Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Facile Construction of All-Bridge-Position-Functionalized 2,4,6,8-Tetraazaadamantane Skeleton and Conversion of Its *N*-Functionalities

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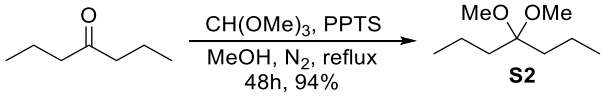
1. General Information

Unless otherwise specified, the chemicals (AR grade) were obtained from commercial sources and were used without further purification, and all reactions were performed in oven dried glassware under a positive pressure of nitrogen. Ozone was produced from a Sankang Ozone Generator. Because of the strong oxidizing properties, ozone can affect especially the eyes and respiratory systems, even at low concentrations. Thus manipulation of ozone must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn at all times. Petroleum ether refers to the fraction boiling in the 60-90°C range. The progress of the reactions was monitored by TLC (silica gel, Polygram SILG/UV 254 plates). Column chromatography was performed on silica gel (200-300 mesh). ^{1}H and ^{13}C NMR spectra were obtained at 500 and 126 MHz, respectively, and $CDCl_3$ was used as the solvent with TMS as the internal standard, Methanol-d_4 was used as the solvent without TMS. All FTIR spectra were obtained using a Nicolet FTIR IS10 Spectrometer. High resolution mass spectra (HRMS) data were measured on an ESI-microTOF II spectrometer. X-ray intensity data were collected on a Bruker D8 CMOS detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å). The known compounds were identified by comparison of their physical and spectral data with those reported in the literature. Yields refers to isolated yield of analytically pure material unless otherwise noted. 3-methylpenta-1,4-dien-3-ol (**1**) [1], 4-methylhepta-2,5-dien-4-ol (**2**) [2], 2,2-dipropenyl-1,3-dioxolane (**4**) [3] and benzoquinone bis(ethylene ketal) (**S1**) [4] were prepared according to reported procedures.

2. Experimental Procedures

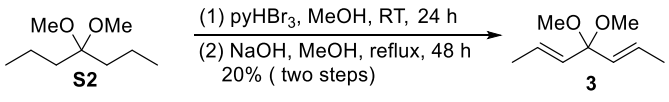
4,4-dimethoxyheptane (S2)



To a solution of 4-heptanone (40.0 mmol, 5.6 mL) in methanol (20 mL) with pyridinium *p*-toluenesulfonate (0.2 eq., 8 mmol, 2.01 g) was added trimethyl orthoformate (100 mmol, 11.4 mL, 2.5 eq) and the reaction mixture was heated to reflux for 48 h. After cooling to room temperature, the reaction mixture was poured into 30 g ice-water, stirred for 30 min, then extracted with *n*-pentane (3 × 50 mL). The combined organic phases were washed with brine, dried (Na_2SO_4). Ketal **S2** (6.05 g, 94%) was obtained by rotary evaporation under reduced pressure below 42 ºC and at 500 mbar as a colorless liquid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.14 (s, 6H), 1.57 – 1.50 (m, 4H), 1.32 – 1.32 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 103.34, 47.72, 34.90, 17.15, 14.50.

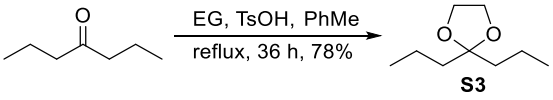
(2*E*,5*E*)-4,4-dimethoxyhepta-2,5-diene (3)



Pyridinium tribromide (20.5 mmol, 7.13 g) was added to the methanol solution (40 mL) of 4,4-dimethoxyheptane (**S2**) (10 mmol, 1.6 g) in an ice bath, then stirred at room temperature for 24 h, the color of the reaction solution became light, poured into ice water to quench, extracted with *n*-pentane (50 mL) three times, washed with saturated sodium bicarbonate solution, and brine, dried over anhydrous sodium sulfate, distilled under vacuum to obtain crude dibromide (2.9 g), which was directly carried out to the next step without purification. Sodium hydroxide (82.5 mmol, 3.3 g) was added to dry methanol solution (30 mL) of dibromide, refluxed under nitrogen for 48 h, poured into ice water for quenching, extracted with *n*-pentane (30 mL) three times, the organic phase was washed with water and brine, dried (Na_2SO_4), the diene **3** (0.32 g, 20% over two steps) was obtained by distillation under reduced pressure below 40 ºC at 500 mbar as a pale yellow liquid.

R_f = 0.5 (petroleum ether /EtOAc 20:1). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 5.86 (dq, *J* = 15.5, 6.6 Hz, 2H), 5.35 (dq, *J* = 15.5, 1.7 Hz, 2H), 3.17 (s, 6H), 1.73 (dd, *J* = 6.6, 1.7 Hz, 6H).

2,2-dipropyl-1,3-dioxolane (S3) [5]

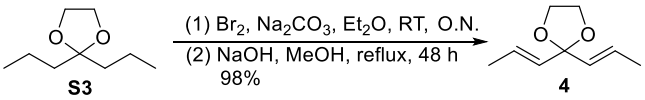


A solution of 4-heptanone (26.3 mmol, 3.7 mL), ethylene glycol (187.9 mmol,11.3 mL) and *p*-TsOH (1.1 mmol, 214.4 mg) in toluene (30 mL) was refluxed for 24 h, with azotropic removal of water (Dean-Stark apparatus). The reaction was then cooled to room temperature and quenched with water and the separated aqueous layer was extracted with ether. The combined organic layers were washed with 10% (wt) NaOH solution, and dried over Na_2SO_4. After filtration, the solution was concentrated under the reduced pressure to furnish ketal **S3** (3.37g, 81%) as a pale yellow oil, which was used for the next step without further purification.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.92 (s, 4H), 1.61 – 1.54 (m, 4H), 1.43 – 1.32 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 6H).

The other analytical data are in accordance with literature values [5].

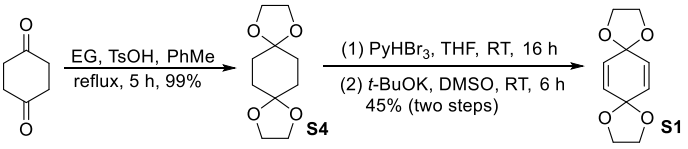
2,2-dipropenyl-1,3-dioxolane (4) [3]



To the ketal **S3** (9.48 mmol, 1.50 g) in Et_2O (15 mL) was added bromine (19.2 mmol, 984 µL) at room temperature. After the addition was complete, Na_2CO_3 (41.7 mmol, 4.42 g) was added in one portion and the resulting mixture was stirred over night at room temperature. The reaction mixture was filtered through cotton and then concentrated to dryness. The obtained dibromo intermediate (3.02 g, >99% crude yield) was dissolved without further purification in methanol (30 mL), and NaOH (82.5 mmol, 3.30 g) was added at room temperature. The mixture was then heated to reflux for 48 h. Once the mixture reached room temperature again, it was diluted with water (60 mL) and extracted with *n*-pentane (4 × 50 mL), then the organic phase was dried over Na_2SO_4. After removal of the solvent the desired diene ketal **4** was obtained (1.44 g, 98%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.88 (dq, *J* = 15.4, 6.6 Hz, 2H), 5.51 (dq, *J* = 15.4, 1.7 Hz, 2H), 3.93 (s, 4H), 1.73 (dd, *J* = 6.6, 1.7 Hz, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 130.34, 128.30, 106.92, 64.61, 17.64.

benzoquinone bis(ethylene ketal) (S1) [4]



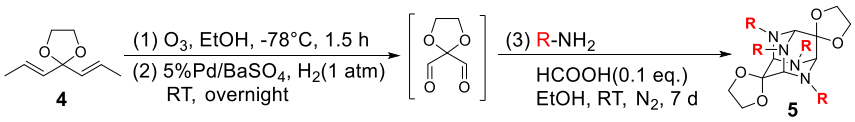
A solution of cyclohexane-1,4-dione (250 mmol, 28.0 g), ethylene glycol (625 mmol, 35 mL) and *p*-TsOH (5 mmol, 2.78 g) in toluene (300 mL) was refluxed for 5 h, with azotropic removal of water (Dean-Stark apparatus). The reaction was then cooled to room temperature and quenched with water and the separated aqueous layer was extracted with ether. The combined organic layers were washed with 10% (wt) NaOH solution, and dried over Na_2SO_4. After filtration, the solution was concentrated under the reduced pressure to furnish diketal **S4** (49.5 g, 99%) as a white solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.95 (s, 8H), 1.79 (s, 8H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 108.26, 64.42, 32.29.

Pyridinium tribromide (20.2 mmol, 7.05 g) was added to the tetrahydrofuran (20 mL) of **S4** (10 mmol, 2 g) in an ice bath, then stirred at room temperature for 16 h, the color of the reaction solution became light, poured into ice water and extracted with ether (30 mL) three times, washed with saturated sodium bicarbonate solution and brine, dried over Na_2SO_4, distilled under vacuum to obtain crude dibromide (3.6 g), which was directly carried out to the next step without purification. Potassium *t*-butoxide (42 mmol, 4.70 g) was added to dry dimethyl sulfoxide solution (45 mL) of dibromide (3.6 g), stirred under nitrogen at room temperature for 6 h, poured into ice water and extracted with ether (30 mL) six times, the organic phase was washed with water and brine, dried (Na_2SO_4), purified on a flash column of silica gel (petroleum ether /EtOAc, v/v 10: 1) to give diene **S1** (0.883 g, 45% over two steps) as a white solid.

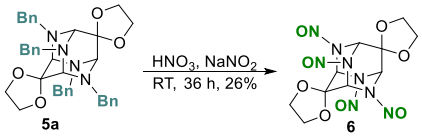
1H NMR (500 MHz, Chloroform-*d*) δ 5.92 (s, 4H), 4.05 (s, 8H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 130.48, 98.52, 65.42.

General procedure for the synthesis of polysubstituted 2,4,6,8-tetraazaadamantanes (5a-e, 5g-5l, 5n-p, 5t-v)



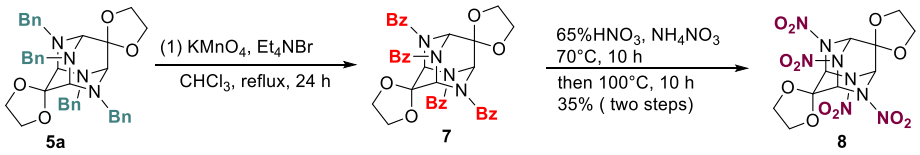
O_3 was passed through the solution of diene ketal **4** (1 mmol) in dry ethanol (25 mL) at -78°C for 1.5 h, then warmed to room temperature and charged with 5%Pd/$BaSO_4$ (5 mol%) under 1 atm of H_2 (balloon), stirred at room temperature overnight. The mixture was filtered through a pad of Celite, and then $BnNH_2$ (6 mmol, 0.66 mL) and HCOOH (0.1 mmol, 0.004 mL) were added. The mixture was allowed to stir at room temperature for 7d and then concentrated in vacuum, which was purified by flash chromatography (ethyl acetate/petroleum ether as eluent) to afford pure products.

Synthesis of 2,4,6,8-tetranitroso-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (6)



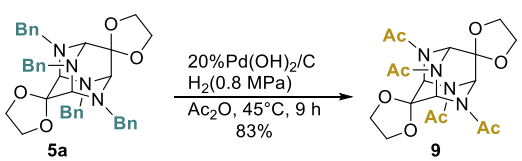
With stirring and cooling, compound **5a** (0.34 mmol, 241 mg), $NaNO_2$ (8.5 mmol, 600 mg) was added over a 5 min period to 65%HNO_3 (10 ml) at 0°C. Then the reaction mixture was stirred for 36 h at room temperature, poured onto 10 g ice-water, and the resulting precipitate was filtered off and dried to give a slight yellow solid, which was purified on a flash column of silica gel (petroleum ether /EtOAc, v/v 5: 2) to give tetranitrosamine **6** (32.9 mg, 26%) as a white solid.

Synthesis of 2,4,6,8-tetranitro-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (8) from 5a



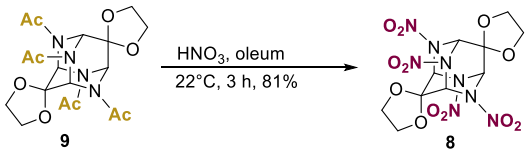
With stirring and cooling, potassium permanganate (6 mmol, 1.42 g) was added over a 10 min period at 0°C to a solution of **5a** (0.5 mmol, 309 mg) and tetraethylammonium bromide (1.67 mmol, 350 mg) in $CHCl_3$ (20 mL). After stirring the reaction mixture for 2 h at 0-10°C, the reaction temperature was raised to reflux for 24 h. Sodium thiosulfate and water were then added to destroy excess $KMnO_4$. Finally, the mixture was extracted with chloroform (4×20 mL), washed with water (4×20 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give the mixtures as a white solid containing tetrabenzamide **7** (269 mg), which was directly carried out to the next step without purification. To a solution of ammonium nitrate (150 mg) in 65% HNO_3 (5 ml), the white solid (269 mg) was added, and the mixture was stirred for 10 h at 70°C, then 10 h at 100°C. The reaction mixture was poured onto 10 g ice-water; the resultant precipitate was filtered off and dried, purified on a flash column of silica gel (petroleum ether /EtOAc, v/v 10: 1) to give tetranitramine **8** (76.3 mg, 35% over two steps) as a white solid.

Synthesis of 2,4,6,8-tetraacetyl-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (9)



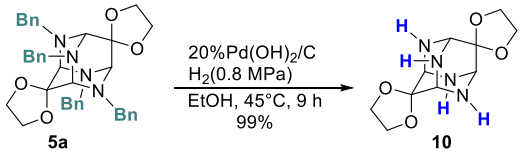
To a 250 mL pressure vessel was charged with **5a** (1 mmol, 0.617 g), $Pd(OH)_2/C$ (0.600 g, 20% Pd), acetic anhydride (50 mL) with an atmosphere of H_2 under the pressure of 0.8 MPa. The reaction mixture was warmed to 45°C and stirred for 9 h, then cooled to room temperature and filtered through a pad of Celite. The filtrate was concentrated in vacuum, and the resulting red solid was purified on a flash column of silica gel (EtOAc/MeOH, v/v 40: 1) to afford tetraacetamide **9** (352.3 mg, 83%) as a white solid.

Synthesis of 2,4,6,8-tetranitro-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (8) from 9



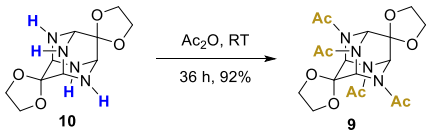
To a mixture of fuming nitric acid (1.86 mL) and 25% oleum (0.90 mL) at 0°C was added tetraacetamide **9** (0.302 g, 0.71 mmol), the reaction was then warmed to 22°C. After stirred for 3 h, the reaction mixture was poured into ice-water (30 mL) with agitation. The white participate was filtered, washed with water and dried in vacuum. The product was purified by flash chromatography (petroleum ether/EtOAc, v/v 10: 1) to afford tetranitramine **8** (250.9 mg, 81%) as a white solid.

Synthesis of 2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (10) from 5a



To a 250 mL pressure vessel was charged with **5a** (0.5 mmol, 0.309 g), $Pd(OH)_2/C$ (0.12 g, 20% Pd), ethanol (50 mL) with an atmosphere of H_2 under the pressure of 0.8 MPa. The reaction mixture was warmed to 45°C and stirred for 9 h, then cooled to room temperature and filtered through a pad of Celite. The filtrate was concentrated in vacuum to afford tetramine**10** (126.9 mg, 99%) as a white solid.

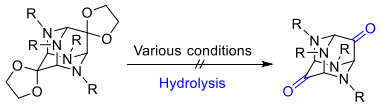
Synthesis of 2,4,6,8-tetraacetyl-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (9) from 10



A solution of compound **10** (0.2 mmol, 52 mg) in acetic anhydride (2 mL) was stirred at room temperature for 36 h, the reaction solution became clear. The solvent was removed by rotary evaporation in vacuum, the residue was purified on a flash column of silica gel (EtOAc/MeOH, v/v 40: 1) to afford tetraacetamide 9 (78.1 mg, 92%) as a white solid.

Attempts for the hydrolysis of ketals

Table S1. Attempts for the hydrolysis of diketals [a].



5a R = Bn
8 R = NO_2
9 R = Ac

11 R = Bn
12 R = NO_2
13 R = Ac

Entry	Hydrolysis Conditions	Reaction temperature (℃)	yield
1	10%HCl, THF, H_2O	RT	-
2	30%HCl, THF, H_2O	RT	-
3	30%HCl, THF, H_2O	reflux	-
4	40%HBr, THF, H_2O	reflux	-

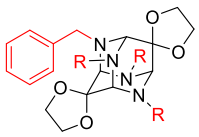
5	98%H_2SO_4, DCM	45	-
6	Acetone, PTSA	RT	-
7	$CeCl_3$, NaI, MeCN	reflux	-
8	$TiCl_4$, LiI, Et_2O	RT	-
9	Acetone, CF_3SO_3H	reflux	-
10	60%$HClO_4$, Acetone	reflux	-
11	Acetone, Oxone, $NaHCO_3$, DCM	18	-
12	CAN, MeCN, H_2O	70	-
13	$PdCl_2(MeCN)_2$, Acetone	reflux	-
14	I_2, Acetone	reflux	-
15	TMSI, $CHCl_3$	RT	-
16	$KMnO_4$, Et_4NBr, $CHCl_3$, H_2O	reflux	-

[a] Reaction conditions: 5a (8 or 9) (0.2 mmol).

3. Analytical Data of Products

Note: the signal assignments for all new products can be found in the copies of NMR spectra.

2,4,6,8-tetrabenzyl-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5a)



5a, R = Bn

Compound **5a** was synthesized following the general procedure.

A white solid, 138.8 mg, 45% yield.

TLC: R_f = 0.5 (petroleum ether/EtOAc = 10:1)

IR (thin film, υ cm^{-1}): 3085, 3003, 3022, 2924, 2889, 2851, 1602, 1494, 1449, 1333, 1134, 1176, 1086, 1026, 1001, 943, 910, 885, 731, 699.

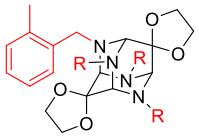
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.46 (m, 8H), 7.30 – 7.30 (m, 8H), 7.22 – 7.15 (m, 4H), 4.34 (d, *J* = 14.9 Hz, 4H), 3.98 (d, *J* = 15.0 Hz, 4H), 3.82 (s, 8H), 3.32 (s, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.16, 128.50, 128.14, 126.50, 103.54, 72.95, 64.23, 55.71.

HRMS (ESI): $C_{38}H_{41}N_4O_4$ $[M+H]^+$: calcd.: 617.3122; found: 617.3120.

Compound **5a** was further determined by X-ray diffraction analysis.

2,4,6,8-tetrakis(2-methylbenzyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5b)



5b, R = 2-MeBn

Compound **5b** was synthesized following the general procedure.

A white solid, 117.7 mg, 35% yield.

TLC: R_f = 0.5 (petroleum ether/EtOAc = 10:1)

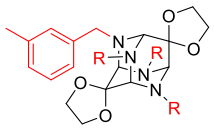
IR (thin film, υ cm^{-1}): 3053, 3014, 2920, 2873, 1605, 1493, 1462, 1331, 1107, 1002, 906, 770, 742, 723.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 7.4 Hz, 4H), 7.15 – 7.09 (m, 8H), 7.09 – 7.02 (m, 4H), 4.20 (d, *J* = 14.5 Hz, 4H), 3.89 (d, *J* = 14.5 Hz, 4H), 3.80 (s, 8H), 3.30 (s, 4H), 2.41 (s, 12H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.50, 137.83, 130.09, 129.49, 126.56, 125.42, 103.93, 72.72, 64.07, 54.18, 19.47.

HRMS (ESI): $C_{42}H_{49}N_4O_4$ $[M+H]^+$: calcd.: 673.3748; found: 673.3742.

2,4,6,8-tetrakis(3-methylbenzyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5c)



5c, R = 3-MeBn

Compound **5c** was synthesized following the general procedure.

A white solid, 131.2 mg, 39% yield.

TLC: R_f = 0.5 (petroleum ether/EtOAc = 10:1)

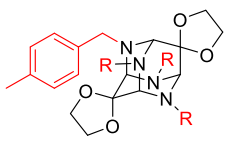
IR (thin film, υ cm^{-1}): 3024, 2953, 2917, 2865, 1605, 1488, 1360, 1195, 1122, 1099, 1081, 901, 851, 773, 692.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.31 (m, 8H), 7.18 (t, *J* = 7.5 Hz, 4H), 6.99 (d, *J* = 7.5 Hz, 4H), 4.31 (d, *J* = 15.0 Hz, 4H), 3.96 (d, *J* = 15.0 Hz, 4H), 3.83 (s, 8H), 3.32 (s, 4H), 2.33 (s, 12H).

^{13}C NMR (126 MHz, Chloroform-d) δ 141.20, 137.53, 129.21, 128.05, 127.17, 125.54, 103.65, 72.96, 64.19, 55.64, 21.64.

HRMS (ESI): $C_{42}H_{49}N_4O_4$ $[M+H]^+$: calcd.: 673.3748; found: 673.3750.

2,4,6,8-tetrakis(4-methylbenzyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5d)



5d, R = 4-MeBn

Compound **5d** was synthesized following the general procedure.

A white solid, 137.9 mg, 41% yield.

TLC: R_f = 0.5 (petroleum ether/EtOAc = 10:1)

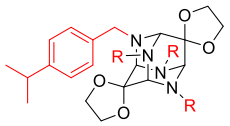
IR (thin film, υ cm^{-1}): 2953, 2922, 2852, 1508, 1488, 1446, 1360, 1211, 1193, 1081, 968, 914, 851, 804, 776.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.8 Hz, 8H), 7.10 – 7.07 (m, 8H), 4.29 (d, *J* = 14.8 Hz, 4H), 3.91 (d, *J* = 14.8 Hz, 4H), 3.81 (s, 8H), 3.30 (s, 4H), 2.31 (s, 12H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.14, 135.87, 128.82, 128.47, 103.60, 72.84, 64.17, 55.43, 21.24.

HRMS (ESI): $C_{42}H_{49}N_4O_4$ $[M+H]^+$: calcd.: 673.3748; found: 673.3747.

2,4,6,8-tetrakis(4-isopropylbenzyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5e)



5e, R = 4-*i*-PrBn

Compound **5e** was synthesized following the general procedure.

A white solid, 149.2 mg, 38% yield.

TLC: R_f = 0.6 (petroleum ether/EtOAc = 10:1)

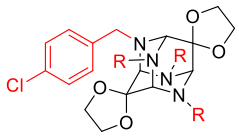
IR (thin film, υ cm^{-1}): 2959, 2925, 2867, 1508, 1462, 1415, 1329, 1094, 1047, 1005, 906, 890, 836, 809.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.9 Hz, 8H), 7.14 (d, *J* = 7.8 Hz, 8H), 4.30 (d, *J* = 15.0 Hz, 4H), 3.93 (d, *J* = 15.0 Hz, 4H), 3.83 (s, 8H), 3.32 (s, 4H), 2.87 (hept, *J* = 6.9 Hz, 4H), 1.23 (d, *J* = 6.9 Hz, 24H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.91, 138.62, 128.35, 126.13, 103.65, 72.90, 64.16, 55.34, 33.88, 24.29, 24.21.

HRMS (ESI): $C_{50}H_{65}N_4O_4$ $[M+H]^+$: calcd.: 785.5000; found: 785.5006.

2,4,6,8-tetrakis(4-chlorobenzyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5g)



5g, R = 4-ClBn

Compound **5g** was synthesized following the general procedure.

A white solid, 162.2 mg, 43% yield.

TLC: R_f = 0.3 (petroleum ether/EtOAc = 10:1)

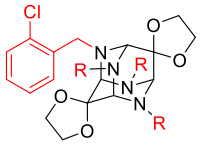
IR (thin film, υ cm^{-1}): 2956, 2923, 2868, 1597, 1493, 1365, 1339, 1211, 1193, 1125, 1081, 1010, 906, 859, 820, 796, 776.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.1 Hz, 8H), 7.25 (d, *J* = 8.2 Hz, 8H), 4.24 (d, *J* = 15.0 Hz, 4H), 3.91 (d, *J* = 15.0 Hz, 4H), 3.83 (s, 8H), 3.22 (s, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.27, 132.23, 129.76, 128.33, 103.23, 72.86, 64.37, 55.04.

HRMS (ESI): $C_{38}H_{37}Cl_4N_4O_4$ $[M+H]^+$: calcd.: 753.1563; found: 753.1560.

2,4,6,8-tetrakis(2-chlorobenzyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5h)



5h, R = 2-ClBn

Compound **5h** was synthesized following the general procedure.

A white solid, 139.6 mg, 37% yield.

TLC: R_f = 0.3 (petroleum ether/EtOAc = 10:1)

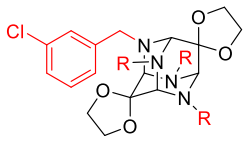
IR (thin film, υ cm^{-1}): 3066, 2937, 2882, 1567, 1472, 1434, 1340, 1303, 1265, 1127, 1101, 1089, 1039, 1001, 951, 913, 890, 764, 744.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 7.4, 1.7 Hz, 4H), 7.30 (dd, *J* = 7.9, 1.3 Hz, 4H), 7.26 – 7.22 (m, 4H), 7.14 (td, *J* = 7.5, 1.8 Hz, 4H), 4.58 (d, *J* = 16.4 Hz, 4H), 3.92 - 3.88 (m, 12H), 3.35 (s, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.54, 134.07, 130.05, 129.27, 127.60, 126.63, 103.22, 73.56, 64.48, 53.02.

HRMS (ESI): $C_{38}H_{37}Cl_4N_4O_4$ $[M+H]^+$: calcd.: 753.1563; found: 753.1568.

2,4,6,8-tetrakis(3-chlorobenzyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5i)



5i, R = 3-ClBn

Compound **5i** was synthesized following the general procedure.

A white solid, 150.9 mg, 40% yield.

TLC: R_f = 0.3 (petroleum ether/EtOAc = 10:1)

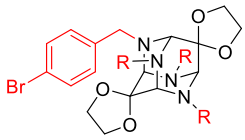
IR (thin film, υ cm^{-1}): 3058, 2922, 2887, 2844, 1595, 1572, 1469, 1424, 1385, 1333, 1295, 1212, 1190, 1112, 1089, 1043, 1026, 945, 918, 895, 882, 865, 782, 711, 684.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (s, 4H), 7.31 (d, *J* = 7.4 Hz, 4H), 7.23 – 7.12 (m, 8H), 4.31 (d, *J* = 15.5 Hz, 4H), 3.95 (d, *J* = 15.5 Hz, 4H), 3.90 (s, 8H), 3.25 (s, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.10, 134.28, 129.46, 128.35, 126.79, 126.46, 103.25, 73.07, 64.52, 55.13.

HRMS (ESI): $C_{38}H_{37}Cl_4N_4O_4$ $[M+H]^+$: calcd.: 753.1563; found: 753.1565.

2,4,6,8-tetrakis(4-bromobenzyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5j)



5j, R = 4-BrBn

Compound **5j** was synthesized following the general procedure.

A white solid, 214.4 mg, 46% yield.

TLC: R_f = 0.4 (petroleum ether/EtOAc = 10:1)

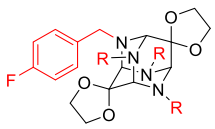
IR (thin film, υ cm^{-1}): 3066, 2937, 2882, 1567, 1472, 1434, 1340, 1303, 1265, 1127, 1101, 1089, 1039, 1001, 951, 913, 890, 764, 744.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.38 (m, 8H), 7.34 (d, *J* = 8.2 Hz, 8H), 4.22 (d, *J* = 15.1 Hz, 4H), 3.88 (d, *J* = 15.1 Hz, 4H), 3.84 (s, 8H), 3.21 (s, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.80, 131.29, 130.17, 120.39, 103.22, 72.89, 64.39, 55.09.

HRMS (ESI): $C_{38}H_{37}Br_4N_4O_4$ $[M+H]^+$: calcd.: 932.9502; found: 932.9500.

2,4,6,8-tetrakis(4-fluorobenzyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5k)



5k, R = 4-FBn

Compound **5k** was synthesized following the general procedure.

A white solid, 96.4 mg, 28% yield.

TLC: R_f = 0.4 (petroleum ether/EtOAc = 10:1)

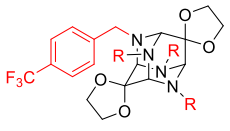
IR (thin film, υ cm^{-1}): 2956, 2849, 1602, 1511, 1446, 1331, 1216, 1120, 1093, 1000, 911, 820, 812, 767.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 8.5, 5.7 Hz, 8H), 6.96 (t, *J* = 8.7 Hz, 8H), 4.23 (d, *J* = 14.7 Hz, 4H), 3.93 (d, *J* = 14.7 Hz, 4H), 3.82 (s, 8H), 3.24 (s, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.86 (d, *J* = 243.8 Hz), 136.40 (d, *J* = 2.7 Hz), 129.89 (d, *J* = 7.7 Hz), 114.91 (d, *J* = 21.1 Hz), 103.40, 72.76, 64.31, 55.04.

HRMS (ESI): $C_{38}H_{37}F_4N_4O_4$ $[M+H]^+$: calcd.: 689.2745; found: 689.2749.

2,4,6,8-tetrakis(4-trifluoromethylbenzyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5l)



5l, R = 4-CF_3Bn

Compound **5l** was synthesized following the general procedure.

A white solid, 84.4 mg, 19% yield.

TLC: R_f = 0.4 (petroleum ether/EtOAc = 10:1)

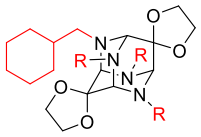
IR (thin film, υ cm^{-1}): 2922, 2894, 2859, 1618, 1416, 1318, 1308, 1273, 1160, 1104, 1064, 1013, 953, 910, 835, 817.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.9 Hz, 8H), 7.57 (d, *J* = 8.0 Hz, 8H), 4.41 (d, *J* = 15.4 Hz, 4H), 4.05 (d, *J* = 15.4 Hz, 4H), 3.92 (s, 8H), 3.28 (s, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.97, 129.07 (q, *J* = 32.0 Hz), 128.55, 125.20 (q, *J* = 3.8 Hz), 124.50 (q, *J* = 271.7 Hz),103.24, 73.23, 64.57, 55.38.

