CHEMISTRY
AN ASIAN JOURNAL

Supporting Information

Supporting Information

Chiral Imidazoline Promoted Baylis-Hillman Reaction

*Junye Xu, Yanyi Guan, Shihui Yang, Yurui Ng, Guangrong Peh, Choon-Hong Tan**

Department of Chemistry, 3 Science Drive 3, National University of Singapore,

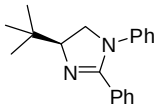
Singapore 117543

chmtanch@nus.edu.sg

Supporting Information

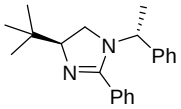
1. Characterization of chiral imidazoline.

(3d) (*S*)-4-*tert*-Butyl-1, 2-diphenyl-4, 5-dihydro-1*H*-imidazole



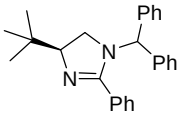
F. Menges, M. Neuburger, A. Pfaltz, *Org. Lett.* **2002**, *4*, 4713-4716.

(3g) (*S*)-4-*tert*-Butyl-2-phenyl-1-[-(*R*)-1-phenylethyl)-4, 5-dihydro-1*H*-imidazole]



Pale yellow solid; $\mathbf{R_f}$ = 0.40 (hexane/ethyl acetate 1:1); **m.p.** 111.6-112.4 ^{o}C; **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) d 0.96 (s, 9H), 1.43 (d, 3H, *J* = 6.8 Hz), 3.07-3.24 (m, 2H), 3.79 (dd, 1H, *J* = 11.2, 9.4 Hz), 4.83 (q, 1H, *J* = 6.8 Hz), 7.24-7.58 (m, 10H); **^{13}C NMR** (300 MHz, $CDCl_3$, ppm) d 16.5, 26.0, 34.5, 44.9, 53.3, 73.5, 126.7, 127.1, 128.2, 128.5 (two peaks), 129.6, 132.1, 141.4, 165.4; **IR** (film, cm^{-1}) 3021, 2965, 1620, 1216; $\mathbf{[a]^{25}_{,D}}$ -1.5 (c *2.59*, $CHCl_3$); **LRMS** (FAB) *m/z* 307.1 ($M+H^+$); **HRMS** (FAB) calcd. for $[C_{21}H_{26}N_2+H]^+$ requires *m/z* 307.2174. Found 307.2174.

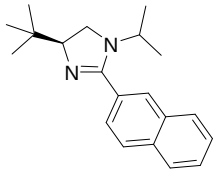
(3h) (*S*)-1-Benzhydryl-4-*tert*-butyl-2-phenyl-4, 5-dihydro-1*H*-imidazole



Colorless oil; $\mathbf{R_f}$ = 0.40 (hexane/ethyl acetate 4:1); **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) d 0.79 (s, 9H), 3.01 (t, 1H, *J* = 9.6 Hz), 3.37 (t, 1H, *J* = 10.4 Hz), 3.85 (m, 1H), 6.01 (s, 1H), 7.02-7.05 (m, 2H), 7.21-7.42 (m, 13H), 7.53-7.56 (m, 2H); **^{13}C NMR** (300 MHz, $CDCl_3$, ppm) d 25.9, 34.2, 46.2, 63.3, 73.9, 126.9 (two peaks), 127.3 (two peaks), 127.4, 127.5, 128.1, 128.2, 128.4, 128.6, 129.0, 129.9, 131.8, 139.1, 139.7, 165.6; **IR** (film, cm^{-1}) 2958, 2925, 2866, 1618, 1596; $\mathbf{[a]^{25}_{,D}}$ -33.8 (c *1.27*, $CHCl_3$);

LRMS (FAB) *m/z* 369.1 ($M+H^+$); **HRMS** (FAB) calcd. for $[C_{26}H_{28}N_2+H]^+$ requires *m/z* 369.2331. Found 369.2334.

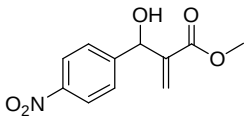
(3j) (*S*)-4-*tert*-Butyl-1-isopropyl-2-(naphthalen-2-yl)-4, 5-dihydro-1*H*-imidazole



Yellow oil; $\mathbf{R_f}$ = 0.40 (hexane/ethyl acetate 1:1); **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) d 1.01 (s, 9H), 1.04 (d, 3H, *J* = 6.6 Hz), 1.17 (d, 3H, *J* = 6.6 Hz), 3.34 (t, 1H, *J* = 9.4 Hz), 3.52 (t, 1H, *J* = 10.1 Hz), 3.83-3.97 (m, 2H), 7.50-7.55 (m, 3H), 7.83-7.91 (m, 3H), 8.05 (s, 1H); **^{13}C NMR** (300 MHz, $CDCl_3$, ppm) d 19.5, 20.6, 25.8, 34.6, 44.2, 47.0, 71.6, 125.0, 126.5, 127.0, 127.7, 128.2, 128.3, 128.5, 132.8, 133.9, 165.8; **IR** (film, cm^{-1}) 2959, 2869, 1591; $\mathbf{[a]^{25}_{,D}}$ -13.2 (c *0.19*, $CHCl_3$); **LRMS** (FAB) *m/z* 295.3 ($M+H^+$); **HRMS** (FAB) calcd. for $[C_{26}H_{28}N_2+H]^+$ requires *m/z* 295.2174. Found 295.2170.

