Anion-directed Assembly of a Rectangular Supramolecular Cage in the Solid State with Electron-deficient Phenoxylated Oxacalix[2]arene[2]triazine

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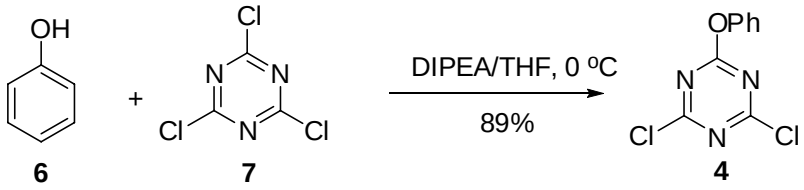
1. General Information

^{1}H and ^{13}C NMR spectra were recorded on 300, 400 or 600MHz NMR spectrometer. Chemical shifts are reported in ppm versus tetramethylsilane with either tetramethylsilane or the residual solvent resonance used as an internal standard. All solvents were dried according to standard procedures prior to use. All other major chemicals were obtained from commercial sources and used without further purification. The single crystal of **5a**, **5b** and the complex of [**5a**·Et_4NCl] were obtained by slow evaporation of a mixture of dichloromethane and hexane, acetone and hexane, dichloromethane and methanol, respectively.

2. Experimental details and characterization of products



6 **7** **4**

Scheme S1 Synthesis of **4**.

Preparation of **4**: To a solution of 2,4,6-trichloro-1,3,5-triazine **7** (5 mmol, 922 mg) in 15 mL THF, phenol **6** (5 mmol, 470 mg) in 20 mL THF and DIPEA (5.5 mmol, 709 mg) were added dropwise during 2 h. The mixture was stirring under icebath. After the reaction was finised, the resulting mixture was concentrated and was chromatographed on a silica gel (200-300 meshes) column eluting with a mixture of petroleum ether and acetone (6 : 1). Pure **4** was obtained as a white solid (1.08 g, 89%): ^{1}H NMR （400MHZ, $CDCl_3$） δ7.49-7.43 (2H, m), 7.37-7.31(1H, m), 7.20-7.15(2H, m); ^{13}C NMR (100MHZ, $CDCl_3$) δ173.2, 171.2, 151.1, 130.0, 127.1, 121.1.

Preparation of **5a**. Mixing **4** (2 mmol, 484 mg), **3** (2 mmol, 220 mg) and anhydrous K_2CO_3 (50 mL) in 20 mL acetonitrile. The mixture was refluxed for 24 h. After filtration and concentration, the residue was chromatographed on a silica gel (200-300

meshes) column eluting with a mixture of petroleum ether and ethyl acetate. Pure product **5a** (219 mg, 39%) was obtained as white solids: mp 176-178 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54-7.46 (m, 4H), 7.38-7.24 (m, 8H), 7.02-6.98 (2H, d, J = 1.8 Hz), 6.98-6.92 (4H, dd, J_1 = 8.3 Hz, J_2 = 1.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.6, 173.7, 152.3, 152.1, 130.5, 129.7, 126.2, 121.7, 119.0, 116.6; IR (KBr) ν 1566, 1483, 1367, 1199 cm^{-1}; MS (MALDI-TOF) *m/z* 559.2 ($M+H^+$), 581.2 ($M+Na^+$). Anal. Calcd. for $C_{30}H_{18}N_6O_6$: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.82; H, 3.40; N, 14.93.

Preparation of cage molecule **5b**. Mixing **2** (1 mmol, 184 mg) and anhydrous K_2CO_3 (2.2 mmol, 304 mg) in 20 mL dired acetonitrile. After stirring at room temperature for 30 min, a solution **1** (0.5 mmol, 222 mg) in 20 mL dired acetonitrile was added dropwise. The mixture was then stirred for another 30 min. After filtration and concentration, the residue was chromatographed on a silica gel (200-300 meshes) column eluting with a mixture of petroleum ether, ethyl acetate and dichlomethane (12 : 1 : 1). Pure **5b** (353 mg, 96%) was then obtained as white solids : mp 269-270 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.29 (2H, t, J_1 = 8.10 Hz), 6.89 (4H, dd, J_1 = 8.10 Hz, J_2 = 2.10 Hz), 6.74 (2H, t, J_2 = 2.10 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.0, 173.1, 151.9, 141.4 (dm, J_1 = 254.3 Hz, J_2 = 13.6 Hz), 140.1 (dm, J_1 = 254.3 Hz, J_2 = 13.6 Hz), 138.1 (dm, J_1 = 254.3 Hz, J_2 = 13.6 Hz), 130.7, 126.1(t, J_2 = 13.6 Hz), 119.6, 116.2; IR (KBr) ν 1589, 1521, 1485, 1449 cm^{-1}; MS (MALDI-TOF) *m/z* 739.2 ($M+H^+$). Anal. Calcd. for $C_{30}H_8F_{10}N_6O_6$: C, 48.80; H, 1.09; N, 11.38. Found: C, 48.67; H, 1.31; N, 11.26.

3. Crystal structure

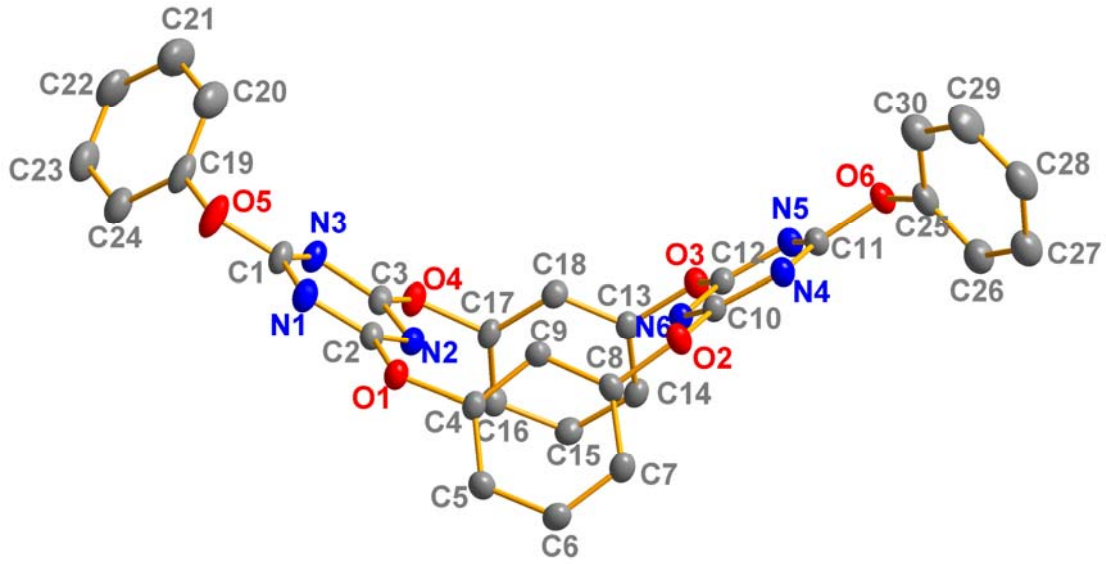
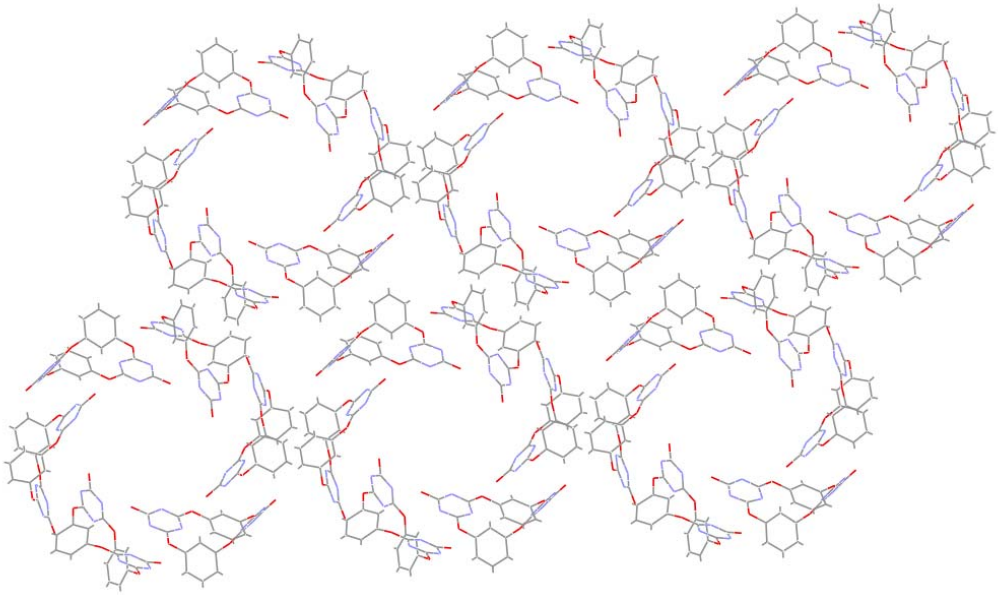


Figure S1 Crystal structure of **5a**. Selected bond length [Å]: C4-O1 1.414, O1-C2 1.337, C8-O2 1.420, O2-C10 1.340, C12-O3 1.339, O3-C13 1.408, C17-O4 1.417, O4-C3 1.337. Selected distances [Å]: C1···C11 9.082, N2···N6 4.574, C18···C9 4.295, C15···C6 6.233.



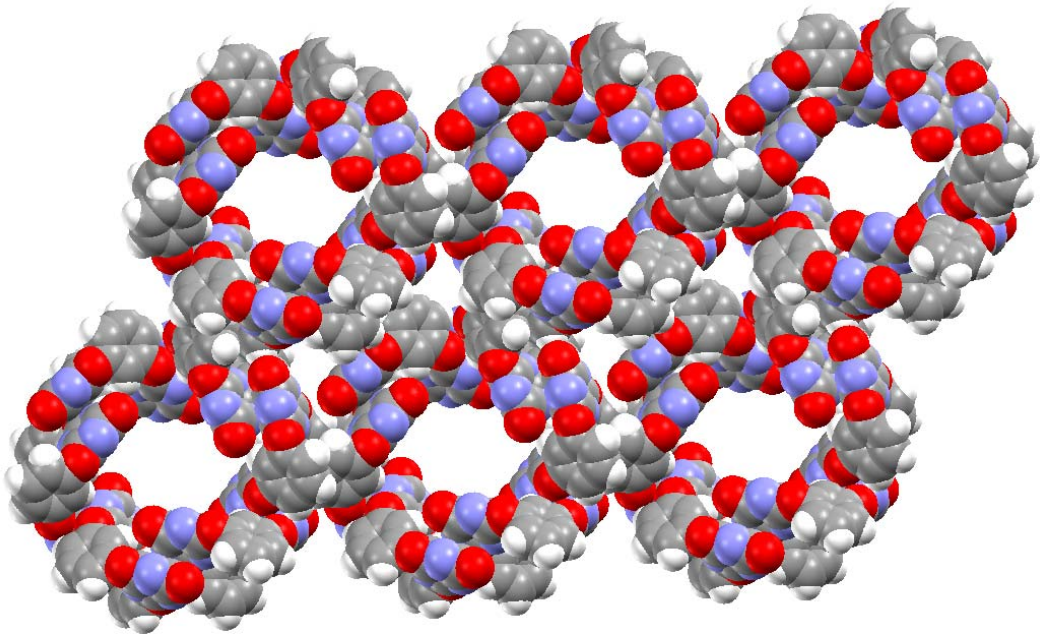


Figure S2 Self assembly of **5a**.

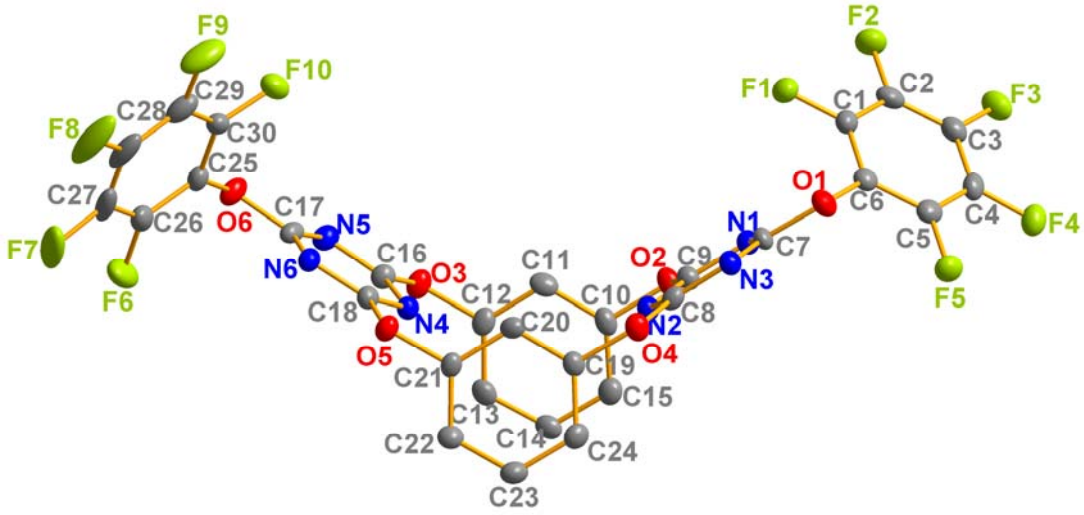


Figure S3 Crystal structure of **5b**. Selected bond length [Å]: C9-O2 1.326, O2-C10 1.431, C12-O3 1.420, O3-C16 1.330, C18-O5 1.351, O5-C21 1.412, C19-O4 1.420, O4-C8 1.341. Selected distances [Å]: C7···C17 9.027, N4···N2 4.600, C20···C11 4.435, C23···C14 4.925.

