Electronic Supplementary Material (ESI) for Dalton Transactions.

Site-selective cation-π-interaction as a way of selective recognition of caesium cation with sumanene-functionalized ferrocenes

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Supplementary Information

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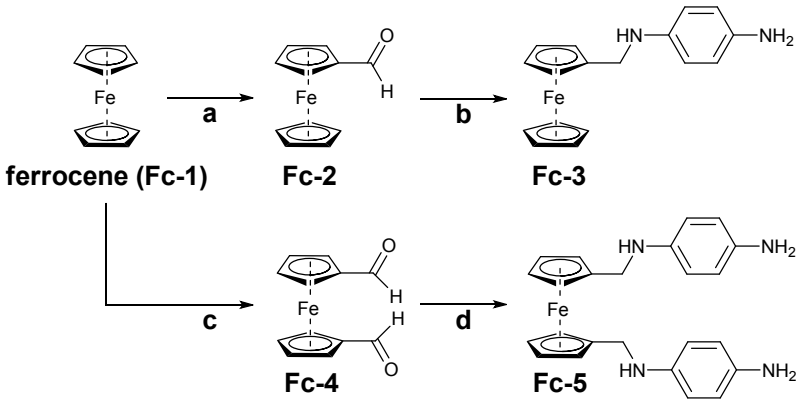
S1. Experimental section

S1.1 Materials and methods

Chemical reagents and solvents were commercially purchased and purified according to the standard methods, if necessary. Air- and moisture-sensitive reactions were carried out using commercially available anhydrous solvents under an inert atmosphere of nitrogen. The NMR experiments were carried out using JEOL JNM-ECZS spectrometer operating at 400 MHz (^{1}H NMR at 400 MHz or ^{13}C{^{1}H} NMR at 100 MHz). Unless otherwise stated, the spectra were recorded at 23 °C. Standard 5 mm NMR tubes were used. ^{1}H and ^{13}C chemical shifts (δ) were reported in parts per million (ppm) relative to the solvent signals: $CDCl_3$, δ_H (residual $CHCl_3$) 7.26 ppm, δ_C 77.23 ppm, or $(CD_3)_2CO$, δ_H (residual $(CH_3)_2CO$) 2.05 ppm. Melting points were determined on Standford Research Systems MPA 100 and were uncorrected. Infrared (IR) spectra were recorded on a JASCO FT IR-4100 spectrometer with a spectral resolution of 2 cm^{-1} (80 scans) in the wavelength range of 2000-600 cm^{-1}. UV–visible (UV–Vis) absorption spectra were recorded on a JASCO V-670 spectrometer with the spectral resolution of 1 nm. Fluorescence spectra were recorded on a JASCO FP6500 spectrometer with the spectral resolution of 1 nm. Cyclic voltammetry (CV) was measured with a ALS/CH Instruments Electrochemical Analyzer Model 600A. Elemental analyses were performed using CHNS Elementar Vario EL III apparatus. Each elemental composition was reported as an average of two analyses. APCI-MS spectra were measured with ACQUITY ultra performance LC instrument. Gel permeable chromatography (GPC) was conducted on JAIGEL 2H using a JAI Recycling Preparative HPLC LC-908W with $CHCl_3$ as eluent. TLC analysis was performed using Merck Silica gel 60 F254 and PTLC was conducted using Wako Wakogel B-5F or with Al_2O_3 (neutral) plates.

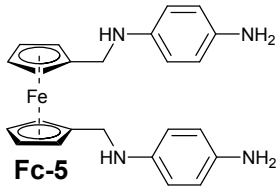
Sumanene (**1**)[1], formylsumanene (**2**)[2], nitrosumanene (**6**)[2], formylferrocene (**Fc-2**)[3], 1,1'-diformylferrocene (**Fc-4**)[4], *N*-(ferrocenylmethyl)benzene-1,4-diamine (**Fc-3**)[5], were synthesized according to the literature procedures.

S1.2 Synthesis



Scheme S1. Synthesis of the ferrocene derivatives: (**a**) ferrocene 100 mol%, DMF 200 mol%, $POCl_3$ 200 mol%, $CHCl_3$, 55°C, 24 h, 69% yield; (**b**) formylferrocene 100 mol%, *p*-phenylenediamine 500 mol%, MeOH, reflux, 6 h then $NaBH_4$ 200 mol%, reflux, 1h, 70% yield; (**c**) ferrocene 100 mol%, TMEDA 200%, ^{n}BuLi 220 mol%, hex, 27°C, 24 h then DMF 220 mol% in diethyl ether, -78°C, 2 h, 72% yield; (**d**) 1,1'-diformylferrocene 100 mol%, *p*-phenylenediamine 600 mol%, MeOH, reflux, 6 h then $NaBH_4$ 800 mol%, reflux, 1h, 73% yield.

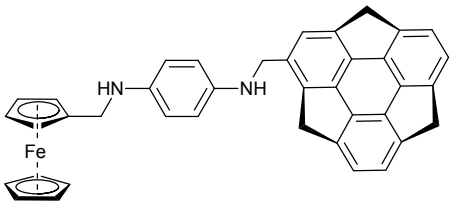
N^{1},*N*$^{1'}$-(1,1'-bis(methyl)ferrocenyl)bis(benzene-1,4-diamine) (Fc-5)



A solution of 1,1'-diformylferrocene (24.2 mg, 0.1 mmol) and *p*-phenylenediamine (64.9 mg, 0.6 mmol) in methanol[6] (5 mL) was refluxed for 6 h. Sodium borohydride (30.2 mg, 0.8 mmol) was then added and the mixture was further refluxed for 1 h. The reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with water (5 mL), brine (3 mL), dried over Na_2SO_4, filtered and evaporated in vacuum. The crude product was purified by PTLC (SiO_2; CH_2Cl_2/MeOH, 95:5 *v*/*v*) to give compound *N*^{1},*N*^{1}-(1,1'-bis(methyl)ferrocenyl)bis(benzene-1,4-diamine) (**Fc-5**; 31.1 mg ; 73% yield) as a dark-orange solid.

Mp: 132 °C (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm), δ_H 6.64-6.62 (m, 4H), 6.58-6.54 (m, 4H), 4.23-4.22 (t, *J* = 1.8 Hz, 2H), 4.14–4.13 (t, *J* = 1.9 Hz, 2H), 3.92 (s, 4H), 3.29 (bs, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm), δ_C 114.7 (2C), 138.8 (2C), 138.2 (2C), 116.9 (2C),114.9 (2C), 87.4 (2C), 68.8 (4C), 68.5 (4C), 68.0 (2C), 44.7 (2C); IR (ATR), *v* 1565, 1510, 1485, 1300, 1245, 1105, 815 cm^{-1}; Elemental analysis: calculated for $C_{24}H_{26}FeN_4$: C (67.61%), H (6.15%), N (13.14%); found: C (67.50%), H (6.13%), N (13.28%); APCI-MS calcd. for $C_{24}H_{26}FeN_4$ $[M]^+$ = 426.15, found: m/z 426.16; R_f (SiO_2; CH_2Cl_2/MeOH, 95:5 *v*/*v*) = 0.55

***N*[1]-(ferrocenylmethyl)-*N*[4]-(sumanenylmethyl)benzene-1,4-diamine (3)**

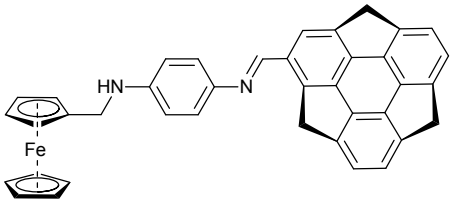


3

A solution of *N*-(ferrocenylmethyl)benzene-1,4-diamine (**Fc-3**; 2.5 mg, 0.0082 mmol) in MeOH[6] (0.8 mL) was added to a stirred solution of formylsumanene (**2**; 2.4 mg, 0.0082 mmol) in dry THF (1.0 mL). Formic acid (85%; 10 µL) was added and the mixture was stirred at 27 °C for 24 h. Then, sodium borohydride (1.2 mg, 0.0248 mmol) was added and the mixture was further stirred at 27°C for 3 h. CH_2Cl_2 (15 mL) was added and the organic layer was washed with saturated $NaHCO_3$ (2 mL), water (2 mL), brine (2 mL), dried with Na_2SO_4, filtered, and the solvent was removed in vacuum. The resultant residue was purified by column chromatography (Al_2O_3; CH_2Cl_2/MeOH = 99.5:0.5 *v/v*) to give *N*[1]-(ferrocenylmethyl)-*N*[4]-(sumanenylmethyl)benzene-1,4-diamine (**3**; 3.6 mg, 75% yield) as the light-orange solid.

Mp: 195 °C (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm), δ_H 7.16 (s, 1H), 7.11-7.09 (m, 4H), 6.63-6.62 (m, 4H), 4.35-4.22 (m, 5H), 4.24-4.23 (t, *J* = 1.9 Hz, 2H), 4.17 (s, 5H), 4.13–4.12 (t, *J* = 1.9 Hz, 2H), 3.91 (s, 2H), 3.52 (d, *J* = 19.9 Hz, 1H), 3.44 (d, *J* = 15.0 Hz, 1H), 3.39 (d, *J* = 15.1 Hz, 1H); ^{1}H NMR ($(CD_3)_2CO$, 400 MHz, ppm), δ_H 7.25 (s, 1H), 7.16-7.14 (m, 4H), 6.60-6.54 (m, 4H), 4.72-4.64 (m, 4H), 4.40-4.27 (m, 4H), 4.23-4.22 (t, *J* = 1.9 Hz, 2H), 4.16 (s, 5H), 4.12-4.10 (t, *J* = 5.9 Hz, 1H), 4.07–4.05 (t, *J* = 1.9 Hz, 2H), 3.91 (d, *J* = 5.9 Hz, 2H), 3.64 (d, *J* = 20.0 Hz, 1H), 3.48 (d, *J* = 15.1 Hz, 1H), 3.44 (d, *J* = 15.0 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm), δ_C 150.3, 149.2, 149.2, 149.1, 149.0, 148.9, 148.8 (2C), 148.2, 147.1, 141.3, 141.2, 135.9, 123.6, 123.5 (2C), 123.4 (2C), 115.1 (2C), 115.0 (2C), 87.2, 87.2, 68.7 (5C), 68.3 (2C), 68.0 (2C), 49.0, 45.0, 42.0 (2C), 41.0; IR (ATR), *v* 1560, 1510, 1460, 1300, 1225, 1100, 1000, 800, 750 cm^{-1}; UV-Vis, λ_{max} ($CHCl_3$:MeOH = 1:1 *v/v*) 250, 280, 360, 395 nm; Elemental analysis: calculated for $C_{39}H_{30}FeN_2$: C (80.41%), H (5.19%), N (4.81%); found: C (80.07%), H (5.28%), N (4.65%); APCI-MS: calcd. for $C_{39}H_{30}FeN_2$ $[M]^+$ = 582.81, found: m/z 582.83; R_f (Al_2O_3; CH_2Cl_2/MeOH, 99.5:0.5 *v/v*) = 0.40

(*E*)-*N*[1]-(ferocenylmethyl)-*N*[4]-(sumenenylmethyl)benzene-1,4-diamine (4)



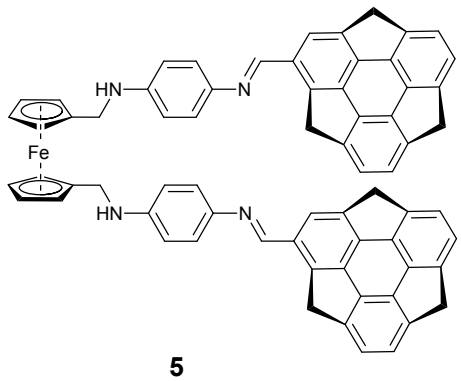
4

A solution of *N*-(ferrocenylmethyl)benzene-1,4-diamine (**Fc-3**; 2.5 mg, 0.0082 mmol) in MeOH[6] (0.8 mL) was added to a stirred solution of formylsumanene (**2**; 2.4 mg,

0.0082 mmol) in dry THF (1.0 mL). Formic acid (85%; 10 µL) was added and the mixture was stirred at 27 °C for 24 h. CH_2Cl_2 (15 mL) was added and the organic layer was washed with saturated $NaHCO_3$ (2 mL), water (2 mL), brine (2 mL), dried with Na_2SO_4, filtered, and the solvent was removed in vacuum. The resultant residue was purified by using a recycling GPC (chloroform as eluting solvent) to give (*E*)-*N*^{1}-(ferocenylmethyl)-*N*^{4}-(sumenenylmethyl)benzene-1,4-diamine (**4**; 4.5 mg, 94% yield) as the dark yellow solid.

Mp: 178°C (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm), 8.60 (s, 1H), 7.61 (s, 1H), 7.25-7.23 (m, 2H), 7.17-7.11 (m, 4H), 6.71-6.69 (m, 2H), 4.98 (d, *J* = 20.6 Hz, 1H), 4.75 (d, *J* = 19.6 Hz, 1H), 4.72 (d, *J* = 19.6 Hz, 1H), 4.27-4.26 (t, *J* = 1.9 Hz, 2H), 4.20 (s, 5H), 4.17–4.16 (t, *J* = 1.9 Hz, 2H), 4.00-3.98 (bm, 3H), 3.66 (d, *J* = 20.6 Hz, 1H), 3.50 (d, *J* = 19.6 Hz, 1H), 3.45 (d, *J* = 19.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm), δ_C 156.1, 150.1, 149.5, 149.4 (2C), 149.1, 149.0, 148.9, 148.8, 148.6, 148.2, 147.5, 147.3, 147.1, 142.6, 133.7, 124.9, 124.1, 124.0, 123.6 (2C), 122.7 (2C), 113.4 (2C), 86.5, 68.7 (5C), 68.4 (2C), 68.2 (2C), 43.8, 43.0, 42.0, 41.8; IR (ATR), *v* 1635, 1555, 1510, 1455, 1300, 1250, 1100, 995, 805, 755 cm^{-1}; UV-Vis, λ_{max} ($CHCl_3$:MeOH = 1:1 *v/v*) 255, 295, 360, 390 nm; Elemental analysis: calculated for $C_{39}H_{28}FeN_2$: C (80.69%), H (4.86%), N (4.83%); found: C (80.15%), H (4.59%), N (4.60%); APCI-MS: calcd. for $C_{39}H_{28}FeN_2$ [M]$^+$ = 580.49, found: m/z 582.48. R_f (SiO_2; CH_2Cl_2) = 0.56

(*N*^{4}*E*,*N*$^{4'}$*E*)-*N*^{1},*N*$^{1'}$-(1,1'-bis(methyl)ferrocenyl)bis(*N*^{4}-(sumanenylmethyl)benzene-1,4-diamine) (5)



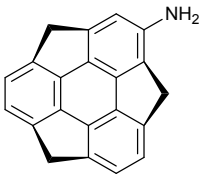
5

A solution of *N*^{1},*N*^{1}-(1,1'-bis(methyl)ferrocenyl)bis(benzene-1,4-diamine) (**Fc-5**; 3.1 mg, 0.0072 mmol) in MeOH[6] (1.0 mL) was added to a stirred solution of formylsumanene (**2**; 4.2 mg, 0.0144 mmol) in dry THF (2.0 mL). Formic acid (85%; 20 µL) was added and the mixture was stirred at 27 °C for 24 h. CH_2Cl_2 (20 mL) was added and the organic layer was washed with saturated $NaHCO_3$ (3 mL), water (2 mL), brine (3 mL), dried with Na_2SO_4, filtered, and the solvent was removed in vacuum. The resultant residue was purified by using a recycling GPC (chloroform as eluting solvent) to give (*N*^{4}*E*, *N*$^{4'}$*E*)-*N*^{1},*N*$^{1'}$-(1,1'-bis(methyl)ferrocenyl)bis(*N*^{4}-(sumanenylmethyl)benzene-1,4-diamine) (**5**; 5.0 mg, 72% yield) as the yellow solid.[7]

Mp: 171°C (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm), δ 8.57 (s, 1H), 8.55 (s, 1H), 7.59 (s, 1H), 7.56 (s, 1H), 7.23-7.20 (m, 4H), 7.11-7.06 (m, 8H), 6.67-6.63 (m, 4H),

4.94-4.84 (m, 2H), 4.72-4.59 (m, 4H), 4.29-4.28 (t, *J* = 1.8 Hz, 2H), 4.21–4.20 (t, *J* = 1.8 Hz, 2H), 4.02-4.00 (bm, 6H), 3.84-3.69 (m, 2H), 3.45-3.29 (m, 4H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, ppm), δ_C 156.3, 156.1, 149.5 (2C), 149.4 (2C), 149.3 (4C), 149.2 (2C), 149.1 (2C), 149.0 (2C), 148.9 (2C), 148.2 (2C), 148.0 (2C), 147.8 (2C), 147.5 (4C), 147.4 (2C), 147.3 (2C), 135.5 (2C), 124.9 (2C), 124.4 (2C), 124.1 (2C), 123.9 (2C), 123.5 (2C), 122.8 (4C), 113.50 (6C), 87.0 (2C), 68.8 (2C), 68.7 (2C), 43.0 (2C), 42.8 (2C), 42.0 (2C), 41.7 (2C); IR (ATR), *v* 1650, 1605, 1510, 1460, 1395, 1255, 1085, 1020, 795 cm^{-1}; UV-Vis, λ_{max} ($CHCl_3$:MeOH = 1:1 *v/v*) 255, 295, 395 nm; Elemental analysis: calculated for $C_{68}H_{46}FeN_4$: C (83.77%), H (4.76%), N (5.75%); found: C (84.02%), H (4.85%), N (5.60%); APCI-MS: calcd. for $C_{68}H_{46}FeN_4$ $[M]^+$ = 974.97, found: m/z 974.96. R_f (SiO_2; CH_2Cl_2) = 0.75

Aminosumanene (7)

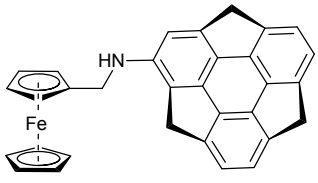


7

A mixture containing nitrosumanene (**6**; 4.0 mg, 0.0121 mmol) and Pd/C (10% Pd; 8.0 mg, 200 w/w%) in the solvent (EtOH/AcOEt = 1:1 v/v, 4.0 mL)[8] was stirred at 27 °C for 3 h. The mixture was filtered through celite and washed with CH_2Cl_2 (15 mL). The volatiles were distilled off in vacuum to give aminosumanene (**7**; 3.4 mg, 99% yield) as a yellow-white solid.

Mp: 118 °C (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm), δ 7.12-7.10 (m, 3H), 7.03-6.96 (m, 2H), 6.42 (bs, 2H), 4.70-4.49 (m, 3H), 3.41-3.28 (m, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, ppm), δ_C 153.0, 150.7, 150.1, 149.3, 149.1, 149.0, 148.4, 147.9, 147.4, 143.2, 140,8, 129.4, 123.6, 123.5, 123.3, 121.7, 121.7, 111.7, 41.8, 41.6, 39.7; IR (ATR), *v* 1585, 1535, 1320, 1250, 985, 815, 750 cm^{-1}; Elemental analysis: calculated for $C_{21}H_{13}N$: C (90.29%), H (4.70%), N (5.01%); found: C (90.20%), H (4.59%), N (5.21%); APCI-MS: calcd. for $C_{21}H_{13}N$ $[M]^+$ = 279.33, found: m/z 279.34. R_f (SiO_2; CH_2Cl_2) = 0.67

***N*-(ferrocenylmethyl)sumanene (8)**



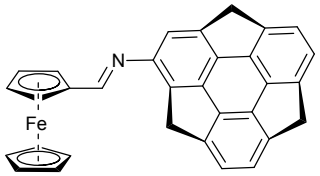
8

A solution of formylferrocene (3.0 mg, 0.0140 mmol), aminosumanene (3.9 mg, 0.0140 mmol) and formic acid (85%; 20 µL) in THF/methanol solvent system (1:2 *v/v*)[8] (2.5 mL) was refluxed for 6 hours at nitrogen atmosphere. Sodium borohydride (1.7 mg, 0.0420 mmol, 3 eq) was then added and the mixture was further refluxed for 1 h. The

reaction mixture was diluted with CH_2Cl_2 (15 mL), washed saturated $NaHCO_3$ (2 mL), water (2 mL), brine (2 mL), dried over Na_2SO_4, filtered and evaporated in vacuum. The resultant residue was purified by using a recycling GPC (chloroform as eluting solvent) to give *N*-(ferrocenylmethyl)sumanene (**8**; 4.6 mg, 69%) as the light-orange solid.[9]

Mp: 221 °C (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm), δ_H 7.10-7.09 (m, 3H), 7.04-6.94 (m, 2H), 6.45 (bs, 1H), 4.68 (d, *J* = 19.2 Hz, 1H), 4.63 (d, *J* = 19.1 Hz, 1H), 4.59 (d, *J* = 19.4 Hz, 1H), 4.27-4.26 (t, *J* = 1.8 Hz, 2H), 4.21 (s, 5H), 4.18–4.17 (t, *J* = 1.8 Hz, 2H), 4.01 (d, *J* = 7.8 Hz, 2H), 3.41 (d, *J* = 19.2 Hz, 1H), 3.36 (d, *J* = 19.1 Hz, 1H), 3.32 (d, *J* = 19.4 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm), δ_C 153.1, 149.8, 149.5, 149.2, 148.4, 148.3, 148.0, 147.9, 147.5, 147.4 (2C), 147.1, 146.9, 146.6, 136.0, 134.6, 123.4, 108.0, 98.4, 68.73 (5C), 68.33, (2C), 68.2 (2C), 51.2, 42.7, 41.7, 40.6; IR (ATR), *v* 1545, 1515, 1465, 1290, 1245, 1130, 1105, 995, 810 cm^{-1}; UV-Vis, λ_{max} ($CHCl_3$:MeOH = 1:1 *v/v*) 250, 280, 370 nm; Elemental analysis: calculated for $C_{32}H_{23}FeN$: C (80.51%), H (4.86%), N (2.93%); found: C (80.71%), H (4.72%), N (3.04%); APCI-MS: calcd. for $C_{32}H_{23}FeN$ $[M]^+$ = 477.38, found: m/z 477.36. R_f (SiO_2; CH_2Cl_2/hexane, 95:5 *v*/*v*) = 0.82

(*E*)-*N*-(ferrocenylmethyl)sumanene (9)

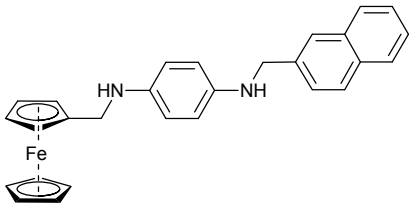


9

A solution of formylferrocene (3.0 mg, 0.0140 mmol), aminosumanene (3.9 mg, 0.0140 mmol) and formic acid (85%; 20 µL) in THF/methanol solvent system (1:2 *v/v*)[8] (2.5 mL) was refluxed for 6 h. The reaction mixture was diluted with CH_2Cl_2 (15 mL), washed saturated $NaHCO_3$ (2 mL), water (2 mL), brine (2 mL), dried over Na_2SO_4, filtered and evaporated in vacuum. The resultant residue was purified by using a recycling GPC (chloroform as eluting solvent) to give (*E*)-*N*-(ferrocenylmethyl)sumanene (**9**; 4.1 mg, 61%) as the orange solid.

Mp: 202 °C (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm), δ_H 8.56 (s, 1H), 7.13-7.09 (m, 4H), 6.96 (s, 1H), 4.80 (d, *J* = 19.9 Hz, 1H), 4.82-4.81 (t, *J* = 1.9 Hz, 2H), 4.72 (d, *J* = 19.6 Hz, 2H), 4.50 (t, *J* = 1.9 Hz, 2H), 4.25 (s, 5H), 3.56 (d, *J* = 19.9 Hz, 1H), 3.47 (d, *J* = 19.6 Hz, 1H), 3.42 (d, *J* = 19.6 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm), δ_C 162.1, 151.7, 149.5, 149.3, 149.2, 149.1, 149.0, 148.9, 148.7, 148.6, 148.5, 148.4 (2C),123.8, 123.6, 123.5 (2C), 123.1, 119.3, 71.5, 69.6 (5C), 69.3 (2C), 69.2 (2C), 41.9, 41.8, 41.5; IR (ATR), *v* 1630, 1520, 1465, 1395, 1295, 1255, 1120, 1005, 815 cm^{-1}; UV-Vis, λ_{max} ($CHCl_3$:MeOH = 1:1 *v/v*) 240, 280, 375 nm; Elemental analysis: calculated for $C_{32}H_{21}FeN$: C (80.85%), H (4.45%), N (2.95%); found: C (80.99%), H (4.28%), N (3.09%); APCI-MS: calcd. for $C_{32}H_{21}FeN$ $[M]^+$ = 475.36, found: m/z 475.35. R_f (SiO_2; CH_2Cl_2/hexane, 90:10 *v*/*v*) = 0.85

***N*^{1}-(ferrocenylmethyl)-*N*^{4}-(naphthalen-2-ylmethyl)benzene-1,4-diamine (10)**



A solution of *N*-(ferrocenylmethyl)benzene-1,4-diamine (**Fc-3**; 5.6 mg, 0.0082 mmol), 2-napthaldehyde (2.9 mg, 0.0183 mmol) and formic acid (85%; 30 µL) in MeOH[6] (2.0 mL) was stirred at 27 °C for 24 h. Then, sodium borohydride (1.2 mg, 0.0248 mmol) was added and the mixture was further stirred at 27 °C for 3 h. CH_2Cl_2 (20 mL) was added and the organic layer was washed with saturated $NaHCO_3$ (2 mL), water (2 mL), brine (2 mL), dried with Na_2SO_4, filtered, and the solvent was removed in vacuum. The resultant residue was purified by PTLC (SiO_2; CH_2Cl_2) to give *N*^{1}-(ferrocenylmethyl)-*N*^{4}-(naphthalen-2-ylmethyl)benzene-1,4-diamine (**10**; 5.5 mg, 67% yield) as the light-orange solid.

Mp: 110 °C (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz, ppm), δ_H 7.86-7.80 (m, 4H), 7.52-7.45 (m, 3H), 6.66-6.60 (m, 4H), 4.87 (bs, 1H), 4.44-4.455 (bm, 2H), 4.24-4.23 (t, *J* = 1.9 Hz, 2H), 4.17 (s, 5H), 4.13–4.12 (t, *J* = 1.9 Hz, 2H), 3.90-3.89 (bm, 2H), 3.64 (bs, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm), δ_C 141.2, 141.0, 137.7, 132.9, 128.4, 128.1, 128.0, 127.9, 126.3 (2C), 126.2 (2C), 125.8, 125.4, 115.0 (2C), 87.13, 68.6 (5C), 68.3 (2C), 67.9 (2C), 49.9, 44.9; IR (ATR), *v* 1555, 1515, 1460, 1295, 1250, 1130, 1095, 1005, 810, 745 cm^{-1}; UV-Vis, λ_{max} ($CHCl_3$:MeOH = 1:1 *v/v*) 260, 265, 270, 380 nm; Elemental analysis: calculated for $C_{28}H_{26}FeN_2$: C (75.34%), H (5.87%), N (6.28%); found: C (75.83%), H (5.26%), N (6.36%); APCI-MS: calcd. for $C_{28}H_{26}FeN_2$ $[M]^+$ = 446.36, found: m/z 446.35; R_f (SiO_2; CH_2Cl_2) = 0.31.

