

## Electronic Supplementary Information (ESI)

### Simple Transformation of Crystalline Chiral Natural Anions to Liquid Medium and Their Use to Induce Chirality

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#### General Remarks

The following chemicals were purchased from Aldrich and used as supplied: Rh<sub>2</sub>(OAc)<sub>4</sub>, cyclohexene, styrene, 1-hexene, K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub>, *N*-methyl-morpholine oxide (NMO) and *t*-butanol. Tetrahydrofuran (THF), triethylamine, and dichloroethane were freshly distilled over calcium hydride. *p*-Toluenesulfonylazide was prepared from *p*-toluenesulfonylchloride and sodium azide. Sodium hydride was used as 55% dispersion in mineral oil. All reactions were performed in oven-dried glassware under an atmosphere of argon. The diazo substrate **1** and the lactam **2** has been reported by us elsewhere.<sup>1</sup> Tetra-*n*-hexyl-dimethylguanidinium chloride [(di-h)<sub>2</sub>dmg] Cl was prepared according to our reported procedure.<sup>2</sup>

Flash chromatography was carried out on silica gel 60 M from MN (Ref. 815381) or on aluminium oxide basic from MN (Ref. 815010, Brockmann activity 1). Reaction mixtures were analysed by TLC using ALUGRAM<sup>®</sup> SIL G/UV<sub>254</sub> from MN (Ref. 818133, silica gel 60) and aluminiumoxid 60F<sub>254</sub> neutral plates (type E) from Merck (Ref. 5550). Infrared spectra (IR) spectra were recorded on a Mattson Instruments model Satellite FTIR as thinly dispersed films. High and low resolution mass spectra (EI, FAB) were carried out by mass spectrometry service of University of Santiago de Compostela (Spain). NMR spectra were recorded in a Bruker AMX 400 using CDCl<sub>3</sub> as solvent and (CH<sub>3</sub>)<sub>4</sub>Si (<sup>1</sup>H) as internal standard. <sup>31</sup>P chemical shifts are reported in ppm relative to H<sub>3</sub>PO<sub>4</sub> (external standard). All coupling constants are expressed in Hz. Infrared spectra (IR) were recorded with a Jasco FT/IR-430 or with a Mattson Instruments Satellite FTIR model as thinly dispersed films. Gas liquid chromatography (GLC) was carried out on a Varian Star 3400 Cx gas chromatograph, using He as carrier gas and chiral capillary column Supelco β-dex 120 (30m x 0.25 mm). HPLC analyses were carried out using Dionex components P680 and UVD340S on a

### General procedure for the anion exchange of [(di-h)<sub>2</sub>dmg] Cl

The Ionic Liquid tetra-*n*-hexyl-dimethylguanidinium chloride [(di-h)<sub>2</sub>dmg]Cl was prepared following the reported procedure.<sup>2</sup> The IL [(di-h)<sub>2</sub>dmg]Cl (1g, 2.18 mmol) was dissolved in dichloromethane and then the desired chiral organic anion (2 equiv) was added as a salt or as an acid. When the organic anion was added as an acid, it was firstly transformed to the salt by addition of equimolar NaOH solution in methanol. The mixture was stirred at room temperature during 24 hours. The resulting solid was collected by filtration and washed with dichloromethane (2 × 20 mL). The combined organic layers were collected, dried (MgSO<sub>4</sub>) and filtered. The salt was then recovered after passing through a column with silica and activated carbon and the solvent removed under vacuum. The product was stirred under vacuum overnight.

