SUPPORTING INFORMATION for

Substituent Effects in CH Hydrogen Bond Interactions: Linear Free Energy Relationships and Influence of Anions

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Part I: Experimental Procedures

General Comments. ^{1}H and ^{13}C NMR spectra were obtained on a Varian 300 MHz (^{1}H 299.95 MHz, ^{13}C 75.43 MHz), Inova 500 MHz (^{1}H 500.10 MHz, ^{13}C 125.75 MHz) or Bruker Avance-III-HD 600 MHz (^{1}H 599.98 MHz, ^{13}C 150.87 MHz) spectrometer with a Prodigy multinuclear broadband BBO CryoProbe. Chemical shifts (δ) are expressed in ppm relative to tetramethylsilane (TMS) using residual non-deuterated solvent ($CDCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.0 ppm; CD_2Cl_2: ^{1}H 5.32 ppm, ^{13}C 54.0 ppm; DMSO–d_6: ^{1}H 2.50 ppm, ^{13}C 39.51 ppm). UV-Vis spectra were recorded on an HP 8453 UV-Vis spectrophotometer using a 265 nm high-pass filter. Dry solvents were obtained from distillation using published literature procedures directly before use. 2-(Trimethylsilyl)ethynyl-4-*t*-butylaniline (**3**),[1] 1,3-dibromo-5-nitrobenzene (**4b**),[2] 1-*t*-butyl-3,5-diiodobenzene (**4e**),[3] and *N*,*N*-dimethyl-3,5-diiodoaniline (**4g**)[4] were synthesized as previously reported. All other reagents were purchased and used as received.

Dianiline 2a (R=H). A suspension of ethynylaniline **3** (2.262 g, 9.22 mmol) and K_2CO_3 (6.37 g, 46.1 mmol) in Et_2O (15 mL) and MeOH (30 mL) was stirred at 25 °C and monitored by TLC until completion (30 min). The solution was diluted with CH_2Cl_2 and washed three times with water and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dissolved in minimal THF and added to an N_2-purged solution of 1,3-diiodobenzene (**4a**, 1.39 g, 4.20 mmol), $Pd(PPh_3)_4$ (0.49 g, 0.42 mmol) and CuI (0.16 g, 0.84 mmol) in dry THF (45 mL) and *i*-Pr_2NH (45 mL). After stirring at 50 °C for 8 h, the cooled reaction was concentrated *in vacuo* and the residue was taken up into CH_2Cl_2. The solution was filtered through a 3 cm silica gel plug and washed with additional CH_2Cl_2. The combined organics were concentrated *in vacuo* and the product was purified by column chromatography (2:1 hexanes/CH_2Cl_2) to afford **2a** (1.01 g, 57%) as a pale brown solid. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.71 (t, J = 1.7 Hz, 1H), 7.50 (dd, J = 7.7, 1.7 Hz, 2H), 7.34-7.40 (m, 3H), 7.21 (dd, J = 8.5, 2.4

Hz, 2H), 6.69 (d, J = 8.5 Hz, 2H), 4.22 (br s, 4H), 1.28 (s, 18H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 146.37, 141.29, 134.56, 131.37, 129.26, 129.22, 128.00, 124.40, 114.73, 107.30, 93.69, 87.78, 34.35, 31.68. HRMS (ESI) for $C_{30}H_{33}N_2$ $[M+H]^+$: calcd 421.2625, found 421.2644.

Dianiline 2b (R=NO_2). A suspension of ethynylaniline **3** (2.07 g, 8.43 mmol) and K_2CO_3 (5.3 g, 38.3 mmol) in Et_2O (15 mL) and MeOH (30 mL) was stirred at 25 °C and monitored by TLC until completion (30 min). The solution was diluted with CH_2Cl_2 and washed three times with water and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dissolved in minimal THF and added to an N_2-purged solution of 1-nitro-1,3-dibromo-5-nitrobenzene[2] (**4b**, 1.067 g, 3.8 mmol), $Pd(PPh_3)_4$ (0.22 g, 0.19 mmol) and CuI (0.156 g, 0.82 mmol) in dry THF (40 mL) and *i*-Pr_2NH (40 mL). After stirring at 50 °C for 24 h, the cooled reaction was concentrated *in vacuo* and the residue was taken up into CH_2Cl_2. The solution was filtered through a 3 cm silica gel plug and washed with additional CH_2Cl_2. The combined organics were concentrated *in vacuo* and the product was purified by column chromatography (2:1 hexanes:CH_2Cl_2) to afford **2b** (1.7 g, 95%) as an orange solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.46 (d, J = 1.5 Hz, 2H), 8.32 (t, J = 1.4 Hz, 1H), 7.27 (d, J = 2.4 Hz, 2H), 7.19 (dd, J = 8.6, 2.4 Hz, 2H), 6.69 (d, J = 8.6 Hz, 2H), 5.61 (s, 4H), 1.23 (s, 18H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 148.16 (overlapping peaks), 138.94, 137.86, 128.29, 128.07, 125.21, 124.46, 114.06, 103.56, 90.86, 90.84, 33.47, 31.23. HRMS (ESI) for $C_{30}H_{32}N_3O_2$ $[M+H]^+$: calcd 466.2495, found 466.2515.

Dianiline 2c (R=Cl). A suspension of ethynylaniline **5** (2.701 g, 10.98 mmol) and K_2CO_3 (7.554 g, 54.7 mmol) in Et_2O (20 mL) and MeOH (40 mL) was stirred at 25 °C and monitored by TLC until completion (30 min). The solution was diluted with CH_2Cl_2 and washed three times with water and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dissolved in minimal THF and added to an N_2-purged solution of 1,3-dibromo-5-

chlorobenzene (**4c**, 1.615 g, 5.97 mmol), $Pd(PPh_3)_4$ (0.245 g, 0.21 mmol) and CuI (0.025 g, 0.13 mmol) in dry THF (50 mL) and *i*-Pr_2NH (50 mL). After stirring at 50 °C for 8 h, the cooled reaction was concentrated *in vacuo* and the residue was taken up into CH_2Cl_2. The solution was filtered through a 3 cm silica gel plug and washed with additional CH_2Cl_2. The combined organics were concentrated *in vacuo* and the product was purified by column chromatography (2:1 hexanes/CH_2Cl_2) to afford **2c** (1.440 g, 53%) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.46 (d, *J* = 1.5 Hz, 2H), 7.37 (d, *J* = 2.0 Hz, 2H), 7.22 (dd, *J* = 8.5, 2.1 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 4.16 (s, 4H), 1.29 (s, 18H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.85, 137.89, 133.26, 132.04, 129.83, 128.08, 127.75, 125.36, 114.02, 103.96, 91.35, 89.78, 33.44, 31.22. HRMS (ESI) for $C_{30}H_{32}N_2Cl$ $[M+H]^+$: calcd 455.2254, found 455.2242.

Dianiline 2d (R=F). A suspension of ethynylaniline **3** (1.231 g, 5.018 mmol) and K_2CO_3 (3.468 g, 25.09 mmol) in Et_2O (15 mL) and MeOH (30 mL) was stirred at 25 °C and monitored by TLC until completion (30 min). The solution was diluted with CH_2Cl_2 and washed three times with water and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dissolved in minimal THF and added to an N_2-purged solution of 1,3-dibromo-5-fluorobenzene (**4d**, 0.637 g, 2.509 mmol), $Pd(PPh_3)_4$ (0.100 g, 0.0865 mmol) and CuI (0.014 g, 0.735 mmol) in dry THF (20 mL) and *i*-Pr_2NH (20 mL). After stirring at 50 °C for 8 h the cooled reaction was concentrated *in vacuo* and the residue was taken up into CH_2Cl_2. The solution was filtered through a 3 cm silica gel plug and washed with additional CH_2Cl_2. The combined organics were concentrated *in vacuo* and the product was purified by column chromatography (2:1 hexanes/CH_2Cl_2) to afford **2d** (0.715 g, 65%) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (t, *J* = 1.4 Hz, 1H), 7.38 (d, *J* = 2.3 Hz, 2H), 7.22 (dd, *J* = 8.5, 2.3 Hz, 2H), 7.19 (dd, *J* = 9.1, 1.4 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 4.16 (s, 4H), 1.30 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.05 (d, *J* = 244 Hz), 145.76, 141.13, 130.49, 130.47, 128.98, 127.85, 125.61 (d, *J* =

10.5 Hz), 118.05 (d, J = 22.9 Hz), 114.57, 106.79, 92.44 (d, J = 3.5 Hz), 88.33, 34.09, 31.53. HRMS (ESI) for $C_{30}H_{32}N_2F$ $[M+H]^+$: calcd 439.2550, found 439.2531.

Dianiline 2e (R=*t*-Bu). A suspension of ethynylaniline **3** (2.0 g, 8.15 mmol) and K_2CO_3 (5.63 g, 40.74 mmol) in Et_2O (20 mL) and MeOH (40 mL) was stirred at 25 °C and monitored by TLC until completion (30 min). The solution was diluted with CH_2Cl_2 and washed three times with water and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dissolved in minimal THF and added to an N_2-purged solution of 1-*t*-butyl-3,5-diiodobenzene[3] (1.19 g, 3.08 mmol), $Pd(PPh_3)_4$ (0.178 g, 0.15 mmol) and CuI (0.12 g, 0.62 mmol) in dry THF (10 mL) and *i*-Pr_2NH (10 mL). After stirring at 50 °C for 23 h, the cooled reaction was concentrated *in vacuo* and the residue was taken up into CH_2Cl_2. The solution was filtered through a 3 cm silica gel plug and washed with additional CH_2Cl_2. The combined organics were concentrated *in vacuo* and the product was purified by column chromatography (3:2 hexanes/EtOAc) to afford **2e** (0.903 g, 61%) as a pale brown solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.63–7.52 (m, 3H), 7.39 (d, J = 2.3 Hz, 2H), 7.21 (dd, J = 8.5, 2.3 Hz, 2H), 6.70 (d, J = 8.5 Hz, 2H), 4.23 (s, 4H), 1.37 (s, 9H), 1.29 (s, 18H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 152.51, 146.34, 141.29, 131.77, 129.27, 128.90, 127.89, 123.96, 114.73, 107.47, 94.26, 87.10, 35.24, 34.36, 31.71, 31.45. HRMS (ESI) for $C_{34}H_{41}N_2$ $[M+H]^+$: calcd 477.3270, found 477.3263.

Dianiline 2f (R=OMe). A suspension of ethynylaniline **3** (0.808 g, 4.27 mmol) and K_2CO_3 (2.95 g, 21.33 mmol) in Et_2O (15 mL) and MeOH (30 mL) was stirred at at 25 °C and monitored by TLC until completion (30 min). The solution was diluted with CH_2Cl_2 and washed three times with water and brine. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was dissolved in minimal THF and added to an N_2-purged solution of 3,5-dibromoanisole (0.250 g, 0.940 mmol), $Pd(PPh_3)_4$ (0.100 g, 0.0865 mmol) and CuI (0.010 g, 0.0525 mmol) in dry THF (50 mL) and *i*-Pr_2NH (50 mL). After stirring at 50 °C for 8 h, the

cooled reaction was concentrated *in vacuo* and the residue was taken up into CH_2Cl_2. The solution was filtered through a 3 cm silica gel plug and washed with additional CH_2Cl_2. The combined organics were concentrated *in vacuo* and the product was purified by column chromatography (CH_2Cl_2) to afford **2f** (0.182 g, 43%) as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 1.9 Hz, 2H), 7.33 (s, 1H), 7.20 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.04 (s, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 4.17 (s, 4H), 3.85 (s, 3H), 1.29 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.45, 145.68, 141.07, 128.92, 127.50, 127.24, 124.82, 116.92, 114.50, 107.25, 93.50, 87.10, 55.66, 34.07, 31.54. HRMS (ESI) for $C_{31}H_{35}N_2O$ $[M+H]^+$: calcd 451.2749, found 451.2729.

Dianiline 2g (R=NMe$_2$). A suspension of ethynylaniline **3** (0.312 g, 1.24 mmol) and K_2CO_3 (0.856 g, 6.195 mmol) in Et_2O (10 mL) and MeOH (20 mL) was stirred at 25 °C and monitored by TLC until completion (30 min). The solution was diluted with CH_2Cl_2 and washed three times with water and brine. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dissolved in minimal THF and added to an N_2-purged solution of *N*,*N*-dimethyl-3,5-diiodoaniline[4] (0.20 g, 0.59 mmol), $Pd(PPh_3)_4$ (0.014 g, 0.012 mmol) and CuI (0.005 g, 0.02 mmol) in dry THF (15 mL) and *i*-Pr_2NH (5 mL). After stirring at 50 °C for 8 h, the cooled reaction was concentrated *in vacuo* and the residue was taken up into CH_2Cl_2. The solution was filtered through a 3 cm silica gel plug and washed with additional CH_2Cl_2. The combined organics were concentrated *in vacuo* and the product was purified by column chromatography (3:1 hexanes/EtOAc followed by 100% EtOAc) to afford **2g** (0.111 g, 41%) as a pale brown solid. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.37 (d, *J* = 2.4 Hz, 2H), 7.19 (dd, *J* = 8.5, 2.4 Hz, 2H), 7.05 (t, *J* = 1.3 Hz, 1H), 6.86 (d, *J* = 1.3 Hz, 2H), 6.69 (d, *J*=8.5, 2H), 4.22 (s, 4H), 3.00 (s, 4H), 1.28 (s, 18H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 150.94, 146.30, 141.24, 129.23, 127.76, 124.60, 122.69, 115.30, 114.67, 107.57, 94.74, 86.39, 40.78, 34.34, 31.69. HRMS (ESI) for $C_{32}H_{38}N_3$ $[M+H]^+$: calcd 464.3066, found 464.3055.

Bisurea 1a (R=H). All glassware was dried in a 150 °C oven for at least 1 h. Dianiline **2a** (200 mg, 0.5 mmol) and *p*-methoxyphenyl isocyanate (177 mg, 1.2 mmol) in toluene (50 mL) were stirred at 50 °C for 8 h. The reaction became cloudy upon completion and acetone was added until the turbidity was removed. Hexanes was added until a slight turbidity returned and the suspension was left to precipitate overnight in the refrigerator. Filtration afforded **1a** (320 mg, 93%) as a fine white powder. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.28 (s, 2H), 8.11 (s, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.99 (t, J = 1.7 Hz, 1H), 7.72 (dd, J = 7.6, 1.7 Hz, 2H), 7.55 (t, J = 7.8 Hz, 1H), 7.50 (d, J = 2.4 Hz, 2H), 7.42 (dd, J = 8.8, 2.4 Hz, 2H), 7.37 (d, J = 8.9 Hz, 4H), 6.86 (d, J = 8.9 Hz, 4H), 3.70 (s, 6H), 1.29 (s, 18H). ^{13}C NMR (151 MHz, DMSO-d_6): δ 154.61, 152.40, 144.38, 138.04, 134.33, 132.43, 131.77, 129.16, 128.69, 126.96, 122.94, 120.22, 119.64, 114.03, 110.73, 93.69, 86.75, 55.13, 33.94, 31.02. HRMS (ESI) for $C_{46}H_{47}N_4O_4$ $[M+H]^+$: calcd 719.3563, found 719.3597.

Bisurea 1b (R=NO_2). All glassware was dried in a 150 °C oven for at least 1 h. Dianiline **1b** (0.100 g, 0.215 mmol) and *p*-methoxyphenyl isocyanate (0.08 mg, 0.536 mmol) in toluene (50 mL) were stirred at 80 °C for 8 h. The reaction became cloudy upon completion and filtration afforded **1b** (100 mg, 47%) as a fine yellow powder. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.25 (s, 2H), 8.55 (s, 2H), 8.40 (s, 1H), 8.19 (s, 2H), 8.05 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 2.3 Hz, 2H), 7.47 (dd, J = 8.8, 2.4 Hz, 2H), 7.39 (d, J = 8.7 Hz, 4H), 6.87 (d, J = 8.7 Hz, 4H), 3.70 (s, 6H), 1.30 (s, 18H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 154.65, 152.36, 148.18, 144.47, 139.77, 138.41, 132.35, 129.03, 127.63, 125.72, 124.55, 120.25, 119.71, 114.06, 110.03, 91.79, 89.11, 55.14, 33.99, 31.01. HRMS (ESI) for $C_{46}H_{46}N_5O_6$ $[M+H]^+$: calcd 764.3448, found 764.3412.

Bisurea 1c (R=Cl). All glassware was dried in a 150 °C oven for at least 1 h. Dianiline **2c** (125 mg, 0.274 mmol) and *p*-methoxyphenyl isocyanate (94 mg, 0.632 mmol) in toluene (50 mL) were stirred at 50 °C for 8 h. The reaction became cloudy upon completion and filtration

afforded **1c** (186 mg, 90%) as a fine white powder. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.25 (s, 2H), 8.11 (s, 2H), 8.04 (d, J = 8.6 Hz, 2H), 7.95 (s, 1H), 7.84 (s, 2H), 7.53 (s, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.3 Hz, 4H), 6.86 (d, J = 8.3 Hz, 4H), 3.71 (s, 6H), 1.29 (s, 18H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.64, 152.36, 144.41, 138.25, 133.52, 132.85, 132.38, 131.07, 128.83, 127.34, 124.77, 120.26, 119.67, 114.04, 110.29, 92.34, 88.16, 55.13, 33.95, 30.99. HRMS (ESI) for $C_{46}H_{46}N_4O_4Cl$ $[M+H]^+$: calcd 753.3208, found 753.3215.

Bisurea 1d (R=F). All glassware was dried in a 150 °C oven for at least 1 h. Dianiline **2d** (250 mg, 0.570 mmol) and *p*-methoxyphenyl isocyanate (177 mg, 1.2 mmol) in toluene (50 mL) were stirred at 50 °C for 8 h. The reaction became cloudy upon completion and filtration afforded **1d** (400 mg, 95%) as a fine white powder. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.25 (s, 2H), 8.11 (s, 2H), 8.03 (d, J = 9.0 Hz, 2H), 7.85 (s, 1H), 7.63 (d, J = 9.2 Hz, 2H), 7.52 (s, 2H), 7.44 (d, J = 7.2 Hz, 2H), 7.38 (d, J = 8.8 Hz, 4H), 6.86 (d, J = 8.8 Hz, 4H), 3.70 (s, 6H), 1.29 (s, 18H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.6 (d, J = 245.2), 155.12, 152.85, 144.90, 138.71, 132.86, 131.34, 129.26, 127.80, 124.83 (d, J = 11.0 Hz), 120.75, 120.17, 119.00, 114.51, 110.78, 92.55 (d, J = 3.8 Hz), 88.32, 55.61, 34.43, 31.48. HRMS (ESI) for $C_{46}H_{46}N_4O_4F$ $[M+H]^+$: calcd 737.3503, found 737.3487.

Bisurea 1e (R=*t*-Bu). Dianiline **2e** (300 mg, 0.63 mmol) and *p*-methoxyphenyl isocyanate (235 mg, 1.57 mmol) in dry toluene (50 mL) were stirred at 50 °C for 48 h. The reaction was evaporated to dryness in vacuo and purified by column chromatography (3:2 hexanes:EtOAc, 410 mg, 84%). Trituration with EtOH afforded analytically pure **1e** (40 mg, 10%) as a fine white powder. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.29 (s, 2H), 8.13 (s, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.84 (t, J = 1.4 Hz, 1H), 7.73 (d, J = 1.5 Hz, 2H), 7.52 (d, J = 2.3 Hz, 2H), 7.42 (dd, J = 8.9, 2.4 Hz, 2H), 7.38 (d, J = 8.7 Hz, 4H), 6.86 (d, J = 8.6 Hz, 4H), 3.70 (s, 6H), 1.35 (s, 9H), 1.29 (s, 18H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.06, 152.90, 152.24, 144.89, 138.49, 132.97,

132.21, 129.37, 129.18, 127.32, 123.18, 120.58, 120.23, 114.52, 111.48, 94.64, 86.76, 55.60, 35.11, 34.42, 31.50, 31.29. HRMS (ESI) for $C_{50}H_{55}N_4O_4$ $[M+H]^+$: calcd 775.4223, found 775.4191.

Bisurea 1f (R=OMe). Dianiline **2f** (150 mg, 0.33 mmol) and *p*-methoxyphenyl isocyanate (105 mg, 0.70 mmol) in dry toluene (40 mL) were stirred at 50 °C for 8 h. The reaction became cloudy upon completion and acetone was added until the turbidity was removed. Hexanes was added until a slight turbidity returned and the suspension was left to precipitate overnight in the refrigerator. Filtration afforded **1f** (215 mg, 87%) as a fine white powder. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.28 (s, 2H), 8.09 (s, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.59 (s, 1H), 7.50 (d, J = 2.4 Hz, 2H), 7.42 (dd, J = 8.7, 2.4 Hz, 2H), 7.37 (d, J = 8.9 Hz, 4H), 7.32 (s, 2H), 6.85 (d, J = 8.9 Hz, 4H), 3.86 (s, 3H), 3.70 (s, 6H), 1.29 (s, 18H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 159.19, 154.60, 152.39, 144.37, 138.06, 132.44, 128.87, 128.70, 126.97, 123.94, 120.19, 119.68, 117.45, 114.02, 110.71, 93.68, 86.56, 55.64, 55.12, 33.93, 31.01. HRMS (ESI) for $C_{46}H_{46}N_4O_4F$ $[M+H]^+$: calcd 737.3503, found 737.3487.

Bisurea 1g (R=NMe$_2$). Dianiline **2g** (50 mg, 0.11 mmol) and *p*-methoxyphenyl isocyanate (37 mg, 0.25 mmol) in toluene (20 mL) were stirred at 50 °C for 48 h. The reaction became cloudy upon completion and was cooled overnight at –20 °C. Filtration afforded **1g** (47 mg, 57%) as a fine white powder.^{1}H NMR (600 MHz, DMSO-d_6) δ 9.30 (s, 2H), 8.08 (s, 2H), 8.00 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 2.4 Hz, 2H), 7.41 (dd, J = 8.8, 2.4 Hz, 2H), 7.37 (d, J = 9.0 Hz, 4H), 7.28 (s, 1H), 7.04 (d, J = 1.3 Hz, 2H), 6.85 (d, J = 9.0 Hz, 4H), 3.70 (s, 6H), 2.98 (s, 6H), 1.29 (s, 18H). ^{13}C NMR (151 MHz, DMSO) δ 154.57, 152.43, 150.20, 144.40, 137.93, 132.50, 128.67, 126.72, 123.25, 122.16, 120.12, 119.73, 115.28, 114.04, 111.13, 94.82, 85.46, 55.14, 39.97, 33.95, 31.04. HRMS (ESI) for $C_{48}H_{52}N_5O_4$ $[M+H]^+$: calcd 762.4019, found 762.3986.

Part II: X-Ray Crystallography

Diffraction intensities were collected at 173(2) K on a Bruker Apex2 CCD diffractometer using CuKα radiation λ= 1.54178 Å. The space group was determined based on systematic absences. Absorption corrections were applied by SADABS.[5] The structure was solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. All H atoms were treated in calculated positions, except those at the N atoms involved in H-bonds, which were found from the residual density map and refined with restrictions on their N-H distances; the value of 1 Å was used in the refinement as a target for the corresponding N-H bonds. In addition to **1b** the crystal structure includes solvent acetonitrile molecules. The refinement showed that position of the acetonitrile is not fully occupied; in the structure there is a half of acetonitrile molecule per one main molecule. Crystals of the investigated compound were very small needles and diffraction at high angles was very weak. Even using a strong *Incoatec IμS* Cu source we could collect visible diffraction data only up to θ_{max} = 100.0°. While the final structure is not very precise, it clearly represents all chemical results. All calculations were performed by the Bruker SHELXTL (v. 6.10)[6] and SHELXL-2013 packages.[7] The crystal structure of TBA^+ **(1a**⊂Cl)$^-$ has been reported previously[8] and the data deposited with the CCDC as structure #929532.

Crystallographic data for **1b**: $C_{46}H_{46.5}N_{5.5}O_6$ [$C_{46}H_{45}N_5O_6$·0.5(CH_3CN)], M = 784.39, 0.14 x 0.04 x 0.03 mm, T = 173(2) K, Monoclinic, space group *P*2/*c*, *a* = 16.7165(16) Å, *b* = 9.0824(8) Å, *c* = 29.495(3) Å, *β* = 101.756(7)°, *V* = 4384.2(8) Å^3, *Z* = 4, D_c = 1.188 Mg/m^3, *μ* = 0.642 mm^{-1}, *F*(000) = 1660, $2\theta_{max}$ = 100.0°, 15027 reflections, 4362 independent reflections [R_{int} = 0.0699], R1 = 0.1023, wR2 = 0.2840 and GOF = 1.083 for 4362 reflections (557 parameters) with I>2σ(I), R1 = 0.1270, wR2 = 0.3018 and GOF = 1.083 for all reflections, max/min residual electron density +0.432/–0.298 eÅ^3.

Part III: Titrations

^{1}H NMR Titrations

NMR Titration Conditions. ^{1}H NMR titrations were carried out on an Inova 500 MHz spectrometer (^{1}H 500.10 MHz). Chemical shifts (δ) are expressed in ppm relative to tetramethylsilane (TMS) using residual non-deuterated solvent ($CDCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.0 ppm). $CDCl_3$ was prepared by passing over activated alumina. 1:1 v/v $CDCl_3$ and deionized water was mixed in a separatory funnel and the organic layer was collected. Association constants were determined using non-linear regression fitting in MatLab.[9] Titration data for **1a** with halides has been previously reported.[8]

A stock solution of **1a-g** in $CDCl_3$ (3 mL) was prepared and used in the preparation of a TBA salt solution (2.4 mL). The remaining stock solution (0.6 mL) was used as the starting volume in an NMR tube. Spectra were recorded after each addition of TBA salt on a 500 MHz spectrometer and the Δδ of urea proton H_g was used to follow the progress of the titration.

Table S1. Titration of **1a** with NO_3^-. (Stock $[NO_3^-]$ = 20.1 mM)

	Guest (μL)	[**1a**] (M)	$[NO_3^-]$ (M)	Equiv.	δ (ppm)
0	0	7.42E-04	0.00E+00	0.00	7.443
1	5	7.42E-04	1.01E-07	0.22	7.570
2	10	7.42E-04	2.01E-07	0.44	7.688
3	15	7.42E-04	3.02E-07	0.66	7.770
4	20	7.42E-04	4.02E-07	0.87	7.853
5	25	7.42E-04	5.03E-07	1.08	7.919
6	35	7.42E-04	7.04E-07	1.49	8.005
7	45	7.42E-04	9.05E-07	1.89	8.068
8	55	7.42E-04	1.11E-06	2.28	8.109
9	65	7.42E-04	1.31E-06	2.65	8.137
10	75	7.42E-04	1.51E-06	3.01	8.158
11	85	7.42E-04	1.71E-06	3.36	8.172
12	100	7.42E-04	2.01E-06	3.87	8.190
13	125	7.42E-04	2.51E-06	4.67	8.208
14	150	7.42E-04	3.02E-06	5.42	8.221
15	200	7.42E-04	4.02E-06	6.78	8.235
16	250	7.42E-04	5.03E-06	7.97	8.244
17	350	7.42E-04	7.04E-06	9.98	8.257
18	450	7.42E-04	9.05E-06	11.61	8.265

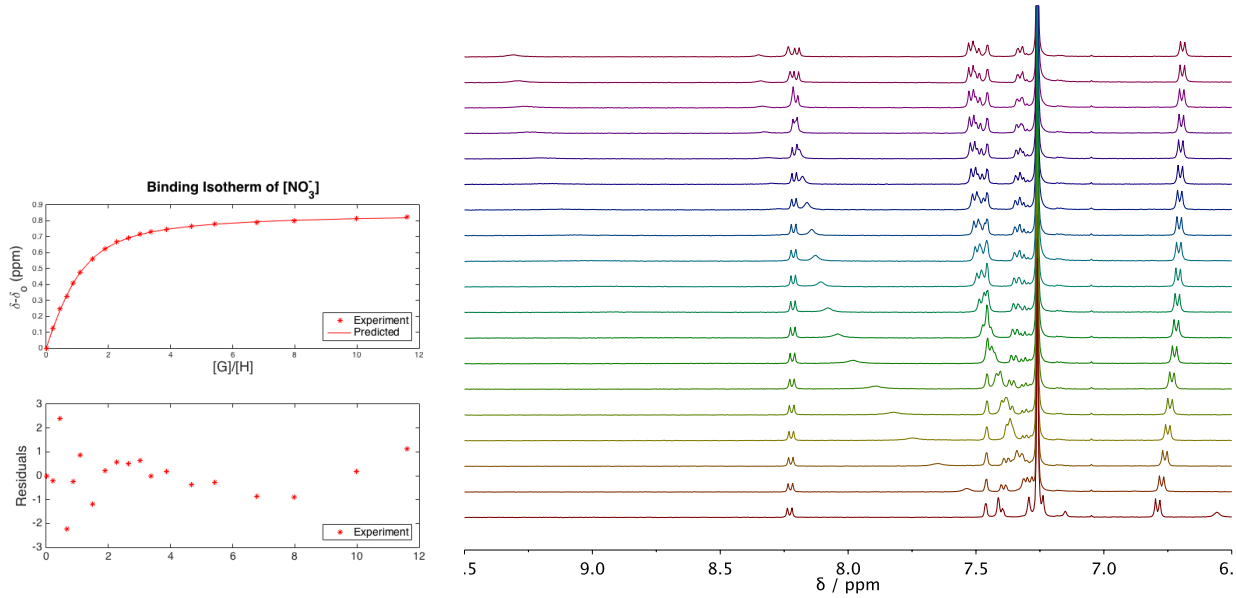

Figure S1. Binding isotherm for NO_3^- titration of **1a** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1a** (0.742 mM) titrated with TBA NO_3^- (0-11.6 equiv., bottom to top) in $CDCl_3$.

Table S2. Titration of **1b** with Cl^-. (Stock [Cl^-] = 12.1 mM)

	Guest (μL)	[**1b**] (M)	[Cl^-] (M)	Equiv.	δ (ppm)
0	0	3.77E-04	0.00E+00	0.00	7.467
1	4	3.77E-04	7.99E-05	0.21	7.550
2	8	3.77E-04	1.59E-04	0.42	7.655
3	12	3.77E-04	2.37E-04	0.63	7.832
4	16	3.77E-04	3.13E-04	0.83	7.940
5	20	3.77E-04	3.89E-04	1.03	8.000
6	24	3.77E-04	4.64E-04	1.23	8.033
7	28	3.77E-04	5.38E-04	1.43	8.053
8	32	3.77E-04	6.11E-04	1.62	8.066
9	37	3.77E-04	7.01E-04	1.86	8.076
10	45	3.77E-04	8.42E-04	2.23	8.086
11	55	3.77E-04	1.01E-03	2.69	8.093
12	65	3.77E-04	1.18E-03	3.13	8.098
13	80	3.77E-04	1.42E-03	3.76	8.102
14	100	3.77E-04	1.72E-03	4.57	8.106
15	125	3.77E-04	2.08E-03	5.52	8.108
16	150	3.77E-04	2.41E-03	6.40	8.110
17	200	3.77E-04	3.02E-03	8.00	8.112
18	250	3.77E-04	3.55E-03	9.41	8.113
19	350	3.77E-04	4.44E-03	11.79	8.115
20	450	3.77E-04	5.17E-03	13.71	8.116

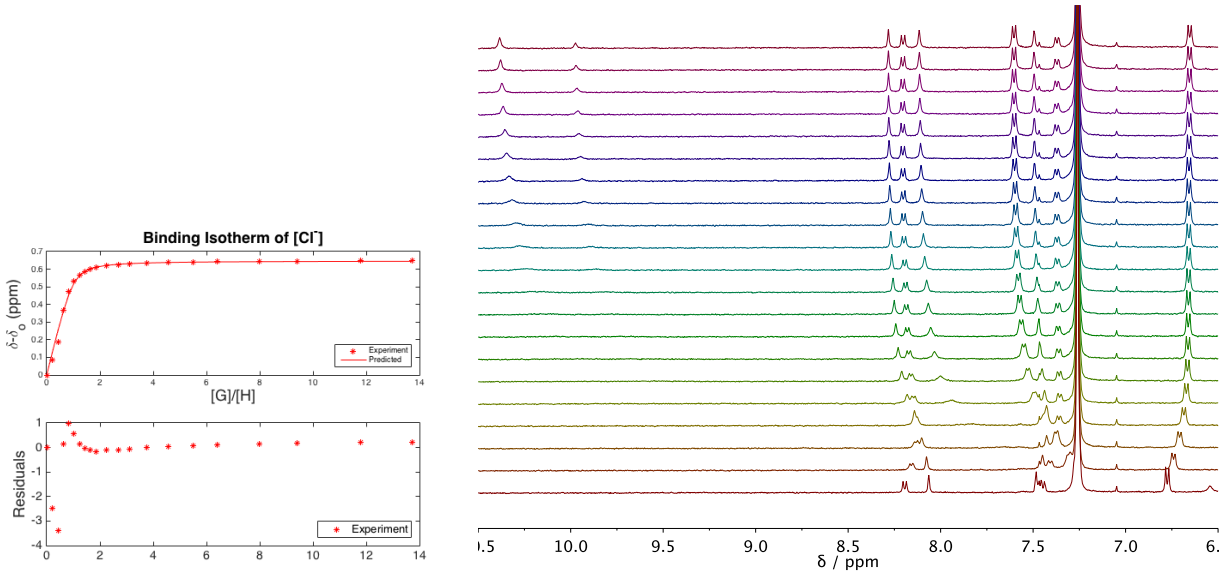

Figure S2. Binding isotherm for Cl^- titration of **1b** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1b** (0.377 mM) titrated with TBA Cl^- (0-13.7 equiv., bottom to top) in $CDCl_3$.

Table S3. Titration of **1b** with Br^-. (Stock [Br^-] = 18.8 mM)

	Guest (μL)	[**1b**] (M)	[Cl^-] (M)	Equiv.	δ (ppm)
0	0	4.76E-04	0.00E+00	0.00	7.486
1	5	4.76E-04	9.39E-08	0.33	7.524
2	10	4.76E-04	1.88E-07	0.65	7.683
3	15	4.76E-04	2.82E-07	0.96	7.769
4	20	4.76E-04	3.76E-07	1.27	7.820
5	30	4.76E-04	5.64E-07	1.88	7.877
6	40	4.76E-04	7.51E-07	2.47	7.906
7	50	4.76E-04	9.39E-07	3.04	7.924
8	60	4.76E-04	1.13E-06	3.59	7.935
9	80	4.76E-04	1.50E-06	4.65	7.949
10	100	4.76E-04	1.88E-06	5.64	7.958
11	125	4.76E-04	2.35E-06	6.81	7.965
12	150	4.76E-04	2.82E-06	7.90	7.969
13	200	4.76E-04	3.76E-06	9.87	7.975
14	300	4.76E-04	5.64E-06	13.17	7.981
15	400	4.76E-04	7.51E-06	15.80	7.984
16	600	4.76E-04	1.13E-05	19.75	7.988
17	800	4.76E-04	1.50E-05	22.57	7.989
18	1000	4.76E-04	1.88E-05	24.69	7.990

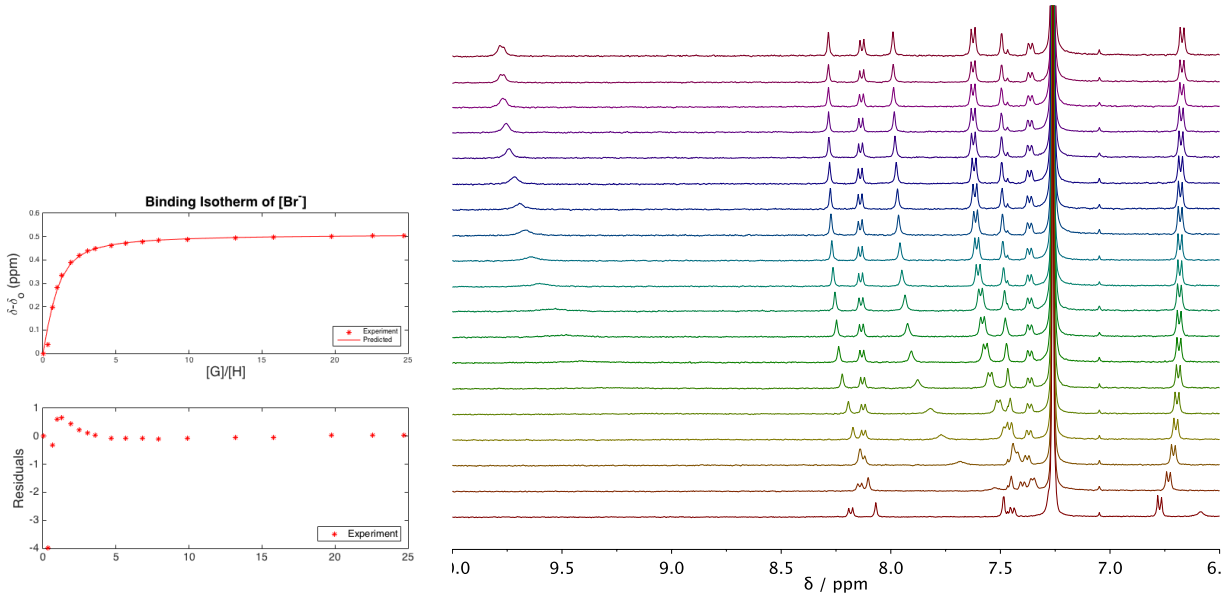

Figure S3. Binding isotherm for Br^- titration of **1b** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1b** (0.476 mM) titrated with TBA Br^- (0-24.7 equiv., bottom to top) in $CDCl_3$.

