Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information:

Methanesulfonyl-Polarized Halogen Bonding Enables Strong Halide Recognition in an Arylethynyl Anion Receptor

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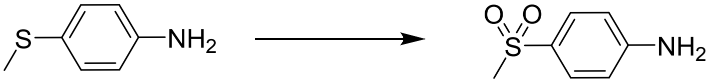
S1 Experimental Procedures

General Procedures. ^{1}H and ^{13}C NMR spectra were obtained on a Varian 500 MHz spectrometer (^{1}H 500.10 MHz, ^{13}C 125.75 MHz). ^{1}H and ^{13}C NMR chemical shifts (δ) are reported in parts per million (ppm) and referenced to residual solvent resonances ($CDCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.16 ppm; $(CD_3)_2CO$: ^{1}H 2.05 ppm, ^{13}C 29.84 ppm & 206.26 ppm; DMSO-d_6: ^{1}H 2.50 ppm, ^{13}C 39.52 ppm). Masses for new compounds were determined with a Waters Xevo G2-XS ToF spectrometer. Compoumd UV-Vis spectra were recorded on an Agilent Carey 100 UV-Vis spectrophotometer. Additional details regarding UV-Vis titrations are provided in Section 2. Spectroscopic data were collected in DMSO-1.5±0.5 wt% water.[1] Unless otherwise specified, all reagents were purchased and used as received. Tetrabutylammonium salts were dried under vacuum for 24 h.

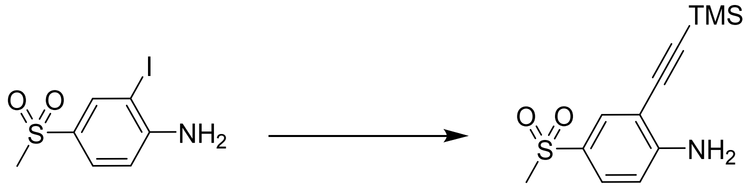
Synthesis



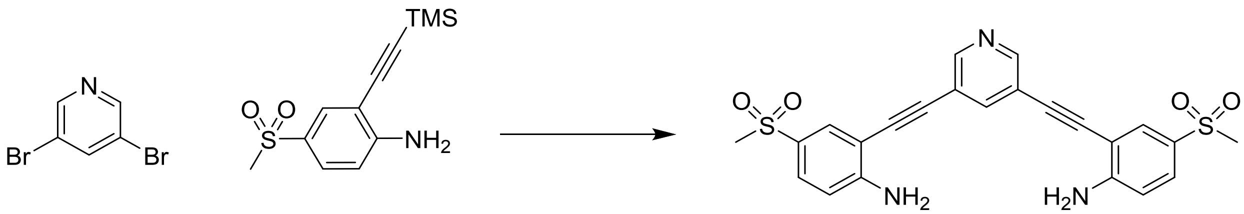
4-(Methanesulfonyl)aniline. To a solution of 4-(methylthio)benzenamine (4.48 g, 32.2 mmol) in MeOH (70 mL) was added ZnCl (0.451 g, 3.22 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (1.2 mL, 8.04 mmol). 30% H_2O_2 solution (20 mL) was slowly added, then the reaction was refluxed for 8 h. After cooling to room temperature, the solution was diluted with H_2O (60 mL) and the product was extracted with CH_2Cl_2 (4x). The combined organics were dried ($MgSO_4$), filtered and concentrated to give the desired sulfone (3.15 g, 57%) whose spectral data matched that previously reported.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, J = 8.0 Hz, 2H), 6.64 (d, J = 8.0 Hz, 2H), 3.63 (s, 2H), 2.41 (s, 3H).

2-Iodo-4-(methanesulfonyl)aniline (2). To a solution of 4-(methanesulfonyl)aniline (3.15 g, 18.4 mmol) in MeOH (60 mL) was added a mixture of KI (2.05 g, 12.3 mmol) and KIO_3 (1.38 g, 6.45 mmol) in deionized water (100 mL). HCl (1M, 20.3 mL) was slowly added dropwise over 30 min as the solution turned dark red. The reaction was then stirred overnight at room temperature. The product was extracted

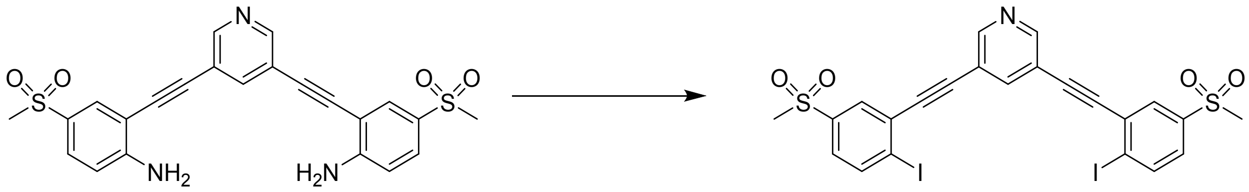
EtOAc (4x) and the combined organic layers were washed twice each with sat. $Na_2S_2O_3$ solution, water and brine, and then dried ($MgSO_4$). The crude product was purified by column chromatography (5:1 CH_2Cl_2:EtOAc) to afford **1** (2.72 g, 50%) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 4.68 (s, 2H), 3.02 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.24, 138.69, 130.21, 128.97, 113.35, 81.98, 45.02; HRMS (TOF-MS-ES+) for $C_7H_9INO_2S$ $[M+H]^+$: calcd 297.9399, found 297.9429.



4-(Methanesulfonyl)-2-((trimethylsilyl)ethynyl)aniline (3). Iodoaniline **2** (2.48 g, 8.33 mmol) was dissolved in a degassed solution of THF (30 mL) and *i*-Pr_2NH (30 mL) under N_2. CuI (71.2 mg, 0.333 mmol), $Pd(PPh_3)_2Cl_2$ (111 mg, 0.167 mmol), and (trimethylsilyl)acetylene (TMSA, 4.6 mL, 33.3 mmol) were added to the solution and the reaction was then stirred at 50 °C under N_2 for 12 h. After cooling the solvent was removed *in vacuo*. The resultant solid was dissolved in minimal CH_2Cl_2 and then purified through a silica plug to yield **2** (1.31 g, 59%) as a brown solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 4.78 (s, 2H), 2.99 (s, 3H), 0.27 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.06, 132.35, 128.89, 128.32, 113.36, 107.52, 102.02, 99.21, 44.80, –0.17; HRMS (TOF-MS-ES+) for $C_{12}H_{18}NO_2SSi$ $[M+H]^+$: calcd 268.0828, found 268.0847.

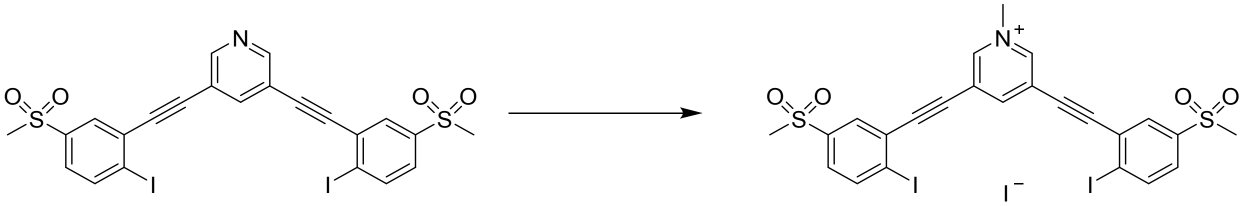


Bis-aniline 4. Ethynylaniline **3** (1.305 g, 4.87 mmol) was dissolved in a solution of THF (20 mL) and MeOH (20 mL) with 5 equiv. of K_2CO_3 (3.37 g, 24.4 mmol) was added and the mixture was stirred for 1 h. The solvent was removed *in vacuo* then the residue was redissolved in CH_2Cl_2. The organic solution was washed twice with water and with brine, dried ($MgSO_4$), then concentrated *in vacuo*. The deprotected residue was dissolved in a degassed solution of THF (25 mL) and *i*-Pr_2NH (25 mL) under N_2. A solution of 3,5-dibromopyridine (417 mg, 1.77 mmol), CuI (64.2 mg, 0.4 mmol), $Pd(PPh_3)_4$ (217 mg, 0.188 mmol) in degassed THF (30 mL) and *i*-Pr_2NH (30 mL) was prepared under N_2 to which the deprotected aniline was added via cannula. The reaction was heated at 50 °C and stirred for 12 h. After cooling the solvent was removed *in vacuo*. The resultant solid was dissolved in minimal CH_2Cl_2 and then purified through a silica plug eluting with EtOAc as well to remove impurities. The desired product was removed from the plug using with acetone and concentrated *in vacuo* to yield **3** (863 mg, 60%) as a yellow solid. ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 8.79 (s, 2H), 8.26 (s, 1H), 7.85 (s, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.21 (s, 4H), 3.05 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.53, 151.63, 141.13, 133.26, 130.45, 129.16, 120.69, 114.64, 105.96, 91.92, 89.37, 44.88; HRMS (TOF-MS-ES+) for $C_{23}H_{20}N_3O_4S_2$ $[M+H]^+$: calcd 466.0895, found 466.0923.

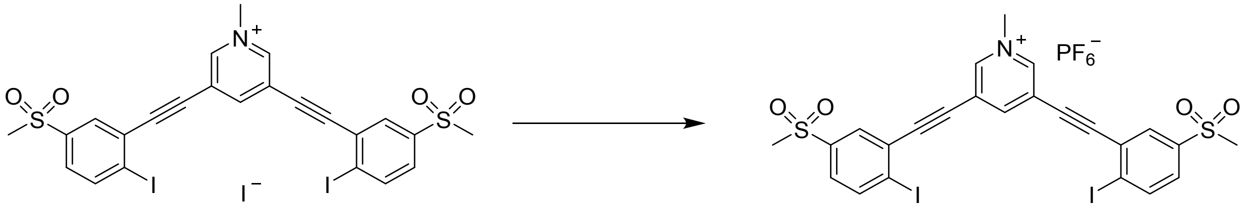


Diiodide 5. Bis-aniline **4** (863 mg, 1.85 mmol) was dissolved in CH_3CN (7 mL) and concentrated HCl (5 mL) was added to the solution. After cooling to 0 ºC, a solution of $NaNO_2$ (549 mg, 7.95 mmol) in CH_3CN (5 mL) and H_2O (15 mL) was added dropwise to the dianiline solution, which was stirred at room temperature for 1 h. The reaction was then transferred to a 0 °C solution of KI (1.539 g, 9.27 mmol) in H_2O (50 mL) and CH_3CN (10 mL) and the mixture stirred overnight allowing to return to room temperature. The product was extracted with CH_2Cl_2 (4x) then washed twice each with a saturated $Na_2S_2O_3$ solution, H_2O, and brine. After drying ($MgSO_4$), the solution was purified though a silica plug to yield **4** (376 mg, 30%) as an off white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 2H), 8.15 (d, *J* = 8.4 Hz, 2H), 8.09 (s, 2H), 8.06 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 3.09 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.84, 141.02, 140.91,

140.29, 131.16, 130.77, 128.01, 119.38, 108.21, 93.94, 90.86, 44.62; HRMS (TOF-MS-ES+) for $C_{23}H_{16}I_2NO_4S_2$ $[M+H]^+$: calcd 687.8610, found 687.8631.



