

*Electronic Supplementary Information for*

# **Regioselective Aerobic Oxidative Heck Reactions with Electronically Unbiased Alkenes: Efficient Access to $\alpha$ -Alkyl Vinylarenes**

**Changwu Zheng and Shannon S. Stahl\***

*Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706,  
United States*

## **Table of Contents**

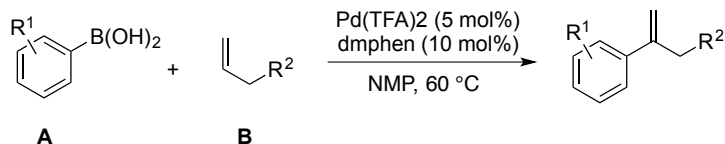
General Information.....	S2
Typical Procedure for Palladium-Catalyzed Oxidative Heck Reactions.....	S2
Procedure for 1 mmol-Scale Reactions.....	S2
Table S1. Comparison of Different Arylboronic Acid to Alkene Ratios.....	S3
Spectral Data for Products.....	S3
Spectra for the New Products.....	S10

**General Information.** All commercially available compounds were purchased and used as received. Solvents were dried over activated-alumina columns prior to use; however, purification and drying of commercial solvents is not required for the catalytic reactions described here.  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded on Bruker AC-300 or Varian MercuryPlus 300 instruments, and  $\text{CDCl}_3$ ,  $\text{Pd}(\text{TFA})_2$ , dmphen, 1-octene, and *N*-methylpyrrolidone were purchased from Sigma-Aldrich and used as received. Arylboronic acids were purchased from Sigma-Aldrich, Combi-Blocks or Frontier Scientific and used as received. The chemical shift values are given in parts per million relative to  $\text{CDCl}_3$  (7.26 ppm for  $^1\text{H}$ , and 77.23 ppm for  $^{13}\text{C}$ ). Gas chromatographic analysis of reactions was conducted with a Shimadzu GC-17A or GC-2010Plus gas chromatograph with either a DB-Wax or a RTX-5 column. Flash chromatography was performed using SiliaFlash® P60 (Silicycle, particle size 40-63  $\mu\text{m}$ , 230-400 mesh).

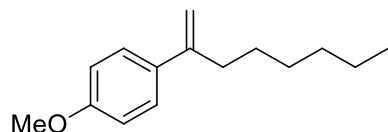
**Typical Procedure for Palladium-Catalyzed Oxidative Heck Reactions.** In a disposable culture tube,  $\text{Pd}(\text{TFA})_2$  (3.3 mg, 0.01 mmol) and dmphen (4.2 mg, 0.02 mmol) were dissolved in NMP (0.2 mL). The reaction tube was placed into an aluminum block mounted on a Large Capacity Mixer (Glas-Col) that enabled several reactions to be performed simultaneously under a constant pressure of (approx.) 1 atm with controlled temperature and orbital agitation. The headspace above the tubes was purged with oxygen gas for ca. 5 min. Then a solution of terminal alkene (0.2 mmol) and arylboronic acid (0.3 mmol) in NMP (0.3 mL) was added. The temperature was slowly raised to 60  $^\circ\text{C}$  and continued for 6 hours. After completion, EtOAc (5 mL) was added to the reaction mixture, followed by aq.  $\text{NH}_4\text{Cl}$  (5 mL). The solution was extracted 3 times with EtOAc (5 mL $\times$ 3), dried over  $\text{Na}_2\text{SO}_4$  and filtered. The solvent was removed at reduced pressure. The residue was loaded onto a silica gel column and purified by flash chromatography (hexanes/ether mixture).

#### **Procedure for 1 mmol-Scale Reactions.**

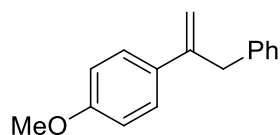
To a 25 mL three-neck round bottom flask with a stir bar was added  $\text{Pd}(\text{TFA})_2$  (16 mg, 0.05 mmol), dmphen (21 mg, 0.1 mmol) and NMP (1.5 mL). The flask was evacuated briefly under vacuum, filled with oxygen gas and sealed with a septum. A balloon was filled with  $\text{O}_2$  and connected to a 6-inch needle. The needle attached to the  $\text{O}_2$  balloon was inserted through the septum, and the solution was sparged with  $\text{O}_2$  gas for ca. 10 min. A solution of arylboronic acid (1.5 mmol) and alkene (1 mmol) in NMP (1 mL) was added. The reaction was heated for 6 h at 60  $^\circ\text{C}$  using an oil bath with vigorous stirring under an  $\text{O}_2$  atmosphere supplied by the balloon. Pure product was isolated by using the same procedure described above.

**Table S1.** Comparison of Different Arylboronic Acid to Alkene Ratios.

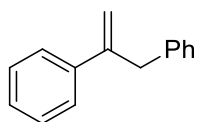
A	B	Yield (A/B = 1.5)	Yield (A/B = 1)	Yield (A/B = 0.5)
		83	57	72
		79	43	63
		85	51	68
		66	38	60

**Spectral data for products****1-Methoxy-4-(oct-1-en-2-yl)benzene<sup>1</sup> 3a**

Yield: 70%, >20:1 regioselectivity. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.18 (d, *J* = 1.2 Hz, 1H), 4.96 (d, *J* = 1.2 Hz, 1H), 3.80 (s, 3H), 2.46 (t, *J* = 7.2 Hz, 2H), 1.27-1.49 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 159.2, 148.3, 134.1, 127.4, 113.8, 110.7, 55.5, 35.7, 31.9, 29.3, 28.5, 22.9, 14.3.

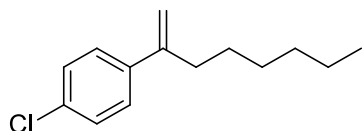
**1-Methoxy-4-(3-phenylprop-1-en-2-yl)benzene<sup>2</sup> 3b**

Yield: 81%, 10:1 regioselectivity. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 9.0 Hz, 2H), 7.23-7.26 (m, 5H), 6.81 (d, *J* = 9.0 Hz, 2H), 5.43 (d, *J* = 1.2 Hz, 1H), 4.94 (d, *J* = 1.2 Hz, 1H), 3.81 (s, 2H), 3.77 (s, 3H).



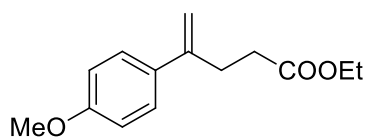
### Prop-2-ene-1,2-diyl dibenzene<sup>3</sup> 3c

Yield: 76%, 10:1 regioselectivity. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.22-7.47 (m, 10H), 5.52 (s, 1H), 5.04 (s, 1H), 3.86 (s, 2H).



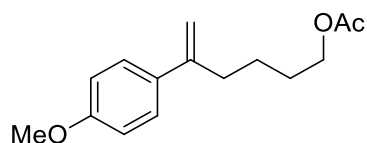
### 1-Chloro-4-(oct-1-en-2-yl)benzene<sup>4</sup> 3d

Yield: 71%, 10:1 regioselectivity. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.25-7.34 (m, 4H), 5.23 (d, *J* = 1.2 Hz, 1H), 5.06 (d, *J* = 1.2 Hz, 1H), 2.46 (t, *J* = 7.5 Hz, 2H), 1.27-1.44 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H).



