

# Supporting Information

## **Iridium Catalyzed Hydrocarboxylation of 1,1-Dimethylallene: Byproduct-Free Reverse Prenylation of Carboxylic Acids**

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## **General Methods**

All reactions were run under one atmosphere of argon gas unless otherwise indicated. 1,2-Dichloroethane (DCE) was distilled from Pure-Solv MD-5 Solvent Purification System (Innovative Technology, inc). Anhydrous solvents were transferred by an oven-dried syringe. Reaction vessels were dried in oven for overnight and cooled under a stream of nitrogen. [Ir(cod)<sub>2</sub>Cl] and BIPHEP were used as received from Umicore or Strem Chemicals. Cesium Carbonate was purchased from Aldrich. Carboxylic acids (**1a-11a**) were commercially available and were used directly without further purification. *N*-Boc-protected (–)-phenylalanine (**12a**) was prepared according to literature procedure.<sup>1</sup> Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F<sub>254</sub>). Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+1, M or M-1) or a suitable fragment ion. Nuclear magnetic resonance spectra (<sup>1</sup>H NMR and <sup>13</sup>C NMR) spectra were recorded with a Varian Gemini (300 MHz) spectrometer for CDCl<sub>3</sub> solutions and chemical shifts are reported as parts per million (ppm) relative to, respectively, residual CHCl<sub>3</sub> δ<sub>H</sub> (7.26 ppm) and CDCl<sub>3</sub> δ<sub>C</sub> (77.0 ppm) as internal standards. Coupling constants are reported in hertz (Hz).

## **General Procedure for the Coupling of Carboxylic Acids and 1,1-Dimethylallene**

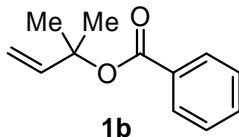
To an oven-dried reaction vessel under one atmosphere of argon gas charged with carboxylic acids **1a-12a** (100 mol%), [Ir(cod)Cl]<sub>2</sub> (1 mol%), BIPEHP (2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (120 mol% or 240 mol%). The reaction mixture was allowed to stir at 60 °C until complete consumption of starting material was observed, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes) provided **1b-12b**.

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<sup>1</sup> Čaplar, V.; Žinić, M.; Pozzo, J.-L.; Fages, F.; Mieden-Gundert, G.; Vögtle, F. *Eur. J. Org. Chem.* **2004**, 4048–4059.

## **Detailed Procedure and Spectral Data of All Compounds (1b–12b)**

### **2-Methylbut-3-en-2-yl benzoate<sup>2</sup> (1b)**



To an oven-dried reaction vessel under one atmosphere of argon gas charged with benzoic acid (**1a**) (36.6 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (24.5 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 24 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:30) provided **1b** (48 mg, 0.252 mmol) as a clear oil in 84% yield.

**TLC (SiO<sub>2</sub>)**: R<sub>f</sub> = 0.30 (ethyl acetate:hexanes, 1:30).

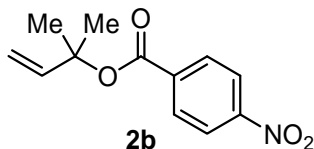
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 6.22 (dd, *J* = 17.4, 10.5 Hz, 1H), 5.29 (d, *J* = 17.4 Hz, 1H), 5.16 (d, *J* = 10.5 Hz, 1H), 1.69 (s, 6H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 165.6, 142.8, 132.8, 131.8, 129.7, 128.5, 113.1, 81.5, 26.8.

**FTIR** (neat): ν 2979, 2927, 2360, 2339, 1716, 1700, 1683, 1669, 1558, 1472, 1417, 1313, 1284, 1235, 1165, 1109, 1069, 1026, 921, 847, 711 cm<sup>-1</sup>.

<sup>2</sup> Sedighi, M.; Calimsiz, S.; Lipton, M. A. *J. Org. Chem.* **2006**, *71*, 9517–9518.

## 2-Methylbut-3-en-2-yl 4-nitrobenzoate<sup>3</sup> (**2b**)



To an oven-dried reaction vessel under one atmosphere of argon gas charged with *p*-nitrobenzoic acid (**2a**) (50.1 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (24.5 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 16 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:15) provided **2b** (60 mg, 0.255 mmol) as pale yellow solid in 85% yield.

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.38 (ethyl acetate:hexanes, 1:8).

**MP:** 112–114 °C (hexanes/CH<sub>2</sub>Cl<sub>2</sub>)

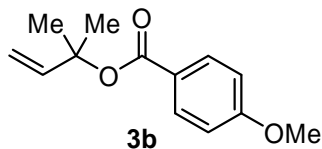
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 8.28 (d, *J* = 8.7 Hz, 2H), 8.19 (d, *J* = 8.7 Hz, 2H), 6.21 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.31 (d, *J* = 17.4 Hz, 1H), 5.20 (d, *J* = 10.8 Hz, 1H), 1.71 (s, 6H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 163.6, 150.6, 142.0, 137.3, 130.8, 123.7, 113.9, 83.0, 26.7.

**FTIR** (neat): ν 3114, 2982, 1720, 1645, 1606, 1523, 1471, 1415, 1380, 1366, 1348, 1322, 1288, 1265, 1115, 1102, 873, 842, 784, 739, 716 cm<sup>-1</sup>.

<sup>3</sup> Chi, K.-W.; Koo, E.-C. *Bull. Korean. Chem. Soc.* **1994**, *15*, 98–100.

### 2-Methylbut-3-en-2-yl 4-methoxybenzoate<sup>3</sup> (**3b**)



To an oven-dried reaction vessel under one atmosphere of argon gas charged with *p*-anisic acid (**3a**) (45.6 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (24.5 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 16 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:30) provided **3b** (60 mg, 0.272 mmol) as a clear oil in 91% yield.

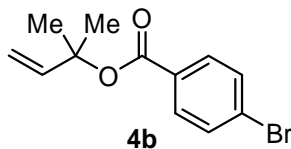
**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.28 (ethyl acetate:hexanes, 1:30).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 7.97 (dd, *J* = 8.7, 2.1 Hz, 2H), 6.91 (dd, *J* = 8.7, 2.1 Hz, 2H), 6.21 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.27 (d, *J* = 17.4 Hz, 1H), 5.14 (d, *J* = 10.8 Hz, 1H), 3.86 (s, 3H), 1.67 (s, 6H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 165.4, 163.3, 143.1, 131.7, 124.3, 113.7, 112.8, 81.1, 55.6, 26.9.

**FTIR** (neat): ν 2978, 1714, 1606, 1509, 1286, 1257, 1168, 1136, 1101, 1031, 847, 771 cm<sup>-1</sup>.

## 2-Methylbut-3-en-2-yl 4-bromobenzoate<sup>3</sup> (**4b**)



To an oven-dried reaction vessel under one atmosphere of argon gas charged with *p*-bromobenzoic acid (**4a**) (60.3 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (24.5 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 24 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:30) provided **4b** (66 mg, 0.245 mmol) as a clear oil in 82% yield.

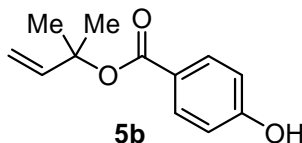
**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.32 (ethyl acetate:hexanes, 1:20).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 7.87 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.57 (dd, *J* = 8.4, 2.1 Hz, 2H), 6.20 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 5.16 (d, *J* = 10.8 Hz, 1H), 1.67 (s, 6H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 164.9, 142.5, 131.8, 131.3, 130.7, 127.9, 113.3, 82.0, 26.8.

**FTIR** (neat): ν 2979, 2926, 1718, 1589, 1483, 1396, 1379, 1364, 1287, 1235, 1166, 1135, 1101, 1068, 1012, 847, 757, 682 cm<sup>-1</sup>.

## 2-Methylbut-3-en-2-yl 4-hydroxybenzoate (**5b**)



To an oven-dried reaction vessel under one atmosphere of argon gas charged with 4-hydroxybenzoic acid (**5a**) (41.4 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (24.5 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 24 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:8) provided **5b** (49 mg, 0.238 mmol) as a clear oil in 79% yield.

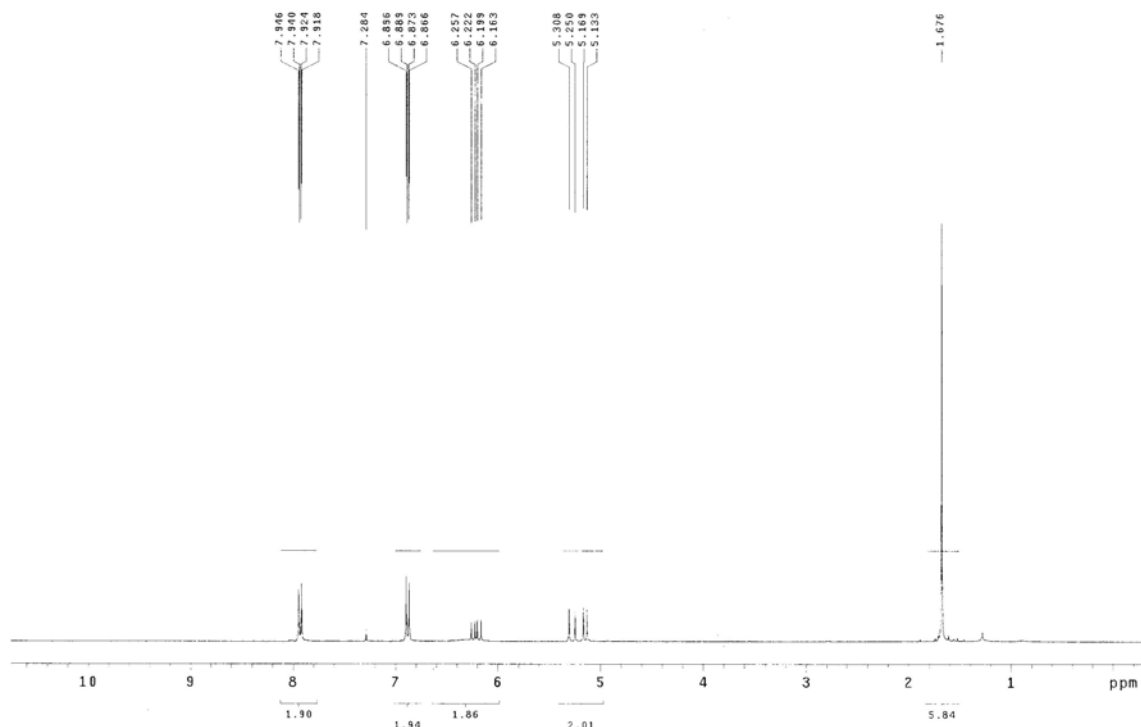
**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.28 (ethyl acetate:hexanes, 1:8).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 7.93 (dd, *J* = 6.6, 1.8 Hz, 2H), 6.88 (dd, *J* = 6.9, 2.1 Hz, 2H), 6.36 (br, 1H), 6.20 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.27 (d, *J* = 17.4 Hz, 1H), 5.14 (d, *J* = 10.8 Hz, 1H), 1.67 (s, 6H).

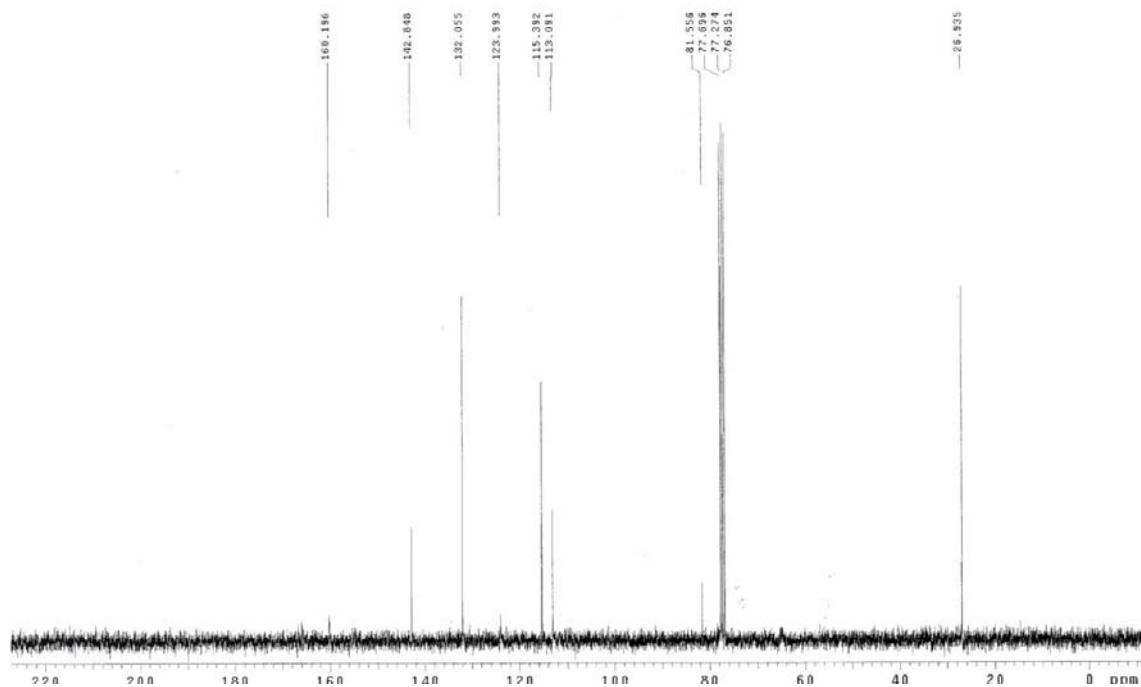
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 160.2, 142.8, 132.1, 124.0, 115.4, 113.1, 81.5, 26.9.