Compound 1·I. Diiodide **5** (166 mg, 0.242 mmol) was added to an N_2-purged bomb flask containing excess iodomethane (5 mL). The flask was seal, then heated to 100 °C, and stirred for 10 h. After cooling to room temperature, the yellow precipitate was collected by filtration, washed with CH_2Cl_2, then dried under vacuum to yield **1·I** (200 mg, 99.7%) as a bright yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.45 (s, 2H), 9.04 (s, 1H), 8.34 (d, *J* = 8.1 Hz, 2H), 8.20 (s, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 4.40 (s, 3H), 3.32 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.83, 147.52, 141.21, 140.32, 131.43, 129.34, 127.96, 122.03, 108.44, 96.83, 86.24, 48.58, 43.25; HRMS (TOF-MS-ES+) for $C_{24}H_{18}I_3NO_4S_2$ $[M+H]^+$: calcd 829.7890, found 829.7834.



Receptor 1·PF₆. Compound **1·I** (24.8 mg, 0.0293 mmol) was dissolved in acetone (40 mL) and deionized H_2O (15 mL). $AgPF_6$ (18.8 mg, 0.0746 mmol) was added and the solution was then stirred at room temperature for 30 min over which time a gray precipitate formed. The precipitate was filtered off and the filtrate was concentrated *in vacuo* to remove the acetone, which allowed **1·PF₆** to precipitate out of the remaining water as a white solid. The white solid was filtered and washed with deionized H_2O (3 x 10 mL) and then hexanes (3 x 10 mL). The white solid was dried under vacuum to yield pure **1·PF₆** (18.6 mg, 75%). ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 9.55 (s, 2H), 9.13 (s, 1H), 8.36 (d, *J* = 8.3 Hz, 2H), 8.16 (s, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 4.79 (s, 3H), 3.23 (s, 6H); ^{13}C NMR (126 MHz, $(CD_3)_2CO$) δ 148.89, 148.02, 142.69, 141.25, 132.33, 130.28, 129.18, 124.29, 107.31, 98.21, 86.46, 49.81, 43.82.

S2. Titrations

General Titration Procedures. A stock solution of **1·PF$_6$** (0.1 mM) was prepared in DMSO-1.4 wt% water and sonicated for 1 minute. The stock solution was then used to prepare experimental host solutions at 30 ± 0.1 µM of which 1.75 mL was transferred to a septum sealed cuvette. To maintain a constant host concentration, remaining experimental host solution was then used to dissolve NBu_4X salts which were prepared in septa-sealed vials. Aliquots of NBu_4X were added to the host cuvette with a gas-tight syringe, and a spectrum was recorded after each addition. Binding constants were determined by non-linear regression fit to a 1:1 model using the Bindfit binding program.[3] Titrations with each anion were performed in triplicate and the average of the resulting binding constants were reported with under 15% error.

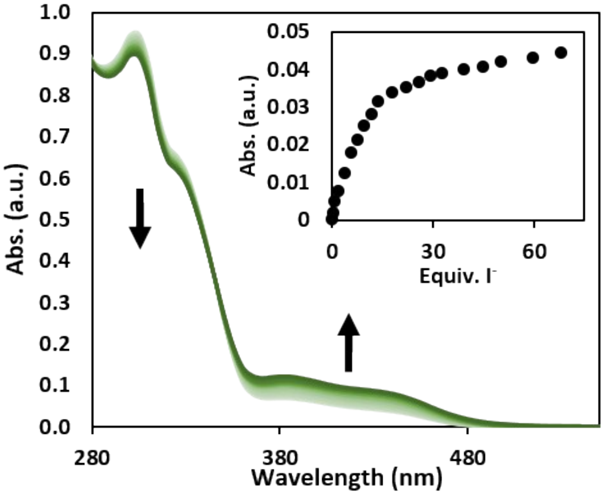


Fig. S1. UV-Vis spectroscopic titration of **1·PF$_6$** with TBA^+I^- in wet DMSO (1.4% water w/w) at a concentration of 30 µM. Inset shows the absorption binding isotherm upon addition of TBA^+I^- at 430 nm).

Table S1. Calculated association constants (K_a) for **1·PF$_6$** in DMSO (1.4% water w/w) obtained by fitting to a 1:1 host-guest model in Bindfit. Error is less than ±15%.[54]

Guest	K_a (M^{-1})[a]
Cl$^-$	940
Br$^-$	690
I$^-$	3900

UV-Vis Titration of I$^-$ with 1·PF$_6$

Table 2S. Titration of **1·PF$_6$** with I$^-$. (Stock [I$^-$] = 5.0 ± 0.2 mM)

	Guest Added (µL)	Equiv. Guest	Host Conc [M]	Guest Conc [M]	Abs at 430nm	Abs at 380nm	Abs at 414nm
1	0	0.00	2.96E-05	0.00E+00	0.036070	0.060334	0.041649
2	5	0.50	2.96E-05	1.51E-05	0.036676	0.061389	0.042183
3	10	1.00	2.96E-05	3.01E-05	0.039053	0.064685	0.045038
4	20	1.99	2.96E-05	5.99E-05	0.043239	0.069963	0.049232
5	40	3.94	2.96E-05	1.18E-04	0.047425	0.076012	0.053750
6	60	5.84	2.96E-05	1.76E-04	0.050363	0.079453	0.057026
7	80	7.71	2.96E-05	2.32E-04	0.053660	0.083928	0.060616
8	100	9.53	2.96E-05	2.86E-04	0.056323	0.086863	0.063051
9	125	11.75	2.96E-05	3.53E-04	0.059144	0.089881	0.066107
10	150	13.92	2.96E-05	4.18E-04	0.061516	0.092103	0.068279
11	200	18.08	2.96E-05	5.43E-04	0.062929	0.093400	0.069748
12	250	22.04	2.96E-05	6.62E-04	0.064585	0.095203	0.071472
13	300	25.80	2.96E-05	7.75E-04	0.065807	0.095883	0.072272
14	350	29.38	2.96E-05	8.83E-04	0.067098	0.097283	0.073663
15	400	32.80	2.96E-05	9.86E-04	0.067759	0.097173	0.074048
16	500	39.17	2.96E-05	1.18E-03	0.068250	0.098463	0.074765
17	600	45.01	2.96E-05	1.35E-03	0.069275	0.099647	0.076093
18	700	50.37	2.96E-05	1.51E-03	0.069568	0.100833	0.076376
19	900	59.87	4.70E-06	1.80E-03	0.070444	0.102412	0.076990
20	1100	68.04	5.74E-06	2.04E-03	0.071747	0.105058	0.078748

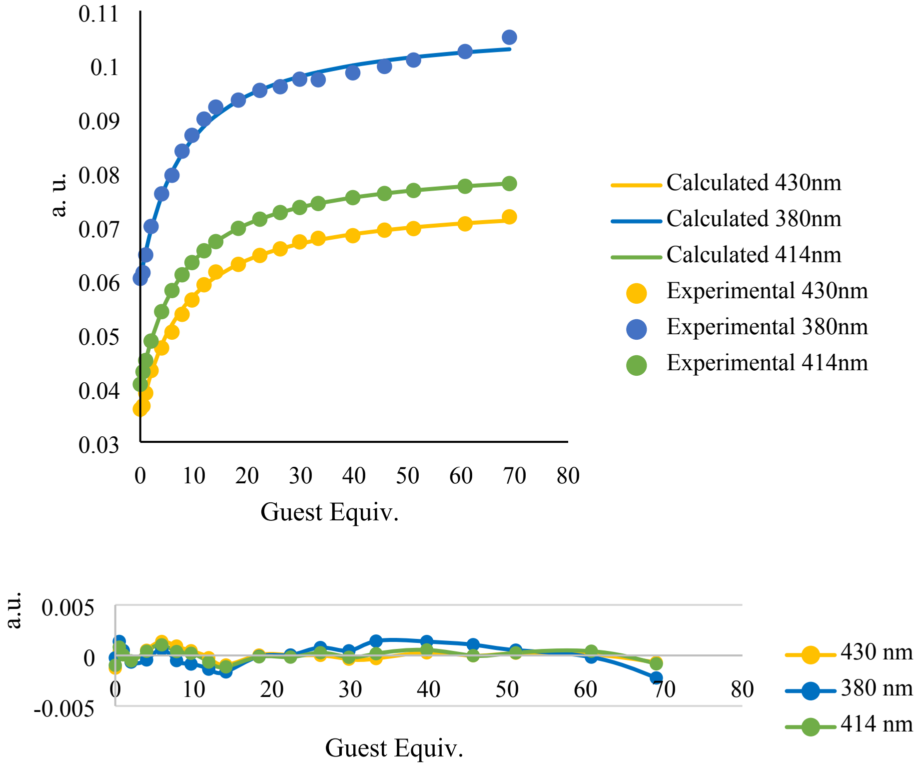


Fig. S2 Representative binding isotherm for I⁻ titration of **1·PF$_6$** in DMSO-1.4 wt% water determined by UV-Vis spectroscopy.

