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Asymmetric Arylboron Additions to Enones Using Novel Rhodium-Dicyclophane Imidazolium Carbene Catalysis**

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All the reactions were carried out under argon gas. Dioxane and THF were distilled from sodium benzophenone ketyl before use. $Rh(acac)(C_2H_4)_2$ could be prepared from $RhCl_3$ according to the literature procedure or it is available commercially. NMR spectra were recorded on a Bruker AMX 300 (300 MHz) or a DMX 600 (MHz) instrument.

General Procedure for Rh catalyzed enone addition:

A 10 ml round-bottom flask under argon was charged with $Rh(acac)(C_2H_4)_2$ (2.1 mg, 0.008 mmol), $PhB(OH)_2$ (73.5 mg, 0.6 mmol), and the bis-cyclophane imidazolium salt (9.4 mg, 0.012 mmol), containing THF (2 mL) and cyclohexenone (39 mg, 0.4 mmol). The mixture was stirred at rt for 10 min, and H_2O (0.2 mL) was added. The mixture was stirred magnetically at 60 °C for indicated time. The solution was cooled to rt and saturated sodium bicarbonate (5 mL) was added and the mixture was stirred for 15 min. The mixture was extracted with ethyl acetate (2 x 5 mL). The combined ethyl acetate fractions were washed 3 times with aqueous brine (5 mL) and dried over anhydrous magnesium sulphate. The solvent was removed by rotary evaporation and hexane (10 mL) was added to the crude material which was filtered through a pad of silicon gel (2 g). The concentrated filtrate was purified by silica gel chromatography using ethyl acetate/hexanes (5-15 %). The known compounds, with the isolated yields indicated, were characterized by the individual data:

***S*-3-Phenylcyclohexanone**: ^{1}H NMR ($CDCl_3$) δ 7.26-7.36 (m, 2H), 7.16-7.25 (m, 3H), 3.01 (m, 1H), 2.30-2.66 (m, 4H), 2.03-2.18 (m, 2H), 1.70-1.93 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 211.2, 144.5, 128.6, 126.6, 126.3, 49.2, 44.6, 41.3, 32.7, 25.6; MS (EI) *m/z* 174; $[\alpha]_D$ –21° ($CHCl_3$, c 0.97), chiral HPLC (OD-H column, hept/*i*-PrOH, 98/2, 1 mL/min, rt) 8.32 min (major), 9.45 (minor).

***S*-3-(4-Methoxyphenyl) cyclohexanone**: ^{1}H NMR ($CDCl_3$) δ 7.09 (d, *J*=8.6 Hz, 2H), 6.81 (d, *J*=8.6 Hz, 2H), 3.75 (s, 3H), 2.91 (m, 1H), 2.23-2.52 (m, 4H), 2.00-2.07 (m, 2H), 1.68-1.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 211.1, 159.2, 136.3, 127.6, 126.8, 113.3, 56.0, 49.2, 44.1, 41.2, 32.8, 25.3; MS (EI) *m/z* 204. $[\alpha]_D$ –17° ($CHCl_3$, c 0.95), chiral HPLC (OD-H column, hept/*i*-PrOH, 90/10, 1 mL/min, rt) 10.87 min (major), 13.04 (minor).

***S*-3-*o*-Tolyl-cyclohexanone:** ^{1}H NMR ($CDCl_3$) δ 7.15-7.18 (m, 4H), 3.11 (m, 1H), 2.37-2.42 (m, 4H), 2.27 (s, 3H), 2.12 (m, 1H), 1.90-1.93 (m, 1H), 1.72 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 211.2, 142.5, 135.2, 131.0, 126.3, 126.0, 48.3, 41.5,41.3, 32.2, 25.9, 19.3; MS (EI) *m/z* 188. $[\alpha]_D$ –15° ($CHCl_3$, c 0.87); chiral HPLC (OD-H column, hept/*i*-PrOH, 98/2, 1 mL/min, rt) 9.36 min (major), 11.73 (minor).