### Ethyl 4-(4-methoxyphenyl)pent-4-enoate 3e

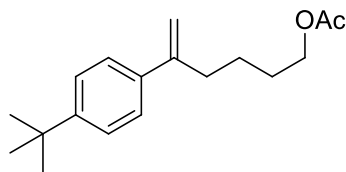
Yield: 84%, 8:1 regioselectivity. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 5.23 (d, *J* = 1.5 Hz, 1H), 5.00 (d, *J* = 1.2 Hz, 1H), 4.12 (q, *J* = 6.9 Hz, 2H), 3.81 (s, 3H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.46 (t, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 173.4, 159.4, 146.4, 133.2, 127.4, 113.9, 111.5, 60.6, 55.5, 33.6, 30.7, 14.4; HRMS (EI) Calcd. for C<sub>14</sub>H<sub>19</sub>O<sub>3</sub> ([M+H]<sup>+</sup>): 235.1329, found: 235.1332.



### 5-(4-Methoxyphenyl)hex-5-en-1-yl acetate 3f

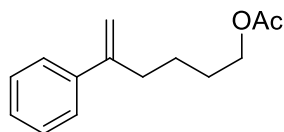
Yield: 80%, 8:1 regioselectivity. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 5.21 (d, *J* = 1.5 Hz, 1H), 4.98 (d, *J* = 1.2 Hz, 1H), 4.05 (t, *J* = 6.3 Hz, 2H), 3.81 (s, 3H), 2.51 (t, *J* = 6.3 Hz, 2H), 2.02 (s, 3H), 1.63-1.68 (m, 2H), 1.48-1.56 (m, 2H); <sup>13</sup>C NMR (75 MHz,

CDCl<sub>3</sub>)  $\delta$  171.4, 159.3, 147.5, 133.7, 127.4, 113.9, 111.3, 64.5, 55.5, 35.1, 28.4, 24.7, 21.2; **HRMS (EI)** Calcd. for C<sub>15</sub>H<sub>21</sub>O<sub>3</sub> ([M+H]<sup>+</sup>): 249.1486, found: 249.1485.



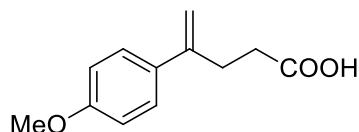
### 5-(4-(*tert*-Butyl)phenyl)hex-5-en-1-yl acetate **3g**

Yield: 83%, 10:1 regioselectivity. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (s, 4H), 5.28 (s, 1H), 5.02 (s, 1H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.02 (s, 3H), 1.62-1.71 (m, 2H), 1.48-1.55 (m, 2H), 1.32 (s, 9H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>)  $\delta$  171.4, 150.6, 147.9, 138.2, 125.9, 124.4, 112.1, 64.6, 35.0, 34.7, 31.5, 28.4, 24.7, 21.2; **HRMS (EI)** Calcd. for C<sub>18</sub>H<sub>27</sub>O<sub>2</sub> ([M+H]<sup>+</sup>): 275.2006, found: 275.2008.



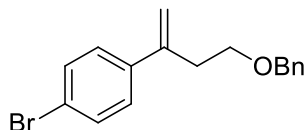
### 5-Phenylhex-5-en-1-yl acetate **3h**

Yield: 79%, 8:1 regioselectivity. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.26-7.40 (m, 5H), 5.28 (s, 1H), 5.07 (s, 1H), 4.05 (t, *J* = 6.6 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.04 (s, 3H), 1.61-1.71 (m, 2H), 1.46-1.56 (m, 2H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>)  $\delta$  171.4, 148.3, 141.3, 128.5, 127.6, 126.3, 112.8, 64.5, 35.1, 28.4, 24.7, 21.2; **HRMS (EI)** Calcd. for C<sub>14</sub>H<sub>22</sub>NO<sub>2</sub> ([M+NH<sub>4</sub>]<sup>+</sup>): 236.1646, found: 236.1640.



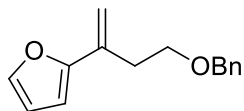
### 4-(4-Methoxyphenyl)pent-4-enoic acid<sup>5</sup> **3i**

Yield: 76%, 12:1 regioselectivity. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>OD = 3:1)  $\delta$  7.35 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 5.21 (s, 1H), 4.99 (s, 1H), 3.78 (s, 3H), 2.77 (t, *J* = 7.8 Hz, 2H), 2.41 (t, *J* = 8.1 Hz, 2H).



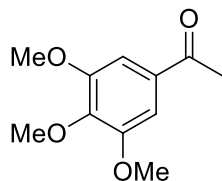
### 1-(4-(Benzyloxy)but-1-en-2-yl)-4-bromobenzene **3j**

Yield: 68%, 4:1 regioselectivity. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (dd, *J* = 6.6, 1.8 Hz, 2H), 7.25-7.32 (m, 7H), 5.34 (s, 1H), 5.15 (s, 1H), 4.48 (s, 2H), 3.57 (t, *J* = 6.9 Hz, 2H), 2.80 (t, *J* = 6.6 Hz, 2H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>)  $\delta$  144.5, 140.1, 138.5, 131.6, 128.6, 128.0, 127.81, 127.80, 121.6, 114.7, 73.2, 69.1, 35.8; **HRMS (EI)** Calcd. for C<sub>17</sub>H<sub>17</sub>BrO ([M]<sup>+</sup>): 316.0458, found: 316.0446.



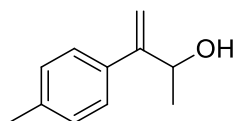
### 2-(4-(Benzyloxy)but-1-en-2-yl)furan 3k

Yield: 66%, 7:1 regioselectivity.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25-7.35 (m, 6H), 6.36-6.37 (m, 1H), 6.31 (d,  $J = 3.3$  Hz, 1H), 5.58 (s, 1H), 5.03 (s, 1H), 4.53 (s, 2H), 3.68 (t,  $J = 6.9$  Hz, 2H), 2.70 (t,  $J = 7.2$  Hz, 2H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  154.6, 142.1, 138.6, 134.4, 128.6, 127.9, 127.8, 111.3, 110.9, 106.4, 73.2, 69.6, 33.8; **HRMS (EI)** Calcd. for  $\text{C}_{15}\text{H}_{17}\text{O}_2$  ( $[\text{M}+\text{H}]^+$ ): 229.1224, found: 229.1226.



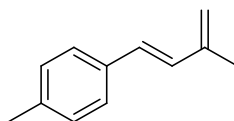
### 1-(3,4,5-Trimethoxyphenyl)ethanone<sup>6</sup> 3l

Yield: 67%.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (s, 2H), 3.93 (s, 9H), 2.60 (s, 3H).



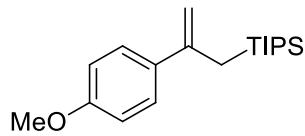
### 3-(*p*-Tolyl)but-3-en-2-ol<sup>7</sup> 3m

Yield: 41%, 20:1 regioselectivity.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (d,  $J = 8.1$  Hz, 2H), 7.15 (d,  $J = 8.4$  Hz, 2H), 5.32 (s, 1H), 5.26 (s, 1H), 4.78-4.85 (m, 1H), 2.35 (s, 3H), 1.67 (d,  $J = 4.2$  Hz, 1H), 1.33 (d,  $J = 6.3$  Hz, 3H).