UV-Vis Titration of Br⁻ with 1·PF$_6$

Table S3. Titration of **1·PF$_6$** with Br⁻. (Stock [Br⁻] = 5.1 ± 0.7 mM)

	Guest Added (µL)	Equiv. Guest	Host Conc [M]	Guest Conc [M]	Abs at 430nm	Abs at 380nm	Abs at 414nm
1	0	0.00	2.96E-05	0.00E+00	0.046561	0.073172	0.052984
2	5	0.57	2.96E-05	1.69E-05	0.047132	0.073774	0.053700
3	10	1.14	2.96E-05	3.37E-05	0.048172	0.0748	0.054473
4	20	2.26	2.96E-05	6.71E-05	0.049047	0.075502	0.055346
5	40	4.48	2.96E-05	1.33E-04	0.051469	0.078229	0.057868
6	60	6.64	2.96E-05	1.97E-04	0.054131	0.081509	0.060412
7	80	8.76	2.96E-05	2.59E-04	0.055564	0.083381	0.062042
8	100	10.83	2.96E-05	3.21E-04	0.057097	0.085191	0.063635
9	125	13.36	2.96E-05	3.96E-04	0.058981	0.087514	0.065643
10	150	15.82	2.96E-05	4.69E-04	0.060908	0.089861	0.067461

11	200	20.55	2.96E-05	6.09E-04	0.063129	0.092288	0.069840
12	250	25.04	2.96E-05	7.42E-04	0.065631	0.094813	0.072298
13	300	29.32	2.96E-05	8.69E-04	0.067444	0.096967	0.074137
14	350	33.39	2.96E-05	9.89E-04	0.069428	0.099662	0.076310
15	400	37.27	2.96E-05	1.10E-03	0.070554	0.101284	0.077205
16	500	44.52	2.96E-05	1.32E-03	0.072513	0.104910	0.079745
17	600	51.15	2.96E-05	1.52E-03	0.074517	0.108016	0.081932
18	700	57.24	2.96E-05	1.70E-03	0.076821	0.111062	0.084230
19	900	68.04	2.96E-05	2.02E-03	0.078521	0.114307	0.086145
20	1100	77.33	2.96E-05	2.74E-03	0.080512	0.117874	0.088661

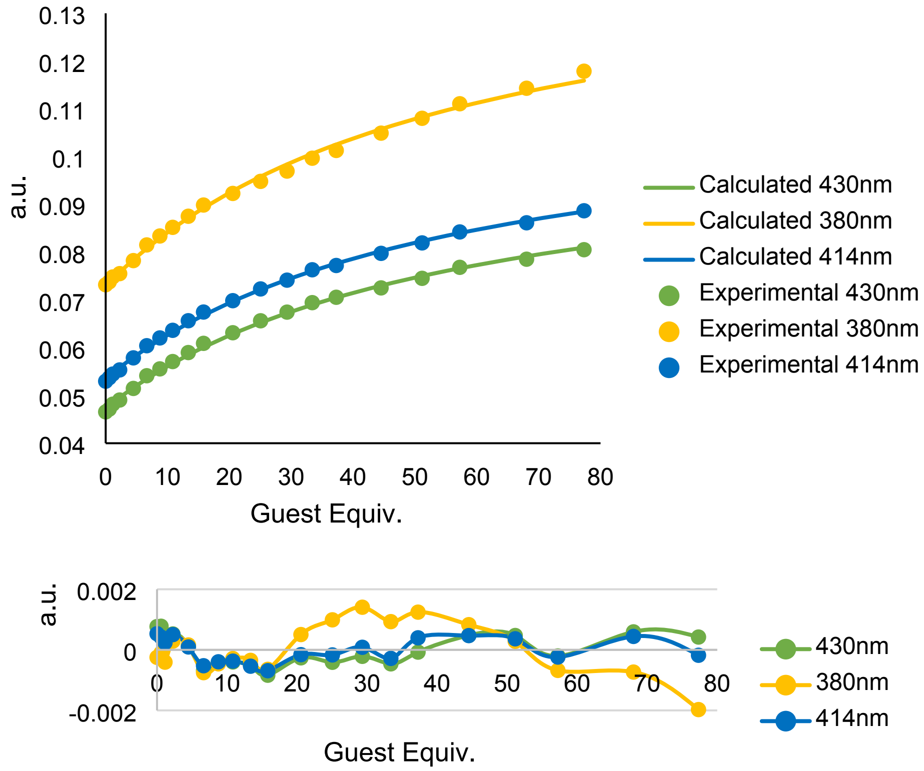


Fig. S3 Representative binding isotherm for Br⁻ titration of **1·PF$_6$** in DMSO-1.4 wt% water determined by UV-Vis spectroscopy.

UV-Vis Titration of Cl⁻ with 1·PF$_6$

Table S4. Titration of **1·PF$_6$** with Cl⁻. (Stock [Cl⁻] = 5.0 ± 1.0 mM)

	Guest Added (μL)	Equiv. Guest	Host Conc [M]	Guest Conc [M]	Abs at 430nm	Abs at 380nm	Abs at 414nm
1	0	0.00	2.96E-05	0.00E+00	0.047583	0.059292	0.049926

2	5	0.46	2.96E-05	1.35E-05	0.048717	0.060809	0.050813
3	10	0.91	2.96E-05	2.69E-05	0.049710	0.061000	0.051383
4	20	1.80	2.96E-05	5.35E-05	0.050999	0.062343	0.052381
5	40	3.57	2.96E-05	1.06E-04	0.053042	0.064519	0.054489
6	60	5.29	2.96E-05	1.57E-04	0.054029	0.065232	0.055247
7	80	6.98	2.96E-05	2.07E-04	0.055211	0.066604	0.057027
8	100	8.63	2.96E-05	2.56E-04	0.057021	0.069085	0.058683
9	125	10.65	2.96E-05	3.15E-04	0.058143	0.070495	0.059819
10	150	12.61	2.96E-05	3.74E-04	0.060231	0.072777	0.061763
11	200	16.38	2.96E-05	4.85E-04	0.060864	0.073135	0.062298
12	250	19.97	2.96E-05	5.91E-04	0.061986	0.074720	0.063737
13	300	23.37	2.96E-05	6.92E-04	0.063037	0.076083	0.064809
14	350	26.62	2.96E-05	7.89E-04	0.064137	0.077728	0.065924
15	400	29.72	2.96E-05	8.80E-04	0.065021	0.079145	0.067072
16	500	35.49	2.96E-05	1.05E-03	0.066267	0.081133	0.068374
17	600	40.78	2.96E-05	1.21E-03	0.067405	0.083067	0.069659
18	800	50.11	2.96E-05	1.48E-03	0.068722	0.085426	0.071280
19	900	54.25	2.96E-05	1.61E-03	0.074790	0.098192	0.078932
20	1100	61.65	2.96E-05	1.83E-03	0.077444	0.103316	0.082143

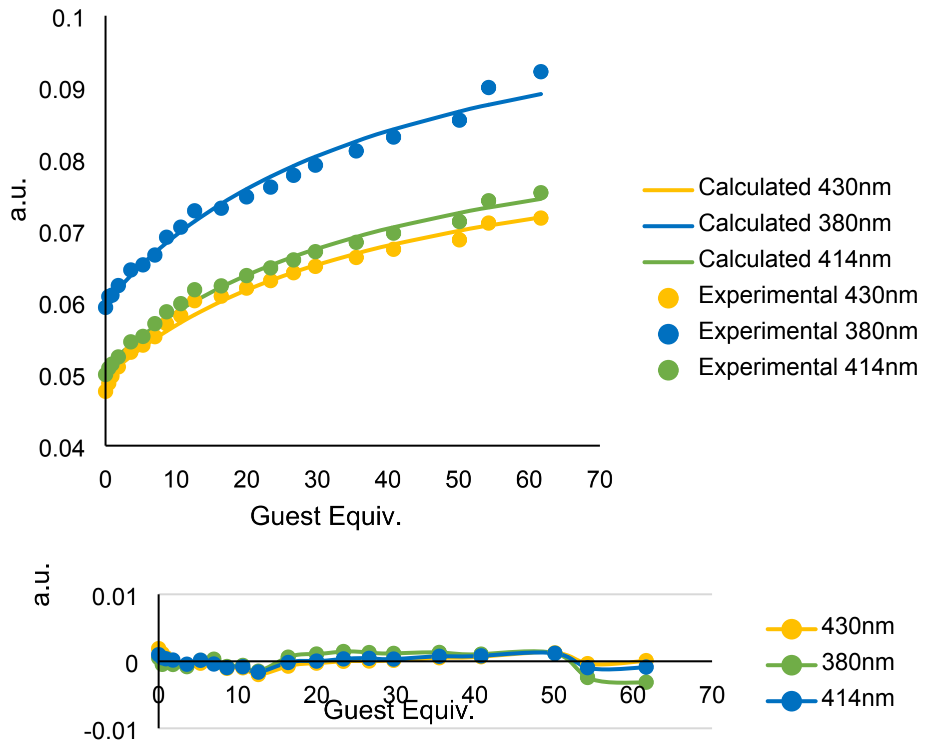


Fig. S4 Representative binding isotherm for Cl⁻ titration of **1·PF$_6$** in DMSO-1.4 wt% water determined by UV-Vis spectroscopy.

S3. X-ray Crystallography

General. Diffraction intensities for **1·PF$_6$**, **1·Cl**, **1·Br**, and **1·I** were collected at 173 K on a Bruker Apex2 DUO CCD diffractometer using CuKα radiation, λ= 1.54178 Å. Absorption corrections were applied by SADABS.[4] Space groups were determined based on intensity statistics (**1·Cl**, **1·Br, 1·I**) and systematic absences (**1·PF$_6$**). Structures were 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. H atoms were refined in calculated positions in a rigid group model. H atoms in solvent water molecule in **1·Cl** were not found and not taken into consideration. H atoms in solvent water in **1·Br** were found on the residual density map and refined with restrictions on O-H bond distances. All calculations were performed by the Bruker SHELXL-2014/7 package. [5] CCDC 1868183-1868185, 1875924 contain the supplementary crystallographic data for these compounds. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystals suitable for x-ray diffraction were grown as follows: (a) for **1·PF$_6$** through slow evaporation of the compound in acetone over time; (b) for **1·I** through slow evaporation of the compound in a MeOH/MeCN solvent mixture; (c) for **1·Cl** and **1·Br** by dissolving **1·PF$_6$** in acetone and adding 2 equiv. of TBA$^+$Cl$^-$ or TBA$^+$Br$^-$, then filtering the resulting precipitated **1·Cl** and **1·Br** salts, which were then re-dissolved in a MeOH/MeCN mixture and evaporated slowly over time.

X-ray Structure of Analysis of 1·Br. A nearly identical binding mode was observed in the crystal structure of **1·Br**. While the adopted conformation remains the same as found in **1·Cl**, the Br$^-$ is held at a distance and angle of 3.407(4) Å and 167°, respectively, owing to an 14% reduction of the ionic and van der Waals radii (Fig. S8).[6] A second Br$^-$ species is found in the molecular plane forming a hydrogen bond with a pyridinium C(H) on the side opposite to the halogen bonding at a C(H)··· Br$^-$ distance of 3.495 Å, thus balancing the complex charge between the two receptors and two anions. The second halogen bond donor is pointed inward towards the central pocked and halogen bonding with the methanesulfonyl oxygen from an adjacent receptor scaffold in the stack.

