Inherently dinuclear iridium(III) *meso* architectures accessed by cyclometalation of calix[4]arene-based bis(aryltriazoles)

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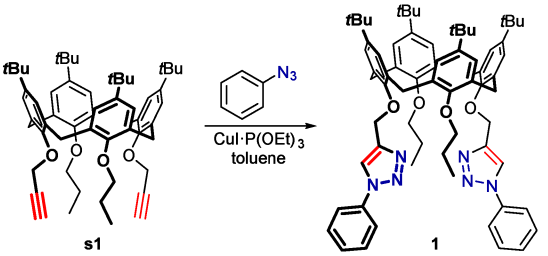
Supplementary Information

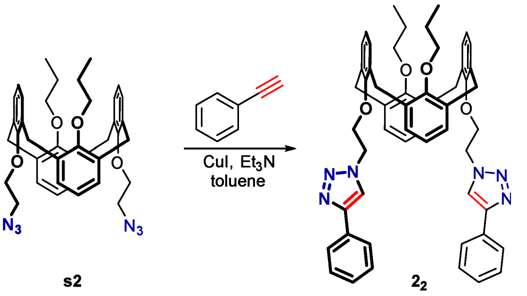
Contents

Synthesis and characterization of novel compounds

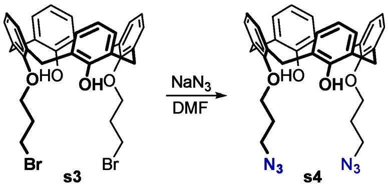
General experimental methods: NMR spectra were acquired on a Bruker Avance 400 instrument at 20 ºC if not stated otherwise, and chemical shifts are reported as ppm referenced to solvent signals. ESI mass spectra were obtained from Sciex TripleTOF 5600+ spectrometers. Chemicals received from commercial sources were used without further purification. Calixarenes **s1**,[Ref1] **s2**,[Ref2] **s3**,[Ref3] **s6**, **s7**,[Ref2] **s9**, **s10**[Ref4] and **3_2a**[Ref5] were prepared according to the published procedures.



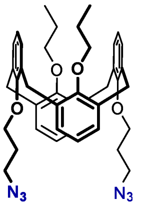
Bis(phenyltriazole) ***1***. A mixture of calixarene **s1** (0.200 g, 0.25 mmol), phenylazide (0.087 g, 0.57 mmol) and CuI·P(OEt)$_3$ (0.011 g, 0.03 mmol) in toluene (20 ml) was stirred at 95 °C for 7 h. The solvent was removed under reduced pressure, and the residue was stirred vigorously for 2 h with dichloromethane and aq. HCl (2 M). The organic layer was separated, washed with aq. Na_2SO_3 (5%) and water and dried with $MgSO_4$. After removal of the solvent, the product was purified by column chromatography on silica (gradient from dichloromethane to dichloromethane/ethanol (40:1)). Yield 0.209 g (81%), white solid. M. p. 256–258 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.17 (s, 2H; ArH$_{Trz}$), 7.83–7.78 (m, 4H; ArH$_{Ph}$), 7.56–7.49 (m, 4H; ArH$_{Ph}$), 7.46–7.40 (m, 2H; ArH$_{Ph}$), 6.86 (s, 4H; ArH), 6.63 (s, 4H; ArH), 5.36 (s, 4H; OCH$_2$Trz), 4.26 (d, 4H, ^2J = 12.6 Hz; ArCH$_2$Ar), 3.64–3.58 (m, 4H; O$\underline{\text{CH}_2}$CH$_2$), 3.06 (d, 4H, ^2J = 12.6 Hz; ArCH$_2$Ar), 1.72–1.60 (m, 4H; OCH$_2$$\underline{\text{CH}_2}$), 1.15 (s, 18H; C(CH$_3$)$_3$), 0.98 (18H; C(CH$_3$)$_3$), 0.63 (t, 6H; ^3J = 7.5 Hz; CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 153.48, 152.92, 145.89, 145.02, 144.18, 137.23, 134.62, 132.98 (C$_{Ar}$), 129.70, 128.49, 125.25, 124.67, 122.00, 120.43 (CH$_{Ar}$), 76.89 (O$\underline{\text{C}}$H$_2$CH$_2$), 66.68 (OCH$_2$Trz), 33.91, 33.70 ($\underline{\text{C}}$(CH$_3$)$_3$), 31.60 (ArCH$_2$Ar), 31.49, 31.32 (C(CH$_3$)$_3$), 22.94 (OCH$_2$$\underline{\text{C}}H_2$), 9.92 (CH$_3$) ppm. ESI-MS *m*/*z*: 1047.6473 [M+H]$^+$ for $C_{68}H_{83}N_6O_4$ (1047.6470).



Bis(phenyltriazole) ***2_2***. A mixture of calixarene **s2** (0.323 g, 0.50 mmol), phenylacetylene (0.121 ml, 1.10 mmol), CuI (0.014 g, 0.075 mmol), triethylamine (7 ml) and toluene (25 ml) was stirred at room temperature for 72 h. The solvent was removed under reduced pressure, and the residue was stirred vigorously for 2 h with dichloromethane and aq. HCl (2 M). The organic layer was separated, washed with water and dried with $MgSO_4$. After removal of the solvent, the product was purified by column chromatography on silica (gradient from dichloromethane to dichloromethane/ethanol (40:1)). Yield 0.280 g (66%), white solid. M. p. 203–205 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.90–7.85 (m, 4H; ArH$_{\mathrm{Ph}}$), 7.80 (s, 2H; ArH$_{\mathrm{Trz}}$), 7.45–7.38 (m, 4H; ArH$_{\mathrm{Ph}}$), 7.35–7.29 (m, 2H; ArH$_{\mathrm{Ph}}$), 7.05 (d, 4H, ^{3}J = 7.5 Hz; ArH), 6.83 (t, 2H, ^{3}J = 7.5 Hz; ArH), 6.82 (d, 4H, ^{3}J = 7.5 Hz; ArH), 6.67–6.62 (m, 2H; ArH), 4.09–4.03 (m, 4H, NCH$_2$), 3.82 (d, 4H, ^{2}J = 15.7 Hz; ArCH$_2$Ar), 3.72 (d, 4H, ^{2}J = 15.7 Hz; ArCH$_2$Ar), 3.59–3.54 (m, 4H; OCH$_2$), 3.47–3.41 (m, 4H; OCH$_2$), 1.38–1.27 (m, 4H; $\mathrm{C\underline{H}_2CH_3}$), 0.73 (t, 6H; ^{3}J = 7.5 Hz; CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 157.29, 155.04, 147.66, 134.41, 133.65, 130.59 (C$_{\mathrm{Ar}}$), 130.24, 129.21, 128.85, 128.09, 125.65, 122.88, 122.52, 120.71 (CH$_{\mathrm{Ar}}$), 72.36, 68.23 (OCH$_2$), 49.83 (NCH$_2$), 37.75 (ArCH$_2$Ar), 22.58 ($\mathrm{\underline{C}H_2CH_3}$), 10.02 (CH$_3$) ppm. ESI-MS *m*/*z*: 851.4277 $[\mathrm{M+H}]^+$ for $\mathrm{C_{54}H_{55}N_6O_4}$ (851.4279).

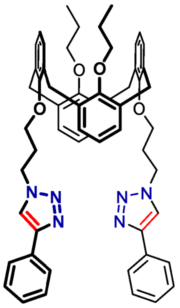


Bis(azide) **s4**. A mixture of calixarene **s3** (0.573 g, 0.86 mmol), sodium azide (0.224 g, 3.45 mmol) and DMF (10 ml) was stirred at 60 °C for 4 h and cooled to room temperature. Water was added, and the solid formed was collected, washed with water and cold methanol and dried. Yield 0.446 g (88%), white solid. M. p. 191–193 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.95 (m, 2H; OH), 7.06 (d, 4H, ^{3}J = 7.5 Hz; ArH), 6.91 (d, 4H, ^{3}J = 7.5 Hz; ArH), 6.78–6.73 (m, 2H; ArH), 6.65 (t, 2H, ^{3}J = 7.5 Hz; ArH), 4.23 (d, 4H, ^{2}J = 13.0 Hz; ArCH$_2$Ar), 4.10–4.05 (m, 4H; OCH$_2$), 3.94–3.88 (m, 4H; CH$_2$N$_3$), 3.40 (d, 4H, ^{2}J = 13.0 Hz; ArCH$_2$Ar), 2.32–2.24 (m, 4H; $\mathrm{CH_2C\underline{H}_2}$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 153.00, 151.18, 133.13 (C$_{\mathrm{Ar}}$), 129.05, 128.53 (CH$_{\mathrm{Ar}}$), 127.85 (C$_{\mathrm{Ar}}$), 125.67, 119.25 (CH$_{\mathrm{Ar}}$), 72.78 (OCH$_2$), 48.05 (CH$_2$N$_3$), 31.28 (ArCH$_2$Ar), 29.56 ($\mathrm{CH_2\underline{C}H_2}$) ppm. ESI-MS *m*/*z*: 608.2976 $[\mathrm{M+NH_4}]^+$ for $\mathrm{C_{68}H_{83}N_6O_4}$ (608.2980).

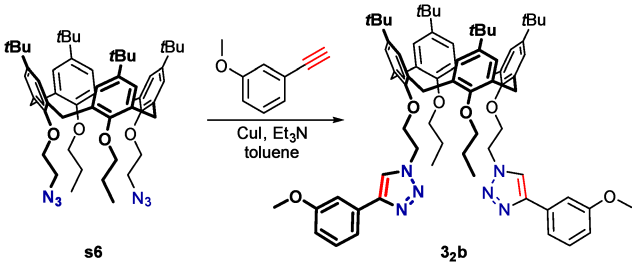


Bis(azide) **s5**. A mixture of calixarene **s4** (0.446 g, 0.76 mmol), Cs$_2$CO$_3$ (0.991 g, 3.04 mmol) and 1-iodopropane (0.290 ml, 3.04 mmol) in DMF (30 ml) was stirred at room temperature for 48 h. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane and washed with aq. HCl (2 M), aq. Na$_2$SO$_3$ (5%) and water and dried with MgSO$_4$. After removal of the solvent, the product was purified by column chromatography on silica (dichloromethane). Yield 0.338 g (66%), white solid. M. p. 146–147 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.03 (d, 4H, ^{3}J = 7.5 Hz; ArH), 7.02 (d, 4H, ^{3}J = 7.5 Hz; ArH), 6.82 (t, 2H, ^{3}J = 7.5 Hz; ArH), 6.79 (t, 2H, ^{3}J = 7.5 Hz; ArH), 3.80 (d, 4H, ^{2}J = 15.8 Hz; ArCH$_2$Ar), 3.75 (d, 4H, ^{2}J = 15.8 Hz; ArCH$_2$Ar), 3.58 (t, 4H, ^{3}J = 6.6 Hz; OCH$_2$), 3.42–3.37 (m, 4H; OCH$_2$), 3.06 (t, 4H, ^{3}J = 7.0 Hz; CH$_2$N$_3$), 1.67–1.58 (m, 4H; $\mathrm{CH_2C\underline{H}_2}$), 1.31–1.20 (m, 4H; $\mathrm{CH_2C\underline{H}_2}$), 0.73 (t, 6H, ^{3}J = 7.6 Hz; CH$_3$) ppm. ^{13}C NMR

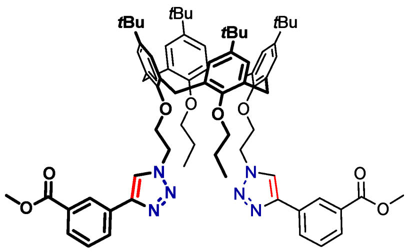
(100 MHz, $\mathrm{CDCl_3}$): δ = 156.90, 156.38, 134.07, 133.68 ($\mathrm{C_{Ar}}$), 129.62, 129.33, 122.29, 121.95 ($\mathrm{CH_{Ar}}$), 72.21, 67.24 ($\mathrm{OCH_2}$), 48.21 ($\mathrm{CH_2N_3}$), 37.77 ($\mathrm{ArCH_2Ar}$), 29.12, 22.60 ($\mathrm{CH_2\underline{C}H_2}$), 10.06 ($\mathrm{CH_3}$) ppm. ESI-MS *m*/*z*: 675.3653 $[\mathrm{M+H}]^+$ for $\mathrm{C_{40}H_{47}N_6O_4}$ (675.3653).



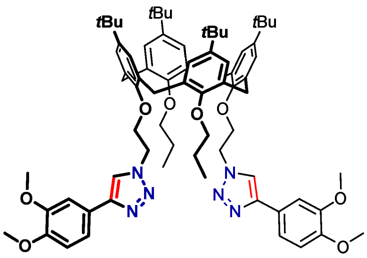
Bis(phenyltriazole) $\boldsymbol{2_3}$ was prepared as described for the bis(phenyltriazole) $\mathbf{2_2}$ from bis(azide) **s5** (0.300 g, 0.45 mmol), phenylacetylene (0.109 ml, 0.99 mmol) and CuI (0.012 g, 0.063 mmol) in the mixture of triethylamine (7 ml) and toluene (28 ml). Yield 0.352 g (90%), white solid. M. p. 225–227 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ = 7.86–7.82 (m, 4H; $\mathrm{ArH_{Ph}}$), 7.75 (s, 2H; $\mathrm{ArH_{Trz}}$), 7.44–7.38 (m, 4H; $\mathrm{ArH_{Ph}}$), 7.35–7.29 (m, 2H; $\mathrm{ArH_{Ph}}$), 7.01 (d, 4H, ^3J = 7.5 Hz; ArH), 6.97 (d, 4H, ^3J = 7.5 Hz; ArH), 6.83 (t, 2H, ^3J = 7.5 Hz; ArH), 6.81 (d, 4H, ^3J = 7.5 Hz; ArH), 3.95–3.88 (m, 4H, $\mathrm{NCH_2}$), 3.82 (d, 4H, ^2J = 16.1 Hz; $\mathrm{ArCH_2Ar}$), 3.77 (d, 4H, ^2J = 16.1 Hz; $\mathrm{ArCH_2Ar}$), 3.60 (t, 4H, ^3J = 6.9 Hz; $\mathrm{OCH_2}$), 3.37–3.31 (m, 4H; $\mathrm{OCH_2}$), 1.81–1.71 (m, 4H; $\mathrm{OCH_2C\underline{H}_2}$), 1.18–1.06 (m, 4H; $\mathrm{OCH_2C\underline{H}_2}$), 0.66 (t, 6H; ^3J = 7.5 Hz; $\mathrm{CH_3}$) ppm. ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ = 157.10, 156.23, 147.66, 134.34, 133.55, 130.61 ($\mathrm{C_{Ar}}$), 129.49, 129.08, 128.88, 128.07, 125.58, 122.55, 122.07, 119.63 ($\mathrm{CH_{Ar}}$), 71.76, 66.77 ($\mathrm{OCH_2}$), 47.11 ($\mathrm{NCH_2}$), 38.13 ($\mathrm{ArCH_2Ar}$), 30.44, 22.30 ($\mathrm{OCH_2\underline{C}H_2}$), 9.94 ($\mathrm{CH_3}$) ppm. ESI-MS *m*/*z*: 879.4590 $[\mathrm{M+H}]^+$ for $\mathrm{C_{56}H_{59}N_6O_4}$ (879.4592).



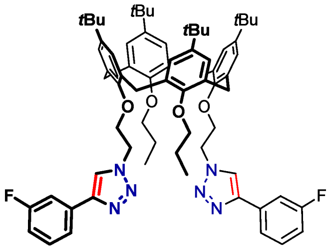
Bis(aryltriazole) $\boldsymbol{3_2b}$ was prepared as described for the bis(phenyltriazole) $\mathbf{2_2}$ from bis(azide) **s6** (0.100 g, 0.115 mmol), 3-methoxyphenylacetylene (0.032 g, 0.24 mmol) and CuI (0.003 g, 0.016 mmol) in the mixture of triethylamine (1.75 ml) and toluene (7 ml). Yield 0.055 g (42%), white solid. M. p. 130–132 °C. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ = 8.11 (s, 2H; $\mathrm{ArH_{Trz}}$), 7.55 (bs, 2H; $\mathrm{ArH_{Ph}}$), 7.49–7.44 (m, 2H; $\mathrm{ArH_{Ph}}$), 7.35–7.28 (m, 2H; $\mathrm{ArH_{Ph}}$), 7.17 (s, 4H; ArH), 6.91–6.85 (m, 2H; $\mathrm{ArH_{Ph}}$), 6.47 (s, 4H; ArH), 5.29–5.22 (m, 4H; $\mathrm{NCH_2}$), 4.67–4.59 (m, 4H; $\mathrm{OCH_2}$), 4.34 (d, 4H, ^2J = 12.7 Hz; $\mathrm{ArCH_2Ar}$), 3.86 (s, 6H; $\mathrm{OCH_3}$), 3.71–3.63 (m, 4H; $\mathrm{C\underline{H}_2CH_2CH_3}$), 3.22 (d, 4H, ^2J = 12.7 Hz; $\mathrm{ArCH_2Ar}$), 1.89–1.78 (m, 4H; $\mathrm{CH_2C\underline{H}_2}$), 1.36 (s, 18H; $\mathrm{C(CH_3)_3}$), 0.90 (t, 6H, ^3J = 7.6 Hz; $\mathrm{CH_3}$), 0.83 (s, 18H; $\mathrm{C(CH_3)_3}$) ppm. ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ = 159.99, 153.36, 151.94, 147.76, 146.20, 144.50, 135.31, 131.97, 131.52 ($\mathrm{C_{Ar}}$), 129.81, 125.86, 124.61, 120.46, 118.19, 114.18, 110.63 ($\mathrm{CH_{Ar}}$), 77.87, 71.52 ($\mathrm{OCH_2}$), 55.30 ($\mathrm{OCH_3}$), 49.29 ($\mathrm{NCH_2}$), 34.15, 33.57 ($\mathrm{\underline{C}(CH_3)_3}$), 31.64 ($\mathrm{C(\underline{C}H_3)_3}$), 31.07 ($\mathrm{ArCH_2Ar}$), 31.04 ($\mathrm{C(\underline{C}H_3)_3}$), 23.51 ($\mathrm{CH_2\underline{C}H_2}$), 10.51 ($\mathrm{CH_3}$) ppm. ESI-MS *m*/*z*: 1135.6996 $[\mathrm{M+H}]^+$ for $\mathrm{C_{72}H_{91}N_6O_6}$ (1135.6995).



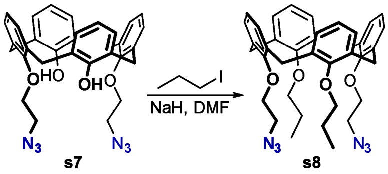
Bis(aryltriazole) ***3*****$_2$*****c*** was prepared as described for the bis(phenyltriazole) **2**$_2$ from bis(azide) **s6** (0.100 g, 0.115 mmol), methyl 3-ethynylbenzoate (0.039 g, 0.24 mmol) and CuI (0.003 g, 0.016 mmol) in the mixture of triethylamine (1.75 ml) and toluene (7 ml). The product was purified by crystallization from methanol. Yield 0.097 g (71%), white solid. M. p. 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58–8.55 (m, 2H; ArH_{Ph}), 8.21 (s, 2H; ArH_{Trz}), 8.20–8.17 (m, 2H; ArH_{Ph}), 8.02–7.98 (m, 2H; ArH_{Ph}), 7.54–7.48 (m, 2H; ArH_{Ph}), 7.17 (s, 4H; ArH), 6.47 (s, 4H; ArH), 5.29–5.23 (m, 4H; NCH_2), 4.69–4.62 (m, 4H; OCH_2), 4.34 (d, 4H, $^2J = 12.8$ Hz; $ArCH_2Ar$), 3.90 (s, 6H; OCH_3), 3.72–3.64 (m, 4H; OCH_2), 3.23 (d, 4H, $^2J = 12.8$ Hz; $ArCH_2Ar$), 1.88–1.77 (m, 4H; $CH_2C\underline{H}_2$), 1.35 (s, 18H; $C(CH_3)_3$), 0.90 (t, 6H, $^3J = 7.5$ Hz; CH_3), 0.83 (s, 18H; $C(CH_3)_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.81 (C=O), 153.32, 151.95, 146.94, 146.22, 144.52, 135.28, 131.50, 131.08, 130.73 (C_{Ar}), 130.13, 129.06, 128.95, 126.63, 125.88, 124.62, 120.70 (CH_{Ar}), 77.85, 71.47 (OCH_2), 52.11 (OCH_3), 49.38 (NCH_2), 34.14, 33.57 ($\underline{C}(CH_3)_3$), 31.63 ($C(\underline{C}H_3)_3$), 31.10 ($ArCH_2Ar$), 31.04 ($C(\underline{C}H_3)_3$), 23.51 ($CH_2\underline{C}H_2$), 10.49 (CH_3) ppm. ESI-MS *m*/*z*: 1191.6892 $[M+H]^+$ for $C_{74}H_{91}N_6O_8$ (1191.6893).



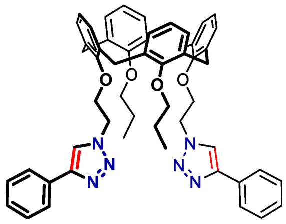
Bis(aryltriazole) ***3*****$_2$*****d*** was prepared as described for the bis(phenyltriazole) **2**$_2$ from bis(azide) **s6** (0.087 g, 0.10 mmol), 3,4-dimethoxyphenylacetylene (0.049 g, 0.30 mmol) and CuI (0.004 g, 0.020 mmol) in the mixture of triethylamine (2 ml) and toluene (8 ml). The product was purified by column chromatography (gradient from dichloromethane to dichloromethane/ethanol (65:1)). Yield 0.106 g (89%), white solid. M. p. 154–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 2H; ArH_{Trz}), 7.54 (d, 2H, $^4J = 2.0$ Hz; ArH_{Ph}), 7.33 (dd, 2H, $^3J = 8.2$ Hz, $^4J = 2.0$ Hz; ArH_{Ph}), 7.16 (s, 4H; ArH), 6.84 (d, 2H, $^3J = 8.2$ Hz; ArH_{Ph}), 6.47 (s, 4H; ArH), 5.27–5.19 (m, 4H; NCH_2), 4.64–4.56 (m, 4H; OCH_2), 4.34 (d, 4H, $^2J = 12.7$ Hz; $ArCH_2Ar$), 3.95 (s, 6H; OCH_3), 3.89 (s, 6H; OCH_3), 3.72–3.65 (m, 4H; OCH_2), 3.22 (d, 4H, $^2J = 12.7$ Hz; $ArCH_2Ar$), 1.91–1.78 (m, 4H; $CH_2C\underline{H}_2$), 1.35 (s, 18H; $C(CH_3)_3$), 0.91 (t, 6H, $^3J = 7.4$ Hz; CH_3), 0.82 (s, 18H; $C(CH_3)_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.35, 151.93, 149.24, 148.96, 147.83, 146.22, 144.52, 135.31, 131.53 (C_{Ar}), 125.86, 124.63 (CH_{Ar}), 123.67 (C_{Ar}), 119.58, 118.24, 111.25, 108.88 (CH_{Ar}), 77.87, 71.56 (OCH_2), 55.99, 55.86 (OCH_3), 49.27 (NCH_2), 34.16, 33.58 ($\underline{C}(CH_3)_3$), 31.64 ($C(\underline{C}H_3)_3$), 31.07 ($ArCH_2Ar$), 31.05 ($C(\underline{C}H_3)_3$), 23.53 ($CH_2\underline{C}H_2$), 10.55 (CH_3) ppm. ESI-MS *m*/*z*: 1195.7211 $[M+H]^+$ for $C_{74}H_{95}N_6O_8$ (1195.7206).



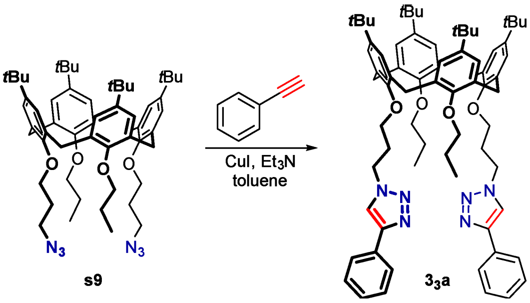
Bis(aryltriazole) ***3$_2$e*** was prepared as described for the bis(phenyltriazole) **2$_2$** from bis(azide) **s6** (0.100 g, 0.115 mmol), 3-fluorophenylacetylene (0.029 g, 0.24 mmol) and CuI (0.003 g, 0.016 mmol) in the mixture of triethylamine (1.75 ml) and toluene (7 ml). The product was purified by precipitation with hexane from a dichloromethane solution. Yield 0.077 g (60%), white solid. M. p. 255–257 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 2H; ArH_{Trz}), 7.76–8.71 (m, 4H; ArH_{Ph}), 7.43–7.36 (m, 2H; ArH_{Ph}), 7.18 (s, 4H; ArH), 7.07–7.00 (m, 2H; ArH_{Ph}), 6.47 (s, 4H; ArH), 5.29–5.22 (m, 4H; NCH_2), 4.68–4.61 (m, 4H; OCH_2), 4.34 (d, 4H, ^2J = 12.6 Hz; $ArCH_2Ar$), 3.71–3.63 (m, 4H; OCH_2), 3.23 (d, 4H, ^2J = 12.6 Hz; $ArCH_2Ar$), 1.87–1.76 (m, 4H; $CH_2C\underline{H}_2$), 1.37 (s, 18H; $C(CH_3)_3$), 0.89 (t, 6H, ^3J = 7.4 Hz; CH_3), 0.83 (s, 18H; $C(CH_3)_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.22 (d, $^1J_{C,F}$ = 245.5 Hz; C_{Ar}), 153.37, 151.96, 146.87, 146.28, 144.56, 135.32 (C_{Ar}), 132.82 (d, $^3J_{C,F}$ = 8.6 Hz; C_{Ar}), 131.47 (C_{Ar}), 130.38 (d, $^3J_{C,F}$ = 8.6 Hz; CH_{Ar}), 125.91, 124.63 (CH_{Ar}), 121.29 (d, $^4J_{C,F}$ = 2.8 Hz; CH_{Ar}), 120.80 (CH_{Ar}), 114.87 (d, $^2J_{C,F}$ = 21.3 Hz; CH_{Ar}), 112.63 (d, $^2J_{C,F}$ = 23.3 Hz; CH_{Ar}), 77.87, 71.50 (OCH_2), 49.35 (NCH_2), 34.17, 33.58 ($\underline{C}(CH_3)_3$), 31.65 ($C(\underline{C}H_3)_3$), 31.13 ($ArCH_2Ar$), 31.05 ($C(\underline{C}H_3)_3$), 23.52 ($CH_2\underline{C}H_2$), 10.50 (CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –112.65 ppm. ESI-MS *m*/*z*: 1111.6594 $[M+H]^+$ for $C_{70}H_{85}F_2N_6O_4$ (1111.6595).



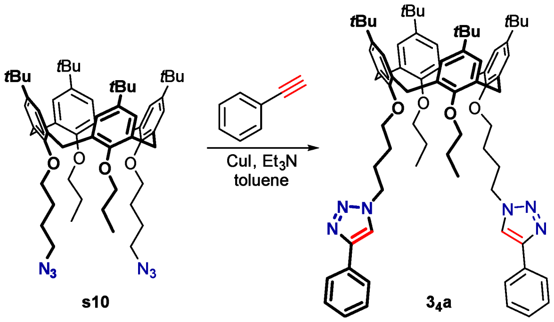
Bis(azide) ***s8***. A mixture of calixarene **s7** (0.562 g, 1.00 mmol) and NaH (60%, 0.240 g, 6.00 mmol) in DMF (25 ml) was stirred at room temperature for 1 h. 1-iodopropane was added and the mixture was stirred at room temperature for 48 h. The reaction was quenched with methanol, the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and washed with aq. HCl (2 M) and water and dried with $MgSO_4$. After removal of the solvent, the product was purified by column chromatography on silica (dichloromethane). Yield 0.400 g (62%), white solid. M. p. 98–100 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99–6.95 (m, 4H; ArH), 6.87–6.82 (m, 2H; ArH), 6.36–6.31 (m, 2H; ArH), 6.28–6.24 (m, 4H; ArH), 4.38 (d, 4H, ^2J = 13.5 Hz; $ArCH_2Ar$), 4.16 (t, 4H, ^3J = 6.6 Hz; OCH_2), 3.80 (t, 4H, ^3J = 6.6 Hz; OCH_2), 3.74 (t, 4H, ^3J = 7.2 Hz; CH_2N_3), 3.20 (d, 4H, ^2J = 13.5 Hz; $ArCH_2Ar$), 1.97–1.86 (m, 4H; $CH_2C\underline{H}_2$), 1.05 (t, 6H, ^3J = 7.5 Hz; CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.68, 155.07, 135.96, 133.43 (C_{Ar}), 128.88, 127.73, 122.68, 122.25 (CH_{Ar}), 77.16, 71.52 (OCH_2), 50.78 (CH_2N_3), 30.79 ($ArCH_2Ar$), 23.39 ($CH_2\underline{C}H_2$), 10.61 (CH_3) ppm. ESI-MS *m*/*z*: 647.3336 $[M+H]^+$ for $C_{38}H_{43}N_6O_4$ (647.3340).



