Supplementary Information

Synthesis of bambusurils with perfluoroalkylthiobenzyl groups as highly potent halide receptors

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Table of Contents

1. Materials and methods

All reagents and solvents were purchased from commercial suppliers and used without further purification. Compounds **2**, **5** and **19** were prepared using the previously described procedures.[1–3] Mili-Q grade water was prepared by a Barnstead™ MicroPure™ Water Purification System. All reactions that require increased temperature were heated with a DrySyn heating block on an electromagnetic stirrer. Mixing of the reaction mixtures was done by a magnetic stirrer. TLC data were recorded on VWR TLC Aluminium Plates – Silica F254, 200 µm layer thickness.

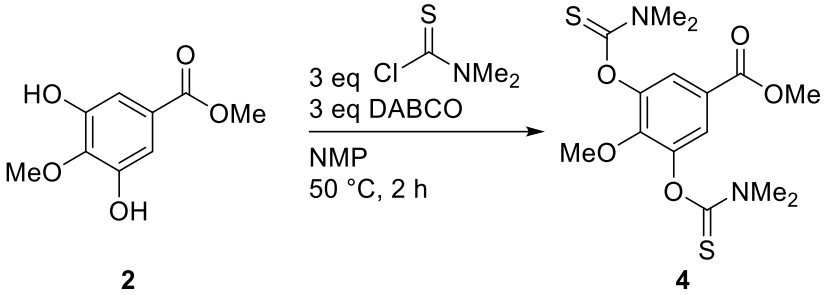
The NMR spectra were measured on one of the following spectrometers at 25 °C: Bruker Avance III 300 MHz (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{19}F: 282 MHz), Bruker Avance III 500 MHz (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F 471 MHz); Jeol JNM-ECZ600R/S3 (^{1}H: 600 MHz, ^{19}F 565 MHz) was used to measure competition experiments described in the Section 4. Chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (*J*) are given in Hertz (Hz). The ^{1}H and ^{13}C NMR spectra were referenced to the solvent residual signals; ^{19}F NMR spectra were either unreferenced.[4] The NMR spectra were processed using MestReNova 14.3.3.

HRMS spectra were recorded on an Agilent 6224 Accurate-Mass TOF mass spectrometer. Samples were ionized by electrospray ionization (ESI) or atmospheric-pressure chemical ionization (APCI). For recording MALDI-TOF mass spectra MALDI-TOF Axima CFR spectrometer was used. Samples were ionized with the aid of a nitrogen laser (wavelength 337 nm, maximum power 6 MW). Gentisic acid (DHB) or α-cyano-4-hydroxycinnamic acid (HCCA) were used as matrices.

Mass spectra of the compounds **9**-**16**, **24**, **25** and **27** could not be recorded due to poor ionizability of these compounds.

2. Synthetic procedures

2.1. Methyl 3,5-bis((dimethylcarbamothioyl)oxy)-4-methoxybenzoate 4

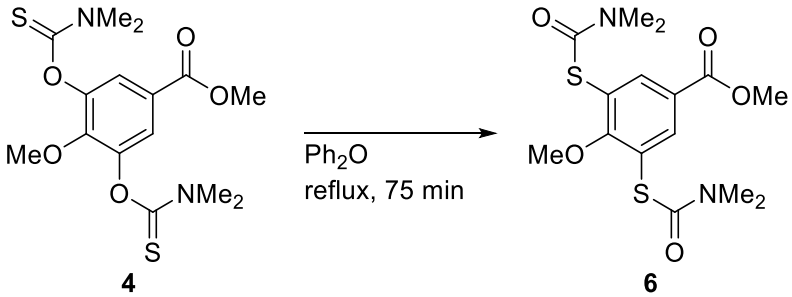


2 **4**

2 (7.93 g, 40 mmol, 1 eq) and DABCO (13.46 g, 120 mmol, 3 eq) were heated in dry NMP (80 mL) to 50 °C forming a dark yellow solution under an inert atmosphere. Dimethylthiocarbamoyl chloride (14.83 g, 120 mmol, 3 eq) dissolved in dry NMP (40 mL) was added. The reaction mixture was stirred at 50 °C for 4 h under an inert atmosphere. The yellow suspension was diluted with MeOH (140 mL) and poured into vigorously stirred cold water (700 mL). The mixture was sonicated until a fine precipitate was obtained. The solid was collected by filtration and redissolved in a boiling EtOAc (100 mL). Cyclohexane (350 mL) was added, the resulting mixture was sonicated, then cooled to 4 °C. The product was collected by filtration and displacement washed with hexane (200 mL). Compound **4** was obtained as a white solid (10.73 g, 72%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (s; 2H; Ar-H), 3.92 (s; 3H; OCH_3), 3.86 (s; 3H; OCH_3), 3.45 (s; 6H; NCH_3), 3.36 (s; 6H; NCH_3). **^{13}C{^{1}H} APT NMR** (75 MHz, $CDCl_3$): 187.2, 165.5, 149.0, 146.6, 124.4, 124.0, 61.5, 52.3, 43.6, 38.9. **HRMS** (APCI): m/z calc. for $C_{15}H_{20}N_2O_5S_2+H^+$: 373.0886 $[M+H]^+$; found: 373.0889. **TLC**: R_F = 0.52 ($CHCl_3$/MeCN 9:1).

2.2. Methyl 3,5-bis((dimethylcarbamoyl)thio)-4-methoxybenzoate 6

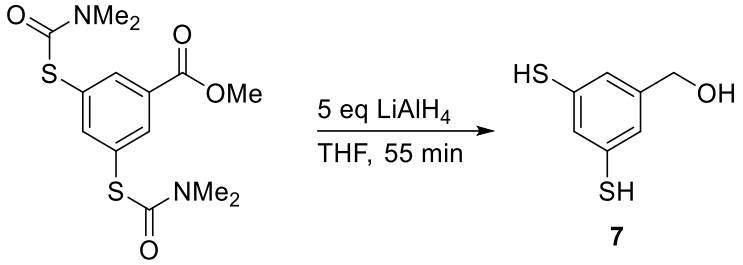


4 **6**

4 (9.86 g, 26.5 mmol) with Ph_2O (295 mL) were heated to reflux for 75 min while N_2 was bubbled through the reaction mixture for the whole time. After cooling down, a brown solution was diluted with hexane (600 mL) and filtered through a SiO_2 plug (4.0×8.0 cm). The plug was washed with EtOAc/hexane (1:2, 200 mL), and then the product was eluted with EtOAc/hexane (5:1 600 mL). The filtrate was evaporated, and the residue was purified by column chromatography (cyclohexane/EtOAc 1:1 to 4:1). Compound **6** was obtained as an orangish solid (7.15 g, 73%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (s; 2H; Ar-H), 3.89 (s; 3H; OCH_3), 3.87 (s; 3H; OCH_3), 3.08 (br s; 12H; NCH_3). **^{13}C{^{1}H} APT NMR** (75 MHz, $CDCl_3$): 166.6, 165.7, 165.5, 141.4, 126.8, 124.5, 62.2, 52.4, 37.2. **HRMS** (APCI): m/z calc. for $C_{15}H_{20}N_2O_5S_2+H^+$: 373.0886 $[M+H]^+$; found: 373.0887. **TLC**: R_F = 0.26 ($CHCl_3$/MeCN 9:1).

2.3. 3,5-Dimercaptobenzylalcohol 7

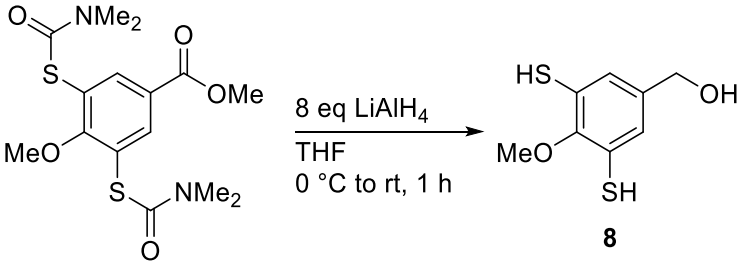


5 **7**

$LiAlH_4$ (1898 mg, 50 mmol, 5 eq) was suspended in dry THF (60 mL) under an inert atmosphere. Dropwise addition of **5** (3424 mg, 10 mmol, 1 eq) in dry THF (40 mL) caused heating of the reaction mixture to reflux. After further stirring for 55 min, the reaction mixture was cooled in an ice bath and quenched by slowly adding EtOAc (20 mL) and water (50 mL). The volatiles were evaporated at 40 °C and the mixture was acidified with aqueous HCl (10%, 100 mL) and extracted with CH_2Cl_2 (4×75 mL). The organic extracts were dried over $MgSO_4$. Evaporation at 40 °C yielded compound **7** as a white solid (1650 mg, 96%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09 (s; 1H; Ar-H), 7.04 (s; 2H; Ar-H), 4.57 (s; 2H; SH), 3.45 (s; 2H; CH_2), 1.89 (s; 1H; OH). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): 142.8, 132.5, 128.4, 124.8, 64.5. **HRMS** (ESI): m/z calc. for $C_7H_8OS_2-H^-$: 170.9944 $[M-H]^-$; found: 170.9933. **TLC**: R_F = 0.32 ($CHCl_3$/MeCN 9:1); 0.27 (cyclohexane/EtOAc 1:1); 0.08 (cyclohexane/EtOAc 5:1).

2.4. 3,5-Dimercapto-4-methoxybenzylalcohol 8

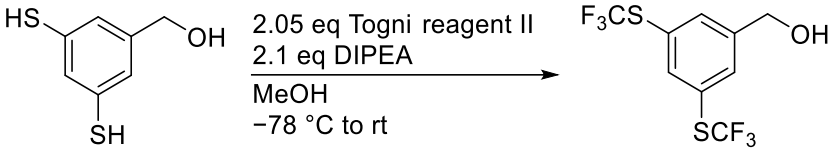


6 **8**

$LiAlH_4$ (911 mg, 24 mmol, 5 eq) was suspended in dry THF (100 mL) under an inert atmosphere. **6** (1117 mg, 3 mmol, 1 eq) in dry THF (50 mL) was added dropwise at 0 °C. The reaction mixture was stirred for 1.5 h at ambient temperature. Then it was cooled in an ice bath and quenched by slow addition of EtOAc (30 mL) and water (50 mL). The volatiles were evaporated at 40 °C and the mixture was acidified with aqueous HCl (10%, 150 mL) and extracted with CH_2Cl_2 (4×50 mL). The organic extracts were dried over $MgSO_4$ + Na_2SO_3. Evaporation at 40 °C yielded oil, which was purified by dry column vacuum chromatography (SiO_2, 20% EtOAc in hexane to EtOAc). Compound **8** was obtained as a colourless oil (382 mg, 62%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.04 (s; 2H; Ar-H), 4.53 (s; 2H; SH), 3.84 (s; 3H; OCH_3), 3.74 (s; 2H; CH_2), 1.74 (s; 1H; OH). **HRMS** (ESI): m/z calc. for $C_8H_{10}O_2S_2$–H^-: 201.0049 [M−H]$^-$; found: 201.0045. **TLC**: R_F = 0.37 ($CHCl_3$/MeCN 9:1); 0.27 (cyclohexane/EtOAc 1:1); 0.08 (cyclohexane/EtOAc 5:1).

2.5. 3,5-Bis((trifluoromethyl)thio)benzylalcohol 9

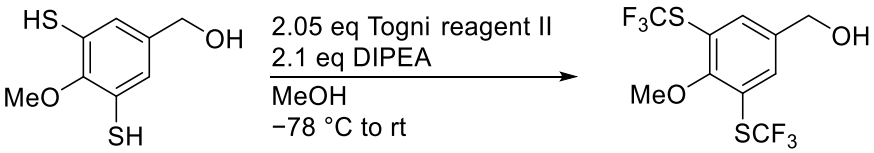


7 **9**

Togni reagent II (4535 mg, 14.35 mmol, 2.05 eq) was suspended in dry MeOH (100 mL) and the mixture was degassed with N_2 by bubbling. Then it was cooled to −78 °C (dry ice/acetone bath) and DIPEA (2.56 mL, 14.7 mmol, 2.1 eq) was added, followed by dropwise addition of **7** (1206 mg, 7 mmol, 1 eq) dissolved in dry MeOH (20 mL) over 30 min. The reaction mixture was mixed at −78 °C for an additional 60 min, then left to reach ambient temperature. It was loaded on SiO_2 and purified by column chromatography (SiO_2, cyclohexane/EtOAc 7:1) to yield compound **9** as a yellowish liquid (1892 mg, 88%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (s; 1H; Ar-H), 7.77 (s; 2H; Ar-H), 4.76 (s; 2H; CH_2), 2.25 (s; 1H; OH). **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ = 145.0, 142.5, 136.9, 129.9 (q; *J* = 308.3 Hz), 126.5 (q; *J* = 2.3 Hz), 63.9. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −42.3. **TLC**: R_F = 0.53 (cyclohexane/EtOAc 1:1); 0.21 (cyclohexane/EtOAc 5:1).

2.6. 4-Methoxy-3,5-bis((trifluoromethyl)thio)benzylalcohol 10

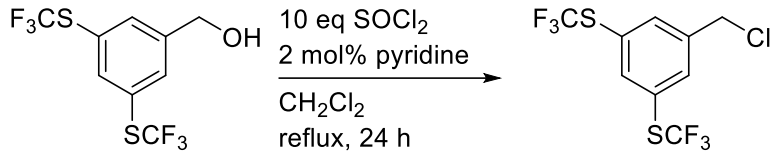


8 **10**

Togni reagent II (6456 mg, 19.41 mmol, 2.05 eq) was suspended in dry MeOH (100 mL) and the mixture was degassed with N_2 by bubbling. Then it was cooled to −78 °C (dry ice/acetone bath) and DIPEA (3.47 mL, 19.88 mmol, 2.1 eq) was added. It was followed by the addition of **8** (1915 mg, 9.47 mmol, 1 eq) dissolved in dry MeOH (25 mL) using a syringe pump at a rate of 1 mL min^{-1}. The reaction mixture was mixed at −78 °C for an additional 60 min, then left to reach ambient temperature. It was evaporated yielding a brown oil, which was purified by column chromatography (SiO_2, cyclohexane/EtOAc 5:1) to yield compound **10** as a yellowish oil (2671 mg, 83%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (s; 2H; Ar-H), 4.72 (d; *J* = 308.3 Hz 2H; CH_2), 3.96 (s; 3H; OCH_3), 1.82 (t; *J* = 5.8 Hz; 1H; OH). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 162.1, 138.7, 138.1, 129.4 (q, *J* = 309.1 Hz), 121.1 (q, *J* = 1.8 Hz), 63.7, 62.8. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = −41.3. **TLC**: R_F = 0.55 (cyclohexane/EtOAc 1:1); 0.24 (cyclohexane/EtOAc 5:1).

2.7. 3,5-Bis((trifluoromethyl)thio)benzylchloride 11

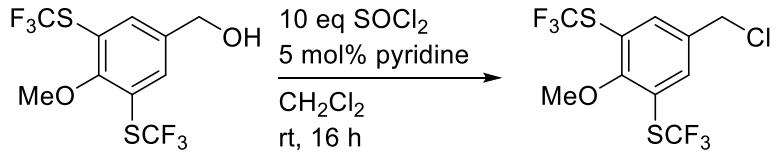


9 **11**

9 (4194 mg, 13.6 mmol, 1 eq) was dissolved in CH_2Cl_2 (136 mL), then $SOCl_2$ (9.9 mL, 136 mmol, 10 eq) and pyridine (21.9 µL, 0.27 mmol, 0.02 eq) were added. The reaction mixture was heated to reflux for 24 h. After that, the reaction mixture was cooled to ambient temperature, and quenched by the addition of cold water (200 mL) and vigorous stirring for 20 min. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2×100 mL). The combined organic phases were washed with brine (200 mL), dried over $MgSO_4$ and loaded on Celite. The Celite with adsorbed compounds was placed on the top of a SiO_2 plug and the product was eluted with hexane (200 mL). Evaporation yielded compound **11** as a colourless liquid (3268 mg, 74%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (s; 1H; Ar-H), 7.82 (s; 2H; Ar-H), 4.61 (s; 2H; CH_2). **^{13}C{^{1}H} NMR** (126 MHz, acetone-d_6): δ = 143.6, 142.7, 139.8, 130.5 (q; J = 307.4 Hz), 126.9 (q; J = 2.3 Hz), 44.7. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −42.2. **TLC**: R_F = 0.40 (cyclohexane); 0.51 (pentane).

2.8. 4-Methoxy-3,5-bis((trifluoromethyl)thio)benzylchloride 12

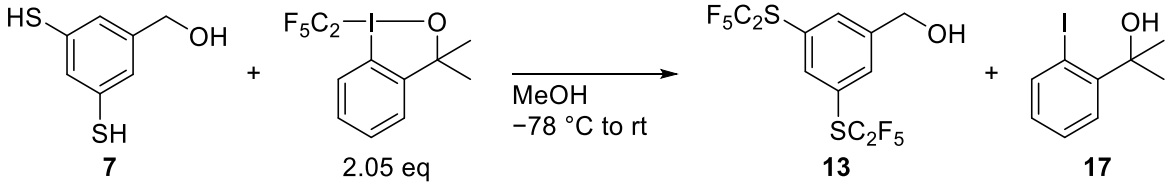


10 **12**

10 (2482 mg, 7.34 mmol, 1 eq) was dissolved in CH_2Cl_2 (75 mL), then $SOCl_2$ (5.3 mL, 73.4 mmol, 10 eq) and pyridine (29.6 µL, 0.37 mmol, 0.05 eq) were added. The reaction mixture was mixed at ambient temperature for 16 h. After that, the reaction mixture was cooled to ambient temperature, and quenched by the addition of cold water (45 mL) and vigorous stirring for 20 min. The organic phase was separated away, and the aqueous phase was extracted with CH_2Cl_2 (2×20 mL). Combined organic phases were washed with brine (100 mL) and dried over Na_2SO_4. The drying agent was filtered off, the filtrate was redissolved in Et_2O (30 mL) and filtered through a SiO_2 plug. It was washed with additional Et_2O (2×20 mL). Filtrates were evaporated to yield **12** as a colourless oil (2406 mg, 92%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78 (s; 2H; Ar-H), 4.56 (s; 2H; CH_2), 3.98 (s; 3H; OCH_3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 162.7, 139.7, 135.3, 129.3 (q, J = 309.0 Hz), 121.5 (q, J = 2.2 Hz), 62.9, 44.2. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = −41.2. **TLC**: R_F = 0.28 (cyclohexane).

2.9. 3,5-Bis((pentafluoroethyl)thio)benzylalcohol 13

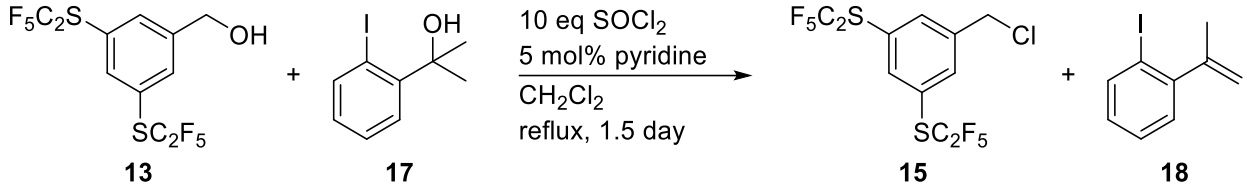


7 **13** **17**

C_2F_5-Togni reagent (1558 mg, 4.1 mmol, 2.05 eq) was dissolved in dry MeOH (45 mL) and the mixture was degassed with N_2 by bubbling. Then it was cooled to −78 °C (dry ice/acetone bath). **7** (345 mg, 2 mmol, 1 eq) dissolved in dry MeOH (10 mL) was added using a syringe pump at a rate of 0.7 mL min^{-1}. The reaction mixture was mixed at −78 °C for an additional 30 min, then left to reach ambient temperature. It was loaded on SiO_2 and purified by column chromatography (SiO_2, cyclohexane/acetone 19:1) to yield a mixture of **17** (686 mg) and **13** (695 mg, 85%) as a colourless oil. It was used in the following reaction without further separation.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (s; 1H; Ar-H), 7.80 (s; 2H; Ar-H), 4.79 (s; 2H; CH_2), 1.95 (s; 1H; OH). **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −82.5 (t; *J* = 3.4 Hz; 6F; CF_3), −91.5 (q; *J* = 3.6 Hz; 4F; CF_2). **TLC**: R_F = 0.24 (cyclohexane/EtOAc 5:1).

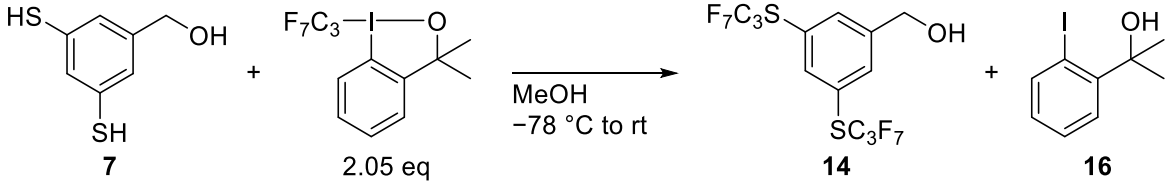
2.10. 3,5-Bis((pentafluoroethyl)thio)benzylchloride 15



A mixture of **13** (695 mg, 1.7 mmol, 1 eq) and **17** (686 mg) was dissolved in CH_2Cl_2 (40 mL), then $SOCl_2$ (1.23 mL, 17 mmol, 10 eq) and pyridine (6.9 µL, 0.085 mmol, 0.05 eq) were added. The reaction mixture was heated to reflux for 1.5 days. After that, the reaction mixture was quenched by the addition of cold water (50 mL) and vigorous stirring for 20 min. The organic phase was washed with phosphate buffer (0.05 M, pH = 7, 2×30 mL), brine (50 mL) and dried over magnesium sulphate. The filtrate was evaporated to yield a brown liquid. It was redissolved in Et_2O (100 mL) and filtered through a SiO_2 plug. The filtrate was evaporated to yield a mixture of **18** (460 mg) and **15** (700 mg, 96%) as a brown liquid. It was used in the following reaction without further separation.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (s; 1H; Ar-H), 7.83 (s; 2H; Ar-H), 4.61 (s; 2H; CH_2). **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −82.4 (t; *J* = 3.4 Hz; 6F; CF_3), −91.4 (q; *J* = 3.4 Hz; 4F; CF_2). **TLC**: R_F = 0.40 (cyclohexane).

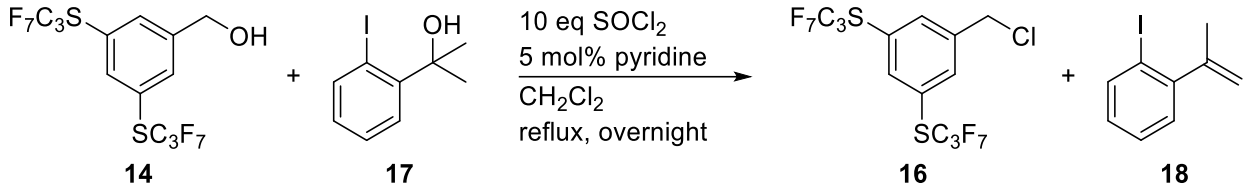
2.11. 3,5-Bis((heptafluoropropyl)thio)benzylalcohol 14



C_3F_7-Togni reagent (2645 mg, 6.15 mmol, 2.05 eq) was dissolved in dry MeOH (70 mL) and the mixture was degassed with N_2 by bubbling. Then it was cooled to −78 °C (dry ice/acetone bath). **7** (517 mg, 3 mmol, 1 eq) dissolved in dry MeOH (15 mL) was added using a syringe pump at a rate of 0.5 mL min^{-1}. The reaction mixture was mixed at −78 °C for an additional 30 min, then left to reach ambient temperature. It was loaded on SiO_2 and purified by column chromatography (SiO_2, cyclohexane/acetone 19:1) to yield a mixture of **16** (1558 mg) and **14** (1371 mg, 90%) as a colourless oil. It was used in the following reaction without further separation.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (s; 1H; Ar-H), 7.81 (s; 2H; Ar-H), 4.79 (d; *J* = 4.8 Hz; 2H; CH_2), 2.05 (t; *J* = 5.6 Hz; 1H; OH). **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −80.2 (t; *J* = 9.2 Hz; 6F; CF_3), −80.2 (qt; *J* = 9.2, 3.3 Hz; 4F; CF_2), −123.5 (t; *J* = 3.4 Hz; 4F; CF_2). **TLC**: R_F = 0.24 (cyclohexane/EtOAc 5:1).

2.12. 3,5-Bis((heptafluoropropyl)thio)benzylchloride 16

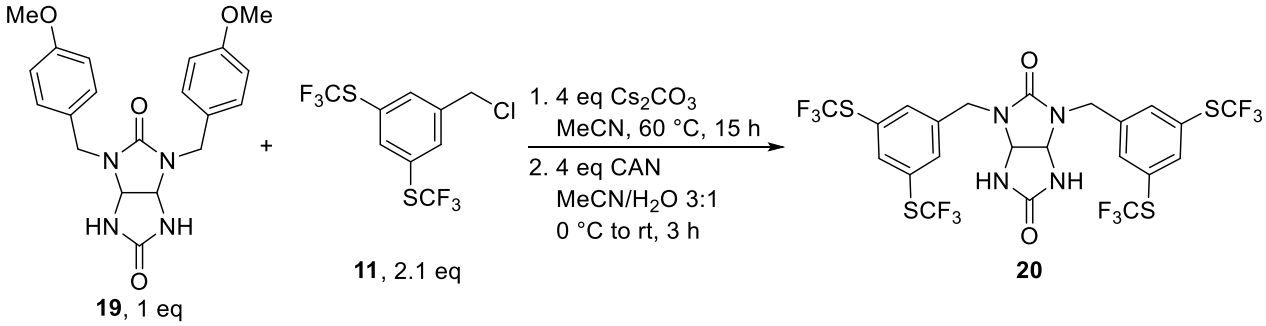


14 **17** **16** **18**

A mixture of **14** (1150 mg, 2.26 mmol, 1 eq) and **17** (1549 mg) was dissolved in CH_2Cl_2 (50 mL), then $SOCl_2$ (1.64 mL, 22.6 mmol, 10 eq) and pyridine (9.1 µL, 0.113 mmol, 0.05 eq) were added. The reaction mixture was heated to reflux overnight. After that, the reaction mixture was quenched by the addition of cold water (50 mL) and vigorous stirring for 20 min. The organic phase was washed with phosphate buffer (0.05 M, pH = 7, 2×30 mL), brine (50 mL) and dried over magnesium sulphate. The filtrate was evaporated to yield a yellow liquid. It was purified by column chromatography (SiO_2, pentane) to yield a mixture of **18** (637 mg) and **16** (982 mg, 82%) as a colourless transparent oil. It was used in the following reaction without further separation.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (t; *J* = 1.8 Hz; 1H; Ar-H), 7.85 (d; *J* = 1.7 Hz; 2H; Ar-H), 4.61 (s; 2H; CH_2). **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −80.2 (t; *J* = 9.3 Hz; 6F; CF_3), −87.3 (qt; *J* = 9.2, 3.1 Hz; 4F; CF_2), −123.5 (t; *J* = 3.4 Hz; 4F; CF_2). **TLC**: R_F = 0.40 (cyclohexane).

2.13. 2,4-Bis(3,5-bis((trifluoromethyl)thio)benzyl)glycoluril 20



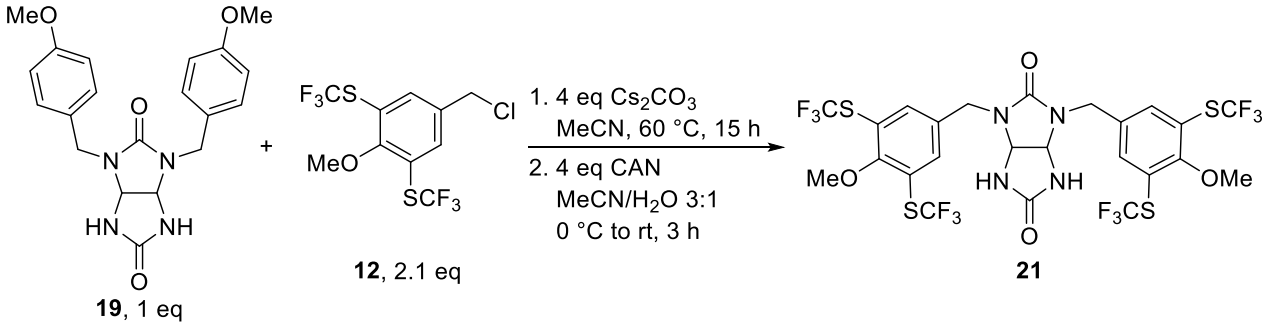
19, 1 eq **11**, 2.1 eq **20**

19 (1147 mg, 3 mmol, 1 eq), Cs_2CO_3 (3910 mg, 12 mmol, 4 eq) and **11** (2026 mg, 6.2 mmol, 2.1 eq) were mixed in dry MeCN (35 mL) for 15 h at 60 °C under an inert atmosphere. The orange mixture was filtered through a Celite pad, and the filtration cake was washed with additional MeCN (2×5 mL). The orange filtrate was cooled to −20°C and a solution of CAN (6579 mg, 12 mmol, 4 eq) in cold water (15 mL) was added. The reaction mixture was mixed at ambient temperature for 3 h. Then it was diluted with water (200 mL), extracted with CH_2Cl_2 (3×75 mL) and the combined extracts were dried over $MgSO_4$. The drying agent was filtered off, the filtrate was loaded on Celite and purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 29:1) yielding compound **20** as a white solid (1577 mg, 73%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (s; 2H; Ar-H), 7.74 (s; 4H; Ar-H), 5.65 (s; 2H; NH), 5.25 (s; 2H; CH), 4.82 (d; *J* = 15.9 Hz; 2H; CH_2), 4.39 (d; *J* = 15.9 Hz; 2H; CH_2). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-d_6): δ = 160.5, 157.4,

141.6, 141.2, 137.7, 129.3 (q; *J* = 308.2 Hz), 125.1 (d; *J* = 2.3 Hz), 65.9, 43.6. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −42.1. **HRMS** (APCI): m/z calc. for $C_{22}H_{14}F_{12}N_4O_2S_4$+$H^+$: 722.9881 $[M+H]^+$; found: 722.9877. **TLC**: R_F = 0.17 (CH_2Cl_2/MeOH 19:1).

2.14. 2,4-Bis(4-methoxy-3,5-bis((trifluoromethyl)thio)benzyl)glycoluril 21

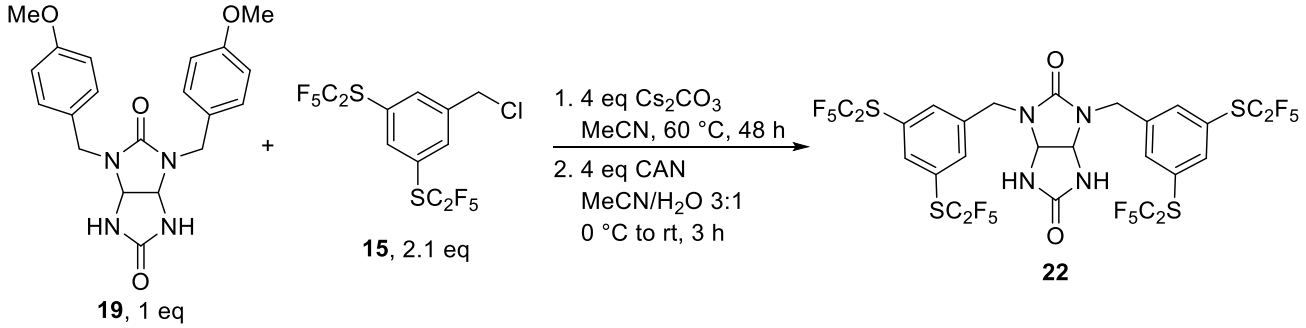


19, 1 eq + **12**, 2.1 eq → **21**

19 (2022 mg, 5.3 mmol, 1 eq), Cs_2CO_3 (6891 mg, 21.2 mmol, 4 eq) and **12** (3961 mg, 11.1 mmol, 2.1 eq) were mixed in dry MeCN (74 mL) for 15 h at 60 °C under an inert atmosphere. The orange mixture was filtered through a Celite pad and the filtration cake was washed with additional MeCN (2×15 mL). The orange filtrate was evaporated yielding an orange sticky foam. It was redissolved in MeCN (79 mL) and cooled to −24°C. A solution of CAN (11622 mg, 21.2 mmol, 4 eq) in cold water (26 mL) was added. The reaction mixture was mixed at ambient temperature for 3 h. Then it was diluted with water (250 mL), extracted with CH_2Cl_2 (3×60 mL) and the combined extracts were washed with brine (80 mL) and dried over Na_2SO_4. The drying agent was filtered off, the filtrate was evaporated, and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 29:1) yielding compound **21** as a yellowish solid (3464 mg, 84%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (s; 4H; Ar-H), 6.30 (s; 2H; NH), 5.17 (s; 2H; CH), 4.75 (d; *J* = 15.7 Hz; 2H; CH_2), 4.26 (d; *J* = 15.7 Hz; 2H; CH_2), 3.96 (s; 6H; OCH_3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 162.5, 161.2 157.3, 139.2, 134.1, 129.3 (q, *J* = 309.0 Hz), 121.7 (q, *J* = 2.0 Hz), 66.2, 62.9, 44.6. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = −41.3. **HRMS** (APCI): m/z calc. for $C_{24}H_{18}F_{12}N_4O_4S_4$+$H^+$: 783.0092 $[M+H]^+$; found: 783.0088. **TLC**: R_F = 0.21 (CH_2Cl_2/MeOH 19:1).

2.15. 2,4-Bis(3,5-bis((pentafluoroethyl)thio)benzyl)glycoluril 22



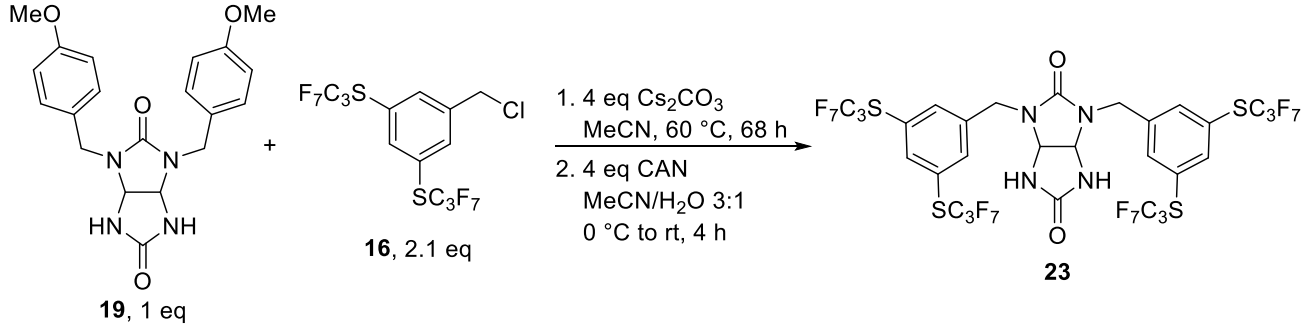
19, 1 eq + **15**, 2.1 eq → **22**

19 (299 mg, 0.78 mmol, 1 eq), Cs_2CO_3 (1018 mg, 3.12 mmol, 4 eq) and a mixture of **15** (700 mg, 1.64 mmol, 2.1 eq) and **18** (460 mg) were mixed in dry MeCN (10 mL) for 48 h at 60 °C under an inert atmosphere. The reaction mixture was filtered through a Celite pad, and the filtration cake was washed with an additional MeCN (2×10 mL). Combined filtrates were loaded on SiO_2 and purified by column

chromatography (SiO_2, cyclohexane/EtOAc 3:1) to yield a yellow honey-like liquid (738 mg). It was dissolved in MeCN (8.1 mL) and cooled to −20°C. A solution of CAN (1188 mg, 2.17 mmol, 4 eq) in cold water (2.7 mL) was added. The reaction mixture was mixed at ambient temperature for 3 h. Then it was diluted with water (50 mL), extracted with EtOAc (3×50 mL) and combined extracts were dried over $MgSO_4$. The drying agent was filtered off, the filtrate was loaded on SiO_2 and purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 39:1) yielding compound **22** as a white solid (289 mg, 47%).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.95 (s; 2H; Ar-H), 7.84 (s; 4H; Ar-H), 6.05 (s; 2H; NH), 5.19 (s; 2H; CH), 4.62 (d; *J* = 16.2 Hz; 2H; CH_2), 4.37 (d; *J* = 16.2 Hz; 2H; CH_2). **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN): δ = 161.6, 158.9, 144.7, 142.6, 140.1, 125.1 (t; *J* = 3.0 Hz), 121.1 (tq; *J* = 288.3, 40.5 Hz), 119.7 (qt; *J* = 286.1, 36.8 Hz), 67.7, 45.4. **^{19}F NMR** (282 MHz, CD_3CN): δ = −83.3 (t; *J* = 3.5 Hz; 12F; CF_3), −92.3 (d; *J* = 3.6 Hz; 8F; CF_2). **HRMS** (APCI): m/z calc. for $C_{26}H_{14}F_{20}N_4O_2S_4$+$H^+$: 922.9753 $[M+H]^+$; found: 922.9745. **TLC**: R_F = 0.17 (CH_2Cl_2/MeOH 19:1).

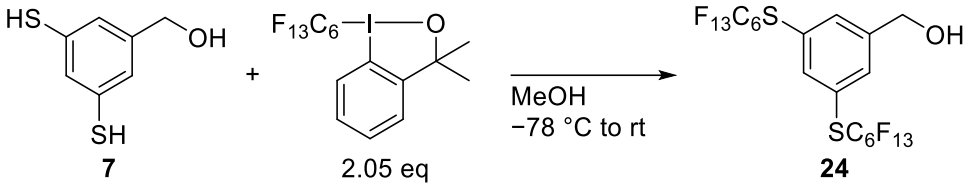
2.16. 2,4-Bis(3,5-bis((heptafluoropropyl)thio)benzyl)glycoluril 23



19 (340 mg, 0.888 mmol, 1 eq), Cs_2CO_3 (1158 mg, 3.55 mmol, 4 eq) and a mixture of **16** (982 mg, 1.87 mmol, 2.1 eq) and **18** (637 mg) were mixed in dry MeCN (10 mL) for 68 h at 60 °C under an inert atmosphere. The reaction mixture was loaded on SiO_2 and purified by column chromatography (SiO_2, cyclohexane/EtOAc 2:1) to yield a yellowish viscous liquid (1039 mg). It was dissolved in MeCN (11.4 mL) and cooled to −20°C. A solution of CAN (1672 mg, 2.17 mmol, 4 eq) in cold water (3.8 mL) was added. The reaction mixture was mixed at ambient temperature for 4 h. Then it was diluted with water (50 mL), extracted with EtOAc (3×50 mL) and combined extracts were dried over $MgSO_4$. The drying agent was filtered off, the filtrate was loaded on SiO_2 and purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 29:1) yielding compound **23** as an orangish solid (494 mg, 58%).

^{1}H NMR (500 MHz, CD_3CN): δ = 7.96 (s; 2H; Ar-H), 7.85 (s; 4H; Ar-H), 5.95 (s; 2H; NH), 5.19 (s; 2H; CH), 4.62 (d; *J* = 16.2 Hz; 2H; CH_2), 4.37 (d; *J* = 16.3 Hz; 2H; CH_2). **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN): δ = 161.5, 159.0, 144.9, 142.6, 140.3, 124.9 (t; *J* = 3.0 Hz), 123.4 (tt; *J* = 289.5, 33.3 Hz), 118.7 (qt; *J* = 287.4, 3.1 Hz), 110.0 (tqt; *J* = 265.3, 35.3, 36.6 Hz), 67.7, 45.4. **^{19}F NMR** (282 MHz, CD_3CN): δ = −81.0 (t; *J* = 9.5 Hz; 12F; CF_3), −88.2 (qt; *J* = 9.5, 3.5 Hz; 8F; CF_2), −124.1 (d, *J* = 3.9 Hz, 8F; CF_2). **HRMS** (APCI): m/z calc. for $C_{30}H_{14}F_{28}N_4O_2S_4$+$H^+$: 1122.9625 $[M+H]^+$; found: 1122.9609. **TLC**: R_F = 0.17 (CH_2Cl_2/MeOH 19:1).

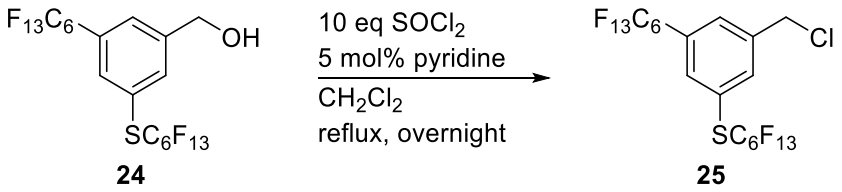
2.17. 3,5-Bis((tridecafluorohexyl)thio)benzylalcohol 24



C_6F_{13}-Togni reagent (2379 mg, 4.1 mmol, 2.05 eq) was dissolved in dry MeOH (55 mL) and the mixture was degassed with N_2 by bubbling. Then it was cooled to −78 °C (dry ice/acetone bath). **7** (345 mg, 2 mmol, 1 eq) dissolved in dry MeOH (10 mL) was added using a syringe pump at a rate of 0.5 mL min^{-1}. The reaction mixture was mixed at −78 °C for an additional 30 min, then left to reach ambient temperature. It was loaded on SiO_2 and purified by column chromatography (SiO_2, cyclohexane/acetone 19:1) to yield compound **24** as a colourless oil (993 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.90 (s; 1H; Ar-H), 7.81 (s; 2H; Ar-H), 4.80 (d; *J* = 5.1 Hz; 2H; CH_2), 1.88 (t; *J* = 5.7 Hz; 2H; OH). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 144.4, 144.0, 137.8, 125.3 (t; *J* = 34.7 Hz), 124.8, 123.0 (t; *J* = 34.6 Hz), 121.0–120.4 (m), 118.5 (t; *J* = 33.1 Hz), 116.2 (t; *J* = 33.0 Hz), 114.3–112.3 (m), 111.6–109.9 (m), 109.2–107.9 (m), 106.9–106.0 (m), 63.8. **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −80.9 (tt; *J* = 9.7, 2.6 Hz; 12F; CF_3), −86.6 (tq; *J* = 13.9, 3.2 Hz; 8F; CF_2), −119.0 (tdq; *J* = 13.6, 6.8, 3.5 Hz; 8F; CF_2), −121.4 – −121.6 (m; 8F; CF_2) −122.8 (br s; 8F; CF_2) −126.2 (tdd; *J* = 14.9, 7.1, 3.7 Hz; 8F; CF_2). **TLC**: R_F = 0.14 (cyclohexane/EtOAc 9:1).

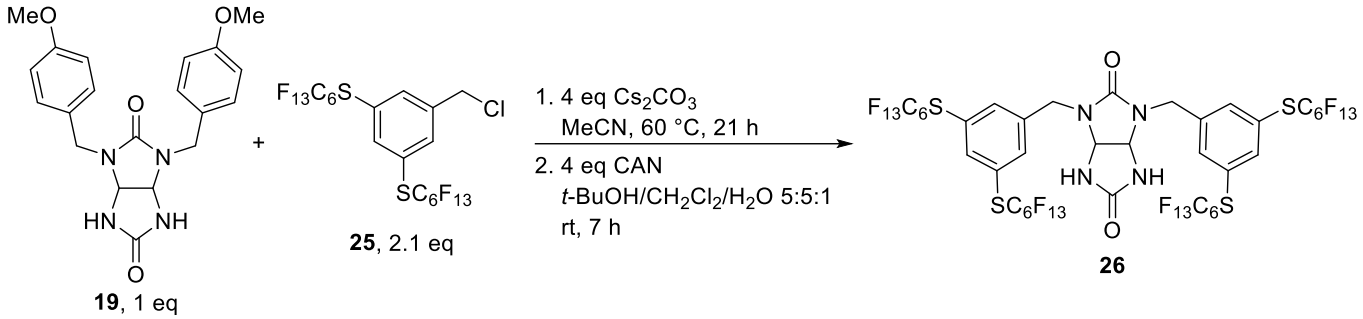
2.18. 3,5-Bis((tridecafluorohexyl)thio)benzylchloride 25



24 (954 mg, 1.18 mmol, 1 eq) was dissolved in CH_2Cl_2 (35 mL), then $SOCl_2$ (0.86 mL, 11.8 mmol, 10 eq) and pyridine (4.8 µL, 0.059 mmol, 0.05 eq) were added. The reaction mixture was heated to reflux overnight. After that, the reaction mixture was loaded on Celite. The Celite with absorbed compounds was placed on the top of a SiO_2 plug and the product was eluted using pentane (2×50 mL). Evaporation of filtrates yielded compound **25** as a colourless transparent oil (746 mg, 76%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (t; *J* = 1.7 Hz; 1H; Ar-H), 7.834 (d; *J* = 1.7 Hz; 2H; Ar-H), 2.07 (s; 2H; CH_2). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 145.2, 140.5, 139.7, 125.2 (t; *J* = 3.1 Hz), 122.9 (t; *J* = 34.6 Hz), 120.9–120.3 (m), 118.5 (t; *J* = 33.2 Hz), 116.2 (t; *J* = 33.0 Hz), 113.9–112.3 (m), 111.6–110.2 (m), 109.2–108.2 (m), 106.6–106.0 (m), 44.2. **^{19}F NMR** (282 MHz, CD_3CN): δ = −126.2 – −126.3 (m; 6F; CF_3), −86.5 (ddd; *J* = 17.4, 10.4, 3.3 Hz; 4F; CF_2), −119.0 (br s; 4F; CF_2), −121.4 (br s; 4F; CF_2), −122.8 (br s; 4F; CF_2), −126.1 – −126.3 (m; 4F; CF_2), **TLC**: R_F = 0.46 (cyclohexane/EtOAc 9:1); 0.39 (cyclohexane); 0.55 (pentane).