***S*-3-(4-Acetylphenyl)cyclohexanone:** ^{1}H NMR ($CDCl_3$) δ 7.25-7.60 (d, *J*= 8.4 Hz, 2H), 7.18-7.21 (d, *J*=8.4 Hz, 2H), 3.12 (m, 1H), 2.32-2.45 (m, 7H), 2.19 (m, 1H), 1.87-1.91 (m, 1H), 1.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 211.5, 196.7, 148.0, 134.7, 127.9, 127.5, 126.0, 48.1, 41.3, 39.0, 32.2, 25.9, 24.8; MS (EI) *m/z* 216. $[\alpha]_D$ – 23° ($CHCl_3$, c 0.78); chiral HPLC (OD-H column, hept/*i*-PrOH, 95/5, 1 mL/min, rt) 10.52 min (major), 13.76 (minor).

***S*-3-(4-Trifluoromethyl) cyclohexanone**: ^{1}H NMR ($CDCl_3$) δ 7.57-7.59 (d, *J*=8.4 Hz, 2H), 7.32-7.34 (d, *J*=8.4 Hz, 2H), 3.09 (tt, *J*= 11.9/4.2 Hz, 1H), 2.37-2.61 (m, 4H), 2.13-2.20 (m, 1H), 2.08-2.10 (m, 1H), 1.78-1.92(m, 2H); ^{13}C NMR ($CDCl_3$) δ 210.0, 148.2, 129.0, 126.9, 125.6, 124.0, 48.3, 44.6, 41.0, 32.8, 25.2; MS (EI) *m/z* 242. $[\alpha]_D$ -18° ($CHCl_3$, c 0.97); chiral HPLC (OD-H column, hept/*i*-PrOH, 90/10, 1 mL/min, rt) 8.73 min (major), 10.21 (minor).

***S*-3-Phenylcycloheptanone**: ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 2H), 7.15-7.21 (m, 3H), 2.82-2.87 (m, 2H), 2.53-2.66 (m, 3H), 1.91-1.97(m, 3H), 1.63-1.70 (m, 2H), 1.40-1.46 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 213.6, 146.7, 128.5, 126.2, 126.0, 51.6, 43.2, 42.7, 39.8, 30.2, 23.9; MS (EI) *m/z* 188. $[\alpha]_D$ –59° ($CHCl_3$, c 0.78), chiral HPLC (OD-H column, hept/*i*-PrOH, 95/5, 1 mL/min, rt) 7.45 min (major), 8.21 (minor).

***S*-3-(4-Methoxyphenyl) cycloheptanone**: ^{1}H NMR ($CDCl_3$) δ 7.12 (d, *J*=8.6 Hz, 2H), 6.83 (d, *J*=8.6 Hz, 2H), 3.73 (s, 3H), 2.85-2.88 (m, 2H), 2.52-2.56 (m, 3H), 1.90-1.93(m, 3H), 1.67-1.71 (m, 2H), 1.39 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 214.1, 158.9, 138.5, 128.3, 126.8, 126.2, 113.7, 56.6, 43.2, 42.5, 39.6, 30.3, 25.1; MS (EI) *m/z* 218. $[\alpha]_D$ –51° ($CHCl_3$, c 0.77), chiral HPLC (OD-H column, hept/*i*-PrOH, 90/10, 1 mL/min, rt) 9.78 min (major), 12.16 (minor).

***S*-3-*o*-Tolyl-cycloheptanone**: ^{1}H NMR ($CDCl_3$) $\delta\,\delta$ 7.03-7.17 (m, 4H), 2.83-2.87 (m, 2H), 2.43-2.48 (m, 6H), 1.87-1.90(m, 3H), 1.66-1.73 (m, 2H), 1.42 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 211.2, 142.4, 132.9, 132.7, 130.2, 125.5, 50.0, 43.6, 42.5, 37.8, 27.7, 24.2, 21.6; MS (EI) *m/z* 202. $[\alpha]_D$ –57° ($CHCl_3$, c 0.83), chiral HPLC (OD-H column, hept/*i*-PrOH, 95/5, 1 mL/min, rt) 7.83 min (major), 9.76 (minor).