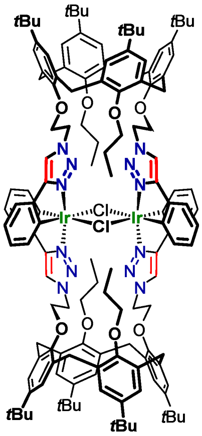
Bis(phenyltriazole) ***3'$_2$a*** was prepared as described for the bis(phenyltriazole) **2$_2$** from bis(azide) **s8** (0.323 g, 0.50 mmol), phenylacetylene (0.121 ml, 1.10 mmol) and CuI (0.014 g, 0.075 mmol) in the mixture of triethylamine (7 ml) and toluene (28 ml). Yield 0.230 g (54%), white solid. M. p. 280–282 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 2H; ArH_{Trz}), 7.98–7.94 (m, 4H; ArH_{Ph}), 7.45–7.40 (m, 4H; ArH_{Ph}), 7.36–7.31 (m, 2H; ArH_{Ph}), 7.16 (d, 4H, ^3J = 7.5 Hz; ArH), 7.03–6.98 (m, 2H; ArH), 6.30–6.24 (m, 2H; ArH), 6.19–6.15 (m, 4H; ArH), 5.09–5.02 (m, 4H; NCH_2), 4.67–4.60 (m, 4H; OCH_2), 4.36 (d, 4H, ^2J = 13.6 Hz; $ArCH_2Ar$), 3.67 (t, 4H, ^3J = 7.4 Hz; OCH_2), 3.25 (d, 4H, ^2J = 13.6 Hz; $ArCH_2Ar$), 1.86–1.74 (m, 4H; $CH_2C\underline{H}_2$), 0.91 (t, 6H, ^3J = 7.4 Hz; CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.58, 154.55, 147.81, 136.55, 132.76, 130.68 (C_{Ar}), 129.40, 128.78, 128.03, 127.65, 125.74, 123.30, 122.48, 120.64 (CH_{Ar}), 77.39, 72.10 (OCH_2), 48.99 (NCH_2), 30.93 ($ArCH_2Ar$), 23.41 ($CH_2\underline{C}H_2$), 10.52 (CH_3) ppm. ESI-MS *m/z*: 851.4272 $[M+H]^+$ for $C_{54}H_{55}N_6O_4$ (851.4279).



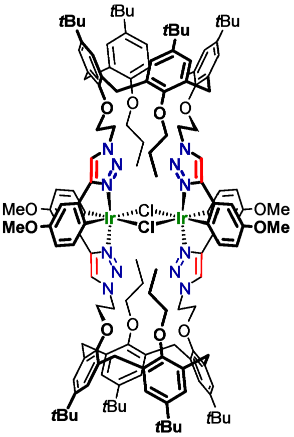
Bis(phenyltriazole) ***3$_3$a*** was prepared as described for the bis(phenyltriazole) **2$_2$** from bis(azide) **s9** (0.224 g, 0.25 mmol), phenylacetylene (0.060 ml, 0.55 mmol) and CuI (0.007 g, 0.037 mmol) in the mixture of triethylamine (3.5 ml) and toluene (14 ml). The product was purified by precipitation with hexane from a dichloromethane solution. Yield 0.220 g (80%), white solid. M. p. 262–264 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (s, 2H; ArH_{Trz}), 7.86–7.82 (m, 4H; ArH_{Ph}), 7.43–7.38 (m, 4H; ArH_{Ph}), 7.35–7.29 (m, 2H; ArH_{Ph}), 7.06 (s, 4H; ArH), 6.49 (s, 4H; ArH), 4.59–4.51 (m, 4H; NCH_2), 4.31 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 4.12–4.05 (m, 4H; OCH_2), 3.65–3.58 (m, 4H; OCH_2), 3.13 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 2.75–2.65 (m, 4H; $CH_2C\underline{H}_2$), 1.83–1.70 (m, 4H; $CH_2C\underline{H}_2$), 1.29 (s, 18H; $C(CH_3)_3$), 0.90 (t, 6H, ^3J = 7.2 Hz; CH_3), 0.85 (s, 18H; $C(CH_3)_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.76, 152.34, 147.57, 145.29, 144.18, 135.17, 131.96, 130.66 (C_{Ar}), 128.84, 128.04, 125.58, 125.53, 124.56, 120.13 (CH_{Ar}), 77.50, 71.38 (OCH_2), 47.82 (NCH_2), 34.03, 33.58 ($\underline{C}(CH_3)_3$), 31.63, 31.13 ($C(\underline{C}H_3)_3$), 31.03 ($ArCH_2Ar$), 30.99, 23.54 ($CH_2\underline{C}H_2$), 10.51 (CH_3) ppm. ESI-MS *m/z*: 1103.7092 $[M+H]^+$ for $C_{72}H_{91}N_6O_4$ (1103.7096).



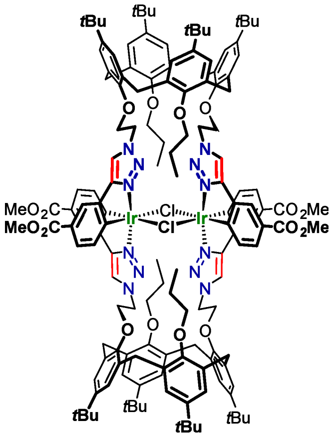
Bis(phenyltriazole) ***3$_4$a*** was prepared as described for the bis(phenyltriazole) **2$_2$** from bis(azide) **s10** (0.231 g, 0.25 mmol), phenylacetylene (0.060 ml, 0.55 mmol) and CuI (0.007 g, 0.037 mmol) in the mixture of triethylamine (3.5 ml) and toluene (14 ml). The product was purified by precipitation with hexane from a dichloromethane solution. Yield 0.218 g (77%), white solid. M. p. 210–212 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.94 (s, 2H; ArH$_{Trz}$), 7.87–7.83 (m, 4H; ArH$_{Ph}$), 7.43–7.37 (m, 4H; ArH$_{Ph}$), 7.34–7.28 (m, 2H; ArH$_{Ph}$), 6.88 (s, 4H; ArH), 6.65 (s, 4H; ArH), 4.51–4.46 (m, 4H; NCH$_2$), 4.33 (d, 4H, $^2J = 12.5$ Hz; ArCH$_2$Ar), 4.01–3.93 (m, 4H; OCH$_2$), 3.73–3.66 (m, 4H; OCH$_2$), 3.11 (d, 4H, $^2J = 12.5$ Hz; ArCH$_2$Ar), 2.16–2.07 (m, 8H; $CH_2C\underline{H}_2$), 1.90–1.78 (m, 4H; $CH_2C\underline{H}_2$), 1.16 (s, 18H; C(CH$_3$)$_3$), 0.98 (s, 18H; C(CH$_3$)$_3$), 0.91 (t, 6H, $^3J = 7.2$ Hz; CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 153.49, 153.03, 147.76, 144.73, 144.21, 134.26, 132.93, 130.65 (C$_{Ar}$), 128.80, 128.05, 125.64, 125.17, 124.73, 119.74 (CH$_{Ar}$), 77.05, 73.89 (OCH$_2$), 50.41 (NCH$_2$), 33.88, 33.69 ($\underline{C}(CH_3)_3$), 31.49, 31.30 ($C(\underline{C}H_3)_3$), 31.04 (ArCH$_2$Ar), 27.17, 27.15, 23.38 ($CH_2\underline{C}H_2$), 10.44 (CH$_3$) ppm. ESI-MS *m*/*z*: 1131.7405 [M+H]$^+$ for $C_{74}H_{95}N_6O_4$ (1131.7409).



Complex ***4a***. A mixture of calixarene **3$_2$a** (0.215 g, 0.20 mmol) and IrCl$_3$·3H$_2$O (0.071 g, 0.20 mmol) in 2-ethoxyethanol (8 ml) was stirred at 130 °C for 48 h in an argon-flushed capped flask. The solid formed was collected, washed with 2-ethoxyethanol and dissolved in dichloromethane. The solution was filtered to remove traces of iridium black and concentrated to almost dryness. Hexane was added and the solid formed was collected, washed with hexane and dried. Yield 0.105 g (40%), light yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.65 (s, 4H; ArH$_{Trz}$), 7.26 (d, 4H, $^4J = 2.6$ Hz; ArH), 7.24 (d, 4H, $^4J = 2.6$ Hz; ArH), 7.10–7.06 (m, 4H; ArH$_{Ph}$), 6.65–6.59 (m, 4H; ArH$_{Ph}$), 6.55 (s, 4H; ArH), 6.55–6.50 (m, 4H; ArH$_{Ph}$), 6.50 (s, 4H; ArH), 5.93–5.87 (m, 4H; ArH$_{Ph}$), 5.70–5.60 (m, 4H; NCH$_2$), 5.47–5.31 (m, 8H; $NCH_2{+}NCH_2C\underline{H}_2$), 4.52 (d, 4H, $^2J = 12.5$ Hz; ArCH$_2$Ar), 4.49 (d, 4H, $^2J = 12.5$ Hz; ArCH$_2$Ar), 4.47–4.39 (m, 4H; $NCH_2C\underline{H}_2$), 3.87–3.75 (m, 8H; $C\underline{H}_2CH_2CH_3$), 3.34 (d, 4H, $^2J = 12.5$ Hz; ArCH$_2$Ar), 3.31 (d, 4H, $^2J = 12.5$ Hz; ArCH$_2$Ar), 2.34–2.22 (m, 4H; $C\underline{H}_2CH_3$), 2.04–1.91 (m, 4H; $C\underline{H}_2CH_3$), 1.39 (s, 36H; C(CH$_3$)$_3$), 1.11 (t, 6H, $^3J = 7.5$ Hz; CH$_3$), 0.88 (s, 18H; C(CH$_3$)$_3$), 0.83 (s, 18H; C(CH$_3$)$_3$), 0.54 (t, 6H, $^3J = 7.5$ Hz; CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 157.87, 154.05, 152.66, 151.65, 146.41, 144.70, 144.24, 142.11, 135.86, 135.54, 135.22, 131.85, 131.55 (C$_{Ar}$), 126.71, 126.15, 125.56, 124.75, 124.70, 120.74, 120.54, 116.44 (CH_{Ar}), 79.46, 78.02 ($\underline{C}H_2CH_2CH_3$), 71.34 (OCH_2), 50.33 (NCH_2), 34.26, 33.65, 33.63 ($\underline{C}(CH_3)_3$), 31.73 ($C(\underline{C}H_3)_3$), 31.54 ($ArCH_2Ar$), 31.11 ($C(\underline{C}H_3)_3$), 30.88 ($ArCH_2Ar$), 24.07, 24.06 ($CH_2\underline{C}H_2CH_3$), 10.57, 10.56 (CH_3) ppm. ESI-MS *m*/*z*: 2567.2066 $[M–Cl]^+$ for $C_{140}H_{168}ClIr_2N_{12}O_8$ (2567.2083).

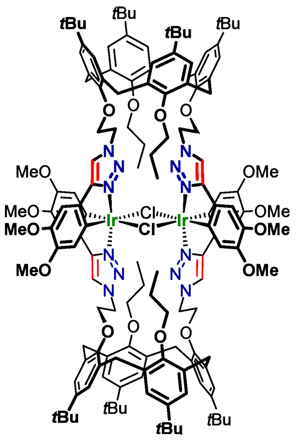


Complex ***4b*** was prepared as described for the complex **4a** from calixarene $\mathbf{3_2b}$ (0.041 g, 0.036 mmol) and $IrCl_3·3H_2O$ (0.013 g, 0.036 mmol) in 2-ethoxyethanol (1.45 ml). Yield 0.015 g (31%), greenish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (s, 4H; ArH_{Trz}), 7.26 (d, 4H, $^4J = 2.2$ Hz; ArH), 7.24 (d, 4H, $^4J = 2.2$ Hz; ArH), 6.73 (d, 4H, $^4J = 2.4$ Hz; ArH_{Ph}), 6.55 (s, 4H; ArH), 6.51 (s, 4H; ArH), 6.26 (dd, 4H, $^3J = 8.5$ Hz, $^4J = 2.7$ Hz; ArH_{Ph}), 5.77 (d, 4H, $^3J = 8.5$ Hz; ArH_{Ph}), 5.67–5.60 (m, 4H; NCH_2), 5.43–5.33 (m, 8H; NCH_2+$NCH_2C\underline{H}_2$), 4.53 (d, 4H, $^2J = 12.7$ Hz; $ArCH_2Ar$), 4.48 (d, 4H, $^2J = 12.7$ Hz; $ArCH_2Ar$), 4.46–4.39 (m, 4H; $NCH_2C\underline{H}_2$), 3.87–3.77 (m, 8H; $C\underline{H}_2CH_2CH_3$), 3.60 (s, 12H; OCH_3), 3.34 (d, 4H, $^2J = 12.7$ Hz; $ArCH_2Ar$), 3.32 (d, 4H, $^2J = 12.7$ Hz; $ArCH_2Ar$), 2.35–2.20 (m, 4H; $C\underline{H}_2CH_3$), 2.05–1.91 (m, 4H; $C\underline{H}_2CH_3$), 1.40 (s, 36H; $C(CH_3)_3$), 1.11 (t, 6H, $^3J = 7.4$ Hz; CH_3), 0.89 (s, 18H; $C(CH_3)_3$), 0.83 (s, 18H; $C(CH_3)_3$), 0.59 (t, 6H, $^3J = 7.4$ Hz; CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.81, 154.86, 154.02, 152.61, 151.64, 146.42, 144.70, 144.25, 135.85, 135.56, 135.20, 131.83, 131.53, 131.33 (C_{Ar}), 126.13, 125.57, 124.75, 124.69, 116.51, 113.37, 106.99 (CH_{Ar}), 79.41, 78.01 ($\underline{C}H_2CH_2CH_3$), 71.29 (OCH_2), 55.32 (OCH_3), 50.33 (NCH_2), 34.25, 33.64, 33.63 ($\underline{C}(CH_3)_3$), 31.72 ($C(\underline{C}H_3)_3$), 31.53 ($ArCH_2Ar$), 31.10 ($C(\underline{C}H_3)_3$), 30.90 ($ArCH_2Ar$), 24.05, 24.03 ($CH_2\underline{C}H_2CH_3$), 10.67, 10.55 (CH_3) ppm. ESI-MS *m*/*z*: 1407.1945 $[M–2Cl+4CH_3CN]^{2+}$ for $C_{152}H_{188}Ir_2N_{16}O_{12}$ (1407.1925).

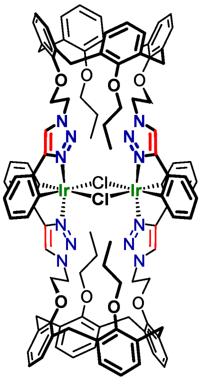


Complex ***4c*** was prepared as described for the complex **4a** from calixarene $\mathbf{3_2c}$ (0.090 g, 0.076 mmol) and $IrCl_3·3H_2O$ (0.027 g, 0.076 mmol) in 2-ethoxyethanol (3.02 ml). Yield 0.035 g (33%), light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (s, 4H; ArH_{Trz}), 7.79 (d, 4H, $^4J = 1.9$ Hz; ArH_{Ph}), 7.28 (d, 4H, $^4J = 2.4$ Hz; ArH), 7.26 (d, 4H, $^4J = 2.4$ Hz; ArH), 7.19 (dd, 4H, $^3J = 8.3$ Hz, $^4J = 1.9$ Hz; ArH_{Ph}), 6.57 (s, 4H; ArH), 6.53 (s, 4H; ArH), 5.97 (d, 4H, $^3J = 8.3$ Hz; ArH_{Ph}), 5.75–5.63 (m, 4H; NCH_2), 5.51–5.39 (m, 8H; NCH_2+$NCH_2C\underline{H}_2$), 4.51 (d, 4H, $^2J = 12.7$ Hz; $ArCH_2Ar$), 4.49 (d, 4H, $^2J = 12.7$ Hz; $ArCH_2Ar$), 4.47–4.40 (m, 4H; $NCH_2C\underline{H}_2$), 3.88–3.82 (m, 4H; $C\underline{H}_2CH_2CH_3$), 3.81–

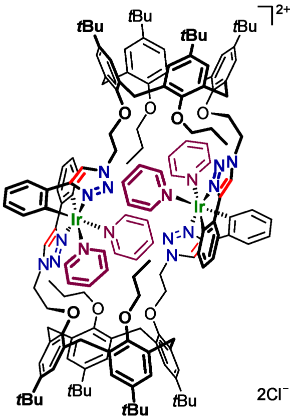
3.75 (m, 4H; $C\underline{H}_2CH_2CH_3$), 3.75 (s, 12H; OCH_3), 3.38 (d, 4H, ${}^2J$ = 12.7 Hz; $ArCH_2Ar$), 3.36 (d, 4H, ${}^2J$ = 12.7 Hz; $ArCH_2Ar$), 2.33–2.21 (m, 4H; $C\underline{H}_2CH_3$), 2.04–1.92 (m, 4H; $C\underline{H}_2CH_3$), 1.41 (s, 36H; $C(CH_3)_3$), 1.14 (t, 6H, ${}^3J$ = 7.5 Hz; CH_3), 0.90 (s, 18H; $C(CH_3)_3$), 0.85 (s, 18H; $C(CH_3)_3$), 0.51 (t, 6H, ${}^3J$ = 7.5 Hz; CH_3) ppm. ${}^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 167.89 (C=O), 156.87, 153.92, 152.51, 151.55, 151.52, 146.59, 144.79, 144.40, 135.93, 135.74, 135.12, 131.76 (C_{Ar}), 131.55 (CH_{Ar}), 131.49 (C_{Ar}), 127.95, 126.25, 125.57, 124.78, 124.77 (CH_{Ar}), 123.04 (C_{Ar}), 121.70, 117.56 (CH_{Ar}), 79.33, 78.06 ($\underline{C}H_2CH_2CH_3$), 71.15 (OCH_2), 51.52 (OCH_3), 50.55 (NCH_2), 34.26, 33.64, 33.63 ($\underline{C}(CH_3)_3$), 31.70 ($C(\underline{C}H_3)_3$), 31.57 ($ArCH_2Ar$), 31.09, 31.08 ($C(\underline{C}H_3)_3$), 30.85 ($ArCH_2Ar$), 24.14, 24.13 ($CH_2\underline{C}H_2CH_3$), 10.60, 10.58 (CH_3) ppm. ESI-MS *m/z*: 2799.2286 $[M–Cl]^+$ for $C_{148}H_{176}ClIr_2N_{12}O_{16}$ (2799.2302).



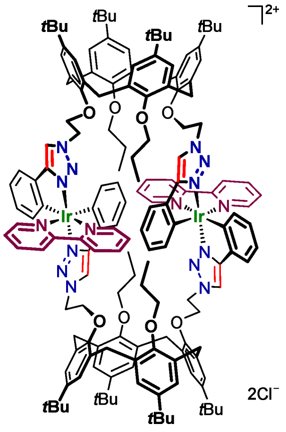
Complex ***4d*** was prepared as described for the complex **4a** from calixarene **3_2d** (0.106 g, 0.089 mmol) and $IrCl_3{\cdot}3H_2O$ (0.031 g, 0.089 mmol) in 2-ethoxyethanol (3.56 ml). Yield 0.031 g (25%), gray-green solid. ${}^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.56 (s, 4H; ArH_{Trz}), 7.25 (d, 4H, ${}^4J$ = 2.5 Hz; ArH), 7.24 (d, 4H, ${}^4J$ = 2.5 Hz; ArH), 6.73 (s, 4H; ArH_{Ph}), 6.53 (bs, 8H; ArH), 5.72–5.60 (m, 4H; NCH_2), 5.64 (s, 4H; ArH_{Ph}), 5.50–5.41 (m, 4H; $NCH_2C\underline{H}_2$), 5.38–5.28 (m, 4H; NCH_2), 4.46 (d, 4H, ${}^2J$ = 12.6 Hz; $ArCH_2Ar$), 4.38 (d, 4H, ${}^2J$ = 12.6 Hz; $ArCH_2Ar$), 4.36–4.28 (m, 4H; $NCH_2C\underline{H}_2$), 3.83–3.77 (m, 4H; $C\underline{H}_2CH_2CH_3$), 3.75–3.68 (m, 4H; $C\underline{H}_2CH_2CH_3$), 3.68 (s, 12H; OCH_3), 3.60 (s, 12H; OCH_3), 3.33 (d, 4H, ${}^2J$ = 12.6 Hz; $ArCH_2Ar$), 3.25 (d, 4H, ${}^2J$ = 12.6 Hz; $ArCH_2Ar$), 2.51–2.39 (m, 4H; $C\underline{H}_2CH_3$), 2.04–1.93 (m, 4H; $C\underline{H}_2CH_3$), 1.39 (s, 36H; $C(CH_3)_3$), 1.12 (t, 6H, ${}^3J$ = 7.5 Hz; CH_3), 0.86 (s, 18H; $C(CH_3)_3$), 0.84 (s, 18H; $C(CH_3)_3$), 0.60 (t, 6H, ${}^3J$ = 7.5 Hz; CH_3) ppm. ${}^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 158.26, 154.00, 152.54, 151.53, 147.76, 146.52, 144.82, 144.48, 144.20, 135.49, 135.04, 133.91, 131.52, 131.45, 126.68 (C_{Ar}), 126.36, 125.49, 124.85, 124.79, 115.25, 114.06, 105.69 (CH_{Ar}), 79.72, 78.06 ($\underline{C}H_2CH_2CH_3$), 71.63 (OCH_2), 56.14, 54.99 (OCH_3), 50.33 (NCH_2), 34.29, 33.66, 33.63 ($\underline{C}(CH_3)_3$), 31.72, 31.10, 31.08 ($C(\underline{C}H_3)_3$), 30.92, 30.67 ($ArCH_2Ar$), 24.49, 24.20 ($CH_2\underline{C}H_2CH_3$), 10.61, 10.58 (CH_3) ppm. ESI-MS *m/z*: 2807.2920 $[M–Cl]^+$ for $C_{148}H_{184}ClIr_2N_{12}O_{16}$ (2807.2928).



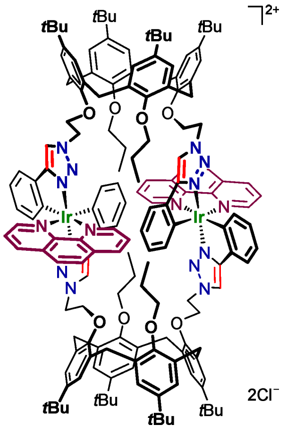
Complex ***4'a*** was prepared as described for the complex **4a** from calixarene **3'$_2$a** (0.223 g, 0.26 mmol) and $IrCl_3 \cdot 3H_2O$ (0.092 g, 0.26 mmol) in 2-ethoxyethanol (11 ml). Yield 0.123 g (44%), light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (s, 4H; ArH_{Trz}), 7.30–7.25 (m, 8H; ArH), 7.09 (t, 4H, ^3J = 7.4 Hz; ArH), 7.08–7.05 (m, 4H; ArH_{Ph}), 6.64–6.59 (m, 4H; ArH_{Ph}), 6.55–6.50 (m, 4H; ArH_{Ph}), 6.36–6.28 (m, 8H; ArH), 6.25–6.21 (m, 4H; ArH), 5.90–5.86 (m, 4H; ArH_{Ph}), 5.55–5.38 (m, 8H; NCH_2+$NCH_2C\underline{H}_2$), 5.30–5.18 (m, 4H; NCH_2), 4.54 (d, 4H, ^2J = 13.4 Hz; $ArCH_2Ar$), 4.50 (d, 4H, ^2J = 13.4 Hz; $ArCH_2Ar$), 4.43–4.33 (m, 4H; $NCH_2C\underline{H}_2$), 3.87–3.81 (m, 4H; $C\underline{H}_2CH_2CH_3$), 3.81–3.75 (m, 4H; $C\underline{H}_2CH_2CH_3$), 3.37 (d, 4H, ^2J = 13.4 Hz; $ArCH_2Ar$), 3.34 (d, 4H, ^2J = 13.4 Hz; $ArCH_2Ar$), 2.21–2.09 (m, 4H; $C\underline{H}_2CH_3$), 2.03–1.92 (m, 4H; $C\underline{H}_2CH_3$), 1.14 (t, 6H, ^3J = 7.5 Hz; CH_3), 0.59 (t, 6H, ^3J = 7.4 Hz; CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.90, 157.23, 154.84, 153.87, 141.87, 137.04, 136.34, 135.42, 132.93, 132.75 (C_{Ar}), 131.81, 131.80, 129.66, 129.05, 127.85, 126.75, 123.64, 122.67, 122.30, 120.78, 120.68, 116.76 (CH_{Ar}), 78.88, 77.72 ($\underline{C}H_2CH_2CH_3$), 71.84 (OCH_2), 50.14 (NCH_2), 31.00, 30.63 ($ArCH_2Ar$), 23.94, 23.91 ($CH_2\underline{C}H_2CH_3$), 10.72, 10.52 (CH_3) ppm. ESI-MS *m*/*z*: 2117.7019 $[M{-}Cl]^+$ for $C_{108}H_{104}ClIr_2N_{12}O_8$ (2117.7050).



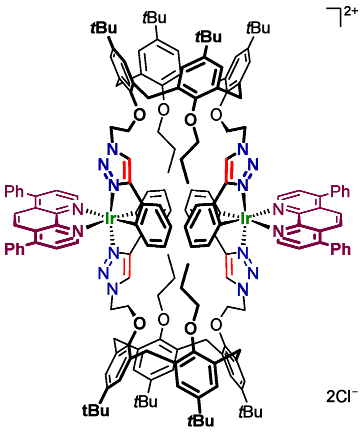
Complex *5*. A mixture of complex **4a** (0.020 g, 0.0075 mmol) and pyridine (0.006 ml, 0.075 mmol) in methanol (2.0 ml) and dichloromethane (0.5 ml) was stirred at room temperature for 48 h. The solvents were removed under reduced pressure, and diethyl ether was added to the residue. The solid formed was collected, washed with diethyl ether and dried. Yield 0.021 g (quant.), white solid. ^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD (5:1)): δ = 8.14 (s, 4H; ArH_{Trz}), 8.10 (bd, 8H; ArH_{Py}), 7.22–7.18 (m, 4H, ArH_{Ph}), 7.08–6.99 (bs, 4H; ArH_{Py}), 7.04 (s, 4H; ArH), 7.03 (s, 4H; ArH), 6.67–6.62 (m, 4H; ArH_{Ph}), 6.65–6.49 (bs, 8H; ArH_{Py}); 6.50–6.44 (m, 4H; ArH_{Ph}), 6.38 (d, 4H, ^4J = 2.4 Hz; ArH), 6.22 (d, 4H, ^4J = 2.4 Hz; ArH), 6.18–6.14 (m, 4H; ArH_{Ph}), 4.77–4.54 (m, 12H; NCH_2+$ArCH_2Ar$), 4.18 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 4.18–4.09 (m, 4H; $NCH_2C\underline{H}_2$), 3.85–3.74 (m, 4H; $C\underline{H}_2CH_2CH_3$), 3.69–3.58 (m, 4H; $NCH_2C\underline{H}_2$), 3.15 (d, 4H, ^2J = 12.8 Hz; $ArCH_2Ar$), 2.86 (bd, 4H; $ArCH_2Ar$), 2.69 (bs, 4H; $C\underline{H}_2CH_2CH_3$), 1.84–1.72 (m, 4H; $C\underline{H}_2CH_3$), 1.62–1.51 (m, 4H; $C\underline{H}_2CH_3$), 1.23 (s, 18H; $C(CH_3)_3$), 1.22 (s, 18H; $C(CH_3)_3$), 0.79 (bt, 6H; CH_3), 0.66 (s, 36H; $C(CH_3)_3$), 0.42 (t, 6H, ^3J = 7.6 Hz; CH_3) ppm. ESI-MS *m*/*z*: 1424.2070 $[M{-}2Cl]^{2+}$ for $C_{160}H_{188}Ir_2N_{16}O_8$ (1424.2039).



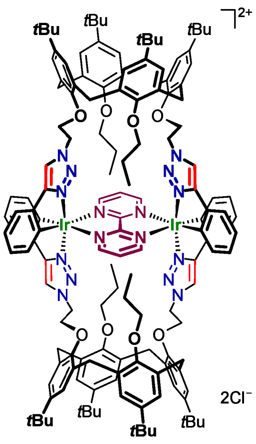
Complex ***6*** was prepared as described for the complex **5** from complex **4a** (0.020 g, 0.0075 mmol) and 2,2′-bipyridyl (0.003 g, 0.018 mmol) in methanol (2.0 ml) and dichloromethane (0.5 ml). Yield 0.022 g (quant.), bright yellow solid. M. p. 329–330 °C (decomp.). For ^{1}H NMR spectrum see Figure S43. ESI-MS *m*/*z*: 1422.1881 $[M{-}2Cl]^{2+}$ for $C_{160}H_{184}Ir_2N_{16}O_8$ (1421.1870).



Complex ***7*** was prepared as described for the complex **5** from complex **4a** (0.020 g, 0.0075 mmol) and 1,10-phenanthroline (0.003 g, 0.018 mmol) in methanol (2.0 ml) and dichloromethane (0.5 ml). Yield 0.022 g (quant.), bright yellow solid. M. p. 324–326 °C (decomp.) For ^{1}H NMR spectrum see Figure S44. ESI-MS *m*/*z*: 1446.1886 $[M{-}2Cl]^{2+}$ for $C_{164}H_{184}Ir_2N_{16}O_8$ (1446.1882).