**[(di-h)<sub>2</sub>dmg][(S)-mand];** This compound was obtained as an orange viscous liquid (1.10 g, 88 %) IR  $\nu_{\text{max}}$  (film): 3749, 3444, 3062, 3032, 2931, 2862, 1732, 1651, 1574, 1543, 1458, 1419, 1361, 1242, 1188, 1092, 1065, 930, 895, 729, 698, 667  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR  $\delta$  (CDCl<sub>3</sub>, 400MHz): 7.37 (2H, d, J = 3.5 Hz); 7.20 (3H, t, J = 6.6 Hz); 5.04 (1H, s); 3.05–2.91 (8H, m); 2.72 (6H, s); 1.60–1.10 (32H, m); 0.85 (12H, t, J = 9.2 Hz). <sup>13</sup>C-NMR  $\delta$  (100 MHz, CDCl<sub>3</sub>): 175.92; 163.13; 139.70; 128.07, 127.57 and 126.78; 73.03; 49.95 and 49.25 (rotamers); 47.95; 40.20; 31.43 and 31.27 (rotamers); 27.72 and 27.27 (rotamers); 26.39 and 26.14 (rotamers); 22.39; 13.85. Analysis: Calc. for C<sub>35</sub>H<sub>65</sub>N<sub>3</sub>O<sub>3</sub>·2H<sub>2</sub>O: N 6.86, C 68.63, H 11.27. Found: N 6.69, C 69.05, H 11.45 %.

**[(di-h)<sub>2</sub>dmg][lactic];** This compound was obtained as a yellow viscous liquid (0.95g, 85 %)

IR  $\nu_{\text{max}}$  (film): 3749, 3398, 2931, 2858, 1736, 1716, 1701, 1651, 1581, 1539, 1462, 1419, 1377, 1315, 1269, 1200, 1138, 1061, 968, 879, 798, 729, 667  $\text{cm}^{-1}$ . <sup>1</sup>H-NMR  $\delta$  (CDCl<sub>3</sub>, 400MHz): 3.83 (1H, m); 3.00–2.85 (8H, m); 2.76 (6H, s); 1.47–1.35 (32H, m); 1.02 (3H, s); 0.60 (12H, t, J = 6.1

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Hz).  $^{13}\text{C-NMR } \delta$  (100 MHz,  $\text{CDCl}_3$ ): 179.25; 163.10; 67.26; 49.88 and 49.18 (rotamers); 47.72; 40.26; 31.25 and 30.98 (rotamers); 27.57 and 27.16 (rotamers); 26.19 and 25.57 (rotamers); 22.14; 20.71; 13.58. Analysis: Calc. for  $\text{C}_{30}\text{H}_{63}\text{N}_3\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ : N 7.28, C 62.39, H 12.13. Found: N 6.83, C 62.56, H 11.76 %.

**[(di-h)<sub>2</sub>dmg][quinic]**; This compound was obtained as a yellow pale viscous liquid (1.22 g, 91 %) IR  $\nu_{\text{max}}$  (film): 3676, 3398, 2929, 2858, 2729, 2422, 1581, 1539, 1464, 1419, 1377, 1315, 1269, 1242, 1198, 1169, 1144, 1119, 1063, 970, 908, 879, 796, 727  $\text{cm}^{-1}$ .  $^1\text{H-NMR } \delta$  ( $\text{CDCl}_3$ , 400MHz): 3.17 (1H, t,  $J = 7.2$  Hz); 3.03 (2H, t,  $J = 6.8$  Hz); 2.96–2.76 (8H, m); 2.71 (6H, s); 2.10 (4H, s); 1.88–1.85 (2H, m); 1.73–1.23 (32H, m); 0.83 (12H, t,  $J = 6.7$  Hz).  $^{13}\text{C-NMR } \delta$  (100 MHz,  $\text{CDCl}_3$ ): 179.78; 163.34; 121.84; 69.13; 49.92 and 49.39 (rotamers); 48.17 and 48.00 (rotamers); 40.76; 38.59; 31.55 and 31.35 (rotamers); 27.85 and 27.41 (rotamers); 26.65 and 26.46 (rotamers); 22.51; 13.84. Analysis: Calc. for  $\text{C}_{34}\text{H}_{69}\text{N}_3\text{O}_6$ : N 6.85, C 66.23, H 12.20. Found: N 7.68, C 66.90, H 12.74 %.

