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Crystal structure and characterization of a co-product in the syntheses of a Schiff base give evidence of its zwitterionic nature in the solid state.

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Electronic Supplementary Information

Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for (o-VA)$_2$TPNH2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C(1)	2513(3)	6235(3)	-2398(2)	35(1)
C(11)	2499(3)	3704(3)	-2371(2)	34(1)
C(12)	1703(3)	2099(3)	-2687(2)	39(1)
C(13)	142(4)	1331(3)	-3555(3)	50(1)
C(14)	-634(3)	2138(4)	-4080(3)	55(1)
C(15)	115(3)	3702(3)	-3742(2)	47(1)
C(16)	1703(3)	4510(3)	-2878(2)	37(1)
C(17)	1829(5)	-164(3)	-2322(3)	58(1)
O(1)	4048(2)	4408(2)	-1521(2)	37(1)
O(11)	2591(3)	1459(2)	-2066(2)	48(1)
C(2)	4870(3)	6051(2)	-1382(2)	35(1)
C(21)	4562(3)	6812(3)	-3382(2)	37(1)
C(22)	5125(3)	7212(3)	-4395(2)	44(1)
C(23)	6522(4)	7069(3)	-4526(3)	53(1)
C(24)	7343(4)	6549(4)	-3673(3)	54(1)
C(25)	6811(3)	6190(3)	-2666(3)	45(1)
C(26)	5416(3)	6339(2)	-2512(2)	37(1)
C(27)	4717(7)	8111(5)	-6195(4)	77(1)
O(2)	3166(2)	6940(2)	-3299(2)	40(1)
O(21)	4207(3)	7681(3)	-5161(2)	60(1)
C(3)	3252(3)	6557(3)	-114(2)	40(1)
C(31)	2443(3)	7548(3)	211(2)	37(1)
C(32)	641(3)	7022(2)	-68(2)	36(1)
C(33)	455(4)	8384(4)	464(3)	57(1)
C(34)	1855(5)	9665(3)	1026(3)	58(1)
S	3545(1)	9423(1)	981(1)	58(1)
N	3830(2)	6774(2)	-1217(2)	34(1)

Table S2. Full bond lengths [Å] and angles [º] for (o-VA)$_2$TPNH2.

C(1)-O(2)	1.438(3)	O(11)-C(12)-C(11)	114.5(2)
C(1)-N	1.453(3)	C(13)-C(12)-C(11)	118.9(2)
C(1)-C(16)	1.516(3)	C(12)-C(13)-C(14)	120.2(3)
C(11)-O(1)	1.369(3)	C(15)-C(14)-C(13)	121.0(2)
C(11)-C(16)	1.392(3)	C(14)-C(15)-C(16)	120.1(3)
C(11)-C(12)	1.409(3)	C(11)-C(16)-C(15)	119.0(2)
C(12)-O(11)	1.370(3)	C(11)-C(16)-C(1)	119.2(2)
C(12)-C(13)	1.384(4)	C(15)-C(16)-C(1)	121.6(2)
C(13)-C(14)	1.388(5)	C(11)-O(1)-C(2)	112.83(16)
C(14)-C(15)	1.371(4)	C(12)-O(11)-C(17)	117.1(2)
C(15)-C(16)	1.402(3)	N-C(2)-O(1)	112.19(18)
C(17)-O(11)	1.429(3)	N-C(2)-C(26)	109.10(18)
O(1)-C(2)	1.468(3)	O(1)-C(2)-C(26)	110.54(18)
C(2)-N	1.432(3)	O(2)-C(21)-C(26)	122.5(2)
C(2)-C(26)	1.503(3)	O(2)-C(21)-C(22)	116.9(2)
C(21)-O(2)	1.370(3)	C(26)-C(21)-C(22)	120.6(2)
C(21)-C(26)	1.385(3)	O(21)-C(22)-C(23)	126.4(2)
C(21)-C(22)	1.412(3)	O(21)-C(22)-C(21)	114.9(2)
C(22)-O(21)	1.345(4)	C(23)-C(22)-C(21)	118.6(3)
C(22)-C(23)	1.393(4)	C(24)-C(23)-C(22)	120.5(3)
C(23)-C(24)	1.387(5)	C(25)-C(24)-C(23)	120.8(3)
C(24)-C(25)	1.382(4)	C(24)-C(25)-C(26)	119.6(3)
C(25)-C(26)	1.402(3)	C(21)-C(26)-C(25)	119.9(2)
C(27)-O(21)	1.422(4)	C(21)-C(26)-C(2)	119.3(2)
C(3)-N	1.476(3)	C(25)-C(26)-C(2)	120.8(2)
C(3)-C(31)	1.496(3)	C(21)-O(2)-C(1)	112.59(17)
C(31)-C(32)	1.484(3)	C(22)-O(21)-C(27)	117.6(3)
C(31)-S	1.690(2)	N-C(3)-C(31)	112.61(18)
C(32)-C(33)	1.474(4)	C(32)-C(31)-C(3)	125.2(2)
C(33)-C(34)	1.340(5)	C(32)-C(31)-S	112.92(17)
C(34)-S	1.685(4)	C(3)-C(31)-S	121.91(19)
		C(33)-C(32)-C(31)	105.0(2)
O(2)-C(1)-N	108.88(18)	C(34)-C(33)-C(32)	115.9(3)
O(2)-C(1)-C(16)	111.82(18)	C(33)-C(34)-S	112.9(2)
N-C(1)-C(16)	111.34(18)	C(34)-S-C(31)	93.26(14)
O(1)-C(11)-C(16)	122.6(2)	C(2)-N-C(1)	107.56(18)
O(1)-C(11)-C(12)	116.7(2)	C(2)-N-C(3)	112.45(18)
C(16)-C(11)-C(12)	120.7(2)	C(1)-N-C(3)	114.02(19)
O(11)-C(12)-C(13)	126.6(2)		

