# Catalytic Platinum-Initiated Cation-Olefin Reactions with Alkene Terminating Groups

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## **Table of Contents**

1)	Substrate Synthesis	S2
2)	Cyclization Optimization	S9
3)	Cyclization Experimental	S11
4)	NMR Spectra	S17

## 1. Substrate Synthesis

All reagents were reagent grade quality and used as received from Aldrich unless otherwise indicated. The piperidinomethyl polystyrene resin was purchased from NovaBiochem and used without further purification. All reactions were conducted under inert conditions (Ar or N<sub>2</sub>) or in a nitrogen filled glove box unless otherwise indicated. All glassware was oven dried unless otherwise indicated. Anhydrous CH<sub>2</sub>Cl<sub>2</sub>, ether, and toluene were passed through a column of alumina. Anhydrous diisopropylamine ( $iPr_2NH$ ) and triethylamine (Et<sub>3</sub>N) were distilled from CaH<sub>2</sub> prior to use. Anhydrous nitroethane (EtNO<sub>2</sub>) was distilled from P<sub>2</sub>O<sub>5</sub> and degassed by freeze-pump-thaw prior to use. Column chromatography was performed using SilaFlash P60 40-63 µm (230-400 mesh). All NMR spectra were recorded on Bruker Avance 400 or 600 MHz spectrometer at STP. All deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>31</sup>P NMR chemical shifts are reported in  $\delta$  units, parts per million (ppm) relative to the chemical shift of residual solvent or an external standard. <sup>31</sup>P reference peak was set at 0 ppm for phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85%) as an external standard. High resolution mass spectra (HRMS) were obtained using a Micromass Q-ToF Ultima. Compounds 1, 3, 7, 9, 11, 18 and 19 have previously been reported and characterized.<sup>1,2</sup>

<sup>&</sup>lt;sup>1</sup> **1**, **3**, **7**, **9**, and **11** in Sokol, J. G.; Korapala, C. S.; White, P. S.; Becker, J. J.; Gagné, M. R. *Angew. Chem. Int. Ed.* **2011**, *50*, 5658-5661.

<sup>&</sup>lt;sup>2</sup> **18** and **19** in Koh, J. H.; Gagné, M. R. *Angew. Chem. Int. Ed.* **2004**, *43*, 3459-3461.



(*E*)-5-methyl-1-phenylnona-4,8-dien-1-one: A solution of *n*-butyllithium (6.6 mL, 1.6 M in hexanes) was added to a solution of diisopropylamine (1.55 mL, 11.0 mmol) in 20 mL THF at -78 °C. The reaction was stirred for one hour. The acetophenone (1.2 mL, 10.3 mmol) was then added and the solution was stirred for an additional hour. The (*E*)-7-bromo-5-methylhepta-1,5-diene<sup>1</sup> (2.3 g, 12.2 mmol) was then added and the temperature of the reaction mixture was brought to room temperature. The reaction was left to stir overnight. The reaction was quenched using 0.5 M HCl (5 mL) and the product was extracted using ether (5 mL) three times. The organics were then washed with brine (50 mL), dried with MgSO<sub>4</sub>, and the volatiles were removed under vacuum resulting in a yellow oil (1.87 g, 8.2 mmol, 75%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  7.97 (d, *J* = 7.6 Hz, 2 H), 7.57 (t, *J* = 7.1 Hz, 1 H), 7.45 (t, *J* = 7.3 Hz, 2 H), 5.84-5.73 (m, 1 H), 5.21 (t, *J* = 8.0 Hz, 1 H), 5.00 (d, *J* = 17.4 Hz, 1 H), 4.93 (d, *J* = 9.5 Hz, 1 H), 3.01 (t, *J* = 7.4 Hz, 2 H), 2.45 (dt, *J* = 7.6 Hz, 7.4 Hz, 2 H), 2.19-2.13 (m, 2 H), 2.09-2.03 (m, 2 H), 1.64 (s, 3 H).