Table S4. Titration of **1b** with I⁻. (Stock [I⁻] = 62.5 mM)

	Guest (μL)	[**1b**] (M)	[I⁻] (M)	Equiv.	δ (ppm)
0	0	1.27E-03	0.00E+00	0.00	8.062
1	5	1.27E-03	3.13E-07	0.41	8.094
2	10	1.27E-03	6.25E-07	0.81	8.115
3	15	1.27E-03	9.38E-07	1.20	8.133
4	20	1.27E-03	1.25E-06	1.59	8.147
5	30	1.27E-03	1.88E-06	2.35	8.169
6	40	1.27E-03	2.50E-06	3.09	8.184
7	50	1.27E-03	3.13E-06	3.80	8.196
8	65	1.27E-03	4.06E-06	4.83	8.209
9	80	1.27E-03	5.00E-06	5.81	8.218
10	100	1.27E-03	6.25E-06	7.06	8.227
11	120	1.27E-03	7.50E-06	8.23	8.234
12	160	1.27E-03	1.00E-05	10.40	8.243
13	200	1.27E-03	1.25E-05	12.35	8.248
14	250	1.27E-03	1.56E-05	14.53	8.252
15	300	1.27E-03	1.88E-05	16.47	8.255
16	400	1.27E-03	2.50E-05	19.76	8.259
17	600	1.27E-03	3.75E-05	24.70	8.262
18	800	1.27E-03	5.00E-05	28.23	8.263
19	1200	1.27E-03	7.50E-05	32.93	8.264

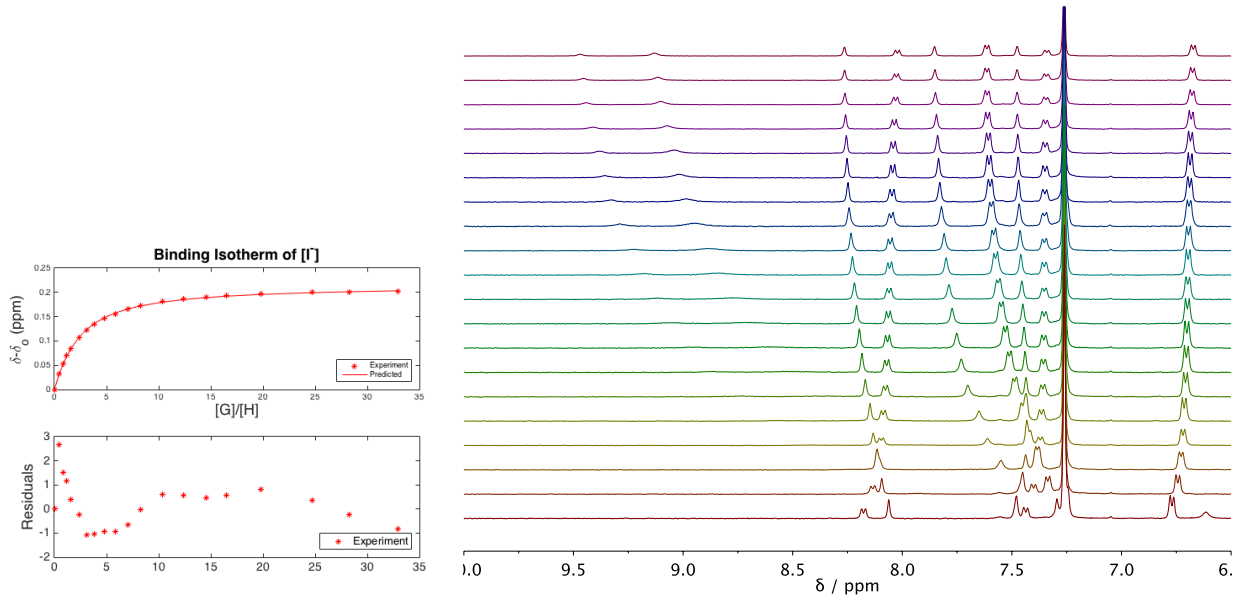

Figure S4. Binding isotherm for I⁻ titration of **1b** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1b** (1.27 mM) titrated with TBA I⁻ (0-32.9 equiv., bottom to top) in $CDCl_3$.

Table S5. Titration of **1b** with NO_3^-. (Stock $[NO_3^-]$ = 27.1 mM)

	Guest (μL)	[**1b**] (M)	$[NO_3^-]$ (M)	Equiv.	δ (ppm)
0	0	4.45E-04	0.00E+00	0.00	7.284
1	5	4.45E-04	1.35E-07	0.50	7.719
2	10	4.45E-04	2.71E-07	1.00	7.997
3	15	4.45E-04	4.06E-07	1.48	8.105
4	20	4.45E-04	5.42E-07	1.96	8.15
5	25	4.45E-04	6.77E-07	2.43	8.174
6	30	4.45E-04	8.13E-07	2.90	8.188
7	35	4.45E-04	9.48E-07	3.35	8.197
8	40	4.45E-04	1.08E-06	3.80	8.204
9	50	4.45E-04	1.35E-06	4.68	8.213
10	60	4.45E-04	1.63E-06	5.53	8.219
11	80	4.45E-04	2.17E-06	7.16	8.228
12	100	4.45E-04	2.71E-06	8.69	8.231
13	150	4.45E-04	4.06E-06	12.17	8.238
14	200	4.45E-04	5.42E-06	15.22	8.244
15	300	4.45E-04	8.13E-06	20.29	8.248
16	400	4.45E-04	1.08E-05	24.34	8.251
17	600	4.45E-04	1.63E-05	30.43	8.254

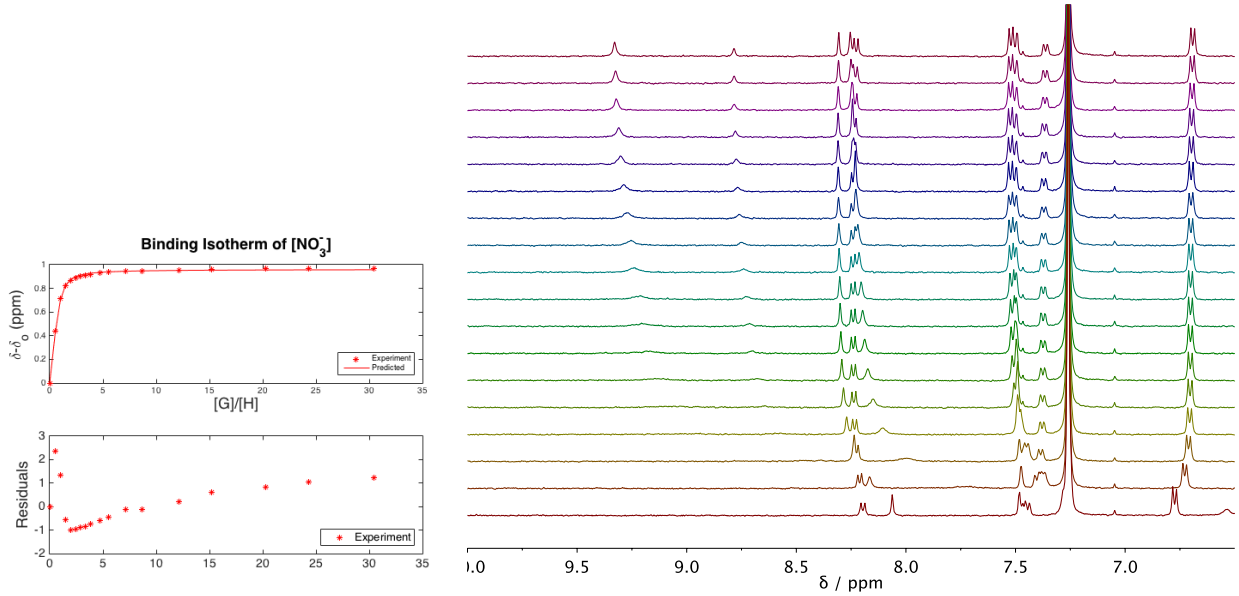

Figure S5. Binding isotherm for NO_3^- titration of **1b** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1b** (0.445 mM) titrated with TBA NO_3^- (0-30.4 equiv., bottom to top) in $CDCl_3$.

Table S6. Titration of **1c** with Cl^-. (Stock $[Cl^-]$ = 27.4 mM)

	Guest (µL)	[**1c**] (M)	$[Cl^-]$ (M)	Equiv.	δ (ppm)
0	0	7.43E-04	0.00E+00	0.00	7.027
1	5	7.43E-04	2.26E-04	0.30	7.573
2	10	7.43E-04	4.49E-04	0.60	7.791
3	15	7.43E-04	6.68E-04	0.90	7.92
4	20	7.43E-04	8.83E-04	1.19	7.989
5	25	7.43E-04	1.10E-03	1.47	8.02
6	30	7.43E-04	1.30E-03	1.75	8.037
7	40	7.43E-04	1.71E-03	2.30	8.053
8	50	7.43E-04	2.11E-03	2.83	8.062
9	60	7.43E-04	2.49E-03	3.35	8.067
10	80	7.43E-04	3.22E-03	4.33	8.073
11	100	7.43E-04	3.91E-03	5.26	8.077
12	150	7.43E-04	5.48E-03	7.37	8.084
13	200	7.43E-04	6.84E-03	9.21	8.087
14	300	7.43E-04	9.13E-03	12.28	8.093
15	400	7.43E-04	1.10E-02	14.73	8.097
16	600	7.43E-04	1.37E-02	18.41	8.102
17	1100	7.43E-04	1.77E-02	23.83	8.106
18	1600	7.43E-04	1.99E-02	26.78	8.106

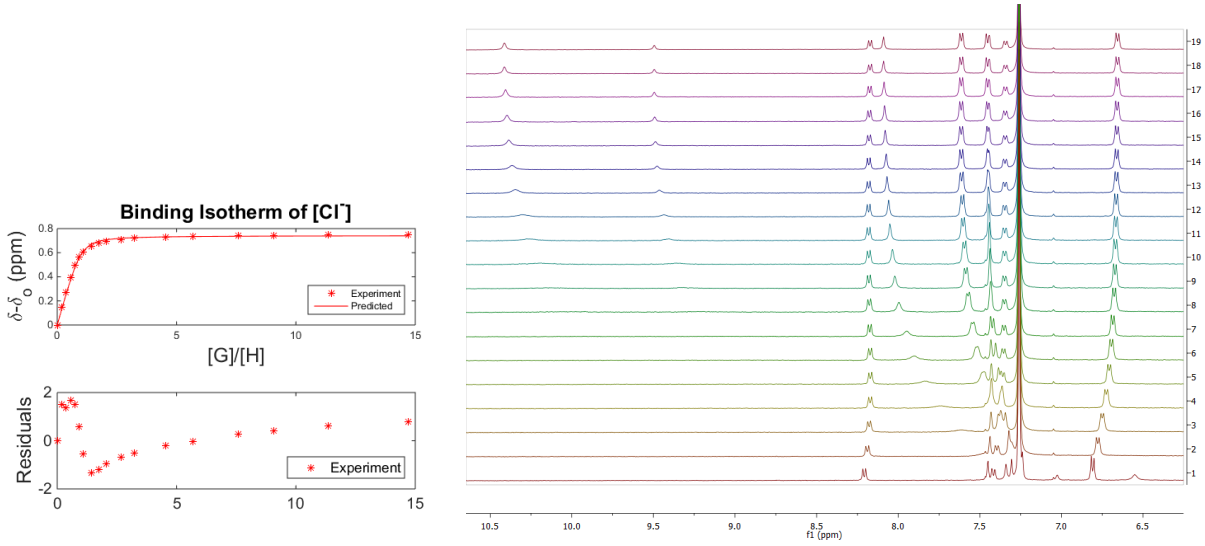

Figure S6. Binding isotherm for Cl^- titration of **1c** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1c** (0.743 mM) titrated with TBA Cl^- (0-26.78 equiv., bottom to top) in $CDCl_3$.

Table S7. Titration of **1c** with Br^-. (Stock [Br^-] = 24.5 mM)

	Guest (μL)	[**1c**] (M)	[Br^-] (M)	Equiv.	δ (ppm)
0	0	5.18E-04	0.00E+00	0.00	7.042
1	5	5.18E-04	2.03E-04	0.39	7.479
2	10	5.18E-04	4.02E-04	0.78	7.592
3	15	5.18E-04	5.98E-04	1.16	7.672
4	20	5.18E-04	7.91E-04	1.53	7.722
5	25	5.18E-04	9.81E-04	1.89	7.761
6	30	5.18E-04	1.17E-03	2.26	7.79
7	40	5.18E-04	1.53E-03	2.96	7.828
8	50	5.18E-04	1.89E-03	3.64	7.852
9	60	5.18E-04	2.23E-03	4.31	7.87
10	80	5.18E-04	2.88E-03	5.57	7.891
11	150	5.18E-04	4.90E-03	9.47	7.905
12	200	5.18E-04	6.13E-03	11.84	7.924
13	300	5.18E-04	8.17E-03	15.79	7.935
14	400	5.18E-04	9.81E-03	18.95	7.946
15	600	5.18E-04	1.23E-02	23.68	7.952
16	1000	5.18E-04	1.53E-02	29.60	7.958
17	1500	5.18E-04	1.75E-02	33.83	7.962

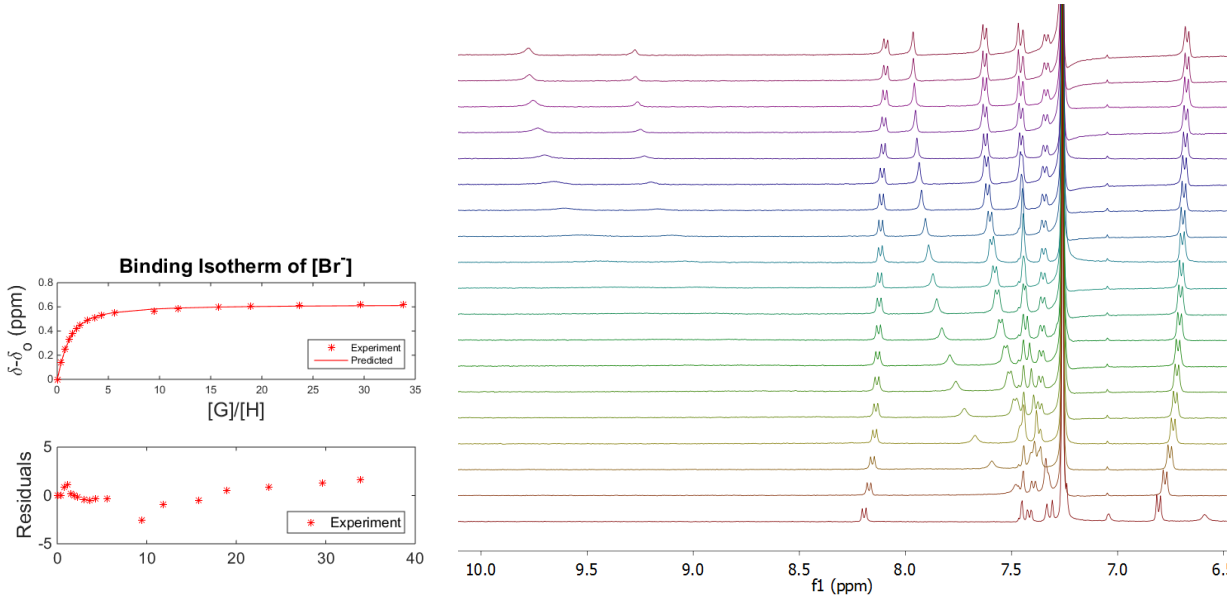

Figure S7. Binding isotherm for Br^- titration of **1c** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1c** (0.518 mM) titrated with TBA Br^- (0-33.83 equiv., bottom to top) in $CDCl_3$.

Table S8. Titration of **1c** with I⁻. (Stock [I⁻] = 70.3 mM)

	Guest (μL)	[**1c**] (M)	[I⁻] (M)	Equiv.	δ (ppm)
0	0	7.35E-04	0.00E+00	0	7.339
1	5	7.35E-04	5.81E-04	0.79	7.41
2	10	7.35E-04	1.15E-03	1.57	7.463
3	15	7.35E-04	1.72E-03	2.34	7.506
4	20	7.35E-04	2.27E-03	3.09	7.537
5	25	7.35E-04	2.81E-03	3.83	7.567
6	30	7.35E-04	3.35E-03	4.56	7.592
7	40	7.35E-04	4.40E-03	5.98	7.627
8	50	7.35E-04	5.41E-03	7.37	7.654
9	60	7.35E-04	6.39E-03	8.70	7.673
10	80	7.35E-04	8.27E-03	11.26	7.703
11	100	7.35E-04	1.00E-02	13.68	7.723
12	150	7.35E-04	1.41E-02	19.15	7.754
13	200	7.35E-04	1.76E-02	23.94	7.774
14	300	7.35E-04	2.34E-02	31.92	7.789
15	400	7.35E-04	2.81E-02	38.30	7.809
16	600	7.35E-04	3.52E-02	47.88	7.813
17	900	7.35E-04	4.22E-02	57.45	7.817

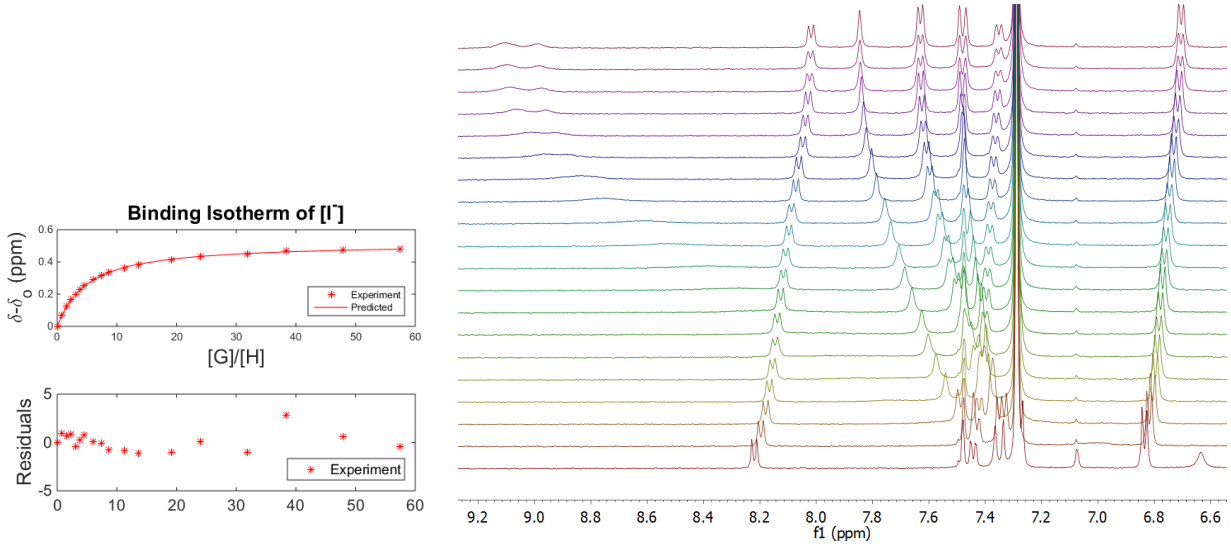

Figure S8. Binding isotherm for I⁻ titration of **1c** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1c** (0.734 mM) titrated with TBA I⁻ (0-57.45 equiv., bottom to top) in $CDCl_3$.

Table S9. Titration of **1d** with Cl^-. (Stock [Cl^-] = 26.4 mM)

	Guest (µL)	[**1d**] (M)	[Cl^-] (M)	Equiv.	δ (ppm)
0	0	6.65E-04	0.00E+00	0	7.342
1	5	6.65E-04	2.19E-04	0.33	7.586
2	10	6.65E-04	4.33E-04	0.65	7.78
3	15	6.65E-04	6.45E-04	0.97	7.904
4	20	6.65E-04	8.53E-04	1.28	7.971
5	25	6.65E-04	1.06E-03	1.59	8.013
6	30	6.65E-04	1.26E-03	1.89	8.034
7	40	6.65E-04	1.65E-03	2.48	8.055
8	50	6.65E-04	2.03E-03	3.06	8.071
9	60	6.65E-04	2.40E-03	3.61	8.079
10	80	6.65E-04	3.11E-03	4.68	8.089
11	100	6.65E-04	3.78E-03	5.68	8.095
12	150	6.65E-04	5.29E-03	7.95	8.104
13	200	6.65E-04	6.61E-03	9.94	8.11
14	300	6.65E-04	8.81E-03	13.25	8.117
15	400	6.65E-04	1.06E-02	15.90	8.121
16	600	6.65E-04	1.32E-02	19.88	8.126
17	900	6.65E-04	1.59E-02	23.86	8.127

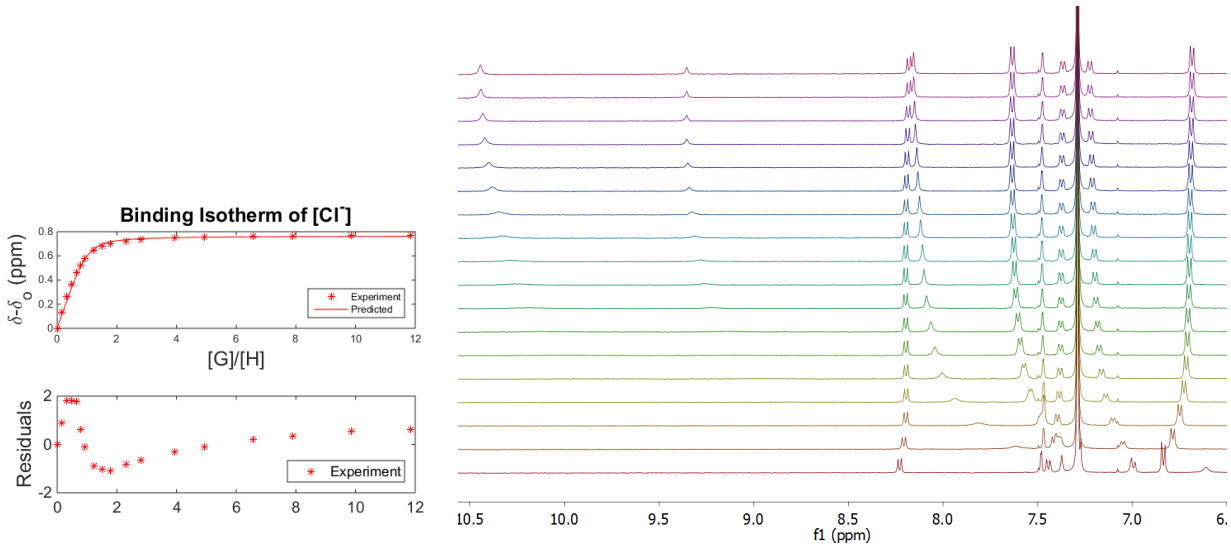

Figure S9. Binding isotherm for Cl^- titration of **1d** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1d** (0.665 mM) titrated with TBA Cl^- (0-23.86 equiv., bottom to top) in $CDCl_3$.

Table S10. Titration of **1d** with Br^-. (Stock [Br^-] = 31.8 mM)

	Guest (μL)	[**1d**] (M)	[Br^-] (M)	Equiv.	δ (ppm)
0	0	9.32E-04	0.00E+00	0	7.338
1	5	9.32E-04	2.63E-04	0.28	7.473
2	10	9.32E-04	5.22E-04	0.56	7.58
3	15	9.32E-04	7.77E-04	0.83	7.669
4	20	9.32E-04	1.03E-03	1.10	7.726
5	25	9.32E-04	1.27E-03	1.37	7.768
6	30	9.32E-04	1.52E-03	1.63	7.806
7	40	9.32E-04	1.99E-03	2.14	7.841
8	50	9.32E-04	2.45E-03	2.63	7.869
9	60	9.32E-04	2.90E-03	3.11	7.886
10	80	9.32E-04	3.75E-03	4.02	7.91
11	100	9.32E-04	4.55E-03	4.89	7.924
12	150	9.32E-04	6.37E-03	6.84	7.944
13	200	9.32E-04	7.97E-03	8.55	7.955
14	300	9.32E-04	1.06E-02	11.40	7.97
15	400	9.32E-04	1.27E-02	13.68	7.975
16	600	9.32E-04	1.59E-02	17.10	7.982
17	900	9.32E-04	1.91E-02	20.52	7.987
18	1300	9.32E-04	2.18E-02	23.40	7.989
19	1800	9.32E-04	2.40E-02	25.65	7.991

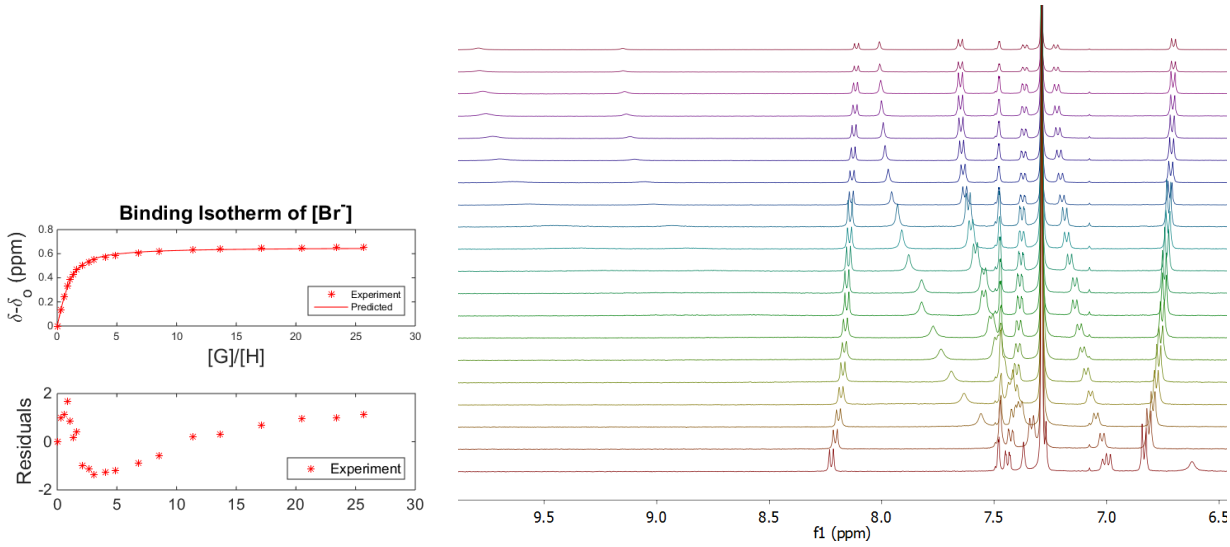

Figure S10. Binding isotherm for Br^- titration of **1d** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1d** (0.932 mM) titrated with TBA Br^- (0-25.65 equiv., bottom to top) in $CDCl_3$.

Table S11. Titration of **1d** with I⁻. (Stock [I⁻] = 90.2 mM)

	Guest (μL)	[**1d**] (M)	[I⁻] (M)	Equiv.	δ (ppm)
0	0	8.73E-04	0.00E+00	0	7.342
1	5	8.73E-04	7.46E-04	0.85	7.421
2	10	8.73E-04	1.48E-03	1.69	7.477
3	15	8.73E-04	2.20E-03	2.52	7.519
4	20	8.73E-04	2.91E-03	3.33	7.556
5	25	8.73E-04	3.61E-03	4.13	7.583
6	30	8.73E-04	4.30E-03	4.92	7.609
7	40	8.73E-04	5.64E-03	6.46	7.642
8	50	8.73E-04	6.94E-03	7.95	7.669
9	60	8.73E-04	8.20E-03	9.40	7.689
10	80	8.73E-04	1.06E-02	12.16	7.721
11	110	8.73E-04	1.40E-02	16.01	7.742
12	150	8.73E-04	1.80E-02	20.67	7.773
13	200	8.73E-04	2.26E-02	25.84	7.79
14	300	8.73E-04	3.01E-02	34.45	7.808
15	400	8.73E-04	3.61E-02	41.34	7.817
16	600	8.73E-04	4.51E-02	51.68	7.825
17	900	8.73E-04	5.41E-02	62.01	7.83
18	1300	8.73E-04	6.17E-02	70.72	7.832
19	1650	8.73E-04	6.62E-02	75.79	7.832

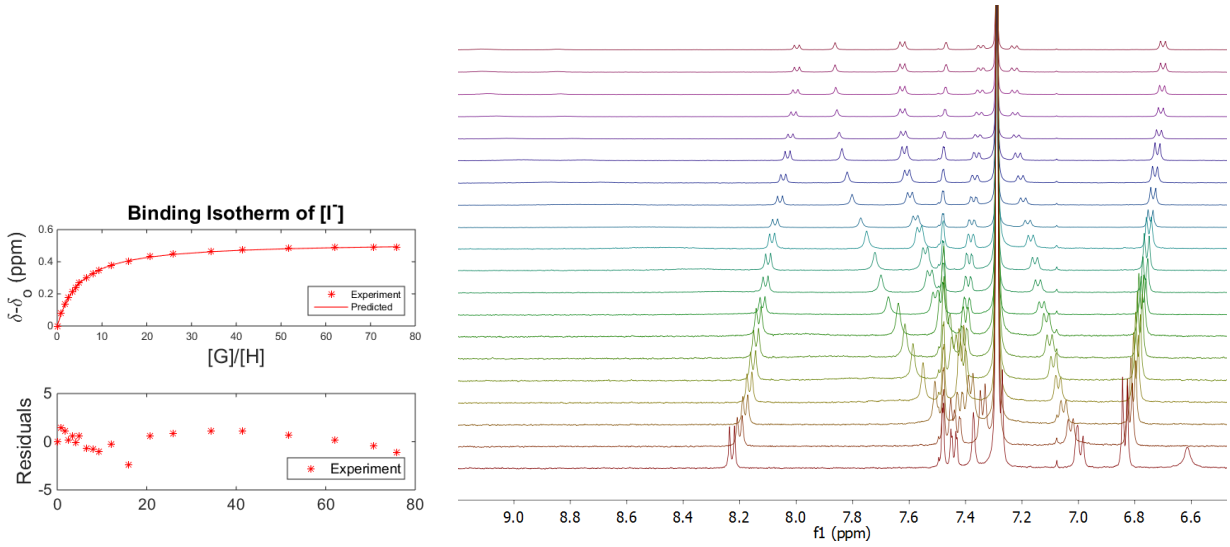

Figure S11. Binding isotherm for I⁻ titration of **1d** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1d** (0.873 mM) titrated with TBA I⁻ (0-75.79 equiv., bottom to top) in $CDCl_3$.

Table S12. Titration of **1e** with Cl^-. (Stock [Cl^-] = 39.1 mM)

	Guest (µL)	[**1e**] (M)	[Cl^-] (M)	Equiv.	δ (ppm)
0	0	7.74E-04	7.74E-04	0.00	7.453
1	5	7.74E-04	7.74E-04	0.42	7.743
2	10	7.74E-04	7.74E-04	0.83	7.911
3	15	7.74E-04	7.74E-04	1.23	7.988
4	20	7.74E-04	7.74E-04	1.63	8.021
5	25	7.74E-04	7.74E-04	2.02	8.039
6	30	7.74E-04	7.74E-04	2.40	8.050
7	40	7.74E-04	7.74E-04	3.16	8.064
8	50	7.74E-04	7.74E-04	3.88	8.072
9	60	7.74E-04	7.74E-04	4.59	8.077
10	80	7.74E-04	7.74E-04	5.94	8.083
11	100	7.74E-04	7.74E-04	7.21	8.087
12	150	7.74E-04	7.74E-04	10.10	8.092
13	200	7.74E-04	7.74E-04	12.62	8.095
14	300	7.74E-04	7.74E-04	16.83	8.098
15	400	7.74E-04	7.74E-04	20.20	8.100
16	600	7.74E-04	7.74E-04	25.25	8.103

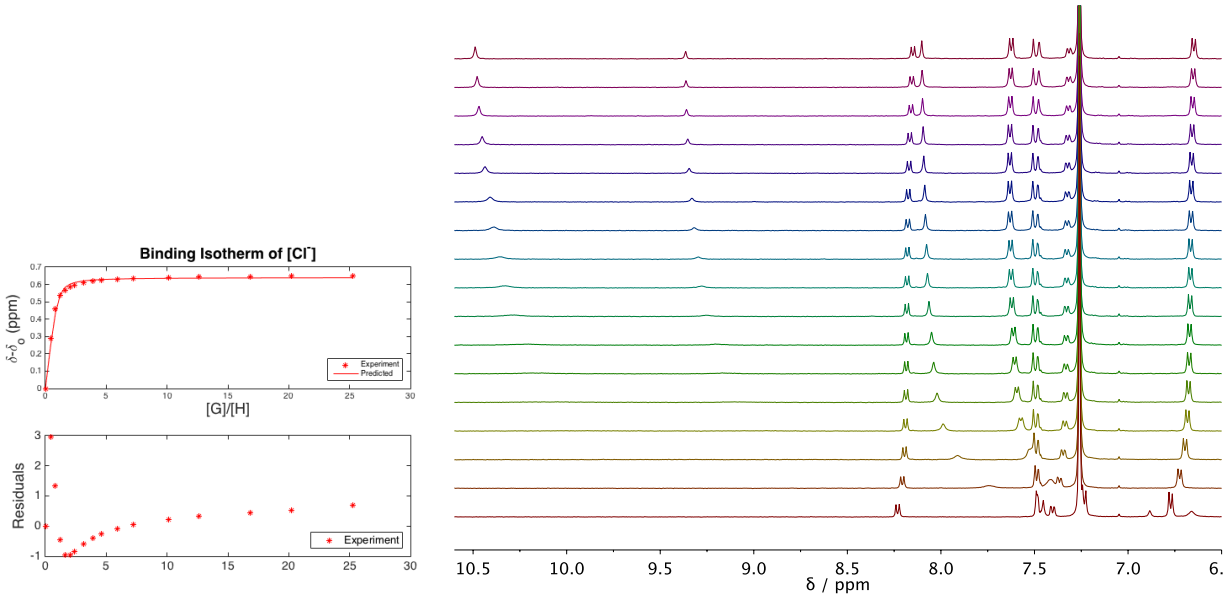

Figure S12. Binding isotherm for Cl^- titration of **1e** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1e** (0.774 mM) titrated with TBA Cl^- (0-25 equiv., bottom to top) in $CDCl_3$.

Table S13. Titration of **1e** with Br^- (Stock [Br^-] = 44.4 mM).

