

## Supporting Information

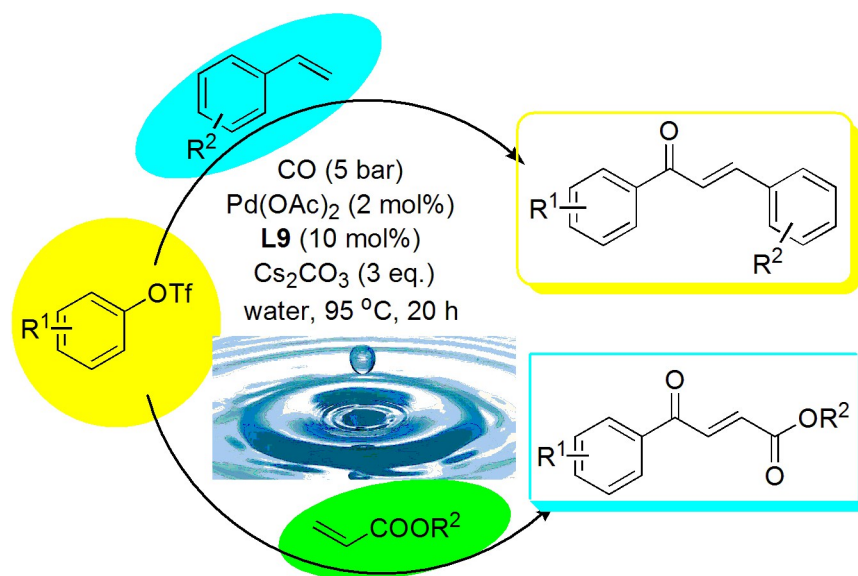
# A Robust Multifunctional Ligand-controlled Palladium-Catalyzed Carbonylation Reactions in Water

Pei-Sen Gao<sup>a,b</sup>, Kan Zhang<sup>a</sup>, Ming-Ming Yang<sup>a</sup>, Shan Xu<sup>a</sup>, Hua-Ming Sun<sup>a</sup>, Jin-Lei Zhang<sup>a</sup>, Zi-Wei

Gao<sup>a\*</sup>, Wei-Qiang Zhang<sup>a\*</sup>, Li-Wen Xu<sup>a,b\*</sup>

<sup>a</sup> Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education (MOE) and School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, P. R. China

<sup>b</sup> Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, P. R. China



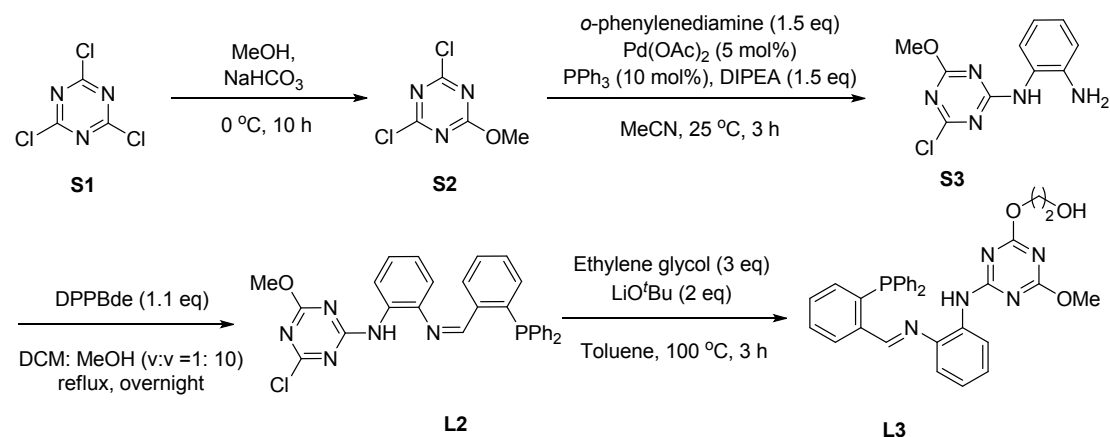
# Table of Contents

S-1. General Information.....	3
S-2. Synthetic Routes for Schiff-Based ligands.....	4-10
S-2.1 Experimental procedure for synthesis of L3.....	4
S-2.2 Experimental procedure for synthesis of L5.....	5
S-2.3 Experimental procedure for synthesis of L6.....	6
S-2.4 Experimental procedure for synthesis of L7.....	7
S-2.5 Experimental procedure for synthesis of L8.....	8
S-2.6 Experimental procedure for synthesis of L9.....	9
S-3. Optimization of Carbonylative Heck Coupling reaction between 1a, CO and 2a.....	10-12
S-3.1 Optimization of different Pd sources in the titled reaction of 1a, CO and 2a.....	10
S-3.2 Optimization of different solvents in the titled reaction of 1a, CO and 2a.....	11
S-3.3 Optimization of different phosphine ligands in the carbonylative Heck coupling of 1a, CO and 2a....	12
S-4. General procedure for Carbonylative Heck coupling reaction of aromatic triflates, CO and styrenes in water (GP1) .....	13
S-5. General procedure for Carbonylative Heck coupling reaction of aromatic triflates, CO and acrylates in water (GP2).....	14
S-6. General procedure for [3+2] cycloaddition of substituted chalcones leading to $\gamma$ -lactams (GP3).....	15
S-7. Investigation of recyclability performance of Pd(OAc) <sub>2</sub> /L9 catalytic system on the carbonylative Heck reaction of 1a, CO and 2a.....	16
S-8. Mechanism Study of Carbonylative Heck Reaction.....	17-21
S-9. NMR-Data of products 3, 5, 7 and ligands.....	22-36
S-10. NMR Spectrums of products and novel <i>N,P</i> ligands.....	37-78
S-11. References.....	79

## S-1. General Information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by thin layer chromatography using silica gel. All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. <sup>1</sup>H-NMR was recorded at 400 MHz or 600 MHz: chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl<sub>3</sub> at 7.26 ppm). <sup>13</sup>C-NMR was recorded at 100 MHz or 126 MHz: chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl<sub>3</sub> at 77.20 ppm). <sup>31</sup>P-NMR were recorded at 202 MHz or 243 MHz: chemical shifts for phosphorous are reported in parts per million (ppm, δ scale) referenced to the phosphorous resonance of phosphoric acid (δ = 0). The ESI - MS analysis of the samples was operated on an LCQ advantage mass spectrometer (ThermoFisher Company, USA), equipped with an ESI ion source in the positive ionization mode, with data acquisition using the Xcalibur software (Version 1.4). High resolution mass spectral analyses (LRMS and HRMS) were performed at Chemical Instrument Center, Sha'an Xi Normal University (Bruker Daltonics micrOTOF-QII). Elemental Analysis was performed at Bruker Vario EL III. FT-IR measurement was performed at Bruker Tensor 27. Reagents, such as tetrahydrofuran, toluene (with Na and benzophenone) and MeCN (CaH<sub>2</sub>), were freshly distilled in prior to use. Aromatic triflates were synthesized according to literature reports <sup>[1]</sup>. **L1**, **L2** and **L4** were synthesized by the methods developed by our groups <sup>[2]</sup>.

## S-2. Synthetic Routes for Schiff-Based ligands



Scheme S1. Synthetic routes of **L3**

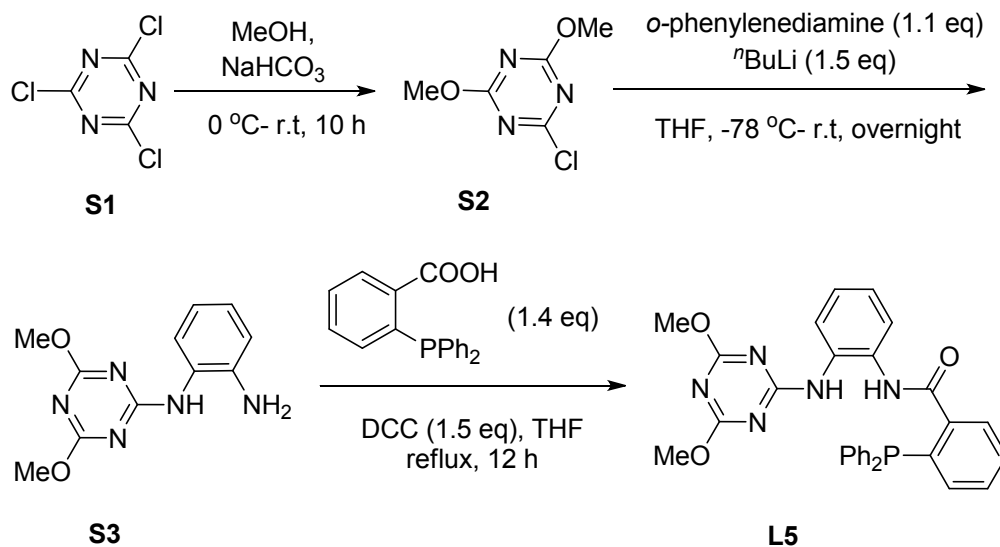
### S-2.1 Experimental procedure for synthesis of **L3**

Procedure for synthesis of **L3** : Given that **L2** could be synthesized according to the previous report by our group<sup>[2]</sup>, the procedure for synthesis of **L2** was not described in detail herein. With **L2** in hand, **L3** could be obtained via a nucleophilic substitution with ethylene glycol under strong basic conditions. The procedure for synthesis of **L3** was listed as following.

To a dried Schlenk flask, **L2** (2 mmol, 1.05 g) and LiO<sup>t</sup>Bu (56.2 mg, 4 mmol) were added under nitrogen atmosphere. Subsequently, dried toluene (3 mL) was added via syringe. The mixture was stirred at room temperature for 10 min. Then ethylene glycol (334  $\mu$ L, 6 mmol) in anhydrous toluene (3 mL) was added at the same temperature. The reaction mixture was heated at 100 °C for about 3 h until **L2** was completely consumed. After cooling to room temperature, the reaction mixture was diluted with 15 mL of ethyl acetate and filtered through a plug of celite, followed by washed with 15 mL of ethyl acetate. The combined residue was concentrated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel to afford 550 mg of the target product **L3** as yellow solid. Yield : 50% . <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  9.24 (s, 1H), 9.04 (s, 1H), 8.59 (s, 1H), 8.12 (s, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.31 (s, 10H), 7.22 (s, 1H), 7.02 – 6.98 (m, 1H), 6.96 (t, *J* = 6.9 Hz, 1H), 6.90 (s, 1H), 4.55 (s, 2H), 4.12 (t, *J* = 10.7 Hz, 2H), 3.94 (d, *J* = 78.3 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  171.16, 165.89, 158.08, 139.13, 138.79, 138.68, 136.52, 134.21, 134.00, 133.87, 133.42, 131.07, 129.01, 128.94, 128.72, 128.67, 127.60, 123.01, 119.54, 116.74, 65.32, 60.41, 54.96. <sup>31</sup>P NMR

(243 MHz, CDCl<sub>3</sub>)  $\delta$  -12.24. HR-MS (ESI):  $m/z$ : calcd. for C<sub>31</sub>H<sub>29</sub>N<sub>5</sub>O<sub>3</sub>P<sup>+</sup> 550.1930 [M+H]<sup>+</sup> and 572.1827 [M+Na]<sup>+</sup>. Found: 550.1928 and 572.1826.

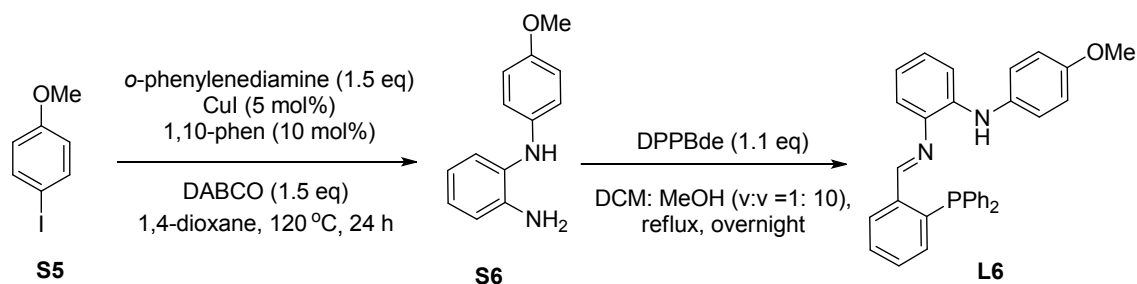
### S-2.2 Experimental procedure for synthesis of L5



Scheme S4. Synthetic routes of L5

Given that S3 could be synthesized according to the previous work reported by our group<sup>[2]</sup>, the procedure for synthesis of S3 was not described in detail herein. To a solution of S3 (5 mmol, 1.24 g) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added 2-(diphenylphosphino) benzoic acid (7 mmol, 2.14 g) and dicyclohexylcarbodiimide (DCC, 7 mmol, 1.359 g) at 0 °C. The reaction mixture were stirred at this temperature for 30 minutes and further stirred at 40 °C for another 4 h. After S3 was completed consumed, the mixture were filtrate through a plug of celite. The filtrates were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: petroleum ether: ethyl acetate = 5:1 to 1:1), to give 802.76 mg of the desired product L5 as white solid. Yield: 30%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.42 (s, 1H), 7.85 (s, 1H), 7.64 (s, 1H), 7.54 (d,  $J$  = 7.8 Hz, 1H), 7.38 (d,  $J$  = 6.4 Hz, 1H), 7.31 (s, 1H), 7.27 (d,  $J$  = 7.4 Hz, 1H), 7.25 – 7.17 (m, 10H), 7.11 (t,  $J$  = 7.5 Hz, 1H), 7.07 (d,  $J$  = 7.3 Hz, 1H), 6.94 (s, 1H), 3.81 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  172.49, 167.67, 167.13, 156.93, 140.79, 136.46, 136.40, 134.24, 133.95, 133.82, 130.69, 130.52, 128.98, 128.95, 128.67, 128.62, 128.41, 128.38, 126.16, 126.05, 125.70, 125.13, 54.83. <sup>31</sup>P NMR (243 MHz, CDCl<sub>3</sub>)  $\delta$  -10.68. HR-MS (ESI):  $m/z$ : calcd. for C<sub>30</sub>H<sub>26</sub>N<sub>5</sub>O<sub>3</sub>PNa<sup>+</sup> 558.1665 [M+Na]<sup>+</sup>. Found: 558.1663.

### S-2.3 Experimental procedure for synthesis of L6



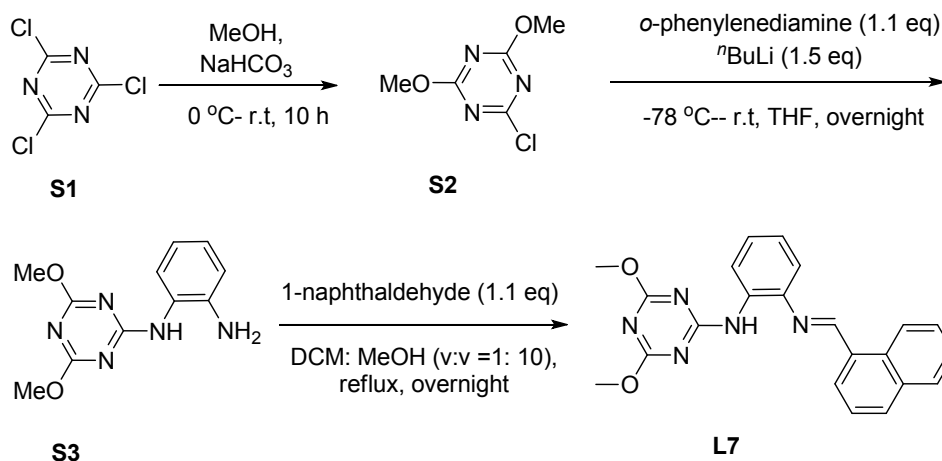
Scheme S3. Synthetic routes of L6

Procedure for synthesis of L6: *p*-Iodoanisole (5 mmol, 1.17 g), CuI (0.025 mmol, 5 mol%, 4.78 g), 1,10-phen (0.05 mmol, 10 mol%, 9.42 g) and DABCO (7.5 mmol, 1.5 eq, 841.28 mg) were charged into a dried schlenk flask. Then, anhydrous 1,4-dioxane (10 mL) was added into the schlenk flask by syringe. The mixture was stirred at room temperature for 0.5 h. Then, a solution of *o*-phenylenediamine (7.5 mmol, 1.5 eq, 811.05 mg) in anhydrous 1,4-dioxane (5 mL) was added into the reaction mixture. The reaction mixture was heated at 100 °C for about 24 h until *p*-iodoanisole was completely consumed. After cooling to room temperature, the reaction mixture was diluted with 15 mL of CH<sub>2</sub>Cl<sub>2</sub> and filtered through a plug of celite, followed by washed with 15 mL of CH<sub>2</sub>Cl<sub>2</sub>. The combined residue was concentrated under reduced pressure, and the resulting crude product was purified by column chromatography on silica gel to provide the corresponding amine. The amine was characterized by HR-MS. calcd. for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O<sup>+</sup> 215.1179 [M+H]<sup>+</sup>. Found: 215.1178.

2-(diphenylphosphino)-benzaldehyde (DPPBde, 1 mmol, 270.2 mg) was dissolved in 2 mL of CH<sub>2</sub>Cl<sub>2</sub>, which was warmed to 40 °C. The freshly prepared amine (1 mmol, 214.26 mg) in 20 mL of MeOH was added to above solution during 0.5 h. The resulting mixture was left standing at the same temperature for 1 h and then refluxed overnight. After DPPBde was completely consumed, the mixture was cooled to room temperature and concentrated under reduced pressure. Then the residue was purified by column chromatography on silica gel to afford 107.1 mg of target product L6 as white solid. Yield : 22%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.03 (s, 1H), 8.06 (d, *J* = 6.7 Hz, 1H), 7.80 (d, *J* = 3.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.37 – 7.35 (m, 1H), 7.29 (dd, *J* = 15.4, 9.3 Hz, 10H), 7.13 (d, *J* = 12.1 Hz, 2H), 6.96 – 6.94 (m, 2H),

6.87 (d,  $J = 9.0$  Hz, 2H), 3.81 (s, 3H), 3.74 (s, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  155.66, 139.35, 137.13, 135.38, 134.04, 133.90, 130.46, 128.79, 128.60, 128.55, 124.15, 122.32, 119.76, 119.51, 118.69, 117.96, 117.13, 114.50, 114.37, 112.41, 55.56.  $^{31}\text{P}$  NMR (243 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.51. HR-MS (ESI):  $m/z$ : calcd. for  $\text{C}_{32}\text{H}_{28}\text{N}_2\text{OP}^+$  487.1934  $[\text{M}+\text{H}]^+$ . Found: 487.1933.

### S-2.4 Experimental procedure for synthesis of L7



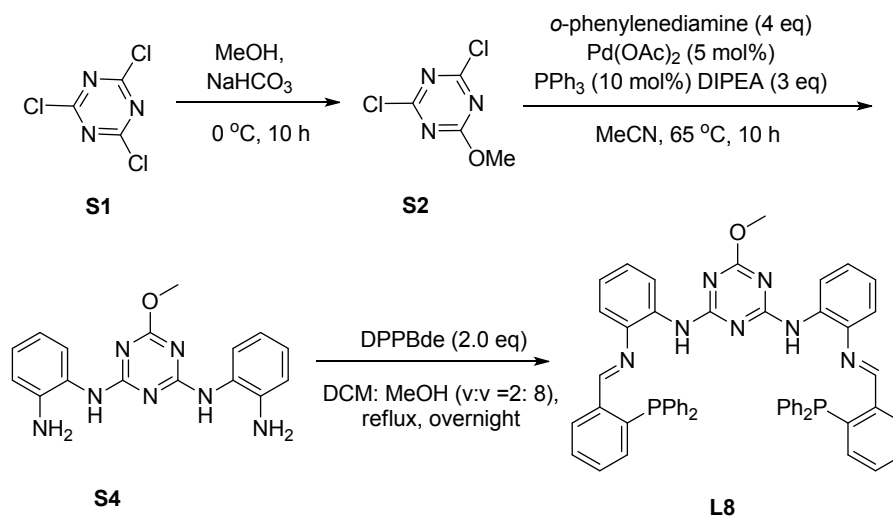
Scheme S4. Synthetic routes of L7

Given that **S3** was synthesized according to the previous literature by our group<sup>[2]</sup>, the procedure for synthesis of **S3** was not described in detail herein. The procedure for synthesis of **L7** was listed as following.

2-(diphenylphosphino)- benzaldehyde (DPPBde, 1 mmol, 270.2 mg ) was dissolved in 2 mL of  $\text{CH}_2\text{Cl}_2$ , which was warmed to 40 °C. **S3** (1.2 mmol, 296.8 mg) in 20 mL of MeOH was added to above solution during 0.5 h. The resulting mixture was left standing at the same temperature for 1 h and then refluxed overnight. After DPPBde was completely consumed, the mixture was cooled to room temperature. The residue was concentrated under reduced pressure , and then the resulting crude product was purified by column chromatography on silica gel to afford 127.2 mg of the target product **L7** as red solid. Yield: 32%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.25 (s, 1H), 8.90 (d,  $J = 8.5$  Hz, 1H), 8.62 (s, 2H), 8.21 (d,  $J = 7.1$  Hz, 1H), 8.00 (d,  $J = 8.1$  Hz, 1H), 7.92 (d,  $J = 8.2$  Hz, 1H), 7.79 – 7.69 (m, 1H), 7.63 (t,  $J = 7.5$  Hz, 1H), 7.59 – 7.54 (m, 2H), 7.32 (t,  $J = 7.5$  Hz, 1H), 7.12 (t,  $J = 7.5$  Hz, 1H), 3.97 (d,  $J = 40.0$  Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  172.43, 167.42, 165.94, 158.67, 139.90, 132.47, 131.62, 131.10, 130.33, 129.83, 128.98, 127.56, 125.40, 123.61, 123.34, 119.86, 116.81, 54.91. HR-MS (ESI):  $m/z$ : calcd.for  $\text{C}_{22}\text{H}_{20}\text{N}_5\text{O}_2^+$  386.1612  $[\text{M}+\text{H}]^+$ .

Found: 386.1611.

### S-2.5 Experimental procedure for synthesis of L8



Scheme S2. Synthetic routes of L8

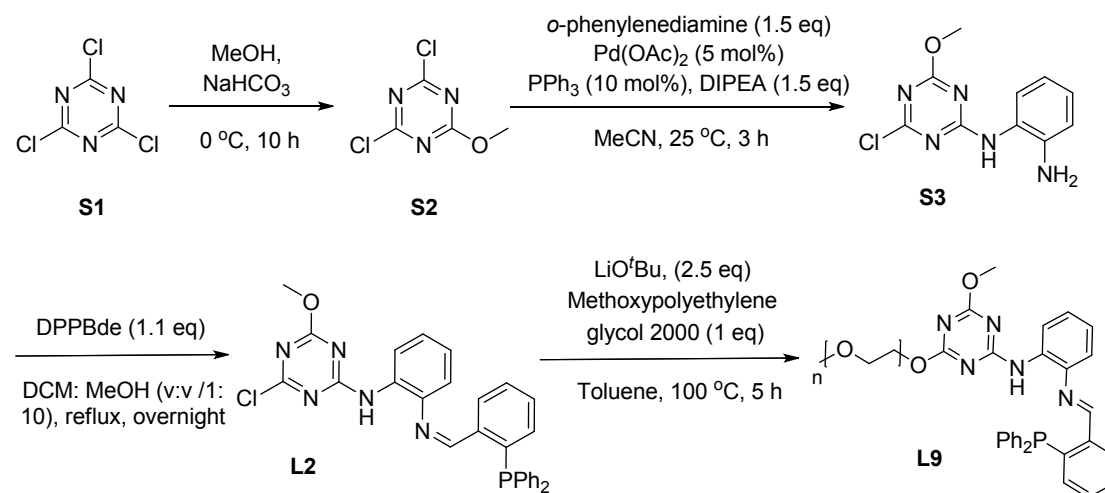
Procedure for synthesis of **L8**: To a dried Schlenk flask, **S2** (2 mmol, 502.1mg ) and *o*-phenylenediamine (324 mg, 3 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (975.5 mg, 3 mmol) were added at room temperature. Dried Toluene (5 mL) was subsequent added. The mixture was stirred at 100 °C for 10 h. After cooling to room temperature, the reaction mixture was diluted with 20 ml of CH<sub>2</sub>Cl<sub>2</sub> and filtered through a plug of celite, followed by washed with 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. The combined residue was concentrated under reduced pressure, and then the resulting crude product was purified by column chromatography (eluent: ethyl acetate : petroleum ether= 1:1) on silica gel to provide the target product **S4** 420.7 mg as yellow solid. Yield: 46%.

2-(Diphenylphosphino)-benzaldehyde (DPPBde, 2 mmol, 580.3 mg ) was dissolved in 2 mL of CH<sub>2</sub>Cl<sub>2</sub>, which was warmed to 40 °C. Freshly prepared **S4** (1 mmol, 323.4 mg) in 8 mL of MeOH was added to the above solution during 0.5 h. The resulting mixture was left standing at the same temperature for 1 h and then refluxed overnight. After DPPBde was completely consumed, the mixture was cooled to room temperature. The residue was concentrated under reduced pressure , and then the resulting crude product was purified by column chromatography on silica gel to provide the target product **L8** 477.2 mg as yellow solid. Yield: 53%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.00 (d, *J* = 4.5 Hz, 2H), 8.08 (dd, *J* = 7.3, 3.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 3H), 7.34 – 7.28 (m, 26H), 7.00 – 6.97 (m, 2H), 6.94 (dd, *J* = 7.5, 4.6 Hz, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.64 (dd, *J* = 17.2, 7.7 Hz, 4H), 4.01 (s, 4H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 156.53, 156.43, 142.41, 139.67,



139.56, 138.21, 138.07, 137.33, 137.27, 137.23, 134.09, 133.96, 130.45, 129.58, 128.81, 128.75, 128.67, 128.62, 127.72, 118.19, 117.43, 115.26, 60.41.  $^{31}\text{P}$  NMR (243 MHz,  $\text{CDCl}_3$ )  $\delta$  -11.71. HR-MS (ESI):  $m/z$ : calcd. for  $\text{C}_{54}\text{H}_{44}\text{N}_7\text{OP}_2^+$  868.3077  $[\text{M}+\text{H}]^+$ . Found: 868.3071.

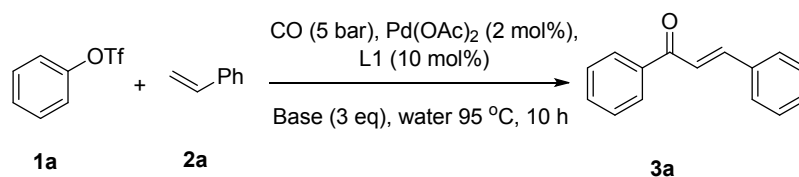
### S-2.6 Experimental procedure for synthesis of L9



Scheme S4. Synthetic routes of L9

To a dried Schlenk flask, **L2** (2 mmol, 1.05 g) and  $\text{LiO}^t\text{Bu}$  (56.2 mg, 4 mmol) were added under nitrogen atmosphere. Dried toluene (6 mL) was subsequently added by syringe. The mixture was stirred at room temperature for 10 min. Then methoxypolyethylene-2000 (3.2 g, 1.6 mmol) was added and then heated at 100 °C for about 3 h. After cooling to room temperature, the reaction mixture was filtered. The filtrate was then poured into a beaker with 30 mL of cooled *n*-hexane, a large amount of precipitate was formed immediately. Then the mixture was filtered and the precipitate was washed with 5 mL of cooled ethyl acetate and 5 mL of cooled water twice. Then, the precipitate was collected, dried over 24 hours under reduced pressure to afford 2.95 g of **L9** as pale-yellow solid. Yield: 75%.

### S-3 Optimization of Carbonylative Heck Coupling reaction between **1a** and **2a**

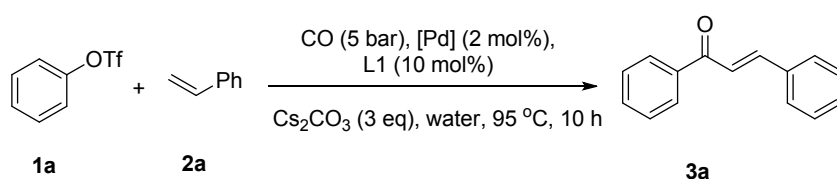


**Table S1.** Investigation of the influence of bases on the titled reaction between **1a** and **2a**

Entry <sup>a</sup>	[Pd]	[P]	Base	Solvent	Yield <sup>b</sup> of <b>3a</b> (%)
<b>1</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	K <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	67
<b>2</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	KOH	1,4-dioxane	10
<b>3</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	NaOH	1,4-dioxane	N.d
<b>4</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	K <sup>t</sup> OBu	1,4-dioxane	44
<b>5</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	Na <sup>t</sup> OBu	1,4-dioxane	43
<b>6</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	DABCO	1,4-dioxane	25
<b>7</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	DIPEA	1,4-dioxane	14
<b>8</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	1,4-dioxane	<b>90</b>
<b>9</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	Et <sub>3</sub> N	1,4-dioxane	11
<b>10</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	NaH	1,4-dioxane	85
<b>11</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	LiHMDS	1,4-dioxane	17
<b>12</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	KHMDS	1,4-dioxane	71

a. the reaction was performed in 0.2 mmol scale at 95 °C. **L1** were all used in 10 mol% , Pd(OAc)<sub>2</sub> 2 mol%, **1a** 0.2 mmol, **2a** 0.6 mmol, CO 5 bar, bases 0.6 mmol, and water 0.5 mL. b. yields of **3a** were determined by <sup>1</sup>H-NMR analysis.

### S-3.1 Optimization of different Pd sources in the titled reaction of 1a and 2a

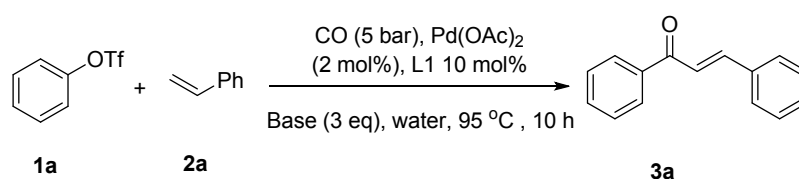


**Table S2.** Optimization of different [Pd] sources in the titled reaction between **1a** and **2a**

Entry <sup>a</sup>	[Pd]	[P]	Base	Solvent	Yield <sup>b</sup> of 3a
<b>1</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	<b>44%</b>
<b>2</b>	[(cinnamyl)PdCl]	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	34%
<b>3</b>	<sup>2</sup> [Pd(C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	33%
<b>4</b>	Pd <sub>2</sub> (Dba) <sub>3</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	trace
<b>5</b>	PdCl <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	42%
<b>6</b>	Pd(MeCN) <sub>2</sub> Cl <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	trace
<b>7</b>	Pd(acac) <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	trace
<b>8</b>	Pd(OOCCF <sub>3</sub> ) <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	41%
<b>9</b>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	N. R

a. the reaction was performed in 0.2 mmol scale at 95 °C. **L1** were all used in 10 mol% , Pd(OAc)<sub>2</sub> 2 mol%, **1a** 0.2 mmol, **2a** 0.6 mmol, CO 5 bar, bases 0.6 mmol, and water 0.5 mL. b. yields of **3a** were determined by <sup>1</sup>H-NMR analysis.

### S-3.2 Optimization of different solvents in the titled reaction of 1a and 2a

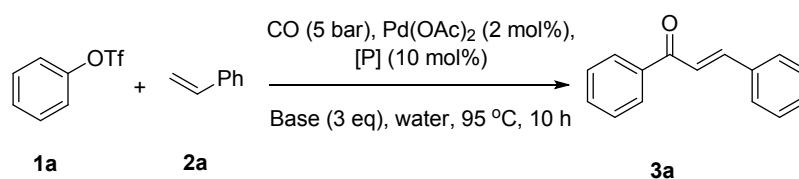


**Table S3.** Optimization of different solvents in the titled reaction between 1a and 2a

Entry <sup>a</sup>	[Pd]	[P]	Solvent	Yield <sup>b</sup> of 3a
1	Pd(OAc) <sub>2</sub>	L1	DMAc	52%
2	Pd(OAc) <sub>2</sub>	L1	THF	11%
3	Pd(OAc) <sub>2</sub>	L1	Toluene	77%
4	Pd(OAc) <sub>2</sub>	L1	<i>o</i> -xylene	81%
5	Pd(OAc) <sub>2</sub>	L1	1,4-dioxane	90%
6	Pd(OAc) <sub>2</sub>	L1	MeCN	21%
7	Pd(OAc) <sub>2</sub>	L1	DMSO	55%
8	Pd(OAc) <sub>2</sub>	L1	DMF	41%

a. the reaction was performed in 0.2 mmol scale at 95 °C. L1 were all used in 10 mol% , Pd(OAc)<sub>2</sub> 2 mol%, 1a 0.2 mmol, 2a 0.6 mmol, CO 5 bar, base 0.6 mmol, and water 0.5 mL. b. NMR- yield.

### S-3.3 Optimization of different phosphine ligands in the carbonylative Heck coupling of **1a** and **2a**

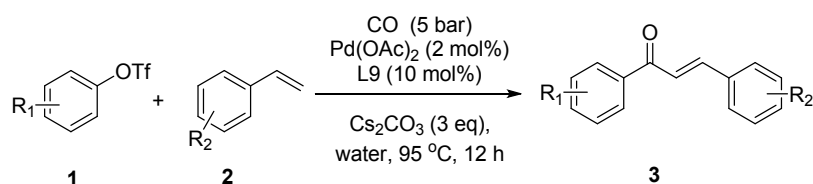


**Table S4.** Screening different phosphine ligands in the titled reaction between **1a** and **2a** in water

Entry <sup>a</sup>	[Pd]	[P]	Base	Solvent	Yield <sup>b</sup> of <b>3a</b>
<b>1</b>	Pd(OAc) <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	44%
<b>2</b>	Pd(OAc) <sub>2</sub>	<b>L2</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	0%
<b>3</b>	Pd(OAc) <sub>2</sub>	<b>L3</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	42%
<b>4</b>	Pd(OAc) <sub>2</sub>	<b>L4</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	27%
<b>5</b>	Pd(OAc) <sub>2</sub>	<b>L5</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	32%
<b>6</b>	Pd(OAc) <sub>2</sub>	<b>L6</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	15%
<b>7</b>	Pd(OAc) <sub>2</sub>	<b>L7</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	0%
<b>8</b>	Pd(OAc) <sub>2</sub>	<b>L8</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	44%
<b>10</b>	Pd(OAc) <sub>2</sub>	<b>L6</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	5%
<b>11</b>	Pd(OAc) <sub>2</sub>	<b>Dppp</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	7%
<b>12</b>	Pd(OAc) <sub>2</sub>	<b>Dppf</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	2%
<b>13</b>	Pd(OAc) <sub>2</sub>	<b>XantPhos</b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	6%
<b>14</b>	Pd(OAc) <sub>2</sub>	<b>PCy<sub>3</sub></b>	Cs <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	0%

a. the reaction was performed in 0.2 mmol scale at 95 °C. **L1** were all used in 10 mol%, Pd(OAc)<sub>2</sub> 2 mol%, **1a** 0.2 mmol, **2a** 0.6 mmol, CO 5 bar, base 0.6 mmol, and water 0.5 mL. b. yields of **3a** were determined by <sup>1</sup>H-NMR analysis

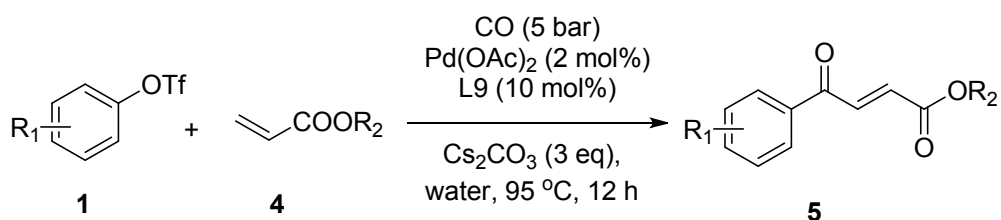
#### S-4. General procedure for Carbonylative Heck coupling reaction of aromatic triflate with Styrene in water (GP1)



**Scheme S7.** Pd(OAc)<sub>2</sub>/ **L9** catalyzed carbonylative Heck coupling of **1** with **2** in water

Take **3b** for example: To a 25 mL of Schlenk tube equipped with a magnetic stirring bar under N<sub>2</sub> were added Pd(OAc)<sub>2</sub> (2.3 mg, 0.01 mmol, 2 mol%), **L9** (124.4 mg, 0.05 mmol, 10 mol%), Cs<sub>2</sub>CO<sub>3</sub> (488.7 mg, 1.5 mmol, 3 eq), 4-methoxyphenyl trifluoromethanesulfonate **4a** (128.1 mg, 0.5 mmol, 1.0 eq) and 2 mL of deionized water. Then styrene (177 μL, 1.5 mmol, 3 eq) was added successively to the mixture. Then, the atmosphere was replaced with 5 bar of CO. The reaction mixture was stirring at 35 °C. After stirring for 1 h, the reaction mixture was further stirred at 95 °C for about 12 h. After **1b** was completely consumed, the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl and then diluted with 5 mL of ethyl acetate twice, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude product was purified by silica gel column chromatography (eluent; petroleum ether: ethyl acetate = 20:1 to 10:1), affording 96.5 mg of desired product **3b** as colorless solid. Yield : 82 % .

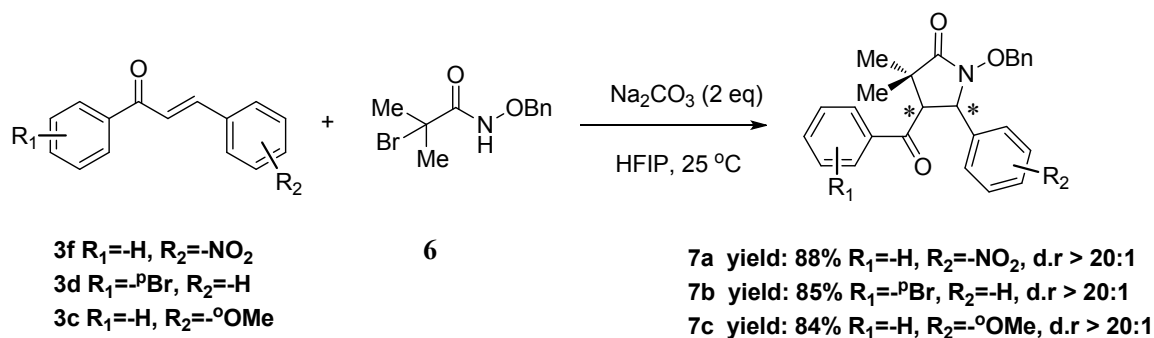
### S-5. General procedure for Carbonylative Heck coupling reaction of aromatic triflates, CO and acrylates in water (GP2)



**Scheme S8.** Pd(OAc)<sub>2</sub>/L9 catalyzed carbonylative Heck coupling of 1, CO and 4 in pure water

Take **5j** for example: To a 5 mL of Schlenk tube equipped with a magnetic stirring bar under N<sub>2</sub> were added Pd(OAc)<sub>2</sub> (2.3 mg, 0.01 mmol, 2 mol%), **L9** (124.4 mg, 0.05 mmol, 10 mol%), Cs<sub>2</sub>CO<sub>3</sub> (488.7 mg, 1.5 mmol, 3 eq), 4-methylphenyl trifluoro- methanesulfonate (120.1 mg, 0.5 mmol, 1.0 eq) and 1.25 mL of deionized water. Then ethylacrylate (320 μL, 3.0 mmol, 6 eq) was added successively to the mixture. Then the atmosphere was replaced with 5 bar of carbon monoxide. The reaction mixture was stirred at 35 °C for 1 h and further stirred at 95 °C for about 12 h. Then the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl, diluted with 5 mL of ethyl acetate twice, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. Finally, the crude product was purified by silica gel column chromatography (eluent; petroleum ether: ethyl acetate = 15:1 to 10:1), affording 99.5 mg of **5j** as colorless oil. Yield : 91 % .

**S-6. General procedure for [3+2] cycloaddition of substituted chalcones leading to  $\gamma$ -lactams (GP3)**

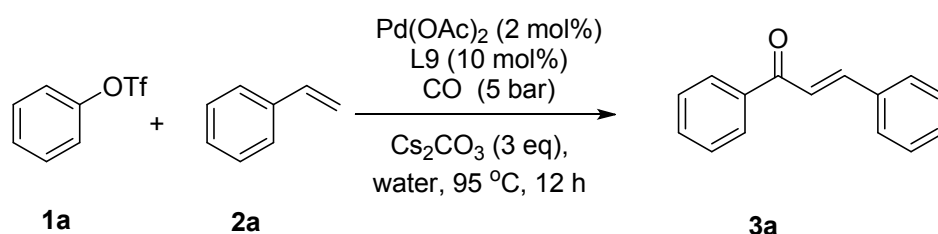


Scheme S9.  $Na_2CO_3$ -Prompted [3+2] cycloaddition of **3**

Take **7a** for example: To a 5 mL of Schlenk tube equipped with a magnetic stirring bar under  $N_2$  were added **3a** (208 mg, 1.0 mmol), **6** (135.4 mg, 0.5 mmol),  $Na_2CO_3$  (160 mg, 1.5 mmol, 3 eq), and 5 mL of HFIP (1,1,1,3,3,3-Hexafluoroisopropanol). Then the mixture was stirred at room temperature for about 24 h. After **6** was completely consumed, the reaction mixture was quenched by a slice of ice. Then the mixture was washed with saturated aqueous  $NH_4Cl$ , diluted with 5 mL of ethyl acetate twice, washed with brine, dried over  $Na_2SO_4$ , filtered and concentrated. The crude product was purified by silica gel column chromatography (eluent; petroleum ether: ethyl acetate = 10:1), to give the desired product **7a** 195.5 mg as pale yellow solid. Yield : 88 % .



