Supporting Information

Highly Enantioselective Synthesis of α -Alkyl-alanines via the Catalytic Phase-Transfer Alkylation of 2-Naphthyl aldimine *tert*-butyl ester by using *O*(9)-Allyl-*N*(1)-2',3',4'-trifluorobenzylhydrocinchonidinium bromide

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L-2-[(Naphthalen-2-ylmethylene)amino]propionic acid *tert*-butyl ester (1E): ^1H -NMR (300 MHz, C_6D_6) δ 8.24 (dd, 1H, J = 7.1, 1.4 Hz), 8.16 (s, 1H), 7.78 (s, 1H), 7.61~7.41 (m, 3H), 7.23~7.17 (m, 2H), 4.03 (q, 1H, J = 6.7 Hz), 1.56 (d, 3H, J = 6.8 Hz), 1.37 (s, 9H); ^{13}C -NMR (75 MHz, C_6D_6) δ 171.3, 162.3, 135.2, 134.5, 133.5, 130.8, 128.8, 128.7, 127.2, 126.5, 124.4, 80.4, 69.2, 27.9, 19.6; MS (EI) m/z 283 $[\text{M}]^+$.

O(9)-Allyl-N(1)-2',3',4'-trifluorobenzylhydrocinchonidinium bromide (6): IR (KBr) 3434, 2960, 1635, 1515, 1493, 1460, 1309, 1165, 1133, 1066, 1023, 814, 758, 685, 517 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.02 (d, J = 4.4 Hz, 1 H), 8.32 (d, J = 8.4 Hz, 1 H), 8.14 (d, J = 8.4 Hz, 1 H), 7.89~7.85 (m, 1 H), 7.79~7.75 (m, 2 H), 7.71 (d, J = 4.4 Hz, 1 H), 7.62~7.60 (m, 1 H), 6.45 (s, 1 H), 6.16~6.10 (m, 1 H), 5.45 (d, J = 17.2 Hz, 1 H), 5.31~5.23 (m, 2 H), 5.02 (d, J = 12.9 Hz, 1 H), 4.30 (dd, J = 12.6, 5.3 Hz, 1 H), 4.12~4.02 (m, 3 H), 3.58~3.52 (m, 1 H), 3.46~3.44 (m, 1 H), 3.35~3.30 (m, 1 H), 2.28~2.21 (m, 1 H), 2.13~2.05 (m, 1 H), 2.01~1.95 (m, 1 H), 1.77~1.74 (m, 1 H), 1.47~1.38 (m, 1 H), 1.25~1.16 (m, 2 H), 0.71 (t, J = 7.3 Hz, 3 H) ppm; ^{13}C NMR (400 MHz, $\text{DMSO}-d_6$) δ 150.6, 148.4, 141.3, 134.4, 130.8, 130.3, 130.1, 127.8, 125.5, 124.2, 120.1, 118.1, 113.9, 113.7, 72.7, 69.7, 67.8, 61.8, 56.6, 51.4, 35.6, 25.7, 25.4, 23.9, 21.2 ppm; m.p. 152 $^\circ\text{C}$; $[\alpha]_D^{23}$ -113 (c 1.050, CHCl_3); MS (FAB): 481 $[\text{M}]^+$; HRMS (ESI) calcd for $[\text{C}_{29}\text{H}_{32}\text{F}_3\text{N}_2\text{O}]^+$: 481.2468, found: 481.2437.

(S)-2-Benzoylamino-2-methylpent-4-enoic acid *tert*-butyl ester (N-benzoyl 3a): ^1H -NMR (300 MHz, CDCl_3) δ 8.11~8.08 (m, 1H), 7.77~7.74 (m, 2H), 7.48~7.37 (m, 2H), 7.13 (s, 1H), 5.72~5.58 (m, 1H), 5.13~5.04 (m, 2H), 3.24 (dd, 1H, J = 15.0, 7.1 Hz), 2.56 (dd, 1H, J = 15.0, 7.1 Hz), 1.70 (s, 3H), 1.48 (s, 9H); ^{13}C -NMR (75 MHz, CDCl_3) δ 173.4, 166.4, 135.0, 134.5, 133.5, 132.6, 131.3, 130.5, 130.0, 129.6, 128.9, 128.4, 128.3, 126.8, 118.9, 82.4, 60.6, 40.2, 27.9, 23.0; MS (EI) m/z 289 $[\text{M}]^+$.