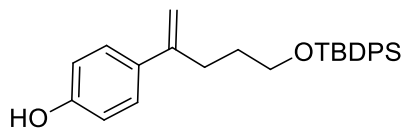
### (*E*)-1-Methyl-4-(3-methylbuta-1,3-dien-1-yl)benzene<sup>8</sup> 3n

Yield: 43%, <1:20 regioselectivity.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 8.4$  Hz, 2H), 7.12 (d,  $J = 8.1$  Hz, 2H), 6.83 (d,  $J = 16.2$  Hz, 1H), 6.50 (d,  $J = 16.2$  Hz, 1H), 5.09 (s, 1H), 5.04 (s, 1H), 2.33 (s, 3H), 1.97 (s, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  142.4, 137.5, 134.8, 131.0, 129.5, 128.8, 126.6, 117.0, 21.4, 18.8; **HRMS (EI)** Calcd. for  $\text{C}_{12}\text{H}_{14}$  ( $[\text{M}]^+$ ): 158.1091, found: 158.1087.



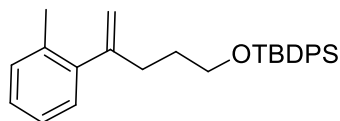
### Triisopropyl(2-(4-methoxyphenyl)allyl)silane 3o

Yield: 72%, 20:1 regioselectivity.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 8.4$  Hz, 2H), 6.84 (d,  $J = 9.0$  Hz, 2H), 5.01 (s, 1H), 4.92 (s, 1H), 3.81 (s, 3H), 2.07 (s, 2H), 1.05-1.08 (m, 3H), 0.97 (s, 18H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  External: 159.1, 147.0, 136.3, 127.8, 113.6, 110.5, 55.46, 18.9, 18.5, 11.5; Internal: 159.2, 152.3, 137.7, 126.9, 120.9, 113.5, 55.55, 22.6, 19.3, 12.6; **HRMS (EI)** Calcd. for  $\text{C}_{19}\text{H}_{33}\text{OSi}$  ( $[\text{M}+\text{H}]^+$ ): 305.2296, found: 305.2298.



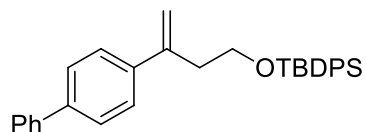
### 4-(5-((*tert*-Butyldiphenylsilyl)oxy)pent-1-en-2-yl)phenol 3p

Yield: 49%, 10:1 regioselectivity.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64-7.67 (m, 4H), 7.26-7.42 (m, 8H), 6.77 (d,  $J = 9.0$  Hz, 2H), 5.19 (s, 1H), 4.96 (s, 1H), 4.73 (s, 1H), 3.68 (t,  $J = 6.3$  Hz, 2H), 2.57 (t,  $J = 7.2$  Hz, 2H), 1.66-1.75 (m, 2H), 1.05 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.1, 147.5, 135.8, 134.2, 134.0, 129.7, 127.8, 127.6, 115.3, 111.0, 63.6, 31.8, 31.6, 27.1, 19.5; **HRMS (EI)** Calcd. for  $\text{C}_{27}\text{H}_{31}\text{O}_2\text{Si}$  ( $[\text{M}-\text{H}]^+$ ): 415.2098, found: 415.2108.



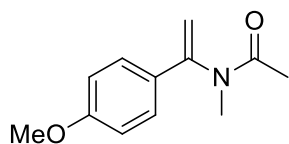
### *tert*-Butyldiphenyl((4-(*o*-tolyl)pent-4-en-1-yl)oxy)silane 3q

Yield: 85%, 7:1 regioselectivity.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.65 (m, 4H), 7.36-7.44 (m, 6H), 7.02-7.15 (m, 4H), 5.16 (d,  $J = 1.2$  Hz, 1H), 4.85 (d,  $J = 1.5$  Hz, 1H), 3.66 (t,  $J = 6.0$  Hz, 2H), 2.44 (t,  $J = 7.8$  Hz, 2H), 2.27 (s, 3H), 1.60-1.69 (m, 2H), 1.03 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  150.0, 143.3, 135.8, 135.0, 134.3, 130.3, 129.7, 128.6, 127.8, 126.9, 125.6, 114.0, 63.7, 34.2, 31.0, 27.1, 20.1, 19.4; **HRMS (EI)** Calcd. for  $\text{C}_{28}\text{H}_{38}\text{NOSi}$  ( $[\text{M}+\text{NH}_4]^+$ ): 432.2718, found: 432.2710.



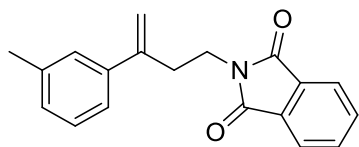
### ((3-([1,1'-Biphenyl]-4-yl)but-3-en-1-yl)oxy)(*tert*-butyl)diphenylsilane 3r

Yield: 82%, 4:1 regioselectivity.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24-7.67 (m, 19H), 5.40 (s, 1H), 5.10 (s, 1H), 3.80 (t,  $J = 6.9$  Hz, 2H), 2.80 (t,  $J = 6.9$  Hz, 2H), 1.03 (s, 9H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  144.8, 141.0, 140.3, 139.9, 135.8, 134.1, 129.8, 129.0, 127.8, 127.5, 127.21, 127.18, 126.6, 114.3, 63.3, 38.7, 27.0, 19.4; **HRMS (EI)** Calcd. for  $\text{C}_{32}\text{H}_{38}\text{NOSi}$  ( $[\text{M}+\text{NH}_4]^+$ ): 480.2718, found: 480.2739.



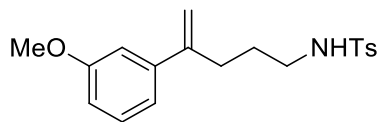
### ***N*-(1-(4-Methoxyphenyl)vinyl)-*N*-methylacetamide<sup>9</sup> 3s**

Yield: 83%, 20:1 regioselectivity. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 5.57 (s, 1H), 5.11 (s, 1H), 3.83 (s, 3H), 3.09 (s, 3H), 2.03 (s, 3H).



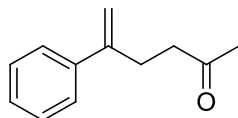
### **2-(3-(*m*-Tolyl)but-3-en-1-yl)isoindoline-1,3-dione 3t**

Yield: 72%, 4:1 regioselectivity. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.78-7.81 (m, 2H), 7.67-7.69 (m, 2H), 7.17-7.26 (m, 3H), 7.00 (d, *J* = 7.5 Hz, 1H), 5.33 (d, *J* = 0.9 Hz, 1H), 5.12 (d, *J* = 0.9 Hz, 1H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.32 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 168.4, 145.4, 140.4, 138.1, 134.0, 132.3, 128.5, 127.0, 123.5, 123.3, 114.6, 37.7, 34.2, 21.7; HRMS (EI) Calcd. for C<sub>19</sub>H<sub>17</sub>NO<sub>2</sub> ([M]<sup>+</sup>): 291.1254, found: 291.1249.