Table S3. Anisotropic displacement parameters ($Å^2 \times 10^3$) for (o-VA)$_2$TPNH2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	34(1)	40(1)	36(1)	14(1)	13(1)	21(1)
C(11)	32(1)	36(1)	32(1)	8(1)	11(1)	13(1)
C(12)	43(1)	37(1)	39(1)	10(1)	17(1)	16(1)
C(13)	46(1)	38(1)	49(1)	3(1)	13(1)	7(1)
C(14)	36(1)	59(2)	46(1)	3(1)	1(1)	9(1)
C(15)	39(1)	59(2)	41(1)	13(1)	7(1)	22(1)
C(16)	34(1)	41(1)	35(1)	10(1)	11(1)	17(1)
C(17)	73(2)	34(1)	68(2)	15(1)	26(2)	21(1)
O(1)	32(1)	32(1)	43(1)	10(1)	5(1)	15(1)
O(11)	51(1)	35(1)	59(1)	14(1)	15(1)	19(1)
C(2)	30(1)	31(1)	38(1)	6(1)	5(1)	12(1)
C(21)	37(1)	32(1)	40(1)	7(1)	14(1)	12(1)
C(22)	46(1)	40(1)	42(1)	9(1)	19(1)	13(1)
C(23)	51(2)	48(1)	55(2)	7(1)	30(1)	12(1)
C(24)	40(1)	52(2)	65(2)	3(1)	24(1)	17(1)
C(25)	33(1)	42(1)	55(1)	5(1)	12(1)	15(1)
C(26)	32(1)	31(1)	42(1)	5(1)	10(1)	12(1)
C(27)	109(3)	78(2)	60(2)	38(2)	47(2)	37(2)
O(2)	41(1)	47(1)	41(1)	20(1)	16(1)	24(1)
O(21)	74(2)	72(1)	52(1)	34(1)	34(1)	37(1)
C(3)	50(1)	43(1)	38(1)	15(1)	18(1)	27(1)
C(31)	42(1)	38(1)	33(1)	11(1)	15(1)	19(1)
C(32)	36(1)	29(1)	50(1)	11(1)	17(1)	20(1)
C(33)	55(2)	65(2)	69(2)	21(2)	32(1)	37(1)
C(34)	76(2)	44(1)	60(2)	8(1)	28(2)	33(1)
S	58(1)	48(1)	62(1)	7(1)	17(1)	21(1)
N	36(1)	35(1)	35(1)	11(1)	11(1)	19(1)

Table S4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for $(o\text{-VA})_2$TPNH2.

Atom	x	y	z	U(eq)
H(1)	1678	6557	-2250	41
H(13)	-388	271	-3788	60
H(14)	-1677	1611	-4669	66
H(15)	-432	4226	-4088	56
H(17A)	770	-494	-2191	88
H(17B)	2509	-468	-1766	88
H(17C)	1695	-620	-3180	88
H(2)	5847	6515	-636	42
H(23)	6908	7323	-5190	64
H(24)	8262	6441	-3781	65
H(25)	7376	5852	-2095	54
H(27A)	5817	8921	-5888	116
H(27B)	3986	8452	-6649	116
H(27C)	4694	7250	-6747	116
H(3A)	4182	6782	605	48
H(3B)	2477	5497	-289	48
H(32)	-190	6046	-487	43
H(33)	-572	8356	412	68
H(34)	1891	10591	1402	69

Table S5. Torsion angles [°] for (o-VA)$_2$TPNH2.

