Heck Reaction of Electronically Diverse Tertiary Alkyl Halides

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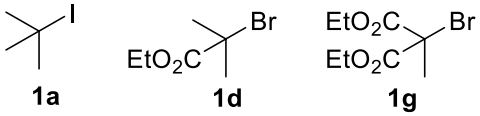
1. General Information

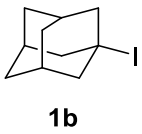
NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) or DPX-400 (400 MHz) instrument. ^{1}H signals are referenced to residual $CHCl_3$ at 7.26 ppm. ^{13}C signals are referenced to $CDCl_3$ at 77.16 ppm. GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle Silica-P flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. Anhydrous solvents purchased from Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system and/or stored over calcium hydride. Benzene was degassed by freeze-pump-thaw method prior to use. All starting materials were purchased from Strem Chemicals, Aldrich, Gelest Inc., TCI America, or Alfa Aesar, or synthesized via known literature procedures. The 34 W Blue LED lamp (Kessil KSH150B LED Grow Light) and Vornado 133 Small Air Circulator fan were purchased from amazon.com. All manipulations with transition metal catalysts were conducted in oven-dried glassware under inert atmosphere using a combination of glovebox and standard Schlenk techniques.

2. Synthesis of starting materials

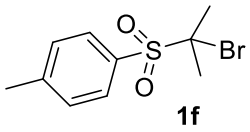
Synthesis of Alkyl halides (1):

The following alkyl halides were purchased from commercial sources.

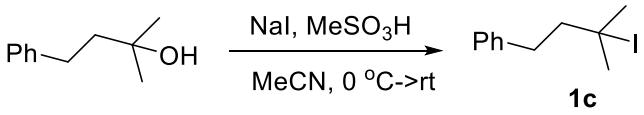




Compound **1b** was prepared according to a literature procedure[1].

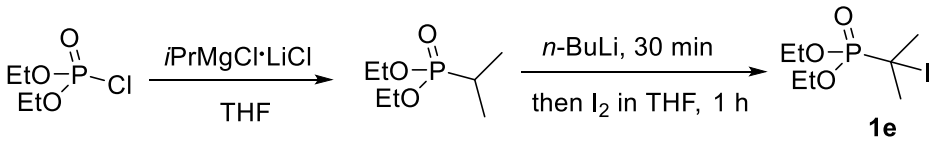


Compound **1f** was prepared according to a literature procedure[2-3].



Compound **1c** was prepared according to a slightly modified literature procedure:[4]

$MeSO_3H$ (650 µL, 10 mmol, 2.0 equiv) was added dropwise to a solution of NaI (1.5 g, 10 mmol, 2.0 equiv) and 2-methyl-4-phenylbutan-2-ol (850 µL, 5 mmol, 1 equiv) in MeCN (20 mL, 0.2 M) at 0 °C. The reaction mixture was allowed to warm to rt, and then stirred for an additional 30 min. Next, the reaction mixture was diluted with hexane and passed through a pad of silica gel. After it was concentrated on a rotary evaporator, the residue was purified by flash chromatography in hexanes. Yield: 1.1 g (82%). Spectroscopic data for **1f** were in accordance with the literature data.[4]

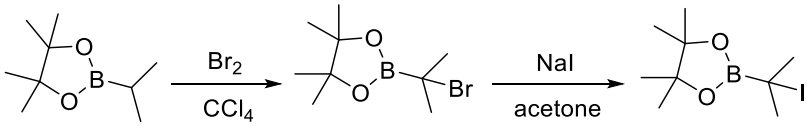


Compound **1e** was prepared according to the following procedure:

To diethyl chlorophosphate (2.89 mL, 20 mmol, 1 equiv) dissolved in THF (40 mL, 0.5 M) was added 1.3 M THF solution of *i*PrMgCl·LiCl (20 mL, 26 mmol, 1.3 equiv) over 30 min at −78 °C under inert atmosphere. The reaction was allowed to warm up to rt overnight. Then it was quenched

with saturated NH_4Cl solution (15 mL) and extracted with Et_2O (3×30 mL). The resulting organic layer was washed with brine (2×10 mL), dried with $MgSO_4$ and concentrated *in vacuo*. The product was used in the next step without further purification. Yield: 2.8 g (78%).

To diethyl isopropylphosphate (721 mg, 4 mmol, 1 equiv) dissolved in THF (40 mL, 0.1 M) was added dropwise 2.5 M hexane solution of *n*-BuLi (3.2 mL, 8 mmol, 2 equiv) at −78 °C under inert atmosphere. The reaction was stirred at this temperature for 30 min. Next, solution of I_2 (2.03 g, 8 mmol, 2 equiv) in THF (10 mL) was added in portions. The resulting reaction mixture was warmed up to r.t. and after 1 h, quenched with saturated NH_4Cl solution (10 mL). Subsequent extraction with Et_2O (3×30 mL) and concentration *in vacuo* led to the crude iodide **1e** that was purified by column chromatography (Hex:Acetone: 5:1 to 1:1). R_f (Hex:Acetone: 1:1) = 0.73. Yield: 0.6 g (50%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 – 4.19 (m, 4H), 2.09 (d, *J* = 15.5 Hz, 6H), 1.35 (td, *J* = 7.1, 0.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 63.94 (d, *J* = 7.2 Hz), 32.29 (s), 16.42 (d, *J* = 5.6 Hz). HRMS (ESI+) calcd. for $C_7H_{17}IO_3P$ [M+H]: 306.9960, found: 306.9948.



1h

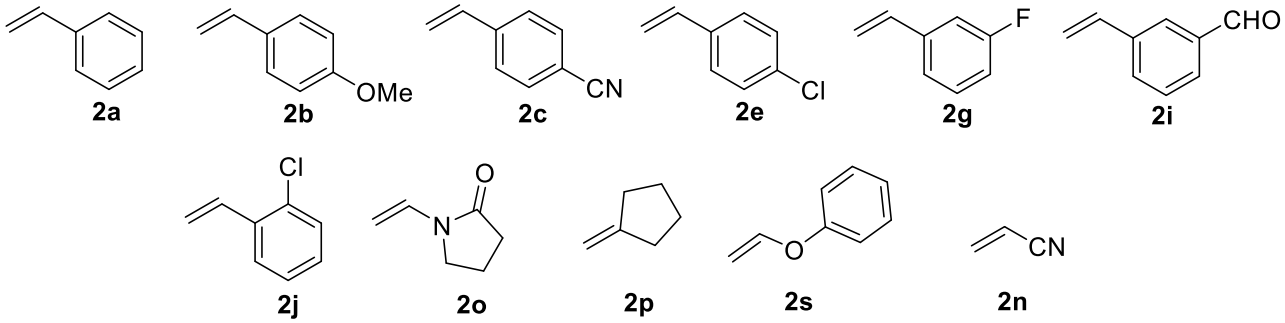
Compound **1h** was prepared according to the following procedure:

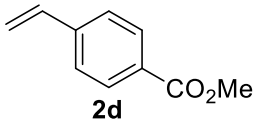
To a solution of 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.1 mL, 11 mmol, 1.1 equiv) in CH_2Cl_2 (30 mL) was added Br_2 (515 μL, 10 mmol, 1 equiv) under inert atmosphere. The reaction was stirred at room temperature for 3 h. The reaction mixture was concentrated *in vacuo* to provide the corresponding brominated substrate that was used for the next step without any purification. Yield: 2.4 g (96%)

To a solution of NaI (2.8 g, 19 mmol, 2 equiv) in acetone (20 mL) under inert atmosphere was added the alkyl bromide (2.4 g, 9.5 mmol, 1 equiv) dissolved in acetone (5 mL). After 2 h, the resulting reaction mixture was quenched with saturated $Na_2S_2O_3$ solution (10 mL) and washed with water (10 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to afford alkyl halide **1h**. Yield: 2.4 g (85%). R_f (Hex:Acetone=10:1): 0.67. Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.94 (s, 6H), 1.28 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 83.98, 32.73, 24.24. HRMS (ESI+) calcd. for $C_9H_{19}BIO_2$ [M+H]: 297.05232, found: 297.05184.

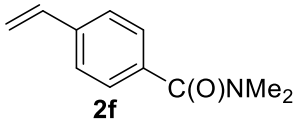
Synthesis of Alkenes (2):

The following alkenes were purchased from commercial sources.

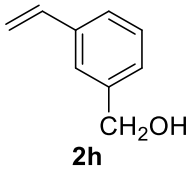




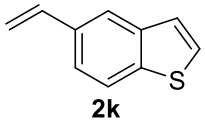
Compound **2d** was prepared according to a literature procedure.[5]



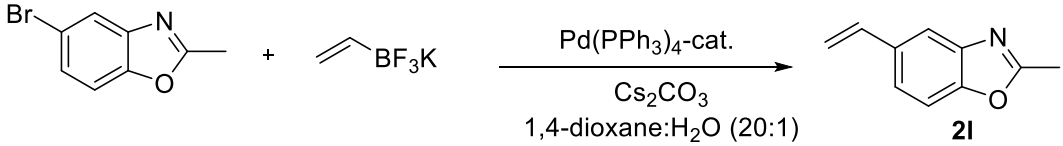
Compound **2f** was prepared according to a literature procedure.[6]



Compound **2k** was prepared according to a literature procedure.[7]

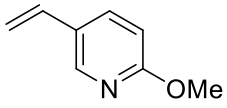


Compound **2l** was prepared according to a literature procedure.[8]



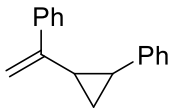
Compound **2l** was prepared according to the following procedure:
To a suspension of 5-bromo-2-methylbenzoxazole (1 g, 4.7 mmol, 1 equiv) in 1,4-dioxane (20 mL) and water (1 mL) was added potassium vinyltrifluoroborate (764 mg, 5.7 mmol, 1.2 equiv),

Cs_2CO_3 (3.08 g, 9.4 mmol, 2 equiv) and tetrakis(triphenylphosphorus) palladium(0) (273 mg, 0.24 mmol, 0.05 equiv). The mixture was stirred at reflux under nitrogen for 5 h. The mixture was then poured onto ice-water (20 mL) and extracted with EtOAc (3×30 mL). The organic phases were combined, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo, the residue was purified by chromatography on silica gel (Hex:EA=20:1>10:1) to afford **2l** as yellow oil. Yield: 0.59 g (79%). All analytical data were in accordance with the literature.[9]



2m

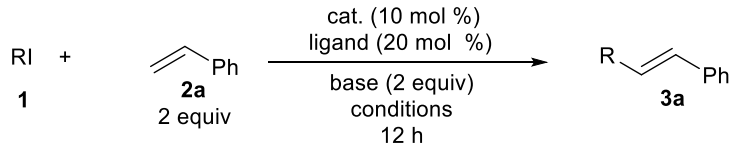
Compound **2m** was prepared according to a literature procedure.[5]

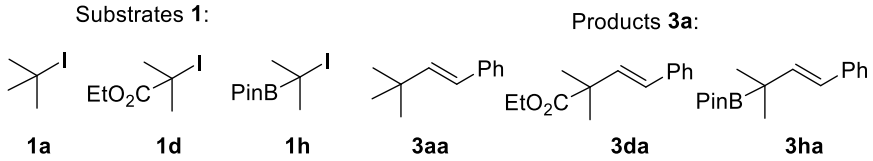


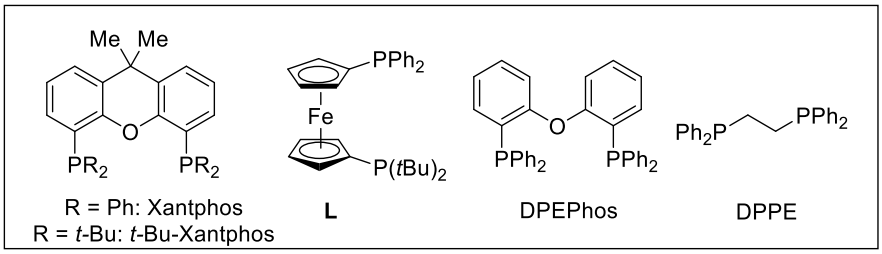
2t

Compound **2t** was prepared according to a literature procedure.[10]

3. Optimization Table







#	Substrate **1**	Catalyst	Ligand	Base	Conditions	Product **3a**	Yield,[b] %
1	**1a**	$Pd(PPh_3)_4$	-	Cs_2CO_3	[0.1] $PhCH_3$, 50 °C	**3aa**	Dec.
2	**1a**	$Pd(dppf)Cl_2$	-	Cy_2NMe	[0.1] $PhCF_3$, 110 °C	**3aa**	Dec.
3	**1a**	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	[0.5] PhH, BLED	**3aa**	87
4[c]	**1a**	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	[0.5] PhH, BLED	**3aa**	92[d]
5[e]	**1a**	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	[0.5] PhH, BLED	**3aa**	53
6	**1a**	$Pd(OOCCF_3)_2$	Xantphos	Cs_2CO_3	[0.5] PhH, BLED	**3aa**	81
7[f]	**1a**	$Pd(OAc)_2$ (5 mol %)	Xantphos (10 mol %)	Cs_2CO_3	[0.5] PhH, BLED	**3aa**	82
8	**1a**	$Pd(OAc)_2$ (5 mol %)	Xantphos (10 mol %)	Cs_2CO_3	[0.5] THF, BLED	**3aa**	64
9	**1a**	$Pd(OAc)_2$ (2 mol %)	Xantphos (5 mol %)	Cs_2CO_3	[0.5] PhH, BLED	**3aa**	42
10	**1a**	Pd Xantphos G3	-	iPr_2NEt	[0.5] PhH, BLED	**3aa**	59
11	**1a**	$Pd(PPh_3)_4$	-	Cs_2CO_3	[0.5] PhH, BLED	**3aa**	7
12	**1a**	$Pd(PPh_3)_4$	-	Cs_2CO_3	[0.5] THF, BLED	**3aa**	14
13	**1a**	$Pd(PPh_3)_4$	-	Cs_2CO_3	[0.1] THF, BLED	**3aa**	46
14	**1a**	$Pd(OAc)_2$	DPEPhos	Cs_2CO_3	[0.5] PhH, BLED	**3aa**	7
15	**1a**	$Pd(OAc)_2$	*t*-Bu-Xantphos	Cs_2CO_3	[0.5] PhH, BLED	**3aa**	0
16	**1a**	$Pd(OAc)_2$	**L**	Cs_2CO_3	[0.5] PhH, BLED	**3aa**	7
17	**1a**	$Ni(COD)_2$	DPPE	Cs_2CO_3	[0.5] PhH, BLED	**3aa**	0
18	**1a**	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	[0.5] PhH, 40 °C	**3aa**	traces
19	**1a**	-	Xantphos	Cs_2CO_3	[0.5] PhH, BLED	**3aa**	0
20	**1d**	$Pd(dppf)Cl_2$	-	Cy_2NMe	[0.1] $PhCF_3$, 110 °C	**3da**	Dec.
21	**1d**	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	[0.5] PhH, BLED	**3da**	67

22	**1d**	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	[0.5] PhH, no light, rt	**3da**	88
23	**1h**	$Pd(dppf)Cl_2$	-	Cy_2NMe	[0.1] $PhCF_3$, 110 ^oC	**3ha**	Dec.
24	**1h**	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	[0.5] PhH, BLED	**3ha**	30
25	**1h**	Pd Xantphos G3	-	*i*Pr_2NEt	[0.5] PhH, BLED	**3ha**	86
26	**1h**	Pd Xantphos G3	-	*i*Pr_2NEt	[0.5] PhH, no light, 40 ^oC	**3ha**	96

[a] Conditions: **1a** 0.1 mmol scale, 34 W blue LED; [b]GC-MS yield; [c]2 equiv of *t*-BuI and 1 equiv of styrene were used. [d] Isolated yield, 0.5 mmol scale. [e] *t*-BuBr was used and reaction time was 48 h. [f] 5 mol % $Pd(OAc)_2$ and 10 mol % Xantphos work well for the reaction when **1a** is the limiting reagent. However, for the isolation purpose, since styrenes were found to be barely separable from the corresponding Heck products, we used **1a** in excess and 10 mol % $Pd(OAc)_2$/20 mol % Xantphos (conditions in entry 4).

4. Heck Reaction of Tertiary Alkyl Halides

General Procedure I:

An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 10 mol %), Xantphos (57.9 mg, 0.1 mmol, 20 mol %) and Cs_2CO_3 (326 mg, 1 mmol, 2 equiv) under N_2 atmosphere (glovebox). Next, alkyl halide **1** (1 mmol, 2 equiv), alkene **2** (0.5 mmol, 1 equiv) and dry/degassed benzene (1 mL) were added to reaction vessel via syringes. The vessel was capped with a pressure screw cap. The vial was irradiated with 34 W Blue LED lamp (Kessil KSH150B LED Grow Light) for 6-12 h (monitored by GC/MS), with cooling by a fan (vial temperature reached 37 °C). The vial distance from the lamp was about 1-2 cm. The resulting mixture was purified by column chromatography, affording the corresponding products **(3)**.

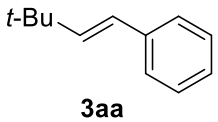
General Procedure II:

An oven dried 1 mL Wheaton V-vial containing a stirring bar was charged with $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 10 mol %), Xantphos (29.0 mg, 0.05 mmol, 20 mol %) and Cs_2CO_3 (163 mg, 0.5 mmol, 2 equiv) under N_2 atmosphere (glovebox). Next, alkyl halide **1** (0.25 mmol, 1 equiv), alkene **2** (0.5 mmol, 2 equiv) and dry/degassed benzene (0.5 mL) were added to reaction vessel via syringes. The vessel was capped with a pressure screw cap. The reaction was stirred at rt, covered with foil, for 6-12 h (monitored by GC/MS). The resulting mixture was purified by column chromatography, affording the corresponding products **(3)**.

General Procedure III:

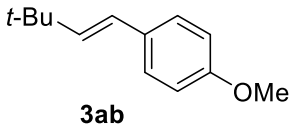
An oven dried 1 mL Wheaton V-vial containing a stirring bar was charged with alkyl halide **1** (0.5 mmol, 2 equiv), and Xantphos Pd G3 (23.8 mg, 0.025 mmol, 10 mol %) under N_2 atmosphere (glovebox). Next, alkene **2** (0.25 mmol, 1 equiv) and dry/degassed benzene (0.5 mL) and *i*Pr_2NEt (87 μL, 0.5 mmol, 2 equiv) were added to the reaction vessel via syringes. The vessel was capped with a pressure screw cap. The reaction was stirred at 40 °C in a preheated aluminum block for 6-12 h (monitored by GC/MS). The resulting mixture was purified by column chromatography, affording the corresponding products **(3)**.

Alkyl Heck Products (3) Analytics:



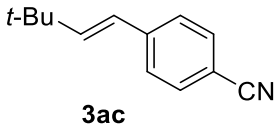
3aa

3aa was prepared according to the general procedure **I**. Yellow oil (73.5 mg, 92%). All analytical data for **3aa** were in accordance with the literature data[11]. R_f (Petroleum ether): 0.73. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.22 – 7.17 (m, 1H), 6.33 (d, *J* = 16.2 Hz, 1H), 6.27 (d, *J* = 16.2 Hz, 1H), 1.14 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.84, 138.05, 128.45, 126.72, 126.00, 124.56, 33.32, 29.58.



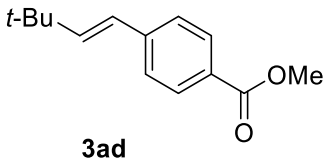
3ab

3ab was prepared according to the general procedure **I**. White solid (92.5 mg, 97%). All analytical data for **3ab** were in accordance with the literature data[12]. R_f (Petroleum ether:EA = 10:1): 0.73. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 6.88 – 6.79 (m, 2H), 6.26 (d, *J* = 16.2 Hz, 1H), 6.13 (d, *J* = 16.2 Hz, 1H), 3.81 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.60, 139.82, 130.85, 127.04, 123.86, 113.90, 55.27, 33.21, 29.68.



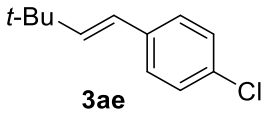
3ac

3ac was prepared according to the general procedure **I**. White solid (96.0 mg, >99%). All analytical data for **3ac** were in accordance with the literature data[13]. R_f (Petroleum ether:EA = 10:1): 0.49. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 2H), 7.42 (m, 2H), 6.39 (d, *J* = 16.2 Hz, 1H), 6.30 (d, *J* = 16.2 Hz, 1H), 1.13 (s, 9H). ^{13}C NMR (101 MHz, CDCl3) δ 146.07, 142.82, 132.46, 126.66, 123.62, 119.32, 110.06, 33.86, 29.47. HRMS (ESI+) calcd. for $C_{13}H_{16}N$ [M+H]: 186.1283, found: 186.1286.



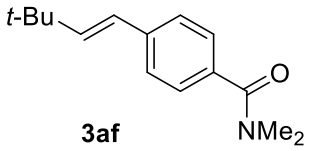
3ad

3ad was prepared according to the general procedure **I**. Yellow oil (100 mg, 92%). R_f (Petroleum ether:EA = 10:1): 0.9. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (m, 2H), 7.40 (m, 2H), 6.39 (d, *J* = 16.2 Hz, 1H), 6.32 (d, *J* = 16.2 Hz, 1H), 3.89 (s, 3H), 1.13 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.10, 144.71, 142.76, 129.96, 125.98, 124.09, 52.05, 33.69, 29.52. HRMS (ESI+) calcd. for $C_{14}H_{19}O_2$ [M+H]: 219.1385, found 218.1387.



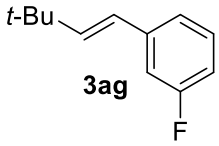
3ae

3ae was prepared according to the general procedure **I**. Clear oil (81.6 mg, 84%). All analytical data for **3ae** were in accordance with the literature data[14]. R_f (Hexanes): 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 4H), 6.34 – 6.17 (m, 2H), 1.09 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.52, 136.57, 132.24, 128.56, 127.23, 123.50, 33.40, 29.51.



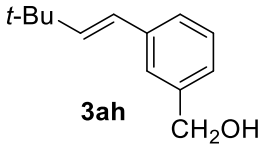
3af

3af was prepared according to the general procedure **I**. Yellow oil (101.6 mg, 88%). R_f (Hex:EA = 1:1): 0.28. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.26 (m, 5H), 6.29 (s, 2H), 3.07 (s, 3H), 2.96 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.86, 143.52, 139.69, 134.67, 127.81, 126.12, 124.27, 39.90, 35.69, 33.77, 29.80. HRMS (ESI+) calcd. for $C_{15}H_{22}NO$ [M+H]: 232.1701, found: 232.1703.



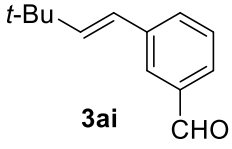
3ag

3ag was prepared according to the general procedure **I**. Clear oil (69.4 mg, 78%). R_f (Hexanes): 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.19 (m, 1H), 7.10 (m, 1H), 7.08 – 7.03 (m, 1H), 6.90 – 6.83 (m, 1H), 6.26 (s, 2H), 1.12 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.37 (s), 143.20 (s), 140.51 (d, J = 7.5 Hz), 129.80 (d, J = 8.4 Hz), 123.68 (s), 121.90 (s), 113.45 (d, J = 21.5 Hz), 112.39 (d, J = 21.6 Hz), 33.40 (s), 29.46 (s). HRMS (EI+) calcd. for $C_{12}H_{15}F$ [M]: 178.11578, found: 178.11617.



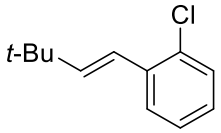
3ah

3ah was prepared according to the general procedure **I**. Yellow oil (66.0 mg, 69%). R_f (Hex:EA = 5:1): 0.19. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.29 (d, J = 4.5 Hz, 2H), 7.18 (m, 1H), 6.36 – 6.25 (m, 2H), 4.67 (s, 2H), 1.13 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.24, 141.04, 138.40, 128.70, 125.48, 125.35, 124.49, 124.34, 65.36, 33.37, 29.56. HRMS (ESI+) calcd. for $C_{13}H_{18}ONa$ [M+Na]: 213.1255, found: 213.1249.



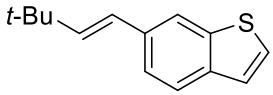
3ai

3ai was prepared according to the general procedure **I**. Clear oil (92.0 mg, 98%). R_f (Hex:EA = 5:1): 0.78. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.87 (s, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 6.41 – 6.26 (m, 2H), 1.14 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.64, 143.96, 139.23, 136.80, 132.22, 129.25, 128.26, 126.97, 123.56, 33.66, 29.60. HRMS (ESI+) calcd. for $C_{13}H_{17}O$ [M+H]: 189.1279, found: 189.1280.



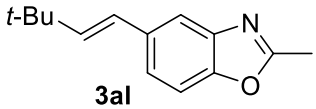
3aj

3aj was prepared according to the general procedure **I**. Yellow oil (77.0 mg, 79%). R_f (Hex): 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 1H), 7.36 – 7.33 (m, 1H), 7.23 – 7.12 (m, 2H), 6.72 (d, *J* = 16.1 Hz, 1H), 6.25 (d, *J* = 16.1 Hz, 1H), 1.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.65, 136.14, 132.83, 129.55, 127.75, 126.69, 126.57, 121.14, 33.76, 29.50. HRMS (EI+) calcd. for $C_{12}H_{15}Cl$ [M]: 194.08623, found: 194.08650.



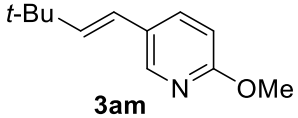
3ak

3aj was prepared according to the general procedure **I**. White solid (62.4 mg, 58%). R_f (Hex:EA = 5:1): 0.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.42 (q, *J* = 3.3 Hz, 1H), 7.37 (d, *J* = 5.4 Hz, 1H), 7.28 (t, *J* = 6.2 Hz, 1H), 6.42 (d, *J* = 16.1 Hz, 1H), 6.33 (d, *J* = 16.2 Hz, 1H), 1.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.43, 140.80, 138.94, 135.05, 126.43, 124.97, 124.13, 123.88, 123.02, 120.36, 33.93, 30.10. HRMS (EI+) calcd. for $C_{14}H_{16}S$ [M]: 216.09727, found: 216.09769.



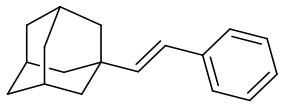
3al

3ak was prepared according to the general procedure **I**. Clear oil (86.2 mg, 80%). R_f (Hex:EA = 5:1): 0.37. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.32 – 7.27 (m, 1H), 6.38 (d, *J* = 16.1 Hz, 1H), 6.23 (d, *J* = 16.1 Hz, 1H), 2.60 (s, 3H), 1.13 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.10, 150.11, 141.98, 141.56, 134.76, 124.31, 122.73, 116.54, 109.83, 31.56, 29.58, 14.52. HRMS (ESI+) calcd. for $C_{14}H_{18}NO$ [M+H]: 216.1388, found: 216.1387.



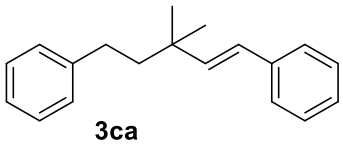
3am

3al was prepared according to the general procedure **I**. Yellow oil (92.6 mg, 97%). R_f (Hex:EA = 5:1): 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 2.3 Hz, 1H), 7.64 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.68 (d, *J* = 8.6 Hz, 1H), 6.22 (d, *J* = 16.2 Hz, 1H), 6.12 (d, *J* = 16.2 Hz, 1H), 3.92 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.14, 144.97, 141.26, 135.24, 127.11, 120.69, 110.65, 53.38, 33.37, 29.54. HRMS (ESI+) calcd. for $C_{12}H_{17}NO$ [M+H]: 192.1388, found: 192.1387.



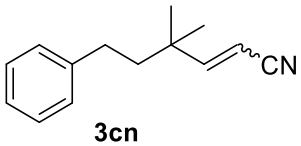
3ba

3ba was prepared according to the general procedure **I**, using 2 equiv of styrene **2a** and 1 equiv of alkyl iodide **1b**. White solid (100 mg, 84%). R_f (Hex:EA = 5:1): 0.67. All analytical data for **3ac** were in accordance with the literature data[15]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 2H), 7.29 (m, 2H), 7.18 (m, 1H), 6.25 (d, *J* = 16.3 Hz, 1H), 6.11 (d, *J* = 16.3 Hz, 1H), 2.04 (s, 3H), 1.27 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.09, 138.20, 128.43, 126.67, 125.96, 124.49, 42.23, 36.89, 29.69, 28.48.



3ca

3ca was prepared according to the general procedure **I**, using 2 equiv of styrene **2a** and 1 equiv of alkyl iodide **1c**. Clear oil (89.8 mg, 72%). R_f (Hexanes): 0.54. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.36 – 7.26 (m, 4H), 7.21 (m, 4H), 6.38 (d, *J* = 16.2 Hz, 1H), 6.27 (d, *J* = 16.2 Hz, 1H), 2.60 (m, 2H), 1.78 – 1.68 (m, 2H), 1.21 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.18, 140.20, 137.96, 128.52, 128.32, 126.88, 126.26, 126.07, 125.59, 45.31, 36.46, 31.36, 29.72, 27.25. HRMS (EI+) calcd. for $C_{19}H_{22}$ [M]: 250.17215, found: 250.17158.