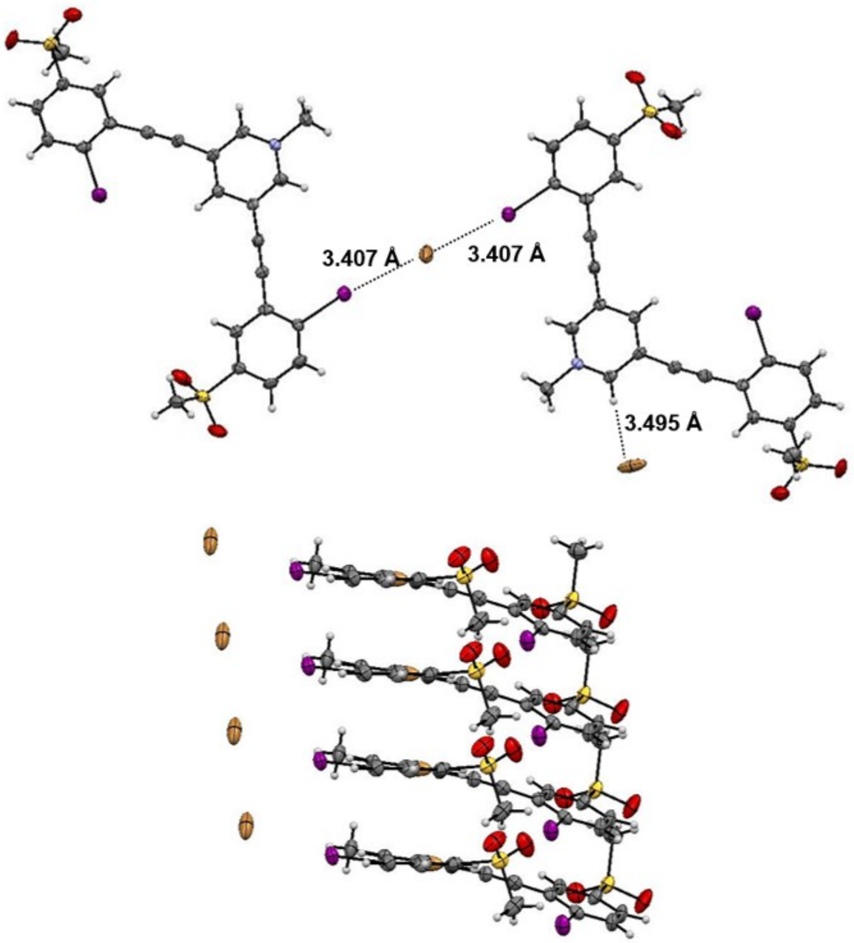


Fig. S5 ORTEP representation (50% probability ellipsoid) of the X-ray crystal structure of **1·Br**.

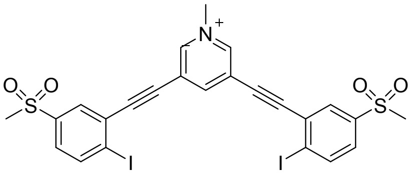
Table S5. X-ray diffraction details for **1•I**, **1•Cl**, **1•Br**, and **1•PF$_6$**.

Compound	**1·I**	**1·Cl**	**1·Br**	**1·PF$_6$**
Empirical formula	$C_{24}H_{18}I_3NO_4S_2$	$C_{24}H_{20}ClI_2NO_5S_2$	$C_{24}H_{20}BrI_2NO_5S_2$	$C_{27}H_{24}F_6I_2NO_5PS_2$
Formula weight	829.21	755.78	800.24	905.36
Temperature	173(2) K	173(2) K	173(2) K	173(2) K
Wavelength	1.54178 Å	1.54178 Å	1.54178 Å	1.54178 Å
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	P2$_1$/n
Unit cell dimensions	a = 8.5565(5) Å	a = 5.057(3) Å	a = 5.1366(3) Å	a = 15.0002(8) Å
	b = 13.3964(8) Å	b = 15.197(9) Å	b = 15.3534(7) Å	b = 8.6636(5) Å
	c = 13.6335(8) Å	c = 17.789(11) Å	c = 17.7446(9) Å	c = 25.9025(10) Å
	α = 64.031(4)°	α = 79.501(15)°	α = 78.460(3)°	α= 90°
	β= 79.229(4)°	β = 89.107(15)°	β = 89.369(4)°	β = 102.518(3)°
	γ = 86.953(4)°	γ = 85.63(2)°	γ = 86.064(4)°	γ = 90°
Volume	1379.49(15) Å^3	1340.3(14) Å^3	1367.89(12) Å^3	3286.2(3) Å^3
Z	2	2	2	4
Density (calculated)	1.996 Mg/m^3	1.873 Mg/m^3	1.943 Mg/m^3	1.830 Mg/m^3
Absorption coefficient	28.358 mm^{-1}	21.106 mm^{-1}	21.494 mm^{-1}	17.326 mm^{-1}
F(000)	784	732	768	1760
⍰ range for data collection	3.667 to 66.871°	2.526 to 67.081°	2.541 to 66.650°	3.142 to 66.712°
Reflections collected	13406	14065	15563	21649
Independent reflections	4799 [R(int) = 0.0634]	4611 [R(int) = 0.1041]	4812 [R(int) = 0.0624]	5781 [R(int) = 0.0978]
Completeness to = 66.871°	97.9%	96.6%	99.6%	99.2%
Max. and min. transmission	0.7528 and 0.4856	0.7528 and 0.4651	0.5842 and 0.3375	0.7528 and 0.5144
Data / restraints / parameters	4799 / 0 / 307	4611 / 0 / 319	4812 / 2 / 327	5781 / 0 / 397
Goodness-of-fit on F^2	1.057	1.062	1.029	1.005
Final R indices [I>2⍰(I)]	R1 = 0.0394 wR2 = 0.0973	R1 = 0.0681 wR2 = 0.1670	R1 = 0.0389 wR2 = 0.0841	R1 = 0.0636 wR2 = 0.1439
R indices (all data)	R1 = 0.0535 wR2 = 0.1037	R1 = 0.1023 wR2 = 0.1913	R1 = 0.0580 wR2 = 0.0907	R1 = 0.1026 wR2 = 0.1654
Residual e$^-$ density	0.924/–0.899	0.917/–1.294	0.732/-0.643	1.529/–1.029

S4. Computational Details

General. Receptors **1**, **5** was optimized by carrying out the DFT calculations using the B97-D3 functional[7] along with the Def2-TZVP basis set[8] in gas phase, which were performed with Gaussian 09 software package.[9] The frequency calculation was also performed on the structure to ensure no imaginary frequency. Electrostatic potential surface (ESP) was created at the B97-D3/Def2-TZVP level of theory and determined at an electron density of 0.001 electrons bohr^{-3}. The most positive V_S(r) values ($V_{S,max}$) for electrostatic potential surface energies were calculated using the Multiwfn program.[10]

Table S6 Cartesian coordinates for **1**



	X	Y	Z
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C	-1.21935095	2.39133654	0.00445153
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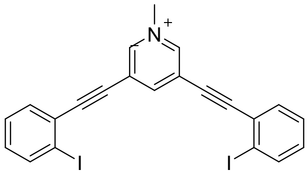
C	1.22374198	2.39877106	0.00483574
C	1.18025355	3.80074636	-0.05870542
N	-0.00444254	4.45007784	-0.08954520
C	-2.44300974	1.69895279	0.02604350
C	2.44880299	1.70869284	0.02695670
C	-3.43697616	0.99575807	0.03007039
C	3.44128022	1.00348094	0.03123757
C	-4.58838950	0.18300330	0.01556854
C	4.59040761	0.18740515	0.01702968
C	-5.86580439	0.78517831	0.01934902
C	-7.00480238	-0.00188494	-0.03029290
C	-6.91351957	-1.39535730	-0.08712520
C	-5.66182413	-2.00931781	-0.07377718
C	-4.50516499	-1.23208284	-0.02187823
C	4.50254717	-1.22743212	-0.01806177
C	5.65656374	-2.00855994	-0.06970905

C	6.91022994	-1.39868199	-0.08518167
C	7.00612067	-0.00545255	-0.03081338
C	5.86971956	0.78544922	0.01860762
I	-2.63179811	-2.20442215	-0.02012742
I	2.62592880	-2.19366207	-0.01305789
S	-8.62018594	0.79846288	-0.09467893
S	8.62415953	0.78926441	-0.09824434
C	0.01078308	5.93311156	-0.14973617
C	-9.22252359	0.63093691	1.58516603
O	-8.38813875	2.20528276	-0.35512354
O	-9.45866491	-0.00456133	-0.95885963
C	9.22710674	0.62375370	1.58159011
O	9.45925219	-0.01876904	-0.96103835
O	8.39676583	2.19621789	-0.36196502
H	-2.08321748	4.39618331	-0.08934529
H	0.00662454	0.61491424	0.08047578
H	2.07438890	4.41044201	-0.08913494
H	-5.95481163	1.86637705	0.03630773
H	-7.81512753	-1.99565767	-0.16475951
H	-5.58883461	-3.09080354	-0.11697436
H	5.58003740	-3.08986964	-0.11104214
H	7.80981539	-2.00204466	-0.16254355
H	5.96218350	1.86638942	0.03363355
H	-1.00991824	6.29479664	-0.26278342
H	0.44336532	6.32118438	0.77475131
H	0.61108317	6.24591532	-1.00585839
H	-10.21049148	1.09962416	1.59387710
H	-9.30230468	-0.42907411	1.83404149
H	-8.54403506	1.15278111	2.26278073
H	10.21660432	1.08923130	1.58849760
H	8.55079720	1.14945045	2.25840551
H	9.30357475	-0.43591613	1.83294595