O(1)-C(11)-C(12)-O(11)	1.5(3)	O(2)-C(21)-C(26)-C(2)	-4.2(3)
C(16)-C(11)-C(12)-O(11)	-176.4(2)	C(22)-C(21)-C(26)-C(2)	174.7(2)
O(1)-C(11)-C(12)-C(13)	-179.2(2)	C(24)-C(25)-C(26)-C(21)	1.4(4)
C(16)-C(11)-C(12)-C(13)	2.9(3)	C(24)-C(25)-C(26)-C(2)	-176.2(2)
O(11)-C(12)-C(13)-C(14)	177.7(3)	N-C(2)-C(26)-C(21)	-17.7(3)
C(11)-C(12)-C(13)-C(14)	-1.5(4)	O(1)-C(2)-C(26)-C(21)	106.1(2)
C(12)-C(13)-C(14)-C(15)	-0.7(5)	N-C(2)-C(26)-C(25)	159.9(2)
C(13)-C(14)-C(15)-C(16)	1.5(4)	O(1)-C(2)-C(26)-C(25)	-76.3(3)
O(1)-C(11)-C(16)-C(15)	-180.0(2)	C(26)-C(21)-O(2)-C(1)	-12.4(3)
C(12)-C(11)-C(16)-C(15)	-2.2(3)	C(22)-C(21)-O(2)-C(1)	168.6(2)
O(1)-C(11)-C(16)-C(1)	-5.1(3)	N-C(1)-O(2)-C(21)	50.3(2)
C(12)-C(11)-C(16)-C(1)	172.7(2)	C(16)-C(1)-O(2)-C(21)	-73.2(2)
C(14)-C(15)-C(16)-C(11)	0.0(4)	C(23)-C(22)-O(21)-C(27)	-1.6(5)
C(14)-C(15)-C(16)-C(1)	-174.8(2)	C(21)-C(22)-O(21)-C(27)	179.6(3)
O(2)-C(1)-C(16)-C(11)	106.4(2)	N-C(3)-C(31)-C(32)	103.8(3)
N-C(1)-C(16)-C(11)	-15.7(3)	N-C(3)-C(31)-S	-77.6(2)
O(2)-C(1)-C(16)-C(15)	-78.9(3)	C(3)-C(31)-C(32)-C(33)	178.2(2)
N-C(1)-C(16)-C(15)	159.1(2)	S-C(31)-C(32)-C(33)	-0.6(3)
C(16)-C(11)-O(1)-C(2)	-10.2(3)	C(31)-C(32)-C(33)-C(34)	-0.1(4)
C(12)-C(11)-O(1)-C(2)	171.95(19)	C(32)-C(33)-C(34)-S	0.7(4)
C(13)-C(12)-O(11)-C(17)	-0.9(4)	C(33)-C(34)-S-C(31)	-0.8(3)
C(11)-C(12)-O(11)-C(17)	178.3(2)	C(32)-C(31)-S-C(34)	0.8(2)
C(11)-O(1)-C(2)-N	47.8(2)	C(3)-C(31)-S-C(34)	-178.0(2)
C(11)-O(1)-C(2)-C(26)	-74.2(2)	O(1)-C(2)-N-C(1)	-68.6(2)
O(2)-C(21)-C(22)-O(21)	0.2(3)	C(26)-C(2)-N-C(1)	54.2(2)
C(26)-C(21)-C(22)-O(21)	-178.8(2)	O(1)-C(2)-N-C(3)	57.7(2)
O(2)-C(21)-C(22)-C(23)	-178.8(2)	C(26)-C(2)-N-C(3)	-179.43(18)
C(26)-C(21)-C(22)-C(23)	2.3(4)	O(2)-C(1)-N-C(2)	-73.7(2)
O(21)-C(22)-C(23)-C(24)	-179.1(3)	C(16)-C(1)-N-C(2)	50.0(2)
C(21)-C(22)-C(23)-C(24)	-0.3(4)	O(2)-C(1)-N-C(3)	160.86(18)
C(22)-C(23)-C(24)-C(25)	-1.2(4)	C(16)-C(1)-N-C(3)	-75.4(2)
C(23)-C(24)-C(25)-C(26)	0.6(4)	C(31)-C(3)-N-C(2)	169.0(2)
O(2)-C(21)-C(26)-C(25)	178.3(2)	C(31)-C(3)-N-C(1)	-68.2(3)
C(22)-C(21)-C(26)-C(25)	-2.8(3)		

Table S6. Hydrogen bond distances [Å] and angles [°] for (o-VA)$_2$TPNH2.

D-H...A	**d(D-H)**	**d(H...A)**	**d(D...A)**	**<(DHA)**
C(3)-H(3A)...O(1)#1	0.97	2.51	3.321(3)	141
C(27)-H(27B)...S#2	0.96	2.99	3.746(4)	136

Symmetry transformations: (#1) -x+1, -y+1, -z; (#2) x, y, z-1.

