

Electronic Supplementary Information (ESI) of

Rotaxanes of a Macrocyclic Ferrocenophane with Dialkylammonium Axle Components

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Experimental Section

(C₆H₄-4-tBu)₃CC₆H₄-4-OC₆H₄-4-CHO

An *N*-methyl-2-pyrrolidone (NMP) solution (24 cm³) containing (C₆H₄-4-tBu)₃CC₆H₄-4-OH (3.0 g, 6.0 mmol), 4-fluorobenzaldehyde (1.3 g, 12 mmol), CsF (2.2 g, 13 mmol) was stirred for 24 h at 100 °C. The crude product was collected by filtration, which was washed with hexane and Et₂O to give (C₆H₄-4-tBu)₃CC₆H₄-4-OC₆H₄-4-CHO as white solid in quantitative yield; δ_H(250 MHz; CDCl₃; r.t.) 1.31 (27 H, s, CH₃), 6.95 (2 H, d, *J* 9, C₆H₄O), 7.08-7.11 (8 H, ^tBuC₆H₄, C₆H₄O), 7.21-7.27 (8 H, ^tBuC₆H₄, C₆H₄O), 7.85 (2 H, d, *J* 8, C₆H₄O) and 9.92 (1 H, s, CHO); δ_C(100 MHz; CDCl₃; r.t.) 31.4 (CH₃), 34.4 (C(CH₃)), 63.4 (C(^tBuC₆H₄)₃), 117.6 (C₆H₄), 118.7 (C₆H₄), 124.1 (^tBuC₆H₄), 130.6 (^tBuC₆H₄), 131.2 (C₆H₄), 131.8 (C₆H₄), 132.9

(C₆H₄), 143.6 (C₆H₄), 144.0 (C₆H₄), 148.5 (C₆H₄), 152.8 (C₆H₄), 163.1 (C₆H₄) and 190.6 (CHO); *m/z* (HRFABMS) 609.3737 ([M + H]⁺. C₄₄H₄₉O₂ requires 609.3733).

(C₆H₄-4-tBu)₃CC₆H₄-4-OC₆H₄-4-C=NCH₂C₆H₄-4-OCH₂CH₂CH=CH₂

A solution of (C₆H₄-4-tBu)₃CC₆H₄-4-OC₆H₄-4-CHO (1.8 g, 3.0 mmol) and H₂NCH₂C₆H₄OCH₂CH₂CH=CH₂ (0.53 g, 3.0 mmol) in toluene (50 cm³) was stirred under reflux condition in the presence of MS4A (Molecular sieves 4 Å, 1.2 g). After removal of MS4A, evaporation of the solution to dryness produced (C₆H₄-4-tBu)₃CC₆H₄-4-OC₆H₄-4-C=NCH₂C₆H₄-4-OCH₂CH₂CH=CH₂ as a white solid which was washed with hexane (1.7 g, 2.2 mmol, 74%) (Found: C, 85.42; H, 7.83; N, 1.87. C₅₅H₆₁NO₂(H₂O)_{0.25} requires C, 85.50; H, 8.02; N, 1.81%); δ_H(300 MHz; CDCl₃; r.t.) 1.33 (27 H, s, CH₃), 2.56 (2 H, dt, *J* 7 and 7, CH₂CH=CH₂), 4.03 (2 H, t, *J* 7, OCH₂), 4.76 (2 H, s, NCH₂), 5.13 (1 H, d, *J* 10, cis-CH=CH₂), 5.19 (1 H, d, *J* 17, trans-CH=CH₂), 5.93 (1 H, ddt, *J* 17, 10 and 7, CH=CH₂), 6.89-6.93 (4 H, C₆H₄), 7.06 (2 H, d, *J* 8, C₆H₄), 7.12 (6 H, d, *J* 9, ^tBuC₆H₄), 7.19 (6 H, d, *J* 9, C₆H₄), 7.24-7.29 (8 H, ^tBuC₆H₄, C₆H₄), 7.76 (2 H, d, *J* 8, C₆H₄) and 8.34 (1 H, s, CH=N); δ_C(75.5 MHz; CDCl₃; r.t.) 31.3 (CH₃), 33.6 (CH₂CH=CH₂), 34.3 (C(CH₃)), 63.2 (C(^tBuC₆H₄)₃), 64.4 (NCH₂), 67.2 (OCH₂), 114.6, 117.0, 117.8, 118.4, 124.1 (^tBuC₆H₄), 129.1, 129.8, 130.7 (^tBuC₆H₄), 131.1, 131.4, 132.7, 134.5, 142.9, 143.8, 148.5, 154.1, 157.9, 159.6 and 160.8.

(C₆H₄-4-tBu)₃CC₆H₄-4-OC₆H₄-4-CH₂NHCH₂C₆H₄-4-OCH₂CH₂CH=CH₂

(C₆H₄-4-tBu)₃CC₆H₄-4-OC₆H₄-4-C=NCH₂C₆H₄-4-OCH₂CH₂CH=CH₂ (1.0 g, 1.3 mmol) was dissolved in THF (18 cm³) at room temperature then the solution was cooled to 0 °C. LiAlH₄ (0.25 g, 6.5 mmol) was added to the solution at 0 °C and the mixture was stirred for 19 h under reflux condition then the solution was cooled to room temperature. The reaction mixture was quenched with 3 M aqueous solution of KOH (20 cm³) and the product was extracted by CH₂Cl₂. The separated organic phase was dried over MgSO₄ and evaporation of the solution gave crude product which was purified by SiO₂ column chromatography (eluent:

hexane/AcOEt/CH₂Cl₂ 6:1:1) to give (C₆H₄-4-tBu)₃CC₆H₄-4-OC₆H₄-4-CH₂NHCH₂C₆H₄-4-OCH₂CH₂CH=CH₂ as a white solid (0.60 g, 0.78 mmol, 60%) (Found: C, 85.28; H, 8.26; N, 1.81. C₅₅H₆₃NO₂(H₂O)_{0.25} requires C, 85.00; H, 8.14; N, 1.86%); δ_H(300 MHz; CDCl₃; r.t.) 1.30 (27 H, s, CH₃), 2.54 (2H, dtt, *J* 7, 7 and 2, CH₂CH=CH₂), 3.74 (2 H, s, NCH₂), 3.75 (2 H, s, NCH₂), 4.01 (2 H, t, *J* 7, OCH₂), 5.11 (1 H, ddt, *J* 10, 2 and 2, 1H, cis-CH=CH₂), 5.17 (ddt, *J* = 17, 2 and 2, 1H, trans-CH=CH₂), 5.91 (ddt, *J* = 17, 10, 7, CH=CH₂), 6.83-6.88 (4 H, C₆H₄), 6.99 (2 H, d, *J* 8, C₆H₄), 7.09 (6 H, d, *J* 9, ^tBuC₆H₄), 7.12 (2 H, d, *J* 9, C₆H₄), 7.29 (2 H, d, *J* 8, C₆H₄) and 7.73 (2 H, d, *J* 8, C₆H₄); δ_C(75.5 MHz; CDCl₃; r.t.) 31.4 (CH₃), 33.6 (CH₂CH=CH₂), 34.3 (C(CH₃)), 52.4 (NCH₂), 52.5 (NCH₂), 63.2 (C(^tBuC₆H₄)₃), 67.2 (OCH₂), 114.4, 116.9, 117.0, 119.1, 124.1 (^tBuC₆H₄), 129.3, 129.5, 130.7 (^tBuC₆H₄), 132.3, 132.5, 134.5, 135.2, 142.0, 143.9, 148.4, 155.3, 155.9 and 157.9; R_f 0.21 (hexane/AcOEt/CH₂Cl₂ 6:1:1).

[(C₆H₄-4-tBu)₃CC₆H₄-4-OC₆H₄-4-CH₂NH₂CH₂C₆H₄-4-OCH₂CH₂CH=CH₂](Cl)

(C₆H₄-4-tBu)₃CC₆H₄-4-OC₆H₄-4-CH₂NHCH₂C₆H₄-4-OCH₂CH₂CH=CH₂ (0.30 g, 0.39 mmol) was dissolved in CH₂Cl₂/MeOH (10 cm³/10 cm³) at room temperature then 4 M aqueous solution of HCl (30 cm³) and MeOH (60 cm³) were added to the solution. The stirring the mixture for 5 h at room temperature causes separation of crude product from the solution. The solid product was collected by filtration and washed with MeOH, hexane then Et₂O and dried under reduced pressure to give [(C₆H₄-4-tBu)₃CC₆H₄-4-OC₆H₄-4-CH₂NH₂CH₂C₆H₄-4-OCH₂CH₂CH=CH₂](Cl) as a white solid (0.30 g, 0.37 mmol, 95%) (Found: C, 81.28; H, 7.91; N, 1.79. C₅₅H₆₄NO₂Cl(H₂O)_{0.25} requires C, 81.45; H, 8.02; N, 1.73%); δ_H(300 MHz; CDCl₃; r.t.) 1.30 (27 H, s, CH₃), 2.45 (2 H, dt, *J* 7 and 7, CH₂CH=CH₂), 3.78 (2 H, s, NCH₂), 3.80 (2 H, s, NCH₂), 3.85 (2 H, t, *J* 7, OCH₂), 5.07 (1 H, dd, *J* 10 and 2, cis-CH=CH₂), 5.11 (1 H, dd, *J* 17 and 2, trans-CH=CH₂), 5.82 (1 H, ddt, *J* 17, 10 and 7, CH=CH₂), 6.78 (2 H, d, *J* 9, C₆H₄), 6.84 (2 H, d, *J* 8, C₆H₄), 6.97 (2 H, d, *J* 8, C₆H₄), 7.07 (6 H, d, *J* 8, ^tBuC₆H₄), 7.12 (2 H, d, *J* 9, C₆H₄), 7.24 (6 H, d, *J* 8, ^tBuC₆H₄), 7.40 (2 H, d, *J* 9, C₆H₄), 7.45 (2 H, d, *J* 8, C₆H₄)

and 10.1 (2 H, br s, NH₂); δ_C (100 MHz; CDCl₃; r.t.) 31.4 (CH₃), 33.5 (CH₂CH=CH₂), 34.4 (C(CH₃)), 48.0 (NCH₂), 48.1 (NCH₂), 63.2 (C(^tBuC₆H₄)₃), 67.1 (OCH₂), 114.9, 117.1 (CH₂CH=CH₂), 118.0, 118.5, 121.8, 124.1 (^tBuC₆H₄), 130.6 (^tBuC₆H₄), 131.8, 131.9, 132.6, 134.0, 143.0, 143.7, 148.4, 153.6, 158.4 and 159.5.