**S-7. Investigation of Recyclability performance of Pd(OAc)<sub>2</sub>/L9 catalytic system on the carbonylative Heck reaction of 1a, CO and 2a**



Runs <sup>a</sup>	Fresh	1 <sup>b</sup>	2	3	4	5
Yield <sup>c</sup> (%)	90%	90%	82%	82%	75%	63%

<sup>a</sup> All the reaction was performed at 0.5mmol scale. **1a** (0.5 mmol), **2a** (1.5 mmol), 2 mol% of Pd(OAc)<sub>2</sub>, 10 mol% of **L9**, 3 eq of Cs<sub>2</sub>CO<sub>3</sub> and 3 mL of pure water. <sup>b</sup> The Pd(OAc)<sub>2</sub>/**L9** catalytic system was used in the reaction between **1a**, CO (5 bar) and **2a** <sup>c</sup> isolated yields

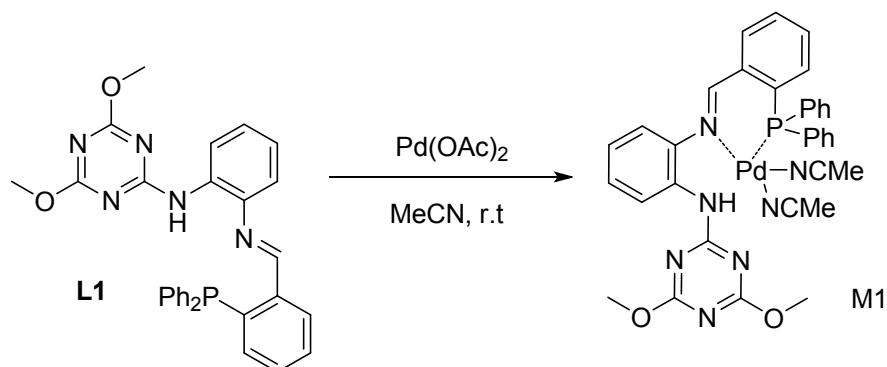
Procedure for recyclable experiment on the carbonylative Heck coupling reaction between PhOTf, CO and **2a** under Pd(OAc)<sub>2</sub>/**L9** catalytic system in pure water: After completion of the carbonylative Heck coupling reaction between PhOTf, CO and **2a**, the reaction mixture was extracted with 5 mL of ethyl acetate twice. The organic phase was collected. The Pd(OAc)<sub>2</sub>/**L9** catalytic system in water phase was subjected to the next run by charging with **1a** (0.5 mmol), styrene (3 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (358.4 mg, 2.2 eq). After five runs, the yield of **3a** was decreased to 63% .

**Description:** The moderate recyclability of Pd/**L9** catalytic system after five runs in water maybe caused by the following reasons. I) The loss of activated Pd species II) The oxidation of **L9** by water.

## S-8. Mechanism Study of Carbonylative Heck Reaction

### Investigation of coordination behavior of Pd(OAc)<sub>2</sub> and s-triazine based *N, P*- Ligands (**L1** or **L9**):

Initially, we explored the possible coordination form of Pd(OAc)<sub>2</sub> and **L1** (the mother ligand of **L9**). Based on our previous work on the coordination behavior of **L1** with Pd(OAc)<sub>2</sub>, we believe the chelation effect is key for the carbonylative Heck coupling between **1a**, CO and **2a**. The formation of complex **M1** (Scheme S10) was studied by HR-MS and <sup>31</sup>P-NMR.



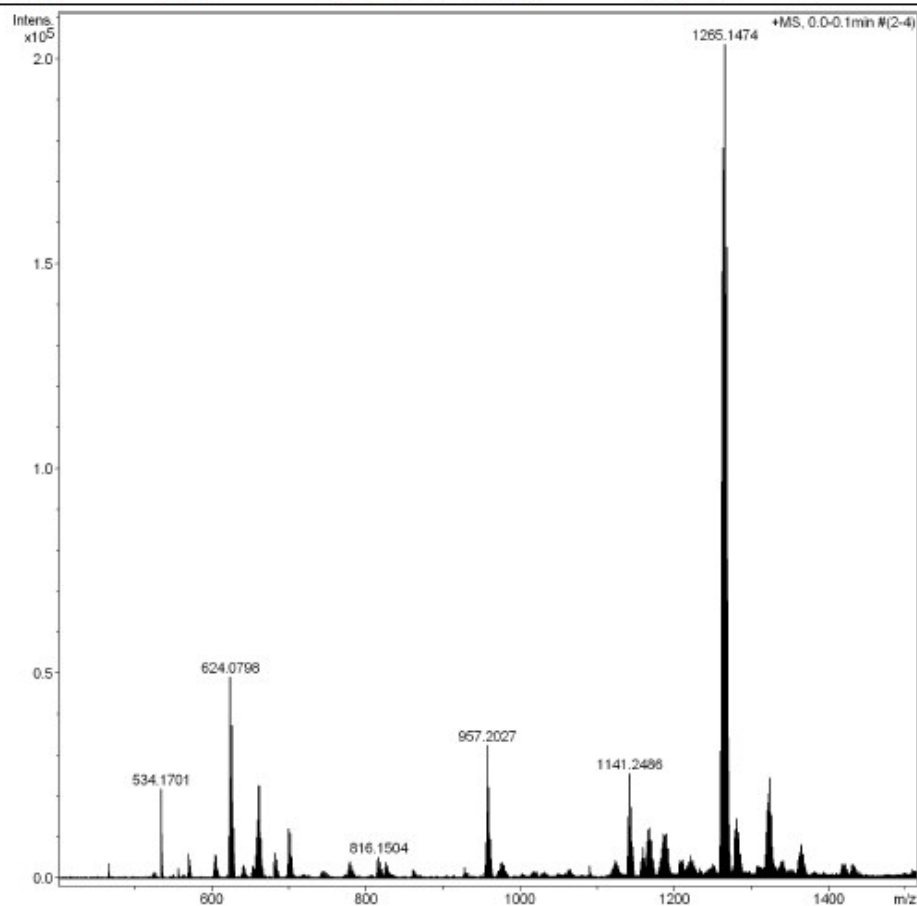
**Scheme S10.** Investigation of coordination behavior of Pd(OAc)<sub>2</sub> and **L1**

When 0.1 mmol of **L1**, 0.1 mmol of Pd(OAc)<sub>2</sub> and 0.5 mL of MeCN was mixed at room temperature, the color of solution became dark red. The mixture was analyzed by HR-MS analysis (Fig S3). HR-MS analysis of the Pd / **L1** catalytic system was conducted. As seen in the Fig S3, the peak at 622.0794 and 1265.1474 were assigned to the [I+H]<sup>+</sup> and [2I+Na]<sup>+</sup>, respectively. These figures indicated that Pd(OAc)<sub>2</sub> and **L1**-Phos likely coordinated in 1:1 of mol ratio to form an active palladium species (Fig S4). The N and P atoms of the **L1**-Phos coordinated to the Palladium center. The amplifying signals at 620-629 were shown below, which indicating that presence of mono palladium species.

## Display Report

<b>Analysis Info</b>		Acquisition Date	7/12/2016 4:49:03 PM	
Analysis Name	D:\Data\FAN\data\2016\0712\gps-2.d	Operator	Fan	
Method	tune_wide_20151116.m	Instrument	maXis	10103
Sample Name	gaopeisen	Comment		

<b>Acquisition Parameter</b>					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	200 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2900 m/z	Set Collision Cell RF	1500.0 Vpp	Set Divert Valve	Waste



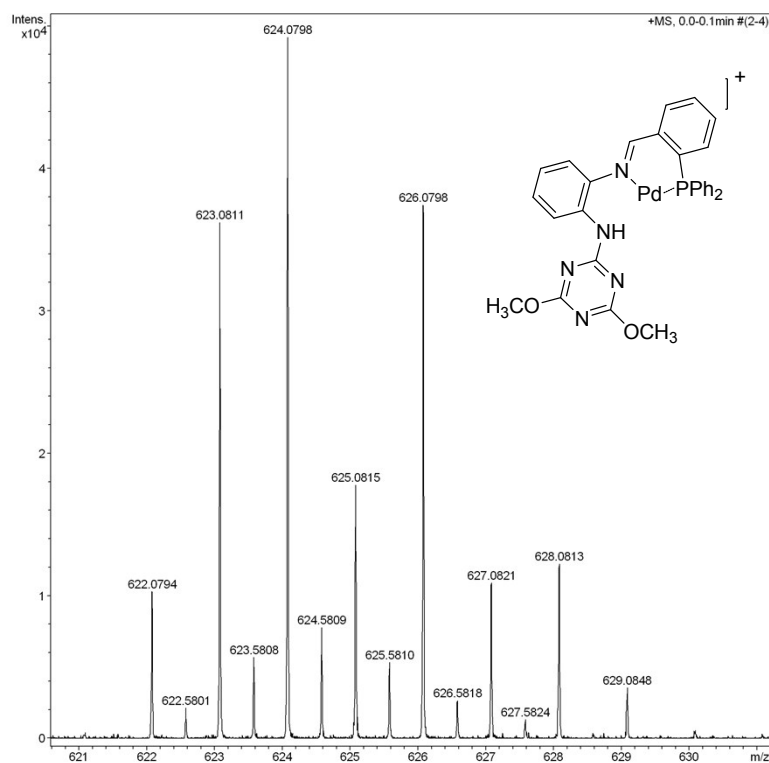
Bruker Compass DataAnalysis 4.0

printed: 7/12/2016 4:52:06 PM

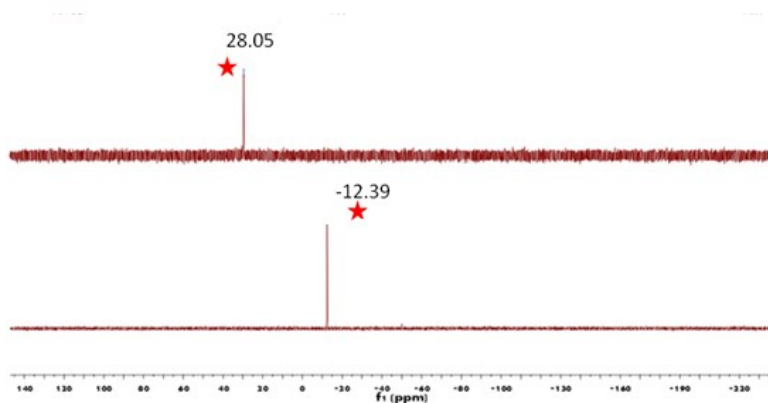
Page 1 of 1

**Fig S3.** HR-MS of Pd(OAc)<sub>2</sub> + L1-Phos (mol ratio= 1:1) (Abstrated from our previous work <sup>[2]</sup>)

Aiming at gaining more information on the coordination mode of Pd(OAc)<sub>2</sub> and L1, the reaction between Pd(OAc)<sub>2</sub> (0.05 mmol) and L1 (0.05 mmol) in CDCl<sub>3</sub> was investigated by <sup>31</sup>P-NMR analysis. After 5 min in room temperature, the <sup>31</sup>P-NMR spectrum of a 1:1 reaction showed only one signal (28.05 ppm). The signal at -12.39 ppm was assigned to -PPh<sub>2</sub> of L1 (Fig S5). These results supported that both N and P unit of L1 coordinated to the center of Pd(II) forming a tetra-coordinated palladium activated species.

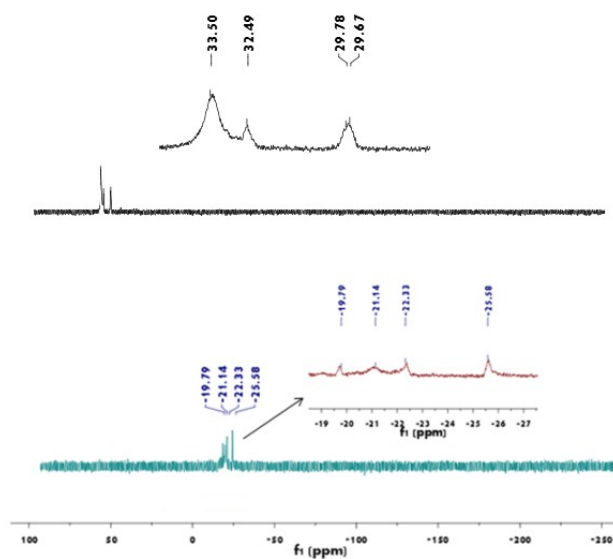


**Figure S4.** The HR-MS of Pd/L1 complexes (Abstrated from our previous work <sup>[2]</sup> )



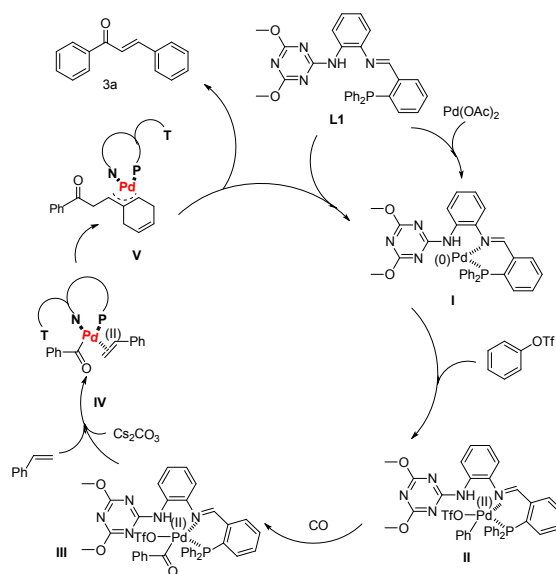
**Figure S5.** The comparison of <sup>31</sup>P-NMR spectrum of Pd/ L1 complex (above) and <sup>31</sup>P-NMR spectrum of L1 (bottom) (Abstrated from our previous work <sup>[2]</sup> )

Also, we conducted the <sup>31</sup>P-NMR analysis of Pd(OAc)<sub>2</sub> / L9 complex and <sup>31</sup>P-NMR analysis of L9. (Figure S6). The <sup>31</sup>P-NMR spectrum of L9 in CDCl<sub>3</sub> showed four signals at -19.79, -21.14, -22.33, -25.58 ppm. The <sup>31</sup>P-NMR spectrum of L9/ Pd(OAc)<sub>2</sub> in CDCl<sub>3</sub> of a 1:1 reaction showed four signals appeared at 33.50, 32.49, 29.87 and 29.67 ppm. These results suggested that L9 showed the similar coordination mode with its mother ligand L1.



**Figure S6.** The comparison of  $^{31}\text{P}$ -NMR spectrum of Pd/ **L9** complex (above) and  $^{31}\text{P}$ -NMR spectrum of **L9** (bottom)

Finally, based on our study on the coordination of Pd/**L1** and the general accepted Pd-catalyzed Heck-type Carbonylative reaction by Wu and Beller, we have made a proposed mechanism for Pd/**L1** catalyzed Heck-type Carbonylative reaction (**Figure S11**)



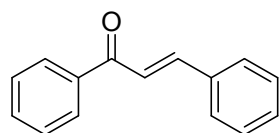
**Scheme S11.** A proposed mechanism for *s*-triazine based *N,P*- ligand **L1** controlled Pd-catalyzed Heck-Typed carbonylative reaction of **1**, CO and **2**.

Based on the investigation of the coordination behavior of Pd(OAc)<sub>2</sub> with **L1** and the generally accepted mechanism for Pd-catalyzed Heck-type carbonylative reaction posed by Wu and Beller,

we proposed a mechanism for *s*-triazine based *N,P*- ligands controlled Pd-catalyzed Heck-type carbonylative reaction of **1a**, CO and **2a**. We suppose that **L1** coordinated with Pd(OAc)<sub>2</sub> to give **(I)** species. Then **(I)** underwent oxidative addition of the aryl triflate to form **(II)**, After CO insertion process, the acylpalladium **(III)** intermediate was formed. Then, Coordination and insertion of the alkene followed by β-hydride elimination produces the desired chalcone **3a** and the active Pd species was regenerated by reaction with Cs<sub>2</sub>CO<sub>3</sub> to complete the catalytic cycle.

## S.9 NMR-Data of products and novel N,P-ligands

### S-9.1 NMR-Data of Carbonylative Heck coupling products 3

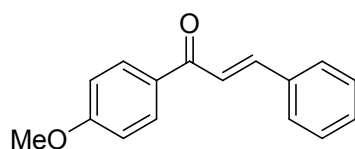


3a

In accordance with **GP1**, **3a** was obtained as colorless solid. Yield: 85%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 7.1$  Hz, 2H), 7.77 (d,  $J = 15.7$  Hz, 1H), 7.55 (d,  $J = 2.9$  Hz, 1H), 7.54 (s, 1H), 7.49 (d,  $J = 9.4$  Hz, 1H), 7.48 (s, 1H), 7.42 (s, 1H), 7.41 (d,  $J = 7.4$  Hz, 1H), 7.32 (d,  $J = 2.0$  Hz, 1H),

7.31 (d,  $J = 1.9$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  190.23, 165.75, 144.71, 138.21, 134.89, 132.85, 130.59, 129.00, 128.68, 128.57, 128.54, 122.01.

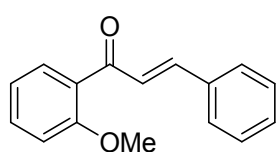


3b

In accordance with **GP1**, **3b** was obtained as pale yellow solid.

Yield: 82%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.5$  Hz, 2H), 7.74 (d,  $J = 15.6$  Hz, 1H), 7.53 (d,  $J = 8.8$  Hz, 2H), 7.50 (d,  $J = 7.3$  Hz, 1H), 7.43 (t,  $J = 7.7$  Hz, 2H), 7.37 (d,  $J = 15.6$  Hz, 1H),

6.86 (d,  $J = 8.8$  Hz, 2H), 3.74 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  190.50, 161.71, 144.74, 138.45, 132.62, 130.29, 128.59, 128.43, 127.54, 119.64, 114.44, 55.34.

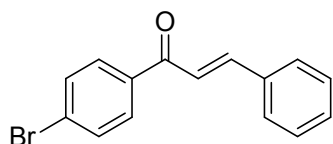


3c

In accordance with **GP1**, **3c** was obtained as yellow oil. Yield: 81%.  $^1\text{H}$

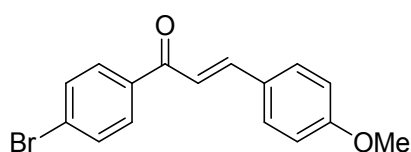
NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 3.8$  Hz, 1H), 7.51 (d,  $J = 6.0$  Hz, 1H), 7.49 (d,  $J = 3.8$  Hz, 1H), 7.48 (d,  $J = 1.7$  Hz, 1H), 7.38 (t,  $J = 7.8$  Hz, 1H), 7.31 – 7.28 (m, 3H), 7.16 (s, 1H), 6.94 (t,  $J = 7.4$  Hz, 1H), 6.91 (d,  $J$

= 8.3 Hz, 1H), 3.80 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  191.98, 157.12, 142.22, 134.17, 131.82, 129.34, 129.20, 128.34, 127.86, 127.38, 126.12, 119.75, 110.66, 54.76.



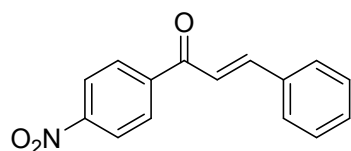
**3d**

In accordance with **GP1**, **3d** was obtained as pale yellow solid. Yield: 88%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 15.7 Hz, 1H), 7.59 – 7.55 (m, 3H), 7.54 (s, 1H), 7.42 (d, *J* = 15.7 Hz, 1H), 7.37 – 7.32 (m, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 189.00, 145.26, 136.86, 134.67, 131.90, 130.77, 130.06, 129.68, 129.02, 128.88, 128.74, 128.59, 127.92, 127.49, 121.31.



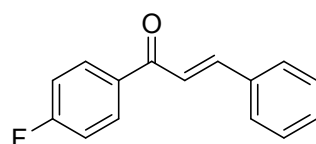
**3e**

In accordance with **GP1**, **3e** was obtained as yellow solid. Yield: 86%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.04 (d, *J* = 8.9 Hz, 2H), 7.80 (d, *J* = 15.6 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 15.6 Hz, 1H), 7.40 (s, 3H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 188.71, 163.46, 143.97, 135.10, 131.11, 130.85, 130.36, 128.95, 128.39, 121.89, 113.88, 55.51.



**3f**

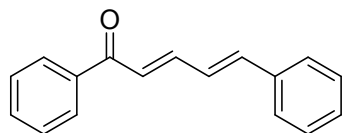
In accordance with **GP1**, **3f** was obtained as yellow solid. Yield: 44%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.26 (d, *J* = 8.7 Hz, 2H), 8.03 (d, *J* = 7.2 Hz, 2H), 7.79 (dd, *J* = 17.2, 12.2 Hz, 3H), 7.63 (dd, *J* = 19.9, 11.6 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 189.64, 148.56, 141.51, 141.06, 137.54, 133.40, 128.97, 128.85, 128.62, 125.73, 124.23.



**3g**

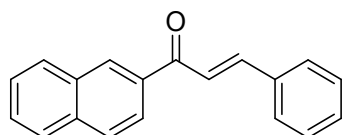
In accordance with **GP1**, **3g** was obtained as yellow solid. Yield: 35%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 15.7 Hz, 1H), 7.57 (dd, *J* = 8.6, 5.5 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 9.7 Hz, 1H), 7.05 (t, *J* = 8.6 Hz, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 190.08, 164.85 (d, *J* = 252.2 Hz), 163.18, 143.38, 138.10, 132.87, 131.17, 130.43 (d, *J* = 9.1 Hz), 128.66, 121.69, 116.16 (d, *J* = 21.1 Hz).





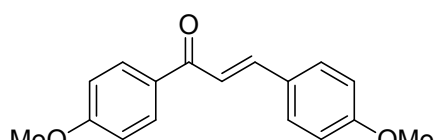
3h

In accordance with **GPI**, **3h** was obtained as yellow solid. Yield: 77%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 7.2$  Hz, 2H), 7.41 (dd,  $J = 14.9, 10.8$  Hz, 1H), 7.34 (t,  $J = 7.3$  Hz, 1H), 7.27 (t,  $J = 7.5$  Hz, 4H), 7.16 (t,  $J = 7.4$  Hz, 2H), 7.11 (t,  $J = 7.3$  Hz, 1H), 6.89 (d,  $J = 14.9$  Hz, 1H), 6.80 (dd,  $J = 15.5, 10.8$  Hz, 1H), 6.73 (d,  $J = 15.6$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  190.25, 144.84, 141.95, 138.26, 136.14, 132.74, 129.30, 128.93, 128.67, 128.47, 127.42, 127.01, 125.39.



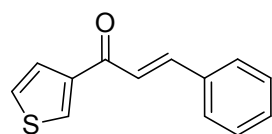
3i

In accordance with **GPI**, **3i** was obtained as yellow solid. Yield: 80%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.57 (d,  $J = 15.4$  Hz, 1H), 8.15 (d,  $J = 8.4$  Hz, 1H), 7.98 (d,  $J = 7.3$  Hz, 2H), 7.83 – 7.76 (m, 3H), 7.52 (d,  $J = 15.5$  Hz, 1H), 7.50 – 7.45 (m, 2H), 7.42 (dt,  $J = 7.6, 6.1$  Hz, 4H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  190.32, 141.76, 138.22, 133.78, 132.92, 132.41, 131.81, 130.86, 128.81, 128.72, 128.63, 127.02, 126.35, 125.49, 125.14, 124.71, 123.53.



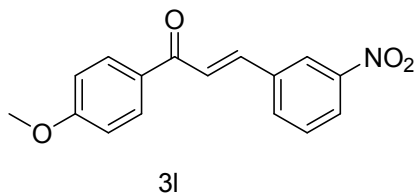
3j

In accordance with **GPI**, **3j** was obtained as yellow solid. Yield: 82%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.7$  Hz, 2H), 7.72 (d,  $J = 15.5$  Hz, 1H), 7.50 (d,  $J = 8.2$  Hz, 2H), 7.38 (d,  $J = 15.5$  Hz, 1H), 6.88 (d,  $J = 8.6$  Hz, 2H), 6.83 (d,  $J = 8.3$  Hz, 2H), 3.75 (s, 3H), 3.72 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  188.49, 163.26, 161.48, 143.72, 131.21, 130.68, 130.14, 127.67, 119.29, 114.35, 113.77, 55.37, 55.27.

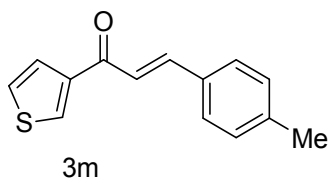


3k

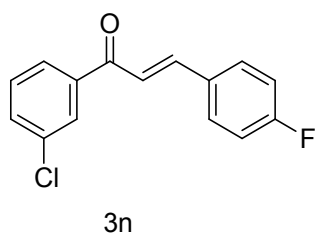
In accordance with **GPI**, **3k** was obtained as pale-yellow solid. Yield: 85%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 – 7.99 (m, 2H), 7.81 (d,  $J = 15.6$  Hz, 1H), 7.59 (d,  $J = 1.6$  Hz, 1H), 7.57 (d,  $J = 7.3$  Hz, 1H), 7.49 (t,  $J = 7.5$  Hz, 2H), 7.43 (d,  $J = 4.6$  Hz, 1H), 7.39 – 7.33 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.22, 139.73, 139.65, 139.60, 134.19, 130.70, 130.07, 129.89, 128.53, 126.70, 123.22.



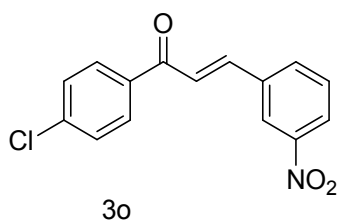
In accordance with **GP1**, **3l** was obtained as pale-yellow solid. Yield: 86%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (s, 1H), 7.84 (d,  $J = 7.8$  Hz, 1H), 7.76 (d,  $J = 15.6$  Hz, 1H), 7.55 (d,  $J = 8.7$  Hz, 2H), 7.48 (d,  $J = 8.0$  Hz, 1H), 7.38 (t,  $J = 7.8$  Hz, 1H), 7.31 (d,  $J = 15.6$  Hz, 1H), 6.89 (d,  $J = 8.8$  Hz, 2H), 3.79 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  188.87, 161.91, 145.48, 140.06, 134.80, 132.41, 130.41, 129.86, 128.44, 127.31, 126.45, 118.92, 114.45, 55.32.



In accordance with **GP1**, **3m** was obtained as pale-yellow solid. Yield: 81%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.1$  Hz, 2H), 7.77 (d,  $J = 15.6$  Hz, 1H), 7.55 (d,  $J = 2.0$  Hz, 1H), 7.39 (d,  $J = 5.0$  Hz, 1H), 7.32 (dd,  $J = 13.3, 10.3$  Hz, 2H), 7.25 (d,  $J = 8.0$  Hz, 2H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  190.38, 143.62, 138.20, 137.98, 135.55, 129.30, 129.09, 128.59, 126.98, 125.28, 121.69, 21.57.

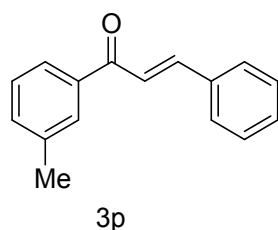


In accordance with **GP1**, **3n** was obtained as pale-yellow solid. Yield: 77%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (dd,  $J = 8.7, 5.5$  Hz, 2H), 7.73 (s, 1H), 7.66 (d,  $J = 15.7$  Hz, 1H), 7.49 (s, 1H), 7.46 (t,  $J = 10.0$  Hz, 2H), 7.24 (t,  $J = 7.8$  Hz, 1H), 7.14 (t,  $J = 8.6$  Hz, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  188.18, 166.53 (d,  $J = 255.2$  Hz), 143.06, 136.85, 134.19, 133.29, 131.20 (d,  $J = 9.1$  Hz), 131.14, 130.83, 130.46, 127.27, 123.08 (d,  $J = 61.9$  Hz), 122.67, 115.87 (d,  $J = 22.7$  Hz).



In accordance with **GP1**, **3o** was obtained as pale-yellow solid. Yield: 38%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (s, 1H), 8.24 (d,  $J = 8.2$  Hz,

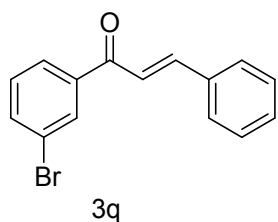
1H), 7.89 (d,  $J = 7.8$  Hz, 1H), 7.61 (t,  $J = 8.0$  Hz, 1H), 7.53 (d,  $J = 13.2$  Hz, 1H), 7.52 – 7.50 (m, 1H), 7.47 (s, 1H), 7.46 (d,  $J = 1.5$  Hz, 1H), 7.41 – 7.38 (m, 1H), 7.26 (d,  $J = 16.1$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  192.83, 148.73, 142.45, 138.56, 136.27, 133.96, 131.97, 130.45, 129.55, 128.65, 127.07, 124.91, 122.86.



In accordance with **GP1**, **3p** was obtained as pale-yellow solid. Yield: 78%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 7.8$  Hz, 2H), 7.76 (d,  $J = 15.7$  Hz, 1H), 7.51 (dd,  $J = 16.7, 11.4$  Hz, 2H), 7.44 (t,  $J = 7.6$  Hz, 2H), 7.39 (d,  $J = 7.3$  Hz, 2H), 7.24 (d,  $J = 7.5$  Hz, 1H), 7.16 (d,  $J = 7.5$  Hz, 1H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  190.43, 145.05, 138.57, 138.23,

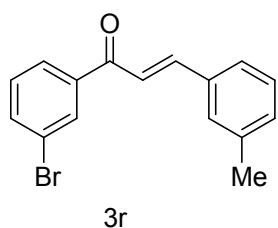
134.82, 132.80, 131.48, 129.17, 128.87, 128.64, 128.55, 125.75, 121.76, 21.32.



In accordance with **GP1**, **3q** was obtained as pale-yellow solid. Yield: 73%.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 7.7$  Hz, 2H), 7.70 (s, 1H), 7.64 (d,  $J = 15.7$  Hz, 1H), 7.53 (t,  $J = 7.2$  Hz, 1H), 7.48 (s, 1H), 7.45 (s, 3H), 7.44 (s, 1H), 7.20 (t,  $J = 7.8$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$

189.83, 142.84, 137.83, 136.98, 133.21, 133.06, 130.89, 130.47, 128.72, 128.59, 127.25, 123.13, 123.08.

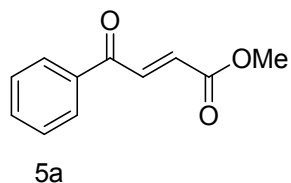


In accordance with **GP1**, **3r** was obtained as pale-yellow solid. Yield: 75%.

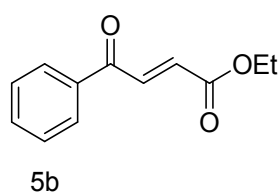
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (s, 2H), 7.73 (s, 1H), 7.66 (d,  $J = 15.6$  Hz, 1H), 7.49 (d,  $J = 13.9$  Hz, 3H), 7.36 (s, 2H), 7.23 (d,  $J = 6.8$  Hz, 1H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  189.87, 142.57, 138.49,

137.90, 137.07, 133.83, 133.13, 130.86, 130.44, 129.09, 128.56, 127.22, 125.80, 123.30, 123.07, 21.43.

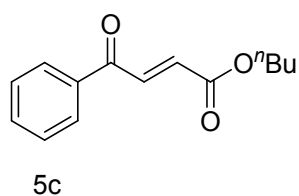
## S-9.2 NMR-Data of Carbonylative Heck coupling products 5



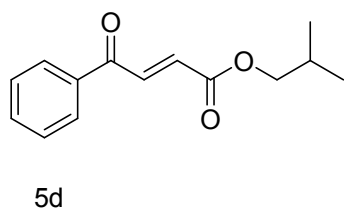
In accordance with **GP2**, 85.6 mg of **5a** was obtained as colorless oil. Yield: 90%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 6.75 (d, *J* = 15.6 Hz, 1H), 3.71 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.17, 165.86, 136.49, 136.46, 133.81, 131.93, 128.83, 128.78, 52.24. HR-MS (ESI positive ion mode): *m/z*: calcd. for C<sub>11</sub>H<sub>11</sub>O<sub>3</sub><sup>+</sup> : 191.0703 [M+H]<sup>+</sup>. Found: 191.0701.



In accordance with **GP2**, 89.8 mg of **5b** was obtained as red oil. Yield: 88%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 15.6 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 6.77 (d, *J* = 15.6 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 189.42, 165.48, 136.57, 136.32, 133.79, 132.53, 129.08, 128.84, 128.82, 61.33, 14.14. HR-MS (ESI positive ion mode): *m/z*: calcd. for C<sub>12</sub>H<sub>13</sub>O<sub>3</sub><sup>+</sup> : 205.0859 [M+H]<sup>+</sup>. Found: 205.0855.

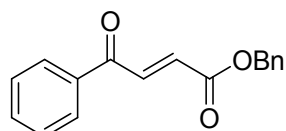


In accordance with **GP2**, 98.6 mg of **5c** was obtained as colorless oil. Yield: 85%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.93 – 7.86 (m, 2H), 7.82 (dd, *J* = 15.6, 2.9 Hz, 1H), 7.52 (dd, *J* = 11.1, 7.2 Hz, 1H), 7.41 (dd, *J* = 11.8, 7.5 Hz, 2H), 6.80 (dd, *J* = 15.6, 3.6 Hz, 1H), 4.15 (td, *J* = 6.6, 3.5 Hz, 2H), 1.66 – 1.54 (m, 2H), 1.34 (ddd, *J* = 14.8, 7.5, 3.4 Hz, 2H), 0.87 (td, *J* = 7.4, 3.4 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 189.48, 165.62, 136.61, 136.35, 133.81, 132.58, 128.86, 65.24, 30.56, 19.11, 13.68. HR-MS (ESI positive ion mode): *m/z*: calcd. for C<sub>14</sub>H<sub>17</sub>O<sub>3</sub><sup>+</sup> : 233.1772 [M+H]<sup>+</sup>. Found: 233.1772.



In accordance with **GP2**, 102.1 mg of **5d** was obtained as colorless oil. Yield: 88%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 8.1 Hz,

2H), 7.83 (d,  $J = 13.8$  Hz, 1H), 7.54 (t,  $J = 8.0$  Hz, 1H), 7.43 (t,  $J = 7.1$  Hz, 2H), 6.82 (d,  $J = 15.5$  Hz, 1H), 3.95 (dd,  $J = 6.7, 1.8$  Hz, 2H), 1.94 (dp,  $J = 13.4, 6.7$  Hz, 1H), 0.90 (d,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  189.55, 165.63, 136.62, 136.40, 133.84, 132.59, 128.89, 128.86, 71.42, 27.73, 19.07. HR-MS (ESI positive ion mode):  $m/z$ : calcd. for  $\text{C}_{14}\text{H}_{17}\text{O}_3^+$  : 233.1772  $[\text{M}+\text{H}]^+$ . Found: 233.1770.

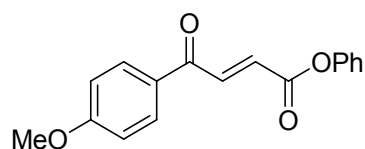


5e

In accordance with **GP2**, 109.2 mg of **5e** was obtained as colorless oil.

Yield: 82%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 7.3$  Hz, 2H), 7.86 (d,  $J = 15.6$  Hz, 1H), 7.53 (t,  $J = 7.4$  Hz, 1H), 7.41 (t,  $J = 7.8$  Hz, 2H), 7.31 (q,  $J = 8.0$  Hz, 3H), 7.28 – 7.24 (m, 2H), 6.85 (d,  $J = 15.6$  Hz, 1H),

5.19 (s, 2H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  189.47, 165.41, 136.90, 136.57, 135.36, 133.90, 132.22, 128.92, 128.90, 128.70, 128.55, 128.42, 67.16. HR-MS (ESI positive ion mode):  $m/z$ : calcd. for  $\text{C}_{17}\text{H}_{15}\text{O}_3^+$  : 267.1016  $[\text{M}+\text{H}]^+$ . Found: 267.1016.

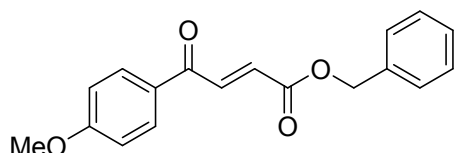


5f

In accordance with **GP4**, 127.1 mg of **10f** was obtained as red solid.

Yield: 90%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 15.6$  Hz, 1H), 8.00 (d,  $J = 7.8$  Hz, 2H), 7.60 (t,  $J = 7.2$  Hz, 1H), 7.49 (t,  $J = 7.6$  Hz, 2H), 7.08 (d,  $J = 8.9$  Hz, 2H), 6.90 (d,  $J = 8.9$  Hz, 2H),

3.76 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  189.16, 164.34, 157.55, 143.95, 137.75, 136.51, 134.00, 131.73, 128.97, 128.93, 122.14, 116.07, 114.78, 114.57, 55.57. HR-MS (ESI positive ion mode):  $m/z$ : calcd. for  $\text{C}_{17}\text{H}_{15}\text{O}_4^+$  : 283.0965  $[\text{M}+\text{H}]^+$ . Found: 283.0964.

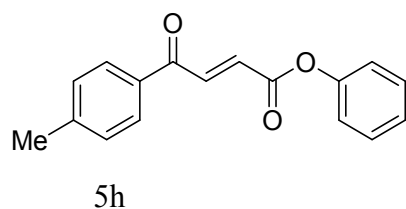


5g

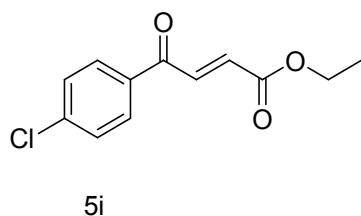
In accordance with **GP2**, 118.5 mg of **5g** was obtained as red solid.

Yield: 78%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J = 8.0$  Hz, 2H), 8.00 (d,  $J = 15.5$  Hz, 1H), 7.66 (t,  $J =$

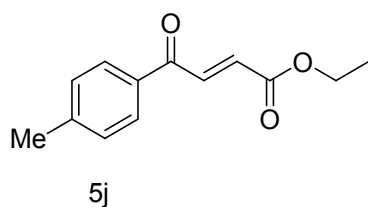
7.3 Hz, 1H), 7.54 (t,  $J = 7.6$  Hz, 2H), 7.44 (d,  $J = 8.4$  Hz, 2H), 7.03 – 6.95 (m, 3H), 5.30 (s, 2H), 3.85 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  189.19, 165.33, 159.86, 136.58, 133.78, 132.25, 130.31, 129.01, 128.85, 128.83, 128.64, 127.54, 114.05, 66.91, 55.16. HR-MS (ESI positive ion mode):  $m/z$ : calcd. for  $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Na}^+$  : 319.0941  $[\text{M}+\text{Na}]^+$ . Found: 319.0940.



In accordance with **GP2**, 117.2 mg of **5h** was obtained as colorless oil. Yield: 88%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 15.6$  Hz, 1H), 7.89 (d,  $J = 7.9$  Hz, 2H), 7.48 (t,  $J = 7.4$  Hz, 1H), 7.37 (t,  $J = 7.6$  Hz, 2H), 7.06 (d,  $J = 8.1$  Hz, 2H), 6.96 – 6.89 (m, 3H), 2.21 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  189.16, 164.19, 148.27, 137.78, 136.52, 135.91, 134.01, 131.78, 130.10, 128.98, 128.95, 121.06, 20.92. HR-MS (ESI positive ion mode):  $m/z$ : calcd. for  $\text{C}_{17}\text{H}_{14}\text{O}_3\text{Na}^+$  : 289.0835  $[\text{M}+\text{Na}]^+$ . Found: 289.0835.

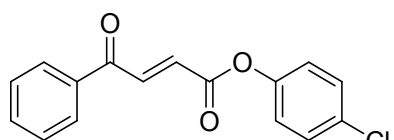


In accordance with **GP2**, 82.4 mg of **5i** was obtained as yellow oil. Yield: 69%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.4$  Hz, 2H), 7.77 (d,  $J = 15.5$  Hz, 1H), 7.40 (d,  $J = 8.4$  Hz, 2H), 6.80 (d,  $J = 15.5$  Hz, 1H), 4.22 (q,  $J = 7.1$  Hz, 2H), 1.27 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  188.23, 165.38, 140.43, 135.79, 134.96, 133.01, 130.22, 129.24, 61.45, 14.15. HR-MS (ESI positive ion mode):  $m/z$ : calcd. for  $\text{C}_{12}\text{H}_{11}\text{ClO}_3\text{Na}^+$  : 261.0289  $[\text{M}+\text{Na}]^+$ . Found: 261.0289.