(*E*)-(6-methyldeca-1,5,9-trien-2-yl)benzene, 5: (Trimethylsilyl)methylmagnesium chloride (20 mL, 1.0 M in diethyl ether) was added to a solution of (*E*)-5-methyl-1-phenylnona-4,8-dien-1-

one (2 g, 8.7 mmol) in 100 mL diethyl ether. The reaction mixture was heated to reflux for 24 hours. The mixture was cooled to 0 °C and thionyl chloride (3 mL, 40 mmol) was added. The reaction was stirred for one hour at 0 °C. The reaction was quenched using saturated NH<sub>4</sub>Cl<sub>(aq)</sub> (50 mL). The reaction mixture was vacuum filtered through a fritted funnel, and the aqueous layer was removed and extracted with ether (25 mL) three times. The combined organics were then dried with MgSO<sub>4</sub> and the volatiles were removed under vacuum. Silica gel flash column chromatography was performed using hexanes as the eluent (Rf = 0.6) resulting in a colorless oil (0.9 g, 3.9 mmol, 45 %). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  7.41 (dt, *J* = 7.8 Hz, 1.5 Hz, 2 H), 7.32 (tt, *J* = 7.6 Hz, 1.5 Hz, 2 H), 7.27 (dt, *J* = 7.3 Hz, 1.4 Hz, 1 H), 5.86-5.75 (m, 1 H), 5.27 (d, *J* = 1.5 Hz, 1 H), 5.17 (t, *J* = 6.4 Hz, 1 H), 5.06 (d, *J* = 1.4 Hz, 1 H), 5.01 (dd, *J* = 17.1 Hz, 1.8 Hz, 1 H), 4.93 (dd, *J* = 10.2 Hz, 2.0 Hz 1 H), 2.53 (t, *J* = 7.2 Hz, 2 H), 2.13 (q, *J* = 4.0 Hz, 2 H), 2.12 (q, *J* = 3.8 Hz, 2 H), 2.05 (q, *J* = 7.8 Hz, 2 H), 1.53 (s, 3 H). <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)  $\delta_{\rm C}$  148.3, 141.4, 138.8, 135.0, 128.1 (2C), 127.3, 126.2 (2C), 124.1, 114.4, 112.4, 39.1, 35.5, 32.4, 26.9, 16.1. HRMS calculated for C<sub>17</sub>H<sub>22</sub> [M] = 226.17215 calculated, found 226.17168.



(*E*)-1-(4-methoxyphenyl)-5-methylnona-4,8-dien-1-one: A solution of *n*-butyllithium (20 mL, 1.6 M in hexanes) was added to a solution of diisopropylamine (5.2 mL, 34 mmol) in 30 mL THF at -78 °C. The reaction was stirred for one hour. The acetanisole (4.3 mL, 31 mmol) was then added and the solution was stirred for an additional hour. The (*E*)-7-bromo-5-methylhepta-

1,5-diene<sup>1</sup> (7.0 g, 37 mmol) was then added and the temperature of the reaction mixture was brought to room temperature. The reaction was left to stir overnight. The reaction was quenched using 0.5 M HCl (5 mL) and the product was extracted using ether (5 mL) three times. The organics were then washed with brine (50 mL), dried with MgSO<sub>4</sub>, and the volatiles were removed under vacuum resulting in a yellow oil (4.1 g, 16 mmol, 52%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  7.95 (d, *J* = 8.7 Hz, 2 H), 6.94 (d, *J* = 8.7 Hz, 2 H), 5.84-5.74 (m, 1 H), 5.21 (t, *J* = 7.1 Hz, 1 H), 5.00 (dd, *J* = 17.0 Hz, 1.2 Hz, 1 H), 4.93 (dd, *J* = 10.1 Hz, 1.0 Hz, 1 H), 3.88 (s, 3 H), 2.95 (t, *J* = 7.6 Hz, 2 H), 2.45 (dt, *J* = 7.4 Hz, 7.3 Hz, 2 H), 2.14 (t, *J* = 7.3 Hz, 2 H), 2.07 (dt, *J* = 7.8 Hz, 3.4 Hz, 2 H), 1.64 (s, 3 H).



