Supplementary Material (ESI) for Chemical Communications
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Tunable Asymmetric Copper-Catalyzed Allylic Amination and Oxidation Reactions

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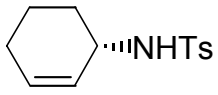
Supporting Information

General procedure for asymmetric allylic amination and oxidation reactions

A solution of $Cu(MeCN)_4PF_6$ (0.1 equiv.) and ligand (0.11 equiv.) in the appropriate solvent (5 mL per mmol peroxycarbamate) was stirred at RT for 10 minutes. The alkene (5 equiv.) was added to the pale blue solution, followed by the addition of the peroxycarbamate **6** (1 equiv.). The reaction mixture was stirred at RT and gradually changed from blue to green or dark brown during the course of the reaction. On completion of the reaction, as indicated by the disappearance of the peroxycarbamate by TLC, it was quenched with a saturated aqueous solution of $NaHCO_3$ and extracted with ethyl acetate. The combined organic extracts were washed with a saturated aqueous solution of $NaHCO_3$ and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the crude product and this was purified by flash column chromatography on silica gel.

Enantiomeric excesses were determined using chiral HPLC (Chiralpak AD or ADH column) and the absolute configuration of the major enantiomer was established by comparison with literature data in cases where this was possible.

***N*-[(1*S*)-2-Cyclohexen-1-yl]-4-methylbenzenesulfonamide (*S*)-3a**[1]

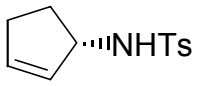


Following the general procedure, cyclohexene (100 μL) was reacted with the peroxycarbamate **2a** (57.4 mg) the complex generated from $Cu(MeCN)_4PF_6$ (7.4 mg) and the ligand (*S*,*S*)-**1b** (7.4 mg) in dichloromethane (1.0 mL) at room temperature over 20 h. Flash column chromatography on silica gel (pet. ether-ether, 100:0→50:50) afforded the allylic amine **3a** (22 mg, 44%) as an oil.

$[\alpha]^{19}_D$ = –34 (*c* = 0.78, $CHCl_3$) {Lit. *R*-enantiomer (18% ee) $[\alpha]^{20}_D$ = +11.6 (*c* = 1.0, $CHCl_3$)}[1]; HPLC (Chiralpak AD 7%, *i*PrOH-hexane, flow rate 1 $mLmin^{-1}$) $t_R(R)$ = 27.6 min, $t_R(S)$ = 29.4 min, ee = 51 %; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.49–1.65 (m, 3 H), 1.70–1.80 (m, 1 H), 1.82–2.00 (m,

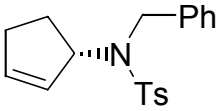
2 H), 2.43 (s, 3 H), 3.75–3.87 (m, 1 H), 4.47 (d, 1 H), 5.34 (dddd, J = 10.0, 3.4, 2.2, 2.2 Hz, 1 H), 5.76 (dddd, J = 10.0, 3.7, 3.7, 1.8 Hz, 1 H), 7.30 (d, J = 8.5 Hz, 2 H), 7.77 (d, J = 8.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 19.6 (CH_2), 21.8 (CH_3), 24.8 (CH_2), 30.6 (CH_2), 49.3 (CH), 127.3 (CH), 127.4 (CH), 130.0 (CH), 131.8 (CH), 138.7 (C), 143.5 (C); IR ($CHCl_3$) 3382, 2927, 2864, 1599, 1328, 1154, 884 cm^{-1}; HRMS (EI+) for $C_{13}H_{17}NO_2S$ calcd 251.0980, found 251.0979.

_N_-[(1_S_)-2-Cyclopenten-1-yl]-4-methylbenzenesulfonamide (_S_)-4a[1]