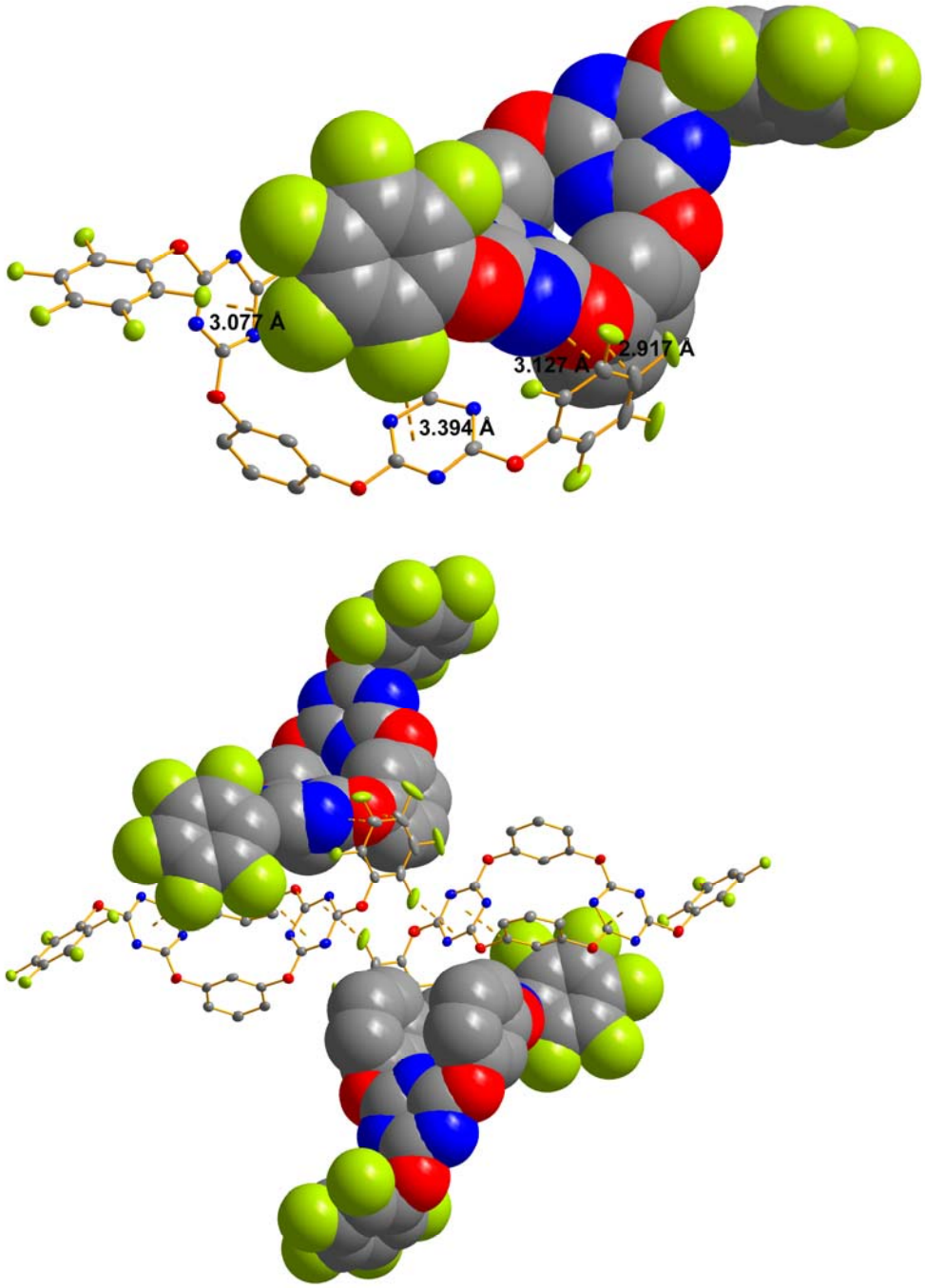


Figure S4 Self assembly of **5b** through multiple lone pair electrons-π interactions.

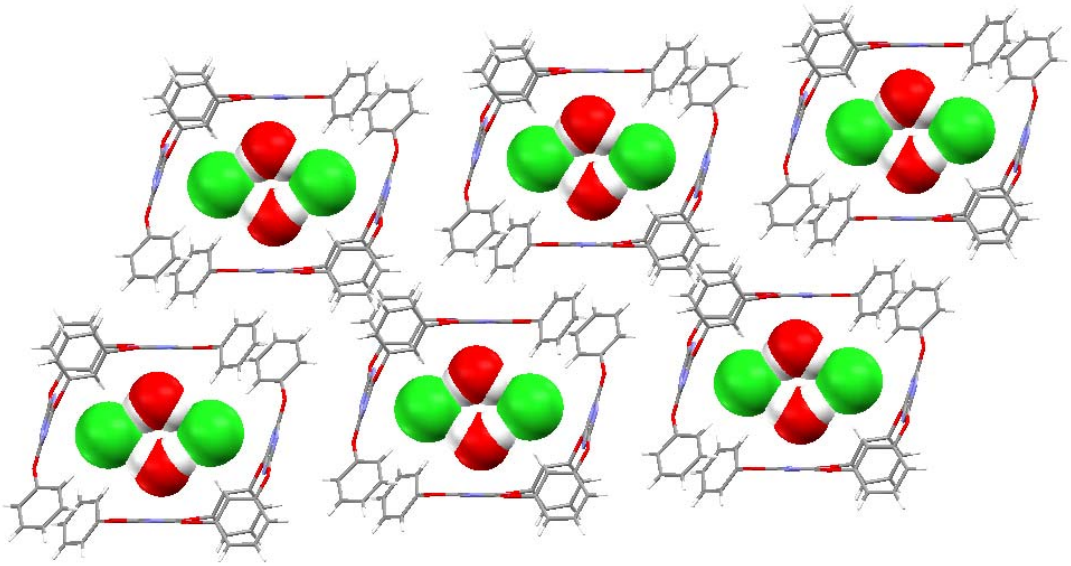


Figure S5 Self assembled cage structure of [**5a**·Cl^-·H_2O] complex through multple weak interactions.

4. Spectroscopic titration data

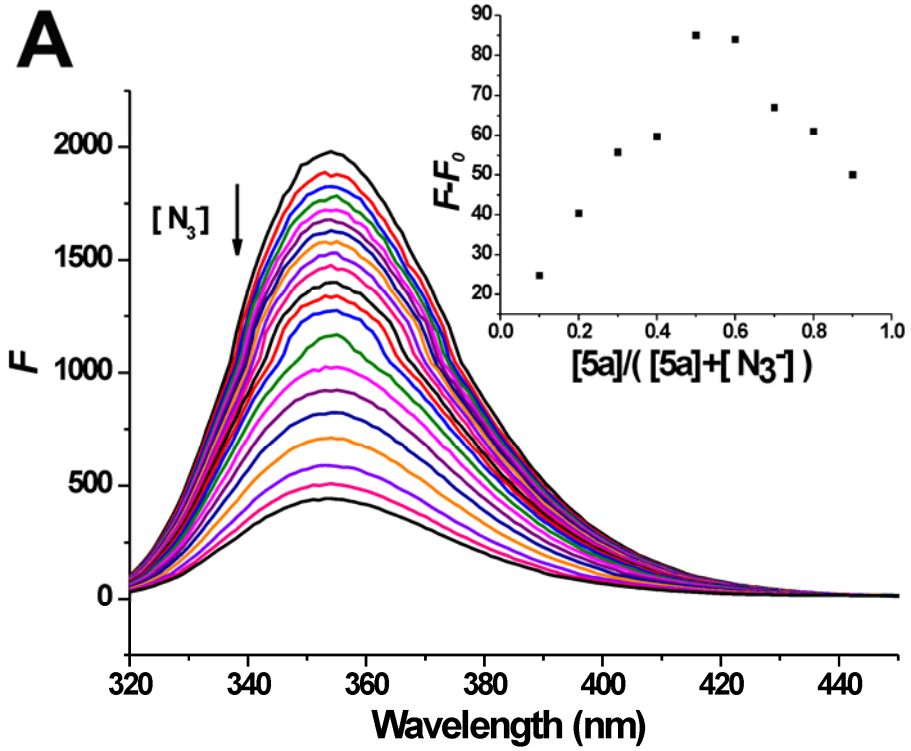


Figure S6 Fluorescence titration curves of **5a** (5.68×10^{-4} M in 2.0 mL acetonitrile) upon the addition of tetrabutylammonium azide (0, 1.11, 2.23, 3.37, 4.45, 5.569, 6.67, 7.79, 8.90, 10.0, 11.1, 13.4, 15.6, 16.7, 17.8, 18.9, 20.0, 21.1, 22.3 $\times 10^{-4}$ M), respectively. The excitation wavelength was 298 nm. Insert is the Job's plot of the complex.

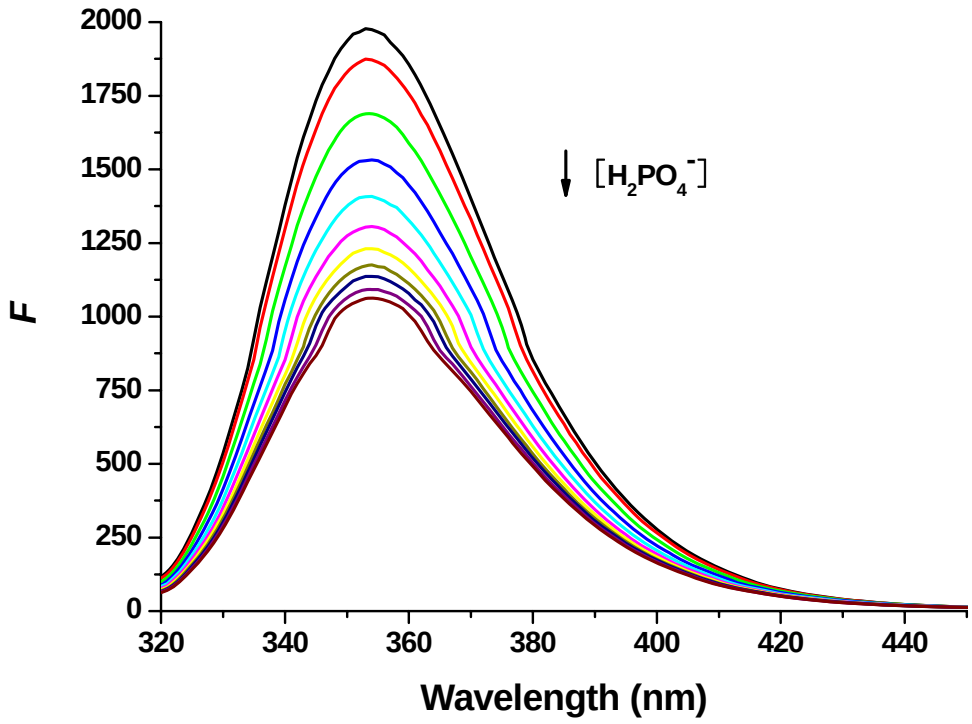


Figure S7 Fluorescence titration curves of **5a** (5.68×10^{-4} M in 2.0 mL acetonitrile) upon the addition of tetrabutylammonium phosphate (0, 0.18, 0.36, 0.54, 0.715, 0.89, 1.07, 1.25, 1.43, 1.61, 1.79×10^{-4} M), respectively. The excitation wavelength was 298 nm. The excitation and emission band widths were both 10 nm and the scan speed was set at 240 nm/min, respectively.

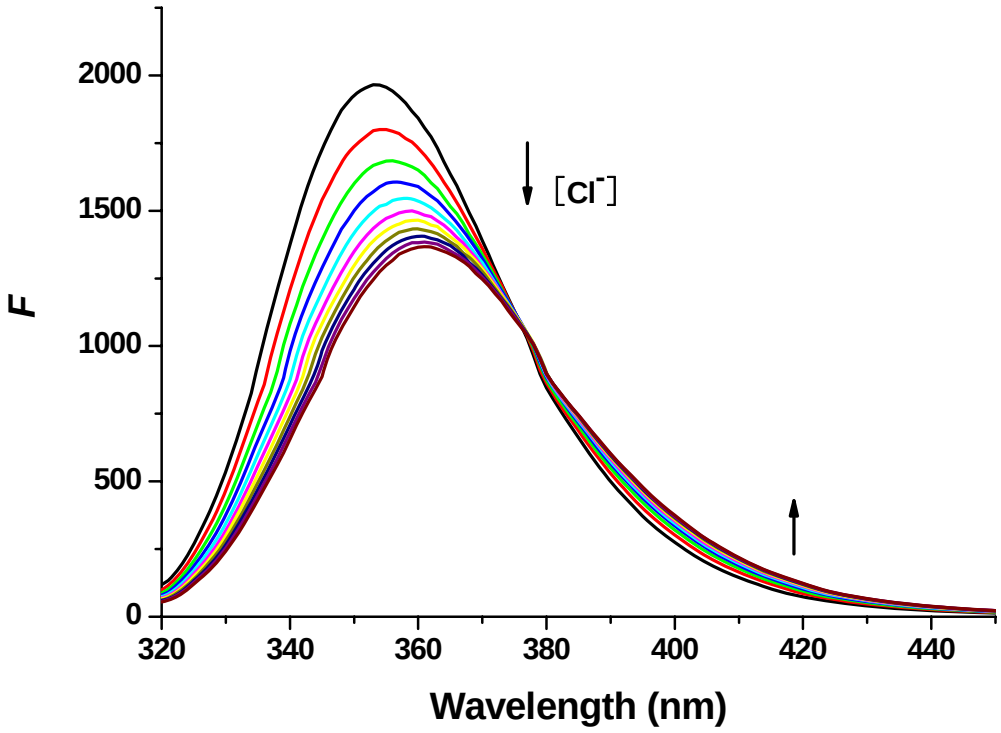


Figure S8 Fluorescence titration curves of **5a** (5.68×10^{-4} M in 2.0mL acetonitrile) upon the addition of tetrabutylammonium chloride (0, 0.37, 0.74, 1.11, 1.48, 1.85, 2.23, 2.60, 2.97, 3.34, 3.71×10^{-3} M), respectively. The excitation wavelength was 298 nm. The excitation and emission band widths were both 10 nm and the scan speed was set at 240 nm/min, respectively.

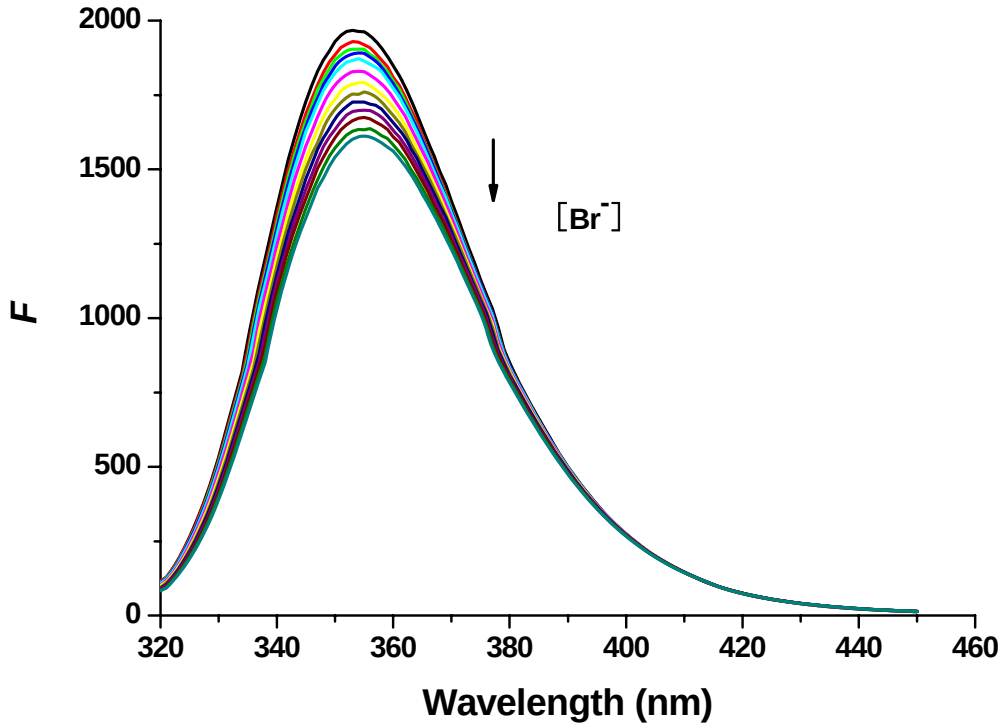


Figure S9 Fluorescence titration curves of **5a** (5.68×10^{-4} M in 2.0mL acetonitrile) upon the addition of tetrabutyl ammonium bromide (0, 0.18, 0.35, 0.527, 0.70, 1.05, 1.41, 1.78, 2.11, 2.46, 2.81, 3.16, 3.51×10^{-3} M), respectively. The excitation wavelength was 298 nm. The excitation and emission band widths were both 10 nm and the scan speed was set at 240nm/min, respectively.

