Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information for:

Photo-switchable anion binding and catalysis with a visible light responsive halogen bonding receptor

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Contents

1 Materials and methods

All reagents and solvents were purchased from commercial sources and used without further purification. Where necessary, solvents were dried by passing through an MBraun MPSP-800 column and degassed with nitrogen. Triethylamine was distilled from and stored over potassium hydroxide. Column chromatography was carried out on Merck® silica gel 60 under a positive pressure of nitrogen. Where mixtures of solvents were used, ratios are reported by volume. NMR spectra were recorded on a Bruker AVIII 400, Bruker AVII 500 (with cryoprobe) and Bruker AVIII 500 spectrometers. Chemical shifts are reported as δ values in ppm. Mass spectra were carried out on a Waters Micromass LCT and Bruker microTOF spectrometers. UV-vis spectra were recorded on a V-770 UV-Visible/NIR Spectrophotometer equipped with Peltier temperature controller and stirrer using quartz cuvettes of 1 cm path length.

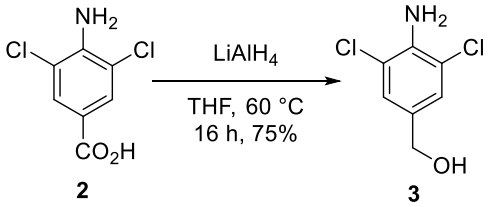
All novel compounds were characterised by ^{1}H, ^{19}F (where appropriate), and ^{13}C NMR, and high-resolution mass spectrometry. Azobenzene derivatives were formed as a mixture of *E* and *Z* isomers. Peaks for the *E* isomer are reported (major product). Thermal relaxation to achieve 100% *E* isomer was achieved by heating the sample at 70 °C prior to NMR titration experiments.

MM optimisation carried out using Avogadro 1.1.1 using UFF force field.

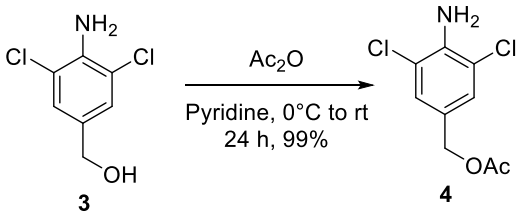
Abbreviations

Ac: Acetyl BAr^{F}_{4}: Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate; DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene; DCM: Dichloromethane; DMF: *N*,*N*-Dimethylformamide; DMSO: Dimethylsulfoxide; HRMS: High resolution mass spectrometry; MeCN: Acetonitrile; MeOH: Methanol; NCS: N-Chlorosuccinimide; rt: Room temperature; TBTA: Tris((1-benzyl-4-triazolyl)methyl)amine; Tf: Triflate; THF: Tetrahydrofuran; Ts: Tosyl

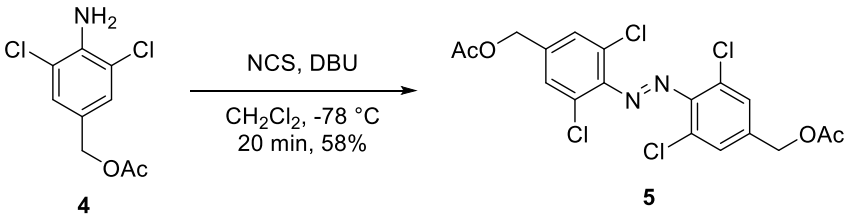
2 Synthesis and characterization



Compound 3: $LiAlH_4$ (4.60 g, 121.2 mmol, 2.5 equiv.) was suspended in dry THF (143 mL) under nitrogen. Acid **2** (10.0 g, 48.5 mmol) was suspended in dry THF (100 mL) and this was added to the solution of $LiAlH_4$ over 15 mins at 0 °C. The reaction mixture was then heated at 60 °C for 16 h, resulting in a colour change from brown to grey. The reaction mixture was diluted with ether (200 mL) and cooled to 0 °C. 5 mL water was added dropwise, then 5 mL NaOH was added dropwise before adding a further 15 mL water, resulting in a light brown suspension (Fieser workup). The reaction mixture was stirred for 15 minutes, then $MgSO_4$ was added. The solids were filtered under vacuum and the filtrate concentrated. The residue was purified by silica gel flash chromatography (50% EtOAc in hexane) to afford the title compound as a yellow solid (6.99 g, 36.4 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 2H), 4.54 (s, 2H), 4.43 (br s, 2H), 1.59 (br s, 1H) Data in agreement with literature values.[1]

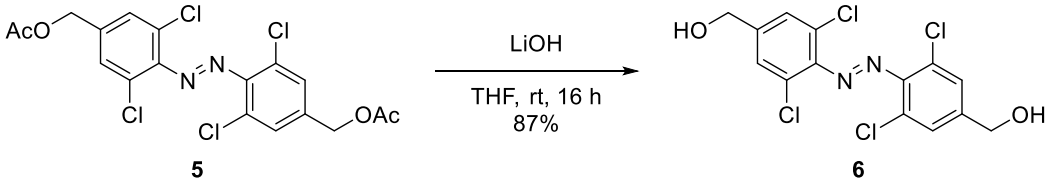


Compound 4: To a solution of **3** (4.45 g, 23.2 mmol) in pyridine (15 mL) was added acetic anhydride (2.19 mL, 32.3 mmol, 1.0 equiv.). The reaction mixture was stirred at 0 °C and allowed to warm to rt before stirring for 24 h. The product was extracted into EtOAc (20 mL) and the mixture was washed with water (2 ×20 mL) and HCl (15 mL), then dried over $MgSO_4$. The solvent was removed *in vacuo* afford the title compound as a yellow oil without further purification (5.41 g, 23.1 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 2H), 4.93 (s, 2H), 4.75 – 4.14 (m, 2H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.90, 140.28, 128.44, 126.14, 119.46, 65.25, 21.15. HRMS-ESI (*m/z*) for $[M+H]^+$, $C_9H_{10}Cl_2NO_2^+$: calculated 231.9938; found 231.9931.



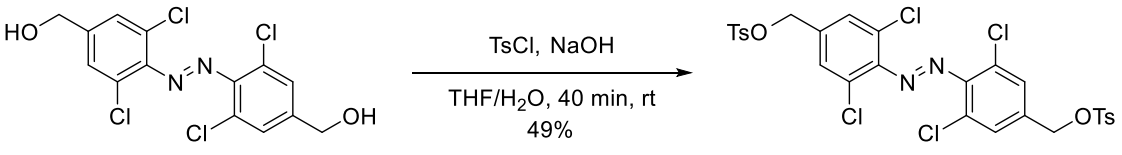
4 5

Compound 5: Conditions taken from Lin and co-workers.[2] To a solution of **4** (4.32 g, 18.5 mmol) in CH_2Cl_2 (290 mL) was added DBU (5.63 g, 37.0 mmol, 2 equiv.) with stirring at rt for 5 mins. NCS (4.92 g, 36.9 mmol, 2 equiv.) was added at -78 °C and the reaction mixture was stirred for 20 mins at -78 °C with occasional brief sonication, before quenching by addition of saturated $NaHCO_3$ (250 mL). The dark orange reaction mixture was washed with water (3 × 250 mL) and 1 M HCl (250 mL). The organic layer was concentrated *in vacuo* and was purified by silica gel flash chromatography (30% Hexane in CH_2Cl_2) to afford the title compound as an orange solid as a mixture of isomers (2.48 g, 5.34 mmol, 58%). ***E*-5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 4H), 5.10 (s, 4H), 2.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.59, 147.20, 138.58, 128.82, 127.67, 64.33, 20.99. HRMS-ESI (*m/z*) for $[M+H]^+$, $C_{18}H_{15}Cl_4N_2O_4^+$: calculated 464.9751; found 464.9751.



5 6

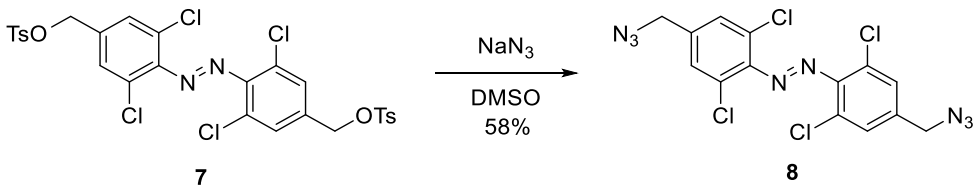
Compound 6: To a solution of **5** (2.48 g, 5.3 mmol) in THF (20 mL) was added LiOH (632.7 mg, 26.4 mmol, 5 equiv.) in water (5 mL). The reaction mixture was stirred at rt for 16 h and monitored by TLC before diluting in DCM (100 mL) and washing with water (3 × 100 mL). The solvent was removed *in vacuo*, then was purified by silica gel flash chromatography (3% MeOH in CH_2Cl_2) to afford the title compound as an orange solid as a mixture of isomers (1.76 g, 4.63 mmol, 87%). ***E*-6**: ^{1}H NMR (400 MHz, Acetone) δ 7.61 (t, *J* = 0.8 Hz, 4H), 4.79 – 4.73 (m, 4H), 4.66 (dd, *J* = 6.3, 5.4 Hz, 2H). ^{13}C NMR (101 MHz, Acetone) δ 147.21, 146.60, 128.07, 127.65, 62.94. HRMS-ESI (*m/z*) for $[M+H]^+$, $C_{14}H_{11}Cl_4N_2O_2^+$: calculated 380.9540; found 380.9541.



6 7

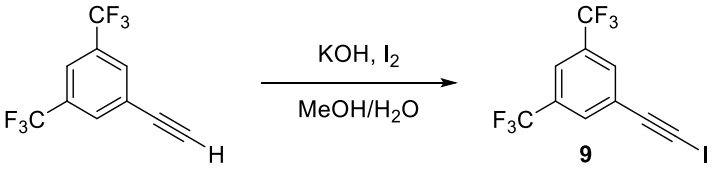
Tosylate 7. 6 (173 mg, 455 µmol) was dissolved in 7:3 THF/H_2O (20 mL). NaOH (91 mg, 2.28 mmol, 5 eq) was added. Then TsCl (261 mg, 1.37 mmol, 3 eq) was added. The reaction was stirred at room temperature for 40 minutes. The reaction was diluted with CH_2Cl_2, then washed with H_2O (3x). The

organic layer was concentrated, then purified by silica gel flash chromatography (dry load, 50% to 100% CH_2Cl_2 in hexane) to afford the title compound as an orange solid as a mixture of isomers (3:1 **E:Z**) (154.3 mg, 223 µmol, 49%). ***E*-6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 4H), 7.35 (dd, *J* = 8.0, 5.0 Hz, 4H), 7.30 (s, 4H), 5.06 (s, 4H), 2.45 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.67, 145.59, 135.96, 133.08, 130.14, 129.00, 128.14, 127.69, 69.53, 21.83. HRMS-ESI (m/z) Calculated for $C_{28}H_{22}N_2O_6S_2Cl_4$ $[M+H]^+$, 688.9717; found 685.4355.



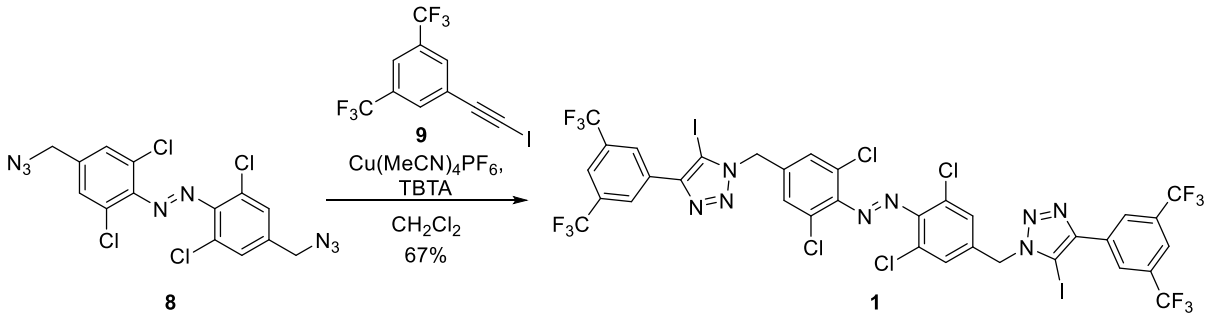
7 **8**

Azide 8. Tosylate 7 (150 mg, 218 µmol) was dissolved in dry DMSO (3.5 mL) under N_2. Sodium azide (71 mg, 1.09 mmol, 5 eq) was added and the reaction was stirred at room temperature for 16 hours. Water was added (5 mL) and the reaction was extracted with Et_2O (3x 10 mL). The combined organic layers were washed with water (3 x 10 mL) then dried with $MgSO_4$. The organic layer was concentrated and left without further purification to afford the title compound as an orange solid (54 mg, 126 µmol, 58%). ***E*-8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 4H), 4.41 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.26, 138.19, 128.79, 128.00, 53.34. HRMS-ESI (m/z) Calculated for $C_{14}H_9Cl_4N_8$ $[M+H]^+$, 428.9699; found 428.9700.

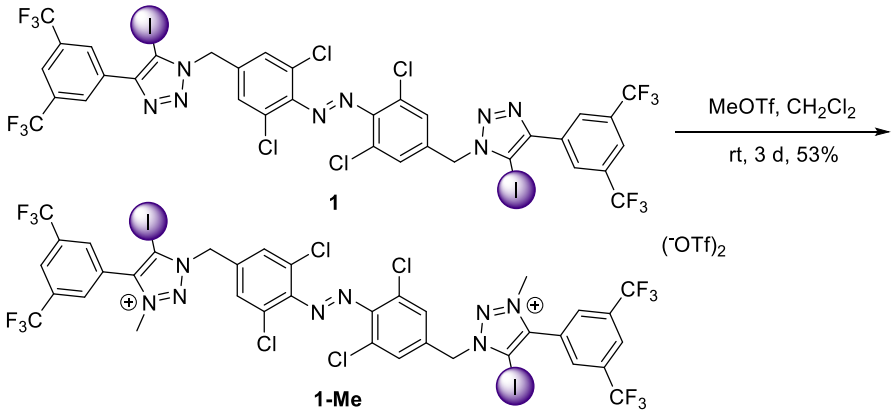


9

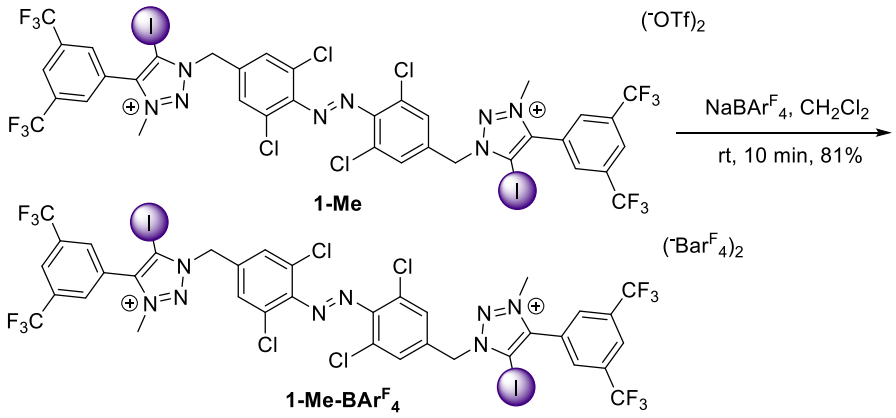
1-iodoethynyl-3,5-bis(trifluoromethyl)benzene 9. This known compound was prepared according a literature procedure.[3] 1-ethynyl-3,5-bis(trifluoromethyl) benzene (165 mg, 0.69 mmol) and KOH (185 mg in 0.5 mL H_2O, 1.73 mmol, 2.5 eq) were stirred in MeOH (4 mL) at 0°C for 10 mins. Iodine (361 mg, 0.76 mmol, 1.1 eq) was added and the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was diluted with water (25 mL) and the product was extracted with ethyl acetate (2 x 25 mL). The organic layer was dried with $MgSO_4$, then concentrated to afford a yellow oil (206 mg, 0.56 mmol, 82%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.81 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.22. Data in agreement with literature values.[3]



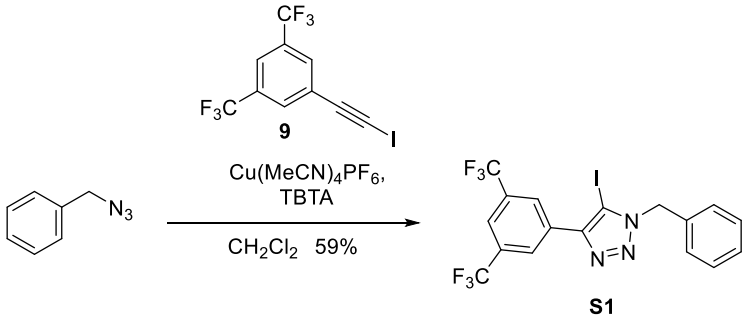
Triazole 1. Azide **8** (53 mg, 123 µmol), Iodoalkyne **9** (180 mg, 492 µmol, 4 eq), Tris((1-benzyl-4-triazolyl)methyl)amine [TBTA] (13 mg, 24.6 µmol, 0.2 eq) and Tetrakis(acetonitrile)copper(I) hexafluorophosphate (9 mg, 24.6 µmol, 0.2 eq) were placed in a flask and purged with N_2. Degassed CH_2Cl_2 (3 mL) was added and the reaction was stirred at room temperature overnight. The mixture was diluted with CH_2Cl_2, then washed with ammonia / EDTA solution. The organic layer was concentrated and the residue was purified by silica gel flash chromatography (dry load, 50% to 70% CH_2Cl_2 in hexane) to afford the title compound as an orange solid as a mixture of isomers (95 mg, 82 µmol, 67%). ***E*-1**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 4H), 7.92 (s, 2H), 7.43 (s, 4H), 5.71 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.06, 147.74, 136.15, 132.26 (q, *J* = 33.5 Hz), 128.92, 128.34, 127.39 (m), 124.21, 123.30 (q, *J* = 272.8 Hz), 122.54 (m), 77.68, 53.22. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.96. HRMS-ESI (m/z) Calculated for $C_{34}H_{13}N_8F_{12}Cl_4I_2$ $[M-H]^-$, 1156.7896; found 1156.7876.



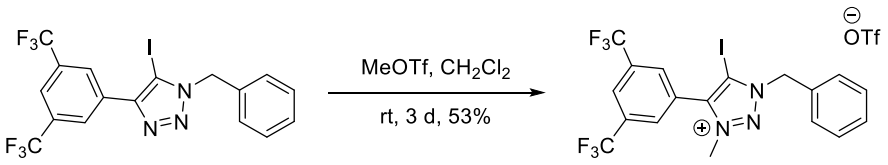
1-Me. To a suspension of **1** (25 mg, 21.6 µmol) in dry CH_2Cl_2 (1 mL) under N_2 in a sealed tube was added methyl triflate (7 µL, 64.8 µmol, 3 eq). The reaction was stirred under protection from light for 3 days. Then, Et_2O (10 mL) was added, and the precipitate was collected *via* filtration. The solid was collected and dried to afford the title compound as an orange solid (17 mg, 11.4 µmol, 53%). ***E*-1-Me**: ^{1}H NMR (400 MHz, DMSO) δ 8.59 (s, 2H), 8.41 (s, 4H), 7.86 (s, 4H), 6.20 (s, 4H), 4.32 (s, 6H). ^{13}C NMR (151 MHz, DMSO) δ 146.53, 144.32, 135.95, 131.59 (m), 131.31 (d, *J* = 33.4 Hz), 129.95, 126.45, 125.97 (m), 125.66, 122.81 (d, *J* = 273.2 Hz), 95.75, 55.19, 40.05. ^{19}F NMR (377 MHz, DMSO) δ -61.28, -77.75. HRMS-ESI (m/z) Calculated for $C_{36}H_{20}N_8F_{12}Cl_4I_2$ $[M]^{2+}$, 593.9214; found 593.9197



1-Me-BAr$^F_4$. 1-Me (50 mg, 33.6 µmol) was suspended in CH_2Cl_2 (2 mL). $NaBAr^F_4$ (59.62 mg, 67.3 µmol, 2 eq) was added, and the mixture turned into an orange solution, which was stirred for a further 10 minutes. The reaction was diluted with CH_2Cl_2 (20 mL). The organic layer was washed with water twice, then dried and concentrated to afford the title compound as a sparkly orange solid (79 mg, 27.1 µmol, 81%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.35 (s, 2H), 7.94 (s, 4H), 7.71 (br s, 24H), 7.63 (s, 4H), 7.55 (q, *J* = 1.4 Hz, 12H), 5.83 (s, 4H), 4.32 (s, 6H). ^{19}F NMR (377 MHz, CD_2Cl_2) δ -62.81, -63.54.

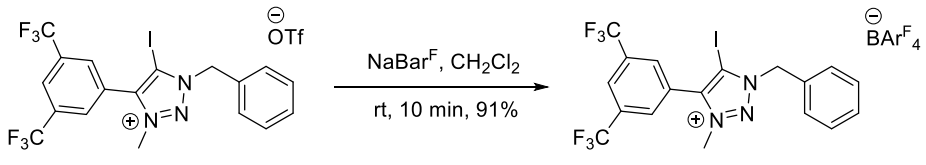


S1. Benzyl azide (165 µL, 1.32 mmol, 3 eq), Iodoalkyne **9** (160 mg, 440 µmol, 4 eq), Tris((1-benzyl-4-triazolyl)methyl)amine [TBTA] (45 mg, 85 µmol, 0.2 eq) and Tetrakis(acetonitrile)copper(I) hexafluorophosphate (31 mg, 85 µmol, 0.2 eq) were placed in a flask and purged with N_2. Degassed CH_2Cl_2 (5 mL) was added and the reaction was stirred at room temperature overnight. The mixture was diluted with CH_2Cl_2, then washed with ammonia / EDTA solution. The organic layer was concentrated and the residue was purified by silica gel flash chromatography (dry load, 10% Acetone in hexane) to afford the title compound as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (d, *J* = 1.7 Hz, 2H), 7.89 (s, 1H), 7.40 – 7.34 (m, 3H), 7.34 – 7.30 (m, 2H), 5.71 (s, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.95. ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.63, 133.95, 132.51, 132.17 (d, *J* = 33.4 Hz), 129.20, 128.92, 128.00, 127.35 (q, *J* = 3.7 Hz), 123.35 (q, *J* = 272.8 Hz), 122.25 (h, *J* = 3.8 Hz), 77.42, 54.81. HRMS-ESI (m/z) Calculated for $C_{17}H_{11}F_6IN_3$ $[M+H]^+$, 497.9896; found 497.9883.



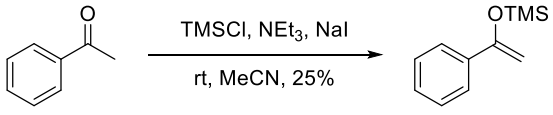
S1 **S1-Me**

S1-Me. To a suspension of **S1** (100 mg, 201.13 µmol) in dry CH_2Cl_2 (1 mL) under N_2 in a sealed tube was added methyl triflate (65 µL, 603 µmol, 3 eq). The reaction was stirred for 2 days. Then, Et_2O (10 mL) was added, and the precipitate was collected *via* filtration. The solid was collected and dried to afford the title compound a white solid (68 mg, 103 µmol, 53%). ^{1}H NMR (600 MHz, DMSO) δ 8.54 (s, 1H), 8.43 (d, *J* = 1.7 Hz, 2H), 7.53 – 7.43 (m, 5H), 6.04 (s, 2H), 4.26 (s, 3H). ^{19}F NMR (377 MHz, DMSO) δ -61.34, -77.77. ^{13}C NMR (151 MHz, DMSO) δ 144.21, 132.40, 131.76 (m), 131.33 (q, *J* = 33.8 Hz), 129.16, 129.10, 128.45, 125.89, 125.81, 122.87 (d, *J* = 273.2 Hz), 94.76, 57.04, 40.05. HRMS-ESI (m/z) Calculated for $C_{18}H_{14}N_3F_6I$ $[M]^+$, 513.0068; found 513.0131



S1 **10**

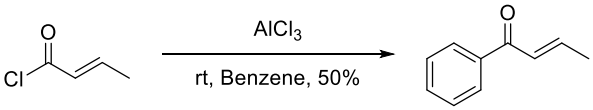
1-Me-BAr$^F_4$. 1-Me (31 mg, 46.9 µmol) was suspended in CH_2Cl_2 (3 mL). $NaBAr^F_4$ (41.5 mg, 46.9 µmol, 1 eq) was added, and the mixture turned into a colourless solution, which was stirred for a further 10 minutes. The reaction was diluted with CH_2Cl_2 (20 mL). The organic layer was washed with water twice, then dried and concentrated to afford the title compound as a sparkly white solid (96 mg, 43.9 µmol, 91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.89 (s, 2H), 7.68 (dt, *J* = 5.5, 2.4 Hz, 6H), 7.49 (s, 3H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 5.62 (s, 2H), 4.10 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.40, -63.17.



14

14. Prepared according to a modified literature procedure.[4] To a mixture of acetophenone (0.97 mL, 8.32 mmol), triethylamine (1.45 mL, 10.4 mmol, 1.25 eq) and TMSCl (1.32 mL, 10.4 mmol) in dry acetonitrile was added NaI (1.56 g, 1.25 eq) under nitrogen. The reaction was stirred at room temperature for 1 hour. The reaction was poured onto pentane (20 mL) and ice water (20 mL). The organic layer was concentrated, then quickly purified by silica gel flash chromatography (petroleum ether) to afford the title compound as a clear oil (400 mg, 2.08 mmol, 25%). ^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.61 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.37 – 7.27 (m, 3H), 4.93 (d, *J* = 1.6 Hz, 1H), 4.45 (d, *J* = 1.7 Hz, 1H), 0.29 (s, 9H). Data in agreement with literature values.[4]



S2

S2. Prepared according to a modified literature procedure.[5] trans-Crotonylchloride (6.50 g, 62.2 mmol, 1 eq) was suspended in benzene (18.0 mL) and $AlCl_3$ (13.6 g, 101 mmol, 1.62 eq) was added while cooling. The mixture was stirred overnight and was quenched by pouring into a mixture of 1 M HCl (100 mL) and ice (100 mL). Extraction with dichloromethane (3 × 50 mL) followed by washing with 1 M NaOH (30 mL) and drying over Na_2SO_4 yielded the crude product after removal of the solvent. The organic layer was concentrated and the residue was purified by silica gel flash chromatography (3% EtOAc in pentane) to afford the title compound as a clear oil (4.6 g, 31.3 mmol, 50 %).[1]H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 2H), 7.58 – 7.50 (m, 1H), 7.50 – 7.42 (m, 2H), 7.08 (dq, *J* = 15.5, 6.8 Hz, 1H), 6.91 (dq, *J* = 15.3, 1.6 Hz, 1H), 2.00 (dd, *J* = 6.8, 1.6 Hz, 3H). Data in agreement with literature values.[5]

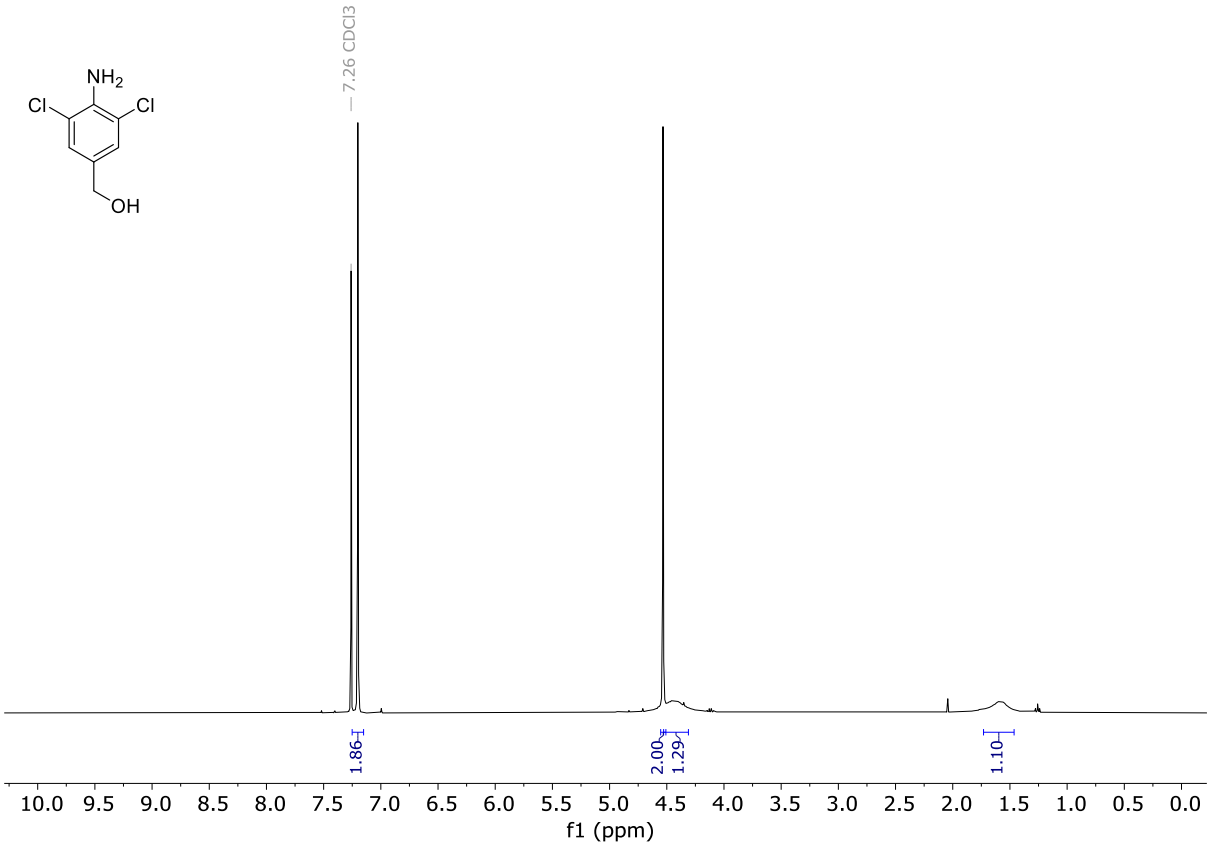


Figure S1. [1]H NMR spectrum of **3** (Chloroform-*d*, 298 K).

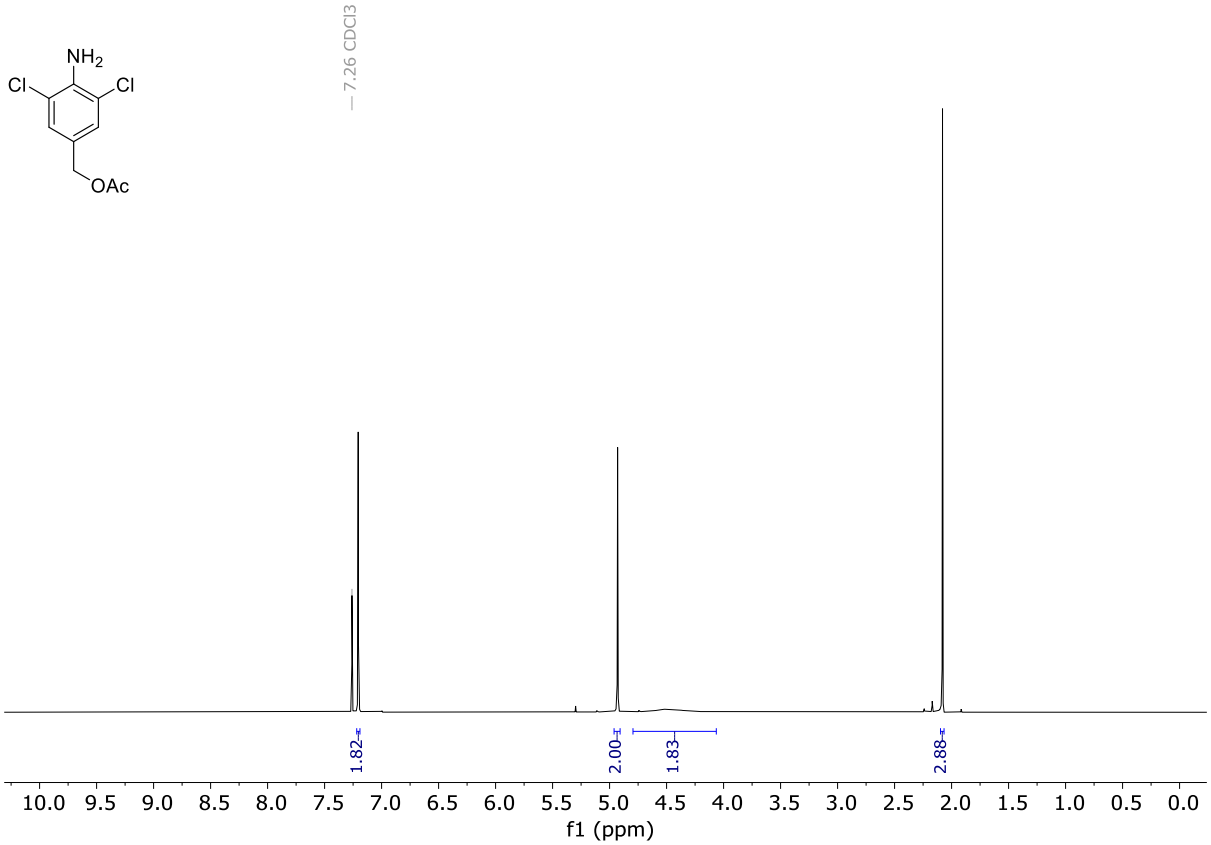


Figure S2. [1]H NMR spectrum of **4** (Chloroform-*d*, 298 K).

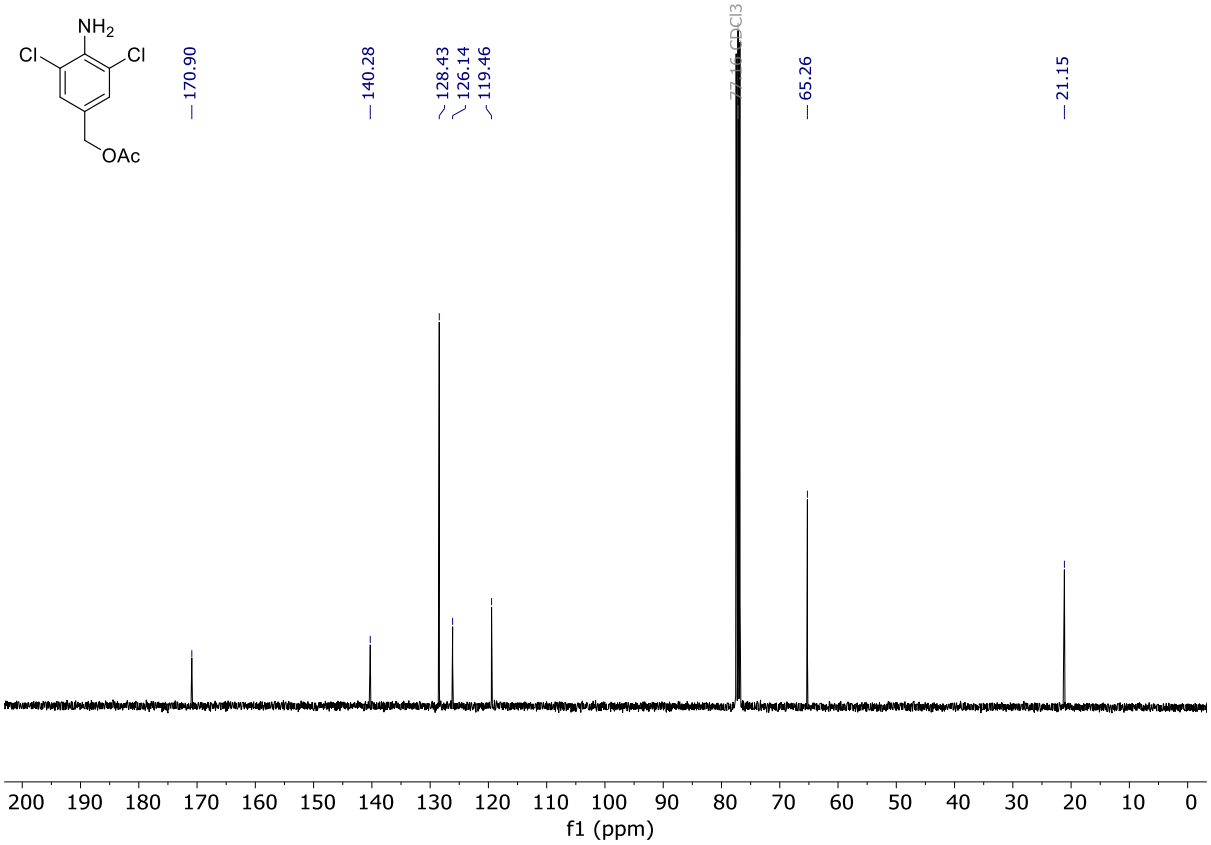


Figure S3. [13]C NMR spectrum of **4** (Chloroform-*d*, 298 K).

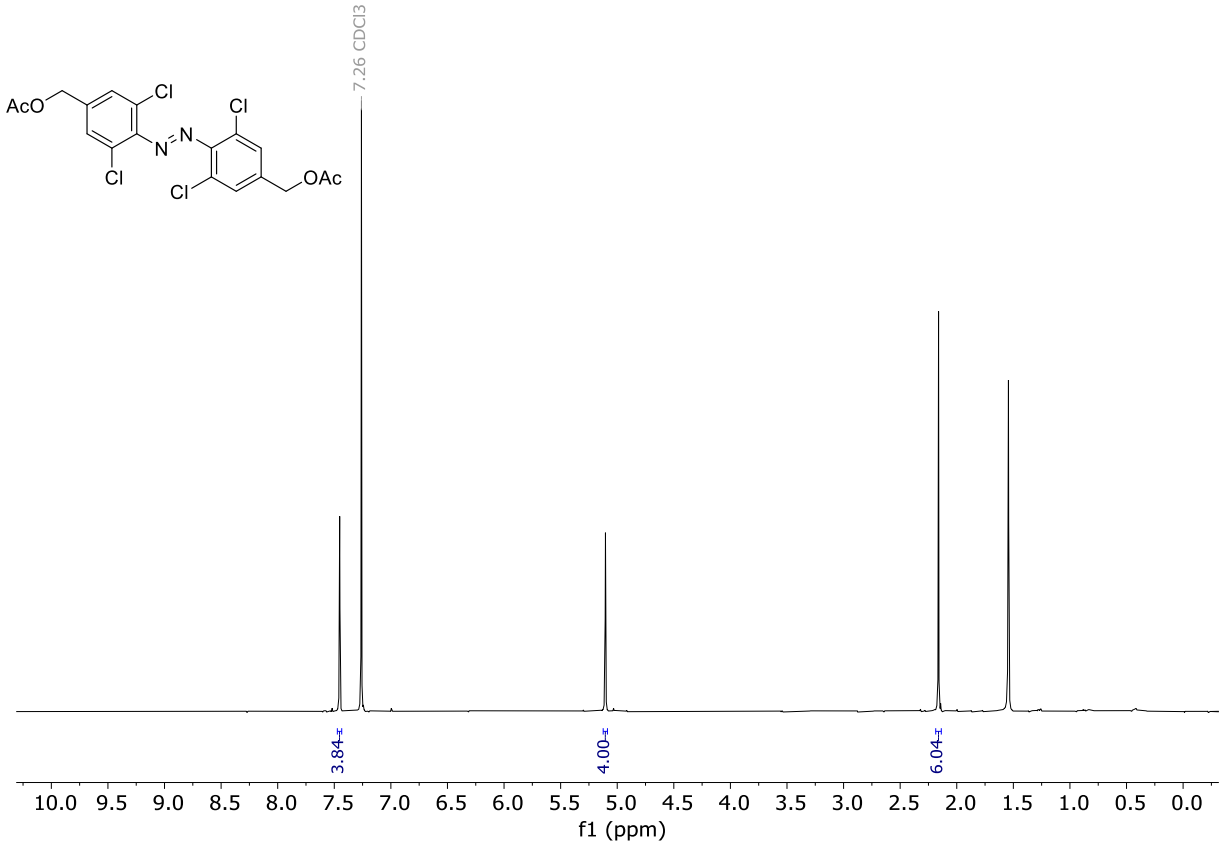


Figure S4. [1]H NMR spectrum of **5** (Chloroform-*d*, 298 K).

