

## Iron(II) PNP Complexes as Catalysts for the Selective Formation of 3-Hydroxyacrylates from Aromatic Aldehydes and Ethyldiazoacetate

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### Supporting Information

#### Experimental Section

**General.** The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker AVANCE-250 spectrometer and were referenced to SiMe<sub>4</sub>.

**General Procedure for the Iron(II) Catalyzed Synthesis of 3-Hydroxyacrylates.** Aldehyde (1 equiv.) and ethyldiazoacetate (1 equiv) were added to a solution of the catalyst (10 mol%) in CH<sub>3</sub>NO<sub>2</sub> (5 mL) and the mixture was stirred at room temperature for 16 h. The mixture was then filtered through a plug of silica to remove the catalyst and the product was purified by chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>).

**3-Hydroxy-2-(4-methoxyphenyl)acrylic acid ethyl ester** (Table 2, entries 1 and 2): <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 20°C): 12.05 (d, *J* = 12.6 Hz, 1H, CHOH), 7.23 (d, *J* = 12.6 Hz, 1H, CHOH), 7.17 (d, *J* = 8.7 Hz, Ph<sup>2,6</sup>), 6.86 (d, *J* = 8.9 Hz, 2H, Ph<sup>3,5</sup>), 4.26 (q, *J* = 7.1 Hz, 2H, COOCH<sub>2</sub>CH<sub>3</sub>), 3.78 (s, 3H, OCH<sub>3</sub>), 1.27 (t, *J* = 7.2 Hz, 3H, COOCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>, 20°C): 171.8 (COOCH<sub>2</sub>CH<sub>3</sub>), 162.8 (CHOH), 158.7 (Ph), 130.5 (Ph), 126.4 (Ph), 113.6 (Ph), 108.1 (CCHOH), 60.8 (COOCH<sub>2</sub>CH<sub>3</sub>), 55.1 (OCH<sub>3</sub>), 14.1 (COOCH<sub>2</sub>CH<sub>3</sub>).

**3-Hydroxy-2-(4-fluorophenyl)acrylic acid ethyl ester** (Table 2, entries 3 and 4): <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 20°C): 12.08 (d, *J* = 12.6 Hz, 1H, CHOH), 7.25 – 7.17 (m, 3H, CHOH and Ph<sup>2,6</sup>), 6.98 (t, *J* = 8.8 Hz, 2H, Ph<sup>3,5</sup>), 4.25 (q, *J* = 7.2 Hz, 2H, COOCH<sub>2</sub>CH<sub>3</sub>), 1.25 (t, *J* = 7.1 Hz, 3H, COOCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>, 20°C): 171.4 (COOCH<sub>2</sub>CH<sub>3</sub>), 163.3 (CHOH), 160.0 (Ph), 131.0 (Ph), 127.6 (Ph), 114.9 (Ph), 107.6 (CCHOH), 60.9 (COOCH<sub>2</sub>CH<sub>3</sub>), 14.0 (COOCH<sub>2</sub>CH<sub>3</sub>).

**3-Hydroxy-2-(4-chlorophenyl)acrylic acid ethyl ester** (Table 2, entries 5 and 6):  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ): 12.13 (d,  $J = 12.6$  Hz, 1H,  $\text{CHOH}$ ), 7.29 – 7.15 (m, 5H,  $\text{CHOH}$  and Ph), 4.27 (q,  $J = 7.2$  Hz, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 1.27 (t,  $J = 7.2$  Hz, 3H,  $\text{COOCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ): 171.2 ( $\text{COOCH}_2\text{CH}_3$ ), 163.5 ( $\text{CHOH}$ ), 132.7 (Ph), 130.6 (Ph), 128.3 (Ph), 107.6 ( $\text{CCHOH}$ ), 61.1 ( $\text{COOCH}_2\text{CH}_3$ ), 14.1 ( $\text{COOCH}_2\text{CH}_3$ ).

**3-Hydroxy-2-(4-bromophenyl)acrylic acid ethyl ester** (Table 2, entries 7 and 8):  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ): 12.13 (d,  $J = 12.6$  Hz, 1H,  $\text{CHOH}$ ), 7.44 (d,  $J = 8.5$  Hz, 2H,  $\text{Ph}^{3,5}$ ), 7.27 (d,  $J = 12.6$  Hz, 1H,  $\text{CHOH}$ ), 7.13 (d,  $J = 8.5$  Hz, 2H,  $\text{Ph}^{2,6}$ ), 4.28 (q,  $J = 7.2$  Hz, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 1.28 (t,  $J = 7.2$  Hz, 3H,  $\text{COOCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ): 171.2 ( $\text{COOCH}_2\text{CH}_3$ ), 163.5 ( $\text{CHOH}$ ), 133.0 (Ph), 131.3 (Ph), 131.0 (Ph), 121.0 (Ph), 107.7 ( $\text{CCHOH}$ ), 61.1 ( $\text{COOCH}_2\text{CH}_3$ ), 14.1 ( $\text{COOCH}_2\text{CH}_3$ ).

