# **Supplementary Information**

# Enantioselective Pd-Catalyzed Tandem Allylic Alkylation Reaction Using Monodentate Phosphoramidite Ligands for the Formal Total Synthesis of Huperzine A

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# **General Information:**

All solvents used as reaction media were purified using the Solvent Purification System 400-4 from Innovative Technology, Inc. or distilled under nitrogen immediately before use. Ether and THF were distilled from Na/benzophenone ketyl. Toluene and CH<sub>2</sub>Cl<sub>2</sub> were distilled from CaH<sub>2</sub>. Solvents for extraction and chromatography were reagent grade and used as received. All chemicals were purchased from Aldrich or Acros Chemical Co., and were used without further purification unless otherwise noted. Microwave-assisted reactions were carried out with CEM Discover S series microwave reactor. 1H and <sup>13</sup>C NMR spectra were measured on Bruker Avance III HD-Nanobay 400 (400 MHz 1H; 100 MHz <sup>13</sup>C; 161.9 MHz <sup>31</sup>P), Varian Inova-400 (400 MHz 1H; 100 MHz<sup>13</sup>C), or Varian Gemini-2300 (300 MHz 1H; 75 MHz<sup>13</sup>C) spectrometer in a deuterated solvent using residual protons (CHCl<sub>3</sub>: 1H, 7.26 ppm; <sup>13</sup>C, 77.0 ppm) as the internal standard. Melting points were measured on a Thomas Hoover Capillary melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer Model 241 polarimeter. TLC was performed on Merck DC-Alufolien Kieselgel 60F 254 and flash column chromatography was carried out on Silicyle SiliaFlashP60®. Analytical HPLC was carried out with a Shimadzu LC-2010A HPLC system. Low-Resolution Mass Spectrometry was performed on Agilent 6890GC/5973 Mass Selective Detector. High-resolution mass spectrometric analyses were carried out at the Mass Spectrometry Laboratories, University of Illinois Urbana-Champaign, Urbana, IL or the Bioanalytical Laboratory of the Institute of Chemical Biology and Drug Discovery at Stony

Brook University. All reactions were carried out under nitrogen atmosphere in oven-dried glassware using standard Schlenck technique unless otherwise noted.

#### Methyl 6-hydroxy-2-methoxy-7,8-dihydroquinoline-5-carboxylate (1)<sup>1</sup>

1,4-Cyclohexanedione monoethylene ketal (3.00 g, 19.20 mmol), methyl propiolate (3.23 g, 38.41 mmol) were placed into a round bottom flask. A 7 N solution of ammonia in methanol (60 mL) was added to the reaction flask and the flask was sealed with a septum. Two 18 gauge needles were placed in the septum to vent. The round bottom flask was then placed into a stainless steel Parr reaction vessel and heated to 100 °C for 10 hours. After which point the pressure typically reached approximately 100 psi. After the 10 hour heating period the vessel was evacuated and the solvent was removed *in vaccuo*. The resulting red-orange solid was adhered to silica gel and subjected to column chromatography on silica gel (MeOH:CH<sub>2</sub>Cl<sub>2</sub> = 1:19) to give 1,5,7,8-tetrahydro-2H-spiro[quinoline-6,2'-[1,3]dioxolan]-2-one (**5**) as a light yellow solid (72%, 2.85 g): mp dec >220 °C, (lit.<sup>2</sup> mp dec >220 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  1.90 (t, 2 H, *J* = 4.8 Hz), 2.70 (s, 2 H), 2.86 (t, 2 H), 4.01 (s, 4 H), 6.38 (d, 1H, *J* = 6.9 Hz), 7.12 (d, 1 H, *J* = 6.9 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  26.1, 30.2, 36.4, 64.9, 107.5, 112.0, 117.9, 141.8, 143.6. All data are in agreement with the literature values.<sup>2</sup>