Complex ***8*** was prepared as described for the complex **5** from complex **4a** (0.020 g, 0.0075 mmol) and bathophenanthroline (0.006 g, 0.018 mmol) in methanol (2.0 ml) and dichloromethane (0.5 ml). Yield 0.024 g (quant.), bright orange solid. M. p. 317–319 °C (decomp.) ^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD (10:1)): δ = 8.26 (d, 4H, ^3J = 5.3 Hz; ArH_{Phen}), 8.09 (s, 4H; ArH_{Trz}), 7.99 (s, 4H; ArH_{Phen}), 7.30 (d, 4H, ^3J = 5.3 Hz; ArH_{Phen}), 7.51–7.41 (m, 20H; ArH_{Phen}), 7.24 (s, 4H; ArH), 7.25–7.22 (m, 4H, ArH_{Ph}), 7.10 (s, 4H; ArH), 6.82–6.74 (m, 4H; ArH_{Ph}), 6.39 (d, 4H, ^4J = 2.5 Hz; ArH), 6.37 (d, 4H, ^4J = 2.5 Hz; ArH), 6.27–6.21 (m, 8H; ArH_{Ph}), 4.82–4.69 (m, 4H; NCH_2), 4.55–4.44 (m, 4H; $NCH_2C\underline{H}_2$), 4.25 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 4.10–3.96 (m, 8H; NCH_2+$NCH_2C\underline{H}_2$), 4.07 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 3.94–3.86 (m, 4H; $C\underline{H}_2CH_2CH_3$), 3.37–3.27 (m, 4H; $C\underline{H}_2CH_2CH_3$), 3.22 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 3.19 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 2.24–2.10 (m, 4H; $C\underline{H}_2CH_3$), 1.42 (s, 18H; $C(CH_3)_3$), 1.29 (s, 18H; $C(CH_3)_3$), 1.12 (bt, 6H; CH_3), 0.87–0.76 (m, 4H; $C\underline{H}_2CH_3$), 0.73 (s, 36H; $C(CH_3)_3$), –1.26 (bs, 6H; CH_3) ppm. ESI-MS *m*/*z*: 1598.2524 $[M{-}2Cl]^{2+}$ for $C_{188}H_{200}Ir_2N_{16}O_8$ (1598.2518).



Complex **9** was prepared as described for the complex **5** from complex **4a** (0.020 g, 0.0075 mmol) and 2,2′-bipyrimidine (0.0014 g, 0.009 mmol) in methanol (2.0 ml) and dichloromethane (0.5 ml). Yield 0.021 g (quant.), pale green solid. M. p. 246–248 °C (decomp.) ^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD (10:1)): δ = 8.51 (d, 4H, ^3J = 5.4 Hz; ArH_{Bipyr}), 8.18 (bt, 2H; ArH_{Bipyr}), 7.97 (s, 4H; ArH_{Trz}), 7.45–7.41 (m, 4H; ArH_{Ph}), 7.18–7.10 (m, 8H, ArH), 7.00–6.93 (m, 4H; ArH_{Ph}), 6.87–6.81 (m, 4H; ArH_{Ph}), 6.45 (s, 4H; ArH), 6.40 (s, 4H; ArH), 6.30–6.24 (m, 4H; ArH_{Ph}), 5.08–4.91 (m, 8H; NCH_2+$NCH_2C\underline{H}_2$), 4.49–4.38 (m, 4H; NCH_2^*), 4.34–4.23 (m, 12H; $NCH_2C\underline{H}_2^*$+$ArCH_2Ar$), 3.75–3.67 (m, 4H; $C\underline{H}_2CH_2CH_3$), 3.63–3.57 (m, 4H; $C\underline{H}_2CH_2CH_3$), 3.21 (d, 4H, ^2J = 12.5 Hz; $ArCH_2Ar$), 3.19 (d, 4H, ^2J = 12.6 Hz; $ArCH_2Ar$), 1.77–1.59 (m, 8H; $C\underline{H}_2CH_3$), 1.29 (s, 36H; $C(CH_3)_3$), 0.90 (t, 6H, ^3J = 7.4 Hz; CH_3), 0.84 (t, 6H, ^3J = 7.4 Hz; CH_3), 0.78 (s, 18H; $C(CH_3)_3$), 0.74 (s, 18H; $C(CH_3)_3$) ppm. ESI-MS *m*/*z*: 1345.1543 $[M–2Cl]^{2+}$ for $C_{148}H_{174}Ir_2N_{16}O_8$ (1345.1491).

NMR spectra of novel compounds

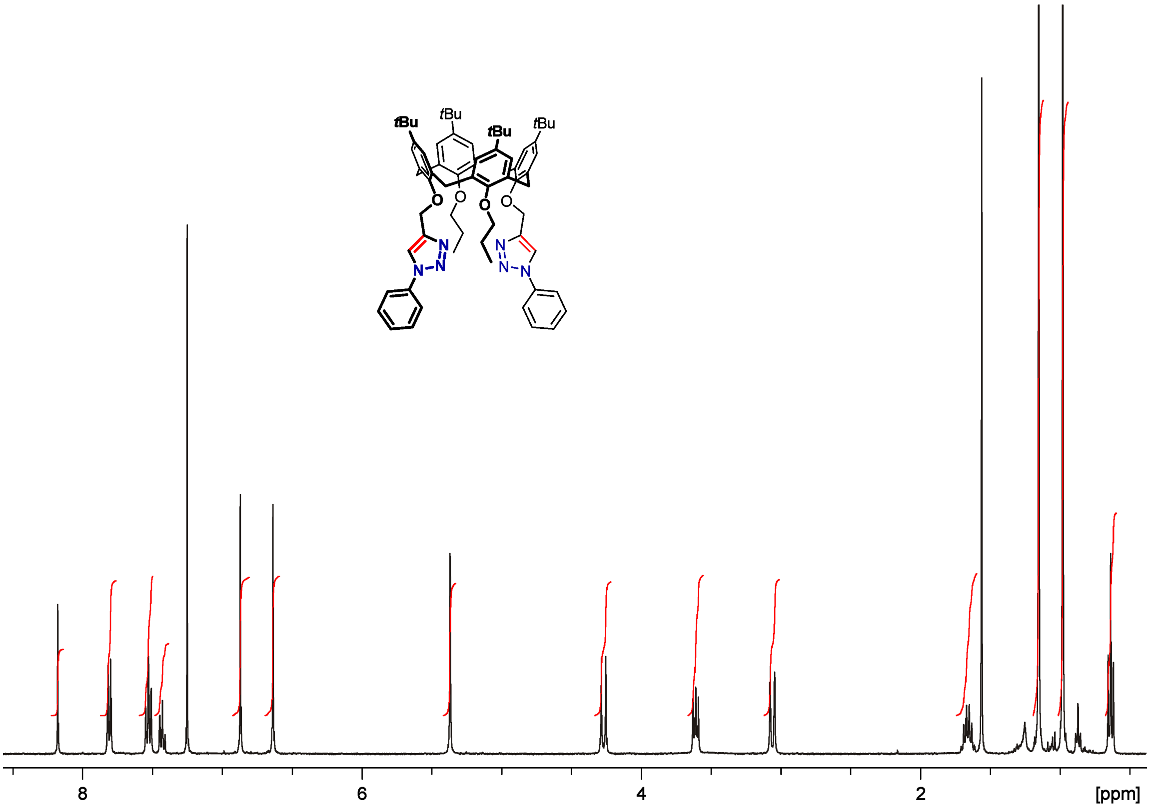


Figure S1. ^{1}H NMR spectrum of calixarene **1** (400 MHz, $CDCl_3$).

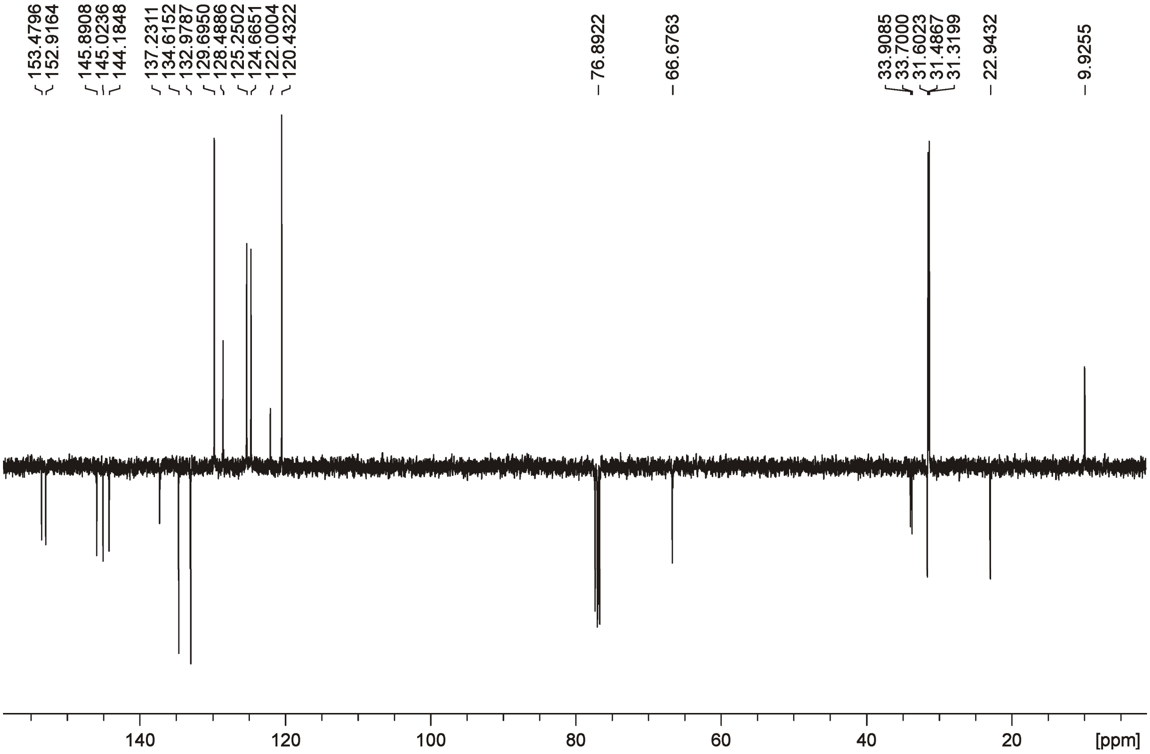


Figure S2. ^{13}C NMR spectrum (APT) of calixarene **1** (100 MHz, $CDCl_3$).

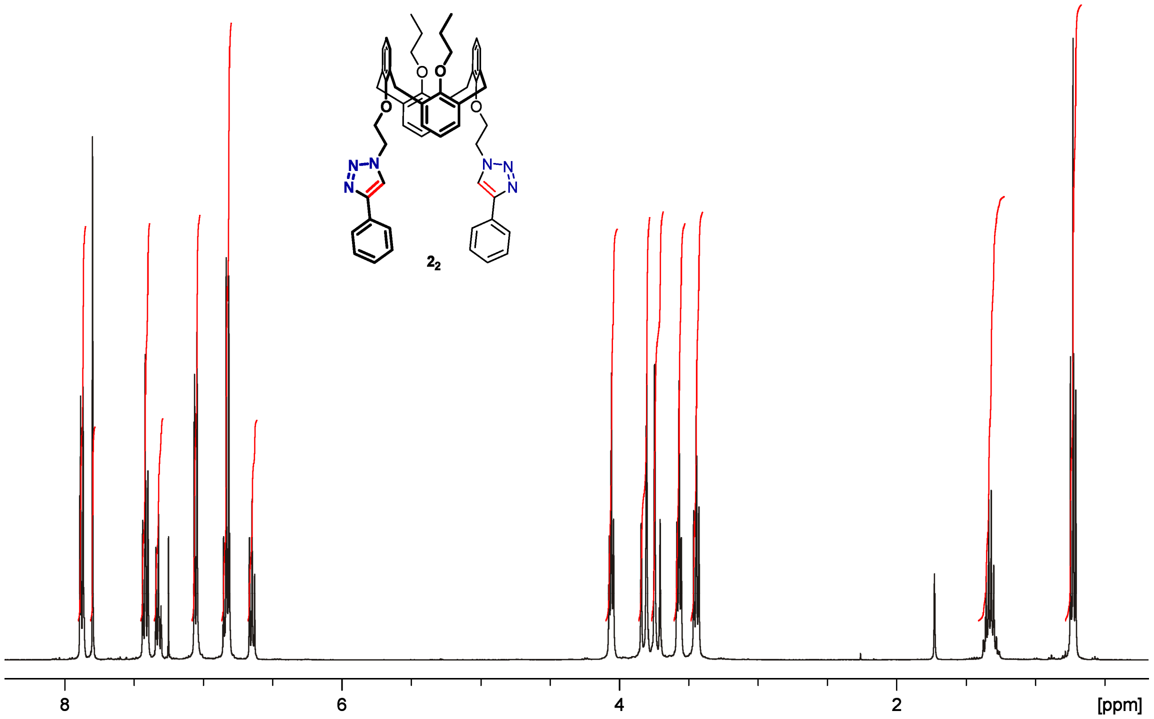


Figure S3. ^{1}H NMR spectrum of calixarene **2_2** (400 MHz, $CDCl_3$).

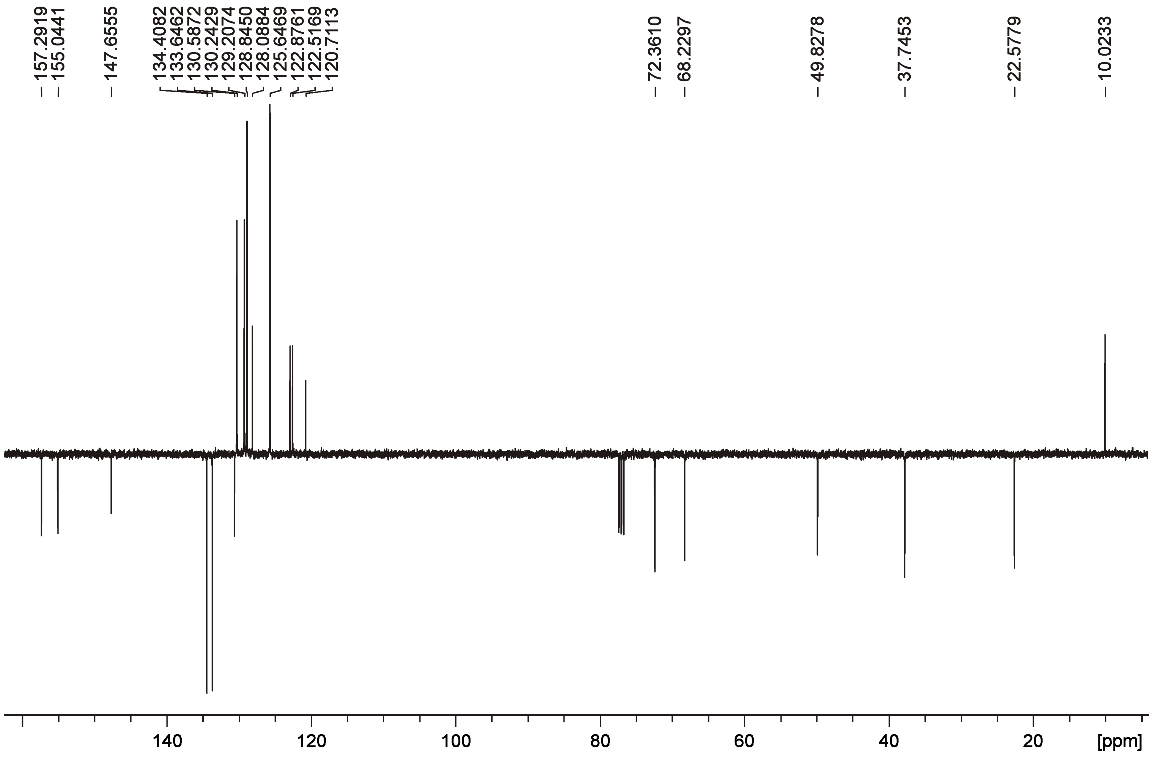


Figure S4. ^{13}C NMR spectrum (APT) of calixarene **2_2** (100 MHz, $CDCl_3$).

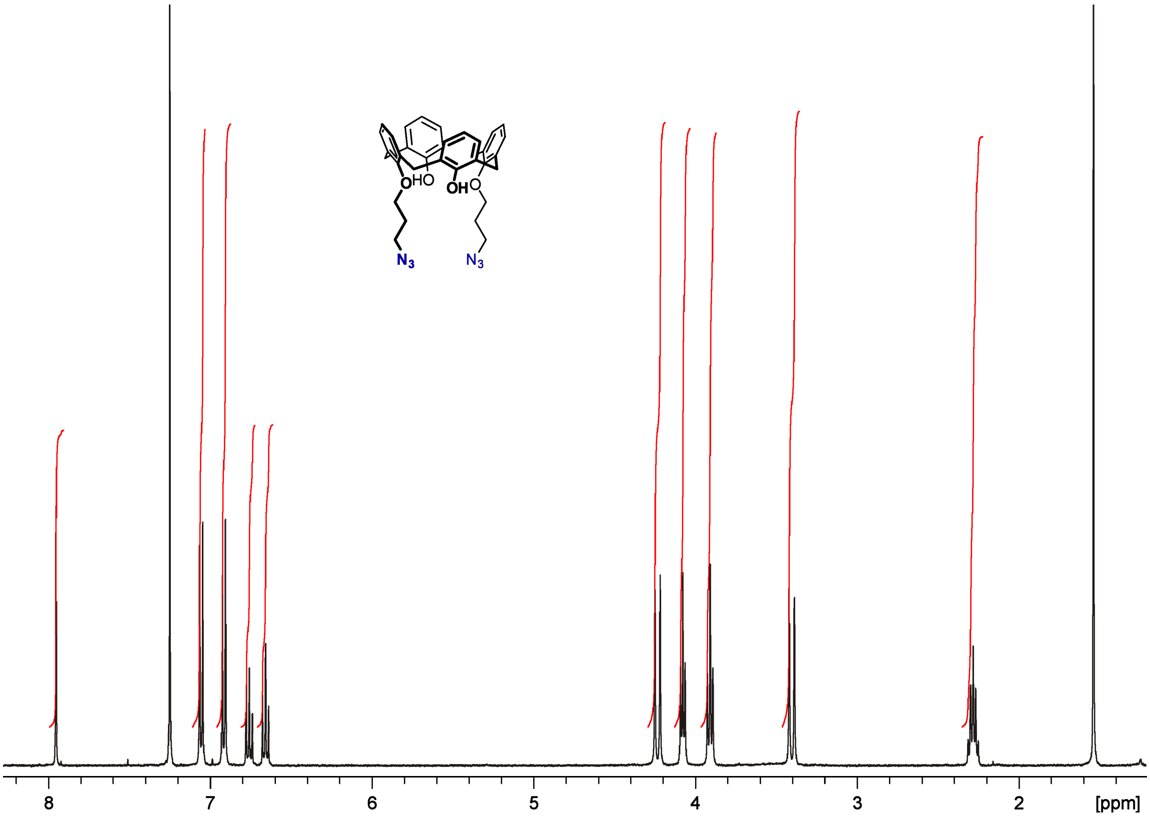


Figure S5. ^{1}H NMR spectrum of calixarene **s4** (400 MHz, $CDCl_3$).

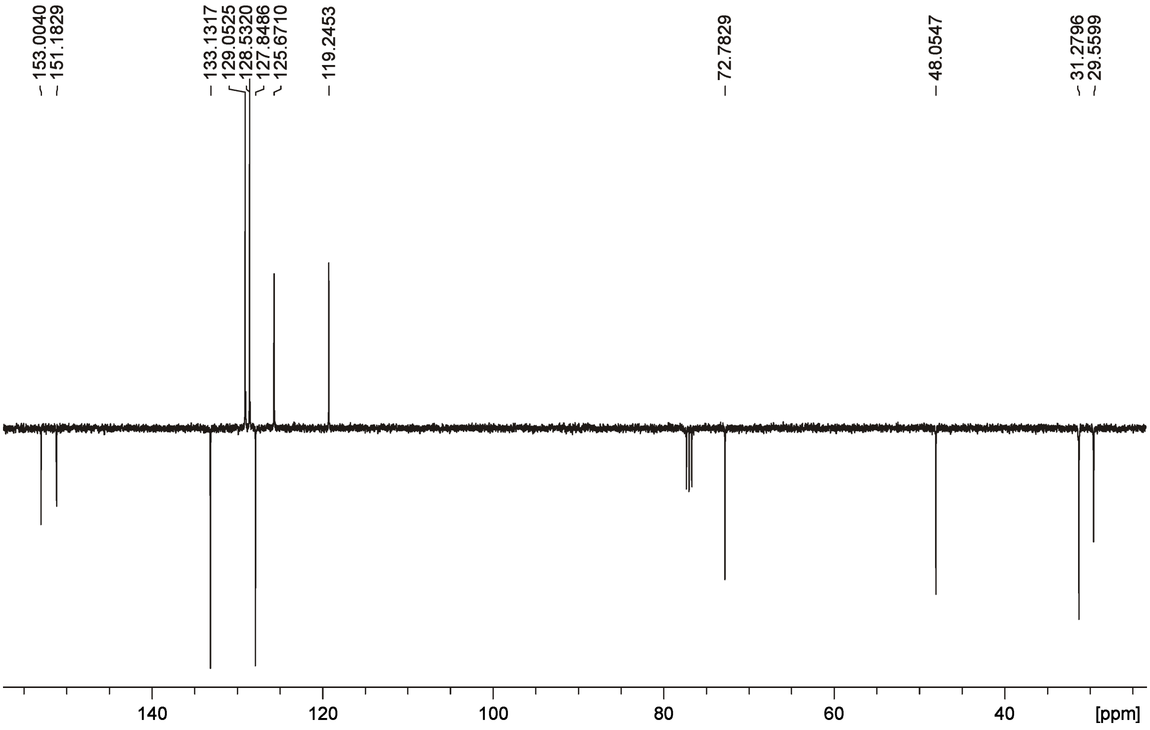


Figure S6. ^{13}C NMR spectrum (APT) of calixarene **s4** (100 MHz, $CDCl_3$).

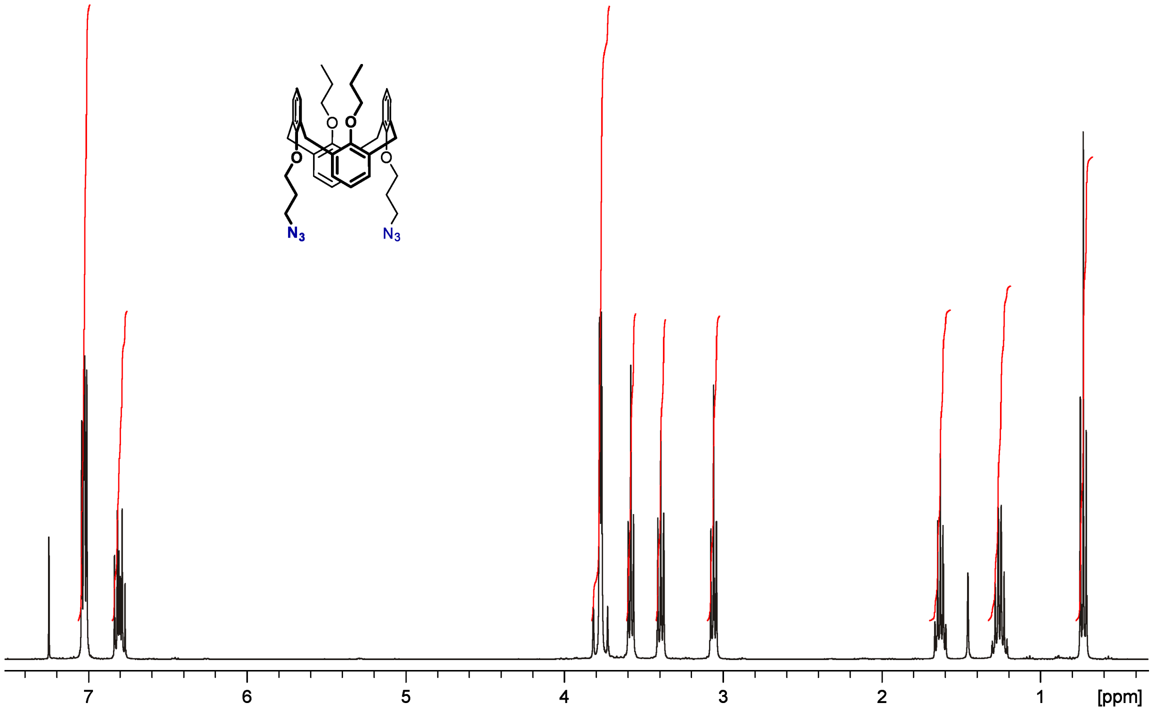


Figure S7. ^{1}H NMR spectrum of calixarene **s5** (400 MHz, $CDCl_3$).

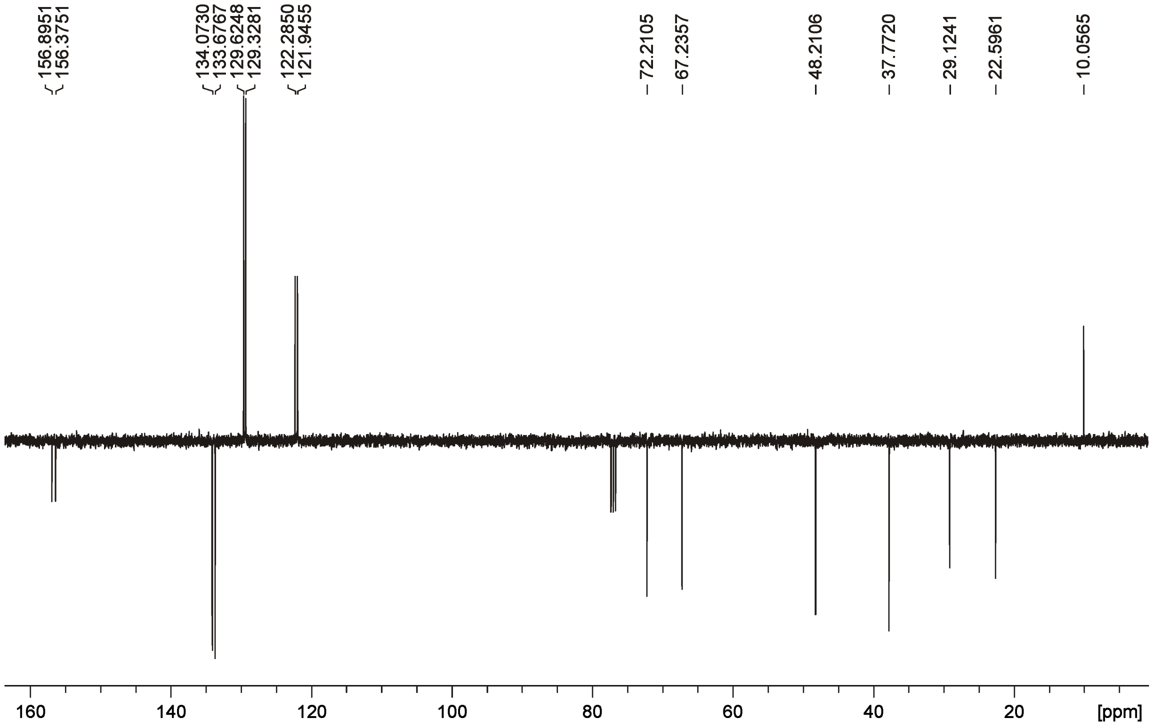


Figure S8. ^{13}C NMR spectrum (APT) of calixarene **s5** (100 MHz, $CDCl_3$).

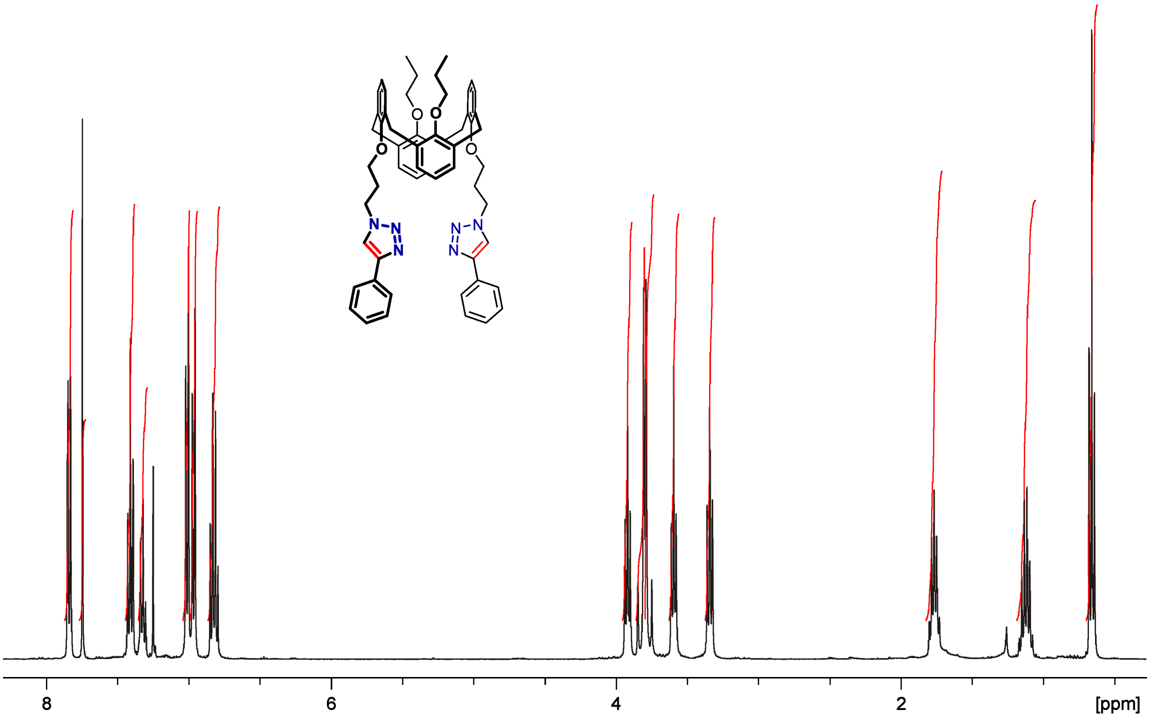


Figure S9. ^{1}H NMR spectrum of calixarene **2**$_3$ (400 MHz, CDCl$_3$).