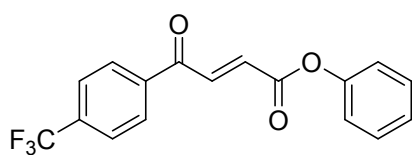
In accordance with **GP2**, 97.4 mg of **5j** was obtained as colorless oil. Yield: 91%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 8.5$  Hz, 2H), 7.81 (d,  $J = 15.5$  Hz, 1H), 7.22 (d,  $J = 7.9$  Hz, 2H), 6.78 (d,  $J$

= 15.5 Hz, 1H), 4.21 (q,  $J = 7.1$  Hz, 2H), 2.35 (s, 3H), 1.26 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  188.97, 165.63, 144.88, 136.54, 132.18, 129.57, 129.00, 61.29, 21.73, 14.16. HR-MS (ESI positive ion mode):  $m/z$ : calcd. for  $\text{C}_{13}\text{H}_{15}\text{O}_3^+$  : 219.1016  $[\text{M}+\text{Na}]^+$ . Found: 219.1016.



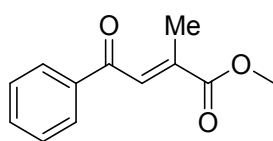
**5k**

In accordance with **GP2**, 126.2 mg of **5k** was obtained as colorless oil. Yield: 88%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 15.5$  Hz, 1H), 7.89 (d,  $J = 7.4$  Hz, 2H), 7.50 (t,  $J = 7.4$  Hz, 1H), 7.38 (t,  $J = 7.7$  Hz, 2H), 7.23 (d,  $J = 8.8$  Hz, 2H), 7.00 (d,  $J = 8.8$  Hz, 2H), 6.93 (d,  $J = 15.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  188.91, 163.74, 148.88, 138.23, 136.38, 134.12, 131.60, 131.22, 129.63, 129.00, 128.94, 122.80. HR-MS (ESI positive ion mode):  $m/z$ : calcd. for  $\text{C}_{16}\text{H}_{11}\text{ClO}_3\text{Na}^+$  : 309.0289  $[\text{M}+\text{Na}]^+$ . Found: 309.0288.



**5l**

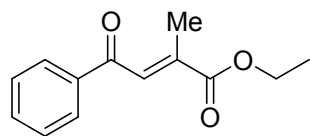
In accordance with **GP2**, 145.7 mg of **5l** was obtained as yellow solid. Yield: 91%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 15.5$  Hz, 1H), 7.92 (d,  $J = 7.7$  Hz, 2H), 7.57 (d,  $J = 8.4$  Hz, 2H), 7.53 (t,  $J = 7.3$  Hz, 1H), 7.41 (t,  $J = 7.6$  Hz, 2H), 7.20 (d,  $J = 8.3$  Hz, 2H), 6.97 (d,  $J = 15.5$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  188.88, 163.47, 152.87, 138.59, 136.37, 134.14, 130.96, 129.01, 128.93, 128.82 (q,  $J = 262$  Hz, Cquat), 126.97 (q, Cquat), 121.94. HR-MS (ESI positive ion mode):  $m/z$ : calcd. for  $\text{C}_{17}\text{H}_{12}\text{F}_3\text{O}_3^+$  : 321.0733  $[\text{M}+\text{H}]^+$ . Found: 321.0733.



**5m**

In accordance with **GP2**, 145.7 mg of **5m** was obtained as yellow liquid. Yield: 71%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.5$  Hz, 2H), 7.62 (s, 1H), 7.47 (t,  $J = 7.4$  Hz, 1H), 7.37 (t,  $J = 7.8$  Hz, 2H), 3.74 (s, 3H), 2.08 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  191.27, 166.77, 139.37, 136.40,

132.52, 130.90, 127.72, 127.55, 51.50, 13.68.



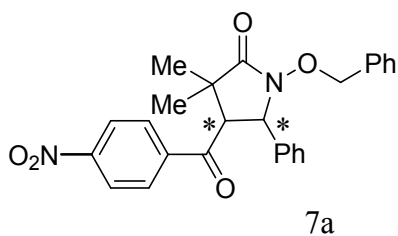
5n

In accordance with **GP2**, 145.7 mg of **5n** was obtained as yellow liquid.

Yield: 70%.  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.77 (m, 2H), 7.59 (d,  $J = 1.5$  Hz, 1H), 7.42 (t,  $J = 7.4$  Hz, 1H), 7.32 (t,  $J = 7.8$  Hz, 2H), 4.15 (dd,  $J = 14.4, 7.2$  Hz, 2H), 2.05 (s, 3H), 1.25 – 1.16 (m, 3H).  $^{13}\text{C NMR}$

(151 MHz,  $\text{CDCl}_3$ )  $\delta$  192.18, 167.16, 140.68, 137.42, 133.40, 131.57, 128.66, 128.48, 61.42, 14.60, 14.09.

### S-9.3 NMR-Data of [3+2] cycloaddition products 7a-7c

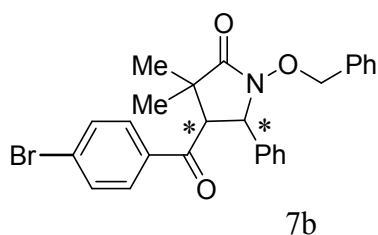


7a

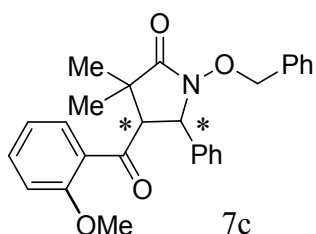
In accordance with **GP3**, 195.5 mg of **7a** was obtained as yellow solid. Yield: 88%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09



(d,  $J = 8.7$  Hz, 2H), 7.55 (dd,  $J = 6.5, 2.8$  Hz, 2H), 7.44 – 7.35 (m, 5H), 7.23 – 7.15 (m, 5H), 6.80 (d,  $J = 16.1$  Hz, 1H), 6.59 (d,  $J = 16.1$  Hz, 1H), 4.92 (d,  $J = 9.6$  Hz, 1H), 4.39 (d,  $J = 9.6$  Hz, 1H), 1.44 (d,  $J = 6.7$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.04, 147.51, 142.00, 139.00, 133.90, 132.82, 130.64, 129.86, 129.62, 129.14, 128.67, 128.49, 127.65, 126.96, 124.04, 92.34, 78.89, 78.16, 26.05, 25.48.

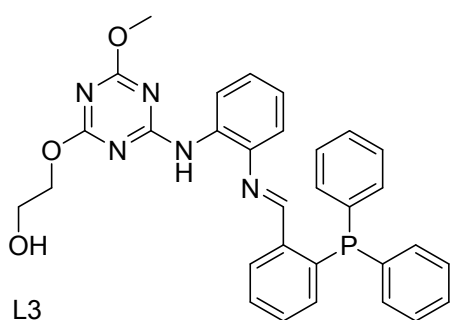


In accordance with **GP3**, 202.5 mg of **7b** was obtained as yellow solid. Yield: 85%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (q,  $J = 8.7$  Hz, 4H), 7.39 – 7.24 (m, 10H), 6.77 (d,  $J = 16.1$  Hz, 1H), 6.45 (d,  $J = 16.1$  Hz, 1H), 4.98 (d,  $J = 9.7$  Hz, 1H), 4.66 (d,  $J = 9.7$  Hz, 1H), 1.51 (s, 3H), 1.46 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.43, 138.89, 135.39, 133.87, 133.85, 131.65, 129.80, 129.13, 128.91, 128.79, 128.77, 128.53, 127.58, 127.10, 123.64, 92.70, 79.01, 78.11, 25.93, 25.55.



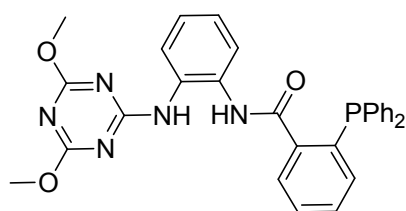
In accordance with **GP3**, 202.5 mg of **7c** was obtained as yellow solid. Yield: 84%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 6.3$  Hz, 1H), 7.31 – 7.21 (m, 1H), 7.17 – 7.02 (m, 2H), 6.75 (d,  $J = 7.5$  Hz, 0H), 6.68 (d,  $J = 8.3$  Hz, 0H), 6.53 (d,  $J = 16.2$  Hz, 0H), 4.87 (d,  $J = 9.5$  Hz, 0H), 4.48 (d,  $J = 9.5$  Hz, 0H), 3.59 (s, 3H), 1.39 (d,  $J = 24.6$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.14, 157.39, 140.29, 134.30, 129.66, 129.63, 129.19, 128.93, 128.80, 128.72, 128.47, 128.44, 127.85, 127.27, 124.82, 120.68, 111.03, 93.19, 78.83, 77.93, 55.44, 26.05, 25.67.

#### S-9.4 NMR-Data of Novel s-triazine derived Schiff-base *N,P* ligands



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.24 (s, 1H), 9.04 (s, 1H), 8.59 (s, 1H), 8.12 (s, 1H), 7.48 (t,  $J = 7.3$  Hz, 1H), 7.36 (t,  $J = 7.1$  Hz, 1H), 7.31 (s, 10H), 7.22 (s, 1H), 7.02 – 6.98 (m, 1H), 6.96 (t,  $J = 6.9$  Hz, 1H), 6.90 (s, 1H), 4.55 (s, 3H)

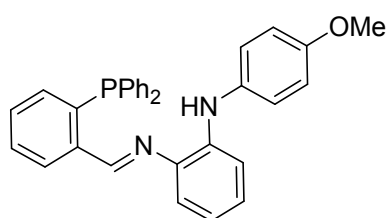
2H), 4.12 (t,  $J = 10.7$  Hz, 2H), 3.94 (d,  $J = 78.3$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  171.16, 165.89, 158.08, 139.13, 138.79, 138.68, 136.52, 134.21, 134.00, 133.87, 133.42, 131.07, 129.01, 128.94, 128.72, 128.67, 127.60, 123.01, 119.54, 116.74, 65.32, 60.41, 54.96.  $^{31}\text{P}$  NMR (243 MHz,  $\text{CDCl}_3$ )  $\delta$  -12.24. HR-MS (ESI):  $m/z$ : calcd. for  $\text{C}_{31}\text{H}_{29}\text{N}_5\text{O}_3\text{P}^+$  550.1930  $[\text{M}+\text{H}]^+$  and 572.1827  $[\text{M}+\text{Na}]^+$ . Found: 550.1928 and 572.1826.



L5

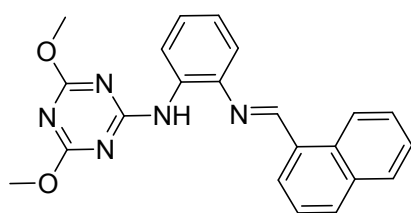
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (s, 1H), 7.85 (s, 1H), 7.64 (s, 1H), 7.54 (d,  $J = 7.8$  Hz, 1H), 7.38 (d,  $J = 6.4$  Hz, 1H), 7.31 (s, 1H), 7.27 (d,  $J = 7.4$  Hz, 1H), 7.25 – 7.17 (m, 10H), 7.11 (t,  $J = 7.5$  Hz, 1H), 7.07 (d,  $J = 7.3$  Hz, 1H), 6.94 (s, 1H), 3.81 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  172.49, 167.67, 167.13,

156.93, 140.79, 136.46, 136.40, 134.24, 133.95, 133.82, 130.69, 130.52, 128.98, 128.95, 128.67, 128.62, 128.41, 128.38, 126.16, 126.05, 125.70, 125.13, 54.83.  $^{31}\text{P}$  NMR (243 MHz,  $\text{CDCl}_3$ )  $\delta$  -10.68. HR-MS (ESI):  $m/z$ : calcd. for  $\text{C}_{30}\text{H}_{26}\text{N}_5\text{O}_3\text{PNa}^+$  558.1665  $[\text{M}+\text{Na}]^+$ . Found: 558.1663.



L6

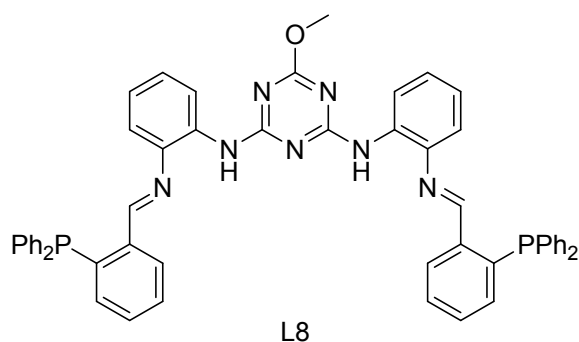
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.03 (s, 1H), 8.06 (d,  $J = 6.7$  Hz, 1H), 7.80 (d,  $J = 3.6$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 1H), 7.39 (d,  $J = 7.0$  Hz, 2H), 7.37 – 7.35 (m, 1H), 7.29 (dd,  $J = 15.4, 9.3$  Hz, 10H), 7.13 (d,  $J = 12.1$  Hz, 2H), 6.96 – 6.94 (m, 2H), 6.87 (d,  $J = 9.0$  Hz, 2H), 3.81 (s, 3H), 3.74 (s, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  155.66, 139.35, 137.13, 135.38, 134.04, 133.90, 130.46, 128.79, 128.60, 128.55, 124.15, 122.32, 119.76, 119.51, 118.69, 117.96, 117.13, 114.50, 114.37, 112.41, 55.56.  $^{31}\text{P}$  NMR (243 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.51. HR-MS (ESI):  $m/z$ : calcd. for  $\text{C}_{32}\text{H}_{28}\text{N}_2\text{OP}^+$  487.1934  $[\text{M}+\text{H}]^+$ . Found: 487.1933.



L7

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.25 (s, 1H), 8.90 (d,  $J = 8.5$  Hz, 1H), 8.62 (s, 2H), 8.21 (d,  $J = 7.1$  Hz, 1H), 8.00 (d,  $J = 8.1$  Hz, 1H), 7.92 (d,  $J = 8.2$  Hz, 1H), 7.79 – 7.69 (m, 1H), 7.63 (t,  $J = 7.5$  Hz, 1H), 7.59 – 7.54 (m, 2H), 7.32 (t,  $J = 7.5$  Hz, 1H), 7.12 (t,  $J = 7.5$  Hz, 1H), 3.97 (d,  $J = 40.0$  Hz, 6H).

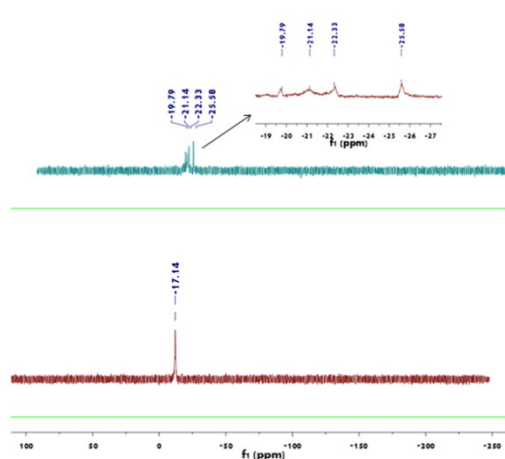
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  172.43, 167.42, 165.94, 158.67, 139.90, 132.47, 131.62, 131.10, 130.33, 129.83, 128.98, 127.56, 125.40, 123.61, 123.34, 119.86, 116.81, 54.91. HR-MS (ESI):  $m/z$ : calcd. for  $\text{C}_{22}\text{H}_{20}\text{N}_5\text{O}_2^+$  386.1612  $[\text{M}+\text{H}]^+$ . Found: 386.1611.



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.00 (d,  $J = 4.5$  Hz, 2H), 8.08 (dd,  $J = 7.3, 3.5$  Hz, 2H), 7.44 (t,  $J = 7.5$  Hz, 3H), 7.34 – 7.28 (m, 26H), 7.00 – 6.97 (m, 2H), 6.94 (dd,  $J = 7.5, 4.6$  Hz, 2H), 6.75 (d,  $J = 8.9$  Hz, 2H), 6.64 (dd,  $J = 17.2, 7.7$  Hz, 4H), 4.01 (s, 4H).  $^{13}\text{C}$  NMR (151 MHz,

$\text{CDCl}_3$ )  $\delta$  156.53, 156.43, 142.41, 139.67, 139.56, 138.21, 138.07, 137.33, 137.27, 137.23, 134.09, 133.96, 130.45, 129.58, 128.81, 128.75, 128.67, 128.62, 127.72, 118.19, 117.43, 115.26, 60.41.  $^{31}\text{P}$  NMR (243 MHz,  $\text{CDCl}_3$ )  $\delta$  -11.71. HR-MS (ESI):  $m/z$ : calcd. for  $\text{C}_{54}\text{H}_{44}\text{N}_7\text{OP}_2^+$  868.3077  $[\text{M}+\text{H}]^+$ . Found: 868.3071.

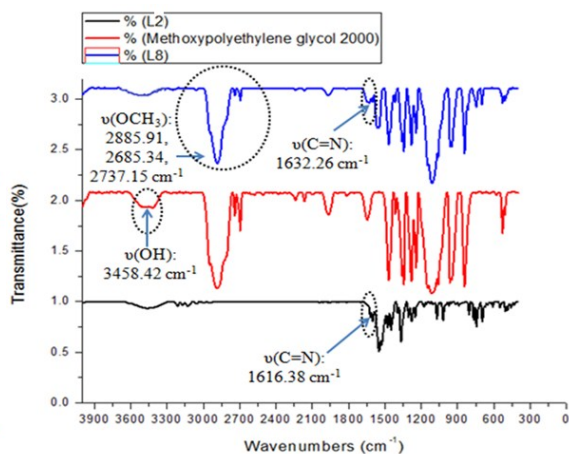
**Characterization:** **L9** was characterized by  $^{31}\text{P}$ -NMR, elemental analysis and FT-IR analysis. Initially, we made comparison of  $^{31}\text{P}$ -NMR of **L2** (starting material) with **L8** (Fig S1). The peak ( $\delta = -17.14$  ppm) was assigned to the **L2**-Phos Ligand. When **L2** underwent nucleophilic substitution with methoxypolyethylene-2000 under strong base conditions, the **L9** was formed. Through  $^{31}\text{P}$ -NMR analysis, the signals ( $\delta = -19.79, -21.14, -22.33$  and  $-25.58$  ppm) was assigned to the **L9**-Phos ligand. No positive signals were observed at  $^{31}\text{P}$ -NMR spectrum, indicating that the **L9** was not been oxidativated to  $\text{P}=\text{O}$  compound. Then, FT-IR analysis was conducted (Fig S2). Through the comparison of **L9**, **L2** and methoxypolyethylene-2000, we clearly observed that the peak ( $\nu(\text{OH}) = 3458.42 \text{ cm}^{-1}$ ) of methoxypolyethylene-2000 was disappeared as the result of the nucleophilic substitution with **L7**. Simultaneously, the new peaks ( $\nu(-\text{OCH}_3) = 2885.91, 2685.34, 2737.15 \text{ cm}^{-1}$ ) appeared. Compared with the spectrum of **L2**, these peaks was slightly blueshifted. Also, the peak ( $\nu(-\text{C}=\text{N}) = 1632.26 \text{ cm}^{-1}$ ) of **L2** was slightly red-shifted to  $1632.26 \text{ cm}^{-1}$ , which indicating that the s-triazinal unit was grafted at the end of methoxypolyethylene glycol-2000.



**Fig S1.** Comparison of  $^{31}\text{P}$ -NMR of L9 (blue line) with L2 (red line)

**Fig S3.** The elemental analysis of L9 at C,H,O,N mode.

Finally, in order to identify the structure of **L9**, elemental analysis was conducted (Fig S3). The results demonstrate that the **L9** has been synthesized successfully.

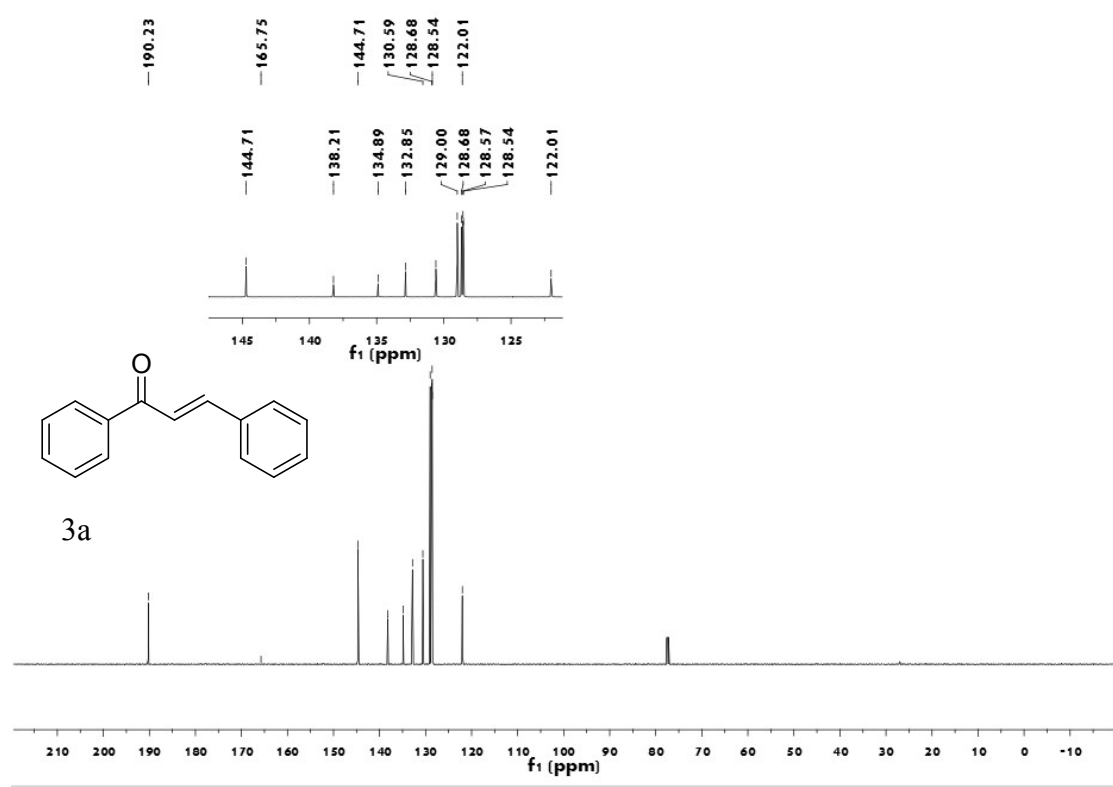
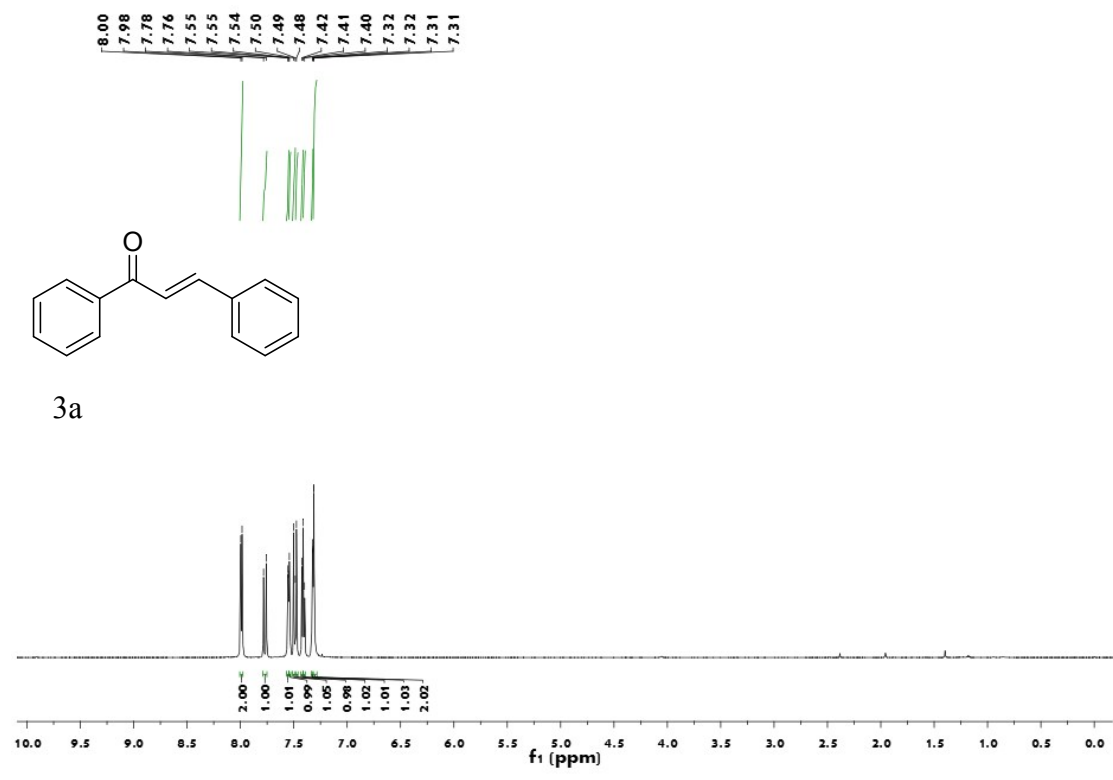


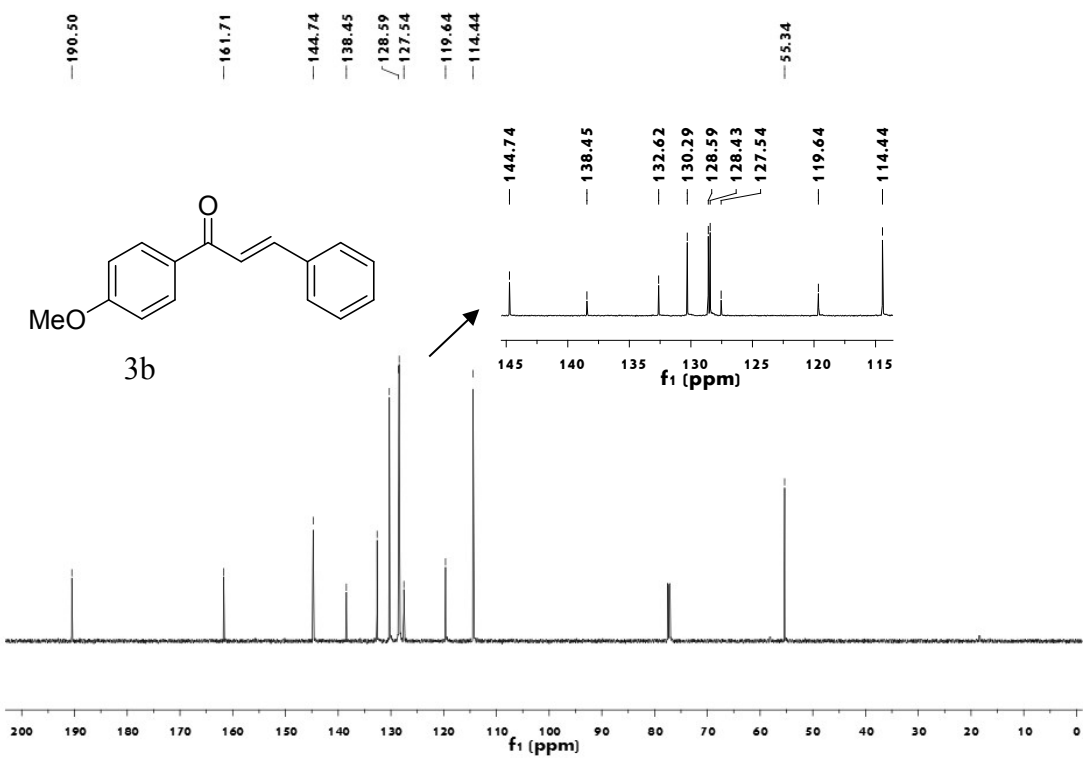
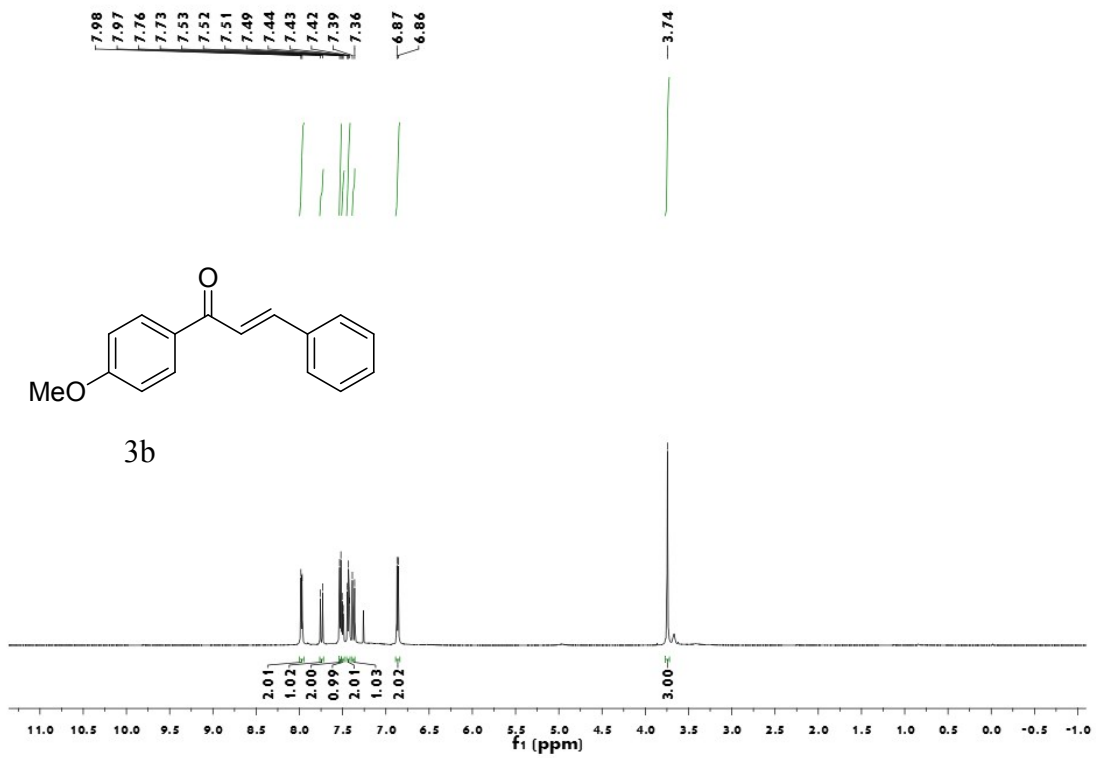
**Fig S2.** Comparison of FT-IR spectrum of L9 with that of L2 and methoxypolyethylene.

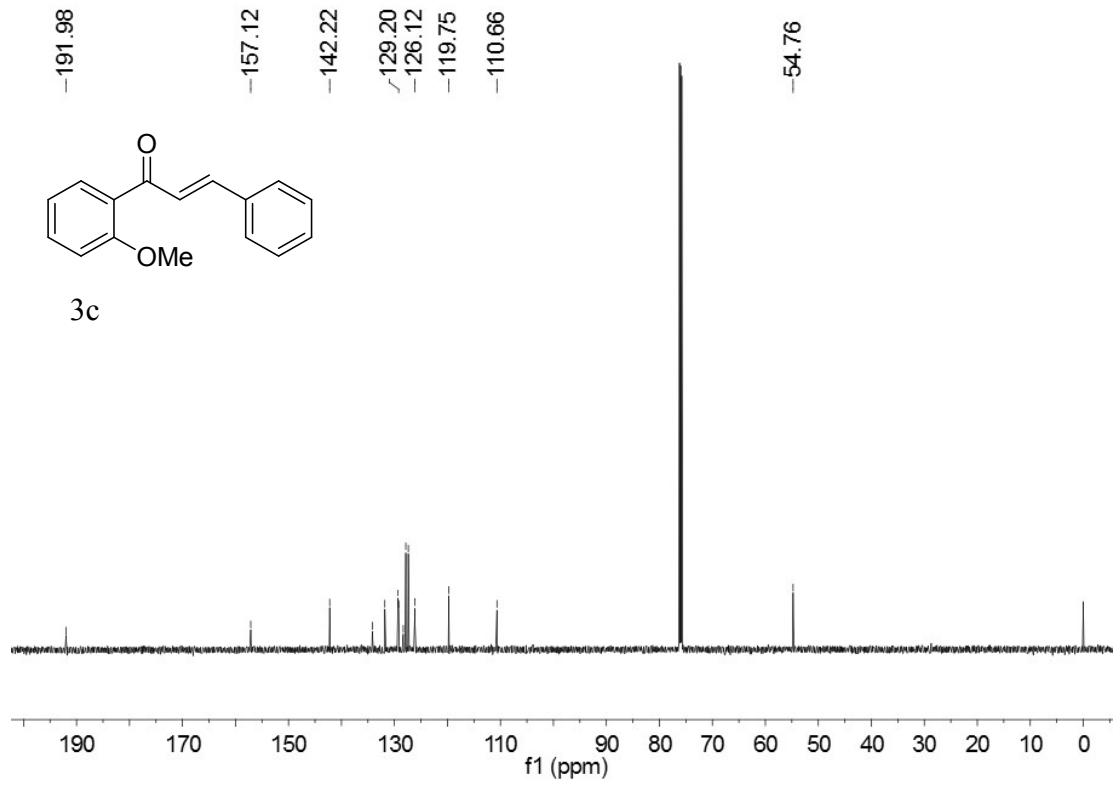
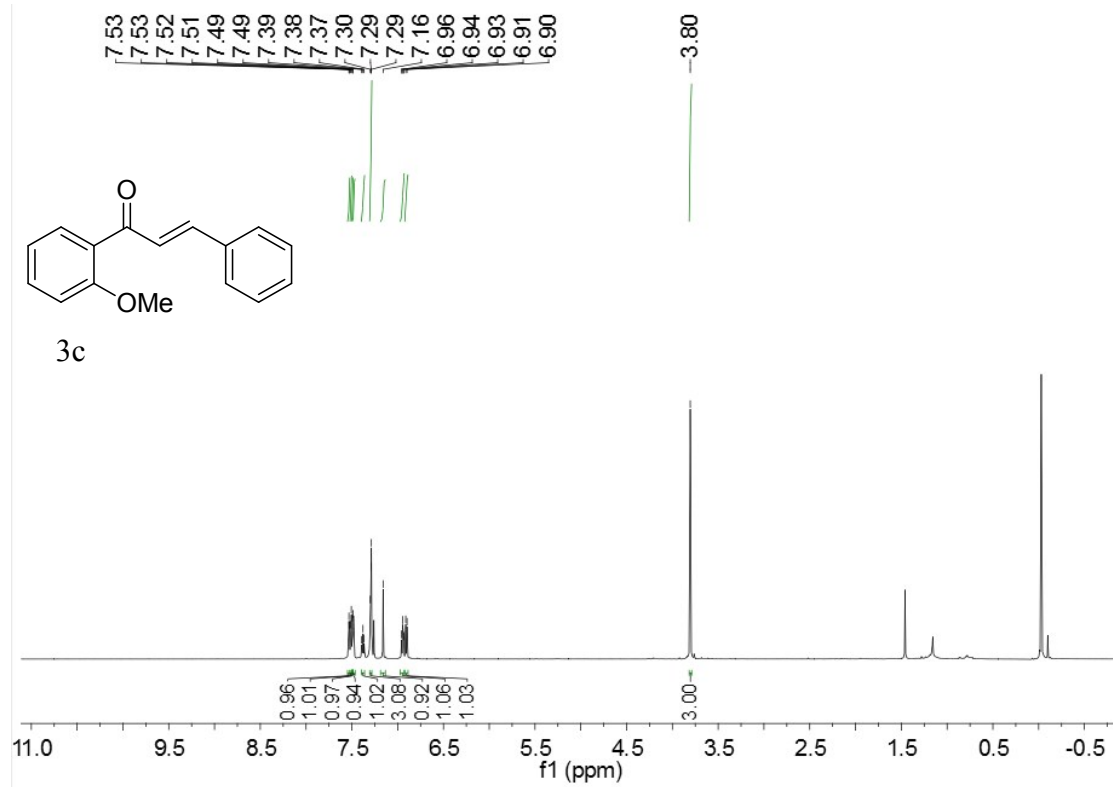
	C%	H%	N%	O%	P%
Measured	57.18	8.37	2.80	30.35	1.30
Calculated	57.20	8.35	2.81	30.40	1.24

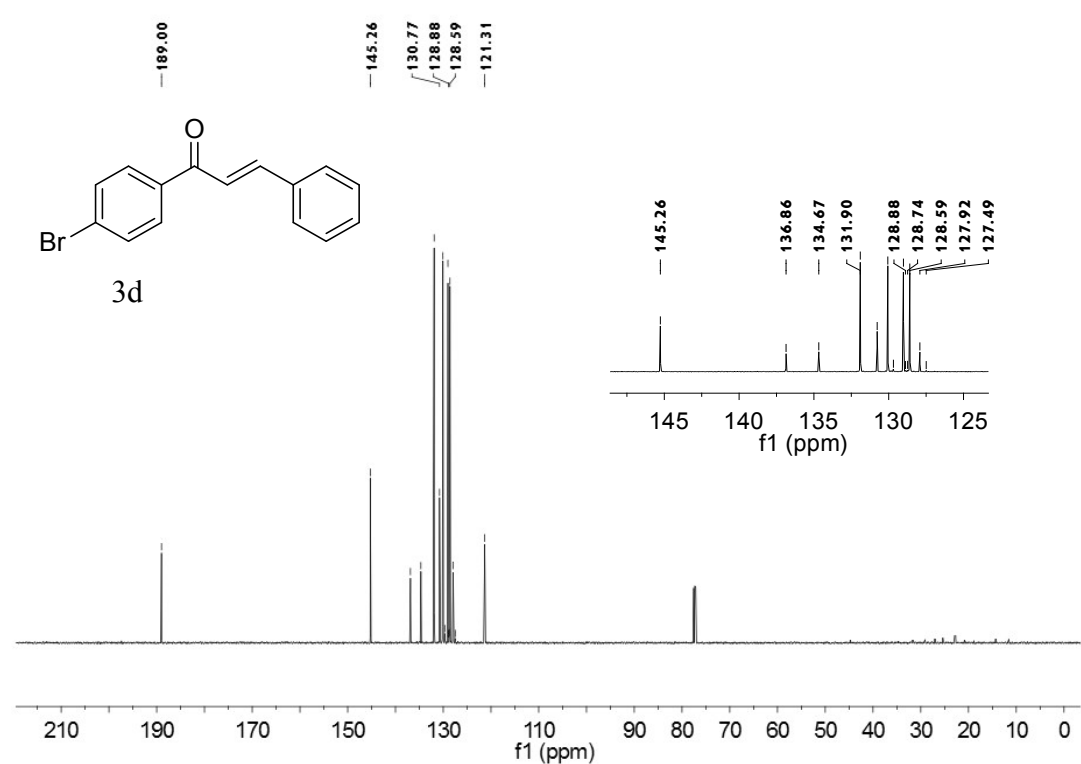
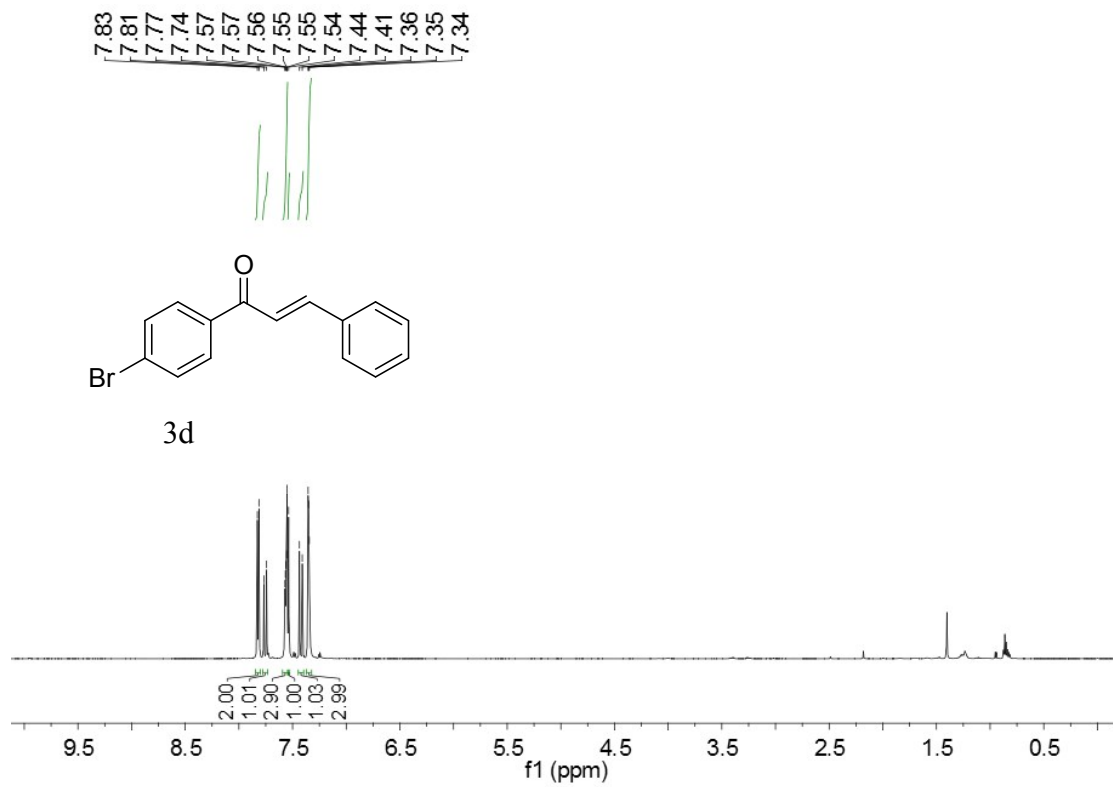
## S-10. NMR Spectrum of products and ligands