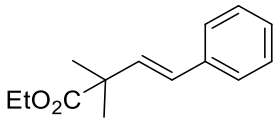


3cn

E(**a**)/Z(**b**) = 1.5 : 1

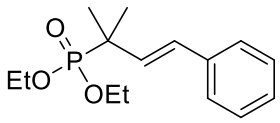
3cn was prepared according to the general procedure **I**, 2 equiv of acrylonitrile **2n** and 1 equiv of alkyl iodide **1c**. Colorless oil (58.4 mg, 59%). R_f (Hx:EA = 9:1): 0.36. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.22 (m), 7.17 (m), 6.73 (dd, J = 16.7, 3.1 Hz, 1H(**a**)), 6.34 (dd, J = 12.3, 3.2 Hz, 1H(**b**)), 5.33 (dd, J = 12.3, 3.2 Hz, 1H(**a**)), 5.28 (dd, J = 16.7, 3.1 Hz, 1H(**b**)), 2.62 – 2.54 (m, 2H(**a**)), 2.54 – 2.46 (m, 2H(**b**)), 1.84 – 1.72 (m, 2H(**a**)), 1.72 – 1.61 (m, 2H(**b**)), 1.33 (d, J = 3.2 Hz, 6H(**a**)), 1.13 (d, J = 3.1 Hz, 6H(**b**)). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.35, 162.31, 142.02, 141.83, 128.49, 128.45, 128.28, 128.20, 126.01, 125.92, 117.84, 116.62, 109.57, 97.06, 96.59, 44.87, 43.94, 38.80,

38.16, 31.21, 31.03, 29.69, 26.91, 26.72, 25.78. HRMS (ESI+) calcd. for $C_{14}H_{18}N$ [M+H]: 200.1439, found: 200.1445.



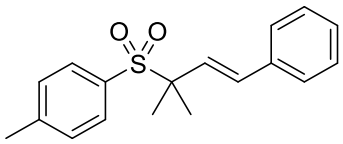
3da

3da was prepared according to the general procedure **II**. Colorless oil (50.7 mg, 92%). R_f (Hex:EA = 5:1): 0.52. All analytical data for **3ac** were in accordance with the literature data[16]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 2H), 7.31 (m, 2H), 7.24 (m, 1H), 6.42 (m, 2H), 4.15 (q, J = 7.1 Hz, 2H), 1.41 (s, 6H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.42, 143.45, 137.30, 134.65, 128.65, 128.05, 127.50, 126.46, 60.92, 44.51, 25.21, 14.30.



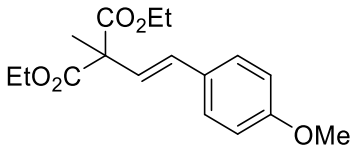
3ea

3ea was prepared according to the general procedure **III**, using 5 mol % Xantphos Pd G3, 2 equiv of styrene **2a** and 1 equiv of **1e**. Brown oil (60.0 mg, 85%). R_f (Hex:Acetone = 1:1): 0.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.30 (m, 2H), 7.24 – 7.18 (m, 1H), 6.46 (dd, *J* = 16.2, 4.8 Hz, 1H), 6.34 (dd, *J* = 16.2, 5.7 Hz, 1H), 4.10 (p, *J* = 7.1 Hz, 4H), 1.40 (d, *J* = 16.7 Hz, 6H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.14 (s), 131.88 (d, *J* = 8.7 Hz), 129.74 (d, *J* = 11.8 Hz), 128.52 (s), 127.42 (s), 126.34 (s), 62.39 (d, *J* = 7.4 Hz), 22.38 (d, *J* = 4.4 Hz), 16.51 (d, *J* = 5.5 Hz). HRMS (EI+) calcd. for $C_{15}H_{24}O_3P$ [M+H]: 283.1463, found: 283.1459.



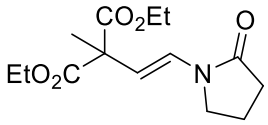
3fa

3fa was prepared according to the general procedure **III**, using 2 equiv of styrene **2a** and 1 equiv of **1f** on a 0.5 mmol scale. White solid (128 mg, 85%). R_f (Hex:EA = 5:1): 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (m, 2H), 7.36 – 7.31 (m, 4H), 7.26 (m, 3H), 6.41 – 6.20 (m, 2H), 2.41 (s, 3H), 1.55 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.51, 136.12, 133.30, 132.38, 130.53, 129.06, 128.67, 128.23, 128.01, 126.62, 64.53, 21.60, 21.20. HRMS and LRMS failed to provide the HR mass for this compound.



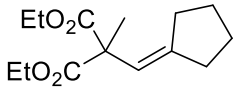
3gb

3gb was prepared according to the general procedure **II**, using 2 equiv of **2b** and 1 equiv of **1g**. Colorless oil (41.3 mg, 54%). R_f (Hex:EA = 5:1): 0.15. All analytical data for **3gb** were in accordance with the literature data[17]. 1H NMR (400 MHz, CDCl3) δ 7.34 (m, 2H), 6.85 (m, 2H), 6.55 (d, *J* = 16.4 Hz, 1H), 6.44 (d, *J* = 16.4 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 4H), 3.81 (s, 3H), 1.65 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.44, 159.57, 130.32, 127.94, 125.57, 114.10, 61.76, 55.75, 55.45, 29.85, 20.54, 14.18. HRMS (ESI+) calcd. for $C_{17}H_{22}O_5$ [M+H]: 307.1545, found: 307.1552.



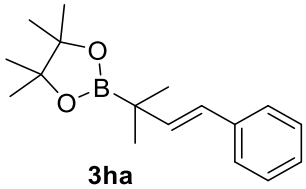
3go

3go was prepared according to the general procedure **III**, using 2 equiv of **2o** and 1 equiv of **1g**. Yellow oil (33.0 mg, 47%). R_f (Hex:EA = 3:1): 0.1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 14.9 Hz, 1H), 5.39 (d, *J* = 14.9 Hz, 1H), 4.19 (dd, *J* = 13.6, 6.7 Hz, 4H), 3.55 (t, *J* = 7.1 Hz, 2H), 2.48 (t, *J* = 8.1 Hz, 2H), 2.18 – 2.03 (m, 2H), 1.60 (s, 3H), 1.25 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.49, 171.41, 125.45, 110.01, 61.83, 54.33, 45.26, 31.33, 29.82, 20.08, 17.56, 14.13. HRMS (ESI+) calcd. for $C_{14}H_{22}NO_5$ [M+H]: 284.1511, found: 284.1509.



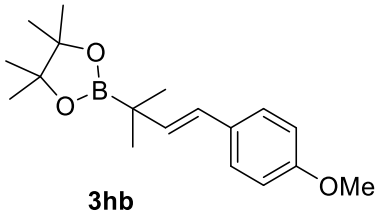
3gp

3gp was prepared according to the general procedure **III**, using 2 equiv of **2p** and 1 equiv of **1g**. Clear oil (32.3 mg, 51%). R_f (Hex:EA = 10:1, $KMnO_4$ stain): 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.42 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 4H), 2.73 (s, 2H), 2.25 (m, 2H), 2.14 (m, 2H), 1.84 – 1.78 (m, 2H), 1.37 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.55, 139.22, 129.28, 61.46, 61.33, 53.33, 37.02, 35.78, 32.44, 29.83, 23.88, 20.12, 14.15. HRMS (ESI+) calcd. for $C_{14}H_{23}O_4$ [M+H]: 255.1586, found: 255.1587.



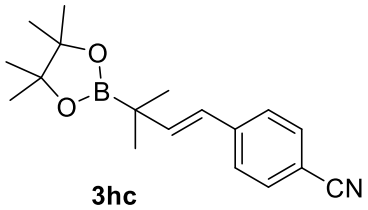
3ha

3ha was prepared according to the general procedure **III** and purified on silica gel that was dried in the oven at 180 °C overnight. White solid (68.0 mg, >99%). R_f (Hex:Acetone = 10:1): 0.53. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 2H), 7.28 (m, 2H), 7.17 (m, 1H), 6.38 (d, *J* = 16.2 Hz, 1H), 6.29 (d, *J* = 16.1 Hz, 1H), 1.23 (s, 12H), 1.18 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.95, 138.40, 128.36, 126.45, 125.95, 125.64, 83.24, 29.69, 24.56, 23.91. HRMS (EI+) calcd. for $C_{17}H_{25}BO_2$ [M]: 272.19477, found: 272.19495.



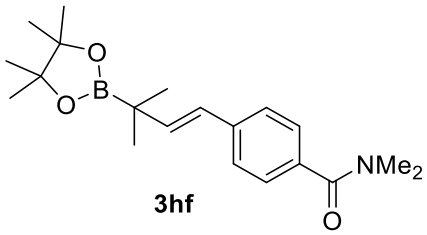
3hb

3hb was prepared according to the general procedure **III** and purified on silica gel that was dried in the oven at 180 °C overnight. White solid (68.0 mg, 90%). R_f (Hex:Acetone = 10:1): 0.72. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2H), 6.83 (m, 2H), 6.23 (m, 2H), 3.79 (s, 3H), 1.22 (s, 12H), 1.16 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.57, 136.97, 131.43, 127.52, 127.14, 125.17, 114.04, 113.96, 111.71, 83.34, 55.42, 43.97, 24.91, 24.85, 24.72, 24.17. HRMS (ESI+) calcd. for $C_{28}H_{28}BO_3$ [M+H]: 303.2132, found: 303.2126.



3hc

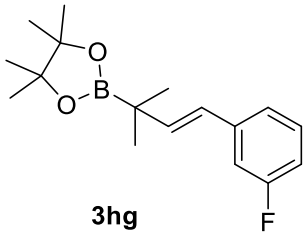
3hc was prepared according to the general procedure **III** and purified on silica gel that was dried in the oven at 180 °C overnight. White solid (65.0 mg, 88%). R_f (Hex:Et_2O = 1:1): 0.63. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (m, 2H), 7.40 (m, 2H), 6.52 (d, *J* = 16.1 Hz, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 1.21 (s, 12H), 1.17 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.49, 132.29, 126.47, 124.35, 119.29, 109.60, 83.52, 24.62, 23.73. HRMS (ESI+) calcd. for $C_{18}H_{25}BNO_2$ [M+H]: 298.1978, found 298.1971.



3hf

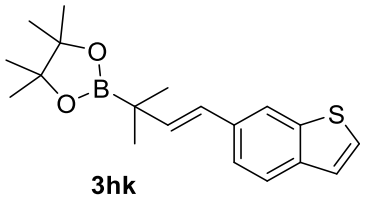
3hf was prepared according to the general procedure **III** and purified on silica gel that was dried in the oven at 180 °C overnight. Brown solid (80.9 mg, 94%). R_f (Hex:Acetone = 7:3): 0.33. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4H), 6.42 (d, *J* = 16.1 Hz, 1H), 6.27 (d, *J* = 16.1 Hz, 1H), 3.08

(s, 3H), 2.98 (s, 3H), 1.21 (s, 12H), 1.16 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.72, 140.58, 139.84, 134.21, 127.55, 125.84, 125.08, 83.43, 39.72, 35.49, 24.67, 23.94. HRMS (ESI+) calcd. for $C_{20}H_{31}BNO_3$ [M+H]: 344.2397, found: 344.2413.



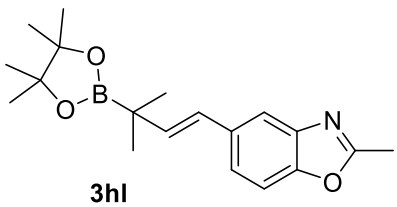
3hg

3hg was prepared according to the general procedure **III** and purified on silica gel that was dried in the oven at 180 °C overnight. Yellow solid (65.0 mg, 90%). R_f (Hex:Acetone = 20:1): 0.38. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 14.1, 7.8 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 10.3 Hz, 1H), 6.85 (td, *J* = 8.3, 1.9 Hz, 1H), 6.39 (d, *J* = 16.1 Hz, 1H), 6.24 (d, *J* = 16.1 Hz, 1H), 1.23 (s, 12H), 1.17 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.94 (d, *J* = 291.0 Hz), 140.83 (d, *J* = 7.7 Hz), 140.46 (s), 129.70 (d, *J* = 8.4 Hz), 124.65 (s), 121.86 (s), 113.16 (d, *J* = 21.4 Hz), 112.29 (d, *J* = 21.5 Hz), 83.32 (s), 24.55 (s), 24.24 (s), 23.80 (s). HRMS (EI+) calcd. for $C_{17}H_{24}BFO_2$ [M]: 290.18534, found: 290.18541.



3hk

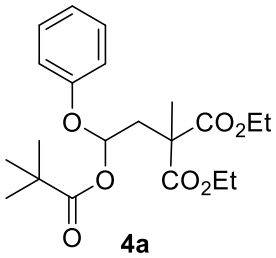
3hj was prepared according to the general procedure **III** and purified on silica gel that was dried in the oven at 180 °C overnight. White solid (66.6 mg, 81%). R_f (Hex:Acetone = 20:1): 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.42 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.35 (d, *J* = 5.4 Hz, 1H), 7.27 (d, *J* = 5.5 Hz, 1H), 6.45 (d, *J* = 16.1 Hz, 1H), 6.39 (d, *J* = 16.1 Hz, 1H), 1.24 (s, 12H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.27, 139.11, 138.28, 134.96, 125.79, 125.57, 123.63, 123.29, 122.61, 119.73, 83.27, 24.58, 23.97. HRMS (ESI+) calcd. for $C_{19}H_{26}BO_2S$ [M+H]: 329.1747, found: 329.1755.



3hl

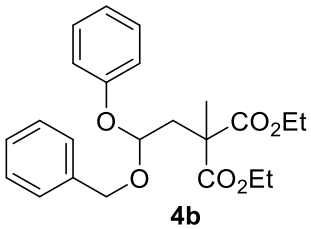
3hk was prepared according to the general procedure **III** and purified on silica gel that was dried in the oven at 180 °C overnight. White solid (73.8 mg, 98%). R_f (Hex:Acetone = 10:1): 0.17 . ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 6.40 – 6.30 (m, 2H), 2.60 (s, 3H), 1.22 (s, 12H), 1.18 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.02,

149.98, 141.92, 138.73, 135.16, 125.38, 122.75, 116.45, 109.75, 24.56, 23.92, 14.55. HRMS (ESI+) calcd. for $C_{19}H_{27}BNO_3$ [M+H]: 328.2084, found 328.2077.



4a

4a was prepared according to the general procedure **III** in the presence of 2 equiv of CsOPiv instead of N(*i*Pr)Me_2 on a 0.5 mmol scale. Colorless oil (162 mg, 82%). R_f (Hex:EA = 9:1): 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 2H), 7.01 (m, 1H), 6.89 (m, 2H), 6.62 – 6.50 (m, 1H), 4.28 – 4.06 (m, 4H), 2.64 (dd, *J* = 14.5, 8.0 Hz, 1H), 2.42 (dd, *J* = 14.5, 3.0 Hz, 1H), 1.53 (s, 3H), 1.22 (dt, *J* = 12.6, 7.1 Hz, 6H), 1.13 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.26, 171.72, 171.43, 155.91, 129.64, 123.19, 117.04, 94.04, 61.73, 61.58, 51.54, 39.54, 38.98, 26.97, 20.18, 14.10, 14.04. HRMS (ESI+) calcd. for $C_{21}H_{30}O_7Na$ [M+Na]: 417.1889, found: 417.1884.

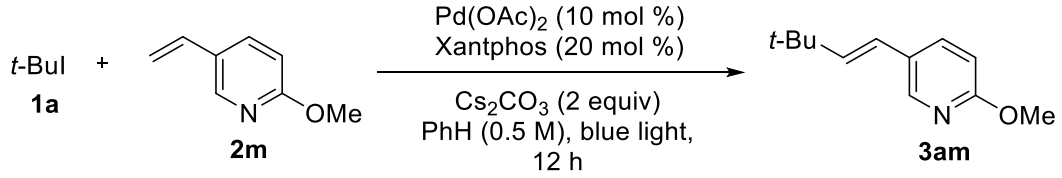


4b

Compound **4b** was prepared according to the general procedure **III** in the presence of 2 equiv of benzyl alcohol on a 0.5 mmol scale. Yellow oil (80.2 mg, 40%). R_f (Hex:EA = 5:1): 0.6 ($KMnO_4$ stain). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.26 (m, 7H), 7.04-6.9 (m, 3H), 5.51 (t, *J* = 5.2 Hz, 1H), 4.72 (d, *J* = 11.4 Hz, 1H), 4.52 (d, *J* = 11.2 Hz, 1H), 4.19-4.05 (m, 4H), 2.57-2.48 (m, 2H), 1.50 (s, 3H), 1.23-1.12 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.77, 156.89, 137.18, 129.53, 128.26, 128.10, 127.70, 122.13, 117.19, 99.46, 68.25, 61.36, 51.56, 39.44, 29.68, 20.53, 13.93, 13.87. HRMS (ESI+) calcd. for $C_{23}H_{28}O_6Na$ [M+Na]: 423.1784, found: 423.1785.

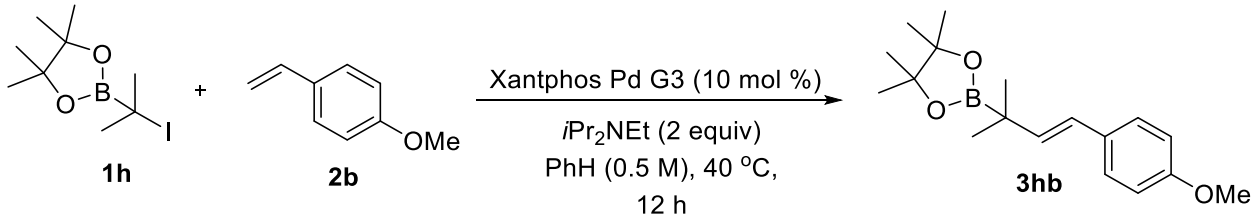
5. Representative Procedures for 1 mmol Scale Reactions

Synthesis of compound 3am:



An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with $Pd(OAc)_2$ (22.5 mg, 0.1 mmol, 10 mol %), Xantphos (116 mg, 0.2 mmol, 20 mol %) and Cs_2CO_3 (652 mg, 2 mmol, 2 equiv) under N_2 atmosphere (glovebox). Next, dry benzene (2 mL), *tert*-butyl iodide **1a** (240 µL, 2 mmol, 2 equiv), and alkene **2m** (135 µL, 1 mmol, 1 equiv) were added to reaction vessel via syringes. The vessel was capped with a pressure screw cap. The vial was irradiated with 34 W Blue LED lamp (Kessil KSH150B LED Grow Light) for 12 h, with cooling by a fan (vial temperature reached 37 °C). The resulting mixture was directly loaded on silica gel, the vial was washed with CH_2Cl_2, and column chromatography was performed using gradient from pure hexane to hexane:ethyl acetate (5:1). The product **3am** was obtained in isolated 93% yield (178 mg) as orange oil.

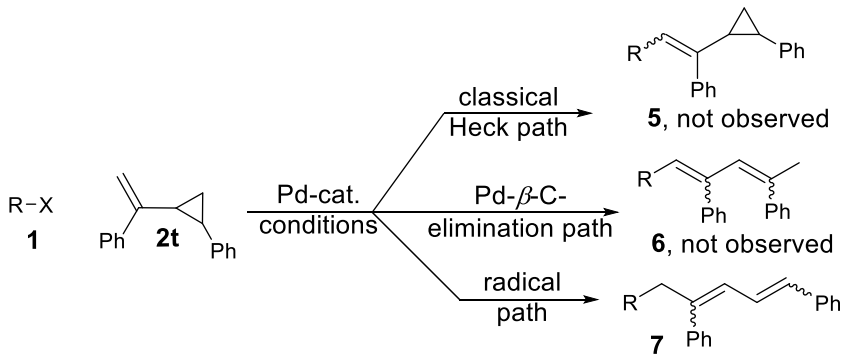
Synthesis of compound 3hb:



An oven dried 3 mL Wheaton V-vial containing a stirring bar was charged with alkyl halide **1h** (444 mg, 1.5 mmol, 1.5 equiv), and Xantphos Pd G3 (95.0 mg, 0.010 mmol, 10 mol %) under N_2 atmosphere (glovebox). Next, dry benzene (2 mL), 4-vinylanisole **2b** (133 µL,1 mmol, 1 equiv), and *i*Pr_2NEt (350 µL, 2 mmol, 2 equiv) were added to the reaction vessel via syringes. The vessel was capped with a pressure screw cap. The reaction was stirred at 40 ^oC in a preheated aluminum block for 12 h. At that point, GC-MS showed only presence of the product **3hb** in the reaction mixture. The resulting mixture was directly loaded on silica gel (dried at 180 ^oC in the oven overnight), the vial was washed with acetone, and column chromatography was performed using gradient from pure hexane to hexane:acetone (10:1). The product **3hb** was obtained in 96% isolated yield (290 mg) as white solid.

6. Mechanistic Studies

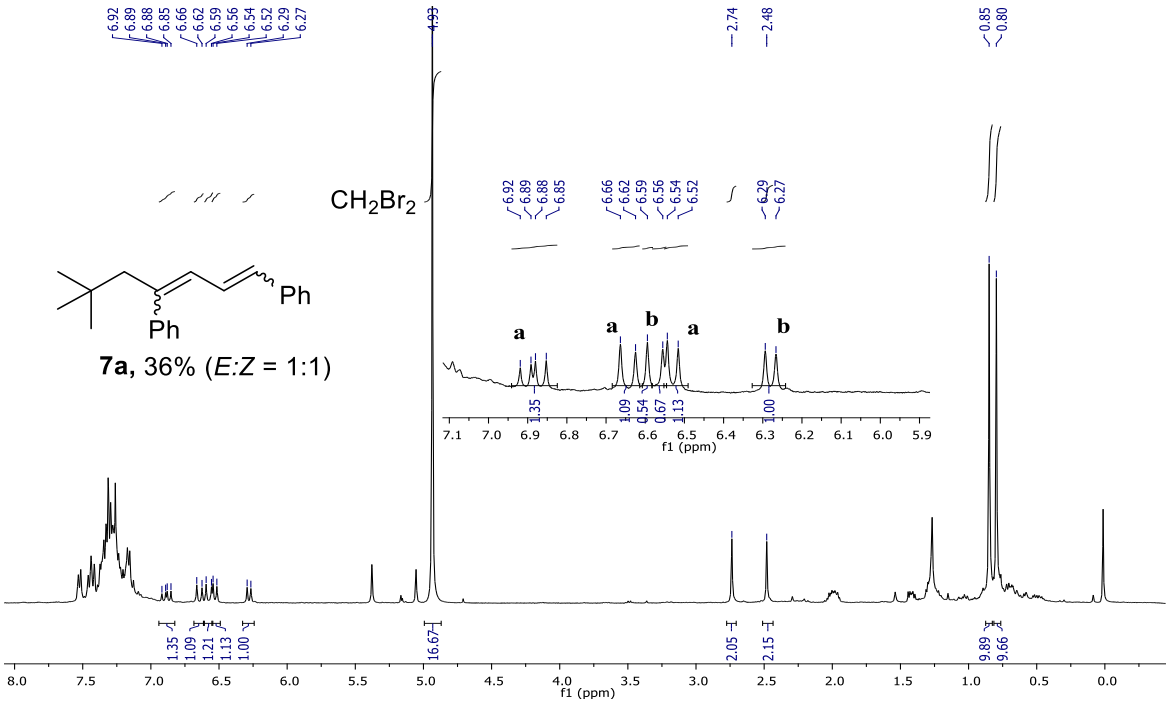
Radical clock experiment:



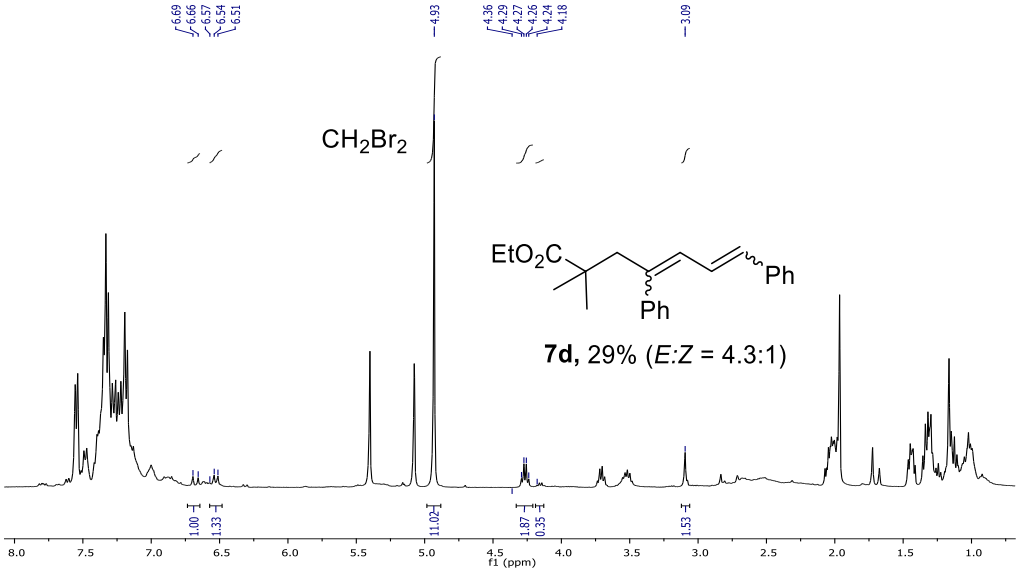
R-X	NMR yiled of **7**
1a	36% (**7a**)
1d	29% (**7d**)
1h	37% (**7h**)

Reaction of electronically different alkyl halides **1** with the radical clock **2t** resulted in regioselective radical-ring opening of the cyclopropyl unit **7**. Formation of a product of Pd-*β*-C elimination[18] of the cyclopropane component (**6**), or the coupling adduct possessing an intact cyclopropane unit (**5**), was not detected.

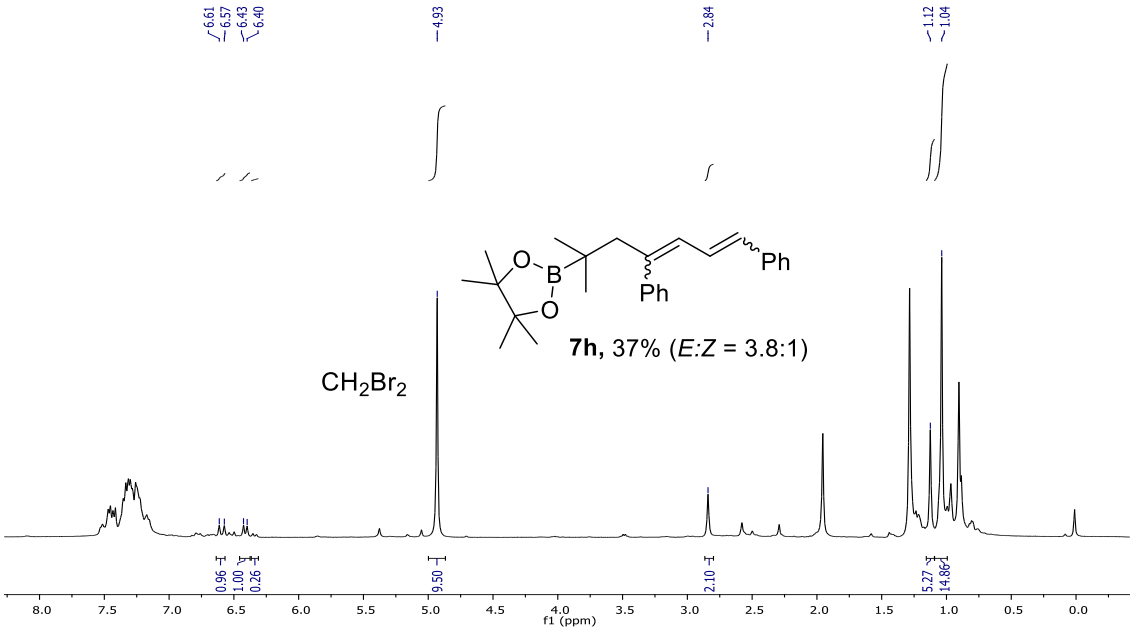
Compound **7a** was obtained in 36% NMR (*E:Z* = 1:1) yield using general procedure **I** on a 0.1 mmol scale and CH_2Br_2 as standard (10 μL). Characteristic NMR data are provided for both isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (dd, *J* = 15.6, 11.0 Hz, 1H(**a**)), 6.64 (d, *J* = 15.5 Hz, 1H(**a**)), 6.57 (d, *J* = 15.7 Hz, 1H(**b**)), 6.53 (d, *J* = 11.1 Hz, 1H(**a**)), 6.28 (d, *J* = 10.9 Hz, 1H(**b**)), 2.74 (s, 2H), 2.48 (s, 2H), 0.85 (s, 7H), 0.80 (s, *J* = 8.7 Hz, 9H).