S1.3 Florescence spectra titration

The 0.5 mM stock solution of the sumanene-ferrocene conjugate and 2 mM stock solution of Cs^+ (in the form of CsCl) in the solvent system ($CHCl_3$:MeOH = 1/1 *v/v*) were prepared. The concentration of sumanene-ferrocene conjugate was kept constant (0.1 mM), whilst the samples varied in the molar equivalent of Cs^+ added (eq = 0, 0.5, 1, 2, 4, 6 or 12).

S1.4 ^{1}H NMR titration

The 3.0 mM stock solution of the sumanene-ferrocene conjugate and 9 mM stock solution of Cs^+ (in the form of CsCl) in the solvent system ($CDCl_3$:CD_3OD = 1/1 *v/v*) were prepared. The concentration of sumanene-ferrocene conjugate was kept constant (1.5 mM), whilst the samples varied in the molar equivalent of Cs^+ added (eq = 0, 0.5, 1, 2, 3).

S1.5 Cyclic voltammetry

Measurements were conducted in CH_2Cl_2 with tetrabutylammonium perchlorate (TBAP; 0.1 M) as a supporting electrolyte, with a sumanene-ferrocene conjugate concentration of 0.5 mM and a scan rate of 0.05 V/s. The voltammograms were referenced against the ferrocene/ferrocenium couple (Fc/Fc^+). The glassy carbon electrode (GCE) played a role of the working electrode, Ag/AgCl electrode was used as the reference electrode and a platinum wire was used as the counter electrode. The working electrode was polished with Al_2O_3 slurry on a wet pad before the measurement. After the polishing step, the electrode was rinsed with the pure solvent.

For the Cs^+ recognition tests, cyclic voltammograms were measured in the solvent system ($CHCl_3$:MeOH = 1/1 *v/v*) with TBAP as a supporting electrolyte (0.1 M). Two tests were run: (1) with the solution of pristine sumanene-ferrocene conjugate (0.5 mM), (2) with the solution of sumanene-ferrocene conjugate (0.5 mM) containing 12 molar equivalents of Cs^+ (in the form of its corresponding chloride).

S2. NMR spectra

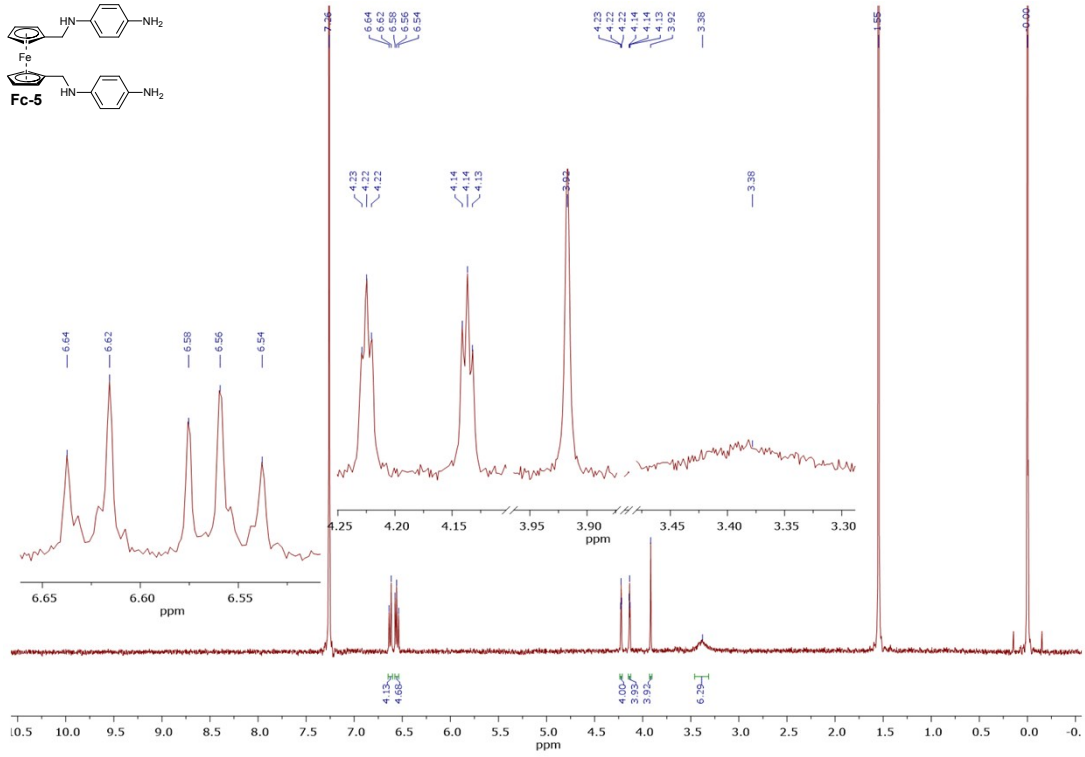


Fig. S1. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **Fc-3**.

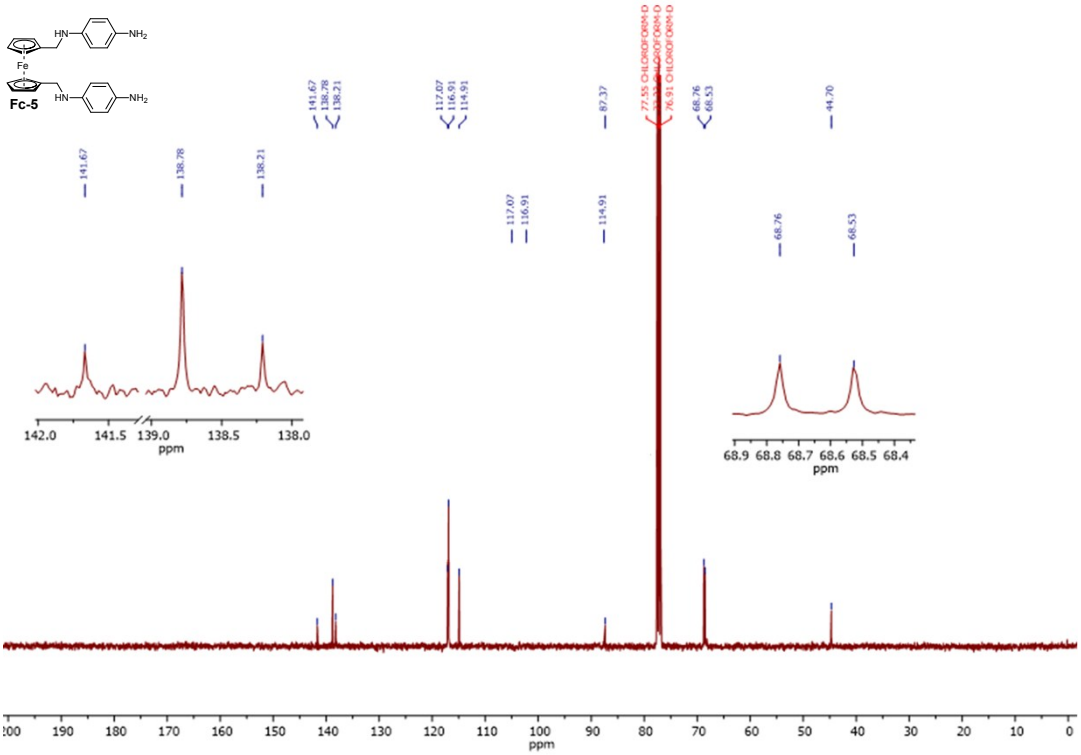


Fig. S2. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **Fc-3**.

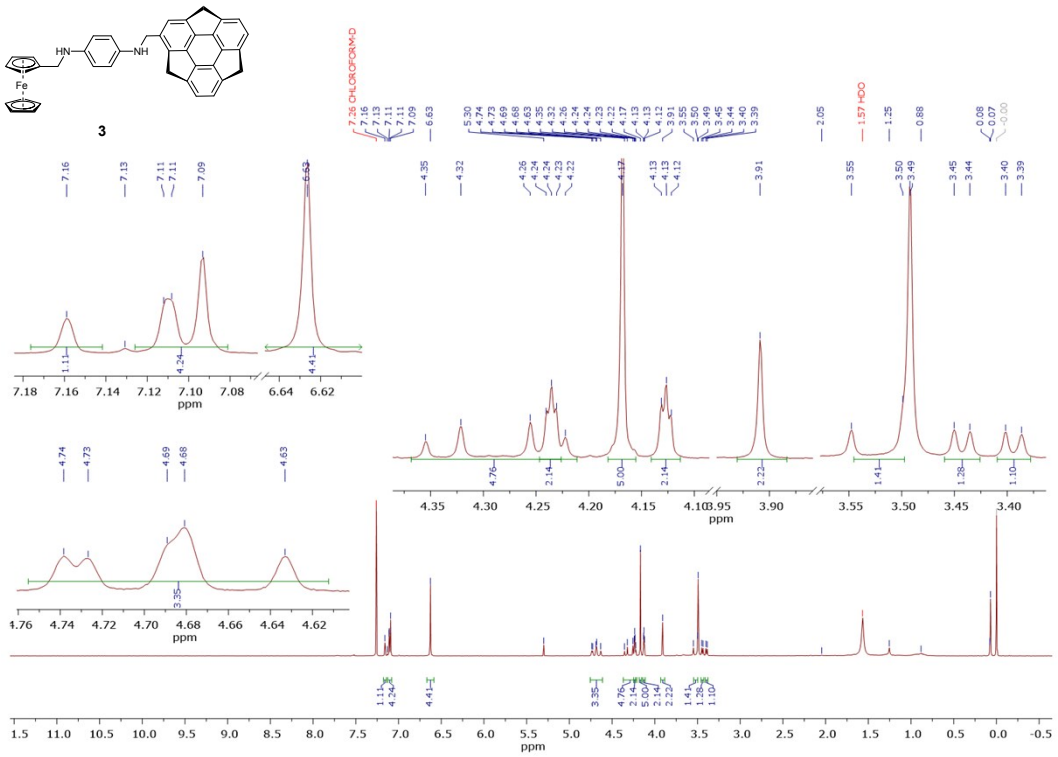


Fig. S3. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **3**.

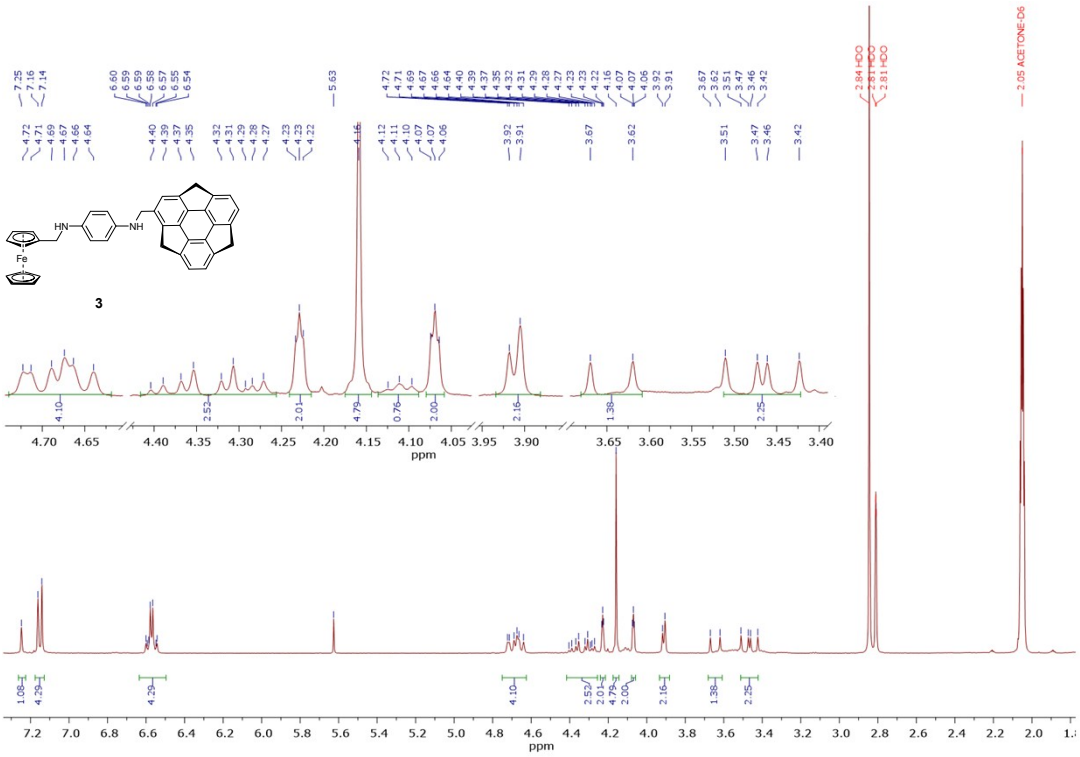


Fig. S4. ^{1}H NMR ($(CD_3)_2CO$, 400 MHz) spectrum of compound **3**.

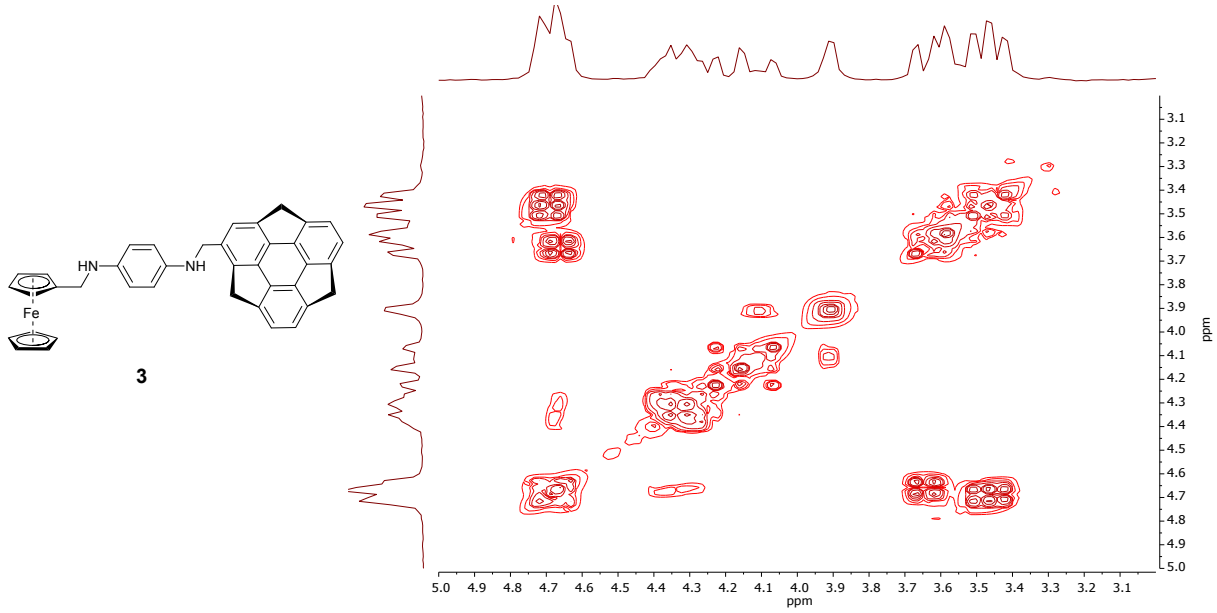


Fig. S5. Inset of ^{1}H-^{1}H COSY NMR ($(CD_3)_2CO$, 400 MHz) spectrum of compound **3**.

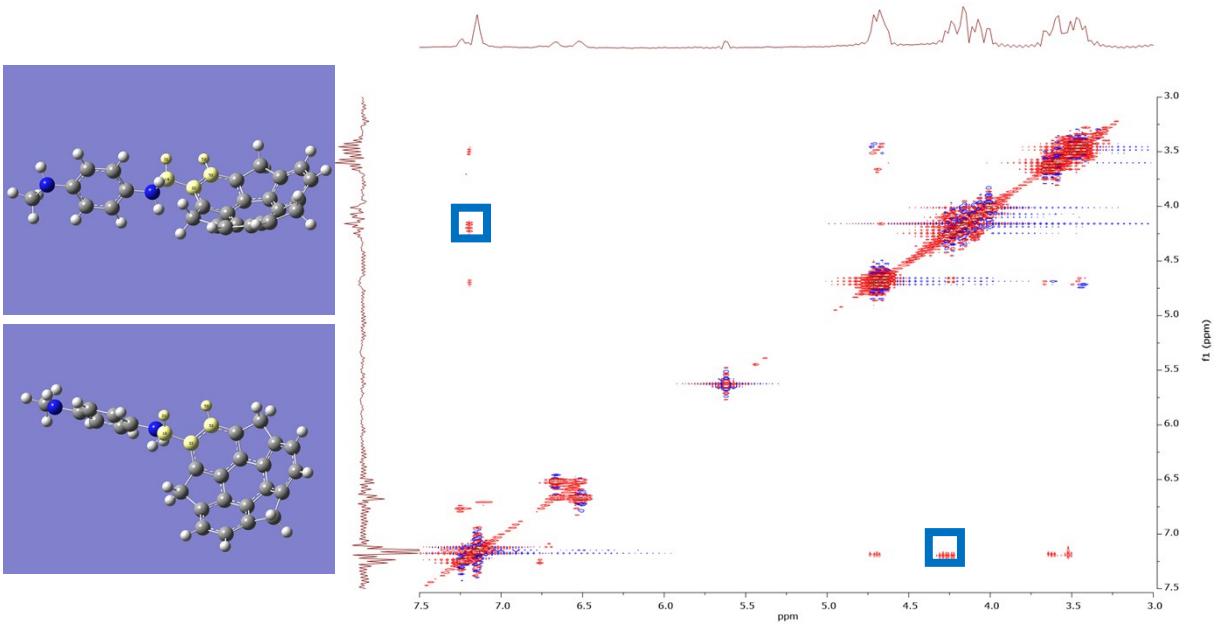
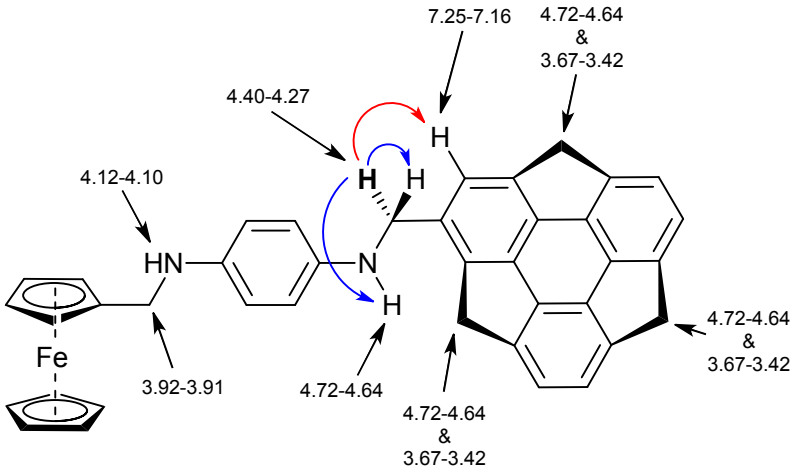


Fig. S6. ^{1}H-^{1}H TOCSY NMR ($(CD_3)_2CO$, 400 MHz) spectrum of compound **3** together with the representation of the optimized partial structure of compound **3**.[10] The crucial cross-correlations are marked in blue.

Table S1. Graphical representation and summary of the data on the crucial cross-correlations observed in the ^{1}H-^{1}H COSY (marked blue) and ^{1}H-^{1}H TOCSY (marked red) spectra of compound **3** (spectra recorded in $(CD_3)_2CO$). The chemical shifts for the respective protons are also presented. Cross-correlation between C**H$_2$**-sumanene (4.40-4.27 ppm) and **H**-Ar of sumanene (7.25-7.16 ppm) observed in the ^{1}H-^{1}H TOCSY experiment, confirmed that the C**H$_2$**-sumanene diastereotopic protons and **H**-Ar of sumanene are included in the same spin system (U-shaped system, see the graphical representation in Fig. S6). This feature stands for the signal multiplicity of C**H$_2$**-sumanene (multiplet, 4.40-4.27 ppm).



Chemical shift [ppm] and peak assignment		7.25-7.16 (m) Ar (sumanene)	4.72-4.64 (m) benzylic exo + NH-CH$_2$-sumanene	4.40-4.27 (m) C**H$_2$**-sumanene	4.12-4.10 (t) Fc-CH$_2$-N**H**	3.92-3.91 (d) Fc-C**H$_2$**	3.67-3.42 (3 x d) benzylic endo
7.25-7.16 (m)	Ar (sumanene)			**X**			
4.72-4.64 (m)	benzylic exo + N**H**-CH$_2$-sumanene			**X**			**X**
4.40-4.27 (m)	C**H$_2$**-sumanene	**X**	**X**				
4.12-4.10 (t)	Fc-CH$_2$-N**H**					**X**	
3.92-3.91 (d)	Fc-C**H$_2$**				**X**		
3.67-3.42 (3 x d)	benzylic endo		**X**				

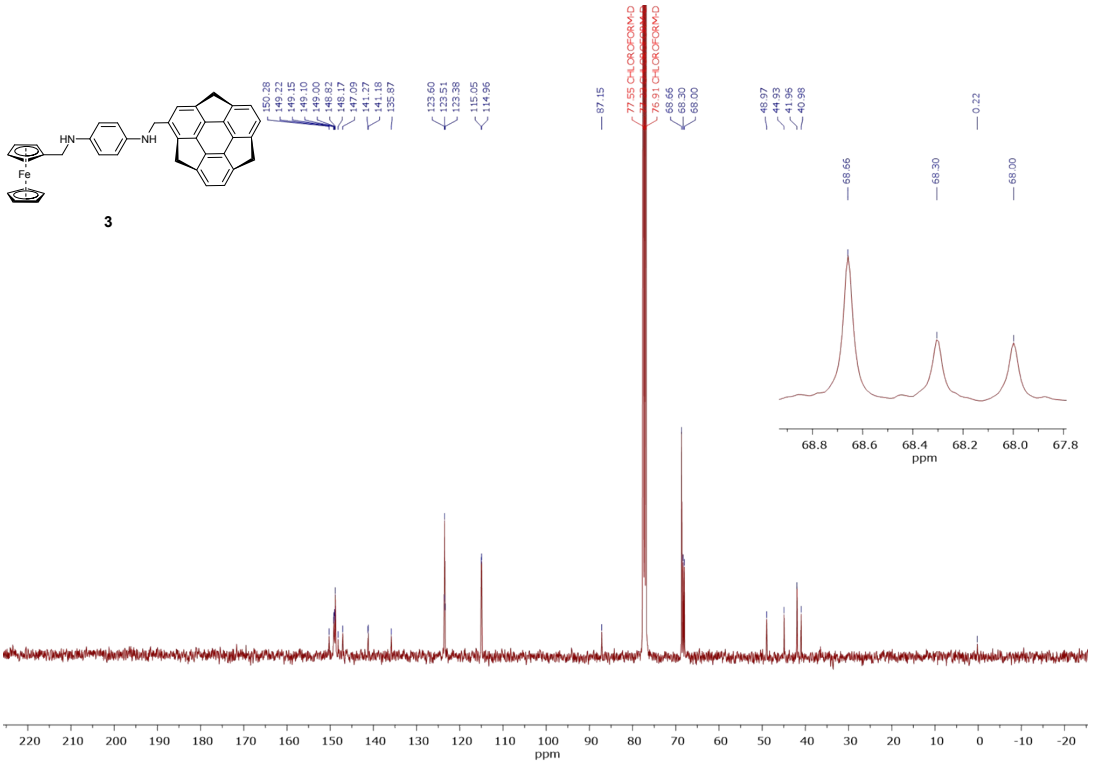


Fig. S7. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **3**.

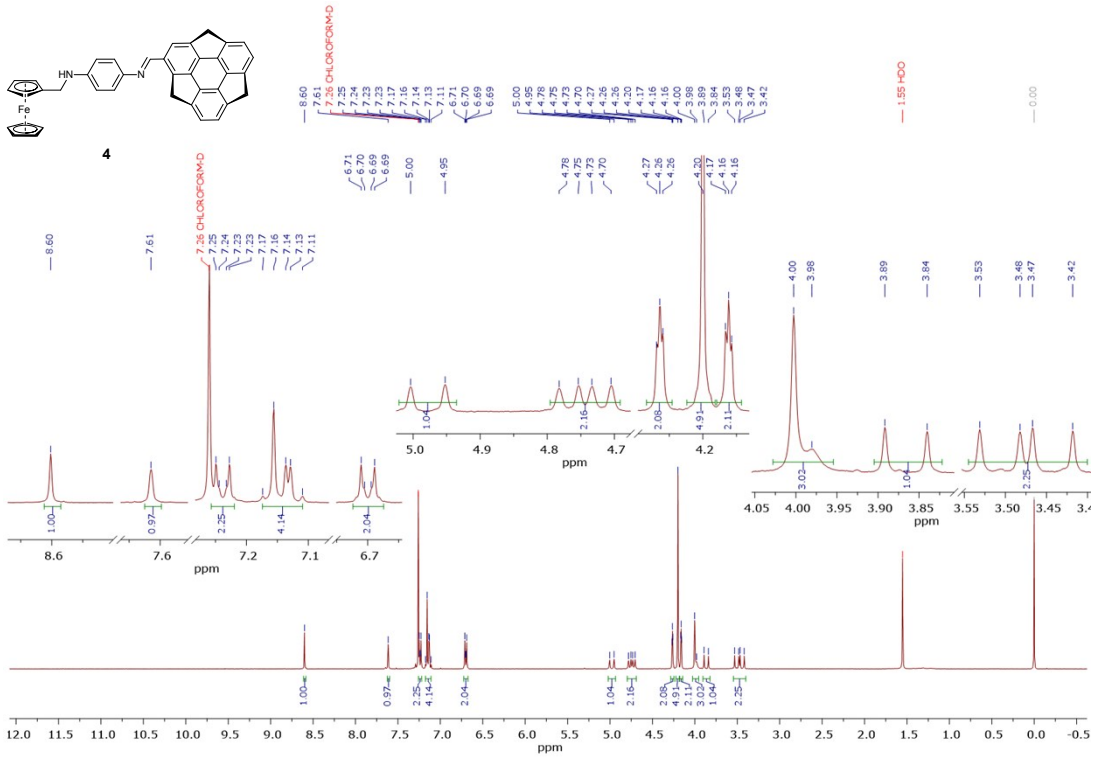


Fig. S8. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **4**.