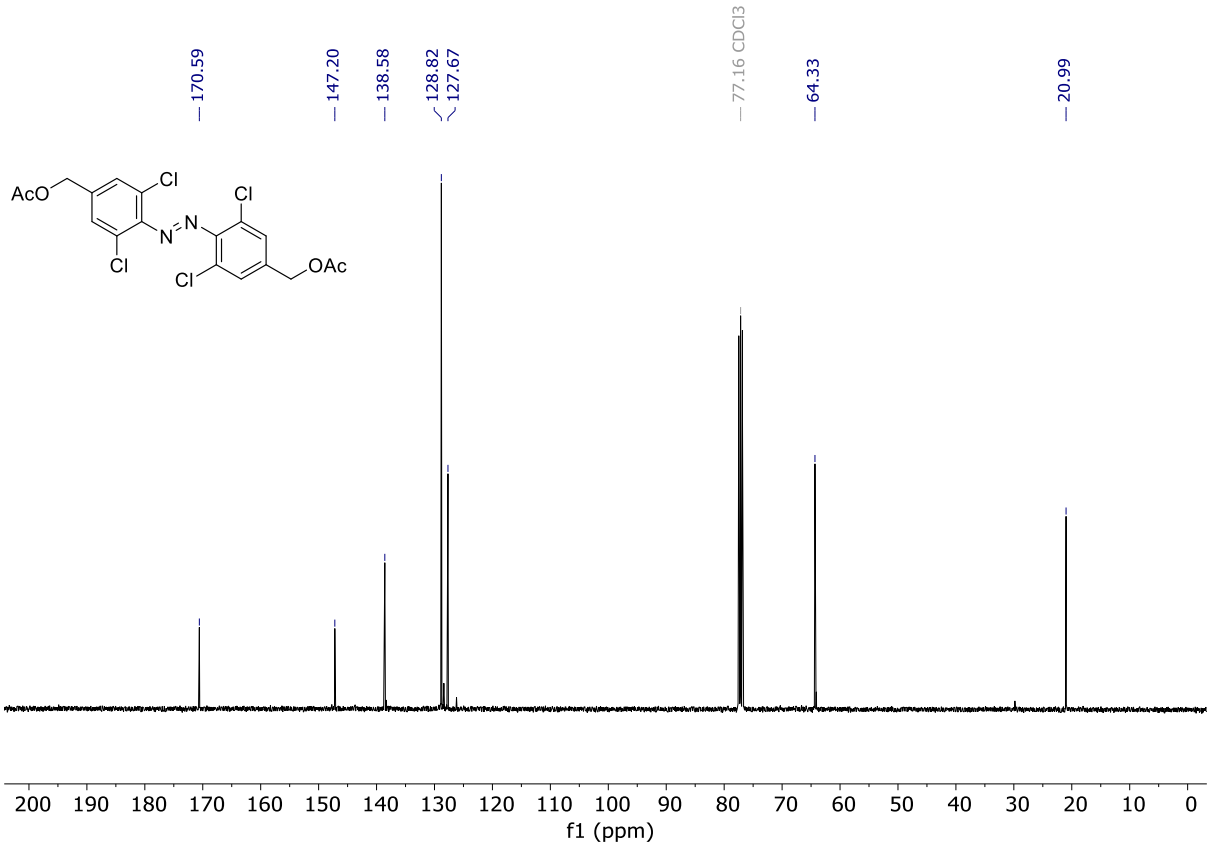


Figure S5. [13]C NMR spectrum of **5** (Chloroform-*d*, 298 K).

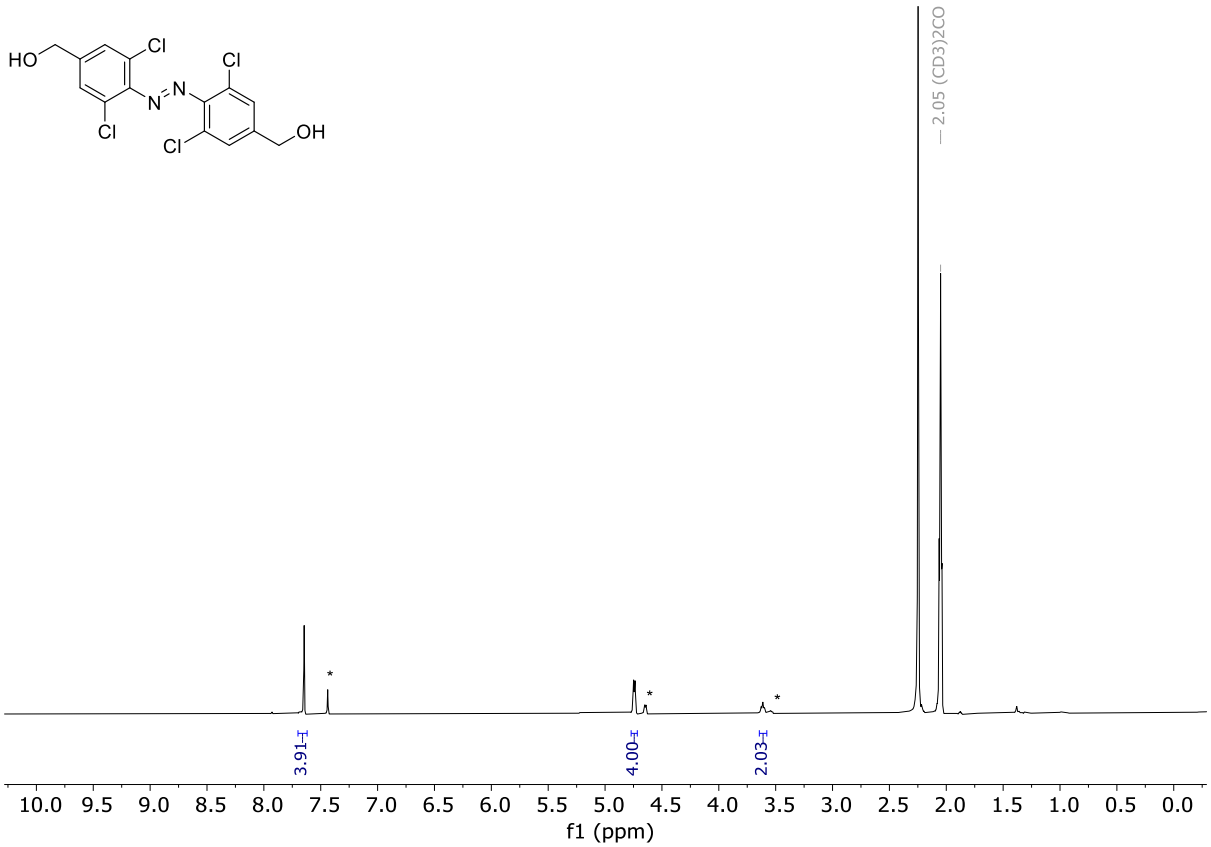


Figure S6. [1]H NMR spectrum of **6** (acetone-d_6, 298 K). **6^{Z}** signals labelled as *

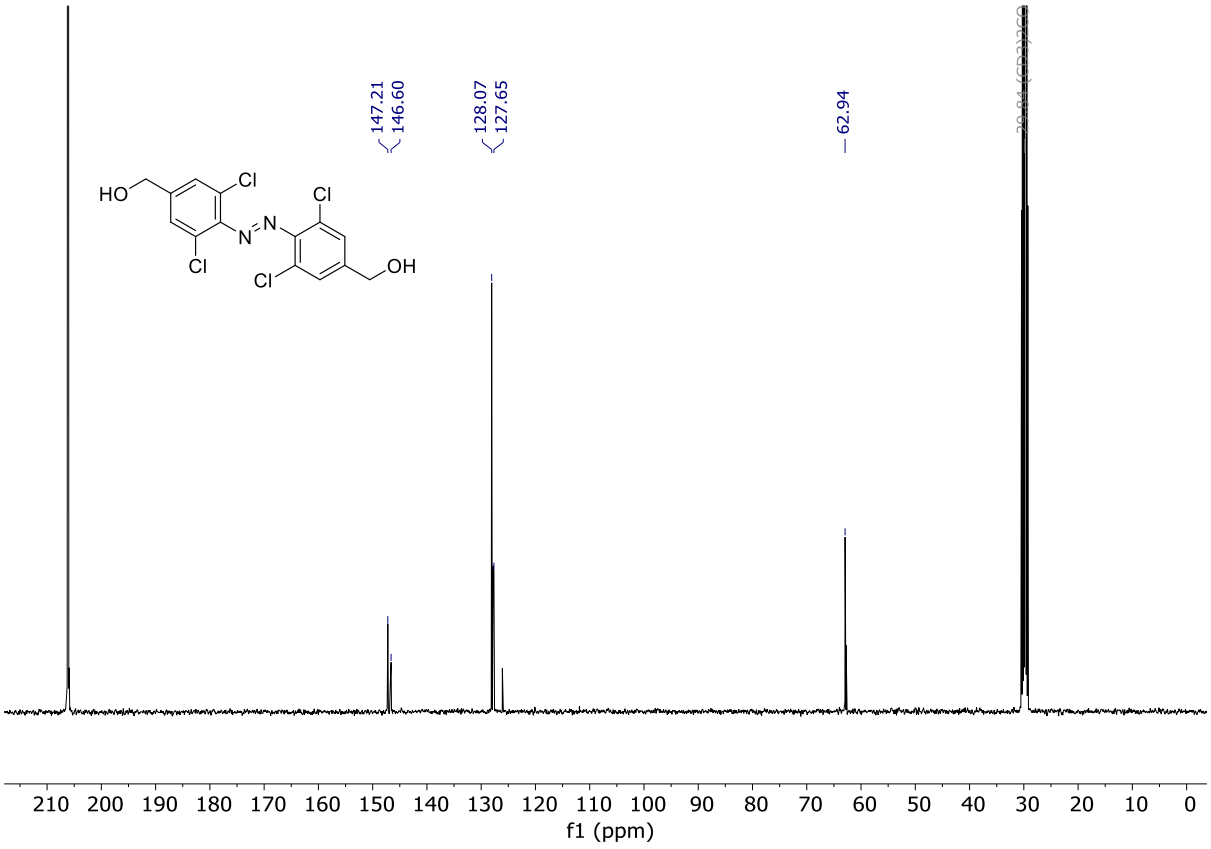


Figure S7. [13]C NMR spectrum of **6** (acetone-d_6, 298 K).

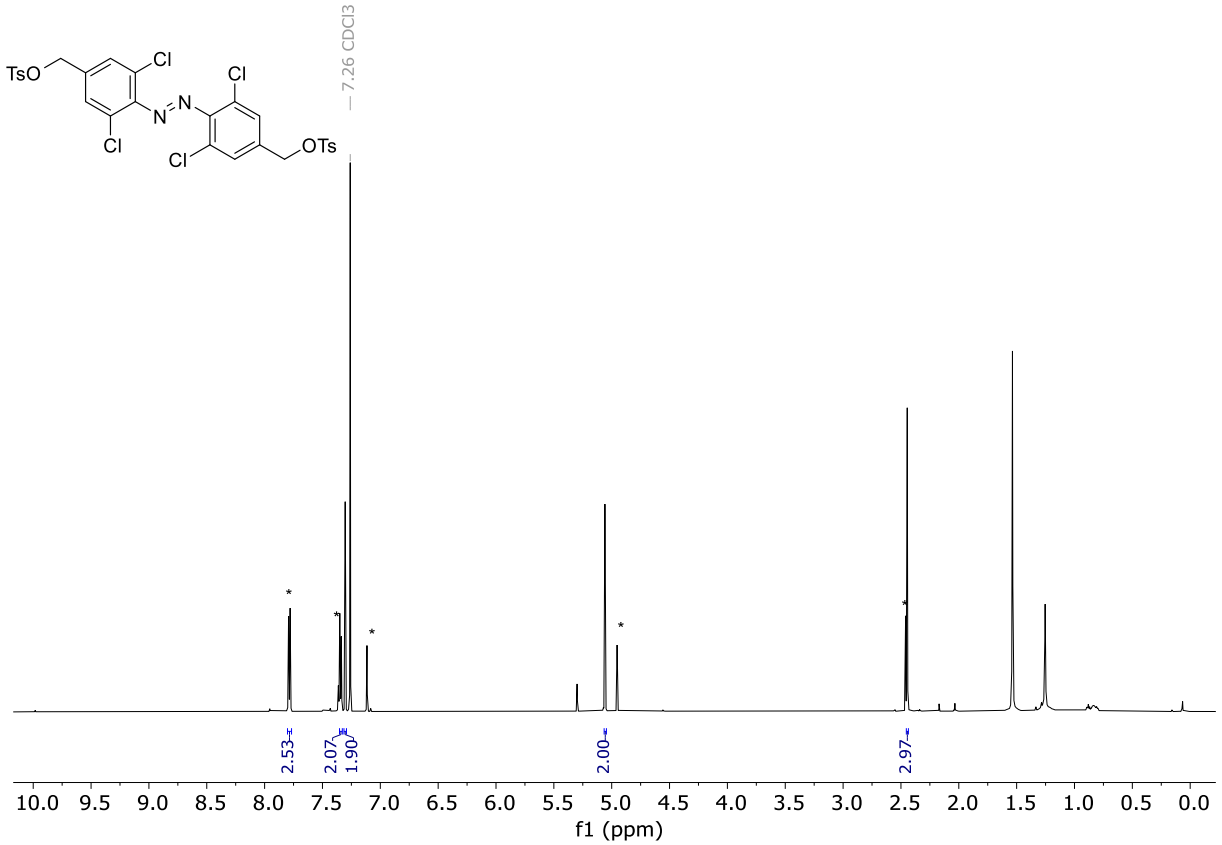


Figure S8. [1]H NMR spectrum of **7** (Chloroform-*d*, 298 K). **7** **Z** signals labelled as *

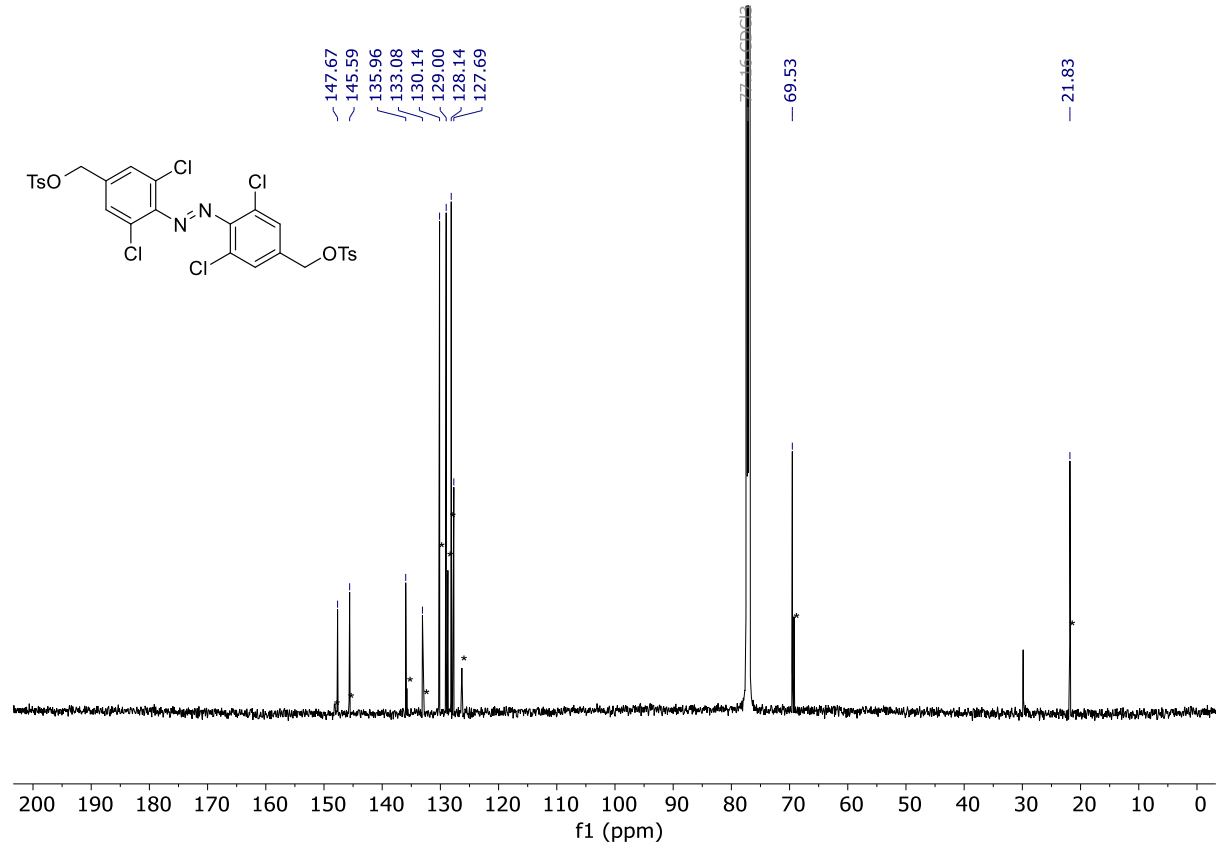


Figure S9. [13]C NMR spectrum of **7** (Chloroform-*d*, 298 K). **7** **Z** signals labelled as *

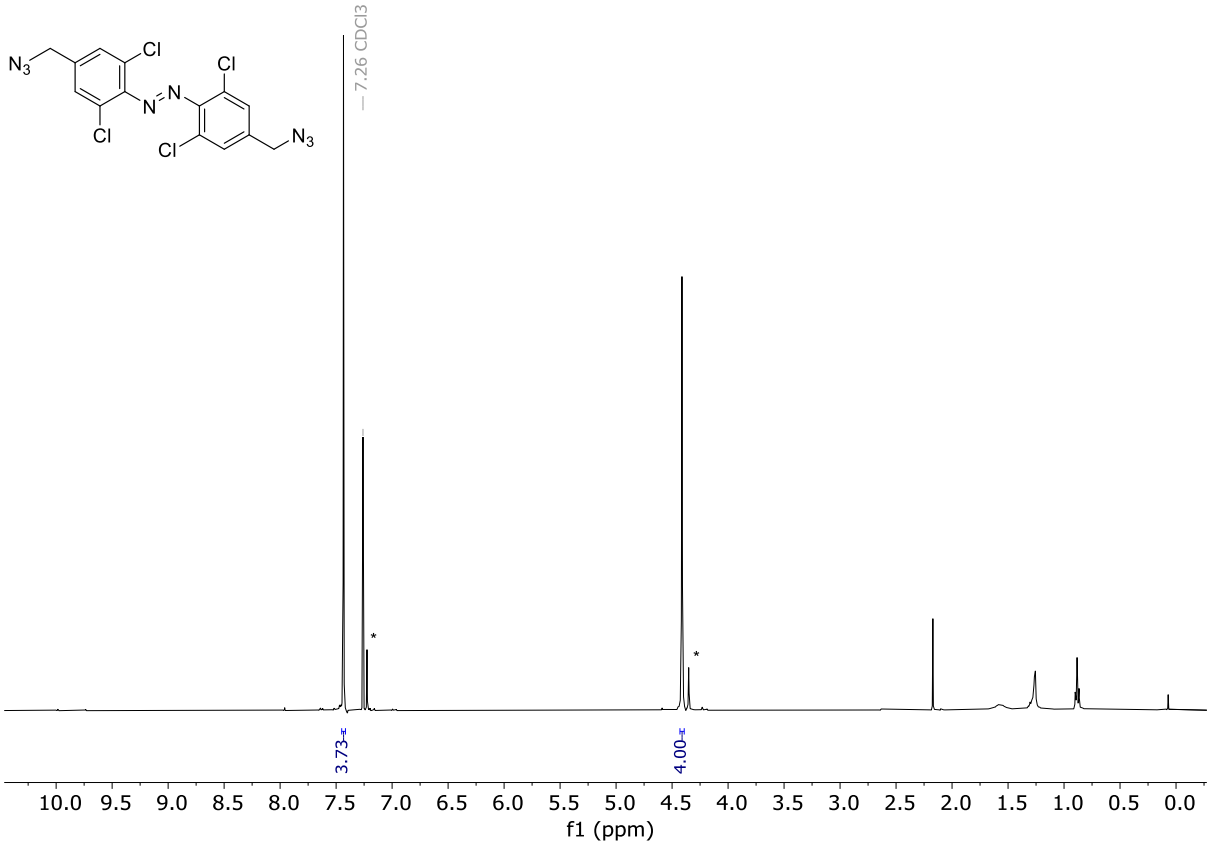


Figure S10. ^{1}H NMR spectrum of **8** (Chloroform-*d*, 298 K). **8**$^{\mathbf{Z}}$ signals labelled as *

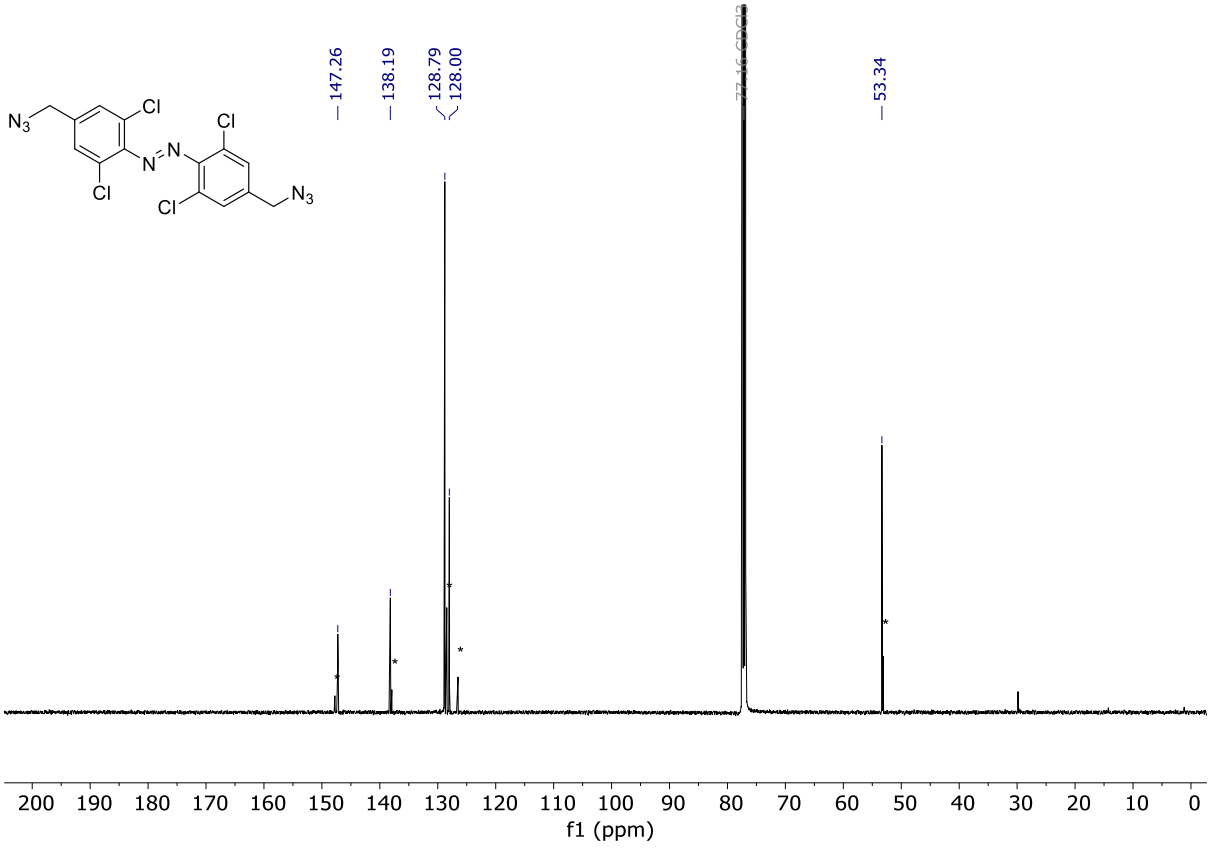


Figure S11. ^{13}C NMR spectrum of **8** (Chloroform-*d*, 298 K). **8**$^{\mathbf{Z}}$ signals labelled as *

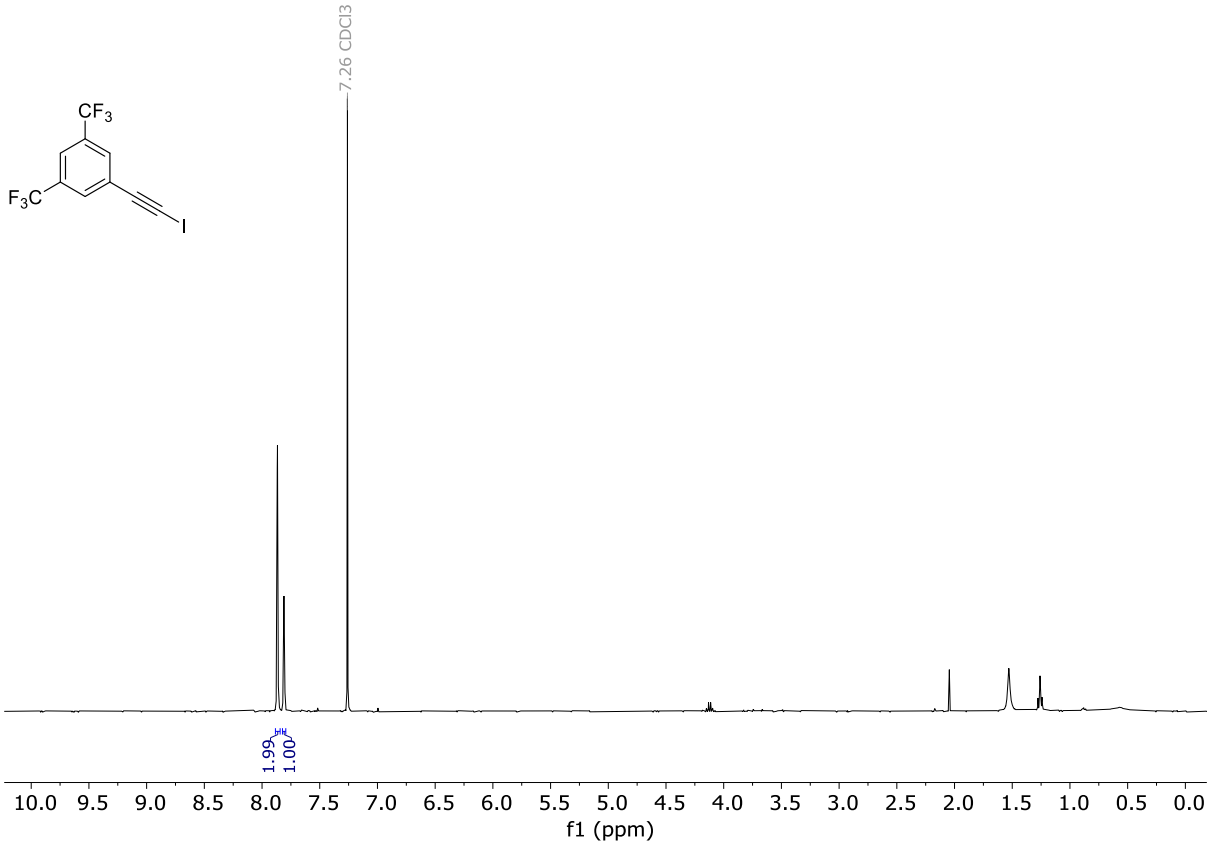


Figure S12. ^{1}H NMR spectrum of **9** (Chloroform-*d*, 298 K).

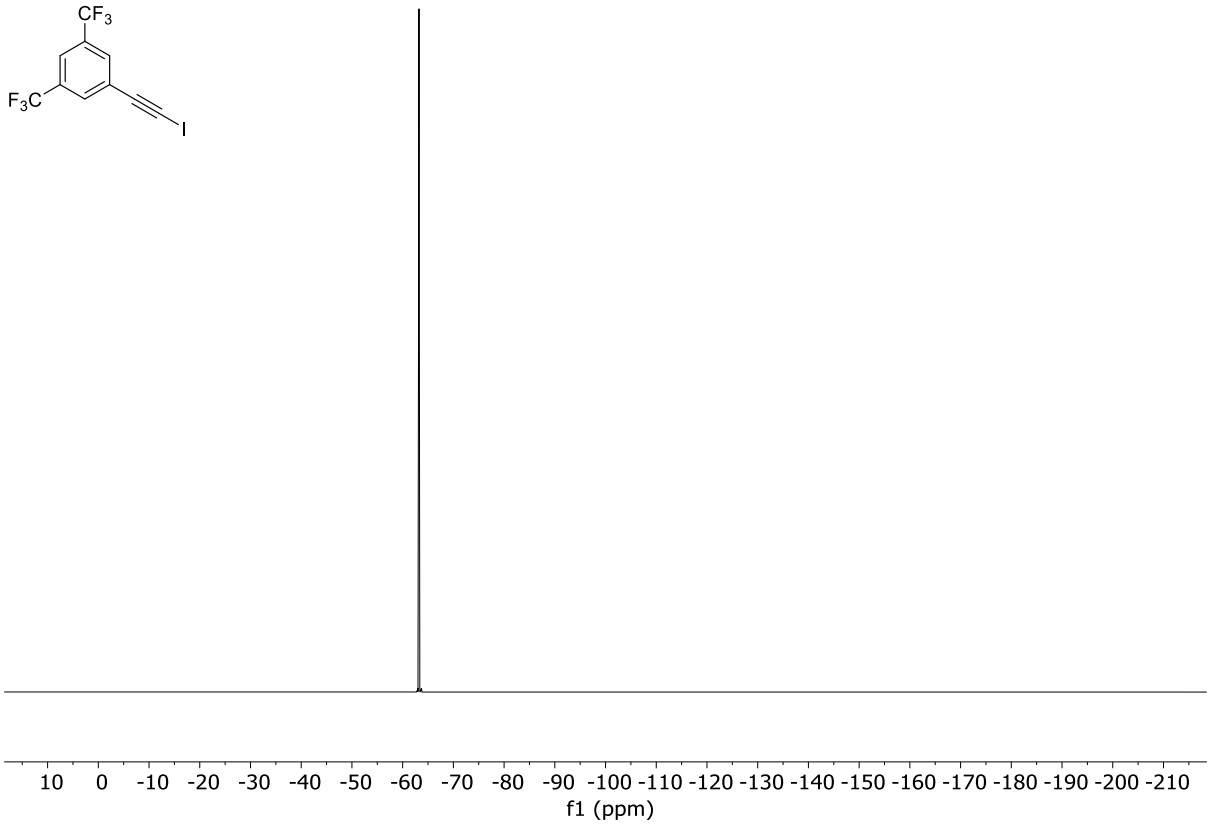


Figure S13. ^{19}F NMR spectrum of **9** (Chloroform-*d*, 298 K).

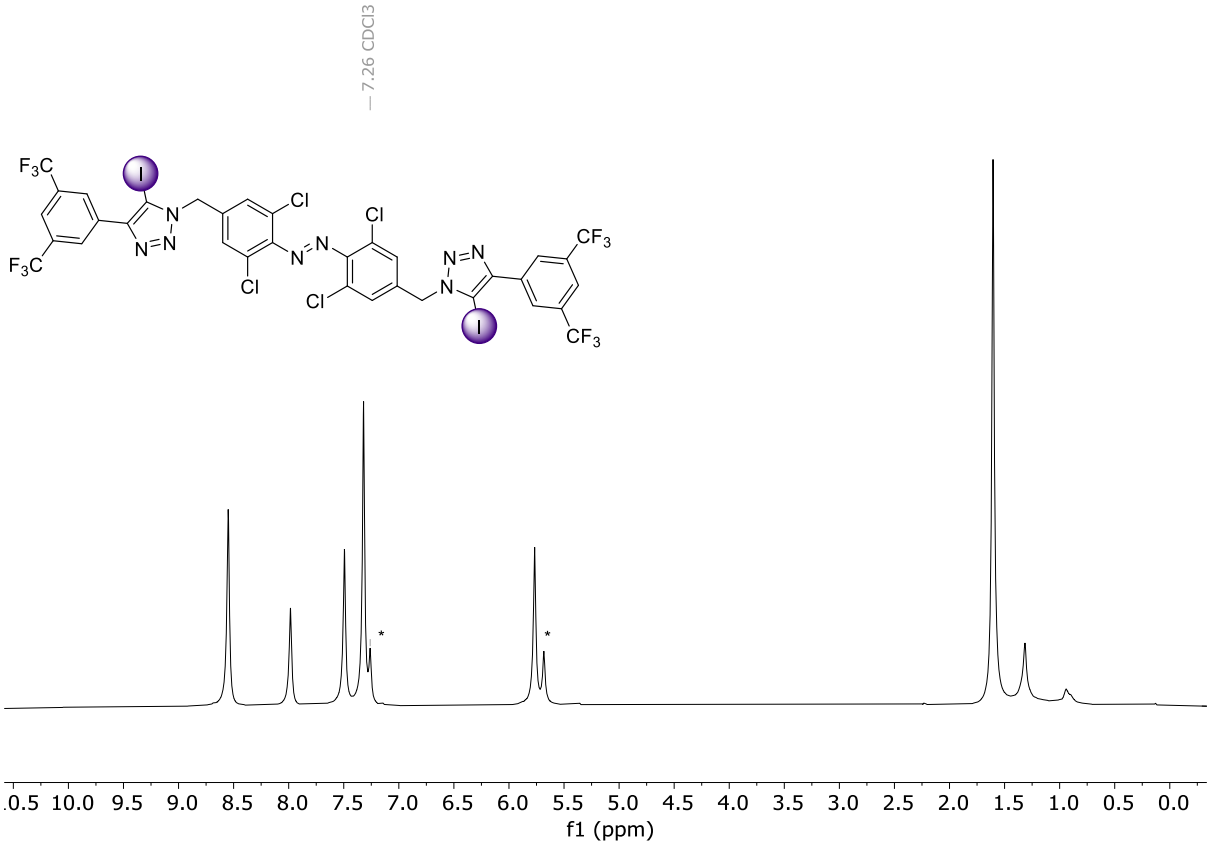


Figure S14. ^{1}H NMR spectrum of **1** (Chloroform-*d*, 298 K). **1^{Z}** signals labelled as *

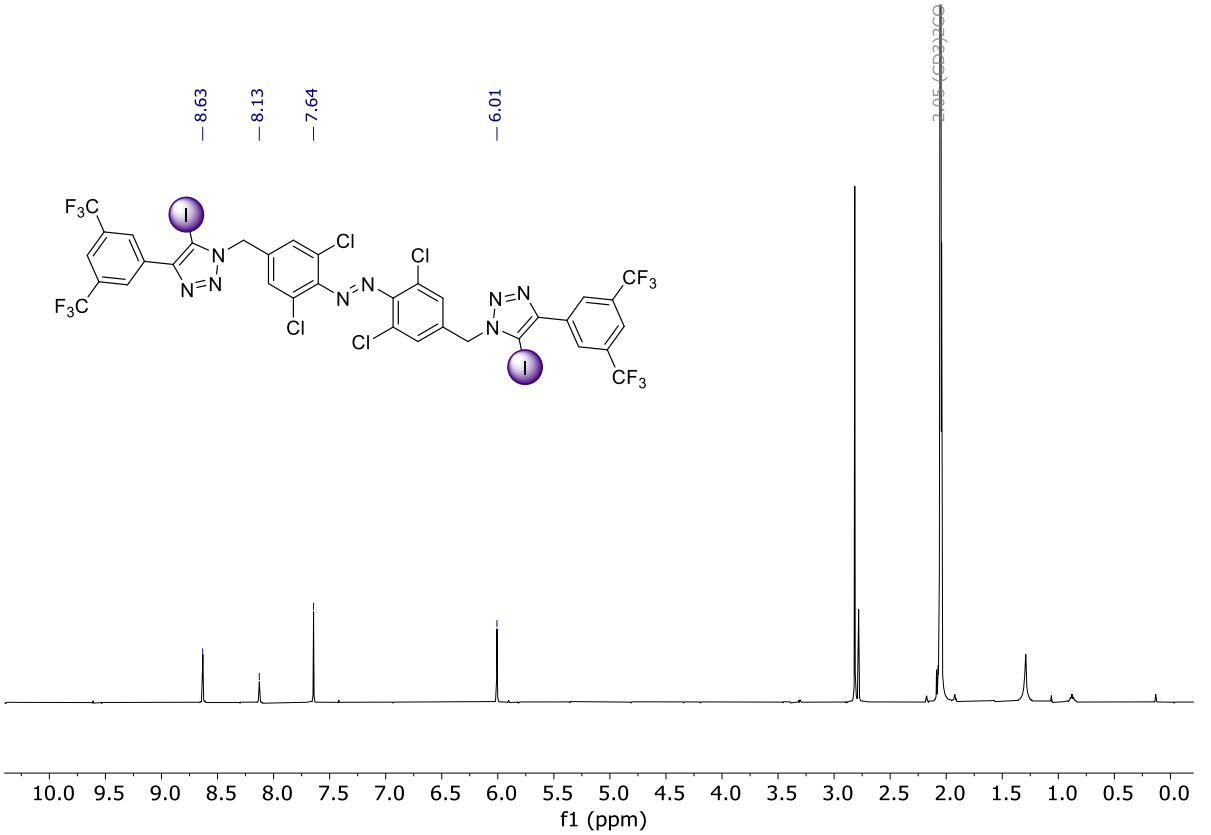


Figure S15. ^{1}H NMR spectrum of **1** (Acetone-d_6, 298 K).

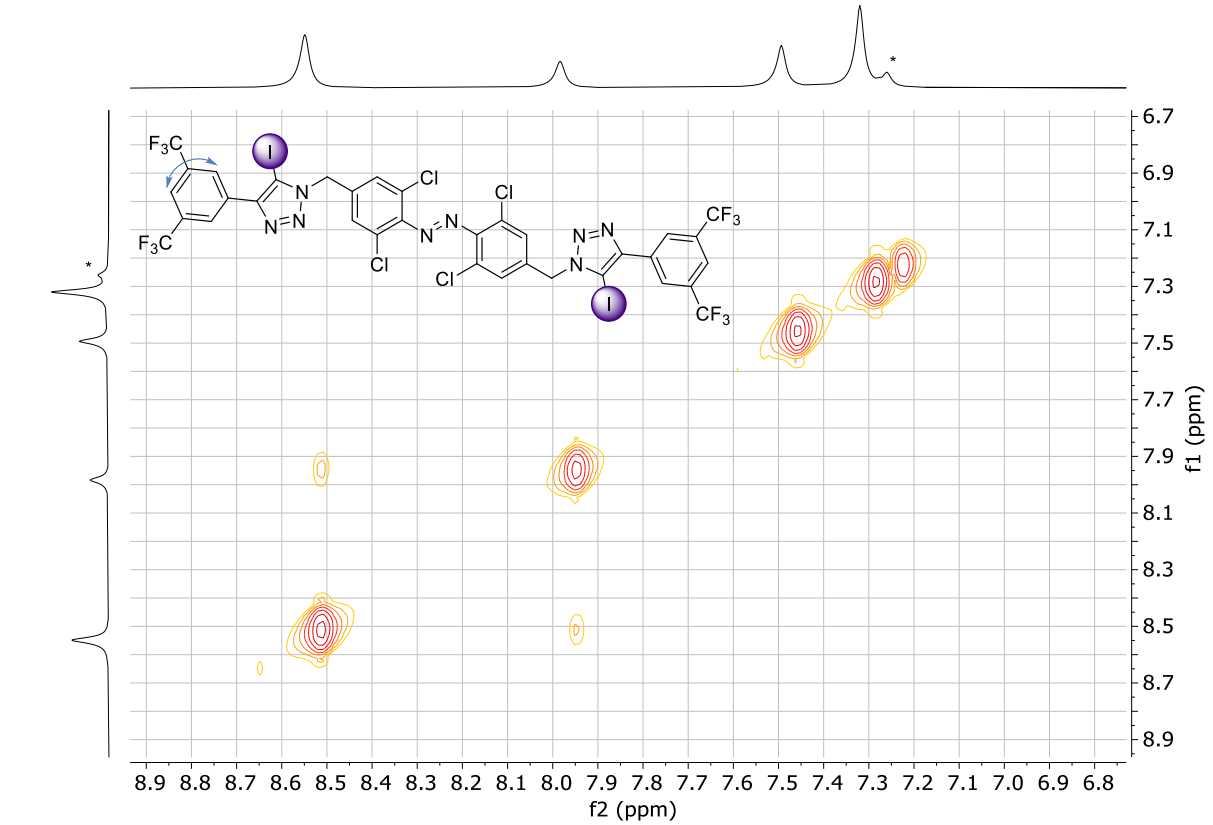


Figure S16. COSY NMR spectrum of **1** (Chloroform-*d*, 298 K). $\mathbf{1}^{\mathbf{Z}}$ signals labelled as *

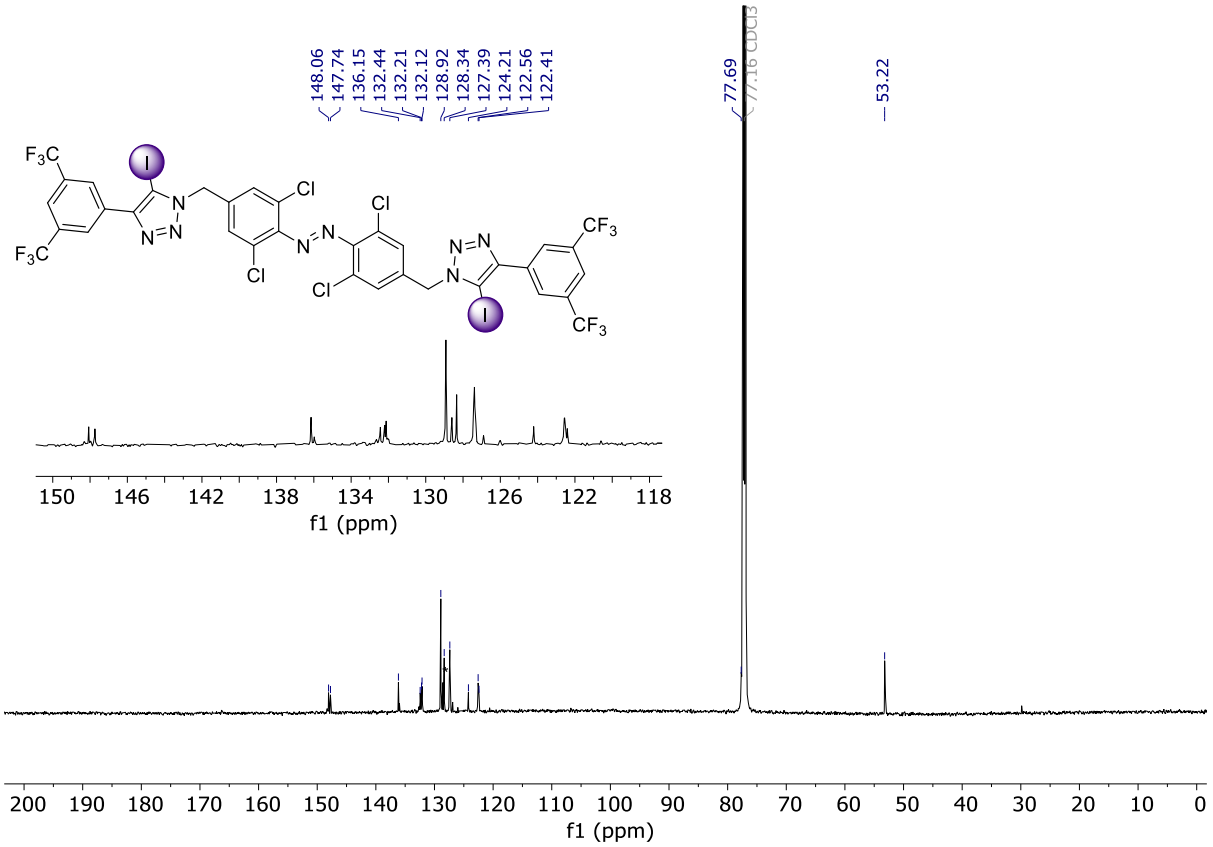


Figure S17. ^{13}C NMR spectrum of **1** (Chloroform-*d*, 298 K).