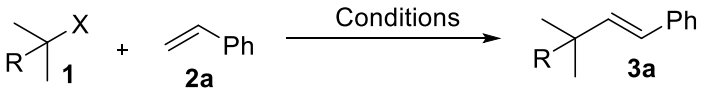
Compound **7d** was obtained in 29% NMR (*E:Z* = 4.3:1) yield using general procedure **II** on a 0.1 mmol scale and CH_2Br_2 as standard (10 μL). Characteristic NMR data are provided only for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (d, *J* = 15.3 Hz, 1H), 6.53 (d, *J* = 10.9 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.09 (s, 2H).



Compound **7h** was obtained in 37% NMR (*E:Z* = 3.8:1) yield using general procedure **III** on a 0.1 mmol scale and CH_2Br_2 as standard (10 μL). Characteristic NMR data are provided only for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (d, *J* = 15.6 Hz, 1H), 6.41 (d, *J* = 11.2 Hz, 1H), 2.84 (s, 2H), 1.12 (s, 6H), 1.04 (s, 12H).



Trapping with TEMPO:



R	X	Conditions	yield of **3a**, %	+ TEMPO (1 equiv)
Me (**1a**)	I	Conditions I	92% (**3aa**)	0% (**3aa**)
CO_2Et (**1d**)	Br	Conditions II	88% (**3da**)	0% (**3da**)
BPin (**1h**)	I	Conditions III	96% (**3ha**)	0% (**3ha**)

Photophysical studies:

Photophysical studies was conducted in order to understand the role of visible light. For these studies, $Pd(PPh_3)_4$ was used since it was found to be a competent catalyst for the tertiary Heck reaction reaction (see Optimization Table, entry 12). The absorption spectra of $Pd(PPh_3)_4$, *tert*-butyl iodide **1a** and styrene **2a** showed that Pd(0) is the only light absorbing species between 400 and 500 nm (Fig. 1). Next, emission spectrum was recorded by irradiated Pd(0) catalyst at 450 nm (Kessil blue LED's maximum absorption), to show the emission band at 620 nm. Subsequently, different amounts of *tert*-butyl iodide **1a** were added to Pd(0) catalyst. The emission intensity decreased gradually by increasing concentration of **1a** (Fig. 2). The obtained linear correlation between I_0/I and concentration of **1a** for Stern−Volmer studies (Fig. 3) indicated that the alkyl iodide presumably engages in an SET event with Pd(0) species.

Fig. 1. Abroption of $Pd(PPh_3)_4$ (8.65×10^{-4} M in THF) (black line); *tert*-butyl iodide (**1a**) (red line) and styrene (**2a**) (blue line).

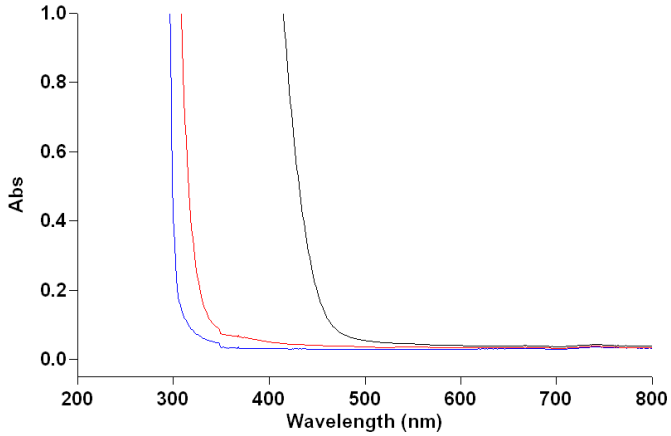


Fig. 2. Emission quenching of $Pd(PPh_3)_4$ (8.65×10^{-4} M in THF) by the concentration range of 0-300 mol % of *tert*-butyl iodide (**1a**) with respect to $Pd(PPh_3)_4$ after irradiation at 450 nm at 25 °C.

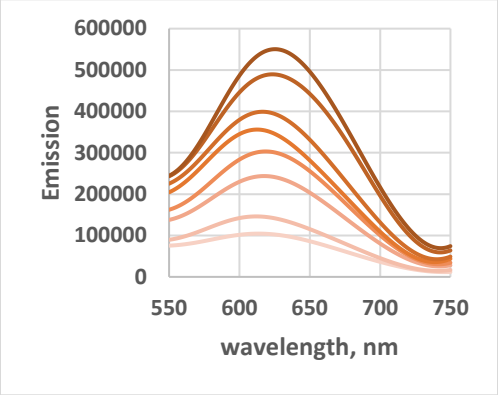
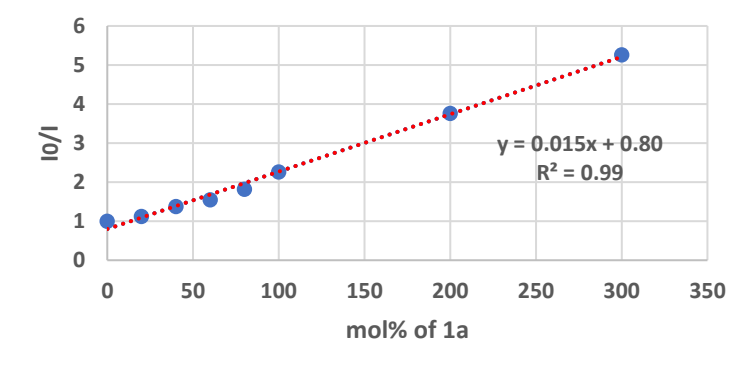
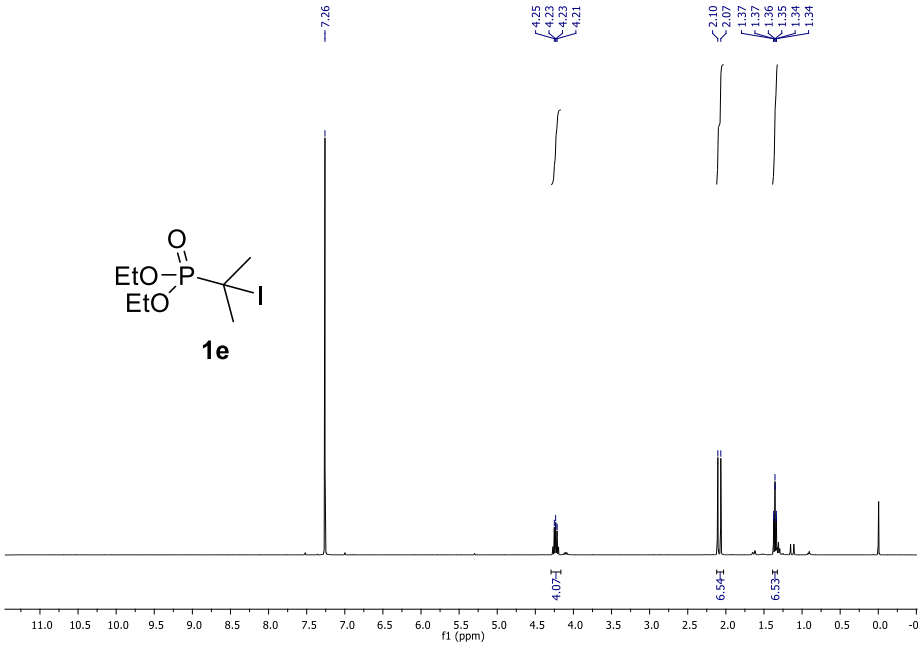


Fig. 3. Stern-Volmer plot for the emission quenching of $Pd(PPh_3)_4$ by various concentrations of *tert*-butyl iodide **1a** (from 0 to 300 mol % with respect to $Pd(PPh_3)_4$ in THF).

