Supplementary Information

‘AND’-based fluorescence scaffold for the dual-analyte detection of ROS/RNS and a second analyte

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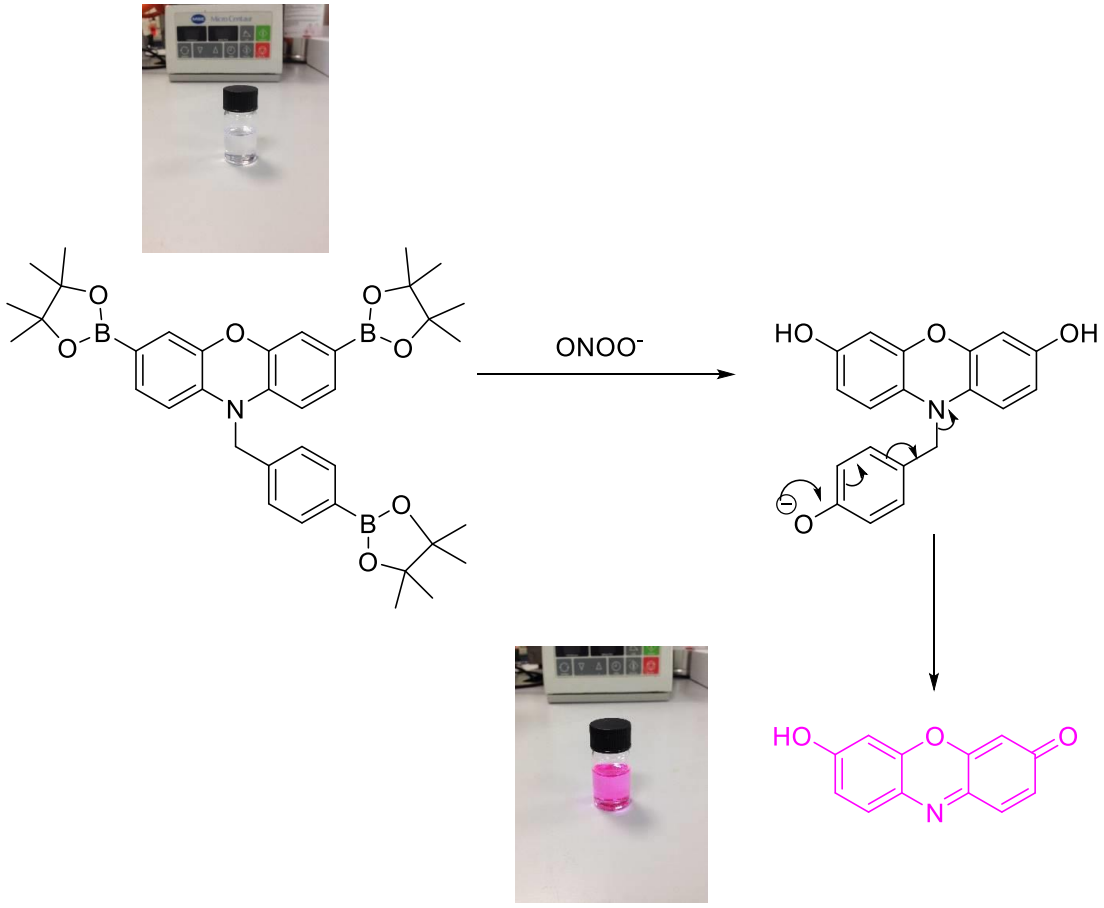
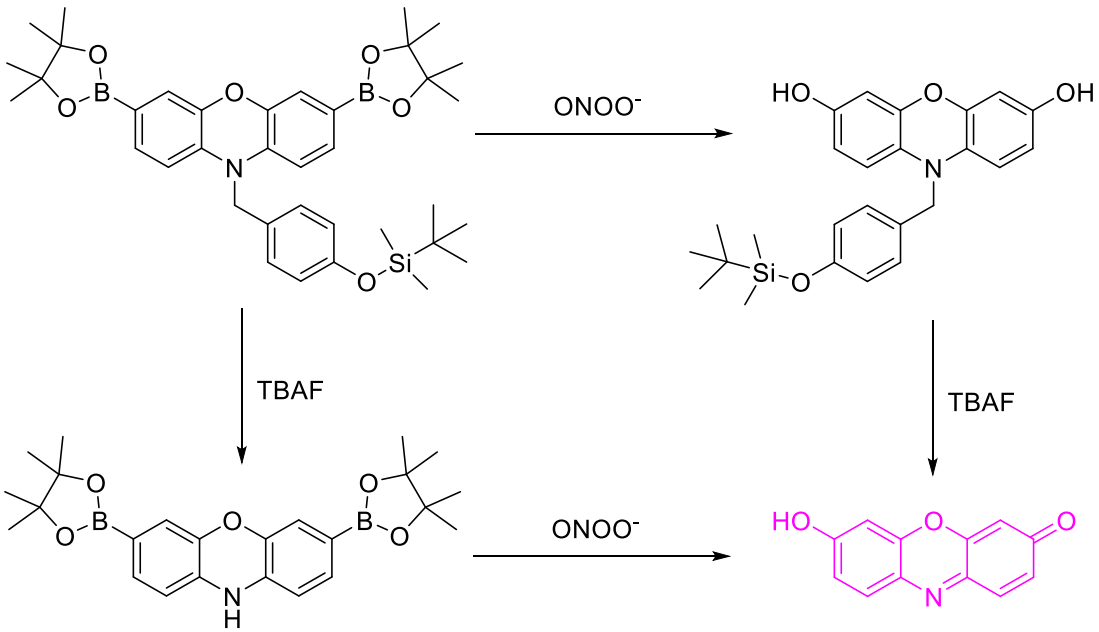
Content

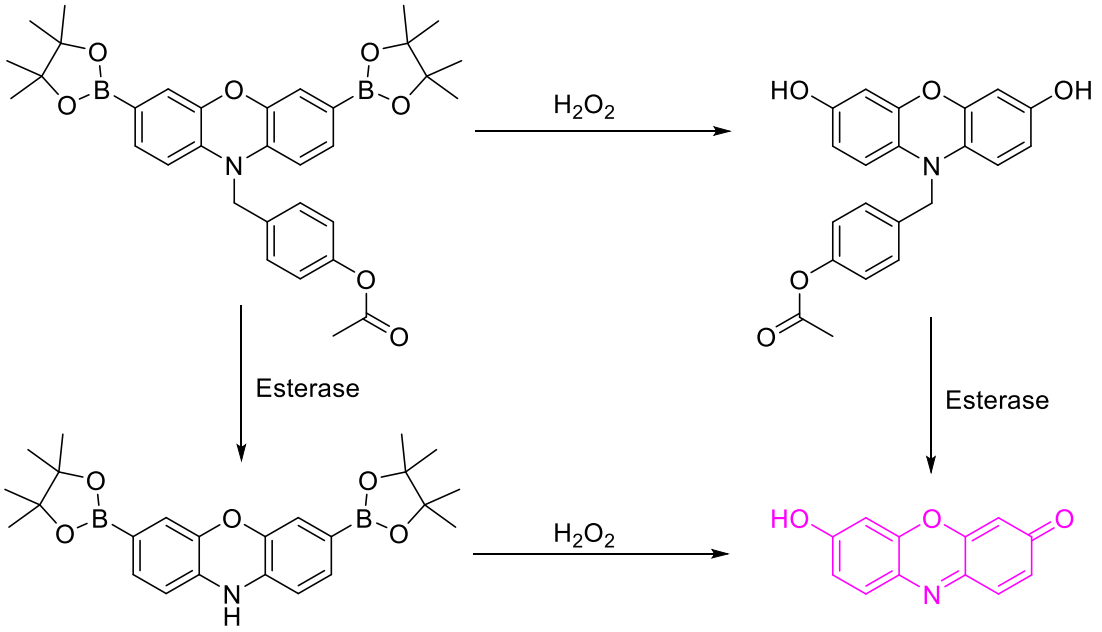
1. Reaction mechanism of pinkments



Scheme S1 – Reaction mechanism of **Pinkment** with the addition of $ONOO^-$



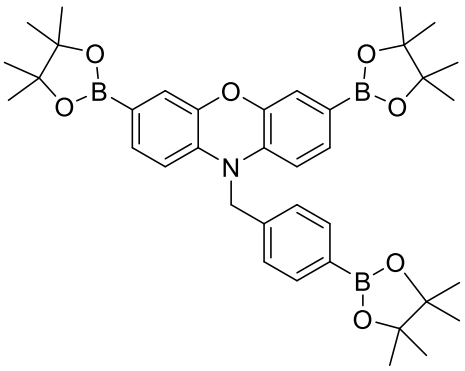
Scheme S2 – Reaction of **Pinkment-OTBS** with F^- and $ONOO^-$



Scheme S3 – Reaction of **Pinkment-OAc** with esterase$^-$ and H_2O_2

2. Fluorescence analysis

Pinkment



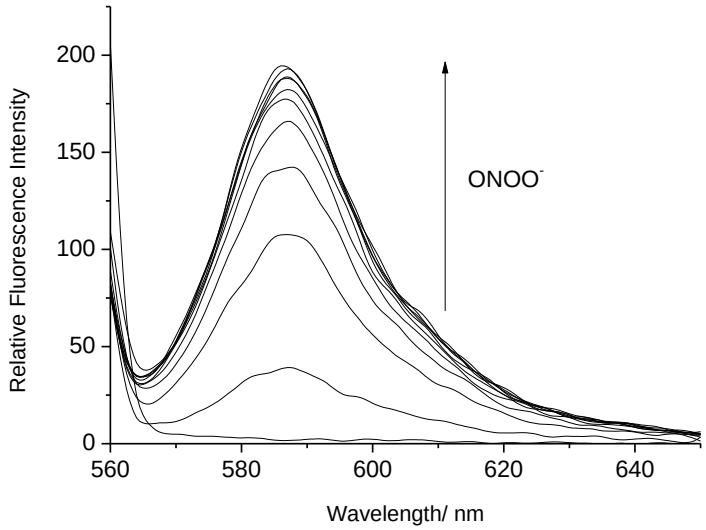


Fig. S1- Fluorescence spectra of **Pinkment** (50 nM) with addition of $ONOO^-$ (0 – 10 μM) in pH 8.2 buffer solution [52 wt% methanol]. Fluorescence intensities were measured with λex = 550 nm with slit widths ex 10 nm and em 10 nm

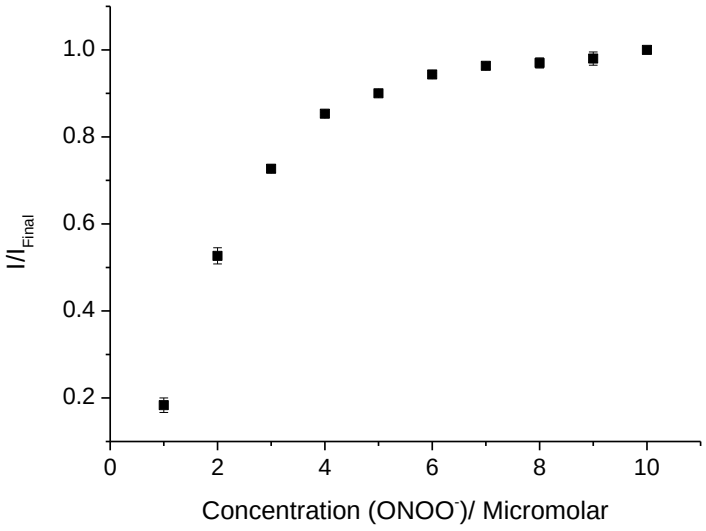


Fig. S2 - Fluorescence intensity changes (I/I_{Final}) with **Pinkment** (50 nM) and additions of $ONOO^-$ (0 – 10 µM) in pH 8.2 buffer solution [52 wt% methanol]. Fluorescence intensities were measured with λex = 550 nm/λem 590 nm with slit widths ex 10 nm and em 10 nm

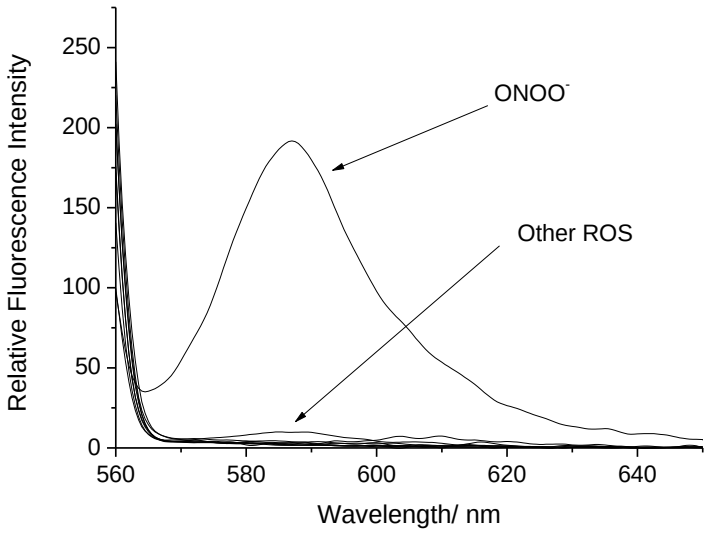


Fig. S3 - Fluorescence spectra of **Pinkment** (50 nM) in the presence of various ROS/RNS: $ONOO^-$ (10 μM, 1 min), ^-OCl (100 μM, 30 min), H_2O_2 (500 μM, 30 min), $ROO^\cdot$ (100 μM, 30 min), $^1O_2$ (100 μM, 1 min), NO (100 μM, 1 min), $^-O_2$ (100 μM, 1 min), OH (100 μM, 1 min) λex 550 nm/ λem 590 nm in pH 8.2 buffer solution [52 wt% methanol] with slit widths ex 10 nm and em 10 nm

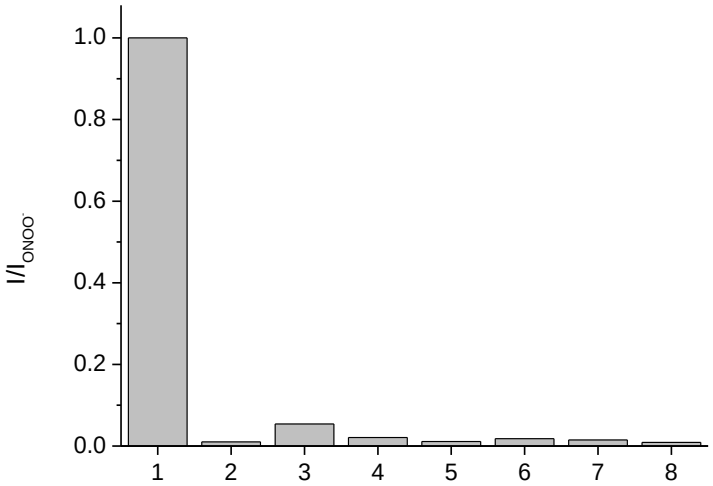
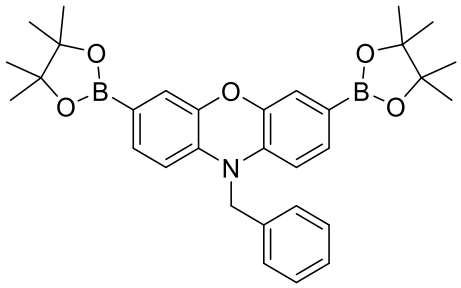


Fig. S4 - Selectivity bar chart of **Pinkment** (50 nM) in the presence of various ROS/RNS: 1 - $ONOO^-$ (10 μM, 1 min), 2 - ^-OCl (100 μM, 30 min), 3 - H_2O_2 (500 μM, 30 min), 4 - $^-O_2$ (100 μM, 1 min), 5 - $ROO^\cdot$ (100 μM, 30 min), 6 - $^\cdot OH$ (100 μM, 1 min), 7 - $^1O_2$ (100 μM, 1 min), 8 - NO (100 μM, 1 min). λex 550 nm/ λem 590 nm in pH 8.2 buffer solution [52 wt% methanol] with slit widths ex 10 nm and em 10 nm

Pinkment-Bn



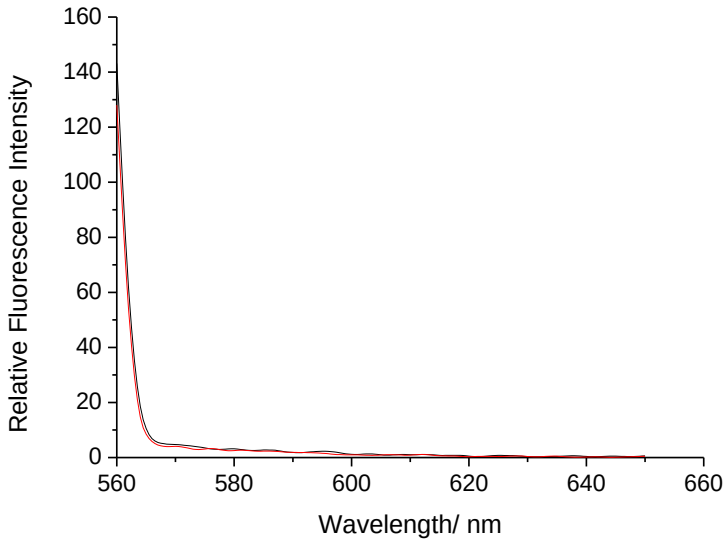


Fig. S5 - Fluorescence spectra of **114** (50 nM) with $ONOO^-$ (10 µM) in pH 8.21 buffer solution [52.1 wt% methanol. Fluorescence intensity were measured with λ_{ex} = 550nm with slit widths ex slit: 10 nm and em slit:10 nm

Pinkment-OH

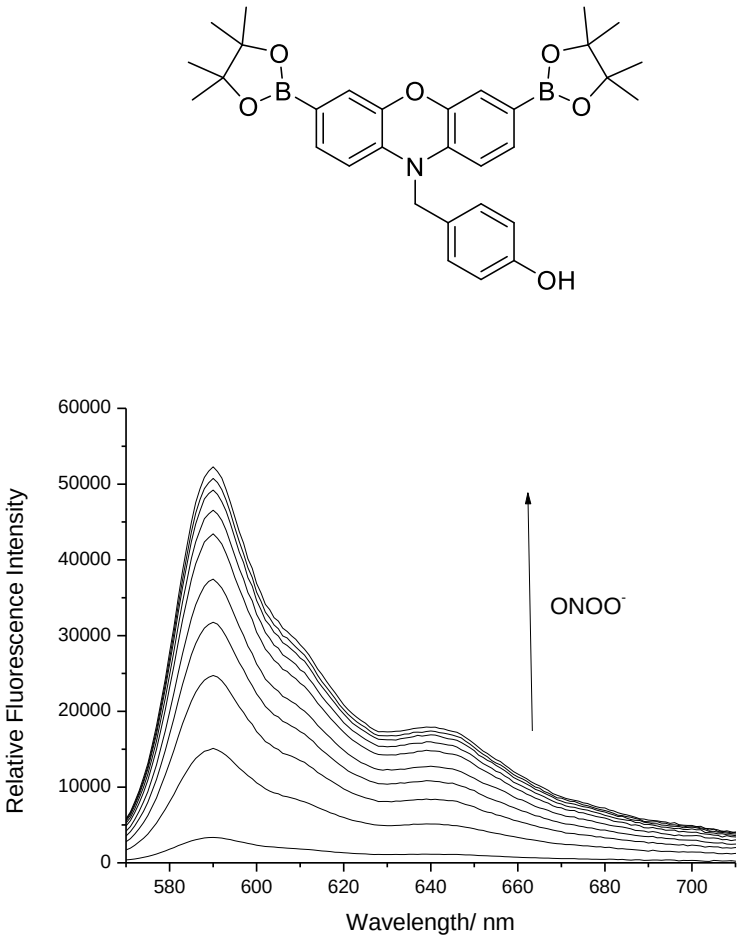


Fig. S6 – Fluorescence spectra of **Pinkment-OH** (0.5 μM) with the addition of ONOO- (0-10 μM) in PBS (52% w/w H2O:MeOH) pH=8.2 at 25 °C; λex= 545-20 nm