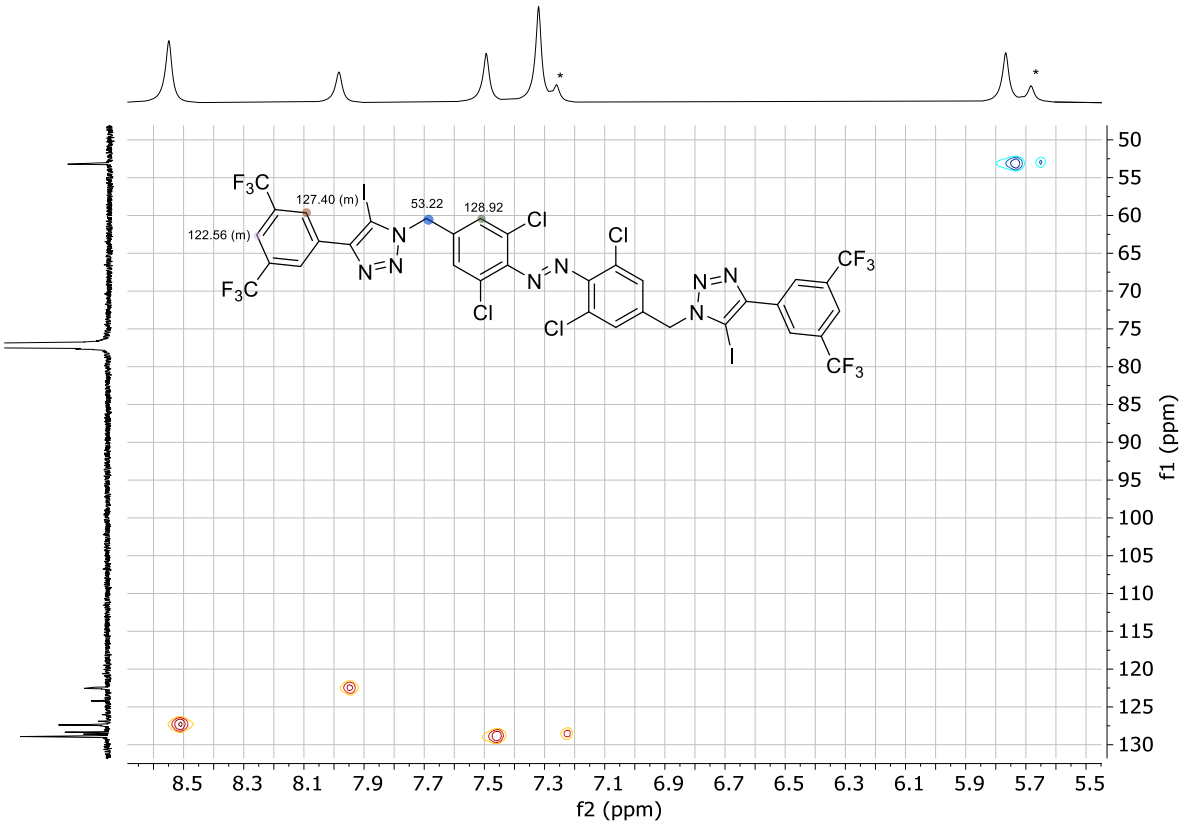


Figure S18. HSQC NMR spectrum of **1** (Chloroform-*d*, 298 K). **1** ^{Z} signals labelled as *

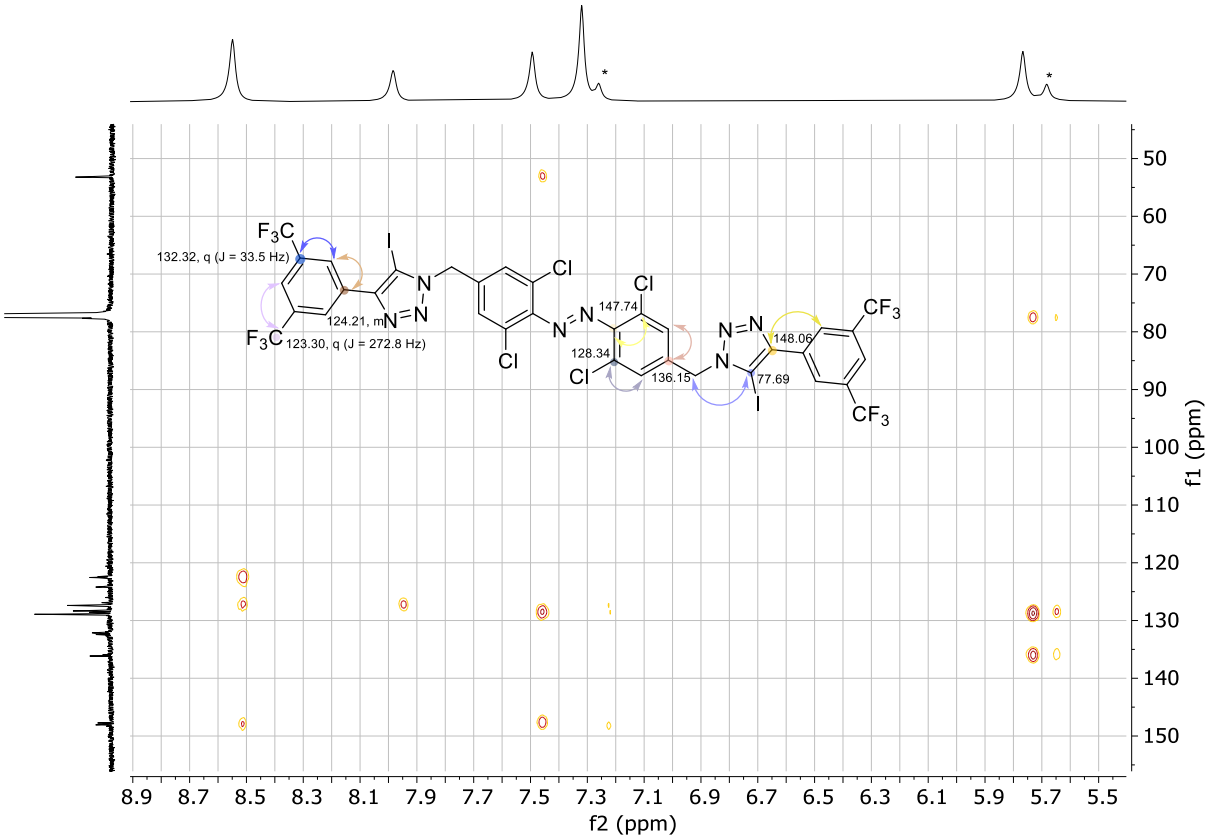


Figure S19. HMBC NMR spectrum of **1** (Chloroform-*d*, 298 K). **1**^{Z} signals labelled as *

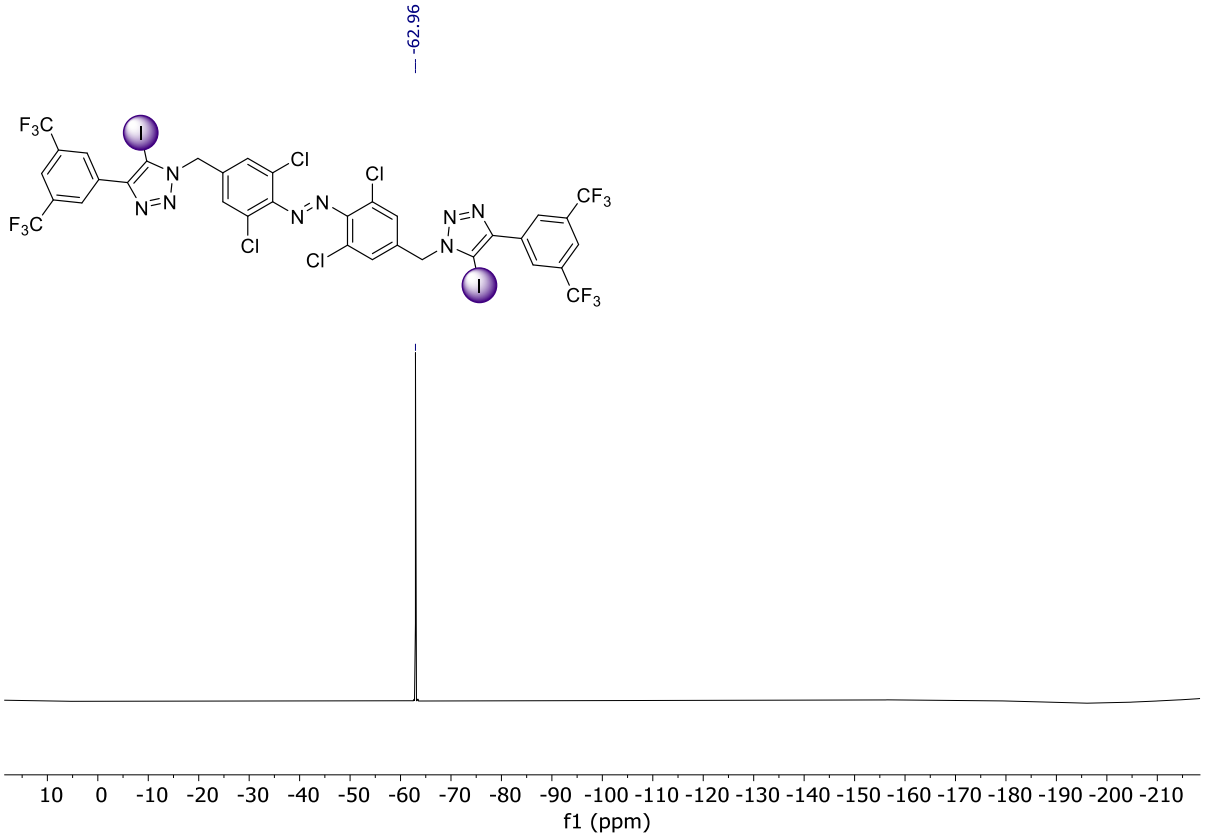


Figure S20. ^{19}F NMR spectrum of **1** (Chloroform-*d*, 298 K).

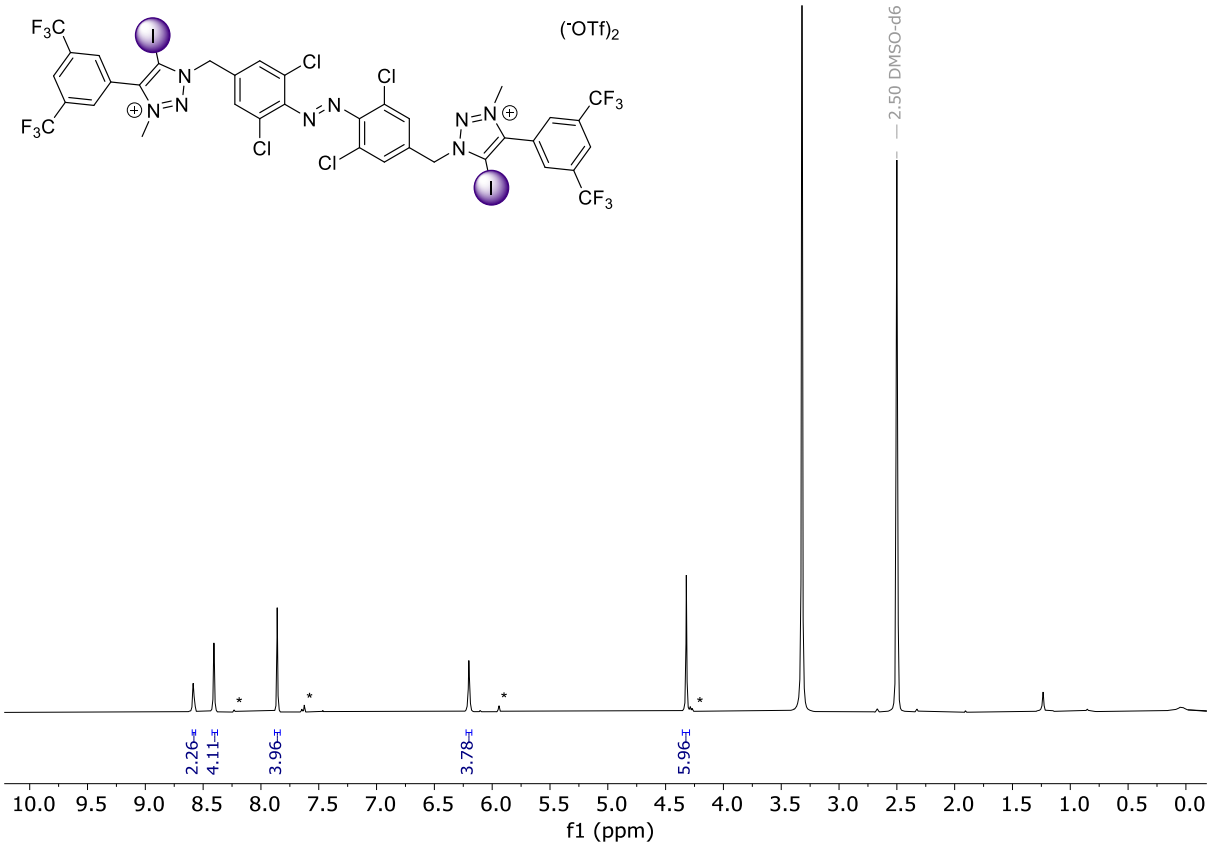


Figure S21. ^{1}H NMR spectrum of **1-Me** (DMSO-d_6, 298 K). **1^{Z}-Me** signals labelled as *

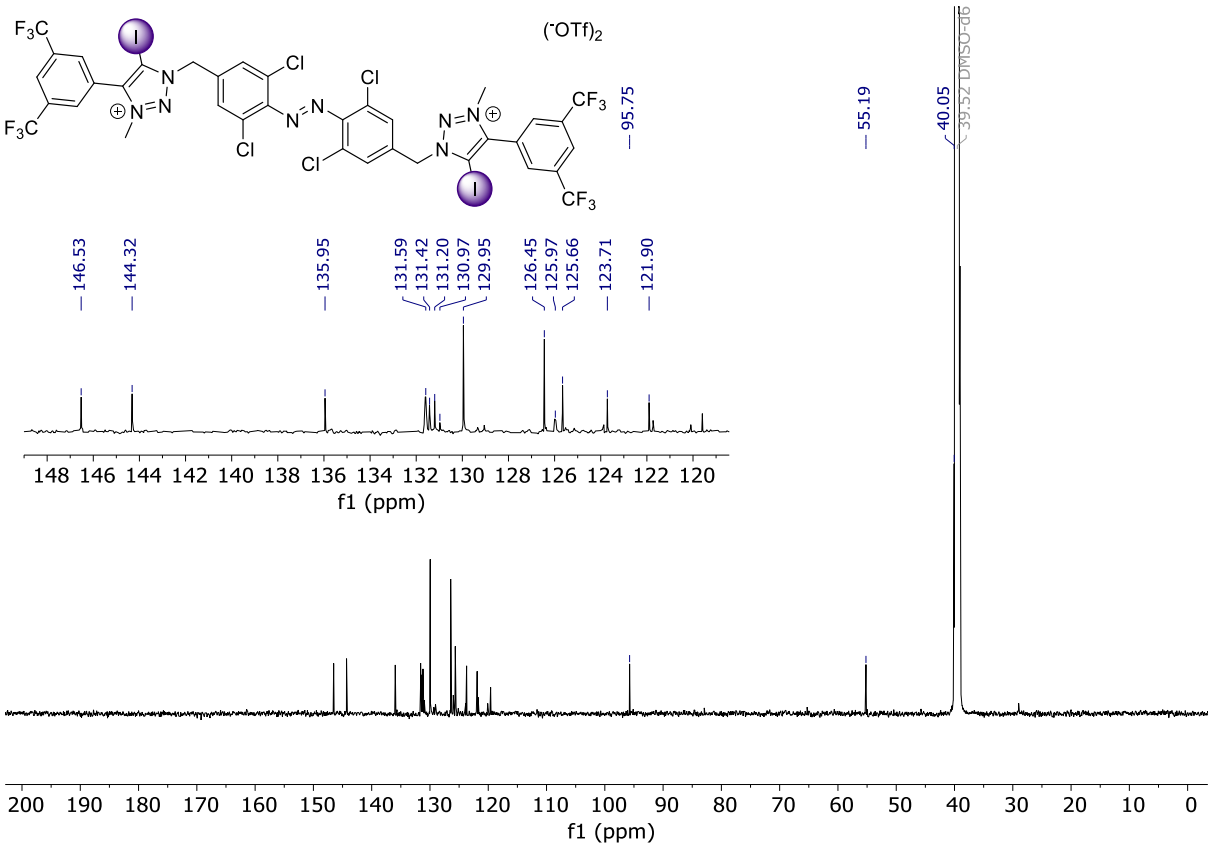


Figure S22. ^{13}C NMR spectrum of **1-Me** (DMSO-d_6, 298 K).

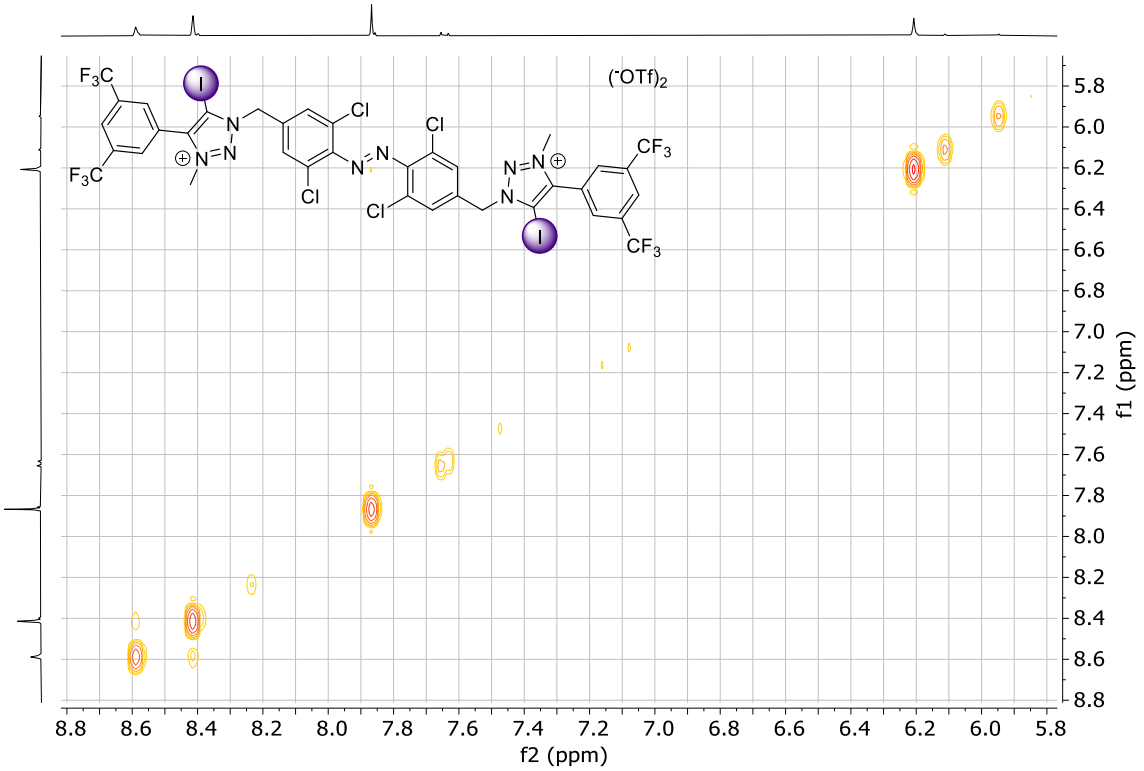


Figure S23. COSY NMR spectrum of **1-Me** (DMSO-d_6, 298 K). **1^{Z}-Me** signals labelled as *

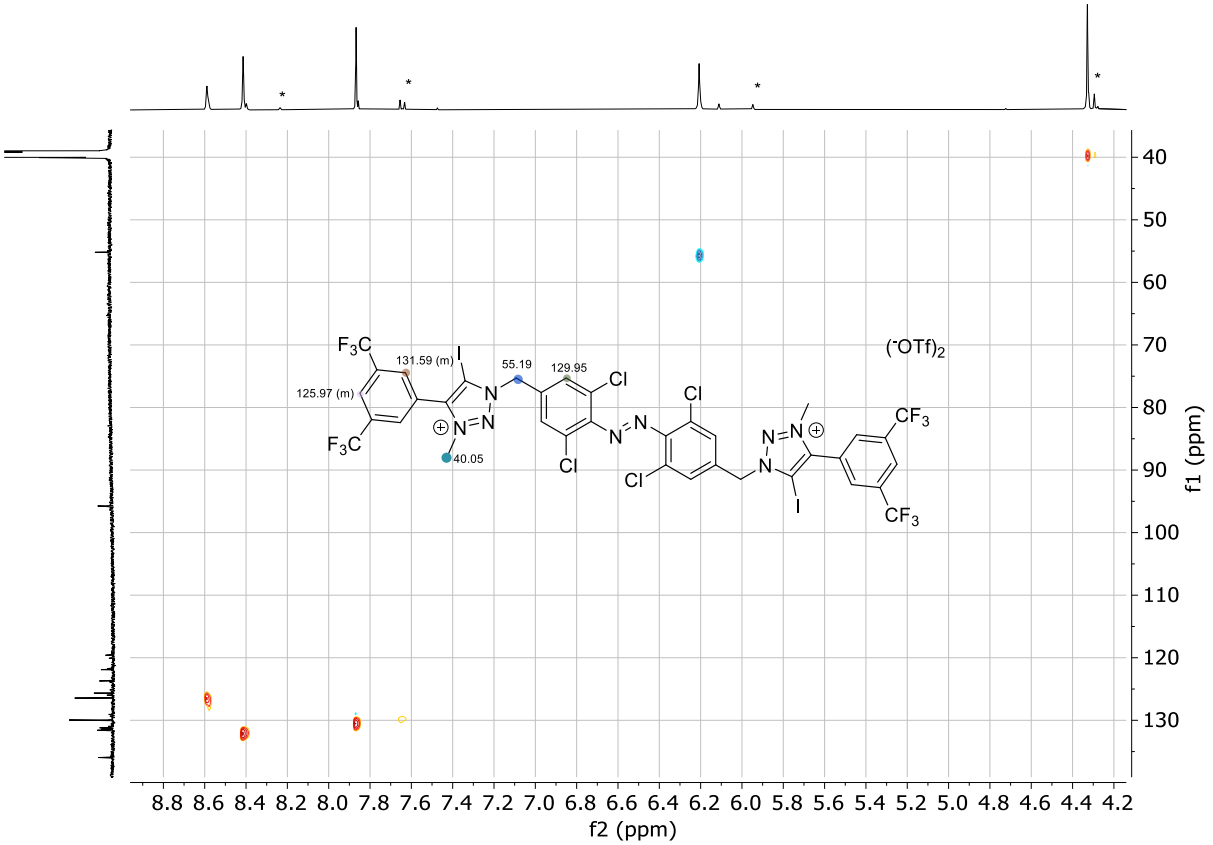


Figure S24. HSQC NMR spectrum of **1-Me** (DMSO-d_6, 298 K). **1^{Z}-Me** signals labelled as *

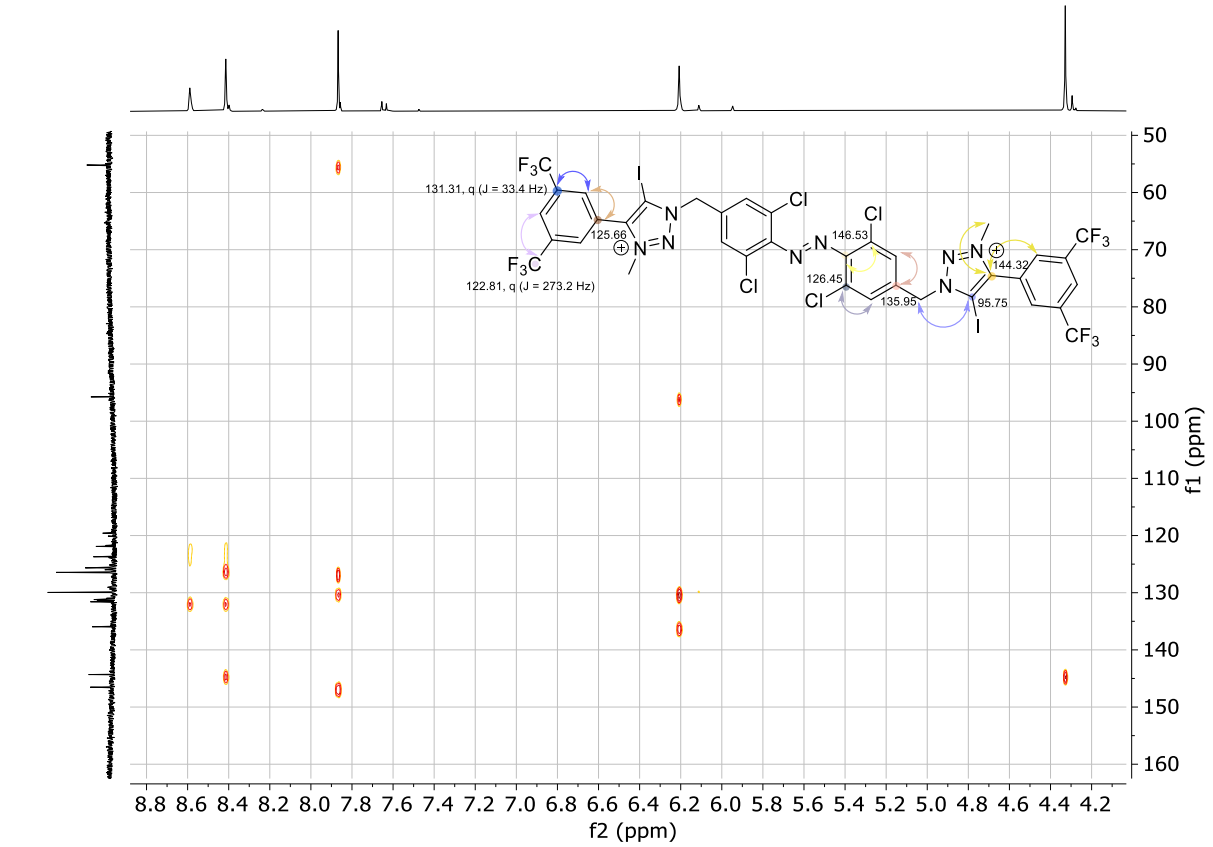


Figure S25. HMBC NMR spectrum of **1-Me** (DMSO-d_6, 298 K). **1^{Z}-Me** signals labelled as *

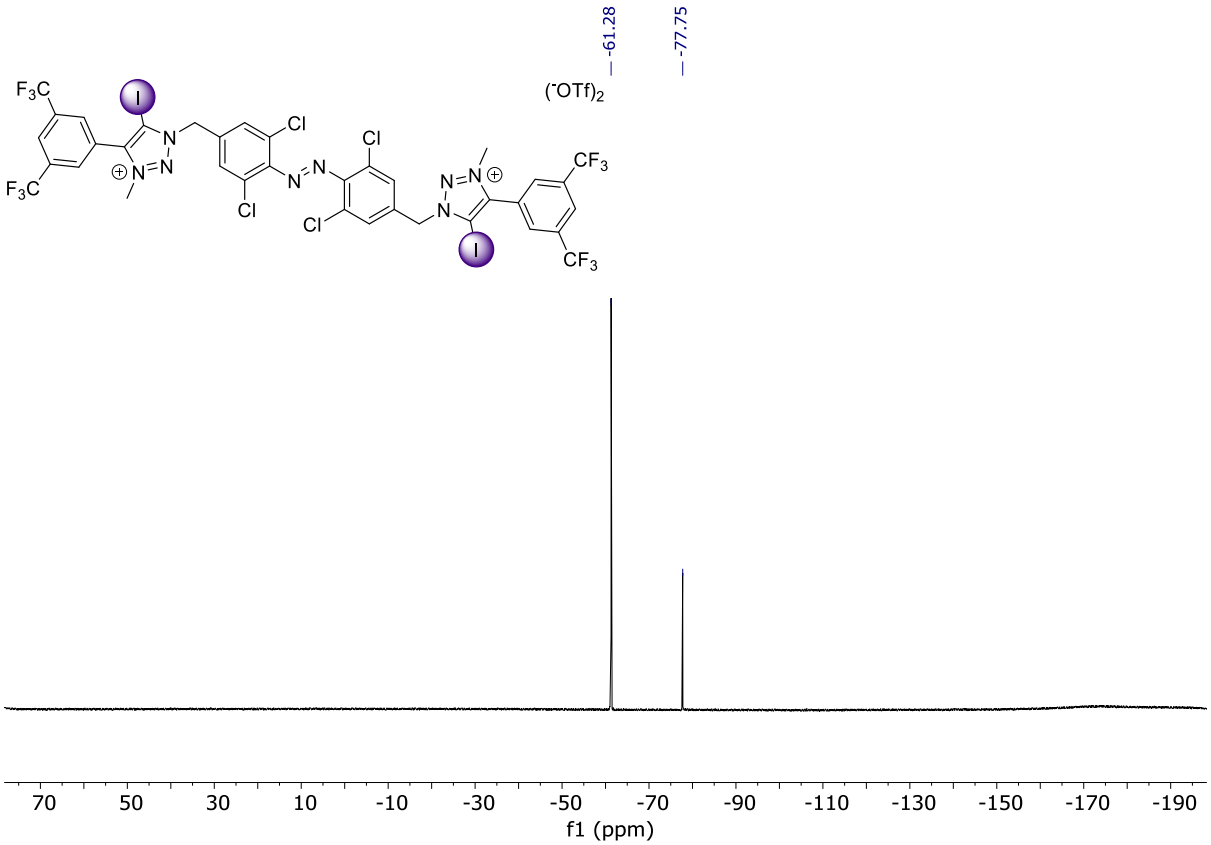


Figure S26. ^{19}F NMR spectrum of **1-Me** (DMSO-d_6, 298 K).

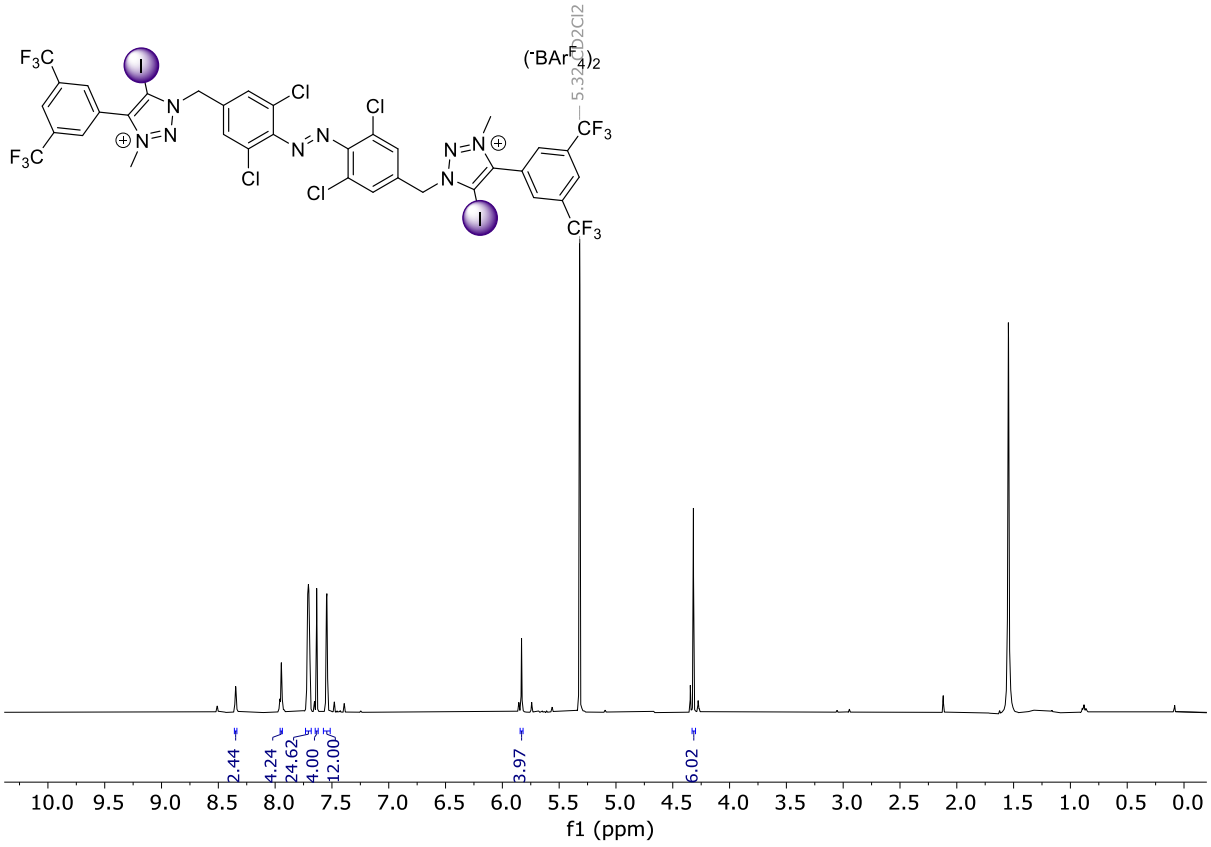


Figure S27. ^{1}H NMR spectrum of **1-Me-BAr$^{F}_{4}$** (CD_2Cl_2, 298 K). **1^{Z}-Me** signals labelled as *

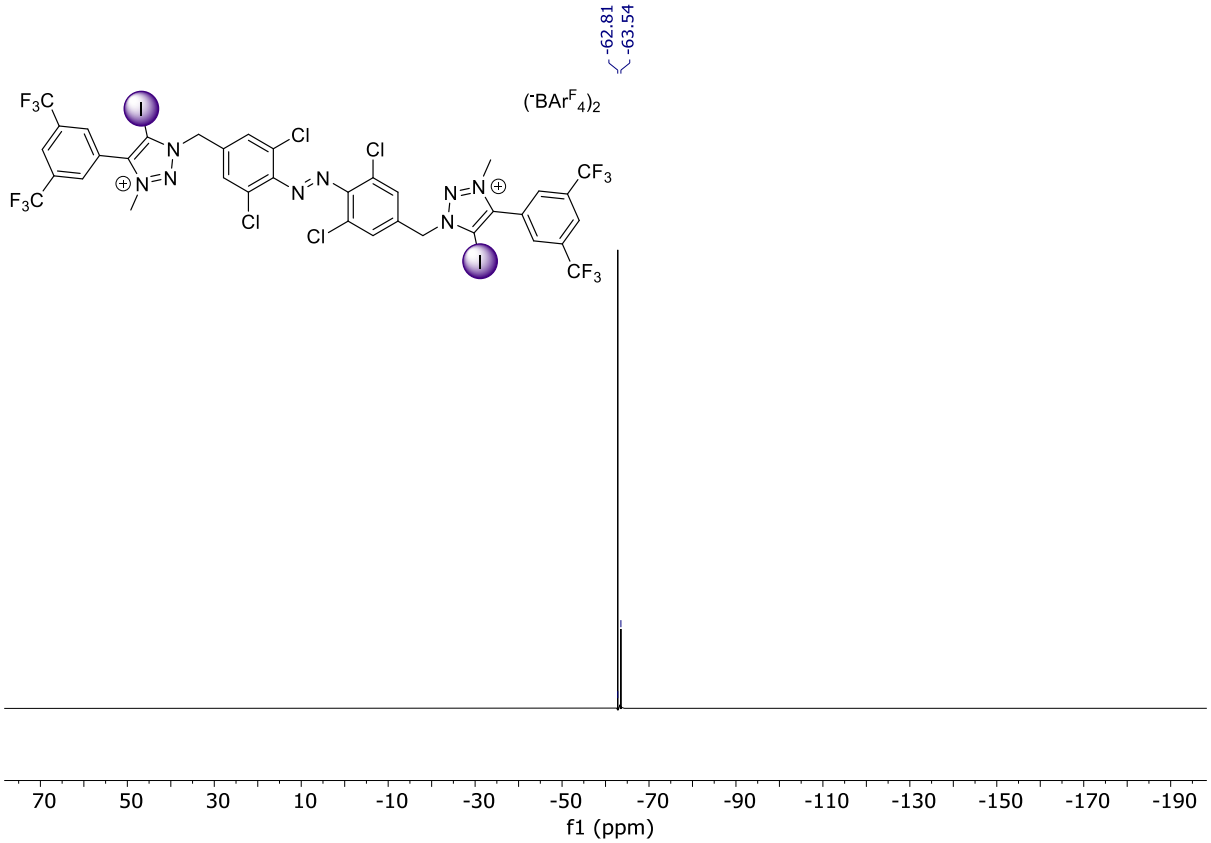


Figure S28. ^{19}F NMR spectrum of **1-Me-BAr$^{F}_{4}$** (CD_2Cl_2, 298 K).

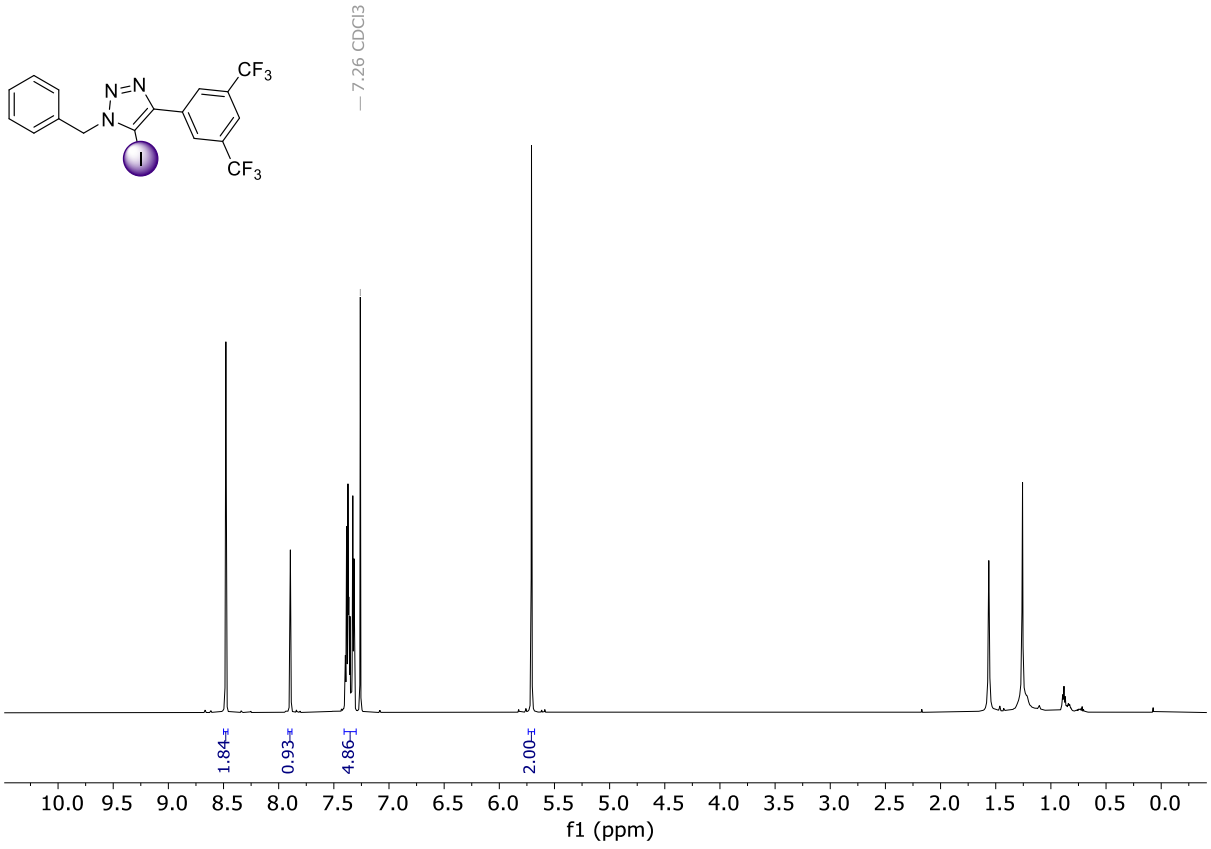


Figure S29. ^{1}H NMR spectrum of **S1** (Chloroform-*d*, 298 K).