**FTIR** (neat): ν 3363, 2981, 1710, 1688, 1680, 1608, 1592, 1513, 1443, 1366, 1315, 1285, 1233, 1166, 1135, 1114, 851, 773 cm<sup>-1</sup>.

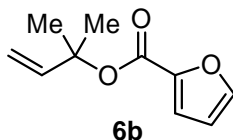
**HRMS** (CI) Calcd. for C<sub>12</sub>H<sub>15</sub>O<sub>3</sub> [M+1]: 207.1021, Found: 207.1024.



KIS 32-11  
Pulse Sequence: s2pu1



## 2-Methylbut-3-en-2-yl furan-2-carboxylate (**6b**)



To an oven-dried reaction vessel under one atmosphere of argon gas charged with 2-furoic acid (**6a**) (33.6 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (24.5 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 16 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:30) provided **6b** (44 mg, 0.244 mmol) as a clear oil in 81% yield.

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.30 (ethyl acetate:hexanes, 1:30).

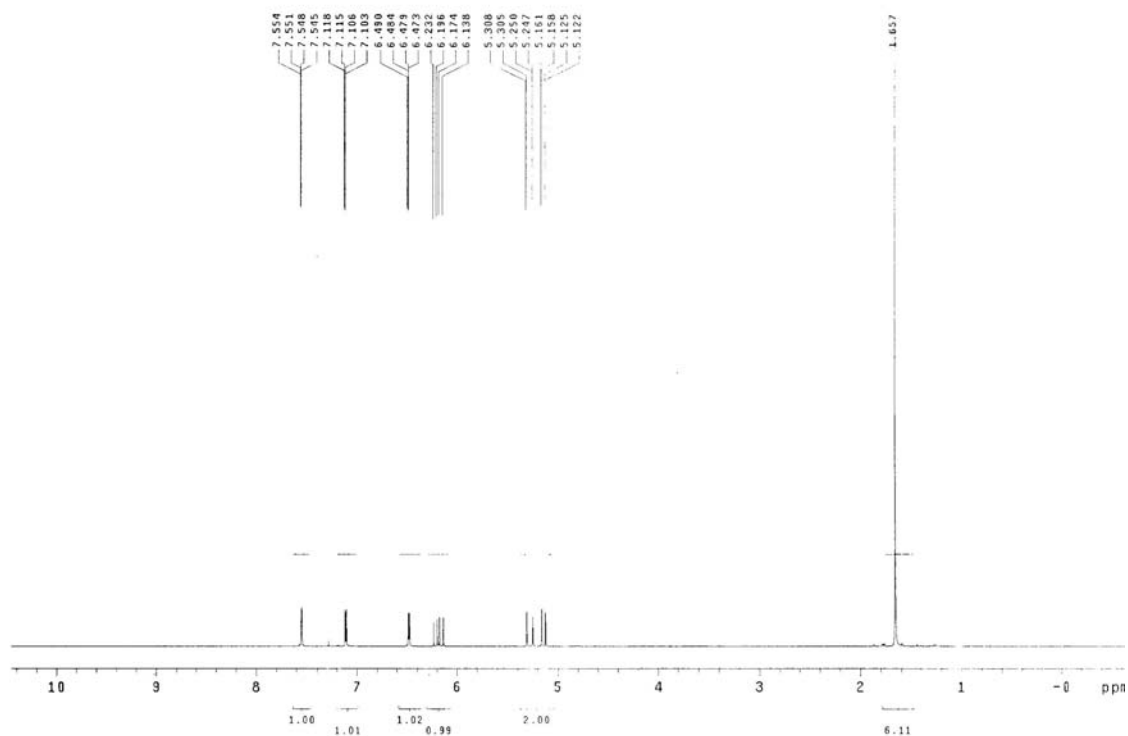
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 7.54 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.11 (dd, *J* = 3.6, 0.9 Hz, 1H), 6.48 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.18 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.27 (d, *J* = 17.4 Hz, 1H), 5.13 (d, *J* = 10.8 Hz, 1H), 1.66 (s, 6H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 157.9, 146.1, 145.9, 142.4, 117.5, 113.4, 111.9, 82.3, 26.8.

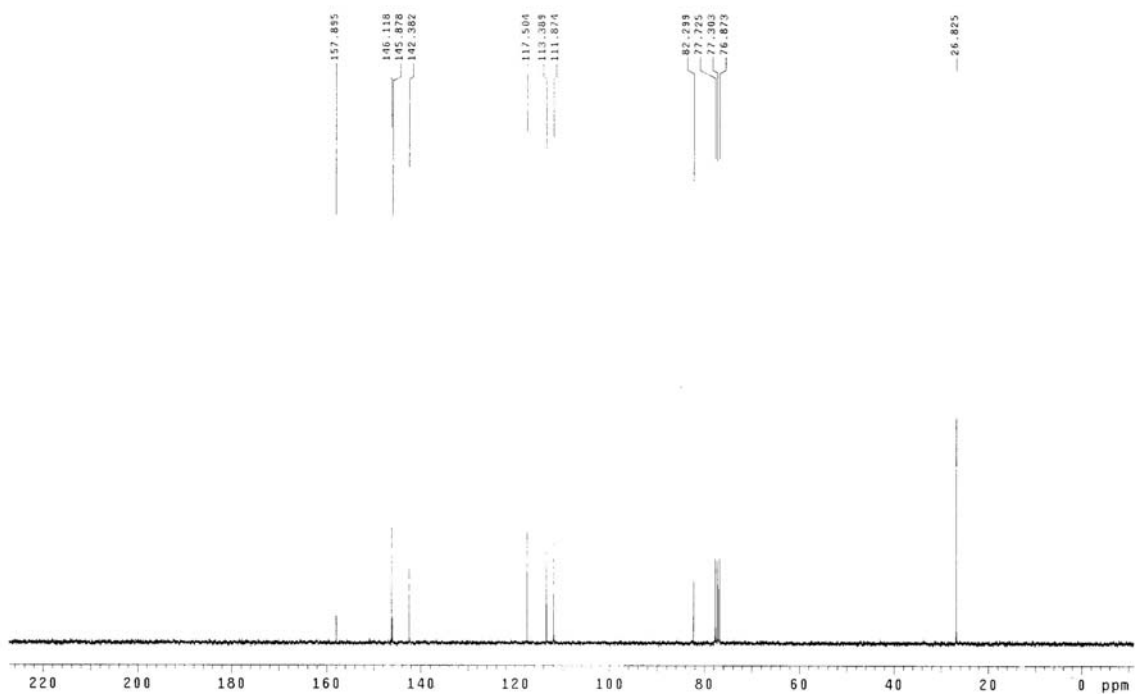
**FTIR** (neat): ν 2980, 2930, 1705, 1525, 1469, 1456, 1417, 1360, 1269, 1233, 1200, 1166, 1134, 1092, 1076, 1035, 923, 862, 823, 751, 718 cm<sup>-1</sup>.

**HRMS** Calcd. for C<sub>12</sub>H<sub>13</sub>O<sub>3</sub> (M+1): 181.0865, Found: 181.0869.

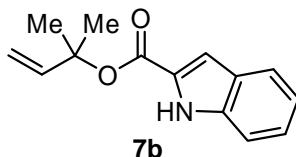
K1S 35-7  
Pulse Sequence: s2pul



K1S 35-7  
Pulse Sequence: s2pul



## 2-Methylbut-3-en-2-yl 1*H*-indole-2-carboxylate (**7b**)



To an oven-dried reaction vessel under one atmosphere of argon gas charged with indole-2-carboxylic acid (**7a**) (48.3 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (24.5 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 8 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:15) provided **7b** (63 mg, 0.275 mmol) as a clear syrup in 92% yield.

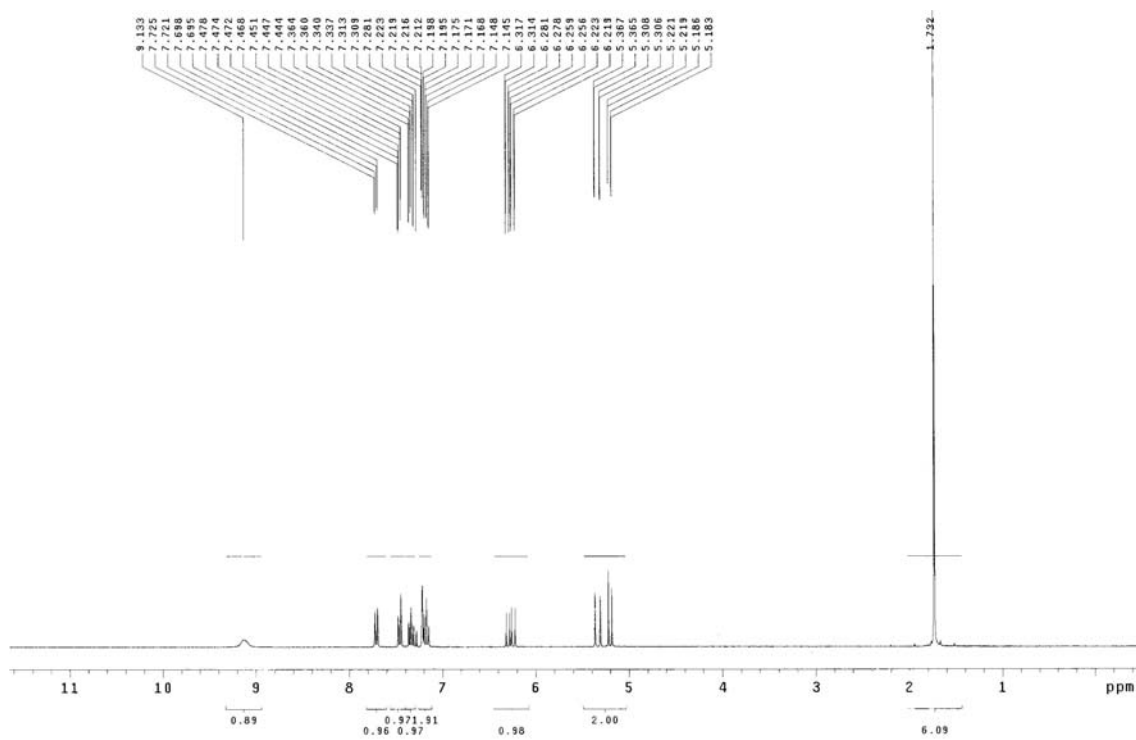
**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.32 (ethyl acetate:hexanes, 1:15).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 9.13 (br, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 8.1 Hz, 1H), 6.21 (s, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.26 (dd, *J* = 17.7, 10.8 Hz, 1H), 5.33 (d, *J* = 17.7 Hz, 1H), 5.19 (d, *J* = 10.8 Hz, 1H), 1.73 (s, 6H).

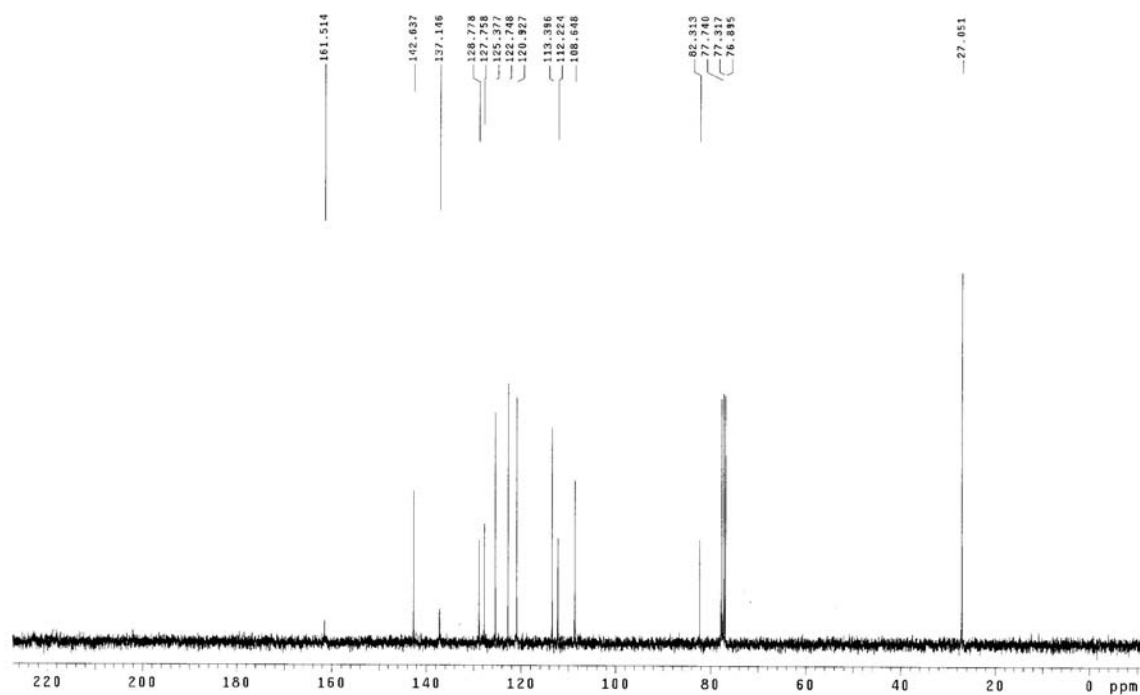
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 161.5, 142.6, 137.1, 128.8, 127.7, 125.4, 122.7, 120.9, 113.4, 112.2, 108.6, 82.3, 27.1.