Following the general procedure, cyclopentene (88 μL) was reacted with the peroxycarbamate **2a** (57.4 mg) the complex generated from $Cu(MeCN)_4PF_6$ (7.4 mg) and the ligand (*S*,*S*)-**1b** (7.4 mg) in dichloromethane (1.0 mL) at room temperature over 40 h. Flash column chromatography on silica gel (pet. ether-ether, 100:0→50:50) afforded the allylic amine **3a** (14 mg, 30%) as an oil.
$[\alpha]^{26}_D$ = –21 (c = 0.56, $CHCl_3$) {Lit. *R*-enantiomer (64% ee) $[\alpha]^{20}_D$ = +15.4 (c = 1.0, $CHCl_3$)}[1]; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42–1.58 (m, 1 H), 2.10–2.27 (m, 2 H), 2.30–2.41 (m, 1 H), 2.43 (s, 3 H), 4.35–4.50 (m, 2 H), 5.41–5.47 (m, 1 H), 5.84–5.90 (m, 1 H), 7.31 (d, J = 8.3 Hz, 2 H), 7.77 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 21.9 (CH_3), 31.2 (CH_2), 31.9 (CH_2), 60.2 (CH), 127.4 (CH), 129.8 (CH), 130.8 (CH), 135.4 (CH), 138.5 (C), 143.7 (C); IR ($CHCl_3$) 3374, 2928, 2857, 1599, 1353, 1154, 897 cm^{-1}; HRMS (EI+) for $C_{12}H_{15}NO_2S$ calcd 237.0824, found 237.0834.

_N_-Benzyl-_N_-[(1_S_)-2-cyclopenten-1-yl]-4-methylbenzenesulfonamide



$[\alpha]^{21}_D$ = –11 (c = 0.75, $CHCl_3$); HPLC (Chiralpak ADH, 7% *i*PrOH-hexane, flow rate 1 mLmin^{-1}) t_R(*S*) = 38.0 min, t_R(*R*) = 40.7 min, ee = 46 %; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.30–1.42 (m, 1 H), 1.91–2.02 (m, 1 H), 2.07–2.15 (m, 2 H), 2.40 (s, 3 H), 4.15 (d, J = 16.2 Hz, 1H), 4.22 (d, J = 16.2 Hz, 1 H), 5.09–5.19 (m, 2 H), 5.79 (dddd, J = 5.5, 2.3, 2.2, 2.1 Hz, 1 H), 7.17–7.29 (m, 5 H), 7.30–7.35 (m, 2 H), 7.70 (d, J = 7.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 21.9 (CH_3), 27.7 (CH_2), 31.6 (CH_2), 47.6 (CH_2), 65.0 (CH), 127.4 (CH), 127.6 (CH), 127.8 (CH), 128.5 (CH), 129.6 (CH), 130.0 (CH), 136.2 (CH), 138.0 (C), 139.4 (C), 143.5 (C); IR ($CHCl_3$) 2926, 2854, 1598, 1342, 1150, 867 cm^{-1}; HRMS (EI+) for $C_{19}H_{21}NO_2S$ calcd 327.1293, found 327.1291.

Carbamate (_R_)-5b[2]

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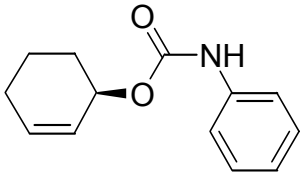
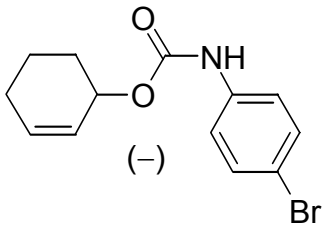


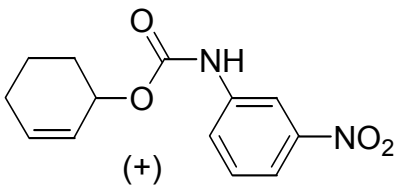
$[\alpha]^{30}_{D}$ = +137 (*c* = 0.68, $CHCl_3$); HPLC (Chiralpak AD, 3 % *i*PrOH-hexane, flow rate 1 mLmin^{-1}) t_R(*R*) = 23.8 min, t_R(*S*) = 28.3 min, ee = 61 %; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.60–1.88 (m, 3 H), 1.90–2.20 (m, 3 H), 5.25–5.32 (m, 1 H), 5.78 (dddd, *J* = 10.0, 3.6, 1.8, 1.8 Hz, 1H), 5.98 (m, *J* = 10.0, 4.1, 3.7, 1.2 Hz, 1 H), 6.52–6.60 (br s, 1 H), 7.03–7.07 (m, 1 H), 7.27–7.33 (m, 2 H), 7.35–7.41 (m, 2 H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 19.1 (CH_2), 25.2 (CH_2), 28.9 (CH_2), 69.2 (CH), 118.9 (CH), 123.6 (CH), 126.1 (CH), 129.4 (CH), 133.2 (CH), 138.4 (C), 153.6 (C); IR ($CHCl_3$) 3434, 2935, 2868, 1728, 1596 cm^{-1}; HRMS (EI+) for $C_{13}H_{15}NO_2$ calcd 217.1103, found 217.1099. Anal. calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.70; H, 6.94; N, 6.25.