AnCH=NC₆H₄OCH₂CH₂CH=CH₂ (An = 9-anthryl)

A solution of 9-anthracenecarboxaldehyde (1.1 g, 5.3 mmol) and H₂NCH₂C₆H₄OCH₂CH₂CH=CH₂ (0.92 g, 5.2 mmol) in toluene (50 cm³) was heated at 120 °C for 10 h in the presence of MS4A (4 Å molecular sieves, 1.0 g). Evaporation of the solution to dryness produced AnCH=NC₆H₄OCH₂CH₂CH=CH₂ which was extracted with CH₂Cl₂. The solution was filtered to remove MS4A and reprecipitation from CH₂Cl₂/hexane at -20 °C gave AnCH=NC₆H₄OCH₂CH₂CH=CH₂ as a brown solid which was washed with hexane and dried under reduced pressure (1.9 g, 5.2 mmol, quant) (Found: C, 84.72; H, 6.37; N, 3.96. C₂₆H₂₃NO requires C, 85.45; H, 6.34; N, 3.83%); δ_H (300 MHz; C₆D₆; r.t.) 2.30 (2 H, dt, *J* 7 and 7, OCH₂CH₂), 3.63 (2 H, t, *J* 7, OCH₂), 4.86 (2 H, s, NCH₂), 5.00 (1 H, d, *J* 11, =CH₂), 5.02 (1 H, d, *J* 17, =CH₂), 5.75 (1 H, ddt, *J* 17, 11 and 7, CH=CH₂), 6.88 (2 H, d, *J* 9, C₆H₄), 7.20-7.30 (4 H, H₂-An, H₃-An), 7.36 (2 H, d, *J* 9, C₆H₄), 7.76 (2 H, d, *J* 8, H₄-An), 8.15 (1 H, s, H₁₀-An), 8.77 (2 H, d, *J* 9, H₁-An) and 9.27 (1 H, s, NCH); δ_C (75.5 MHz; C₆D₆; r.t.) 34.0 (OCH₂CH₂), 66.5 (NCH₂), 67.1 (OCH₂), 114.9 (C₆H₄), 116.8 (=CH₂), 125.4, 125.6, 126.8, 129.1, 129.5, 129.9, 130.8, 131.7, 132.2 (An), 134.9 (CH=CH₂), 158.6 (C₆H₄) and 160.3 (NCH).

(C₆H₃-3,5-Me₂)C(=O)NHCH₂C₆H₄-4-OCH₂CH₂CH=CH₂

To a CH₂Cl₂ solution (15 cm³) containing H₂NCH₂C₆H₄-4-CH₂CH₂CH=CH₂ (1.5 g, 8.6 mmol) and Et₃N (1.2 g, 12 mmol) was added 3,5-dimethylbenzoyl chloride (1.5 g, 8.6 mmol) at 0 °C. The temperature of the reaction mixture was allowed to rise room temperature during and the mixture was stirred for further 12 h. The reaction mixture was quenched with water and the product was extracted by CH₂Cl₂. The separated organic phase was dried over

MgSO₄ and evaporation of the solution gave crude product which was washed with hexane to give (C₆H₃-3,5-Me₂)C(=O)NHCH₂C₆H₄-4-OCH₂CH₂CH=CH₂ as a white solid (0.70 g, 2.3 mmol, 26%) (Found: C, 77.60; H, 7.34; N, 4.29. C₂₀H₂₃NO₂ requires C, 77.64; H, 7.49; N, 4.53%); δ_H(300 MHz; CDCl₃; r.t.) 2.34 (6 H, s, CH₃), 2.54 (2 H, dtt, *J* 6, 6 and 2, CH₂CH=CH₂), 4.01 (2 H, t, *J* 6, OCH₂), 4.56 (2 H, d, *J* 5, NCH₂), 5.11 (1 H, ddt, *J* 10, 2 and 2, cis-CH=CH₂), 5.17 (1 H, ddt, *J* 17, 2 and 2, trans-CH=CH₂), 5.90 (1 H, ddt, *J* 17, 10 and 6, CH=CH₂), 6.28 (1 H, br s, NH), 6.88 (2 H, d, *J* 8, C₆H₄), 7.12 (1 H, s, para-C₆H₃), 7.27 (2 H, d, *J* 8, C₆H₄) and 7.37 (2 H, s, ortho-C₆H₃); δ_H(100 MHz; CDCl₃; r.t.) 21.2 (CH₃), 33.6 (CH₂CH=CH₂), 43.5 (NCH₂), 67.2 (OCH₂), 114.7, 116.9 (CH₂CH=CH₂), 124.6, 129.1, 130.3, 132.9, 134.2, 134.3, 138.1, 158.2 and 167.5 (C=O).

(C₆H₃-3,5-Me₂)CH₂NHCH₂C₆H₄-4-OCH₂CH₂CH=CH₂

(C₆H₃-3,5-Me₂)C(=O)NHCH₂C₆H₄-4-OCH₂CH₂CH=CH₂ (1.6 g, 5.0 mmol) was dissolved in THF (60 cm³) at room temperature then the solution was cooled to 0 °C. LiAlH₄ (0.76 g, 20 mmol) was added to the solution at 0 °C and the mixture was stirred for 12 h under reflux condition then the solution was cooled to room temperature. The reaction mixture was quenched with 3 M aqueous solution of KOH (10 cm³) and the product was extracted by CH₂Cl₂. The separated organic phase was dried over MgSO₄ and evaporation of the solution gave crude product which was purified by SiO₂ column chromatography (eluent: hexane/AcOEt 6:1) to give (C₆H₃-3,5-Me₂)CH₂NHCH₂C₆H₄-4-OCH₂CH₂CH=CH₂ as a yellow oil (0.30 g, 1.0 mmol, 20%) (Found: C, 81.11; H, 8.34; N, 4.78. C₂₀H₂₅NO requires C, 81.31; H, 8.53; N, 4.74%); δ_H(300 MHz; CDCl₃; r.t.) 2.31 (6 H, s, CH₃), 2.54 (2 H, dtt, *J* 7, 7 and 2, CH₂CH=CH₂), 3.72 (2 H, s, NCH₂), 3.74 (2 H, s, NCH₂), 4.01 (2 H, t, *J* 7, OCH₂), 5.11 (1 H, ddt, *J* 10, 2 and 2, cis-CH=CH₂), 5.18 (1 H, ddt, *J* 17, 2 and 2, trans-CH=CH₂), 5.91 (1 H, ddt, *J* 17, 10 and 7, CH=CH₂), 6.87 (2 H, d, *J* 9, C₆H₄), 6.89 (1 H, s, para-C₆H₃), 6.95 (2 H, s, ortho-C₆H₃) and 7.27 (2 H, d, *J* 9, C₆H₄); δ_C(75.5 MHz; CDCl₃; r.t.) 21.2 (CH₃), 33.6

(CH₂CH=CH₂), 52.6 (NCH₂), 53.0 (NCH₂), 67.1 (OCH₂), 114.3, 116.9, 125.9, 128.4, 129.2, 132.4, 134.4, 137.8, 140.1 and 157.8.

CH₂=CHCOOC₆H₄-4-C(C₆H₄-4-tBu)₃

To a solution of (C₆H₄-4-tBu)₃CC₆H₄-4-OH (1.3 g, 6.0 mmol) and Et₃N (0.42 cm³, 3.0 mmol) in CH₂Cl₂ (5.0 cm³) was added acryloyl chloride (0.25 cm³, 3.0 mmol) in CH₂Cl₂ (1.0 cm³). After stirring the mixture for 1 h at room temperature, the solution was diluted by CH₂Cl₂ and the insoluble solid was removed by filtration. Removal of solvent by evaporation gave CH₂=CHCOOC₆H₄-4-C(C₆H₄-4-tBu)₃ as a white solid which was washed with Et₂O, water and dried under reduced pressure (1.1 g, 2.0 mmol, 79 mmol) (Found: C, 84.53; H, 8.53. C₄₀H₄₆O₂(H₂O)_{0.5} requires C, 84.61; H, 8.34%); δ_H(300 MHz; CDCl₃; r.t.) 1.30 (27 H, s, CH₃), 5.99 (1 H, dd, *J* 11 and 2, cis-CH₂=CH), 6.31 (1 H, dd, *J* 17 and 11, CH₂=CH), 6.59 (1 H, dd, *J* 17 and 2, trans-CH₂=CH), 7.00 (2 H, d, *J* 9, C₆H₄), 7.06-7.16 (6 H, C₆H₄) and 7.19-7.29 (10 H, C₆H₄); δ_C(75.5 MHz; CDCl₃; r.t.) 31.3 (CH₃), 34.3 (CH₂), 63.3 (C(CH₃)₃), 119.9, 124.1, 128.0, 130.7, 132.2, 132.4, 143.7, 144.9, 148.3, 148.4 and 164.5 (C=O); *R*_f 0.41 (hexane/AcOEt 5:1).