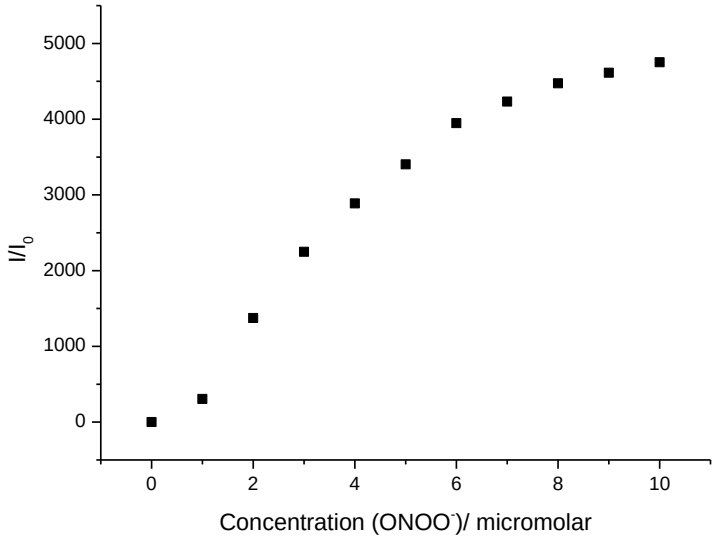


Fig. S7 - Fluorescence intensity changes (I/I_{Final}) with **Pinkment-OH** (0.5 µM) and additions of $ONOO^-$ (0 – 10 µM) in pH 8.2 buffer solution [52 wt% methanol]. Fluorescence intensities were measured with λex = 545-20 nm/λem = 590

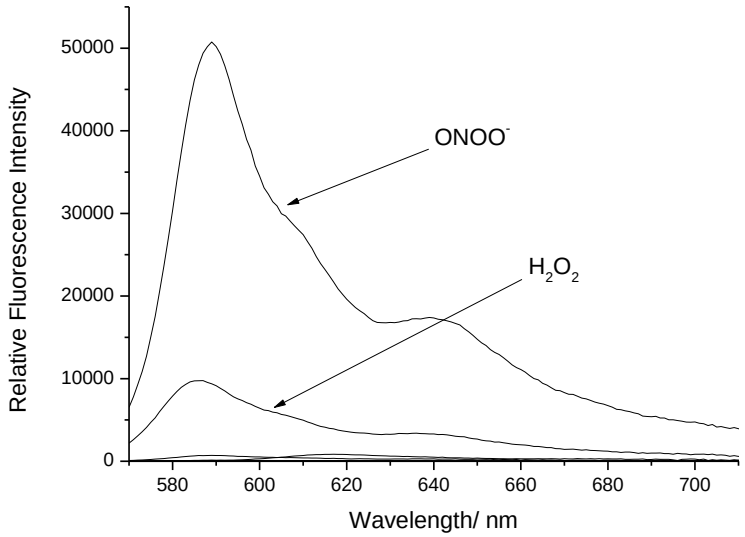


Fig. S8 - Fluorescence spectra of **Pinkment-OH** (0.5 µM) in the presence of various ROS/RNS: $ONOO^-$ (10 µM, 1 min), ^-OCl (500 µM, 30 min), H_2O_2 (500 µM, 30 min), $ROO^\cdot$ (500 µM, 30 min), $^1O_2$ (500 µM, 30 min), $^-O_2$ (500 µM, 30 min), OH (500 µM, 30 min). λex = 545-20 nm in pH 8.2 buffer solution [52 wt% methanol]

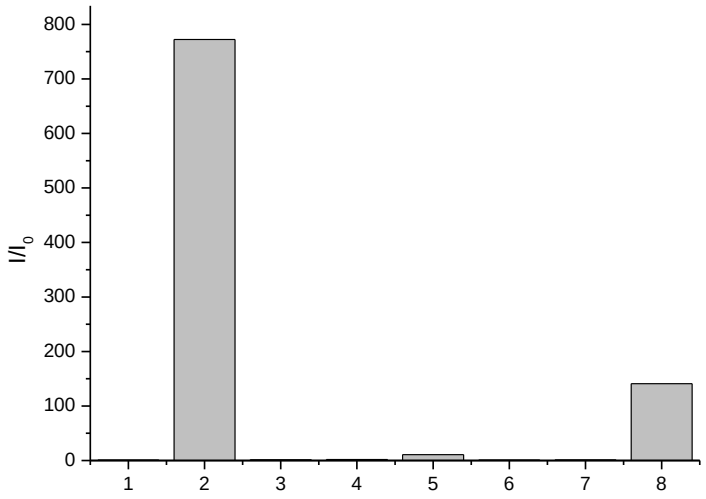
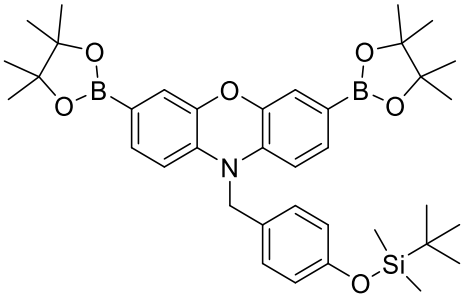


Fig. S9 - Selectivity bar chart of **Pinkment-OH** (0.5 µM) in the presence of various ROS/RNS: 1 – Sensor only, 2- $ONOO^-$ (10 µM, 1 min), 3 - $^{\cdot}OH$ (500 µM, 1 min), 4 - $^-O_2$ (500 µM, 1 min), 5 - $^1O_2$ (500 µM, 1 min). 6 - $ROO^\cdot$ (500 µM, 30 min), 7 - ^-OCl (500 µM, 30 min), 8 - H_2O_2 (1 mM, 30 min), λex = 545-20 nm / λem = 590 nm in pH 8.2 buffer solution [52 wt% methanol]

Pinkment-OTBS



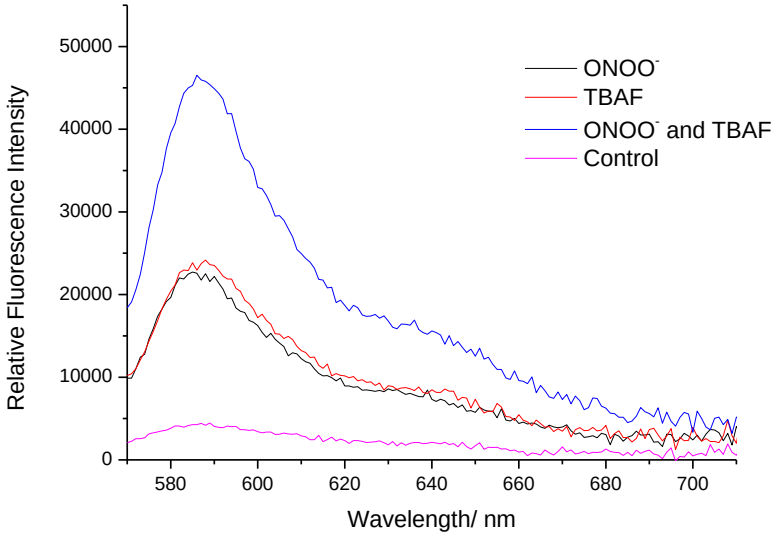


Fig. S10 – Fluorescence spectra of **Pinkment-TBS** (0.5 µM) in the presence of $ONOO^-$ (200 µM), TBAF (10 mM) and both analytes (200 µM and 10 mM, respectively). The data was obtained in PBS pH=7.4 (100% w/w H_2O), λex = 545-20 nM at 25 ºC. Measure immediately for $ONOO^-$. 1 h wait before measurement with TBAF.

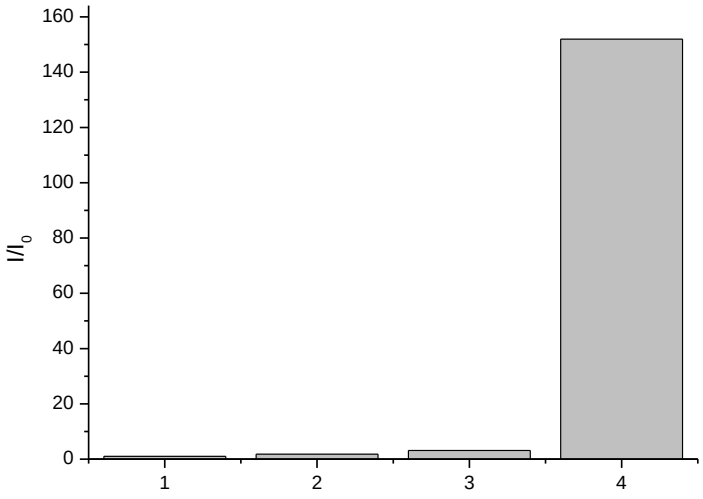


Fig. S11 – Bar chart of **Pinkment-OTBS** (0.5 µM) 1 – sensor only, 2 - $ONOO^-$ (50 µM), 3 -TBAF (10 mM) and 4 – TBAF and $ONOO^-$ (10 mM and 50 µM, respectively). The data was obtained in PBS buffer (52% w/w MeOH:H_2O), pH = 8.2 at 25 ºC. λex =545-20 nm/ λem = 590 nm

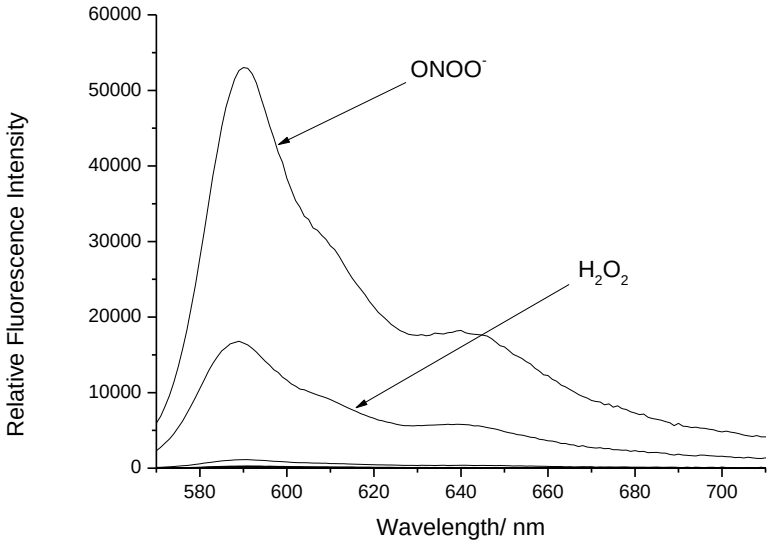


Fig. S12 - Fluorescence spectra of **Pinkment-OTBS** (0.5 µM) with TBAF (10 mM) in the presence of $ONOO^-$ (50 µM) OH·(500 µM), superoxide (500 µM), singlet oxygen (500 µM) and measured after 5 mins. H_2O_2 (1 mM), ROO· (500 µM) and ClO^- (500 µM) were measured after 30 mins. The data was obtained in PBS buffer (52% w/w MeOH:H_2O), pH = 8.2 at 25 ºC. λ_{ex}=545-20 nm.

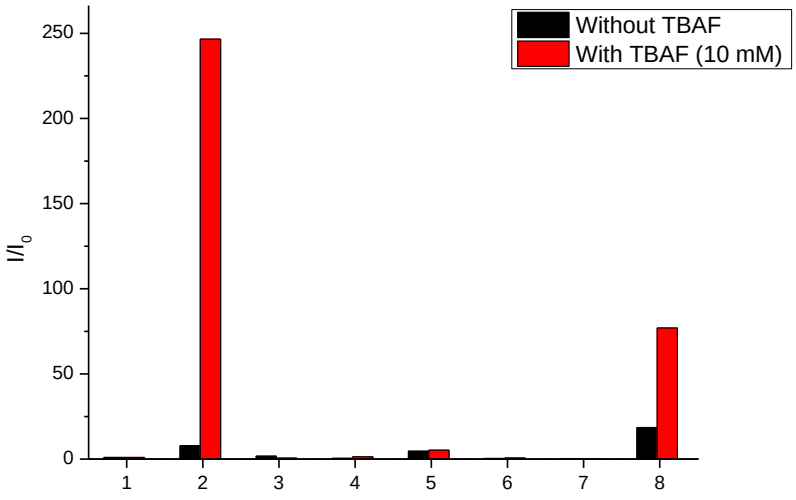


Fig. S13 - Selectivity bar chart of **Pinkment-OTBS** (0.5 µM) with (red) and without (black) TBAF (10 mM) with 1 – Sensor only, 2 - $ONOO^-$ (50 µM), 3 - OH·(500 µM), 4 - superoxide (500 µM), 5 - singlet oxygen (500 µM) after 5 mins. 6 - ROO·(500 µM) 7 - ClO^- (500 µM), 8 - H_2O_2 (1 mM), were measured after 30 mins. The data was obtained in PBS buffer (52% w/w MeOH:H_2O), pH = 8.2 at 25 ºC. λex = 545-20 nm/λem = 590

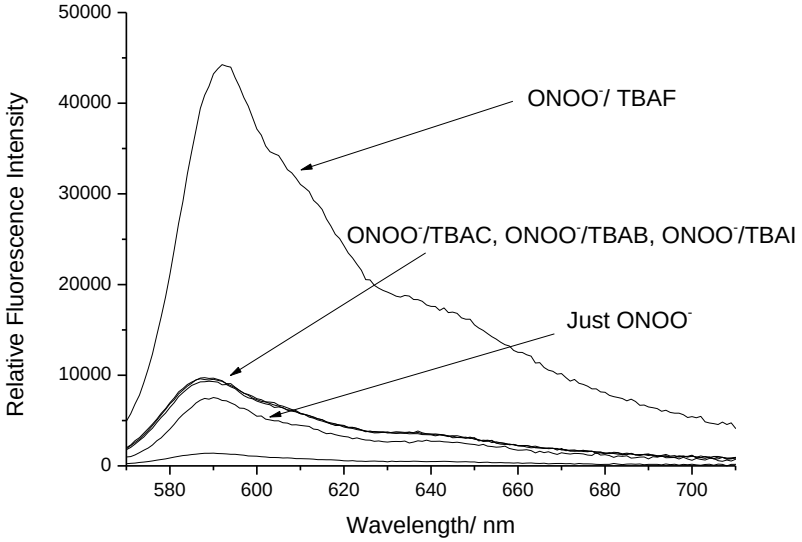
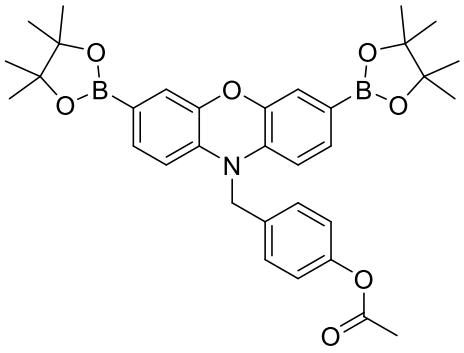


Fig. S14 -Fluorescence spectra of **Pinkment-OTBS** (0.5 µM) with just $ONOO^-$ (20 µM). Then the combination of TBAF (10 mM), TBAB (10 mM), TBAC (10 mM), TBAI (10 mM) with $ONOO^-$ (20 µM), respectively. The data was obtained in PBS buffer 52% H2O:MeOH, pH=8.2 at 25 °C after 90 mins. λex = 545-20 nm/λem = 590

Pinkment-OAc



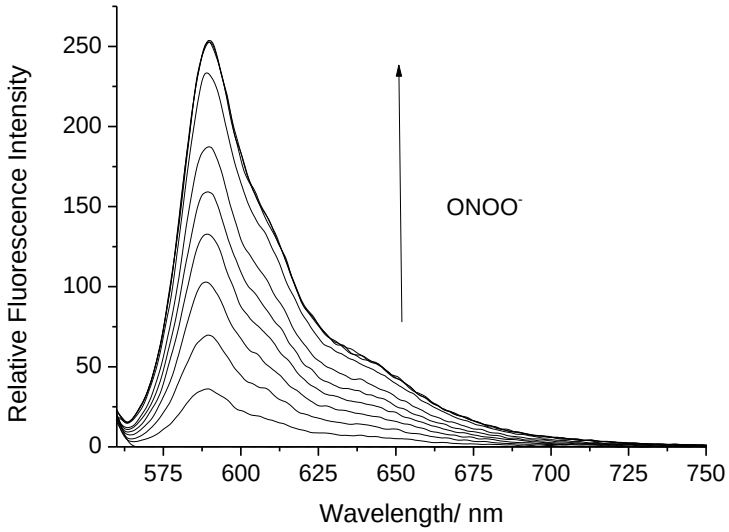


Fig. S15- Fluorescence spectra of **Pinkment-OAc** (0.5 μM) with addition of $ONOO^-$ (0 – 100 μM) in pH = 8.21 buffer solution [52 wt% methanol] at 25 °C. Fluorescence intensities were measured with λ_{ex} = 550nm with Slit Widths Ex slit: 10 nm and Em slit: 5 nm

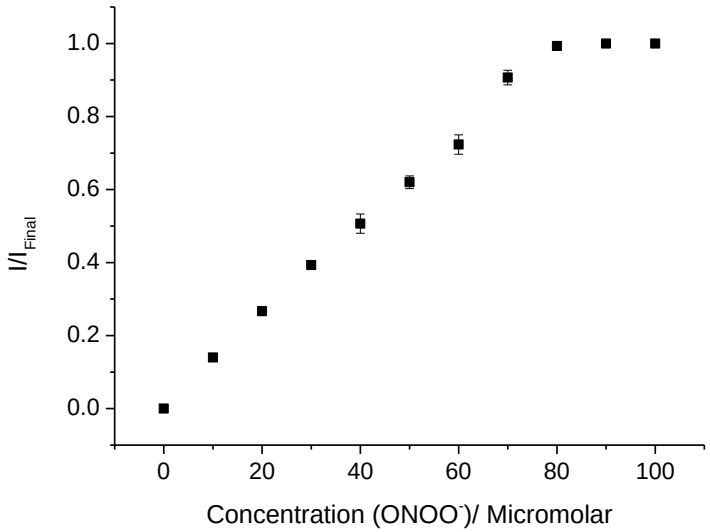


Fig. S16 - Fluorescence intensity changes (I/I_{Final}) with **Pinkment-OAc** (0.5 µM) and additions of $ONOO^-$ (0 – 100 µM in pH = 8.21 buffer solution [52 wt% methanol] at 25 ºC. Fluorescence intensities were measured with λ_{ex} = 550nm/ λ_{em} 590 nm with slit widths ex: 10 nm and em 5 nm

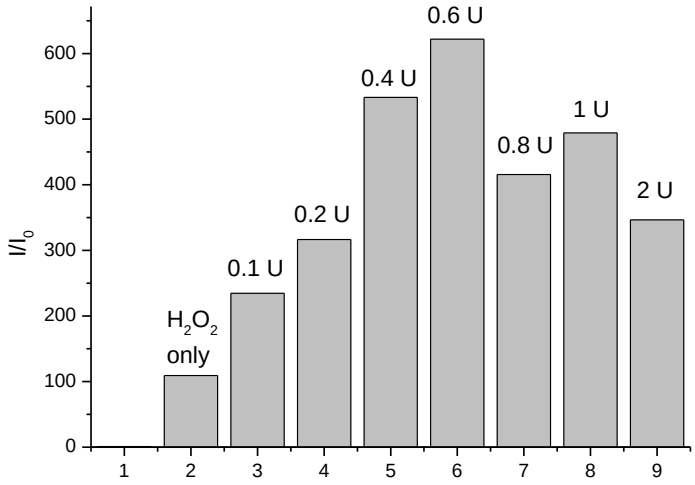


Fig. S17 - Fluorescence intensity changes of **Pinkment-OAc** (0.5 µM) following incubation of various concentrations of PLE (0 – 2 U) for 15 mins and subsequent addition of H_2O_2 (1 mM). (1 – sensor only, 2 – just H_2O_2, 3 - 0.1 U, 4 - 0.2 U, 5 - 0.4 U, 6 - 0.6 U, 7 - 0.8 U, 8 -1 U and 9 - 2 U) The data was obtained in PBS (100% w/w H_2O), pH = 7.4 at 25 ºC. λex=545-20 nm/ λem = 590