**FTIR** (neat): ν 3342, 2977, 1685, 1619, 1577, 1527, 1413, 1381, 1341, 1313, 1262, 1206, 1125, 973, 921, 824, 775, 749, 669 cm<sup>-1</sup>.

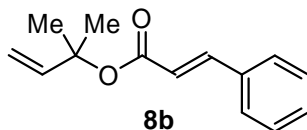
**HRMS** (CI) Calcd. for C<sub>14</sub>H<sub>16</sub>NO<sub>2</sub> [M+1]: 230.1181, Found: 230.1186.



KIS 35-13  
Pulse Sequence: s2pu1



## 2-Methylbut-3-en-2-yl cinnamate (**8b**)



To an oven-dried reaction vessel under one atmosphere of argon gas charged with *trans*-cinnamic acid (**8a**) (44.4 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (24.5 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 16 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:20) provided **8b** (53 mg, 0.245 mmol) as a clear oil in 82% yield.

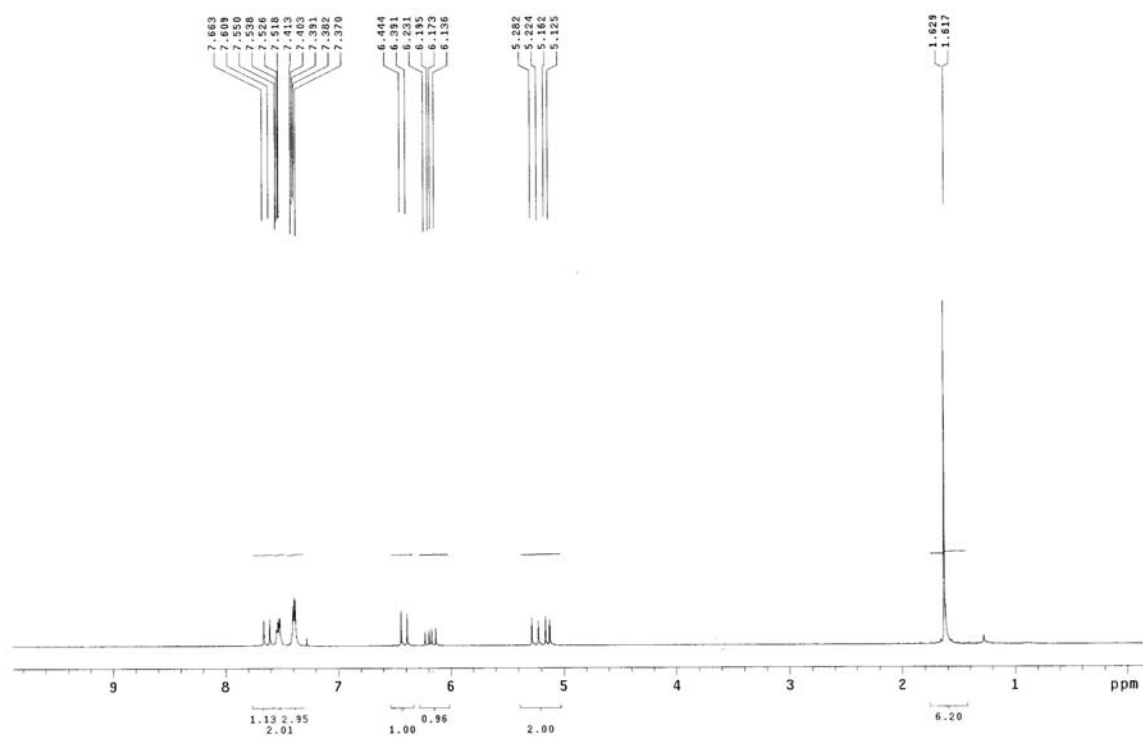
**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.28 (ethyl acetate:hexanes, 1:20).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 7.63 (d, *J* = 15.9 Hz, 1H), 7.55-7.51 (m, 2H), 7.42-7.37 (m, 2H), 6.41 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 17.4, 11.1 Hz, 1H), 5.25 (d, *J* = 17.4 Hz, 1H), 5.14 (d, *J* = 11.1 Hz, 1H), 1.62 (s, 6H).

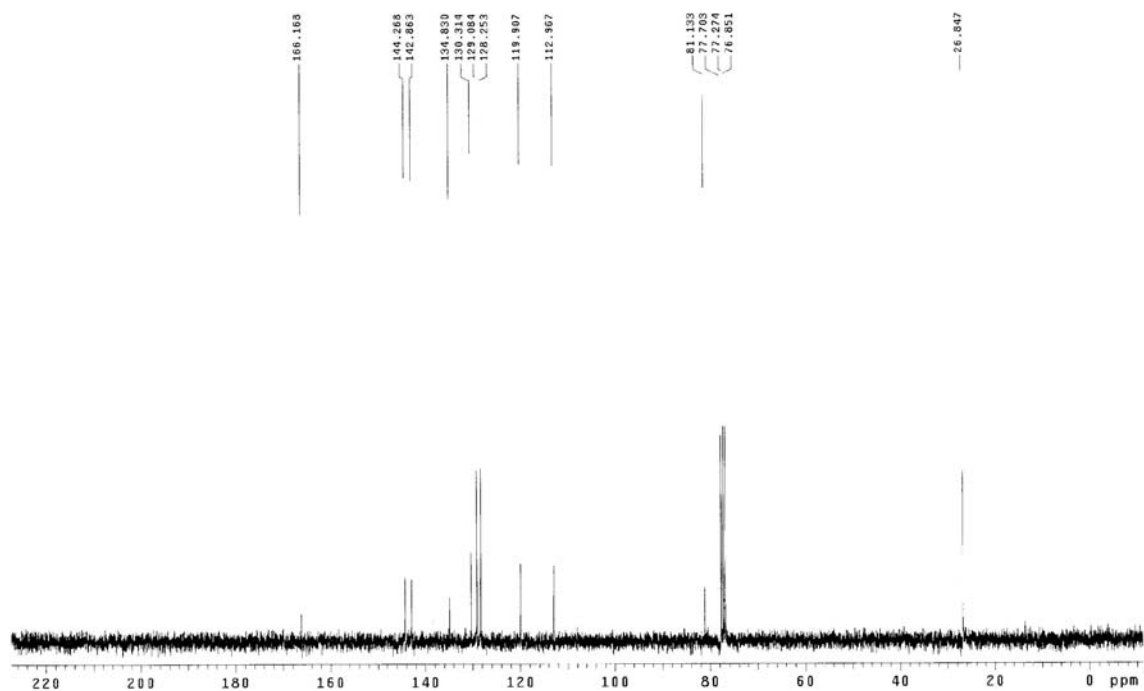
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 166.2, 144.3, 142.9, 134.8, 130.3, 129.1, 128.3, 119.9, 112.9, 81.1, 26.8.

**FTIR** (neat): ν 2980, 1712, 1637, 1449, 1378, 1364, 1328, 1314, 1281, 1203, 1186, 1126, 979, 768, 685 cm<sup>-1</sup>.

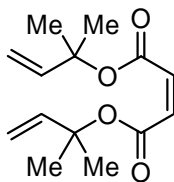
**HRMS** (CI) Calcd. for C<sub>14</sub>H<sub>17</sub>O<sub>2</sub> [M+1]: 217.1229, Found: 217.1231.



KIS 32-3  
Pulse Sequence: s2pu1



**Bis(2-methylbut-3-en-2-yl) maleate (**9b**)**



**9b**

To an oven-dried reaction vessel under one atmosphere of argon gas charged with maleic acid (**9a**) (34.8 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (49 mg, 0.720 mmol, 240 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 36 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:10) provided **9b** (62 mg, 0.246 mmol) as a clear oil in 82% yield.

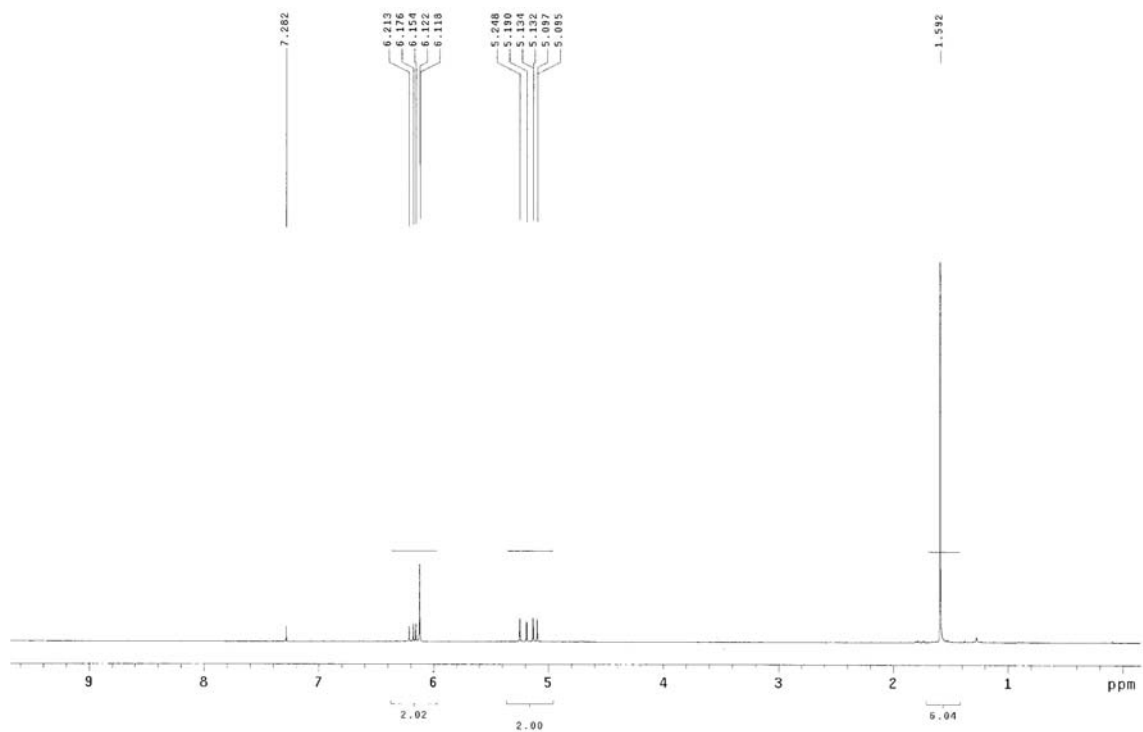
**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.28 (ethyl acetate:hexanes, 1:10).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 6.16 (dd, *J* = 17.4, 11.1 Hz, 2H), 6.12 (s, 2H), 5.22 (d, *J* = 17.4 Hz, 2H), 5.11 (d, *J* = 11.1 Hz, 2H), 1.59 (s, 12H).