***S*-3-(4-Acetylphenyl) cycloheptanone**: ^{1}H NMR ($CDCl_3$) δ 7.56-7.62 (d, *J*=8.6 Hz, 2H), 7.17-7.21 (d, *J*=8.6 Hz, 2H), 2.80-2.83 (m, 2H), 2.47-2.53 (m, 6H), 1.89-1.93(m, 3H), 1.69-1.72 (m, 2H), 1.42 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 210.9, 198.2, 150.7, 134.7, 127.8, 127.6, 49.8, 45.8, 43.7, 37.8, 27.6, 25.8, 24.1; MS (EI) *m/z* 230. $[\alpha]_D$ –53° ($CHCl_3$, c 0.71), chiral HPLC (OD-H column, hept/*i*-PrOH, 90/10, 1 mL/min, rt) 9.34 min (major), 11.59 (minor).

***S*-3-(4-Trifluoromethyl)cycloheptanone**: ^{1}H NMR ($CDCl_3$) δ 7.48-7.54 (d, *J*=8.6 Hz, 2H), 7.26-7.30 (d, *J*=8.6 Hz, 2H), 2.79-2.88 (m, 1H), 2.36-2.48 (m, 2H), 2.01-2.21(m, 2H), 1.90-1.93(m, 2H), 1.37-1.82 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 212.5, 156.7, 135.1, 129.7, 129.3, 123.7, 123.5, 120.8, 113.7, 49.6, 45.7, 43.2, 37.9, 27.6, 24.1; MS (EI) *m/z* 256. $[\alpha]_D$ –48° ($CHCl_3$, c 0.72), chiral HPLC (OD-H column, hept/*i*-PrOH, 95/5, 1 mL/min, rt) 10.25 min (major), 12.85 (minor).

***S*-3-Phenylcyclopentanone:** ^{1}H NMR ($CDCl_3$) δ 7.32-7.37 (m, 2H), 7.22-7.26 (m, 3H), 3.38-3.45 (m, 1H), 267 (m, 1H), 2.40-2.48(m, 2H), 2.25-2.37(m, 2H), 1.91-2.03(m, 1H); ^{13}C NMR ($CDCl_3$) δ 218.2, 143.5, 128.7, 128.3, 126.8, 126.5, 121.4, 45.7, 42.3, 38.9, 31.7; MS (EI) *m/z* 160. $[\alpha]_D$ –87° ($CHCl_3$, c 1.07), chiral HPLC (OD-H column, hept/*i*-PrOH, 98/2, 1 mL/min, rt) 8.52 min (major), 10.76 (minor).

***S*-4-Phenylpentan-2-one:** ^{1}H NMR ($CDCl_3$) δ 7.17-7.36 (m, 5H), 3.52 (m, 1H), 3.29 (m, 1H), 3.18 (m, 1H), 267 (m, 1H), 2.03 (s, 3H), 1.34(d, 3H); ^{13}C NMR ($CDCl_3$) δ 210.2, 145.7, 144.1, 137.2, 133.5, 128.6, 128.3, 127.8, 126.5, 45.8, 44.5; MS (EI) *m/z* 162. $[\alpha]_D$ –37° ($CHCl_3$, c 1.01), chiral HPLC (OD-H column, hept/*i*-PrOH, 98/2, 1 mL/min, rt) 9.37 min (major), 10.89 (minor).