	Guest (μL)	[**1e**] (M)	[Br^-] (M)	Equiv.	δ (ppm)
0	0	1.08E-03	0.00E+00	0.00	7.473
1	5	1.08E-03	3.67E-04	0.34	7.588
2	10	1.08E-03	7.28E-04	0.67	7.676
3	15	1.08E-03	1.08E-03	1.00	7.739
4	20	1.08E-03	1.43E-03	1.32	7.785
5	25	1.08E-03	1.78E-03	1.64	7.821
6	30	1.08E-03	2.11E-03	1.95	7.847
7	40	1.08E-03	2.77E-03	2.56	7.884
8	50	1.08E-03	3.42E-03	3.15	7.907
9	60	1.08E-03	4.04E-03	3.72	7.925
10	80	1.08E-03	5.22E-03	4.82	7.946
11	100	1.08E-03	6.34E-03	5.85	7.961
12	150	1.08E-03	8.88E-03	8.19	7.978
13	200	1.08E-03	1.11E-02	10.24	7.994
14	300	1.08E-03	1.48E-02	13.65	8.001
15	400	1.08E-03	1.78E-02	16.39	8.005
16	600	1.08E-03	2.22E-02	20.48	8.008
17	800	1.08E-03	2.54E-02	23.41	8.009
18	1000	1.08E-03	2.77E-02	25.60	8.01

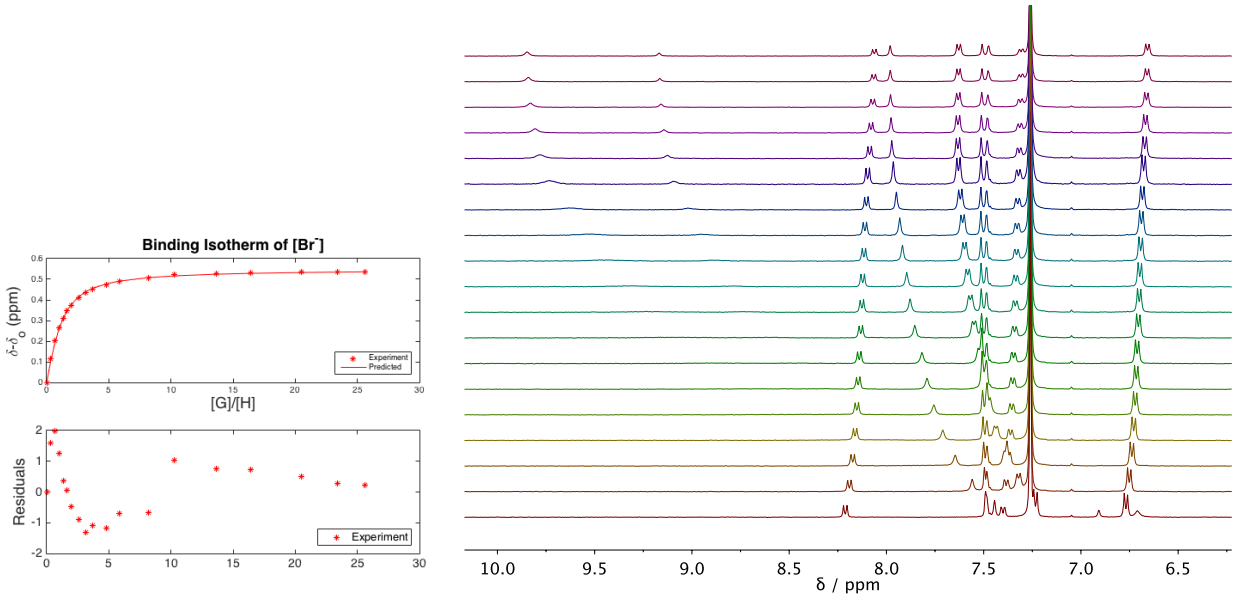

Figure S13. Binding isotherm for Br^- titration of **1e** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1e** (1.08 mM) titrated with TBA Br^- (0-26 equiv., bottom to top) in $CDCl_3$.

Table S14. Titration of **1e** with I⁻. (Stock [I⁻] = 99.1 mM)

	Guest (μL)	[**1e**] (M)	[I⁻] (M)	Equiv.	δ (ppm)
0	0	1.15E-03	0.00E+00	0.00	7.445
1	5	1.15E-03	8.19E-04	0.71	7.493
2	10	1.15E-03	1.62E-03	1.41	7.523
3	20	1.15E-03	3.20E-03	2.78	7.573
4	30	1.15E-03	4.72E-03	4.11	7.612
5	40	1.15E-03	6.19E-03	5.39	7.641
6	50	1.15E-03	7.62E-03	6.64	7.665
7	60	1.15E-03	9.01E-03	7.85	7.684
8	80	1.15E-03	1.17E-02	10.15	7.713
9	100	1.15E-03	1.42E-02	12.33	7.733
10	150	1.15E-03	1.98E-02	17.26	7.764
11	200	1.15E-03	2.48E-02	21.58	7.782
12	300	1.15E-03	3.30E-02	28.77	7.799
13	400	1.15E-03	3.96E-02	34.52	7.808
14	500	1.15E-03	4.51E-02	39.23	7.813
15	600	1.15E-03	4.96E-02	43.15	7.816
16	800	1.15E-03	5.66E-02	49.32	7.819
17	1000	1.15E-03	6.19E-02	53.94	7.820
18	1500	1.15E-03	7.08E-02	61.65	7.821

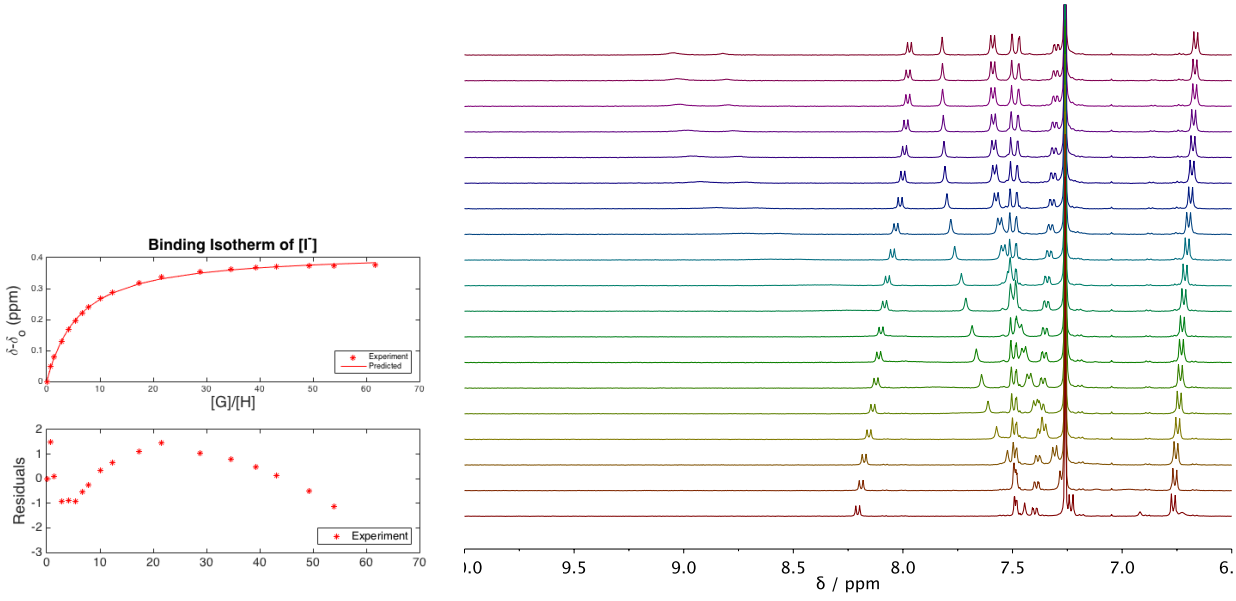

Figure S4. Binding isotherm for I⁻ titration of **1e** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1b** (1.15 mM) titrated with TBA I⁻ (0-62 equiv., bottom to top) in $CDCl_3$.

Table S15. Titration of **1e** with NO_3^-. (Stock $[NO_3^-]$ = 40.6 mM)

	Guest (μL)	[**1e**] (M)	$[NO_3^-]$ (M)	Equiv.	δ (ppm)
0	0	9.46E-04	0.00E+00	0.00	7.495
1	5	9.46E-04	3.36E-04	0.35	7.692
2	10	9.46E-04	6.66E-04	0.70	7.864
3	15	9.46E-04	9.91E-04	1.05	7.977
4	20	9.46E-04	1.31E-03	1.38	8.05
5	25	9.46E-04	1.63E-03	1.72	8.099
6	30	9.46E-04	1.93E-03	2.04	8.131
7	40	9.46E-04	2.54E-03	2.68	8.172
8	50	9.46E-04	3.13E-03	3.30	8.194
9	60	9.46E-04	3.69E-03	3.90	8.211
10	80	9.46E-04	4.78E-03	5.05	8.229
11	100	9.46E-04	5.80E-03	6.13	8.243
12	150	9.46E-04	8.13E-03	8.59	8.256
13	200	9.46E-04	1.02E-02	10.73	8.264
14	300	9.46E-04	1.35E-02	14.31	8.272
15	400	9.46E-04	1.63E-02	17.17	8.275
16	600	9.46E-04	2.03E-02	21.47	8.28
17	800	9.46E-04	2.32E-02	24.53	8.282
18	1000	9.46E-04	2.54E-02	26.83	8.283

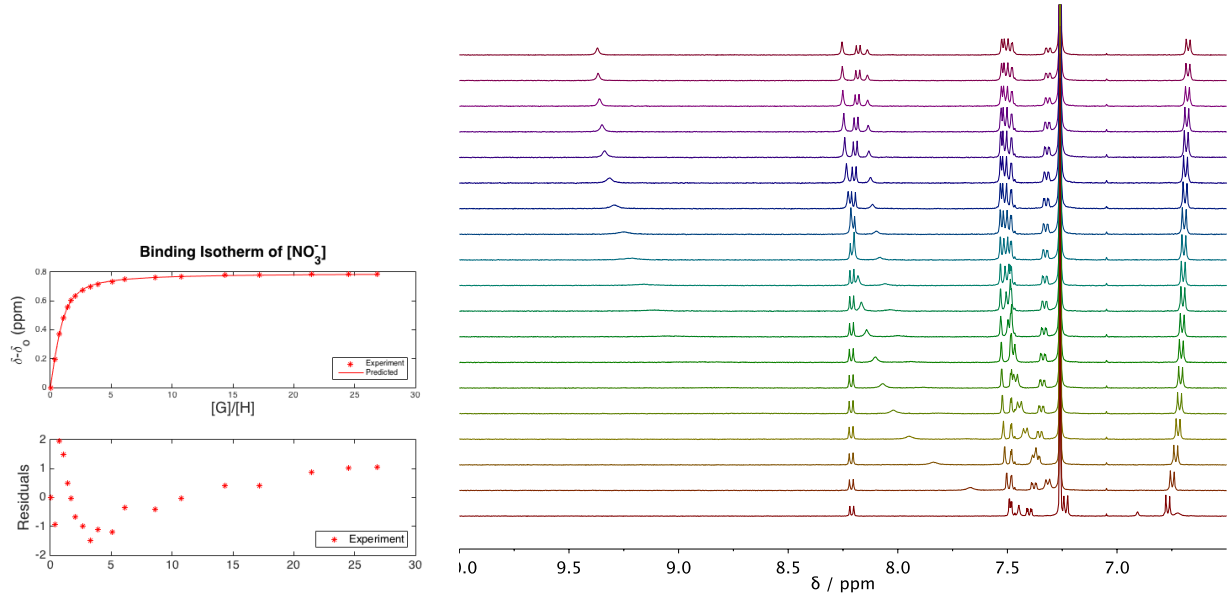

Figure S15. Binding isotherm for NO_3^- titration of **1e** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1e** (0.946 mM) titrated with TBA NO_3^- (0-27 equiv., bottom to top) in $CDCl_3$.

Table S16. Titration of **1f** with Cl^-. (Stock $[Cl^-]$ = 41.2 mM)

	Guest (μL)	[**1f**] (M)	$[Cl^-]$ (M)	Equiv.	δ (ppm)
0	0	7.12E-04	0.00E+00	0	7.399
1	5	7.12E-04	3.41E-04	0.48	7.676
2	10	7.12E-04	6.76E-04	0.95	7.859
3	15	7.12E-04	1.01E-03	1.41	7.955
4	20	7.12E-04	1.33E-03	1.87	8.004
5	25	7.12E-04	1.65E-03	2.32	8.032
6	30	7.12E-04	1.96E-03	2.76	8.048
7	40	7.12E-04	2.58E-03	3.62	8.068
8	50	7.12E-04	3.17E-03	4.45	8.078
9	60	7.12E-04	3.75E-03	5.26	8.086
10	80	7.12E-04	4.85E-03	6.81	8.095
11	100	7.12E-04	5.89E-03	8.27	8.103
12	150	7.12E-04	8.24E-03	11.58	8.114
13	200	7.12E-04	1.03E-02	14.47	8.123
14	300	7.12E-04	1.37E-02	19.29	8.134
15	400	7.12E-04	1.65E-02	23.15	8.14
16	600	7.12E-04	2.06E-02	28.94	8.148
17	800	7.12E-04	2.36E-02	33.08	8.15
18	1100	7.12E-04	2.67E-02	37.45	8.151
19	1500	7.12E-04	2.94E-02	41.34	8.151

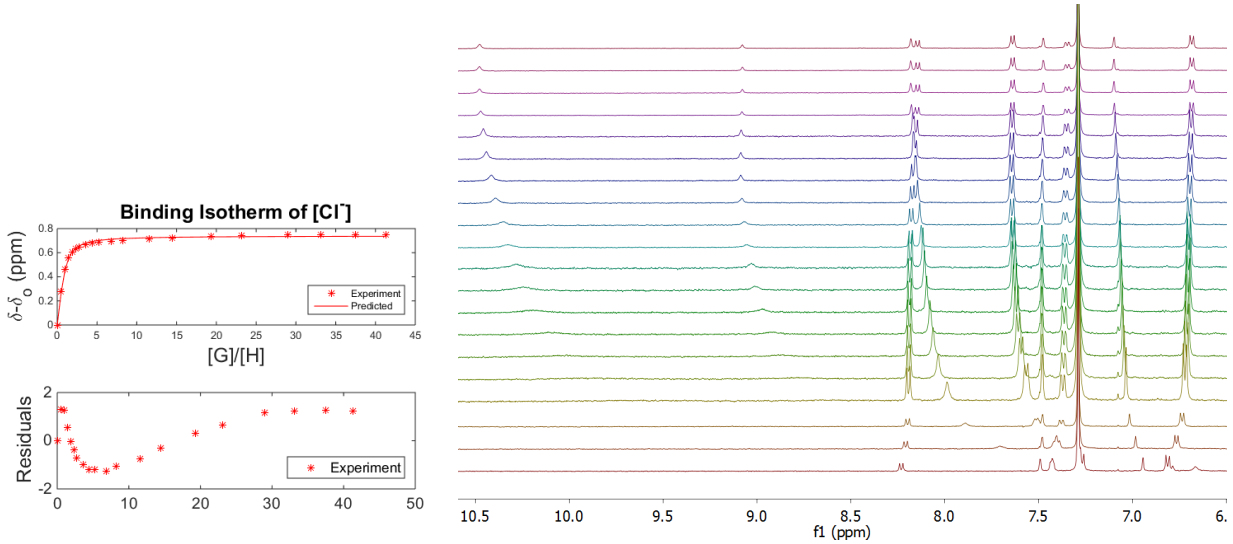

Figure S16. Binding isotherm for Cl^- titration of **1f** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1f** (0.712 mM) titrated with TBA Cl^- (0-41.34 equiv., bottom to top) in $CDCl_3$.

Table S17. Titration of **1f** with Br^-. (Stock [Br^-] = 35.2 mM)

	Guest (μL)	[**1f**] (M)	[Br^-] (M)	Equiv.	δ (ppm)
0	0	7.34E-04	0.00E+00	0	7.399
1	5	7.34E-04	2.91E-04	0.40	7.514
2	10	7.34E-04	5.78E-04	0.79	7.599
3	15	7.34E-04	8.60E-04	1.17	7.663
4	20	7.34E-04	1.14E-03	1.55	7.711
5	25	7.34E-04	1.41E-03	1.92	7.75
6	30	7.34E-04	1.68E-03	2.29	7.779
7	40	7.34E-04	2.20E-03	3.00	7.819
8	50	7.34E-04	2.71E-03	3.69	7.846
9	60	7.34E-04	3.20E-03	4.36	7.871
10	80	7.34E-04	4.15E-03	5.65	7.897
11	100	7.34E-04	5.03E-03	6.86	7.912
12	150	7.34E-04	7.05E-03	9.60	7.94
13	200	7.34E-04	8.81E-03	12.00	7.955
14	300	7.34E-04	1.17E-02	16.00	7.972
15	400	7.34E-04	1.41E-02	19.19	7.981
16	600	7.34E-04	1.76E-02	23.99	7.99
17	800	7.34E-04	2.01E-02	27.42	7.994
18	1100	7.34E-04	2.28E-02	31.05	7.994
19	1500	7.34E-04	0.025173	34.27	7.994

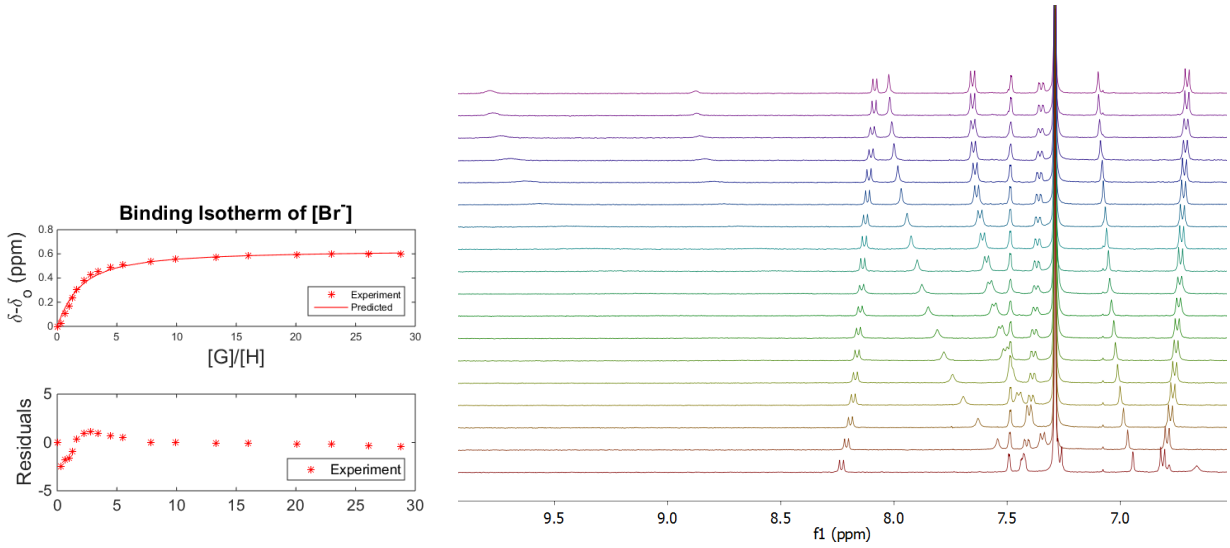

Figure S17. Binding isotherm for Br^- titration of **1f** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1f** (0.734 mM) titrated with TBA Br^- (0-34.27 equiv., bottom to top) in $CDCl_3$.

Table S18. Titration of **1f** with I^-. (Stock [I^-] = 81.2 mM)

	Guest (µL)	[**1f**] (M)	[I^-] (M)	Equiv.	δ (ppm)
0	0	6.54E-04	0.00E+00	0	7.394
1	5	6.54E-04	6.71E-04	1.03	7.44
2	10	6.54E-04	1.33E-03	2.03	7.478
3	15	6.54E-04	1.98E-03	3.03	7.508
4	20	6.54E-04	2.62E-03	4.00	7.535
5	25	6.54E-04	3.25E-03	4.96	7.556
6	30	6.54E-04	3.86E-03	5.91	7.575
7	40	6.54E-04	5.07E-03	7.75	7.608
8	50	6.54E-04	6.24E-03	9.54	7.635
9	60	6.54E-04	7.38E-03	11.28	7.658
10	80	6.54E-04	9.55E-03	14.59	7.689
11	100	6.54E-04	1.16E-02	17.72	7.711
12	150	6.54E-04	1.62E-02	24.81	7.748
13	200	6.54E-04	2.03E-02	31.01	7.771
14	300	6.54E-04	2.71E-02	41.35	7.797
15	400	6.54E-04	3.25E-02	49.62	7.811
16	600	6.54E-04	4.06E-02	62.02	7.821
17	800	6.54E-04	4.64E-02	70.88	7.826
18	1100	6.54E-04	5.25E-02	80.26	7.827
19	1500	6.54E-04	5.80E-02	88.6	7.825

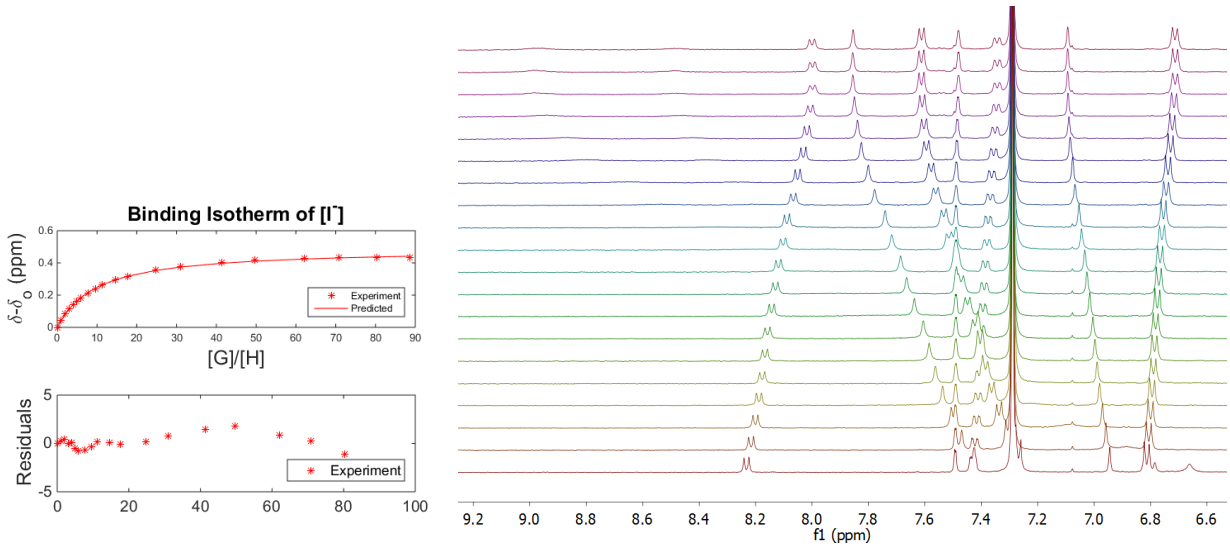

Figure S18. Binding isotherm for I^- titration of **1f** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1f** (0.654 mM) titrated with TBA I^- (0-88.60 equiv., bottom to top) in $CDCl_3$.

Table S19. Titration of **1g** with Cl^-. (Stock [Cl^-] = 48.3 mM).

	Guest (μL)	[**1g**] (M)	[Cl^-] (M)	Equiv.	δ (ppm)
0	0	8.27E-04	0.00E+00	0.00	7.468
1	5	8.27E-04	4.00E-04	0.48	7.720
2	10	8.27E-04	7.92E-04	0.96	7.870
3	20	8.27E-04	1.56E-03	1.89	7.946
4	30	8.27E-04	2.30E-03	2.78	7.988
5	50	8.27E-04	3.72E-03	4.50	8.014
6	70	8.27E-04	5.05E-03	6.11	8.032
7	90	8.27E-04	6.31E-03	7.63	8.054
8	110	8.27E-04	7.49E-03	9.06	8.068
9	130	8.27E-04	8.61E-03	10.41	8.078
10	150	8.27E-04	9.67E-03	11.69	8.091
11	190	8.27E-04	1.16E-02	14.06	8.100
12	240	8.27E-04	1.38E-02	16.70	8.114
13	300	8.27E-04	1.61E-02	19.49	8.123
14	400	8.27E-04	1.93E-02	23.39	8.135
15	500	8.27E-04	2.20E-02	26.58	8.143

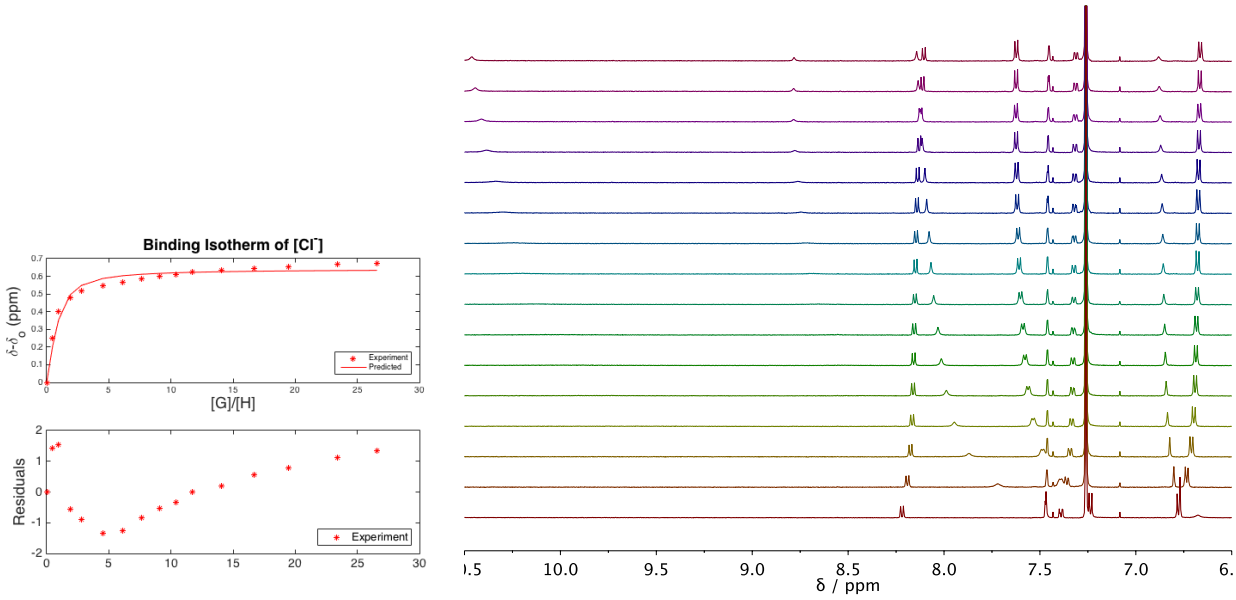

Figure S19. Binding isotherm for Cl^- titration of **1g** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1g** (0.827 mM) titrated with TBA Cl^- (0-27 equiv., bottom to top) in $CDCl_3$.

Table S20. Titration of **1g** with Br^-. (Stock [Br^-] = 46.9 mM)

	Guest (μL)	[**1g**] (M)	[Br^-] (M)	Equiv.	δ (ppm)
0	0	1.17E-03	0.00E+00	0.00	7.466
1	5	1.17E-03	3.87E-04	0.33	7.557
2	10	1.17E-03	7.68E-04	0.66	7.629
3	15	1.17E-03	1.14E-03	0.97	7.685
4	20	1.17E-03	1.51E-03	1.29	7.730
5	30	1.17E-03	2.23E-03	1.90	7.792
6	40	1.17E-03	2.93E-03	2.50	7.832
7	50	1.17E-03	3.61E-03	3.07	7.861
8	60	1.17E-03	4.26E-03	3.63	7.882
9	80	1.17E-03	5.51E-03	4.70	7.910
10	100	1.17E-03	6.70E-03	5.71	7.930
11	125	1.17E-03	8.08E-03	6.89	7.947
12	150	1.17E-03	9.37E-03	7.99	7.959
13	200	1.17E-03	1.17E-02	9.99	7.975
14	300	1.17E-03	1.56E-02	13.32	7.994
15	400	1.17E-03	1.87E-02	15.99	8.005
16	600	1.17E-03	2.34E-02	19.99	8.013
17	800	1.17E-03	2.68E-02	22.84	8.022
18	1000	1.17E-03	2.93E-02	24.98	8.036

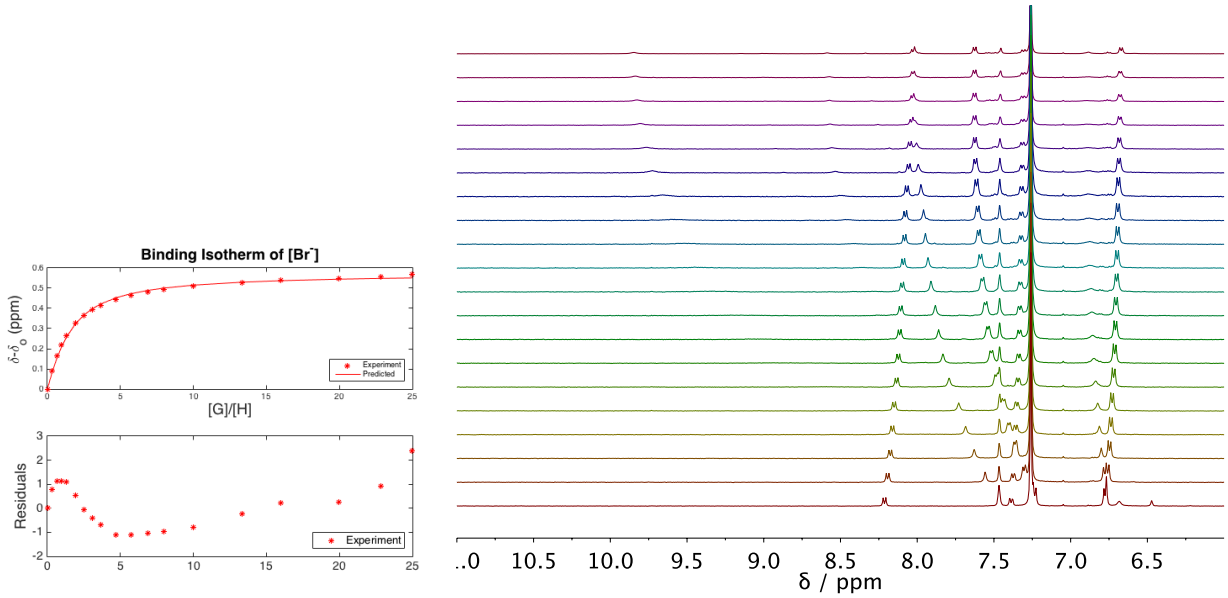

Figure S20. Binding isotherm for Br^- titration of **1g** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1g** (1.17 mM) titrated with TBA Br^- (0-25 equiv., bottom to top) in $CDCl_3$.

Table S21. Titration of **1g** with I⁻. (Stock [I⁻] = 113 mM)

	Guest (μL)	[**1g**] (M)	[I⁻] (M)	Equiv.	δ (ppm)
0	0	1.21E-03	0.00E+00	0.00	7.466
1	5	1.21E-03	9.38E-04	0.78	7.498
2	10	1.21E-03	1.86E-03	1.54	7.524
3	20	1.21E-03	3.66E-03	3.03	7.565
4	30	1.21E-03	5.40E-03	4.48	7.6
5	40	1.21E-03	7.09E-03	5.87	7.628
6	50	1.21E-03	8.73E-03	7.23	7.651
7	60	1.21E-03	1.03E-02	8.54	7.671
8	80	1.21E-03	1.33E-02	11.06	7.701
9	100	1.21E-03	1.62E-02	13.43	7.724
10	150	1.21E-03	2.27E-02	18.80	7.761
11	200	1.21E-03	2.84E-02	23.49	7.782
12	300	1.21E-03	3.78E-02	31.33	7.804
13	400	1.21E-03	4.54E-02	37.59	7.815
14	500	1.21E-03	5.16E-02	42.72	7.822
15	600	1.21E-03	5.67E-02	46.99	7.826
16	800	1.21E-03	6.48E-02	53.70	7.83
17	1000	1.21E-03	7.09E-02	58.74	7.831

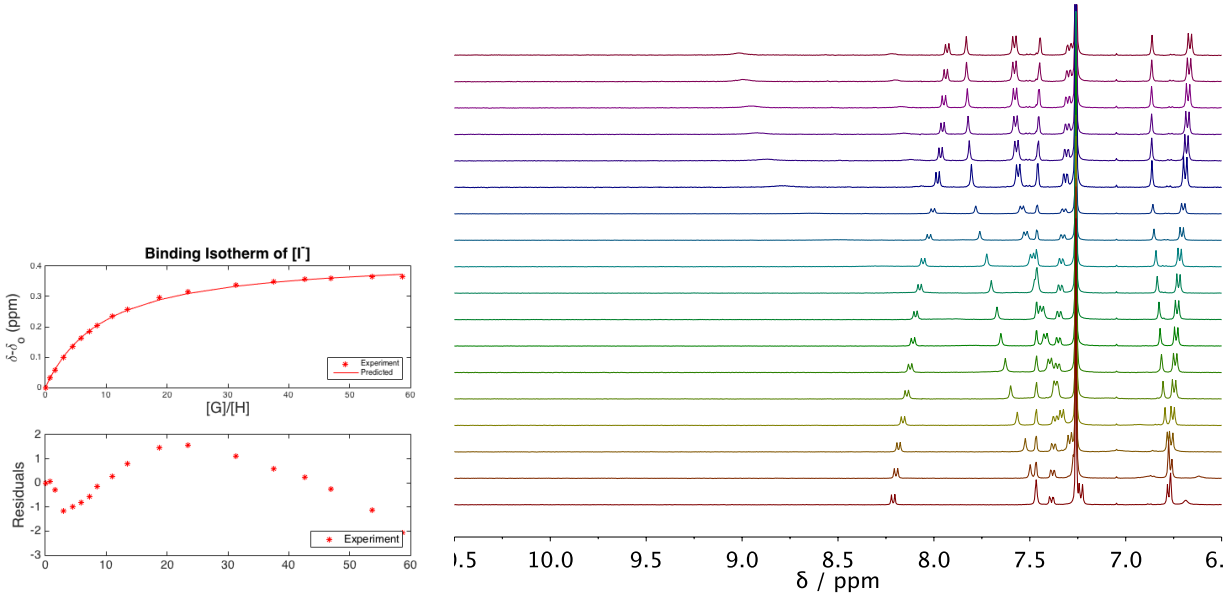

Figure S21. Binding isotherm for I⁻ titration of **1g** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1g** (1.21 mM) titrated with TBA I⁻ (0-59 equiv., bottom to top) in $CDCl_3$.