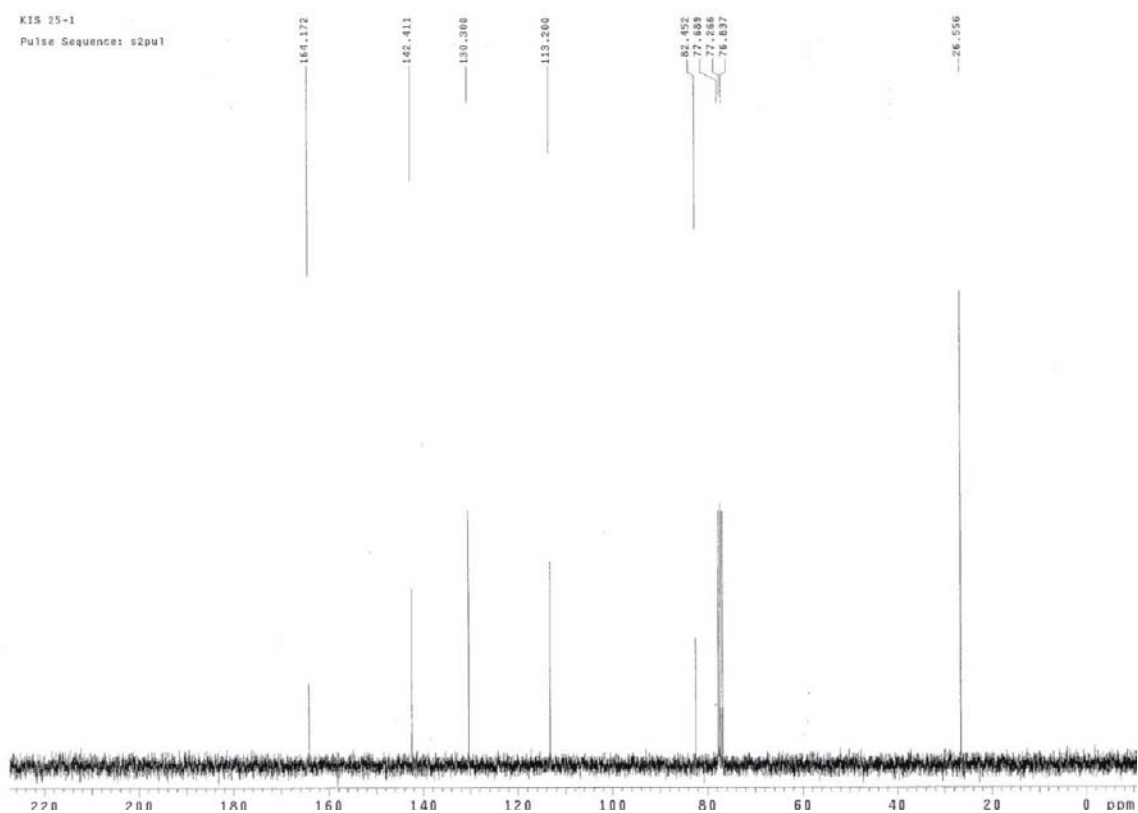
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 164.2, 142.4, 130.3, 113.2, 82.4, 26.5.

**FTIR** (neat): ν 2983, 2934, 1731, 1644, 1470, 1414, 1394, 1365, 1263, 1218, 1121, 979, 922, 835, 807 cm<sup>-1</sup>.

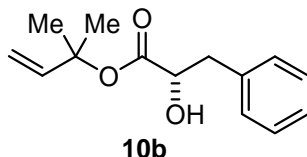
**HRMS** (CI) Calcd. for C<sub>14</sub>H<sub>21</sub>O<sub>4</sub> [M+1]: 253.1440, Found: 253.1444.



KIS 25-1  
Pulse Sequence: s2pul



## 2-Methylbut-3-en-2-yl 2-(*S*)-hydroxy-3-phenylpropanoate (**10b**)



To an oven-dried reaction vessel under one atmosphere of argon gas charged with (–)-3-phenyllactic acid (**10a**) (49.9 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (24.5 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 24 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:6) provided **10b** (52 mg, 0.222 mmol) as a clear oil in 74% yield.

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.30 (ethyl acetate:hexanes, 1:6).

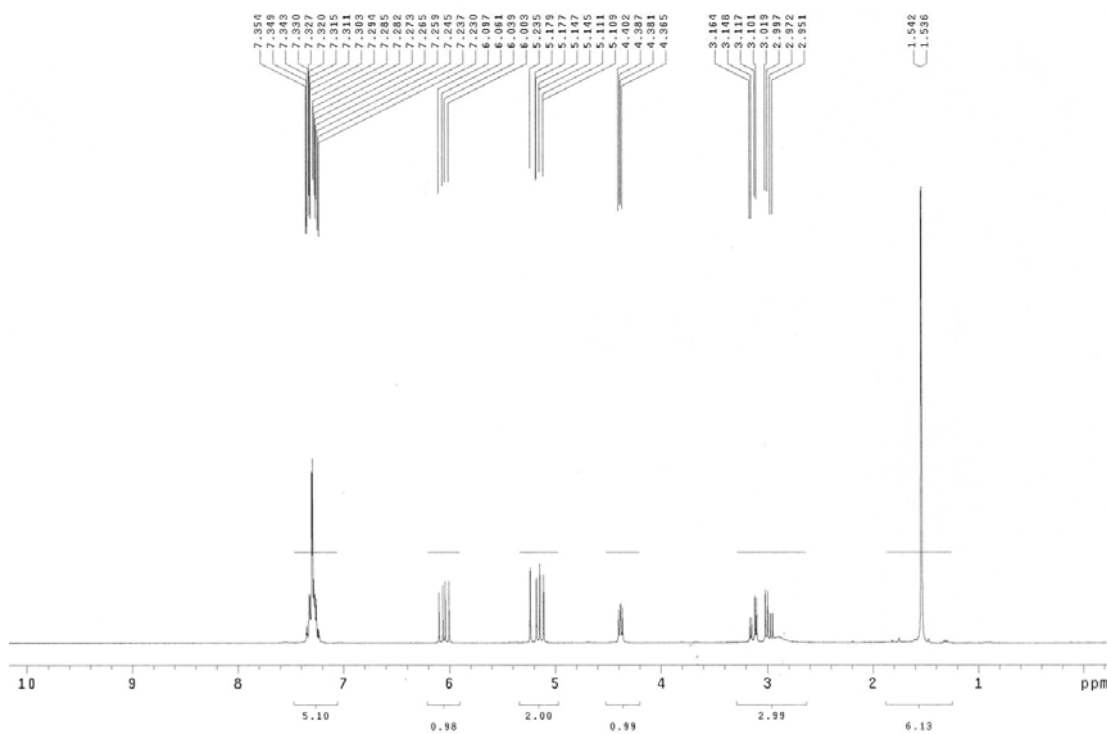
[α]<sub>D</sub><sup>24</sup> –31.0° (*c* 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 7.35-7.23 (m, 5H), 6.04 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.20 (d, *J* = 17.4 Hz, 1H), 5.12 (d, *J* = 10.8 Hz, 1H), 4.38 (dd, *J* = 6.3, 4.5 Hz, 1H), 3.13 (dd, *J* = 14.1, 4.8 Hz, 1H), 2.98 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.90 (br, 1H), 1.54 (s, 6H).

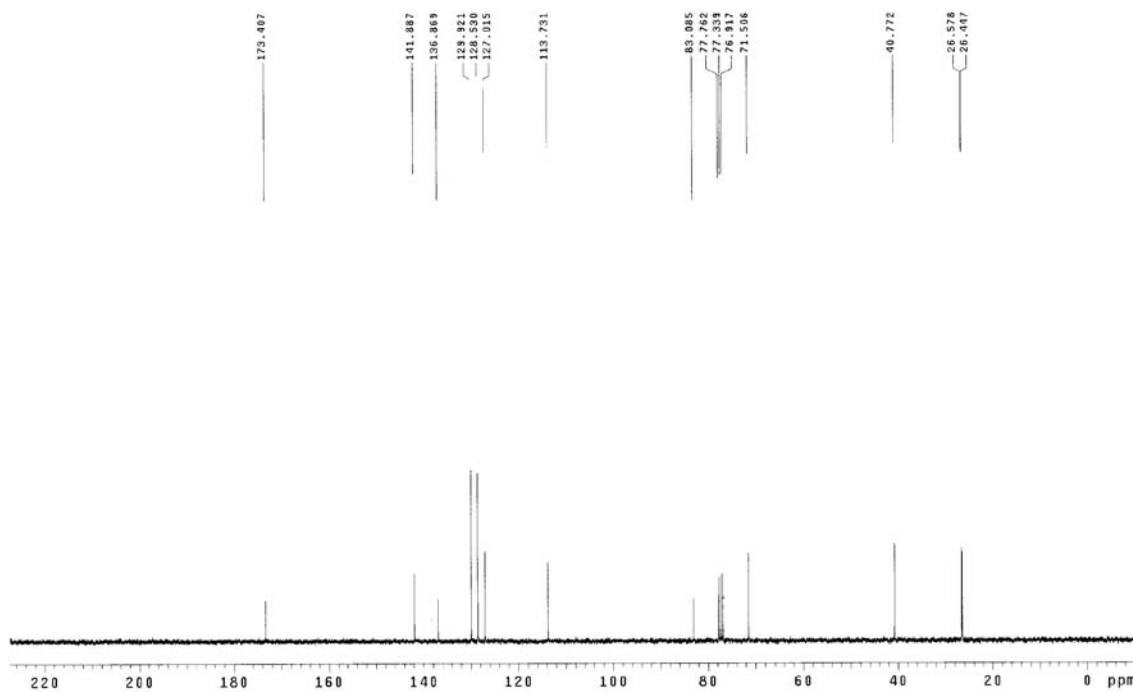
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 173.4, 141.9, 136.8, 129.92, 128.5, 127.0, 113.7, 83.1, 71.5, 40.8, 26.6, 26.4.

**FTIR** (neat): ν 3493, 3029, 2981, 2930, 1731, 1496, 1454, 1414, 1380, 1365, 1264, 1203, 1161, 1127, 1093, 927, 750, 700 cm<sup>–1</sup>.

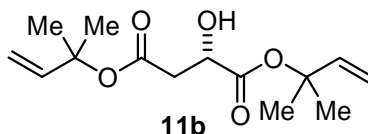
**HRMS** (CI) Calcd. for C<sub>14</sub>H<sub>19</sub>O<sub>3</sub> [M+1]: 235.1334, Found: 235.1337.



KIS 35-16  
Pulse Sequence: s2pu1



**Bis(2-methylbut-3-en-2-yl) 2-(S)-hydroxysuccinate (**11b**)**



To an oven-dried reaction vessel under one atmosphere of argon gas charged with (–)-malic acid (**11a**) (40.2 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (49 mg, 0.720 mmol, 240 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 36 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:6) provided **11b** (62 mg, 0.229 mmol) as a clear oil in 77% yield.

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.28 (ethyl acetate:hexanes, 1:6).

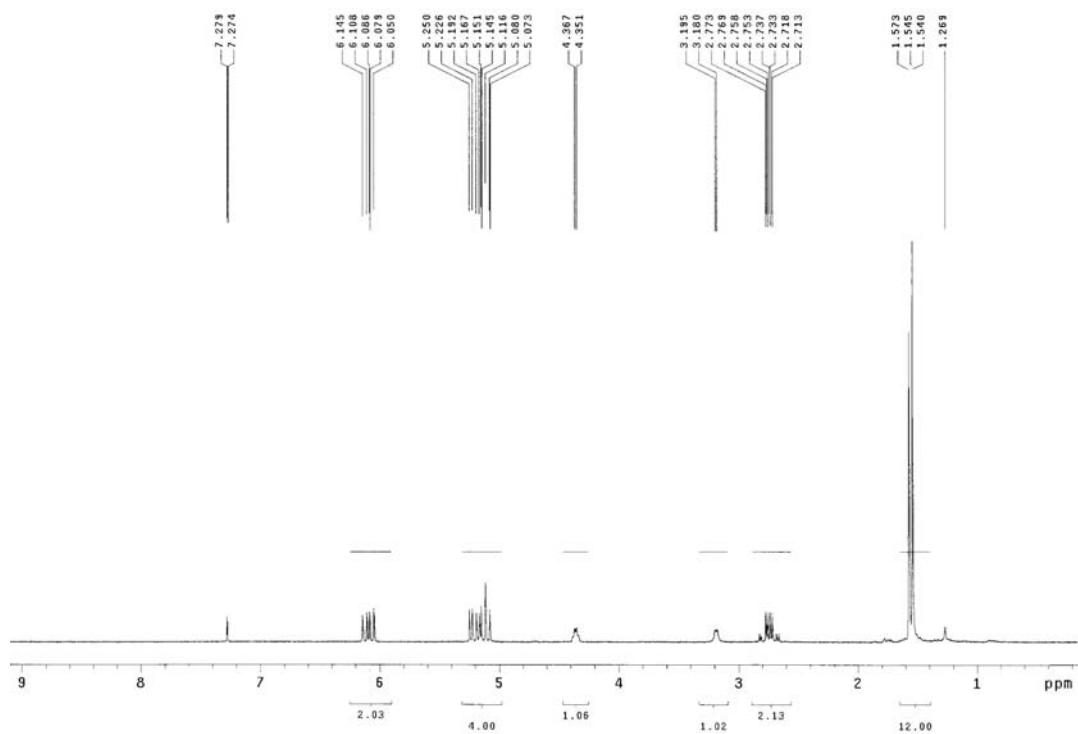
[α]<sub>D</sub><sup>24</sup> +45.0° (c 0.2, CH<sub>2</sub>Cl<sub>2</sub>).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 6.15-6.05 (m, 2H), 5.25-5.07 (m, 2H), 4.35 (br d, *J* = 4.8 Hz, 1H), 3.18 (d, *J* = 4.8 Hz, 1H), 2.79 (dd, *J* = 16.5, 4.5 Hz, 1H), 2.69 (dd, *J* = 16.5, 6.0 Hz, 1H), 1.57 (s, 6H), 1.54 (s, 6H).