### S-10.1 NMR-Spectrum of carbonylative Heck products **3**

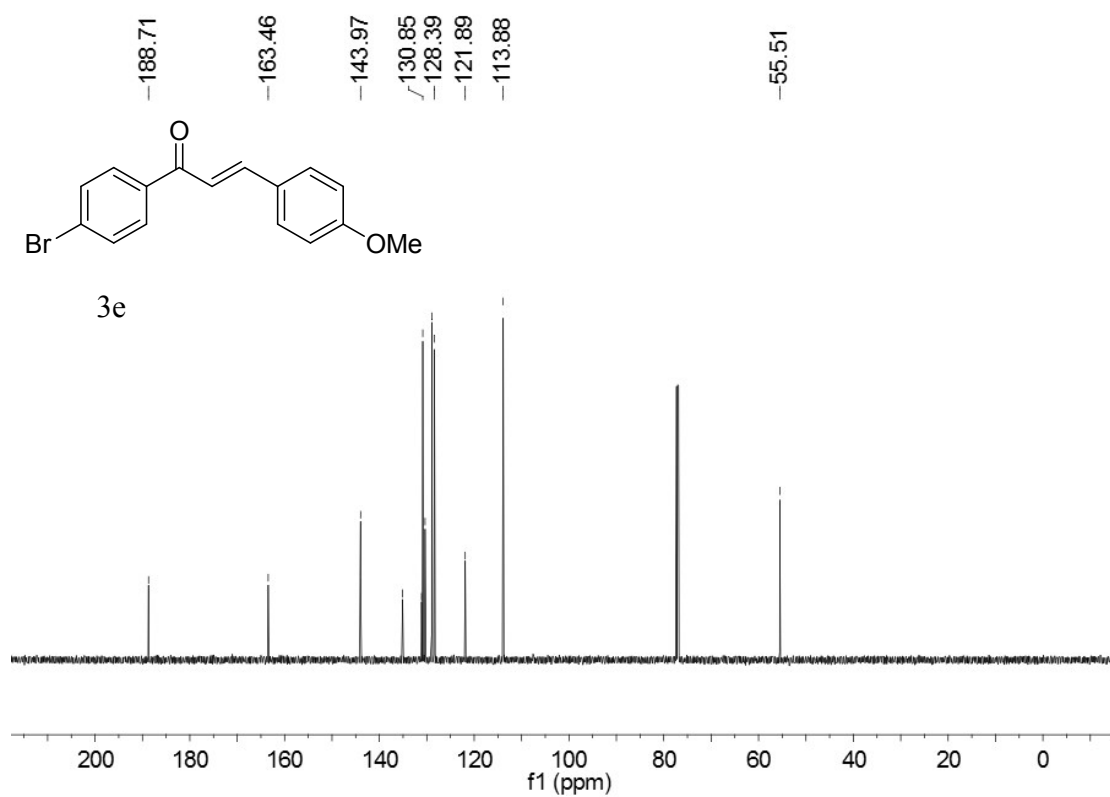
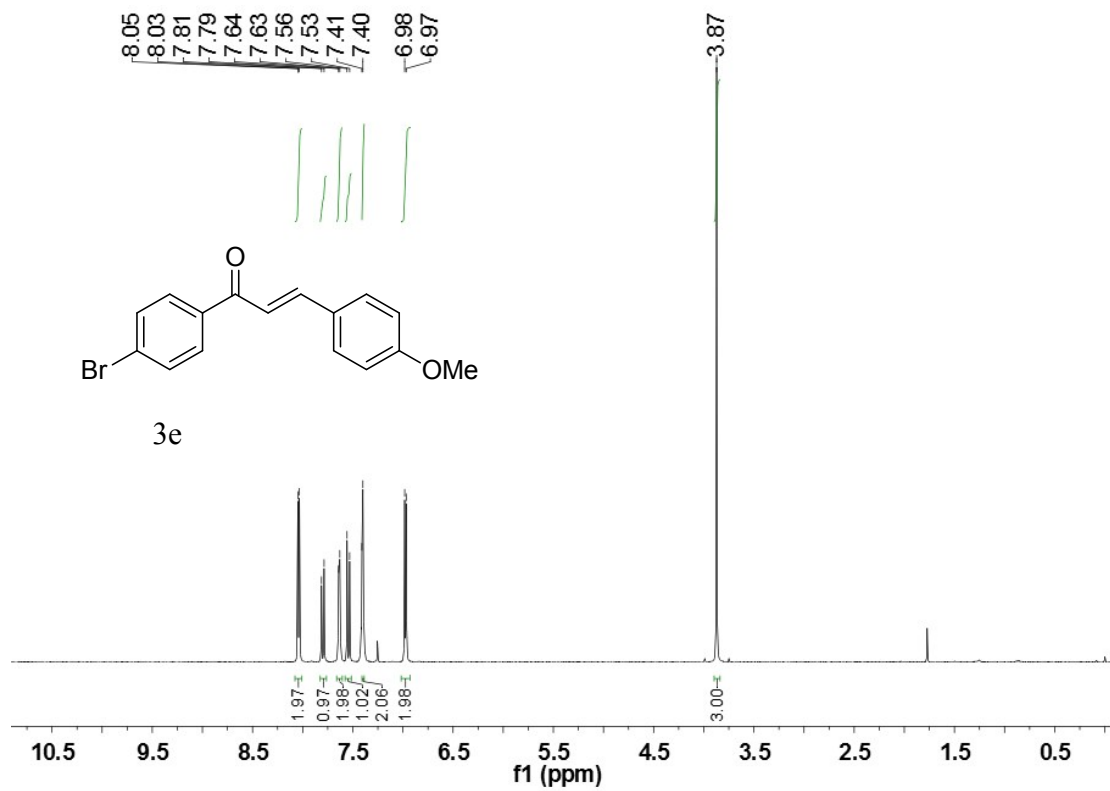


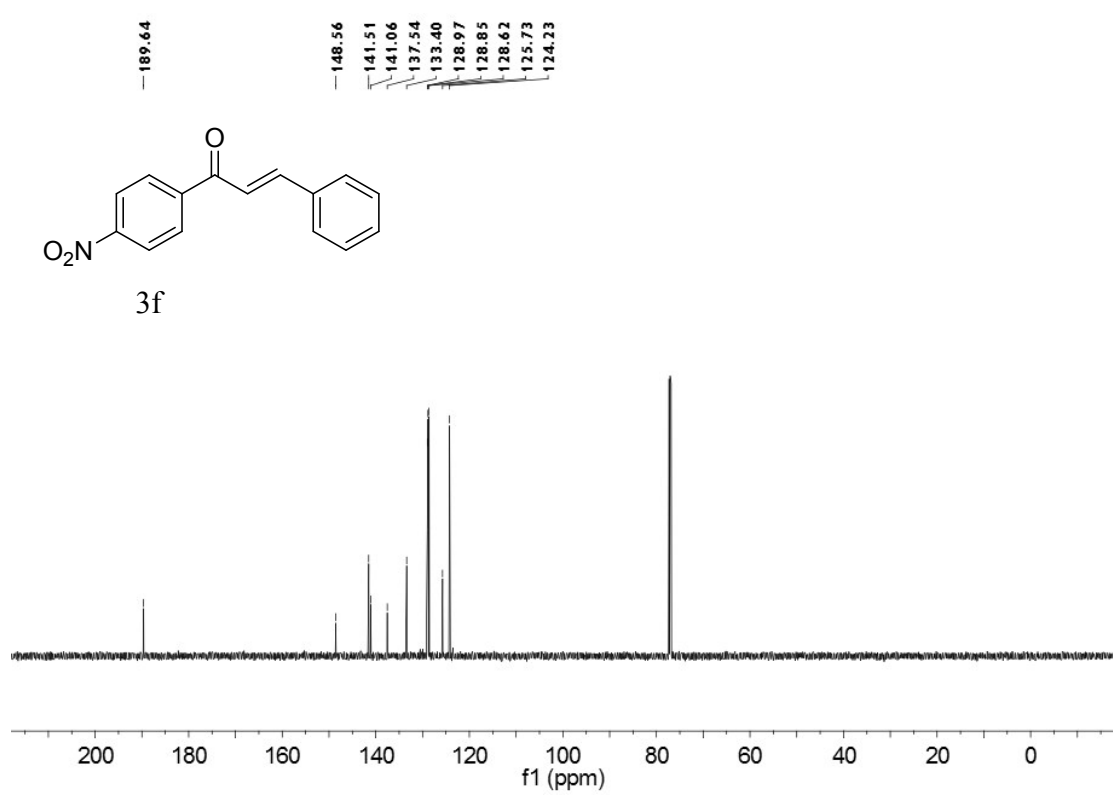
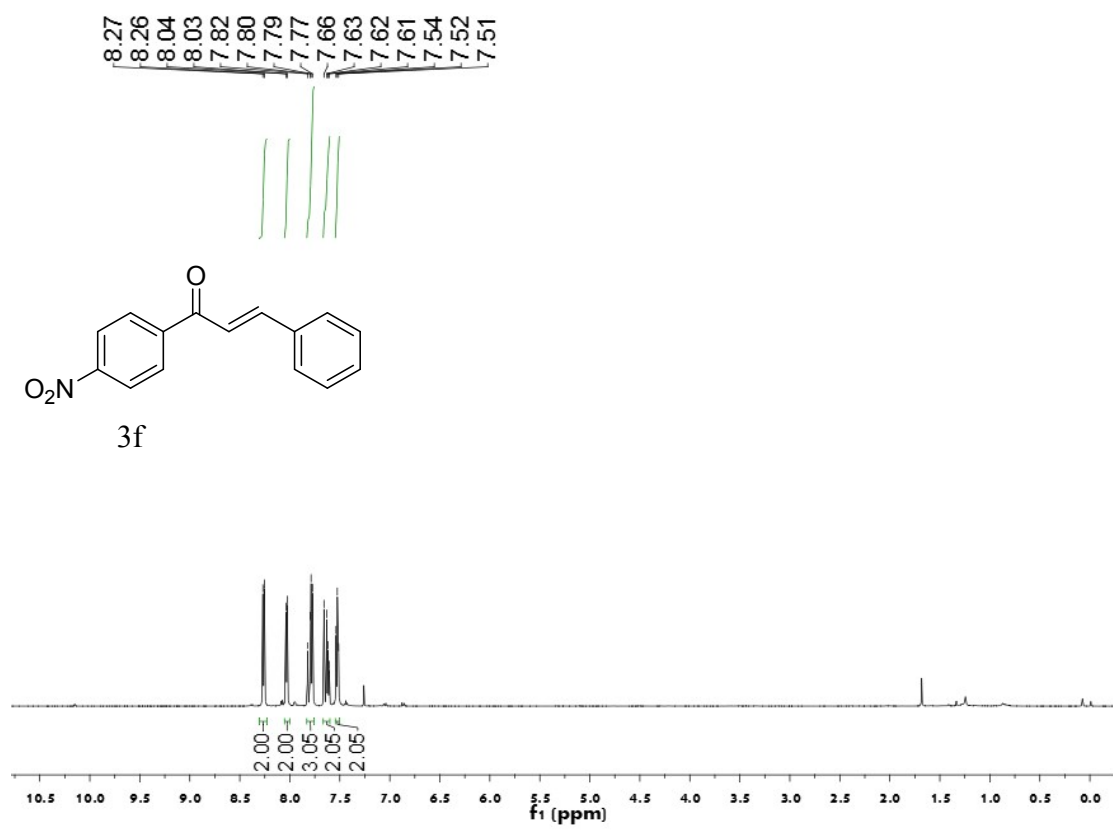


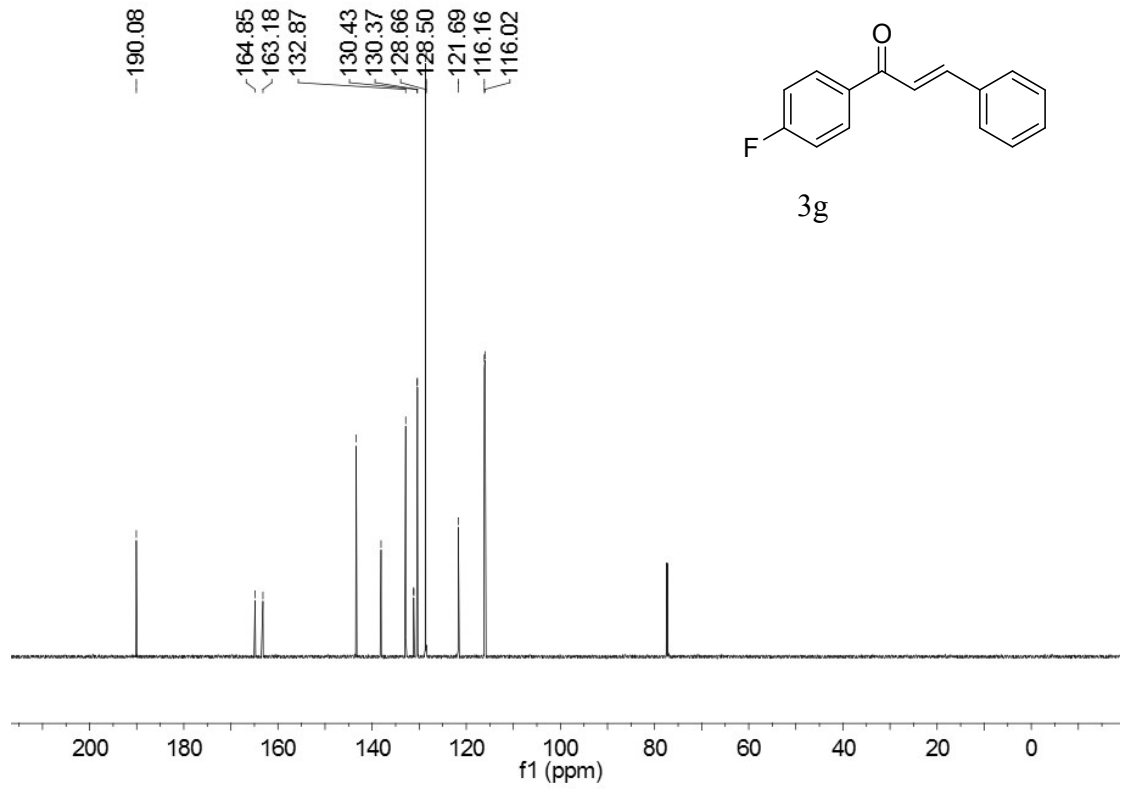
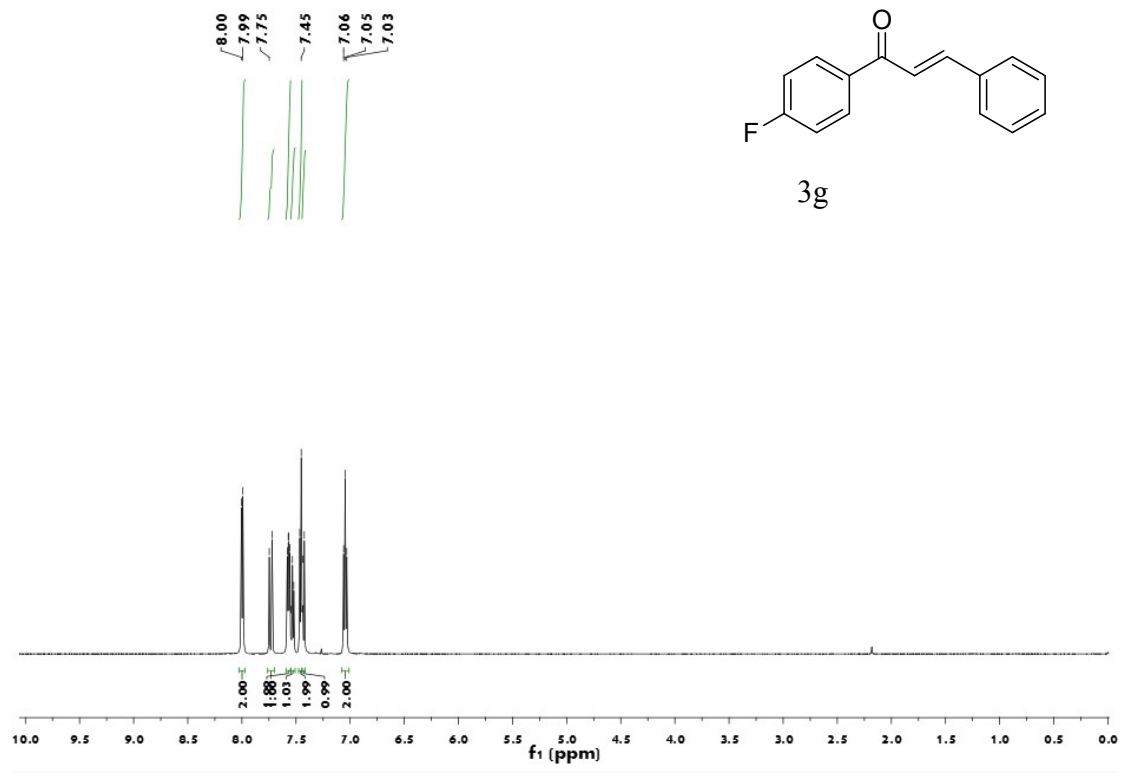


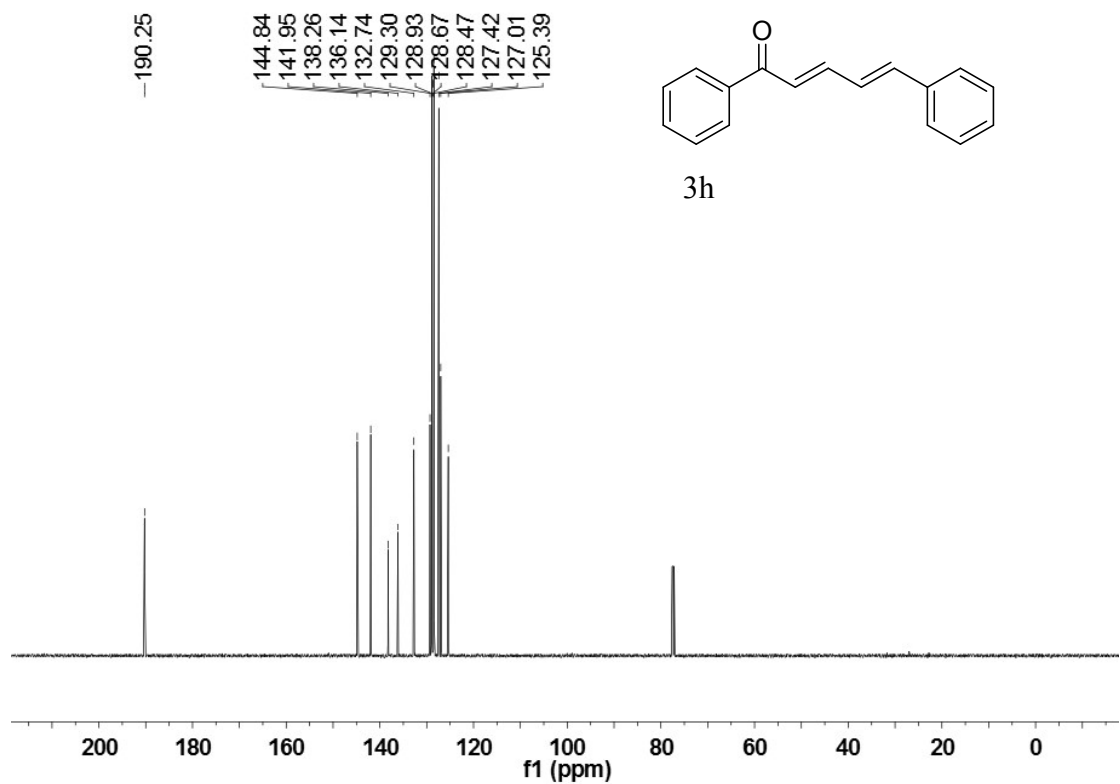
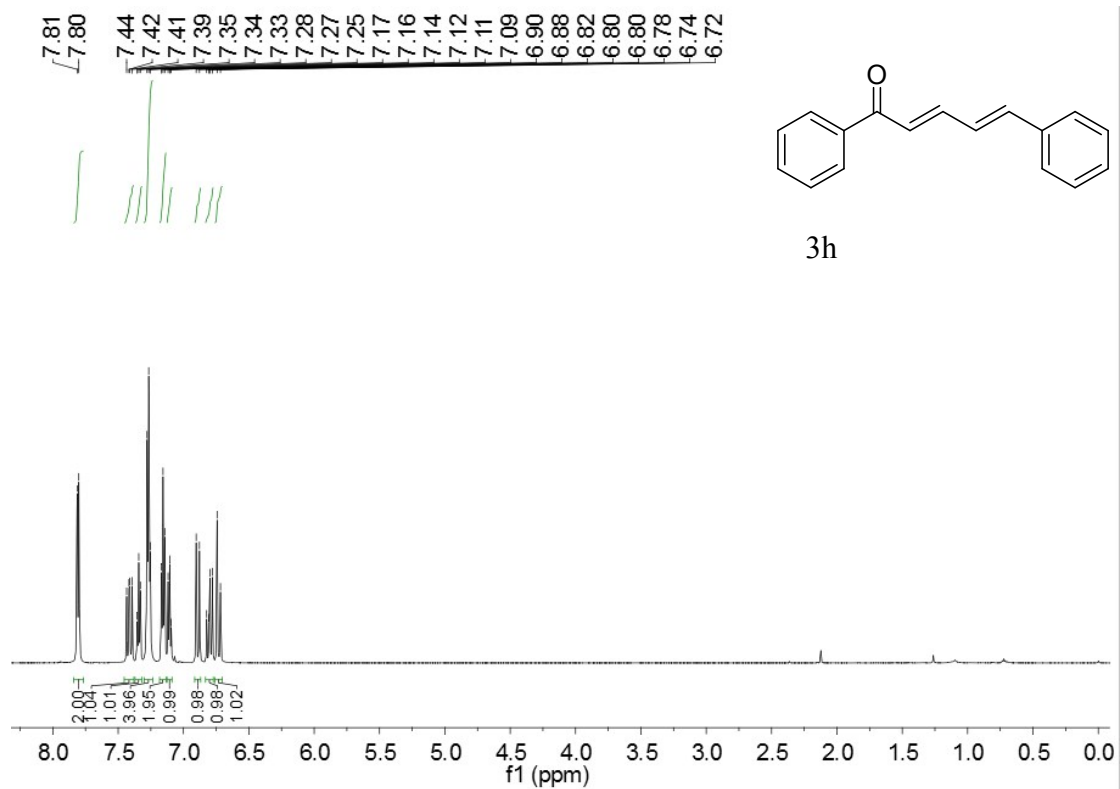


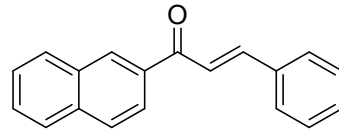
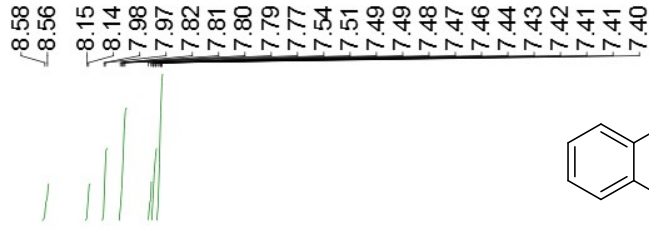




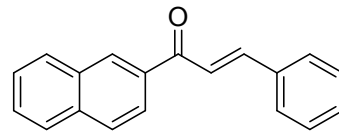
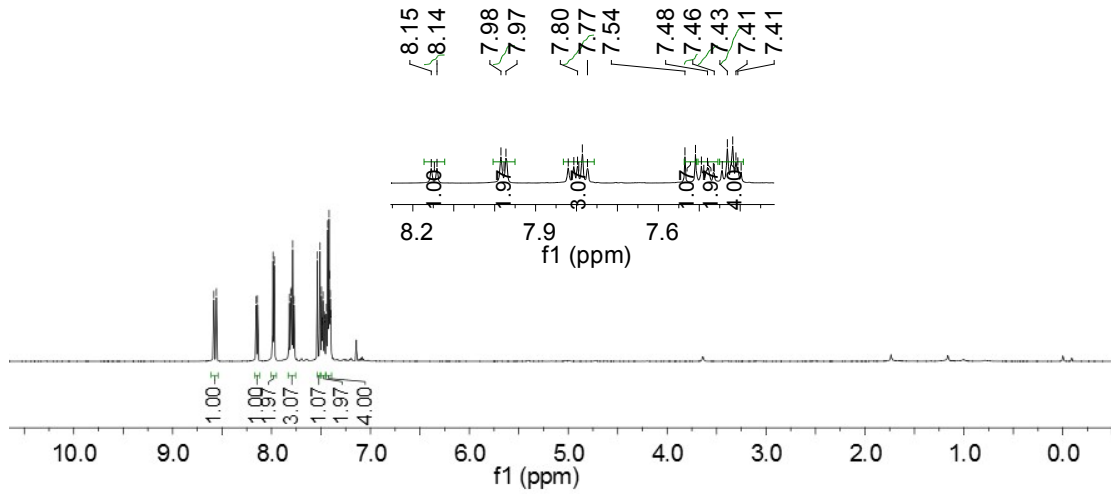




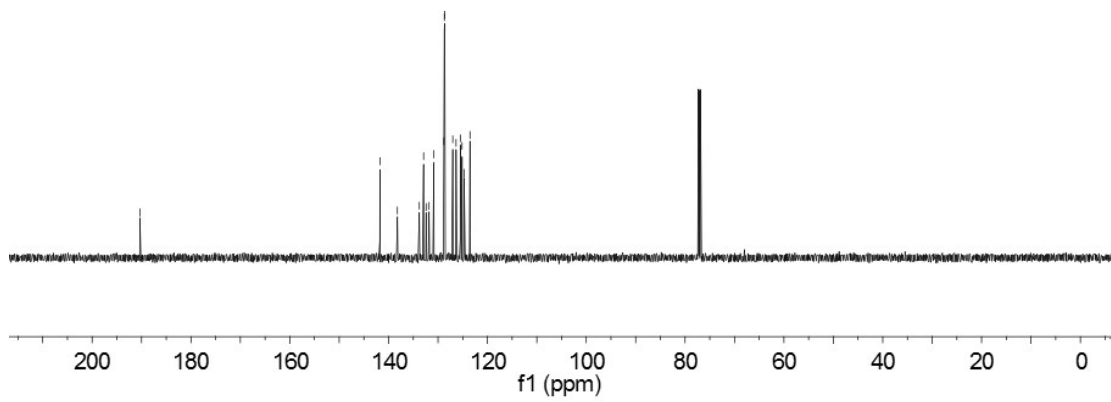


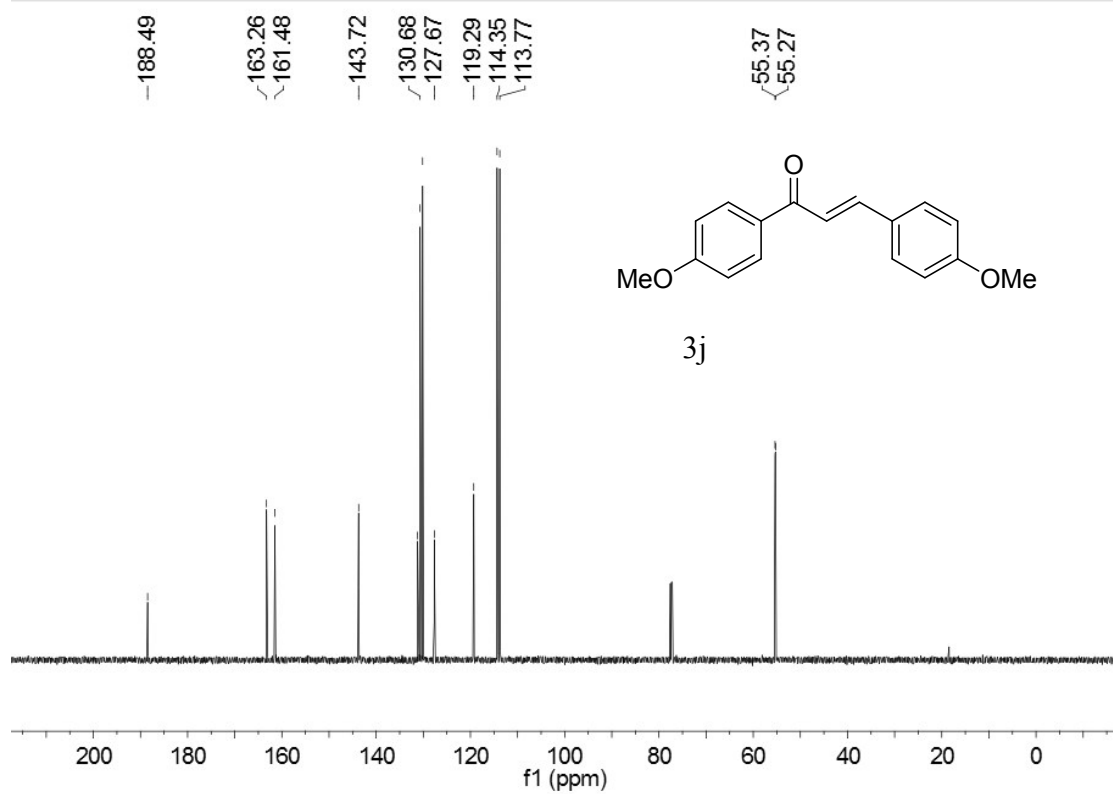
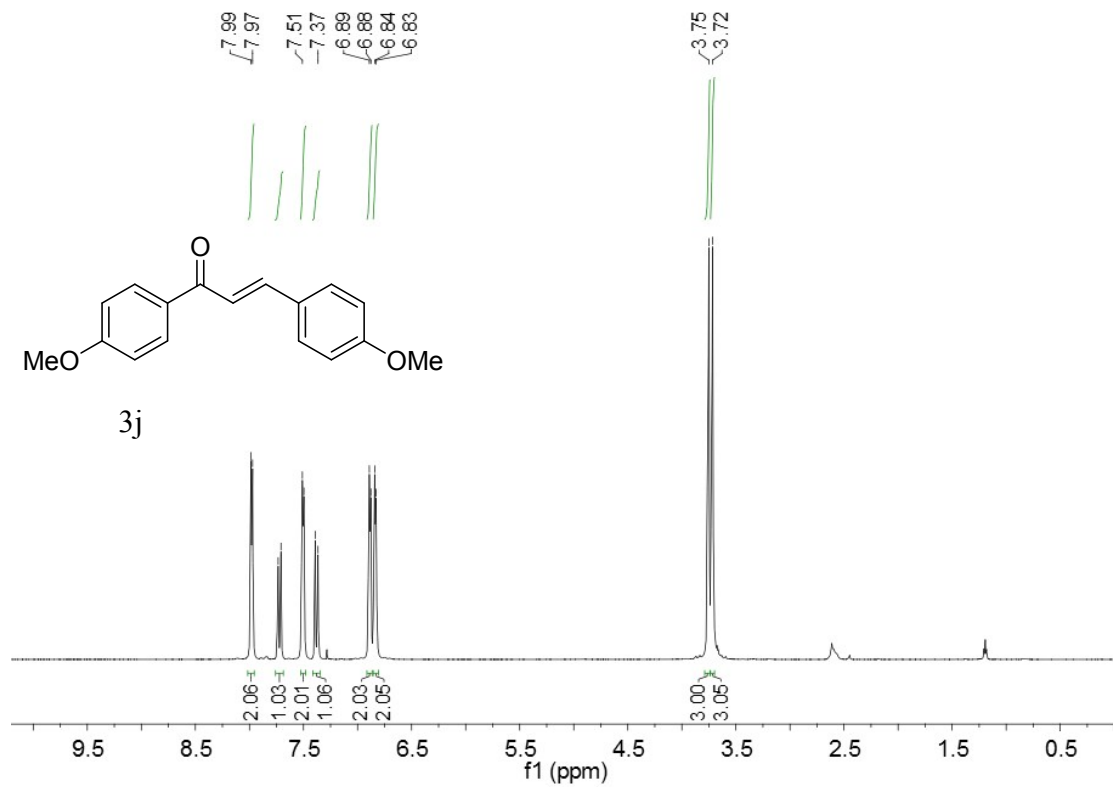


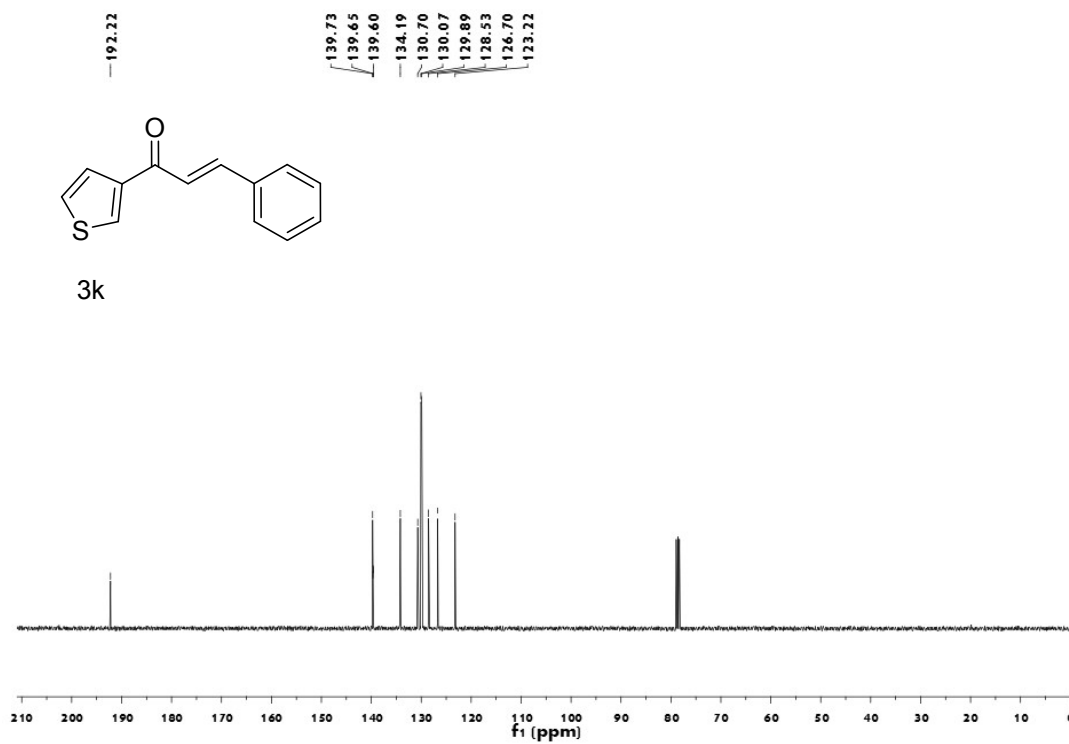
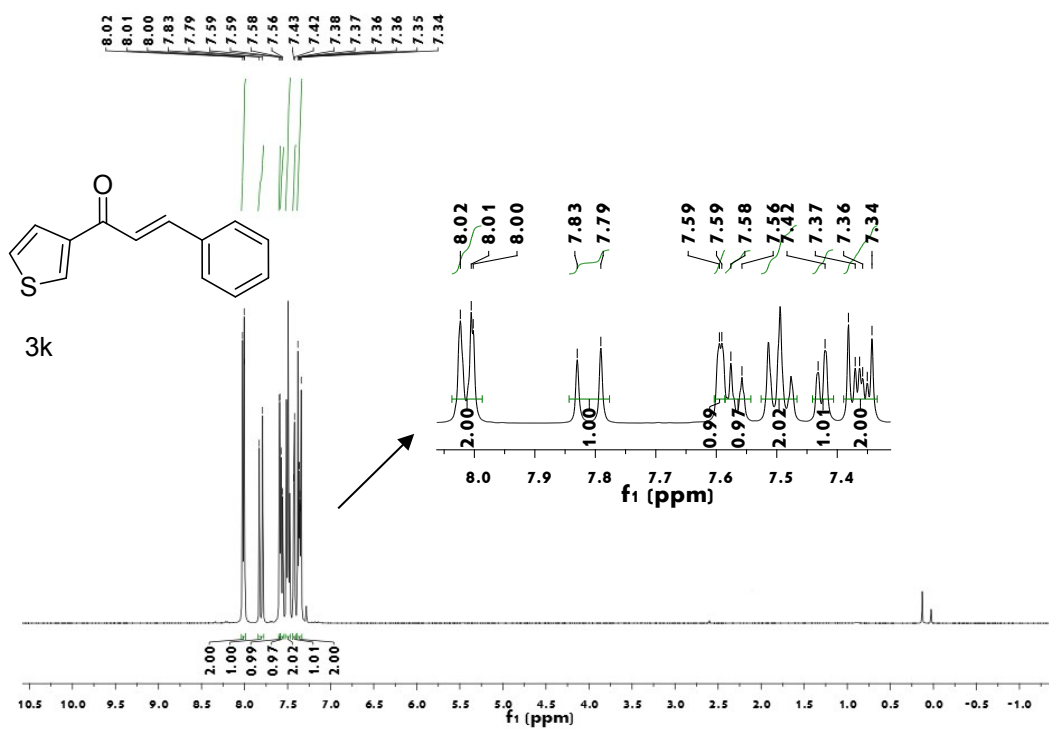
3i

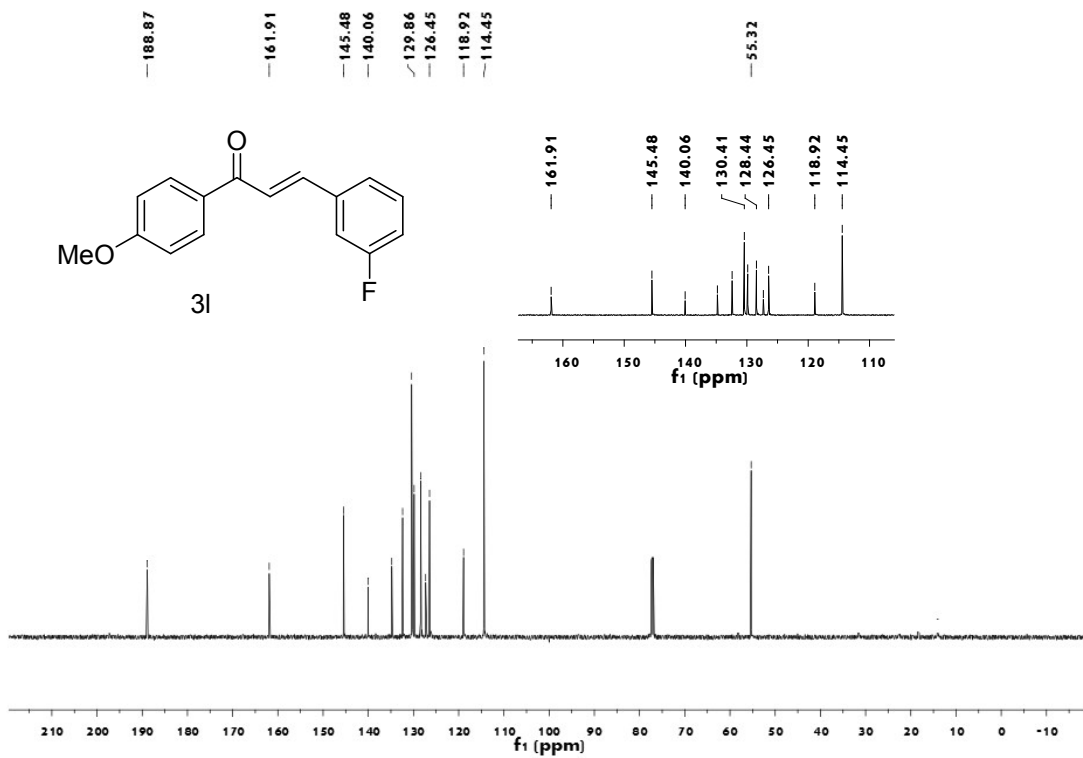
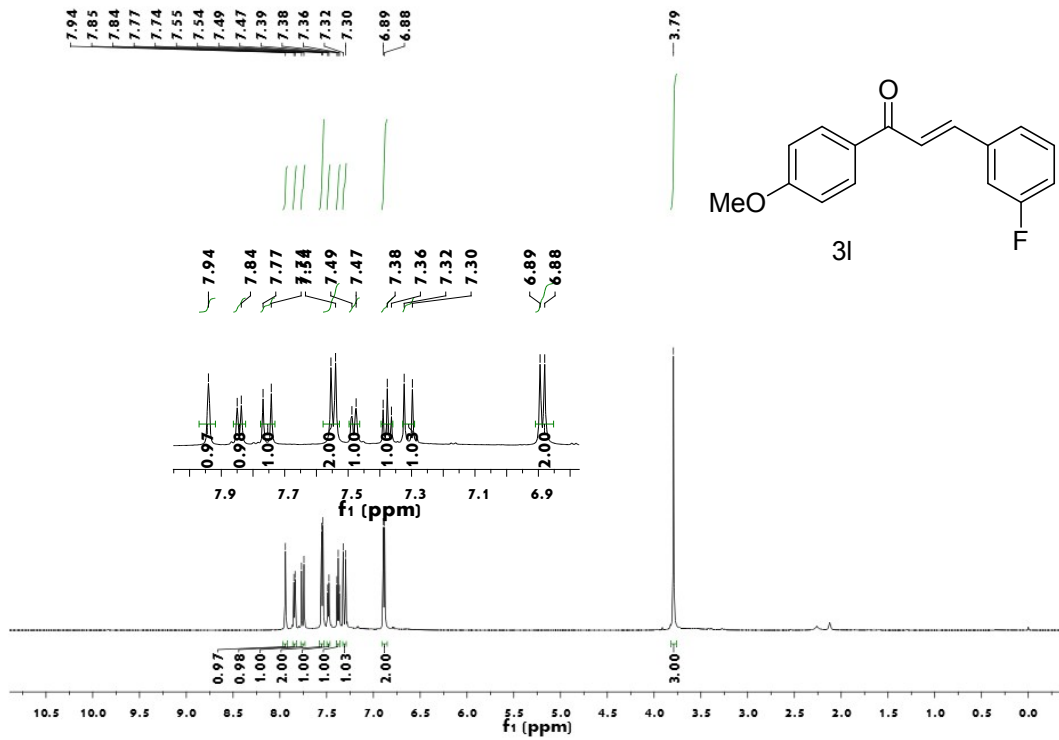