Table S7. Assignment of the experimental FTIR and Raman spectra of o-HVATPNH2 and calculated frequencies (cm^{-1}). Reactants are included for comparison.

o-HVA			TPNH2			o-HVATPNH2			
FTIR	**Calc.**	**Assignment**	**FTIR**	**Calc.**	**Assignment**	**FTIR**	**Raman**	**Calc.**	**Assignment**
			3369^{vs}	3551	$\nu_{as}\ NH_2$				
			3293^{s}	3476	$\nu_{s}\ NH_2$				
3014^{vw}	3318	ν OH							
						3003^{vw}	3005^{w}	3153	$\nu N \cdots H \cdots O$
2939^{w}		νCH^{aldh}				2937^{vw}			νCH^{aldh}
			2919^{s}	3071	$\nu_{as}\ CH_2$	2923^{sh}	2928^{m}	3045	$\nu_{as}\ CH_2$
2884^{w}	3016	$\nu_{s}\ CH_3$				2888^{vw}	2892^{w}	2998	$\nu_{s}CH_3 + \nu CH^{aldh}$
			2852^{vs}	3036	$\nu_{s}\ CH_2$			2965	$\nu_{s}\ CH_2$
2839^{w}	2943	νCH^{aldh}				2834^{w}	2838^{w}	3000	νCH^{aldh}
1645^{vs}	1704	ν C=O							
						1631^{vs}	1635^{vs}	1685	ν C=N
			1598^{vs}	1665	$\delta\ NH_2$				
1591^{m}	1649 1622	$\nu^{R} + \delta OH$				1583^{sh}	1587^{m}	1660 1618	$[\nu^{R} + \delta N\text{-}H \cdots O]^{o\text{-}HVA}$
1471^{m}	1510	$\delta_{as}\ CH_3$				1462^{vs}	1472^{m}	1505	$\delta_{as}\ CH_3$
1455^{s}	1489	$\delta_{as}\ CH_3$						1493	$\delta_{as}\ CH_3$
1433^{sh}	1480	$\delta_{s}\ CH_3 + \delta$ OH				1433^{sh}	1440^{m}	1497	$[\delta(CH_3 + N\text{-}H \cdots O) + \nu^{R}]^{o\text{-}HVA}$
	1472	$\delta_{s}\ CH_3 + \nu^{R}$						1460	$[\delta(N\text{-}H \cdots O + CH^{R} + CH_3)]^{o\text{-}HVA}$
			1439^{s}	1483	$\delta\ CH_2$	$1415^{m,b}$		1480	δCH_2
			1381^{s}	1377	$\delta CH^{R} + \rho_{r}\ NH_2$	1378^{w}		1394	$[\delta CH^{R}]^{TPNH2}$
1388^{s}	1422	δOH				1361^{m}	1365^{w}	1370	$[\delta N\text{-}H \cdots O + \nu^{R}]^{o\text{-}HVA}$
			1330^{w}	1362	$\rho_{w}\ CH_2$	$1333^{m\text{-}w}$	1337^{s}	1355	$\rho_{w}CH_2$
1327^{s}	1306	$[\nu C\text{-}O]^{ArOH} + \delta CH$				1313^{m}		1315	$[\nu C\text{-}O]^{ArOH} + [\delta CH]^{o\text{-}HVA}$
1270^{sh} 1257^{s}	1284	$\nu C\text{-}OCH_3 + \delta CH^{R}$				1269^{s} 1255^{vs}	1258^{vw}	1282	$[\nu C\text{-}OCH_3 + \delta CH^{R}]^{o\text{-}HVA}$
			1079^{w}	1075	νC-N	1097^{sh}		1050	$\nu C\text{-}N + [\gamma CH]^{aldh}$
			900^{sh}	888	$\rho_{t}\ [NH_2 + CH_2]$	902^{vw}		958	$\rho_{t}\ CH_2$
895^{w}	958	γCH^{R}				884^{vw}		920 882	$[\gamma CH^{R}]^{o\text{-}HVA}$
			849^{w}	840	γCH^{R}	853^{vw}	856^{vw}	842	$[\gamma CH^{R}]^{TPNH2}$
			826^{m}	850	$\rho_{w}\ NH_2$				
838^{m}	822	γ OH				$832^{vs,b}$	838^{w}	851	$\gamma N\text{-}H \cdots O$
			747^{sh}	749	ν S-CH + δC-C-C(CH_2)	750^{md}	757^{w}	762	ν S-CH + δ C-C-C(CH_2)
737^{m}	752	γCH^{R}				736^{s}	735^{m}	740	$[\gamma CH^{R}]^{o\text{-}HVA}$
717^{s}	709	δ^{R}				725^{s}		742	$[\delta^{R}]^{o\text{-}HVA}$
			$698^{s,b}$	707	γCH^{R}	704^{sh}		710	$[\gamma CH^{R}]^{TPNH2}$
			616^{w}	628	δ^{R}	615^{vw}	620^{m}	627	$[\delta^{R}]^{TPNH2}$

***References**: R: ring; ν: stretching; δ: in-plane deformation; γ: out-of-plane deformation; ρ_w: wagging; ρ_r: rocking; ρ_t: twisting; as: asymmetric; s: symmetric. Bands Intensities: vs: very strong; s: strong; m: medium; w: weak; vw: very weak; b: broad; sh: shoulder.*