To a solution of **5** (1.75 g, 8.44 mmol) and Ag<sub>2</sub>CO<sub>3</sub> (4.66 g, 16.88 mmol) in CHCl<sub>3</sub> (50 mL) was added dropwise iodomethane (5.25 mL, 84.40 mmol). The reaction mixture was refluxed for 3 h. The resulting mixture was filtered through Celite and concentrated *in vacuo* to afford crude product as a yellow solid. The crude product was purified by column chromatography on silica gel (EtOAc:hexanes = 1:10 to 1:4) to give 2-methoxy-7,8-dihydro-5H-spiro[quinoline-6,2'-[1,3]dioxolane] (**6**) as a white needle crystal (1.56 g, 84% yield): mp 73–75 °C (lit.<sup>1</sup> 77.5–78.5 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  1.97 (t, 2 H, J = 6.9 Hz), 2.88 (s, 2 H), 2.97 (t, 2 H, J = 6.9 Hz), 3.87 (s, 3 H), 4.02 (s, 2H), 6.49 (d, 1 H, J = 8.1 Hz), 7.20 (d, 1 H, J = 8.1 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  31.0, 31.7, 53.5, 64.8, 108.1, 108.3, 121.7, 140.0, 152.9, 162.5. All data are in agreement with the literature values.<sup>1</sup>

Compound **6** (966 mg, 4.37 mmol) was dissolved in a 5%  $HCl_{(aq)}$  solution in acetone (1:1) and refluxed for 16 h. All volatiles were evaporated *in vacuo*. The aqueous layer was then basified with sat. NaHCO<sub>3(aq)</sub> until no more gas evolution was noted. The resulting solution was extracted with EtOAc (20 mL x 3). The combined organic layer was washed with brine, dried over anhydrous

MgSO<sub>4</sub>. The drying agent was removed by filtration and the solvent was evaporated *in vacuo* to afford 2-methoxy-7,8-dihydroquinolin-6(5H)-one (7) as a light yellow oil. The resulting 7 was used without further purification.

To a solution of **7** in dimethyl carbonate (25 mL) was added a solution of sodium hydride (60% w/v in mineral oil, 1.75 g, 43.7 mmol) in 10 mL of dimethyl carbonate. The reaction mixture was refluxed for 3 h and the reaction was quenched with MeOH (10 mL). All volatiles were removed *in vacuo* and the resulting solution was neutralized with sat. NH<sub>4</sub>Cl<sub>(aq)</sub> (10 mL). The resulting solution was then extracted with EtOAc (20 mL x 3). The combined organic layers were washed with brine and dried over anhydrous MgSO4. The drying agent was removed by filtration and the solvent was evaporated *in vacuo* to afford the crude product as a light yellow solid. The crude product was purified by column chromatography on silica gel (EtOAc:hexanes = 1:30 to 1:20) to give compound **1** as a light yellow solid (788 mg, 77% yield for two steps): mp 73–74 °C (lit.<sup>1</sup> mp 71–72 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.06 (t, *J* = 6.9 Hz, 2H), 2.91 (t, *J* = 8.1 Hz, 2H), 3.90 (s, 6H), 6.55 (d, *J* = 8.7 Hz, 1H) 7.89 (d, *J* = 8.4 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  29.3, 30.2, 52.0, 53.6, 98.5, 107.5, 120.0, 136.3, 151.3, 161.3, 172.2, 177.0. All data are in agreement with the literature values.<sup>1</sup>

# 2-Methylenepropane-1,3-diyl diacetate (2a)<sup>3</sup>

1,3-(2-Methylene)propandiol (407 mg, 4.62 mmol) and 0.033 mL of pyridine were placed in a 10 mL round-bottomed flask. To this solution 3 mL of acetic anhydride was added. The reaction mixture was then refluxed overnight. The excess acetic anhydride was removed *in vacuo* and ice water was added to the resulting solution. The aqueous layer was then basified with sat. NaHCO<sub>3(aq)</sub> until no more gas evolution was noted. The aqueous layer was separated and extracted with Et<sub>2</sub>O (10 mL x 3). The combined organic layer was washed with water (20 mL) and brine (20 mL), and dried over anhydrous MgSO<sub>4</sub>. The drying agent was removed by filtration and the solvent was evaporated *in vacuo* to afford the product **2a** as colorless oil. (694 mg, 87% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.16 (s, 6H), 4.67 (s, 4H), 5.35 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  21.1, 64.7, 116.9, 138.8, 170.1. All data are in agreement with the literature values.<sup>3</sup>