HRMS (ESI): $C_{42}H_{37}F_{12}N_4O_4$ $[M+H]^+$: calcd.: 889.2618; found: 889.2618.

2,4,6,8-tetrakis(cyclohexylmethyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5n)



5n, R = $CyCH_2$

Compound **5n** was synthesized following the general procedure.

A white solid, 60.1 mg, 20% yield.

TLC: R_f = 0.4 (petroleum ether/EtOAc = 10:1)

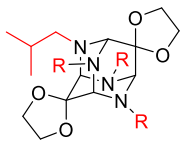
IR (thin film, υ cm^{-1}): 2915, 2847, 1454, 1336, 1283, 1263, 1117, 1071, 1061, 1021, 923, 903, 882.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.90 (s, 8H), 3.13 (s, 4H), 2.88 (dd, *J* = 13.5, 5.0 Hz, 4H), 2.32 (dd, *J* = 13.5, 8.8 Hz, 4H), 2.05 (d, *J* = 13.0 Hz, 4H), 1.72 – 1.62 (m, 12H), 1.32 – 1.09 (m, 18H), 0.93 – 0.76 (m, 10H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 103.73, 74.49, 63.99, 58.88, 38.12, 31.76, 31.44, 27.23, 26.55, 26.46.

HRMS (ESI): $C_{38}H_{65}N_4O_4$ $[M+H]^+$: calcd.: 641.5000; found: 641.4997.

2,4,6,8-tetraisobutyl-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5o)



5o, R = *i*-Bu

Compound **5o** was synthesized following the general procedure.

A white solid, 69.7 mg, 29% yield.

TLC: R_f = 0.3 (petroleum ether/EtOAc = 5:1)

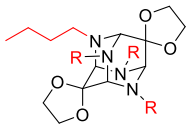
IR (thin film, υ cm^{-1}): 2942, 2889, 2867, 1467, 1384, 1361, 1343, 1326, 1306, 1288, 1258, 1132, 1109, 1074, 1039, 1018, 951, 905, 893.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.90 (s, 8H), 3.15 (s, 4H), 2.90 (dd, *J* = 13.5, 5.1 Hz, 4H), 2.29 (dd, *J* = 13.5, 8.8 Hz, 4H), 1.56 (dtt, *J* = 11.8, 8.7, 5.9 Hz, 5H), 0.94 (d, *J* = 6.6 Hz, 12H), 0.86 (d, *J* = 6.7 Hz, 12H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 103.72, 74.53, 64.09, 60.22, 28.46, 20.84, 20.63.

HRMS (ESI): $C_{26}H_{49}N_4O_4$ $[M+H]^+$: calcd.: 481.3748; found: 481.3746.

2,4,6,8-tetrakis(*n*-butyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5p)



5p, R = *n*-Bu

Compound **5p** was synthesized following the general procedure.

A white solid, 76.9 mg, 32% yield.

TLC: R_f = 0.3 (petroleum ether/EtOAc = 5:1)

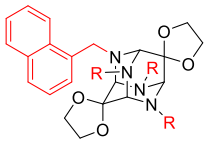
IR (thin film, υ cm^{-1}): 2955, 2935, 2859, 1472, 1459, 1374, 1338, 1311, 1122, 1104, 1074, 1036, 910, 890.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.92 (s, 8H), 3.29 (s, 4H), 2.85 (m, 8H), 1.46 – 1.30 (m, 16H), 0.90 (t, *J* = 7.0 Hz, 12H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 103.46, 73.14, 64.29, 51.91, 31.39, 20.42, 14.28.

HRMS (ESI): $C_{26}H_{49}N_4O_4$ $[M+H]^+$: calcd.: 481.3748; found: 481.3750.

2,4,6,8-tetrakis(naphthalen-1-ylmethyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5t)



5t, R = 1-NpCH_2

Compound **5t** was synthesized following the general procedure.

A white solid, 85.8 mg, 21% yield.

TLC: R_f = 0.5 (petroleum ether/EtOAc = 8:1)

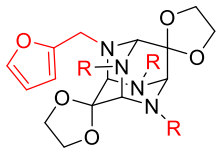
IR (thin film, υ cm^{-1}): 3066, 3033, 2988, 2963, 2925, 2874, 1728, 1593, 1505, 1464, 4396, 1348, 1330, 1260, 1230, 1102, 1086, 1066, 1006, 908, 875, 799.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.42 – 8.33 (m, 4H), 7.81 (m, 4H), 7.68 (m, 4H), 7.47 (m, 8H), 7.32 – 7.24 (m, 8H), 4.56 (d, *J* = 14.2 Hz, 4H), 4.43 (d, *J* = 14.2 Hz, 4H), 3.74 (s, 8H), 3.49 (s, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.95, 133.95, 132.71, 128.27, 127.31, 126.85, 125.61, 125.51, 125.42, 125.31, 103.85, 72.98, 64.22, 54.24.

HRMS (ESI): $C_{54}H_{49}N_4O_4$ $[M+H]^+$: calcd.: 817.3748; found: 817.3742.

2,4,6,8-tetrakis(furan-2-ylmethyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5u)



5u, R = 2-furfuryl

Compound **5u** was synthesized following the general procedure.

A white solid, 118.2 mg, 41% yield.

TLC: R_f = 0.4 (petroleum ether/EtOAc = 3:1)

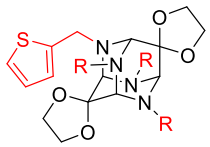
IR (thin film, υ cm^{-1}): 3063, 2955, 2932, 2884, 1570, 1505, 1474, 1434, 1366, 1338, 1293, 1104, 1039, 1001, 915, 807, 759, 744.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.30 (m, 4H), 6.31 – 6.21 (m, 8H), 4.16 (d, *J* = 15.2 Hz, 4H), 4.03 (d, *J* = 15.2 Hz, 4H), 3.87 (s, 8H), 3.35 (s, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.46, 141.70, 110.04, 107.24, 102.93, 72.70, 64.41, 49.52.

HRMS (ESI): $C_{30}H_{33}N_4O_8$ $[M+H]^+$: calcd.: 577.2293; found: 577.2291.

2,4,6,8-tetrakis(thiophen-2-ylmethyl)-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (5v)



5v, R = 2-thienyl-CH_2

Compound **5v** was synthesized following the general procedure.

A white solid, 112.1 mg, 35% yield.

TLC: R_f = 0.4 (petroleum ether/EtOAc = 4:1)

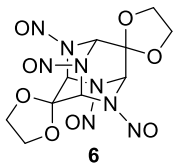
IR (thin film, υ cm^{-1}): 3063, 2960, 2935, 2922, 2892, 2847, 1447, 1437, 1374, 1351, 1326, 1290, 1220, 1109, 1079, 1039, 1006, 910, 855, 850, 817, 711, 709, 694.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 – 7.17 (m, 4H), 6.96 (d, *J* = 3.4 Hz, 4H), 6.90 (dd, *J* = 5.1, 3.4 Hz, 4H), 4.49 (d, *J* = 15.1 Hz, 4H), 4.15 (d, *J* = 15.1 Hz, 4H), 3.86 (s, 8H), 3.45 (s, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.82, 126.41, 124.68, 124.49, 103.08, 72.64, 64.41, 51.44.

HRMS (ESI): $C_{30}H_{33}N_4O_4S_4$ $[M+H]^+$: calcd.: 641.1379; found: 641.1380.

2,4,6,8-tetranitroso-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (6)



6

Compound **6**

A white solid

TLC: R_f = 0.6 (petroleum ether/EtOAc = 1:1)

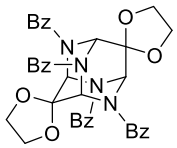
IR (thin film, υ cm^{-1}): 3038, 2968, 2900, 1582, 1333, 1275, 1250, 1117, 1094, 966, 940, 903, 872, 777, 754.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.10 (dt, *J* = 18.4, 1.5 Hz, 2H), 5.05 (t, *J* = 2.1 Hz, 2H), 4.29 – 4.11 (m, 6H), 4.08 – 4.08 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 96.96, 96.92, 94.58, 94.26, 83.57, 73.09, 66.65, 66.61, 66.46, 66.34.

HRMS (ESI): $C_{10}H_{13}N_8O_8$ $[M+H]^+$: calcd.: 373.0851; found: 373.0850.

2,4,6,8-tetrabenzoyl-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (7)

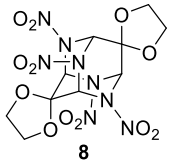


7

Compound **7**, as an intermediate, was difficult to isolate from the reaction mixture, its NMR spectrum was absent, but could be detected by mass spectrometry.

HRMS (ESI): $C_{38}H_{32}N_4NaO_8$ $[M+Na]^+$: calcd.: 695.2112; found: 695.2110.

2,4,6,8-tetranitro-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (8)



8

Compound **8**

A white solid

TLC: R_f = 0.4 (petroleum ether/EtOAc = 4:1)

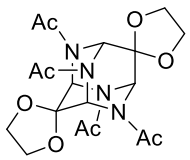
IR (thin film, υ cm^{-1}): 3061, 3041, 2975, 2902, 2852, 1583, 1482, 1469, 1336, 1273, 1245, 1117, 1094, 963, 943, 903, 870, 779, 757.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.91 (s, 4H), 4.22 (s, 8H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 101.15, 67.39, 67.03.

The molecular ion peak of compound **8** could not be found in the ESI ionization source, but its structure was further determined by X-ray diffraction analysis.

2,4,6,8-tetraacetyl-2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (9)



9

Compound **9**

A white solid.

TLC: R_f = 0.4 (EtOAc/MeOH = 40:1)

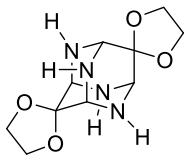
IR (thin film, υ cm^{-1}): 3036, 2978, 2899, 1663, 1439, 1391, 1358, 1333, 1303, 1167, 1117, 1086, 1029, 1016, 996, 948, 903, 872.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.13 (s, 4H), 4.23 – 4.06 (m, 8H), 2.24 (s, 12H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.26, 99.63, 66.71, 61.58, 21.10.

HRMS (ESI): $C_{18}H_{24}N_4NaO_8$ $[M+Na]^+$: calcd.: 447.1486; found: 447.1483.

2,4,6,8-tetraazaadamantane-9,10-dione bis(ethylene ketal) (10)



10

Compound **10**

A white solid, 126.9 mg, 99% yield.

TLC: R_f = 0.4 (MeOH)

IR (thin film, υ cm^{-1}): 3281, 3224, 2970, 2934, 2892, 1657, 1456, 1396, 1336, 1328, 1211, 1129, 1116, 1089, 1017, 996, 945, 891, 860, 815, 794, 760.

^{1}H NMR (500 MHz, Methanol-d_4) δ 4.07 (s, 8H), 3.68 (s, 4H).

^{13}C NMR (126 MHz, Methanol-d_4) δ 101.04, 66.61, 66.31.

HRMS (ESI): $C_{10}H_{17}N_4O_4$ $[M+H]^+$: calcd.: 257.1244; found: 257.1242.

4. X-Ray Crystallographic Analysis

X-ray structure of 5a

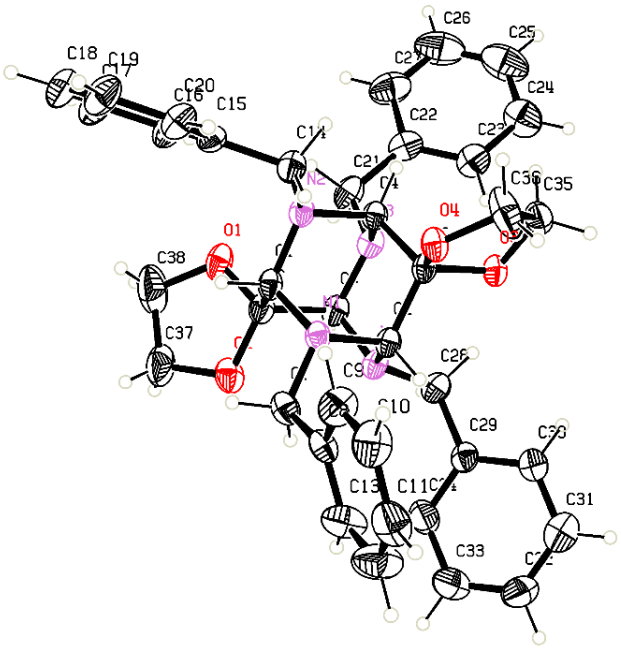


Figure S1. X-ray structure of **5a**.

Table S2. Crystal data and structure refinement for **5a**.

Compound	**5a**	
Empirical formula	$C_{38}H_{40}N_4O_4$	
Formula weight	616.74	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 30.685(13) Å	α = 90°.
	b = 14.167(6) Å	β = 119.995(5)°.
	c = 17.295(7) Å	γ = 90°.
Volume	6511(5) $Å^3$	
Z	8	
Density (calculated)	1.258 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	2624	
Crystal size	0.200 x 0.150 x 0.150 mm^3	
Theta range for data collection	1.533 to 27.316°.	
Index ranges	-39<=h<=38, -16<=k<=17, -21<=l<=21	
Reflections collected	25069	
Independent reflections	6749 [R(int) = 0.0330]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.988 and 0.985	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6749 / 7 / 415	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0569, wR2 = 0.1396	

R indices (all data)	R1 = 0.0978, wR2 = 0.1635
Extinction coefficient	n/a
Largest diff. peak and hole	0.476 and -0.392 e.Å^{-3}
CCDC	2070225

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **5a.**

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	X	Y	Z	U(eq)
C(1)	2039(1)	9806(2)	3010(1)	43(1)
C(2)	1215(1)	10285(2)	2712(1)	41(1)
C(3)	1287(1)	9394(2)	1598(1)	47(1)
C(4)	1466(1)	8618(2)	2961(1)	42(1)
C(5)	1172(1)	9378(2)	3139(1)	40(1)
C(6)	1840(1)	9684(2)	2006(1)	48(1)
C(7)	1843(1)	11510(2)	3052(2)	52(1)
C(8)	1724(1)	12176(2)	3602(2)	50(1)
C(9)	1894(1)	12013(2)	4491(2)	72(1)
C(10)	1809(1)	12640(2)	5008(2)	80(1)
C(11)	1553(1)	13450(2)	4645(2)	81(1)
C(12)	1373(2)	13622(2)	3760(2)	98(1)
C(13)	1457(1)	12981(2)	3243(2)	78(1)
C(14)	2321(1)	8774(2)	4309(1)	50(1)
C(15)	2868(1)	8650(2)	4569(1)	44(1)
C(16)	3010(1)	8257(2)	4001(2)	65(1)
C(17)	3511(1)	8168(2)	4250(2)	79(1)
C(18)	3878(1)	8462(2)	5073(2)	74(1)
C(19)	3743(1)	8833(2)	5657(2)	72(1)
C(20)	3241(1)	8928(2)	5403(2)	58(1)
C(21)	1335(1)	7641(2)	1689(2)	59(1)
C(22)	1027(1)	6827(2)	1717(2)	58(1)
C(23)	591(1)	6955(2)	1746(2)	67(1)
C(24)	305(1)	6196(2)	1733(2)	87(1)
C(25)	450(2)	5303(3)	1677(3)	114(1)
C(26)	876(2)	5159(3)	1640(3)	124(2)
C(27)	1166(1)	5912(2)	1663(2)	94(1)
C(28)	483(1)	10151(2)	1154(2)	52(1)
C(29)	237(1)	11083(2)	1103(1)	49(1)
C(30)	-117(1)	11177(2)	1353(2)	90(1)
C(31)	-361(1)	12029(3)	1249(3)	103(1)
C(32)	-249(1)	12791(2)	908(2)	90(1)
C(33)	103(1)	12713(2)	663(2)	83(1)

C(34)	346(1)	11866(2)	759(2)	70(1)
C(35)	634(1)	8667(2)	3507(2)	58(1)
C(36)	1059(1)	9090(3)	4332(2)	94(1)
C(37)	2279(1)	10423(3)	1434(2)	100(1)
C(38)	2466(2)	9444(3)	1688(3)	111(1)
N(1)	1750(1)	10529(1)	3180(1)	41(1)
N(2)	1998(1)	8888(1)	3345(1)	43(1)
N(3)	1227(1)	8523(1)	1990(1)	46(1)
N(4)	1030(1)	10177(1)	1744(1)	45(1)
O(1)	2113(1)	8989(1)	1834(1)	61(1)
O(2)	1882(1)	10532(1)	1615(1)	61(1)
O(3)	659(1)	9132(1)	2803(1)	47(1)
O(4)	1375(1)	9511(1)	4076(1)	47(1)

Table S4. Bond lengths [Å] and angles [°] for **5a**.

C(1)-N(2)	1.454(3)	N(1)-C(7)-H(7B)	109.2
C(1)-N(1)	1.475(3)	C(8)-C(7)-H(7B)	109.2
C(1)-C(6)	1.536(3)	H(7A)-C(7)-H(7B)	107.9
C(1)-H(1)	0.98	C(13)-C(8)-C(9)	117.2(2)
C(2)-N(1)	1.465(2)	C(13)-C(8)-C(7)	121.1(2)
C(2)-N(4)	1.484(3)	C(9)-C(8)-C(7)	121.6(2)
C(2)-C(5)	1.520(3)	C(10)-C(9)-C(8)	122.0(3)
C(2)-H(2)	0.98	C(10)-C(9)-H(9)	119
C(3)-N(4)	1.455(3)	C(8)-C(9)-H(9)	119
C(3)-N(3)	1.465(3)	C(11)-C(10)-C(9)	120.0(3)
C(3)-C(6)	1.532(3)	C(11)-C(10)-H(10)	120
C(3)-H(3)	0.98	C(9)-C(10)-H(10)	120
C(4)-N(3)	1.463(3)	C(10)-C(11)-C(12)	119.2(3)
C(4)-N(2)	1.473(3)	C(10)-C(11)-H(11)	120.4
C(4)-C(5)	1.533(3)	C(12)-C(11)-H(11)	120.4
C(4)-H(4)	0.98	C(11)-C(12)-C(13)	120.3(3)
C(5)-O(3)	1.421(2)	C(11)-C(12)-H(12)	119.8
C(5)-O(4)	1.429(2)	C(13)-C(12)-H(12)	119.8
C(6)-O(2)	1.417(3)	C(8)-C(13)-C(12)	121.2(3)
C(6)-O(1)	1.417(3)	C(8)-C(13)-H(13)	119.4
C(7)-N(1)	1.457(3)	C(12)-C(13)-H(13)	119.4
C(7)-C(8)	1.509(3)	N(2)-C(14)-C(15)	111.81(17)

C(7)-H(7A)	0.97	N(2)-C(14)-H(14A)	109.3
C(7)-H(7B)	0.97	C(15)-C(14)-H(14A)	109.3
C(8)-C(13)	1.360(4)	N(2)-C(14)-H(14B)	109.3
C(8)-C(9)	1.373(3)	C(15)-C(14)-H(14B)	109.3
C(9)-C(10)	1.373(4)	H(14A)-C(14)-H(14B)	107.9
C(9)-H(9)	0.93	C(20)-C(15)-C(16)	118.1(2)
C(10)-C(11)	1.356(4)	C(20)-C(15)-C(14)	119.7(2)
C(10)-H(10)	0.93	C(16)-C(15)-C(14)	122.26(19)
C(11)-C(12)	1.363(4)	C(15)-C(16)-C(17)	121.0(2)
C(11)-H(11)	0.93	C(15)-C(16)-H(16)	119.5
C(12)-C(13)	1.387(4)	C(17)-C(16)-H(16)	119.5
C(12)-H(12)	0.93	C(18)-C(17)-C(16)	120.4(2)
C(13)-H(13)	0.93	C(18)-C(17)-H(17)	119.8
C(14)-N(2)	1.461(3)	C(16)-C(17)-H(17)	119.8
C(14)-C(15)	1.514(3)	C(17)-C(18)-C(19)	119.4(2)
C(14)-H(14A)	0.97	C(17)-C(18)-H(18)	120.3
C(14)-H(14B)	0.97	C(19)-C(18)-H(18)	120.3
C(15)-C(20)	1.376(3)	C(18)-C(19)-C(20)	120.1(2)
C(15)-C(16)	1.376(3)	C(18)-C(19)-H(19)	120
C(16)-C(17)	1.381(4)	C(20)-C(19)-H(19)	120
C(16)-H(16)	0.93	C(15)-C(20)-C(19)	121.1(2)
C(17)-C(18)	1.364(4)	C(15)-C(20)-H(20)	119.5
C(17)-H(17)	0.93	C(19)-C(20)-H(20)	119.5
C(18)-C(19)	1.373(4)	N(3)-C(21)-C(22)	112.63(19)
C(18)-H(18)	0.93	N(3)-C(21)-H(21A)	109.1
C(19)-C(20)	1.381(3)	C(22)-C(21)-H(21A)	109.1
C(19)-H(19)	0.93	N(3)-C(21)-H(21B)	109.1
C(20)-H(20)	0.93	C(22)-C(21)-H(21B)	109.1
C(21)-N(3)	1.455(3)	H(21A)-C(21)-H(21B)	107.8
C(21)-C(22)	1.508(4)	C(23)-C(22)-C(27)	117.6(3)
C(21)-H(21A)	0.97	C(23)-C(22)-C(21)	122.6(2)
C(21)-H(21B)	0.97	C(27)-C(22)-C(21)	119.7(3)
C(22)-C(23)	1.377(4)	C(22)-C(23)-C(24)	121.2(3)
C(22)-C(27)	1.382(4)	C(22)-C(23)-H(23)	119.4
C(23)-C(24)	1.380(4)	C(24)-C(23)-H(23)	119.4
C(23)-H(23)	0.93	C(25)-C(24)-C(23)	119.9(4)

C(24)-C(25)	1.360(5)	C(25)-C(24)-H(24)	120.1
C(24)-H(24)	0.93	C(23)-C(24)-H(24)	120.1
C(25)-C(26)	1.358(6)	C(26)-C(25)-C(24)	120.0(4)
C(25)-H(25)	0.93	C(26)-C(25)-H(25)	120
C(26)-C(27)	1.375(5)	C(24)-C(25)-H(25)	120
C(26)-H(26)	0.93	C(25)-C(26)-C(27)	120.4(4)
C(27)-H(27)	0.93	C(25)-C(26)-H(26)	119.8
C(28)-N(4)	1.465(3)	C(27)-C(26)-H(26)	119.8
C(28)-C(29)	1.500(3)	C(26)-C(27)-C(22)	120.9(4)
C(28)-H(28A)	0.97	C(26)-C(27)-H(27)	119.5
C(28)-H(28B)	0.97	C(22)-C(27)-H(27)	119.5
C(29)-C(30)	1.362(3)	N(4)-C(28)-C(29)	112.66(18)
C(29)-C(34)	1.377(3)	N(4)-C(28)-H(28A)	109.1
C(30)-C(31)	1.384(4)	C(29)-C(28)-H(28A)	109.1
C(30)-H(30)	0.93	N(4)-C(28)-H(28B)	109.1
C(31)-C(32)	1.355(5)	C(29)-C(28)-H(28B)	109.1
C(31)-H(31)	0.93	H(28A)-C(28)-H(28B)	107.8
C(32)-C(33)	1.346(4)	C(30)-C(29)-C(34)	117.6(2)
C(32)-H(32)	0.93	C(30)-C(29)-C(28)	121.6(2)
C(33)-C(34)	1.379(4)	C(34)-C(29)-C(28)	120.7(2)
C(33)-H(33)	0.93	C(29)-C(30)-C(31)	120.7(3)
C(34)-H(34)	0.93	C(29)-C(30)-H(30)	119.6
C(35)-O(3)	1.420(3)	C(31)-C(30)-H(30)	119.6
C(35)-C(36)	1.495(4)	C(32)-C(31)-C(30)	120.8(3)
C(35)-H(35A)	0.97	C(32)-C(31)-H(31)	119.6
C(35)-H(35B)	0.97	C(30)-C(31)-H(31)	119.6
C(36)-O(4)	1.385(3)	C(33)-C(32)-C(31)	119.4(3)
C(36)-H(36A)	0.97	C(33)-C(32)-H(32)	120.3
C(36)-H(36B)	0.97	C(31)-C(32)-H(32)	120.3
C(37)-O(2)	1.410(3)	C(32)-C(33)-C(34)	120.3(3)
C(37)-C(38)	1.481(5)	C(32)-C(33)-H(33)	119.8
C(37)-H(37A)	0.97	C(34)-C(33)-H(33)	119.8
C(37)-H(37B)	0.97	C(29)-C(34)-C(33)	121.2(3)
C(38)-O(1)	1.387(3)	C(29)-C(34)-H(34)	119.4
C(38)-H(38A)	0.97	C(33)-C(34)-H(34)	119.4
C(38)-H(38B)	0.97	O(3)-C(35)-C(36)	103.72(19)

N(2)-C(1)-N(1)	111.24(16)	O(3)-C(35)-H(35A)	111
N(2)-C(1)-C(6)	106.49(17)	C(36)-C(35)-H(35A)	111
N(1)-C(1)-C(6)	111.41(17)	O(3)-C(35)-H(35B)	111
N(2)-C(1)-H(1)	109.2	C(36)-C(35)-H(35B)	111
N(1)-C(1)-H(1)	109.2	H(35A)-C(35)-H(35B)	109
C(6)-C(1)-H(1)	109.2	O(4)-C(36)-C(35)	106.5(2)
N(1)-C(2)-N(4)	109.79(15)	O(4)-C(36)-H(36A)	110.4
N(1)-C(2)-C(5)	106.08(15)	C(35)-C(36)-H(36A)	110.4
N(4)-C(2)-C(5)	112.59(16)	O(4)-C(36)-H(36B)	110.4
N(1)-C(2)-H(2)	109.4	C(35)-C(36)-H(36B)	110.4
N(4)-C(2)-H(2)	109.4	H(36A)-C(36)-H(36B)	108.6
C(5)-C(2)-H(2)	109.4	O(2)-C(37)-C(38)	106.6(3)
N(4)-C(3)-N(3)	110.93(17)	O(2)-C(37)-H(37A)	110.4
N(4)-C(3)-C(6)	106.73(18)	C(38)-C(37)-H(37A)	110.4
N(3)-C(3)-C(6)	112.22(17)	O(2)-C(37)-H(37B)	110.4
N(4)-C(3)-H(3)	109	C(38)-C(37)-H(37B)	110.4
N(3)-C(3)-H(3)	109	H(37A)-C(37)-H(37B)	108.6
C(6)-C(3)-H(3)	109	O(1)-C(38)-C(37)	105.5(3)
N(3)-C(4)-N(2)	110.43(16)	O(1)-C(38)-H(38A)	110.6
N(3)-C(4)-C(5)	106.73(16)	C(37)-C(38)-H(38A)	110.6
N(2)-C(4)-C(5)	111.00(17)	O(1)-C(38)-H(38B)	110.6
N(3)-C(4)-H(4)	109.5	C(37)-C(38)-H(38B)	110.6
N(2)-C(4)-H(4)	109.5	H(38A)-C(38)-H(38B)	108.8
C(5)-C(4)-H(4)	109.5	C(7)-N(1)-C(2)	113.03(17)
O(3)-C(5)-O(4)	105.22(15)	C(7)-N(1)-C(1)	116.69(16)
O(3)-C(5)-C(2)	110.86(16)	C(2)-N(1)-C(1)	110.20(16)
O(4)-C(5)-C(2)	110.22(16)	C(1)-N(2)-C(14)	114.11(17)
O(3)-C(5)-C(4)	112.84(16)	C(1)-N(2)-C(4)	110.41(16)
O(4)-C(5)-C(4)	110.71(16)	C(14)-N(2)-C(4)	116.97(16)
C(2)-C(5)-C(4)	107.03(16)	C(21)-N(3)-C(4)	114.68(18)
O(2)-C(6)-O(1)	106.47(16)	C(21)-N(3)-C(3)	116.93(17)
O(2)-C(6)-C(3)	110.57(17)	C(4)-N(3)-C(3)	110.28(16)
O(1)-C(6)-C(3)	110.65(18)	C(3)-N(4)-C(28)	113.08(17)
O(2)-C(6)-C(1)	111.34(19)	C(3)-N(4)-C(2)	109.88(16)
O(1)-C(6)-C(1)	111.95(17)	C(28)-N(4)-C(2)	116.57(16)
C(3)-C(6)-C(1)	105.94(16)	C(38)-O(1)-C(6)	108.3(2)

N(1)-C(7)-C(8)	111.94(17)	C(37)-O(2)-C(6)	108.0(2)
N(1)-C(7)-H(7A)	109.2	C(35)-O(3)-C(5)	106.65(15)
C(8)-C(7)-H(7A)	109.2	C(36)-O(4)-C(5)	109.11(17)

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5a**.