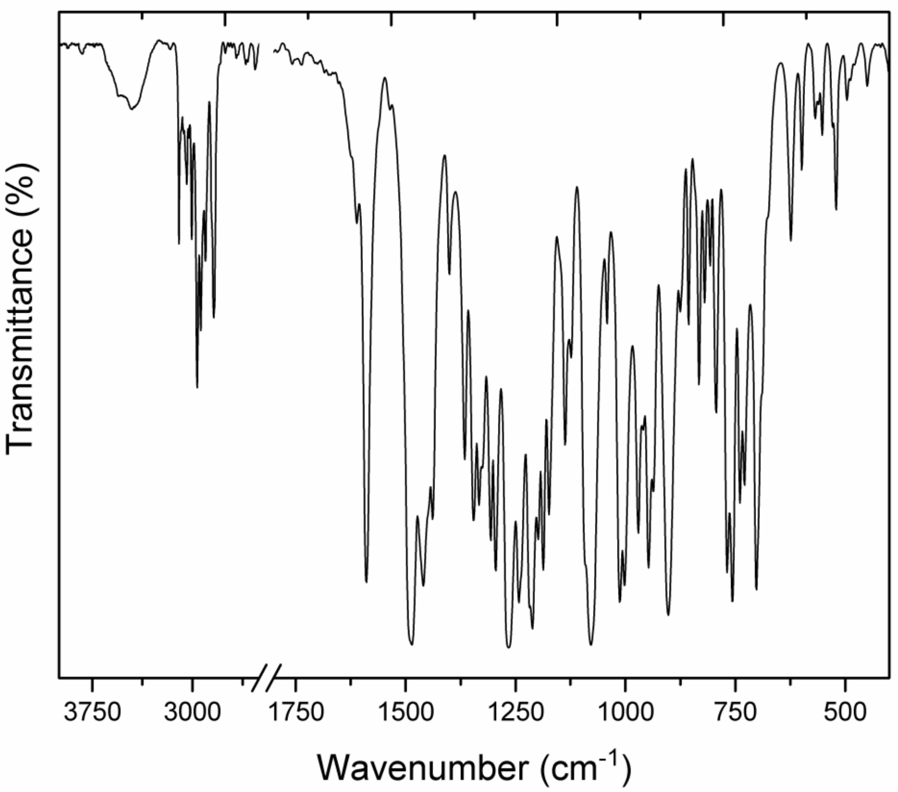
Transmittance (%)
3750
3000
1750
1500
1250
1000
750
500
Wavenumber (cm-1)

Figure S1 FTIR spectrum of (o-VA)$_2$TPNH2

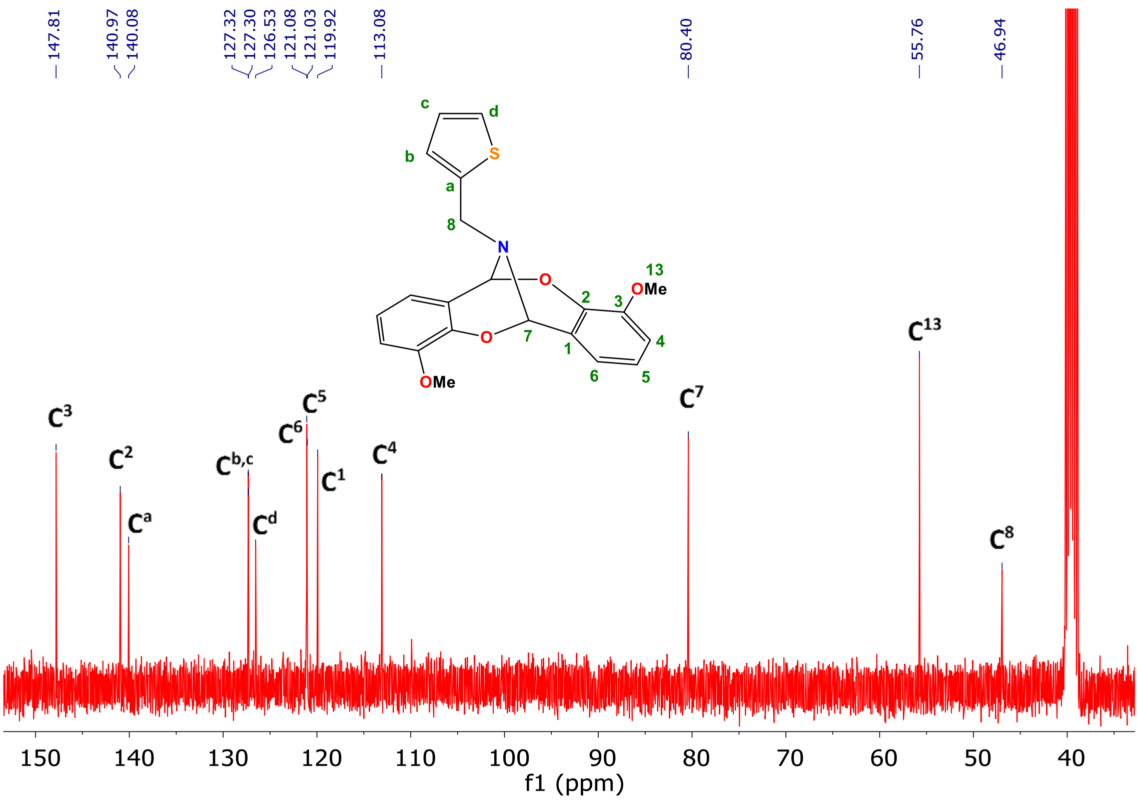

Figure S2. ^{13}C NMR spectrum of (o-VA)$_2$TPNH2 in DMSO-d_6 at room temperature