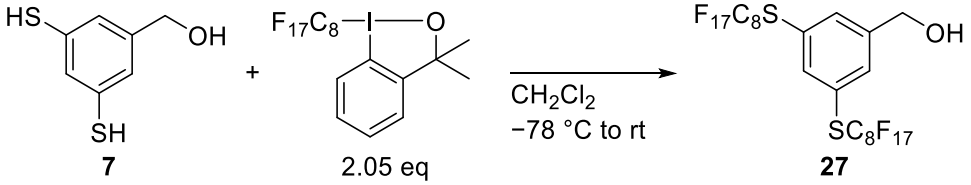
2.19. 2,4-Bis(3,5-bis((tridecafluorohexyl)thio)benzyl)glycoluril 26



19 (150 mg, 0.393 mmol, 1 eq), Cs_2CO_3 (513 mg, 1.57 mmol, 4 eq) and **25** (730 mg, 0.826 mmol, 2.1 eq) were mixed in dry MeCN (10 mL) for 21 h at 60 °C under an inert atmosphere. The reaction mixture was filtered, and solids were washed with additional MeCN (2×10 mL). The filter cake was taken into CH_2Cl_2 (40 mL) and washed with water (2×30 mL). The organic phase was dried over $MgSO_4$ and evaporated. The residue was redissolved in CH_2Cl_2 (5 mL) and cooled to −20 °C. Solution of CAN (863 mg, 1.57 mmol, 4 eq) in cold *t*-BuOH/H_2O (5:1, 6 mL) was added and the reaction mixture was mixed at ambient temperature for 7 h. The reaction mixture was loaded on SiO_2 and purified by column chromatography (SiO_2, PhMe/MeCN 4:1) yielding compound **26** as a yellow solid (245 mg, 36%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (s; 2H; Ar-H), 7.76 (s; 4H; Ar-H), 6.29 (s; 2H; NH), 5.16 (s; 2H; CH), 4.83 (d; *J* = 15.9 Hz; 2H; CH_2), 4.31 (d; *J* = 15.7 Hz; 2H; CH_2). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 161.1, 157.3, 144.9, 139.4, 139.3, 125.5, 125.3–125.1 (m), 123.0 (t; *J* = 34.7 Hz), 120.9–120.4 (m), 118.4 (t; *J* = 33.0 Hz), 116.1 (t; *J* = 33.1 Hz), 114.1–112.3 (m), 111.6–110.1 (m), 109.4–108.2 (m), 106.9–106.3 (m), 66.2, 44.9. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = −81.0 (t; *J* = 10.3 Hz; 12F; CF_3), −86.5 (t; *J* = 14.0 Hz; 8F; CF_2), −119.0 (br s; 8F; CF_2), −121.5 (br s; 8F; CF_2), −122.9 (br s; 8F; CF_2), −126.2 – −126.3 (m; 8F; CF_2). **HRMS** (APCI): m/z calc. for $C_{42}H_{14}F_{52}N_4O_2S_4$+$H^+$: 1722.9242 $[M+H]^+$; found: 1722.9253. **TLC**: R_F = 0.15 (CH_2Cl_2/MeOH 19:1).

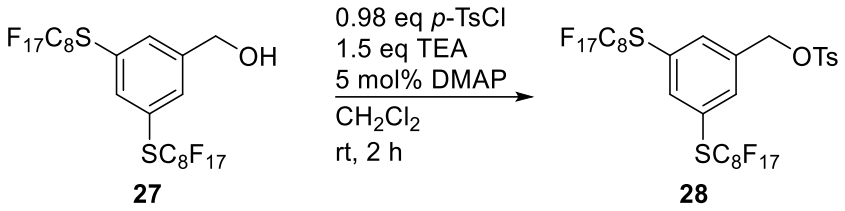
2.20. 3,5-Bis((heptadecafluorooctyl)thio)benzylalcohol 27



7 (536 mg, 3.1 mmol, 1 eq) was dissolved in dry CH_2Cl_2 (40 mL) and the mixture was degassed with N_2 by bubbling. Then it was cooled to −78 °C (dry ice/acetone bath). C_6F_{13}-Togni reagent (4340 mg, 6.4 mmol, 2.05 eq) dissolved in dry CH_2Cl_2 (50 mL) was added over 40 min. The reaction mixture was mixed at −78 °C for an additional 30 min, then left to reach ambient temperature. It was loaded on SiO_2 and purified by column chromatography (SiO_2, cyclohexane/CH_2Cl_2/acetone 18:1:1) to yield compound **27** as a white solid (785 mg, 25%), with impurities **17** and **18**.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (s; 1H; Ar-H), 7.81 (s; 2H; Ar-H), 4.80 (d; *J* = 5.5 Hz; 2H; CH_2). **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −80.9 (t; *J* = 10.3 Hz; 6F; CF_3), −86.6 (t; *J* = 14.2 Hz; 4F; CF_2), −118.9 (br s; 4F; CF_2), −121.2 (br s; 4F; CF_2), −121.9 (br s; 8F; CF_2), −122.8 (br s), −126.2 (br s; 4F; CF_2).

2.21. 3,5-Bis((heptadecafluorooctyl)thio)benzyltosylate 28

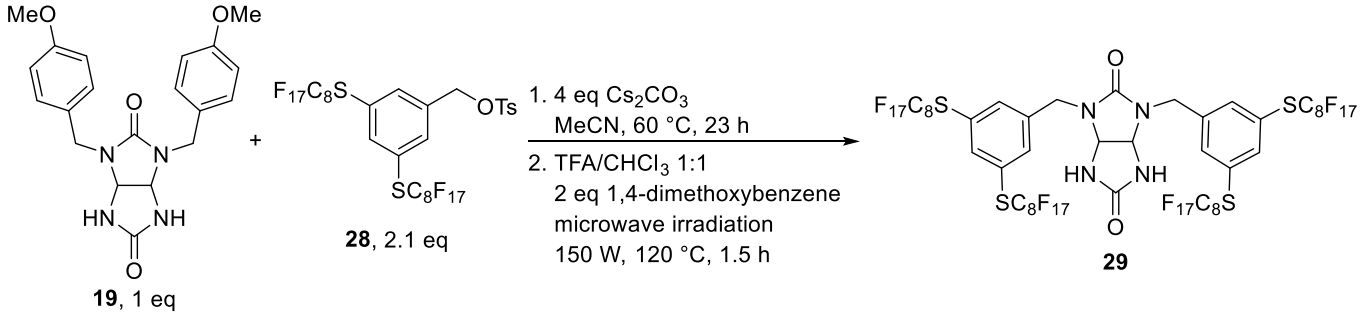


27 **28**

27 (785 mg, 0.78 mmol, 1 eq) was dissolved in CH_2Cl_2 (10 mL), then TEA (0.16 mL, 1.17 mmol, 1.5 eq) and DMAP (4.8 mg, 0.039 mmol, 0.05 eq) were added. TsCl (145 mg, 0.76 mmol, 0.98 eq) was added portionwise, while the reaction mixture was cooled in an ice bath. The reaction mixture was mixed at ambient temperature for 2 h. After that, the reaction mixture was washed with aqueous HCl (5%, 10 mL), saturated aqueous NH_4Cl (10 mL) and water (10 mL). The organic phase was dried over $MgSO_4$. After evaporation, a yellowish solid was obtained, it was loaded on SiO_2 and purified by column chromatography (petroleum ether/EtOAc 9:1). The product **28** was obtained as a white solid (482 mg, 54%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 (t; *J* = 1.6 Hz; 1H; Ar-H), 7.79–7.77 (m; 2H; Ar-H), 7.65 (d; *J* = 1.8 Hz; 2H; Ar-H), 7.32 (d; *J* = 7.9 Hz; 2H; Ar-H), 5.12 (s; 2H; CH_2), 2.43 (s; 3H; CH_3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = 145.6, 145.5, 139.1, 136.9, 133.1, 130.2, 128.1, 125.3, 122.9 (t; *J* = 34.7 Hz), 121.0–120.3 (m), 118.4 (t; *J* = 32.9 Hz), 116.1 (t; *J* = 33.1 Hz), 114.1–110.1 (m), 111.6–112.3 (m), 109.3–108.0 (m), 106.9–105.9 (m), 69.6, 21.7. **^{19}F NMR** (471 MHz, CD_3CN): δ = −80.9 (t; *J* = 10.0 Hz; 6F; CF_3), −86.5 (t; *J* = 14.3 Hz; 4F; CF_2), −118.9 (br s; 4F; CF_2), −121.2 (br s; 4F; CF_2), −121.8 (br s; 4F; CF_2), −121.9 (br s; 4F; CF_2), −122.8 (br s; 4F; CF_2), −126.2 (dq; *J* = 14.7, 6.9 Hz; 6F; CF_3). **HRMS** (APCI): m/z calc. for $C_{26}H_{14}F_{20}N_4O_2S_4$+$H^+$: 922.9753 $[M+H]^+$; found: 922.9745. **TLC**: R_F = 0.29 (cyclohexane/EtOAc 9:1).

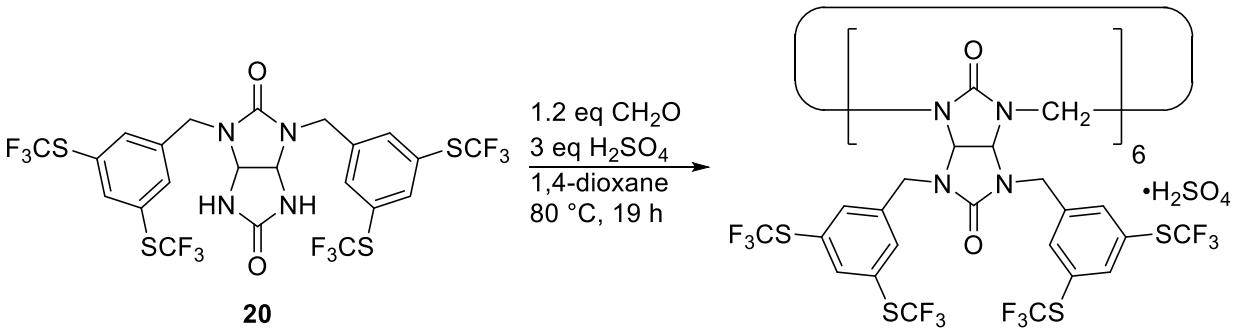
2.22. 2,4-Bis(3,5-bis((heptadecafluorooctyl)thio)benzyl)glycoluril 29



19 (57 mg, 0.150 mmol, 1 eq), Cs_2CO_3 (195 mg, 0.600 mmol, 4 eq) and **28** (366 mg, 0.315 mmol, 2.1 eq) were mixed in dry MeCN (5 mL) for 23 h at 60 °C under an inert atmosphere. The reaction mixture was diluted with MeOH (5 mL), and filtered, and solids were washed with MeOH (2×5 mL). The obtained white solid (300 mg of a tetrasubstituted glycoluril intermediate) and 1,4-dimethoxybenzene (41 mg, 0.300 mmol, 2 eq) were dissolved in $CHCl_3$/TFA (1:1, 10 mL) forming a green solution. It was subjected to microwave irradiation (150 W maximal power) at 120 °C for 90 min. The resulting brown solution was loaded on SiO_2 and purified by column chromatography (SiO_2, hexane/EtOAc 3:1) yielding compound **28** as a brownish solid (93 mg, 29%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (s; 2H; Ar-H), 7.74 (s; 4H; Ar-H), 5.59 (s; 2H; NH), 5.22 (s; 2H; CH), 4.81 (d; *J* = 16.0 Hz; 2H; CH_2), 4.38 (d; *J* = 16.1 Hz; 2H; CH_2). **^{19}F NMR** (282 MHz, $CDCl_3$): δ = −80.9 (t; *J* = 9.8 Hz; 12F; CF_3), −86.5 (br s; 8F; CF_2), −118.9 (br s; 8F; CF_2), −121.2 (br s; 8F; CF_2), −121.9 (br s; 16F; CF_2), −122.8 (br s; 8F; CF_2), −126.2 (br s; 8F; CF_2). **HRMS** (APCI): m/z calc. for $C_{50}H_{14}F_{68}N_4O_2S_4$+$H^+$: 2122.8987 $[M+H]^+$; found: 2122.9006.

2.23. Bambusuril BU1

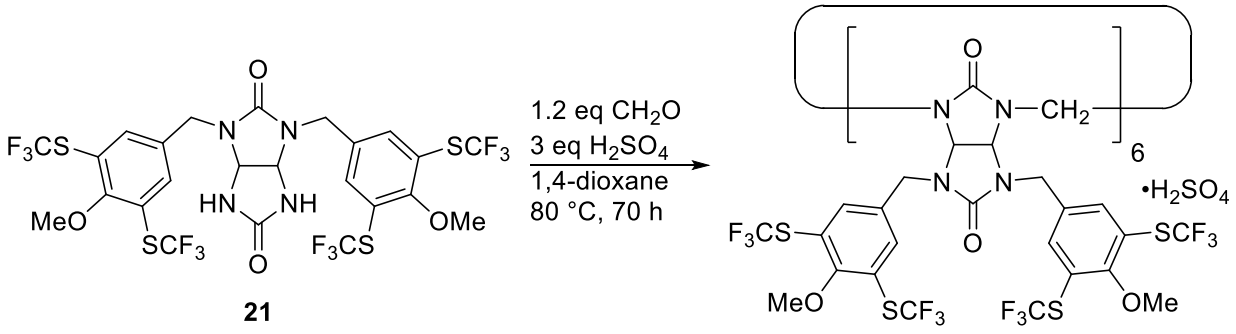


20 **BU1**

20 (415 mg, 574 µmol, 1 eq) and paraformaldehyde (21 mg, 689 µmol, 1.2 eq) were suspended in 1,4-dioxane (1.5 mL). Concentrated H_2SO_4 (97.2 µL, 1810 µmol, 3 eq) was added to a warm mixture which dissolved all reactants. The yellow solution was heated to 80 °C for 19 h. Then dioxane (2 mL) was added to the brown suspension and the solid was collected by filtration and washed with 1,4-dioxane (2×1 mL). The solid was dissolved in MeOH (5 mL) and mili-Q water was added (15 mL). The precipitated solid was collected by filtration and washed with mili-Q water (3×5 mL). The product **BU1** was obtained as a white solid (288 mg, 63%). (The product was obtained as a mixture of anion-free BU and BU·H_2SO_4 complex; therefore Me_4NI was added for NMR analysis.)

^{1}H NMR (500 MHz, acetone-d_6): δ = 7.96 (s; 24H; Ar-H), 7.93 (s; 12H; Ar-H), 5.95 (s; 12H; CH), 5.14 (d; *J* = 16.5 Hz; 12H; CH_2), 4.99 (d; *J* = 16.7 Hz; 12H; CH_2), 4.15 (s; 12H; CH_2). **^{13}C{^{1}H} NMR** (126 MHz, acetone-d_6): δ = 160.6, 159.9, 144.1, 142.4, 137.72, 130.4 (q; *J* = 307.5 Hz), 126.8 (d; *J* = 1.8 Hz), 70.9, 48.1, 47.9. **^{19}F NMR** (471 MHz, acetone-d_6): δ = −43.4. **MS** (MALDI): m/z calcd. for $C_{138}H_{84}F_{72}N_{24}O_{12}S_{24}$+$Na^+$: 4426.875 $[M+Na]^+$; found: 4426.825.

2.24. Bambusuril BU2



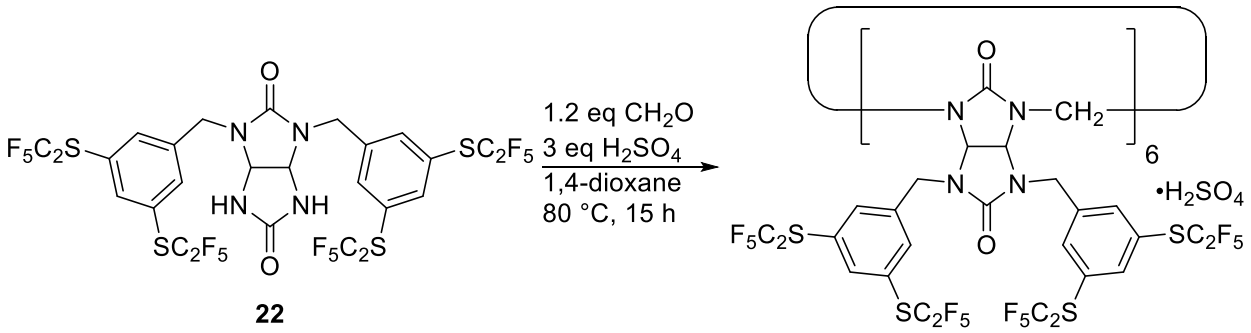
21 **BU2**

21 (1565 mg, 2 mmol, 1 eq) and paraformaldehyde (72 mg, 2.4 µmol, 1.2 eq) were suspended in 1,4-dioxane (4.0 mL). Concentrated H_2SO_4 (322 µL, 6 mmol, 3 eq) was added to a warm mixture which dissolved all reactants. The yellow solution was heated to 80 °C for 70 h. The resulting brown suspension was filtered and the solid was washed with mili-Q water (3×10 mL). It was then purified by column chromatography (SiO_2, CH_2Cl_2/acetone 9:1 to 4:1). The product **BU2** was obtained as a white solid (1180 mg, 74%).

HSO_4^- templating anion was removed from the **BU2** cavity as follows. **BU2**·H_2SO_4 (40 mg) was dissolved in $CHCl_3$/acetone (8+1 mL) in a 15 mL centrifugal tube. It was filled to full volume with mili-Q water and the resulting mixture was shaken. Phase separation was accelerated by centrifugation and the aqueous phase was discarded. This was repeated 60 times. The remaining organic solution was transferred to a clean 5 mL round-bottomed flask and evaporated to dryness yielding anion-free **BU2** as a white solid (35 mg, 88% recovery).

^{1}H NMR (500 MHz, MeCN-d_3): δ = 7.84 (s; 24H; Ar-H), 5.30 (s; 12H; CH), 4.91 (d; *J* = 16.3 Hz; 12H; CH_2), 4.66 (d; *J* = 16.4 Hz; 12H; CH_2), 4.17 (s; 12H; CH_2), 3.91 (s; 36H; OCH_3). **^{13}C{^{1}H} NMR** (126 MHz, MeCN-d_3): δ = 163.0, 161.5, 159.5, 139.8, 137.6, 130.4 (q; *J* = 308.2 Hz), 71.5, 63.7, 48.7, 48.5. **^{19}F NMR** (471 MHz, MeCN-d_3): δ = −42.5. **MS** (ESI): m/z calcd. for $C_{150}H_{108}F_{72}N_{24}O_{24}S_{24}$+$Cl^-$: 4802.9818 $[M+Cl]^-$; found: 4802.9677.

2.25. Bambusuril BU3

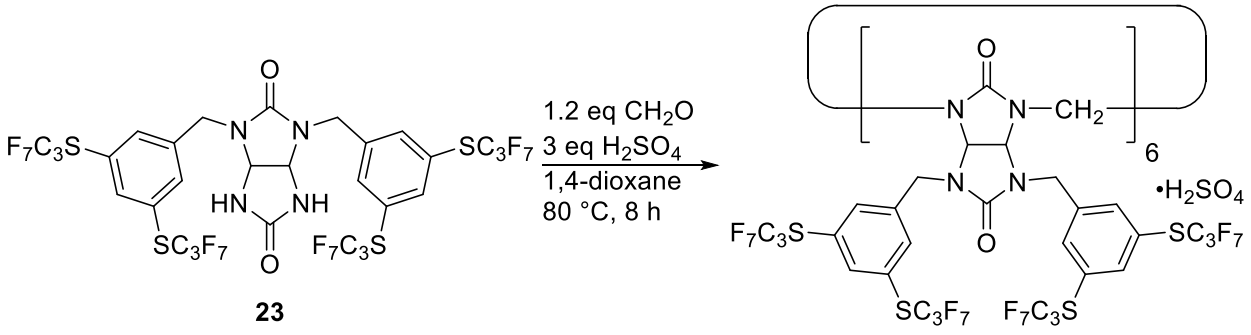


22 **BU3**

Glycoluril **22** (92 mg, 100 µmol, 1 eq) and paraformaldehyde (3.6 mg, 120 µmol, 1.2 eq) were suspended in 1,4-dioxane (200 µL). Concentrated H_2SO_4 (16.1 µL, 300 µmol, 3 eq) was added to a warm mixture which dissolved all reactants. The yellow solution was heated to 80 °C for 15 h. The reaction mixture was diluted with Et_2O (10 mL) and washed with mili-Q water (2×10 mL). The organic phase was evaporated, and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/acetone 6:1 to 4:1). The product **BU3**·H_2SO_4 was obtained as an off-white solid (51 mg, 54%).

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.00 (s; 24H; Ar-H), 7.96 (s; 12H; Ar-H), 5.89 (s; 12H; CH), 5.22 (d; *J* = 17.4 Hz; 12H; CH_2), 5.03 (d; *J* = 16.8 Hz; 12H; CH_2), 4.40 (s; 12H; CH_2). **^{13}C{^{1}H} NMR** (126 MHz, acetone-d_6): δ = 160.4, 159.6, 144.0, 144.0, 125.2, 123.5–115.8 (m), 70.1, 48.4, 48.1. **^{19}F NMR** (471 MHz, acetone-d_6): δ = −83.2 (t; *J* = 3.9 Hz; 72F; CF_3), −92.3 (s; 48F; CF_2). **MS** (ESI): m/z calcd. for $C_{162}H_{84}F_{120}N_{24}O_{12}S_{24}$+$Na^+$: 5629.7997 $[M+Na]^+$; found: 5629.6603.

2.26. Bambusuril BU4



23 **BU4**

Glycoluril **23** (112 mg, 100 µmol, 1 eq) and paraformaldehyde (3.6 mg, 120 µmol, 1.2 eq) were suspended in 1,4-dioxane (200 µL). Concentrated H_2SO_4 (16.1 µL, 300 µmol, 3 eq) was added to a warm mixture which dissolved all reactants. The yellow solution was heated to 80 °C for 8 h. The reaction mixture was loaded on SiO_2 and purified by column chromatography (SiO_2, hexane/acetone 3:1 to 2:1). The obtained product was sonicated in hexane/Et_2O (4:1, 15 mL) and collected by centrifugation. The product **BU4**·H_2SO_4 was obtained as a white solid (75 mg, 65%).

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.02 (s; 24H; Ar-H), 7.97 (s; 12H; Ar-H), 5.91 (s; 12H; CH), 5.23 (d; *J* = 16.3 Hz; 12H; CH_2), 5.06 (d; *J* = 16.6 Hz; 12H; CH_2), 4.49 (s; 12H; CH_2). **^{13}C{^{1}H} NMR** (126 MHz, acetone-d_6): δ = 160.7, 159.7, 144.3, 144.0, 125.0, 125.7–107.2 (m), 70.2, 48.4, 48.3. **^{19}F NMR** (471 MHz, acetone-d_6): δ = −81.1 (t; *J* = 9.1 Hz; 72F; CF_3), −88.2 (dq; *J* = 10.2, 4.9 Hz; 48F; CF_2), −124.2 (d; *J* = 3.9 Hz; 48F; CF_2). **MS** (MALDI): m/z calcd. for $C_{186}H_{84}F_{168}N_{24}O_{12}S_{24}$+$Na^+$: 6826.7213 $[M+Na]^+$; found: 6828.318.

2.27. Anion exchange

BU1·H_2SO_4 (~10 mg) was dissolved together with Bu_4NX (~10 mg mL^{-1}, X = Cl, Br, I) in acetone (1-3 mL) in a 15 mL centrifuge tube. The solution was shaken, the solid was precipitated with mili-Q water (10 mL), sonicated and collected by centrifugation. This was repeated 5 times. The solid was then washed with $CHCl_3$ (2×1 mL) and Et_2O (5 mL). The solid was then transferred to a glass vial and dried in a vacuum. The recovery of **BU1**·BU_4NX was 30-60%.

3. Characterization

3.1. 4

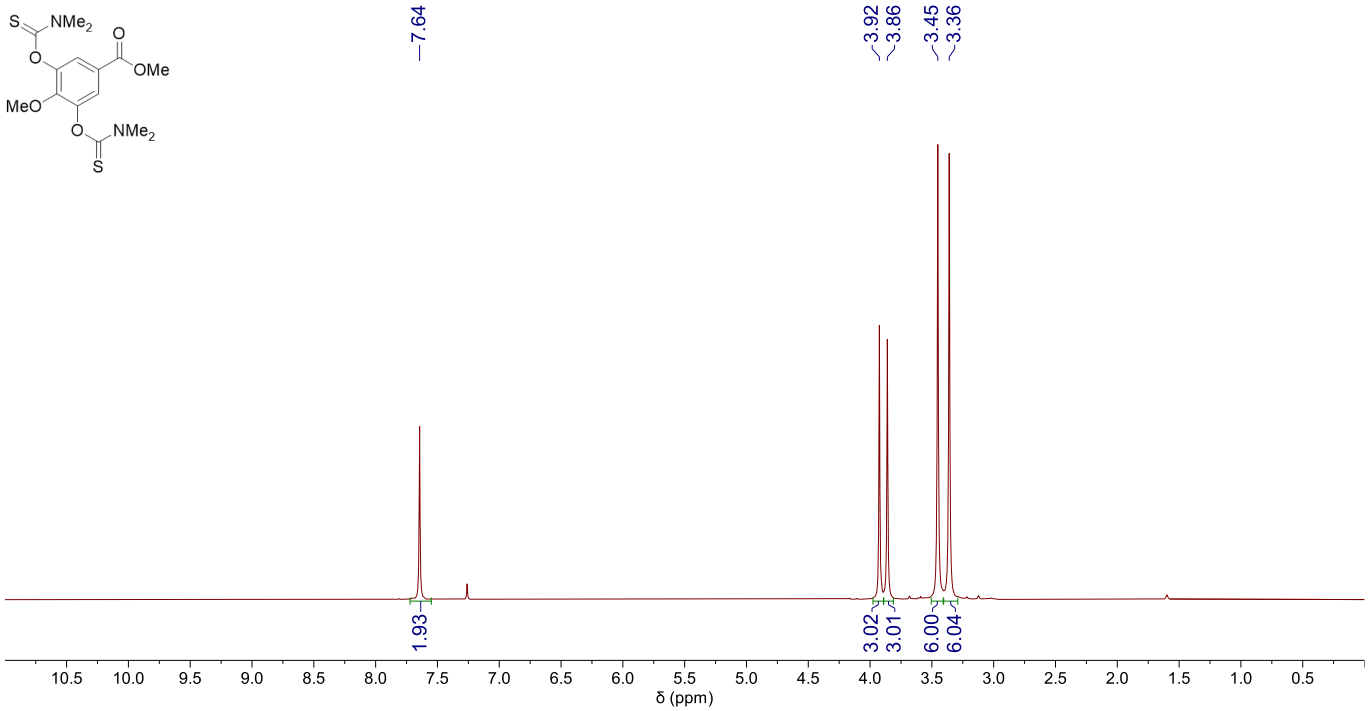


Figure S1: ^{1}H NMR spectrum of **4** (300 MHz, $CDCl_3$).

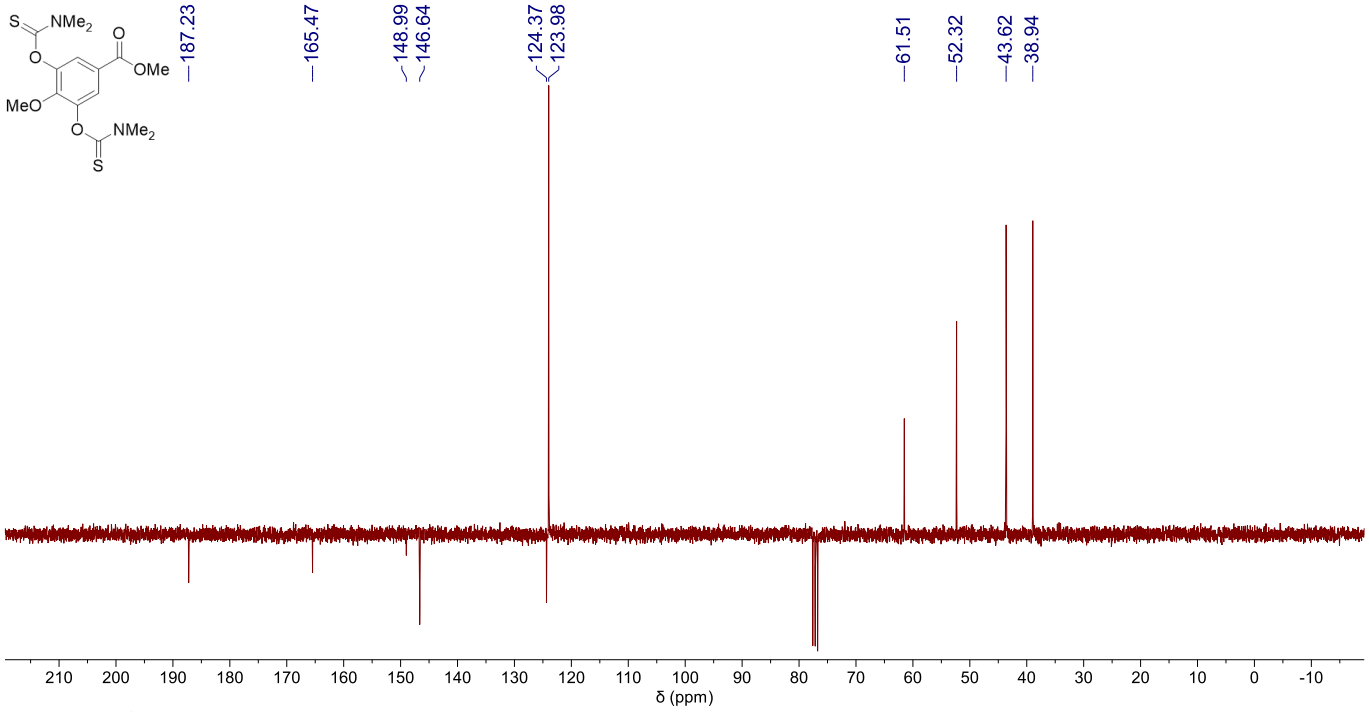


Figure S2: $^{13}C\{^{1}H\}$ APT NMR spectrum of **4** (75 MHz, $CDCl_3$).

3.2. 6

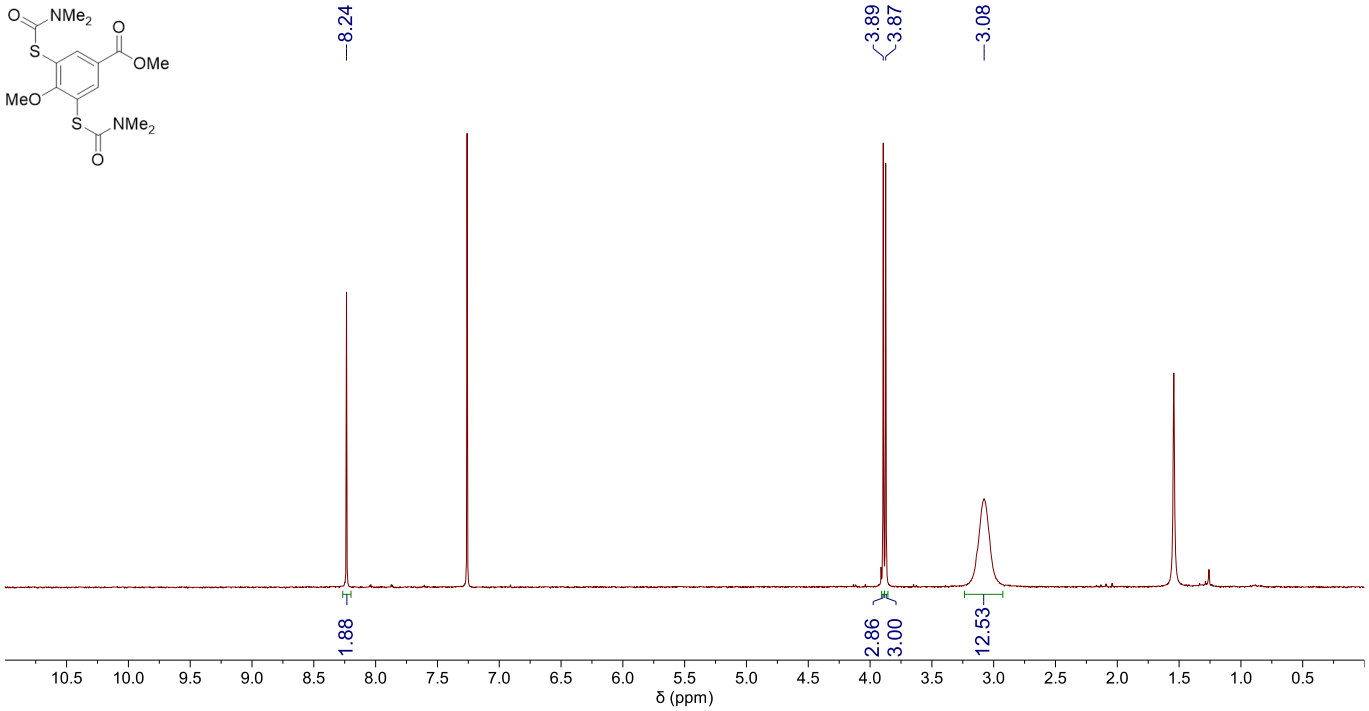


Figure S3: ^{1}H NMR spectrum of **6** (300 MHz, $CDCl_3$).

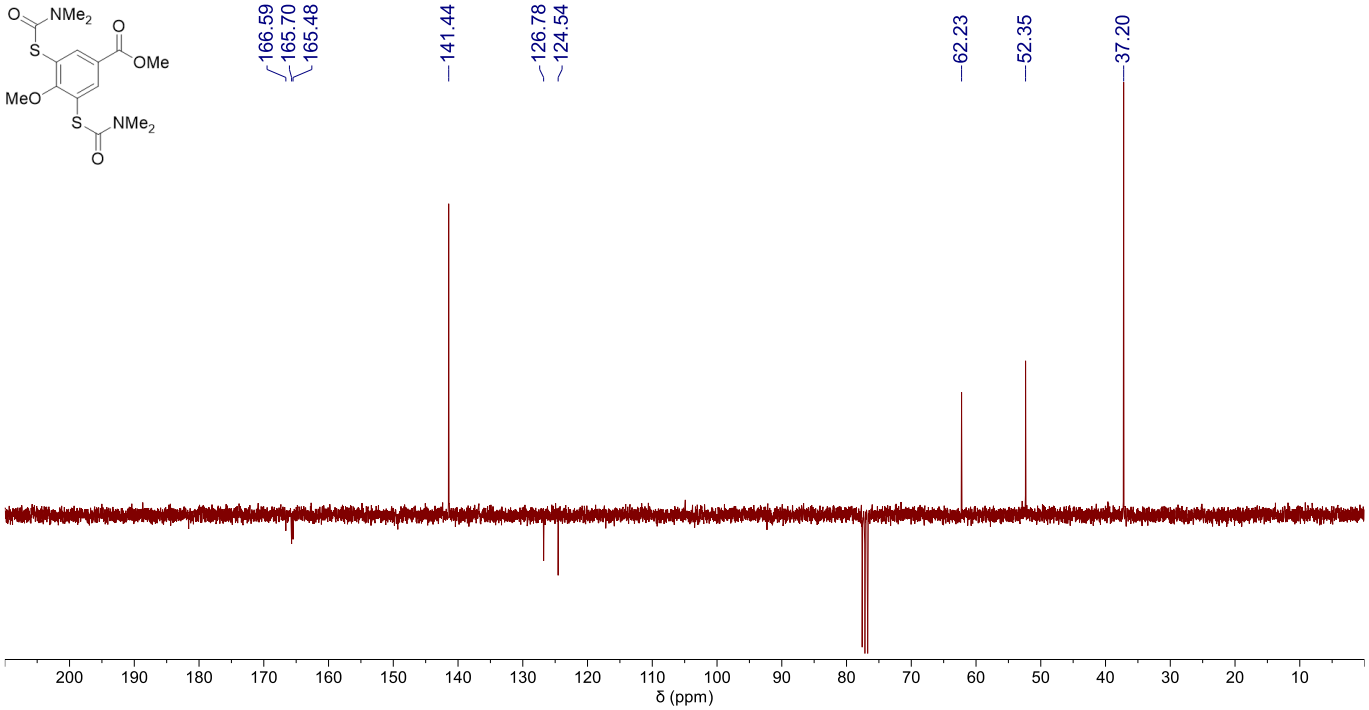


Figure S4: $^{13}C\{^{1}H\}$ APT NMR spectrum of **6** (75 MHz, $CDCl_3$).

3.3. 7

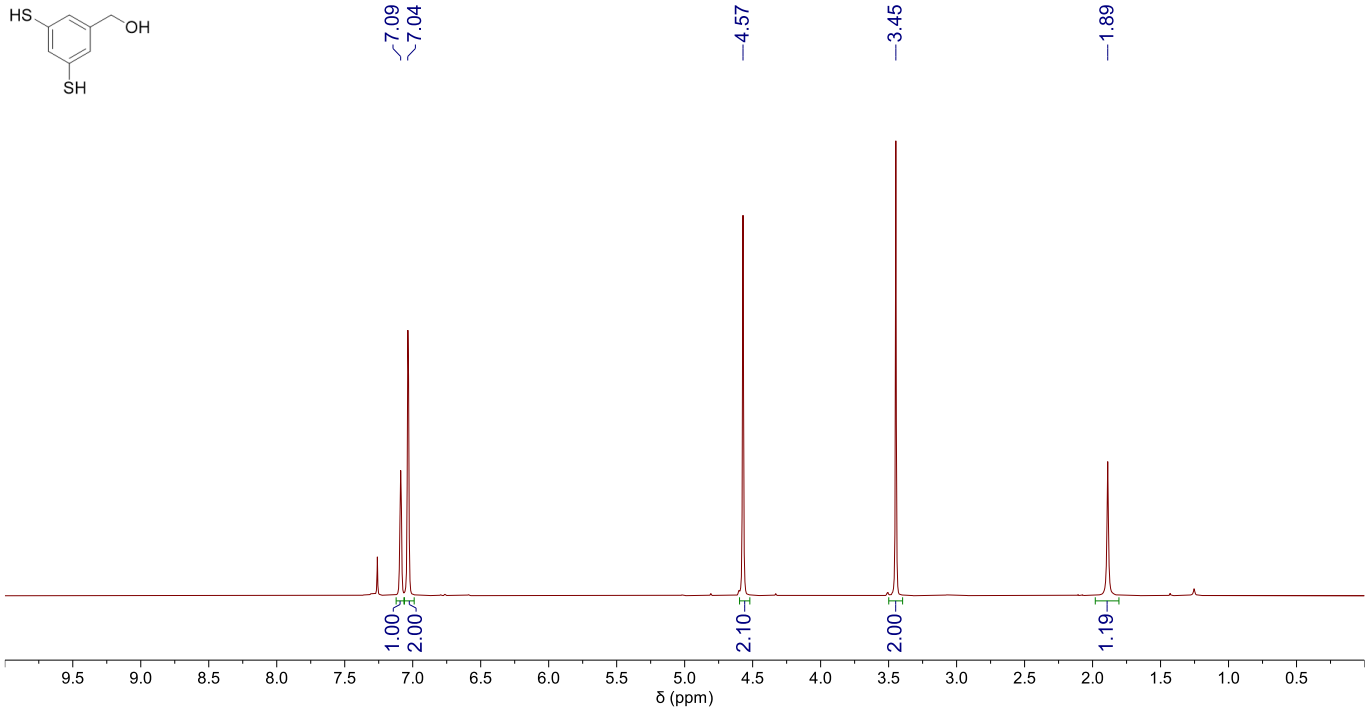


Figure S5: ^{1}H NMR spectrum of **7** (300 MHz, $CDCl_3$).

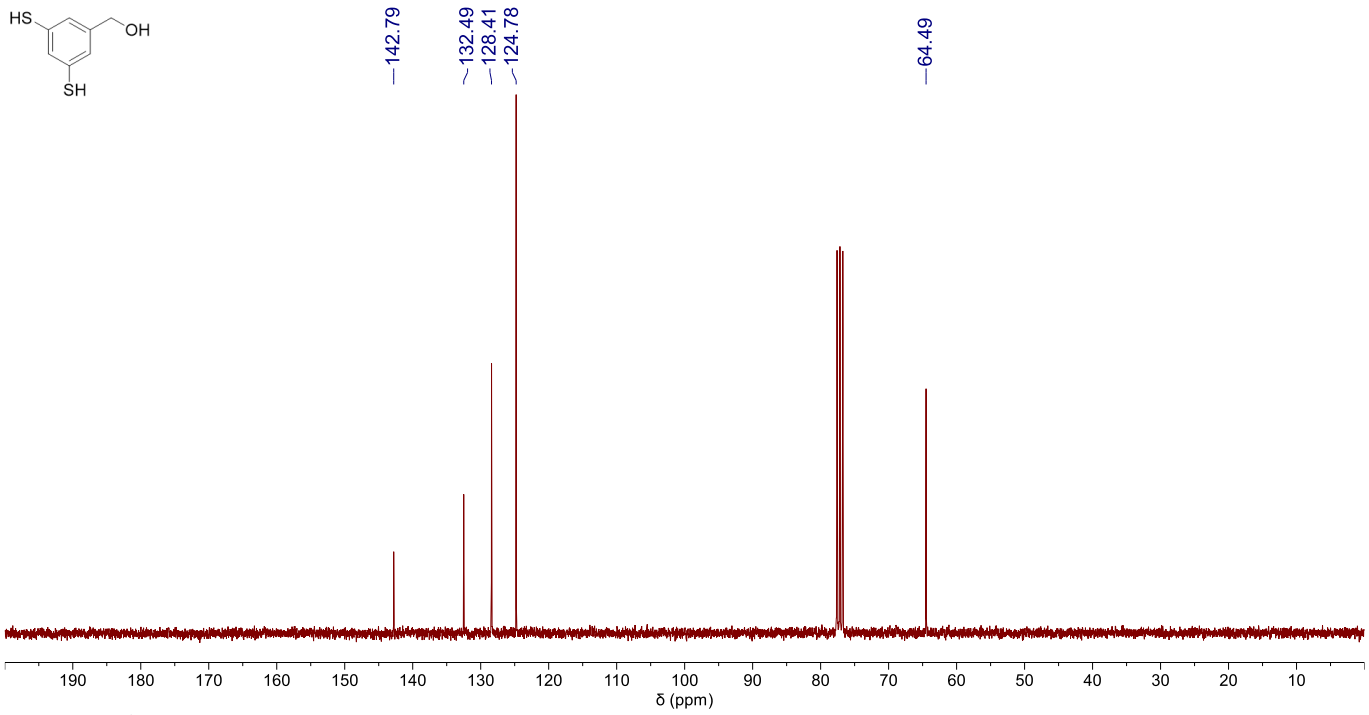


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of **7** (75 MHz, $CDCl_3$).

3.4. 8

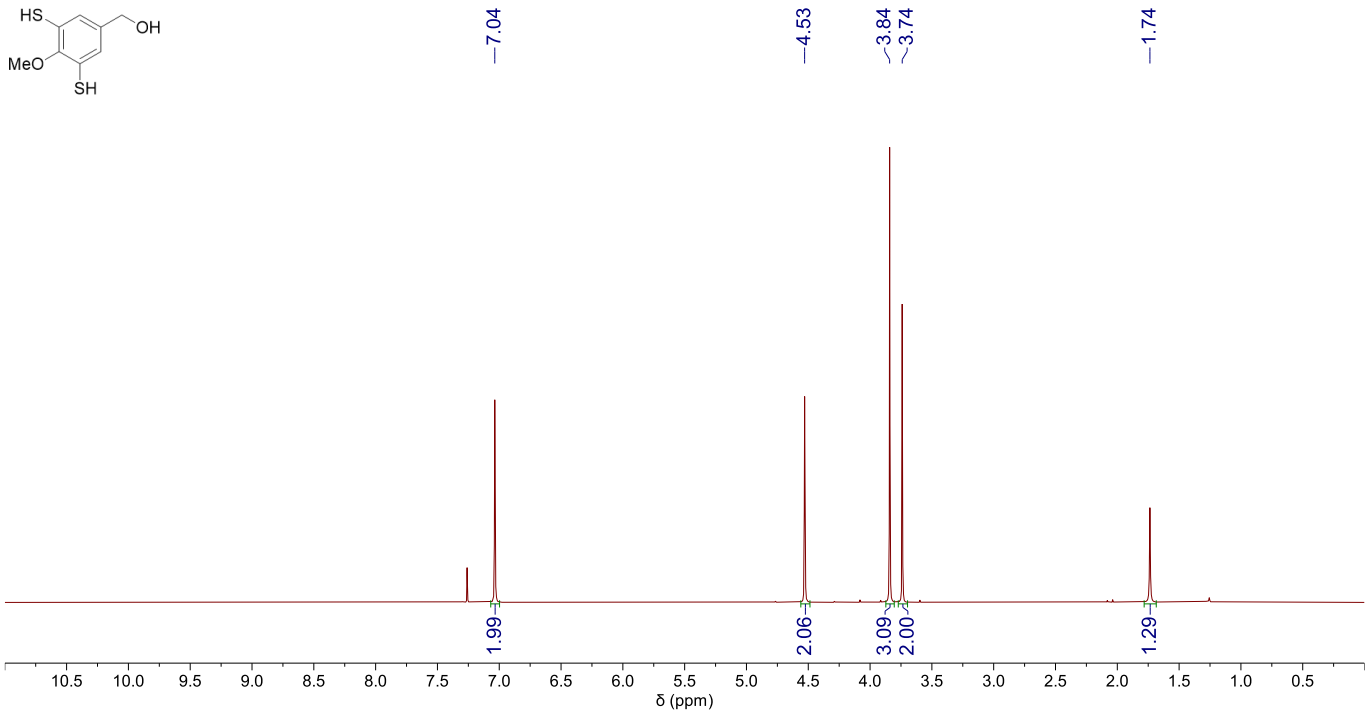


Figure S7: ^{1}H NMR spectrum of **8** (300 MHz, $CDCl_3$).

3.5. 9

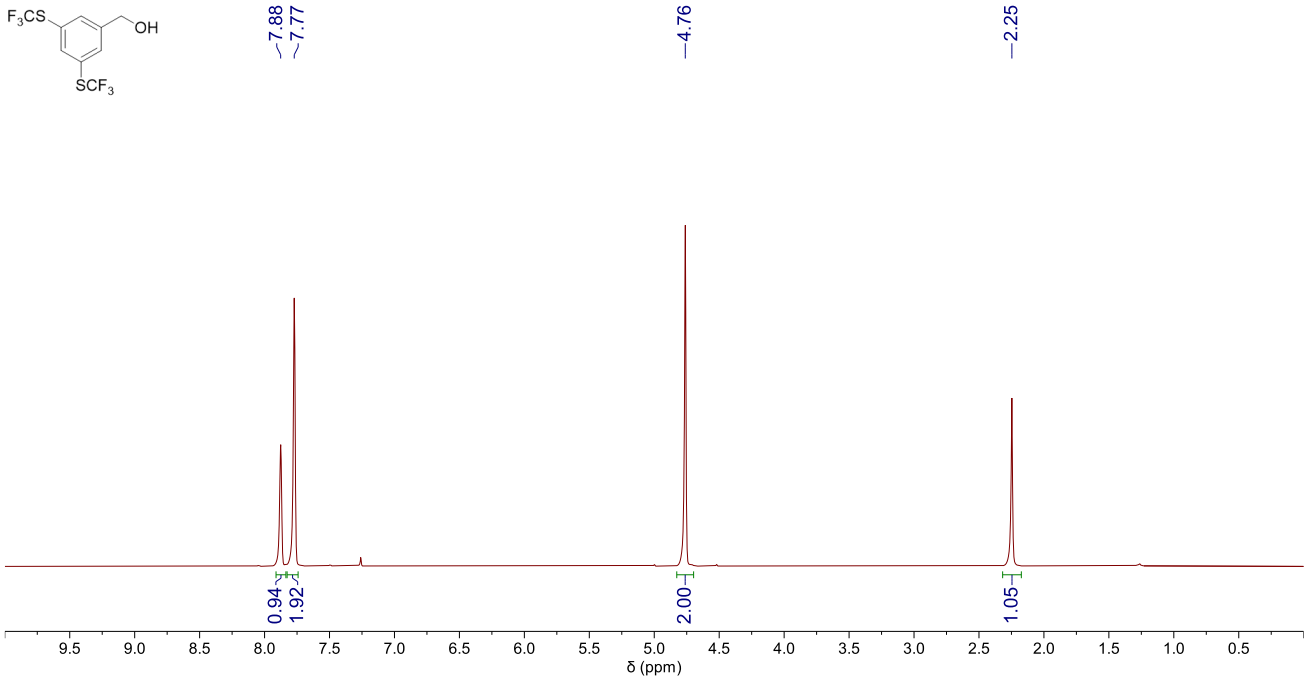


Figure S8: ^{1}H NMR spectrum of **9** (300 MHz, $CDCl_3$).