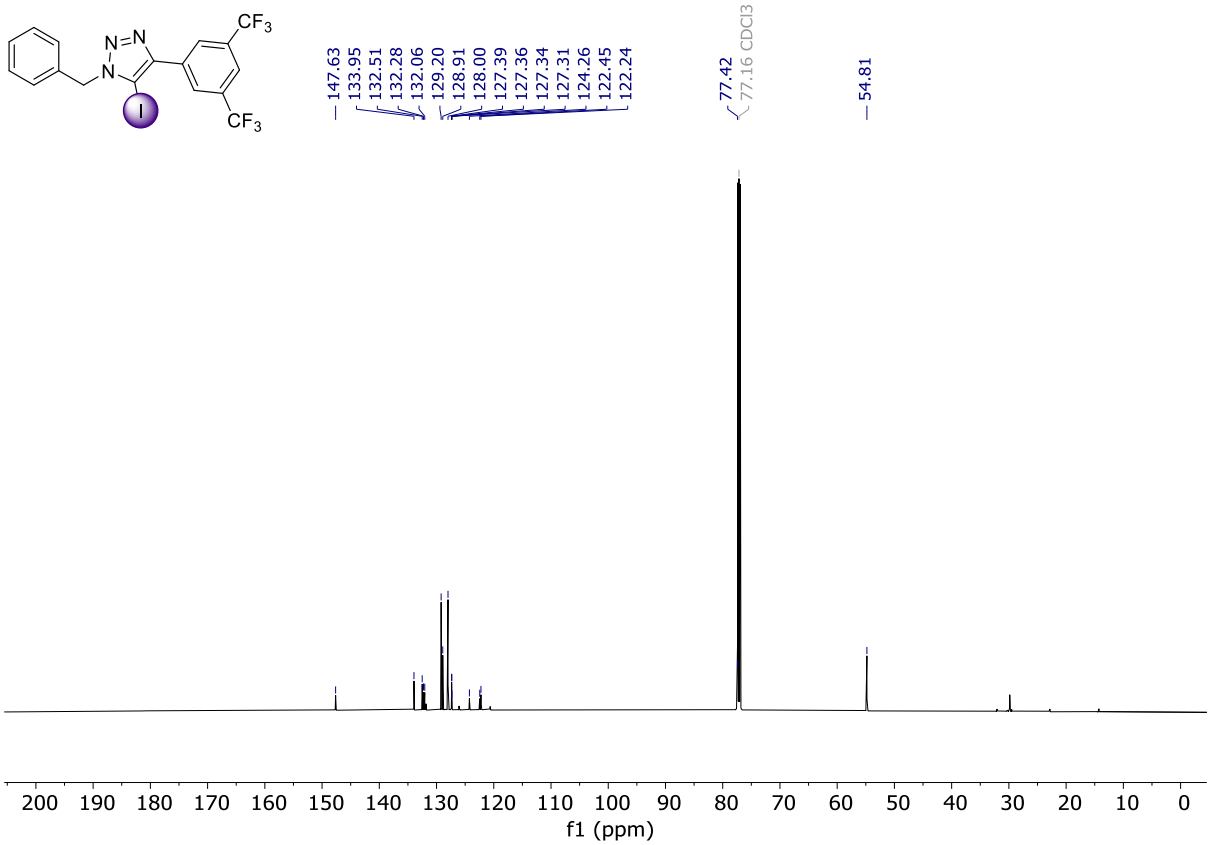


Figure S30. ^{13}C NMR spectrum of **S1** (Chloroform-*d*, 298 K).

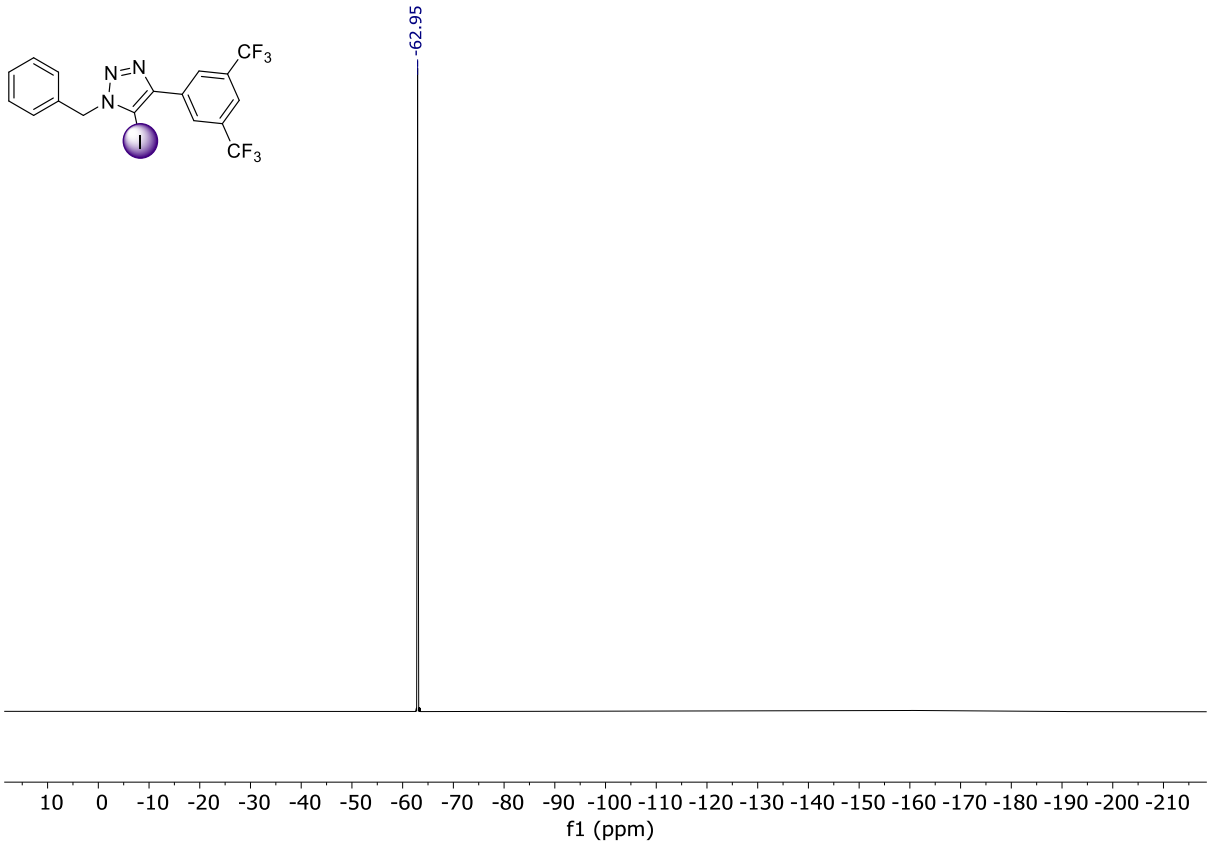


Figure S31. ^{19}F NMR spectrum of **S1**(Chloroform-*d*, 298 K).

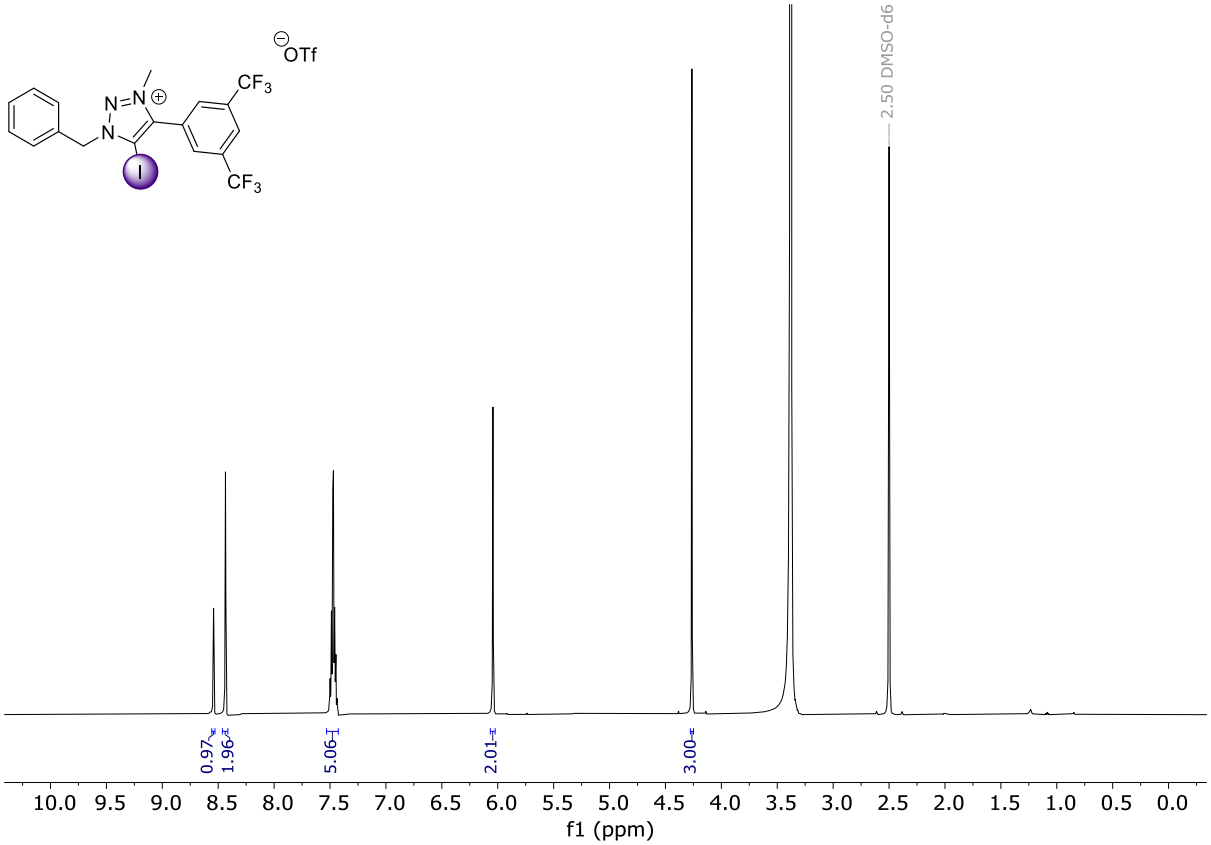


Figure S32. [1]H NMR spectrum of **S1-Me** (DMSO-d_6, 298 K).

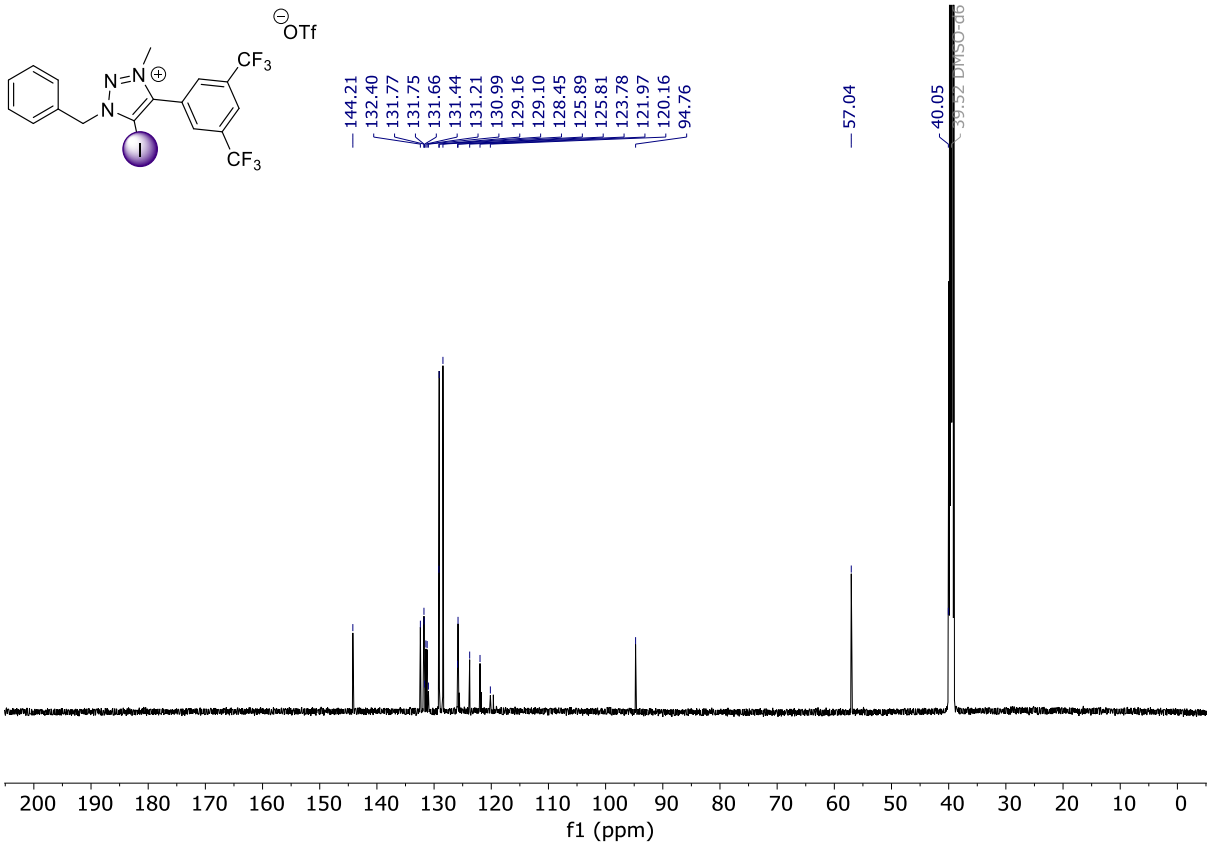


Figure S33. [13]C NMR spectrum of **S1-Me** (DMSO-d_6, 298 K).

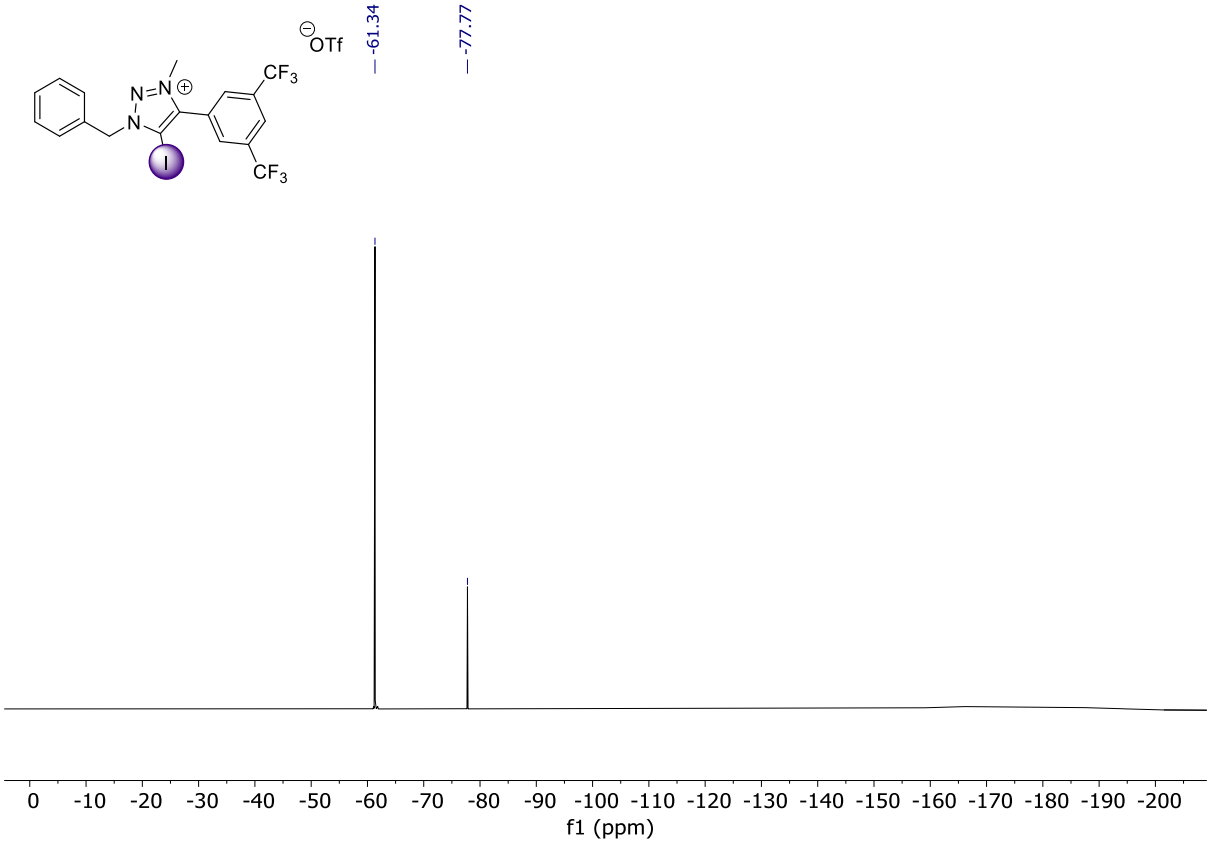


Figure S34. ^{19}F NMR spectrum of **S1-Me** (DMSO-d_6, 298 K).

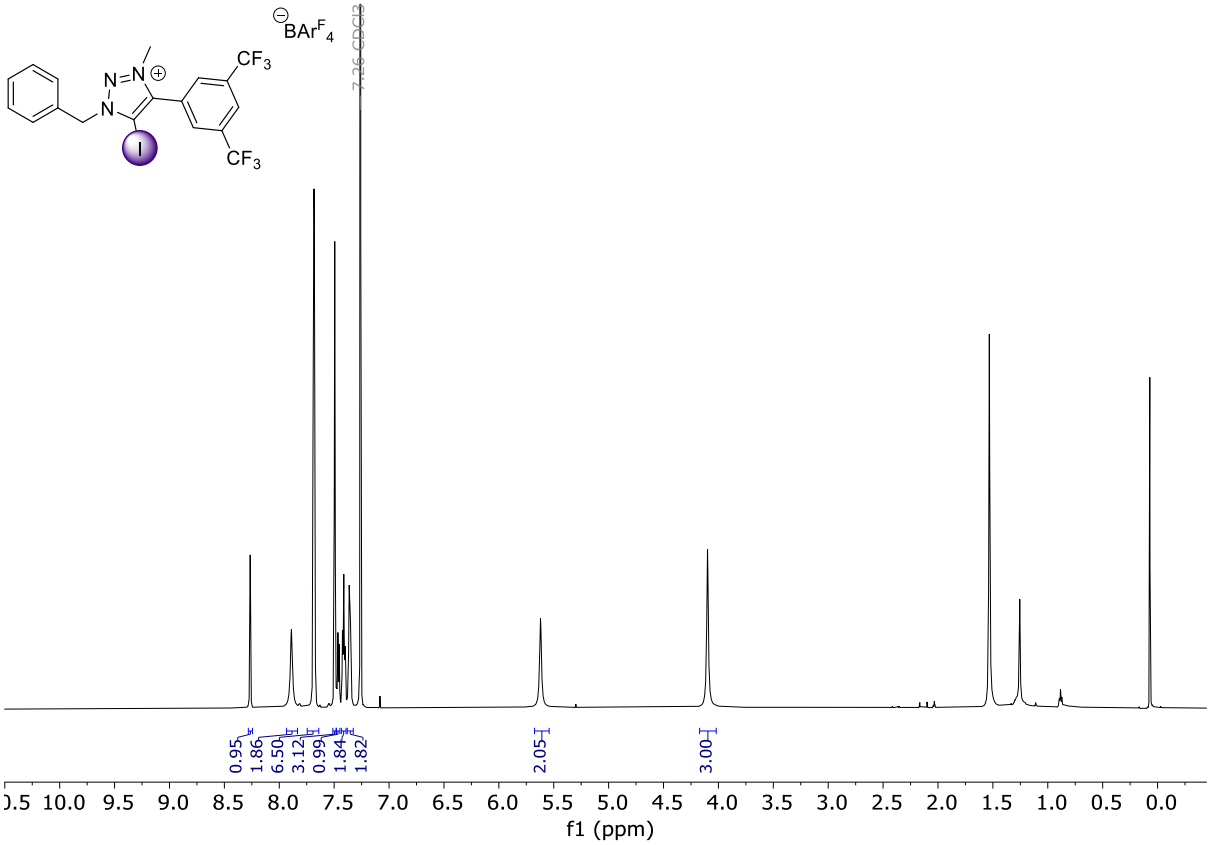


Figure S35. ^{1}H NMR spectrum of **10** (Chloroform-*d*, 298 K).

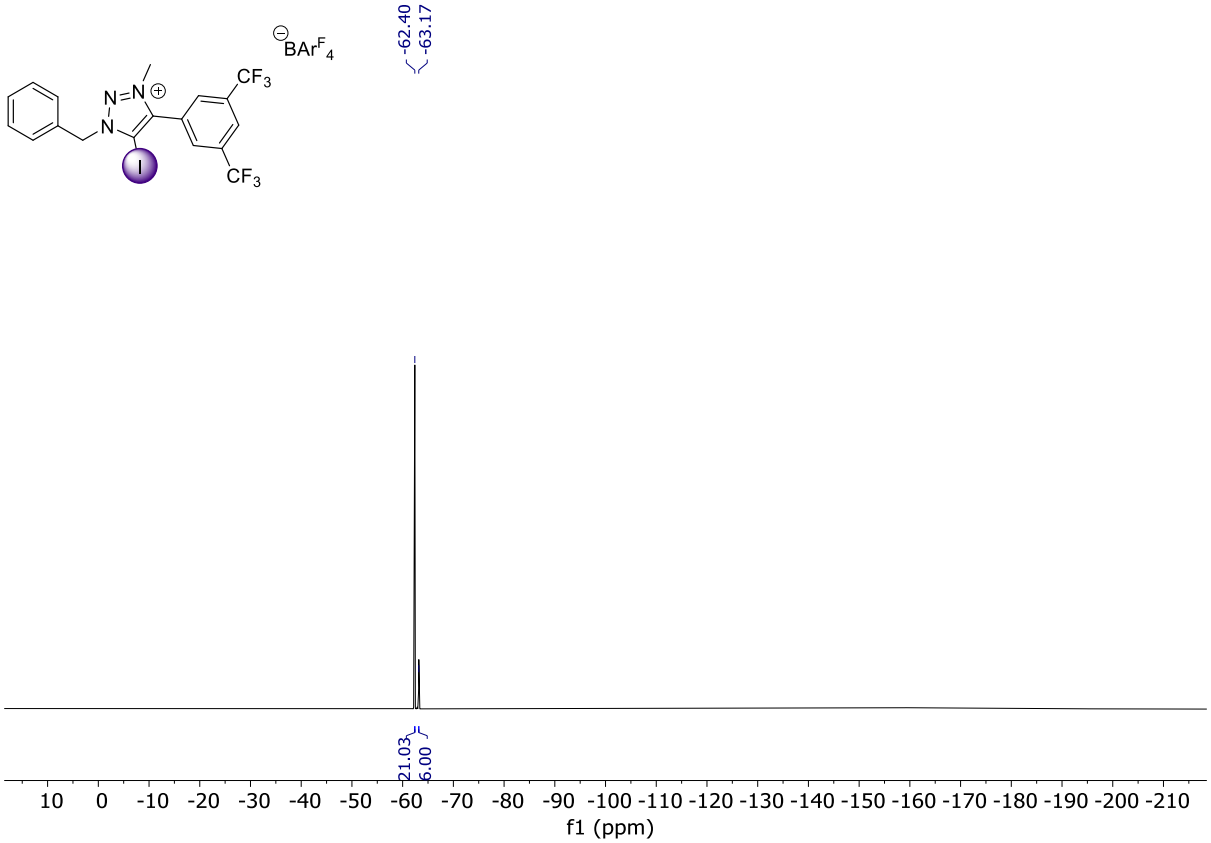


Figure S36. ^{19}F NMR spectrum of **10** (Chloroform-*d*, 298 K).

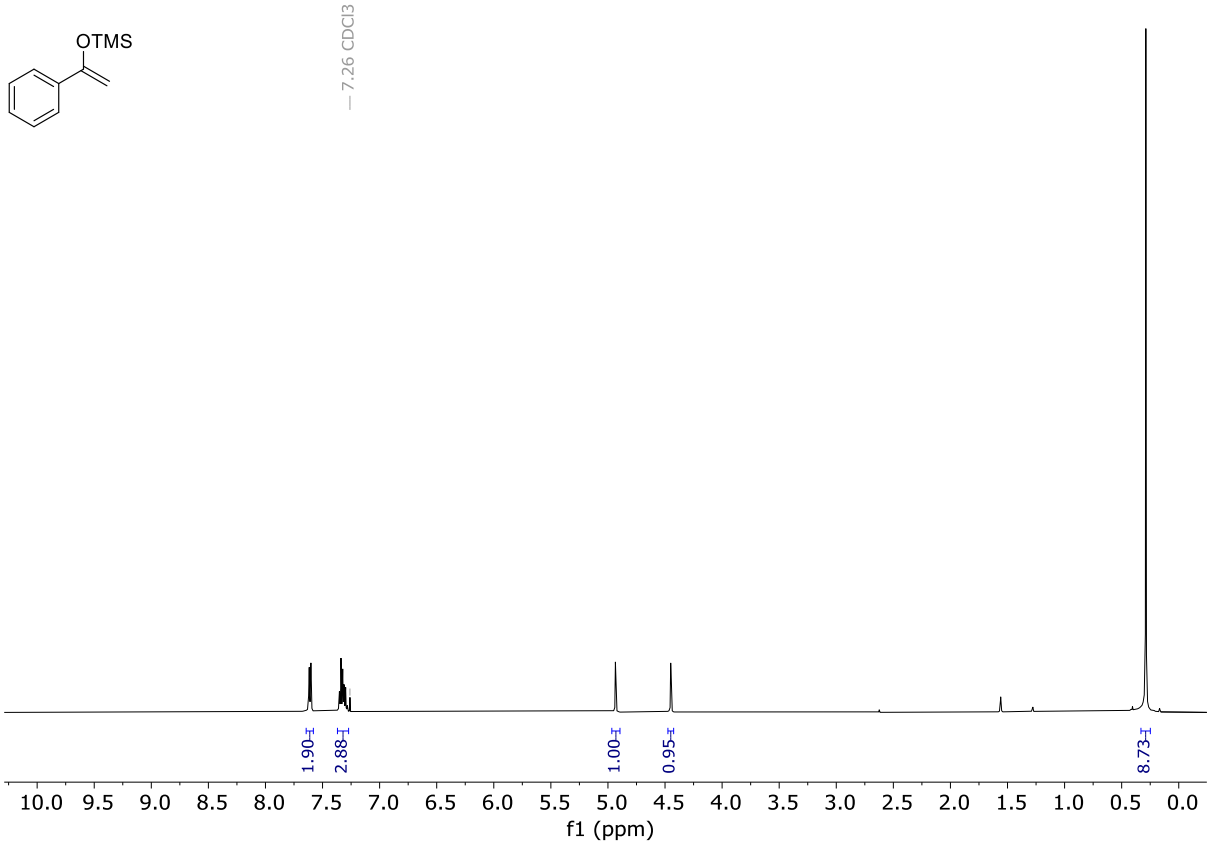


Figure S37. ^{1}H NMR spectrum of **S2** (Chloroform-*d*, 298 K).

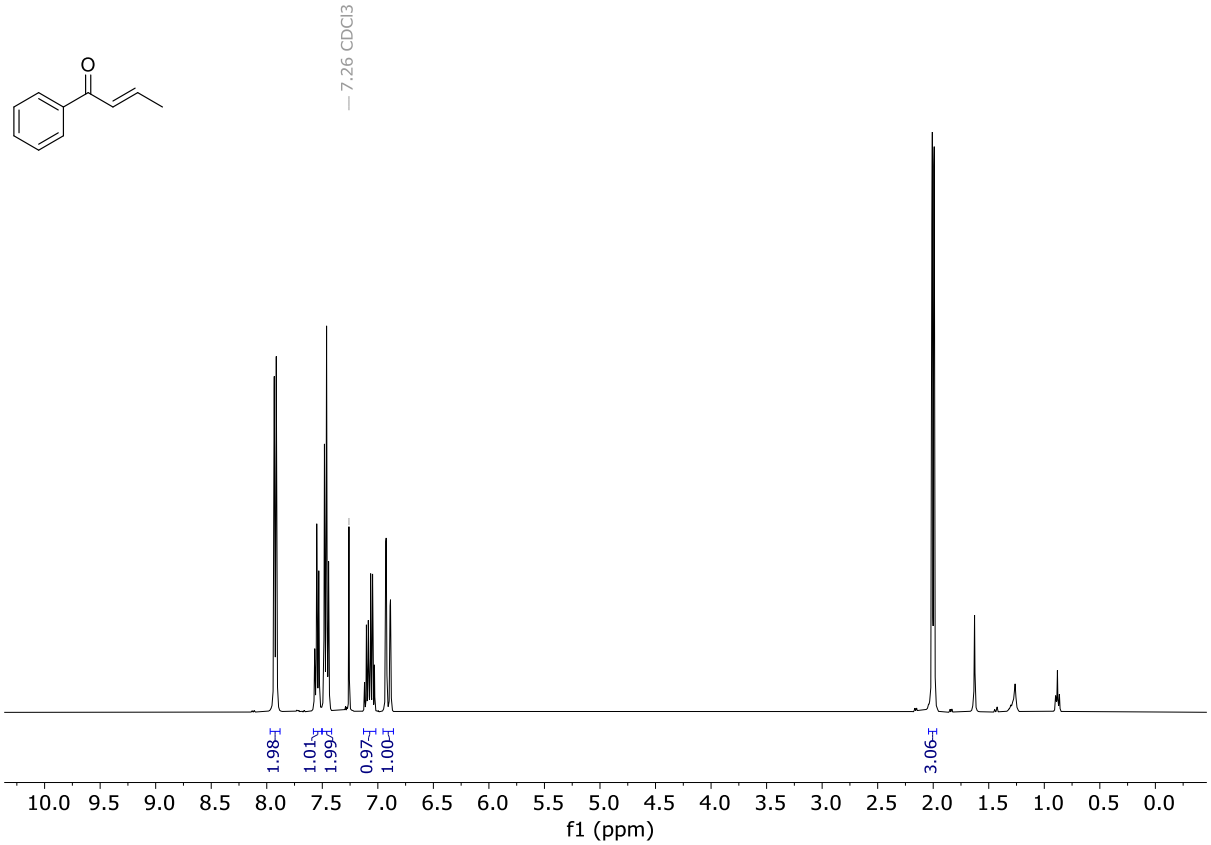


Figure S38. ^{1}H NMR spectrum of **S2** (Chloroform-*d*, 298 K).

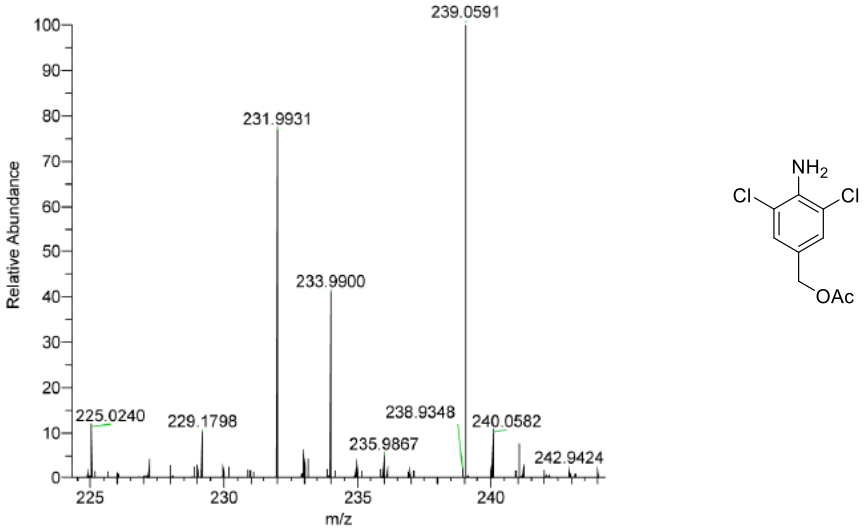
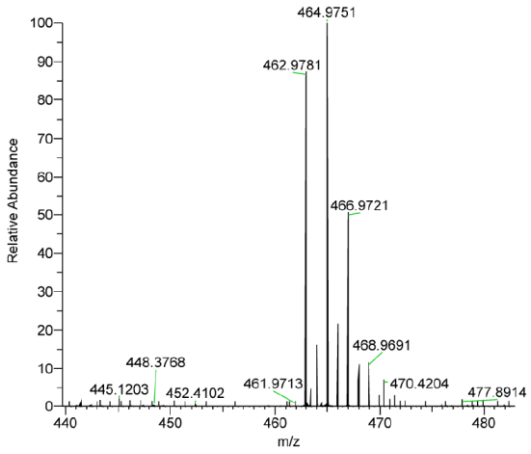


Figure S39. HRMS spectrum of **4**. HRMS-ESI (*m/z*) calculated for $C_9H_{10}Cl_2NO_2^+$ $[M+H]^+$, 231.9938; found 231.9931.



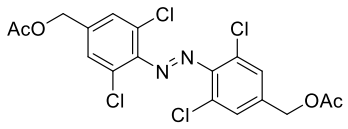
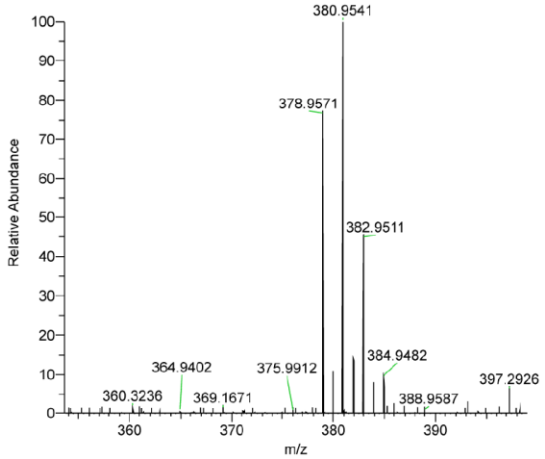


Figure S40. HRMS spectrum of **5**. HRMS-ESI (*m/z*) calculated for $C_{18}H_{15}Cl_4N_2O_4^+$ $[M+H]^+$, 464.9751; found 464.9751.



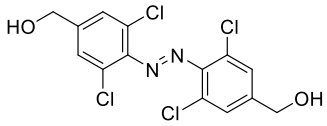
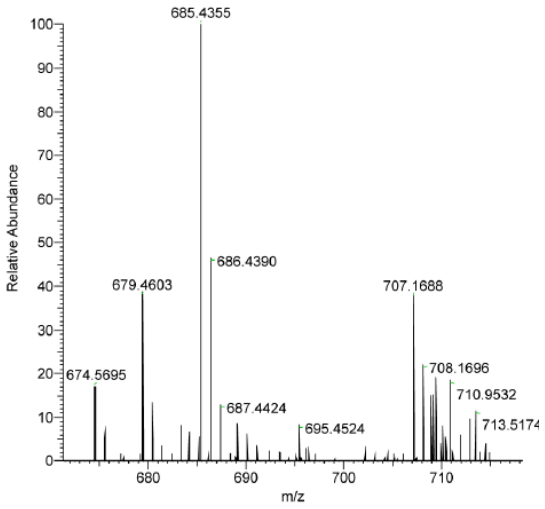


Figure S41. HRMS spectrum of **6**. HRMS-ESI (*m/z*) calculated for $C_{14}H_{11}Cl_4N_2O_2^+$ $[M+H]^+$, 380.9540; found 380.9541.



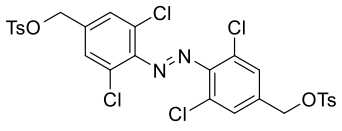
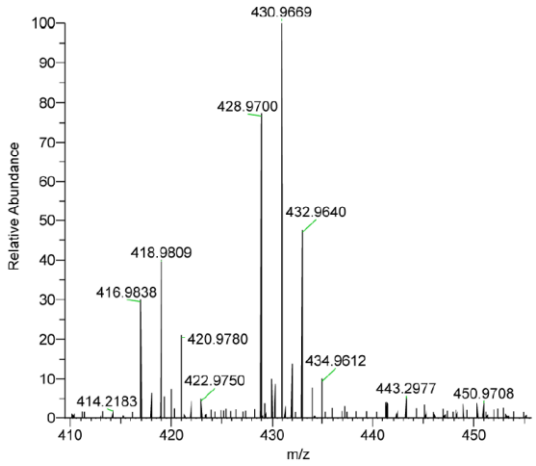


Figure S42. HRMS spectrum of **7**. HRMS-ESI (*m/z*) calculated for $C_{28}H_{23}N_2O_6S_2Cl_4^+$, $[M+H]^+$, 688.9717; found 685.4355.



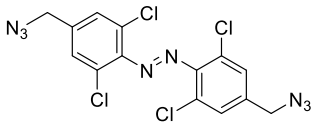
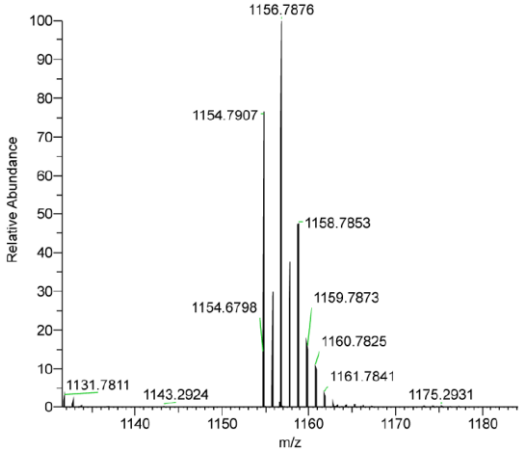


Figure S43. HRMS spectrum of **8**. HRMS-ESI (*m/z*) calculated for $C_{14}H_9Cl_4N_8$ $[M+H]^+$, 428.9699; found 428.9700.



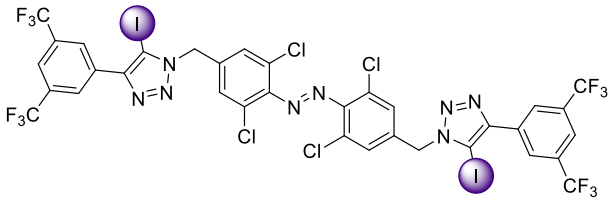
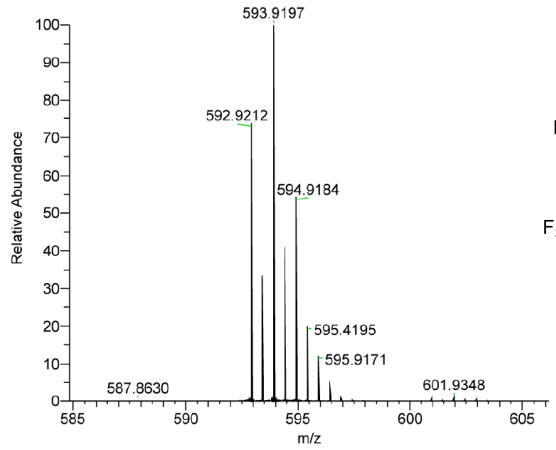


Figure S44. HRMS spectrum of **1**. HRMS-ESI (*m/z*) calculated for $C_{34}H_{13}Cl_4F_{12}I_2N_8^-$ $[M-H]^-$, 1156.7896; found 1156.7876.



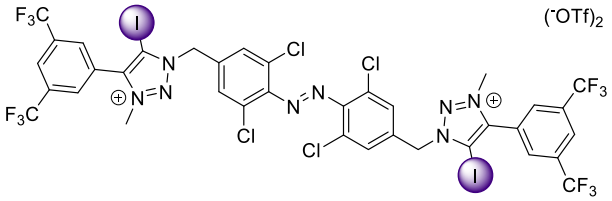


Figure S45. HRMS spectrum of **1-Me**. HRMS-ESI (*m/z*) calculated for $C_{36}H_{20}Cl_4F_{12}I_2N_8^{2+}$ $[M]^{2+}$, 593.9214; found 593.9197.

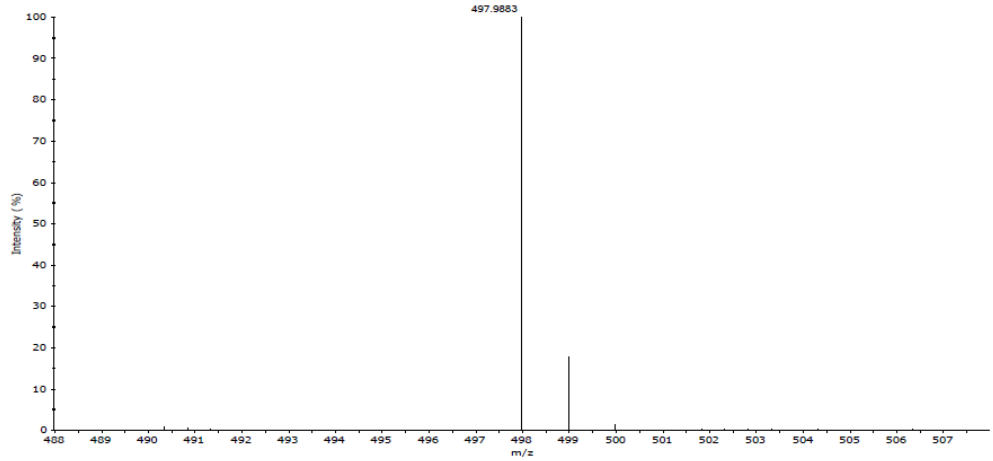


Figure S46. HRMS spectrum of **S1.** HRMS-ESI (m/z) Calculated for $C_{17}H_{11}F_6IN_3$ $[M+H]^+$, 497.9896; found 497.9883.

