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Supporting Information

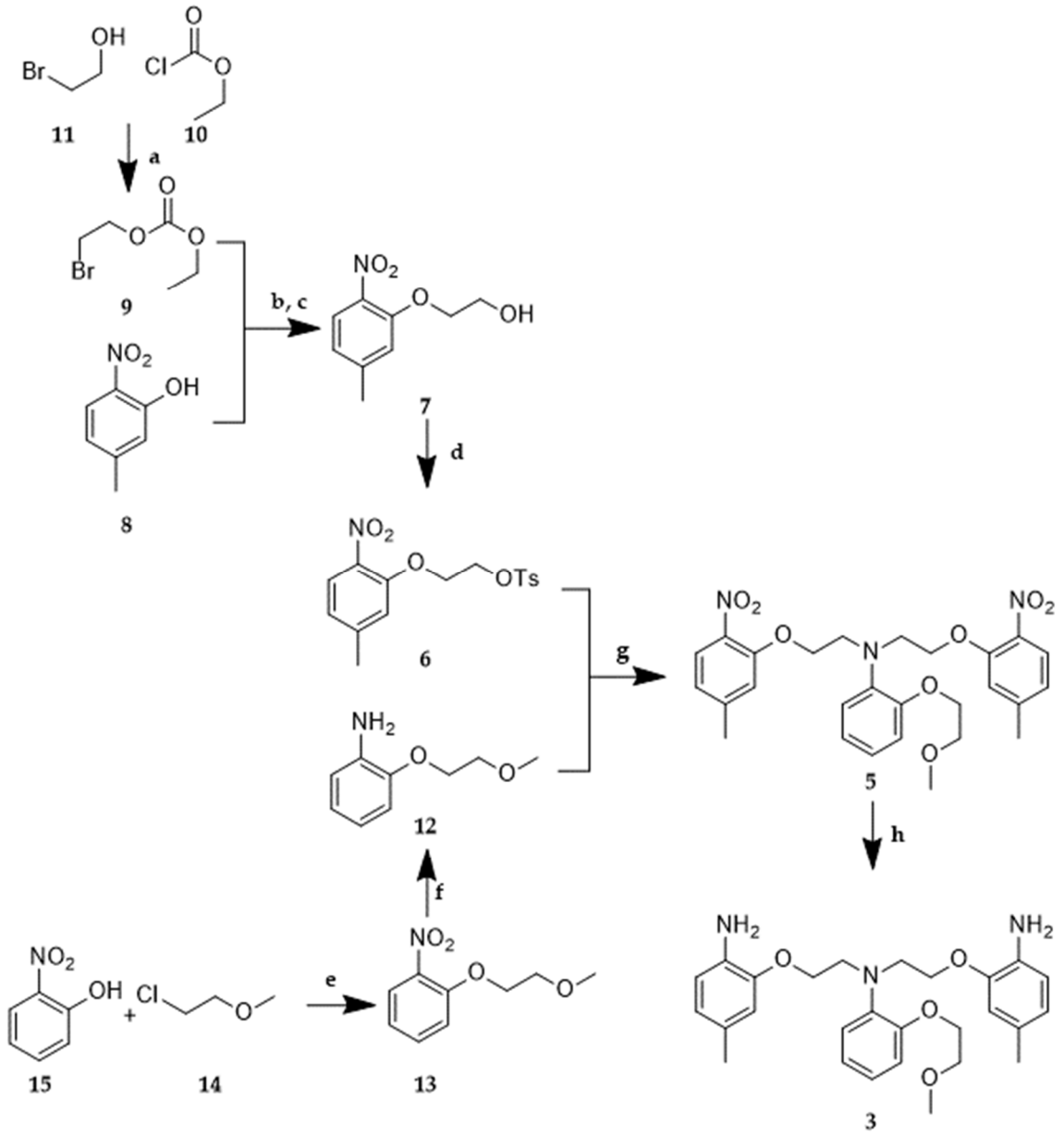
6-(2'-(4''-Oxabutyloxy)phenyl)-1,6,11-triaza-3,9,14,17,22,25-hexaoxa-2(1,2)(4-methylbenzena)-10(1,2)(5-methylbenzena)tricyclo(9.8.8)heptacosaphan·Sodiumbromide·Methylenechloride

Matthias Jochem, Dieter Schollmeyer and Heiner Detert *

Department Chemistry, Johannes Gutenberg-Universität, 55122 Mainz, Germany; majochem@uni-mainz.de (M.J.); scholli@uni-mainz.de (D.S.)
* Correspondence: Correspondence: detert@uni-mainz.de

Inhalt

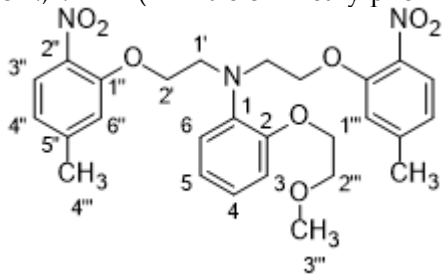
1. Synthesis



***Scheme S1**: Complete synthesis scheme to the precursor (3) of the title compound.*

Steps **e,f** were carried out according to literature [1], step **h** according to literature [2]. Experimental data was verified by literature comparison.

5 *N,N*-2′-Di(2′′-nitro-5′′-methylphen-1-oxy)ethyl-2-methoxyethoxyaniline (**g**)



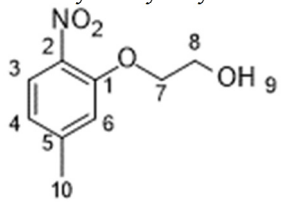
A three-necked flask (1 L) equipped with a Dimroth condenser, a magnetic stirrer and a fine dosing funnel was flushed with nitrogen. The flask was charged with calcium carbonate (5.840 g, 58.0 mmol, 2.0 eq), potassium iodide

(4.81 g, 29.0 mmol, 1.0 eq) and water (150 mL). The dropping funnel was charged with 2-(2'(methoxy)ethoxy)aniline (**12**) (5.00 g, 29.9 mol, 1.0 eq) and *O*-(2'-*para*-tosyloxyethyl)-5-methyl-2-nitrophenol (**6)** (31.5 g, 89.9 mmol, 3.0 eq) dissolved in dioxane (60 mL). The aqueous suspension was heated to reflux and then the second solution was added dropwise over a course of 1.6 hours. Thereafter the mixture was heated to reflux for another 27.5 hours. After 22 hours an additional portion of (**6)** (5.0 g, 13.9 mmol, 0.3 eq). The precipitate was removed by suction filtration, then taken up in water (150 mL) and hot ethyl acetate (150 mL) for hot extraction which was repeated twice. The filter cake was boiled twice with ethyl acetate (50 mL) as well. All organic phases were combined, and the volume reduced to approximately 200 mL. The desired compound started crystallising upon cooling of the ethyl acetate mixture to room temperature. The first fraction was obtained via suction filtration, after which the mother liquor was washed with 2M hydrochloric acid, boiled with active charcoal, filtrated and concentrated until no more yellow crystals formed. These crystals were isolated by suction filtration, after firther concentration of the mother liquor, a dark brown oil formed. This oil still contained traces of the product via TLC and 1H-NMR analysis but was discarded.