Table S7 Cartesian coordinates for **1** without methanesulfonyl substituents



	X	Y	Z
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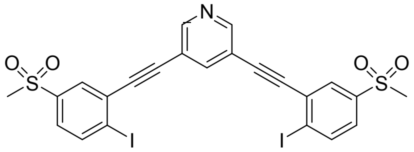
C	1.22219170	2.70212823	-0.00468481
C	-0.00026685	2.00590902	0.00550140
C	-1.22267767	2.70219970	0.01854435
C	-1.18250631	4.10745099	0.02207490
N	-0.00015346	4.75927184	0.01281708
C	2.44300556	2.00625468	-0.01469848
C	-2.44345871	2.00627265	0.02901310
C	3.41980488	1.27825563	-0.02134719
C	-3.42019519	1.27816187	0.03278422
C	4.53431602	0.41746547	-0.02890619
C	-4.53453255	0.41711202	0.03636628
C	5.84185483	0.95384551	-0.07873359
C	6.95033559	0.12063741	-0.08870561
C	6.77754716	-1.26535676	-0.04836926
C	5.49786179	-1.82234568	0.00192233
C	4.38151573	-0.99130889	0.01165137
C	-4.38142096	-0.99140983	-0.01165288
C	-5.49755608	-1.82275995	-0.00632629
C	-6.77735977	-1.26634888	0.04718589
C	-6.95044217	0.11936660	0.09507953
C	-5.84216213	0.95289102	0.08934152
I	2.45999189	-1.87305909	0.09107121
I	-2.45969773	-1.87232078	-0.09610468
C	-0.00020114	6.24152384	-0.03768847
H	2.07829816	4.71383597	-0.00882177
H	-0.00033516	0.92092422	0.00546971
H	-2.07865560	4.71393355	0.03028904
H	5.95768702	2.03299854	-0.10954764

H	7.64156803	-1.92395702	-0.05569604
H	5.37442828	-2.89961048	0.03337201
H	-5.37388704	-2.89981019	-0.04371108
H	-7.64122719	-1.92518095	0.05113422
H	-5.95825980	2.03183450	0.12595471
H	0.89240030	6.61361207	0.46493706
H	-0.00369151	6.56214127	-1.08223766
H	-0.88923997	6.61383877	0.47093996
H	-7.94832679	0.54501050	0.13657671
H	7.94813671	0.54671951	-0.12765156

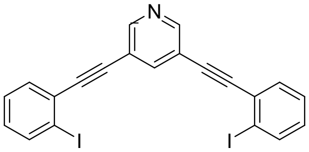
Table S8 Cartesian coordinates for **5**



	X	Y	Z
C	-1.14515546	3.90010676	-0.23089188
C	-1.20946353	2.48991625	-0.16988730
C	-0.00001788	1.78085473	-0.13991571
C	1.20943736	2.48990864	-0.16971430
C	1.14514316	3.90010056	-0.23072255
N	-0.00000204	4.58337779	-0.26033890
C	-2.44268466	1.79833907	-0.13758173
C	2.44265683	1.79833767	-0.13720892
C	-3.46159516	1.13438611	-0.10600783
C	3.46158476	1.13441607	-0.10552536
C	-4.63101905	0.34341883	-0.06426834
C	4.63101167	0.34343781	-0.06405193
C	-5.90089016	0.95863084	-0.04983131
C	-7.05479672	0.18754866	-0.00589179
C	-6.99451099	-1.20730146	0.01371305
C	-5.75035326	-1.83539268	-0.00277465
C	-4.58304665	-1.07319462	-0.03605326

C	4.58304444	-1.07318019	-0.03602375
C	5.75035511	-1.83538166	-0.00296554
C	6.99451411	-1.20729137	0.01348335
C	7.05479598	0.18756136	-0.00593039
C	5.90088366	0.95864862	-0.04965121
I	-2.72234952	-2.07712550	-0.05393270
I	2.72234819	-2.07710897	-0.05382658
S	-8.65288073	1.00410936	0.02903728
S	8.65288200	1.00411980	0.02896537
C	-8.93641888	1.23175510	1.78784281
O	-8.50158033	2.31669480	-0.56795499
O	-9.64350446	0.06622329	-0.46288071
C	8.93657462	1.23153467	1.78777556
O	9.64346382	0.06629926	-0.46316220
O	8.50152757	2.31678338	-0.56784133
H	-2.06639325	4.47957932	-0.25679824
H	-0.00003075	0.69673595	-0.09362516
H	2.06638826	4.47956718	-0.25648598
H	-5.96772298	2.04073711	-0.09126455
H	-7.90998134	-1.79006381	0.02120756
H	-5.69004044	-2.91866090	0.00526549
H	5.69004473	-2.91865121	0.00493560
H	7.90998568	-1.79005424	0.02080861
H	5.96771128	2.04076121	-0.09093317
H	-9.90555420	1.73040991	1.87448164
H	-8.96138086	0.25442523	2.27386721
H	-8.14228332	1.85965995	2.19658807
H	9.90571745	1.73017838	1.87439412
H	8.14247510	1.85938572	2.19667357
H	8.96157956	0.25414079	2.27366904

Table S9 Cartesian coordinates for **5** without methanesulfonyl substituents.



	X	Y	Z
C	1.14524966	4.29065789	0.00014357
C	1.21021832	2.87937426	0.00019317
C	0.00002348	2.17046557	0.00005627
C	-1.21017437	2.87936859	-0.00011879
C	-1.14521184	4.29065290	-0.00014282
N	0.00001722	4.97507954	-0.00001652
C	2.44166166	2.18354551	0.00038253
C	-2.44161452	2.18353421	-0.00027193
C	3.45162654	1.50483414	0.00047930
C	-3.45157981	1.50482345	-0.00036079
C	4.60614225	0.69036327	0.00026154
C	-4.60611554	0.69038103	-0.00027723
C	5.89155029	1.27739207	0.00042520
C	7.03933130	0.49597552	0.00024403
C	6.93548185	-0.89654466	-0.00011124
C	5.67996025	-1.50633558	-0.00027595
C	4.52823315	-0.72304235	-0.00009119
C	-4.52824081	-0.72302661	0.00003337
C	-5.67998803	-1.50629088	0.00009770
C	-6.93549434	-0.89646880	-0.00014838
C	-7.03930934	0.49605410	-0.00046206
C	-5.89150896	1.27744192	-0.00052333
I	2.64394813	-1.69329696	-0.00034558
I	-2.64397922	-1.69332867	0.00041664
H	2.06657337	4.87078408	0.00025008
H	0.00002589	1.08535016	0.00008379
H	-2.06653849	4.87077455	-0.00027806
H	5.95868198	2.36130347	0.00070199
H	7.82889604	-1.51514729	-0.00025743

H	5.59848542	-2.58835071	-0.00054730
H	-5.59854019	-2.58830805	0.00033932
H	-7.82892413	-1.51504908	-0.00009580
H	-5.95861351	2.36135492	-0.00076595
H	-8.01589045	0.97202935	-0.00065807
H	8.01592400	0.97192700	0.00037886

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S6. NMR Spectra

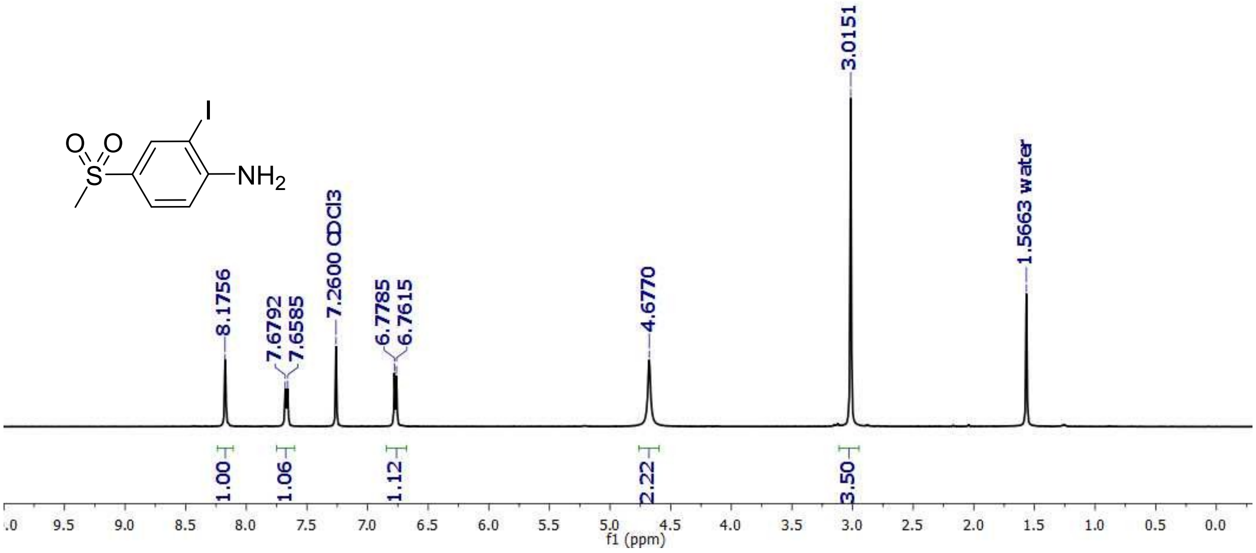

Fig. S6 ^{1}H NMR spectrum **2** (500 MHz, $CDCl_3$, 298 K).

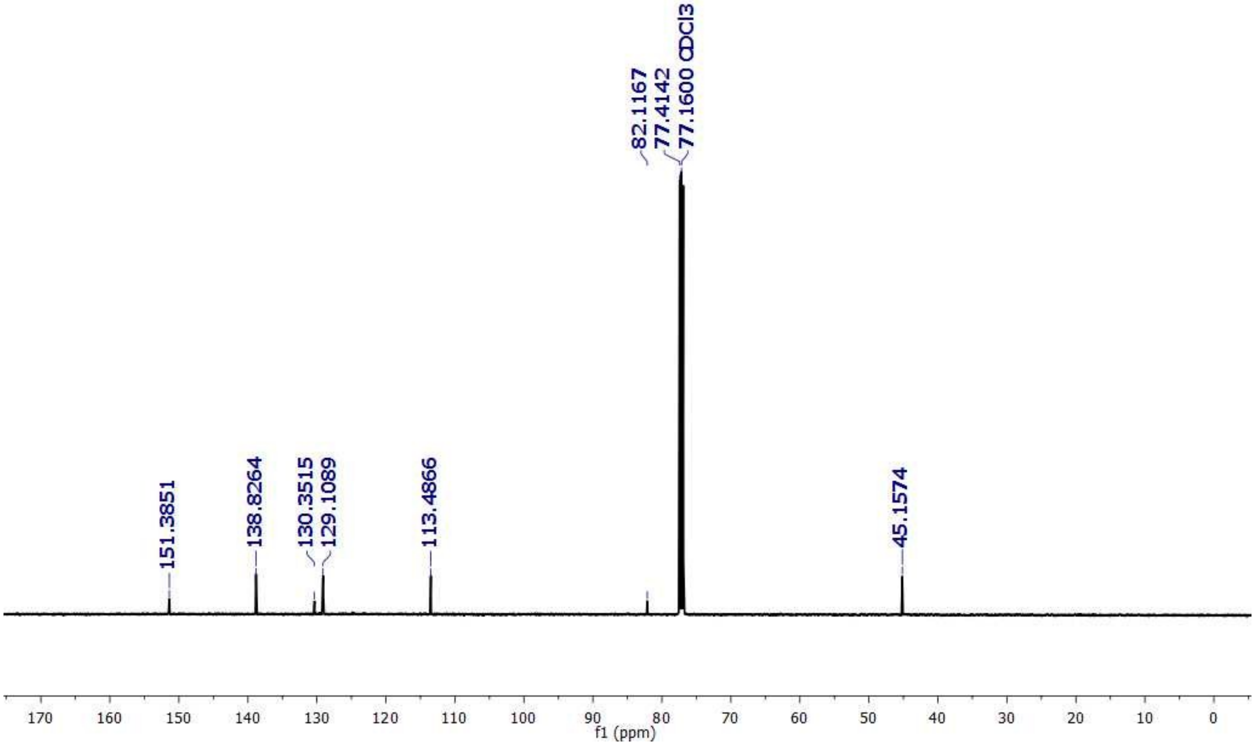

Fig. S7 ^{13}C NMR spectrum of **2** (126 MHz, $CDCl_3$, 298 K).