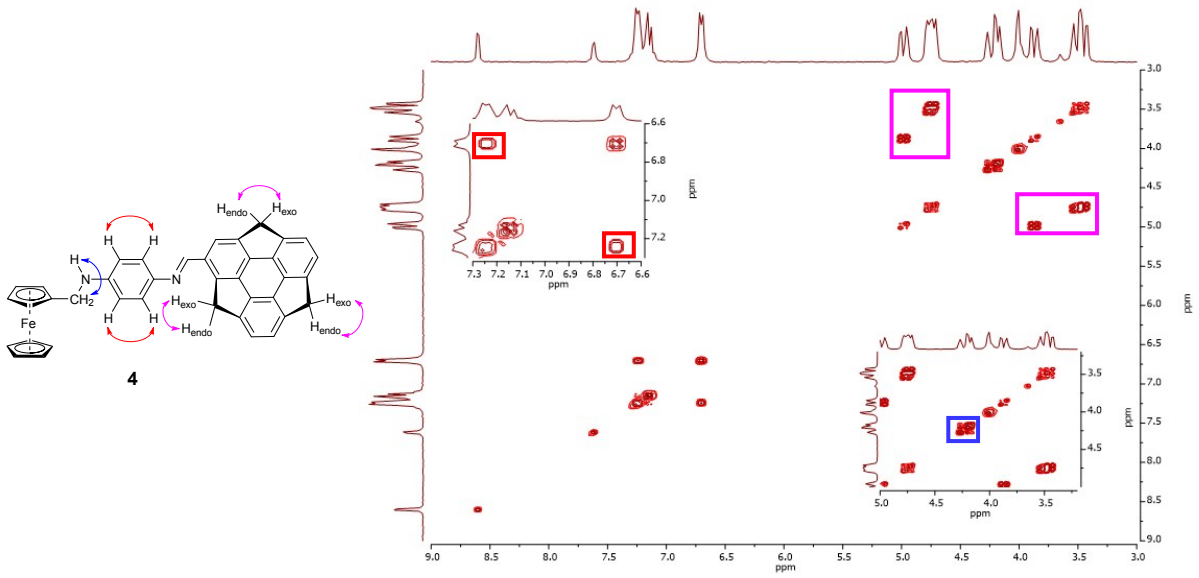


Fig. S9. ^{1}H-^{1}H COSY NMR ($CDCl_3$, 400 MHz) spectrum of compound **4**. The crucial cross correlations are also marked.

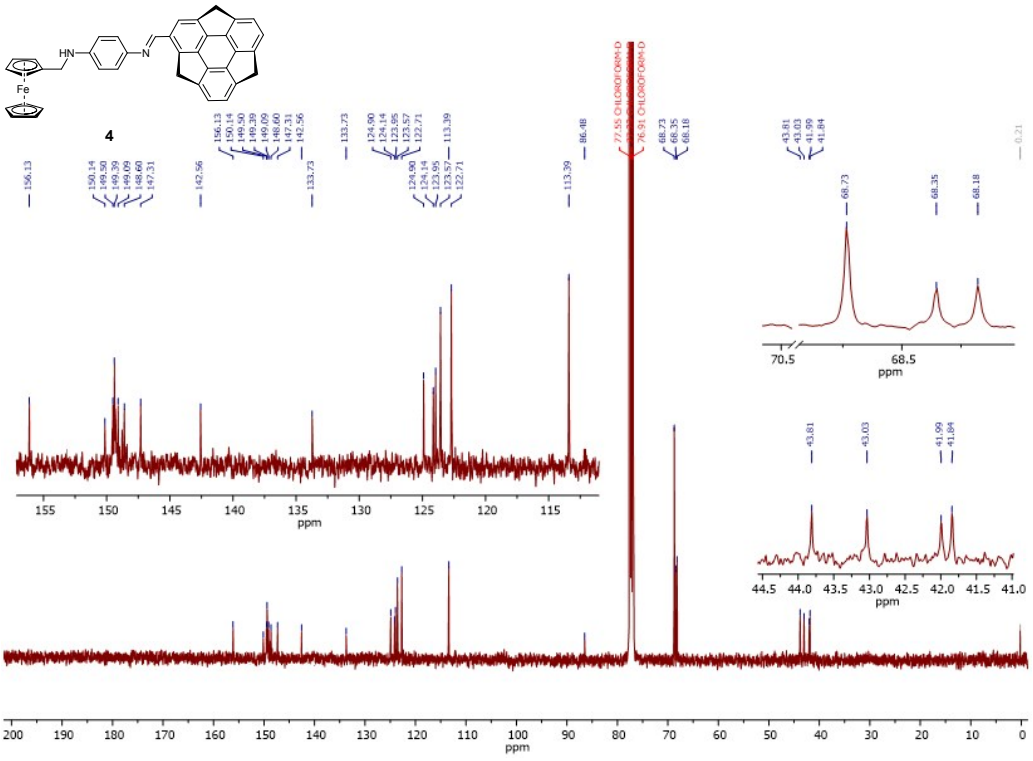


Fig. S10. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **4**.

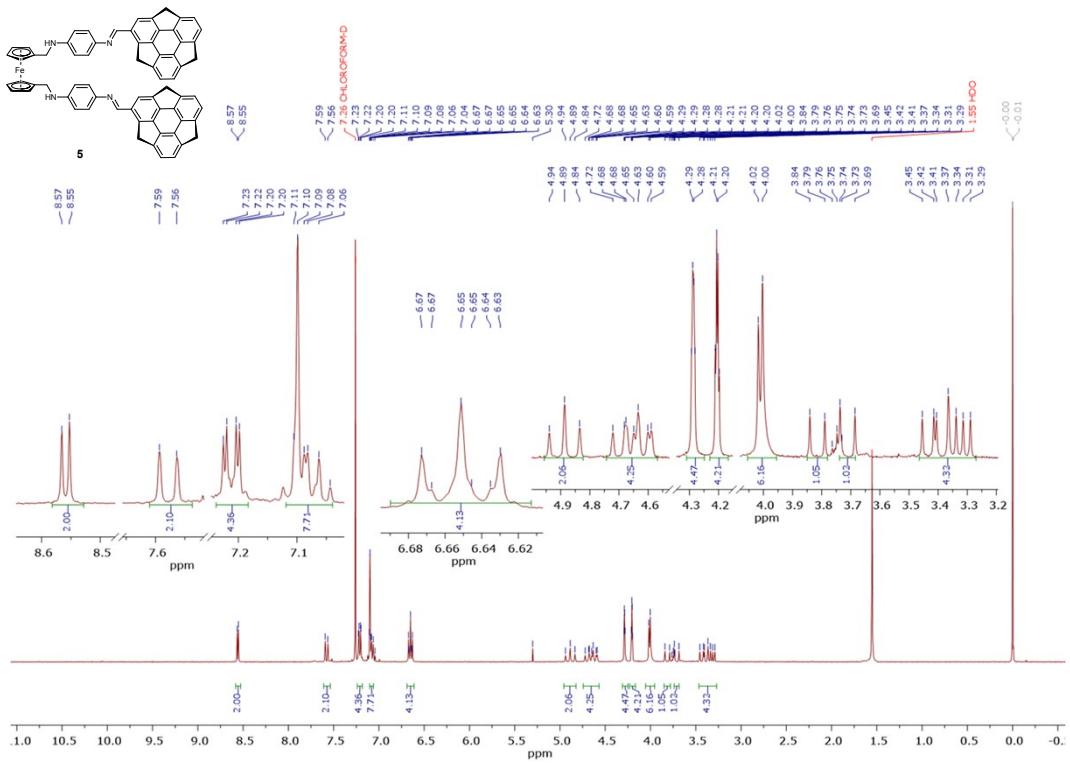


Fig. S11. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **5**.

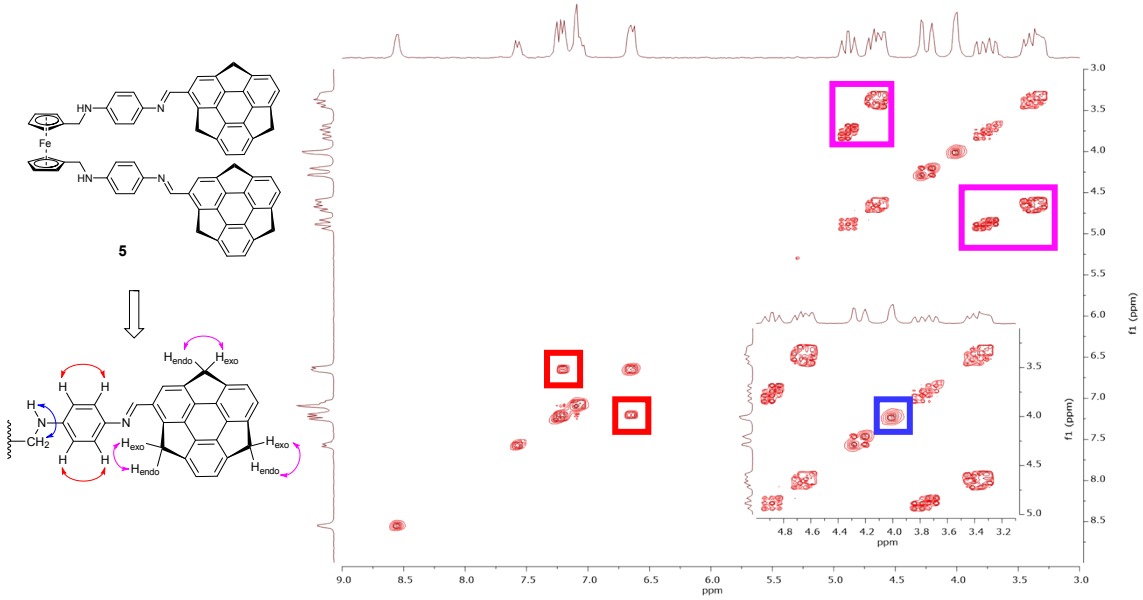


Fig. S12. ^{1}H-^{1}H COSY NMR ($CDCl_3$, 400 MHz) spectrum of compound **5**. The crucial cross correlations are also marked.

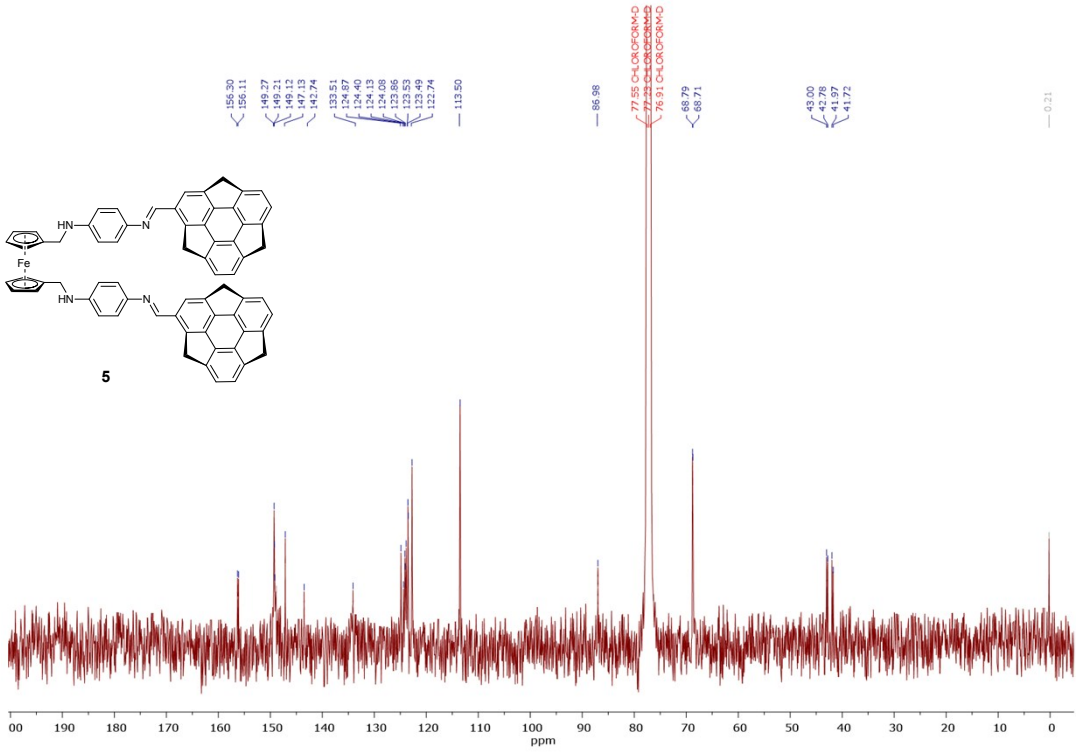


Fig. S13. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **5**.

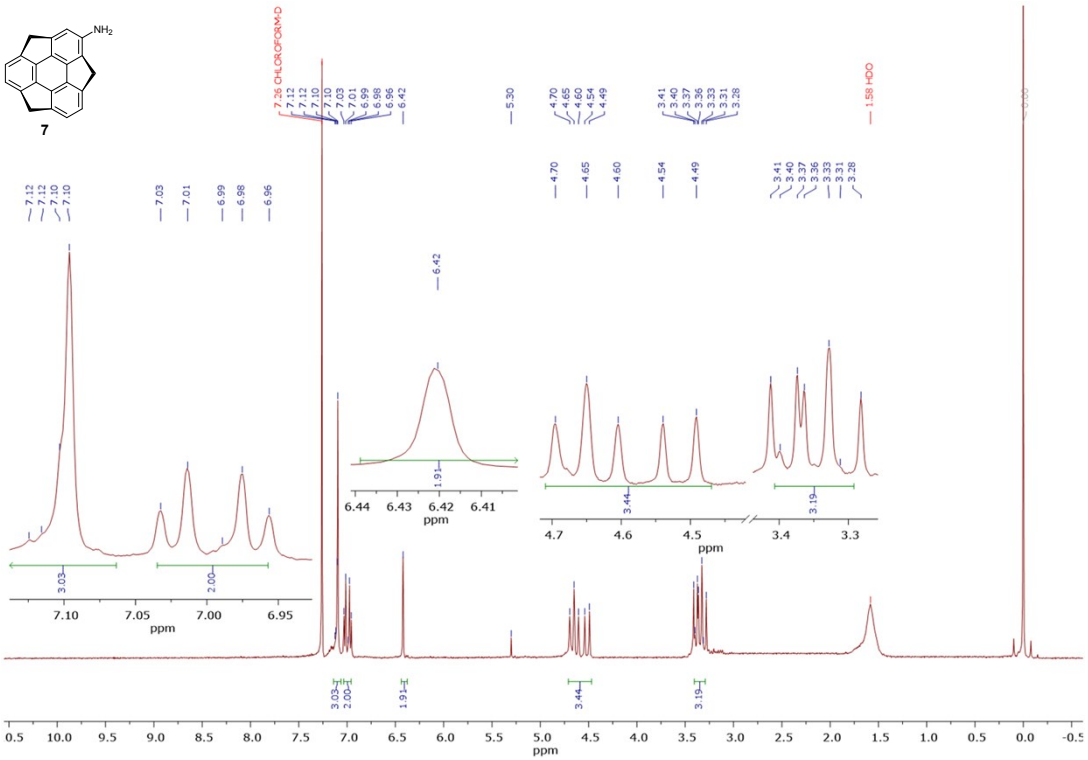


Fig. S14. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **7**.

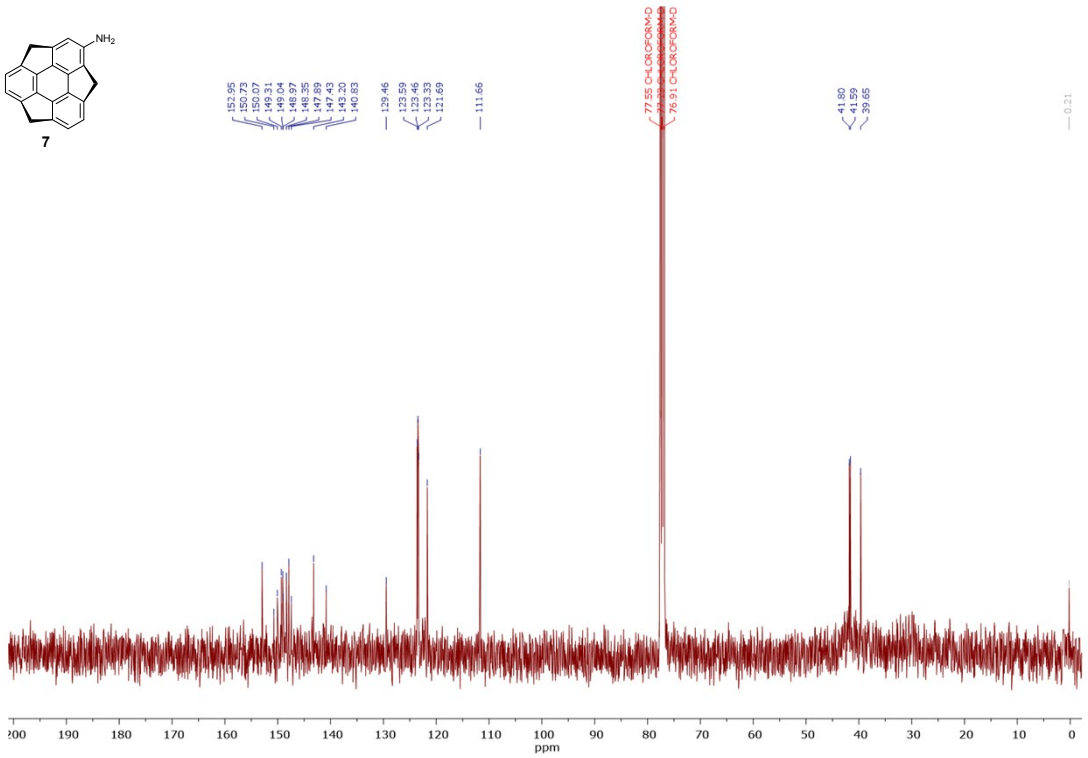


Fig. S15. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **7**.

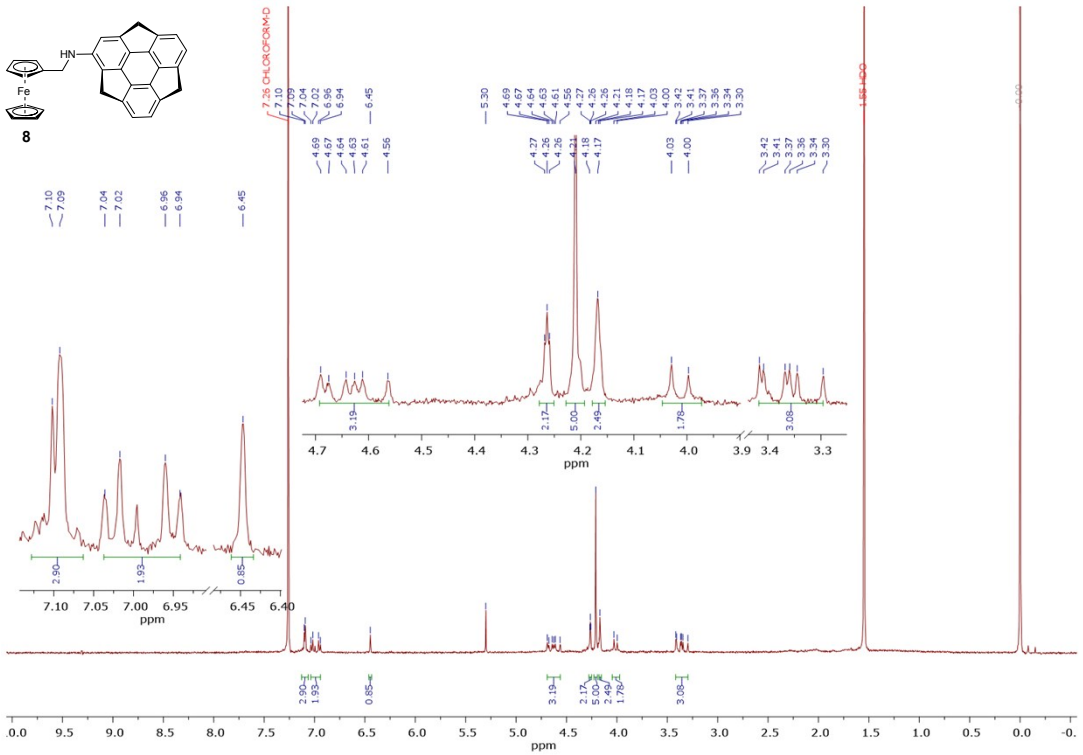


Fig. S16. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **8**.

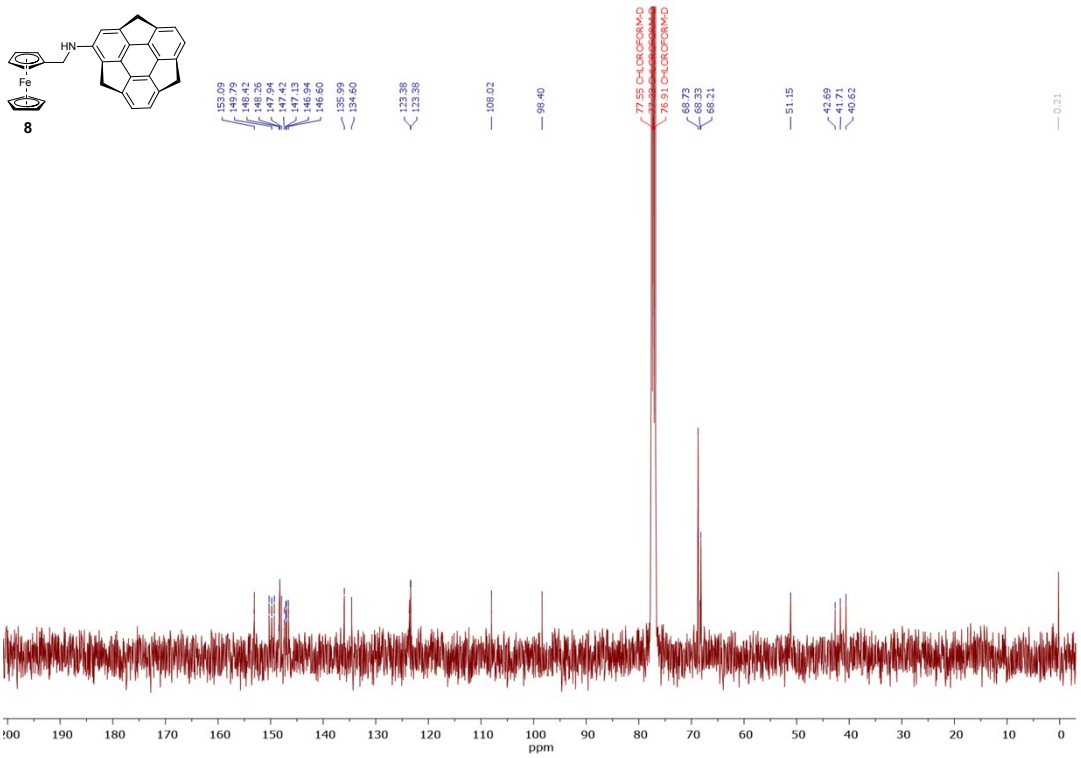


Fig. S17. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **8**.

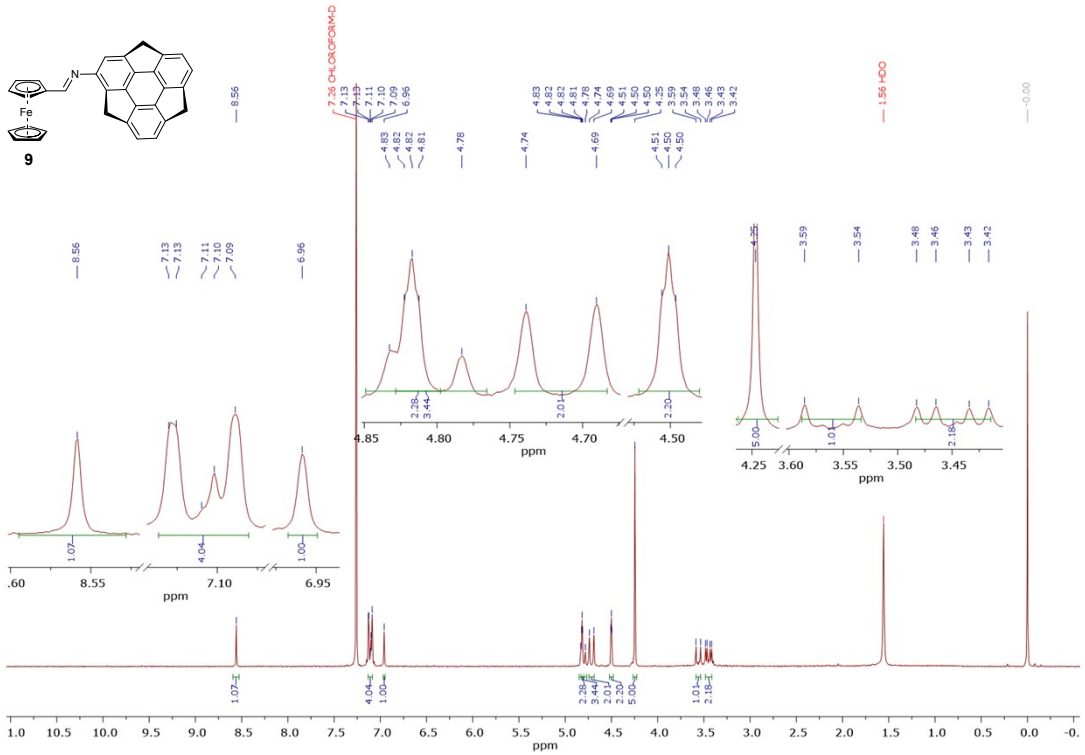


Fig. S18. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **9**.

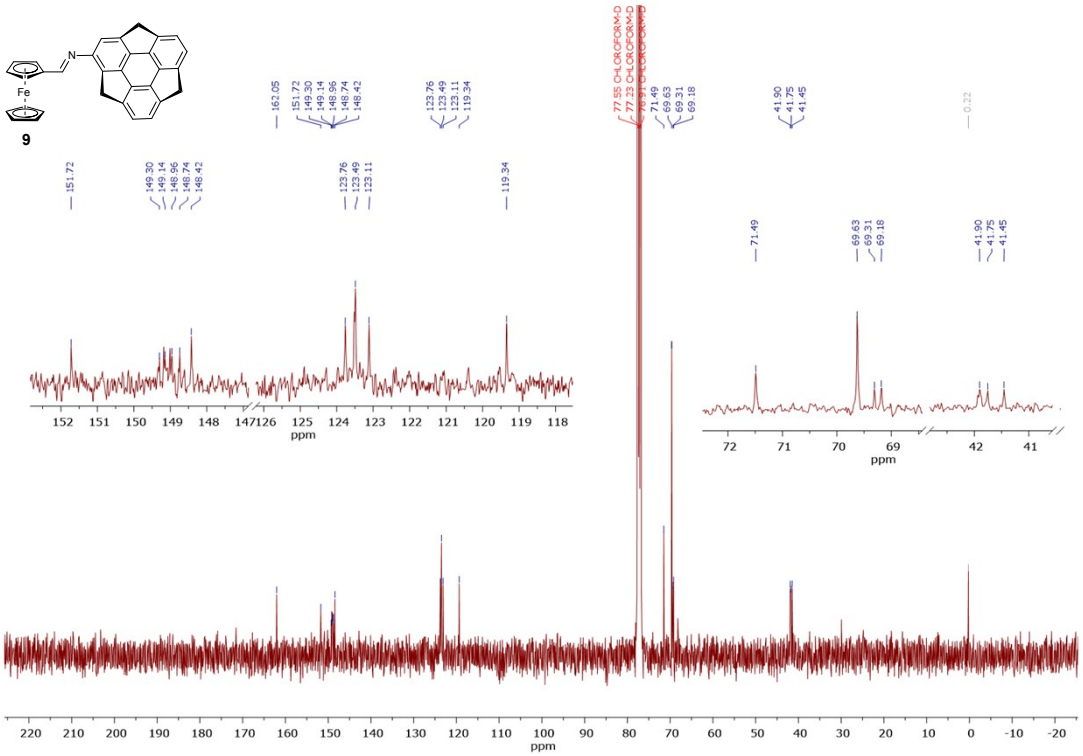


Fig. S19. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **9**.