The desired product was thus obtained as yellow crystals (10.65 g, 20.3 mol, 68%).

HR-ESIMS *m*/*z* 526.2179 $[M+H]^+$ (calcd for $C_{27}H_{32}N_3O_8^+$, 526.2184), 548.1996 $[M+Na]^+$(calcd for $C_{27}H_{31}N_3NaO_8^+$, 548.2003); IR(**1**) ν_{max}/cm^{-1}: 3070, 2925, 2878, 2585, 2437, 2249, 1607, 1590, 1510, 1499, 1449, 1417, 1340, 1308, 1273, 1238, 1178, 1126, 1091, 1030, 967, 916, 841, 817, 745; 1H NMR (400 MHz, CDCl3) δ: 7.73 (d, J = 8.3 Hz, 2H, H3''), 7.07 (dd, J = 7.6, 1.6 Hz, 1H, H4), 6.98—6.86 (m, 3H, H3,5,6), 6.84 (s, 2H, H6''), 6.75 (dd, J = 8.3, 0.6 Hz, 2H, H4''), 4.21 (t, J = 5.6 Hz, 4H, H2'), 4.12—4.07 (AA'BB', 2H, H1'''), 3.75 (t, J = 5.6 Hz, 4H, H2'''), 3.72—3.68 (AA'BB', 2H, H1'), 3.35 (s, 3H, H3'''), 2.36 (s, 6H, H4'''); 13C NMR (101 MHz, CDCl3) δ: 13C NMR (101 MHz, CDCl3) δ 152.85 (C2), 152.69 (C1''), 145.93 (C5''), 139.08 (C1), 137.45 (C2''), 125.78 (C3''), 123.17 (C5), 122.05 (C4), 121.66 (C6), 120.85 (C4''), 115.20 (C6''), 114.60 (C3), 71.28 (C2'''), 68.31 (C2'), 67.97(C1'''), 59.00 (C3'''), 52.38 (C1'), 21.96 (C4''').

7 *O*-Hydroxyethyl-5-methyl-2-nitrophenol (**b,c**)



In a three-necked flask equipped with a magnetic stirrer, a dropping funnel and a Dimroth-condenser with calcium chloride drying tube 2-Nitro-5-methylphenol (**8**) (15.34 g, 0.100 mol, 1.0 eq) was dissolved in N,N-dimethylformamide (100 mL) and potassium carbonate (15.10 g, 0.110 mol, 1.1 eq) was added. The dropping funnel was charged with a solution of 2-bromoethyl ethyl carbonate (**9**) (21.60 g, 0.110 mol, 1.1 eq) in N,N-dimethylformamide(35 mL). The suspension was heated to reflux at which point the second solution was added over a course of 40 minutes, after which stirring was continued for another 10 minutes. After TLC control little educt was still present, so another portion of 2-bromoethyl ethyl carbonate (0.85 g, 0.004 mol, 0.004 eq) and heated to reflux again for 30 minutes. At that time the red colour caused by deprotonated nitrophenol had turned into an orange colour.

To the hot suspension water (200 mL in 4 portions) was added until no more precipitate formed. The precipitate was freed from the liquid by suction filtration to give the still wet crude product in 40.30 g, which was deprotected by boiling the mass in ammonia solution (150 mL of 25 % ammonium hydroxide (aq) with 260 mL water). The desired compound (**6**) was obtained by suction filtration and rinsing with water (2x200 mL) as a beige solid (18.35 g, 93.05 mmol, 93% over two steps).

1H NMR (400 MHz, CDCl3) δ: 7.81 (d, ^3J = 8.3 Hz, 1H, H-3), 6.88 (d, ^4J = 1.0 Hz, 1H, H-6), 6.86—6.84 (m, 1H, H-4), 4.24 – 4.20 (AA'BB', 2H, H-7), 4.04—3.90 (m, 2H, H-8), 2.59 (s, 1H, H-9), 2.41 (s, 3H, H-10); 13C NMR (101 MHz, CDCl3) δ: 152.60 (C-1), 146.35 (C-5), 137.08 (C-2), 128.49 (C-3), 126.17 (C-3), 121.84 (C-4), 115.85 (C-6), 70.42 (C-7), 58.07 (C-8), 22.04 (C-10); HR-ESIMS *m*/*z* 220.0575 $[M+Na]^+$ (calcd for $C_9H_{11}NNaO_4^+$, 220.0580).

6 *O*-(2'-*para*-Tosyloxyethyl)-5-methyl-2-nitrophenol (**d**)

A 500 mL round-bottomed flask equipped with a magnetic stirrer, reflux condenser with a drying tube (calcium chloride) and a dropping funnel was charged with compound **6** (17.67 g, 0.090 mol, 1.0 eq) which was dissolved in dichloromethane (200 mL).The flask was cooled in an ice bath. To this was added *para*-tosylchloride (17.08 g, 0.090 mol, 1.0 eq) and *N*,*N*-dimethyl-4-aminopyridine (180 mg). Over a course of 20 minutes triethylamine (20 mL, 0.143 mol,1.6 eq) was added droprowise with stirring at 0—5 °C. The mixture was then warmed to room temperature

and stirred for 16 hours. An additional portion of *para*-tosylchloride (1.60 g, 0.006 mol, 0.09 eq) was added and stirring continued for 3 hours. The mixture was then extracted with water (3x200 mL) and 2 M hydrochloric acid (200 mL), the organic phase was concentrated under reduced pressure to a yellow oil which solidified upon trituration with petroleum ether (50 mL) to yield the desired product **5** (30.5 g, 0.087 mol, 97%); 1H NMR (300 MHz, CDCl3) δ 7.83—7.78 (AA'XX', 2H), 7.76 (d, J = 8.3 Hz, 1H), 7.38— 7.32 (AA'XX', 2H), 6.86 (ddd, J = 8.3, 1.7, 0.8 Hz, 1H), 6.81 (d, J = 1.6 Hz, 1H), 4.41— 4.35 (AA'BB', 2H), 4.33— 4.28 (AA'BB', 2H), 2.44 (s, 3H), 2.39 (s, 3H); HR-APCIMS *m*/*z* 369.1108 $[M+NH_4]^+$ (calcd for $C_{16}H_{21}N_2O_6S^+$ 351.1112).

9 bromoethyl ethyl carbonate (**a**)

A three-necked round-bottomed flask (250 mL), equipped with a thermometer, a Dimroth condenser and a dropping funnel, was charged with 2-bromoethanol (**11**) (50.0 g, 0.400 mol, 1.0 eq) and dichloromethane (40 mL). To this, *N*,*N*-dimethyl-4-aminopyridine (450 mg) and pyridine (32 mL) were added. The mxitrue was cooled in an ice-salt-bath, to which a solution of ethyl chloroformiate (**10**) (43.6 g, 0.400 mol, 1.0 eq) in dichloromethane (20 mL) was added dropwise via the funnel. The rate was adjusted so that the temperature remained below 9 °C, which took 1 hour. After that time the temperature dropped to 2 °C; the mixture was allowed to warm to room temperature. The warm mixture was poured on ice cold aqueous hydrochloric acid (150 mL, 0.7 M). The organic phase was separated cold and the aqueous phase extracted while cold with dichloromethane (2x100 mL). The combined organic phases were dried over sodium sulfate and the concentrated under reduced pressure to give a crude product of 80 g (n_D^{22}=1.4655), which was then purified by distillation under reduced pressure. The desired product was obtained at a boiling point of 78—81 °C as a colourless liquid (58.4 g, 0.296 mol, 74 %); n_D^{22}=1.4498; 1H NMR (400 MHz, CDCl3) δ: 4.42 (t, J = 6.2 Hz, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.52 (t, J = 6.2 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H).