### ***N*-(4-(3-Methoxyphenyl)pent-4-en-1-yl)-4-methylbenzenesulfonamide 3u**

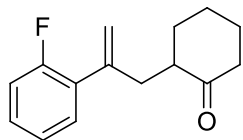
Yield: 61%, >20:1 regioselectivity. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.19-7.29 (m, 3H), 6.80-6.91 (m, 3H), 5.24 (d, *J* = 0.6 Hz, 1H), 5.00 (d, *J* = 1.2 Hz, 1H), 4.43 (br, 1H), 3.81 (s, 3H), 2.91-2.98 (m, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.54-1.64 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 159.8, 147.3, 143.6, 142.4, 137.2, 129.9, 129.6, 127.3, 118.8, 113.6, 113.0, 112.3, 55.4, 42.9, 32.6, 28.2, 21.7; HRMS (EI) Calcd. for C<sub>19</sub>H<sub>27</sub>N<sub>2</sub>O<sub>3</sub>S ([M+NH<sub>4</sub>]<sup>+</sup>): 363.1737, found: 363.1746.



### **5-Phenylhex-5-en-2-one 3v**

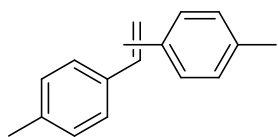
Yield: 73%, 10:1 regioselectivity. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.26-7.41 (m, 5H), 5.28 (s, 1H), 5.07 (s, 1H), 2.79 (t, *J* = 7.2 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.12 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 208.3, 147.4, 140.8, 128.6, 127.8, 126.3, 113.0, 42.6, 30.2, 29.5; HRMS (EI) Calcd. for C<sub>12</sub>H<sub>18</sub>NO ([M+NH<sub>4</sub>]<sup>+</sup>): 192.1383, found: 192.1379.





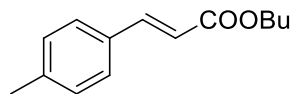
### 2-(2-(2-Fluorophenyl)allyl)cyclohexanone **3w**

Yield: 69%, 4:1 regioselectivity.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20-7.28 (m, 2H), 7.00-7.12 (m, 2H), 5.22 (d,  $J = 8.7$  Hz, 2H), 3.13-3.23 (m, 1H), 1.97-2.42 (m, 6H), 1.78-1.85 (m, 1H), 1.37-1.72 (m, 2H), 1.26-1.36 (m, 1H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  212.7, 161.7, 158.4, 142.5, 130.2, 130.1, 129.5, 129.3, 129.1, 129.0, 124.3, 124.2, 118.1, 118.0, 116.2, 115.9, 48.8, 42.3, 36.7, 36.6, 33.5, 28.2, 25.1; **HRMS (EI)** Calcd. for  $\text{C}_{15}\text{H}_{17}\text{FO}_2$  ( $[\text{M}]^+$ ): 232.1258, found: 232.1254.



### *di-p*-Tolylene ( $\alpha:\beta = 1:1$ )<sup>11,10</sup> **3x**

Yield: 93%, 1:1 regioselectivity.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$   $\alpha$ -product: 7.24 (d,  $J = 8.1$  Hz, 4H), 7.14 (d,  $J = 7.5$  Hz, 4H), 5.38 (s, 2H), 2.37 (s, 6H);  $\beta$ -product: 7.40 (d,  $J = 8.1$  Hz, 4H), 7.16 (d,  $J = 7.8$  Hz, 4H), 7.04 (s, 2H), 2.36 (s, 6H).



### (*E*)-Butyl 3-(*p*-tolyl)acrylate<sup>11</sup> **3y**

Yield: 95%, <1:20 regioselectivity.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J = 16.2$  Hz, 1H), 7.43 (d,  $J = 7.5$  Hz, 2H), 7.19 (d,  $J = 7.8$  Hz, 2H), 6.40 (d,  $J = 16.2$  Hz, 1H), 4.20 (t,  $J = 6.6$  Hz, 2H), 2.37 (s, 3H), 1.64-1.71 (m, 2H), 1.40-1.48 (m, 2H), 0.97 (t,  $J = 7.2$  Hz, 3H).

<sup>1</sup> Alacid, E.; Najera, C. *J. Org. Chem.* **2008**, *73*, 2315.

<sup>2</sup> Sabarre, A.; Love, J. *Org. Lett.* **2008**, *10*, 3941.

<sup>3</sup> Alacid, E.; Najera, C. *Org. Lett.* **2008**, *10*, 5011.

<sup>4</sup> Shirakawa, E.; Imazaki, Y.; Hayashi, T. *Chem. Lett.* **2008**, *37*, 654.

<sup>5</sup> Whitehead, D. C.; Yousefi, R.; Jaganathan, A.; Borhan, B. *J. Am. Chem. Soc.* **2010**, *132*, 3298.

<sup>6</sup> Paredes, M. D.; Alonso, R. *J. Org. Chem.* **2000**, *65*, 2292.

<sup>7</sup> Katritzky, A. R.; Toader, D.; Chassaing, C.; Aslan, D. C. *J. Org. Chem.* **1999**, *64*, 6080.