Table S22. Titration of **1g** with NO_3^-. (Stock $[NO_3^-]$ = 37.3 mM)

	Guest (μL)	[**1g**] (M)	$[NO_3^-]$ (M)	Equiv.	δ (ppm)
0	0	9.19E-04	0.00E+00	0.00	7.467
1	5	9.19E-04	3.09E-04	0.34	7.638
2	10	9.19E-04	6.12E-04	0.67	7.772
3	15	9.19E-04	9.11E-04	0.99	7.877
4	20	9.19E-04	1.21E-03	1.31	7.946
5	30	9.19E-04	1.78E-03	1.94	8.034
6	40	9.19E-04	2.33E-03	2.54	8.084
7	50	9.19E-04	2.87E-03	3.13	8.117
8	60	9.19E-04	3.40E-03	3.70	8.139
9	80	9.19E-04	4.39E-03	4.78	8.167
10	100	9.19E-04	5.34E-03	5.81	8.185
11	125	9.19E-04	6.44E-03	7.01	8.2
12	150	9.19E-04	7.47E-03	8.13	8.209
13	200	9.19E-04	9.34E-03	10.17	8.221
14	300	9.19E-04	1.25E-02	13.55	8.234
15	400	9.19E-04	1.49E-02	16.26	8.241
16	600	9.19E-04	1.87E-02	20.33	8.248
17	800	9.19E-04	2.13E-02	23.24	8.251
18	1000	9.19E-04	2.33E-02	25.41	8.253

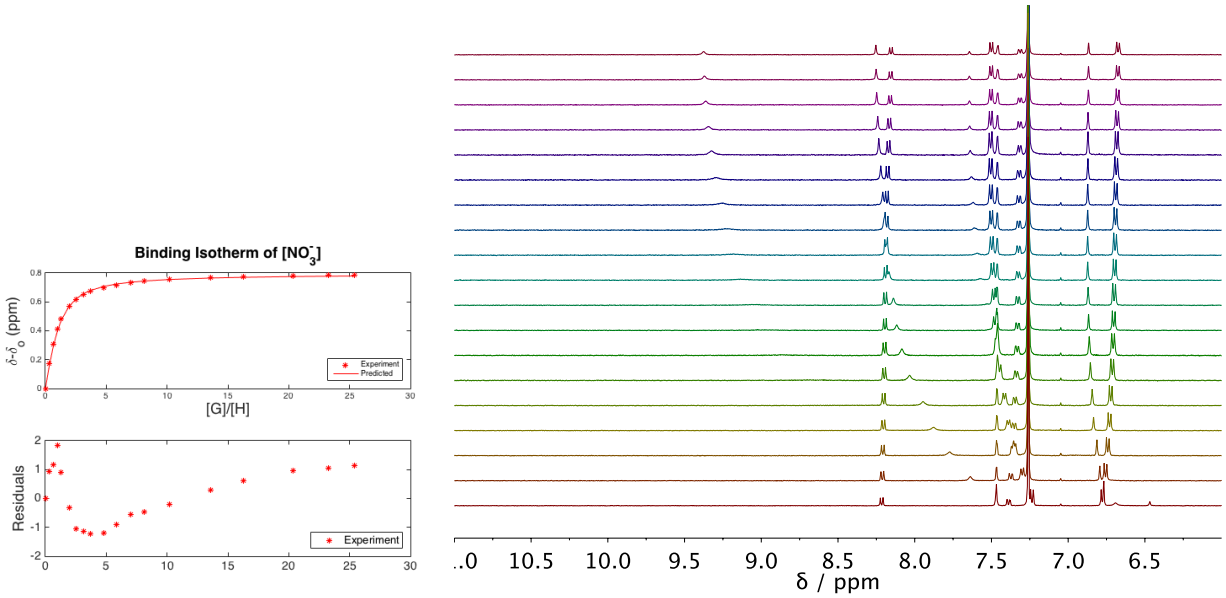

Figure S22. Binding isotherm for NO_3^- titration of **1g** in $CDCl_3$ by ^1H NMR. ^1H NMR stacked plot of **1g** (0.919 mM) titrated with TBA NO_3^- (0-25 equiv., bottom to top) in $CDCl_3$.

UV-VIS Titrations

UV-Vis Titration Conditions. UV-Vis titrations were carried out on an HP 8453 UV-Vis spectrometer equipped with a 265 nm high-pass filter. Water-saturated $CHCl_3$ was prepared in the same manner as for ^1H titrations. Association constants were determined by non-linear regression in HYPERquad fitting the complete spectrum simultaneously.[10] Hamilton gas-tight micro-syringes were used during serial dilutions and titrations. The reported association constants and errors were obtained from the average and standard deviation of three repeated titrations. Single representative titrations for each host/anion pair are included below. Titration data for **1a** with halides has been previously reported.[8]

A stock solution of **1a-g** was prepared by serial dilution from 1 mL to a final volume of 5 mL in $CHCl_3$. An aliquot (2.0 mL) of the stock host solution was transferred to a quartz cuvette with septum cap as the starting volume. Guest solutions were prepared by taking a TBA salt up in the host stock solution (1 mL) then serial diluting to the final concentration (2.0 mL) using the host stock solution. Aliquots of guest solution were added to the cuvette and a spectrum recorded after each addition.

Table S23. Titration of **1a** with NO_3^-. (Stock [NO_3^-] = 2.97 mM).

	Guest (µL)	[**1a**] (M)	[NO_3^-] (M)	Equiv.
0	0	1.14E-05	0.00E+00	0.00
1	5	1.14E-05	7.41E-06	0.65
2	20	1.14E-05	2.94E-05	2.59
3	30	1.14E-05	4.39E-05	3.87
4	50	1.14E-05	7.25E-05	6.39
5	70	1.14E-05	1.01E-04	8.86
6	90	1.14E-05	1.28E-04	11.28
7	110	1.14E-05	1.55E-04	13.65
8	130	1.14E-05	1.81E-04	15.98
9	150	1.14E-05	2.07E-04	18.27
10	190	1.14E-05	2.58E-04	22.72
11	230	1.14E-05	3.07E-04	27.01
12	270	1.14E-05	3.54E-04	31.15
13	310	1.14E-05	3.99E-04	35.14
14	360	1.14E-05	4.53E-04	39.94
15	410	1.14E-05	5.06E-04	44.55
16	510	1.14E-05	6.04E-04	53.21
17	710	1.14E-05	7.79E-04	68.61
18	910	1.14E-05	9.30E-04	81.89
19	1110	1.14E-05	1.06E-03	93.46

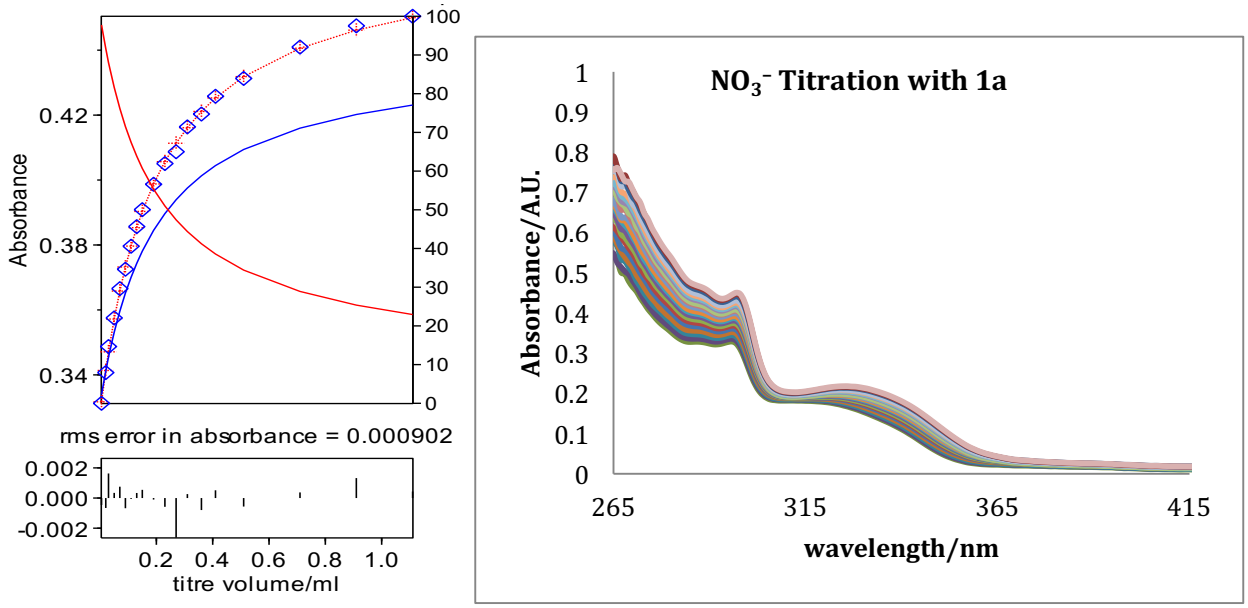

Figure S23. Binding isotherm for NO_3^- titration of **1a** in $CHCl_3$ by UV-vis. Stacked spectra of **1a** (11.4 µM) titrated with TBA NO_3^- (0-93 equiv., increasing abs.) in $CDCl_3$.

Table S24. Titration of **1b** with Cl^-. (Stock [Cl^-] = 2.42 mM)

	Guest (µL)	[1b] (M)	[Cl^-] (M)	Equiv.
0	0	1.04E-05	0.00E+00	0.00
1	5	1.04E-05	6.03E-06	0.58
2	10	1.04E-05	1.20E-05	1.16
3	25	1.04E-05	2.99E-05	2.88
4	40	1.04E-05	4.74E-05	4.57
5	55	1.04E-05	6.47E-05	6.24
6	70	1.04E-05	8.18E-05	7.89
7	85	1.04E-05	9.86E-05	9.51
8	100	1.04E-05	1.15E-04	11.11
9	120	1.04E-05	1.37E-04	13.20
10	140	1.04E-05	1.58E-04	15.26
11	160	1.04E-05	1.79E-04	17.27
12	180	1.04E-05	2.00E-04	19.26
13	200	1.04E-05	2.20E-04	21.20
14	250	1.04E-05	2.69E-04	25.91
15	300	1.04E-05	3.15E-04	30.42
16	400	1.04E-05	4.03E-04	38.87
17	500	1.04E-05	4.84E-04	46.64
18	700	1.04E-05	6.27E-04	60.46
19	900	1.04E-05	7.50E-04	72.38
20	1100	1.04E-05	8.58E-04	82.75

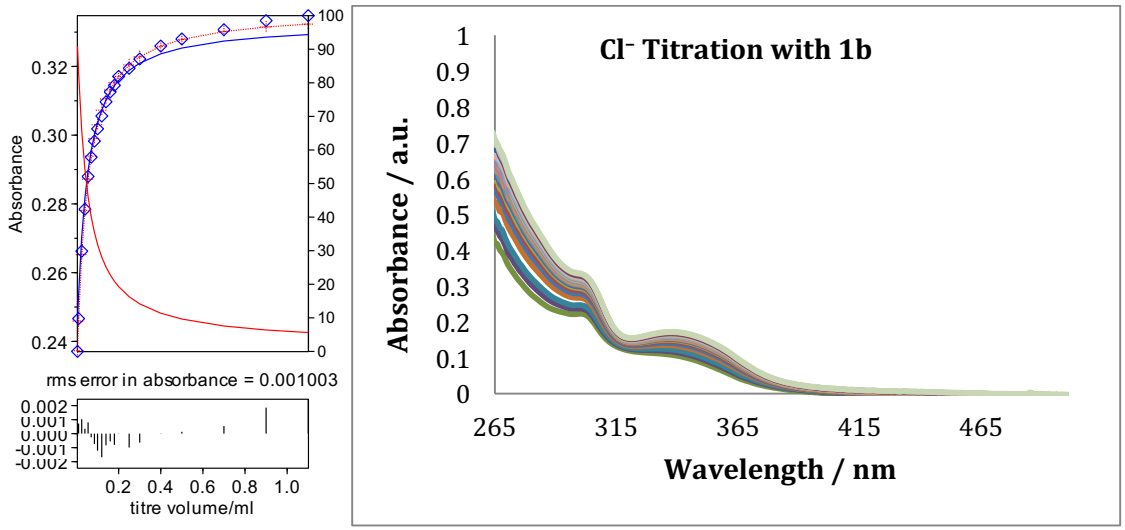

Figure S24. Binding isotherm for Cl^- titration of **1b** in $CHCl_3$ by UV-vis. Stacked spectra of **1b** (10.4 µM) titrated with TBA Cl^- (0-83 equiv., increasing abs.) in $CDCl_3$.

Table S25. Titration of **1b** with Br^-. (Stock [Br^-] = 2.61 mM)

	Guest (µL)	[**1b**] (M)	[Br^-] (M)	Equiv.
0	0	9.72E-06	0.00E+00	0.00
1	5	9.72E-06	6.52E-06	0.67
2	10	9.72E-06	1.30E-05	1.34
3	25	9.72E-06	3.23E-05	3.32
4	40	9.72E-06	5.12E-05	5.27
5	55	9.72E-06	6.99E-05	7.20
6	70	9.72E-06	8.84E-05	9.09
7	85	9.72E-06	1.07E-04	10.96
8	100	9.72E-06	1.24E-04	12.81
9	120	9.72E-06	1.48E-04	15.22
10	140	9.72E-06	1.71E-04	17.59
11	160	9.72E-06	1.94E-04	19.92
12	180	9.72E-06	2.16E-04	22.21
13	200	9.72E-06	2.38E-04	24.45
14	250	9.72E-06	2.90E-04	29.88
15	300	9.72E-06	3.41E-04	35.08
16	400	9.72E-06	4.36E-04	44.82
17	500	9.72E-06	5.23E-04	53.79
18	700	9.72E-06	6.78E-04	69.72
19	900	9.72E-06	8.11E-04	83.46
20	1100	9.72E-06	9.27E-04	95.43
21	1300	9.72E-06	1.03E-03	105.94

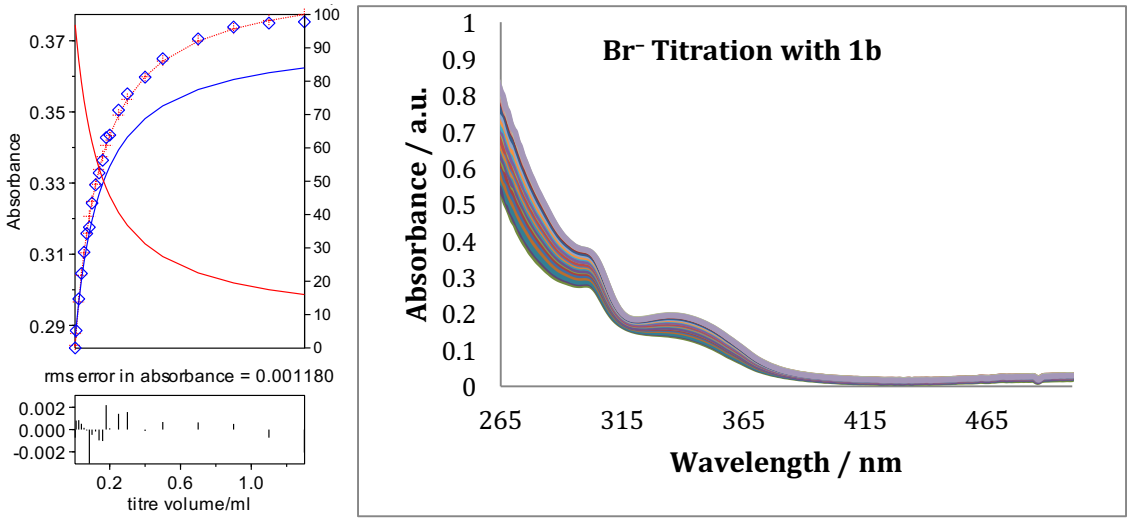

Figure S25. Binding isotherm for Br^- titration of **1b** in $CHCl_3$ by UV-vis. Stacked spectra of **1b** (9.72 µM) titrated with TBA Br^- (0-105 equiv., increasing abs.) in $CDCl_3$.

Table S26. Titration of **1b** with NO_3^-. (Stock [NO_3^-] = 2.35 mM).

	Guest (µL)	[**1b**] (M)	[NO_3^-] (M)	Equiv.
00	0	1.02E-05	0.00E+00	0.00
01	5	1.02E-05	5.87E-06	0.58
02	10	1.02E-05	1.17E-05	1.15
03	25	1.02E-05	2.91E-05	2.85
04	40	1.02E-05	4.62E-05	4.52
05	55	1.02E-05	6.30E-05	6.17
06	70	1.02E-05	7.96E-05	7.80
07	85	1.02E-05	9.60E-05	9.40
08	100	1.02E-05	1.12E-04	10.98
09	130	1.02E-05	1.44E-04	14.08
10	160	1.02E-05	1.74E-04	17.08
11	190	1.02E-05	2.04E-04	20.01
12	220	1.02E-05	2.33E-04	22.86
13	250	1.02E-05	2.62E-04	25.63
14	300	1.02E-05	3.07E-04	30.08
15	400	1.02E-05	3.92E-04	38.44
16	500	1.02E-05	4.71E-04	46.13
17	700	1.02E-05	6.11E-04	59.79
18	900	1.02E-05	7.31E-04	71.58
19	1100	1.02E-05	8.36E-04	81.84

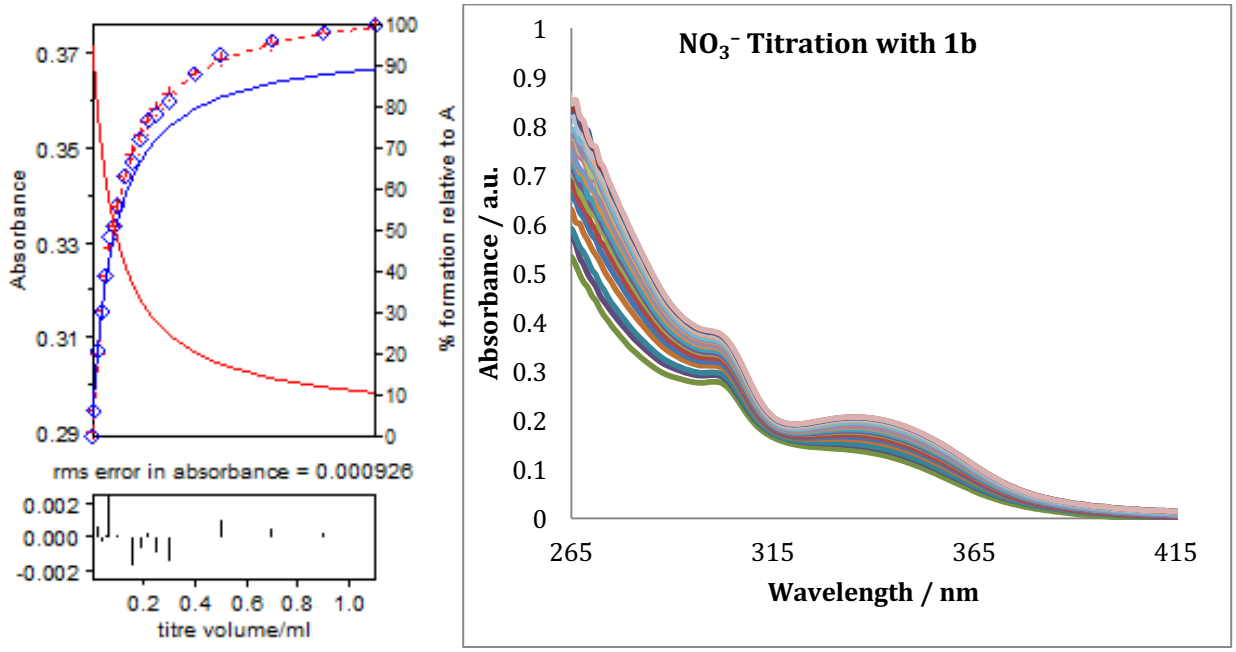

Figure S26. Binding isotherm for NO_3^- titration of **1b** in $CHCl_3$ by UV-vis. Stacked spectra of **1b** (10.2 µM) titrated with TBA NO_3^- (0-82 equiv., increasing abs.) in $CDCl_3$.

Table S27. Titration of **1c** with Cl^-. (Stock [Cl^-] = 2.39 mM).

	Guest (µL)	[**1c**] (M)	[Cl^-] (M)	Equiv.
00	0	1.02E-05	0.00E+00	0.00
01	5	1.02E-05	5.97E-06	0.59
02	10	1.02E-05	1.19E-05	1.17
03	25	1.02E-05	2.95E-05	2.90
04	40	1.02E-05	4.69E-05	4.61
05	55	1.02E-05	6.40E-05	6.29
06	70	1.02E-05	8.09E-05	7.95
07	85	1.02E-05	9.75E-05	9.58
08	100	1.02E-05	1.14E-04	11.19
09	130	1.02E-05	1.46E-04	14.34
10	160	1.02E-05	1.77E-04	17.41
11	190	1.02E-05	2.08E-04	20.39
12	220	1.02E-05	2.37E-04	23.29
13	250	1.02E-05	2.66E-04	26.11
14	300	1.02E-05	3.12E-04	30.65
15	400	1.02E-05	3.99E-04	39.17
16	500	1.02E-05	4.79E-04	47.00
17	700	1.02E-05	6.20E-04	60.93
18	900	1.02E-05	7.43E-04	72.94
19	1100	1.02E-05	8.49E-04	83.39

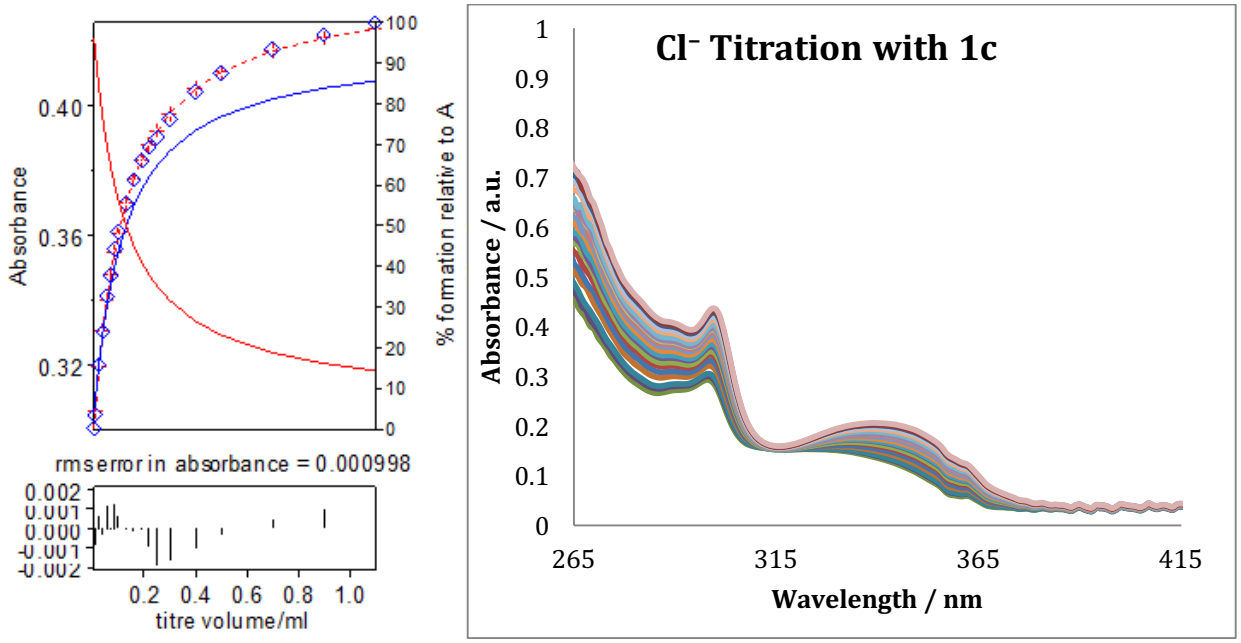

Figure S27. Binding isotherm for Cl^- titration of **1c** in $CHCl_3$ by UV-vis. Stacked spectra of **1c** (10.2 µM) titrated with TBA Cl^- (0-83 equiv., increasing abs.) in $CDCl_3$.

Table S28. Titration of **1c** with Br^-. (Stock [Br^-] = 2.36 mM).

	Guest (µL)	[**1c**] (M)	[Br–] (M)	Equiv.
00	0	1.02E-05	0.00E+00	0.00
01	5	1.02E-05	5.88E-06	0.58
02	10	1.02E-05	1.17E-05	1.15
03	25	1.02E-05	2.91E-05	2.87
04	40	1.02E-05	4.62E-05	4.55
05	55	1.02E-05	6.31E-05	6.21
06	70	1.02E-05	7.97E-05	7.85
07	85	1.02E-05	9.61E-05	9.46
08	100	1.02E-05	1.12E-04	11.05
09	130	1.02E-05	1.44E-04	14.16
10	160	1.02E-05	1.75E-04	17.19
11	190	1.02E-05	2.04E-04	20.13
12	220	1.02E-05	2.34E-04	23.00
13	250	1.02E-05	2.62E-04	25.79
14	300	1.02E-05	3.07E-04	30.27
15	400	1.02E-05	3.93E-04	38.68
16	500	1.02E-05	4.71E-04	46.41
17	700	1.02E-05	6.11E-04	60.17
18	900	1.02E-05	7.31E-04	72.02
19	1100	1.02E-05	8.36E-04	82.35

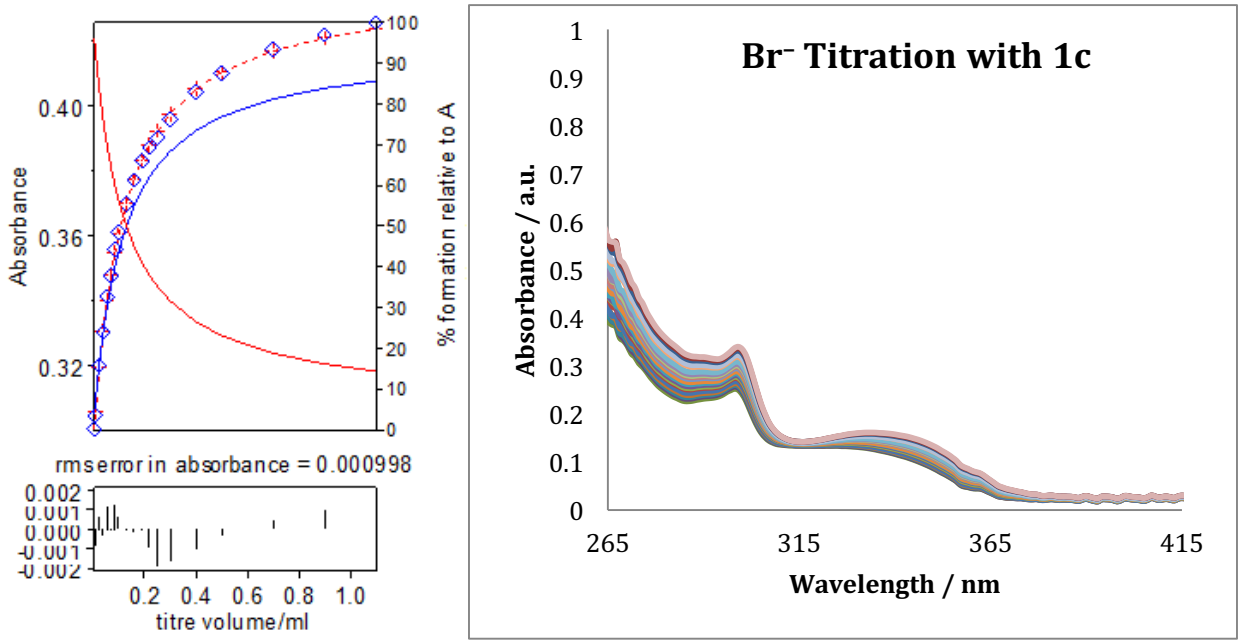

Figure S28. Binding isotherm for Br^- titration of **1c** in $CHCl_3$ by UV-vis. Stacked spectra of **1c** (10.2 µM) titrated with TBA Br^- (0-82 equiv., increasing abs.) in $CDCl_3$.

Table S29. Titration of **1c** with NO_3^-. (Stock [NO_3^-] = 2.35 mM).

	Guest (µL)	[**1c**] (M)	[NO_3^-] (M)	Equiv.
00	0	1.02E-05	0.00E+00	0.00
01	5	1.02E-05	5.85E-06	0.57
02	10	1.02E-05	1.17E-05	1.14
03	25	1.02E-05	2.90E-05	2.83
04	40	1.02E-05	4.60E-05	4.49
05	55	1.02E-05	6.28E-05	6.13
06	70	1.02E-05	7.94E-05	7.75
07	85	1.02E-05	9.57E-05	9.34
08	100	1.02E-05	1.12E-04	10.91
09	130	1.02E-05	1.43E-04	13.98
10	160	1.02E-05	1.74E-04	16.97
11	190	1.02E-05	2.04E-04	19.87
12	220	1.02E-05	2.33E-04	22.70
13	250	1.02E-05	2.61E-04	25.45
14	300	1.02E-05	3.06E-04	29.88
15	400	1.02E-05	3.91E-04	38.18
16	500	1.02E-05	4.69E-04	45.81
17	700	1.02E-05	6.09E-04	59.39
18	900	1.02E-05	7.28E-04	71.09
19	1100	1.02E-05	8.33E-04	81.28

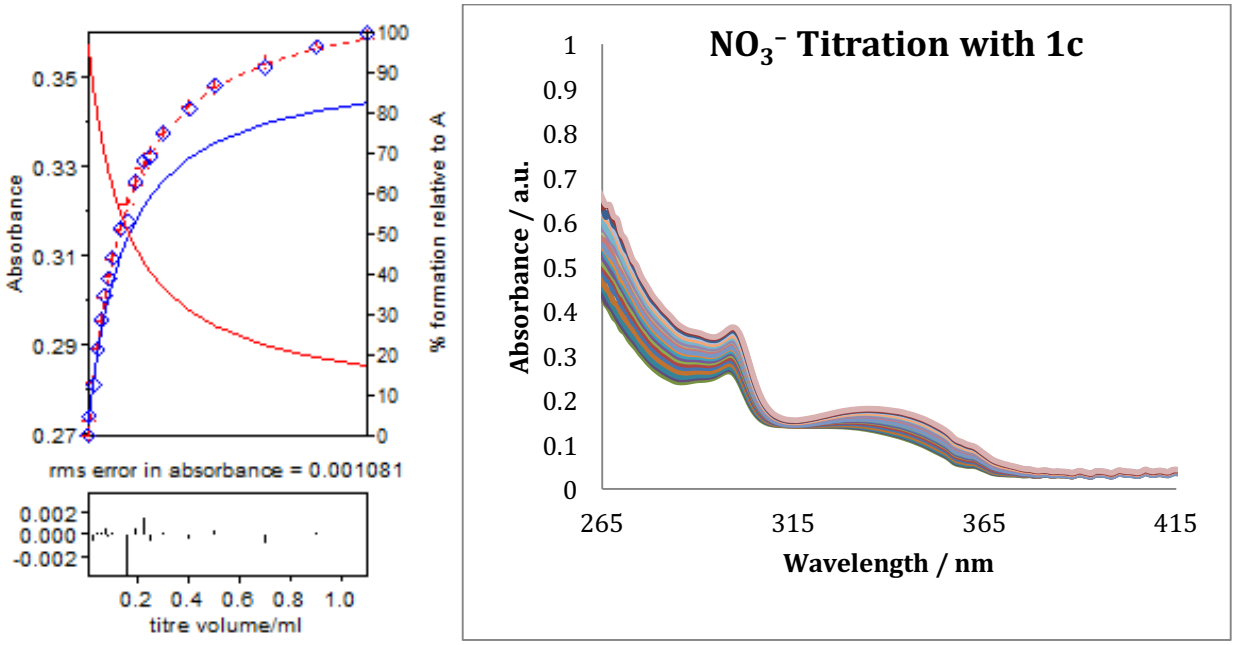

Figure S29. Binding isotherm for NO_3^- titration of **1c** in $CHCl_3$ by UV-vis. Stacked spectra of **1c** (10.2 µM) titrated with TBA NO_3^- (0-81 equiv., increasing abs.) in $CDCl_3$.

Table S30. Titration of **1d** with Cl^-. (Stock [Cl^-] = 2.46 mM).

	Guest (µL)	[**1d**] (M)	[Cl^-] (M)	Equiv.
00	0	1.08E-05	0.00E+00	0.00
01	5	1.08E-05	6.13E-06	0.57
02	10	1.08E-05	1.22E-05	1.13
03	25	1.08E-05	3.03E-05	2.81
04	40	1.08E-05	4.82E-05	4.46
05	55	1.08E-05	6.58E-05	6.09
06	70	1.08E-05	8.31E-05	7.69
07	85	1.08E-05	1.00E-04	9.28
08	100	1.08E-05	1.17E-04	10.83
09	130	1.08E-05	1.50E-04	13.89
10	160	1.08E-05	1.82E-04	16.85
11	190	1.08E-05	2.13E-04	19.74
12	220	1.08E-05	2.44E-04	22.55
13	250	1.08E-05	2.73E-04	25.28
14	300	1.08E-05	3.21E-04	29.68
15	400	1.08E-05	4.10E-04	37.92
16	500	1.08E-05	4.92E-04	45.50
17	700	1.08E-05	6.37E-04	58.99
18	900	1.08E-05	7.63E-04	70.61
19	1100	1.08E-05	8.72E-04	80.73

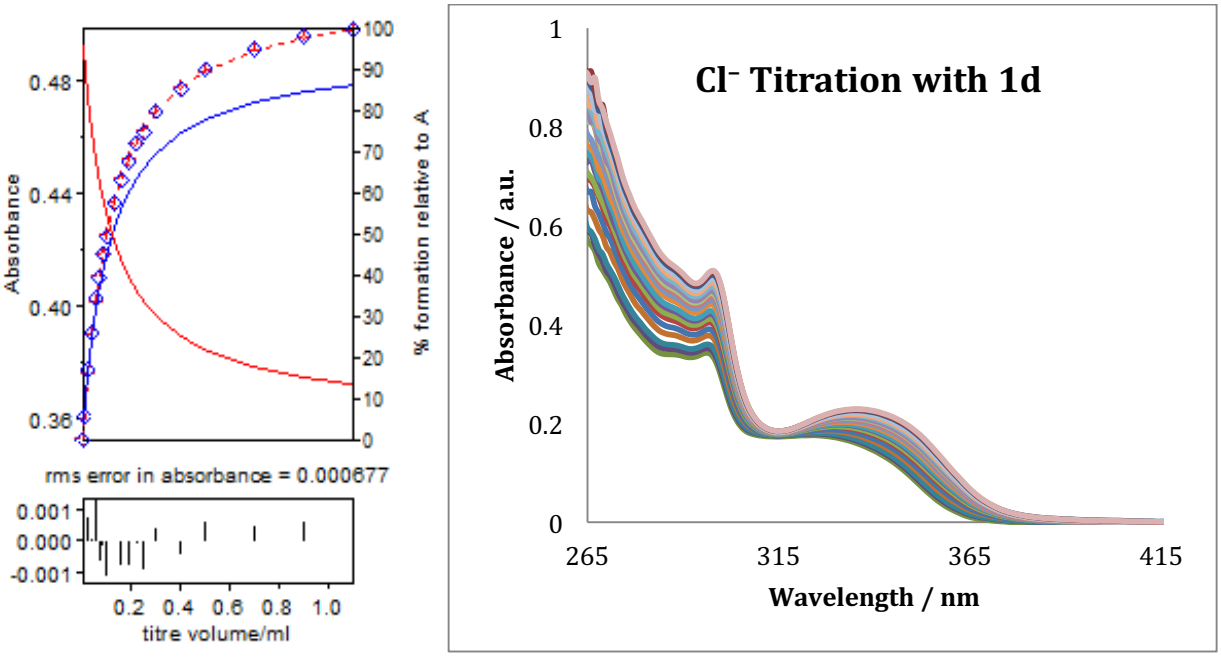

Figure S30. Binding isotherm for Cl^- titration of **1d** in $CHCl_3$ by UV-vis. Stacked spectra of **1d** (10.8 µM) titrated with TBA Cl^- (0-81 equiv., increasing abs.) in $CDCl_3$.

Table S31. Titration of **1d** with Br^-. (Stock [Br^-] = 2.39 mM).

