Supporting Information

Anionic Head Containing Oxacalix[2]arene[2]triazines: Synthesis and Anion-π Directed Self-assembly in Solution and Solid State

Rui-Bin Xu,[1,2] Qi-Qiang Wang,[1,2,*] Yu-Fei Ao,[1] Zhi-Yan Li,[1] Zhi-Tang Huang,[1] De-Xian Wang[1,2,*]

[1] Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[2] University of Chinese Academy of Sciences, Beijing 100049, China

Table of Contents

1. General information

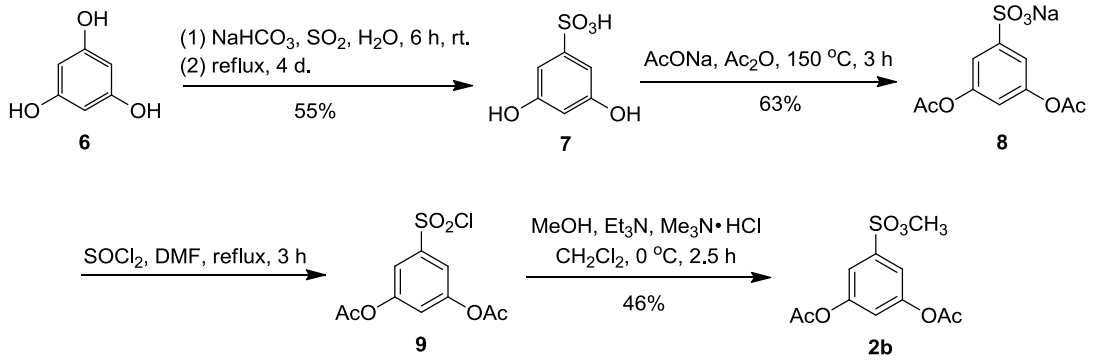
^{1}H and ^{13}C NMR spectra were recorded on 300, 400, 500 and 600 MHz NMR spectrometers. Chemical shifts are reported in ppm with either tetramethylsilane or the residual solvent as an internal standard. Melting points are uncorrected. Elemental analyses were performed with Vario ELIII and Carlo Erba 1106 analytical instruments. The fluorescence spectra were measured with a Hitachi F-7000 fluorescence spectrophotometer. All anhydrous solvents were dried according to standard procedures prior to use. All chemicals were obtained from commercial sources and used without further purification.

Fluorescence titration experiments were carried out with the concentration of oxacalix[2]arene[2]triazine being constant, spectral changes were recorded with the increase of anion concentrations (in tetraalkylammonium salts). The spectroscopic titration data were fitted by a Hyperquad 2003 program to calculate the association constants.

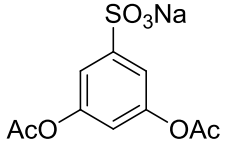
Colorless single crystal of **5a** was obtained by slowly cooling the hot saturated solution of **5a** in acetonitrile. Slow evaporation of the sample solutions from acetonitrile/toluene/hexane and dichloromethane/toluene/hexane afforded the colorless single crystals of **5b** and **5c** respectively.

2. Synthesis procedure

Scheme S1 Synthesis of **2b**



Synthesis of 8

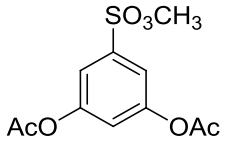


A mixture of 3,5-dihydroxybenzene sulfonic acid **7**[S1] (1 g, 5.30 mmol), sodium acetate (1.30 g, 15.90 mmol) and acetic anhydride (25 mL) was heated at reflux for 3 h, then cooled to room temperature. To the mixture was added ether/hexane (75

[S1] Ghosh, A. K.; Bilcer, G. M.; Devasamudram, T. *PCT Int. Appl.* **2003**, *224*.

mL/75 mL), the solids were collected by filtration and redissolved in methanol and purified with a column of silica gel (100-200 mesh, dichloromethane/methanol = 10:1) to afford the compound **8** as a light yellow solid (1.13 g, 78%): mp 195-196 ^{o}C; IR (KBr) 1765, 1441, 1199 cm^{-1}; ^{1}H NMR (400 MHz, d_6-DMSO, ppm) 7.22 (d, J = 2 Hz, 2H), 6.93 (t, J = 2 Hz, 1H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, d_6-DMSO, ppm) 168.9, 150.4, 150.1, 116.5, 115.9, 20.8; HRMS (ESI, positive): *m/z* Calcd. for $C_{10}H_{10}NaO_7S$ $[M+H]^+$ 297.00449, found 297.00394; Calcd. for $C_{10}H_9Na_2O_7S$ $[M+Na]^+$ 318.98644, found 318.98584.

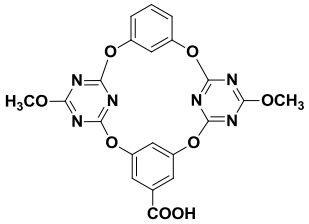
Synthesis of 2b



A mixture of compound **8** (296 mg, 1 mmol) and $SOCl_2$ (5 mL) was refluxed in the presence of DMF (0.1 mL) for 3 h. The resulting mixture was concentrated to afford the compound **9** which was directly used in the next step.

To a solution of triethylamine (0.76 mL, 5.14 mmol)、trimethylamine hydrochloride (325 mg, 3.42 mmol) and methanol (0.28 mL, 6.85 mmol) in anhydrous dichloromethane (30 mL) at 0^{o}C was added a solution of **9** (1 g, 3.42 mL) in anhydrous dichloromethane (10 mL). The reaction mixture was stirred for another 2.5 h, then washed with H_2O (30 mL×2) and brine (20 mL). The organic layer was dried with Na_2SO_4, concentrated *in vacuo* and the residue was purified by chromatography on silica gel (100-200 mesh, petroleum ether/ethyl acetate = 1:1) to yield pure compound **2b** as a light yellow solid (450 mg, 46% for the two steps): mp 101-102 ^{o}C; IR (KBr) 1774, 1368, 1179, 1130 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) 7.55 (d, J = 2 Hz, 2H), 7.26 (t, J = 2.2 Hz, 1H), 3.81 (s, 3H), 2.33 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) 168.4, 151.5, 137.0, 121.3, 118.9, 57.1, 21.1; HRMS (ESI, positive): *m/z* Calcd. for $C_{11}H_{12}NaO_7S$ $[M+Na]^+$ 311.02014, found 311.01970. Anal. Calcd. for $C_{11}H_{12}O_7S$: C, 45.83; H, 4.20; S, 11.12. Found: C, 45.78; H, 4.11; S, 10.99.

Synthesis of 3a

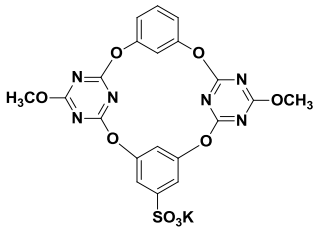


To a three-necked flask containing potassium carbonate (1.55 g, 11.2 mmol) and acetonitrile (400 mL) was added dropwise a mixed solution of trimer **1**[S2] (1.85 g, 4.68 mmol) and benzyl 3,5-dihydroxybenzoate **2a** (1.14 g, 4.68 mmol) in acetonitrile

[S2] Pan, S.; Wang, D.-X.; Zhao, L.; Wang, M.-X. *Tetrahedron* **2012**, *68*, 9464-9477.

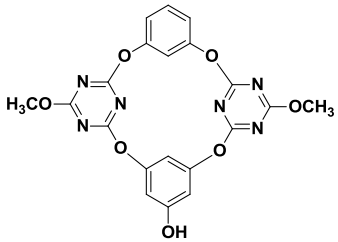
(200 mL) within 5 h. The mixture was stirred for another 2 h under reflux, then cooled to room temperature. After filtration, the filtrate was concentrated and the residue was dissolved in tetrahydrofuran/methanol (50 mL/50 mL). To this solution was added 10% Pd/C (500 mg, 0.2 equiv.). The mixture was stirred overnight at room temperature under H_2 (1 atm, balloon). The resulting mixture was filtered and the filtrate was concentrated. The residue was then purified by a column of silica gel (100-200 mesh, acetone/dichloromethane = 1:10) to afford the compound **3a** as a white solid (828 mg, 37%): mp 156-157 ^oC; IR (KBr) 3461, 1715, 1574, 1362 cm^{-1}; ^1H NMR (400 MHz, d_6-DMSO, ppm) 13.41 (br, s, 1H), 7.47 (d, J = 2.4 Hz, 2H), 7.37 (t, J = 2.2 Hz, 1H), 7.31 (t, J = 8 Hz, 1H), 7.04 (t, J = 2.2 Hz, 1H), 7.00-6.98 (dd, J_1 = 2.4 Hz, J_2 = 8 Hz, 2H), 4.03 (s, 6H); ^{13}C NMR (100 MHz, d_6-DMSO, ppm) 174.2, 172.6, 172.5, 165.5, 151.7, 151.6, 133.4, 130.4, 121.3, 119.7, 118.9, 116.4, 55.8; HRMS (ESI, negative): m/z Calcd. for $C_{21}H_{13}N_6O_8$ $[M-H]^-$ 477.07949, found 477.07779. Anal. Calcd. for $C_{21}H_{14}N_6O_8$ $0.1CH_2Cl_2$: C, 52.05; H, 2.94; N, 17.26. Found: C, 52.32; H, 3.16; N, 16.85.

Synthesis of 3b



A mixture of compound **2b** (50 mg, 0.17 mmol), trimer **1** (69 mg, 0.17 mmol), K_2CO_3 (144 mg, 1.05 mmol) and acetonitrile (50 mL) was heated at reflux for 2 h, then cooled to room temperature. The resulting mixture was filtered and the filtrate was concentrated and purified on a column of silica gel (100-200 mesh, dichloromethane/methanol = 10:1) to afford the compound **3b** as a white solid (17 mg, 18%): ^1H NMR (400 MHz, d_6-DMSO, ppm) 7.37 (t, J = 8.4 Hz, 1H), 7.11 (m, 4H), 7.02-7.00 (dd, J_1 = 1.6 Hz, J_2 = 8 Hz, 2H), 4.04 (s, 6H); ^{13}C NMR (100 MHz, d_6-DMSO, ppm) 174.1, 172.5, 172.4, 151.5, 150.8, 150.6, 130.6, 118.9, 116.6, 116.3, 115.7, 55.7; HRMS (ESI, negative): m/z Calcd. for $C_{20}H_{13}N_6O_9S$ $[M-K]^-$ 513.04647, found 513.04492.

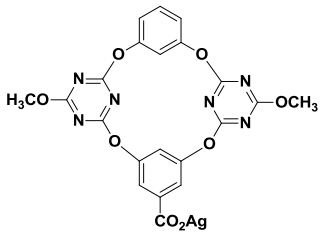
Synthesis of 3c



To a three-necked flask containing potassium carbonate (994 mg, 7.2 mmol) and

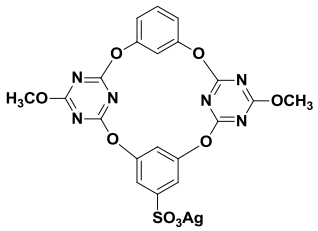
acetonitrile (400 mL) was added dropwise a solution of 5-(benzyloxy)-benzene-1,3-diol **2c** (648 mg, 3 mmol) and trimer **1** (1.85 g, 4.68 mmol) in acetonitrile (250 mL) under reflux within 5 h. The mixture was stirred for another 2 h, then cooled to room temperature. After filtration, the filtrate was concentrated, and then dissolved in tetrahydrofuran/methanol (50 mL/50 mL). To this solution was added 10% Pd/C (500 mg, 0.2 equiv.), stirred overnight at room temperature under H_2 (1 atm, balloon). After filtration, the filtrate was concentrated, and then purified on a column of silica gel (100-200 mesh, petroleum/ethyl acetate = 2:1) to afford the pure compound **3c** as a white solid (800 mg, 27% for the two steps): mp 207-208 ^{o}C; IR (KBr) 1570, 1430, 1363 cm^{-1}; ^{1}H NMR (400 MHz, d_6-DMSO) 10.04 (s, 1H), 7.38 (t, J = 8.2 Hz, 1H), 7.07 (t, J = 2.2 Hz, 1H), 7.04- 7.02 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 2H), 6.45 (t, J = 2 Hz, 1H), 6.35 (d, J = 2 Hz, 2H), 4.02 (s, 6H); ^{13}C NMR (100 MHz, d_6-DMSO) 174.1, 172.6, 172.5, 158.8, 152.1, 151.7, 130.4, 118.8, 116.5, 106.7, 106.0, 55.7; HRMS (ESI, negative): *m/z* Calcd. for $C_{20}H_{13}N_6O_7$ $[M-H]^-$ 449.08457, found 449.08472. Anal. Calcd. for $C_{20}H_{14}N_6O_7$ $0.5CH_2Cl_2$: C, 49.96; H, 3.07; N, 17.05. Found: C, 50.01; H, 3.12; N, 16.99.

Synthesis of 4a



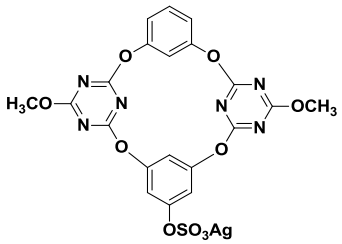
To a solution of **3a** (500 mg, 1.05 mmol) in anhydrous DMF (25 mL) was added sodium hydride (25.2 mg, 1.05 mmol). After stirring at room temperature for 1 h, the resulting mixture was filtered. To the filtrate was added a solution of silver nitrate (268 mg, 1.58 mmol) in water (30 mL). The mixture was stirred at room temperature for another 15 minutes, and the precipitates were collected by filtration to give the compound **4a** as a white solid (550 mg, 90%): ^{1}H NMR (400 MHz, d_6-DMSO, ppm) 7.40 (d, *J* = 2 Hz, 2H), 7.33 (t, *J* = 8 Hz, 1H), 7.12 (s, 1H), 7.05 (s, 1H), 6.98-7.01 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 2H), 4.04 (s, 6H); ^{13}C NMR (100 MHz, d_6-DMSO, ppm) 174.1, 172.6, 172.5, 167.6, 151.6, 151.1, 130.4, 119.4, 118.9, 118.1, 116.4, 55.7. HRMS (ESI, negative): *m/z* Calcd. for $C_{21}H_{13}N_6O_8$ $[M-Ag]^-$ 477.07949, found 477.07999; Calcd. for $C_{42}H_{26}AgN_{12}O_{16}$ $[2M-Ag]^-$ 1063.06373, found 1063.06587.

Synthesis of 4b



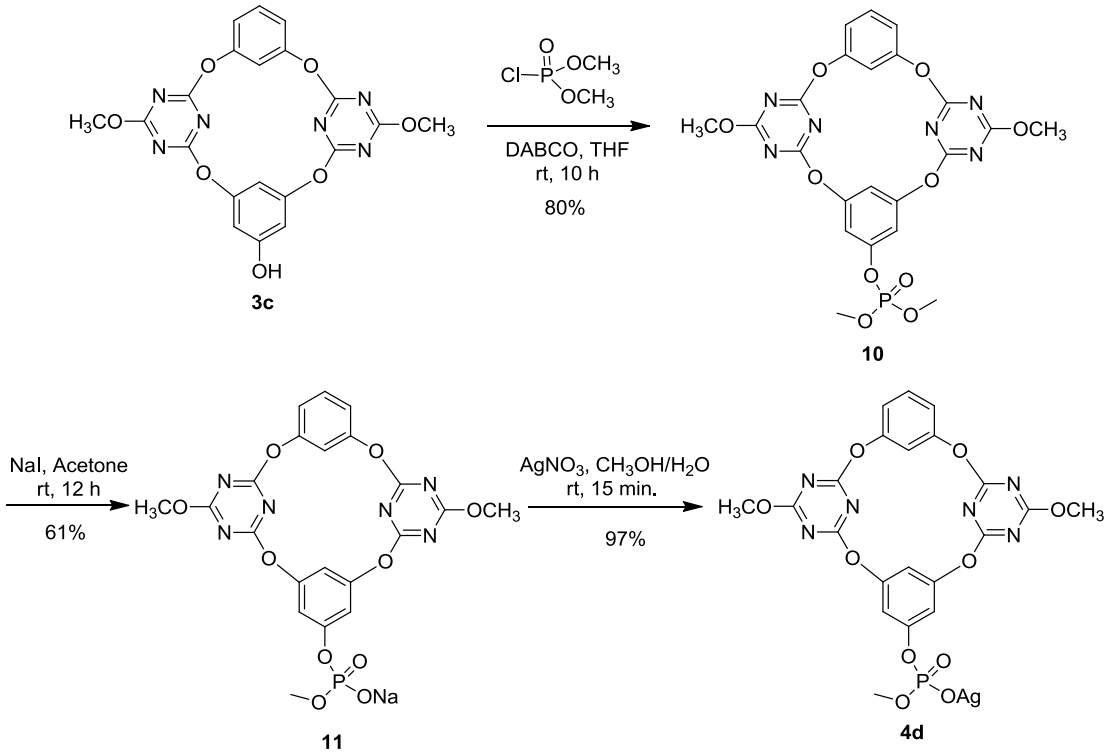
To a solution of **3b** (17 mg, 0.03 mmol) in methanol (10 mL) was added a solution of silver nitrate (44 mg, 0.26 mmol) in DMF (5 mL), the resulting mixture was stirred for 15 minutes at room temperature, then filtered to give compound **4b** (18 mg, 96%) as a white solid: ^{1}H NMR (400 MHz, d_6-DMSO, ppm) 7.37 (t, J = 8 Hz, 1H), 7.10-7.08 (m, 4H), 7.02-7.00 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 2H), 4.04 (s, 6H); ^{13}C NMR (100 MHz, d_6-DMSO, ppm) 174.1, 172.5, 172.4, 151.5, 150.8, 150.7, 55.7. HRMS (ESI, negative): *m/z* Calcd. for $C_{20}H_{13}N_6O_9S$ $[M\text{-}Ag]^-$ 513.04647, found 513.04608; Calcd. for $C_{40}H_{26}AgN_{12}O_{18}S_2$ $[2M\text{-}Ag]^-$ 1134.99770, found 1134.99744.

Synthesis of 4c

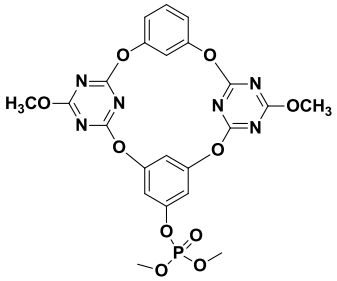


A solution of compound **3c** (150 mg, 0.33 mmol), pyridine sulfur trioxide (530 mg, 3.33 mmol), pyridine (0.27 mL, 3.33 mmol) and anhydrous acetonitrile (25 mL) was heated at reflux for 1 h. After cooling to room temperature, the solution was concentrated, and the residue was redissolved in methanol (30 mL). After filtration, to the filtrate was added a solution of silver nitrate (84 mg, 0.50 mmol) in DMF(10 mL). The mixture was stirred for 15 minutes, then filtered to give the compound **4c** as a white solid (185 mg. 88%): ^{1}H NMR (400 MHz, d_6-DMSO, ppm) 7.38 (t, J = 8 Hz, 1H), 7.11 (s, 1H), 7.04-7.02 (m, 2H), 6.81 (s, 2H), 6.77 (s, 1H), 4.03 (s, 6H); ^{13}C NMR (100 MHz, d_6-DMSO, ppm) 174.1, 172.6, 172.3, 154.8, 151.6, 151.4, 130.6, 118.9, 116.4, 110.4, 110.0, 55.7. HRMS (ESI, negative): *m/z* Calcd. for $C_{20}H_{13}N_6O_{10}S$ $[M\text{-}Ag]^-$ 529.04139, found 529.04161; Calcd. for $C_{40}H_{26}AgN_{12}O_{20}S_2$ $[2M\text{-}Ag]^-$ 1166.98753, found 1166.98807.

Scheme S2 Synthesis of phosphorylated tetraoxacalix[2]arene[2]triazine **4d**

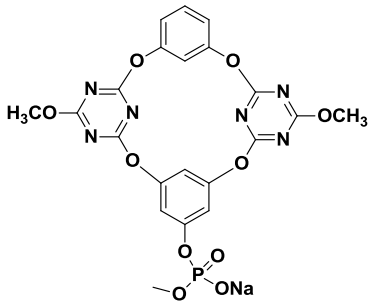


Synthesis of 10



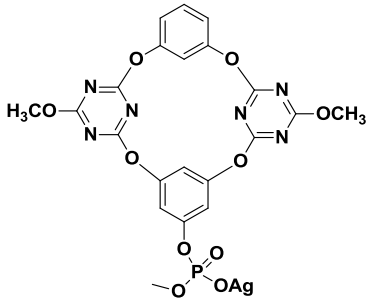
To a solution of **3c** (900 mg, 2 mmol) and 1,4-Diaza[2.2.2]bicyclooctane (DABCO, 336 mg, 3 mmol) in dry THF (25 mL) was added dropwise a solution of dimethyl chlorophosphate (435 mg, 3 mmol) in dry THF (5 mL). The resulting mixture was stirred for 10 h at room temperature, then poured into dichloromethane and washed with aq. HCl (5%) and brine. The organic layer was dried with Na_2SO_4 and filtered. The filtrate was concentrated and the residue was purified by silica gel chromatography (100-200 mesh, petroleum/ethyl acetate = 1 : 2) to give compound **10** as a white solid (889 mg, 80%): mp 111-112 ^{o}C; IR (KBr) 1586, 1427, 1385, 1361, 1148 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, ppm) 7.27 (t, J = 8 Hz, 1H), 6.90-6.88 (dd, J_1 = 2.5 Hz, J_2 = 8 Hz, 2H), 6.81-6.80 (dd, J_1 = 1Hz, J_2 = 2 Hz, 2H), 6.71 (t, J = 2.2 Hz, 1H), 6.58 (t, J = 1 Hz, 1H), 4.13 (s, 6H), 3.77 (d, J = 11.5 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO, ppm) 174.9, 173.5, 173.3, 152.4, 152.0, 151.6, 151.5, 130.4, 119.4, 116.7, 113.9, 111.8, 111.7, 56.1, 55.3, 55.2; HRMS (ESI, positive): m/z Calcd. for $C_{22}H_{20}N_6O_{10}P$ $[M+H]^+$ 559.09809, found 559.09785. Anal. Calcd. for $C_{22}H_{19}N_6O_{10}P$: C, 47.32; H, 3.43; N, 15.05. Found: C, 46.95; H, 3.43; N, 15.05.

Synthesis of 11



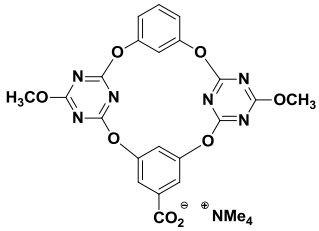
To a solution of **10** (65 mg, 0.1 mmol) in acetone (15 mL) was added sodium iodide (30 mg, 0.2 mmol) and the mixture was stirred at room temperature for 12 h. The solids were collected by filtration and washed by a large excess of ice acetone to give compound **11** as a white solid (38 mg, 61%): mp 235-236 ^{o}C; IR (KBr) 1586, 1429, 1386, 1363, 1150 cm^{-1}; ^{1}H NMR (500 MHz, d_6-DMSO, ppm) 7.37 (t, J = 8 Hz, 1H), 6.08 (t, J = 2 Hz, 1H), 7.03-7.01 (dd, J_1 = 2.5 Hz, J_2 = 8.5 Hz, 2H), 6.79 (d, J = 1.5 Hz, 1H), 6.63 (t, J = 0.5 Hz, 1H), 4.03 (s, 6H), 3.27 (d, J = 11 Hz, 3H); ^{13}C NMR (125 MHz, d_6-DMSO, ppm) 174.1, 172.6, 172.5, 155.7, 155.6, 151.6, 151.4, 130.5, 118.9, 116.5, 109.9, 109.8, 109.1, 55.7, 52.1, 52.0; HRMS (ESI, negative): *m*/*z* Calcd. for $C_{21}H_{16}N_6O_{10}P$ [M-Na]$^-$ 543.06655, found 543.06665.

Synthesis of 4d



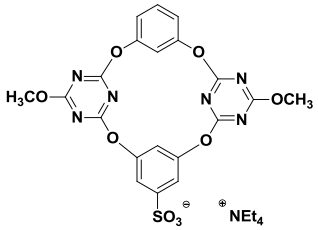
To a solution of **11** (250 mg, 0.44 mmol) in methanol (25 mL) was added a solution of silver nitrate (113 mg, 0.66 mmol) in water (5 mL), the mixture was stirred at room temperature for 15 minutes and filtered to give compound **4d** (279 mg, 97%) as a white solid: ^{1}H NMR (400 MHz, d_6-DMSO, ppm) 7.37 (t, J = 8 Hz, 1H), 7.07 (s, 1H), 7.04-7.02 (m, 2H), 6.81 (s, 1H), 6.68 (s, 1H), 4.03 (s, 6H), 3.32 (d, J = 10.8 Hz, 3H); ^{13}C NMR (100 MHz, d_6-DMSO, ppm) 174.1, 172.6, 172.4, 151.6, 151.5, 130.5, 118.9, 116.5, 110.1, 110.0, 109.6, 55.7, 52.4, 52.3. HRMS (ESI, negative): *m/z* Calcd. for $C_{21}H_{16}N_6O_{10}P$ [M-Ag]$^-$ 543.06655, found 543.06704; Calcd. for $C_{42}H_{32}AgN_{12}O_{20}P_2$ [2M-Ag]$^-$ 1195.03786, found 1195.03947.

Synthesis of 5a



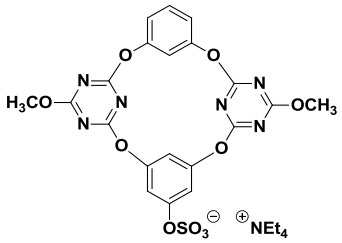
The mixture of compound **4a** (550 mg, 0.94 mmol) and tetramethylammonium chloride (94 mg, 0.86 mmol) in acetonitrile (250 mL) was stirred at room temperature for 10 h. After filtration, the filtrate was concentrated and recrystallized from dichloromethane and hexane to give pure compound **5a** as a white solid (400 mg, 77%): mp 218-219 ^{o}C; IR (KBr) 1568, 1485, 1361 cm^{-1}; ^{1}H NMR (500 MHz, d_3-CD_3CN, ppm) 7.39 (d, J = 2.5 Hz, 2H), 7.33 (t, J = 8 Hz, 1H), 6.95-6.93 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 2H), 6.87 (t, J = 2.2 Hz, 1H), 6.75 (t, J = 2.5 Hz, 1H), 4.05 (s, 6H); ^{13}C NMR (125 MHz, d_3-CD_3CN, ppm) 175.7, 174.4, 174.1, 167.4, 153.0, 152.1, 146.7, 131.3, 120.0, 119.7, 117.8, 117.0, 56.4, 56.0; HRMS (ESI, negative): m/z Calcd. for $C_{21}H_{13}N_6O_8$ $[M\text{-}NMe_4]^-$ 477.07949, found 477.07941. Anal. Calcd. for $C_{21}H_{14}N_6O_8$ $0.25CH_2Cl_2$: C, 52.95; H, 4.49; N, 17.12. Found: C, 52.68; H, 4.79; N, 17.47.