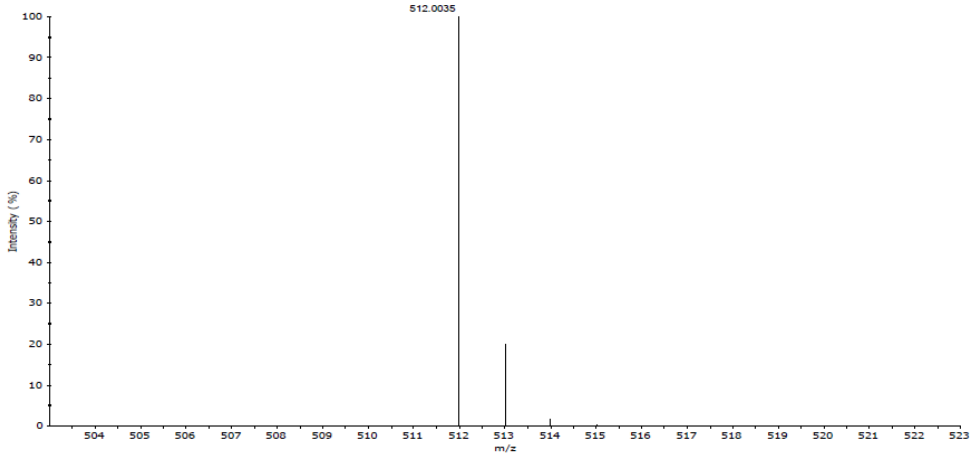


Figure S47. HRMS spectrum of **S1-Me.** HRMS-ESI (m/z) Calculated for $C_{18}H_{14}N_3F_6I$ $[M]^+$, 513.0068; found 513.0131

3 Photo-switching experiments

Photo-irradiation of liquid samples was carried out using Thorlabs high-power mounted LEDs (models M625L4 and M455L4) in in-house custom-built set-ups using optical components supplied by Thorlabs (see Fig S31).

For irradiating small vials of samples or NMR tubes, a Thorlabs cuvette holder (CVH100/M) equipped with mounted LEDs was used. Mirrors opposite to the LED was used to increase the intensity in the sample compartment. A 1A current was supplied to the LED, controlled by a Thorlabs T-Cube LED Driver (LEDD1B). Samples were irradiated for sufficient time to reach the photo-stationary state, as confirmed by NMR or UV-vis experiments.

Figure S48. Apparatus for photo-irradiating small liquid samples

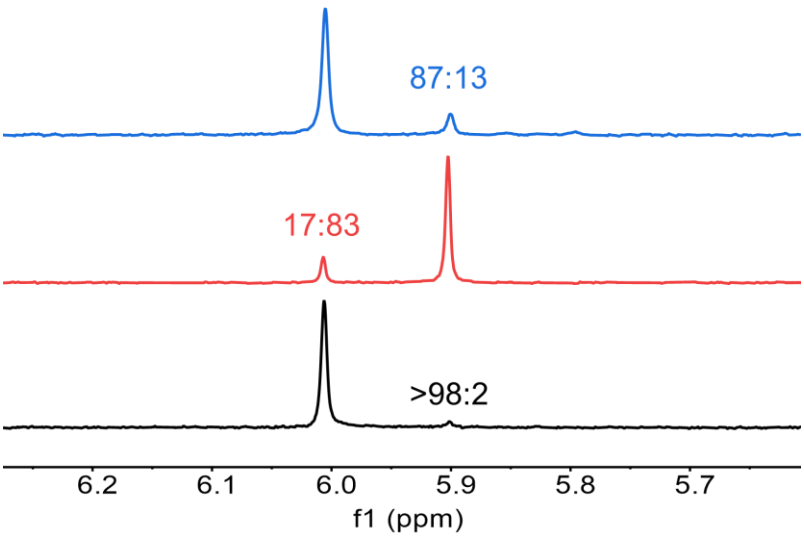
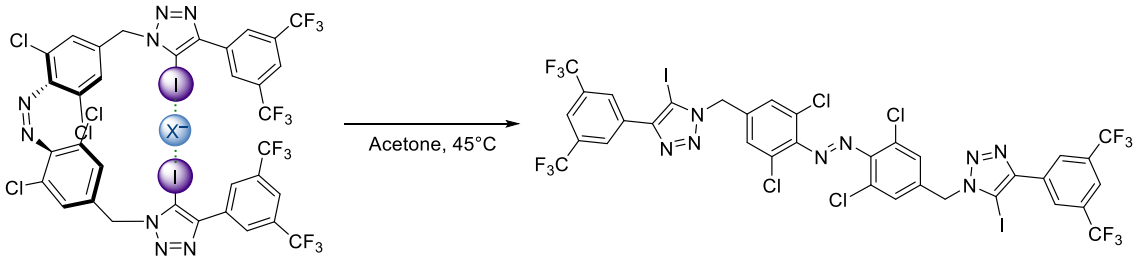


Figure S49. Photostationary states for (A) $\mathbf{1^E}$ at 455 nm (B) $\mathbf{1^Z}$ at 625 nm and (C) **1** Heated at 60 °C in dark for 1 hour (Partial ^{1}H NMR spectra in d_6-Acetone).



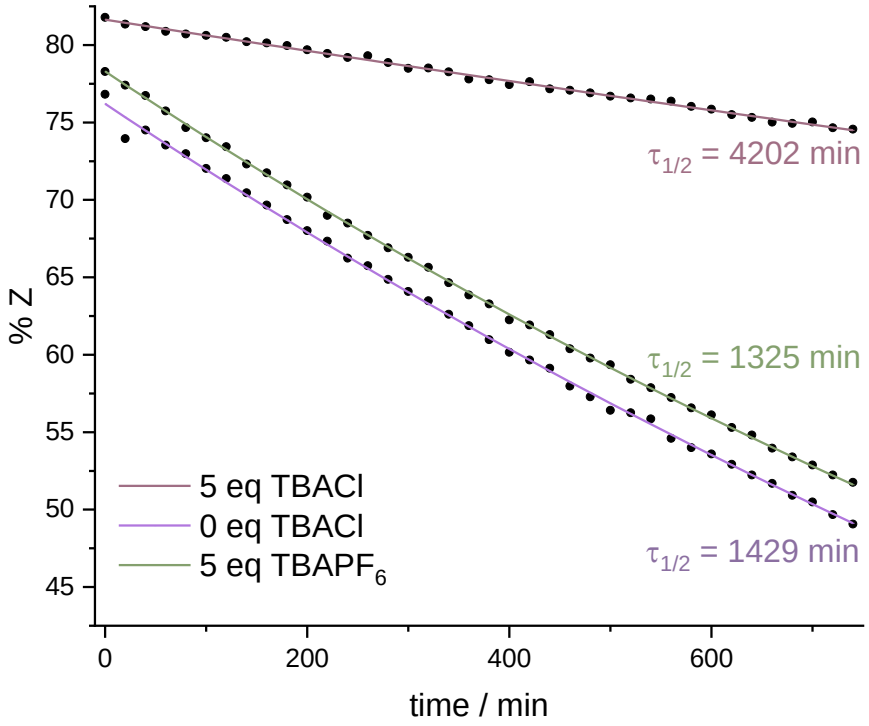


Figure S50. Summary of lifetime plots of $\mathbf{1^Z}$ (PSS at 625 nm) over time (318K, 1 mM; Acetone-d_6) in the presence or absence of anion**.** Data was fitted using Origin Pro using an exponential decay model to determine t_1. The half-life was determined using $\tau_{1/2} = \ln 2(T_1)$. The half-life was ~3x greater in the presence of the strongly binding chloride anion. A control was conducted with $TBAPF_6$ to rule out any charge effects. Experiments were performed at 45 °C to allow measurement over a suitable time-scale.

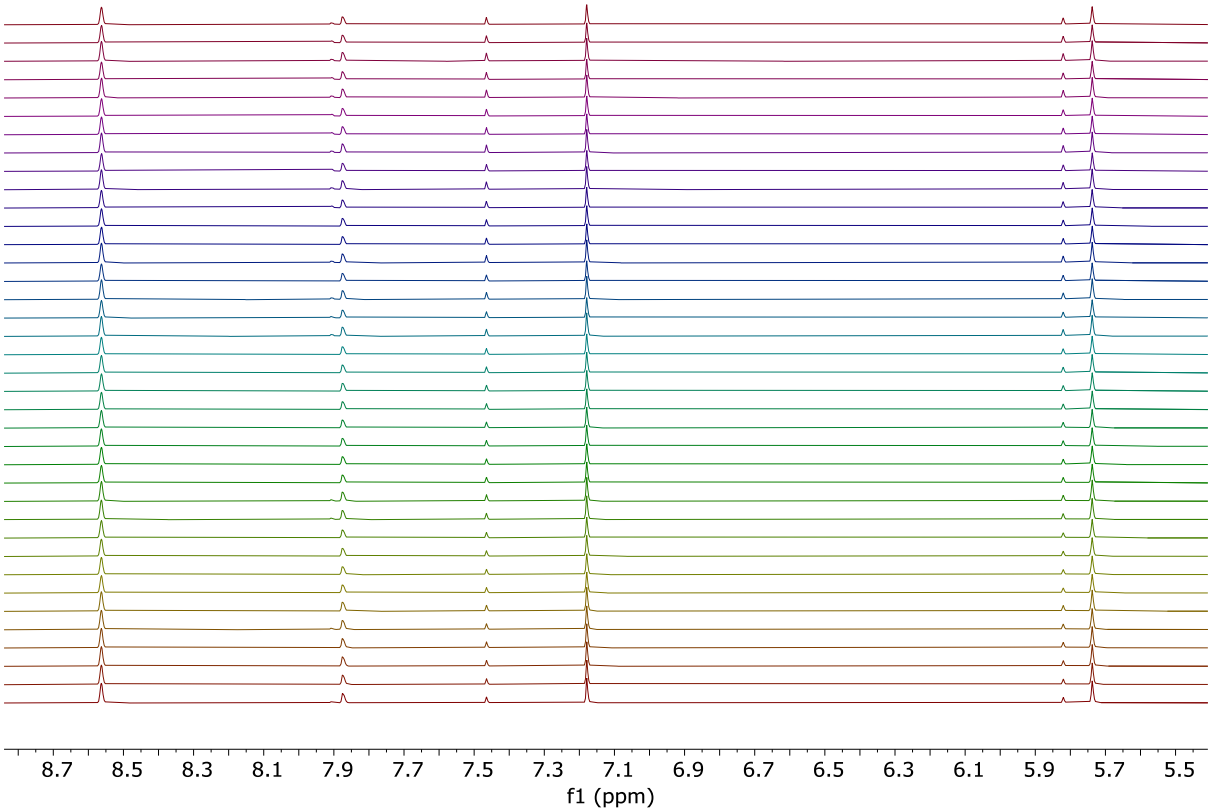


Figure S51. Stacked ^{1}H NMR plot of $\mathbf{1^{Z}}$ (PSS at 625 nm) over time (318K, 1mM Acetone-d_6) in the presence of 5 eq TBACl

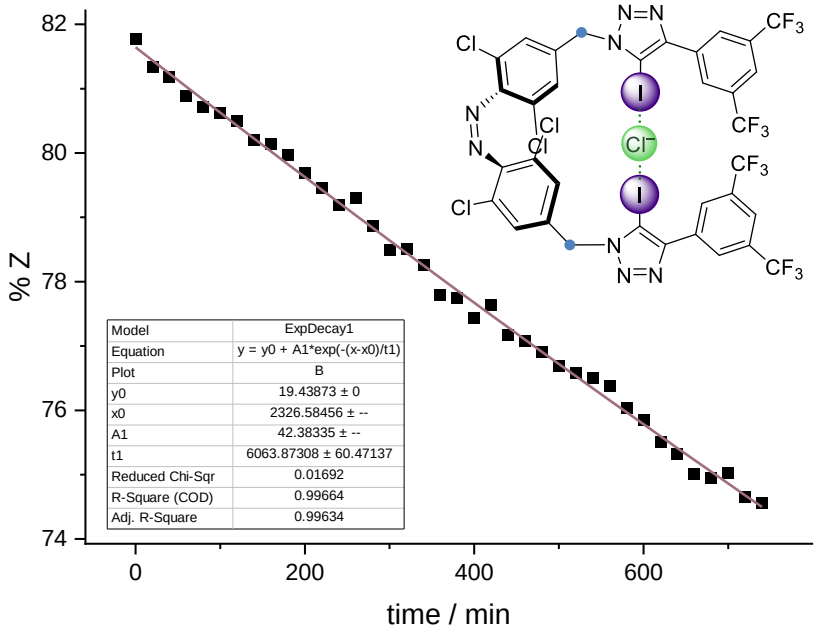


Figure S52. Lifetime plot of $\mathbf{1^{Z}}$ (PSS at 625 nm) over time (318K, 1mM Acetone-d_6) in the presence of 5 eq TBACl**.** Data was fitted using Origin Pro using an exponential decay model to determine t_1.

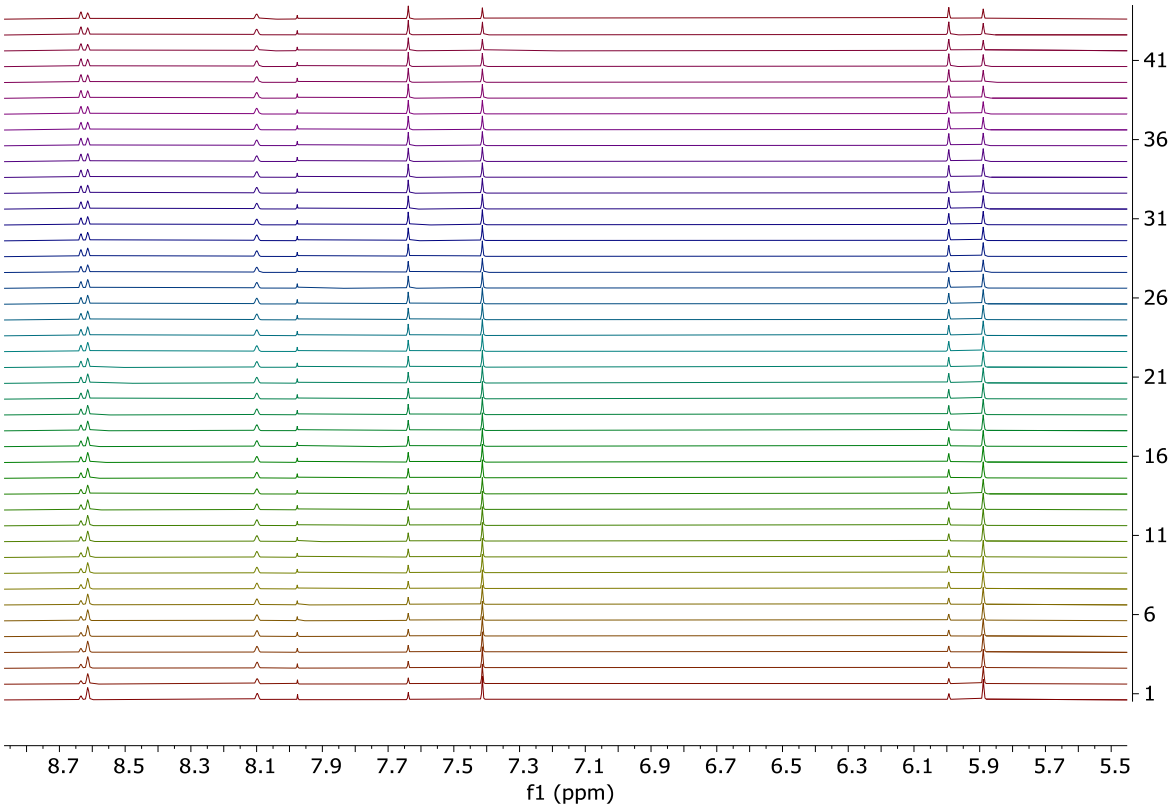


Figure S53. Stacked ^{1}H NMR plot of **1^{Z}** (PSS at 625 nm) over time (318K, 1mM Acetone-d_6)

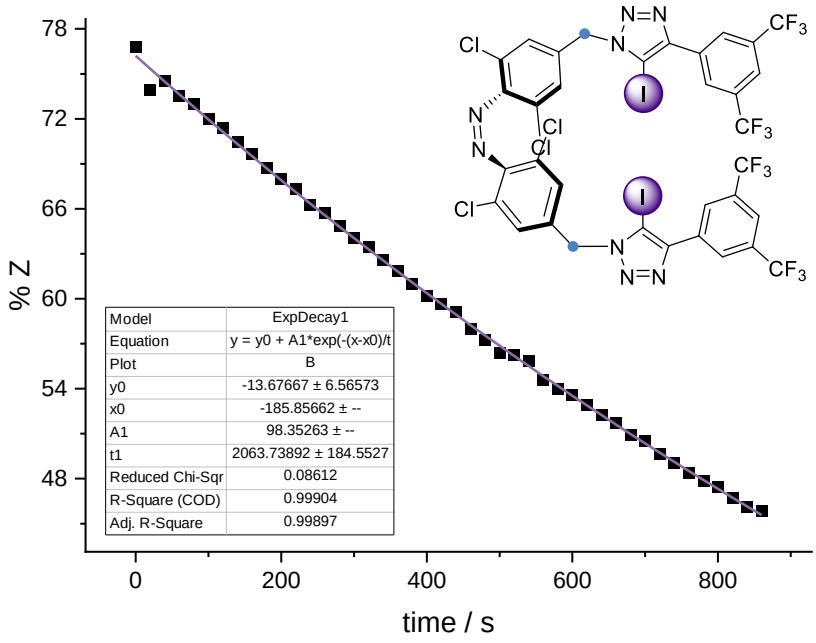


Figure S54. Lifetime plot of **1^{Z}** (PSS at 625 nm) over time (318K, 1mM Acetone-d_6). Data was fitted using Origin Pro using an exponential decay model to determine t_1.

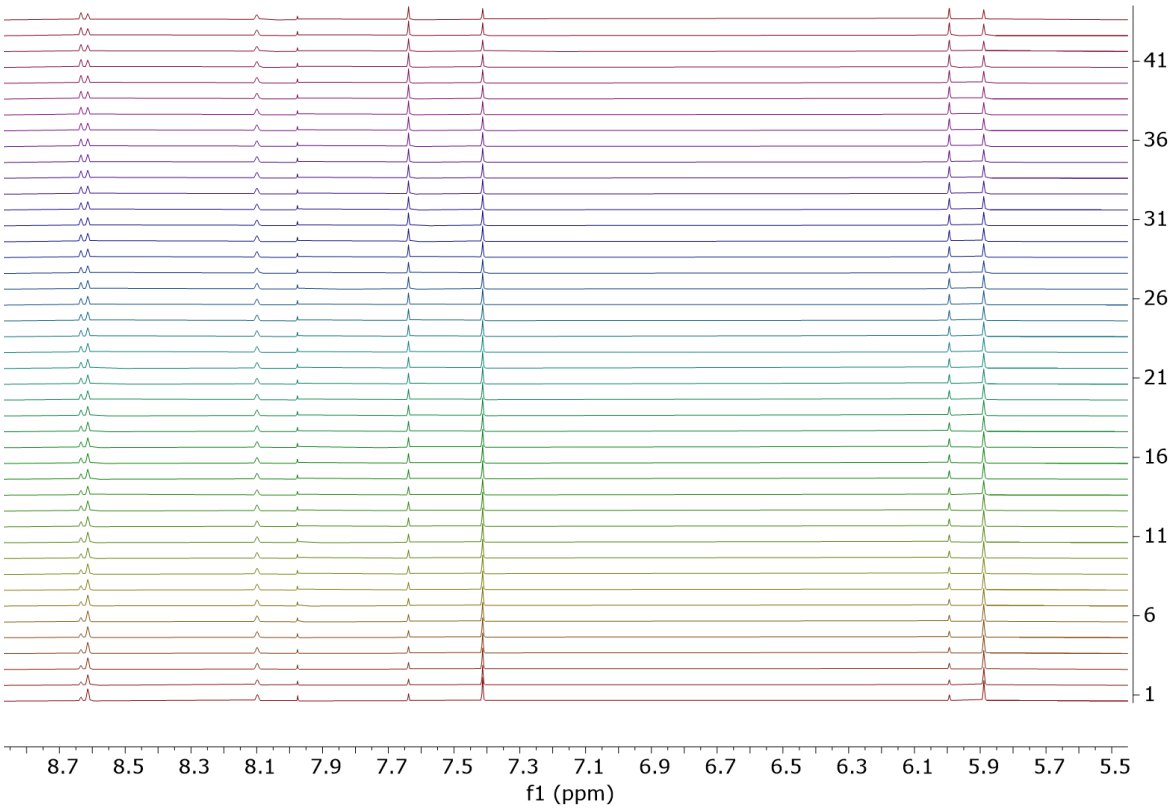


Figure S55. Stacked ^{1}H NMR plot of **1Z** (PSS at 625 nm) over time (318K, 1mM Acetone-d_6) in the presence of 5 eq $TBAPF_6$

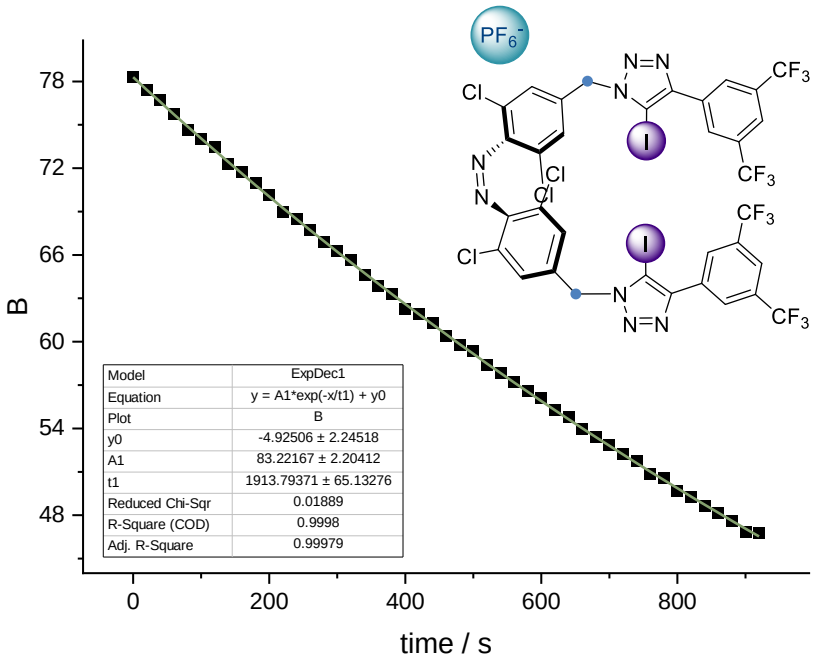
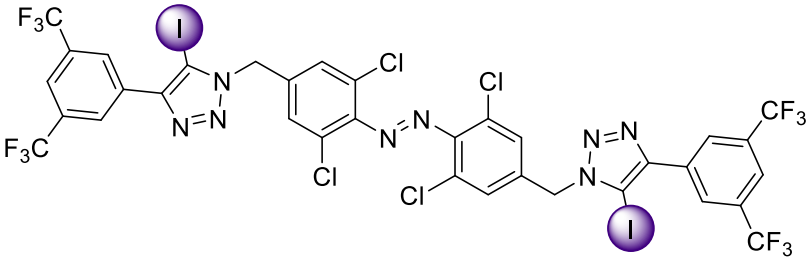


Figure S56. Lifetime plot of $\mathbf{1^Z}$ (PSS at 625 nm) over time (318K, 1mM Acetone-d_6) in the presence of $TBAPF_6$. Data was fitted using Origin Pro using an exponential decay model to determine t_1.

4 UV-Visible absorption spectra.

All UV-vis spectra were determined in DMSO solution. Extinction coefficients were determined by recording a UV-vis spectra for the *E* isomer at 20, 40, 60, 80 µM in DMSO respectively. The absorbance at the maximum of the π - π* transition of the *E*-isomers was plotted against concentration (Beer-Lambert plot) to determine the molar extinction coefficient ε. For each compound, the *E* isomer sample at 40 µM was irradiated with red light to generate the photostationary state, and another spectrum was run. This spectrum was normalised to units of ε and overlaid with the dark (100% *E* isomer) spectrum.



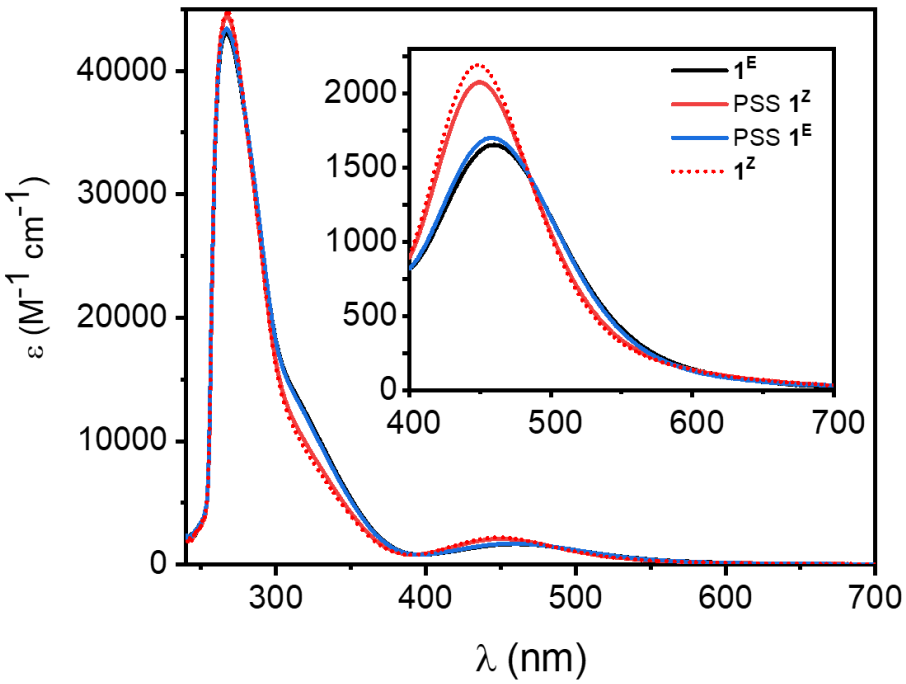


Figure S57. Spectrum of **1** in the dark (100% trans), blue (87% trans) and red (80% cis) state. Pure *Z*-isomer spectrum was calculated from the spectra of pure $\mathbf{1}^{E}$ and the PSS mixture of known composition.

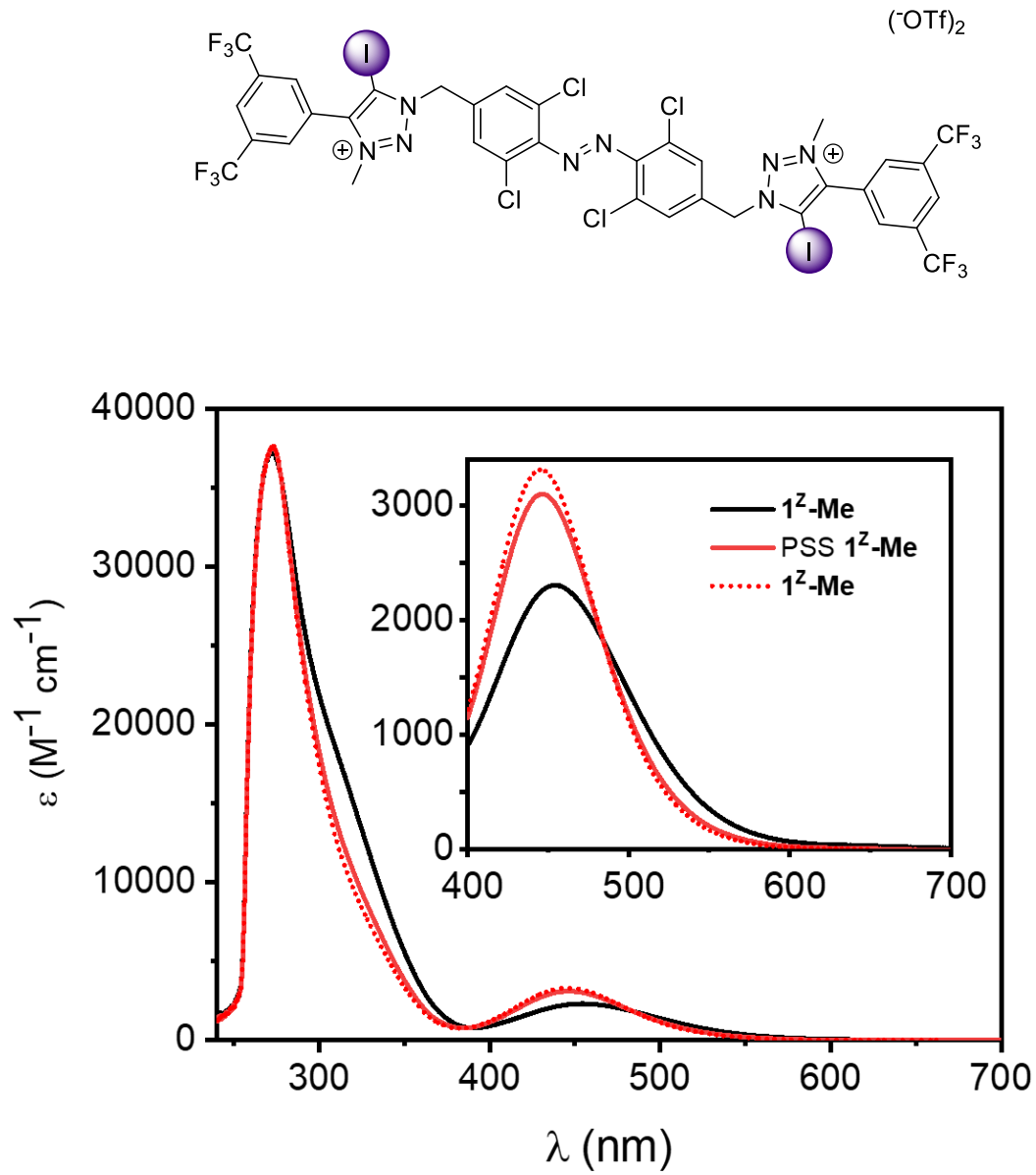


Figure S58. Spectrum of **1-Me** in the dark (100% trans) and red (80% cis) state. Pure *Z*-isomer spectrum was calculated from the spectra of pure $\mathbf{1^{E}}$**-Me** and the PSS mixture of known composition.

5 NMR titration experiments

All binding constants were measured by ^{1}H NMR titrations in a Bruker AVIII 500 spectrometer at 500 MHz and 298 K. Receptor **1** was dissolved in d_6-acetone (Receptor **1-Me** in DMSO-d_6) and added at 1 mM concentration and a known volume (0.5 mL) added to the NMR tube. Known volumes of guest (X^-, added as the TBA salt) in d_6-acetone or DMSO-d_6 were added, and the spectra were recorded after each addition. The chemical shifts of the host spectra, where resolved, were monitored as a function of guest concentration. The data was analysed using a global fit procedure for all three data sets simultaneously in the Dynafit software program,[6] using non-linear least squares analysis to obtain the best fit between observed and calculated chemical shifts. Errors were calculated as two times the standard deviation from the average value of two repeats. In all experiments the association of guest and host was fast on the NMR timescale.

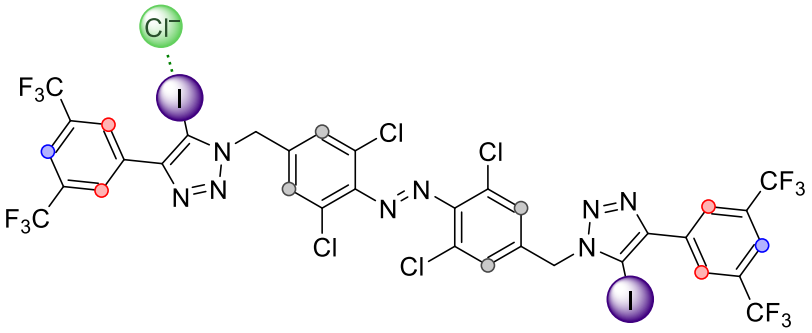
Binding of anions to the *E* isomer was statistical – i.e. binding at each site was independent of the other.

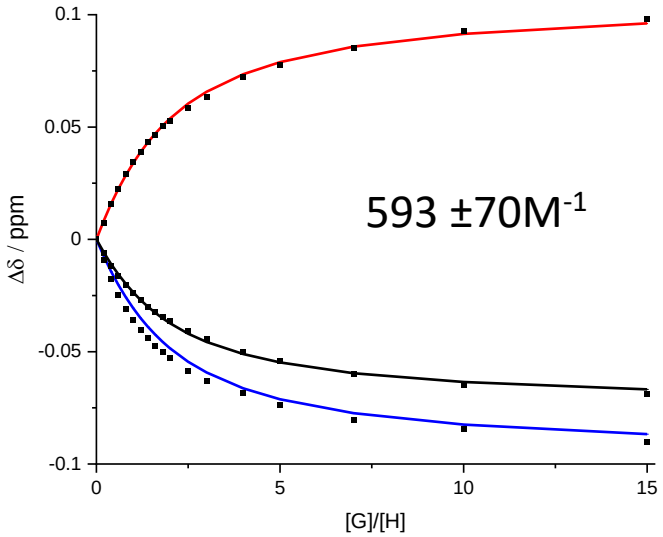
For the Z isomer, a 1 mM sample of **1** in d_6-acetone was irradiated with red light until the PSS was reached, before the titration experiment was conducted as described above. The PSS ratio was maintained throughout the titration. The anion binding constant for $\mathbf{1^Z}$ were obtained by fitting the data, using a global fit procedure, to the following equilibria where K_1^E is fixed, and obtained from the previous titration with the *E* isomer.

$$\mathbf{A}^{\boldsymbol{E}} + \mathrm{Cl}^- \overset{K_{\mathrm{obs}}{}^E}{\rightleftharpoons} \mathbf{A}^{\boldsymbol{E}}\cdot\mathrm{Cl}^-$$

$$\mathbf{A}^{\boldsymbol{Z}} + \mathrm{Cl}^- \overset{K_{\mathrm{obs}}{}^Z}{\rightleftharpoons} \mathbf{A}^{\boldsymbol{Z}}\cdot\mathrm{Cl}^-$$

$[\mathbf{A}^{\boldsymbol{E}}] + [\mathbf{A}^{\boldsymbol{Z}}] = 1$ mM; $[\mathbf{A}^{\boldsymbol{Z}}] = 1\text{-}x^E$ mM; $[\mathbf{A}^{\boldsymbol{E}}] = 1\text{-}x^Z$ mM where x^E and x^Z are the mole-fractions of the *E* and *Z* isomer in the photo-stationary state, respectively.





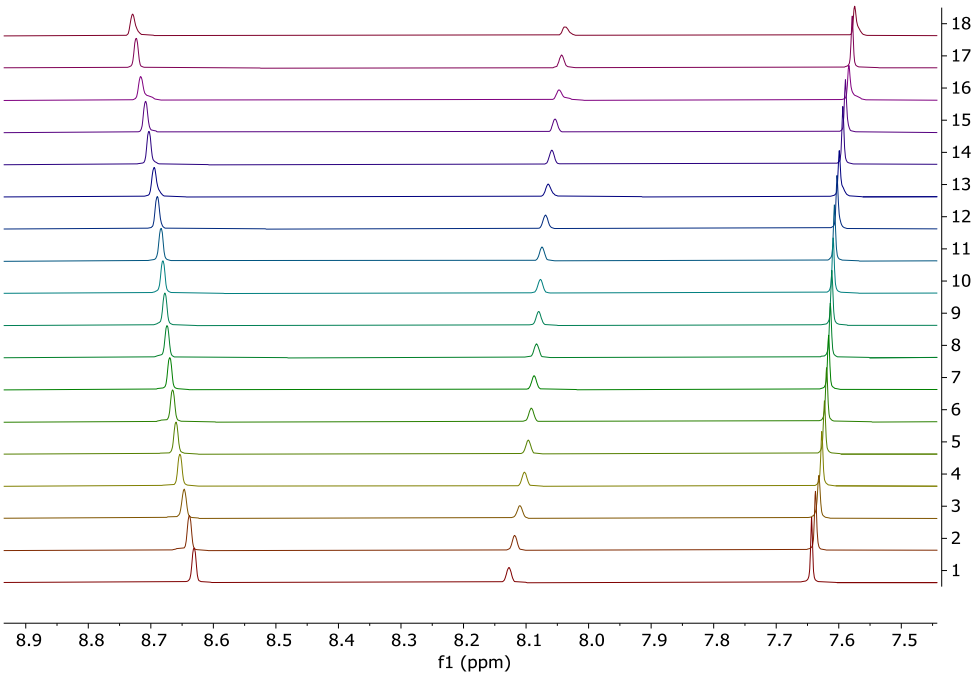
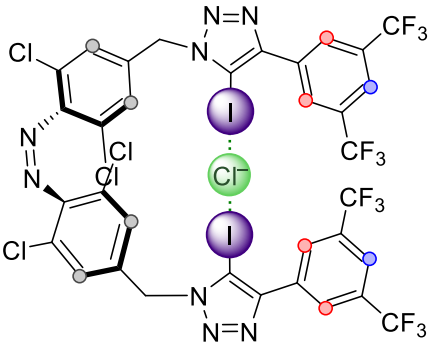
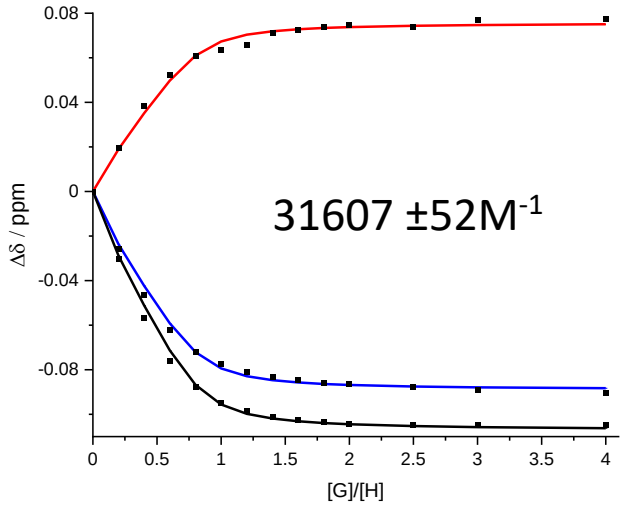


Figure S59. Plots of chemical shift changes of **1**^{E} upon addition of TBACl (Acetone-d_6).





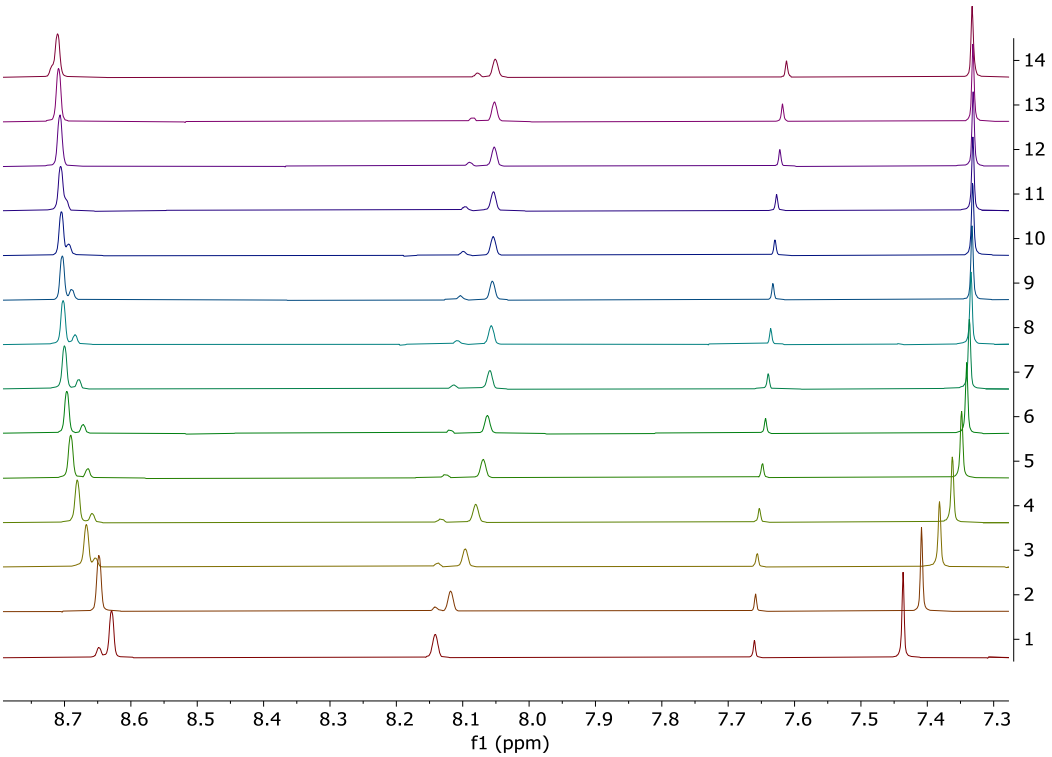
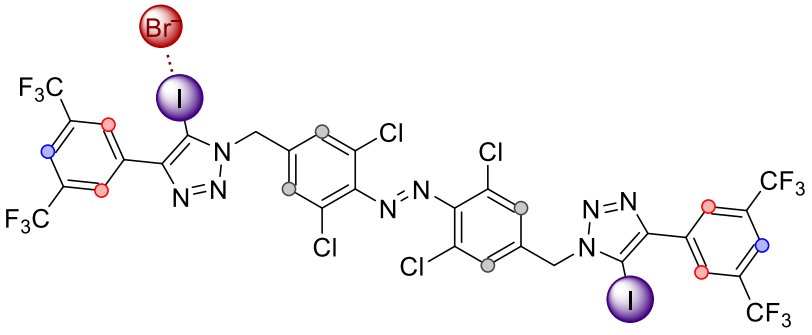
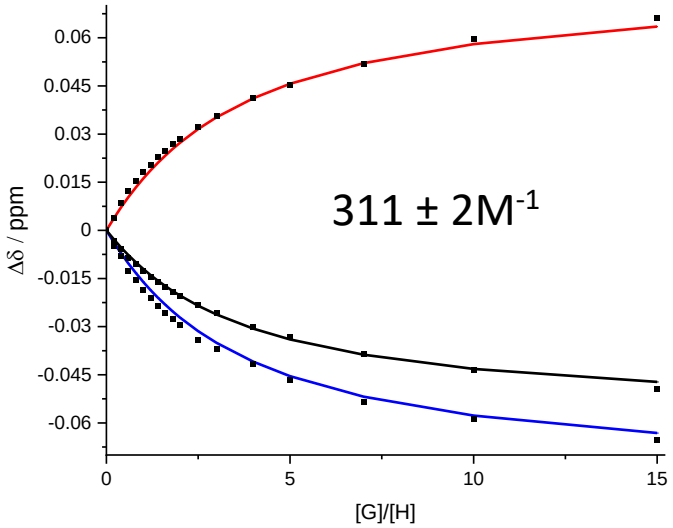


Figure S60. Plots of chemical shift changes of $\mathbf{1^Z}$ upon addition of TBACl (Acetone-d_6).