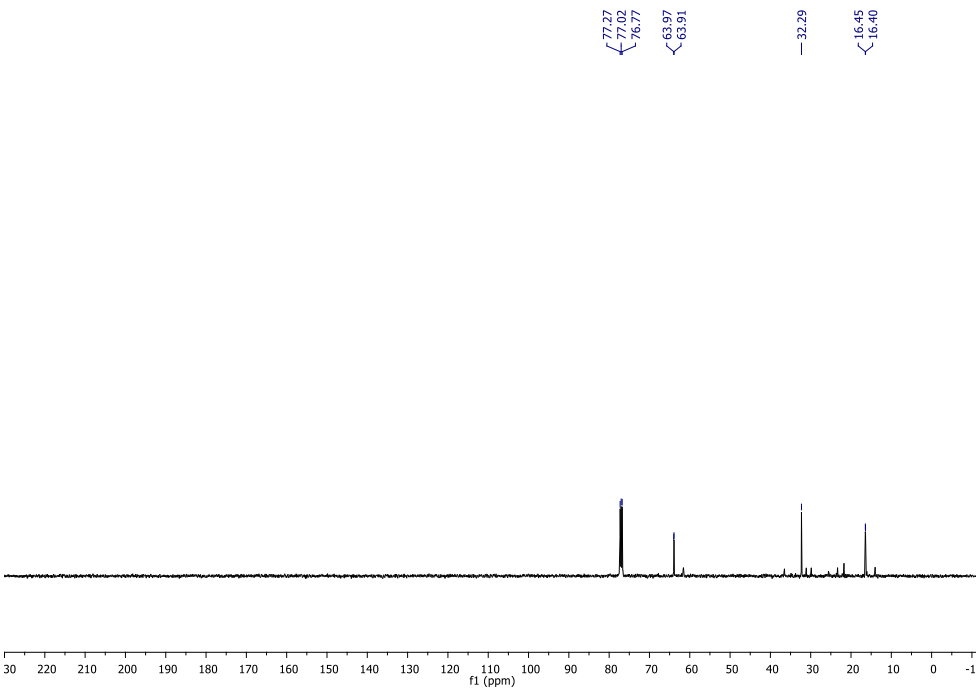


7. NMR Data

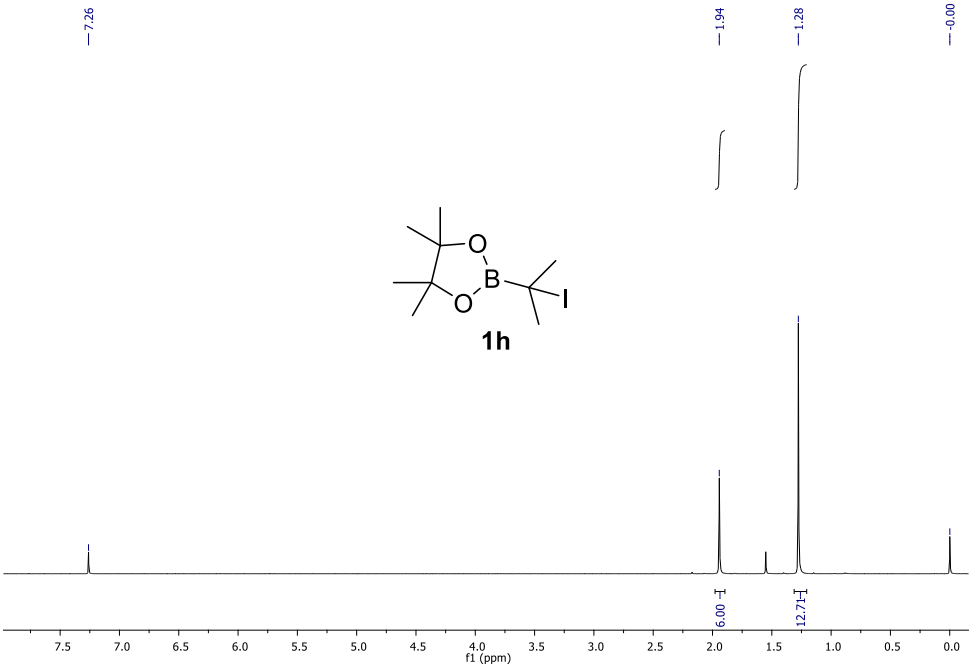
^{1}H NMR of **1h**



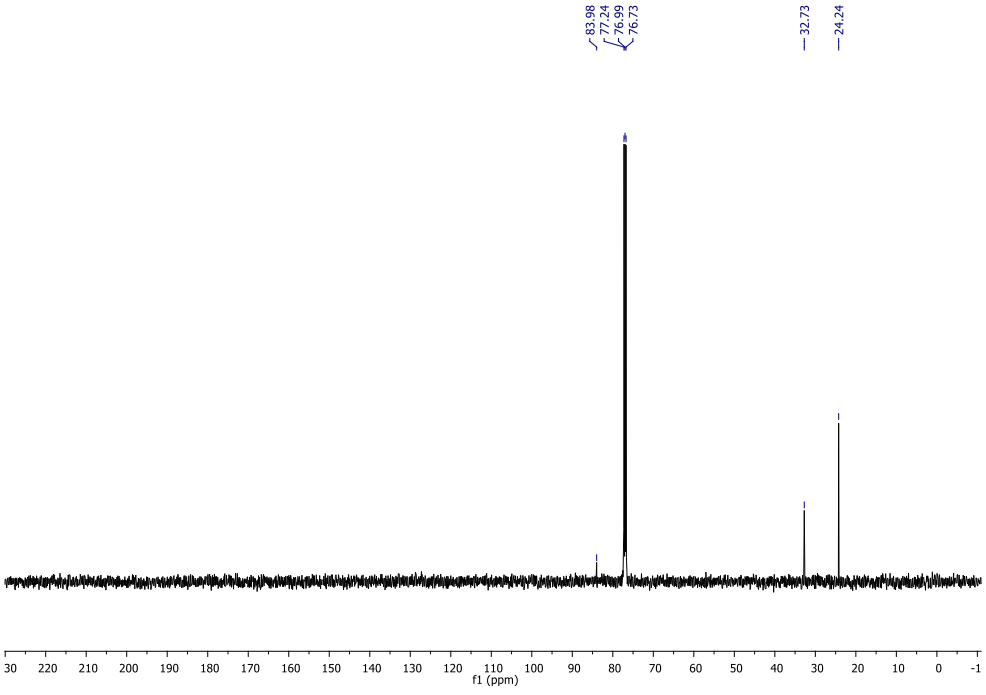
^{13}C NMR of **1e**



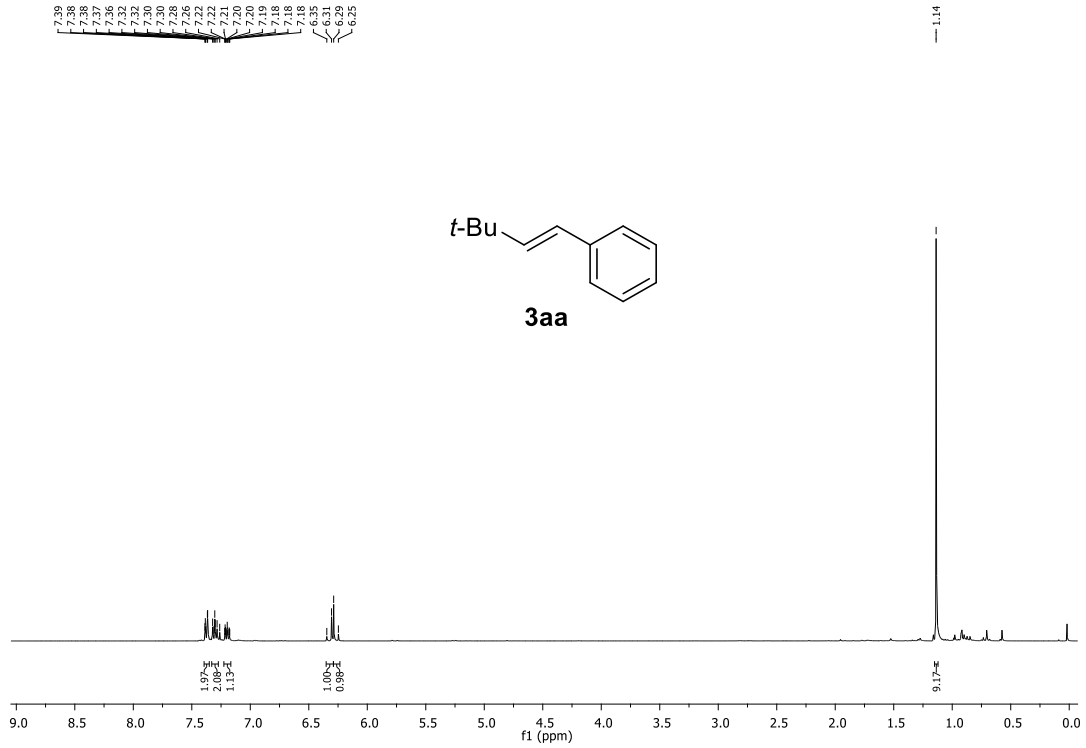
^{1}H NMR of **1h**



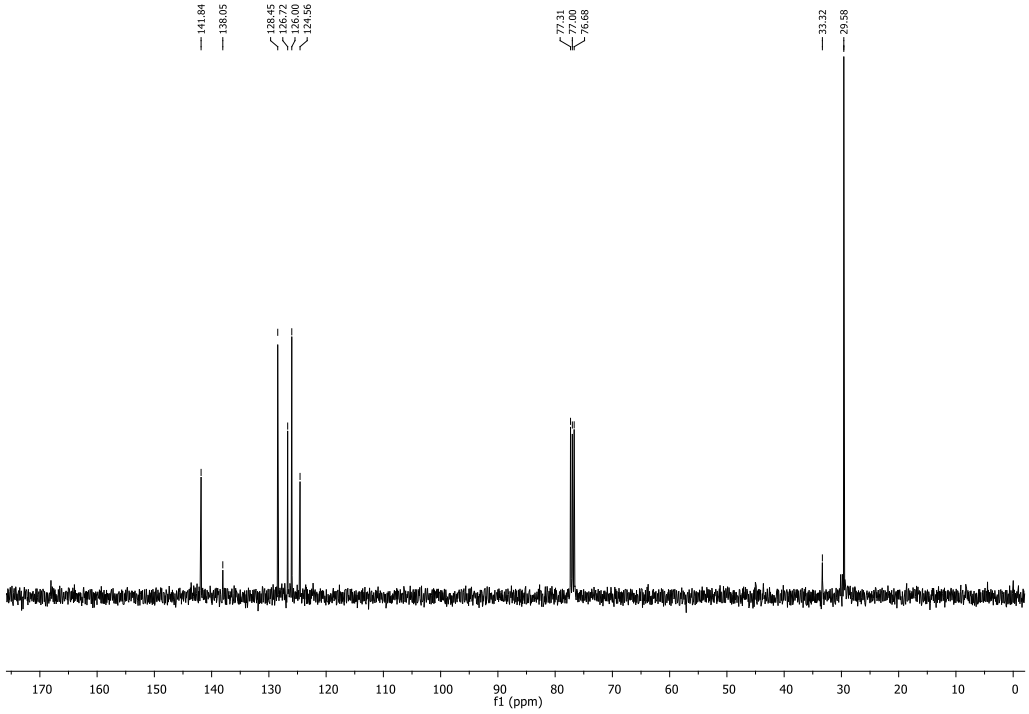
^{13}C NMR of **1h**



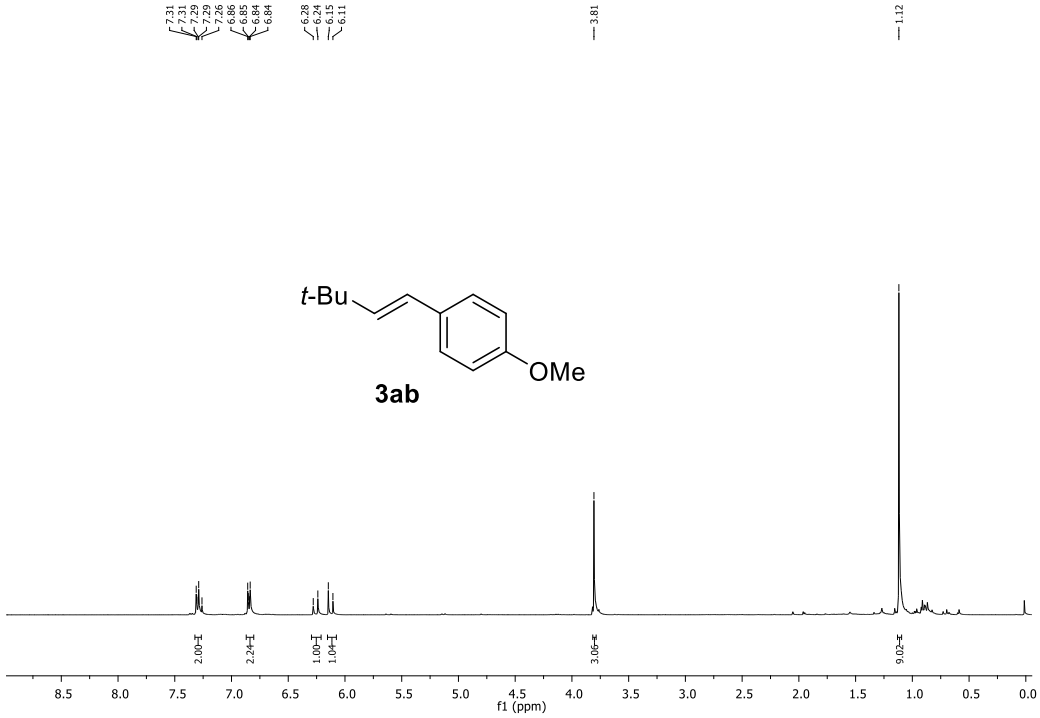
^{1}H NMR of **3aa**



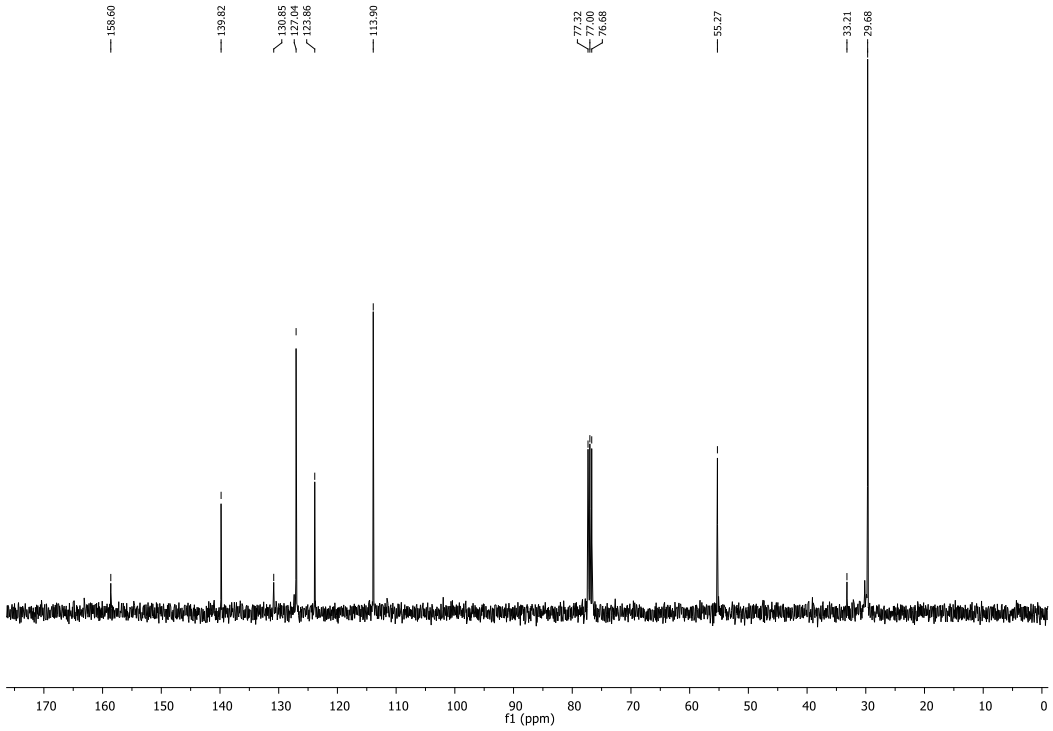
^{13}C NMR of **3aa**



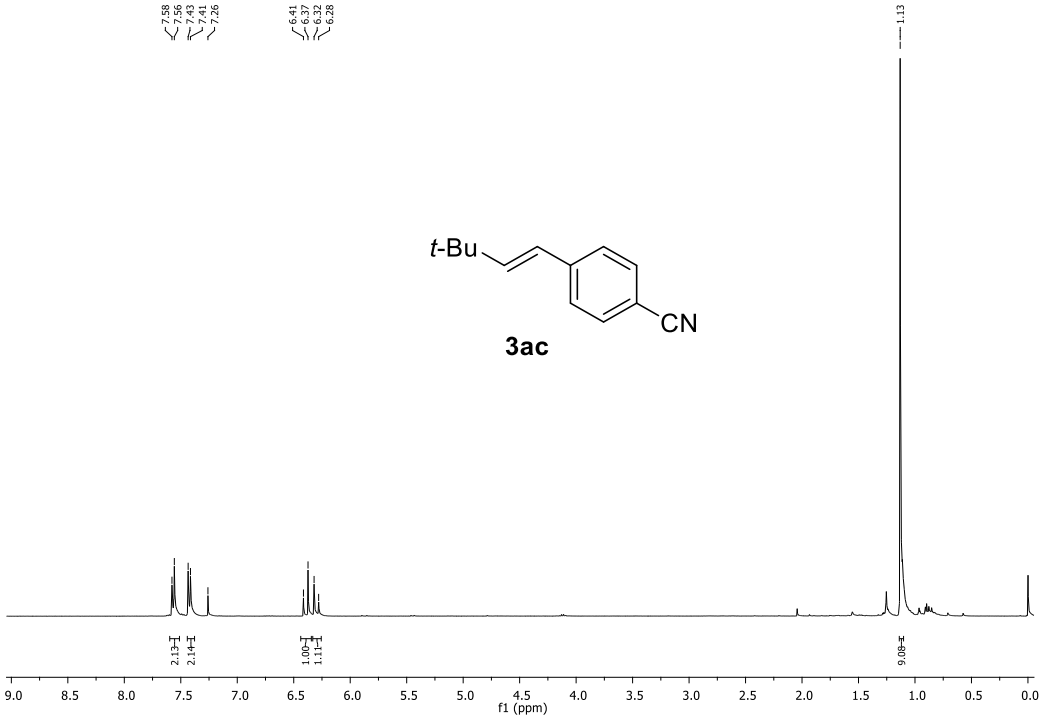
^{1}H NMR of **3ab**



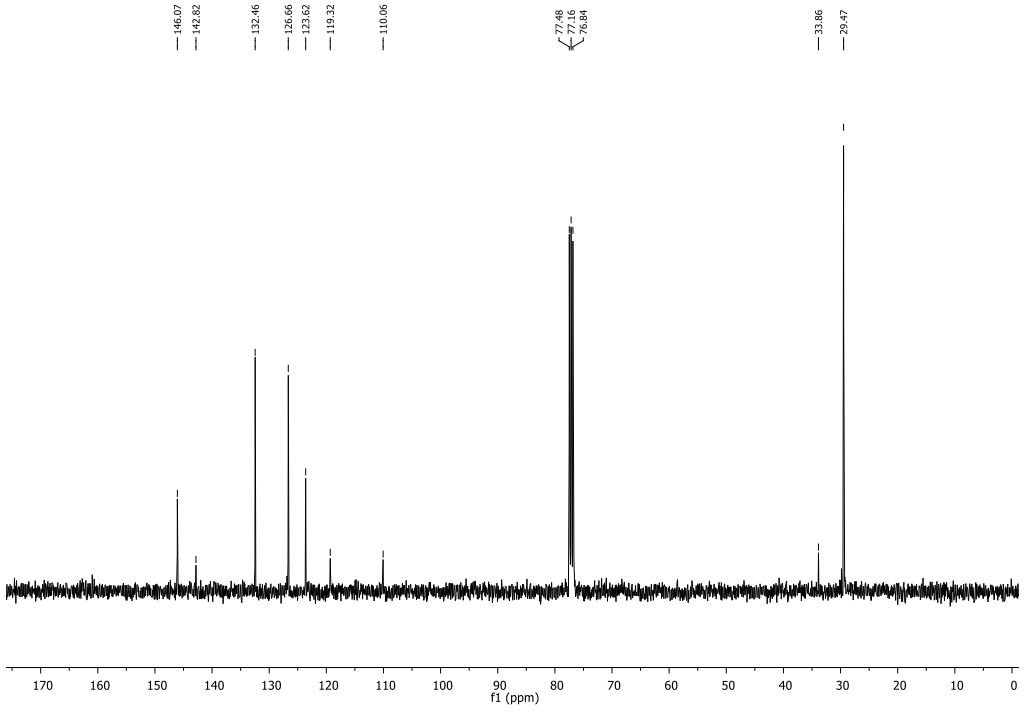
^{13}C NMR of **3ab**



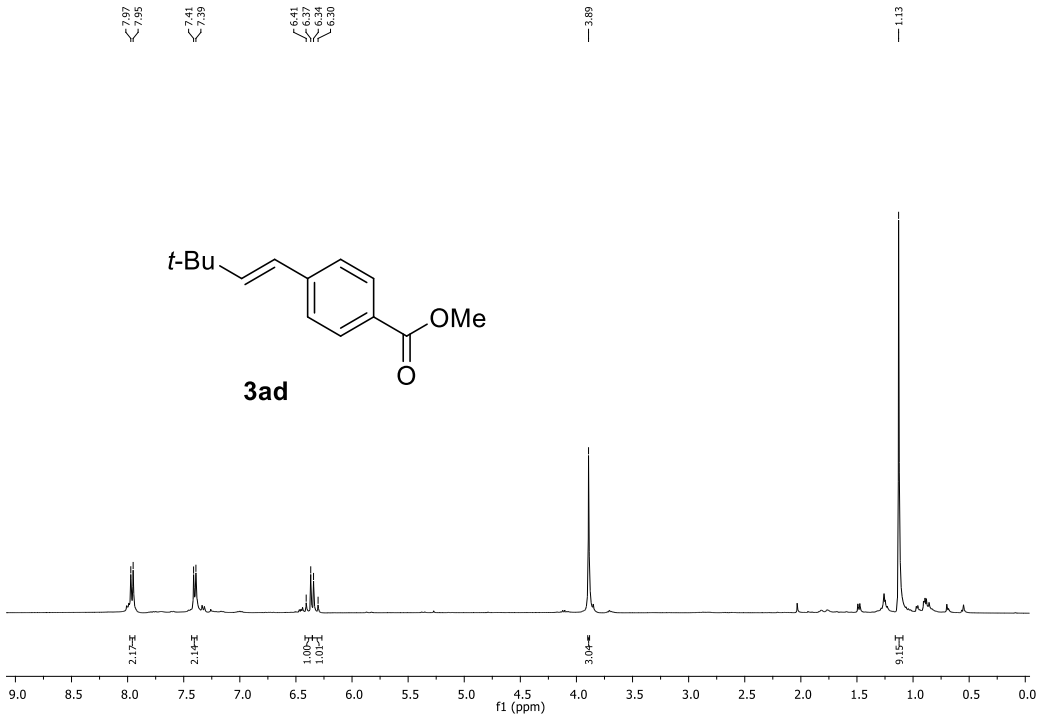
^{1}H NMR of **3ac**



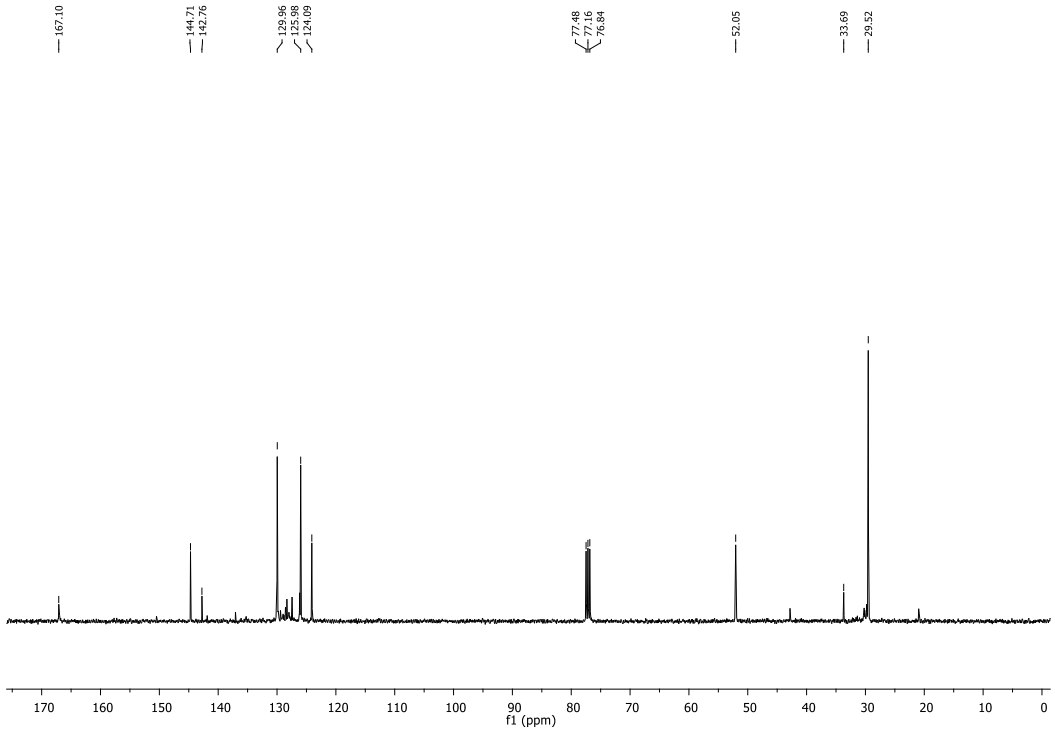
^{13}C NMR of **3ac**



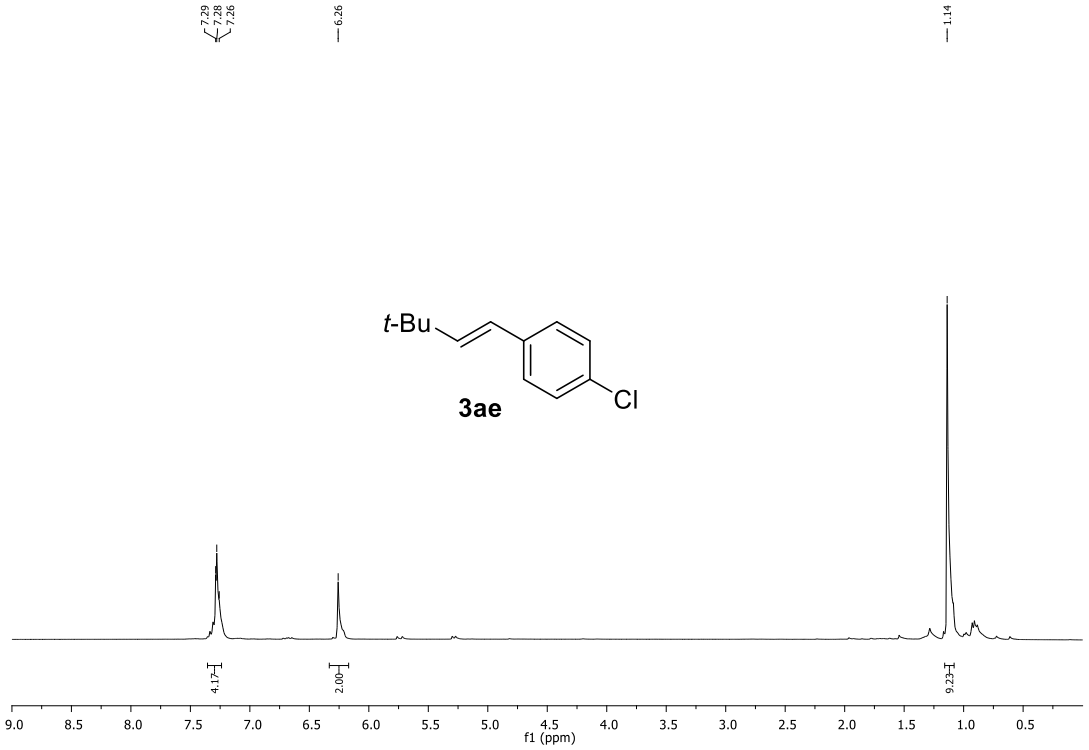
^{1}H NMR of **3ad**



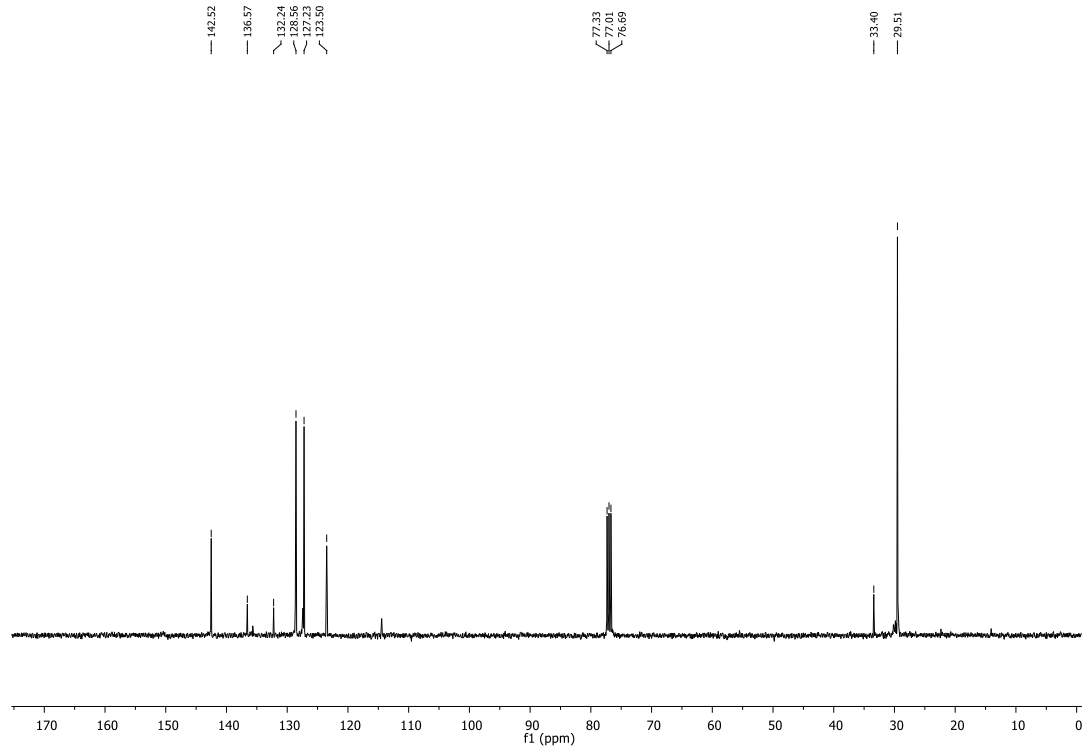
^{13}C NMR of **3ad**



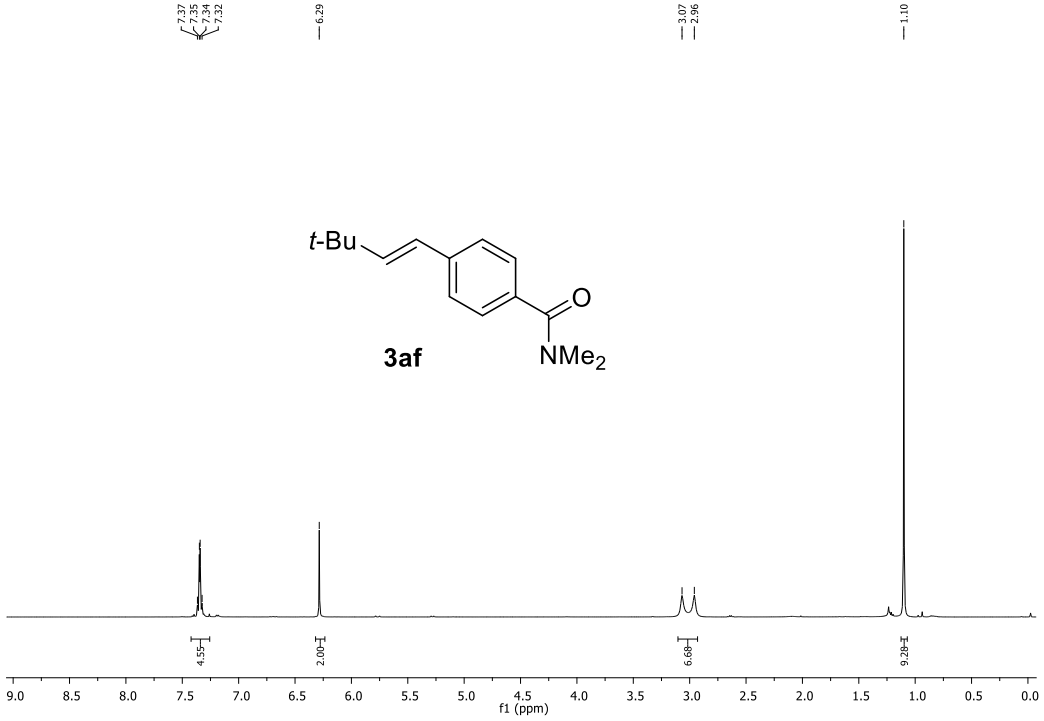
^{1}H NMR of **3ae**



^{13}C NMR of **3ae**



^{1}H NMR of **3af**



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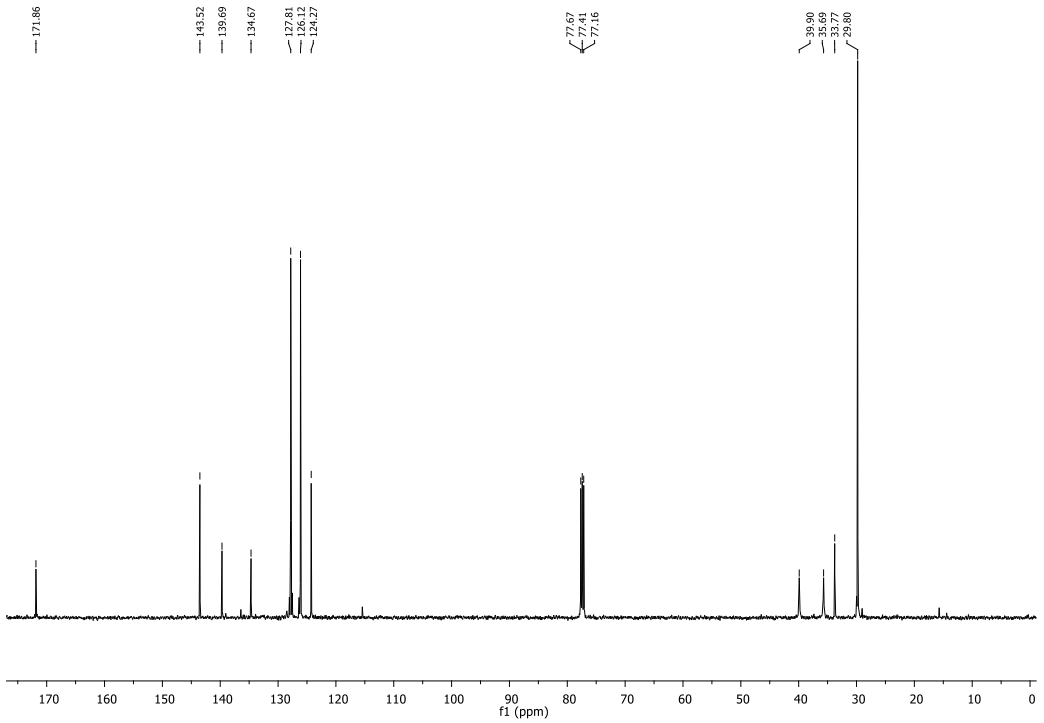
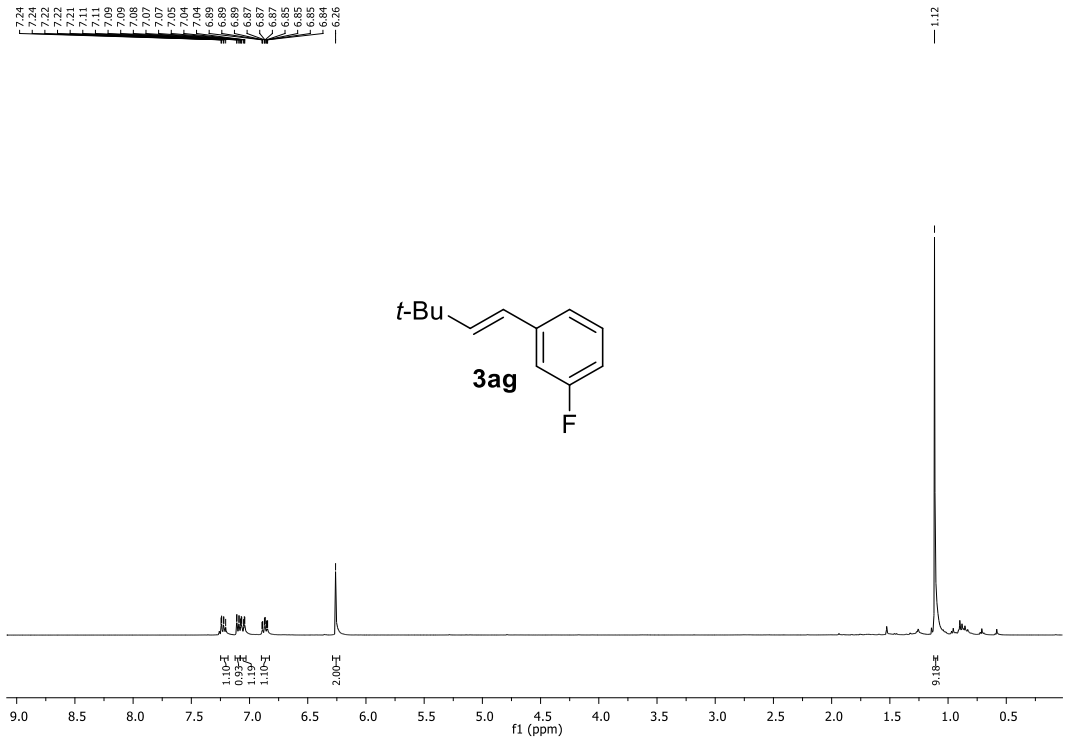
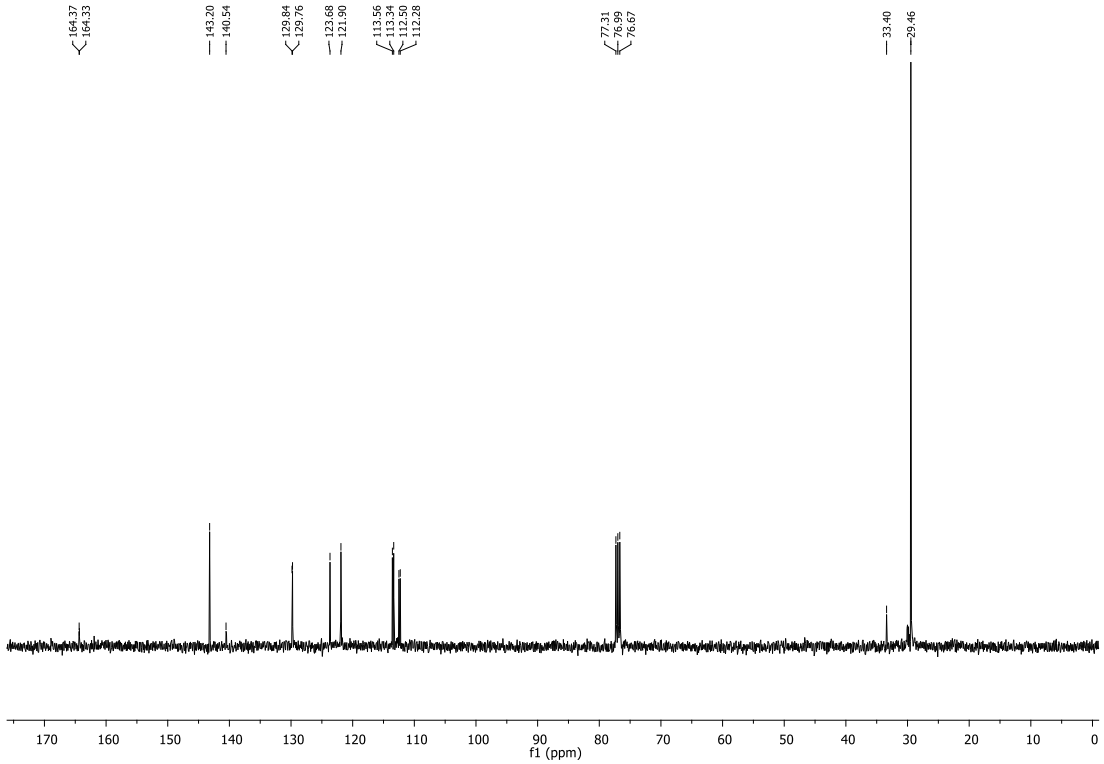


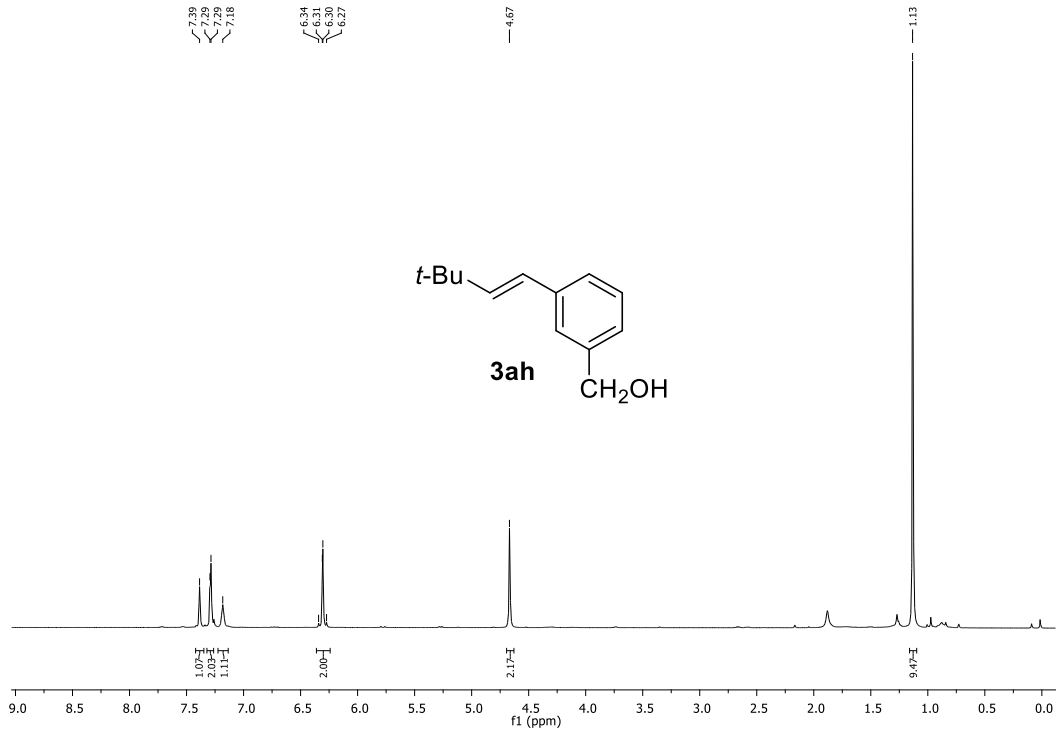
^{1}H NMR of **3ag**



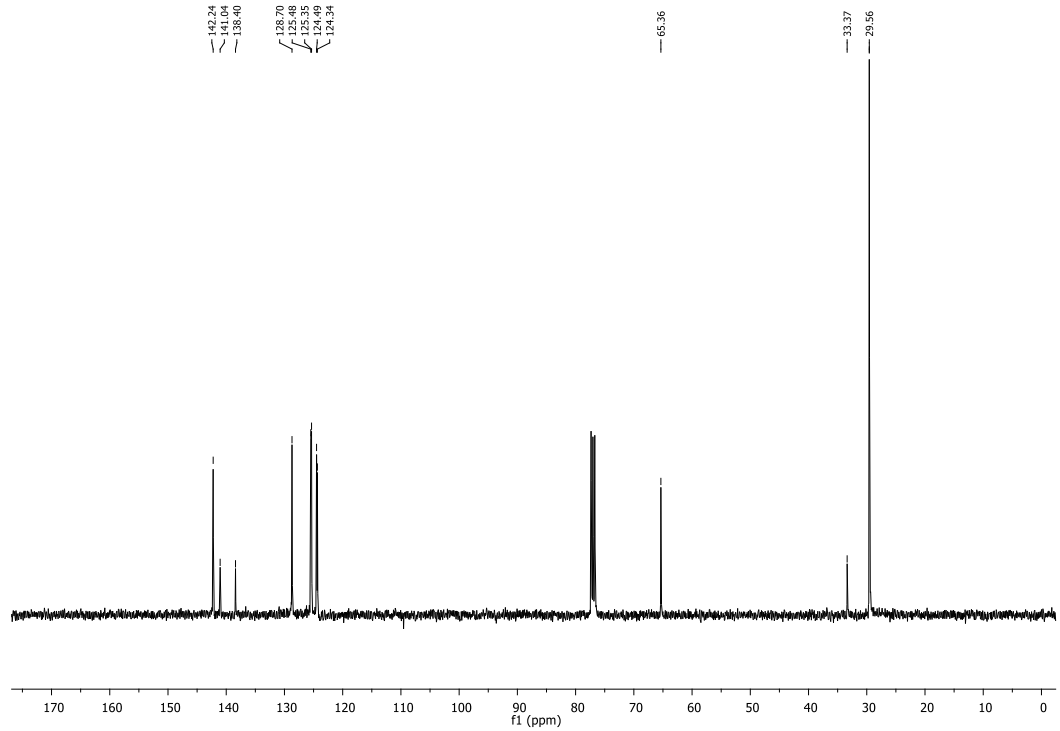
^{13}C NMR of **3ag**



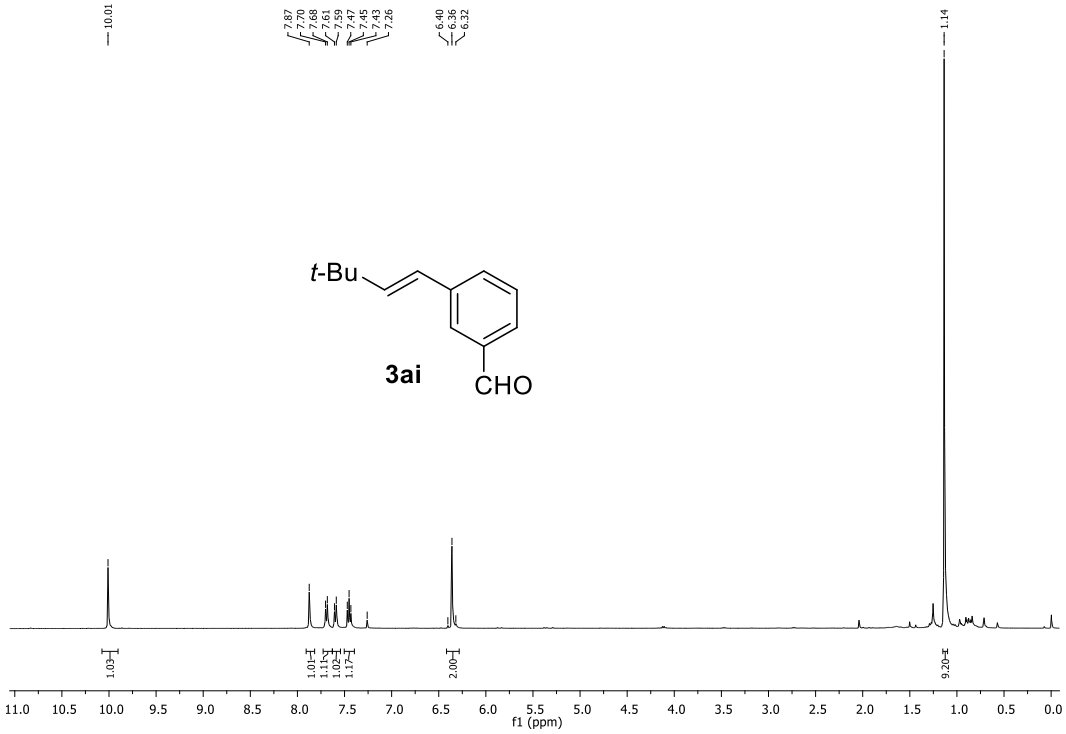
^{1}H NMR of **3ah**



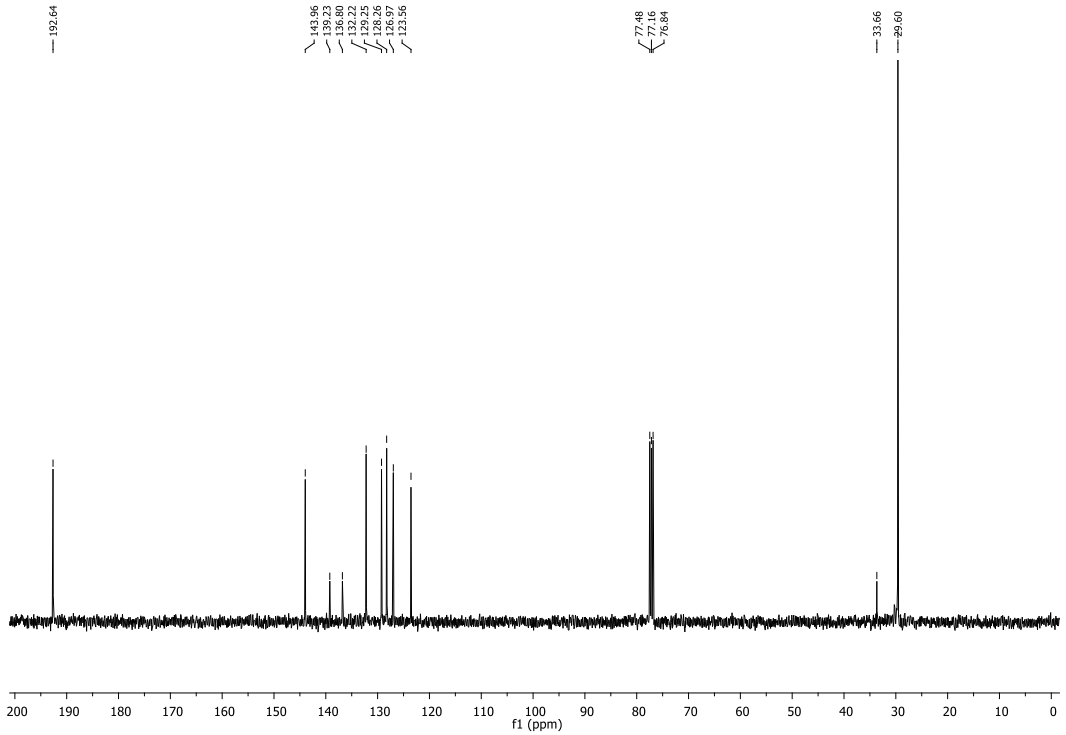
^{13}C NMR of **3ah**



^{1}H NMR of **3ai**



^{13}C NMR of **3ai**



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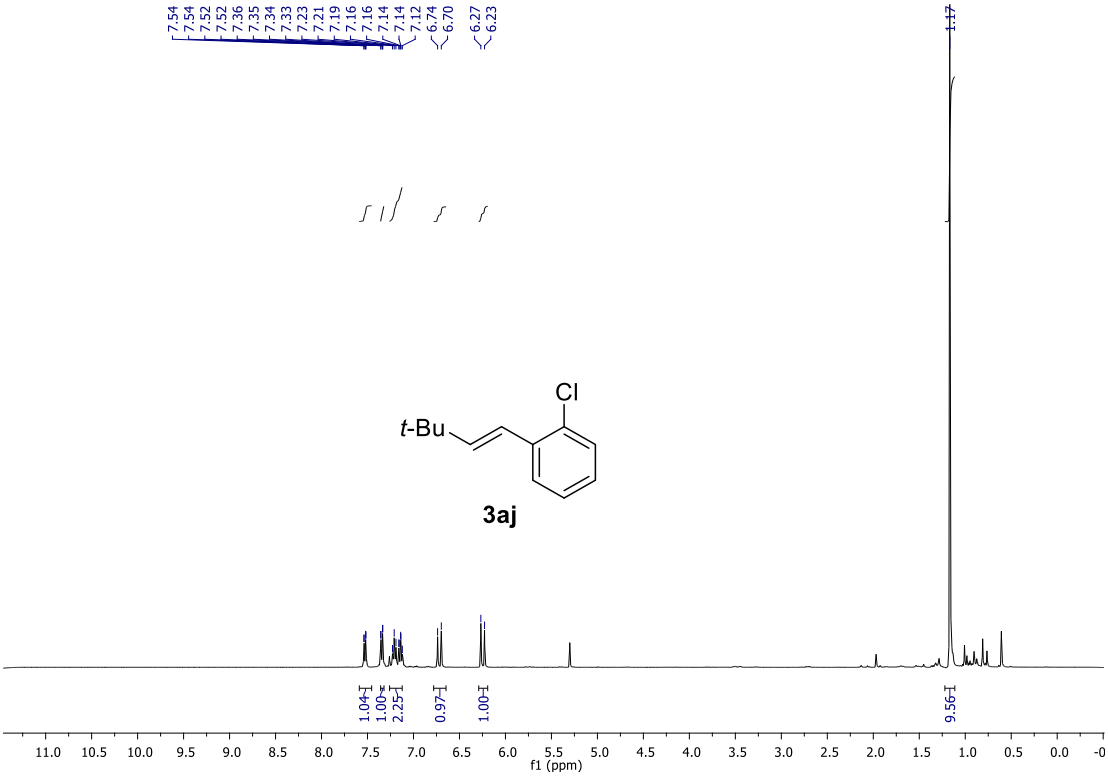