#### (*E*)-1-methoxy-4-(6-methyldeca-1,5,9-trien-2-yl)benzene, 16:

(Trimethylsilyl)methylmagnesium chloride (3.4 mL, 1.0 M in diethyl ether) was added to a solution of (*E*)-1-(4-methoxyphenyl)-5-methylnona-4,8-dien-1-one (0.40 g, 1.6 mmol) in 50 mL diethyl ether. The reaction mixture was heated to reflux for 24 hours. The mixture was cooled to 0 °C and thionyl chloride (0.44 mL, 6 mmol) was added. The reaction was stirred for an additional hour at 0 °C. The reaction was quenched using saturated NH<sub>4</sub>Cl<sub>(aq)</sub> (5 mL). The reaction mixture was vacuum filtered through a fritted funnel, and the aqueous layer was removed and extracted with ether (10 mL) three times. The combined organics were then dried with Na<sub>2</sub>SO<sub>4</sub> and the volatiles were removed under vacuum. Silica gel flash column

chromatography was performed using hexanes as the eluent (Rf = 0.6) resulting in a colorless oil (0.24 g, 0.9 mmol, 56 %). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  7.38 (d, *J* = 8.8 Hz, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 5.88-5.80 (m, 1 H), 5.24 (d, *J* = 3.6 Hz, 1 H), 5.20 (t, *J* = 7.2 Hz, 1 H), 5.05 (dd, *J* = 17.1 Hz, 1.6 Hz 1 H), 5.01 (d, *J* = 3.0 Hz, 1 H), 4.97 (dd, *J* = 10.1 Hz, 1.0 Hz, 1 H), 3.82 (s, 3 H), 2.92 (t, *J* = 7.1 Hz, 2 H), 2.21-2.07 (m, 6 H), 1.70 (s, 3 H). <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)  $\delta_{\rm C}$  158.5, 147.6, 138.8, 134.9, 133.8, 127.9, 127.2, 126.6, 125.6, 124.2, 114.4, 113.5, 55.3, 39.1, 35.5, 32.4, 27.8, 16.0. HRMS calculated for C<sub>18</sub>H<sub>24</sub>O [M] = 256.18272, found 256.18176.



(*E*)-2,2,5-trimethyl-1-phenylnona-4,8-dien-1-one: A solution of *n*-butyllithium (3.0 mL, 1.6 M in hexanes) was added to a solution of diisopropylamine (0.7 mL, 5.0 mmol) in 15 mL THF at -78 °C. The reaction was stirred for one hour. The isobutyrophenone (0.75 mL, 5.0 mmol) was then added and the solution was stirred for an additional hour. The (*E*)-7-bromo-5-methylhepta-1,5-diene<sup>1</sup> (1.0 g, 5.3 mmol) was then added and the temperature of the reaction mixture was brought to room temperature. The reaction was left to stir overnight. The reaction was quenched using 0.5 M HCl (5 mL) and the product was extracted using ether (5 mL) three times. The organics were then washed with brine (30 mL), dried with MgSO<sub>4</sub>, and the volatiles were removed under vacuum resulting in a yellow oil (6.6 g, 32 mmol, 83%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  7.67 (d, *J* = 7.9 Hz, 2 H), 7.56 (t, *J* = 7.0 Hz, 1 H), 7.48 (t, *J* = 7.8 Hz, 2 H), 5.81-5.71 (m, 1 H), 5.10 (t, *J* = 7.3 Hz, 1 H), 4.98 (d, *J* = 16.8 Hz, 1 H), 4.93 (d, *J* = 10.3 Hz, 1 H), 2.45 (d,

*J* = 7.4 Hz, 2 H), 2.08-2.03 (m, 2 H), 1.88-1.82 (m, 2 H), 1.23 (s, 3 H), 0.97 (s, 3 H), 0.74 (s, 3 H).