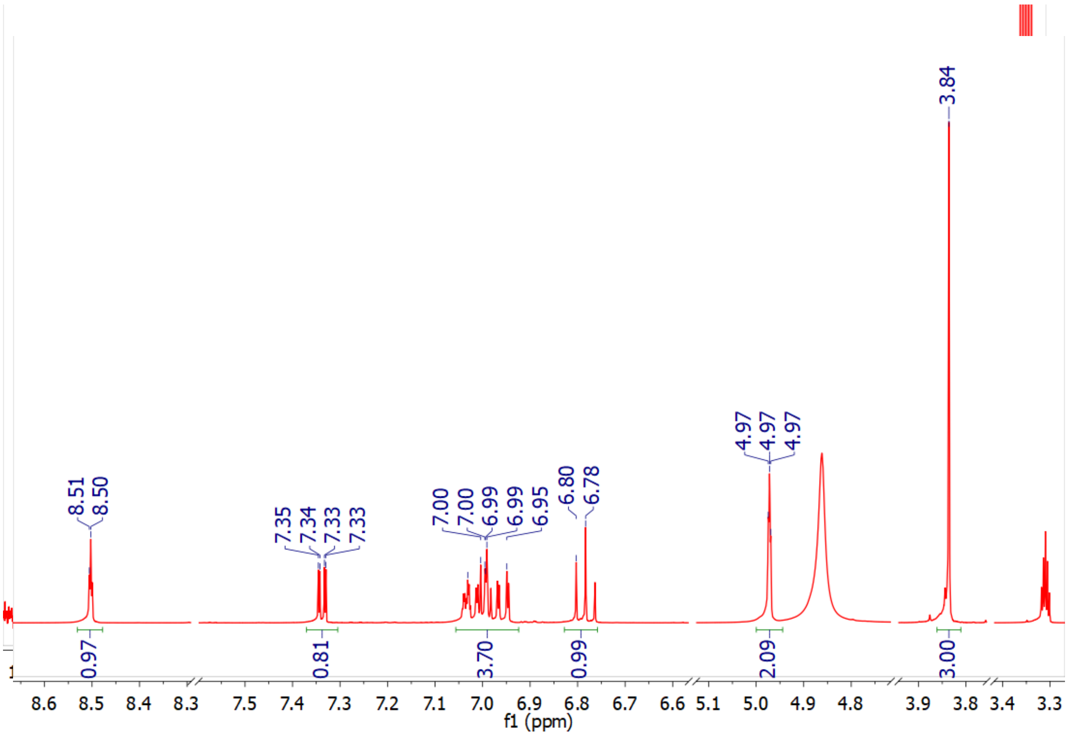

Figura S3. [1]H-NMR spectrum of BS in CD_3OD at 25°C

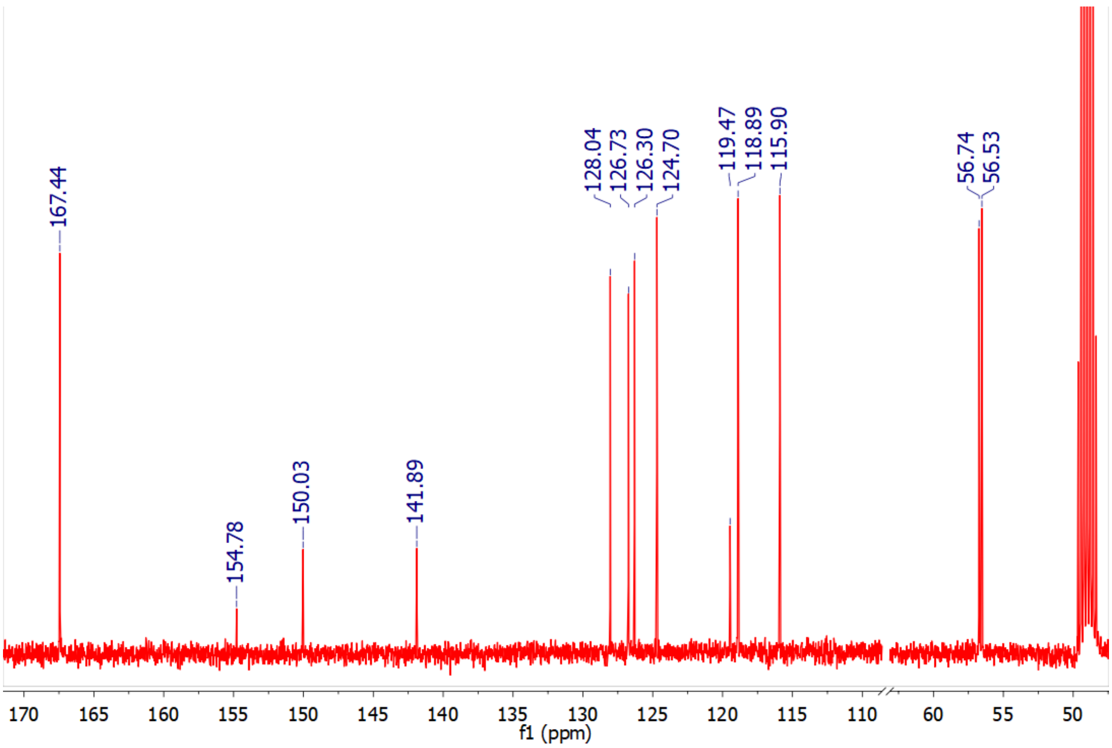

Figure S4. [13]C{[1]H}-NMR spectrum of BS in CD_3OD at 25°