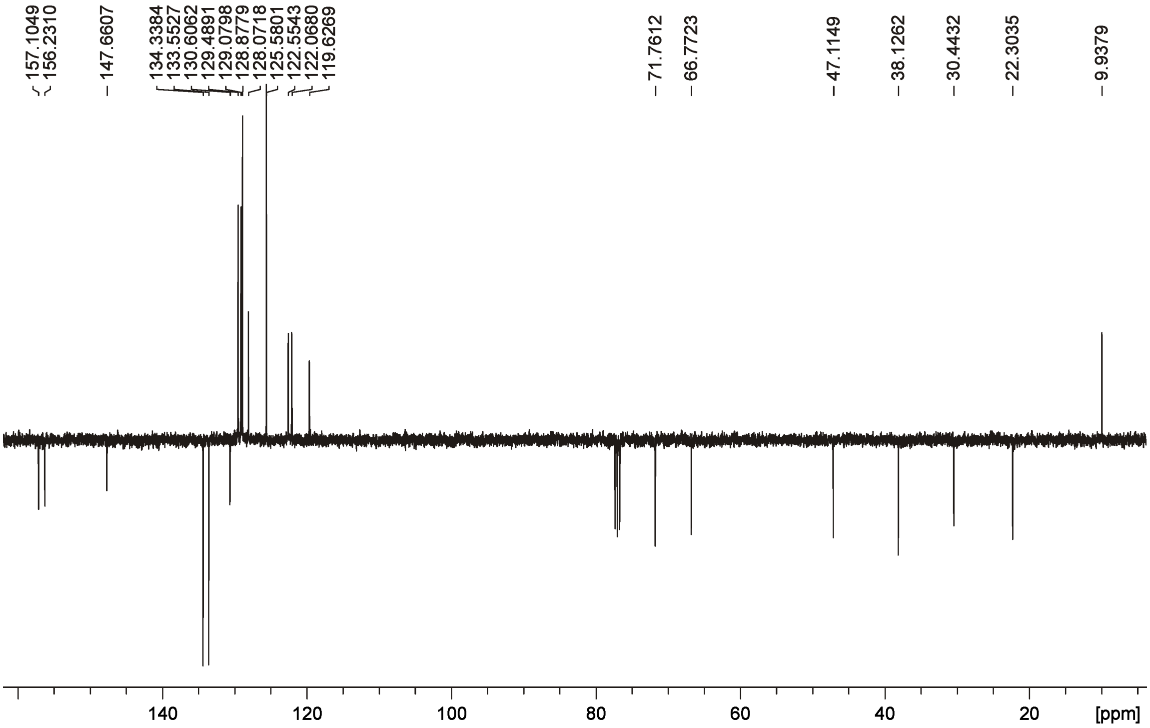


Figure S10. ^{13}C NMR spectrum (APT) of calixarene **2**$_3$ (100 MHz, CDCl$_3$).

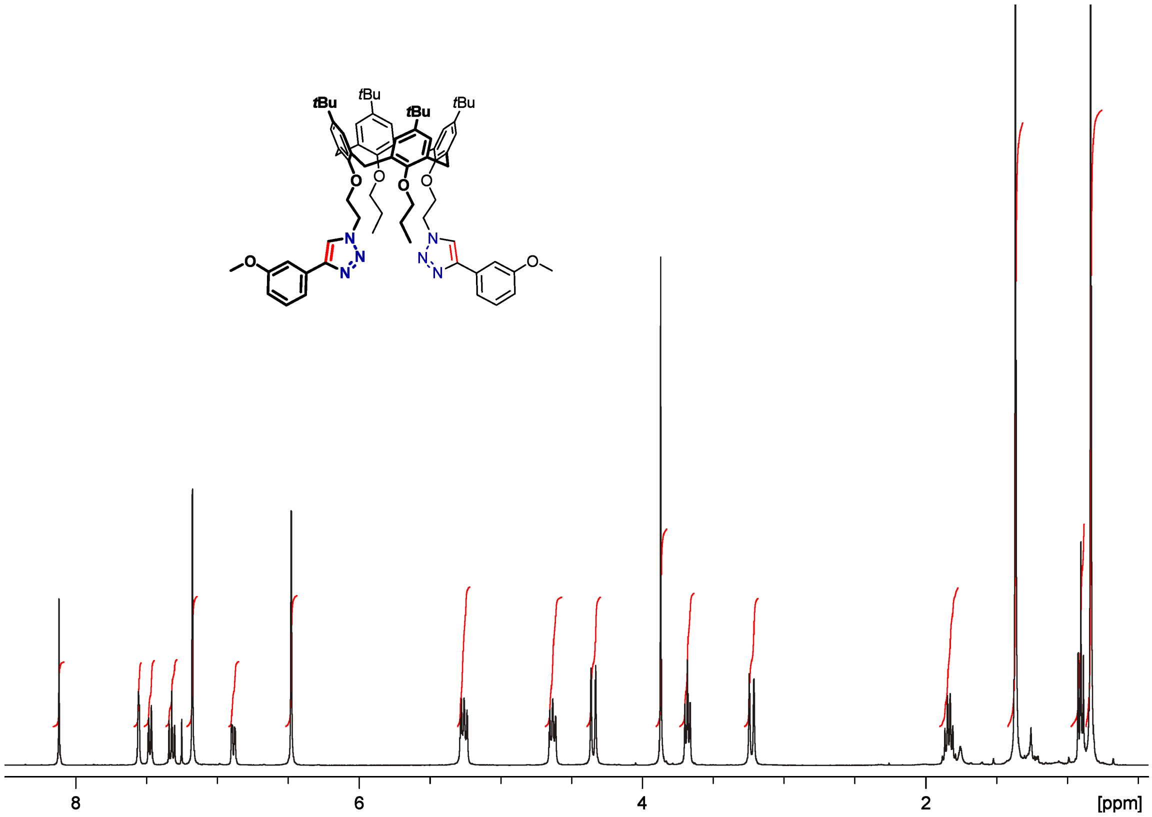


Figure S11. ^{1}H NMR spectrum of calixarene **3_2b** (400 MHz, CDCl$_3$).

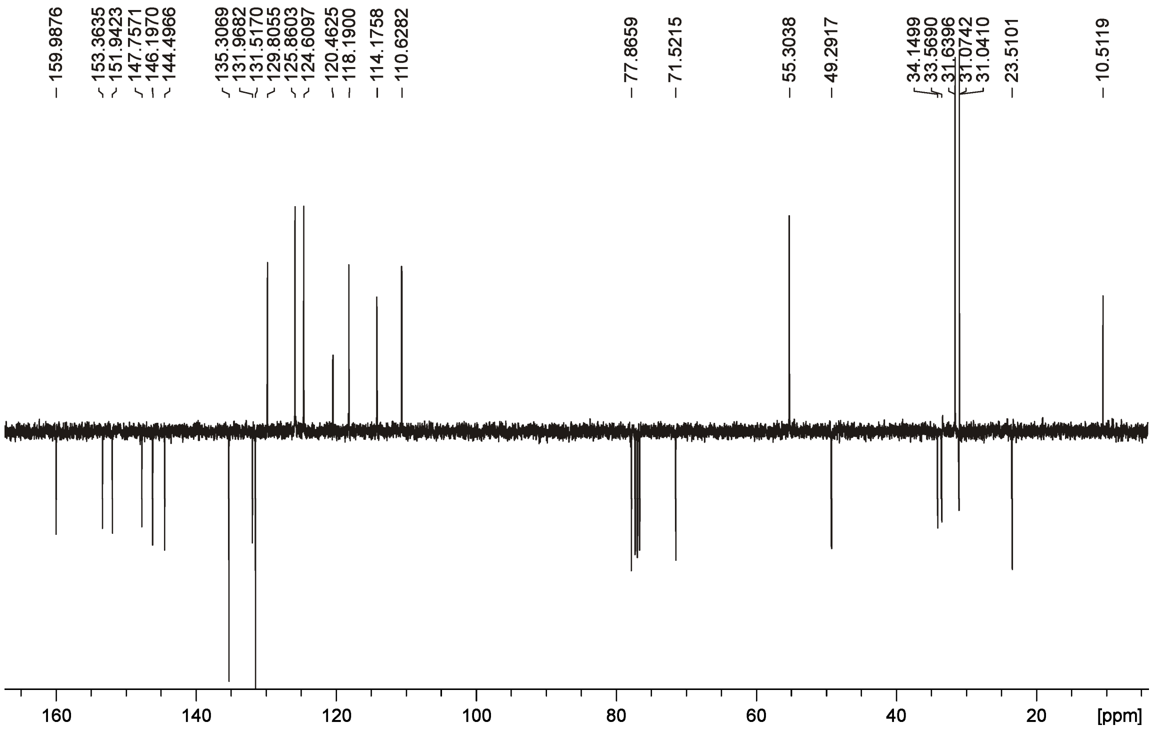


Figure S12. ^{13}C NMR spectrum (APT) of calixarene **3_2b** (100 MHz, CDCl$_3$).

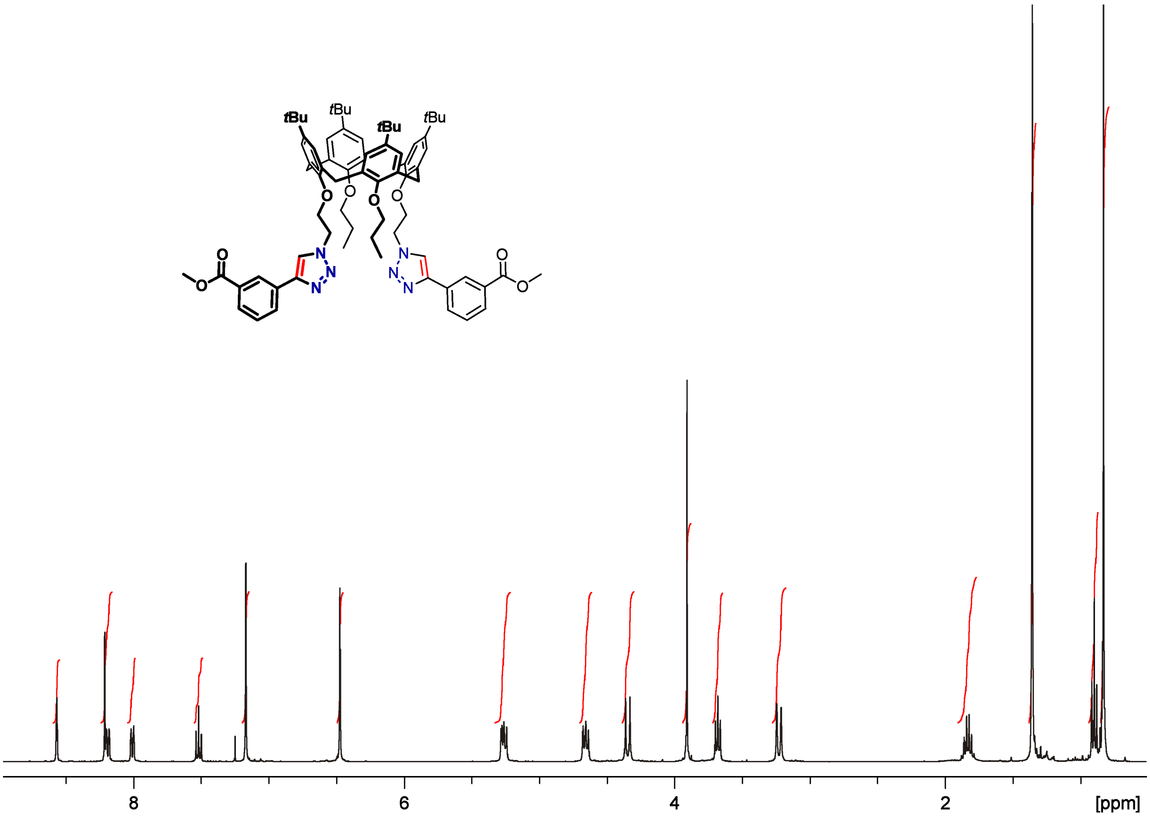


Figure S13. ^{1}H NMR spectrum of calixarene **3$_2$c** (400 MHz, CDCl$_3$).

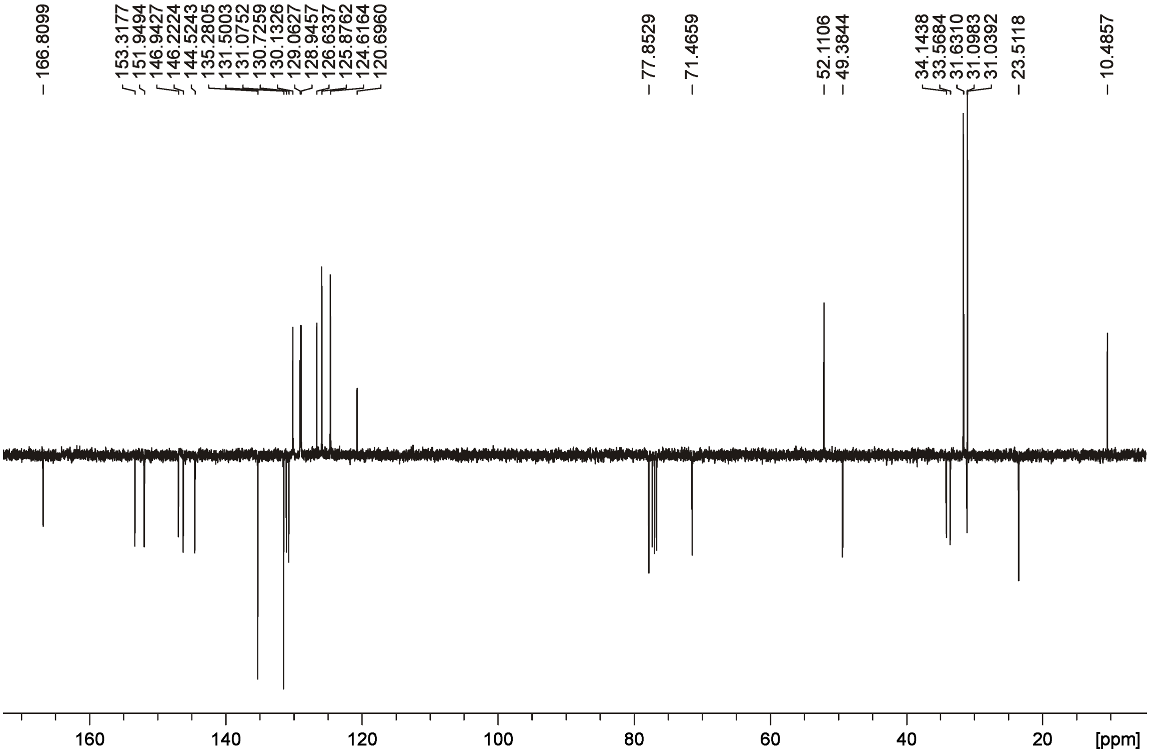


Figure S14. ^{13}C NMR spectrum (APT) of calixarene **3$_2$c** (100 MHz, CDCl$_3$).

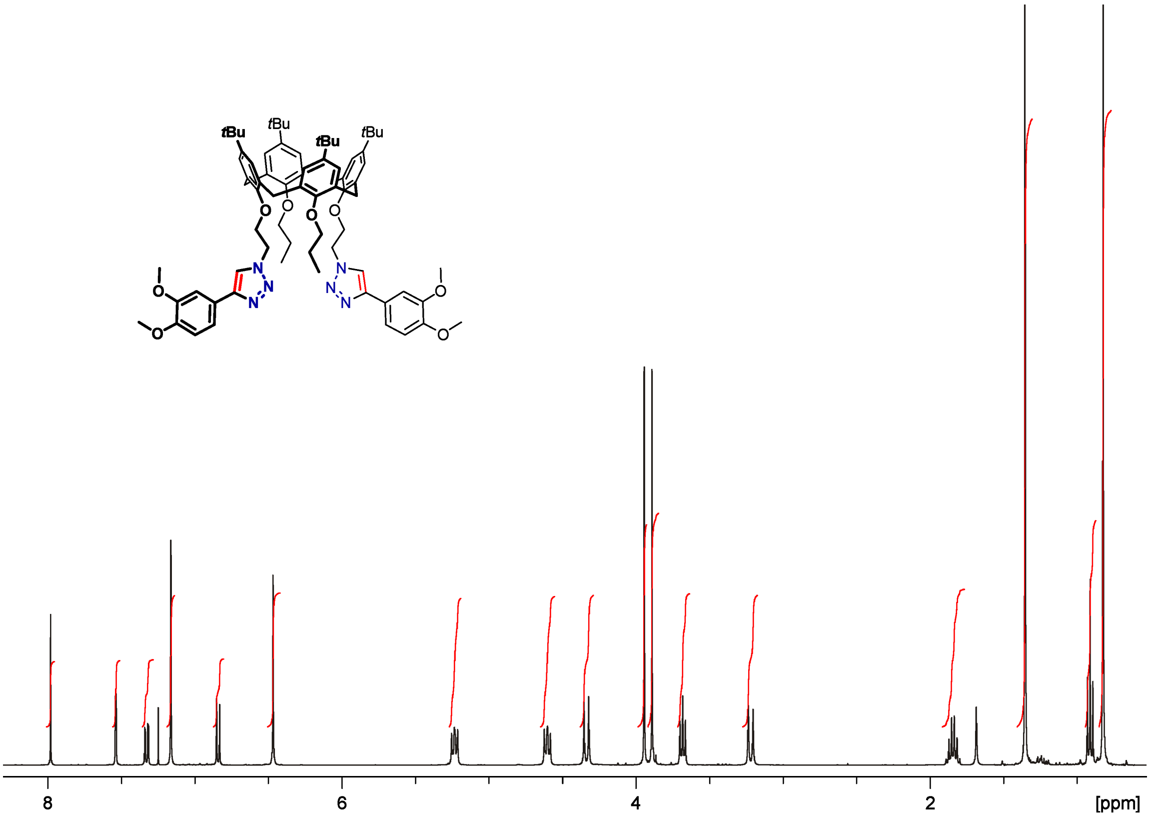


Figure S15. ^{1}H NMR spectrum of calixarene **3_2d** (400 MHz, CDCl$_3$).

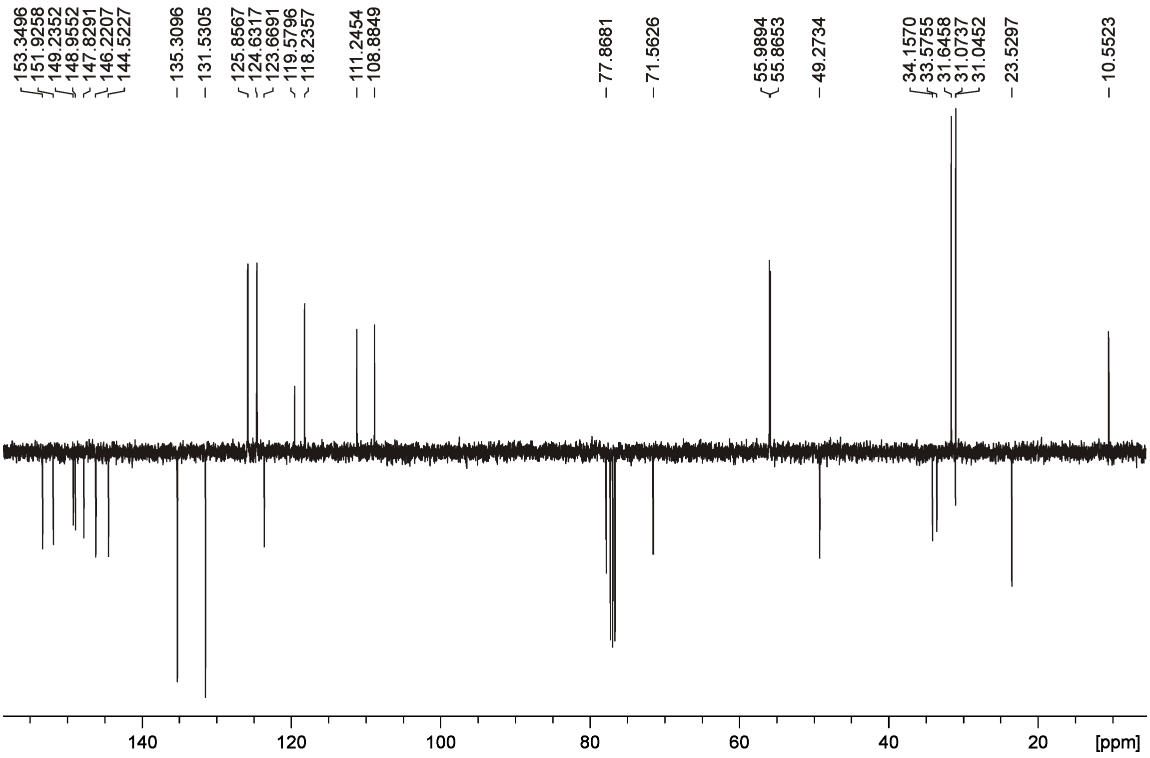


Figure S16. ^{13}C NMR spectrum (APT) of calixarene **3_2d** (100 MHz, CDCl$_3$).

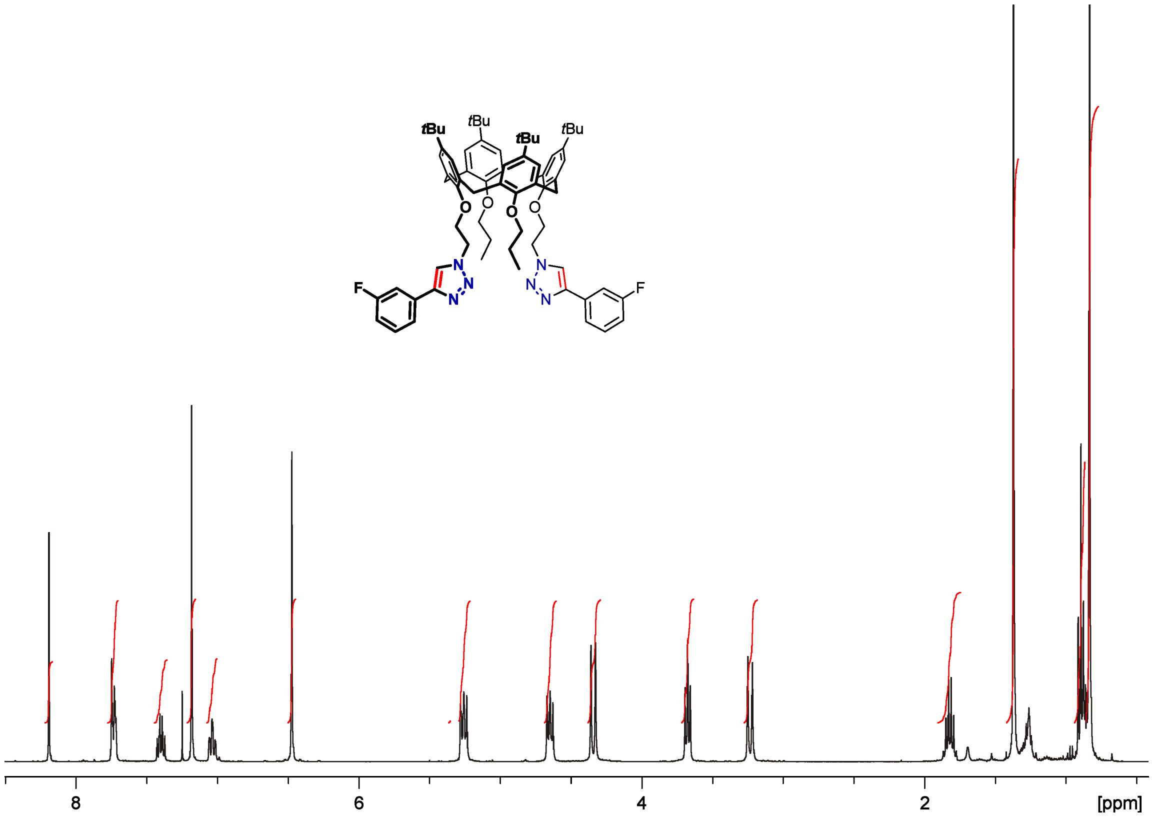


Figure S17. ^{1}H NMR spectrum of calixarene **3_2e** (400 MHz, CDCl$_3$).

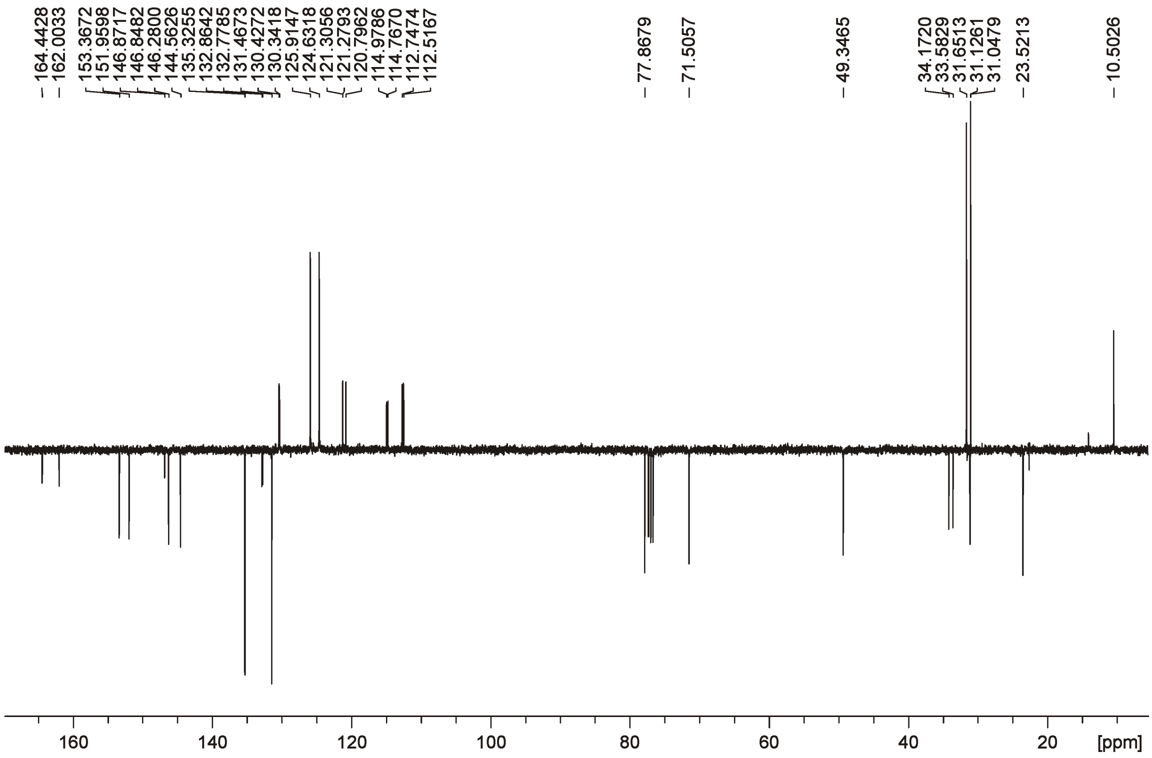


Figure S18. ^{13}C NMR spectrum (APT) of calixarene **3_2e** (100 MHz, CDCl$_3$).

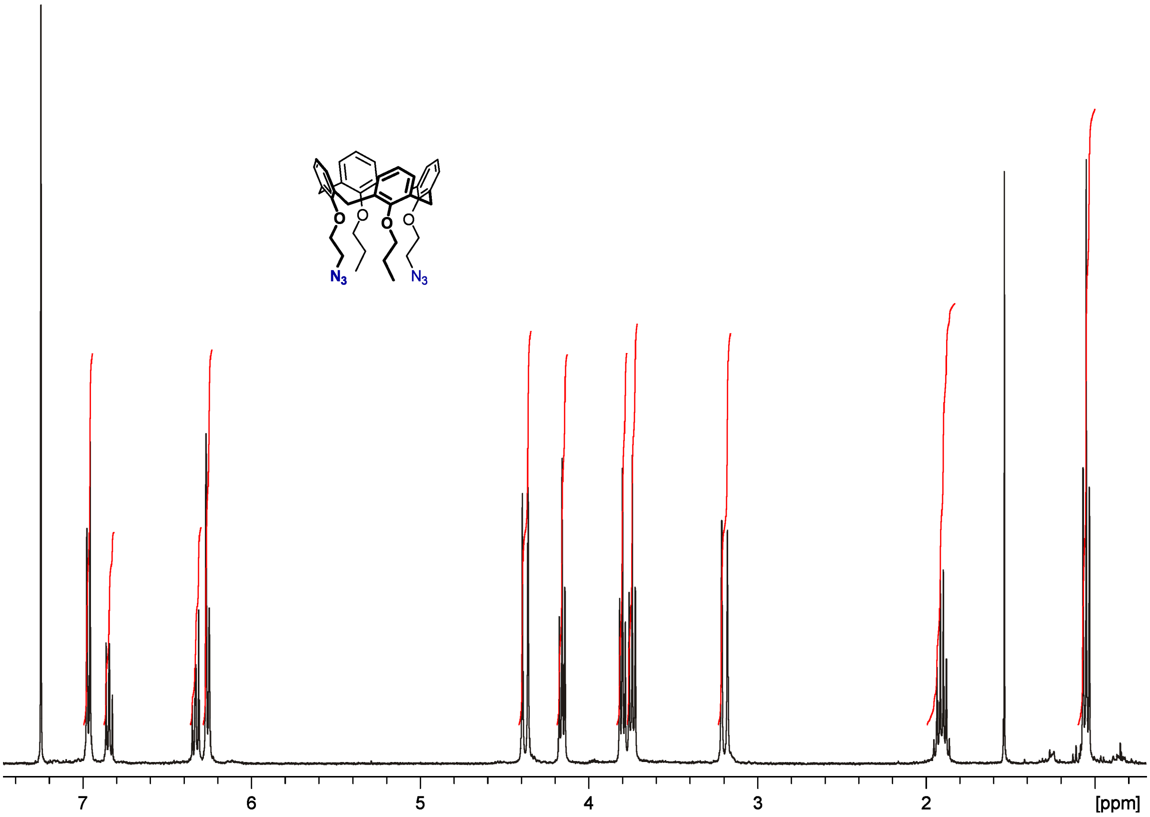


Figure S19. ^{1}H NMR spectrum of calixarene **s8** (400 MHz, $CDCl_3$).