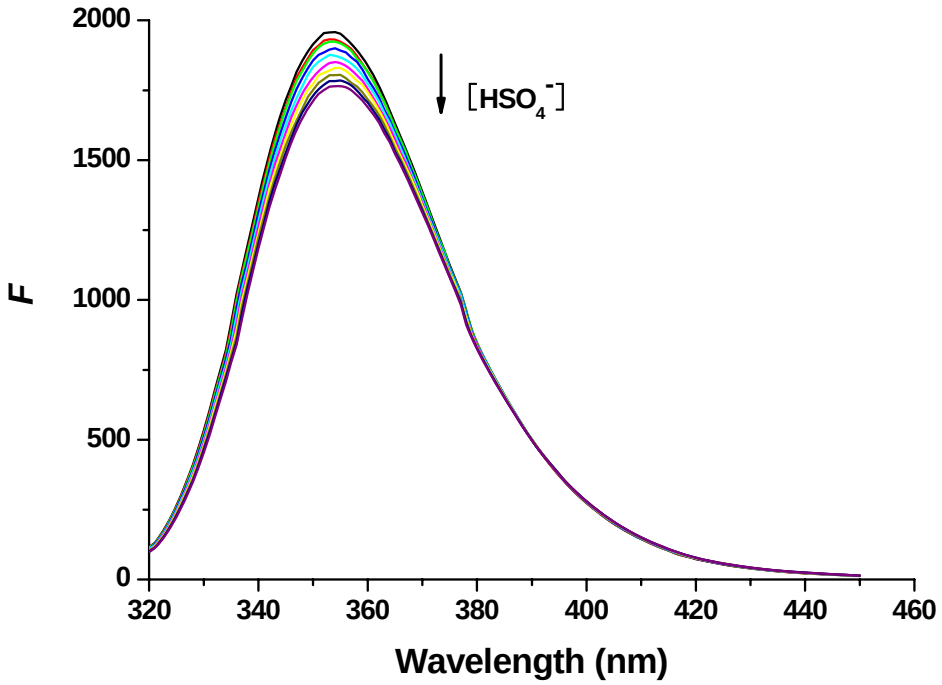


Figure S10 Fluorescence titration curves of **5a** (5.68×10^{-4} M in 2.0mL acetonitrile) upon the addition of tetrabutyl ammonium sulfate (0, 0.19, 0.38, 0.76, 1.14, 1.52, 1.91, 2.285, 2.67, 3.05×10^{-3} M), respectively. The excitation wavelength was 298 nm. The excitation and emission band widths were both 10 nm and the scan speed was set at 240nm/min, respectively.

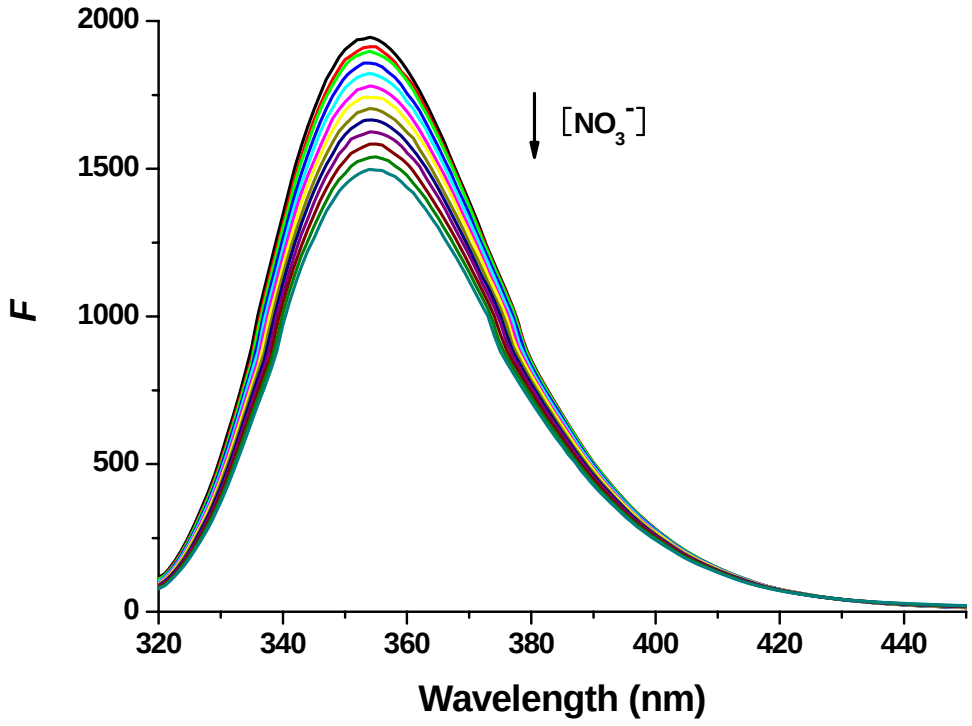


Figure S11 Fluorescence titration curves of **5a** (5.68×10^{-4} M in 2.0mL acetonitrile) upon the addition of tetrabutyl ammonium nitrate (0, 0.35, 0.70, 1.05, 1.40, 1.75, 2.11, 2.456, 2.81, 3.16, 3.51, 3.86, 4.21×10^{-3} M), respectively. The excitation wavelength was 298 nm. The excitation and emission band widths were both 10 nm and the scan speed was set at 240nm/min, respectively.

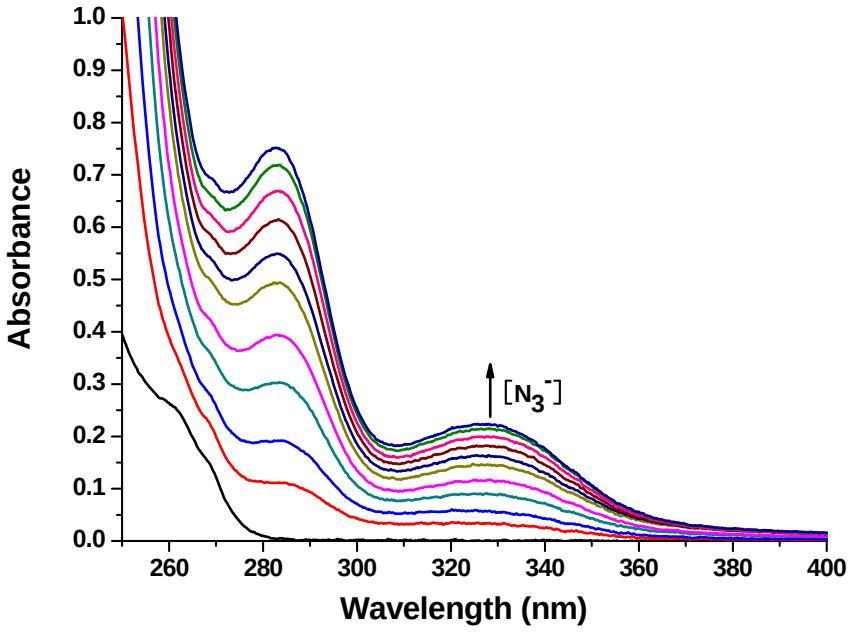


Figure S12 UV-vis titration curves of **5b** (1.76×10^{-4} M in 1 mL acetonitrile) upon the addition of tetrabutylammonium azide (0, 0.39, 0.78, 1.17, 1.560, 1.95, 2.34, 2.73, 3.12, 3.51, 3.90 $\times 10^{-4}$ M), respectively.

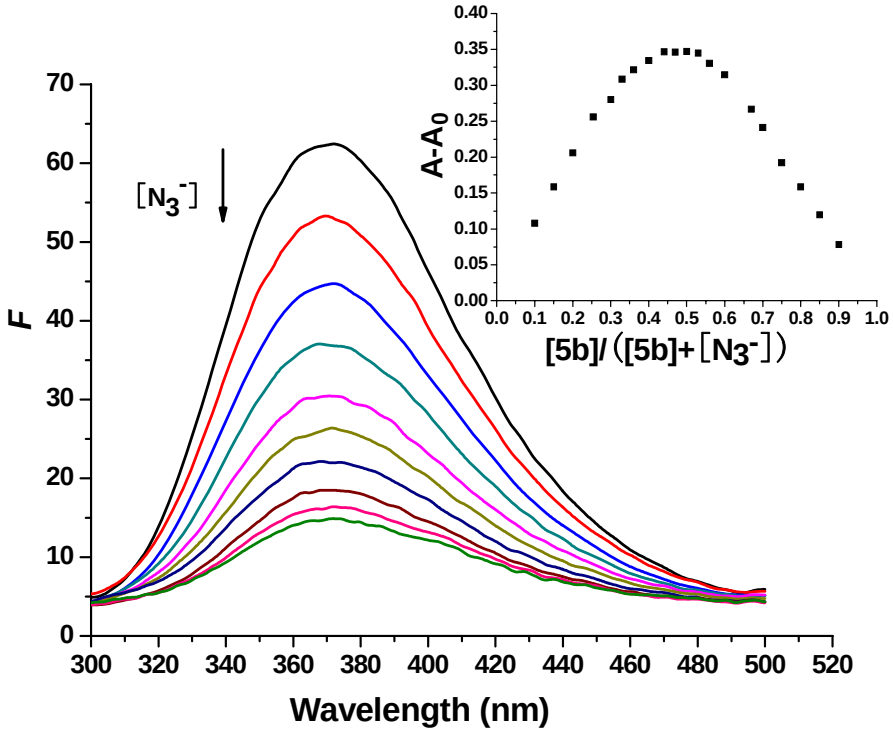


Figure S13 Fluorescence titration curves of **5b** (1.73×10^{-4} M in 1.0mL acetonitrile) upon the addition of tetrabutylammonium azide (0, 0.39, 0.78, 1.17, 1.56, 1.95, 2.34, 2.73, 3.12, 3.51, 3.90×10^{-4} M), respectively. The excitation wavelength was 259 nm. The excitation and emission band widths were both 10 nm and the scan speed was set at 240nm/min, respectively. The insert is the Job plot of the complex and total concentration is 7.10×10^{-4} M.

5. ^{1}H NMR titration data

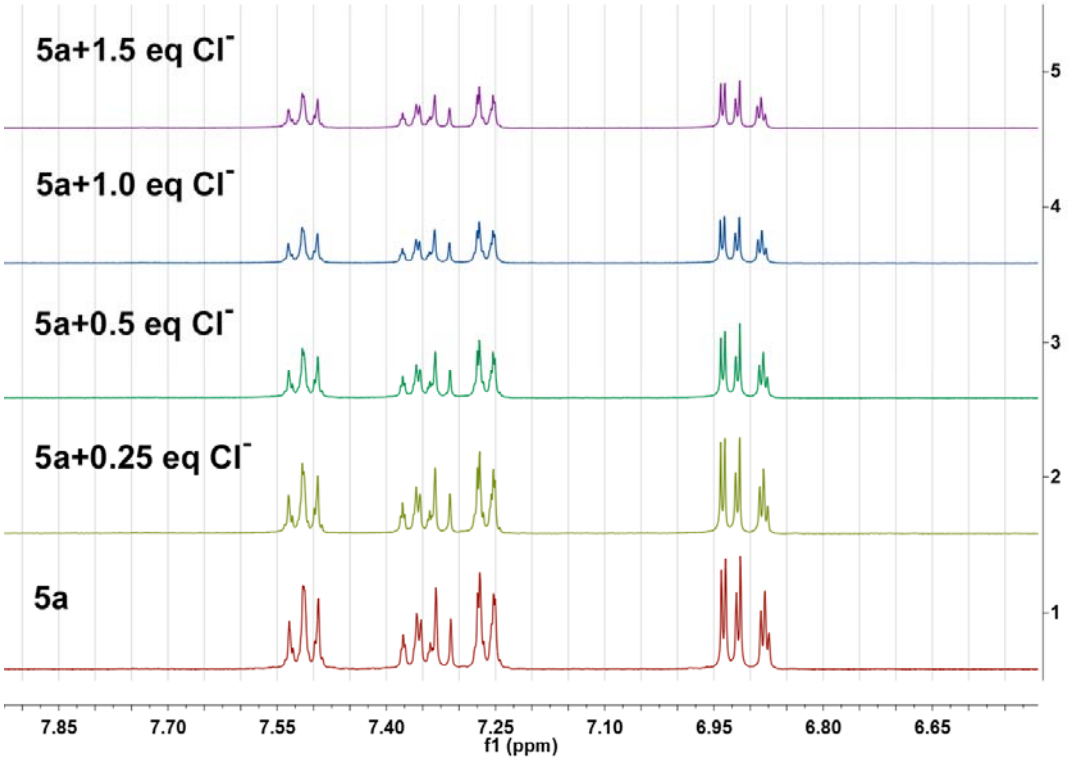


Figure S14 ^{1}H titration of **5a** upon the addition of chloride (in CD_3CN and with 400 MHz NMR spectrometer).