2. Crystallographic Detail on compound 2

Table S1. Anisotropic diffraction parameter (Å2) for compound 2 of Form: -2π2[h2 a*2U11 + ... + 2 h k a* b* U12]

Na1	0.0275(6)	0.0271(6)	0.0242(6)	-0.0015(5)	-0.0042(5)	-0.0110(5)
Br1	0.03539(17)	0.03303(16)	0.03303(17)	-0.00225(12)	-0.00495(13)	-0.01764(13)
C1	0.0291(15)	0.0263(14)	0.0262(14)	-0.0003(11)	-0.0063(12)	-0.0156(12)
C2	0.0290(16)	0.0293(15)	0.0317(16)	-0.0011(12)	-0.0042(13)	-0.0101(13)
C3	0.0330(17)	0.0387(18)	0.0361(18)	0.0016(14)	-0.0119(14)	-0.0134(14)
C4	0.0400(19)	0.0399(18)	0.0289(16)	-0.0003(14)	-0.0116(14)	-0.0163(15)
C5	0.0343(17)	0.0363(17)	0.0283(16)	-0.0047(13)	-0.0057(13)	-0.0148(14)
C6	0.0270(15)	0.0248(14)	0.0259(14)	-0.0008(11)	-0.0052(12)	-0.0129(12)
O7	0.0299(11)	0.0319(11)	0.0245(10)	-0.0026(9)	-0.0029(9)	-0.0147(9)
C8	0.0295(16)	0.0326(16)	0.0282(15)	-0.0027(13)	0.0000(13)	-0.0140(13)
C9	0.0385(18)	0.0316(16)	0.0279(16)	0.0008(13)	-0.0046(13)	-0.0148(14)
O10	0.0612(17)	0.0350(13)	0.0402(14)	-0.0082(11)	0.0010(12)	-0.0238(12)
C11	0.066(3)	0.046(2)	0.088(4)	-0.025(2)	-0.001(3)	-0.002(2)
N12	0.0254(12)	0.0270(12)	0.0218(12)	-0.0004(10)	-0.0035(10)	-0.0118(10)
C13	0.0269(15)	0.0251(14)	0.0265(15)	-0.0019(11)	-0.0047(12)	-0.0130(12)
C14	0.0248(14)	0.0259(14)	0.0280(15)	-0.0021(12)	-0.0066(12)	-0.0101(12)
O15	0.0273(11)	0.0230(10)	0.0288(11)	0.0010(8)	-0.0080(9)	-0.0099(8)
C16	0.0311(16)	0.0325(15)	0.0241(14)	-0.0070(12)	-0.0021(12)	-0.0149(13)
C17	0.0285(15)	0.0235(14)	0.0284(15)	-0.0051(11)	-0.0033(12)	-0.0111(12)
O18	0.0299(11)	0.0255(10)	0.0245(10)	-0.0010(8)	-0.0055(8)	-0.0140(9)
C19	0.0302(15)	0.0252(14)	0.0196(13)	-0.0023(11)	-0.0013(11)	-0.0118(12)
C20	0.0281(15)	0.0261(14)	0.0253(14)	-0.0027(11)	-0.0034(12)	-0.0110(12)
C21	0.0313(16)	0.0261(15)	0.0337(17)	-0.0004(13)	-0.0069(13)	-0.0080(13)
C22	0.0392(18)	0.0236(15)	0.0325(17)	0.0007(12)	-0.0035(14)	-0.0111(13)

C23	0.0375(17)	0.0286(15)	0.0233(14)	-0.0032(12)	-0.0006(12)	-0.0160(13)
C24	0.0294(15)	0.0291(15)	0.0244(14)	-0.0037(12)	-0.0015(12)	-0.0122(12)
C25	0.0218(14)	0.0239(13)	0.0264(14)	-0.0005(11)	-0.0031(11)	-0.0110(11)
C26	0.0251(14)	0.0252(14)	0.0234(14)	-0.0007(11)	-0.0068(11)	-0.0090(11)
C27	0.0299(15)	0.0237(14)	0.0299(15)	-0.0010(12)	-0.0083(12)	-0.0110(12)
C28	0.0294(16)	0.0267(15)	0.0299(16)	0.0009(12)	-0.0042(13)	-0.0119(12)
C29	0.0271(15)	0.0260(14)	0.0245(14)	-0.0009(11)	-0.0035(12)	-0.0087(12)
C30	0.0264(15)	0.0272(14)	0.0284(15)	-0.0047(12)	-0.0058(12)	-0.0099(12)
C31	0.0444(19)	0.0308(16)	0.0329(17)	-0.0030(13)	-0.0003(14)	-0.0203(15)
C32	0.0429(19)	0.0337(17)	0.0274(16)	-0.0022(13)	-0.0031(14)	-0.0165(15)
N33	0.0260(13)	0.0287(12)	0.0242(12)	-0.0024(10)	-0.0051(10)	-0.0106(10)
N34	0.0268(13)	0.0293(13)	0.0230(12)	-0.0044(10)	-0.0021(10)	-0.0124(10)
C35	0.0276(15)	0.0302(15)	0.0299(16)	-0.0064(12)	-0.0033(12)	-0.0095(12)
C36	0.0257(15)	0.0295(15)	0.0314(16)	-0.0046(12)	-0.0037(12)	-0.0077(12)
O37	0.0261(11)	0.0290(11)	0.0307(11)	-0.0019(9)	-0.0046(9)	-0.0097(9)
C38	0.0276(16)	0.0350(16)	0.0339(17)	-0.0028(13)	-0.0001(13)	-0.0137(13)
C39	0.0291(16)	0.0360(17)	0.0403(18)	-0.0022(14)	-0.0092(14)	-0.0147(14)
O40	0.0299(11)	0.0298(11)	0.0308(11)	-0.0014(9)	-0.0076(9)	-0.0114(9)
C41	0.0370(17)	0.0301(15)	0.0301(16)	-0.0039(13)	-0.0086(13)	-0.0160(13)
C42	0.0318(16)	0.0259(14)	0.0284(15)	-0.0028(12)	-0.0074(12)	-0.0117(12)
C43	0.0280(15)	0.0259(14)	0.0260(15)	-0.0002(12)	-0.0047(12)	-0.0092(12)
C44	0.0287(16)	0.0254(14)	0.0308(16)	-0.0037(12)	-0.0020(13)	-0.0085(12)
O45	0.0321(11)	0.0257(10)	0.0238(10)	-0.0033(8)	-0.0047(9)	-0.0093(9)
C46	0.0327(17)	0.0326(16)	0.0249(15)	-0.0067(12)	-0.0028(13)	-0.0075(13)
C47	0.0311(16)	0.0327(16)	0.0254(15)	-0.0014(12)	0.0009(13)	-0.0097(13)
O48	0.0308(11)	0.0262(10)	0.0243(10)	-0.0016(8)	-0.0026(9)	-0.0089(9)
C49	0.0358(17)	0.0279(15)	0.0255(15)	-0.0009(12)	-0.0079(13)	-0.0094(13)
C50	0.0319(16)	0.0284(15)	0.0279(15)	-0.0012(12)	-0.0091(13)	-0.0085(13)
C1L	0.048(2)	0.046(2)	0.043(2)	-0.0024(16)	-0.0056(17)	-0.0255(18)
Cl1	0.1116(10)	0.0442(5)	0.0470(6)	0.0010(4)	-0.0272(6)	-0.0354(6)
Cl2	0.0477(6)	0.1003(9)	0.0467(6)	0.0086(6)	-0.0173(5)	-0.0359(6)

Table S2 Coordinates and isotropic diffraction parameter of hydrogen atoms (Å^2) for compound 2.