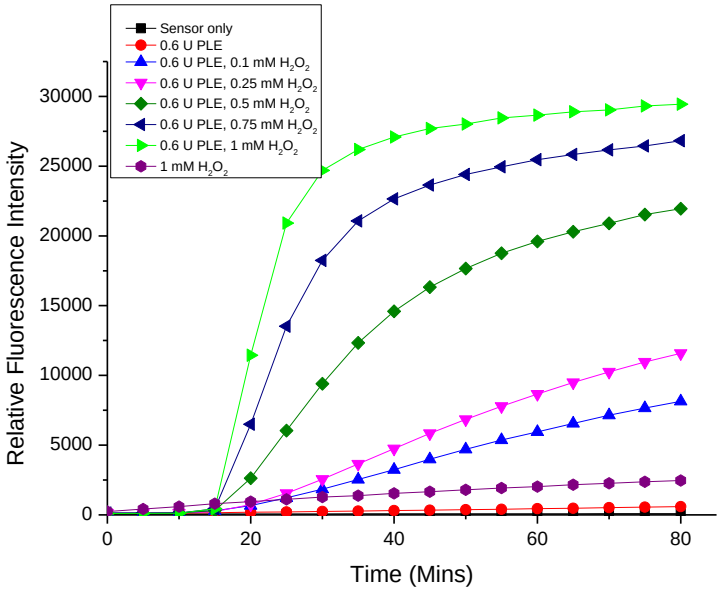
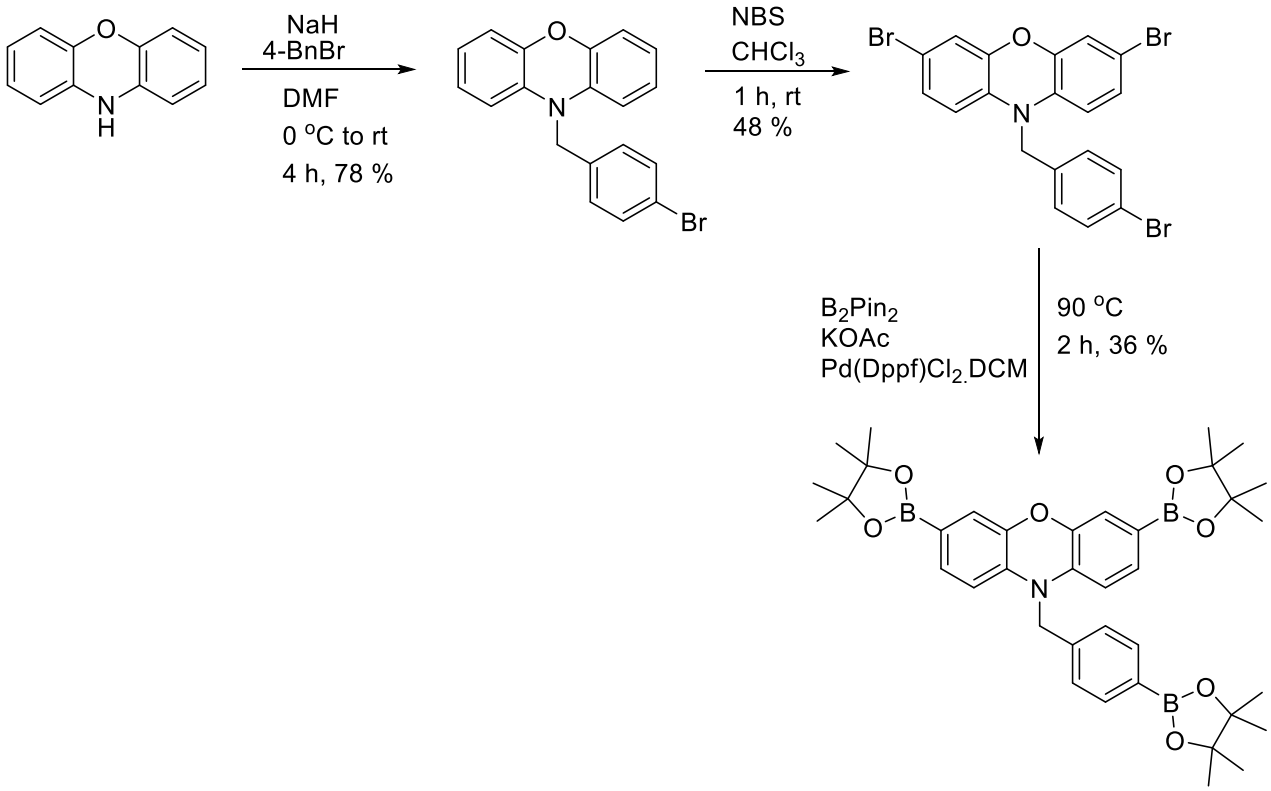
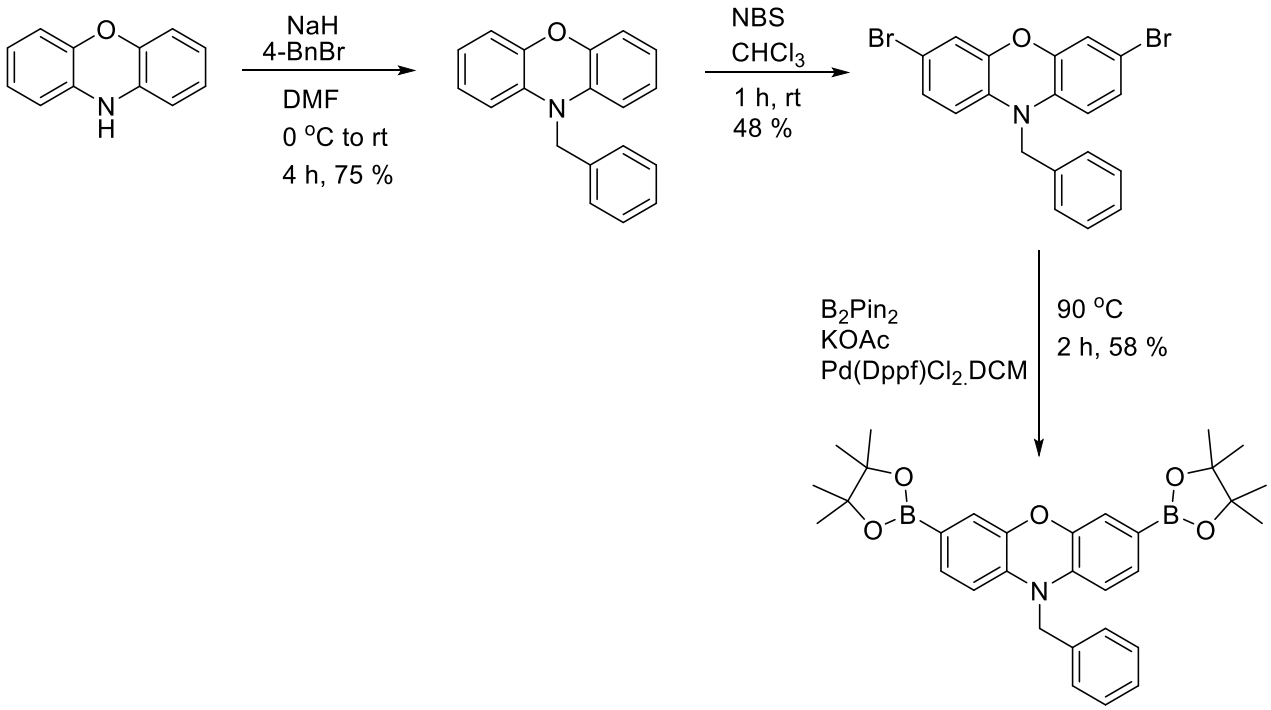


Fig. S18 -Fluorescence intensity changes over time of **Pinkment-OAc** (0.5 µM) with porcine liver esterase, PLE (0.6 U) and various concentrations of H_2O_2 (0.1 light blue, 0.25 pink, 0.5 green, 0.75 dark blue and 1 mM light green). In addition control experiments were carried out - just PLE red (0.6 U) and just H_2O_2 - purple (1 mM) The data was obtained in PBS (100% w/w H_2O), pH = 7.4 at 25 ºC. at 25 °C after 90 mins. λex = 545-20 nm/λem = 590 nm

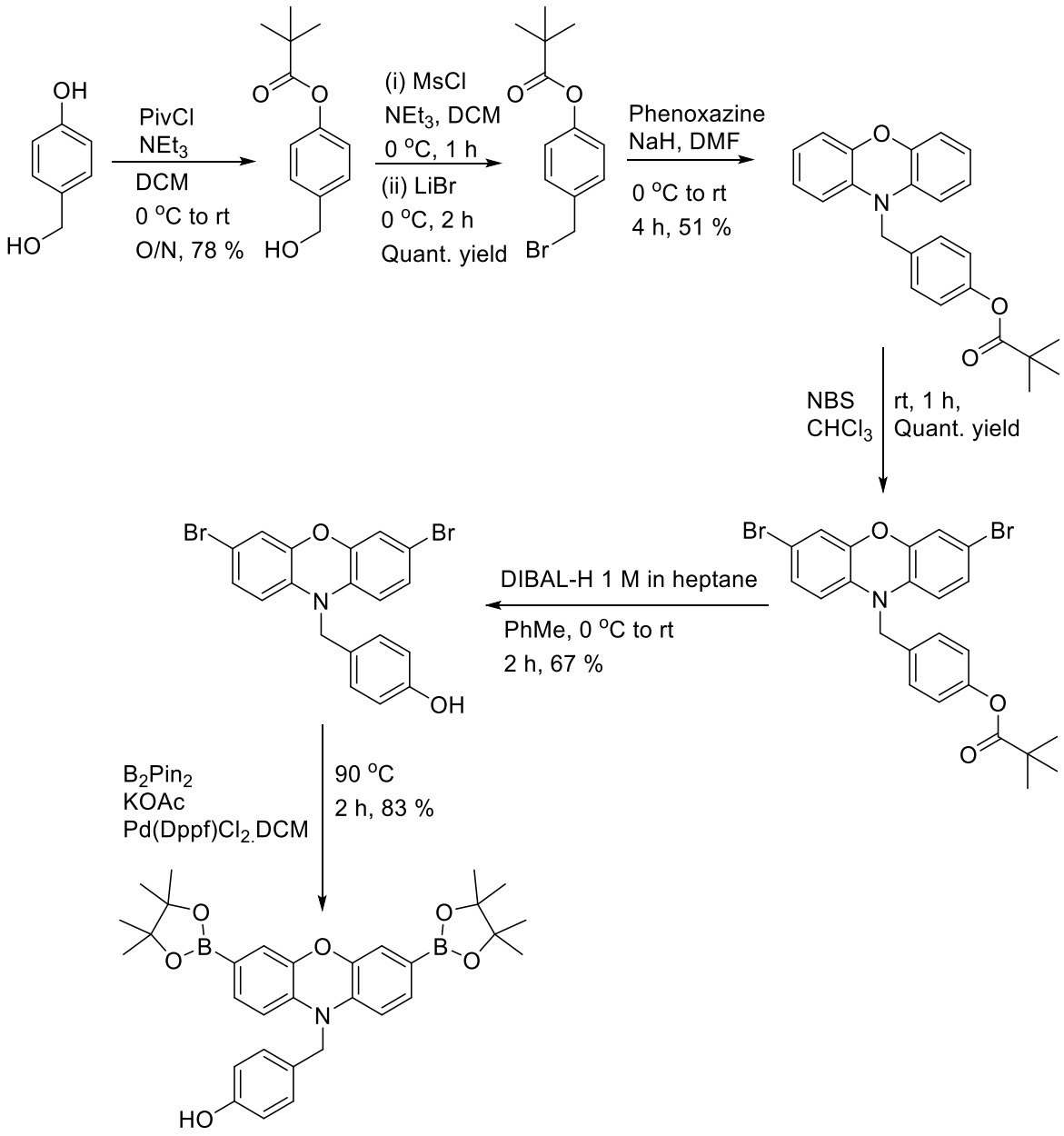
3. Synthetic Schemes



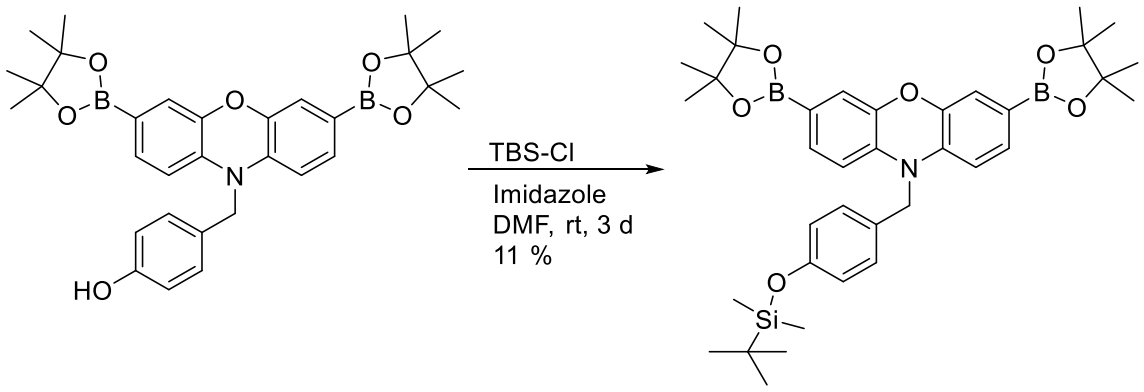
Scheme S4 – Synthetic procedure for the synthesis of **Pinkment**



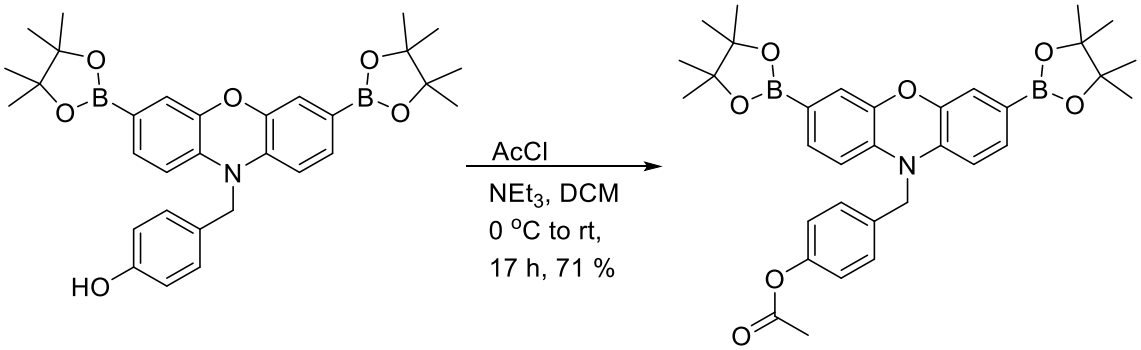
Scheme S5 – Synthetic procedure for the synthesis of **Pinkment-Bn**



Scheme S6 – Synthetic procedure for the synthesis of **Pinkment-OH**



Scheme S7 – Synthetic procedure for the synthesis of **Pinkment-OTBS**



Scheme S8 – Synthetic procedure for the synthesis of **Pinkment-OAc**

4. Crystal structure of Pinkment-OH ·CH_2Cl_2 and its crystallography data

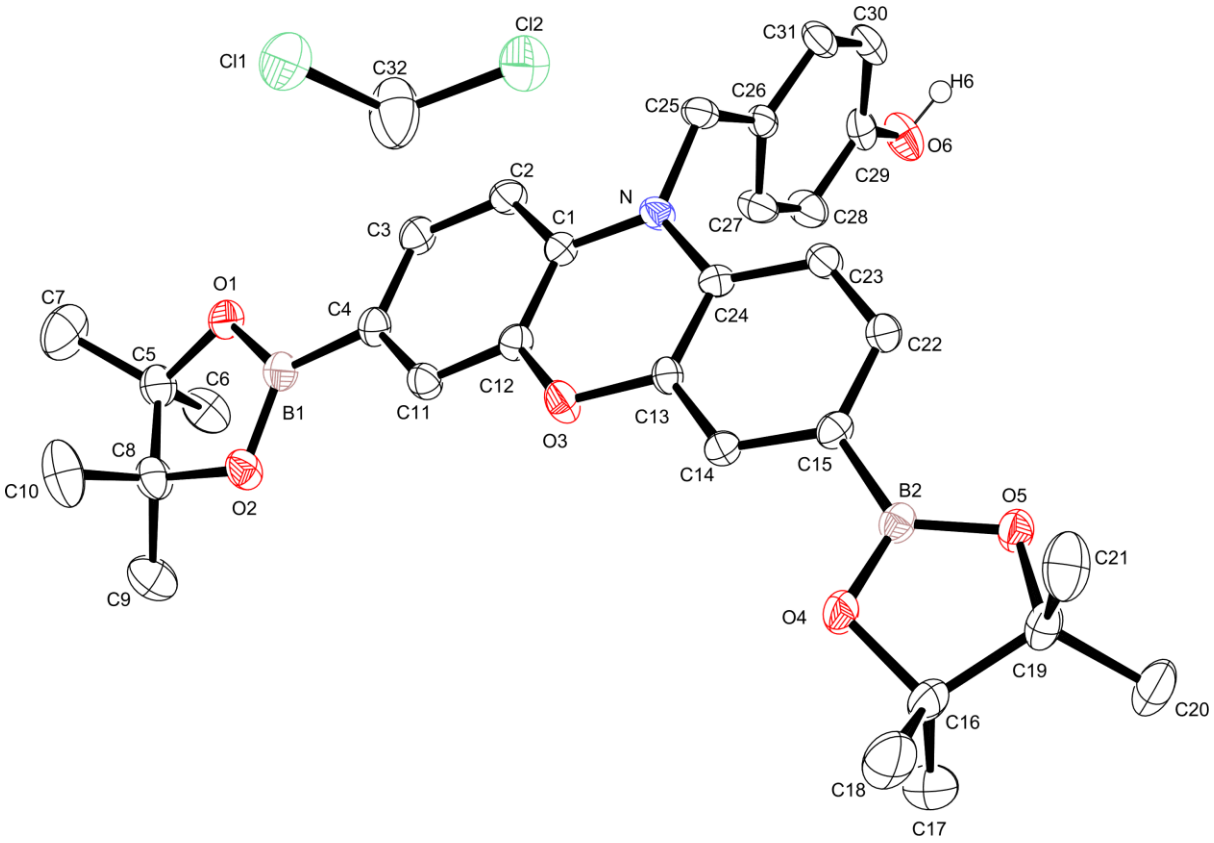


Fig. S19 Pinkment-OH crystallises with one molecule of CH2Cl2 per asymmetric unit Thermal elipsoids shown at 50% probability, H-atoms are omitted for clarity except for the OH hydrogen atom.