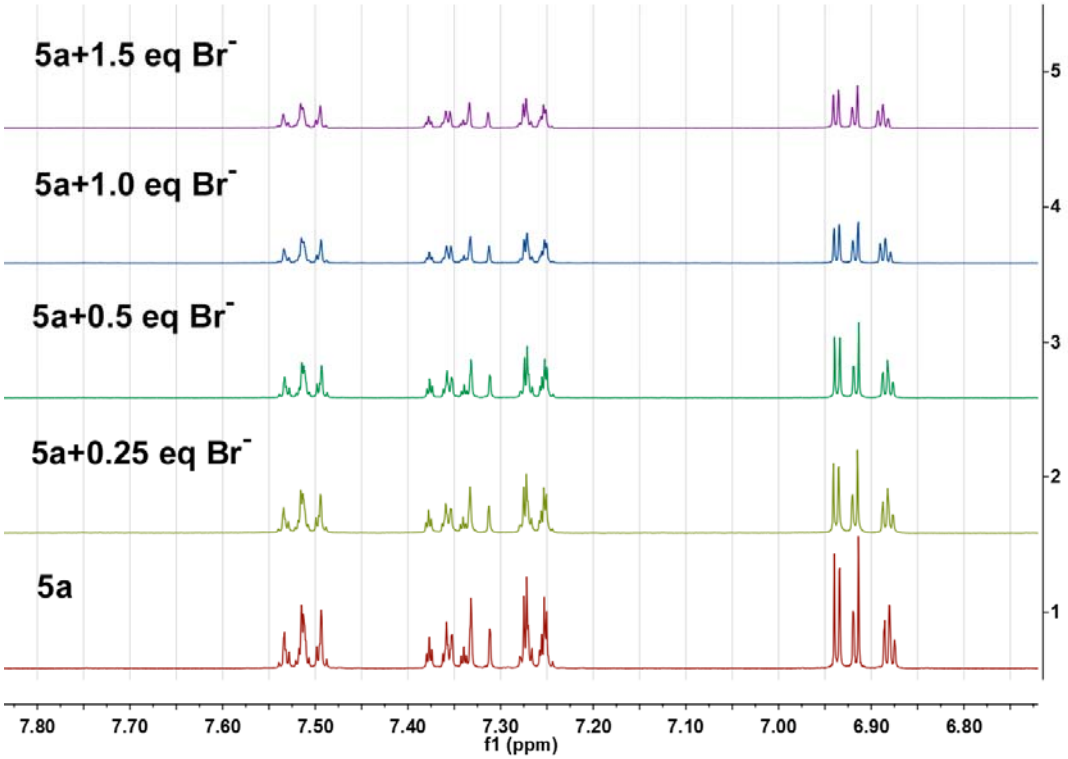


Figure S15 ^{1}H titration of **5a** upon the addition of bromide (in CD_3CN and with 400 MHz NMR spectrometer).

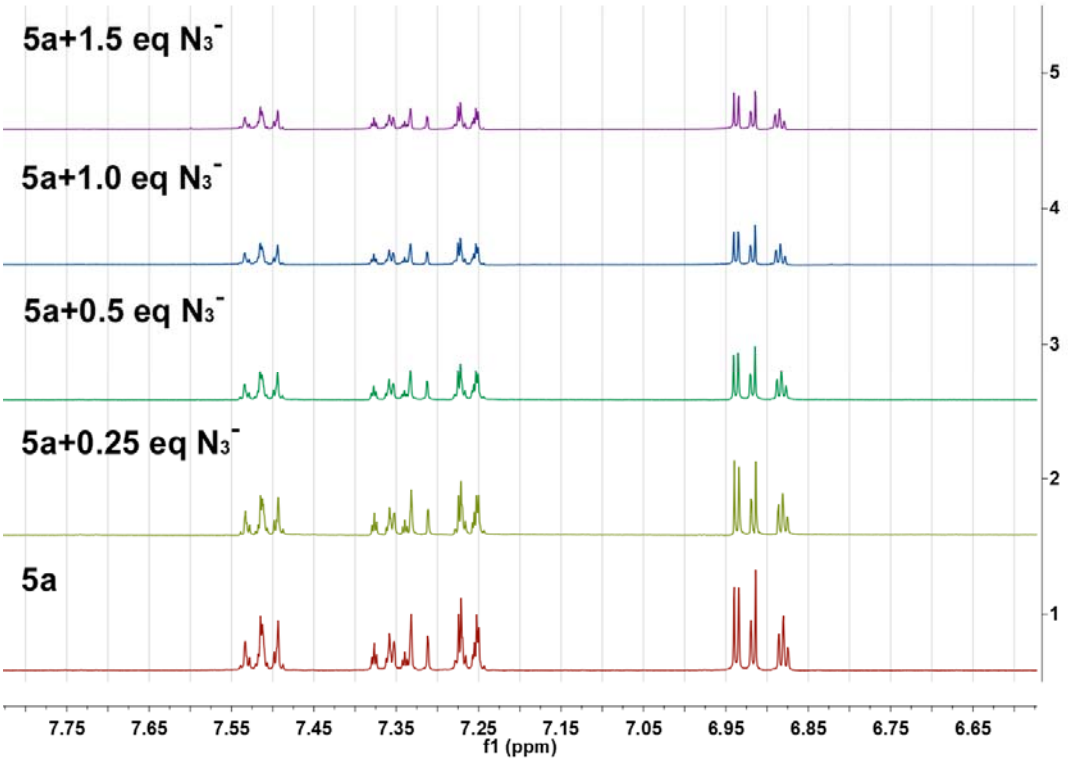


Figure S16 ^{1}H titration of **5a** upon the addition of azide (in CD_3CN and with 400 MHz NMR spectrometer).

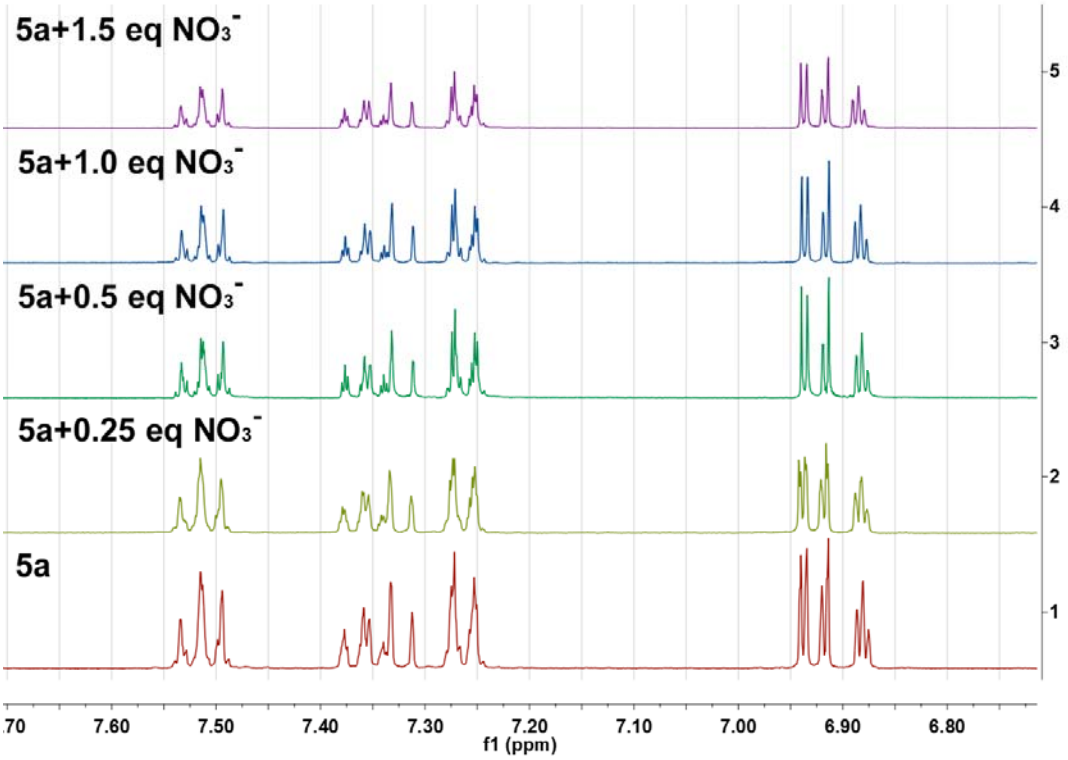


Figure S17 ^{1}H titration of **5a** upon the addition of nitrate (in CD_3CN and with 400 MHz NMR spectrometer).

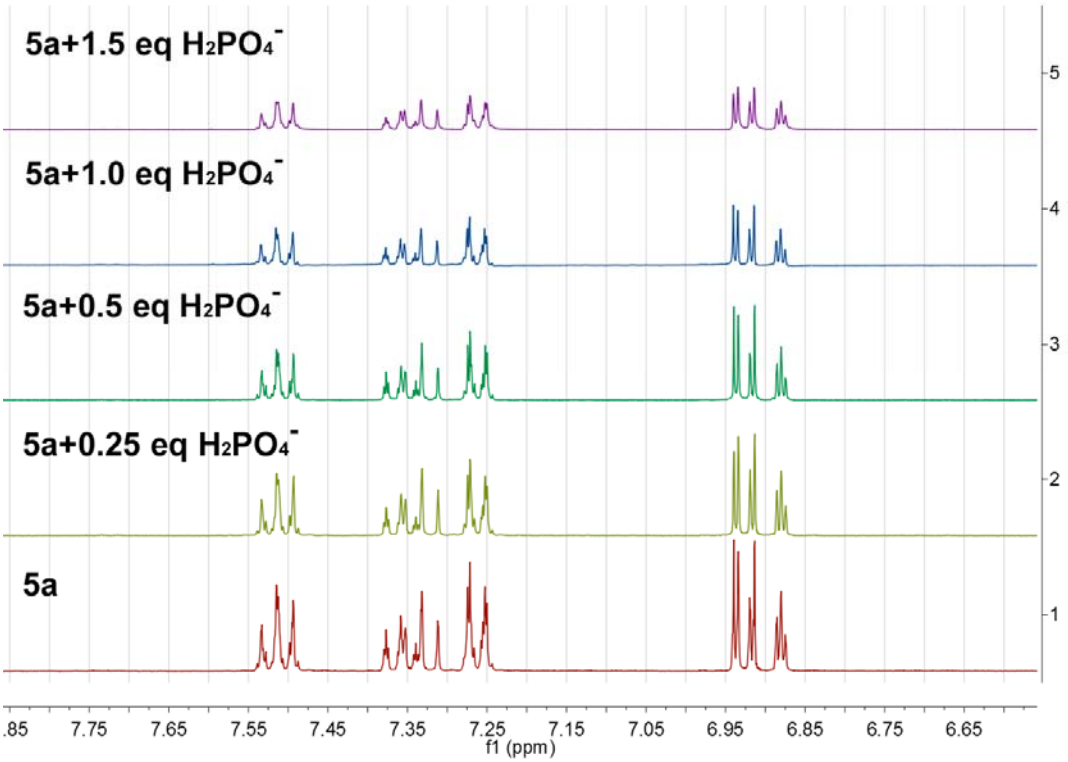


Figure S18 ^{1}H titration of **5a** upon the addition of phosphate (in CD_3CN and with 400 MHz NMR spectrometer).

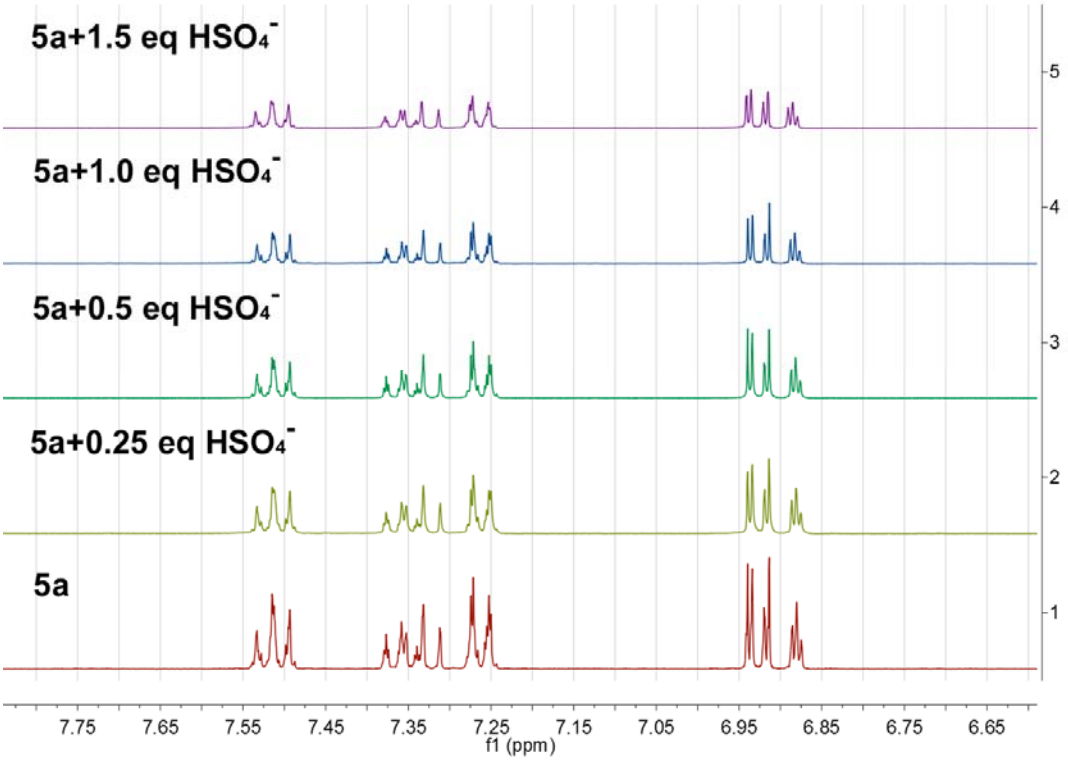


Figure S19 ^{1}H titration of **5a** upon the addition of sulphate (in CD_3CN and with 400 MHz NMR spectrometer).

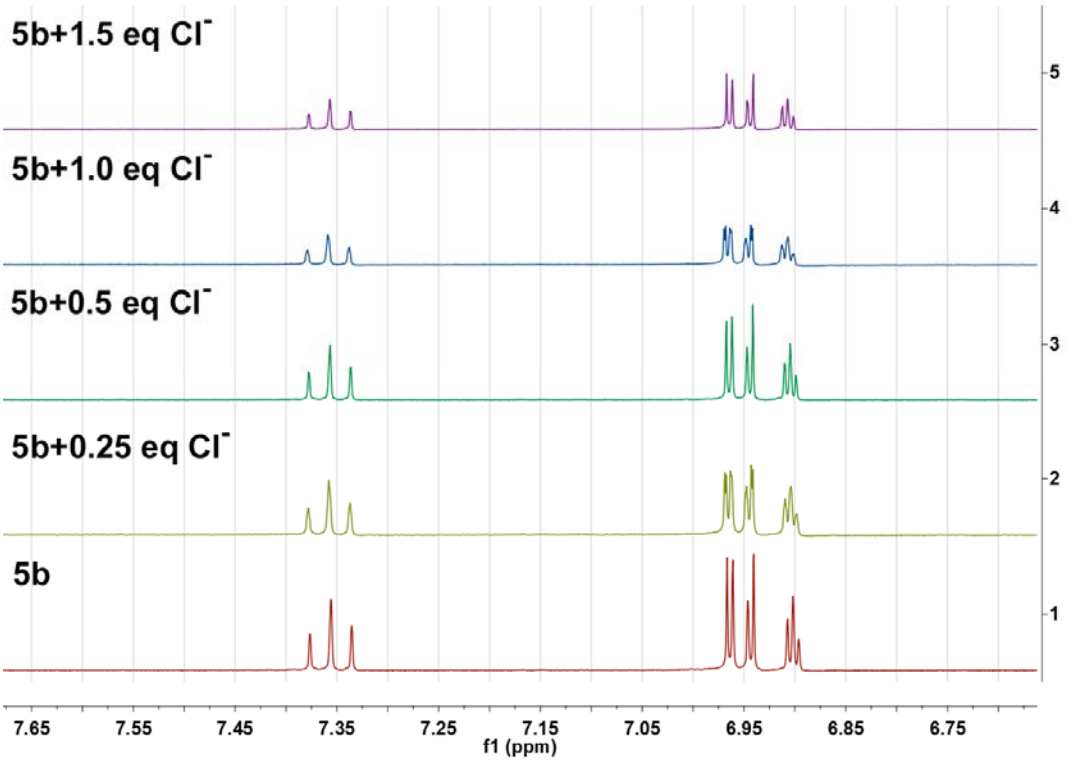


Figure S20 ^{1}H titration of **5b** upon the addition of chloride (in CD_3CN and with 400 MHz NMR spectrometer).