	Guest (µL)	[**1d**] (M)	[Br^-] (M)	Equiv.
00	0	1.26E-05	0.00E+00	0.00
01	5	1.26E-05	5.96E-06	0.47
02	10	1.26E-05	1.19E-05	0.94
03	25	1.26E-05	2.95E-05	2.34
04	40	1.26E-05	4.68E-05	3.71
05	55	1.26E-05	6.39E-05	5.07
06	70	1.26E-05	8.08E-05	6.40
07	85	1.26E-05	9.74E-05	7.72
08	100	1.26E-05	1.14E-04	9.01
09	130	1.26E-05	1.46E-04	11.55
10	160	1.26E-05	1.77E-04	14.02
11	190	1.26E-05	2.07E-04	16.42
12	220	1.26E-05	2.37E-04	18.76
13	250	1.26E-05	2.65E-04	21.03
14	300	1.26E-05	3.12E-04	24.69
15	400	1.26E-05	3.98E-04	31.55
16	500	1.26E-05	4.78E-04	37.86
17	700	1.26E-05	6.19E-04	49.08
18	900	1.26E-05	7.42E-04	58.75
19	1100	1.26E-05	8.48E-04	67.18
20	1300	1.26E-05	9.41E-04	74.58

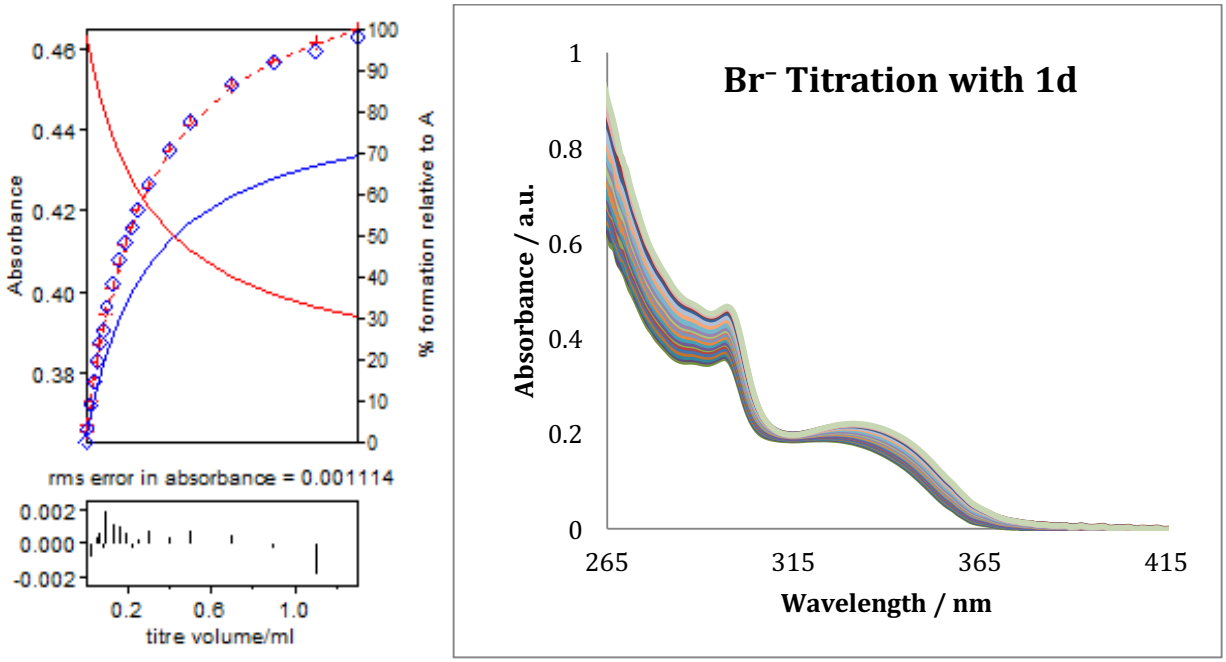

Figure S31. Binding isotherm for Br^- titration of **1d** in $CHCl_3$ by UV-vis. Stacked spectra of **1d** (12.6 µM) titrated with TBA Br^- (0-75 equiv., increasing abs.) in $CDCl_3$.

Table S32. Titration of **1d** with NO_3^-. (Stock [NO_3^-] = 2.35 mM).

	Guest (µL)	[**1d**] (M)	[NO_3^-] (M)	Equiv.
00	0	1.03E-05	0.00E+00	0.00
01	5	1.03E-05	5.86E-06	0.57
02	10	1.03E-05	1.17E-05	1.14
03	25	1.03E-05	2.90E-05	2.83
04	40	1.03E-05	4.60E-05	4.49
05	55	1.03E-05	6.29E-05	6.13
06	70	1.03E-05	7.94E-05	7.74
07	85	1.03E-05	9.57E-05	9.33
08	100	1.03E-05	1.12E-04	10.90
09	130	1.03E-05	1.43E-04	13.97
10	160	1.03E-05	1.74E-04	16.96
11	190	1.03E-05	2.04E-04	19.86
12	220	1.03E-05	2.33E-04	22.68
13	250	1.03E-05	2.61E-04	25.43
14	300	1.03E-05	3.06E-04	29.86
15	400	1.03E-05	3.91E-04	38.15
16	500	1.03E-05	4.70E-04	45.78
17	700	1.03E-05	6.09E-04	59.35
18	900	1.03E-05	7.29E-04	71.04
19	1100	1.03E-05	8.33E-04	81.22

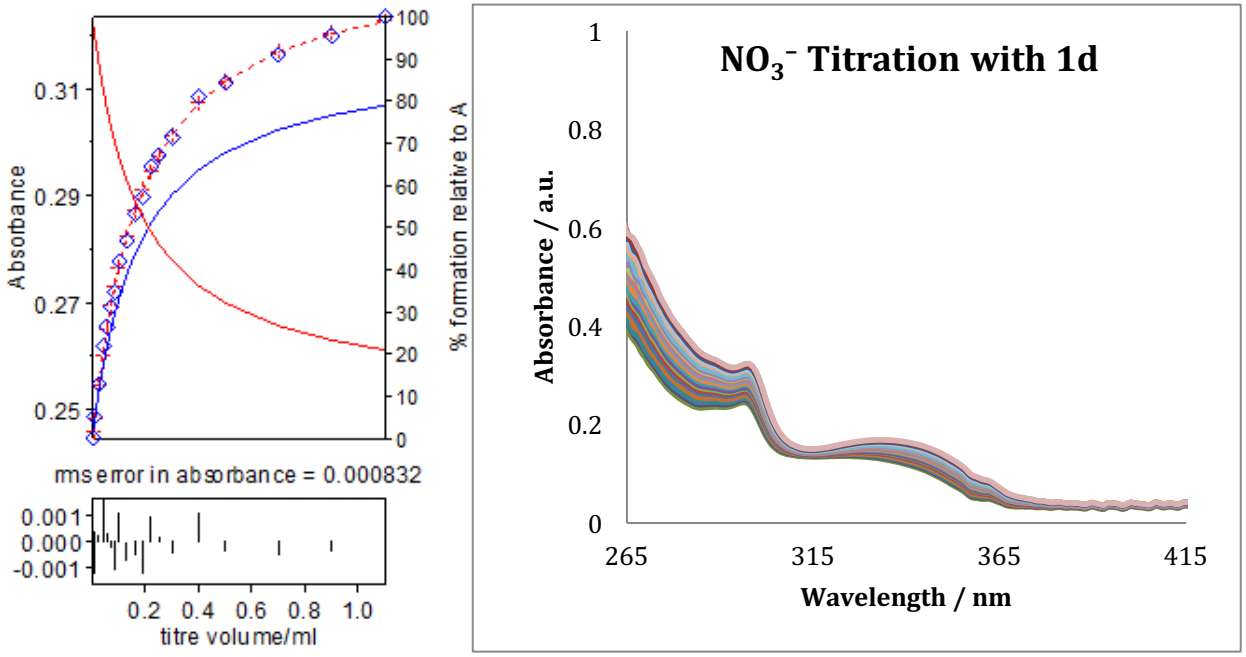

Figure S32. Binding isotherm for NO_3^- titration of **1d** in $CHCl_3$ by UV-vis. Stacked spectra of **1d** (10.3 µM) titrated with TBA NO_3^- (0-81 equiv., increasing abs.) in $CDCl_3$.

Table S33. Titration of **1e** with Cl^-. (Stock [Cl^-] = 5.11 mM)

	Guest (µL)	[**1e**] (M)	[Cl^-] (M)	Equiv.
0	0	2.26E-05	0.00E+00	0.00
1	5	2.26E-05	1.27E-05	0.56
2	10	2.26E-05	2.54E-05	1.12
3	15	2.26E-05	3.80E-05	1.68
4	25	2.26E-05	6.31E-05	2.79
5	50	2.26E-05	1.25E-04	5.50
6	80	2.26E-05	1.97E-04	8.68
7	110	2.26E-05	2.66E-04	11.76
8	150	2.26E-05	3.56E-04	15.74
9	200	2.26E-05	4.64E-04	20.51
10	250	2.26E-05	5.68E-04	25.07
11	300	2.26E-05	6.66E-04	29.43
12	400	2.26E-05	8.52E-04	37.60
13	500	2.26E-05	1.02E-03	45.13
14	700	2.26E-05	1.32E-03	58.50
15	900	2.26E-05	1.59E-03	70.02
16	1300	2.26E-05	2.01E-03	88.88
17	1700	2.26E-05	2.35E-03	103.67

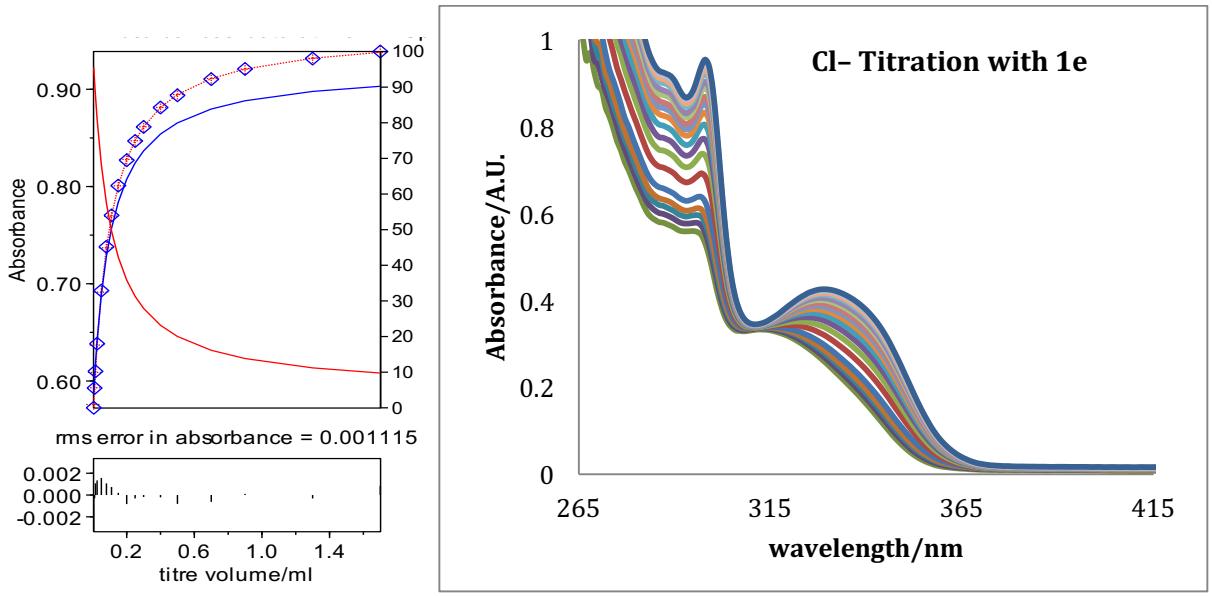

Figure S33. Binding isotherm for Cl^- titration of **1e** in $CHCl_3$ by UV-vis. Stacked spectra of **1e** (22.6 µM) titrated with TBA Cl^- (0-104 equiv., increasing abs.) in $CDCl_3$.

Table S34. Titration of **1e** with Br^-. (Stock [Br^-] = 4.65 mM).

	Guest (µL)	[**1e**] (M)	[Br^-] (M)	Equiv.
0	0	2.28E-05	0.00E+00	0.00
1	5	2.28E-05	1.16E-05	0.51
2	20	2.28E-05	4.60E-05	2.02
3	30	2.28E-05	6.87E-05	3.01
4	50	2.28E-05	1.13E-04	4.97
5	70	2.28E-05	1.57E-04	6.89
6	90	2.28E-05	2.00E-04	8.77
7	110	2.28E-05	2.42E-04	10.62
8	130	2.28E-05	2.84E-04	12.44
9	150	2.28E-05	3.24E-04	14.22
10	190	2.28E-05	4.03E-04	17.68
11	230	2.28E-05	4.79E-04	21.02
12	270	2.28E-05	5.53E-04	24.24
13	310	2.28E-05	6.24E-04	27.35
14	360	2.28E-05	7.09E-04	31.08
15	410	2.28E-05	7.91E-04	34.67
16	510	2.28E-05	9.45E-04	41.40
17	710	2.28E-05	1.22E-03	53.39
18	910	2.28E-05	1.45E-03	63.72
19	1110	2.28E-05	1.66E-03	72.73

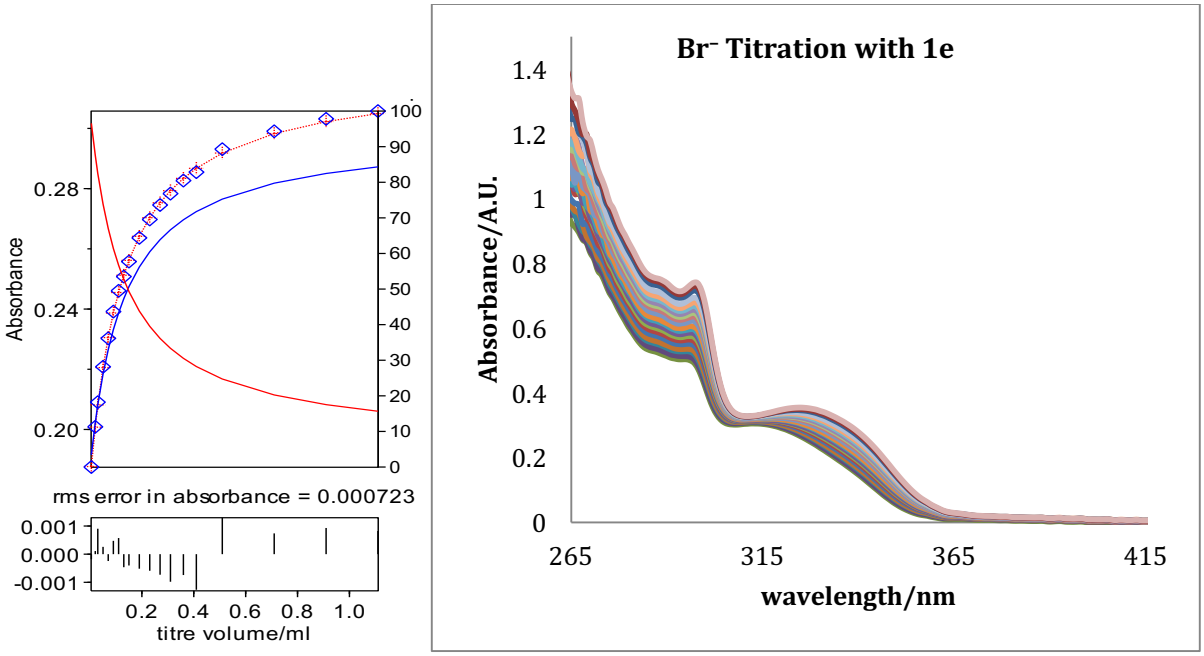

Figure S34. Binding isotherm for Br^- titration of **1e** in $CHCl_3$ by UV-vis. Stacked spectra of **1e** (22.8 µM) titrated with TBA Br^- (0-72 equiv., increasing abs.) in $CDCl_3$.

Table S35. Titration of **1e** with NO_3^-. (Stock [NO_3^-] = 5.05 mM).

	Guest (µL)	[**1e**] (M)	[NO_3^-] (M)	Equiv.
0	0	2.13E-05	0.00E+00	0.00
1	5	2.13E-05	1.26E-05	0.59
2	20	2.13E-05	5.00E-05	2.35
3	30	2.13E-05	7.47E-05	3.50
4	50	2.13E-05	1.23E-04	5.78
5	70	2.13E-05	1.71E-04	8.01
6	90	2.13E-05	2.18E-04	10.20
7	110	2.13E-05	2.63E-04	12.35
8	130	2.13E-05	3.08E-04	14.46
9	150	2.13E-05	3.52E-04	16.53
10	190	2.13E-05	4.38E-04	20.56
11	230	2.13E-05	5.21E-04	24.44
12	270	2.13E-05	6.01E-04	28.19
13	310	2.13E-05	6.78E-04	31.80
14	360	2.13E-05	7.71E-04	36.15
15	410	2.13E-05	8.59E-04	40.31
16	510	2.13E-05	1.03E-03	48.15
17	710	2.13E-05	1.32E-03	62.08
18	910	2.13E-05	1.58E-03	74.10
19	1110	2.13E-05	1.80E-03	84.58

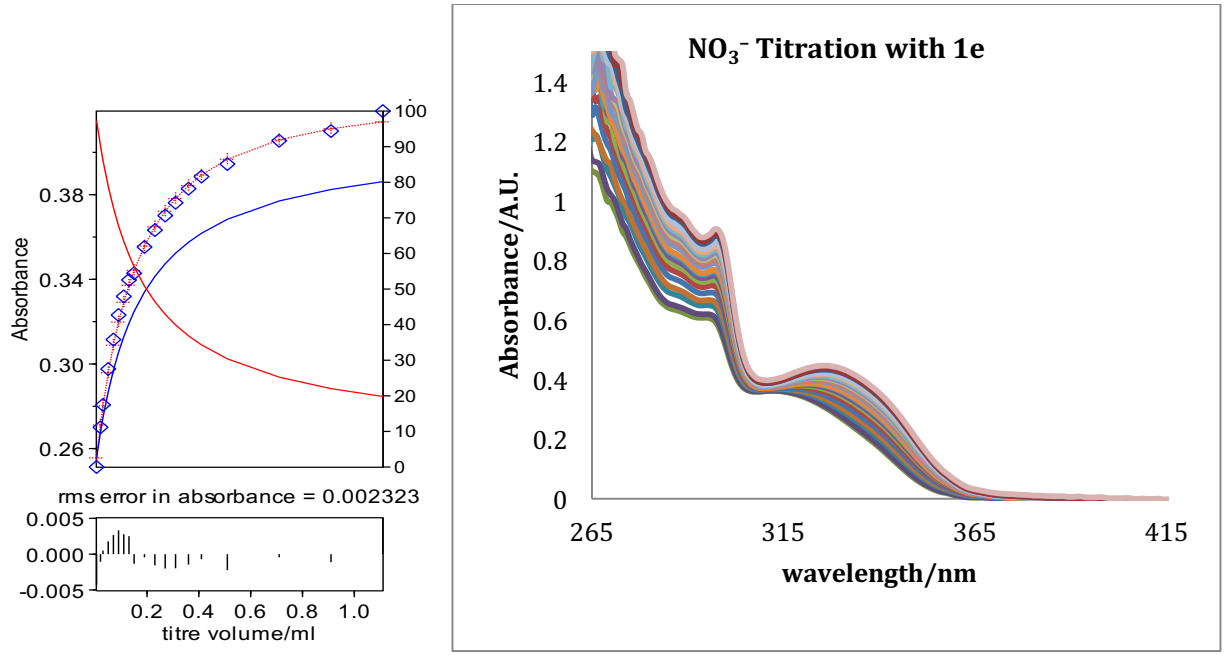

Figure S35. Binding isotherm for NO_3^- titration of **1e** in $CHCl_3$ by UV-vis. Stacked spectra of **1e** (21.3 µM) titrated with TBA NO_3^- (0-85 equiv., increasing abs.) in $CDCl_3$.

Table S36. Titration of **1f** with Cl^-. (Stock [Cl^-] = 2.41 mM)

	Guest (µL)	[**1f**] (M)	[Cl–] (M)	Equiv.
00	0	1.03E-05	0.00E+00	0.00
01	5	1.03E-05	6.01E-06	0.58
02	10	1.03E-05	1.20E-05	1.16
03	25	1.03E-05	2.97E-05	2.88
04	40	1.03E-05	4.72E-05	4.57
05	55	1.03E-05	6.45E-05	6.24
06	70	1.03E-05	8.15E-05	7.88
07	85	1.03E-05	9.82E-05	9.50
08	100	1.03E-05	1.15E-04	11.10
09	130	1.03E-05	1.47E-04	14.23
10	160	1.03E-05	1.78E-04	17.27
11	190	1.03E-05	2.09E-04	20.23
12	220	1.03E-05	2.39E-04	23.10
13	250	1.03E-05	2.68E-04	25.90
14	300	1.03E-05	3.14E-04	30.41
15	400	1.03E-05	4.02E-04	38.85
16	500	1.03E-05	4.82E-04	46.62
17	700	1.03E-05	6.25E-04	60.44
18	900	1.03E-05	7.48E-04	72.35
19	1100	1.03E-05	8.55E-04	82.72

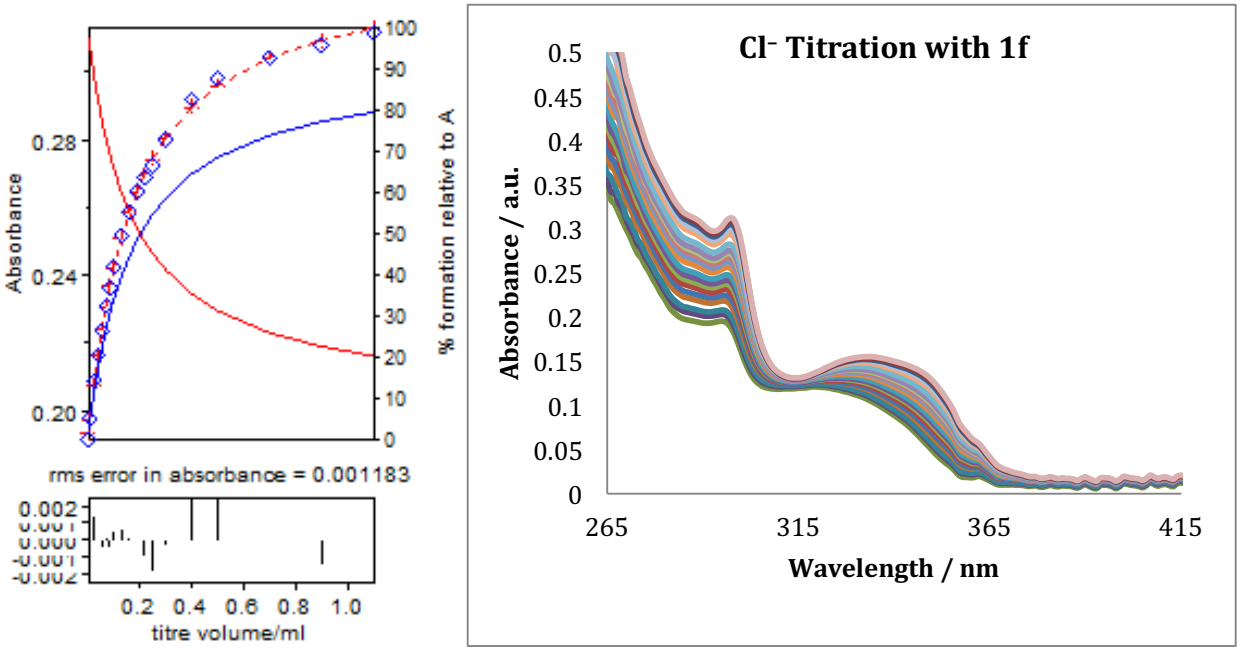

Figure S36. Binding isotherm for Cl^- titration of **1f** in $CHCl_3$ by UV-vis. Stacked spectra of **1f** (10.34 µM) titrated with TBA Cl^- (0-83 equiv., increasing abs.) in $CDCl_3$.

Table S37. Titration of **1f** with Br^-. (Stock [Br^-] = 11.19 mM).

	Guest (µL)	[**1f**] (M)	[Br–] (M)	Equiv.
00	0	1.05E-05	0.00E+00	0.00
01	5	1.05E-05	2.79E-05	2.65
02	10	1.05E-05	5.57E-05	5.29
03	25	1.05E-05	1.38E-04	13.12
04	40	1.05E-05	2.19E-04	20.84
05	55	1.05E-05	3.00E-04	28.44
06	70	1.05E-05	3.78E-04	35.94
07	85	1.05E-05	4.56E-04	43.33
08	100	1.05E-05	5.33E-04	50.61
09	130	1.05E-05	6.83E-04	64.87
10	160	1.05E-05	8.29E-04	78.73
11	190	1.05E-05	9.71E-04	92.21
12	220	1.05E-05	1.11E-03	105.32
13	250	1.05E-05	1.24E-03	118.09
14	300	1.05E-05	1.46E-03	138.62
15	350	1.05E-05	1.67E-03	158.29
16	400	1.05E-05	1.87E-03	177.13
17	500	1.05E-05	2.24E-03	212.56
18	600	1.05E-05	2.58E-03	245.26
19	800	1.05E-05	3.20E-03	303.65
20	1000	1.05E-05	3.73E-03	354.26
21	1200	1.05E-05	4.20E-03	398.55
22	1400	1.05E-05	4.61E-03	437.62
23	1600	1.05E-05	4.97E-03	472.35

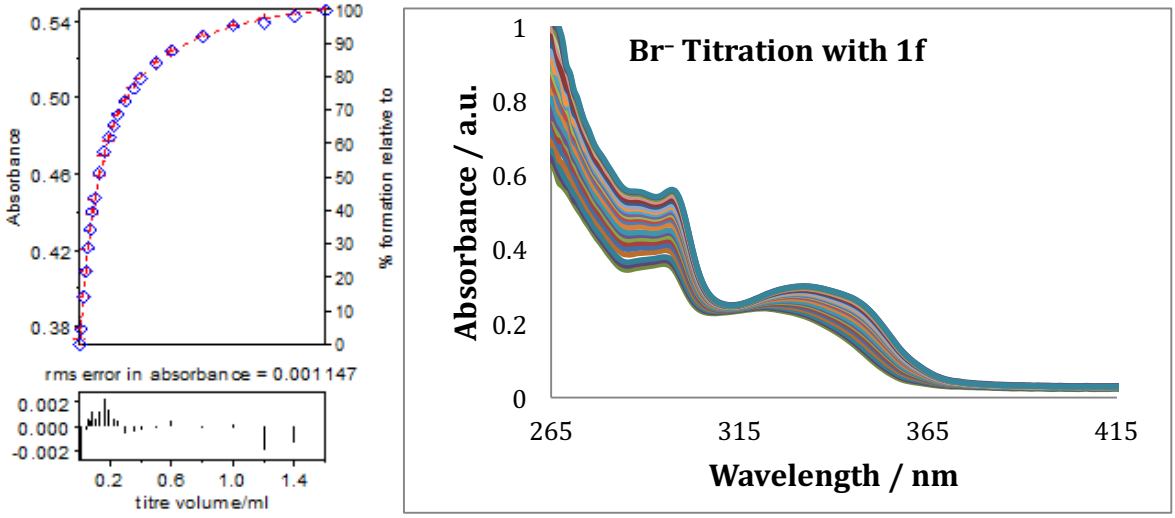

Figure S37. Binding isotherm for Br^- titration of **1f** in $CHCl_3$ by UV-vis. Stacked spectra of **1f** (10.53 µM) titrated with TBA Br^- (0-472 equiv., increasing abs.) in $CDCl_3$.

Table S38. Titration of **1f** with NO_3^-. (Stock [Br^-] = 2.28 mM).

	Guest (µL)	[**1f**] (M)	[NO_3^-] (M)	Equiv.
00	0	1.01E-05	0.00E+00	0.00
01	5	1.01E-05	5.69E-06	0.56
02	10	1.01E-05	1.14E-05	1.13
03	25	1.01E-05	2.82E-05	2.79
04	40	1.01E-05	4.48E-05	4.44
05	55	1.01E-05	6.11E-05	6.05
06	70	1.01E-05	7.72E-05	7.65
07	85	1.01E-05	9.31E-05	9.22
08	100	1.01E-05	1.09E-04	10.77
09	130	1.01E-05	1.39E-04	13.81
10	160	1.01E-05	1.69E-04	16.76
11	190	1.01E-05	1.98E-04	19.63
12	220	1.01E-05	2.26E-04	22.42
13	250	1.01E-05	2.54E-04	25.14
14	300	1.01E-05	2.98E-04	29.51
15	400	1.01E-05	3.81E-04	37.70
16	500	1.01E-05	4.57E-04	45.24
17	700	1.01E-05	5.92E-04	58.65
18	900	1.01E-05	7.09E-04	70.21
19	1100	1.01E-05	8.10E-04	80.27

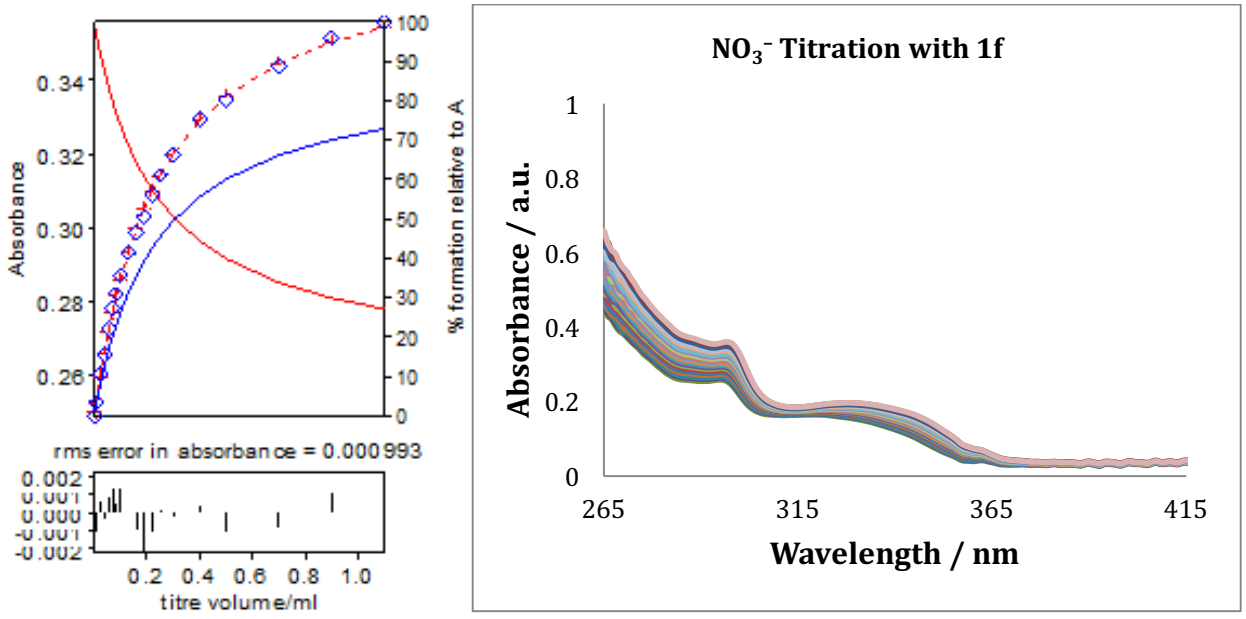

Figure S38. Binding isotherm for NO_3^- titration of **1f** in $CHCl_3$ by UV-vis. Stacked spectra of **1f** (10.1 µM) titrated with TBA NO_3^- (0-80 equiv., increasing abs.) in $CDCl_3$.

Table S39. Titration of **1g** with Cl^-. (Stock [Cl^-] = 9.87 mM).

	Guest (µL)	[**1g**] (M)	[Cl^-] (M)	Equiv.
0	0	3.94E-05	0.00E+00	0.00
1	5	3.94E-05	2.46E-05	0.63
2	10	3.94E-05	4.91E-05	1.25
3	20	3.94E-05	9.77E-05	2.48
4	30	3.94E-05	1.46E-04	3.70
5	50	3.94E-05	2.41E-04	6.11
6	70	3.94E-05	3.34E-04	8.48
7	90	3.94E-05	4.25E-04	10.80
8	110	3.94E-05	5.15E-04	13.07
9	130	3.94E-05	6.02E-04	15.30
10	150	3.94E-05	6.89E-04	17.49
11	190	3.94E-05	8.56E-04	21.75
12	230	3.94E-05	1.02E-03	25.86
13	270	3.94E-05	1.17E-03	29.82
14	310	3.94E-05	1.32E-03	33.64
15	360	3.94E-05	1.51E-03	38.24
16	410	3.94E-05	1.68E-03	42.65
17	510	3.94E-05	2.01E-03	50.94
18	710	3.94E-05	2.59E-03	65.68
19	910	3.94E-05	3.09E-03	78.40

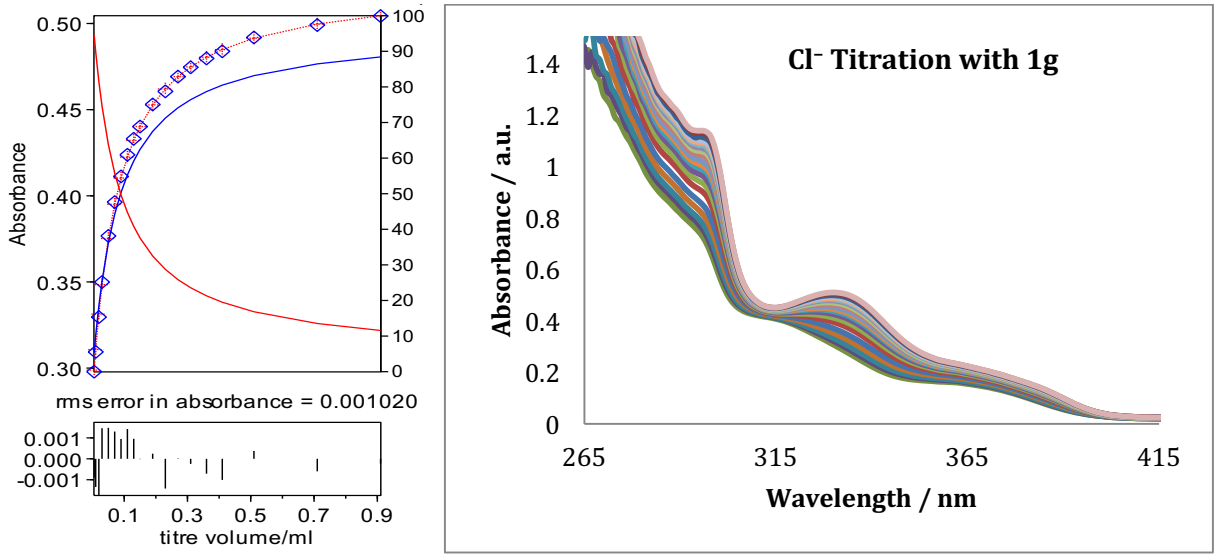

Figure S39. Binding isotherm for Cl^- titration of **1g** in $CHCl_3$ by UV-vis. Stacked spectra of **1g** (39.4 µM) titrated with TBA Cl^- (0-78 equiv., increasing abs.) in $CDCl_3$.

Table S40. Titration of **1g** with Br^-. (Stock [Br^-] = 7.39 mM).