**3-Hydroxy-2-(4-N,N-dimethylaminophenyl)acrylic acid ethyl ester** (Table 2, entries 9 and 10):  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ): 12.00 (d,  $J = 12.6$  Hz, 1H,  $\text{CHOH}$ ), 7.26 (s, 1H, Ph), 7.19 (d,  $J = 12.6$  Hz,  $\text{CHOH}$ ), 7.13 (s, 1H, Ph), 6.74 (d,  $J = 7.9$  Hz, 2H, Ph), 4.29 (q,  $J = 7.2$  Hz, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 2.97 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ), 1.30 (t,  $J = 7.2$  Hz, 3H,  $\text{COOCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ): 172.1 ( $\text{COOCH}_2\text{CH}_3$ ), 162.3 ( $\text{CHOH}$ ), 130.2 (Ph), 129.7 (Ph), 112.9 (Ph), 112.3 (Ph), 108.3 ( $\text{CCHOH}$ ), 60.8 ( $\text{COOCH}_2\text{CH}_3$ ), 40.6 ( $\text{N}(\text{CH}_3)_2$ ), 14.2 ( $\text{COOCH}_2\text{CH}_3$ ).

**3-Hydroxy-2-(biphenyl)acrylic acid ethyl ester** (Table 2, entries 11 and 12):  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ): 12.22 (d,  $J = 12.6$  Hz, 1H,  $\text{CHOH}$ ), 7.65 – 7.58 (m, 4H, Ph), 7.50 – 7.44 (m, 3H, Ph), 7.41 – 7.36 (m, 3H,  $\text{CHOH}$  and Ph), 4.35 (q,  $J = 7.2$  Hz, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 1.34 (t,  $J = 7.1$  Hz, 3H,  $\text{COOCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ): 171.6 ( $\text{COOCH}_2\text{CH}_3$ ), 163.5 ( $\text{CHOH}$ ), 140.7 (Ph), 139.8 (Ph), 133.1 (Ph), 129.7 (Ph), 128.8 (Ph), 127.3 (Ph), 127.0 (Ph), 126.9 (Ph), 108.3 ( $\text{CCHOH}$ ), 61.1 ( $\text{COOCH}_2\text{CH}_3$ ), 14.2 ( $\text{COOCH}_2\text{CH}_3$ ).

**3-Hydroxy-2-(phenyl)acrylic acid ethyl ester** (Table 2 entries 13 and 14):  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ): 12.17 (d,  $J = 12.6$  Hz, 1H,  $\text{CHOH}$ ), 7.34 – 7.28 (m, 5H,  $\text{CHOH}$  and Ph), 4.30 (q,  $J = 7.2$  Hz, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 1.30 (t,  $J = 7.1$  Hz, 3H,  $\text{COOCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ): 171.6 ( $\text{COOCH}_2\text{CH}_3$ ), 163.4 ( $\text{CHOH}$ ), 133.8 (Ph), 129.3 (Ph), 128.1 (Ph), 127.0 (Ph), 108.6 ( $\text{CCHOH}$ ), 60.9 ( $\text{COOCH}_2\text{CH}_3$ ), 14.1 ( $\text{COOCH}_2\text{CH}_3$ ).

**3-Hydroxy-2-(2-methylphenyl)acrylic acid ethyl ester** (Table 2, entries 15 and 16):  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ): 12.07 (d,  $J = 12.6$  Hz, 1H,  $\text{CHOH}$ ), 7.25 – 7.11 (m, 5H,  $\text{CHOH}$  and Ph), 4.27 (q,  $J = 7.1$  Hz, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 2.27 (s, 3H,  $\text{CH}_3$ ), 1.25 (t,  $J = 7.2$  Hz, 3H,  $\text{COOCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ ,

CDCl<sub>3</sub>, 20°C): 171.6 (COOCH<sub>2</sub>CH<sub>3</sub>), 163.1 (CHOH), 138.3 (Ph), 133.4 (Ph), 131.1 (Ph), 129.8 (Ph), 127.9 (Ph), 125.7 (Ph), 107.7 (CCHOH), 60.7 (COOCH<sub>2</sub>CH<sub>3</sub>), 20.0 (CH<sub>3</sub>), 14.2 (COOCH<sub>2</sub>CH<sub>3</sub>).