3i

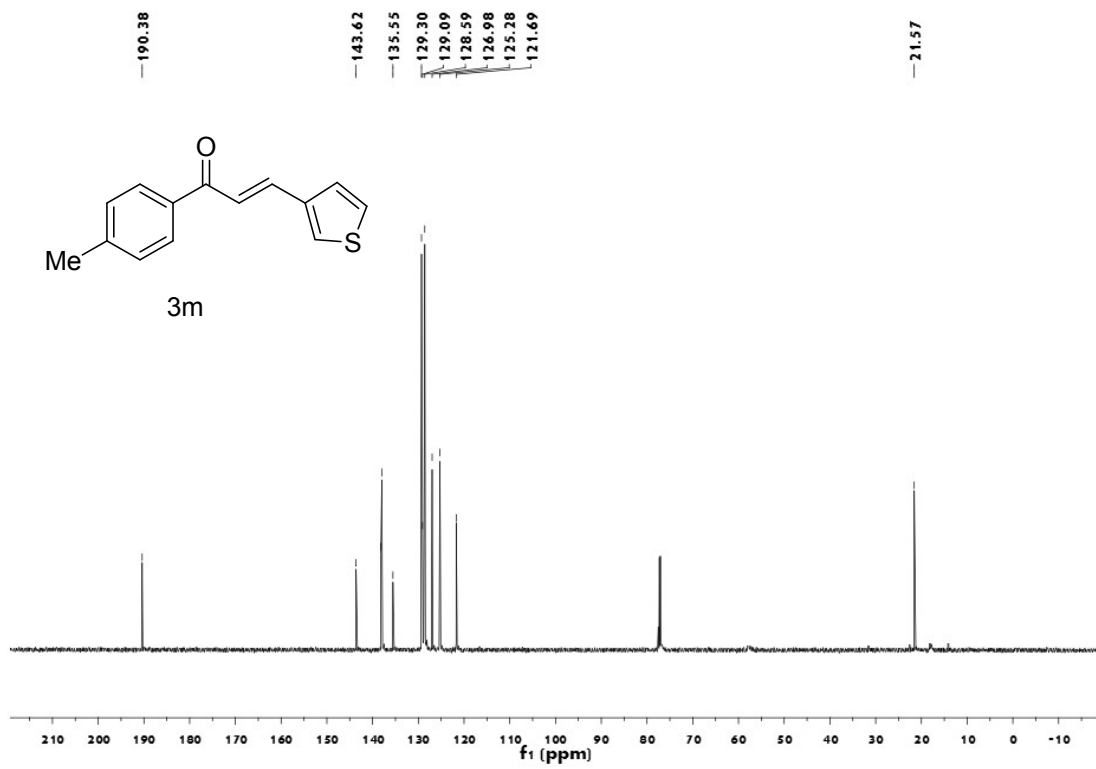
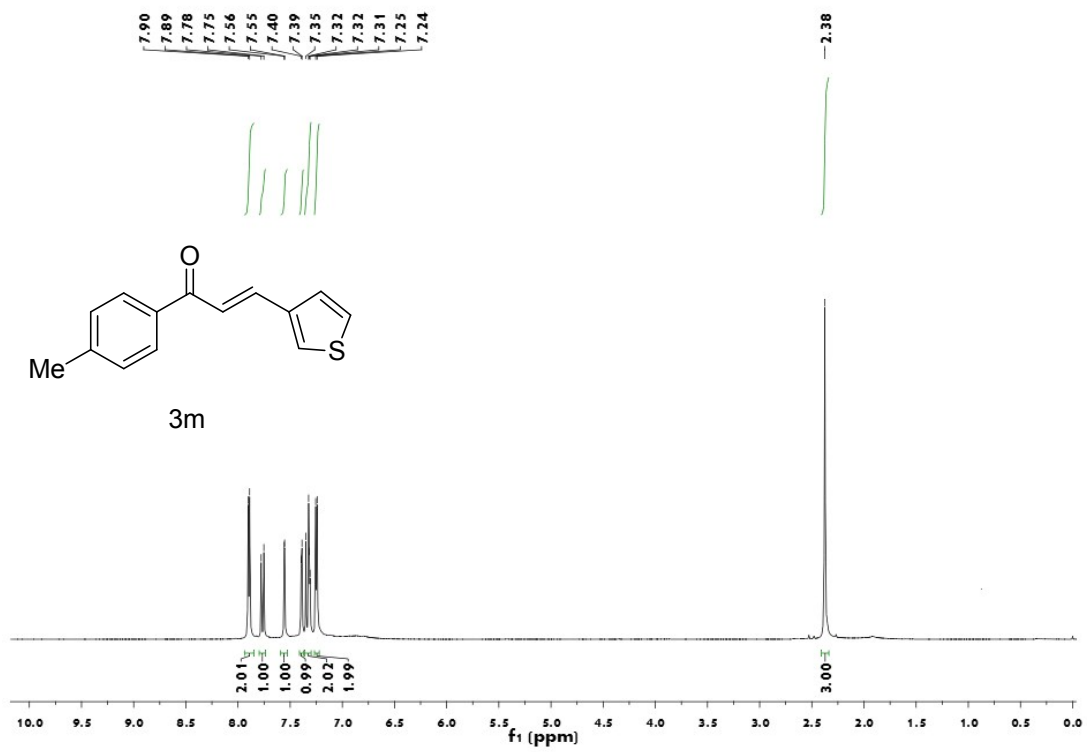


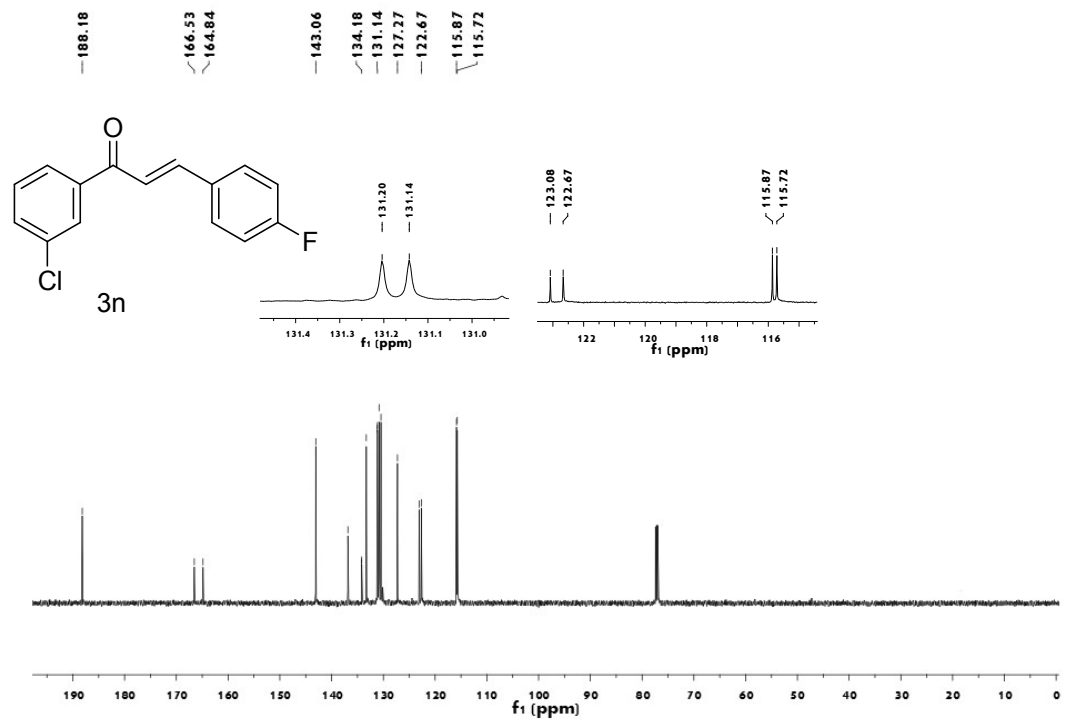
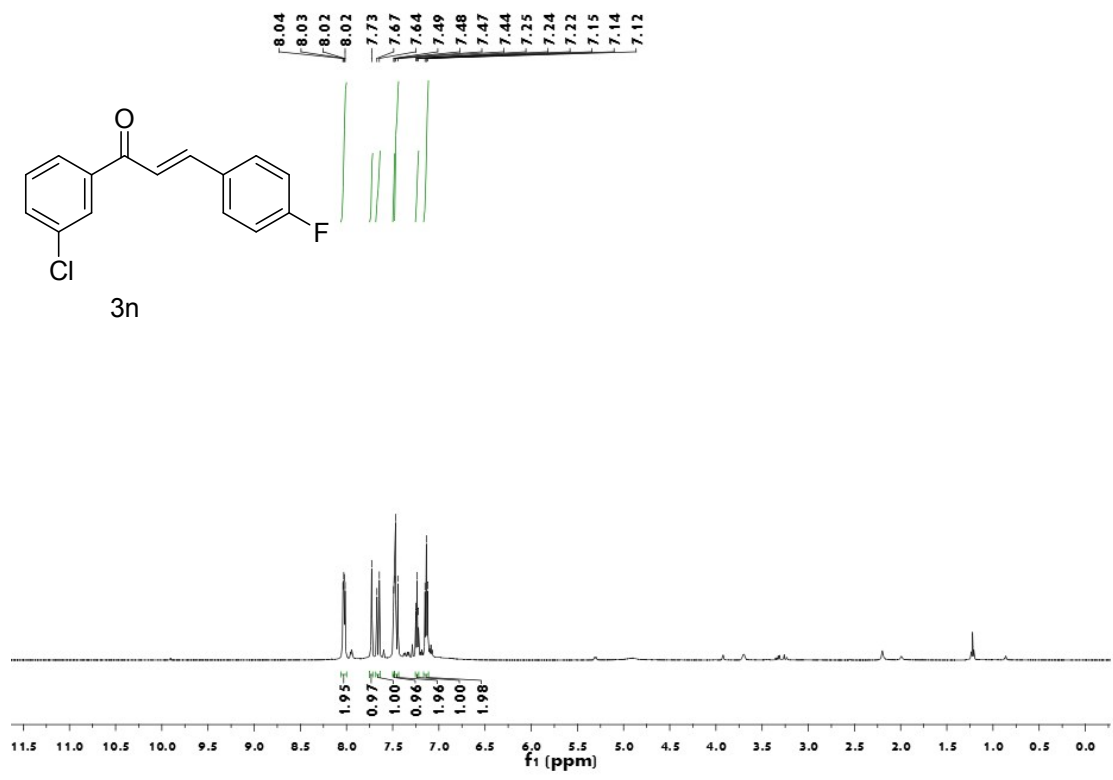


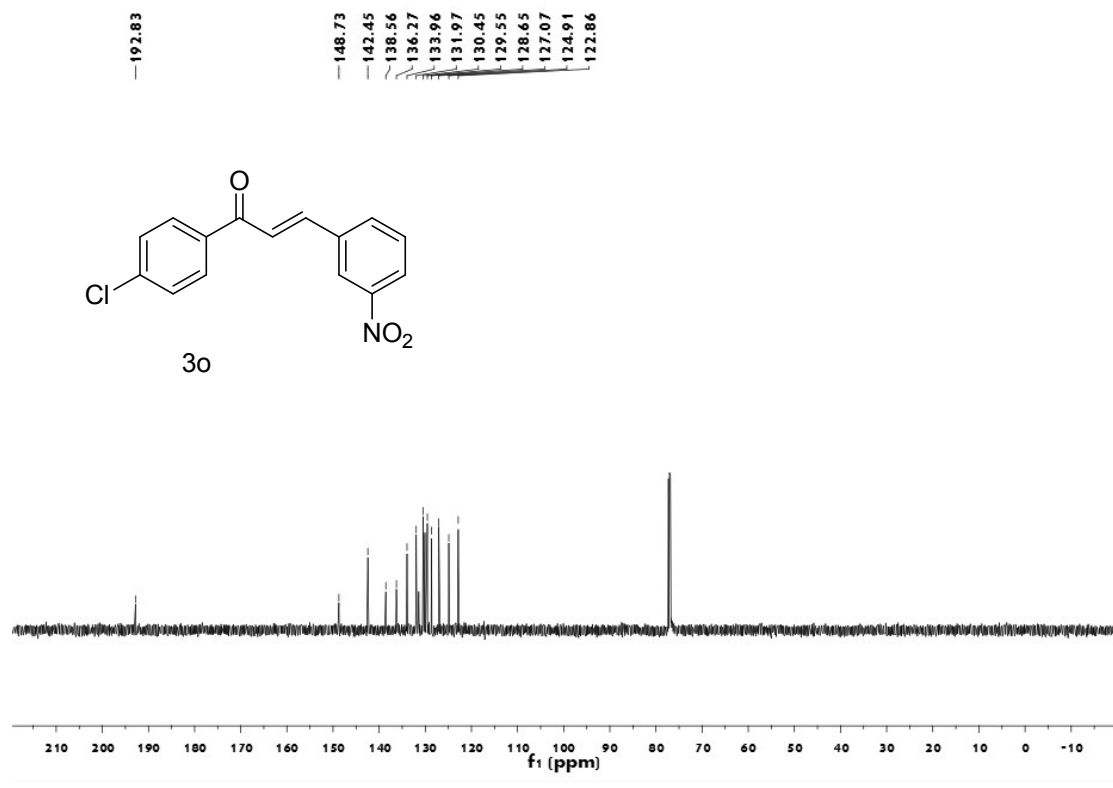
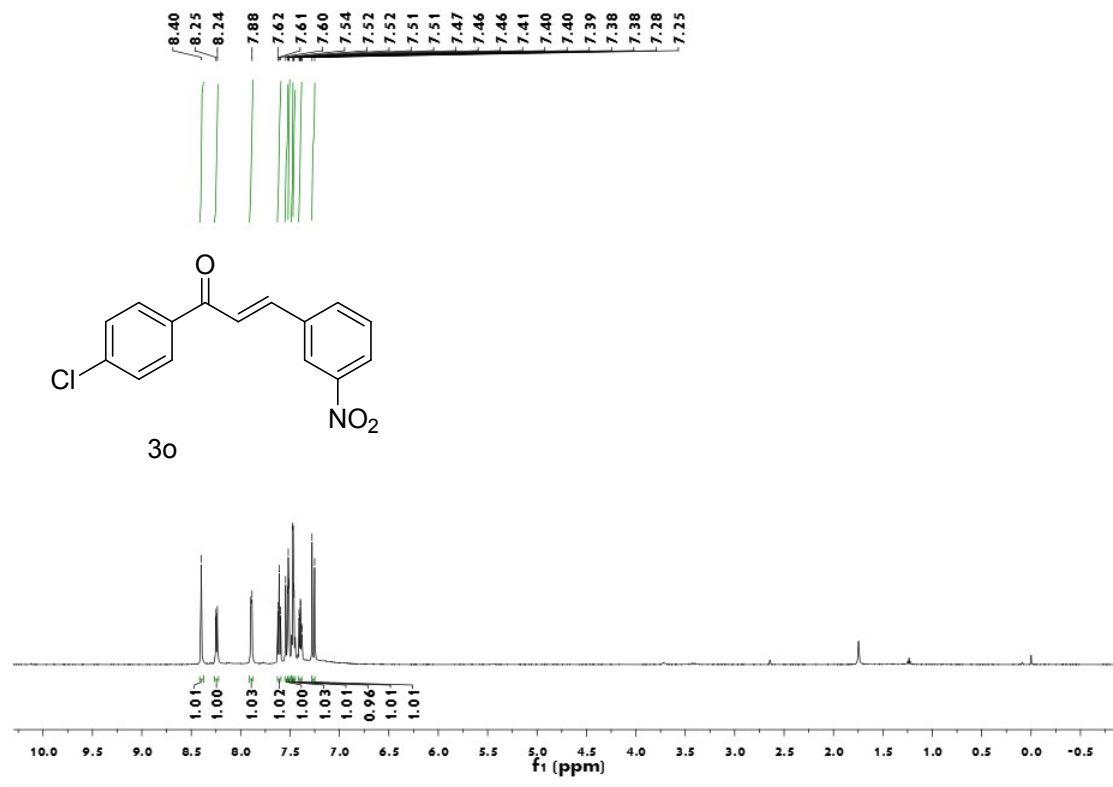


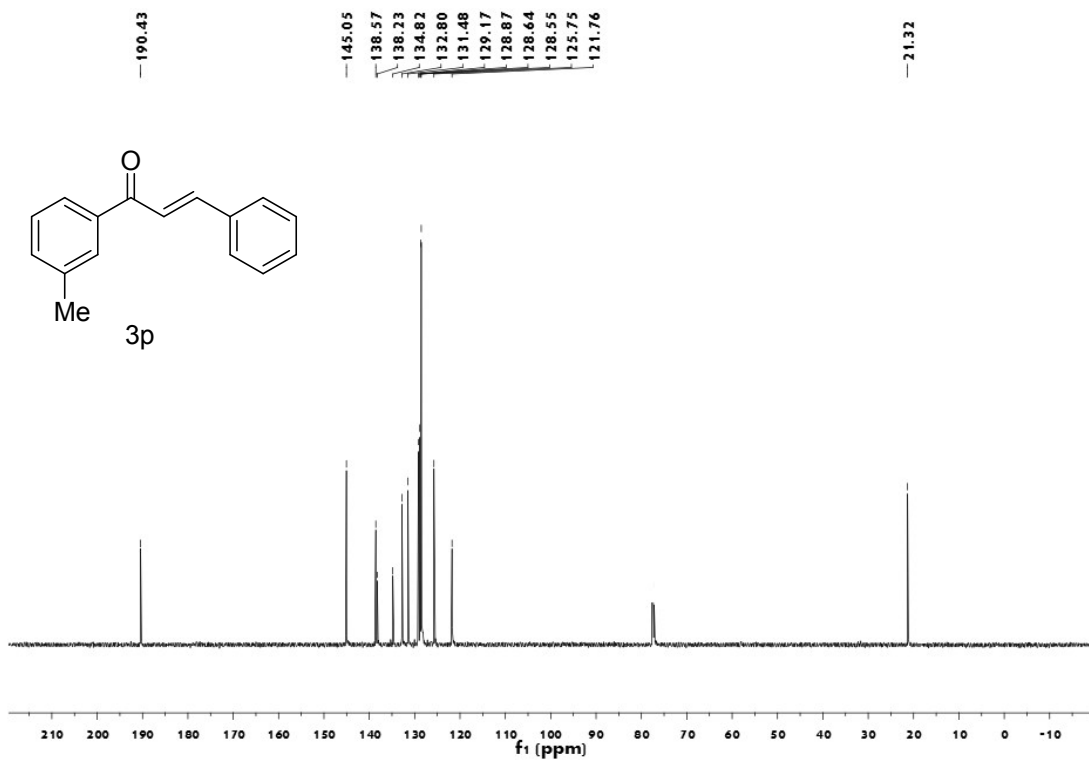
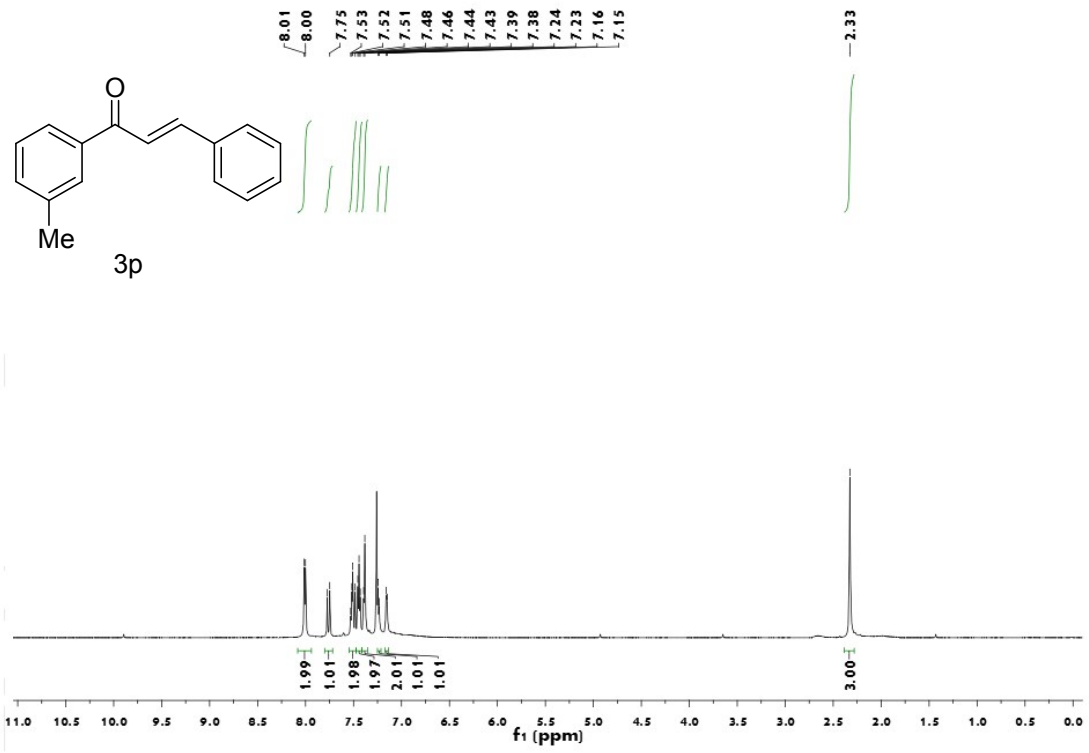


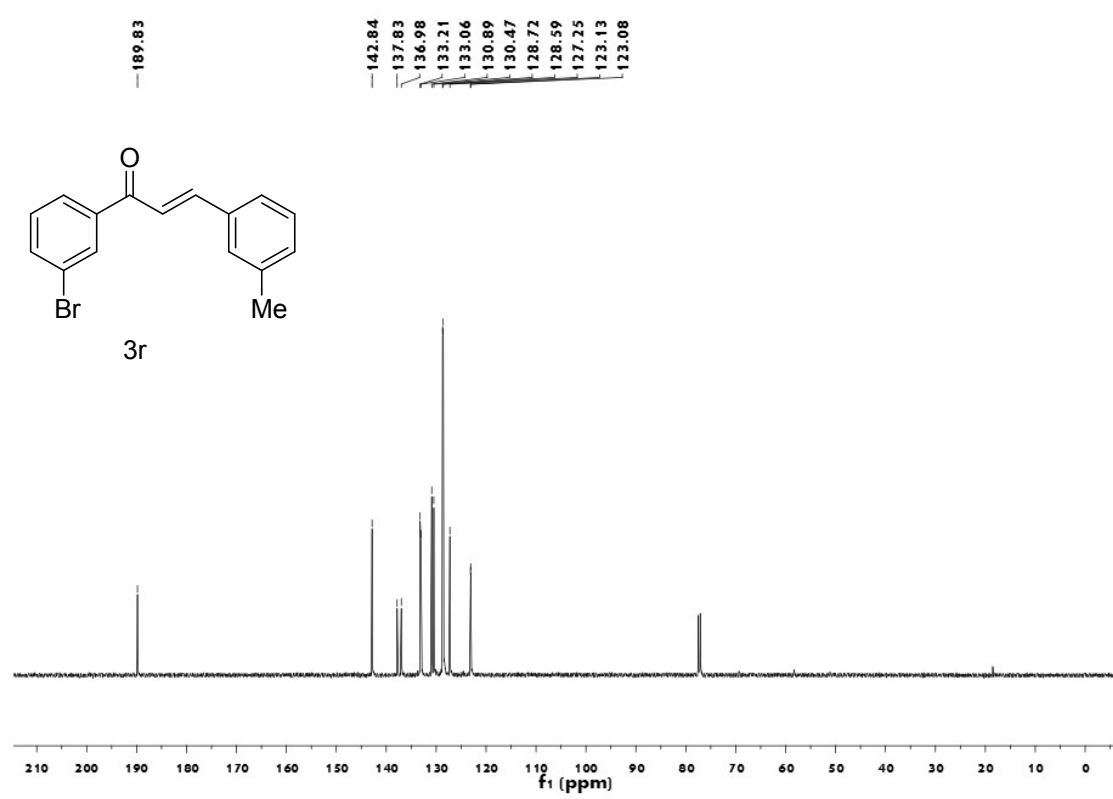
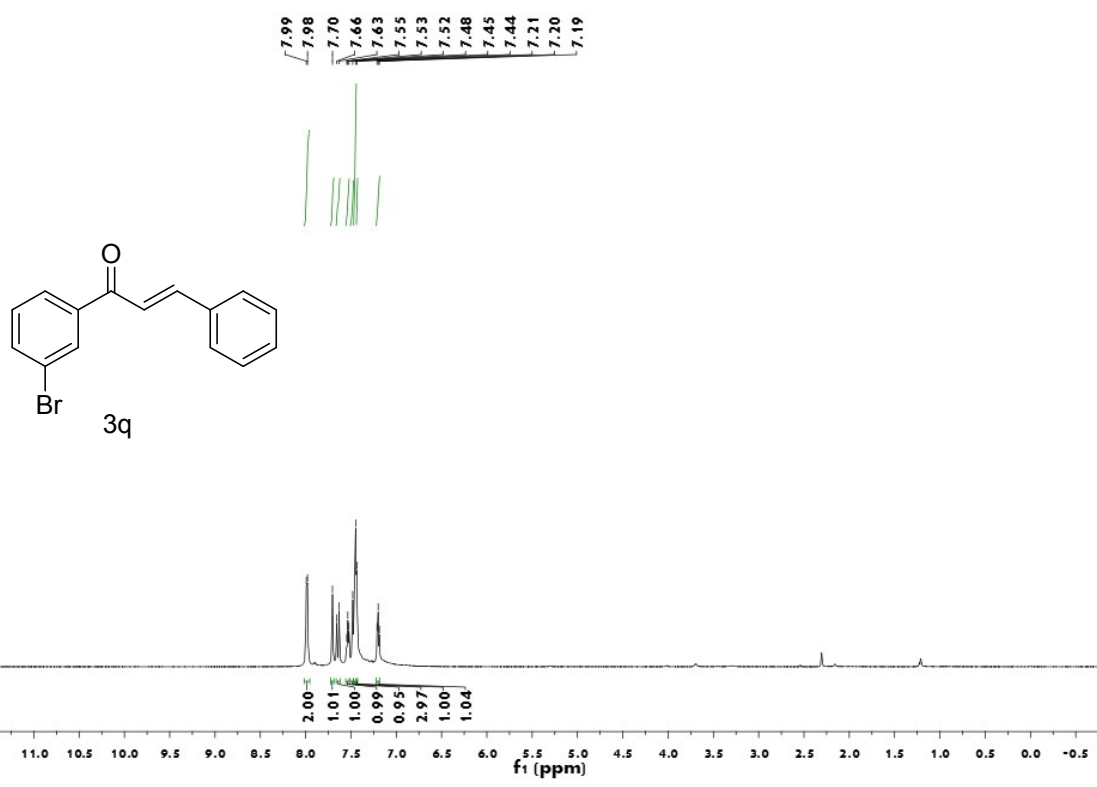


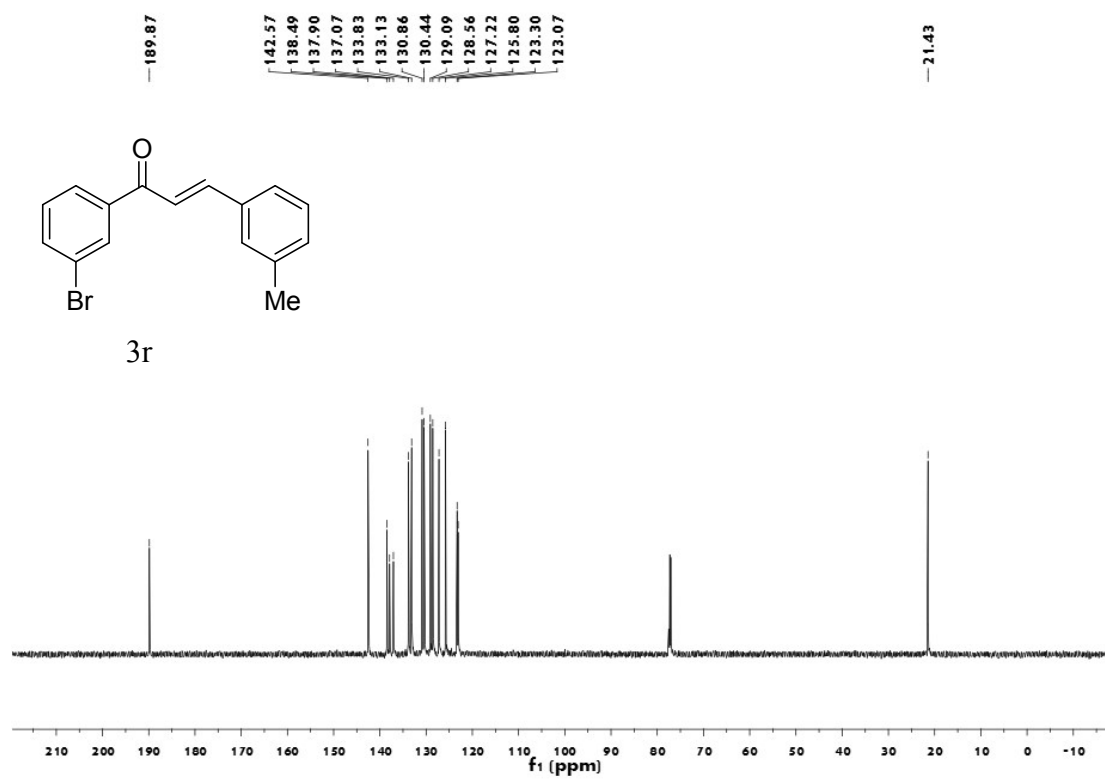
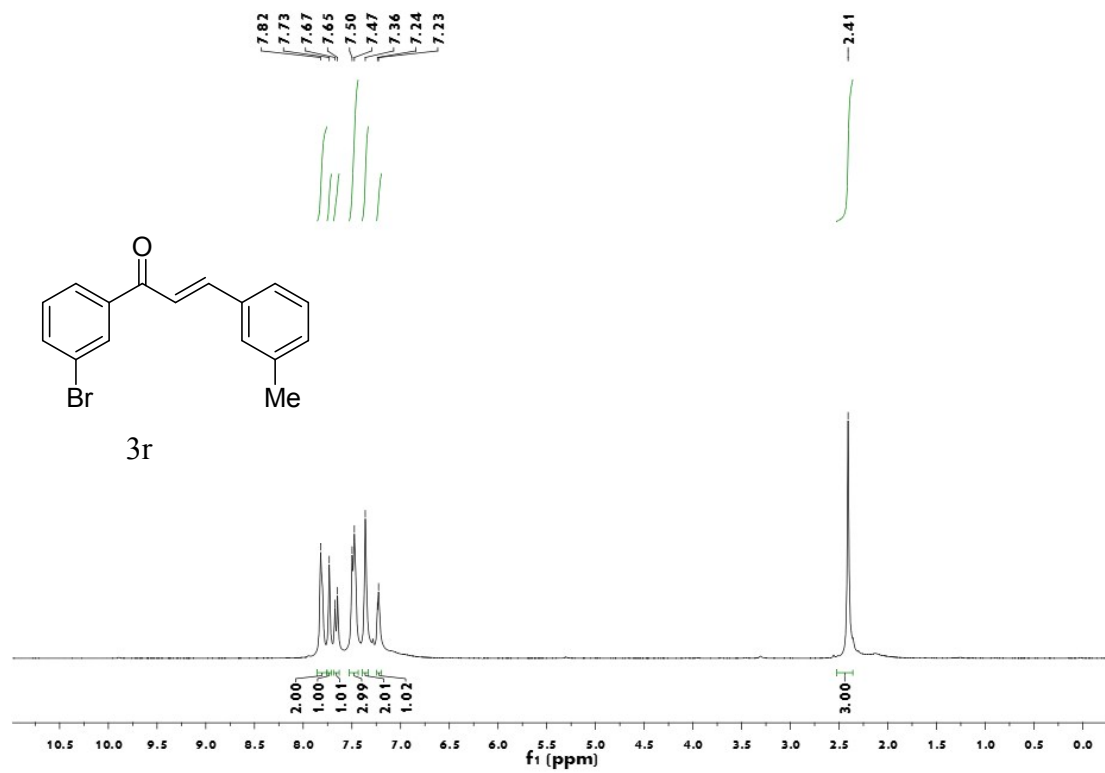




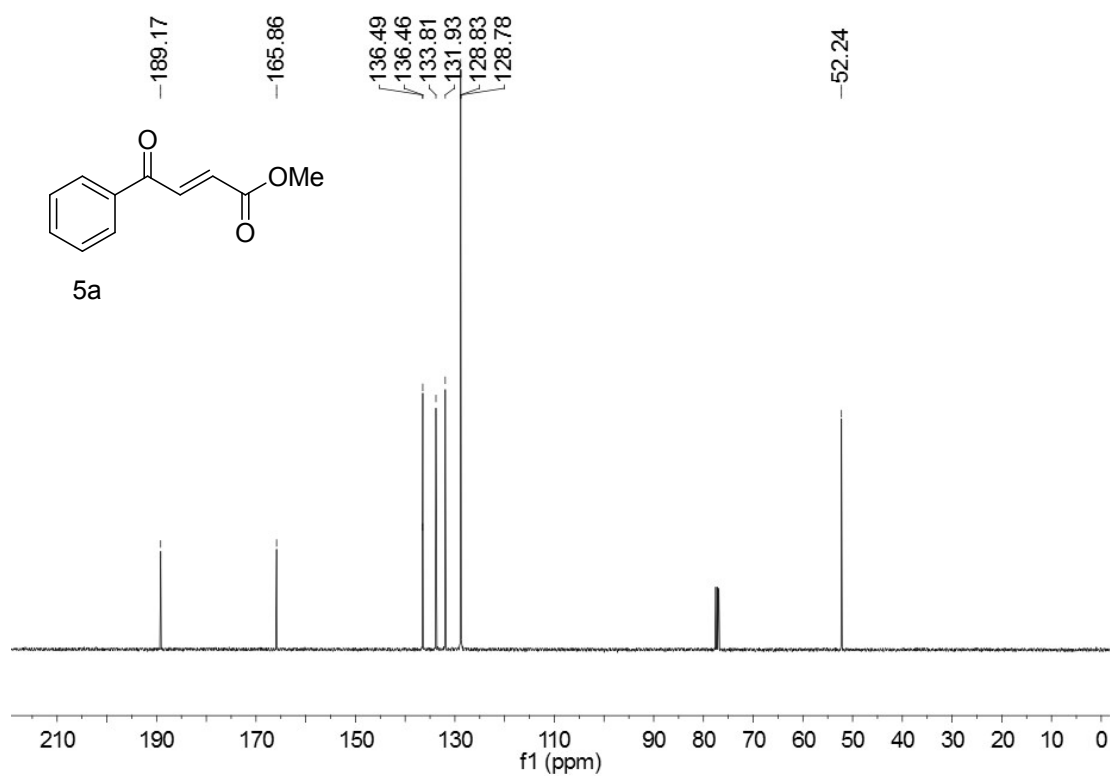
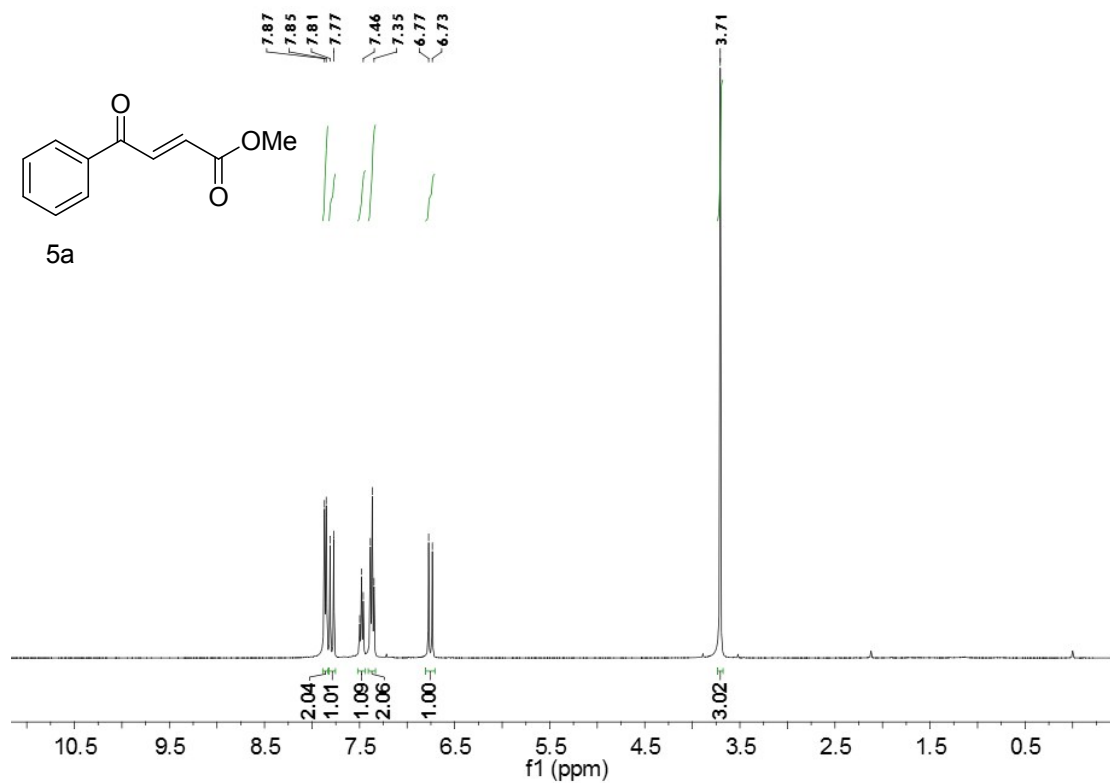


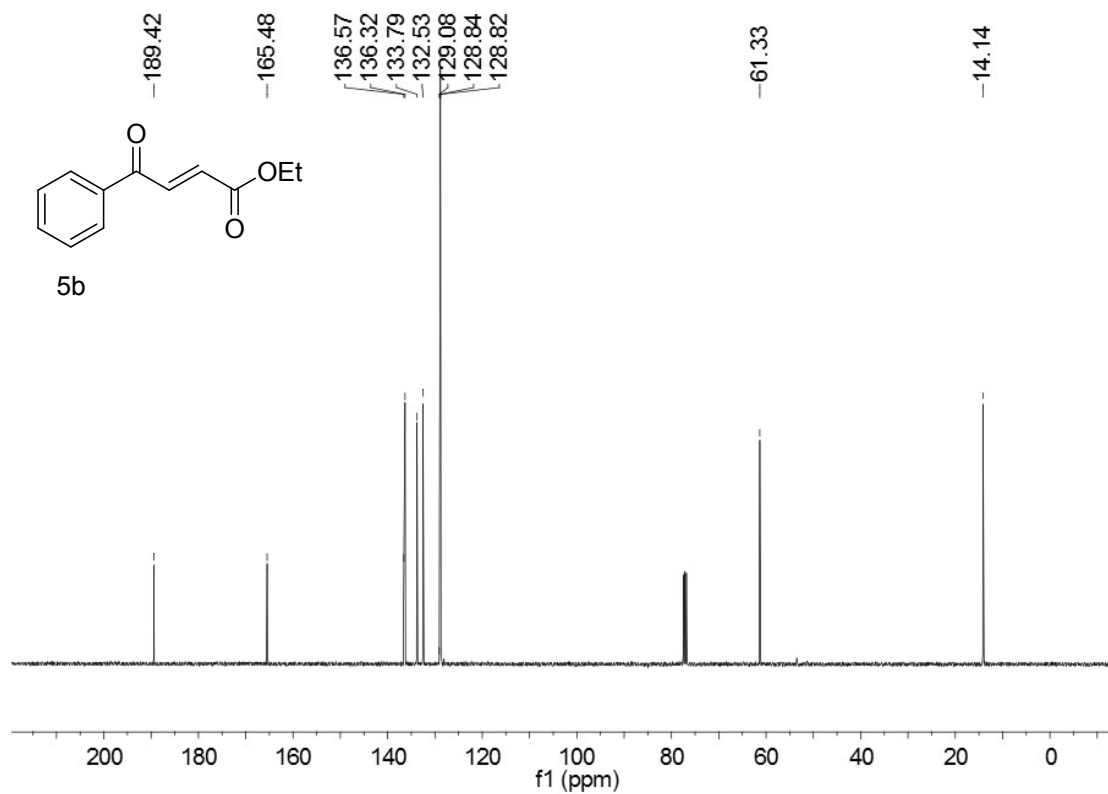
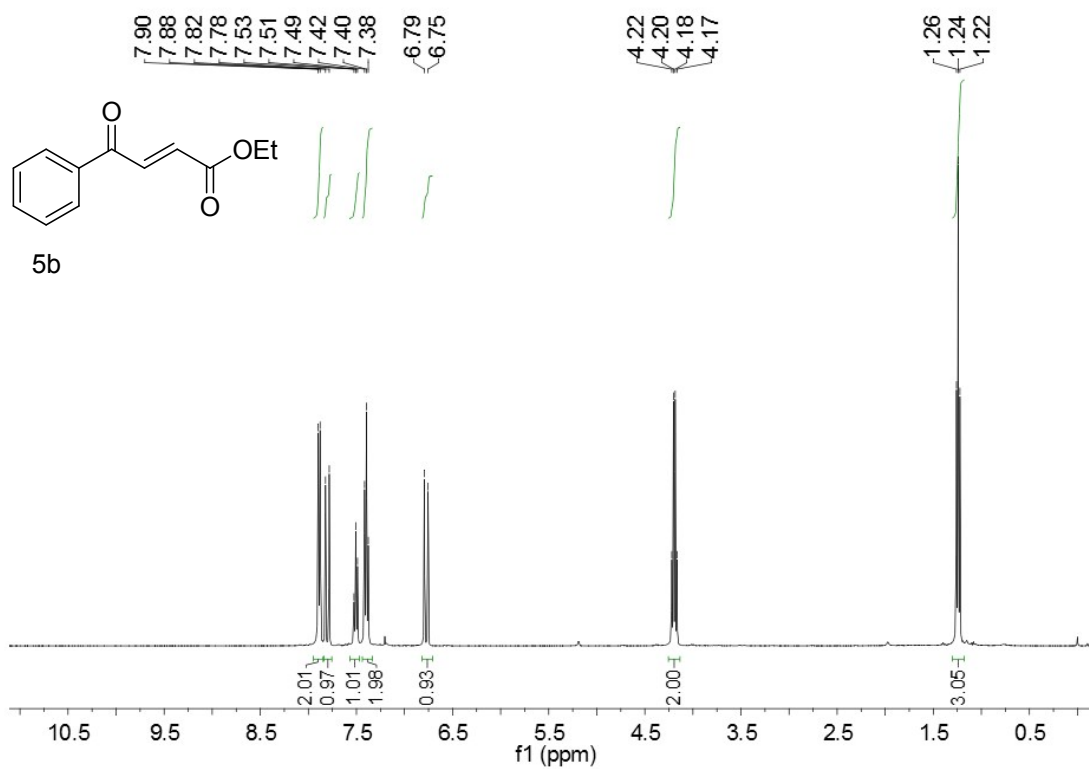