(S)-2-Benzoylamino-2-methylpent-4-ynoic acid *tert*-butyl ester (N-benzoyl 3b): ^1H -NMR (300 MHz, CDCl_3) δ 7.80~7.77 (m, 2H), 7.51~7.38 (m, 3H), 7.15 (s, 1H), 3.37 (dd, 1H, J = 14.2, 2.7 Hz), 2.84 (dd, 1H, J = 14.2, 2.7 Hz), 1.93 (t, 1H, J = 2.7 Hz), 1.69 (s, 3H), 1.49 (s, 9H); ^{13}C -NMR (75 MHz, CDCl_3) δ 172.3, 166.6, 134.9, 131.5, 128.5, 126.9, 82.8, 79.7, 70.7, 60.0, 27.8, 26.2, 22.8; MS (EI) m/z 287 $[\text{M}]^+$.

(S)-2-Benzoylamino-2-methyl-3-phenylpropionic acid *tert*-butyl ester (N-benzoyl 3c): ^1H -NMR (300 MHz, CDCl_3) δ 7.76~7.73 (m, 2H), 7.60~7.25 (m, 3H), 7.23~7.17 (m, 5H), 7.04 (s,

1H), 3.86 (d, 1H, J = 13.6 Hz), 3.27 (d, 1H, J = 13.4 Hz), 1.86 (s, 3H), 1.56 (s, 9H); ^{13}C -NMR (75 MHz, CDCl_3) δ 172.9, 166.5, 136.6, 135.1, 131.1, 129.8, 128.3, 127.8, 126.6, 82.4, 61.5, 40.4, 27.7, 23.6; MS (EI) m/z 339 $[\text{M}]^+$.

(S)-2-Benzoylamino-3-(4-bromophenyl)-2-methylpropionic acid *tert*-butyl ester (N-benzoyl 3d): ^1H -NMR (300 MHz, CDCl_3) δ 7.69~7.66 (m, 2H), 7.50~7.37 (m, 3H), 7.31~7.28 (m, 2H), 6.99~6.96 (m, 2H), 3.78 (d, 1H, J = 13.7 Hz), 3.15 (d, 1H, J = 13.4 Hz), 1.76 (s, 3H), 1.49 (s, 9H); ^{13}C -NMR (75 MHz, CDCl_3) δ 172.9, 166.7, 131.8, 135.1, 131.6, 131.4, 131.1, 128.5, 126.7, 120.7, 82.9, 61.6, 39.7, 27.9, 23.8; MS (EI) m/z 420 $[\text{M}+2]^+$.

(S)-2-Benzoylamino-3-(4-*tert*-butylphenyl)-2-methylpropionic acid *tert*-butyl ester (N-benzoyl 3e): ^1H -NMR (300 MHz, CDCl_3) δ 8.11~8.03 (m, 1H), 7.68~7.65 (m, 2H), 7.49~7.35 (m, 2H), 7.21~7.18 (m, 2H), 7.06~7.03 (m, 2H), 6.95 (s, 1H), 3.71 (d, 1H, J = 13.7 Hz), 3.17 (d, 1H, J = 13.7 Hz), 1.77 (s, 3H), 1.48 (s, 9H), 1.24 (s, 9H); ^{13}C -NMR (75 MHz, CDCl_3) δ 173.3, 171.2, 166.7, 149.5, 135.4, 133.7, 133.6, 131.3, 130.2, 129.6, 129.3, 128.5, 128.4, 126.8, 124.9, 82.6, 61.8, 40.3, 34.3, 31.3, 30.9, 29.7, 28.0, 23.8; MS (EI) m/z 395 $[\text{M}]^+$.