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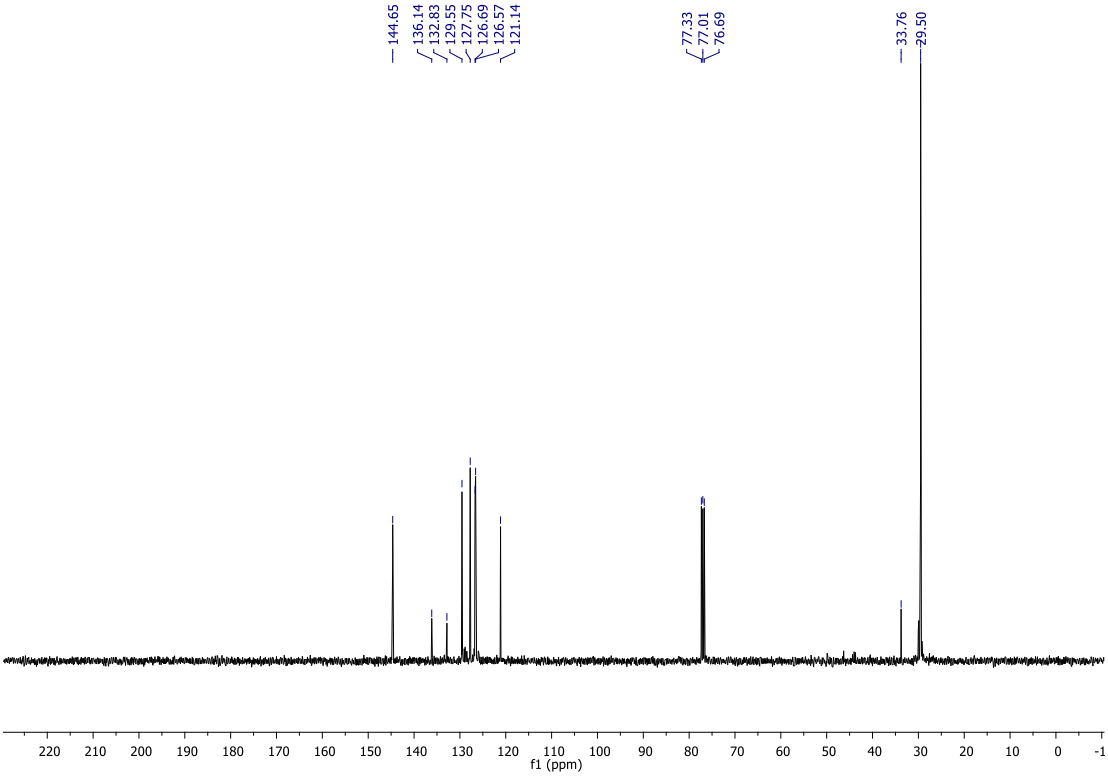

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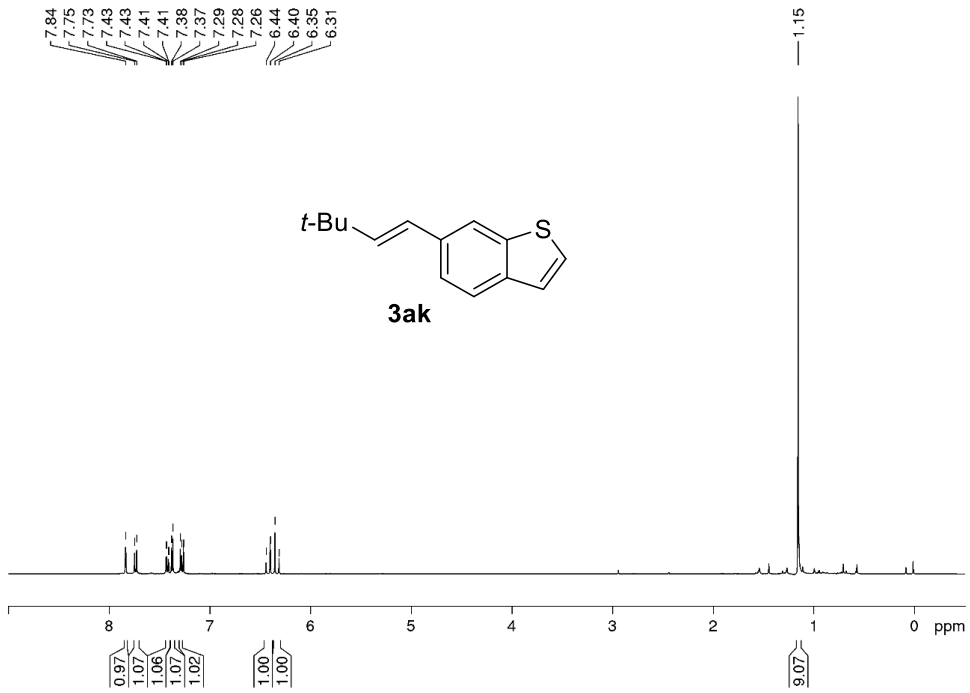
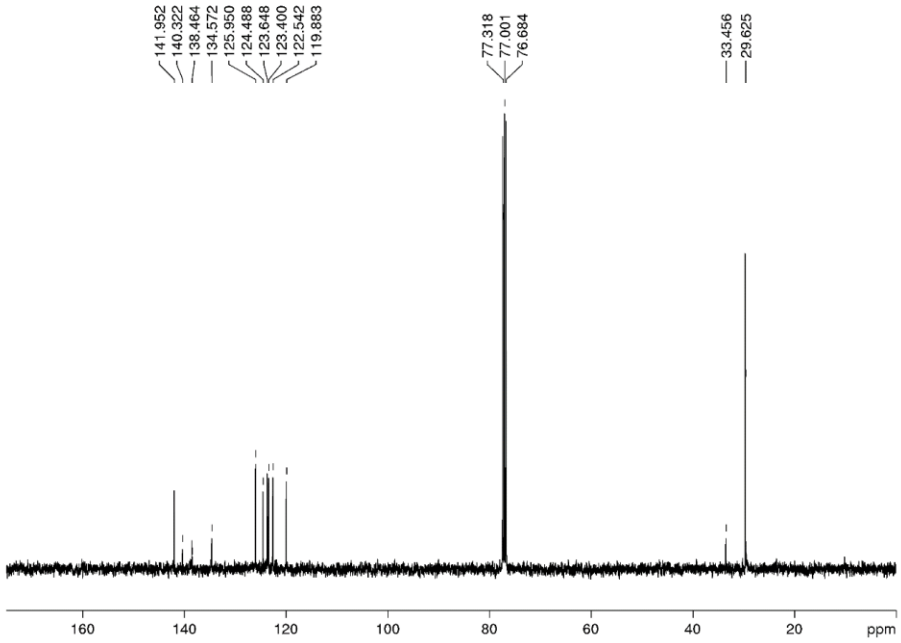
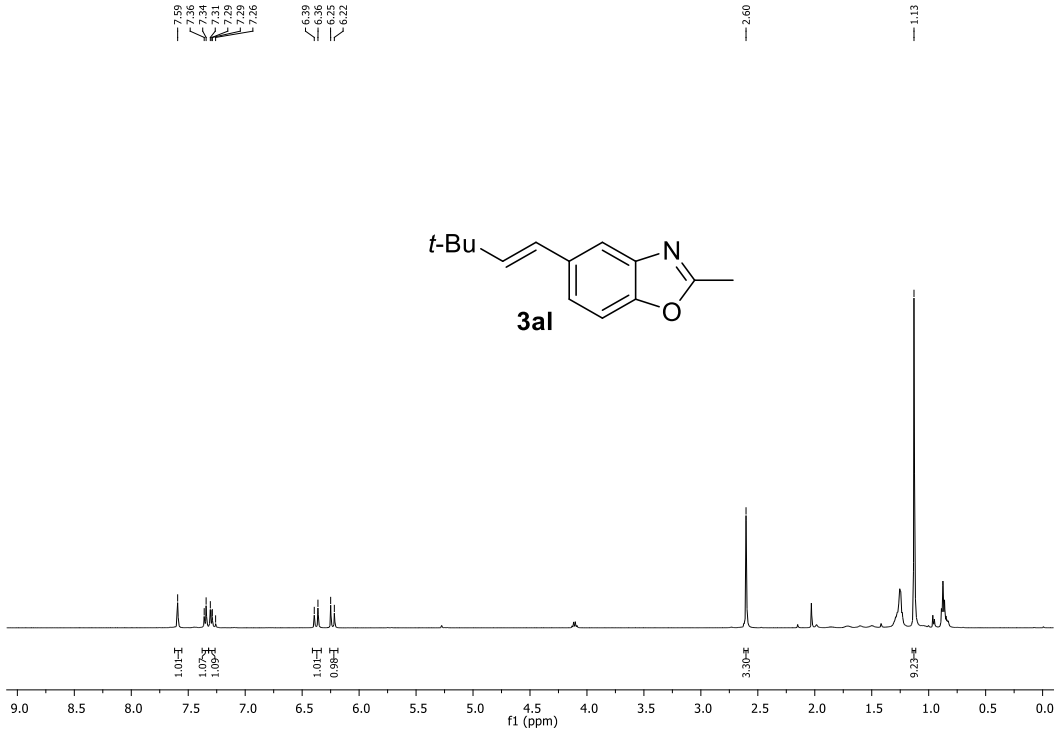


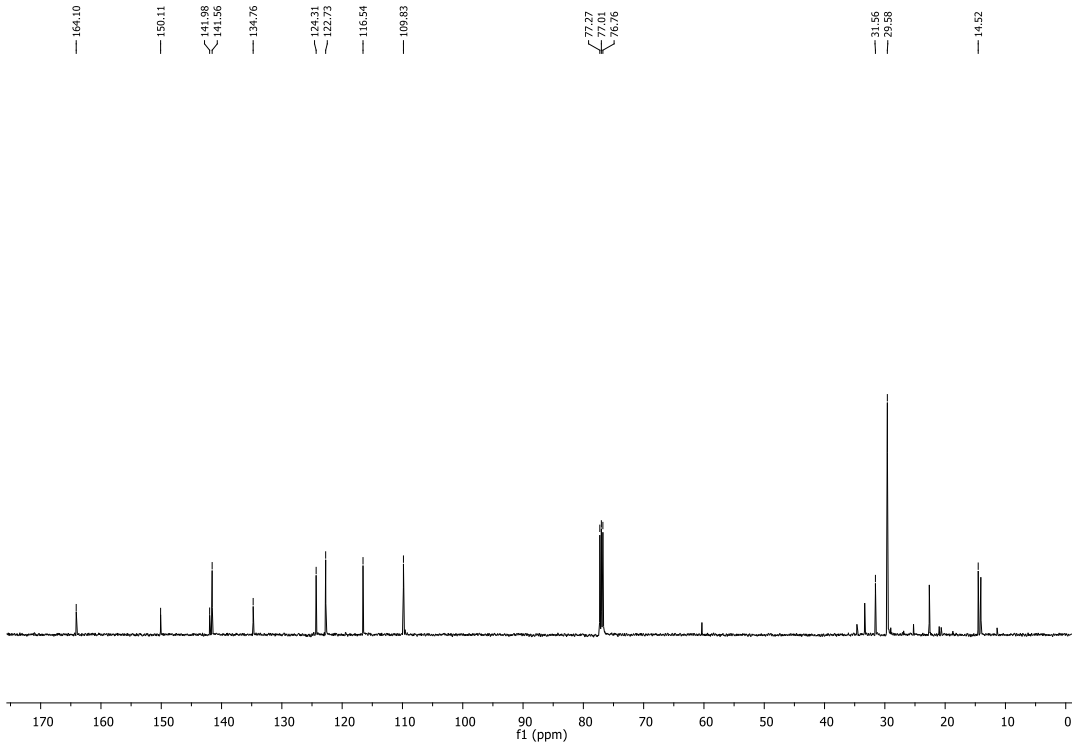
^{13}C NMR of **3ak**



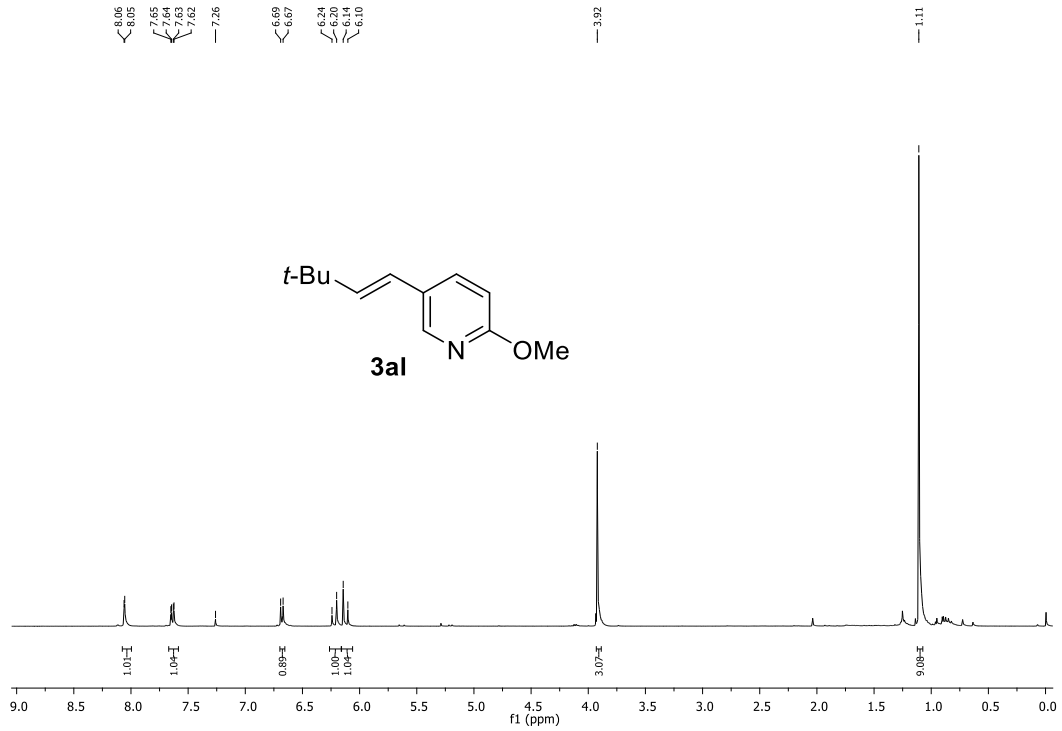
^{1}H NMR of **3al**



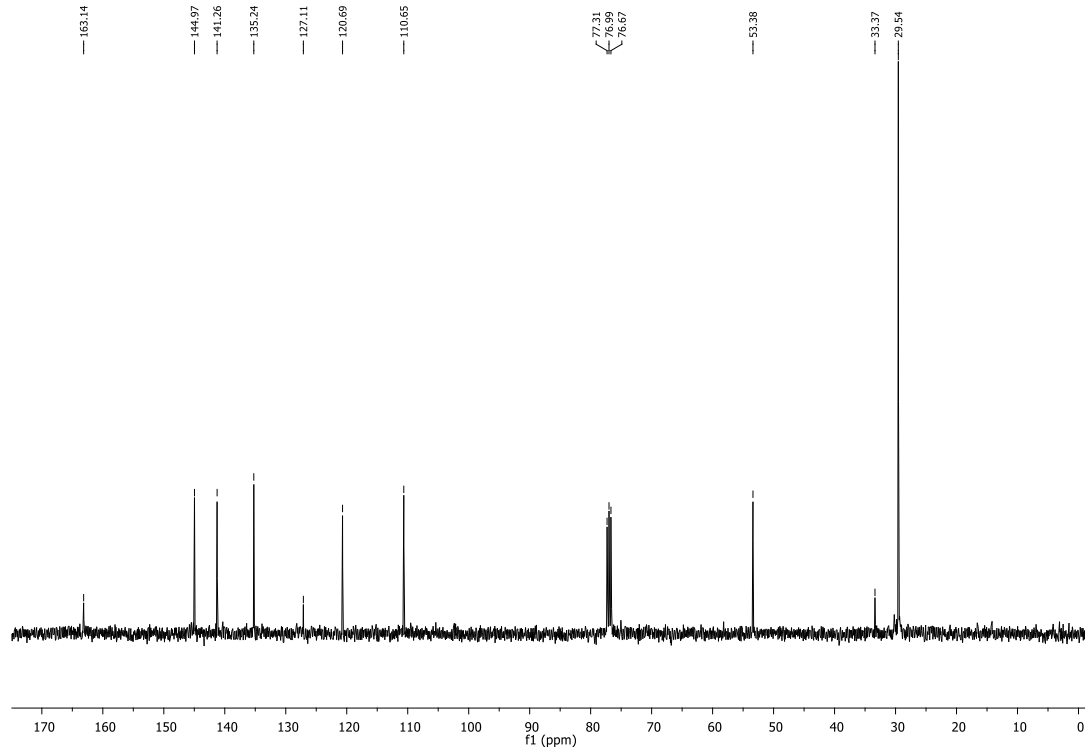
^{13}C NMR of **3al**



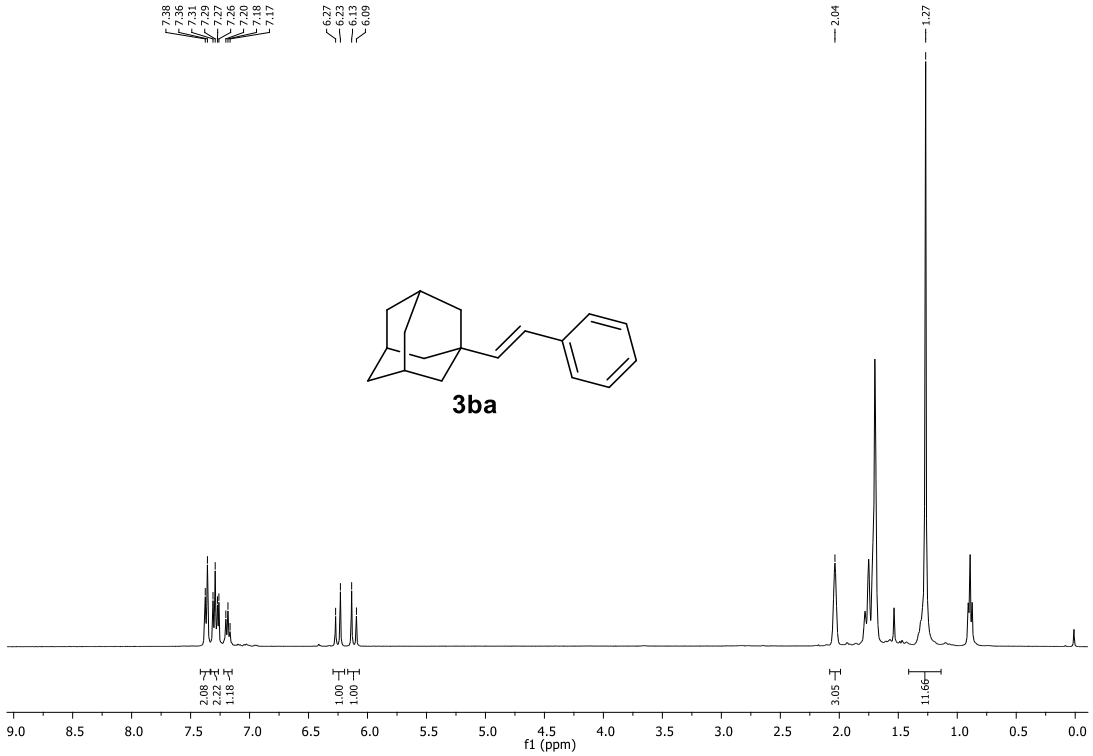
^{1}H NMR of **3am**



^{13}C NMR of **3am**



^{1}H NMR of **3ba**



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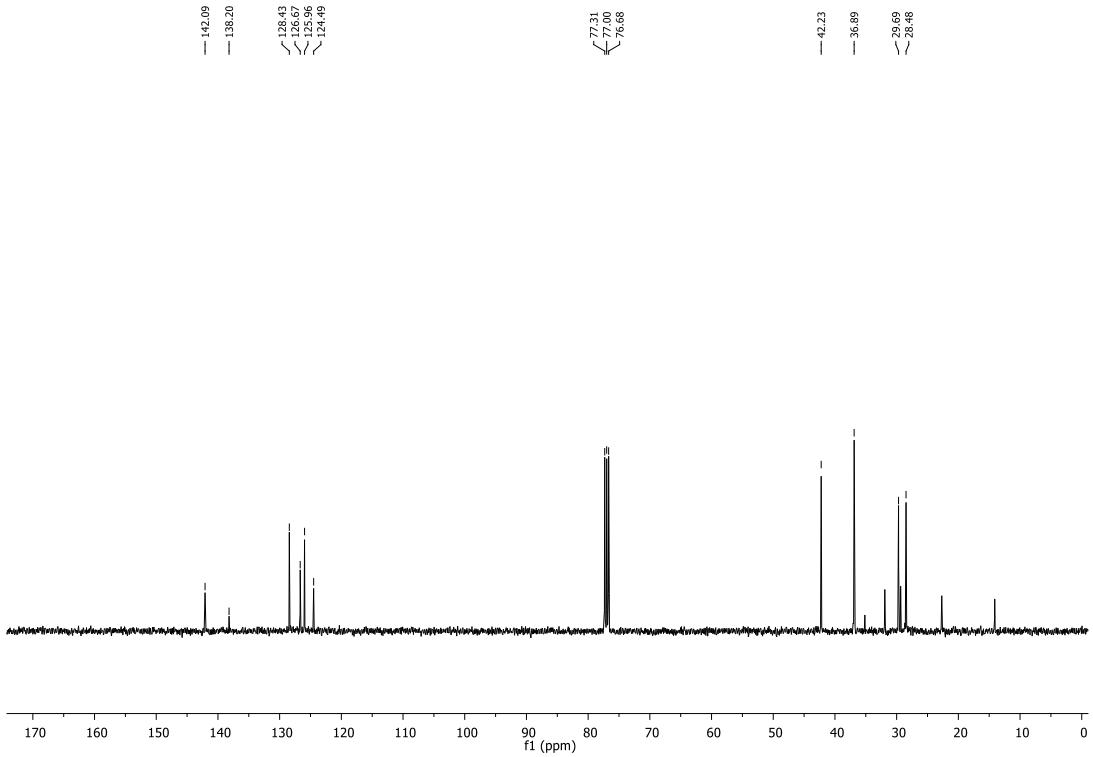
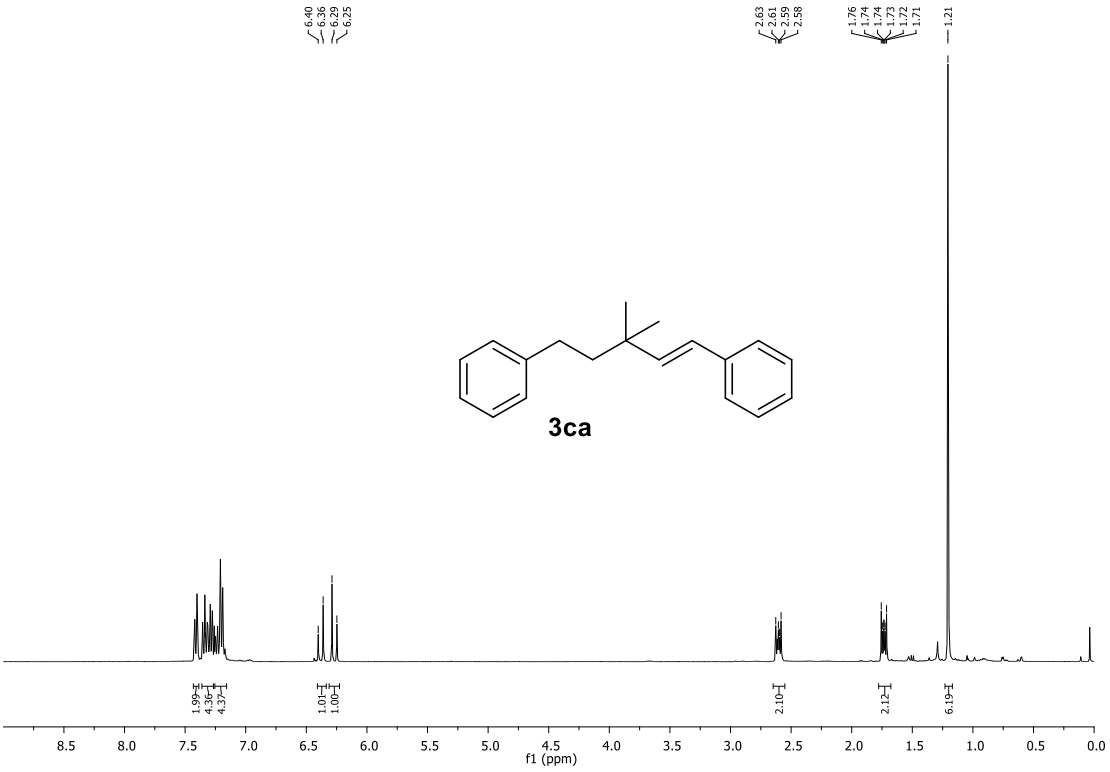
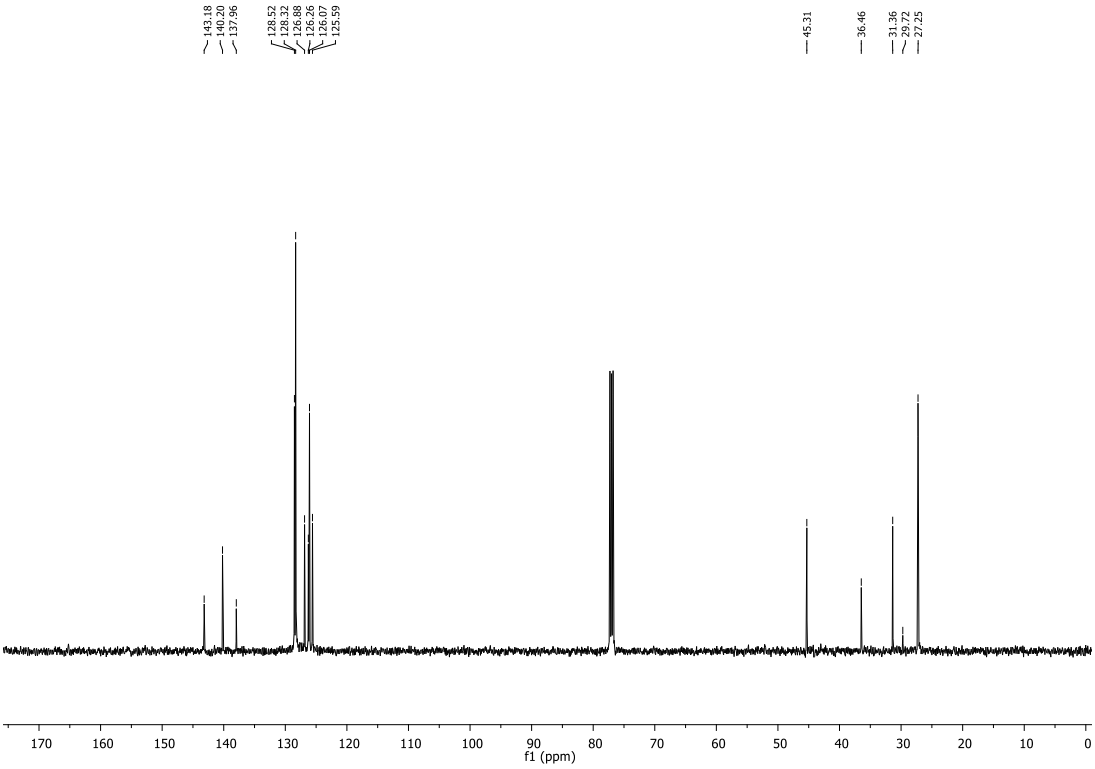