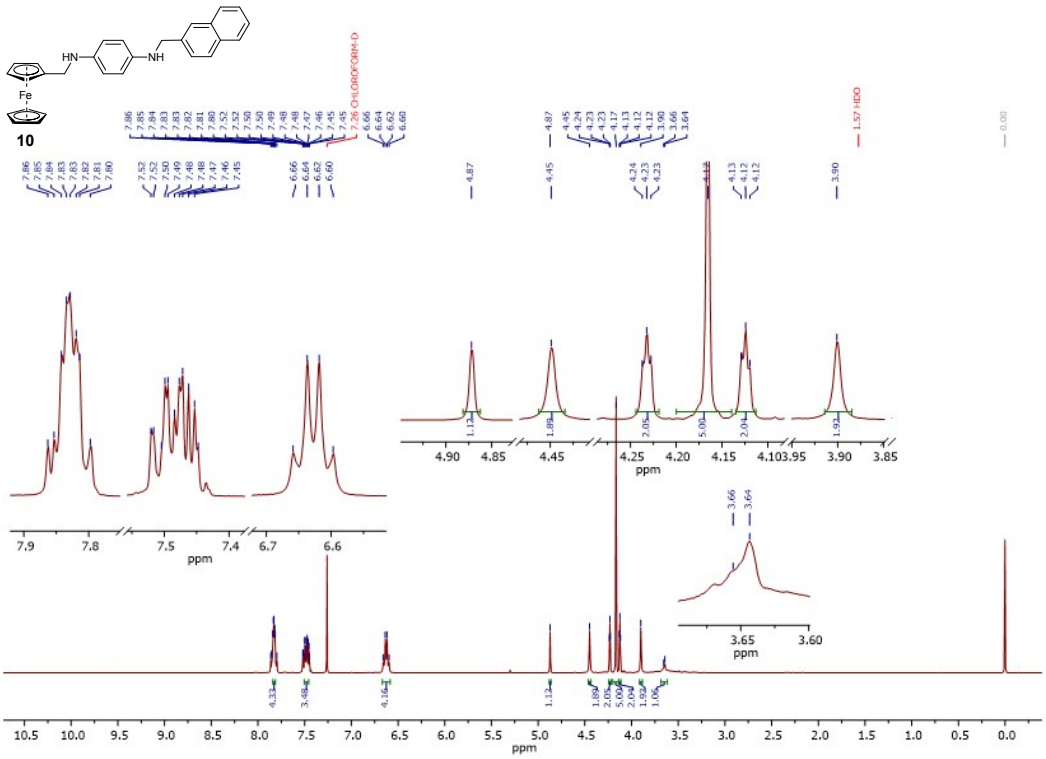


Fig. S20. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of compound **10**.

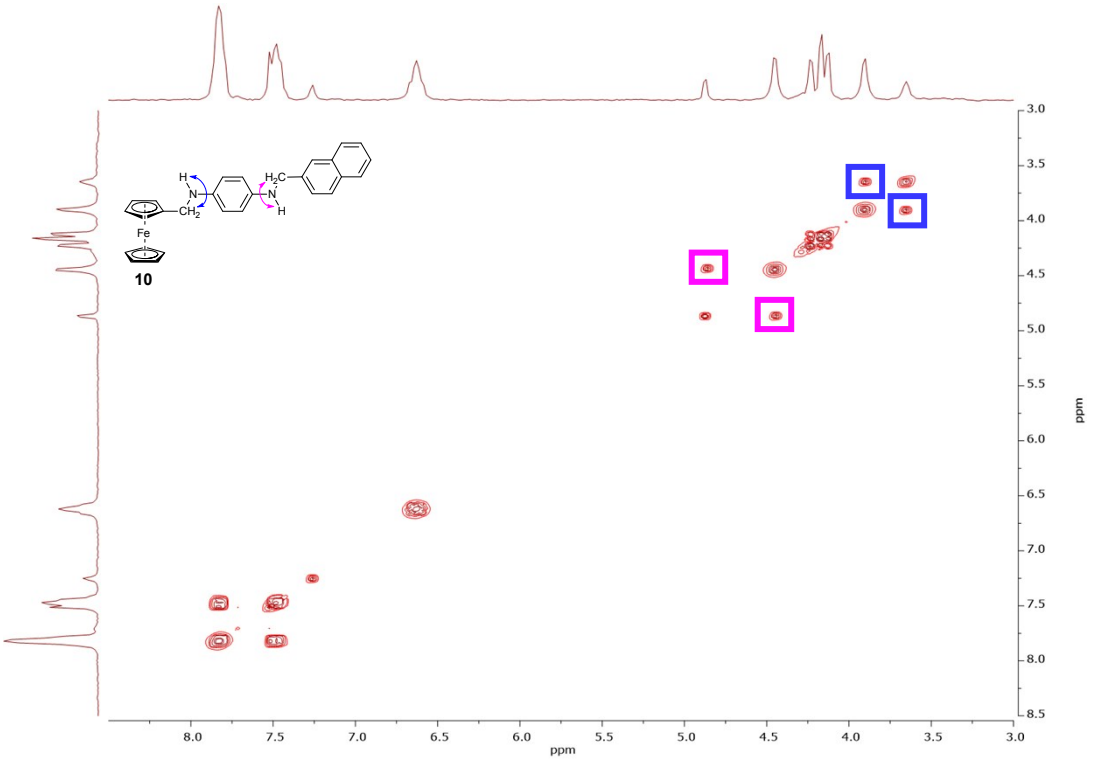


Fig. S21. ^{1}H-^{1}H COSY NMR ($CDCl_3$, 400 MHz) spectrum of compound **10**. The crucial cross correlations are also marked.

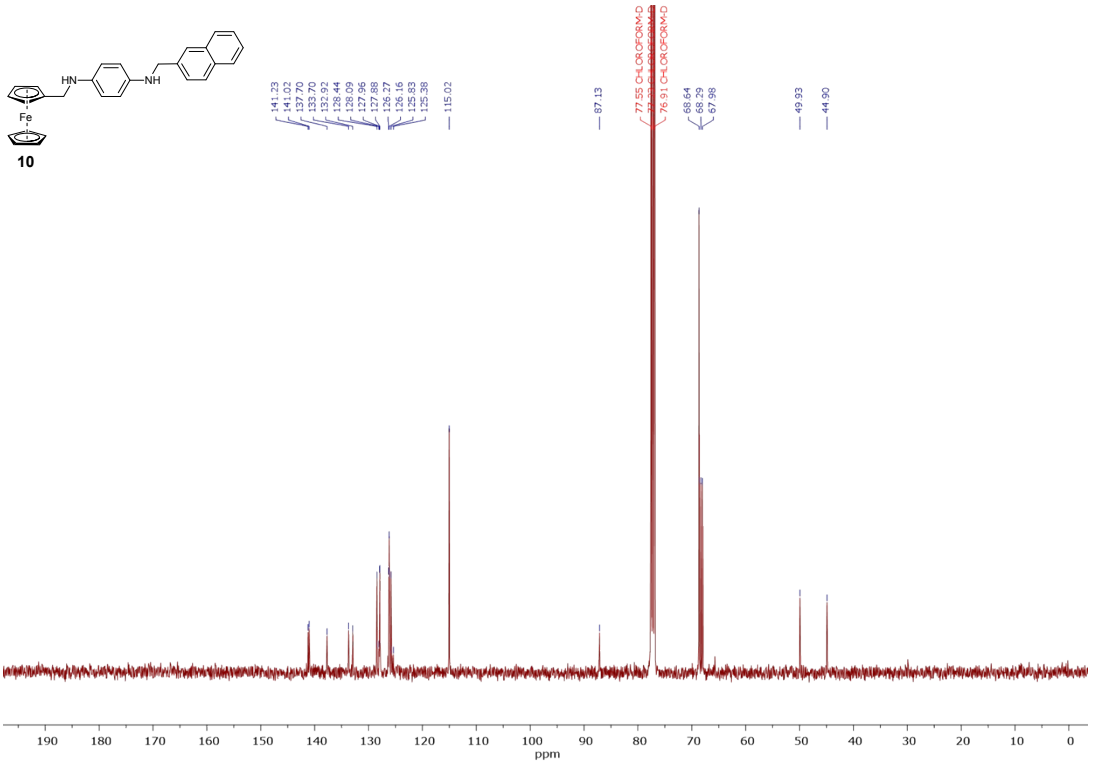


Fig. S22. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of compound **10**.

S3. IR spectra

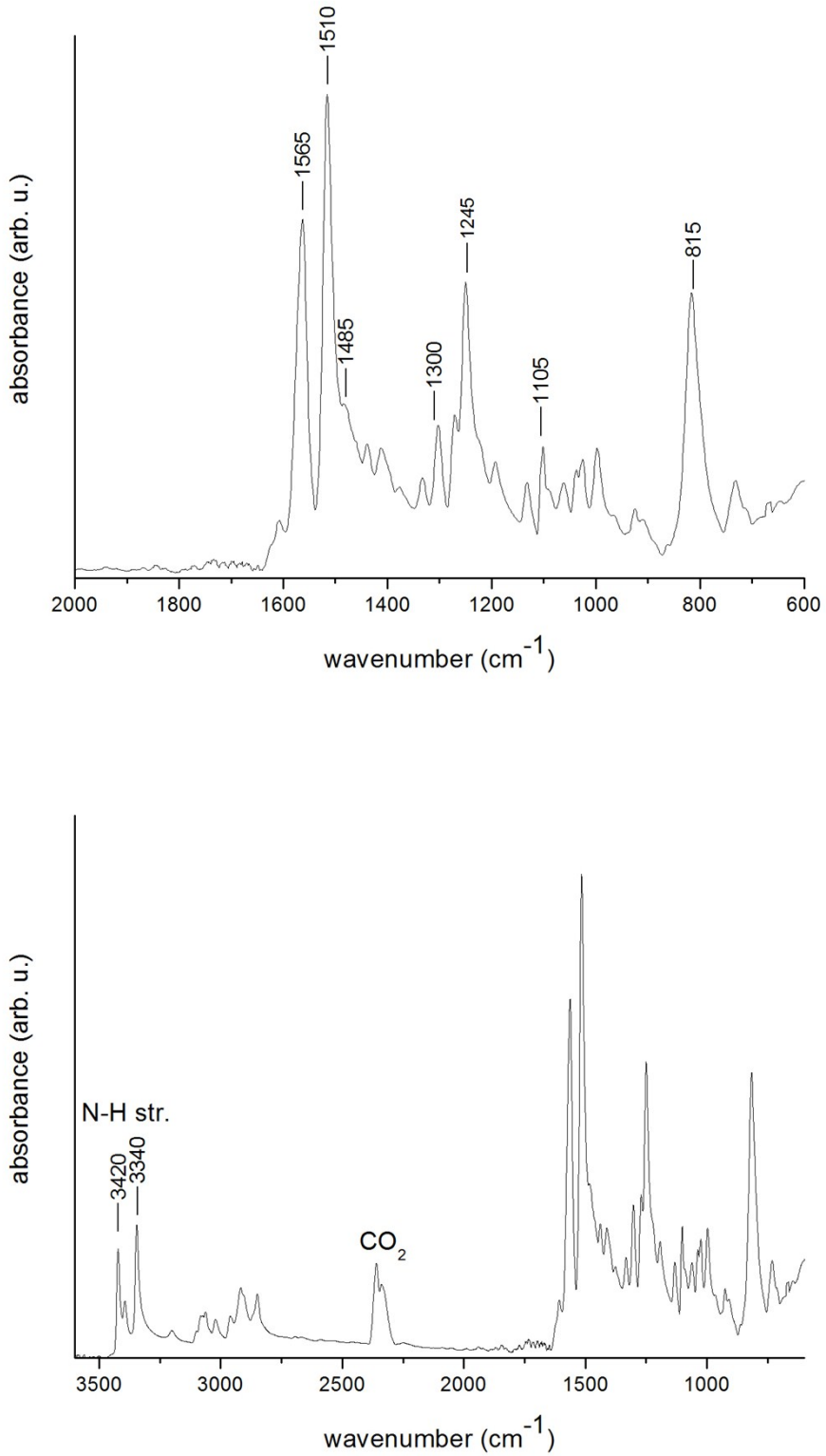


Fig. S23. IR (ATR) spectrum of compound **Fc-5** in the wavenumber range of 2000-600 cm^{-1} (**top**) and in the range of 3600-600 cm^{-1} showing NH stretching vibrations (**bottom**).

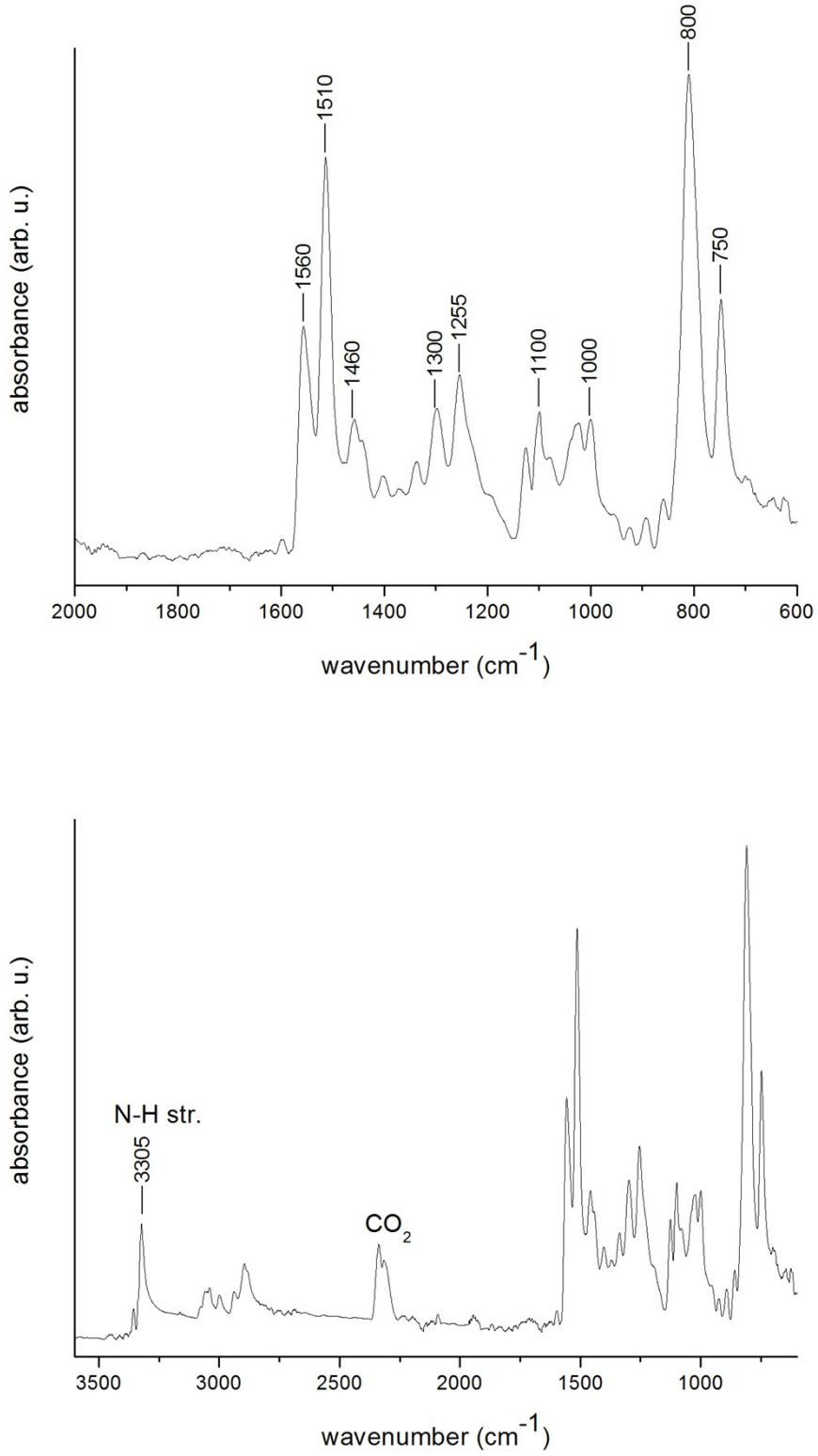


Fig. S24. IR (ATR) spectrum of compound **3** in the wavenumber range of 2000-600 cm^{-1} (**top**) and in the range of 3600-600 cm^{-1} showing NH stretching vibrations (**bottom**).

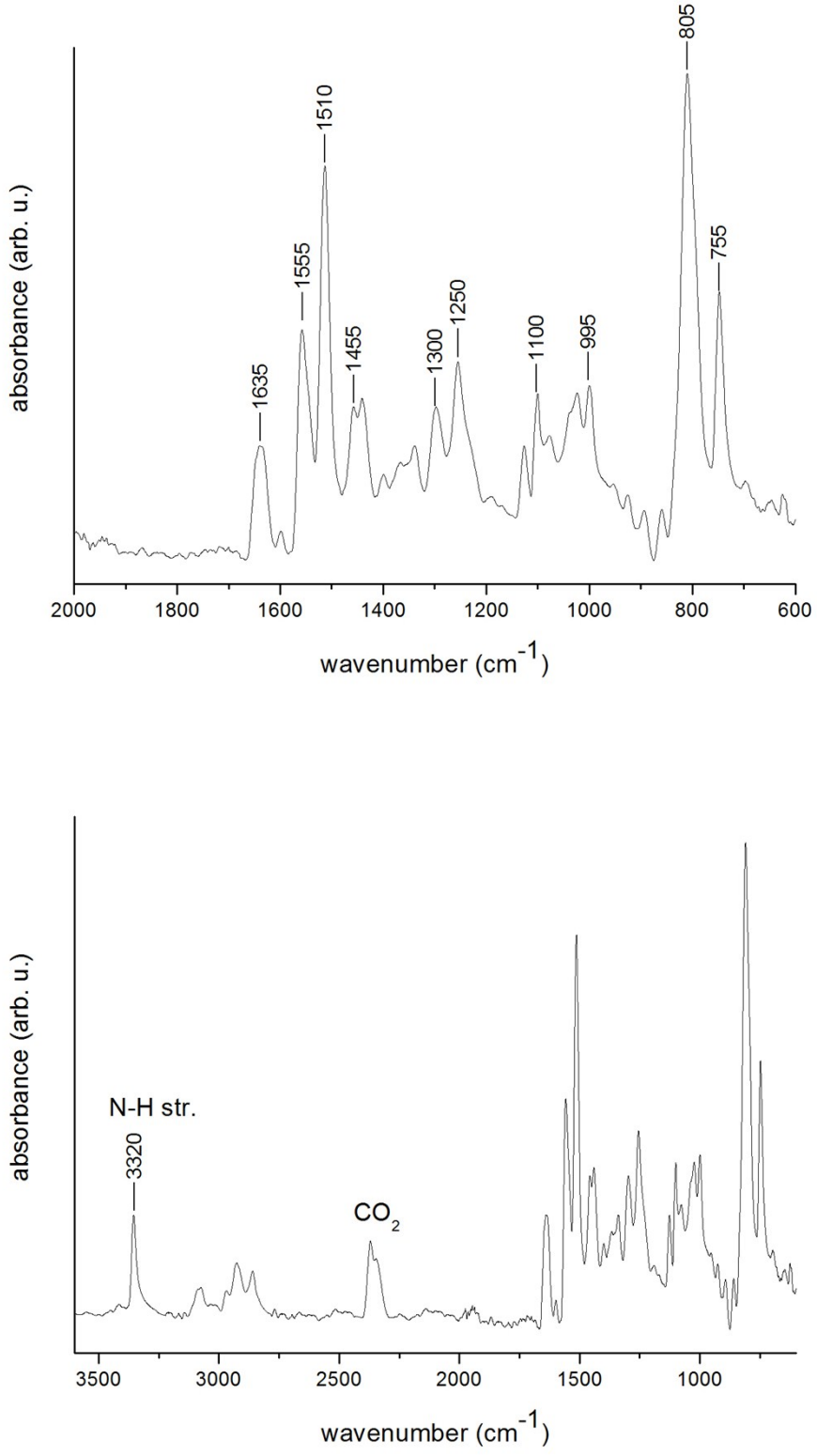


Fig. S25. IR (ATR) spectrum of compound **4** in the wavenumber range of 2000-600 cm^{-1} (**top**) and in the range of 3600-600 cm^{-1} showing NH stretching vibrations (**bottom**).

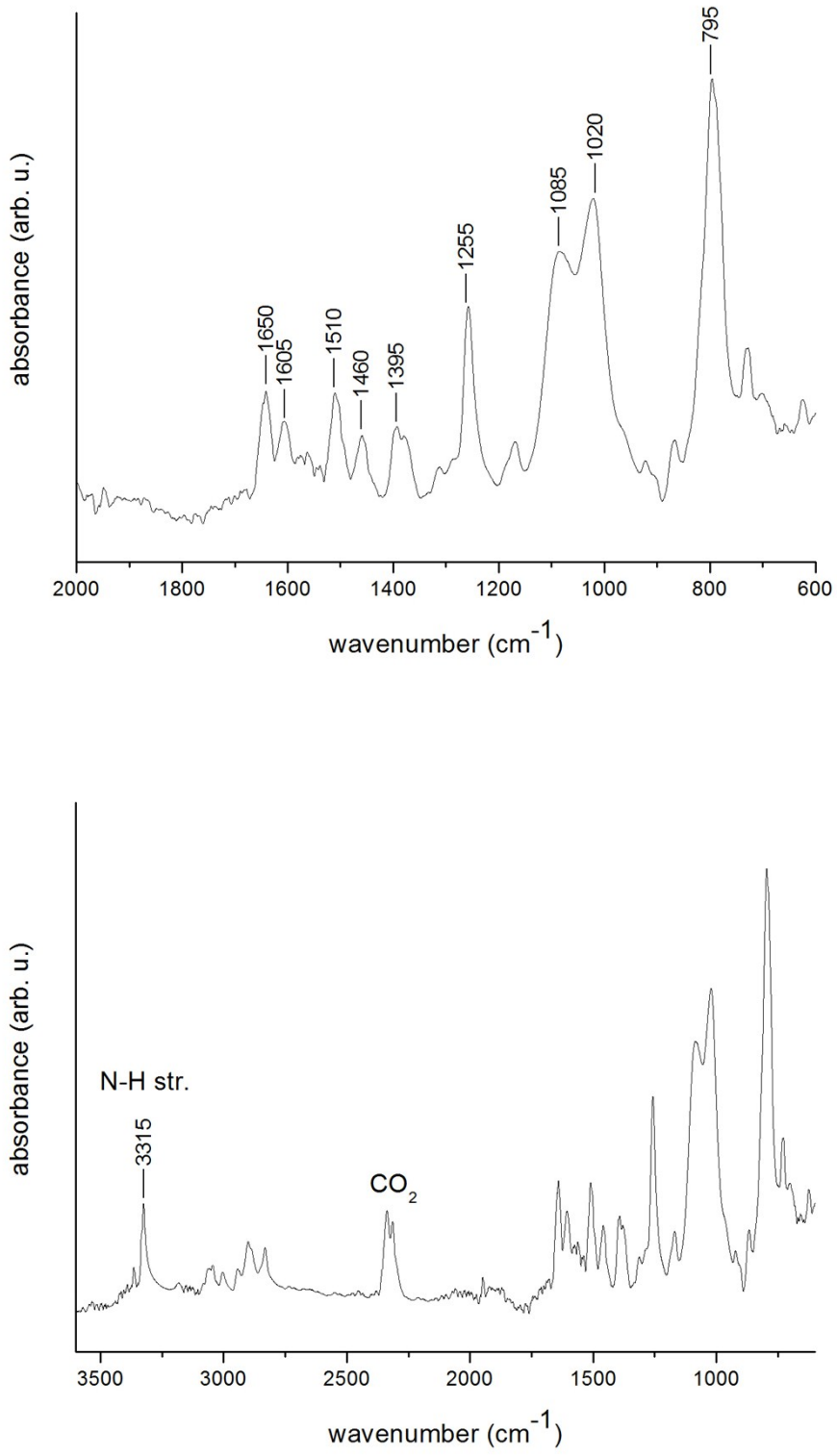


Fig. S26. IR (ATR) spectrum of compound **5** in the wavenumber range of 2000-600 cm^{-1} (**top**) and in the range of 3600-600 cm^{-1} showing NH stretching vibrations (**bottom**).

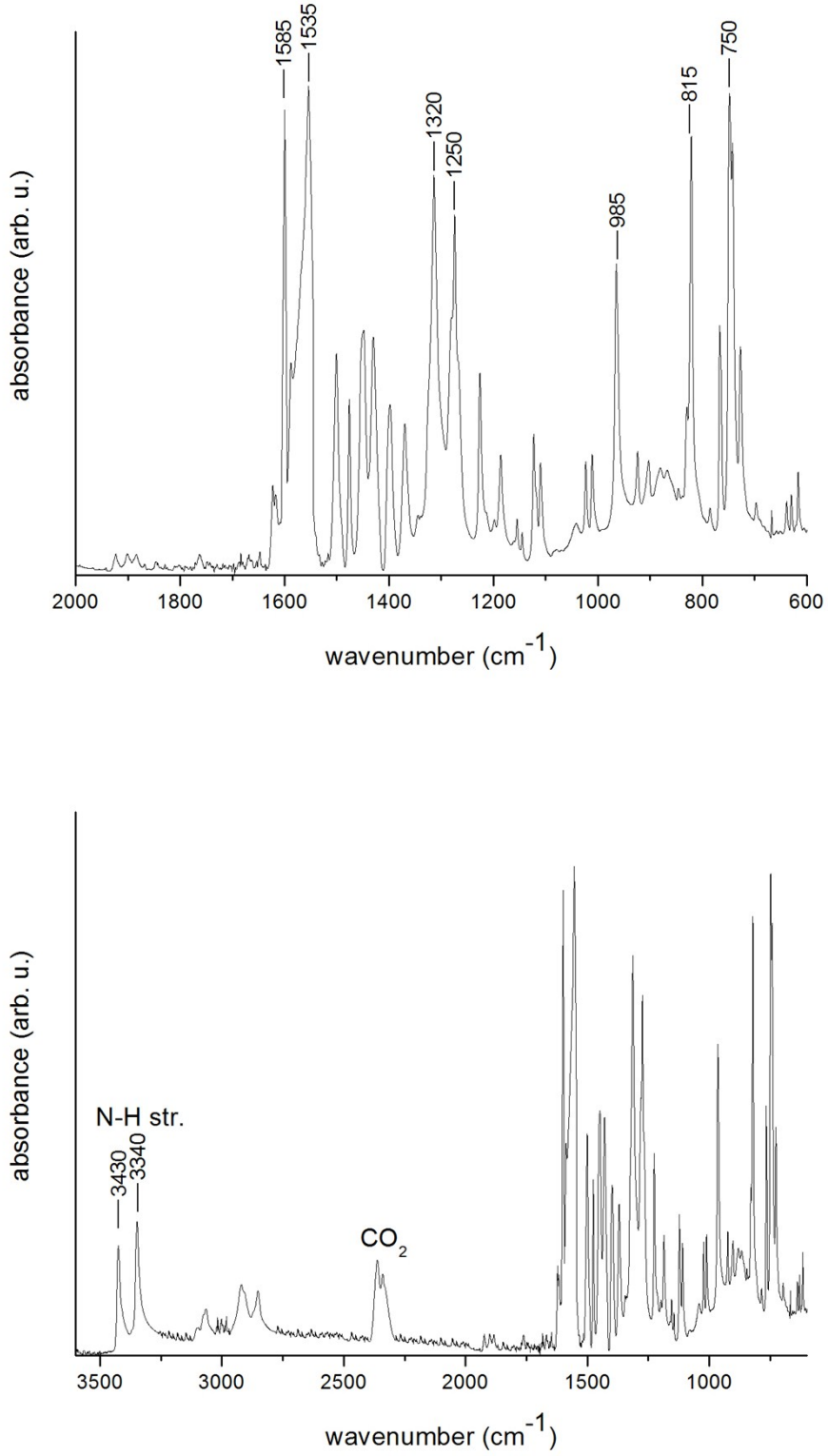


Fig. S27. IR (ATR) spectrum of aminosumanene (**7**) in the wavenumber range of 2000-600 cm^{-1} (**top**) and in the range of 3600-600 cm^{-1} showing NH stretching vibrations (**bottom**).