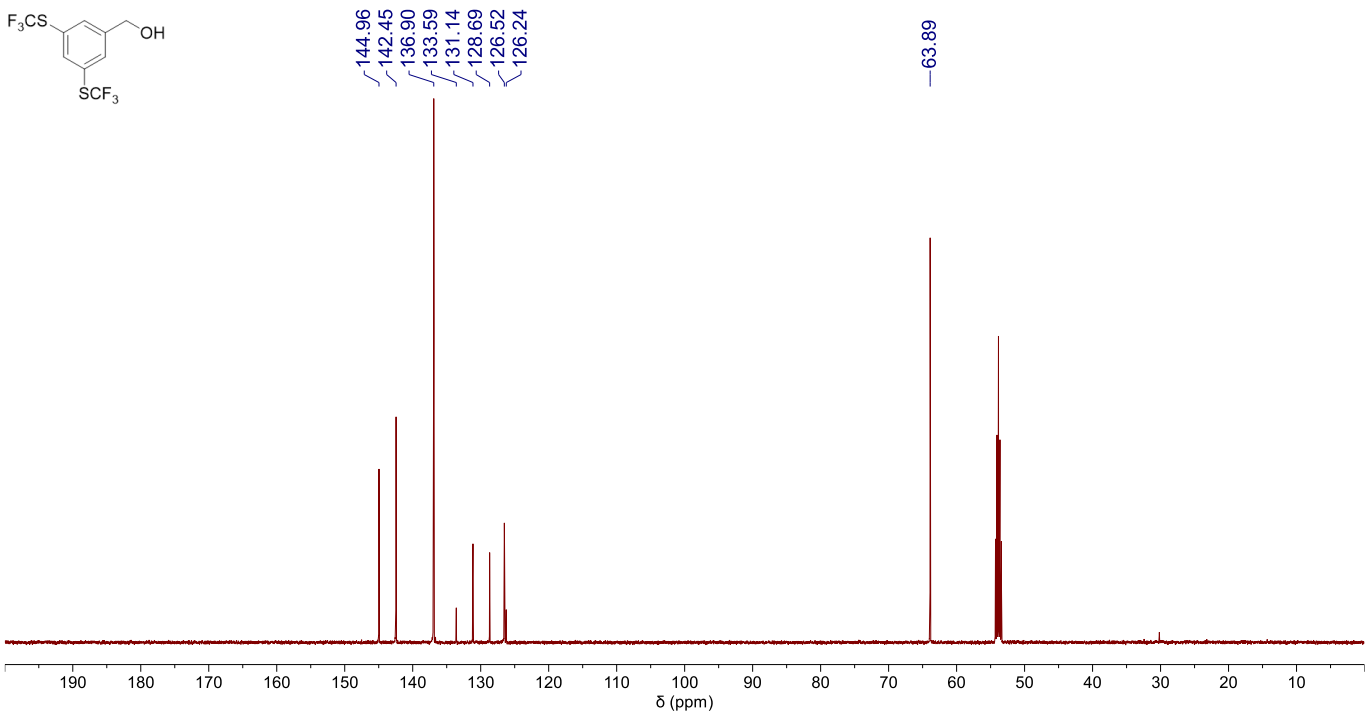


Figure S9: $^{13}C\{^{1}H\}$ NMR spectrum of **9** (126 MHz, CD_2Cl_2).

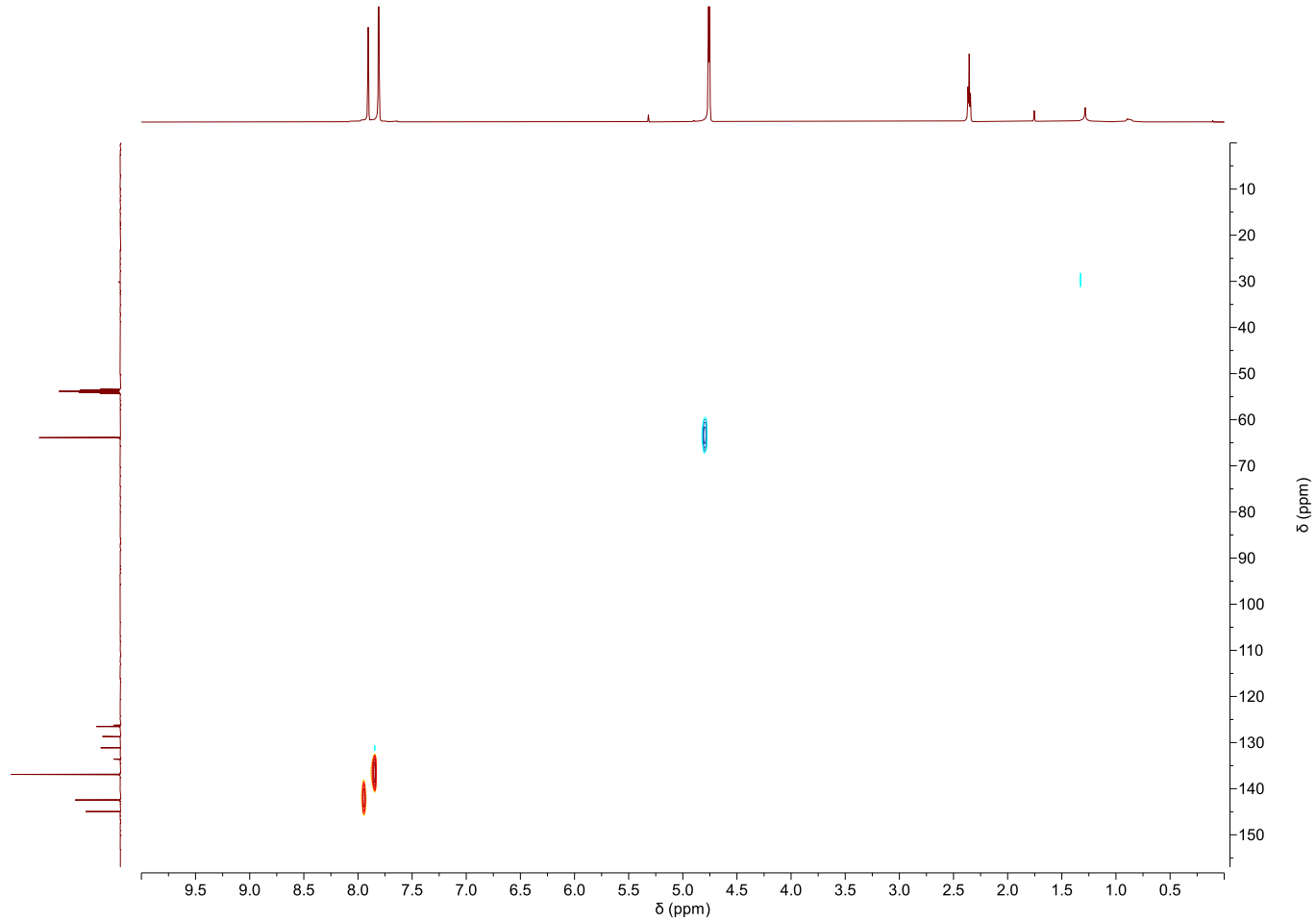


Figure S10: ^{1}H-^{13}C HSQC NMR spectrum of **9** (500 MHz, 126 MHz, CD_2Cl_2).

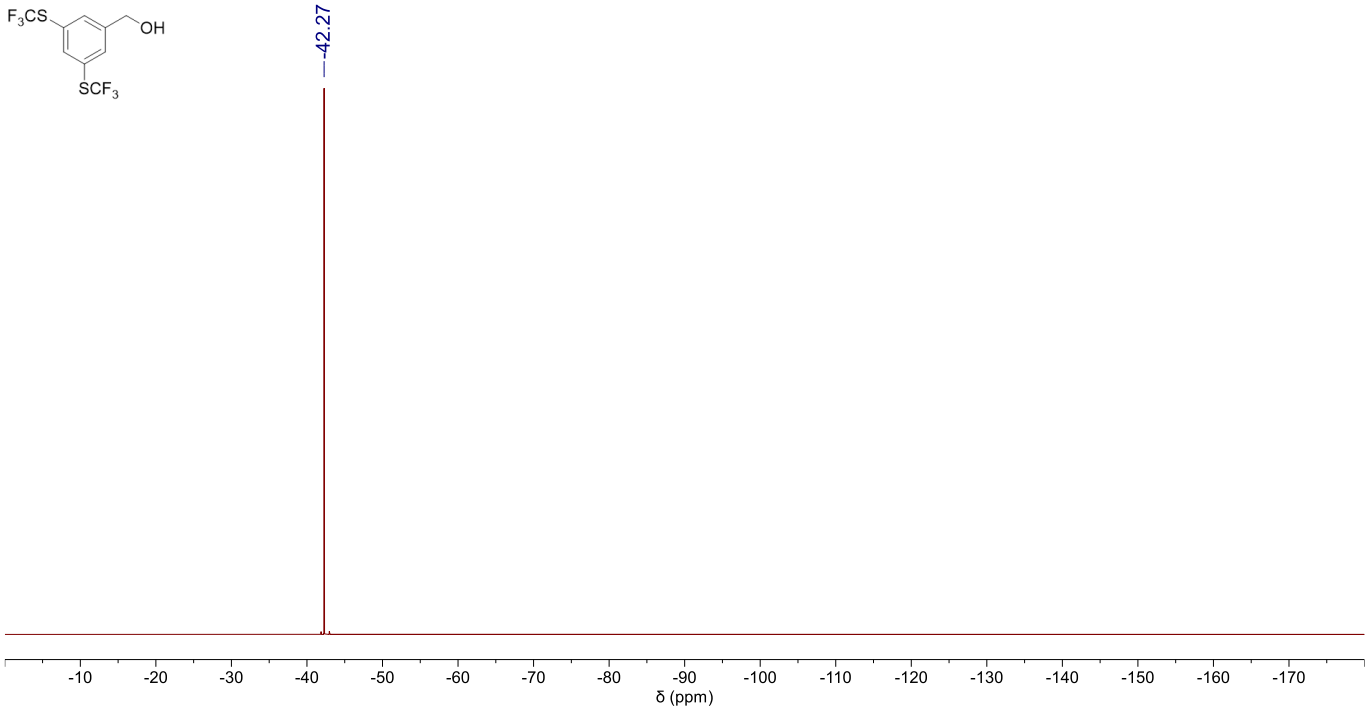


Figure S11: ^{19}F NMR spectrum of **9** (471 MHz, CD_2Cl_2).

3.6. 10

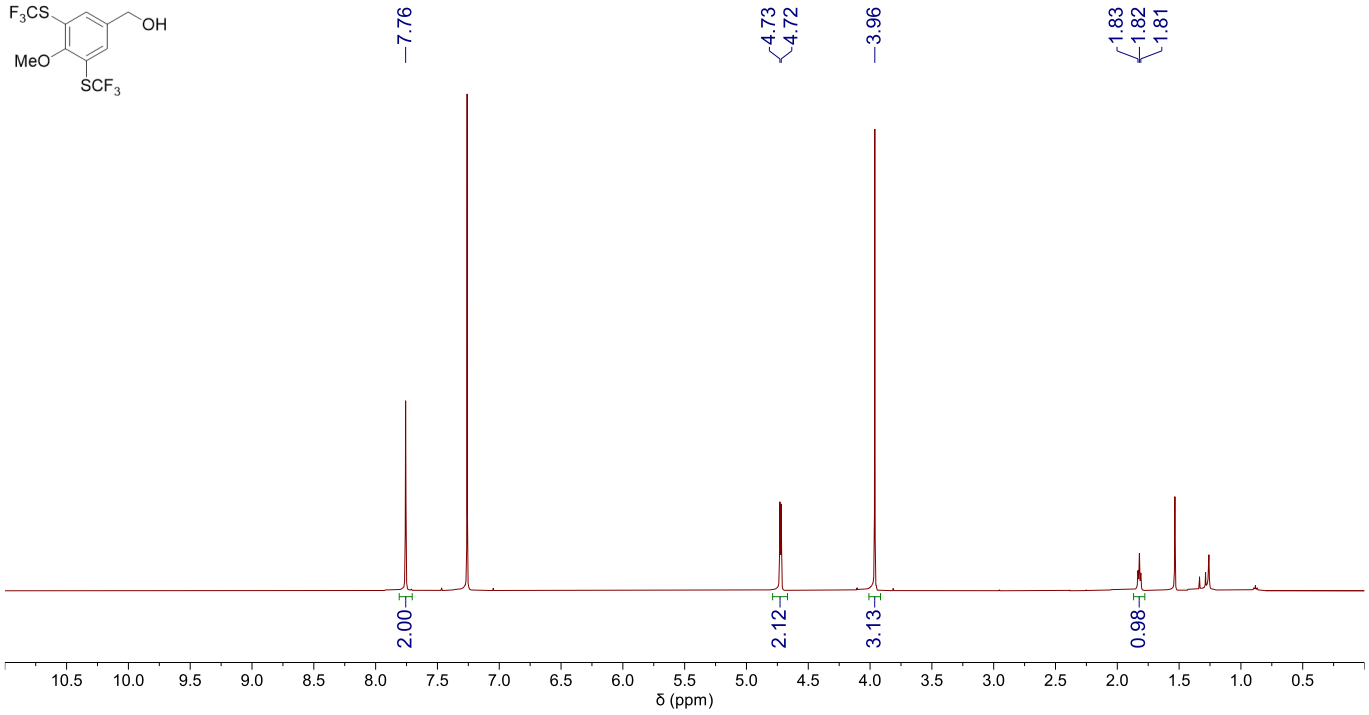


Figure S12: ^{1}H NMR spectrum of **10** (500 MHz, $CDCl_3$).

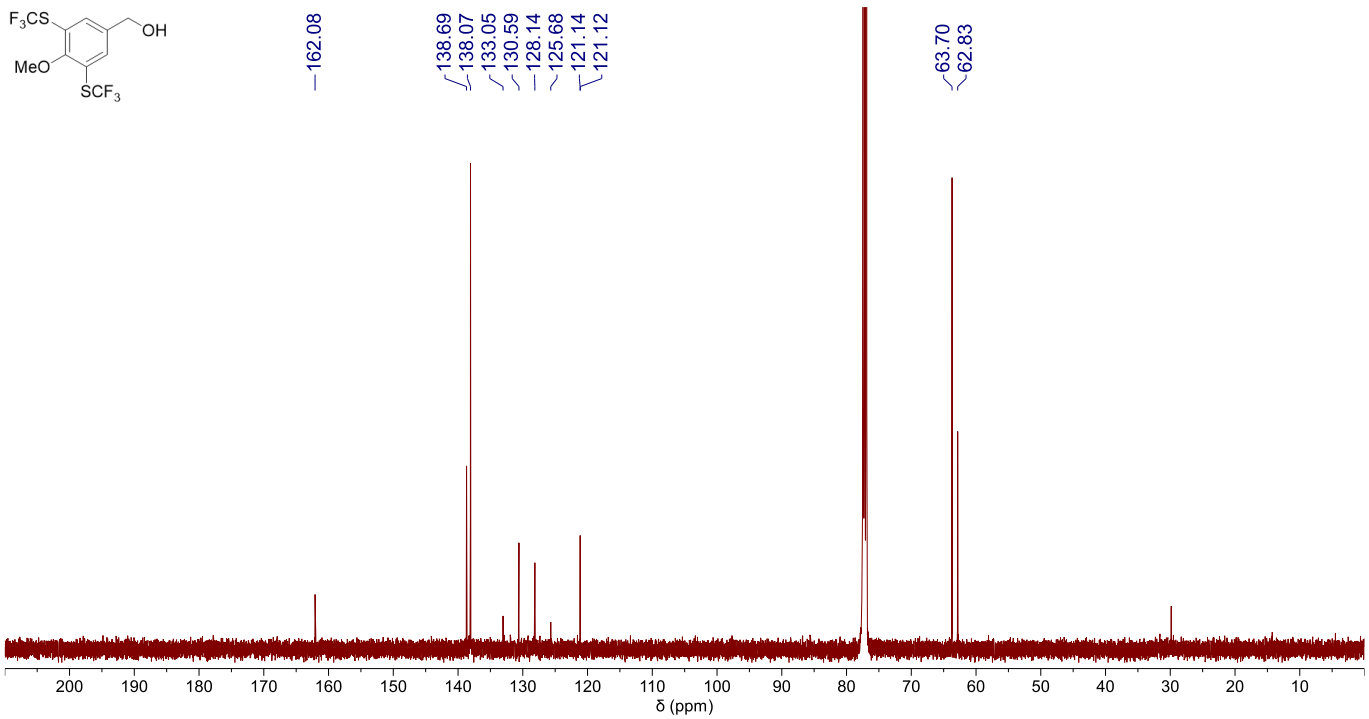


Figure S13: $^{13}C\{^{1}H\}$ NMR spectrum of **10** (126 MHz, $CDCl_3$).

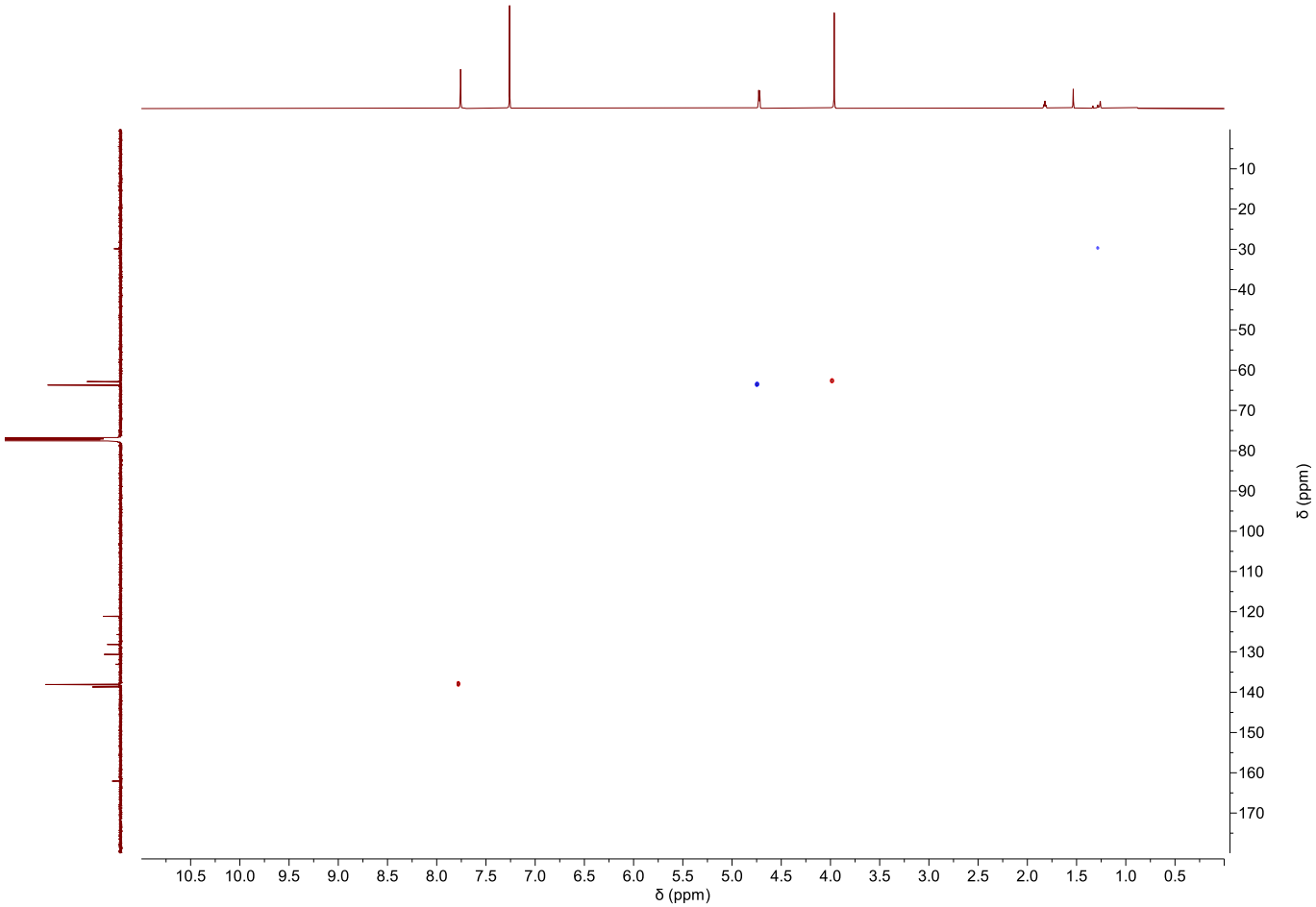


Figure S14: ^{1}H-^{13}C HSQC NMR spectrum of **10** (500 MHz, 126 MHz, $CDCl_3$).

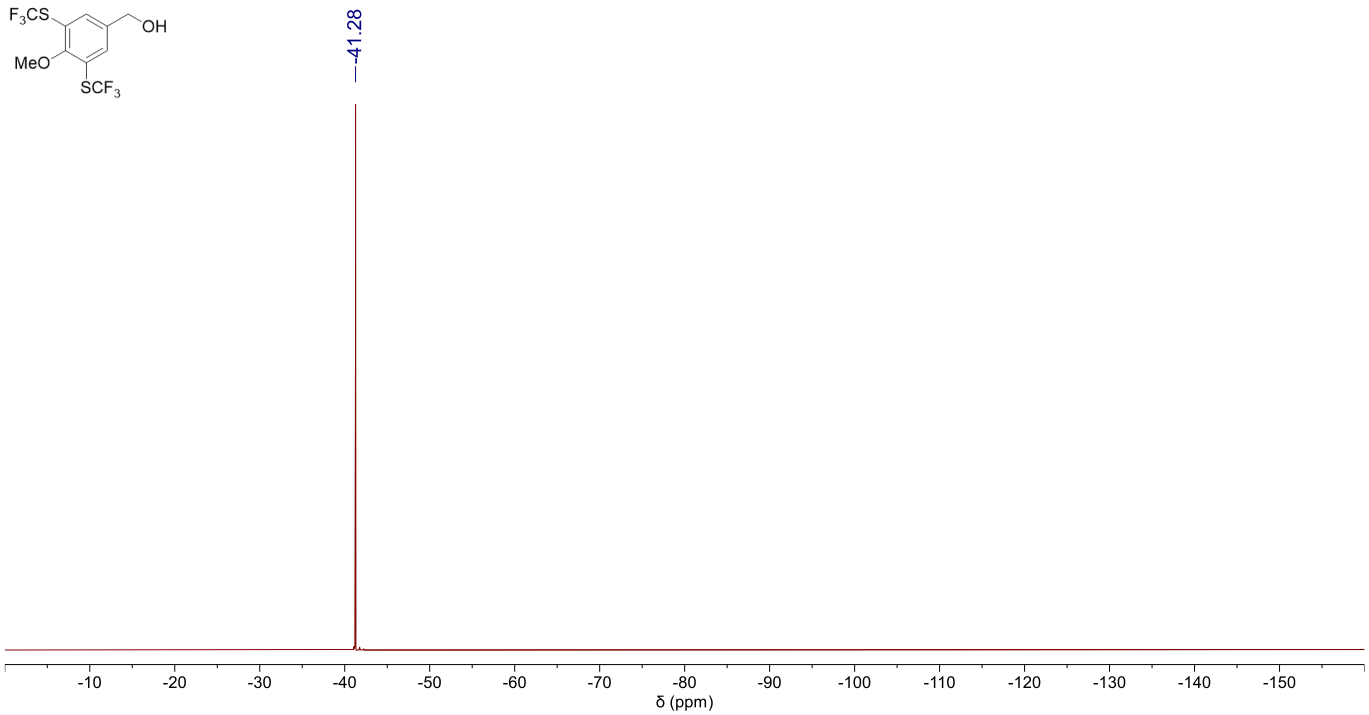


Figure S15: ^{19}F NMR spectrum of **10** (471 MHz, $CDCl_3$).

3.7. 11

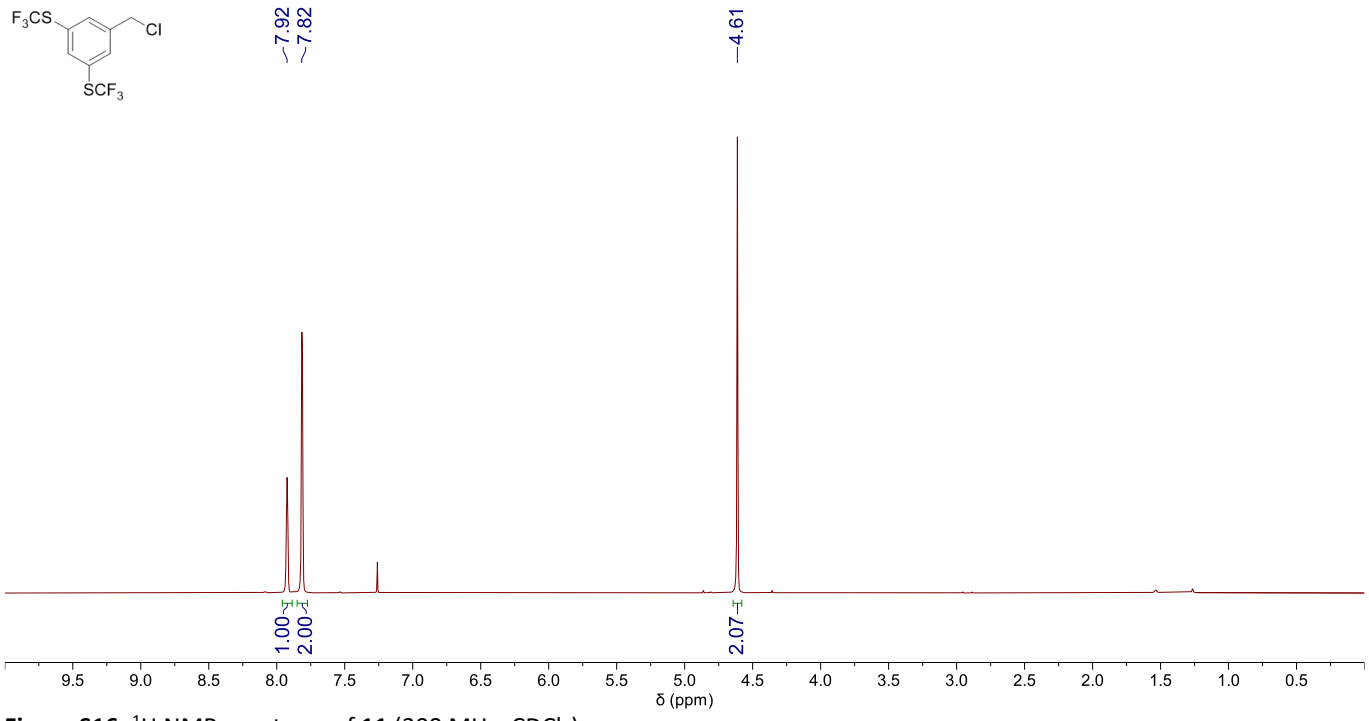


Figure S16: ^{1}H NMR spectrum of **11** (300 MHz, $CDCl_3$).

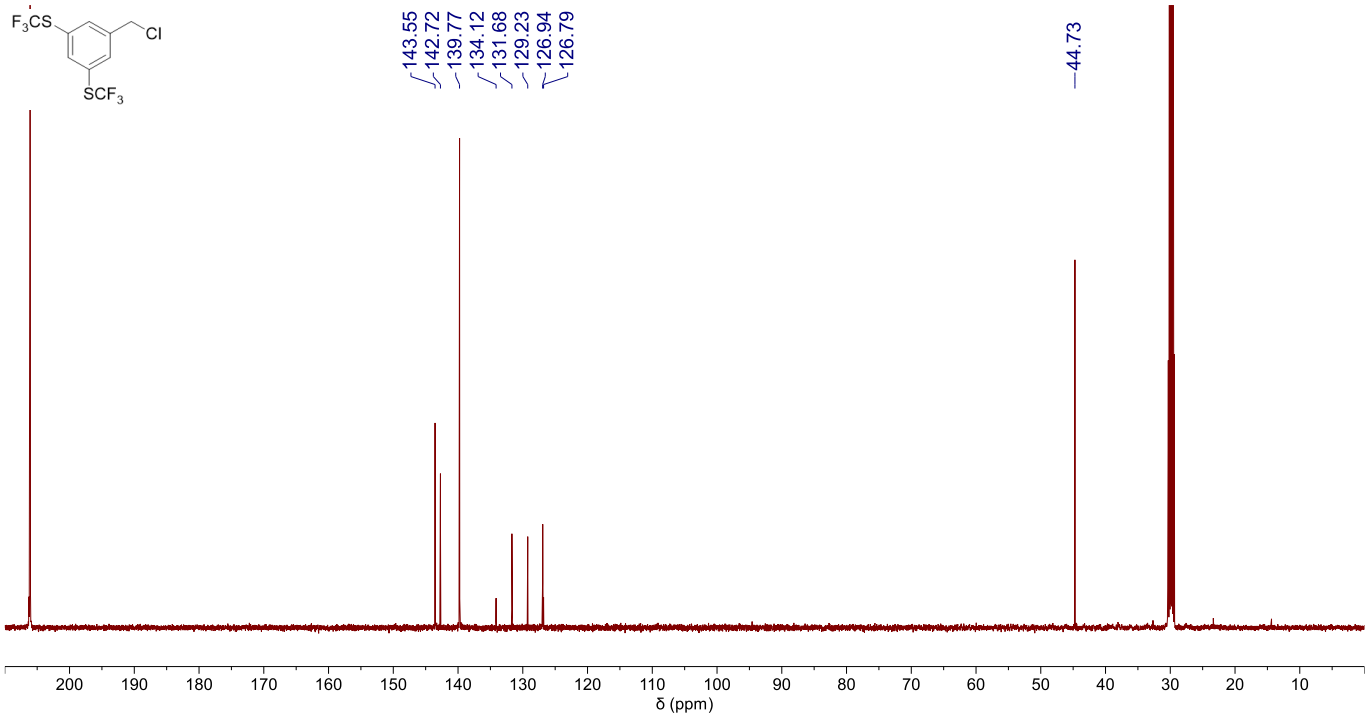


Figure S17: $^{13}C\{^{1}H\}$ NMR spectrum of **11** (126 MHz, acetone-d_6).

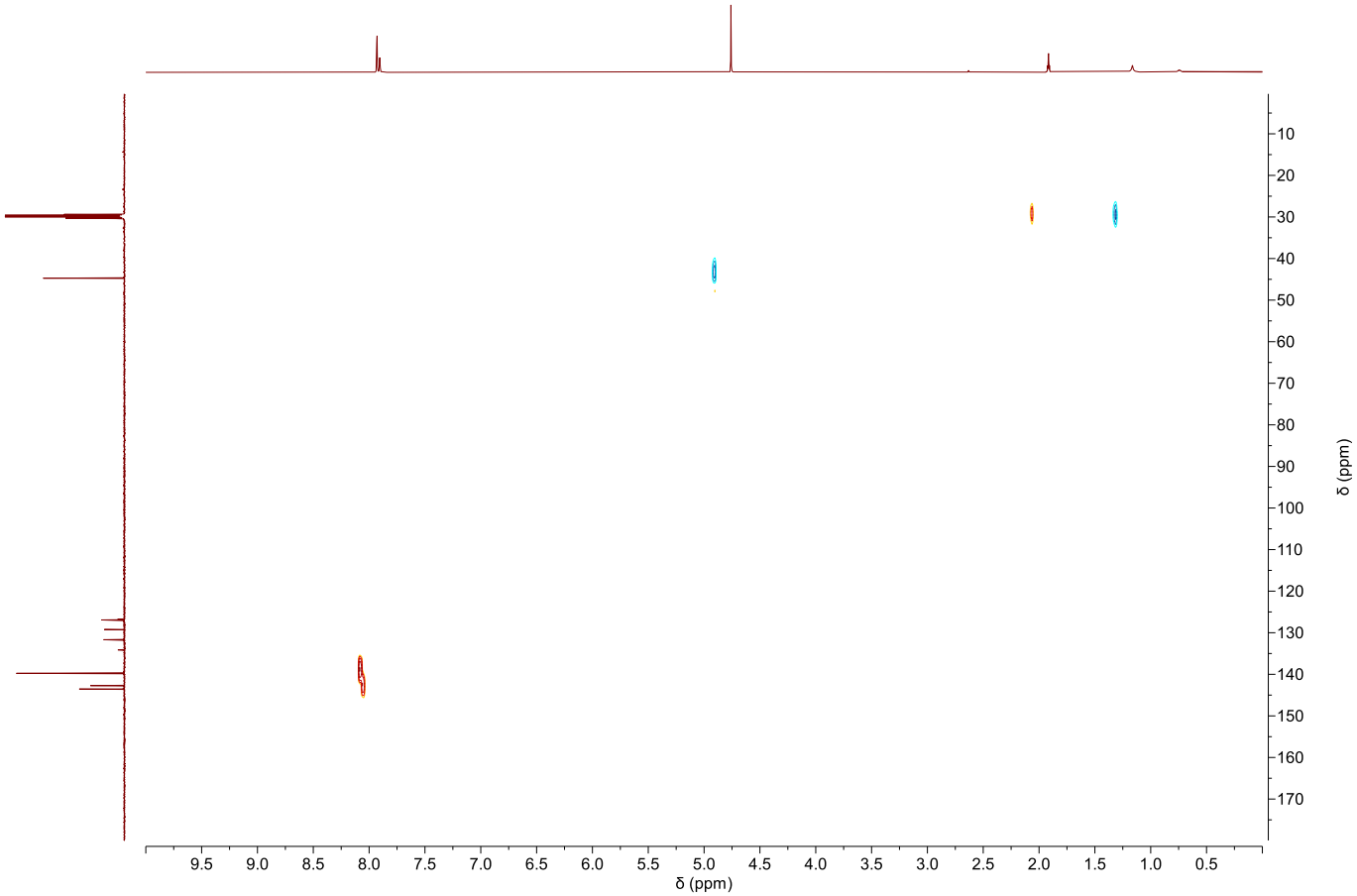


Figure S18: ^{1}H-^{13}C HSQC NMR spectrum of **11** (500 MHz, 126 MHz, acetone-d_6).

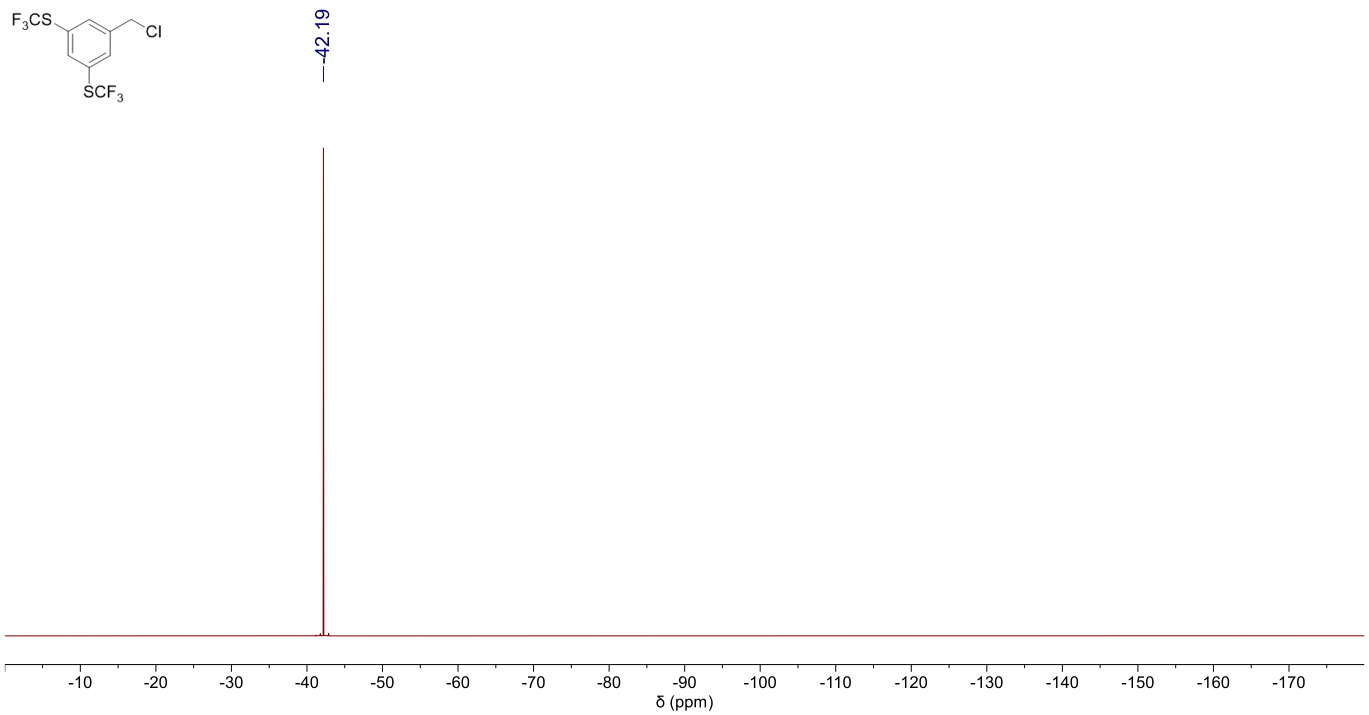


Figure S19: ^{19}F NMR spectrum of **11** (282 MHz, $CDCl_3$).

3.8. 12

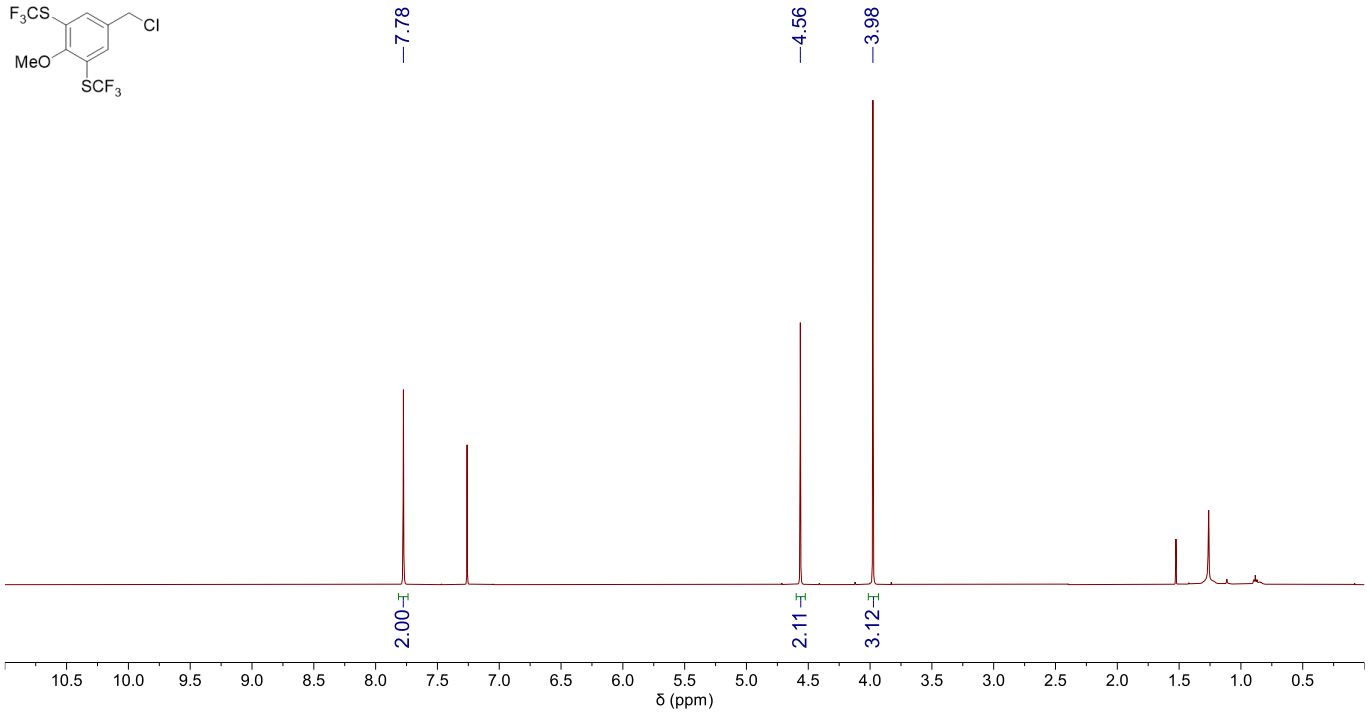


Figure S20: ^{1}H NMR spectrum of **12** (500 MHz, $CDCl_3$).

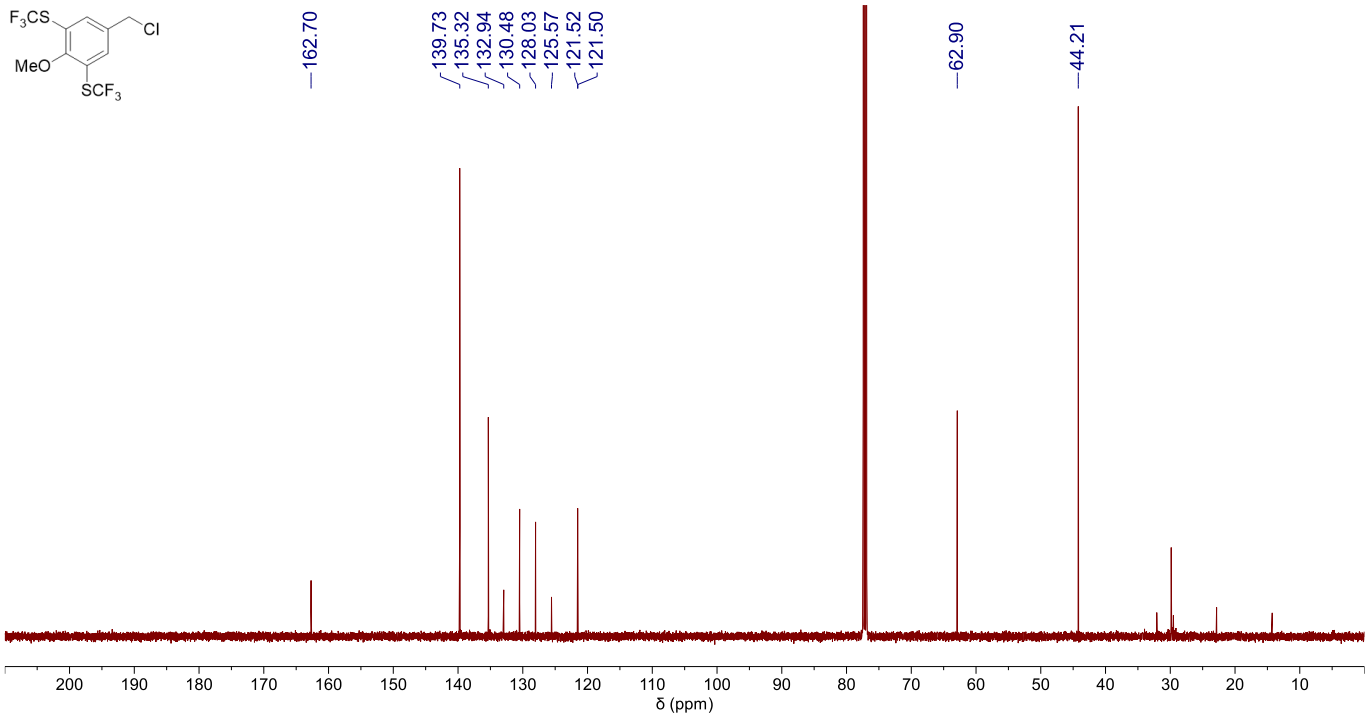


Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum of **12** (126 MHz, $CDCl_3$).

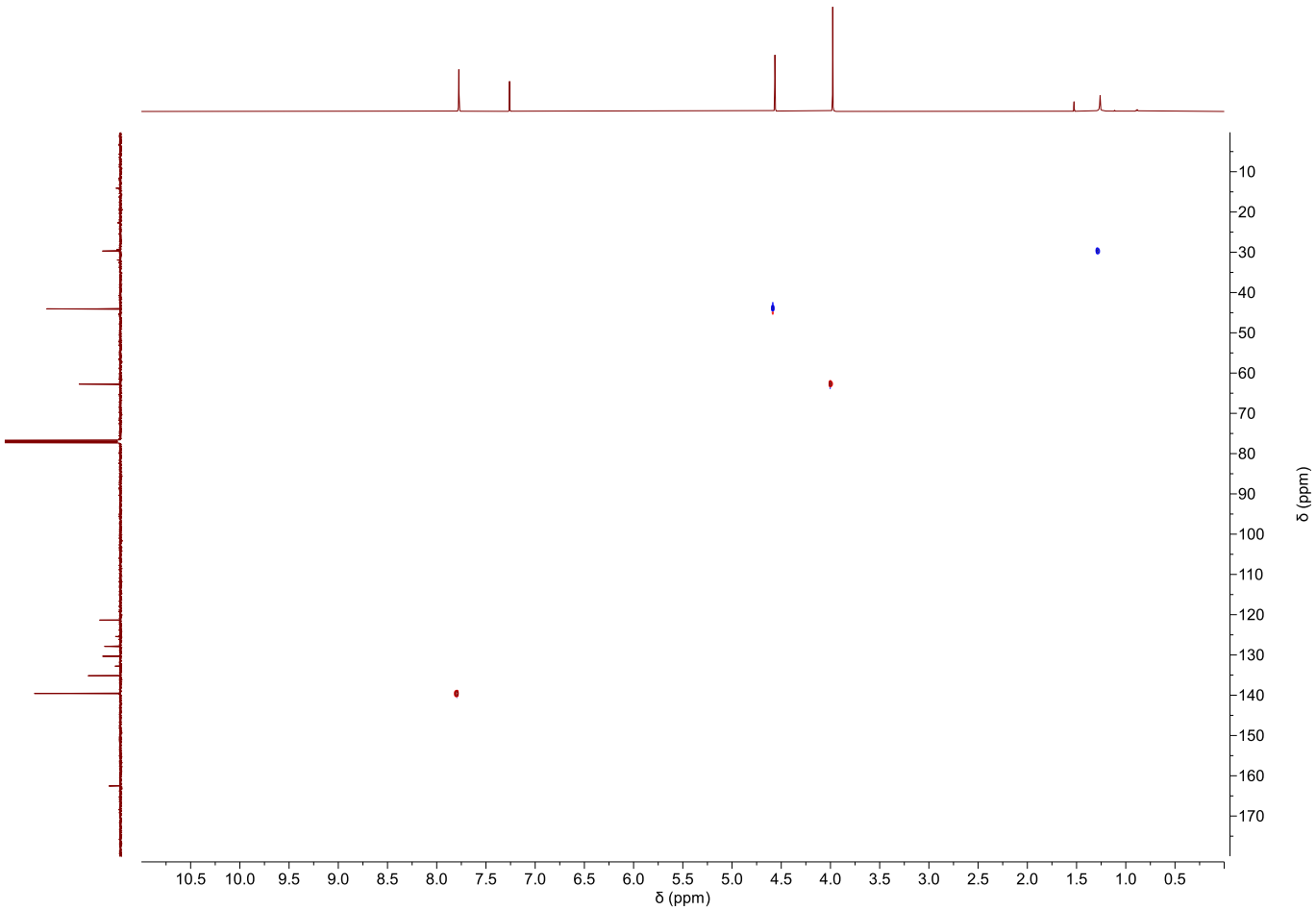


Figure S22: ^{1}H-^{13}C HSQC NMR spectrum of **12** (500 MHz, 126 MHz, $CDCl_3$).