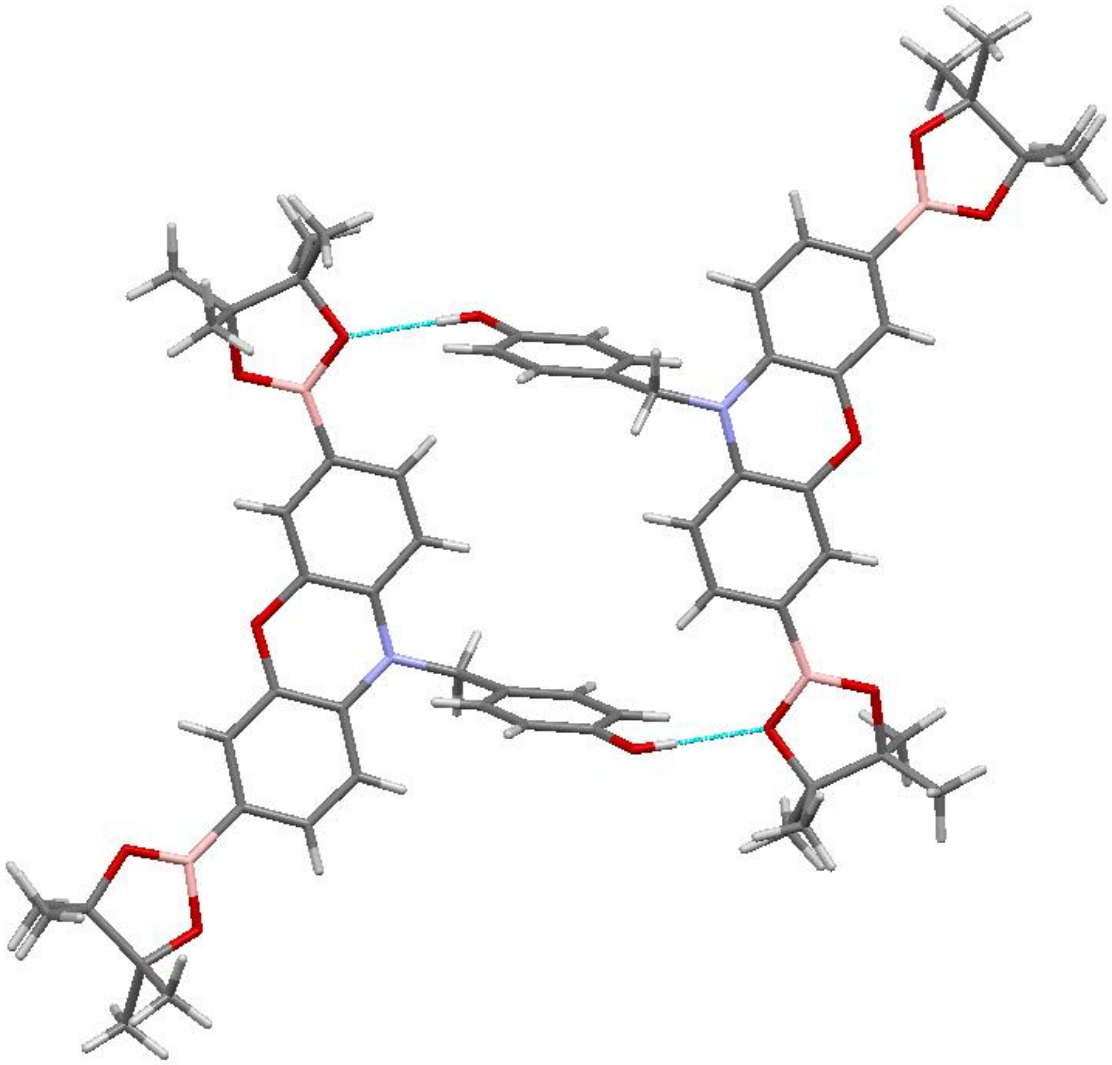


Fig S20. Pinkment-OH forms dimers via the OH hydrogen bond with O5 of a partner molecule see **Table S8**

The BO2(CMe2)2 group comprising atoms B1, O1, O2, C5-C10 is disordered over two sites in the ratio 1:1

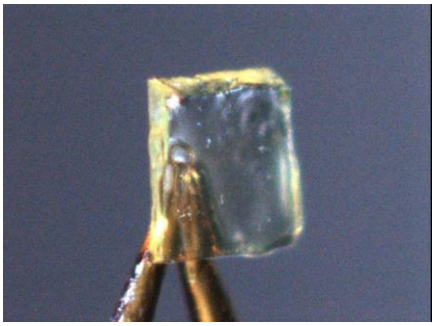


Fig. S21 Crystal of pinkment-OH which was used for data collection.

Table S1 Crystal data and structure refinement for **Pinkment-OH·(CH_2Cl_2)**

Identification code	e16tdj1	
Empirical formula	C32 H39 B2 Cl2 N O6	
Formula weight	626.16	
Temperature	150.00(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 21.0386(6) Å	α= 90°.
	b = 12.0671(3) Å	β= 91.250(3)°.
	c = 12.7442(4) Å	γ = 90°.
Volume	3234.66(16) $Å^3$	
Z	4	
Density (calculated)	1.286 Mg/m^3	
Absorption coefficient	0.244 mm^{-1}	
F(000)	1320	
Crystal size	0.500 x 0.400 x 0.150 mm^3	
Theta range for data collection	3.361 to 30.348°.	
Index ranges	-29<=h<=29, -17<=k<=16, -16<=l<=17	
Reflections collected	46742	
Independent reflections	8960 [R(int) = 0.0329]	
Completeness to theta = 25.242°	99.8 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.85577
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8960 / 0 / 459
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0652, wR2 = 0.1611
R indices (all data)	R1 = 0.0862, wR2 = 0.1737
Extinction coefficient	n/a
Largest diff. peak and hole	0.927 and -0.557 e.$Å^{-3}$

CCDC 1844385 contain the supplementary crystallographic data for **pinkment-OH**

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for e16tdj1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N	2000(1)	7024(1)	5058(1)	21(1)
C(1)	2587(1)	7059(2)	5599(1)	19(1)
C(2)	2687(1)	7674(2)	6514(2)	24(1)
C(3)	3280(1)	7669(2)	7023(2)	25(1)
C(4)	3786(1)	7041(2)	6661(2)	23(1)
B(1)	4424(1)	6969(2)	7284(2)	25(1)
O(1)	4580(4)	7627(7)	8160(8)	28(1)
O(2)	4906(3)	6211(5)	7100(5)	27(1)
C(6)	4964(4)	6574(6)	9614(6)	38(1)
C(7)	5551(3)	8210(6)	9000(6)	51(2)
C(9)	5749(4)	5388(5)	8154(4)	42(2)
C(10)	5912(5)	7074(10)	7085(8)	50(2)

O(1A)	4478(5)	7335(9)	8253(10)	26(2)
O(2A)	4950(3)	6562(7)	6831(6)	31(1)
C(6A)	5225(6)	6854(13)	9637(7)	60(3)
C(7A)	5419(4)	8443(6)	8445(11)	54(3)
C(9A)	5434(5)	5241(6)	8025(7)	46(2)
C(10A)	6064(5)	6780(11)	7241(10)	39(2)
C(5)	5161(1)	7237(2)	8600(2)	32(1)
C(8)	5441(1)	6466(2)	7735(2)	30(1)
C(11)	3682(1)	6427(2)	5739(2)	23(1)
C(12)	3102(1)	6453(2)	5223(1)	20(1)
O(3)	3052(1)	5855(1)	4296(1)	26(1)
C(13)	2450(1)	5689(2)	3878(1)	18(1)
C(14)	2399(1)	4948(2)	3066(1)	19(1)
C(15)	1810(1)	4710(2)	2578(1)	20(1)
B(2)	1791(1)	3827(2)	1704(2)	21(1)
O(4)	2329(1)	3433(1)	1262(1)	27(1)
O(5)	1247(1)	3327(1)	1312(1)	23(1)
C(16)	2154(1)	2469(2)	627(2)	29(1)
C(17)	2292(1)	1455(2)	1295(2)	44(1)
C(18)	2559(1)	2477(2)	-343(2)	45(1)
C(19)	1430(1)	2666(2)	400(2)	25(1)
C(20)	1025(1)	1630(2)	362(2)	39(1)
C(21)	1295(1)	3389(2)	-555(2)	39(1)
C(22)	1278(1)	5269(2)	2953(2)	23(1)
C(23)	1330(1)	6028(2)	3767(2)	22(1)
C(24)	1918(1)	6258(2)	4247(1)	18(1)
C(25)	1473(1)	7719(2)	5379(2)	22(1)
C(26)	1063(1)	7208(2)	6216(2)	21(1)
C(27)	1260(1)	6289(2)	6787(2)	28(1)
C(28)	894(1)	5862(2)	7585(2)	31(1)
C(29)	319(1)	6356(2)	7821(2)	27(1)
C(30)	113(1)	7274(2)	7250(2)	30(1)
C(31)	485(1)	7693(2)	6457(2)	26(1)
O(6)	-14(1)	5909(2)	8626(1)	37(1)
C(32)	3200(2)	9283(3)	4247(3)	60(1)
Cl(1)	3653(1)	10281(1)	3625(1)	57(1)
Cl(2)	2430(1)	9208(1)	3714(1)	48(1)

Table S3. Bond lengths [Å] for e16tdj1.

N-C(24)	1.395(2)
N-C(1)	1.401(2)
N-C(25)	1.456(2)
C(1)-C(2)	1.394(3)
C(1)-C(12)	1.401(3)
C(2)-C(3)	1.394(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.393(3)
C(3)-H(3)	0.9500
C(4)-C(11)	1.402(3)
C(4)-B(1)	1.548(3)
B(1)-O(1A)	1.315(13)
B(1)-O(2A)	1.350(8)
B(1)-O(2)	1.388(6)
B(1)-O(1)	1.403(10)
O(1)-C(5)	1.415(10)
O(2)-C(8)	1.406(6)
C(6)-C(5)	1.584(7)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-C(5)	1.514(6)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(9)-C(8)	1.543(6)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(8)	1.498(11)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
O(1A)-C(5)	1.499(12)
O(2A)-C(8)	1.536(7)
C(6A)-C(5)	1.405(11)

C(6A)-H(6D)	0.9800
C(6A)-H(6E)	0.9800
C(6A)-H(6F)	0.9800
C(7A)-C(5)	1.567(8)
C(7A)-H(7D)	0.9800
C(7A)-H(7E)	0.9800
C(7A)-H(7F)	0.9800
C(9A)-C(8)	1.523(7)
C(9A)-H(9D)	0.9800
C(9A)-H(9E)	0.9800
C(9A)-H(9F)	0.9800
C(10A)-C(8)	1.515(13)
C(10A)-H(10D)	0.9800
C(10A)-H(10E)	0.9800
C(10A)-H(10F)	0.9800
C(5)-C(8)	1.566(3)
C(11)-C(12)	1.373(3)
C(11)-H(11)	0.9500
C(12)-O(3)	1.386(2)
O(3)-C(13)	1.378(2)
C(13)-C(14)	1.370(3)
C(13)-C(24)	1.403(2)
C(14)-C(15)	1.404(3)
C(14)-H(14)	0.9500
C(15)-C(22)	1.401(3)
C(15)-B(2)	1.542(3)
B(2)-O(4)	1.361(3)
B(2)-O(5)	1.379(2)
O(4)-C(16)	1.460(2)
O(5)-C(19)	1.468(2)
C(16)-C(17)	1.514(4)
C(16)-C(18)	1.517(3)
C(16)-C(19)	1.564(3)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800

C(18)-H(18C)	0.9800
C(19)-C(20)	1.514(3)
C(19)-C(21)	1.519(3)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.386(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.395(3)
C(23)-H(23)	0.9500
C(25)-C(26)	1.517(3)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-C(27)	1.384(3)
C(26)-C(31)	1.390(3)
C(27)-C(28)	1.388(3)
C(27)-H(27)	0.9500
C(28)-C(29)	1.387(3)
C(28)-H(28)	0.9500
C(29)-O(6)	1.367(3)
C(29)-C(30)	1.390(3)
C(30)-C(31)	1.387(3)
C(30)-H(30)	0.9500
C(31)-H(31)	0.9500
O(6)-H(6)	0.82(3)
C(32)-Cl(1)	1.738(3)
C(32)-Cl(2)	1.746(3)
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900

Table S4. Bond angles [°] for e16tdj1.

C(24)-N-C(1)	118.57(15)
C(24)-N-C(25)	120.45(15)
C(1)-N-C(25)	120.85(15)
C(2)-C(1)-N	122.86(17)
C(2)-C(1)-C(12)	117.41(17)
N-C(1)-C(12)	119.73(16)
C(1)-C(2)-C(3)	120.28(18)
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-H(2)	119.9
C(4)-C(3)-C(2)	122.04(18)
C(4)-C(3)-H(3)	119.0
C(2)-C(3)-H(3)	119.0
C(3)-C(4)-C(11)	117.31(18)
C(3)-C(4)-B(1)	121.43(18)
C(11)-C(4)-B(1)	121.16(18)
O(1A)-B(1)-O(2A)	118.0(6)
O(2)-B(1)-O(1)	110.4(5)
O(1A)-B(1)-C(4)	121.2(5)
O(2A)-B(1)-C(4)	120.7(3)
O(2)-B(1)-C(4)	125.4(3)
O(1)-B(1)-C(4)	124.1(4)
B(1)-O(1)-C(5)	108.2(7)
B(1)-O(2)-C(8)	109.7(4)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(5)-C(7)-H(7A)	109.5
C(5)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(8)-C(9)-H(9A)	109.5

C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
B(1)-O(1A)-C(5)	108.2(8)
B(1)-O(2A)-C(8)	104.5(5)
C(5)-C(6A)-H(6D)	109.5
C(5)-C(6A)-H(6E)	109.5
H(6D)-C(6A)-H(6E)	109.5
C(5)-C(6A)-H(6F)	109.5
H(6D)-C(6A)-H(6F)	109.5
H(6E)-C(6A)-H(6F)	109.5
C(5)-C(7A)-H(7D)	109.5
C(5)-C(7A)-H(7E)	109.5
H(7D)-C(7A)-H(7E)	109.5
C(5)-C(7A)-H(7F)	109.5
H(7D)-C(7A)-H(7F)	109.5
H(7E)-C(7A)-H(7F)	109.5
C(8)-C(9A)-H(9D)	109.5
C(8)-C(9A)-H(9E)	109.5
H(9D)-C(9A)-H(9E)	109.5
C(8)-C(9A)-H(9F)	109.5
H(9D)-C(9A)-H(9F)	109.5
H(9E)-C(9A)-H(9F)	109.5
C(8)-C(10A)-H(10D)	109.5
C(8)-C(10A)-H(10E)	109.5
H(10D)-C(10A)-H(10E)	109.5
C(8)-C(10A)-H(10F)	109.5
H(10D)-C(10A)-H(10F)	109.5
H(10E)-C(10A)-H(10F)	109.5
C(6A)-C(5)-O(1A)	111.9(6)

O(1)-C(5)-C(7)	109.5(4)
C(6A)-C(5)-C(8)	115.9(5)
O(1)-C(5)-C(8)	104.7(4)
O(1A)-C(5)-C(8)	102.2(5)
C(7)-C(5)-C(8)	119.3(3)
C(6A)-C(5)-C(7A)	113.4(6)
O(1A)-C(5)-C(7A)	102.9(4)
C(8)-C(5)-C(7A)	109.1(4)
O(1)-C(5)-C(6)	104.5(4)
C(7)-C(5)-C(6)	105.5(4)
C(8)-C(5)-C(6)	112.5(3)
O(2)-C(8)-C(10)	108.7(4)
C(10A)-C(8)-C(9A)	110.9(5)
C(10A)-C(8)-O(2A)	104.0(5)
C(9A)-C(8)-O(2A)	104.2(4)
O(2)-C(8)-C(9)	109.9(3)
C(10)-C(8)-C(9)	109.0(4)
O(2)-C(8)-C(5)	103.1(3)
C(10)-C(8)-C(5)	111.1(5)
C(10A)-C(8)-C(5)	119.0(5)
C(9A)-C(8)-C(5)	113.6(4)
O(2A)-C(8)-C(5)	103.1(3)
C(9)-C(8)-C(5)	114.8(3)
C(12)-C(11)-C(4)	120.64(17)
C(12)-C(11)-H(11)	119.7
C(4)-C(11)-H(11)	119.7
C(11)-C(12)-O(3)	116.50(16)
C(11)-C(12)-C(1)	122.28(17)
O(3)-C(12)-C(1)	121.21(16)
C(13)-O(3)-C(12)	117.24(14)
C(14)-C(13)-O(3)	116.30(16)
C(14)-C(13)-C(24)	121.57(16)
O(3)-C(13)-C(24)	122.13(16)
C(13)-C(14)-C(15)	121.38(17)
C(13)-C(14)-H(14)	119.3
C(15)-C(14)-H(14)	119.3
C(22)-C(15)-C(14)	117.12(17)
C(22)-C(15)-B(2)	124.82(17)

C(14)-C(15)-B(2)	118.02(17)
O(4)-B(2)-O(5)	112.90(17)
O(4)-B(2)-C(15)	122.14(17)
O(5)-B(2)-C(15)	124.93(18)
B(2)-O(4)-C(16)	107.84(15)
B(2)-O(5)-C(19)	107.09(15)
O(4)-C(16)-C(17)	106.85(19)
O(4)-C(16)-C(18)	107.93(17)
C(17)-C(16)-C(18)	111.1(2)
O(4)-C(16)-C(19)	102.34(15)
C(17)-C(16)-C(19)	113.65(19)
C(18)-C(16)-C(19)	114.2(2)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(5)-C(19)-C(20)	108.48(17)
O(5)-C(19)-C(21)	105.99(18)
C(20)-C(19)-C(21)	110.72(19)
O(5)-C(19)-C(16)	101.99(15)
C(20)-C(19)-C(16)	115.19(19)
C(21)-C(19)-C(16)	113.56(18)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5

H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-C(15)	121.48(18)
C(23)-C(22)-H(22)	119.3
C(15)-C(22)-H(22)	119.3
C(22)-C(23)-C(24)	120.96(17)
C(22)-C(23)-H(23)	119.5
C(24)-C(23)-H(23)	119.5
N-C(24)-C(23)	123.43(16)
N-C(24)-C(13)	119.08(16)
C(23)-C(24)-C(13)	117.49(16)
N-C(25)-C(26)	114.25(16)
N-C(25)-H(25A)	108.7
C(26)-C(25)-H(25A)	108.7
N-C(25)-H(25B)	108.7
C(26)-C(25)-H(25B)	108.7
H(25A)-C(25)-H(25B)	107.6
C(27)-C(26)-C(31)	118.25(19)
C(27)-C(26)-C(25)	121.88(17)
C(31)-C(26)-C(25)	119.81(17)
C(26)-C(27)-C(28)	121.31(19)
C(26)-C(27)-H(27)	119.3
C(28)-C(27)-H(27)	119.3
C(29)-C(28)-C(27)	119.9(2)
C(29)-C(28)-H(28)	120.1
C(27)-C(28)-H(28)	120.1
O(6)-C(29)-C(28)	117.2(2)
O(6)-C(29)-C(30)	123.19(19)
C(28)-C(29)-C(30)	119.6(2)
C(31)-C(30)-C(29)	119.75(18)
C(31)-C(30)-H(30)	120.1
C(29)-C(30)-H(30)	120.1
C(30)-C(31)-C(26)	121.23(19)
C(30)-C(31)-H(31)	119.4
C(26)-C(31)-H(31)	119.4
C(29)-O(6)-H(6)	109(2)

Cl(1)-C(32)-Cl(2)	111.87(17)
Cl(1)-C(32)-H(32A)	109.2
Cl(2)-C(32)-H(32A)	109.2
Cl(1)-C(32)-H(32B)	109.2
Cl(2)-C(32)-H(32B)	109.2
H(32A)-C(32)-H(32B)	107.9