**3-Hydroxy-2-(3-methylphenyl)acrylic acid ethyl ester** (Table 2, entries 17 and 18): <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 20°C): 12.16 (d, *J* = 12.6 Hz, 1H, CHOH), 7.29 (d, *J* = 12.6 Hz, CHOH), 7.23 – 7.09 (m, 4H, Ph), 4.27 (q, *J* = 7.1 Hz, 2H, COOCH<sub>2</sub>CH<sub>3</sub>), 2.37 (s, 3H, CH<sub>3</sub>), 1.30 (t, *J* = 7.2 Hz, 3H, COOCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>, 20°C): 171.7 (COOCH<sub>2</sub>CH<sub>3</sub>), 163.3 (CHOH), 137.7 (Ph), 134.0 (Ph), 130.1 (Ph), 128.0 (Ph), 127.7 (Ph), 126.6 (Ph), 108.6 (CCHOH), 60.9 (COOCH<sub>2</sub>CH<sub>3</sub>), 21.3 (CH<sub>3</sub>), 14.1 (COOCH<sub>2</sub>CH<sub>3</sub>).

**3-Hydroxy-2-(4-methylphenyl)acrylic acid ethyl ester** (Table 2, entries 19 and 20): <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 20°C): 12.15 (d, *J* = 12.6 Hz, 1H, CHOH), 7.28 (d, *J* = 12.6 Hz, CHOH), 7.22 – 7.17 (m, 4H, Ph), 4.29 (q, *J* = 7.1 Hz, 2H, COOCH<sub>2</sub>CH<sub>3</sub>), 2.36 (s, 3H, CH<sub>3</sub>), 1.29 (t, *J* = 7.1 Hz, 3H, COOCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>, 20°C): 171.8 (COOCH<sub>2</sub>CH<sub>3</sub>), 163.1 (CHOH), 136.6 (Ph), 131.2 (Ph), 129.3 (Ph), 128.9 (Ph), 108.4 (CCHOH), 60.9 (COOCH<sub>2</sub>CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 14.1 (COOCH<sub>2</sub>CH<sub>3</sub>).

**3-Hydroxy-2-(2,5-dimethoxyphenyl)acrylic acid ethyl ester** (Table 2, entries 21 and 22): <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 20°C): 11.95 (d, *J* = 12.6 Hz, 1H, CHOH), 7.18 (d, *J* = 12.6 Hz, CHOH), 6.84 – 6.80 (m, 2H, Ph<sup>3,4</sup>), 6.70 (s, 1H, Ph<sup>6</sup>), 4.23 (q, *J* = 7.0 Hz, 2H, COOCH<sub>2</sub>CH<sub>3</sub>), 3.75 – 3.72 (6H, OCH<sub>3</sub>), 1.22 (t, *J* = 7.1 Hz, 3H, COOCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>, 20°C): 171.6 (COOCH<sub>2</sub>CH<sub>3</sub>), 162.8 (CHOH), 153.2 (Ph), 152.2 (Ph), 124.2 (Ph), 117.7 (Ph), 113.1 (Ph), 111.6 (Ph), 104.5 (CCHOH), 60.5 (COOCH<sub>2</sub>CH<sub>3</sub>), 55.9 (OCH<sub>3</sub>), 55.6 (OCH<sub>3</sub>), 14.2 (COOCH<sub>2</sub>CH<sub>3</sub>).

**3-Hydroxy-2-(3,4-dimethoxyphenyl)acrylic acid ethyl ester** (Table 2, entries 23 and 24): <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 20°C): 12.03 (d, *J* = 12.6 Hz, 1H, CHOH), 7.28 (d, *J* = 12.6 Hz, CHOH), 6.82 – 6.80 (m, 3H, Ph), 4.28 (q, *J* = 7.2 Hz, 2H, COOCH<sub>2</sub>CH<sub>3</sub>), 3.88 – 3.87 (2 x s, 6H, OCH<sub>3</sub>), 1.30 (t, *J* = 7.2 Hz, 3H, COOCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (δ, CDCl<sub>3</sub>, 20°C): 171.7 (COOCH<sub>2</sub>CH<sub>3</sub>), 162.9 (CHOH), 148.4 (Ph), 148.2 (Ph), 126.8 (Ph), 121.6 (Ph), 113.1 (Ph), 110.9 (Ph), 108.2 (CCHOH), 60.9 (COOCH<sub>2</sub>CH<sub>3</sub>), 55.8 (OCH<sub>3</sub>), 55.8 (OCH<sub>3</sub>), 14.2 (COOCH<sub>2</sub>CH<sub>3</sub>).