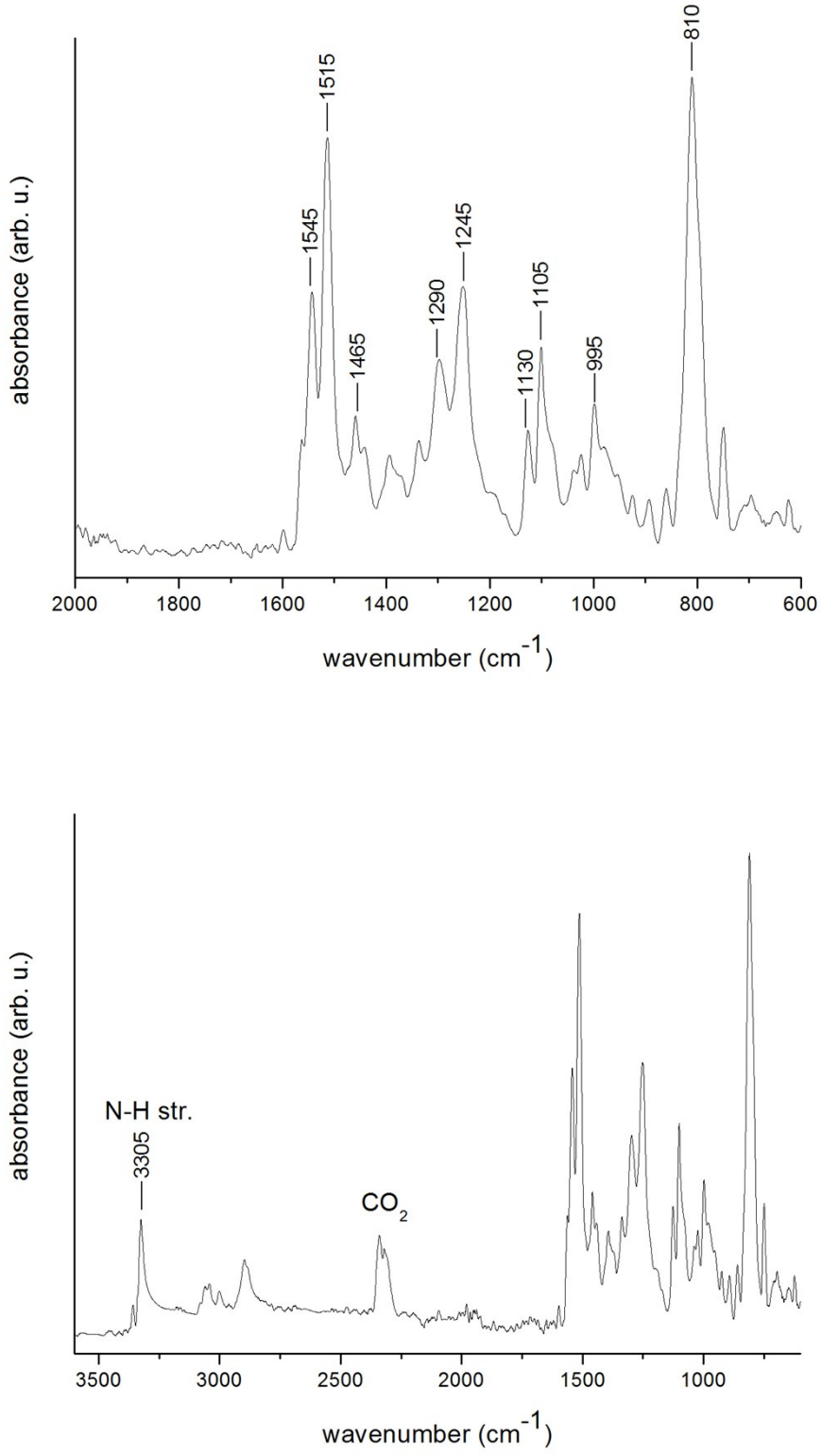


Fig. S28. IR (ATR) spectrum of compound **8** in the wavenumber range of 2000-600 cm^{-1} (**top**) and in the range of 3600-600 cm^{-1} showing NH stretching vibrations (**bottom**).

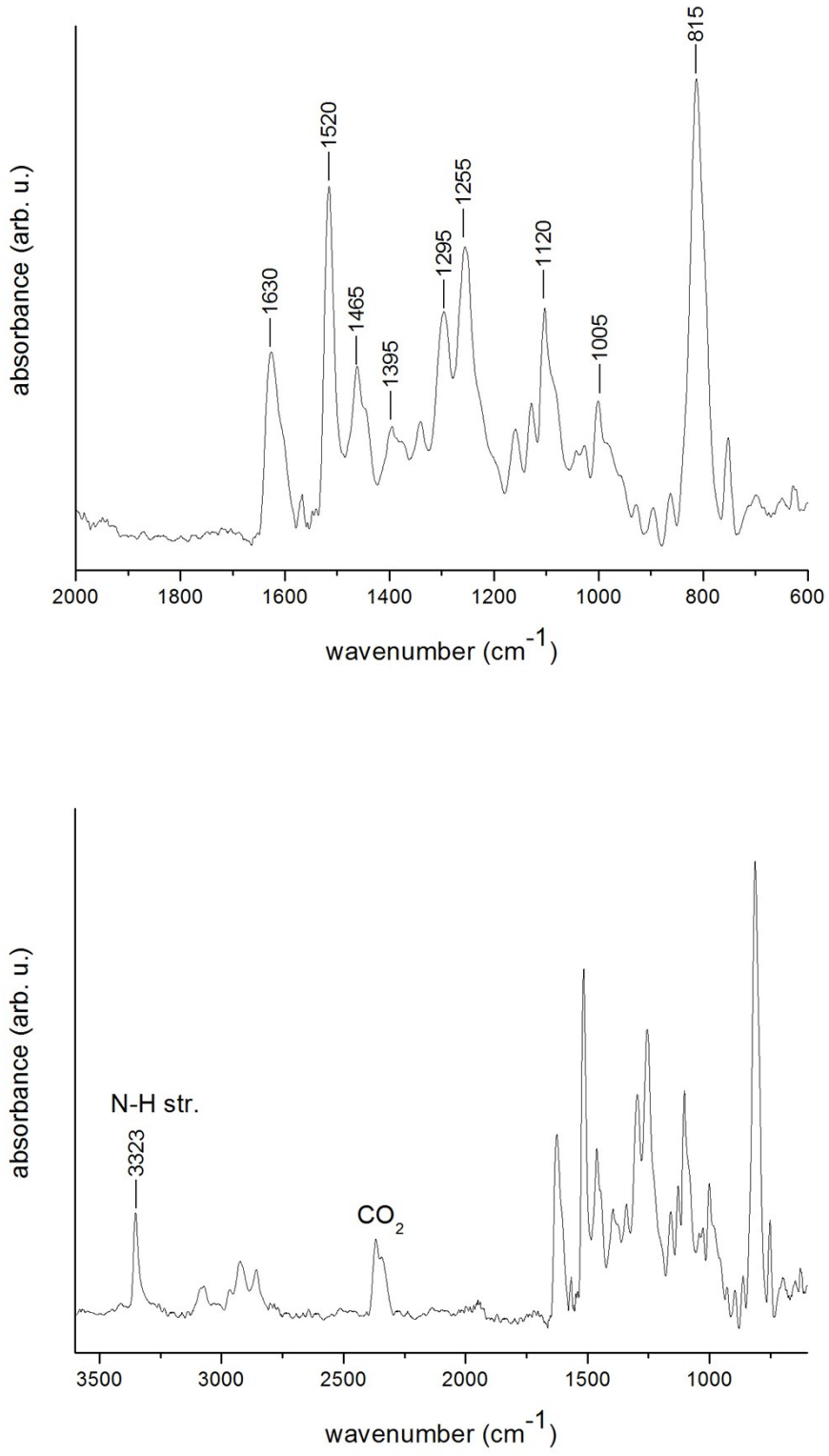


Fig. S29. IR (ATR) spectrum of compound **9** in the wavenumber range of 2000-600 cm^{-1} (**top**) and in the range of 3600-600 cm^{-1} showing NH stretching vibrations (**bottom**).

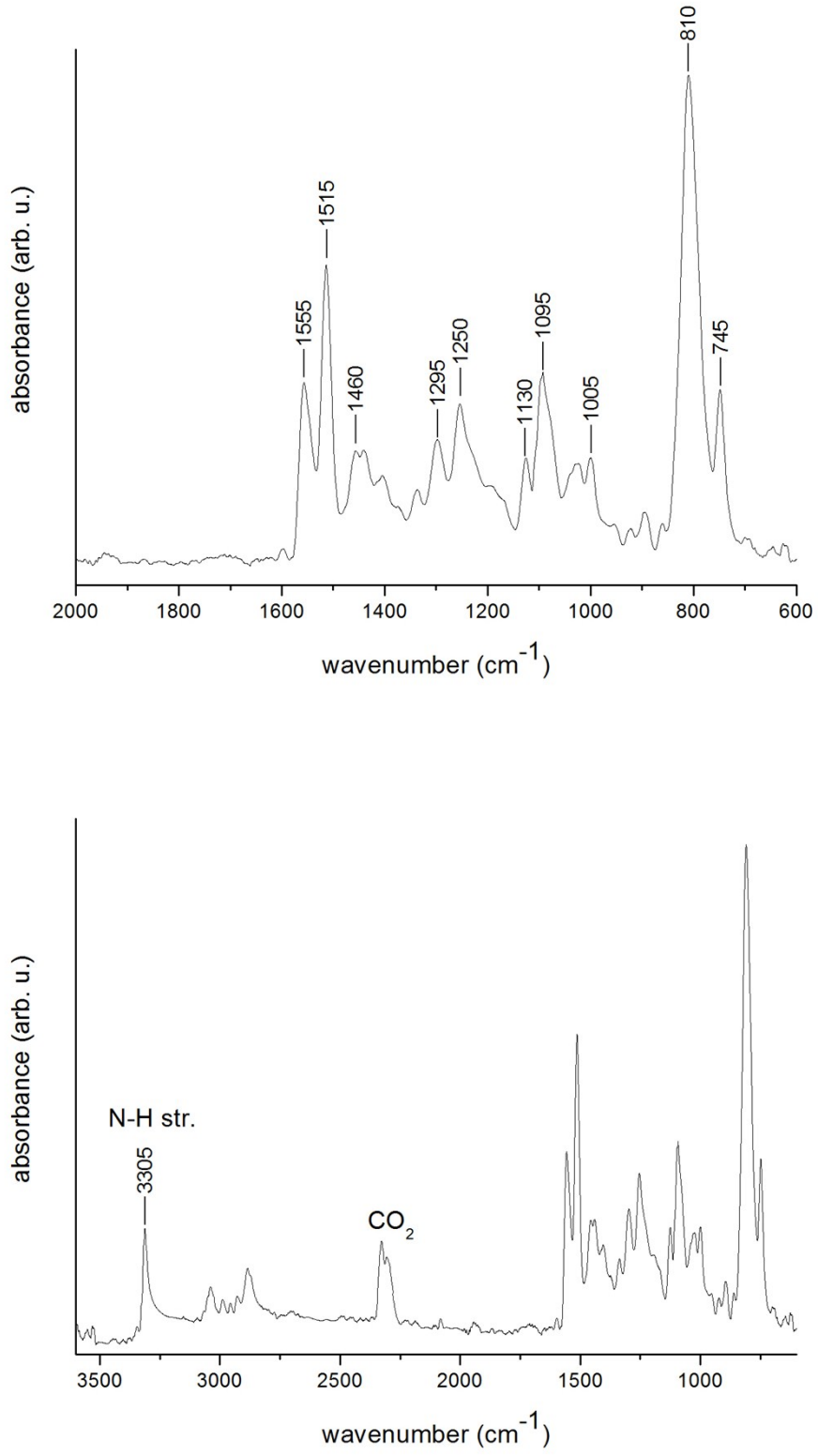


Fig. S30. IR (ATR) spectrum of compound **10** in the wavenumber range of 2000-600 cm^{-1} (**top**) and in the range of 3600-600 cm^{-1} showing NH stretching vibrations (**bottom**).

S4. UV-Vis spectra

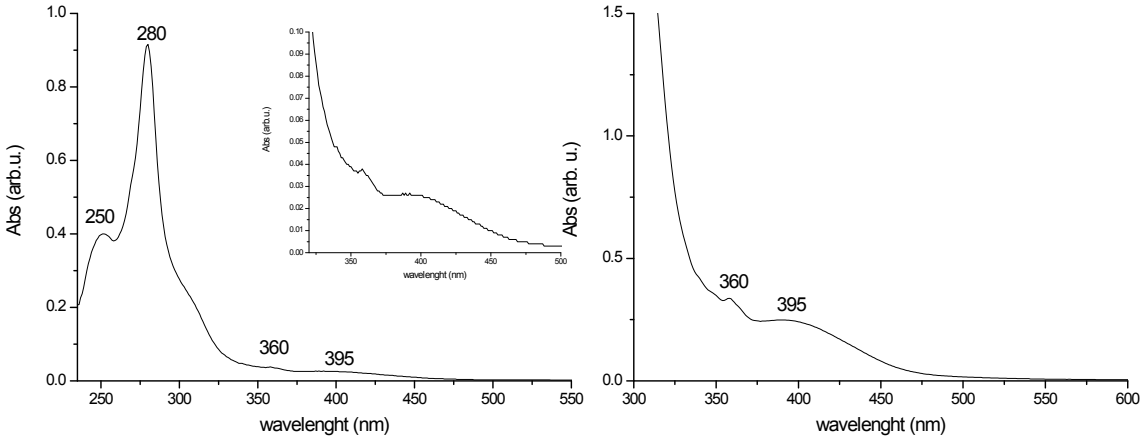


Fig. S31. UV-Vis spectra of compound **3** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; concentration: $1 \cdot 10^{-5}$ M (left), $1 \cdot 10^{-4}$ M (right)).

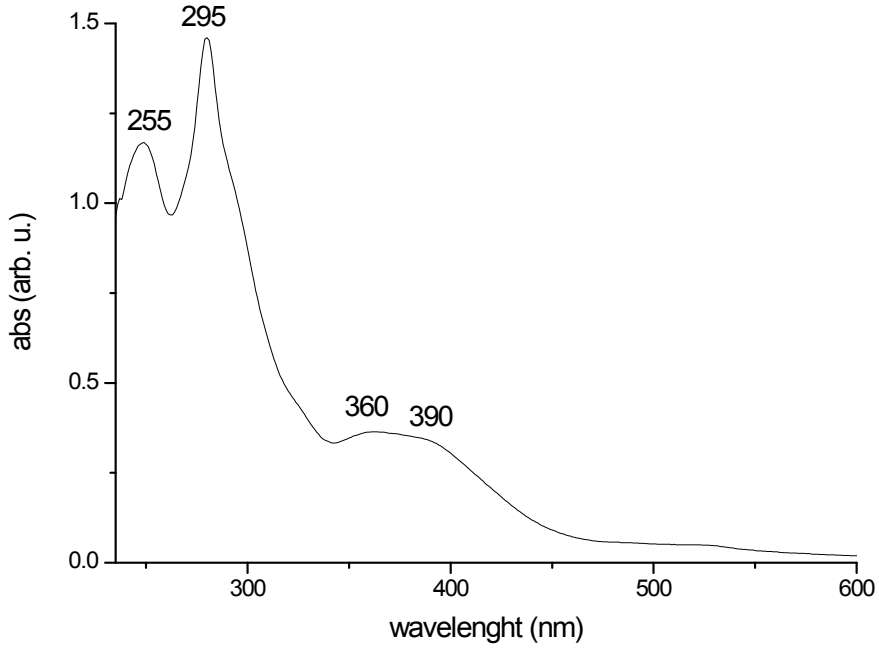


Fig. S32. UV-Vis spectrum of compound **4** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; concentration: $1 \cdot 10^{-4}$ M).

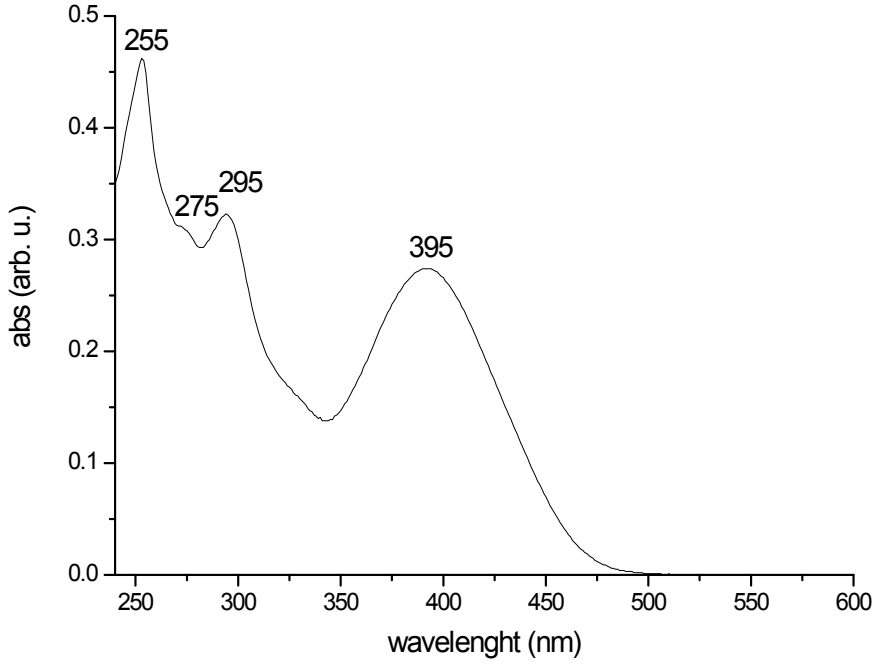


Fig. S33. UV-Vis spectrum of compound **5** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; concentration: $1 \cdot 10^{-5}$ M).

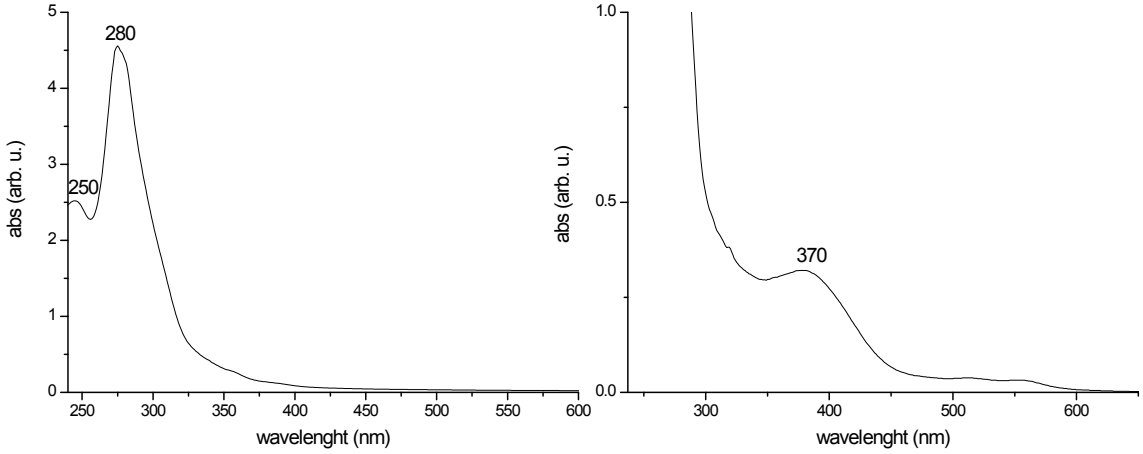


Fig. S34. UV-Vis spectra of compound **8** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; $1 \cdot 10^{-5}$ M (left), $1 \cdot 10^{-4}$ M (right)).

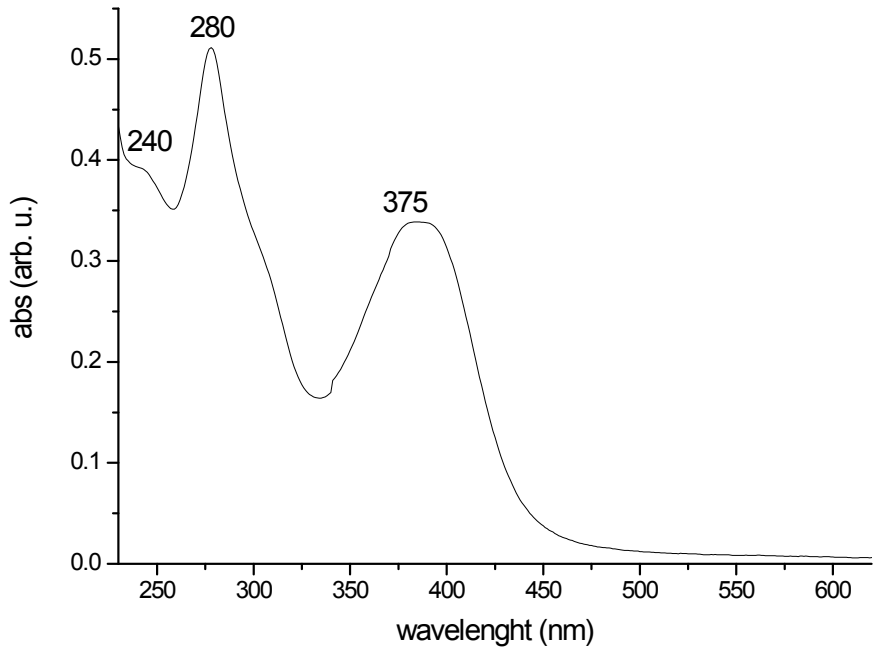


Fig. S35. UV-Vis spectrum of compound **9** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; concentration: $1 \cdot 10^{-4}$ M).

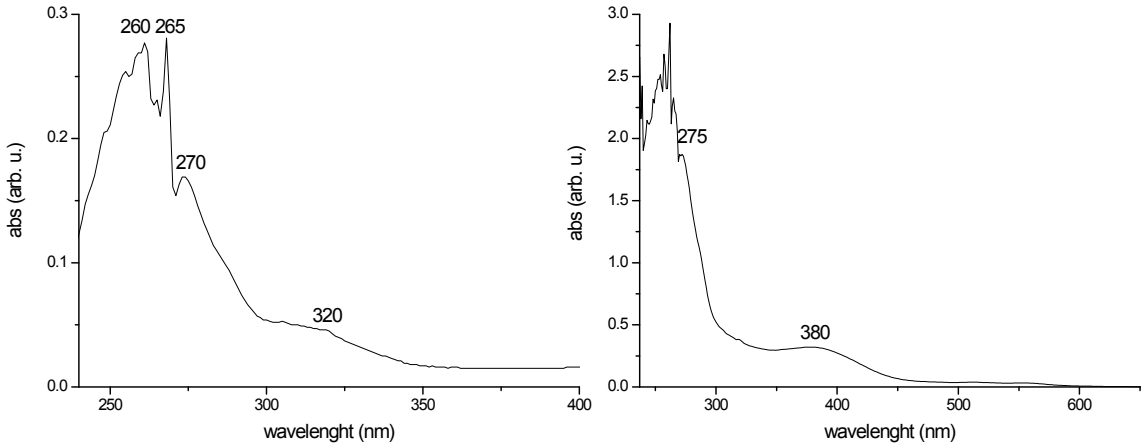


Fig. S36. UV-Vis spectra of compound **10** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; concentration: $1 \cdot 10^{-5}$ M (left), $1 \cdot 10^{-4}$ M (right)).

S5. Fluorescence spectroscopy and titration experiments

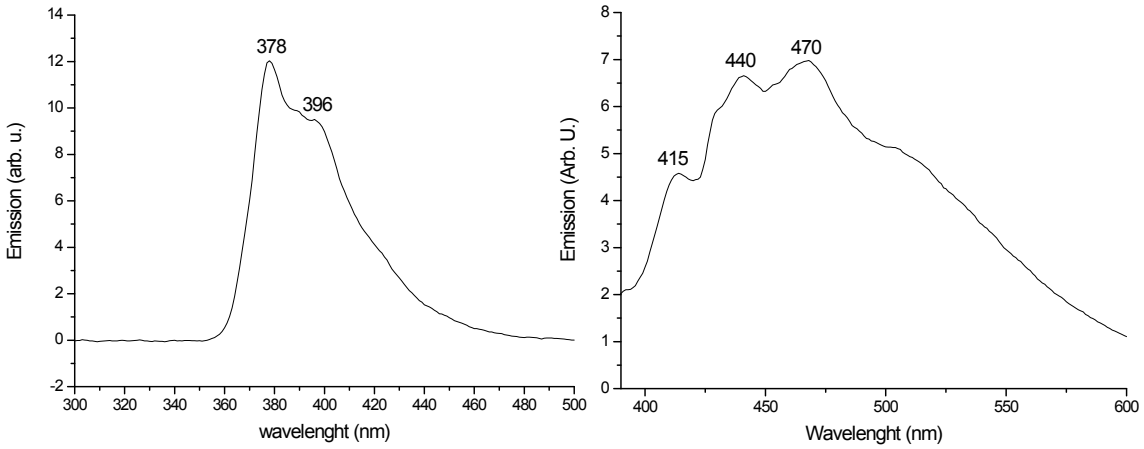


Fig. S37. Emission spectra of compound **3** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm (left), 380 nm (right)).

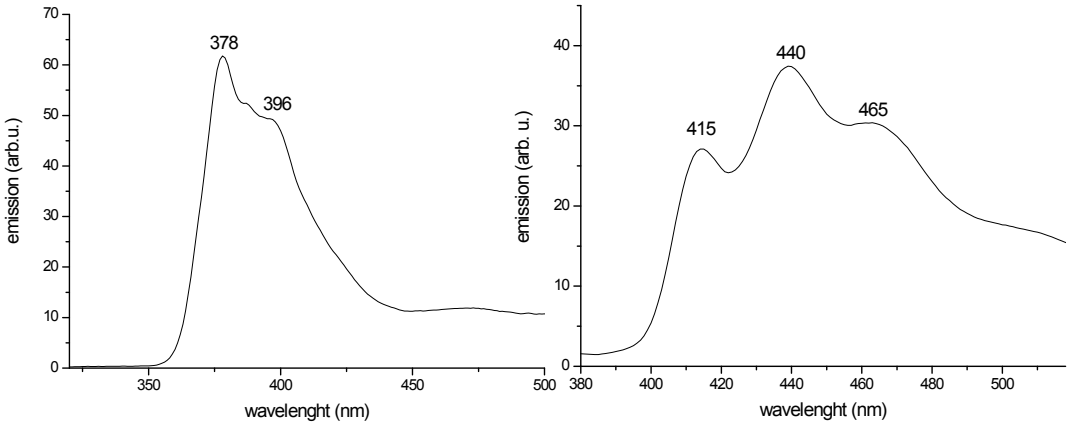


Fig. S38. Emission spectra of compound **4** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm (left), 380 nm (right)).