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for e16tdj1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N	19(1)	23(1)	20(1)	-6(1)	-2(1)	4(1)
C(1)	20(1)	19(1)	17(1)	0(1)	0(1)	0(1)
C(2)	25(1)	24(1)	22(1)	-6(1)	-1(1)	2(1)
C(3)	27(1)	26(1)	22(1)	-7(1)	-2(1)	-2(1)
C(4)	22(1)	26(1)	21(1)	-2(1)	-2(1)	-3(1)
B(1)	24(1)	27(1)	24(1)	-1(1)	-2(1)	-2(1)
O(1)	26(3)	28(3)	28(2)	-6(2)	-13(2)	-1(2)
O(2)	22(2)	35(3)	25(2)	-7(2)	-6(2)	2(2)
C(6)	36(3)	52(3)	26(2)	6(2)	-2(3)	10(3)
C(7)	55(3)	49(3)	48(4)	-3(3)	-22(3)	-12(3)
C(9)	36(3)	50(3)	39(3)	2(2)	-4(2)	11(3)
C(10)	30(5)	81(7)	37(3)	11(4)	-4(3)	-11(4)
O(1A)	18(3)	33(5)	26(3)	-6(3)	-5(2)	-4(3)
O(2A)	23(2)	45(4)	24(3)	0(2)	-8(2)	6(2)
C(6A)	49(6)	103(9)	28(3)	-11(4)	-13(4)	27(6)
C(7A)	37(4)	37(4)	88(8)	-20(4)	1(4)	-7(3)
C(9A)	44(5)	32(3)	59(4)	-2(3)	-10(4)	3(3)
C(10A)	16(4)	53(5)	47(6)	-5(4)	0(3)	4(3)
C(5)	26(1)	36(1)	35(1)	-4(1)	-10(1)	-1(1)
C(8)	23(1)	36(1)	30(1)	3(1)	-6(1)	0(1)
C(11)	19(1)	27(1)	23(1)	-4(1)	1(1)	1(1)
C(12)	22(1)	22(1)	15(1)	-3(1)	1(1)	-2(1)
O(3)	17(1)	39(1)	22(1)	-13(1)	-1(1)	2(1)
C(13)	16(1)	21(1)	16(1)	2(1)	-2(1)	-2(1)
C(14)	20(1)	19(1)	17(1)	-1(1)	1(1)	0(1)
C(15)	24(1)	19(1)	17(1)	0(1)	-2(1)	-1(1)
B(2)	23(1)	20(1)	19(1)	1(1)	-2(1)	-2(1)
O(4)	21(1)	30(1)	31(1)	-14(1)	-1(1)	-3(1)
O(5)	21(1)	26(1)	23(1)	-5(1)	-1(1)	-3(1)
C(16)	28(1)	26(1)	32(1)	-13(1)	1(1)	-4(1)
C(17)	43(1)	32(1)	56(2)	-6(1)	-4(1)	7(1)
C(18)	42(1)	48(2)	45(2)	-24(1)	16(1)	-10(1)
C(19)	27(1)	29(1)	21(1)	-6(1)	1(1)	-8(1)

C(20)	40(1)	34(1)	42(1)	-12(1)	2(1)	-16(1)
C(21)	40(1)	51(1)	26(1)	4(1)	-7(1)	-14(1)
C(22)	21(1)	23(1)	24(1)	-1(1)	-4(1)	0(1)
C(23)	20(1)	24(1)	23(1)	-2(1)	-2(1)	3(1)
C(24)	21(1)	17(1)	16(1)	1(1)	0(1)	1(1)
C(25)	22(1)	21(1)	22(1)	-3(1)	-1(1)	6(1)
C(26)	17(1)	23(1)	22(1)	-6(1)	-4(1)	2(1)
C(27)	24(1)	27(1)	33(1)	0(1)	3(1)	8(1)
C(28)	27(1)	32(1)	34(1)	6(1)	1(1)	5(1)
C(29)	19(1)	37(1)	25(1)	-3(1)	-4(1)	-3(1)
C(30)	16(1)	40(1)	33(1)	-2(1)	-2(1)	6(1)
C(31)	18(1)	31(1)	29(1)	-1(1)	-5(1)	6(1)
O(6)	23(1)	54(1)	35(1)	8(1)	3(1)	1(1)
C(32)	48(2)	64(2)	67(2)	30(2)	-8(1)	-18(1)
Cl(1)	45(1)	42(1)	85(1)	9(1)	10(1)	-8(1)
Cl(2)	38(1)	45(1)	61(1)	2(1)	4(1)	-4(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for e16tdj1.

	x	y	z	U(eq)
H(2)	2349	8099	6791	28
H(3)	3341	8106	7637	30
H(6A)	5346	6305	9985	57
H(6B)	4696	5943	9407	57
H(6C)	4726	7064	10077	57
H(7A)	5954	7940	9304	76
H(7B)	5314	8605	9538	76
H(7C)	5637	8714	8417	76
H(9A)	6131	5570	8572	63
H(9B)	5865	4917	7562	63
H(9C)	5447	4994	8593	63
H(10A)	6292	7240	7515	74
H(10B)	5723	7768	6829	74
H(10C)	6030	6613	6487	74
H(6D)	5005	7362	10107	91
H(6E)	5676	6820	9840	91
H(6F)	5037	6113	9689	91
H(7D)	5875	8462	8619	81
H(7E)	5194	8952	8908	81
H(7F)	5349	8670	7713	81
H(9D)	5741	5107	8601	68
H(9E)	5550	4798	7414	68
H(9F)	5008	5032	8247	68
H(10D)	6408	6741	7771	58
H(10E)	6034	7536	6964	58
H(10F)	6153	6265	6667	58
H(11)	4016	5989	5468	28
H(14)	2771	4588	2827	22
H(17A)	2031	1476	1922	66
H(17B)	2743	1449	1506	66
H(17C)	2192	786	889	66
H(18A)	2530	3205	-682	67
H(18B)	2406	1906	-834	67

H(18C)	3003	2325	-142	67
H(20A)	582	1831	201	58
H(20B)	1050	1254	1043	58
H(20C)	1180	1132	-184	58
H(21A)	846	3601	-575	59
H(21B)	1394	2976	-1193	59
H(21C)	1560	4057	-514	59
H(22)	872	5125	2643	27
H(23)	961	6398	4001	27
H(25A)	1201	7885	4754	26
H(25B)	1645	8431	5647	26
H(27)	1652	5945	6629	34
H(28)	1037	5231	7969	37
H(30)	-282	7614	7402	36
H(31)	343	8323	6073	32
H(6)	-370(16)	6190(30)	8620(20)	49(9)
H(32A)	3179	9462	5004	72
H(32B)	3409	8552	4180	72

Table S7. Torsion angles [°] for e16tdj1.

C(24)-N-C(1)-C(2)	-170.27(18)
C(25)-N-C(1)-C(2)	5.6(3)
C(24)-N-C(1)-C(12)	9.4(3)
C(25)-N-C(1)-C(12)	-174.67(17)
N-C(1)-C(2)-C(3)	179.41(18)
C(12)-C(1)-C(2)-C(3)	-0.3(3)
C(1)-C(2)-C(3)-C(4)	-1.4(3)
C(2)-C(3)-C(4)-C(11)	1.5(3)
C(2)-C(3)-C(4)-B(1)	-174.99(19)
C(3)-C(4)-B(1)-O(1A)	11.8(6)
C(11)-C(4)-B(1)-O(1A)	-164.6(5)
C(3)-C(4)-B(1)-O(2A)	-165.8(5)
C(11)-C(4)-B(1)-O(2A)	17.8(5)
C(3)-C(4)-B(1)-O(2)	166.8(4)
C(11)-C(4)-B(1)-O(2)	-9.5(5)
C(3)-C(4)-B(1)-O(1)	-9.2(5)
C(11)-C(4)-B(1)-O(1)	174.5(4)
O(2)-B(1)-O(1)-C(5)	-3.8(5)
C(4)-B(1)-O(1)-C(5)	172.7(3)
O(1)-B(1)-O(2)-C(8)	-10.0(5)
C(4)-B(1)-O(2)-C(8)	173.6(3)
O(2A)-B(1)-O(1A)-C(5)	2.5(7)
C(4)-B(1)-O(1A)-C(5)	-175.2(3)
O(1A)-B(1)-O(2A)-C(8)	10.6(6)
C(4)-B(1)-O(2A)-C(8)	-171.7(3)
B(1)-O(1)-C(5)-C(7)	143.3(6)
B(1)-O(1)-C(5)-C(8)	14.3(6)
B(1)-O(1)-C(5)-C(6)	-104.1(6)
B(1)-O(1A)-C(5)-C(6A)	-138.7(9)
B(1)-O(1A)-C(5)-C(8)	-14.0(7)
B(1)-O(1A)-C(5)-C(7A)	99.2(8)
B(1)-O(2)-C(8)-C(10)	-100.1(8)
B(1)-O(2)-C(8)-C(9)	140.7(5)
B(1)-O(2)-C(8)-C(5)	17.9(5)
B(1)-O(2A)-C(8)-C(10A)	-143.0(7)
B(1)-O(2A)-C(8)-C(9A)	100.8(7)

B(1)-O(2A)-C(8)-C(5)	-18.1(6)
O(1)-C(5)-C(8)-O(2)	-19.6(6)
C(7)-C(5)-C(8)-O(2)	-142.4(6)
C(6)-C(5)-C(8)-O(2)	93.3(6)
O(1)-C(5)-C(8)-C(10)	96.6(6)
C(7)-C(5)-C(8)-C(10)	-26.2(7)
C(6)-C(5)-C(8)-C(10)	-150.5(6)
C(6A)-C(5)-C(8)-C(10A)	-104.5(10)
O(1A)-C(5)-C(8)-C(10A)	133.5(7)
C(7A)-C(5)-C(8)-C(10A)	25.0(8)
C(6A)-C(5)-C(8)-C(9A)	28.9(10)
O(1A)-C(5)-C(8)-C(9A)	-93.1(7)
C(7A)-C(5)-C(8)-C(9A)	158.4(8)
C(6A)-C(5)-C(8)-O(2A)	141.1(9)
O(1A)-C(5)-C(8)-O(2A)	19.0(7)
C(7A)-C(5)-C(8)-O(2A)	-89.4(8)
O(1)-C(5)-C(8)-C(9)	-139.1(6)
C(7)-C(5)-C(8)-C(9)	98.1(7)
C(6)-C(5)-C(8)-C(9)	-26.2(6)
C(3)-C(4)-C(11)-C(12)	0.0(3)
B(1)-C(4)-C(11)-C(12)	176.57(19)
C(4)-C(11)-C(12)-O(3)	177.47(18)
C(4)-C(11)-C(12)-C(1)	-1.8(3)
C(2)-C(1)-C(12)-C(11)	1.9(3)
N-C(1)-C(12)-C(11)	-177.84(18)
C(2)-C(1)-C(12)-O(3)	-177.33(17)
N-C(1)-C(12)-O(3)	3.0(3)
C(11)-C(12)-O(3)-C(13)	167.48(17)
C(1)-C(12)-O(3)-C(13)	-13.3(3)
C(12)-O(3)-C(13)-C(14)	-169.52(16)
C(12)-O(3)-C(13)-C(24)	11.6(3)
O(3)-C(13)-C(14)-C(15)	179.93(16)
C(24)-C(13)-C(14)-C(15)	-1.1(3)
C(13)-C(14)-C(15)-C(22)	0.5(3)
C(13)-C(14)-C(15)-B(2)	-177.28(17)
C(22)-C(15)-B(2)-O(4)	169.90(19)
C(14)-C(15)-B(2)-O(4)	-12.6(3)
C(22)-C(15)-B(2)-O(5)	-12.5(3)

C(14)-C(15)-B(2)-O(5)	165.02(18)
O(5)-B(2)-O(4)-C(16)	-9.0(2)
C(15)-B(2)-O(4)-C(16)	168.83(18)
O(4)-B(2)-O(5)-C(19)	-10.1(2)
C(15)-B(2)-O(5)-C(19)	172.14(18)
B(2)-O(4)-C(16)-C(17)	-97.1(2)
B(2)-O(4)-C(16)-C(18)	143.4(2)
B(2)-O(4)-C(16)-C(19)	22.6(2)
B(2)-O(5)-C(19)-C(20)	145.06(19)
B(2)-O(5)-C(19)-C(21)	-96.01(19)
B(2)-O(5)-C(19)-C(16)	23.07(19)
O(4)-C(16)-C(19)-O(5)	-27.35(19)
C(17)-C(16)-C(19)-O(5)	87.5(2)
C(18)-C(16)-C(19)-O(5)	-143.69(18)
O(4)-C(16)-C(19)-C(20)	-144.61(18)
C(17)-C(16)-C(19)-C(20)	-29.8(3)
C(18)-C(16)-C(19)-C(20)	99.0(2)
O(4)-C(16)-C(19)-C(21)	86.2(2)
C(17)-C(16)-C(19)-C(21)	-159.0(2)
C(18)-C(16)-C(19)-C(21)	-30.1(3)
C(14)-C(15)-C(22)-C(23)	0.3(3)
B(2)-C(15)-C(22)-C(23)	177.89(18)
C(15)-C(22)-C(23)-C(24)	-0.4(3)
C(1)-N-C(24)-C(23)	169.62(17)
C(25)-N-C(24)-C(23)	-6.3(3)
C(1)-N-C(24)-C(13)	-11.1(3)
C(25)-N-C(24)-C(13)	172.97(16)
C(22)-C(23)-C(24)-N	179.05(18)
C(22)-C(23)-C(24)-C(13)	-0.2(3)
C(14)-C(13)-C(24)-N	-178.31(17)
O(3)-C(13)-C(24)-N	0.6(3)
C(14)-C(13)-C(24)-C(23)	1.0(3)
O(3)-C(13)-C(24)-C(23)	179.87(17)
C(24)-N-C(25)-C(26)	88.5(2)
C(1)-N-C(25)-C(26)	-87.3(2)
N-C(25)-C(26)-C(27)	14.1(3)
N-C(25)-C(26)-C(31)	-168.76(17)
C(31)-C(26)-C(27)-C(28)	-0.3(3)

C(25)-C(26)-C(27)-C(28)	176.8(2)
C(26)-C(27)-C(28)-C(29)	0.1(3)
C(27)-C(28)-C(29)-O(6)	-178.9(2)
C(27)-C(28)-C(29)-C(30)	0.4(3)
O(6)-C(29)-C(30)-C(31)	178.7(2)
C(28)-C(29)-C(30)-C(31)	-0.6(3)
C(29)-C(30)-C(31)-C(26)	0.4(3)
C(27)-C(26)-C(31)-C(30)	0.1(3)
C(25)-C(26)-C(31)-C(30)	-177.13(19)

Table S8. Hydrogen bonds for e16tdj1 [Å and °].

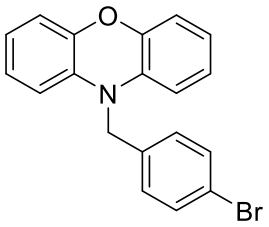
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(6)-H(6)...O(5)#1	0.82(3)	1.94(3)	2.754(2)	173(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

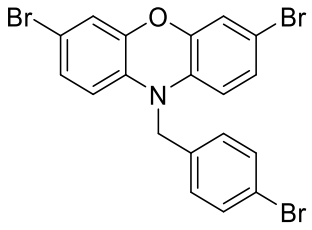
5. Experimental

10-(4-Bromobenzyl)-10H-phenoxazine (1)



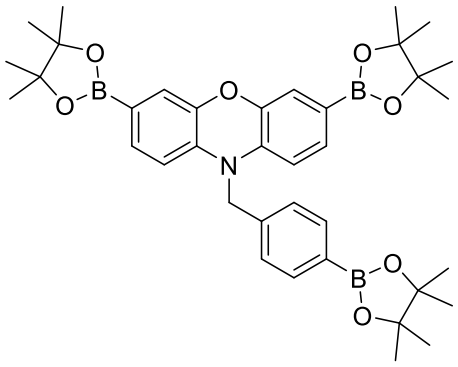
Phenoxazine (1.00 g, 5.46 mmol) was dissolved in DMF (25 mL) before being cooled to 0 ^{o}C. NaH – 60% in mineral oil (0.26 g, 6.60 mmol) was then added portion wise to the solution over the period of 5 min, which was then left to stir at 0 ^{o}C for a further 10 min. 4-Bromobenzyl bromide (1.65 g, 6.60 mmol) was then added portion-wise to the reaction mixture and then was left to stir for 4 hrs at rt. The reaction mixture was then cooled to 0 ^{o}C before being quenched with dropwise addition of H_2O. The reaction mixture was partitioned with EtOAc (100 mL) and H_2O (100 mL). The organic layer was washed with H_2O (3 x 50 mL), brine (50 mL) and dried ($MgSO_4$) and concentrated *in-vacuo* to afford the crude product. **1** was purified via column chromatography 5:95 (EtOAc/Pet ether) to afford a white solid (1.50 g, 4.26 mmol, 78 %). M.p. 109-111 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.8 Hz, 2 H, CH_2Ar*H*), 7.19 (d, *J* = 8.8 Hz, 2 H, CH_2Ar*H*), 6.72 - 6.66 (m, 6 H, Ar*H*), 6.28 (d, *J* = 7.3 Hz, 2 H, Ar*H*), 4.72 (s, 2 H, C*H*$_2$Ar); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 145.1, 132.0, 131.6, 129.3, 127.8, 123.7, 121.5, 121.0, 115.4, 112.0, 48.9; I.R (thinfilm) ν max (cm^{-1}): 3037.8 (C-H sp^2), 2933.66 (C-H Sp^3), 1485.95 (C=C); HRMS (ESI): m/z calculated for $C_{19}H_{14}BrNO$: requires 352.0337 for $[M+H]^+$, found 352.0329

3,7-Dibromo-10-(4-bromobenzyl)-10H-phenoxazine (2)



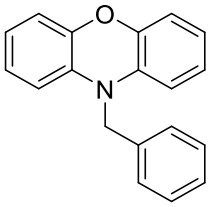
To a solution of **1** (1.50 g, 4.26 mmol) in $CHCl_3$ (120 mL), NBS (1.62 g, 9.08 mmol) was added portion-wise and the reaction was left to stir for 1 hr. The reaction was then quenched with H_2O (100 mL) and the organic layer was washed with H_2O (3 x 100 mL), brine (100 mL) and dried ($MgSO_4$) and concentrated *in-vacuo* to afford the crude product. **2** was purified via trituration (EtOAc) to afford a cream solid (1.11 g, 2.16 mmol, 48 %). M.p. 204-206 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 - 7.43 (d, *J* = 8.3 Hz, 2 H, CH_2ArH), 7.17 - 7.10 (d, *J* = 8.3 Hz, 2 H, CH_2ArH), 6.86 - 6.78 (m, 4 H, Ar*H*), 6.14 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 4.67 (s, 2 H, CH_2Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.3, 134.2, 132.4, 132.3, 127.7, 126.8, 121.4, 118.8, 113.2, 48.8. No mass spec was observed.