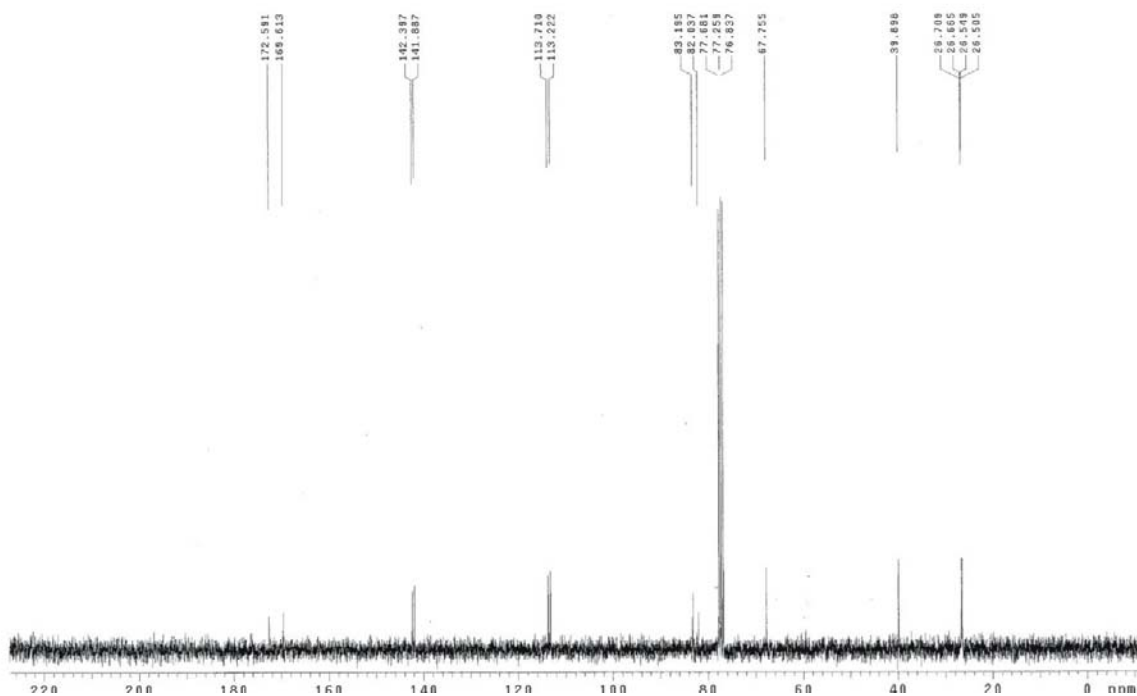
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 172.6, 169.6, 142.4, 141.9, 113.7, 113.2, 83.2, 82.0, 67.7, 39.9, 26.7, 26.6, 26.5, 26.5.

**FTIR** (neat): ν 3501, 2982, 2934, 1733, 1652, 1558, 1471, 1456, 1416, 1380, 1273, 1199, 1161, 1125, 1048, 989, 925, 842, 750 cm<sup>-1</sup>.

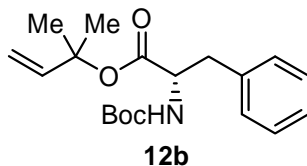
**HRMS** (CI) Calcd. for C<sub>14</sub>H<sub>23</sub>O<sub>5</sub> [M+1]: 271.1545, Found: 271.1550.



KIS 32-5  
Pulse Sequence: s2pu1



## 2-Methylbut-3-en-2-yl 2-(*S*)-(tert-butoxycarbonylamino)-3-phenylpropanoate (**12b**)



To an oven-dried reaction vessel under one atmosphere of argon gas charged with (*S*)-2-(tert-butoxycarbonylamino)-3-phenylpropanoic acid<sup>1</sup> (**12a**) (79.6 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (24.5 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 24 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:8) provided **12b** (74 mg, 0.221 mmol) as a clear syrup in 74% yield.

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.28 (ethyl acetate:hexanes, 1:8).

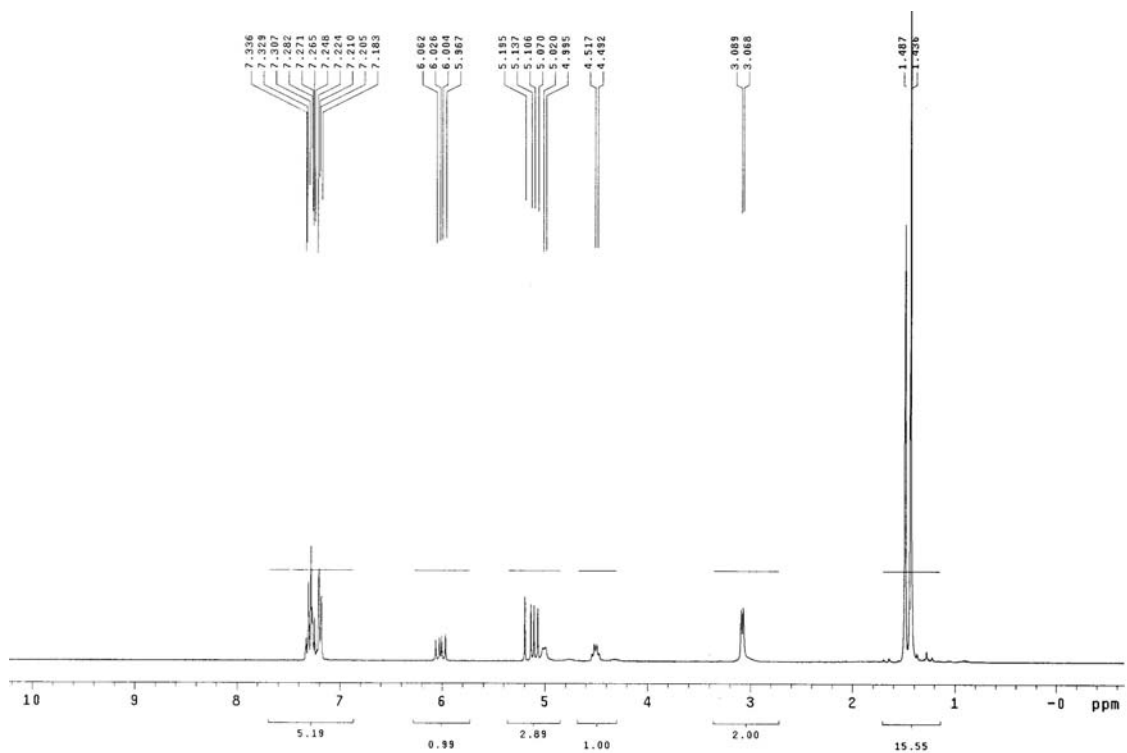
[α]<sub>D</sub><sup>24</sup> +15.0° (c 1.0, CH<sub>2</sub>Cl<sub>2</sub>).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 7.34-7.18 (m, 5H), 6.01 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.16 (d, *J* = 17.4 Hz, 1H), 5.08 (d, *J* = 10.8 Hz, 1H), 5.01 (d, *J* = 7.5 Hz, 1H), 4.50 (dd, *J* = 7.5, 6.3 Hz, 1H), 3.07 (d, *J* = 6.3 Hz, 2H), 1.48 (s, 6H), 1.43 (s, 9H).

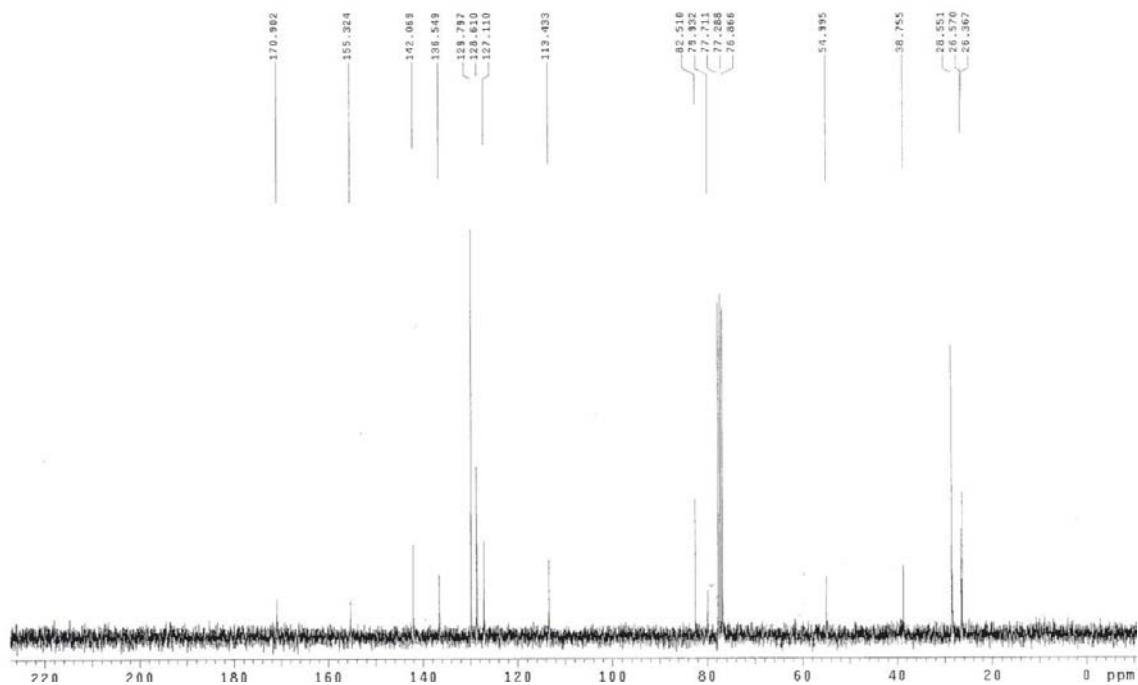
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 170.9, 155.3, 142.1, 136.5, 129.8, 128.6, 127.1, 113.4, 82.5, 79.9, 55.0, 38.7, 28.5, 26.6, 26.4.

**FTIR** (neat): ν 3438, 3369, 3088, 3064, 3029, 2979, 2933, 1736, 1724, 1691, 1679, 1528, 1452, 1413, 1390, 1365, 1256, 1214, 1127, 1079, 1055, 1014, 992, 752, 700 cm<sup>-1</sup>.

**HRMS** (CI) Calcd. for C<sub>19</sub>H<sub>28</sub>NO<sub>4</sub> [M+1]: 334.2018, Found: 334.2017.

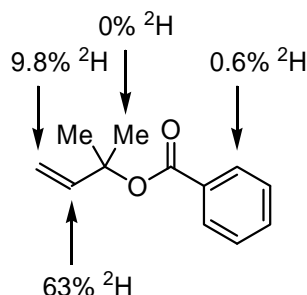


KIS 35-15  
Pulse Sequence: s2pu1



## Experimental Details for Mechanistic Studies

### **3-Deuterio-2-methylbut-3-en-2-yl benzoate ((*O*-<sup>2</sup>H)-1a)**



Benzoic acid-*d* ((*O*-<sup>2</sup>H)-**1a**, 98% deuterium incorporation) was purchased from Aldrich. To an oven-dried reaction vessel under one atmosphere of argon gas charged with benzoic acid-*d* ((*O*-<sup>2</sup>H)-**1a**) (369 mg, 3.000 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (20 mg, 0.030 mmol, 1 mol%), BIPEHP (31 mg, 0.060 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (19.5 mg, 0.060 mmol, 2 mol%) was added 1,2-dichloroethane (30 mL, 0.1 M) followed by 1,1-dimethylallene (245 mg, 3.600 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 24 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:30) provided the title compound (400 mg, 2.090 mmol) as a clear oil in 70% yield.