	Guest (µL)	[**1g**] (M)	[Br^-] (M)	Equiv.
0	0	3.22E-05	0.00E+00	0.00
1	5	3.22E-05	1.84E-05	0.57
2	20	3.22E-05	7.32E-05	2.28
3	30	3.22E-05	1.09E-04	3.40
4	50	3.22E-05	1.80E-04	5.60
5	70	3.22E-05	2.50E-04	7.77
6	90	3.22E-05	3.18E-04	9.90
7	110	3.22E-05	3.85E-04	11.98
8	130	3.22E-05	4.51E-04	14.02
9	150	3.22E-05	5.15E-04	16.03
10	190	3.22E-05	6.41E-04	19.94
11	230	3.22E-05	7.62E-04	23.70
12	270	3.22E-05	8.79E-04	27.33
13	310	3.22E-05	9.92E-04	30.84
14	360	3.22E-05	1.13E-03	35.05
15	410	3.22E-05	1.26E-03	39.09
16	510	3.22E-05	1.50E-03	46.69
17	710	3.22E-05	1.94E-03	60.20
18	910	3.22E-05	2.31E-03	71.86
19	1110	3.22E-05	2.64E-03	82.02

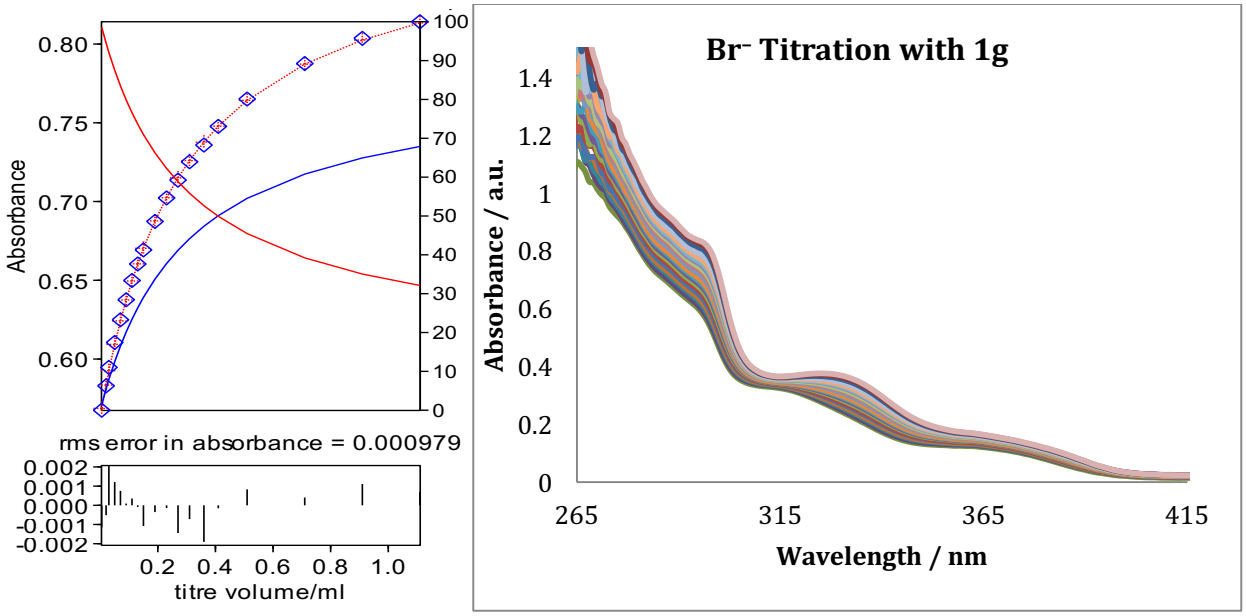

Figure S40. Binding isotherm for Br^- titration of **1g** in $CHCl_3$ by UV-vis. Stacked spectra of **1g** (32.2 µM) titrated with TBA Br^- (0-82 equiv., increasing abs.) in $CDCl_3$.

Table S41. Titration of **1g** with NO_3^-. (Stock [NO_3^-] = 7.91 mM)

	Guest (µL)	[**1g**] (M)	[NO_3^-] (M)	Equiv.
0	0	3.56E-05	0.00E+00	0.00
1	5	3.56E-05	1.97E-05	0.55
2	20	3.56E-05	7.83E-05	2.20
3	30	3.56E-05	1.17E-04	3.28
4	50	3.56E-05	1.93E-04	5.41
5	70	3.56E-05	2.67E-04	7.51
6	90	3.56E-05	3.40E-04	9.56
7	110	3.56E-05	4.12E-04	11.57
8	130	3.56E-05	4.83E-04	13.55
9	150	3.56E-05	5.52E-04	15.49
10	190	3.56E-05	6.86E-04	19.26
11	230	3.56E-05	8.15E-04	22.89
12	270	3.56E-05	9.40E-04	26.40
13	310	3.56E-05	1.06E-03	29.79
14	360	3.56E-05	1.21E-03	33.86
15	410	3.56E-05	1.35E-03	37.76
16	510	3.56E-05	1.61E-03	45.10
17	710	3.56E-05	2.07E-03	58.16
18	910	3.56E-05	2.47E-03	69.42
19	1110	3.56E-05	2.82E-03	79.23

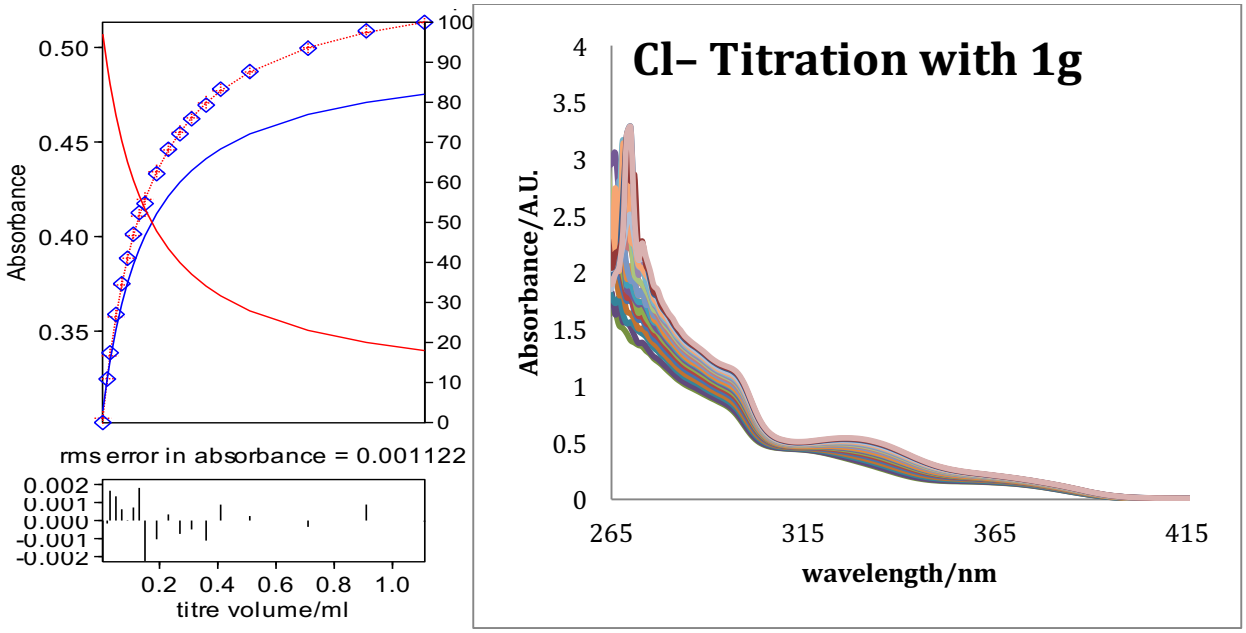

Figure S41. Binding isotherm for NO_3^- titration of **1g** in $CHCl_3$ by UV-vis. Stacked spectra of **1g** (35.6 µM) titrated with TBA NO_3^- (0-79 equiv., increasing abs.) in $CDCl_3$.

Job Plots

UV-Vis Job Plot Conditions. UV-Vis Job plots were carried out on an HP 8453 UV-Vis spectrometer. Water-saturated $CHCl_3$ was prepared in the same manner as for ^1H data. Job plots were obtained by $\Delta\lambda_{max}$ of the anion-bound complex highest peak. Hamilton gas-tight syringes were used during serial dilutions and titrations.

Tetrabutylammonium nitrate with 1b. A stock solution of **1b** was prepared using serial dilution to a final volume of 5 mL (1.32 mg, [**1b**] = 77.76 μM). A 5 mL solution of $TBANO_3$ (6.41 mg, 77.69 μM) was prepared by serial dilution. The volume in the cuvette was 2.0 mL.

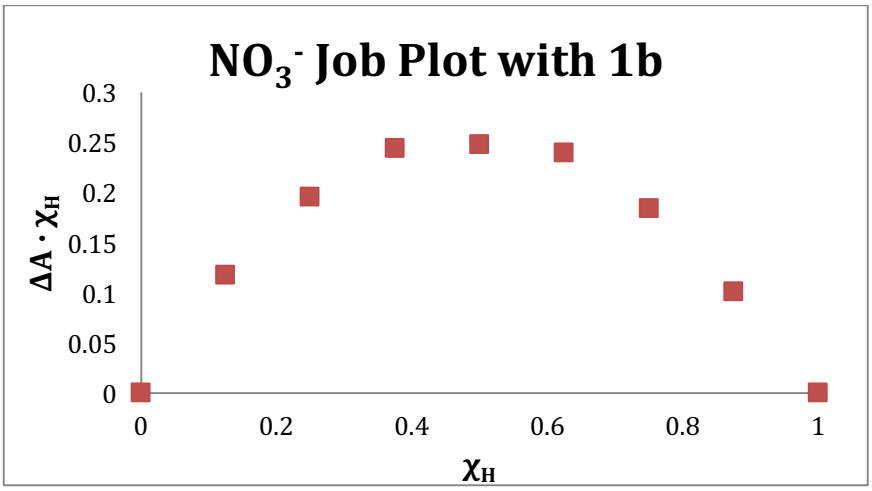

Figure S42. Job plot of **1b** with NO_3^- in water-saturated $CHCl_3$.

Tetrabutylammonium chloride with 1c. A stock solution of **1c** was prepared using serial dilution to a final volume of 5 mL (1.23 mg, [**1c**] = 75.11 μM). A 5 mL solution of TBACl (15.18 mg, 75.10 μM) was prepared by serial dilution. The volume in the cuvette was 2.0 mL.

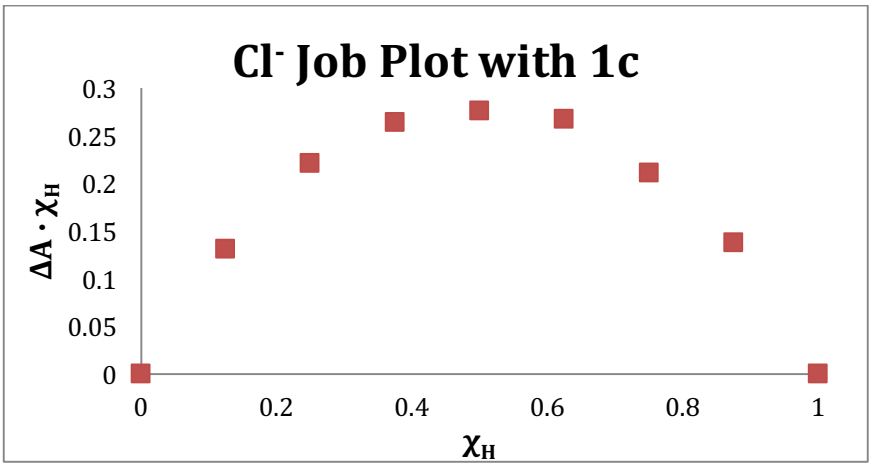

Figure S43. Job plot of **1c** with Cl^- in water-saturated $CHCl_3$.

Tetrabutylammonium bromide with 1c. A stock solution of **1c** was prepared using serial dilution to a final volume of 5 mL (1.25 mg, [**1c**] = 48.95 μM). A 5 mL solution of TBABr (8.96 mg, 48.85 μM) was prepared by serial dilution. The volume in the cuvette was 2.0 mL.

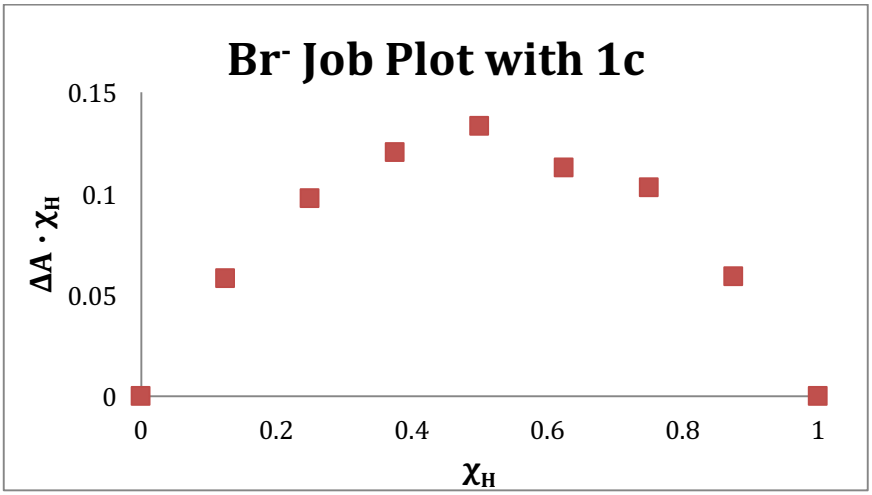

Figure S44. Job plot of **1c** with Br^- in water-saturated $CHCl_3$.

Tetrabutylammonium nitrate with 1c. A stock solution of **1c** was prepared using serial dilution to a final volume of 5 mL (1.36 mg, [**1c**] = 72.21 μM). A 5 mL solution of $TBANO_3$ (7.72 mg, 72.26 μM) was prepared by serial dilution. The volume in the cuvette was 2.0 mL.

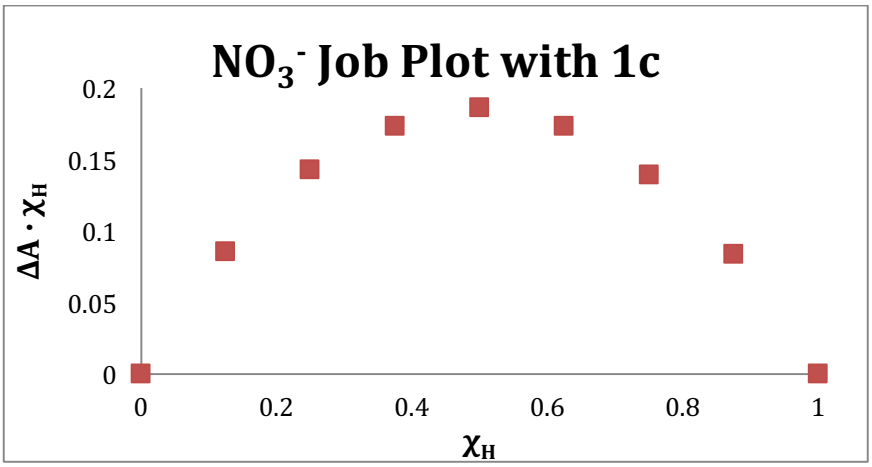

Figure S45. Job plot of **1c** with NO_3^- in water-saturated $CHCl_3$.

Tetrabutylammonium chloride with 1d. A stock solution of **1d** was prepared using serial dilution to a final volume of 5 mL (1.55 mg, [**1d**] = 71.52 μM). A 5 mL solution of TBACl (10.60 mg, 71.51 μM) was prepared by serial dilution. The volume in the cuvette was 2.0 mL.

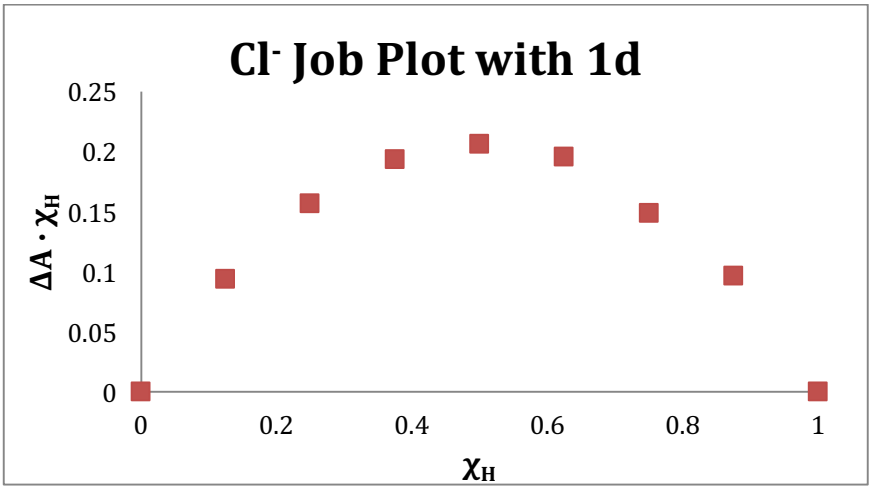

Figure S46. Job plot of **1d** with Cl^- in water-saturated $CHCl_3$.

Tetrabutylammonium bromide with 1d. A stock solution of **1d** was prepared using serial dilution to a final volume of 5 mL (1.18 mg, [**1d**] = 71.26 μM). A 5 mL solution of TBABr (10.07 mg, 71.22 μM) was prepared by serial dilution. The volume in the cuvette was 2.0 mL.

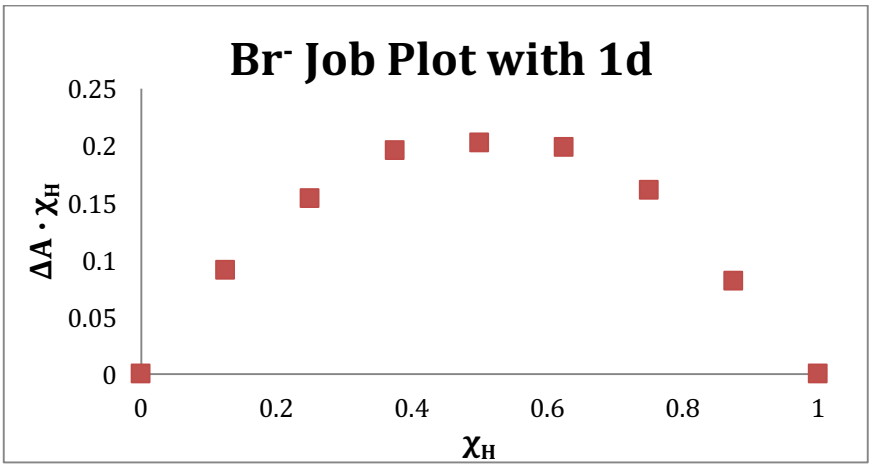

Figure S47. Job plot of **1d** with Br^- in water-saturated $CHCl_3$.

Tetrabutylammonium nitrate with 1d. A stock solution of **1d** was prepared using serial dilution to a final volume of 5 mL (1.65 mg, [**1d**] = 70.53 μM). A 5 mL solution of $TBANO_3$ (5.83 mg, 70.56 μM) was prepared by serial dilution. The volume in the cuvette was 2.0 mL.

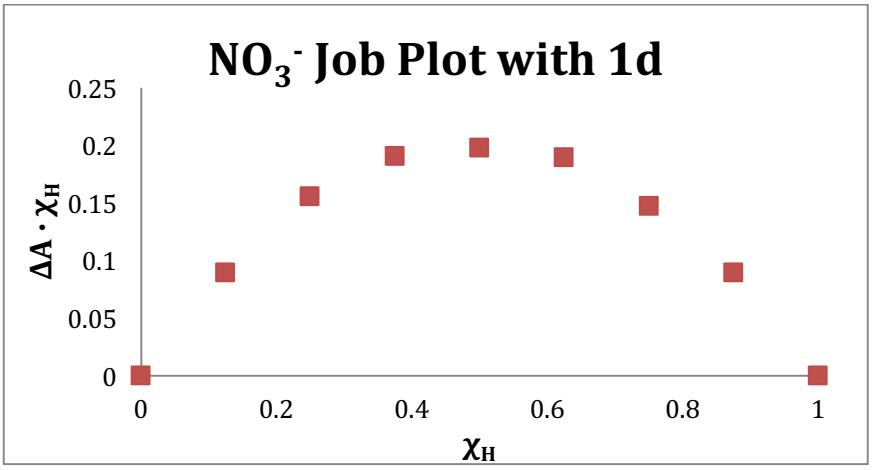

Figure S48. Job plot of **1d** with NO_3^- in water-saturated $CHCl_3$.

Tetrabutylammonium chloride with 1f. A stock solution of **1f** was prepared using serial dilution to a final volume of 5 mL (1.85 mg, [**1f**] = 69.17 μM). A 5 mL solution of TBACl (18.54 mg, 69.16 μM) was prepared by serial dilution. The volume in the cuvette was 2.0 mL.

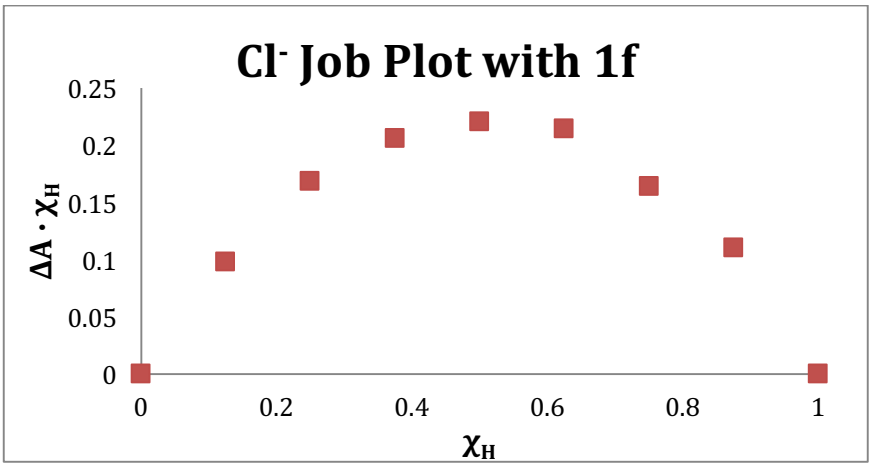

Figure S49. Job plot of **1f** with Cl^- in water-saturated $CHCl_3$.

Tetrabutylammonium bromide with 1f. A stock solution of **1f** was prepared using serial dilution to a final volume of 5 mL (1,76 mg, [**1f**] = 70.50 µM). A 5 mL solution of TBABr (29.32 mg, 70.49 µM) was prepared by serial dilution. The volume in the cuvette was 2.0 mL.

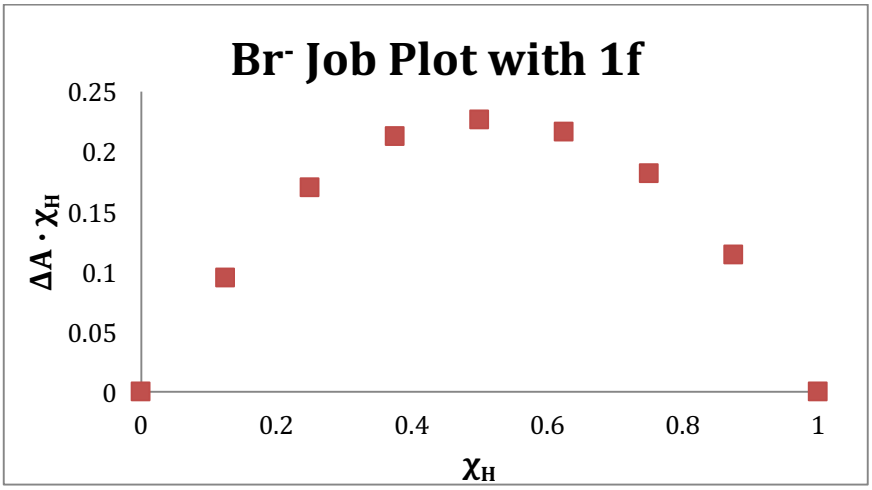

Figure S50. Job plot of **1f** with Br^- in water-saturated $CHCl_3$.

Tetrabutylammonium nitrate with 1f. A stock solution of **1f** was prepared using serial dilution to a final volume of 5 mL (2.12 mg, [**1f**] = 70.77 µM). A 5 mL solution of $TBANO_3$ (6.47 mg, 70.75 µM) was prepared by serial dilution. The volume in the cuvette was 2.0 mL.

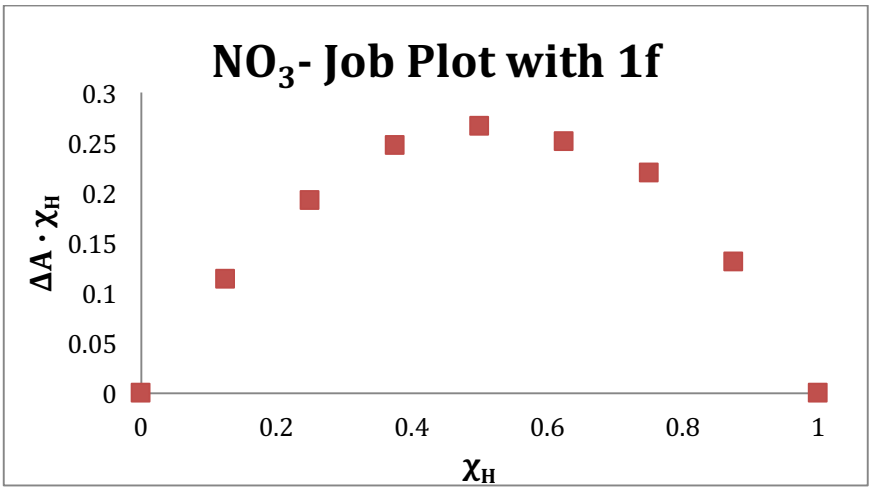

Figure S51. Job plot of **1f** with NO_3^- in water-saturated $CHCl_3$.

Part IV. Fitting Data and Results

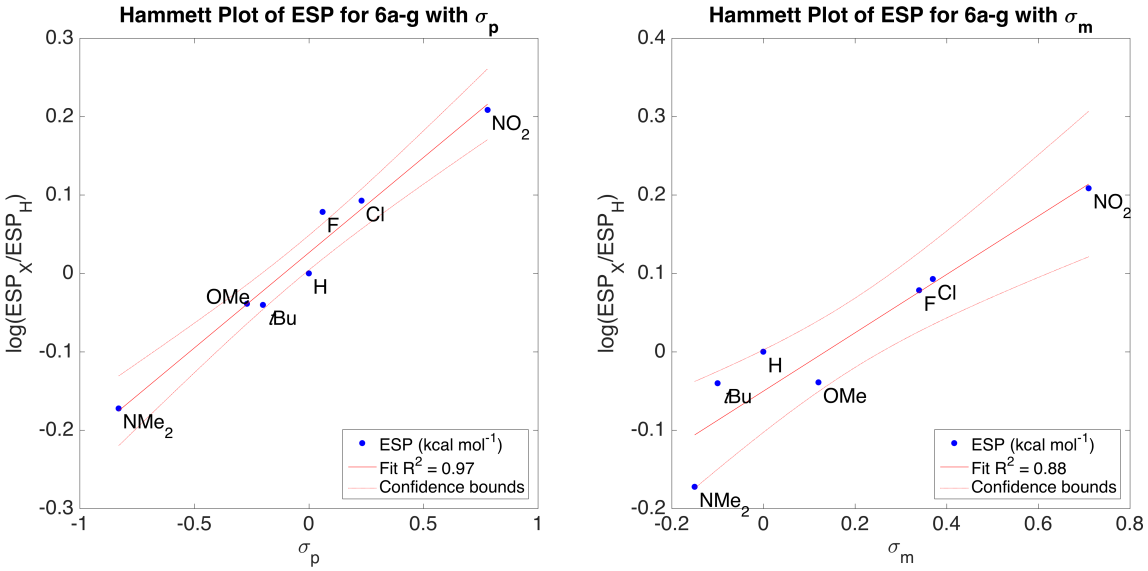

Figure S52. Hammett plots of the ESP for the C-H hydrogen bond donor in **6a-g**. ESP fit with σ_p ($\boldsymbol{\rho}$ = 0.243, i = 0.026) is superior to σ_m ($\boldsymbol{\rho}$ = 0.372, i = -0.050).

Table S42. Mulliken atomic charge and ESP values for 5a-g.

	Mulliken atomic charges							ESP values		
X	H (CH)	C (CH)	H_1	N_1[a]	H_2	H_3	N_2[b]	C–H	N–H_2[c]	N–H_3[c]
$N(Me)_2$	0.168	−0.362	0.388	−0.596	0.382	0.418	−0.789	36.3	55.9	47.5
t-Bu	0.174	−0.321	0.386	−0.605	0.381	0.416	−0.779	39.2	57.0	48.6
H	0.175	−0.273	0.387	−0.613	0.381	0.417	−0.775	39.2	57.8	50.1
F	0.177	−0.279	0.387	−0.613	0.381	0.418	−0.774	43.1	59.5	51.6
NO3	0.186	−0.250	0.385	−0.608	0.381	0.417	−0.775	48.6	62.6	53.6

*Mulliken charges are given as a fraction of one electronic charge. ESP values are reported here in kcal/mol.
[a]Areneethynyl attached nitrogen. [b]Terminal nitrogen. [c]Hydrogens on terminal nitrogen.

Table S43. Coefficients and Fitting Statistics for Mulliken charges and ESP of 5a-g with σ_p.

		ρ	i	N	R^2	F
Charge	**C (CH)**	-0.104(±0.021)	0.029(±0.011)	5	0.90	25.7
	N1	-0.008(±0.005)	-0.607(±0.003)	5	0.43	2.3
	N2	0.005(±0.002)	0.002(±0.001)	5	0.68	6.3
ESP	**C–H**	0.080(±0.015)	0.023(±0.008)	5	0.90	28
	N–H2	0.032(±0.006)	0.007(±0.003)	5	0.91	29
	N–H3	0.034(±0.006)	0.002(±0.003)	7	0.91	29

Table S44. Coefficients and Fitting Statistics for Hammett Plots of σ_+ and σ_-.

K_a (X^-)	ρ	i	N	R^2	F
Cl^- (σ_+)	0.35(±0.07)	0.08(±0.06)	7	0.83	24
Br^- (σ_+)	0.34(±0.07)	0.14(±0.05)	7	0.84	26
I^- (σ_+)	0.27(±0.07)	0.21(±0.06)	7	0.73	14
NO_3^- (σ_+)	0.30(±0.06)	0.15(±0.05)	7	0.81	21
Cl^- (σ_-)	0.52(±0.11)	–0.08(±0.05)	7	0.83	24
Br^- (σ_-)	0.49(±0.12)	–0.02(±0.06)	7	0.77	17
I^- (σ_-)	0.41(±0.10)	–0.08(±0.05)	7	0.77	16
NO_3^- (σ_-)	0.41(±0.12)	–0.02(±0.06)	7	0.71	13

Part V. References

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Part VI: NMR Spectra

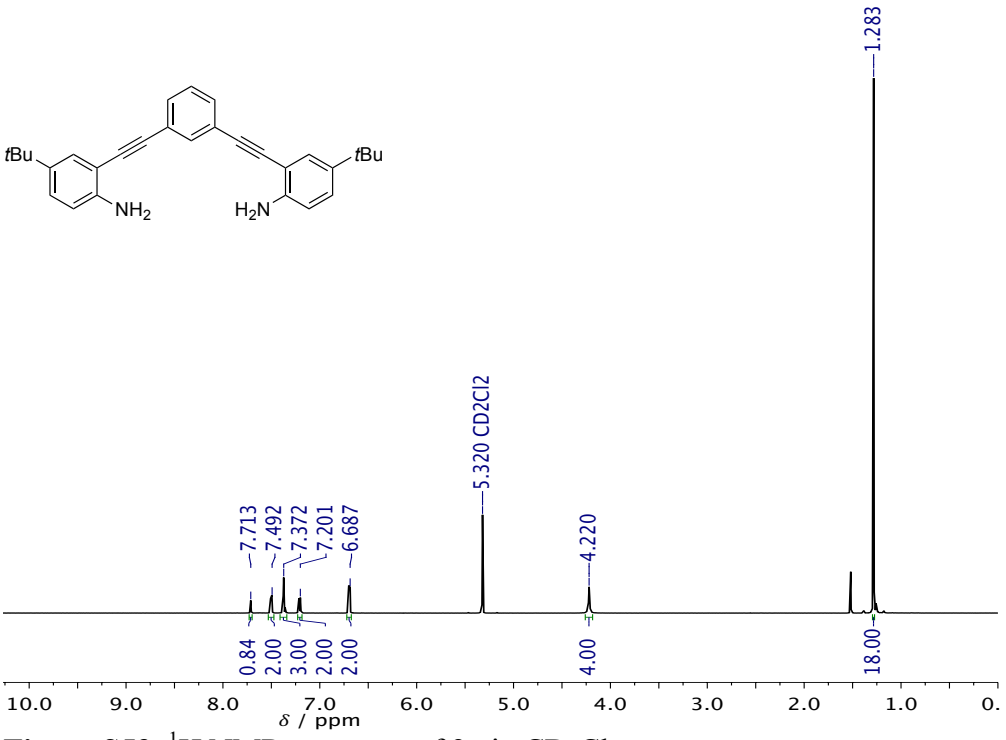

Figure S53. ^{1}H NMR spectrum of **2a** in CD_2Cl_2.

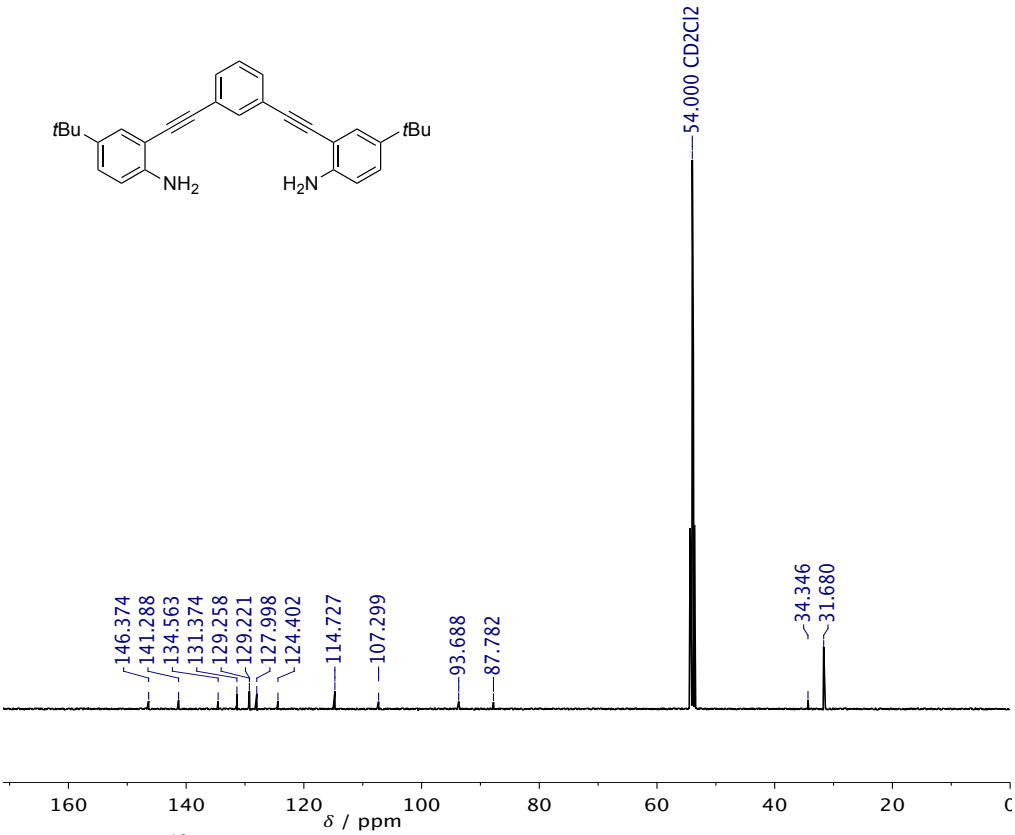

Figure S54. ^{13}C NMR spectrum of **2a** in CD_2Cl_2.

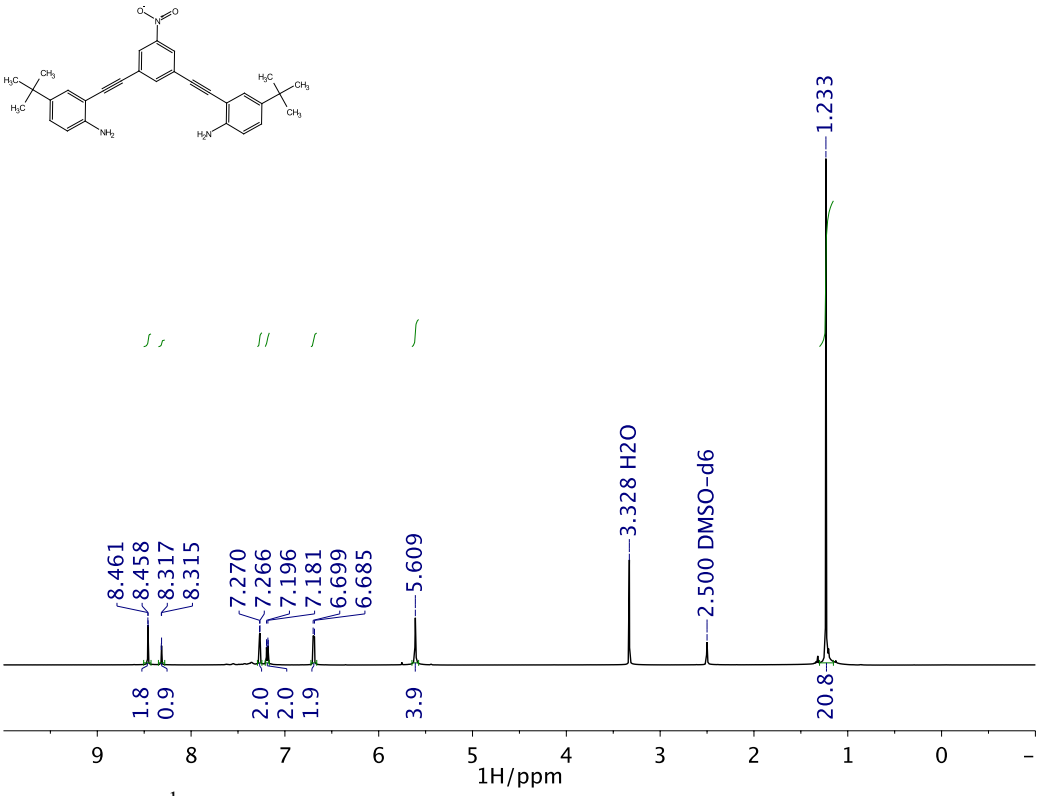

Figure S55. ^{1}H NMR spectrum of **2b** in DMSO-*d6*.