Carbamate (–)-5c



$[\alpha]^{34}_{D}$ = –123 (*c* = 0.65, $CHCl_3$); HPLC (Chiralpak AD, 3 % *i*PrOH-hexane, flow rate 1 mLmin^{-1}) t_R(+) = 27.3 min, t_R(–) = 30.9 min, ee = 67 %; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.60–1.85 (m, 3 H), 1.88–2.18 (m, 3 H), 5.23–5.30 (m, 1 H), 5.77 (dddd, J = 10.0, 3.8, 2.1, 2.1 Hz, 1 H), 5.99 (dddd, J = 10.0, 4.2, 3.2, 1.0 Hz, 1 H), 6.59 (br s, 1 H), 7.26–7.29 (m, 2 H), 7.38–7.42 (m, 2 H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 19.1 (CH_2), 25.2 (CH_2), 28.8 (CH_2), 69.5 (CH), 116.1 (C), 120.5 (CH), 125.9 (CH), 132.3 (CH), 133.4 (CH), 137.5 (C), 153.4 (C); IR ($CHCl_3$) 3433, 2935, 1730, 1590 cm^{-1}; HRMS (EI+) for $C_{13}H_{14}NO_2{}^{81}Br$ calcd 297.0187, found 297.0185, for $C_{13}H_{14}NO_2{}^{79}Br$ calcd 295.0208, found 295.0211. Anal. calcd for $C_{13}H_{14}NO_2Br$: C, 52.72; H, 4.76; N, 4.73. Found: C, 52.26; H, 4.77; N, 4.57.

Carbamate (+)-5d



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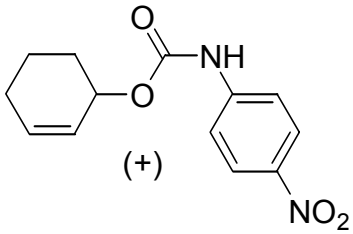
$[\alpha]^{30}_D$ = +110 (*c* = 0.51, $CHCl_3$); HPLC (Chiralpak AD, 7 % *i*PrOH-hexane, flow rate 1 $mLmin^{-1}$) t_R(+) = 21.5 min, t_R(–) = 24.6 min, ee = 65 %; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.60–1.85 (m, 3 H), 1.88–2.18 (m, 3 H), 5.26–5.33 (m, 1 H), 5.74–5.81 (m, 1 H), 5.96–6.03 (m, 1 H), 6.98 (s, 1 H), 7.45 (dd, *J* = 8.4, 8.4 Hz, 1 H), 7.68–7.78 (m, 1 H), 7.89 (dd, *J* = 8.4, 2.1 Hz, 1 H), 8.31 (dd, *J* = 2.1, 2.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 19.0 (CH_2), 25.2 (CH_2), 28.7 (CH_2), 70.0 (CH), 113.6 (CH), 118.2 (CH), 124.4 (CH), 125.6 (CH), 130.1 (CH), 133.7 (CH), 139.7 (C), 149.0 (C), 153.3 (C); IR ($CHCl_3$) 3421, 2947, 2869, 2836, 1732, 1623, 1594, 1548, 912 cm^{-1}; LRMS (EI+) 262, 218, 190, 164, 118, 70, 65; HRMS (EI+) for $C_{13}H_{14}N_2O_4$ calcd 262.0954, found 262.0945. Anal. calcd for $C_{13}H_{14}N_2O_4$: C, 59.54; H, 5.38; N, 10.68. Found: C, 59.36; H, 5.44; N, 10.54.

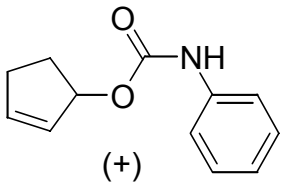
Carbamate (+)-5e



Following the general procedure, cyclohexene (100 μL) was reacted with the peroxycarbamate **2e** (50.8 mg) the complex generated from $Cu(MeCN)_4PF_6$ (7.4 mg) and the ligand (*R*,*R*)-**1b** (7.4 mg) in ethyl acetate (1.0 mL) at room temperature over 16 h. Flash column chromatography on silica gel (pet. ether-ether, 100:0→50:50) afforded the carbamate **5e** (34 mg, 65%) as an oil.