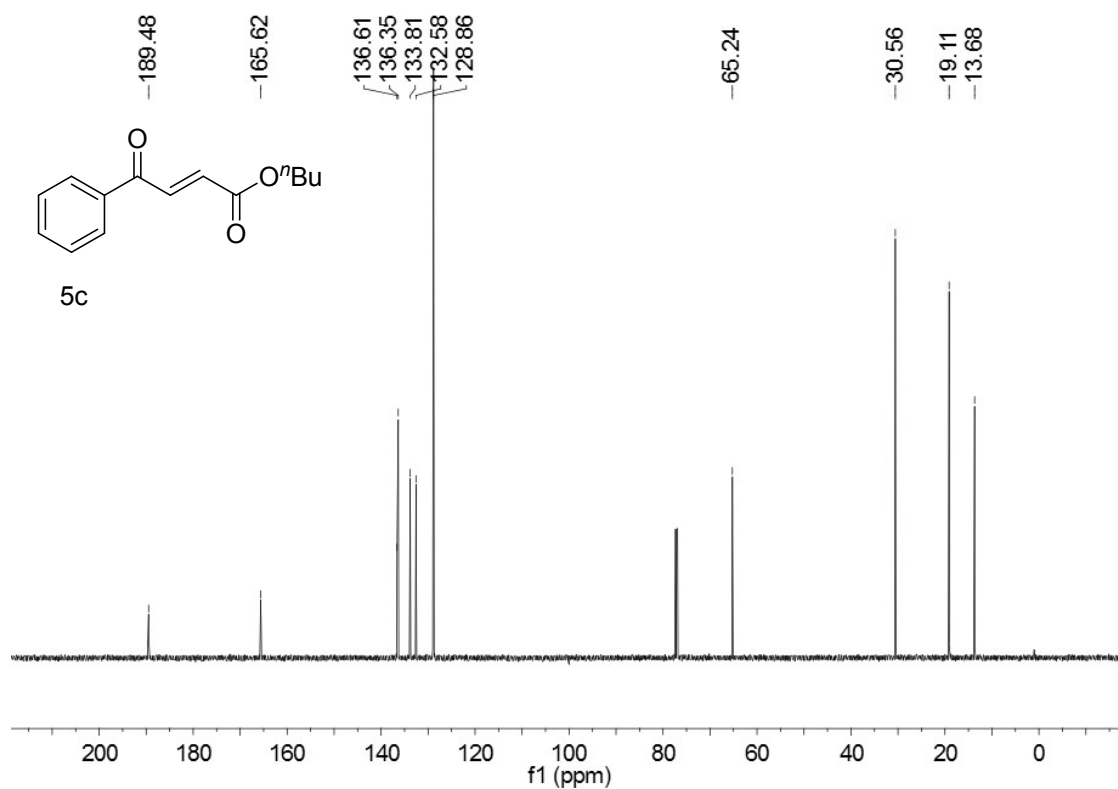
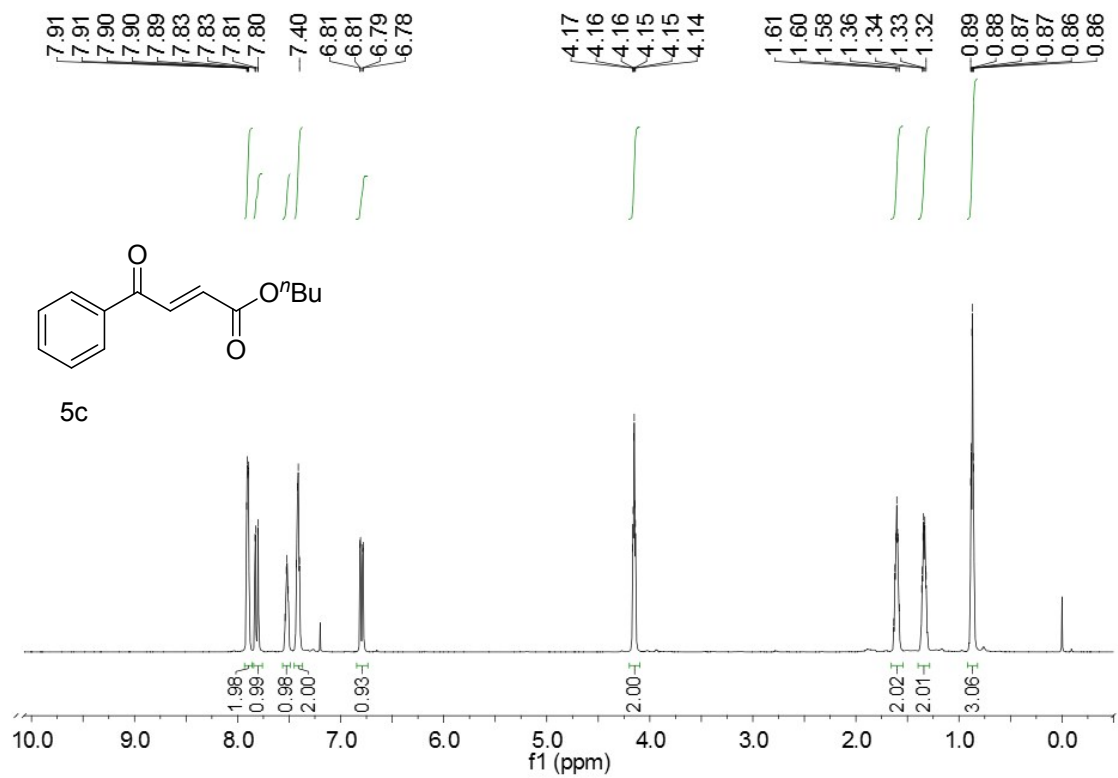


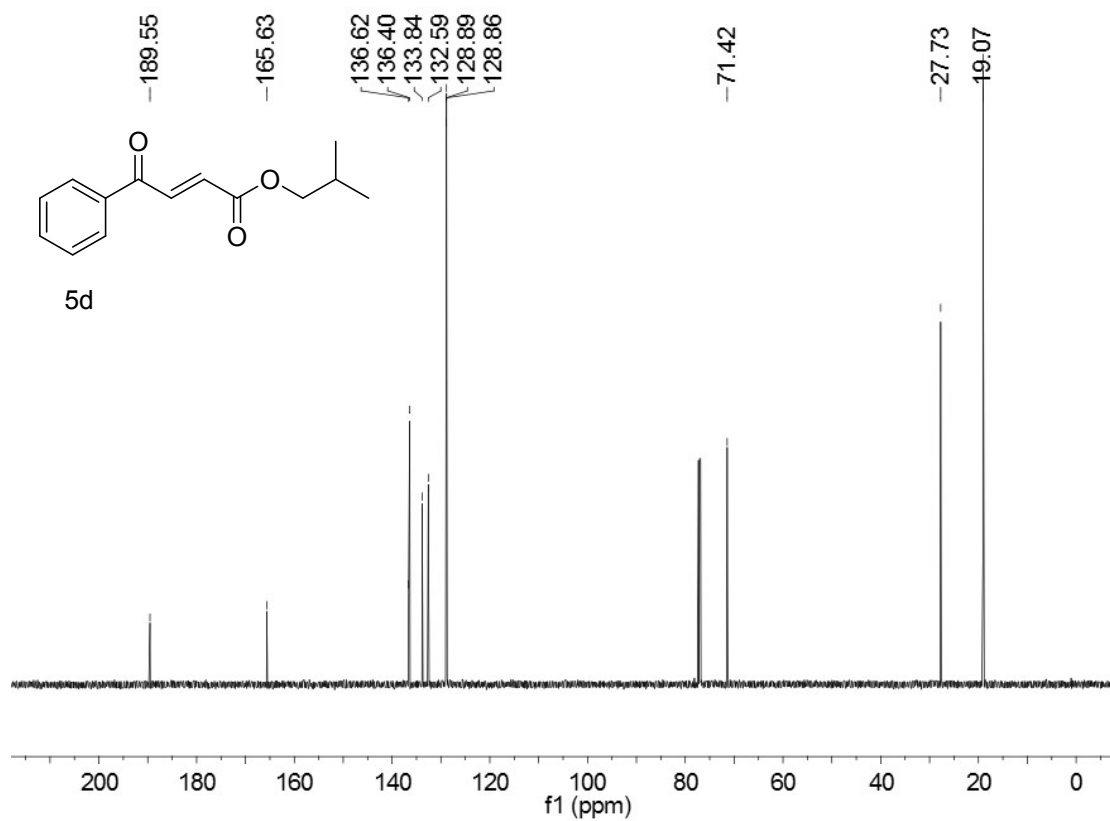
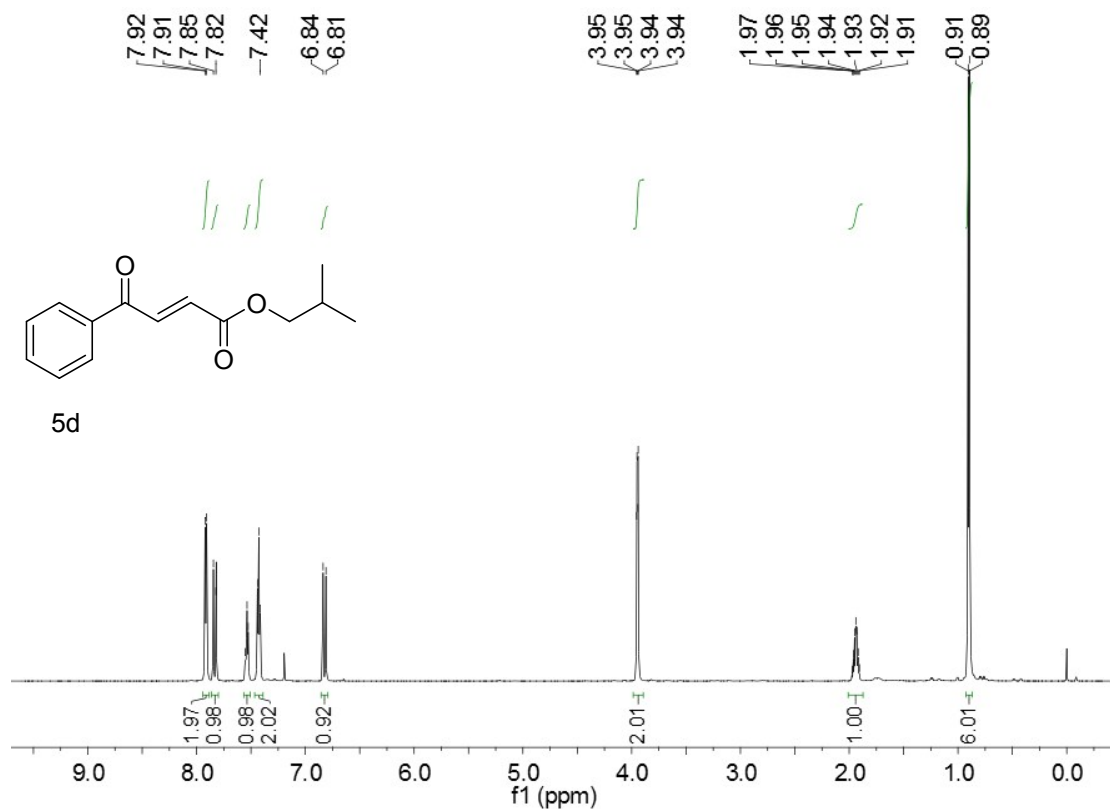
### S-10.2 NMR Spectrum of Carbonylative Heck coupling products 5

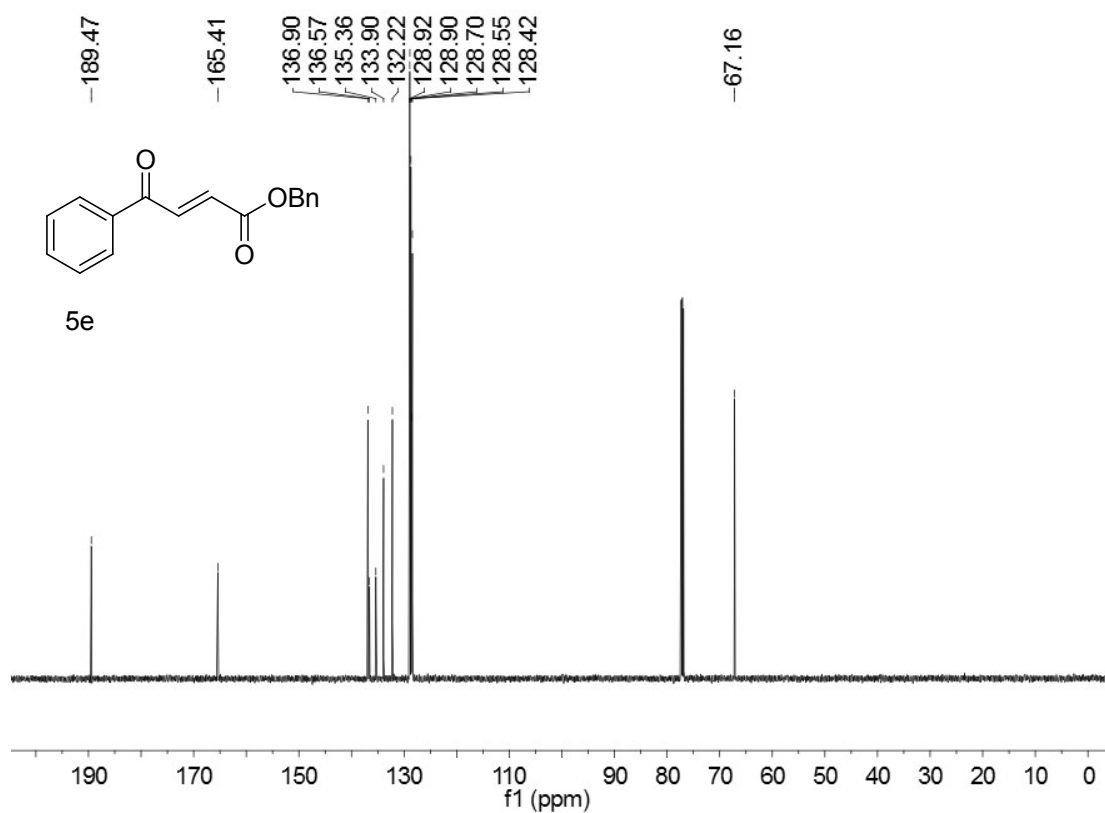
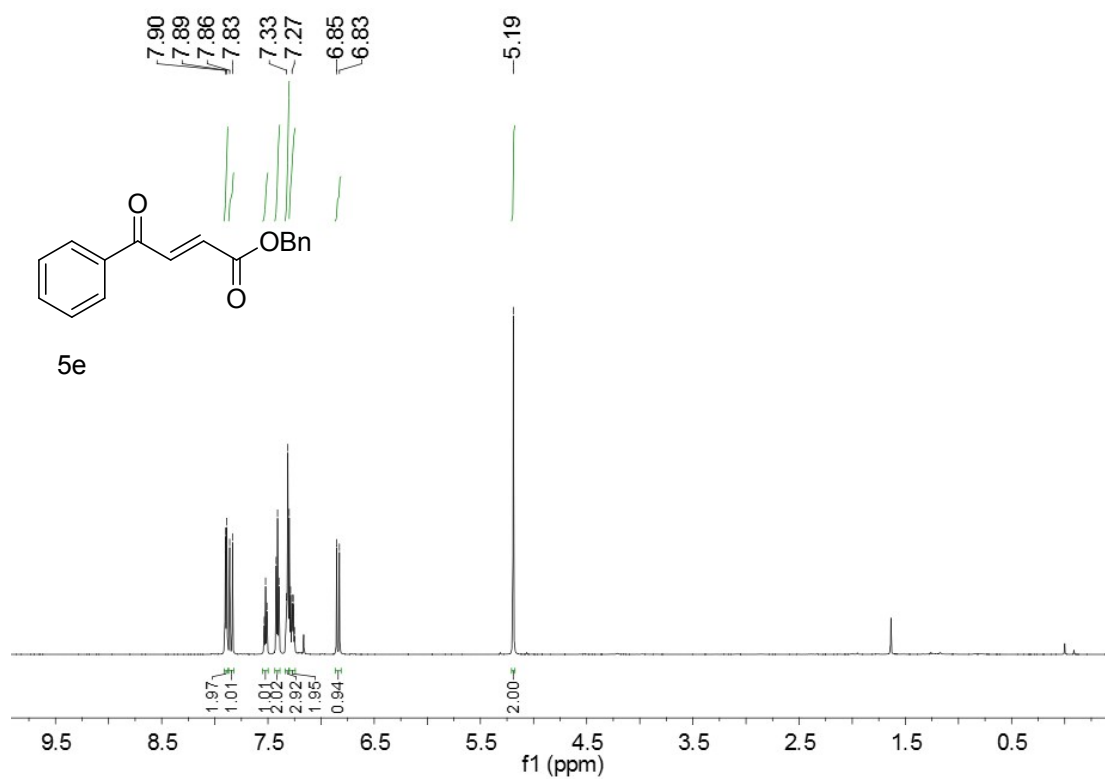


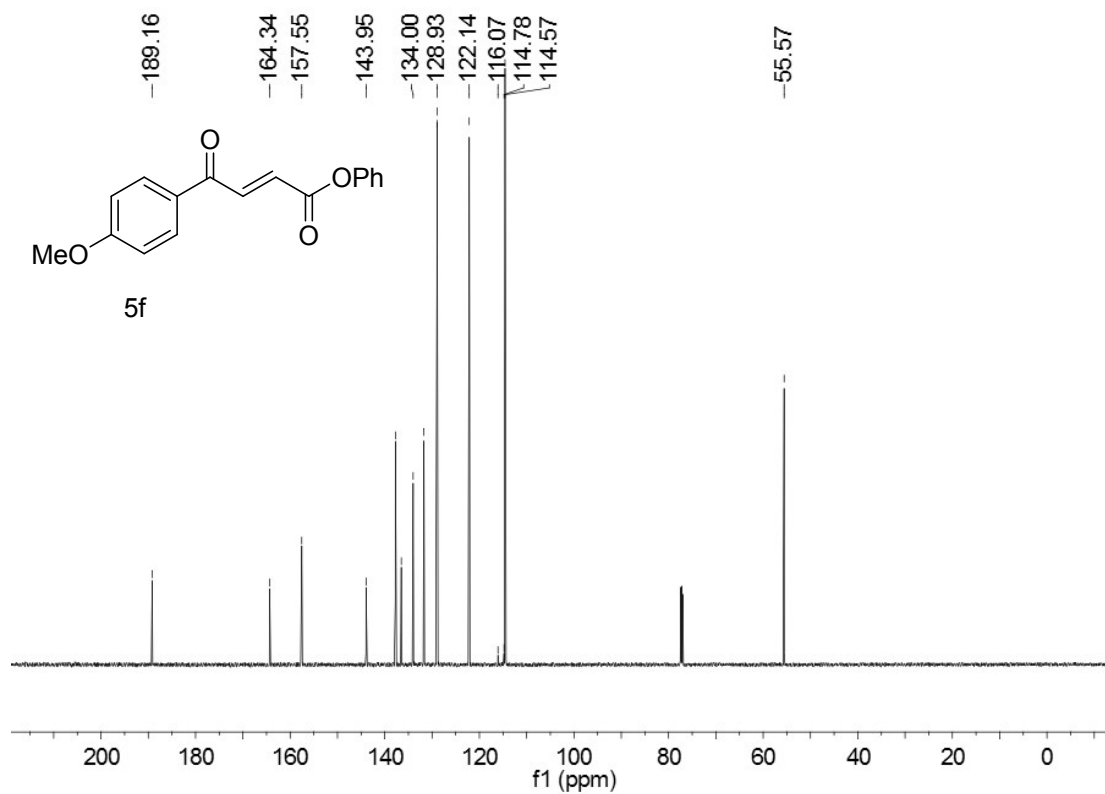
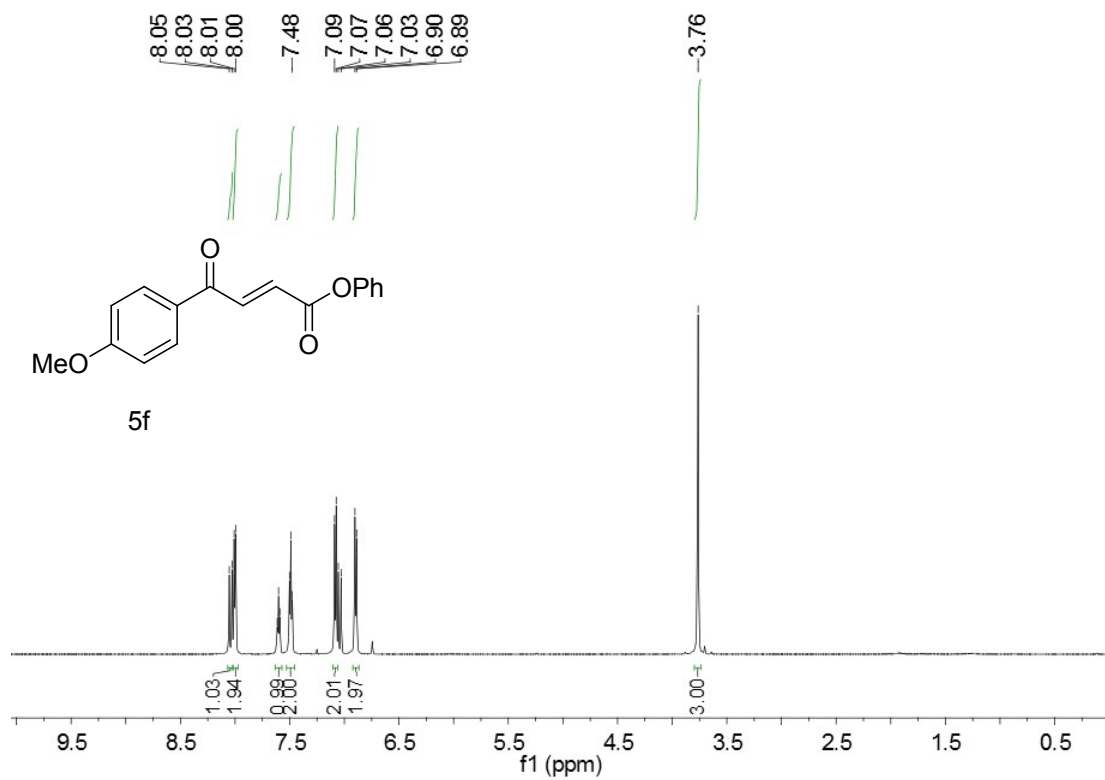


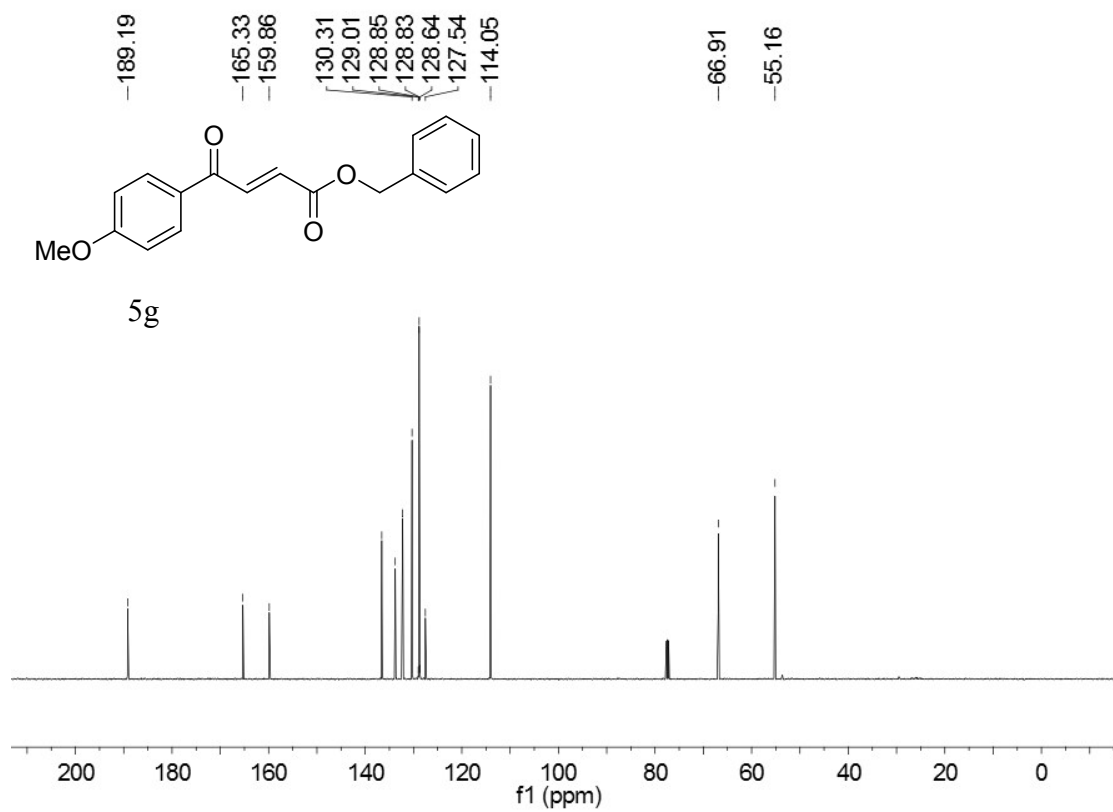
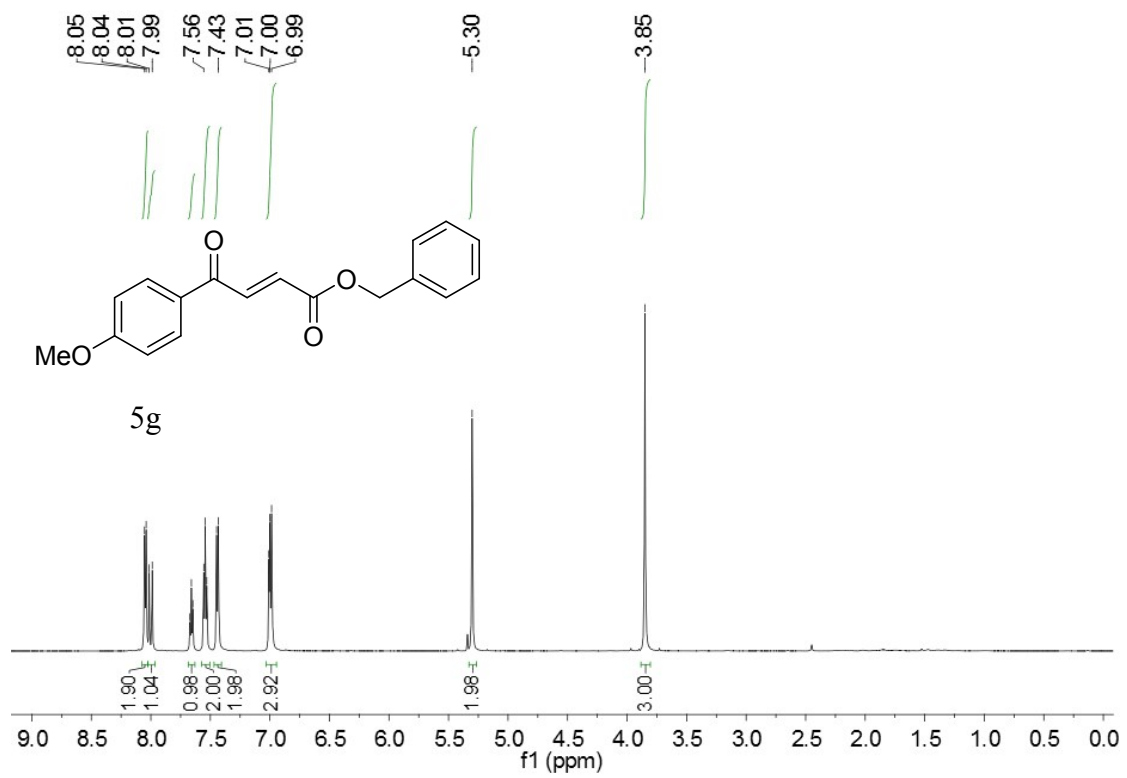


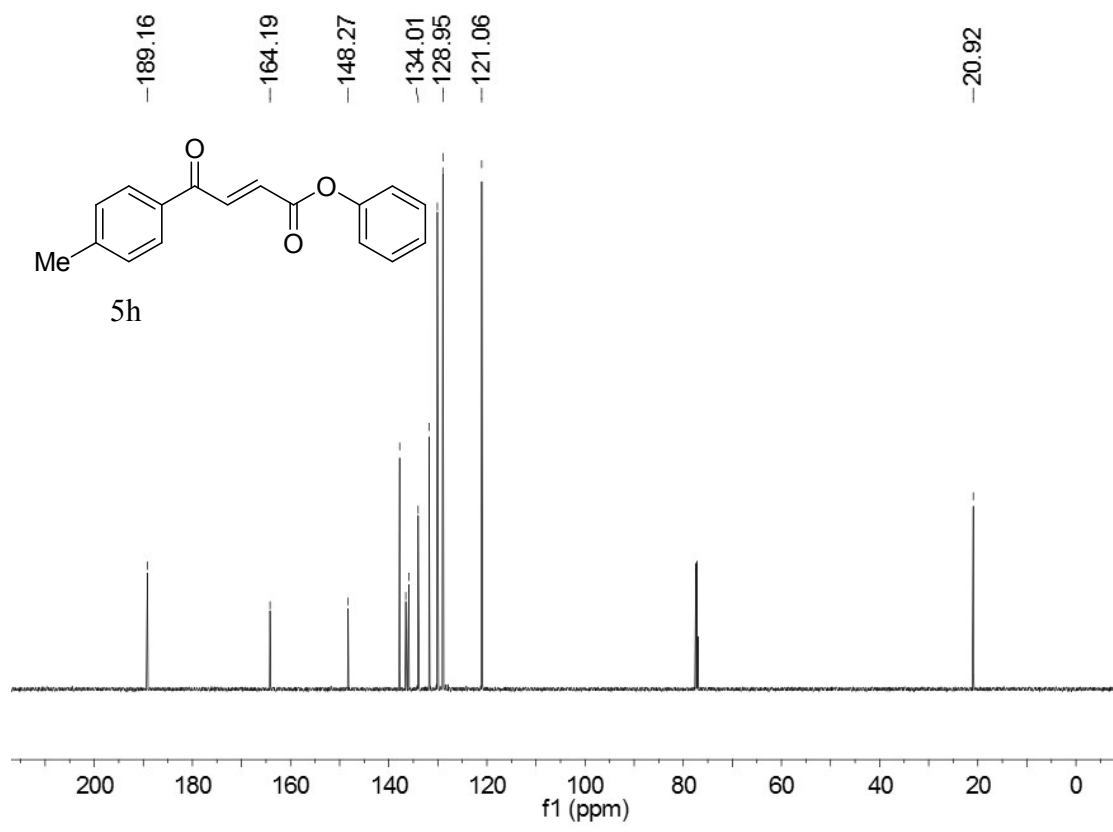
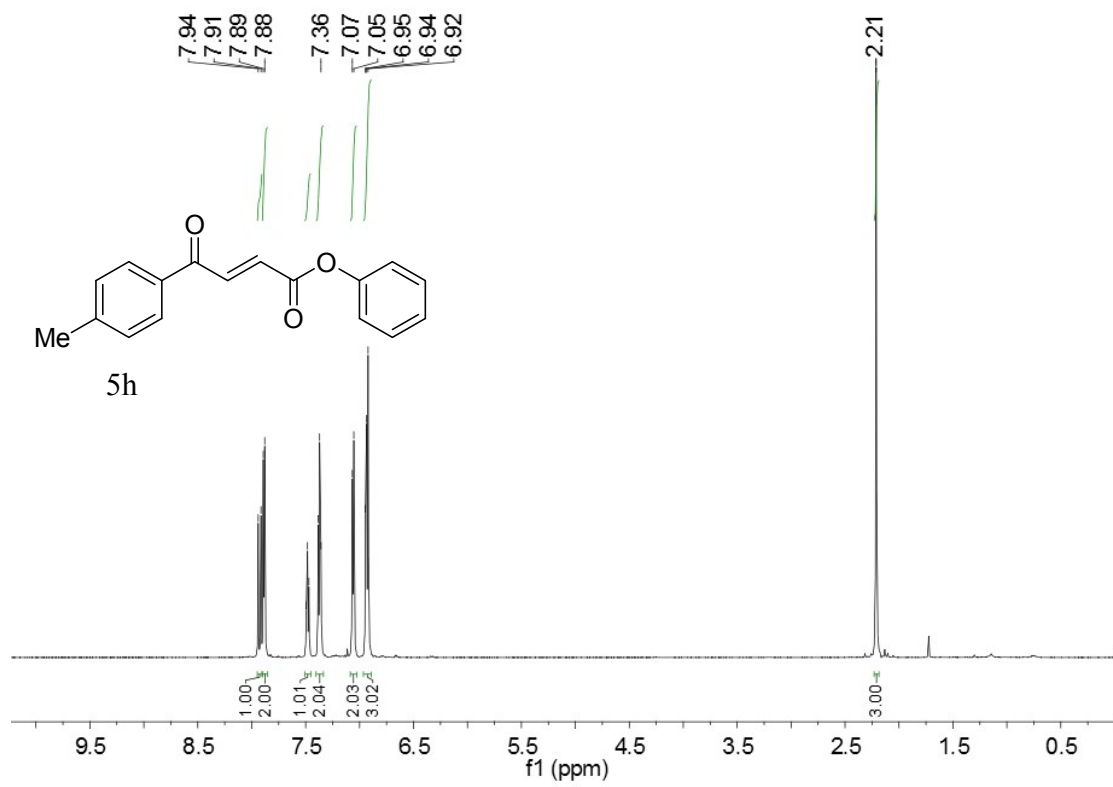


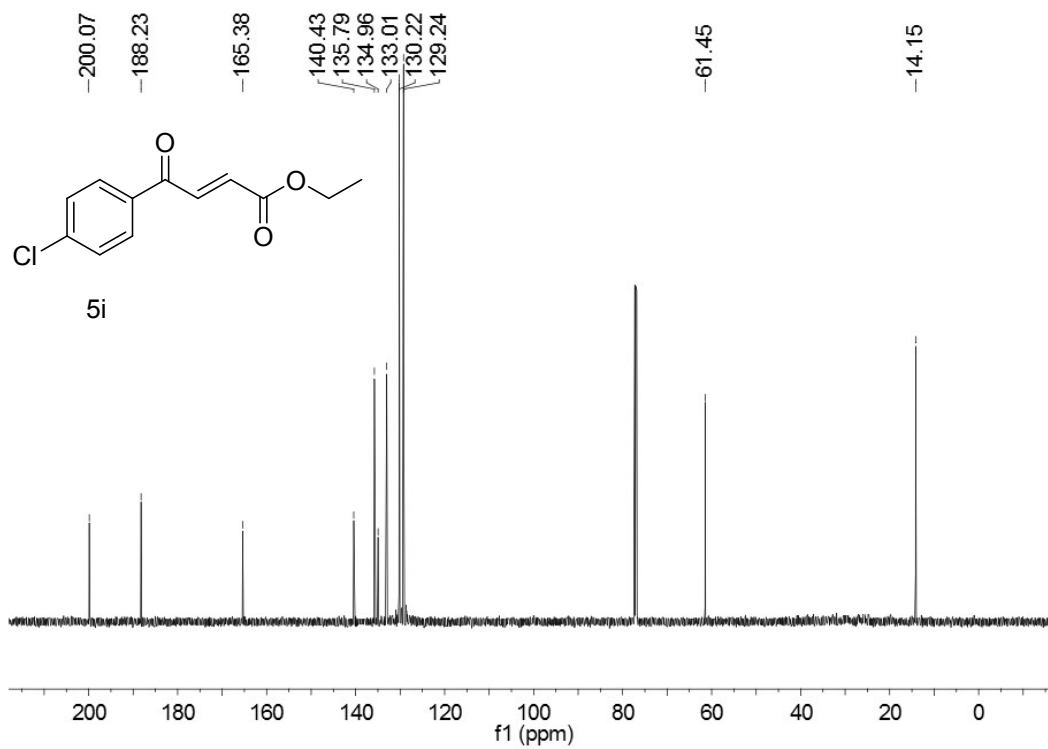
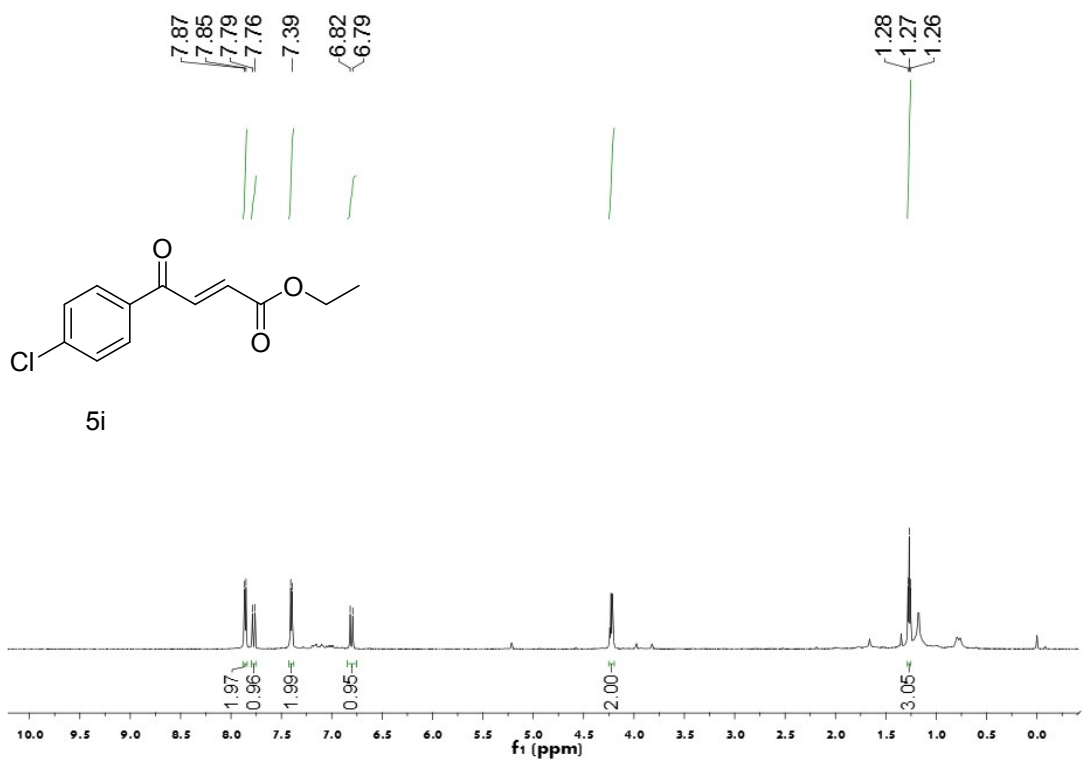