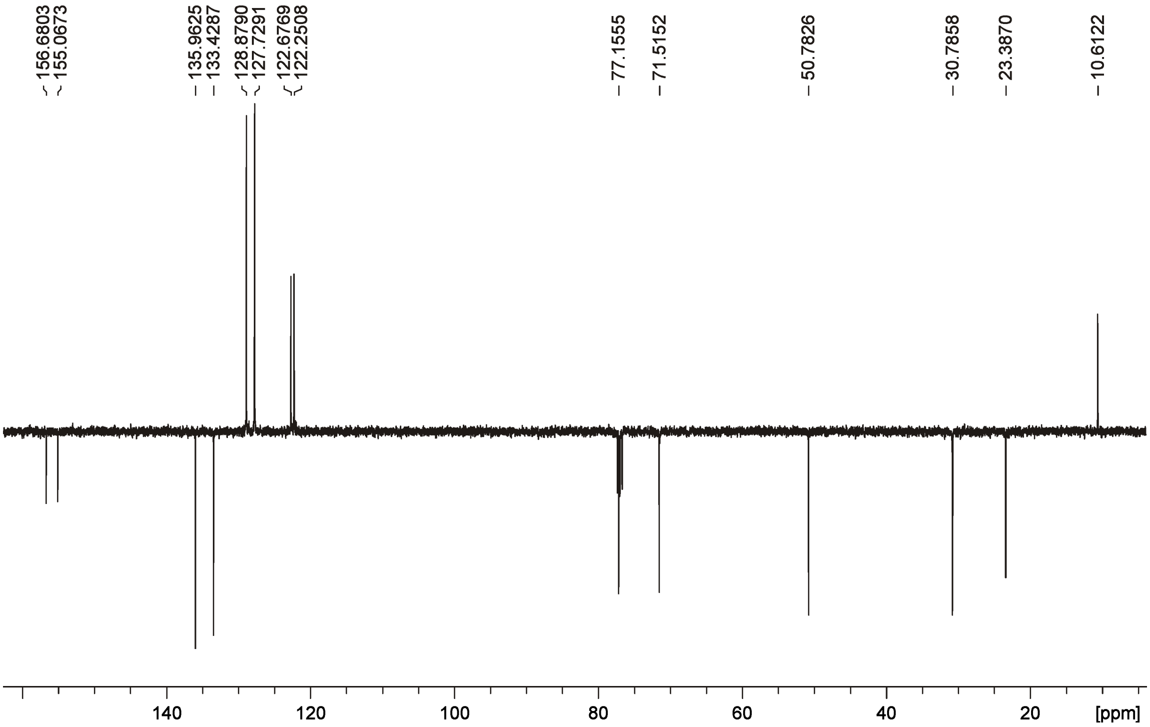


Figure S20. ^{13}C NMR spectrum (APT) of calixarene **s8** (100 MHz, $CDCl_3$).

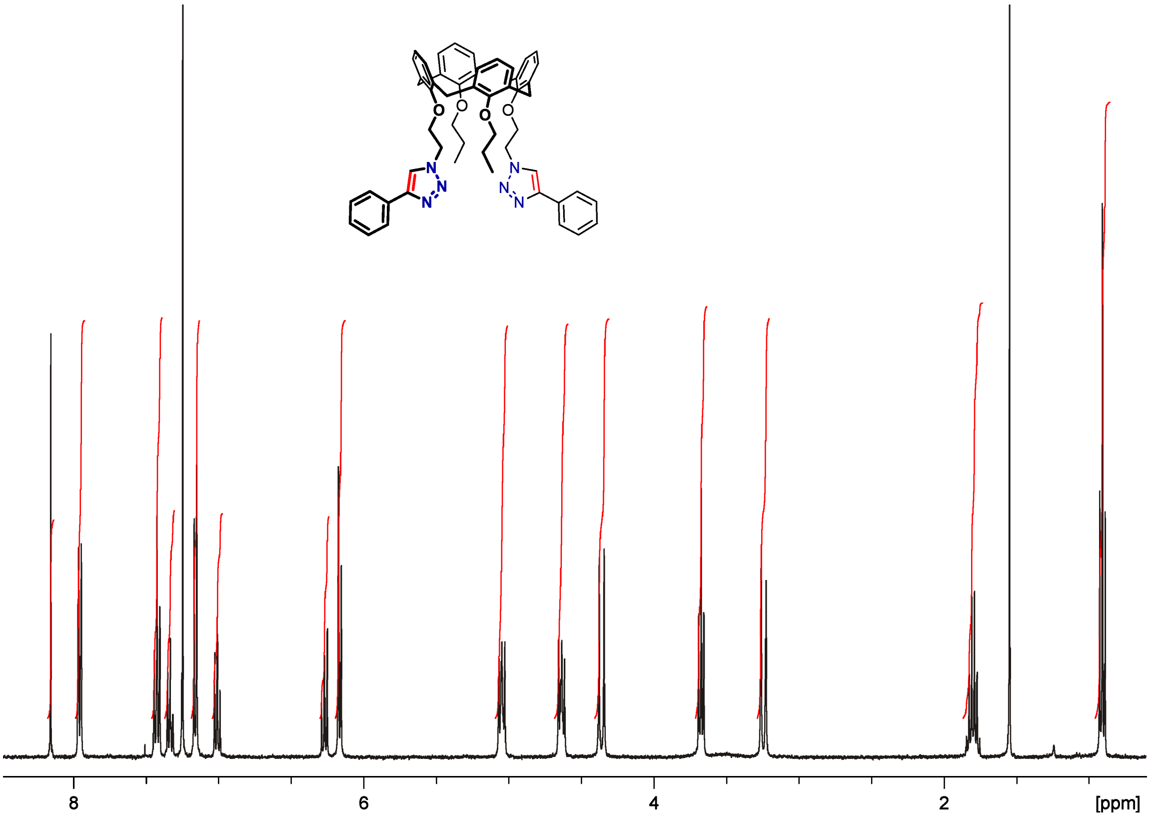


Figure S21. ^{1}H NMR spectrum of calixarene **3'$_2$a** (400 MHz, CDCl$_3$).

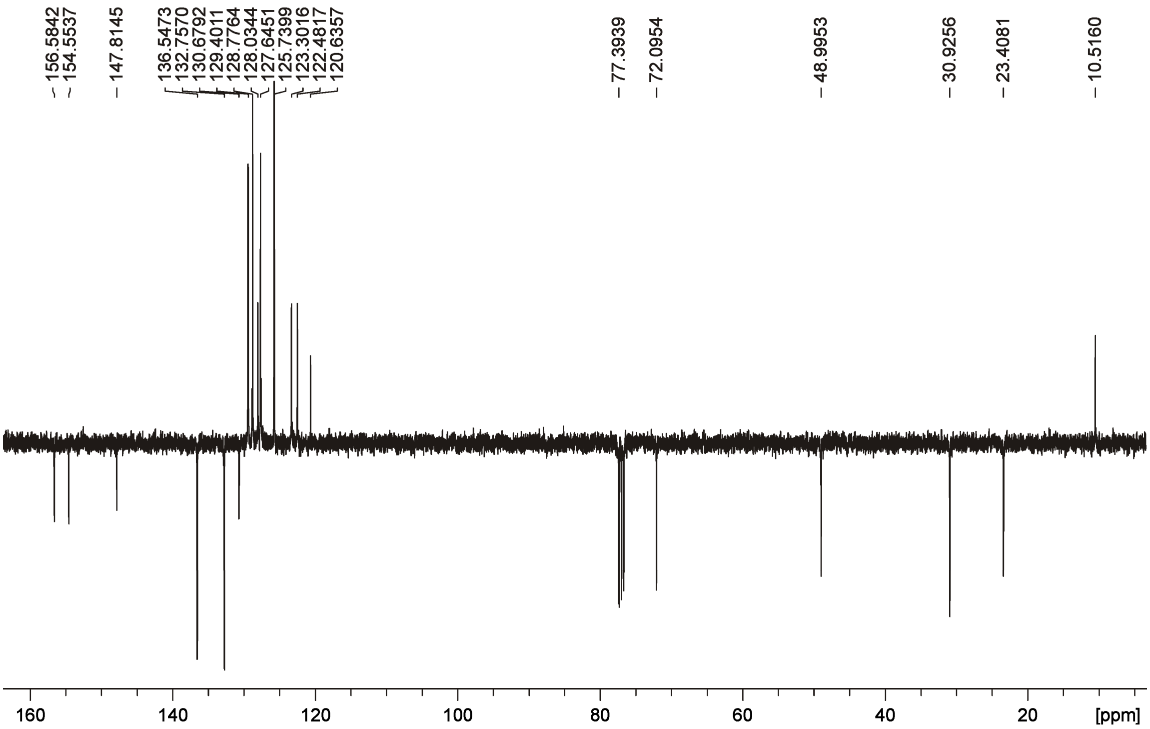


Figure S22. ^{13}C NMR spectrum (APT) of calixarene **3'$_2$a** (100 MHz, CDCl$_3$).

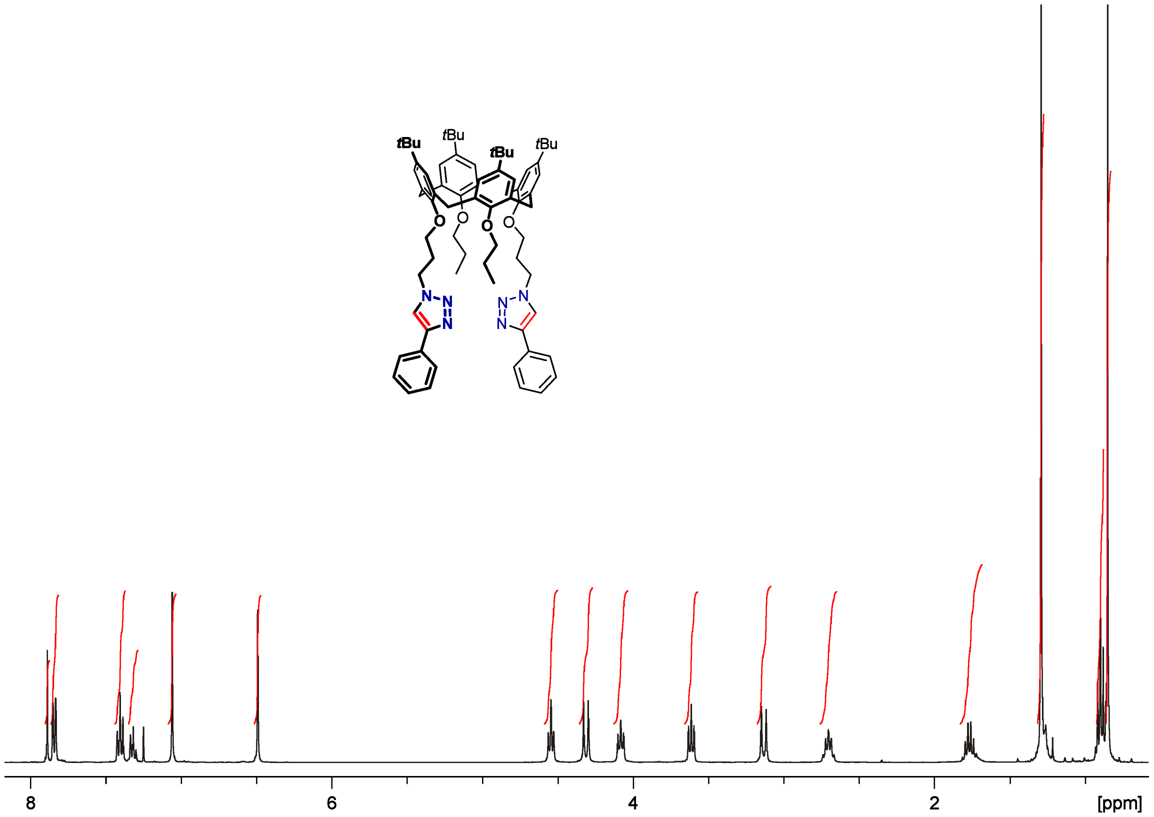


Figure S23. ^{1}H NMR spectrum of calixarene **3_3a** (400 MHz, $CDCl_3$).

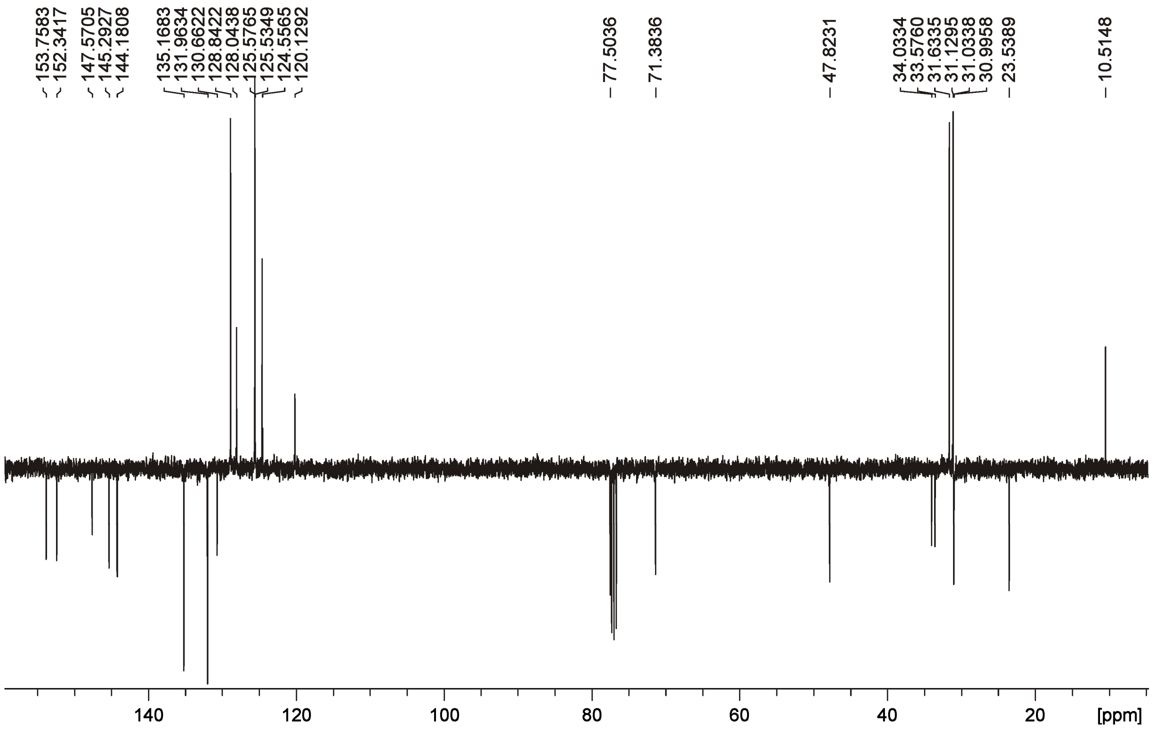


Figure S24. ^{13}C NMR spectrum (APT) of calixarene **3_3a** (100 MHz, $CDCl_3$).

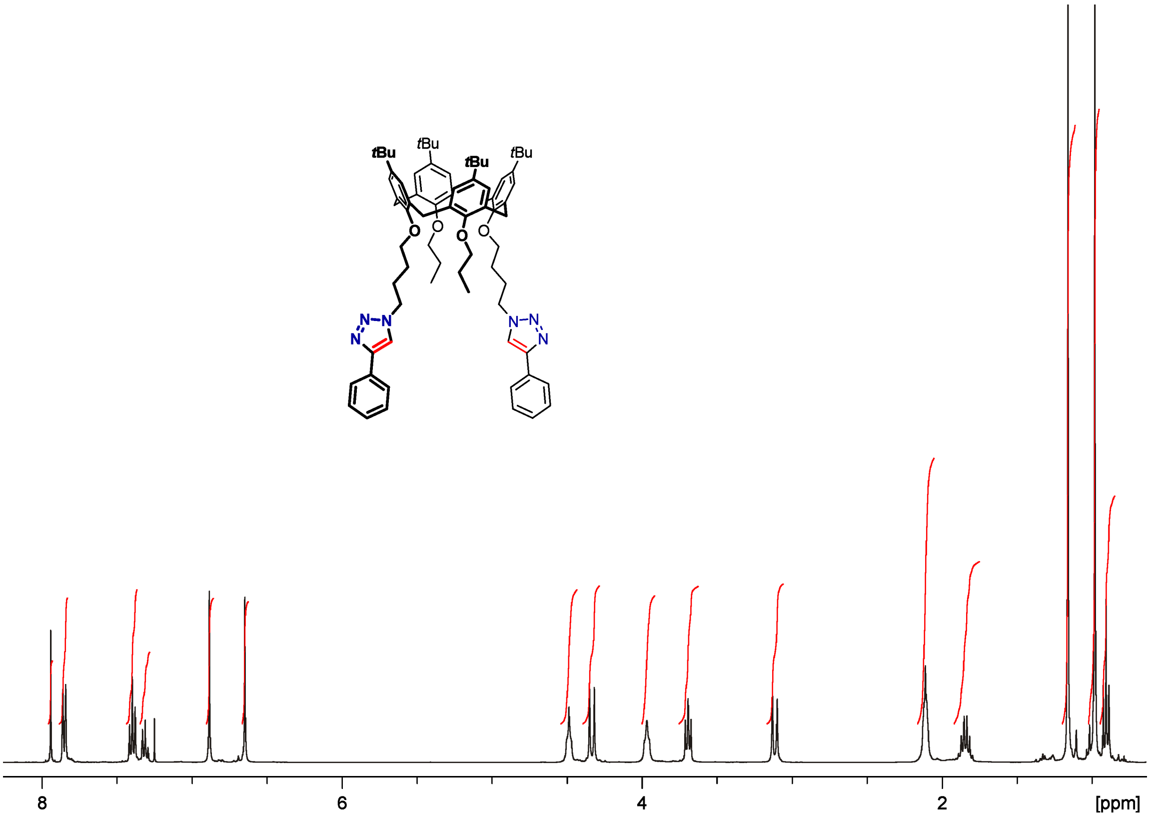


Figure S25. ^{1}H NMR spectrum of calixarene **3$_4$a** (400 MHz, CDCl$_3$).

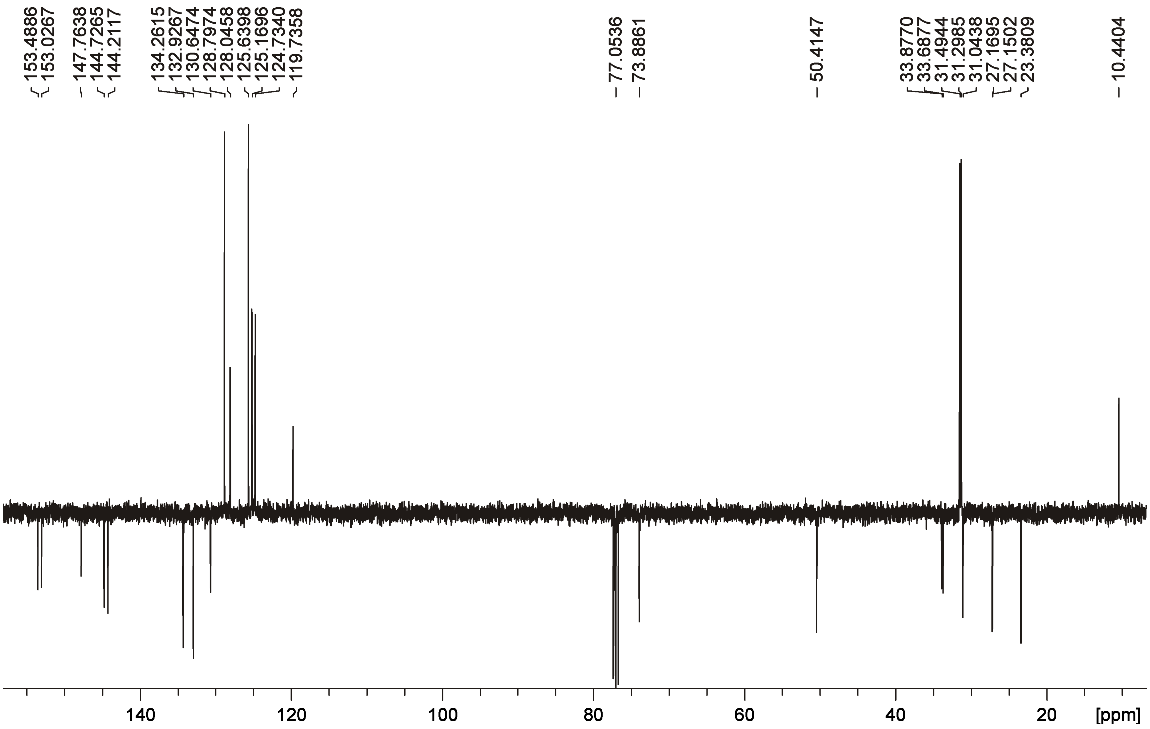


Figure S26. ^{13}C NMR spectrum (APT) of calixarene **3$_4$a** (100 MHz, CDCl$_3$).

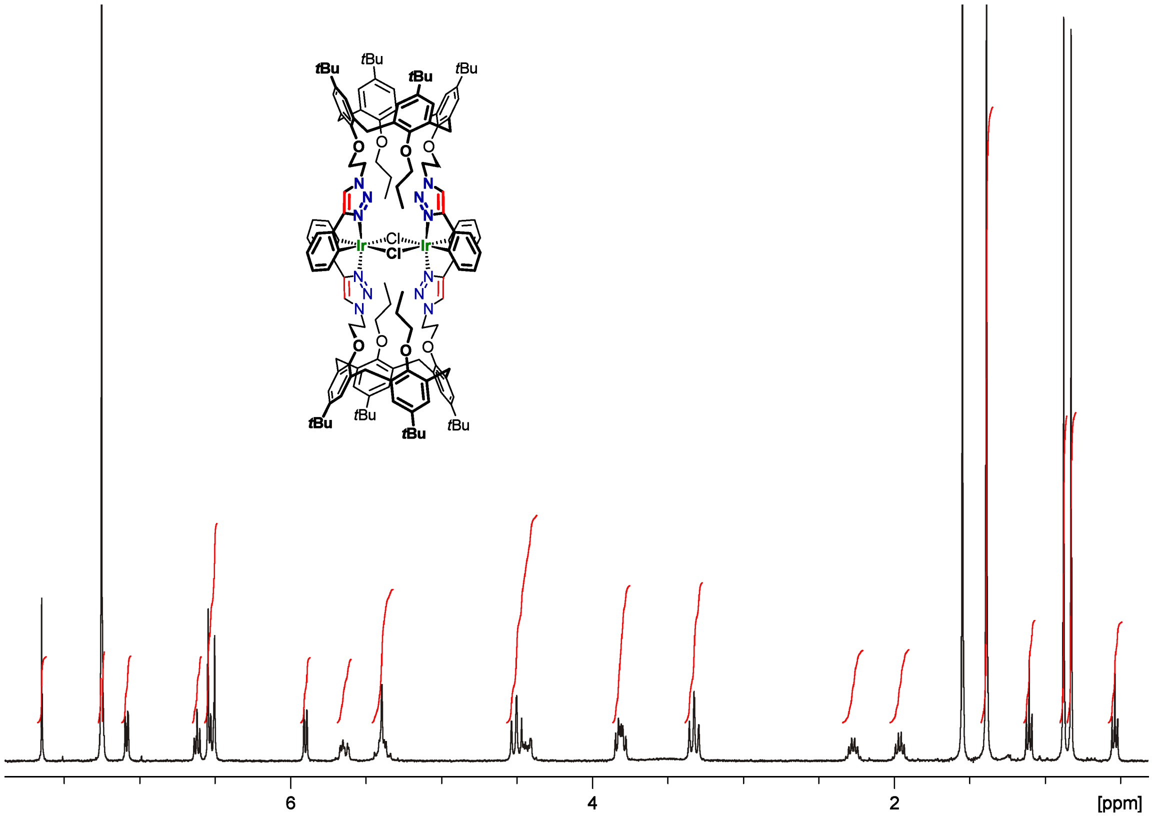


Figure S27. ^{1}H NMR spectrum of complex **4a** (400 MHz, CDCl$_3$).

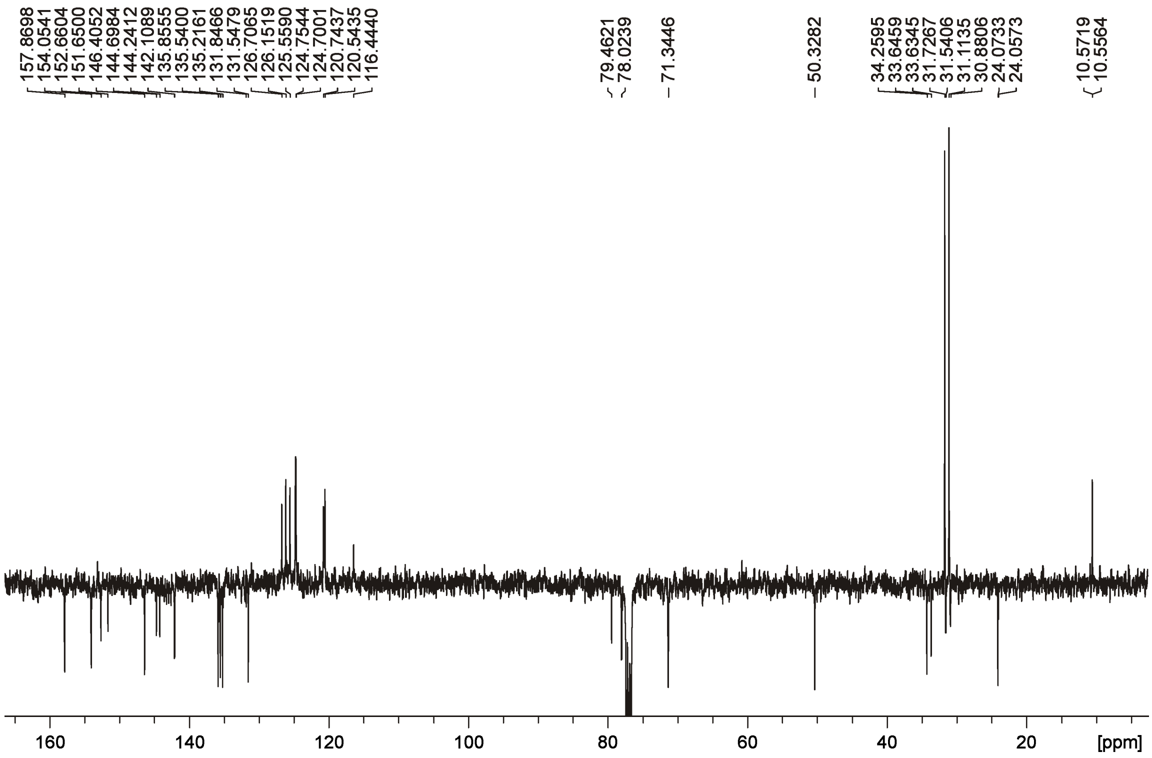


Figure S28. ^{13}C NMR spectrum (APT) of complex **4a** (100 MHz, CDCl$_3$).