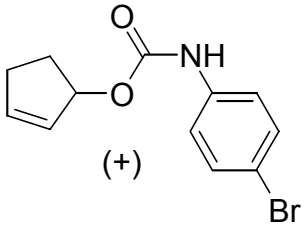
$[\alpha]^{20}_D$ = +132 (*c* = 1.05, $CHCl_3$); HPLC (Chiralpak AD, 7 % *i*PrOH-hexane, flow rate 1 $mLmin^{-1}$) t_R(+) = 25.3 min, t_R(–) = 28.8 min, ee = 72 %; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.61–1.85 (m, 3 H), 1.88–2.20 (m, 3 H), 5.25–5.35 (m, 1 H), 5.76 (dddd, *J* = 10.0, 3.6, 2.2, 2.1 Hz, 1 H), 6.00 (dddd, *J* = 10.0, 4.2, 3.2, 1.0 Hz, 1 H), 7.09 (br s, 1 H), 7.55 (d, *J* = 9.2 Hz, 2 H), 8.18 (d, *J* = 9.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 19.0 (CH_2), 25.2 (CH_2), 28.7 (CH_2), 70.2 (CH), 118.0 (CH), 125.4 (CH), 125.6 (CH), 133.9 (CH), 143.2 (C), 144.4 (C), 152.9 (C); IR ($CHCl_3$) 3426, 2936, 2869, 1738, 1714, 1613, 1594 cm^{-1}; HRMS (EI+) for $C_{13}H_{14}N_2O_4$ calcd 262.0954, found 262.0946. Anal. calcd for $C_{13}H_{14}N_2O_4$: C, 59.54; H, 5.38; N, 10.68. Found: C, 59.55; H, 5.38; N, 10.53.

Carbamate (+)-6b



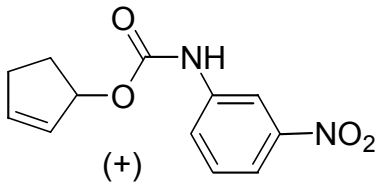
$[\alpha]^{30}_{D}$ = +144 (*c* = 0.50, $CHCl_3$); HPLC (Chiralpak AD, 3% *i*PrOH-hexane, flow rate 1 $mLmin^{-1}$) t_R(+) = 25.5 min, t_R(–) = 28.1 min, ee = 76 %; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.85–1.98 (m, 1 H), 2.30–2.42 (m, 2 H), 2.50–2.63 (m, 1 H), 5.75–5.81 (m, 1 H), 5.88–5.93 (m, 1 H), 6.12–6.17 (m, 1 H), 7.04–7.09 (m, 1 H), 7.28–7.34 (m, 2 H), 7.36–7.40 (m, 2 H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 30.3 (CH_2), 31.4 (CH_2), 81.6 (CH), 118.9 (CH), 123.6 (CH), 129.4 (CH), 129.7 (CH), 138.1 (CH), 138.3 (C), 153.8 (C); IR ($CHCl_3$) 3435, 2933, 2856, 1730, 1603 cm^{-1}; HRMS (EI+) for $C_{12}H_{13}NO_2$ calcd 203.0946, found 203.0939. Anal. calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.70; H, 6.41; N, 6.87.

Carbamate (+)-6c



$[\alpha]^{34}_{D}$ = +101 (*c* = 0.70, $CHCl_3$); HPLC (Chiralpak AD, 3 % *i*PrOH-hexane, flow rate 1 $mLmin^{-1}$) t_R(+) = 38.5 min, t_R(–) = 40.5 min, ee = 70 %; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.85–1.95 (m, 1 H), 2.30–2.42 (m, 2 H), 2.50–2.62 (m, 1 H), 5.73–5.77 (m, 1 H), 5.86–5.90 (m, 1 H), 6.12–6.16 (m, 1 H), 6.56 (br s, 1 H), 7.27 (d, *J* = 7.6 Hz, 2 H), 7.39 (m, 2 H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 30.2 (CH_2), 31.4 (CH_2), 81.9 (CH), 116.1 (C), 120.4 (CH), 129.5 (CH), 132.3 (CH), 137.5 (C), 138.4 (CH), 153.6 (C); IR ($CHCl_3$) 3434, 2933, 2856, 1732, 1591 cm^{-1}; HRMS (CI, NH_3) for $C_{12}H_{12}{}^{81}BrNO_2$+$NH_4^+$ calcd 301.0375, found 301.0364, for $C_{12}H_{12}{}^{79}BrNO_2$+$NH_4^+$ calcd 299.0395, found 299.0388. Anal. calcd for $C_{12}H_{12}BrNO_2$: C, 51.09; H, 4.29; N, 4.96. Found: C, 51.02; H, 4.34; N, 5.17.