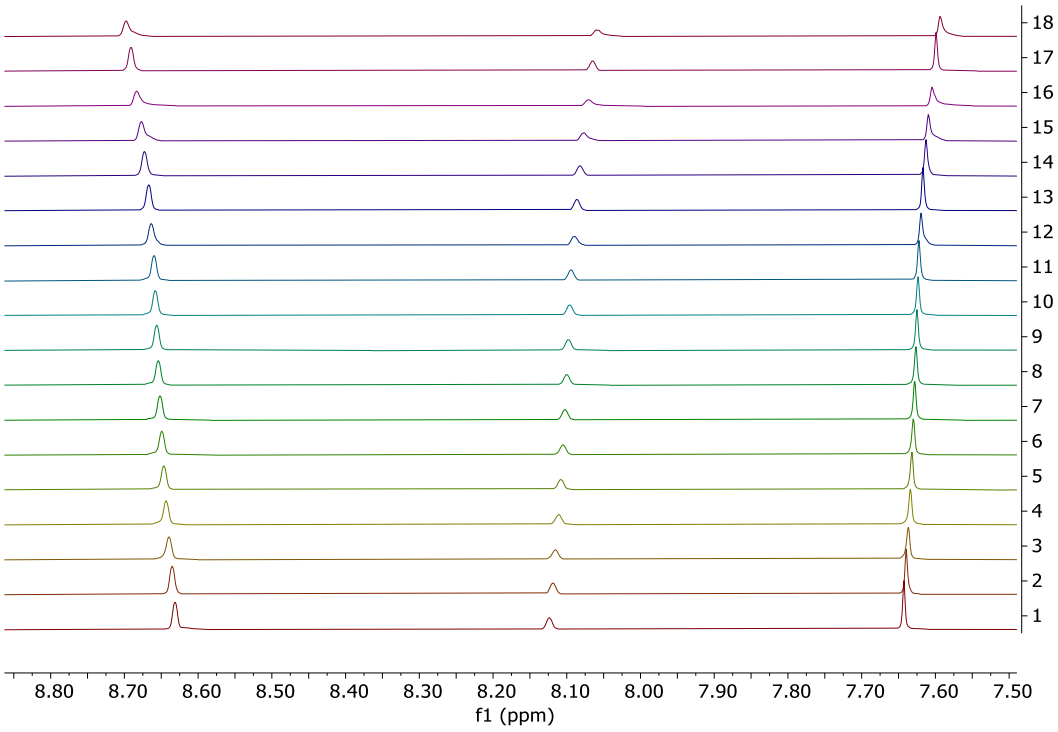
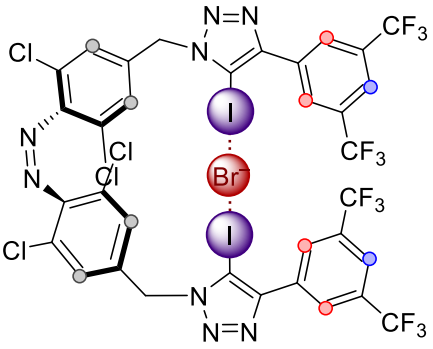
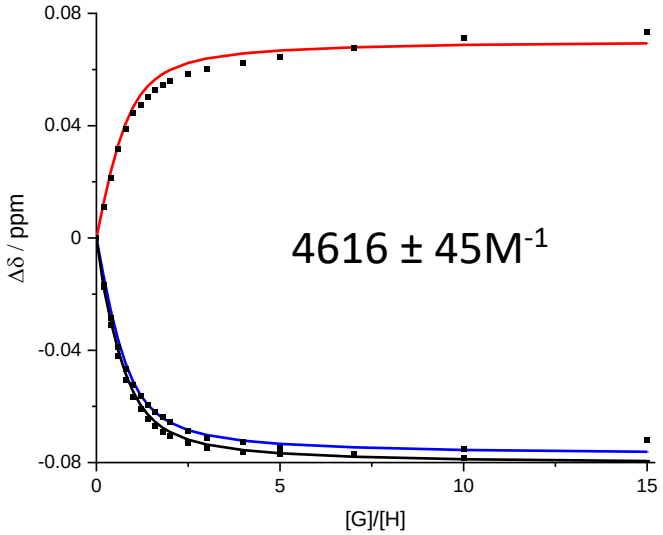


Figure S61. Plots of chemical shift changes of **1**^{E} upon addition of TBABr (Acetone-d_6).





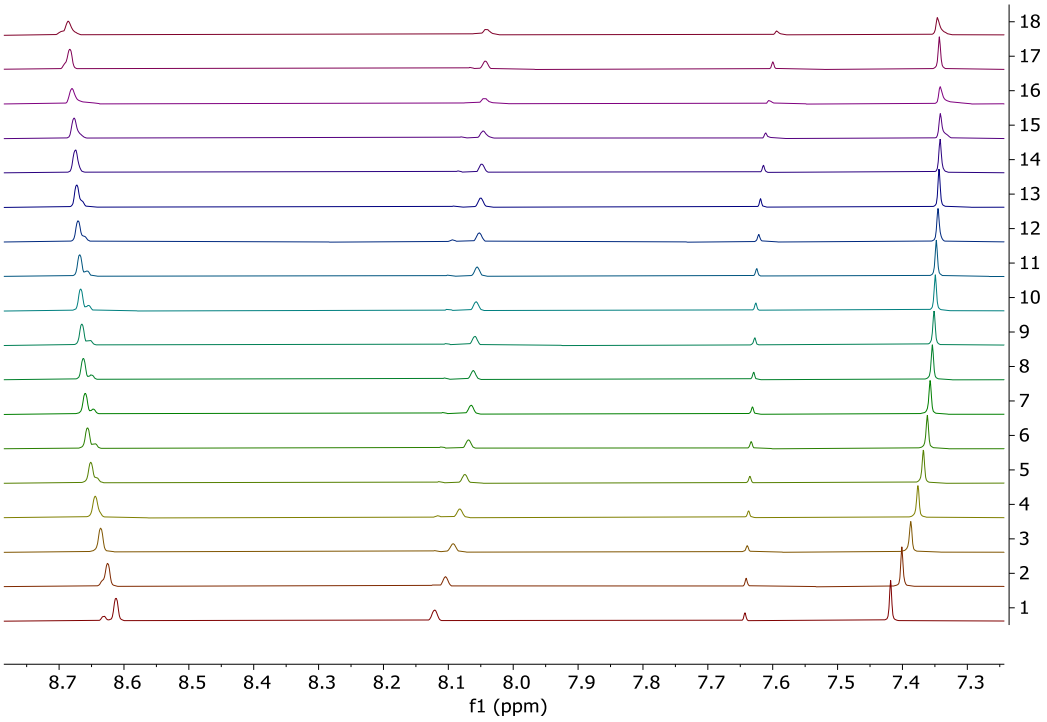
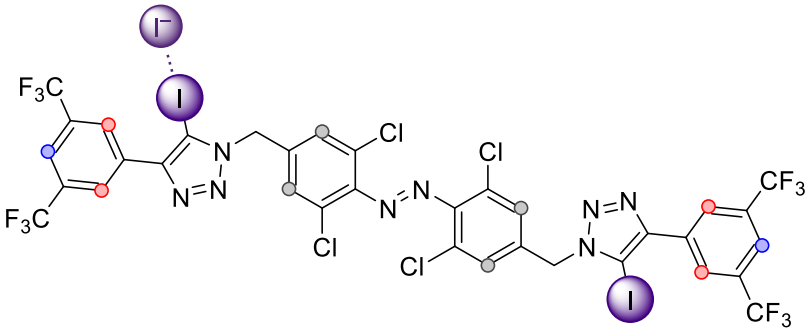
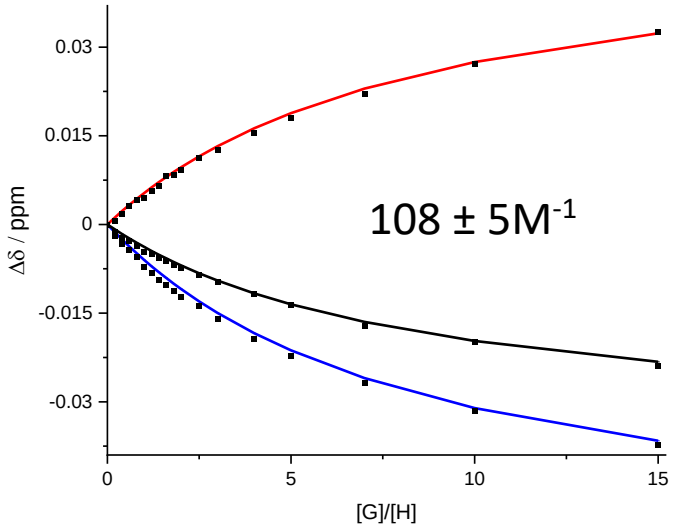


Figure S62. Plots of chemical shift changes of **1**$^{\mathbf{Z}}$ upon addition of TBABr (Acetone-d_6).





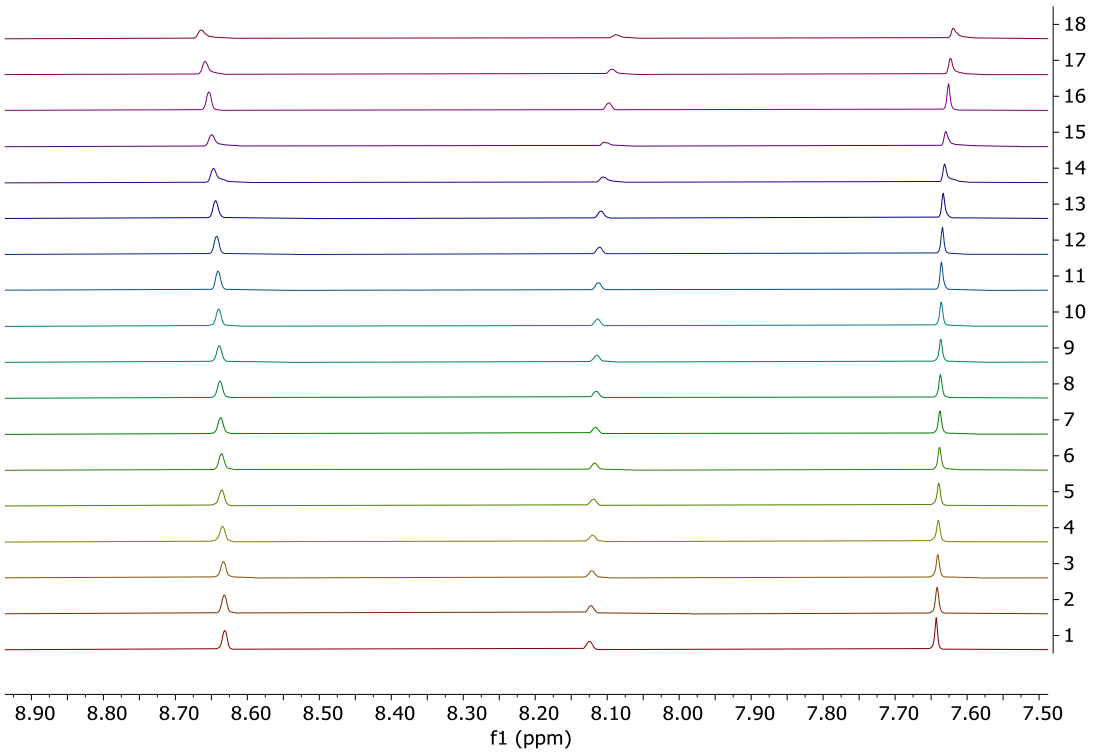
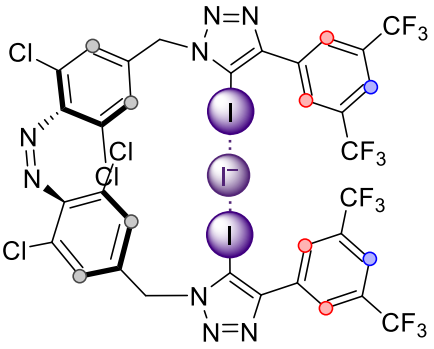
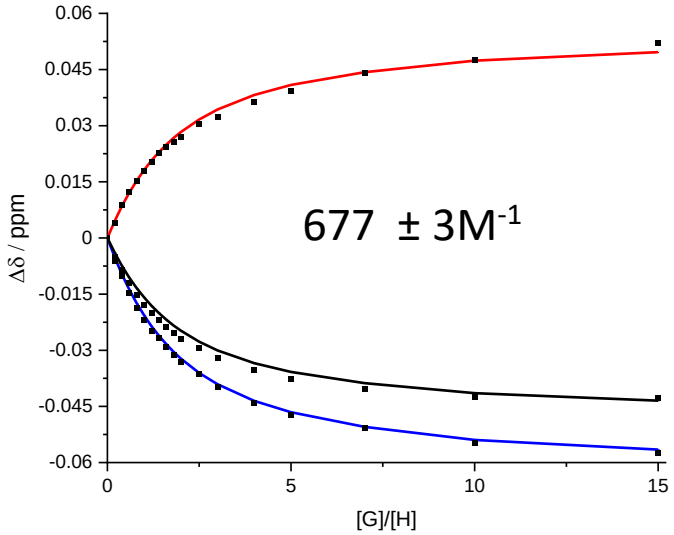


Figure S63. Plots of chemical shift changes of **1**^{E} upon addition of TBAI (Acetone-d_6).





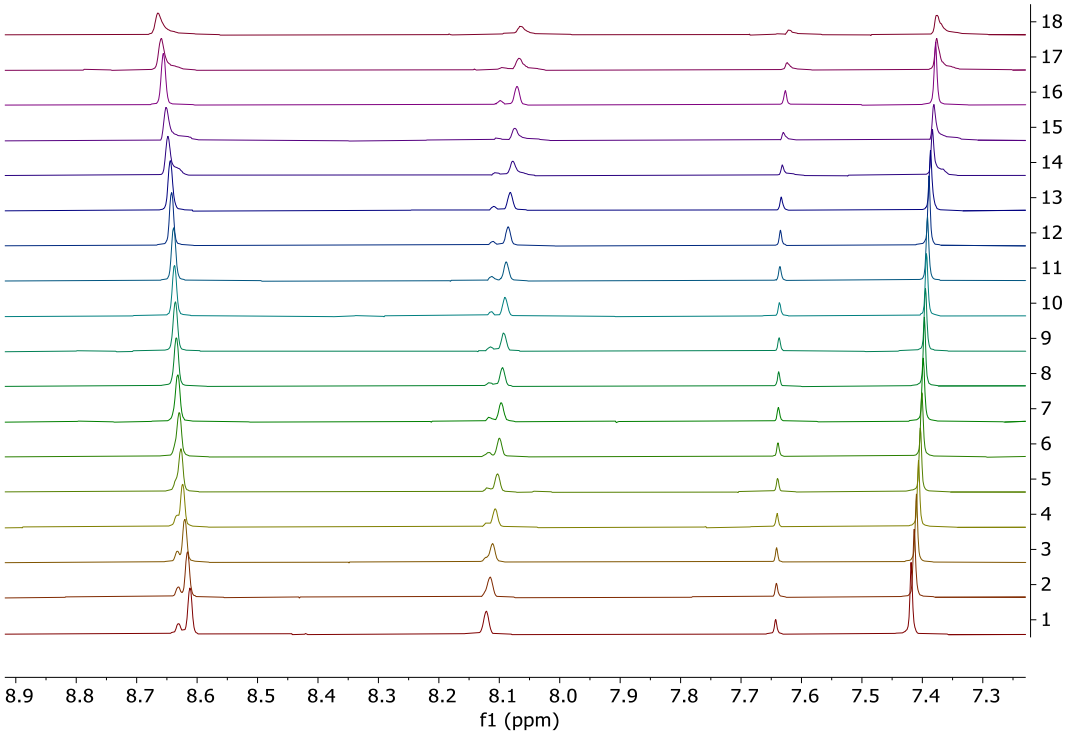


Figure S64. Plots of chemical shift changes of $\mathbf{1^Z}$ upon addition of TBAI (Acetone-d_6).

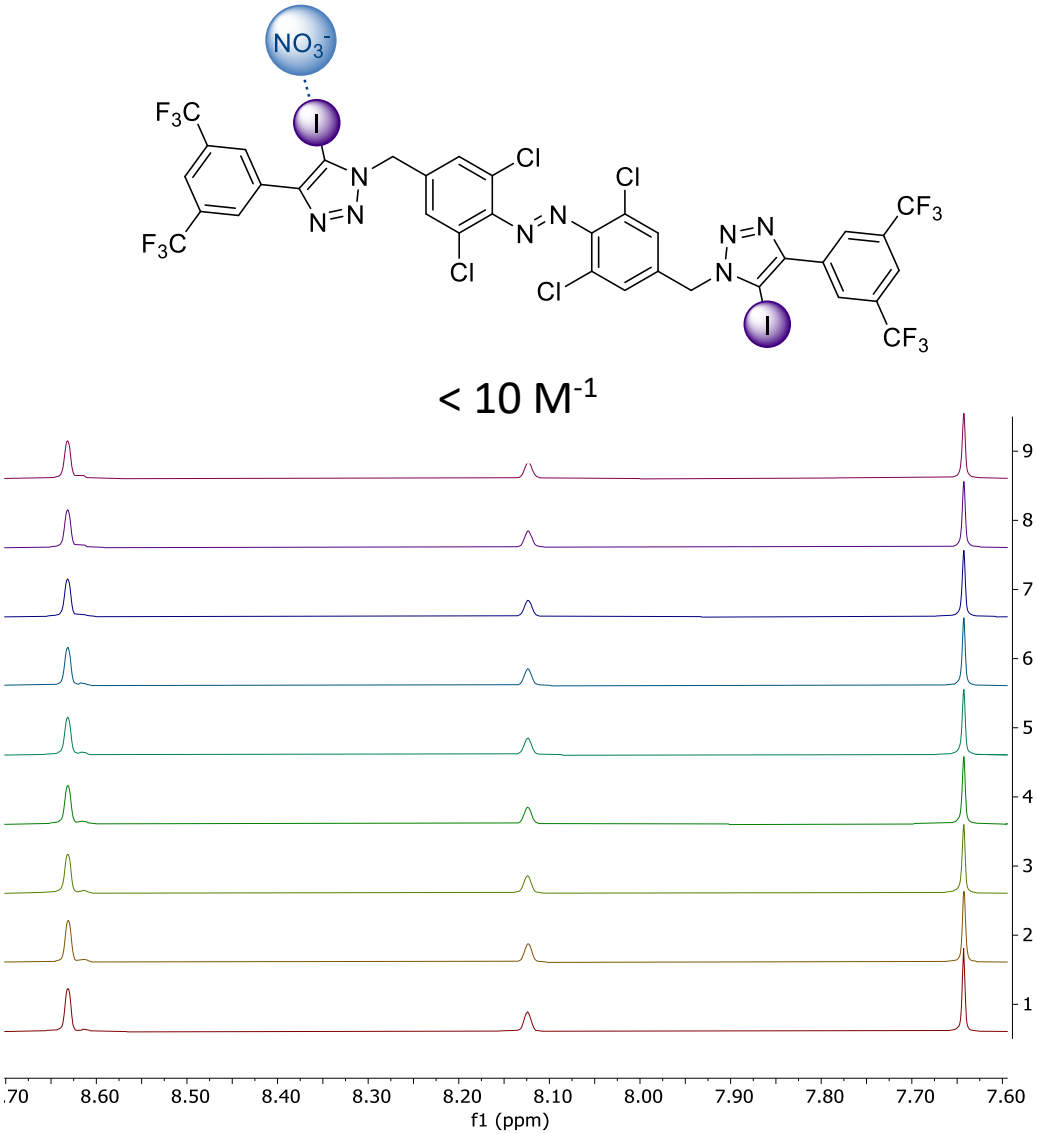
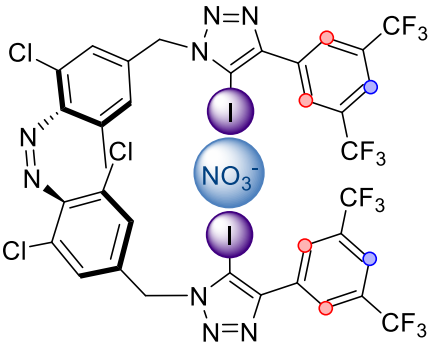
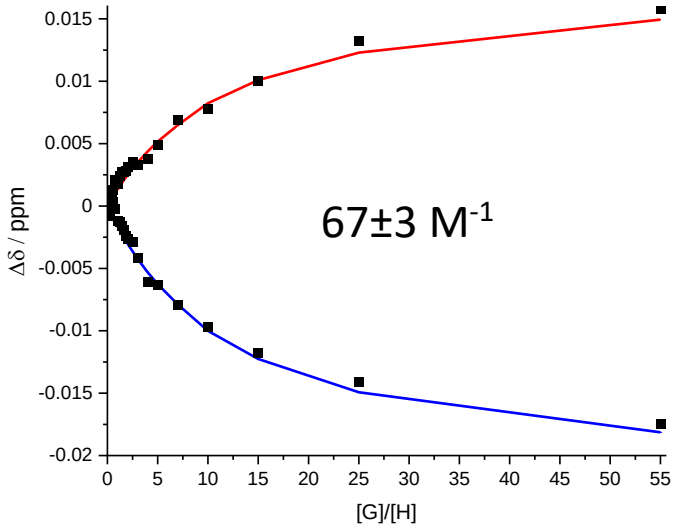


Figure S65. Plots of chemical shift changes of $\mathbf{1^E}$ upon addition of $TBANO_3$ (Acetone-d_6). No binding was observed.





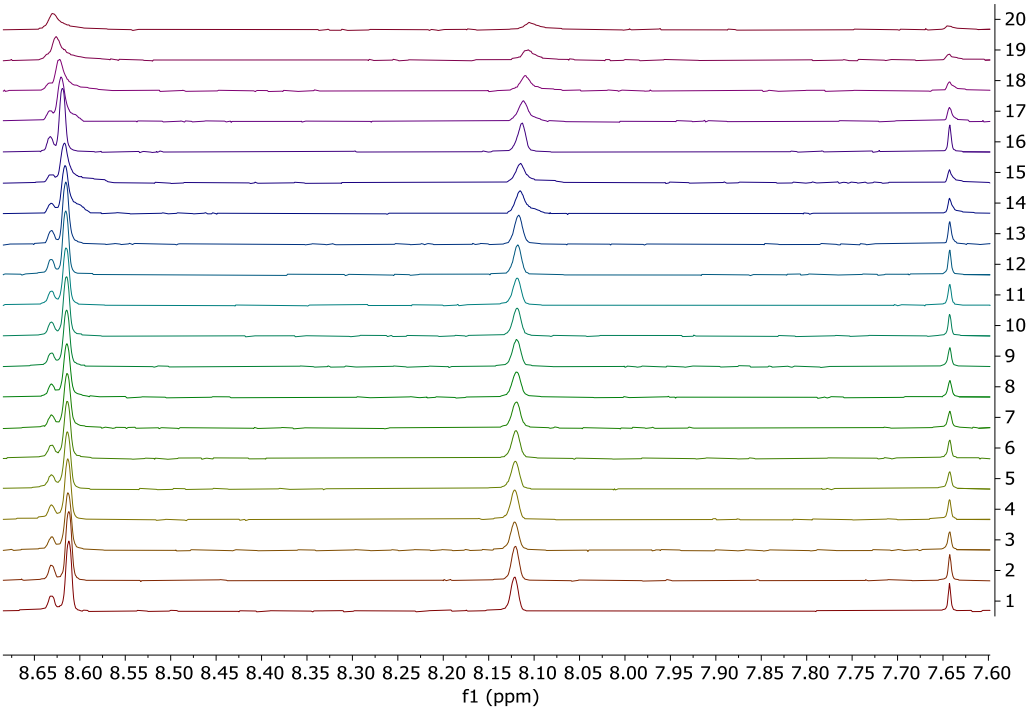


Figure S66. Plots of chemical shift changes of **1**$^{\mathbf{Z}}$ upon addition of $TBANO_3$ (Acetone-d_6).

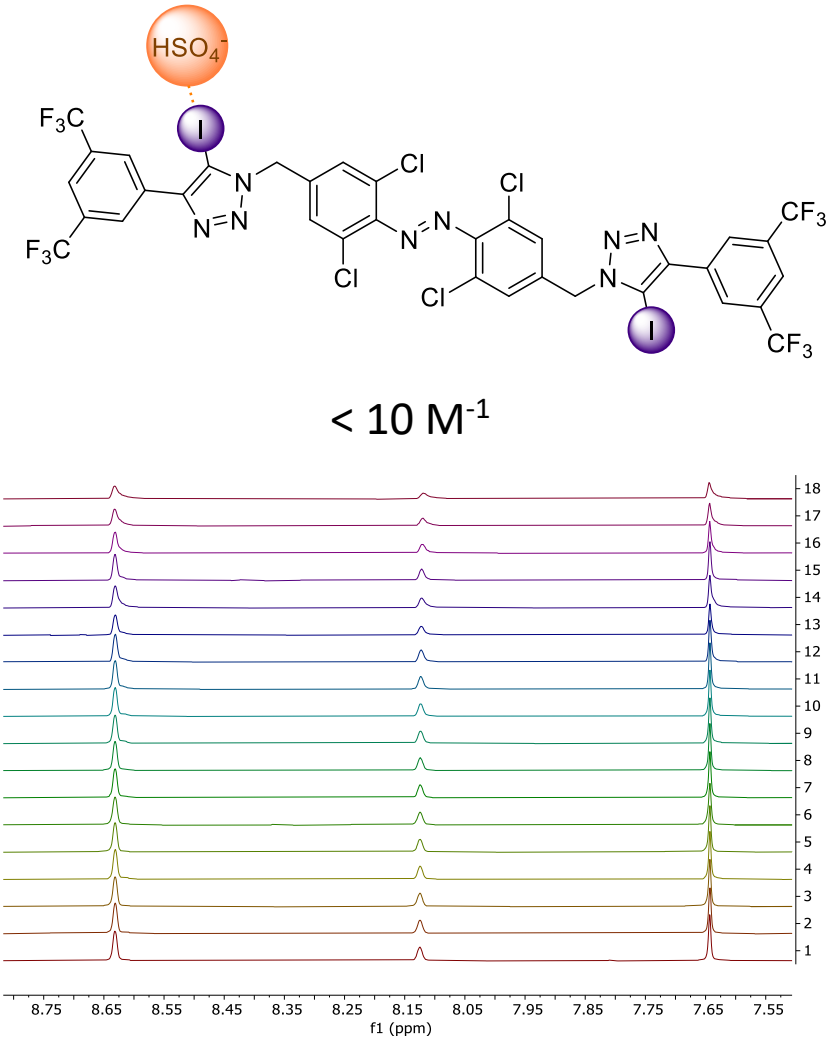
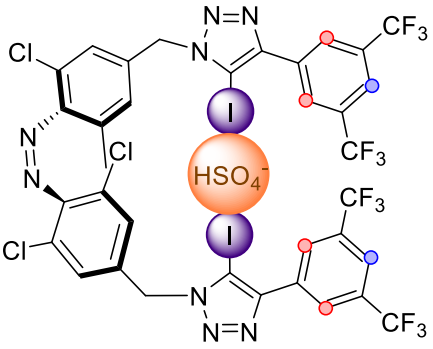
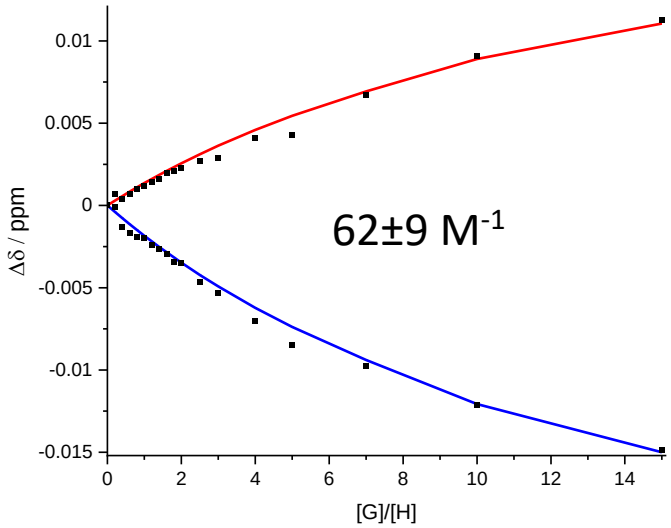


Figure S67. Plots of chemical shift changes of **1**^{E} upon addition of TBAHSO$_4$ (Acetone-d$_6$). No binding was observed.





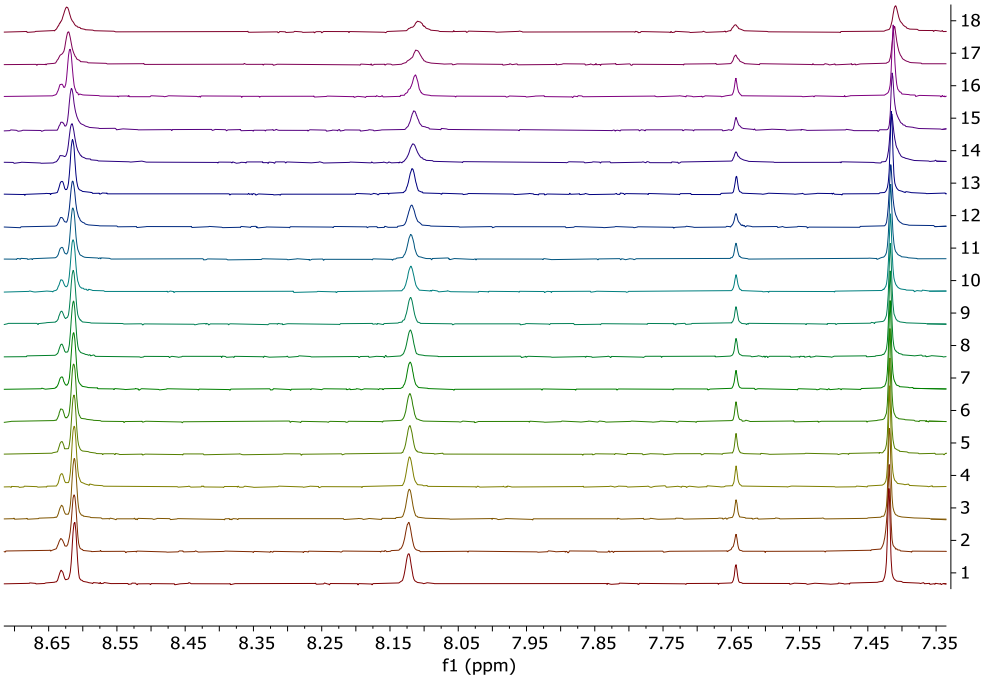
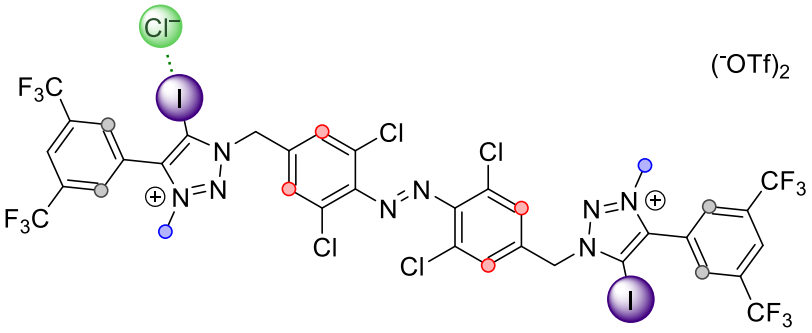
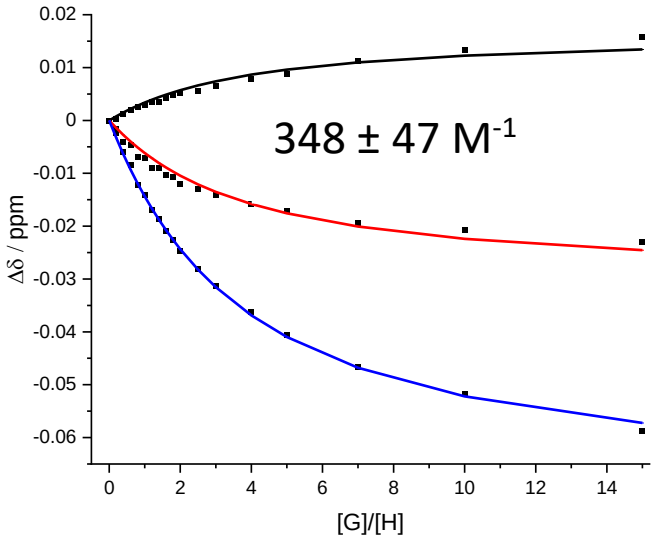


Figure S68. Plots of chemical shift changes of **1**^{Z} upon addition of TBAHSO$_4$. (Acetone-d$_6$)





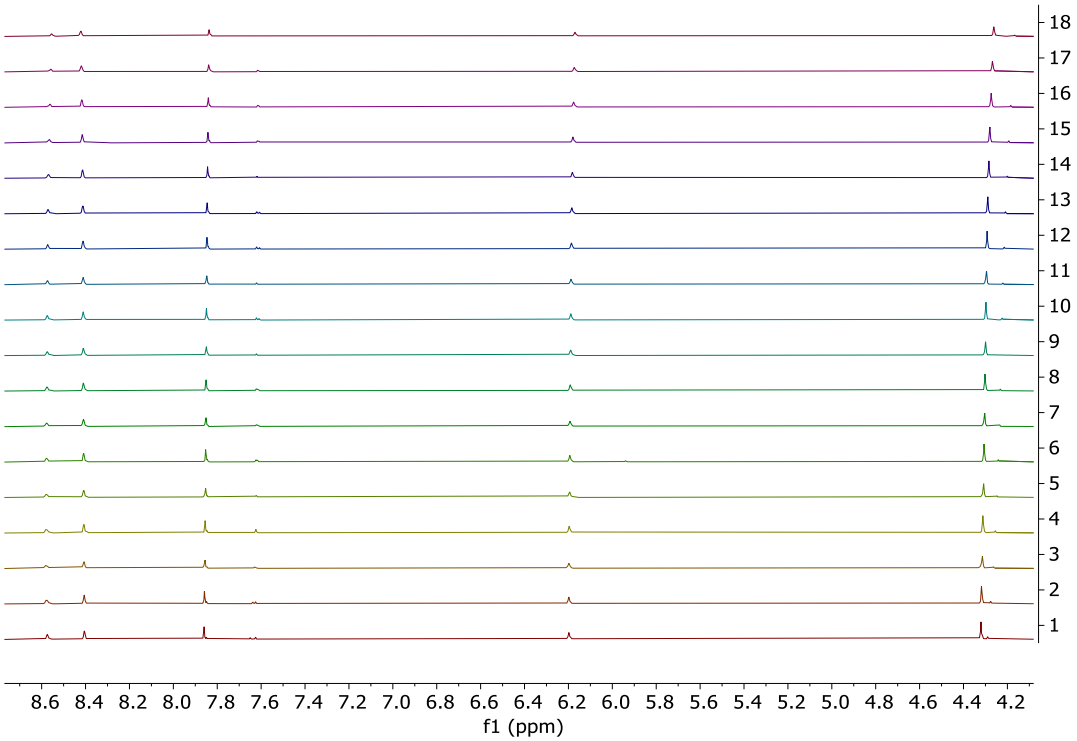
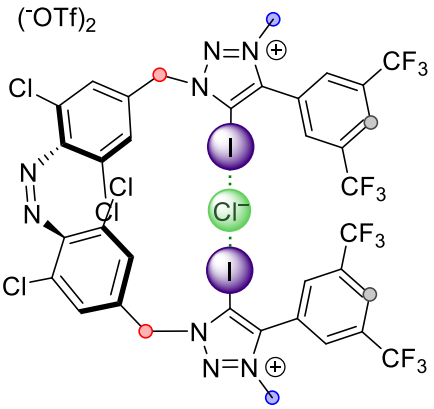
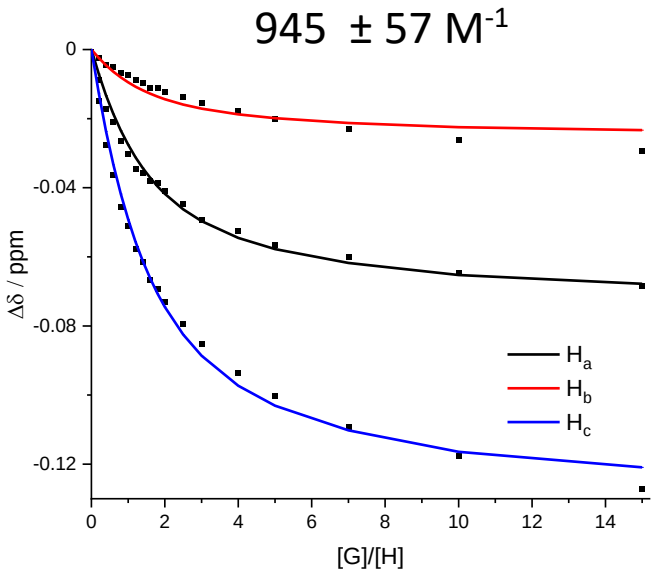


Figure S69. Plots of chemical shift changes of **1-Me^{E}** upon addition of TBACl. (DMSO-d_6)





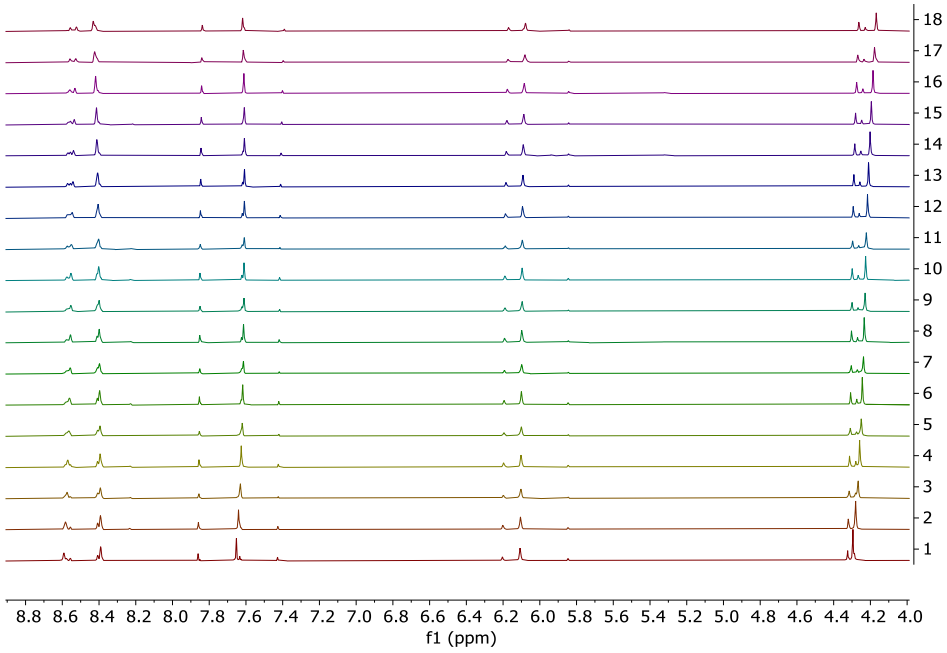


Figure S70. Plots of chemical shift changes of **1-Me^{Z}** upon addition of TBACl. (DMSO-d_6)

6 ^{1}H NMR Kinetics Studies

All ^{1}H NMR experiments were performed on a Bruker AVIII 500 spectrometer at 500 MHz and 298 K. $CDCl_3$ (Sigma, filtered over basic alumina), CD_2Cl_2 (Sigma) and unused NMR-tubes were used. Hamilton gas tight syringes were used for the preparation of the stock solutions.