(C₆H₄-4-tBu)₃CC₆H₄-4-O(CH₂)₁₁OTHP (THP = 2-tetrahydropyranyl). A DMF solution (18 cm³) containing (C₆H₄-4-tBu)₃CC₆H₄-4-OH (0.50 g, 1.0 mmol) and K₂CO₃ (1.4 g, 10 mmol) was stirred for 30 min at 80 °C and Br(CH₂)₁₁OTHP (1.7 g, 5.0 mmol) was added to the solution and stirred for further 16 h. After the evaporation of solvent, the crude product was dissolved in CH₂Cl₂ and the precipitate was removed by filtration. The filtrate was washed with sat. NH₄Cl(aq), dried over MgSO₄, and evaporated. Purification by SiO₂ column chromatography (eluent: hexane/AcOEt 10:1) gave (C₆H₄-4-tBu)₃CC₆H₄-4-O(CH₂)₁₁OTHP as white solid (0.69 g, 0.89 mmol, 91%) (Found: C, 83.77; H, 9.93. C₅₃H₇₄O₃ requires C, 83.85; H, 9.82%); δ_H(300 MHz; CDCl₃; r.t.) 1.30 (27 H, s, CH₃), 1.28-1.88 (24 H, CH₂), 3.34-3.43 (1 H, m, OCH₂), 3.47-3.53 (1 H, m, OCH₂), 3.69-3.77 (1 H, m, OCH₂), 3.84-3.94 (3 H, OCH₂), 4.58 (1 H, t, *J* 4, CH), 6.76 (2 H, d, *J* 9, C₆H₄), 7.07 (2 H, d, *J* 9, C₆H₄), 7.08 (6 H, d,

J 9, ${}^t\text{BuC}_6\text{H}_4$) and 7.23 (6 H, d, J 9, ${}^t\text{BuC}_6\text{H}_4$); δ_{H} (100 MHz; CDCl_3 ; r.t.) 19.8 (CH_2), 25.6 (CH_2), 26.2 (CH_2), 26.3 (CH_2), 29.4-29.6 (6C, CH_2), 29.8 (CH_2), 30.8 (CH_2), 31.4 (CH_3), 34.3 ($\text{C}(\text{CH}_3)$), 62.4 (OCH_2), 63.0 ($\text{C}({}^t\text{BuC}_6\text{H}_4)_3$), 67.7 (OCH_2), 67.8 (OCH_2), 98.8 (CH), 112.9 (C_6H_4), 123.9 (${}^t\text{BuC}_6\text{H}_4$), 130.6 (${}^t\text{BuC}_6\text{H}_4$), 132.1 (C_6H_4), 139.2, 144.1, 148.1 and 156.8.

$(\text{C}_6\text{H}_4\text{-4-tBu})_3\text{CC}_6\text{H}_4\text{-4-O}(\text{CH}_2)_{11}\text{OH}$

To a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ ($20\text{ cm}^3/20\text{ cm}^3$) solution containing $(\text{C}_6\text{H}_4\text{-4-tBu})_3\text{CC}_6\text{H}_4\text{-4-O}(\text{CH}_2)_{11}\text{OTHP}$ (0.60 g, 0.79 mmol) was added 4 M $\text{HCl}(\text{aq})$ (4 cm^3) and stirred for 4 h at room temperature. The solution was participated by addition of CH_2Cl_2 and the organic extract was separated, dried over MgSO_4 , and filtered. The solid obtained by evaporation of the filtrate was washed with hexane to give $(\text{C}_6\text{H}_4\text{-4-tBu})_3\text{CC}_6\text{H}_4\text{-4-O}(\text{CH}_2)_{11}\text{OH}$ as white solid (0.39 g, 0.58 mmol, 73%) (Found: C, 83.06; H, 9.93. $\text{C}_{48}\text{H}_{66}\text{O}_2(\text{H}_2\text{O})$ requires C, 83.19; H, 9.89%); δ_{H} (300 MHz; CDCl_3 ; r.t.) 1.30 (27 H, s, CH_3), 1.30-1.80 (18 H, CH_2), 3.64 (2 H, t, J 7, OCH_2), 3.92 (2 H, t, J 7, OCH_2), 6.75 (2 H, d, J 9, C_6H_4), 7.07 (2 H, d, J 9, C_6H_4), 7.08 (6 H, d, J 9, ${}^t\text{BuC}_6\text{H}_4$) and 7.23 (6 H, d, J 9, ${}^t\text{BuC}_6\text{H}_4$); δ_{C} (100 MHz; CDCl_3 ; r.t.) 25.8 (CH_2), 26.2 (CH_2), 26.3 (CH_2), 29.4-29.6 (6C, CH_2), 29.8 (CH_2), 30.8 (CH_2), 31.4 (CH_3), 32.8 ($\text{C}(\text{CH}_3)$), 34.3 (CH_3), 62.4 (OCH_2), 63.0 ($\text{C}({}^t\text{BuC}_6\text{H}_4)_3$), 67.7 (OCH_2), 67.8 (OCH_2), 112.8 (C_6H_4), 123.9 (${}^t\text{BuC}_6\text{H}_4$), 130.6 (${}^t\text{BuC}_6\text{H}_4$), 132.1 (C_6H_4), 139.2, 144.1, 148.1 and 156.8.

$(\text{C}_6\text{H}_4\text{-4-tBu})_3\text{CC}_6\text{H}_4\text{-4-O}(\text{CH}_2)_{11}\text{O}(\text{CH}_2)_{11}\text{OTHP}$

A toluene (2.0 cm^3) solution containing $(\text{C}_6\text{H}_4\text{-4-tBu})_3\text{CC}_6\text{H}_4\text{-4-O}(\text{CH}_2)_{11}\text{OH}$ (0.14 g, 0.20 mmol) and NaH (0.10 g, 4.0 mmol) was refluxed for 3 h then $\text{Br}(\text{CH}_2)_{11}\text{OTHP}$ (0.080 g, 0.24 mmol) was added to the solution and refluxed for further 21 h. The reaction mixture was quenched with water and the product was extracted by CH_2Cl_2 . The separated organic phase was washed with water, dried over MgSO_4 , filtered, and evaporated. The crude product was purified by SiO_2 column chromatography (eluent: hexane/ AcOEt 10:1) and washing with

methanol to give $(C_6H_4-4-tBu)_3CC_6H_4-4-O(CH_2)_{11}O(CH_2)_{11}OTHP$ as white solid (0.12 g, 0.13 mmol, 66%); δ_H (300 MHz; $CDCl_3$; r.t.) 1.30 (27 H, s, CH_3), 1.30-1.87 (42 H, CH_2), 3.34-3.42 (1 H, m, OCH_2), 3.39 (4 H, OCH_2), 3.46-3.53 (1 H, m, OCH_2), 3.69-3.77 (1 H, m, OCH_2), 3.84-3.87 (1 H, m, OCH_2), 3.92 (2 H, t, J 7, OCH_2), 4.58 (1 H, t, J 4, CH), 6.76 (2 H, d, J 9, C_6H_4), 7.07 (2 H, d, J 9, C_6H_4), 7.08 (6 H, d, J 9, tBuC_6H_4) and 7.23 (6 H, d, J 9, tBuC_6H_4); δ_C (100 MHz; $CDCl_3$; r.t.) 19.8 (CH_2), 25.6 (CH_2), 26.2-26.3 (4C, CH_2), 26.4 (CH_2), 29.4 (2 C, CH_2), 29.6 (9 C, CH_2), 29.8 (2 C, CH_2), 30.8 (CH_2), 31.4 (CH_3), 34.3 ($C(CH_3)$), 62.3 (OCH_2), 63.0 ($C({}^tBuC_6H_4)_3$), 67.7 (OCH_2), 67.8 (OCH_2), 71.0 (2 C, OCH_2), 98.8 (CH), 112.8 (C_6H_4), 123.9 (tBuC_6H_4), 130.6 (tBuC_6H_4), 132.1 (C_6H_4), 139.2, 144.1, 148.1 and 156.8; m/z (HRFABMS) 928.7303 ($[M+H]^+$. $C_{64}H_{96}O_4$ requires 928.7309).

$(C_6H_4-4-tBu)_3CC_6H_4-4-O(CH_2)_{11}O(CH_2)_{11}OH$

To a $CH_2Cl_2/MeOH$ (20 $cm^3/30$ cm^3) solution of $(C_6H_4-4-tBu)_3CC_6H_4-4-O(CH_2)_{11}O(CH_2)_{11}OTHP$ (0.090 g, 0.10 mmol) was added 4 M $HCl(aq)$ (3.0 cm^3) and stirred for 3 h at room temperature. The solution was participated by addition of CH_2Cl_2 and the organic layer was separated, washed with water, dried over $MgSO_4$, filtered, and evaporated. The crude product was washed with methanol to give $(C_6H_4-4-tBu)_3CC_6H_4-4-O(CH_2)_{11}O(CH_2)_{11}OH$ as white solid (0.037 g, 0.044 mmol, 44%) (Found: C, 82.99; H, 10.68. $C_{59}H_{88}O_3(H_2O)_{0.5}$ requires C, 82.95; H, 10.50%); δ_H (300 MHz; $CDCl_3$; r.t.) 1.30 (27 H, s, CH_3), 1.30-1.78 (32 H, CH_2), 3.39 (4 H, t, J 7, OCH_2), 3.63 (2 H, t, J 7, OCH_2), 3.92 (2 H, t, J 7, OCH_2), 6.76 (2 H, d, J 9, C_6H_4), 7.07 (2 H, d, J 9, C_6H_4), 7.08 (6 H, d, J 9, tBuC_6H_4) and 7.23 (6 H, d, J 9, tBuC_6H_4); δ_C (100 MHz; $CDCl_3$; r.t.) 26.2 (CH_2), 26.3 (2 C, CH_2), 29.4-29.6 (11 C, CH_2), 29.8 (2 C, CH_2), 31.4 (CH_3), 34.3 ($C(CH_3)$), 63.0 ($C({}^tBuC_6H_4)_3$), 67.8 (OCH_2), 71.0 (OCH_2), 112.8 (C_6H_4), 123.9 (tBuC_6H_4), 130.6 (tBuC_6H_4), 132.1 (C_6H_4), 139.2, 144.1, 148.1 and 156.8.