#### **Dimethyl 2-methylenepropane-1,3-diyl dicarbonate** (2b)<sup>4</sup>

1,3-(2-Methylene)propandiol (250 mg, 2.84 mmol) and DMAP (1.275 g, 5.68 mmol) were

introduced to a 35 mL microwave reaction vessel, followed by CH<sub>2</sub>Cl<sub>2</sub> (15 mL) under nitrogen at room temperature. The mixture was then cooled to 0 °C and the methyl chloroformate (1.16 g, 8.52 mmol) was added dropwise with stirring. The reaction mixture was warmed to room temperate and placed in a microwave reactor for 90 min at 40 °C. The reaction was quenched by adding sat. NaCl<sub>(aq)</sub> (10 mL). The aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL x 3). The combined organic layer was washed with water (40 mL) and brine (40 mL), and dried over anhydrous MgSO4. The drying agent was removed by filtration and the solvent evaporated *in vacuo* to afford the crude product as yellow oil. The crude product was purified by column chromatography on silica gel (EtOAc:hexanes = 1:10 to 1:4) to give **2b** as a colorless oil (367 mg, 64% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  3.80 (s, 6H), 4.67 (s, 4H), 5.35 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  54.7, 67.4, 117.8, 137.6, 155.2. All data are in agreement with the literature values.<sup>4</sup>

#### Di-*n*-butyl 2-methylenepropane-1,3-diyl di-*n*-butyl dicarbonate (2c)

1,3-(2-Methylene)propandiol (274 mg, 3.11 mmol) and pyridine (2.51 mL, 31.1 mmol) were introduced to a 35 mL microwave reaction vessel, followed by CH<sub>2</sub>Cl<sub>2</sub> (15 mL) under nitrogen at room temperature. The mixture was then cooled to 0 °C and the butyl chloroformate (1.60 mL, 12.4 mmol) was added dropwise with stirring. The reaction mixture was warmed to room temperate and placed in a microwave reactor for 60 min at 50 °C. The reaction was quenched by adding sat. CuSO<sub>4(aq)</sub> (15 mL). The aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL x 3). The combined organic layer was washed with water (40 mL) and brine (40 mL), and dried over anhydrous MgSO<sub>4</sub>. The drying agent was removed by filtration and the solvent was evaporated *in vacuo* to afford the crude product as yellow oil. The crude product was purified by column chromatography on silica gel (EtOAc:hexanes = 1:10 to 1:4) to give **2c** as a colorless oil (858 mg, 96% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  0.88 (t, *J* = 7.5 Hz, 6H) 1.33 (q, *J* = 7.8 Hz, 4H), 1.59 (q, *J* = 8.1 Hz, 4H), 4.09 (t, *J* = 6.9 Hz, 4H), 4.63 (s, 4H), 5.31 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  13.4, 18.7, 67.3, 67.9, 154.8. HRMS (ESI<sup>+</sup>) calcd. for C<sub>14</sub>H<sub>28</sub>NO<sub>6</sub> [M+NH<sub>4</sub>]<sup>+</sup> 306.1911, found 306.1913 ( $\Delta$  = 0.7 ppm).

Compounds **2d** to **2h** were obtained in the same manner as that described for the synthesis of **2c** with some variations.

## 2-Methylenepropane-1,3-diyl divinyl dicarbonate (2d)

Purification of the crude product by column chromatography on silica gel (EtOAc:hexanes = 1:10 to 1:4) afforded **2d** as a colorless oil (58% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  4.58 (dd, J = 5.4, 1.2 Hz, 2H), 4.74 (s, 4H), 4.90 (dd, J = 3.0, 0.9 Hz, 2H), 5.41 (s, 2H), 7.03 (dd, J = 21, 6.0 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  68.0, 98.1, 119.4, 136.7, 142.5, 152.4. HRMS (ESI<sup>+</sup>) calcd. for C<sub>10</sub>H<sub>16</sub>NO<sub>6</sub> [M+NH<sub>4</sub>]<sup>+</sup> 246.0972, found 246.0975 ( $\Delta = 1.2$  ppm).