Synthesis of 5b



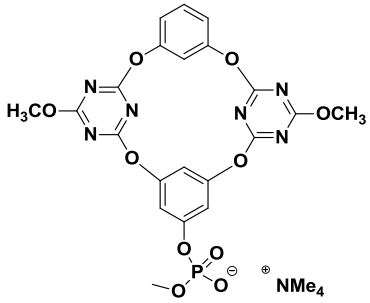
Compound **4b** (91 mg, 0.17 mmol) and tetraethylammonium chloride (26 mg, 0.16 mmol) were dissolved in acetonitrile/methanol (20 mL/20 mL). The resulting solution was stirred at room temperature for 3 h. After filtration, the filtrate was concentrated and recrystallized from dichloromethane/hexane to give pure compound **5b** as a white solid (66 mg, 60%): mp 231-232 ^{o}C; IR (KBr) 1573, 1427, 1385, 1361 cm^{-1}; ^{1}H NMR (500 MHz, d_6-DMSO, ppm) 7.37 (t, J = 8 Hz, 1H), 7.11-7.08 (m, 4H), 7.02-7.00 (dd, J_1 = 2.5 Hz, J_2 = 8 Hz, 2H), 4.04 (s, 6H), 3.20 (q, J = 22 Hz, 8H), 1.17-1.14 (m, 12H); ^{13}C NMR (100 MHz, d_6-DMSO, ppm) 174.1, 172.5, 172.4, 151.5, 150.8, 150.7, 130.6, 118.9, 116.5, 116.3, 115.7, 55.7, 51.4, 7.1; HRMS (ESI, negative): m/z Calcd. for $C_{20}H_{13}N_6O_9S$ $[M\text{-}NEt_4]^-$ 513.04647, found 513.04602. Anal. Calcd. for $C_{28}H_{33}N_7O_9S \cdot H_2O$: C, 50.82; H, 5.33; N, 14.82, S, 4.85. Found: C, 51.19; H, 5.28; N, 14.88, S, 4.77.

Synthesis of 5c



Compound **4c** (170 mg, 0.27 mmol) and tetraethylammonium chloride (40 mg, 0.24 mmol) were dissolved in acetonitrile/methanol (20 mL/20 mL). The mixture was stirred for 3 h at room temperature. After filtration, the filtrate was concentrated and recrystallized from dichloromethane/hexane to afford pure compound **5c** as a white solid (116 mg, 66%): mp 228-229 ^{o}C; IR (KBr) 1574, 1428, 1385, 1361 cm^{-1}; ^{1}H NMR (400 MHz, d_6-DMSO, ppm) 7.38 (t, J = 8 Hz, 1H), 7.10 (t, J = 2.2 Hz, 1H), 7.04-7.01 (dd, J_1 = 2.4 Hz, J_2 = 8 Hz, 2H), 6.80 (d, J = 2 Hz, 2H), 6.76 (t, J = 2 Hz, 1H), 4.03 (s, 6H); ^{13}C NMR (100 MHz, d_6-DMSO, ppm) 174.1, 172.6, 172.4, 154.8, 151.6, 151.4, 130.6, 118.9, 116.4, 110.4, 109.9, 55.7, 51.4, 7.0; HRMS (ESI, negative): m/z Calcd. for $C_{20}H_{13}N_6O_{10}S$ [M-NEt_4]$^-$ 529.04139, found 529.04127. Anal. Calcd. for $C_{28}H_{33}N_7O_{10}S$ $0.5H_2O$: C, 50.29; H, 5.13; N, 14.66, S, 4.80. Found: C, 50.01; H, 5.06; N, 14.61, S, 4.74.

Synthesis of 5d



Compound **4d** (300 mg, 0.46 mmol) and tetramethylammonium chloride (46 mg, 0.42 mmol) were dissolved in acetonitrile/methanol (20 mL/20 mL) and the mixture was stirred at room temperature for 3 h. After filtration, the filtrate was concentrated and recrystallized from dichloromethane/hexane to give pure compound **5d** as a white solid (185 mg, 65%): mp 195-196 ^{o}C; IR (KBr) 1585, 1574, 1428, 1385, 1362, 1150 cm^{-1}; ^{1}H NMR (500 MHz, d_6-DMSO, ppm) 7.37 (t, J = 8 Hz, 1H), 7.08 (s, 1H), 7.03-7.01 (dd, J_1 = 2 Hz, J_2 = 8 Hz, 2H), 6.78 (d, J = 1 Hz, 1H), 6.60 (s, 1H), 4.02 (s, 6H), 3.23 (d, J = 11 Hz, 3H), 3.10 (s, 12H); ^{13}C NMR (125 MHz, d_6-DMSO, ppm) 174.1, 172.6, 172.5, 155.9, 155.8, 151.6, 151.4, 130.5, 118.9, 116.5, 109.8, 108.8, 109.1, 55.7, 54.4, 54.3, 52.0, 51.9; HRMS (ESI, negative): m/z Calcd. for $C_{21}H_{16}N_6O_{10}P$ [M-NMe_4]$^-$ 543.06655, found 543.06595. Anal. Calcd. for $C_{25}H_{28}N_7O_{10}P$ $2.2H_2O$: C, 45.69; H, 4.97; N, 14.92. Found: C, 45.36; H, 4.93; N, 14.85.

3. Spectroscopic titrations

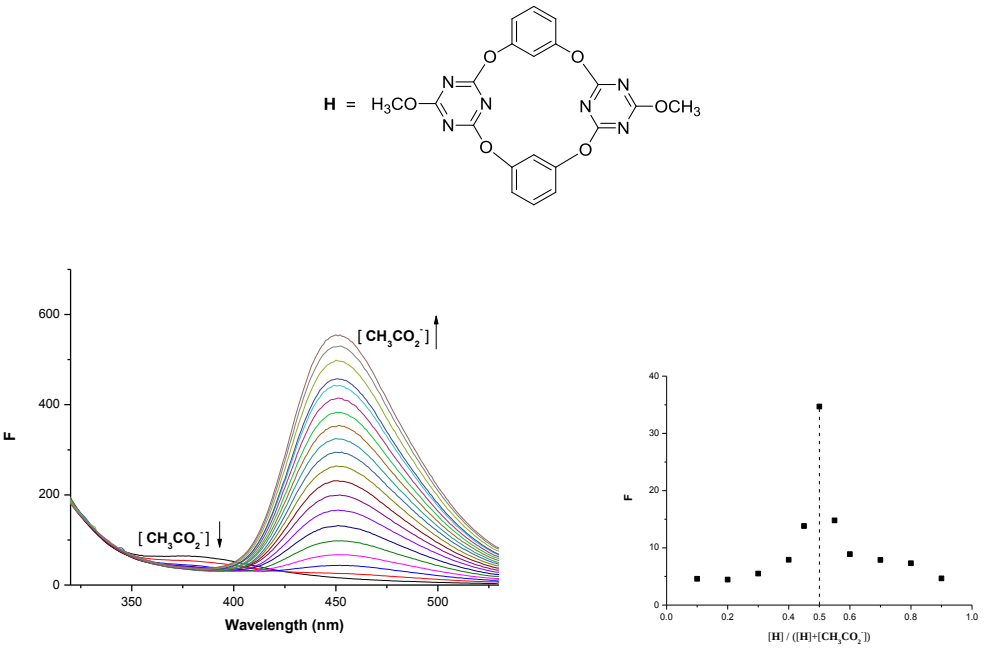


Figure S1. Left: Fluorescence titration of **H** (2.00×10^{-4} M in 2 mL acetonitrile) upon the addition of tetrabutylammonium acetate (0, 0.04, 0.08, 0.12, 0.16, 0.20, 0.24, 0.28, 0.32, 0.36, 0.40, 0.44, 0.48, 0.52, 0.56, 0.60, 0.64, 0.72, 0.8, 0.88, 0.96 $\times10^{-4}$ M), respectively. The excitation wavelength was 278 nm and the excitation and emission slits were set at 10 nm. Right: Job's plot of the complex of **H** and tetrabutylammonium acetate with a total concentration being 5.30×10^{-4} M.
Calculated association constant is 9598 M^{-1}.

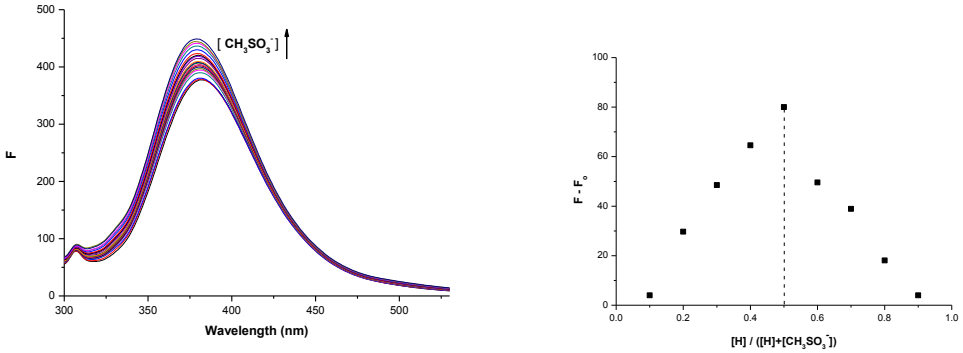


Figure S2. Left: Fluorescence titration of **H** (5.00×10^{-4} M in 2 mL acetonitrile) upon the addition of tetraethylammonium methanesulfonate (0, 0.40, 0.50, 0.80, 0.90, 1.00, 1.10, 1.20, 1.30, 1.40, 1.50, 1.60, 1.70, 1.90, 2.10, 2.30, 2.60, 2.90, 3.20, 3.50 $\times10^{-3}$ M), respectively. The excitation wavelength was 278 nm and the excitation and emission slits were set at 10 nm. Right: Job's plot of the complex of **H** and tetraethylammonium methanesulfonate with a total concentration being 5.00×10^{-4} M.
Calculated association constant is 1089 M^{-1}.

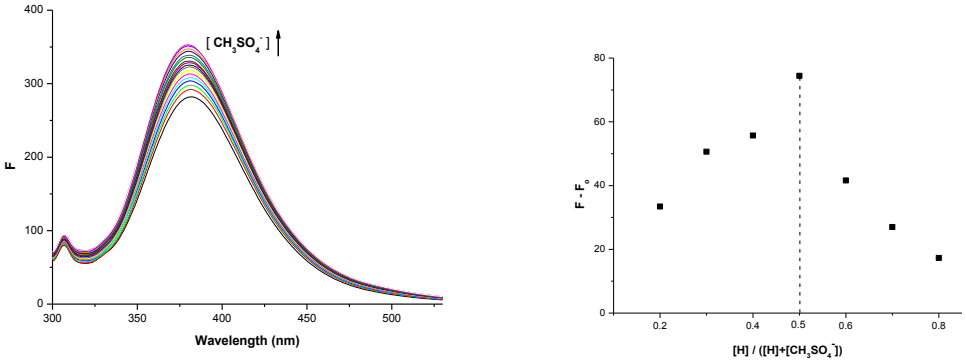


Figure S3. Left: Fluorescence titration of **H** (5.00×10^{-4} M in 2 mL acetonitrile) upon the addition of tetrabutylammonium methylsulfate (0, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.00, 1.10, 1.20, 1.30, 1.40, 1.50, 1.60, 1.70 $\times10^{-3}$ M), respectively. The excitation wavelength was 278 nm and the excitation and emission slits were set at 10 nm. Right: Job's plot of the complex of **H** and tetrabutylammonium methylsulfate with a total concentration being 5.00×10^{-4} M.
Calculated association constant is 2839 M^{-1}.

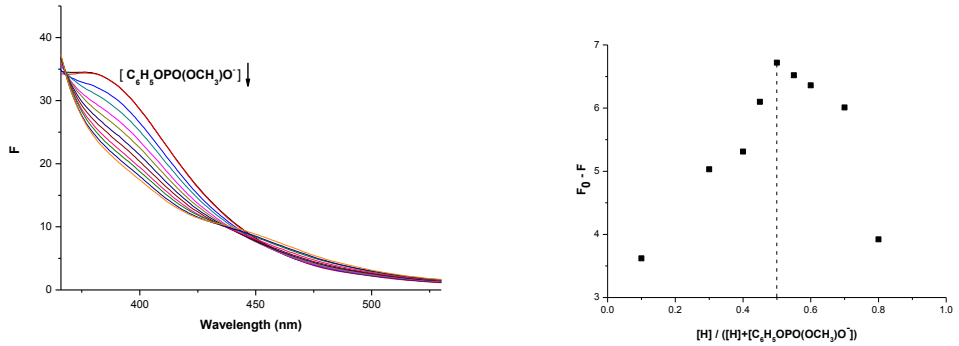


Figure S4. Left: Fluorescence titration of **H** (2.00×10^{-4} M in 2 mL acetonitrile) upon the addition of tetramethylammonium methylphenylphosphate (0, 0.24, 0.44, 0.54, 0.64, 0.74, 0.84, 0.94, 1.04, 1.14, 1.24, 1.34, 1.44, 1.54 $\times10^{-3}$ M), respectively. The excitation wavelength was 278 nm and the excitation and emission slits were set at 10 nm. Right: Job's plot of the complex of **H** and tetramethylammonium methylphenylphosphate with a total concentration being 2.00×10^{-4} M.
Calculated association constant is 1131 M^{-1}.

4. Fluorescent spectra of 5a-5d

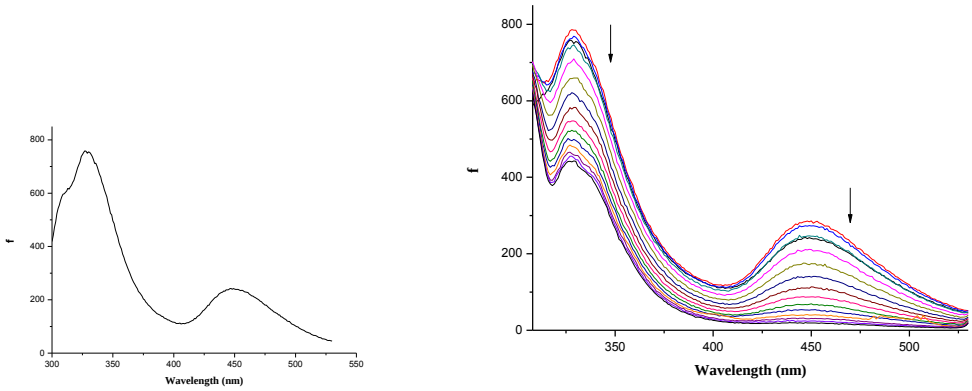


Figure S5. Fluorescent spectroscopy of **5a.** Left: 10^{-3} M in CH_3CN. Right: Fluorescent intensity changes in the range of 1.0×10^{-3} to 1.3×10^{-5} M, ex = 278 nm.

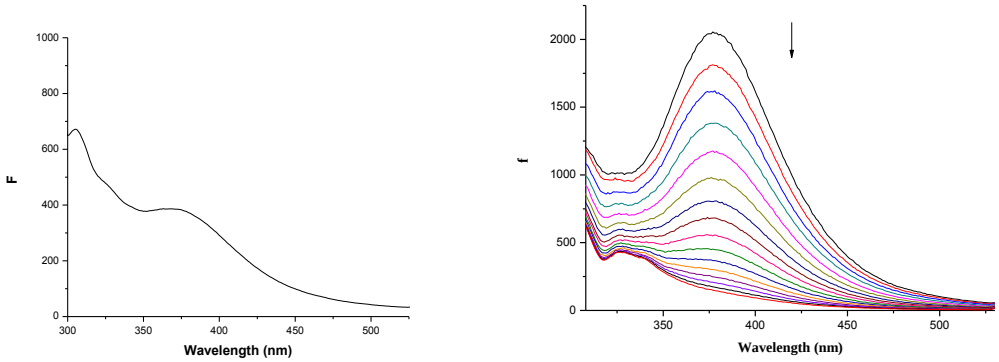


Figure S6. Fluorescent spectroscopy of **5b.** Left: 10^{-3} mol/L in CH_3CN. Right: Fluorescent intensity changes in the range of 1.0×10^{-3} to 1.3×10^{-5} M, ex = 278 nm.

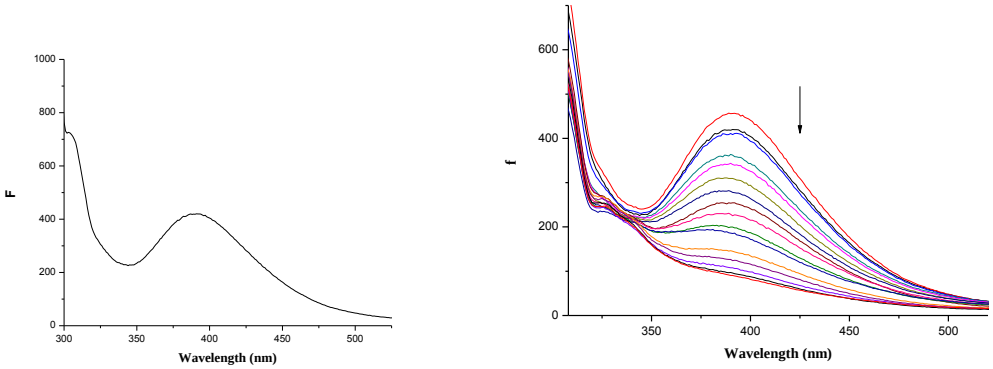


Figure S7. Fluorescent spectroscopy of **5c.** Left: 10^{-3} mol/L in CH_3CN. Right: Fluorescent intensities change in the range of 1.0×10^{-3} to 1.3×10^{-5} M, ex = 278 nm.

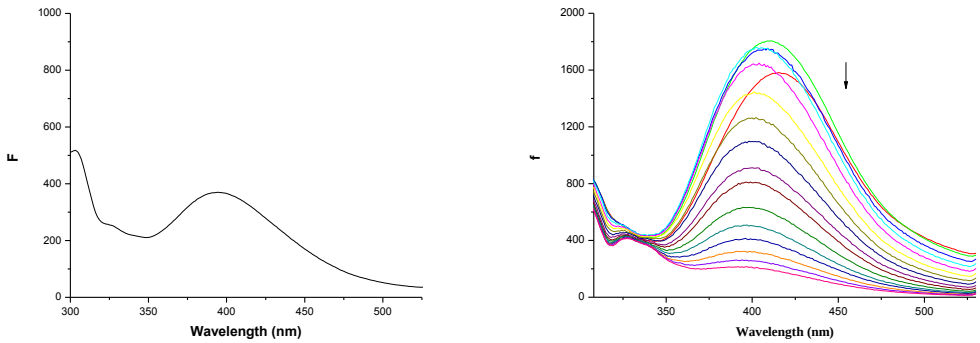


Figure S8. Fluorescent spectroscopy of **5d.** Left: 10^{-3} mol/L in CH_3CN. Right: Fluorescent intensity changes in the range of 1.0×10^{-3} to 1.3×10^{-5} M, ex = 278 nm.

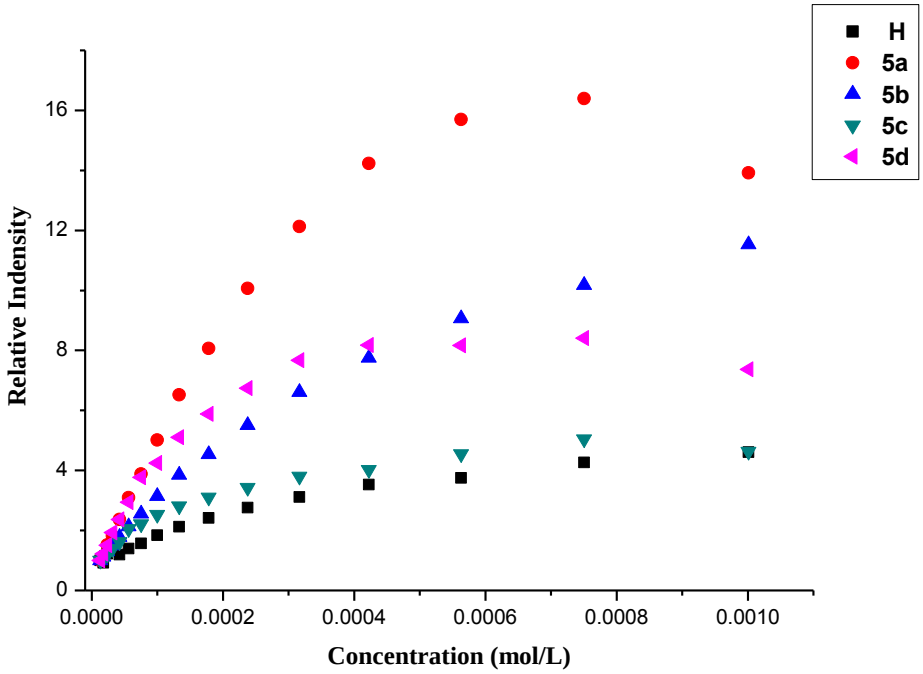


Figure S9. Relative fluorescent intensities of **5a-d** and **H** at different concentrations ranging from 1.0×10^{-3} to 1.3×10^{-5} M. The fluorescent intensities for all the compounds at the initial concentrations of 1.3×10^{-5} M were normalized.

5. Variable temperature and concentration ^{1}H NMR spectra of 5a-d

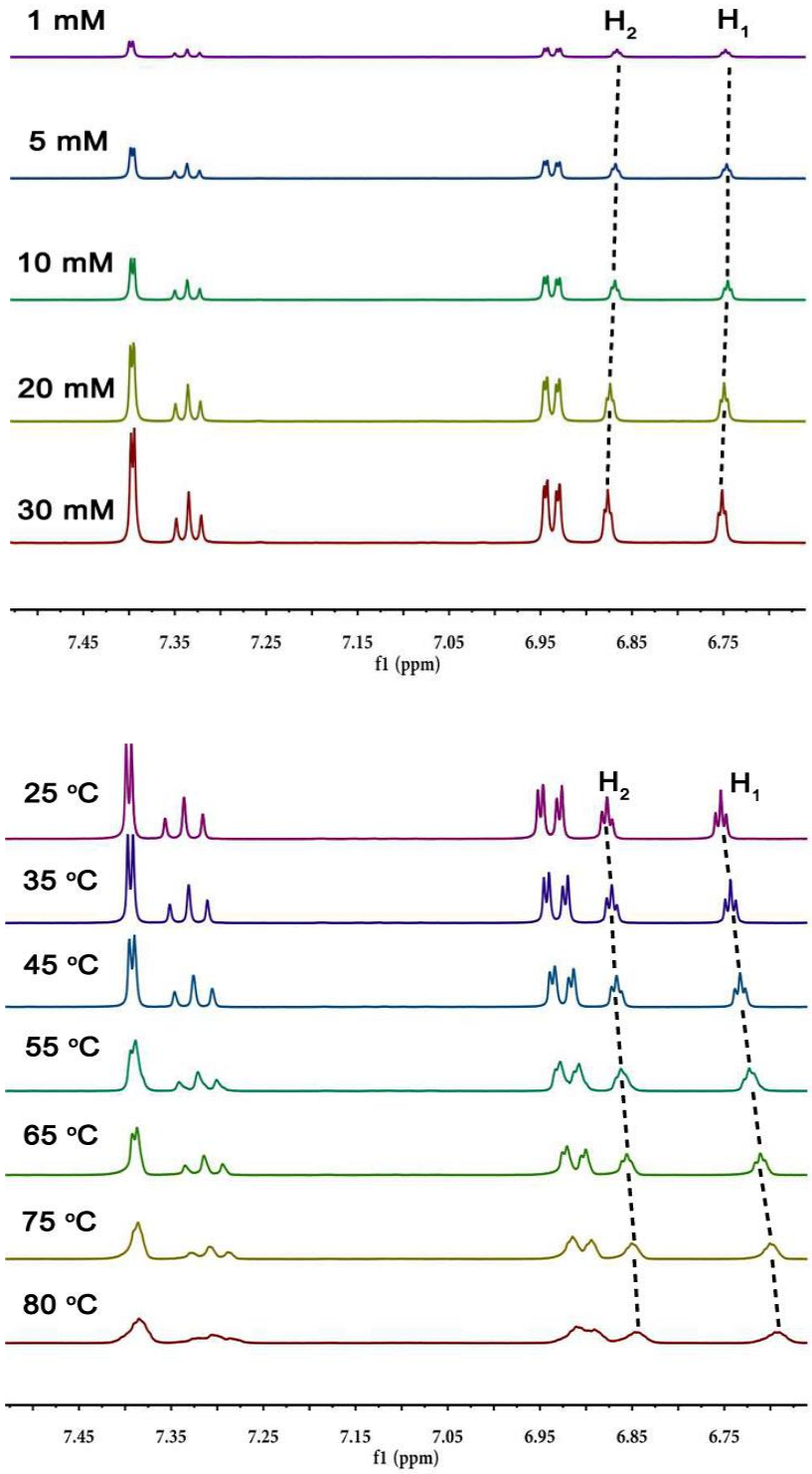


Figure S10. ^{1}H NMR spectra of **5a** in CD_3CN. Top, variable concentrations (298 K). Bottom, variable temperatures (20 mM).

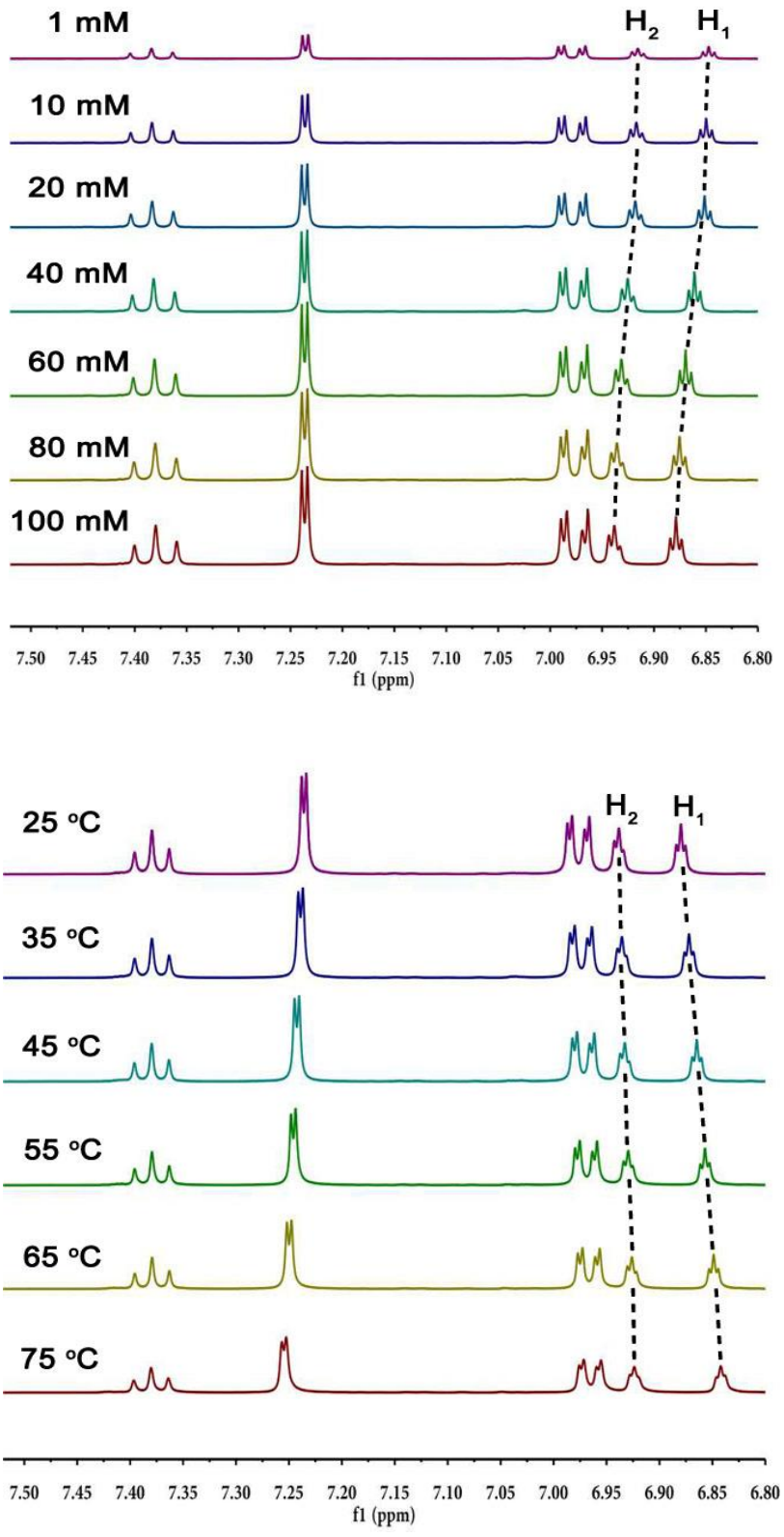


Figure S11. ^{1}H NMR spectra of **5b** in CD_3CN. Top, variable concentrations (298 K). Bottom, variable temperatures (100 mM).