The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
C(1)	32(1)	61(1)	35(1)	-1(1)	16(1)	-2(1)
C(2)	33(1)	51(1)	35(1)	-4(1)	14(1)	-1(1)
C(3)	38(1)	66(2)	29(1)	-4(1)	12(1)	3(1)
C(4)	36(1)	49(1)	38(1)	-3(1)	17(1)	-1(1)
C(5)	30(1)	54(1)	34(1)	-5(1)	13(1)	-4(1)
C(6)	41(1)	67(2)	38(1)	4(1)	22(1)	4(1)
C(7)	52(1)	60(2)	44(1)	-1(1)	25(1)	-11(1)
C(8)	50(1)	50(1)	50(1)	-5(1)	27(1)	-16(1)
C(9)	76(2)	86(2)	56(2)	2(1)	34(1)	12(2)
C(10)	82(2)	103(2)	62(2)	-12(2)	42(2)	-3(2)
C(11)	99(2)	71(2)	95(2)	-31(2)	64(2)	-26(2)
C(12)	147(3)	56(2)	103(3)	2(2)	73(3)	12(2)
C(13)	115(2)	55(2)	67(2)	4(1)	48(2)	1(2)
C(14)	43(1)	69(2)	36(1)	5(1)	18(1)	5(1)
C(15)	41(1)	48(1)	37(1)	6(1)	14(1)	6(1)
C(16)	48(1)	95(2)	42(1)	-6(1)	15(1)	16(1)
C(17)	60(2)	117(3)	59(2)	4(2)	29(1)	30(2)
C(18)	43(1)	93(2)	77(2)	4(2)	24(1)	14(1)
C(19)	43(1)	79(2)	66(2)	-15(1)	6(1)	4(1)
C(20)	49(1)	62(2)	52(1)	-12(1)	17(1)	6(1)
C(21)	51(1)	71(2)	53(1)	-14(1)	24(1)	7(1)
C(22)	63(2)	57(2)	40(1)	-8(1)	16(1)	6(1)
C(23)	58(2)	63(2)	65(2)	-14(1)	20(1)	-7(1)
C(24)	80(2)	85(2)	75(2)	-16(2)	22(2)	-28(2)
C(25)	148(4)	75(3)	100(3)	-10(2)	48(3)	-37(3)
C(26)	178(5)	52(2)	138(4)	-1(2)	76(4)	2(3)
C(27)	113(3)	71(2)	94(2)	0(2)	50(2)	24(2)
C(28)	38(1)	64(2)	39(1)	-1(1)	7(1)	2(1)
C(29)	35(1)	62(2)	39(1)	3(1)	10(1)	0(1)
C(30)	85(2)	80(2)	135(3)	36(2)	79(2)	19(2)
C(31)	91(2)	100(2)	137(2)	9(2)	71(2)	18(1)
C(32)	71(2)	67(2)	124(3)	18(2)	42(2)	18(2)
C(33)	94(2)	64(2)	93(2)	13(2)	48(2)	-1(2)

C(34)	72(2)	67(2)	82(2)	-2(1)	48(2)	-9(1)
C(35)	48(1)	66(2)	63(2)	8(1)	29(1)	-6(1)
C(36)	75(2)	153(3)	56(2)	-2(2)	35(2)	-47(2)
C(37)	66(2)	159(4)	96(2)	52(2)	56(2)	20(2)
C(38)	104(3)	122(3)	158(4)	-37(3)	103(3)	-27(2)
N(1)	34(1)	51(1)	36(1)	-1(1)	15(1)	-5(1)
N(2)	34(1)	58(1)	33(1)	2(1)	14(1)	1(1)
N(3)	40(1)	56(1)	38(1)	-9(1)	16(1)	1(1)
N(4)	34(1)	59(1)	32(1)	-2(1)	10(1)	2(1)
O(1)	49(1)	93(1)	51(1)	-4(1)	31(1)	7(1)
O(2)	60(1)	87(1)	45(1)	9(1)	33(1)	-3(1)
O(3)	36(1)	58(1)	47(1)	-3(1)	21(1)	-6(1)
O(4)	43(1)	64(1)	37(1)	-7(1)	22(1)	-9(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5a**.

	x	y	z	U(eq)
H(1)	2393	9994	3305	52
H(2)	1025	10787	2803	49
H(3)	1143	9302	954	56
H(4)	1444	8018	3220	50
H(7A)	1638	11672	2426	62
H(7B)	2193	11583	3217	62
H(9)	2071	11461	4751	86
H(10)	1928	12508	5607	95
H(11)	1502	13884	4995	98
H(12)	1192	14172	3503	117
H(13)	1328	13104	2639	94
H(14A)	2211	8228	4504	60
H(14B)	2289	9325	4610	60
H(16)	2764	8049	3440	78
H(17)	3600	7905	3856	95
H(18)	4215	8412	5237	88
H(19)	3990	9020	6225	87
H(20)	3153	9185	5801	70
H(21A)	1690	7494	2062	71
H(21B)	1269	7720	1082	71
H(23)	487	7564	1776	81
H(24)	14	6295	1762	105
H(25)	256	4791	1664	137
H(26)	974	4548	1598	148

H(27)	1459	5804	1643	112
H(28A)	341	9676	1369	63
H(28B)	408	9968	559	63
H(30)	-196	10663	1595	107
H(31)	-605	12079	1416	123
H(32)	-413	13362	844	108
H(33)	181	13232	427	100
H(34)	589	11823	589	83
H(35A)	678	7991	3486	70
H(35B)	314	8786	3476	70
H(36A)	934	9555	4585	112
H(36B)	1237	8604	4776	112
H(37A)	2546	10871	1779	120
H(37B)	2160	10527	805	120
H(38A)	2493	9137	1212	133
H(38B)	2794	9439	2225	133

Table S7. Torsion angles [°] for **5a**.

N(1)-C(2)-C(5)-O(3)	173.44(15)	C(30)-C(29)-C(34)-C(33)	-0.7(4)
N(4)-C(2)-C(5)-O(3)	-66.5(2)	C(28)-C(29)-C(34)-C(33)	176.3(2)
N(1)-C(2)-C(5)-O(4)	57.36(19)	C(32)-C(33)-C(34)-C(29)	0.3(5)
N(4)-C(2)-C(5)-O(4)	177.46(15)	O(3)-C(35)-C(36)-O(4)	-17.8(3)
N(1)-C(2)-C(5)-C(4)	-63.11(19)	O(2)-C(37)-C(38)-O(1)	11.2(4)
N(4)-C(2)-C(5)-C(4)	57.0(2)	C(8)-C(7)-N(1)-C(2)	75.9(2)
N(3)-C(4)-C(5)-O(3)	61.5(2)	C(8)-C(7)-N(1)-C(1)	-154.82(17)
N(2)-C(4)-C(5)-O(3)	-178.15(15)	N(4)-C(2)-N(1)-C(7)	75.8(2)
N(3)-C(4)-C(5)-O(4)	179.10(15)	C(5)-C(2)-N(1)-C(7)	-162.27(16)
N(2)-C(4)-C(5)-O(4)	-60.5(2)	N(4)-C(2)-N(1)-C(1)	-56.8(2)
N(3)-C(4)-C(5)-C(2)	-60.75(19)	C(5)-C(2)-N(1)-C(1)	65.16(19)
N(2)-C(4)-C(5)-C(2)	59.6(2)	N(2)-C(1)-N(1)-C(7)	167.41(16)
N(4)-C(3)-C(6)-O(2)	-57.8(2)	C(6)-C(1)-N(1)-C(7)	-73.9(2)
N(3)-C(3)-C(6)-O(2)	-179.51(16)	N(2)-C(1)-N(1)-C(2)	-61.9(2)
N(4)-C(3)-C(6)-O(1)	-175.50(16)	C(6)-C(1)-N(1)-C(2)	56.7(2)
N(3)-C(3)-C(6)-O(1)	62.8(2)	N(1)-C(1)-N(2)-C(14)	-78.8(2)
N(4)-C(3)-C(6)-C(1)	63.0(2)	C(6)-C(1)-N(2)-C(14)	159.68(16)
N(3)-C(3)-C(6)-C(1)	-58.8(2)	N(1)-C(1)-N(2)-C(4)	55.4(2)
N(2)-C(1)-C(6)-O(2)	-177.46(15)	C(6)-C(1)-N(2)-C(4)	-66.16(19)
N(1)-C(1)-C(6)-O(2)	61.1(2)	C(15)-C(14)-N(2)-C(1)	-74.2(2)
N(2)-C(1)-C(6)-O(1)	-58.4(2)	C(15)-C(14)-N(2)-C(4)	154.80(19)
N(1)-C(1)-C(6)-O(1)	-179.86(16)	N(3)-C(4)-N(2)-C(1)	62.8(2)
N(2)-C(1)-C(6)-C(3)	62.3(2)	C(5)-C(4)-N(2)-C(1)	-55.4(2)

N(1)-C(1)-C(6)-C(3)	-59.2(2)	N(3)-C(4)-N(2)-C(14)	-164.50(18)
N(1)-C(7)-C(8)-C(13)	-134.5(2)	C(5)-C(4)-N(2)-C(14)	77.3(2)
N(1)-C(7)-C(8)-C(9)	47.5(3)	C(22)-C(21)-N(3)-C(4)	78.7(2)
C(13)-C(8)-C(9)-C(10)	-1.4(4)	C(22)-C(21)-N(3)-C(3)	-149.90(19)
C(7)-C(8)-C(9)-C(10)	176.6(2)	N(2)-C(4)-N(3)-C(21)	79.1(2)
C(8)-C(9)-C(10)-C(11)	-0.2(5)	C(5)-C(4)-N(3)-C(21)	-160.19(17)
C(9)-C(10)-C(11)-C(12)	1.4(5)	N(2)-C(4)-N(3)-C(3)	-55.5(2)
C(10)-C(11)-C(12)-C(13)	-1.0(5)	C(5)-C(4)-N(3)-C(3)	65.3(2)
C(9)-C(8)-C(13)-C(12)	1.9(4)	N(4)-C(3)-N(3)-C(21)	162.98(17)
C(7)-C(8)-C(13)-C(12)	-176.1(3)	C(6)-C(3)-N(3)-C(21)	-77.7(2)
C(11)-C(12)-C(13)-C(8)	-0.8(5)	N(4)-C(3)-N(3)-C(4)	-63.6(2)
N(2)-C(14)-C(15)-C(20)	152.3(2)	C(6)-C(3)-N(3)-C(4)	55.7(2)
N(2)-C(14)-C(15)-C(16)	-28.1(3)	N(3)-C(3)-N(4)-C(28)	-76.3(2)
C(20)-C(15)-C(16)-C(17)	-1.6(4)	C(6)-C(3)-N(4)-C(28)	161.20(17)
C(14)-C(15)-C(16)-C(17)	178.8(3)	N(3)-C(3)-N(4)-C(2)	55.9(2)
C(15)-C(16)-C(17)-C(18)	0.5(5)	C(6)-C(3)-N(4)-C(2)	-66.6(2)
C(16)-C(17)-C(18)-C(19)	1.2(5)	C(29)-C(28)-N(4)-C(3)	-162.46(18)
C(17)-C(18)-C(19)-C(20)	-1.7(5)	C(29)-C(28)-N(4)-C(2)	68.8(2)
C(16)-C(15)-C(20)-C(19)	1.1(4)	N(1)-C(2)-N(4)-C(3)	63.4(2)
C(14)-C(15)-C(20)-C(19)	-179.3(2)	C(5)-C(2)-N(4)-C(3)	-54.5(2)
C(18)-C(19)-C(20)-C(15)	0.5(4)	N(1)-C(2)-N(4)-C(28)	-166.26(17)
N(3)-C(21)-C(22)-C(23)	19.3(3)	C(5)-C(2)-N(4)-C(28)	75.8(2)
N(3)-C(21)-C(22)-C(27)	-164.4(2)	C(37)-C(38)-O(1)-C(6)	-21.1(4)
C(27)-C(22)-C(23)-C(24)	0.7(4)	O(2)-C(6)-O(1)-C(38)	23.3(3)
C(21)-C(22)-C(23)-C(24)	177.1(2)	C(3)-C(6)-O(1)-C(38)	143.5(3)
C(22)-C(23)-C(24)-C(25)	-1.0(4)	C(1)-C(6)-O(1)-C(38)	-98.6(3)
C(23)-C(24)-C(25)-C(26)	0.4(6)	C(38)-C(37)-O(2)-C(6)	2.9(4)
C(24)-C(25)-C(26)-C(27)	0.3(7)	O(1)-C(6)-O(2)-C(37)	-15.7(3)
C(25)-C(26)-C(27)-C(22)	-0.6(6)	C(3)-C(6)-O(2)-C(37)	-136.0(2)
C(23)-C(22)-C(27)-C(26)	0.0(5)	C(1)-C(6)-O(2)-C(37)	106.6(2)
C(21)-C(22)-C(27)-C(26)	-176.5(3)	C(36)-C(35)-O(3)-C(5)	28.8(3)
N(4)-C(28)-C(29)-C(30)	-120.0(3)	O(4)-C(5)-O(3)-C(35)	-29.2(2)
N(4)-C(28)-C(29)-C(34)	63.2(3)	C(2)-C(5)-O(3)-C(35)	-148.33(18)
C(34)-C(29)-C(30)-C(31)	0.9(5)	C(4)-C(5)-O(3)-C(35)	91.6(2)
C(28)-C(29)-C(30)-C(31)	-176.0(3)	C(35)-C(36)-O(4)-C(5)	0.2(3)
C(29)-C(30)-C(31)-C(32)	-0.8(6)	O(3)-C(5)-O(4)-C(36)	17.6(3)
C(30)-C(31)-C(32)-C(33)	0.4(6)	C(2)-C(5)-O(4)-C(36)	137.2(2)
C(31)-C(32)-C(33)-C(34)	-0.1(5)	C(4)-C(5)-O(4)-C(36)	-104.6(2)

Symmetry transformations used to generate equivalent atoms.

X-ray structure of 8

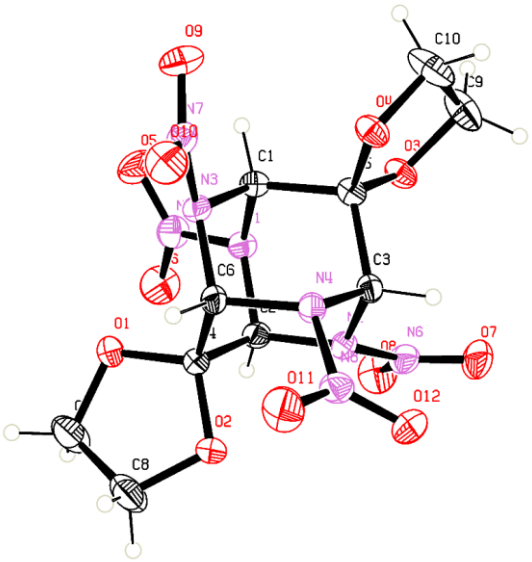


Figure S2. X-ray structure of **8**.

Table S8. Crystal data and structure refinement for **8**.

Compound	**8**	
Empirical formula	$C_{10}H_{12}N_8O_{12}$	
Formula weight	436.28	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.851(6) Å	α = 90°.
	b = 9.892(5) Å	β = 114.106(6)°.
	c = 14.373(7) Å	γ = 90°.
Volume	1667.7(14) $Å^3$	
Z	4	
Density (calculated)	1.738 mg/m^3	
Absorption coefficient	0.161 mm^{-1}	
F(000)	896	
Crystal size	0.200 x 0.150 x 0.150 mm^3	
Theta range for data collection	1.795 to 25.004°.	
Index ranges	-15<=h<=15, -11<=k<=11, -17<=l<=17	
Reflections collected	11663	
Independent reflections	2940 [R(int) = 0.0647]	
Completeness to theta = 25.004°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.976 and 0.971	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2940 / 0 / 271	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0559, wR2 = 0.1176	
R indices (all data)	R1 = 0.0926, wR2 = 0.1299	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.278 and -0.281 $e.Å^{-3}$	
CCDC	2151060	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **8**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	9055(2)	2128(2)	1398(2)	31(1)
C(2)	10094(2)	1100(2)	3085(2)	34(1)
C(3)	11136(2)	2613(2)	2411(2)	31(1)
C(4)	9778(2)	2320(2)	3581(2)	34(1)
C(5)	10206(2)	2386(2)	1323(2)	30(1)
C(6)	9683(2)	3574(2)	2918(2)	31(1)
C(7)	8924(3)	2081(4)	4671(2)	66(1)
C(8)	10069(3)	2666(4)	5213(2)	75(1)
C(9)	10743(3)	1757(3)	64(2)	60(1)
C(10)	10232(3)	3106(3)	-156(2)	68(1)
N(1)	9211(2)	931(2)	2033(1)	33(1)
N(2)	11172(2)	1415(2)	3038(2)	34(1)
N(3)	8801(2)	3298(2)	1912(1)	31(1)
N(4)	10781(1)	3773(2)	2825(1)	32(1)
N(5)	8206(2)	256(2)	1962(2)	46(1)
N(6)	11868(2)	336(2)	3013(2)	43(1)
N(7)	8337(2)	4441(2)	1291(2)	40(1)
N(8)	11646(2)	4403(2)	3669(2)	40(1)
O(1)	8733(1)	2082(2)	3636(1)	44(1)
O(2)	10620(1)	2522(2)	4558(1)	46(1)
O(3)	10484(1)	1270(2)	877(1)	37(1)
O(4)	10121(1)	3529(2)	734(1)	37(1)
O(5)	7322(2)	577(2)	1268(2)	65(1)
O(6)	8336(2)	-630(2)	2582(2)	66(1)
O(7)	12709(2)	636(2)	2877(2)	59(1)
O(8)	11597(2)	-785(2)	3176(2)	65(1)
O(9)	7723(2)	4214(2)	402(2)	57(1)
O(10)	8552(2)	5537(2)	1702(2)	53(1)
O(11)	11344(2)	5352(2)	4032(2)	61(1)
O(12)	12615(1)	3990(2)	3927(1)	50(1)

Table S10. Bond lengths [Å] and angles [°] for **8.**

C(1)-N(1)	1.458(3)	O(1)-C(4)-C(2)	109.59(19)
C(1)-N(3)	1.480(3)	C(6)-C(4)-C(2)	108.37(19)
C(1)-C(5)	1.547(3)	O(4)-C(5)-O(3)	109.58(19)
C(1)-H(1)	0.98	O(4)-C(5)-C(1)	109.70(17)
C(2)-N(2)	1.448(3)	O(3)-C(5)-C(1)	109.48(17)
C(2)-N(1)	1.483(3)	O(4)-C(5)-C(3)	109.45(17)

C(2)-C(4)	1.539(3)	O(3)-C(5)-C(3)	110.01(17)
C(2)-H(2)	0.98	C(1)-C(5)-C(3)	108.61(19)
C(3)-N(4)	1.449(3)	N(3)-C(6)-N(4)	108.60(18)
C(3)-N(2)	1.479(3)	N(3)-C(6)-C(4)	107.31(18)
C(3)-C(5)	1.549(3)	N(4)-C(6)-C(4)	108.94(17)
C(3)-H(3)	0.98	N(3)-C(6)-H(6)	110.6
C(4)-O(2)	1.393(3)	N(4)-C(6)-H(6)	110.6
C(4)-O(1)	1.397(3)	C(4)-C(6)-H(6)	110.6
C(4)-C(6)	1.538(3)	O(1)-C(7)-C(8)	105.3(2)
C(5)-O(4)	1.390(3)	O(1)-C(7)-H(7A)	110.7
C(5)-O(3)	1.395(3)	C(8)-C(7)-H(7A)	110.7
C(6)-N(3)	1.452(3)	O(1)-C(7)-H(7B)	110.7
C(6)-N(4)	1.485(3)	C(8)-C(7)-H(7B)	110.7
C(6)-H(6)	0.98	H(7A)-C(7)-H(7B)	108.8
C(7)-O(1)	1.405(3)	O(2)-C(8)-C(7)	105.9(2)
C(7)-C(8)	1.474(4)	O(2)-C(8)-H(8A)	110.5
C(7)-H(7A)	0.97	C(7)-C(8)-H(8A)	110.5
C(7)-H(7B)	0.97	O(2)-C(8)-H(8B)	110.5
C(8)-O(2)	1.397(3)	C(7)-C(8)-H(8B)	110.5
C(8)-H(8A)	0.97	H(8A)-C(8)-H(8B)	108.7
C(8)-H(8B)	0.97	O(3)-C(9)-C(10)	104.6(2)
C(9)-O(3)	1.424(3)	O(3)-C(9)-H(9A)	110.8
C(9)-C(10)	1.463(4)	C(10)-C(9)-H(9A)	110.8
C(9)-H(9A)	0.97	O(3)-C(9)-H(9B)	110.8
C(9)-H(9B)	0.97	C(10)-C(9)-H(9B)	110.8
C(10)-O(4)	1.408(3)	H(9A)-C(9)-H(9B)	108.9
C(10)-H(10A)	0.97	O(4)-C(10)-C(9)	106.1(2)
C(10)-H(10B)	0.97	O(4)-C(10)-H(10A)	110.5
N(1)-N(5)	1.420(3)	C(9)-C(10)-H(10A)	110.5
N(2)-N(6)	1.403(3)	O(4)-C(10)-H(10B)	110.5
N(3)-N(7)	1.412(3)	C(9)-C(10)-H(10B)	110.5
N(4)-N(8)	1.412(3)	H(10A)-C(10)-H(10B)	108.7
N(5)-O(5)	1.209(3)	N(5)-N(1)-C(1)	116.67(18)
N(5)-O(6)	1.211(3)	N(5)-N(1)-C(2)	114.88(19)
N(6)-O(7)	1.211(3)	C(1)-N(1)-C(2)	113.57(17)
N(6)-O(8)	1.213(3)	N(6)-N(2)-C(2)	118.04(19)
N(7)-O(10)	1.212(3)	N(6)-N(2)-C(3)	117.10(19)
N(7)-O(9)	1.217(3)	C(2)-N(2)-C(3)	114.12(17)
N(8)-O(11)	1.213(3)	N(7)-N(3)-C(6)	115.80(18)
N(8)-O(12)	1.216(3)	N(7)-N(3)-C(1)	115.60(18)

N(1)-C(1)-N(3)	108.89(19)	C(6)-N(3)-C(1)	113.76(17)
N(1)-C(1)-C(5)	106.67(17)	N(8)-N(4)-C(3)	115.66(18)
N(3)-C(1)-C(5)	108.52(17)	N(8)-N(4)-C(6)	115.13(18)
N(1)-C(1)-H(1)	110.9	C(3)-N(4)-C(6)	113.72(17)
N(3)-C(1)-H(1)	110.9	O(5)-N(5)-O(6)	126.7(2)
C(5)-C(1)-H(1)	110.9	O(5)-N(5)-N(1)	117.2(2)
N(2)-C(2)-N(1)	108.96(19)	O(6)-N(5)-N(1)	116.1(2)
N(2)-C(2)-C(4)	106.92(18)	O(7)-N(6)-O(8)	127.0(2)
N(1)-C(2)-C(4)	108.87(18)	O(7)-N(6)-N(2)	116.0(2)
N(2)-C(2)-H(2)	110.7	O(8)-N(6)-N(2)	116.9(2)
N(1)-C(2)-H(2)	110.7	O(10)-N(7)-O(9)	126.7(2)
C(4)-C(2)-H(2)	110.7	O(10)-N(7)-N(3)	117.0(2)
N(4)-C(3)-N(2)	108.75(18)	O(9)-N(7)-N(3)	116.2(2)
N(4)-C(3)-C(5)	106.68(17)	O(11)-N(8)-O(12)	126.6(2)
N(2)-C(3)-C(5)	108.55(17)	O(11)-N(8)-N(4)	115.7(2)
N(4)-C(3)-H(3)	110.9	O(12)-N(8)-N(4)	117.5(2)
N(2)-C(3)-H(3)	110.9	C(4)-O(1)-C(7)	107.7(2)
C(5)-C(3)-H(3)	110.9	C(4)-O(2)-C(8)	107.2(2)
O(2)-C(4)-O(1)	109.64(19)	C(5)-O(3)-C(9)	107.40(18)
O(2)-C(4)-C(6)	109.99(19)	C(5)-O(4)-C(10)	107.45(19)
O(1)-C(4)-C(6)	109.61(18)		
O(2)-C(4)-C(2)	109.63(18)		

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **8**.

The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
C(1)	33(1)	31(1)	27(1)	1(1)	9(1)	-1(1)
C(2)	33(1)	35(1)	31(1)	9(1)	12(1)	2(1)
C(3)	29(1)	33(1)	31(1)	-1(1)	15(1)	0(1)
C(4)	28(1)	47(1)	28(1)	1(1)	12(1)	0(1)
C(5)	38(1)	25(1)	30(1)	0(1)	16(1)	1(1)
C(6)	28(1)	36(1)	32(1)	-3(1)	14(1)	3(1)
C(7)	72(2)	91(2)	46(2)	-20(2)	36(2)	-31(2)
C(8)	68(2)	124(3)	47(2)	-20(2)	38(2)	-27(2)
C(9)	95(2)	49(2)	62(2)	1(2)	58(2)	3(2)
C(10)	120(3)	55(2)	49(2)	13(2)	55(2)	18(2)
N(1)	34(1)	30(1)	33(1)	4(1)	12(1)	-5(1)
N(2)	30(1)	37(1)	33(1)	4(1)	12(1)	8(1)
N(3)	30(1)	32(1)	29(1)	5(1)	10(1)	4(1)

N(4)	29(1)	35(1)	31(1)	-8(1)	13(1)	-4(1)
N(5)	44(1)	44(1)	51(2)	0(1)	19(1)	-12(1)
N(6)	40(1)	47(1)	38(1)	-3(1)	12(1)	13(1)
N(7)	33(1)	40(1)	46(2)	10(1)	16(1)	7(1)
N(8)	38(1)	45(1)	32(1)	-8(1)	12(1)	-9(1)
O(1)	34(1)	66(1)	37(1)	5(1)	20(1)	-1(1)
O(2)	35(1)	74(1)	26(1)	-1(1)	10(1)	2(1)
O(3)	54(1)	30(1)	33(1)	-2(1)	23(1)	3(1)
O(4)	52(1)	29(1)	36(1)	5(1)	24(1)	2(1)
O(5)	38(1)	81(2)	60(1)	11(1)	4(1)	-18(1)
O(6)	68(1)	54(1)	76(2)	23(1)	30(1)	-15(1)
O(7)	42(1)	70(1)	68(1)	-4(1)	26(1)	16(1)
O(8)	76(1)	37(1)	84(2)	9(1)	36(1)	15(1)
O(9)	51(1)	61(1)	42(1)	14(1)	2(1)	9(1)
O(10)	65(1)	34(1)	62(1)	4(1)	28(1)	9(1)
O(11)	62(1)	60(1)	63(1)	-35(1)	27(1)	-9(1)
O(12)	32(1)	65(1)	44(1)	-6(1)	8(1)	-7(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **8**.

	X	Y	Z	U(eq)
H(1)	8443	1987	720	38
H(2)	10159	278	3487	40
H(3)	11880	2773	2394	37
H(6)	9489	4376	3215	38
H(7A)	8896	1167	4905	79
H(7B)	8355	2623	4779	79
H(8A)	10015	3613	5364	90
H(8B)	10482	2190	5848	90
H(9A)	10415	1175	-528	73
H(9B)	11561	1806	268	73
H(10A)	10718	3724	-322	82
H(10B)	9492	3073	-727	82

Table S13. Torsion angles [°] for **8**.

