Supplementary Material for Chemical Communications

Electronic Supporting Information

Shuttling through reversible covalent chemistry

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Experimental procedure for the DA reaction: a solution of 0.025 g of *E*-**1** (0.019 mmol) in 0.5 mL of d_6-DMSO in a NMR tube was treated with ~10 eq. of freshly cracked and distilled cyclopentadiene. The solution was degassed with N_2 and the NMR tube sealed. This solution was heated at 80 ^oC for 16 hrs and then allowed to cool to room temperature, extracted with $CHCl_3$ and washed with water. The organic phase was dried over $MgSO_4$, the solvent evaporated under reduced pressure and the residue purified by column chromatography (silica, $CHCl_3$/MeOH 98:2) to yield *Cp*-**1** as a colourless solid (90%). A similar procedure (8 h reaction time) was used to prepare *Cp*-**2** (93%) from *E*-**2**. Experimental procedure for the r-DA reaction: 0.010 g of *Cp*-**1** (0.007 mmol) in a glass vial were placed in the inlet oven of an FVP apparatus, then heated to 250^oC under reduced pressure (10^{-2} Torr) for 20 minutes, to quantitatively yield *E*-**1**.

Physical data for *Cp*-**1**: Mp 180-182 ^oC; ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ 8.30 (s, 2H, $H_{C \text{ or } C'}$), 8.27 (s, 2H, $H_{C \text{ or } C'}$), 8.19 (m, 8H, $H_{B \text{ and } B'}$), 7.60 (t, J = 7.8Hz, 4H, $H_{A \text{ and } A'}$), 7.46 (bt, 4H, $H_{D \text{ or } D'}$), 7.39 (bt, 4H, $H_{D \text{ or } D'}$), 7.35-7.10 (m, 40 H, H_{Ph}), 7.03 (s, 8H, $H_{F \text{ or } F'}$), 7.01 (s, 8H, $H_{F \text{ or } F'}$), 6.38 (bt, 1H, $H_{k \text{ or } k'}$), 6.31 (m, 3H, $H_{k \text{ or } k'}$, $H_{e \text{ and } e'}$), 6.15 (m, 2H, H_5 and $H_{4'}$), 6.05 (m, 2H, $H_{h \text{ or } h'}$ and $H_{5'}$), 5.85 (bt, 1H, $H_{h \text{ or } h'}$), 5.59 (m, 1H, H_4), 4.64-4.35 (m, 20H, $H_{E \text{ and } E'}$ and $H_{b \text{ and } b'}$), 4.19 (m, 4H, $H_{a \text{ and } a'}$ and $H_{m \text{ and } m'}$), 3.96-3.67 (m, 4H, $H_{l \text{ and } l'}$), 3.01-2.92 (m, 10H, $H_{f \text{ and } f'}$, $H_{g \text{ and } g'}$, $H_{3'}$ and $H_{6'}$), 2.81 (s, 1H, H_6), 2.76 (s, 1H, H_3), 2.63 (m, 1H, H_2), 2.56 (dd, J = 3.8 Hz, J = 1.8 Hz, 1H, $H_{2'}$), 2.20 (d, J = 5.1 Hz, 1H, $H_{1'}$), 2.06 (d, J = 5.5 Hz, 1H, H_1), 1.61-1.08 (m, 52H, H_{alkyl}, $H_{c \text{ and } c'}$, $H_{d \text{ and } d'}$, H_7 and $H_{7'}$);

^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 174.7, 174.6, 174.2, 174.0, 173.8, 173.3, 172.0, 171.9, 166.5, 166.4, 157.8, 141.8, 141.4, 140.7, 140.6, 138.1, 137.7, 137.6, 137.4, 134.7, 134.0, 133.9, 133.8, 133.1, 132.2, 131.4, 131.3, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 127.1, 127.0, 126.9, 126.7, 124.1, 124.0, 67.7, 67.6, 50.9, 50.7, 50.6, 50.4, 49.5, 48.8, 48.5, 48.3, 48.1, 45.1, 45.0, 44.3, 44.0, 43.9, 43.7, 39.9, 39.7, 39.6, 29.4, 29.3, 29.2, 29.1, 29.0, 28.7, 28,5, 26,8; HRMS calcd. for $C_{85}H_{94}N_7O_9$ [M + H^+] 1356.71130 found (FAB, m-NBA matrix) 1356.71261.

Physical data for *Cp*-**2**: Mp 146-148 ^oC; ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 7.35-7.18 (m, 20H, H_{Ph}), 6.34 (m, 2H, $H_{k \text{ and } k'}$), 6.16 (m, 2H, $H_{5 \text{ and } 4'}$), 6.06 (dd, J = 5.7 Hz, J = 2.7 Hz, 1H, $H_{5'}$), 5.82 (bt, 1H, $H_{h \text{ or } h'}$), 5.76 (bt, 1H, $H_{h \text{ or } h'}$), 5.66 (dd, J = 5.7 Hz, 2.7 Hz, H_4), 5.49 (bt, 2H, $H_{e \text{ and } e'}$), 4.63 (d, J = 7.6 Hz, 4H, $H_{b \text{ and } b'}$), 4.35 (t, J = 7.6 Hz, 2H, H_a), 4.23 (t, J = 8.1 Hz, 1H, $H_{m \text{ or } m'}$), 4.19 (t, J = 8.1 Hz, 1H, $H_{m \text{ or } m'}$), 4.01-3.71 (m, 4H, $H_{l \text{ and } l'}$), 3.17 (m, 8H, $H_{f \text{ and } f'}$ and $H_{g \text{ and } g'}$), 2.97 (s, 1H, $H_{6'}$), 2.94 (s, 1H, $H_{3'}$), 2.85 (m, 2H, $H_{3 \text{ and } 6}$), 2.80 (s, 1H, H_2), 2.58 (t, J = 6.9 Hz, 5H, $H_{c \text{ and } c'}$ and $H_{1'}$), 2.33 (t, J = 6.9 Hz, 4H, $H_{d \text{ and } d'}$), 2.24 (dd, J = 5.5 Hz, J = 1.8 Hz, 1H, $H_{2'}$), 2.21 (dd, J = 5.5 Hz, J = 1.8 Hz, 1H, H_1), 1.51-1.14 (m, 44H, H_{alkyl}, H_7 and $H_{7'}$); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 174.6, 174.3, 173.5, 173.2, 172.8, 157.8, 141.8, 141.6, 141.0, 138.0, 137.7, 134.4, 134.0, 128.7, 128.6, 128.5, 128.1, 128.1, 128.0, 127.9, 126.9, 126.8, 126.7, 66.8, 50.9, 50.8, 50.7, 50.5, 49.8, 48.7, 48.6, 48.4, 48.3, 45.4, 45.1, 44.3, 43.8, 43.7, 39.6, 39.5, 31.0, 29.7, 29.6, 29.5, 29.4, 29.2, 26.8; HRMS calcd for $C_{53}H_{66}N_3O_5$ [M + H^+] 824.50025 found (FAB, m-NBA matrix) 824.50116.