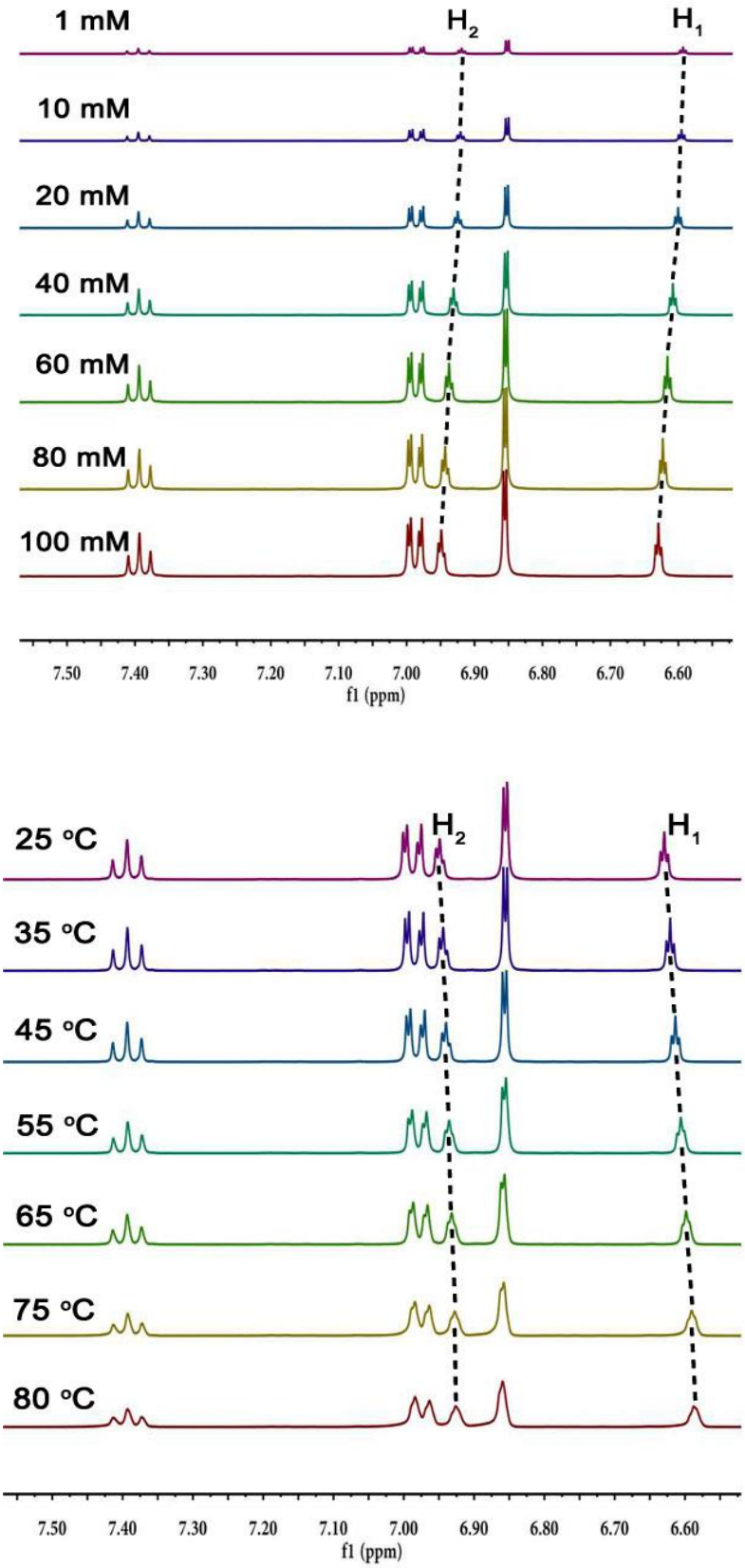


Figure S12. ^{1}H NMR spectra of **5c** in CD_3CN. Top, variable concentrations (298 K). Bottom, variable temperatures (100 mM).

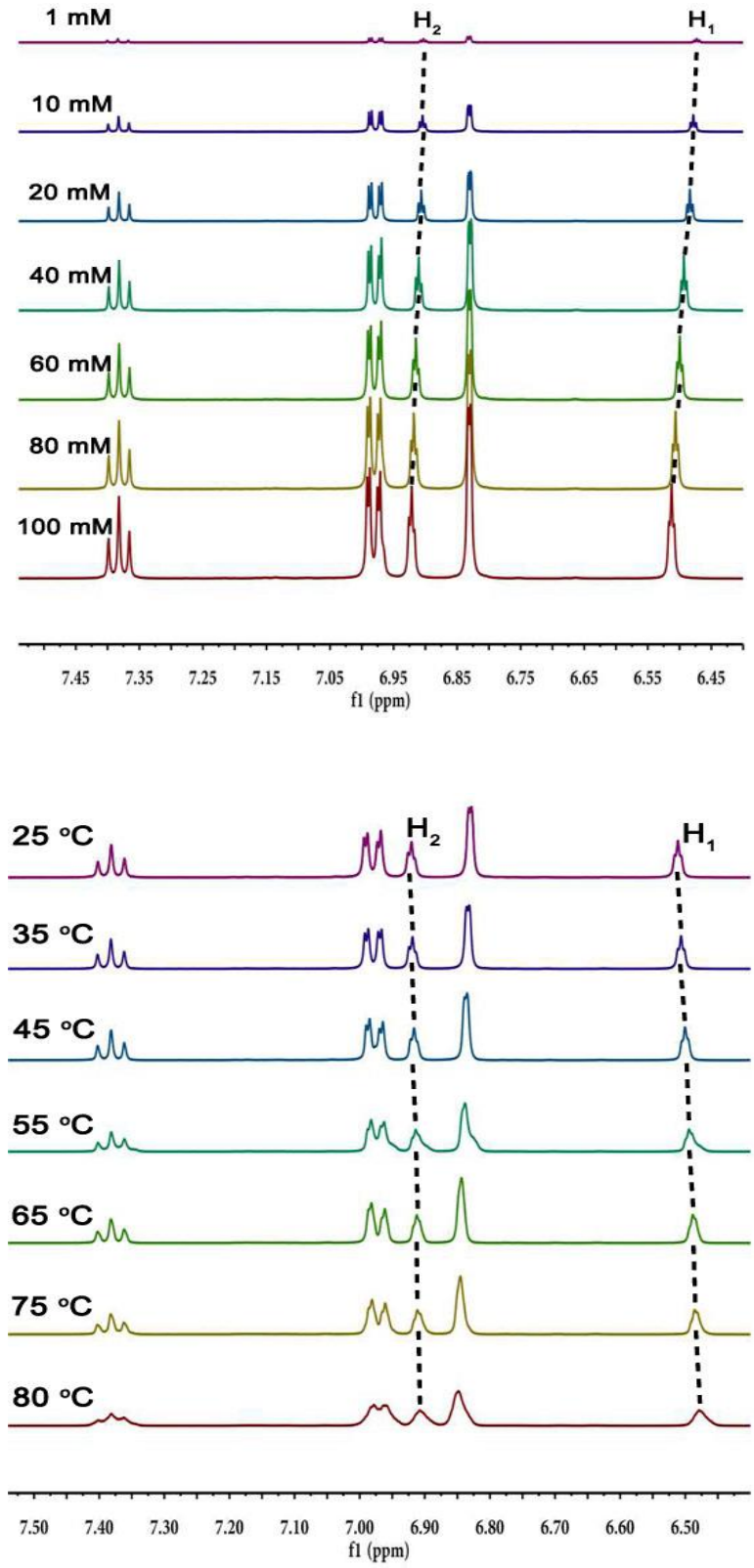


Figure S13. ^{1}H NMR spectra of **5d** in CD_3CN. Top, variable concentrations (298 K). Bottom, variable temperatures (100 mM).

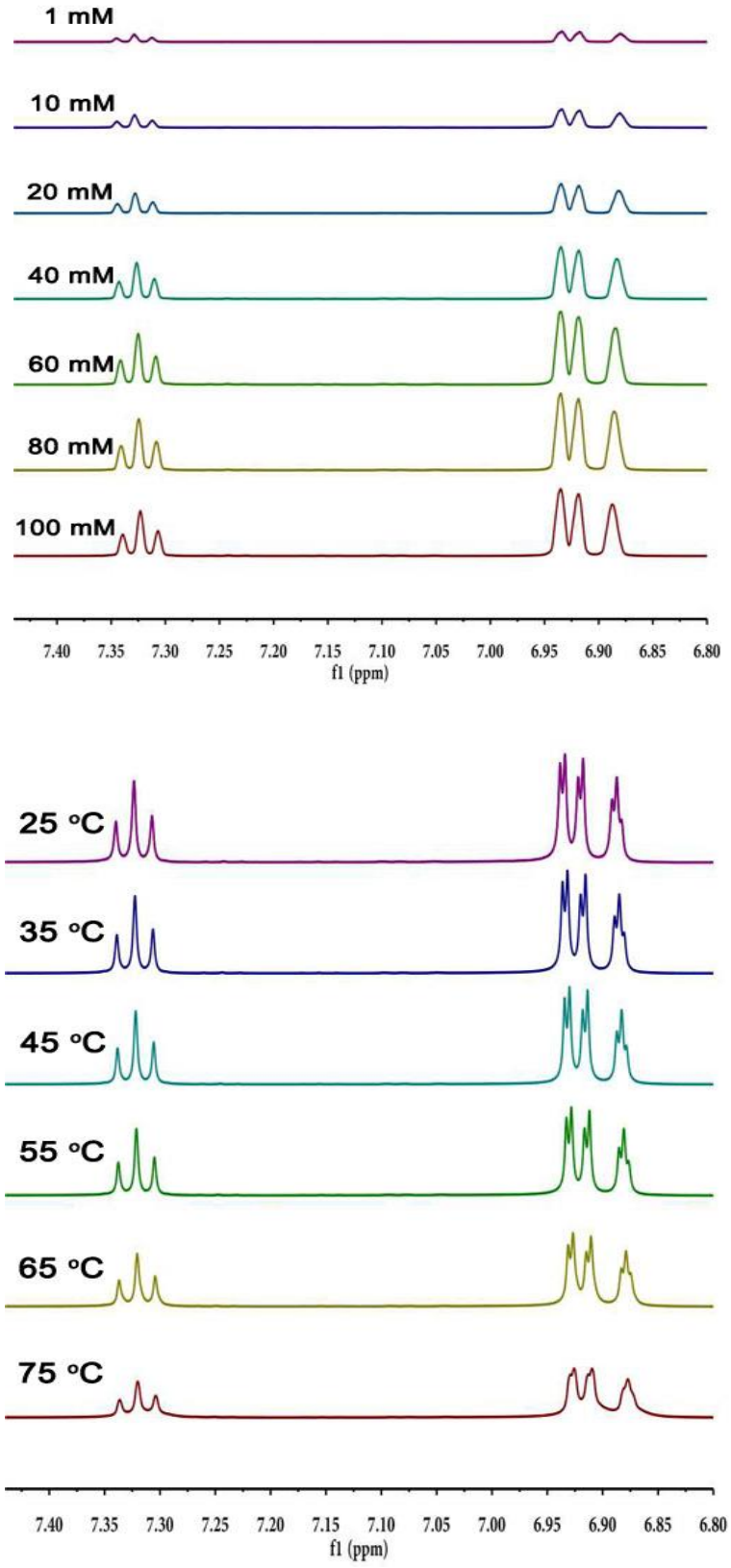


Figure S14. ^{1}H NMR spectra of **H** in CD_3CN. Top, variable concentrations (298 K). Bottom, variable temperatures (100 mM).

6. DOSY results for 5a-d at variable concentrations

Table S1. Diffusion coefficients of **5a** and the solvent CD_2Cl_2 at different concentrations

Concentration (mM)	D(**5a**) (10^{-10} m^2 S^{-1})	D(CH_2Cl_2) (10^{-10} m^2 S^{-1})	D(**5a**)/D(CH_2Cl_2)
0.50	7.42	27.83	0.27
1.00	7.02	27.80	0.25
2.50	6.99	27.76	0.25
5.00	6.85	28.08	0.24
10.00	6.69	27.72	0.24

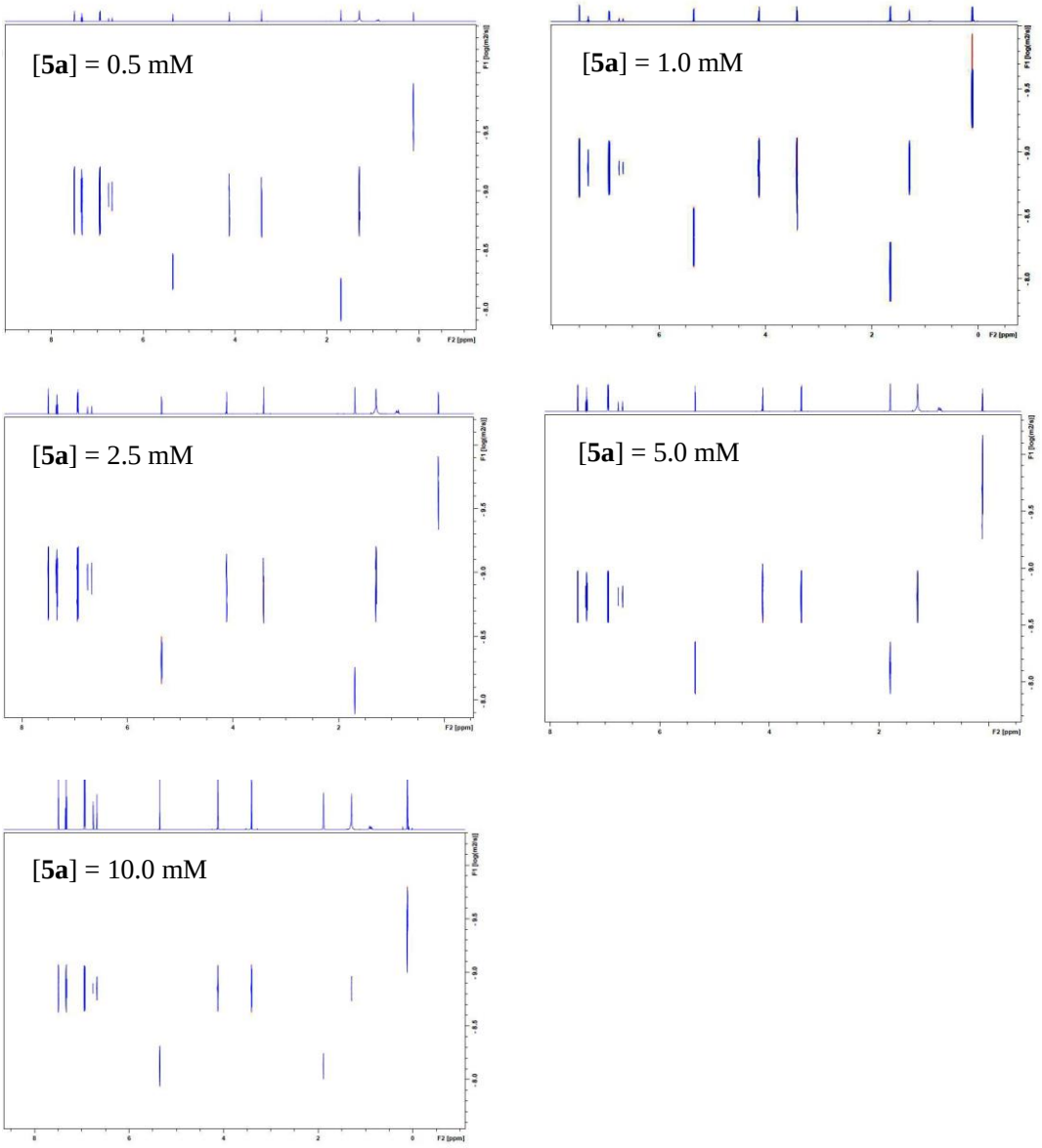


Figure S15. DOSY spectra of **5a** at different concentrations (600 MHz, CD_2Cl_2).

Table S2. Diffusion coefficients of **5b** and the solvent CD_2Cl_2 at different concentrations

Concentration (mM)	D(**5b**) (10^{-10} m^2 S^{-1})	D(CH_2Cl_2) (10^{-10} m^2 S^{-1})	D(**5b**)/D(CH_2Cl_2)
1.00	6.60	27.92	0.24
10.00	6.33	30.40	0.21
20.00	6.19	29.84	0.20
30.00	6.08	34.66	0.18
40.00	5.81	36.89	0.16

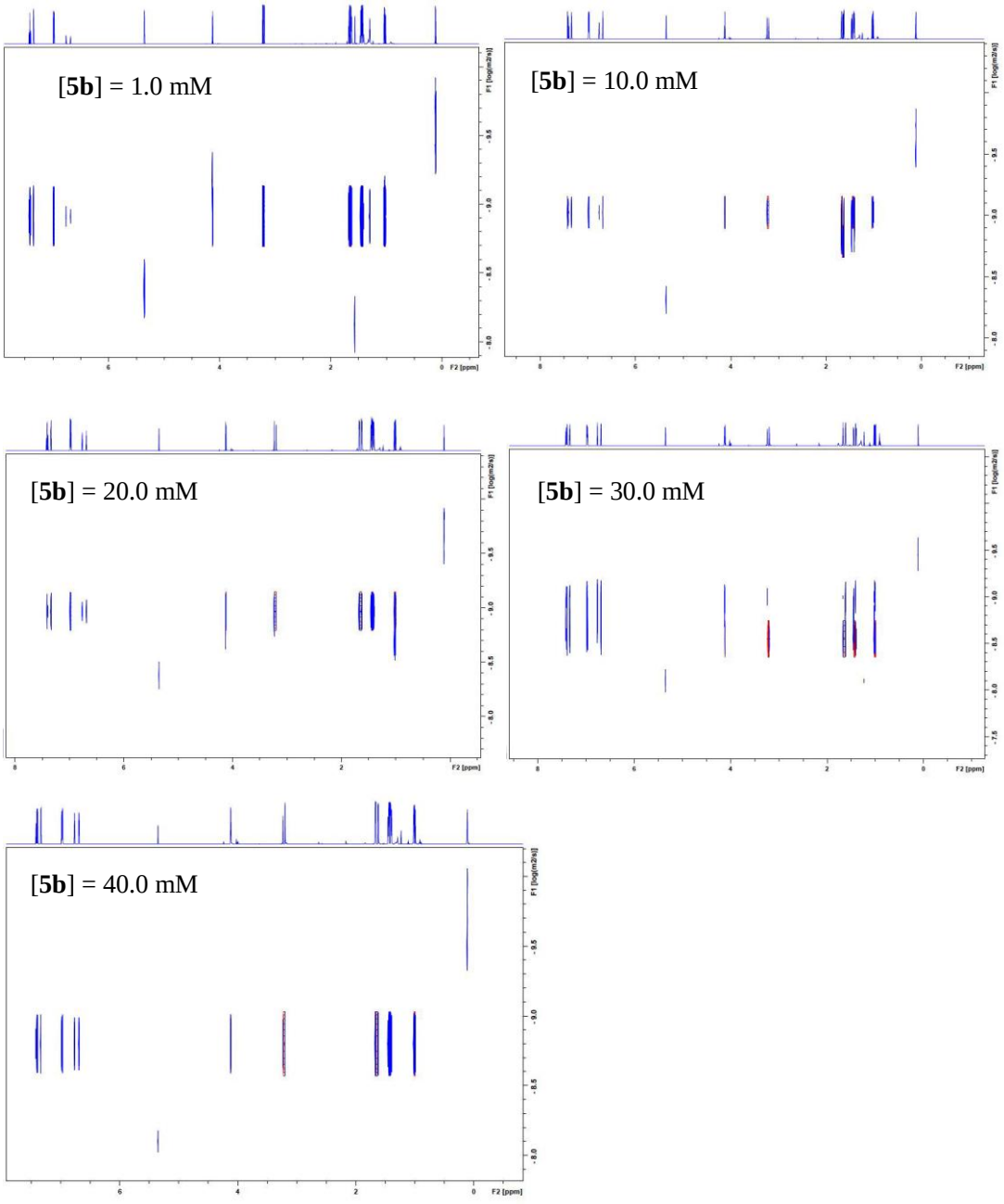


Figure S16. DOSY spectra of **5b** at different concentrations (600 MHz, CD_2Cl_2).

Table S3. Diffusion coefficients of **5c** and the solvent CD_2Cl_2 at different concentrations

Concentration (mM)	D(**5c**) (10^{-10} m^2 S^{-1})	D(CH_2Cl_2) (10^{-10} m^2 S^{-1})	D(**5c**)/D(CH_2Cl_2)
1.00	13.45	37.80	0.36
5.00	10.62	39.02	0.27
10.00	10.36	38.77	0.27
20.00	10.05	39.07	0.26
30.00	10.05	40.33	0.25

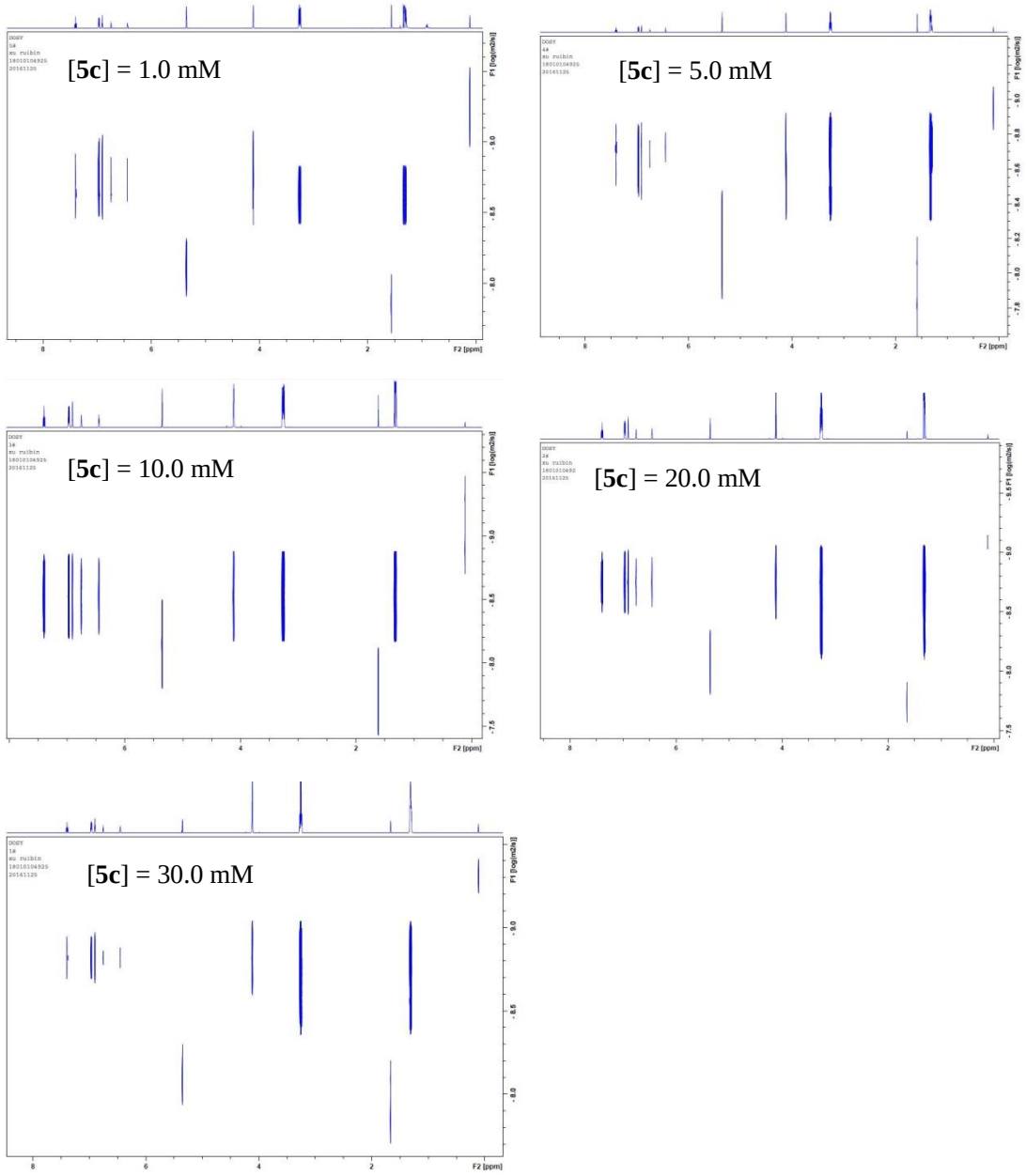


Figure S17. DOSY spectra of **5c** at different concentrations (600 MHz, CD_2Cl_2).