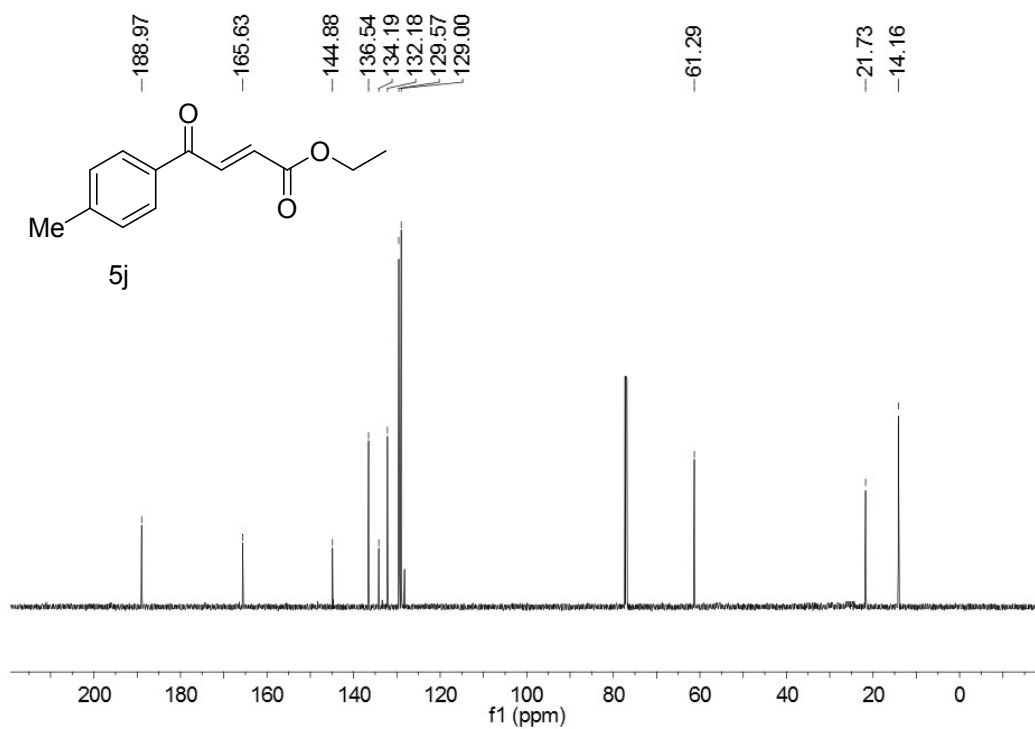
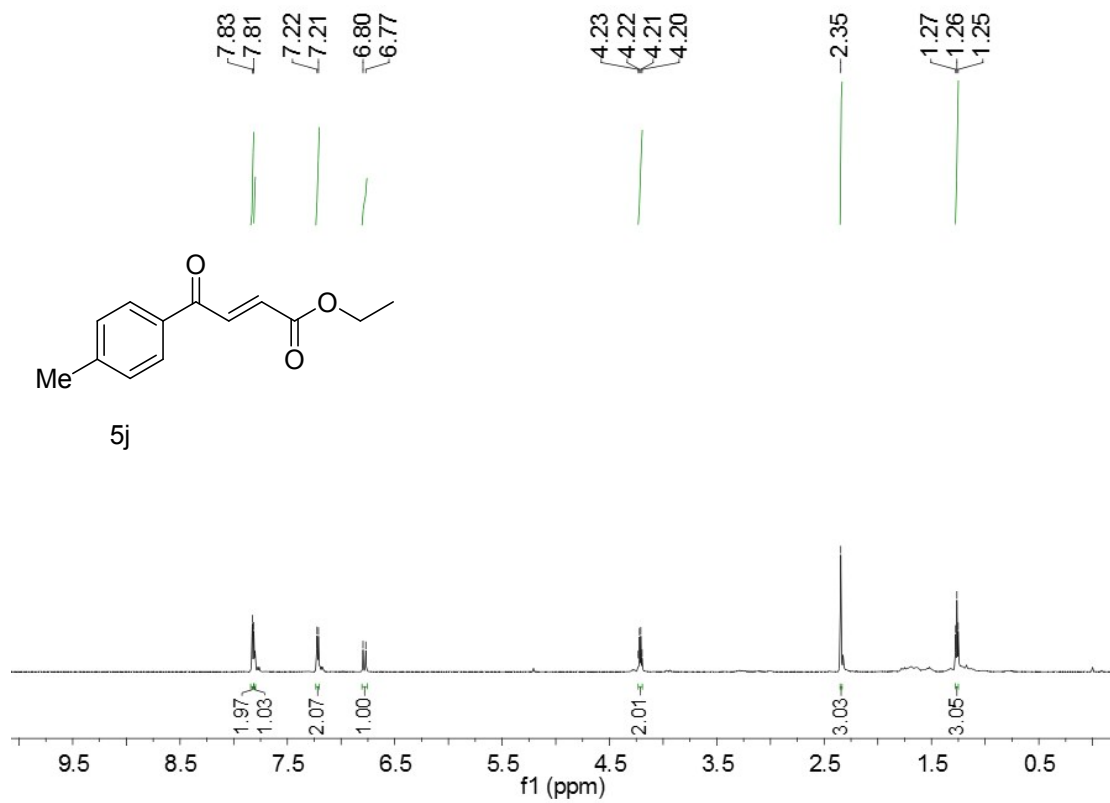




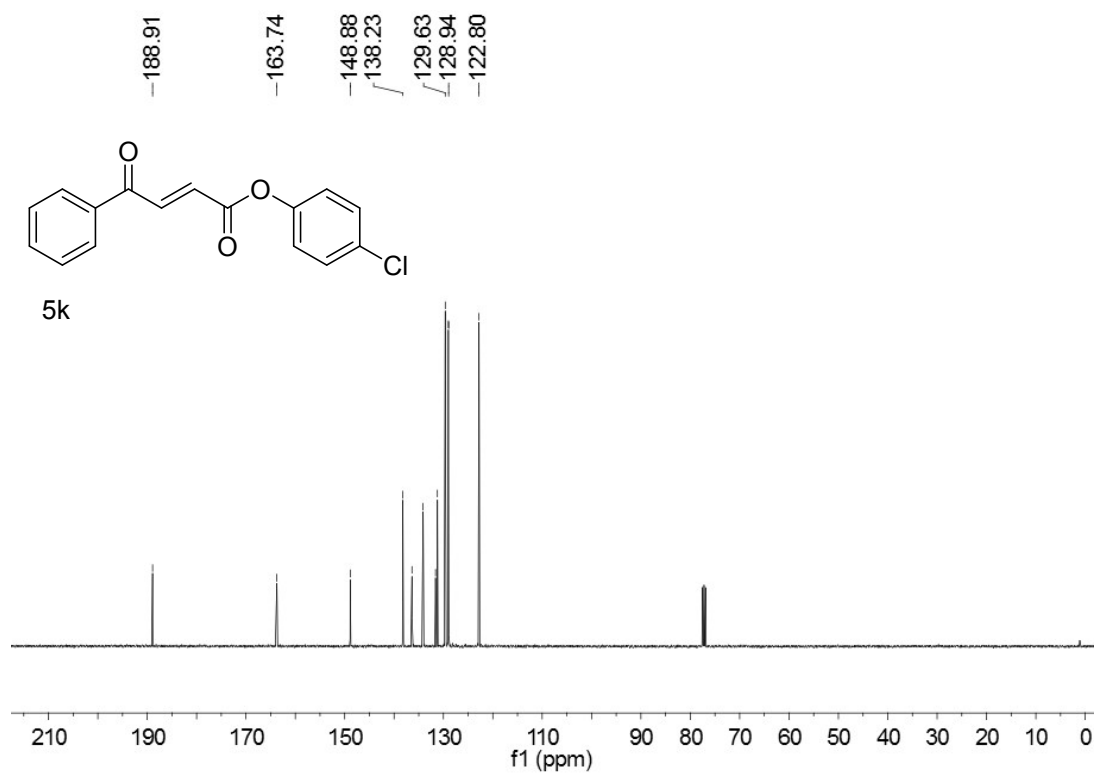
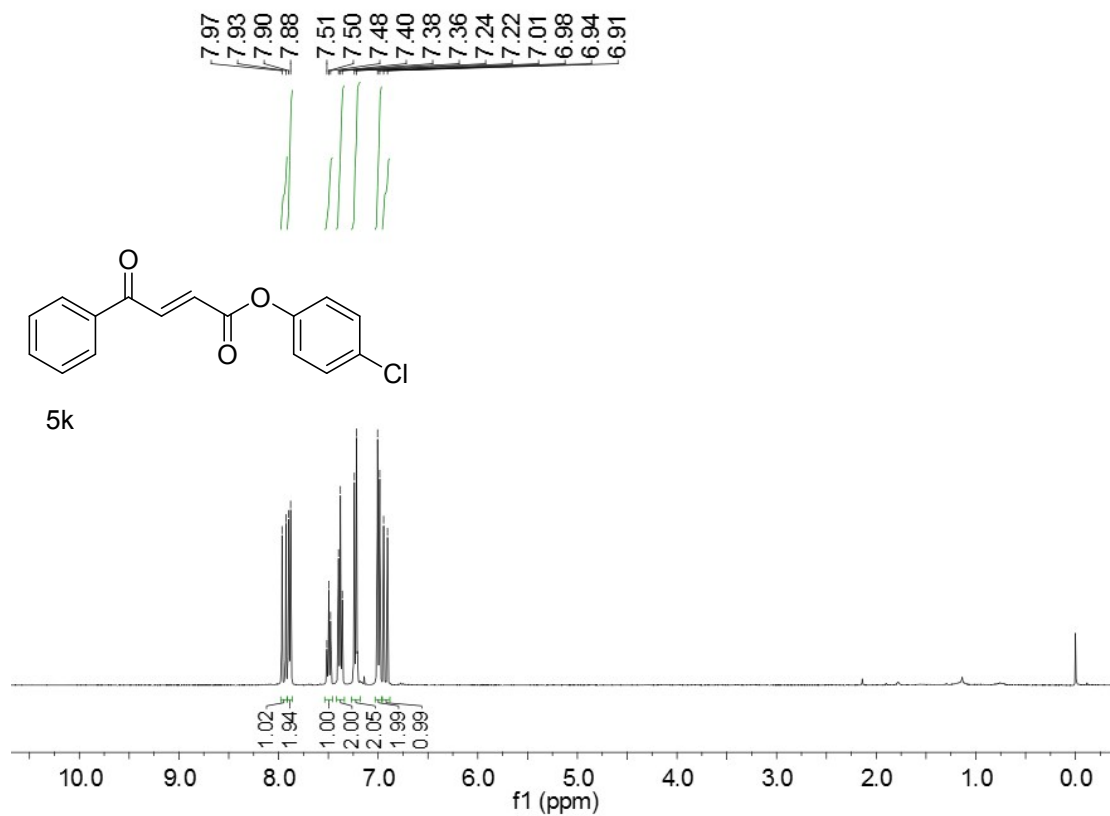


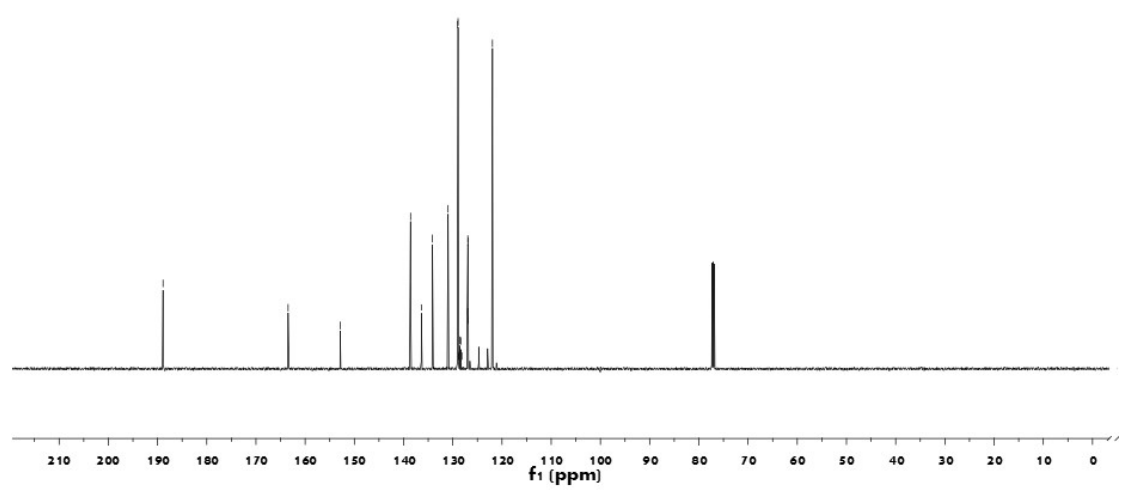
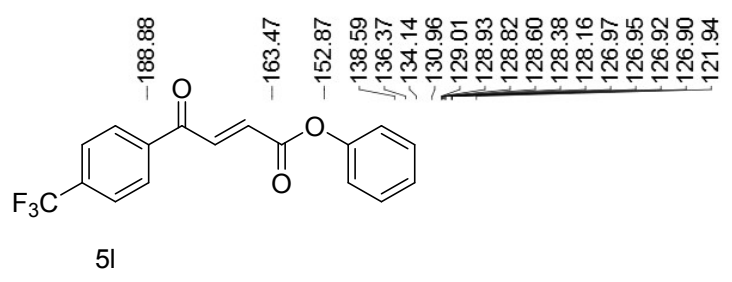
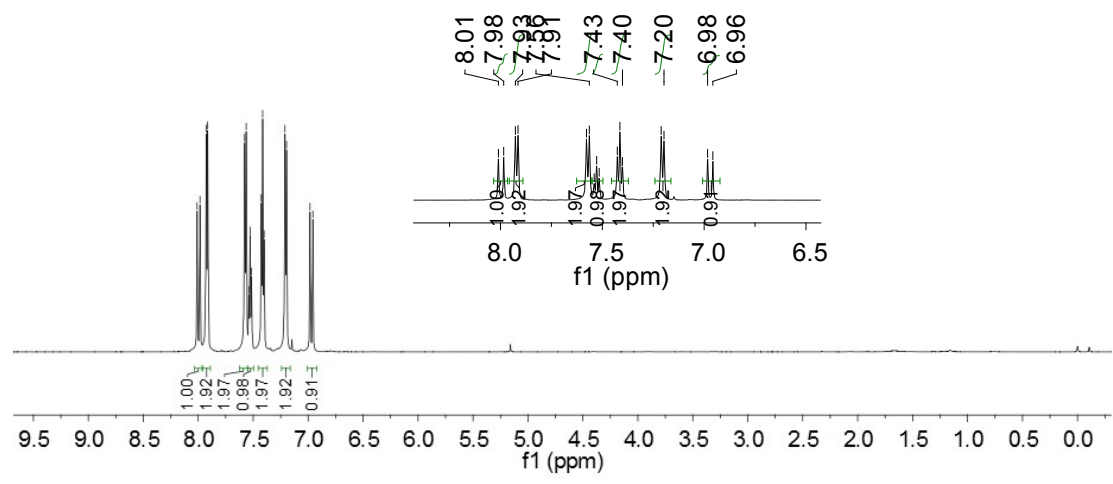
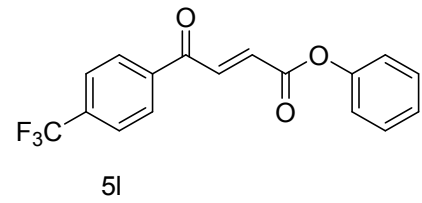
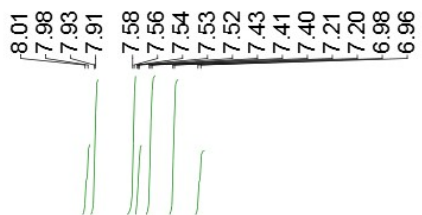


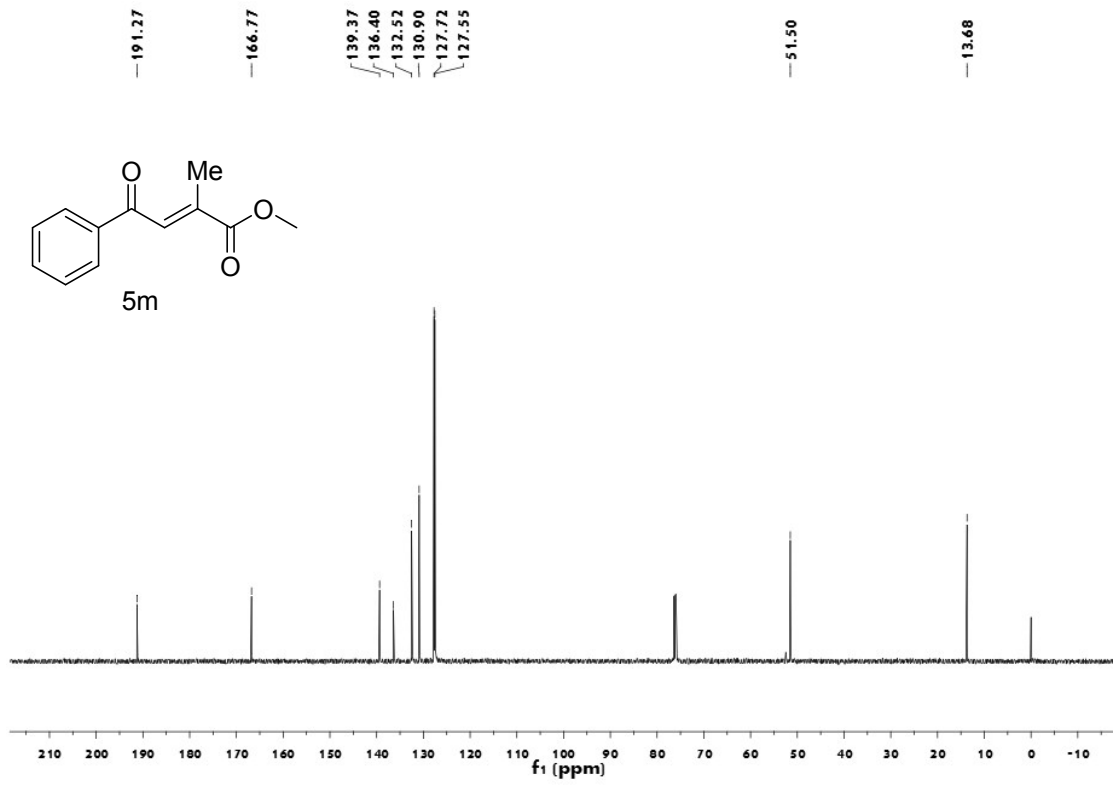
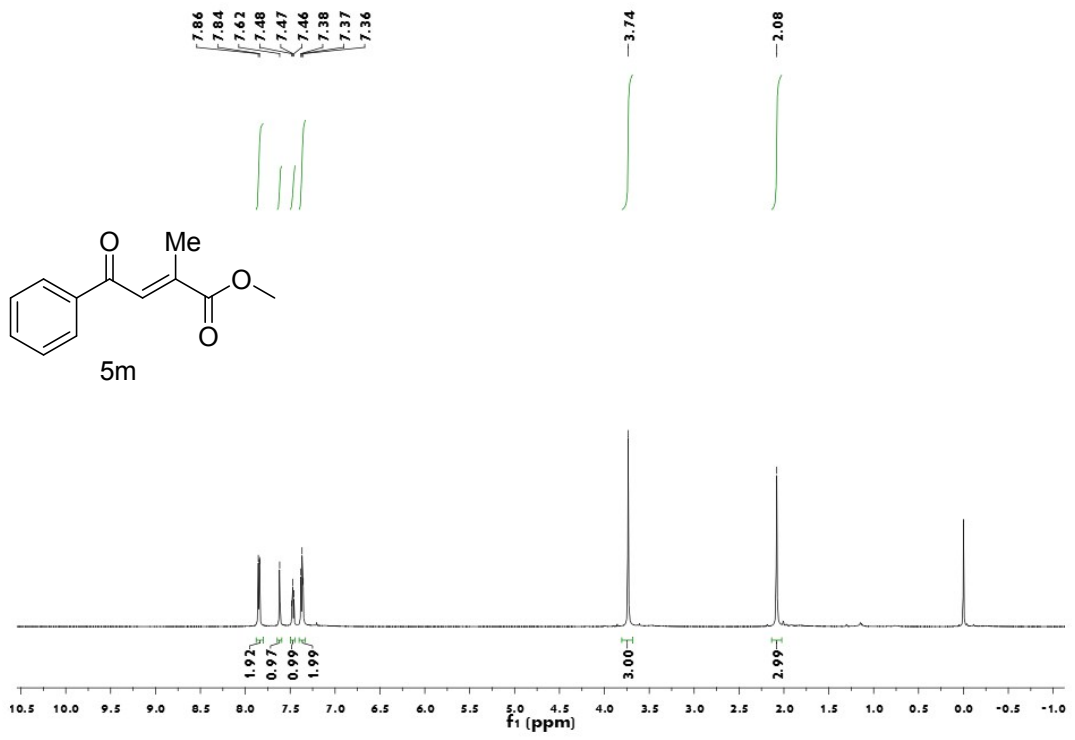


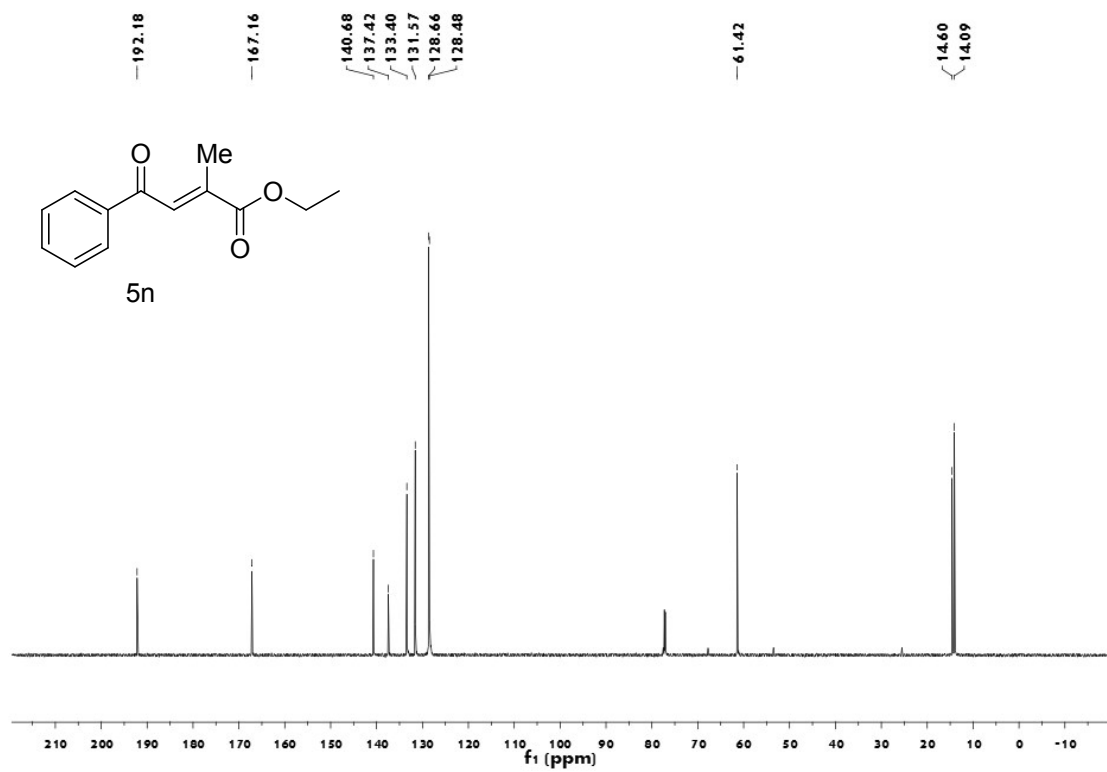
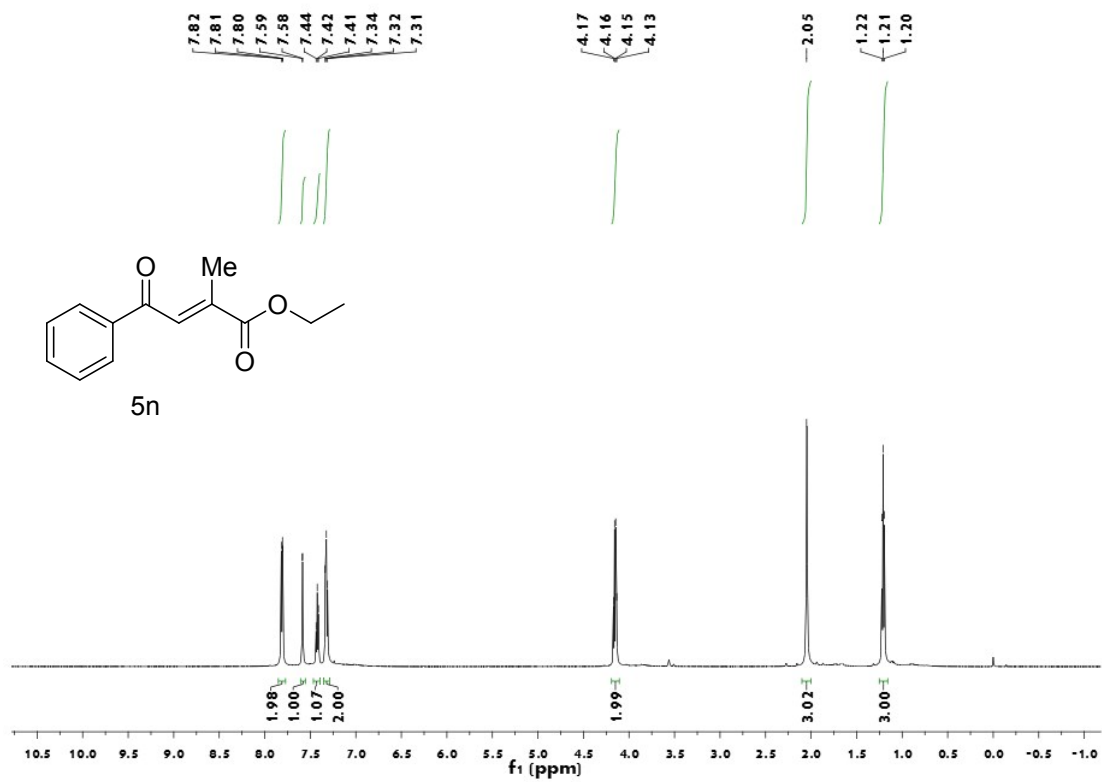




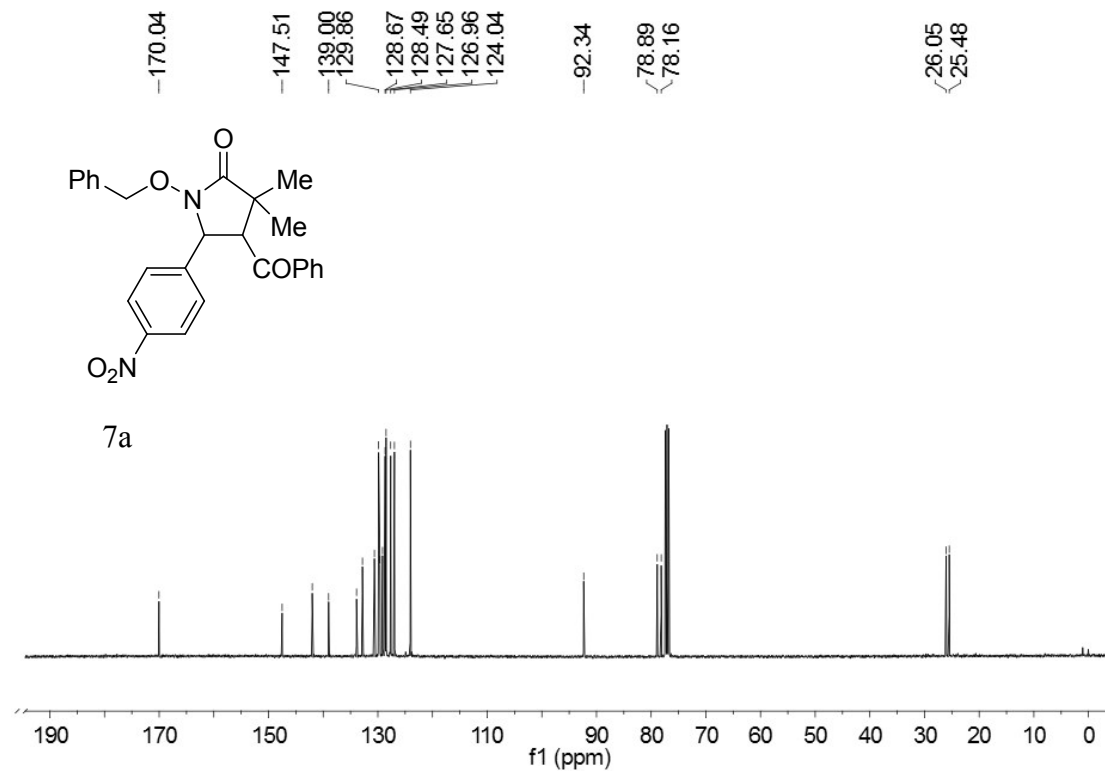
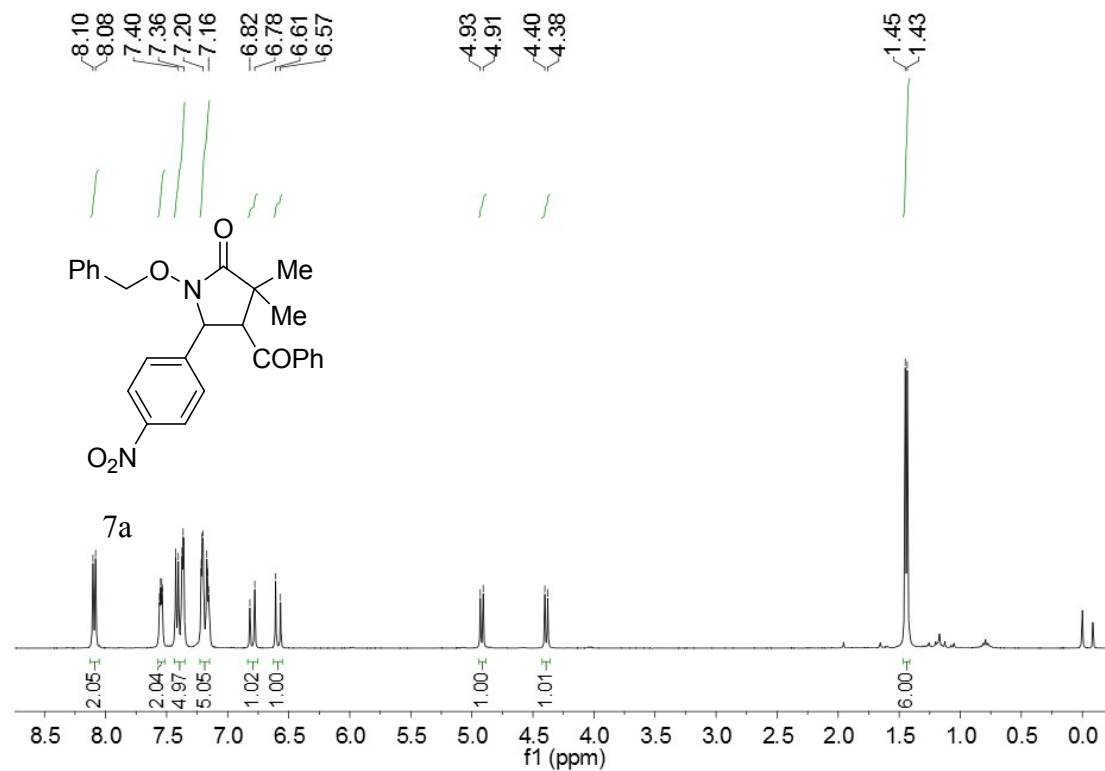


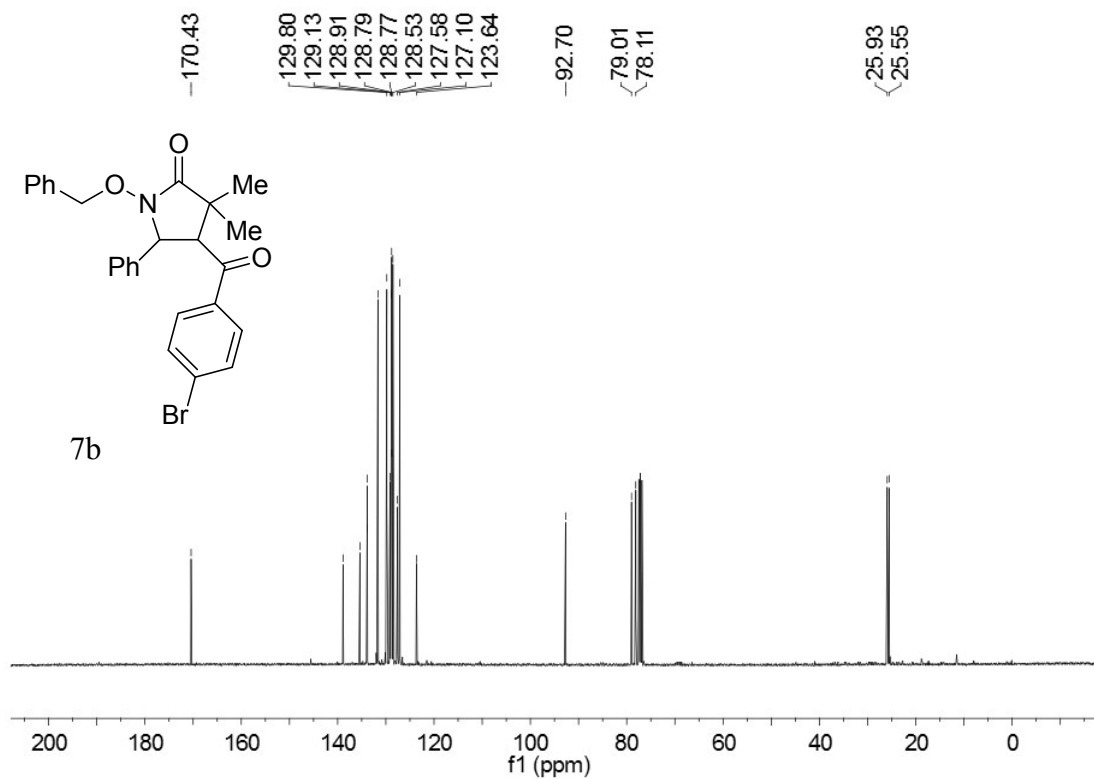
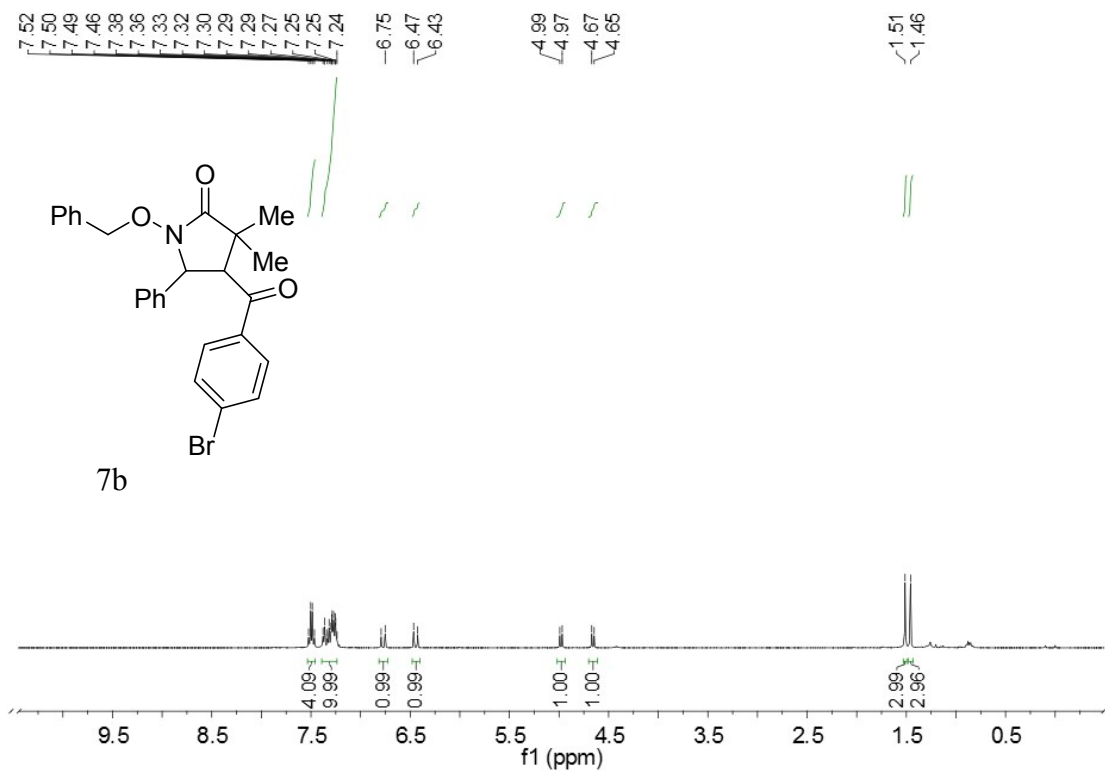


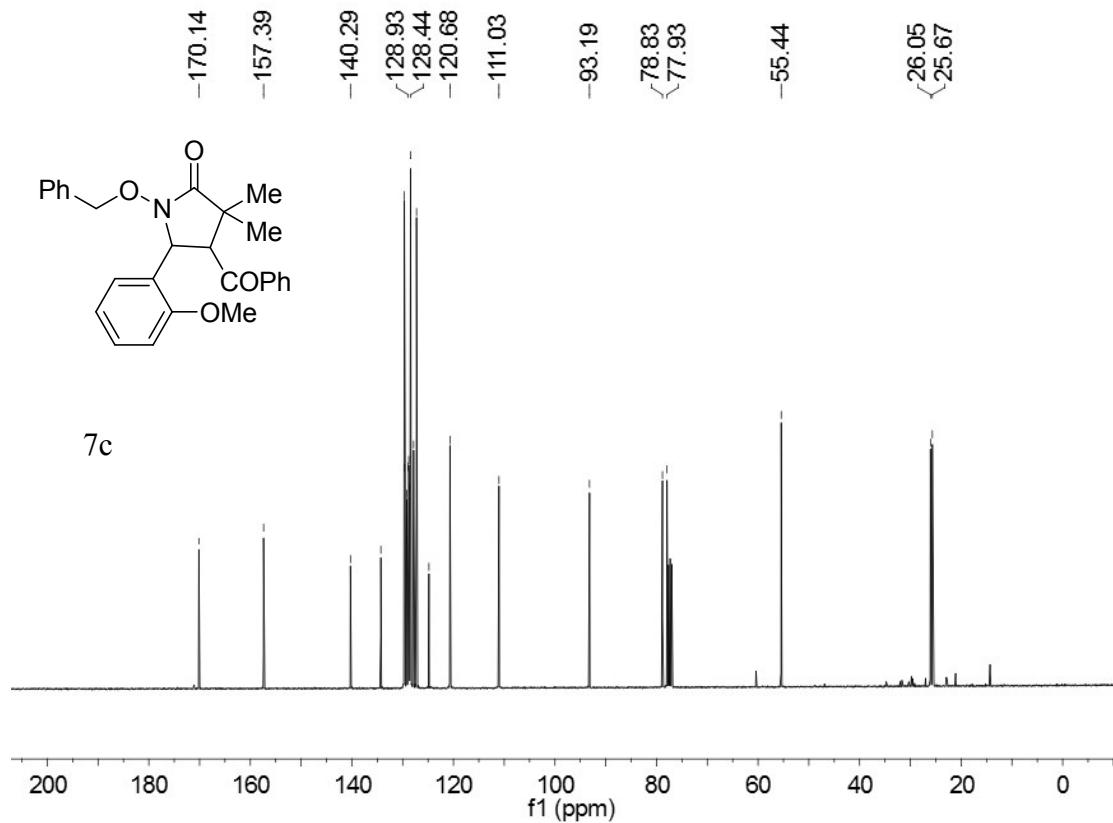
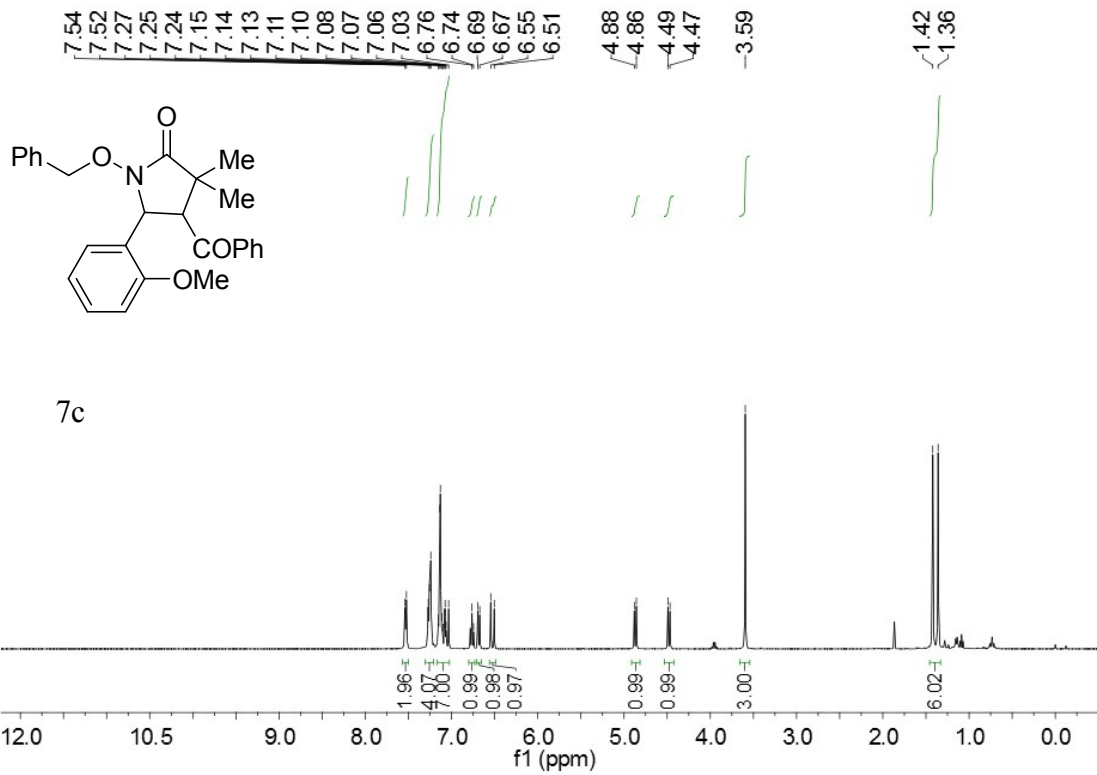