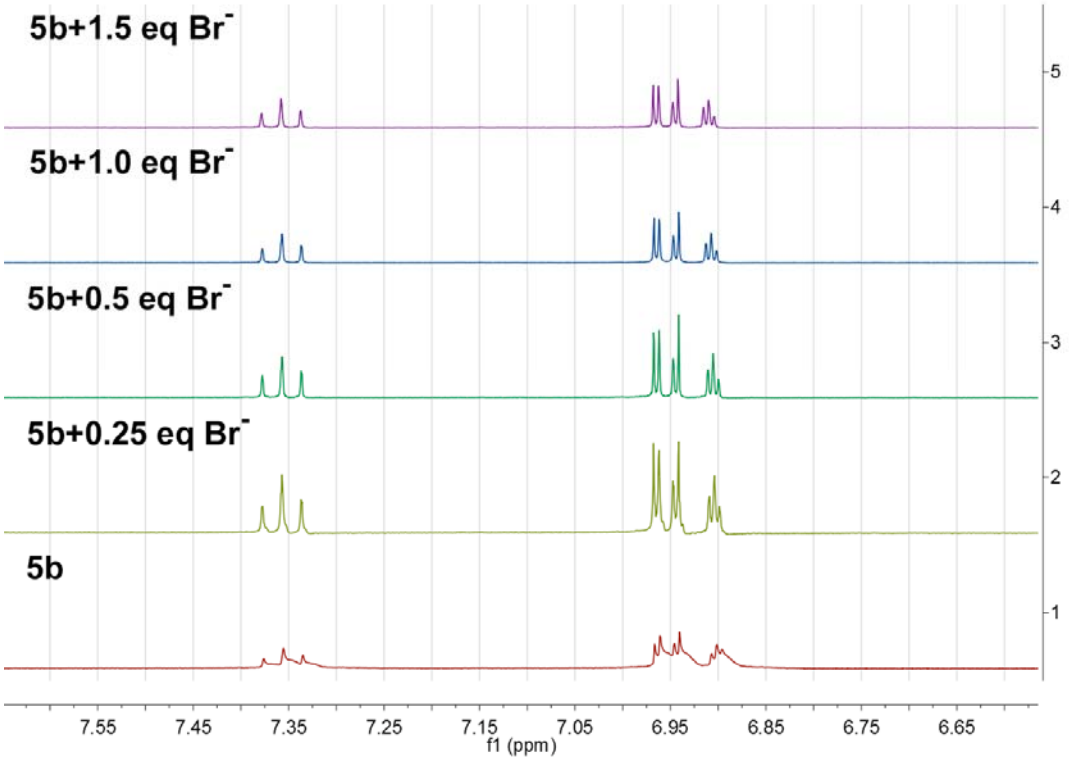


Figure S21 ^{1}H titration of **5b** upon the addition of bromide (in CD_3CN and with 400 MHz NMR spectrometer).

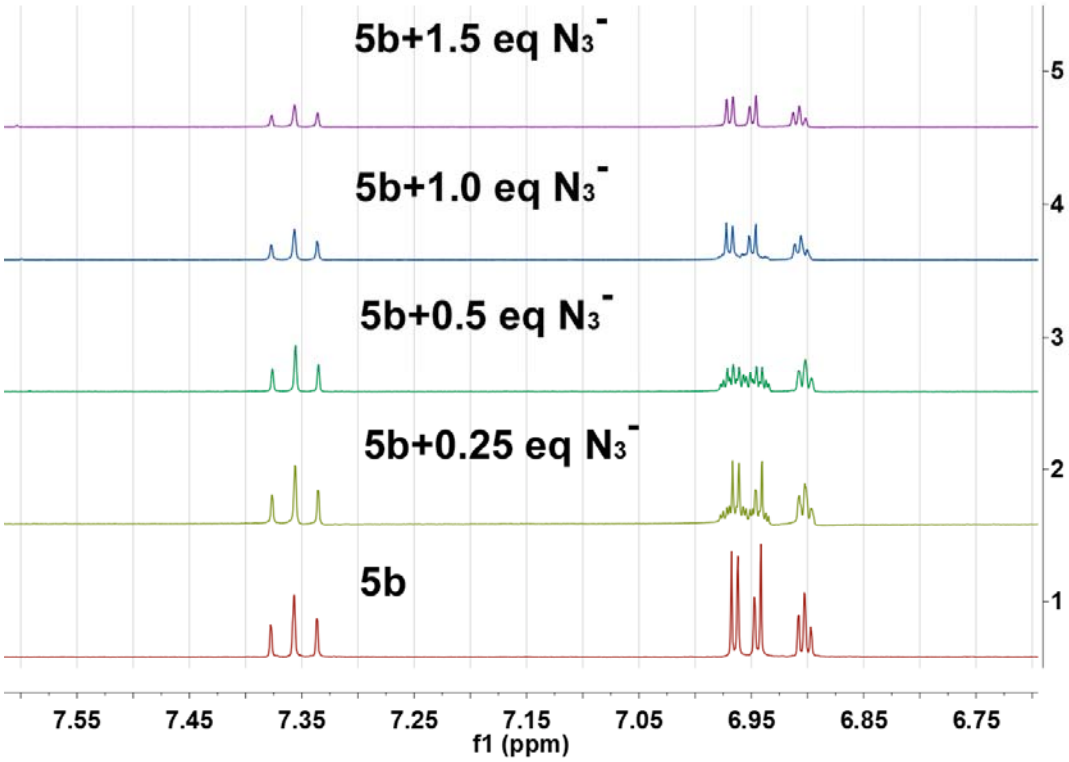


Figure S22 ^{1}H titration of **5b** upon the addition of azide (in CD_3CN and with 400 MHz NMR spectrometer).

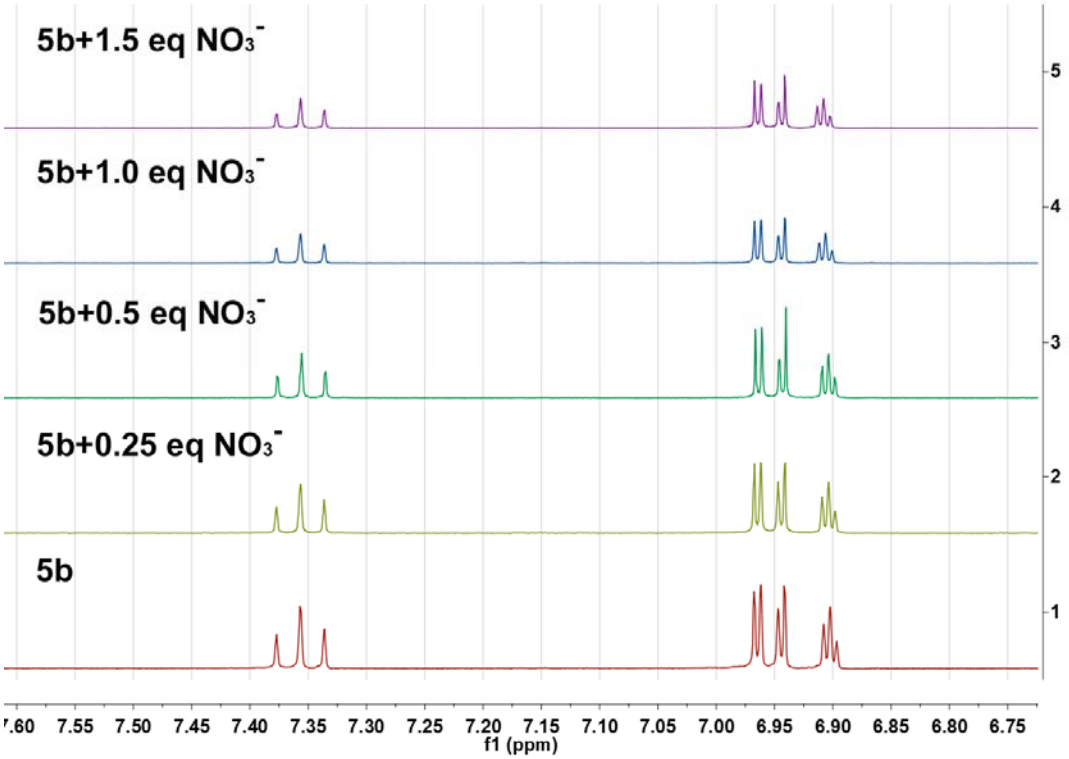


Figure S23 ^{1}H titration of **5b** upon the addition of nitrate (in CD_3CN and with 400 MHz NMR spectrometer).

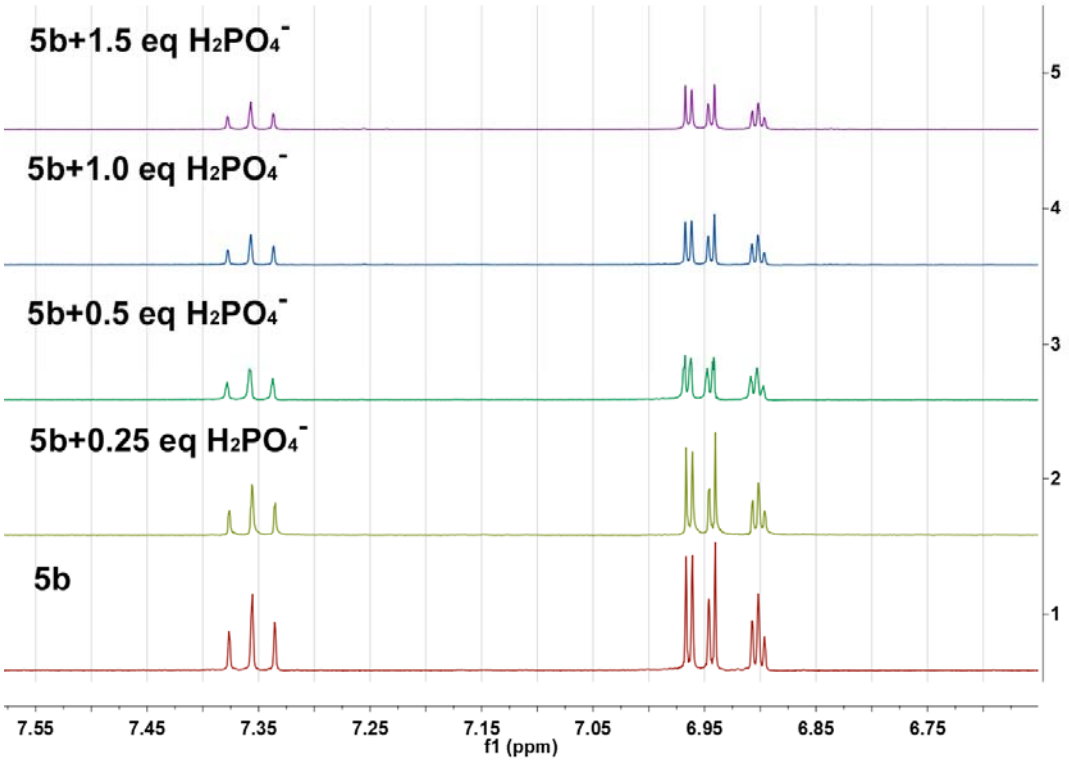


Figure S24 ^{1}H titration of **5b** upon the addition of phosphate (in CD_3CN and with 400 MHz NMR spectrometer).

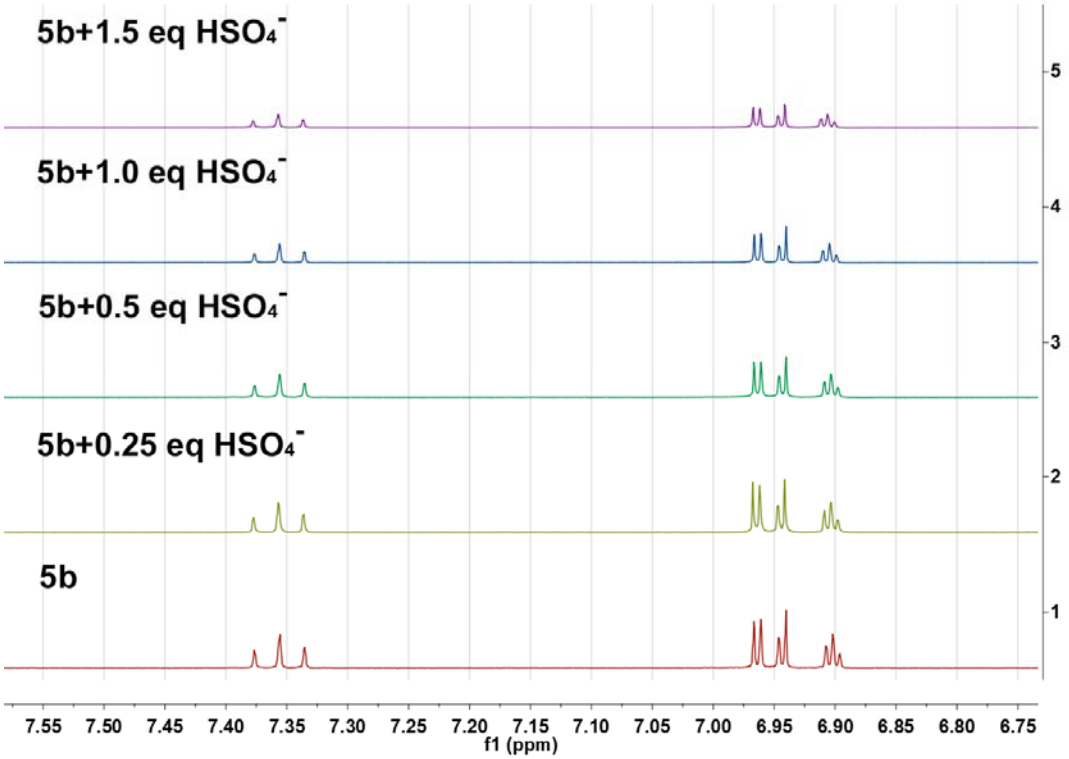


Figure S25 ^{1}H titration of **5b** upon the addition of sulphate (in CD_3CN and with 400 MHz NMR spectrometer).