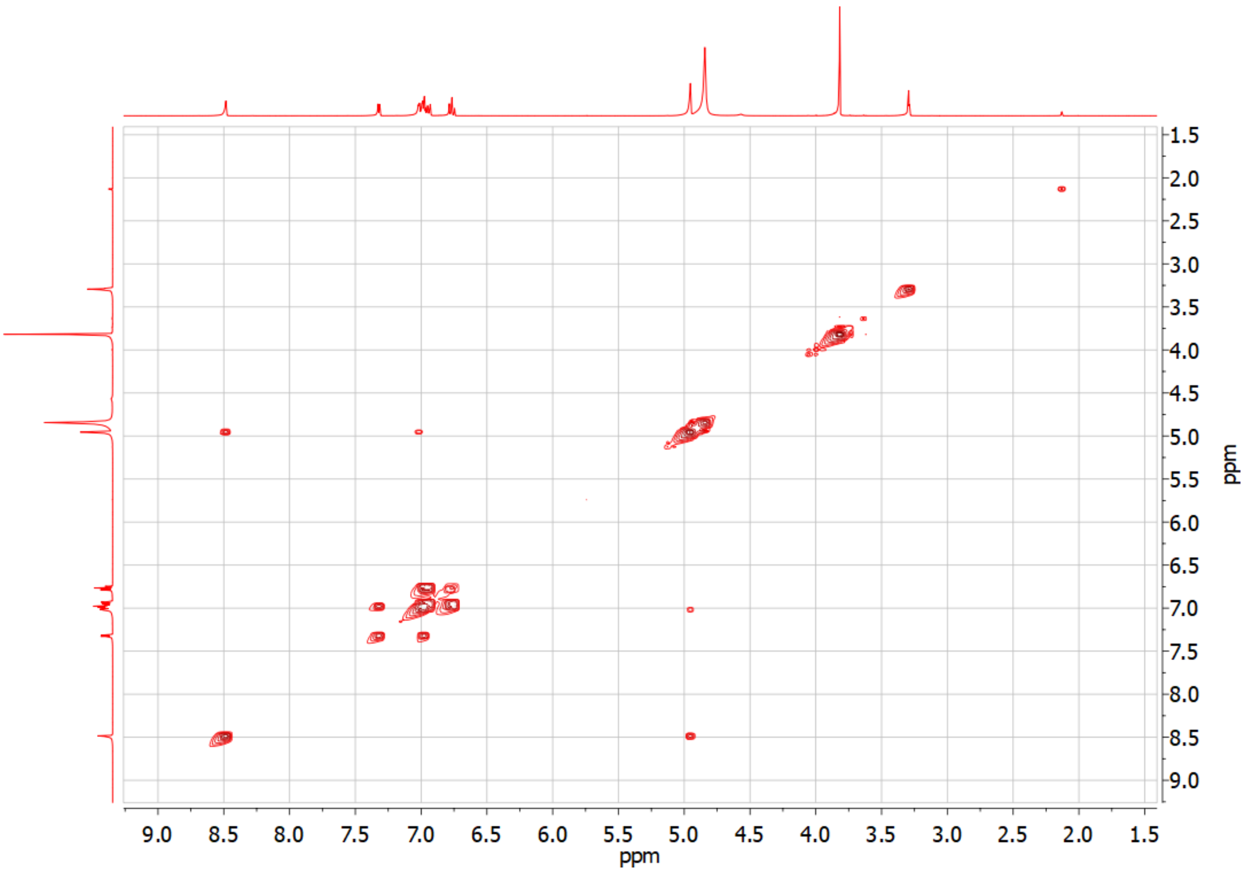

Figure S5. COSY-NMR spectrum of BS in CD_3OD at 25°C

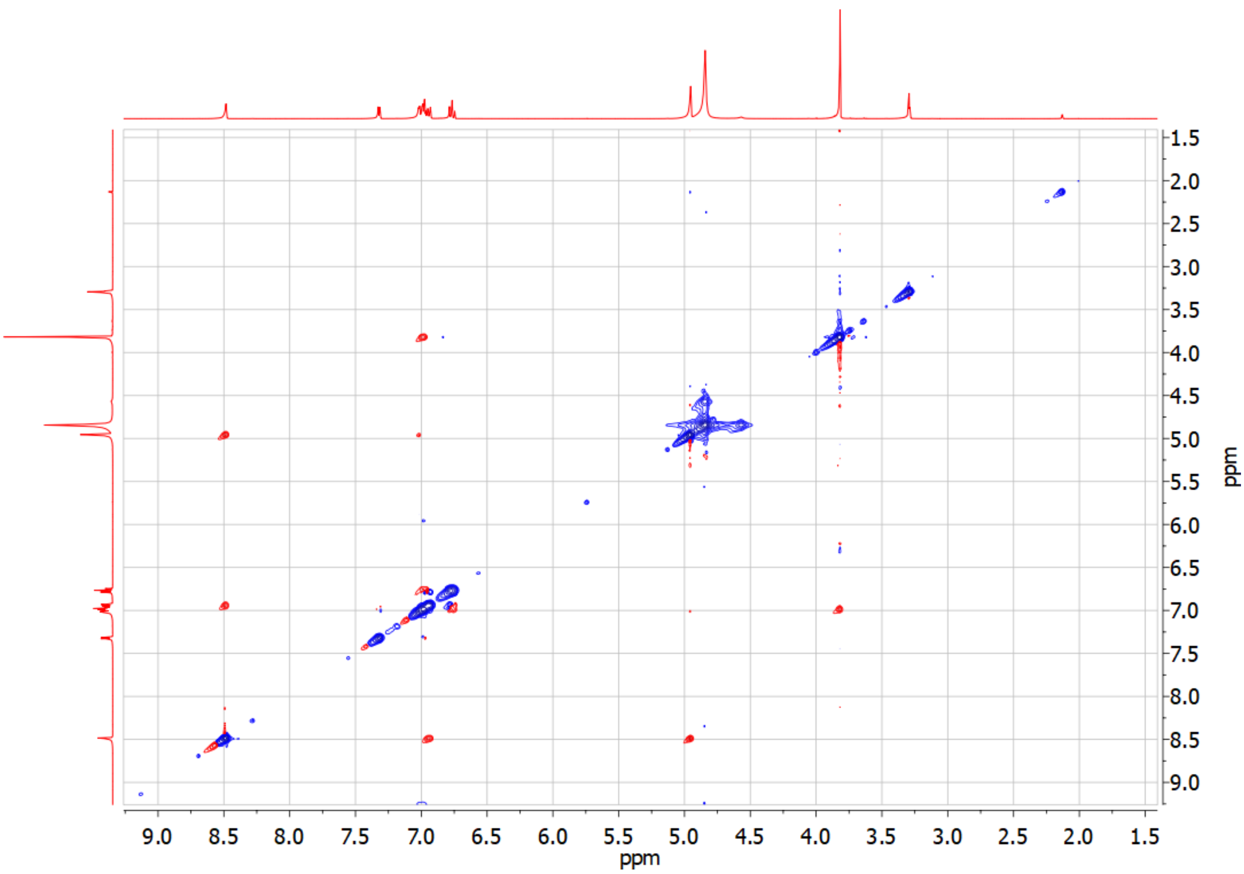