3,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-10H-phenoxazine (Pinkment)



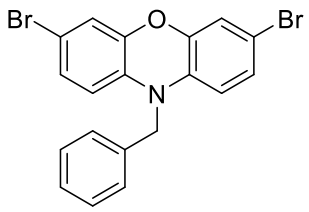
2 (0.20 g, 0.39 mmol), bis(pinacolato) diboron (0.40 g, 1.56 mmol), potassium acetate (0.229 g, 2.34 mmol) and Pd(dppf)Cl_2.DCM (0.028 g, 0.039 mmol) was dissolved in anhydrous DMF (7 mL) and refluxed under argon for 2 h. The reaction was cooled to rt and partitioned with EtOAc (50 mL) and H_2O (50 mL). The organic layer was washed with H_2O (3 x 50 mL), brine (50 mL), dried ($MgSO_4$) and concentrated *in-vacuo* to afford the crude product. **Pinkment** was purified via column chromatography 5:95 (EtOAc/Pet Ether) and trituration (Pet ether) to afford a white solid (0.088 g, 0.14 mmol, 36 %). M.p. 265-268 ^oC (decomposed); ^1H NMR (500 MHz, Acetone-d6) δ 7.76 - 7.71 (d, *J* = 7.8 Hz, 2 H, CH_2Ar*H*), 7.39 - 7.33 (d, *J* = 7.8 Hz, 2 H, CH_2Ar*H*), 7.16 - 7.11 (d, *J* = 7.8 Hz, 2 H, Ar*H*), 6.99 (s, 2 H, Ar*H*), 6.53 - 6.45 (d, *J* = 7.8 Hz, 2 H, Ar*H*), 4.98 (s, 2 H, CH_2Ar), 1.32 (s, 12 H, B*Pin*), 1.29 (s, 24 H, B*Pin*); ^{13}C NMR (75.5MHz, $CDCl_3$) δ 144.8, 139.1, 136.0, 135.5, 131.0, 125.4, 121.0, 111.7, 83.8, 83.6, 83.5, 49.2, 25.1, 24.9, 24.8; HRMS (TOF MS ASAP+): m/z calculated for $C_{37}H_{49}B_3NO_7$: requires 650.3861 for $[M+H]^+$, found 650.3840

10-Benzyl-10H-phenoxazine (3)



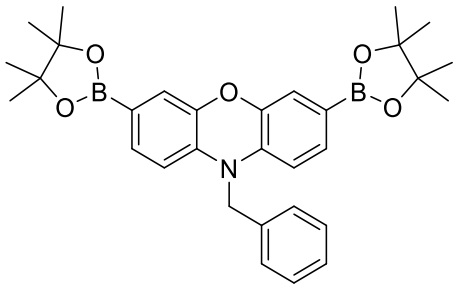
Phenoxazine (1.00 g, 5.46 mmol) was dissolved in DMF (25 mL) before being cooled to 0 ^{o}C. NaH – 60% in mineral oil (0.327 g, 8.18 mmol) was then added portion wise to the solution over the period of 5 min, which was then left to stir at 0 ^{o}C for a further 10 min. Benzyl bromide (1.3 mL, 10.92 mmol) was then added portion-wise to the reaction mixture and then was left to stir for 4 hrs at rt. The reaction mixture was then cooled to 0 ^{o}C before being quenched with dropwise addition of H_2O. The reaction mixture was partitioned with EtOAc (100 mL) and H_2O (100 mL). The organic layer was washed with H_2O (3 x 50 mL), brine (50 mL) and dried ($MgSO_4$) and concentrated *in-vacuo* to afford the crude product. **3** was purified via trituration (Pet ether) to afford a white solid (1.11 g, 4.06 mmol, 75 %). Mp 122- 125 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 - 7.21 (m, 5 H, CH_2Ar*H*), 6.78 - 6.59 (m, 6 H, Ar*H*), 6.35 (d, *J* = 7.0 Hz, 2 H, Ar*H*), 4.80 (br. s., 2 H, C*H*$_2$Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.2, 136.3, 133.9, 129.0, 127.2, 126.0, 123.7, 121.3, 115.3, 112.2, 49.3; HRMS (ESI): m/z calculated for $C_{19}H_{15}NO$: requires 274.1231 for $[M+H]^+$, found 274.1212; requires 296.1051 for $[M+Na]^+$, found 296.1034

10-Benzyl-3,7-dibromo-10H-phenoxazine (4)



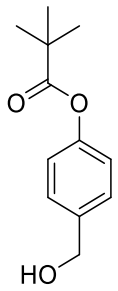
To a solution of **3** (1.10 g, 4.26 mmol) in $CHCl_3$ (100 mL), NBS (1.62 g, 9.08 mmol) was added portion-wise and the reaction was left to stir for 1 hr. The reaction was then quenched with H_2O (100 mL) and the organic layer was washed with H_2O (3 x 100 mL), brine (100 mL) and dried ($MgSO_4$) and concentrated *in-vacuo* to afford **4** as a blue/green solid. No further purification was required (1.11 g, 2.16 mmol, 48 %). M.p. 161-164 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 - 7.22 (m, 5 H, CH_2ArH), 6.86 - 6.78 (m, 4 H, Ar*H*), 6.19 (d, *J* = 9.0 Hz, 2 H, Ar*H*), 4.72 (s, 2 H, CH_2Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.4, 135.1, 132.7, 129.1, 127.6, 126.7, 125.9, 118.6, 113.3, 112.9, 49.2. Mass spec was not observed.

10-Benzyl-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazine (Pinkment-Bn)



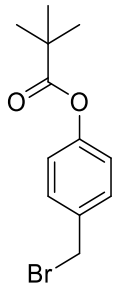
4 (1.14 g, 2.64 mmol), bis(pinacolato) diboron (2.01 g, 7.93 mmol), potassium acetate (1.55 g, 15.84 mmol) and Pd(dppf)Cl_2 (0.193 g, 0.264 mmol) was dissolved in anhydrous DMF (15 mL) and heated at 90 ^oC under argon for 2 h. The reaction was cooled to rt and partitioned with EtOAc (50 mL) and H_2O (50 mL). The organic layer was washed with H_2O (3 x 50 mL), brine (50 mL), dried ($MgSO_4$) and concentrated *in-vacuo* to afford the crude product. **Pinkment-Bn** was purified via column chromatography 5:95 (EtOAc/Pet Ether) and trituration (Pet ether) to afford a white solid (0.81 g, 1.54 mmol, 58 %). M.p. 218-221 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 - 7.23 (m, 5 H, CH_2ArH), 7.20 - 7.11 (d, *J* = 7.9 Hz, 2 H, Ar*H*), 7.08 (s, 2 H, Ar*H*), 6.37 - 6.30 (d, *J* = 7.9 Hz, 2 H, Ar*H*), 4.81 (s, 2 H, CH_2Ar), 1.31 (s, 24 H, B*Pin*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 144.8, 136.0, 135.6, 131.0, 129.0, 127.3, 126.0, 121.0, 111.7, 83.6, 48.7, 24.8; HRMS (TOF MS ASAP+): m/z calculated for $C_{31}H_{38}B_2NO_5$: requires 524.3009 for $[M+H]^+$, found 524.2988

4-(Hydroxymethyl)phenyl pivalate (5)



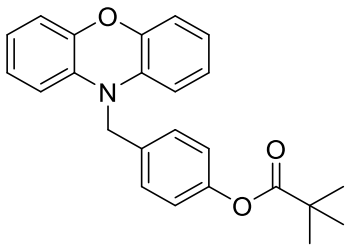
NEt_3 (4.5 mL, 32.22 mmol) was added to a solution of 4-hydroxybenzyl alcohol (2.0 g, 16.11 mmol) in DCM (50 mL). The solution was then cooled to 0 ^oC and trimethylacetyl chloride (2.2 mL, 17.72 mmol) was added dropwise. The reaction mixture was stirred overnight and was allowed to warm to rt. The reaction was partitioned with DCM (100 mL) and H_2O (100 mL). The organic layer was washed with H_2O (3 x 50 mL), brine (50 mL), dried ($MgSO_4$) and concentrated *in-vacuo* to afford the crude material. The title compound (**5**) was purified via column chromatography 5:95 to 20:80 (EtOAc/Pet ether) to afford a clear oil (2.63 g, 12.63 mmol, 78 %) ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 - 7.30 (d, *J* = 8.7 Hz, 2 H, Ar*H*), 7.05 - 6.97 (d, *J* = 8.5 Hz, 2 H, Ar*H*)), 4.62 (s, 2 H, ArC*H*$_2$OH), 1.36 (s, 9H, ArOC(O)C(C*H*$_3$)$_3$); ^{13}C NMR (75MHz, $CDCl_3$) δ 177.3, 150.4, 138.4, 128.0, 121.5, 64.6, 39.1, 27.2; I.R (thinfilm) ν max (cm^{-1}): 3257.85 (br, O-H), 1740.41 (C=O); HRMS (ESI+) m/z calculated for $C_{12}H_{16}O_3$: requires 226.1438 $[M+NH_4]^+$, found 226.1436

4-(Bromomethyl)phenyl pivalate (6)



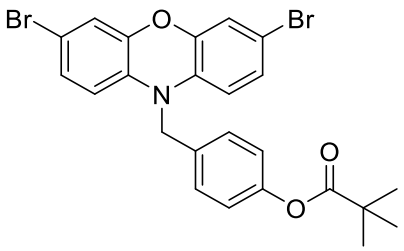
Methanesulfonyl chloride (1.79 mL, 23.1 mmol) was added dropwise to a mixture of 4-(hydroxymethyl)phenyl pivalate (2.3 g, 11 mmol) and NEt_3 (1.8 mL, 23.1 mmol) in DCM (50 mL) at 0 ^oC. The reaction mixture was stirred for 1 h before the addition of LiBr (9.55 g, 110 mmol) and the reaction mixture was stirred for an additional 2 h before H_2O (50 mL) was added. The organic layer was washed with H_2O (3 x 50 mL), brine (50 mL) and dried ($MgSO_4$) and concentrated *in-vacuo* to afford title compound (**6**) as a pale brown solid (2.1 g, 77.1 mmol, 70 %). No further purification was required. ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 - 7.37 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.08 - 7.00 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 4.50 (s, 2 H, ArCH_2Br), 1.36 (s, 9 H, ArOC(O)C(CH_3)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.0, 151.0, 135.1, 130.2, 121.9, 39.1, 32.8, 27.1; I.R (thinfilm) ν max (cm^{-1}): 1743.54 (C=O); HRMS (TOF ASAP+): m/z calculated for $C_{12}H_{15}BrO_2$: requires 271.0334 $[M+H]^+$; found 271.0332

4-((10H-Phenoxazin-10-yl)methyl)phenyl pivalate (7)



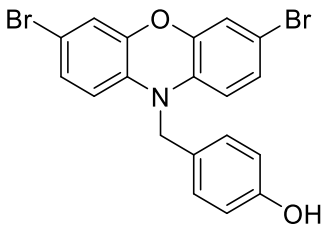
Phenoxazine (1.40 g, 7.56 mmol) was dissolved in DMF (40 mL) before being cooled to 0 ^{o}C. NaH – 60% in mineral oil (0.36 g, 9.07 mmol) was then added portion wise to the solution over the period of 5 min, which was then left to stir at 0 ^{o}C for a further 10 min. 4-(bromomethyl)phenyl pivalate (**6**) (2.05 g, 7.56 mmol) in DMF (10 mL) was then added dropwise to the reaction mixture and then was left to stir for 4 hrs at rt. The reaction mixture was then cooled to 0 ^{o}C before being quenched with dropwise addition of H_2O. The reaction mixture was partitioned with EtOAc (100 mL) and H_2O (100 mL). The organic layer was washed with H_2O (3 x 50 mL), brine (50 mL) and dried ($MgSO_4$) and concentrated *in-vacuo* to afford the crude product. The title compound (**7**) was purified via column chromatography 5:95 to 10:90 (EtOAc/Pet ether) to afford a white solid (1.43 g, 3.83 mmol, 51 %). M.p. 101-103 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 - 7.27 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.10 - 6.99 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 6.75 - 6.64 (m, 6 H, Ar*H*), 6.33 (d, *J* = 8.1 Hz, 2 H, Ar*H*), 4.78 (s, 2 H, NC*H*$_2$Ar), 1.36 (s, 9 H, ArOC(O)C(C*H*$_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 150.2, 145.2, 133.7, 129.0, 127.0, 123.8, 115.3, 112.3, 49.0, 39.1, 27.2; I.R (thinfilm) ν max (cm^{-1}): 1744.94 (C=O);); HRMS (ESI): m/z calculated for $C_{24}H_{23}NO_3$ requires 374.1756 for $[M+H]^+$, found 374.1773; requires 396.1576 for $[M+Na]^+$, found 396.1596

4-((3,7-Dibromo-10H-phenoxazin-10-yl)methyl)phenyl pivalate (8)



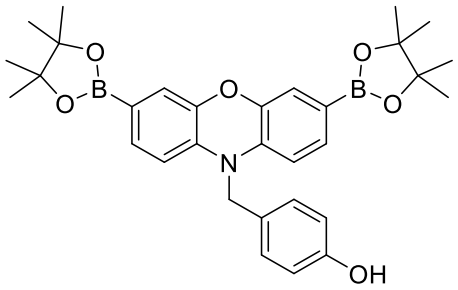
To a solution of **7** (1.22 g, 3.27 mmol) in $CHCl_3$ (100 mL), NBS (1.16 g, 6.54 mmol) was added portion-wise and the reaction was left to stir for 1 hr. The reaction was then quenched with H_2O (100 mL) and the organic layer was washed with H_2O (3 x 100 mL), brine (100 mL) and dried ($MgSO_4$) and concentrated *in-vacuo* to afford the title compound (**8**) as a blue solid (Quantiative yield). Mp. 162-165 ^oC; ^1H NMR (300 MHz, Acetone – d6) δ 7.41 - 7.34 (d, *J* = 8.3 Hz, 2 H, Ar*H*), 7.15 - 7.08 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 6.97 - 6.91 (m, 2 H, Ar*H*), 6.86 (m, 2 H, Ar*H*), 6.51 - 6.42 (m, 2 H, Ar*H*), 4.92 (s, 2 H, NCH_2Ar), 1.33 (s, 9 H, COC(CH_3)$_3$); ^{13}C NMR (75.5 MHz, Acetone – d6) δ 177.5, 151.8, 146.5, 134.0, 128.4, 128.2, 123.4, 119.4, 115.3, 113.5, 48.9, 40.0, 27.7; I.R (thinfilm) ν max (cm^{-1}): 1749.27 (C=O); HRMS (FTMS-NSI): m/z calculated for $C_{24}H_{21}Br_2NO_3$ requires 529.9961 for $[M+H]^+$, found 529.9956

4-((3,7-Dibromo-10H-phenoxazin-10-yl)methyl)phenol (9)



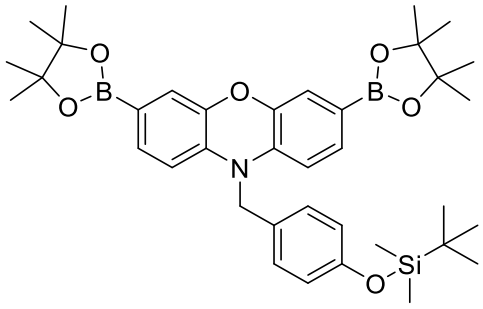
A solution of **8** (1.60 g, 3.01 mmol) in PhMe (100 mL) was cooled to 0 ^{o}C before the dropwise addition of DIBAL – 1 M in Heptane (9.03 mL). The reaction was stirred at 0 ^{o}C for 1 hr before being allowed to warm to rt. The reaction mixture was stirred for another 1 h before being quenched with saturated NH_4Cl (50 mL). EtOAc (100 mL) was then added and the organic layer was washed with H_2O (3 x 100 mL), brine (100 mL) and dried ($MgSO_4$) and concentrated *in-vacuo* to afford the title compound (**9**) as a pink gum (0.9 g, 2.00 mmol, 67 %). ^{1}H NMR (300 MHz, Acetone – d6) δ 7.16 - 7.08 (d, *J* = 8.7 Hz, 2 H, Ar*H*), 6.91 (dd, *J* = 2.3, 8.7 Hz, 2 H, Ar*H*), 6.86 - 6.77 (m, 4 H, Ar*H*), 6.48 - 6.40 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 4.77 (s, 2 H, NC*H*$_2$Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 154.91, 145.36, 144.11, 132.68, 127.67, 127.01, 126.72, 118.59, 115.99, 113.33, 112.84, 48.65; HRMS (TOF ASAP+): m/z calculated for $C_{19}H_{13}Br_2NO_2$ requires 444.9313 for $[M]^+$, found 444.9307

4-((3,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazin-10-yl)methyl)phenol (Pinkment-OH)



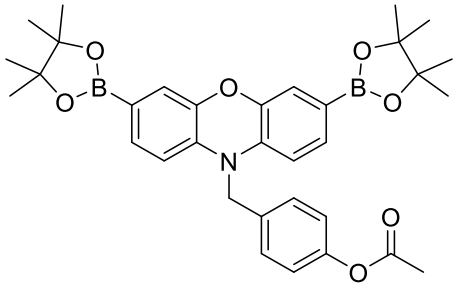
7 (0.9 g, 2.00 mmol), bis(pinacolato) diboron (1.53 g, 6.00 mmol), potassium acetate (1.2 g, 11.94 mmol) and Pd(dppf)Cl_2.DCM (0.145 g, 0.2 mmol) was dissolved in anhydrous DMF (10 mL) and refluxed under argon for 2 hrs. The reaction was cooled to rt and partitioned with EtOAc (50 mL) and H_2O (50 mL). The organic layer was washed with H_2O (3 x 50 mL), brine (50 mL), dried ($MgSO_4$) and concentrated *in-vacuo* to afford the crude product. The title compound was purified via column chromatography 20:80 to 50:50 (EtOAc/Pet Ether) to afford a white solid (0.90 g, 1.66 mmol, 83 %). M.p. 230-233 ^oC; ^1H NMR (300 MHz, Acetone - d6) δ 8.34 (s, 1 H, O-H), 7.16 (m, 4 H, Ar*H*), 6.97 (s, 2 H, Ar*H*), 6.82 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 6.54 (d, *J* = 7.9 Hz, 2 H, Ar*H*), 4.85 (s, 2 H, NCH_2Ar), 1.30 (s, 24 H, BPin); ^{13}C NMR (75 MHz, Acetone – d6) δ 157.9, 145.6, 137.3, 132.4, 128.6, 127.5, 121.7, 116.9, 116.8, 113.5, 84.7, 48.4, 25.5; I.R (thinfilm) ν max (cm^{-1}): 3328.93 (O-H); HRMS (FTMS-NSI): m/z calculated for $C_{31}H_{37}B_2NO_6$ requires 540.2952 for $[M+H]^+$, found 540.2947

10-(4-((*tert*-Butyldimethylsilyl)oxy)benzyl)-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazine (Pinkment-OTBS)



To a solution of **Pinkment-OH** (0.10 g, 0.15 mmol) in DMF (100 mL), *tert*-butyldimethylsilylchloride (0.096 g, 0.6 mmol) and imidazole (0.040 g, 0.6 mmol) was added and the reaction was left to stir overnight. *Tert*-butyldimethylsilylchloride (0.096 g, 0.6 mmol) and imidazole (0.040 g, 0.6 mmol) was then again added and the reaction was stirred for 3 d. H_2O (100 mL) and EtOAc (100 mL) was added and the organic layer was washed with H_2O (3 x 100 mL), brine (100 mL), dried ($MgSO_4$) and concentrated *in-vacuo* to afford the crude material. The title compound was purified via column chromatography 0:100 to 5:95 (EtOAc/Pet ether) to afford a brown oil (0.011 g, 0.017 mmol, 11 %). ^{1}H NMR (300 MHz, Acetone – d6) δ 7.21 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.14 (dd, *J* = 1.3, 7.9 Hz, 2 H, Ar*H*), 6.97 (d, *J* = 1.3 Hz, 2 H, Ar*H*), 6.86 (d, *J* = 8.7 Hz, 2 H, Ar*H*), 6.53 (d, *J* = 8.1 Hz, 2 H, Ar*H*), 4.88 (s, 2 H, NCH_2Ar), 1.29 (s, 24 H, BPin), 0.97 (s, 9 H, OSi$(CH_3)_2$(CCH_3)$_3$), 0.19 (s, 6 H, OSi(CH_3)$_2$$(CCH_3)_3$); ^{13}C NMR (75.5 MHz, Acetone-d6) δ 156.0, 145.6, 137.3, 132.4, 129.8, 128.7, 121.8, 121.5, 113.4, 84.7, 48.3, 26.4, 25.5, 19.1, -3.9; I.R (thinfilm) ν max (cm^{-1}): 2977.24 (C-H, Sp^3); HRMS (TOF ASAP+): m/z calculated for $C_{37}H_{51}B_2NO_6Si$ requires 655.3786 for $[M+H]^+$, found 655.3773

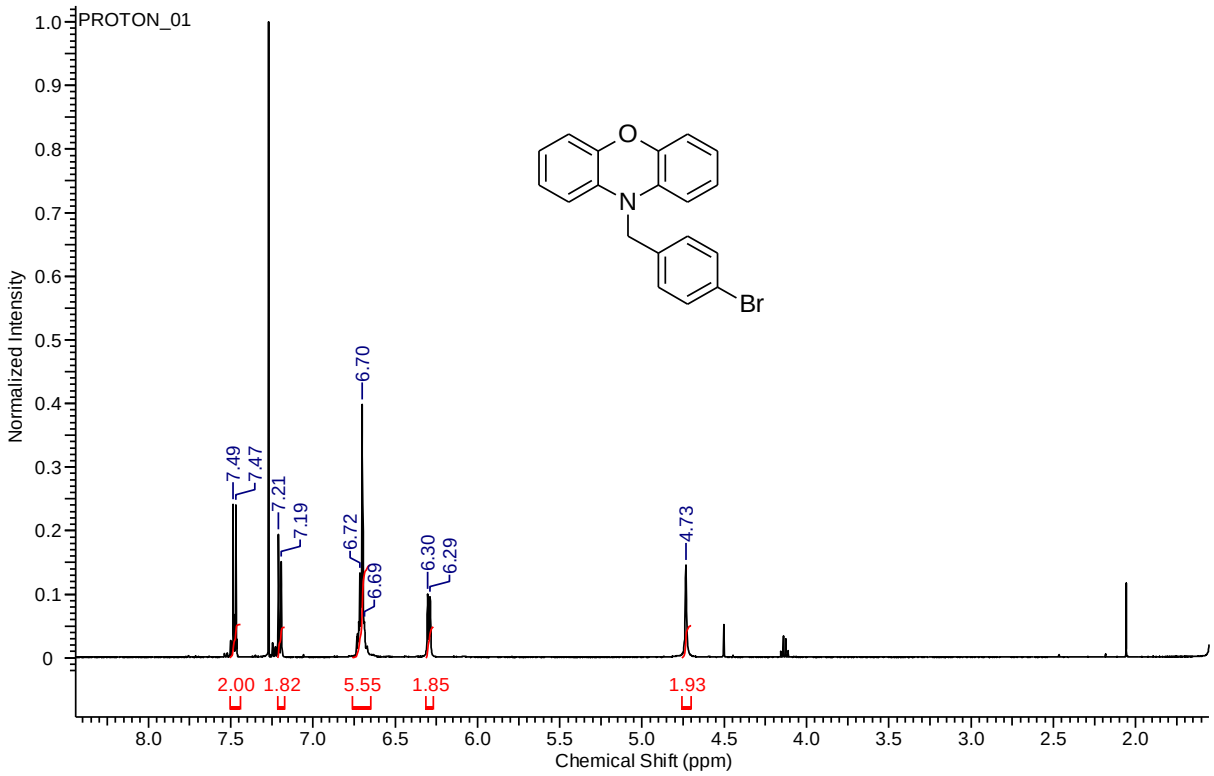
4-((3,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazin-10-yl)methyl)phenyl acetate (Pinkment-OAc)