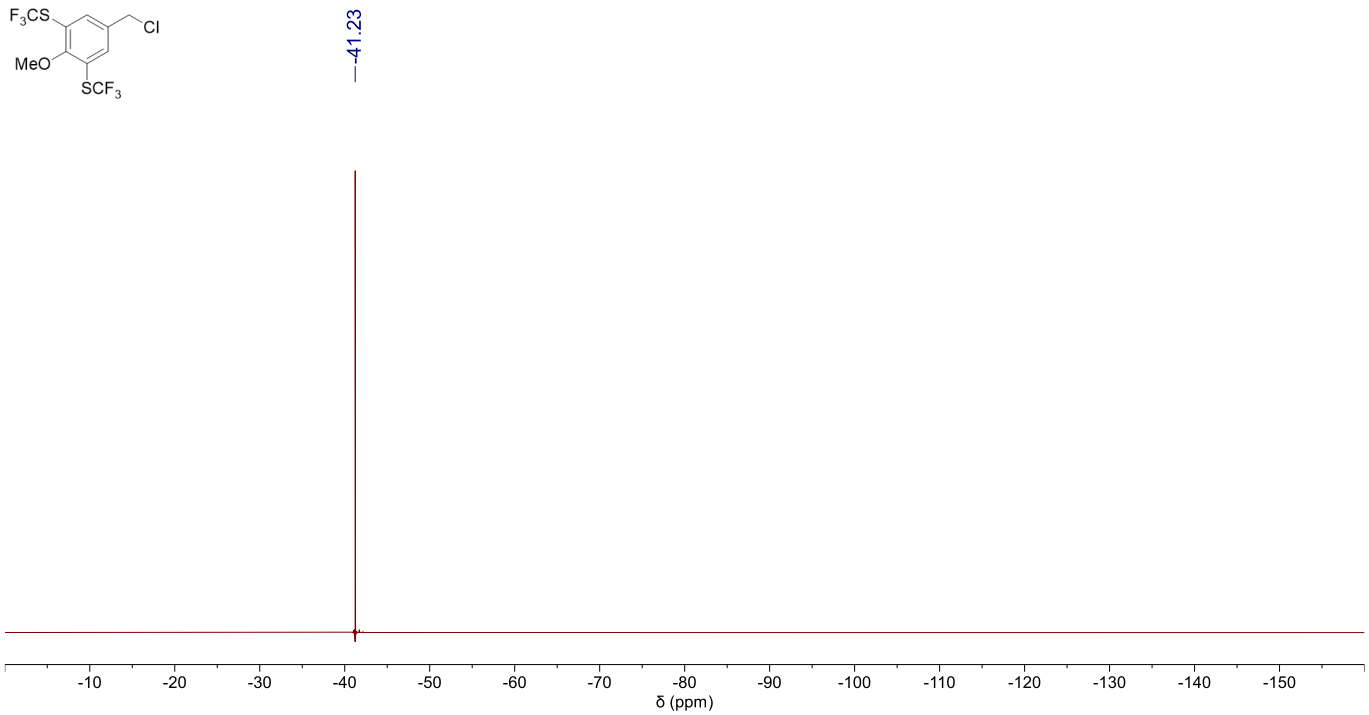


Figure S23: ^{19}F NMR spectrum of **12** (282 MHz, $CDCl_3$).

3.9. 13

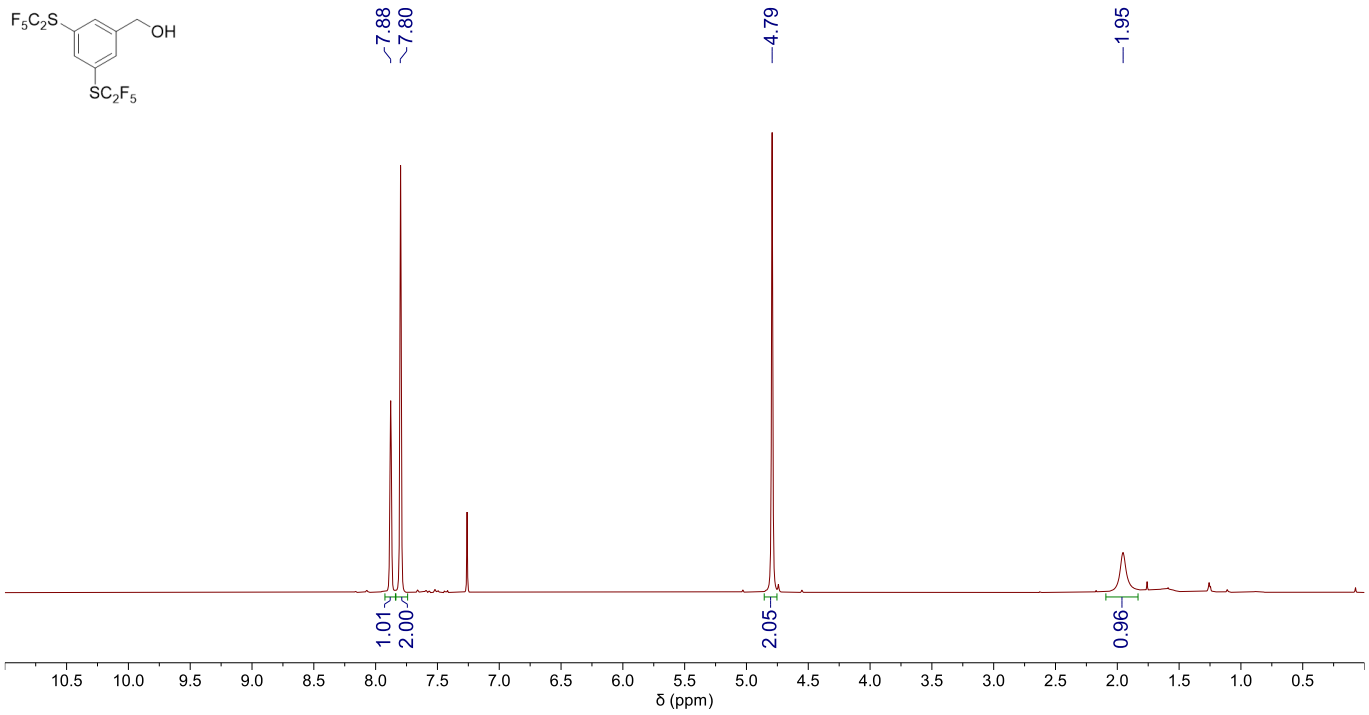


Figure S24: ^{1}H NMR spectrum of a mixture of **13** and **17** (300 MHz, $CDCl_3$).

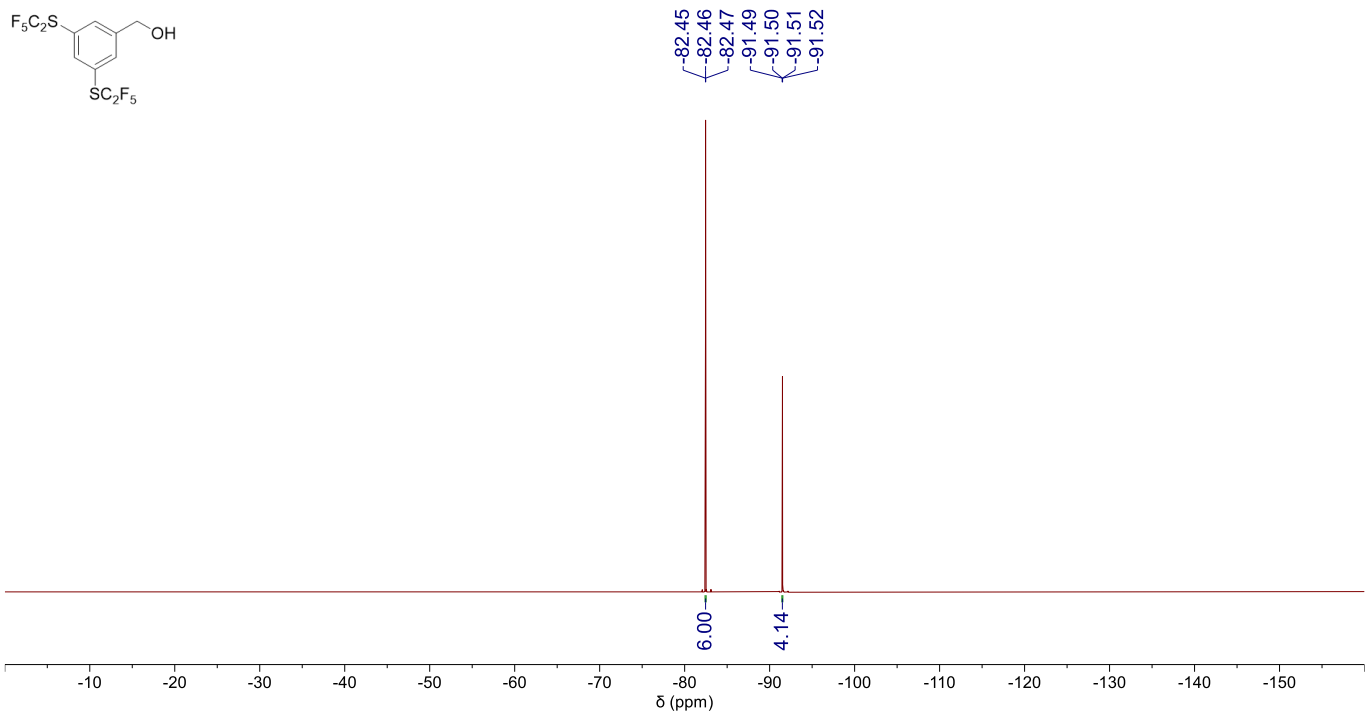


Figure S25: ^{19}F NMR spectrum of a mixture of **13** and **17** (282 MHz, $CDCl_3$).

3.10. 14

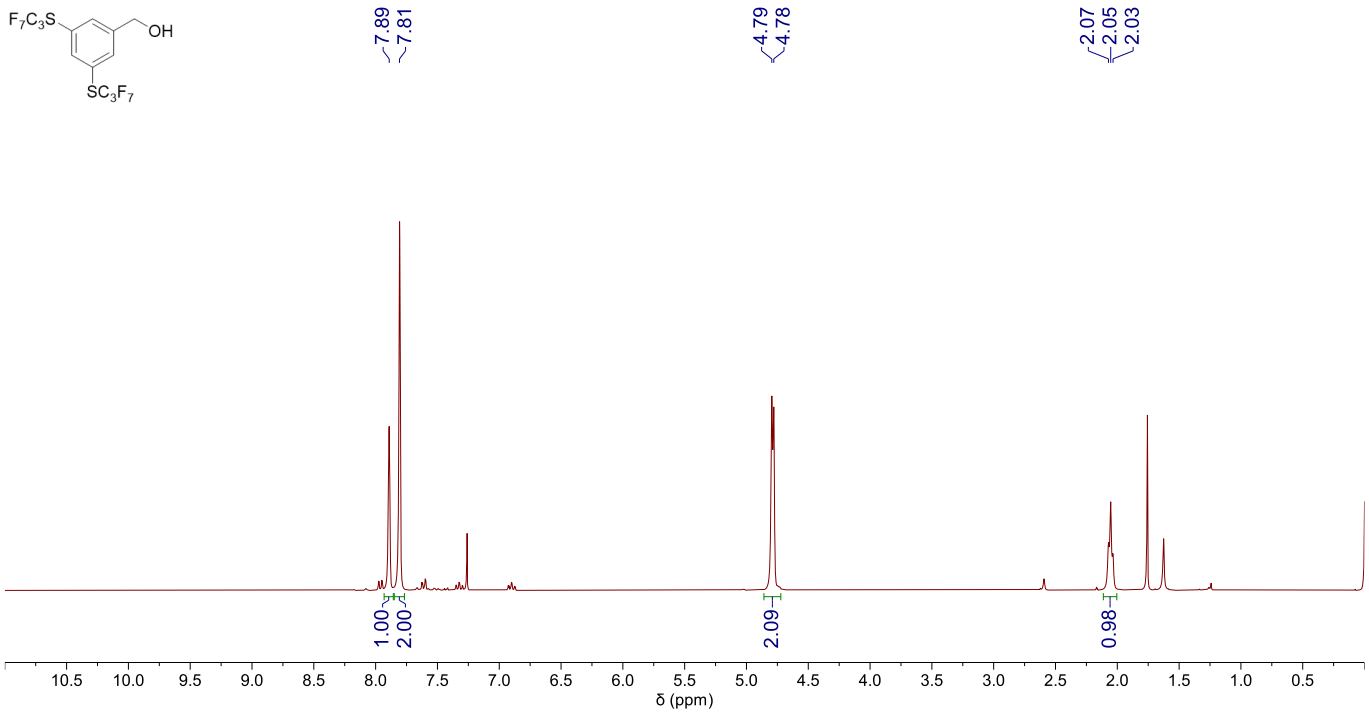


Figure S26: ^{1}H NMR spectrum of a mixture of **14** and **17** (300 MHz, $CDCl_3$).

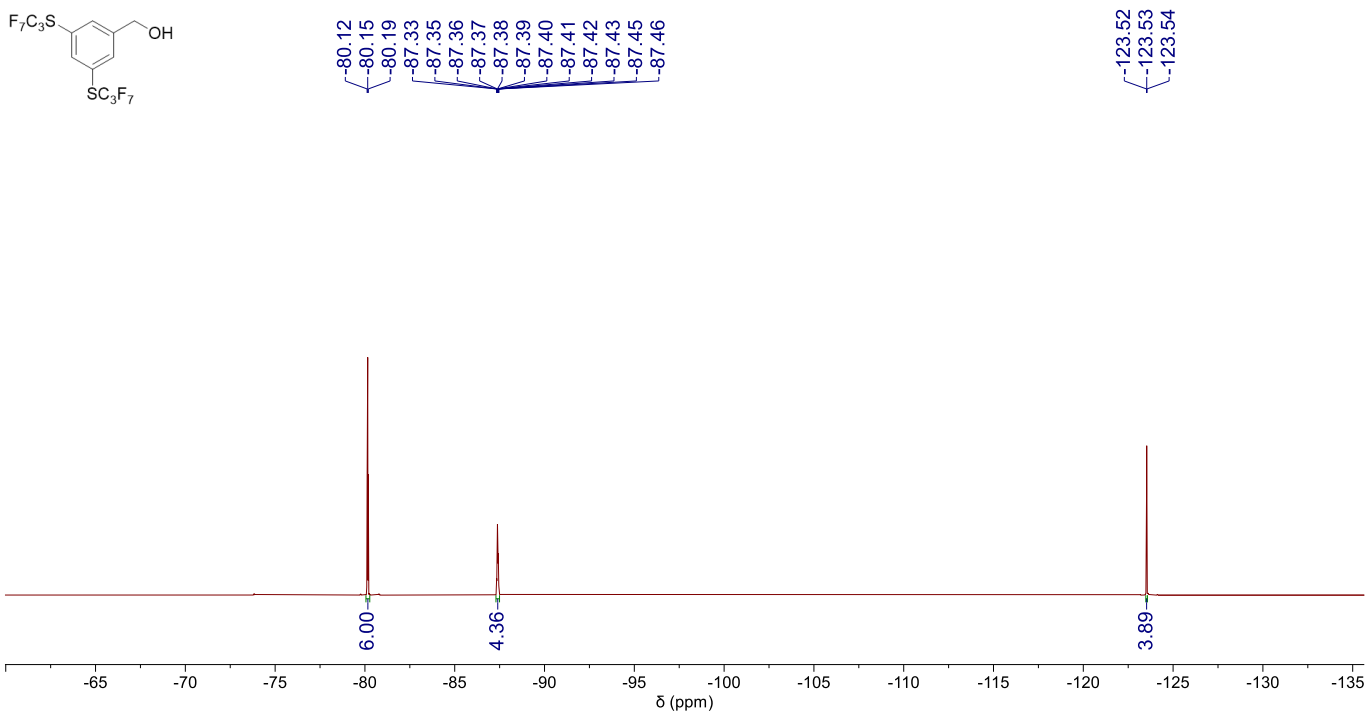


Figure S27: ^{19}F NMR spectrum of a mixture of **14** and **17** (282 MHz, $CDCl_3$).

3.11. 15

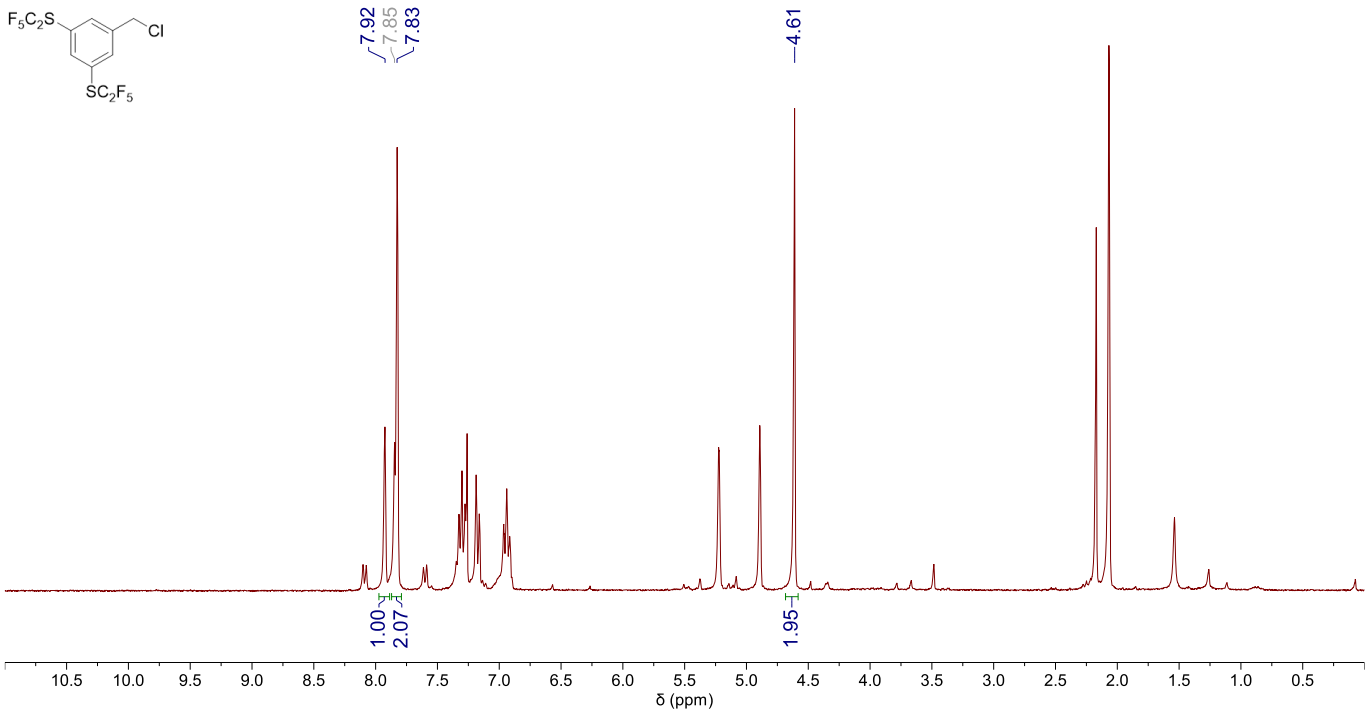


Figure S28: ^{1}H NMR spectrum of a mixture of **15** and **18** (300 MHz, $CDCl_3$).

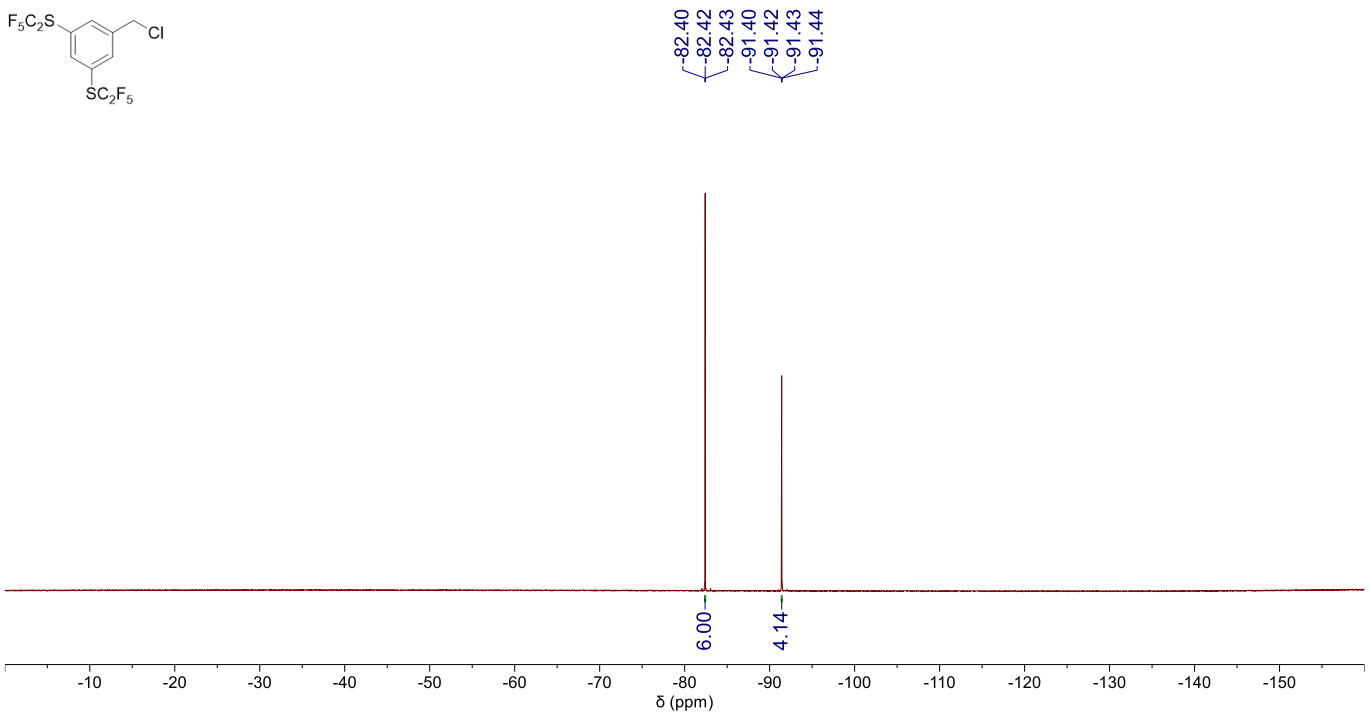


Figure S29: ^{19}F NMR spectrum of a mixture of **15** and **18** (282 MHz, $CDCl_3$).

3.12. 16

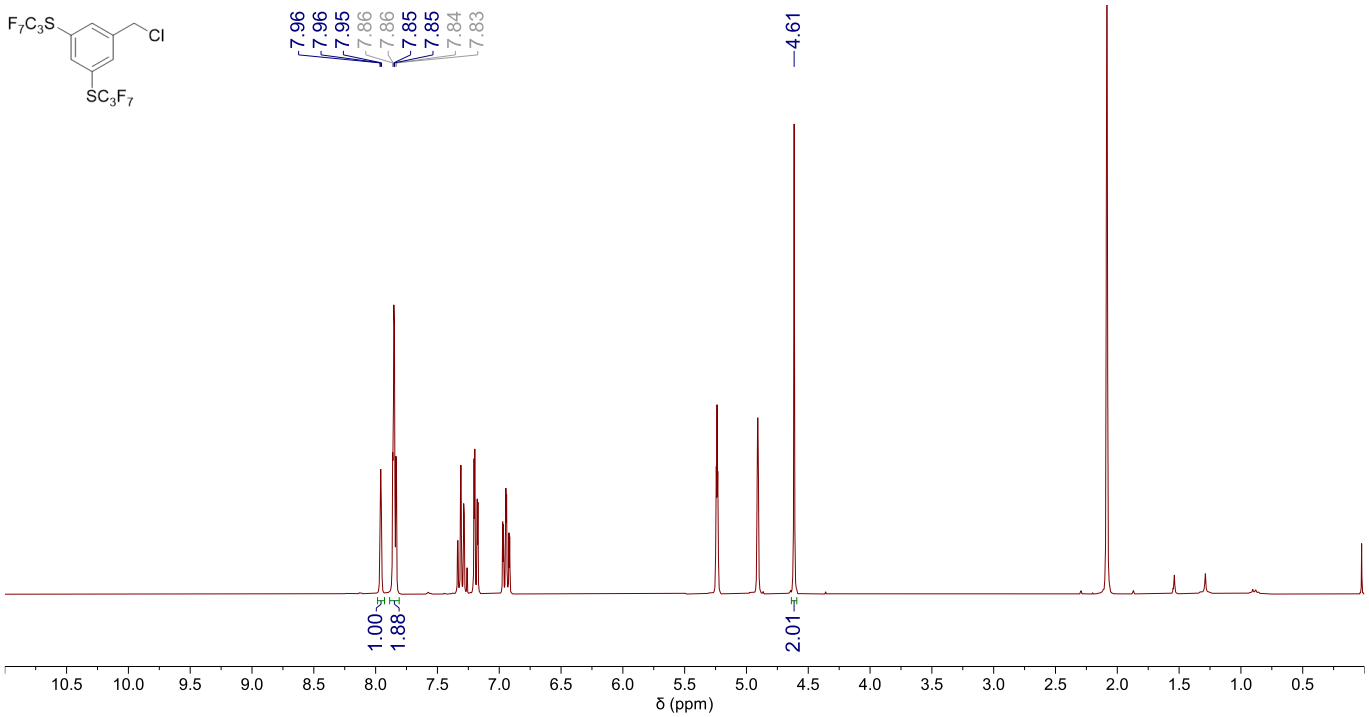


Figure S30: ^{1}H NMR spectrum of a mixture of **16** and **18** (300 MHz, $CDCl_3$).

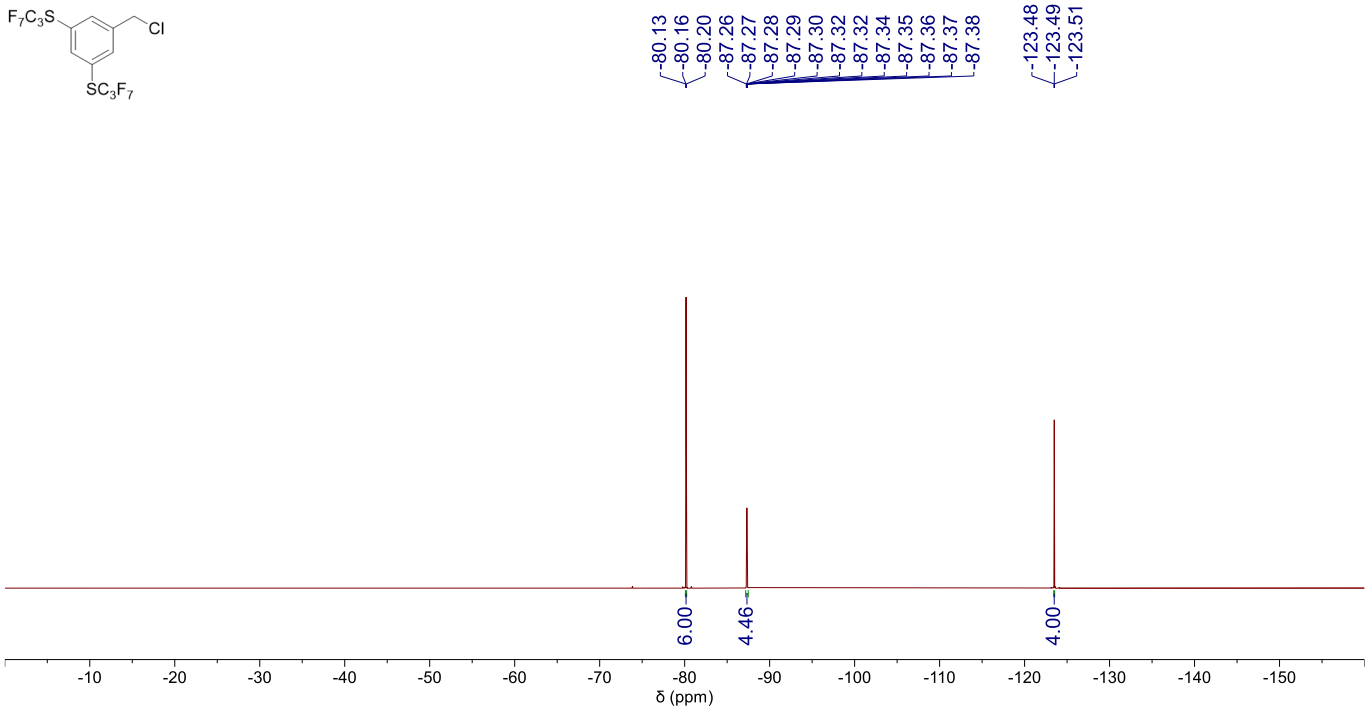


Figure S31: ^{19}F NMR spectrum of a mixture of **16** and **18** (282 MHz, $CDCl_3$).

3.13. 20

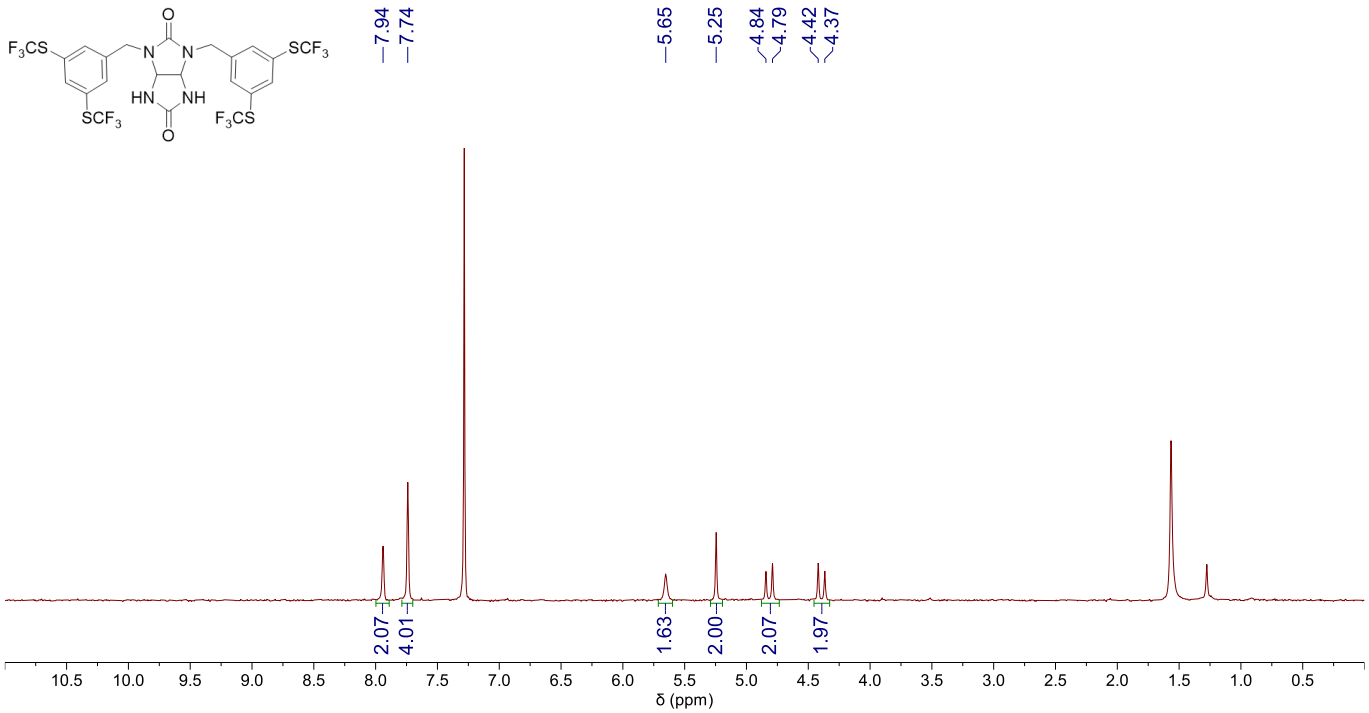


Figure S32: ^{1}H NMR spectrum of **20** (300 MHz, $CDCl_3$).

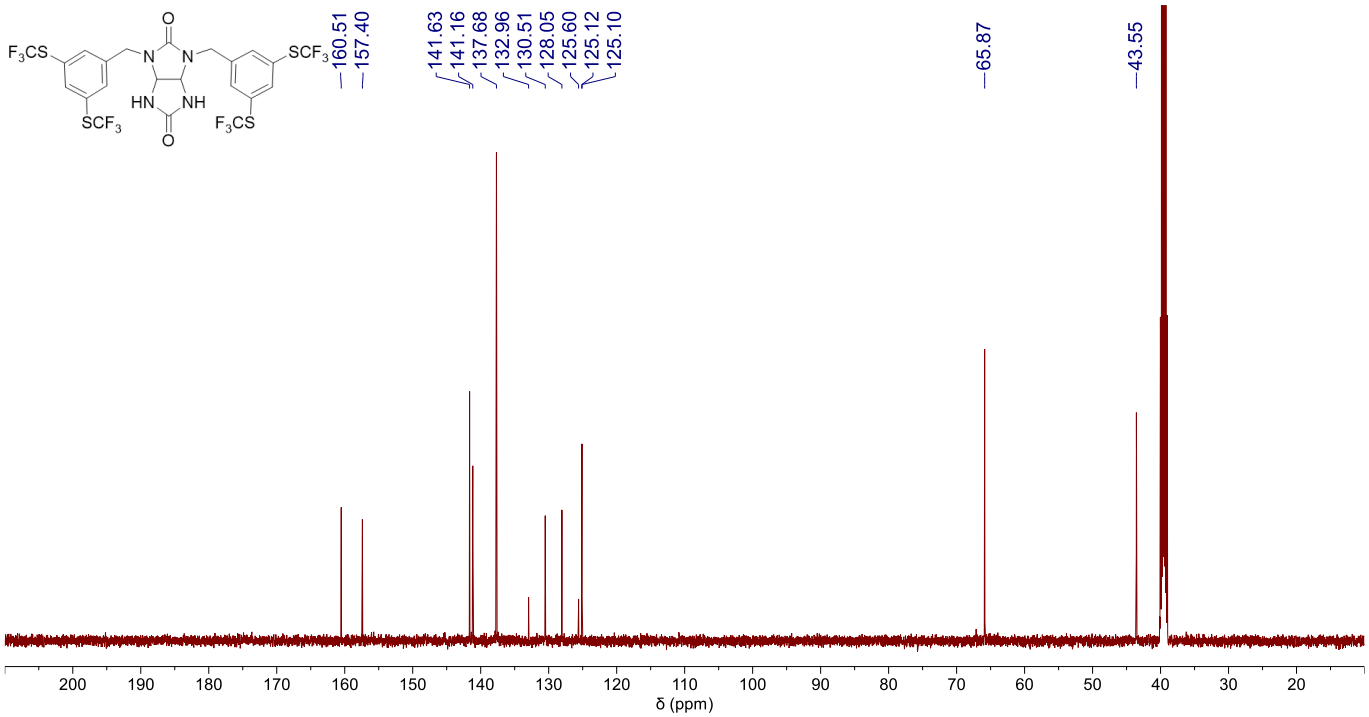


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum of **20** (126 MHz, DMSO-d_6).

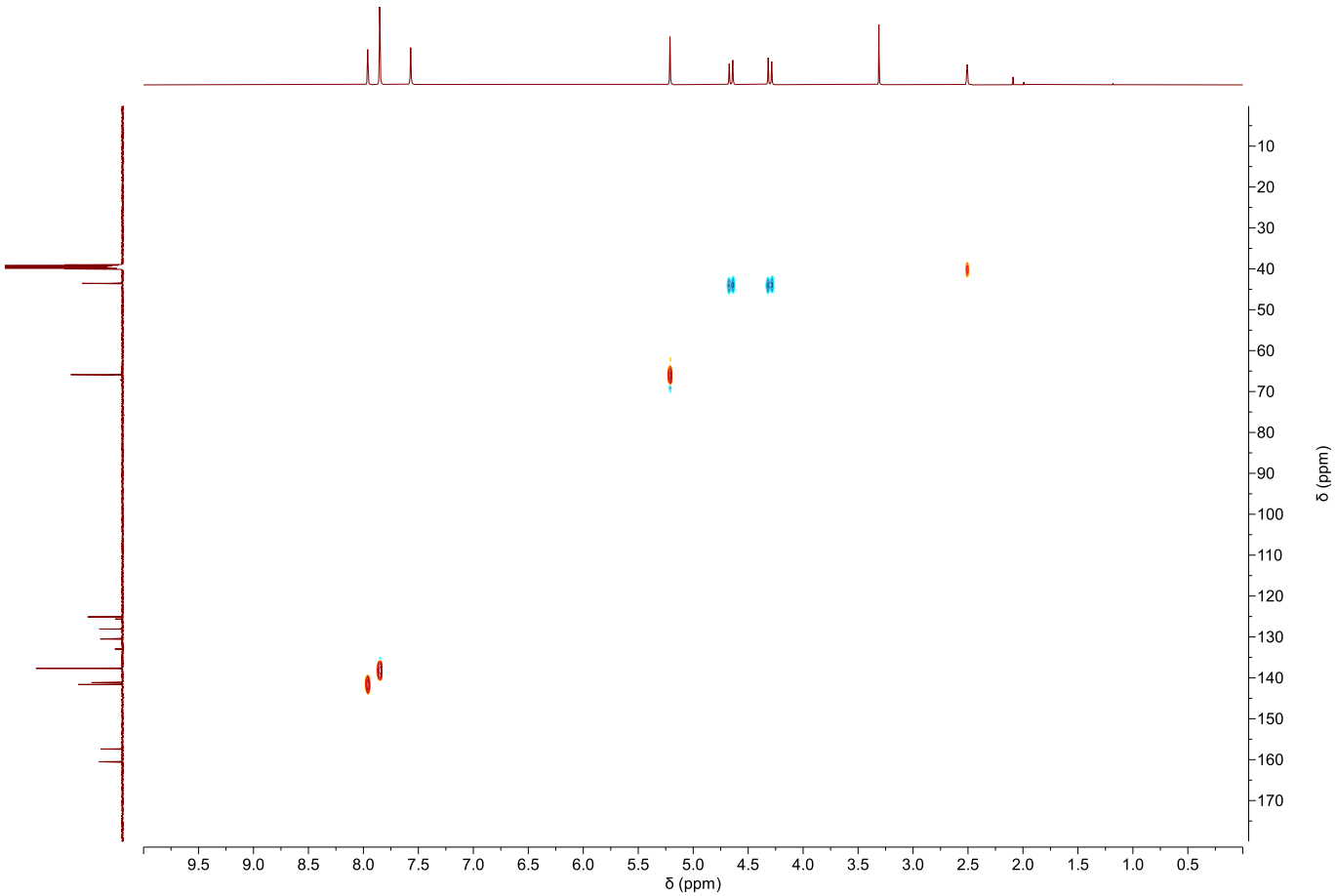


Figure S34: ^{1}H-^{13}C HSQC NMR spectrum of **20** (500 MHz, 126 MHz, DMSO-d_6).

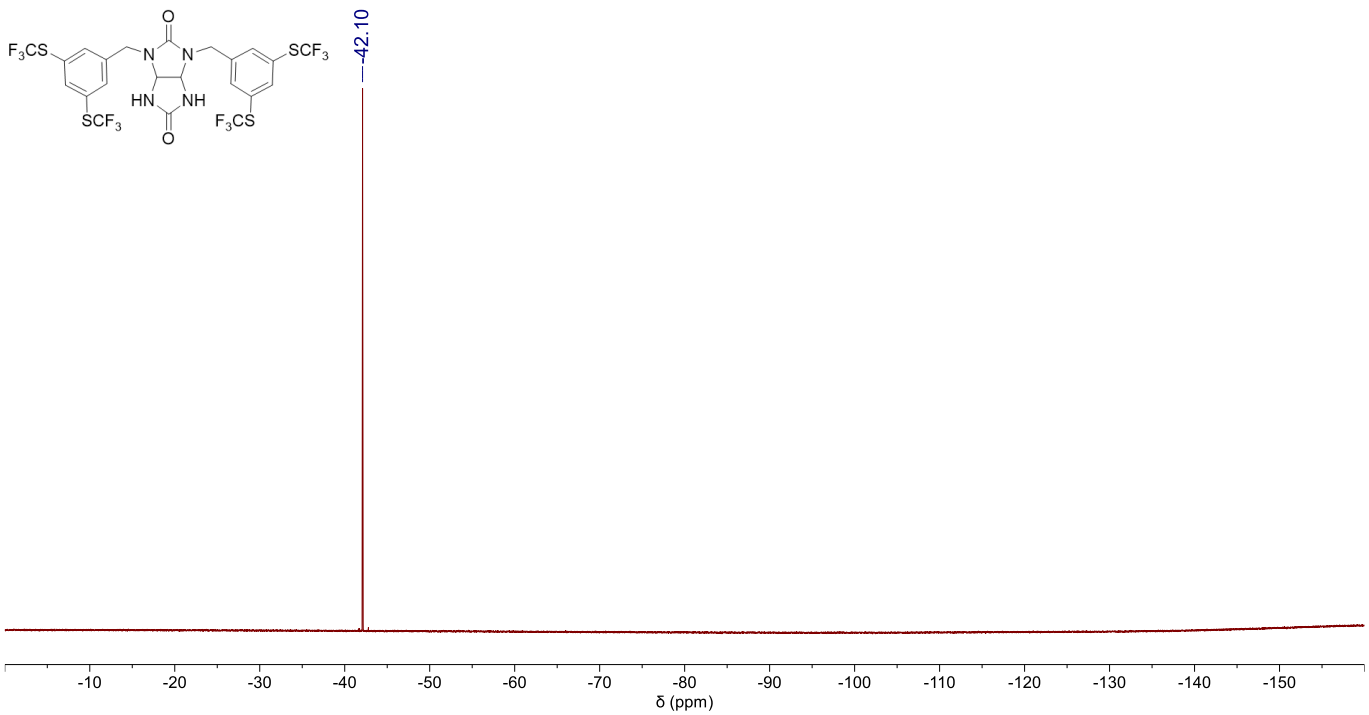


Figure S35: ^{19}F NMR spectrum of **20** (282 MHz, $CDCl_3$).

3.14. 21

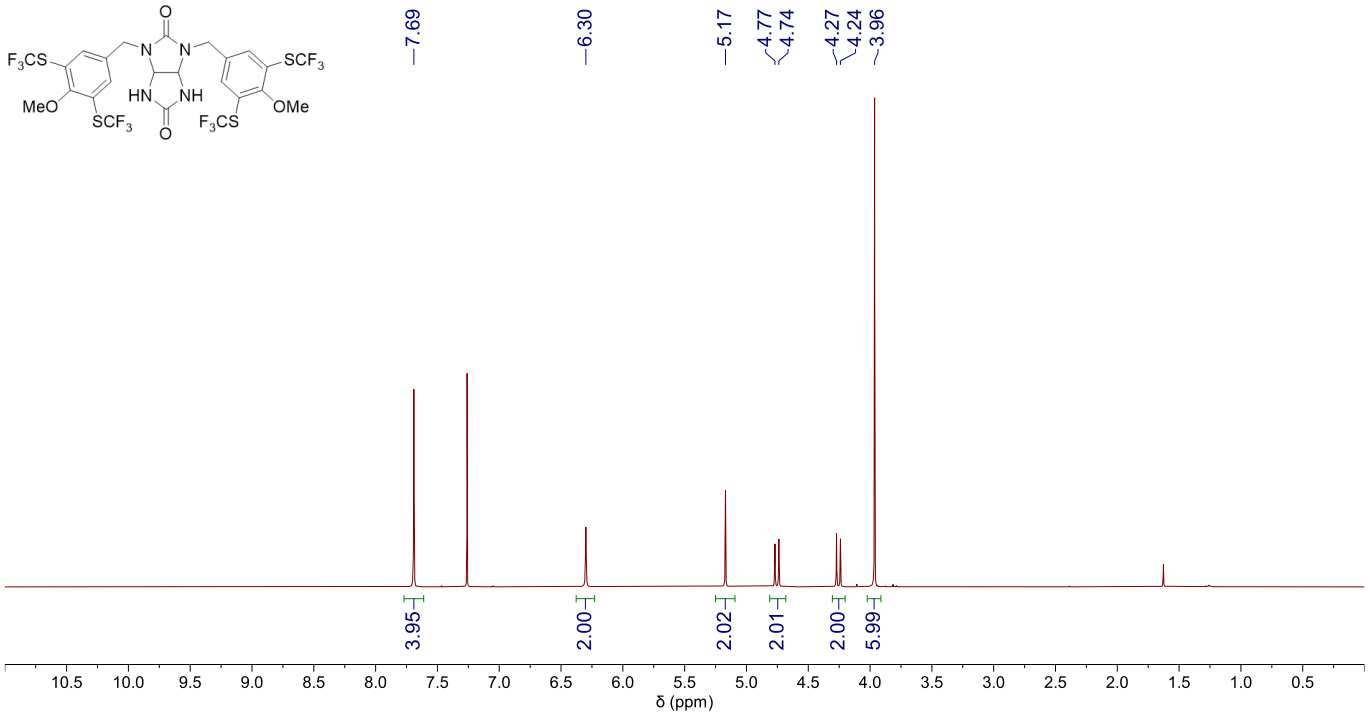


Figure S36: ^{1}H NMR spectrum of **21** (500 MHz, $CDCl_3$).