(C₆H₄-4-tBu)₃CC₆H₄-4-O(CH₂)₁₁O(CH₂)₁₁OCOCH=CH₂

To a solution of (C₆H₄-4-tBu)₃CC₆H₄-4-O(CH₂)₁₁O(CH₂)₁₁OH (0.42 g, 0.50 mmol) and Et₃N (0.077 cm³, 0.55 mmol) in CH₂Cl₂ (5.0 cm³) was added acryloyl chloride (0.045 cm³, 0.55 mmol). After stirring the mixture for 3 h at room temperature, the solution was diluted by CH₂Cl₂. Removal of solvent by evaporation gave (C₆H₄-4-tBu)₃CC₆H₄-4-O(CH₂)₁₁O(CH₂)₁₁OCOCH=CH₂ as a white solid which was washed with methanol, (0.41 g, 0.45 mmol, 90%); δ_H(300 MHz; CDCl₃; r.t.) 1.29 (27 H, s, CH₃), 1.29-1.78 (36 H, CH₂), 3.38 (4 H, t, *J* 7, OCH₂), 3.91 (2 H, t, *J* 7, OCH₂), 4.14 (2 H, t, *J* 7, OCH₂), 5.81 (1 H, dd, *J* 11 and 1, cis-CH=CH₂), 6.16 (1 H, dd, *J* 17 and 11, CH=CH₂), 6.40 (1 H, dd, *J* 17 and 1, trans-CH₂=CH), 6.75 (2 H, d, *J* 9, C₆H₄), 7.07 (2 H, d, *J* 9, C₆H₄), 7.08 (6 H, d, *J* 9, ^tBuC₆H₄) and 7.24 (6 H, d, *J* 9, ^tBuC₆H₄); δ_C(100 MHz; CDCl₃; r.t.) 26.0 (CH₂), 26.2 (3 C, CH₂), 28.7 (CH₂), 29.3-29.6 (9 C, CH₂), 29.6 (2 C, CH₂), 31.4 (CH₃), 34.3 (C(CH₃)), 63.0 (C(^tBuC₆H₄)₃), 64.7 (OCH₂), 67.8 (OCH₂), 71.0 (2 C, OCH₂), 112.8 (C₆H₄), 123.9 (^tBuC₆H₄), 128.6, 130.3, 130.6 (^tBuC₆H₄), 132.1 (C₆H₄), 139.2, 144.1, 148.1, 156.8 and 166.2 (C=O); *m/z* (HRFABMS) 898.6822 ([M+H]⁺. C₆₄H₉₀O₄ requires 898.6839).

AnOCOCH=CH₂

The following manipulation was conducted under Ar atmosphere. To a solution of anthrone (4.9 g, 25 mmol) and NEt₃ (3.8 cm³, 27 mmol) in CH₂Cl₂ (5.0 cm³) was added a CH₂Cl₂ solution (5.0 cm³) of acryloyl chloride (2.2 cm³, 27 mmol) at 0 °C under Ar and then the temperature of the solution was allowed to rise room temperature over 3 h. The insoluble solid formed during the reaction was removed by filtration. The solution was washed with an aqueous solution of 0.1 M NaOH and extracted by CH₂Cl₂. The separated organic layer was dried over MgSO₄, filtered, and evaporated. The product was purified by chromatography on silica gel (eluent: CH₂Cl₂) to give AnOCOCH=CH₂ as yellow solid (2.3 g, 9.3 mmol, 37%) (Found: C, 81.94; H, 4.94. C₁₇H₁₂O₂ requires C, 82.24; H, 4.87%); δ_H(300 MHz; CDCl₃; r.t.)

6.23 (1 H, dd, *J* 10 and 1, CH₂), 6.66 (1 H, dd, *J* 17 and 10, CH=CH₂), 6.89 (1 H, dd, *J* 18 and 1, CH₂), 7.48-7.54 (4 H, H1-An, H4-An), 7.95 (2 H, m, H2-An or H3-An), 8.04 (2 H, m, H2-An or H3-An) and 8.40 (1 H, s, H10-An); δ_{C} (75.5 MHz; CDCl₃; r.t.) 121.3, 123.8, 124.7, 125.5, 126.2, 127.3, 128.3, 131.8, 133.6, 141.8 and 164.6 (C=O); *R*_f 0.49 (CH₂Cl₂).

AnCH₂OCOCH=CH₂

9-anthrylmethyl acrylate was prepared by according to literature method with slight modifications.¹ To a 150 cm³ of methanol solution of anthracene-9-carbaldehyde (1.0 g, 5.0 mmol) was added NaBH₄ (1.5 g, 40 mmol) and the mixture was stirred for 11 h at room temperature before the quenching with sat. NH₄Cl(aq). The product was extracted with CH₂Cl₂, washed with water, dried over MgSO₄, filtered, and evaporation of the solvent yield anthracene-9-methanol (0.80 g, 3.8 mmol, 77%). To a CH₂Cl₂/Et₃N (2.0 cm³/0.3 cm³) solution of anthracene-9-methanol (0.40 g, 2.0 mmol) was added acryloyl chloride (0.20 cm³, 2.2 mmol) in CH₂Cl₂ (0.5 cm³) at 0 °C. The resulting solution was stirred for 1 h and then the temperature was allowed to raise room temperature. The solution was washed with water and extracted by CH₂Cl₂. The separated organic layer was dried over MgSO₄, filtered, and evaporated. The product was purified by SiO₂ column chromatography (eluent: hexane/AcOEt 5:1) to yield 9-anthrylmethyl acrylate (0.15 g, 0.56 mmol, 28%); *R*_f 0.38 (hexane/AcOEt 5:1).

[{AnCH₂NH₂CH₂C₆H₄-4-OCH₂CH₂CH=CHCOOC₆H₄-4-C(C₆H₄-4-tBu)₃}(1)](BAR_F)

(12b)

3 (124 mg, 0.10 mmol) and **1** (61 mg, 0.11 mmol) was dissolved in CH₂Cl₂ (2.0 cm³), followed by addition of CH₂=CHCOOC₆H₄-4-C(C₆H₄-4-tBu)₃ (111 mg, 0.20 mmol) and a Ru-carbene complex ((H₂IMes)(PCy₃)Cl₂Ru=CHPh) (4.2 mg, 5.0 × 10⁻³ mmol). The mixture was refluxed for 14 h and the solvent was removed by evaporation to give a brown oil. The crude product was purified by preparative HPLC (CHCl₃) to give **12b** as a yellow solid (65

mg, 0.065 mmol, 65%) (Found: C, 63.85; H, 5.27; N, 0.62. C₁₂₄H₁₁₆BF₂₄FeNO₁₁(H₂O) requires C, 63.73; H, 5.09; N, 0.60%); δ_{H} (300 MHz; CDCl₃; r.t.) 1.33 (27 H, s, CH₃), 2.78 (2 H, dt, *J* 6 and 6, CH₂CH=CH), 3.30-4.25 (32 H, C₅H₄, OCH₂-Crown), 4.13 (2 H, t, *J* 6, OCH₂-Axle), 5.26 (2 H, m, NCH₂), 5.69 (2 H, m, NCH₂), 5.75 (2 H, m, C₆H₄-Crown), 6.18 (1 H, d, *J* 16, CH₂CH=CH), 6.56 (2 H, m, C₆H₄-Crown), 6.98-7.03 (4 H, m, C₆H₄-Axle), 7.13 (6 H, d, *J* 9, ^tBu-C₆H₄), 7.24-7.28 (9 H, ^tBu-C₆H₄, C₆H₄-Axle, CH₂CH=CH), 7.45 (2 H, dd, *J* 7 and 8, H₃-An), 7.58 (4 H, s, para-C₆H₃), 7.55-7.61 (4 H, H₂-An, C₆H₄-Axle), 7.78 (8 H, br s, ortho-C₆H₃), 7.86 (2 H, d, *J* 8, H₄-An), 7.84 (2 H, br s, NH₂), 8.14 (1 H, s, H₁₀-An) and 8.46 (2 H, d, *J* 9, H₁-An); δ_{C} (100 MHz; CDCl₃; r.t.) 31.4 (CH₃), 32.1 (CH₂CH=CH), 34.3 (C(CH₃)₃), 45.7 (NCH₂), 52.3 (NCH₂), 55.8 (C₅H₄), 57.3 (C₅H₄), 62.5 (C₅H₄), 62.7 (C₅H₄), 63.4 (C(^tBu-C₆H₄)₃), 65.8 (OCH₂-Axle), 67.7 (CH₂-Crown), 70.0 (CH₂-Crown), 70.3 (CH₂-Crown), 70.5 (CH₂-Crown), 71.2 (CH₂-Crown), 71.3 (CH₂-Crown), 110.8 (C₆H₄-Crown), 114.6 (C₆H₄-Axle), 117.4 (para-C₆H₃), 119.9 (C₆H₄-Axle), 120.4, 121.3 (C₆H₄-Crown), 122.9 (CH₂CH=CH), 123.6 (C₁-An), 124.1 (^tBu-C₆H₄), 124.4, 124.5 (quintet, *J*(FC) 271, CF₃), 124.9 (C₃-An), 127.1 (C₆H₄-Axle or C₂-An), 128.2 (C₆H₄-Axle or C₂-An), 128.8 (quintet, *J*(FC) 31, CCF₃), 129.5 (C₄-An), 130.5, 130.6 (^tBu-C₆H₄), 130.8, 131.1 (C₁₀-An), 132.1 (C₆H₄-Axle), 134.7 (ortho-C₆H₃), 143.6, 144.8, 144.9, 146.6 (CH₂CH=CH), 148.3, 148.4, 158.9 (C₆H₄-Axle), 161.6 (quintet, *J*(BC) 50, BC) and 164.5 (C=O).