Bromide Abstraction reaction:

At first, 1 mg Cs_2CO_3 was added in the NMR tube, then 400 µL (2.5 mM) of **1-Me-BAr$^{F}_{4}$** (Pre-heated at 70 degrees for 1 h or PSS at 625 nm) or **10** in $CDCl_3$ and 100 µL (10 mM) 1,3,5-trimethoxybenzene was added. The mixture was mixed by shaking. Finally, 100 µL (10 mM) benzhydryl bromide solution was added and mixed by inversion. The samples were directly transferred and submitted to the NMR spectrometer. The first spectra were measured after approximately 15 minutes and every 15 minutes an additional spectrum was recorded. The conversion was determined by integration of the methoxy signals (3.77 ppm) of 1,3,5-trimethoxybenzene against the two methoxy signals (3.80 ppm and 3.58 ppm) in the product ((2,4,6-trimethoxyphenyl)methylene)dibenzene. The twofold substitution occurred and ((2,4,6-trimethoxy-1,3-phenylene)bis(methanetriyl))tetrabenzene (methoxy signals at 3.41 ppm and 3.03 ppm) was formed as minor product (ca. 13% for both isomers)

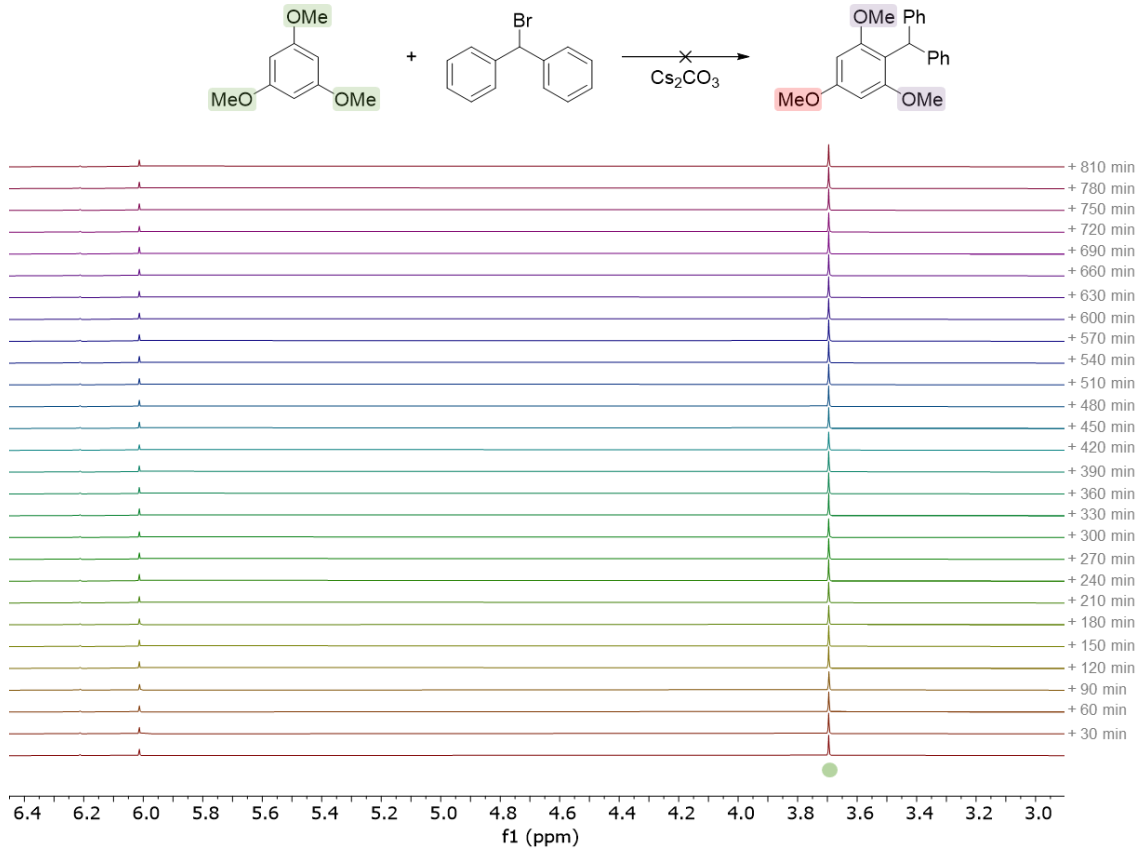


Figure S71. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1,3,5-trimethoxybenzene and benzhydryl bromide in $CDCl_3$ (1.67 mM) in the absence of activator did not occur.

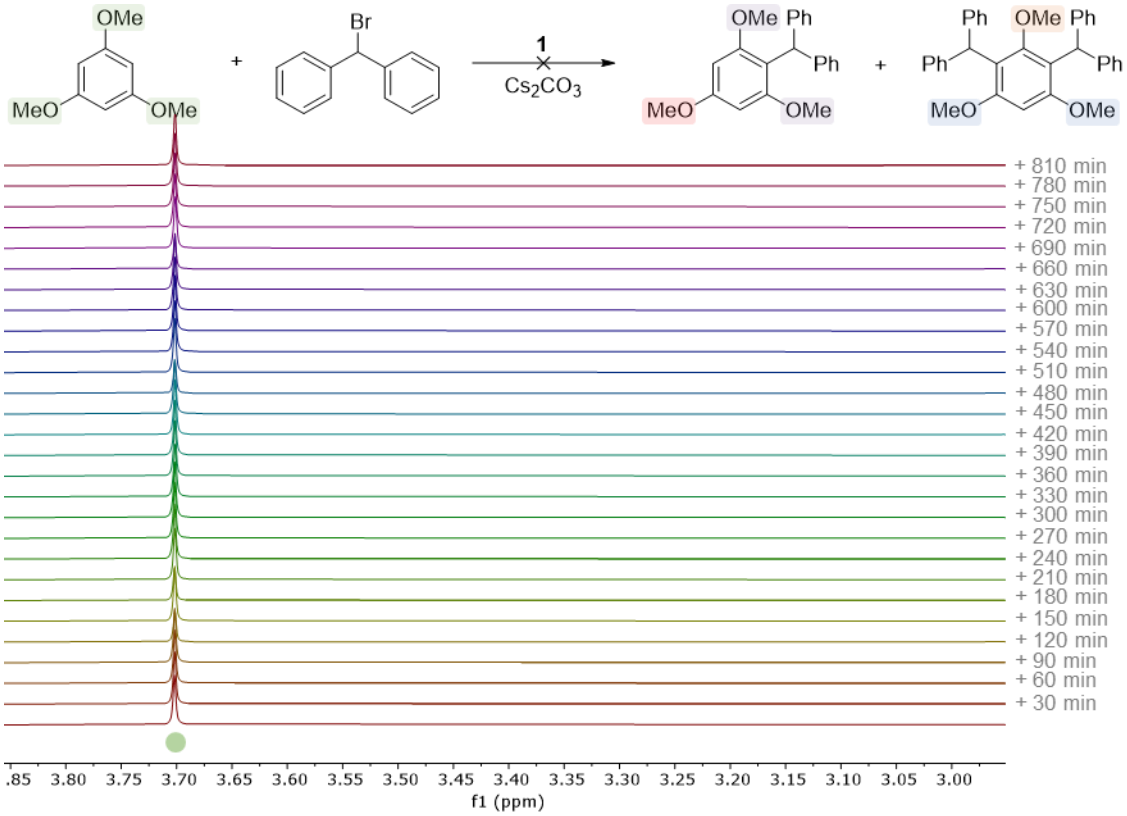


Figure S72. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1,3,5-trimethoxybenzene and benzhydryl bromide in $CDCl_3$ (1.67 mM) in the presence of $\mathbf{1^E}$ did not occur.

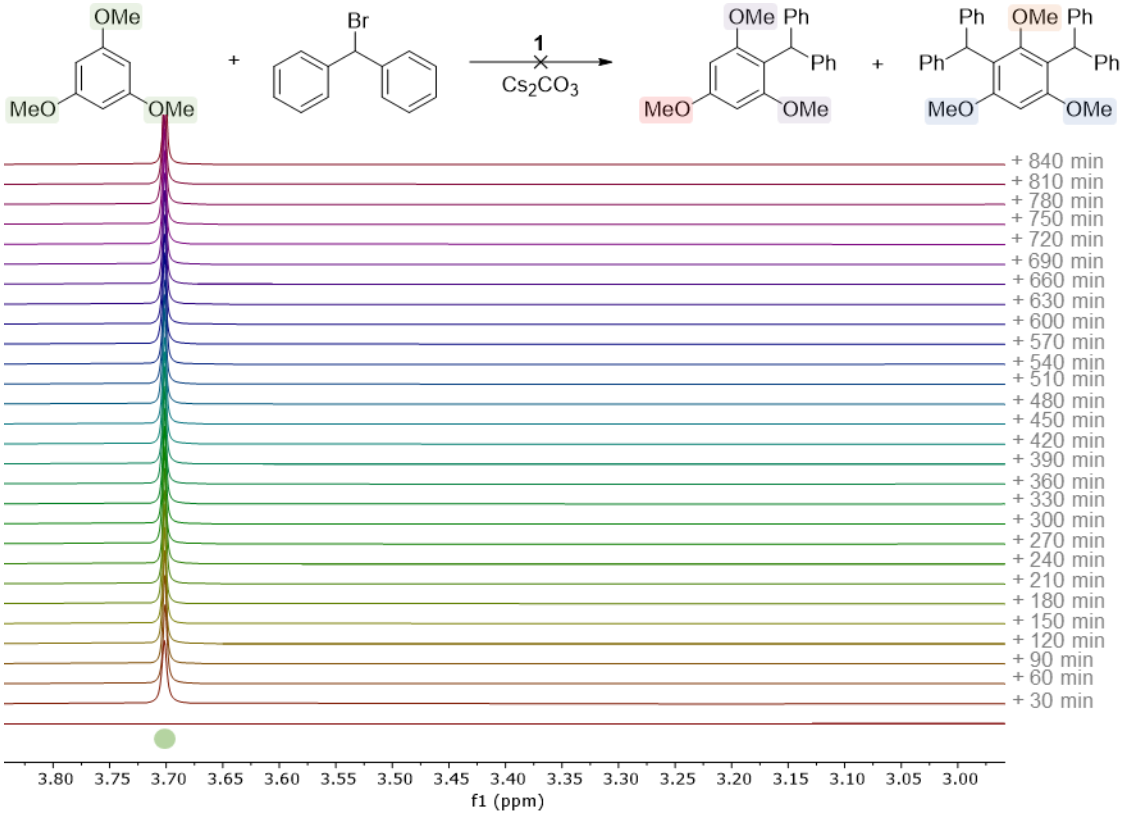


Figure S73. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1,3,5-trimethoxybenzene and benzhydryl bromide in $CDCl_3$ (1.67 mM) in the presence of $\mathbf{1^Z}$ did not occur.

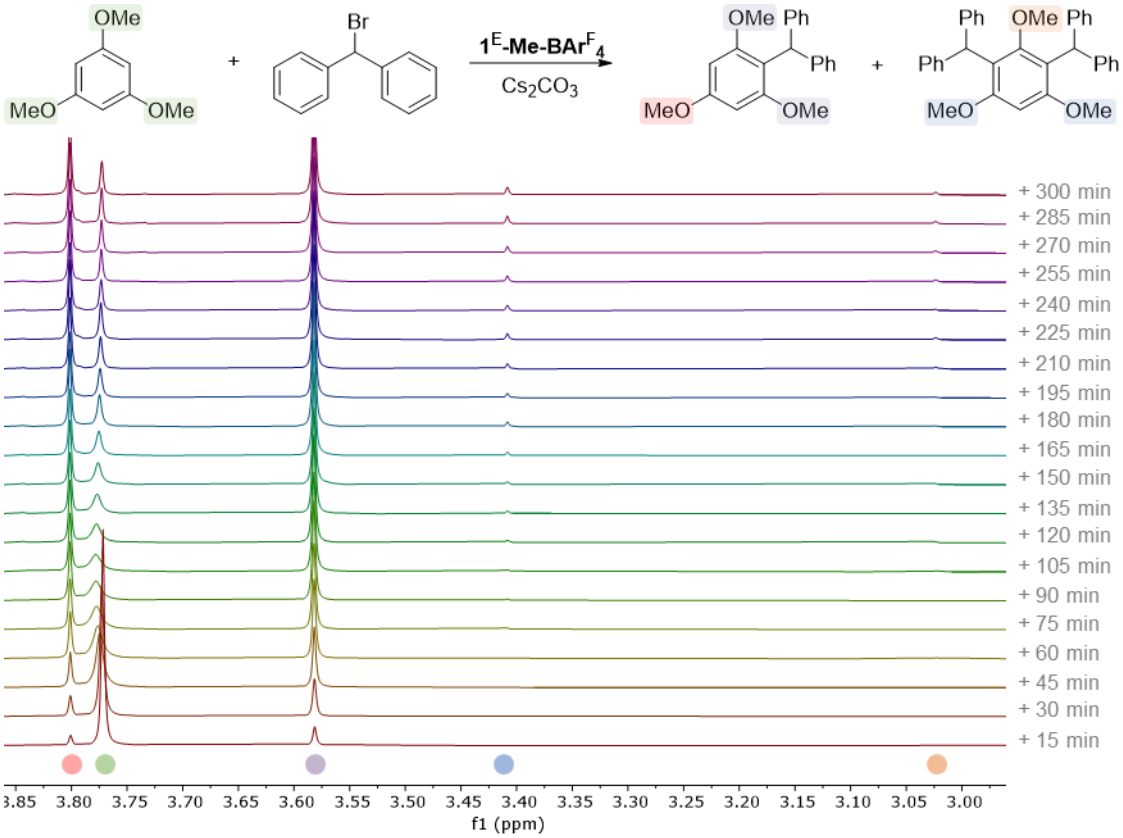


Figure S74. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1,3,5-trimethoxybenzene and benzhydryl bromide in $CDCl_3$ (1.67 mM) in the presence of 1 eq of activator **1^{E}-Me-BAr^{F}**

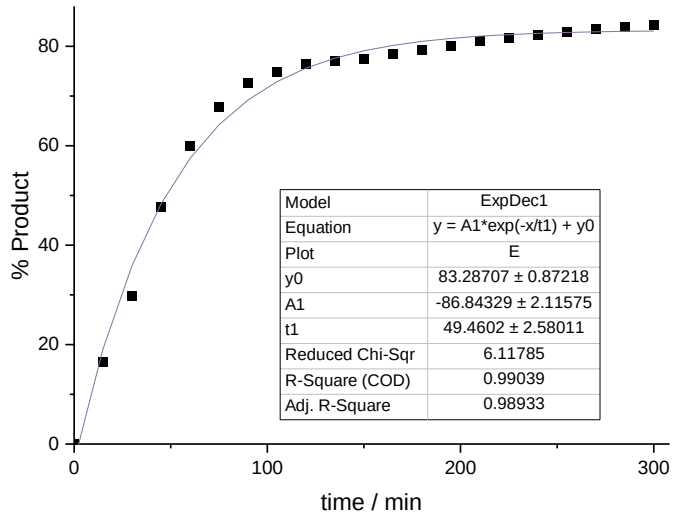


Figure S75. 1st order fit for reaction of 1,3,5-trimethoxybenzene and benzhydryl bromide in $CDCl_3$ (1.67 mM) in the presence of 1 eq of activator **1^{E}-Me-BAr^{F}** to generate ((2,4,6-trimethoxyphenyl)methylene)dibenzene

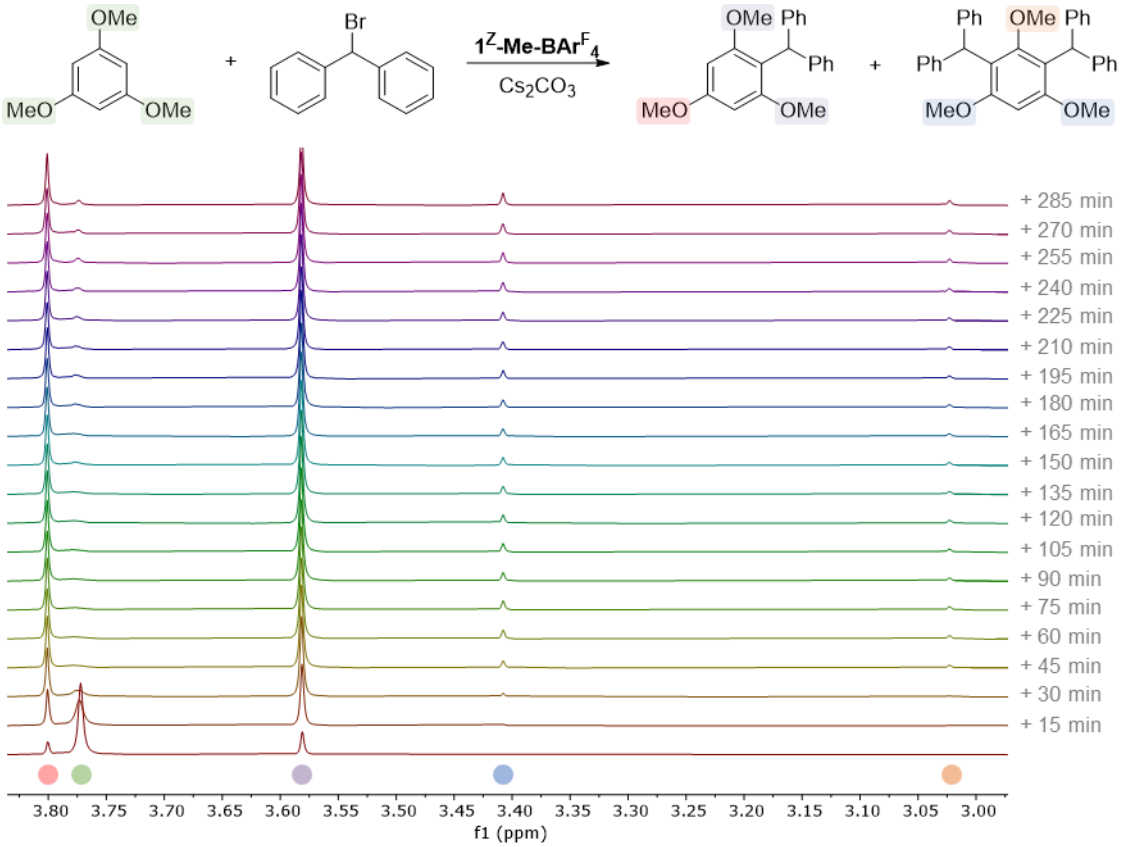


Figure S76. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1,3,5-trimethoxybenzene and benzhydryl bromide in $CDCl_3$ (1.67 mM) in the presence of 1 eq of activator **1^{Z}-Me-BAr^{F}** (80% PSS at 625 nm)

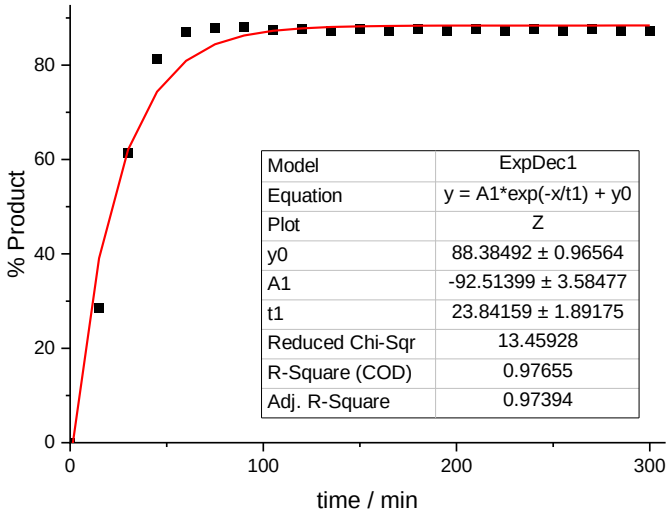


Figure S77. 1st order fit for reaction of 1,3,5-trimethoxybenzene and benzhydryl bromide in $CDCl_3$ (1.67 mM) in the presence of 1 eq of activator **1^{Z}-Me-BAr^{F}** to generate ((2,4,6-trimethoxyphenyl)methylene)dibenzene

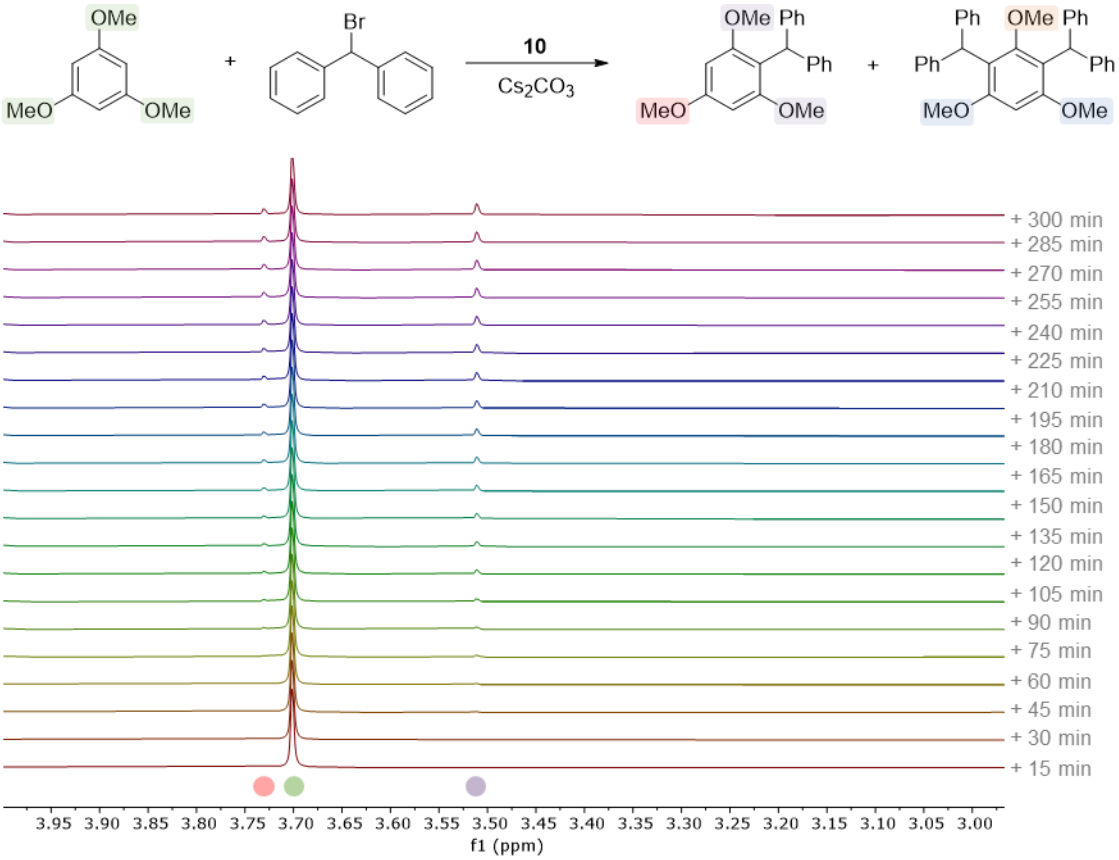


Figure S78. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1,3,5-trimethoxybenzene and benzhydryl bromide in $CDCl_3$ (1.67 mM) in the presence of 2 eq of activator **10.**

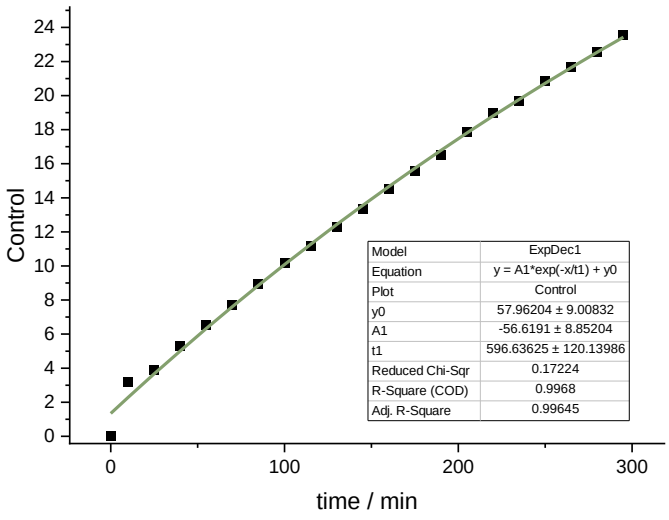


Figure S79. 1st order fit for reaction of 1,3,5-trimethoxybenzene and benzhydryl bromide in $CDCl_3$ (1.67 mM) in the presence of 2 eq of activator **10** to generate ((2,4,6-trimethoxyphenyl)methylene)dibenzene

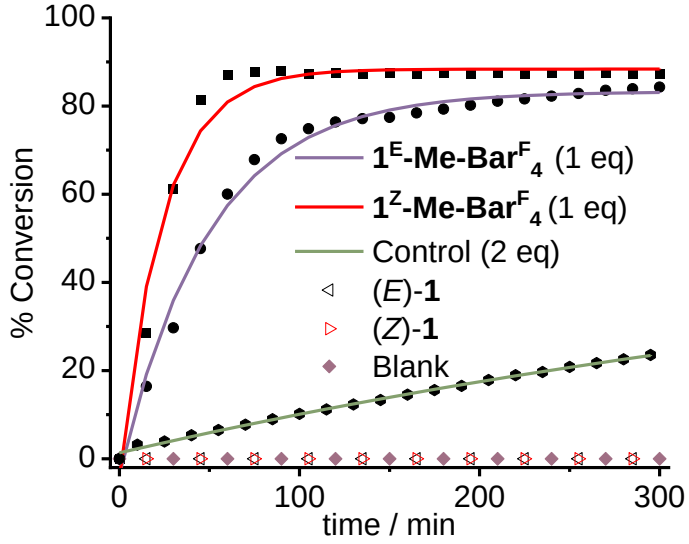


Figure S80. Reaction of 1,3,5-trimethoxybenzene and benzhydryl bromide in $CDCl_3$ (1.67 mM) in the presence **1**, **1-Me-BAr$^F_4$** or **10** to generate ((2,4,6-trimethoxyphenyl)methylene)dibenzene. Blank represents the run without a catalyst.

Chloride abstraction reaction.

At first, 3 mg Cs_2CO_3 was added in the NMR tube, then 200 µL (12 mM) of **1-Me-BAr$^F_4$** (Pre-heated at 70 degrees for 1 h or PSS at 625 nm) or **10** in $CDCl_3$ and 200 µL (12 mM) 1,3,5-trimethoxybenzene was added. The mixture was mixed by shaking. Finally, 200 µL (12 mM) benzhydryl chloride solution was added and mixed by inversion. The samples were directly transferred and submitted to the NMR spectrometer. The first spectra were measured after approximately 30 minutes and every 30 minutes an additional spectrum was recorded. The conversion was determined by integration of the methoxy signals (3.77 ppm) of 1,3,5-trimethoxybenzene against the two methoxy signals (3.80 ppm and 3.58 ppm) in the product ((2,4,6-trimethoxyphenyl)methylene)dibenzene. The two-fold substitution occurred and ((2,4,6-trimethoxy-1,3-phenylene)bis(methanetriyl))tetrabenzene (methoxy signals at 3.41 ppm and 3.03 ppm) was formed as minor product (ca. 6% for both isomers)

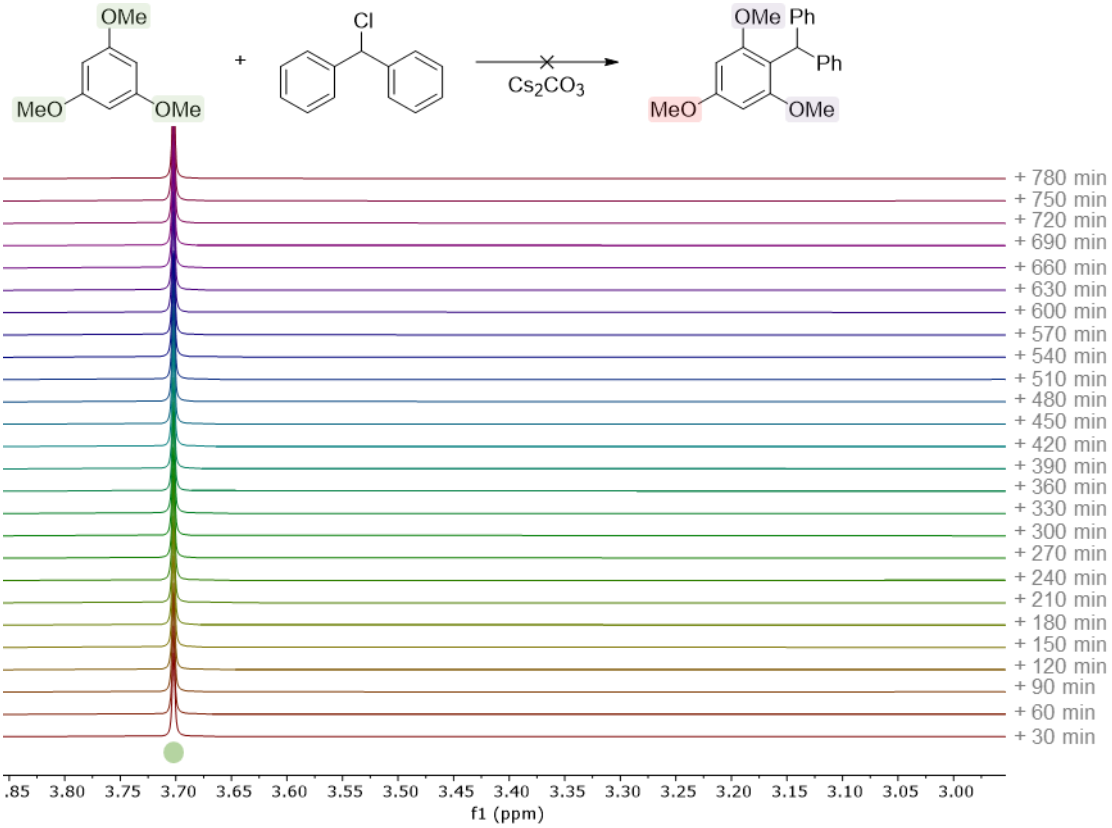


Figure S81. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1,3,5-trimethoxybenzene and benzhydryl chloride in $CDCl_3$ (4 mM) in the absence of activator did not occur.

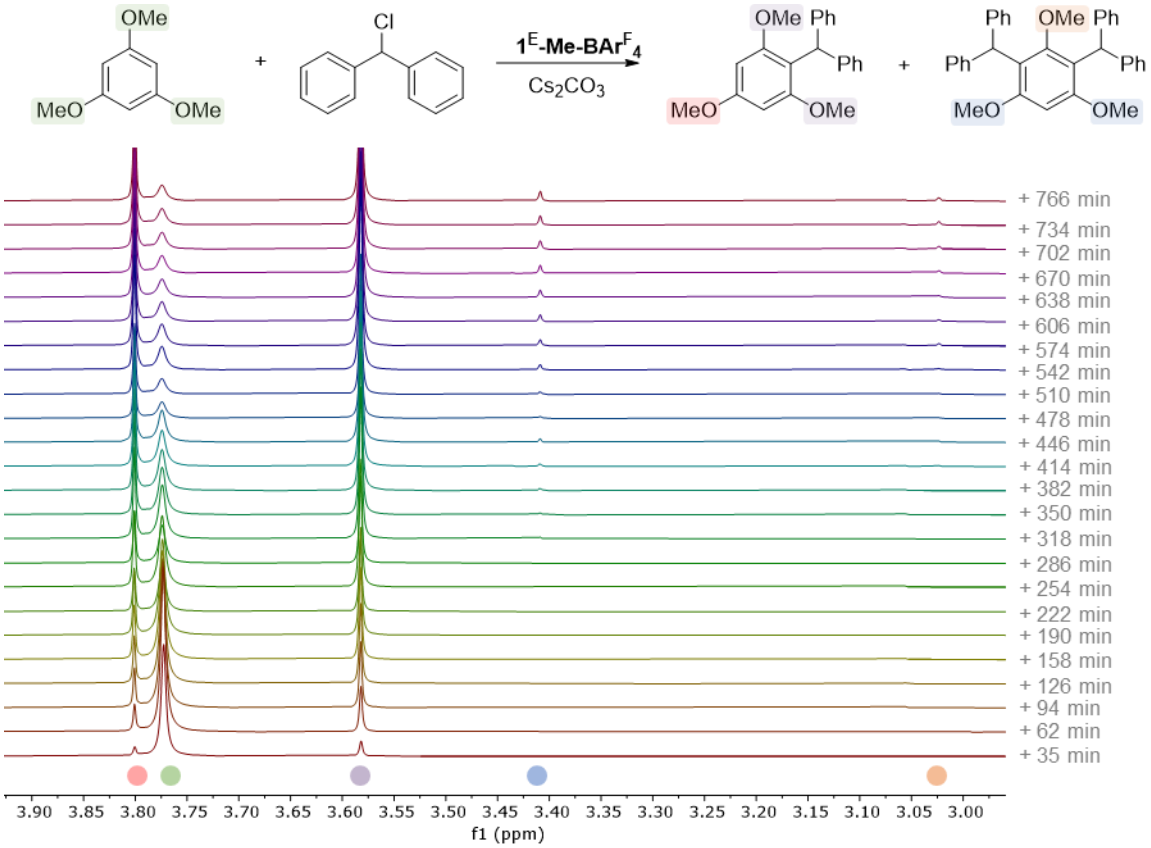


Figure S82. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1,3,5-trimethoxybenzene and benzhydryl chloride in $CDCl_3$ (4 mM) in the presence of 1 eq of activator **1^{E}-Me-BAr$^{F}_{4}$**

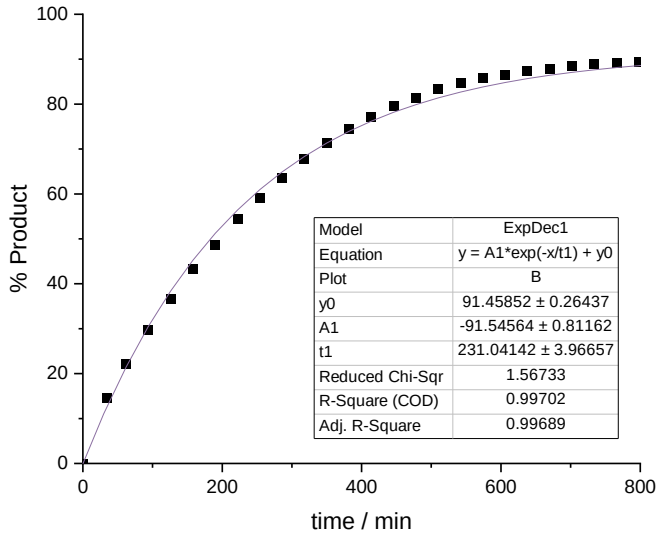


Figure S83. 1st order fit for reaction of 1,3,5-trimethoxybenzene and benzhydryl chloride in $CDCl_3$ (4 mM) in the presence of 1 eq of activator **1^{E}-Me-BAr$^{F}_{4}$** to generate ((2,4,6-trimethoxyphenyl)methylene)dibenzene

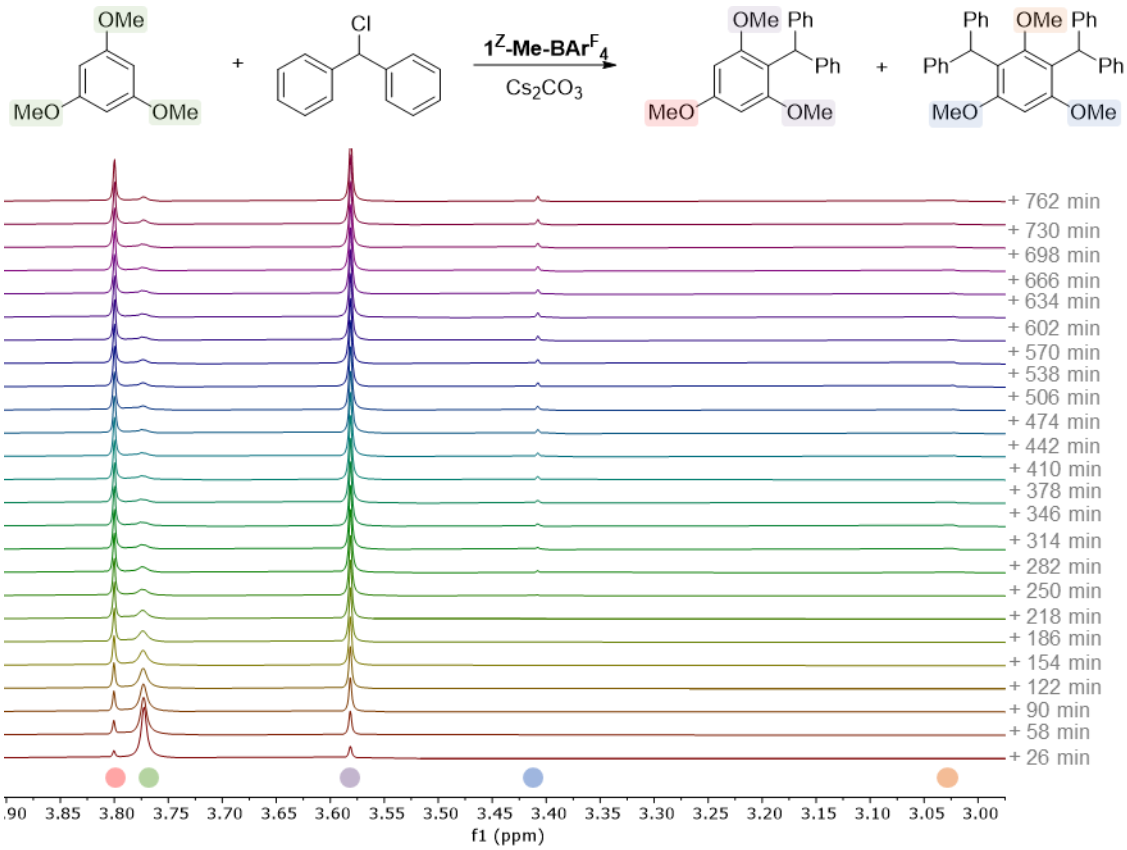


Figure S84. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1,3,5-trimethoxybenzene and benzhydryl chloride in $CDCl_3$ (4 mM) in the presence of 1 eq of activator **1^{Z}-Me-BAr$^{F}_{4}$** (80% PSS at 625 nm)

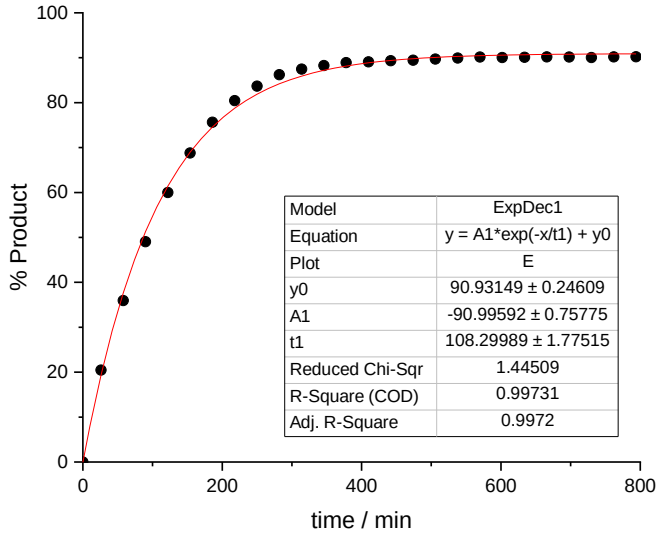


Figure S85. 1st order fit for reaction of 1,3,5-trimethoxybenzene and benzhydryl chloride in $CDCl_3$ (4 mM) in the presence of 1 eq of activator **1^{Z}-Me-BAr$^{F}_{4}$** to generate ((2,4,6-trimethoxyphenyl)methylene)dibenzene

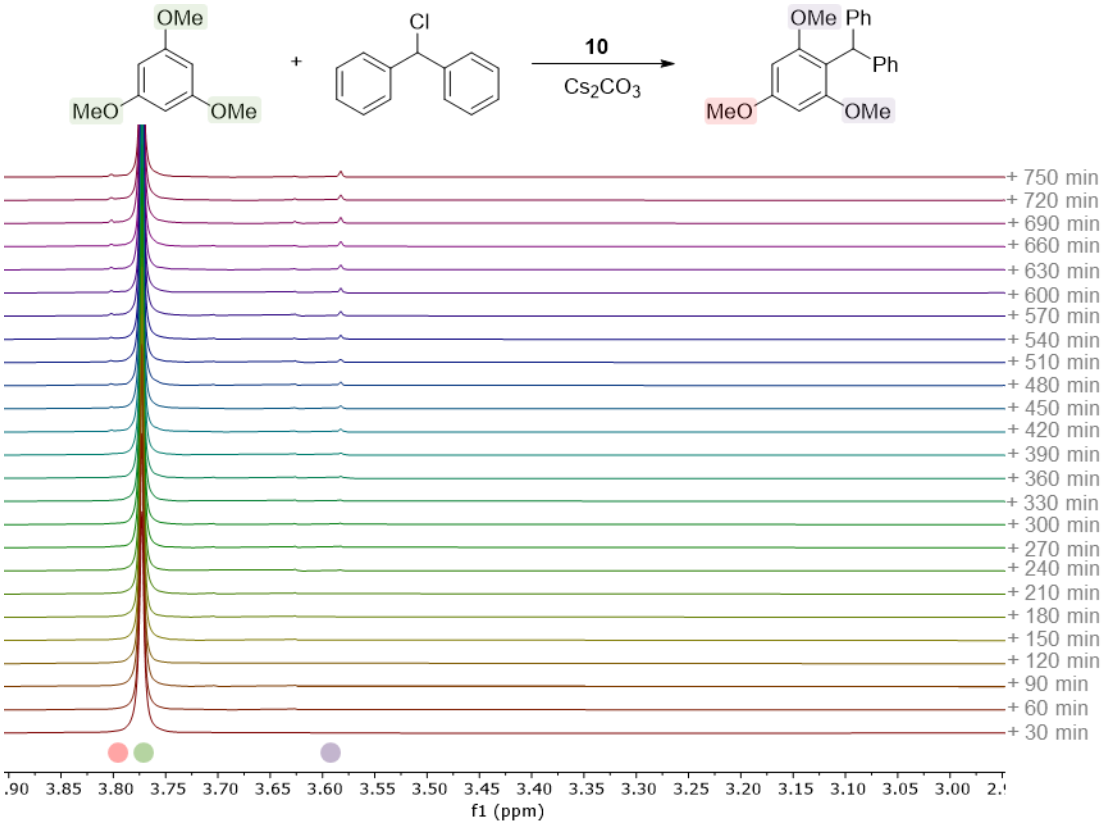


Figure S86. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1,3,5-trimethoxybenzene and benzhydryl chloride in $CDCl_3$ (4 mM) in the presence of 2 eq of activator **10.**

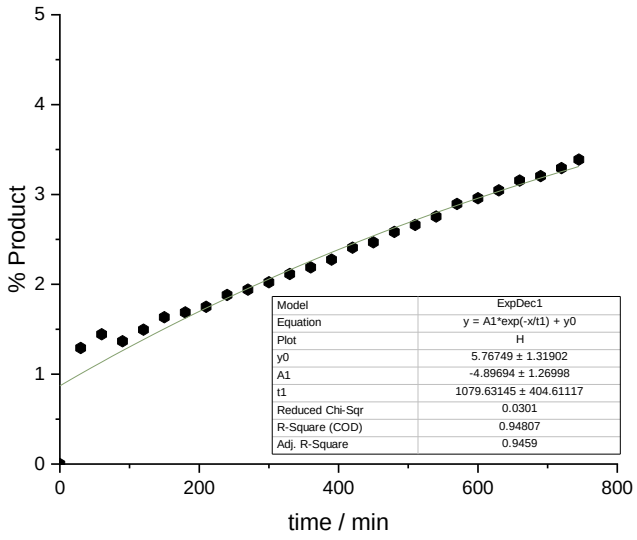


Figure S87. 1st order fit for reaction of 1,3,5-trimethoxybenzene and benzhydryl chloride in $CDCl_3$ (4 mM) in the presence of 2 eq of activator **10** to generate ((2,4,6-trimethoxyphenyl)methylene)dibenzene

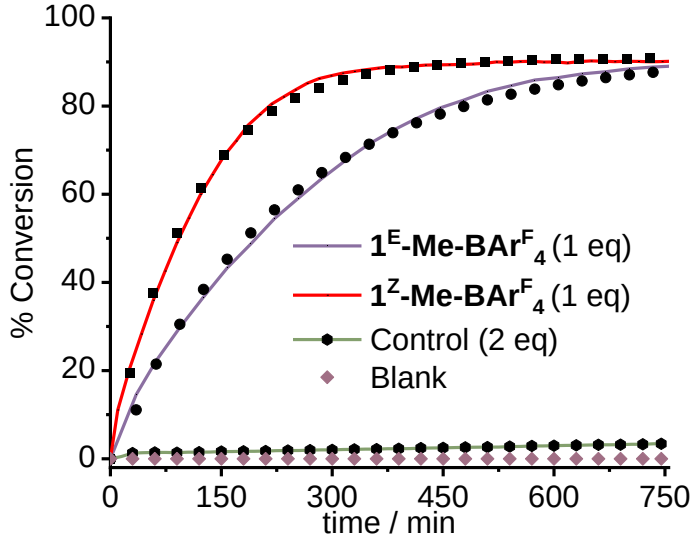


Figure S88. Reaction of 1,3,5-trimethoxybenzene and benzhydryl chloride in $CDCl_3$ (4 mM) in the presence **1-Me-BAr$^F_4$** or **10** to generate ((2,4,6-trimethoxyphenyl)methylene)dibenzene. Blank represents the run without a catalyst.