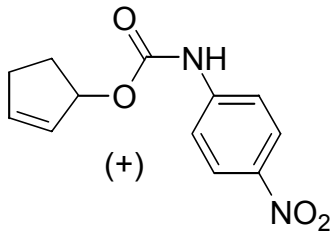
Carbamate (+)-6d



$[\alpha]^{20}_{D}$ = +116 (*c* = 0.91, $CHCl_3$); HPLC (Chiralpak AD, 5 % *i*PrOH-hexane, flow rate 1 $mLmin^{-1}$) t_R(+) = 26.9 min, t_R(–) = 30.2 min, ee = 81 %; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.85–2.00 (m, 1 H), 2.28–2.35 (m, 2 H), 2.50–2.63 (m, 1 H), 5.75–5.81 (m, 1 H), 5.86–5.92 (m, 1 H), 6.13–6.18 (m, 1 H), 6.91 (br s, 1 H), 7.45 (dd, *J* = 8.2, 8.2 Hz, 1 H), 7.70–7.74 (m, 1 H), 7.89 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1 H), 8.30 (dd, *J* = 2.2, 2.1 Hz, 1 H);^{13}C NMR ($CDCl_3$, 500 MHz) δ 30.2 (CH_2), 31.4 (CH_2),

82.4 (CH), 113.6 (CH), 118.2 (CH), 124.4 (CH), 129.3 (CH), 130.1 (CH), 138.6 (CH), 139.6 (C), 149.1 (C), 153.5 (C); IR ($CHCl_3$) 3431, 2934, 2856, 1732, 1353 cm^{-1}; HRMS (EI+) for $C_{12}H_{12}N_2O_4$ calcd 248.0797, found 248.0786. Anal. calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.29. Found: C, 58.09; H, 4.87; N, 11.27.

Carbamate (+)-6e



Following the general procedure, cyclopentene (88 μL) was reacted with the peroxycarbamate **2e** (50.8 mg) the complex generated from $Cu(MeCN)_4PF_6$ (7.4 mg) and the ligand (*R*,*R*)-**1b** (7.4 mg) in ethyl acetate (1.0 mL) at room temperature over 16 h. Flash column chromatography on silica gel (pet. ether-ether, 100:0→50:50) afforded the carbamate **6e** (24 mg, 48%) as an oil.
$[\alpha]^{20}_D$ = +143 (*c* = 0.80, $CHCl_3$); HPLC (Chiralpak ADH, 7 % *i*-PrOH/Hexane, flow rate 1 $mLmin^{-1}$) $t_R(+)$ = 35.0 min, $t_R(-)$ = 37.3 min, ee = 85 %; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.83–1.98 (m, 1 H), 2.25–2.42 (m, 2 H), 2.48–2.62 (m, 1 H), 5.75–5.83 (m, 1 H), 5.85–5.92 (m, 1 H), 6.14–6.21 (m, 1 H), 6.92 (br s, 1 H), 7.53 (d, *J* = 9.2 Hz, 2 H), 8.19 (d, *J* = 9.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 30.2 (CH_2), 31.5 (CH_2), 82.6 (CH), 117.9 (CH), 125.6 (CH), 129.1 (CH), 138.8 (CH), 143.2 (C), 144.4 (C), 153.1 (C); IR ($CHCl_3$) 3426, 2930, 2855, 1732, 1611 cm^{-1}; LRMS 248, 204, 138, 118, 67; LRMS (EI+) *m/z* (rel. intensity) 248 ([M^+], 2), 67 (100); Anal. calcd $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.29. Found: C, 57.85; H, 4.99; N, 11.01.

1 O'Brien, P.; Rosser, C. M.; Caine, D. *Tetrahedron* **2003**, *59*, 9779–9791.

2 Synerholm, M. E.; Gilman, N. W.; Morgan, J. W.; Hill, R. K. *J. Org. Chem.* **1968**, *33*, 1111–1116.