[(1){AnCH₂NH₂CH₂C₆H₄-4-OCH₂CH₂CH=CHCOO(CH₂)₁₁O(CH₂)₁₁OC₆H₄-4-C(C₆H₄-4-tBu)₃]}](BAr_F) (12c)

3 (123 mg, 0.10 mmol) and **1** (61 mg, 0.11 mmol) was dissolved in CH₂Cl₂ (2.0 cm³), followed by addition of (C₆H₄-4-tBu)₃CC₆H₄-4-O(CH₂)₁₁O(CH₂)₁₁OCOCH=CH₂ (99 mg, 0.11 mmol) and a Ru-carbene complex ((H₂IMes)Cl₂Ru=CHC₆H₄-2-OⁱPr) (4.2 mg, 5.0 × 10⁻³ mmol). The mixture was refluxed for 14 h and the solvent was removed by evaporation to give brown oil. The crude product was purified by preparative HPLC (CHCl₃) to give **12c** as

a yellow solid (113 mg, 0.042 mmol, 42%); δ_{H} (300 MHz; CDCl₃; r.t.) 1.29 (27 H, s, CH₃), 1.29-1.80 (36 H, CH₂), 2.70 (2 H, m, CH₂CH=CH), 3.31-4.70 (34 H, OCH₂, C₅H₄), 3.40 (4 H, OCH₂), 3.94 (2 H, t, *J* 7, OCH₂), 4.13 (2 H, t, *J* 7, OCH₂), 5.18 (2 H, m, NCH₂), 5.56 (2 H, m, NCH₂), 5.72 (2 H, m, C₆H₄-Crown), 5.98 (1 H, d, *J* 16, CH=CHCH₂), 6.54 (2 H, m, C₆H₄-Crown), 6.78 (2 H, d, *J* 9, C₆H₄C(^tBuC₆H₄)), 6.96 (2 H, m, C₆H₄CH₂N), 7.03 (1 H, m, CH=CHCH₂), 7.10 (2 H, d, *J* 9, C₆H₄C(^tBuC₆H₄)), 7.11 (6 H, d, *J* 8, ^tBuC₆H₄), 7.25 (6 H, d, *J* 8, ^tBuC₆H₄), 7.46 (2 H, m, C₆H₄CH₂N), 7.56 (4 H, s, para-C₆H₃(CF₃)₂), 7.43-7.60 (4 H, H2-An, H3-An), 7.76 (8 H, br s, ortho-C₆H₃(CF₃)₂), 7.80 (2 H, br s, NH₂), 7.84 (2 H, d, *J* 8, H1 or 4H-An), 8.11 (1 H, s, H10-An) and 8.41 (2 H, m, H1 or H4-An); δ_{C} (100 MHz; CDCl₃; r.t.) 25.9 (CH₂), 26.2 (3 C, CH₂), 28.7 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.5-29.6 (9 C, CH₂), 29.8 (2 C, CH₂), 31.4 (CH₃), 31.9 (CH₂), 34.3 (C(CH₃)), 45.4 (NCH₂), 52.3 (NCH₂), 63.0 (C(^tBuC₆H₄)₃), 64.6 (OCH₂-Axle), 66.0 (OCH₂), 67.6 (OCH₂), 67.8 (OCH₂), 70.2 (2 C, OCH₂), 70.9 (2 C, OCH₂-Axle), 71.1 (OCH₂), 71.3 (2 C, OCH₂), 110.8 (C₆H₄-Crown), 112.8 (C₆H₄C(^tBuC₆H₄)), 114.6 (C₆H₄CH₂N), 117.4 (para-C₆H₃(CF₃)₂), 120.2, 121.3 (C₆H₄-crown), 123.5 (CH=CHCH₂), 123.6 (C1 or C4-An), 123.9 (^tBuC₆H₄), 124.1, 124.5 (quintet, *J*(FC) 271, CF₃), 124.9 (C2 or C3-An), 127.1 (C₆H₄CH₂N), 128.2 (C2 or C3-An), 128.7 (quintet, *J*(FC) 31, CCF₃), 129.5 (C1 or C4-An), 130.4, 130.6 (^tBuC₆H₄), 131.0 (C10-An), 132.1 (C₆H₄C(^tBuC₆H₄)), 134.7 (ortho-C₆H₃(CF₃)₂), 139.2, 144.1, 144.3 (CH=CHCH₂), 144.8, 148.1, 156.8, 158.9, 161.5 (quintet, *J*(BC) 50, BC) and 166.3 (C=O); *m/z* (HRFABMS) 1795.0244 ([M - BAr_F]⁺. C₁₁₄H₁₄₈FeNO₁₃ requires 1795.0300).

[(1)(AnCH₂NH₂CH₂C₆H₄OCH₂CH₂CH=CHCOOC₆H₃Me₂-3,5)](BAr_F) (12d)

[AnCH₂NH₂CH₂C₆H₄OCH₂CH₂CH=CH₂](BAr_F) (**3**) (123 mg, 0.10 mmol) was dissolved in 2 cm³ of CH₂Cl₂ containing **1** (61 mg, 0.11 mmol) and the solution was stirred for 2 h at room temperature, followed by addition of 3,5-dimethylphenyl acrylate (35 mg, 0.20 mmol) and (H₂IMes)(PCy₃)Cl₂Ru=CHPh (H₂Imes = *N,N*-bis(mesityl)-4,5-dihydroimidazol-2-ylidene)

(cat. Ru, 4.2 mg, 5.0×10^{-3} mmol). The mixture was refluxed for 9 h and solvent was removed by evaporation to form brown oil. The crude product was purified by preparative HPLC (eluent: CHCl_3) to give **12d** as yellow solid (125 mg, 0.065 mmol, 65%) (Found: C, 58.44; H, 4.54; N, 0.75. $\text{C}_9\text{H}_8\text{BF}_2\text{FeNO}_{11}(\text{H}_2\text{O})$ requires C, 58.39; H, 4.33; N, 0.72%); δ_{H} (300 MHz; CDCl_3 ; r.t.) 2.31 (6 H, s, CH_3), 2.77 (2 H, dt, J 6 and 6, $\text{CH}_2\text{CH}=\text{CH}$), 3.29-4.22 (34 H, C_5H_4 , CH_2 -Crown, OCH_2 -Axle), 5.24 (2 H, m, NCH_2), 5.66 (2 H, m, NCH_2), 5.74 (2 H, m, C_6H_4 -Crown), 6.16 (1 H, d, J 16, $\text{CH}_2\text{CH}=\text{CH}$), 6.54 (2 H, m, C_6H_4 -Crown), 6.73 (2 H, s, ortho- $\text{C}_6\text{H}_3\text{Me}_2$), 6.88 (1 H, s, para- $\text{C}_6\text{H}_3\text{Me}_2$), 6.98 (2 H, d, J 8, C_6H_4 -Axle), 7.24 (1 H, dt, J 16 and 6, $\text{CH}_2\text{CH}=\text{CH}$), 7.45 (2 H, dd, J 8 and 8, H3-An), 7.56 (4 H, s, para- $\text{C}_6\text{H}_3(\text{CF}_3)_2$), 7.56 (2 H, dd, J 8 and 8, H2-An), 7.56 (2 H, d, J 8, C_6H_4 -Axle), 7.76 (8 H, br s, ortho- $\text{C}_6\text{H}_3(\text{CF}_3)_2$), 7.83 (2 H, br s, NH_2), 7.84 (2 H, d, J 8, H4-An), 8.12 (1 H, s, H10-An) and 8.44 (2 H, d, J 8, H1-An) ; δ_{C} (100 MHz; CDCl_3 ; r.t.) 21.2 (CH_3), 32.0 ($\text{CH}_2\text{CH}=\text{CH}$), 45.7 (NCH_2), 52.4 (NCH_2), 54.8 (C_5H_4), 63.7 (C_5H_4), 65.9, 67.7, 70.1, 70.3, 70.9, 71.2, 71.3, 110.9, 114.7, 117.4, 119.0, 120.3, 124.5 (quintet, $J(\text{FC})$ 271, CF_3), 121.3, 122.9, 123.6, 125.0, 127.1, 127.5, 128.4, 128.9 (quintet, $J(\text{FC})$ 31, $\text{C}(\text{CF}_3)$), 129.6, 130.5, 130.8, 130.8, 131.1, 134.7 (meta- $\text{C}_6\text{H}_3(\text{CF}_3)_2$), 139.2, 144.9, 146.4, 150.4, 158.9 (C_6H_4 -Axle), 161.6 (quinted, $J(\text{BC})$ 50, ipso- $\text{C}_6\text{H}_3(\text{CF}_3)_2$) and 164.7 ($\text{C}=\text{O}$); m/z (FABMS) 1072 ($[\text{M} - \text{BAr}_F]^+$. $\text{C}_{63}\text{H}_{70}\text{FeNO}_{11}$ requires 1072).