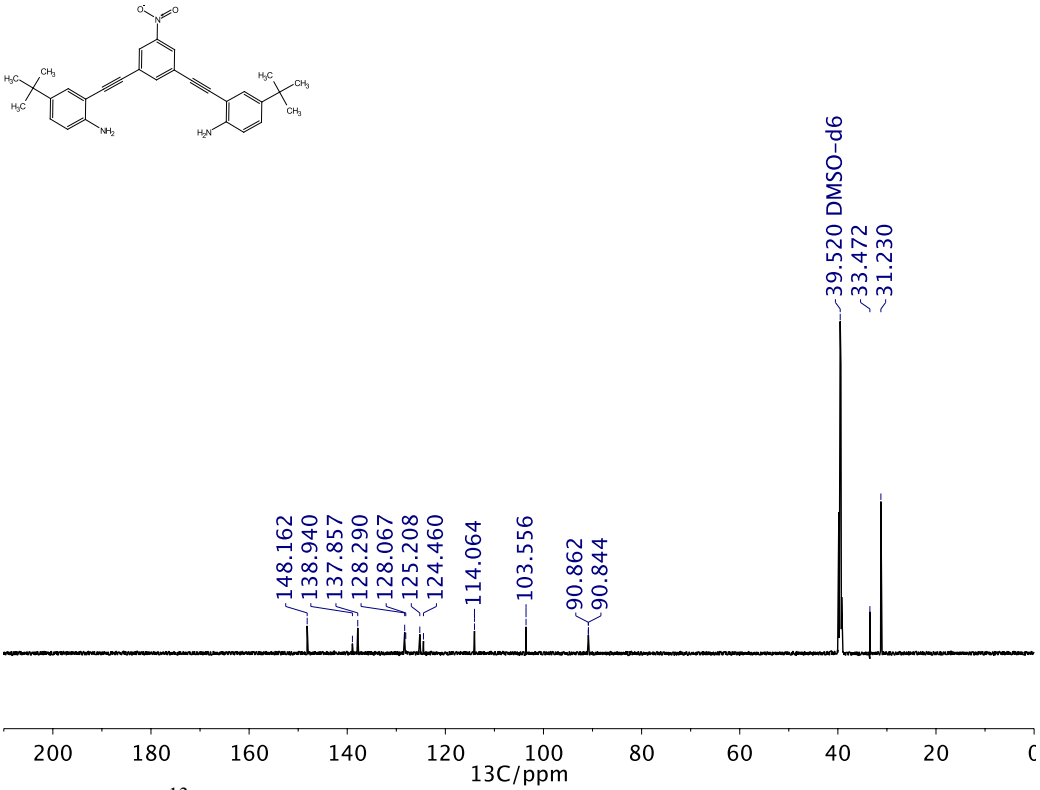

Figure S56. ^{13}C NMR spectrum of **2b** in DMSO-*d6*.

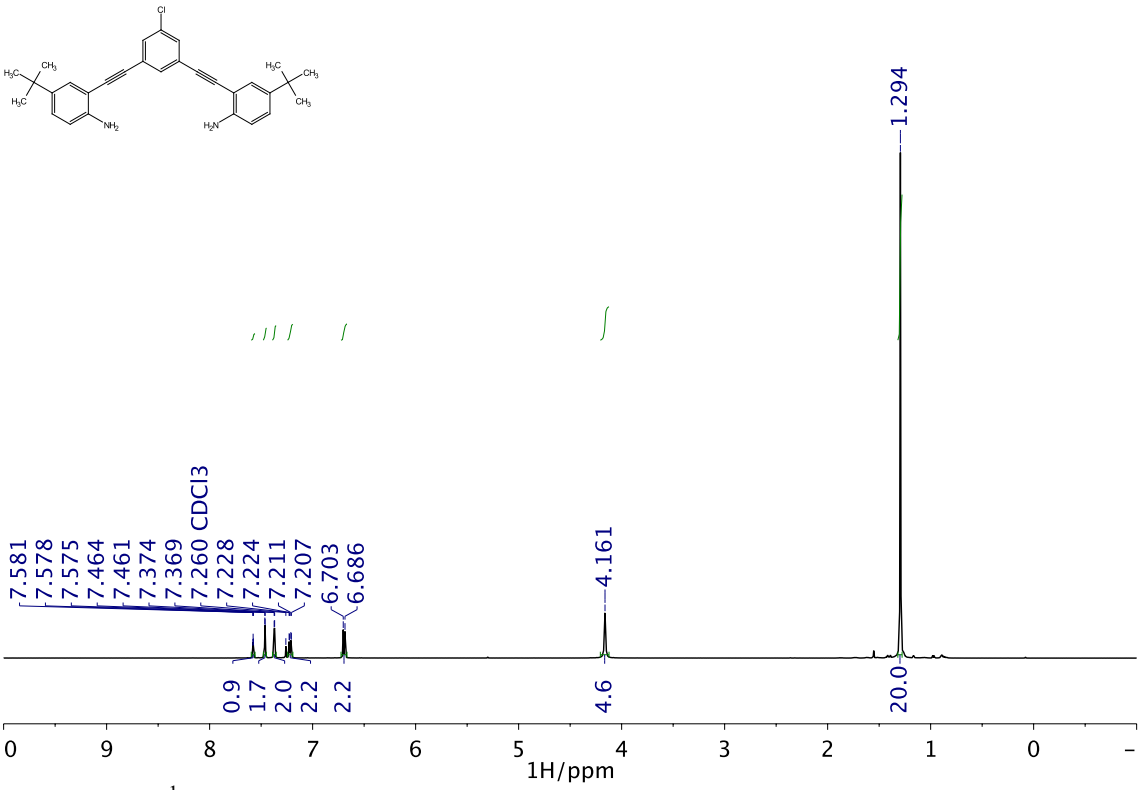

Figure S57. ^{1}H NMR spectrum of **2c** in $CDCl_3$.

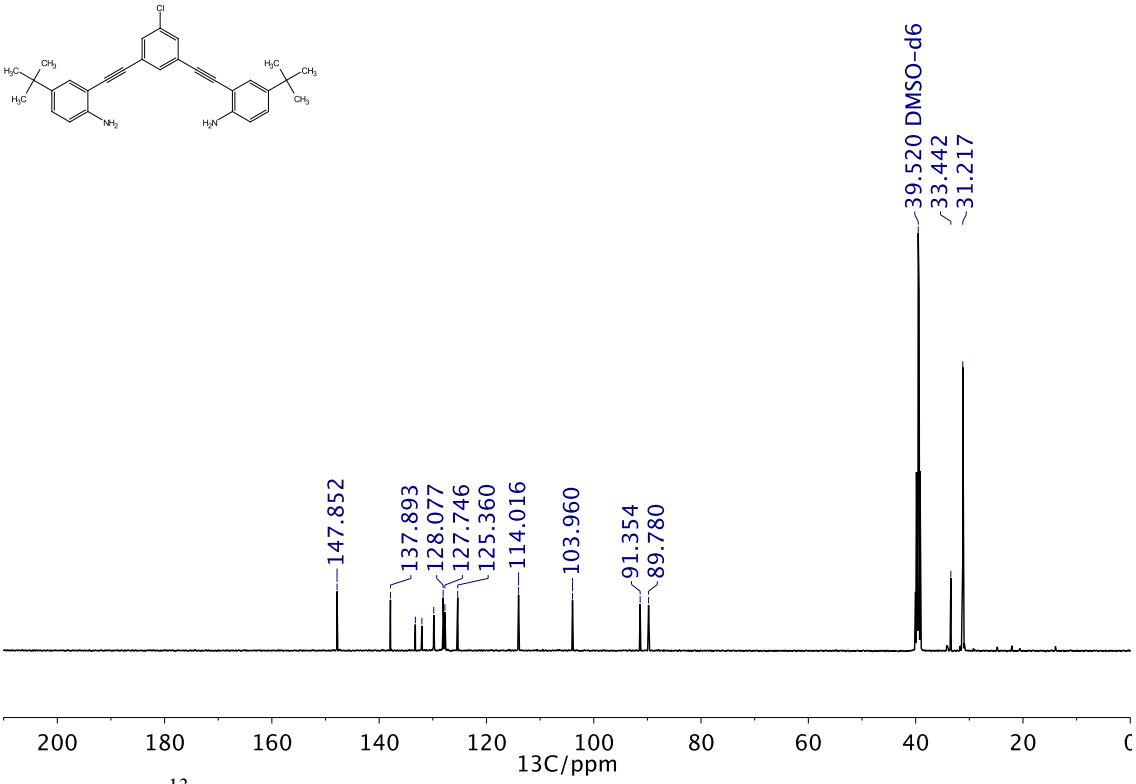

Figure S58. ^{13}C NMR spectrum of **2c** in DMSO-d_6.

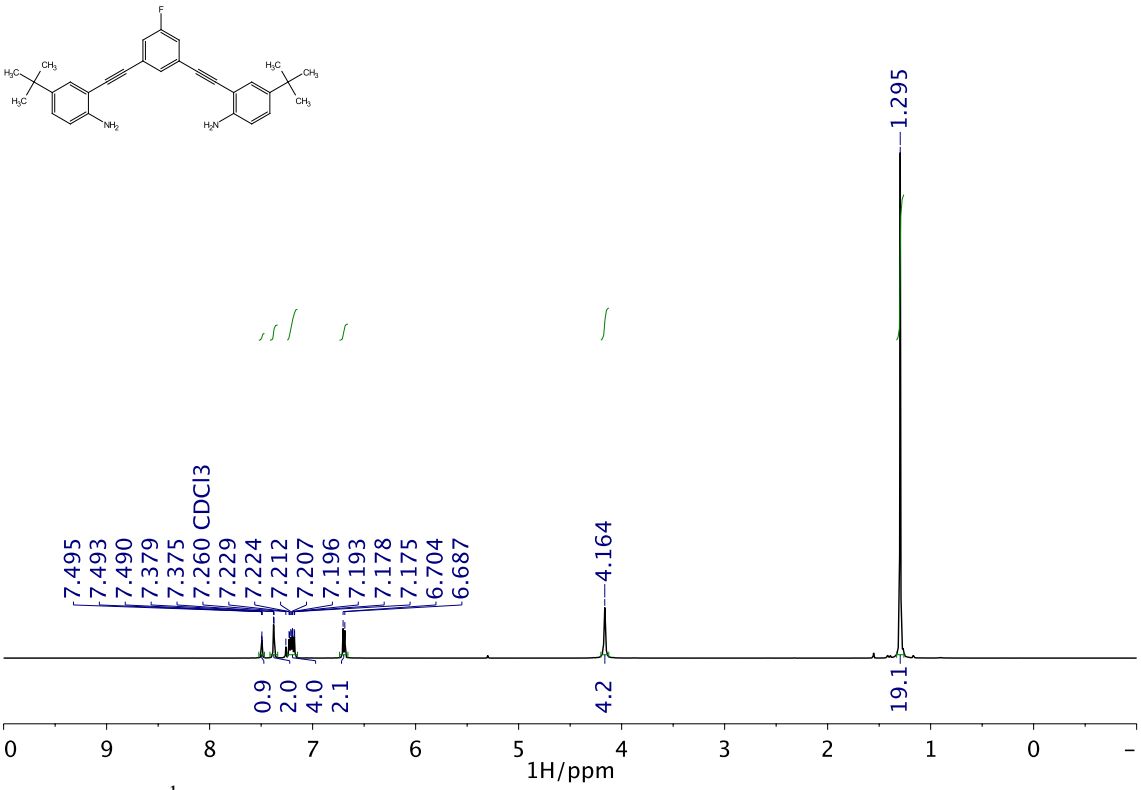

Figure S59. ^{1}H NMR spectrum of **2d** in $CDCl_3$.

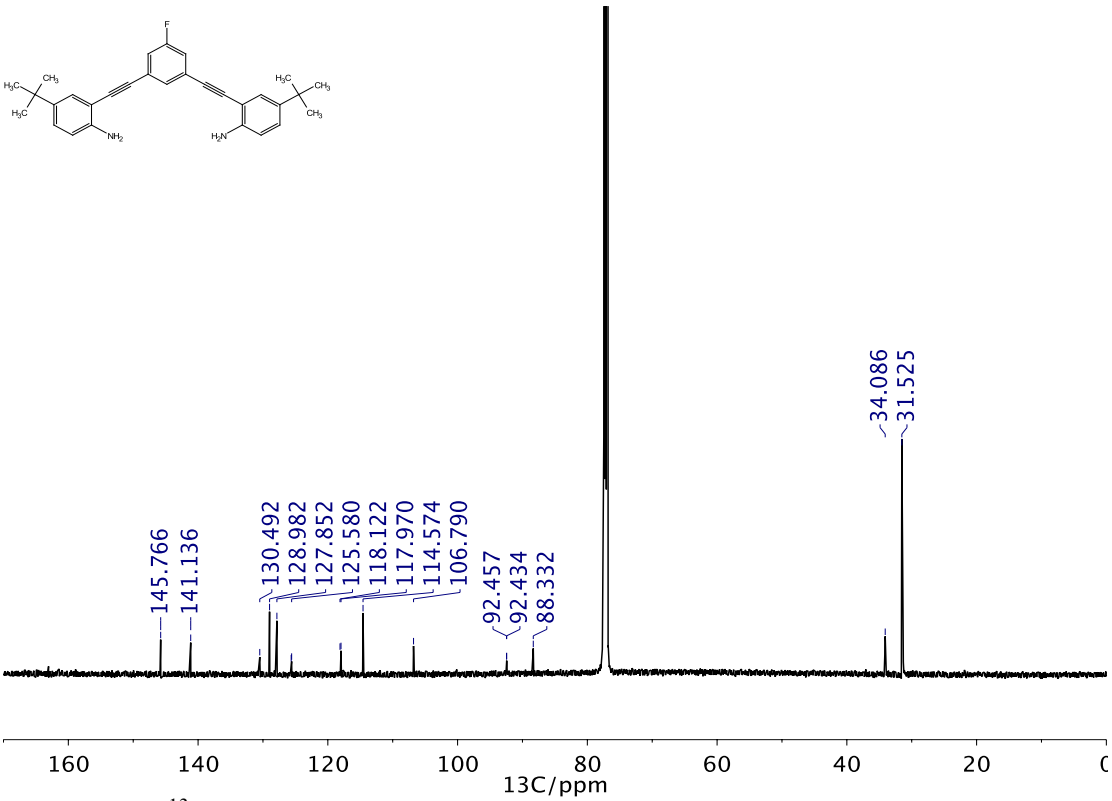

Figure S60. ^{13}C NMR spectrum of **2d** in $CDCl_3$.

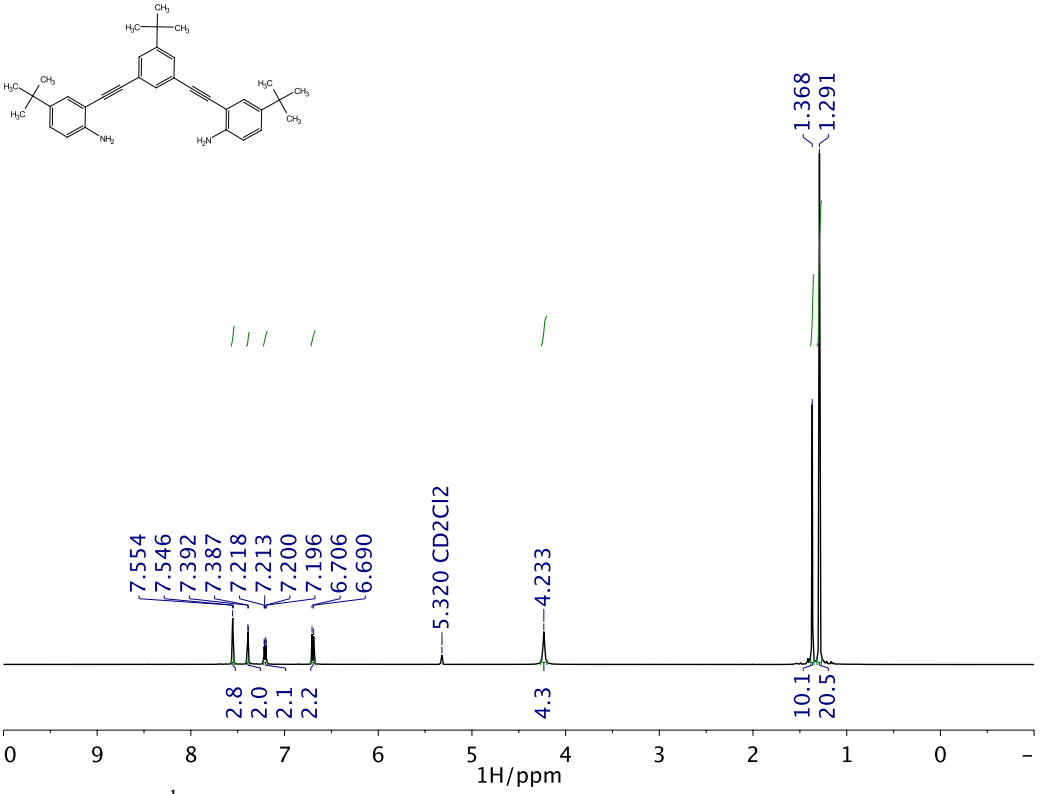

Figure S61. ^{1}H NMR spectrum of **2e** in CD_2Cl_2.

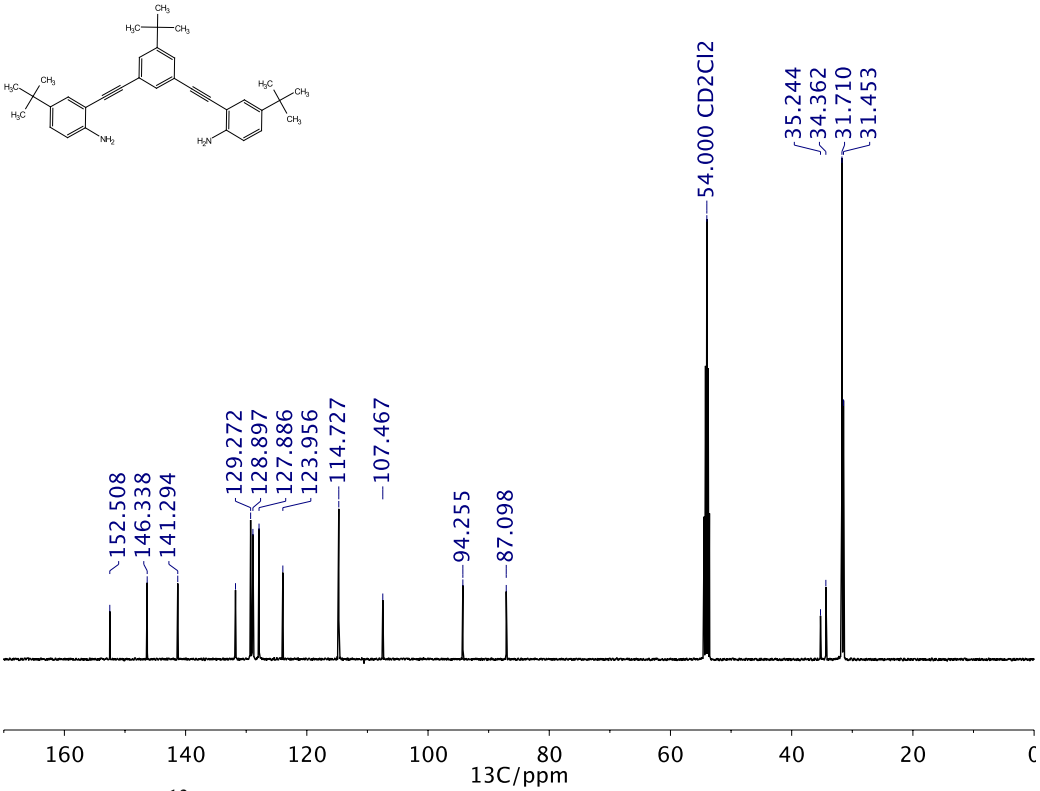

Figure S62. ^{13}C NMR spectrum of **2e** in CD_2Cl_2.

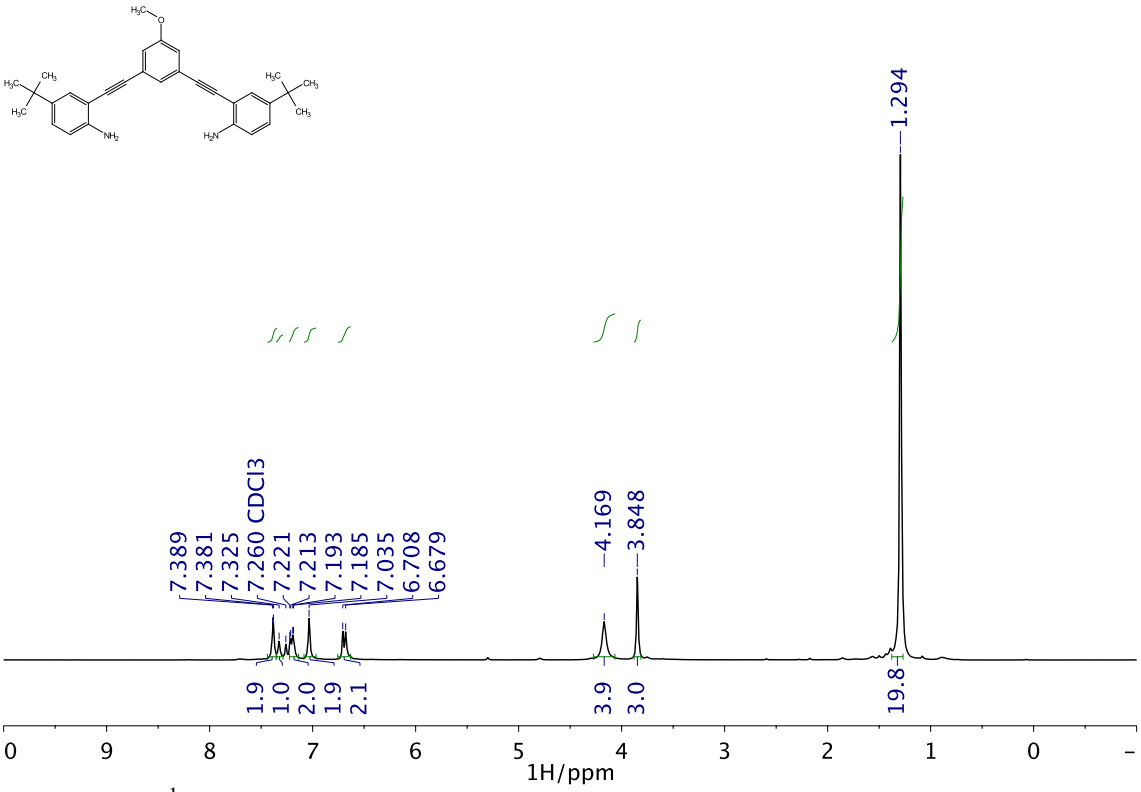

Figure S63. ^{1}H NMR spectrum of **2f** in $CDCl_3$.

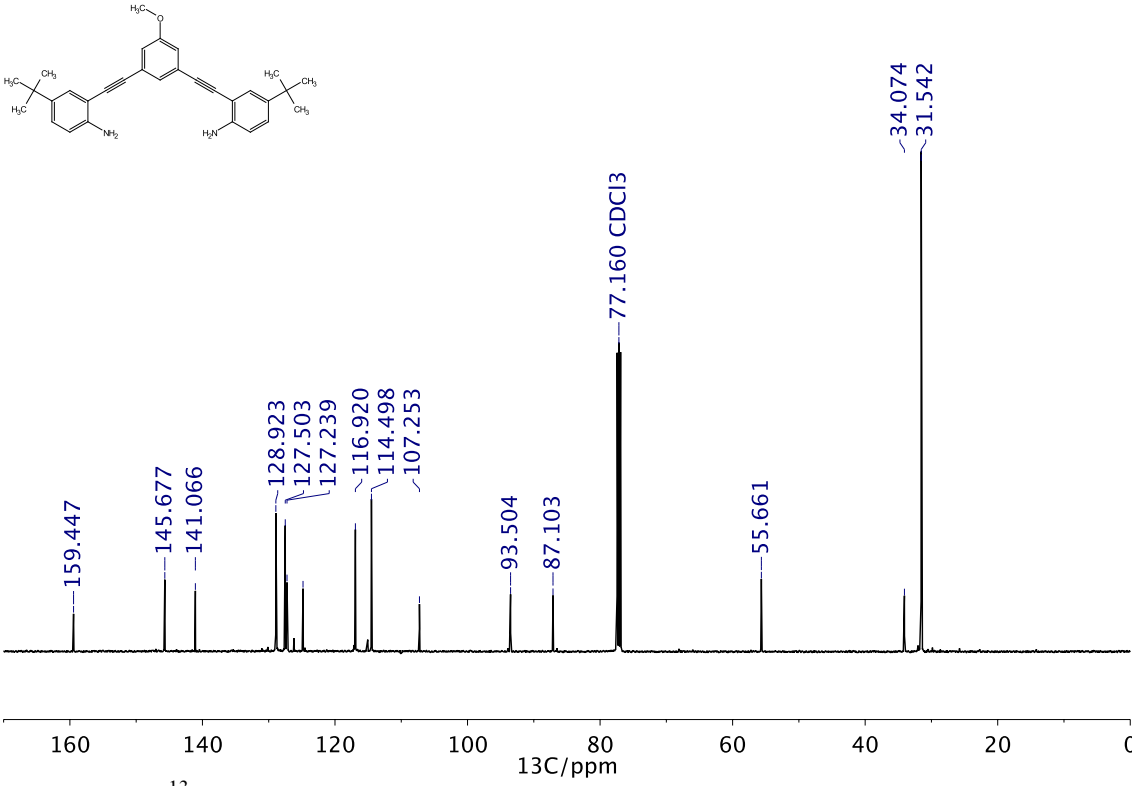

Figure S64. ^{13}C NMR spectrum of **2f** in $CDCl_3$.

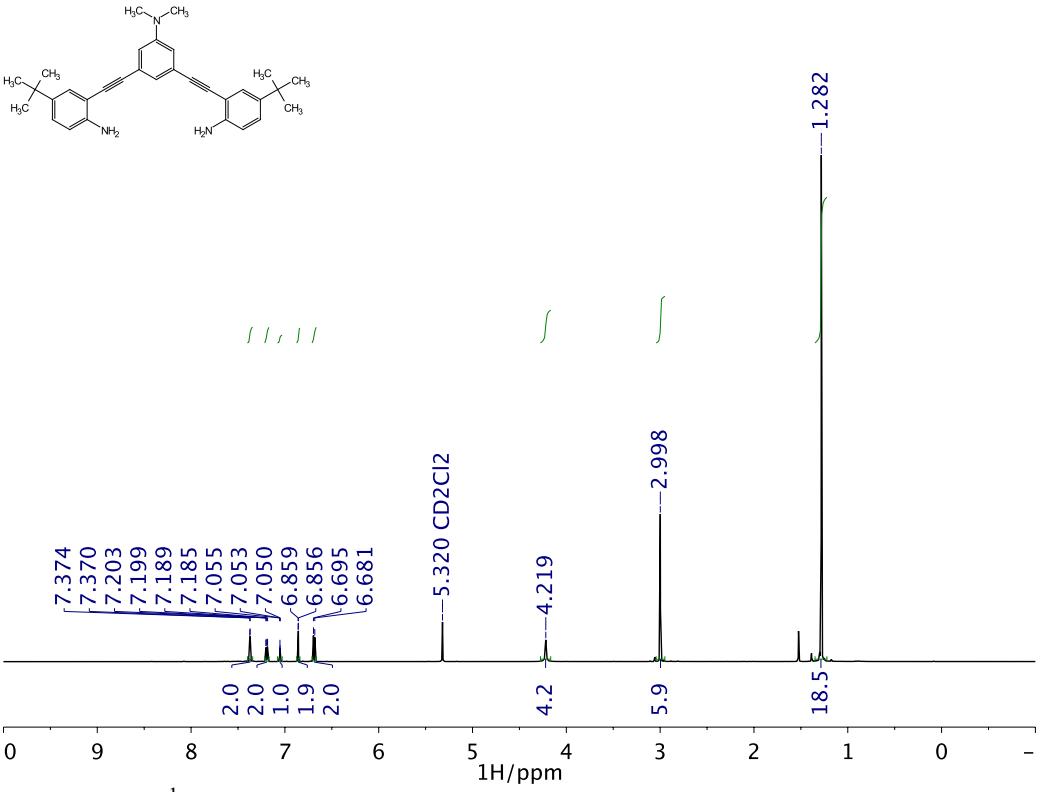

Figure S65. ^{1}H NMR spectrum of **2g** in CD_2Cl_2.

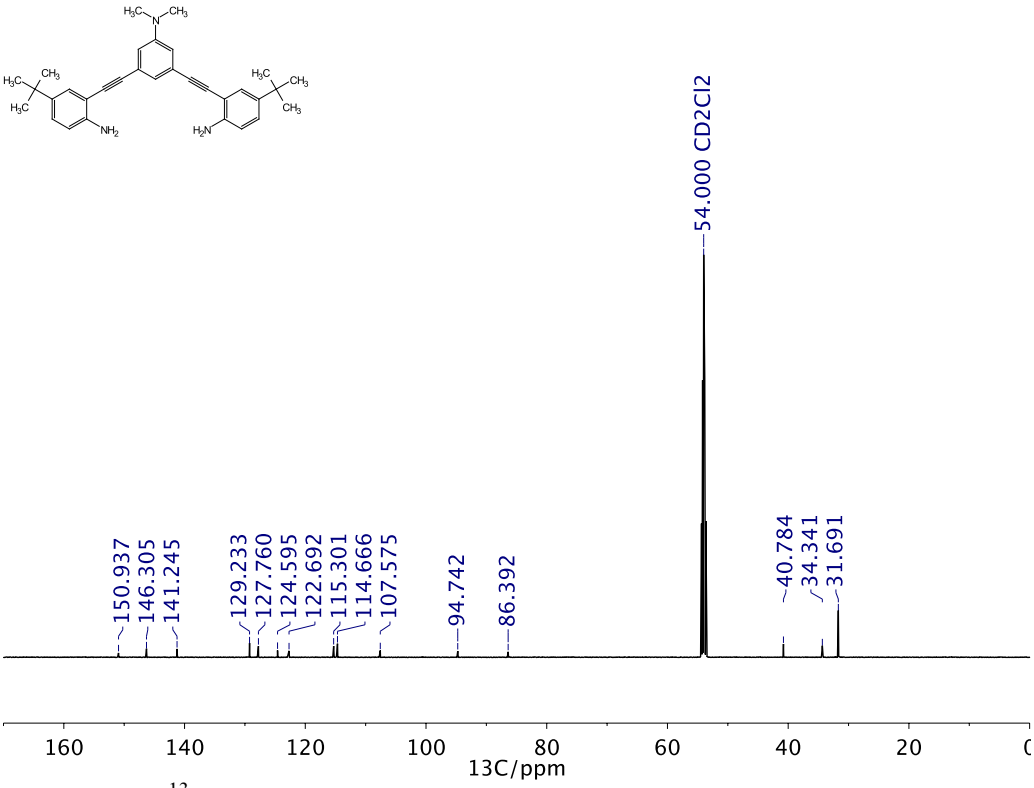

Figure S66. ^{13}C NMR spectrum of **2g** in CD_2Cl_2.

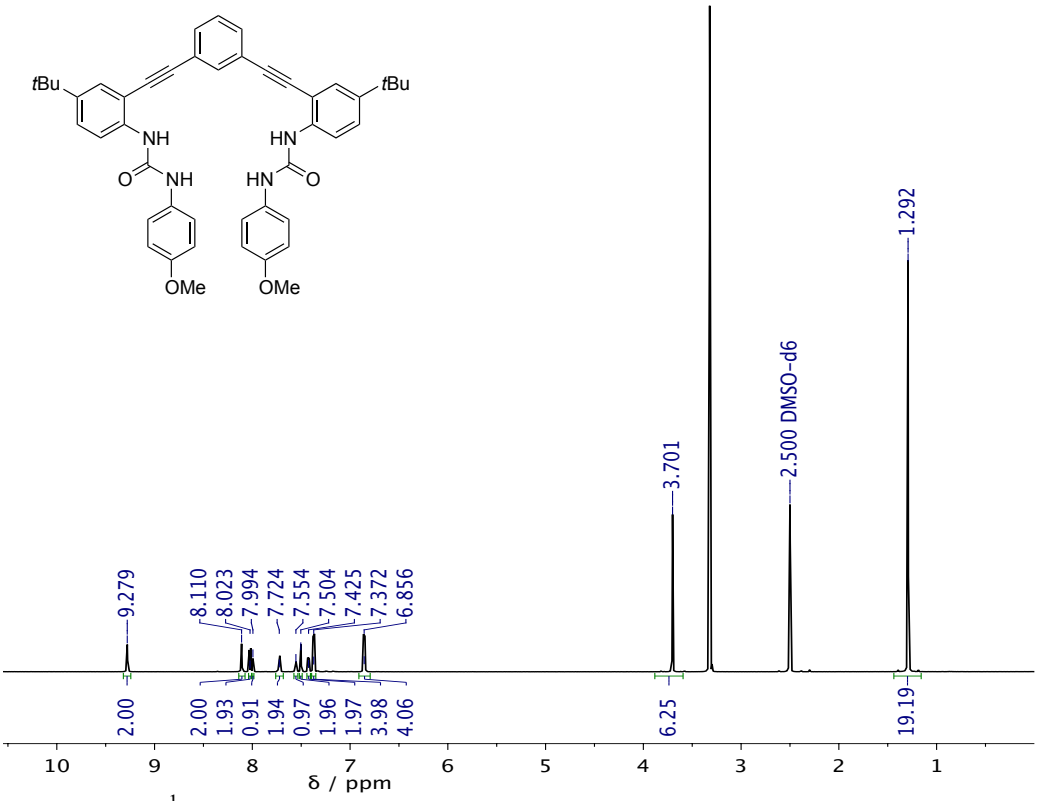

Figure S67. ^{1}H NMR spectrum of **1a** in DMSO–d_6.