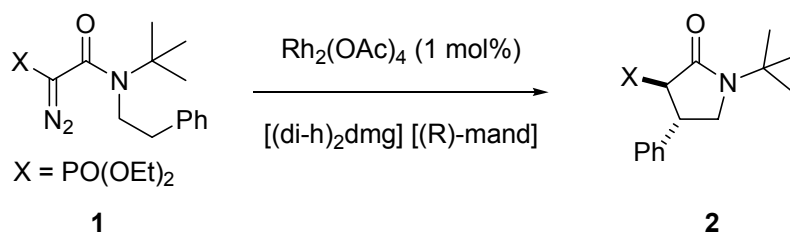
**[(di-h)<sub>2</sub>dmg][(S)-CSA]**; This compound was obtained as a colourless viscous liquid (1.32 g, 92%) IR  $\nu_{\text{max}}$  (film): 3749, 3464, 2931, 2862, 1743, 1701, 1682, 1651, 1577, 1539, 1458, 1419, 1373, 1234, 1173, 1038, 964, 879, 787, 729, 667, 613, 579  $\text{cm}^{-1}$ .  $^1\text{H-NMR } \delta$  ( $\text{CDCl}_3$ , 400MHz): 4.21 (2H, m); 3.15–2.99 (8H, m); 2.96 (6H, s); 2.81 (2H, m); 2.71 (1H, m); 1.81 (2H, m); 1.67–1.38 (32H, m); 1.32 (6H, d,  $J = 3.3$  Hz); 1.22 (6H, s); 0.81 (12H, t,  $J = 6.4$  Hz).  $^{13}\text{C-NMR } \delta$  (100 MHz,  $\text{CDCl}_3$ ): 179.45; 163.35; 121.79; 67.40; 50.01 and 49.38 (rotamers); 47.49; 40.51, 31.56 and 31.31 (rotamers); 30.10; 28.92; 28.83; 27.76 and 27.37 (rotamers); 26.45 and 26.35 (rotamers); 25.72; 22.38; 20.75; 13.93. Analysis: Calc. for  $\text{C}_{37}\text{H}_{73}\text{N}_3\text{O}_4\text{S} \cdot 2\text{H}_2\text{O}$ : N 6.07, C 64.16, H 11.13, S 4.62. Found: N 5.59, C 64.44, H 11.09, S 4.85 %.

**[(di-h)<sub>2</sub>dmg][Boc-ala]**; This compound was obtained as a yellow pale viscous liquid (1.14 g, 85%). IR  $\nu_{\text{max}}$  (film): 3749, 3444, 2931, 2862, 1716, 1701, 1651, 1558, 1539, 1520, 1458, 1419, 1396, 1365, 1338, 1315, 1246, 1169, 1049, 837, 783, 667  $\text{cm}^{-1}$ .  $^1\text{H-NMR } \delta$  ( $\text{CDCl}_3$ , 400MHz): 8.52 (1H,

s); 5.69 (1H, m); 3.06–2.92 (8H, m); 2.86 (6H, s); 1.55–1.25 (32H, m); 1.20 (3H, d,  $J = 3.0$  Hz); 1.13 (6H, s); 1.03 (9H, m) 0.71 (12H, t,  $J = 6.3$  Hz).  $^{13}\text{C-NMR}$   $\delta$  (100 MHz,  $\text{CDCl}_3$ ): 177.54; 163.19; 155.28; 57.35; 50.56; 49.95 and 49.27 (rotamers); 47.26; 40.35; 31.36 and 31.18 (rotamers); 28.23; 27.68 and 27.28 (rotamers); 26.26 and 25.68 (rotamers); 22.24; 19.26; 18.14; 13.69. Analysis: Calc. for  $\text{C}_{35}\text{H}_{72}\text{N}_4\text{O}_4 \cdot 3.7\text{H}_2\text{O}$ : N 8.24, C 61.80, H 11.68. Found: N 8.30, C 61.93, H 11.06 %.