$[(\text{FcCH}_2\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{CH}=\text{CHCOOAn})(1)](\text{BAr}_F)$ (12e**)**

$[\text{FcCH}_2\text{NH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}_2](\text{BARF})$ (**4**) (124 mg, 0.10 mmol) was dissolved in 2.0 cm^3 of CH_2Cl_2 containing **1** (61 mg, 0.12 mmol) and the solution was stirred for 2 h at room temperature, followed by addition of $\text{AnOCOCH}=\text{CH}_2$ (50 mg, 0.20 mmol) and $(\text{H}_2\text{IMes})(\text{PCy}_3)\text{Cl}_2\text{Ru}=\text{CHPh}$ (cat. Ru, 4.2 mg, 5.0×10^{-3} mmol). The mixture was refluxed for 10 h and solvent was removed by evaporation to form brown oil. The crude product was purified by preparative HPLC (eluent: CHCl_3) to give **12e** as purple solid (0.10 g, 0.050 mmol, 50%) (Found: C, 57.28; H, 4.15; N, 0.69. $\text{C}_{97}\text{H}_{82}\text{BF}_2\text{Fe}_2\text{NO}_{11}(\text{H}_2\text{O})$ requires C, 57.27;

H, 4.16; N, 0.69%); δ_{H} (300 MHz; CDCl₃; r.t.) 2.87 (2 H, dt, *J* 6 and 6, CH₂CH=CH), 3.33-4.30 (43 H, m, OCH₂-Axle, C₅H₄-Axle, C₅H₅, C₅H₄-crown), 4.24 (2 H, m, NCH₂), 4.50 (2 H, m, NCH₂), 6.51 (1 H, d, *J* 16, CH₂CH=CH), 6.73 (2 H, m, C₆H₄-Crown), 6.76 (2 H, d, *J* 9, C₆H₄-Axle), 6.94 (2 H, m, C₆H₄-Crown), 7.26 (2 H, d, *J* 9, C₆H₄-Axle), 7.36 (2 H, br s, NH₂), 7.45-7.53 (5 H, m, H₂-An, H₃-An, CH₂CH=CH), 7.58 (4 H, s, para-C₆H₃), 7.77 (8 H, br s, ortho-C₆H₃), 7.96 (2 H, m, H₁-An or H₄-An), 8.04 (2 H, m, H₁-An or H₄-An) and 8.40 (1 H, s, H₁₀-An); δ_{C} (100 MHz; CDCl₃; r.t.) 32.2 (CH₂CH=CH), 48.5 (NCH₂), 51.6 (NCH₂), 55.4 (C₅H₄-Crown), 57.1 (C₅H₄-Crown), 62.8 (C₅H₄-Crown), 63.1 (C₅H₄-Crown), 65.6 (OCH₂-Axle), 68.5 (CH₂-Crown), 68.9 (2C, C₅H₅, C₅H₄-Axle), 69.4 (C₅H₄-Axle), 69.7 (CH₂-Crown), 70.2 (CH₂-Crown), 70.8 (CH₂-Crown), 70.9 (CH₂-Crown), 71.0 (CH₂-Crown), 75.9 (C₅H₄-Axle), 112.3 (C₆H₄-Crown), 114.4 (C₆H₄-Axle), 117.4 (para-C₆H₃), 124.5 (quintet, *J*(FC) 271, CF₃), 121.3 (An), 121.9 (CH₂CH=CH), 123.6, 123.9, 124.7 (10C-An), 125.5 (An), 126.1 (An), 128.4 (An), 128.8 (quintet, *J*(FC) 31, CCF₃), 130.8 (C₆H₄-Axle), 131.8, 134.7 (ortho-C₆H₃), 141.9, 146.7, 148.1 (CH₂CH=CH), 159.3 (C₆H₄-Axle), 161.6 (quintet, *J*(BC) 50, BC) and 164.7 (C=O). Quantry carbons of ferrocenylene group in crown ether was not observed probably due to its weak intensity. *m/z* (FABMS) 1152 ([M - BAr_F]⁺. C₆₅H₇₀NO₁₁ requires 1152).

[[FeCH₂NH₂CH₂C₆H₄-4-OCH₂CH₂CH=CHCOOCH₂An}(1)](BAr_F) (12f)

4 (124 mg, 0.10 mmol) and **1** (61 mg, 0.11 mmol) was dissolved in CH₂Cl₂ (2.0 cm³), followed by addition of CH₂=CHCOOAn (50 mg, 0.20 mmol) and a Ru-carbene complex (H₂IMes)(PCy₃)Cl₂Ru=CHPh (4.2 mg, 5.0 × 10⁻³ mmol). The mixture was refluxed for 10 h and the solvent was removed by evaporation to give a brown oil. The crude product was purified by preparative HPLC (CHCl₃) to give **12f** as a yellow solid (100 mg, 0.050 mmol, 50%) (Found: C, 57.21; H, 4.50; N, 0.76. C₉₈H₈₄BF₂₄Fe₂NO₁₁(H₂O) requires C, 57.47; H, 4.23; N, 0.68%); δ_{H} (300 MHz; CDCl₃; r.t.) 2.61 (2 H, dt, *J* 6 and 6, CH₂CH=CH), 3.30-4.29 (43 H, m, OCH₂-Axle, C₅H₄-Axle, C₅H₅, C₅H₄-Crown), 4.23 (2 H, m, NCH₂), 4.50 (2 H, m,

NCH₂), 5.95 (1 H, d, *J* 16, CH₂CH=CH), 6.24 (2 H, s, AnCH₂), 6.66 (2 H, m, C₆H₄-Crown), 6.85 (2 H, m, C₆H₄-Crown), 7.07 (1 H, dt, *J* 16 and 7, CH₂CH=CH), 7.19 (2 H, d, *J* 9, C₆H₄), 7.31 (2 H, br s, NH₂), 7.46-7.60 (5 H, m, H₂-An, H₃-An), 7.56 (4 H, s, para-C₆H₃), 7.76 (8 H, br s, ortho-C₆H₃), 8.03 (2 H, m, H₁-An or H₄-An), 8.37 (2 H, m, H₁-An or H₄-An) and 8.51 (1 H, s, H₁₀-An); δ_C(100 MHz; CDCl₃; r.t.) 31.7 (CH₂CH=CH), 48.5 (NCH₂), 51.6 (NCH₂), 55.4 (C₅H₄-Crown), 57.1 (C₅H₄-Crown), 58.8 (OCH₂-Axle), 62.6 (C₅H₄-Crown), 62.9 (C₅H₄-Crown), 65.6 (OCH₂), 68.4 (CH₂-Crown), 68.9 (2C, C₅H₅, C₅H₄-Axle), 69.0, 69.4 (C₅H₄-Axle), 69.7 (CH₂-Crown), 70.1 (CH₂-Crown), 70.8 (CH₂-Crown), 71.0 (CH₂-Crown), 75.8 (C₅H₄-Axle), 112.2 (C₆H₄-Crown), 114.3 (C₆H₄-Axle), 117.4 (para-C₆H₃), 121.9 (C₆H₄-Crown), 122.9 (CH₂CH=CH), 123.8 (C₁-An), 123.4, 125.0 (C₂-An or C₃-An), 124.5 (quintet, *J*(FC) 271, CF₃), 126.1, 126.6 (C₂-An or C₃-An), 128.8 (quintet, *J*(FC) 33, CCF₃), 129.0 (C₄-An), 129.2 (C₁₀-An), 130.7 (C₆H₄-Axle), 131.0, 131.3, 134.7 (ortho-C₆H₃), 145.2 (CH₂CH=CH), 146.6, 159.1, 161.6 (quintet, *J*(BC) 50, BC) and 166.3 (C=O); *m/z* (FABMS) 1166 ([M - BAr_F]⁺. C₆₆H₇₂NO₁₁Fe₂ requires 1166).

[(AnCH₂NH₂CH₂C₆H₄OCH₂CH₂CH=CHCOOC₆H₃Me₂-3,5)(DB24C8)](BAr_F) (12g)

[AnCH₂NH₂CH₂C₆H₄OCH₂CH₂CH=CH₂](BAr_F) (**3**) (123 mg, 0.10 mmol) was dissolved in 2.0 cm³ of CH₂Cl₂ containing DB24C8 (54 mg, 0.12 mmol) and the solution was stirred for 15 min at room temperature, followed by addition of 3,5-dimethylphenyl acrylate (35 mg, 0.20 mmol) and (H₂IMes)(PCy₃)Cl₂Ru=CHPh (Cat. Ru, 4.2 mg, 5.0 × 10⁻³ mmol). The mixture was refluxed for 12 h and solvent was removed by evaporation to form brown oil. The crude product was purified by preparative HPLC (eluant: CHCl₃) to give **12g** as purple solid (97 mg, 0.053 mmol, 53%) (Found: C, 59.83; H, 4.59; N, 0.82. C₉₁H₇₈BF₂₄NO₁₁ requires C, 59.78; H, 4.30; N, 0.77%); δ_H(300 MHz; CDCl₃; r.t.) 2.32 (6 H, s, CH₃), 2.76 (2 H, dt, *J* 6 and 6, CH₂CH=CH), 3.34-3.57 (8 H, C₆H₄OCH₂CH₂OCH₂-DB24C8), 3.63-3.82 (8 H, C₆H₄OCH₂CH₂-DB24C8), 3.76-3.91 (8 H, C₆H₄OCH₂-DB24C8), 4.10 (2 H, t, *J* 6, OCH₂-Axle), 5.25 (2 H, m, NCH₂C₆H₄), 5.52 (2 H, m, NCH₂An), 6.16 (1 H, d, *J* 16, CH₂CH=CH),