(*E*)-(3,3,6-trimethyldeca-1,5,9-trien-2-yl)benzene, 8,8-Me<sub>2</sub>-5:

(Trimethylsilyl)methylmagnesium chloride (22 mL, 1.0 M in diethyl ether) was added to a solution of (E)-5-methyl-1-phenylnona-4,8-dien-1-one (2 g, 9.7 mmol) in 100 mL diethyl ether. The reaction mixture was heated to reflux for 24 hours. The mixture was cooled to 0 °C and thionyl chloride (3 mL, 40 mmol) was added. The reaction was stirred for an additional hour at 0 °C. The reaction was quenched using saturated NH<sub>4</sub>Cl<sub>(aq)</sub> (50 mL). The reaction mixture was vacuum filtered through a fritted funnel, and the aqueous layer was removed and extracted with ether (25 mL) three times. The combined organics were then dried with  $MgSO_4$  and the volatiles were removed under vacuum. Silica gel flash column chromatography was performed using hexanes as the eluent (Rf = 0.6) resulting in a colorless oil (1.7 g, 8.3 mmol, 86 %). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  7.43 (t, J = 8.0 Hz, 1 H), 7.35-7.32 (m, 2 H), 7.23 (d, J = 7.8 Hz, 2 H), 5.95-5.89 (m, 1 H), 5.33 (t, J = 7.0 Hz, 1 H), 5.13 (d, J = 1.2 Hz, 1 H), 5.05 (dd, J = 10.1 Hz, 1.0 Hz, 1 H), 5.02 (dd, J = 16.4 Hz, 1.0 Hz, 1 H), 4.96 (d, J = 1.2 Hz, 1 H), 2.30-2.22 (m, 2 H), 2.23-2.20 (m, 2 H), 2.17-2.13 (m, 2 H), 1.66 (s, 3 H), 1.19 (s, 3 H), 1.18 (s, 3 H). <sup>13</sup>C-NMR (151 MHz, CDCl<sub>3</sub>)  $\delta_{\rm C}$  158.0, 143.5, 138.9, 135.8, 129.9, 129.0, 128.2, 127.4, 126.7, 121.9, 114.5, 113.4, 110.1, 41.5, 39.4, 38.9, 32.5, 27.5, 22.1, 16.5. HRMS calculated for  $C_{19}H_{26}$  [M] = 254.2034, 254.20267 found.



(E)-(4-methylocta-3,7-dienyl)benzene, 13: A solution of n-butyllithium (10.5 mL, 1.6 M in hexanes) was added to a solution of methyltriphenylphosphoniumbromide (6.8 g, 19.1 mmol) in 100 mL of THF at -78 °C. The reaction was stirred for one hour at -78 °C. A solution of (E)-4methyl-7-phenylhept-4-enal<sup>3</sup> (3.0 g, 15.1 mmol) in 20 mL THF was added to the phosphonium ylide at -78 °C. The reaction mixture was allowed to warm to room temperature and left to stir overnight. The reaction mixture was quenched using 0.1 M  $HCl_{(aq)}$  (50 mL). The aqueous layer was then removed and extracted with ether (20 mL) three times. The combined organics were then washed with water (50 mL) and brine (50 mL), dried with MgSO<sub>4</sub>, and the volatiles were removed under vacuum. The resulting oil was then extracted using pentane (50 mL) three times. Silica gel flash column chromatography was performed using hexanes as the eluent ( $R_f = 0.5$ ) resulting in a clear oil (2.6 g, 13 mmol, 86 %). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  7.43 (dd, J = 7.3, 7.7 Hz, 2 H), 7.36-7.33 (m, 3 H), 5.99-5.93 (m, 1 H), 5.38 (t, J = 7.1 Hz, 1 H), 5.19 (dd, J = 1.8, 17.1 Hz, 1 H), 5.12 (dd, J = 1.0, 10.2 Hz, 1 H), 2.82 (t, J = 8.0 Hz, 2 H), 2.49 (t, J = 7.6 Hz, 2 H), 2.32 (dt, J = 6.8, 8.0 Hz, 2 H), 2.23 (dt, J = 7.3, 8.0 Hz, 2 H), 1.73 (s, 3 H). <sup>13</sup>C-NMR (151) MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 142.5, 138.8, 135.3, 128.7 (2 H), 128.4 (2 H), 125.8, 124.1, 114.5, 39.2, 36.3, 32.5, 30.1, 16.1. HRMS calculated for  $C_{15}H_{20}$  [M] = 200.15645, 200.15438 found.