# 2-Methylenepropane-1,3-diyl diprop-1-en-2-yl dicarbonate (2e)

Purification of the crude product by column chromatography on silica gel (EtOAc:hexanes = 1:10 to 1:4) afforded **2e** as a light yellow oil (93% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.92 (s, 6H), 4.66 (s, 2H), 4.67 (s, 4H), 5.36 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  18.9, 67.7, 101.8, 118.6, 137.0, 152.4, 152.8; HRMS (ESI<sup>+</sup>) calcd. for C<sub>12</sub>H<sub>20</sub>NO<sub>6</sub> [M+NH<sub>4</sub>]<sup>+</sup> 274.1291, found 274.1285 ( $\Delta$  = -2.2 ppm).

#### 2-Methylenepropane-1,3-diyl dibenzyl dicarbonate (2f)

Purification of the crude product by column chromatography on silica gel (EtOAc:hexanes = 1:10 to 1:4) afforded **2f** as a colorless oil (84% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  4.76 (s, 4H), 5.23 (s, 2H), 5.42 (s 2H), 7.41 (m, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  60.3, 67.7, 69.7, 118.2, 128.3, 128.5, 128.5, 137.4, 154.7. HRMS (ESI<sup>+</sup>) calcd. for C<sub>20</sub>H<sub>24</sub>NO<sub>6</sub> [M+NH<sub>4</sub>]<sup>+</sup> 374.1598, found 374.1598 ( $\Delta$  = 0 ppm).

#### Bis[(9*H*-fluoren-9-yl)methyl] 2-methylenepropane-1,3-diyl dicarbonate (2g)

Purification of the crude product by flash column chromatography on silica gel (EtOAc:hexanes = 1:10 to 1:4) afforded **2g** as a light yellow oil (99% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  4.30 (t, *J* = 7.2 Hz, 2H), 4.47 (d, *J* = 7.2 Hz, 4H), 4.79 (s, 4H), 5.44 (s, 2H), 7.36 (t, *J* = 7.6 Hz, 4H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.66 (d, *J* = 7.6 Hz, 4H), 7.80 (d, *J* = 7.6 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  46.6, 67.7, 69.9, 118.3, 120.0, 125.1, 127.1, 127.8, 137.5, 141.2, 143.2, 154.8; HRMS (ESI<sup>+</sup>) calcd. for C<sub>34</sub>H<sub>32</sub>NO<sub>6</sub> [M+NH<sub>4</sub>]<sup>+</sup> 550.2230, found 550.2224 ( $\Delta$  = -1.1 ppm).

## 2-Methylenepropane-1,3-diyl 4-nitrobenzyl dicarbonate (2h)

Purification of the crude product by flash column chromatography on silica gel (EtOAc:hexanes = 1:10 to 1:4) afforded **2h** as a light yellow oil (82% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  4.70 (s, 4H), 5.23 (s, 4H), 5.37 (s, 2H), 7.51 (d, *J* = 8.8 Hz, 4H), 8.18 (d, *J* = 8.8 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  67.9, 68.0, 118.9, 123.7, 128.2, 136.9, 142.2, 147.7, 154.4; HRMS (ESI<sup>+</sup>) calcd. for C<sub>20</sub>H<sub>22</sub>N<sub>3</sub>O<sub>10</sub> [M+NH<sub>4</sub>]<sup>+</sup> 464.1300, found 464.1300 ( $\Delta$  = 0.0 ppm).

#### tert-Butyl 2-methylenepropane-1,3-diyl dicarbonate (2i)

To a solution of 1,3-(2-methylene)propandiol (535 mg, 6.07 mmol), (*t*-Boc)<sub>2</sub>O (3.58 g, 16.4 mmol) and tetrabutylammonium hydrogen sulfate (350 mg, 1.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added dropwise 6 N NaOH<sub>(aq)</sub> (7 mL) at 0 °C and the mixture was stirred overnight at room temperature. The reaction was quenched by adding water. The aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL x 3). The combined organic layer was washed with water (40 mL) and brine (40 mL), and dried over anhydrous MgSO<sub>4</sub>. The drying agent was removed by filtration and the solvent was evaporated *in vacuo* to afford the crude product as a yellow oil. The crude product was purified by column chromatography on silica gel (EtOAc:hexanes = 1:10 to 1:4) to give **2i** as a colorless oil (1.43 g, 82% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.37 (s, 18H), 4.45 (s, 4H), 5.16 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  27.4, 66.5, 81.7, 116.7, 138.2, 152.8; HRMS (ESI<sup>+</sup>) calcd. for C<sub>14</sub>H<sub>24</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup> 311.1471, found 311.1464 ( $\Delta$  = -2.2 ppm).