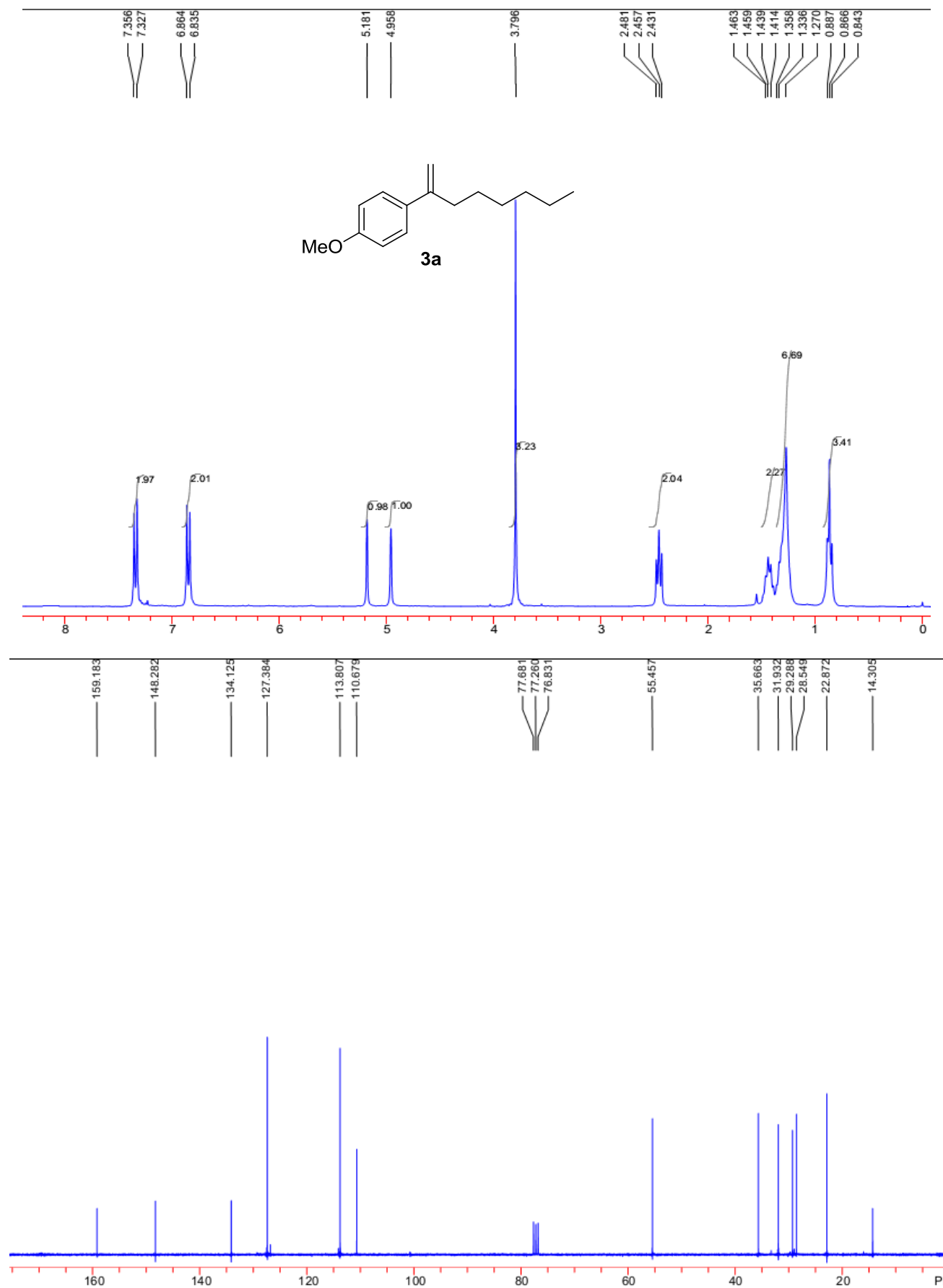
<sup>8</sup> Dubbaka, S. R.; Vogel, P. *Tetrahedron* **2005**, *61*, 1523.

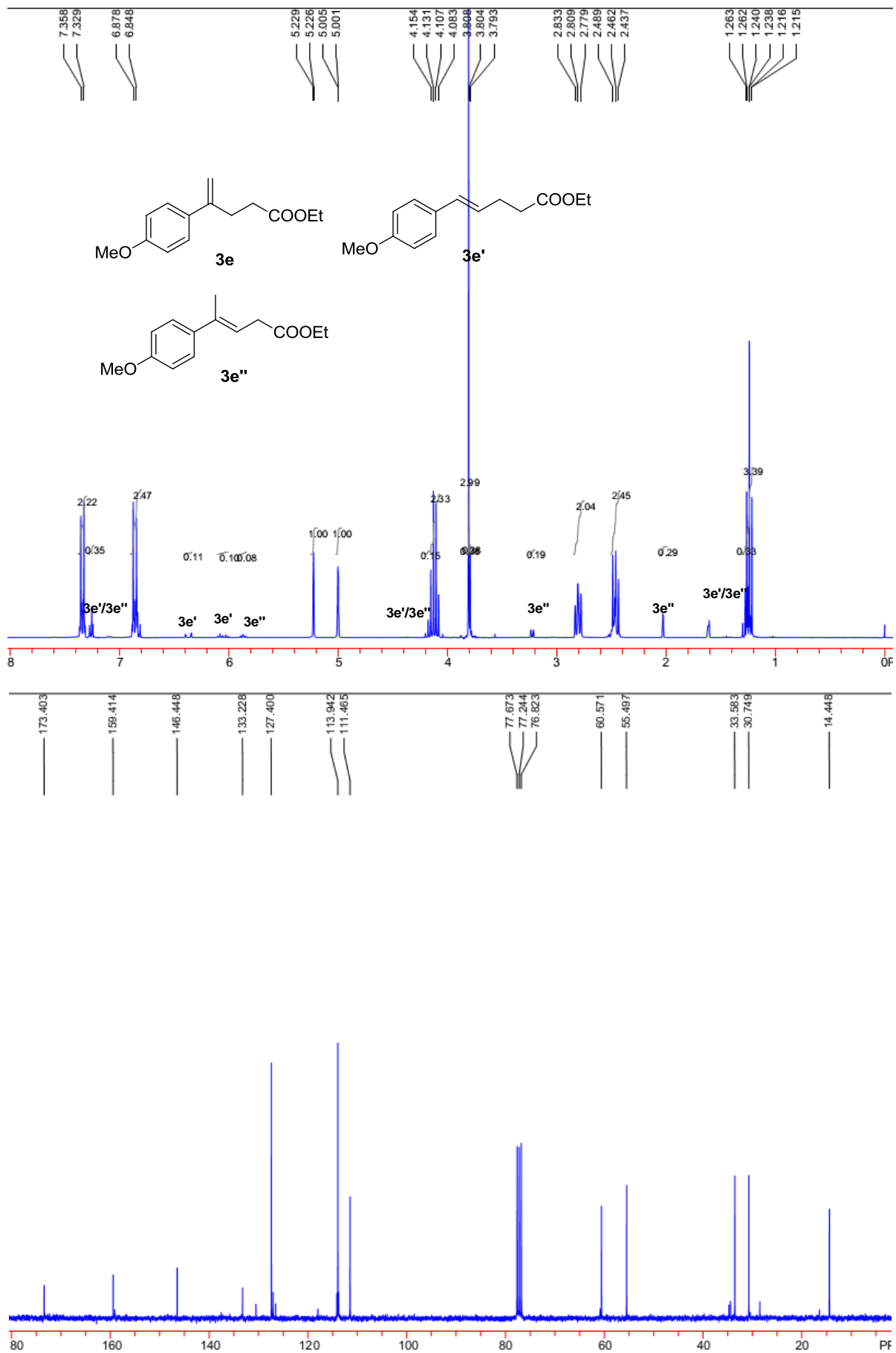
<sup>9</sup> Ruan, J.; Iggo, J. A.; Berry, N. G.; Xiao, J. *J. Am. Chem. Soc.* **2010**, *132*, 16689.