Atom	x	y	z	U(iso)
H2	0.923	0.109	0.375	0.038
H3	0.952	0.089	0.537	0.044
H4	0.794	0.174	0.658	0.043
H5	0.611	0.280	0.616	0.039
H8A	0.892	0.211	0.231	0.037
H8B	0.790	0.333	0.210	0.037
H9A	0.717	0.256	0.121	0.041
H9B	0.843	0.255	0.068	0.041
H11A	0.994	-0.024	0.103	0.110
H11B	0.989	0.048	0.180	0.110

H11C	1.002	0.096	0.062	0.110
H13A	0.623	0.425	0.339	0.031
H13B	0.488	0.493	0.378	0.031
H14A	0.563	0.439	0.202	0.032
H14B	0.538	0.331	0.261	0.032
H16A	0.446	0.418	0.551	0.034
H16B	0.455	0.291	0.576	0.034
H17A	0.268	0.418	0.547	0.032
H17B	0.322	0.464	0.437	0.032
H21	0.128	0.789	0.142	0.039
H22	0.244	0.890	0.109	0.041
H24	0.502	0.610	0.217	0.034
H27	0.271	-0.001	0.514	0.033
H28	0.207	0.004	0.686	0.036
H30	0.270	0.282	0.649	0.033
H31A	0.538	0.777	0.144	0.054
H31B	0.433	0.862	0.212	0.054
H31C	0.442	0.886	0.093	0.054
H32A	0.268	0.143	0.820	0.053
H32B	0.189	0.075	0.832	0.053
H32C	0.133	0.209	0.812	0.053
H35A	0.025	0.700	0.287	0.036
H35B	0.109	0.623	0.365	0.036
H36A	-0.058	0.587	0.411	0.037
H36B	-0.040	0.559	0.302	0.037
H38A	-0.070	0.411	0.436	0.040
H38B	0.045	0.305	0.461	0.040
H39A	-0.026	0.282	0.332	0.042
H39B	-0.007	0.390	0.263	0.042
H41A	0.147	0.102	0.298	0.037
H41B	0.133	0.139	0.402	0.037
H42A	0.324	0.007	0.356	0.034
H42B	0.340	0.088	0.252	0.034
H43A	0.508	0.022	0.377	0.034
H43B	0.496	0.145	0.381	0.034
H44A	0.605	0.103	0.226	0.036
H44B	0.513	0.065	0.205	0.036
H46A	0.435	0.201	0.072	0.039
H46B	0.554	0.217	0.058	0.039
H47A	0.454	0.410	0.057	0.039
H47B	0.411	0.378	-0.024	0.039
H49A	0.200	0.522	0.002	0.037

H49B	0.279	0.565	0.038	0.037
H50A	0.082	0.652	0.112	0.037
H50B	0.079	0.531	0.162	0.037
H1LA	0.221	0.299	0.067	0.054
H1LB	0.212	0.297	-0.044	0.054

Table S3: Bond lengths [Å] and angles [°] for compound 2.

Bond	length	Bond	length
Na1-O48	2.450(2)	C26-N34	1.441(4)
Na1-O18	2.459(2)	C27-C28	1.397(4)
Na1-O45	2.474(2)	C27-H27	0.9500
Na1-O37	2.507(2)	C28-C29	1.384(4)
Na1-O15	2.564(2)	C28-H28	0.9500
Na1-O40	2.602(2)	C29-C30	1.398(4)
Na1-N34	2.648(3)	C29-C32	1.513(4)
Na1-N33	2.669(3)	C30-H30	0.9500
C1-C2	1.381(4)	C31-H31A	0.9800
C1-O7	1.384(3)	C31-H31B	0.9800
C1-C6	1.409(4)	C31-H31C	0.9800
C2-C3	1.385(5)	C32-H32A	0.9800
C2-H2	0.9500	C32-H32B	0.9800
C3-C4	1.380(5)	C32-H32C	0.9800
C3-H3	0.9500	N33-C50	1.472(4)
C4-C5	1.388(5)	N33-C35	1.483(4)
C4-H4	0.9500	N34-C42	1.462(4)
C5-C6	1.395(4)	N34-C43	1.479(4)
C5-H5	0.9500	C35-C36	1.502(4)
C6-N12	1.410(4)	C35-H35A	0.9900
O7-C8	1.440(3)	C35-H35B	0.9900
C8-C9	1.498(4)	C36-O37	1.434(4)
C8-H8A	0.9900	C36-H36A	0.9900
C8-H8B	0.9900	C36-H36B	0.9900
C9-O10	1.420(4)	O37-C38	1.429(4)
C9-H9A	0.9900	C38-C39	1.502(5)
C9-H9B	0.9900	C38-H38A	0.9900
O10-C11	1.418(5)	C38-H38B	0.9900
C11-H11A	0.9800	C39-O40	1.440(4)
C11-H11B	0.9800	C39-H39A	0.9900
C11-H11C	0.9800	C39-H39B	0.9900
N12-C16	1.465(4)	O40-C41	1.427(4)
N12-C13	1.484(4)	C41-C42	1.508(4)