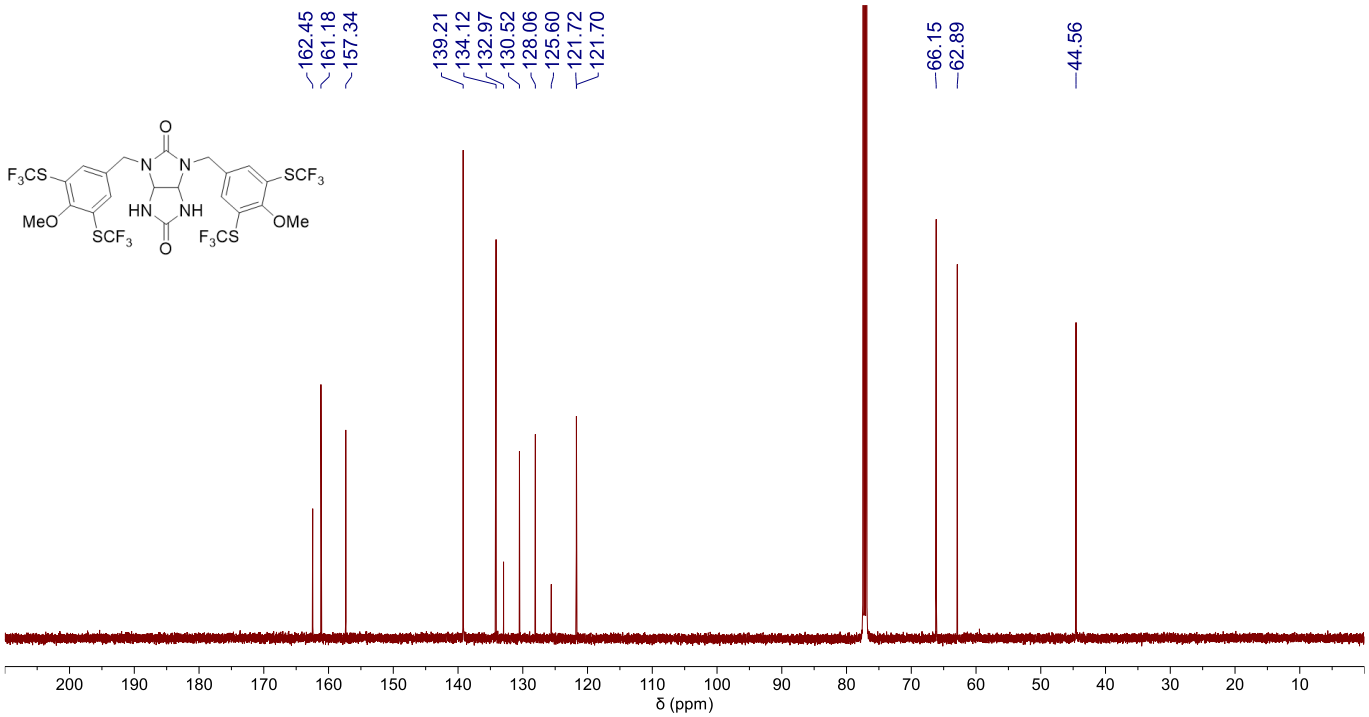


Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of **21** (126 MHz, CD_2Cl_2).

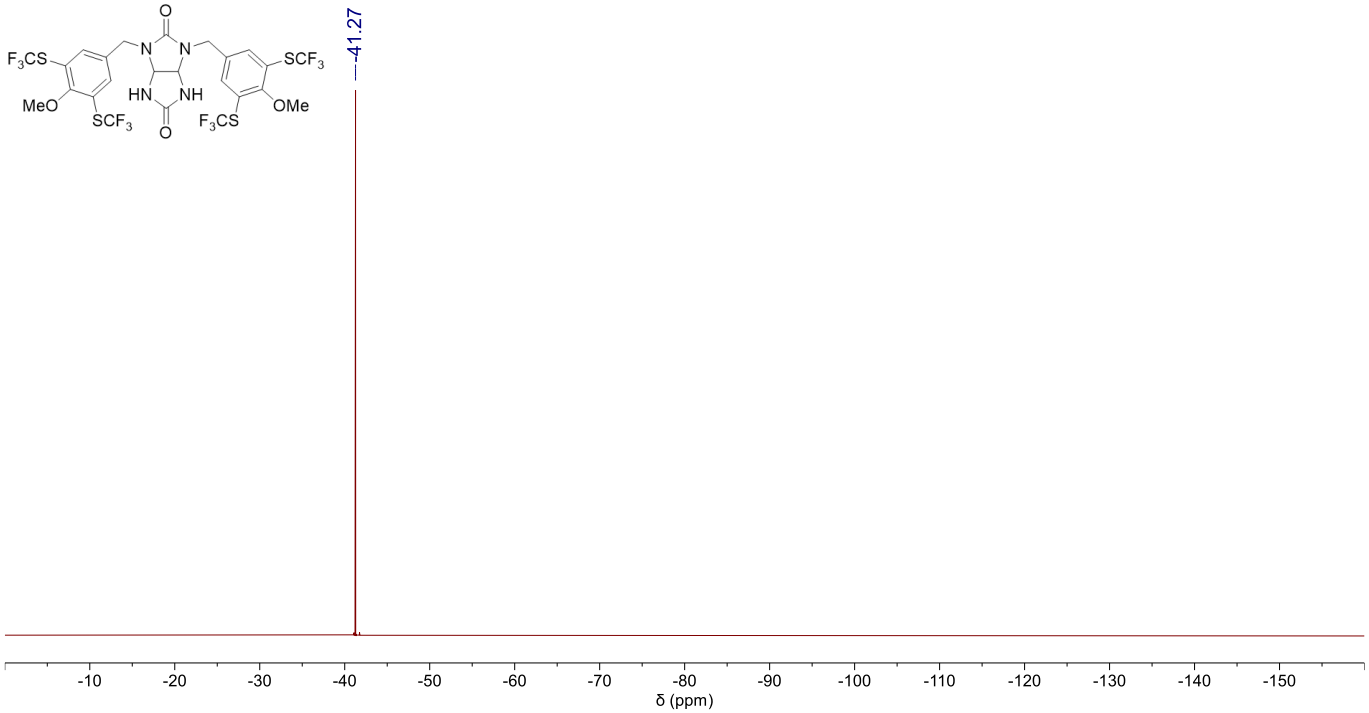


Figure S38: ^{19}F NMR spectrum of **21** (282 MHz, $CDCl_3$).

3.15. 22

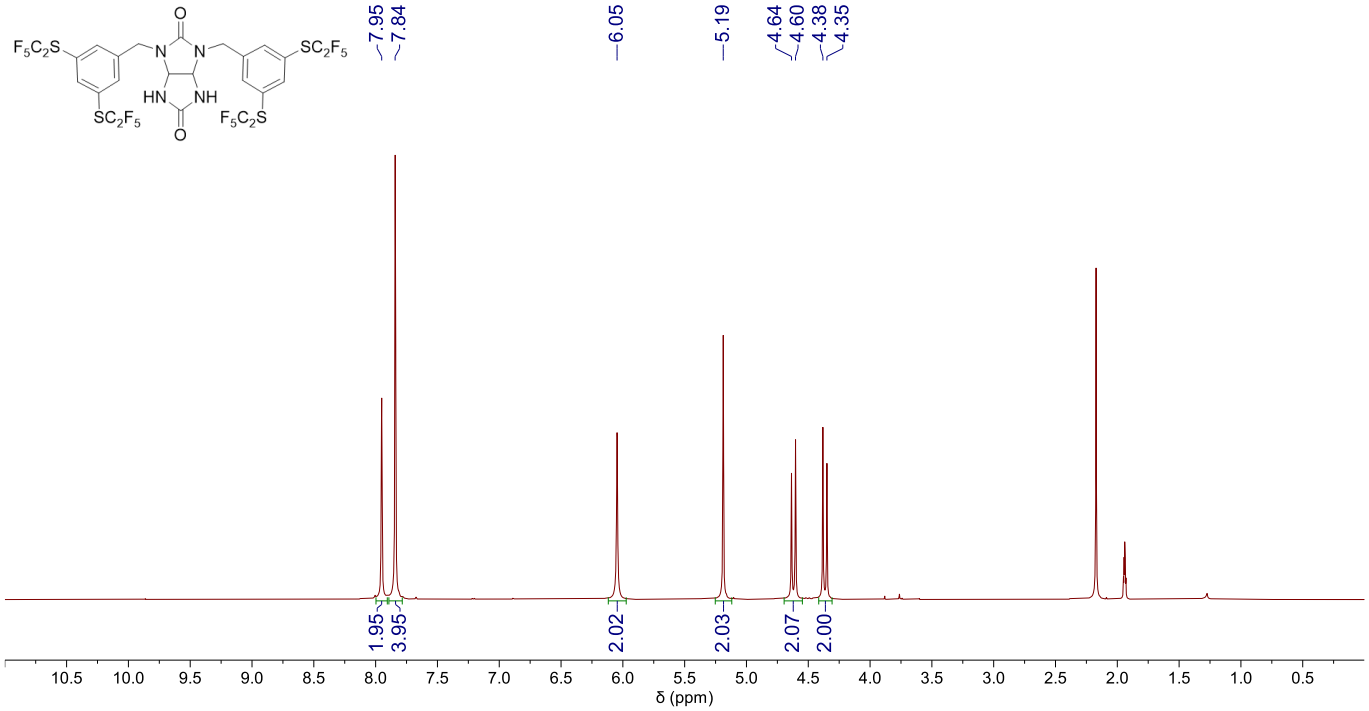


Figure S39: ^{1}H NMR spectrum of **22** (300 MHz, CD_3CN).

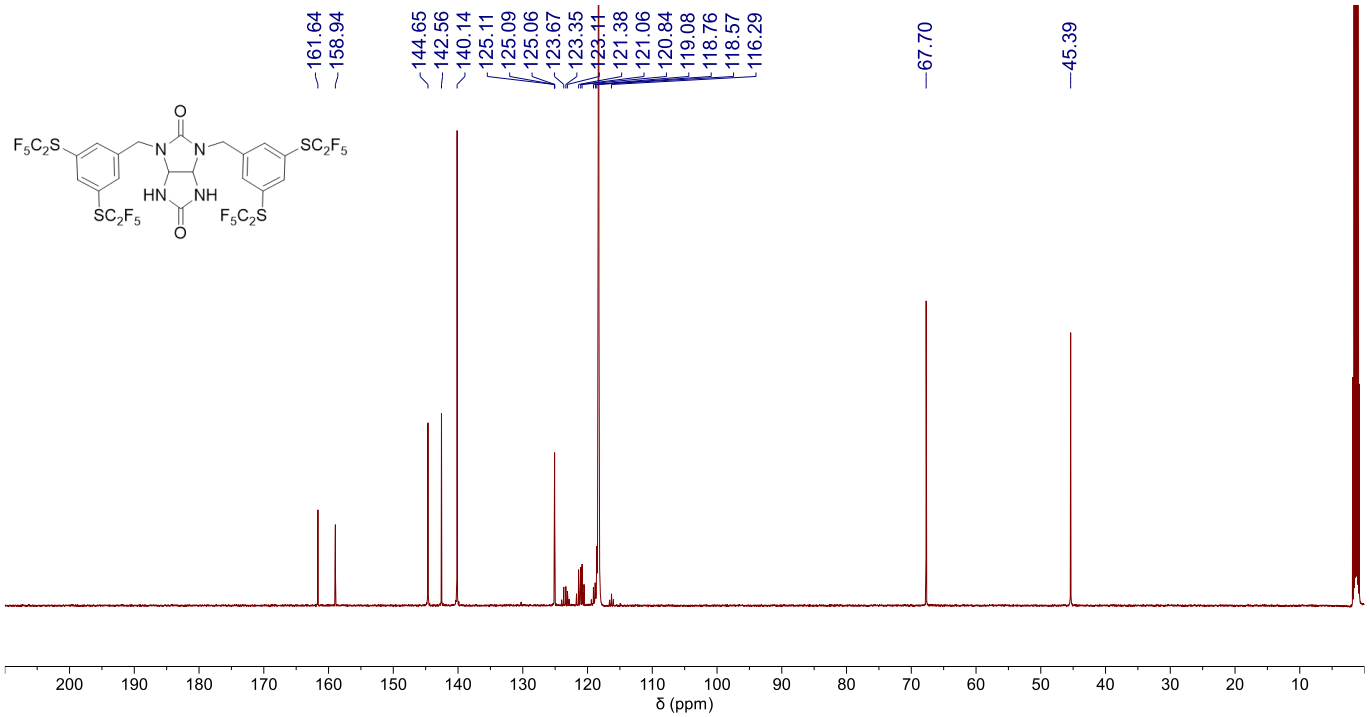


Figure S40: $^{13}C\{^{1}H\}$ NMR spectrum of **22** (126 MHz, CD_3CN).

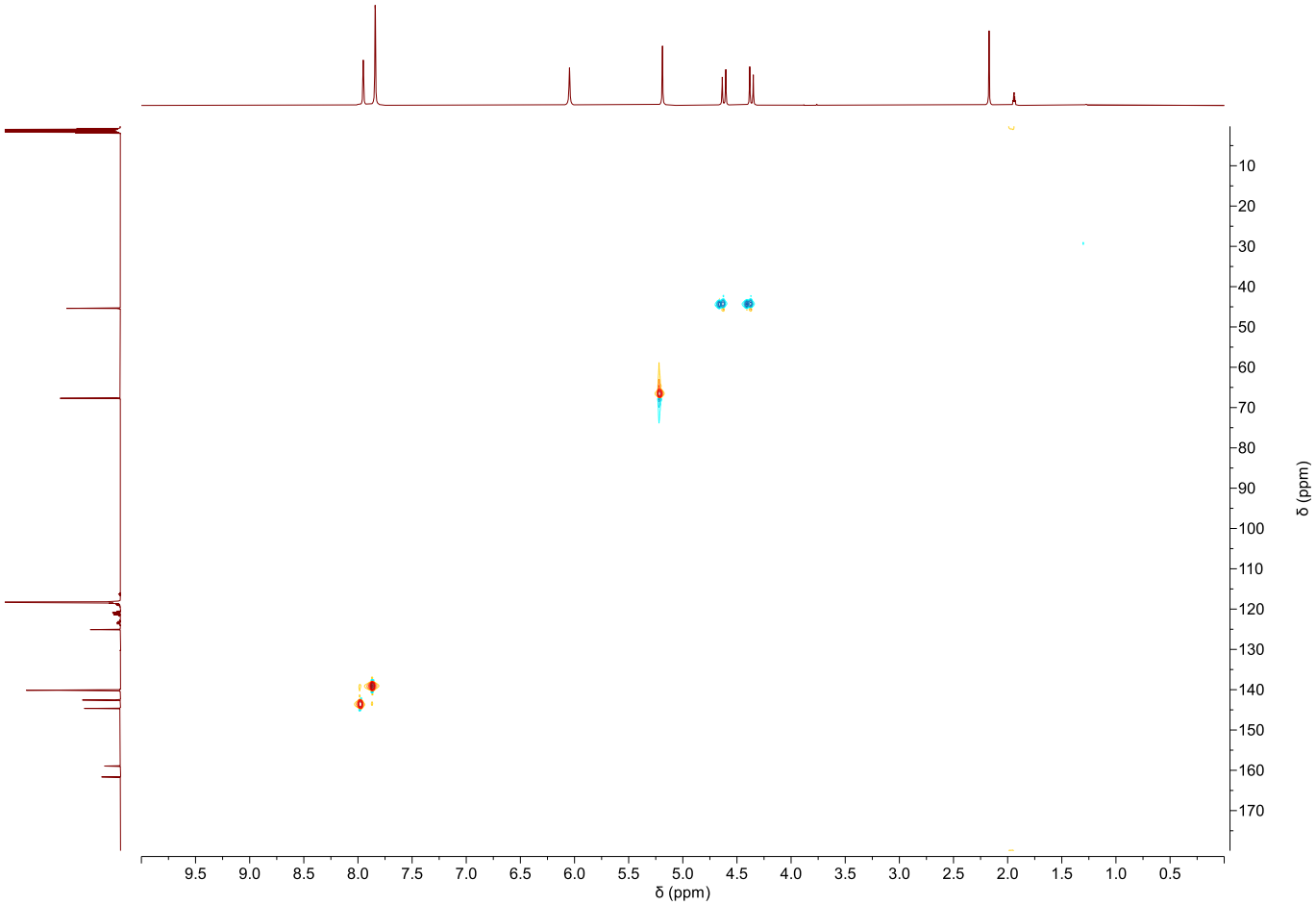


Figure S41: ^{1}H-^{13}C HSQC NMR spectrum of **22** (500 MHz, 126 MHz, CD_3CN).

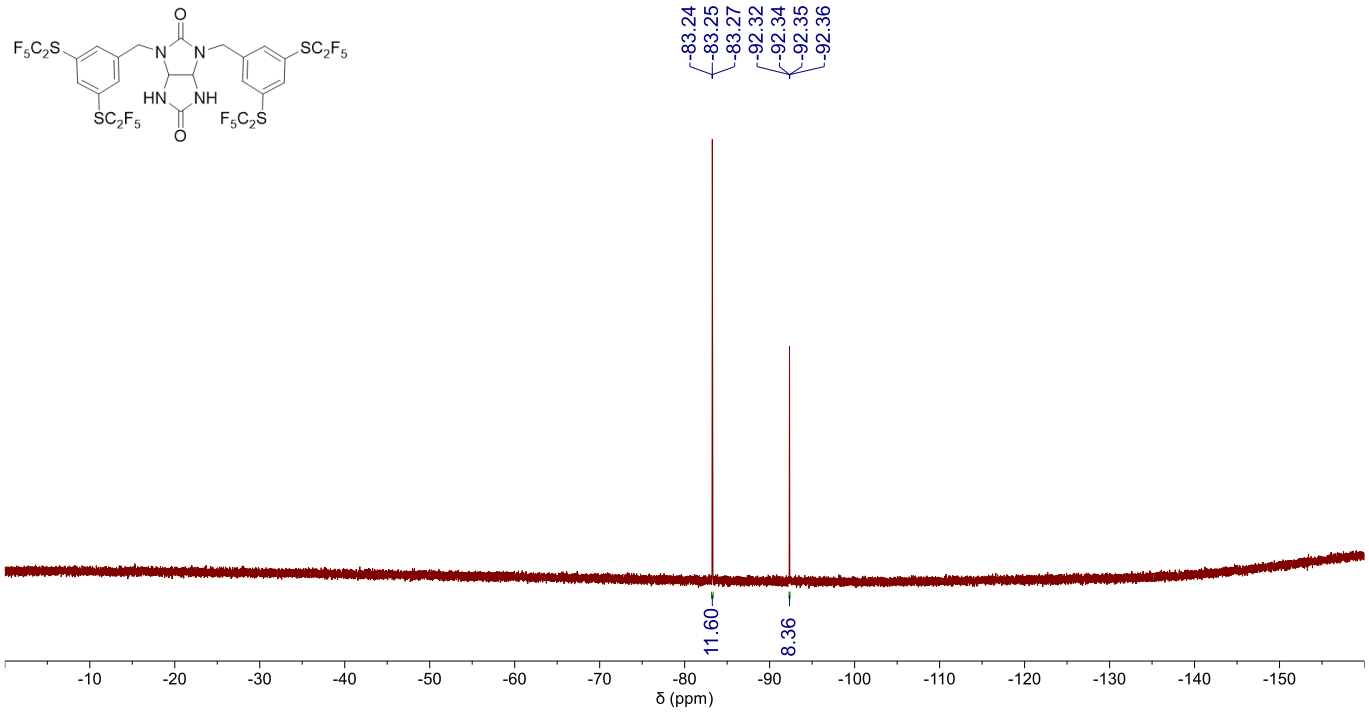


Figure S42: ^{19}F NMR spectrum of **22** (282 MHz, CD_3CN).

3.16. 23

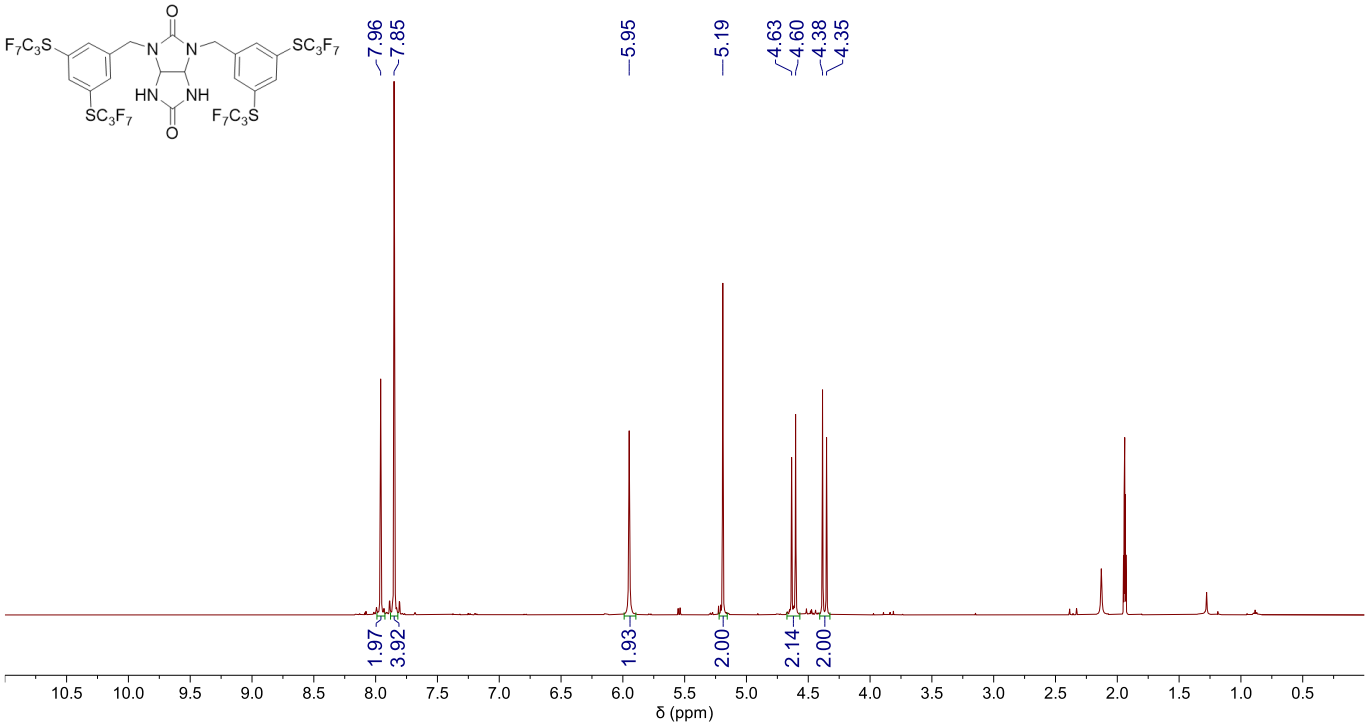


Figure S43: ^{1}H NMR spectrum of **23** (500 MHz, CD_3CN).

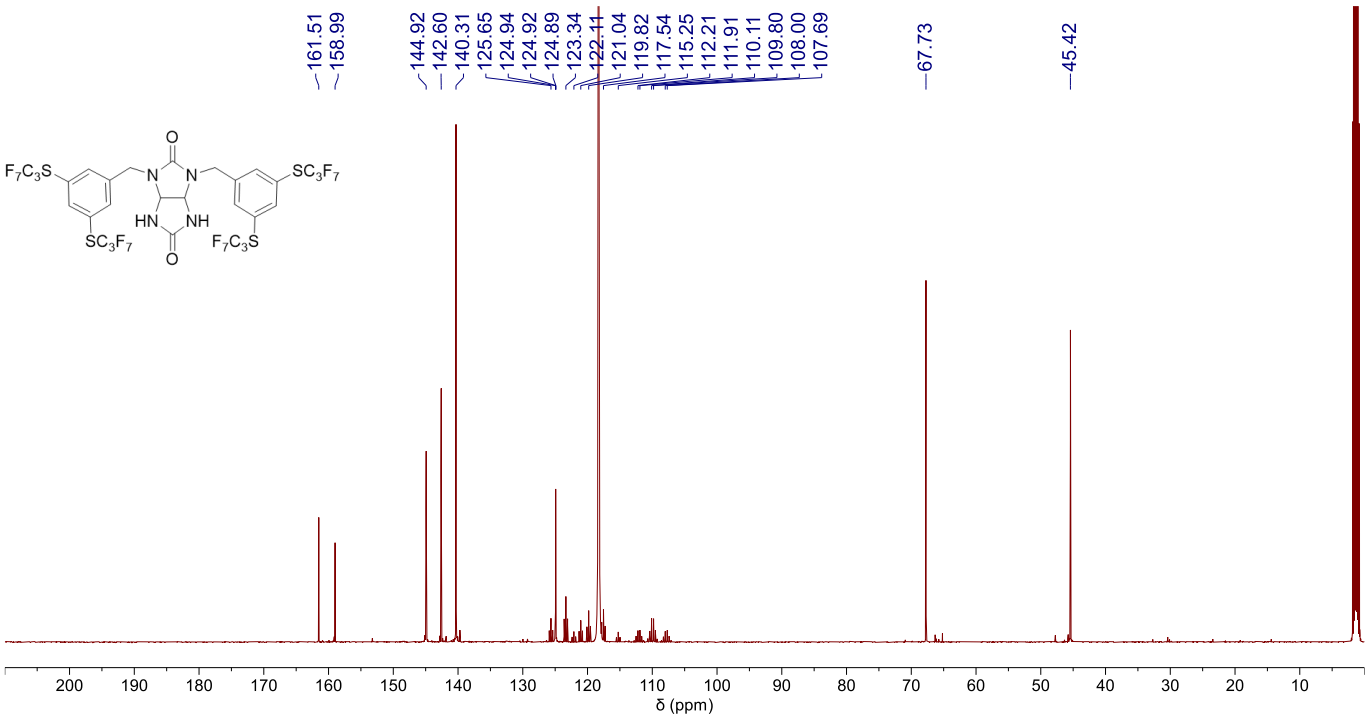


Figure S44: $^{13}C\{^{1}H\}$ NMR spectrum of **23** (126 MHz, CD_3CN).

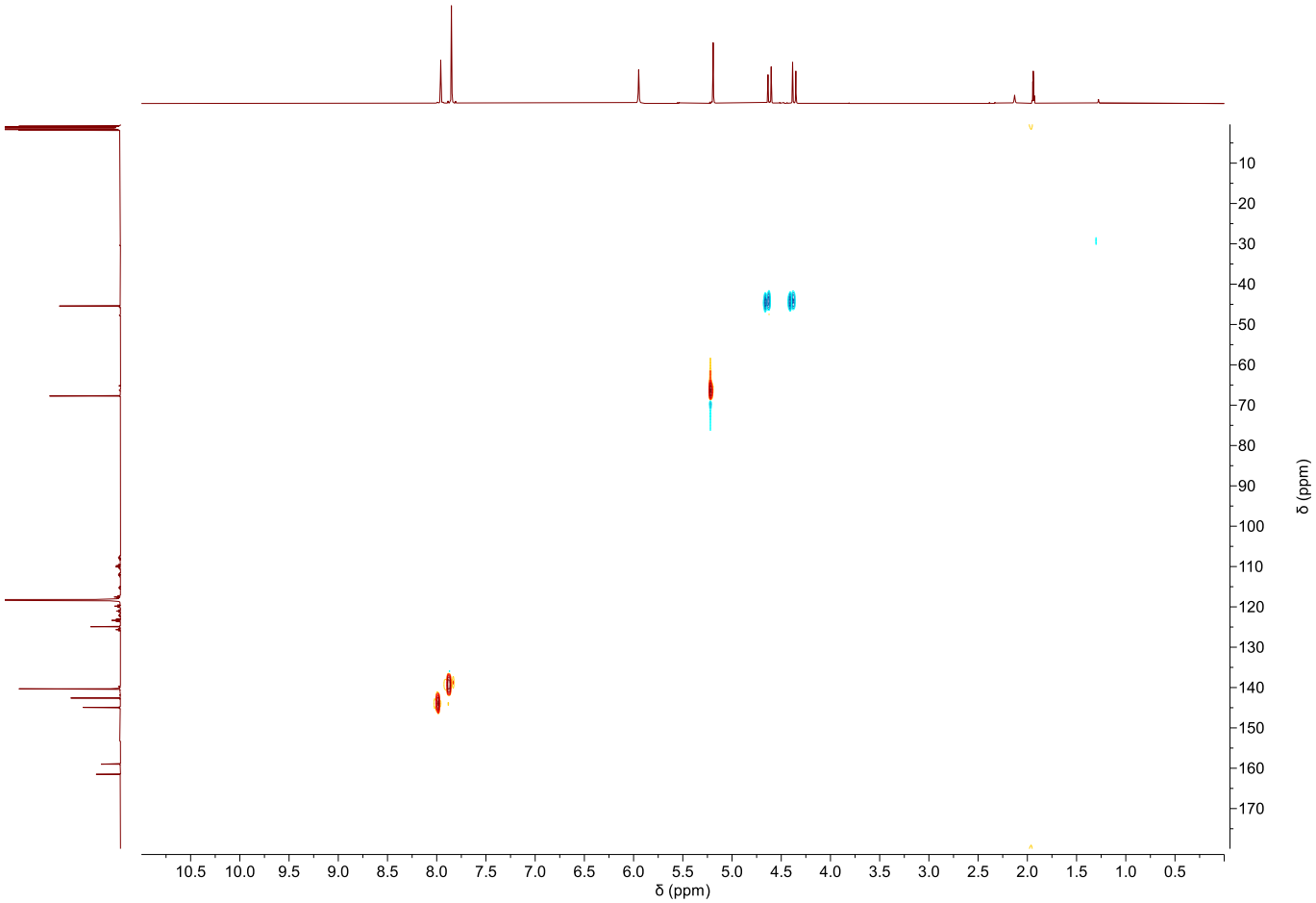


Figure S45: ^{1}H-^{13}C HSQC NMR spectrum of **23** (500 MHz, 126 MHz, CD_3CN).

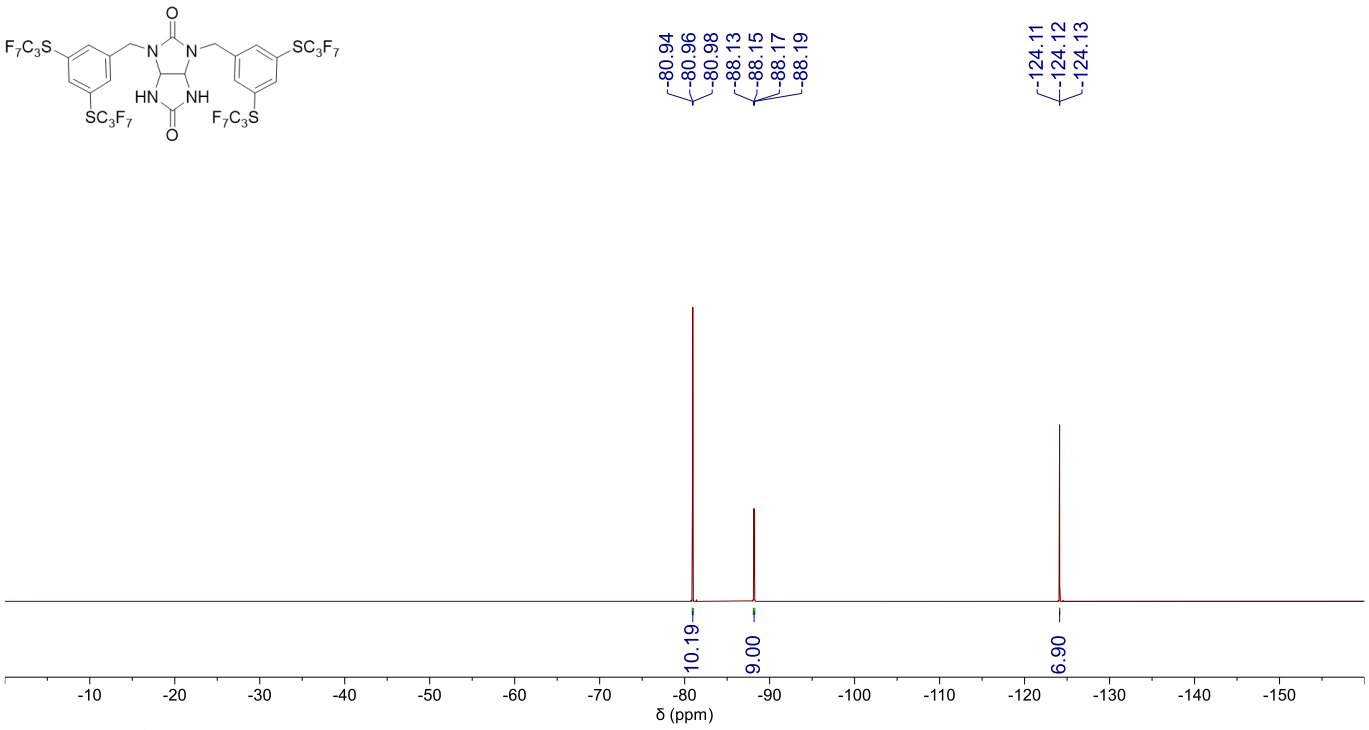


Figure S46: ^{19}F NMR spectrum of **23** (471 MHz, CD_3CN).

3.17. 24

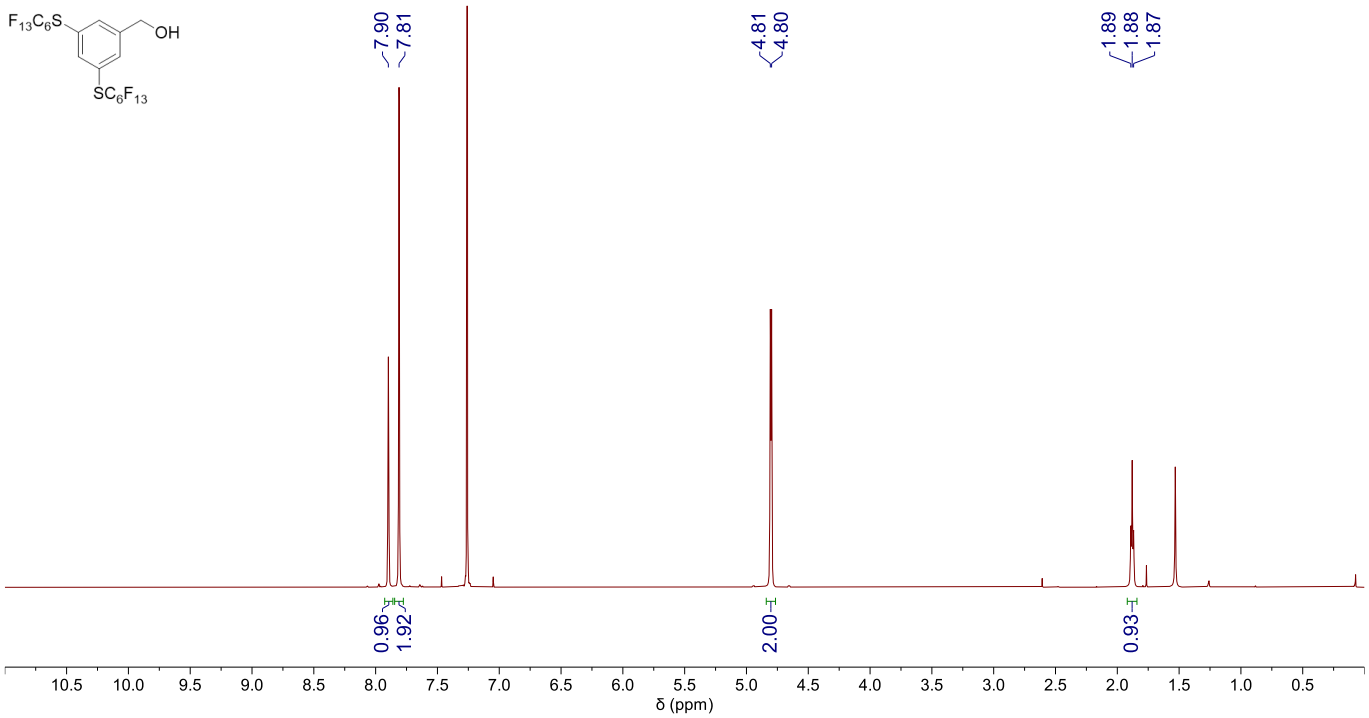


Figure S47: ^{1}H NMR spectrum of **24** (500 MHz, $CDCl_3$).

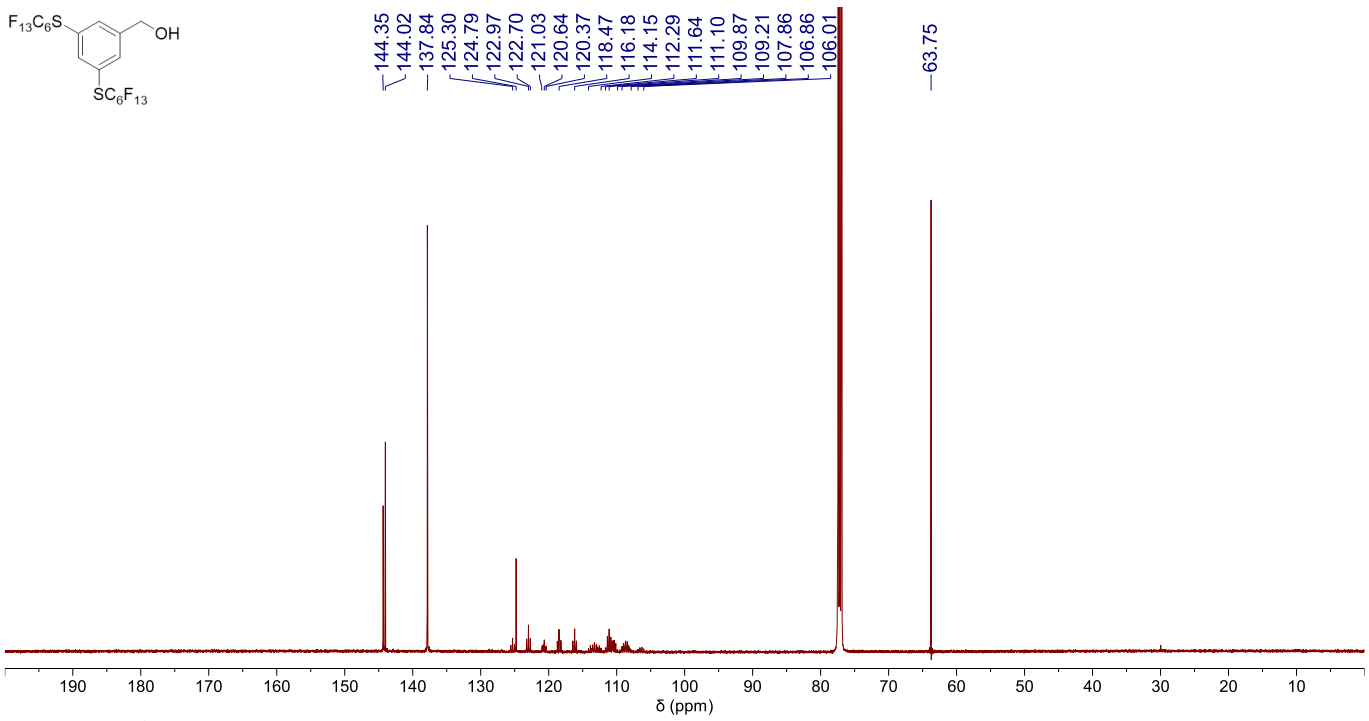


Figure S48: $^{13}C\{^{1}H\}$ NMR spectrum of **24** (126 MHz, $CDCl_3$).

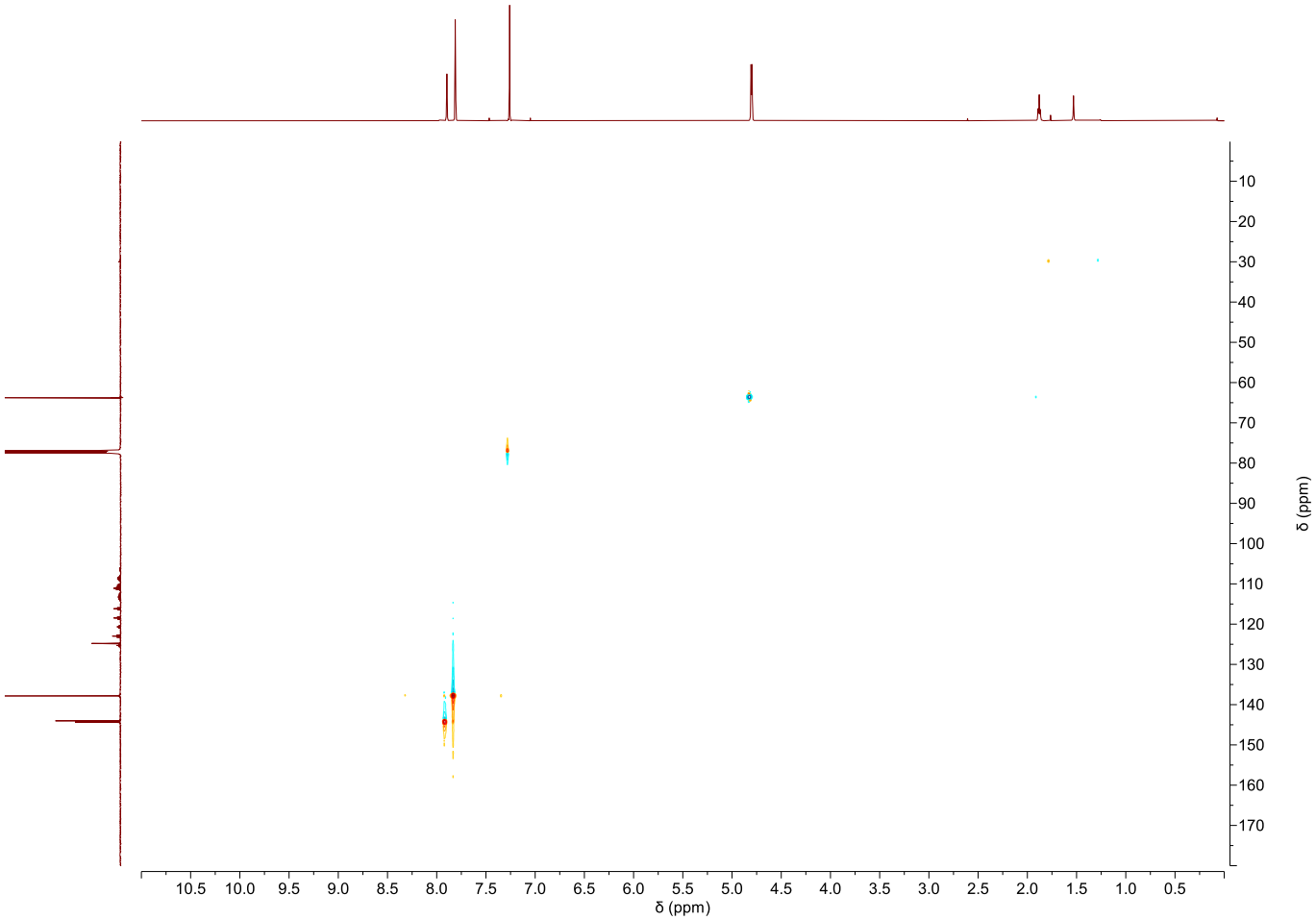


Figure S49: ^{1}H-^{13}C HSQC NMR spectrum of **24** (500 MHz, 126 MHz, $CDCl_3$).

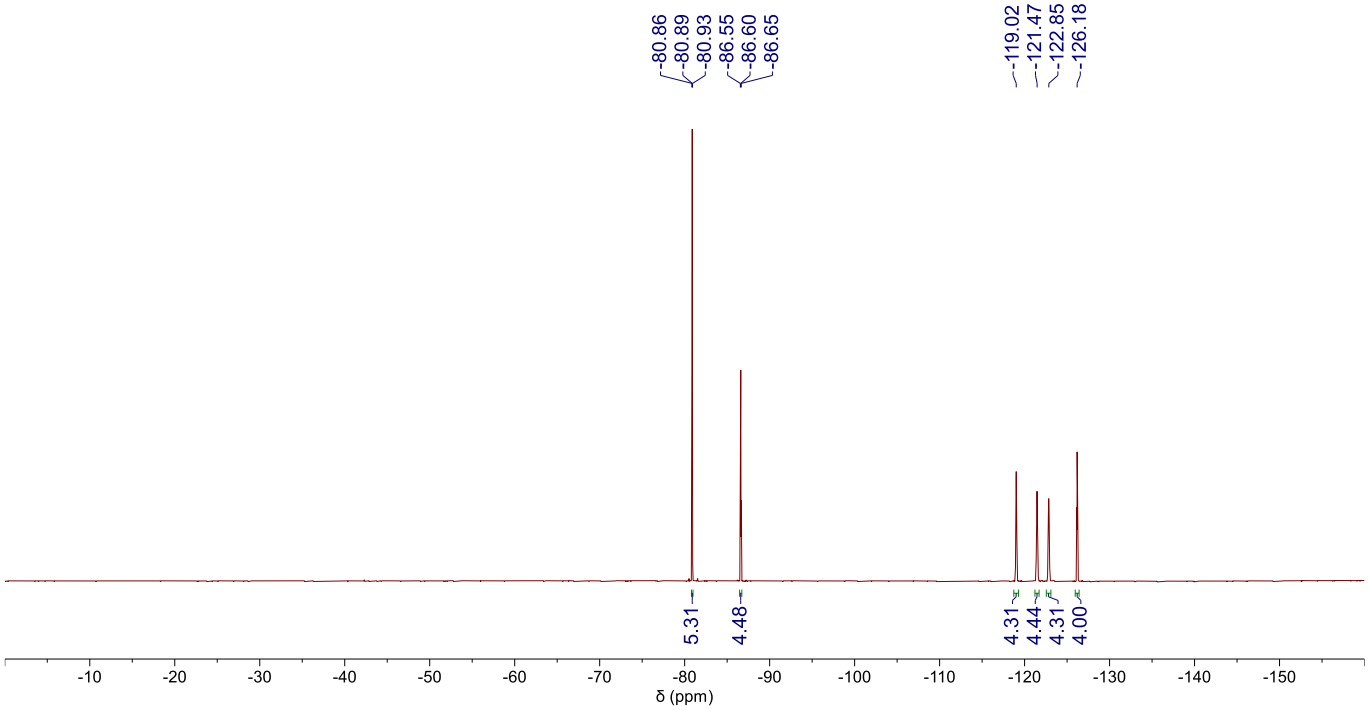


Figure S50: ^{19}F NMR spectrum of **24** (282 MHz, $CDCl_3$).