N(2)-C(2)-C(4)-O(2)	-60.4(2)	C(4)-C(6)-N(3)-C(1)	-61.3(2)
N(1)-C(2)-C(4)-O(2)	-177.95(17)	N(1)-C(1)-N(3)-N(7)	-163.98(17)
N(2)-C(2)-C(4)-O(1)	179.25(17)	C(5)-C(1)-N(3)-N(7)	80.3(2)
N(1)-C(2)-C(4)-O(1)	61.7(2)	N(1)-C(1)-N(3)-C(6)	58.4(2)
N(2)-C(2)-C(4)-C(6)	59.7(2)	C(5)-C(1)-N(3)-C(6)	-57.3(2)
N(1)-C(2)-C(4)-C(6)	-57.9(2)	N(2)-C(3)-N(4)-N(8)	81.5(2)

N(1)-C(1)-C(5)-O(4)	-179.28(17)	C(5)-C(3)-N(4)-N(8)	-161.64(18)
N(3)-C(1)-C(5)-O(4)	-62.1(2)	N(2)-C(3)-N(4)-C(6)	-55.1(2)
N(1)-C(1)-C(5)-O(3)	60.5(2)	C(5)-C(3)-N(4)-C(6)	61.8(2)
N(3)-C(1)-C(5)-O(3)	177.63(17)	N(3)-C(6)-N(4)-N(8)	163.51(18)
N(1)-C(1)-C(5)-C(3)	-59.7(2)	C(4)-C(6)-N(4)-N(8)	-79.9(2)
N(3)-C(1)-C(5)-C(3)	57.5(2)	N(3)-C(6)-N(4)-C(3)	-59.7(2)
N(4)-C(3)-C(5)-O(4)	60.2(2)	C(4)-C(6)-N(4)-C(3)	56.8(2)
N(2)-C(3)-C(5)-O(4)	177.19(17)	C(1)-N(1)-N(5)-O(5)	12.1(3)
N(4)-C(3)-C(5)-O(3)	-179.40(17)	C(2)-N(1)-N(5)-O(5)	148.7(2)
N(2)-C(3)-C(5)-O(3)	-62.4(2)	C(1)-N(1)-N(5)-O(6)	-171.0(2)
N(4)-C(3)-C(5)-C(1)	-59.6(2)	C(2)-N(1)-N(5)-O(6)	-34.5(3)
N(2)-C(3)-C(5)-C(1)	57.4(2)	C(2)-N(2)-N(6)-O(7)	173.3(2)
O(2)-C(4)-C(6)-N(3)	179.60(17)	C(3)-N(2)-N(6)-O(7)	30.8(3)
O(1)-C(4)-C(6)-N(3)	-59.8(2)	C(2)-N(2)-N(6)-O(8)	-10.1(3)
C(2)-C(4)-C(6)-N(3)	59.8(2)	C(3)-N(2)-N(6)-O(8)	-152.5(2)
O(2)-C(4)-C(6)-N(4)	62.2(2)	C(6)-N(3)-N(7)-O(10)	-13.2(3)
O(1)-C(4)-C(6)-N(4)	-177.19(17)	C(1)-N(3)-N(7)-O(10)	-149.9(2)
C(2)-C(4)-C(6)-N(4)	-57.6(2)	C(6)-N(3)-N(7)-O(9)	169.7(2)
O(1)-C(7)-C(8)-O(2)	-20.6(4)	C(1)-N(3)-N(7)-O(9)	33.0(3)
O(3)-C(9)-C(10)-O(4)	22.4(4)	C(3)-N(4)-N(8)-O(11)	-178.2(2)
N(3)-C(1)-N(1)-N(5)	81.8(2)	C(6)-N(4)-N(8)-O(11)	-42.2(3)
C(5)-C(1)-N(1)-N(5)	-161.25(19)	C(3)-N(4)-N(8)-O(12)	5.2(3)
N(3)-C(1)-N(1)-C(2)	-55.3(2)	C(6)-N(4)-N(8)-O(12)	141.1(2)
C(5)-C(1)-N(1)-C(2)	61.6(2)	O(2)-C(4)-O(1)-C(7)	-2.3(3)
N(2)-C(2)-N(1)-N(5)	162.93(18)	C(6)-C(4)-O(1)-C(7)	-123.1(2)
C(4)-C(2)-N(1)-N(5)	-80.8(2)	C(2)-C(4)-O(1)-C(7)	118.1(2)
N(2)-C(2)-N(1)-C(1)	-59.1(2)	C(8)-C(7)-O(1)-C(4)	13.9(4)
C(4)-C(2)-N(1)-C(1)	57.1(2)	O(1)-C(4)-O(2)-C(8)	-11.1(3)
N(1)-C(2)-N(2)-N(6)	-87.7(2)	C(6)-C(4)-O(2)-C(8)	109.5(3)
C(4)-C(2)-N(2)-N(6)	154.81(19)	C(2)-C(4)-O(2)-C(8)	-131.4(2)
N(1)-C(2)-N(2)-C(3)	55.8(2)	C(7)-C(8)-O(2)-C(4)	19.3(4)
C(4)-C(2)-N(2)-C(3)	-61.7(2)	O(4)-C(5)-O(3)-C(9)	8.5(3)
N(4)-C(3)-N(2)-N(6)	-157.30(18)	C(1)-C(5)-O(3)-C(9)	128.8(2)
C(5)-C(3)-N(2)-N(6)	87.0(2)	C(3)-C(5)-O(3)-C(9)	-111.9(2)
N(4)-C(3)-N(2)-C(2)	58.8(2)	C(10)-C(9)-O(3)-C(5)	-18.8(3)
C(5)-C(3)-N(2)-C(2)	-56.9(2)	O(3)-C(5)-O(4)-C(10)	6.0(3)
N(4)-C(6)-N(3)-N(7)	-81.2(2)	C(1)-C(5)-O(4)-C(10)	-114.2(2)
C(4)-C(6)-N(3)-N(7)	161.16(18)	C(3)-C(5)-O(4)-C(10)	126.7(2)
N(4)-C(6)-N(3)-C(1)	56.3(2)	C(9)-C(10)-O(4)-C(5)	-17.7(3)

Symmetry transformations used to generate equivalent atoms:

5. NMR Spectra of Products

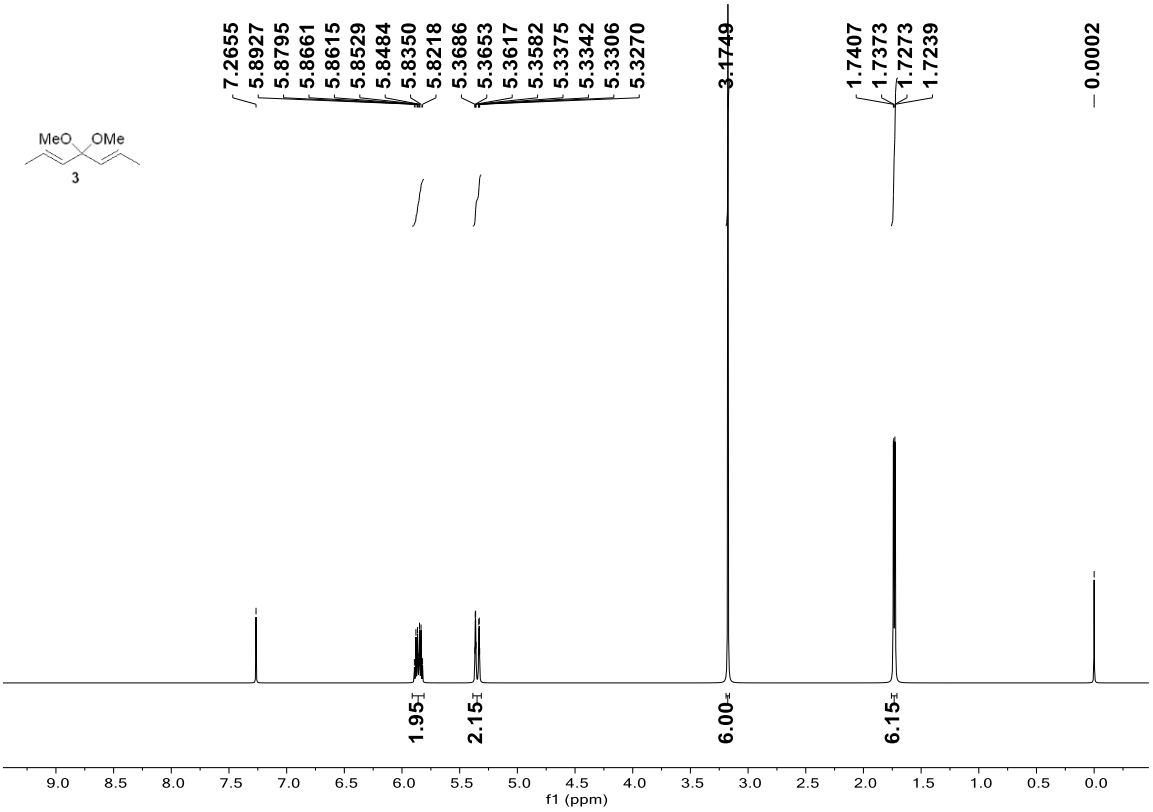


Figure S3. ^{1}H NMR spectrum of **3**.

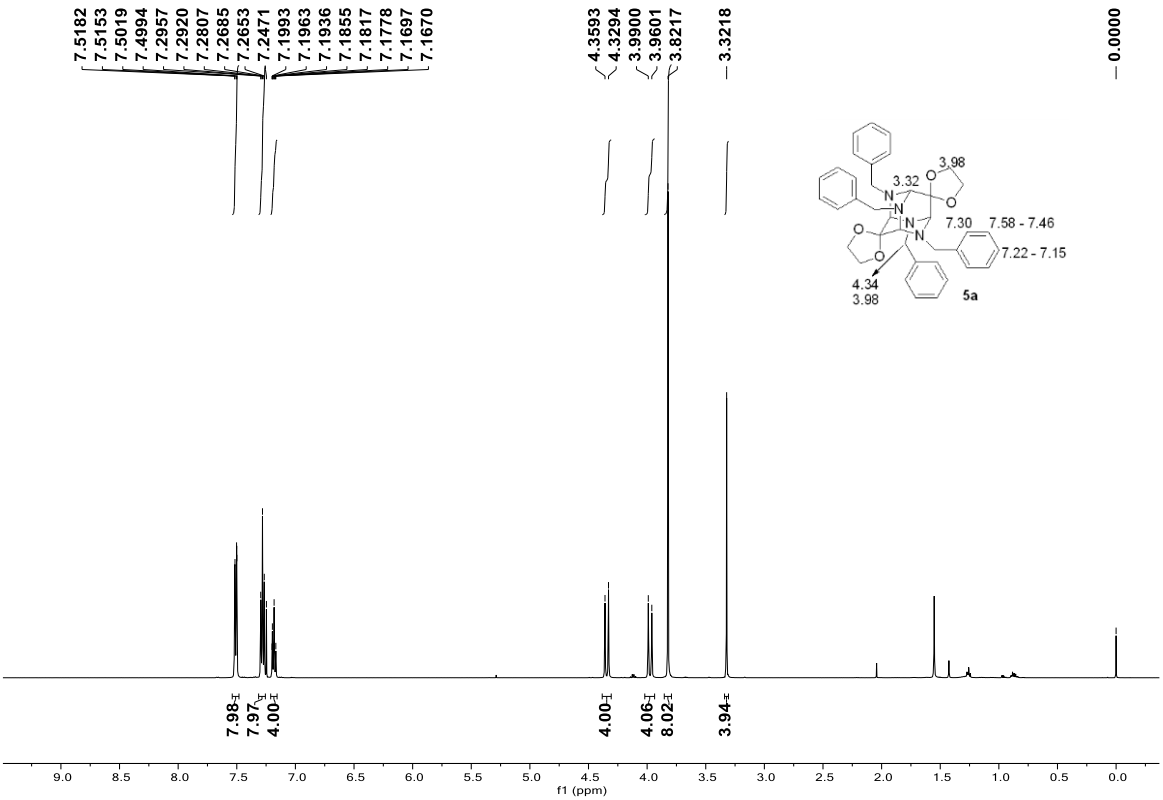


Figure S4. ^{1}H NMR spectrum of compound **5a**.

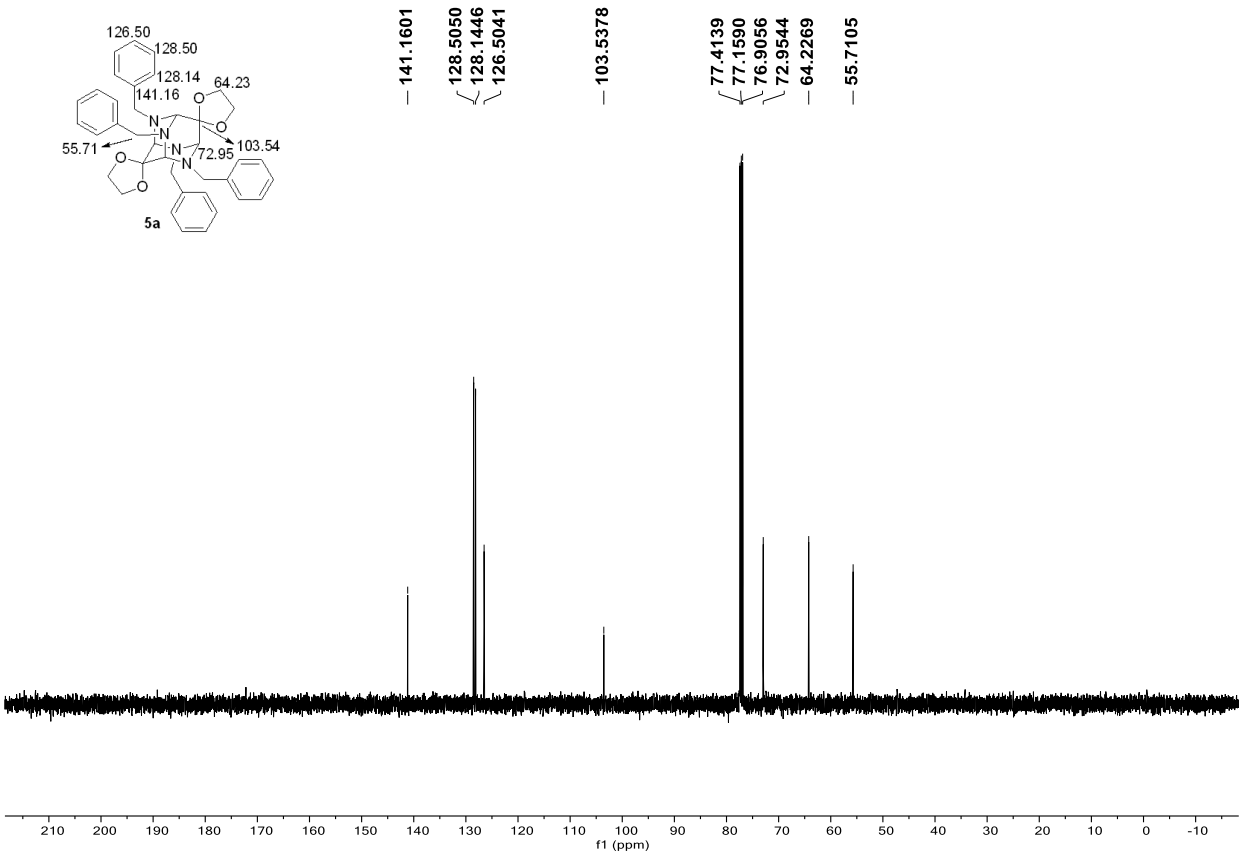


Figure S5. ^{13}C NMR spectrum of compound **5a**.

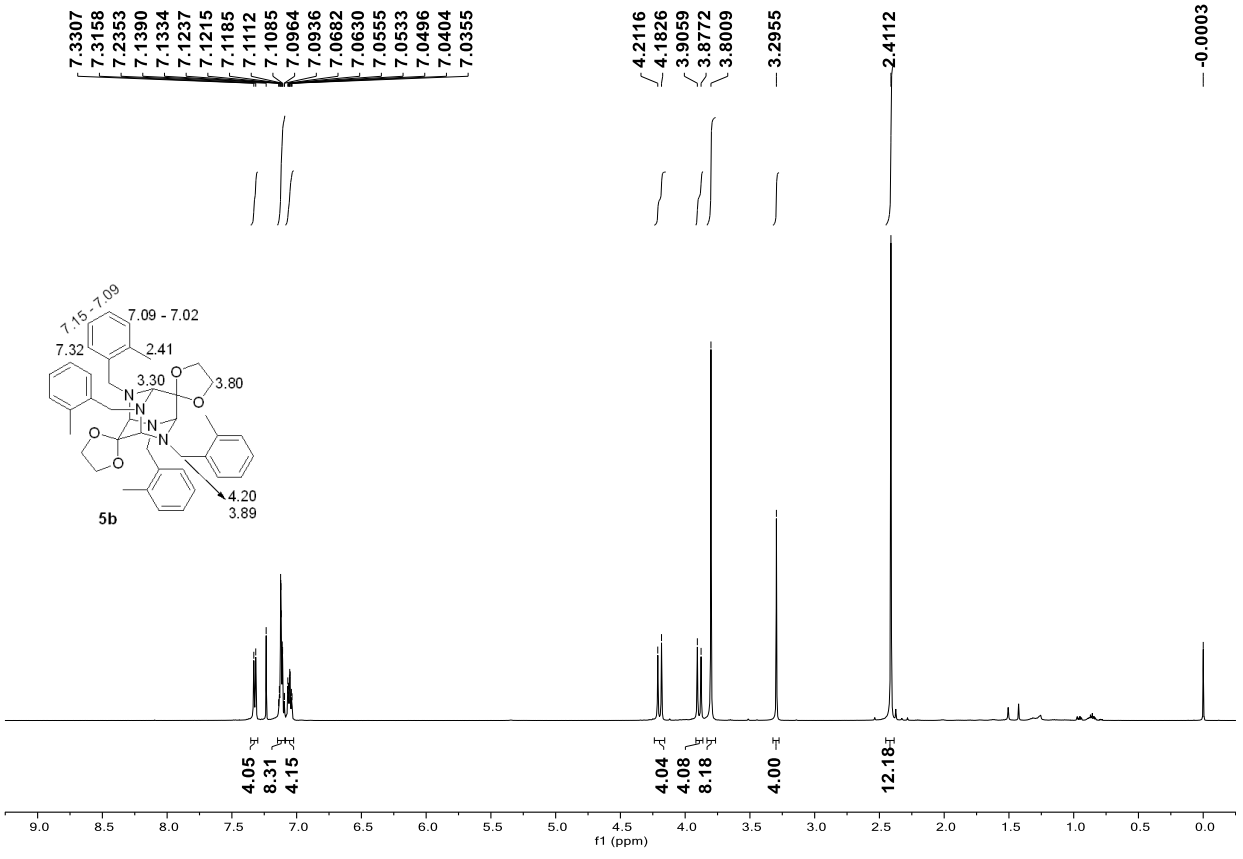


Figure S6. ^{1}H NMR spectrum of compound **5b**.

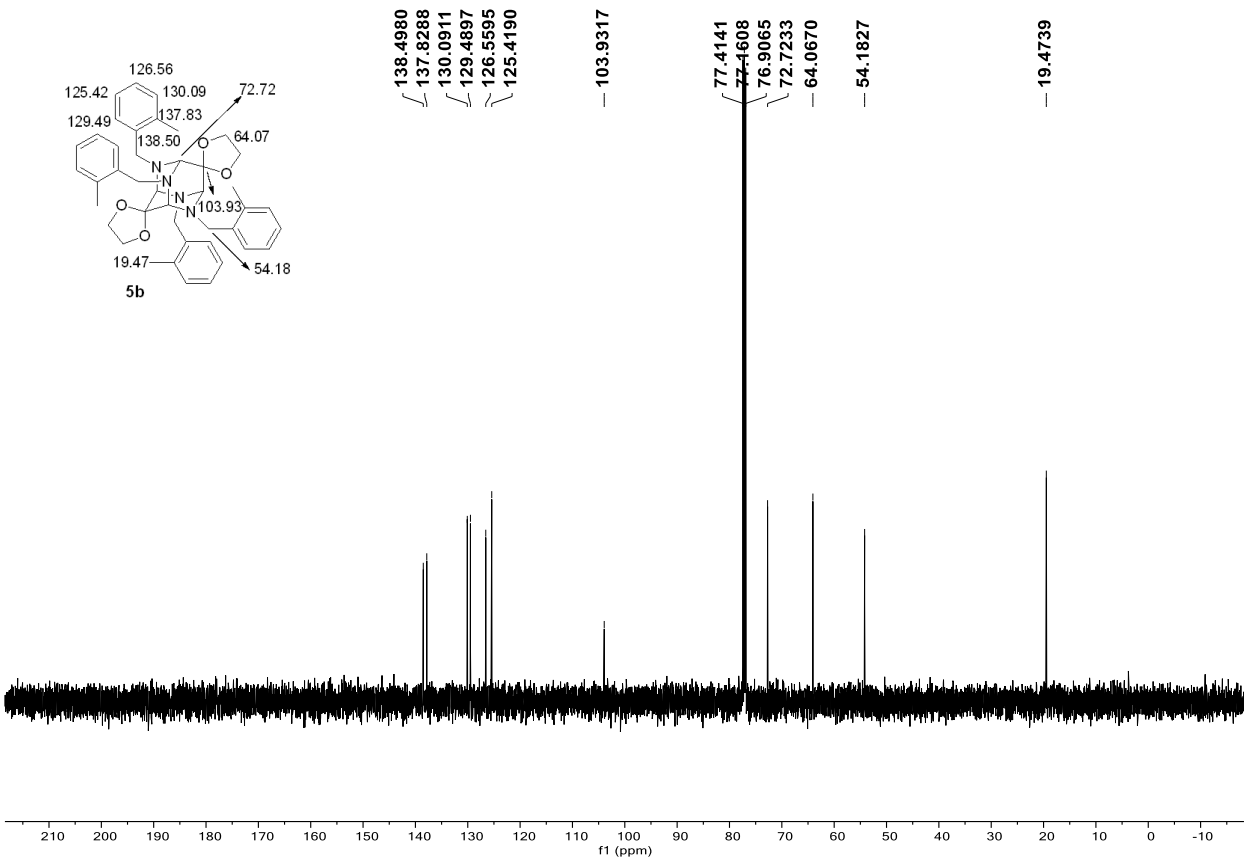


Figure S7. ^{13}C NMR spectrum of compound **5b**.

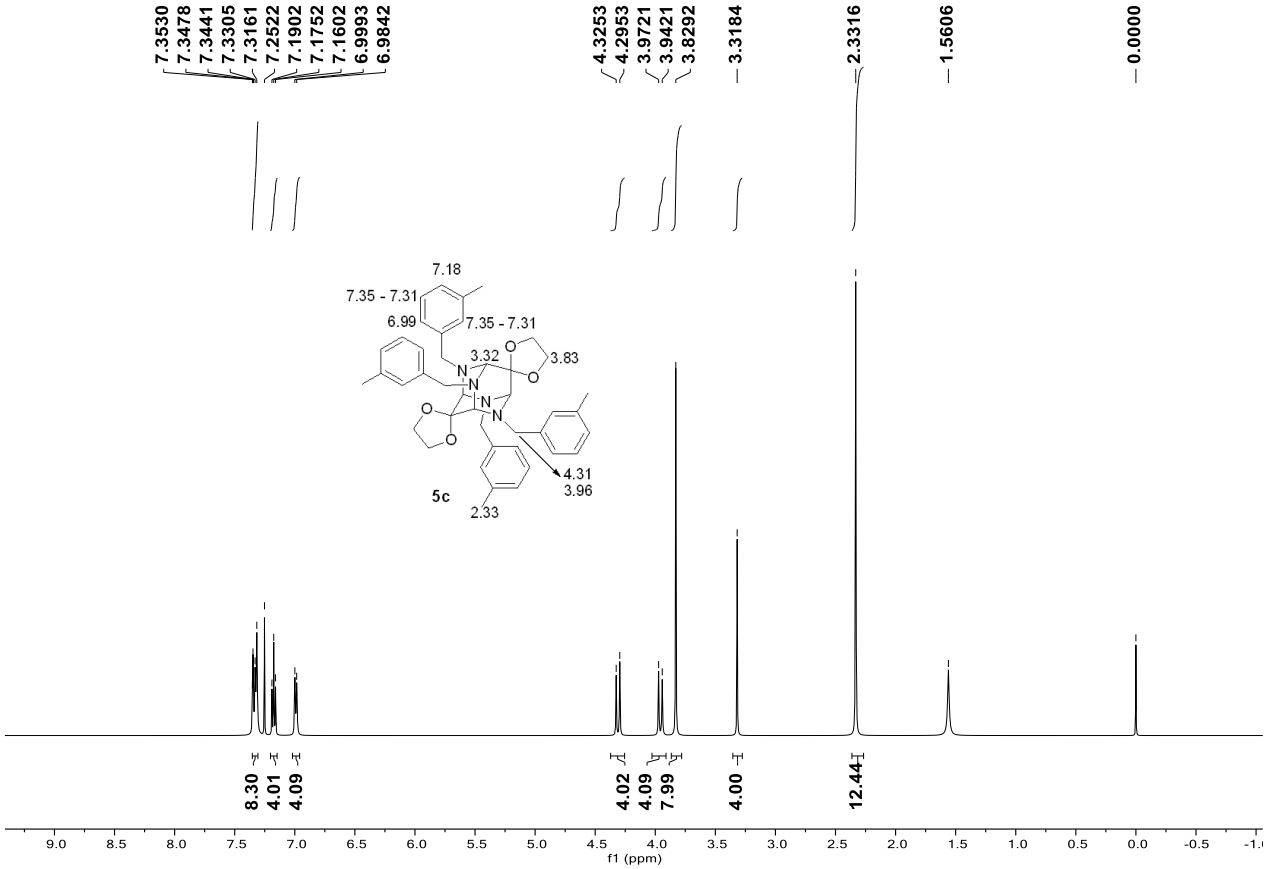


Figure S8. ^{1}H NMR spectrum of compound **5c**.

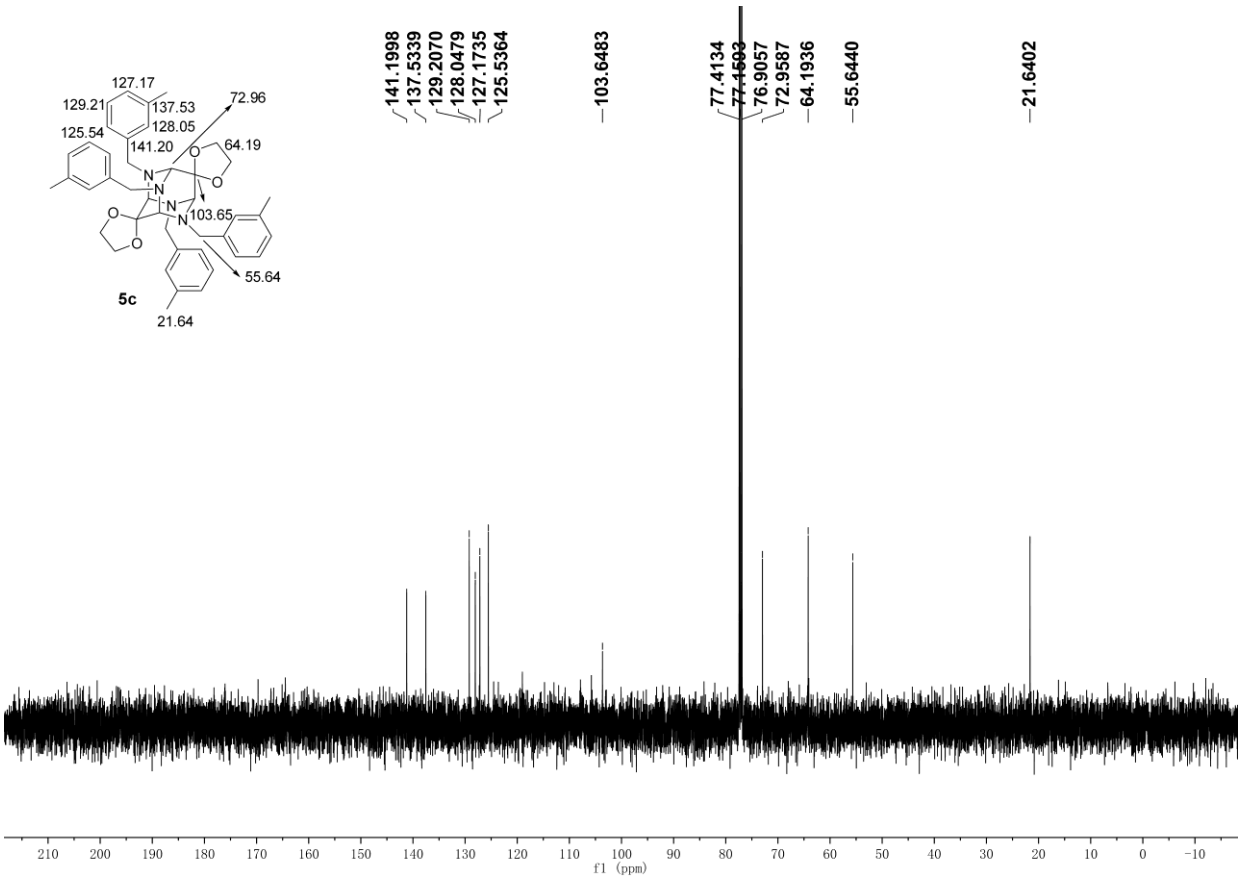


Figure S9. ^{13}C NMR spectrum of compound **5c**.

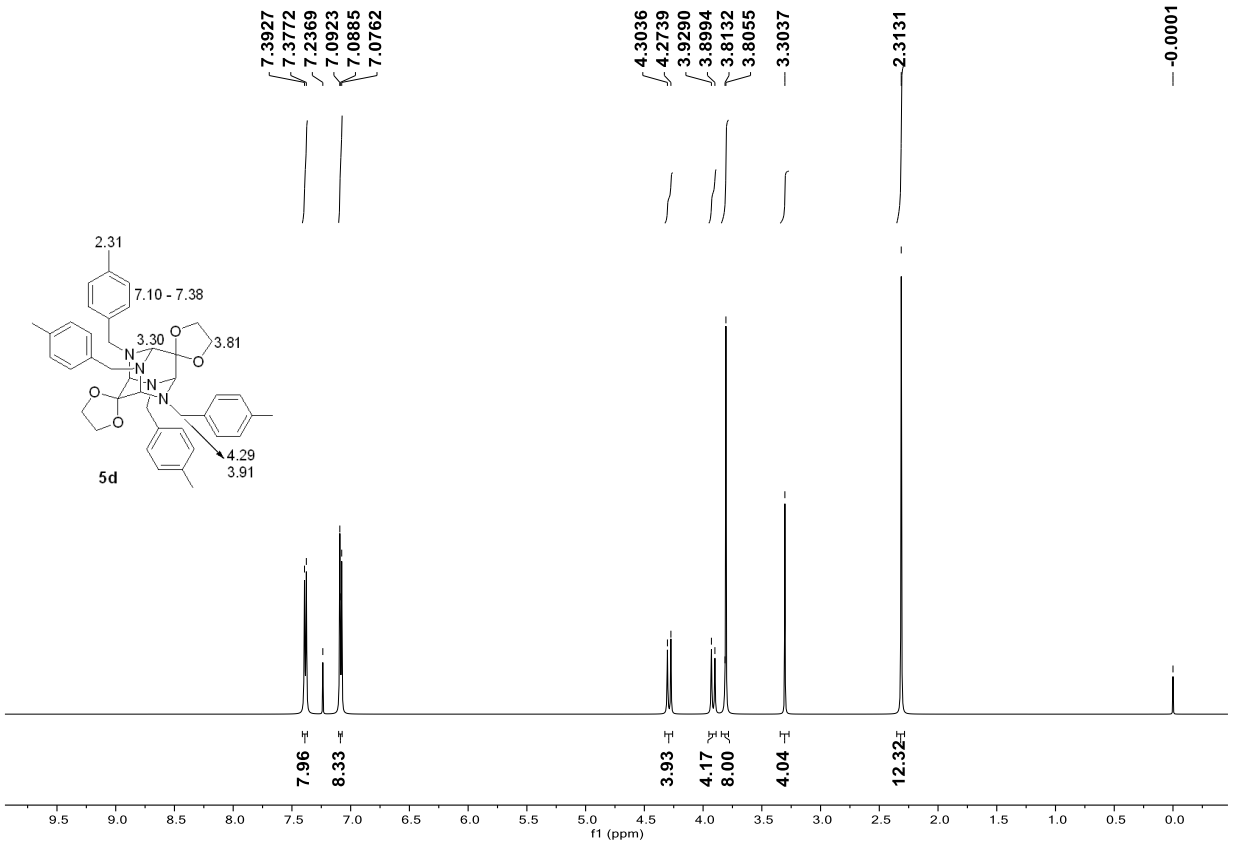


Figure S10. ^{1}H NMR spectrum of compound **5d**.