Table S4. Diffusion coefficients of **5d** and the solvent CD_2Cl_2 at different concentrations

Concentration (mM)	D(**5d**) (10^{-10} m^2 S^{-1})	D(CH_2Cl_2) (10^{-10} m^2 S^{-1})	D(**5d**)/D(CH_2Cl_2)
1.00	6.29	29.44	0.22
5.00	6.03	29.05	0.21
10.00	6.01	29.51	0.20
20.00	5.57	34.61	0.16
30.00	5.33	45.15	0.12

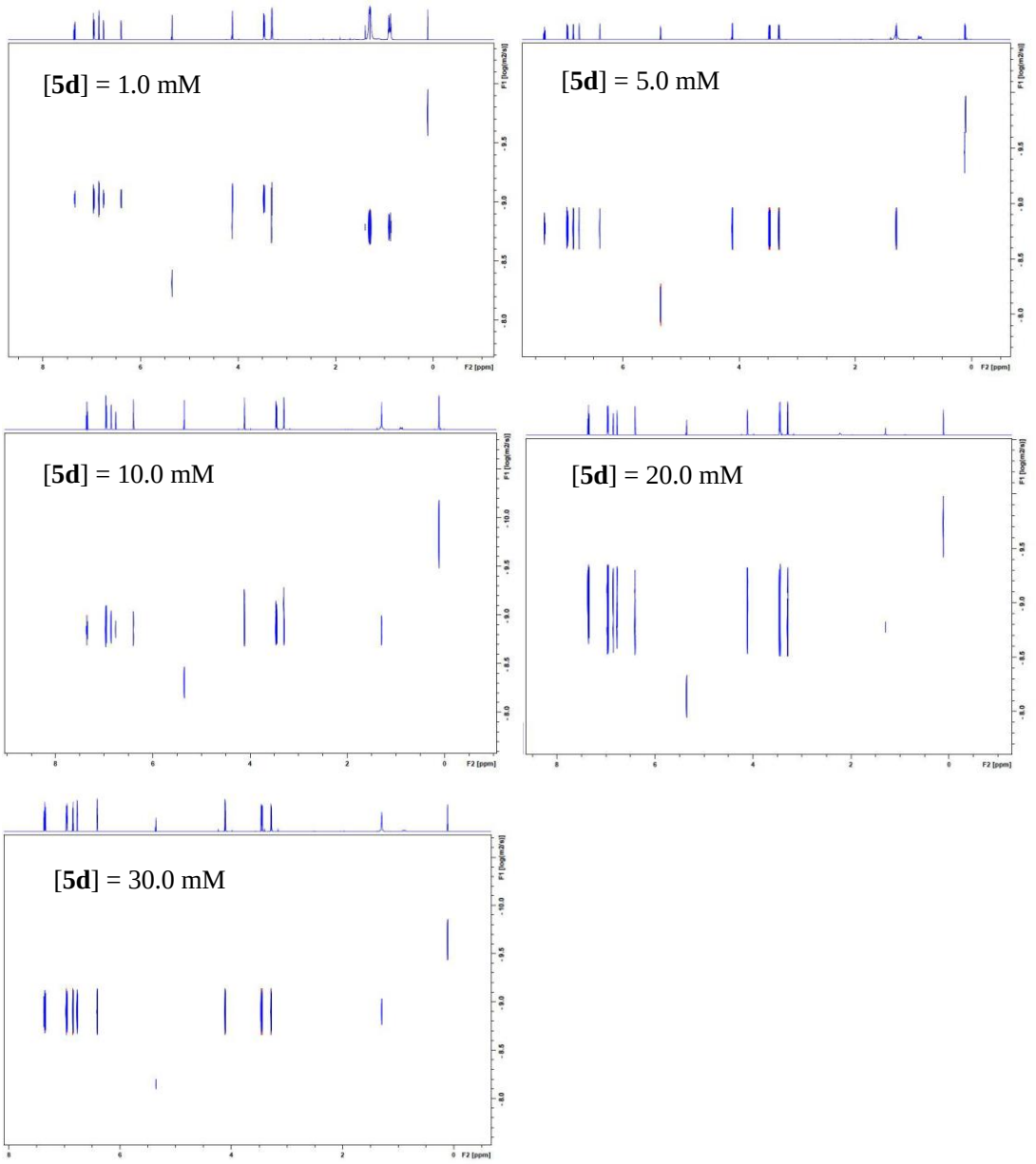


Figure S18. DOSY spectra of **5d** at different concentrations (600 MHz, CD_2Cl_2).

7. DLS measurements for 5a-d at variable concentrations

Measurements were carried out at 25 ± 0.5 °C using an LLS spectrometer (ALV/SP-125) with a multi-τ digital time correlator (ALV-5000). A solid-state He-Ne laser (output power of 22 mW at λ = 632.8 nm) was used as a light source, and the measurements were conducted at a scattering angle of 90°. The freshly prepared samples were injected into a 7 mL glass bottle. The correlation function of scattering data was analyzed via the CONTIN method to obtain the distribution of diffusion coefficients (D) of the solutes, and then the apparent equivalent hydrodynamic radius (R_h) was determined using the Stokes-Einstein equation $R_h = kT/(6\pi\eta D)$, where k is the Boltzmann constant, T is the Kelvin temperature, and η is viscosity of solvent.

Table S5. DLS results for solutions of **5a** in CH_2Cl_2 over a range of concentrations

Concentration (mM)	Hydrodynamic radius (nm)
1.00	0.67
2.50	1.09
5.00	1.38
10.00	1.76

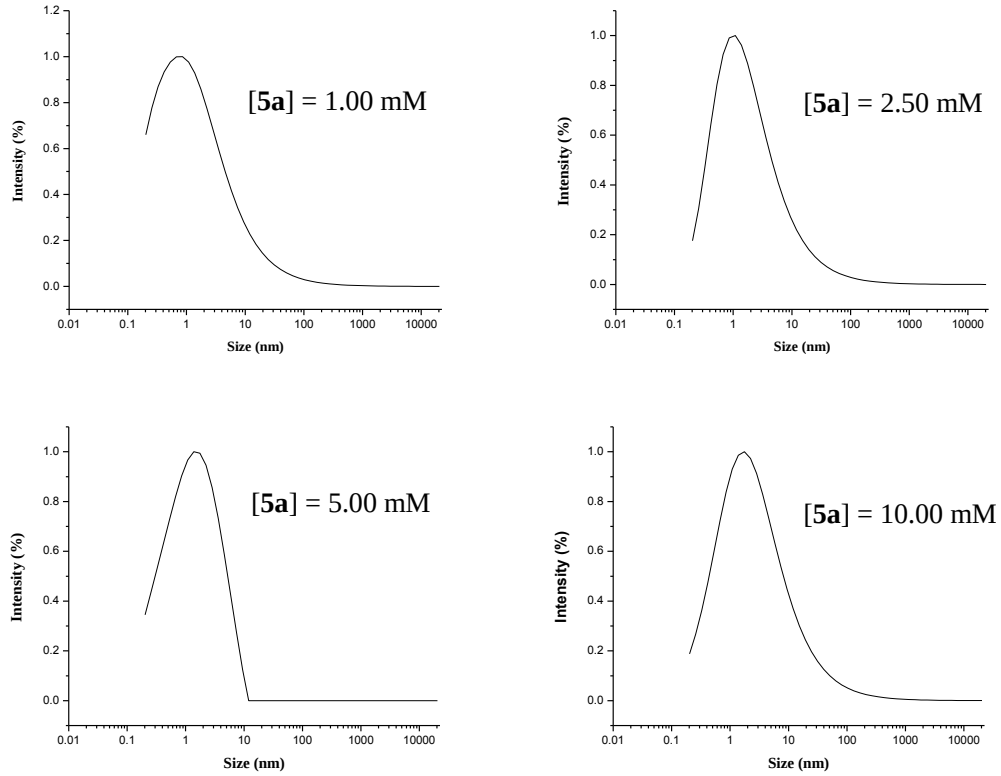


Figure S19. DLS measurements of solutions of **5a** in CH_2Cl_2 over a range of concentrations.

Table S6. DLS results for solutions of **5b** in CH_2Cl_2 over a range of concentrations

Concentration (mM)	Hydrodynamic radius (nm)
5.00	0.86
10.00	1.38
20.00	1.76
30.00	2.24

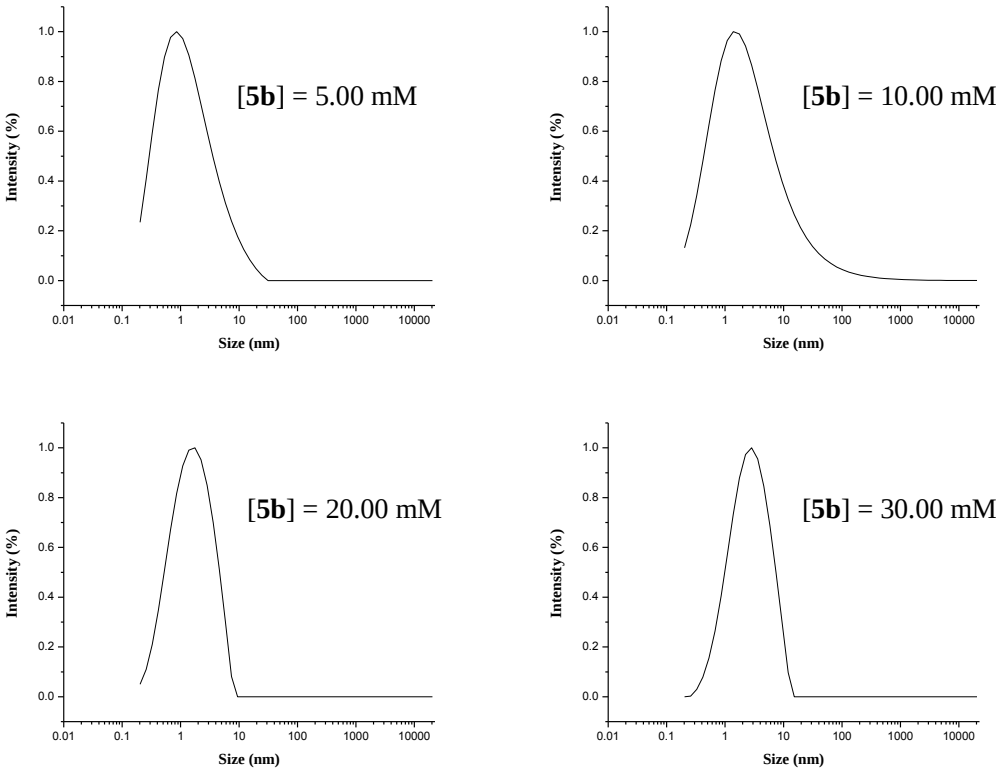


Figure S20. DLS measurements of solutions of **5b** in CH_2Cl_2 over a range of concentrations.

Table S7. DLS results for solutions of **5c** in CH_2Cl_2 over a range of concentrations

Concentration (mM)	Hydrodynamic radius (nm)
5.00	0.85
10.00	1.09
20.00	2.24
30.00	4.59

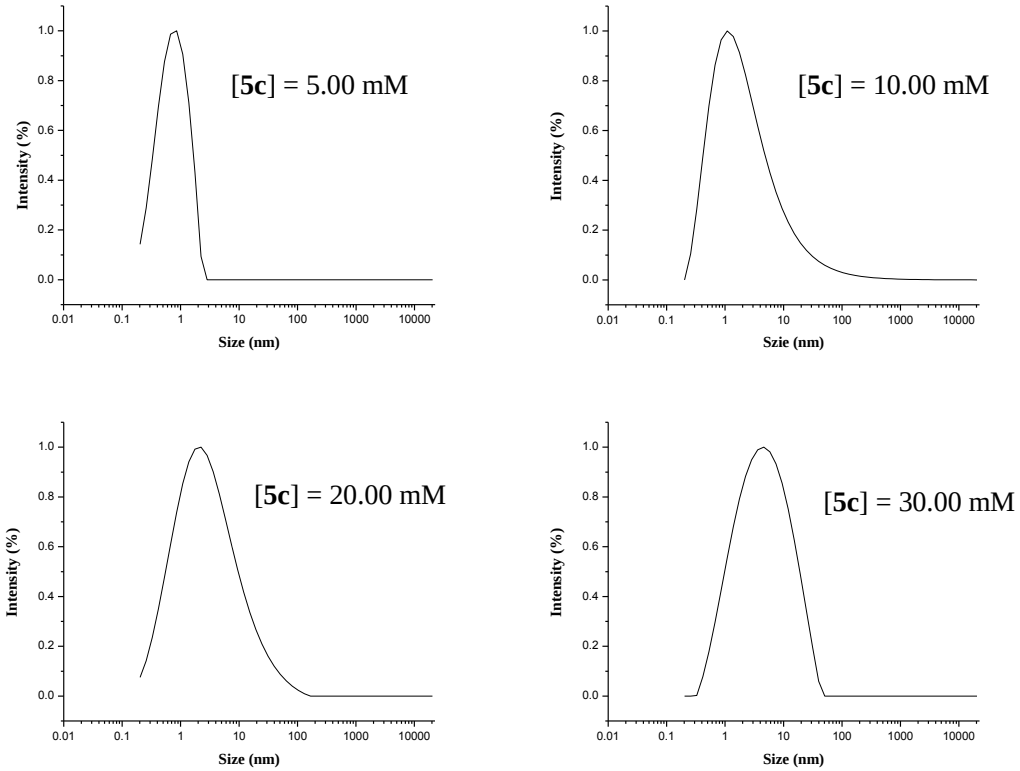


Figure S21. DLS measurements of solutions of **5c** in CH_2Cl_2 over a range of concentrations.

Table S8. DLS results for solutions of **5d** in CH_2Cl_2 over a range of concentrations

Concentration (mM)	Hydrodynamic radius (nm)
5.00	0.78
10.00	1.26
20.00	1.76
30.00	2.84

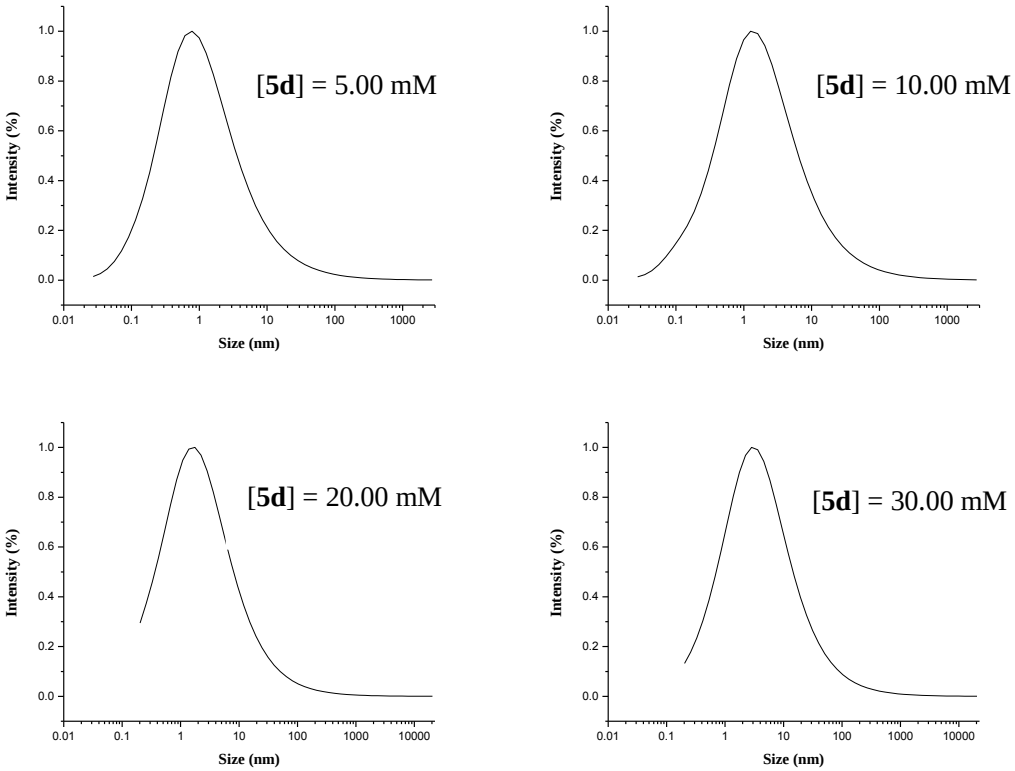


Figure S22. DLS measurements of solutions of **5d** in CH_2Cl_2 over a range of concentrations.

8. ESI-MS spectra

Analysis Info

Analysis Name D:\Data\ESI\2017\2017-01\0116\xrb241B_000001.d

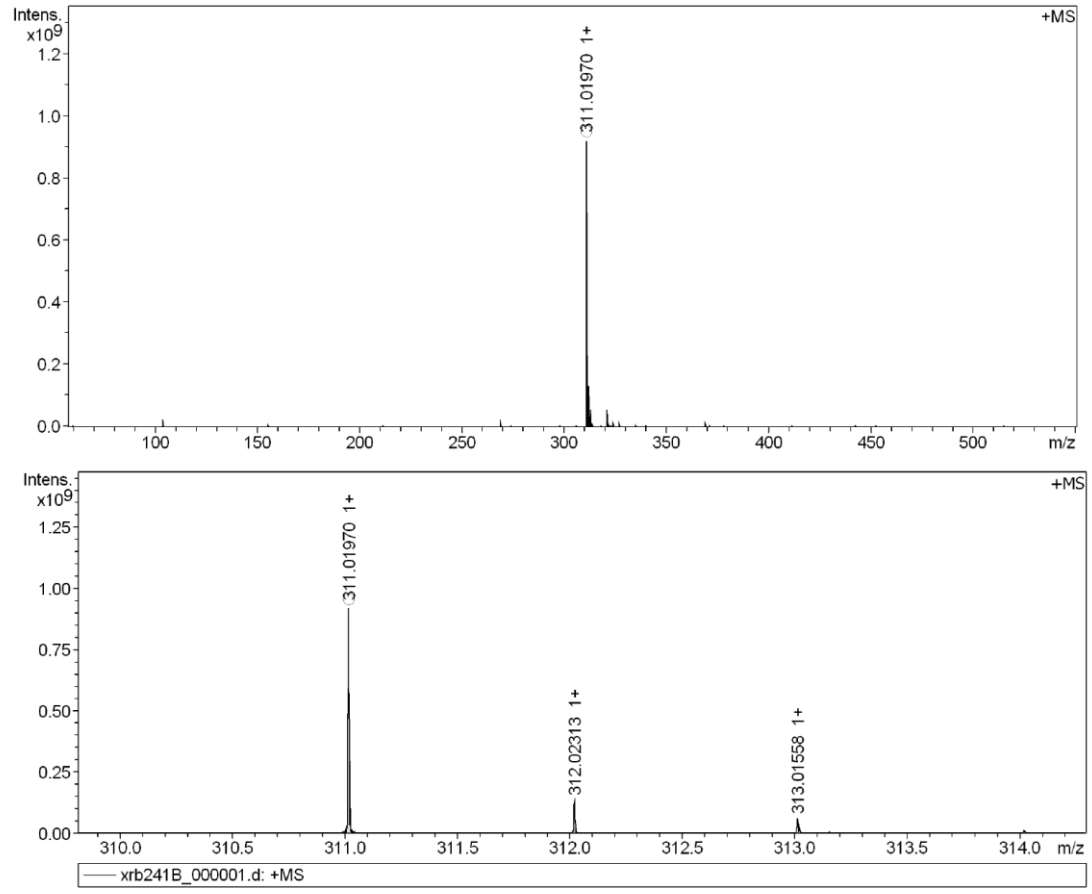
Acquisition Date 1/16/2017 11:23:35 AM

Sample Name xrb241B

Instrument solariX

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	10	Calibration Date	Tue Jan 10 09:21:34
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2048576
Broadband Low Mass	57.7 m/z	Source Accumulation	0.001 sec	Data Processing Size	2097152
Broadband High Mass	550.0 m/z	Ion Accumulation Time	0.050 sec	Apodization	Sine-Bell Multiplication



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
311.019695	1	C11H12NaO7S	100.00	311.019594	-0.3	0.1	6.5	5.5	even	ok

Figure S23. ESI-MS of **2b**.

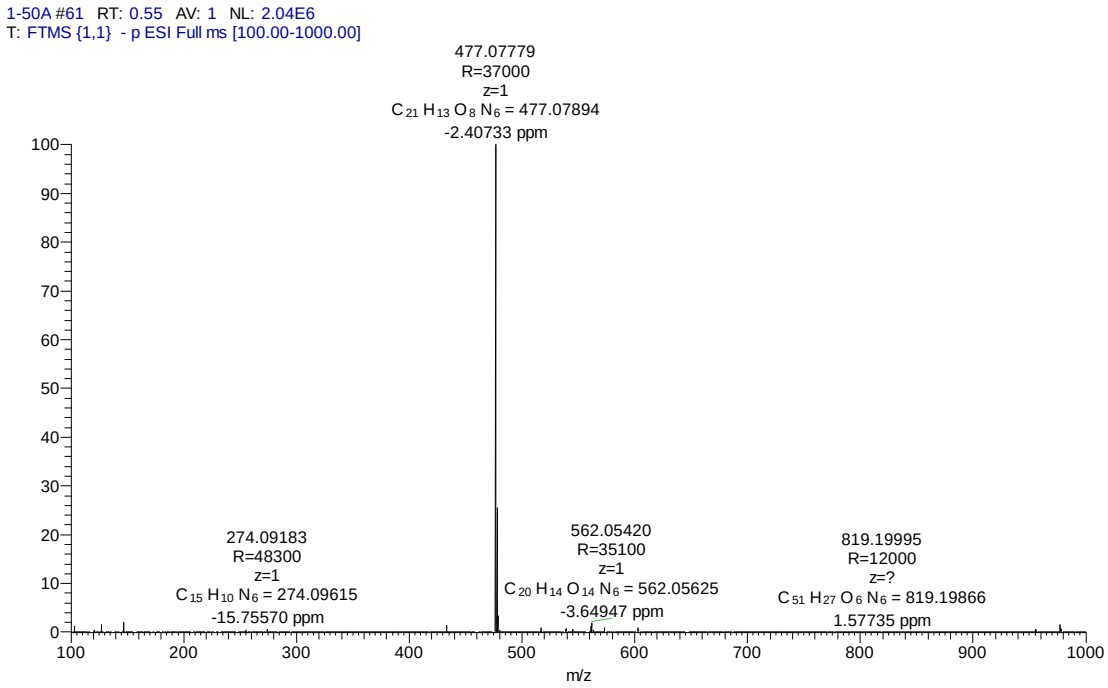


Figure S24. ESI-MS of **3a**.

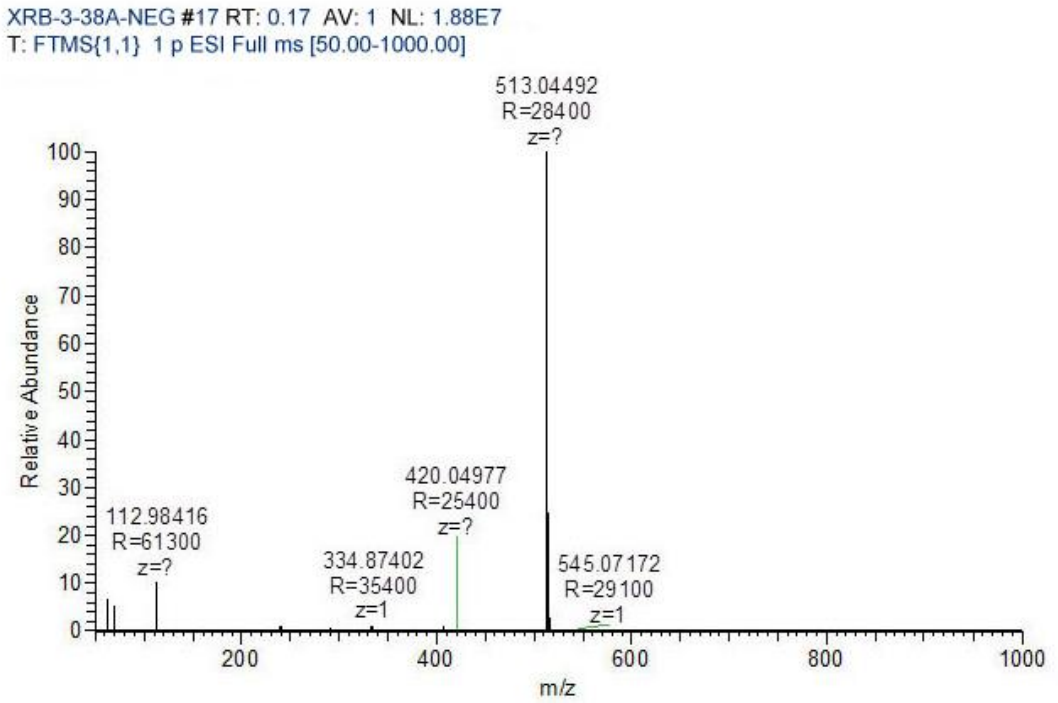


Figure S25. ESI-MS of **3b**.

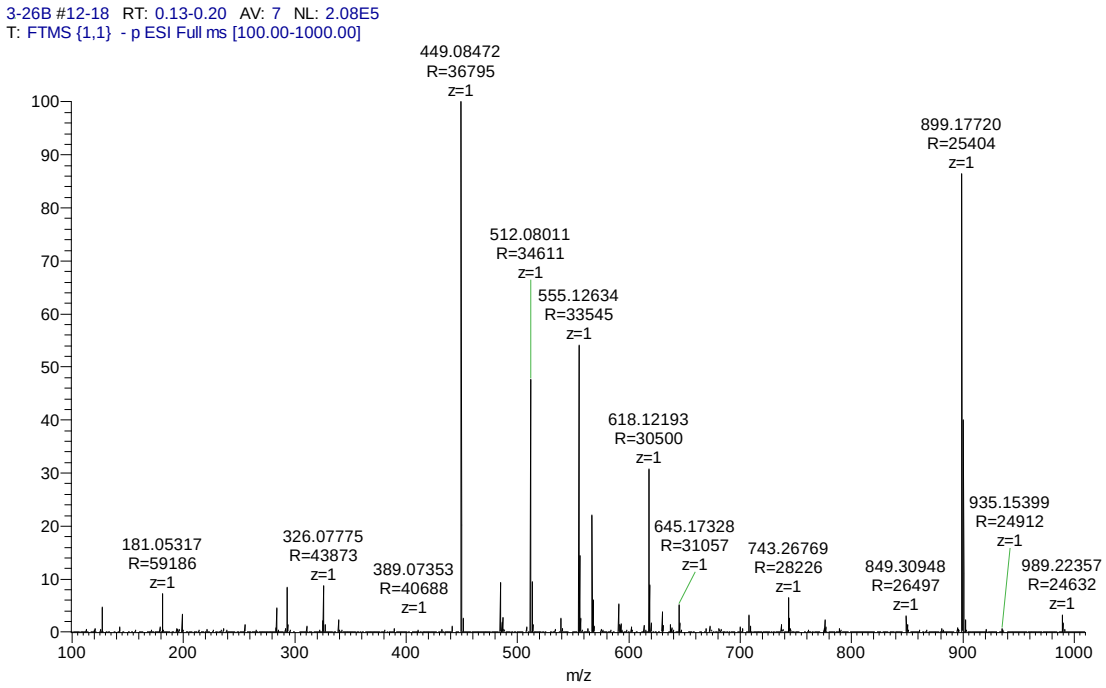


Figure S26. ESI-MS of **3c**.

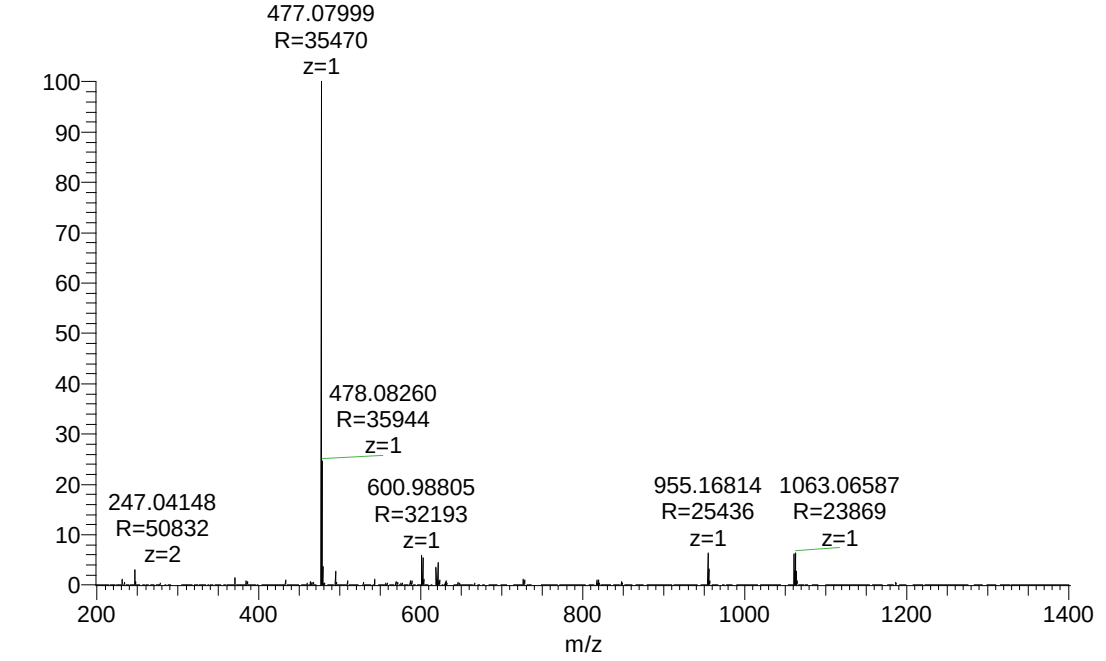


Figure S27. ESI-MS of **4a**.