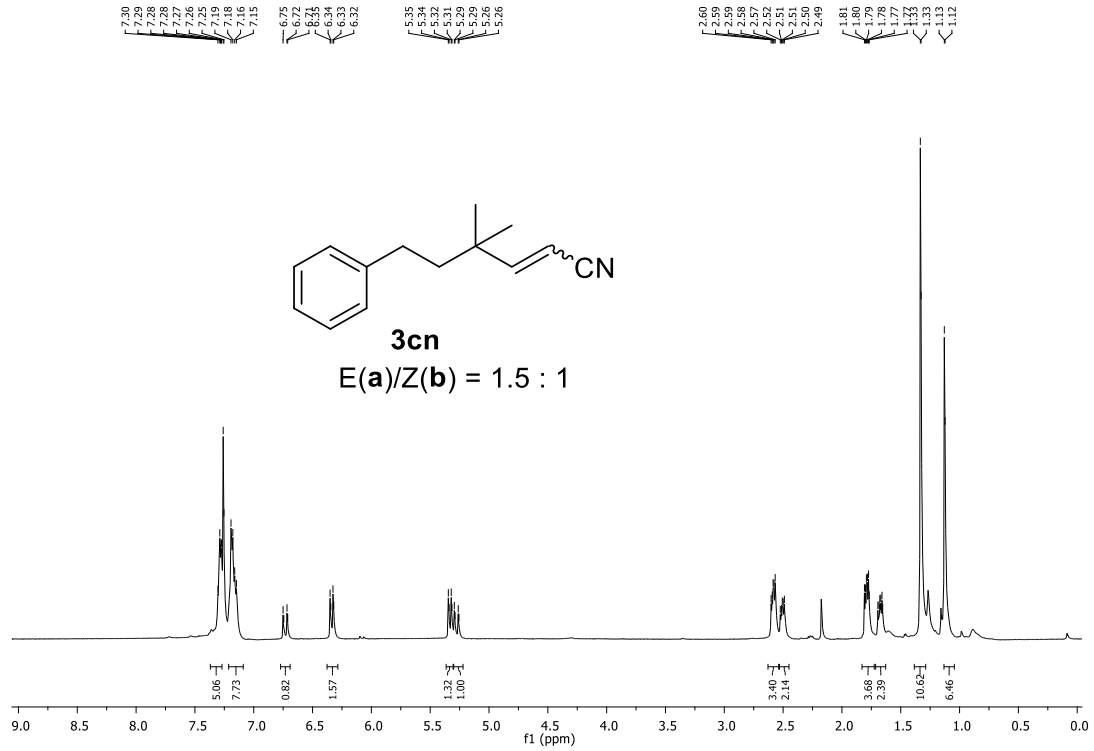
^{1}H NMR of **3ca**



^{13}C NMR of **3ca**



^{1}H NMR of **3cn**



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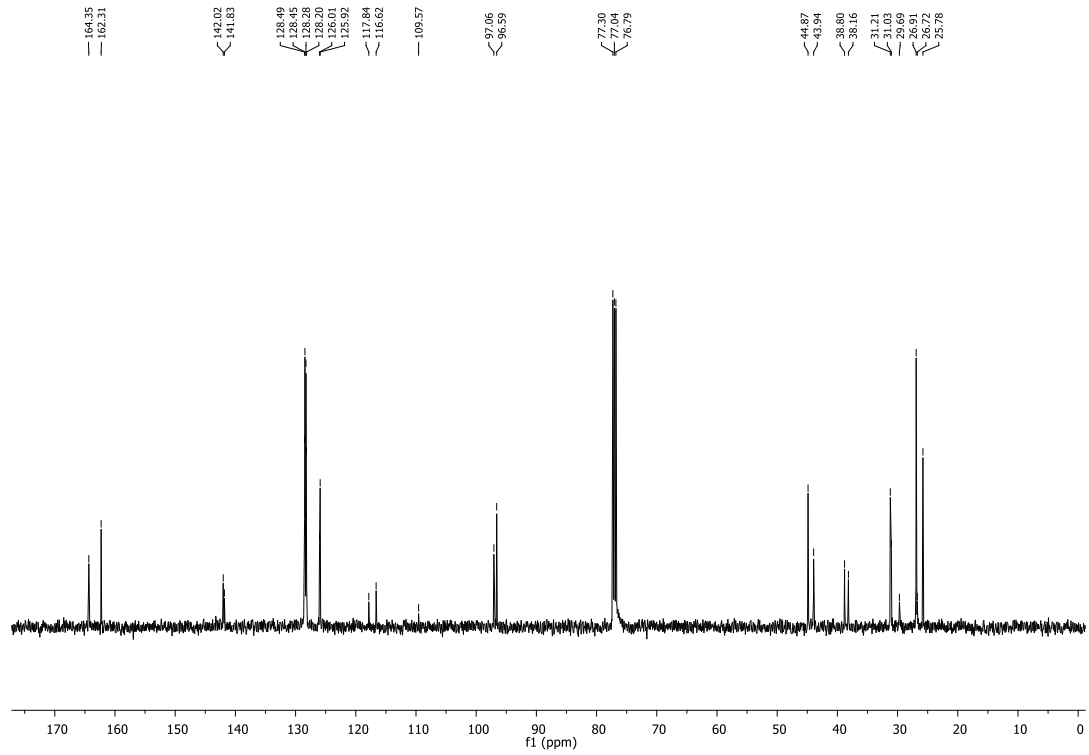
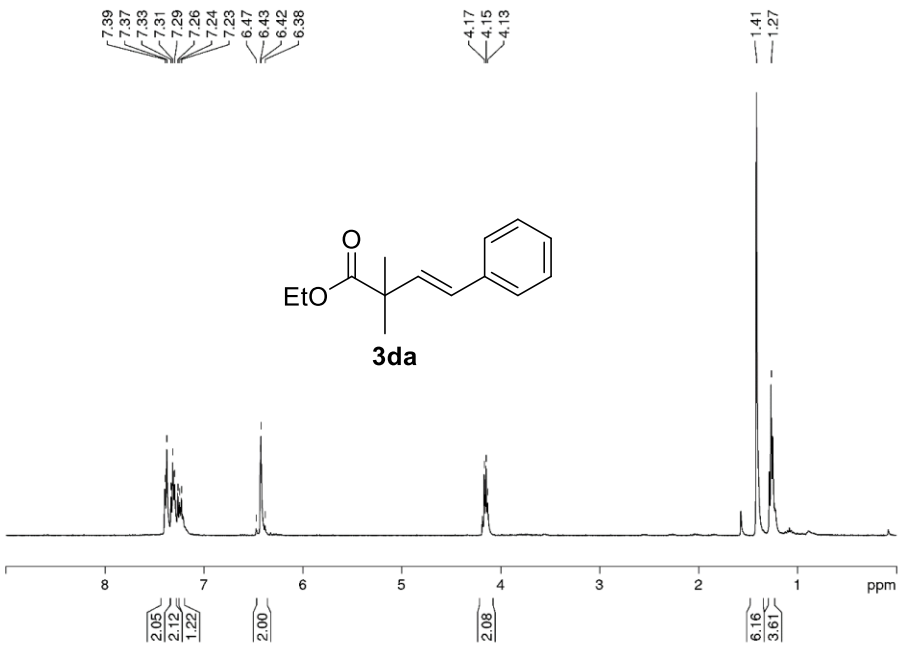
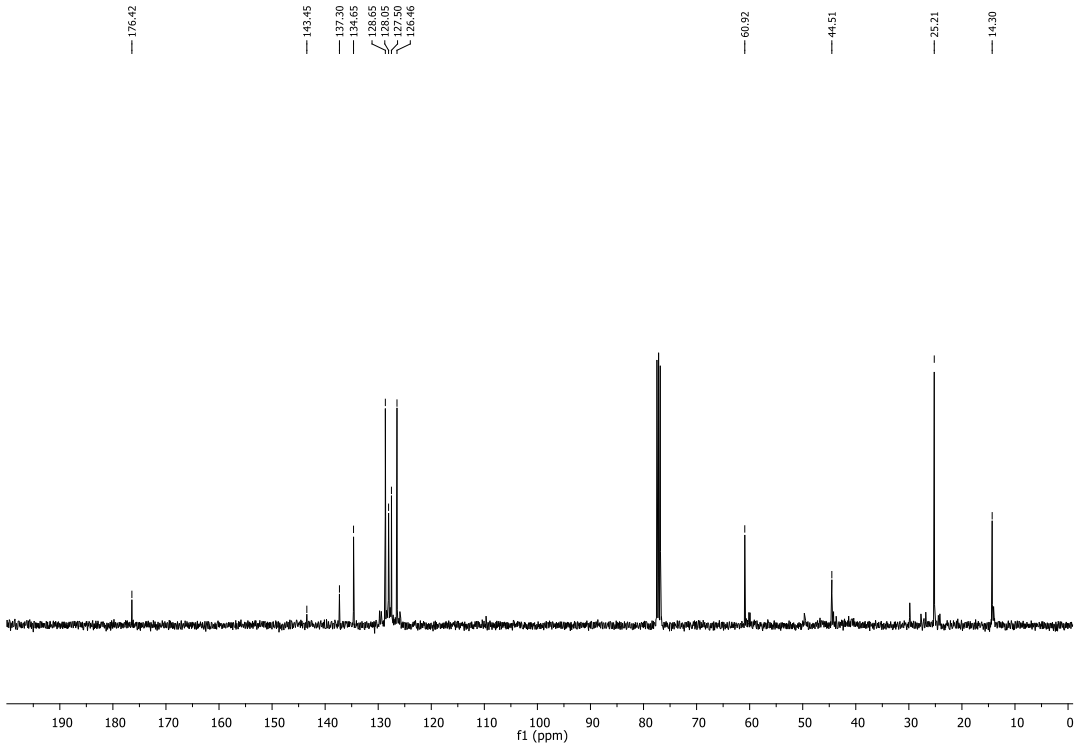


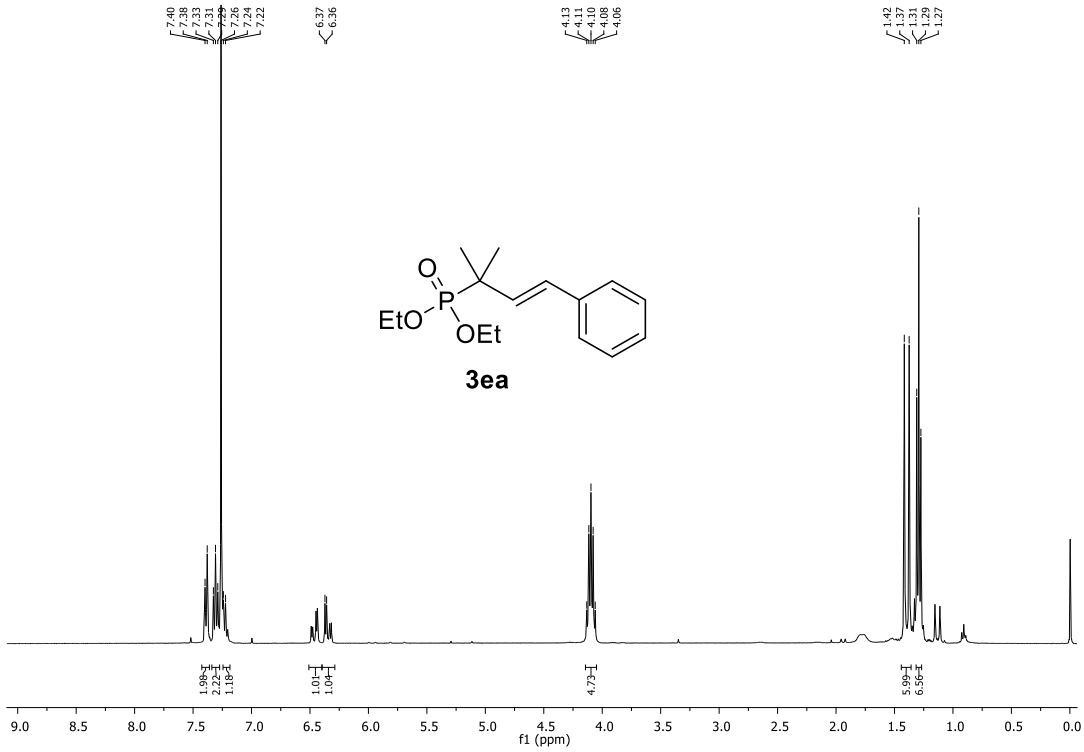
^{1}H NMR of **3da**



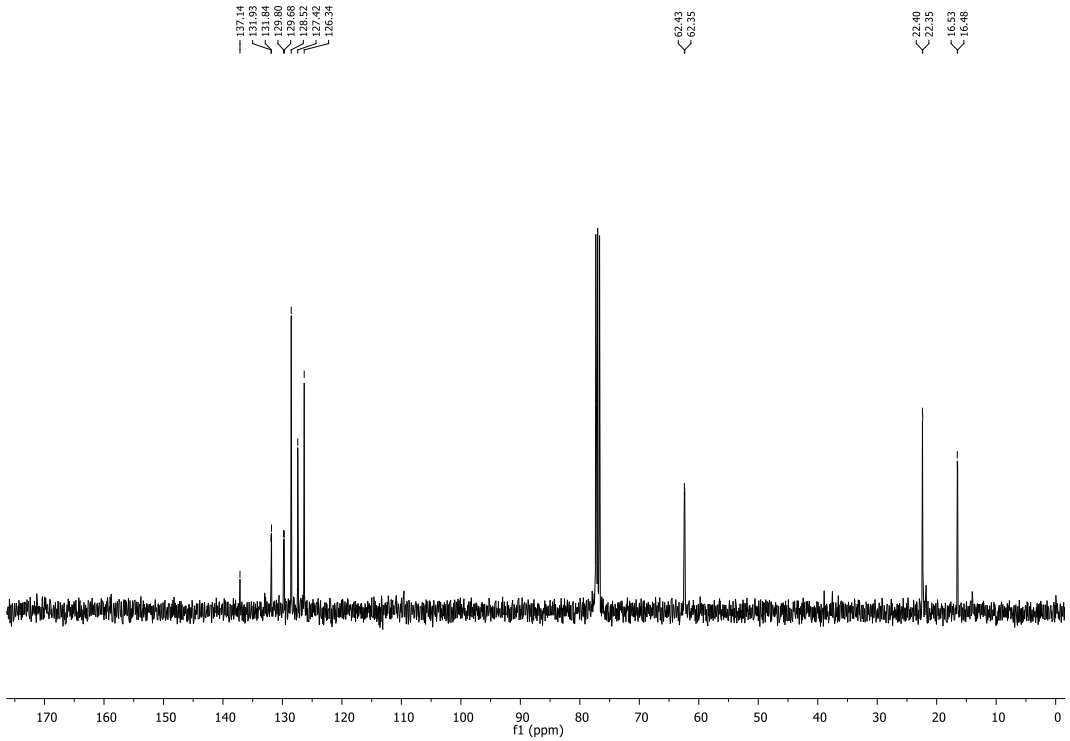
^{13}C NMR of **3da**



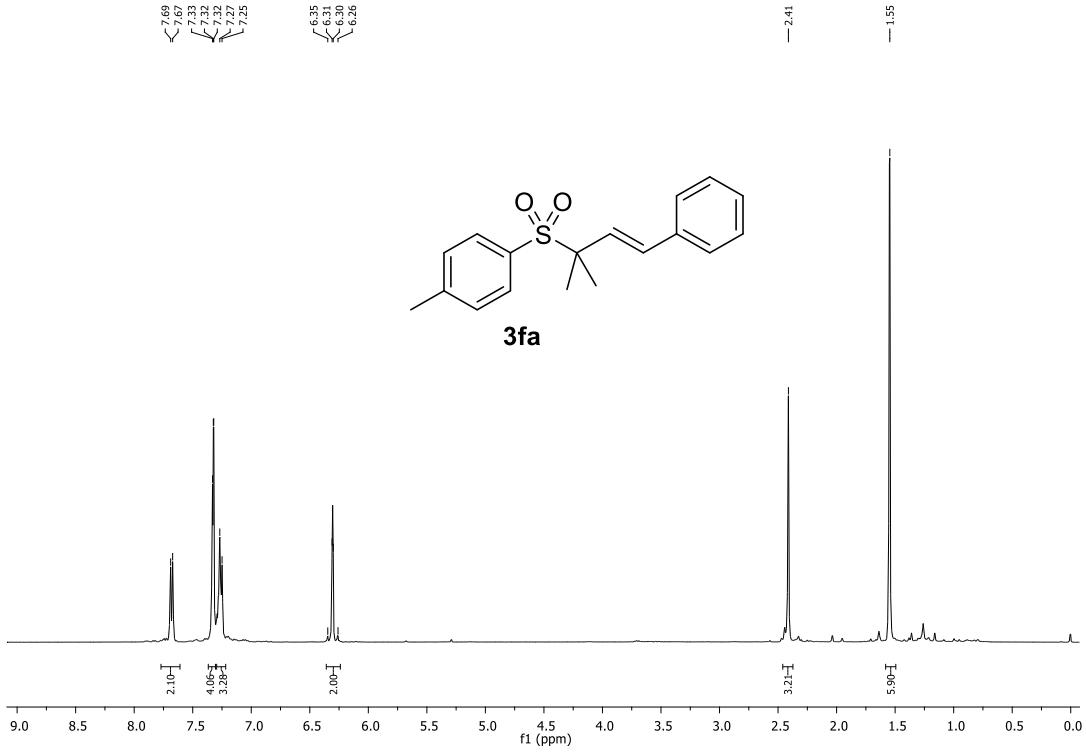
^{1}H NMR of **3ea**



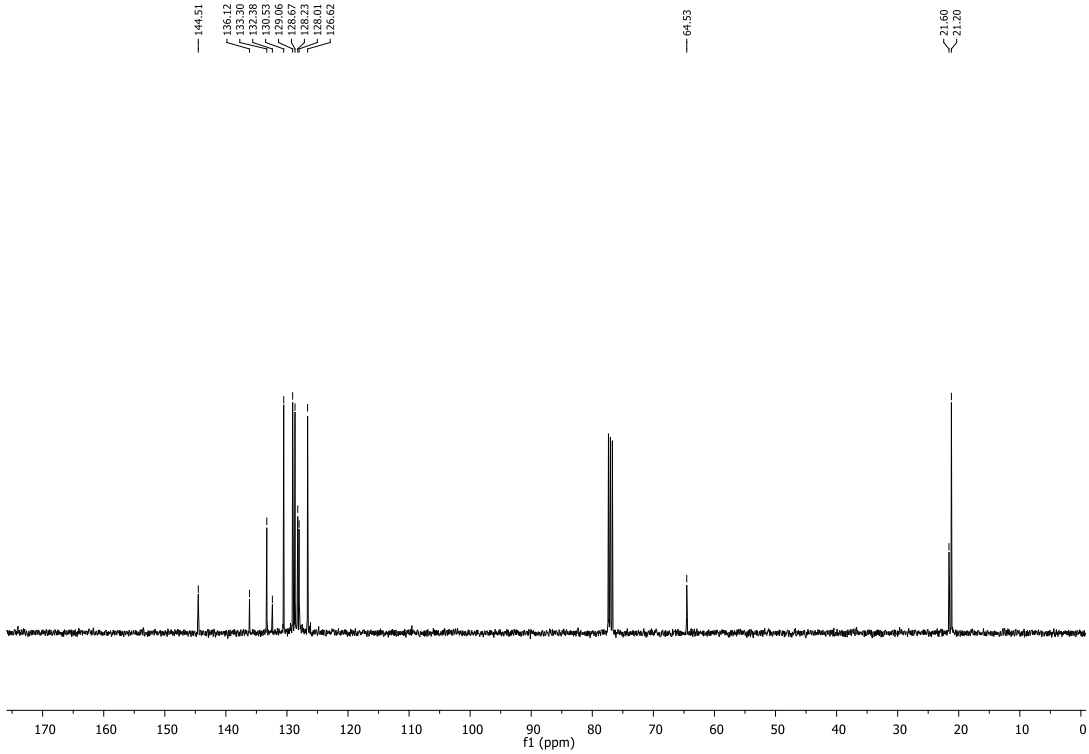
^{13}C NMR of **3ea**



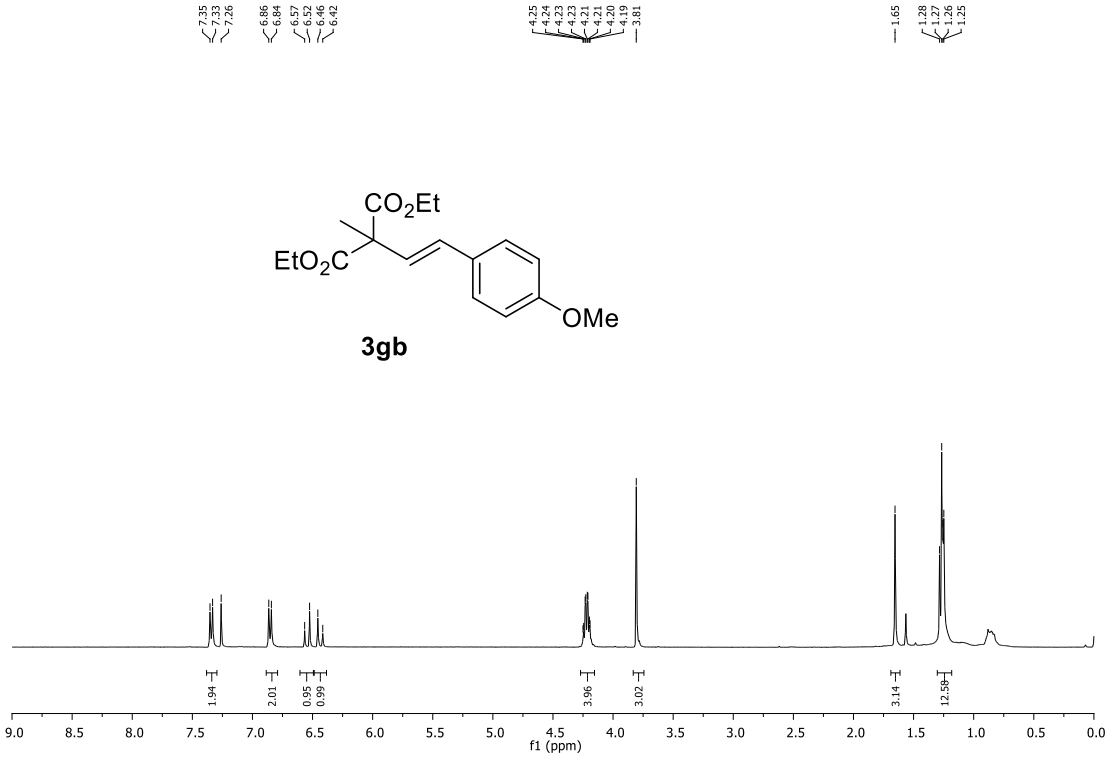
^{1}H NMR of **3fa**



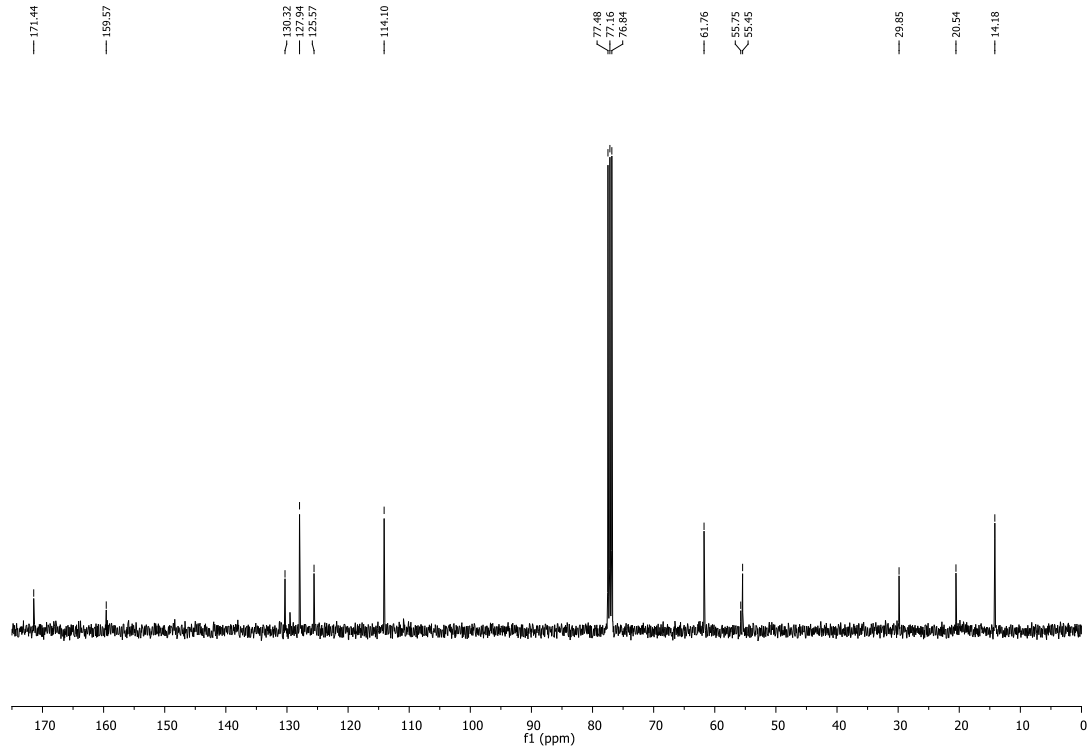
^{13}C NMR of **3fa**



^{1}H NMR of **3gb**



^{13}C NMR of **3gb**



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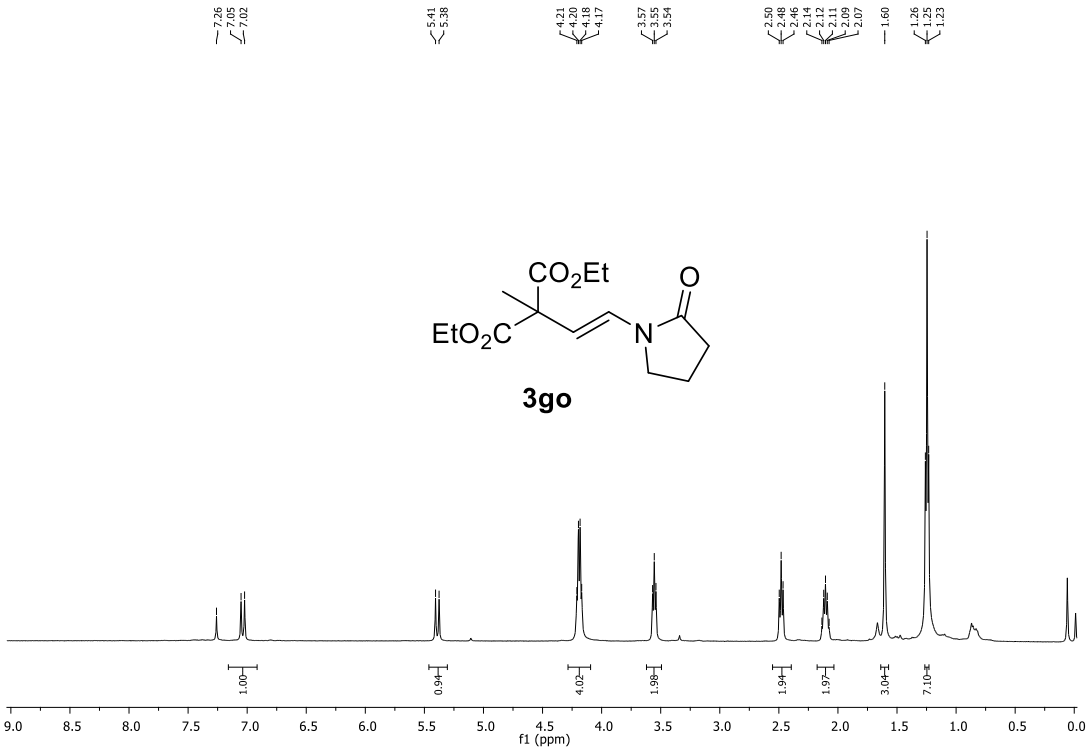