C13-C14	1.525(4)	C41-H41A	0.9900
C13-H13A	0.9900	C41-H41B	0.9900
C13-H13B	0.9900	C42-H42A	0.9900
C14-O15	1.443(3)	C42-H42B	0.9900
C14-H14A	0.9900	C43-C44	1.514(4)
C14-H14B	0.9900	C43-H43A	0.9900
O15-C19	1.375(3)	C43-H43B	0.9900
C16-C17	1.506(4)	C44-O45	1.426(3)
C16-H16A	0.9900	C44-H44A	0.9900
C16-H16B	0.9900	C44-H44B	0.9900
C17-O18	1.436(3)	O45-C46	1.422(4)
C17-H17A	0.9900	C46-C47	1.505(4)
C17-H17B	0.9900	C46-H46A	0.9900
O18-C25	1.379(3)	C46-H46B	0.9900
C19-C24	1.392(4)	C47-O48	1.420(4)
C19-C20	1.403(4)	C47-H47A	0.9900
C20-C21	1.389(4)	C47-H47B	0.9900
C20-N33	1.445(4)	O48-C49	1.434(3)
C21-C22	1.384(4)	C49-C50	1.504(4)
C21-H21	0.9500	C49-H49A	0.9900
C22-C23	1.392(5)	C49-H49B	0.9900
C22-H22	0.9500	C50-H50A	0.9900
C23-C24	1.394(4)	C50-H50B	0.9900
C23-C31	1.515(4)	C1L-Cl2	1.758(4)
C24-H24	0.9500	C1L-Cl1	1.767(4)
C25-C30	1.390(4)	C1L-H1LA	0.9900
C25-C26	1.402(4)	C1L-H1LB	0.9900
C26-C27	1.387(4)		
atoms	angle	atoms	angle
O48-Na1-O18	156.97(9)	C26-C27-H27	119.4
O48-Na1-O45	66.41(7)	C28-C27-H27	119.4
O18-Na1-O45	99.47(8)	C29-C28-C27	120.4(3)
O48-Na1-O37	117.34(8)	C29-C28-H28	119.8
O18-Na1-O37	80.92(8)	C27-C28-H28	119.8
O45-Na1-O37	165.98(8)	C28-C29-C30	118.9(3)
O48-Na1-O15	80.03(7)	C28-C29-C32	122.0(3)
O18-Na1-O15	79.65(7)	C30-C29-C32	119.0(3)
O45-Na1-O15	80.35(7)	C25-C30-C29	120.4(3)
O37-Na1-O15	113.35(8)	C25-C30-H30	119.8
O48-Na1-O40	89.82(8)	C29-C30-H30	119.8
O18-Na1-O40	110.93(8)	C23-C31-H31A	109.5
O45-Na1-O40	98.68(8)	C23-C31-H31B	109.5

O37-Na1-O40	68.44(7)	H31A-C31-H31B	109.5
O15-Na1-O40	169.33(8)	C23-C31-H31C	109.5
O48-Na1-N34	121.19(8)	H31A-C31-H31C	109.5
O18-Na1-N34	62.89(7)	H31B-C31-H31C	109.5
O45-Na1-N34	65.90(8)	C29-C32-H32A	109.5
O37-Na1-N34	102.54(8)	C29-C32-H32B	109.5
O15-Na1-N34	122.41(8)	H32A-C32-H32B	109.5
O40-Na1-N34	65.85(7)	C29-C32-H32C	109.5
O48-Na1-N33	67.56(8)	H32A-C32-H32C	109.5
O18-Na1-N33	111.61(8)	H32B-C32-H32C	109.5
O45-Na1-N33	124.44(8)	C20-N33-C50	112.6(2)
O37-Na1-N33	67.36(8)	C20-N33-C35	108.8(2)
O15-Na1-N33	62.53(7)	C50-N33-C35	113.7(2)
O40-Na1-N33	110.57(8)	C20-N33-Na1	116.46(18)
N34-Na1-N33	169.63(9)	C50-N33-Na1	98.17(17)
C2-C1-O7	121.3(3)	C35-N33-Na1	106.87(17)
C2-C1-C6	120.7(3)	C26-N34-C42	115.8(2)
O7-C1-C6	117.8(3)	C26-N34-C43	109.9(2)
C1-C2-C3	120.8(3)	C42-N34-C43	112.9(2)
C1-C2-H2	119.6	C26-N34-Na1	107.14(17)
C3-C2-H2	119.6	C42-N34-Na1	106.74(17)
C4-C3-C2	119.4(3)	C43-N34-Na1	103.41(16)
C4-C3-H3	120.3	N33-C35-C36	114.0(2)
C2-C3-H3	120.3	N33-C35-H35A	108.8
C3-C4-C5	120.0(3)	C36-C35-H35A	108.8
C3-C4-H4	120.0	N33-C35-H35B	108.8
C5-C4-H4	120.0	C36-C35-H35B	108.8
C4-C5-C6	121.7(3)	H35A-C35-H35B	107.7
C4-C5-H5	119.1	O37-C36-C35	108.9(2)
C6-C5-H5	119.1	O37-C36-H36A	109.9
C5-C6-C1	117.3(3)	C35-C36-H36A	109.9
C5-C6-N12	123.1(3)	O37-C36-H36B	109.9
C1-C6-N12	119.6(3)	C35-C36-H36B	109.9
C1-O7-C8	116.8(2)	H36A-C36-H36B	108.3
O7-C8-C9	108.3(2)	C38-O37-C36	111.4(2)
O7-C8-H8A	110.0	C38-O37-Na1	111.87(17)
C9-C8-H8A	110.0	C36-O37-Na1	118.93(17)
O7-C8-H8B	110.0	O37-C38-C39	110.5(3)
C9-C8-H8B	110.0	O37-C38-H38A	109.6
H8A-C8-H8B	108.4	C39-C38-H38A	109.6
O10-C9-C8	114.0(3)	O37-C38-H38B	109.6
O10-C9-H9A	108.7	C39-C38-H38B	109.6

C8-C9-H9A	108.7	H38A-C38-H38B	108.1
O10-C9-H9B	108.7	O40-C39-C38	110.0(3)
C8-C9-H9B	108.7	O40-C39-H39A	109.7
H9A-C9-H9B	107.6	C38-C39-H39A	109.7
C11-O10-C9	112.6(3)	O40-C39-H39B	109.7
O10-C11-H11A	109.5	C38-C39-H39B	109.7
O10-C11-H11B	109.5	H39A-C39-H39B	108.2
H11A-C11-H11B	109.5	C41-O40-C39	112.1(2)
O10-C11-H11C	109.5	C41-O40-Na1	117.57(17)
H11A-C11-H11C	109.5	C39-O40-Na1	109.03(17)
H11B-C11-H11C	109.5	O40-C41-C42	108.7(2)
C6-N12-C16	116.3(2)	O40-C41-H41A	110.0
C6-N12-C13	114.0(2)	C42-C41-H41A	110.0
C16-N12-C13	114.4(2)	O40-C41-H41B	110.0
N12-C13-C14	114.5(2)	C42-C41-H41B	110.0
N12-C13-H13A	108.6	H41A-C41-H41B	108.3
C14-C13-H13A	108.6	N34-C42-C41	112.2(2)
N12-C13-H13B	108.6	N34-C42-H42A	109.2
C14-C13-H13B	108.6	C41-C42-H42A	109.2
H13A-C13-H13B	107.6	N34-C42-H42B	109.2
O15-C14-C13	113.8(2)	C41-C42-H42B	109.2
O15-C14-H14A	108.8	H42A-C42-H42B	107.9
C13-C14-H14A	108.8	N34-C43-C44	113.0(2)
O15-C14-H14B	108.8	N34-C43-H43A	109.0
C13-C14-H14B	108.8	C44-C43-H43A	109.0
H14A-C14-H14B	107.7	N34-C43-H43B	109.0
C19-O15-C14	117.3(2)	C44-C43-H43B	109.0
C19-O15-Na1	125.06(17)	H43A-C43-H43B	107.8
C14-O15-Na1	117.02(16)	O45-C44-C43	108.4(2)
N12-C16-C17	113.0(2)	O45-C44-H44A	110.0
N12-C16-H16A	109.0	C43-C44-H44A	110.0
C17-C16-H16A	109.0	O45-C44-H44B	110.0
N12-C16-H16B	109.0	C43-C44-H44B	110.0
C17-C16-H16B	109.0	H44A-C44-H44B	108.4
H16A-C16-H16B	107.8	C46-O45-C44	112.3(2)
O18-C17-C16	112.0(2)	C46-O45-Na1	117.39(17)
O18-C17-H17A	109.2	C44-O45-Na1	122.33(17)
C16-C17-H17A	109.2	O45-C46-C47	108.6(2)
O18-C17-H17B	109.2	O45-C46-H46A	110.0
C16-C17-H17B	109.2	C47-C46-H46A	110.0
H17A-C17-H17B	107.9	O45-C46-H46B	110.0
C25-O18-C17	117.8(2)	C47-C46-H46B	110.0