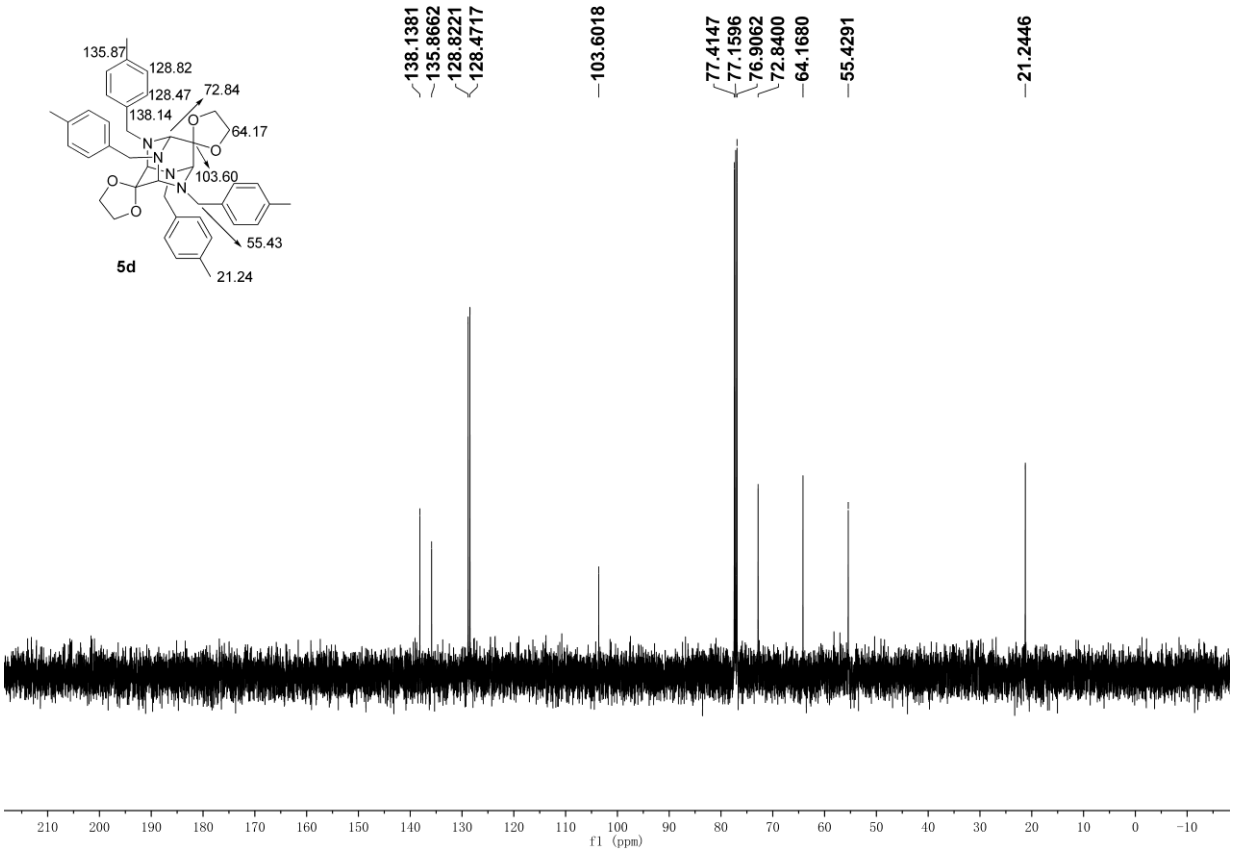


Figure S11. ^{13}C NMR spectrum of compound **5d**.

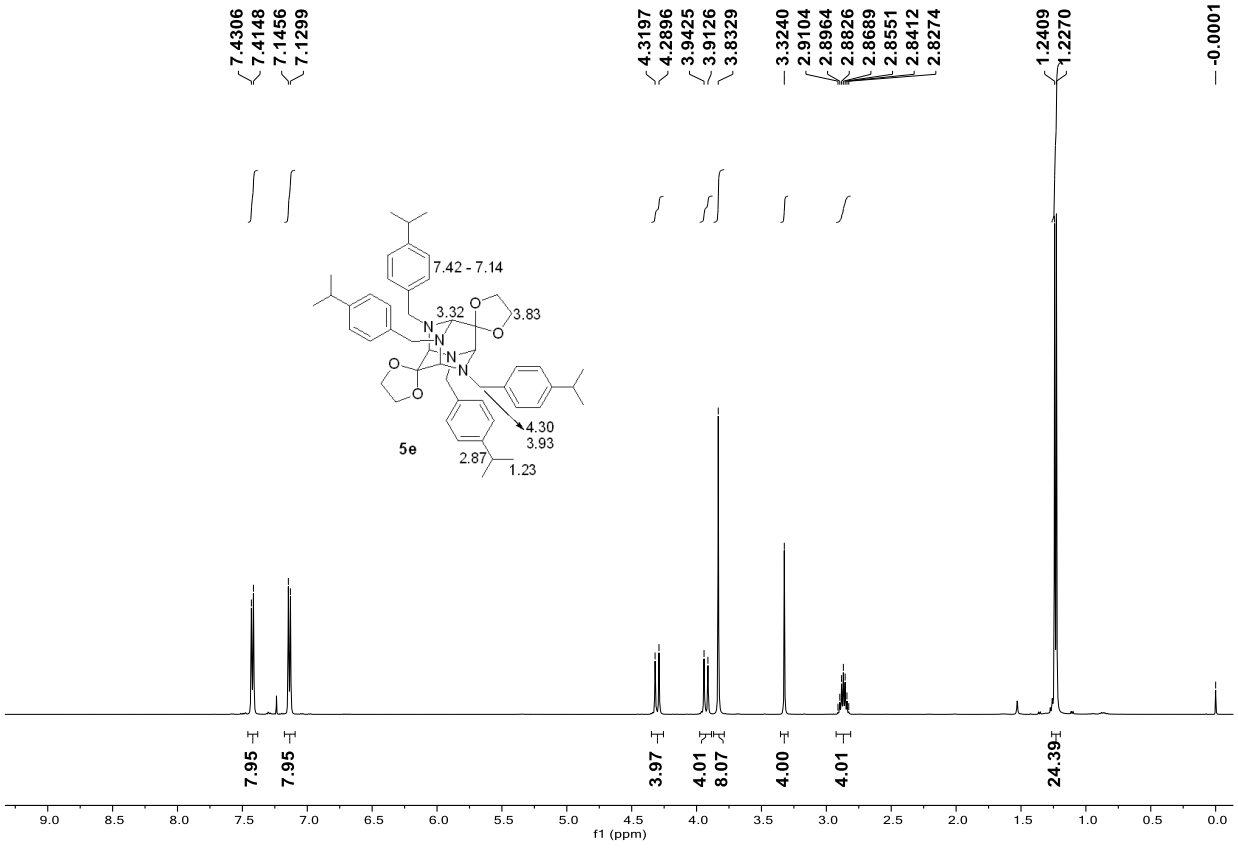


Figure S12. ^{1}H NMR spectrum of compound **5e**.

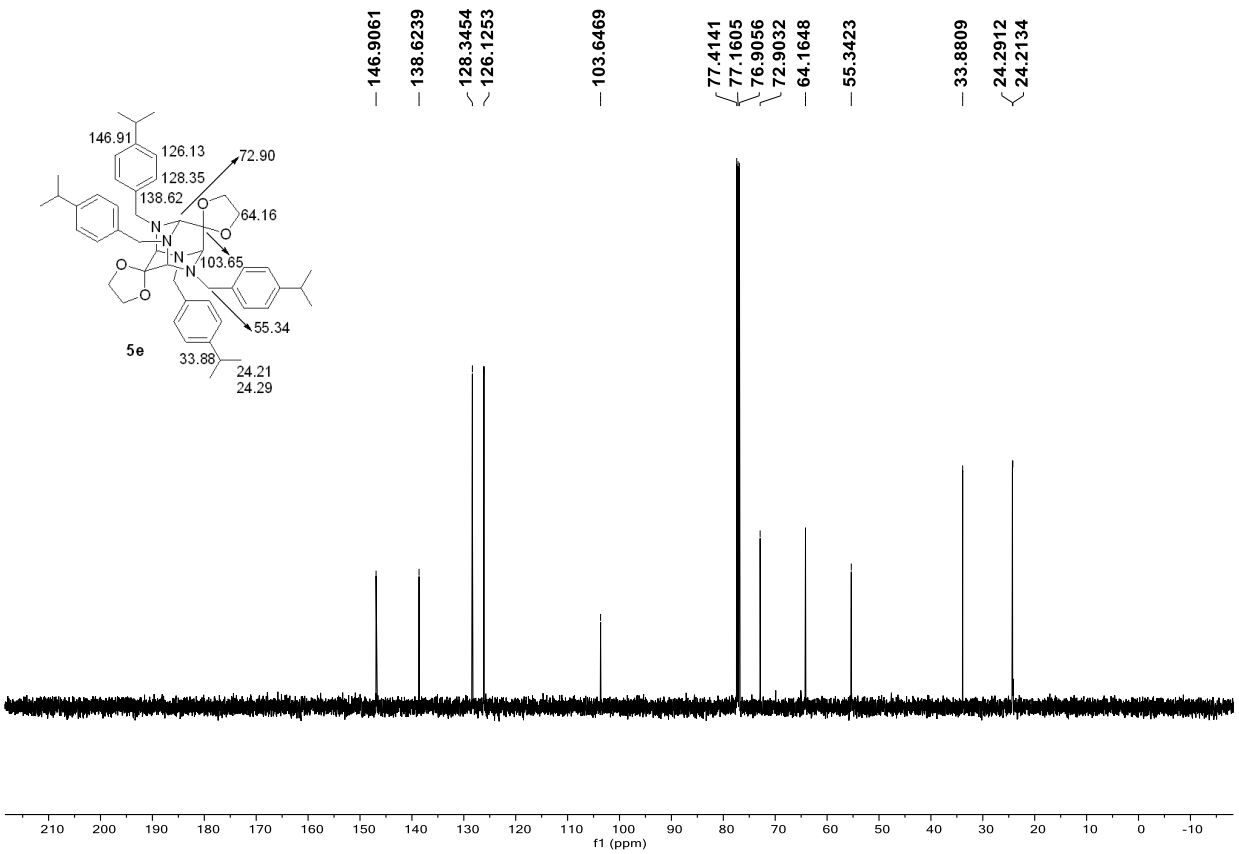


Figure S13. ^{13}C NMR spectrum of compound **5e**.

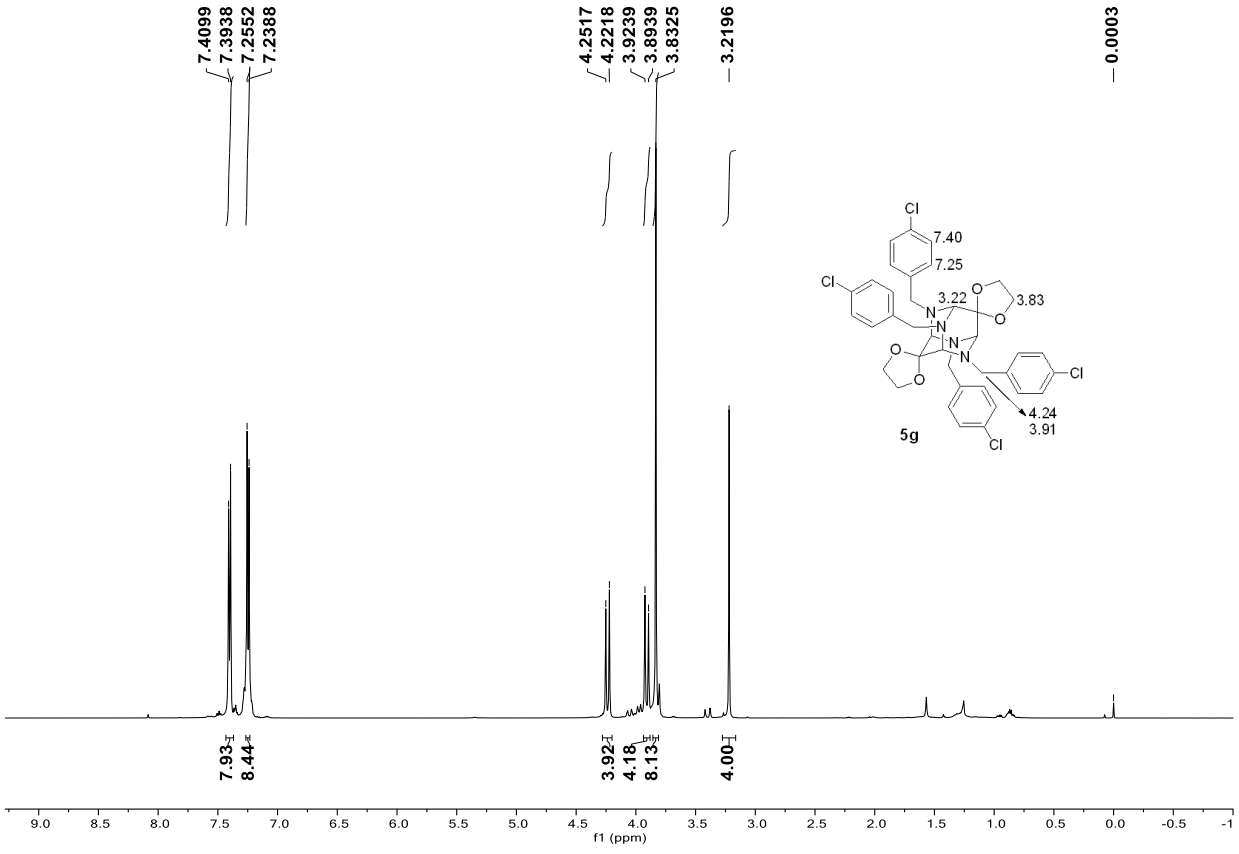


Figure S14. ^{1}H NMR spectrum of compound **5g**.

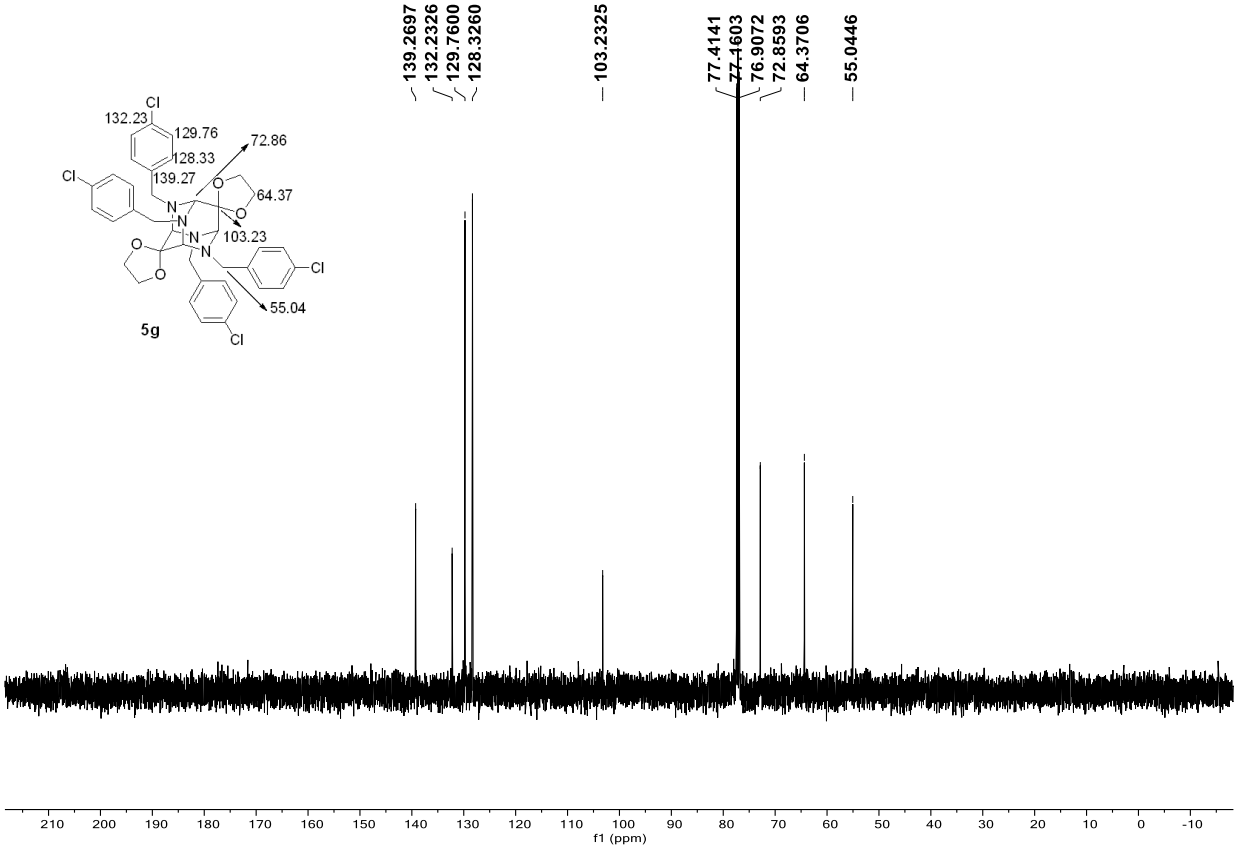


Figure S15. ^{13}C NMR spectrum of compound **5g**.

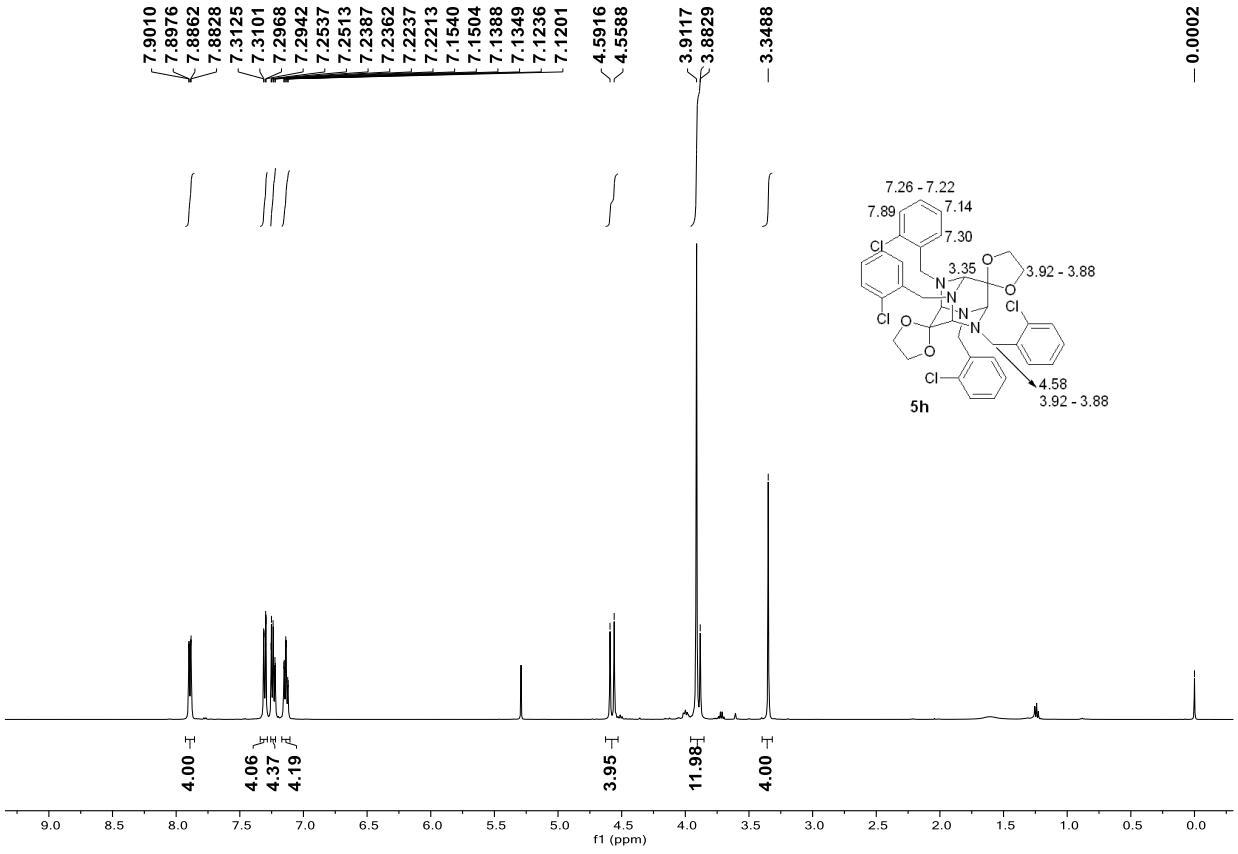


Figure S16. ^{1}H NMR spectrum of compound **5h**.

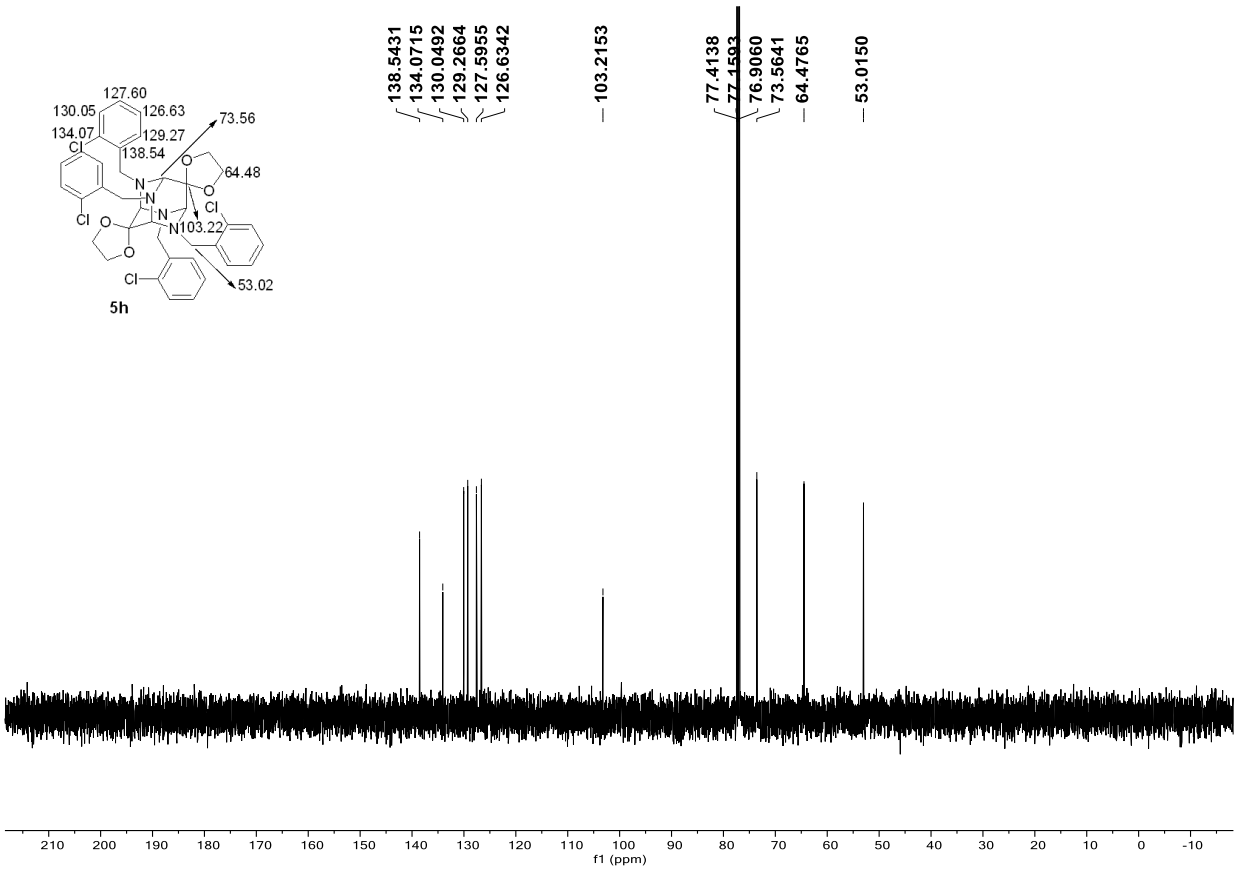


Figure S17. ^{13}C NMR spectrum of compound **5h**.

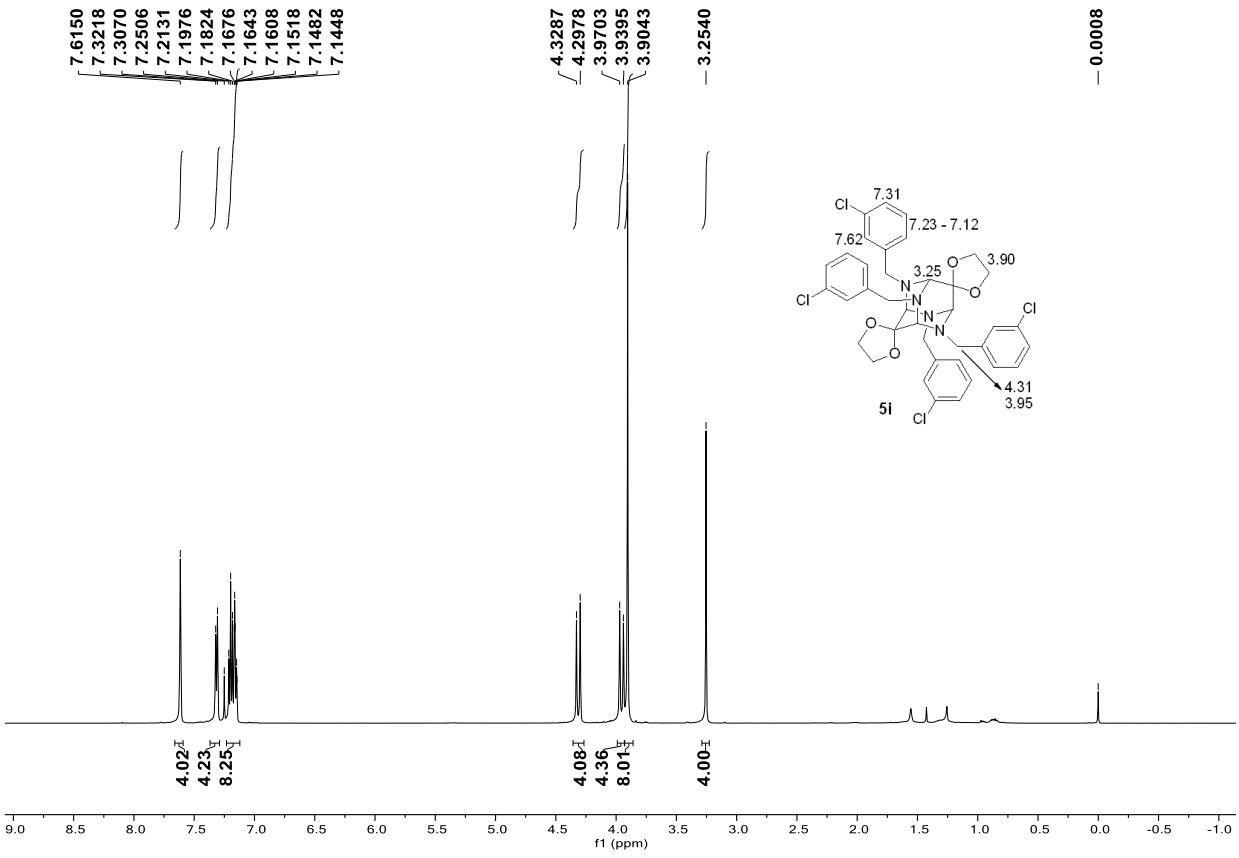


Figure S18. ^{1}H NMR spectrum of compound **5i**.

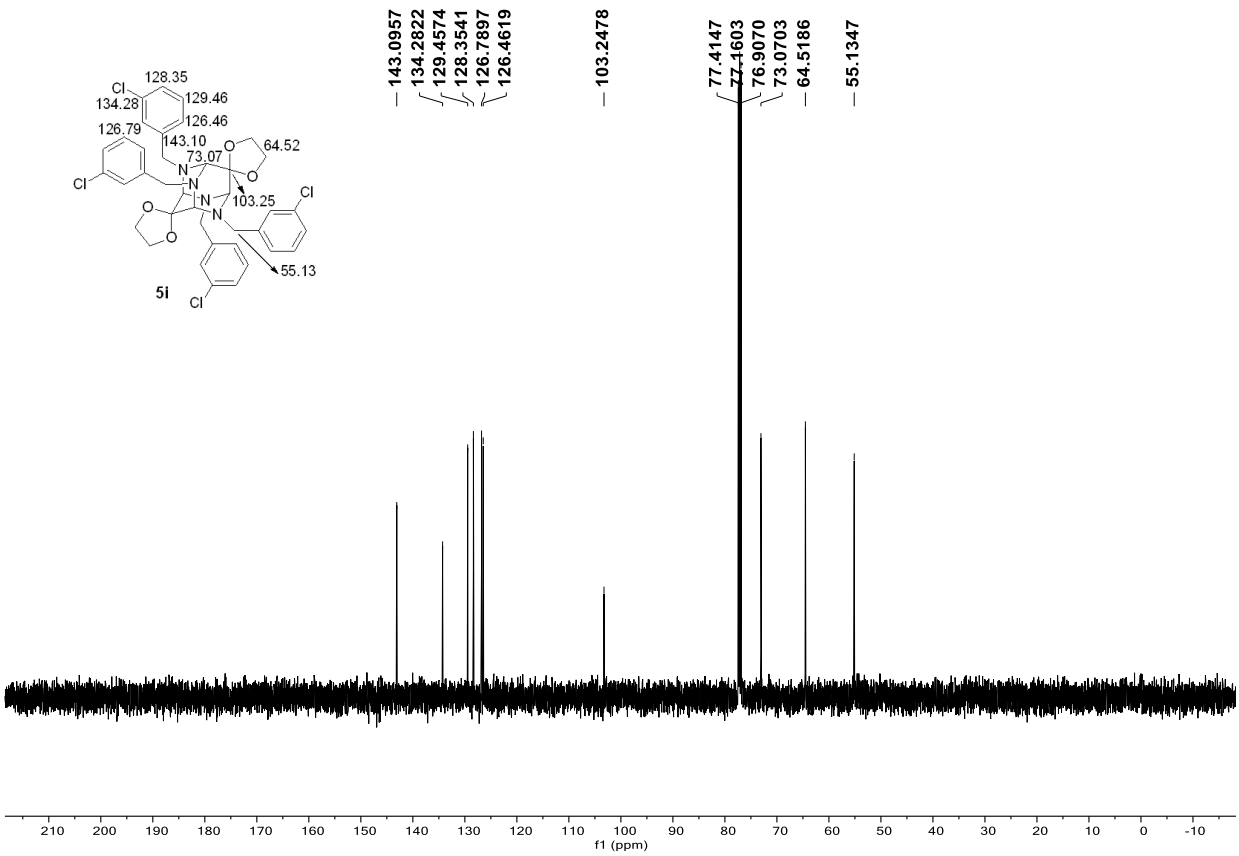


Figure S19. ^{13}C NMR spectrum of compound **5i**.