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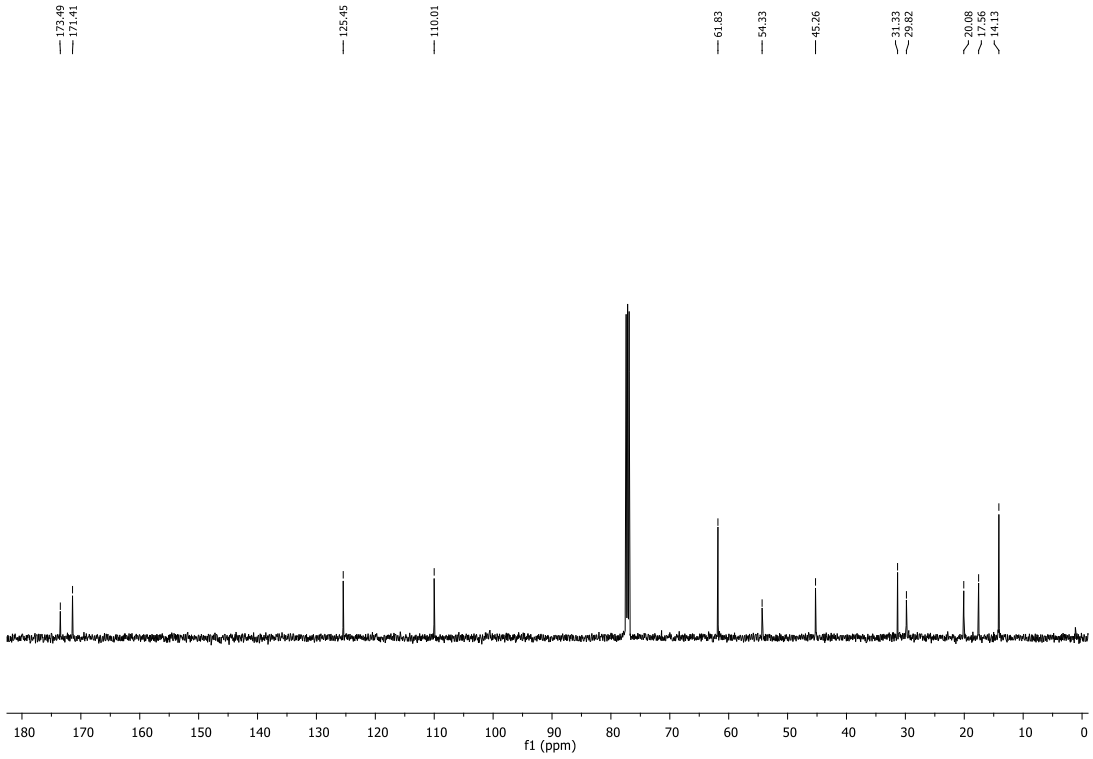
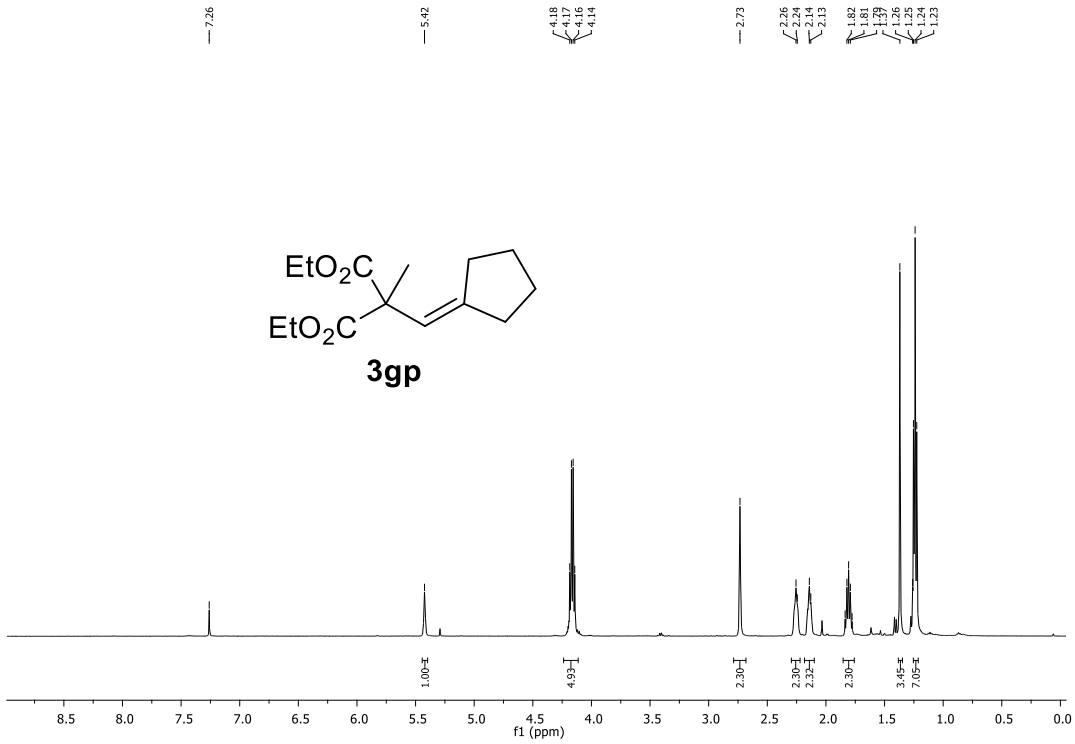
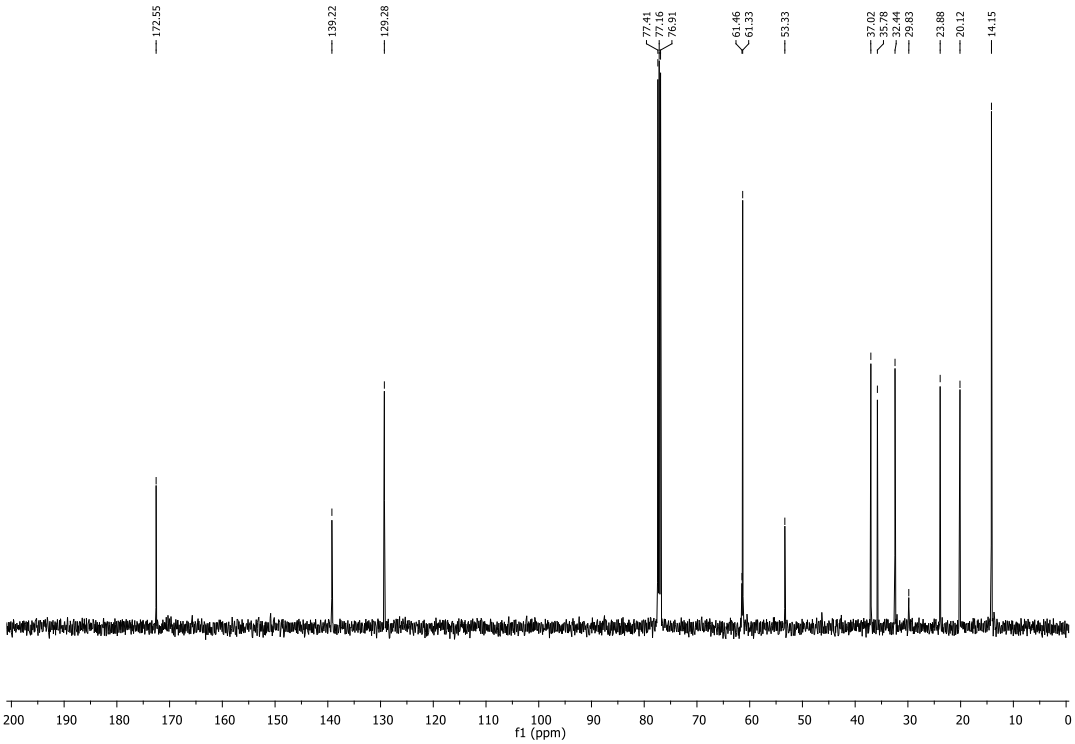