<sup>&</sup>lt;sup>3</sup> Surendra, K.; Qiu, W.; Corey, E. J. J. Am. Chem. Soc. **2011**, 133, 9724-9726.

# 2. Cyclization Optimization



**Optimization:** Further reaction condition optimization included testing multiple silver salts and nitriles. The nitrile acts as a labile ligand and is capable of filling the open coordination site on the platinum and leaving an open site when beta-hydride elimination occurs. The nitrile also affected the product ratios when substrates that went to multiple products were used (Table 3, entries 4-6). This suggests that the nitrile may interact with the active triphenyl carbenium, tempering its activity.

Using different silver salts to activate the platinum diiodide complex had a similar affect to using different nitriles, minimal variance to reaction rate but different product ratios where more prevalent when applicable. The microscopic role of the counterion is less clear as it affects both the catalyst and the cationic hydride abstraction agent. Product isolation is a problem associated with this chemistry due to the similar polarities of the product with starting material, alkene isomers of product and starting material, and the triphenyl methane generated as a result of the reaction. The most efficient method to isolate product was found to be the use of preparative-TLC using hexanes as the eluent. Due to minimal separation of the compounds, multiple separations were often required to obtain spectroscopically pure products. Isolated yields of these high purity products were consequently reduced to 5-20%.

### **3.** Cyclization Experimental



**2:** The (BINAP)PtI<sub>2</sub> (9.8 mg, 10 µmol), AgBF<sub>4</sub> (4.4 mg, 22.5 µmol) and NCC<sub>6</sub>F<sub>5</sub> (5.8 mg, 30 µmol) were mixed in 0.3 mL EtNO<sub>2</sub> for one hour in the dark. The mixture was filtered through a 0.2 µm PTFE syringe filter (rinsing with 0.3 mL EtNO<sub>2</sub>) onto substrate (19.2 mg, 100 µmol), Ph<sub>2</sub>NH (5.1 mg, 30 µmol), TrOMe (27.4 mg, 100 µmol) and TrBF<sub>4</sub> (16.5 mg, 50 µmol). The mixture was stirred in the dark for 48 hours. The mixture was passed through a silica gel plug using hexanes and the volatiles were removed under vacuum. The product was isolated through the use of consecutive preparative-TLC plates using hexanes as the eluent (Rf = 0.6) resulting in a clear oil (2.8 mg, 14.7 µmol, 14.7%). 15 <sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN)  $\delta_{\rm H}$  5.62-5.58 (m, 2 H), 4.88 (dd, *J* = 1.0 Hz, 1.4 Hz, 1 H), 4.70 (d, *J* = 2.2 Hz, 1 H), 1.94-1.78 (m, 4 H), 1.79 (s, 3 H), 1.76-1.69 (m, 2 H), 1.48-1.24 (m, 6 H), 0.84 (s, 3 H). <sup>13</sup>C-NMR (151 MHz, CD<sub>3</sub>CN)  $\delta_{\rm C}$  147.7, 125.8, 125.6, 112.2, 55.9, 41.5, 40.4, 35.6, 30.0, 29.9, 28.1, 26.4, 23.6, 11.3. HRMS calculated for C<sub>14</sub>H<sub>22</sub> [M] = 190.17215, 190.17271 found.