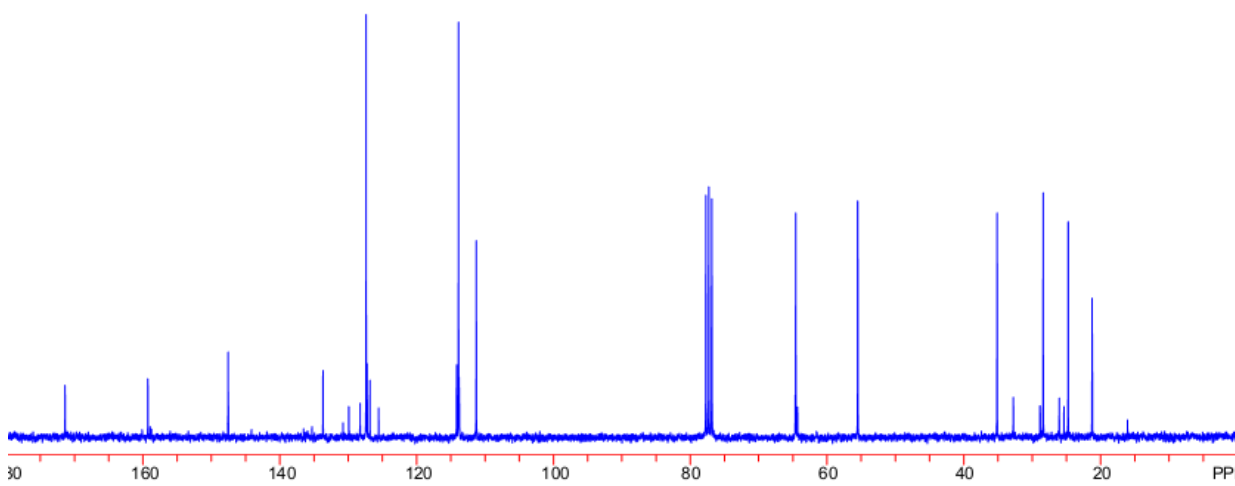
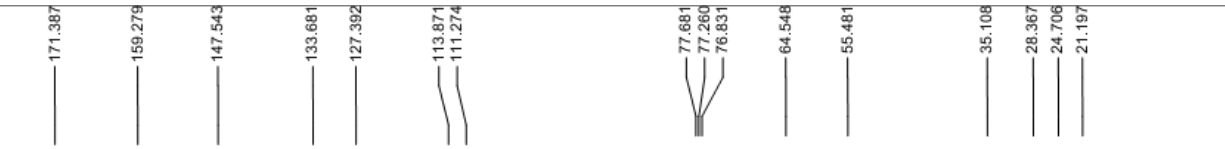
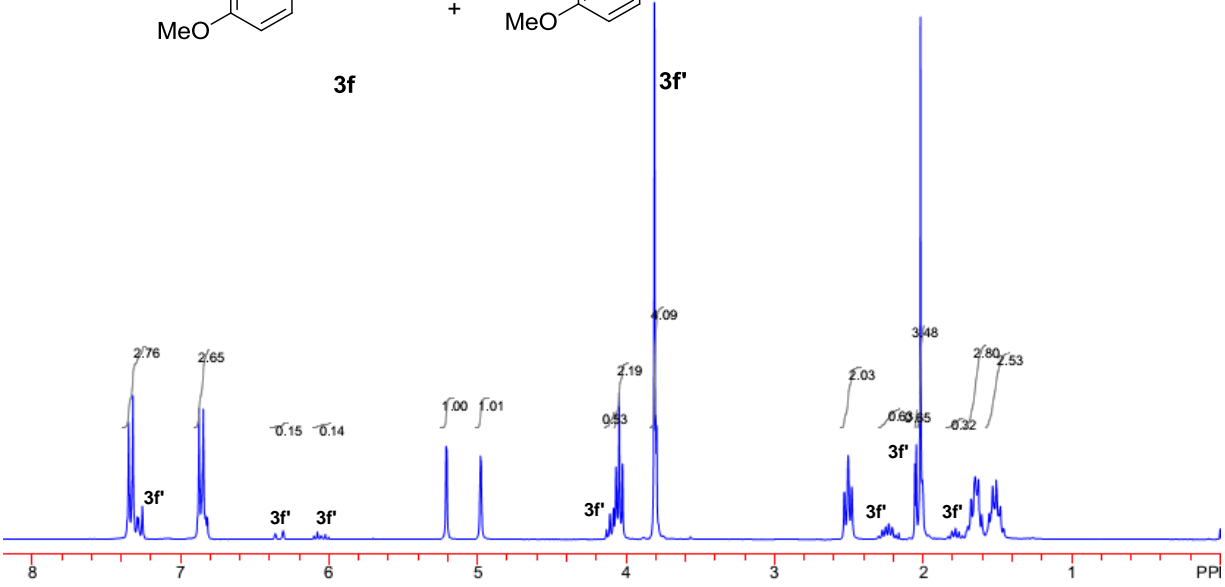
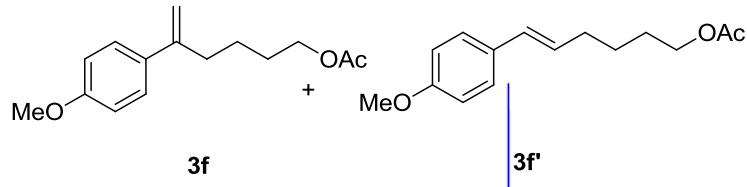
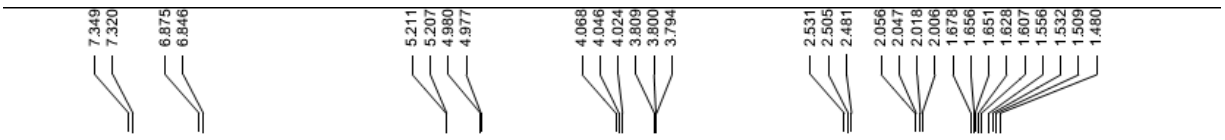
<sup>10</sup> Zhao, X.; Jing, J.; Lu, K.; Zhang, Y.; Wang, J. *Chem. Commun.* **2010**, 1724.

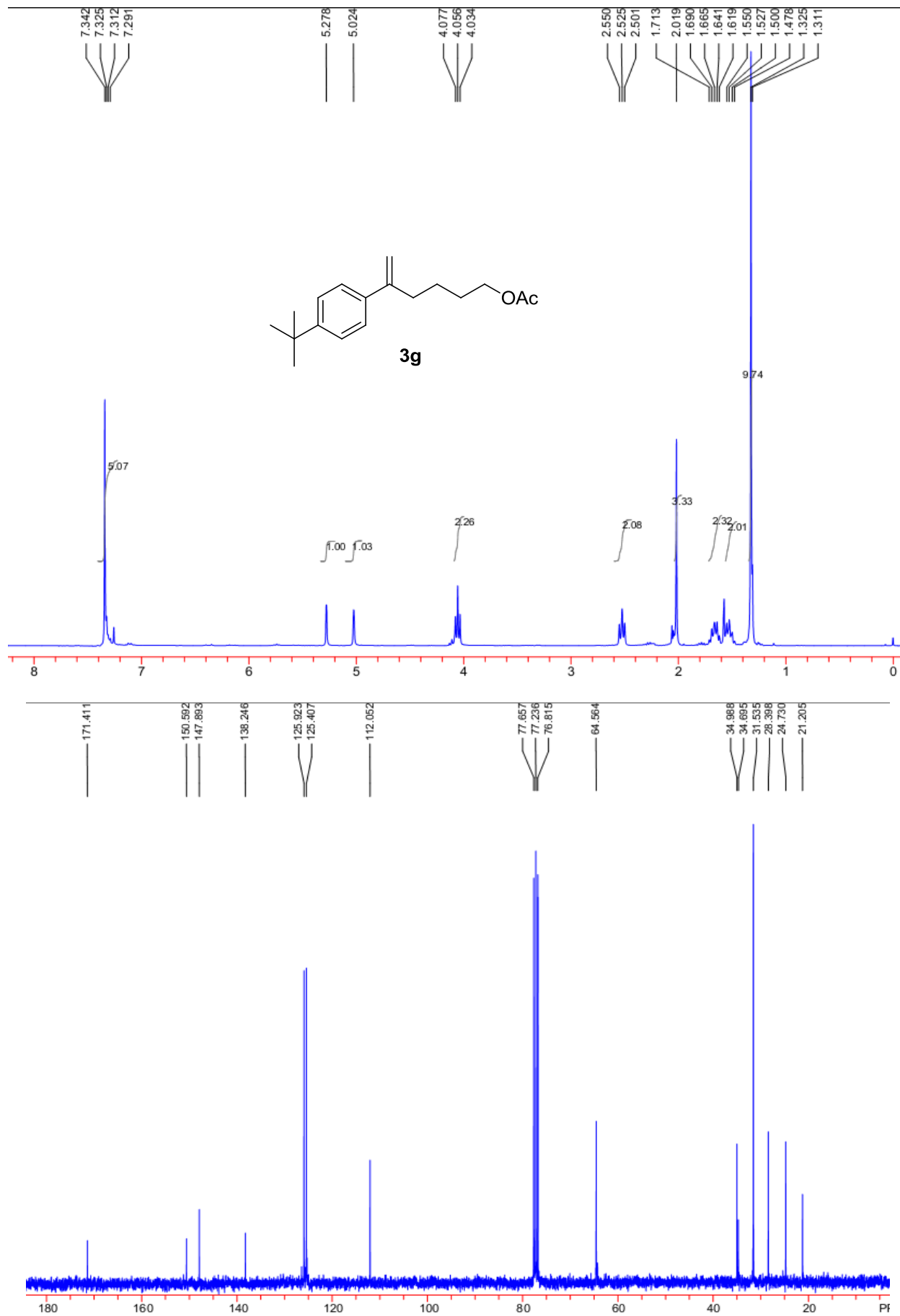
<sup>11</sup> Yang, F.-L.; Ma, X.-T.; Tian, S.-K. *Chem. Eur. J.* **2012**, *18*, 1582.

