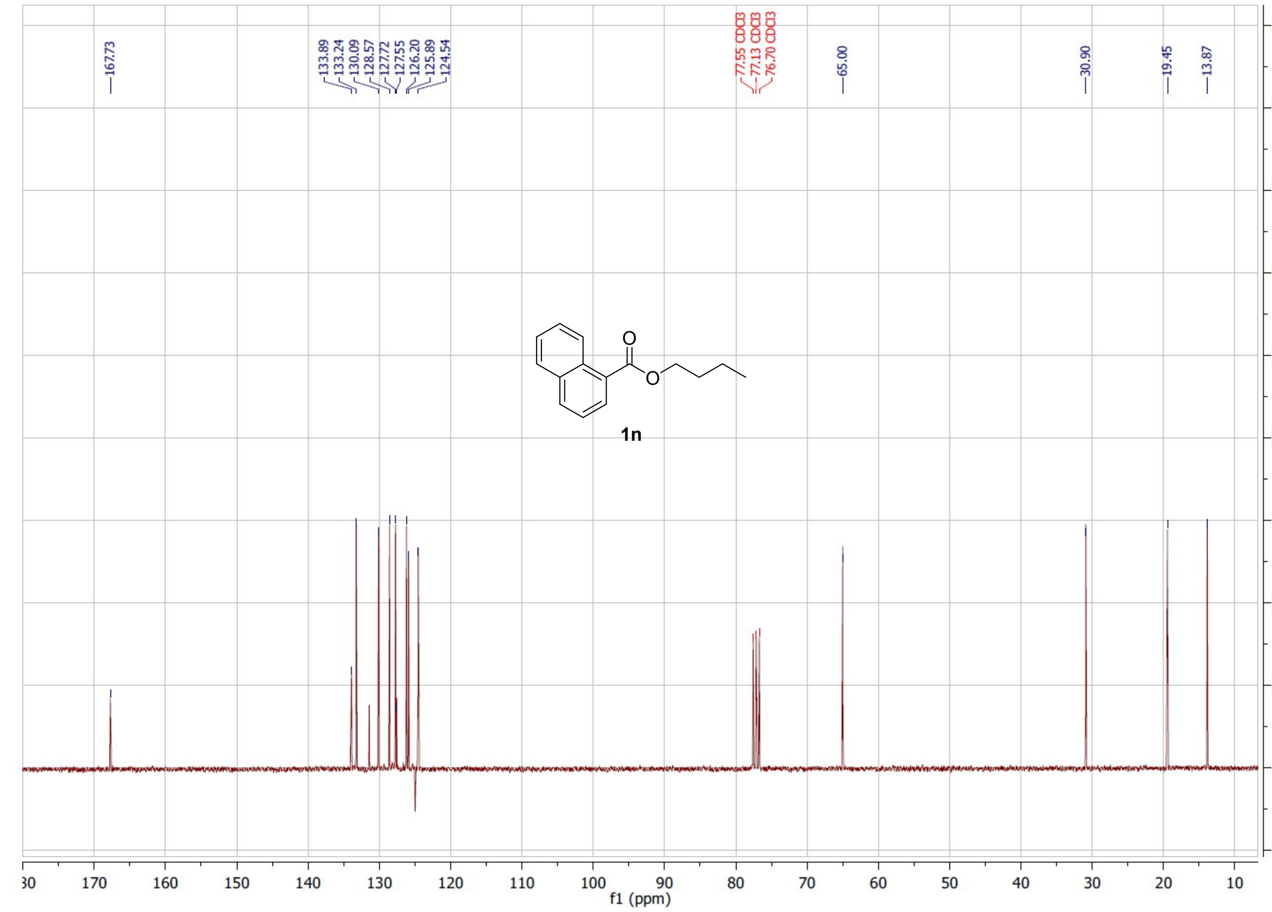

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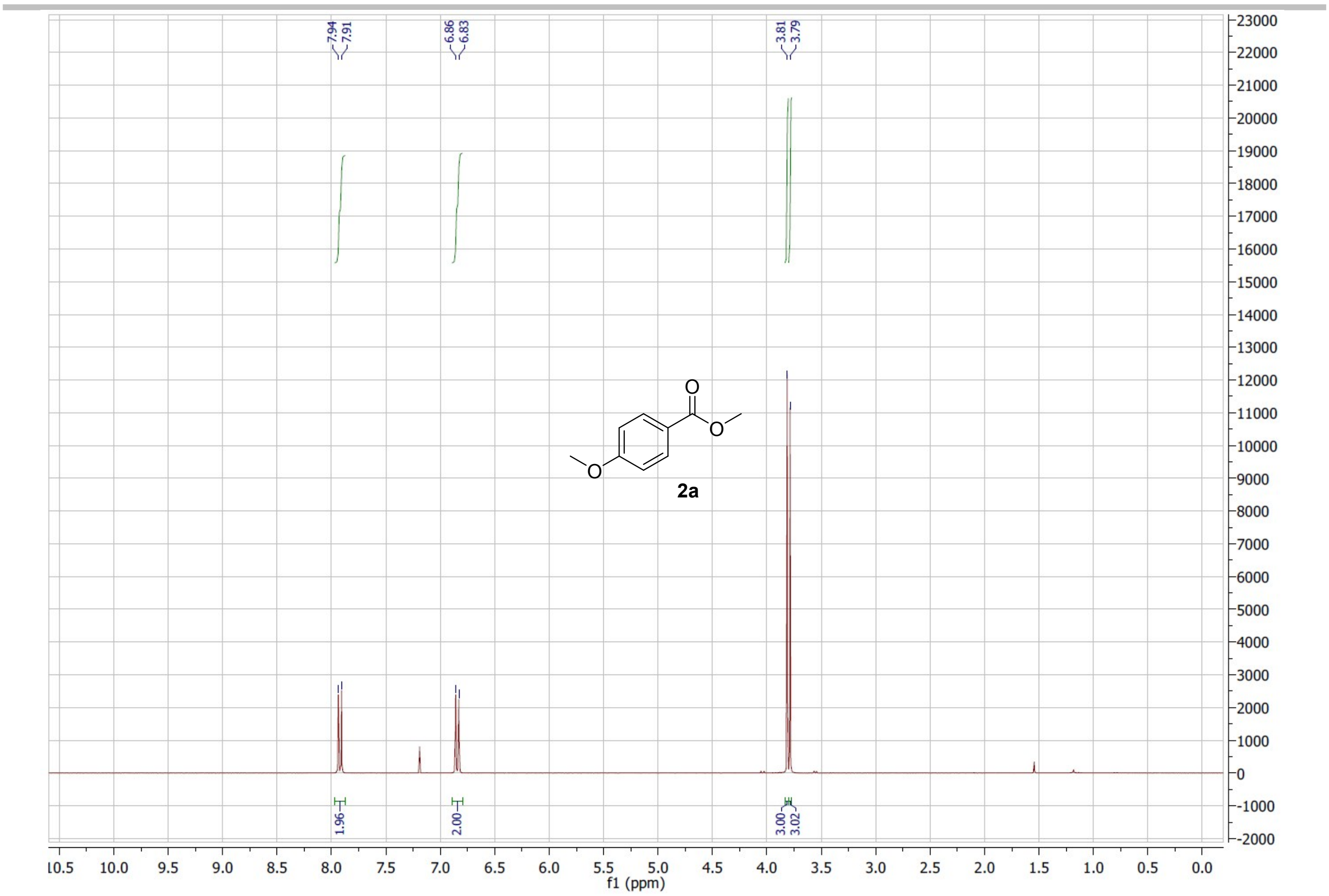

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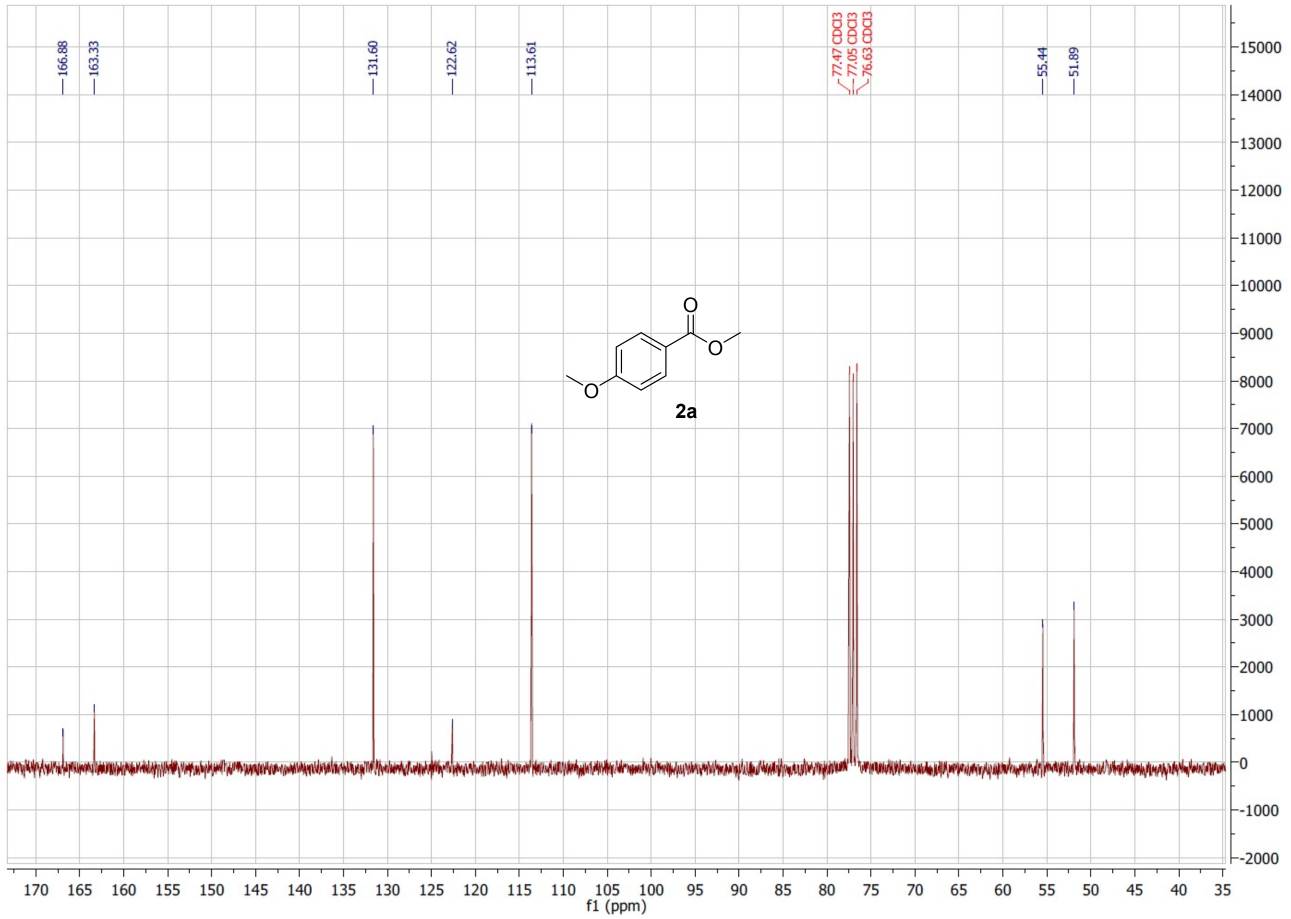

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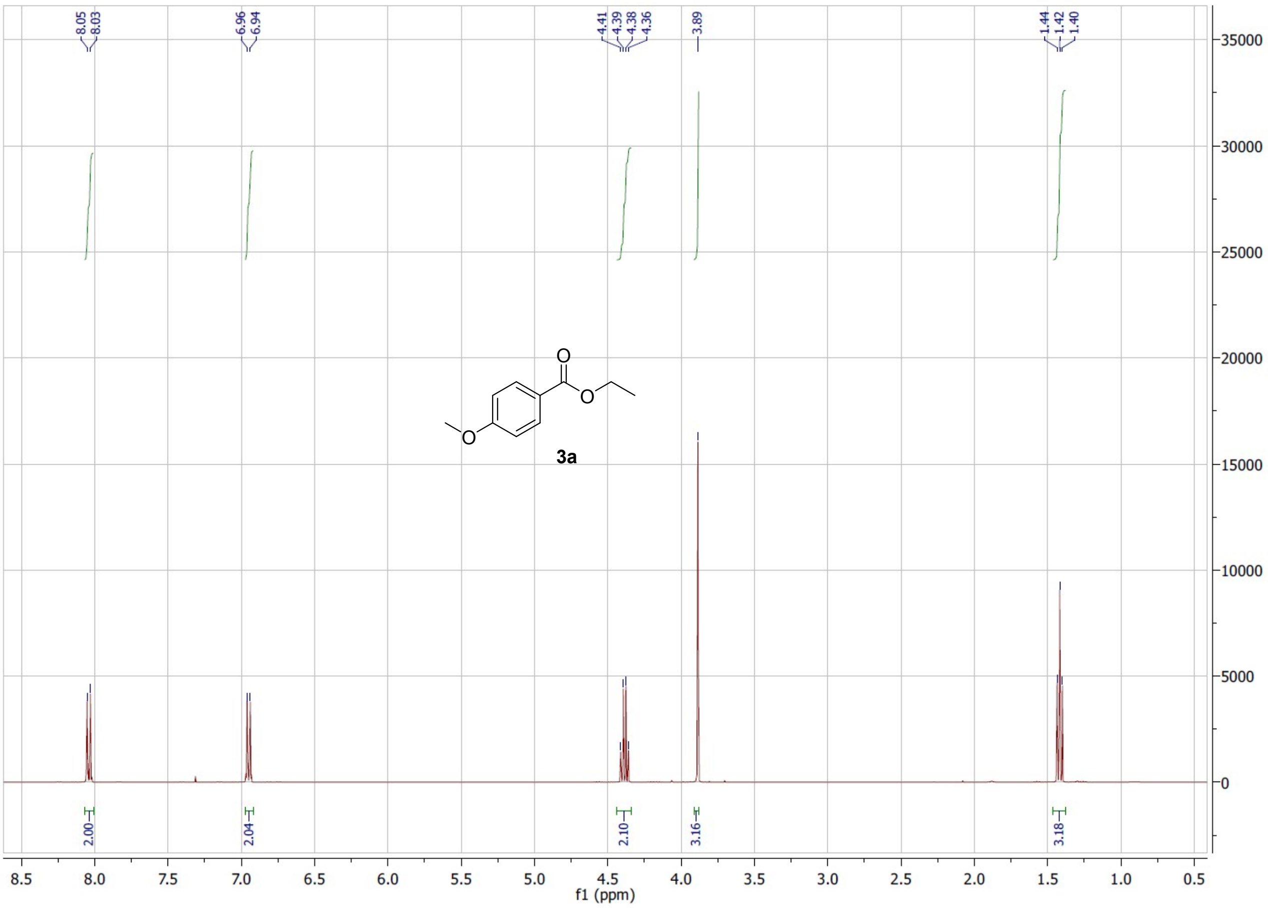

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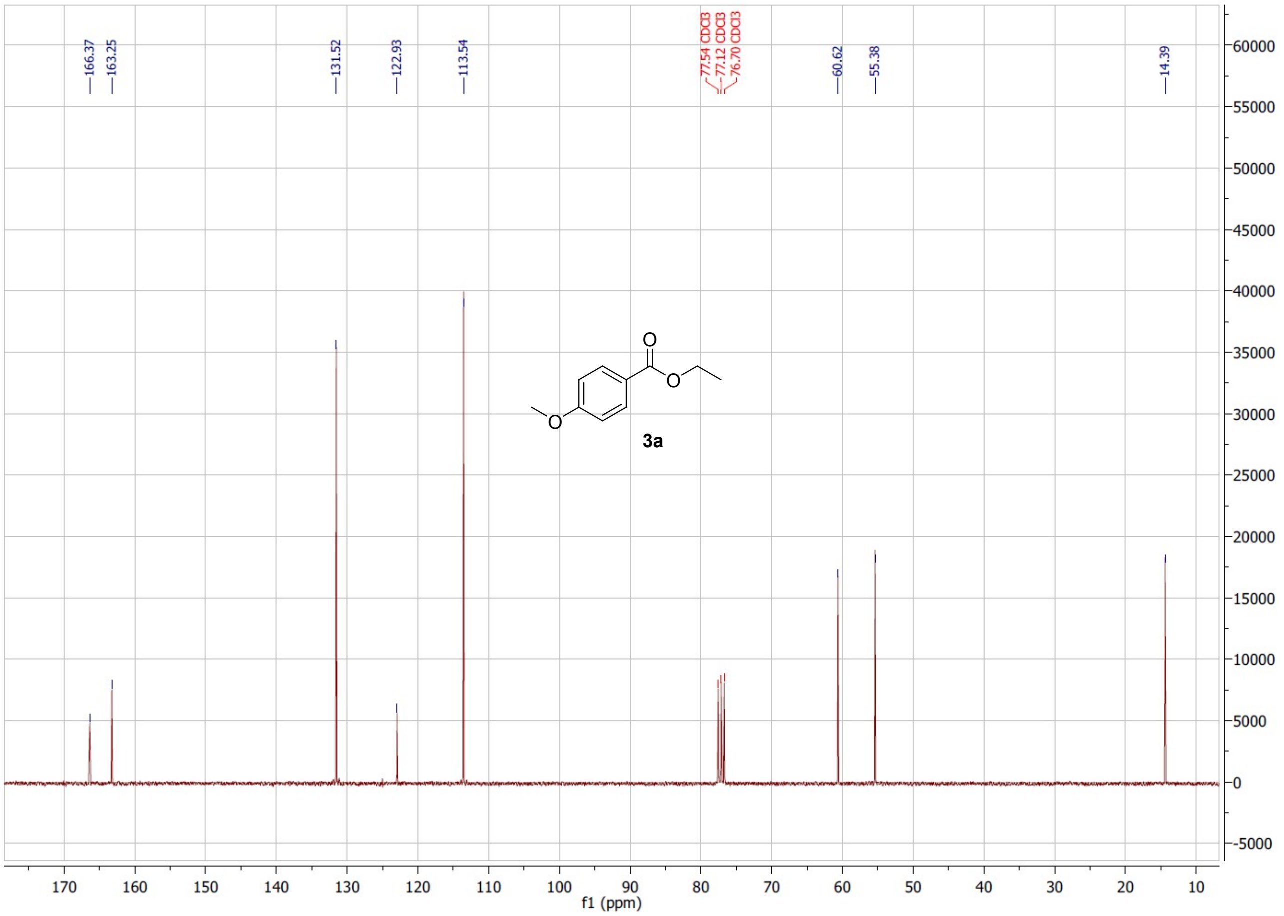

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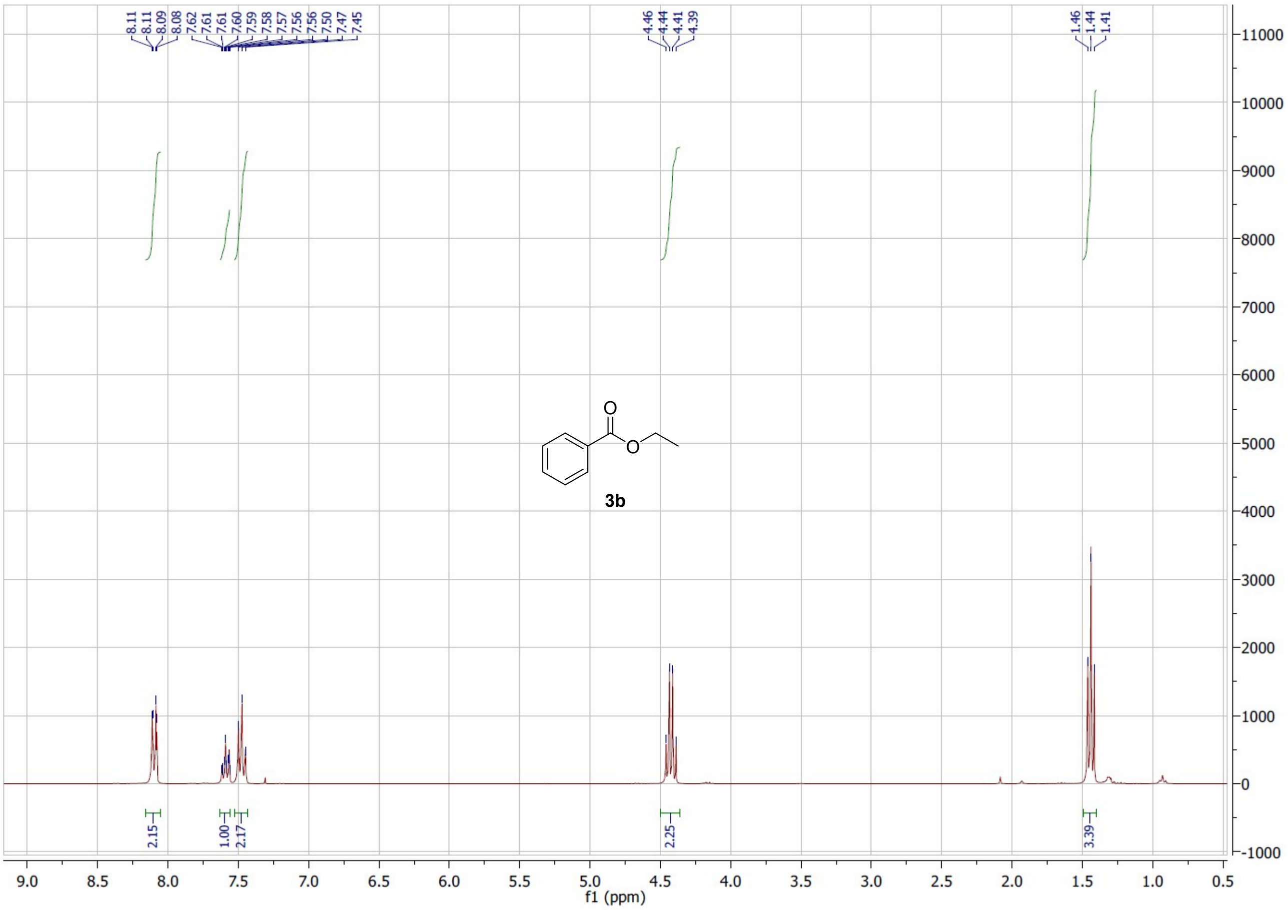

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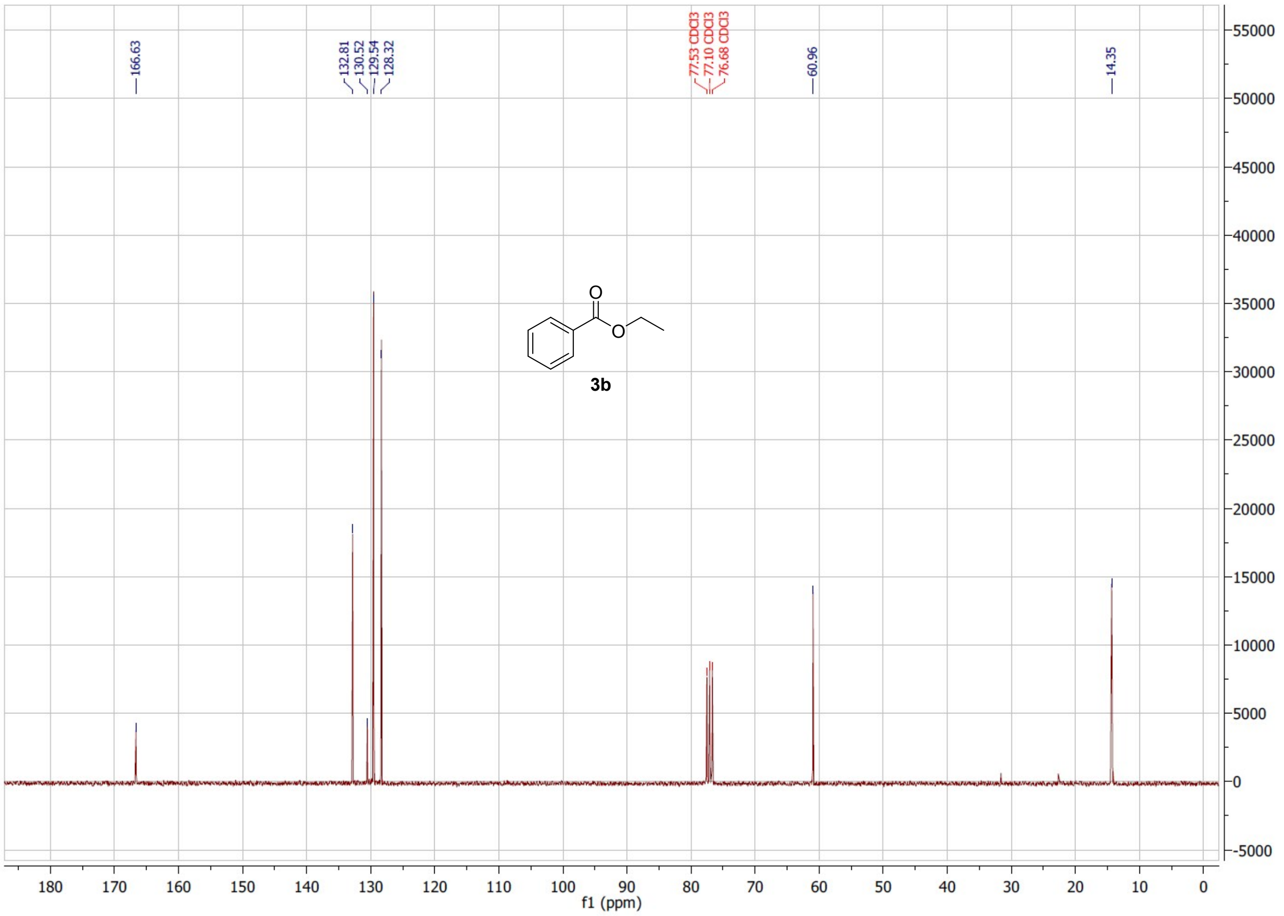

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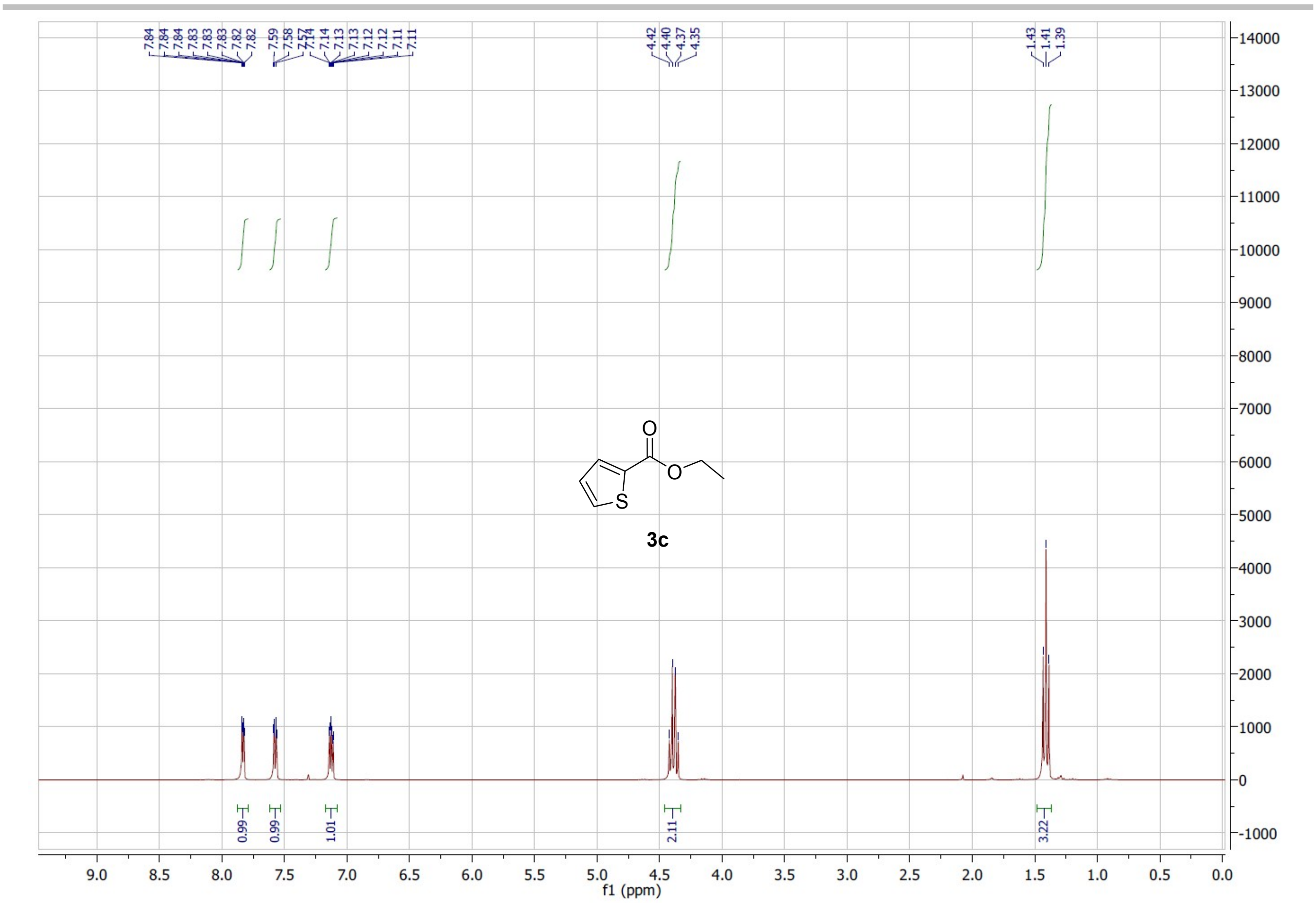