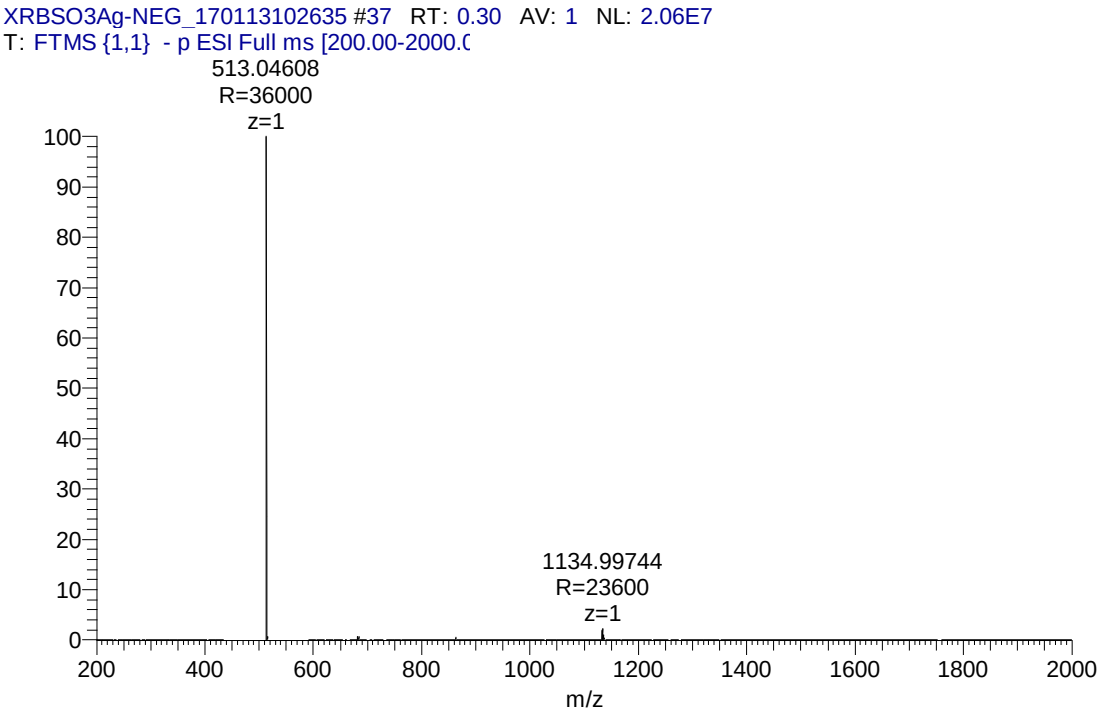


Figure S28. ESI-MS of **4b**.

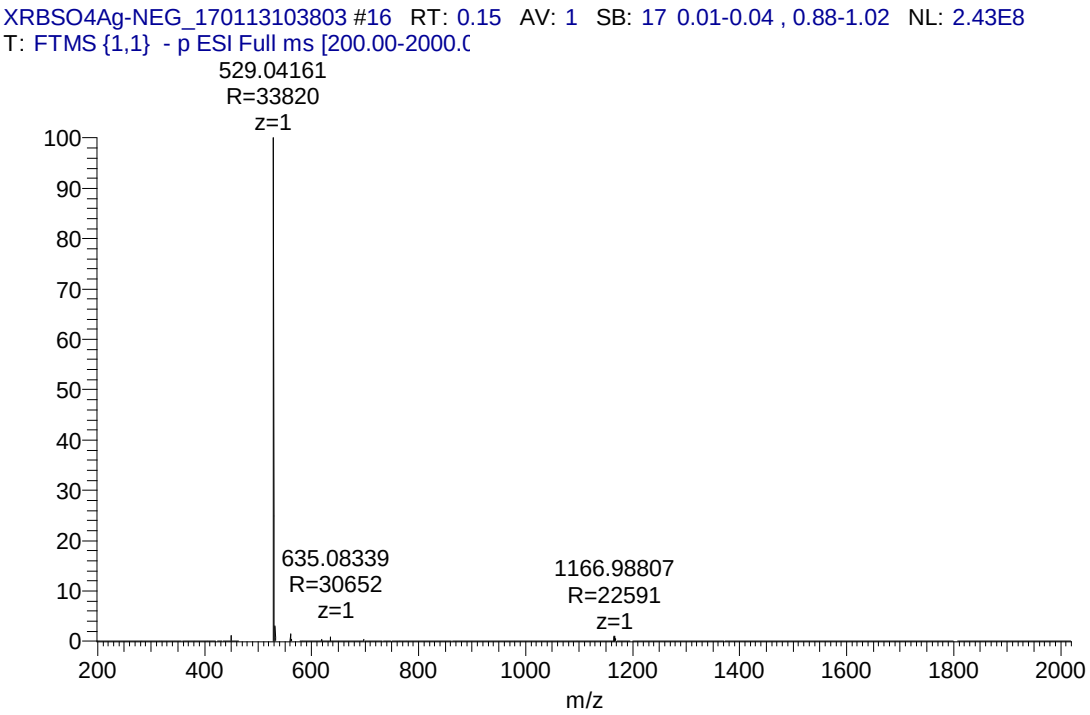


Figure S29. ESI-MS of **4c**.

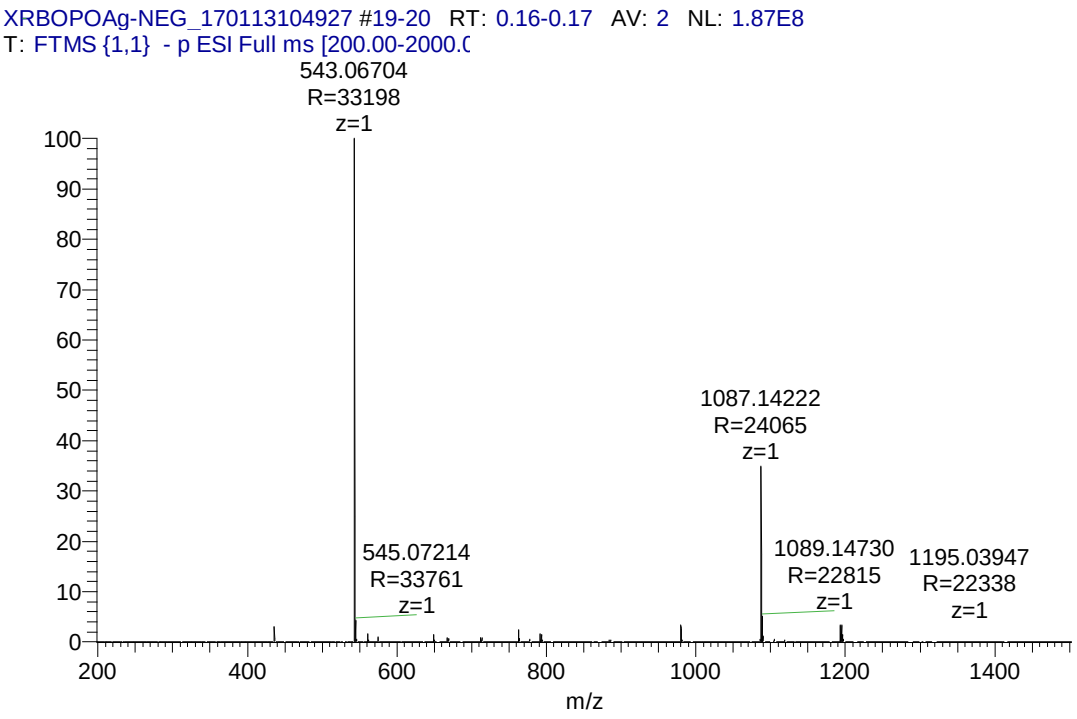


Figure S30. ESI-MS of **4d**.

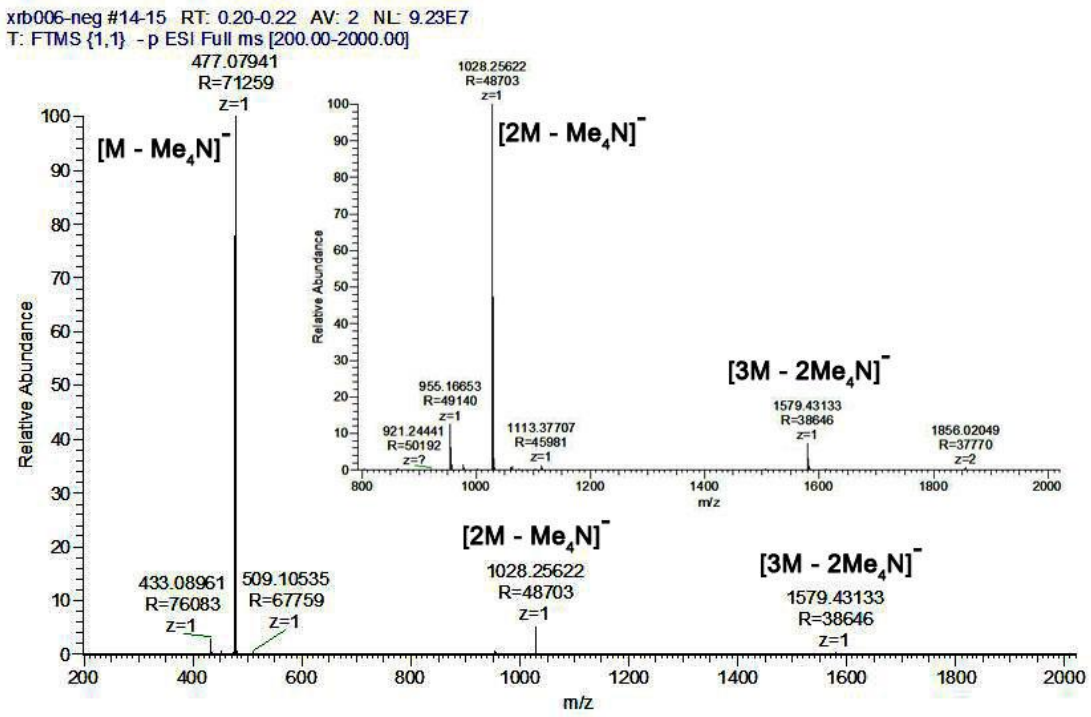


Figure S31. ESI-MS of **5a** (inset: enlarged spectrum showing the dimeric and trimeric peaks).

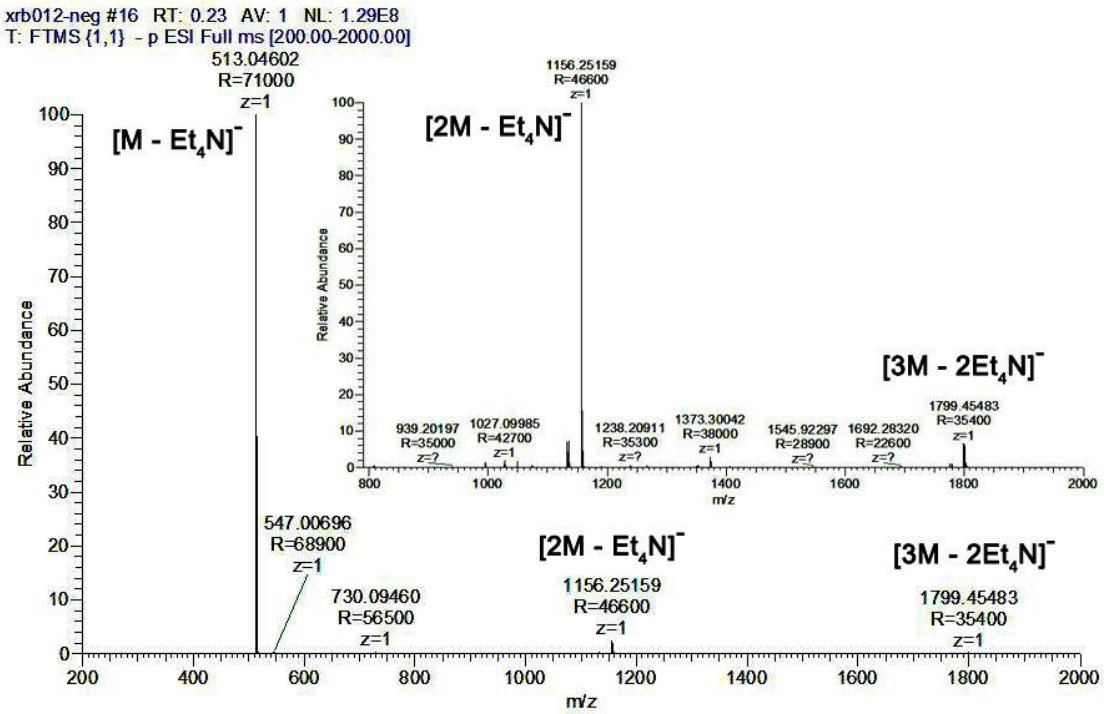


Figure S32. ESI-MS of **5b** (inset: enlarged spectrum showing the dimeric and trimeric peaks).

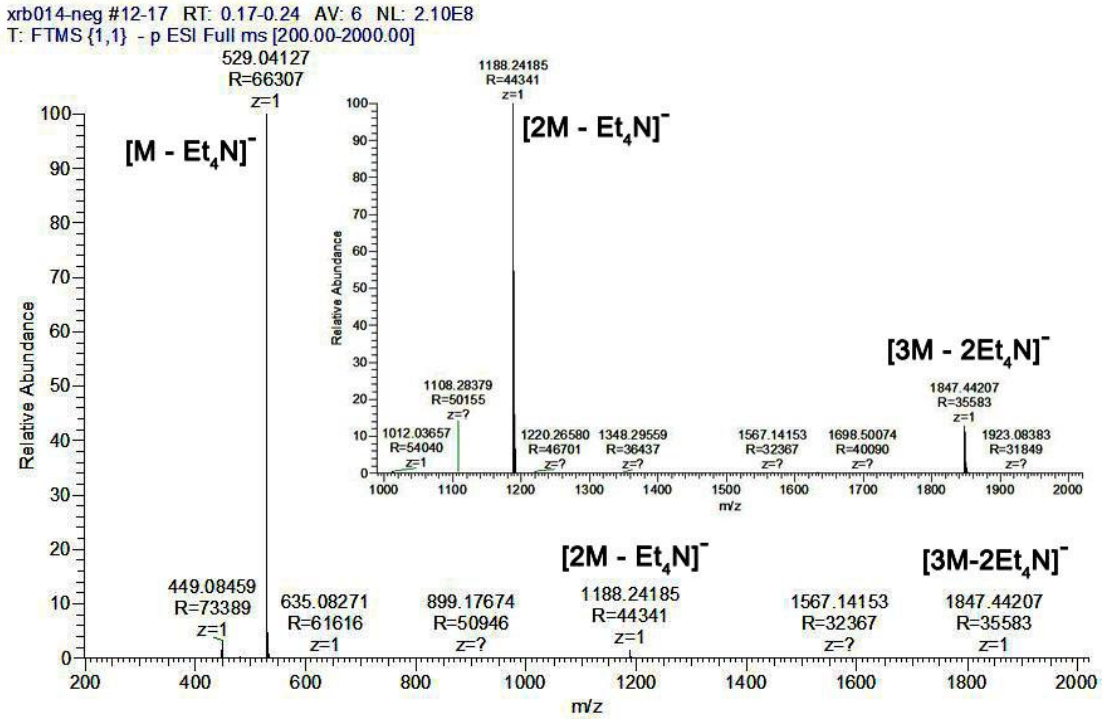


Figure S33. ESI-MS of **5c** (inset: enlarged spectrum showing the dimeric and trimeric peaks).

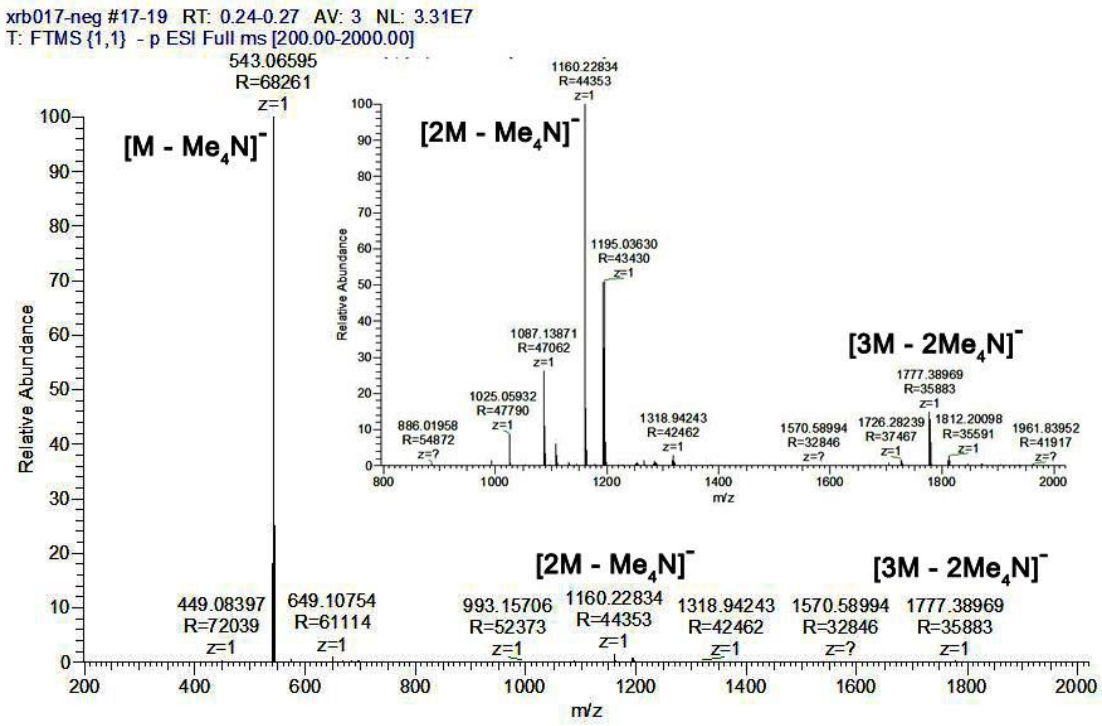


Figure S34. ESI-MS of **5d** (inset: enlarged spectrum showing the dimeric and trimeric peaks).

Analysis Info

Analysis Name D:\Data\ESI\2017\2017-01\0116\xrb239B_000001.d

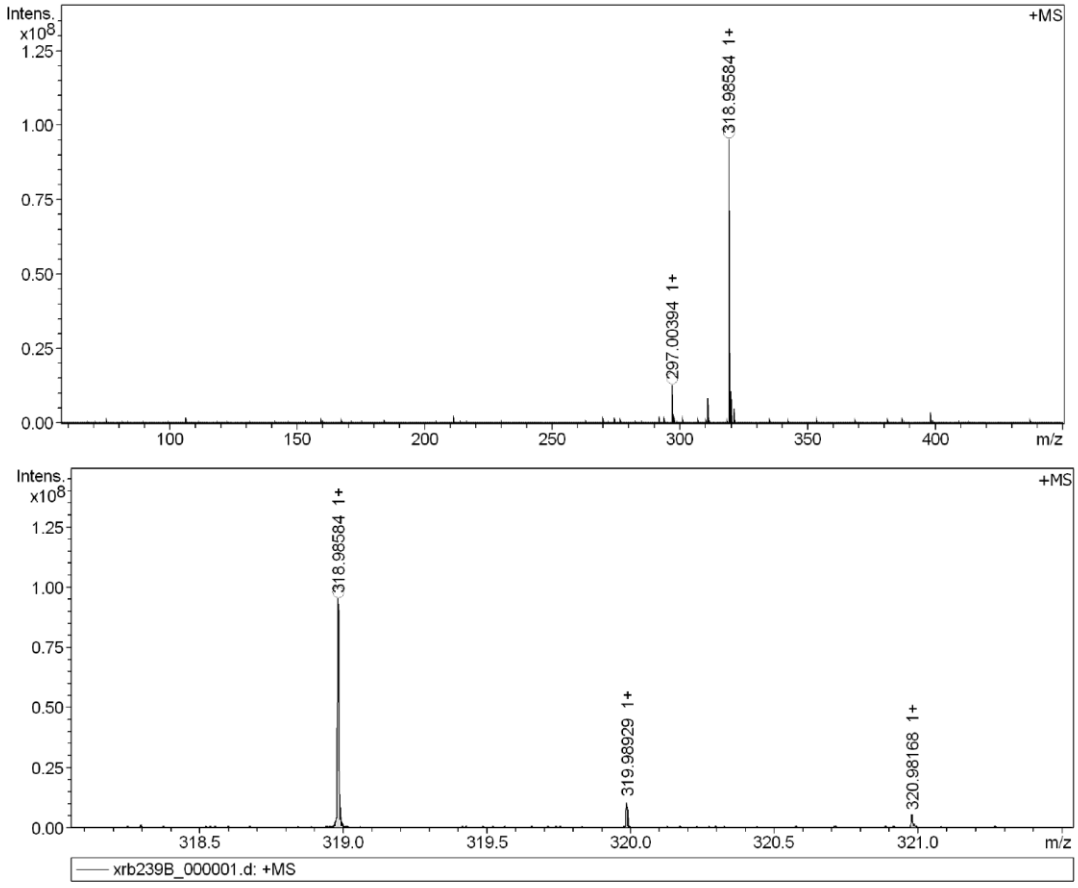
Acquisition Date 1/16/2017 11:42:26 AM

Sample Name xrb239B

Instrument solariX

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	10	Calibration Date	Tue Jan 10 09:21:34
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2048576
Broadband Low Mass	57.7 m/z	Source Accumulation	0.001 sec	Data Processing Size	2097152
Broadband High Mass	450.0 m/z	Ion Accumulation Time	0.050 sec	Apodization	Sine-Bell Multiplication



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
297.003943	1	C10H10NaO7S	100.00	297.003944	0.0	0.3	9.7	5.5	even	ok
318.985845	1	C10H9Na2O7S	100.00	318.985889	-0.1	0.5	5.2	5.5	even	ok

Figure S35. ESI-MS of **8**.

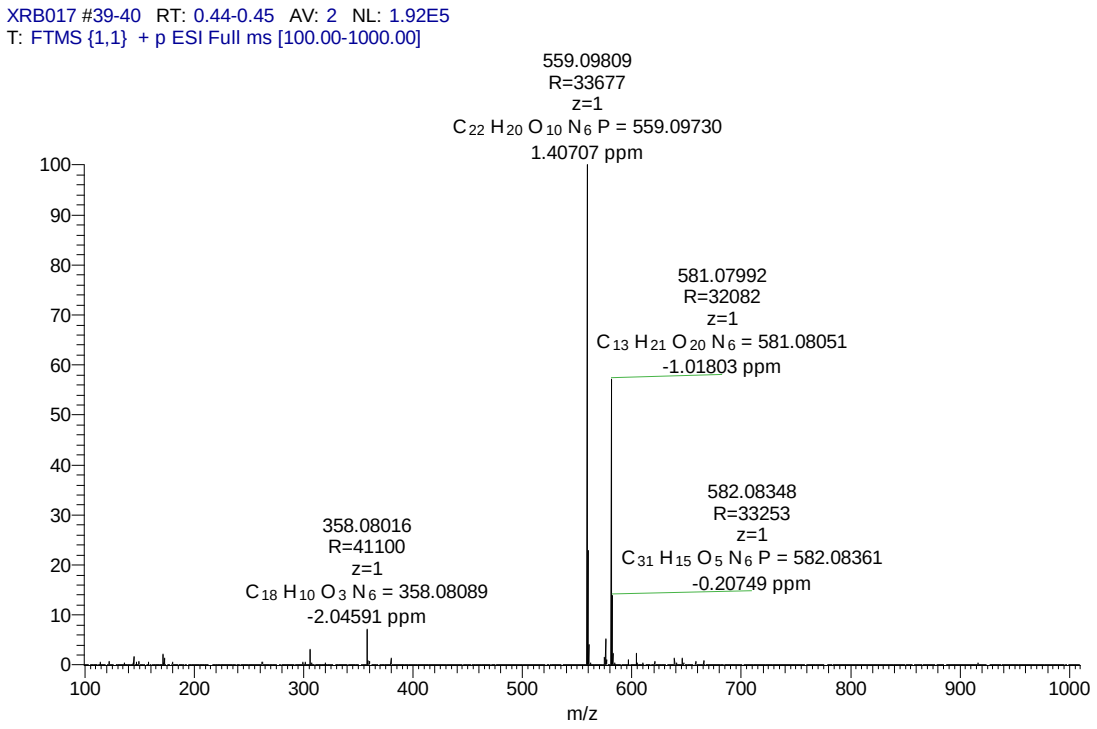


Figure S36. ESI-MS of **10**.

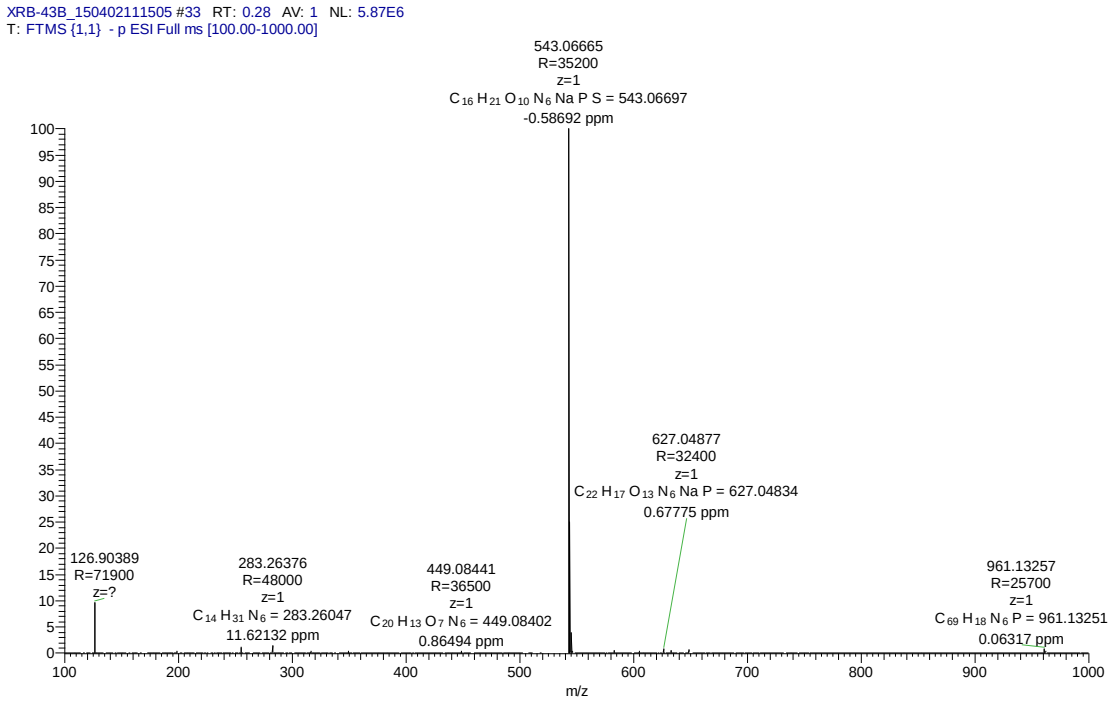


Figure S37. ESI-MS of **11**.