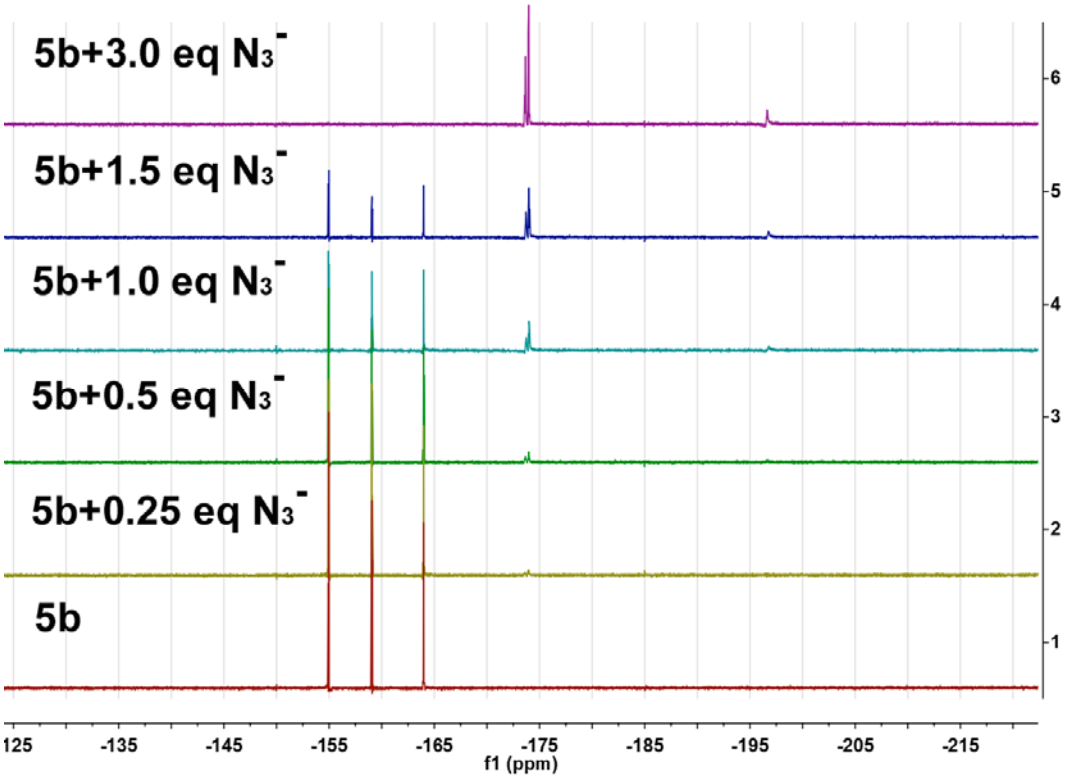


Figure S26 ^{19}F titration of **5b** upon the addition of azide (in CD_3CN and with 400 MHz NMR spectrometer).

6. ESI-MS spectrum

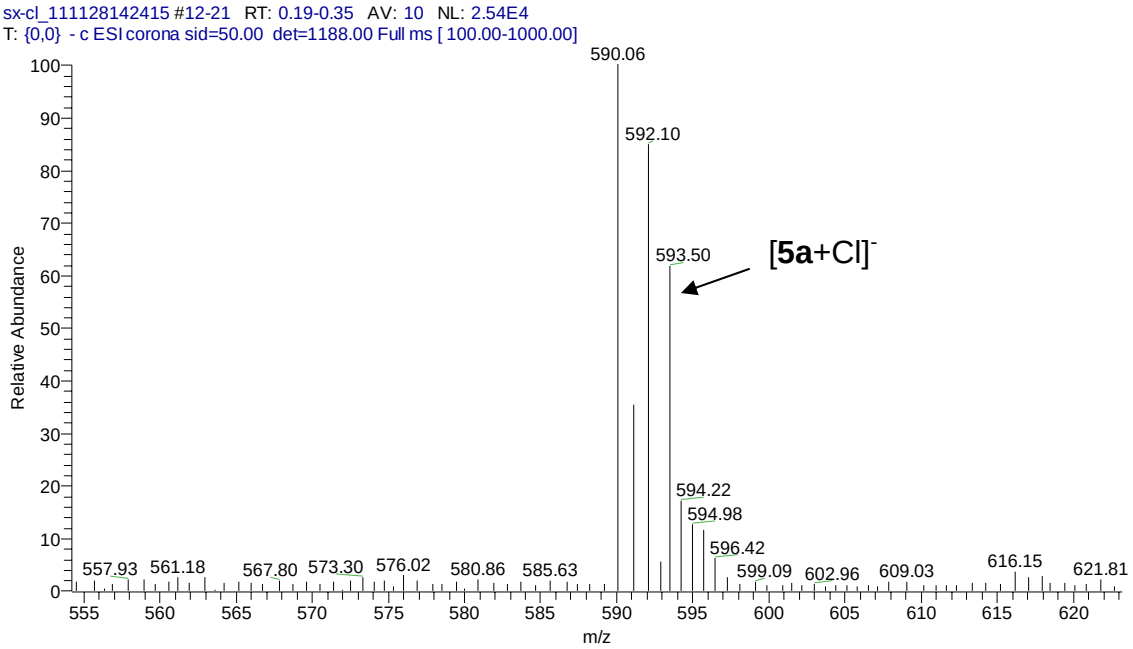


Figure S27 ESI-MS spectrum of **5a** and chloride.

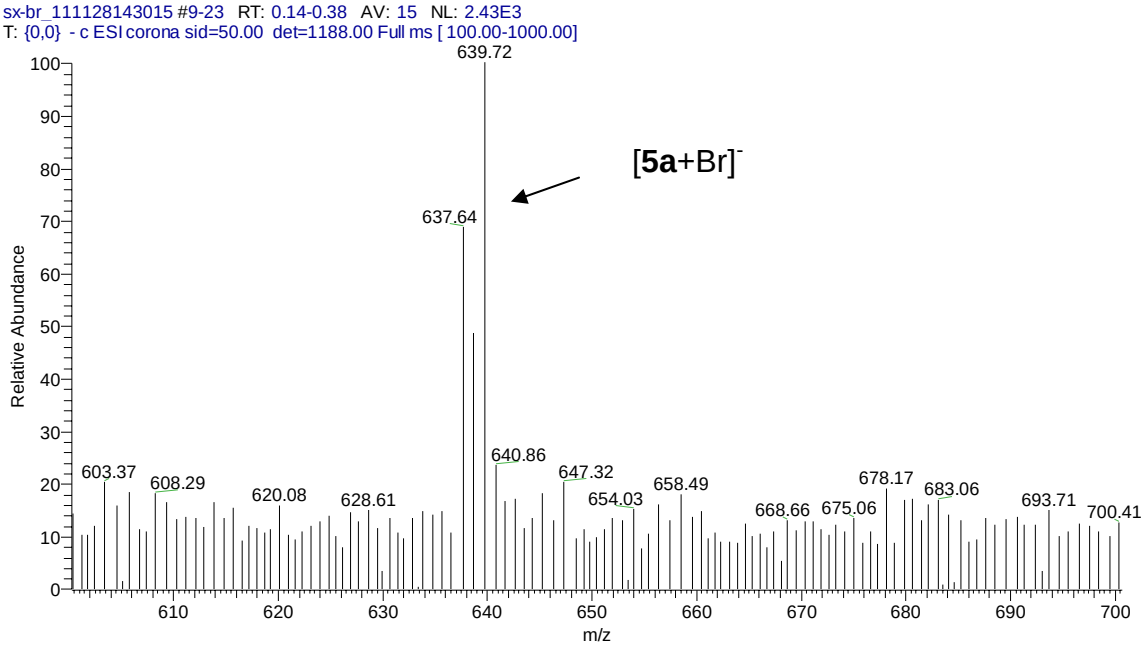


Figure S28 ESI-MS spectrum of **5a** and bromide.

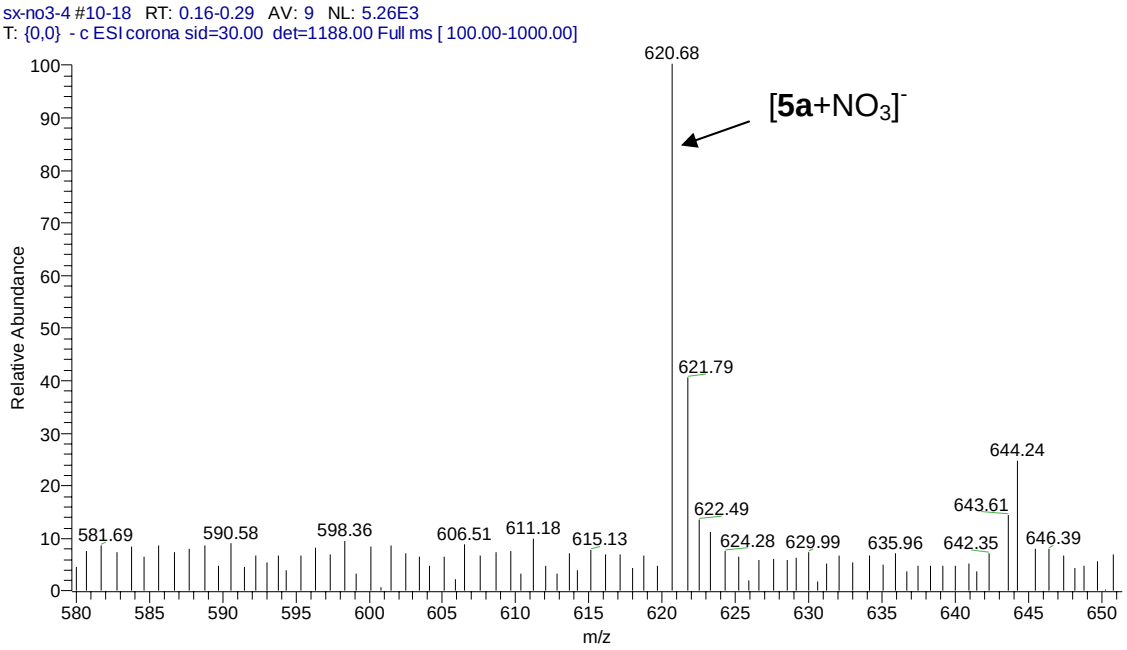


Figure S29 ESI-MS spectrum of **5a** and nitrate.

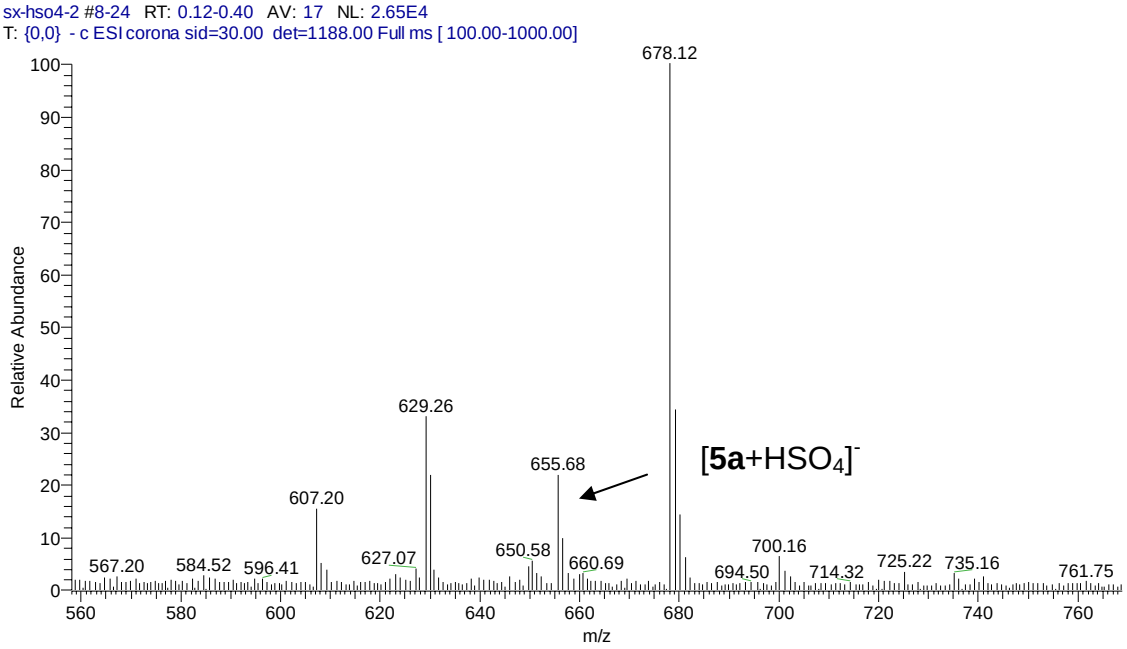


Figure S30 ESI-MS spectrum of **5a** and sulphate.

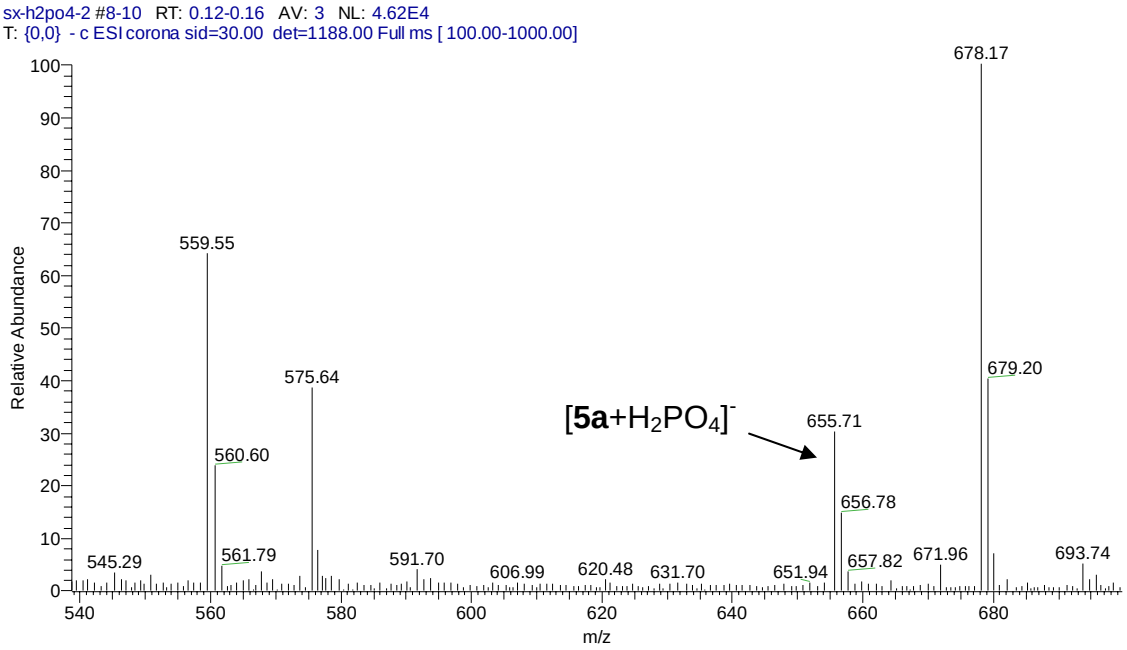


Figure S31 ESI-MS spectrum of **5a** and phosphate.