(S)-2-Benzoylamino-2-methyl-3-(4-trifluoromethylphenyl)propionic acid *tert*-butyl ester (N-benzoyl 3f): ^1H -NMR (300 MHz, CDCl_3) δ 8.02~7.99 (m, 2H), 7.69~7.66 (m, 2H), 7.57~7.37 (m, 4H), 7.23~7.21 (m, 1H), 6.99 (s, 1H), 3.91 (d, 1H, J = 13.7 Hz), 3.27 (d, 1H, J = 13.7 Hz), 1.79 (s, 3H), 1.49 (s, 9H); ^{13}C -NMR (75 MHz, CDCl_3) δ 172.9, 166.8, 134.9, 133.0, 132.9, 131.6, 130.1, 129.5, 128.9, 128.6, 128.3, 126.7, 125.5, 124.9, 83.2, 63.8, 61.7, 40.5, 40.1, 30.5, 29.5, 23.9; MS (EI) m/z 407 $[\text{M}]^+$.

(S)-2-Benzoylamino-3-(2-fluorophenyl)-2-methylpropionic acid *tert*-butyl ester (N-benzoyl 3g): ^1H -NMR (300 MHz, CDCl_3) δ 8.11~8.08 (m, 1H), 7.71~7.68 (m, 2H), 7.47~7.36 (m, 3H), 7.19~7.13 (m, 2H), 7.00~6.94 (m, 2H), 3.62 (d, 1H, J = 13.9 Hz), 3.39 (d, 1H, J = 13.9 Hz), 1.75 (s, 3H), 1.44 (s, 9H); ^{13}C -NMR (75 MHz, CDCl_3) δ 172.8, 166.9, 135.1, 133.5, 132.6, 131.3, 130.0, 129.5, 128.5, 128.4, 126.8, 123.8, 115.2, 115.0, 82.5, 61.0, 34.2, 27.7, 23.5; MS (EI) m/z 357 $[\text{M}]^+$.

(S)-2-Benzoylamino-3-(2,6-difluorophenyl)-2-methylpropionic acid *tert*-butyl ester (N-benzoyl 3h): ^1H -NMR (300 MHz, CDCl_3) δ 8.04~8.01 (m, 2H), 7.74~7.71 (m, 2H), 7.57~7.39 (m, 3H), 6.89~6.82 (m, 2H), 3.95 (d, 1H, J = 5.9 Hz), 3.48 (d, 1H, J = 5.1 Hz), 1.69 (s, 3H),

1.45 (s, 9H); ^{13}C -NMR (75 MHz, CDCl_3) δ 172.3, 167.0, 131.2, 129.5, 128.5, 128.4, 126.8, 111.3, 111.0, 107.6, 82.2, 60.5, 29.2, 27.7, 22.8; MS (EI) m/z 375 $[\text{M}]^+$.

(S)-2-Benzoylamino-3-(2,4-dichlorophenyl)-2-methylpropionic acid *tert*-butyl ester (N-benzoyl 3i): ^1H -NMR (300 MHz, CDCl_3) δ 7.74~7.66 (m, 2H), 7.61~7.34 (m, 4H), 7.24~7.06 (m, 2H), 6.83 (s, 1H), 3.71 (d, 1H, J = 14.6 Hz), 3.52 (d, 1H, J = 14.4 Hz), 1.68 (s, 3H), 1.43 (s, 9H); ^{13}C -NMR (75 MHz, CDCl_3) δ 172.6, 166.8, 135.5, 134.8, 133.5, 132.8, 131.6, 129.3, 128.6, 126.8, 82.6, 60.9, 36.5, 27.8, 23.8; MS (EI) m/z 408 $[\text{M}]^+$.