C25-O18-Na1	117.35(16)	H46A-C46-H46B	108.3
C17-O18-Na1	119.32(16)	O48-C47-C46	108.7(2)
O15-C19-C24	124.0(3)	O48-C47-H47A	109.9
O15-C19-C20	115.8(2)	C46-C47-H47A	109.9
C24-C19-C20	120.2(3)	O48-C47-H47B	109.9
C21-C20-C19	118.3(3)	C46-C47-H47B	109.9
C21-C20-N33	122.0(3)	H47A-C47-H47B	108.3
C19-C20-N33	119.6(3)	C47-O48-C49	111.8(2)
C22-C21-C20	121.6(3)	C47-O48-Na1	115.59(17)
C22-C21-H21	119.2	C49-O48-Na1	118.55(17)
C20-C21-H21	119.2	O48-C49-C50	108.7(2)
C21-C22-C23	119.9(3)	O48-C49-H49A	109.9
C21-C22-H22	120.0	C50-C49-H49A	109.9
C23-C22-H22	120.0	O48-C49-H49B	109.9
C22-C23-C24	119.2(3)	C50-C49-H49B	109.9
C22-C23-C31	121.4(3)	H49A-C49-H49B	108.3
C24-C23-C31	119.5(3)	N33-C50-C49	111.1(3)
C19-C24-C23	120.6(3)	N33-C50-H50A	109.4
C19-C24-H24	119.7	C49-C50-H50A	109.4
C23-C24-H24	119.7	N33-C50-H50B	109.4
O18-C25-C30	123.8(3)	C49-C50-H50B	109.4
O18-C25-C26	115.3(3)	H50A-C50-H50B	108.0
C30-C25-C26	120.9(3)	Cl2-C1L-Cl1	113.6(2)
C27-C26-C25	118.0(3)	Cl2-C1L-H1LA	108.8
C27-C26-N34	124.1(3)	Cl1-C1L-H1LA	108.8
C25-C26-N34	117.9(2)	Cl2-C1L-H1LB	108.8
C26-C27-C28	121.2(3)	Cl1-C1L-H1LB	108.8
		H1LA-C1L-H1LB	107.7

Table S4: Torsion angles [°] for compound 2.

atoms	angle	atoms	angle
O7-C1-C2-C3	-176.5(3)	C25-C26-C27-C28	-1.0(4)
C6-C1-C2-C3	-2.2(5)	N34-C26-C27-C28	178.6(3)
C1-C2-C3-C4	2.2(5)	C26-C27-C28-C29	-2.5(5)
C2-C3-C4-C5	-0.8(5)	C27-C28-C29-C30	2.8(5)
C3-C4-C5-C6	-0.7(5)	C27-C28-C29-C32	-175.9(3)
C4-C5-C6-C1	0.7(4)	O18-C25-C30-C29	174.9(3)
C4-C5-C6-N12	-180.0(3)	C26-C25-C30-C29	-3.9(4)
C2-C1-C6-C5	0.7(4)	C28-C29-C30-C25	0.4(4)
O7-C1-C6-C5	175.2(2)	C32-C29-C30-C25	179.1(3)
C2-C1-C6-N12	-178.6(3)	C21-C20-N33-C50	60.0(4)
O7-C1-C6-N12	-4.1(4)	C19-C20-N33-C50	-121.1(3)
C2-C1-O7-C8	-53.2(4)	C21-C20-N33-C35	-66.9(4)
C6-C1-O7-C8	132.3(3)	C19-C20-N33-C35	112.0(3)
C1-O7-C8-C9	162.7(3)	C21-C20-N33-Na1	172.3(2)
O7-C8-C9-O10	-68.2(3)	C19-C20-N33-Na1	-8.8(3)
C8-C9-O10-C11	-69.6(4)	C27-C26-N34-C42	26.7(4)
C5-C6-N12-C16	-12.7(4)	C25-C26-N34-C42	-153.7(3)
C1-C6-N12-C16	166.5(2)	C27-C26-N34-C43	-102.7(3)
C5-C6-N12-C13	123.6(3)	C25-C26-N34-C43	76.9(3)
C1-C6-N12-C13	-57.1(3)	C27-C26-N34-Na1	145.6(3)
C6-N12-C13-C14	116.7(3)	C25-C26-N34-Na1	-34.8(3)
C16-N12-C13-C14	-106.1(3)	C20-N33-C35-C36	-173.1(3)
N12-C13-C14-O15	95.2(3)	C50-N33-C35-C36	60.6(3)
C13-C14-O15-C19	81.1(3)	Na1-N33-C35-C36	-46.6(3)
C13-C14-O15-Na1	-107.2(2)	N33-C35-C36-O37	56.7(3)
C6-N12-C16-C17	-163.6(2)	C35-C36-O37-C38	-168.7(2)
C13-N12-C16-C17	60.2(3)	C35-C36-O37-Na1	-36.3(3)
N12-C16-C17-O18	60.9(3)	C36-O37-C38-C39	88.6(3)
C16-C17-O18-C25	79.5(3)	Na1-O37-C38-C39	-47.3(3)
C16-C17-O18-Na1	-127.3(2)	O37-C38-C39-O40	64.2(3)
C14-O15-C19-C24	-7.9(4)	C38-C39-O40-C41	86.8(3)
Na1-O15-C19-C24	-178.9(2)	C38-C39-O40-Na1	-45.2(3)
C14-O15-C19-C20	171.8(2)	C39-O40-C41-C42	-157.9(2)
Na1-O15-C19-C20	0.8(3)	Na1-O40-C41-C42	-30.4(3)
O15-C19-C20-C21	-175.5(3)	C26-N34-C42-C41	63.0(3)
C24-C19-C20-C21	4.2(4)	C43-N34-C42-C41	-169.1(2)
O15-C19-C20-N33	5.5(4)	Na1-N34-C42-C41	-56.1(3)
C24-C19-C20-N33	-174.8(3)	O40-C41-C42-N34	59.5(3)