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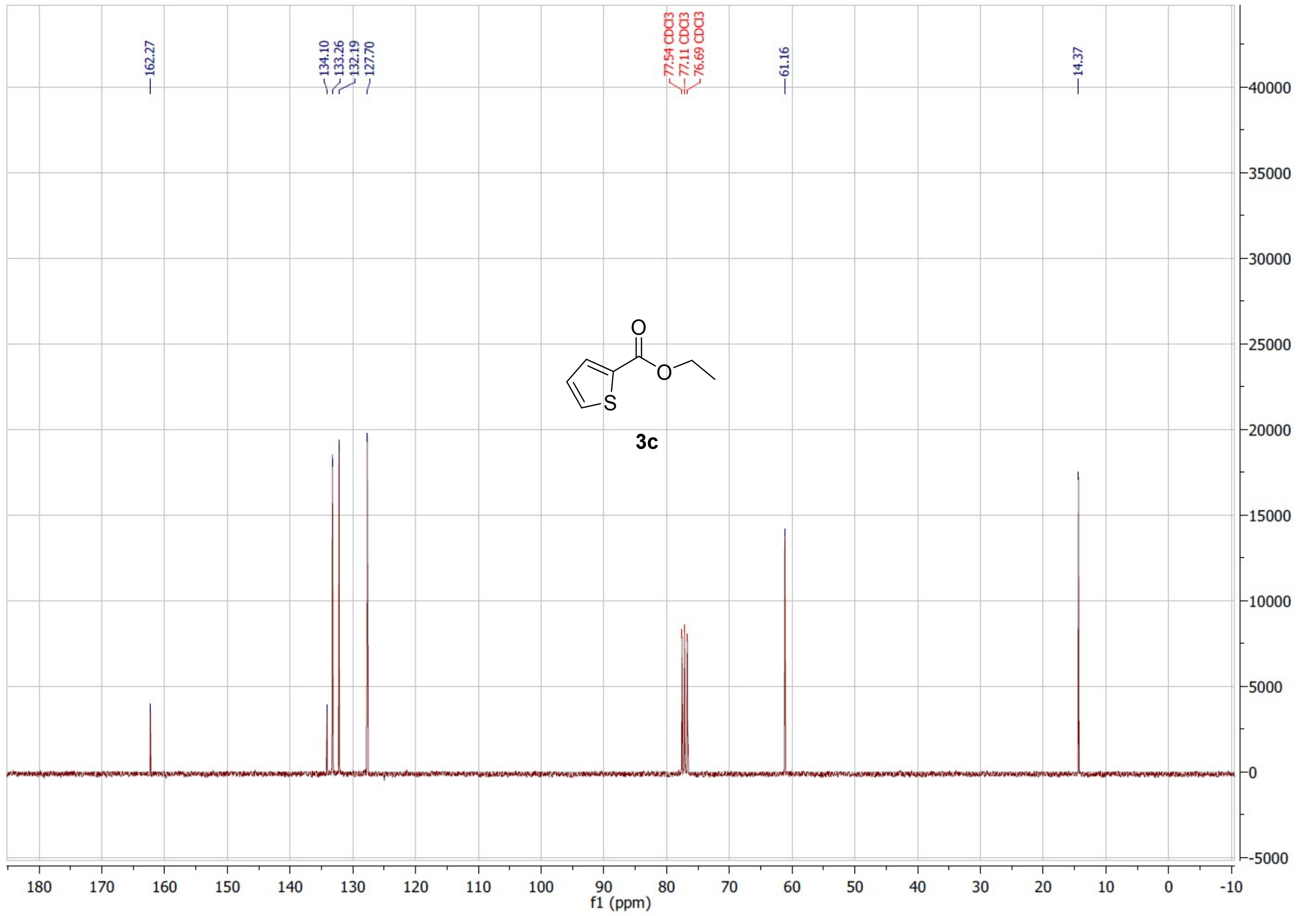

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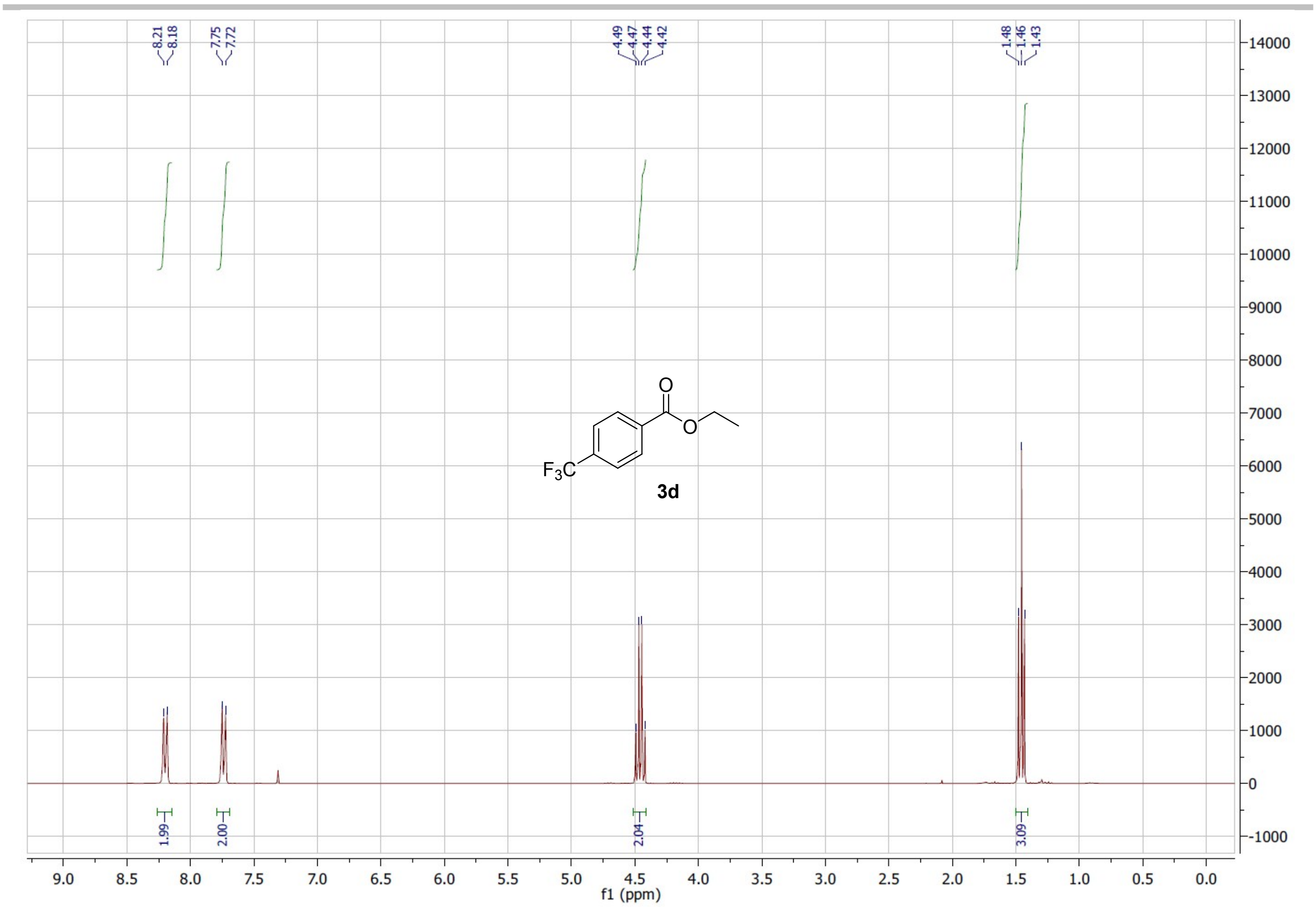
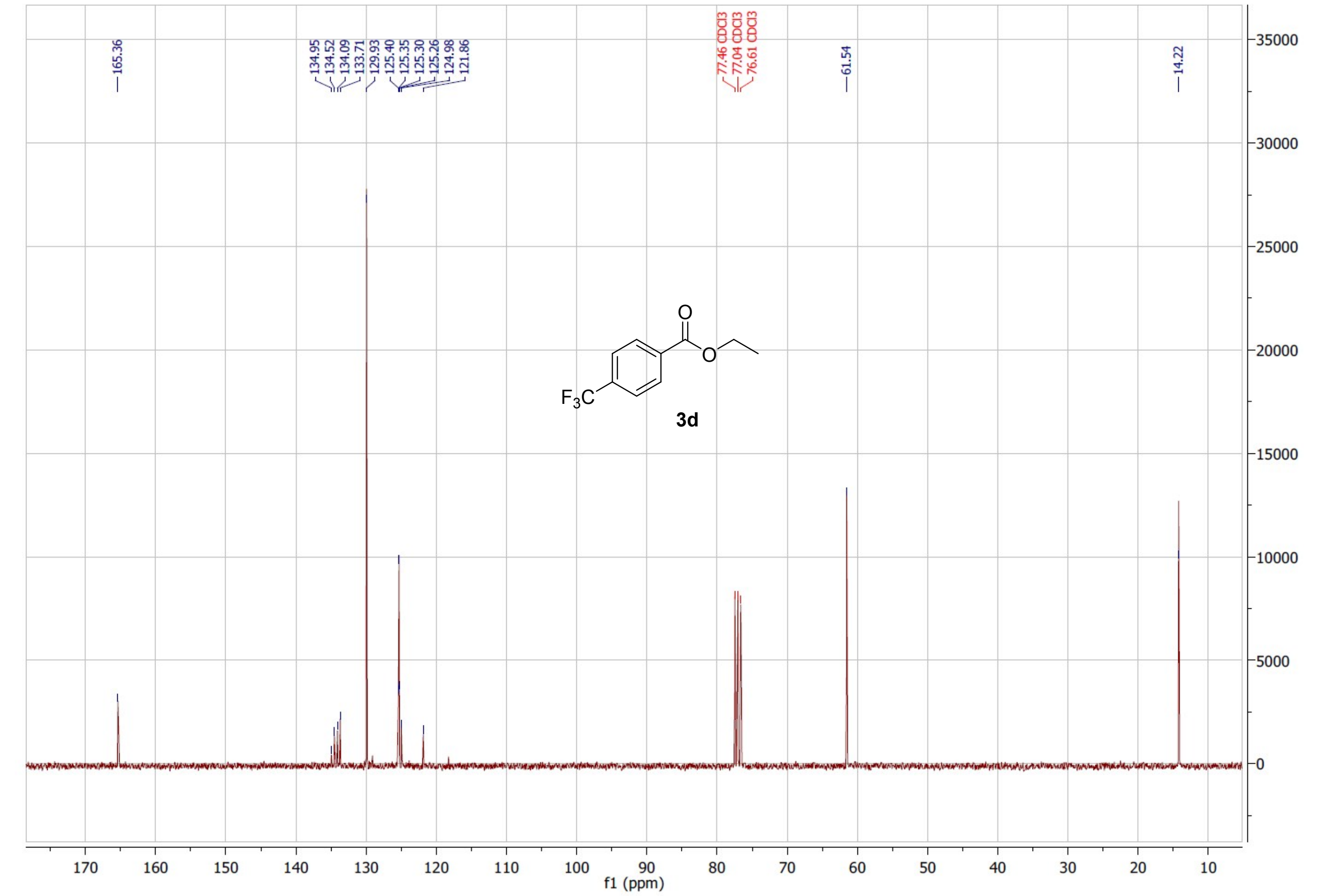
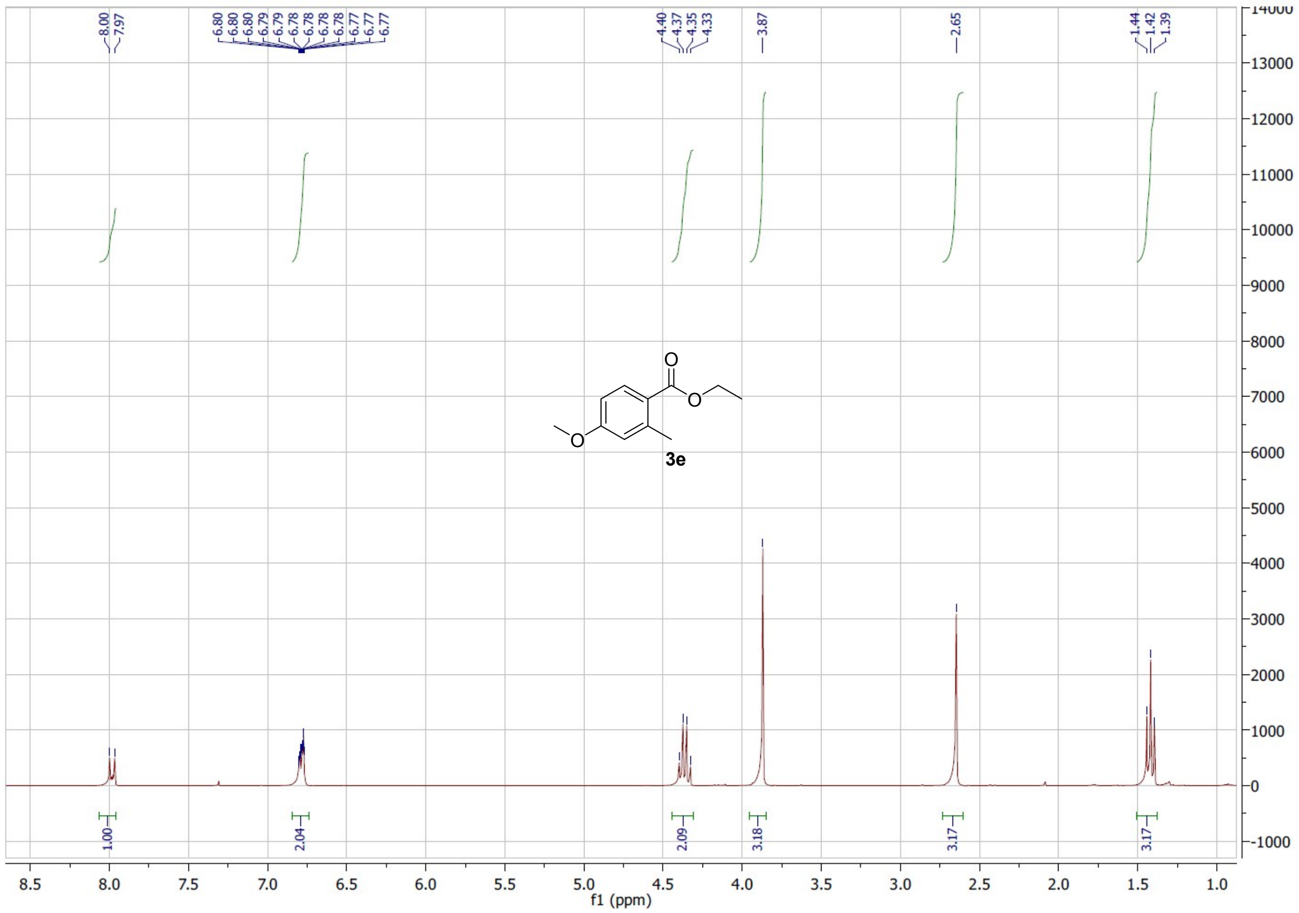


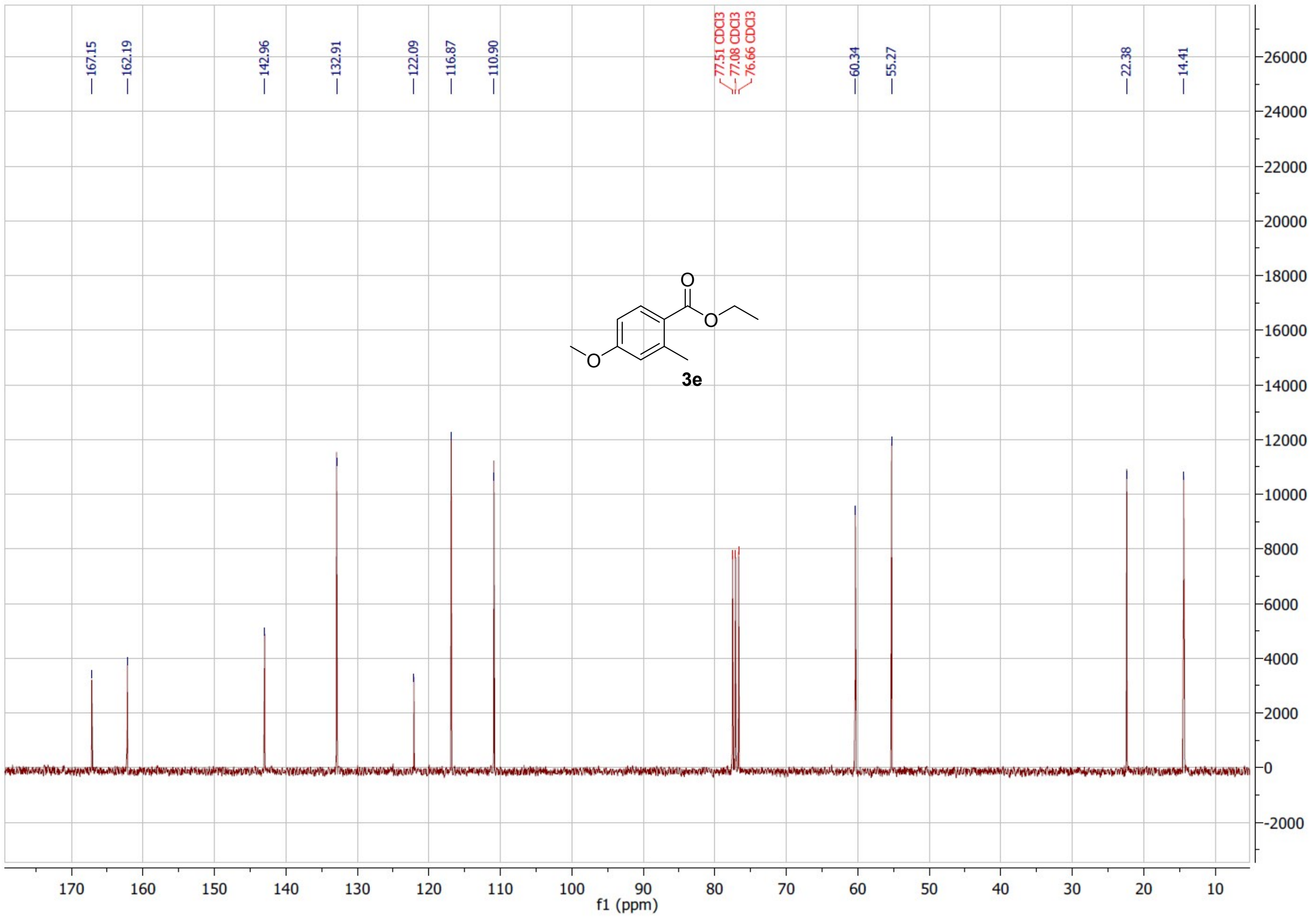
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm)



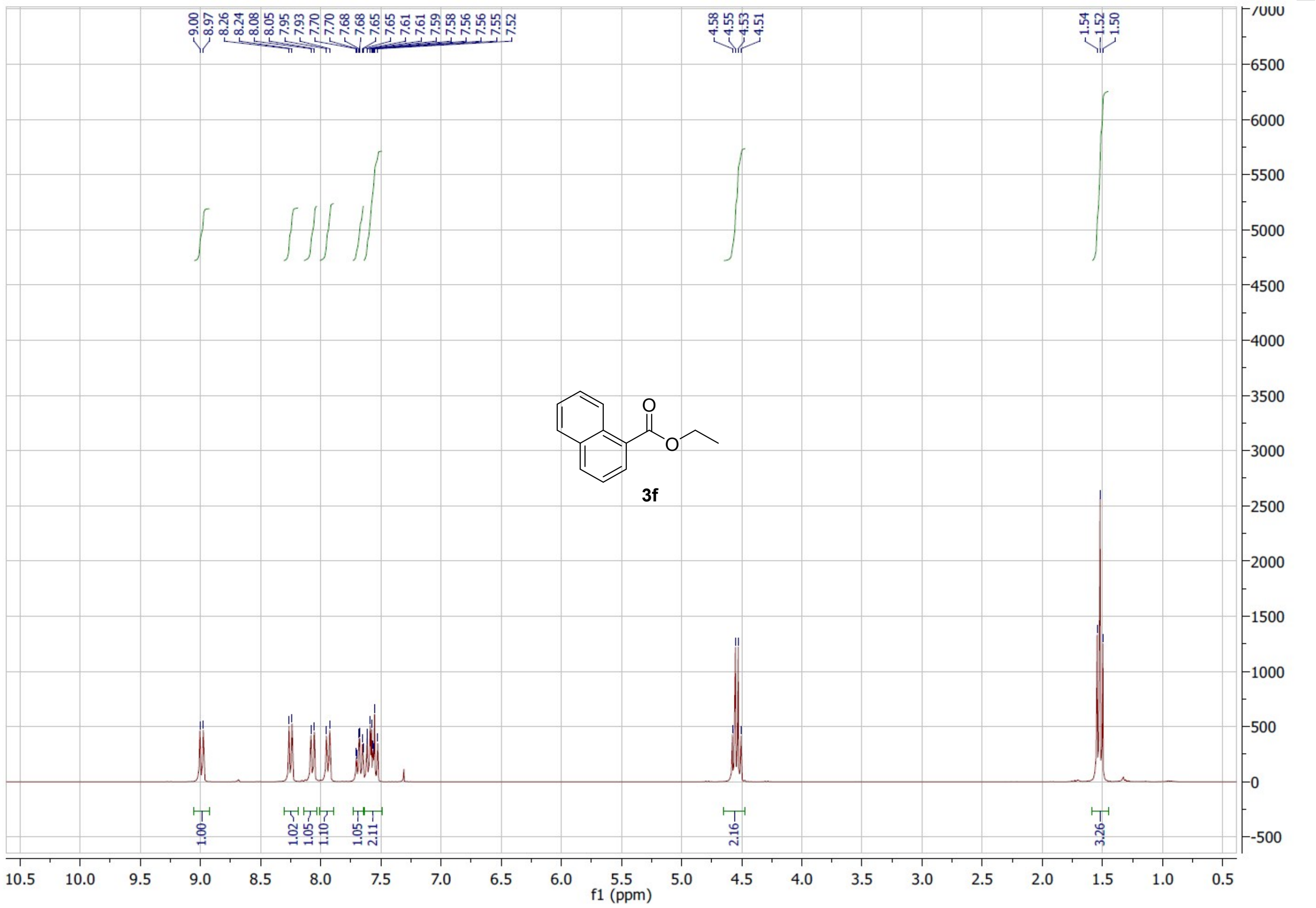
^1H NMR (300MHz, $CDCl_3$, ppm)



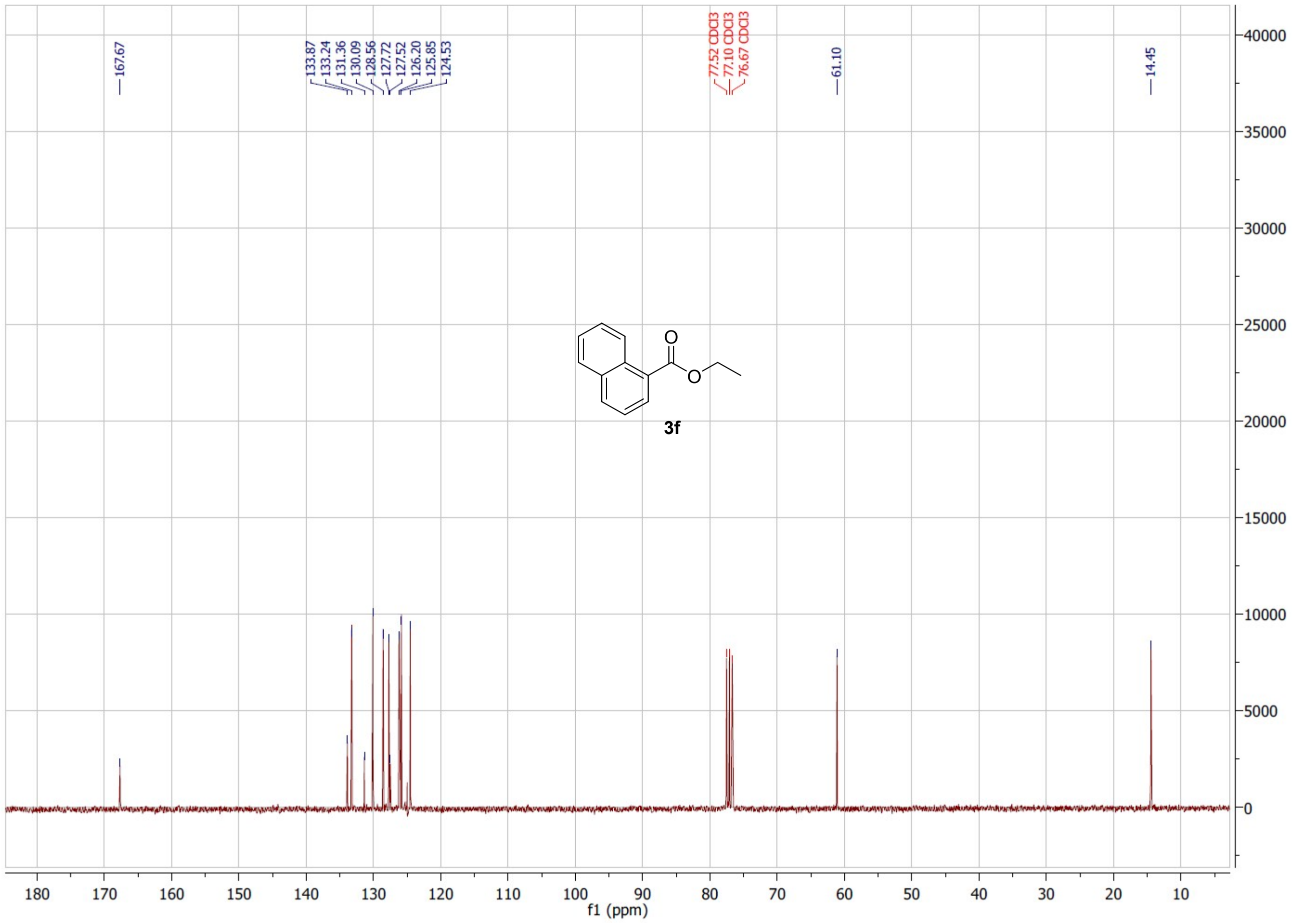
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, ppm)



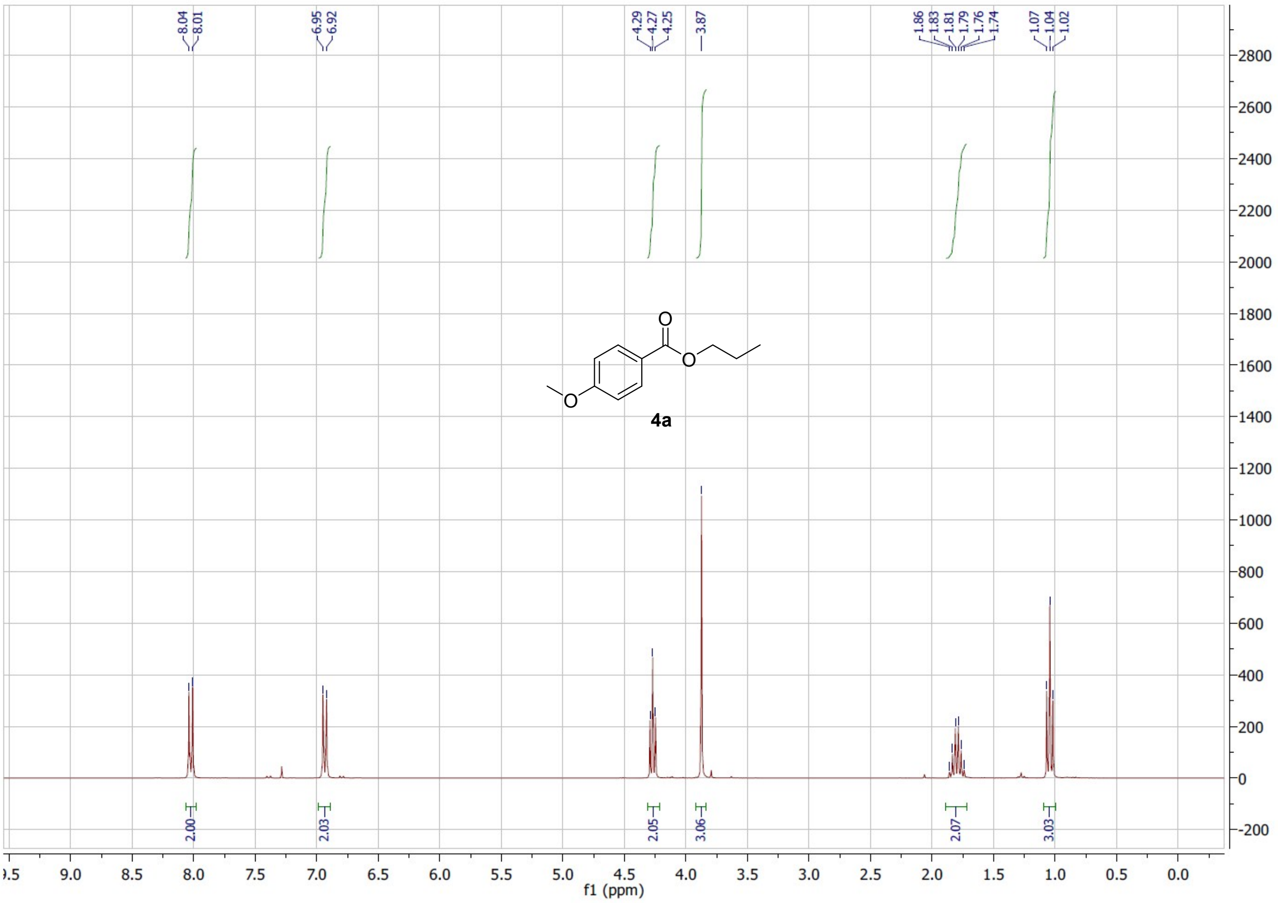
^{1}H NMR (300MHz, $CDCl_3$, ppm)