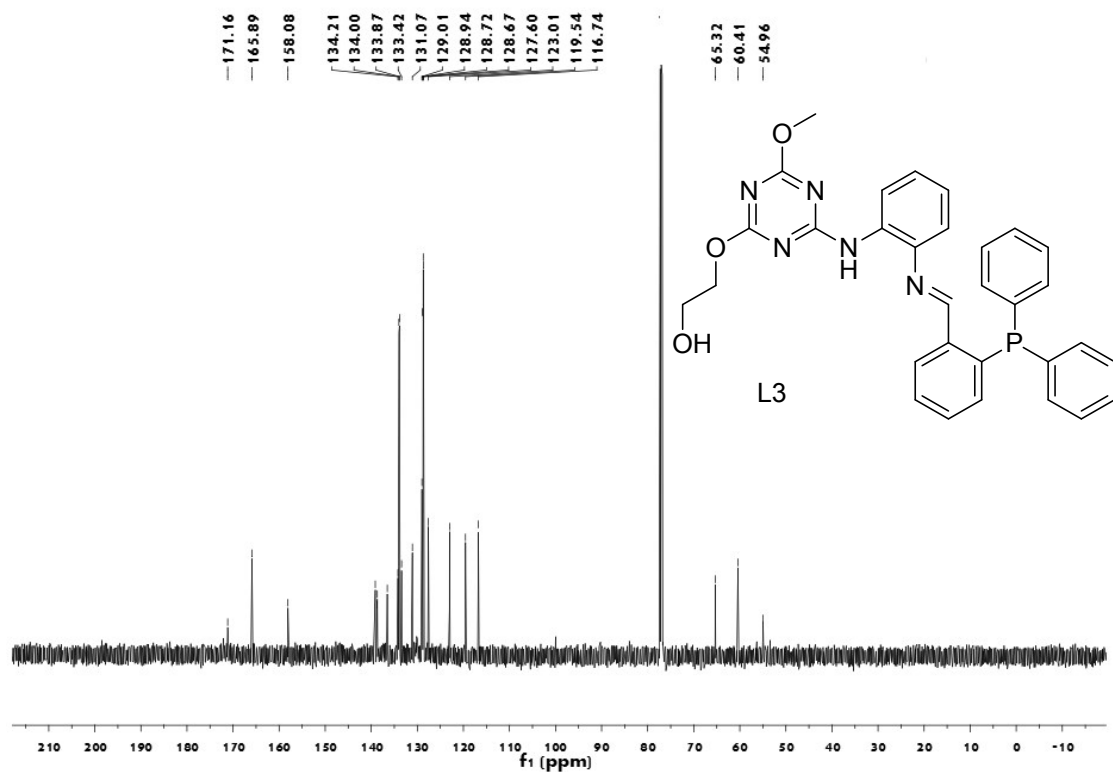
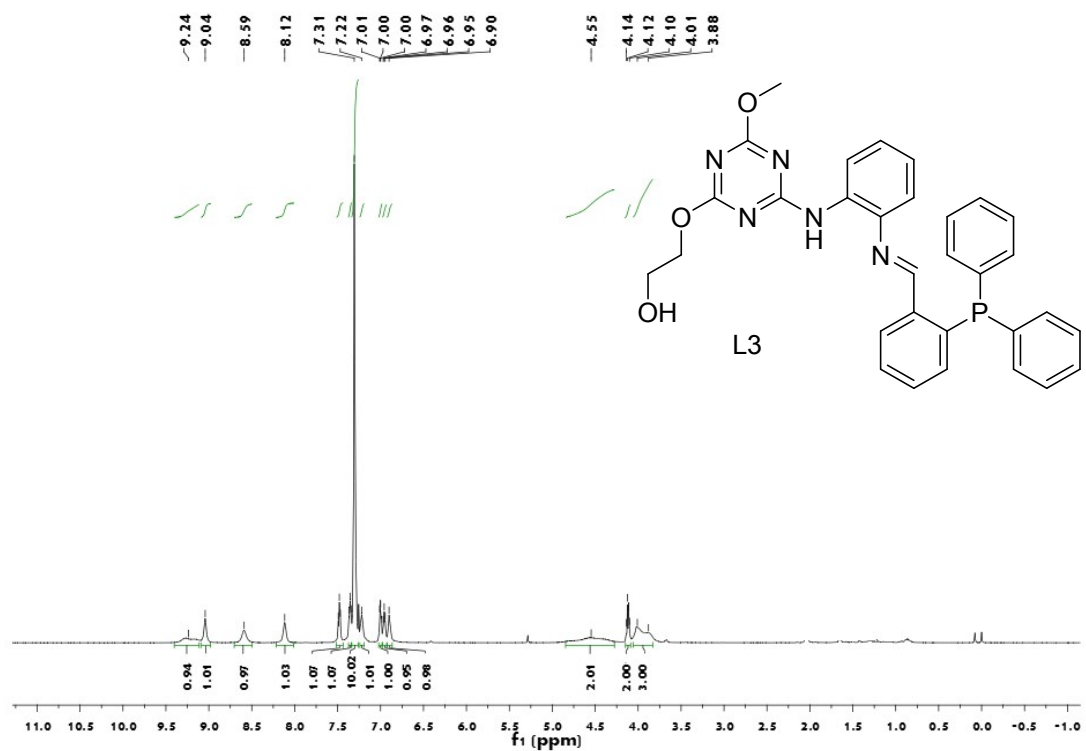
S-10.3. NMR Spectrum of [3+2] cycloaddition product 7



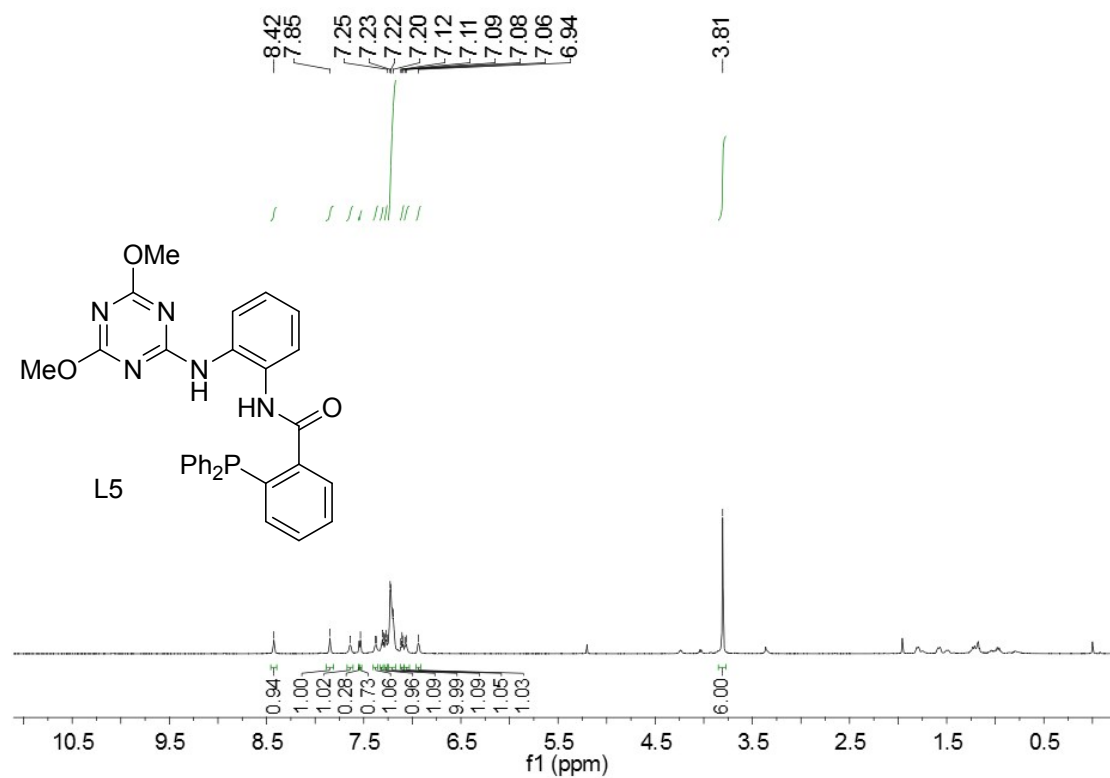
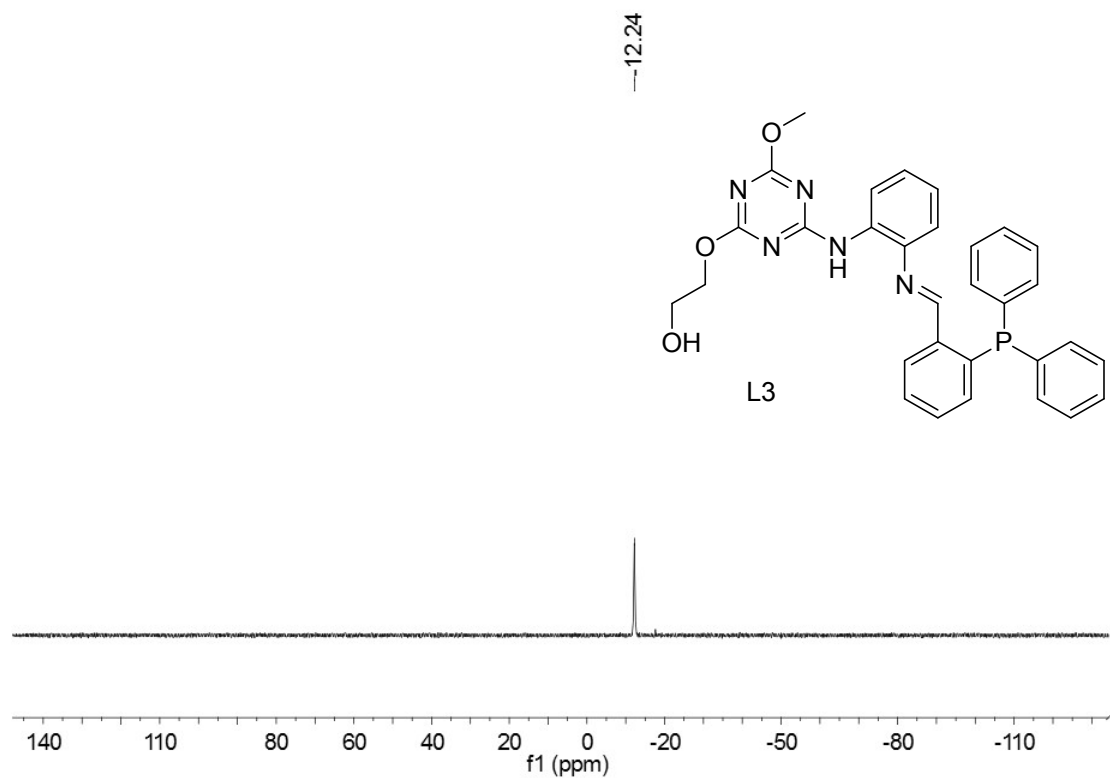


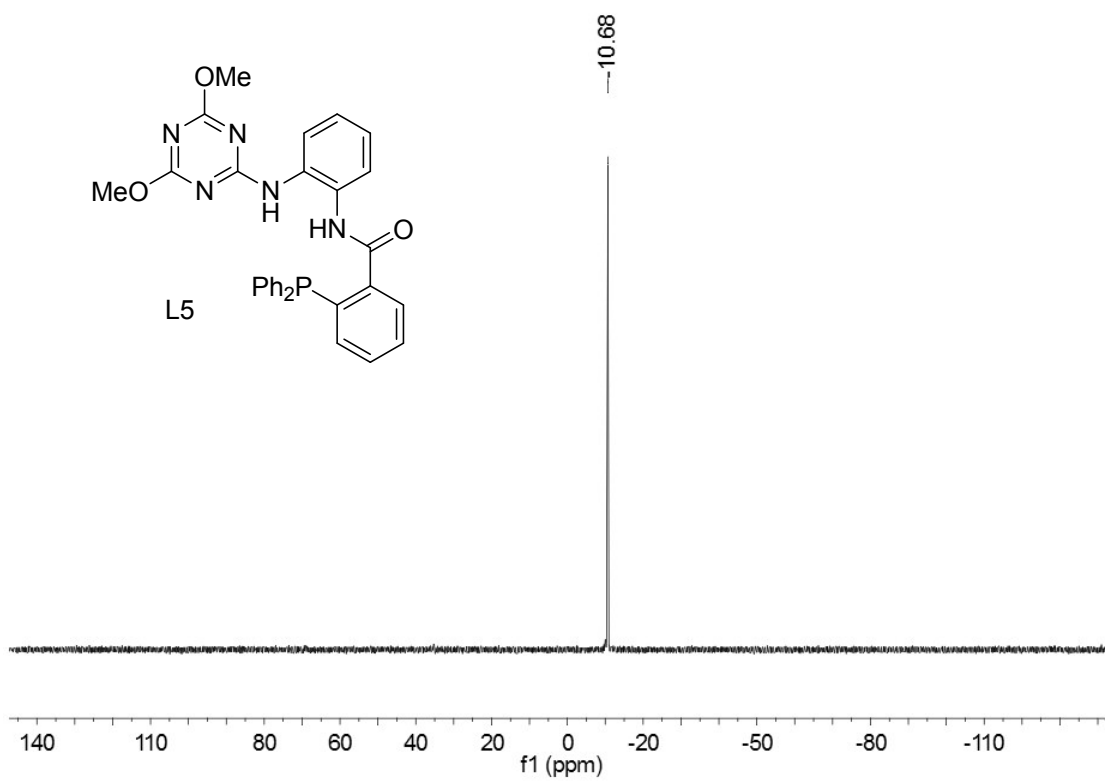
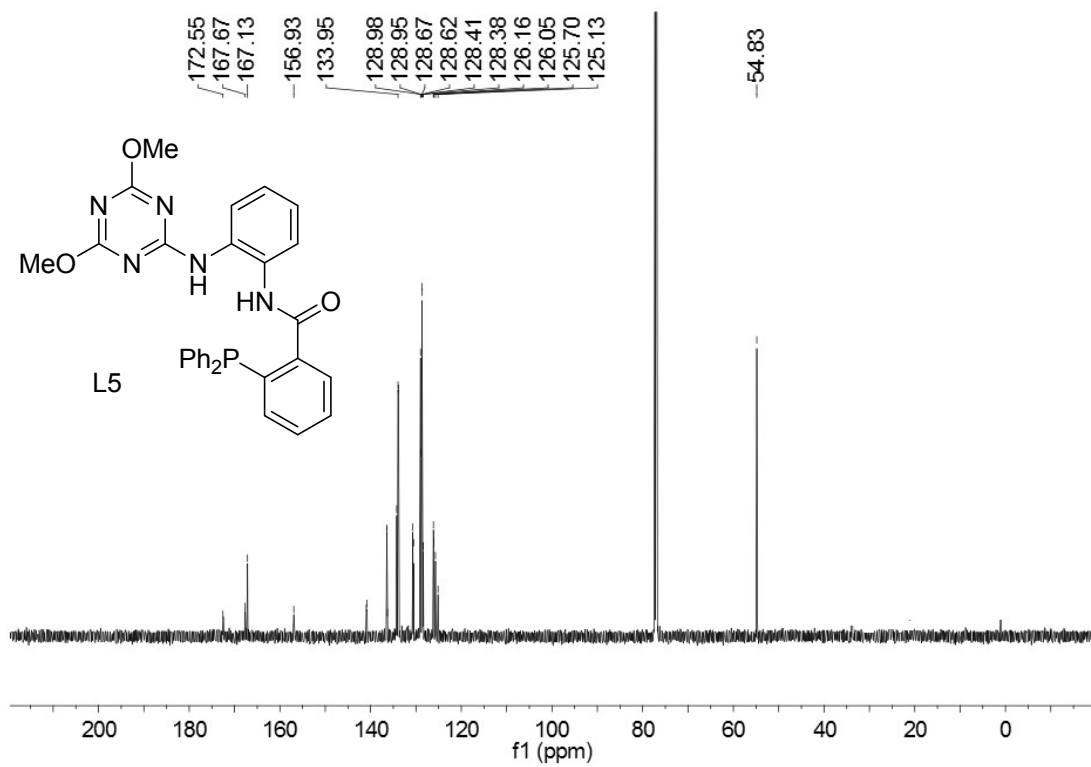


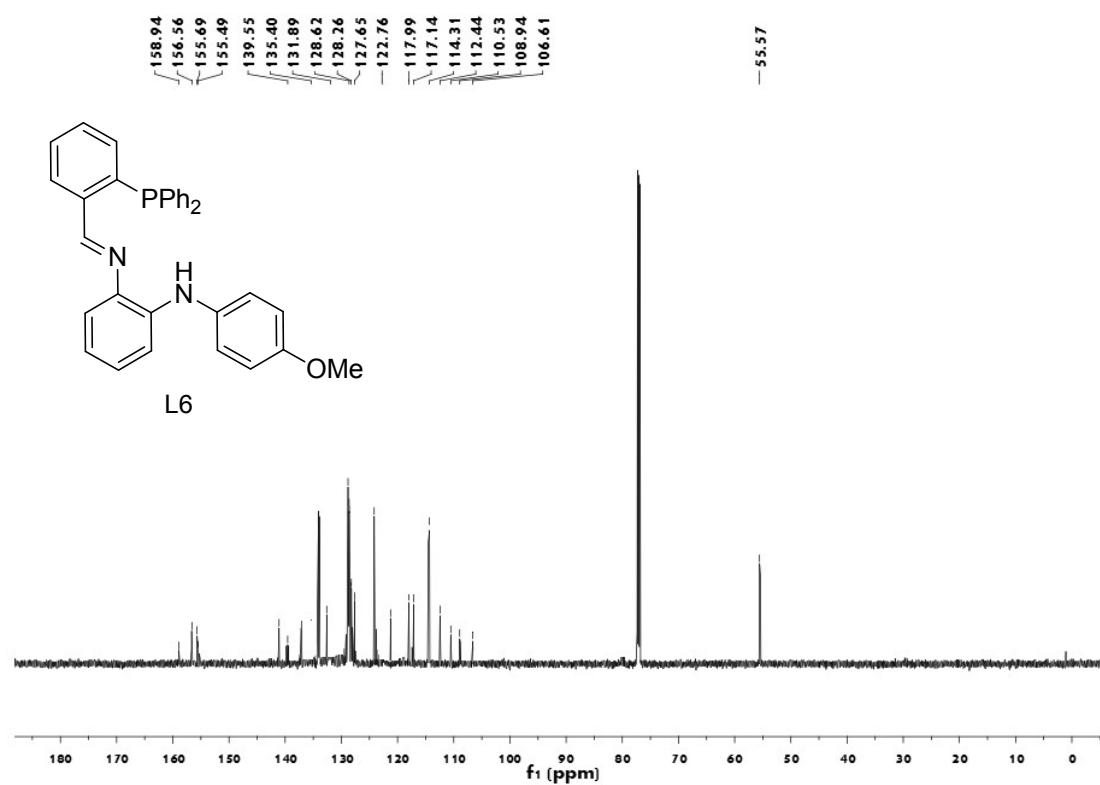
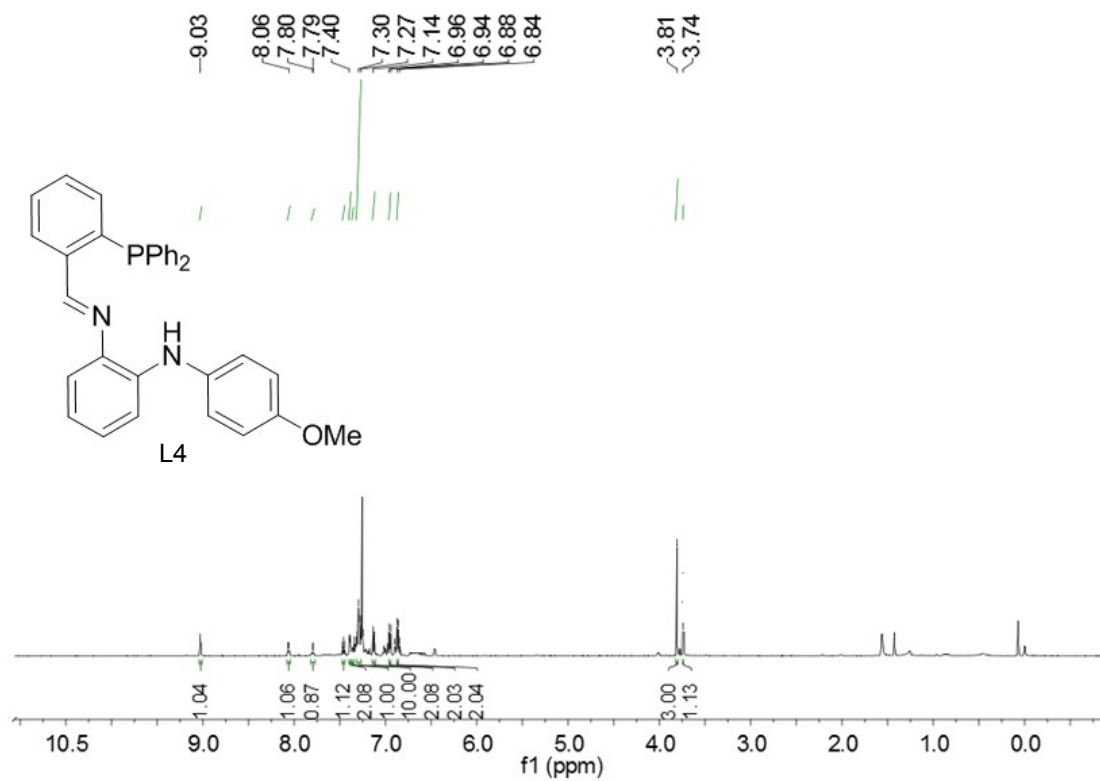
### S-10.4. NMR Spectrum of s-triazine based N,P-ligands L

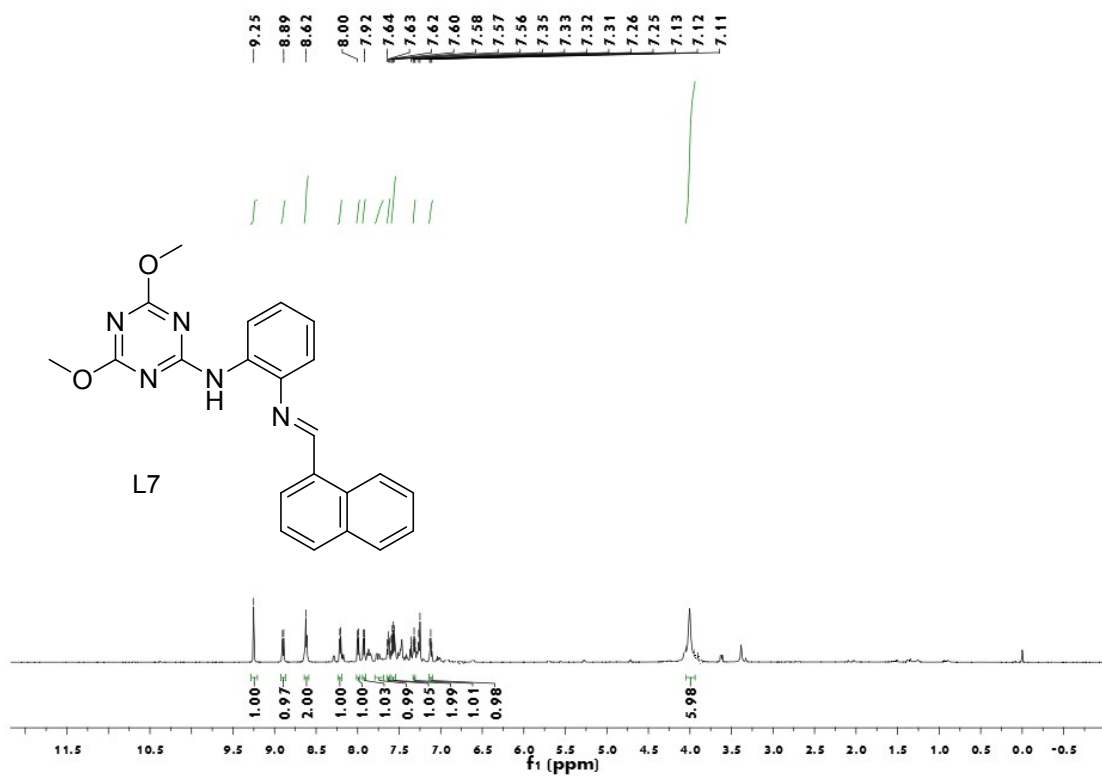
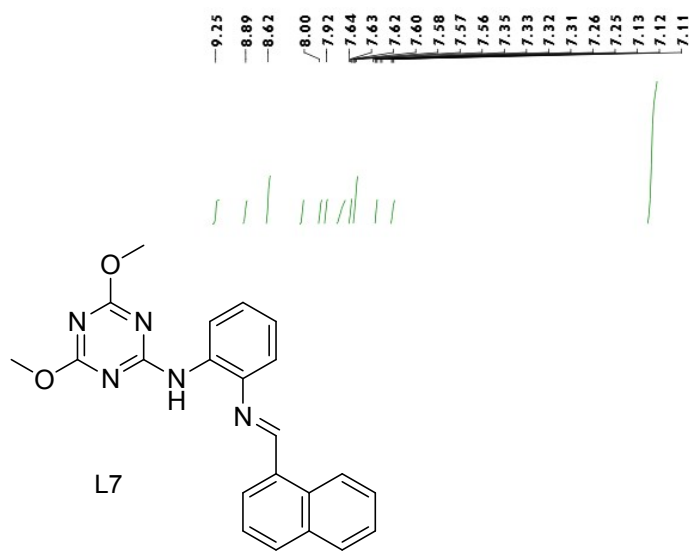
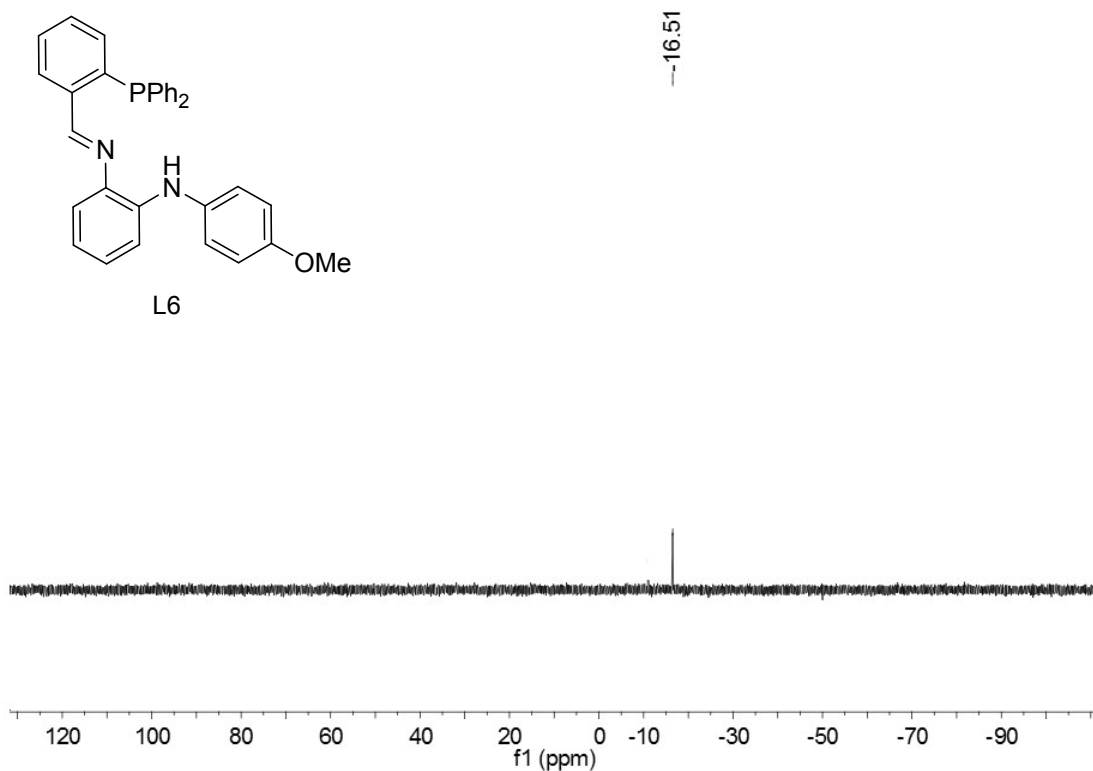
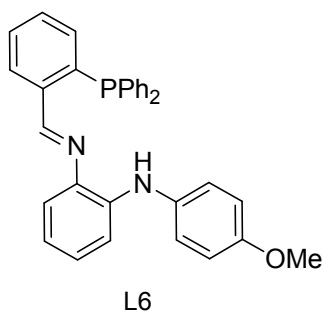


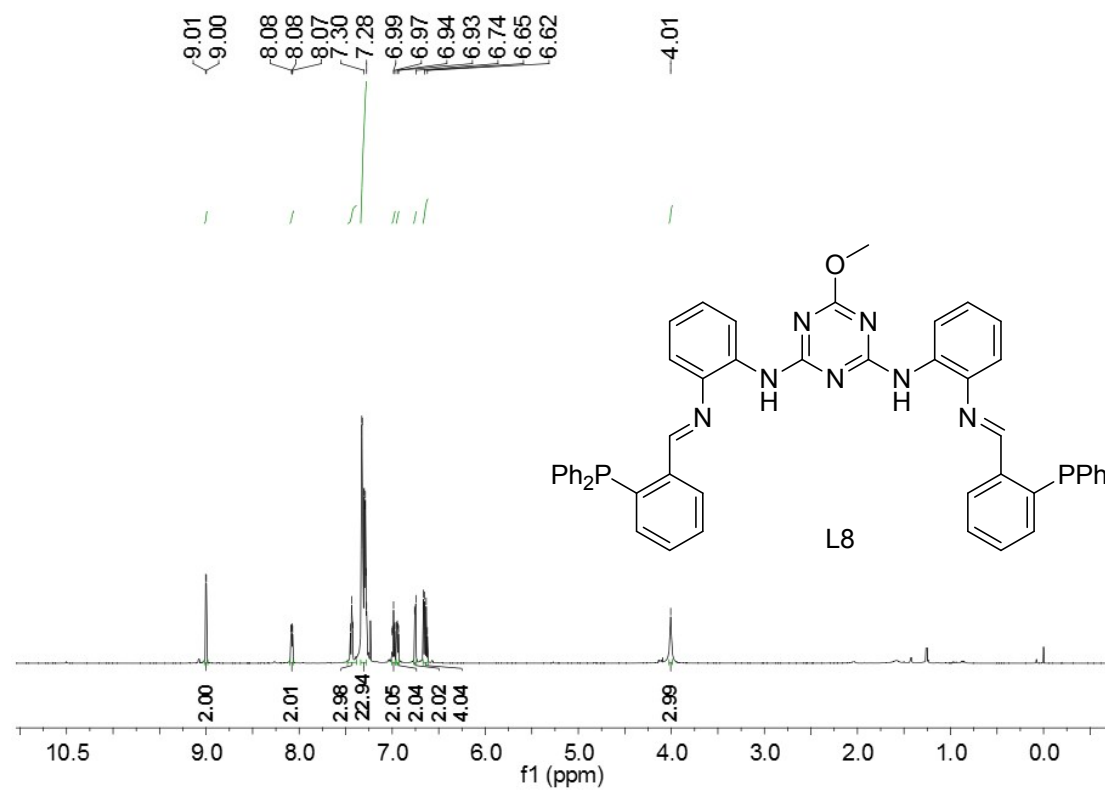
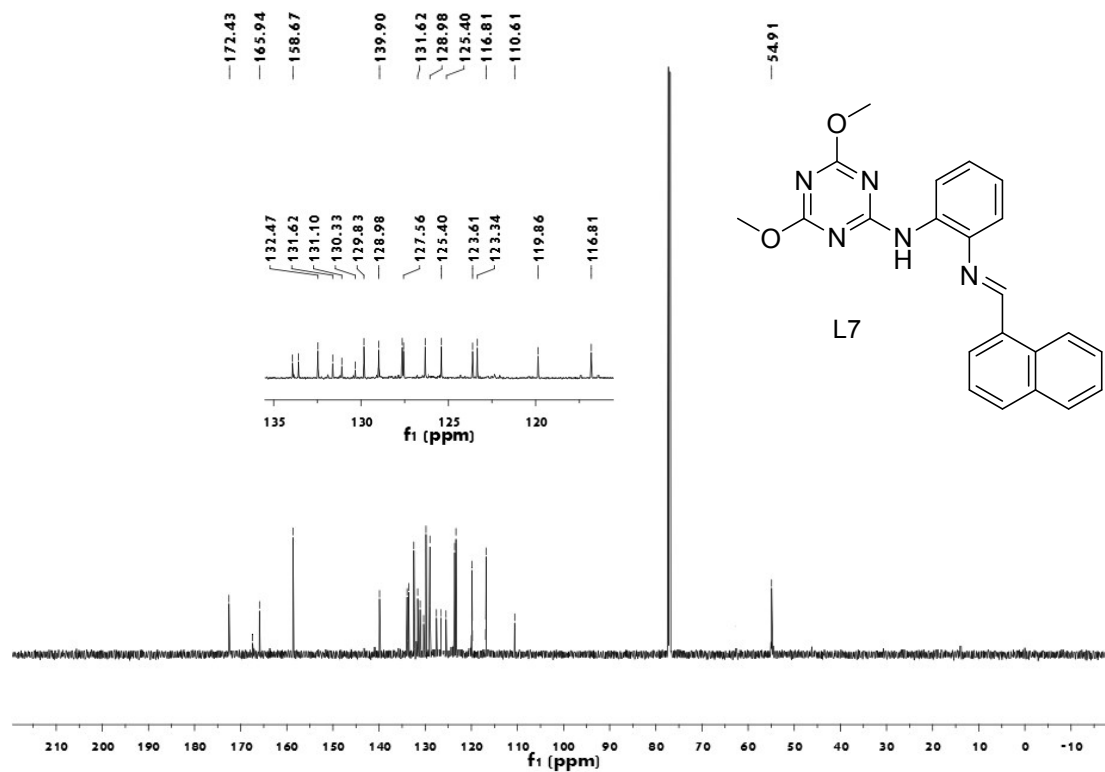


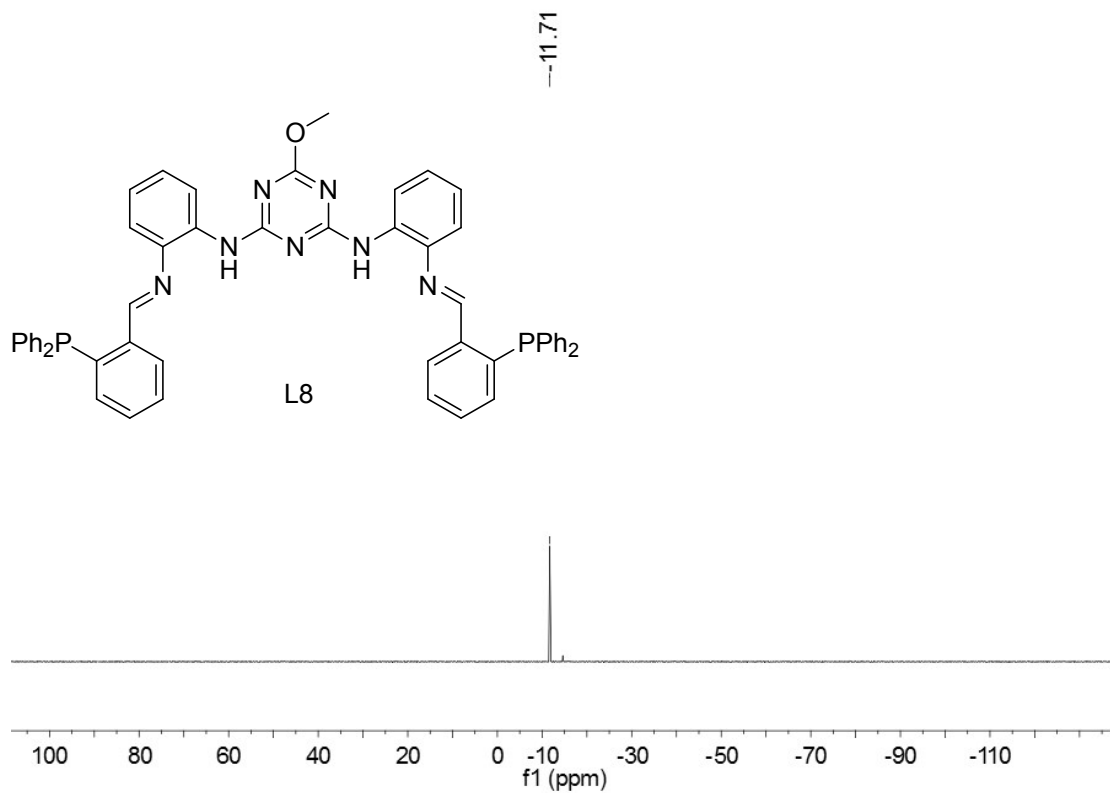
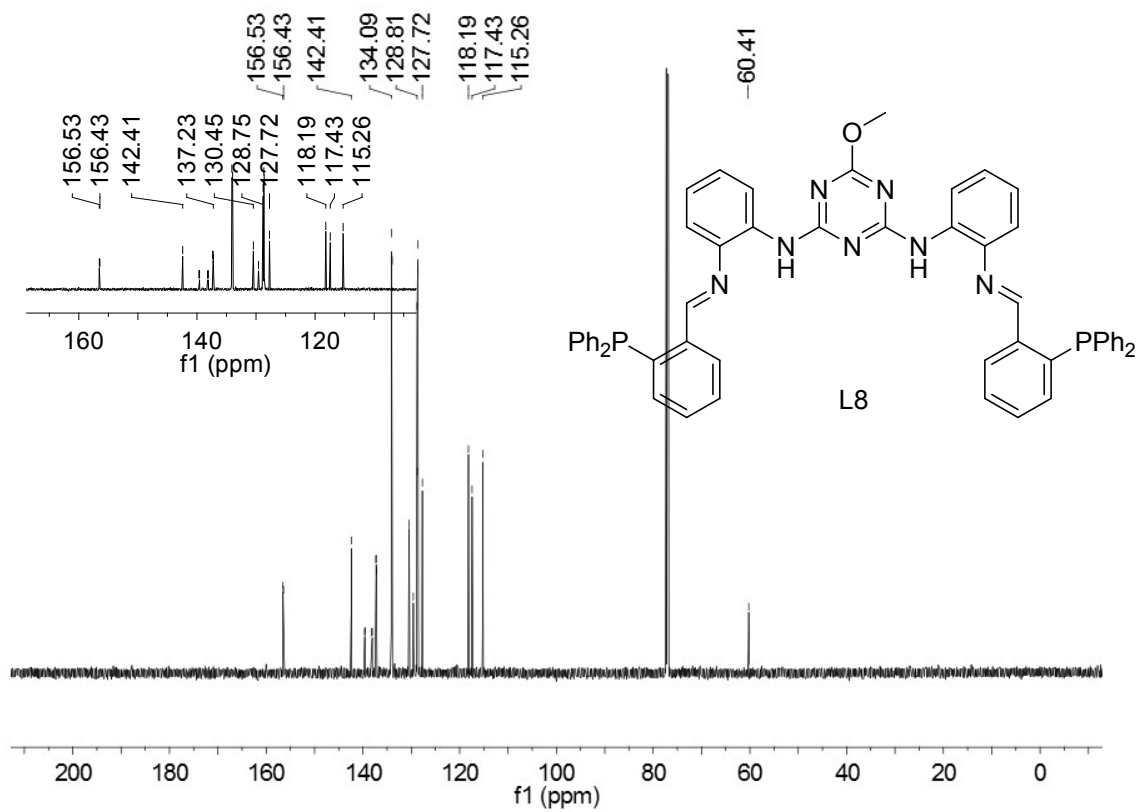












## S-11. References

- [1] D. E. Frantz, D. G. Weaver , J. P. Carey , M. H. Kress and U. H. Dolling. *Org Lett.*, 2002, **4**, 4717-4718.
- [2] P. S. Gao, N. Lin, J. L. Zhang, H. M. Sun, W. Q. Zhang, Z. W. Gao and L. W. Xu. *ChemCatChem*, 2016, **8**, 3466-3474.
- [3] X.-F. Wu, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 5284-5288.