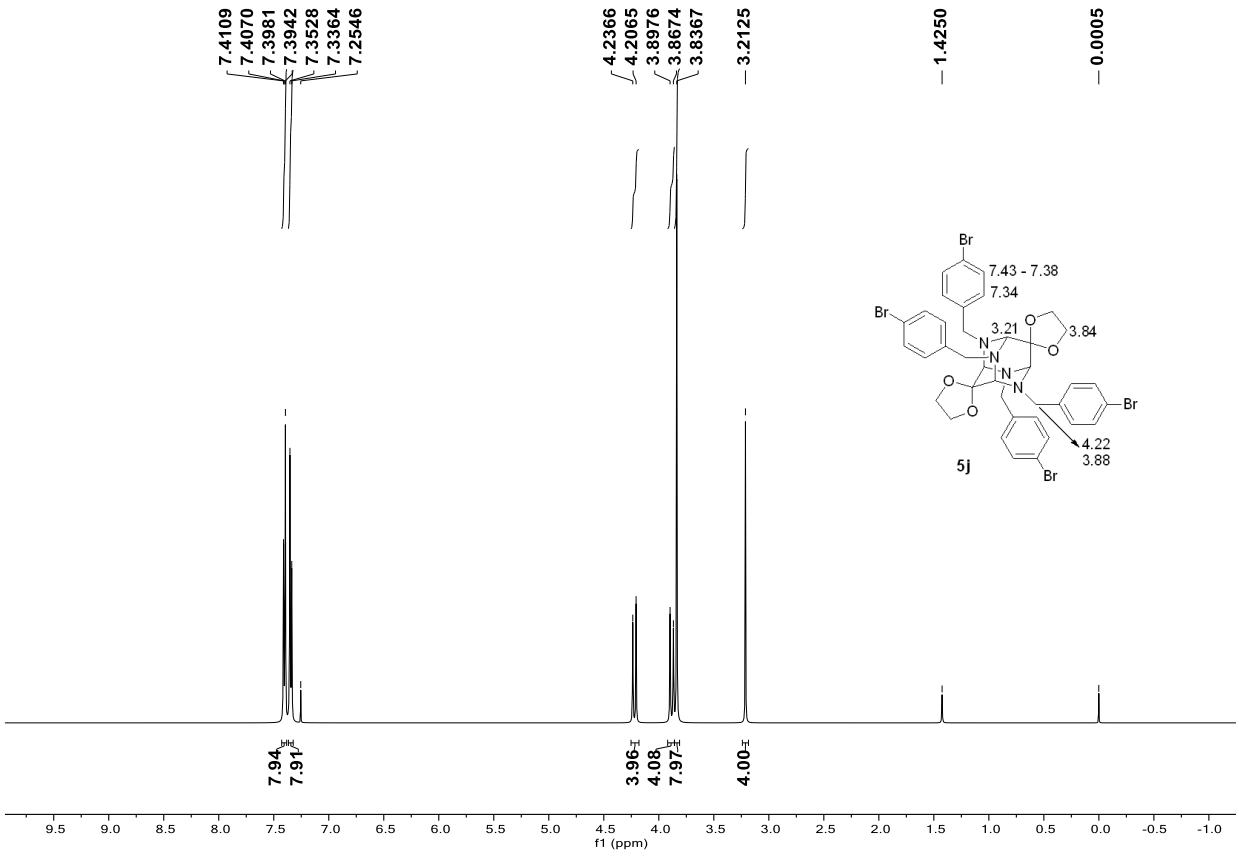


Figure S20. ^{1}H NMR spectrum of compound **5j**.

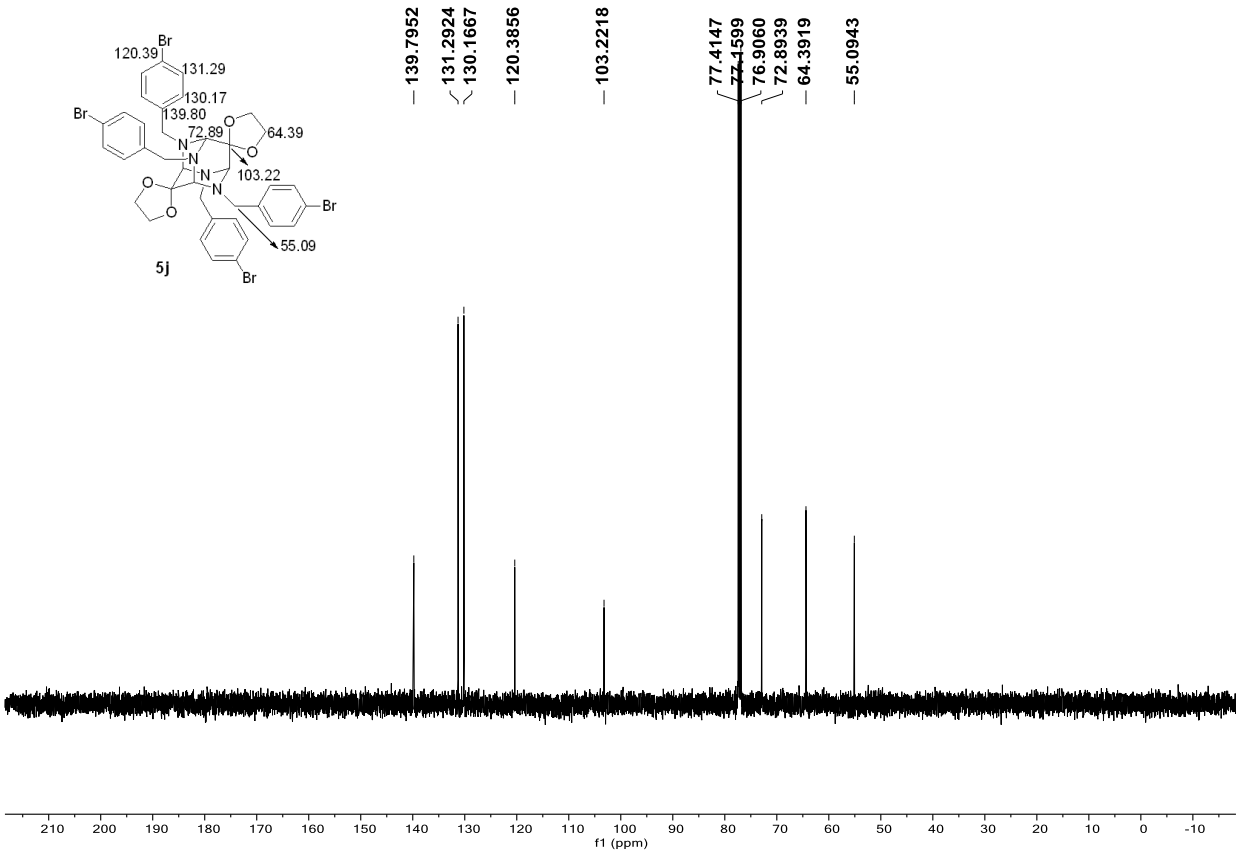


Figure S21. ^{13}C NMR spectrum of compound **5j**.

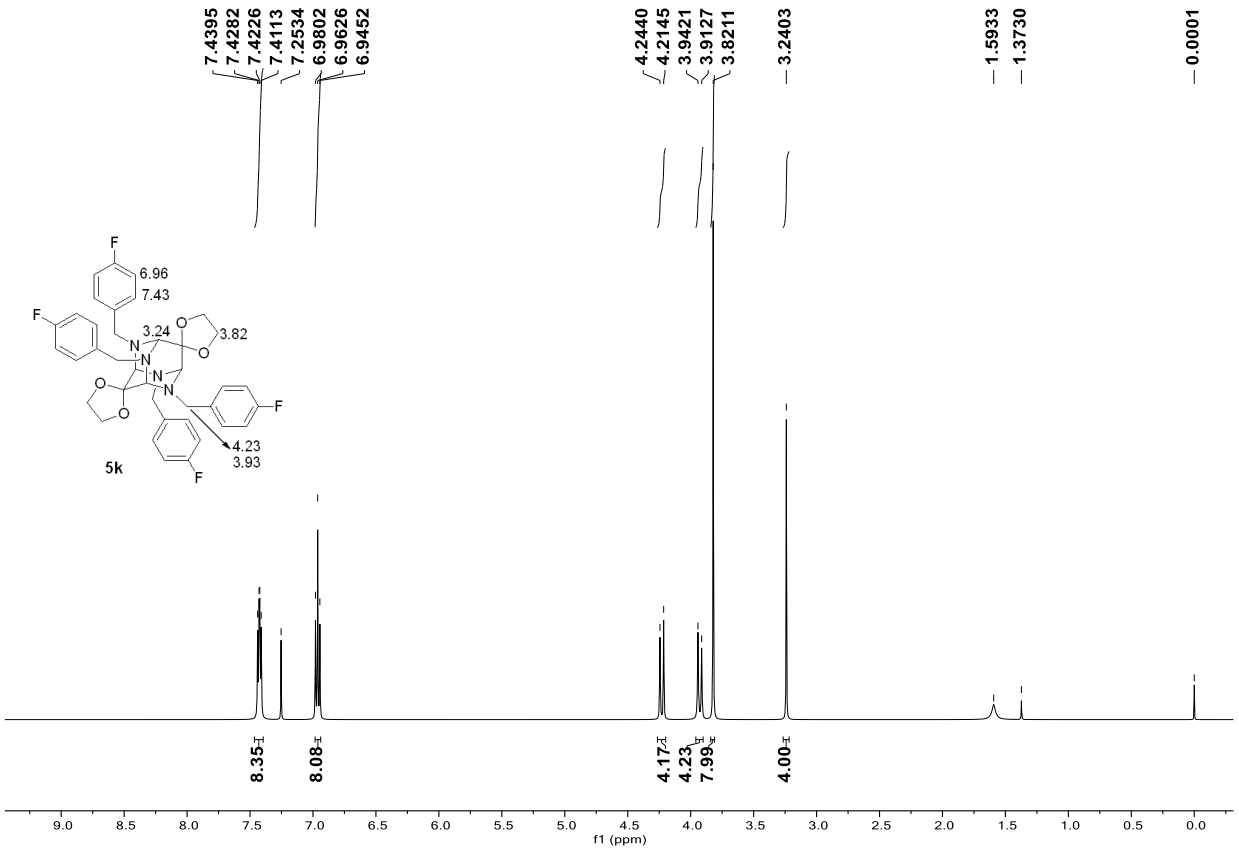


Figure S22. ^{1}H NMR spectrum of compound **5k**.

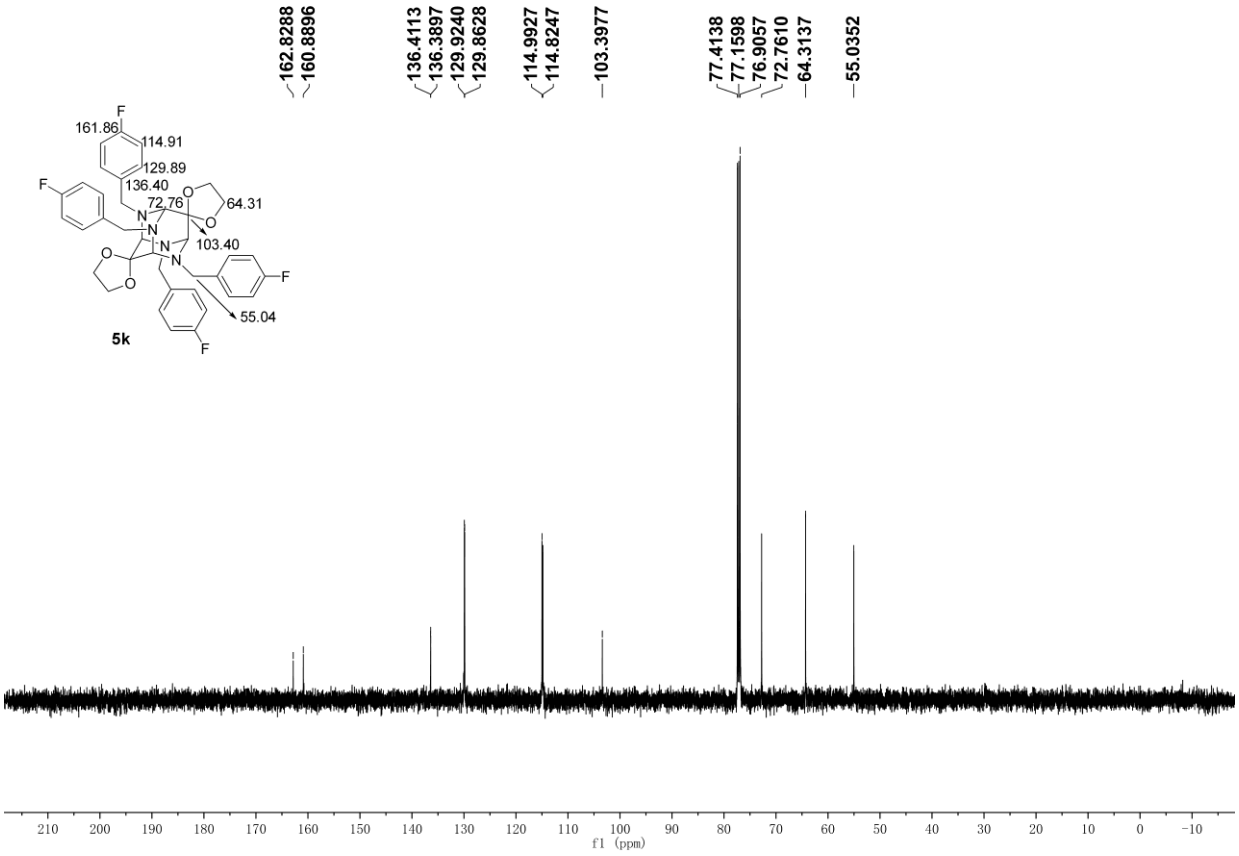


Figure S23. ^{13}C NMR spectrum of compound **5k**.

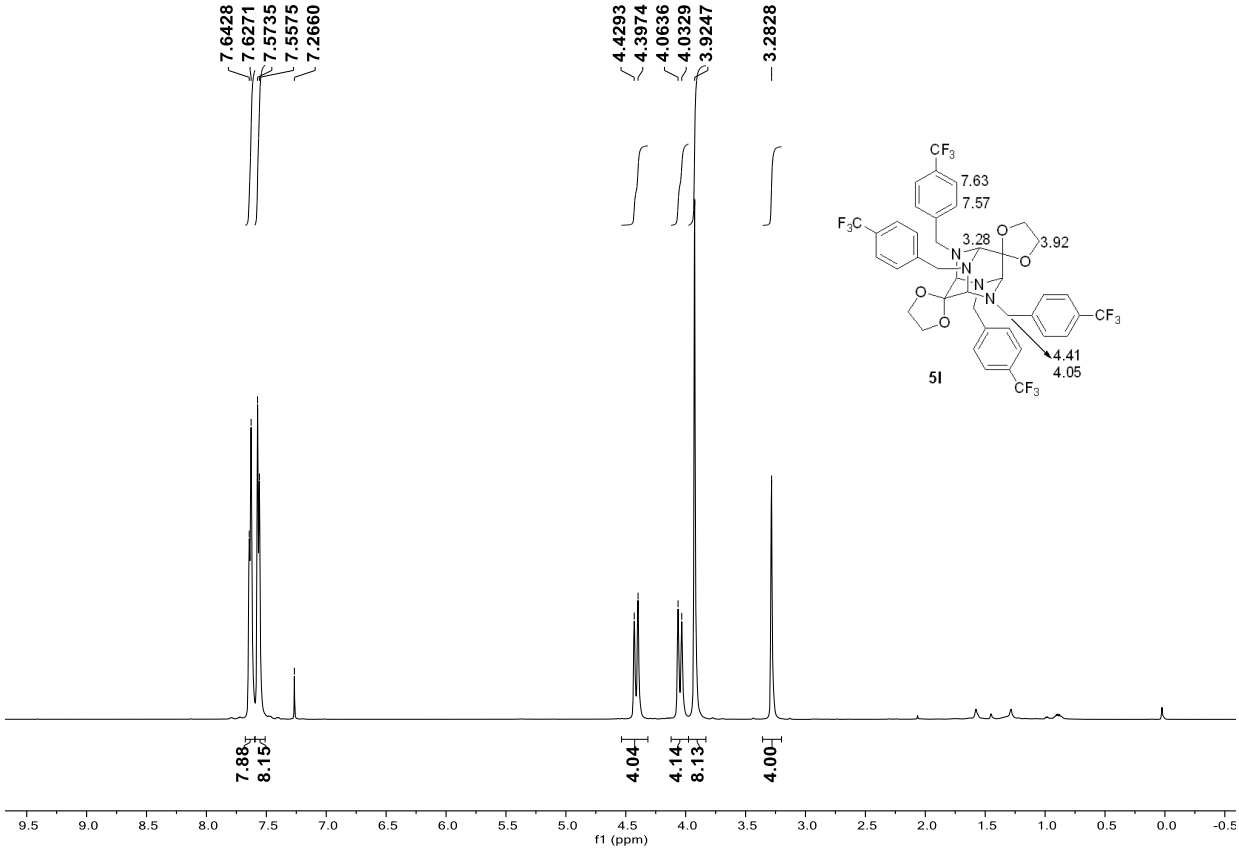


Figure S24. ^{1}H NMR spectrum of compound **5l**.

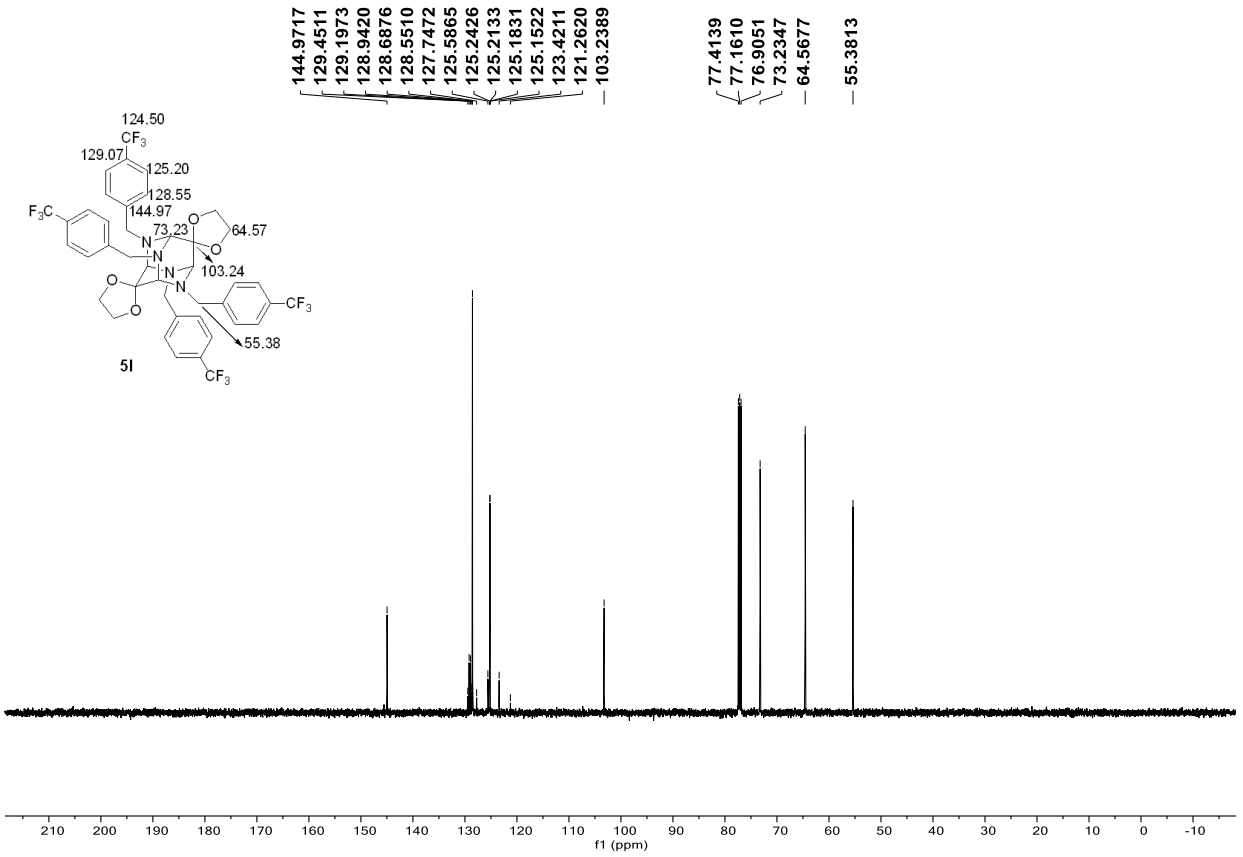


Figure S25. ^{13}C NMR spectrum of compound **5l**.

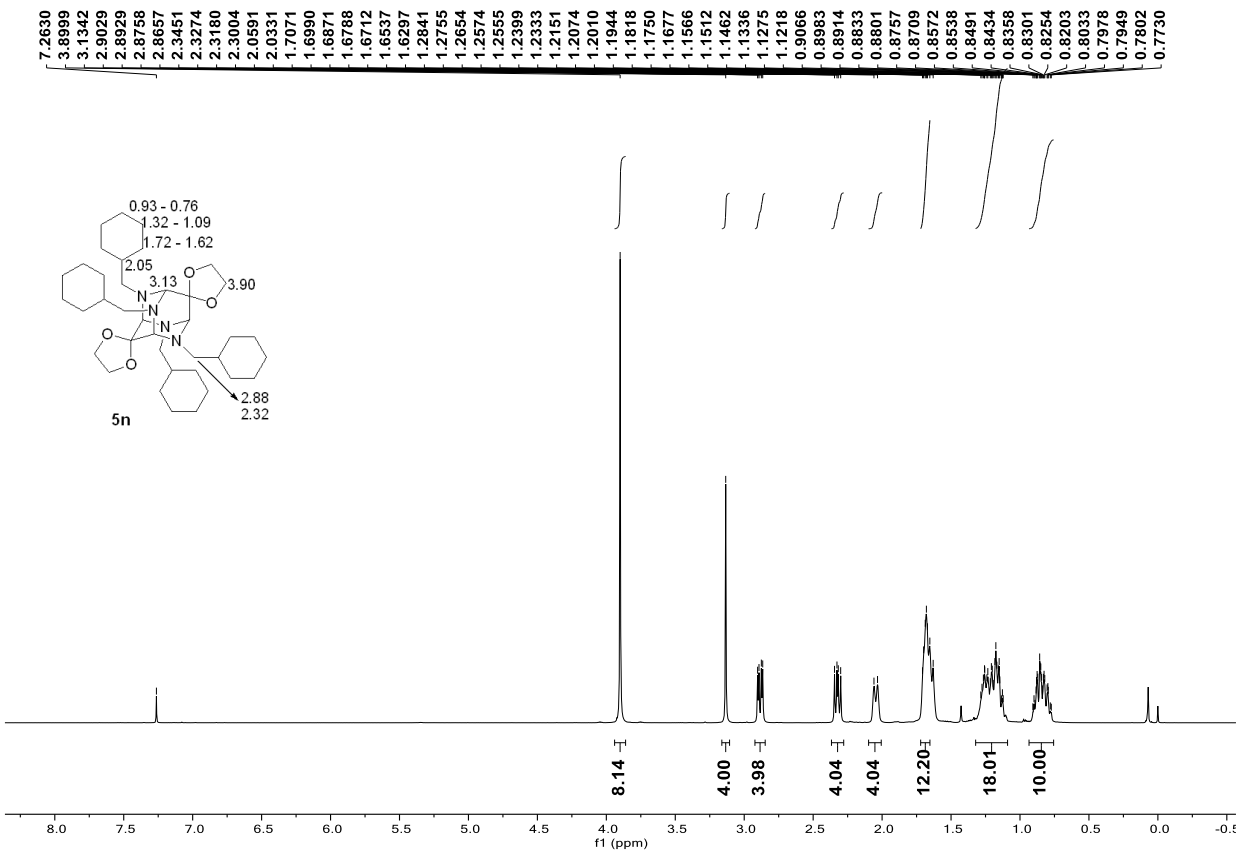


Figure S26. ^{1}H NMR spectrum of compound **5n**.

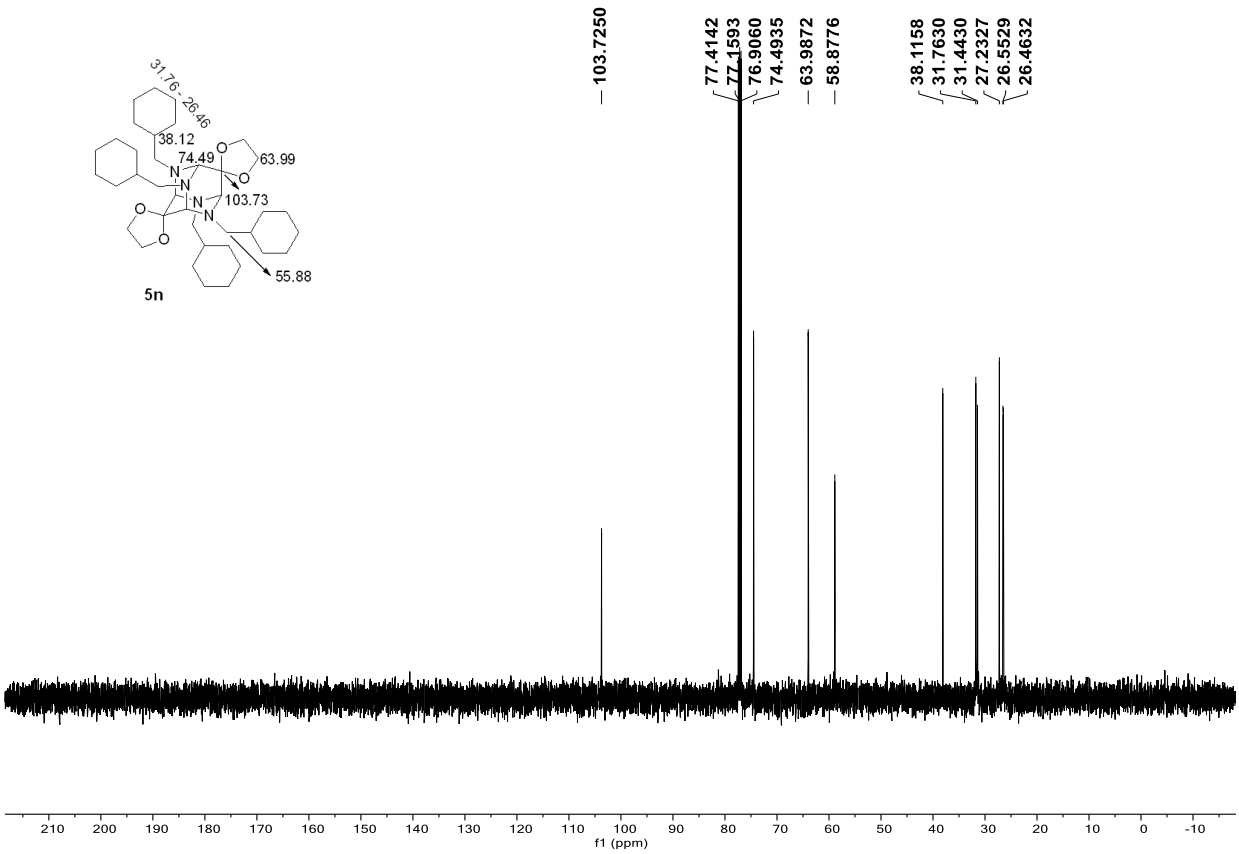


Figure S27. ^{13}C NMR spectrum of compound **5n**.

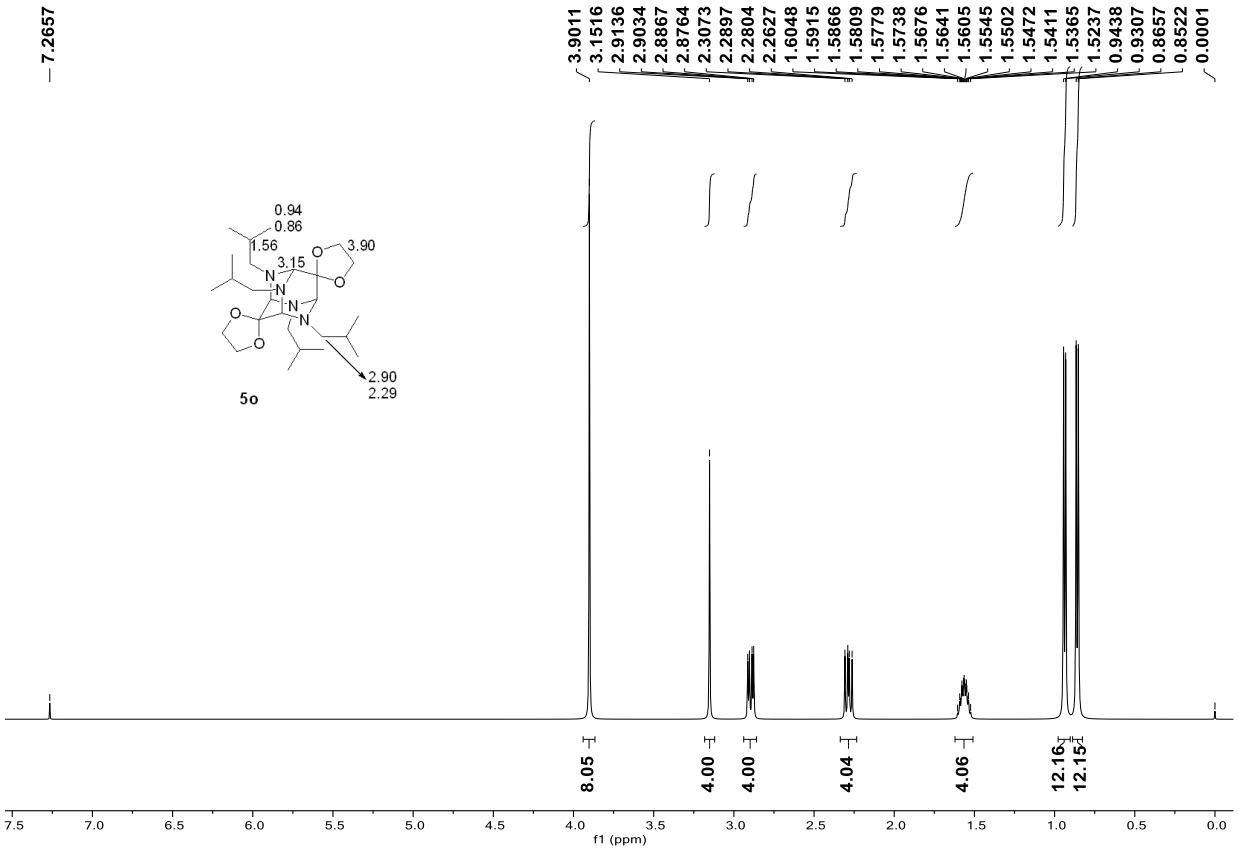


Figure S28. ^{1}H NMR spectrum of compound **5o**.