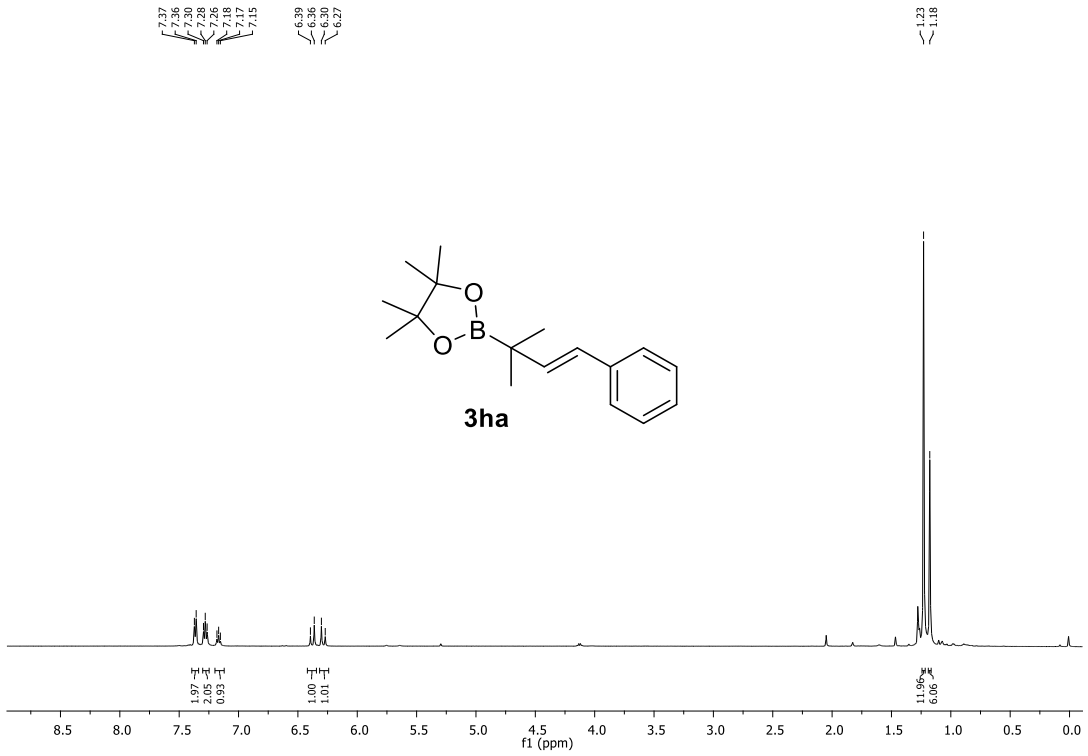
^{1}H NMR of **3gp**



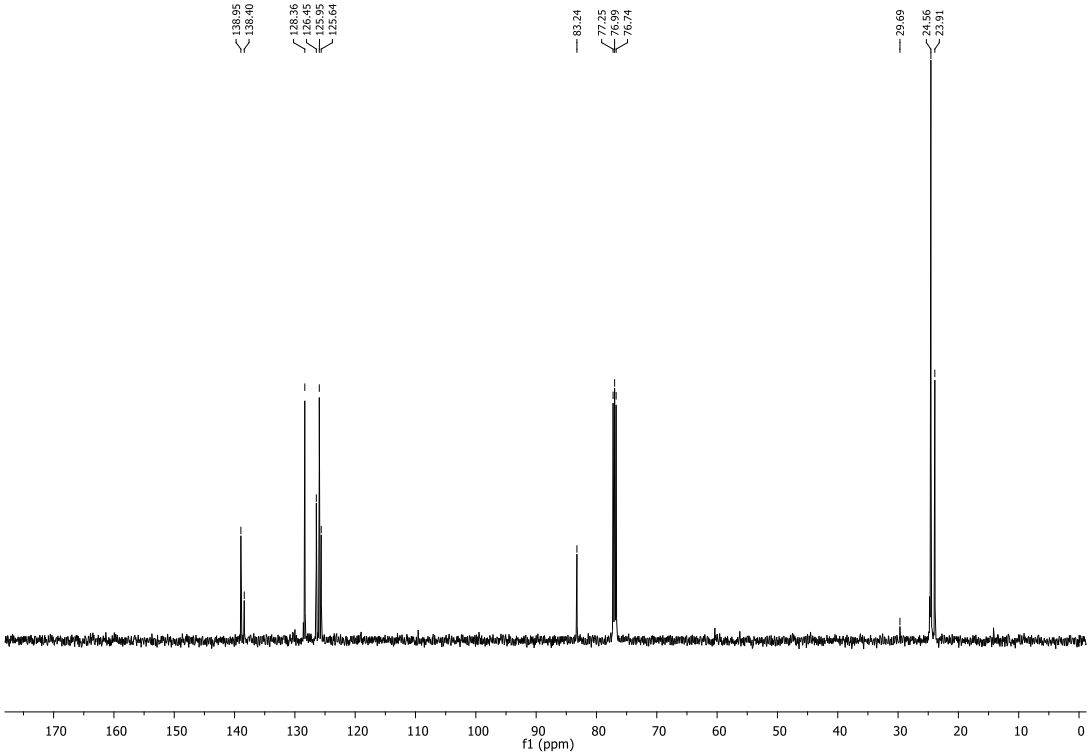
^{13}C NMR of **3gp**



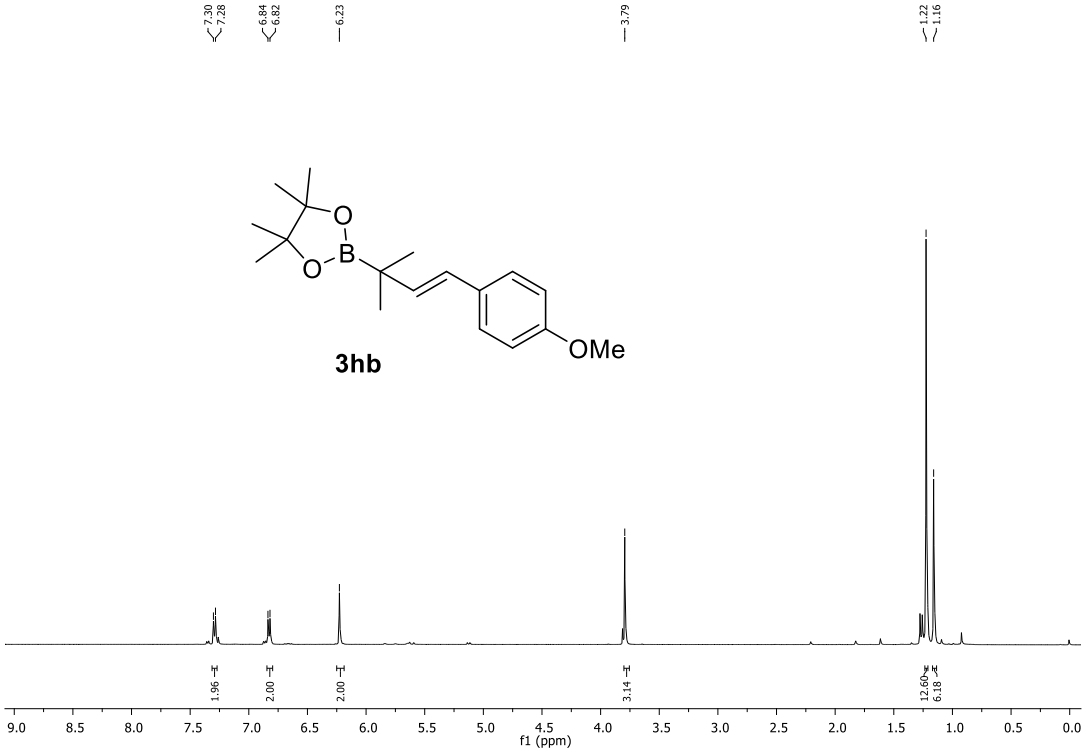
^{1}H NMR of **3ha**



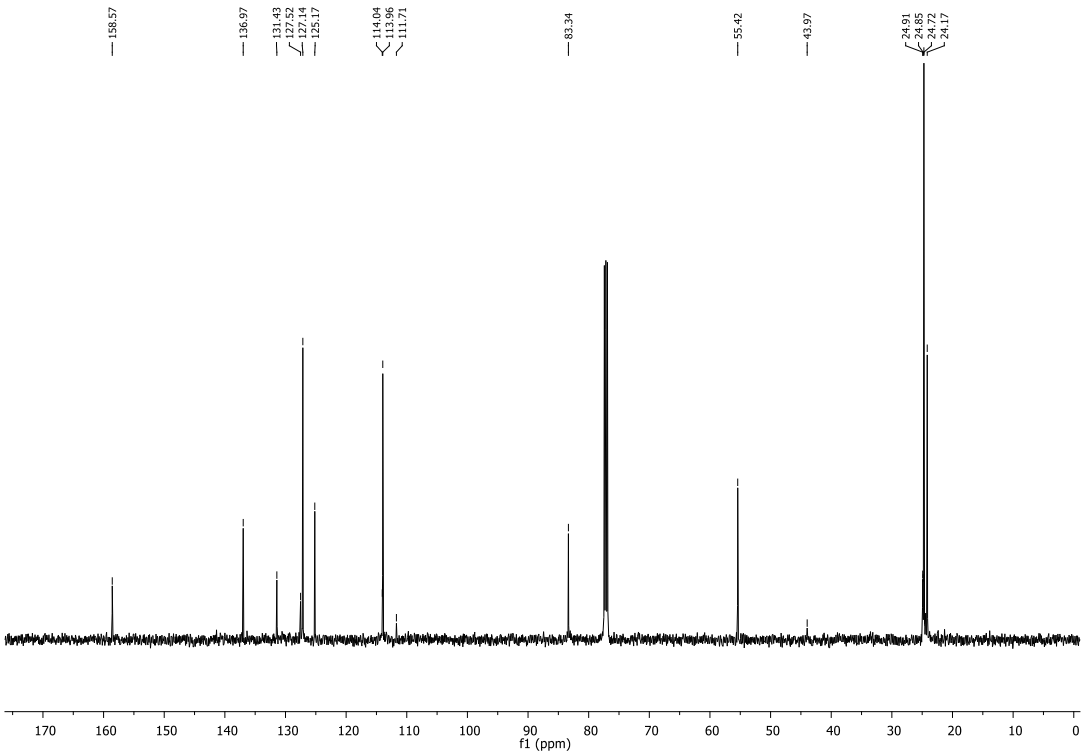
^{13}C NMR of **3ha**



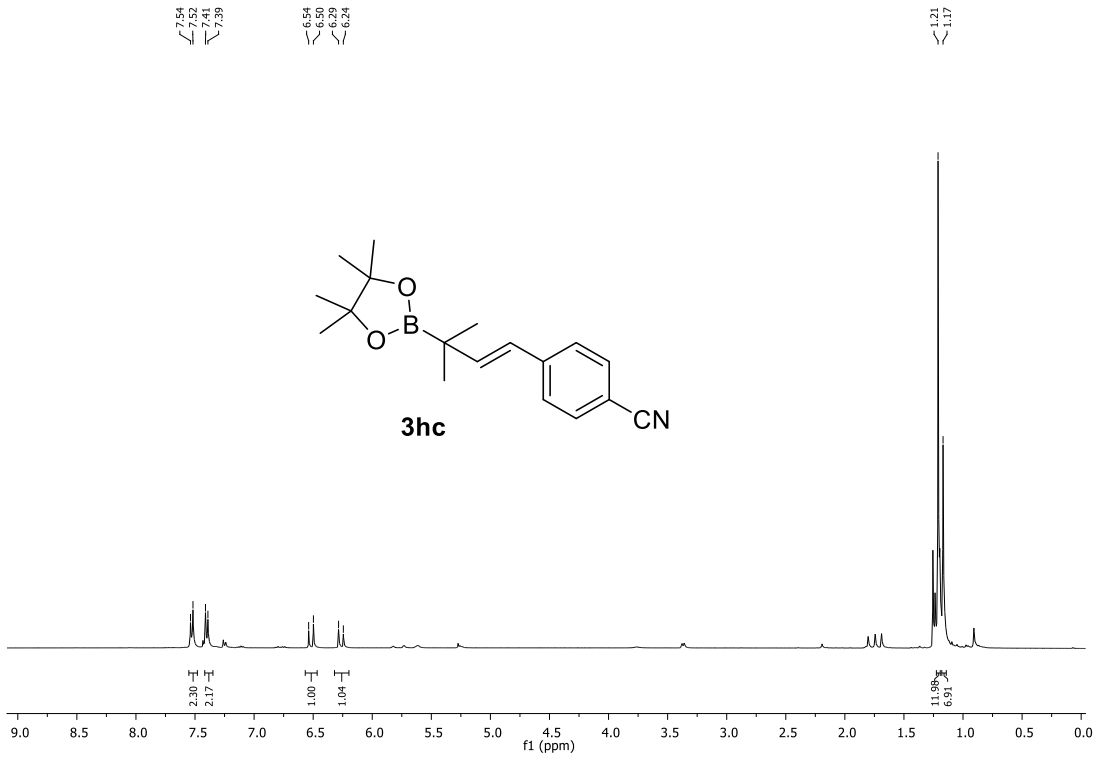
^{1}H NMR of **3hb**



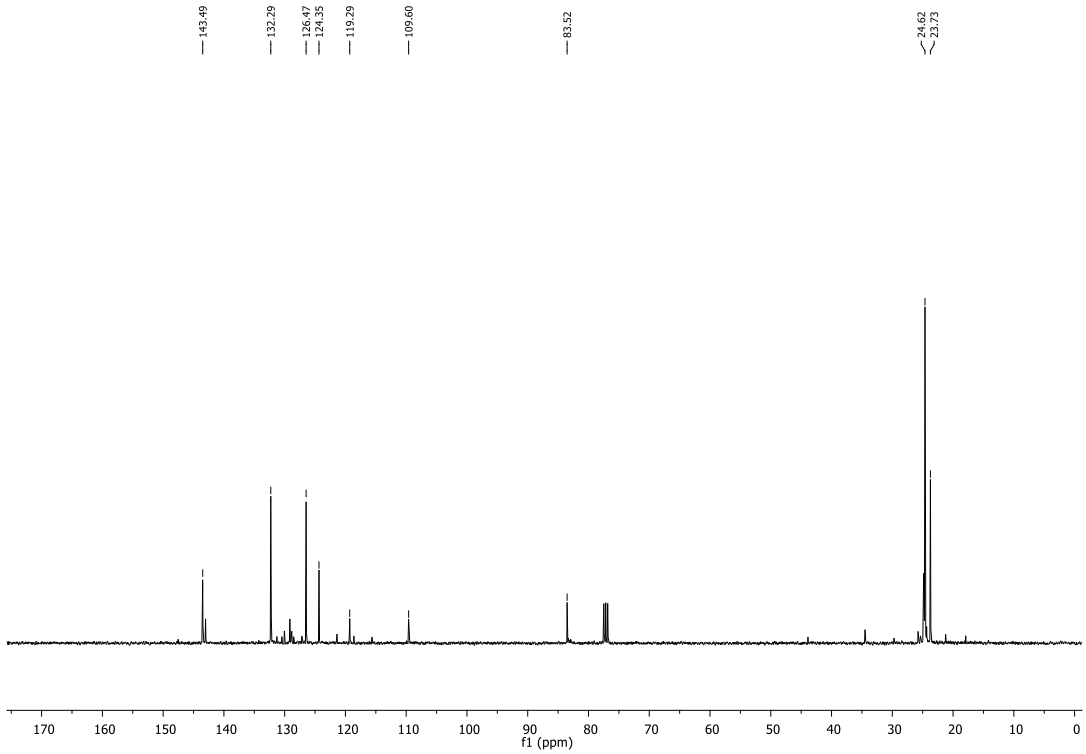
^{13}C NMR of **3hb**



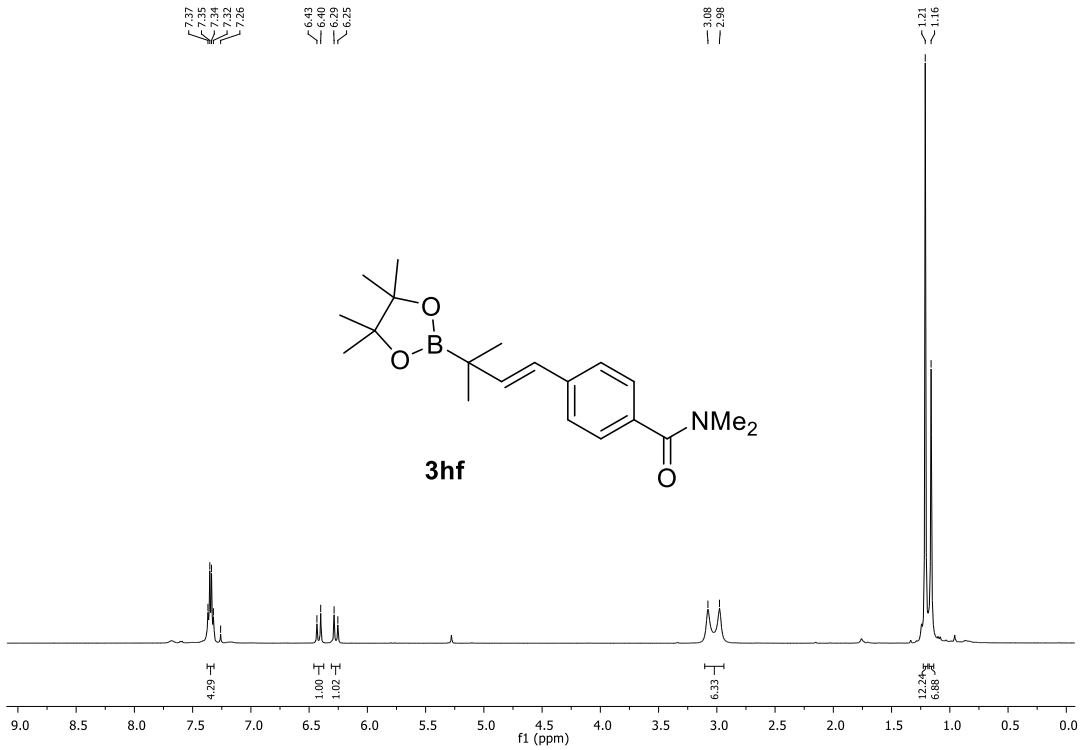
^{1}H NMR of **3hc**



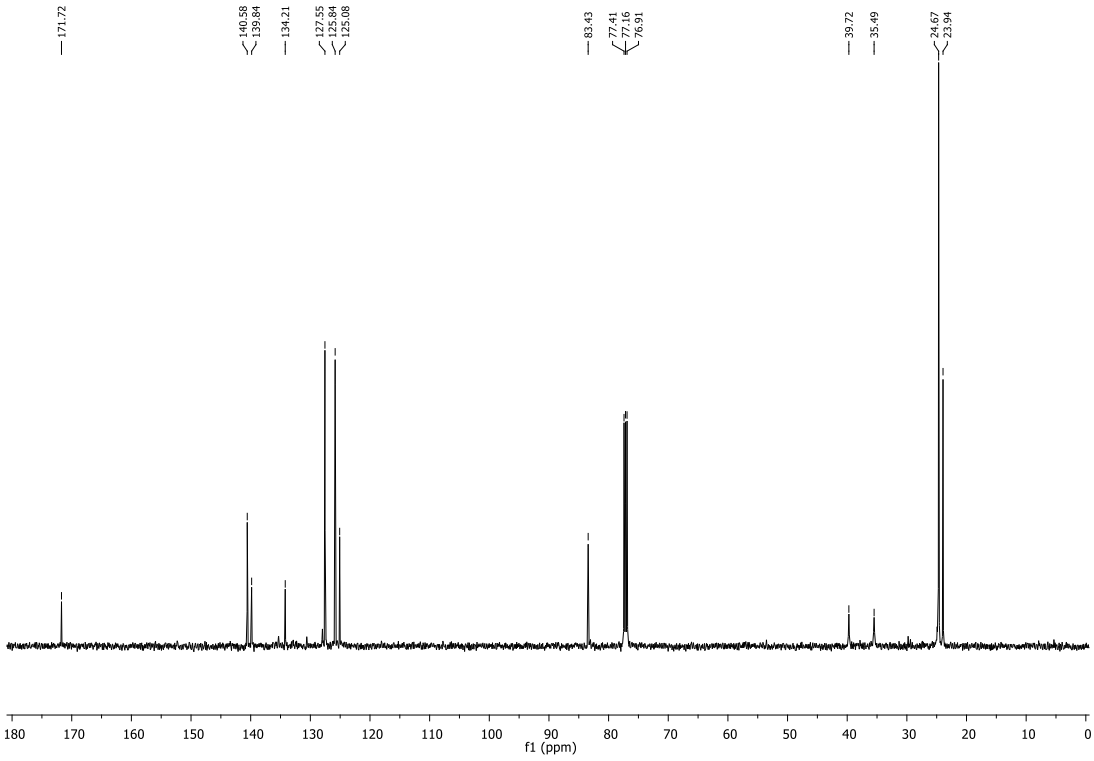
^{13}C NMR of **3hc**



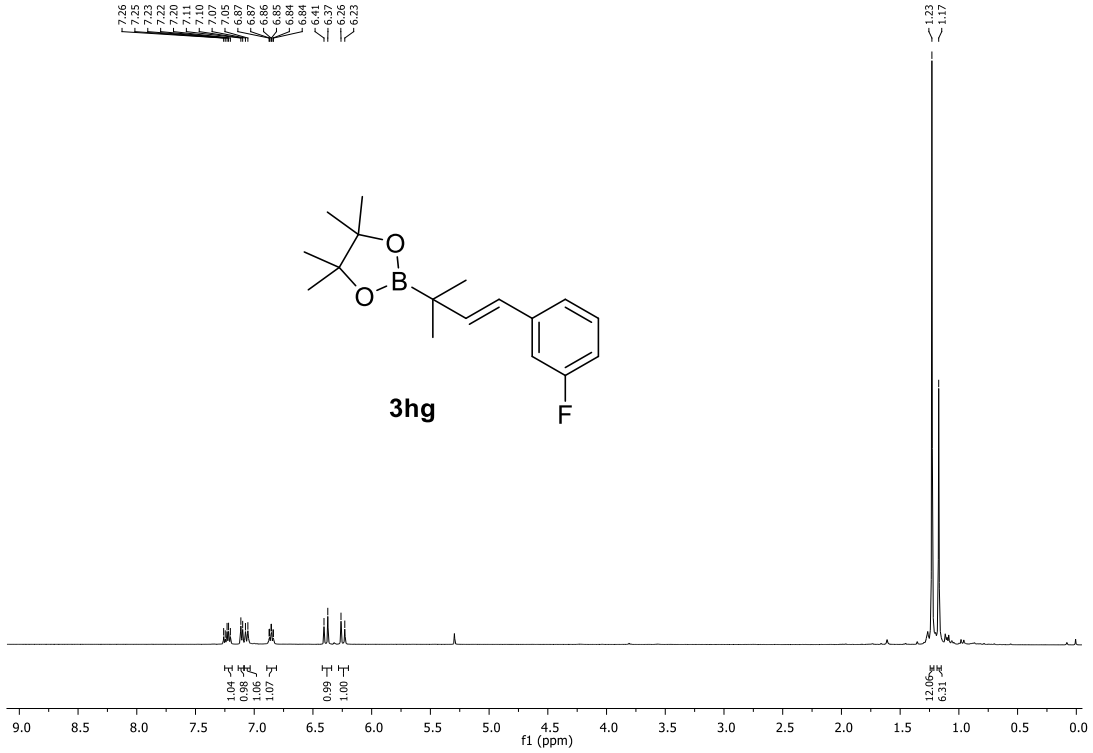
^{1}H NMR of **3hf**



^{13}C NMR of **3hf**



^{1}H NMR of **3hg**



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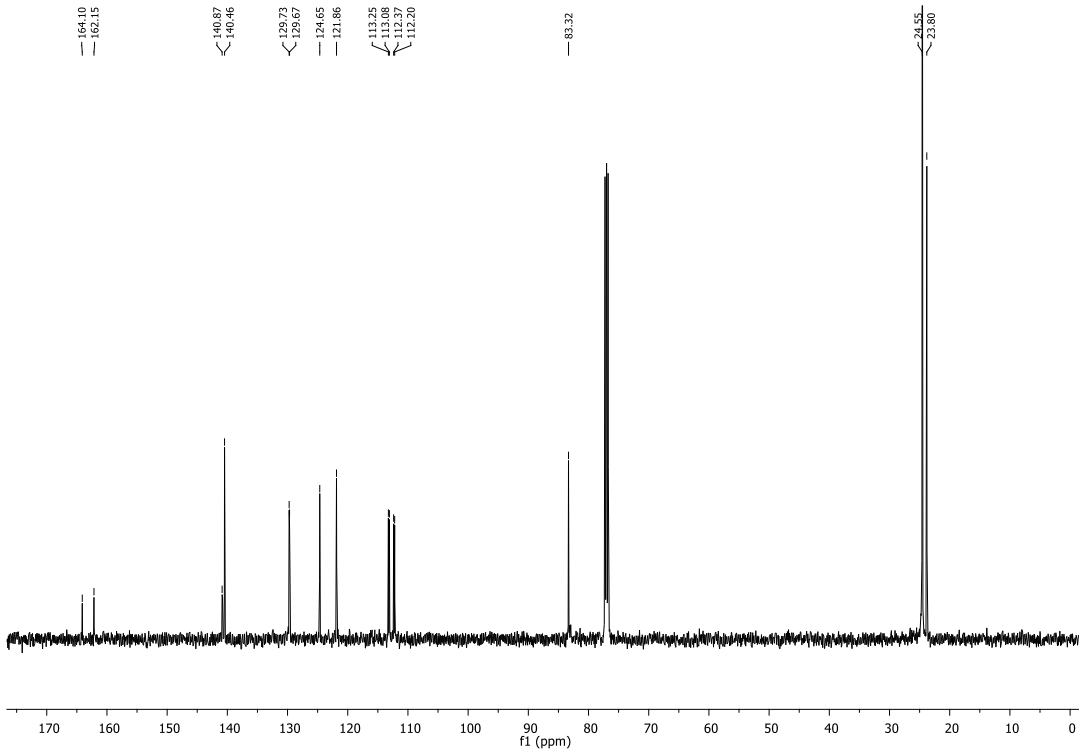
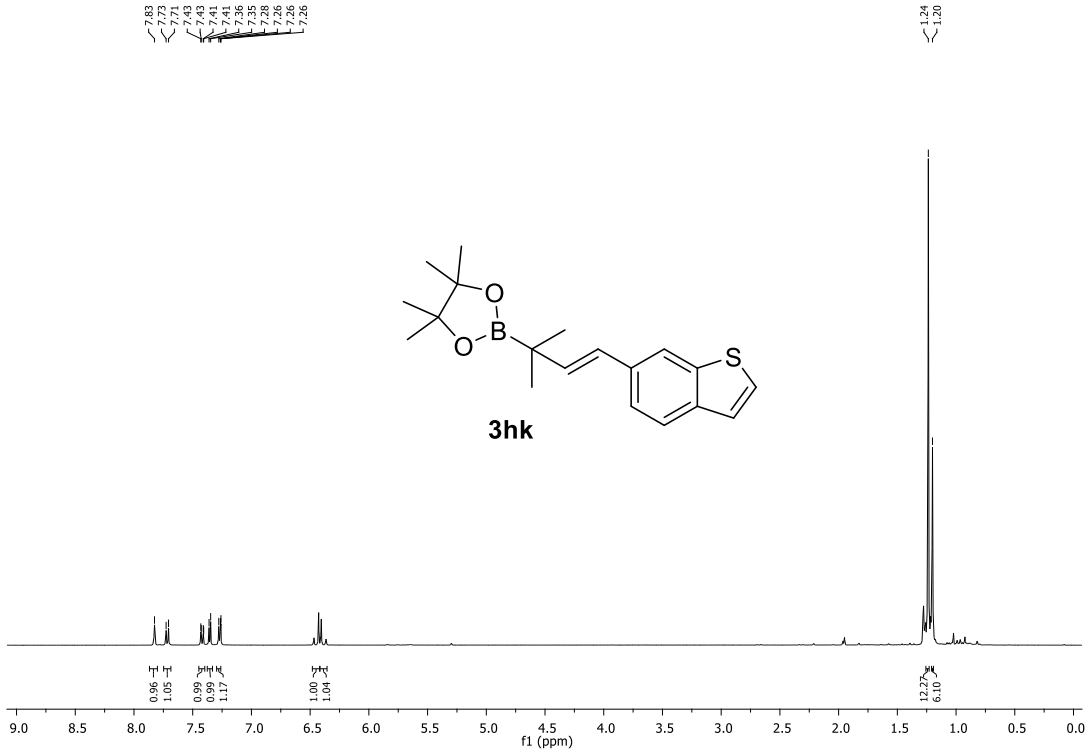


^{1}H NMR of **3hk**



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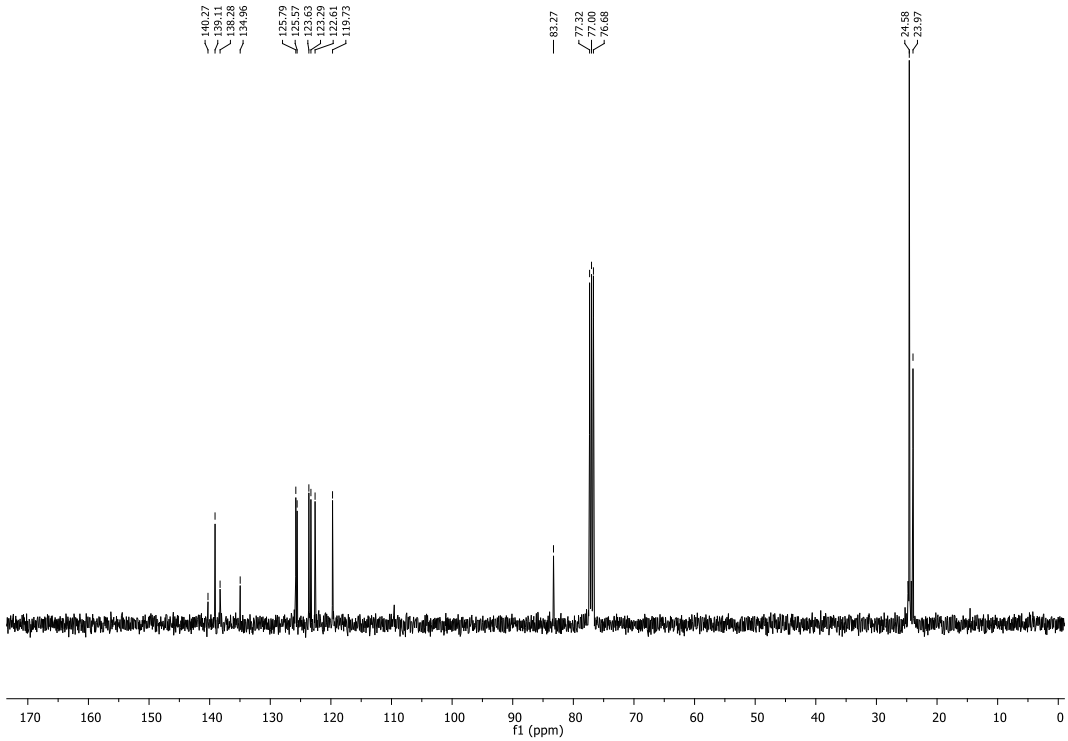
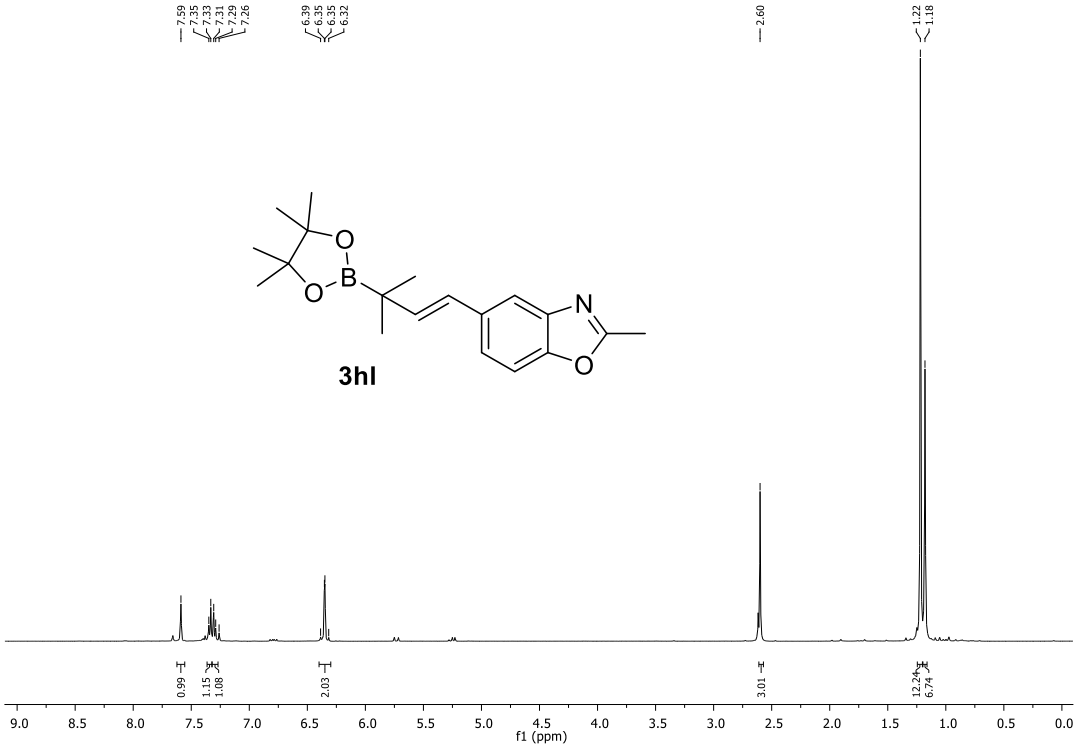
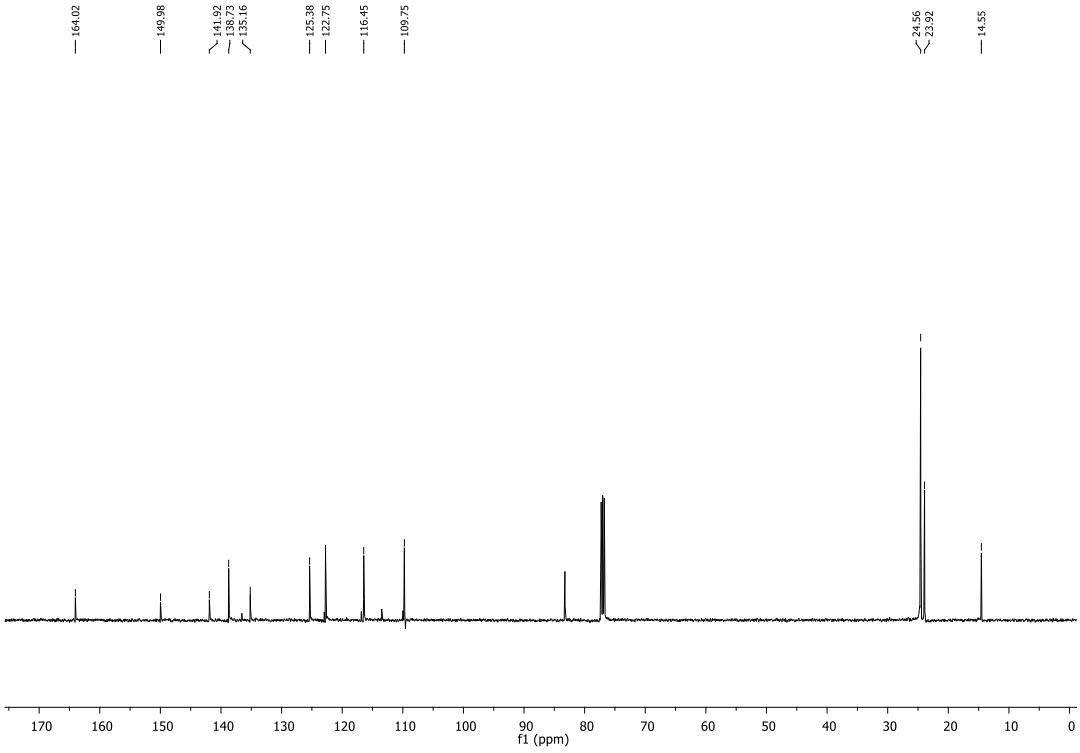


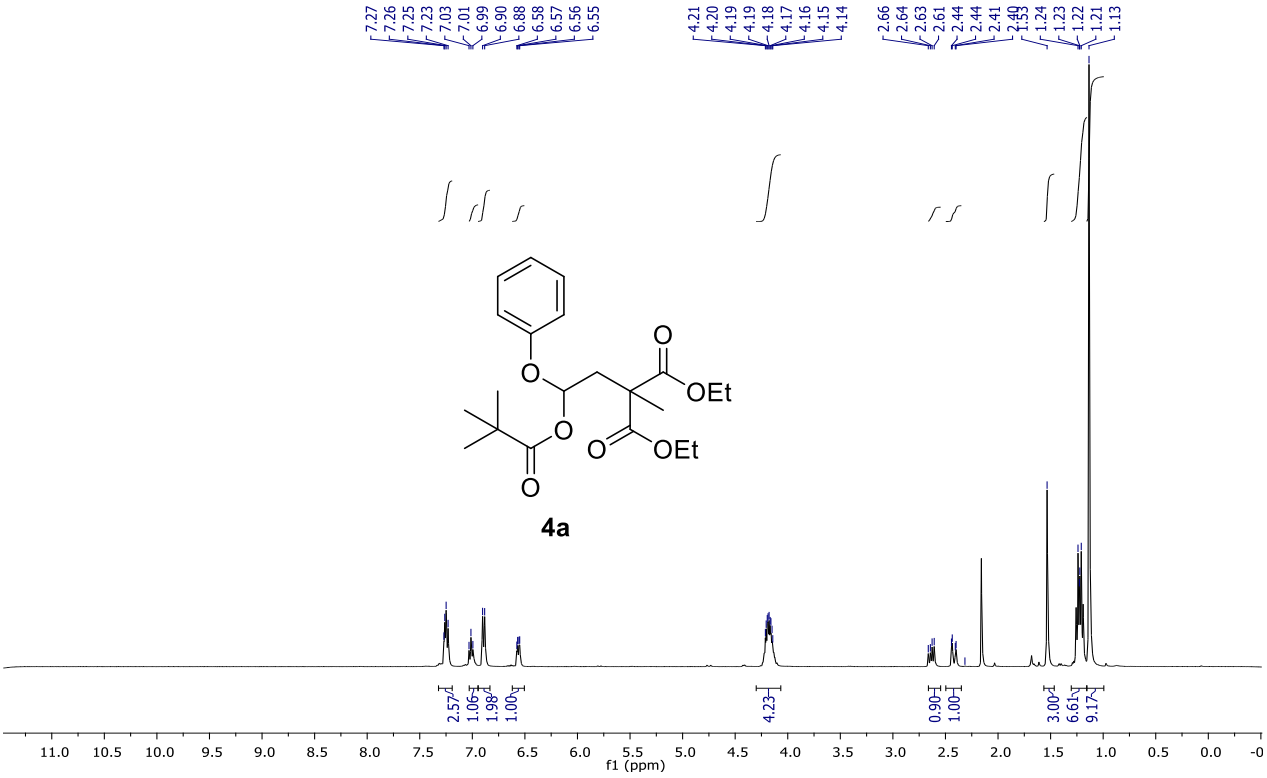
^{1}H NMR of **3hl**



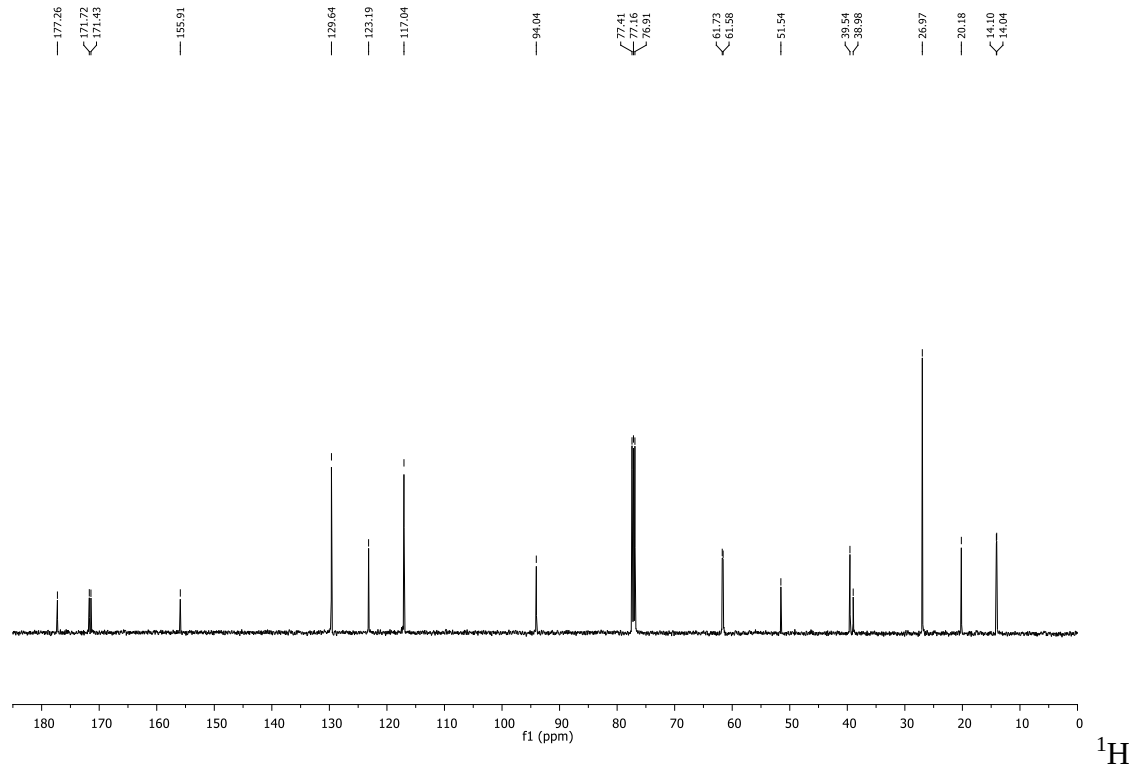
^{13}C NMR of **3hl**



^{1}H NMR of **4a**

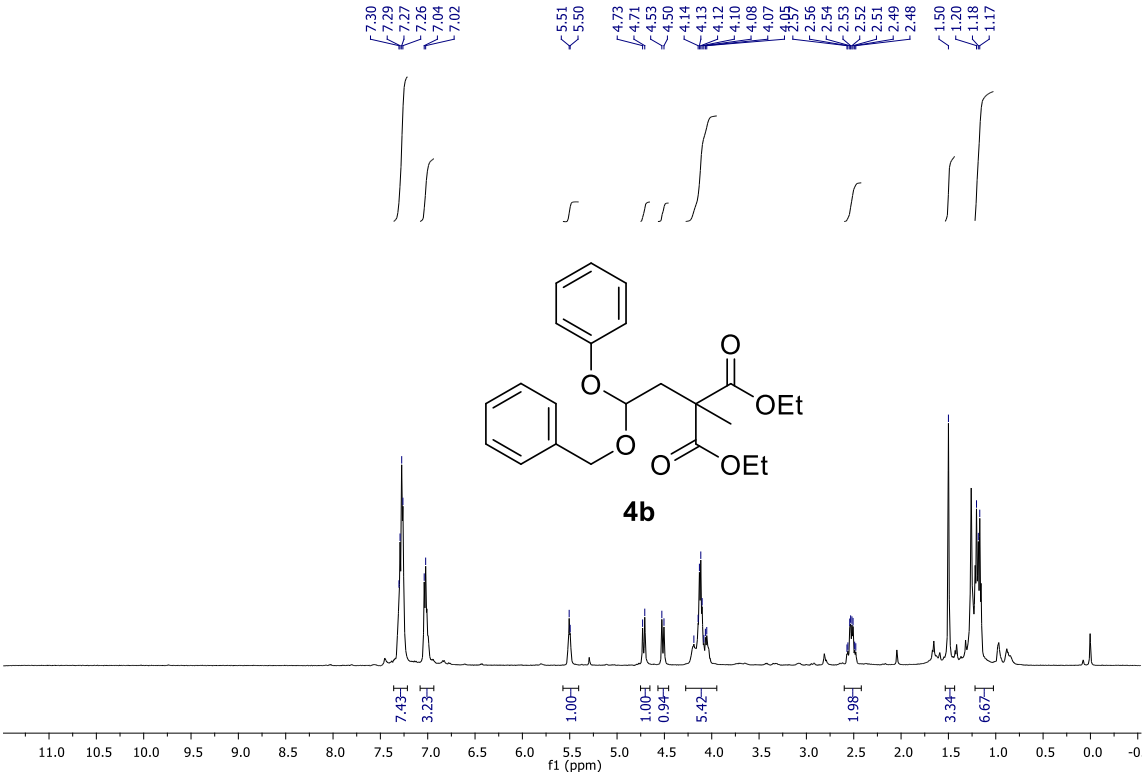


^{1}H NMR of **4a**

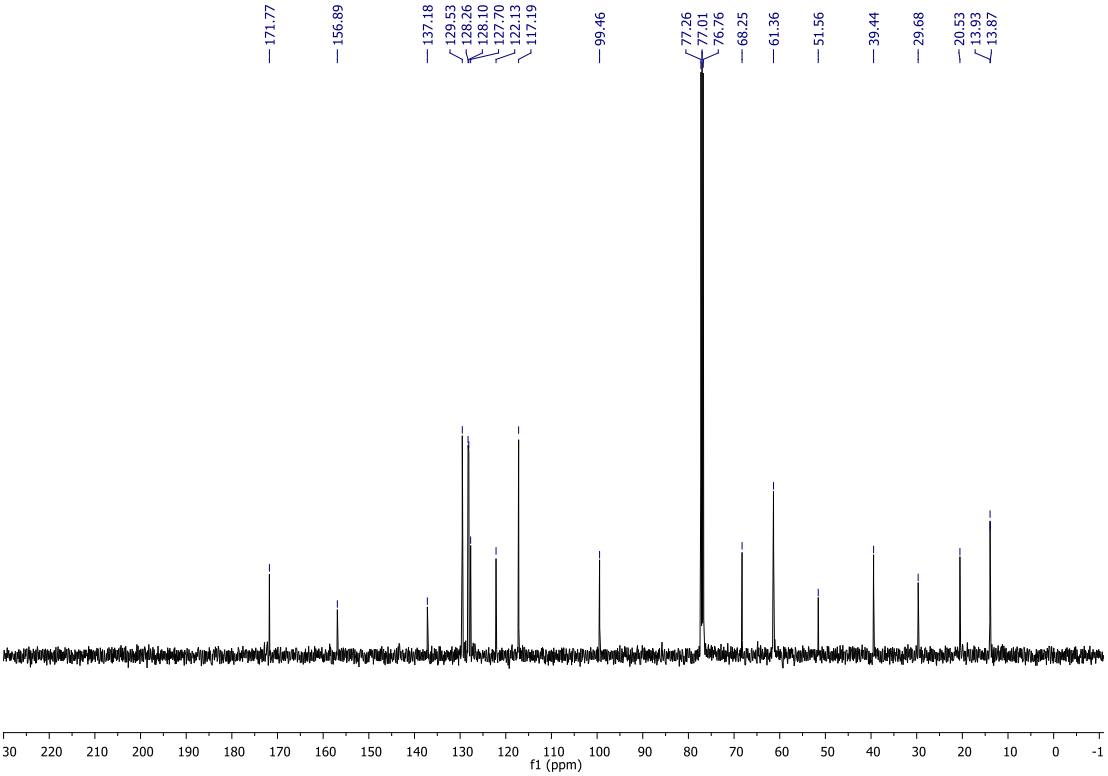


^{1}H

NMR of **4b**



^{13}C NMR of **4b**



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