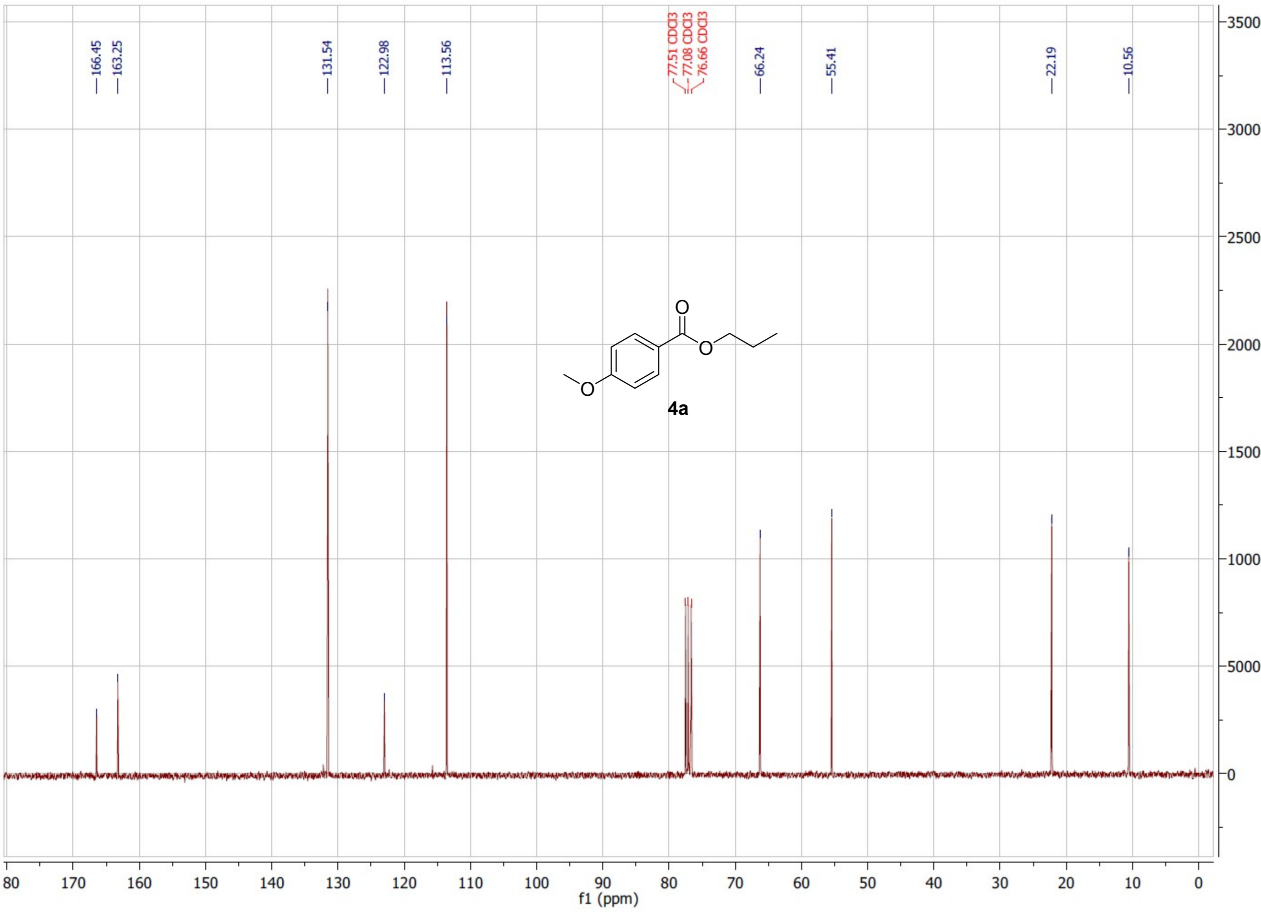
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, ppm)



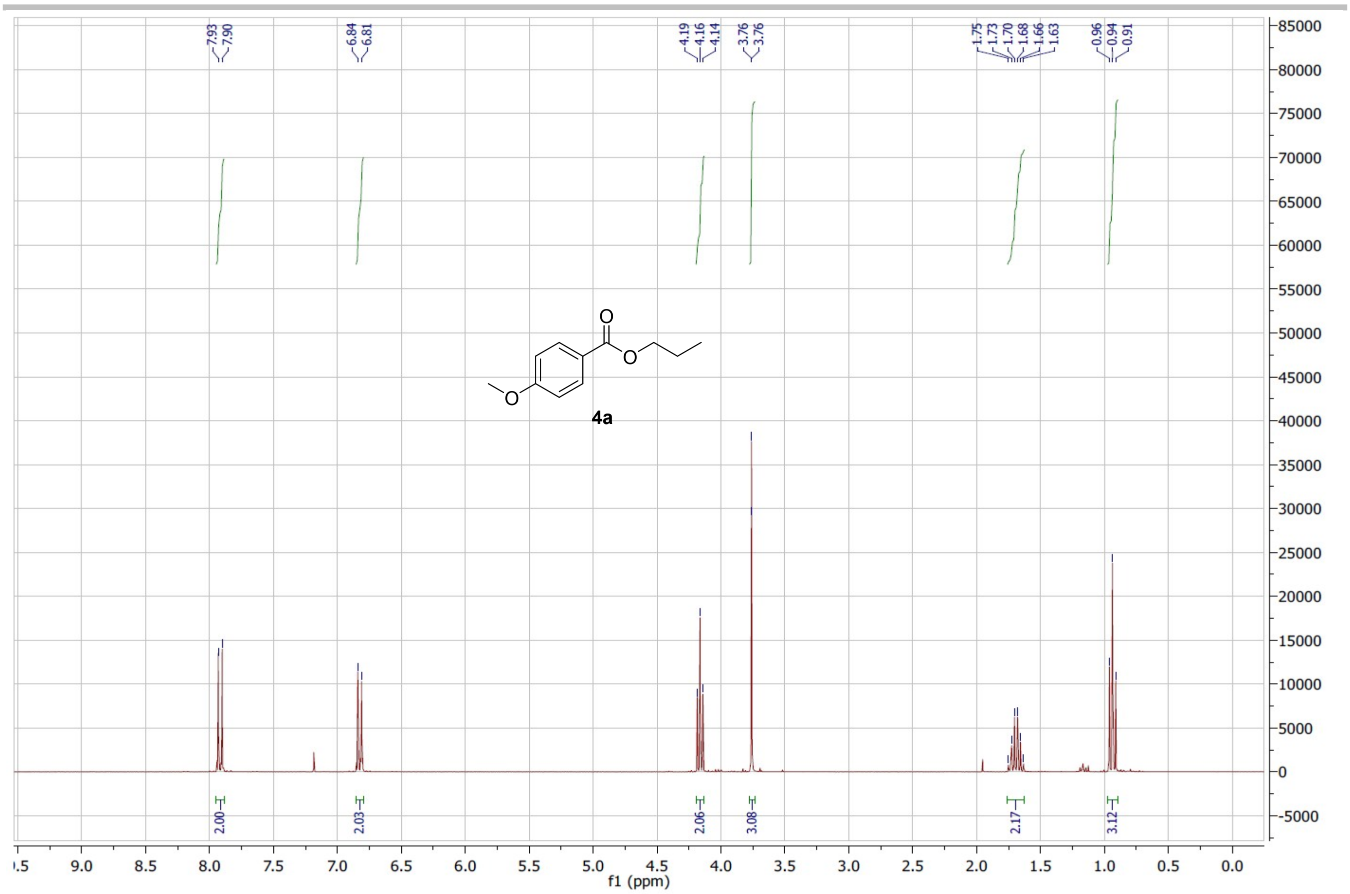
^{1}H NMR (300MHz, $CDCl_3$, ppm)



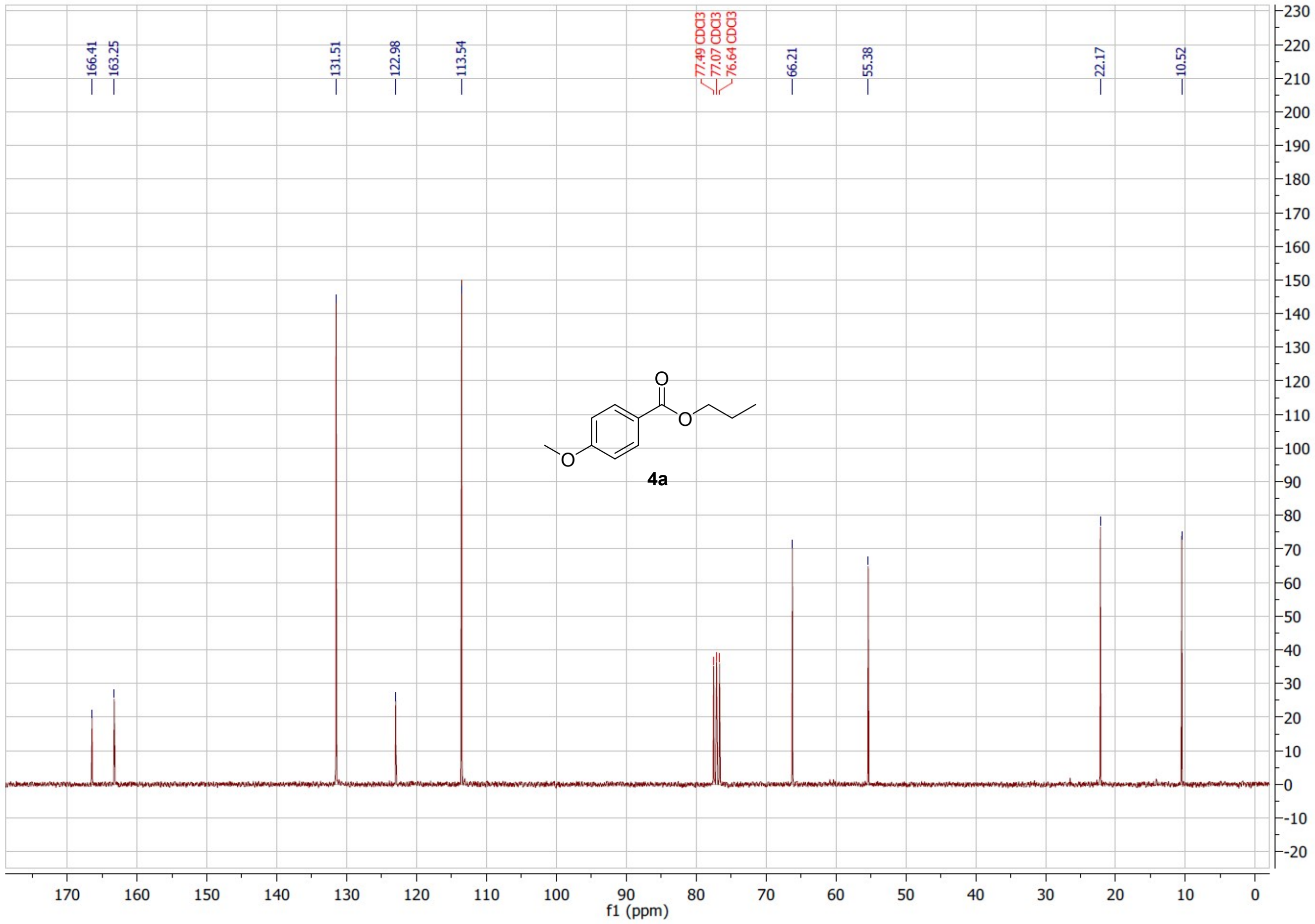
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, ppm)



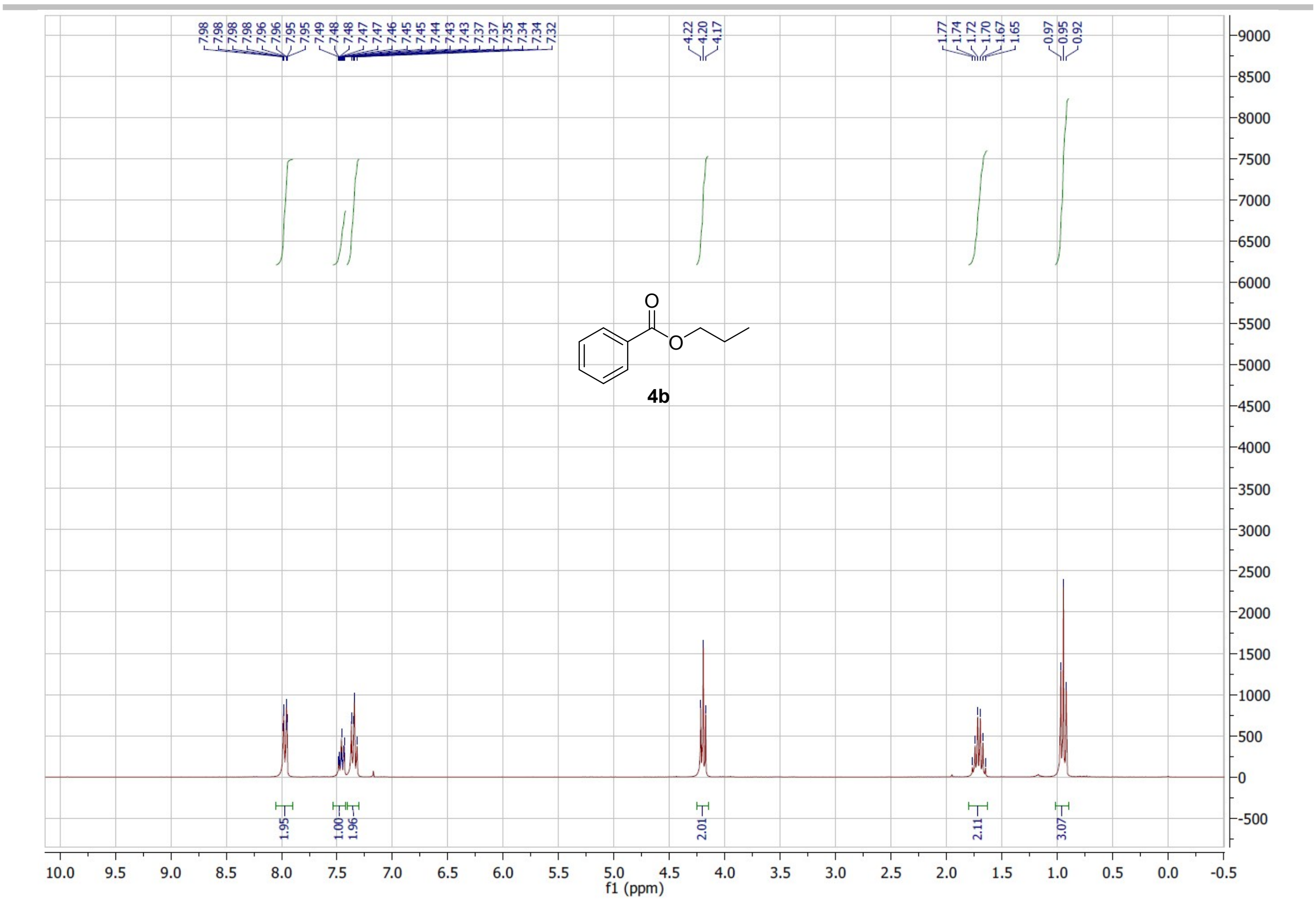
4a, Scale-up, ^{1}H NMR (300MHz, $CDCl_3$, ppm)



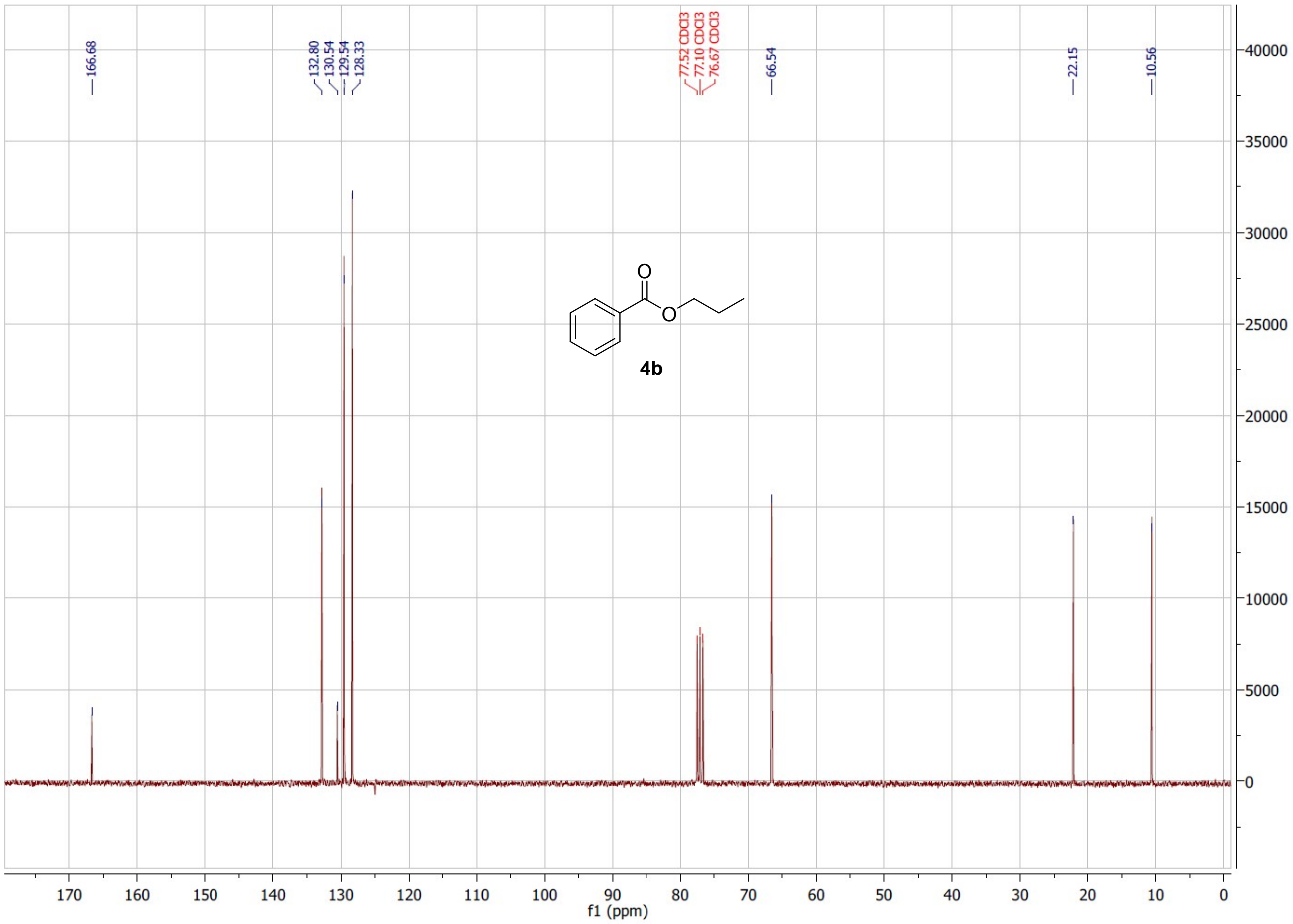
4a, Scale-up, $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, ppm)



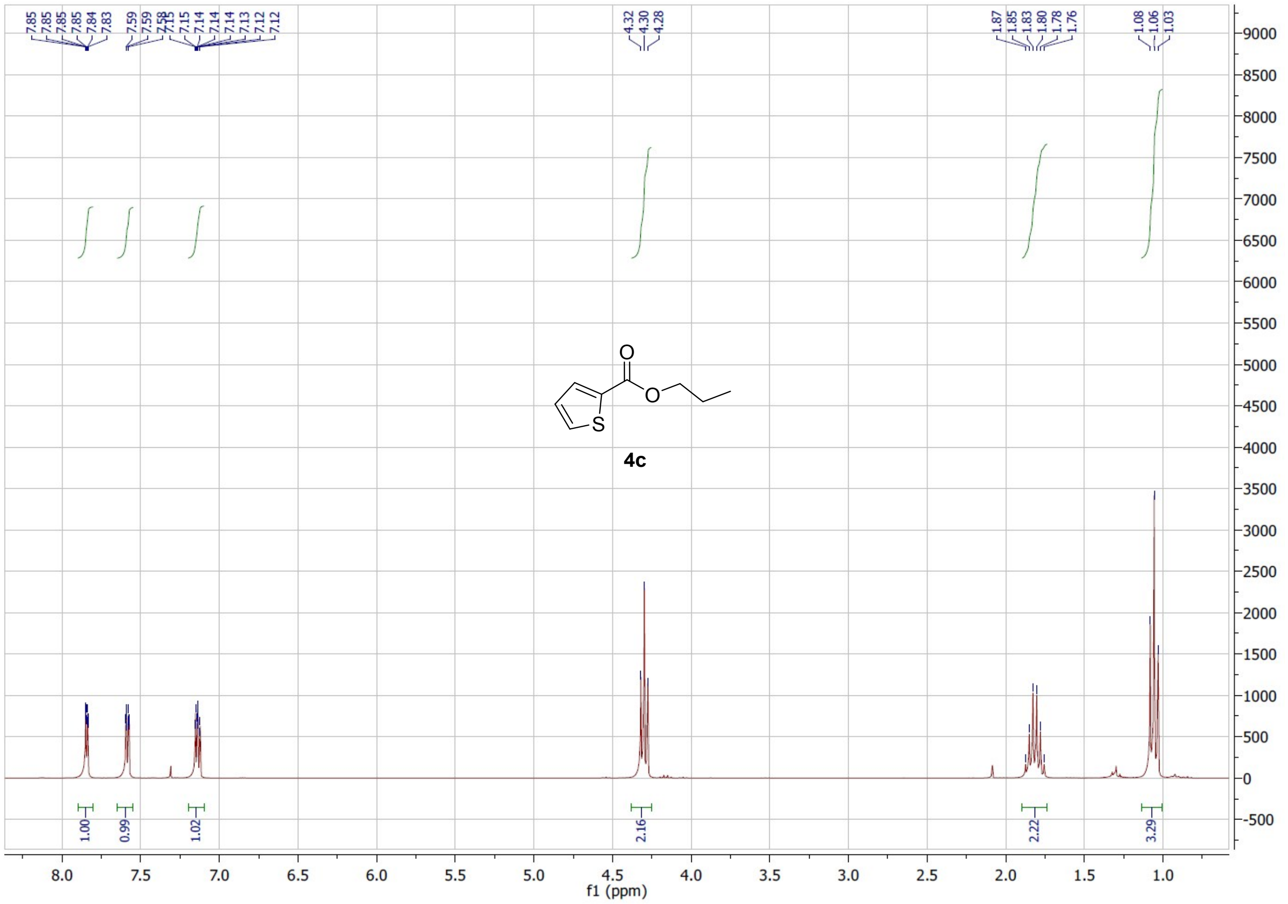
^{1}H NMR (300MHz, $CDCl_3$, ppm)



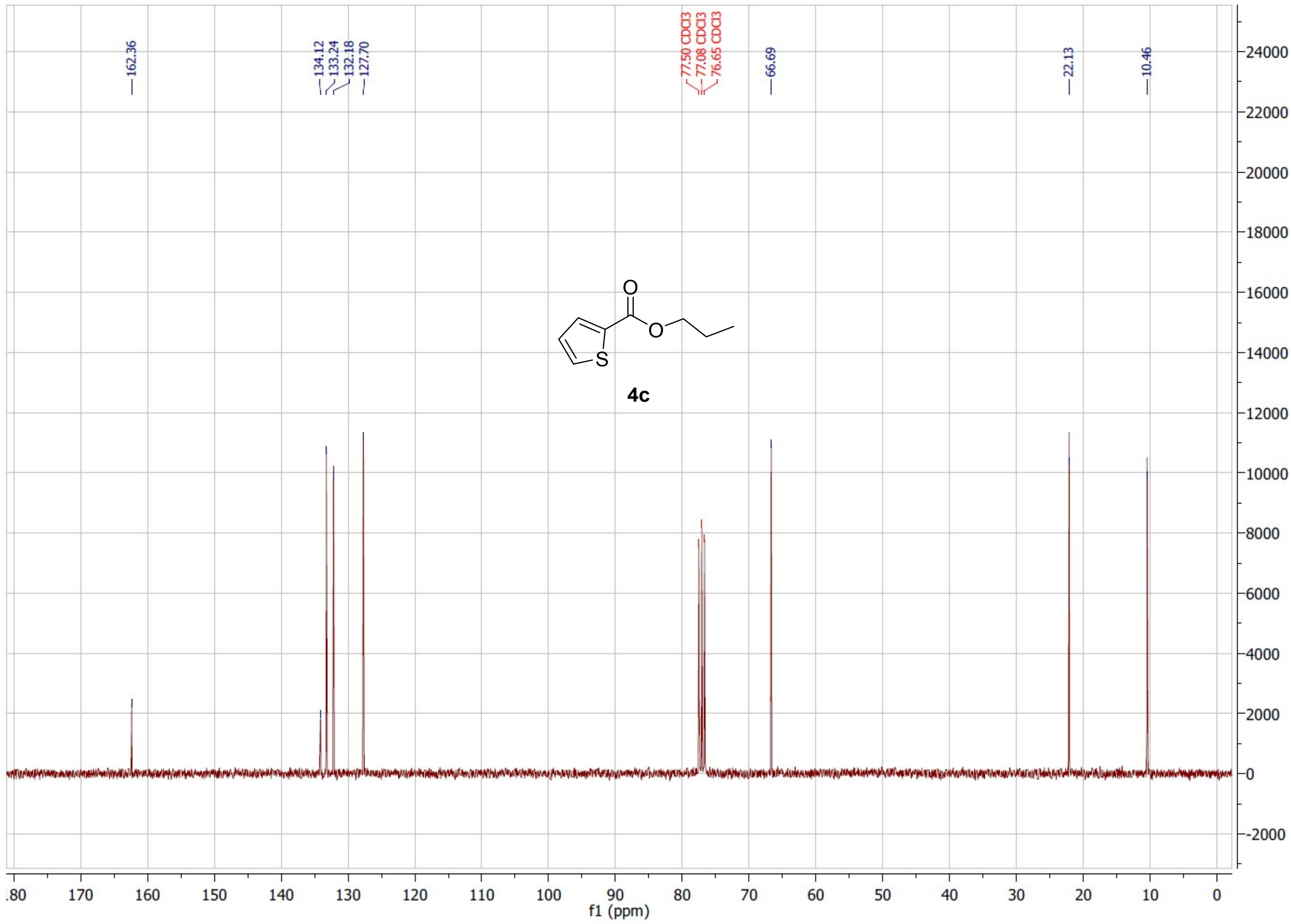
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, ppm)



^{1}H NMR (300MHz, $CDCl_3$, ppm)



$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm)