6.33 (4 H, m, ortho-C₆H₄-DB24C8), 6.71 (4 H, m, meta-C₆H₄-DB24C8), 6.74 (2 H, s, ortho-C₆H₃Me₂), 6.88 (1 H, s, para-C₆H₃Me₂), 6.89 (2 H, d, *J* 8, ortho-C₆H₄-Axle), 7.24 (1 H, dt, *J* 16 and 6, CH₂CH=CH), 7.41 (2 H, d, *J* 8, meta-C₆H₄-Axle), 7.43 (2 H, dt, *J* 8 and 8, H3-An), 7.53 (2 H, dt, *J* 8 and 8, H2-An), 7.56 (4 H, s, para-C₆H₃(CF₃)₂), 7.66 (2 H, br s, NH₂), 7.76 (8 H, br s, ortho-C₆H₃(CF₃)₂), 7.84 (2 H, d, *J* 8, H4-An), 8.14 (1 H, s, H10-An) and 8.43 (2 H, d, *J* 9, H1-An); δ_{C} (100 MHz; CDCl₃; r.t.) 21.2 (CH₃), 32.1 (CH₂CH=CH), 45.5 (NCH₂An), 52.4 (NCH₂C₆H₄), 65.8 (OCH₂-Axle), 67.9 (C₆H₄OCH₂-DB24C8), 70.4 (C₆H₄OCH₂CH₂-DB24C8), 71.0 (C₆H₄OCH₂CH₂OCH₂-DB24C8), 111.9 (ortho-C₆H₄-DB24C8), 114.5 (ortho-C₆H₄-Axle), 117.4 (para-C₆H₃(CF₃)₂), 119.0 (ortho-C₆H₃Me₂), 120.9, 121.5 (meta-C₆H₄-DB24C8), 122.9 (CH₂CH=CH), 123.2, 123.4 (C1-An), 124.1 (quintet, *J*(FC) 271, CF₃), 124.9 (ortho-C₆H₄-Axle or meta-C₆H₄-Axle), 125.9, 127.0 (para-C₆H₃(CF₃)₂), 127.5 (para-C₆H₃Me₂), 128.5 (meta-C₆H₄-Axle or meta-C₆H₄-Axle), 128.9 (quintet, *J*(FC) 31, CCF₃), 129.5 (C3-An), 130.6, 130.8, 130.8, 158.7 (C₆H₄-Axle), 161.6 (quintet, *J*(BC) 50, BC) and 164.7 (C=O); *m/z* (FABMS) 964 ([M - BAr_F]⁺. C₅₉H₆₆NO₁₁ requires 964).

[(FcCH₂NH₂CH₂C₆H₄OCH₂CH₂CH=CHCOOAn)(DB24C8)](BAr_F) (12h)

[FcCH₂NH₂CH₂C₆H₄OCH₂CH₂CH=CH₂](BAr_F) (**4**) (124 mg, 0.10 mmol) was dissolved in 2 cm³ of CH₂Cl₂ containing DB24C8 (54 mg, 0.12 mmol) and the solution was stirred for 15 min at room temperature, followed by addition of AnOCOCH=CH₂ (50 mg, 0.20 mmol) and (H₂IMes)(PCy₃)Cl₂Ru=CHPh (Cat. Ru, 4.2 mg, 5 × 10⁻³ mmol). The mixture was refluxed for 11 h and solvent was removed by evaporation to form brown oil. The crude product was purified by preparative HPLC (eluant: CHCl₃) to give **12h** as yellow solid (100 mg, 0.052 mmol, 52%) (Found: C, 58.02; H, 4.12; N, 0.87. C₉₃H₇₈BF₂₄FeN₁O₁₁(H₂O) requires C, 57.99; H, 4.19; N, 0.73%); δ_{H} (400 MHz; CDCl₃; r.t.) 2.89 (2 H, br, CH₂CH=CH), 3.12-4.50 (37 H), 4.63 (2 H, br s), 6.52 (1 H, br s, CH₂CH=CH), 6.70-7.60 (19 H), 7.54 (4 H, s, para-C₆H₃), 7.73 (8 H, s, ortho-C₆H₃), 7.96 (2 H, br s), 8.03 (2 H, br s) and 8.39 (1 H, s, H10-An); δ_{C} (100 MHz; CDCl₃; r.t.) 32.3 (CH₂CH=CH), 48.9 (NCH₂), 51.6 (NCH₂), 66.0, 68.7, 70.4, 70.9, 72.6

(br, C₅H₅), 113.2, 114.5, 117.3, 121.3, 122.0, 123.8, 124.4, 124.4 (quintet, *J*(FC) 271, CF₃), 124.6, 125.5, 126.1, 128.3, 128.7 (quintet, *J*(FC) 31, meta-C₆H₃), 130.9, 131.7, 134.6, 141.8, 147.4, 148.2, 159.0 (C₆H₄-Axle), 161.5 (quintet, *J*(BC) 50, BC) and 164.6 (C=O); *m/z* (FABMS) 1044 ([M - BAr_F]⁺. C₆₁H₆₆NO₁₁Fe requires 1044).

[[{(C₆H₃-3,5-Me₂)CH₂NH₂CH₂C₆H₄-4-OCH₂CH₂CH=CHCOOAn}(DB24C8)](BAr_F)](12i) 5 (116 mg, 0.10 mmol) and DB24C8 (54 mg, 0.11 mmol) was dissolved in CH₂Cl₂ (2.0 cm³), followed by addition of CH₂=CHCOOAn (50 mg, 0.20 mmol) and a Ru-carbene complex (H₂IMes)(PCy₃)Cl₂Ru=CHPh (4.2 mg, 5.0 × 10⁻³ mmol). The mixture was refluxed for 12 h and the solvent was removed by evaporation to give brown oil. The crude product was purified by preparative HPLC (CHCl₃) to give **12i** as a yellow solid (160 mg, 0.088 mmol, 88%) (Found: C, 59.67; H, 4.34; N, 0.79. C₉₁H₇₈NO₁₁F₂₄B requires C, 59.78; H, 4.30; N, 0.77%); δ_H(300 MHz, CDCl₃, r.t.) 2.17 (6 H, s, CH₃), 2.91 (2 H, dt, *J* 6 and 6, CH₂CH=CH), 3.35 (8 H, m, CH₂-DB24C8), 3.72 (8 H, m, CH₂-DB24C8), 4.10 (8 H, m, CH₂-DB24C8), 4.18 (2 H, t, *J* 6, OCH₂-Axle), 4.42 (2 H, m, NCH₂), 4.63 (2 H, m, NCH₂), 6.56 (1 H, d, *J* 16, CH₂CH=CH), 6.77-6.97 (9 H, C₆H₄-DB24C8, C₆H₄-Axle, ortho-C₆H₃, para-C₆H₃), 7.37 (2 H, d, *J* 9, C₆H₄-Axle), 7.45 (2 H, br s, NH₂), 7.48-7.57 (5 H, CH₂CH=CH, An), 7.62 (4 H, s, para-C₆H₃), 7.82 (8 H, m, ortho-C₆H₃), 8.01-8.07 (4 H, An) and 8.42 (1 H, s, H10-An); δ_C(100 MHz; CDCl₃; r.t.) 21.0 (CH₃), 32.2 (CH₂CH=CH), 52.1 (NCH₂), 52.6 (NCH₂), 65.7 (OCH₂-Axle), 68.1 (CH₂-DB24C8), 70.1 (CH₂-DB24C8), 70.5 (CH₂-DB24C8), 112.7 (C₆H₄-DB24C8), 114.4 (C₆H₄-Axle), 117.4 (para-C₆H₃), 121.3 (An), 121.8 (C₆H₄-DB24C8), 121.9 (CH₂CH=CH), 123.9, 124.1, 124.5 (quintet, *J*(FC) 271, CF₃), 124.6 (10C-An), 125.5 (An), 126.1 (An), 126.4 (ortho-C₆H₄), 128.3 (An), 128.9 (quintet, *J*(FC) 31, CCF₃), 130.7 (para-C₆H₃), 130.9 (C₆H₄-Axle), 131.2, 131.8, 134.7 (ortho-C₆H₃), 138.3, 141.9, 147.3, 148.2 (CH₂CH=CH), 159.2 (C₆H₄-Axle), 161.6 (quintet, *J*(BC) 50, BC) and 164.7 (C=O); *m/z* (FABMS) 965 ([M - BAr_F]⁺. C₅₉H₆₆NO₁₁ requires 965).

[[AnCH₂N(Ac)CH₂C₆H₄-4-OCH₂CH₂CH=CHCOOC₆H₄-4-C(C₆H₄-4-tBu)₃](1)](13b)