***S*-1,3-Diphenylbutan-1-one:** mp: 50-51.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.92 (d, 2H), 7.41-7.57(m, 3H), 7.15-7.33 (m, 5H), 3.50(m, 1H), 3.31 (dd, 1H), 3.16(dd, 1H), 1.32 (d, 3H); ^{13}C NMR ($CDCl_3$) δ 199.1, 146.5, 132.9, 128.7, 128.4, 128.1, 126.9, 126.3, 47.2, 36.1, 21.7; MS (EI) *m/z* 224, $[\alpha]_D$ –15° ($CHCl_3$, c 1.00), chiral HPLC (OD-H column, hept/*i*-PrOH, 98/2, 1 mL/min, rt)

***S*-5-Methyl-4-phenylhexan-2-one:** ^{1}H NMR ($CDCl_3$) δ 7.11-7.30 (m, 5H), 2.86-2.95(m, 1H), 2.75-2.80(m, 2H), 1.98 (s, 3H), 1.75-1.88(m, 1H), 0.92(d, 3H), 0.73(d, 3H); ^{13}C NMR ($CDCl_3$) δ 210.1, 144.5, 128.3, 128.0, 126.2, 48.2, 47.5, 33.1, 20.5, 19.8; MS (EI) *m/z* 190. $[\alpha]_D$ –32° ($CHCl_3$, c 1.15), chiral HPLC (OD-H column, hept/*i*-PrOH, 98/2, 1 mL/min, rt)

Synthesis of the bis-[2.2]paracyclophane ligands

Prepared according to the published procedures:[18]
***S*$_p$-(-)-4-Amino[2.2]paracyclophane**: ^{1}H NMR ($CDCl_3$) δ 7.13 (dd, 1H), 6.00-6.56 (m, 5H), 5.34 (d, 1H), 3.2-3.38 (broad, 2H), 2.56-3.12 (m, 8H); MS (EI) *m/z* 223; $[\alpha]^{20}_D$ 85° ($CHCl_3$, c 0.55), mp: 239-241 °C.

***S*$_p$-(-)-4-Bromo-12-amino[2.2]paracyclophane**: ^{1}H NMR ($CDCl_3$) δ 7.15-7.23 (dd, 1H), 6.10-6.66 (m, 4H), 5.36-5.42 (d, 1H), 3.35-3.62 (broad, 2H), 2.62-3.22 (m, 8H); MS (EI) *m/z* 302.2; $[\alpha]^{20}_D$ –75° ($CHCl_3$, c 0.67).

Synthesis of *S*$_p$-(-)-4-aryl-12-amino[2.2]paracyclophanes 2: To a flame dried flask fitted with a chilled water condenser under nitrogen was added phenylpinacolatoboronic or cyclohexanylpinacolatoboronic ester (15.0 mmol) and the mixture of *S*$_p$-(-)-4-Bromo-12-amino [2.2] paracyclophane (2.72 g, 9.0 mmol), followed by $Pd(OAc)_2$ (41mg, 0. 18 mmol, 2 mol %), dihydroimidazolium chloride salt ligand (Ar=2,6-di-*i*-propylphenyl, 115 mg, 0.27 mmol, 3 mol %) and CsF (2.05 g, 13.5 mmol) in THF (30 mL). The mixture was stirred at 60 °C for 3.5 hr. The mixture was cooled to rt and extracted with ethyl acetate (10 x 2 mL) from added water (20 mL). The combined ethyl acetate fractions were washed with aqueous brine (3 x 10 mL) and dried over anhydrous magnesium sulphate. The solvent was removed by rotary evaporation and the crude material was diluted with ethyl acetate (50 mL). Water was added (50 mL) and the pH value was adjusted to ~1.0 as the solution was vigorously stirred. The water phase was separated and ethyl acetate was added (20 mL). The pH value was adjusted to ~12. The aqueous layer was extracted with ethyl acetate (2 x 20 mL) and the combined organic layers were dried over anhydrous magnesium sulphate. The solvent was removed by rotary evaporation. The crude product was purified by a short silicon gel column (4 g) eluted with 35% ethyl acetate/hexanes to get the light yellow product. LC-MS show the purification to be >95%. The individual compounds were characterized by the data shown below:

2 (R=Ph): Yield: 92%; ^{1}H NMR ($CDCl_3$) δ 7.28-7.52 (m, 3H), 7.11-7.21 (m, 3H), 6.12-6.64 (m, 4H), 5.38-5.45 (d, 1H), 3.49-3.65 (broad, 2H), 2.62-3.23 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 149.7, 145.8, 145.5, 143.7, 140.9, 137.8, 137.3, 130.5, 125.7, 125.4, 120.7, 36.9, 36.6; light-yellow solid; LC-MS: show molecule peak (M+1): 300.