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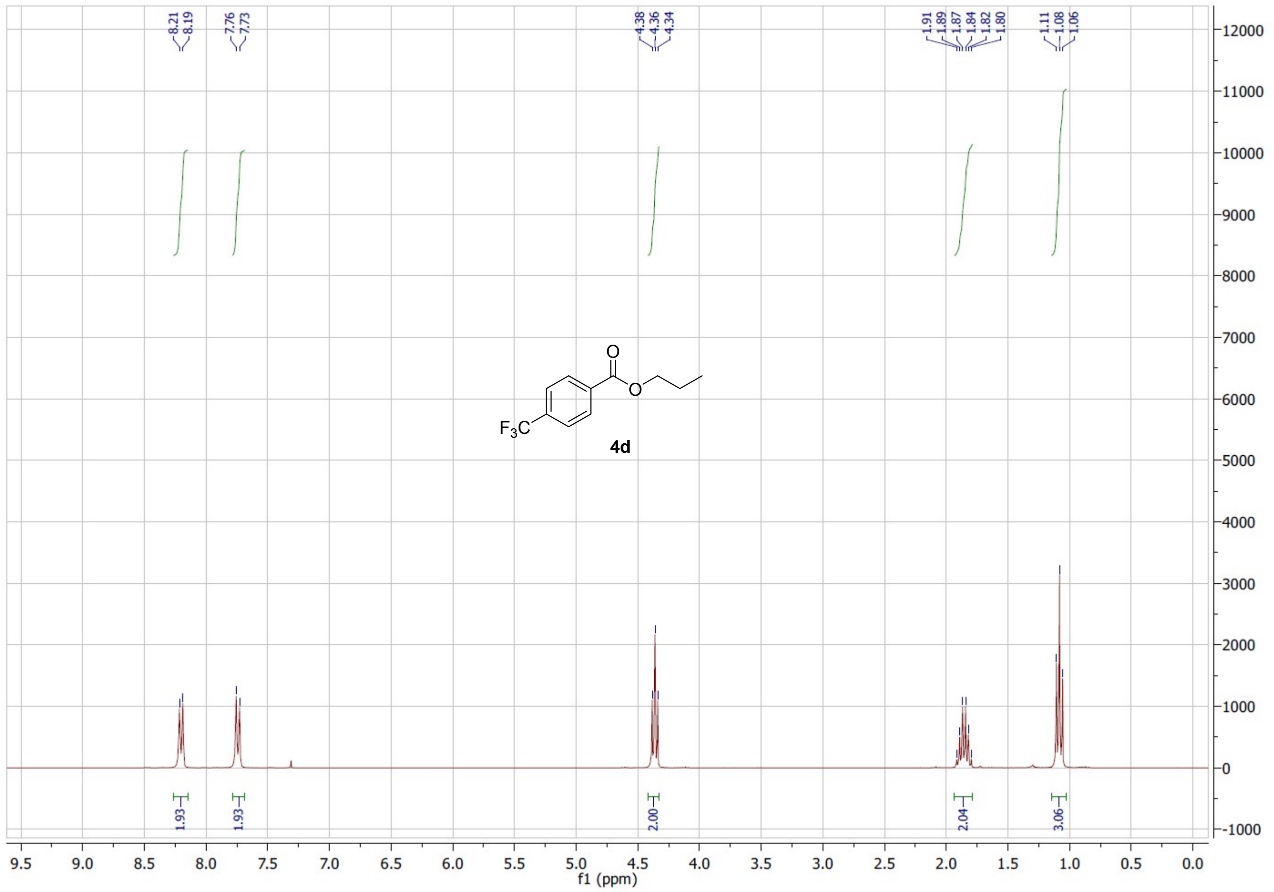
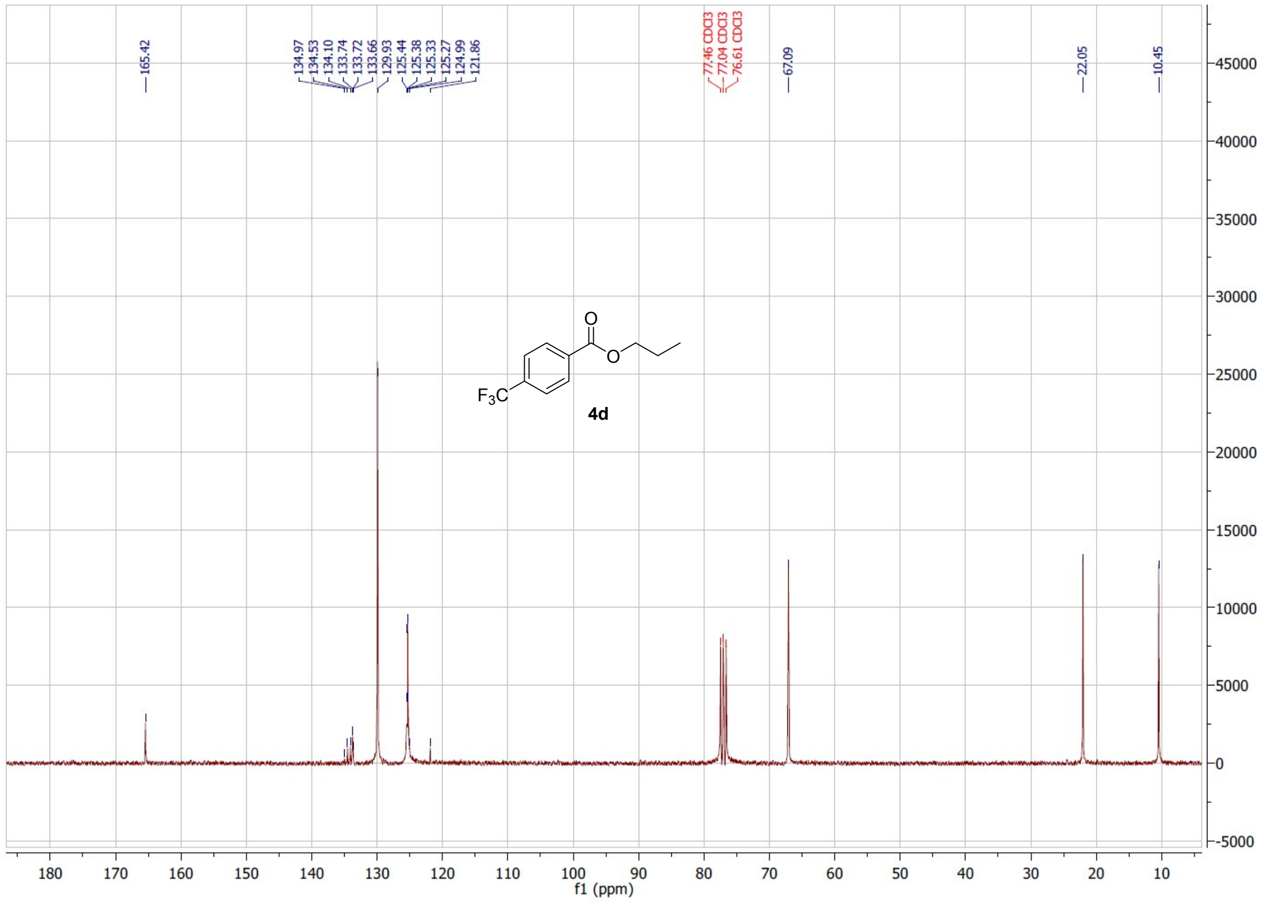


$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm)



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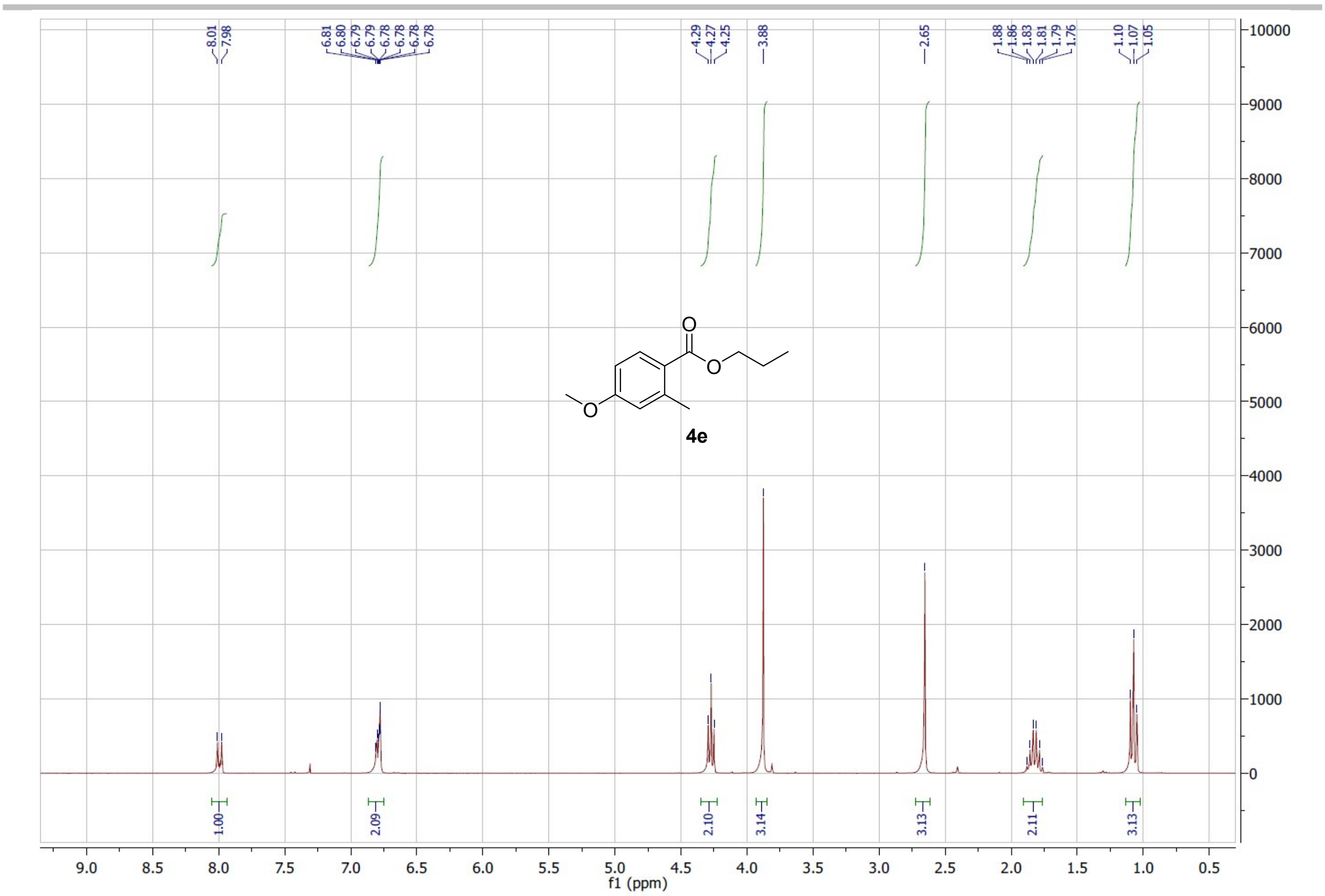

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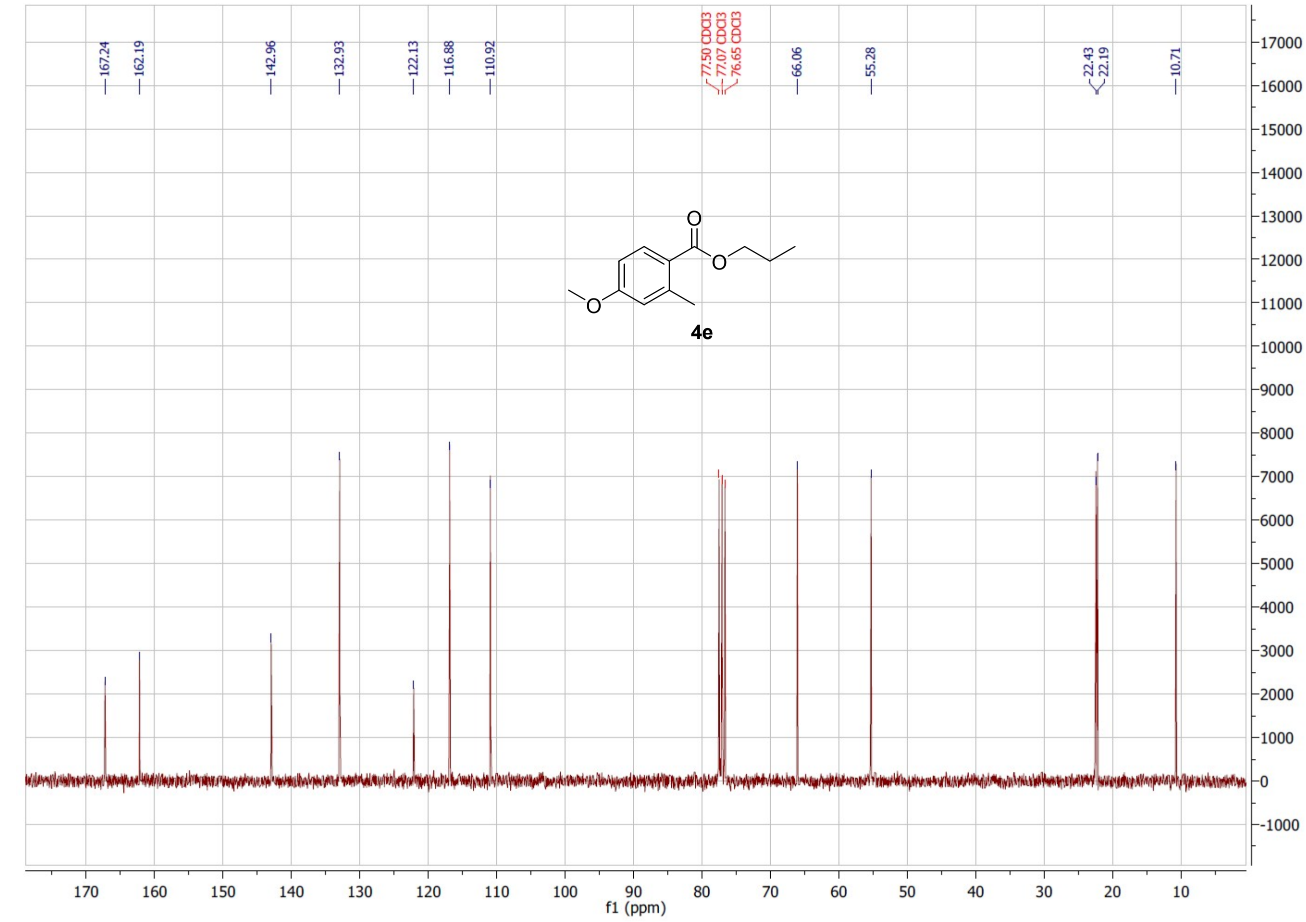

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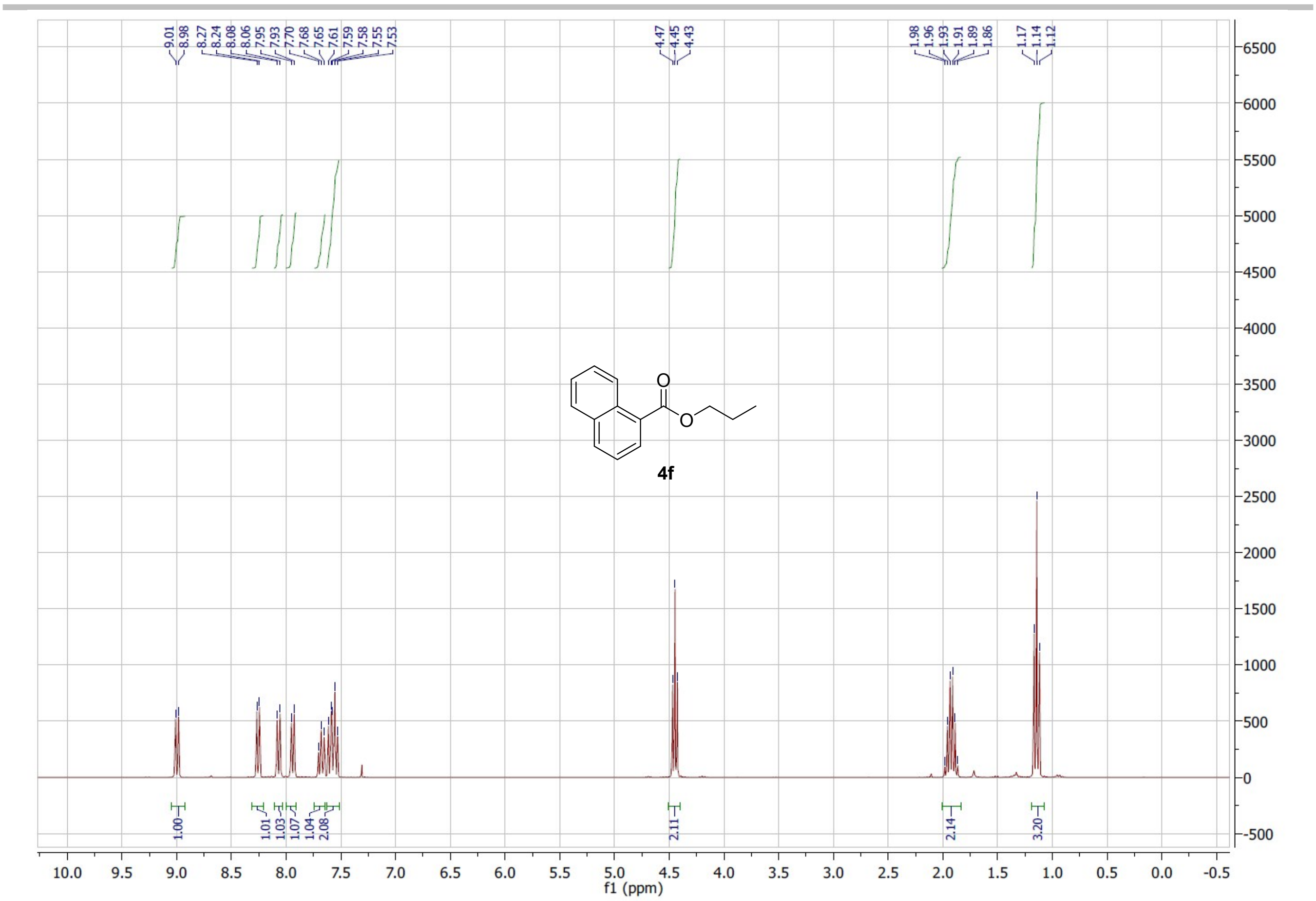

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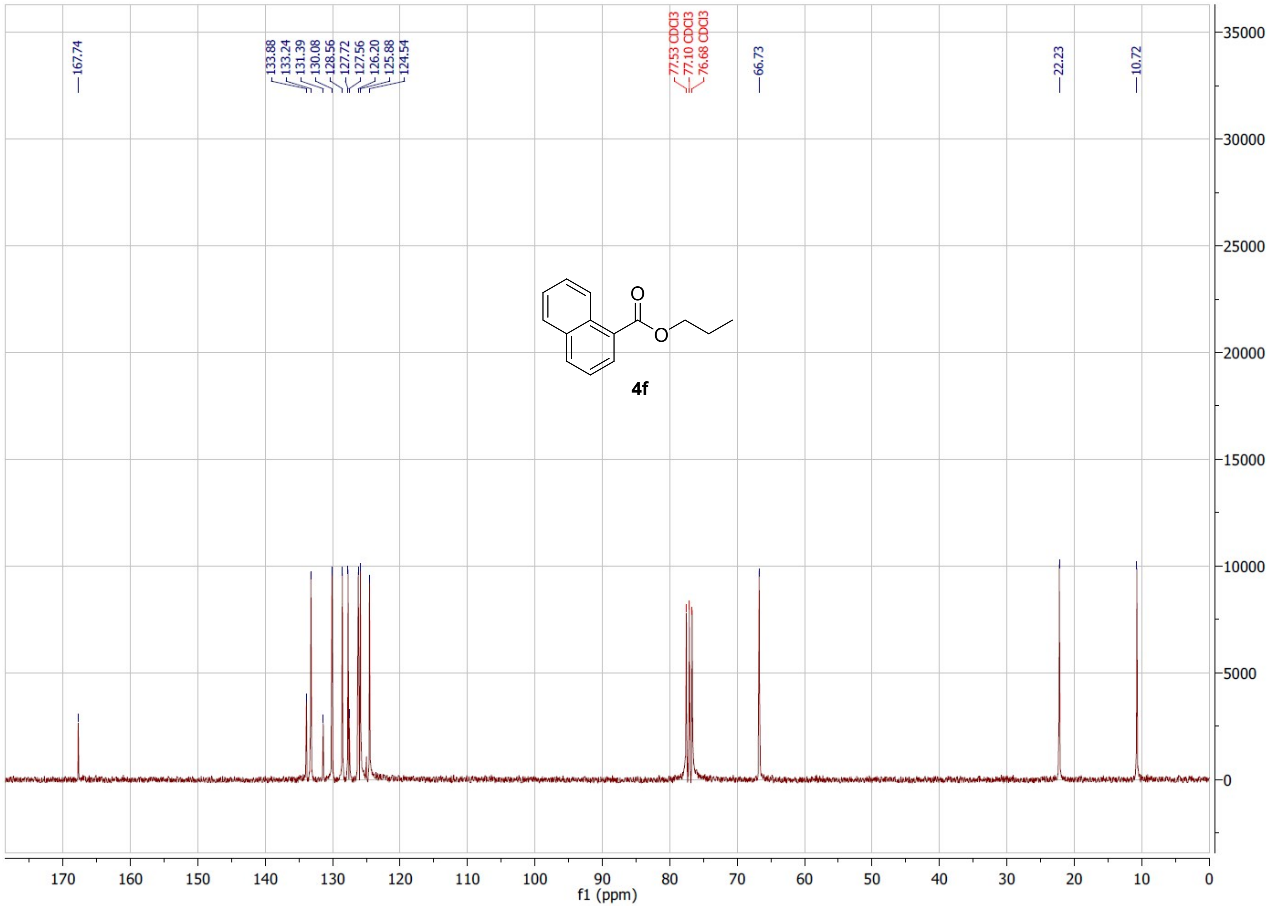

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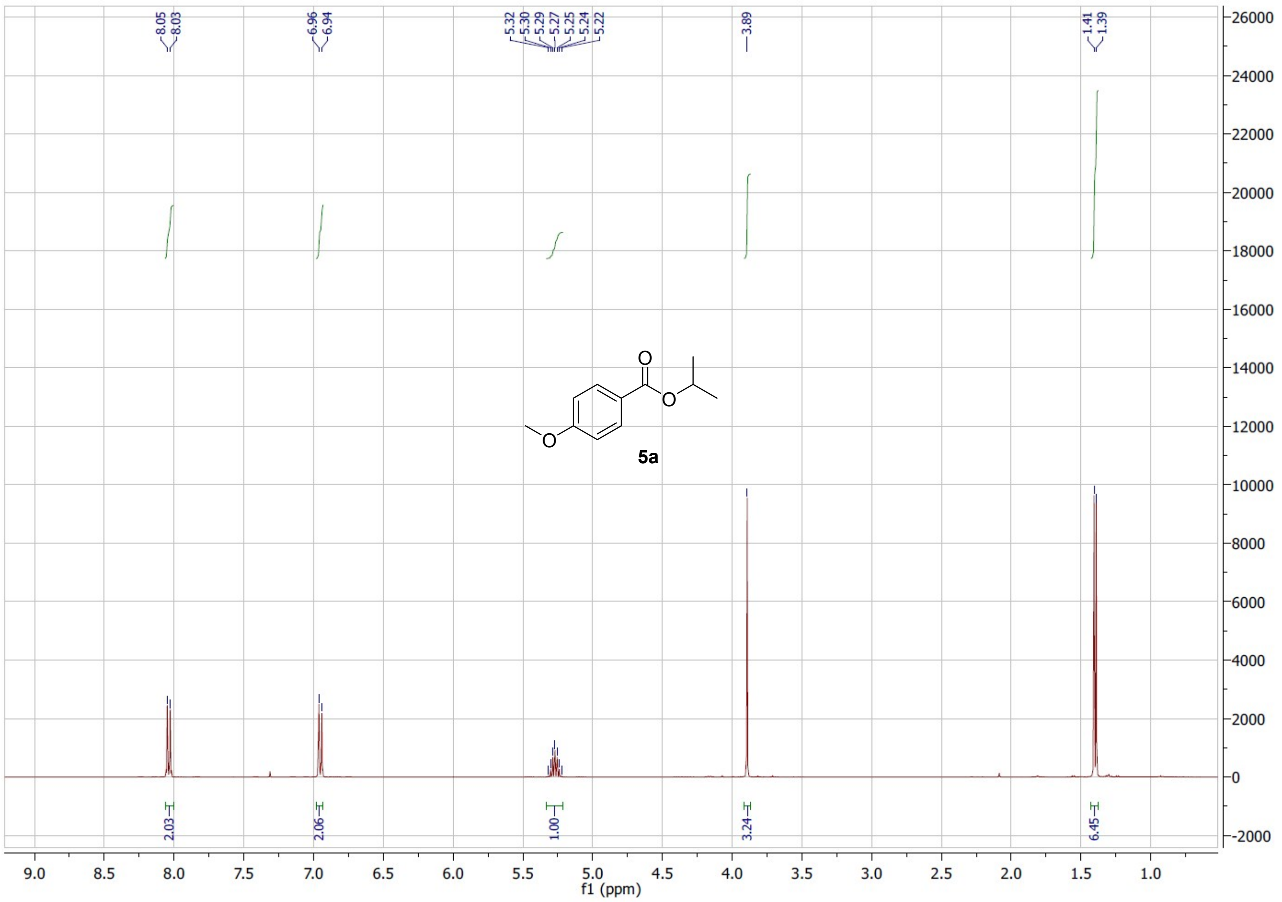

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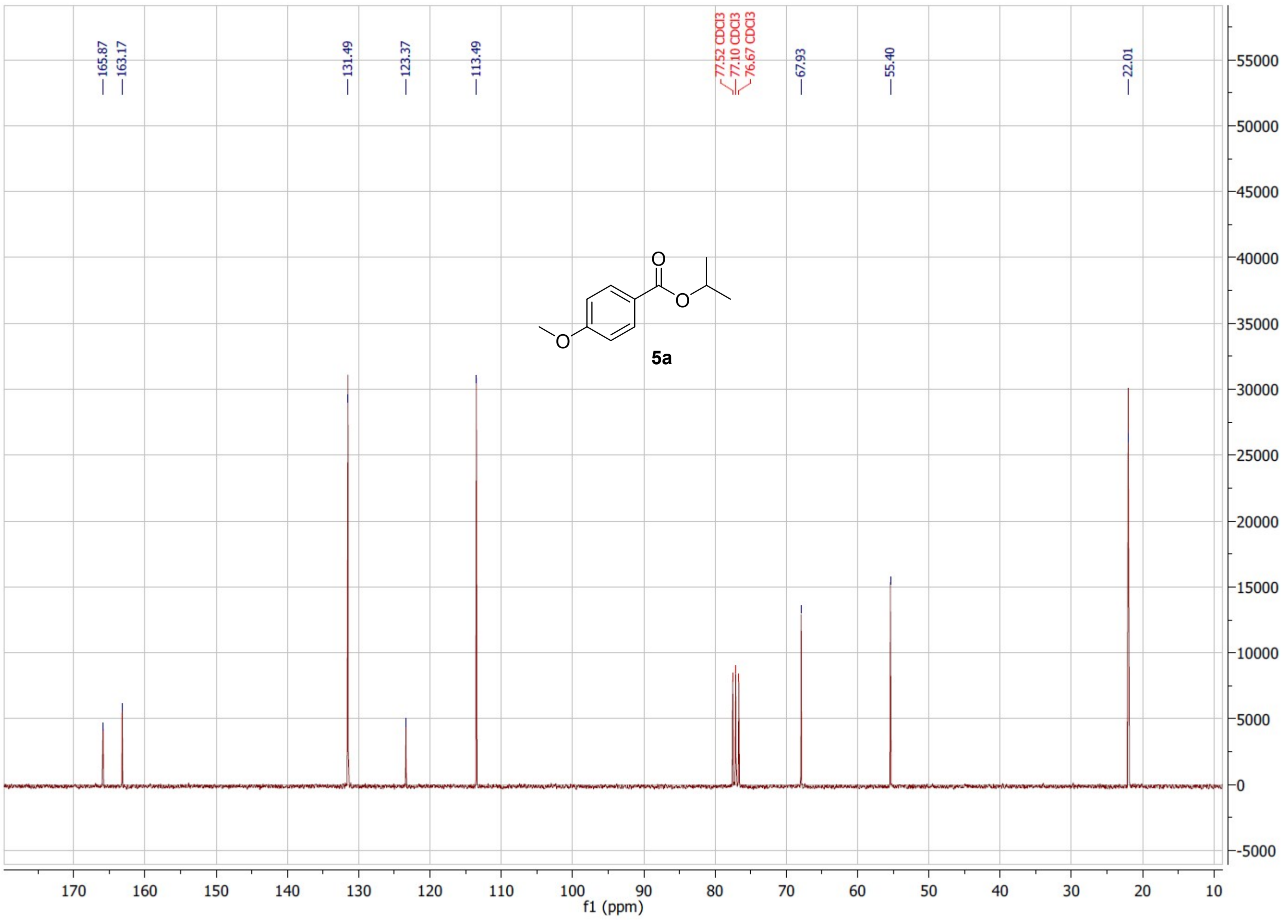