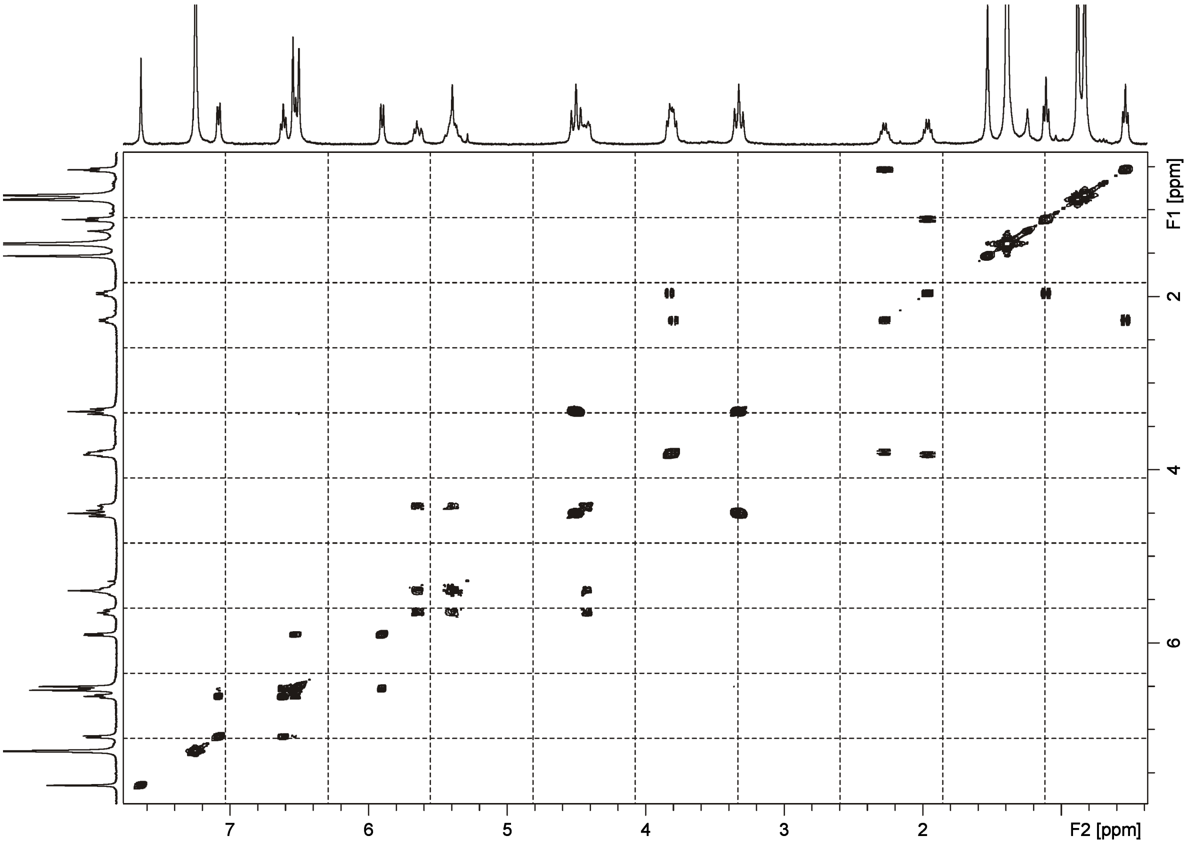


Figure S29. ^{1}H–^{1}H COSY spectrum of complex **4a** (400 MHz, CDCl$_3$).

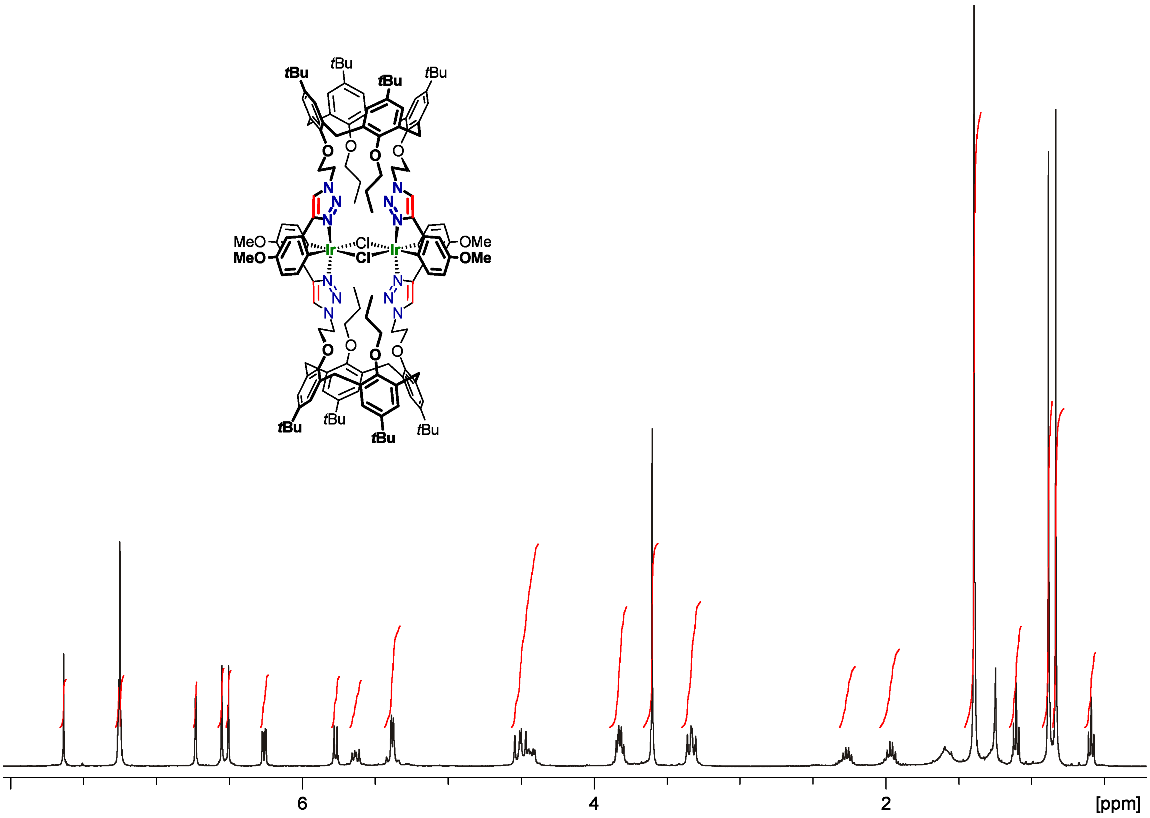


Figure S30. ^{1}H NMR spectrum of complex **4b** (400 MHz, CDCl$_3$).

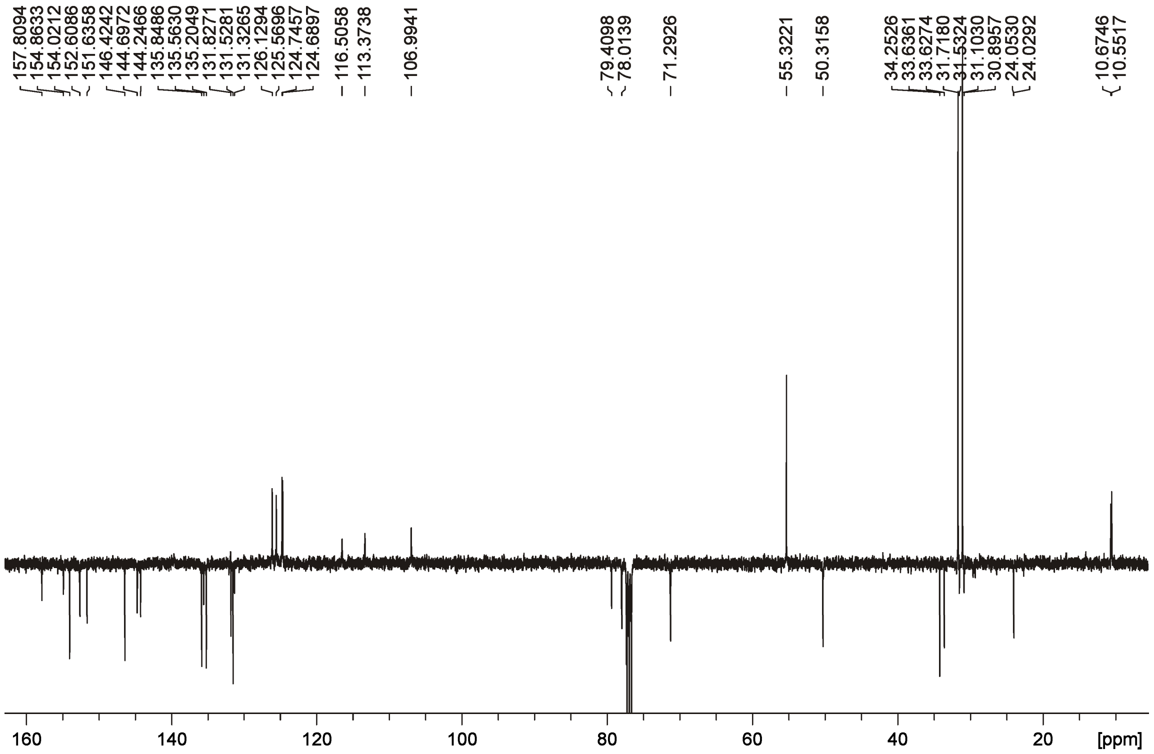


Figure S31. ^{13}C NMR spectrum (APT) of complex **4b** (100 MHz, CDCl$_3$).

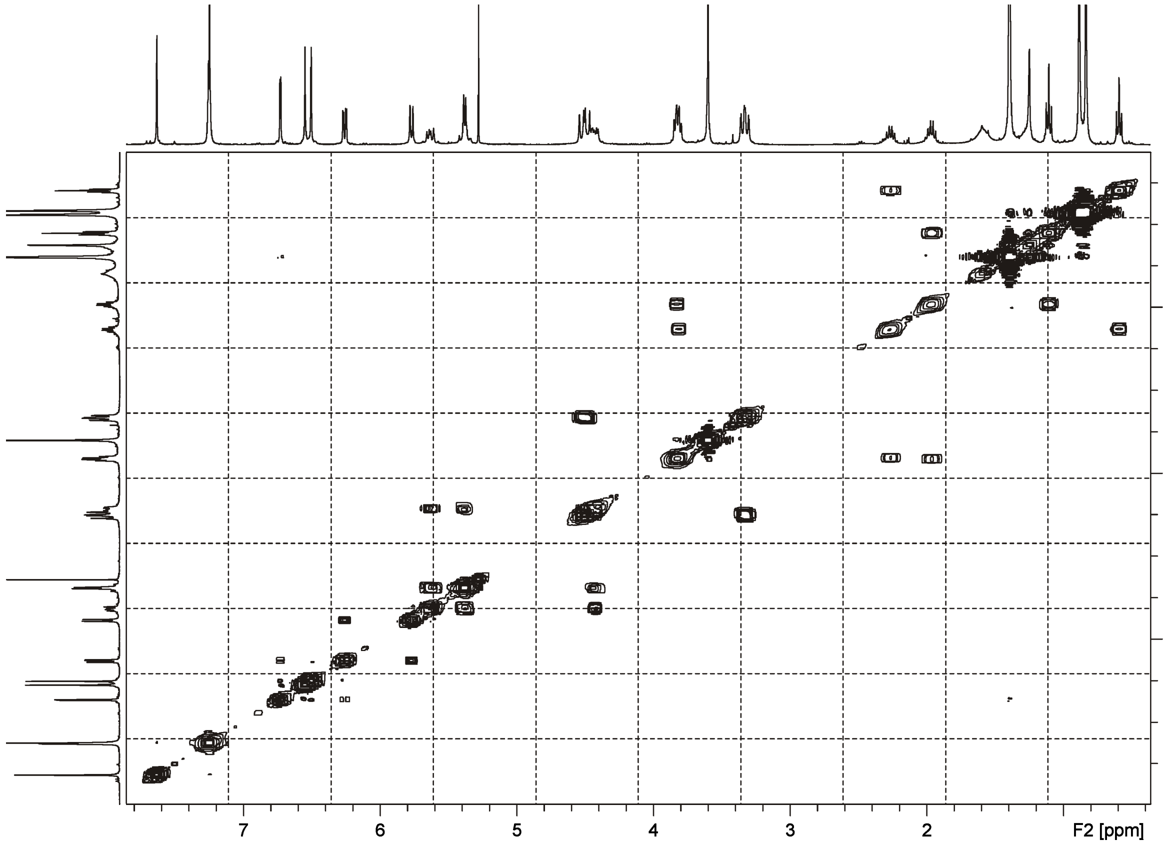


Figure S32. ^{1}H–^{1}H COSY spectrum of complex **4b** (400 MHz, CDCl$_3$).

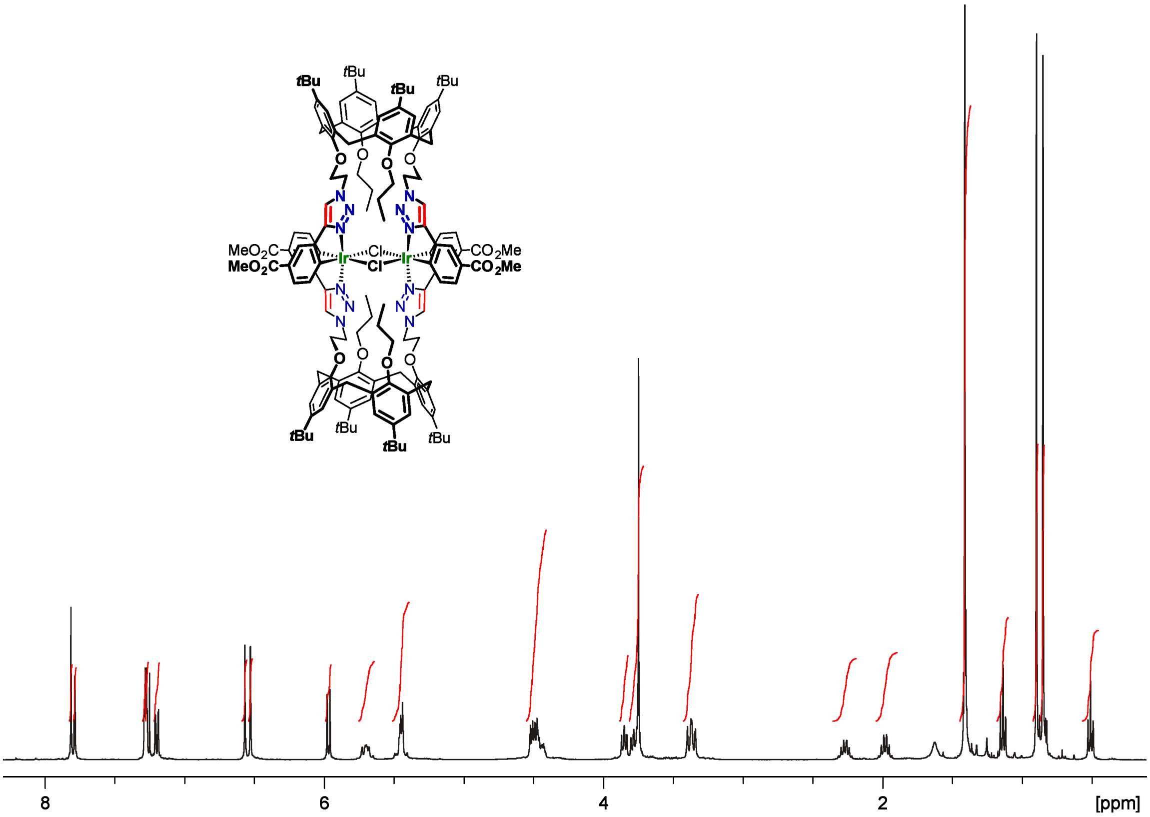


Figure S33. ^{1}H NMR spectrum of complex **4c** (400 MHz, $CDCl_3$).

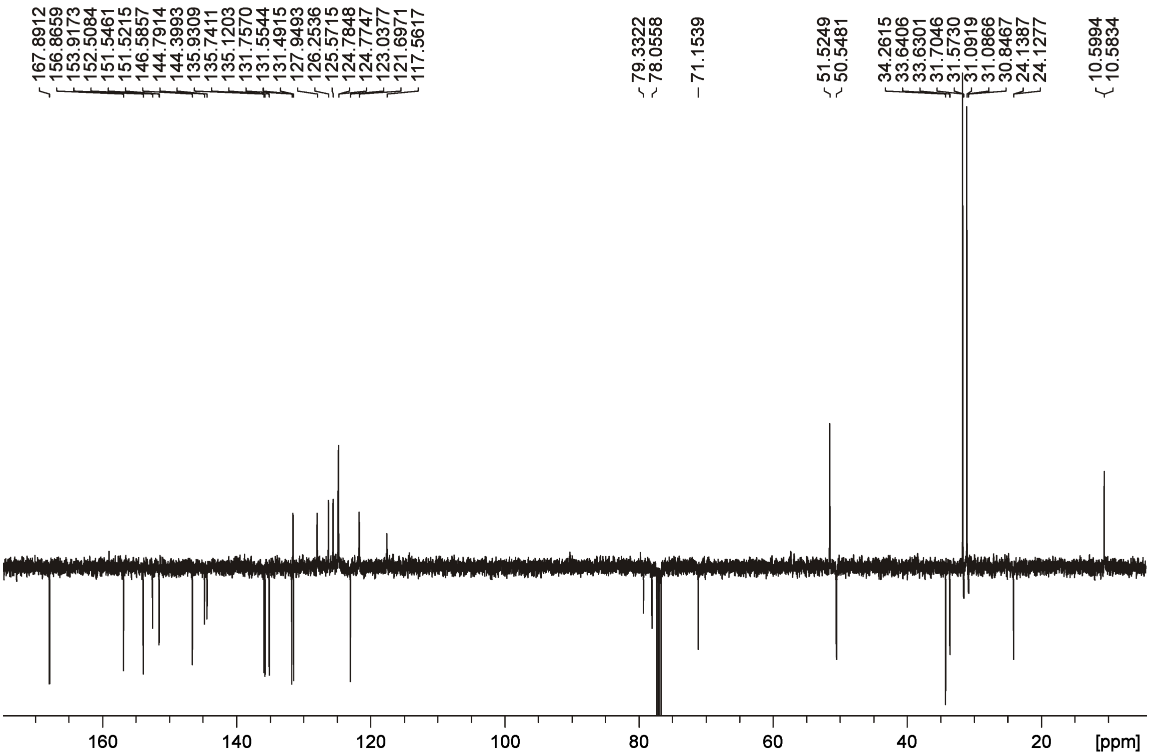


Figure S34. ^{13}C NMR spectrum (APT) of complex **4c** (100 MHz, $CDCl_3$).

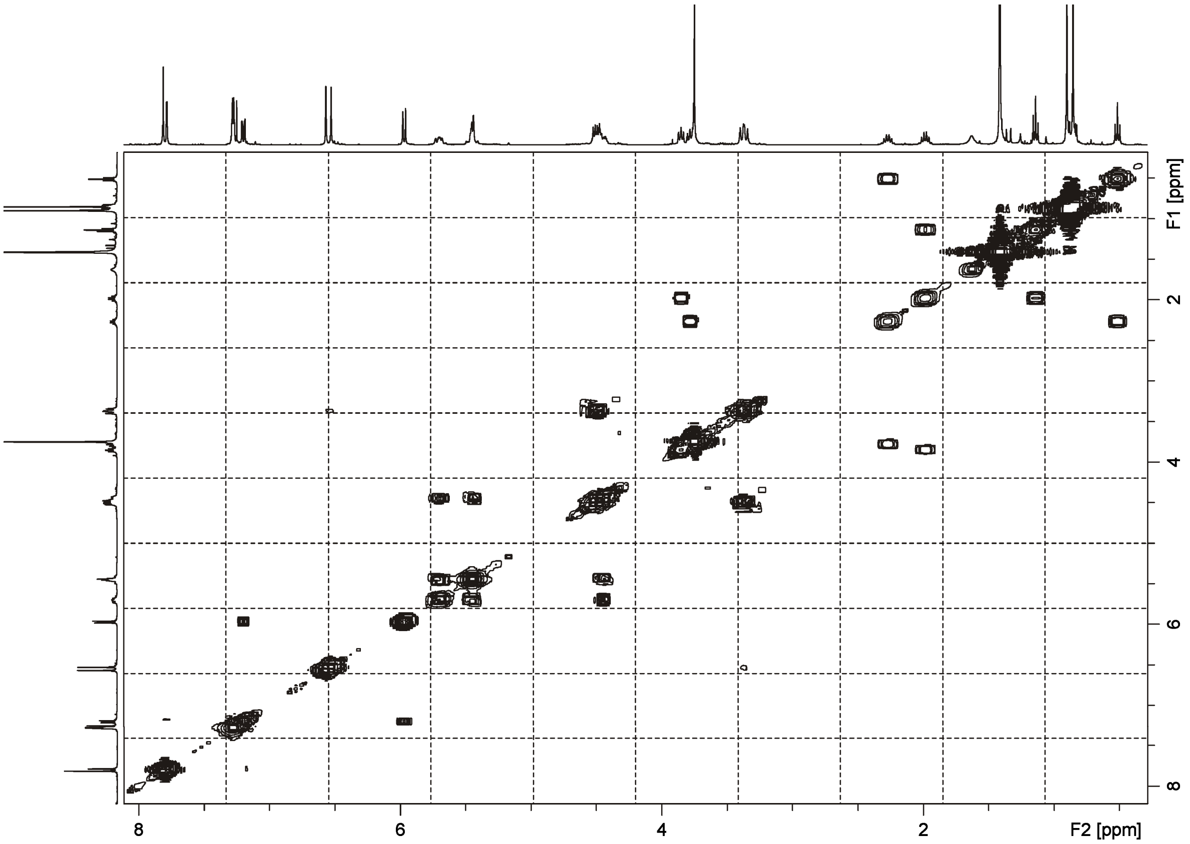


Figure S35. ^{1}H–^{1}H COSY spectrum of complex **4c** (400 MHz, $CDCl_3$).

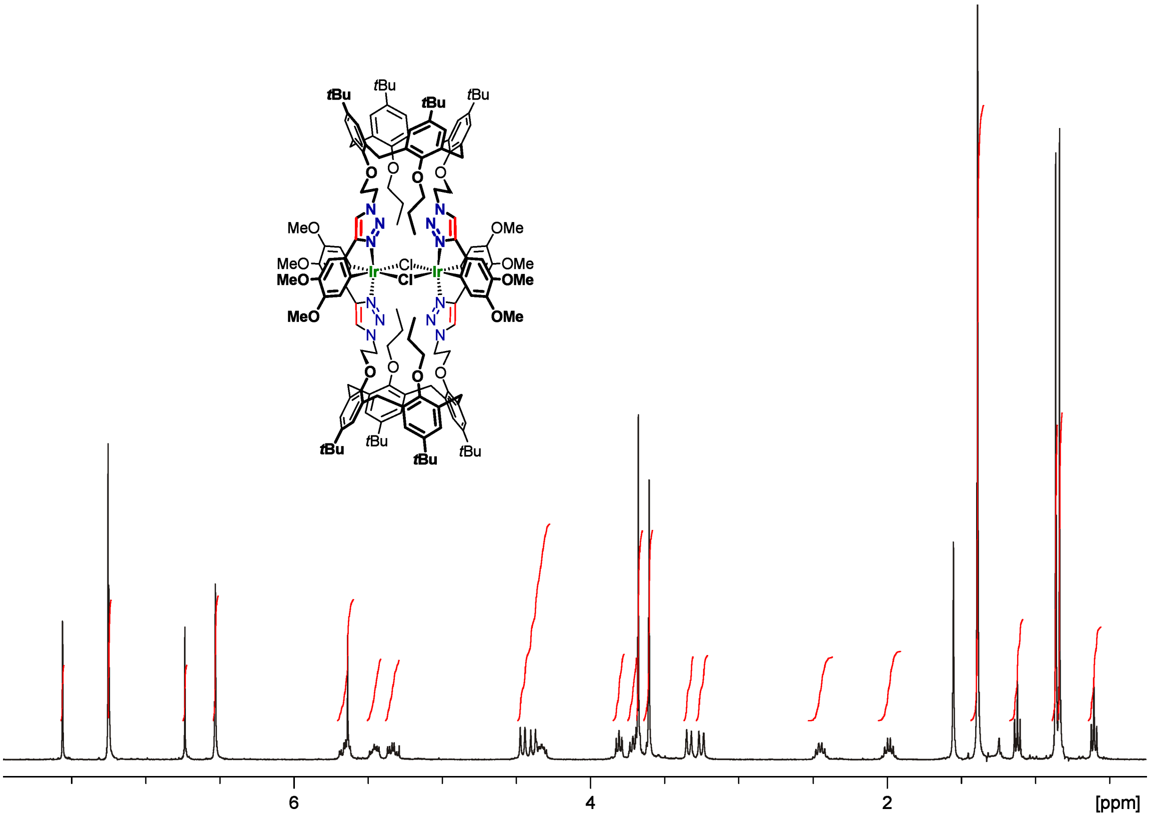


Figure S36. ^{1}H NMR spectrum of complex **4d** (400 MHz, $CDCl_3$).

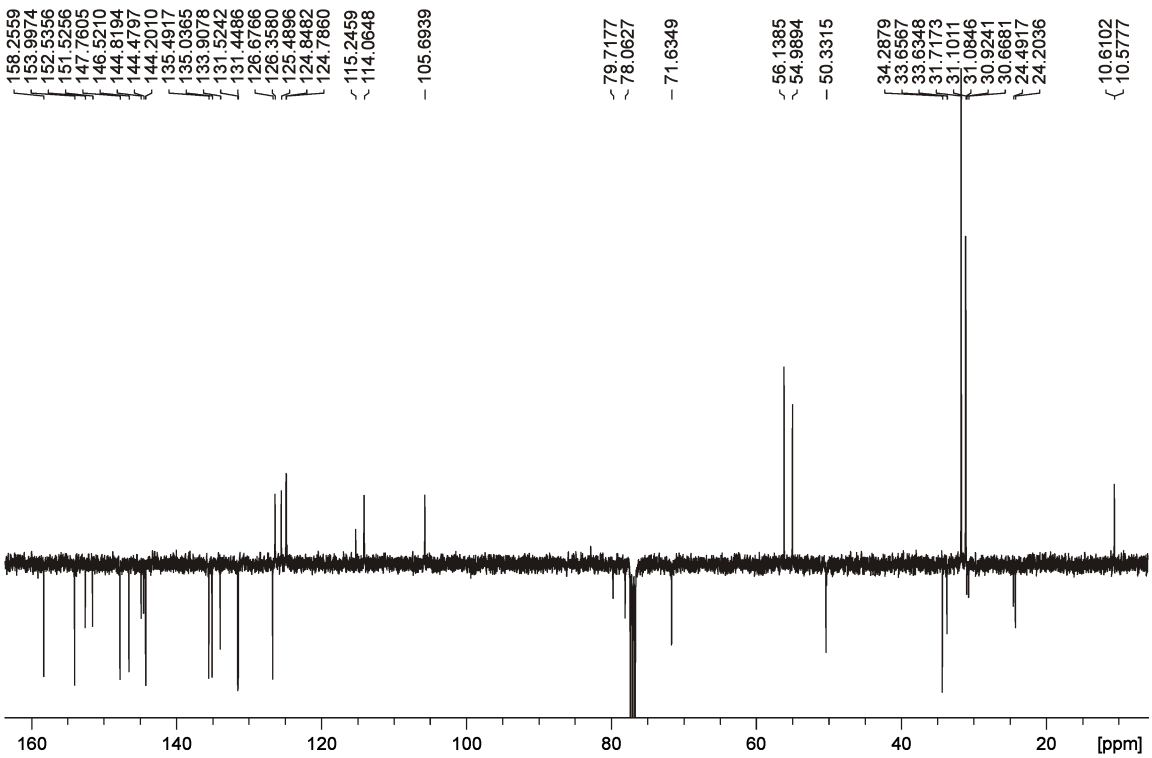


Figure S37. ^{13}C NMR spectrum (APT) of complex **4d** (100 MHz, $CDCl_3$).

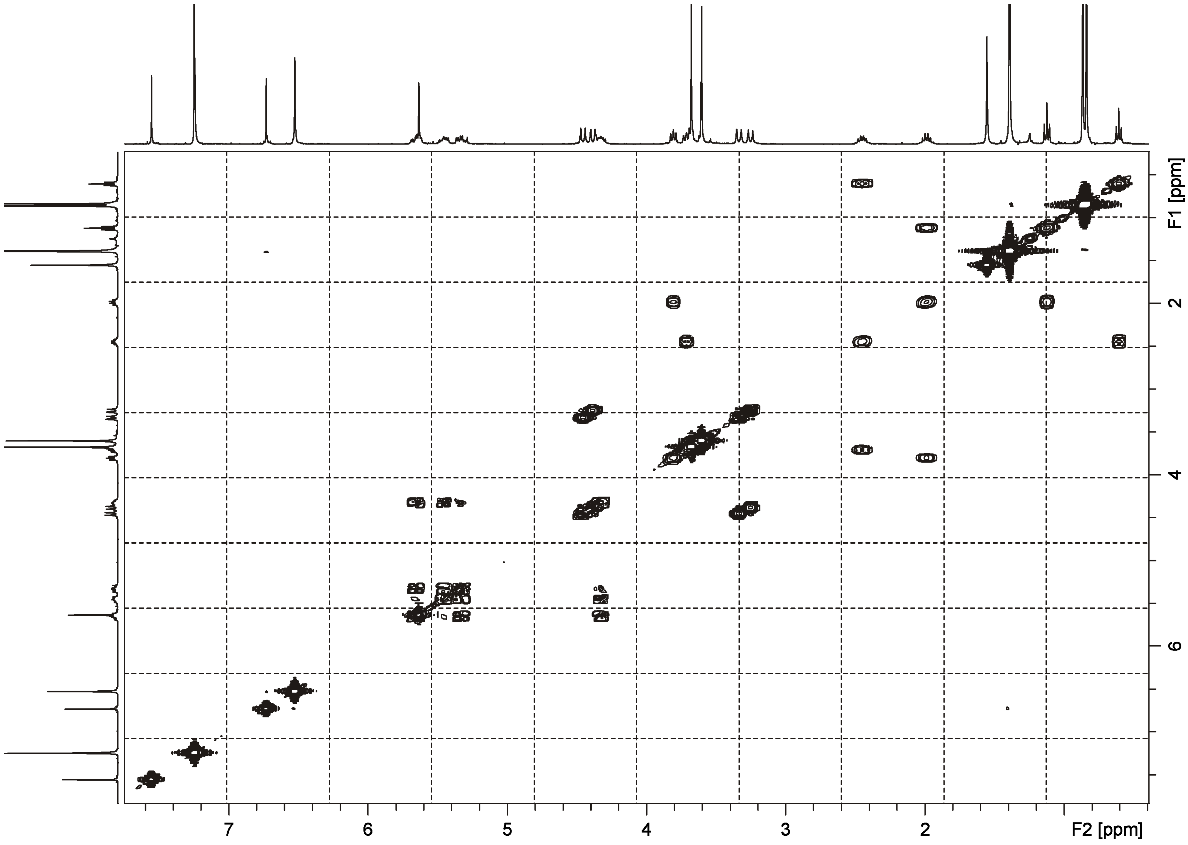


Figure S38. ^{1}H–^{1}H COSY spectrum of complex **4d** (400 MHz, $CDCl_3$).