3.18. 25

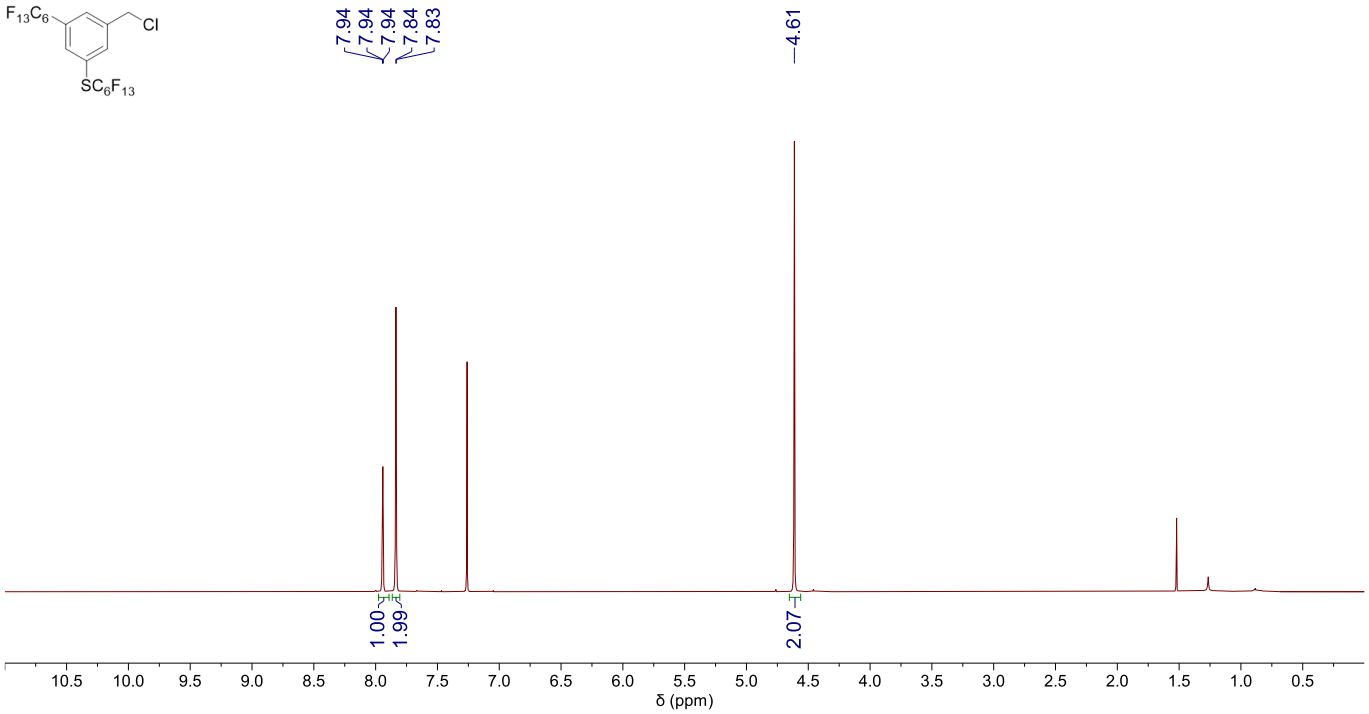


Figure S51: ^{1}H NMR spectrum of **25** (500 MHz, $CDCl_3$).

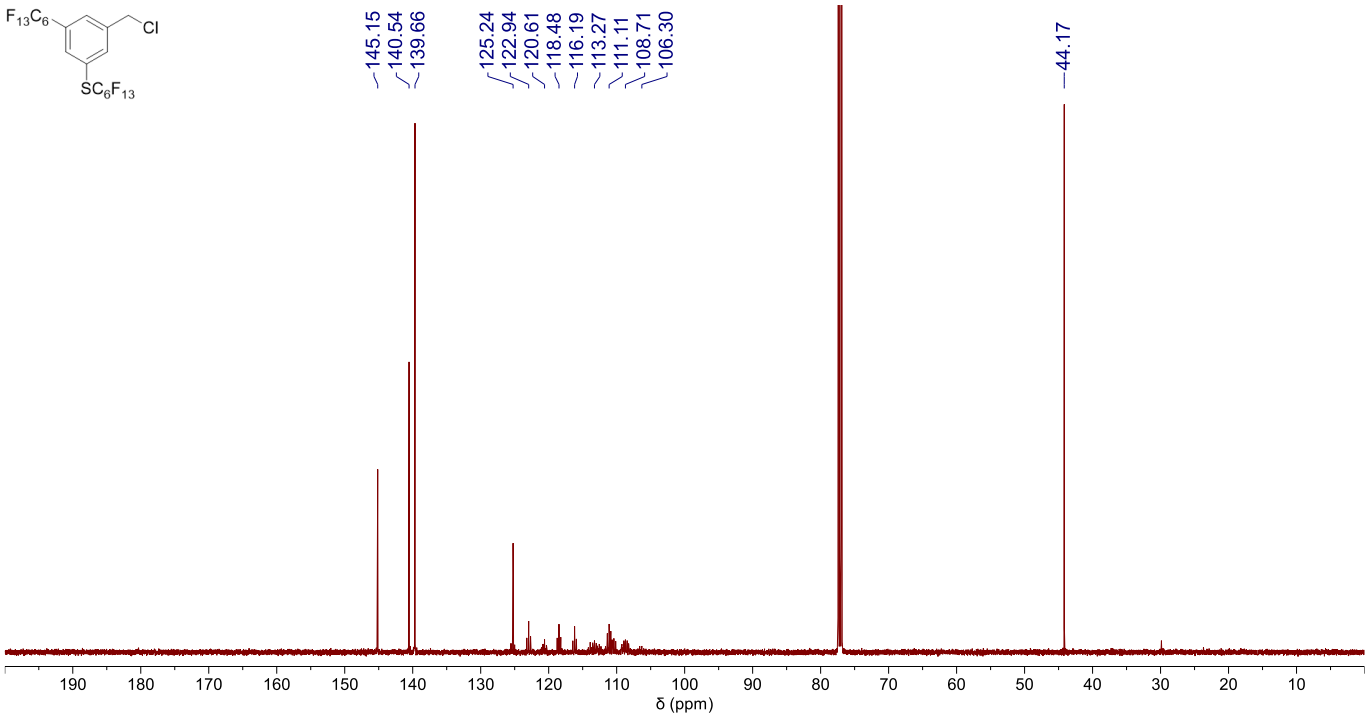


Figure S52: $^{13}C\{^{1}H\}$ NMR spectrum of **25** (126 MHz, $CDCl_3$).

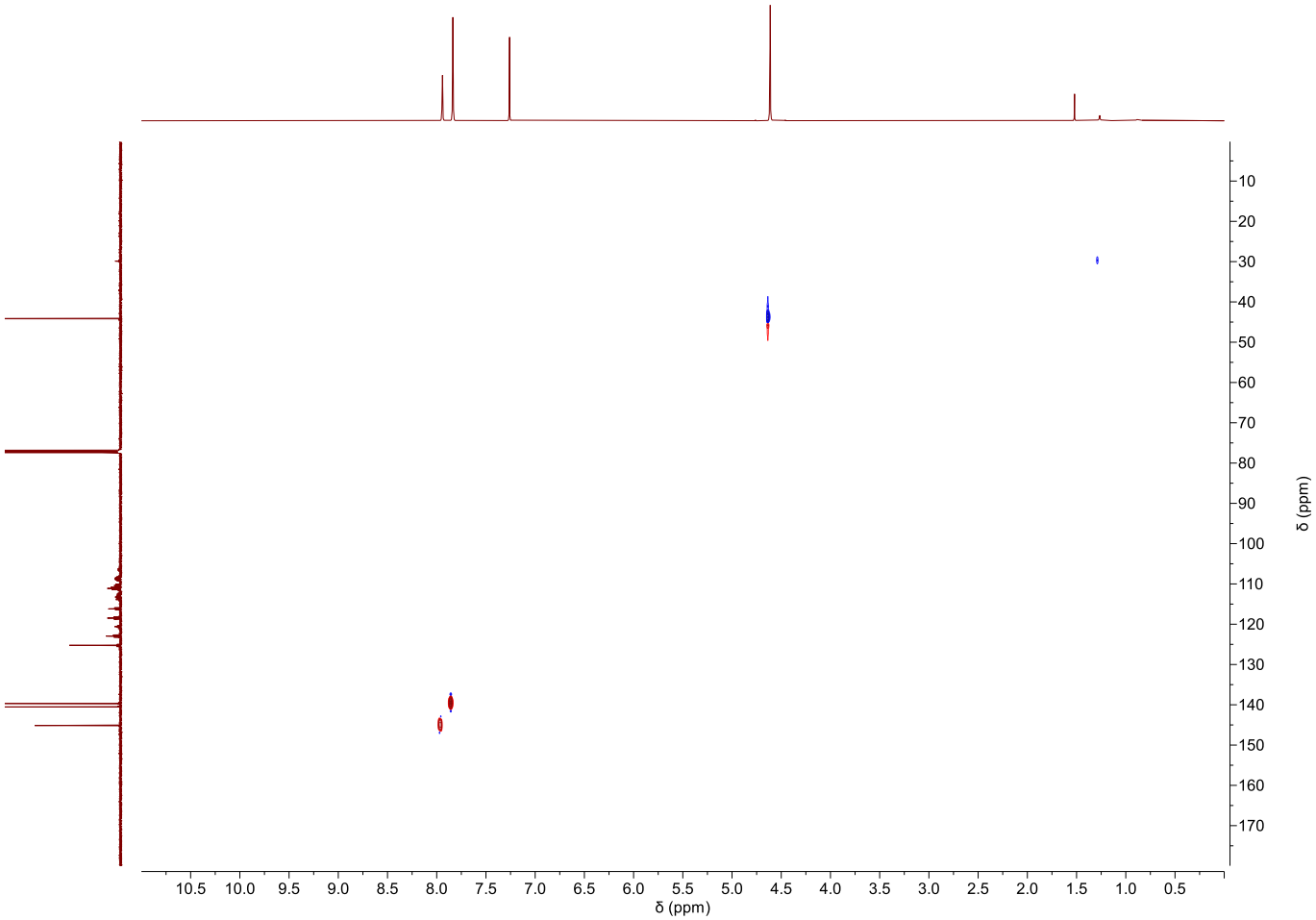


Figure S53: ^{1}H-^{13}C HSQC NMR spectrum of **25** (500 MHz, 126 MHz, $CDCl_3$).

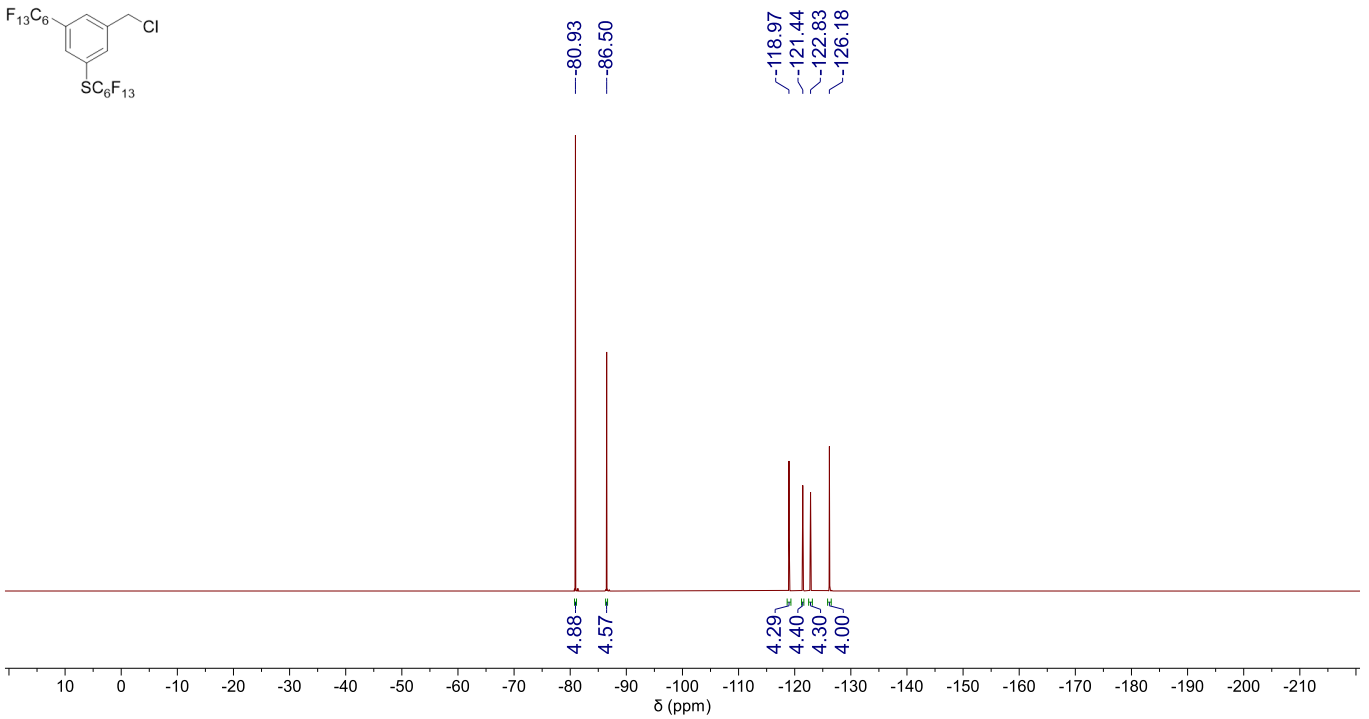


Figure S54: ^{19}F NMR spectrum of **25** (471 MHz, $CDCl_3$).

3.19. 26

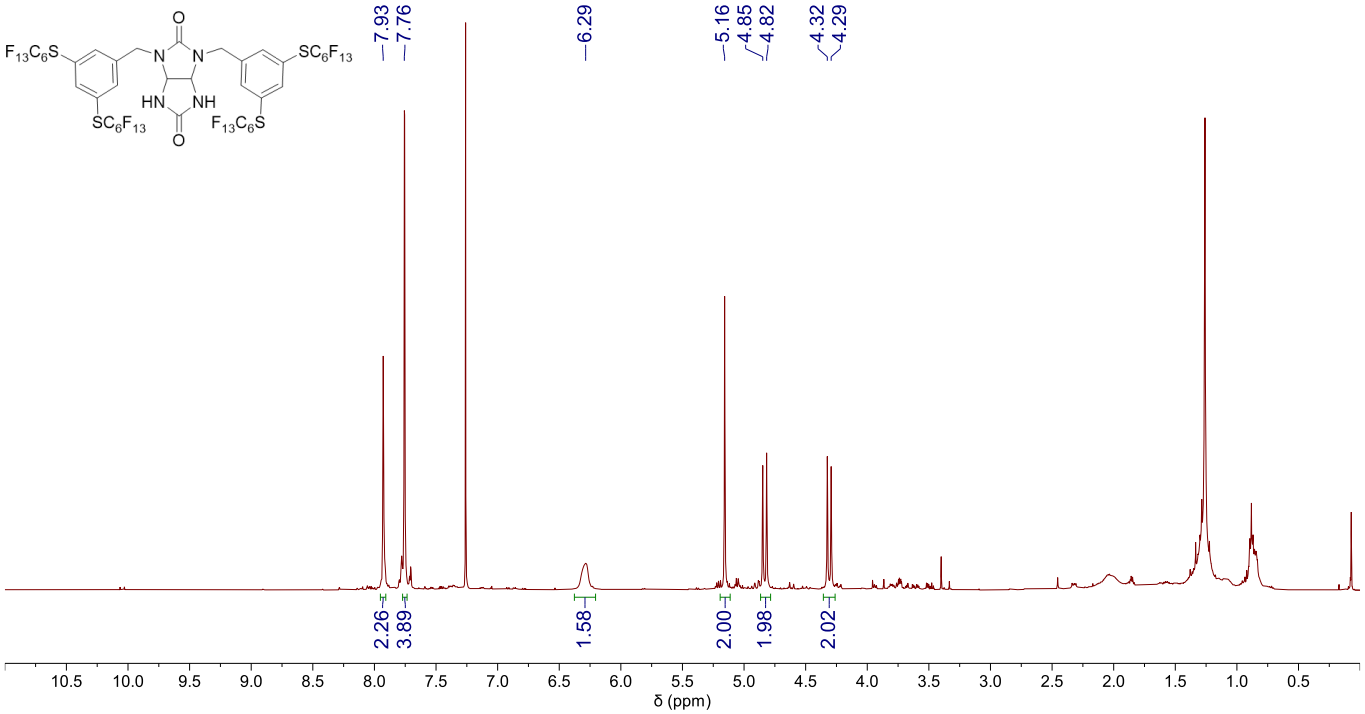


Figure S55: ^{1}H NMR spectrum of **26** (500 MHz, $CDCl_3$).

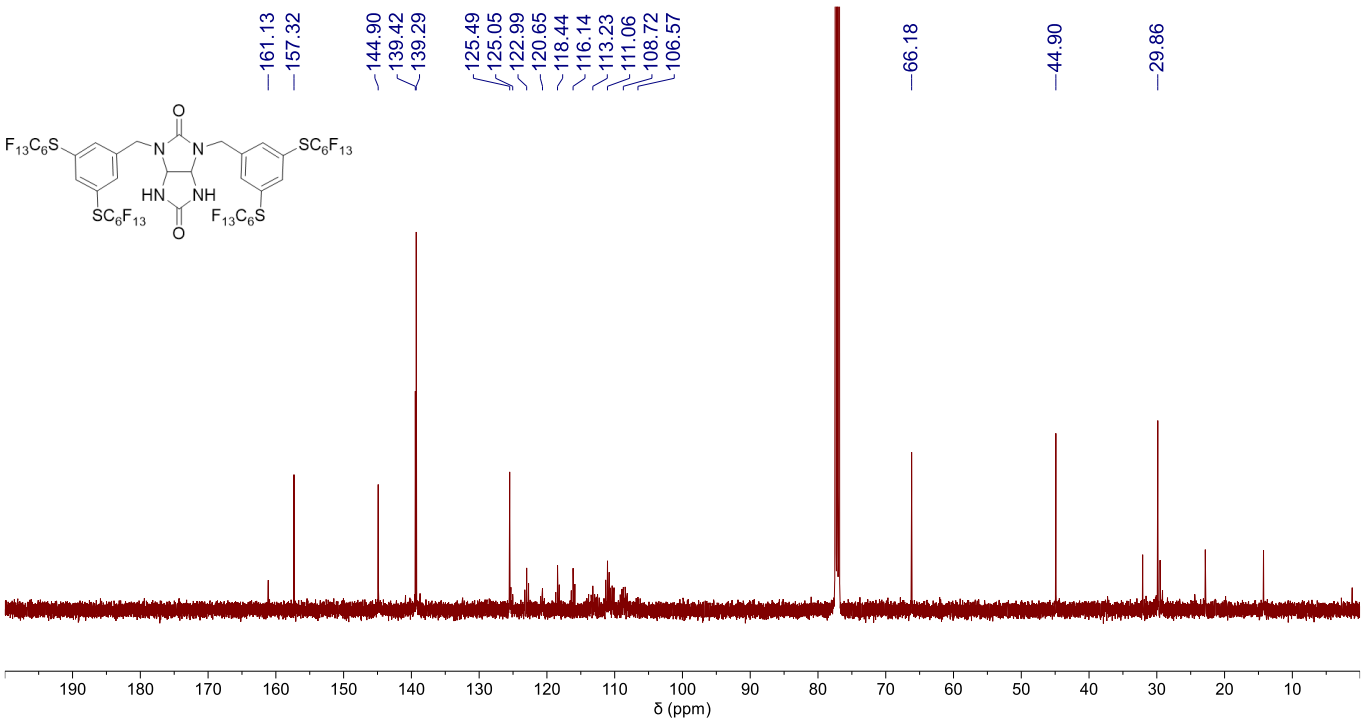


Figure S56: $^{13}C\{^{1}H\}$ NMR spectrum of **26** (126 MHz, $CDCl_3$).

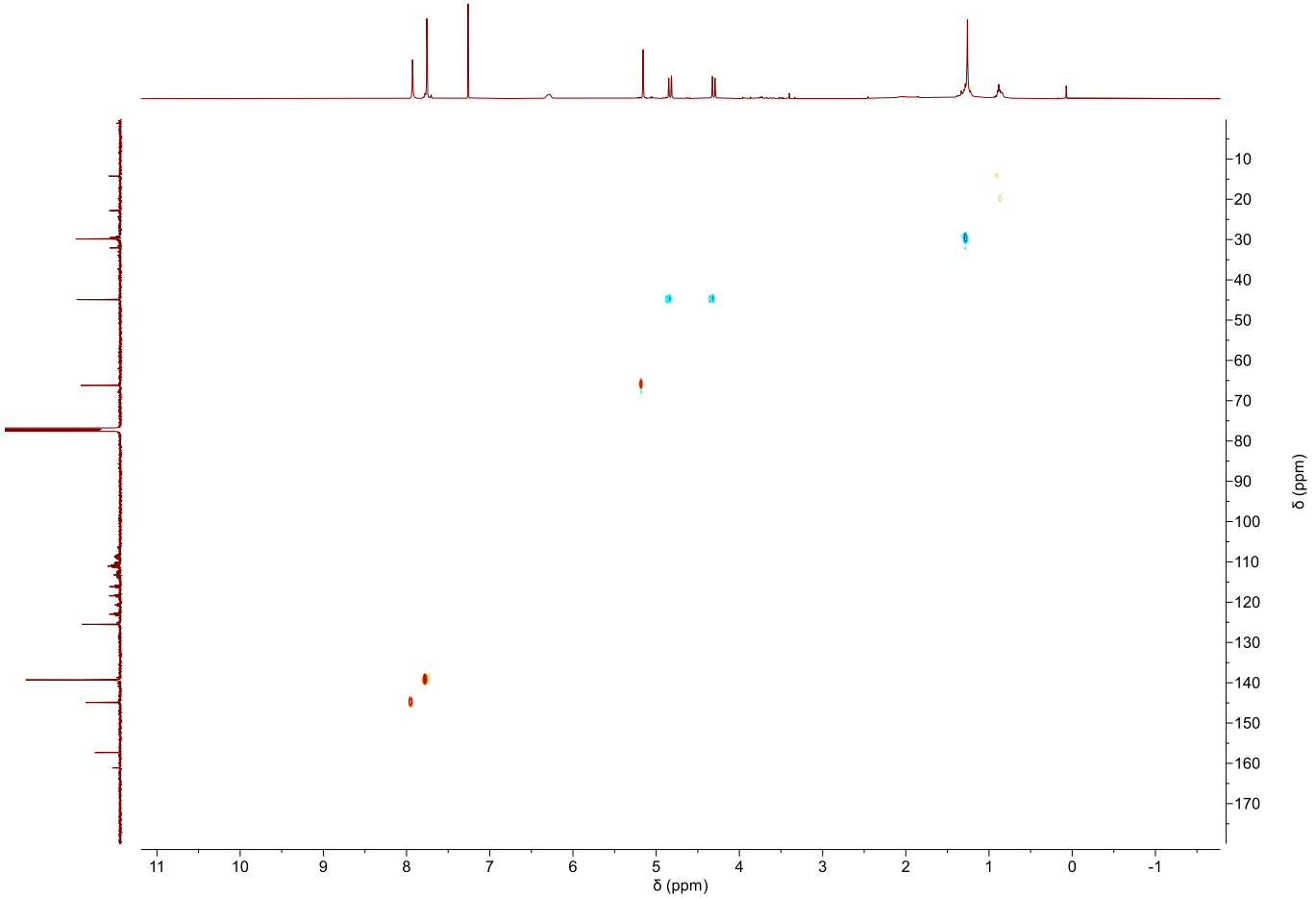


Figure S57: ^{1}H-^{13}C HSQC NMR spectrum of **26** (500 MHz, 126 MHz, $CDCl_3$).

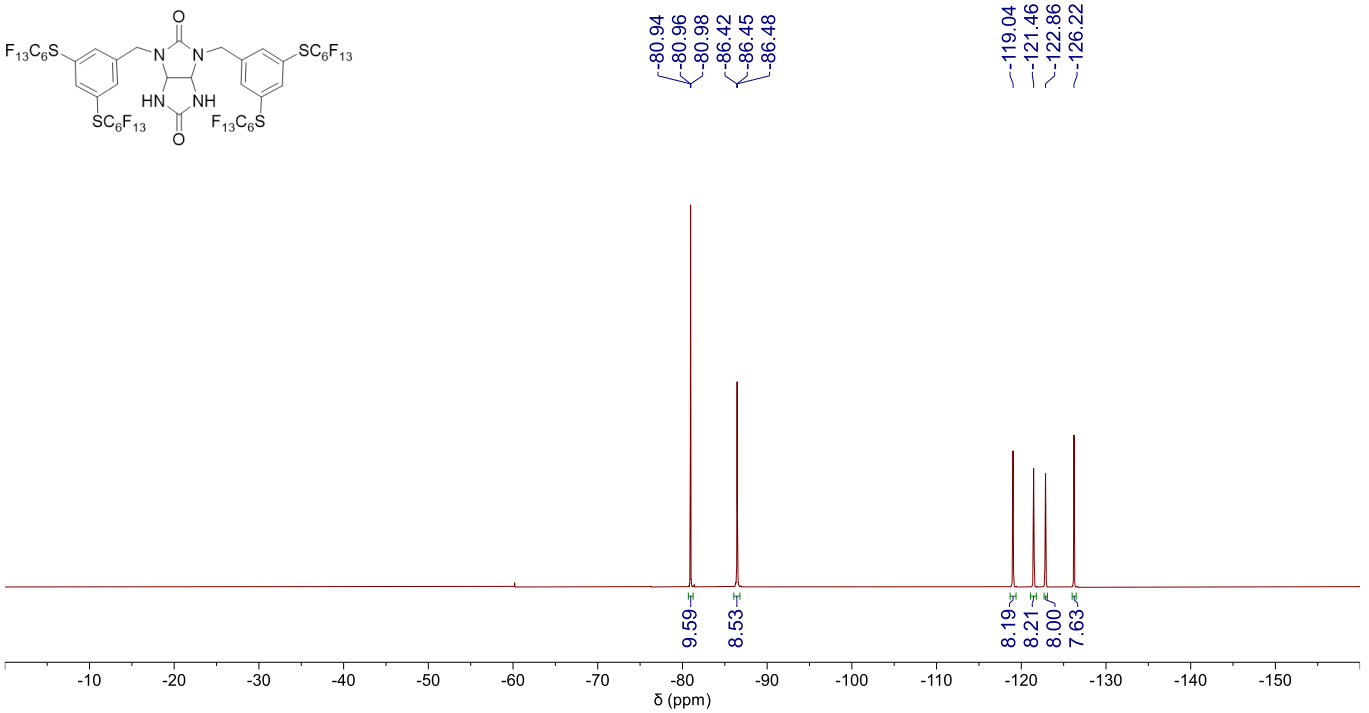


Figure S58: ^{19}F NMR spectrum of **26** (471 MHz, $CDCl_3$).

3.20. 27

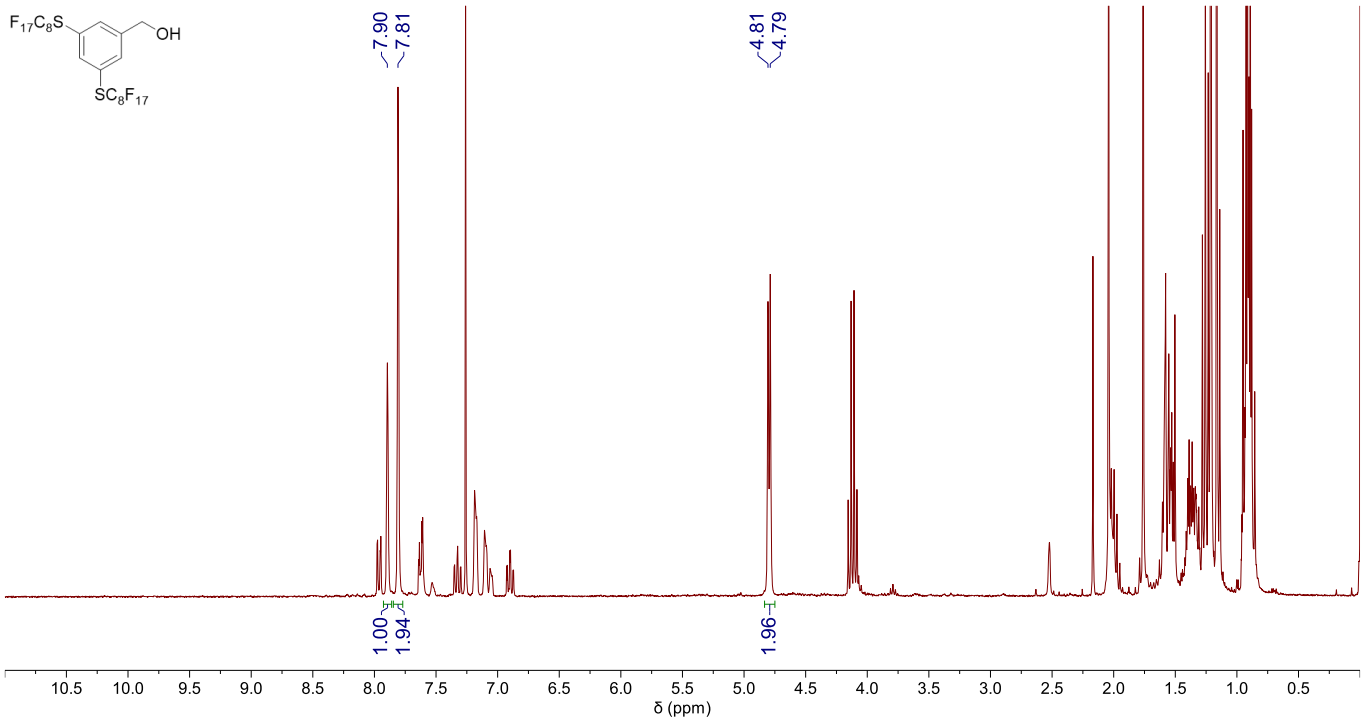


Figure S59: ^{1}H NMR spectrum of a mixture of **17** and **27** (300 MHz, $CDCl_3$).

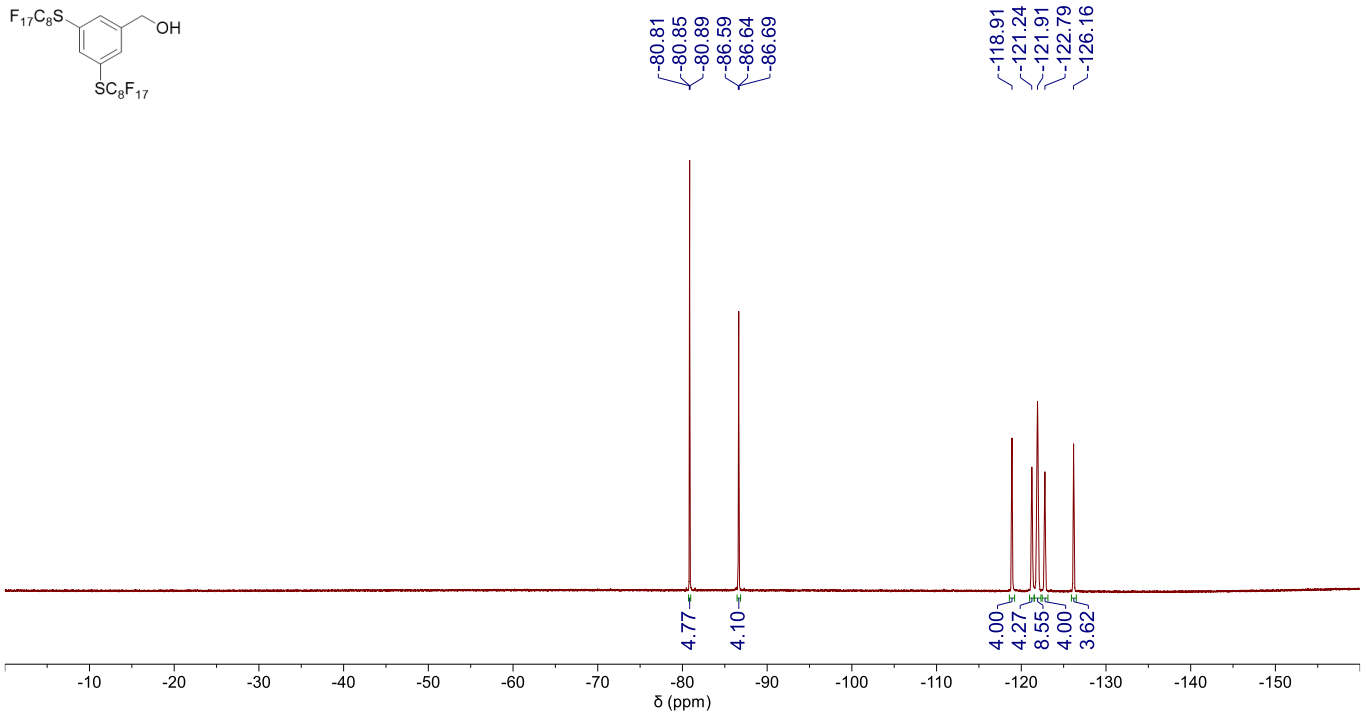


Figure S60: ^{19}F NMR spectrum of a mixture of **17** and **27** (282 MHz, $CDCl_3$).

3.21. 28

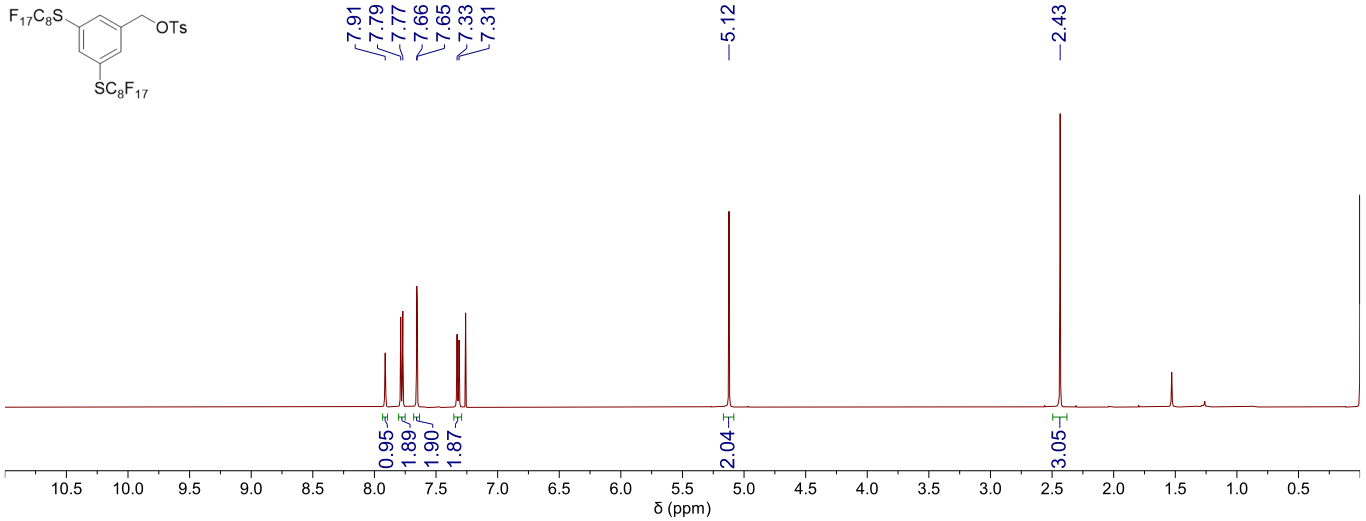


Figure S61: ^{1}H NMR spectrum of **28** (500 MHz, $CDCl_3$).

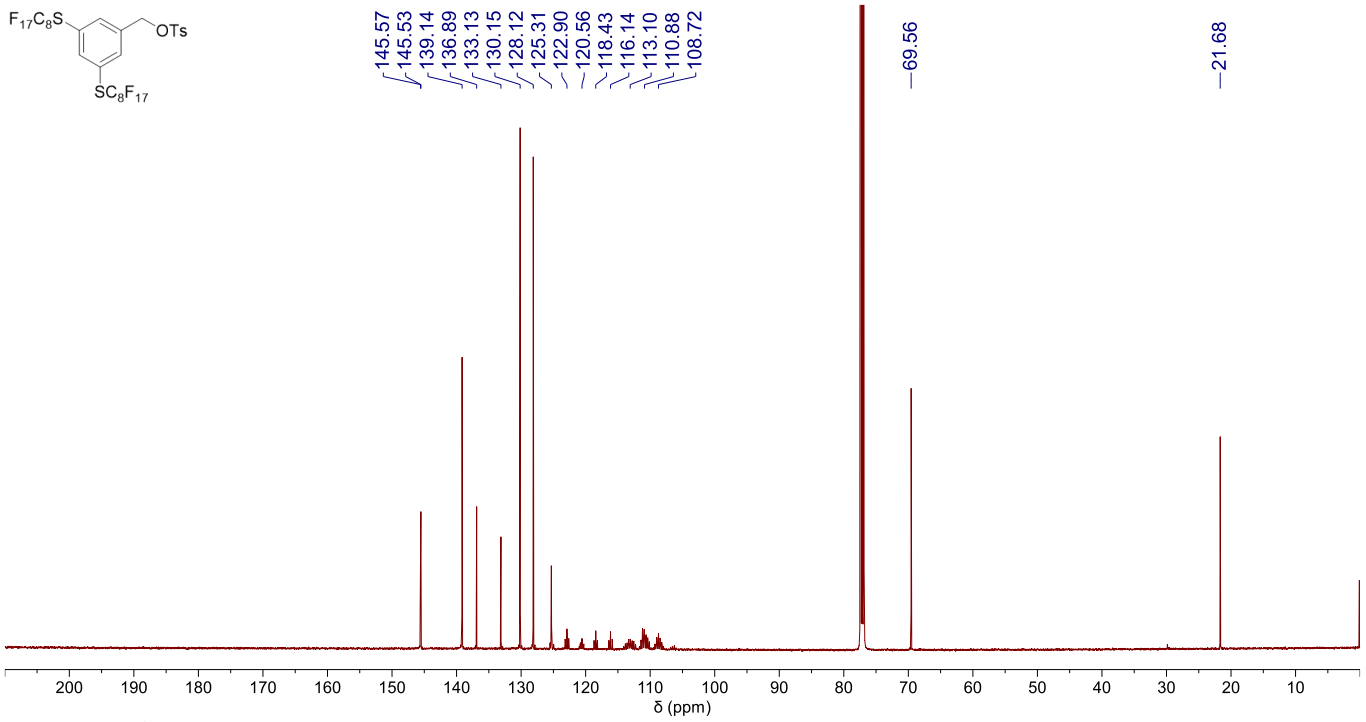


Figure S62: $^{13}C\{^{1}H\}$ NMR spectrum of **28** (126 MHz, $CDCl_3$).

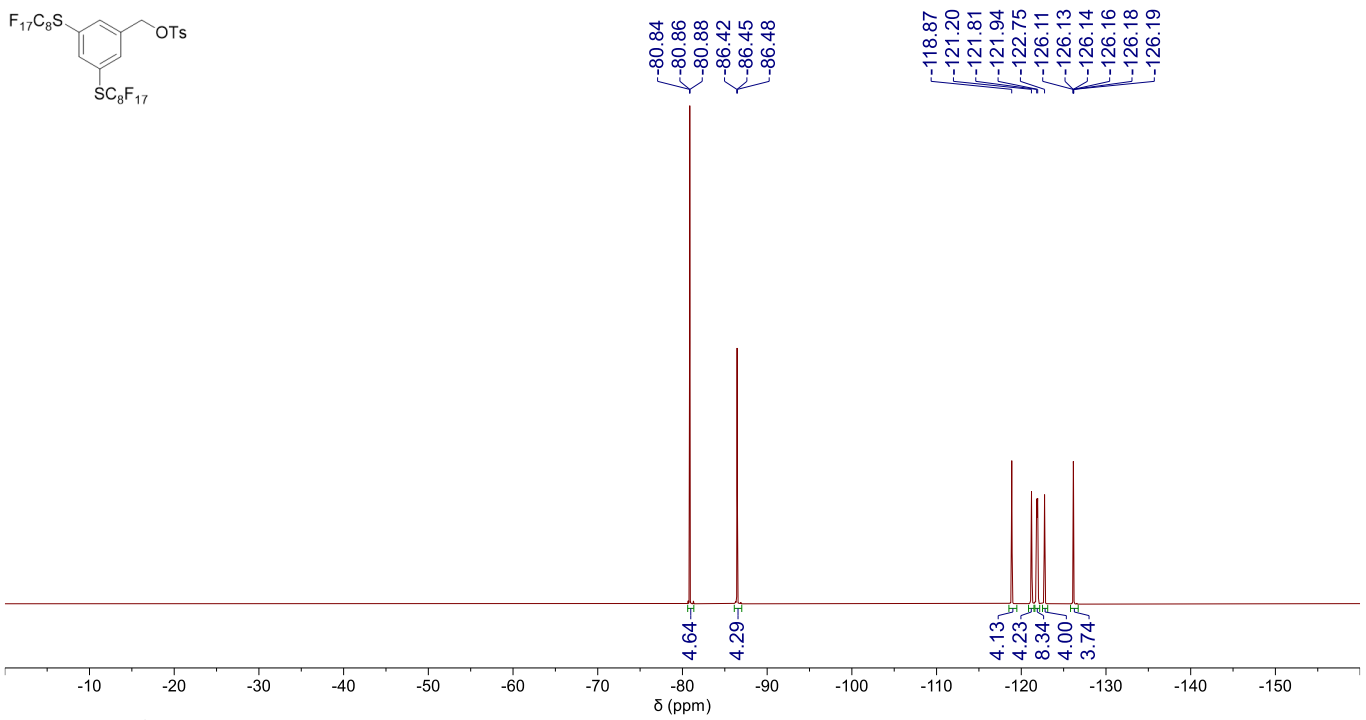


Figure S63: ^{19}F NMR spectrum of **28** (471 MHz, $CDCl_3$).

3.22. 29

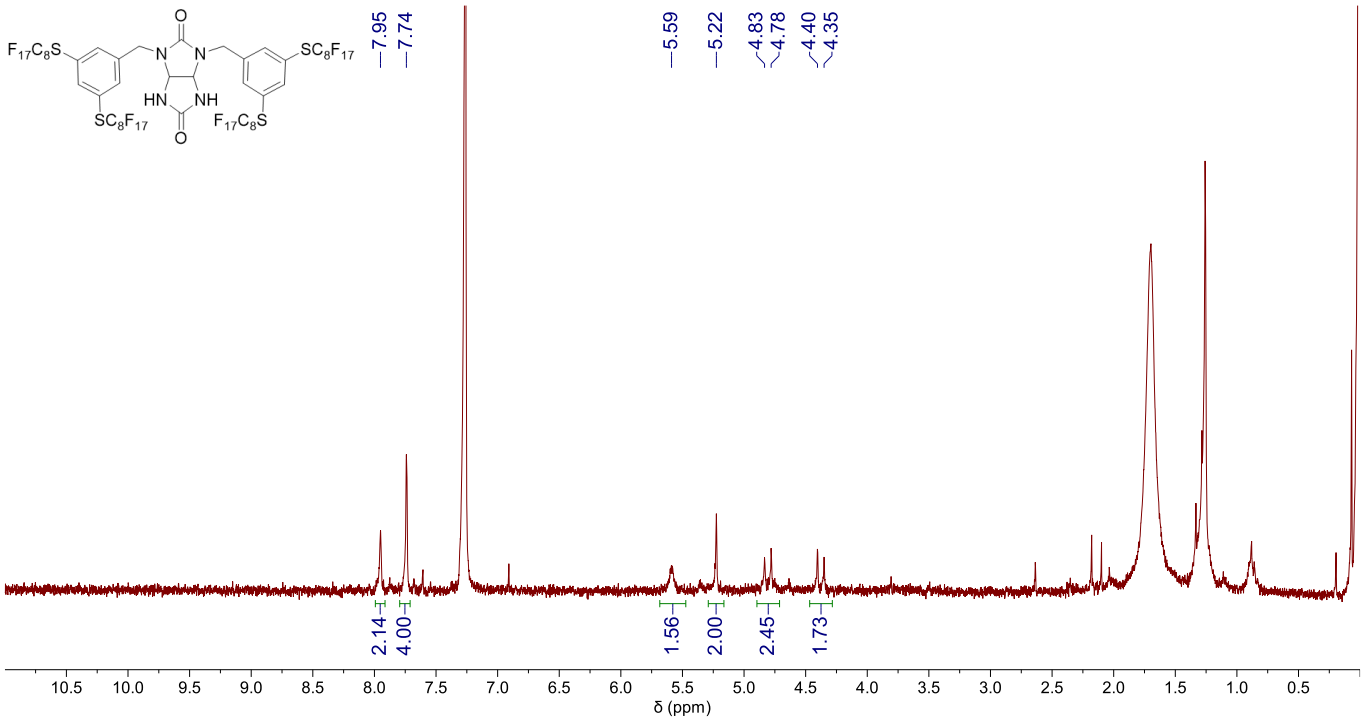


Figure S64: ^{1}H NMR spectrum of **29** (300 MHz, $CDCl_3$).

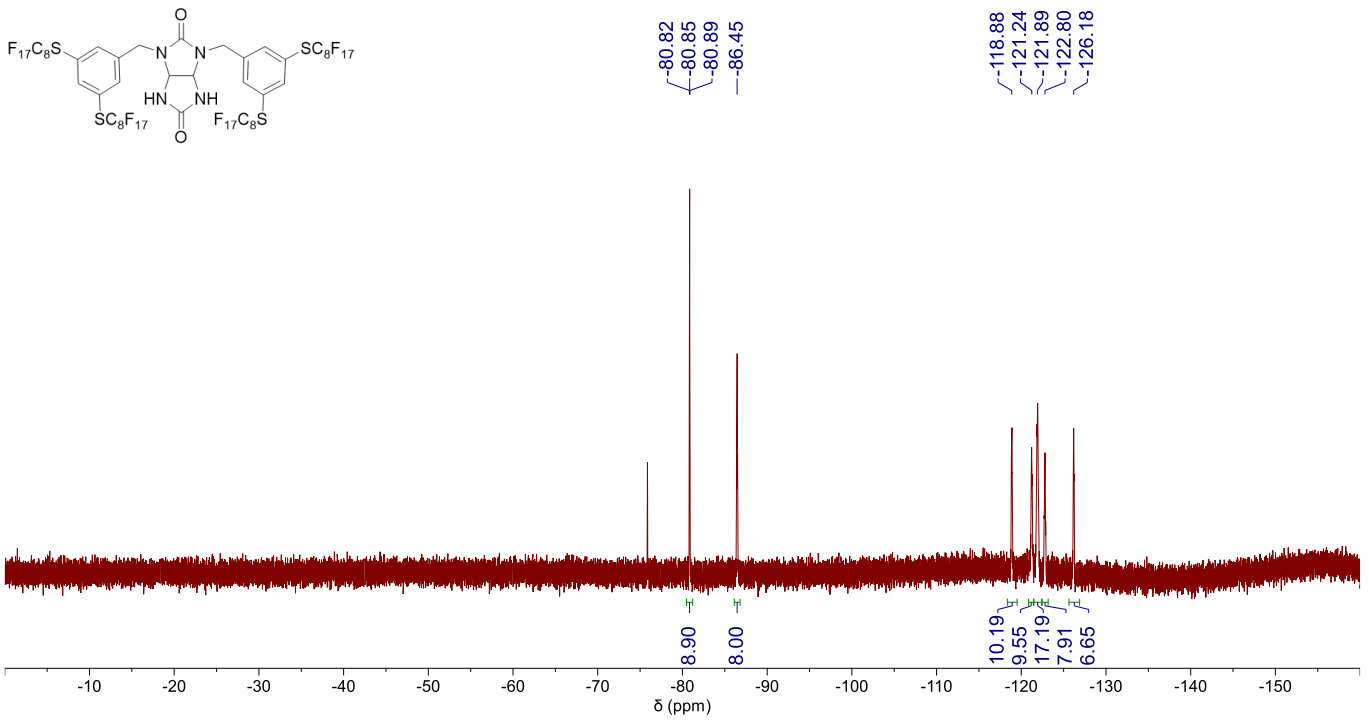


Figure S65: ^{19}F NMR spectrum of **29** (282 MHz, $CDCl_3$).