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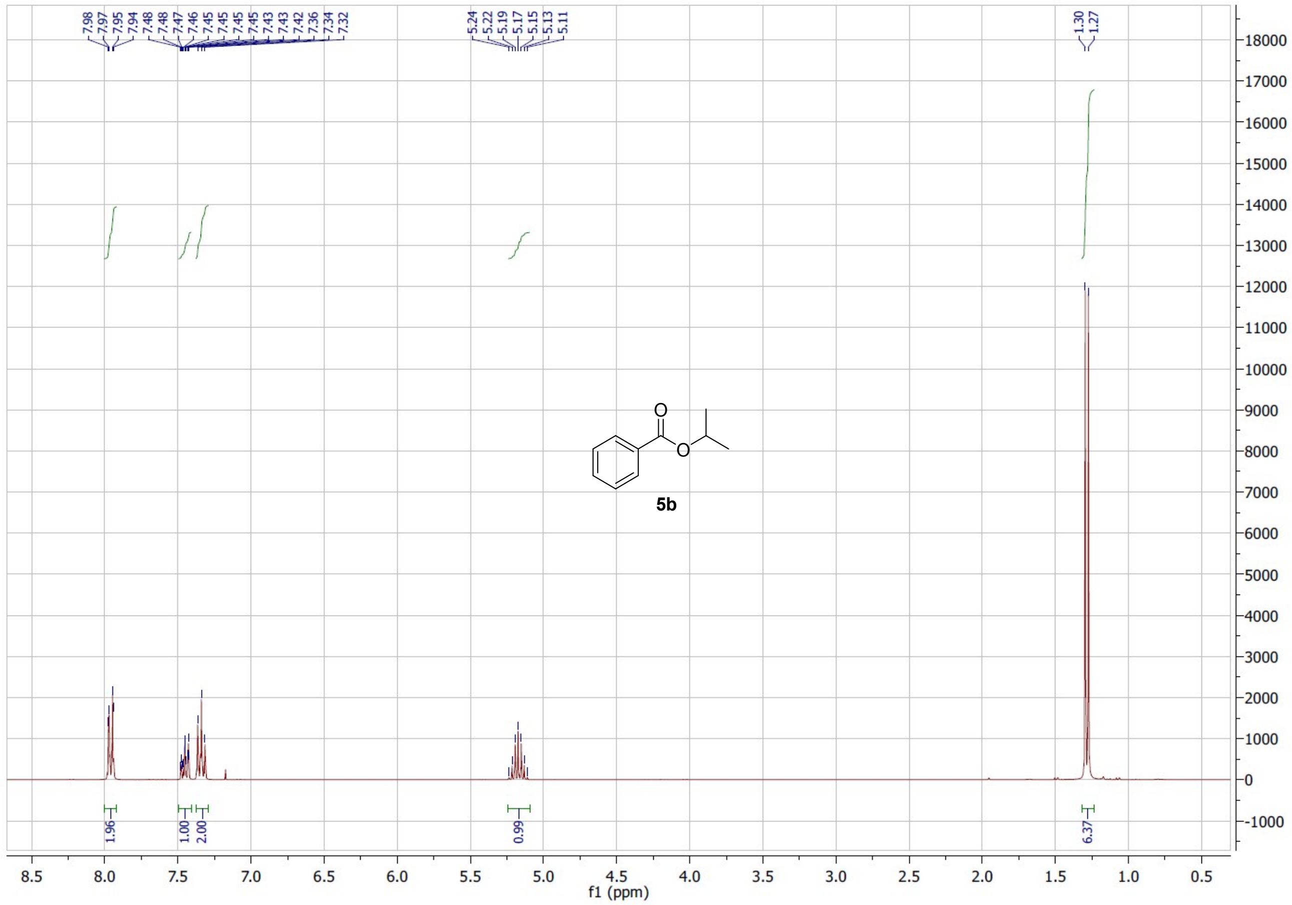

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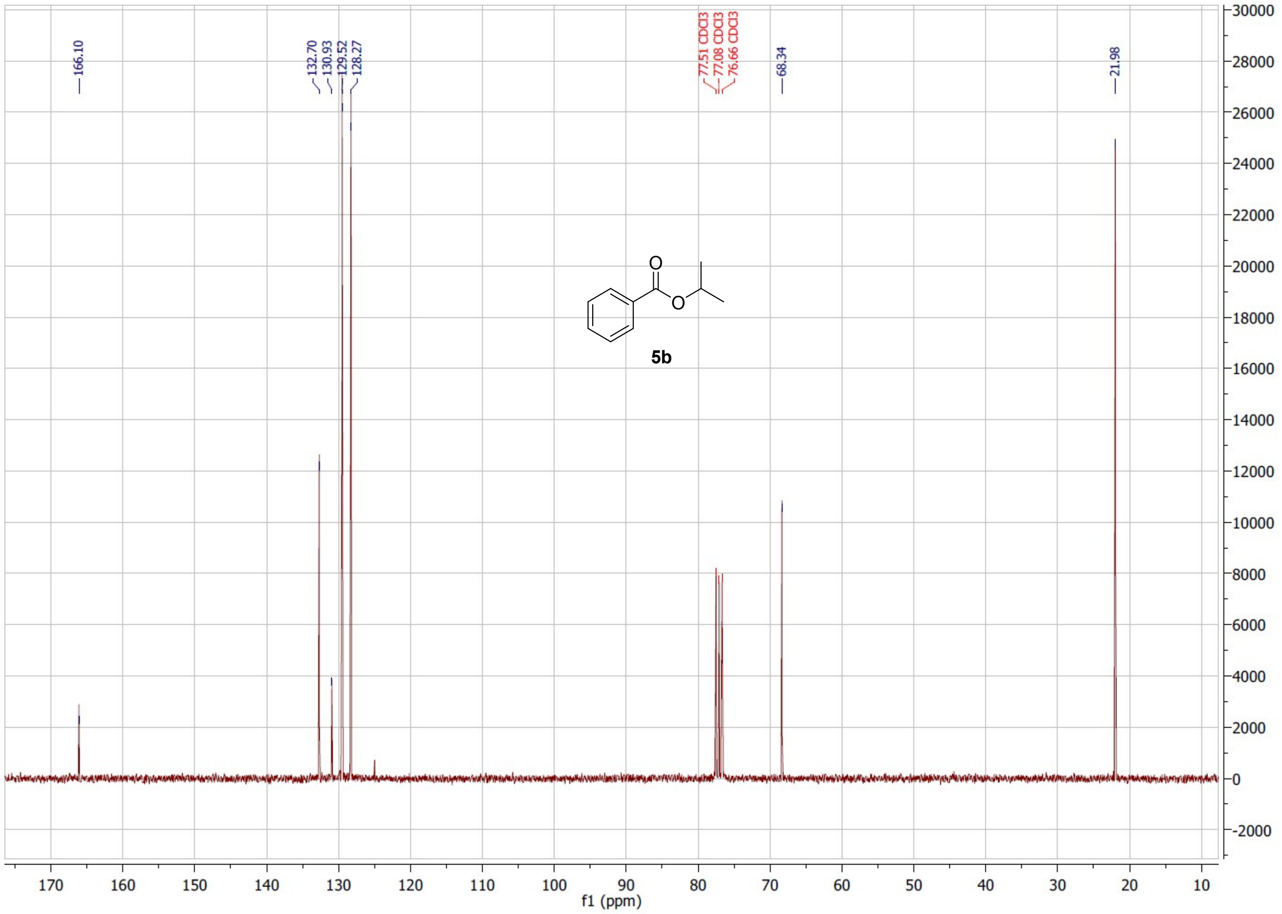

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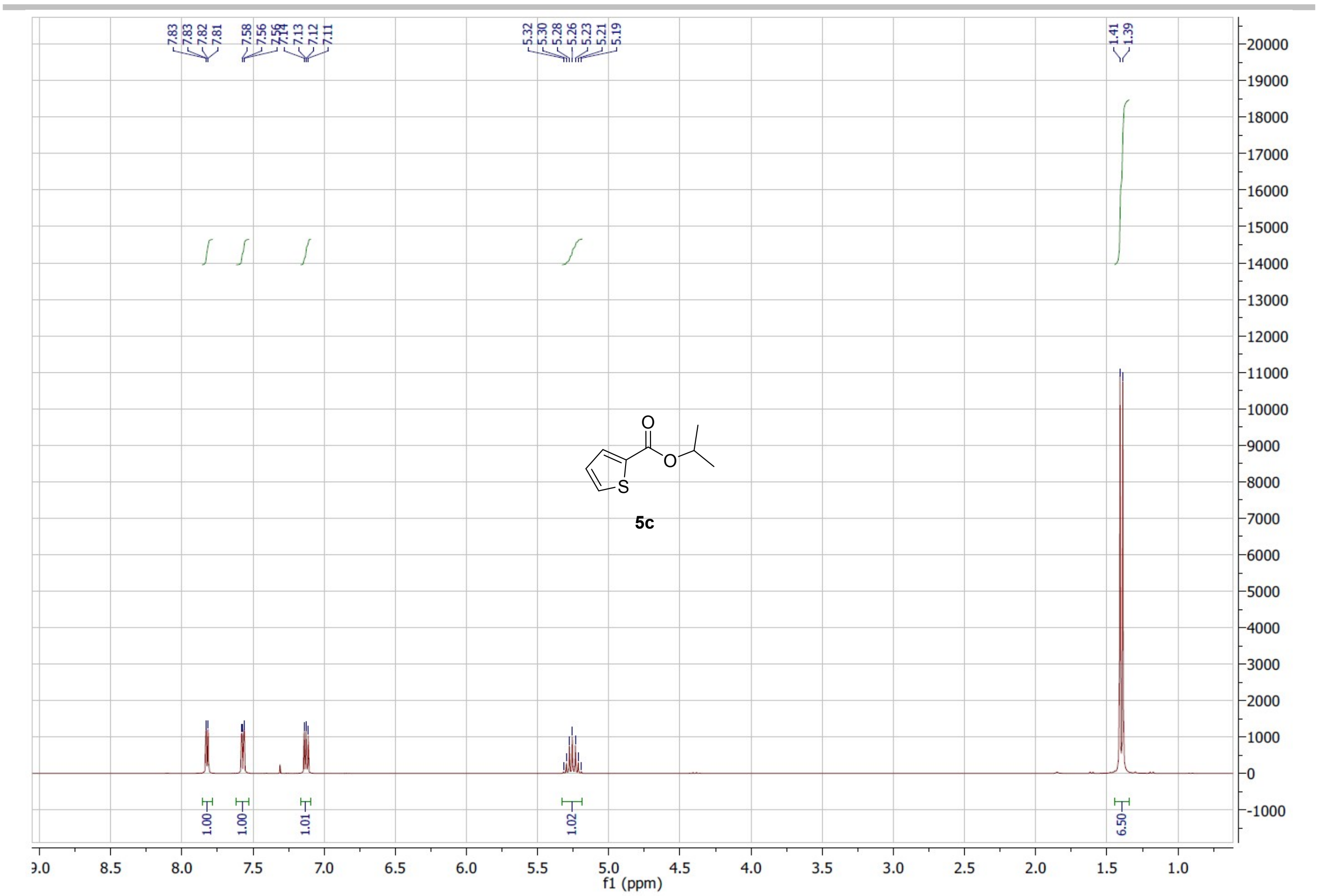

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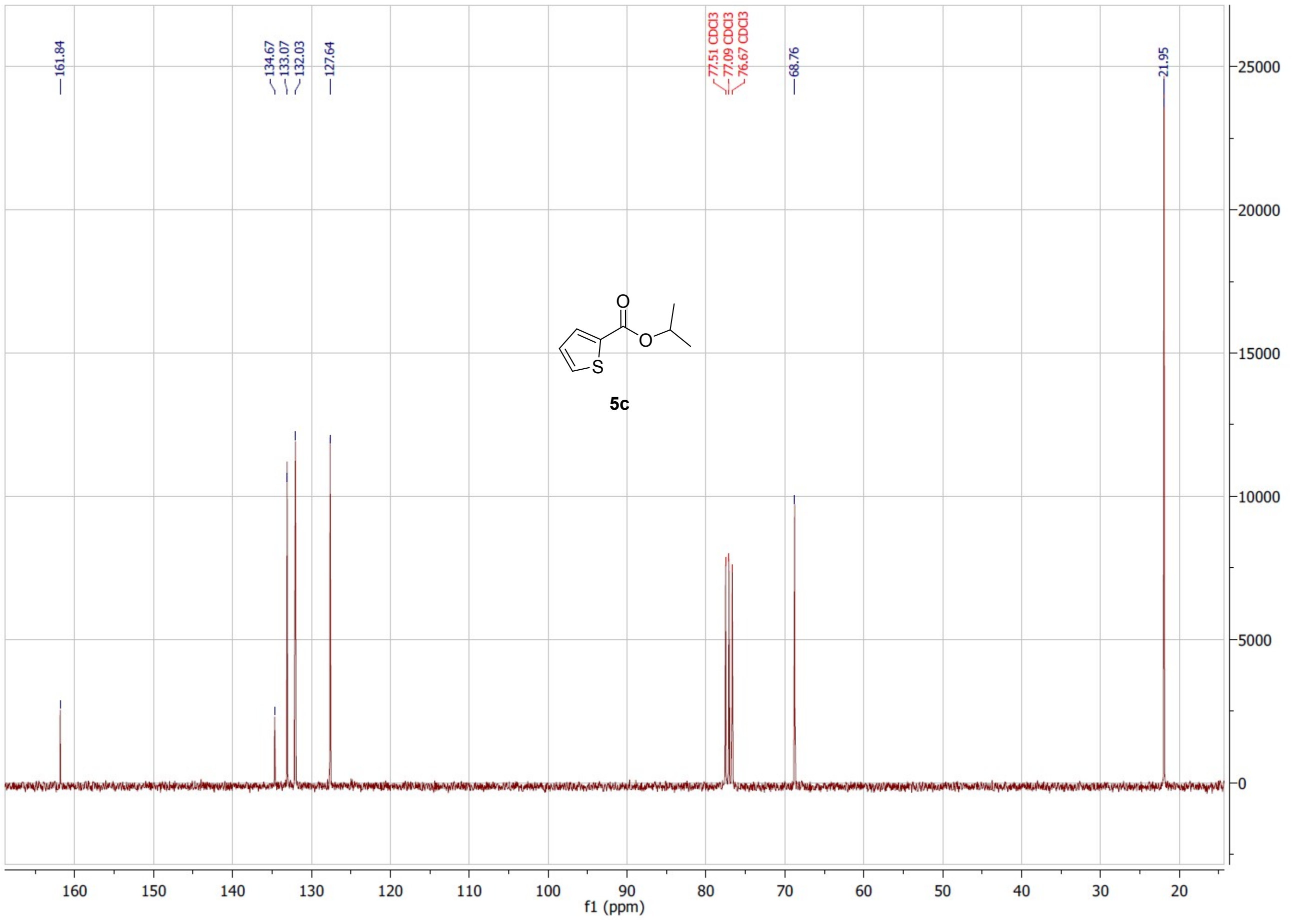

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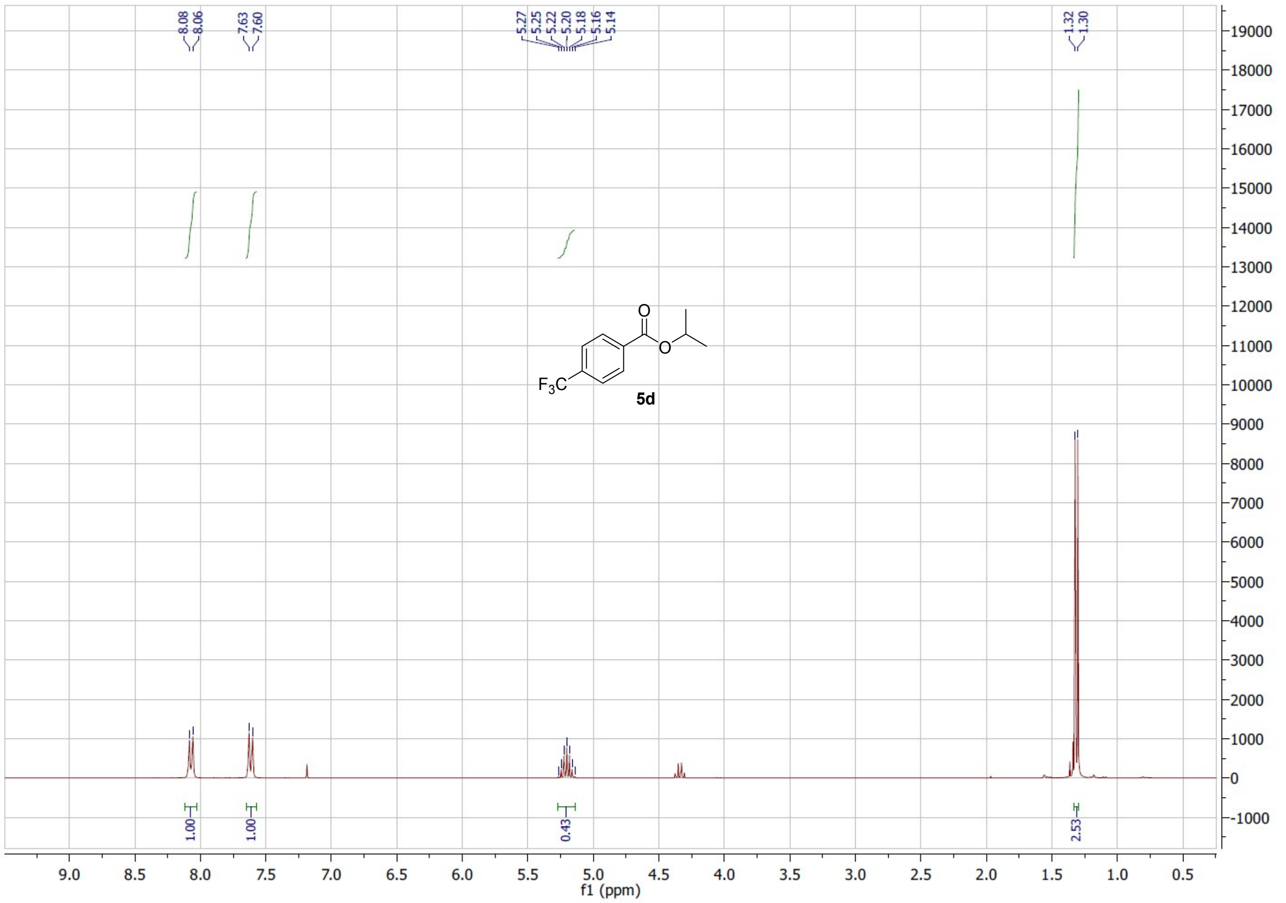

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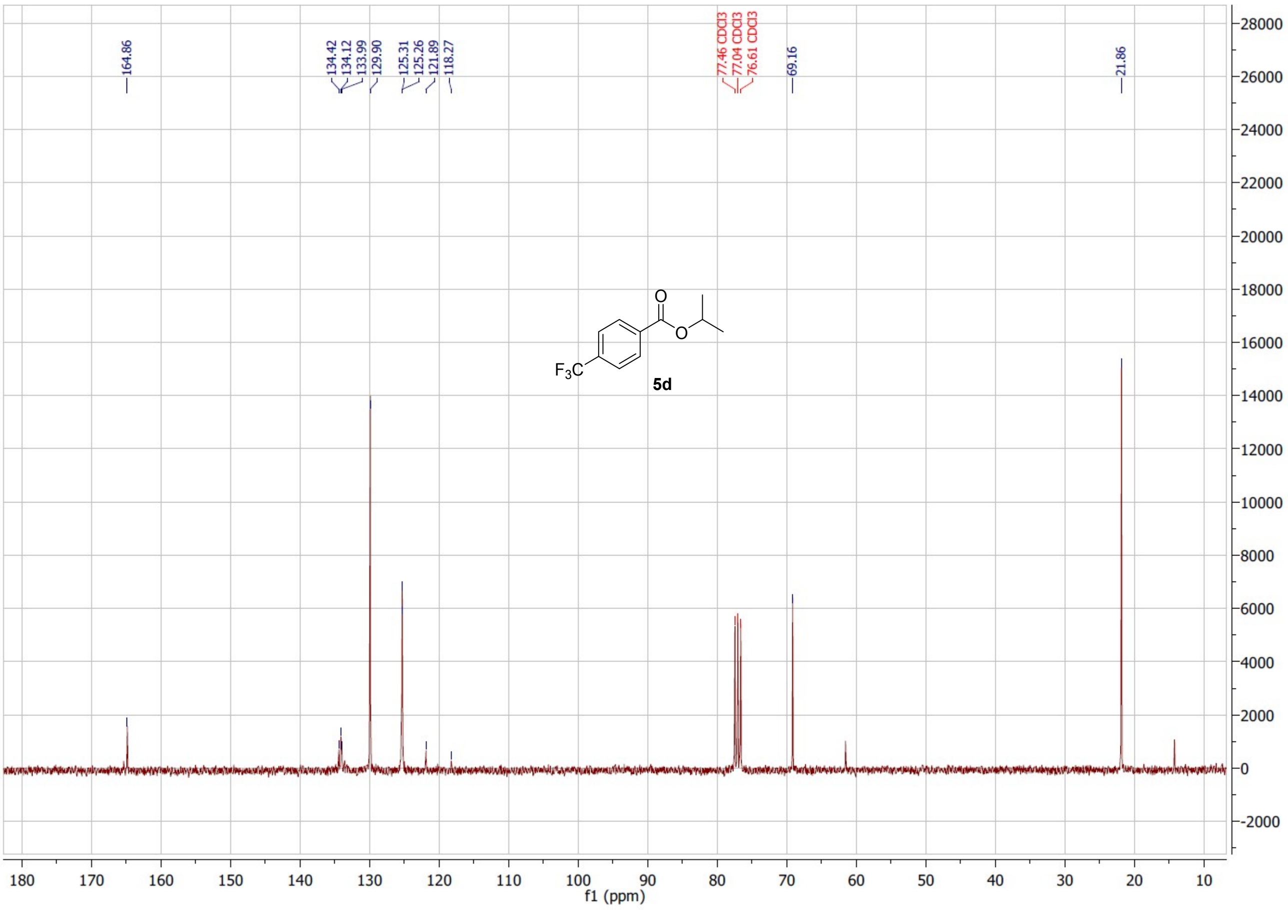

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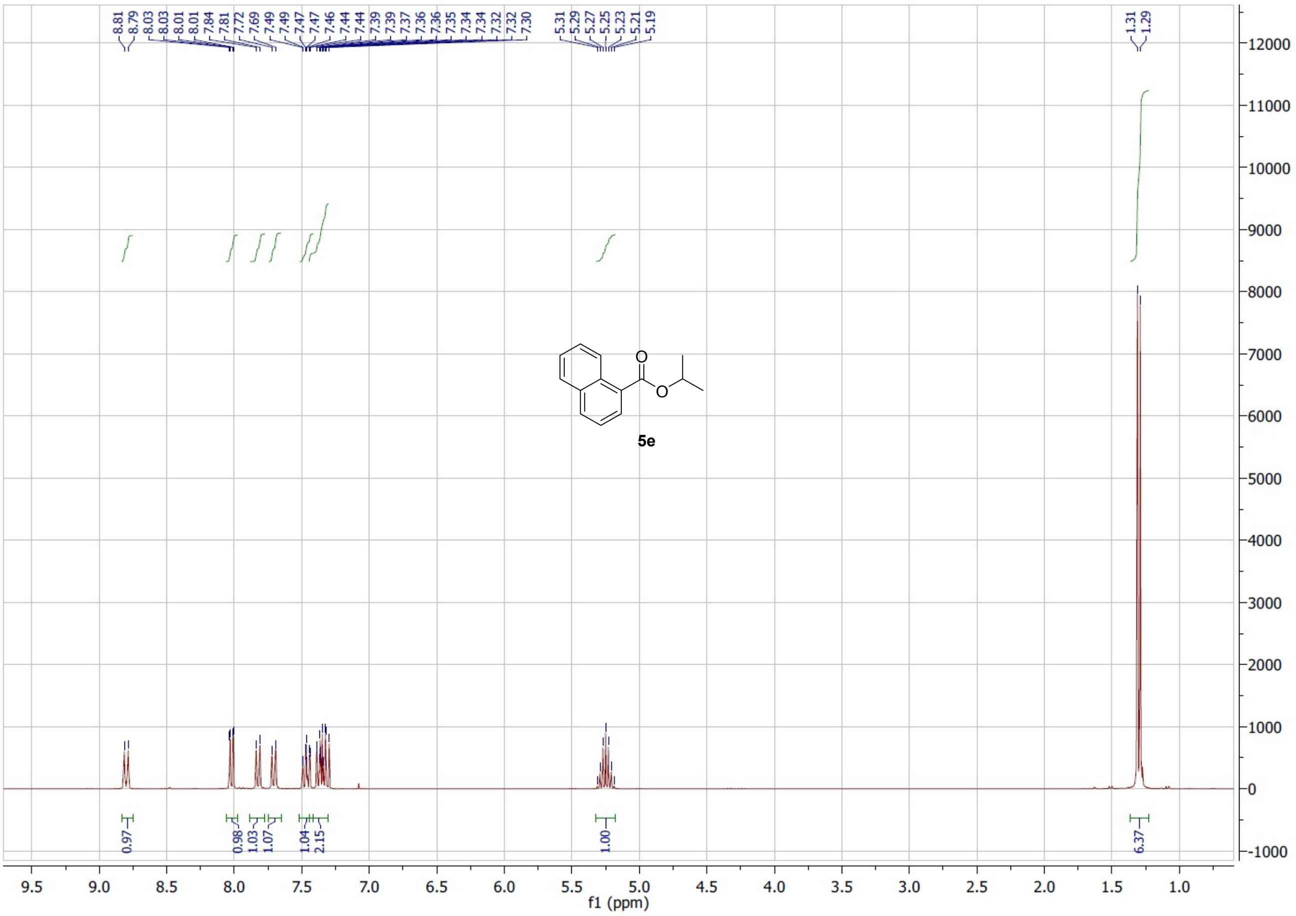

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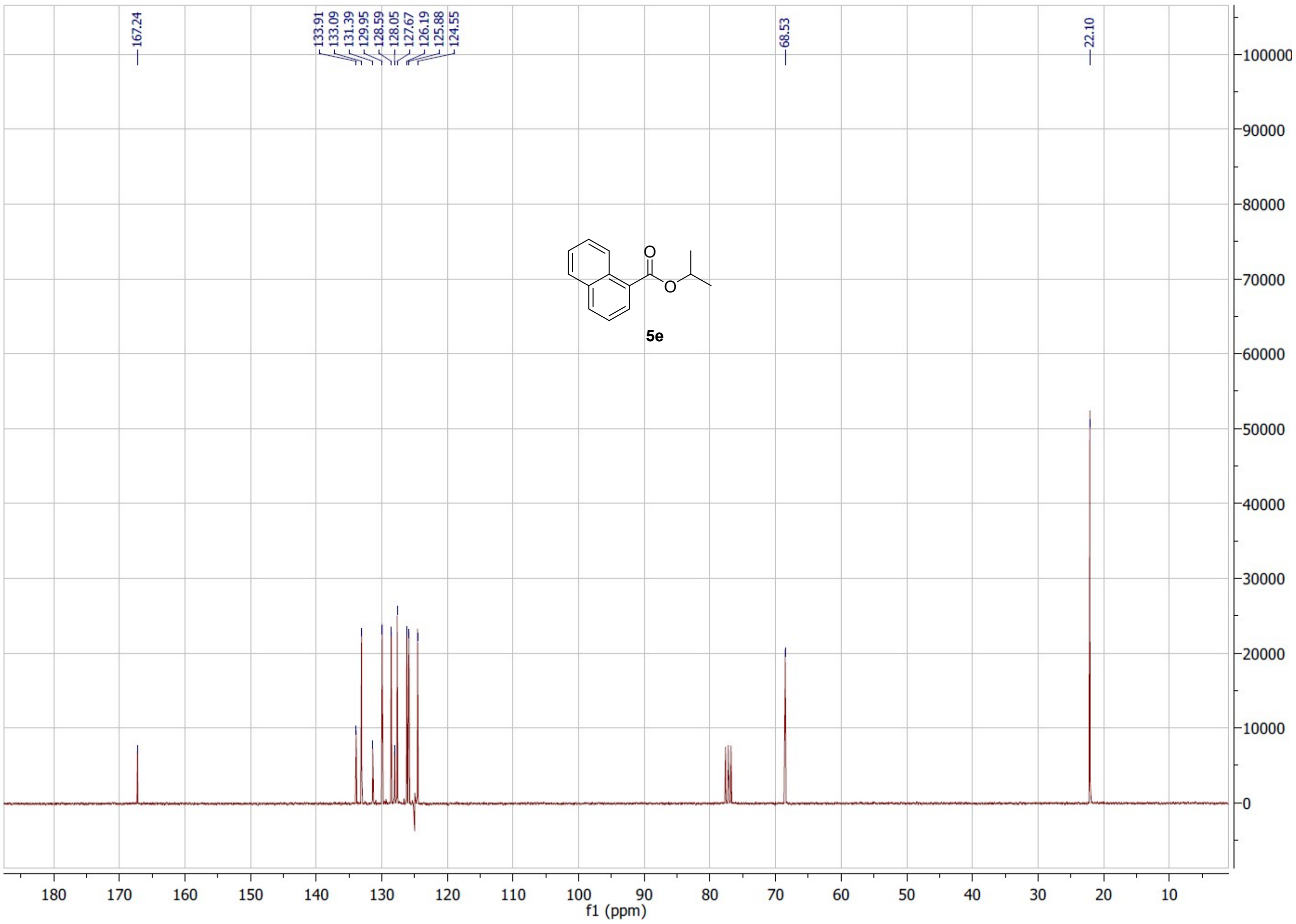