**4**: The (BINAP)PtI<sub>2</sub> (9.8 mg, 10 μmol), AgBF<sub>4</sub> (4.4 mg, 22.5 μmol) and NCC<sub>6</sub>F<sub>5</sub> (5.8 mg, 30 μmol) were mixed in 0.3 mL EtNO<sub>2</sub> for one hour in the dark. The mixture was filtered through a 0.2 μm PTFE syringe filter (rinsing with 0.3 mL EtNO<sub>2</sub>) onto substrate (23.3 mg, 100 μmol), Ph<sub>2</sub>NH (5.1 mg, 30 μmol), TrOMe (27.8 mg, 101 μmol) and TrBF<sub>4</sub> (16.5 mg, 50 μmol). The mixture was stirred in the dark for 36 hours. The mixture was passed through a silica gel plug using hexanes and the volatiles were removed under vacuum. The product was isolated through the use of consecutive preparative-TLC plates using hexanes as the eluent (Rf = 0.6) resulting in a clear oil (3.2 mg, 13.9 μmol, 13.9%). <sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN)  $\delta_{\rm H}$  5.68-5.54 (m, 2 H), 5.39 (m, 1 H), 1.92-1.65 (m, 4 H), 1.62 (s, 3 H), 1.59-1.25 (m, 9 H), 0.92 (s, 3 H), 0.81 (s, 3 H). <sup>13</sup>C-NMR (151 MHz, CD<sub>3</sub>CN)  $\delta_{\rm C}$  131.7, 126.1, 125.6, 120.0, 50.5, 50.3, 42.5, 41.3, 40.8, 29.9, 29.7, 25.2, 23.3, 22.9, 19.0, 12.0. HRMS calculated for C<sub>17</sub>H<sub>26</sub> [M] = 230.20345, 230.20376 found.



**6**: The (BINAP)PtI<sub>2</sub> (9.8 mg, 10  $\mu$ mol), AgBF<sub>4</sub> (4.4 mg, 22.5  $\mu$ mol) and NCC<sub>6</sub>F<sub>5</sub> (6.0 mg, 31  $\mu$ mol) were mixed in 0.3 mL EtNO<sub>2</sub> for one hour in the dark. The mixture was filtered through a 0.2  $\mu$ m PTFE syringe filter (rinsing with 0.3 mL EtNO<sub>2</sub>) onto substrate (22.2 mg, 98  $\mu$ mol),

Ph<sub>2</sub>NH (5.1 mg, 30 μmol), TrOMe (27.3 mg, 100 μmol) and TrBF<sub>4</sub> (16.6 mg, 50 μmol). The mixture was stirred in the dark for 36 hours. The mixture was passed through a silica gel plug using hexanes and the volatiles were removed under vacuum. The product was isolated through the use of consecutive preparative-TLC plates using hexanes as the eluent (Rf = 0.6) resulting in a clear oil (4.2 mg, 18.8 μmol, 19.2%). <sup>1</sup>H-NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_{\rm H}$  7.38 (t, *J* = 8.4 Hz, 2 H), 7.29 (t, *J* = 7.2 Hz, 2 H), 7.20 (d, *J* = 7.2 Hz, 1 H), 6.03 (t, *J* = 2.1 Hz, 1 H), 5.66-5.58 (m, 2 H), 2.32-1.87 (m, 7 H), 0.91 (s, 3 H). <sup>13</sup>C-NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_{\rm C}$  142.7, 135.0, 129.7, 128.1, 126.5, 125.9, 125.3, 125.0, 124.1, 123.2, 43.4, 41.3, 34.9, 31.0, 30.0, 23.1, 17.0. HRMS calculated for C<sub>17</sub>H<sub>20</sub> [M] = 224.15650, 224.15715 found.