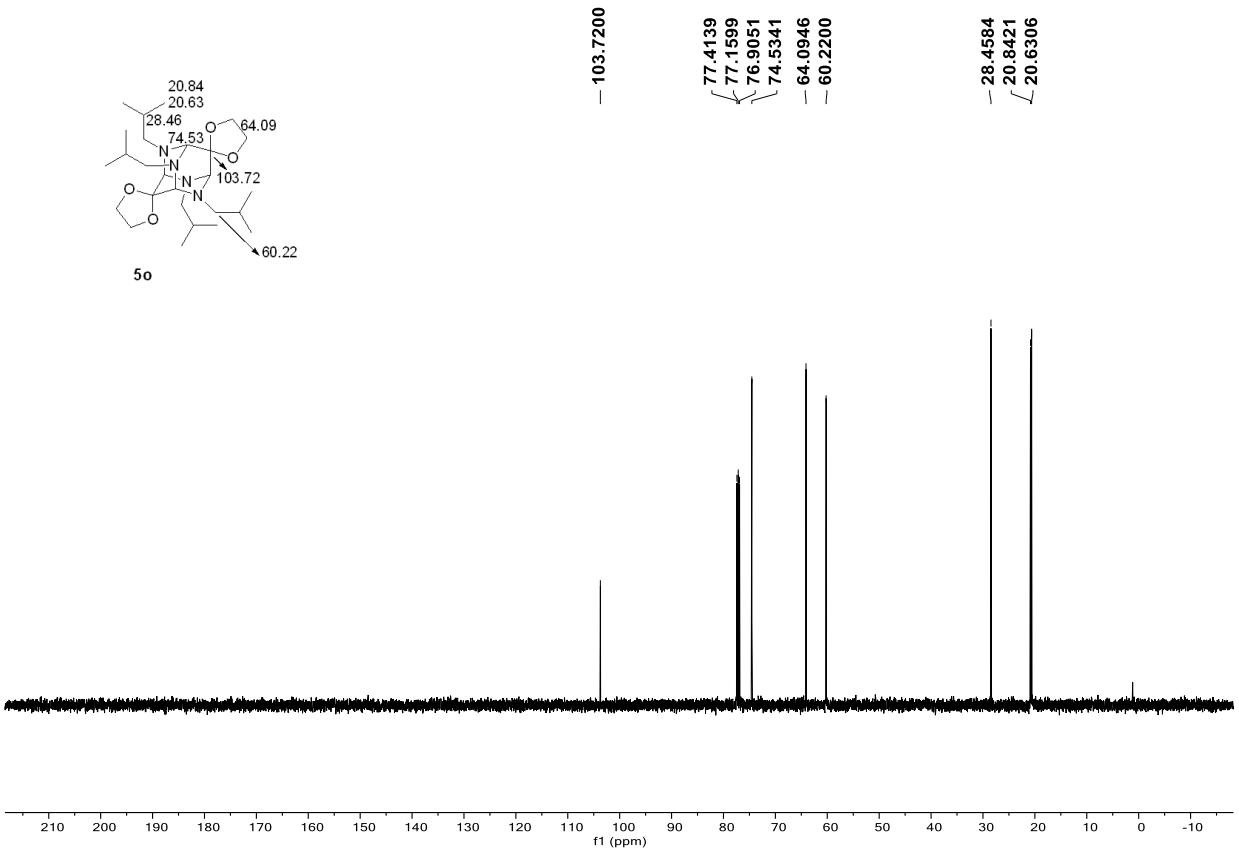


Figure S29. ^{13}C NMR spectrum of compound **5o**.

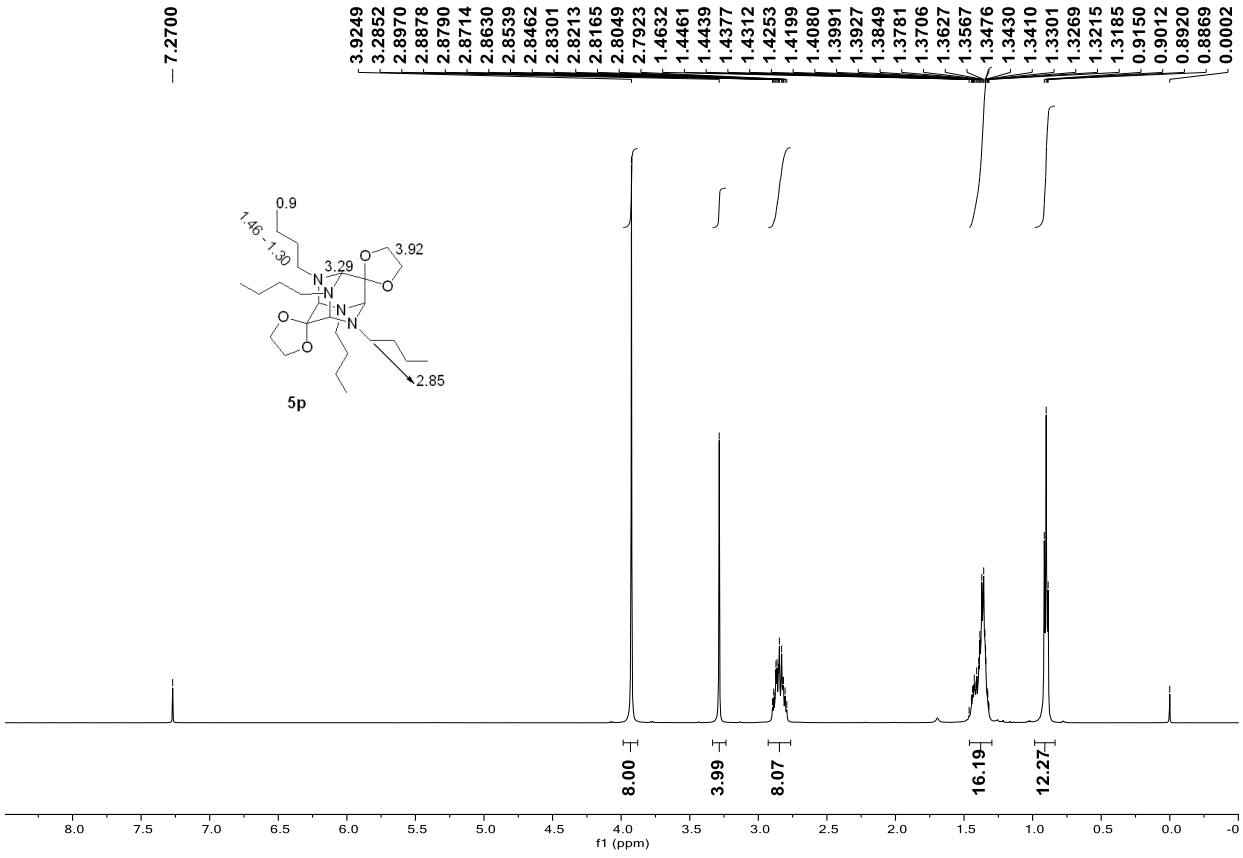


Figure S30. ^{1}H NMR spectrum of compound **5p**.

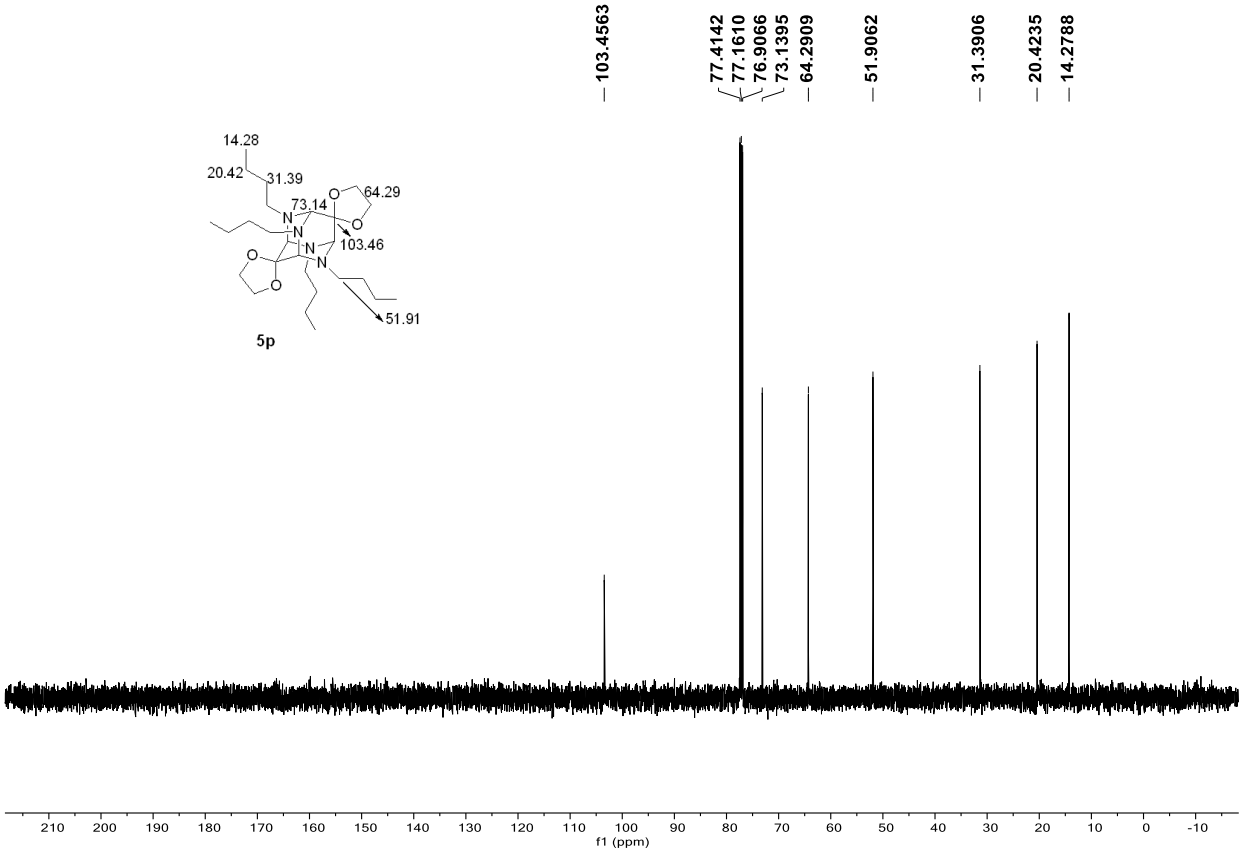


Figure S31. ^{13}C NMR spectrum of compound **5p**.

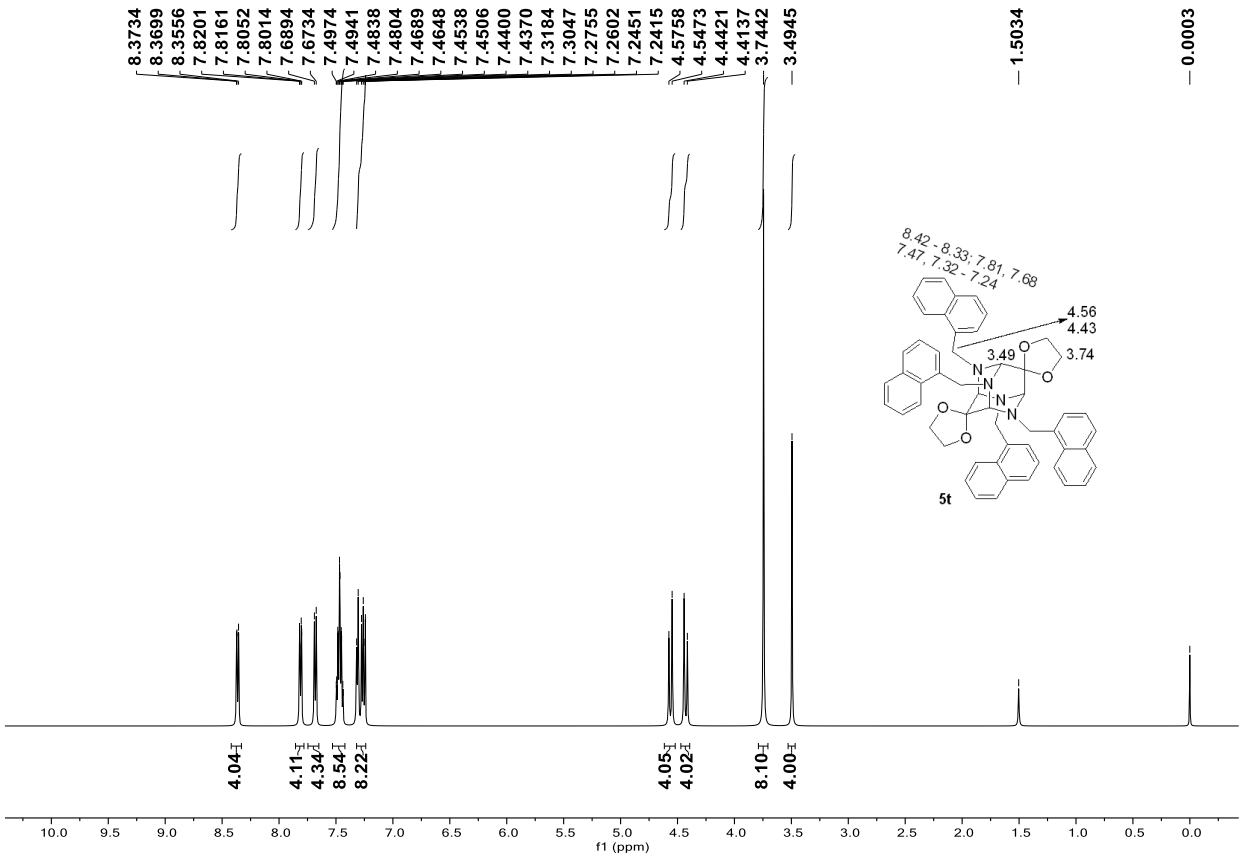


Figure S32. ^{1}H NMR spectrum of compound **5t**.

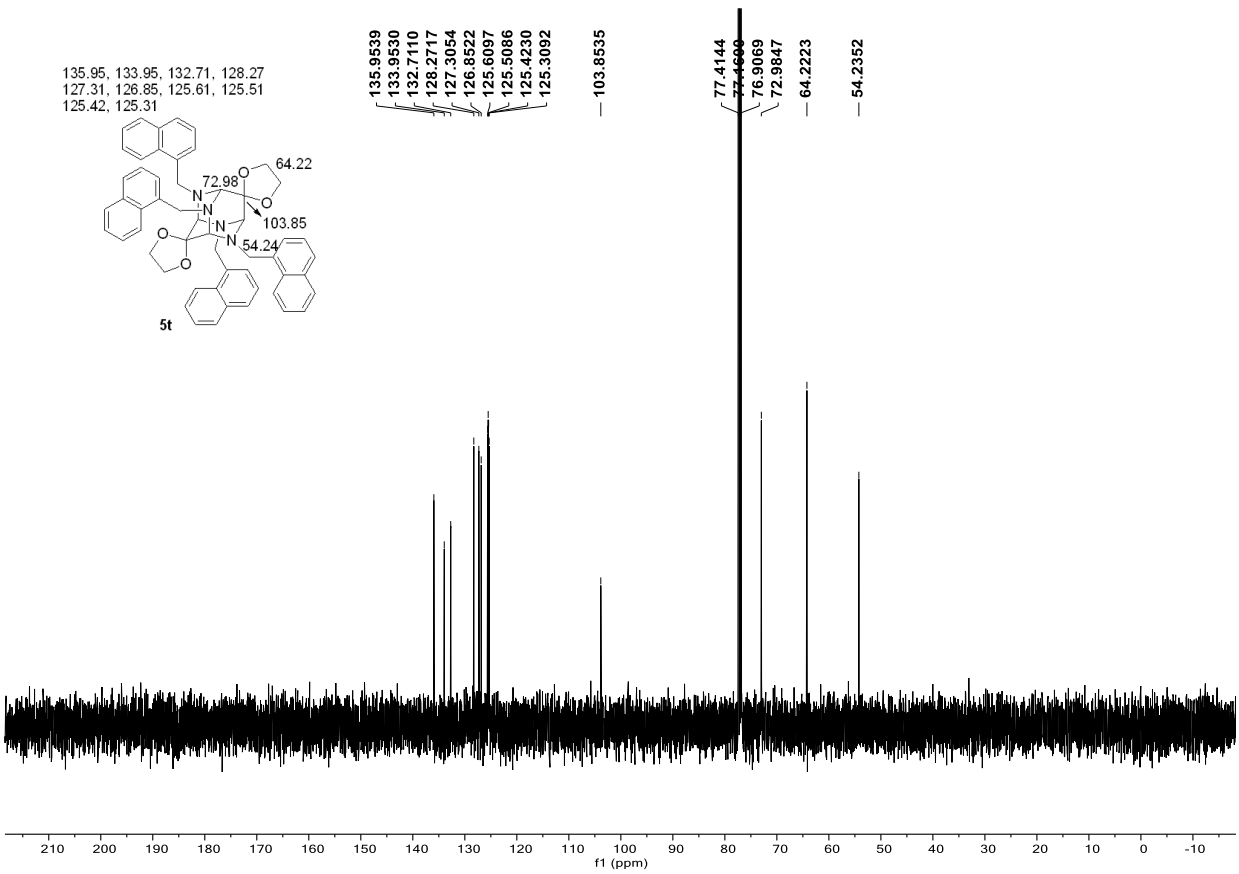


Figure S33. ^{13}C NMR spectrum of compound **5t**.

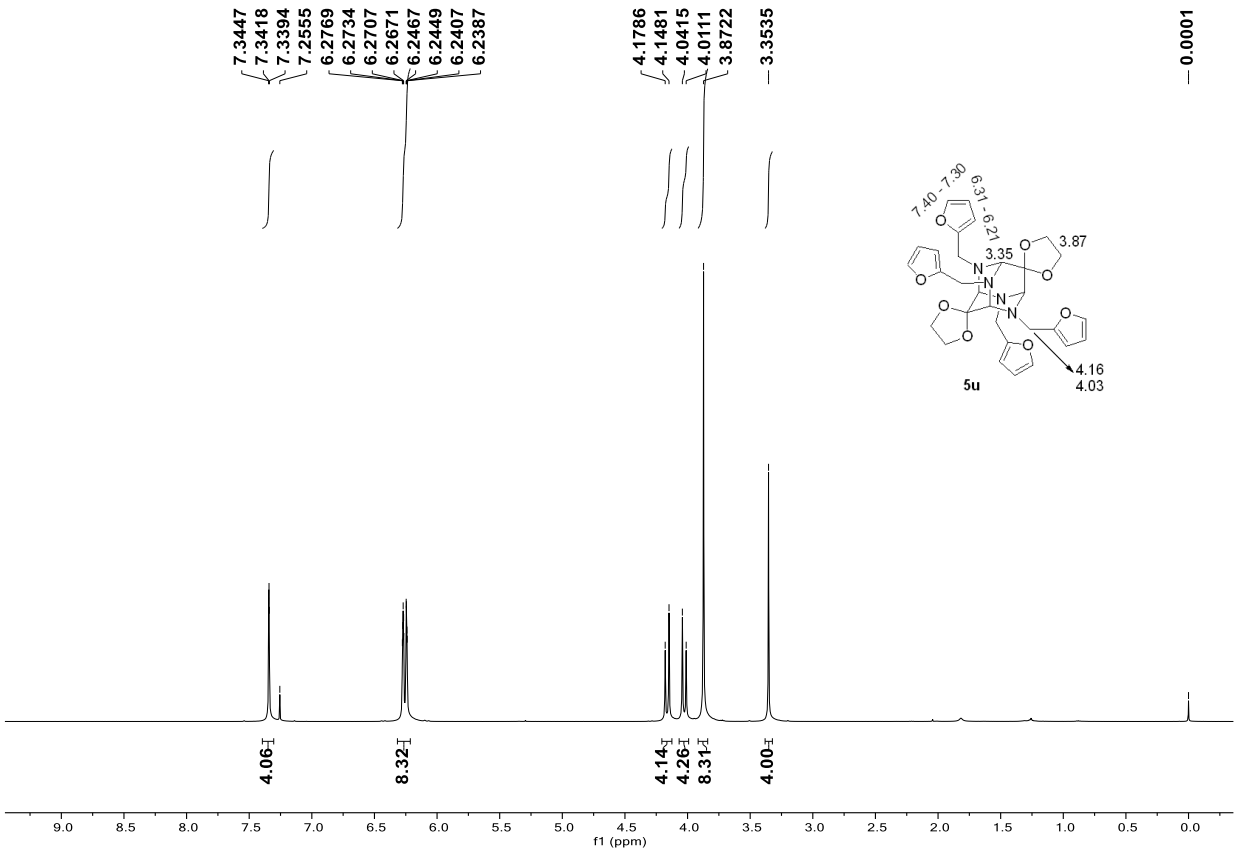


Figure S34. ^{1}H NMR spectrum of compound **5u**.

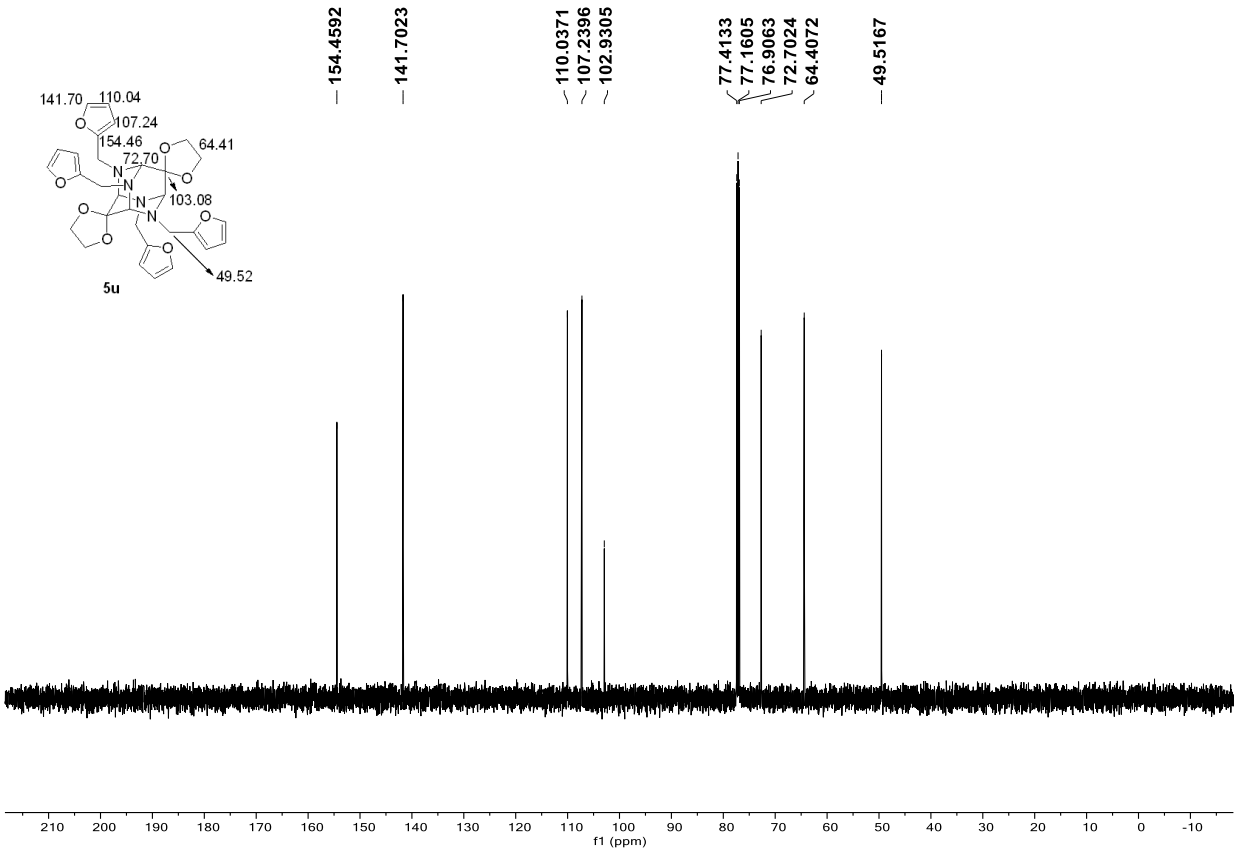


Figure S35. ^{13}C NMR spectrum of compound **5u**.

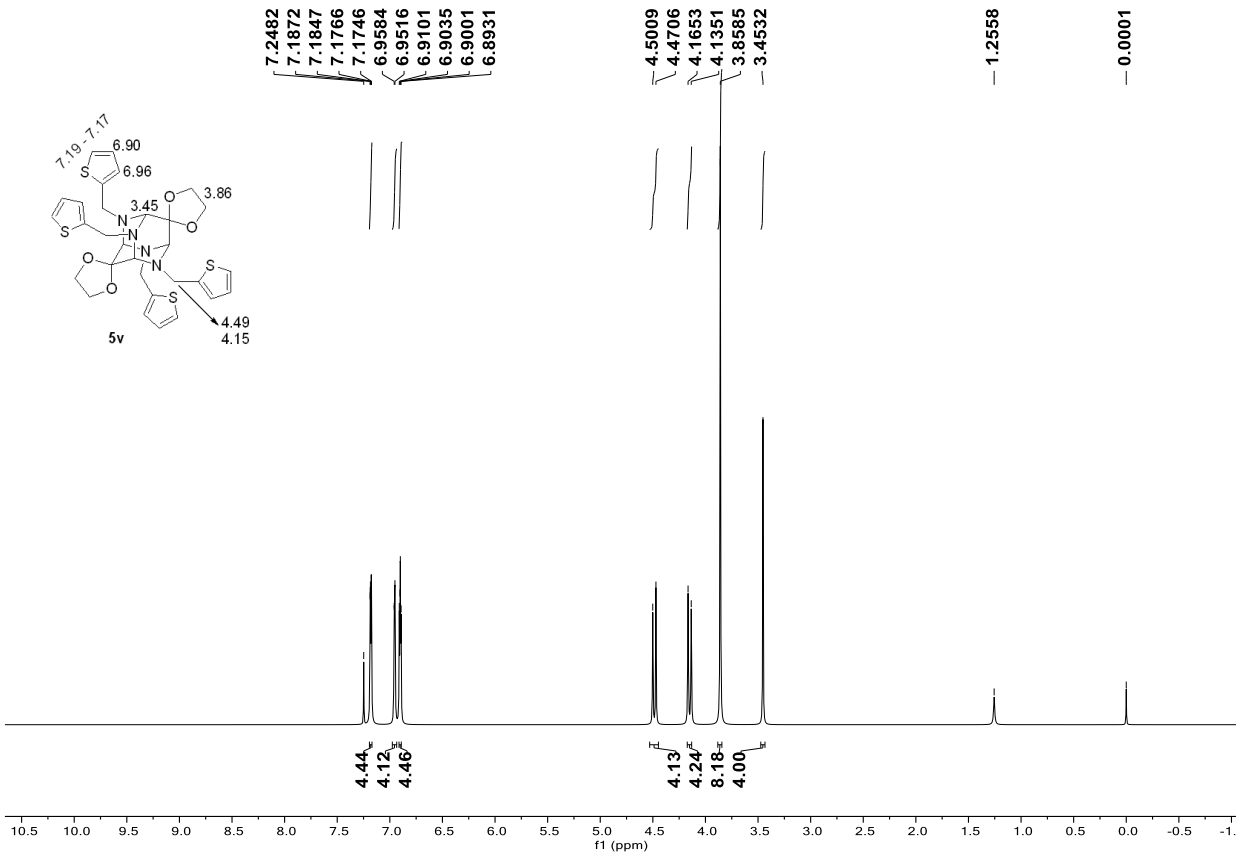


Figure S36. ^{1}H NMR spectrum of compound **5v**.