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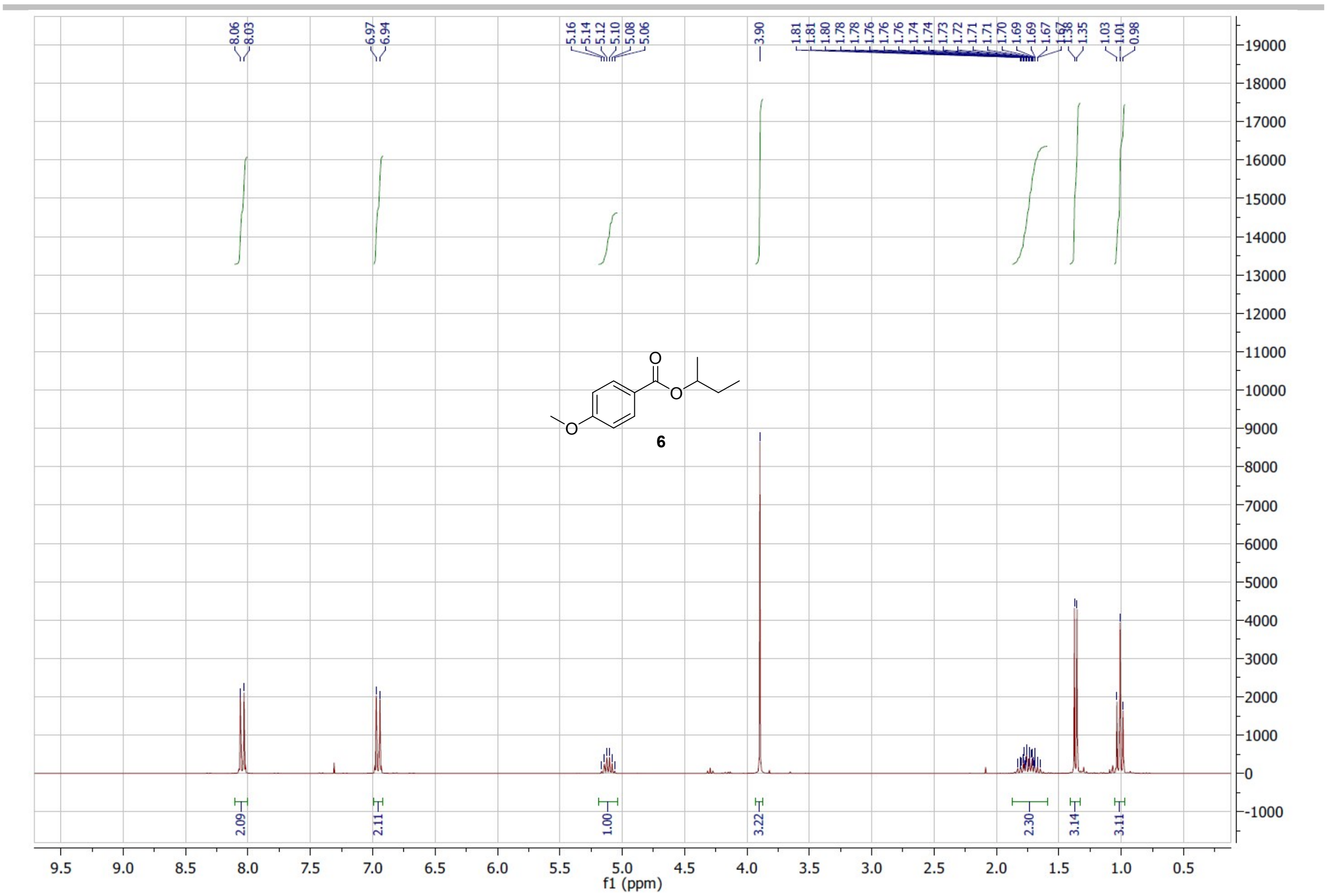
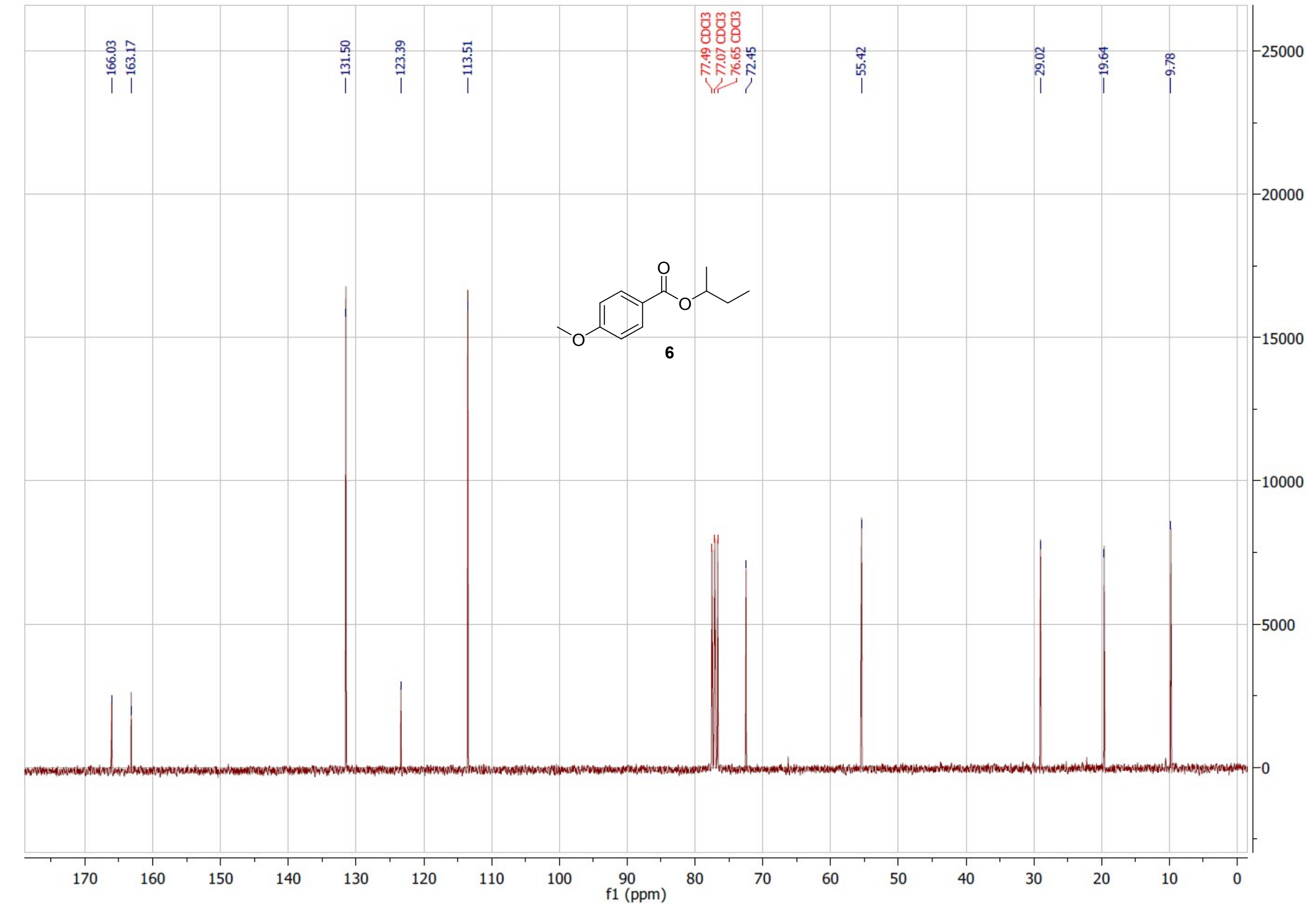
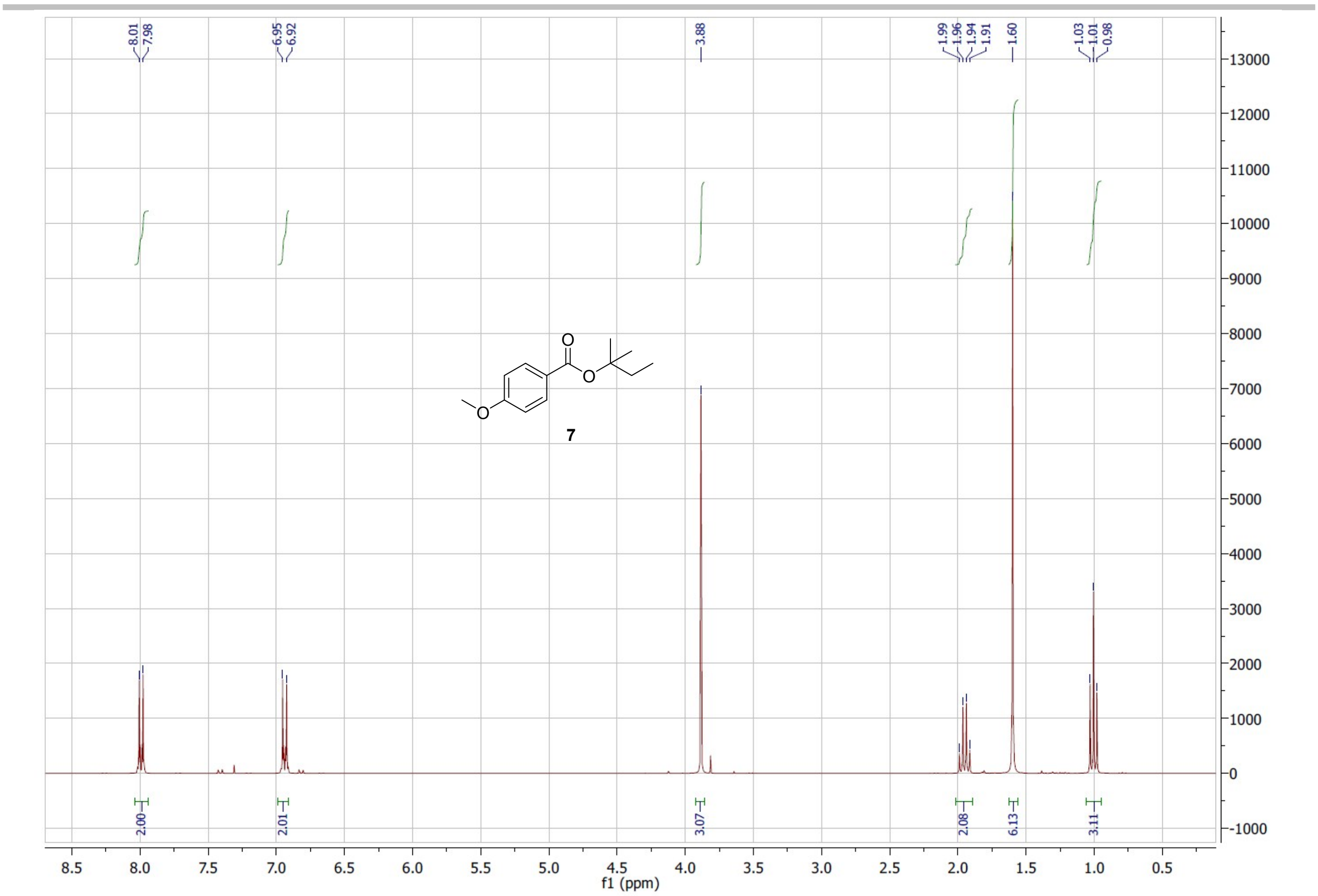


¹³C{¹H} NMR (75 MHz, CDCl₃, ppm)



¹H NMR (300MHz, CDCl₃, ppm)



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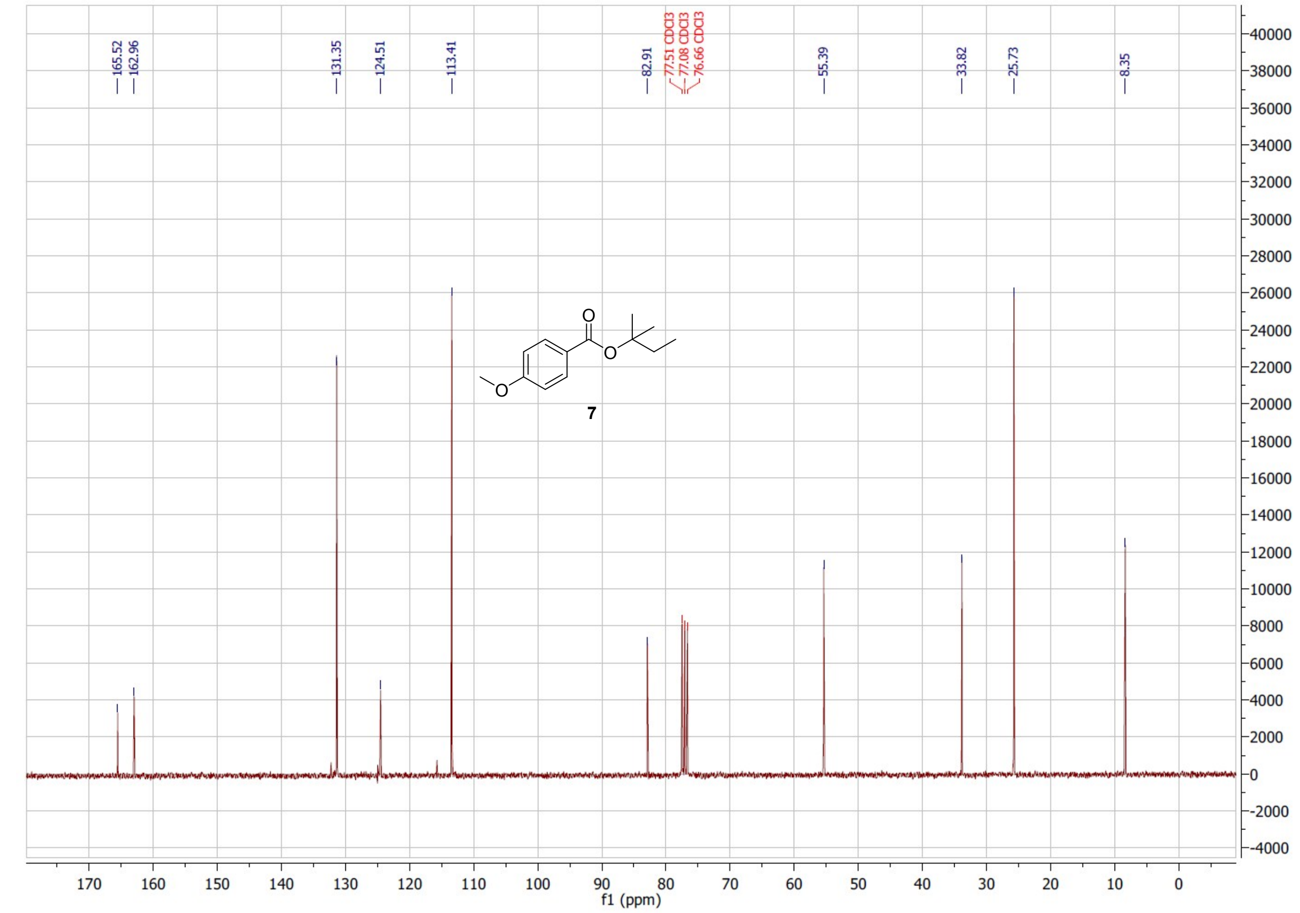

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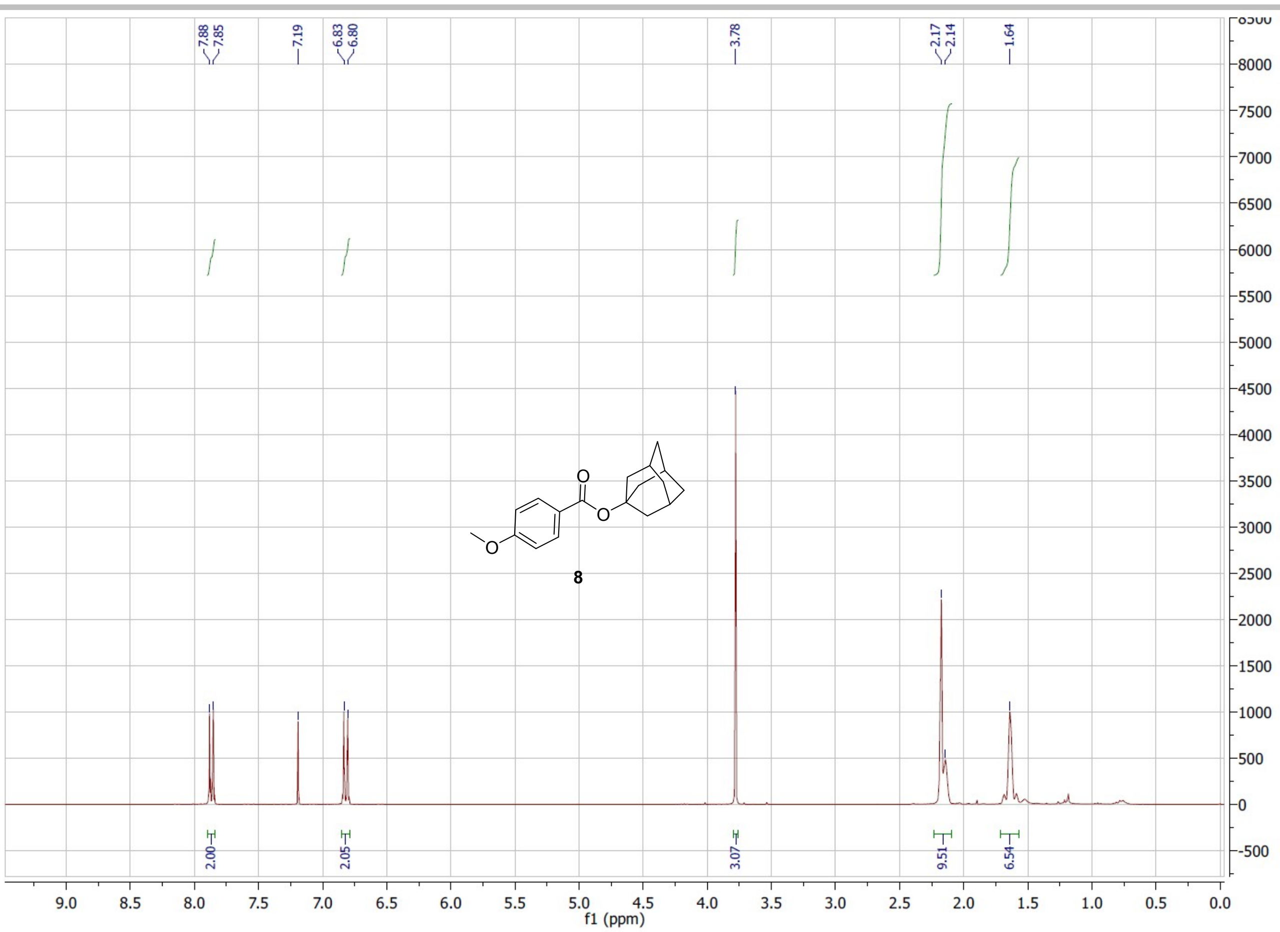

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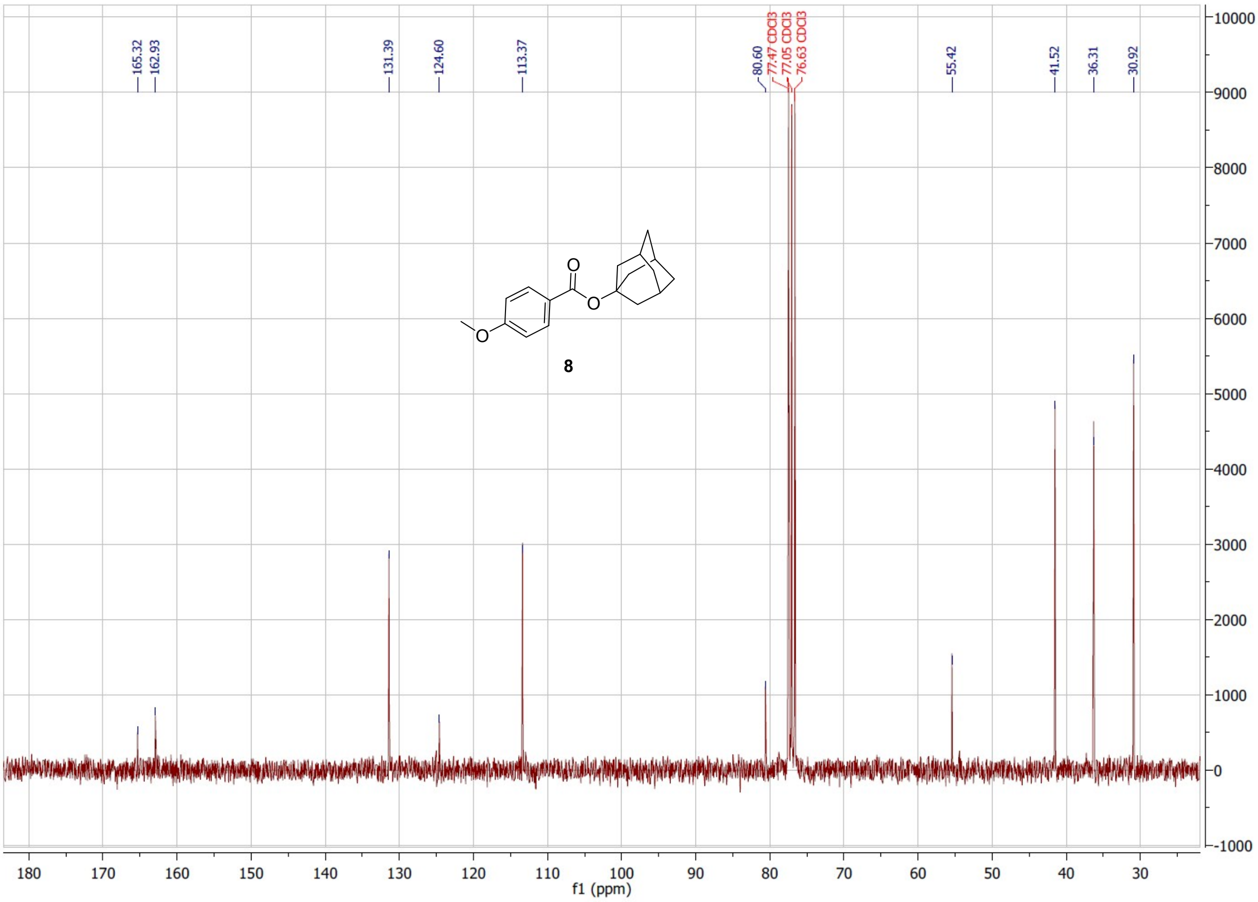

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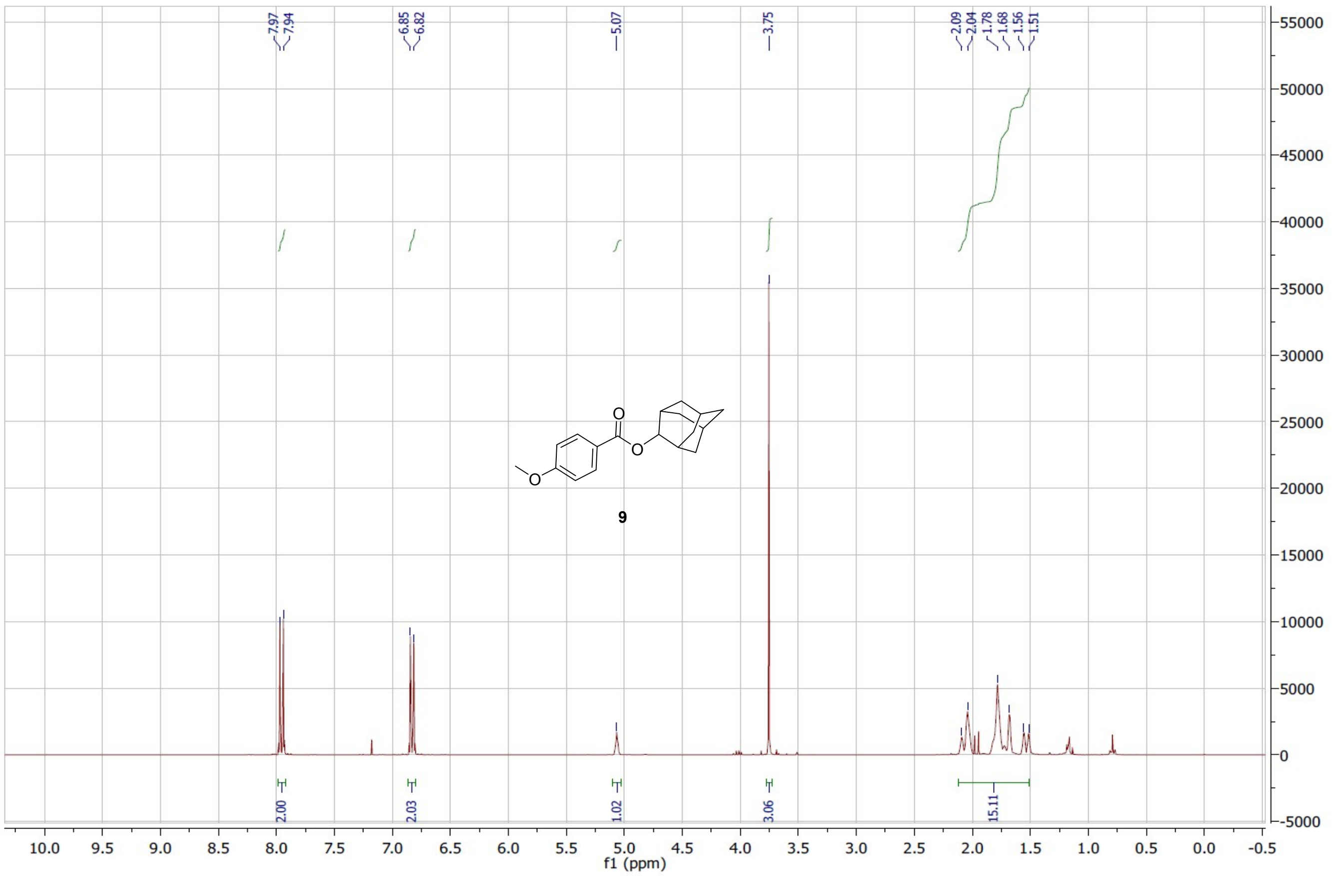

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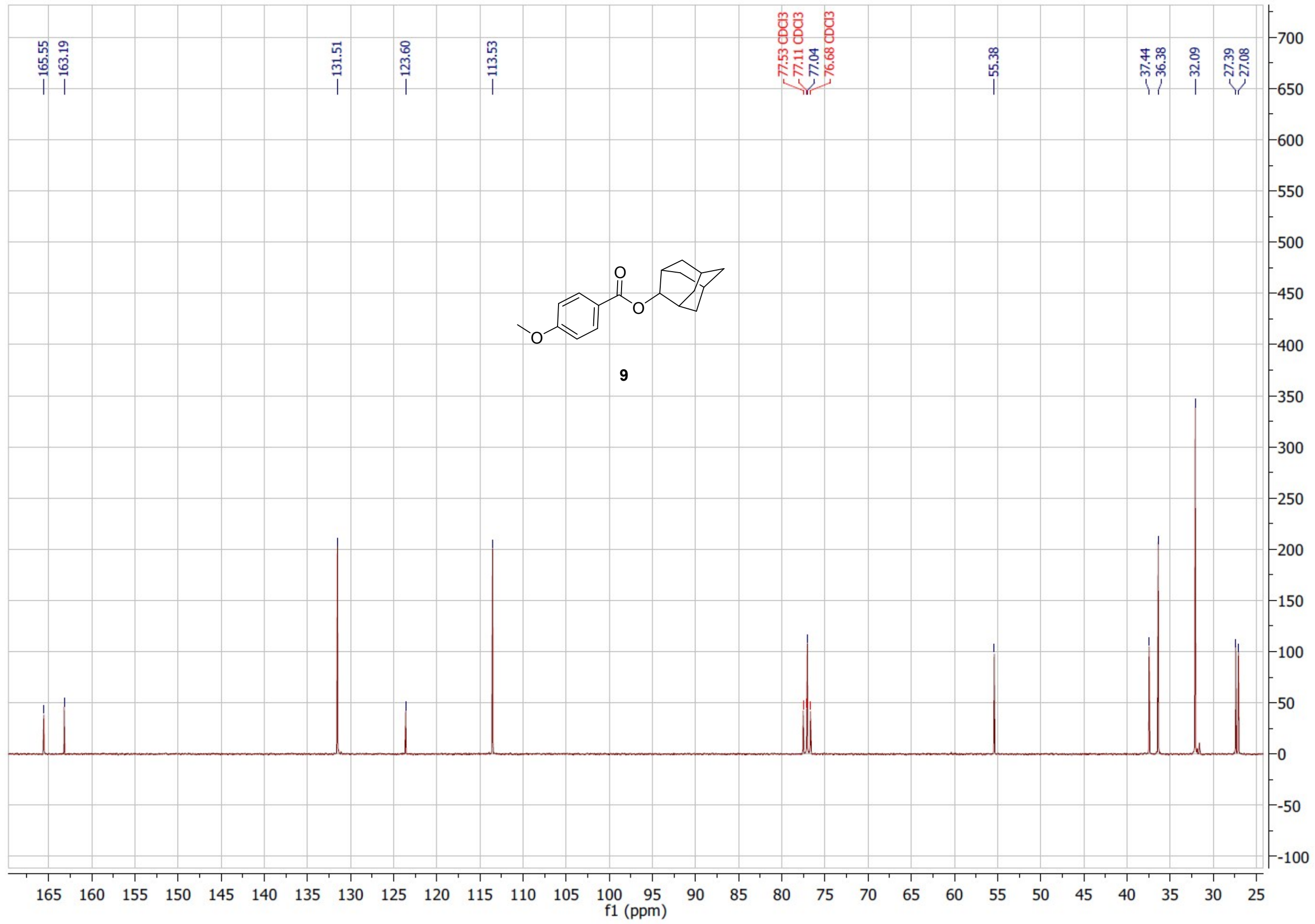