Figure S6. NOESY-NMR spectrum of BS in CD_3OD at 25°C

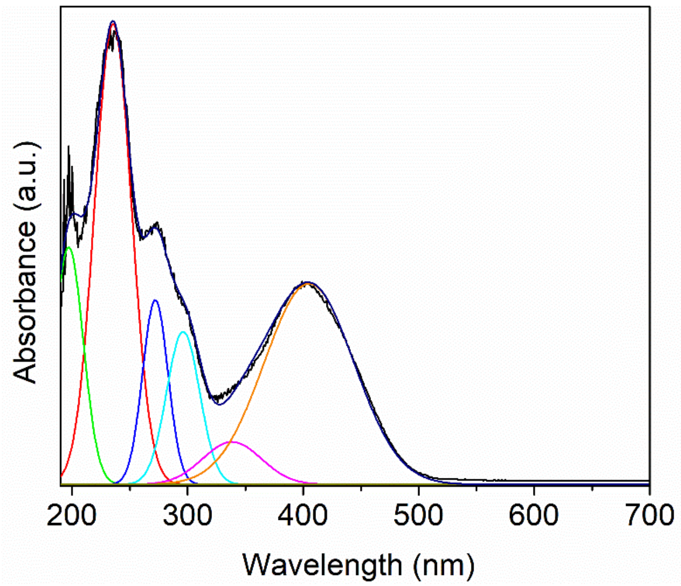

Figure S7. Deconvolved absorption spectra of solid SB registered by DR in 200-700 nm region.