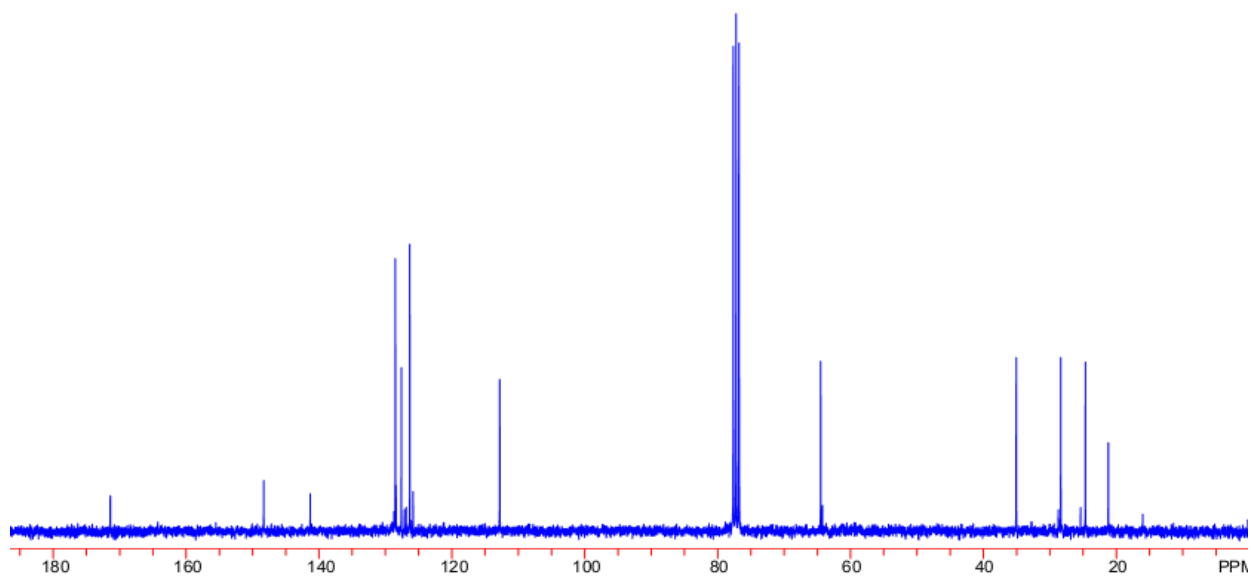
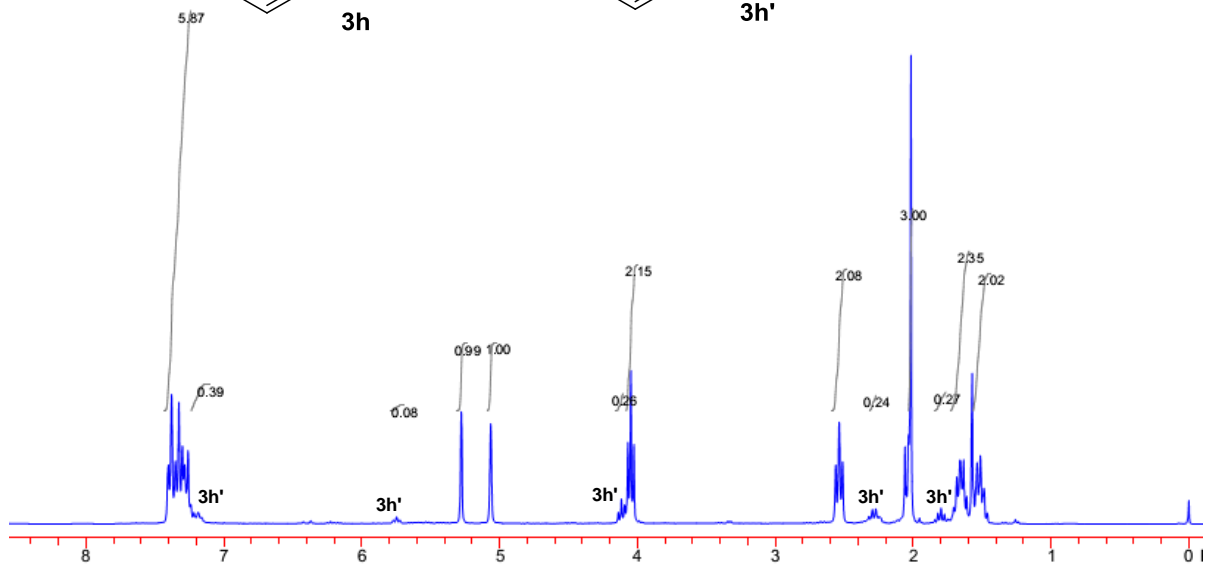
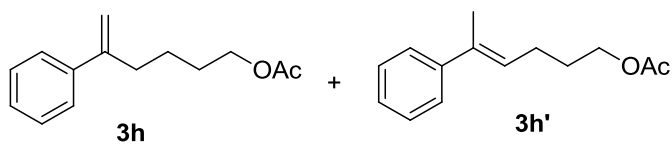
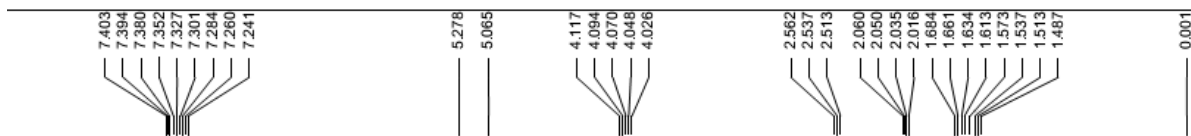
# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra