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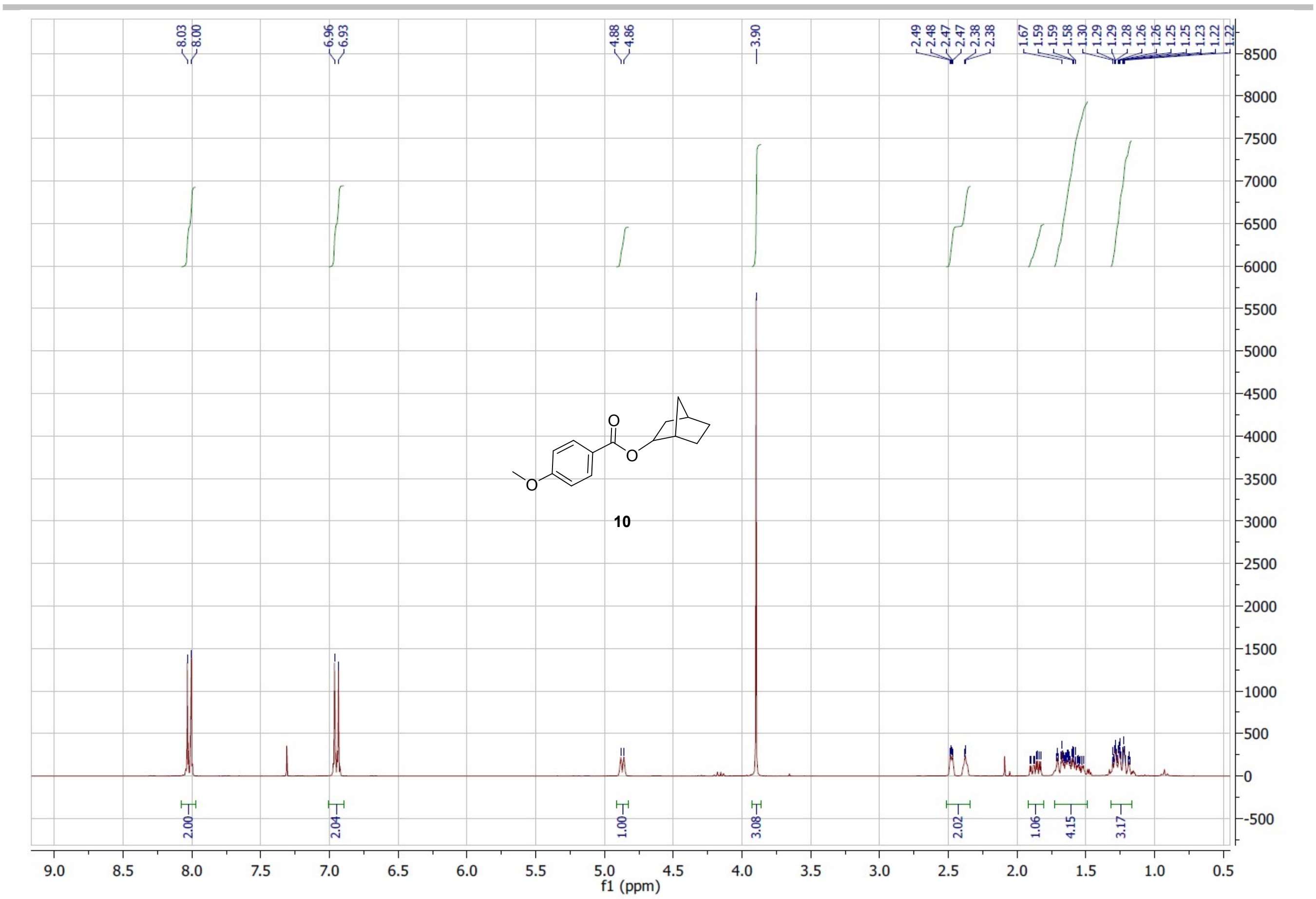
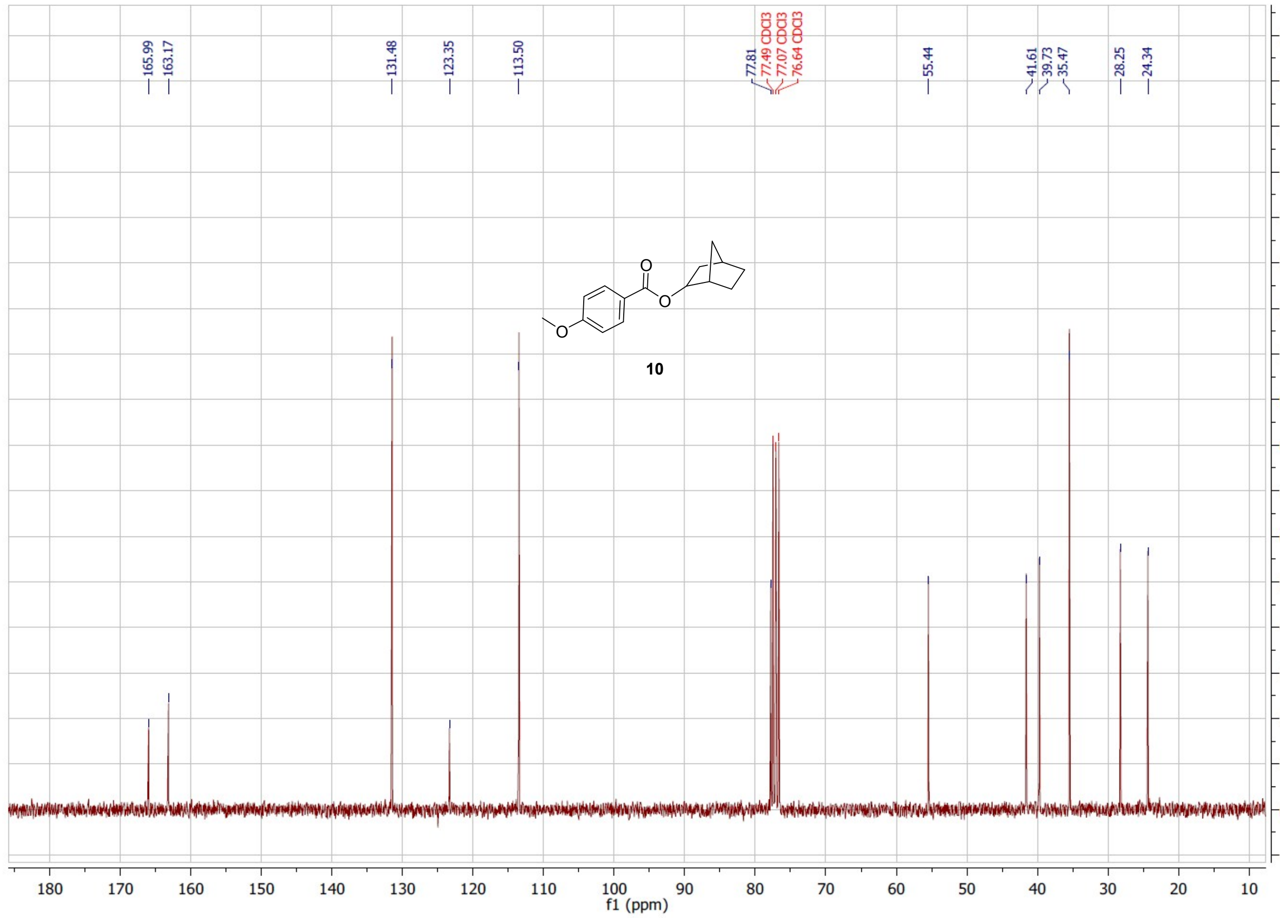


^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm)



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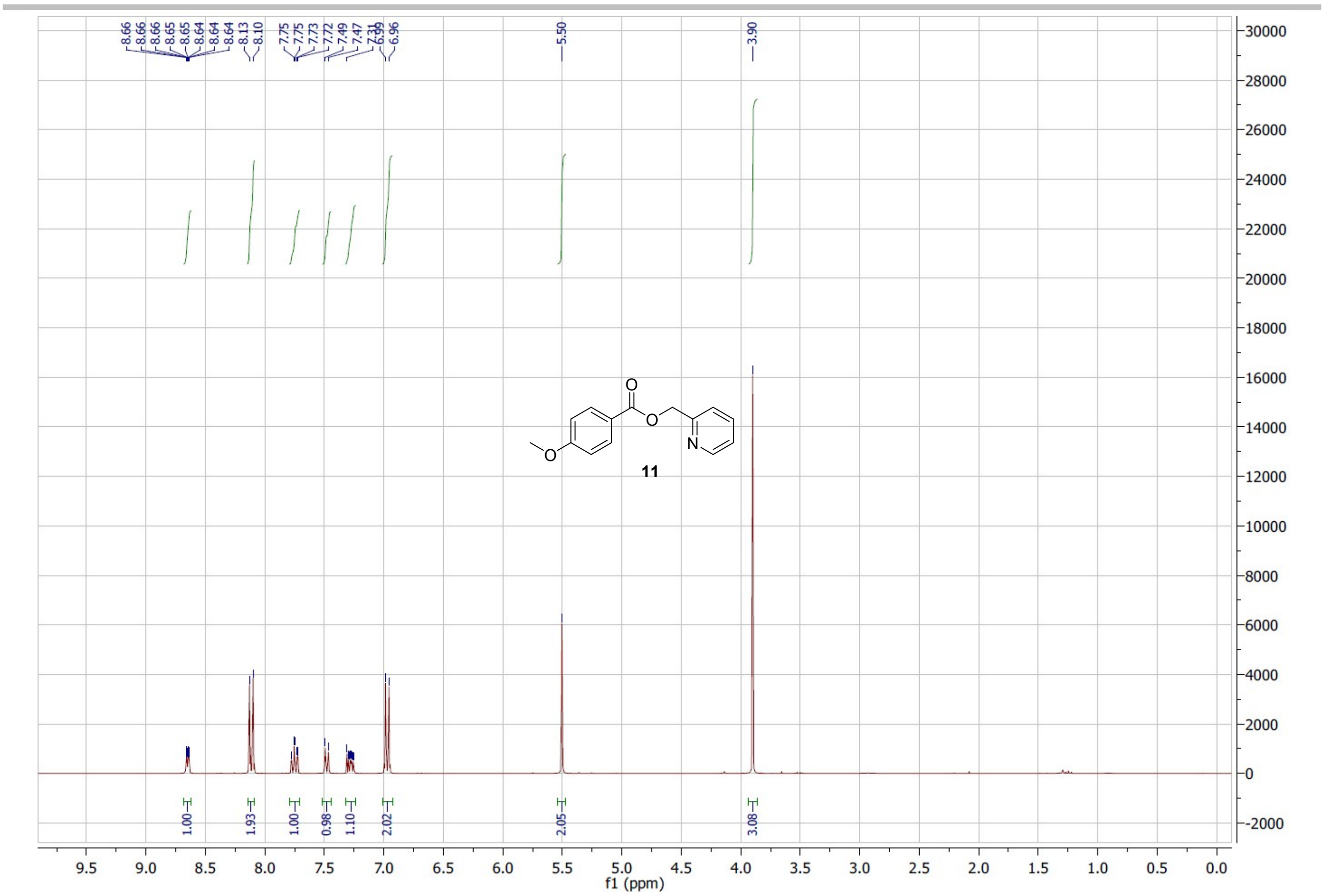

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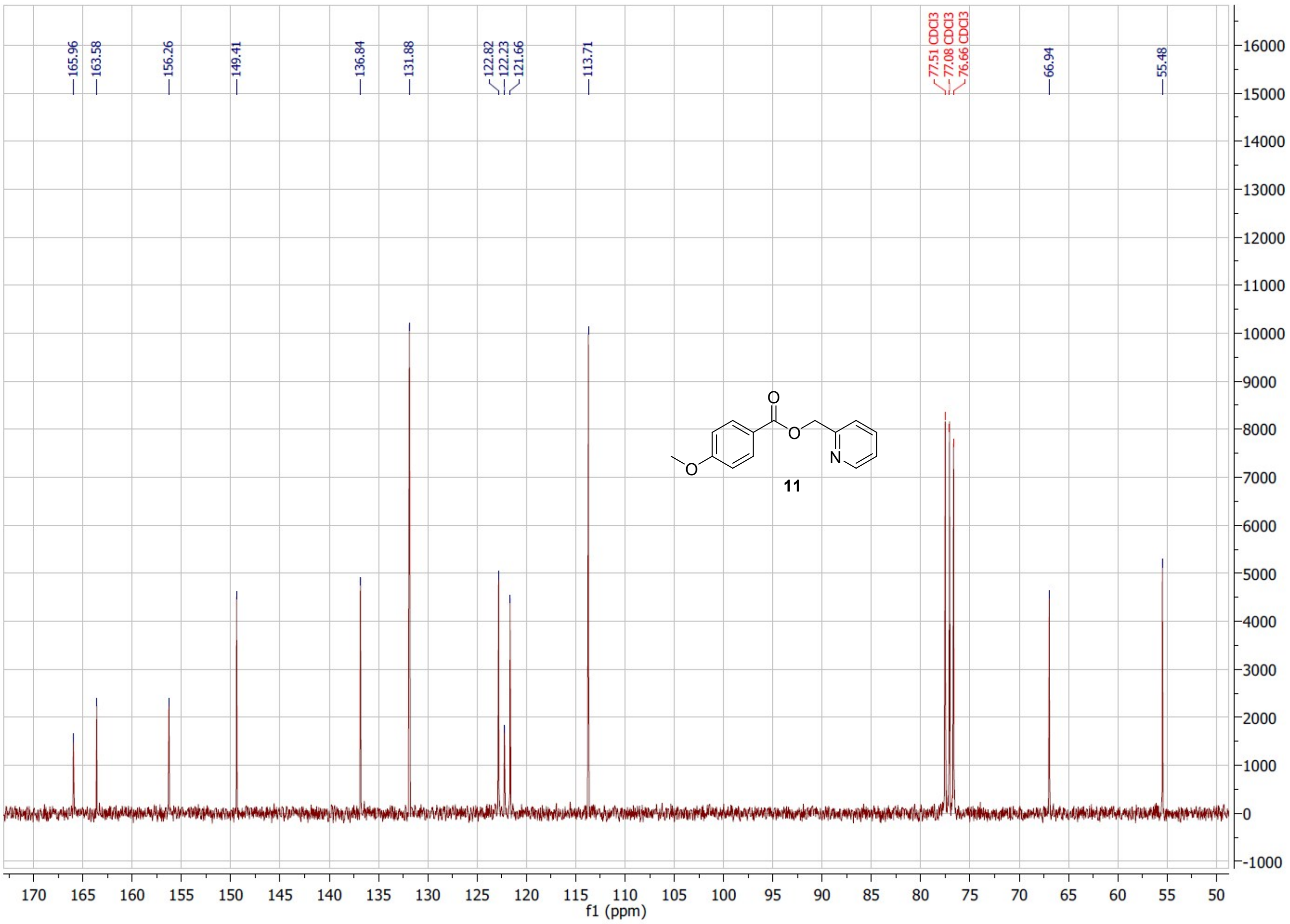
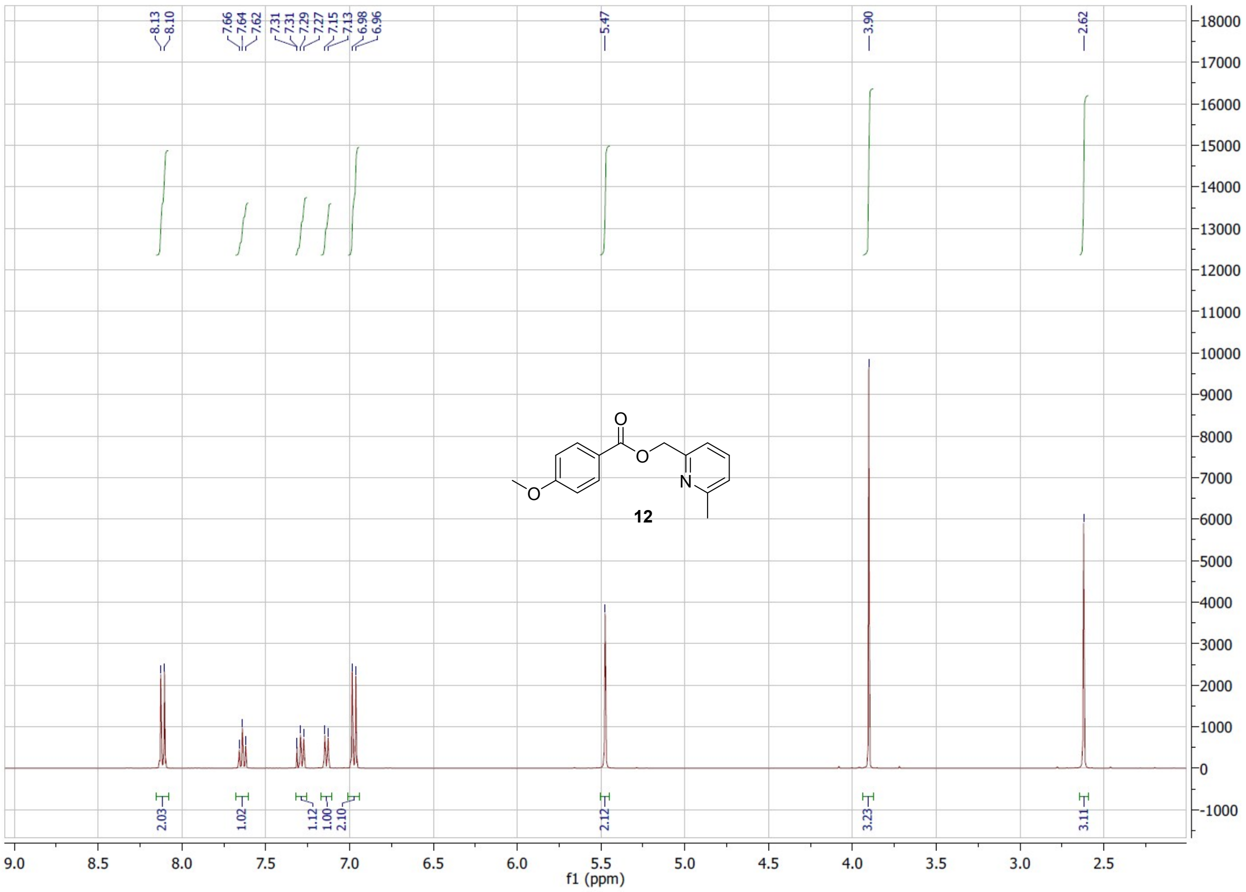
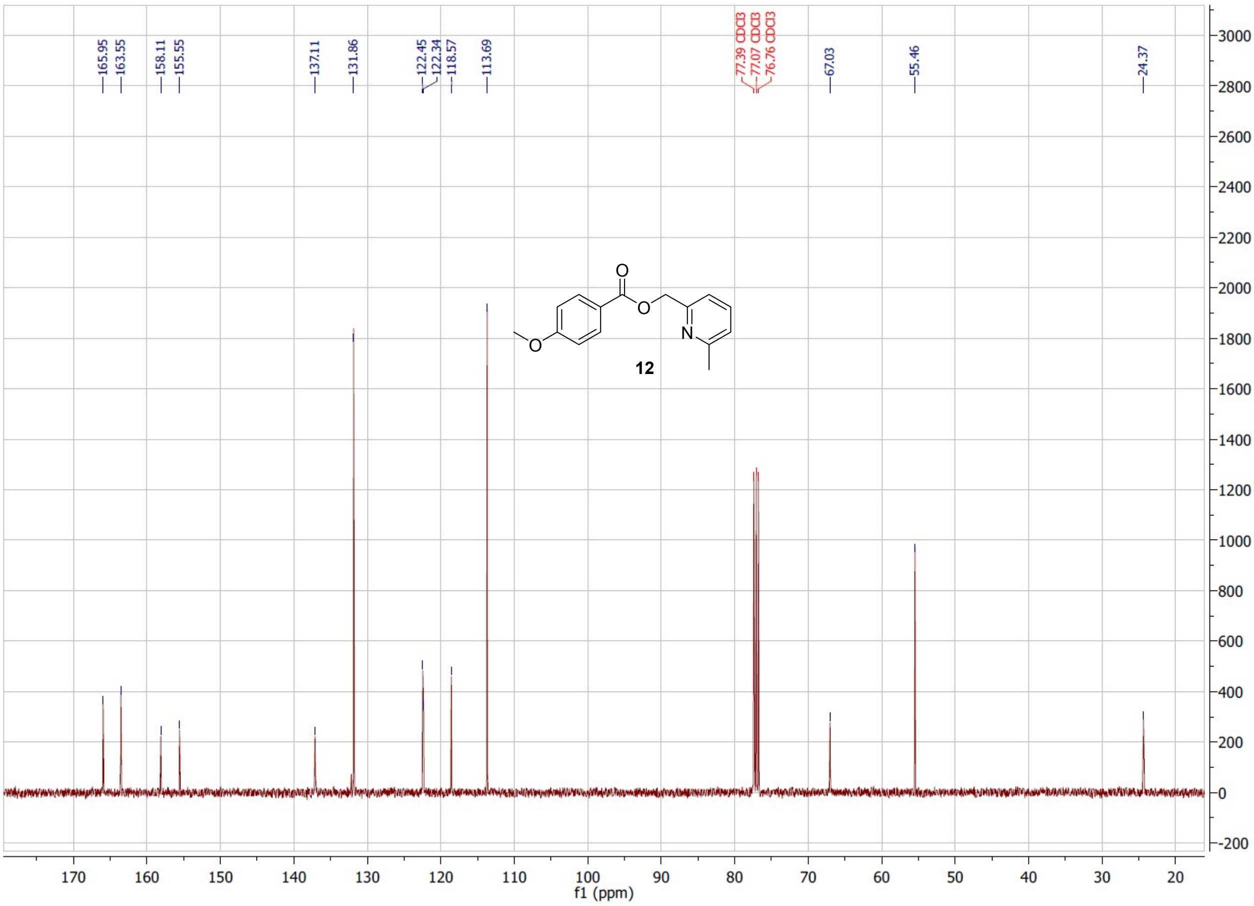


¹H NMR (300MHz, CDCl$_3$, ppm)



^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, ppm)



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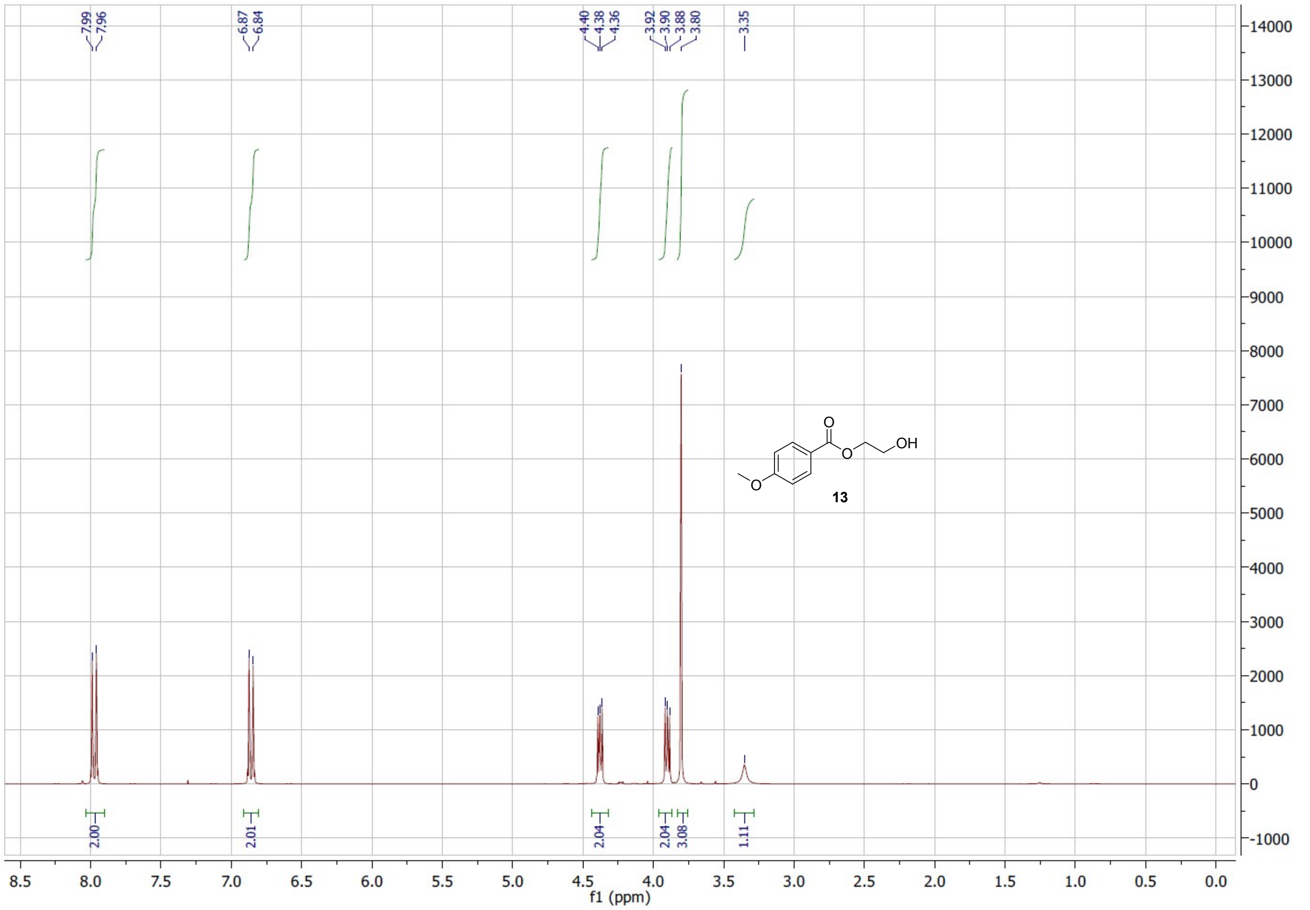

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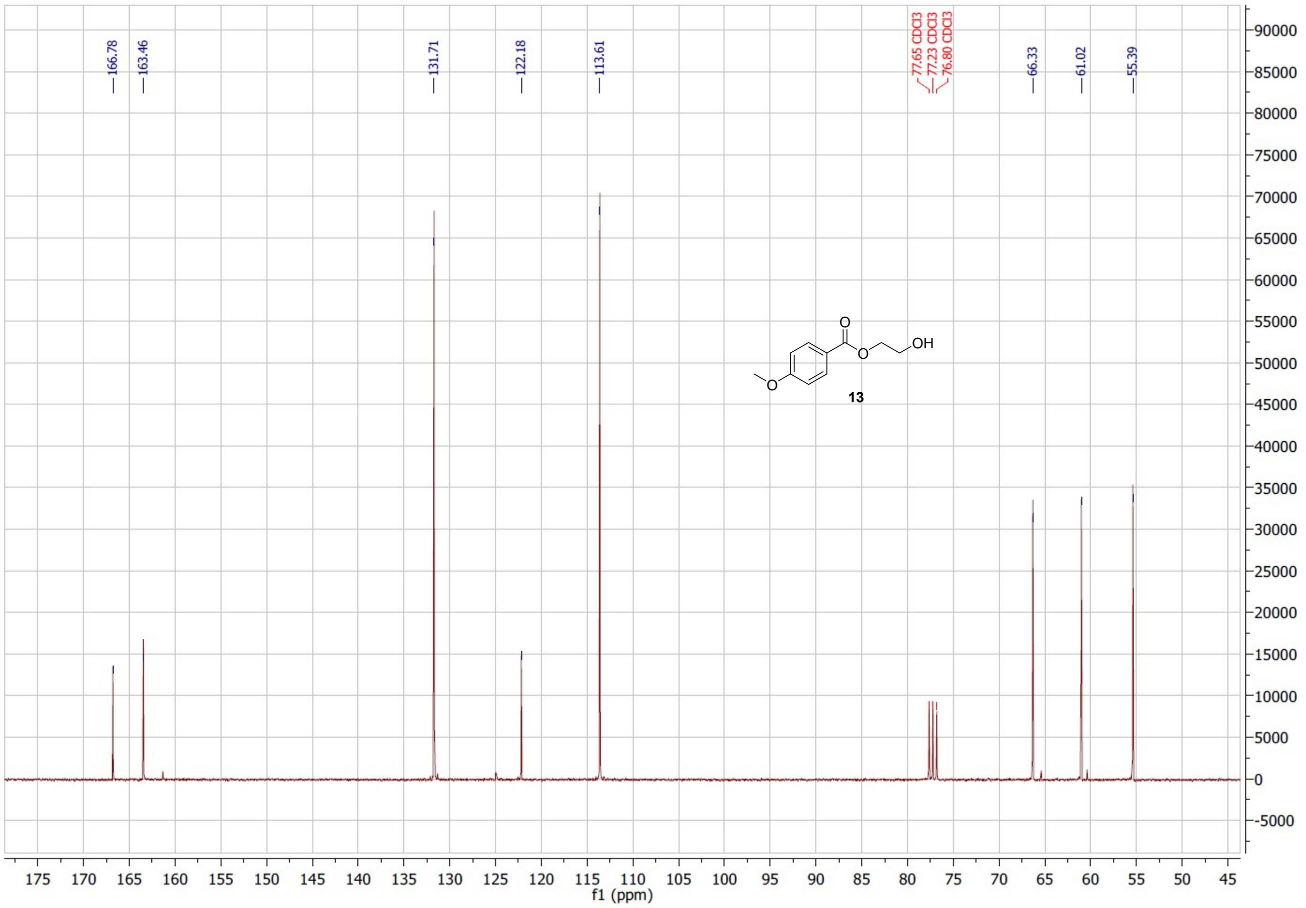