# General procedure for preparations of phosphoramidite ligands<sup>5</sup>

Phosphorous trichloride (87 mL, 1.0 mmol) was added dropwise to Et<sub>3</sub>N (70 mL, 5 mmol) at 0 °C under N<sub>2</sub>. To this mixture was added a solution of an amine (1.0 mmol) in THF (2 mL). The mixture was stirred at room temperature and monitored by <sup>31</sup>P-NMR until the peak of the aminophosphorous dichloride was solely observed together with the disappearance of the peaks of PCl<sub>3</sub> in THF/Et<sub>3</sub>N. The mixture was then cooled to 0 °C and a solution of 5,5',6,6-tetramethylbiphenyl-2,2'-diol (242 mg, 1.0 mmol) in THF (3 mL) was added. The resulting mixture was stirred for 12 h at room temperature. After addition of ether (2 mL), the resulting solid was quickly filtered off on a short pad of silica gel and washed with ether. The combined solution was concentrated *in vacuo* to give a crude product. Purification of the crude product by column chromatography on a short silica gel column using EtOAc/hexanes as eluent afforded the desired phosphoramidite ligand.

# *O,O'-(R)-(5,5',6,6'-Tetramethylbiphenyl-2,2'-diyl)-N,N-[(S)-1-phenylethyl][(S)-1-(2-methoxyphenyl)ethyl]phosphoramidite ((R,S,S)-MPN-L3)*

(*R*,*S*,*S*)-**MPN-L3** (63% yield) was obtained as a white solid: mp 139.0–140.0 °C ; [ $\alpha$ ] $_{D}^{22}$  – 178.0 (*c* 0.50, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.54 (d, *J* = 6.9 Hz, 3H), 1.66 (dd, *J* = 1.6, 7.5 Hz, 3H), 2.01 (s, 3H), 2.03 (s, 3H), 2.26 (s, 3H), 2.31 (s, 3H), 3.53 (s, 3H), 4.53–4.59 (m, 1H), 4.83–4.93 (m, 1H), 6.46 (dd, *J* = 1.1, 8.2 Hz, 1H), 6.77 (td, *J* = 1.1, 7.5 Hz, 1H), 6.83–6.92 (m, 3H), 6.98 (ddd, *J* = 1.7, 7.3, 8.1 Hz, 1H), 7.04–7.23 (m, 6H) 7.44 (dt, *J* = 1.5, 7.7 Hz, 1H); <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>)  $\delta$  139.0; HRMS (ESI<sup>+</sup>) calcd for C<sub>33</sub>H<sub>37</sub>NO<sub>3</sub>P [M+H]<sup>+</sup> 526.2511, found 526.2509 ( $\Delta$  = -0.4 ppm).

# *O,O'-(S)-(3,3',5,5',6,6'-Hexamethylbiphenyl-2,2'-diyl)-N,N-[(S)-1-phenylethyl][(S)-1-(2-methoxyphenyl)ethyl]phosphoramidite ((S,S,S)-MPN-L6)*

(S,S,S)-**MPN-L6** (67% yield) was obtained as a white solid: mp 121.0–123.0 °C ; [ $\alpha$ ]<sub>D</sub><sup>22</sup> +63.9 (*c* 0.72, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.50 (d, *J* = 7.0 Hz, 3H), 1.57 (dd, *J* = 1.3, 7.2 Hz, 3H), 1.85 (s, 3H), 1.89 (s, 3H), 1.98 (s, 3H), 2.21 (s, 3H), 2.25 (s, 3H), 2.43 (d, *J* = 0.9 Hz, 3H), 3.61 (s, 3H), 4.47–4.54 (m, 1H), 4.87–4.95 (m, 1H), 6.63–6.69 (m, 1H), 6.81–6.87 (m, 2H), 7.05–7.19 (m, 7H), 7.64 (dd, *J* = 1.7, 7.6 Hz, 1H); <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>)  $\delta$  142.2; HRMS (ESI<sup>+</sup>) calcd for C<sub>35</sub>H<sub>41</sub>NO<sub>3</sub>P [M+H]<sup>+</sup> 554.2824, found 554.2822 ( $\Delta$  = –0.4 ppm).

# References

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