**TLC** (SiO<sub>2</sub>): R<sub>f</sub> = 0.30 (ethyl acetate:hexanes, 1:30).

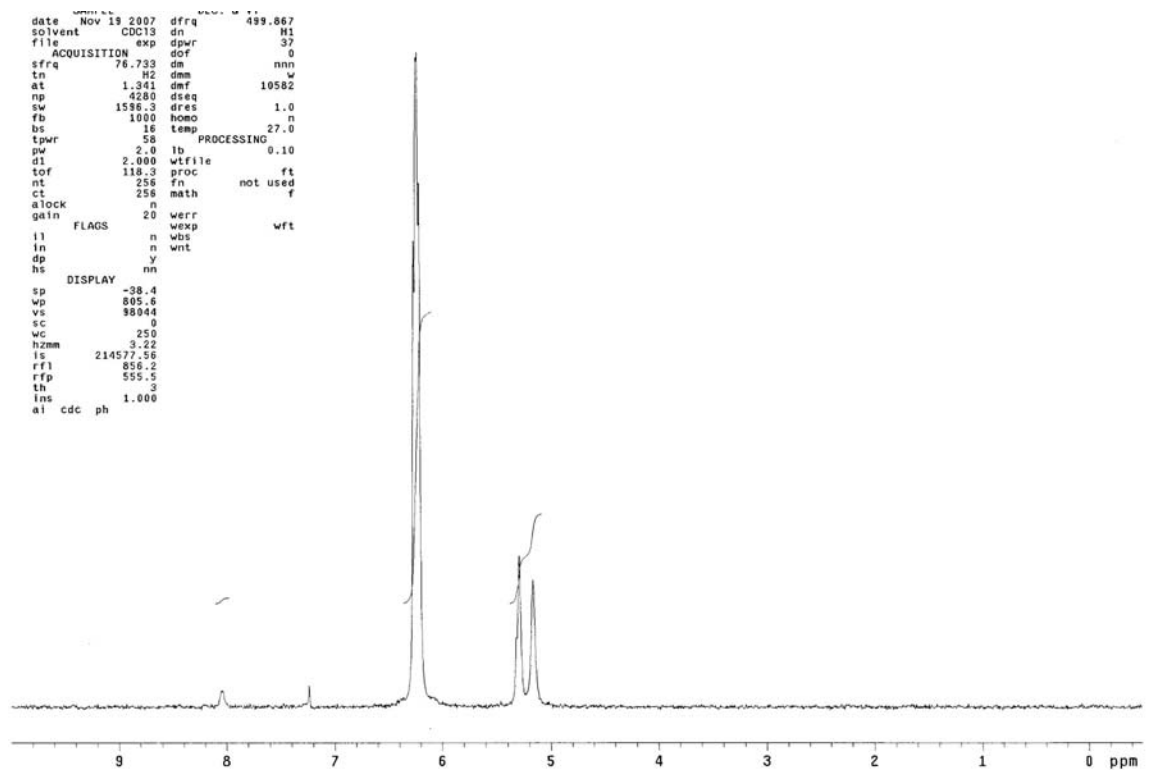
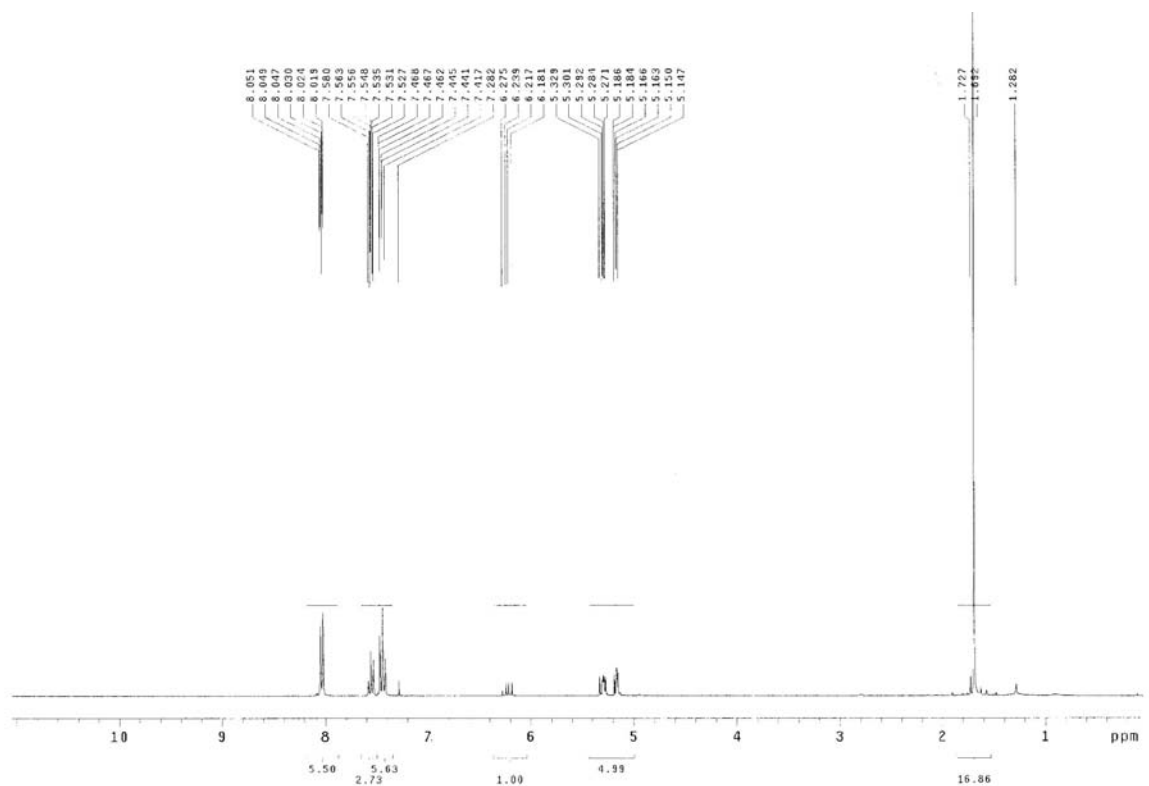
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 8.03 (d, *J* = 6.9 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 6.22 (dd, *J* = 17.4, 10.8 Hz, 0.36H), 5.33-5.14 (m, 1.77H), 1.69 (s, 6H).

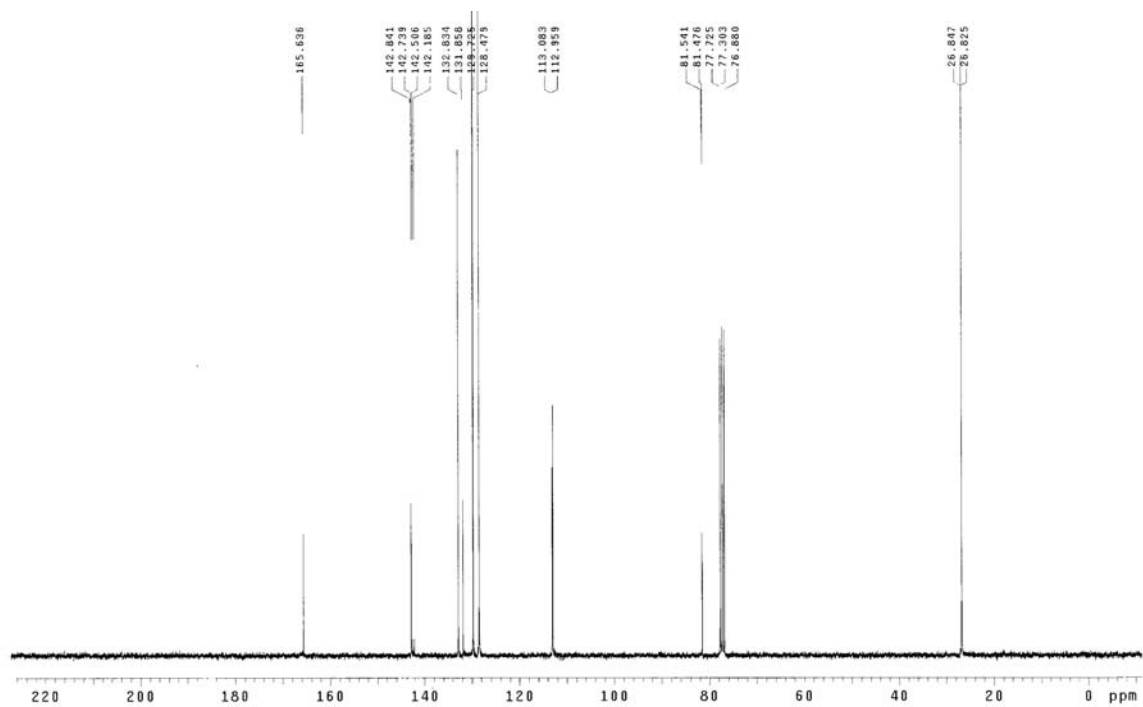
**<sup>2</sup>H NMR** (77 MHz, CHCl<sub>3</sub>): δ 8.04 (s, 0.02<sup>2</sup>H), 6.22 (m, 1.0<sup>2</sup>H), 5.29 (s, 0.15<sup>2</sup>H), 5.16 (s, 0.15<sup>2</sup>H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 165.6, 142.8, 142.7, 142.5, 142.2, 132.8, 131.8, 129.7, 128.5, 113.1, 112.9, 81.5, 81.5, 26.8, 26.8.

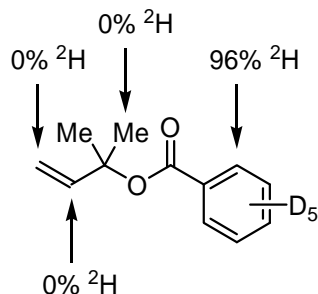
**FTIR** (neat): ν 2981, 1715, 1450, 1379, 1365, 1313, 1285, 1237, 1202, 1134, 1108, 1069, 1026, 921, 846, 711 cm<sup>-1</sup>.

**HRMS** (CI) Calcd. for C<sub>12</sub>H<sub>14</sub><sup>2</sup>HO<sub>2</sub> [M+1]: 192.1135, Found: 192.1134.





## 2-Methylbut-3-en-2-yl pentadeuterio-benzoate ((<sup>2</sup>H)<sub>5</sub>-1a)



Benzoic-*d*<sub>5</sub> acid ((<sup>2</sup>H)<sub>5</sub>-1a, 99% deuterium incorporation) was purchased from Aldrich. To an oven-dried reaction vessel under one atmosphere of argon gas charged with benzoic-*d*<sub>5</sub> acid ((<sup>2</sup>H)<sub>5</sub>-1a) (38.2 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by 1,1-dimethylallene (24.5 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 24 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:30) provided the title compound (48 mg, 0.246 mmol) as a clear oil in 82% yield.

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.30 (ethyl acetate:hexanes, 1:30).

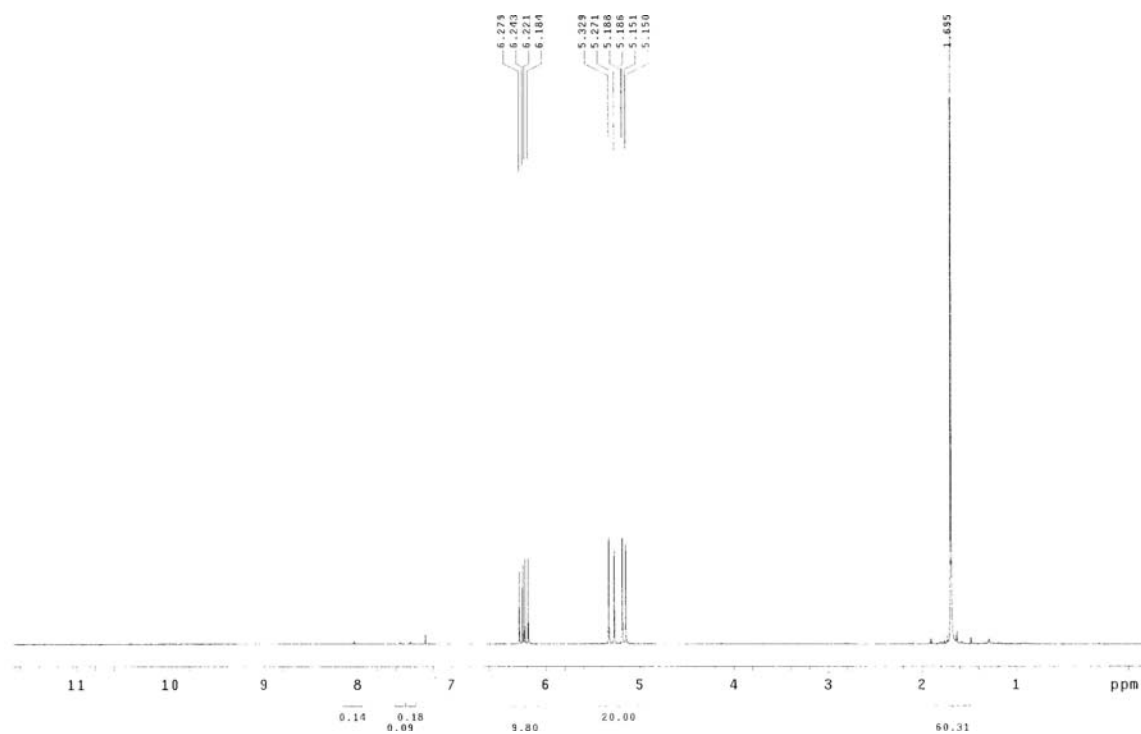
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 6.23 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.29 (d, *J* = 17.4 Hz, 1H), 5.16 (d, *J* = 10.8 Hz, 1H), 1.69 (s, 6H).

**<sup>2</sup>H NMR** (77 MHz, CHCl<sub>3</sub>): δ 8.03 (s, 1.92<sup>2</sup>H), 7.56 (s, 1.0<sup>2</sup>H), 7.44 (s, 2.0<sup>2</sup>H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 165.6, 142.8, 132.6, 132.3, 132.0, 131.7, 129.6, 129.3, 129.0, 128.3, 127.9, 127.6, 113.1, 81.5, 26.8.