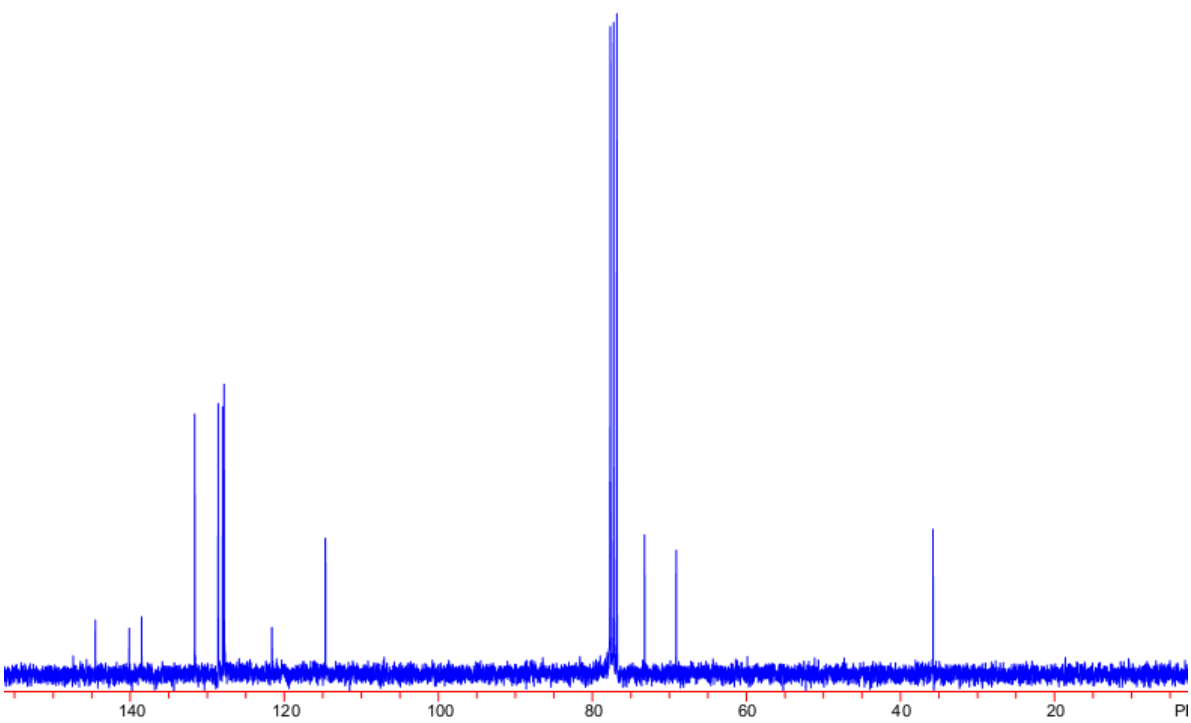
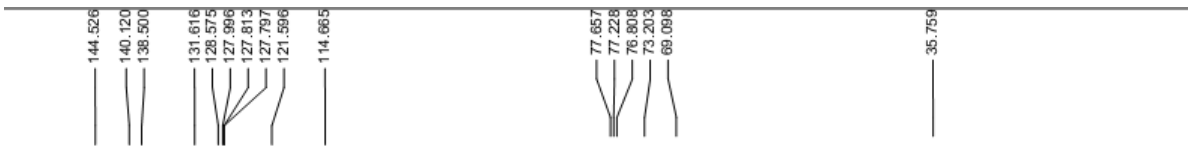
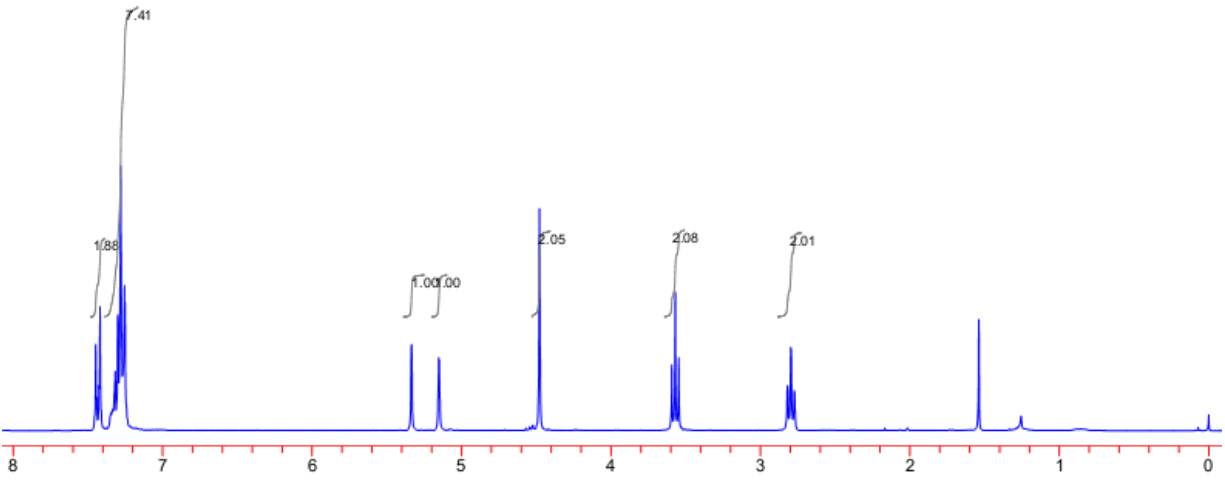
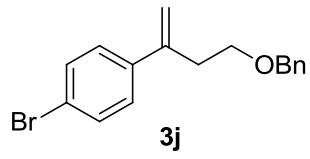
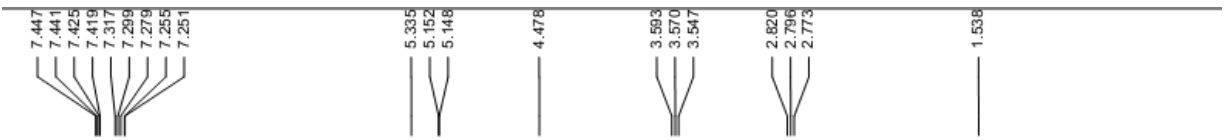


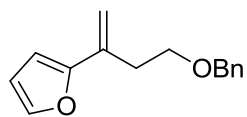
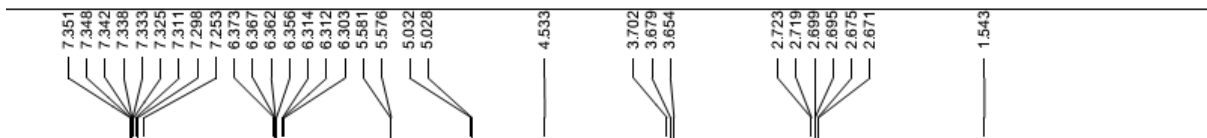












3k