C19-C20-C21-C22	-2.9(5)	C26-N34-C43-C44	-171.7(2)
N33-C20-C21-C22	176.0(3)	C42-N34-C43-C44	57.4(3)
C20-C21-C22-C23	-1.0(5)	Na1-N34-C43-C44	-57.5(2)
C21-C22-C23-C24	3.5(5)	N34-C43-C44-O45	50.0(3)
C21-C22-C23-C31	-174.3(3)	C43-C44-O45-C46	-161.7(2)
O15-C19-C24-C23	178.0(3)	C43-C44-O45-Na1	-13.7(3)
C20-C19-C24-C23	-1.7(4)	C44-O45-C46-C47	-174.5(3)
C22-C23-C24-C19	-2.2(4)	Na1-O45-C46-C47	35.8(3)
C31-C23-C24-C19	175.7(3)	O45-C46-C47-O48	-52.9(3)
C17-O18-C25-C30	6.6(4)	C46-C47-O48-C49	-173.4(2)
Na1-O18-C25-C30	-147.2(2)	C46-C47-O48-Na1	46.8(3)
C17-O18-C25-C26	-174.5(2)	C47-O48-C49-C50	-157.8(3)
Na1-O18-C25-C26	31.7(3)	Na1-O48-C49-C50	-19.4(3)
O18-C25-C26-C27	-174.7(3)	C20-N33-C50-C49	59.3(3)
C30-C25-C26-C27	4.2(4)	C35-N33-C50-C49	-176.4(2)
O18-C25-C26-N34	5.6(4)	Na1-N33-C50-C49	-63.9(2)
C30-C25-C26-N34	-175.4(3)	O48-C49-C50-N33	60.8(3)

3. NMR Spectra of compund 1

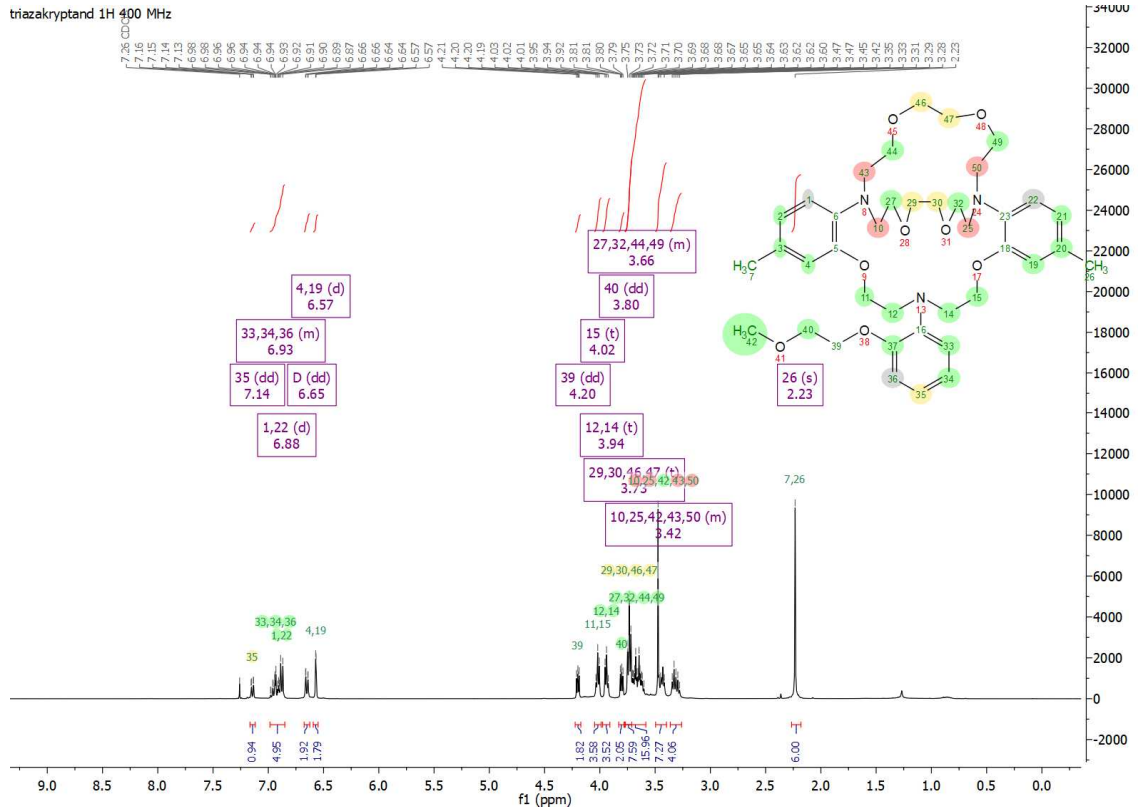


Figure S1: 1H NMR spectrum of compound 1.

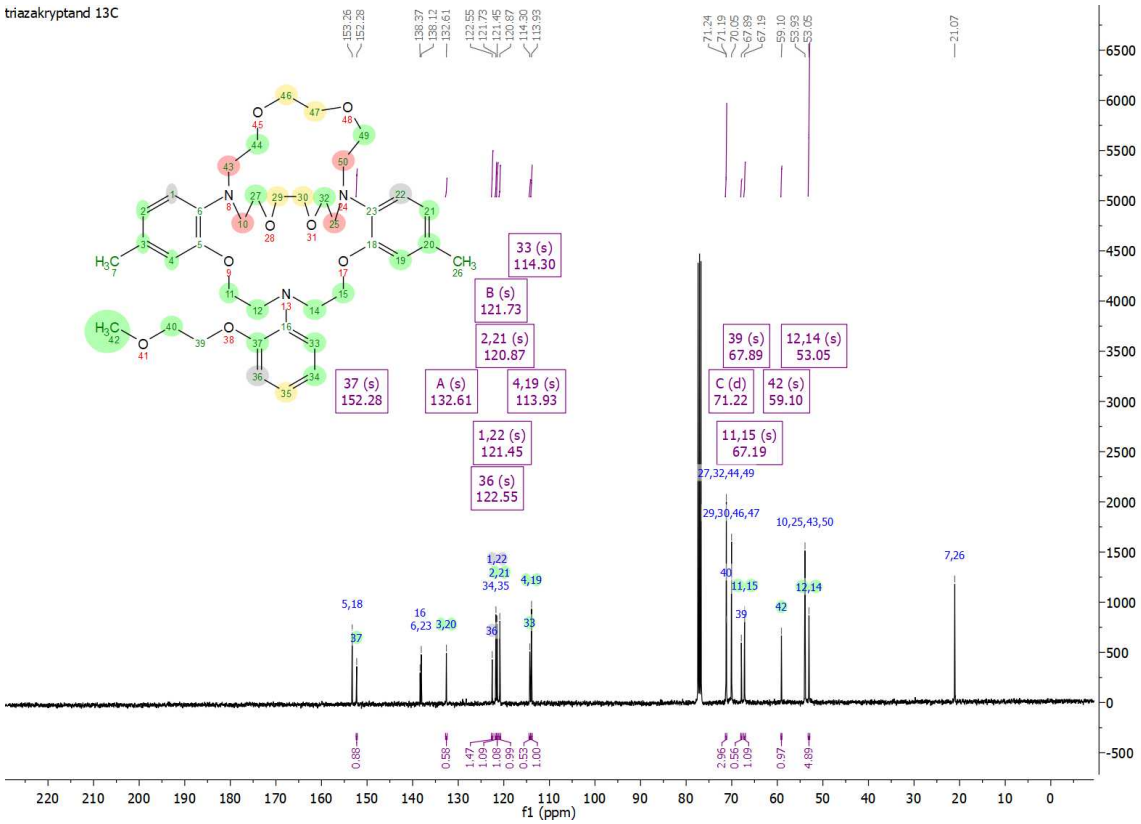


Figure S2: 13C NMR spectrum of compound 1.