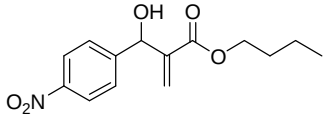
5. Characterization of Baylis-Hillman adducts.

(4a) Methyl 2-(hydroxy (4-nitrophenyl) methyl) acrylate



60% ee. K.-S. Yang, W.-D. Lee, J.-F. Pan, *J. Org. Chem.* **2003**, *68*, 915-919. **HPLC conditions:** Chiralcel OD-H column (Diacel); 96/4 hexane/2-propanol; Flow rate 0.5 mL/min; ? = 254 nm; 46.7 min (major, *R*), 50.6 min (minor, *S*) [a].

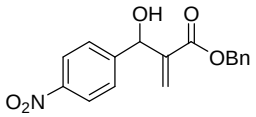
(4b) Butyl 2-(hydroxyl (4-nitrophenyl) methyl) acrylate



[a] Absolute configuration of **4a** was assigned by comparing with the literature data: Y. Iwabuchi, M. Nakatani, N. Yokoyama, S. Hatakeyama, *J. Am. Chem. Soc.* **1999**, *121*, 10219-10220.

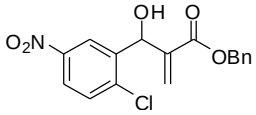
41% ee. D. Basavaiah, M. Krishnamacharyulu, A. J. Rao, *Syn. Comm.* **2000**, *30*, 2061-2069. **HPLC conditions:** Chiralcel OB-H column (Diacel); 95/5 hexane/2-propanol; Flow rate 1.0 mL/min; ? = 254 nm; 23.4 min (minor), 26.2 min (major).

(4c) Benzyl 2-(hydroxy (4-nitrophenyl) methyl) acrylate



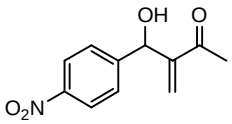
48% ee. K.-S. Yang, W.-D. Lee, J.-F. Pan, *J. Org. Chem.* **2003**, *68*, 915-919. **HPLC conditions:** Chiralcel OD-H column (Diacel); 80/20 hexane/2-propanol; Flow rate 0.5 mL/min; ? = 254 nm; 15.4 min (major), 17.5 min (minor).

(4g) Benzyl 2-((2-chloro-5-nitrophenyl) (hydroxy) methyl) acrylate



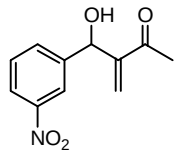
31% ee; Colorless oil; $\mathbf{R_f}$ = 0.40 (hexane/ethyl acetate 4:1); **^{1}H NMR** (300 MHz, $CDCl_3$, ppm) d 3.57 (bs, 1H), 5.21 (dd, 2H, *J* = 16.0, 12.2 Hz), 5.67 (s, 1H), 5.99 (s, 1H), 6.45 (s, 1H), 7.30-7.37 (m, 5H), 7.50 (d, 1H, *J* = 8.7 Hz), 8.09 (dd, 1H, *J* = 8.7, 2.8 Hz), 8.45 (d, 1H, *J* = 2.8 Hz); **^{13}C NMR** (300 MHz, $CDCl_3$, ppm) d 67.0, 69.0, 123.6, 123.7, 128.0, 128.1, 128.4, 128.6, 130.4, 135.1, 139.4, 139.6, 140.5, 146.8, 165.8; **IR** (film, cm^{-1}) 3483, 3020, 1718, 1527, 1462, 1348; **LRMS** (ESI) *m/z* 382.2 ($M+Cl^-$); **HRMS** (ESI) calcd. for $[C_{17}H_{14}ClNO_5+Cl]^-$ requires *m/z* 382.0249. Found 382.0252. **HPLC conditions:** Chiralcel OD-H column (Diacel); 95/5 hexane/2-propanol; Flow rate 1.0 mL/min; ? = 254 nm; 19.3 min (major), 23.3 min (minor).

(6a) 3-(Hydroxy (4-nitrophenyl) methyl) but-3-en-2-one



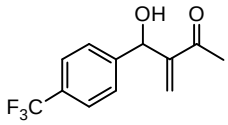
60% ee. M. Shi, J.-K. Jiang, *Tetrahedron: Asymmetry* **2002**, *13*, 1941-1497. **HPLC conditions:** Chiralcel OJ-H column (Diacel); 96/4 hexane/2-propanol; Flow rate 1.0 mL/min; ? = 254 nm; 71.6 min (minor, *S*), 75.6 min (major, *R*).[b]

(6b) 3-(Hydroxy (3-nitrophenyl) methyl) but-3-en-2-one



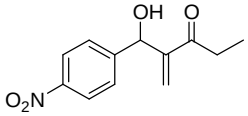
67% ee. M. Shi, C.-Q. Li, J.-K. Jiang, *Chem.Comm.* **2001**, *9*, 833-834. **HPLC conditions:** Chiralcel OD-H column (Diacel); 96/4 hexane/2-propanol; Flow rate 0.5 mL/min; ? = 254 nm; 49.3 min (major), 53.0 min (minor).