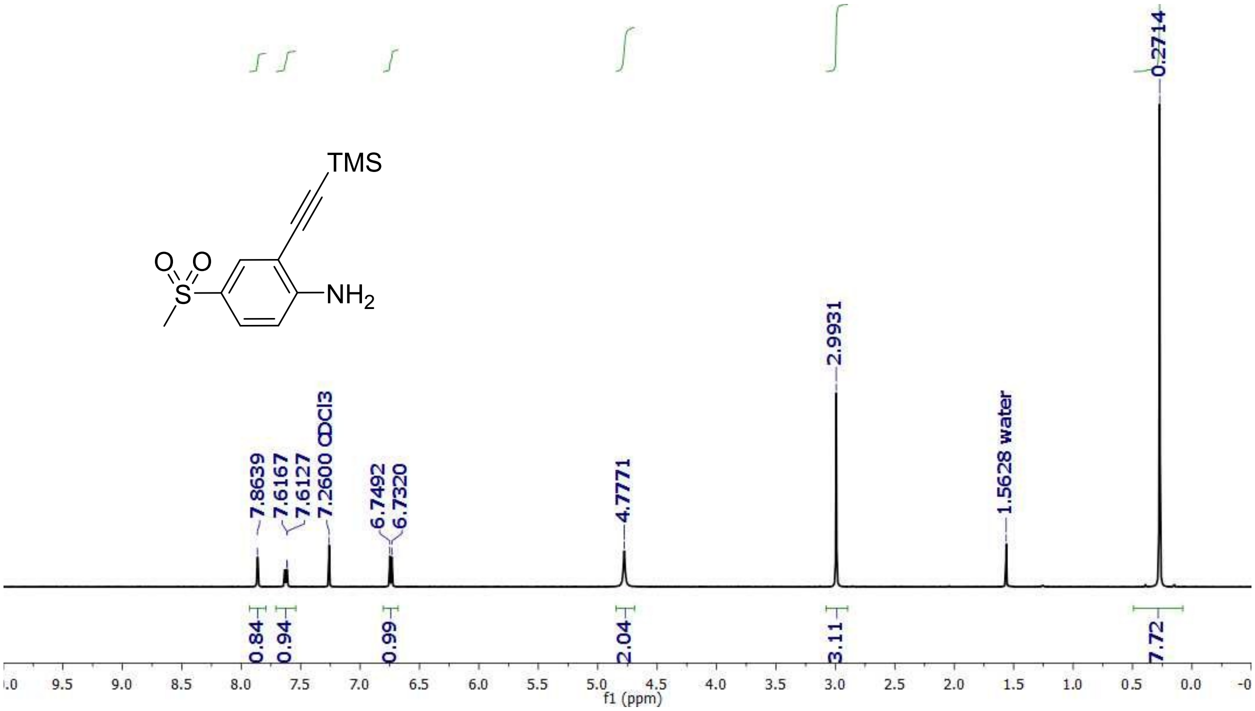

Fig. S8 ^{1}H NMR spectrum of **3** (500 MHz, $CDCl_3$, 298 K).

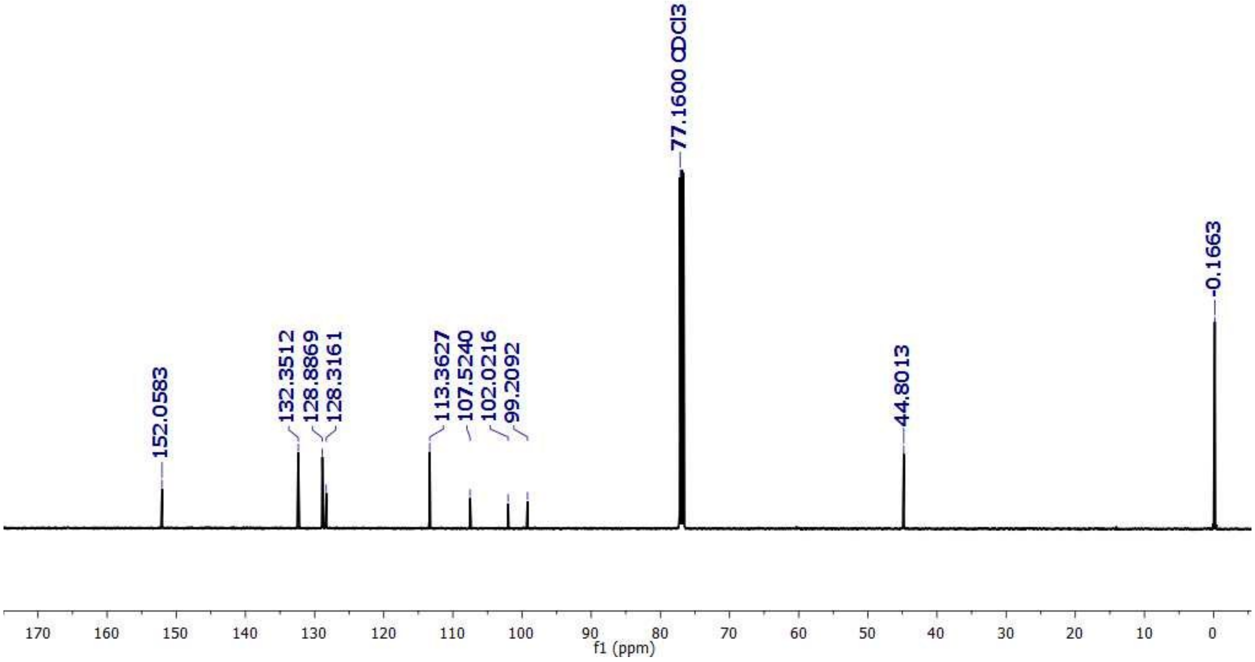

Fig. S9 ^{13}C NMR spectrum of **3** (126 MHz, $CDCl_3$, 298 K).

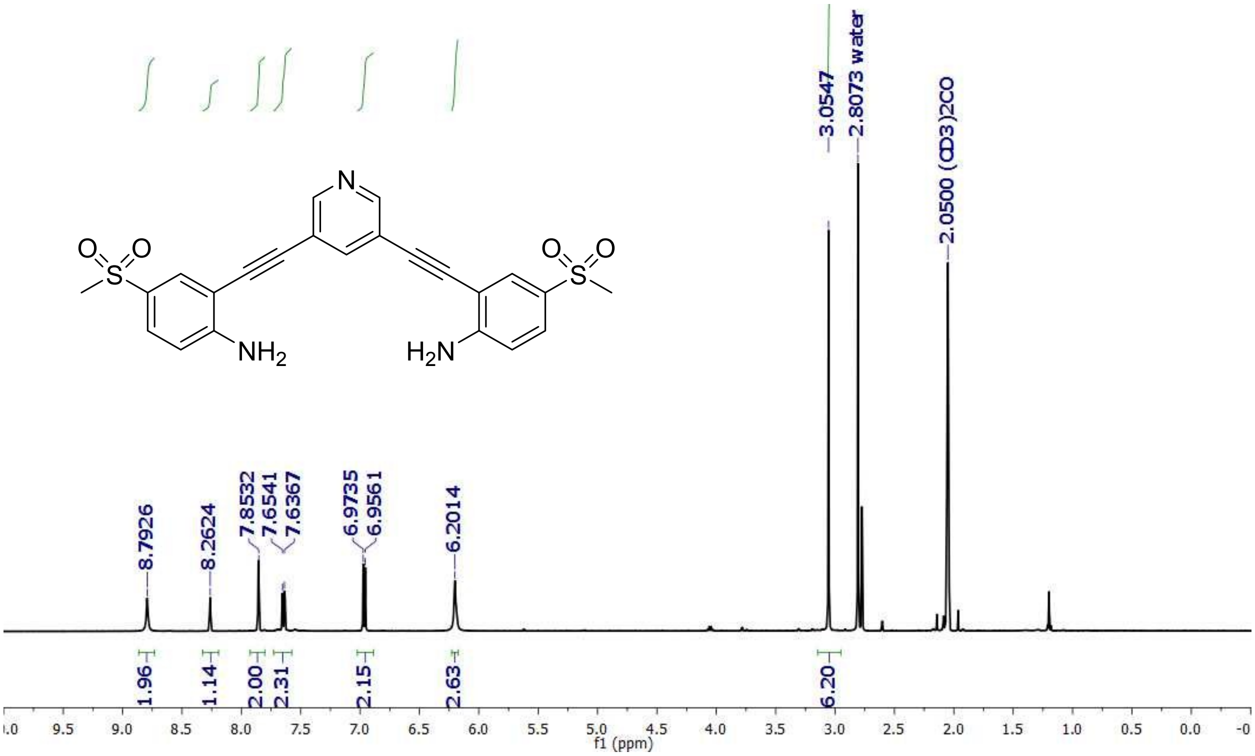

Figure S10. ^{1}H NMR spectrum of **4** (500 MHz, $(CD_3)_2CO$, 298 K).