To a solution of **12b** (0.19 g, 0.080 mmol) in MeCN (3.0 cm³) were added Et₃N (5.6 × 10⁻² cm³, 0.40 mmol) and acetic anhydride (3.8 × 10⁻² cm³, 0.40 mmol), and the reaction mixture was stirred for 14 h at room temperature. After the removal of the solvent by evaporation, the product was purified by SiO₂ column chromatography (hexane/AcOEt 1:1) to give **13b** as a yellow solid (97 mg, 6.5 × 10⁻² mmol, 81%) (Found: C, 72.88; H, 6.89; N, 0.91. C₉₄H₁₀₅FeNO₁₂(H₂O)₃ requires C, 72.81; H, 7.21; N, 0.90%); ν (KBr disk; r.t.)/cm⁻¹ 1651, 1732 (C=O); δ_{H} (300 MHz; CDCl₃; r.t) 1.31 (27 H, s, C(CH₃)₃), 2.19 (3 H, s, COCH₃), 3.16 (2 H, dt, *J* 7 and 7, CH₂CH=CH), 3.54-4.25 (34 H, C₅H₄, CH₂-crown, NCH₂), 4.52 (2 H, t, *J* 8, OCH₂-Axle), 5.71 (2 H, s, NCH₂), 6.43 (1 H, d, *J* 16, CH₂CH=CH), 6.75 (2 H, d, *J* 8, C₆H₄), 6.84 (4 H, m, C₆H₄), 6.95 (2 H, d, C₆H₄), 6.98 (2 H, d, C₆H₄), 7.13 (6 H, d, *J* 8, C₆H₄(^tBuC₆H₄)₃), 7.22 (2 H, d, *J* 8, C₆H₄), 7.25 (6 H, d, *J* 8, ^tBuC₆H₄), 7.35-7.44 (4 H, 2H-An, 3H-An), 7.63 (1 H, dt, *J* 16 and 7, CH₂CH=CH), 7.99 (2 H, d, *J* 8, 4H-An), 8.10 (2 H, d, *J* 9, 1H-An) and 8.45 (1 H, s, 10H-An); δ_{C} (100 MHz; CDCl₃; r.t.) 21.9 (COCH₃), 31.4 (C(CH₃)₃), 32.7 (CH₂CH=CH), 34.3 (C(CH₃)₃), 39.1 (NCH₂), 48.6 (NCH₂), 56.4 (C₅H₄), 56.5 (C₅H₄), 62.1 (2C, C₅H₄), 63.3 (C(^tBuC₆H₄)₃), 66.1 (OCH₂-Axle), 68.1 (CH₂-Crown), 69.6 (CH₂-Crown), 69.7 (CH₂-Crown), 70.0 (CH₂-Crown), 70.6 (CH₂-Crown), 70.9 (CH₂-Crown), 112.2 (C₆H₄), 115.1 (C₆H₄), 120.1 (C₆H₄), 120.7 (C₆H₄), 121.5 (CH₂CH=CH), 124.0 (^tBuC₆H₄), 124.3 (1C-An), 124.9 (2C-An or 3C-An), 126.2 (2C-An or 3C-An), 126.5 (C₆H₄), 127.3, 128.0, 128.1 (10C-An), 128.9 (4C-An), 130.6 (^tBuC₆H₄), 131.2, 131.4, 131.9 (C₆H₄), 143.6, 144.3, 148.2, 148.3, 148.6, 150.0 (CH₂CH=CH), 158.5, 165.3 (NC=O) and 171.0 (C(C=O)); *R*_f 0.25 (hexane/AcOEt 1:1).

[{AnCH₂N(Ac)CH₂C₆H₄-4-OCH₂CH₂CH=CHCOO(CH₂)₁₁O(CH₂)₁₁OC₆H₄-4-C(C₆H₄-4-tBu)₃}(1)] (13c)

To a solution of **12c** (122 mg, 0.046 mmol) in MeCN/CH₂Cl₂ (2.0 cm³/1.0 cm³) were added Et₃N (3.3 × 10⁻² cm³, 0.24 mmol) and acetic anhydride (2.2 × 10⁻² cm³, 0.23 mmol), and the

reaction mixture was stirred for 14 h at room temperature. The solution was diluted with CH_2Cl_2 and the organic layer was washed with water, dried over MgSO_4 , filtered, and evaporated. The product was purified by SiO_2 column chromatography (hexane/AcOEt 1:1) to give **13c** as a yellow solid (71 mg, 3.8×10^{-2} mmol, 84%); δ_{H} (300 MHz; CDCl_3 ; r.t.) 1.28 (27 H, s, CH_3), 1.28-1.76 (36 H, CH_2), 2.19 (3 H, s, COCCH_3), 2.86 (2 H, br s, $\text{CH}_2\text{CH}=\text{CH}$), 3.38-4.13 (40 H, OCH_2 , C_5H_4 , NCH_2), 4.04 (2 H, s, NCH_2), 4.36 (2 H, m, OCH_2), 5.70 (2 H, s, NCH_2), 6.05 (1 H, d, J 15, $\text{CH}=\text{CHCH}_2$), 6.76-6.91 (10 H, C_6H_4 -Crown, $\text{C}_6\text{H}_4\text{C}(\text{tBuC}_6\text{H}_4)$, $\text{C}_6\text{H}_4\text{CH}_2\text{N}$), 7.06-7.11 (1 H, $\text{CH}=\text{CHCH}_2$), 7.07 (2 H, d, J 8, $\text{C}_6\text{H}_4\text{C}(\text{tBuC}_6\text{H}_4)$), 7.10 (6 H, d, J 8, tBuC_6H_4), 7.23 (6 H, d, J 8, tBuC_6H_4), 7.40-7.45 (4 H, H2-An, H3-An), 8.01 (2 H, d, J 7, H1 or 4H-An), 8.10 (2 H, d, J 8, H1 or H4-An), 8.46 (1 H, s, H10-An); δ_{C} (100 MHz; CDCl_3 ; r.t.) 22.0 (COCH_3), 26.0 (CH_2), 26.1 (CH_2), 26.2 (2 C, CH_2), 28.8 (CH_2), 29.4-29.6 (10 C, CH_2), 29.8 (2 C, CH_2), 31.3 (CH_3), 32.3 (CH_2), 34.3 ($\text{C}(\text{CH}_3)$), 39.0 (NCH_2), 48.6 (NCH_2), 56.9 (C_5H_4), 62.9 ($\text{C}(\text{tBuC}_6\text{H}_4)_3$), 64.1 (OCH_2 -Axle), 66.0 (OCH_2 -Axle), 67.7 (OCH_2 -Crown), 67.8 (OCH_2 -Crown), 69.7 (2 C, OCH_2 -Axle, OCH_2 -Crown), 70.4 (OCH_2 -Crown), 70.7 (OCH_2 -Crown), 70.9 (2 C, OCH_2 -Axle), 111.9 (C_6H_4), 112.9, 115.1, 120.5, 122.2 ($\text{CH}=\text{CHCH}_2$), 123.8 (tBuC_6H_4), 124.3 (C1 or C4-An), 124.9 (C2 or C3-An), 126.2 (C2 or C3-An), 126.5, 126.9, 127.3, 127.9, 128.1 (C10-An), 128.9 (C1 or C4-An), 130.5 (tBuC_6H_4), 131.1, 131.3, 131.9 ($\text{C}_6\text{H}_4\text{C}(\text{tBuC}_6\text{H}_4)$), 139.0, 144.0, 146.8 ($\text{CH}=\text{CHCH}_2$), 148.0, 156.7, 158.3, 166.8 ($\text{C}=\text{O}$) and 170.9 ($\text{C}=\text{O}$); m/z (HRFABMS) 1836.0321 ($[\text{M} - \text{BAr}_\text{F}]^+$. $\text{C}_{116}\text{H}_{149}\text{FeNO}_{14}$ requires 1836.0327); R_f 0.40 (hexane/AcOEt 1:1).

Table S1. Crystal data and details of structure refinement of [K(1)]BPh₄.

Compound	[K(1)]BPh ₄
formula	C ₅₂ H ₅₆ BFeKO ₈
molecular weight	914.76
crystal system	monoclinic
space group	<i>P</i> 2 ₁ /n (No. 14)
<i>a</i> /Å	13.846(2)
<i>b</i> /Å	22.065(4)
<i>c</i> /Å	14.893(3)
<i>β</i> /deg	92.6643(8)
<i>U</i> /Å ³	4545(1)
<i>Z</i>	4
<i>F</i> (000)	1928.00
<i>D</i> c/ g cm ⁻³	1.337
crystal size/mm	0.40 x 0.40 x 0.20
unique reflections	10119
used reflections [<i>I</i> ≥ 2.0σ(<i>I</i>)]	8367
no. of variables	635
<i>R</i> [<i>I</i> ≥ 2.0σ(<i>I</i>)]	0.0397
<i>R</i> _w [<i>I</i> ≥ 2.0σ(<i>I</i>)]	0.0624
good of fitness	0.974

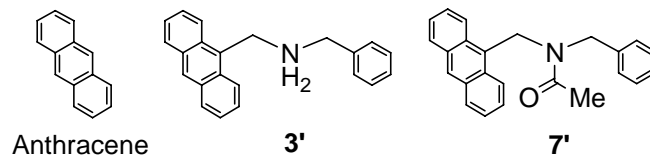
Table S2. Selected bond distances of [K(1)]BPh₄.

Atom	Atom	Distance / Å
K(1)	O(1)	2.779(1)
K(1)	O(2)	2.836(2)
K(1)	O(3)	2.736(1)
K(1)	O(4)	2.822(1)
K(1)	O(5)	2.757(2)
K(1)	O(6)	2.927(2)
K(1)	O(7)	2.822(2)
K(1)	O(8)	2.880(1)

Table S3. Selected bond angles of [K(1)]BPh₄.

Atom	Atom	Atom	Angle / °
K(1)	O(1)	C(5)	110.4(1)
K(1)	O(1)	C(6)	115.6(1)
K(1)	O(2)	C(7)	119.2(1)
K(1)	O(2)	C(8)	117.9(1)
K(1)	O(3)	C(9)	121.5(1)
K(1)	O(3)	C(10)	106.3(1)
K(1)	O(4)	C(11)	118.0(1)
K(1)	O(4)	C(12)	124.6(1)
K(1)	O(5)	C(17)	126.9(1)
K(1)	O(5)	C(18)	107.2(1)
K(1)	O(6)	C(19)	115.3(1)
K(1)	O(6)	C(20)	114.5(2)
K(1)	O(7)	C(21)	108.2(2)
K(1)	O(7)	C(22)	116.5(2)
K(1)	O(7)	C(23)	117.3(1)
K(1)	O(8)	C(24)	113.5(1)
K(1)	O(8)	C(25)	109.5(1)

Table S4. The calculated triplet levels of the compounds.^{a)}



Compound	Triplet level /cm ⁻¹ (calculated)	Triplet level /cm ⁻¹ (experiment)
Anthracene	14 500	14 700, ^{b)} 14 870 ^{c)}
3'	14 300	-
7'	14 100	-

a) The structure of the compounds have been optimized with the B3LYP/6-31G(d) level of theory using the PC GAMESS/Firefly 7.1.F program (Ref S2). The excitation energy have been calculated with TD-B3LYP/6-31+G(d) level of theory using GAMESS (12 JAN 2009(R1)) programs (Ref S3). b) Ref S4. c) Ref S5.

Reference

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