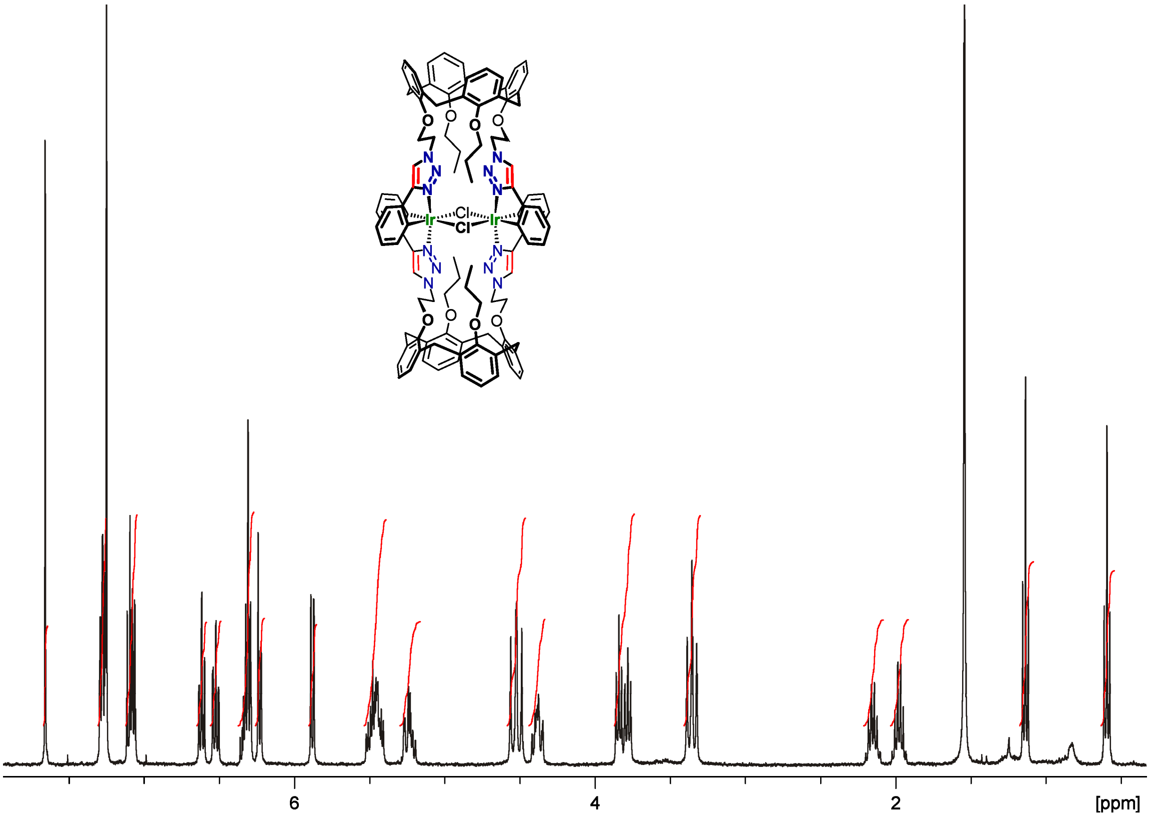


Figure S39. ^{1}H NMR spectrum of complex **4'a** (400 MHz, $CDCl_3$).

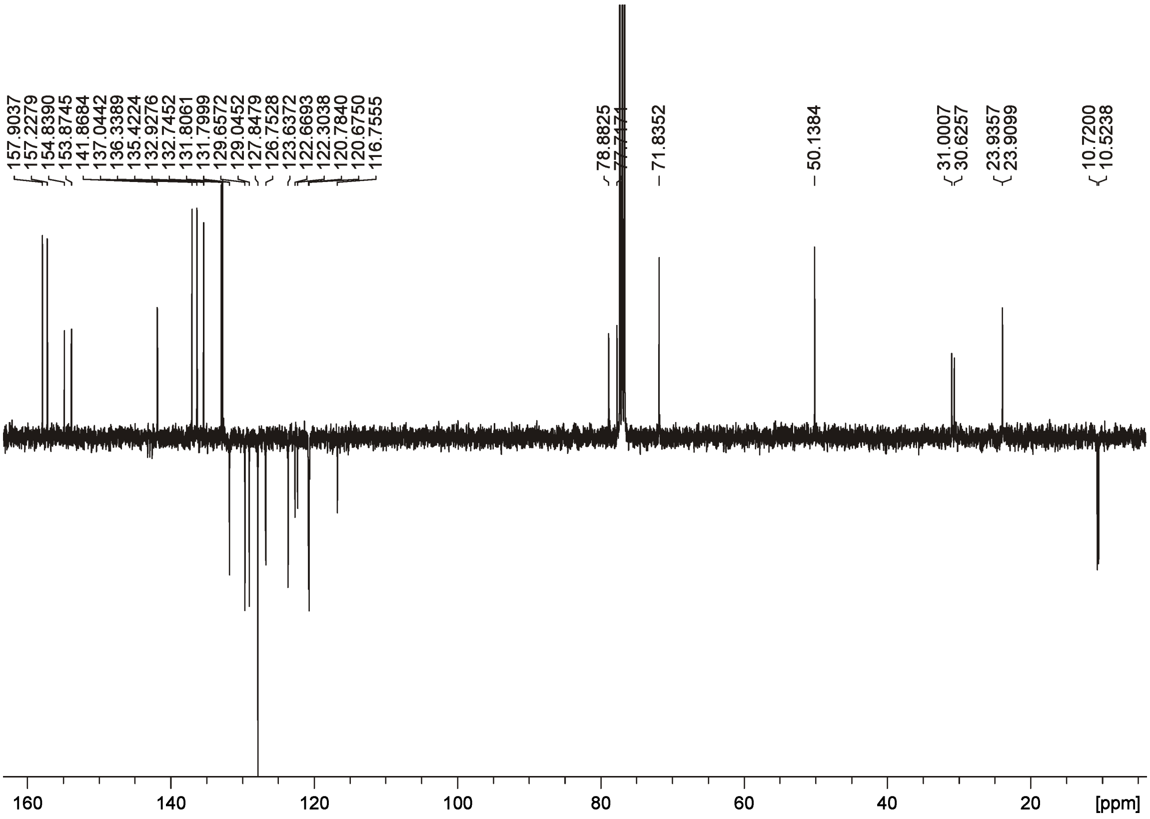


Figure S40. ^{13}C NMR spectrum (APT) of complex **4'a** (100 MHz, $CDCl_3$).

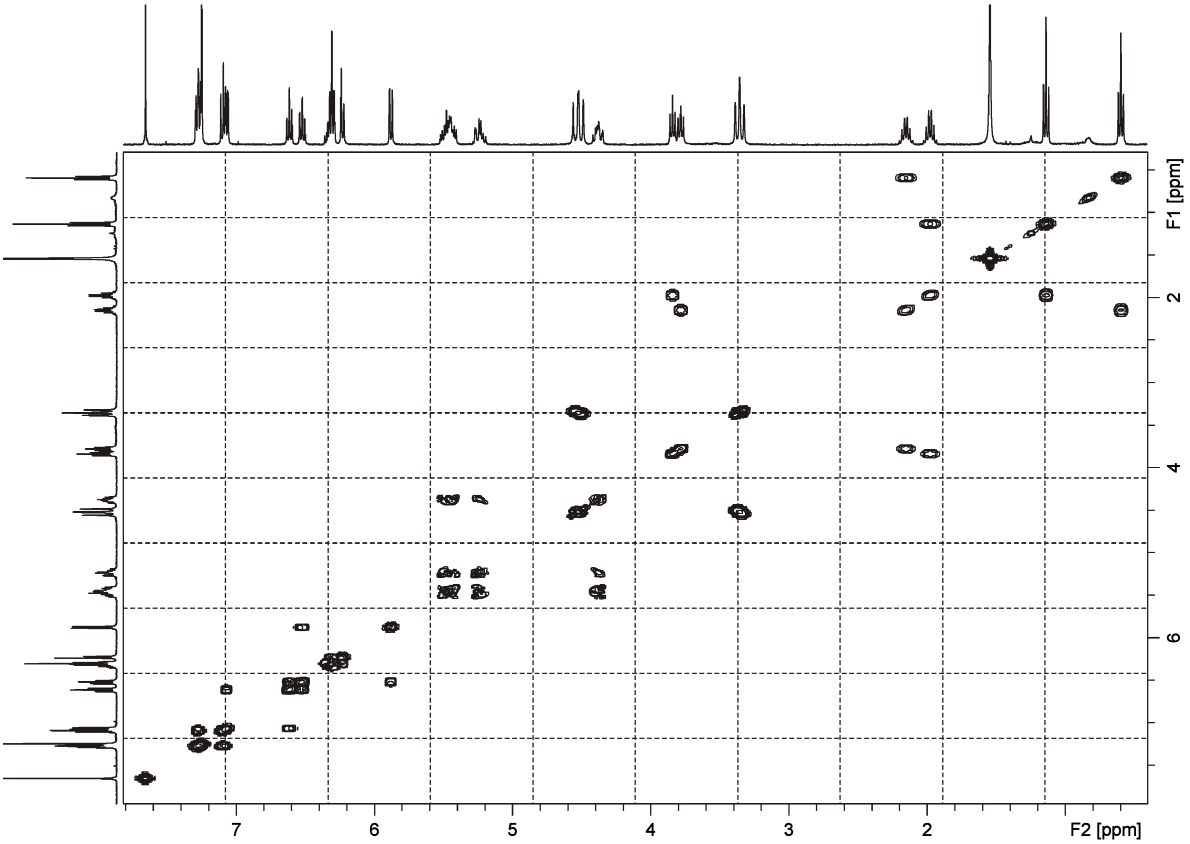


Figure S41. ^1H–^1H COSY spectrum of complex **4'a** (400 MHz, $CDCl_3$).

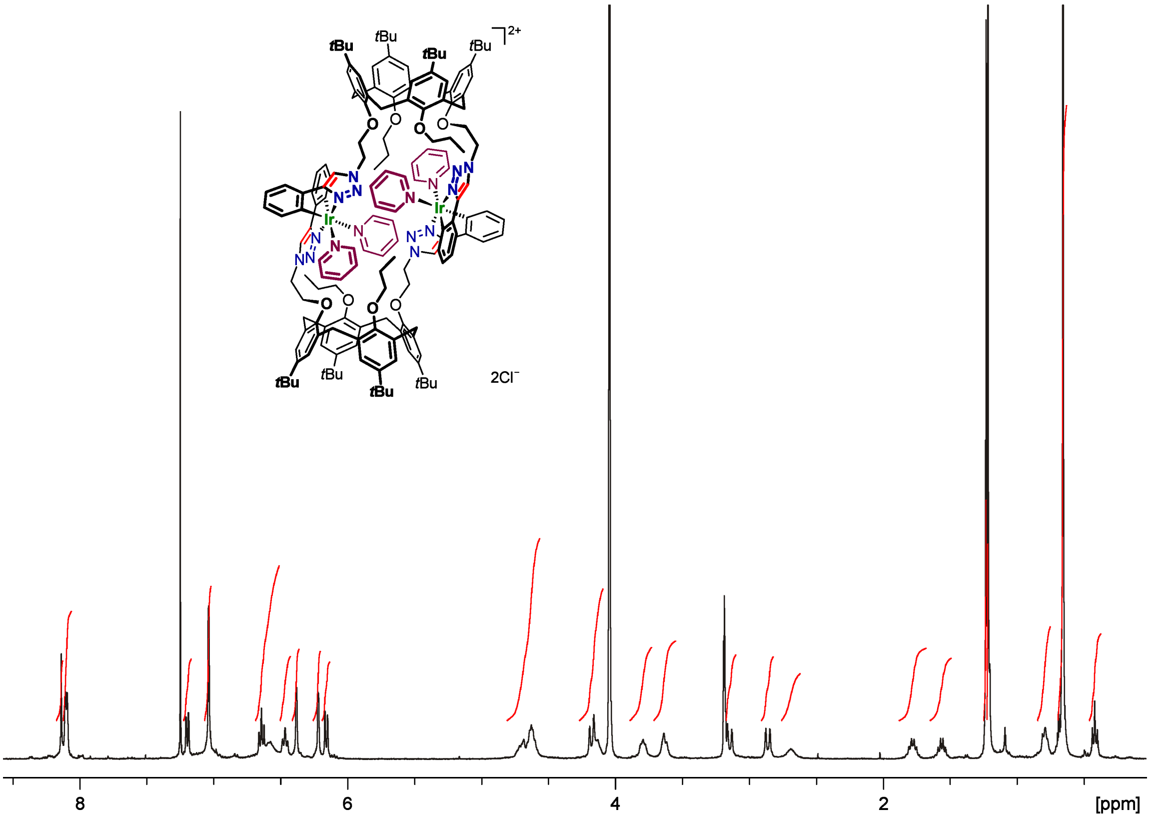


Figure S42. ^1H NMR spectrum of complex **5** (400 MHz, $CDCl_3$+CD_3OD (4:1)).

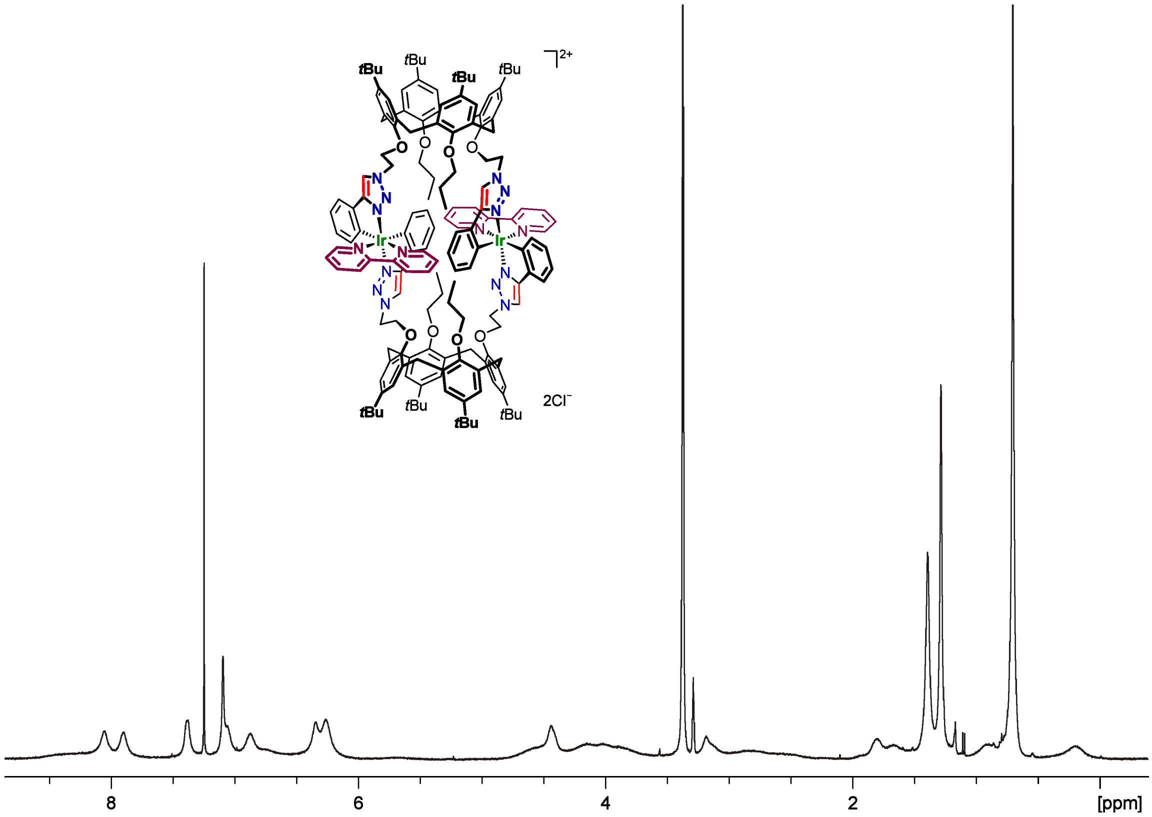


Figure S43. ^{1}H NMR spectrum of complex **6** (400 MHz, $CDCl_3$+CD_3OD (10:1)).

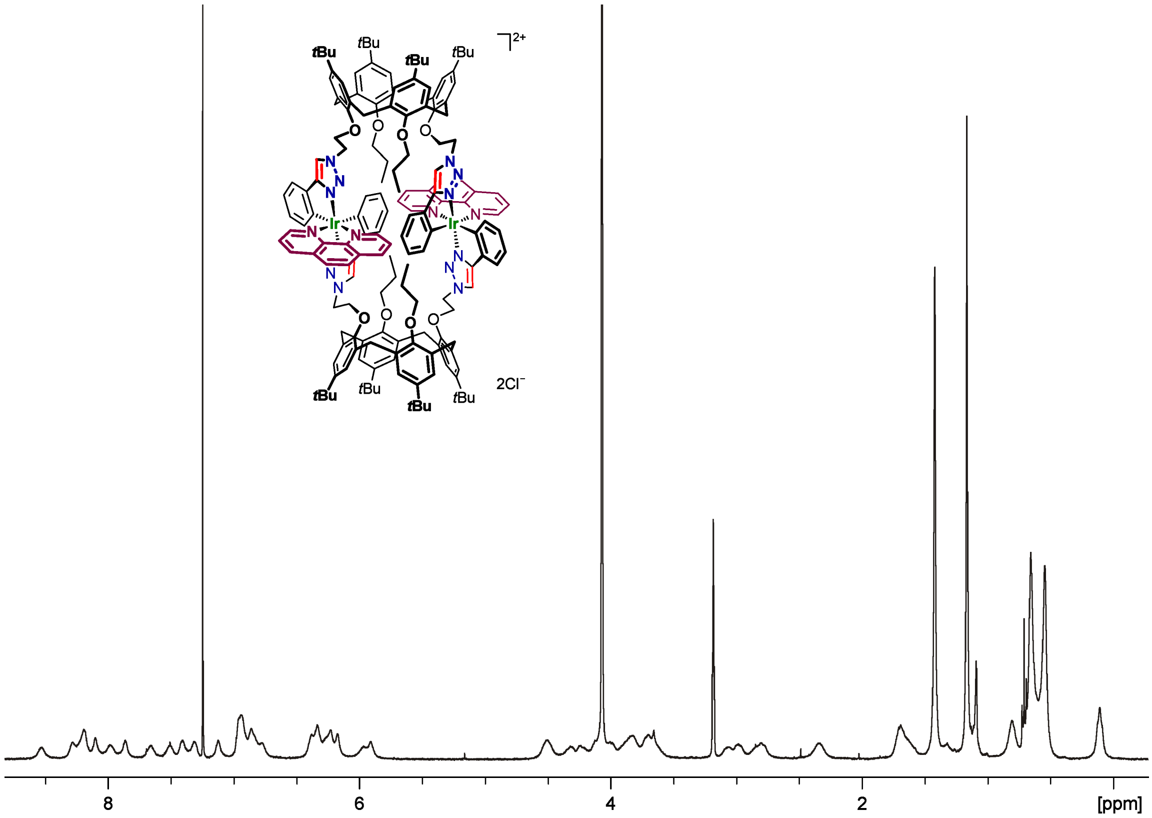


Figure S44. ^{1}H NMR spectrum of complex **7** (400 MHz, $CDCl_3$+CD_3OD (4:1)).

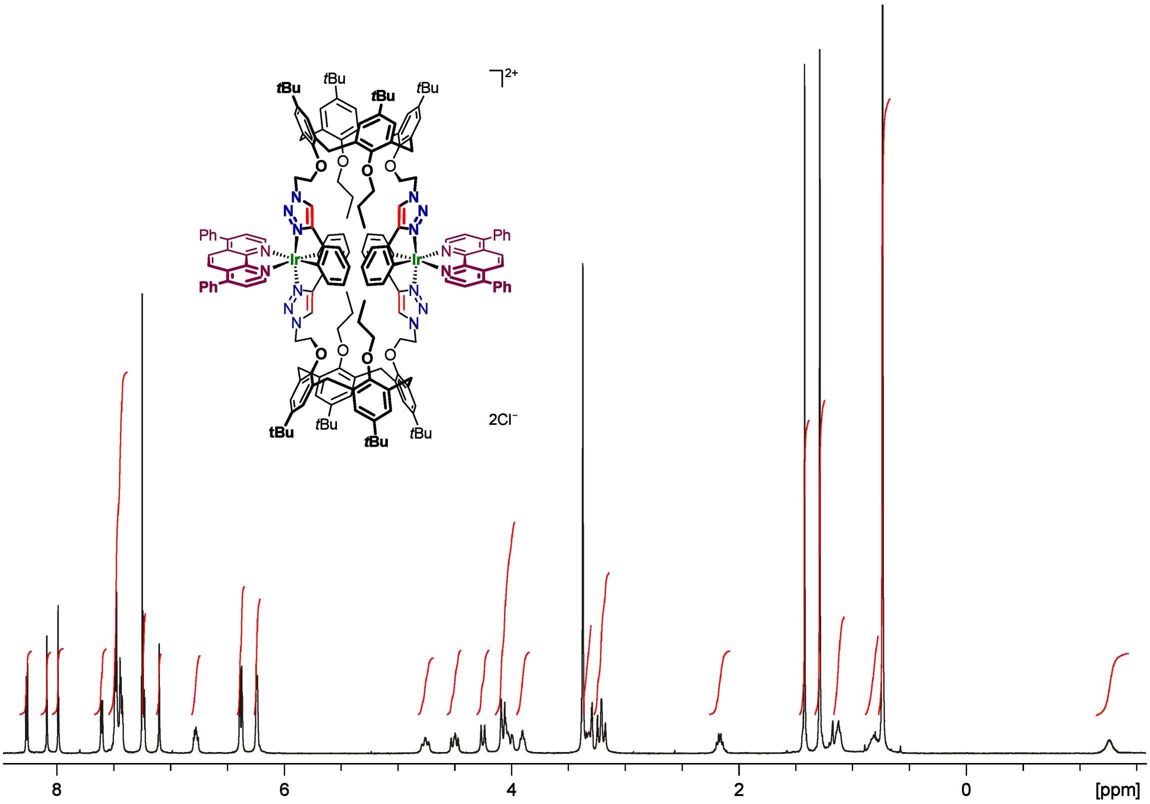


Figure S45. ^{1}H NMR spectrum of complex **8** (400 MHz, $CDCl_3$+CD_3OD (10:1)).

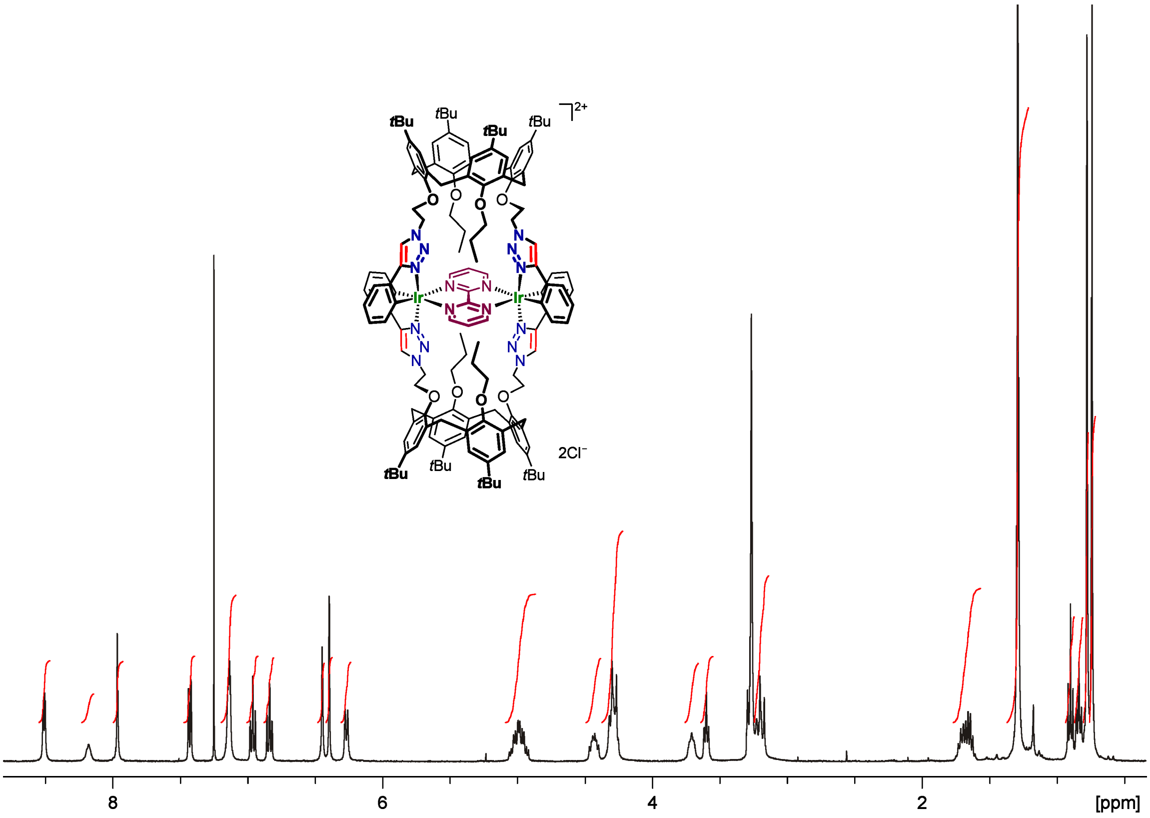


Figure S46. ^{1}H NMR spectrum of complex **9** (400 MHz, $CDCl_3$+CD_3OD (10:1)).

Details of X-ray diffraction measurements

Crystal growth conditions

Complex **4a**: slow evaporation of the solution of complex **4a** in dichloromethane/1,2-dichloroethane mixture;
Complex **4d**: slow evaporation of the solution of complex **4d** in dichloromethane/methanol mixture;
Complex **5**: slow evaporation of the solution of complex **5** in dichloromethane/methanol mixture;
Complex **6**: slow evaporation of the solution of complex **6** in dichloromethane/ethanol mixture;
Complex **7**: slow evaporation of the solution of complex **7** in dichloromethane/methanol mixture;
Complex **8**: diffusion of diethyl ether into the solution of complex **8** in dichloromethane/methanol mixture;
Complex **9**: slow evaporation of the solution of complex **9** and excess $n\text{Bu}_4\text{NPF}_6$ in chloroform; obtained as PF_6-salt.

Crystallographic data were collected on Bruker SMART APEX II (complex **4a** at T=100 K) and D8 Venture (complexes **4d**, **8**, **9** at T=100 K, **5** at T=200 K and **6**, **7** at T=150 K) diffractometers using graphite monochromatized Mo–Kα radiation (λ = 0.71073 Å) using a ω-scan mode. Temperatures above 100 K were used because of the destruction of the crystals at lower temperatures. Absorption correction based on measurements of equivalent reflections was applied.[Ref6] The structures were solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Some components of the disordered propoxy- and *tert*-butyl-groups in the structure of **9** and two C atoms of a partially occupied solvent tetrachloroethane molecule in the structure of **4a** were refined isotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model. In all the structures, part or all of highly disordered solvent dichloromethane, methanol, ethanol and/or ether molecules were not located and their contribution was suppressed by the SQUEEZE procedure.[Ref7] The structure of complex **4d** was completely ordered whereas in all the other structures *tert*-butyl-groups were disordered over two positions with occupancies in the range from 0.66/0.34 to 0.5/0.5. Almost the same occupancy ratios were calculated for propoxy-groups disordered over two sites in the structures of **4a** and **6**–**8**. In the structure of **6**, the main molecule exhibited a conformational disorder of the $\text{O–CH}_2\text{–CH}_2\text{–N(Trz)}$ moiety with equal refined occupancies of the two components. In the structure of **5**, the coordinated pyridine molecule facing outward from the second Ir(III) ion was disordered over two adjacent positions (dihedral angle between the two planes was 15.4(4)°) with the N–C bond being common for the both components. Crystallographic details are presented in Tables S1–S3 and the structures are plotted in Figures S47–S53.

Table S1. Details of the X-ray crystal data collection and structure refinement for complexes **4a**, **4d**, **5** and **6**.