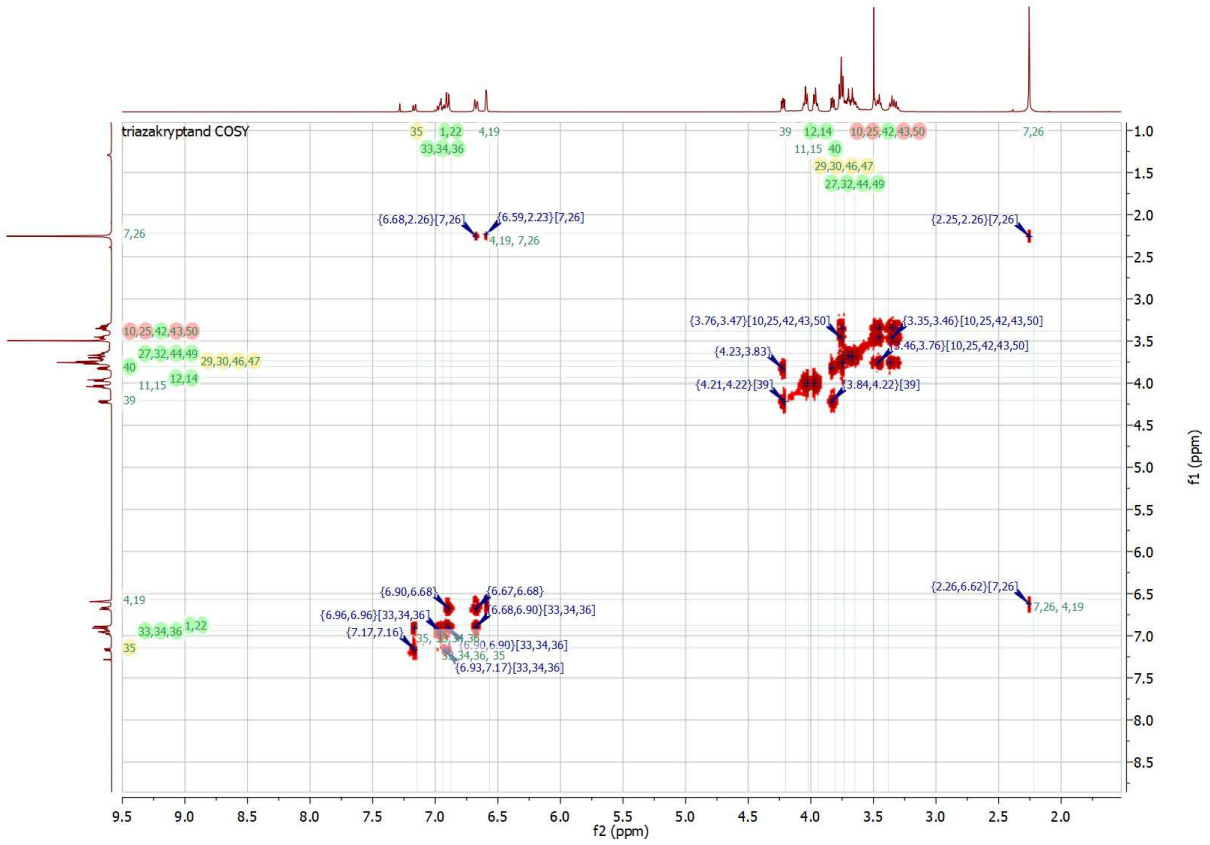


Figure S3: 1H- COSY NMR spectrum of compound 1.

Figure S4: 1H-13C HSQC spectrum of compound 1.

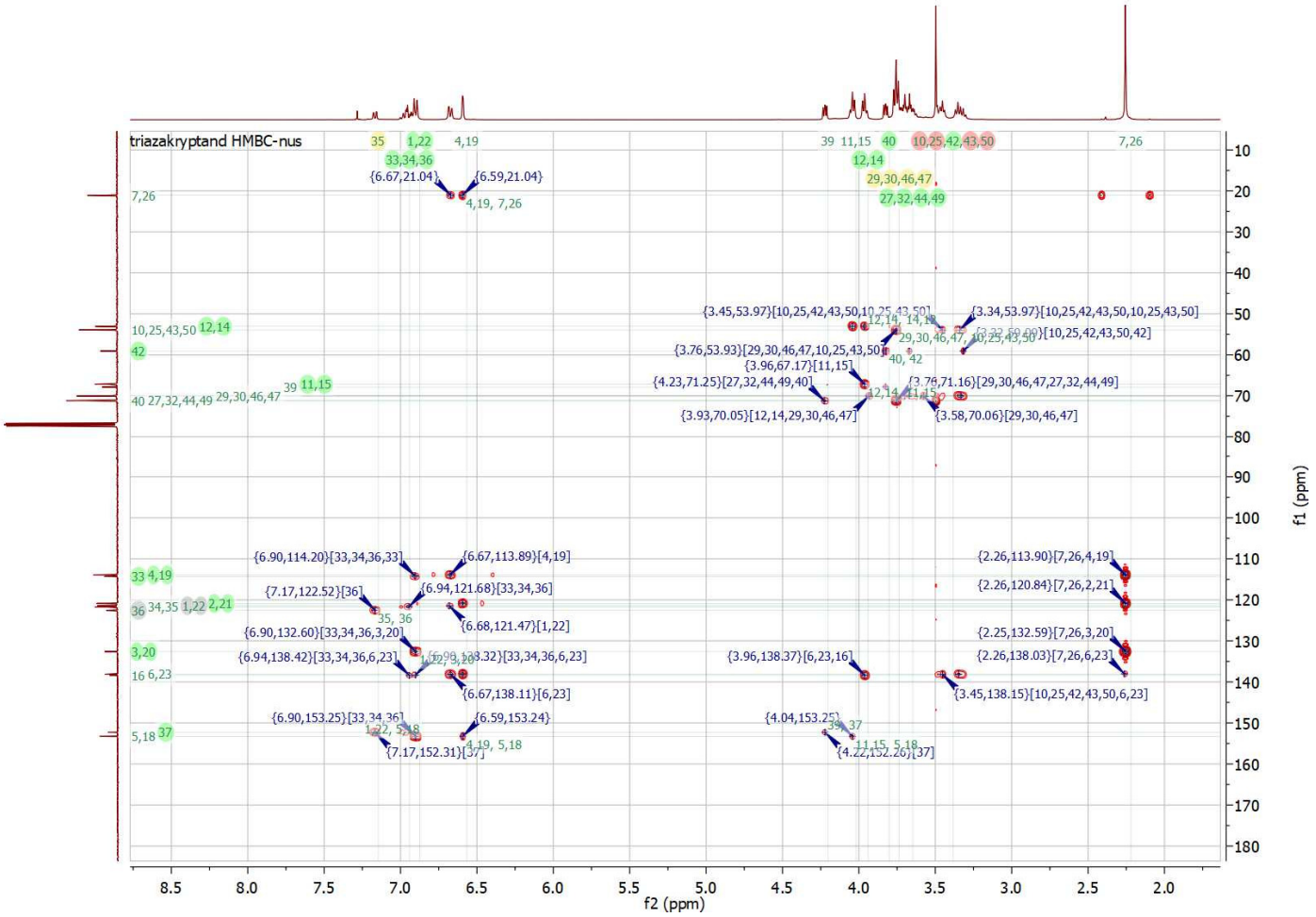


Figure S5: 1H-13C HMBC spectrum of compound 1.

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