**8**: The (BINAP)PtI<sub>2</sub> (9.8 mg, 10 µmol), AgBF<sub>4</sub> (4.5 mg, 23.1 µmol) and NCC<sub>6</sub>F<sub>5</sub> (5.8 mg, 30 µmol) were mixed in 0.3 mL EtNO<sub>2</sub> for one hour in the dark. The mixture was filtered through a 0.2 µm PTFE syringe filter (rinsing with 0.3 mL EtNO<sub>2</sub>) onto substrate (20.3 mg, 100 µmol), Ph<sub>2</sub>NH (5.1 mg, 30 µmol), TrOMe (27.4 mg, 100 µmol) and TrBF<sub>4</sub> (16.4 mg, 50 µmol). The mixture was stirred in the dark for 16 hours. The mixture was passed through a silica gel plug using hexanes and the volatiles were removed under vacuum. The product was isolated through the use of consecutive preparative-TLC plates using hexanes as the eluent (Rf = 0.6) resulting in a clear oil (1.8 mg, 8.9 µmol, 8.9%). <sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN)  $\delta_{\rm H}$  5.632-5.592 (m, 2 H), 2.16-2.04 (m, 2 H), 1.90-1.85 (m, 8 H), 1.71-1.30 (m, 7 H), 0.84 (s, 3 H). <sup>13</sup>C-NMR (151 MHz,

CD<sub>3</sub>CN) δ<sub>C</sub> 126.2, 126.1, 125.8, 125.4, 46.5, 40.8, 35.6, 35.3, 30.7, 30.1, 29.8, 29.5, 23.0, 23.0, 16.6. HRMS calculated for C<sub>15</sub>H<sub>22</sub> [M] = 202.17215, 202.17267 found.



**10**: The (BINAP)PtI<sub>2</sub> (9.8 mg, 10 µmol), AgBF<sub>4</sub> (4.4 mg, 22.5 µmol) and NCC<sub>6</sub>F<sub>5</sub> (5.8 mg, 30 µmol) were mixed in 0.3 mL EtNO<sub>2</sub> for one hour in the dark. The mixture was filtered through a 0.2 µm PTFE syringe filter (rinsing with 0.3 mL EtNO<sub>2</sub>) onto substrate (25.2 mg, 100 µmol), Ph<sub>2</sub>NH (5.1 mg, 30 µmol), TrOMe (27.4 mg, 100 µmol) and TrBF<sub>4</sub> (16.5 mg, 50 µmol). The mixture was stirred in the dark for 24 hours. The mixture was passed through a silica gel plug using hexanes and the volatiles were removed under vacuum. The product was isolated through the use of consecutive preparative-TLC plates using hexanes as the eluent (Rf = 0.6) resulting in a clear oil (1.2 mg, 4.8 µmol, 4.8%). <sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN)  $\delta_{\rm H}$  7.71 (d, *J* = 8.6 Hz, 1 H), 7.24 (d, *J* = 7.7 Hz, 1 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 7.13 (t, *J* = 7.4 Hz, 1 H), 5.75-5.64 (m, 3 H), 2.87-2.55 (m, 4 H), 2.37-2.01 (m, 4 H), 1.89-1.52 (m, 4 H), 1.05 (s, 3 H). <sup>13</sup>C-NMR (151 MHz, CD<sub>3</sub>CN)  $\delta_{\rm C}$  142.2, 129.1, 126.7, 126.6, 126.3, 125.9, 125.7, 125.3, 121.9, 118.7, 48.7, 38.8, 36.0, 29.8, 28.6, 26.3, 24.7, 22.8, 17.1. HRMS calculated for C<sub>19</sub>H<sub>22</sub> [M] = 250.17215, 250.17276 found.