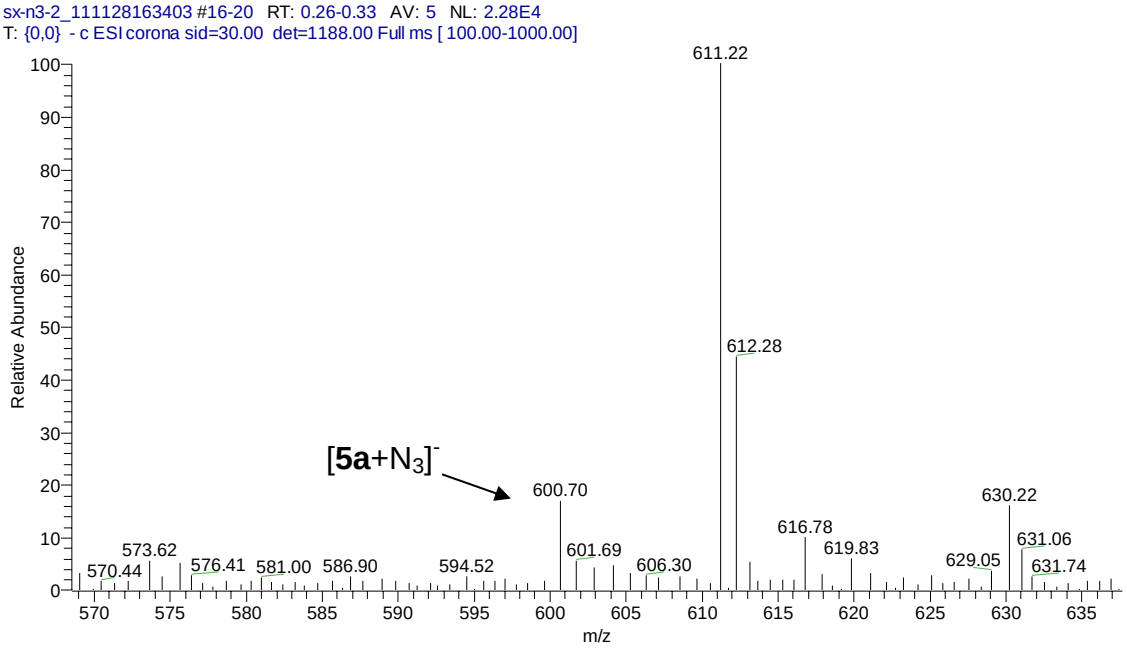


Figure S32 ESI-MS spectrum of **5a** and azide.

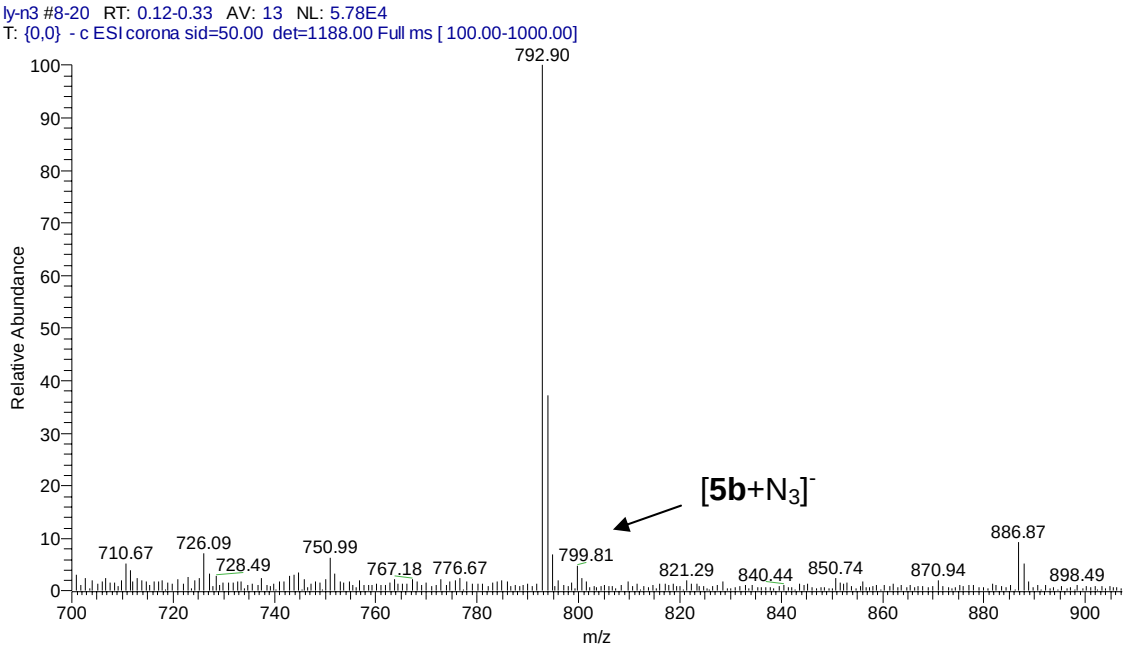


Figure S33 ESI-MS spectrum of **5b** and azide.

7. ^{1}H and ^{13}C NMR spectra of products

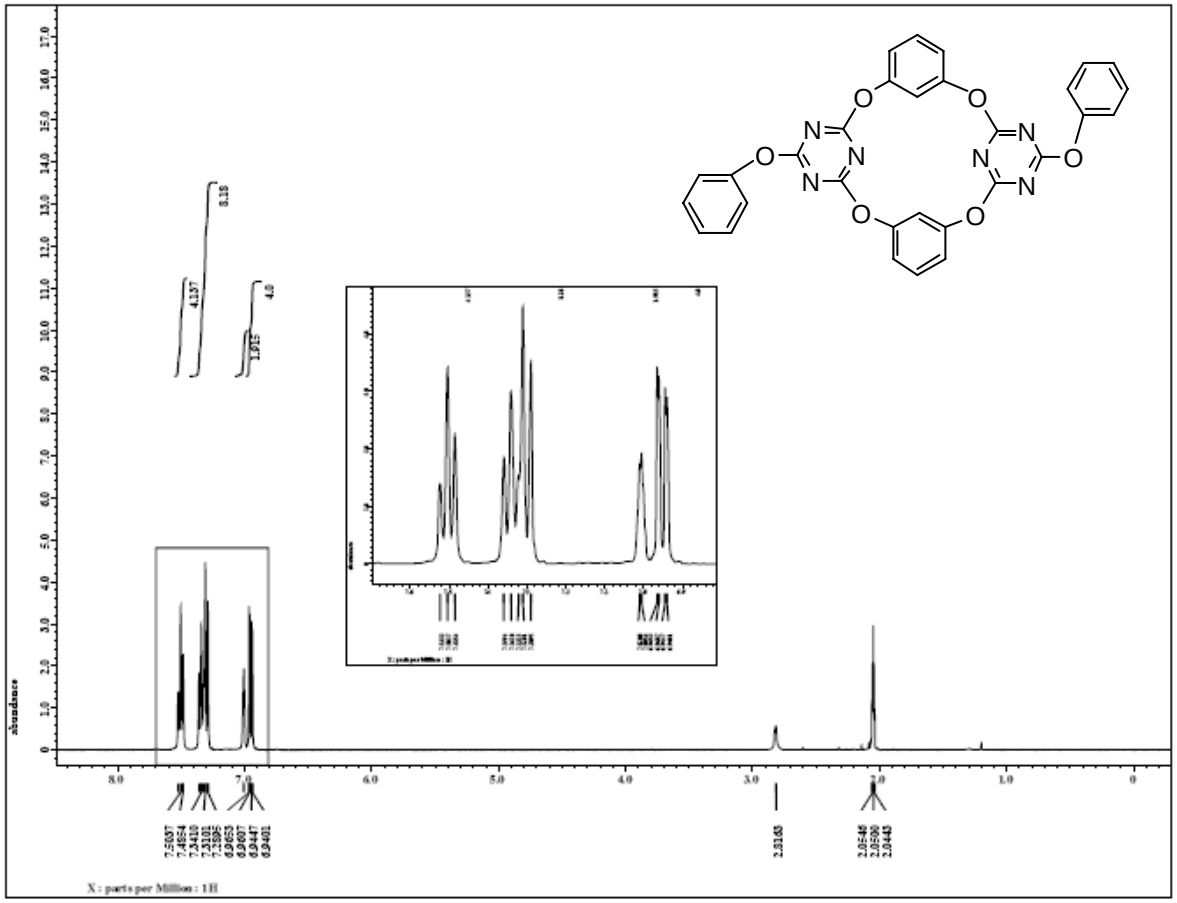


Figure S34 ^{1}H NMR of **5a**.

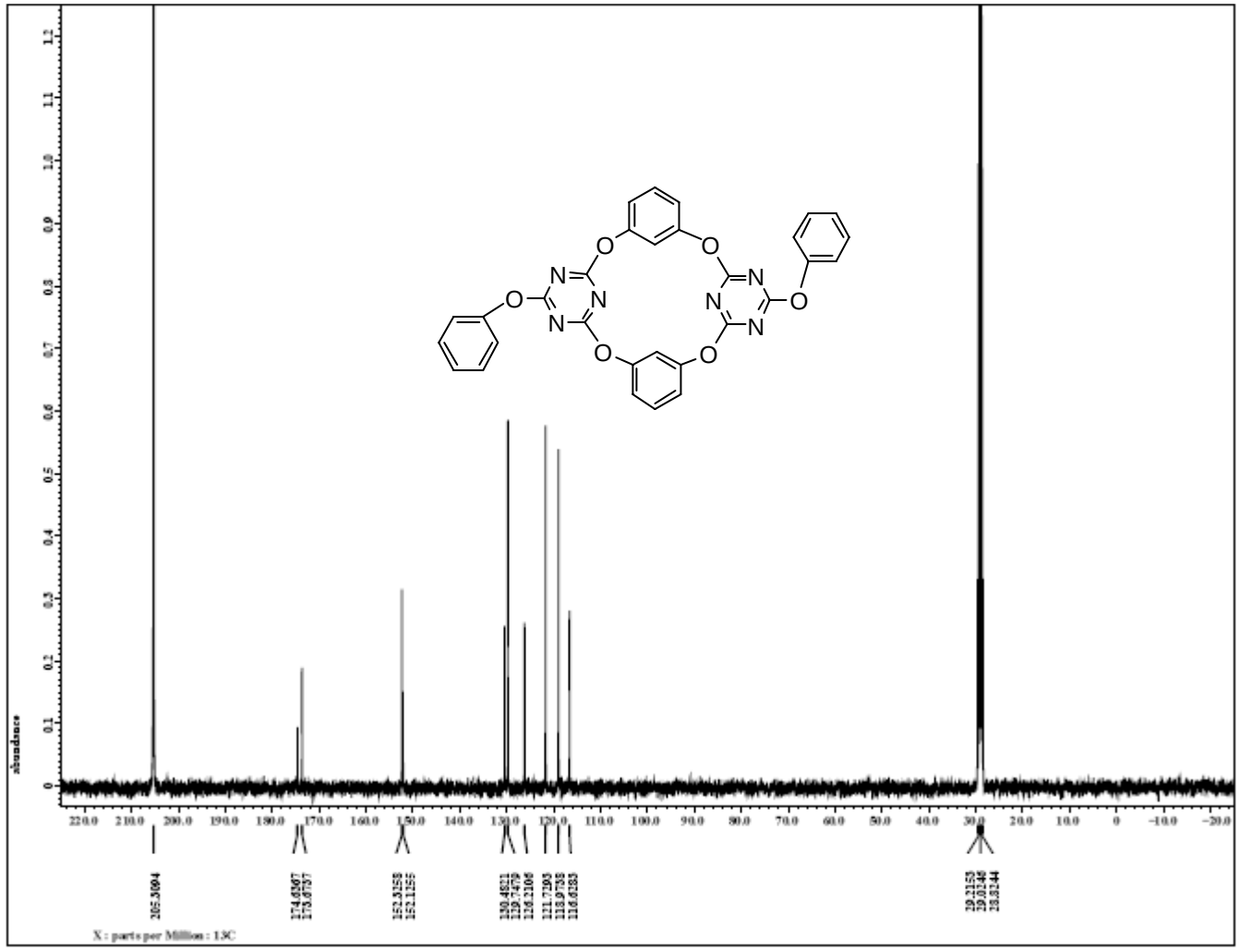
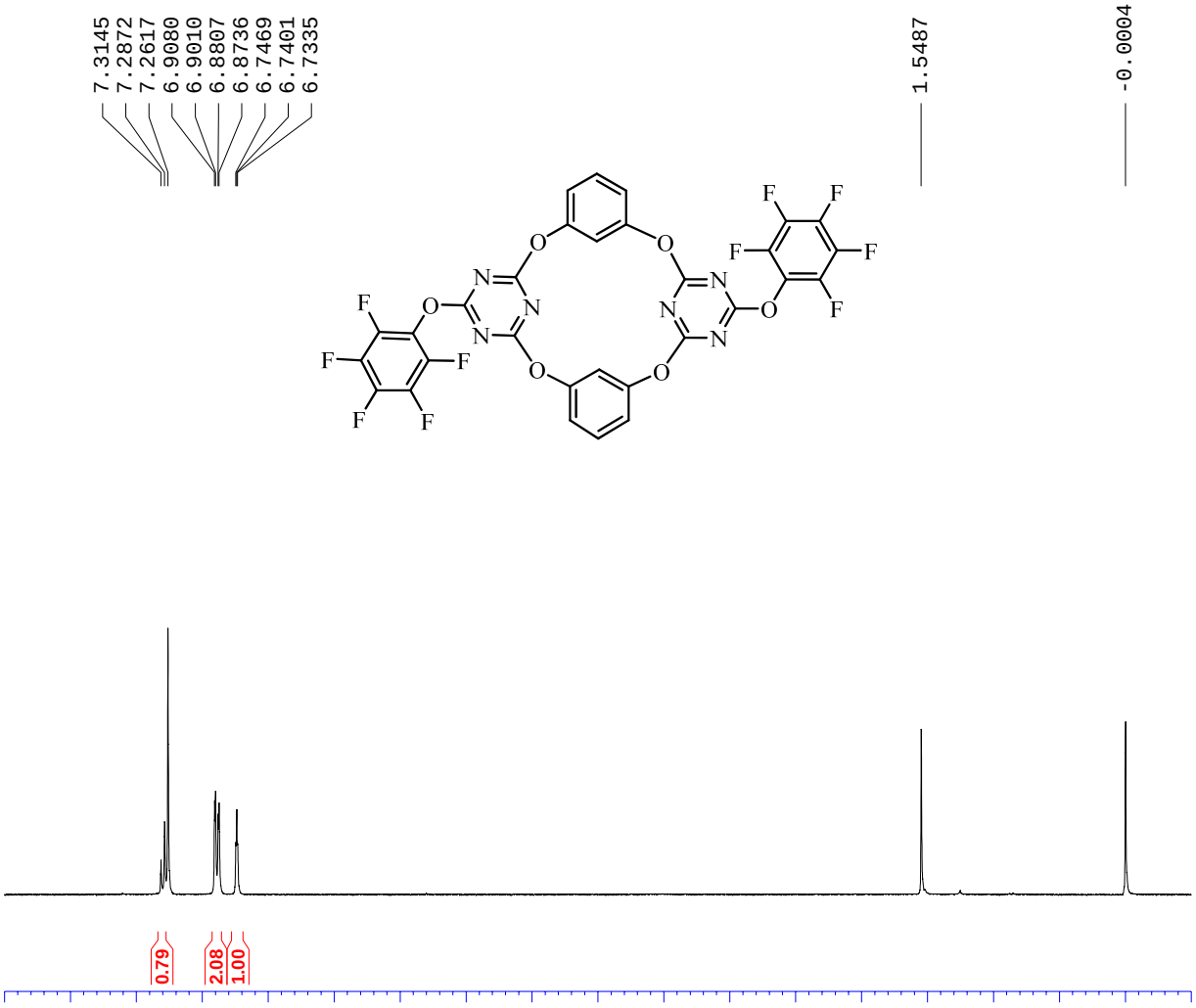