(S)-2-Benzoylamino-2-methyl-3-*m*-tolylpropionic acid *tert*-butyl ester (N-benzoyl 3j): ^1H -NMR (300 MHz, CDCl_3) δ 7.99~7.65 (m, 2H), 7.48~7.35 (m, 4H), 7.09~6.89 (m, 4H), 3.74 (d, 1H, J = 13.4 Hz), 3.15 (d, 1H, J = 13.7 Hz), 2.19 (s, 3H), 1.79 (s, 9H); ^{13}C -NMR (75 MHz, CDCl_3) δ 173.2, 166.9, 131.3, 130.8, 130.0, 128.5, 127.9, 127.5, 126.9, 126.7, 82.7, 61.9, 40.6, 27.9, 23.8, 21.2; MS (EI) m/z 353 $[\text{M}]^+$.

(S)-2-Benzoylamino-2-methyl-3-naphthalen-1-ylpropionic acid *tert*-butyl ester (N-benzoyl 3k): ^1H -NMR (300 MHz, CDCl_3) δ 8.21~8.18 (m, 1H), 7.82~7.78 (m, 1H), 7.73~7.70 (m, 1H), 7.59~7.56 (m, 2H), 7.45~7.30 (m, 7H), 6.81 (s, 1H), 4.04 (d, 1H, J = 14.4 Hz), 3.81 (d, 1H, J = 14.4 Hz), 1.81 (s, 3H), 1.37 (s, 9H); ^{13}C -NMR (75 MHz, CDCl_3) δ 173.0, 166.9, 135.2, 133.8, 133.1, 132.9, 131.3, 128.6, 128.5, 128.4, 127.6, 126.8, 125.9, 125.4, 125.0, 124.5, 82.5, 61.7, 36.9, 27.7, 24.1; MS (EI) m/z 389 $[\text{M}]^+$.

Table S1. HPLC conditions for *N*-benzoyl derivatives of **3a-k**

compound	column	solvent	wavelength	flow rate	retention time (<i>R</i>)-isomer	retention time (<i>S</i>)-isomer
<i>N</i> -benzoyl 3a	Chiralcel OD	Hx : 2-PrOH = 500 : 7.0	254 nm	0.7 ml/min	11.5 min	15.9 min
<i>N</i> -benzoyl 3b	Chiralcel OD	Hx : 2-PrOH = 500 : 7.0	254 nm	0.7 ml/min	15.8 min	22.9 min
<i>N</i> -benzoyl 3c	Chiralcel OD	Hx : 2-PrOH = 500 : 7.0	254 nm	0.7 ml/min	15.9 min	20.0 min
<i>N</i> -benzoyl 3d	Chiralcel OD	Hx : 2-PrOH = 500 : 7.0	254 nm	0.7 ml/min	14.0 min	19.6 min
<i>N</i> -benzoyl 3e	Chiralpak AD	Hx : 2-PrOH = 500 : 7.0	254 nm	1.0 ml/min	16.7 min	19.2 min
<i>N</i> -benzoyl 3f	Chiralcel OD	Hx : 2-PrOH = 500 : 5.0	254 nm	1.0 ml/min	12.0 min	14.0 min
<i>N</i> -benzoyl 3g	Chiralcel OD	Hx : 2-PrOH = 500 : 7.0	254 nm	0.7 ml/min	15.6 min	18.6 min
<i>N</i> -benzoyl 3h	Chiralpak AD	Hx : 2-PrOH = 500 : 10.0	254 nm	1.0 ml/min	23.5 min	25.5 min
<i>N</i> -benzoyl 3i	Chiralcel OD	Hx : 2-PrOH = 500 : 5.0	254 nm	1.0 ml/min	24.9 min	18.3 min
<i>N</i> -benzoyl 3j	Chiralcel OD	Hx : 2-PrOH = 500 : 7.0	254 nm	0.7 ml/min	13.2 min	16.5 min
<i>N</i> -benzoyl 3k	Chiralcel OD	Hx : 2-PrOH = 500 : 10.0	254 nm	1.0 ml/min	15.0 min	26.2 min