**12**: The (BINAP)PtI<sub>2</sub> (9.8 mg, 10 μmol), AgBF<sub>4</sub> (4.4 mg, 22.5 μmol) and NCC<sub>6</sub>F<sub>5</sub> (5.7 mg, 30 μmol) were mixed in 0.3 mL EtNO<sub>2</sub> for one hour in the dark. The mixture was filtered through a 0.2 μm PTFE syringe filter (rinsing with 0.3 mL EtNO<sub>2</sub>) onto substrate (28.0 mg, 99.3 μmol), Ph<sub>2</sub>NH (5.3 mg, 31 μmol), TrOMe (27.3 mg, 100 μmol) and TrBF<sub>4</sub> (16.5 mg, 50 μmol). The mixture was stirred in the dark for 8 hours. The mixture was passed through a silica gel plug using hexanes and the volatiles were removed under vacuum. The product was isolated through the use of consecutive preparative-TLC plates using hexanes as the eluent (Rf = 0.3) resulting in a clear oil (1.4 mg, 5.0 μmol, 5.0%). <sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN) δ<sub>H</sub> 7.55 (d, *J* = 6.6 Hz, 1 H), 7.36 (t, *J* = 7.4 Hz, 1 H), 6.74 (t, *J* = 3.0 Hz, 1 H), 6.73 (s, 1 H), 5.77-5.64 (m, 2 H), 3.78 (s, 3 H), 2.73-2.62 (m, 2 H), 2.36-1.98 (m, 7 H), 1.91-1.65 (m, 3 H), 1.03 (s, 3 H). <sup>13</sup>C-NMR (151 MHz, CD<sub>3</sub>CN) δ<sub>C</sub> 133.7, 130.5, 129.7, 127.8, 126.7, 125.8, 123.1, 112.9, 110.8, 106.6, 54.8, 38.8, 36.2, 30.2, 29.8, 29.0, 26.2, 24.7, 22.7, 17.1. HRMS calculated for C<sub>20</sub>H<sub>24</sub>O [M] = 280.18272, 280.18202 found.



**14**: The (BINAP)PtI<sub>2</sub> (9.8 mg, 10 μmol), AgBF<sub>4</sub> (4.4 mg, 22.5 μmol) and NCC<sub>6</sub>F<sub>5</sub> (5.8 mg, 30 μmol) were mixed in 0.3 mL EtNO<sub>2</sub> for one hour in the dark. The mixture was filtered through a 0.2 μm PTFE syringe filter (rinsing with 0.3 mL EtNO<sub>2</sub>) onto substrate (20.1 mg, 100 μmol), Ph<sub>2</sub>NH (5.3 mg, 31 μmol), TrOMe (27.6 mg, 100 μmol) and TrBF<sub>4</sub> (16.4 mg, 50 μmol). The mixture was stirred in the dark for 16 hours. The mixture was passed through a silica gel plug using hexanes and the volatiles were removed under vacuum. The product was isolated through the use of consecutive preparative-TLC plates using hexanes as the eluent (Rf = 0.6) resulting in a clear oil (0.9 mg, 4.7 μmol, 4.7%). <sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN)  $\delta_{\rm H}$  7.34 (d, *J* = 8.0 Hz, 1 H), 7.16 (t, *J* = 7.6 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 7.08 (t, *J* = 7.0 Hz, 1 H), 5.78-5.73 (m, 2 H), 2.90-2.48 (m, 4 H), 2.14-2.08 (m, 2 H), 1.70-1.66 (m, 3 H), 1.11 (s, 3 H). <sup>13</sup>C-NMR (151 MHz, CD<sub>3</sub>CN)  $\delta_{\rm C}$  135.6, 129.0, 126.5, 126.1, 125.9, 125.4, 125.2, 41.7, 39.6, 30.0, 29.5, 25.0, 21.7. HRMS calculated for C<sub>15</sub>H<sub>18</sub> [M] = 198.1409, 198.1406 found.









Ph

**5** <sup>1</sup>H, 600 MHz CDCl<sub>3</sub>



∠Ph

**5** <sup>13</sup>C, 151 MHz CDCl<sub>3</sub>



















13 <sup>1</sup>H, 600 MHz

CDCl<sub>3</sub>







S33



,Ph

8,8-Me<sub>2</sub>-**5** <sup>1</sup>H, 600 MHz CDCl<sub>3</sub>



Ph

8,8-Me<sub>2</sub>-**5** <sup>13</sup>C, 151 MHz CDCl<sub>3</sub>



,OMe 16

<sup>13</sup>H, 600 MHz CDCl<sub>3</sub>



.OMe 16 <sup>13</sup>C, 151 MHz CDCl<sub>3</sub>



S38