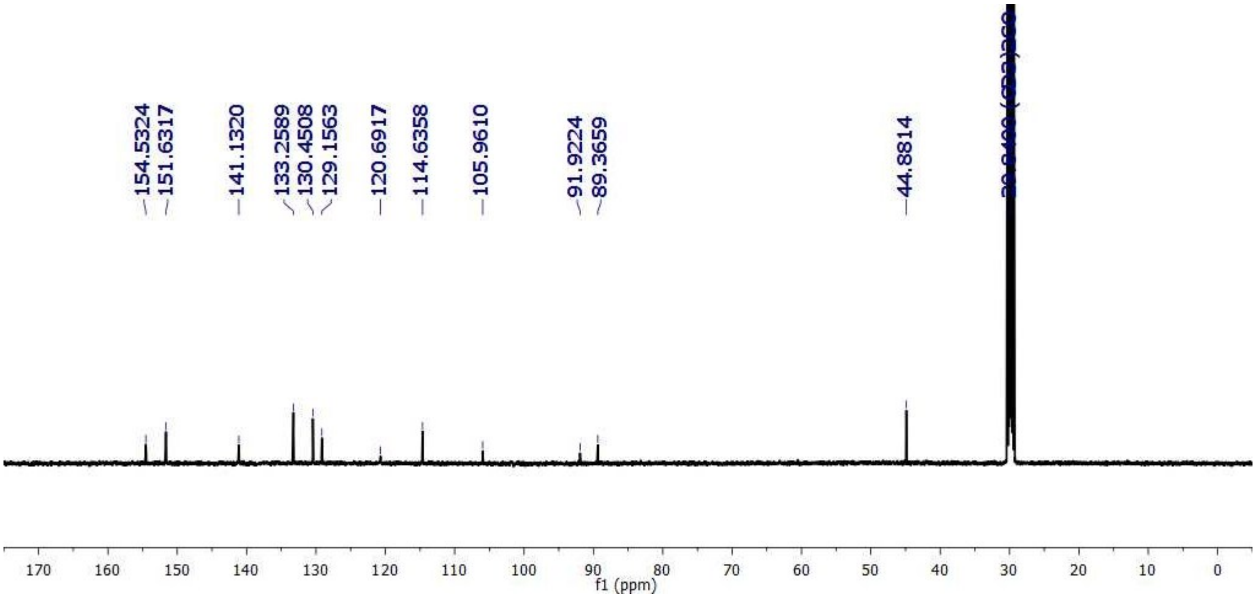

Fig. S11 ^{13}C NMR spectrum of **4** (126 MHz, $(CD_3)_2CO$, 298 K).

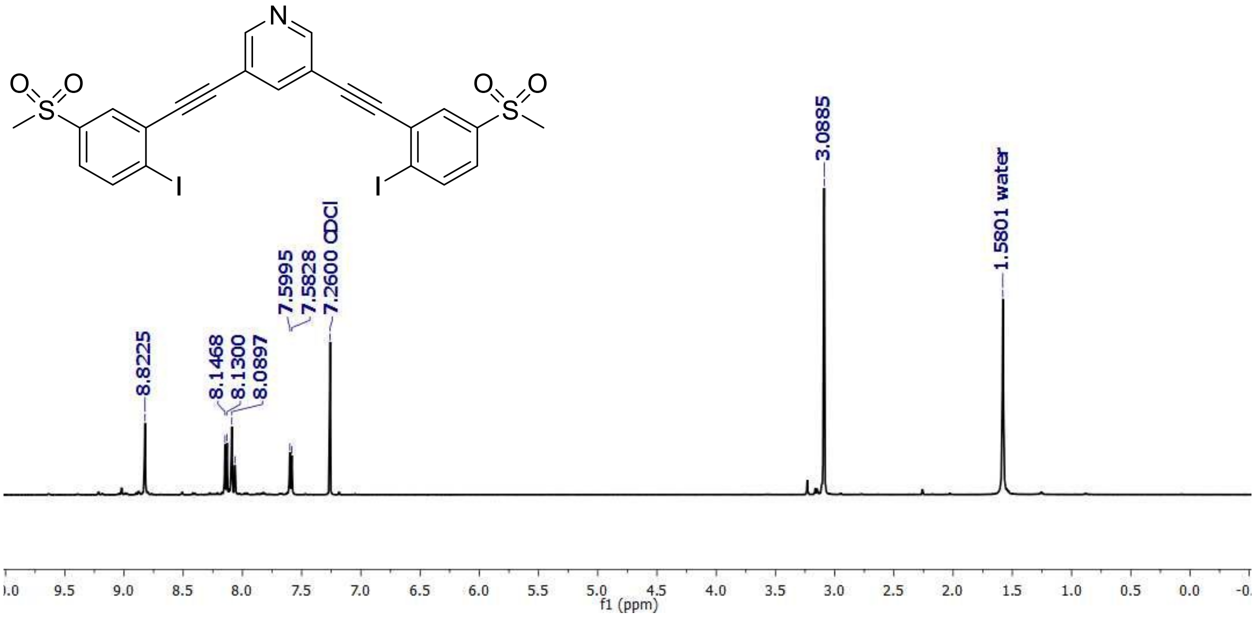

Fig. S12 ^{1}H NMR spectrum of **5** (500 MHz, $CDCl_3$, 298 K).

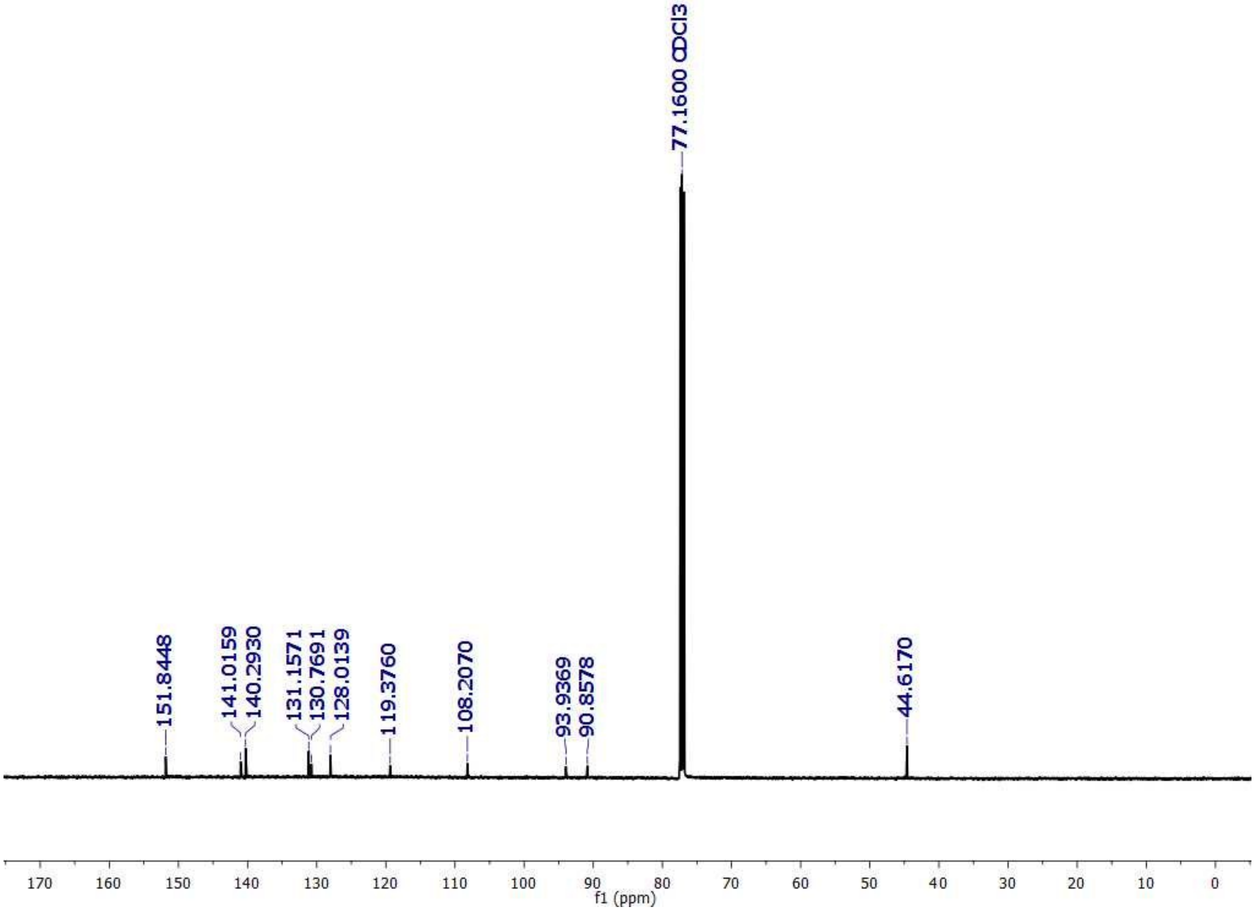

Fig. S13 ^{13}C NMR spectrum of **5** (126 MHz, $CDCl_3$, 298 K).