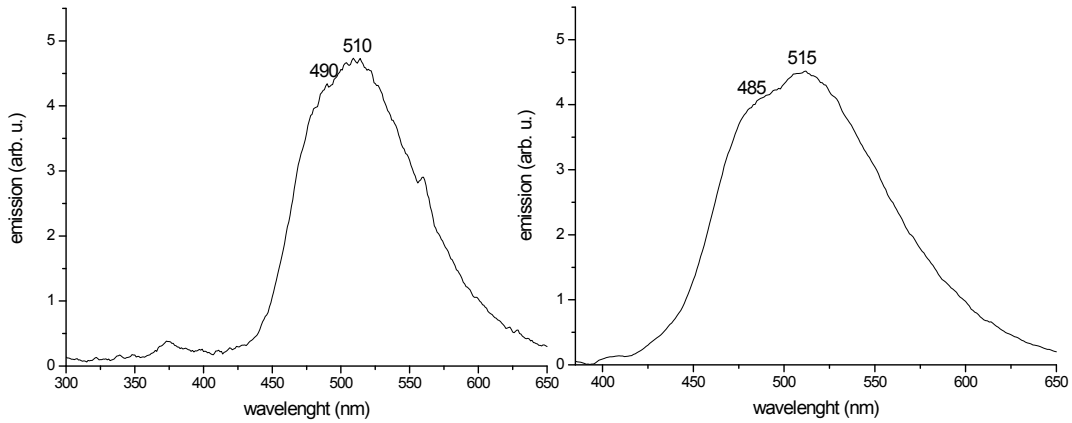


Fig. S39. Emission spectra of compound **5** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm (left), 380 nm (right)).

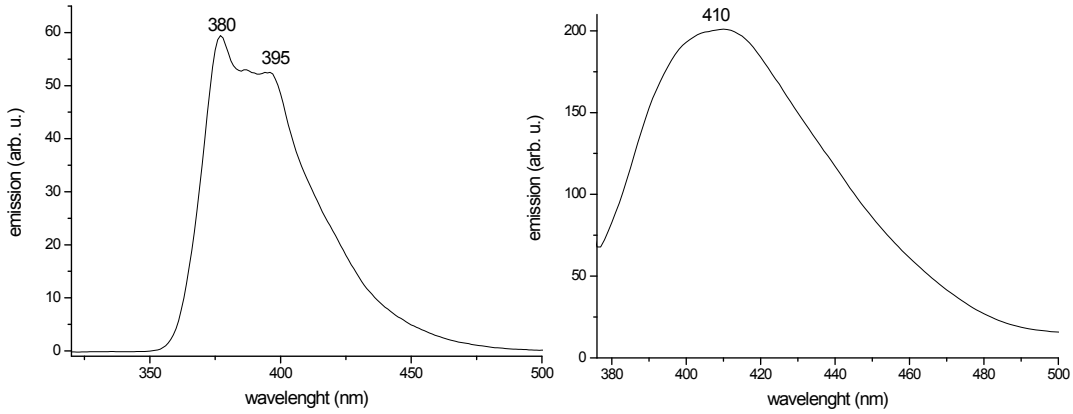


Fig. S40. Emission spectrum of compound **8** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; concentration: $1 \cdot 10^{-4}$M; excitation wavelength: 280 nm (left), 370 nm (right)).

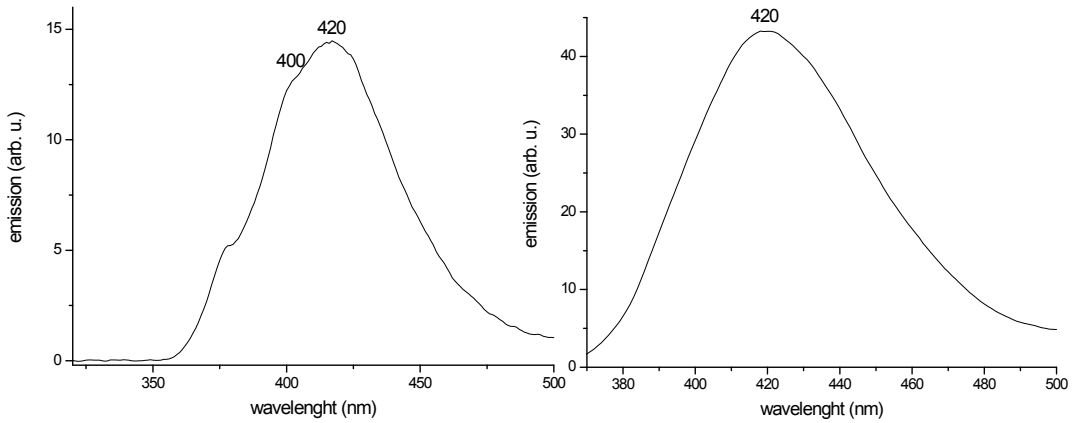


Fig. S41. Emission spectra of compound **9** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm (left), 380 nm (right)).

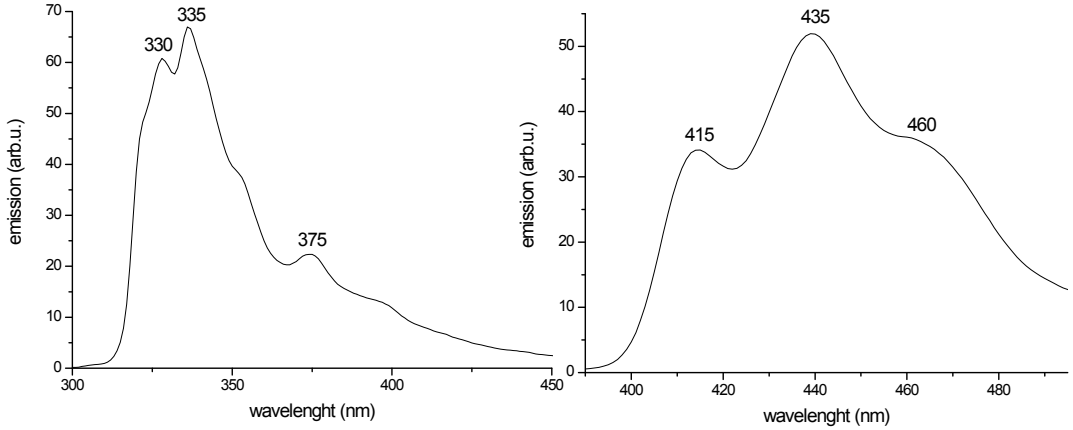


Fig. S42. Emission spectra of compound **10** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm (left), 380 nm (right)).

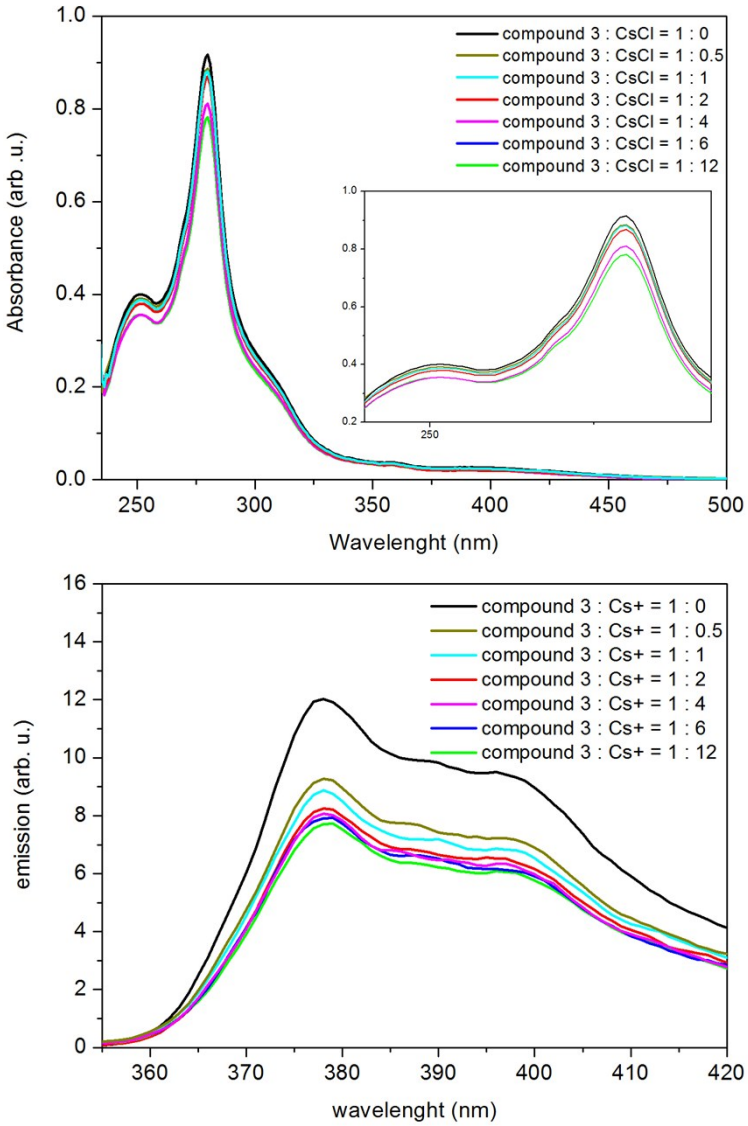


Fig. S43. Comparison between UV-Vis (**top**) or fluorescence (**bottom**) spectra titration methods for caesium cation (Cs^+; in the form of CsCl) binding studies with representative compound **3** (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; compound **3** concentration: $1 \cdot 10^{-4}$ M; excitation wavelength for the fluorescence spectra: 280 nm).

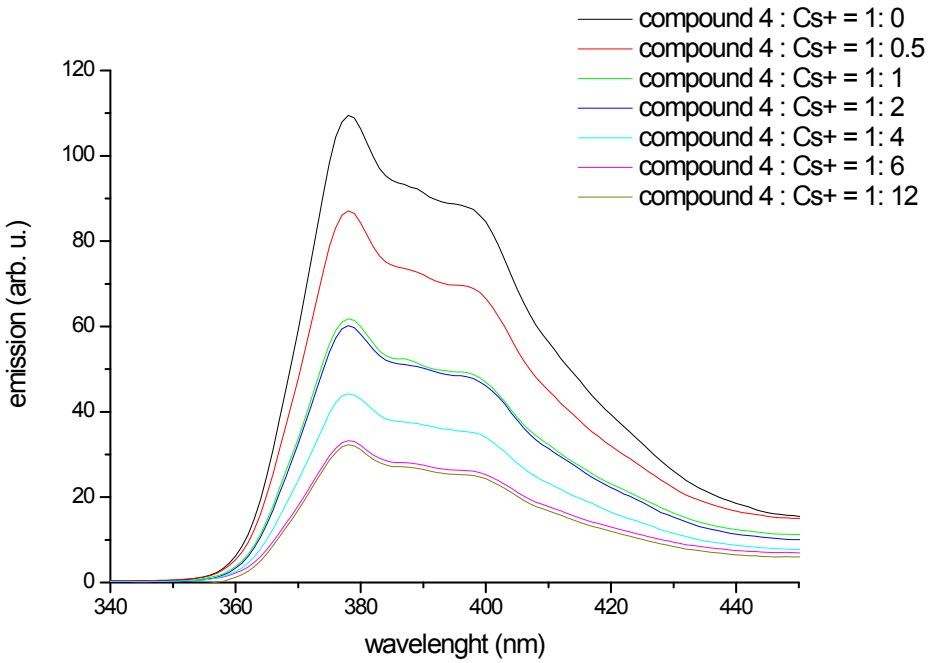


Fig. S44. Caesium cation (Cs^+; in the form of CsCl) binding studies with compound **4** using the fluorescence spectra titration method (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; compound **4** concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm).

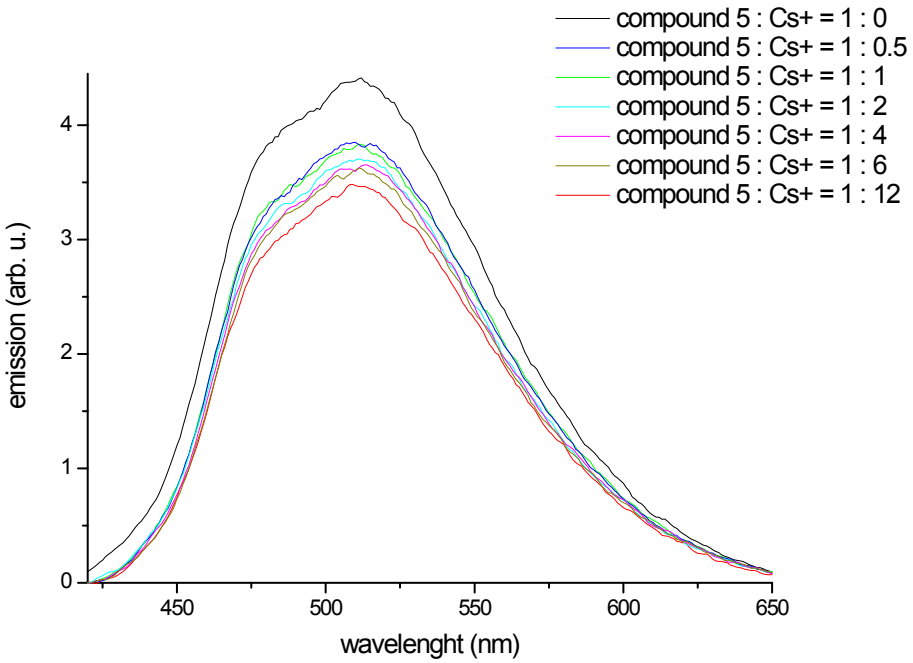


Fig. S45. Caesium cation (Cs^+; in the form of CsCl) binding studies with compound **5** using the fluorescence spectra titration method (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; compound **5** concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm).

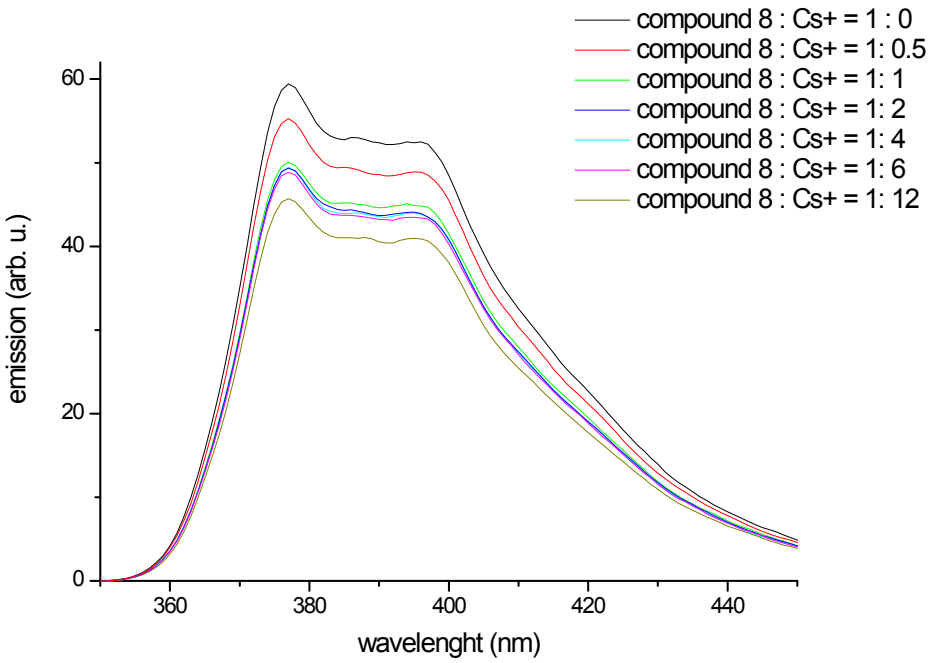


Fig. S46. Caesium cation (Cs^+; in the form of CsCl) binding studies with compound **8** using the fluorescence spectra titration method (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; compound **8** concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm).

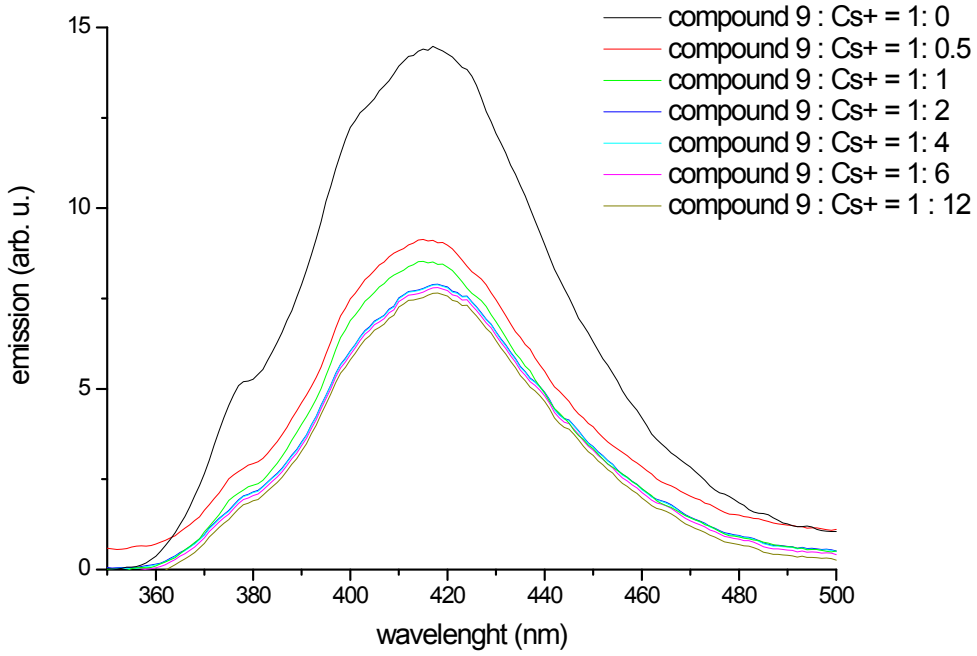


Fig. S47. Caesium cation (Cs^+; in the form of CsCl) binding studies with compound **9** using the fluorescence spectra titration method (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; compound **9** concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm).

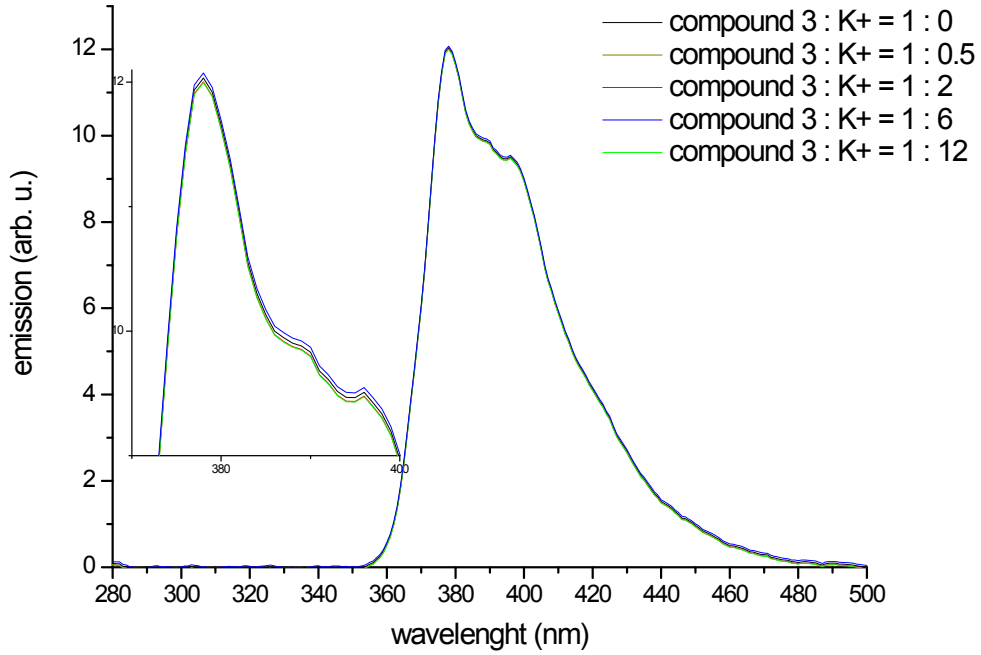


Fig. S48. Potassium cation (K^+; in the form of KCl) binding studies with compound **3** using the fluorescence spectra titration method (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; compound **3** concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm).

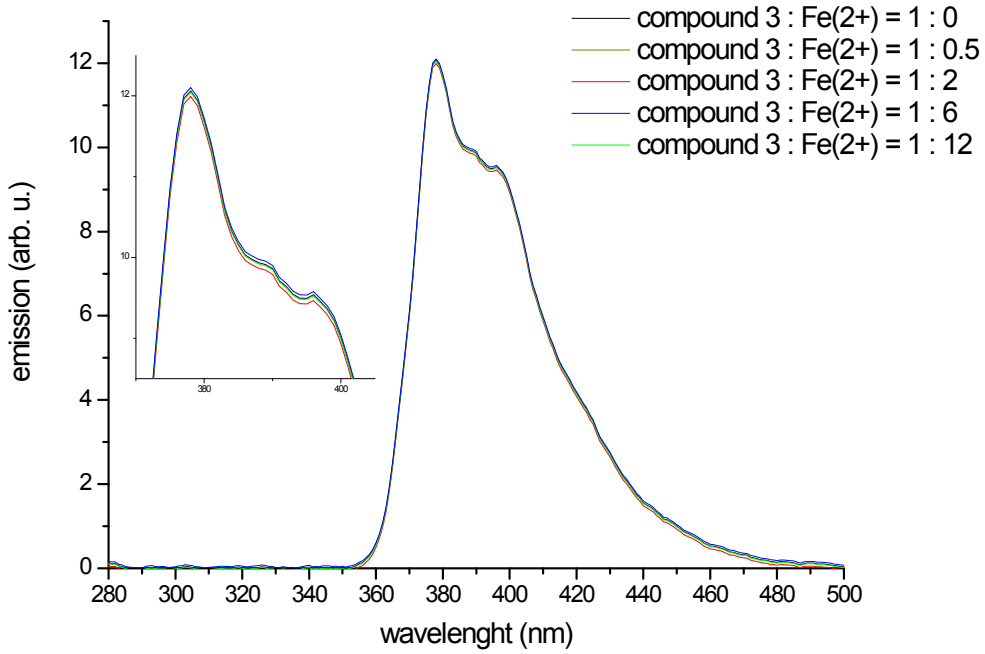


Fig. S49. Iron cation (Fe^{2+}; in the form of $FeCl_2$) binding studies with compound **3** using the fluorescence spectra titration method (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; compound **3** concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm).

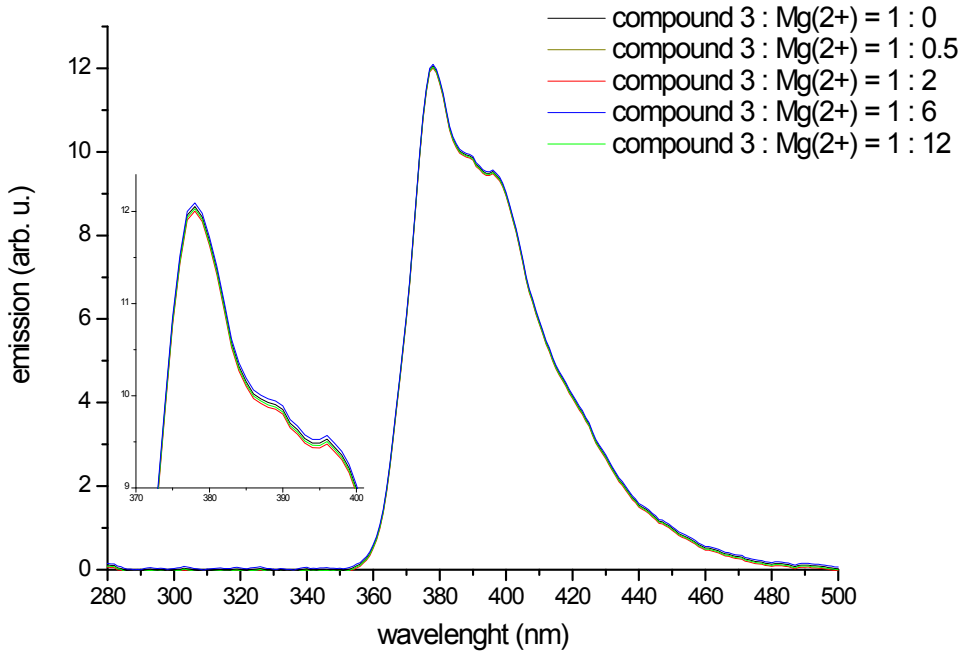


Fig. S50. Magnesium cation (Mg^{2+}; in the form of $MgCl_2$) binding studies with compound **3** using the fluorescence spectra titration method (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; compound **3** concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm).

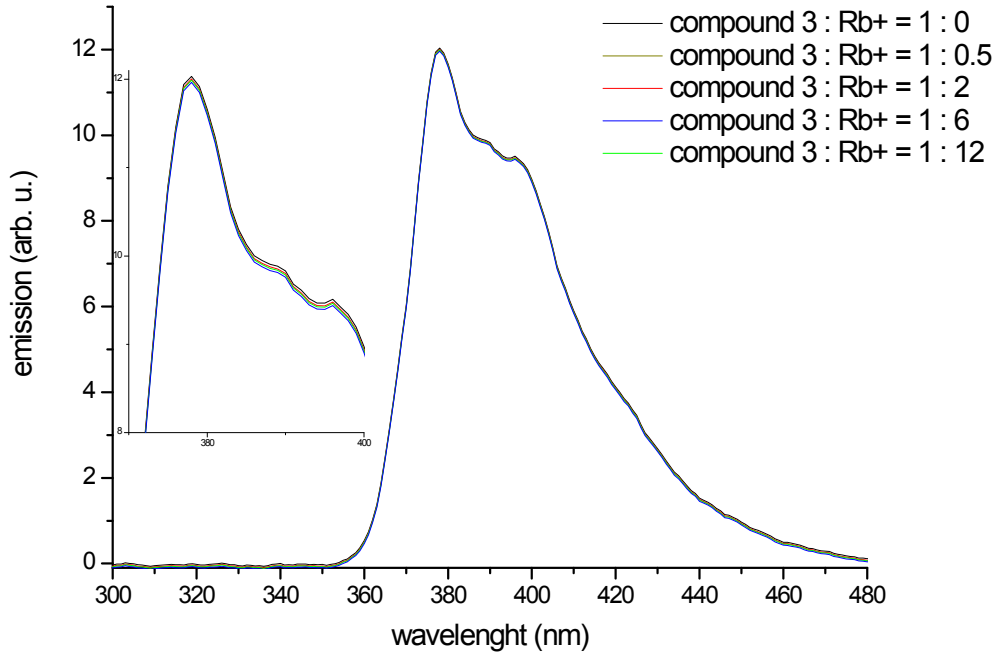


Fig. S51. Rubidium cation (Rb^{+}; in the form of RbCl) binding studies with compound **3** using the fluorescence spectra titration method (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; compound **3** concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm).