9. X-ray crystallography study of 5a-c

Single crystal X-ray diffraction data were collected on a MM007HF Saturn724+ diffractometer for structures **5a**, **5b** and **5c** using MoK/α radition (λ = 0.71073 Å) at a temperature of 173 K. The intensity data were collected by the omega scans techniques, scaled, and reduced with CrystalClear (Rigaku Inc., 2007). Frame counting times of 10 seconds (**5a**), 5 seconds (**5b**) , 20 seconds (**5c**) were used for intensities data collection. X-rays were provided by a fine-focus sealed X-ray tube operated at 50 kV and 24 mA. Lattice constants were determined with the CrystalClear (Rigaku Inc., 2007) using peak centers for 8389 reflections (**5a**), 6849 reflections (**5b**), 6929 reflections (**5c**).

Integrated reflection intensities were produced and the correction of the collected intensities for absorption was done using the CrystalClear (Rigaku Inc., 2007) program. The structures were solved by direct methods using SHELXT (Sheldrick, 2014) and refined using full-matrix least-squares methods in ShelXL (Sheldrick, 2014/2015). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms attached to carbon atoms were fixed at their ideal positions.

Table S9. Crystal data and structure refinement of **5a-c**

	5a	**5b**	**5c**
Empirical formula	$C_{33}H_{37}N_{11}O_8$	$C_{28}H_{33}N_7O_9S$	$C_{28}H_{33}N_7O_{10}S$
Formula weight	715.73	643.67	659.67
Temperature	173.15 K	173(2) K	173.15 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	Pbca	Pbca	P1 21/n1
a	13.944(3) Å	16.9672(19) Å	11.585(2) Å
b	17.897(4) Å	16.6921(19) Å	18.121(3) Å
c	29.542(6) Å	21.140(3) Å	14.653(3) Å
α	90 °	90 °	90 °
β	90 °	90 °	90.339(3) °
γ	90 °	90 °	90 °
Volume	7372(3) $Å^3$	5987.3(12) $Å^3$	3035.2(10) $Å^3$
Z	8	8	4
Density (calculated)	1.290 Mg/m^3	1.428 Mg/m^3	1.444 Mg/m^3
Absorption coefficient	0.095 mm^{-1}	0.174 mm^{-1}	0.176 mm^{-1}
F(000)	3008	2704	1384
Crystal size	0.33 x 0.209 x 0.067 mm^3	0.349 x 0.17x 0.05 mm^3	0.201x 0.18 x 0.039 mm^3
Theta range for data collection	1.976 to 27.424 °	1.964 to 27.489 °	1.802 to 27.578 °
Index ranges	-18<=h<=16 -23<=k<=15 -38<=l<=38	-22<=h<=22 -21<=k<=21 -27<=l<=27	-15<=h<=14 -23<=k<=23 -19<=l<=19
Reflections collected	65235	80056	6929
Independent reflections	8389 [R(int) = 0.0602]	6849 [R(int) = 0.0511]	6929 [R(int) = ?]
Completeness to theta = 25.197 °	99.9%	99.9 %	99.7 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.7260	1.00000 and 0.89169	1.0000 and 0.8400
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8389 / 0 / 479	6849 /0 / 412	6929 / 0 / 422
Goodness-of-fit on F^2	1.324	1.285	1.093
Final R indices [I>2sigma(I)]	R1 = 0.0843, wR2 = 0.1770	R1 = 0.0640, wR2 = 0.1531	R1 = 0.0678, wR2 = 0.1943
R indices (all data)	R1 = 0.0869, wR2 = 0.1785	R1 = 0.0643, wR2 = 0.1533	R1 = 0.0712, wR2 = 0.1972
Extinction coefficient	n/a	n/a	n/a
Largest diff. peak and hole	0.260 and -0.318 $e.Å^{-3}$	0.608 and -0.386 $e.Å^{-3}$	0.456and -0.345$e.Å^{-3}$

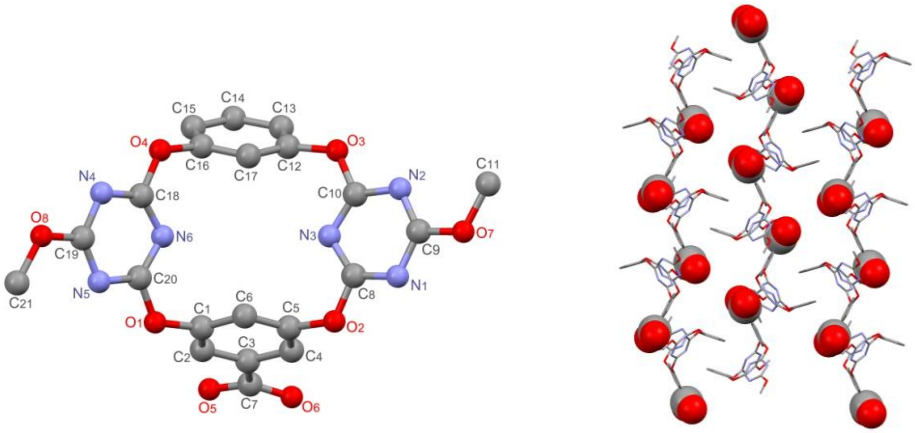


Figure S38. X-ray crystal structure of **5a** and the extended packing motif with the anionic heads highlighted in space filling. Countercation $^{+}NMe_4$ and solvent CH_3CN molecules are omitted for clarity.

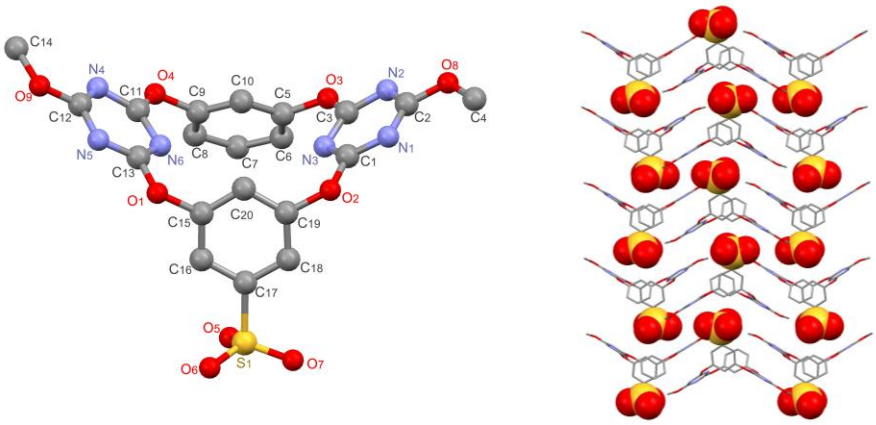


Figure S39. X-ray crystal structure of **5b** and the extended packing motif with the anionic heads highlighted in space filling. Countercation $^{+}NEt_4$ is omitted for clarity.

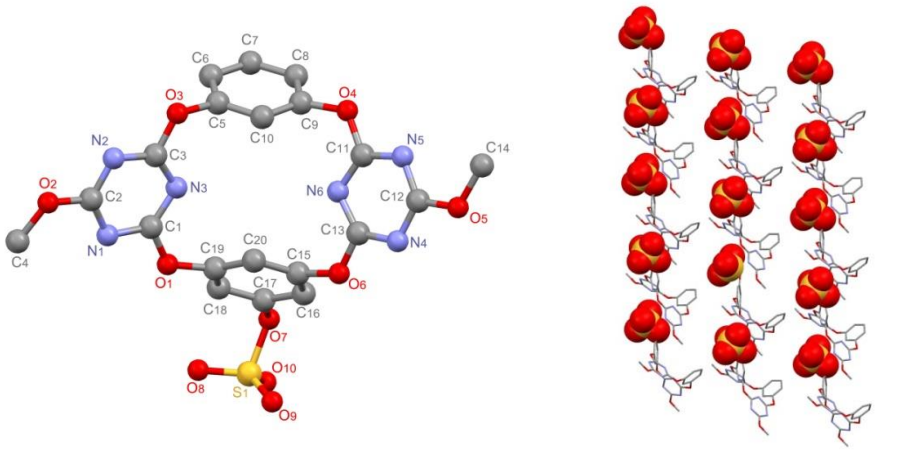
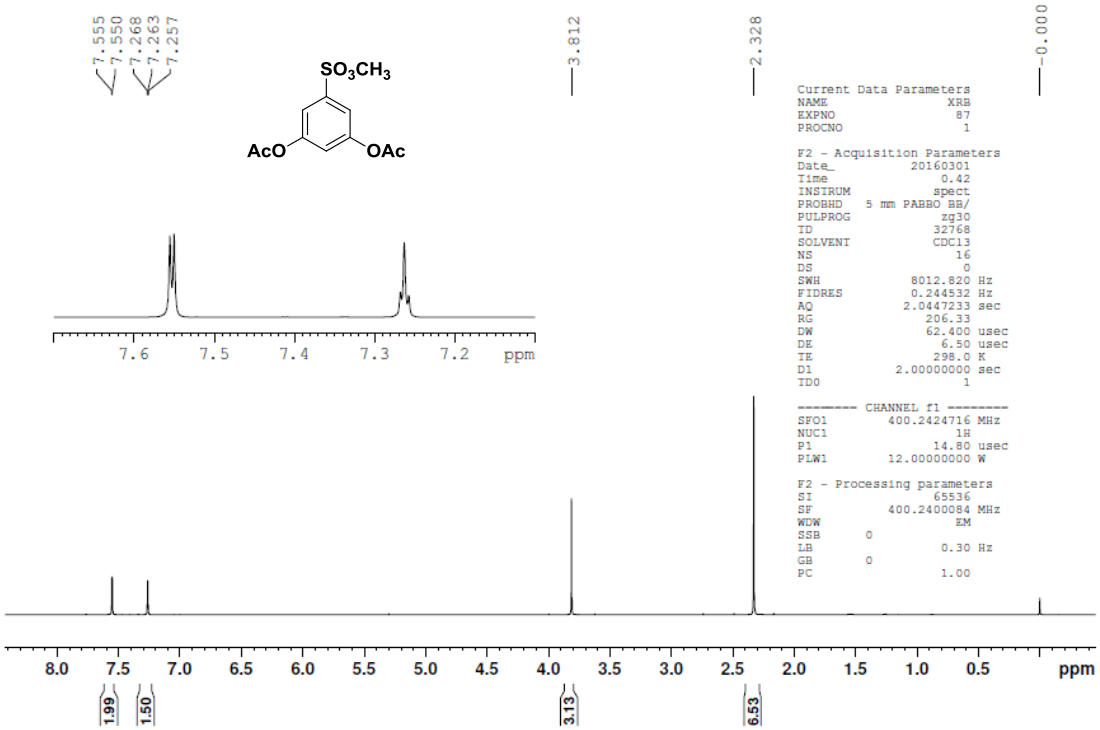


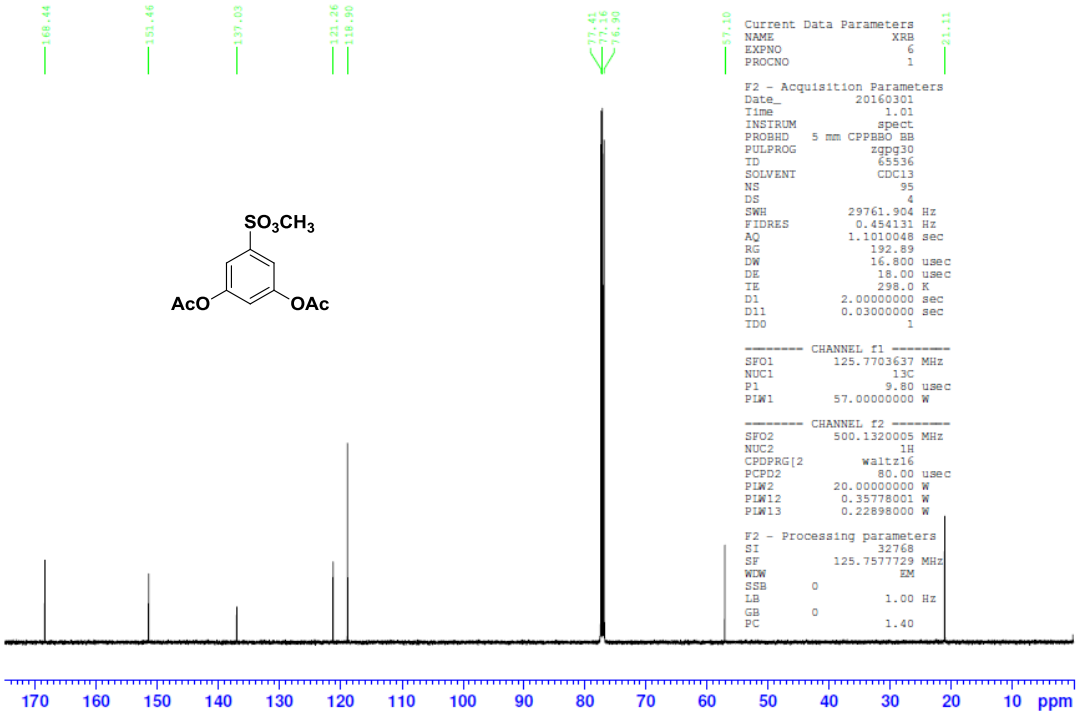
Figure S40. X-ray crystal structure of **5c** and the extended packing motif with the anionic heads highlighted in space filling. Countercation $^{+}NEt_4$ is omitted for clarity.