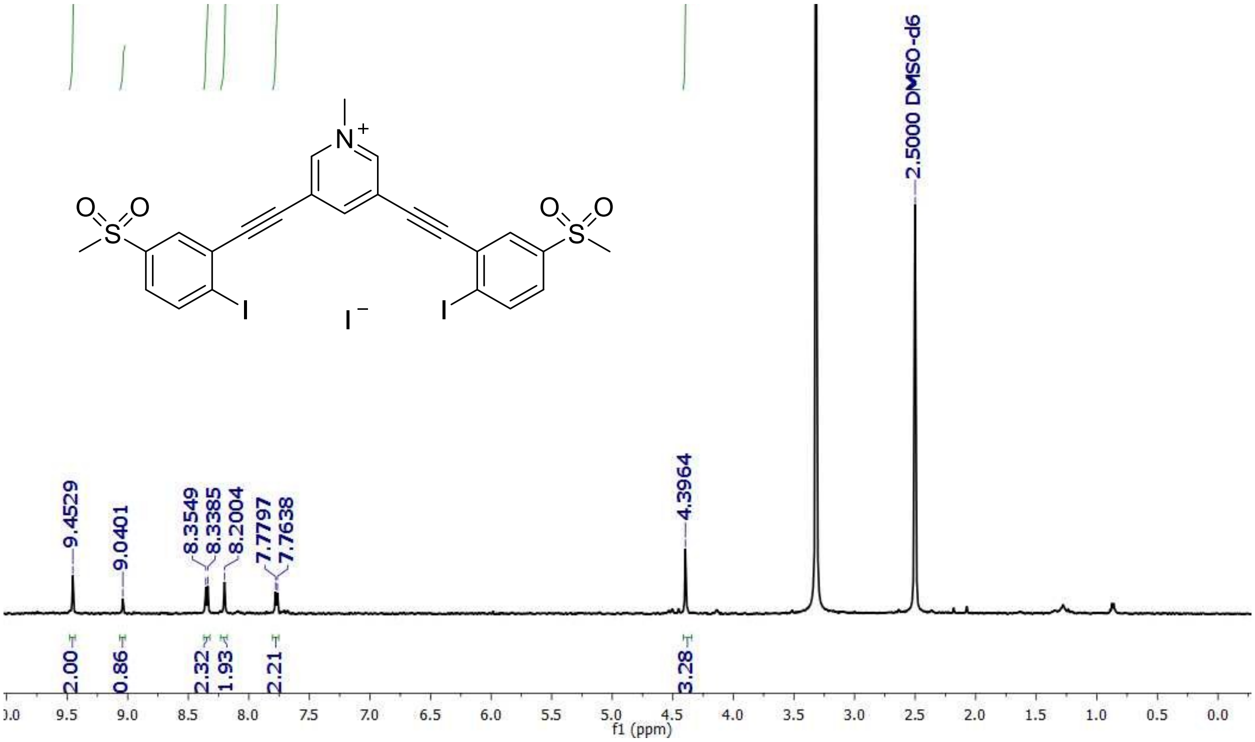

Fig. S14 ^{1}H NMR spectrum of **1·I** (500 MHz, DMSO-d_6, 298 K).

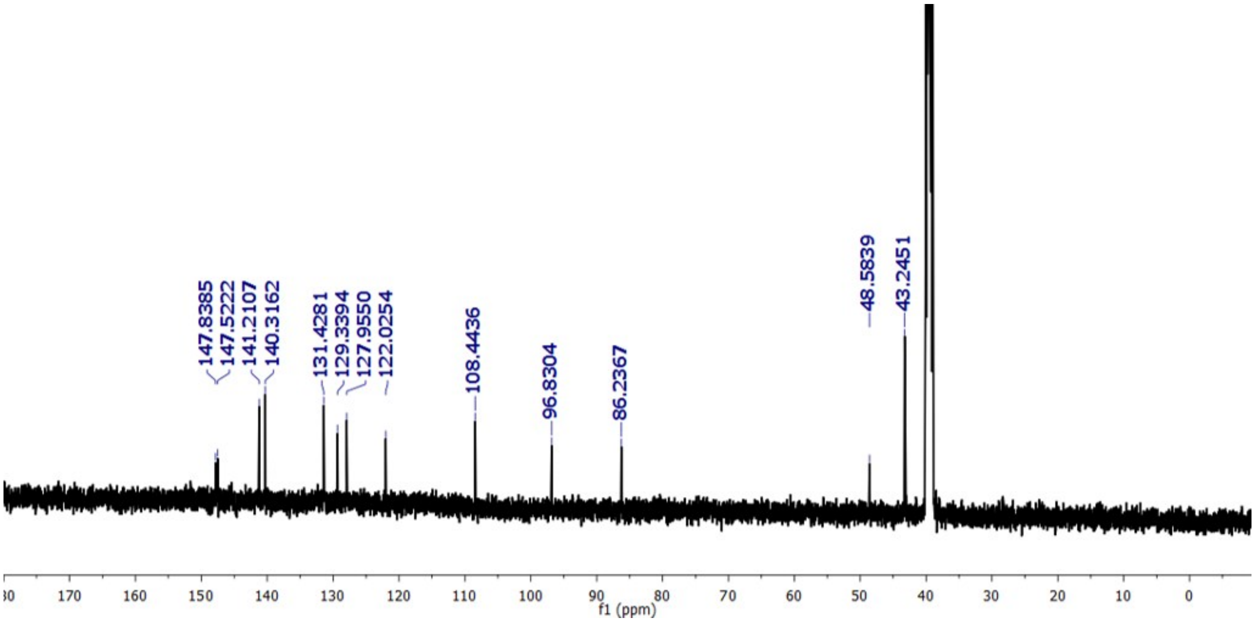

Fig. S15 ^{13}C NMR spectrum of **1·I** (126 MHz, DMSO-d_6, 298 K).

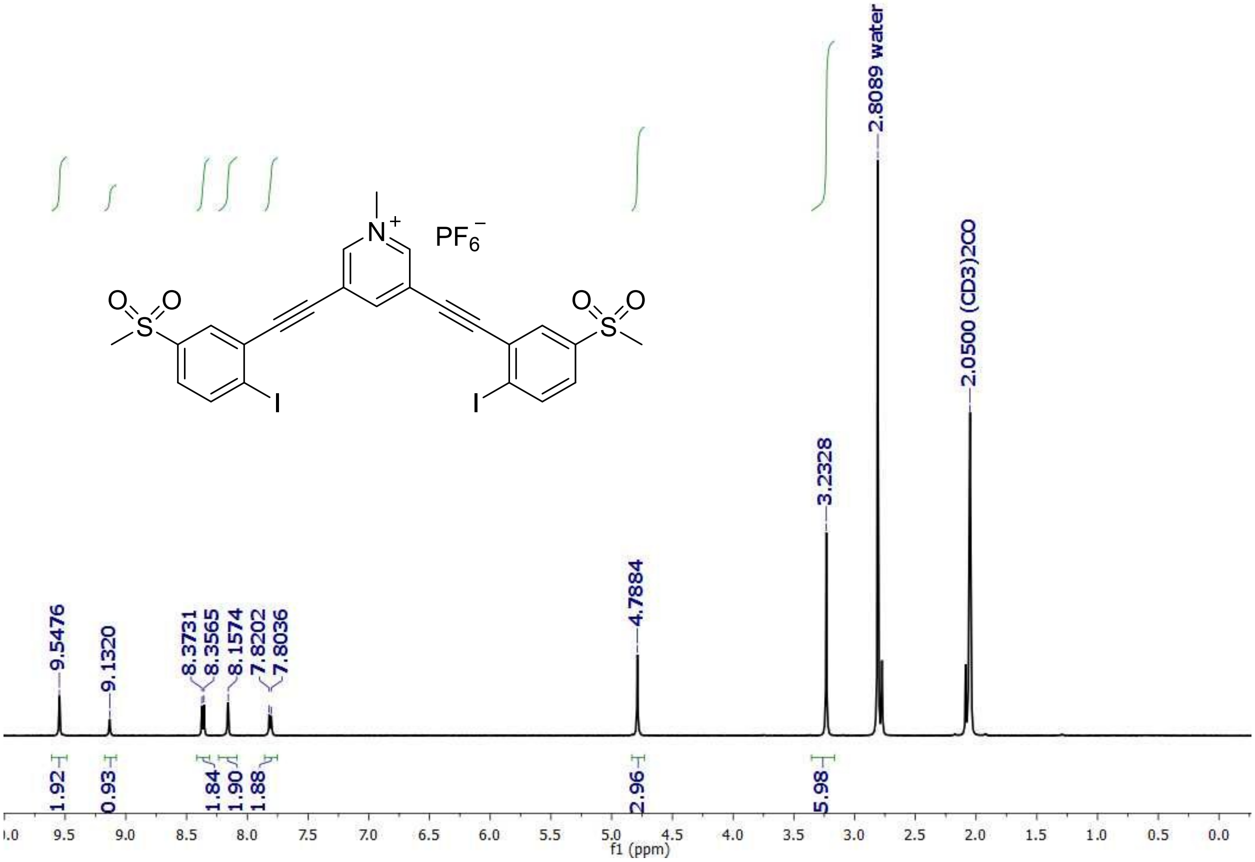

Fig. S16 ^{1}H NMR spectrum of **1·PF$_6$** (500 MHz, $(CD_3)_2CO$, 298 K).

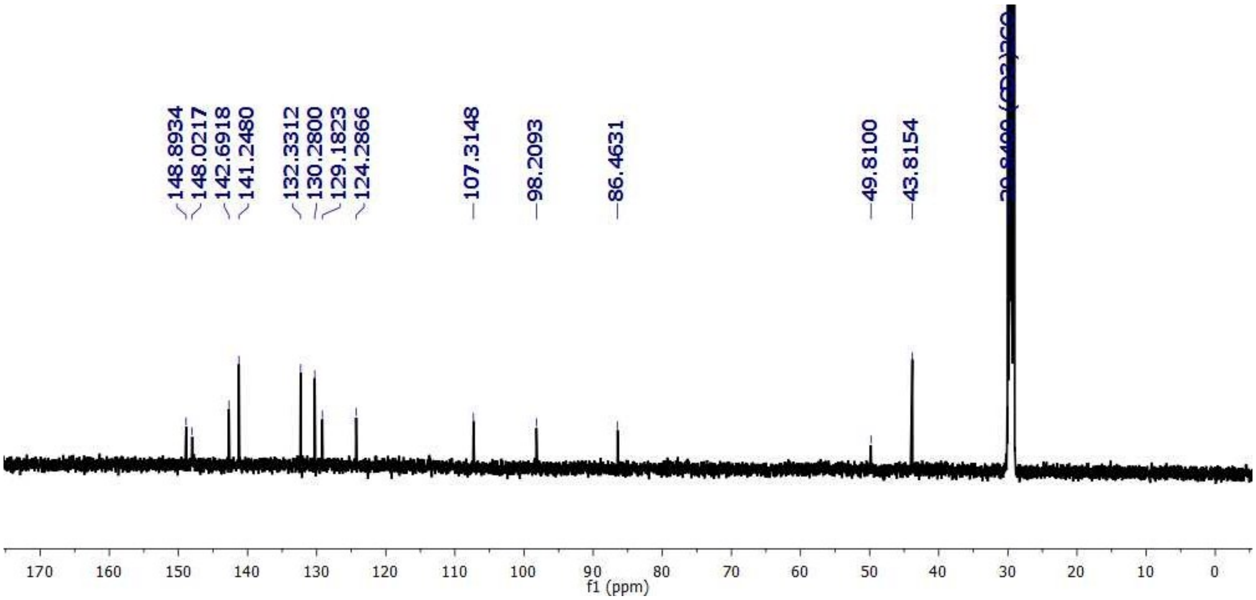

Fig. S17 ^{13}C NMR spectrum of **1·PF$_6$** (126 MHz, $(CD_3)_2CO$, 298 K).