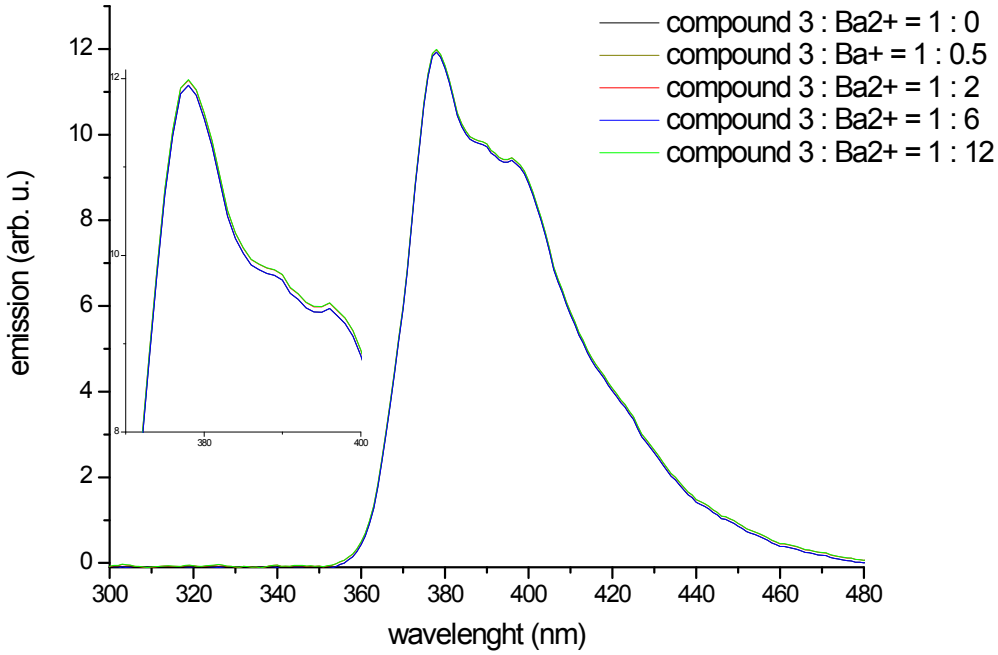


Fig. S52. Barium cation (Ba^{+}; in the form of $BaCl_2$) binding studies with compound **3** using the fluorescence spectra titration method (solvent: $CHCl_3$:MeOH = 1:1 *v/v*; compound **3** concentration: $1 \cdot 10^{-4}$ M; excitation wavelength: 280 nm).

S6. The Job's plots

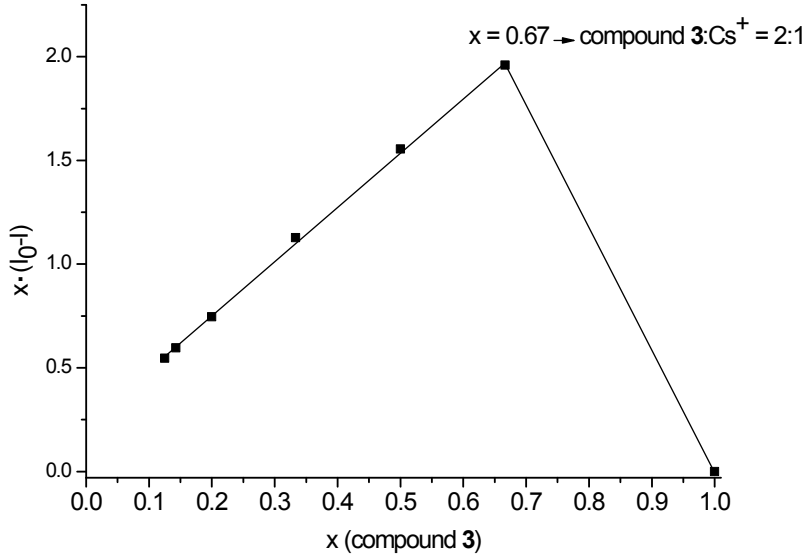


Fig. S53. The Job's plot related to the interactions of the compound **3** with Cs^+ (based on the data from the florescence spectra titration; *x* stands for the molar fraction of compound **3**, I_0 stands for the emission intensity of compound **3** without Cs^+ added, *I* stands for the emission intensity of compound with the given amount of Cs^+ added).

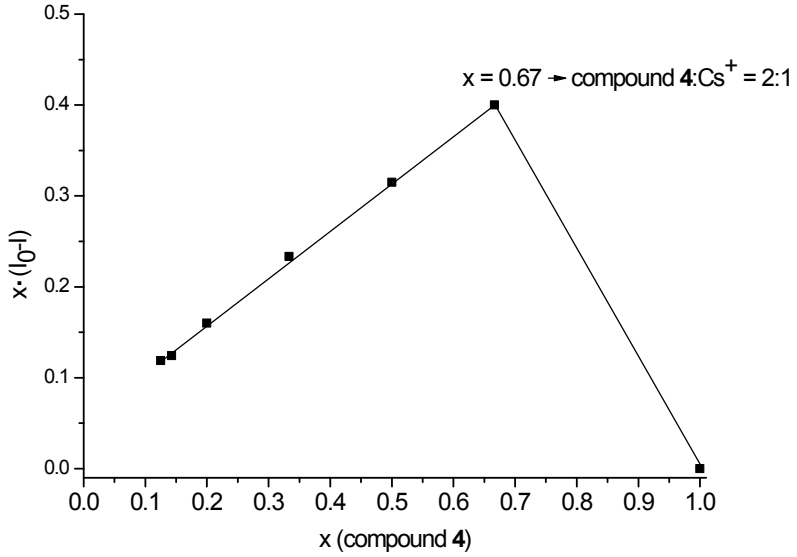


Fig. S54. The Job's plot related to the interactions of the compound **4** with Cs^+ (based on the data from the florescence spectra titration; *x* stands for the molar fraction of compound **4**, I_0 stands for the emission intensity of compound **4** without Cs^+ added, *I* stands for the emission intensity of compound with the given amount of Cs^+ added).

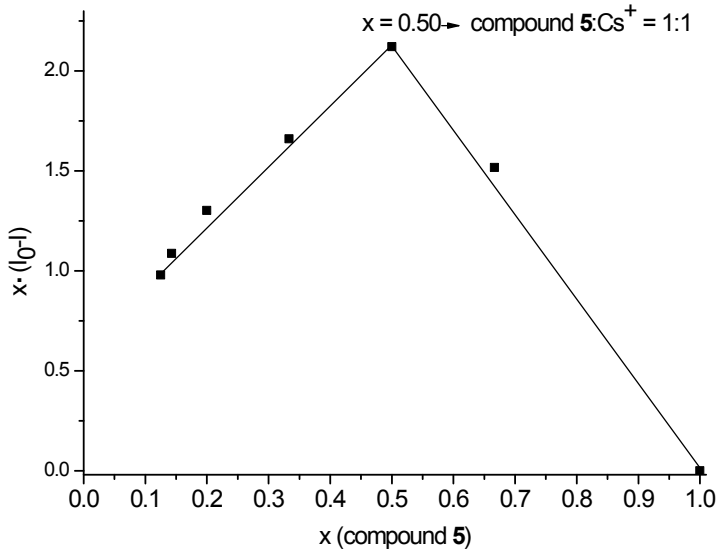


Fig. S55. The Job's plot related to the interactions of the compound **5** with Cs^+ (based on the data from the florescence spectra titration; *x* stands for the molar fraction of compound **5**, I_0 stands for the emission intensity of compound **5** without Cs^+ added, *I* stands for the emission intensity of compound with the given amount of Cs^+ added).

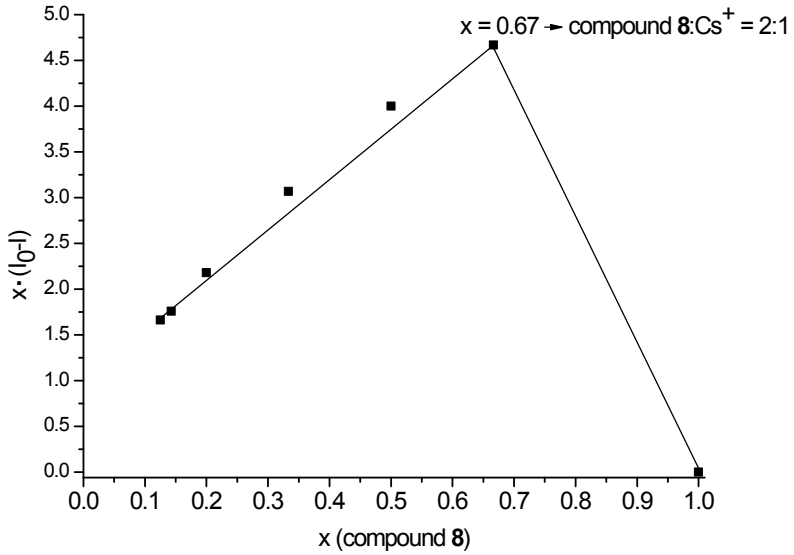


Fig. S56. The Job's plot related to the interactions of the compound **8** with Cs^+ (based on the data from the florescence spectra titration; *x* stands for the molar fraction of compound **8**, I_0 stands for the emission intensity of compound **8** without Cs^+ added, *I* stands for the emission intensity of compound with the given amount of Cs^+ added).

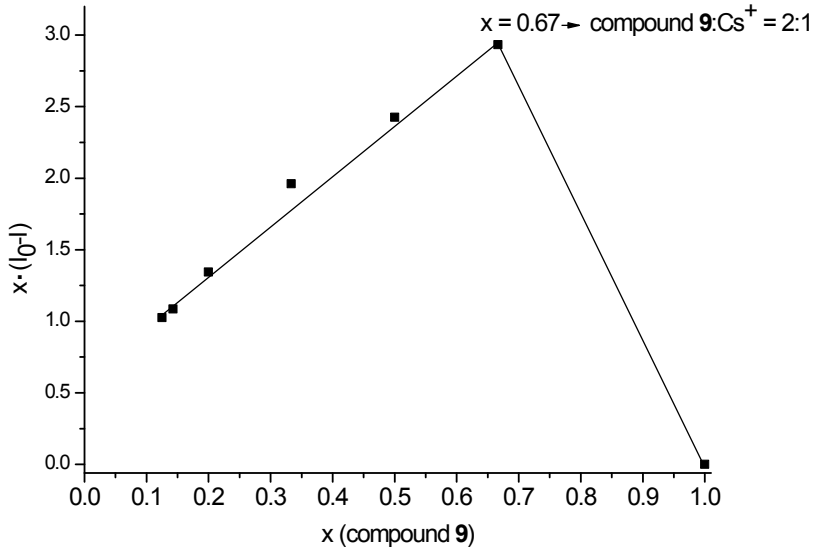


Fig. S57. The Job's plot related to the interactions of the compound **9** with Cs^+ (based on the data from the florescence spectra titration; *x* stands for the molar fraction of compound **9**, I_0 stands for the emission intensity of compound **9** without Cs^+ added, *I* stands for the emission intensity of compound with the given amount of Cs^+ added).

S7. ^{1}H NMR titration experiments

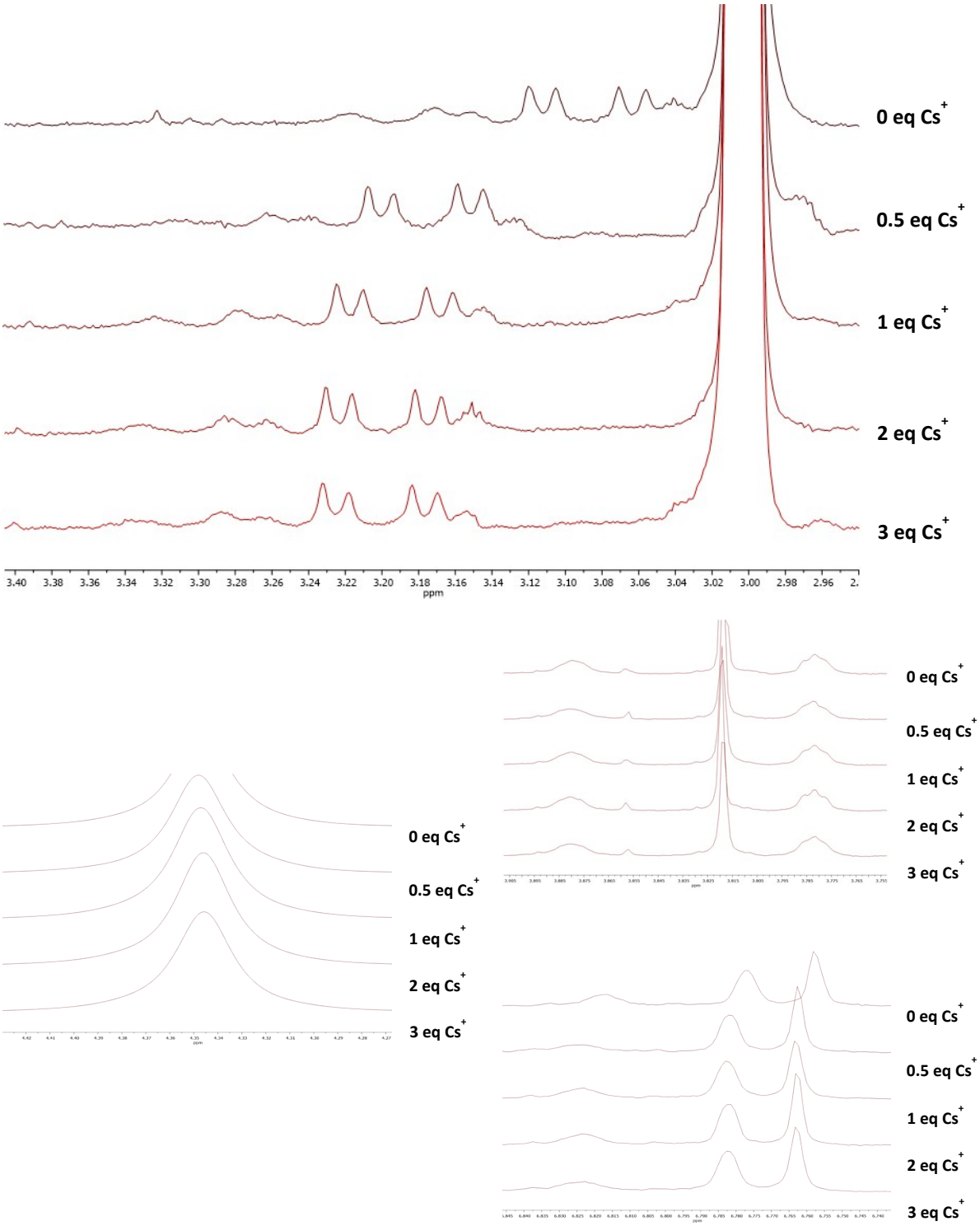


Fig. S58. Caesium cation (Cs^+; in the form of CsCl) binding studies with compound **3** using the ^{1}H NMR titration method (solvent: $CDCl_3$:CD_3OD = 1:1 *v/v*; compound **3** concentration: 1.5 mM). The insets of the spectra are presented.

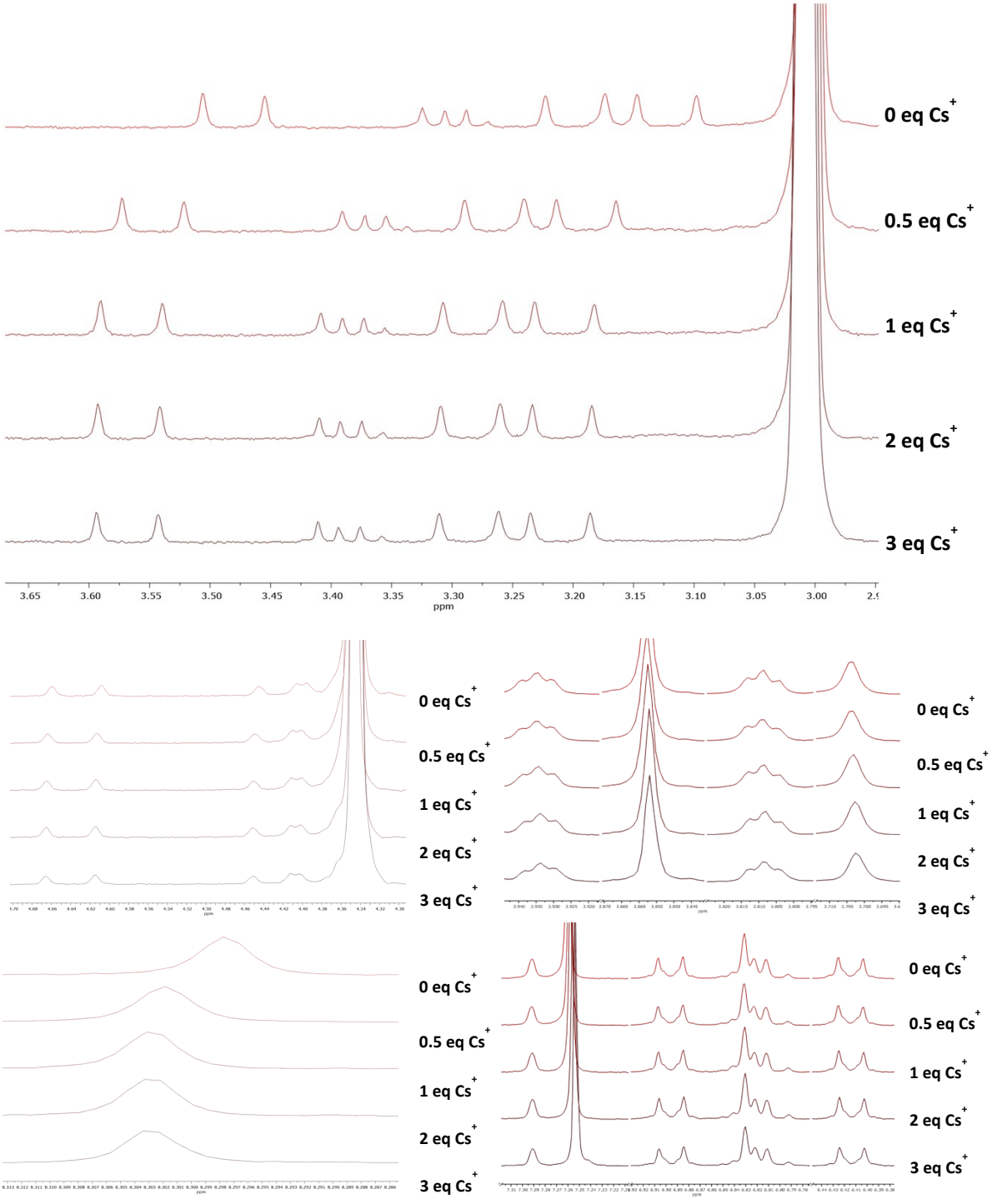


Fig. S59. Caesium cation (Cs^+; in the form of CsCl) binding studies with compound **4** using the ^1H NMR titration method (solvent: $CDCl_3$:CD_3OD = 1:1 *v/v*; compound **4** concentration: 1.5 mM). The insets of the spectra are presented.

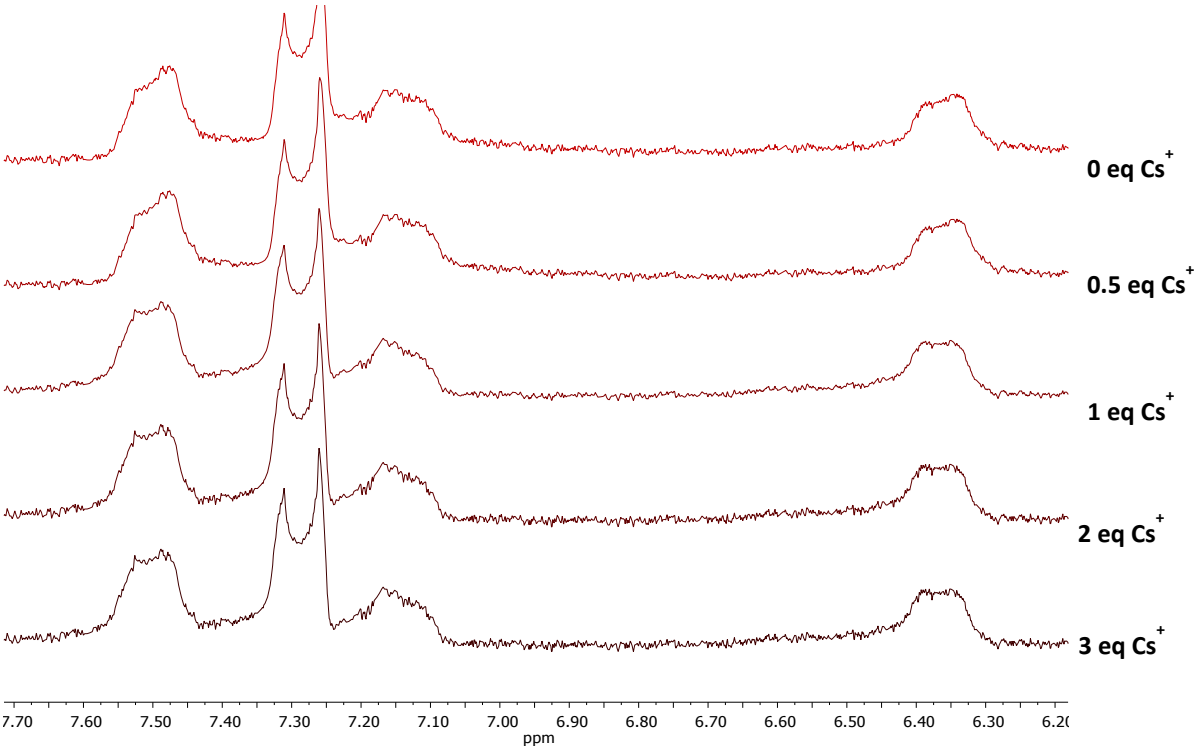


Fig. S60. Caesium cation (Cs^+; in the form of CsCl) binding studies with compound **10** using the ^1H NMR titration method (solvent: $CDCl_3$:CD_3OD = 1:1 *v/v*; compound **10** concentration: 1.5 mM).

S8. Cyclic voltammograms

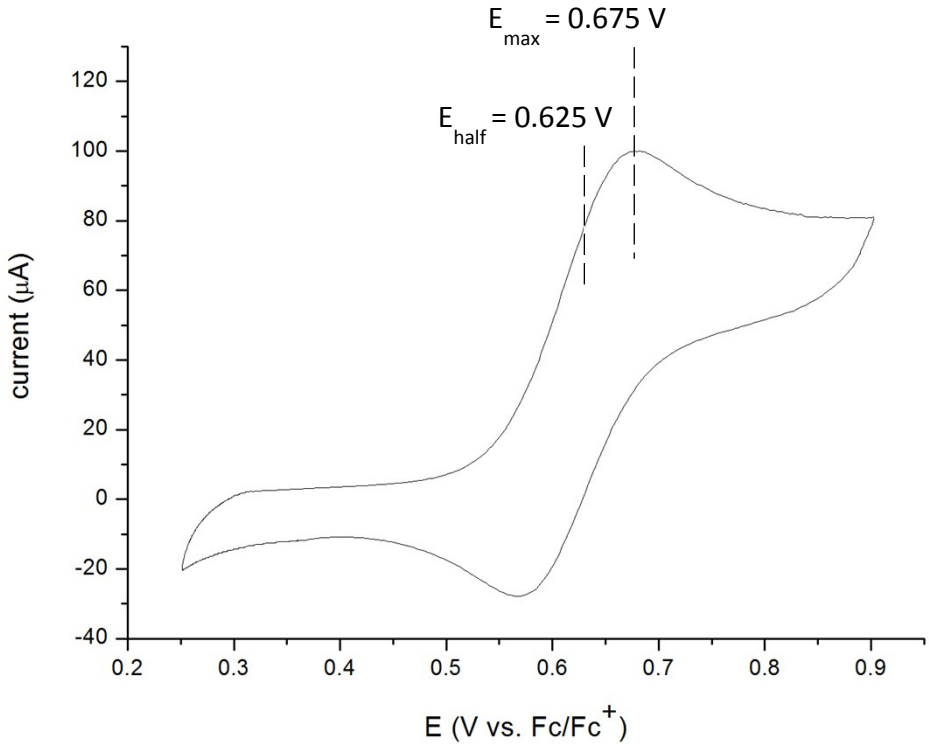


Fig. S61. Cyclic voltammogram of compound **3** in CH_2Cl_2.

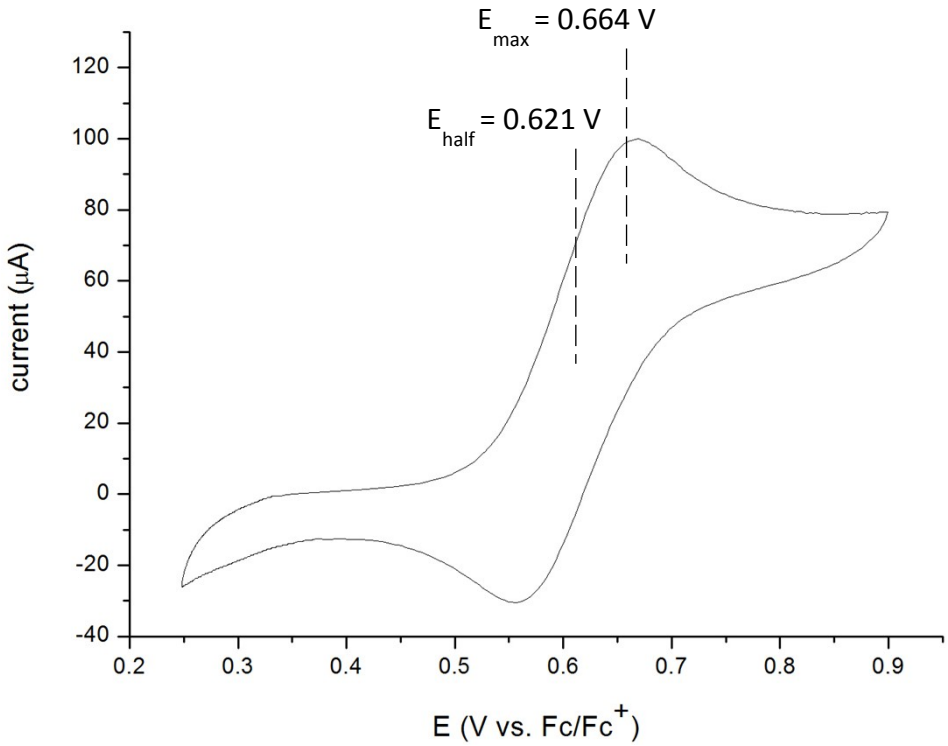


Fig. S62. Cyclic voltammogram of compound **4** in CH_2Cl_2.