2 (R=*c*-hexyl): Yield: 89%; ^{1}H NMR ($CDCl_3$) δ 7.13-7.23 (dd, 1H), 6.12-6.65 (m, 4H), 5.36-5.43 (d, 1H), 3.45-3.66 (broad, 2H), 2.63-3.22 (m, 9H), 1.32-1.65 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 148.6, 145.6, 135.9, 135.7, 135.2, 134.2, 130.7, 129.5, 125.2, 123.6, 120.7, 37.8, 37.6, 27.7, 27.0; light-yellow solid; LC-MS: show molecule peak (M+1): 306.

2 (R=*o*-MeOPh): Yield: 81%; ^{1}H NMR ($CDCl_3$) δ 7.31-7.38 (m, 1H), 7.09-7.22 (m, 3H), 6.92-6.97 (m, 3H), 6.12-6.65 (m, 4H), 5.38-5.45 (d, 1H), 3.72 (s, 3H), 3.52-3.68 (broad, 2H), 2.61-3.23 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 150.6, 148.7, 146.8, 146.5, 145.5, 143.7, 138.2, 126.9, 126.1, 121.3, 56.3, 37.6, 37.2; light-yellow solid; LC-MS: show molecule peak (M+1): 330.

Synthesis of dihydroimidazolium salts 3-6: To a solution of ***S*$_p$**-4-amino-paracyclophane **2** (2.23 mmol) in *n*-propanol (15 mL) were added a mixture of 40% aqueous solution of glyoxal (0.17 g, corresponding to 1.33 mmol of glyoxal), water (10 mL).The mixture was stirred for 16 h at rt and then 4 h at 60 °C. The mixture was cooled to rt. Upon addition of water (18 mL), a light yellow solid precipitated which was collected by filtration and dried by vacuum. The yield for the crude diimine product was from 75% to 88%. No further purication was performed at this point. The material was taken on directly to the next step.

To a solution of glyoxal-bis-(2,9-dicyclohexaphenanthrenyl) ethane diimine (1.55 mmol) in THF (10 mL) at 0 °C were added sodium borohydride (0.35 g, 8.80 mmol) in portions of 0.07 g over a period of 60 min. The mixture was allowed to warm to rt, and the mixture was stirred for 16 h, and subsequently refluxed for an additional 3 h. The mixture was allowed to cool to rt. To the mixture was added ice water (5 mL) over a period of 0.5 h, and then hydrochloric acid (8 mL, 3 M) cautiously. A white solid precipitated as a powder, which was collected by filtration, and dried in vacuum. Yields ranged from 76 to 82%. Again, no further purification was performed at this point. The crude N,N'-bis-[2.2]paracyclophanyl-1,2-diaminoethane dihydrochloride was taken on to the next step.

To a mixture of N,N'-bis-[2.2]paracyclophanyl-1,2-diaminoethane dihydrochloride (5.0 mmol) in triethyl orthoformate (30 mL) was added two drops of 96% formic acid. The mixture was heated at reflux for 60 h. After cooling to rt, a colorless solid precipitated which was collected by filtration and crystallized in toluene/dichloroethane/*n*-propanol (1:1:1) to get an off-white solid powder. Yields ranged from 88-90%. The bis-[2.2]paracyclophanylimidazolium chlorides were taked directly to the next step.