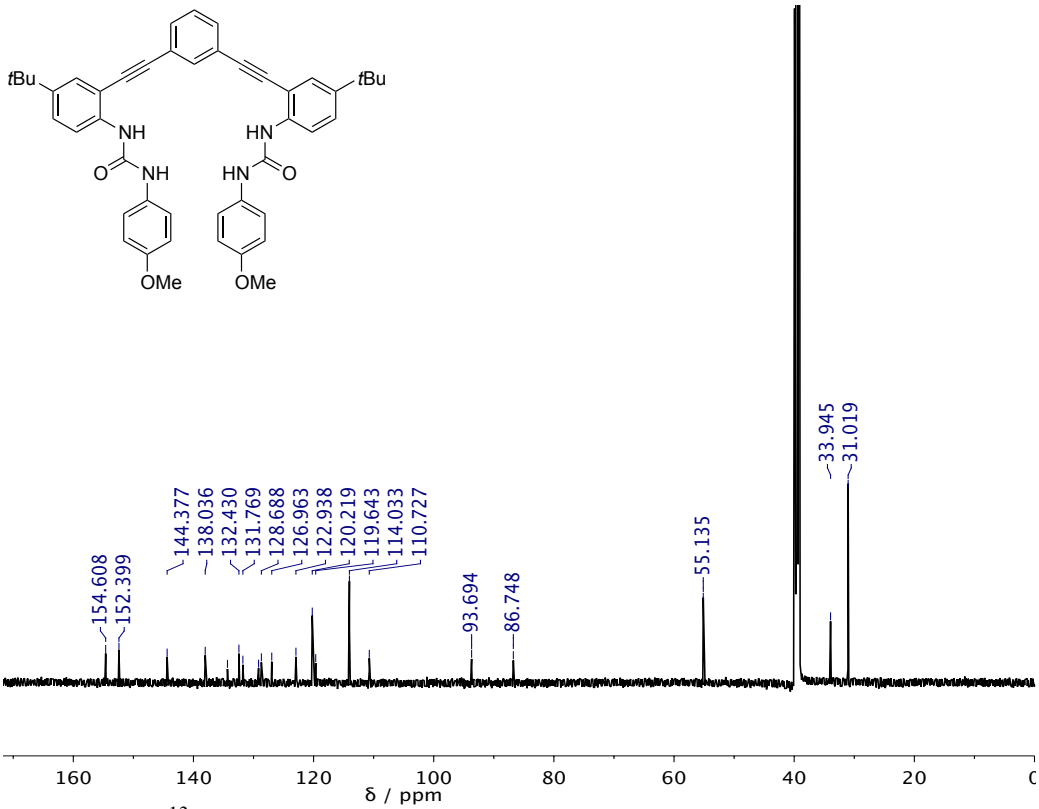

Figure S68. ^{13}C NMR spectrum of **1a** in DMSO–d_6.

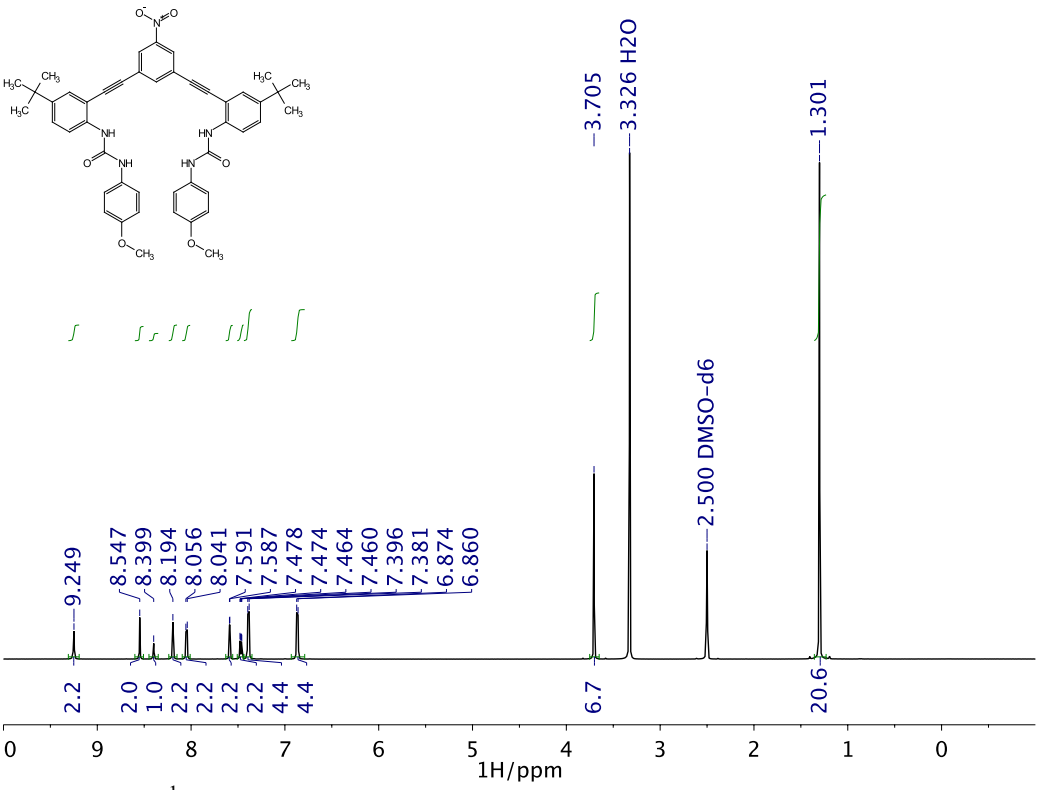

Figure S69. ^{1}H NMR spectrum of **1b** in DMSO–d_6.

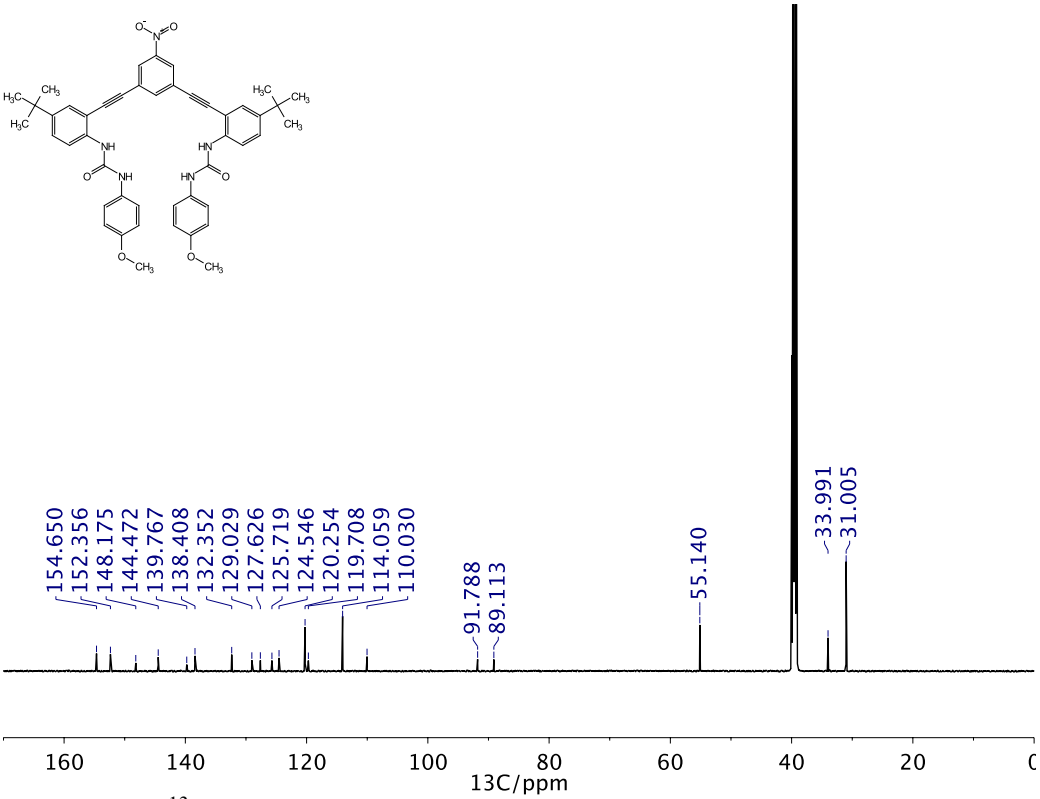

Figure S70. ^{13}C NMR spectrum of **1b** in DMSO–d_6.

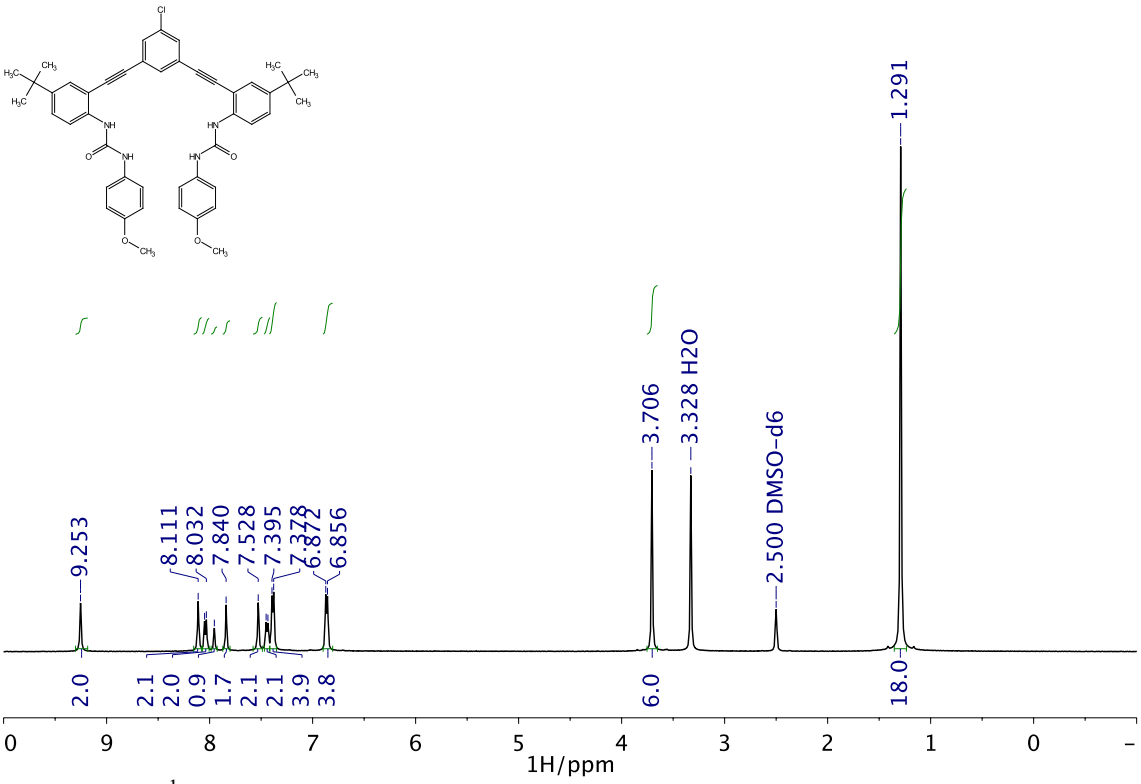

Figure S71. ^{1}H NMR spectrum of **1c** in DMSO–d_6.

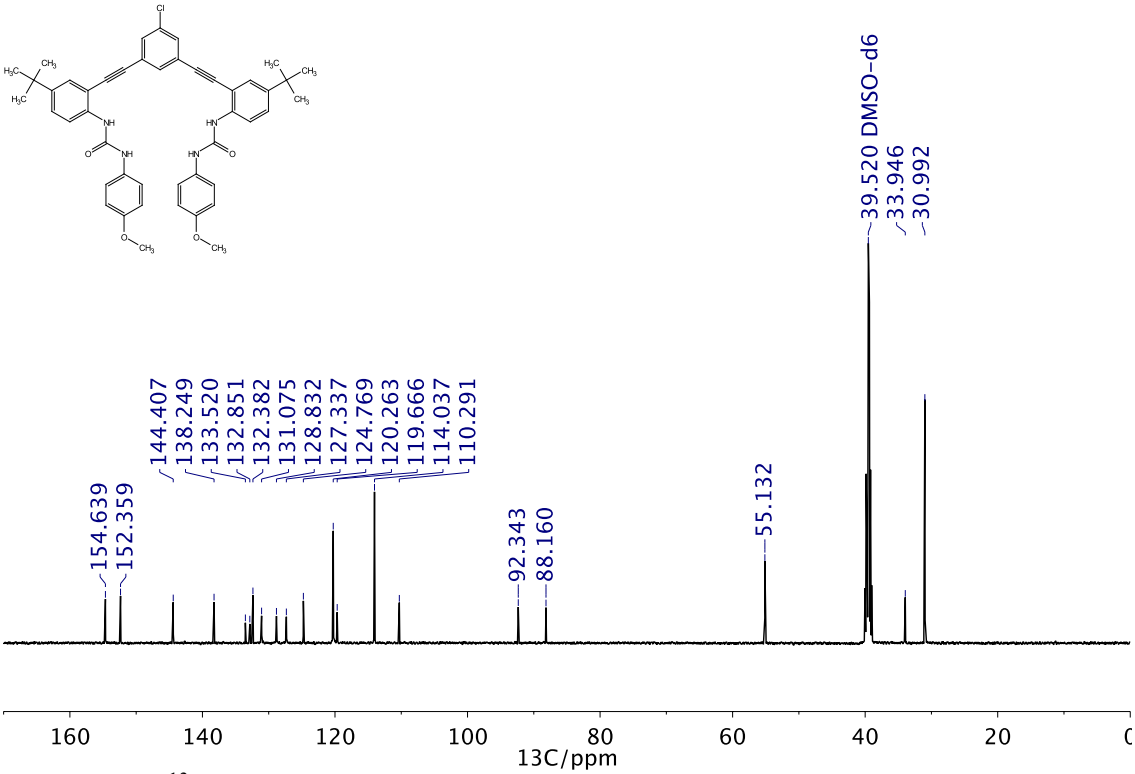

Figure S72. ^{13}C NMR spectrum of **1c** in DMSO–d_6.

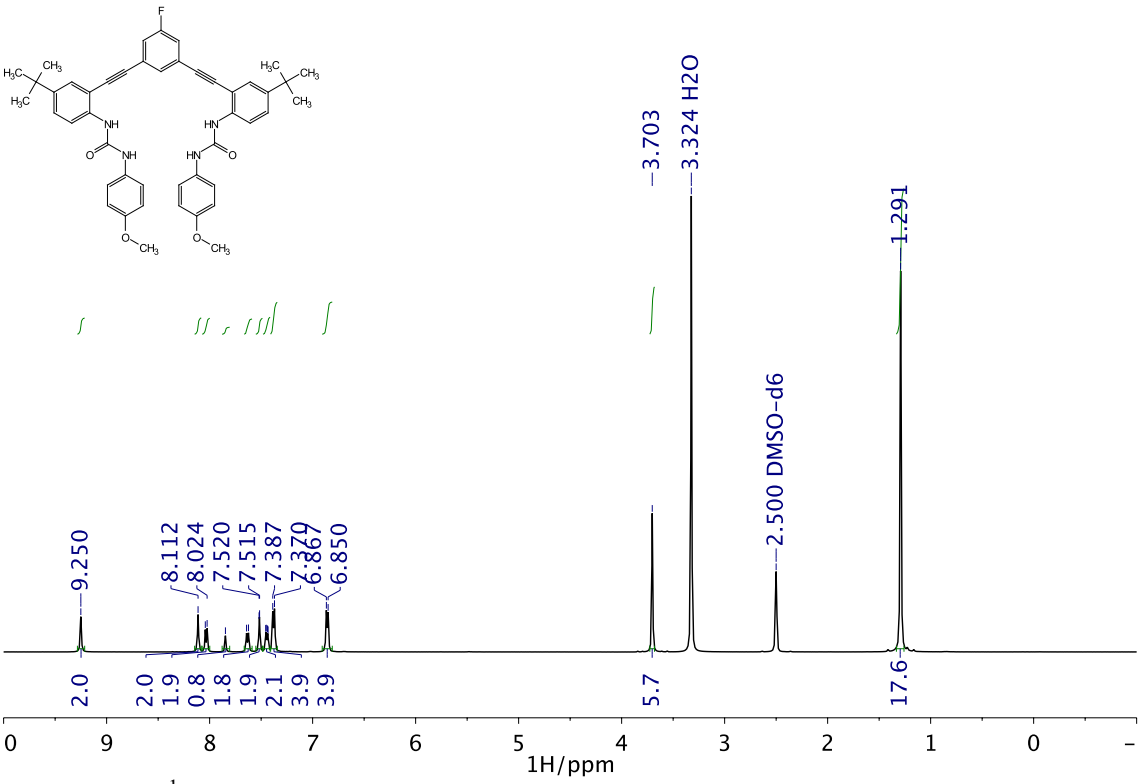

Figure S73. ^{1}H NMR spectrum of **1d** in DMSO–d_6.

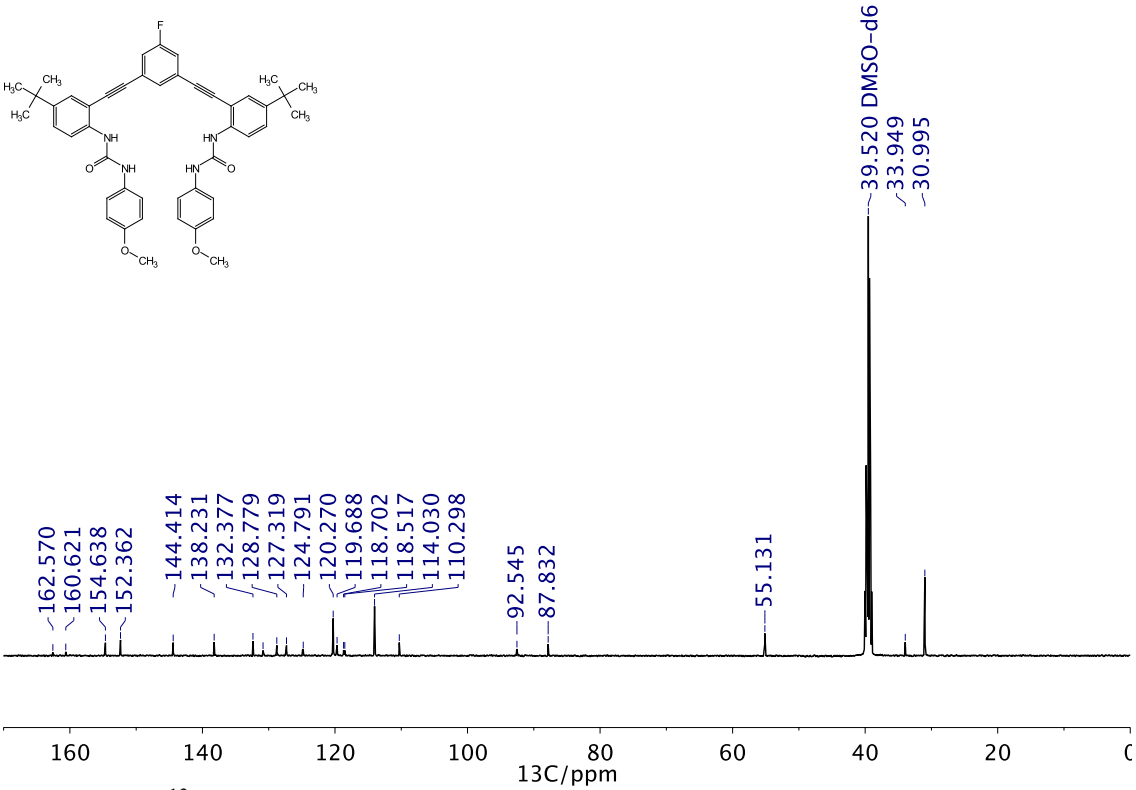

Figure S74. ^{13}C NMR spectrum of **1d** in DMSO–d_6.

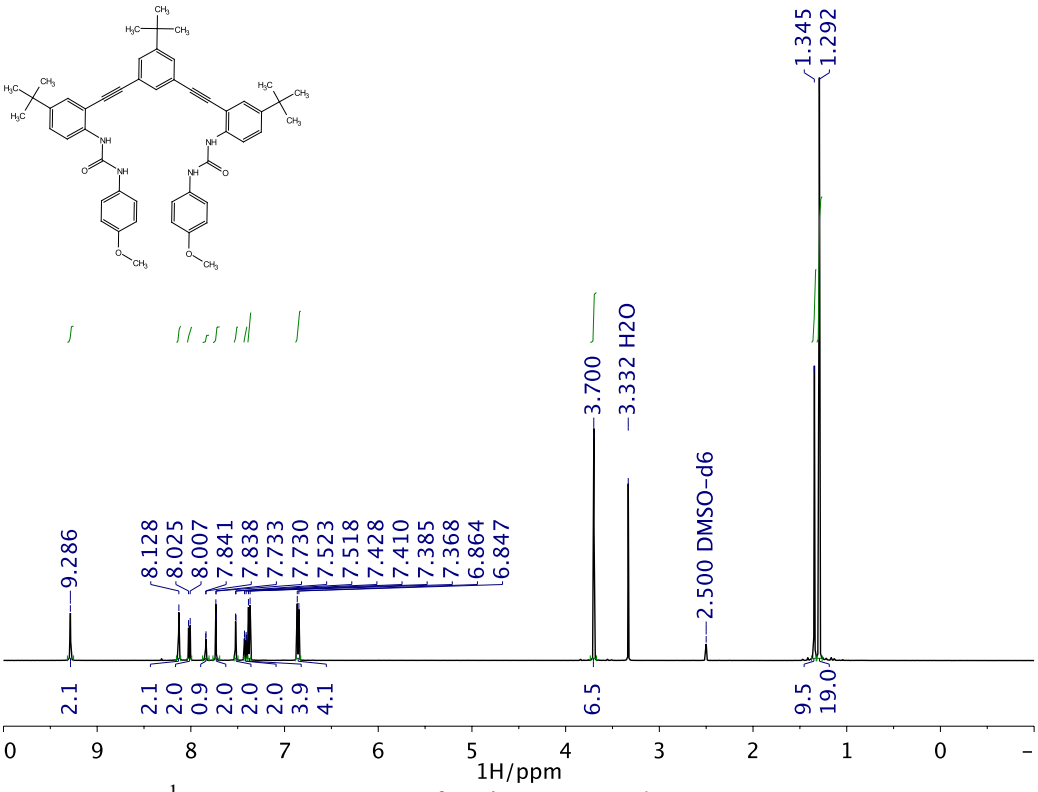

Figure S75. ^{1}H NMR spectrum of **1e** in DMSO–d_6.

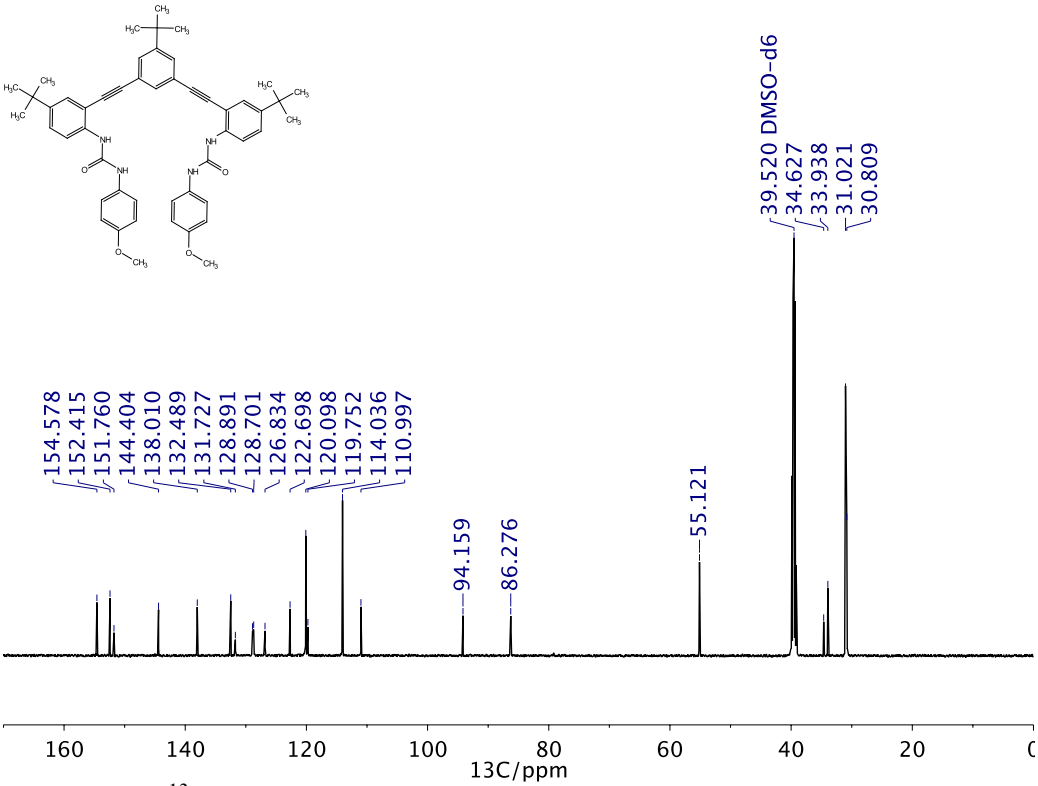

Figure S76. ^{13}C NMR spectrum of **1e** in DMSO–d_6.

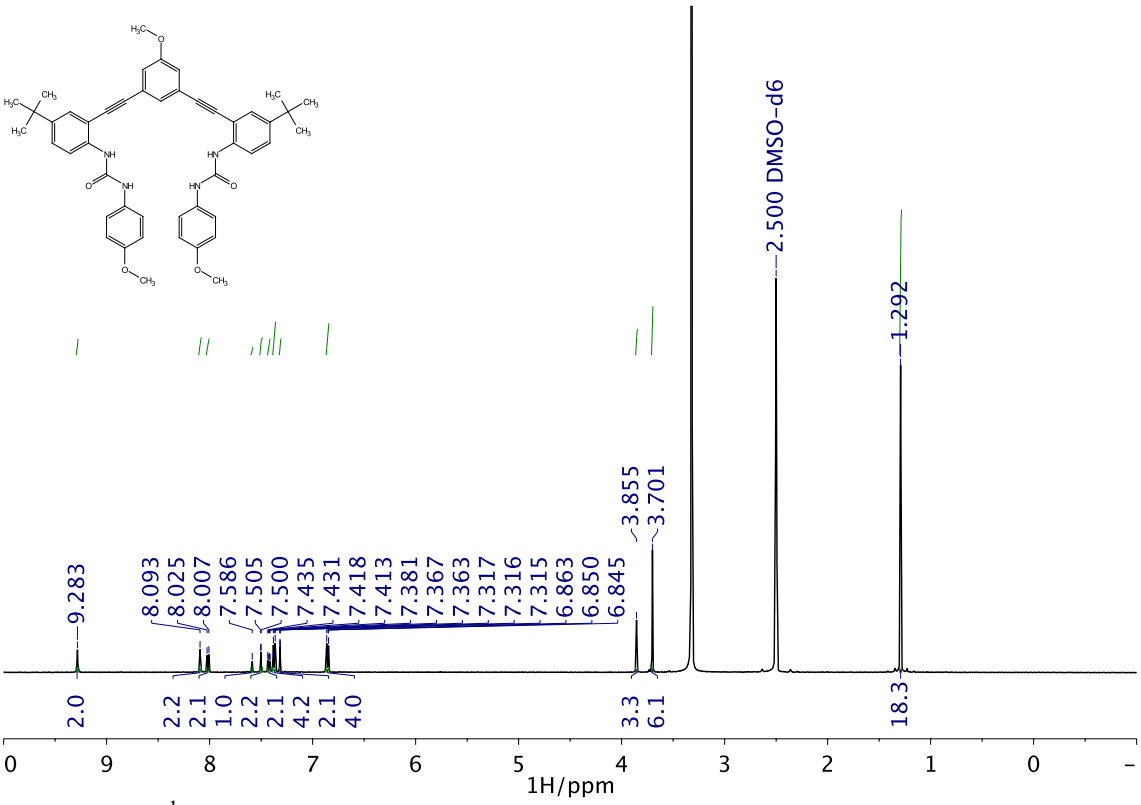

Figure S77. ^{1}H NMR spectrum of **1f** in DMSO–d_6.

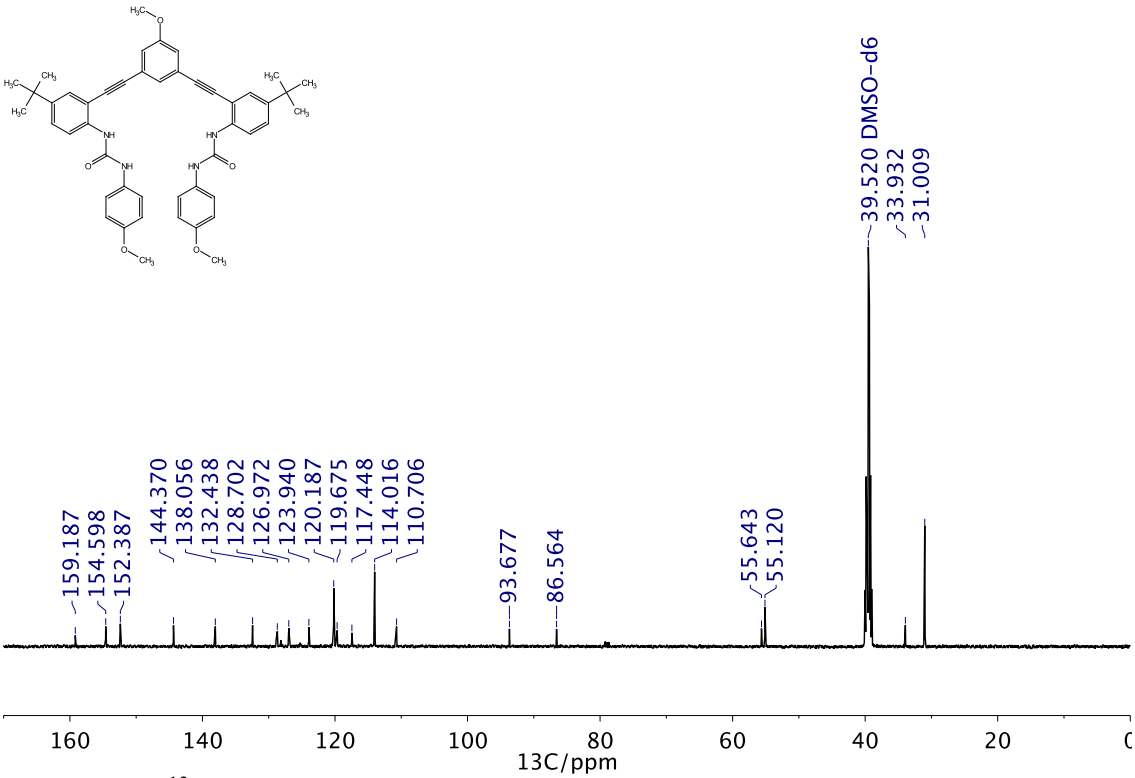

Figure S78. ^{13}C NMR spectrum of **1f** in DMSO–d_6.

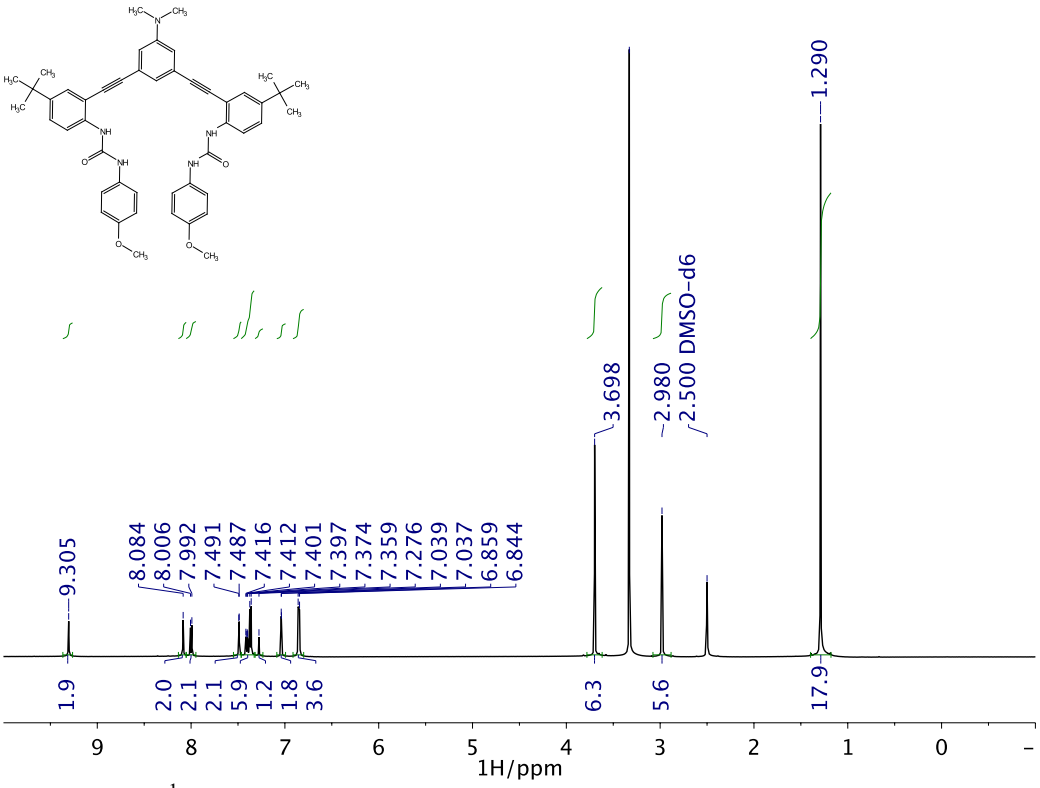

Figure S79. ^{1}H NMR spectrum of **1g** in DMSO–d_6.

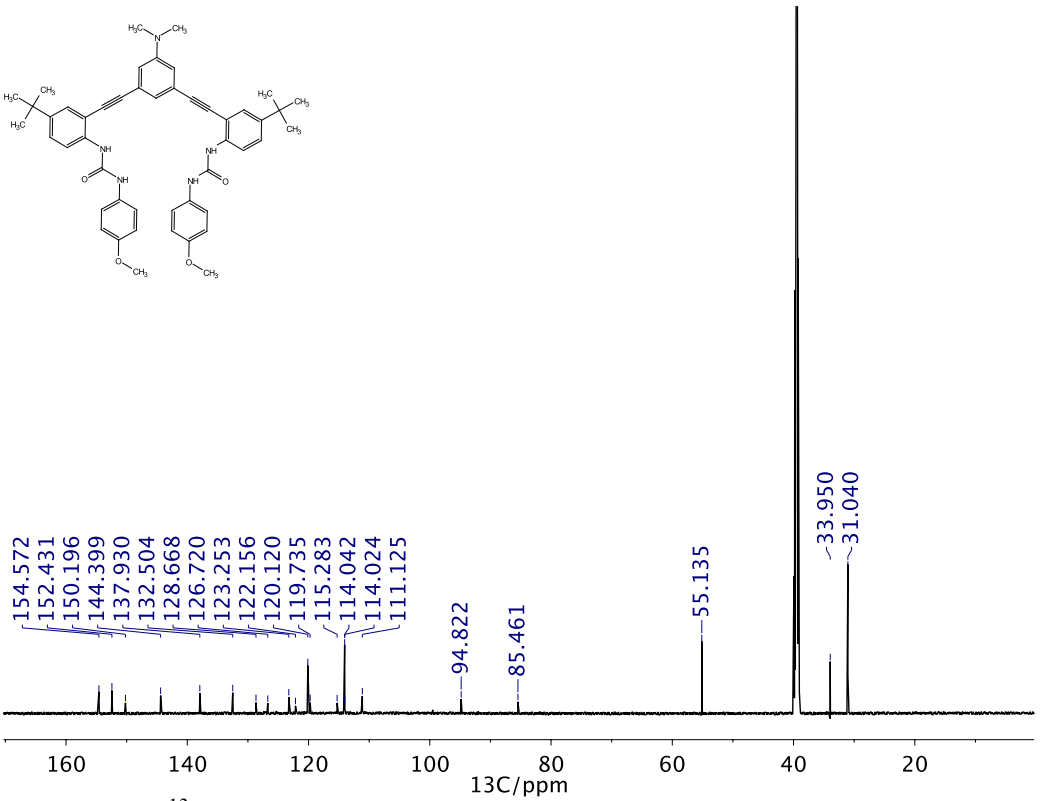

Figure S80. ^{13}C NMR spectrum of **1g** in DMSO–d_6.