10. Copies of NMR spectra for new compounds

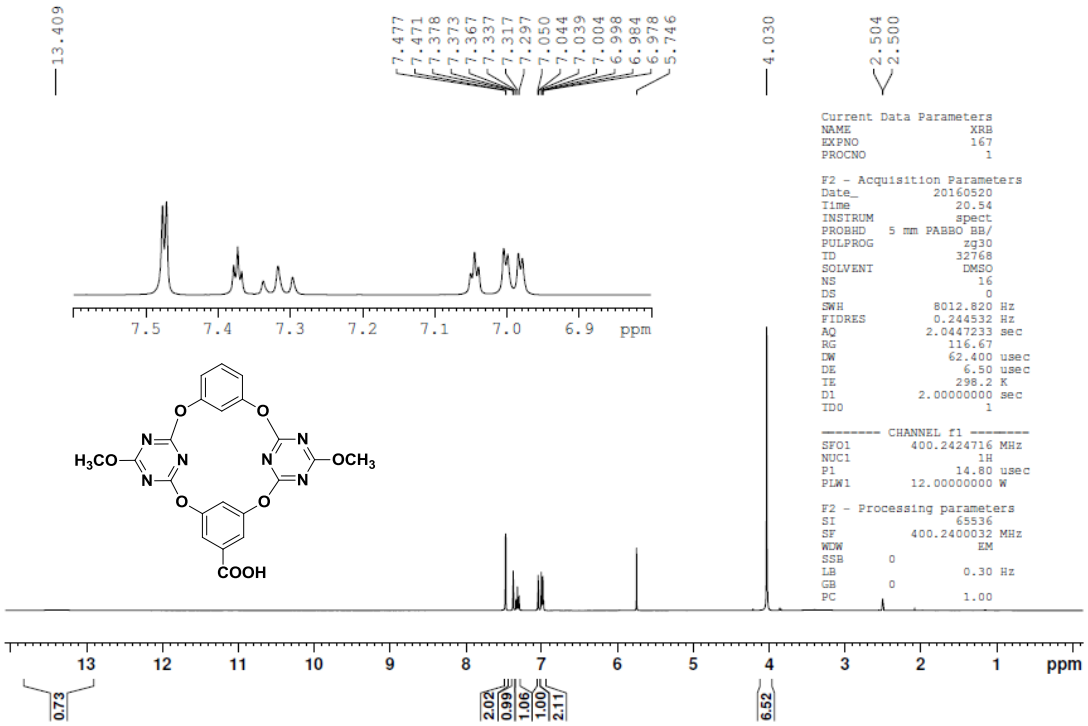
2b - ^{1}H NMR



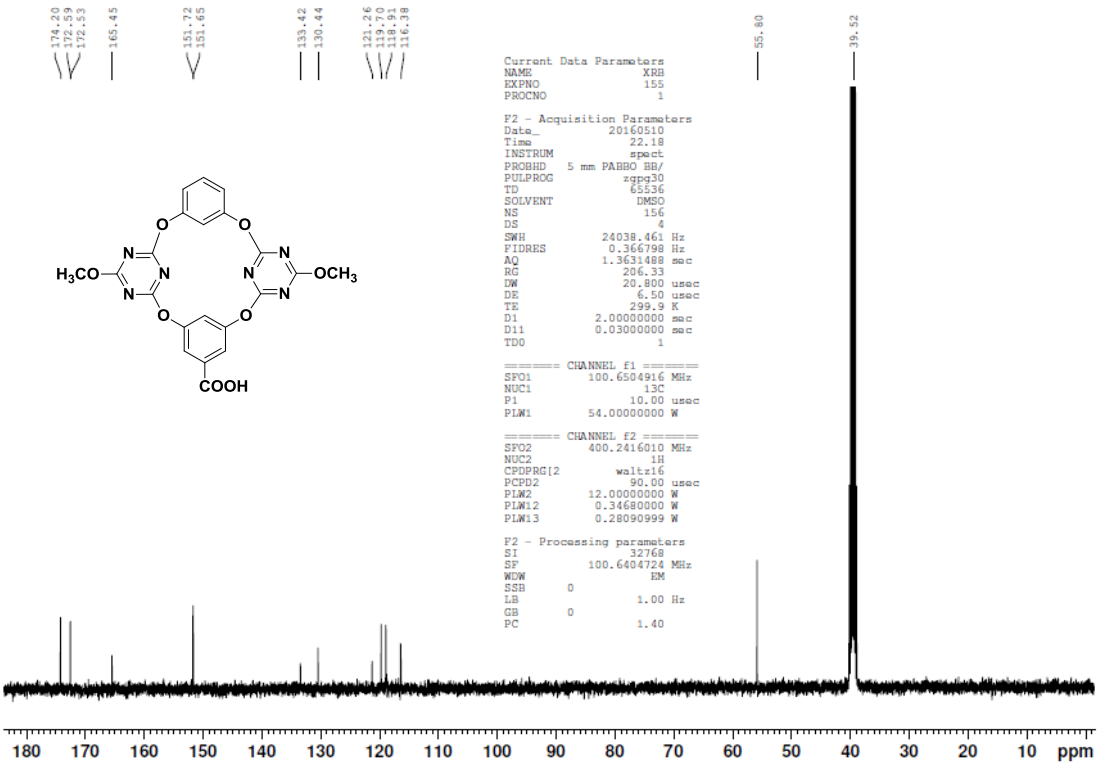
2b - ^{13}C NMR



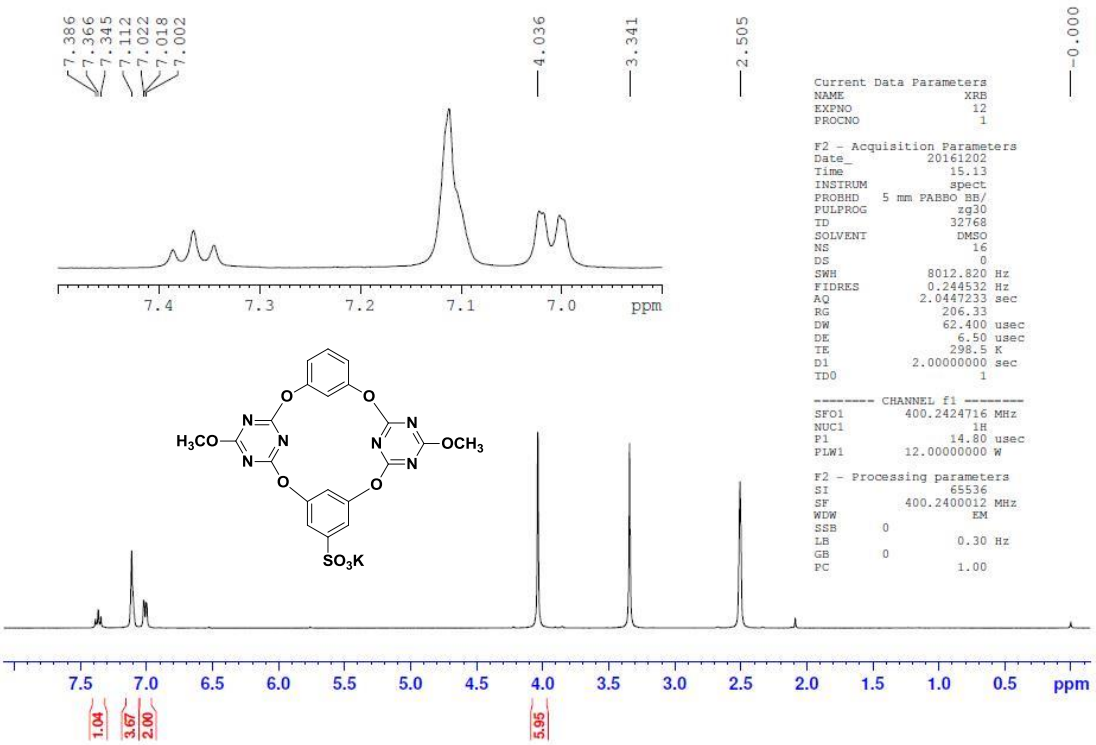
3a - ^{1}H NMR



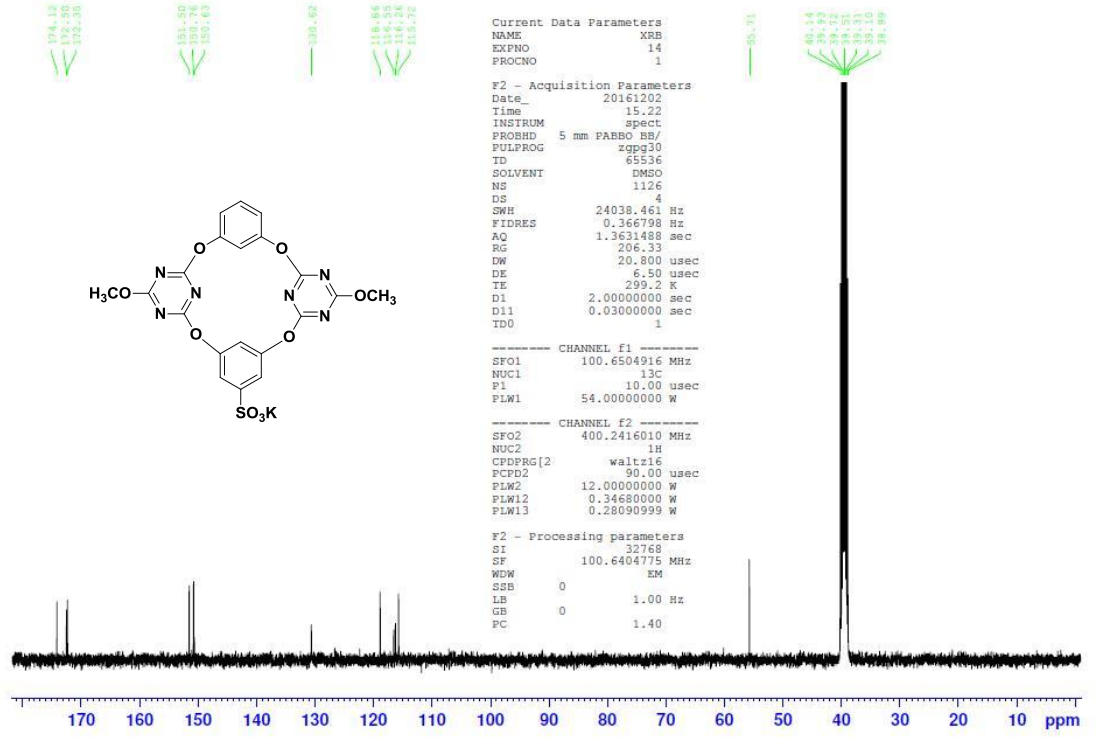
3a - ^{13}C NMR



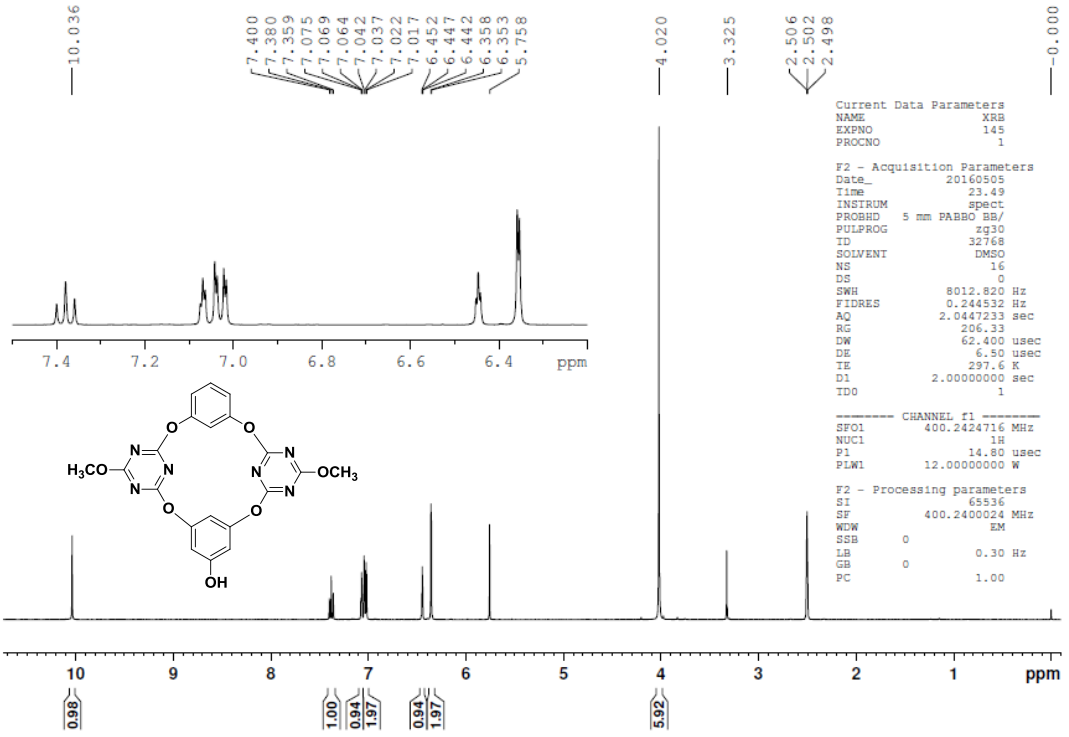
3b - ^{1}H NMR



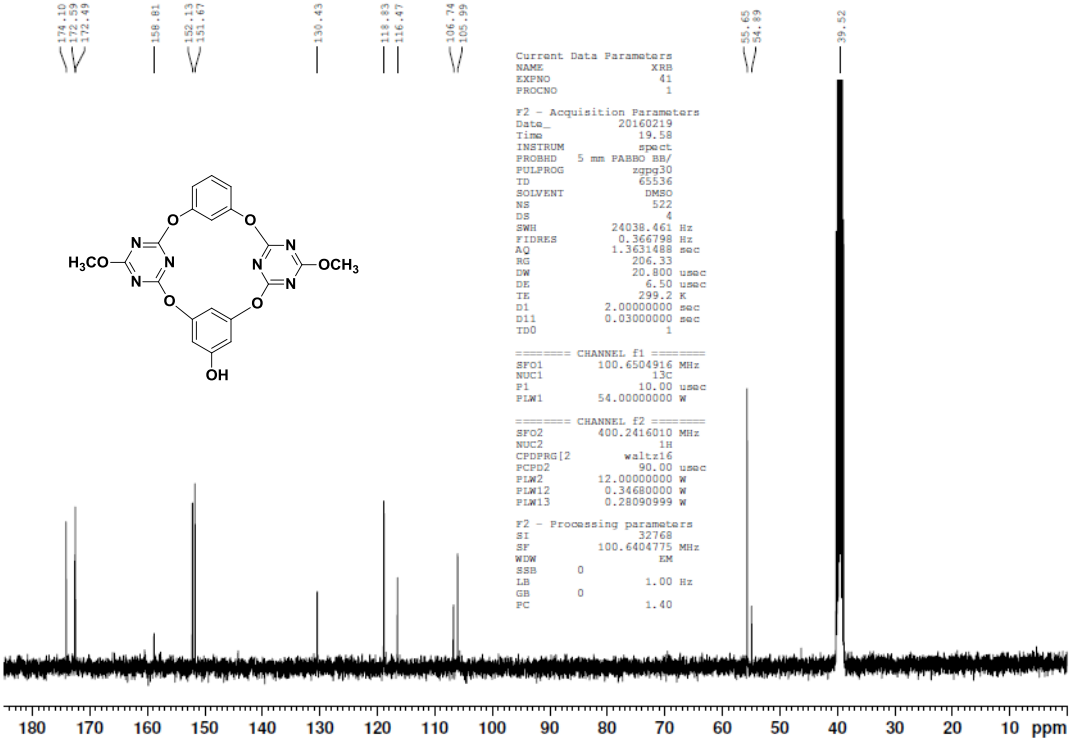
3b – ^{13}C NMR



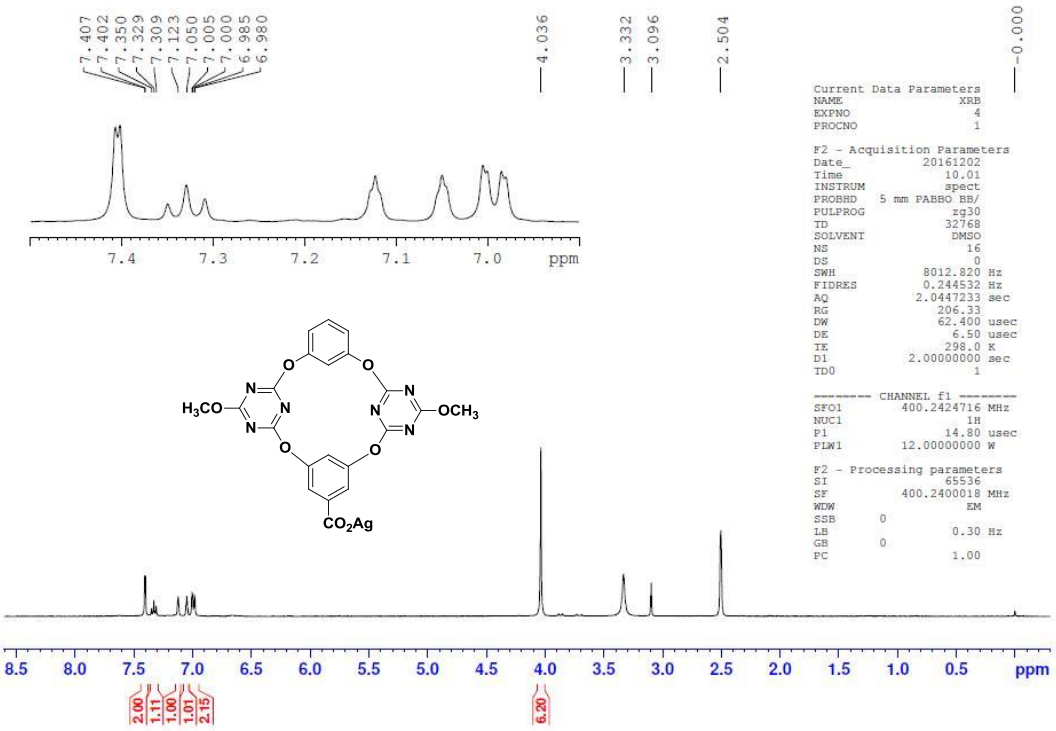
3c - ^{1}H NMR



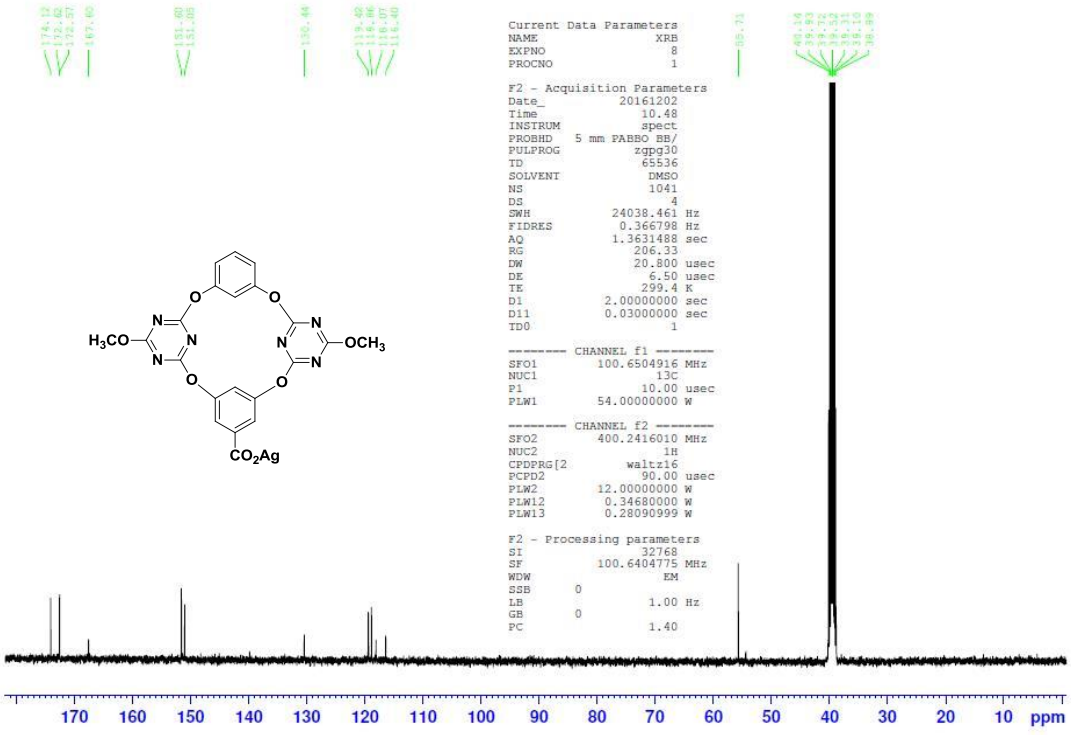
3c - ^{13}C NMR



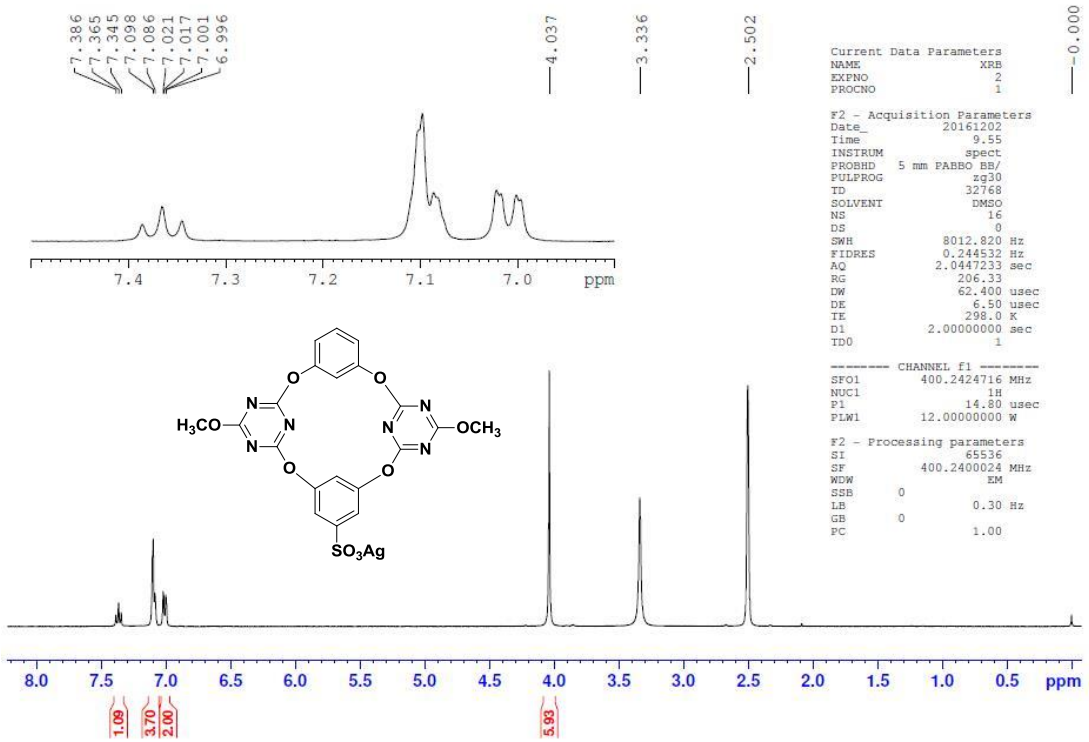
4a - ^{1}H NMR



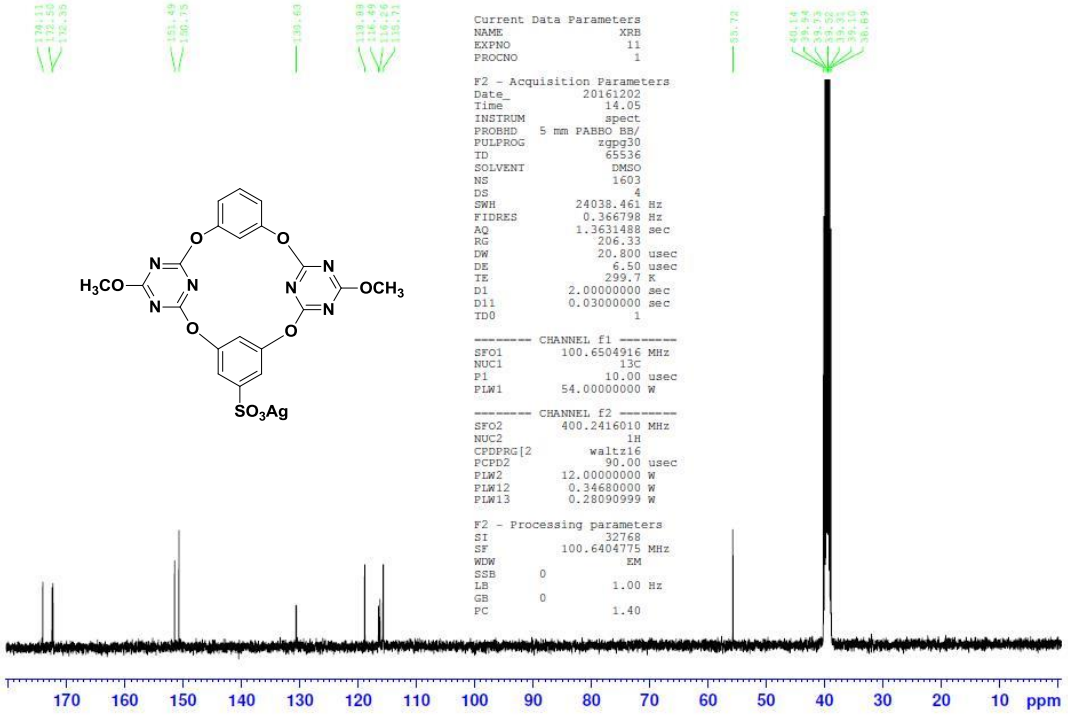
4a – ^{13}C NMR



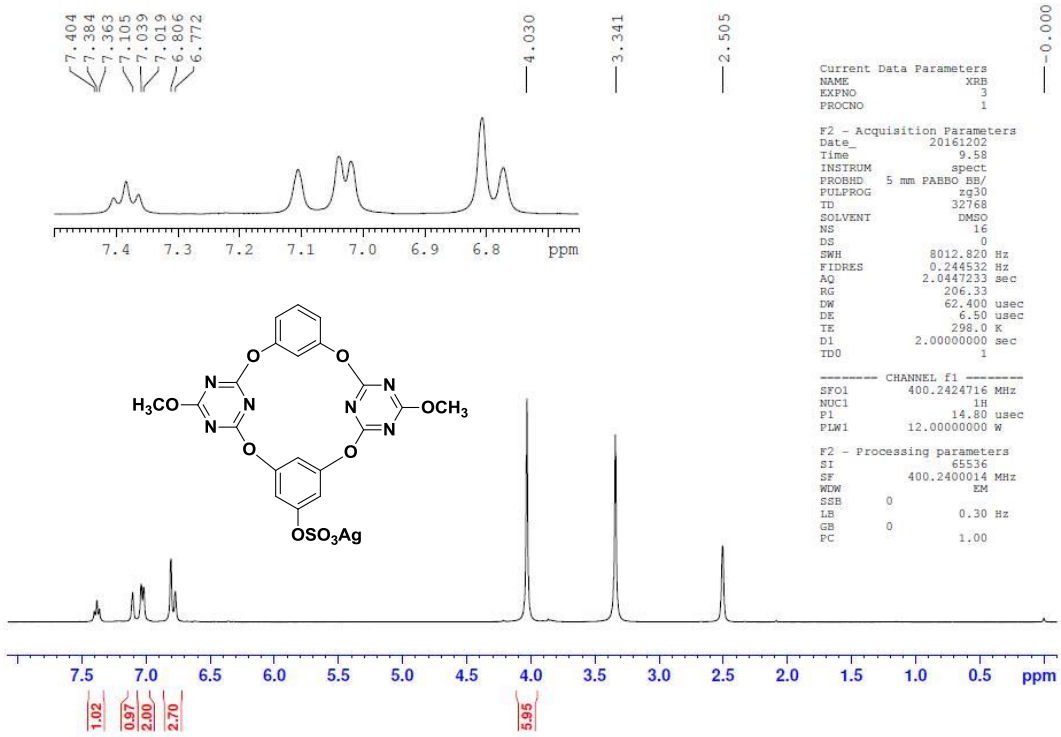
4b - ^{1}H NMR



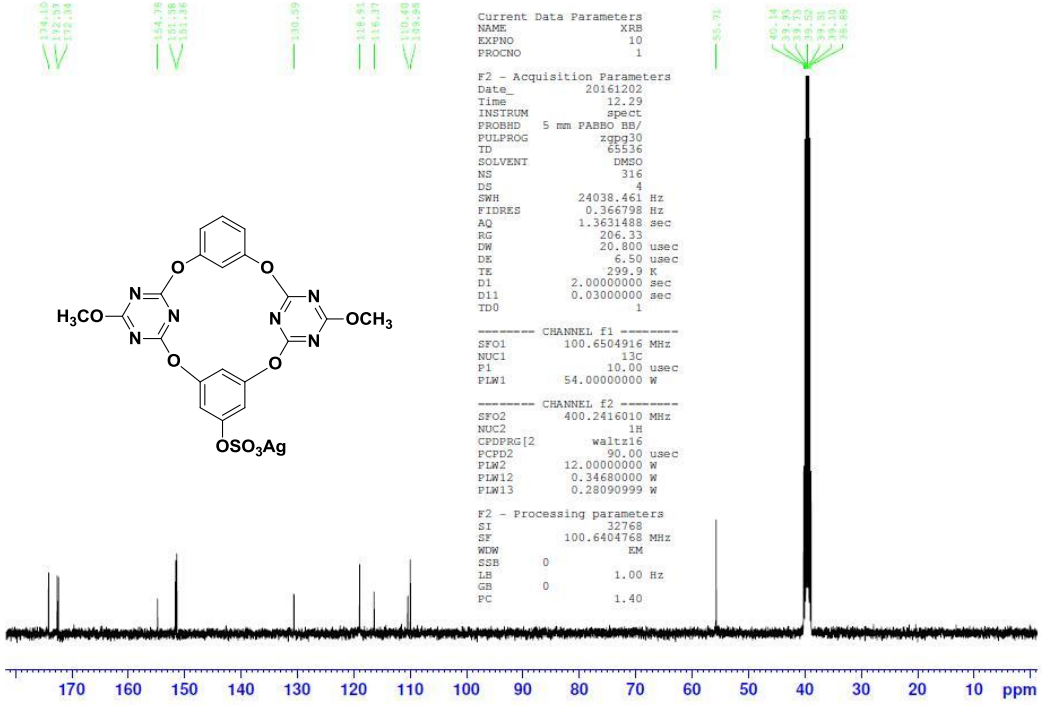
4b – ^{13}C NMR



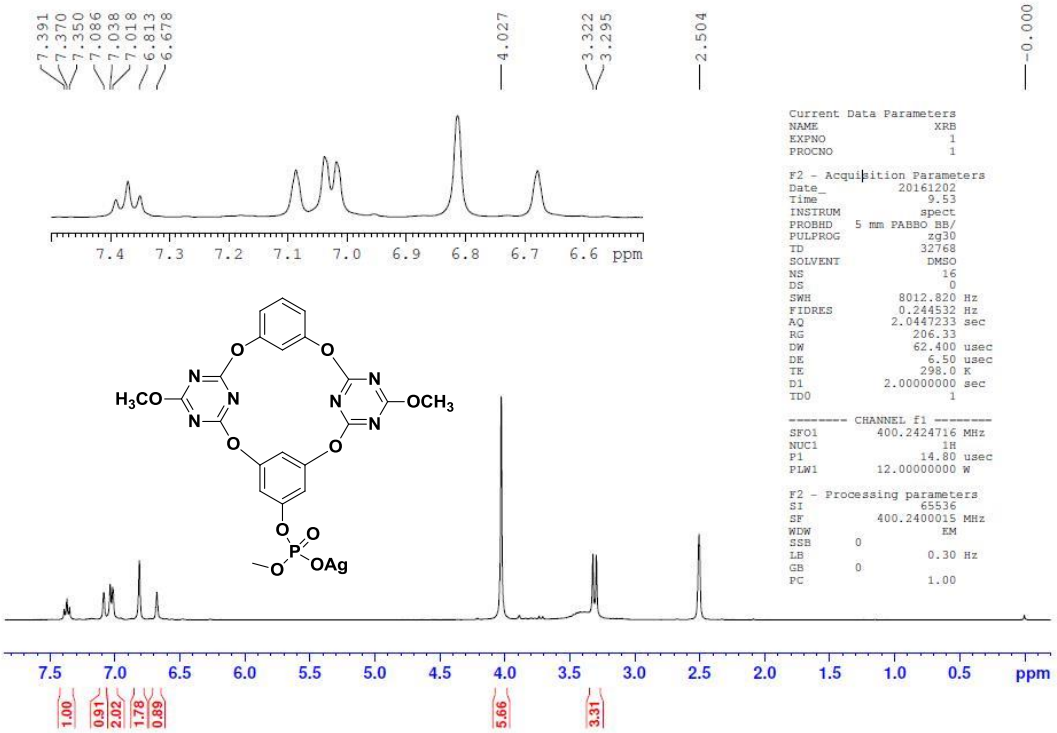
4c - ^{1}H NMR



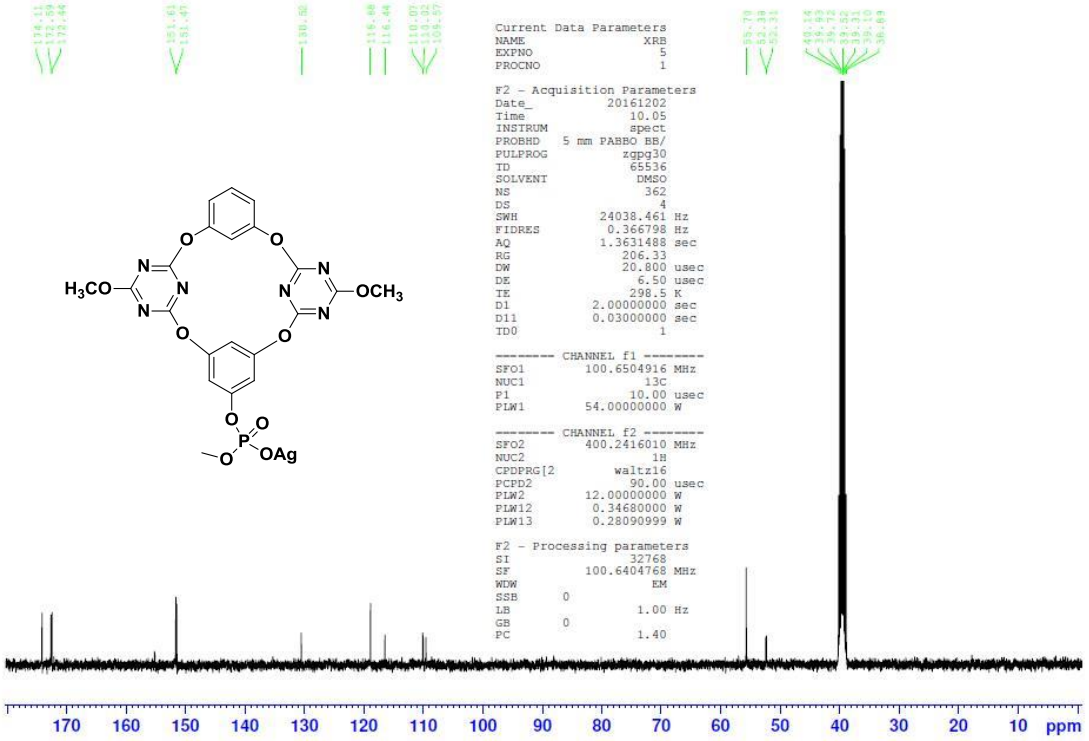