3.23. Bambusuril BU1

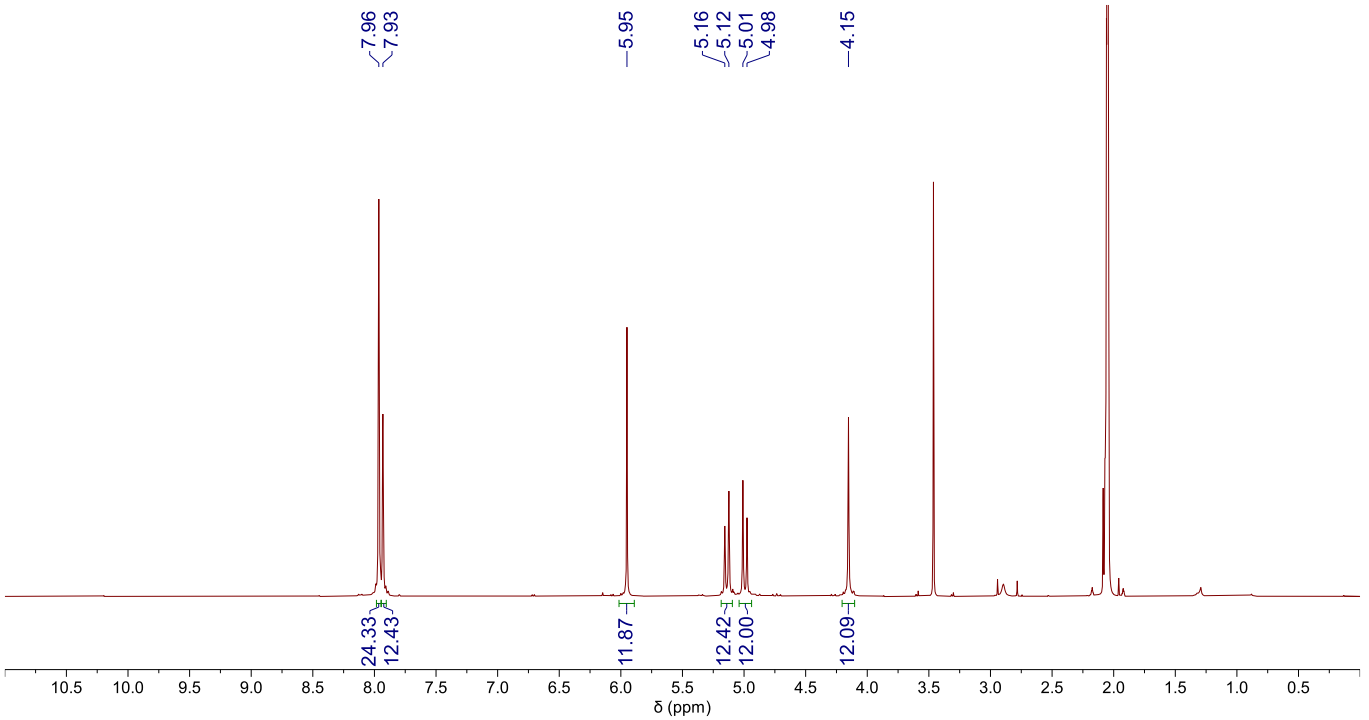


Figure S66: ^{1}H NMR spectrum of **BU1** in the presence of excess Me_4NI (500 MHz, acetone-d_6).

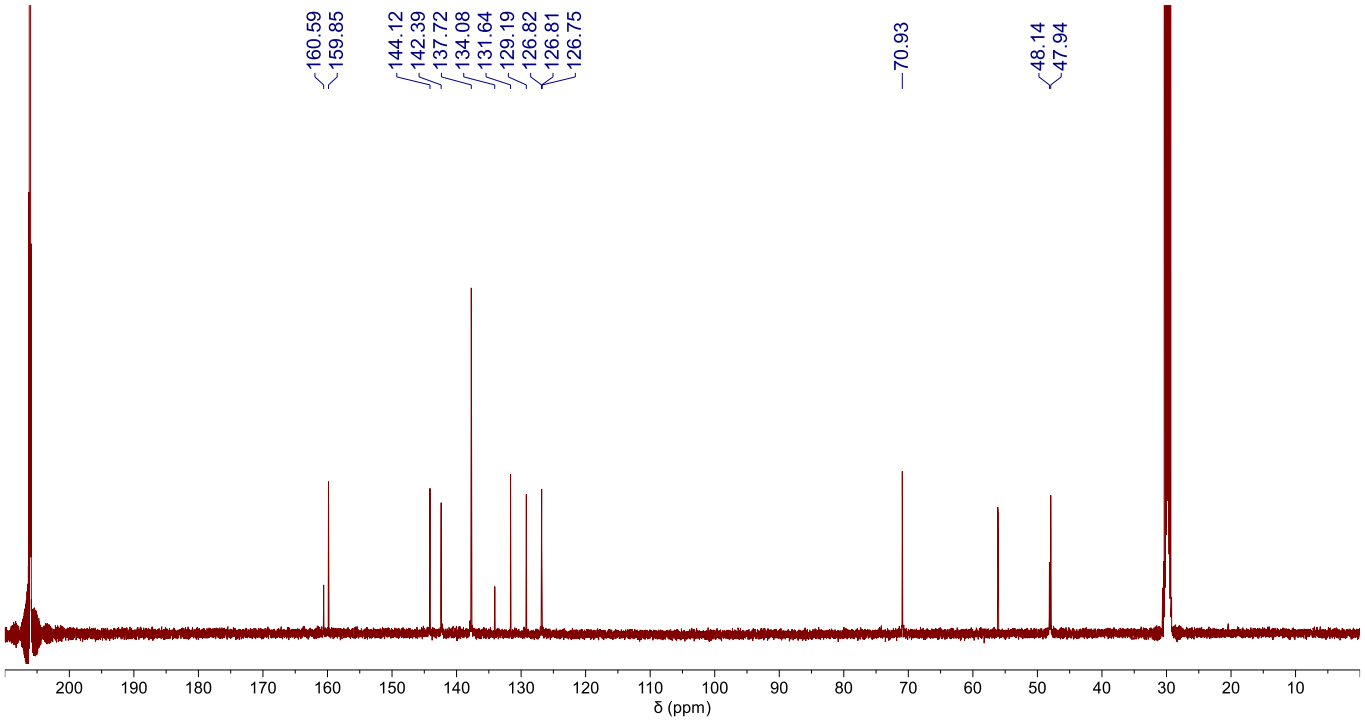


Figure S67: $^{13}C\{^{1}H\}$ NMR spectrum of **BU1** in the presence of excess Me_4NI (126 MHz, acetone-d_6).

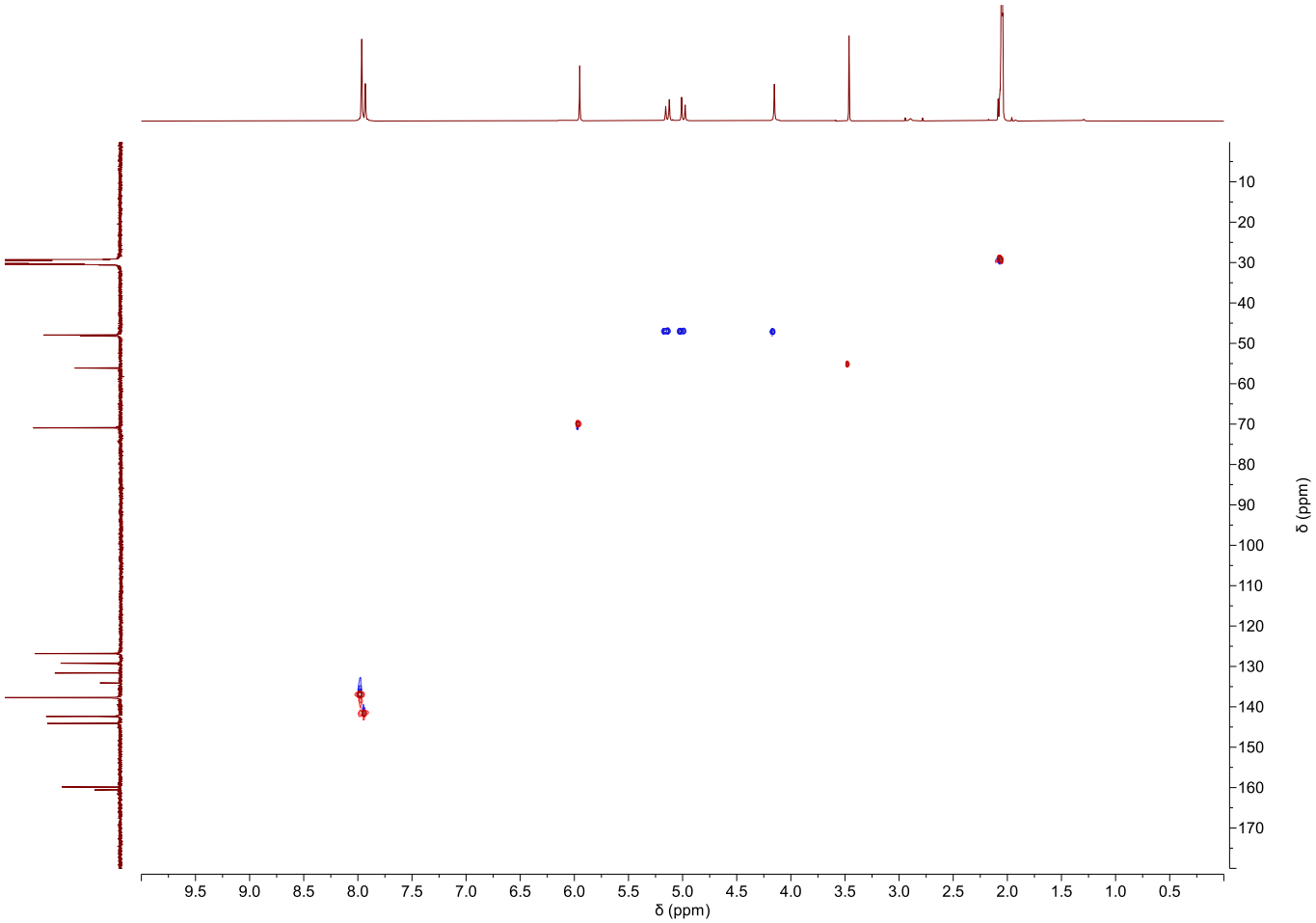


Figure S68: ^{1}H-^{13}C HSQC NMR spectrum of **BU1** in the presence of excess Me_4NI (500 MHz, 126 MHz, acetone-d_6).

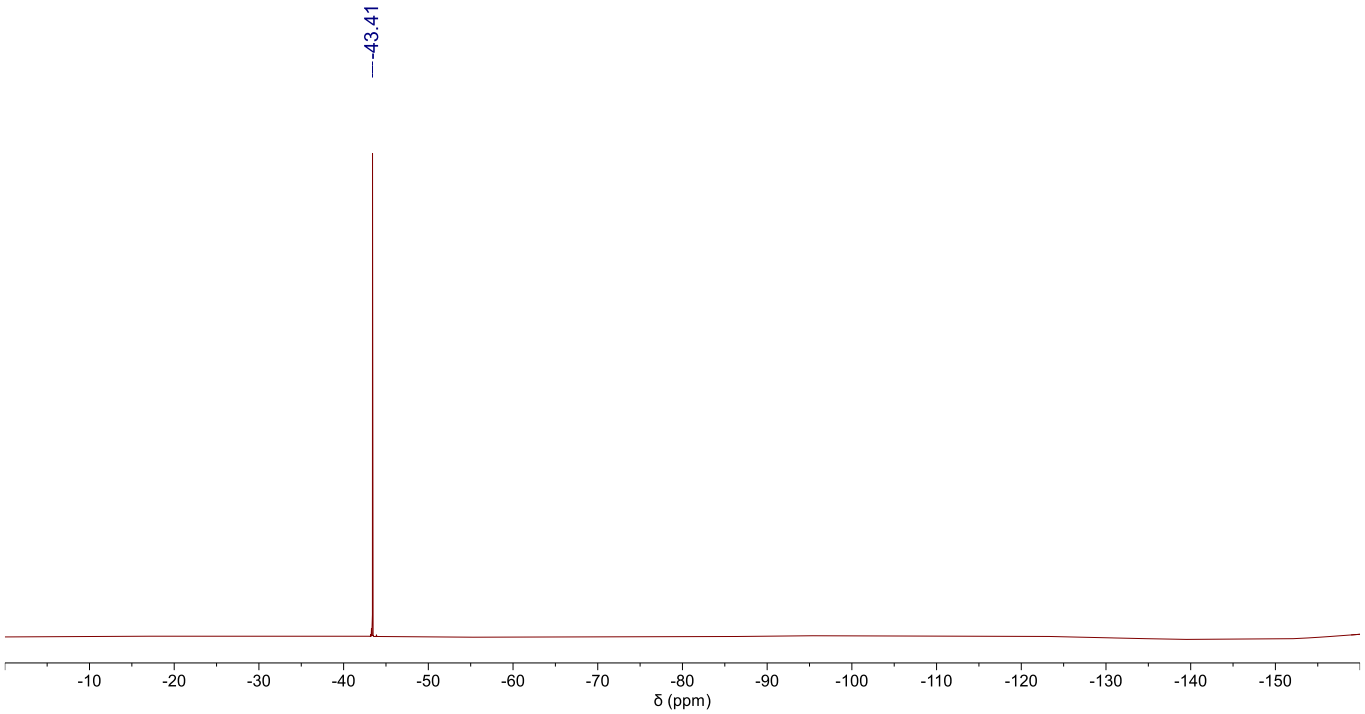


Figure S69: ^{19}F NMR spectrum of **BU1** in the presence of excess Me_4NI (565 MHz, acetone-d_6).

3.24. Bambusuril BU2

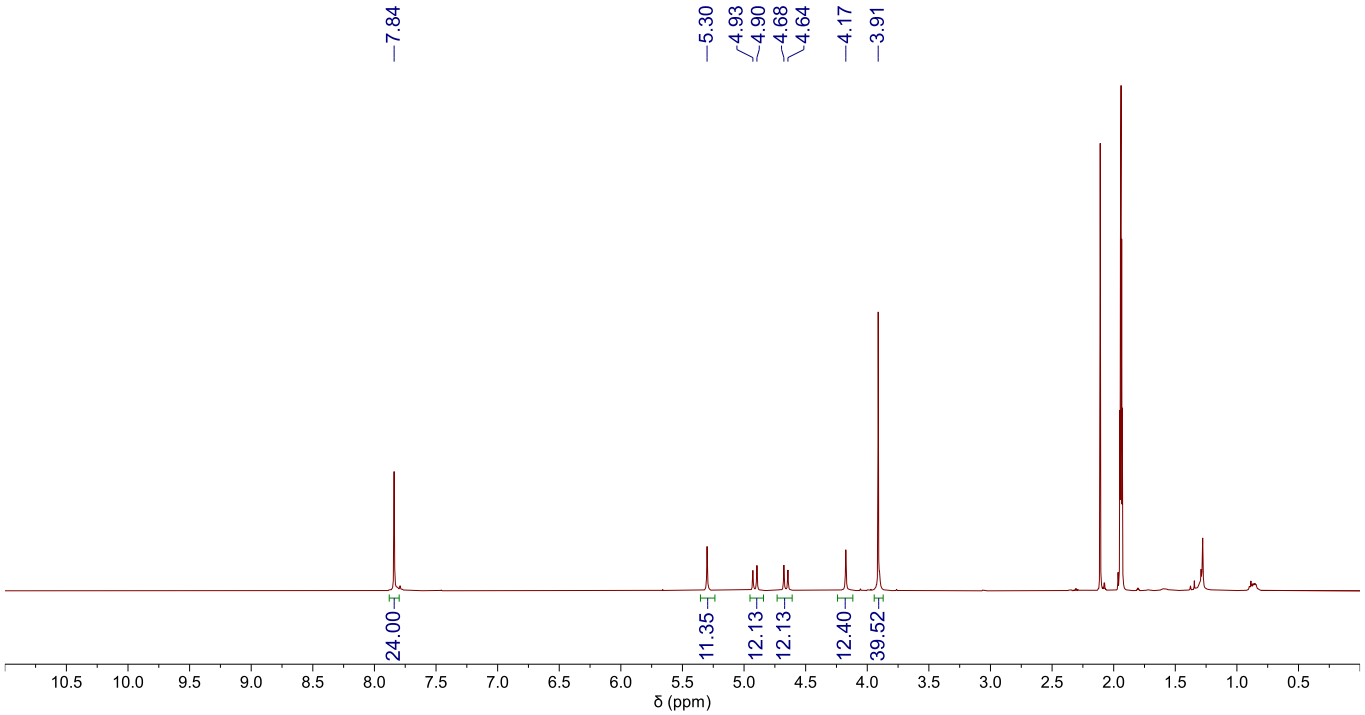


Figure S70: ^{1}H NMR spectrum of **BU2** (500 MHz, MeCN-d_3).

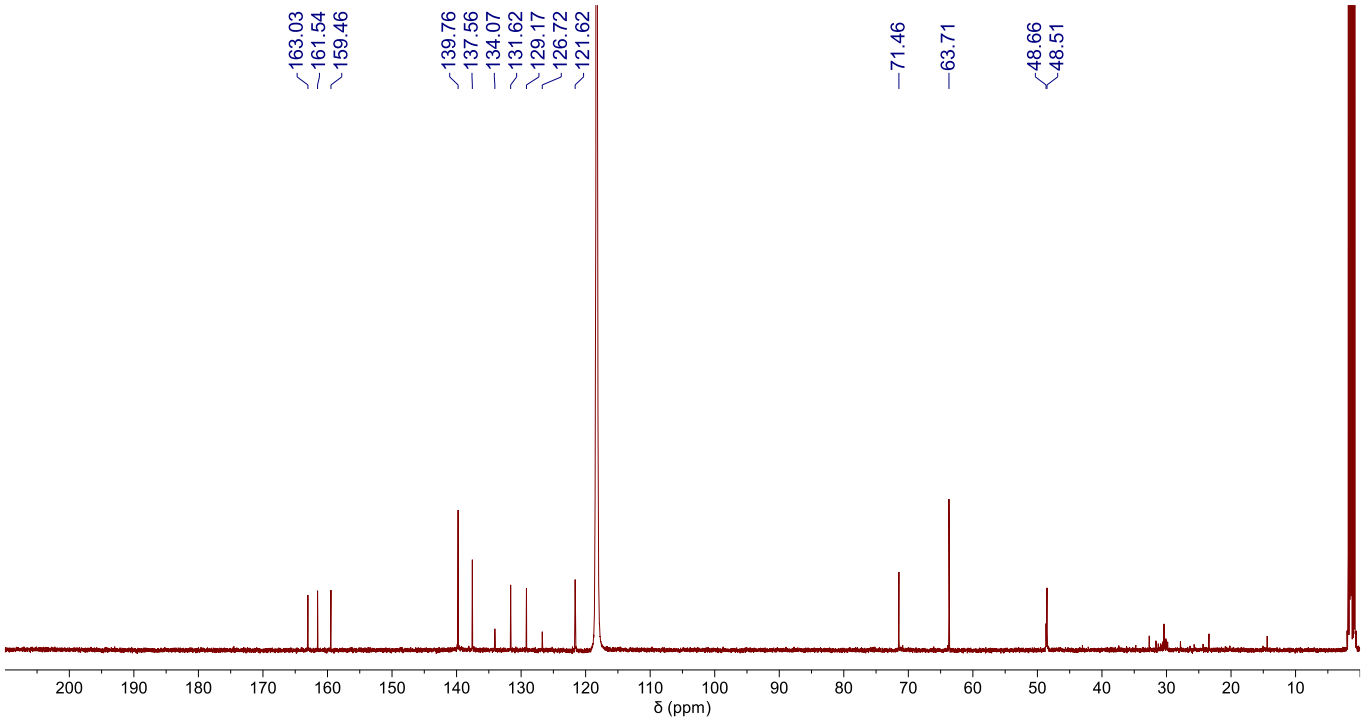


Figure S71: $^{13}C\{^{1}H\}$ NMR spectrum of **BU2** (126 MHz, MeCN-d_3).

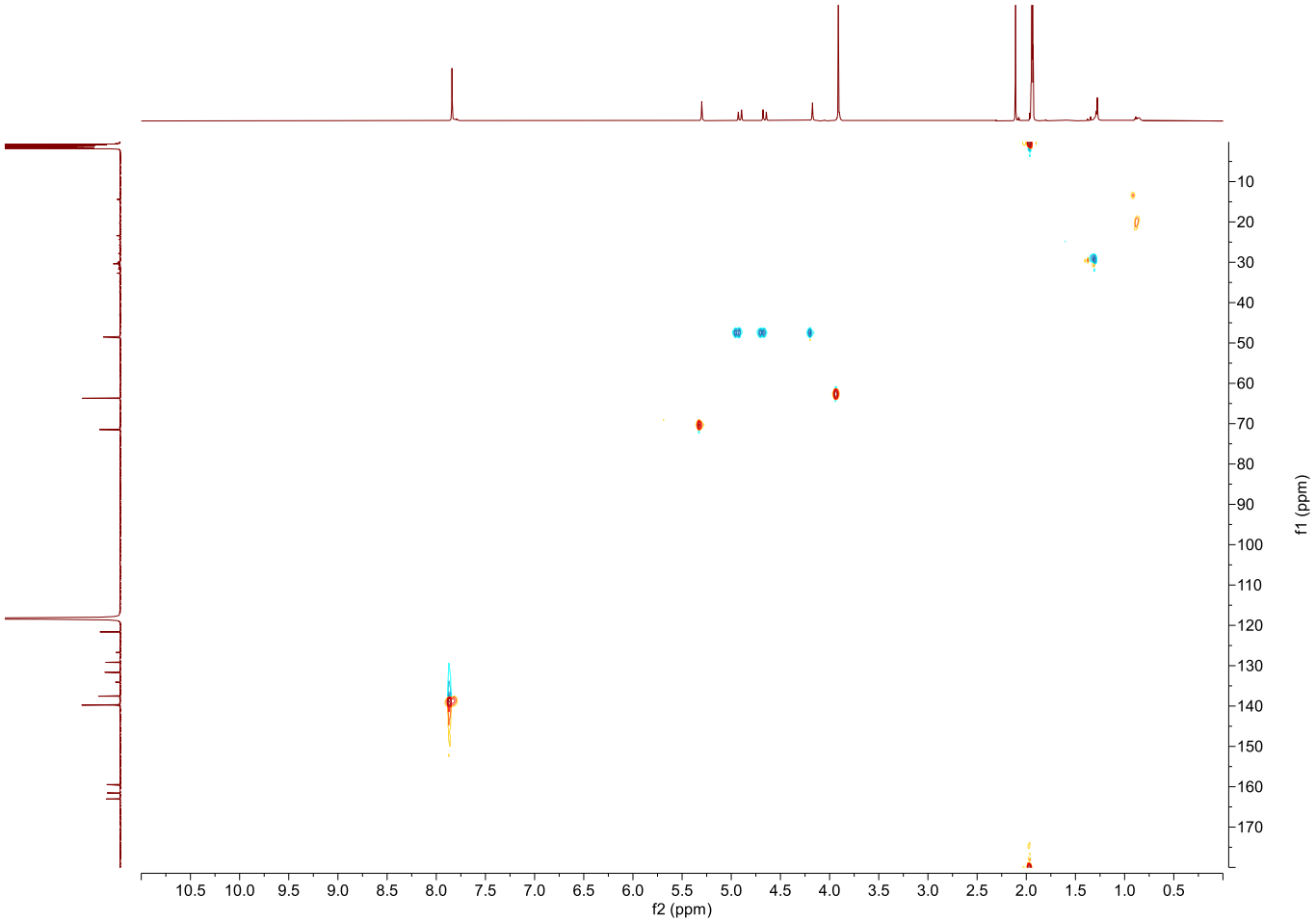


Figure S72: ^{1}H-^{13}C HSQC NMR spectrum of **BU2** (500 MHz, 126 MHz, MeCN-d_3).

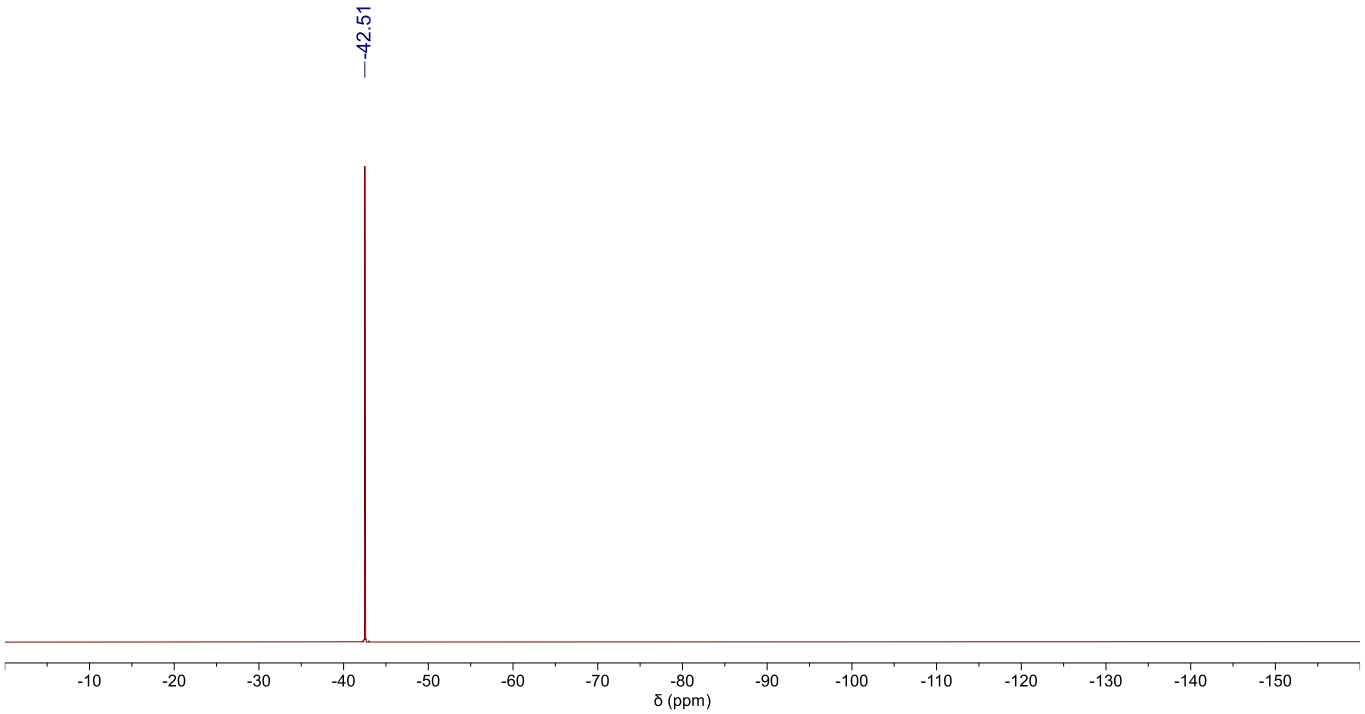


Figure S73: ^{19}F NMR spectrum of **BU2** (471 MHz, MeCN-d_3).

3.25. Bambusuril BU3

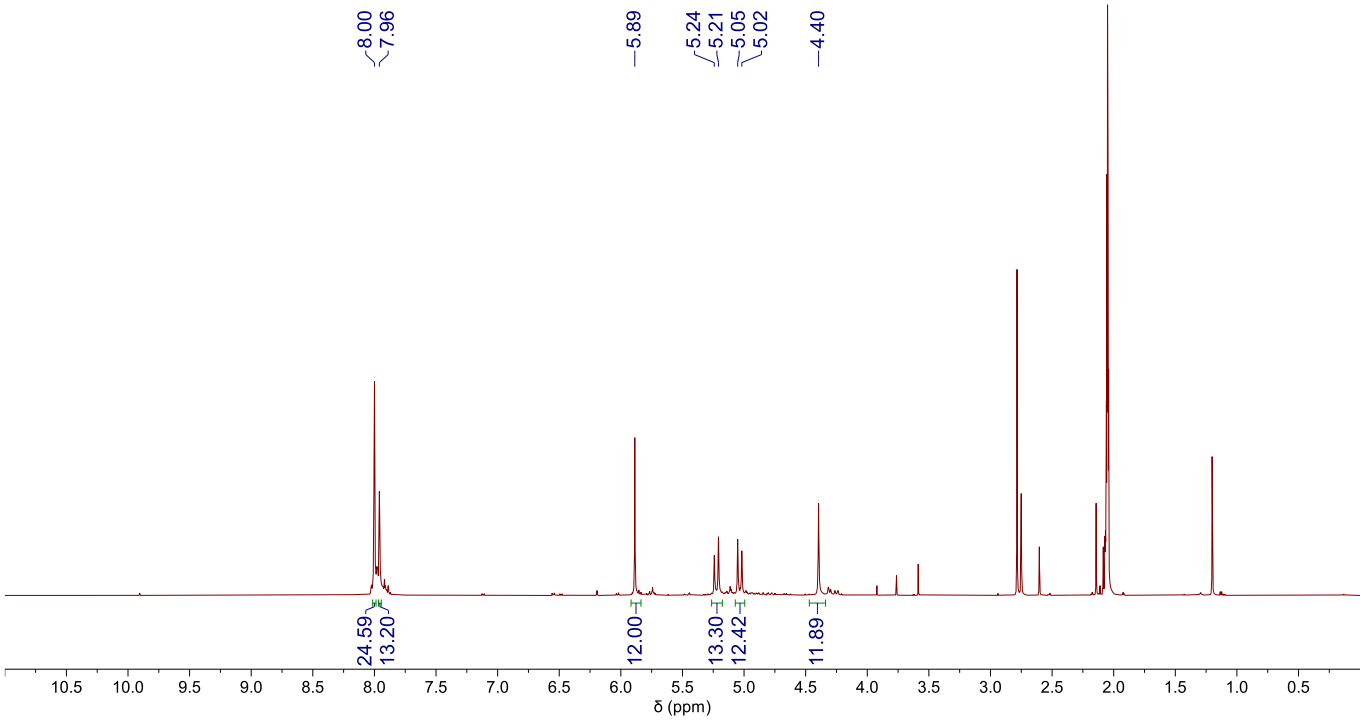


Figure S74: ^{1}H NMR spectrum of **BU3**·H_2SO_4 (500 MHz, acetone-d_6).

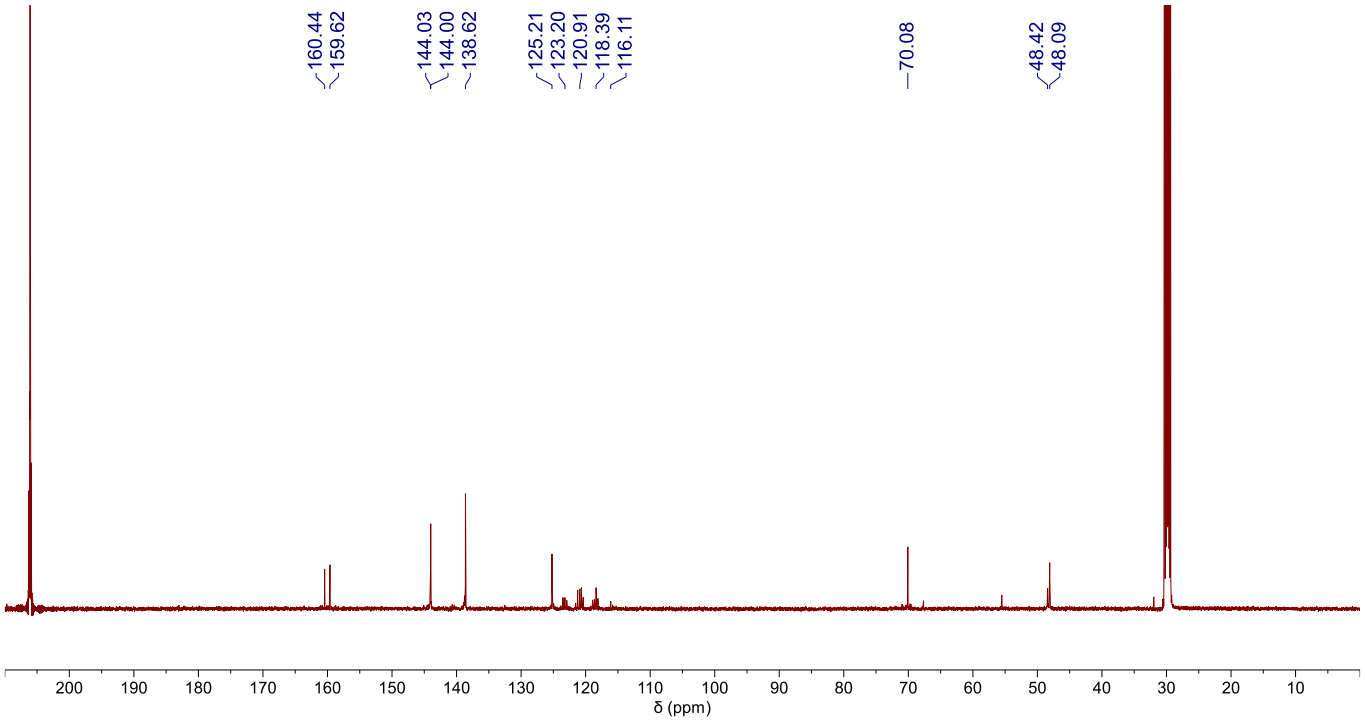


Figure S75: $^{13}C\{^{1}H\}$ NMR spectrum of **BU3**·H_2SO_4 (126 MHz, acetone-d_6).

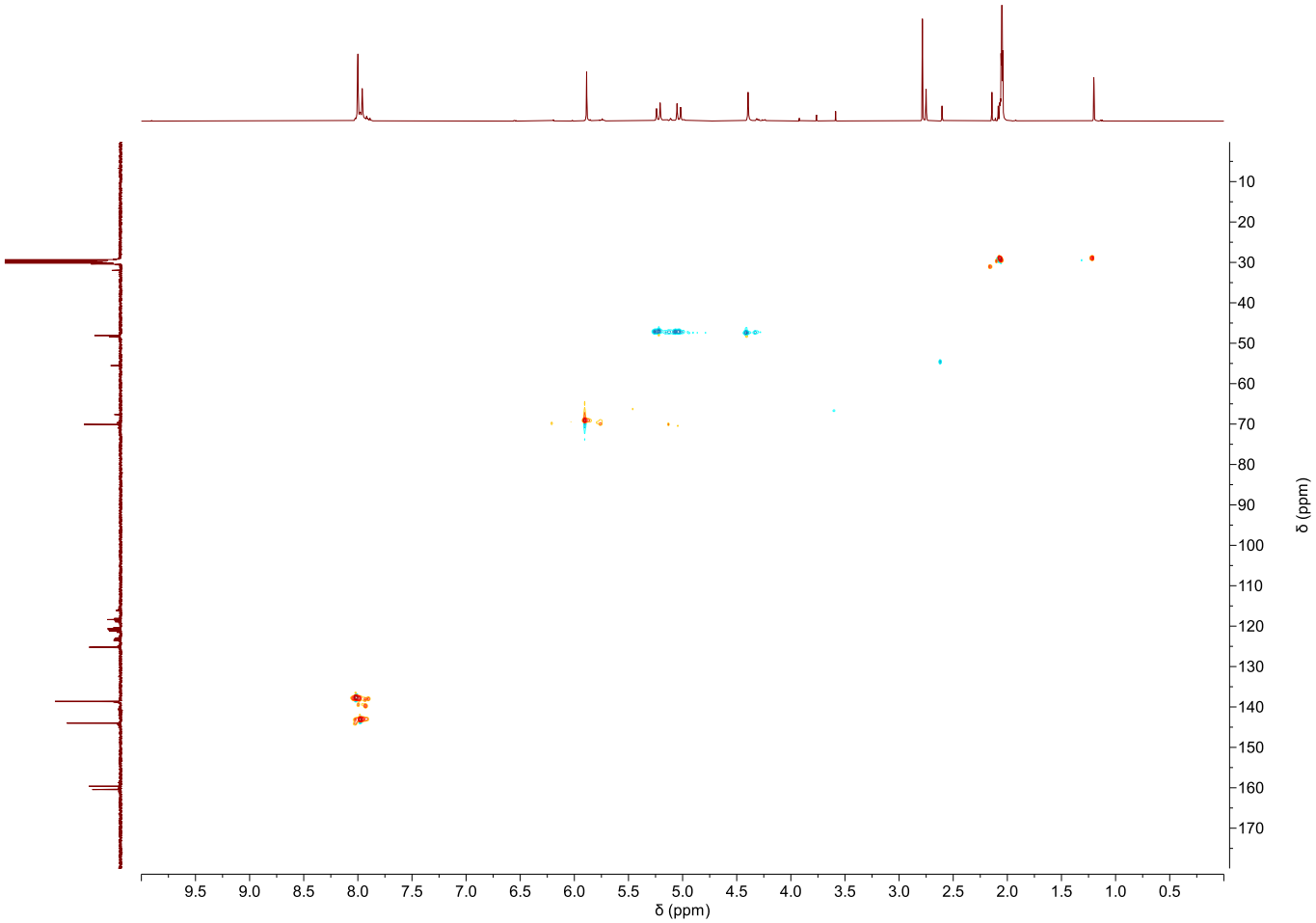


Figure S76: ^{1}H-^{13}C HSQC NMR spectrum of **BU3**·H_2SO_4 (500 MHz, 126 MHz, acetone-d_6).

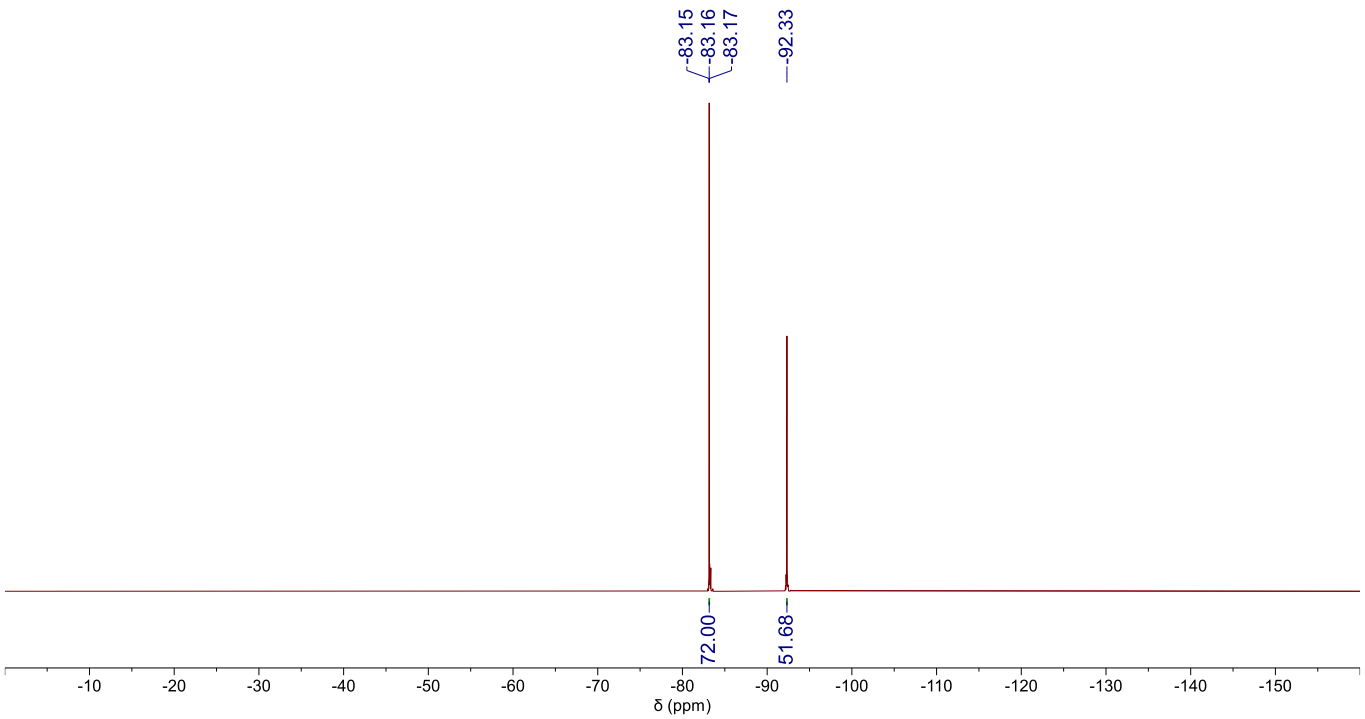


Figure S77: ^{19}F NMR spectrum of **BU3**·H_2SO_4 (471 MHz, acetone-d_6).

3.26. Bambusuril BU4

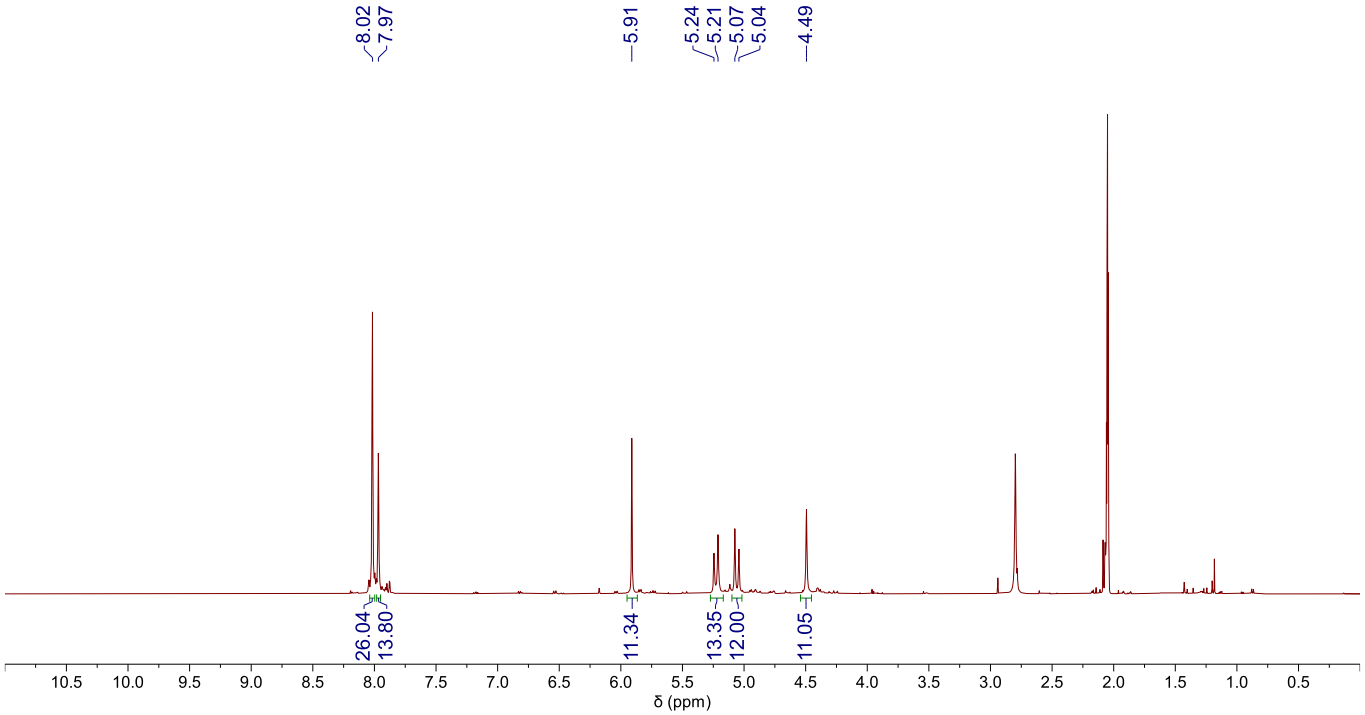


Figure S78: ^{1}H NMR spectrum of **BU4**·H_2SO_4 (500 MHz, acetone-d_6).

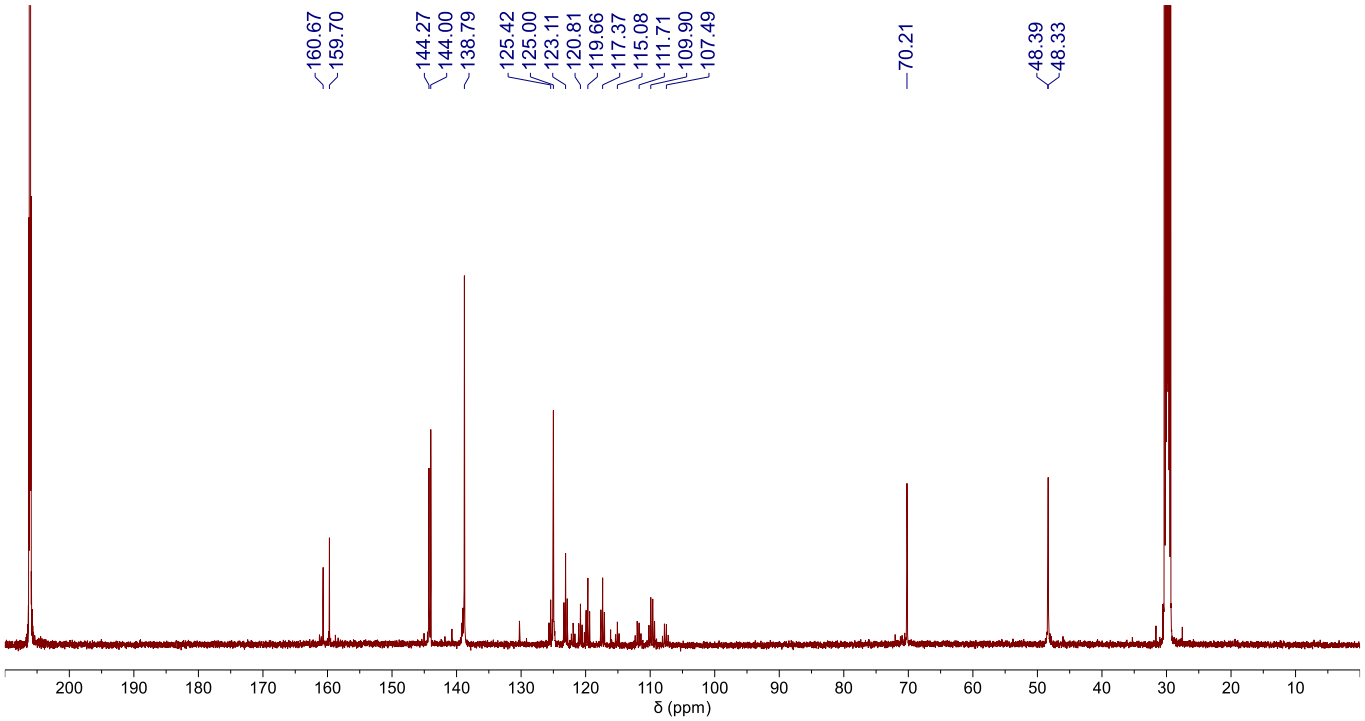


Figure S79: $^{13}C\{^{1}H\}$ NMR spectrum of **BU4**·H_2SO_4 (126 MHz, acetone-d_6).