Compound	**4a**	**4d**	**5**	**6**
Formula	$C_{140}H_{168}N_{12}O_8Cl_2Ir_2\cdot$ $\cdot 6.5C_2H_4Cl_2\cdot 2CH_2Cl_2$	$C_{148}H_{184}N_{12}O_{18}Cl_2Ir_2\cdot$ $\cdot 9.7CH_3OH\cdot 7.9CH_2Cl_2$	$C_{160}H_{188}N_{16}O_8Ir_2^{2+}\cdot 2Cl^{-}$	$C_{160}H_{184}N_{16}O_8Ir_2^{2+}\cdot 2Cl^{-}\cdot$ $\cdot 5.4C_2H_5OH\cdot 3.7H_2O$
M_w	3415.19	3824.08	2918.55	3229.94
Temperature (K)	100(2)	100(2)	200(2)	150(2)
Size (mm)	0.35 x 0.12 x 0.02	0.20 x 0.18 x 0.08	0.22 x 0.20 x 0.05	0.12 x 0.08 x 0.01
Cryst. system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$	$P2_1/c$
a (Å)	19.6360(13)	13.0463(7)	24.2215(6)	24.3502(10)
b (Å)	13.1399(6)	20.2747(12)	20.0567(6)	18.8077(8)
c (Å)	34.199(2)	20.6481(11)	20.2899(7)	20.2321(7)
α (°)	90	103.234(2)	90	90
β (°)	103.304(2)	106.527(2)	106.4790(10)	102.2470(10)
γ (°)	90	96.082(2)	90	90
V (Å^3)	8587.0(9)	5010.6(5)	9452.0(5)	9054.9(6)
Z	2	1	2	2
θ range (deg)	$1.98 < \theta < 25.20$	$1.79 < \theta < 30.00$	$1.70 < \theta < 25.05$	$2.03 < \theta < 25.04$
collected/ /unique rflns	97984 / 15109	83251 / 29156	45618 / 16665	78627 / 15966
Completeness to θ (%)	97.6	99.7	99.6	99.6
data/ /restraints/ /params	15109 / 40 / 819	29156 / 0 / 1018	16665 / 35 / 762	15966 / 61 / 965
Goodness of fit on F^2	1.052	1.045	1.050	0.963
Final R indices ($I > 2\sigma(I)$)	R1 = 0.0741 wR2 = 0.1756	R1 = 0.0485 wR2 = 0.1244	R1 = 0.0603 wR2 = 0.1596	R1 = 0.0625 wR2 = 0.1465
Largest diff peak/hole (e/Å^3)	1.81 / −2.57	3.40 / −2.17	1.61 / −1.26	1.60 / −1.44

Table S2. Details of the X-ray crystal data collection and structure refinement for complexes **7**–**9**.

Compound	**7**	**8**	**9**
Formula	$C_{164}H_{184}N_{16}O_8Ir_2{}^{2+}\cdot 2Cl^-\cdot$ $\cdot 2CH_2Cl_2$	$C_{188}H_{200}N_{16}O_8Ir_2{}^{2+}\cdot 2Cl^-\cdot$ $\cdot 2CH_2Cl_2\cdot 2(C_2H_5)_2O$	$C_{148}H_{174}N_{16}O_8Ir_2{}^{2+}\cdot 2PF_6{}^-$
M_w	3132.41	3510.90	2979.36
Temperature (K)	150(2)	100(2)	100(2)
Size (mm)	0.22 x 0.16 x 0.03	0.22 x 0.10 x 0.02	0.35 x 0.12 x 0.10
Cryst. system	monoclinic	orthorhombic	triclinic
Space group	$P2_1/c$	$Pna2_1$	P-1
a (Å)	19.9988(10)	27.5551(9)	19.3154(12)
b (Å)	16.5267(8)	21.0953(7)	22.6544(13)
c (Å)	29.1477(13)	33.6113(9)	26.8007(15)
α (°)	90	90	105.9690(10)
β (°)	97.424(2)	90	90.215(2)
γ (°)	90	90	114.547(2)
V (Å^3)	9553.0(8)	19537.7(10)	10162.0(10)
Z	2	4	2
θ range (deg)	$1.63 < \theta < 25.05$	$1.76 < \theta < 25.05$	$1.49 < \theta < 25.00$
collected/ /unique rflns	44998 / 16802	94035 / 34200	133799 / 35698
Completeness to θ (%)	99.3	99.0	99.8
data/ /restraints/ /params	16802 / 65 / 889	34200 / 65 / 889	35698 / 134 / 1523
Goodness of fit on F^2	1.032	1.021	1.029
Final R indices ($I > 2\sigma(I)$)	R1 = 0.0701 wR2 = 0.1673	R1 = 0.0504 wR2 = 0.1174	R1 = 0.0593 wR2 = 0.1599
Largest diff peak/hole (e/Å^3)	3.12 / −1.10	1.40 / −1.50	2.49 / −1.47

Table S3. Selected bond lengths (Å) and angles (°) in structures of complexes **4a**, **4d**, **5**–**9**.

4a	Ir$_1$–C$_1$	Ir$_1$–C$_2$	Ir$_1$–N$_1$	Ir$_1$–N$_2$	Ir$_1$–Cl$_1$	Ir$_1$–Cl$_2$		
	2.028(8)	2.031(9)	2.035(8)	2.021(7)	2.5129(19)	2.525(2)		
	Cl$_1$–Ir$_1$–Cl$_2$	C$_1$–Ir$_1$–C$_2$	C$_1$–Ir$_1$–N$_2$	C$_2$–Ir$_1$–N$_1$	C$_1$–Ir$_1$–Cl$_1$	C$_2$–Ir$_1$–Cl$_2$	N$_1$–Ir$_1$–Cl$_1$	N$_2$–Ir$_1$–Cl$_2$
	82.28(7)	91.0(3)	92.8(3)	92.1(3)	92.8(3)	94.3(2)	93.7(2)	91.1(2)
4d	Ir$_1$–C$_1$	Ir$_1$–C$_{20}$	Ir$_1$–N$_1$	Ir$_1$–N$_2$	Ir$_1$–Cl$_1$	Ir$_1$–Cl$_2$		
	2.007(3)	1.998(3)	2.025(3)	2.014(3)	2.5139(8)	2.5247(7)		
	Cl$_1$–Ir$_1$–Cl$_2$	C$_1$–Ir$_1$–C$_2$	C$_1$–Ir$_1$–N$_2$	C$_2$–Ir$_1$–N$_1$	C$_1$–Ir$_1$–Cl$_1$	C$_2$–Ir$_1$–Cl$_2$	N$_1$–Ir$_1$–Cl$_1$	N$_2$–Ir$_1$–Cl$_2$
	82.18(3)	90.25(13)	92.79(12)	93.63(12)	92.53(9)	95.31(9)	90.68(8)	91.91(8)
5	Ir$_1$–C$_1$	Ir$_1$–C$_2$	Ir$_1$–N$_1$	Ir$_1$–N$_2$	Ir$_1$–N$_3$	Ir$_1$–N$_4$		
	2.009(6)	2.032(7)	2.035(5)	2.033(5)	2.124(5)	2.150(5)		
	C$_1$–Ir$_1$–C$_2$	C$_1$–Ir$_1$–N$_2$	C$_2$–Ir$_1$–N$_1$	C$_2$–Ir$_1$–N$_3$	C$_1$–Ir$_1$–N$_4$	N$_1$–Ir$_1$–N$_3$	N$_1$–Ir$_1$–N$_4$	N$_2$–Ir$_1$–N$_3$
	87.4(3)	93.0(2)	93.1(2)	92.3(2)	92.6(3)	96.4(2)	89.2(2)	90.30(19)
6	Ir$_1$–C$_1$	Ir$_1$–C$_2$	Ir$_1$–N$_1$	Ir$_1$–N$_2$	Ir$_1$–N$_3$	Ir$_1$–N$_4$		
	2.001(9)	2.022(8)	2.021(7)	2.047(7)	2.113(7)	2.132(6)		
	C$_1$–Ir$_1$–C$_2$	C$_1$–Ir$_1$–N$_2$	C$_2$–Ir$_1$–N$_1$	C$_2$–Ir$_1$–N$_4$	C$_1$–Ir$_1$–N$_3$	N$_1$–Ir$_1$–N$_3$	N$_1$–Ir$_1$–N$_4$	N$_2$–Ir$_1$–N$_3$
	84.6(3)	94.1(3)	94.5(3)	101.6(3)	97.9(3)	89.4(3)	98.7(3)	96.9(3)
7	Ir$_1$–C$_1$	Ir$_1$–C$_2$	Ir$_1$–N$_1$	Ir$_1$–N$_2$	Ir$_1$–N$_3$	Ir$_1$–N$_4$		
	2.028(9)	2.038(8)	2.024(6)	2.026(6)	2.131(6)	2.141(7)		
	C$_1$–Ir$_1$–C$_2$	C$_1$–Ir$_1$–N$_2$	C$_2$–Ir$_1$–N$_1$	C$_2$–Ir$_1$–N$_3$	C$_1$–Ir$_1$–N$_4$	N$_1$–Ir$_1$–N$_3$	N$_1$–Ir$_1$–N$_4$	N$_2$–Ir$_1$–N$_3$
	87.4(3)	96.0(3)	94.9(3)	100.3(3)	95.1(3)	94.0(2)	93.9(2)	90.2(2)
8	Ir$_1$–C$_1$	Ir$_1$–C$_2$	Ir$_1$–N$_1$	Ir$_1$–N$_2$	Ir$_1$–N$_3$	Ir$_1$–N$_4$		
	2.039(12)	2.009(12)	2.009(8)	2.050(8)	2.110(9)	2.140(9)		
	C$_1$–Ir$_1$–C$_2$	C$_1$–Ir$_1$–N$_2$	C$_2$–Ir$_1$–N$_1$	C$_2$–Ir$_1$–N$_3$	C$_1$–Ir$_1$–N$_4$	N$_1$–Ir$_1$–N$_3$	N$_1$–Ir$_1$–N$_4$	N$_2$–Ir$_1$–N$_3$
	96.1(4)	95.7(5)	93.2(4)	91.6(4)	93.5(4)	96.0(4)	89.0(3)	90.2(4)
	Ir$_2$–C$_3$	Ir$_2$–C$_4$	Ir$_2$–N$_5$	Ir$_2$–N$_6$	Ir$_2$–N$_7$	Ir$_2$–N$_8$		
	2.034(11)	2.049(13)	2.017(8)	2.033(9)	2.144(10)	2.145(9)		
	C$_3$–Ir$_2$–C$_4$	C$_3$–Ir$_2$–N$_6$	C$_4$–Ir$_2$–N$_5$	C$_4$–Ir$_2$–N$_8$	C$_3$–Ir$_2$–N$_7$	N$_5$–Ir$_2$–N$_7$	N$_5$–Ir$_2$–N$_8$	N$_6$–Ir$_2$–N$_8$
	94.8(4)	93.7(4)	92.1(4)	93.9(4)	94.6(4)	90.4(3)	97.8(8)	89.7(4)
9	Ir$_1$–C$_1$	Ir$_1$–C$_2$	Ir$_1$–N$_1$	Ir$_1$–N$_2$	Ir$_1$–N$_3$	Ir$_1$–N$_4$		
	2.043(7)	2.074(7)	2.025(5)	2.003(5)	2.175(5)	2.167(5)		
	C$_1$–Ir$_1$–C$_2$	C$_1$–Ir$_1$–N$_2$	C$_2$–Ir$_1$–N$_1$	C$_2$–Ir$_1$–N$_4$	C$_1$–Ir$_1$–N$_3$	N$_1$–Ir$_1$–N$_3$	N$_1$–Ir$_1$–N$_4$	N$_2$–Ir$_1$–N$_3$
	91.7(2)	95.9(2)	97.4(2)	94.7(2)	96.1(2)	91.0(2)	96.6(2)	93.0(2)
	Ir$_2$–C$_3$	Ir$_2$–C$_4$	Ir$_2$–N$_5$	Ir$_2$–N$_6$	Ir$_2$–N$_7$	Ir$_2$–N$_8$		
	2.048(7)	2.061(7)	2.015(5)	2.025(5)	2.194(5)	2.161(5)		
	C$_3$–Ir$_2$–C$_4$	C$_3$–Ir$_2$–N$_6$	C$_4$–Ir$_2$–N$_5$	C$_4$–Ir$_2$–N$_8$	C$_3$–Ir$_2$–N$_7$	N$_5$–Ir$_2$–N$_7$	N$_5$–Ir$_2$–N$_8$	N$_6$–Ir$_2$–N$_8$
	91.9(3)	98.8(3)	94.8(2)	95.6(2)	94.6(3)	90.21(19)	95.00(19)	87.0(2)

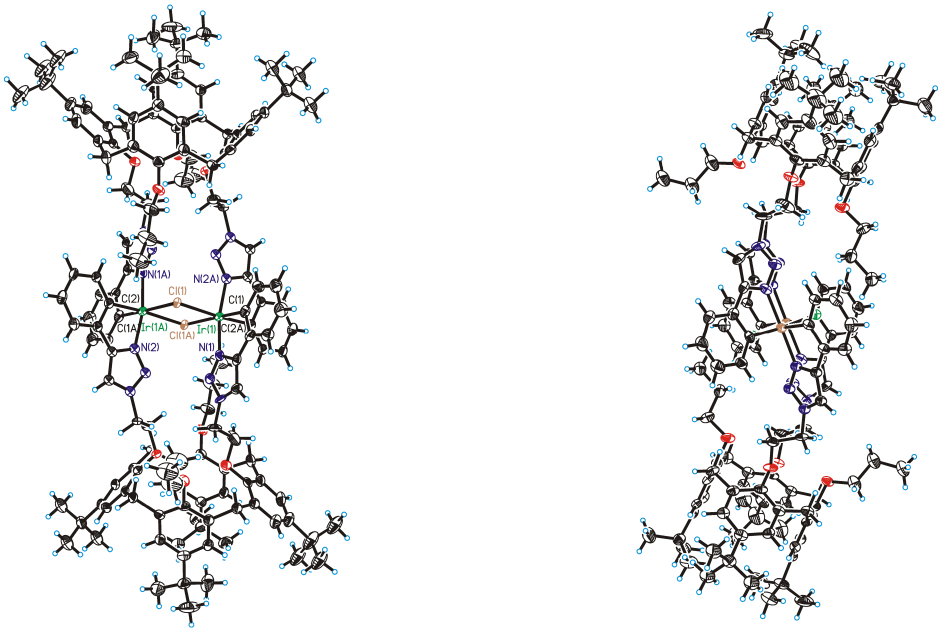


Figure S47. Molecular structure of complex **4a**; thermal ellipsoids are drawn at the 50% probability level.

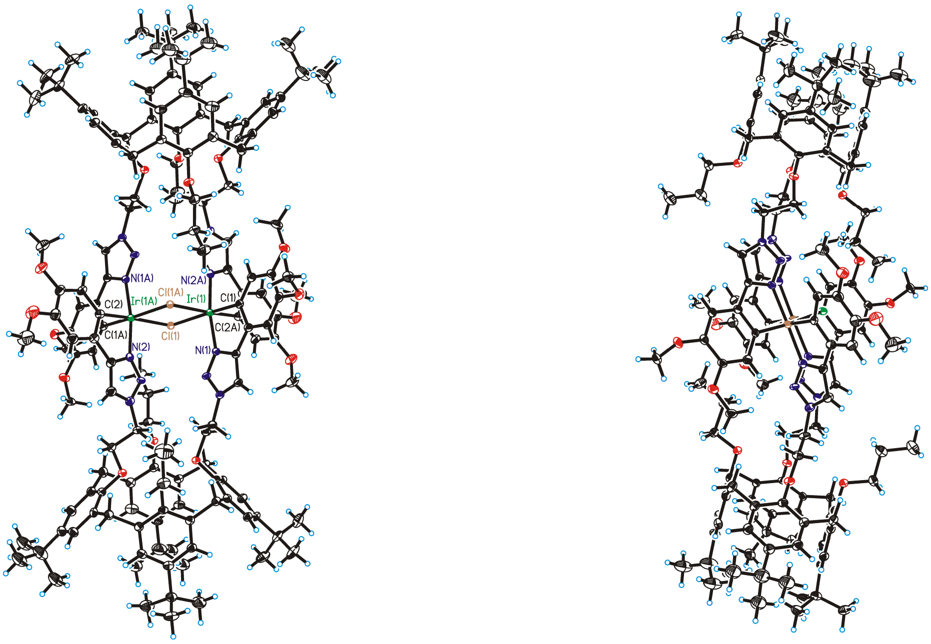


Figure S48. Molecular structure of complex **4d**; thermal ellipsoids are drawn at the 50% probability level.

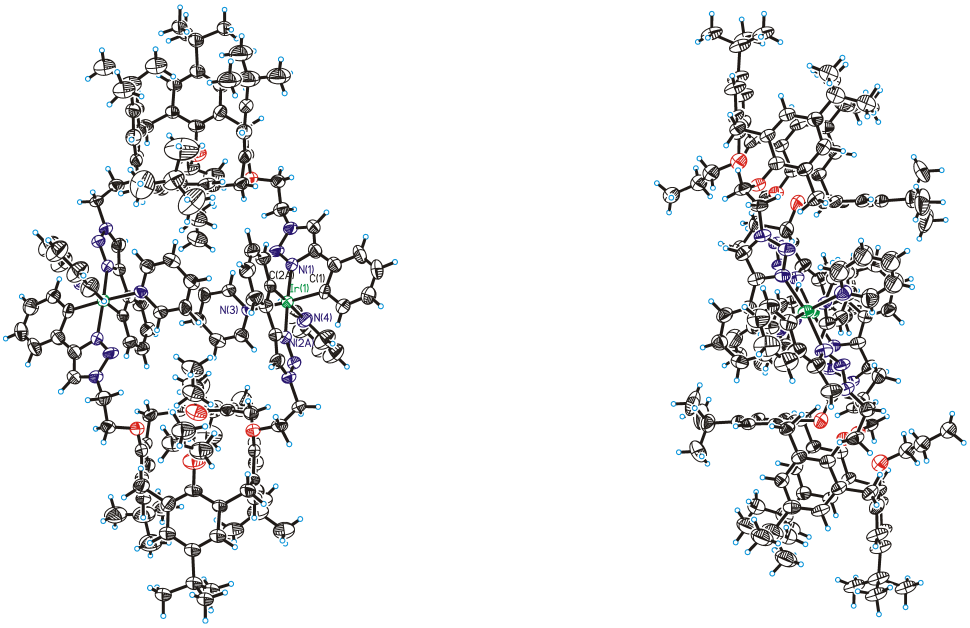


Figure S49. Molecular structure of complex **5**; thermal ellipsoids are drawn at the 50% probability level.

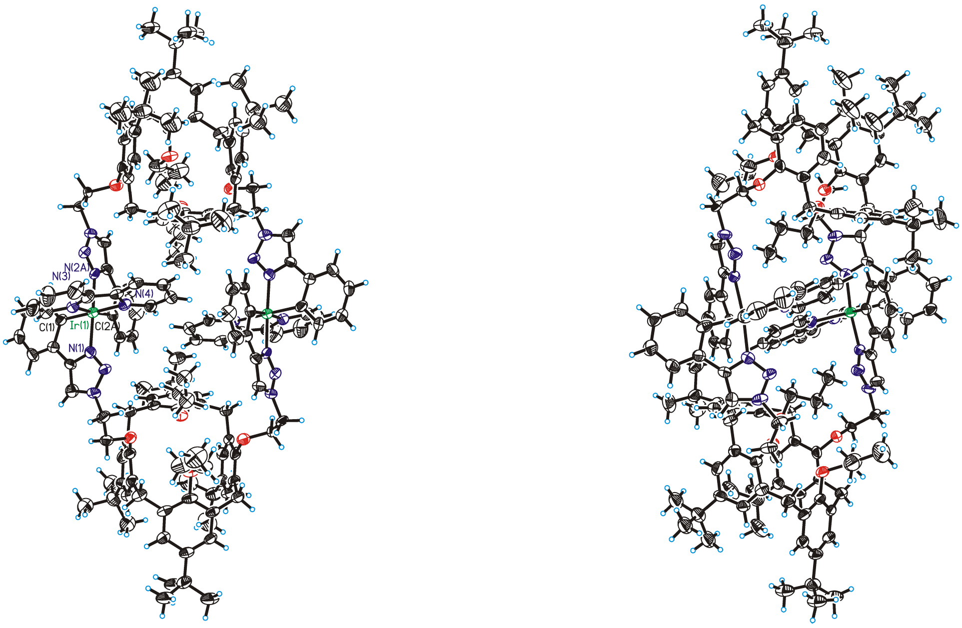


Figure S50. Molecular structure of complex **6**; thermal ellipsoids are drawn at the 50% probability level.

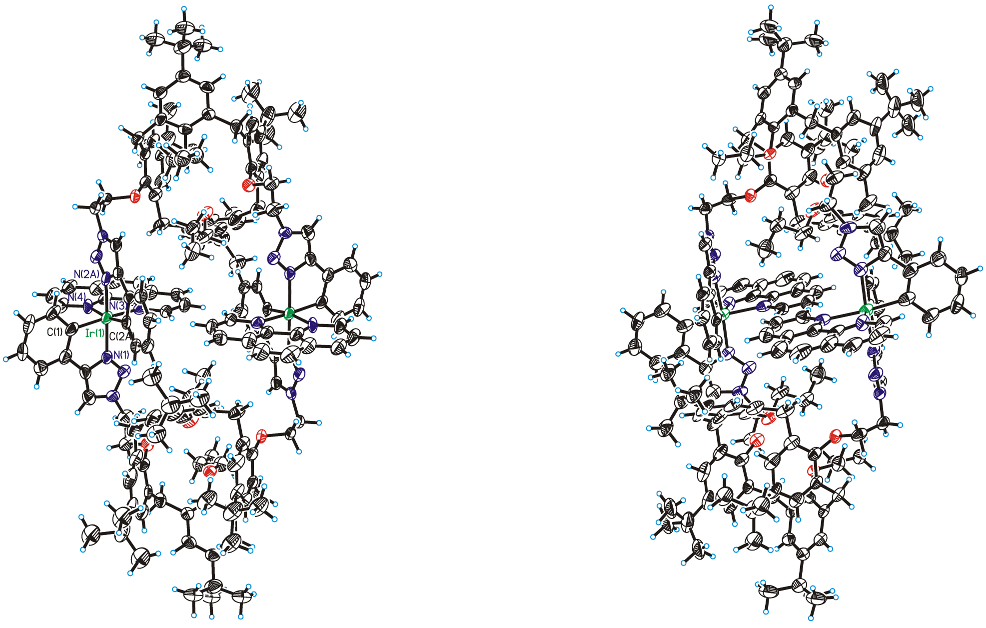


Figure S51. Molecular structure of complex **7**; thermal ellipsoids are drawn at the 50% probability level.

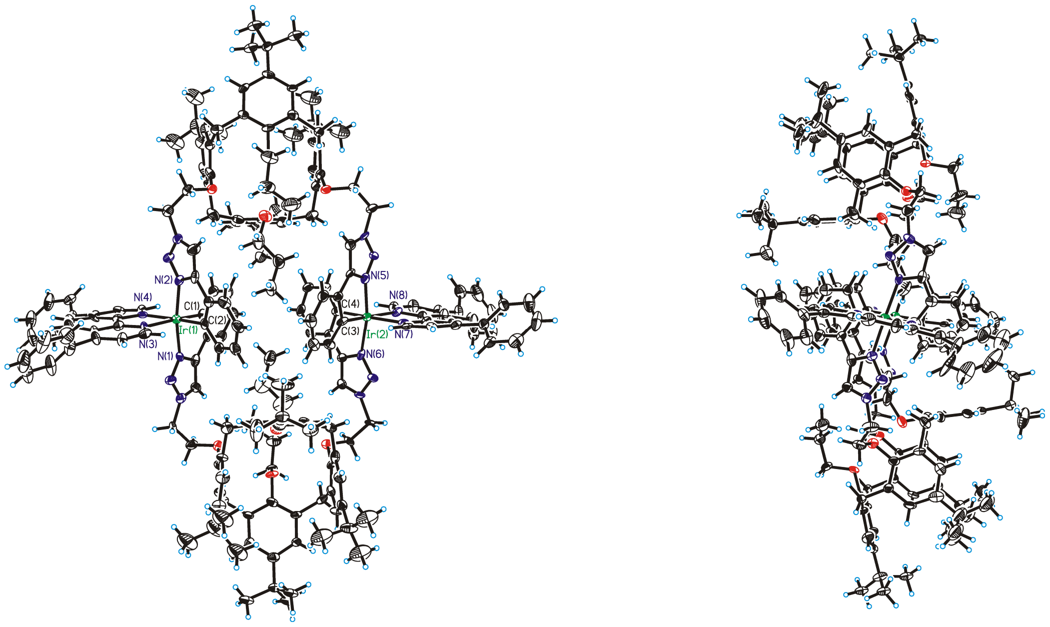


Figure S52. Molecular structure of complex **8**; thermal ellipsoids are drawn at the 50% probability level.

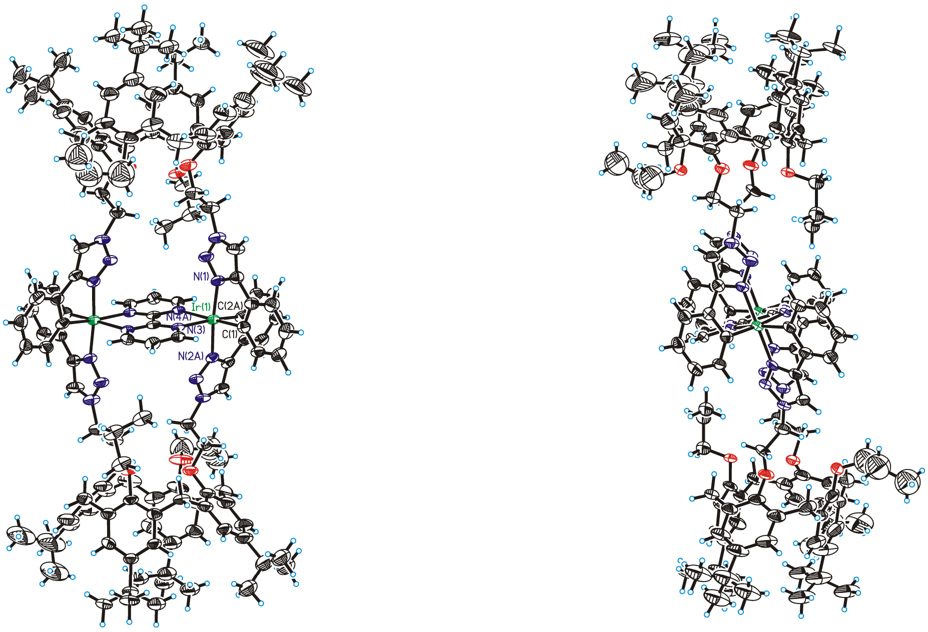


Figure S53. Molecular structure of complex **9**; thermal ellipsoids are drawn at the 50% probability level.

UV/vis and fluorescence data for the heteroleptic complexes

Electronic absorption spectra were measured on an OKB Spectr SF-2000 spectrophotometer. Emission spectra were measured using a Perkin-Elmer LS55 spectrometer over excitation with a xenon lamp.

Table S4. UV/vis and luminescence data for complexes **6**–**9**.

Complex	λ_{abs} / nm ($\varepsilon\cdot 10^{-3}$ / $M^{-1}\cdot cm^{-1}$)[a]	λ_{em} / nm (*PLQY* / *%*)[b]
6	271 (*67.3*), 302 (*39.1*), 336 (*16.7*), 433 (*1.5*)	541 (*3.5*)
7	272 (*88.8*), 318 (*24.2*), 424 (*1.8*)	538 (*4.4*)
8	286 (*74.7*), 327 (*33.4*), 383 (*10.6*), 430 (*3.0*)	548 (*2.4*)
9	308 (*13.0*), 410 (*3.4*), 590 (*0.7*)	

[a] – Measured in Ar-saturated acetonitrile/dichloromethane (4:1) mixture.

[b] – PLQY – photoluminescence quantum yield relative to Rhodamine 6G was measured in Ar-saturated acetonitrile/dichloromethane (4:1) mixture. Estimated error ±15% for rel. PLQY.

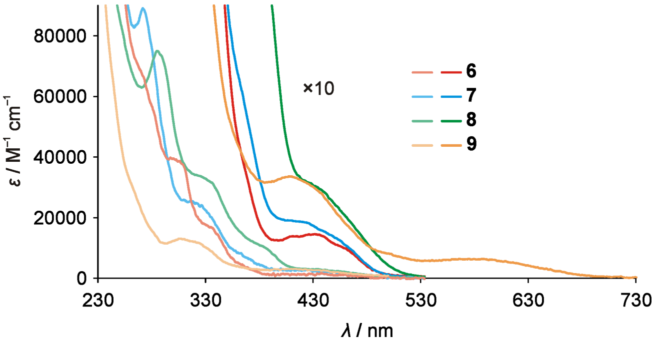


Figure S54. Absorption spectra of heteroleptic complexes **6**–**9**; acetonitrile/dichloromethane (4:1).

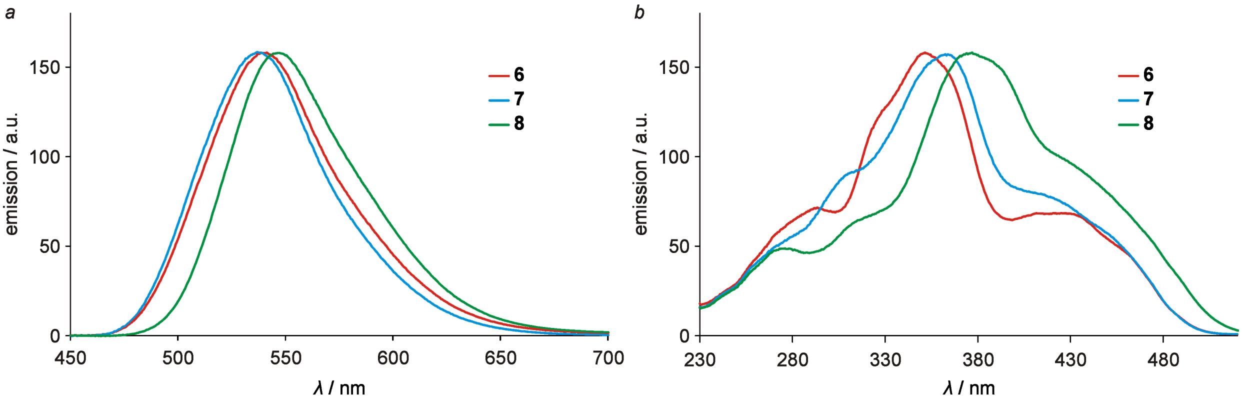


Figure S55. Emission (a) and excitation (b) spectra of heteroleptic complexes **6**–**8**; acetonitrile/dichloromethane (4:1).

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