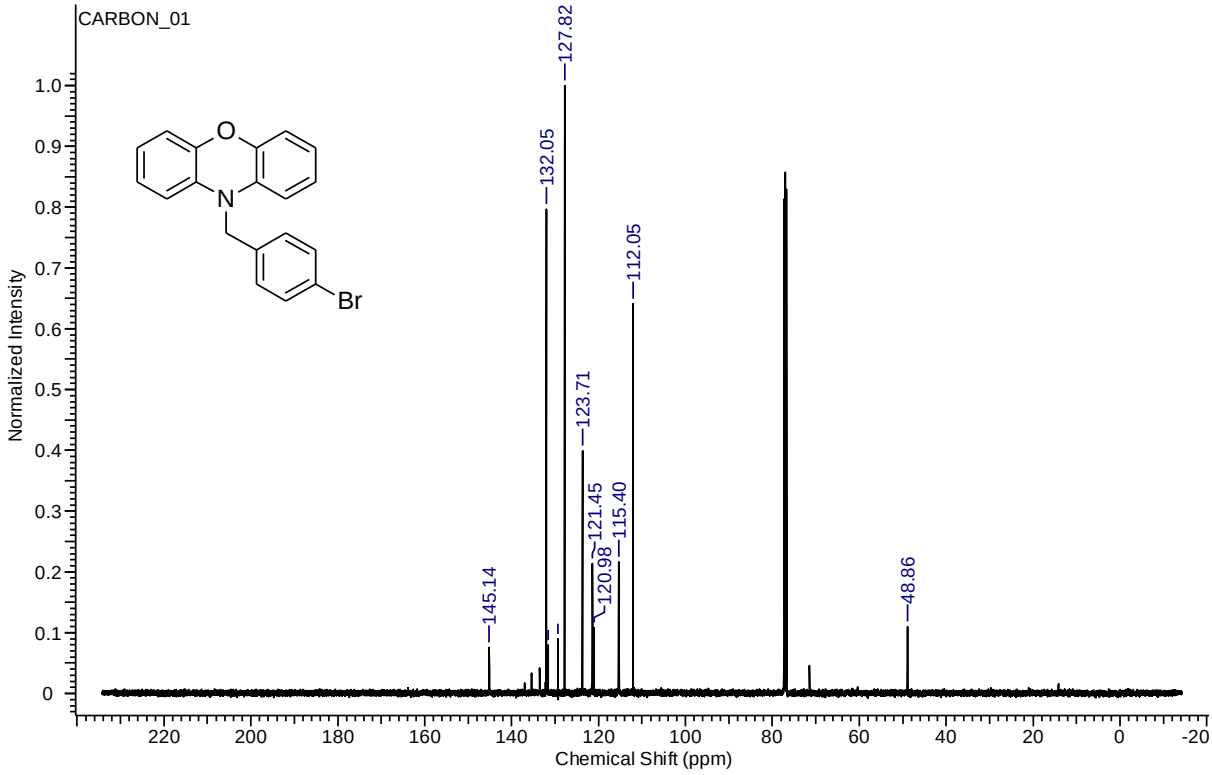
Pinkment-OH (0.10 g, 0.185 mmol) was dissolved in DCM (2 mL) and NEt_3 (0.075 µl, 0.55 mmol) was added. The solution was cooled to 0 ºC before the addition of AcCl (0.040 µl, 0.55 mmol). The reaction mixture was allowed to warm to rt and was stirred for 17 h. The reaction mixture was partitioned with H_2O (20 mL) and the organic layer was washed with H_2O (3 x 20 mL), Brine (1 x 20 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford the title compound as a pale yellow solid, no purification was required (0.077 g, 0.13 mmol, 71 %). M.p. 153-155 ºC. ^{1}H NMR (300 MHz, Acetone) δ 7.39 - 7.30 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.15 (m, 4 H, Ar*H*), 6.99 (d, *J* = 1.3 Hz, 2 H, Ar*H*), 6.59 - 6.48 (d, *J* = 7.9 Hz, 2 H, Ar*H*), 4.95 (s, 2 H, ArC*H*$_2$OAc), 2.24 (s, 3 H, OAc), 1.29 (s, 24 H, BPin); ^{13}C NMR (75 MHz, Acetone) δ 170.1, 151.4, 145.6, 137.1, 134.6, 132.5, 128.4, 123.5, 121.9, 113.4, 84.7, 48.4, 25.6, 21.4; I.R (thinfilm) ν max (cm^{-1}): 1766.00 (C=O); HRMS (FTMS-NSI): m/z calculated for $C_{33}H_{39}B_2NO_7$ requires 584.2985 for $[M+H]^+$, found 584.2974

6. NMR

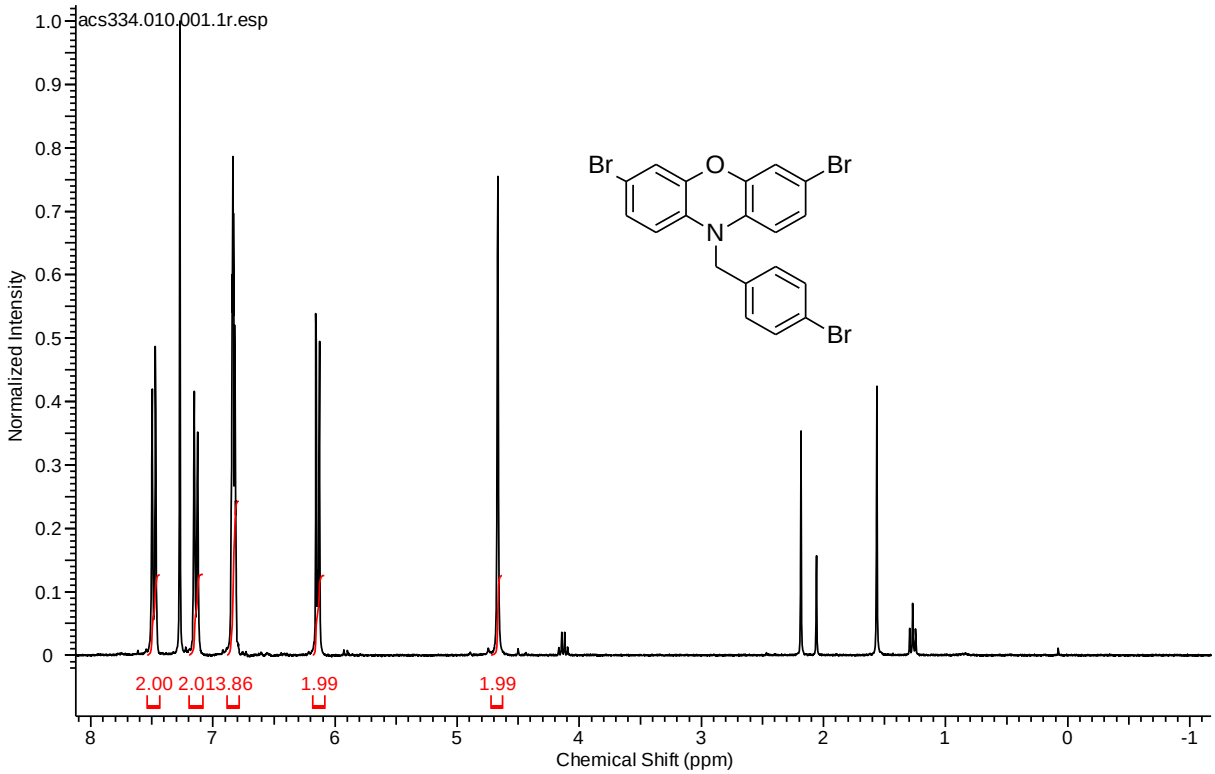
10-(4-bromobenzyl)-10H-phenoxazine (1) (500 MHz, $CDCl_3$)



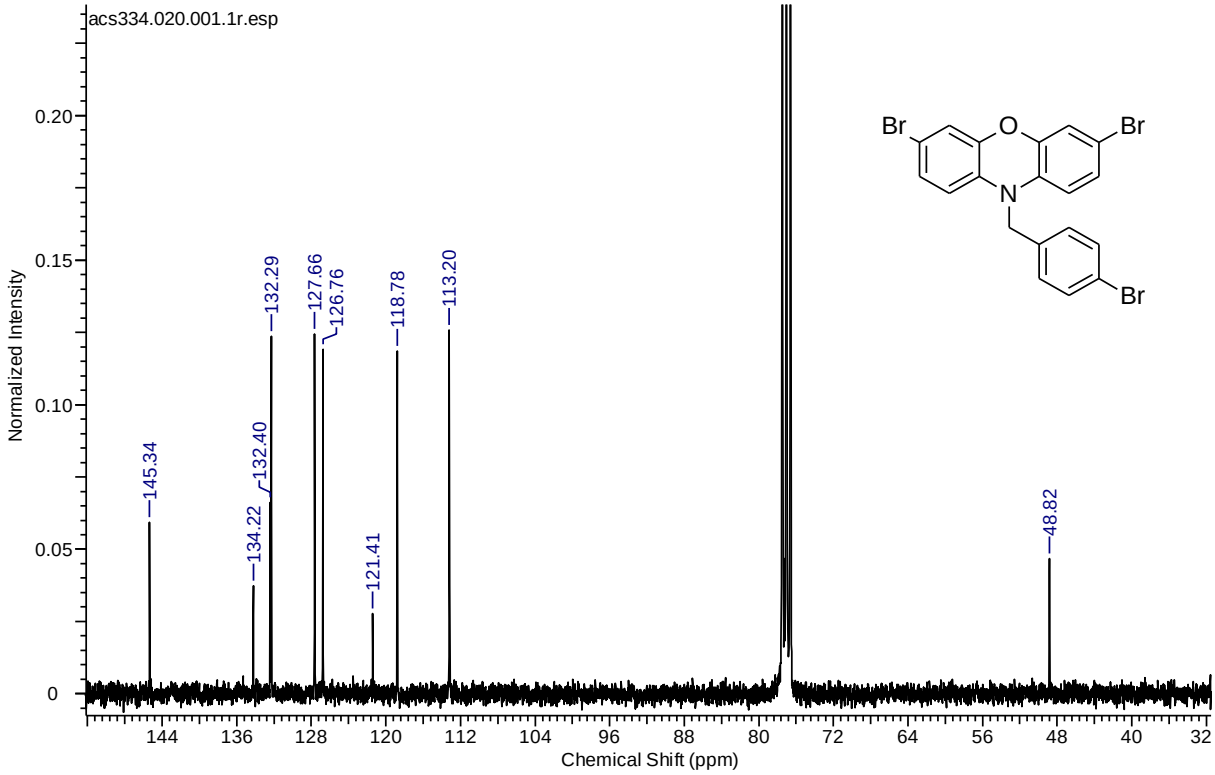
10-(4-bromobenzyl)-10H-phenoxazine (1) (125.75 MHz, $CDCl_3$)



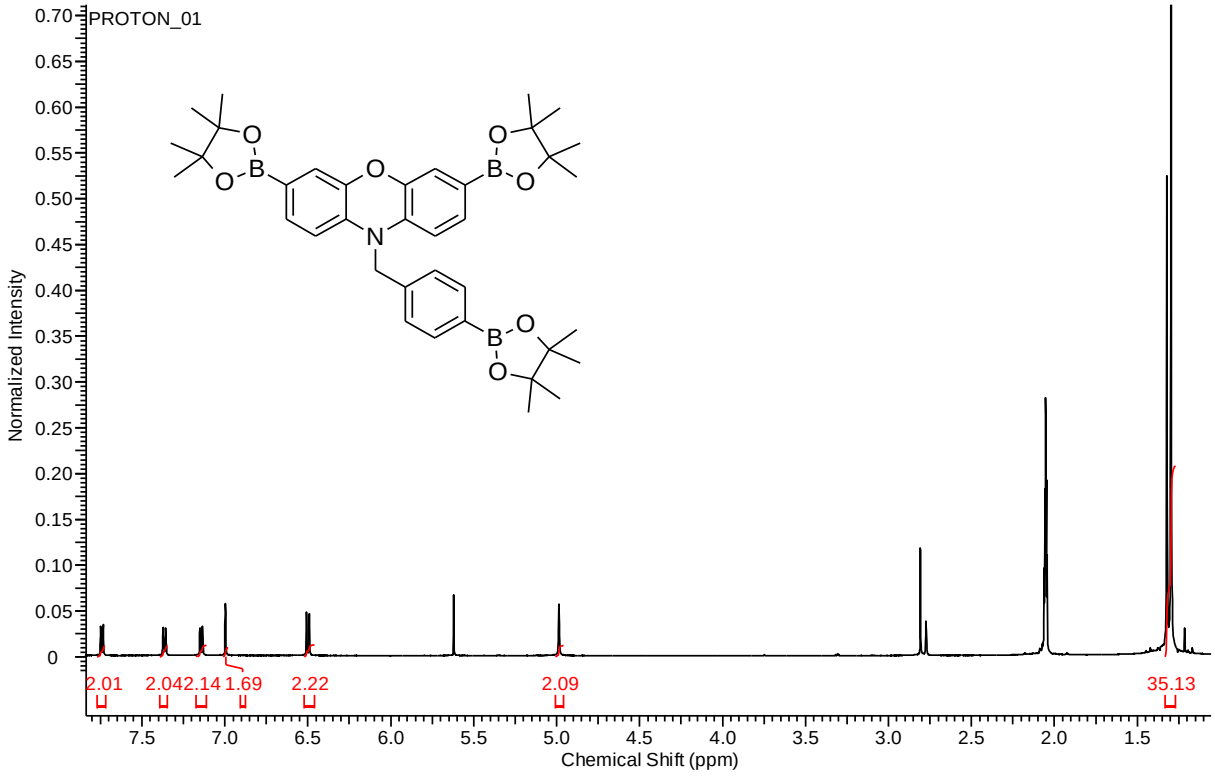
3,7-Dibromo-10-(4-bromobenzyl)-10H-phenoxazine (2) (300 MHz, $CDCl_3$)



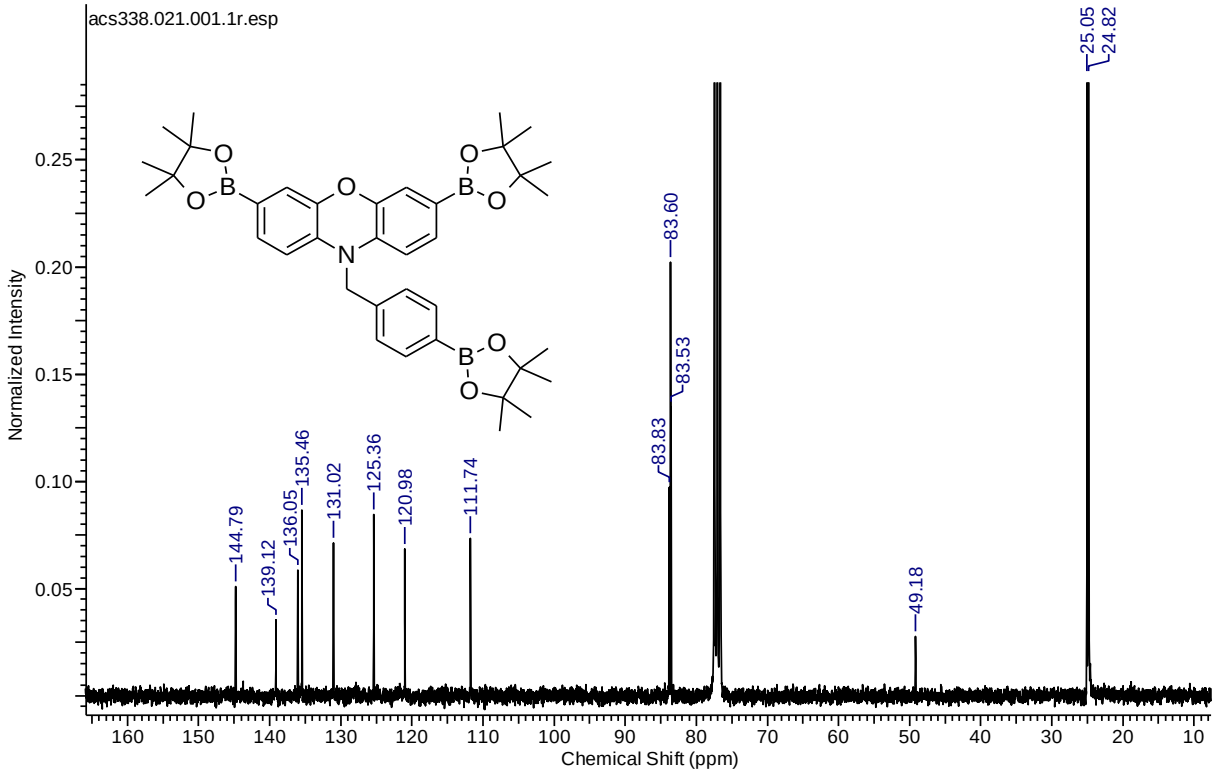
3,7-Dibromo-10-(4-bromobenzyl)-10H-phenoxazine (2) (75.5 MHz, $CDCl_3$)



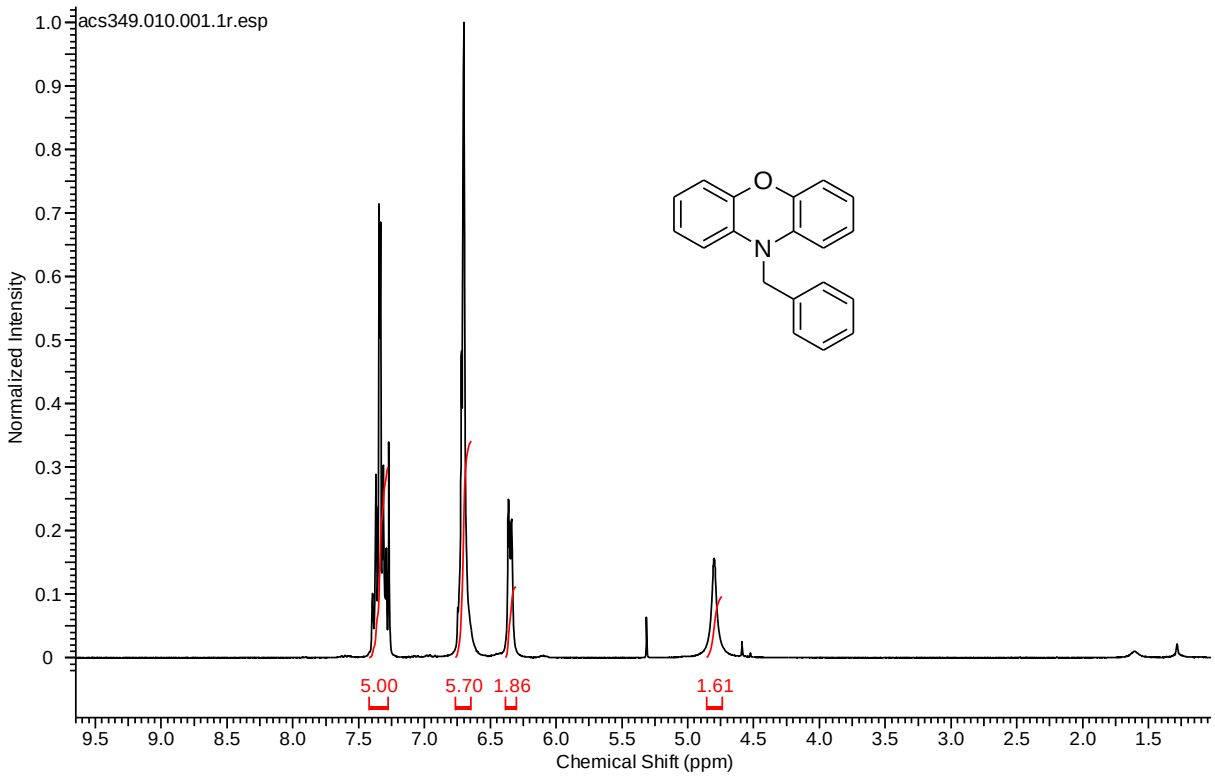
3,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-10H-phenoxazine (Pinkment) (500 MHz, Acetone-d6)