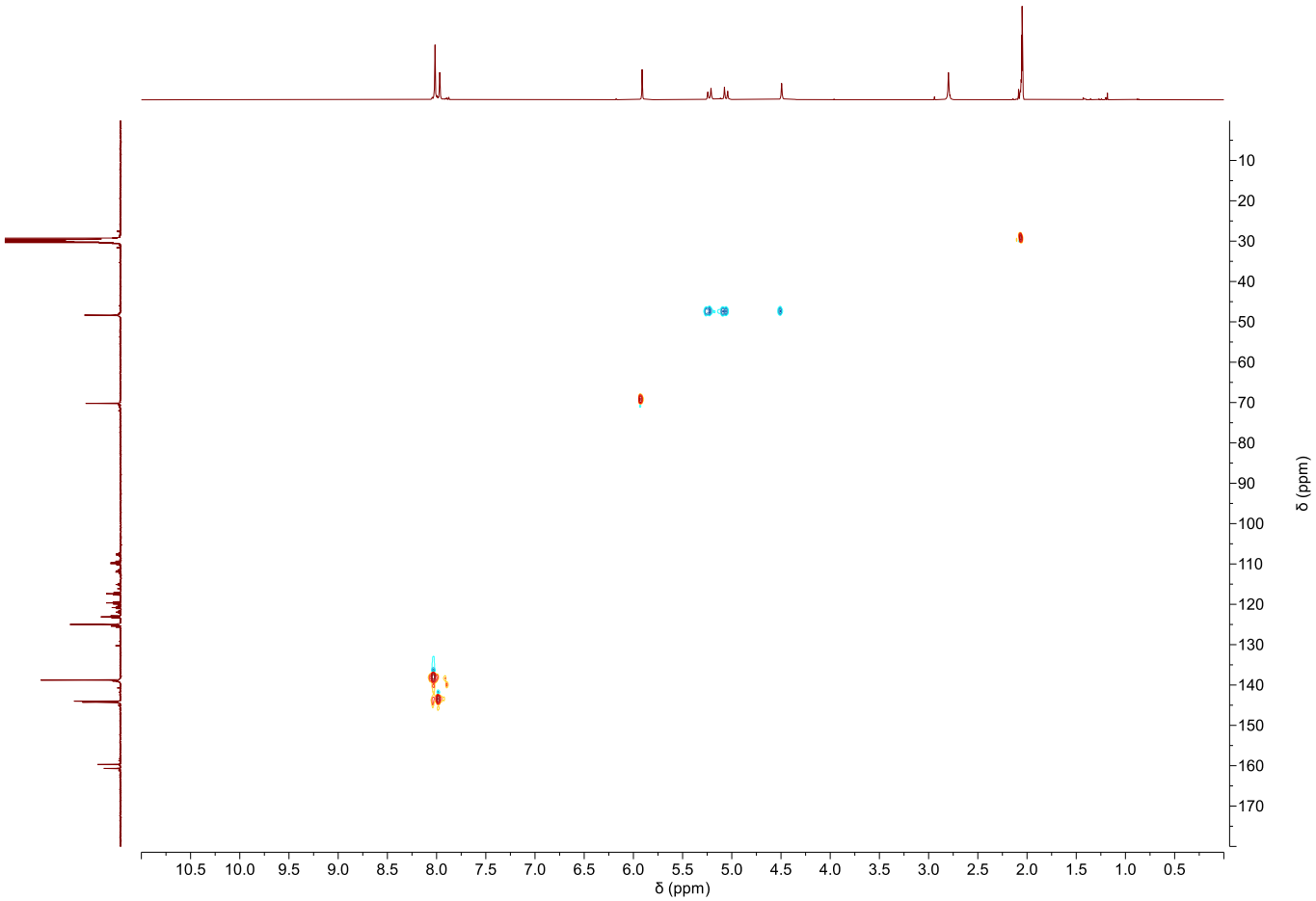


Figure S80: ^{1}H-^{13}C HSQC NMR spectrum of **BU4**·H_2SO_4 (500 MHz, 126 MHz, acetone-d_6).

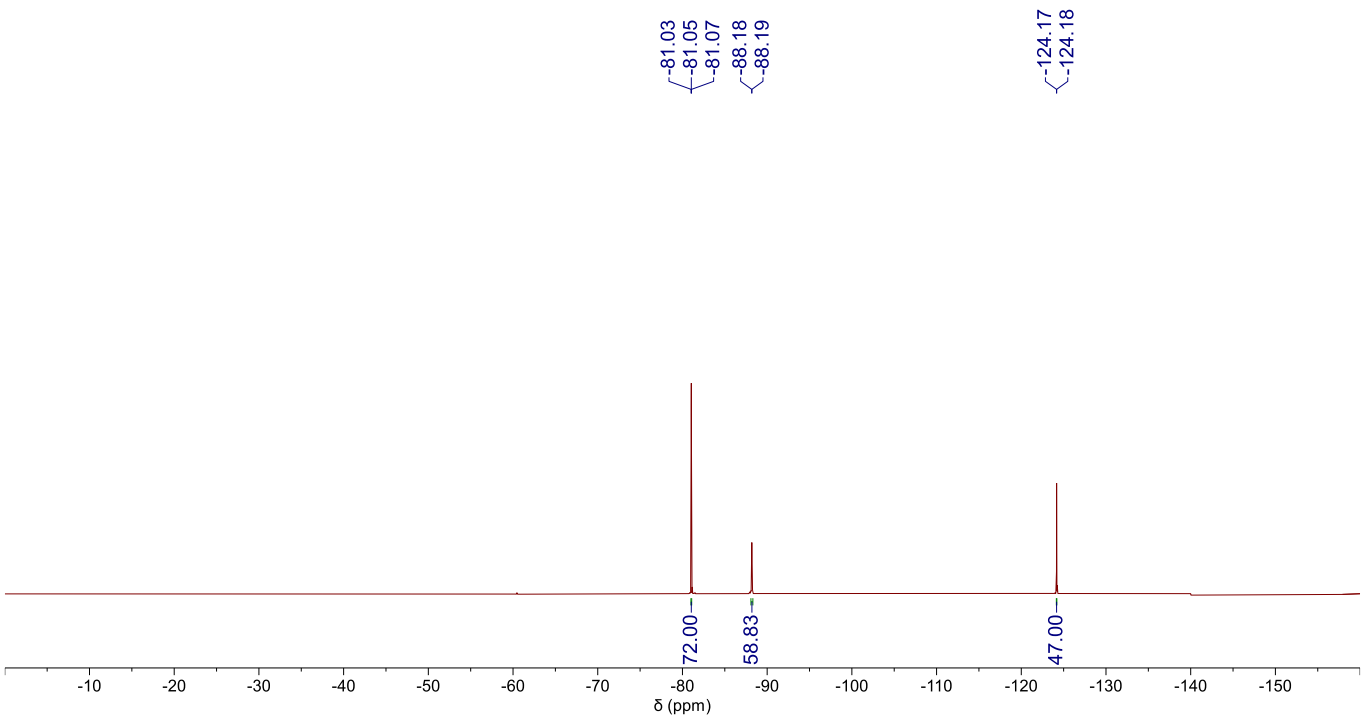


Figure S81: ^{19}F NMR spectrum of **BU4**·H_2SO_4 (471 MHz, acetone-d_6).

3.27. Bambusuril BU1 with various anions

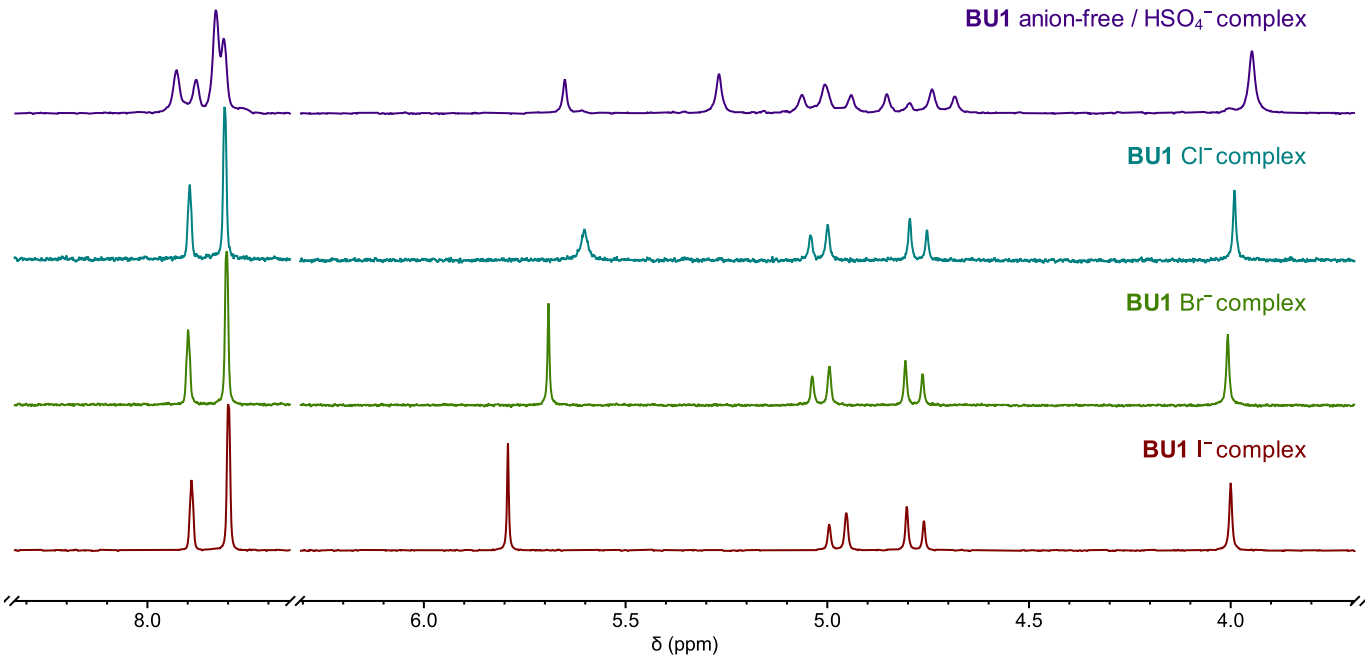


Figure S82: ^{1}H NMR spectra of **BU1** partially complexed by H_2SO_4 and **BU1**·Bu_4NX (1:1 ratio) (300 MHz, MeCN-d_3). Each complex is characterized by unique chemichal shift of macrocyclic protons.[5]

4. Description of the competition experiment between two bambusurils

To obtain binding affinities of **BU1** and **BU2** we have performed a competition experiment with **BU5** as described previously.[6] We took advantage of the great resolution of ^{19}F NMR spectroscopy and the slow exchange rate of BUs with halides. As shown in Figure 2 in the main text, upon mixing anion-free **BU5** with the Bu_4NCl complex of **BU2** in CD_3CN, anion-free **BU5** scavenges a part of the chloride from the **BU2** resulting in the formation of 2 new signals, corresponding to the Bu_4NCl complex of **BU5** and anion-free **BU2**. Simple integration of the corresponding signals and using equation (S1) gives a ratio *R* of association constants of **BU2** and **BU5**.w

$$R = \frac{K_a(\mathbf{BU2}\cdot \mathrm{A}^-)}{K_a(\mathbf{BU5}\cdot \mathrm{A}^-)} = \frac{I(\mathbf{BU5})I(\mathbf{BU2}\cdot \mathrm{A}^-)}{I(\mathbf{BU5}\cdot \mathrm{A}^-)I(\mathbf{BU2})} \tag{S1}$$

Given that the absolute association constant value for **BU5** is known, the absolute association constant for **BU2** can be determined. The uncertainty of the *R* value (described as the standard deviation *σ*) is obtained from several experiments using equation (S2), where R_i are the values obtained from the individual experiments and $\bar{R}$ is the average value.

$$\sigma = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(R_i - \bar{R})^2} \tag{S2}$$

The absolute value K_a of **BU2** and Bu_4NCl and related uncertainty are obtained from equations (S3) and (S4) respectively.

$$K_a(\mathbf{BU2}) = K_a(\mathbf{BU5})\cdot R \tag{S3}$$

$$\sigma_{K_a(\mathrm{A}^-)} = K_a(\mathrm{A}^-)\sqrt{\left(\frac{\sigma_{K_a(\mathbf{BU5})}}{K_a(\mathbf{BU5})}\right)^2 + \left(\frac{\sigma_R}{R}\right)^2} \tag{S4}$$

For the logarithmic scale presented in Table 1 in the main text, the uncertainty (described by the standard deviation) was recalculated using the following equation:

$$\log_{10}\sigma_{K_a(\mathrm{A}^-)} \approx \frac{\sigma_{K_a(\mathrm{A}^-)}}{K_a(\mathrm{A}^-)\ln 10} \tag{S5}$$

4.1. Experimental

For a typical competition experiment, the complex of the first BU with Bu_4NX (X = Cl, Br or I) and an excess of competing anion-free BU are dissolved in CD_3CN by gentle heating. The final concentrations of the bambusurils in the solution range from 50 to 400 µM. The competition is set up in such a way that the total amount of bambusurils is larger than the anion amount in the sample (n(**BU2**)+n(**BU5**)>n(A^-)). The prepared sample is measured by ^{19}F qNMR spectroscopy at 298 K within an hour after its preparation. The experiments were repeated 4-7 times (Table S1) for each combination of the species.

The obtained data were processed by zero-filling to two times the original spectrum size and applying exponential apodization matching average T2*. Automatic baseline correction by polynomial fits (3rd-5th order) was used; only regions of ±10 ppm from the signals of interest were corrected. Phase correction was done when needed. Integration regions were done manually.

Anion-free and complexed forms of the individual bambusurils are characterized by essentially the same T1, which is lower than 1.5 seconds. The usage of a 90° pulse or precisely adjusting the pulse frequency and relaxation delay was found not to be absolutely necessary, as only their ratio is important according to the equation (S1). On the other hand, a good signal-to-noise ratio and good separation and resolution of the integrated signals are required for the experiment. Integration regions were manually picked.

In the ^{19}F NMR spectrum of some BUs (**BU5** and **BU7** in particular), there are a few minor signals with a lower chemical shift than the main peak of the anion-free bambusuril. The nature of these signals is explained in our previous work.[5]

4.2. Ratios of association constants obtained from competition experiments

Table S1: Overview of all *R* values (K_a(BU)/K_a(Competing BU)) obtained from the individual competition experiments.

BU	Competing BU	Anion	*R*
BU1	**BU5**	Chloride	9.493
BU1	**BU5**	Chloride	9.610
BU1	**BU5**	Chloride	9.856
BU1	**BU5**	Chloride	8.402
BU1	**BU5**	Chloride	13.193
BU1	**BU5**	Chloride	14.452
BU1	**BU5**	Chloride	14.766
BU1	**BU5**	Chloride	10.836
Average			**11.33±2.46**
BU2	**BU5**	Chloride	7.100
BU2	**BU5**	Chloride	11.020
BU2	**BU5**	Chloride	9.243
BU2	**BU5**	Chloride	9.112
BU2	**BU5**	Chloride	14.341
BU2	**BU5**	Chloride	14.637
BU2	**BU5**	Chloride	14.588
Average			**11.43±3.11**
BU6	**BU5**	Chloride	3.482
BU6	**BU5**	Chloride	2.123
BU6	**BU5**	Chloride	5.742
BU6	**BU5**	Chloride	4.757
Average			**4.03±1.57**
BU1	**BU2**	Chloride	0.946
BU1	**BU2**	Chloride	0.973
BU1	**BU2**	Chloride	0.949
BU1	**BU2**	Chloride	0.961
Average			**0.96±0.01**
BU1	**BU6**	Chloride	2.465
BU1	**BU6**	Chloride	3.626
BU1	**BU6**	Chloride	2.841
BU1	**BU6**	Chloride	2.999
BU1	**BU6**	Chloride	2.954
Average			**2.98±0.42**

Bambusuril	Competing BU	Anion	*R*
BU2	**BU6**	Chloride	3.296
BU2	**BU6**	Chloride	2.764
BU2	**BU6**	Chloride	2.871
BU2	**BU6**	Chloride	3.528
BU2	**BU6**	Chloride	3.808
Average			**3.25±0.44**
BU1	**BU5**	Iodide	19.468
BU1	**BU5**	Iodide	18.701
BU1	**BU5**	Iodide	27.950
BU1	**BU5**	Iodide	22.483
BU1	**BU5**	Iodide	21.557
BU1	**BU5**	Iodide	24.611
BU1	**BU5**	Iodide	20.619
Average			**22.20±3.20**
BU2	**BU5**	Iodide	29.863
BU2	**BU5**	Iodide	27.973
BU2	**BU5**	Iodide	27.649
BU2	**BU5**	Iodide	28.710
Average			**28.55±0.98**
BU1	**BU2**	Iodide	1.252
BU1	**BU2**	Iodide	1.154
BU1	**BU2**	Iodide	1.027
BU1	**BU2**	Iodide	0.700
BU1	**BU2**	Iodide	0.767
BU1	**BU2**	Iodide	0.918
BU1	**BU2**	Iodide	0.911
Average			**0.96±0.20**
BU2	**BU7**	Iodide	3,597
BU2	**BU7**	Iodide	4,180
BU2	**BU7**	Iodide	3,005
BU2	**BU7**	Iodide	2,361
BU2	**BU7**	Iodide	2,284
Average			**3.09±0.81**

Table S1 (continued): Overview of all *R* values (K_a(BU)/K_a(Competing BU)) obtained from the individual competition experiments.

BU	**Competing BU**	**Anion**	***R***
BU1	**BU5**	Bromide	9.363
BU1	**BU5**	Bromide	7.805
BU1	**BU5**	Bromide	10.790
BU1	**BU5**	Bromide	5.843
BU1	**BU5**	Bromide	7.581
BU1	**BU5**	Bromide	6.670
BU1	**BU5**	Bromide	8.197
Average			**8.04±1.65**
BU2	**BU5**	Bromide	9.385
BU2	**BU5**	Bromide	9.640
BU2	**BU5**	Bromide	11.555
BU2	**BU5**	Bromide	10.552
BU2	**BU5**	Bromide	9.640
Average			**11.28±0.98**
BU5	**BU6**	Bromide	5.466
BU5	**BU6**	Bromide	5.478
BU5	**BU6**	Bromide	5.836
BU5	**BU6**	Bromide	5.266
BU5	**BU6**	Bromide	6.528
BU5	**BU6**	Bromide	6.595
Average			**5.86±0.57**

4.3. Examples of the results obtained from the competition experiments

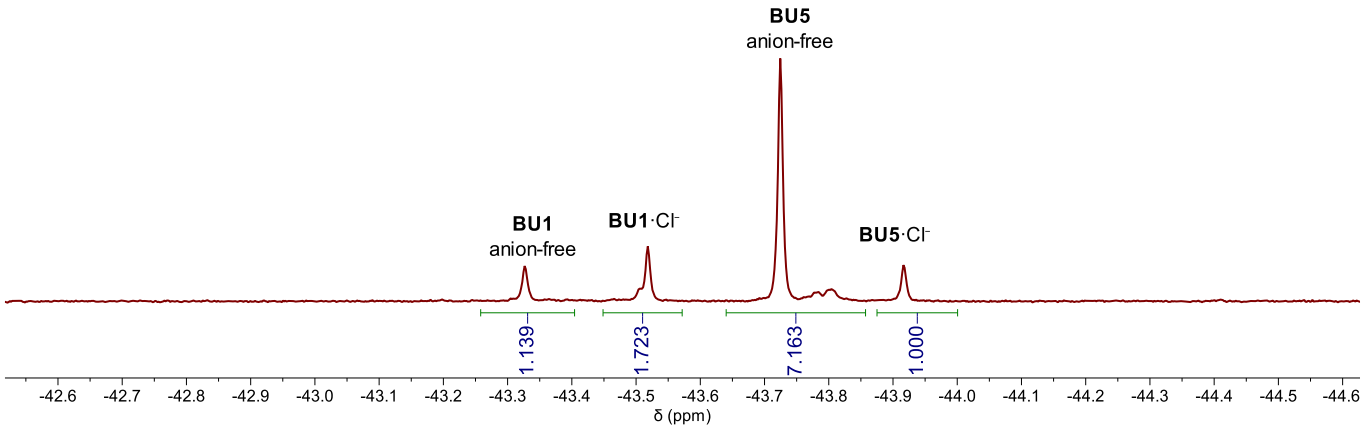


Figure S83: ^{19}F NMR spectrum (CD_3CN) of a competition experiment between **BU1** and **BU5** for Cl^-, giving K_a(**BU1**)/K_a(**BU5**) = 10.84.

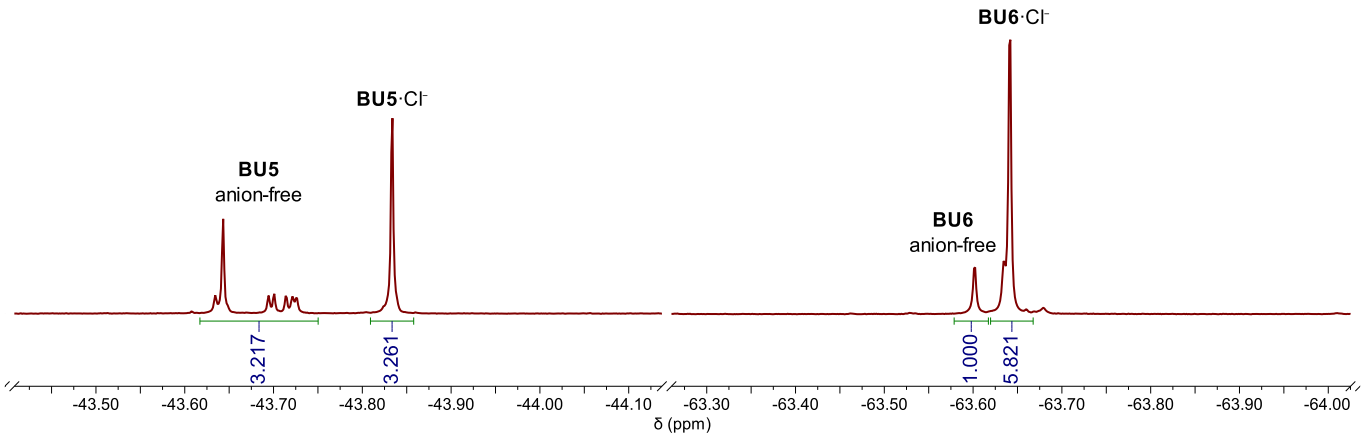


Figure S84: ^{19}F NMR spectrum (CD_3CN) of a competition experiment between **BU5** and **BU6** for Cl^-, giving K_a(**BU6**)/K_a(**BU5**) = 5.74.

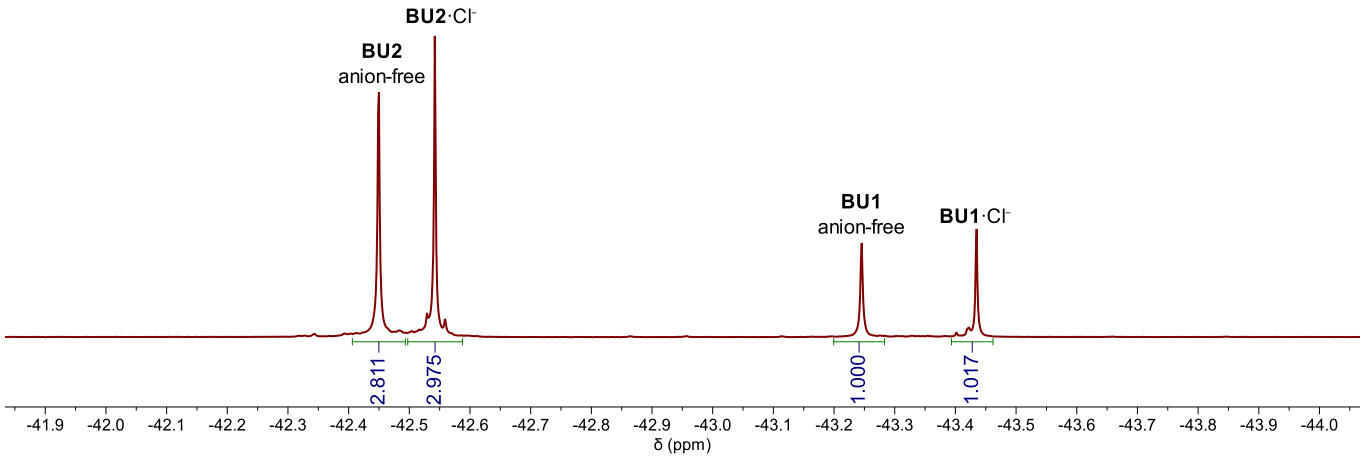


Figure S85: ^{19}F NMR spectrum (CD_3CN) of a competition experiment between **BU1** and **BU2** for Cl^-, giving K_a(**BU1**)/K_a(**BU2**) = 0.96.

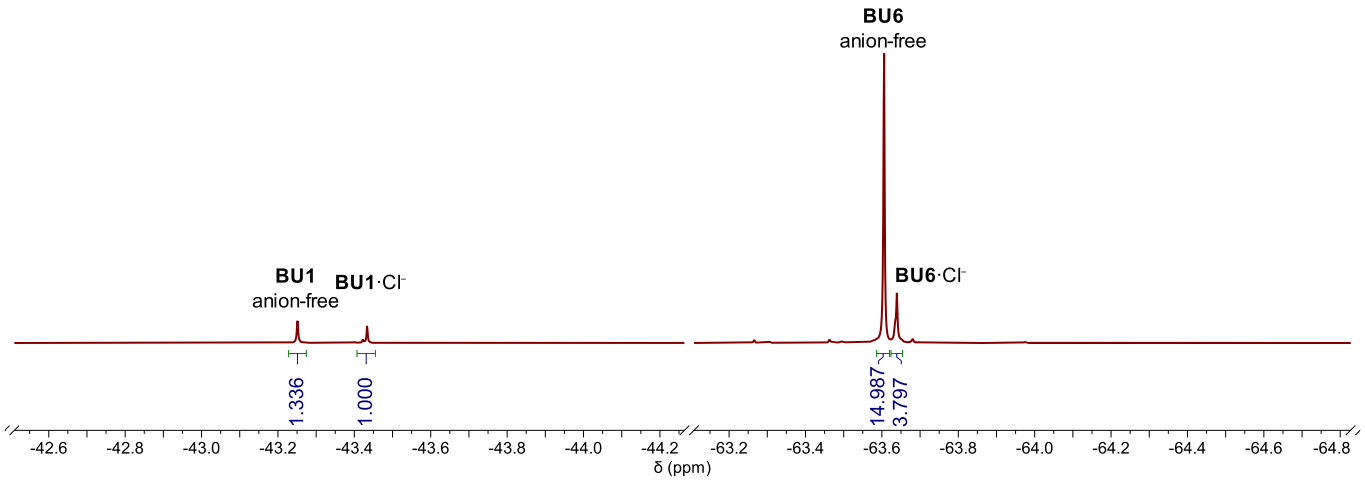


Figure S86: ^{19}F NMR spectrum (CD_3CN) of a competition experiment between **BU1** and **BU6** for Cl^-, giving K_a(**BU1**)/K_a(**BU6**) = 2.95.

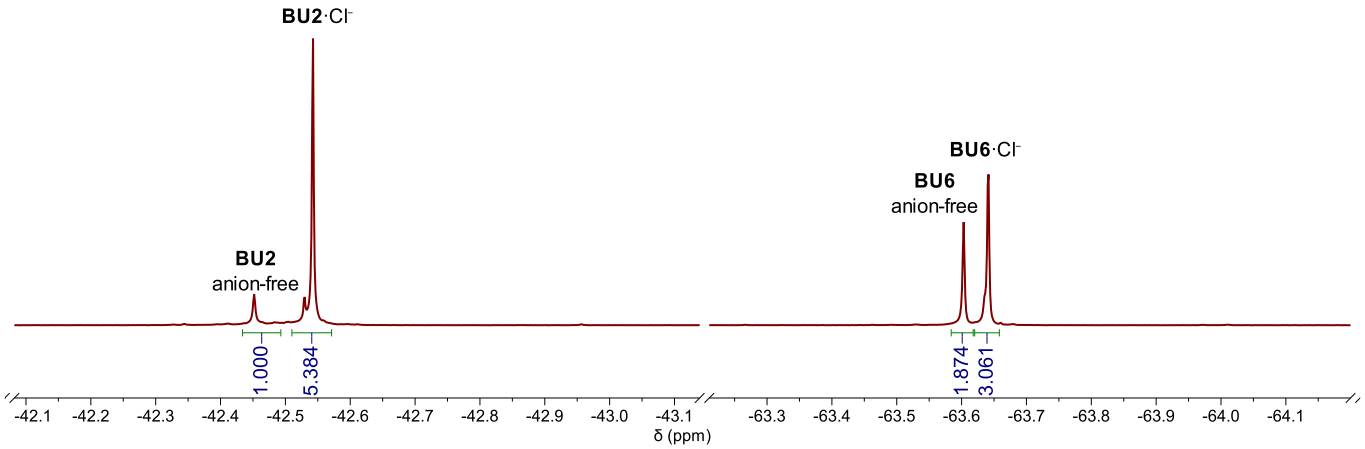


Figure S87: ^{19}F NMR spectrum (CD_3CN) of a competition experiment between **BU2** and **BU6** for Cl^-, giving K_a(**BU2**)/K_a(**BU6**) = 3.30.

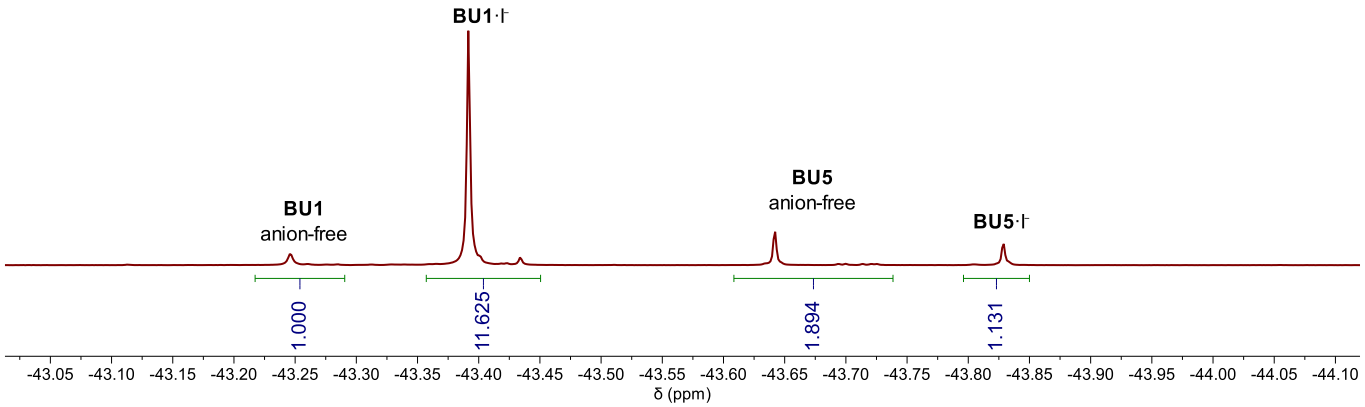


Figure S88: ^{19}F NMR spectrum (CD_3CN) of a competition experiment between **BU1** and **BU5** for I^-, giving K_a(**BU1**)/K_a(**BU5**) = 19.47.

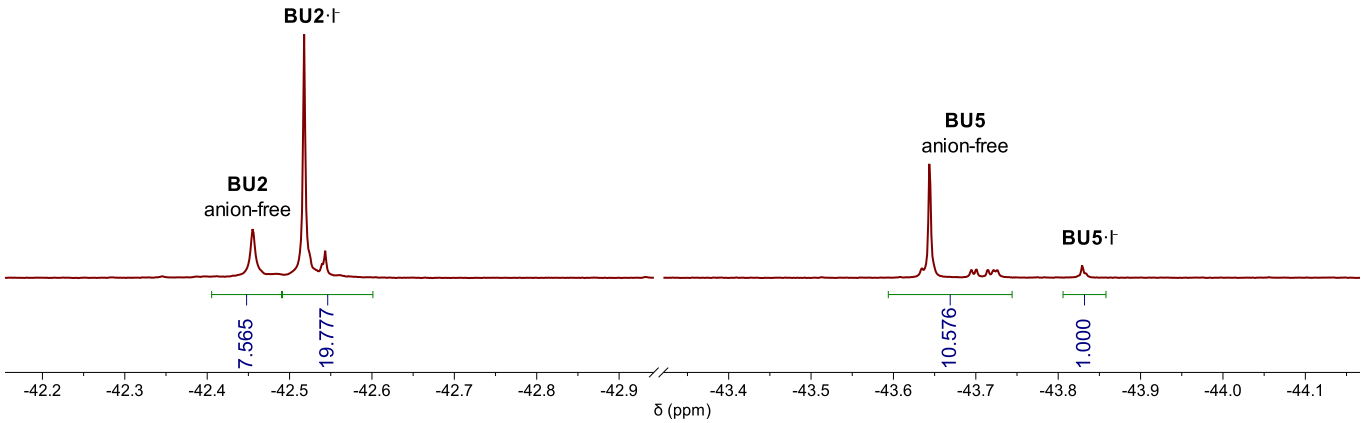


Figure S89: ^{19}F NMR spectrum (CD_3CN) of a competition experiment between **BU2** and **BU5** for I^-, giving K_a(**BU2**)/K_a(**BU5**) = 27.65.

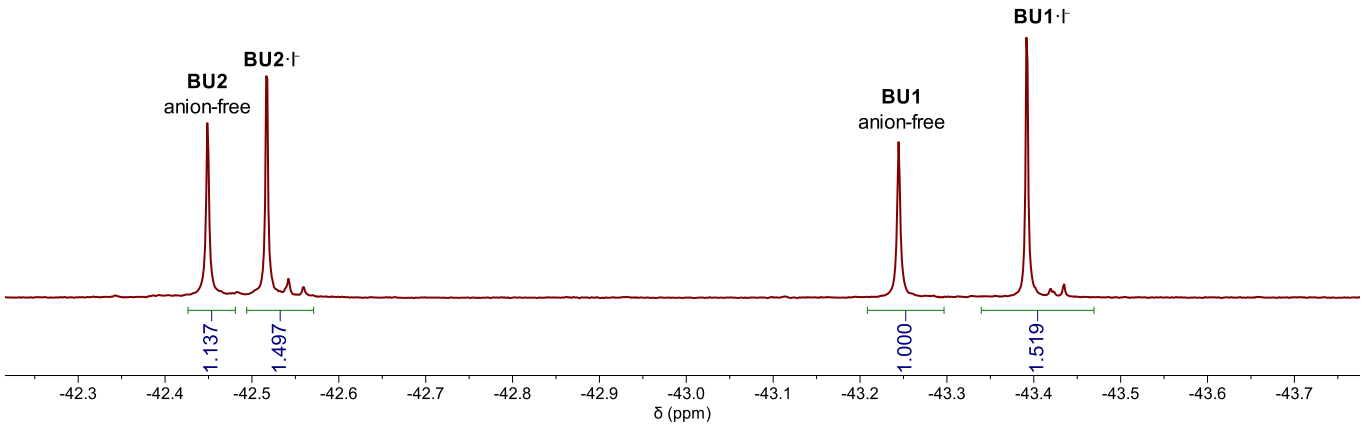


Figure S90: ^{19}F NMR spectrum (CD_3CN) of a competition experiment between **BU1** and **BU2** for I^-, giving K_a(**BU1**)/K_a(**BU2**) = 1.15.

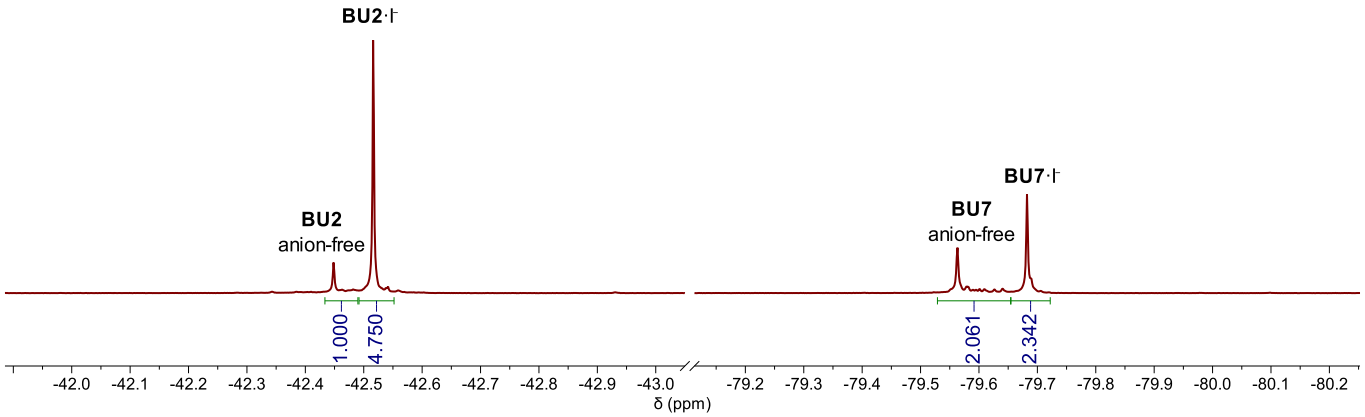


Figure S91: ^{19}F NMR spectrum (CD_3CN) of a competition experiment between **BU2** and **BU7** for I^-, giving K_a(**BU2**)/K_a(**BU7**) = 4.18.

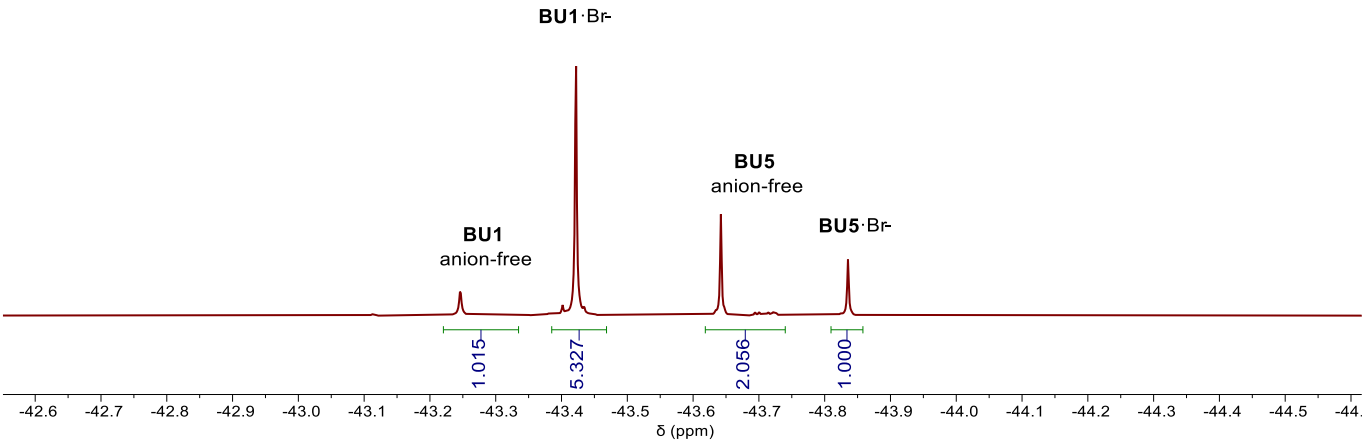


Figure S92: ^{19}F NMR spectrum (CD_3CN) of a competition experiment between **BU1** and **BU5** for Br^-, giving K_a(**BU1**)/K_a(**BU5**) = 10.79.

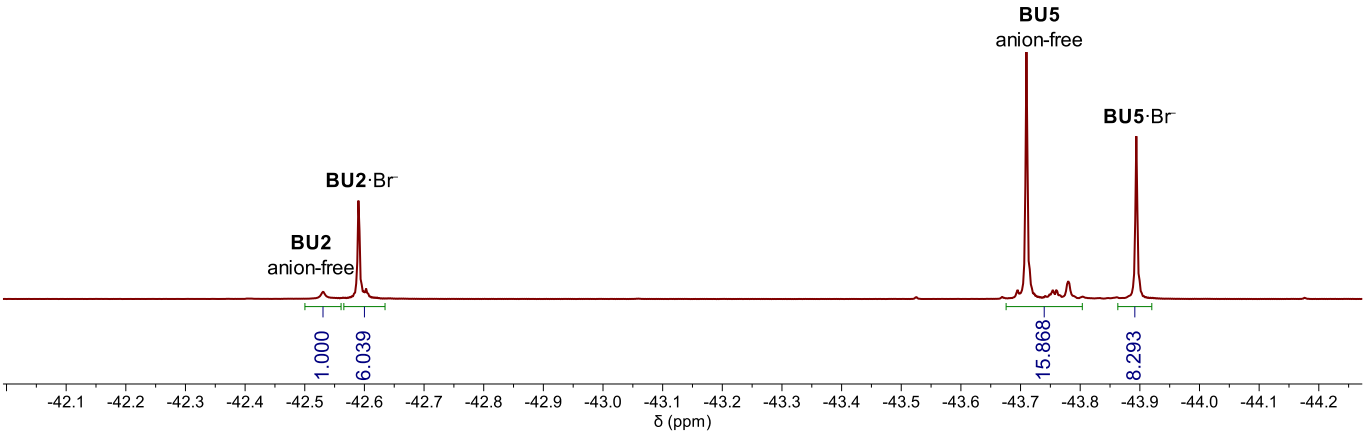


Figure S93: ^{19}F NMR spectrum (CD_3CN) of a competition experiment between **BU2** and **BU5** for Br^-, giving K_a(**BU2**)/K_a(**BU5**) = 11.56.

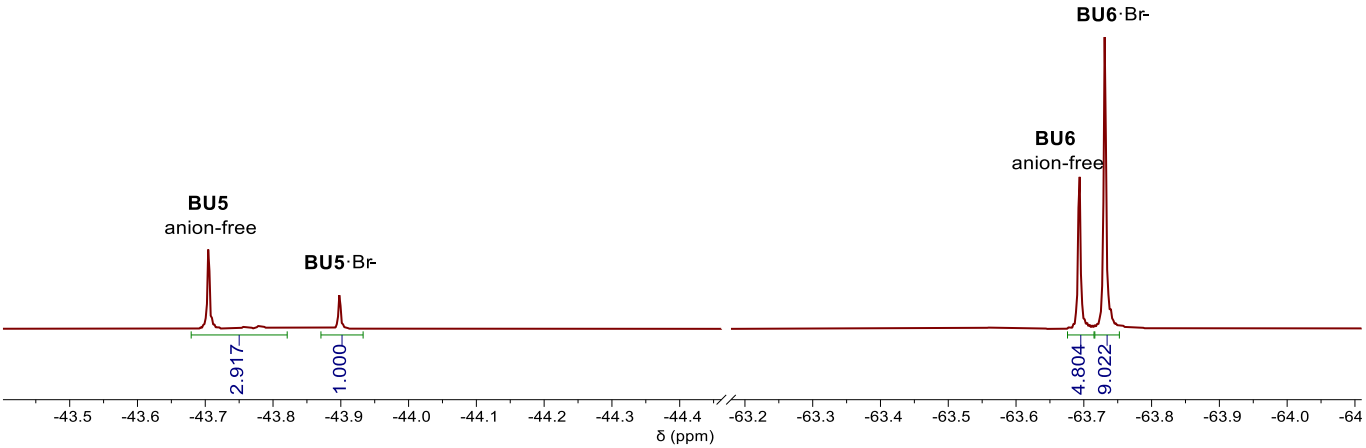


Figure S94: ^{19}F NMR spectrum (CD_3CN) of a competition experiment between **BU5** and **BU6** for Br^-, giving K_a(**BU6**)/K_a(**BU5**) = 5.48.

5. Molecular modelling

The calculations were done in Spartan '18, Version 1.4.4. Geometries of BU structures were optimized using semi-empirical method at PM6 level of theory.

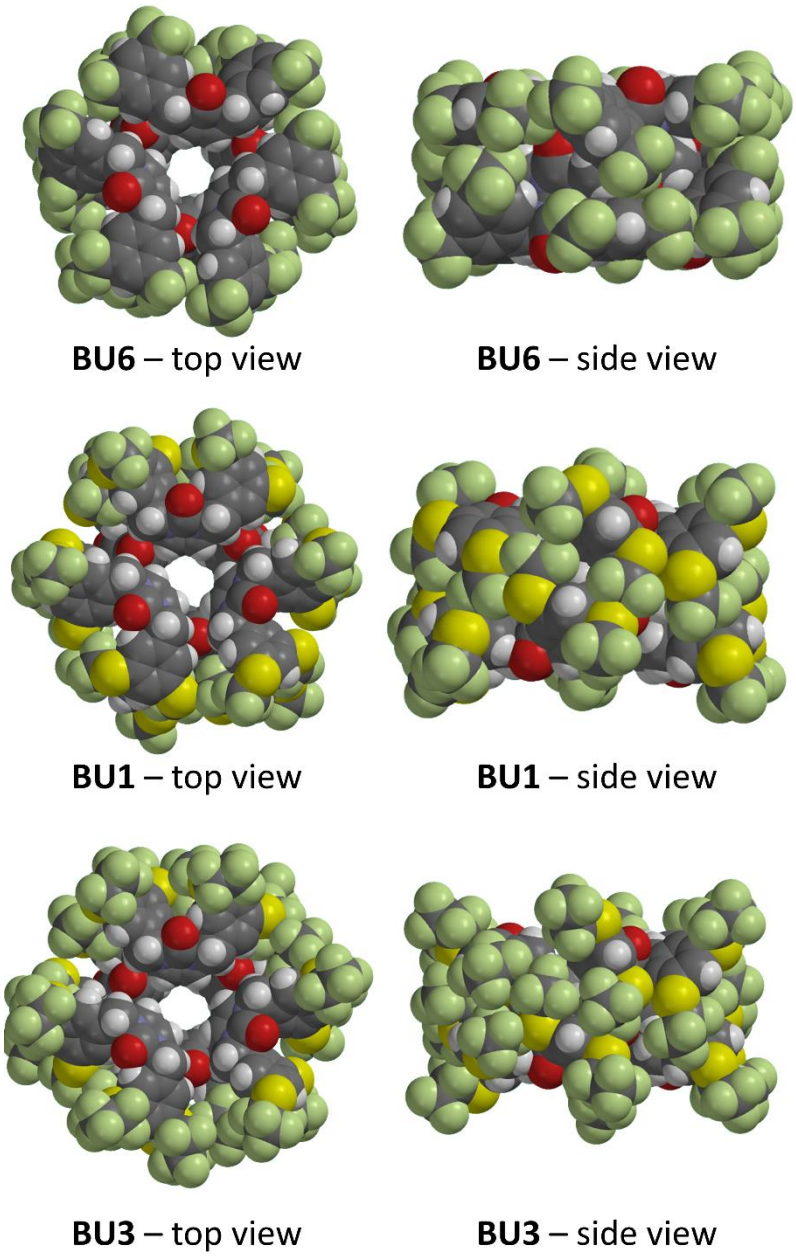


Figure S95: Space-filling models of **BU5** (top), **BU1** (middle) and **BU3** (bottom).

6. References

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