**[(di-h)<sub>2</sub>dmg][Ac-prol-OH]**; This compound was obtained as a yellow pale viscous liquid (1.15 g, 88 %). IR  $\nu_{\text{max}}$  (film): 3749, 3421, 2931, 2862, 1736, 1716, 1701, 1624, 1577, 1539, 1458, 1338, 1273, 1196, 1084, 1038, 1007, 968, 876, 818, 725, 667  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$   $\delta$  ( $\text{CDCl}_3$ , 400MHz): 4.39 (1H, m); 3.66 (1H, m); 3.51-3.40 (2H, m); 3.15–3.02 (8H, m); 2.98 (6H, s); 1.96 (1H, s); 1.89 (1H, s); 1.64–1.31 (32H, m); 1.90 (9H, m), 0.79 (12H, t,  $J = 5.7$  Hz).  $^{13}\text{C-NMR}$   $\delta$  (100 MHz,  $\text{CDCl}_3$ ): 176.50 and 175.59 (rotamers); 171.17 and 170.32 (rotamers); 163.25; 69.34 and 68.25 (rotamers); 60.75 and 58.79 (rotamers); 55.88 and 54.16 (rotamers); 49.82 and 49.29 (rotamers); 47.33; 40.58; 39.96; 37.80; 31.29 and 31.13 (rotamers); 27.70 and 27.32 (rotamers); 26.39 and 26.29 (rotamers); 22.55; 22.32; 21.63; 13.80. Analysis: Calc. for  $\text{C}_{34}\text{H}_{68}\text{N}_4\text{O}_4 \cdot 4.3\text{H}_2\text{O}$ : N 8.27, C 60.27, H 11.31. Found: N 8.07, C 60.57, H 10.78 %.

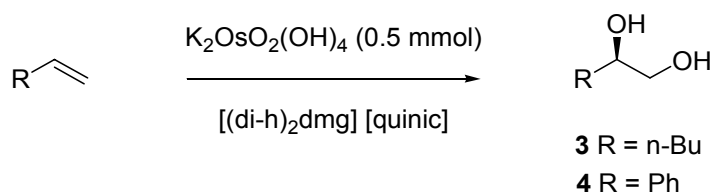
### Representative procedure for the Rh(II) catalysed intramolecular C-H insertion



To a stirred suspension of  $\text{Rh}_2(\text{OAc})_4$  (0.66 mg, 1 mol%) in the chiral ionic liquid [(di-h)<sub>2</sub>dmg] [(*R*)-mand] (0.3 g) under argon atmosphere was added the  $\alpha$ -diazo- $\alpha$ -(diethoxyphosphoryl)acetamide **1** (58.7 mg, 0.15 mmol) and heated at 110 °C during 3 h. The reaction mixture was allowed to cool to room temperature, extracted with *n*-hexane (5 x 2 mL, 5

min for each extraction), evaporated under reduced pressure and the obtained residue (81 % conversion and *trans/cis* ratio of 67:33 by  $^{31}\text{P}$  NMR) was purified by flash chromatography (basic alumina AcOEt/Hex 1:1) to give the  $\gamma$ -lactam **2**<sup>1</sup> (38.0 mg, 72 %), ee 27 % (major enantiomer  $t_{\text{R}}$  = 28.67 min, minor enantiomer  $t_{\text{R}}$  = 15.78 min determined by HPLC, Chiralpak AD column, columns with pre-column at 25°C using 10% of 2-propanol in hexane at 1mL/min)<sup>3</sup>.

### Representative procedure for the Sharpless asymmetric dihydroxylation (AD)



To chiral ionic liquid [(di-h)<sub>2</sub>dmg][quinic] (0.3 mL) was added NMO (100 mg; 0.5 mmol) and the catalyst K<sub>2</sub>OsO<sub>2</sub>(OH)<sub>4</sub> (0.5 mol%). Then the olefin (0.5 mmol) was added to the mixture (formation of a second phase for liquid olefins for some ILs which disappears during the reaction), which was stirred at room temperature during 24 h. The obtained mixture was dissolved in a small amount of dichloromethane (2 mL) and purified by flash chromatography to give the corresponding chiral diols **3** and **4**.<sup>4</sup>

**3**<sup>4</sup> (66.6 mg, 95 %), ee = 85 % (determined by GLC analysis: carrier gas flow: 0.9 mL/min, T(oven)= 102 °C; T(injector)=270 °C; T(detector)=270 °C];  $t_{\text{R}}$  = 25.4 min. (minor);  $t_{\text{R}}$  = 27.1 min. (major))<sup>4</sup>.

**4**<sup>4</sup> (55.3 mg, 92 %), ee = 72 % (determined by by GLC analysis: carrier gas flow: 0.9 mL/min, T(oven)= 140 °C; T(injector)=270 °C; T(detector)=270 °C;  $t_{\text{R}}$  = 25.2 min. (minor);  $t_{\text{R}}$  = 26.3 min. (major))<sup>4</sup>.

### References

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