To the bis-[2.2]paracyclophanylimidazolium chlorides was added an equal equivalent of ammonium tetrafluoroborate in methanol (5 mL). The mixture was heated at reflux for 3 h, and the solution was cooled to rt. The product was collected by filtration to give a solid which was washed by cold methanol to give an off-white solid powder. Data for the individual products are shown below along with the yield for the combined three steps:

3: Yield: 61%; ^{1}H NMR ($CDCl_3$) δ 9.57 (s, 1H), 7.06 (m, 2H), 6.08-6.87 (m, 10H), 5.95 (m, 2H), 4.52 (s, 4H), 2.51-3.09 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 161.2, 149.7, 146.3, 145.7, 145.6, 143.2, 141.3, 137.6, 137.1, 130.7, 125.6, 125.0, 120.7, 54.8, 36.3, 36.1, 35.6; white powder solid; MS (EI) *m/z* 574; $[\alpha]^{20}_{D}$ −157° (DMSO, c 0.15): mp: 268 °C decomposed. $C_{35}H_{37}BF_4N_2$ (572.50) calcd. C: 73.43%, H: 6.51%, N: 4.89%, found: C: 73.27%, H: 6.52%, N: 4.82%.

4: Yield: 62%; ^{1}H NMR ($CDCl_3$) δ 9.61 (s, 1H), 7.15-7.27 (m, 10H), 7.02 (m, 2H), 6.06-6.81 (m, 8H), 5.93 (m, 2H), 4.48-4.56 (m, 4H), 2.52-3.11 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 161.2, 149.7, 146.3, 145.7, 145.6, 143.2, 141.3, 137.6, 137.1, 130.7, 125.6, 125.0, 120.7, 54.8, 36.3, 36.1, 35.6; white powder solid; MS (EI) *m/z* 726; $[\alpha]^{20}_{D}$ –86° (DMSO, c 0.21): mp: 252-253 °C. $C_{47}H_{45}BF_4N_2$ (724.70) calcd: C: 77.90%, H: 6.26%, N: 3.87%, found: C: 77.26%, H: 6.31%, N: 3.79%.

5: Yield: 50%; ^{1}H NMR ($CDCl_3$) δ 9.86 (s, 1H), 7.18-7.26 (m, 8H), 7.07-7.12 (dd, 2H), 6.10-6.73 (m, 8H), 5.36-5.43 (d, 2H), 4.68 (dd, *J*=8.4 Hz, 2H), 4.02 (dd, *J*=8.4 Hz, 2H), 2.62-3.26 (m, 8H), 1.32-1.67 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 162.1, 148.2, 147.6, 145.3, 145.2, 140.6, 139.7, 135.6, 135.1, 135.6, , 134.3, 130.6, 129.5, 125.2, 123.2, 120.6, 55.8, 55.3, 37.5, 37.0, 27.6, 27.0; $[\alpha]^{20}_{D}$ –162° (DMSO, c 0.11); white solid; LC-MS: molecule peak (M+1): 738. mp: 248-250 °C. $C_{47}H_{57}BF_4N_2$ (736.80) calcd: C: 76.62%, H: 7.80%, N: 3.80%, found: C: 76.59%, H: 7.76%, N: 3.82%.

6: Yield: 51%; ^{1}H NMR ($CDCl_3$) δ 10.21 (s, 1H), 7.3-7.11 (m, 8H), 6.16-6.78 (m, 10H), 5.38-5.45 (d, 2H), 4.62 (dd, *J*=8.4 Hz, 2H), 4.32 (dd, *J*=8.4 Hz, 2H), 3.80 (s, 3H), 3.76 (s, 3H), 2.51-3.09 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 162.1, 160.7, 148.6, 145.6, 135.9, 135.7, 135.2, 134.2, 130.7, 129.5, 125.2, 123.6, 120.7, 37.8, 37.6, 27.7, 27.0; white powder solid; $[\alpha]^{20}_{D}$ –138° (DMSO, c 0.09); LC-MS: molecule peak (M+1): 786. mp: 270 °C decomposed. $C_{49}H_{49}BF_4N_2O_2$ (784.75) calcd. C: 75.00%, H: 6.29%, N: 3.57%, O: 4.08%, found: C: 74.95%, H: 6.33%, N: 3.57%, O: 4.03%