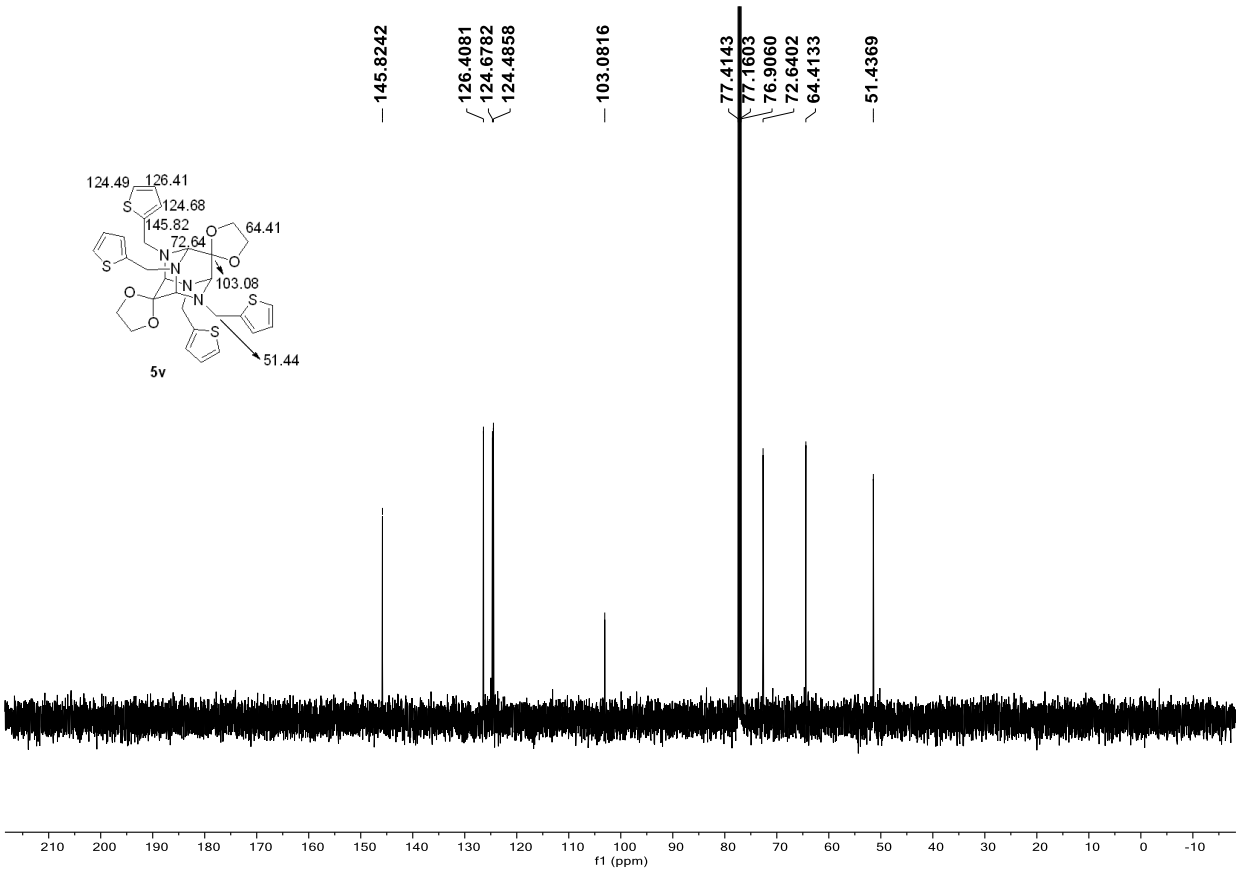


Figure S37. ^{13}C NMR spectrum of compound **5v**.

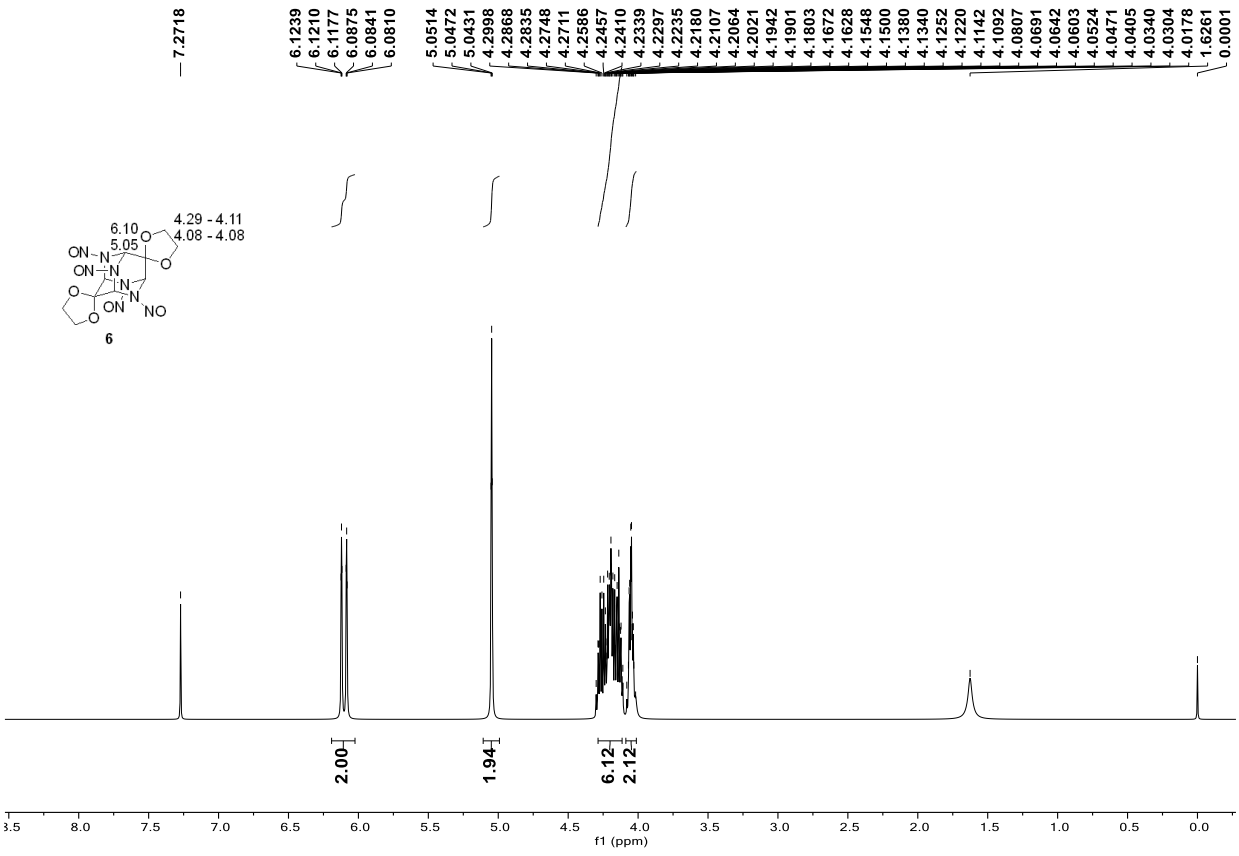


Figure S38. ^{1}H NMR spectrum of compound **6**.

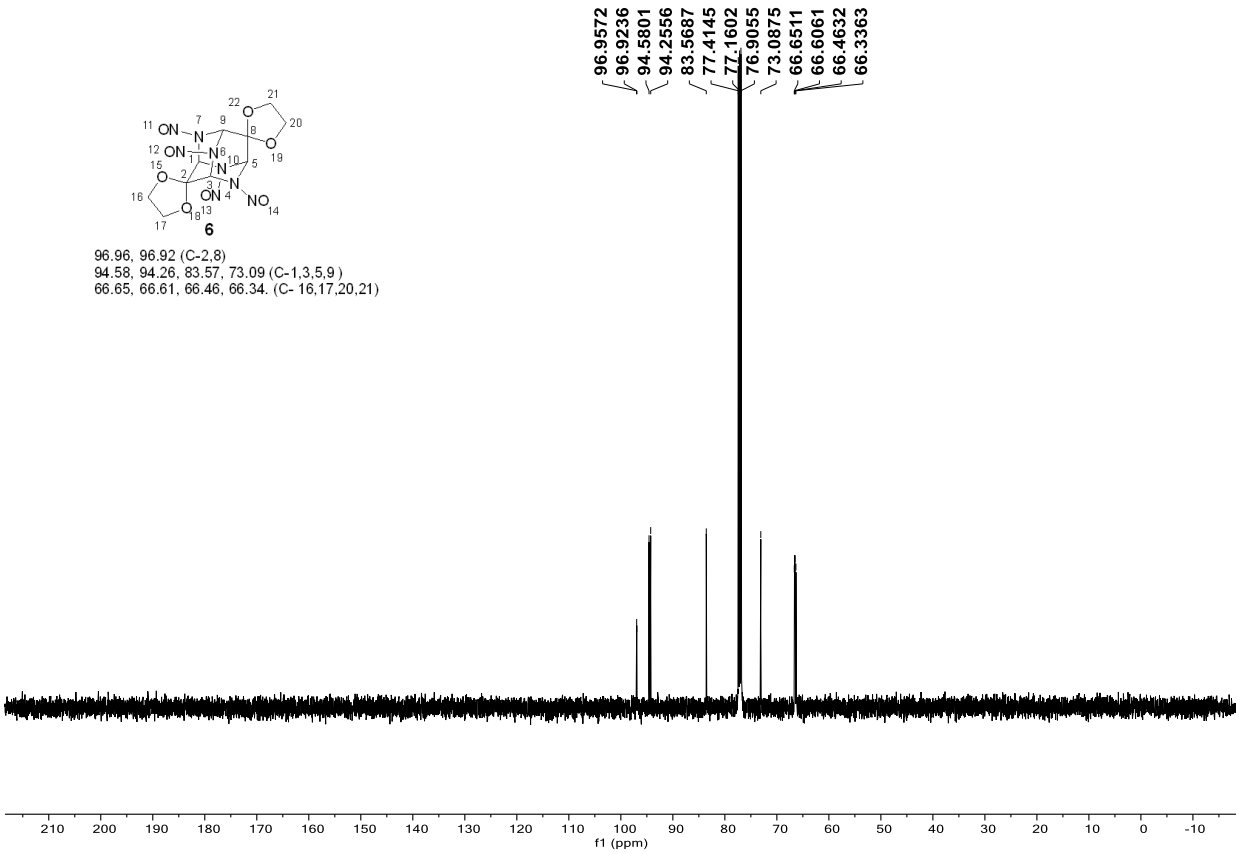


Figure S39. ^{13}C NMR spectrum of compound **6**.

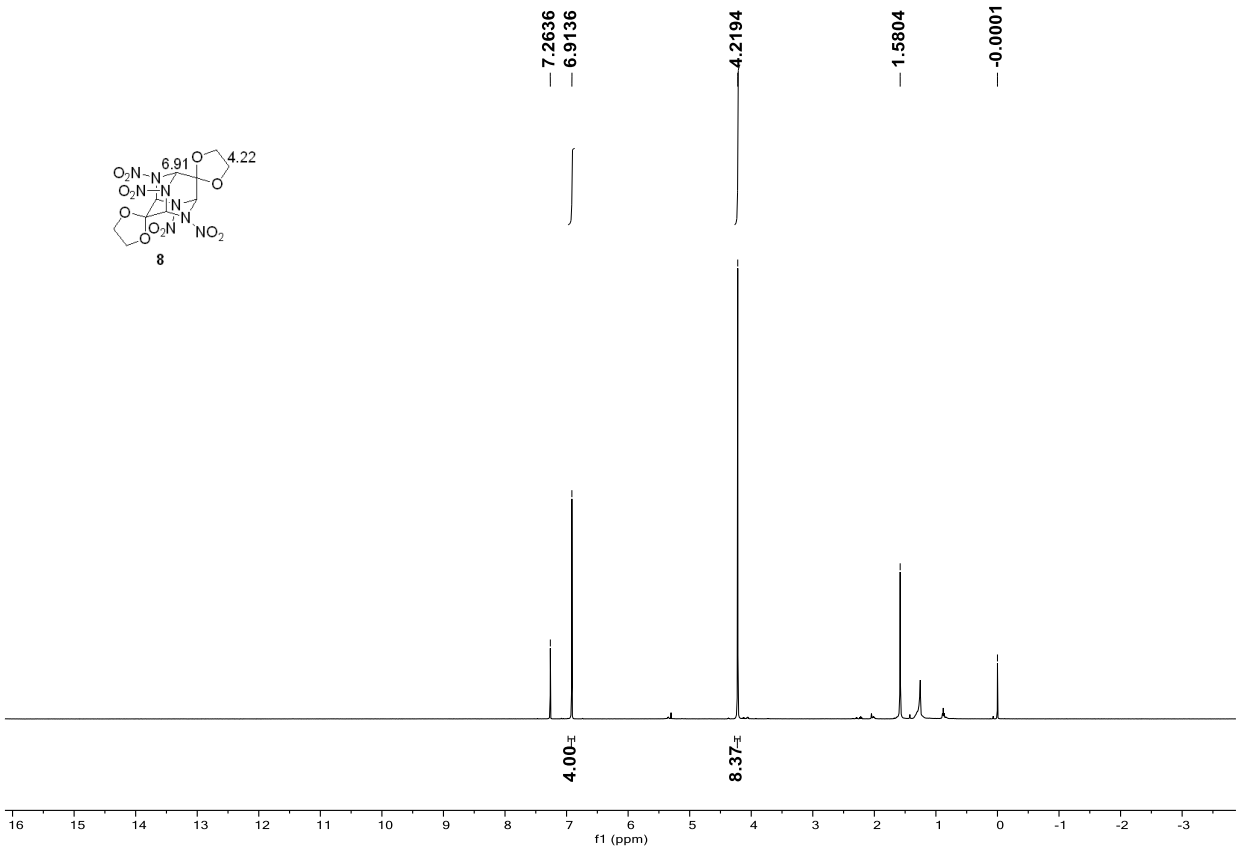


Figure S40. ^{1}H NMR spectrum of compound **8**.

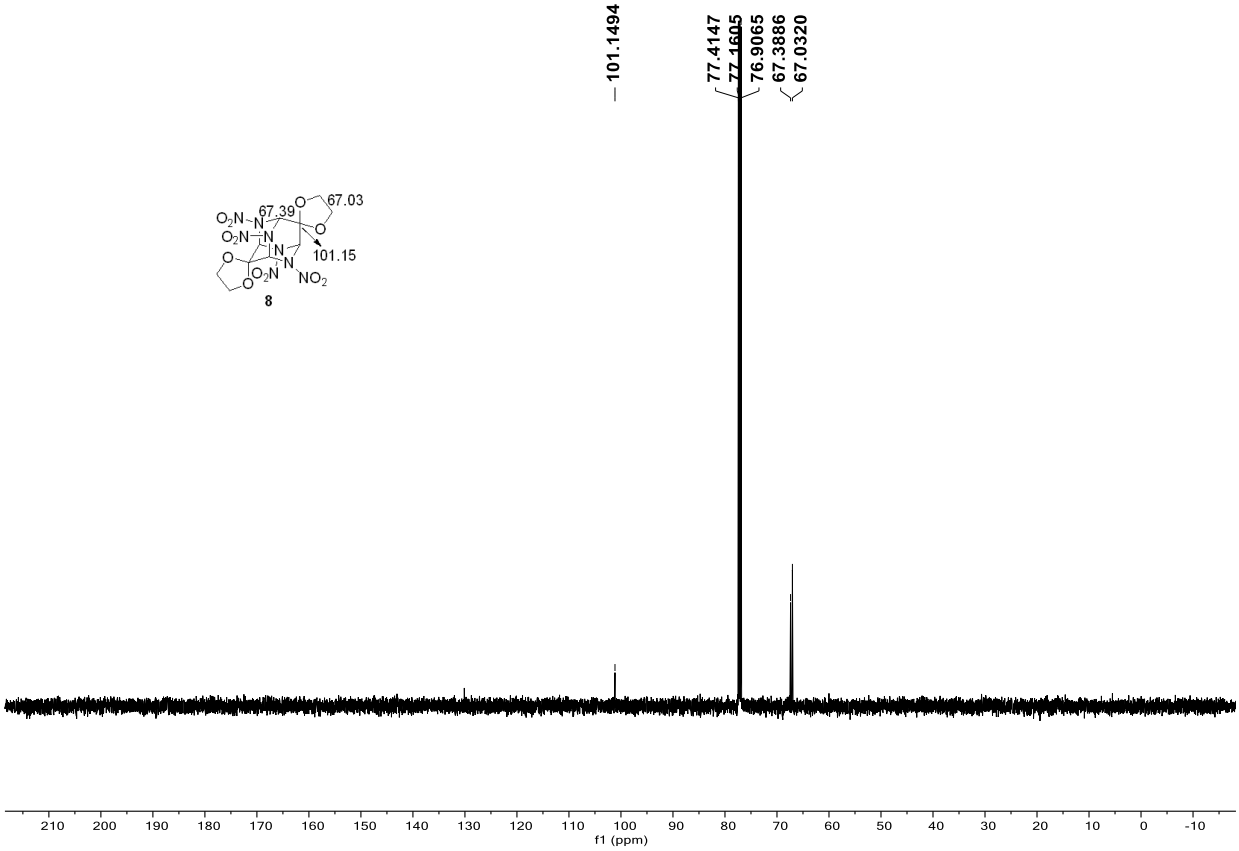


Figure S41. ^{13}C NMR spectrum of compound **8**.

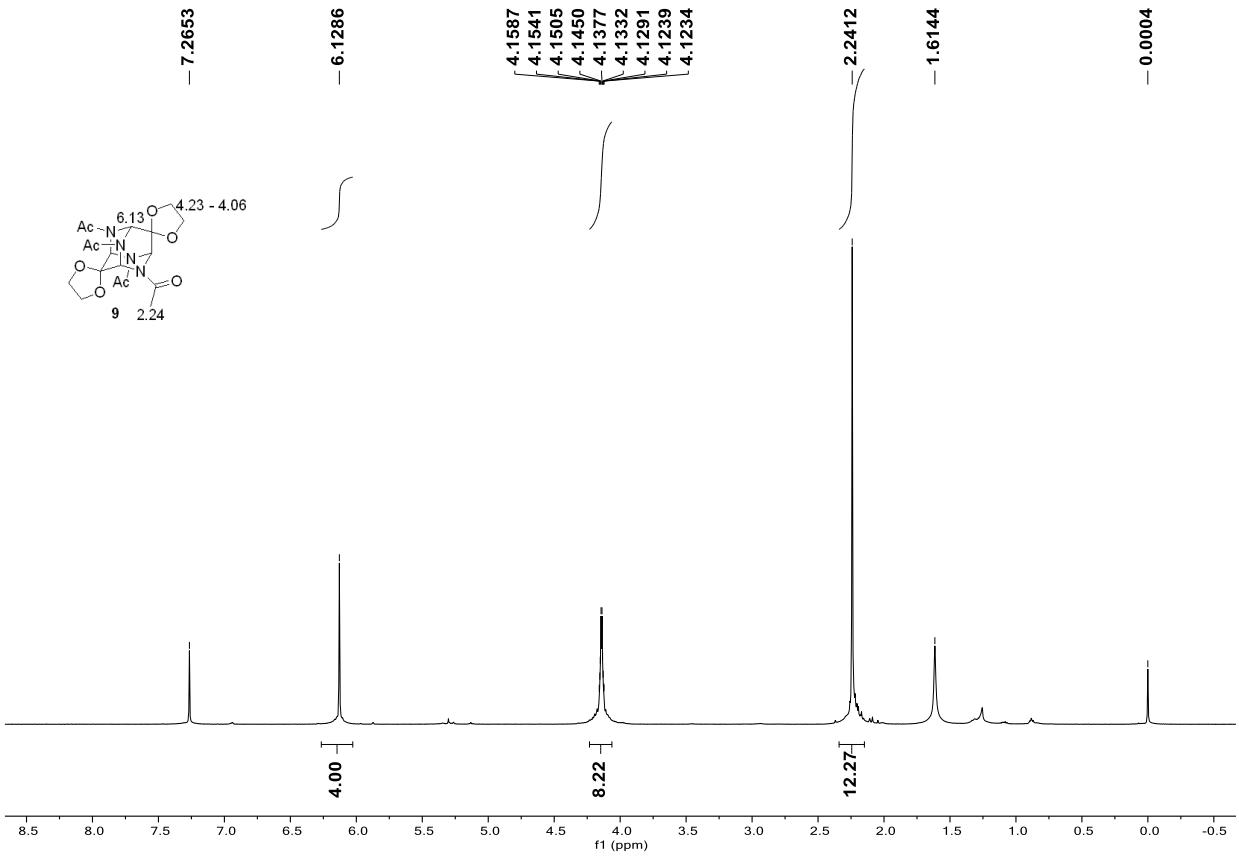


Figure S42. ^{1}H NMR spectrum of compound **9**.

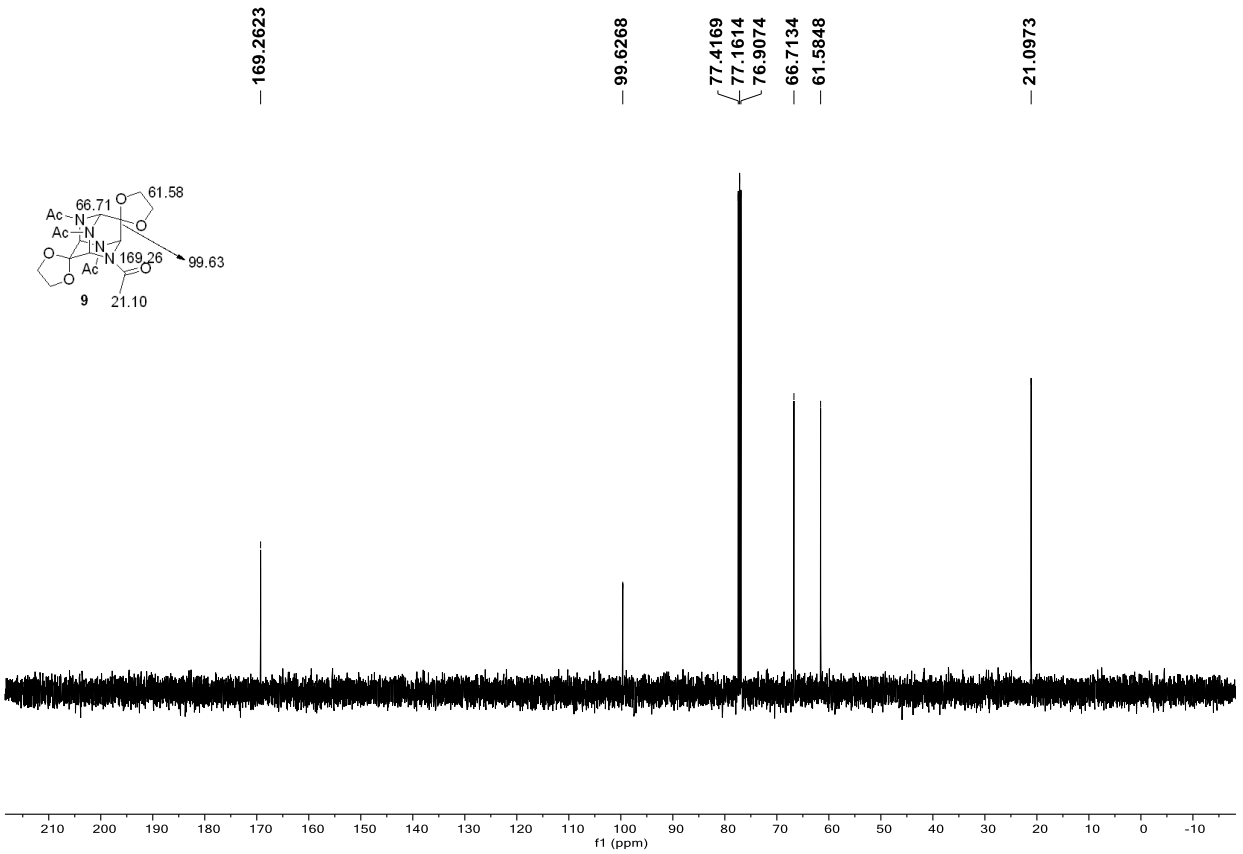


Figure S43. ^{13}C NMR spectrum of compound **9**.

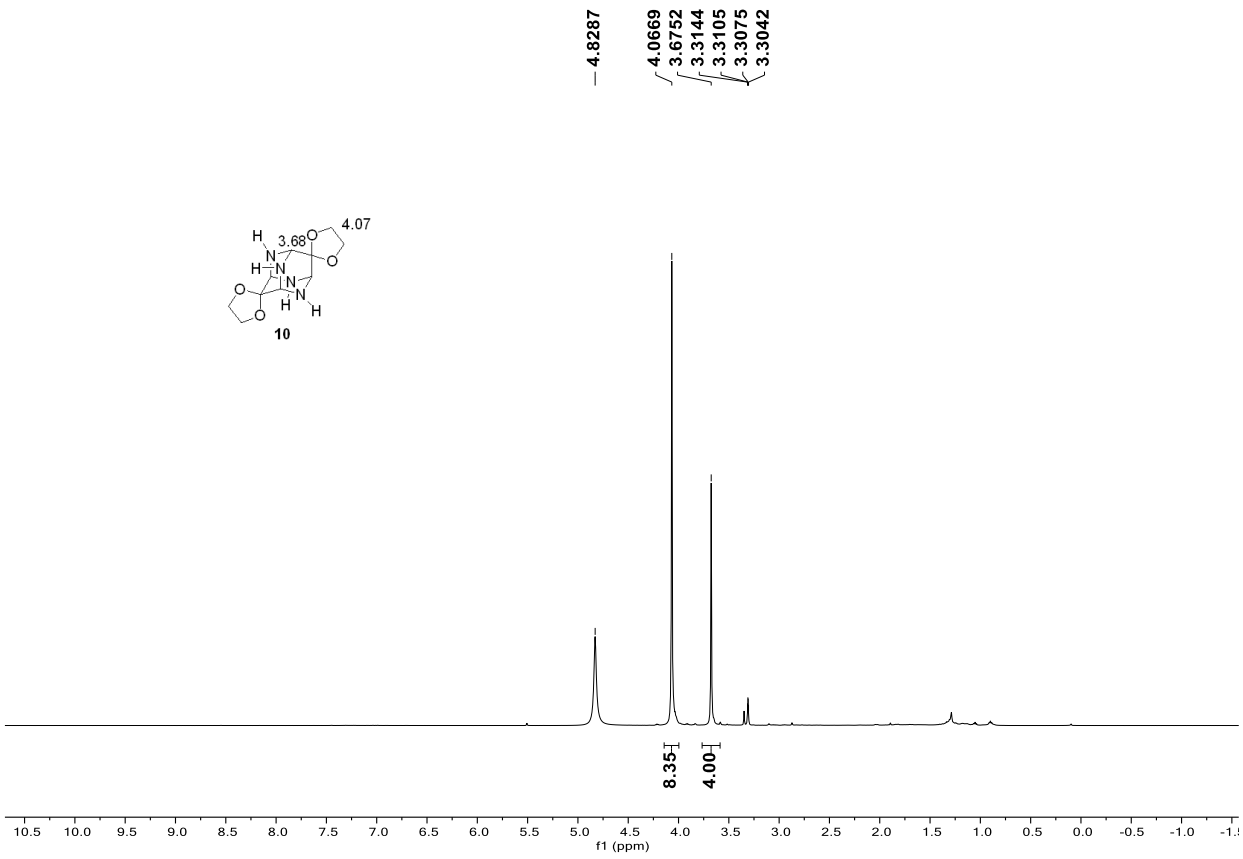


Figure S44. ^{1}H NMR spectrum of compound **10**.

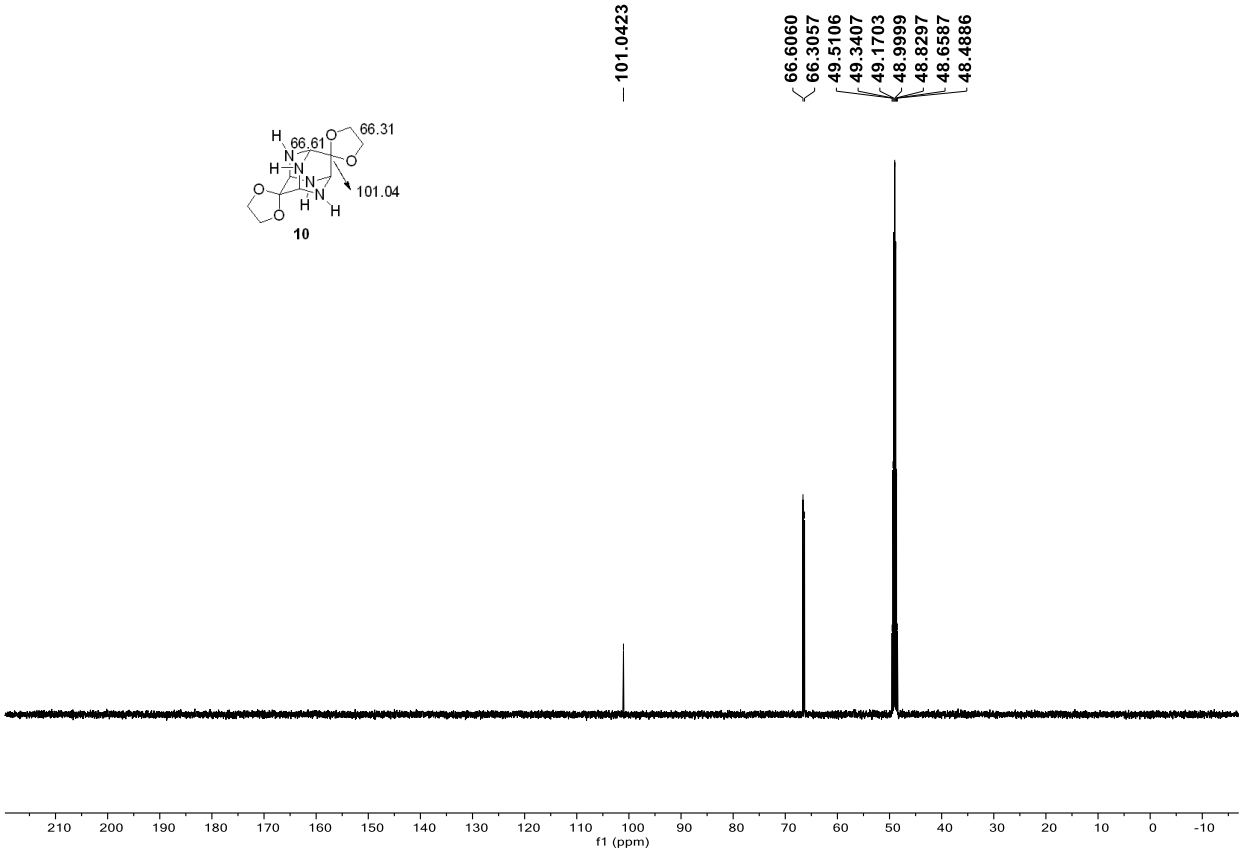


Figure S45. ^{13}C NMR spectrum of compound **10**.

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