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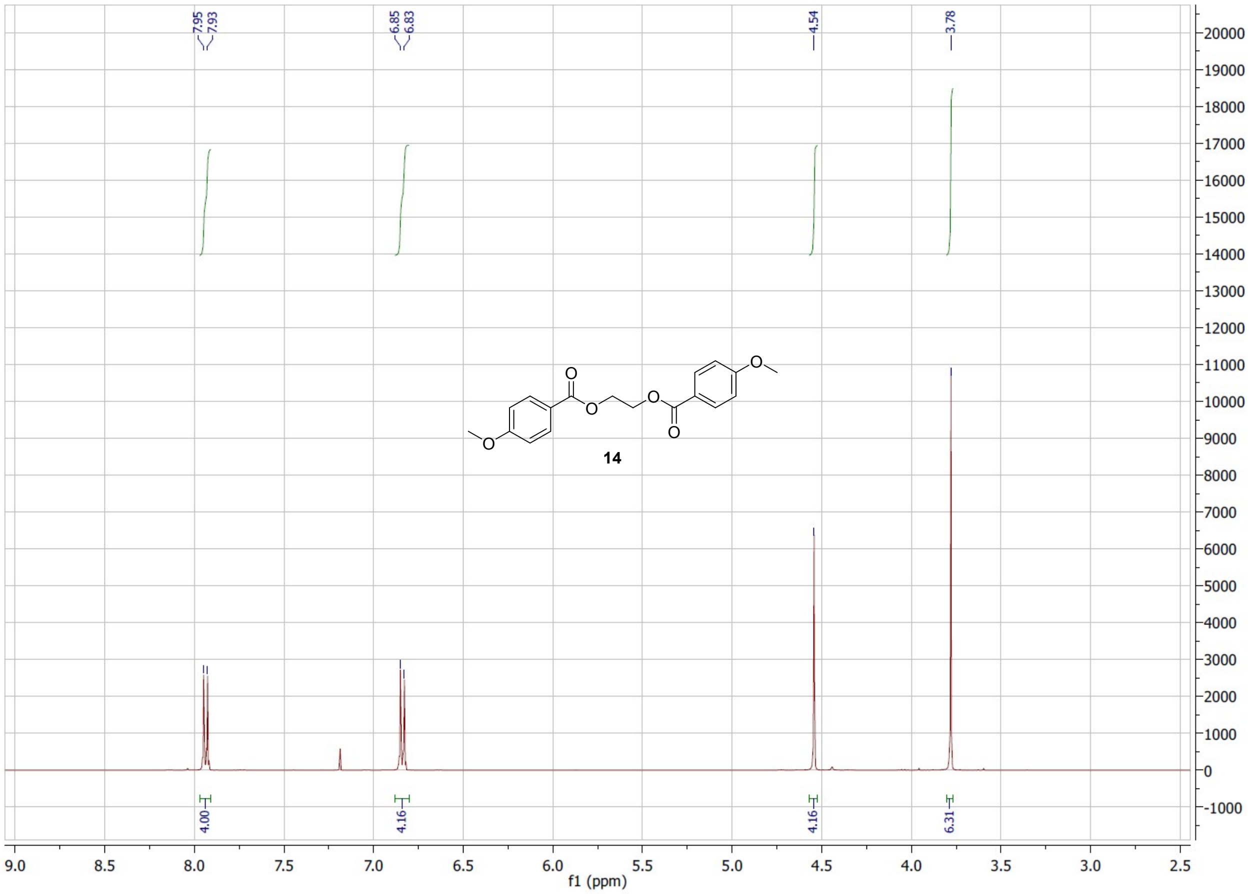

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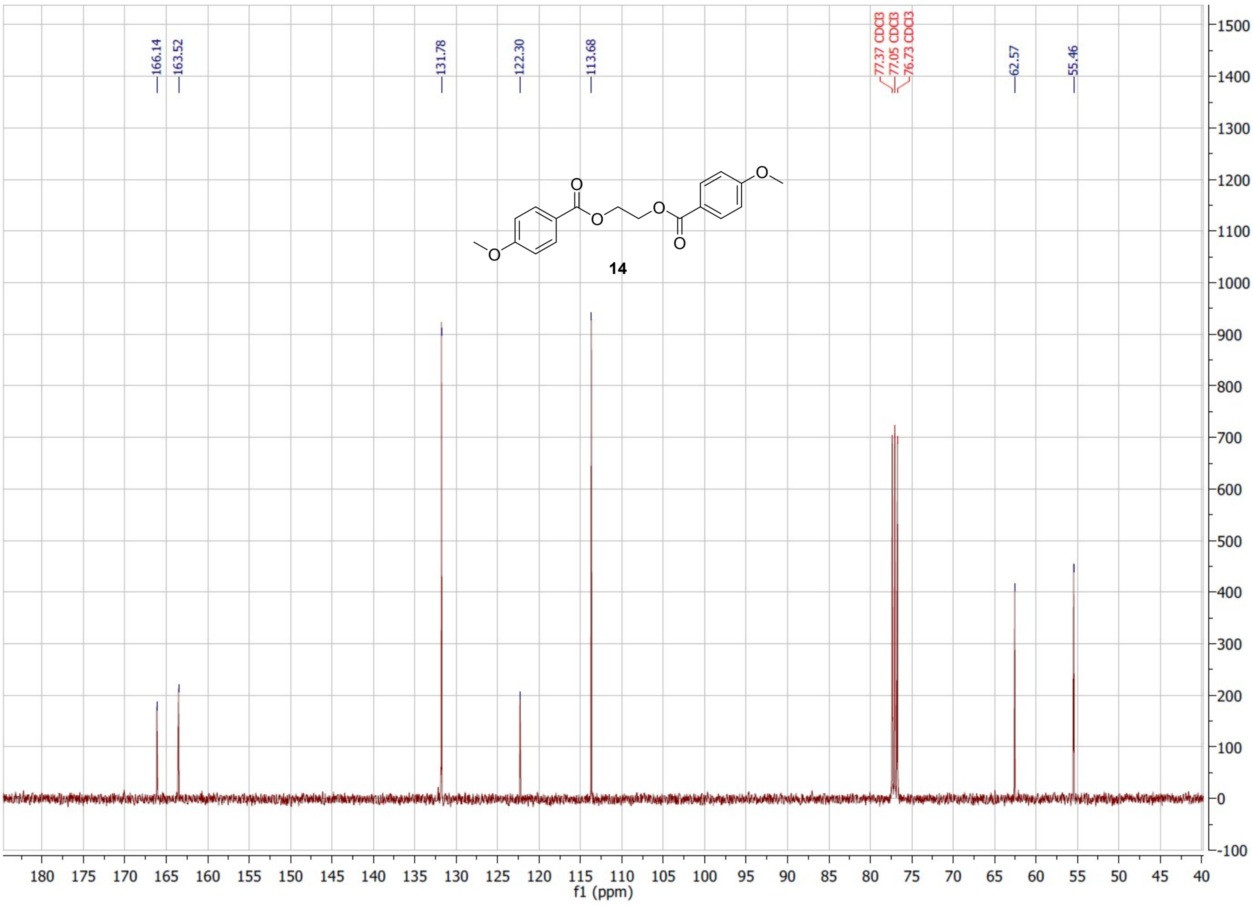
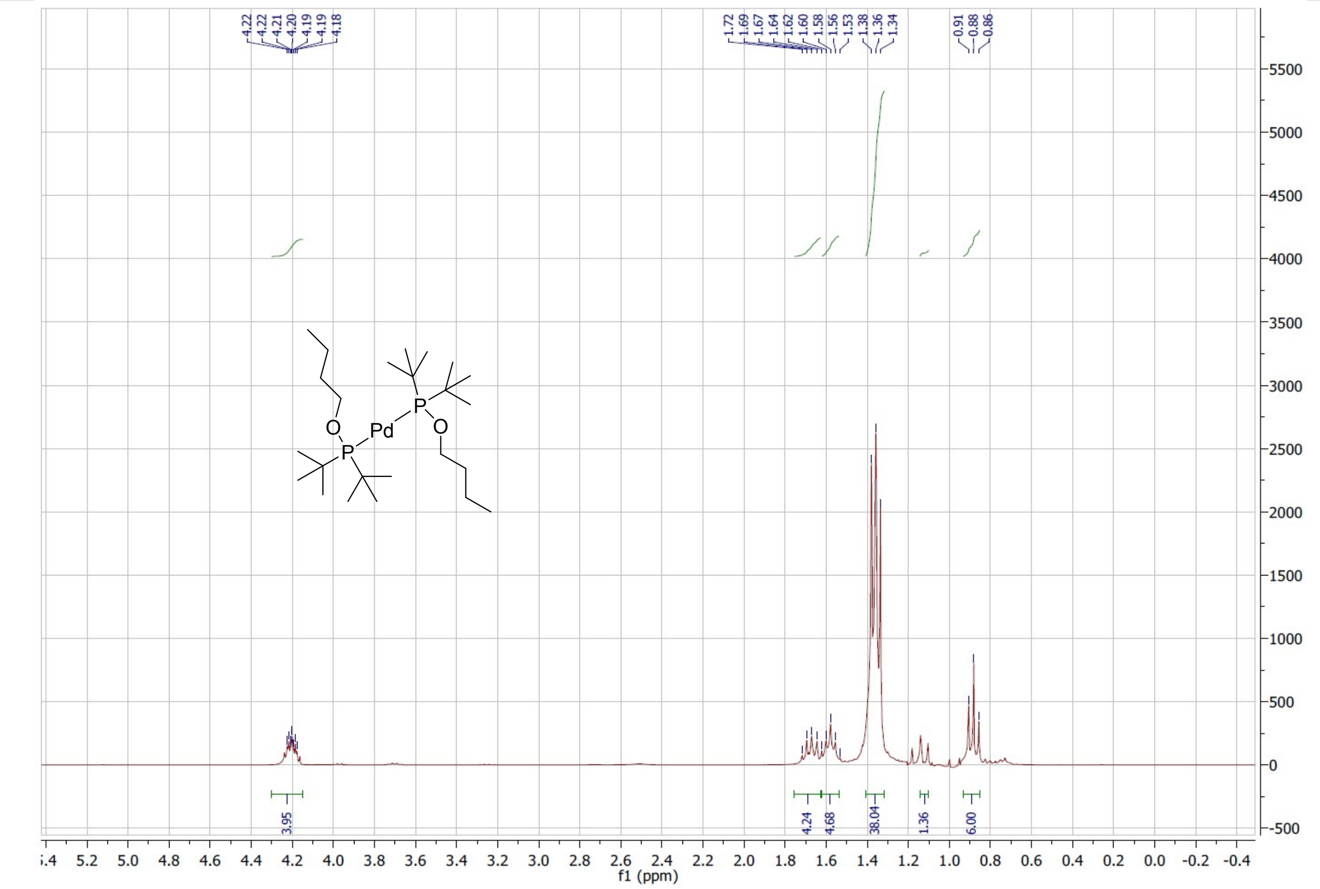
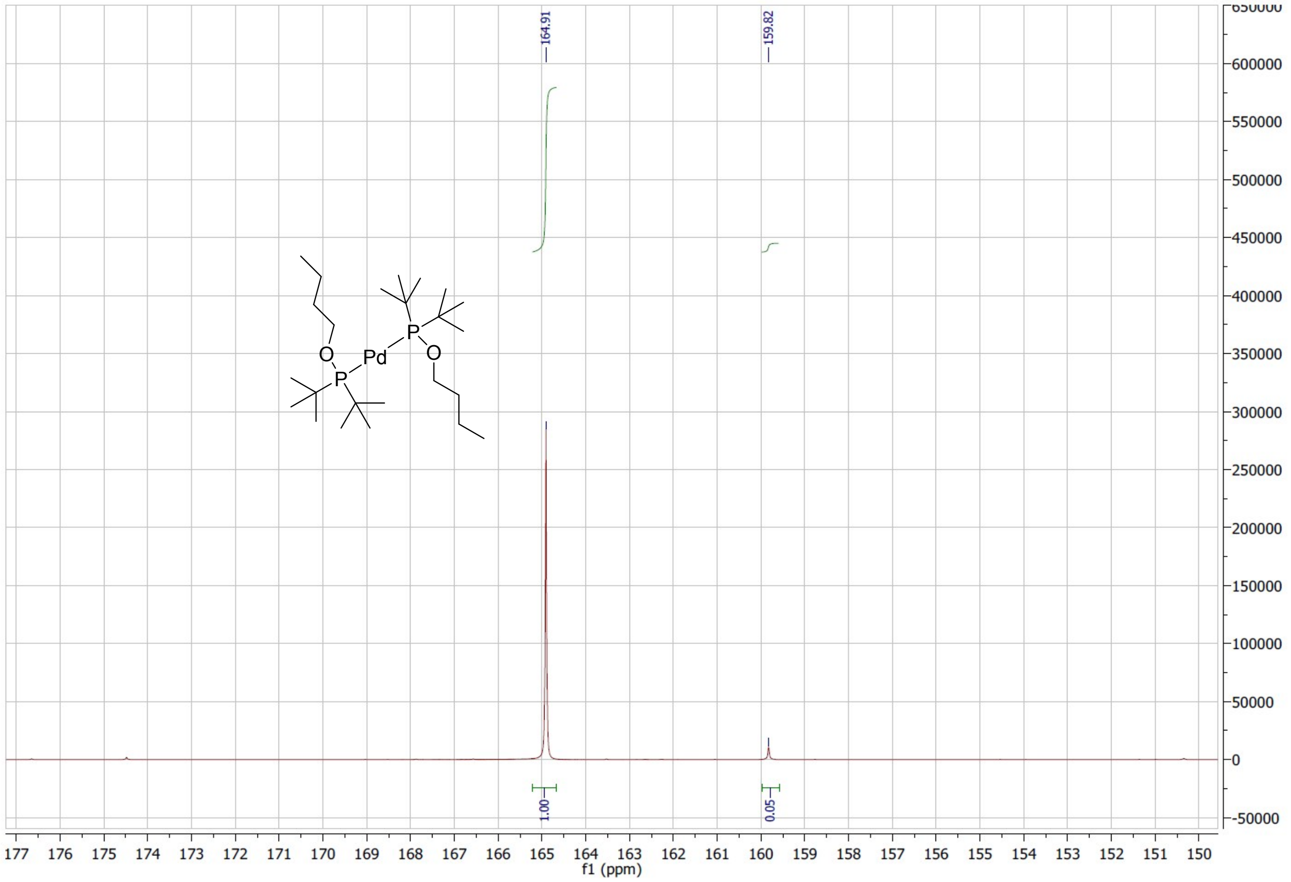


^1H NMR (300MHz, C_6D_6, ppm)

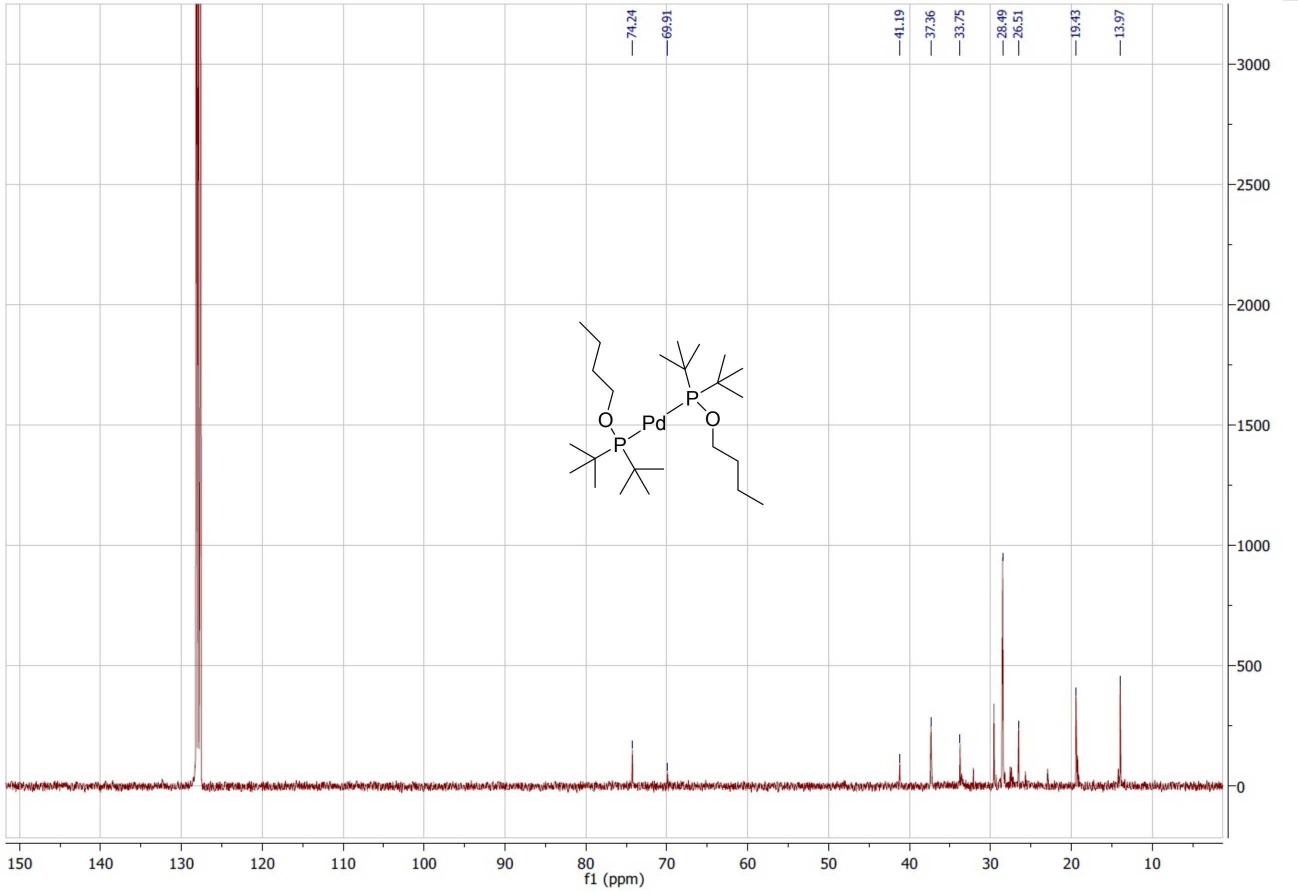


$^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, ppm)

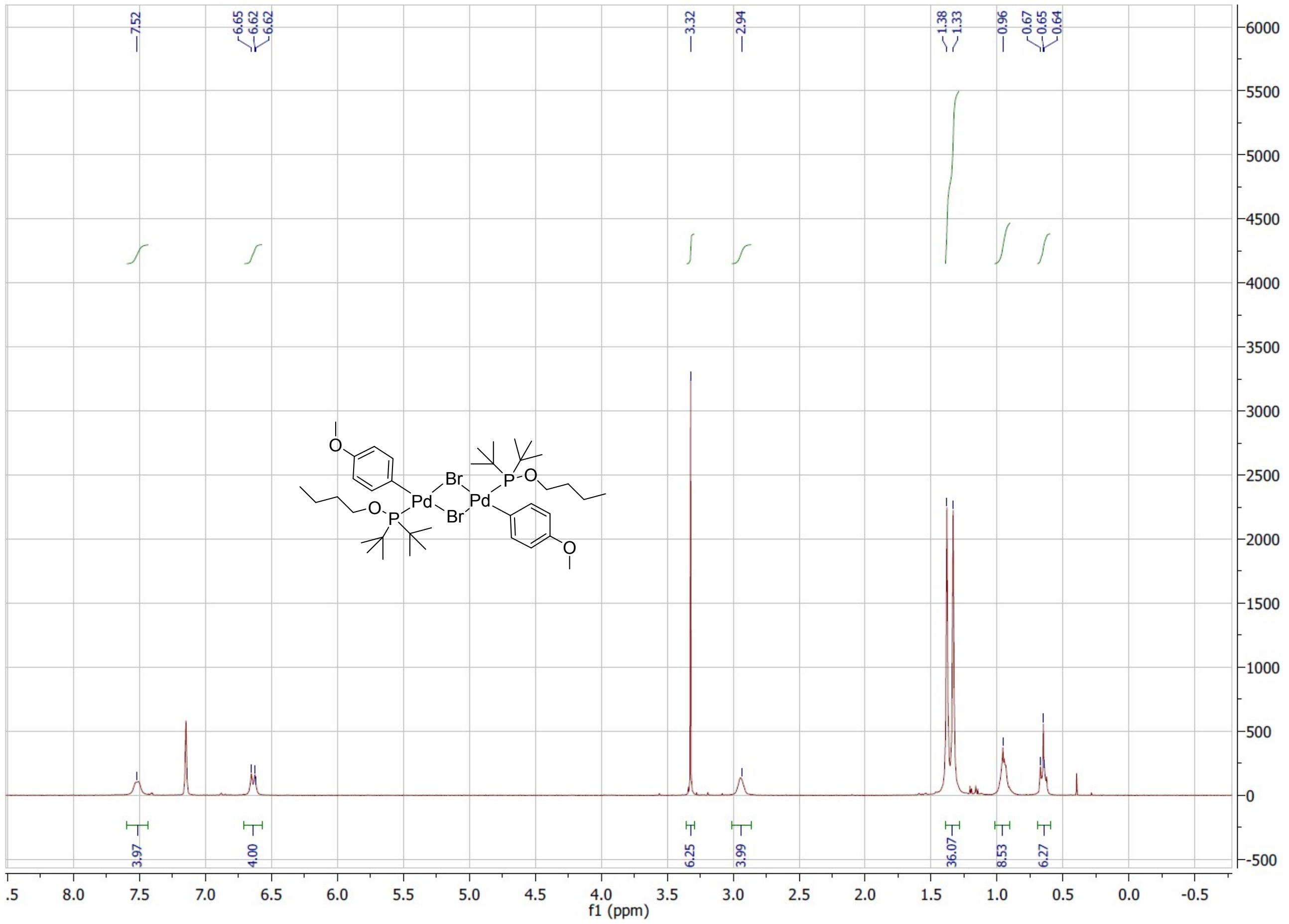


Note: Pd(**L2**)$_2$ would dissociate a **L2** ligand in solution in some extent. Singlet at -159.8 ppm was identified as the dissociated **L2**.

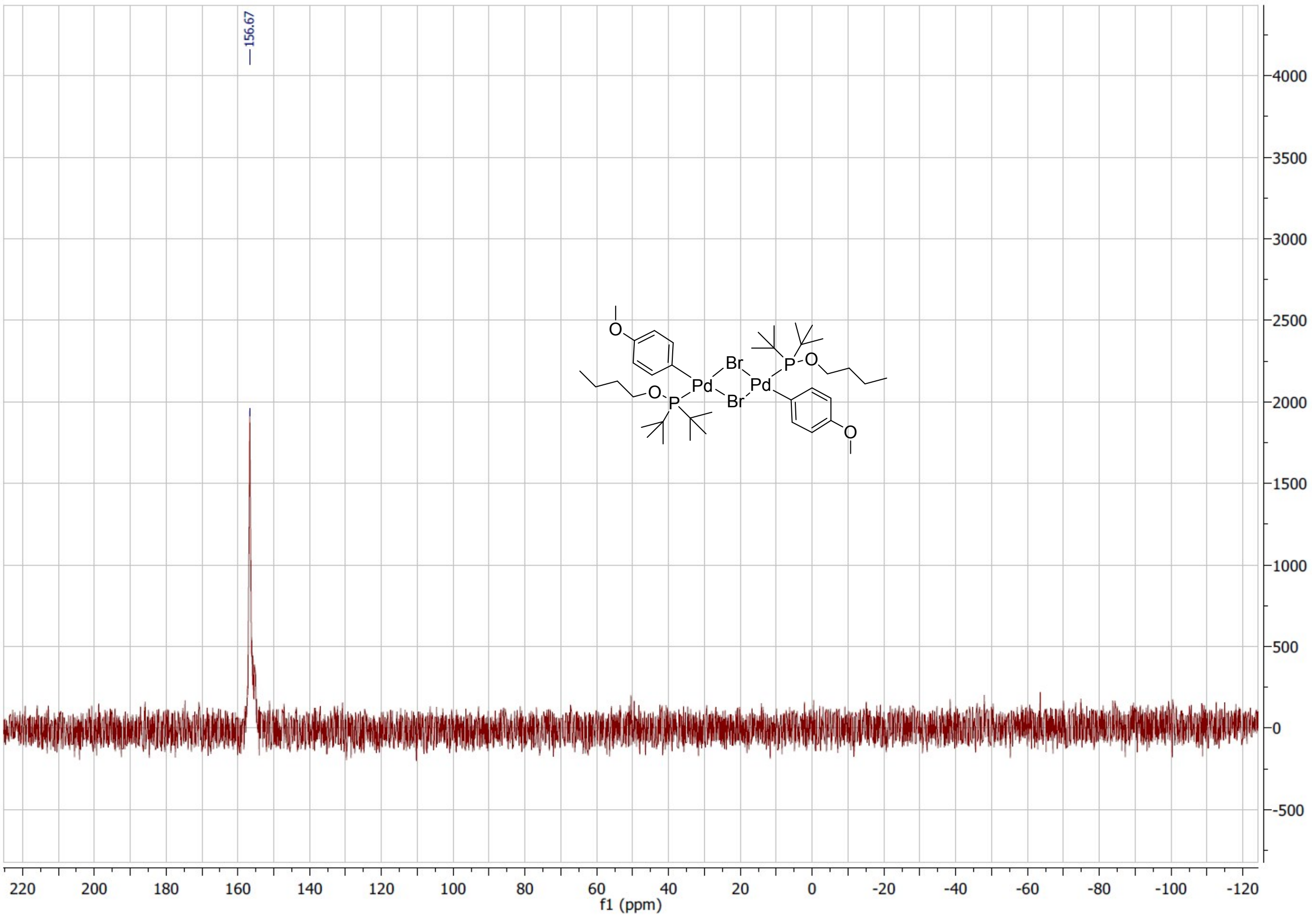
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm)



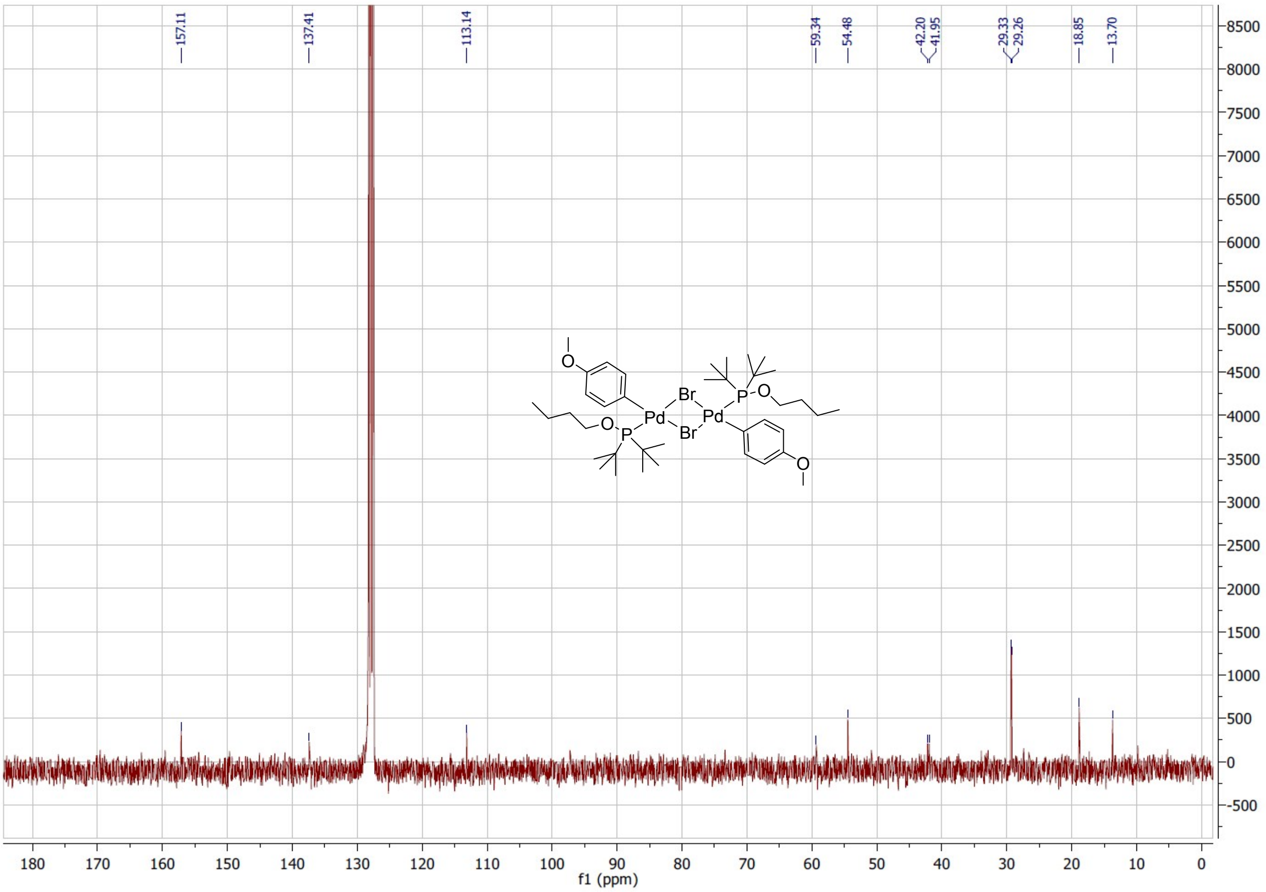
^{1}H NMR (300MHz, C_6D_6, ppm)



$^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, ppm)



$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm)



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