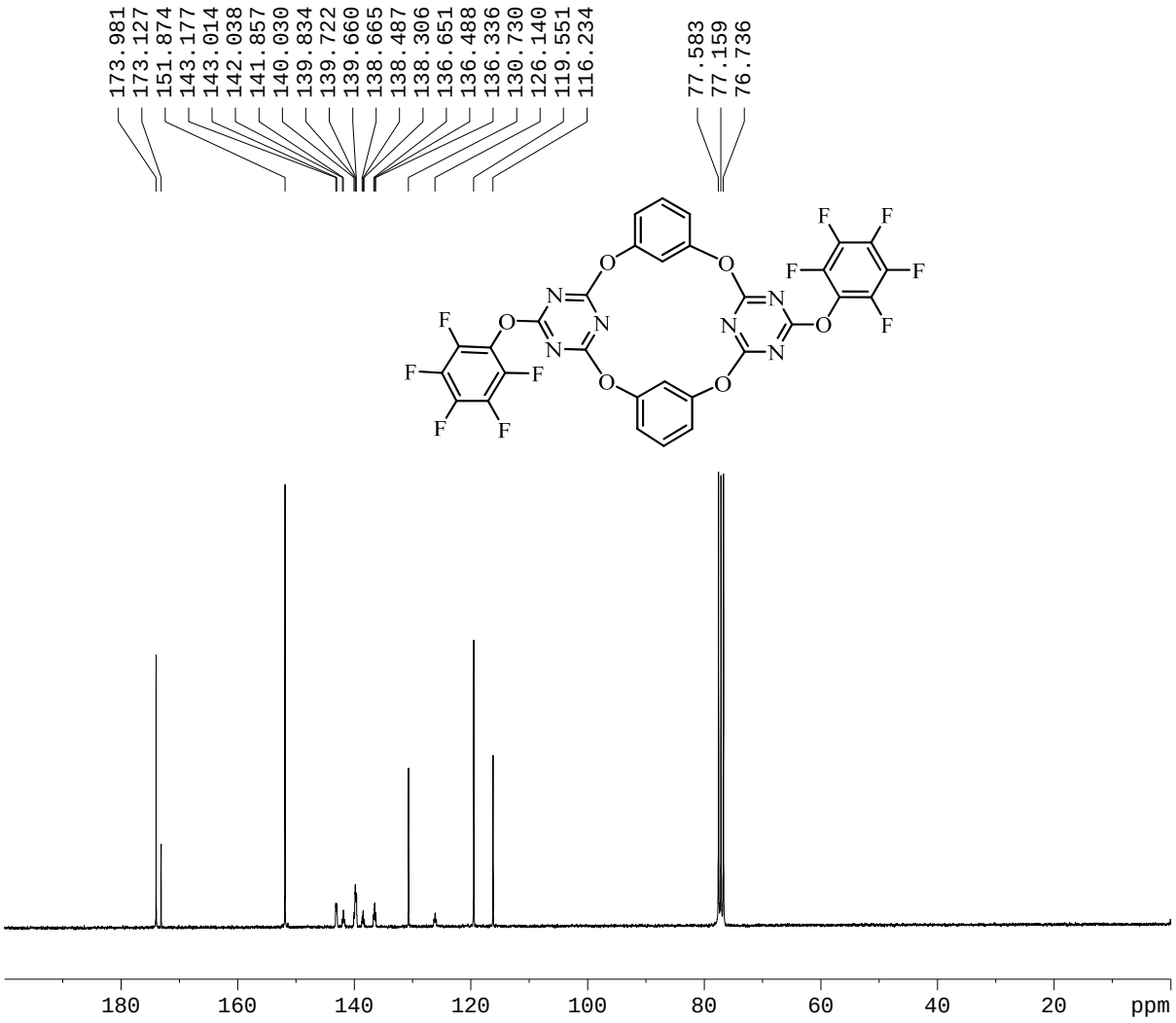
Figure S35 ^{13}C NMR of **5a**.




```
NAME          ly0108-uv
EXPNO                10
PROCNO                1
Date_          20100402
Time              11.07
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            8992.806 Hz
FIDRES        0.137219 Hz
AQ            3.6438515 sec
RG                645.1
DW               55.600 usec
DE                8.00 usec
TE               295.1 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz
SI                32768
SF          300.1300054 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Figure S36 ^{1}H NMR of **5b**.




```
NAME            ly-C6F5
EXPNO                 1
PROCNO                1
Date_          20100405
Time               1.19
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgig30
TD                32768
SOLVENT           CDCl3
NS                10240
DS                    0
SWH           18832.393 Hz
FIDRES         0.574719 Hz
AQ             0.8700404 sec
RG                4597.6
DW                26.550 usec
DE                 8.00 usec
TE                297.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             100.00 usec
PL2                3.00 dB
PL12              22.33 dB
SFO2        300.1312005 MHz
SI                32768
SF           75.4677389 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Figure S37 ^{13}C NMR of **5b**.

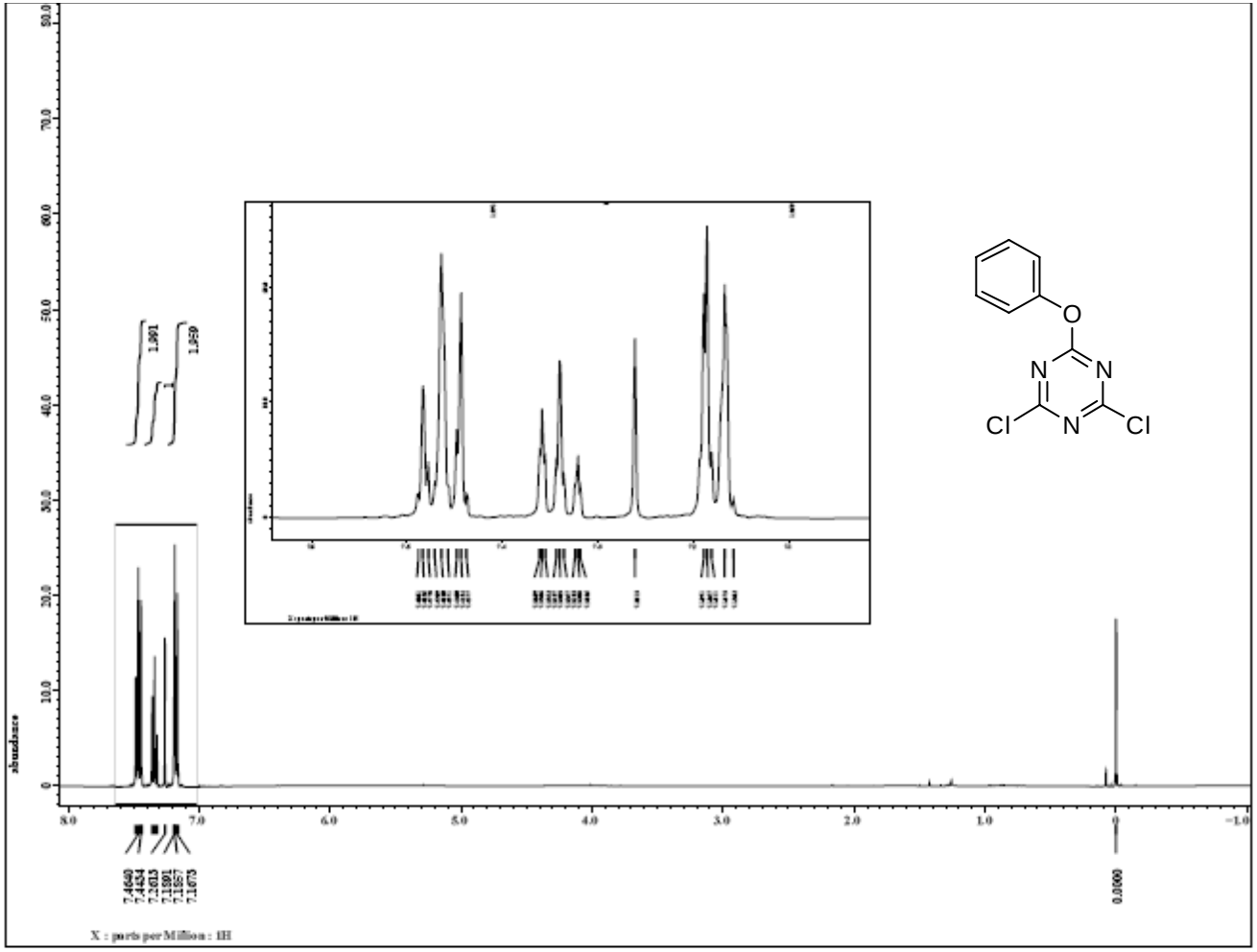


Figure S38 ^{1}H NMR of **4**.

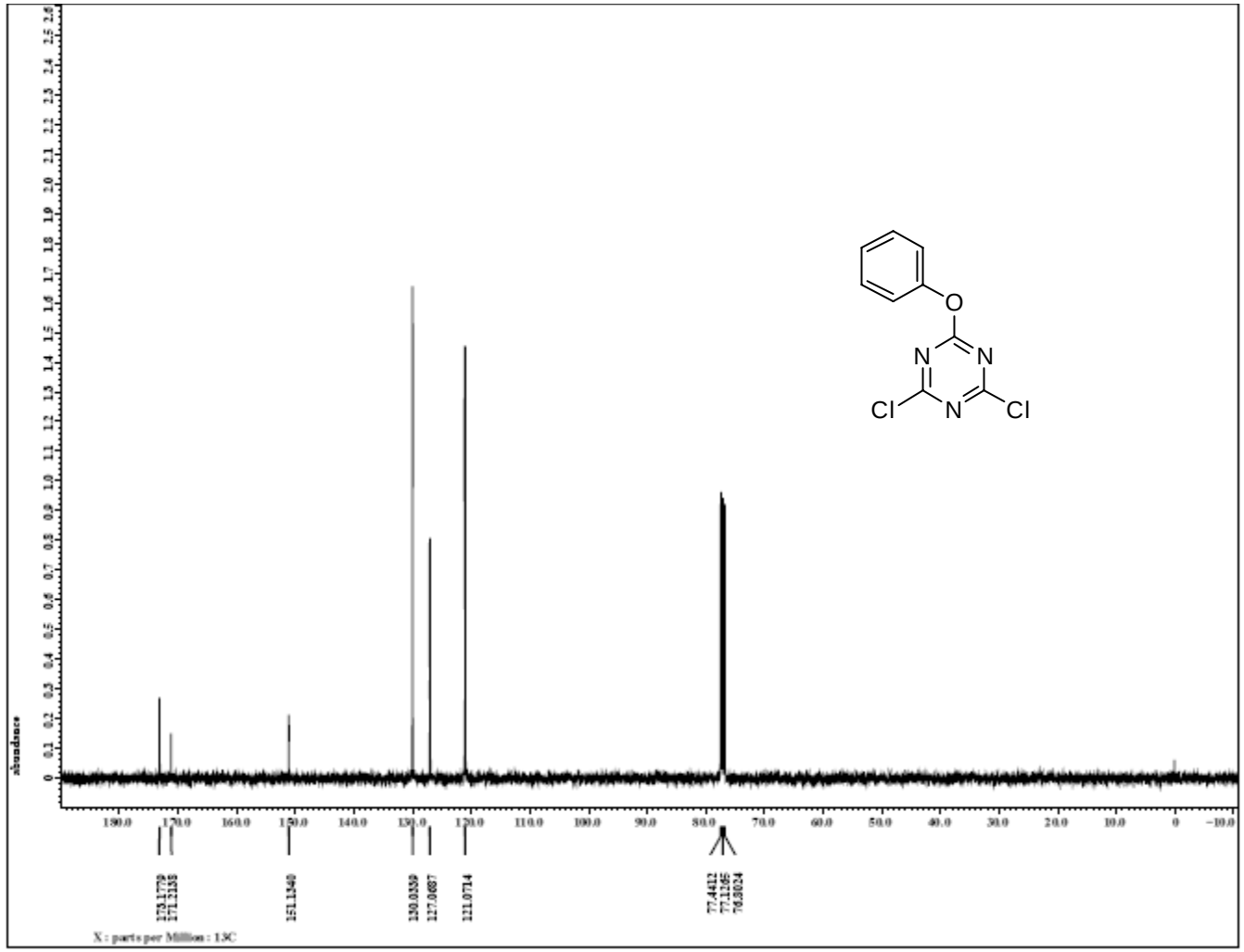


Figure S39 ^{13}C NMR of **4**.