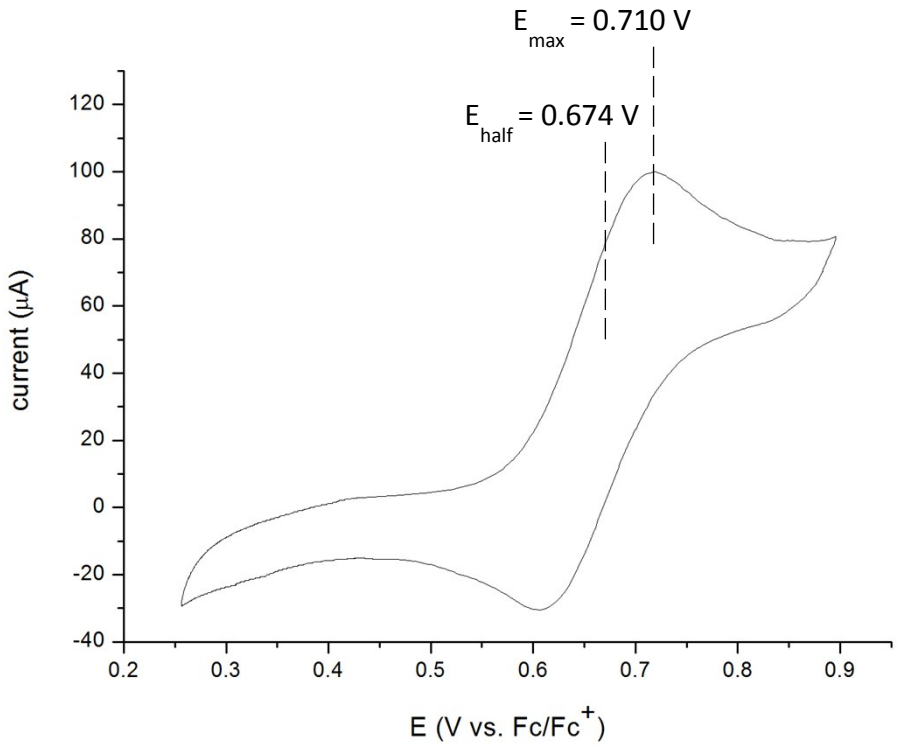


Fig. S63. Cyclic voltammogram of compound **5** in CH_2Cl_2.

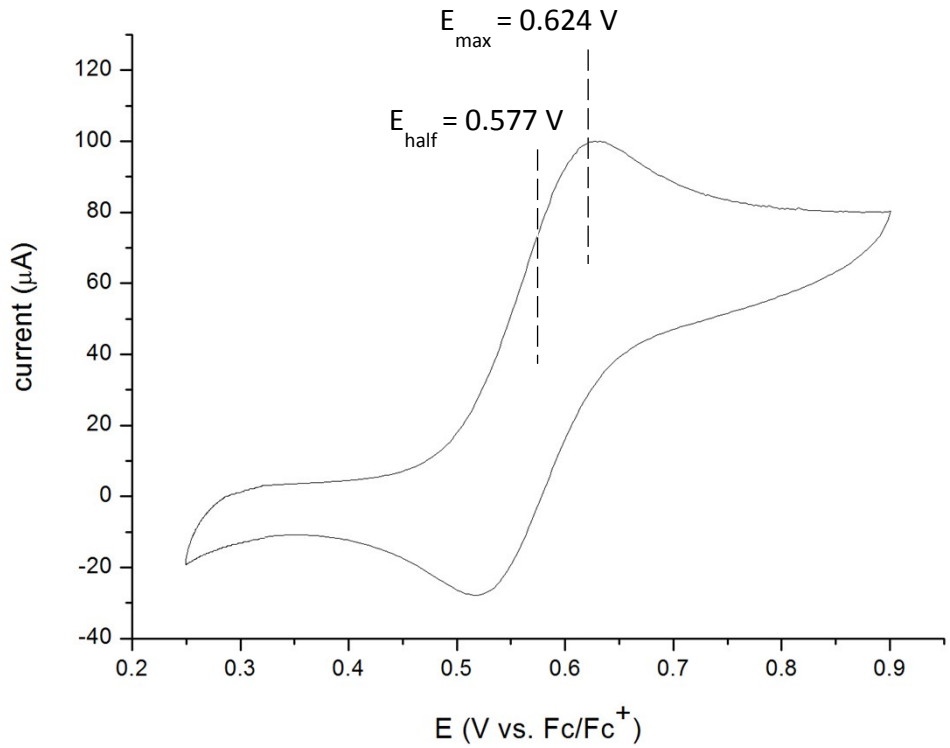


Fig. S64. Cyclic voltammogram of compound **8** in CH_2Cl_2.

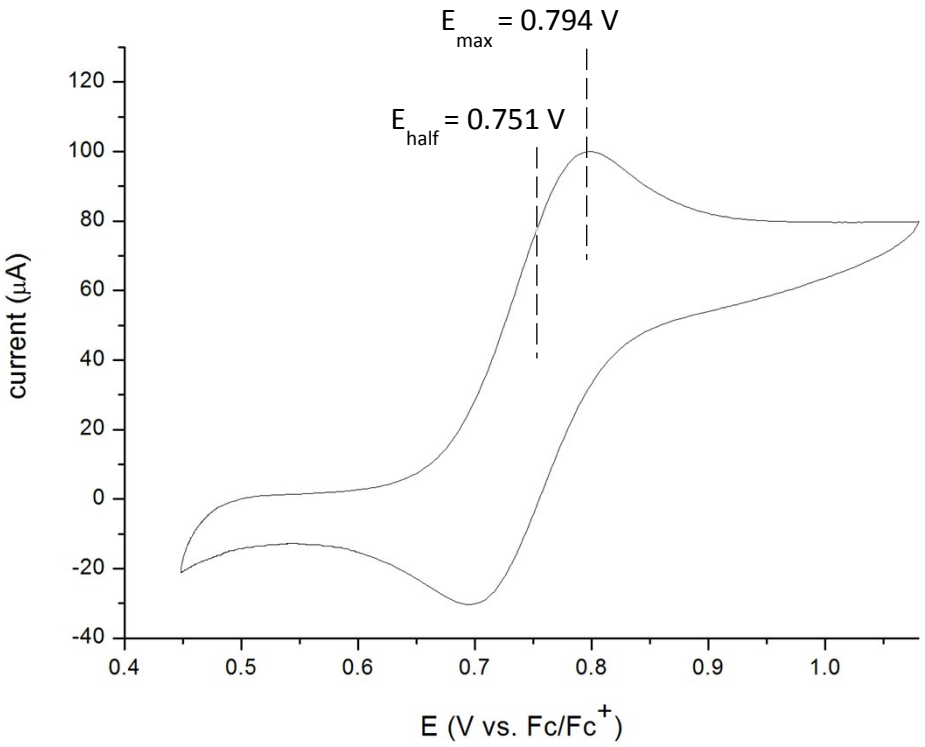


Fig. S65. Cyclic voltammogram of compound **9** in CH_2Cl_2.

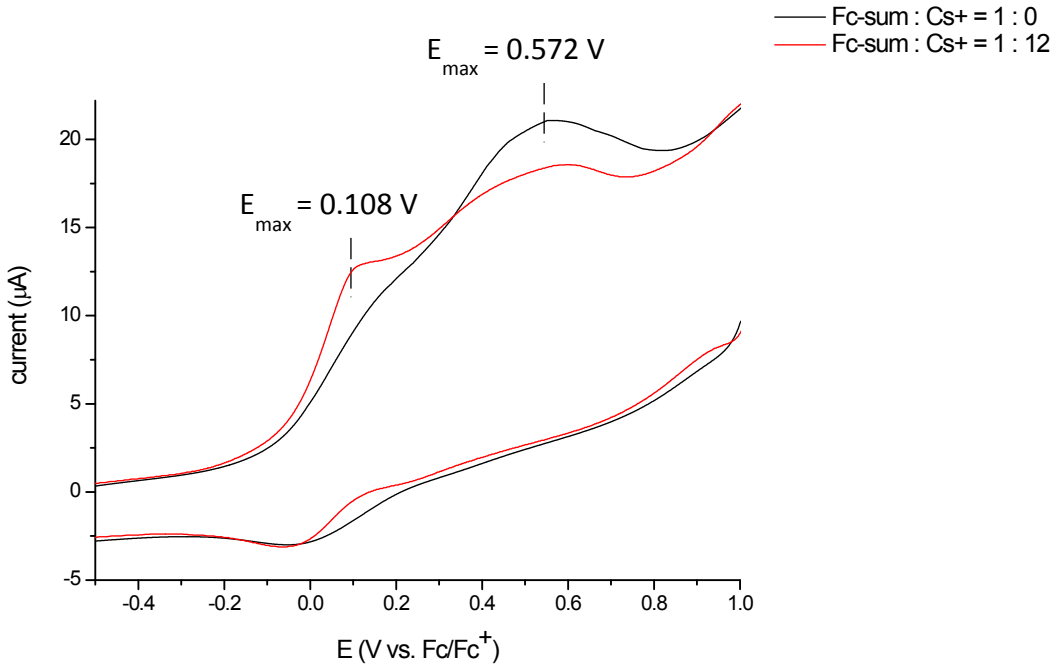


Fig. S66. Cyclic voltammogram of compound **3** in $CHCl_3$:MeOH = 1:1 *v*/*v*, with (black curve) and without (red curve) Cs^+ added (12 eq).

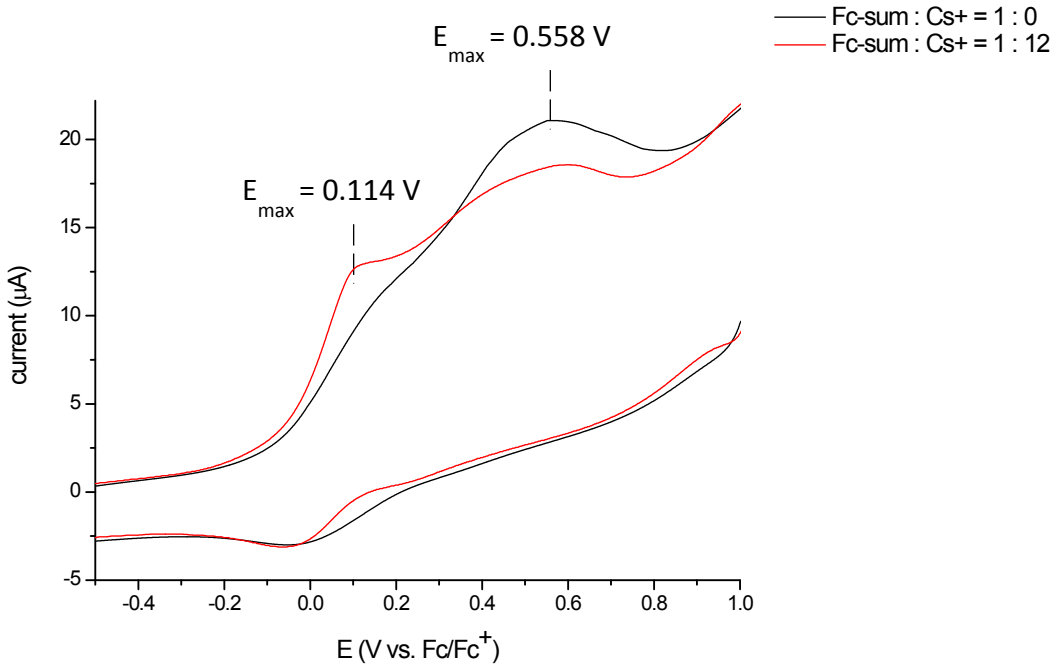


Fig. S67. Cyclic voltammogram of compound **4** in $CHCl_3$:MeOH = 1:1 *v*/*v*, with (black curve) and without (red curve) Cs^+ added (12 eq).

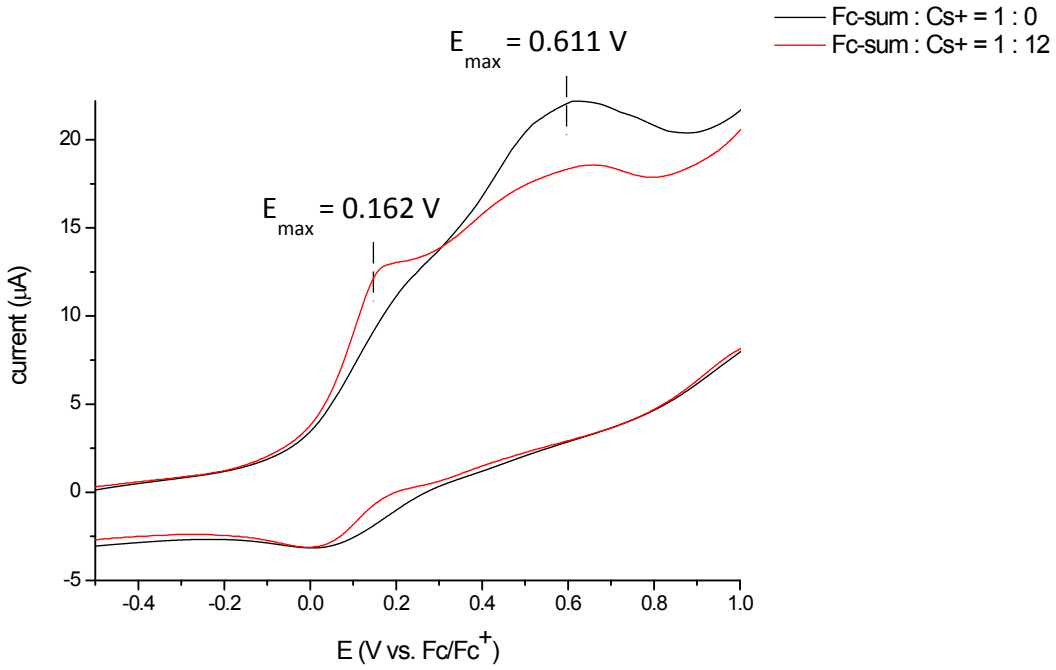


Fig. S68. Cyclic voltammogram of compound **5** in $CHCl_3$:MeOH = 1:1 *v*/*v*, with (black curve) and without (red curve) Cs^+ added (12 eq).

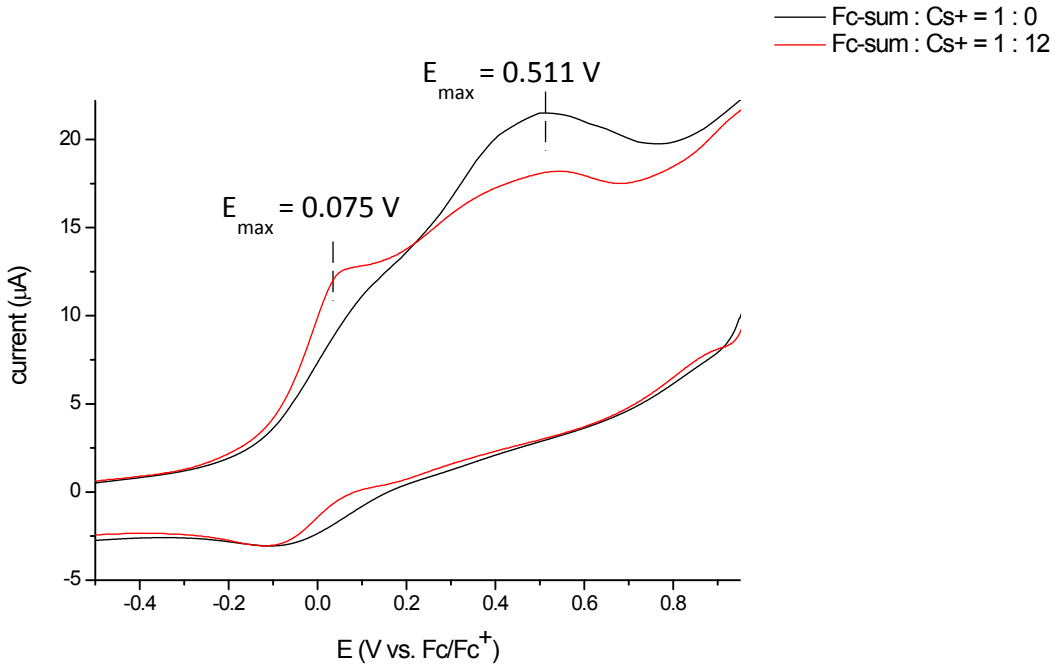


Fig. S69. Cyclic voltammogram of compound **8** in $CHCl_3$:MeOH = 1:1 *v*/*v*, with (black curve) and without (red curve) Cs^+ added (12 eq).

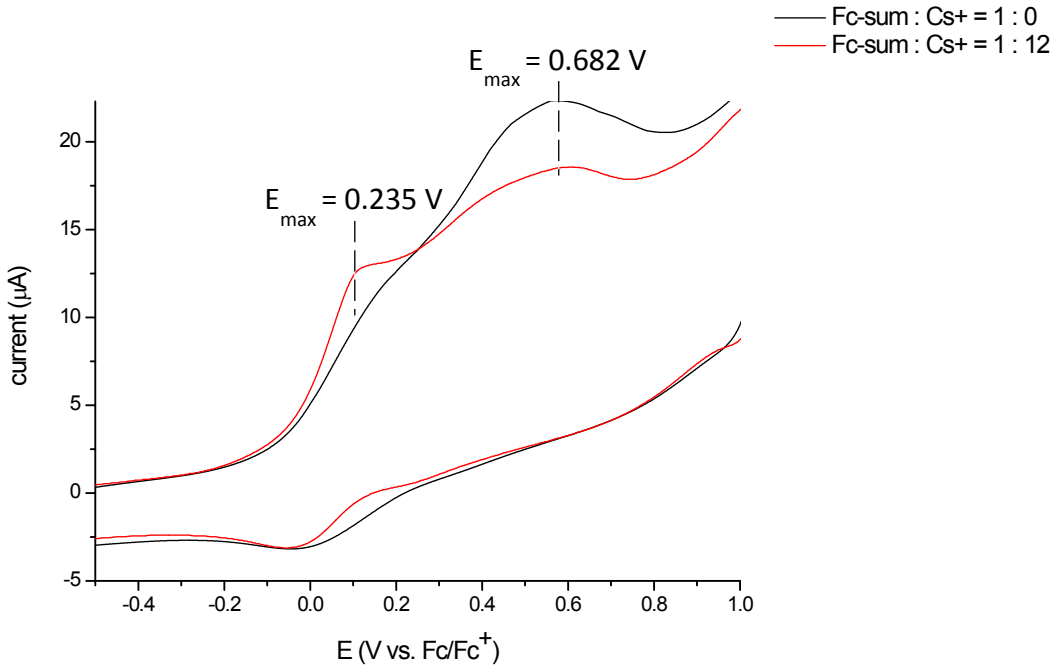


Fig. S70. Cyclic voltammogram of compound **9** in $CHCl_3$:MeOH = 1:1 *v*/*v*, with (black curve) and without (red curve) Cs^+ added (12 eq).

S9. Details on calculation of K_a and LOD

Calculations were based on the Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K_a \cdot C_{cation}$$

, where C_{cation} is the molar concentration of the cation, I_0 and I are the fluorescence intensity of Fc-sumanene derivative in the absence and in the presence of cation, respectively (reference no. 26 in the manuscript). K_a and LOD were calculated as follows:

- K_a value for compound **5** was calculated accordingly on the basis of the I_0/I = f(C_{cation}) linear dependency (Fig. S71). K_a values for compounds **3**, **4**, **8**, **9** were calculated accordingly on the basis of the I_0/I = f(C_{cation}^2) linear dependences (Fig. S72). I_0/I = f(C_{cation}) linear plots for compounds **3**, **4**, **8**, **9** are also presented in Fig. S71. Despite the fact that the Stern-Volmer method fits best for 1:1 interaction model, both I_0/I = f(C_{cation}) and I_0/I = f(C_{cation}^2) plots for compounds **3**, **4**, **8** were linear, thus enabling calculation of K_a. However, the calculated K_a numbers for compounds **3**, **4**, **8**, **9** should be treated as the approximate ones.
- LOD values were calculated accordingly on the basis of the I_0-I/I_0 = f(C_{cation}) linear dependences (Fig. S73).

The plots are given below. The results of calculations are summarized in **Table 2** in the main article file.

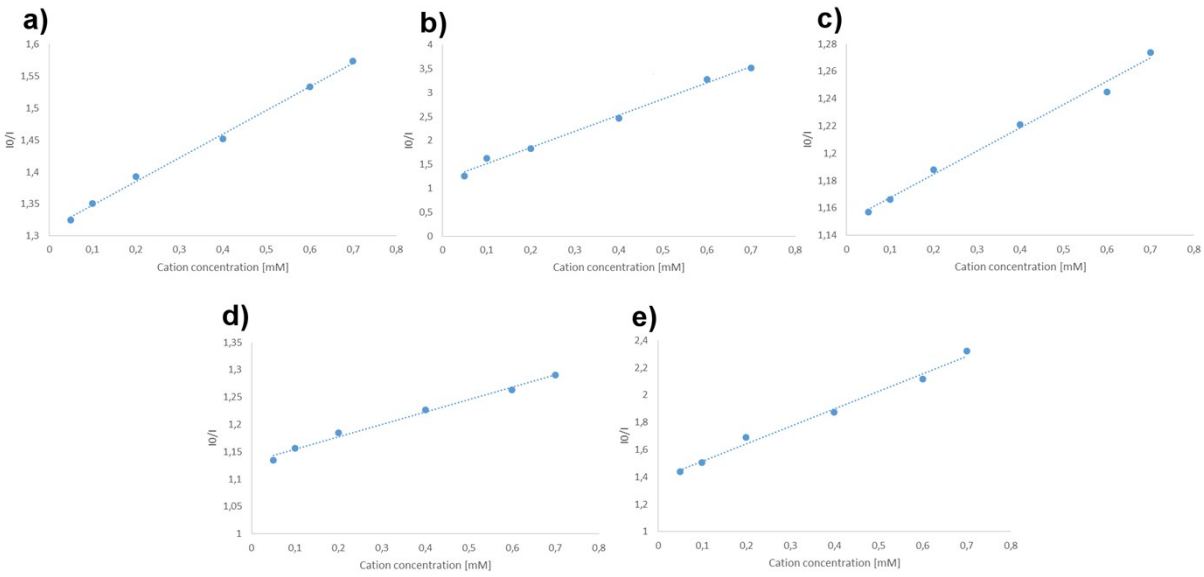


Fig. S71. $I_0/I = f(C_{cation})$ plot for: (**a**) compound **3**, (**b**) compound **4**, (**c**) compound (**5**), (**d**) compound (**8**), (**e**) compound **9**.

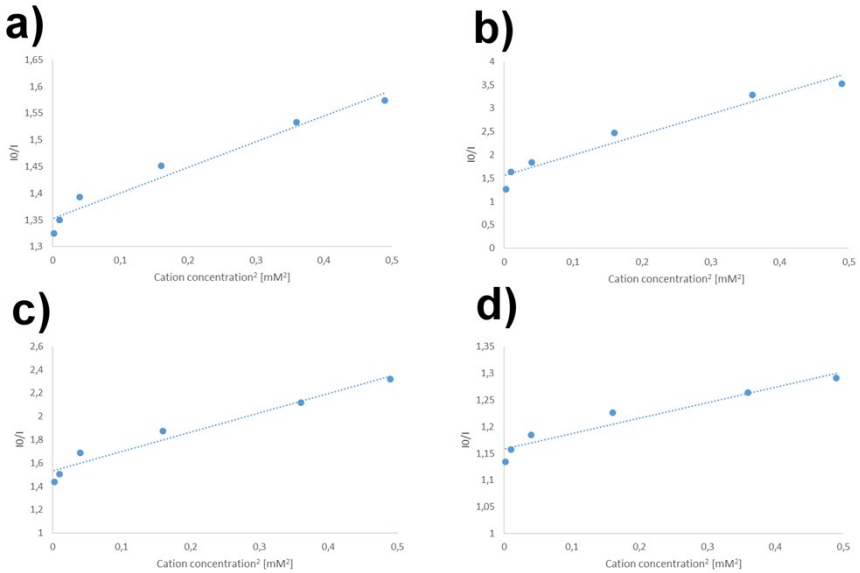


Fig. S72. $I_0/I = f(C_{cation}^2)$ plot for: (**a**) compound **3**, (**b**) compound **4**, (**c**) compound (**8**), (**d**) compound **9**.

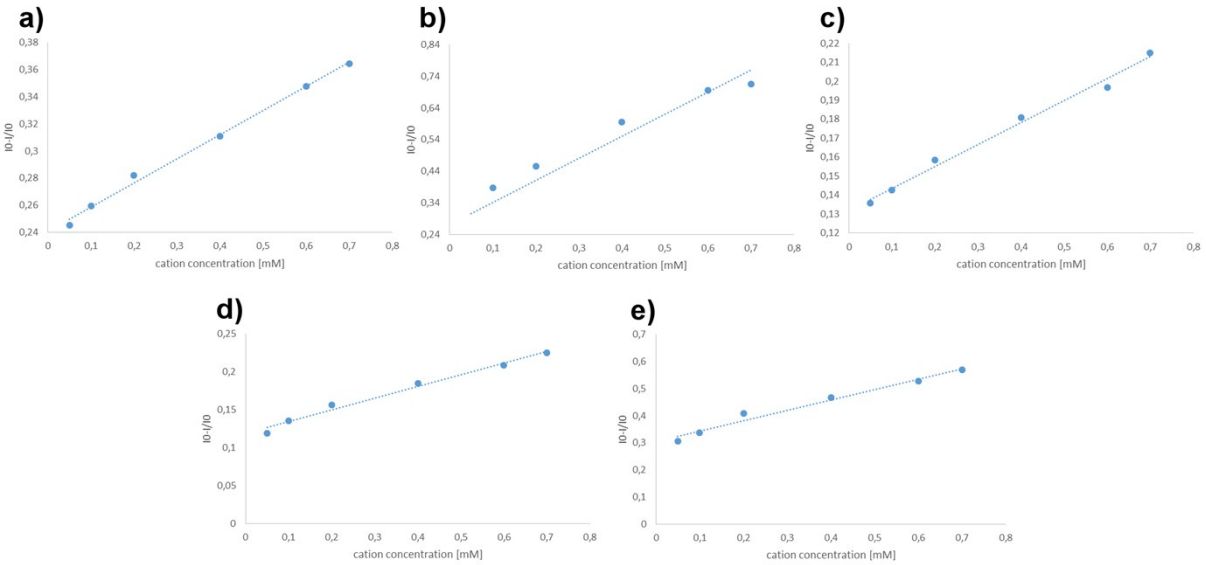


Fig. S73. I_0-I/I = f(C_{cation}) plot for: (**a**) compound **3**, (**b**) compound **4**, (**c**) compound (**5**), (**d**) compound (**8**), (**e**) compound **9**.

S10. References

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[6] MeOH was dried over molecular sieves 3Å and bubbled with N_2 before the reaction.

[7] The compound **5** can be also isolated by means of filtration (67% yield). After filtration of the reaction mixture, the crude product is washed with cold (-30°C) methanol (5 mL), cold (-30°C) THF (1.5 mL) and dried under vacuum.

[8] The solvent was bubbled with N_2 before the reaction.

[9] The compound **8** and be also purified with PTLC (SiO_2; CH_2Cl_2/MeOH = 95:5 *v*/*v*; R_f (**8**) = 0.9; 63% yield).

[10] The optimized partial structure of compound **3** was obtained with Gaussian09 software (M. J. Frisch, et al. *Gaussian 09, Revision B.01, Gaussian Inc., Wallingford, CT*, **2010**).