(6d) 3-(Hydroxy (4-(trifluoromethyl) phenyl) methyl) but-3-en-2-one



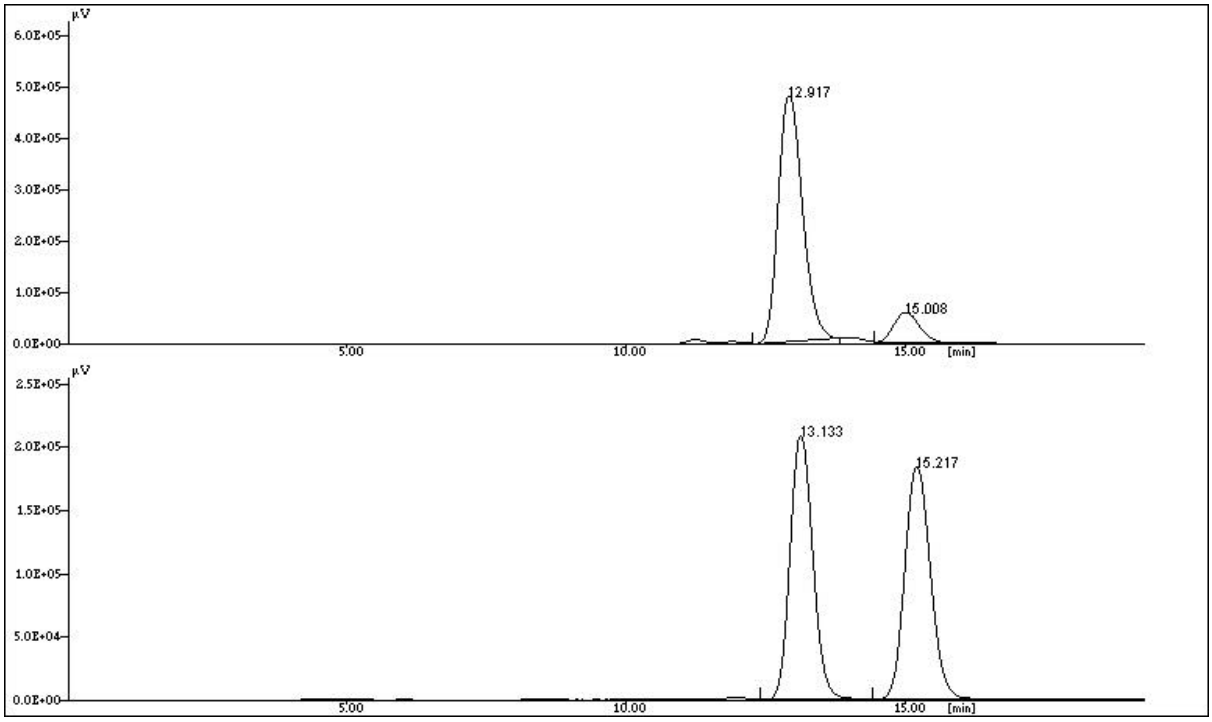
47% ee. Y.-S. Lin, C.-W. Liu, T. Y. R. Tsai, *Tetrahedron Lett.* **2005**, *46*, 1859-1861. **HPLC conditions:** Chiralcel AS-H column (Diacel); 90/10 hexane/2-propanol; Flow rate 0.75 mL/min; ? = 254 nm; 8.5 min (major), 9.9 min (minor).

(6e) 2-(Hydroxy (4-nitrophenyl) methyl) pent-1-en-3-one

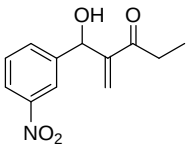


77% ee. M. Shi, C.-Q. Li, J.-K. Jiang, *Tetrahedron* **2003**, *59*, 1181-1189. **HPLC conditions:** Chiralcel OD-H column (Diacel); 90/10 hexane/2-propanol; Flow rate 0.75 mL/min; ? = 254 nm; 13.1 min (major), 15.2 min (minor).

[b] Absolute configuration of **6a** was assigned by comparing with the literature data: M. Shi, J.-K. Jiang, *Tetrahedron: Asymmetry* **2002**, *13*, 1941-1947.



(6f) 2-(Hydroxyl (3-nitrophenyl) methyl) pent-1-en-3-one



75% ee. M. Shi, C.-Q. Li, J.-K. Jiang, *Tetrahedron* **2003**, *59*, 1181-1189. **HPLC conditions:** Chiralcel OD-H column (Diacel); 95/5 hexane/2-propanol; Flow rate 0.75 mL/min; ? = 254 nm; 22.1 min (major), 24.8 min (minor).