**FTIR** (neat): ν 2981, 1716, 1413, 1382, 1364, 1331, 1252, 1230, 1200, 1165, 1132, 1079, 922, 850 cm<sup>-1</sup>.

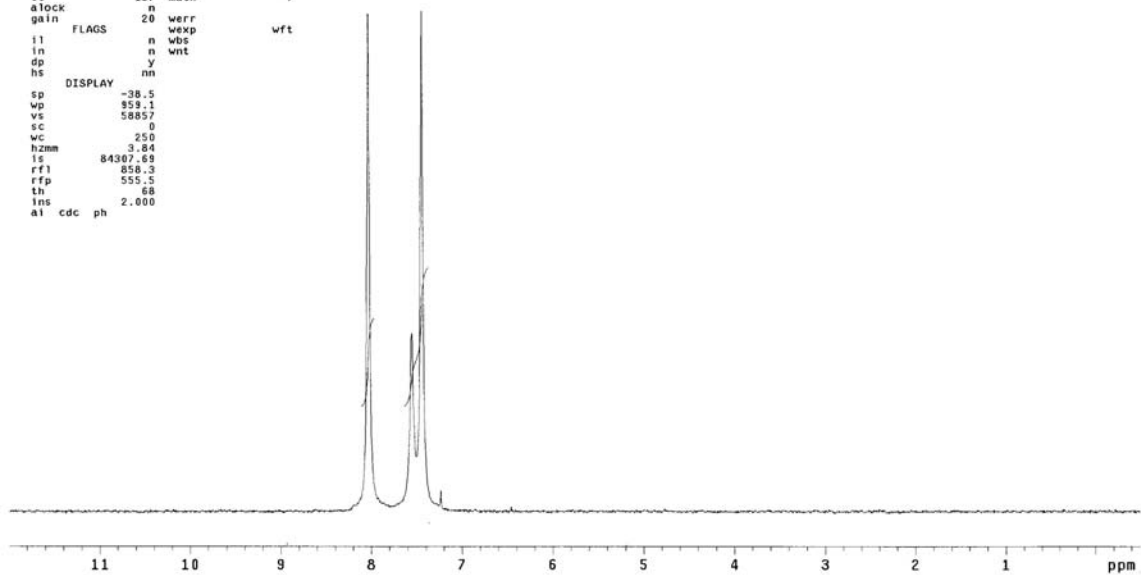
**HRMS** (CI) Calcd. for C<sub>12</sub>H<sub>14</sub><sup>2</sup>HO<sub>2</sub> [M+1]: 196.1386, Found: 196.1388.

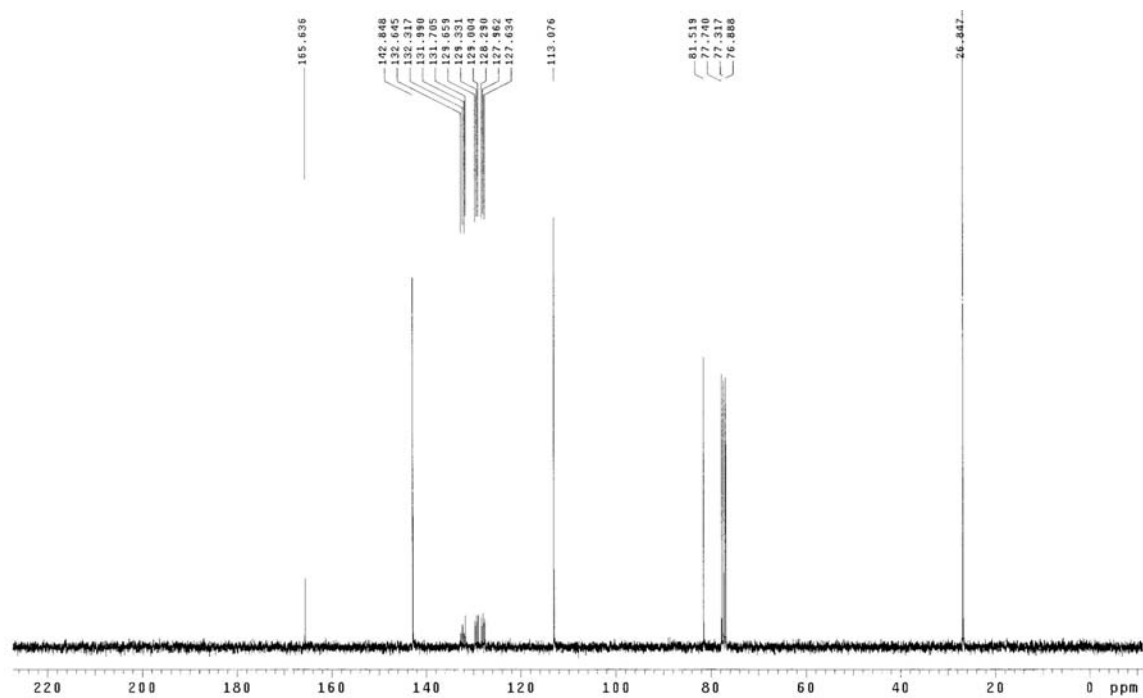


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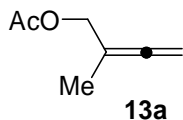
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## **Experimental Procedure and Spectral Data for the Preparation of Allenes (13a and 14a)**

### **2-Methylbuta-2,3-dienyl acetate (13a)**



To a stirred solution of 2-methylbuta-2,3-dien-1-ol<sup>4</sup> (0.2 g, 2.378 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (24 mL) was added acetic anhydride (0.27 mL, 2.853 mmol), triethylamine (0.8 mL, 5.706 mmol) and 4-(dimethylamino)pyridine (15 mg, 0.119 mmol) at 0 °C under one atmosphere of argon gas. The reaction mixture was stirred for 2 h at 0 °C and quenched with H<sub>2</sub>O (5 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the organic layer was washed with H<sub>2</sub>O and brine, dried over MgSO<sub>4</sub> and concentrated in vacuo. Purification of the product by column chromatography (SiO<sub>2</sub>: diethyl ether:pentane, 1:30) provided **13a** (0.21 g, 1.664 mmol) as a clear oil in 70% yield.

**TLC (SiO<sub>2</sub>)**: R<sub>f</sub> = 0.26 (diethyl ether:pentane, 1:30).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 4.75 (sextet, *J* = 2.7 Hz, 2H), 4.54 (t, *J* = 2.4 Hz, 2H), 2.09 (s, 3H), 1.73 (t, *J* = 3.0 Hz, 3H).

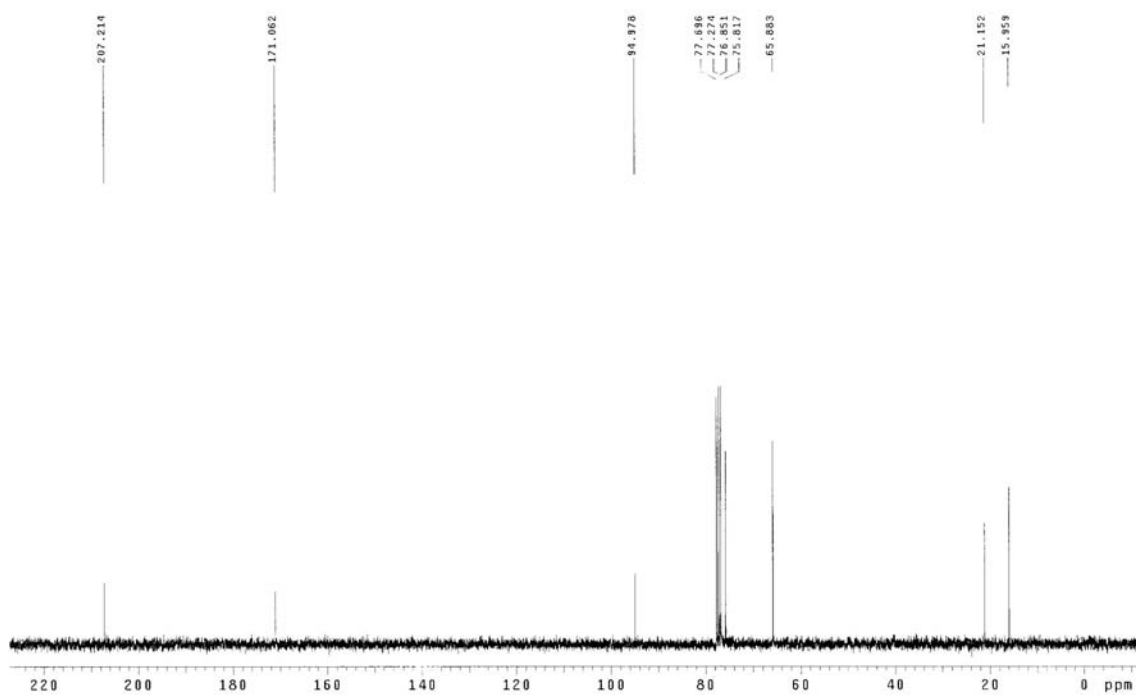
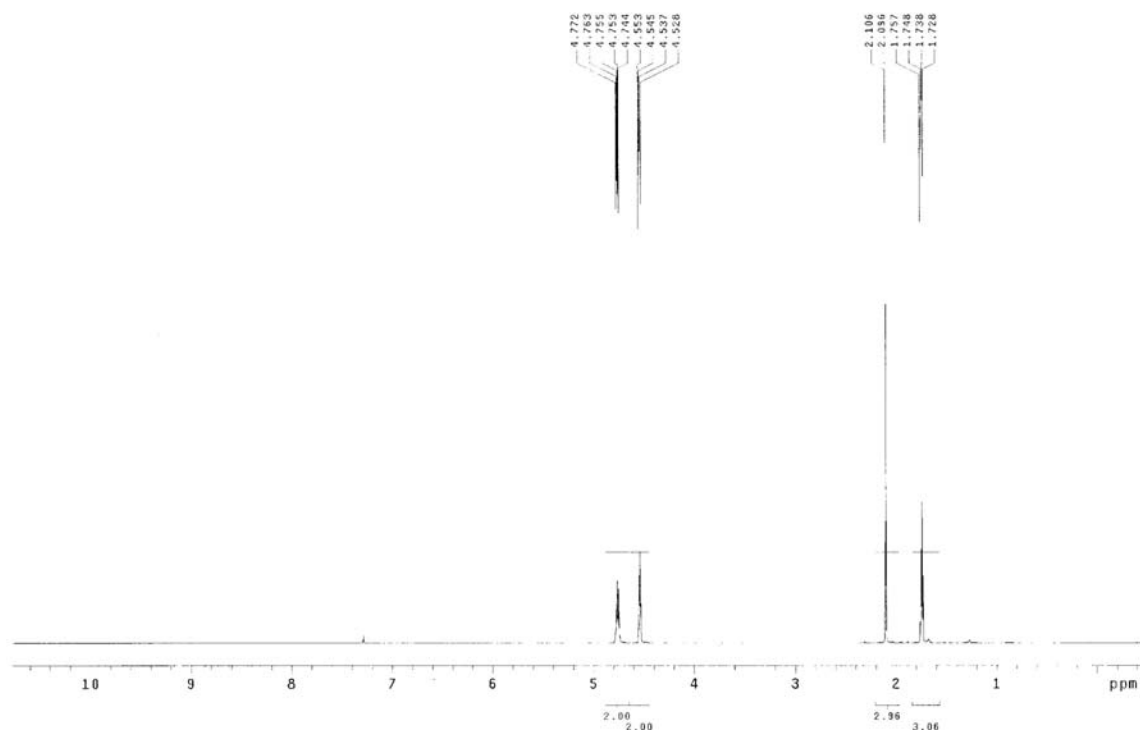
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 207.21, 171.06, 94.97, 75.81, 65.88, 21.15, 15.95.

**FTIR** (neat): ν 2942, 1965, 1765, 1443, 1371, 1231, 1027, 853 cm<sup>-1</sup>.

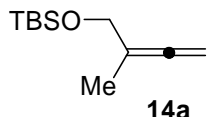
**HRMS** (CI) Calcd. for C<sub>7</sub>H<sub>11</sub>O<sub>2</sub> [M+1]: 127.0759, Found: 127.0762.

<sup>4</sup> For the preparation of 2-methylbuta-2,3-dien-1-ol, see: Cook, S. P.; Danishefsky, S. J. *Org. Lett.* **2006**, 8, 5693–5695.

Pulse Sequence: v2pu1



***tert*-Butyldimethyl(2-methylbuta-2,3-dienyloxy)silane (**14a**)**



To a stirred solution of 2-methylbuta-2,3-dien-1-ol<sup>4</sup> (0.2 g, 2.378 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (24 mL) was added *tert*-butyldimethylsilyl chloride (0.43 g, 2.853 mmol), triethylamine (0.8 mL, 5.706 mmol) and 4-(dimethylamino)pyridine (15 mg, 0.119 mmol) at 0 °C under one atmosphere of argon gas. The reaction mixture was stirred for 4 h at room temperature and quenched with H<sub>2</sub>O (5 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the organic layer was washed with H<sub>2</sub>O and brine, dried over MgSO<sub>4</sub> and concentrated in vacuo. Purification of the product by column chromatography (SiO<sub>2</sub>: diethyl ether:pentane, 1:100) provided **14a** (0.36 g, 1.815 mmol) as a clear oil in 76% yield.