4c – ^{13}C NMR



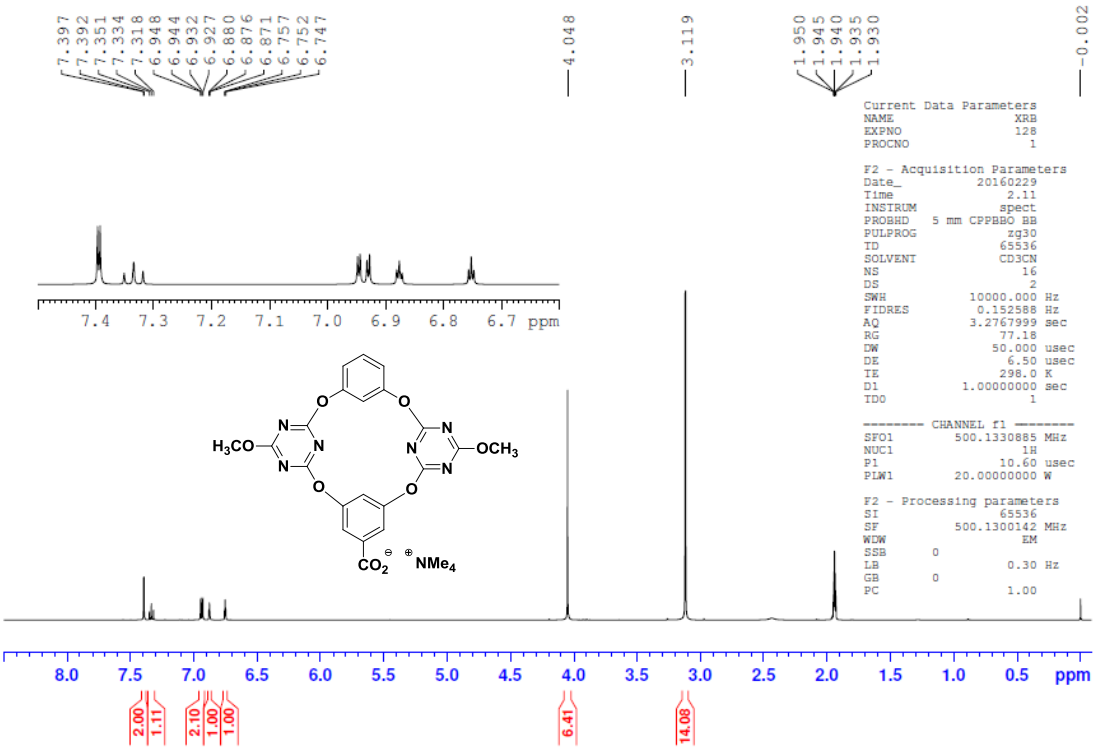
4d - ^{1}H NMR



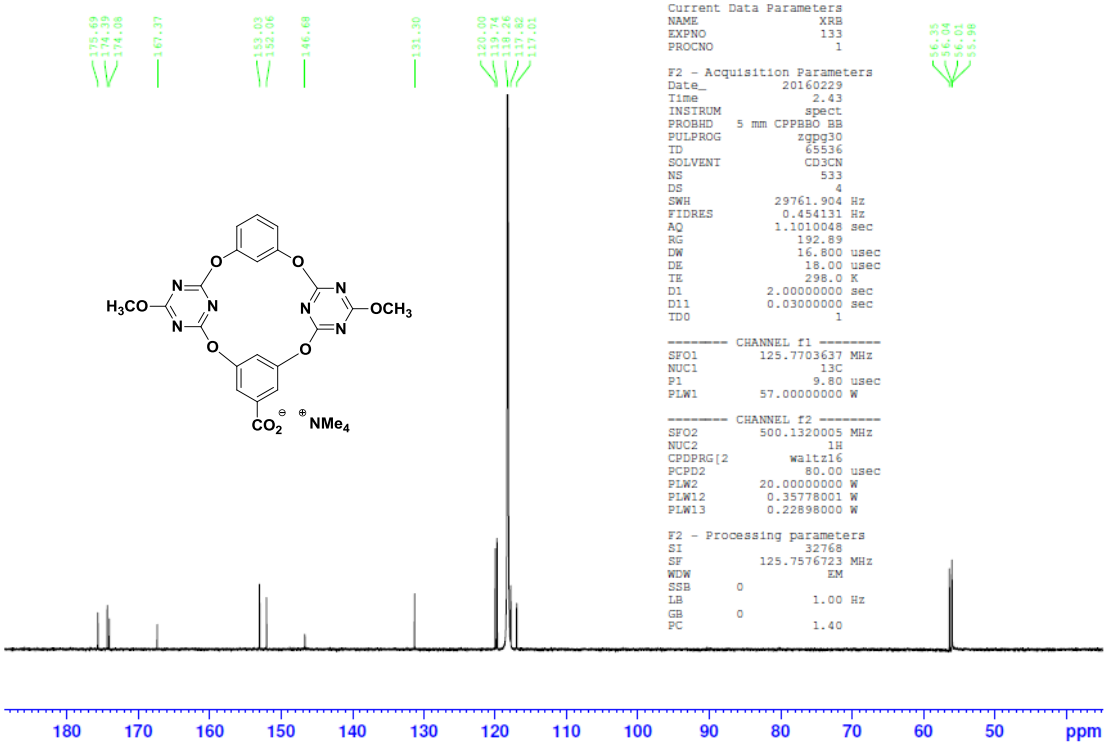
4d – ^{13}C NMR



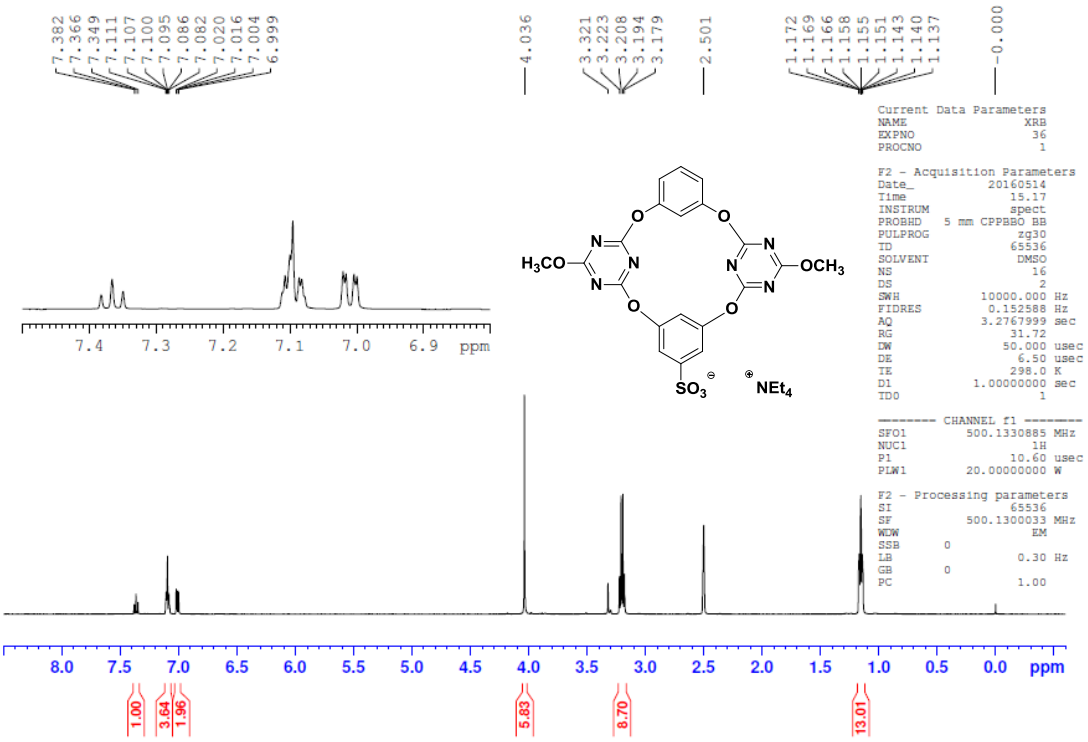
5a - ^{1}H NMR



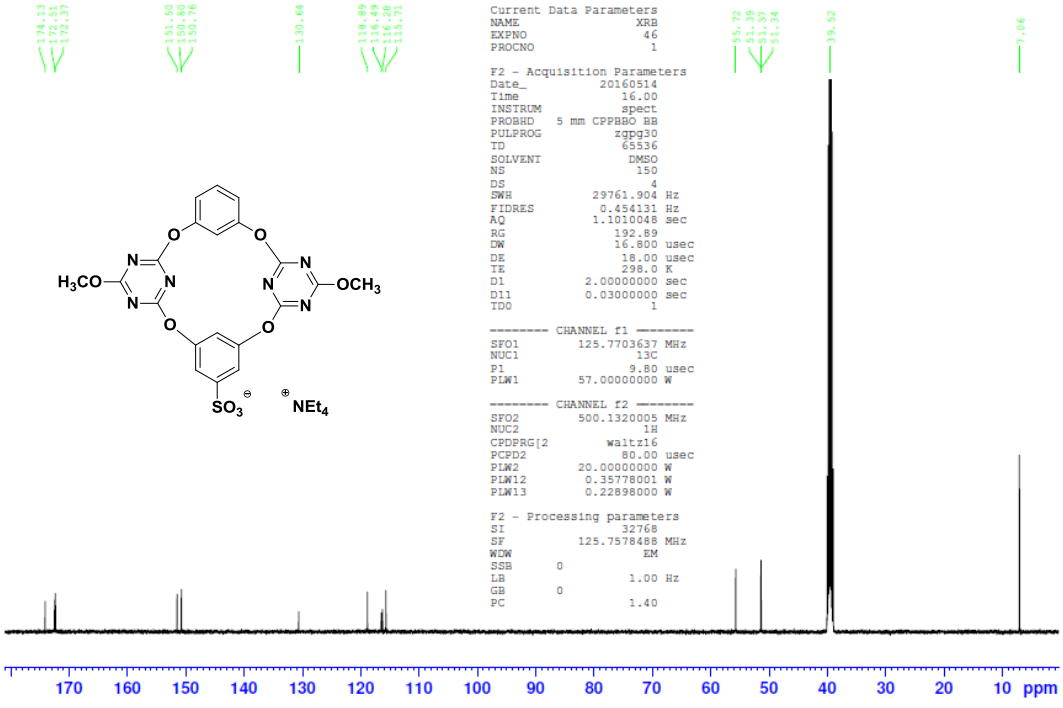
5a - ^{13}C NMR



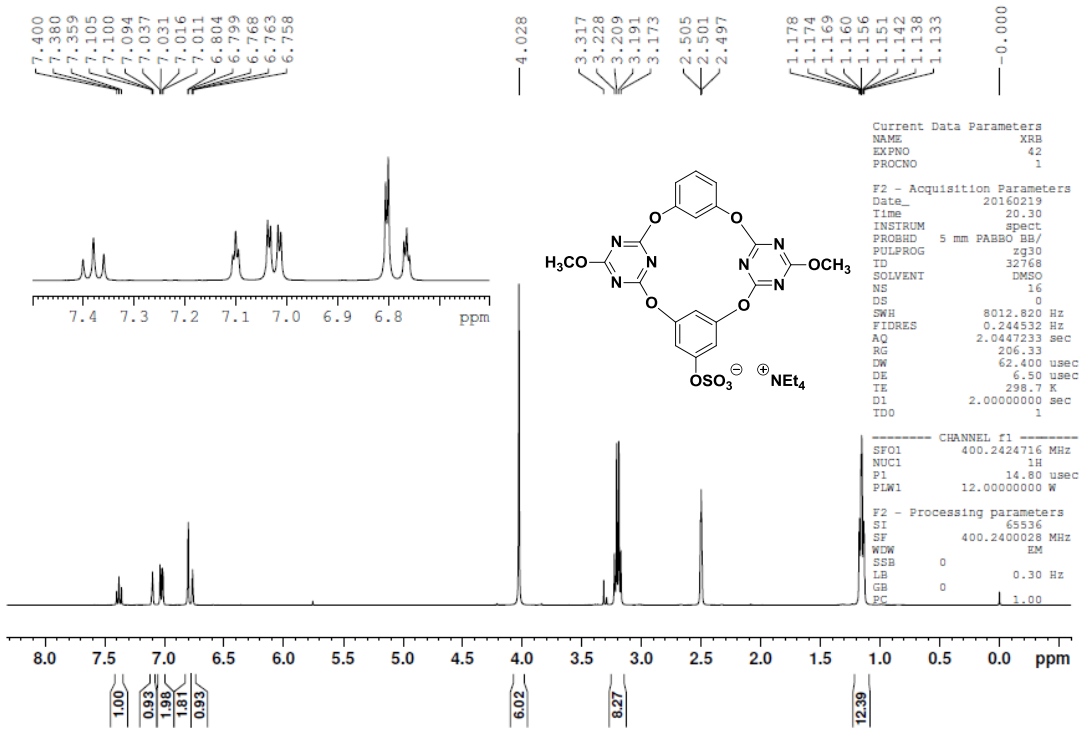
5b - ^{1}H NMR



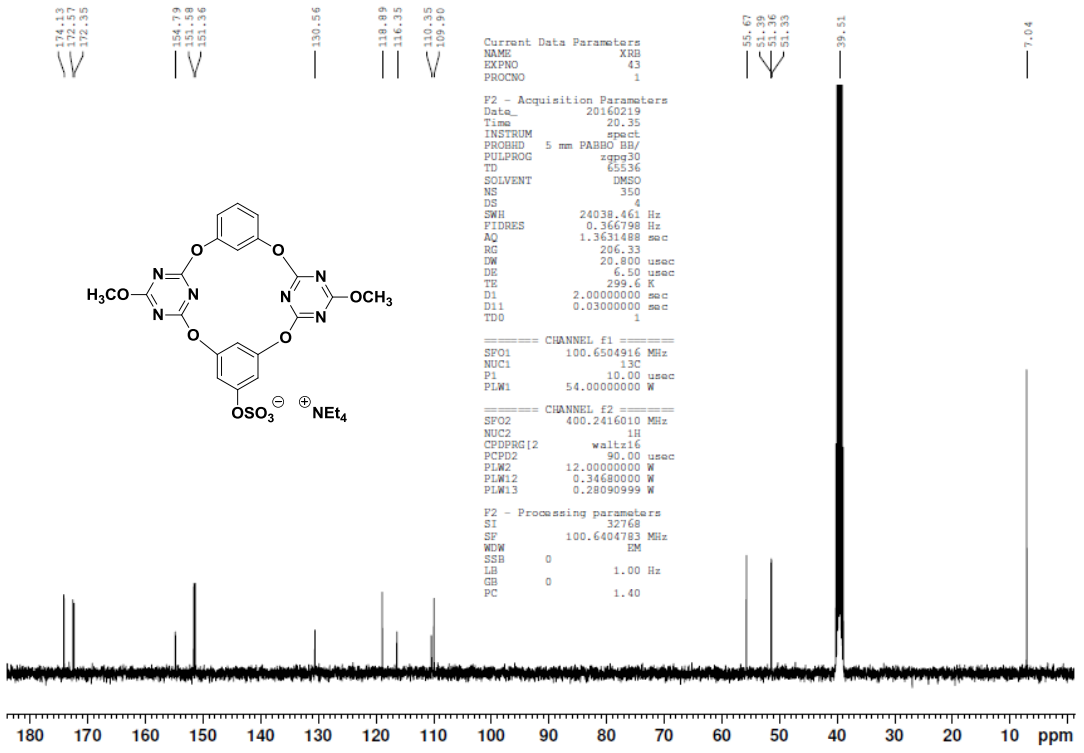
5b - ^{13}C NMR



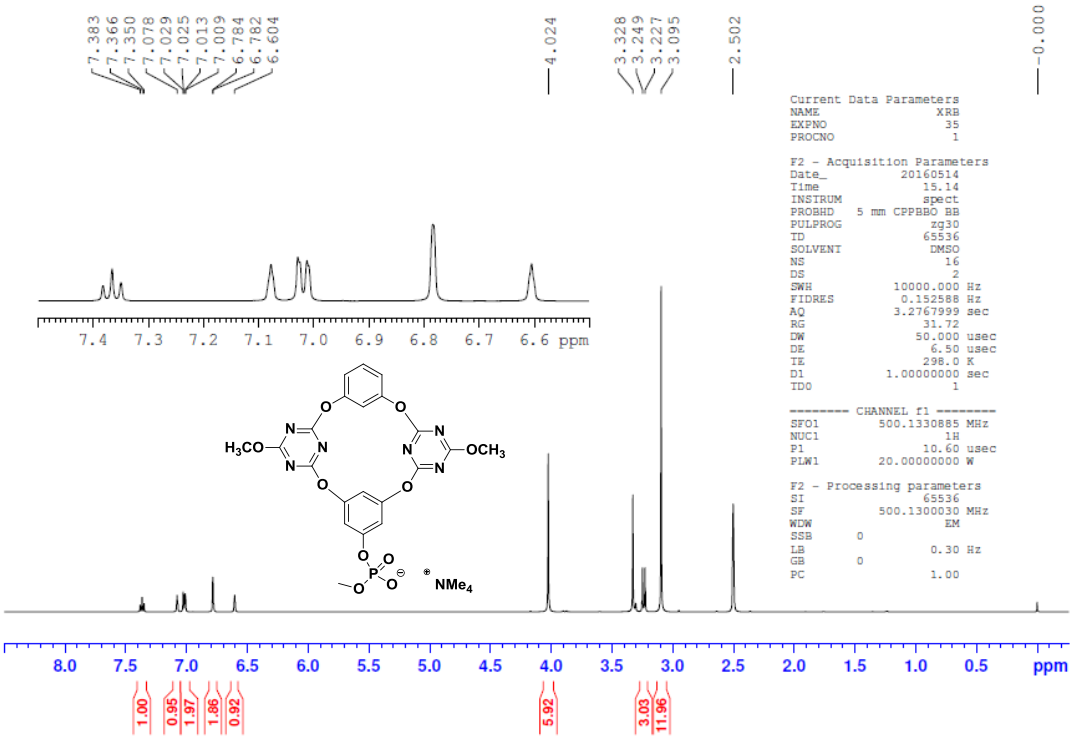
5c - ^{1}H NMR



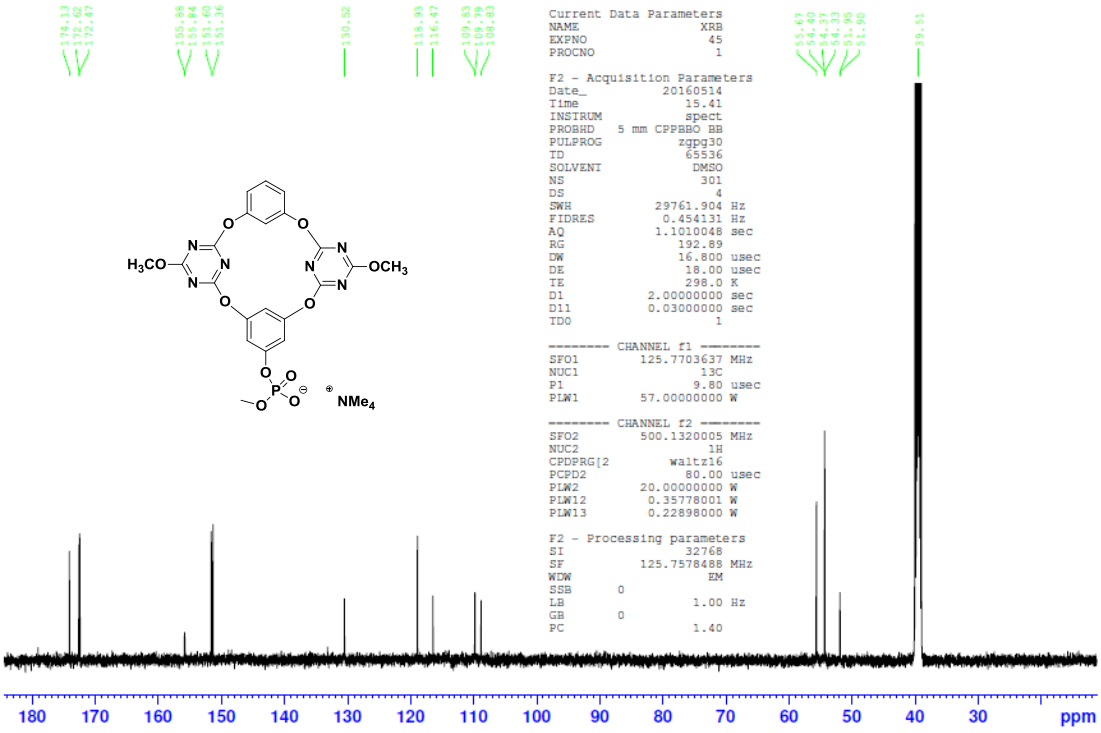
5c - ^{13}C NMR



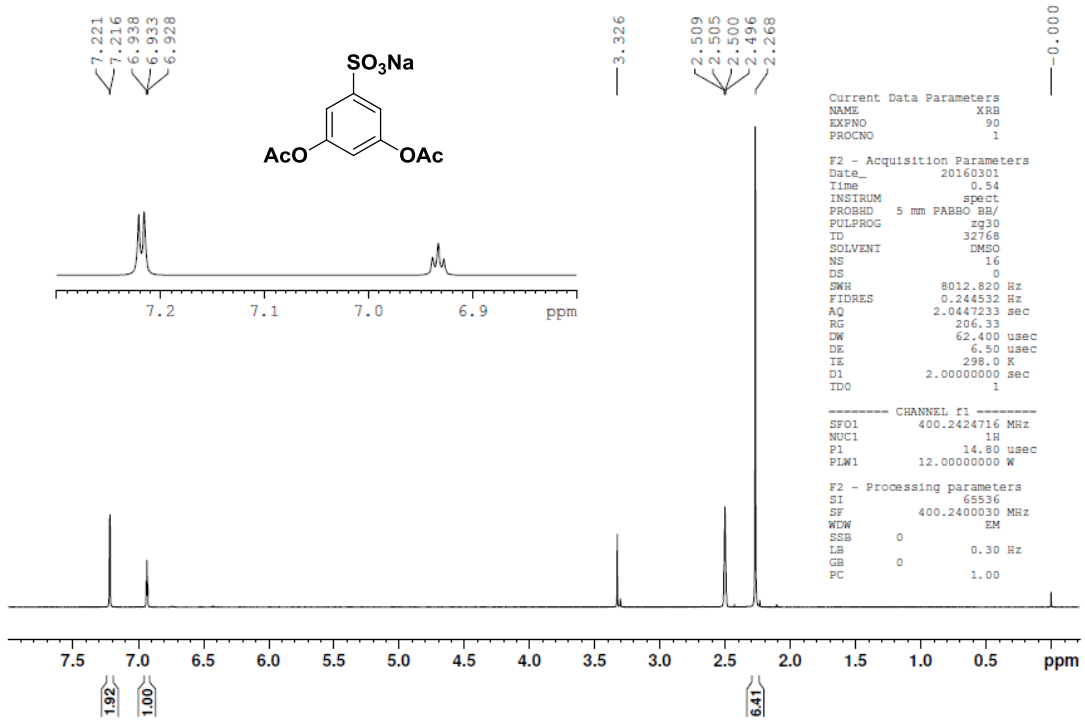
5d - ^{1}H NMR



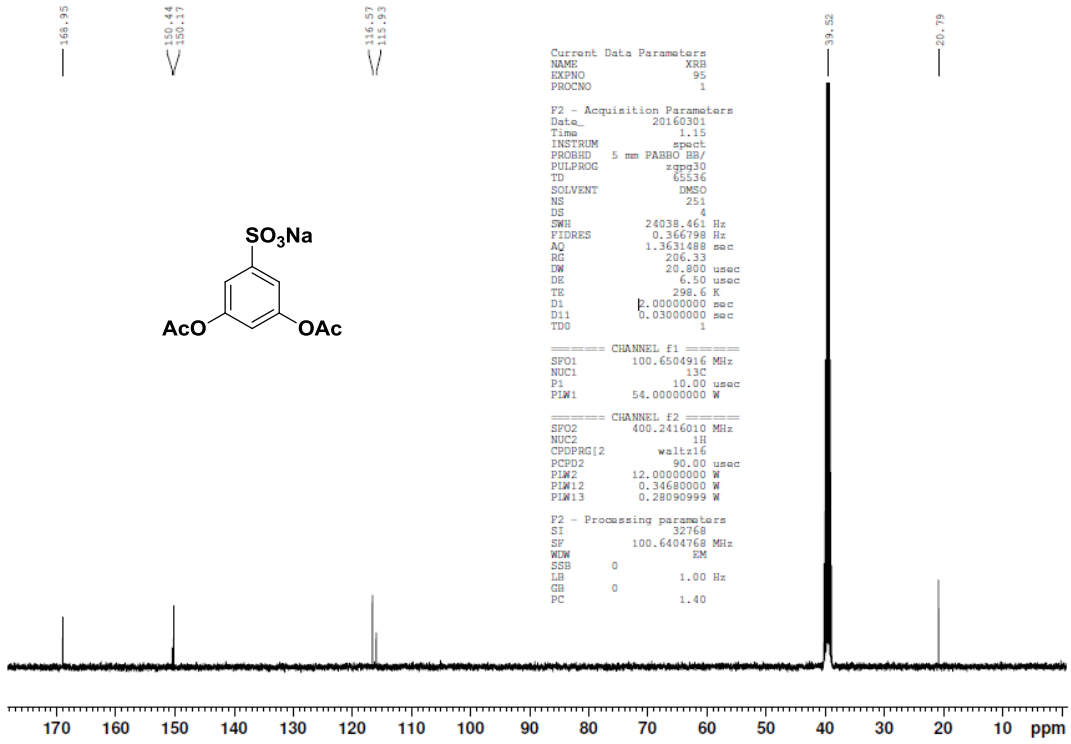
5d - ^{13}C NMR



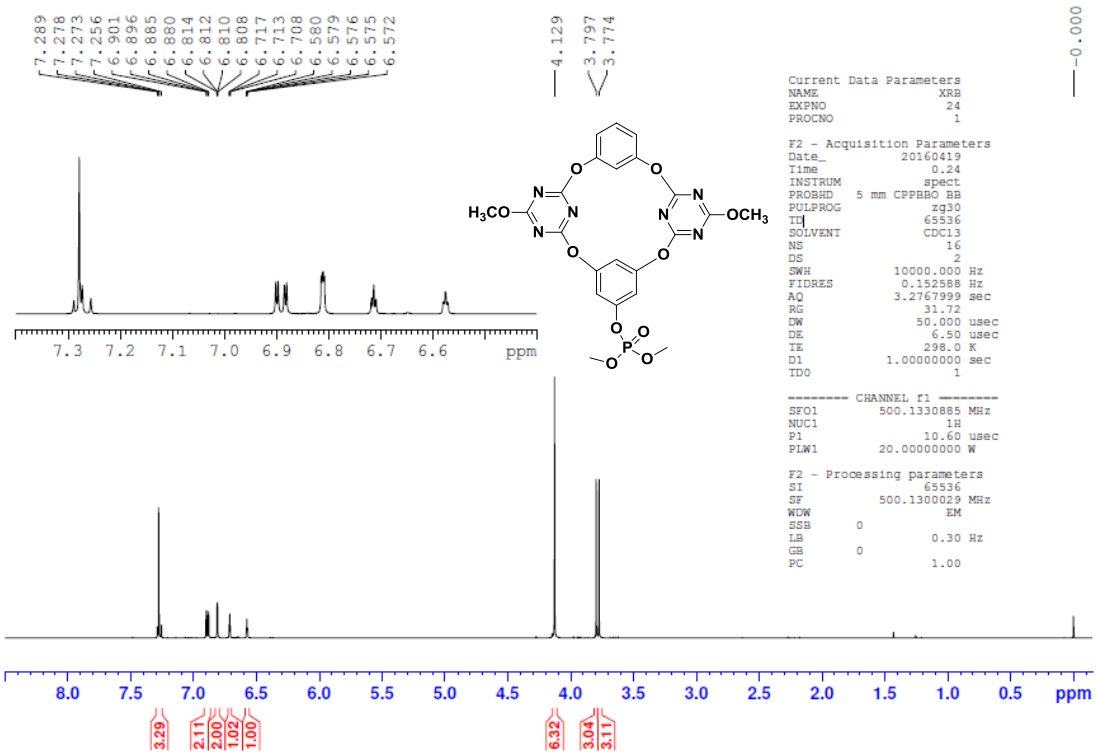
8 - ^{1}H NMR



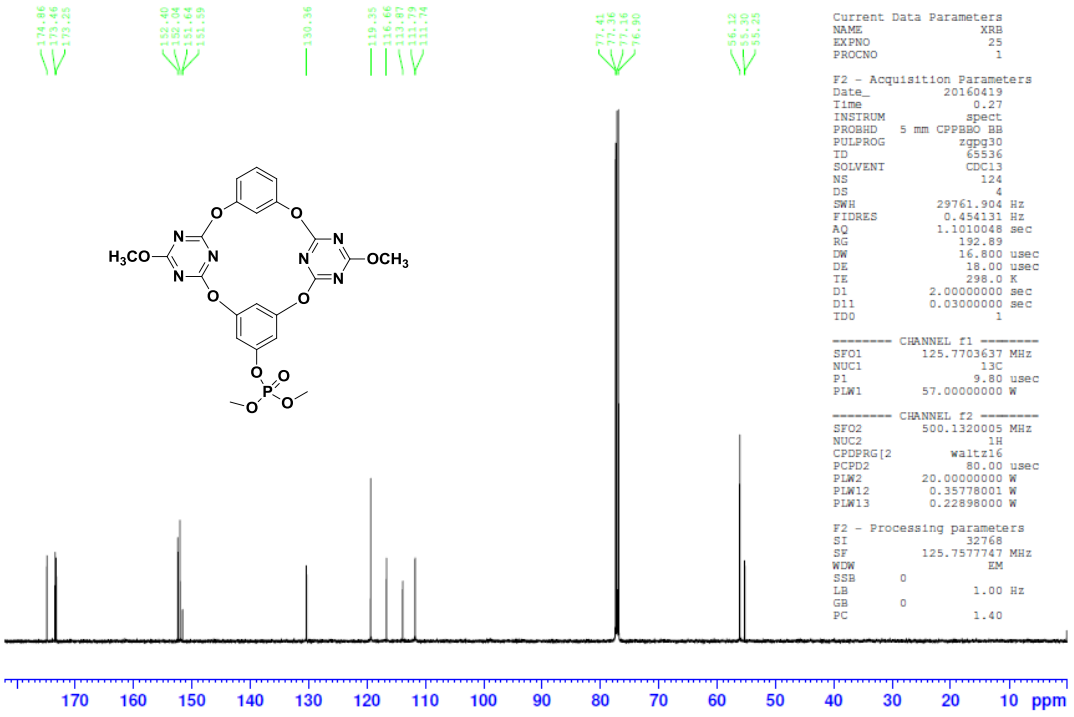
8 - ^{13}C NMR



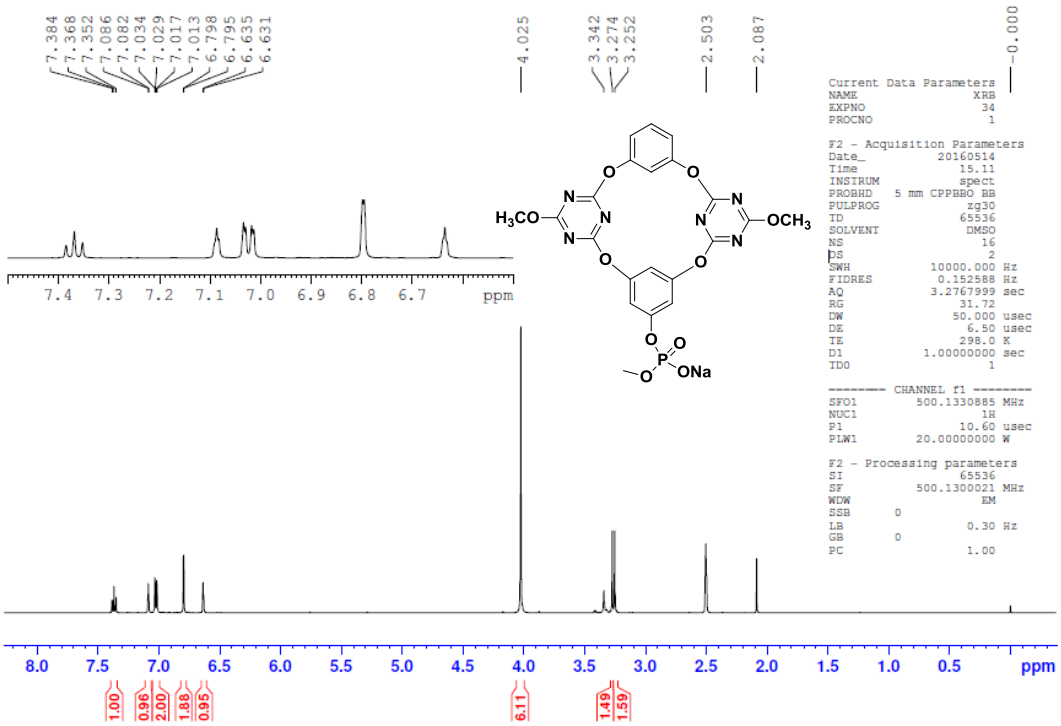
10 - ^{1}H NMR



10 - ^{13}C NMR



11 - ^{1}H NMR



11 - ^{13}C NMR