Mukaiyama Aldol Reaction.

At first, catalyst (0.5 mol% **1-Me-BAr$^{F}_{4}$** or 1 mol% **10**) was added to an NMR tube. The NMR tube was purged with N_2, then degassed, dry $CDCl_3$ (0.5 mL) was added. Benzaldehyde (10.2 µL, 0.1 mmol) was added to it under N_2. The silyl enol ether (30 µL, 0.15 mmol) was added to it and ^{1}H NMR were recorded in 15 minute intervals. Conversions were determined based on the consumption of aldehyde through the measurement of integration of the aldehyde proton relative to that of TMS signal of the product.

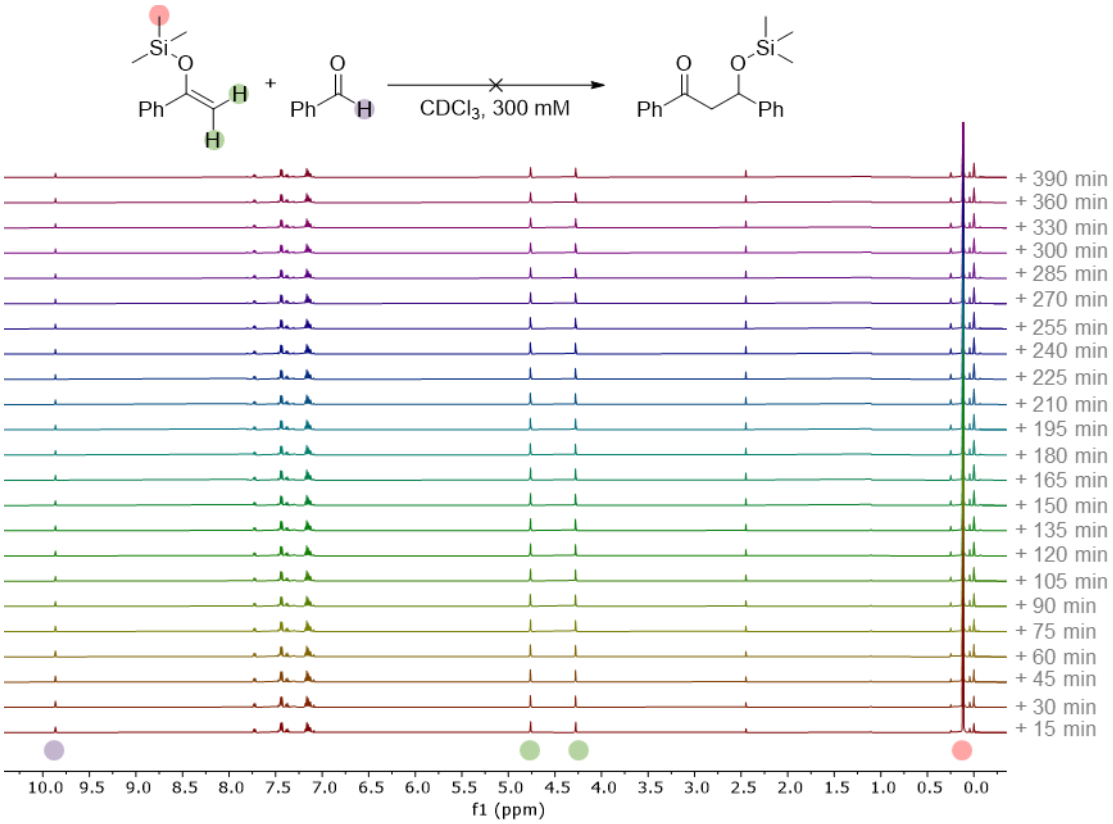


Figure S89. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of silyl enol ether and benzaldehyde in $CDCl_3$ (300 mM) in the absence of activator did not occur.

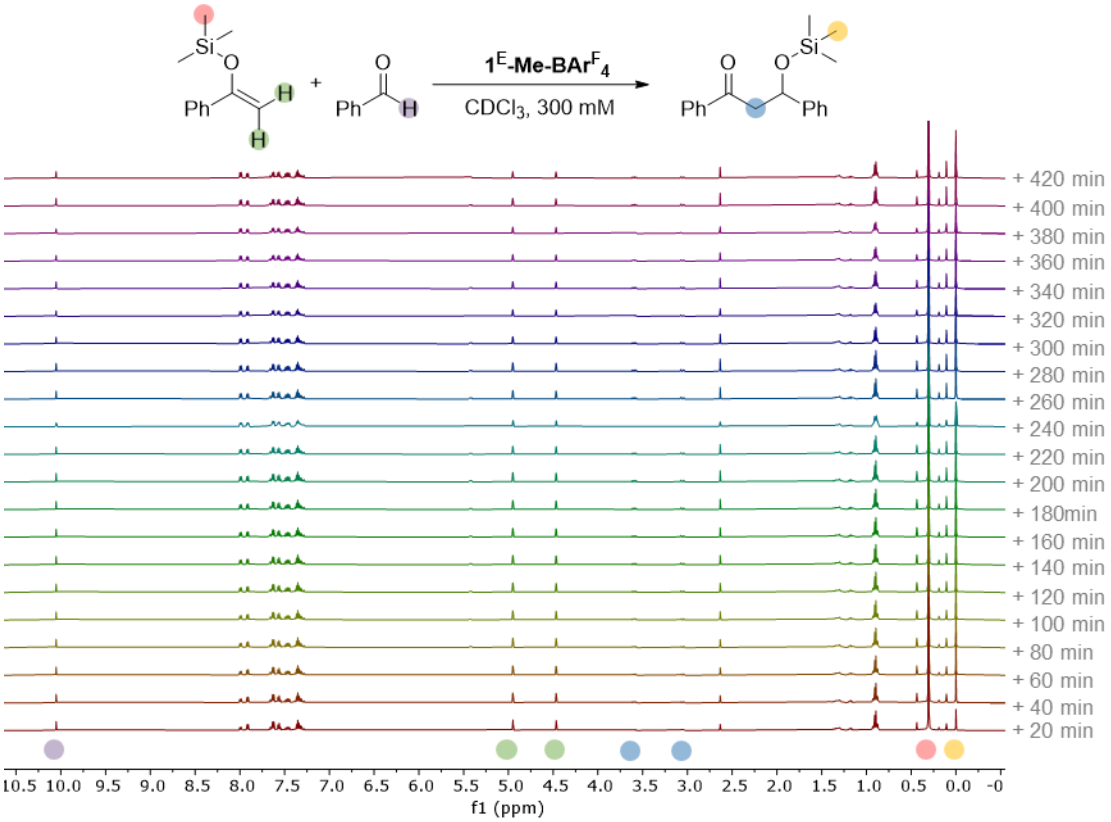


Figure S90. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of silyl enol ether and benzaldehyde in $CDCl_3$ (300 mM) in the presence of 0.5 mol% activator **1^{E}-Me-BAr$^{F}_{4}$**

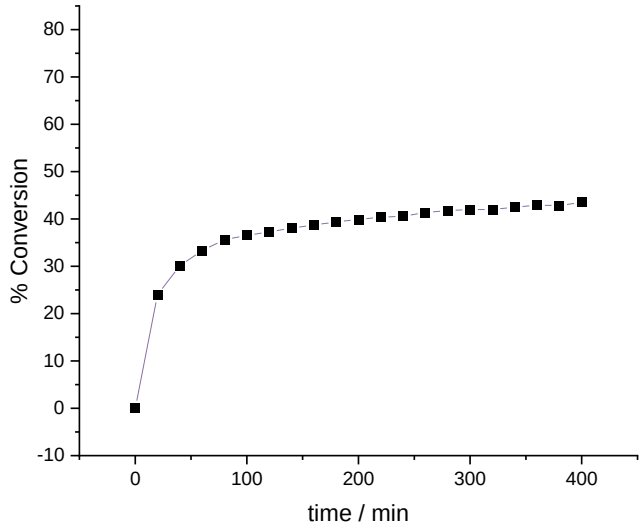


Figure S91. Reaction of silyl enol ether and benzaldehyde in $CDCl_3$ (300 mM) in the presence of 0.5 mol% activator **1^{E}-Me-BAr$^{F}_{4}$**

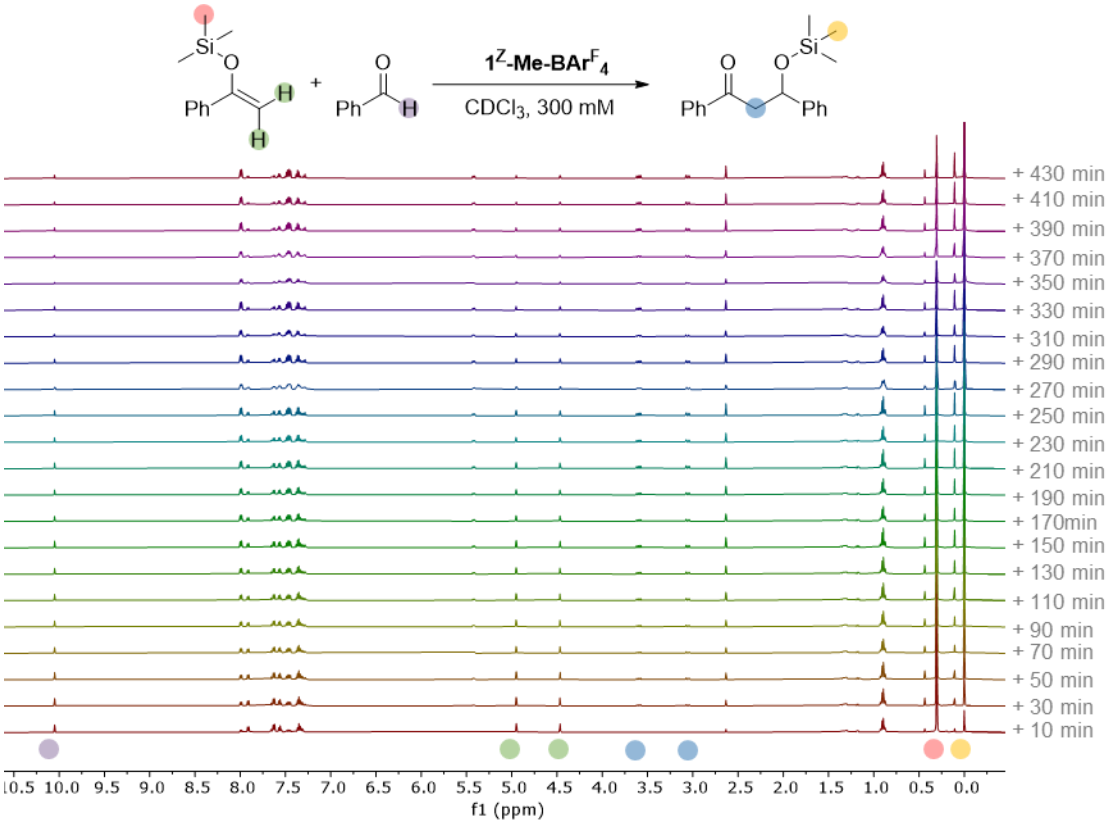


Figure S92. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of silyl enol ether and benzaldehyde in $CDCl_3$ (300 mM) in the presence of 0.5 mol% activator **1^{Z}-Me-BAr$^{F}_{4}$**

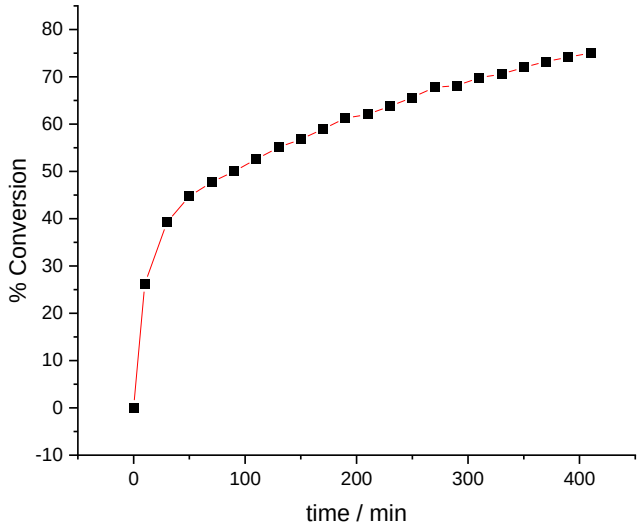


Figure S93. Reaction of silyl enol ether and benzaldehyde in $CDCl_3$ (300 mM) in the presence of 0.5 mol% activator **1^{Z}-Me-BAr$^{F}_{4}$**

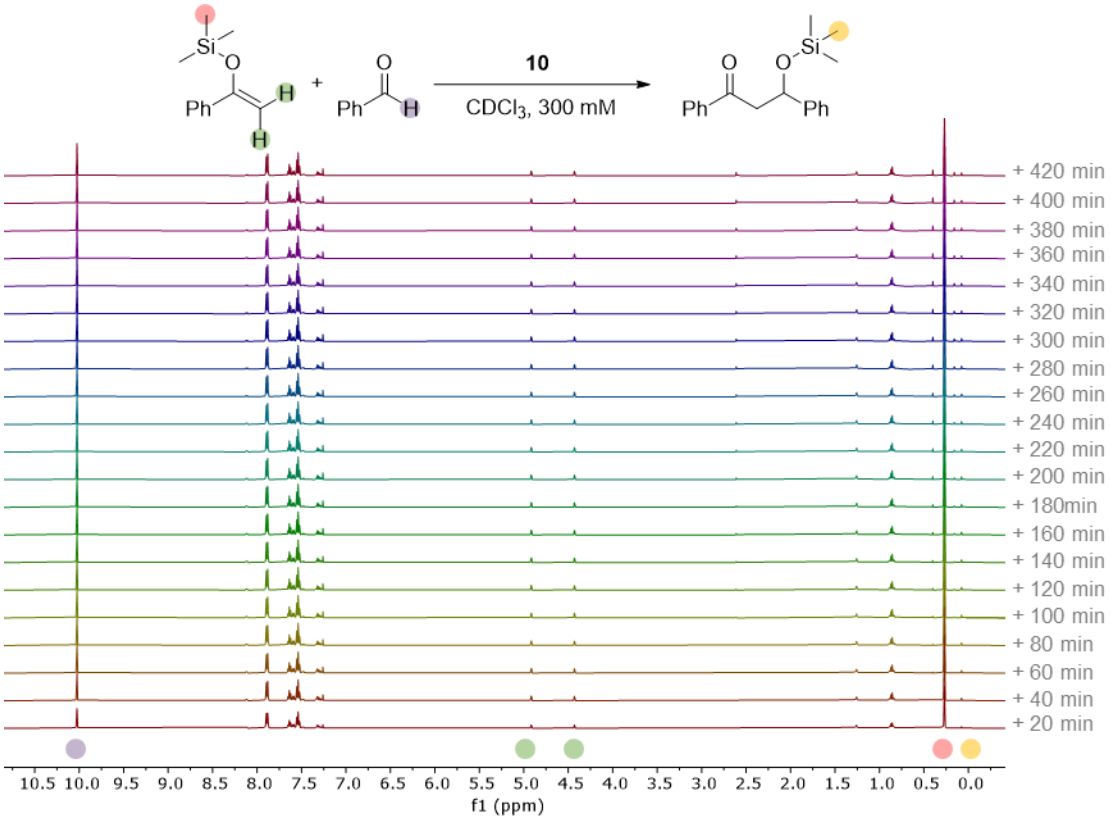


Figure S94. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of silyl enol ether and benzaldehyde in $CDCl_3$ (300 mM) in the presence of 1 mol% activator **10**

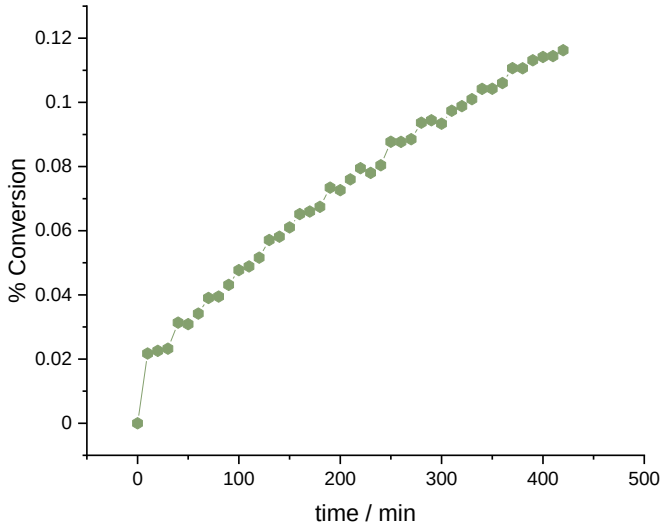


Figure S95. Figure S62. Reaction of silyl enol ether and benzaldehyde in $CDCl_3$ (300 mM) in the presence of 1 mol% activator **10**

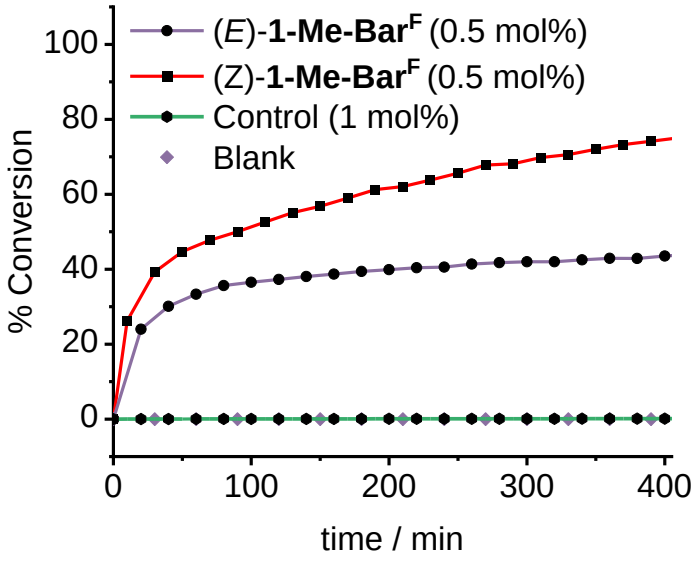


Figure S96. Reaction of silyl enol ether and benzaldehyde in $CDCl_3$ (300 mM) in the presence **1-Me-BAr$^F_4$** or **10.** Blank represents the run without the catalyst.

Michael addition reaction

To a new NMR tube, freshly prepared stock solutions of the respective catalyst (200 µL, 0.1 eq. 15 mM), 1- methylindole (200 µL, 1 eq., 150 mM) and β-trans-crotonophenone (200 µL, 1 eq., 150 mM) in deuterated methylene chloride were added, sealed and the NMR tube shaken. Afterwards, ^{1}H-NMR experiments were performed periodically every 15 minutes at room temperature. Conversions were determined based on the consumption of β-trans-crotonophenone (signal at 1.99 ppm) vs. the formation of product (signal at 1.42).

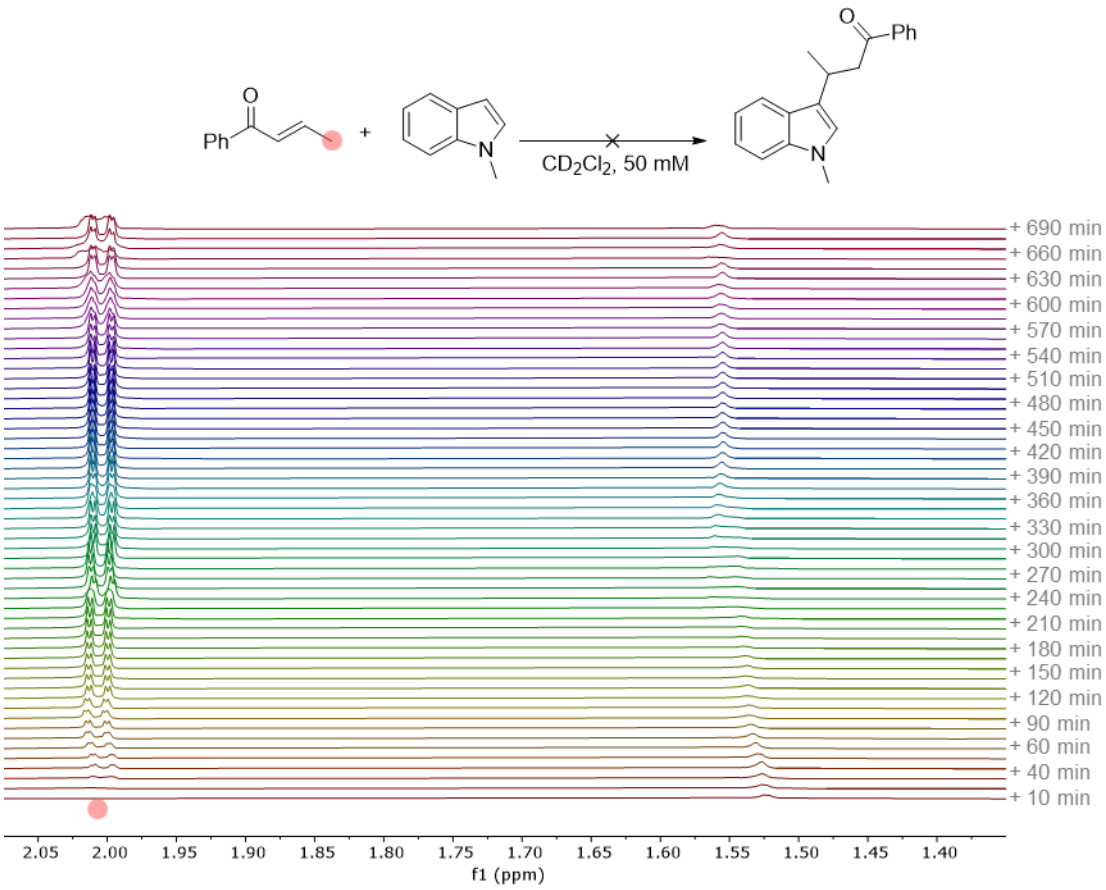


Figure S97. Stacked plot of the ^{1}H NMR kinetic experiments. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1- methylindole and β-trans-crotonophenone in CD_2Cl_2 (50 mM) in the absence of activator did not occur.

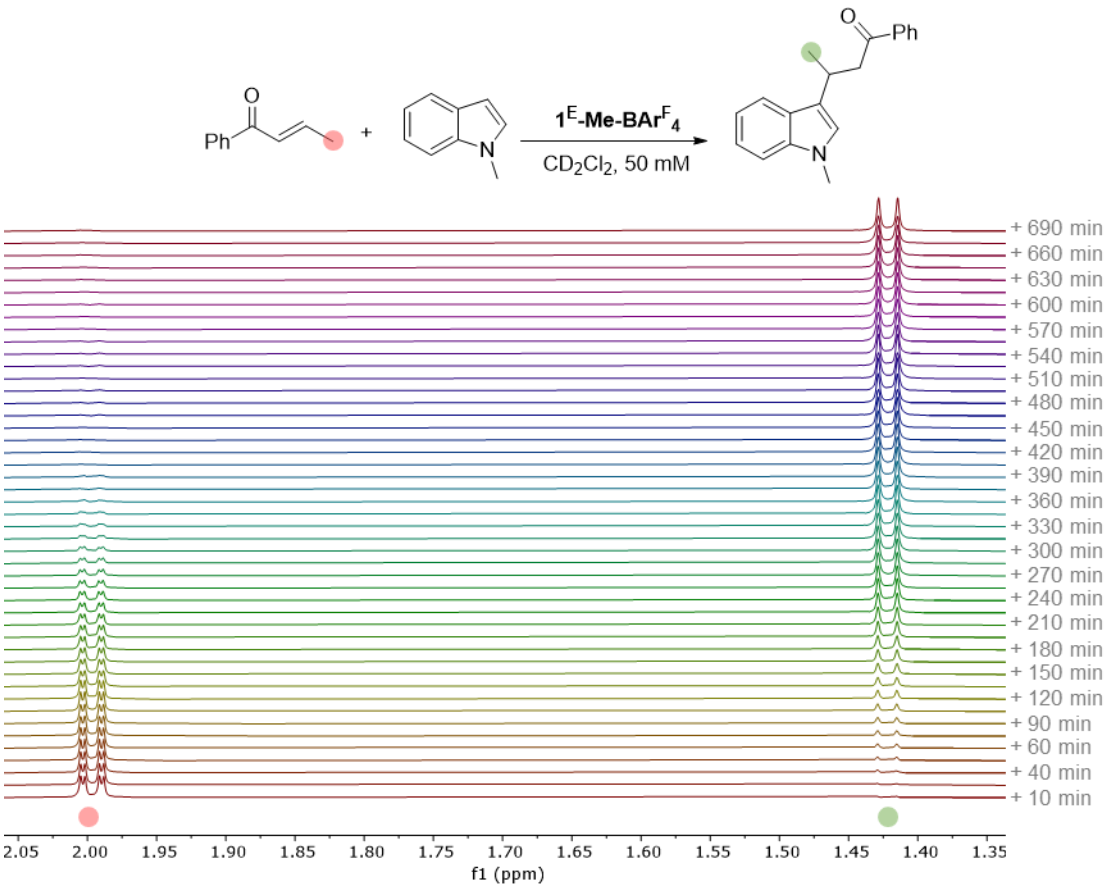


Figure S98. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1- methylindole and β-trans-crotonophenone in CD_2Cl_2 (50 mM) in the presence of 10 mol% activator **1^{E}-Me-BAr$^{F}_{4}$**

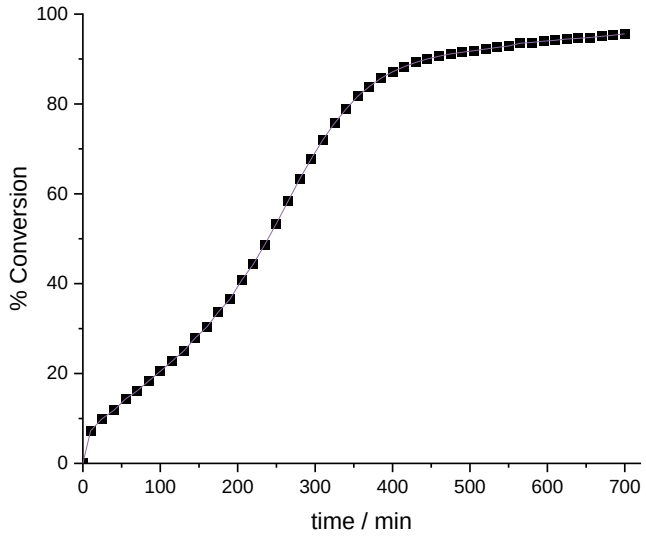


Figure S99. Reaction of 1- methylindole and β-trans-crotonophenone in CD_2Cl_2 (50 mM) in the presence of 10 mol% activator **1^{E}-Me-BAr$^{F}_{4}$**

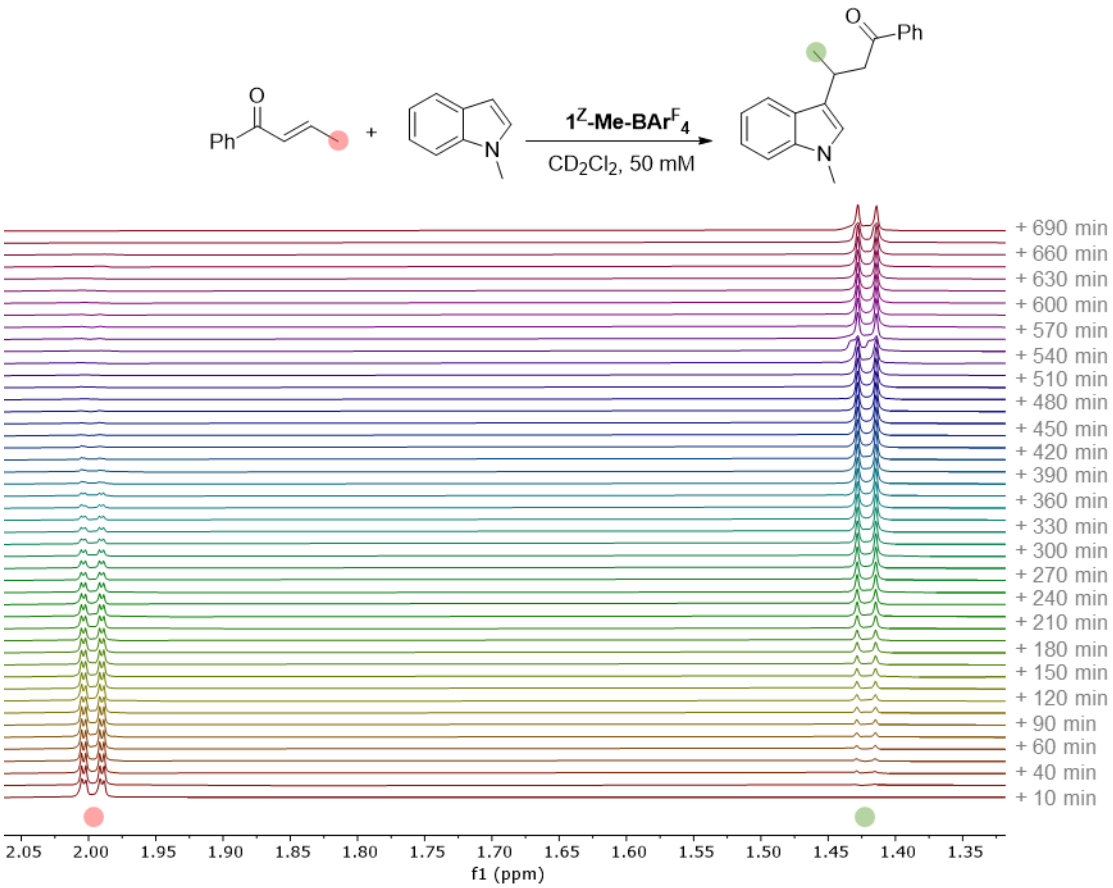


Figure S100. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1- methylindole and β-trans-crotonophenone in CD_2Cl_2 (50 mM) in the presence of 10 mol% activator **1^{Z}-Me-BAr$^{F}_{4}$**

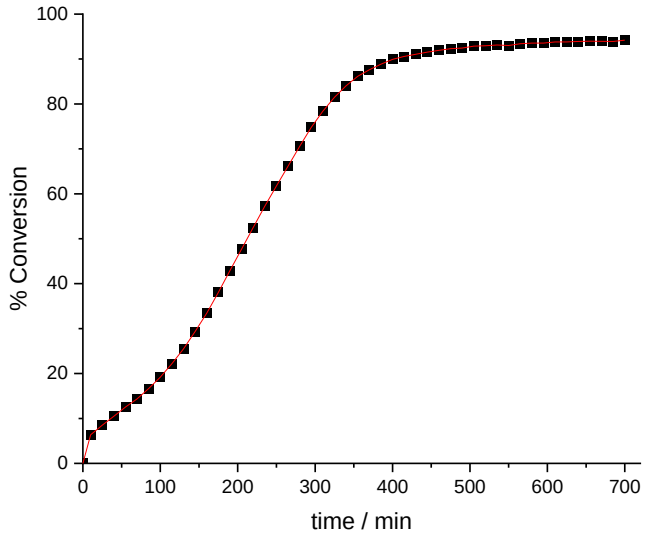


Figure S101. Reaction of 1- methylindole and β-trans-crotonophenone in CD_2Cl_2 (50 mM) in the presence of 10 mol% activator **1^{Z}-Me-BAr$^{F}_{4}$**

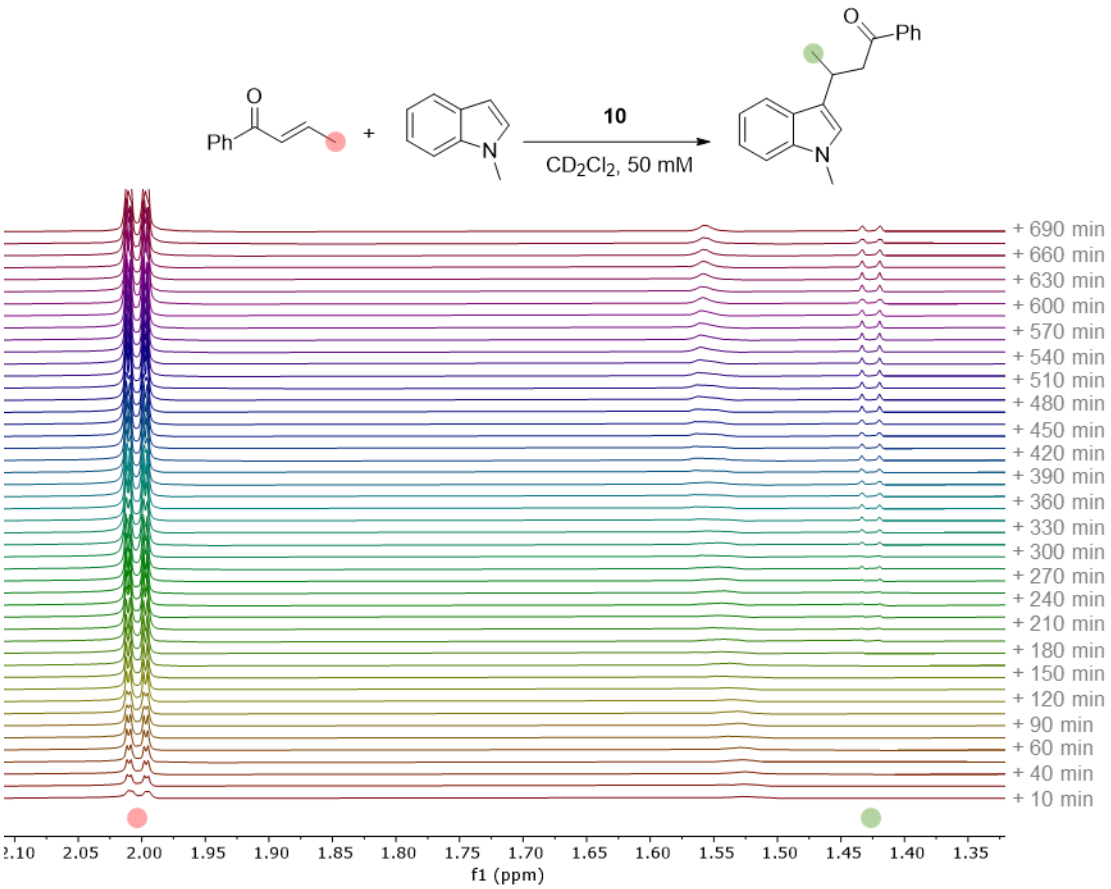


Figure S102. Stacked plot of the ^{1}H NMR kinetic experiments. Reaction of 1- methylindole and β-trans-crotonophenone in CD_2Cl_2 (50 mM) in the presence of 20 mol% activator **10**

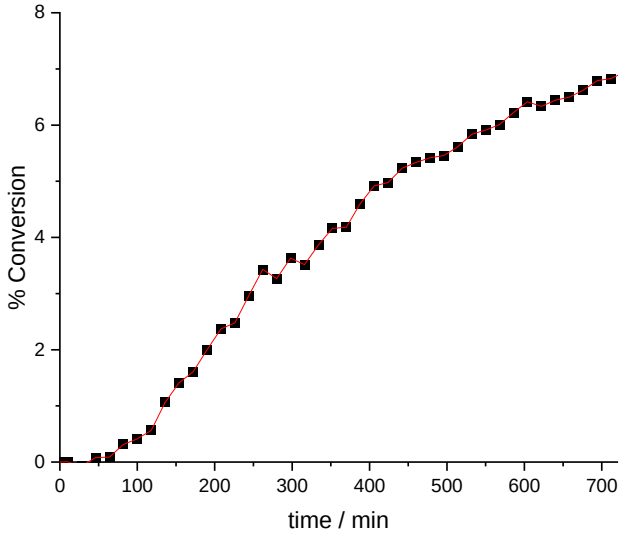


Figure S103. Reaction of 1- methylindole and β-trans-crotonophenone in CD_2Cl_2 (50 mM) in the presence of 20 mol% activator **10**

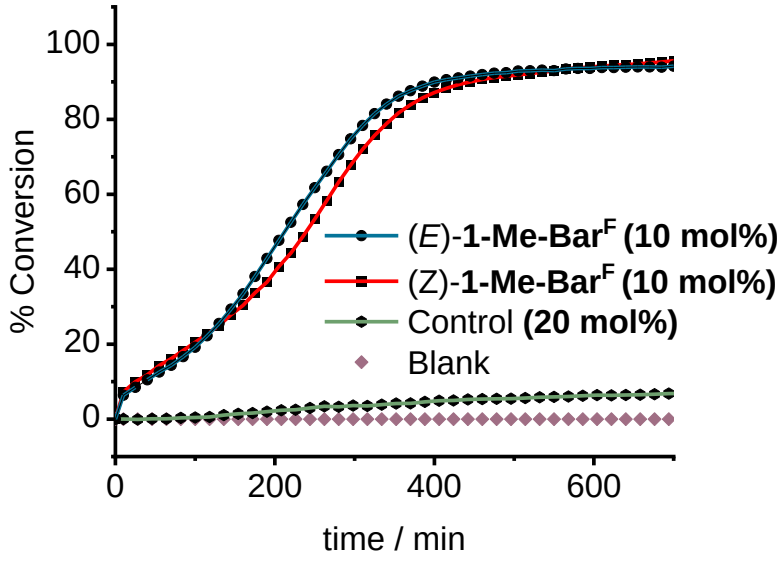


Figure S104. Reaction of N-methylindole and β-trans-crotonophenone in CD_2Cl_2 (50 mM) in the presence **1-Me-BAr$^F{}_4$** or **10.** Blank represents the run without the catalyst.

7 References

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