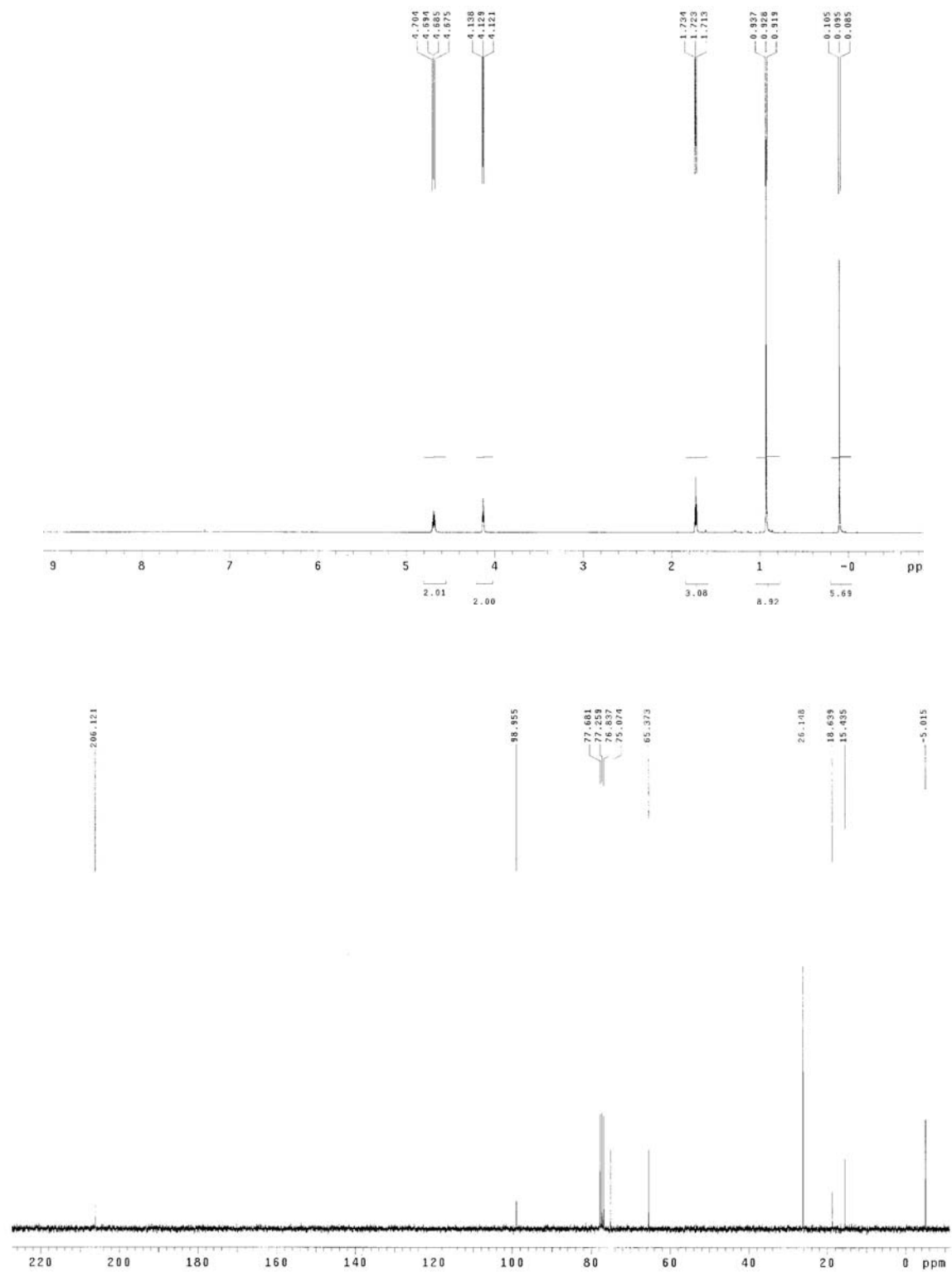
**TLC (SiO<sub>2</sub>)**: R<sub>f</sub> = 0.30 (diethyl ether:pentane, 1:100).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 4.68 (sextet, *J* = 3.0 Hz, 2H), 4.12 (t, *J* = 2.7 Hz, 2H), 1.72 (t, *J* = 3.0 Hz, 3H), 0.92 (s, 9H), 0.95 (s, 6H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 206.12, 98.95, 75.07, 65.37, 26.14, 18.63, 15.43, −5.01.

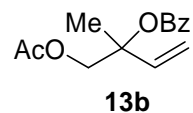
**FTIR** (neat): ν 2929, 2857, 1963, 1463, 1256, 1077, 839, 775 cm<sup>−1</sup>.

**HRMS** (CI) Calcd. for C<sub>11</sub>H<sub>23</sub>OSi [M+1]: 199.1518, Found: 199.1523.



## **Experimental Procedure and Spectral Data for the Coupling of Benzoic Acid and Allenes (13a and 14a)**

### **1-Acetoxy-2-methylbut-3-en-2-yl benzoate (13b)**



To an oven-dried reaction vessel under one atmosphere of argon gas charged with benzoic acid (**1a**) (36.6 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by **13a** (45.4 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 24 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:15) provided **13b** (54 mg, 0.218 mmol) as a clear oil in 73% yield.

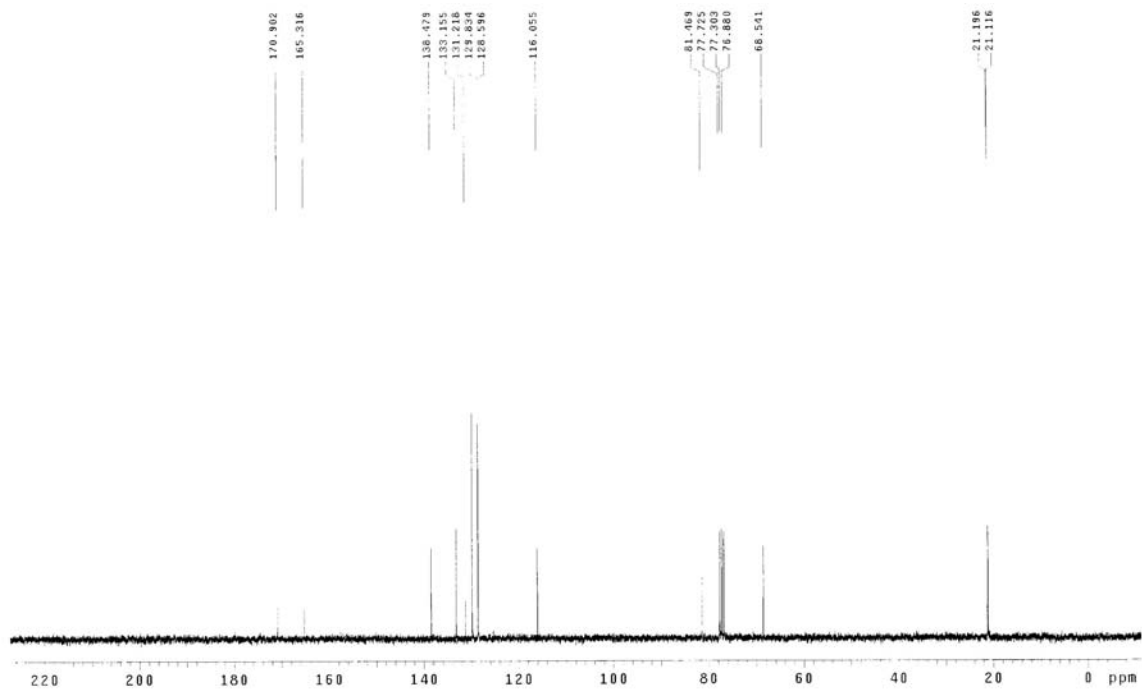
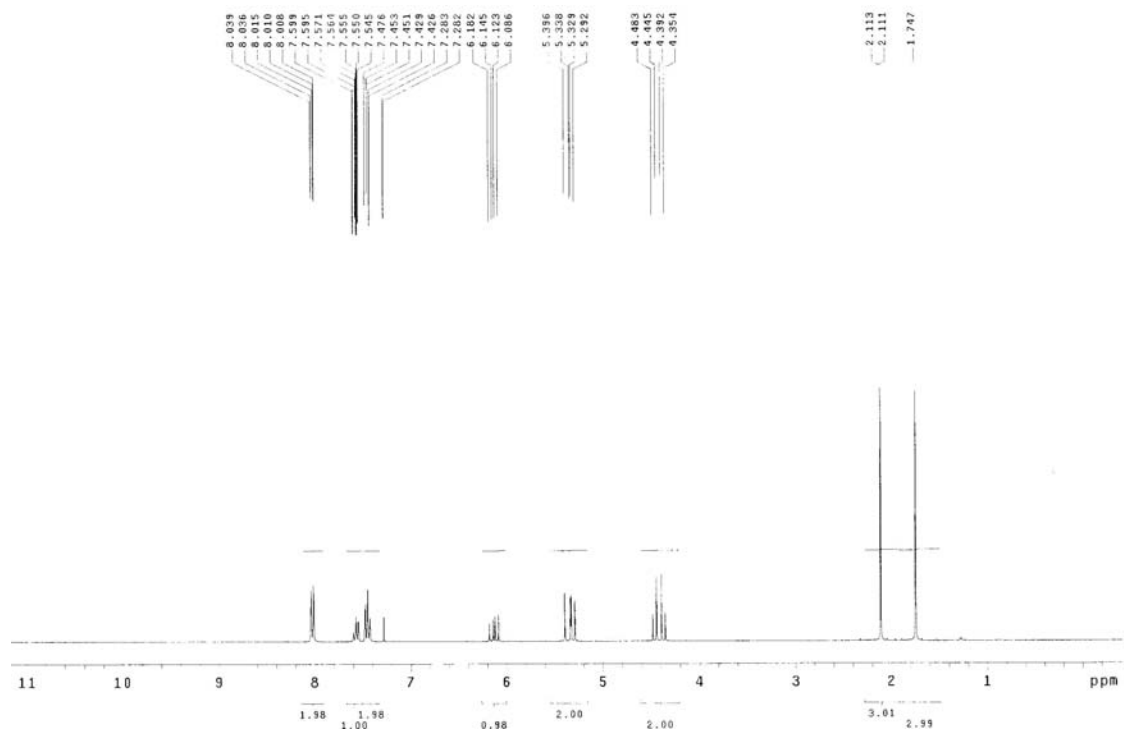
**TLC (SiO<sub>2</sub>)**: R<sub>f</sub> = 0.28 (ethyl acetate:hexanes, 1:15).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 6.13 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.36 (d, *J* = 17.7 Hz, 1H), 5.30 (d, *J* = 11.1 Hz, 1H), 4.46 (d, *J* = 11.4 Hz, 1H), 4.37 (d, *J* = 11.4 Hz, 1H), 2.11 (s, 3H), 1.74 (s, 3H).

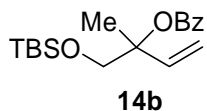
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 170.90, 165.31, 138.47, 133.15, 131.21, 129.83, 128.59, 116.05, 81.46, 68.54, 21.19, 21.11.

**FTIR** (neat): ν 2989, 1747, 1720, 1601, 1451, 1414, 1372, 1315, 1278, 1239, 1176, 1112, 1070, 1047, 1026, 991, 928, 882, 852, 712 cm<sup>-1</sup>.

**HRMS** (CI) Calcd. for C<sub>14</sub>H<sub>17</sub>O<sub>4</sub> [M+1]: 249.1127, Found: 249.1127.



**1-(*tert*-Butyldimethylsilyloxy)-2-methylbut-3-en-2-yl benzoate (**14b**)**



To an oven-dried reaction vessel under one atmosphere of argon gas charged with benzoic acid (**1a**) (36.6 mg, 0.300 mmol, 100 mol%), [Ir(cod)Cl]<sub>2</sub> (2.0 mg, 0.003 mmol, 1 mol%), BIPEHP (3.1 mg, 0.006 mmol, 2 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (1.95 mg, 0.006 mmol, 2 mol%) was added 1,2-dichloroethane (3.0 mL, 0.1 M) followed by **14a** (71.4 mg, 0.360 mmol, 120 mol%). The reaction mixture was allowed to stir at 60 °C for a period of 36 hours, at which point the reaction mixture was evaporated onto silica gel. Purification of the product by column chromatography (SiO<sub>2</sub>: ethyl acetate:hexanes, 1:30) provided **14b** (72 mg, 0.225 mmol) as a clear oil in 75% yield.

**TLC (SiO<sub>2</sub>):** R<sub>f</sub> = 0.26 (ethyl acetate:hexanes, 1:30).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 6.17 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.31 (d, *J* = 17.7 Hz, 1H), 5.25 (d, *J* = 11.1 Hz, 1H), 3.95 (d, *J* = 9.9 Hz, 1H), 3.81 (d, *J* = 9.9 Hz, 1H), 1.70 (s, 3H), 0.90 (s, 9H), 0.08 (s, 6H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ 165.60, 139.68, 132.85, 131.75, 129.78, 128.45, 114.99, 83.62, 68.41, 26.02, 21.05, 18.45, −5.19.

**FTIR** (neat): ν 2954, 2929, 2857, 1720, 1471, 1451, 1314, 1277, 1256, 1113, 1069, 1026, 837, 776, 710 cm<sup>−1</sup>.

**HRMS** (CI) Calcd. for C<sub>18</sub>H<sub>29</sub>O<sub>3</sub>Si [M+1]: 321.1886, Found: 321.1891.