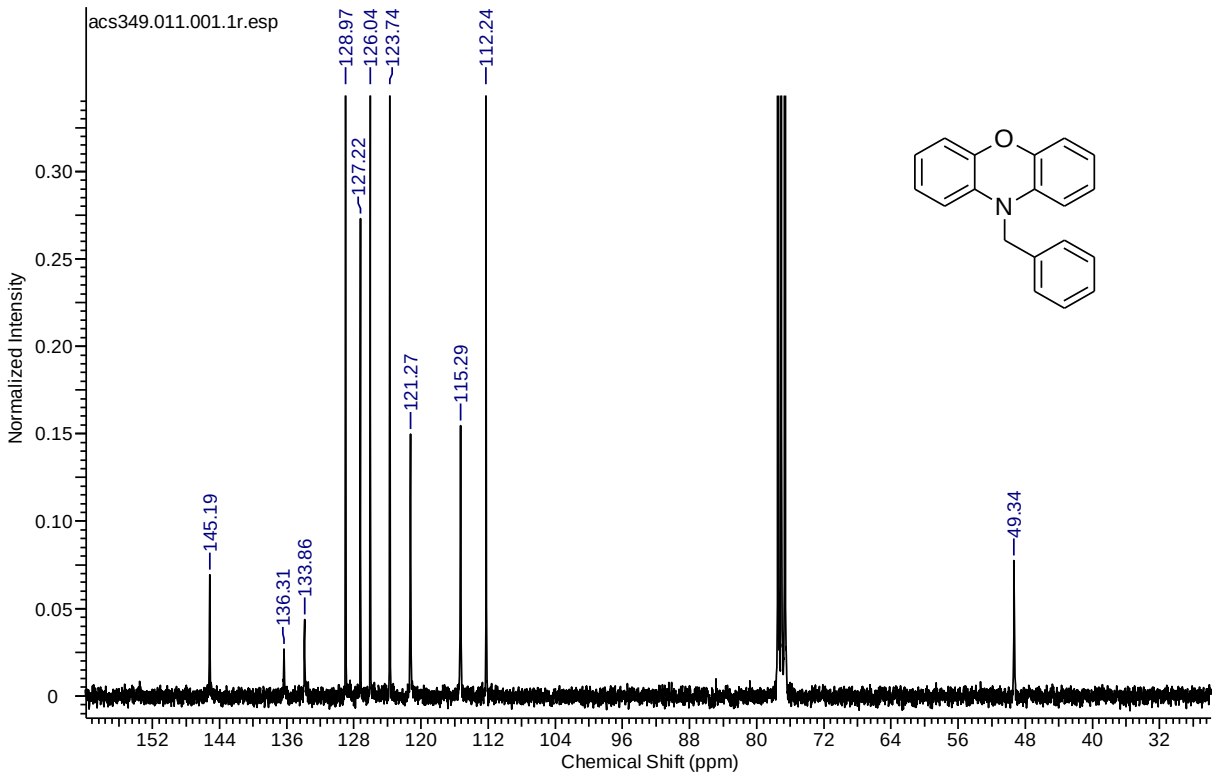
3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-10H-phenoxazine (Pinkment) (75.5 MHz, $CDCl_3$)



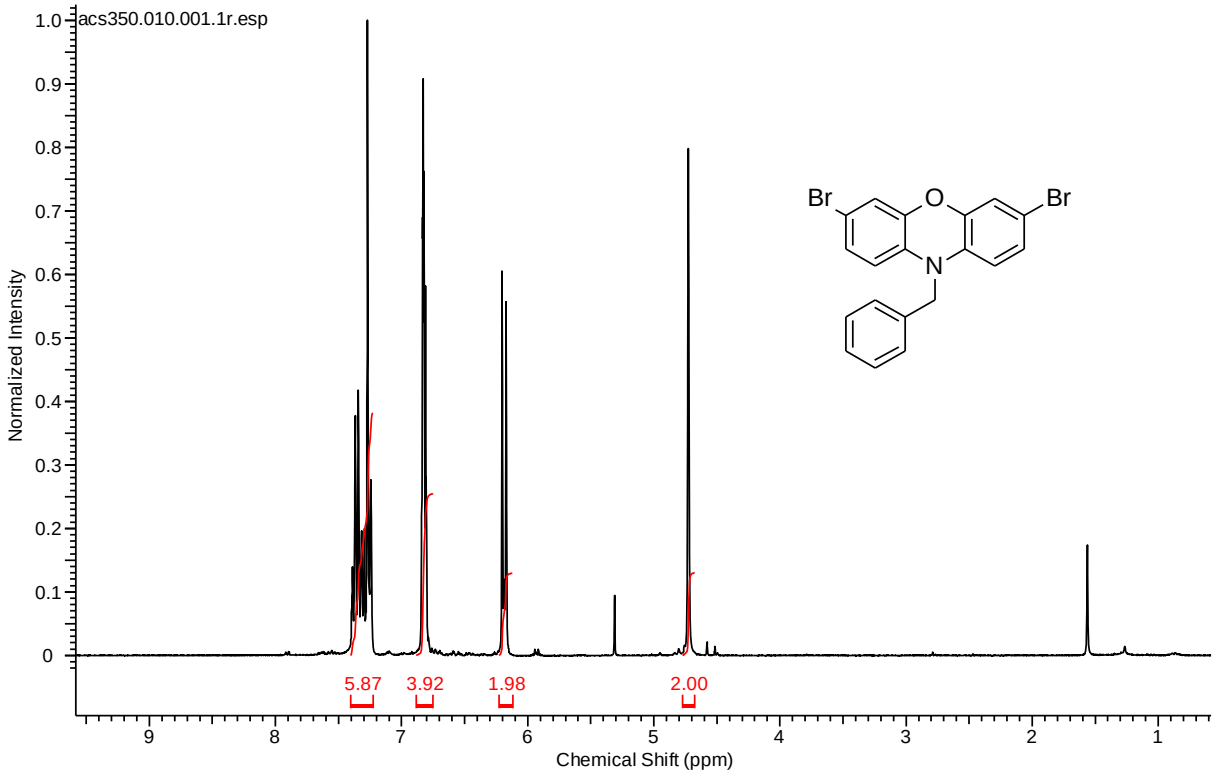
10-benzyl-10H-phenoxazine (3) (300 MHz, $CDCl_3$)



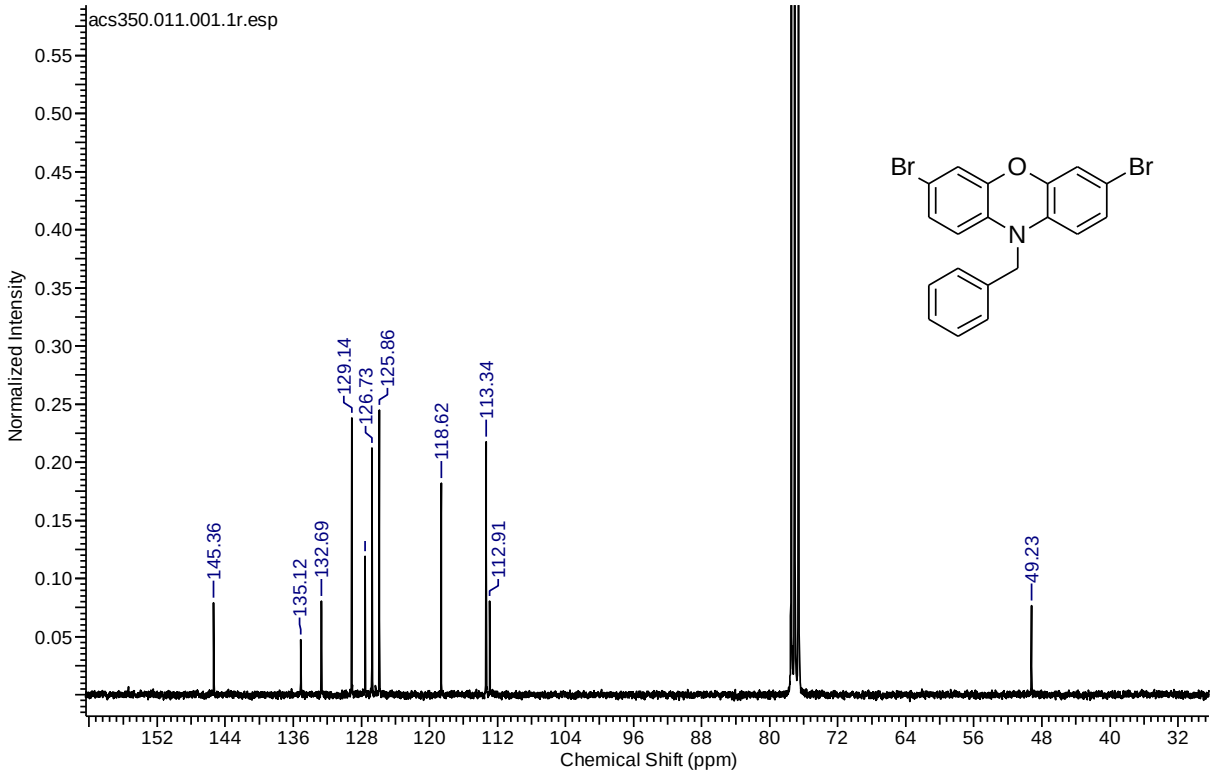
10-benzyl-10H-phenoxazine (3) (75.5 MHz, $CDCl_3$)



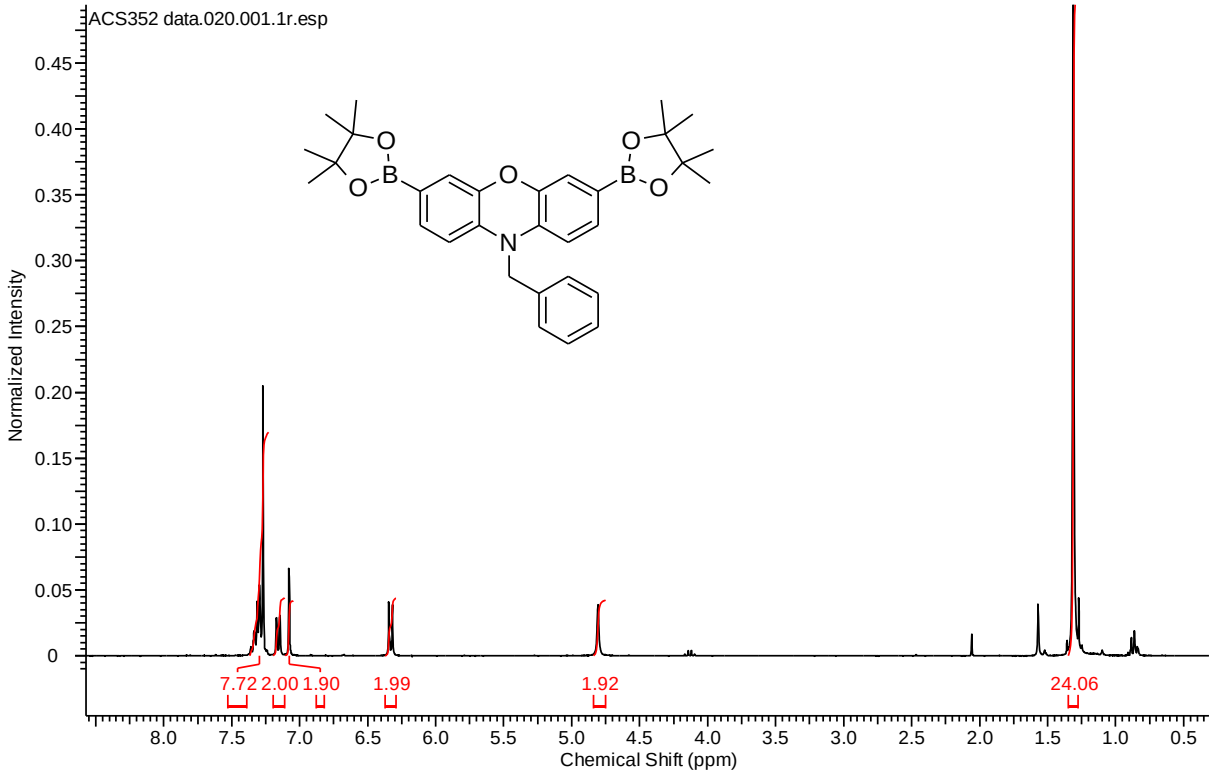
10-benzyl-3,7-dibromo-10H-phenoxazine (4) (300 MHz, $CDCl_3$)



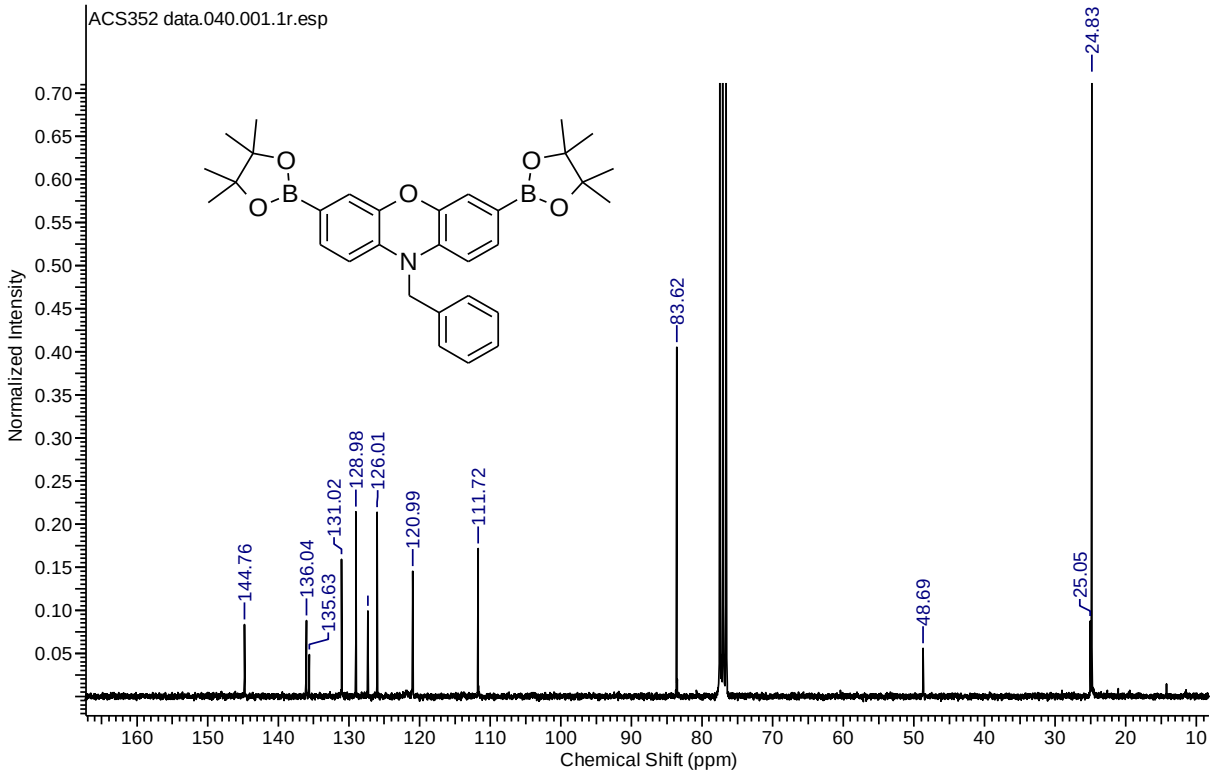
10-benzyl-3,7-dibromo-10H-phenoxazine (4) (75.5 MHz, $CDCl_3$)



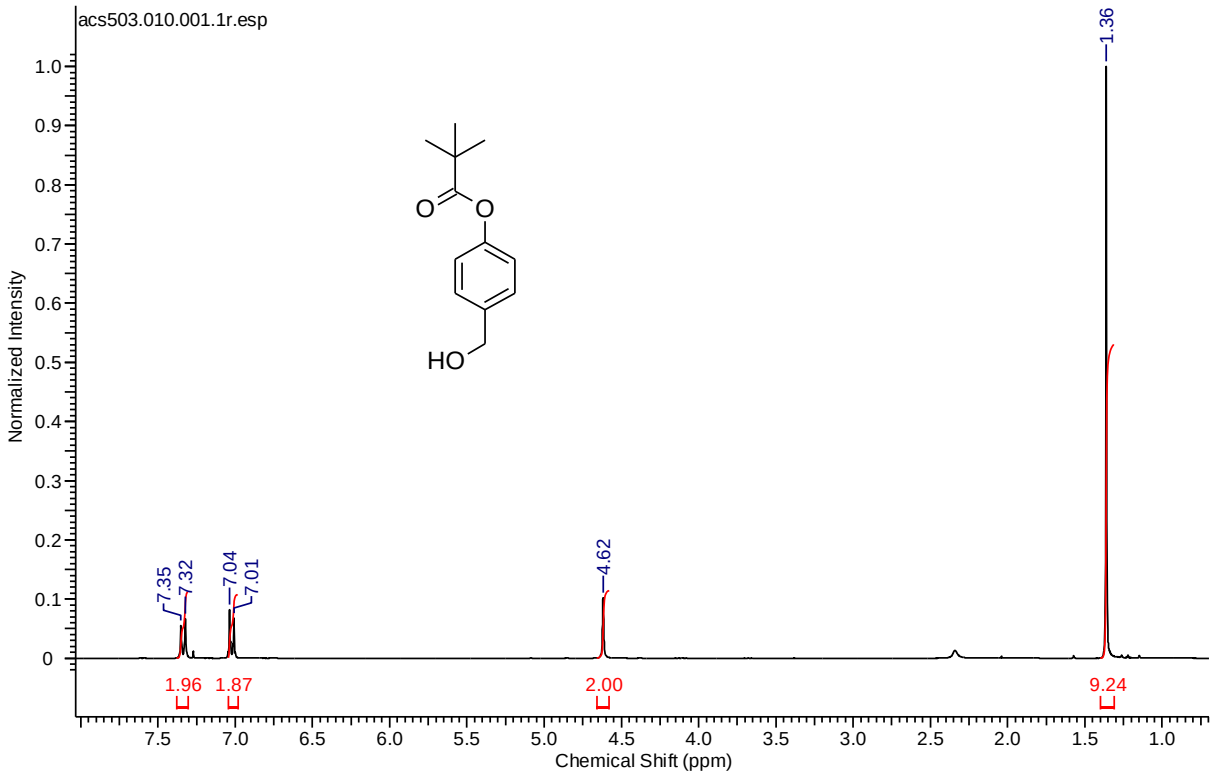
10-benzyl-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazine (Pinkment-Bn) (300 MHz, $CDCl_3$)



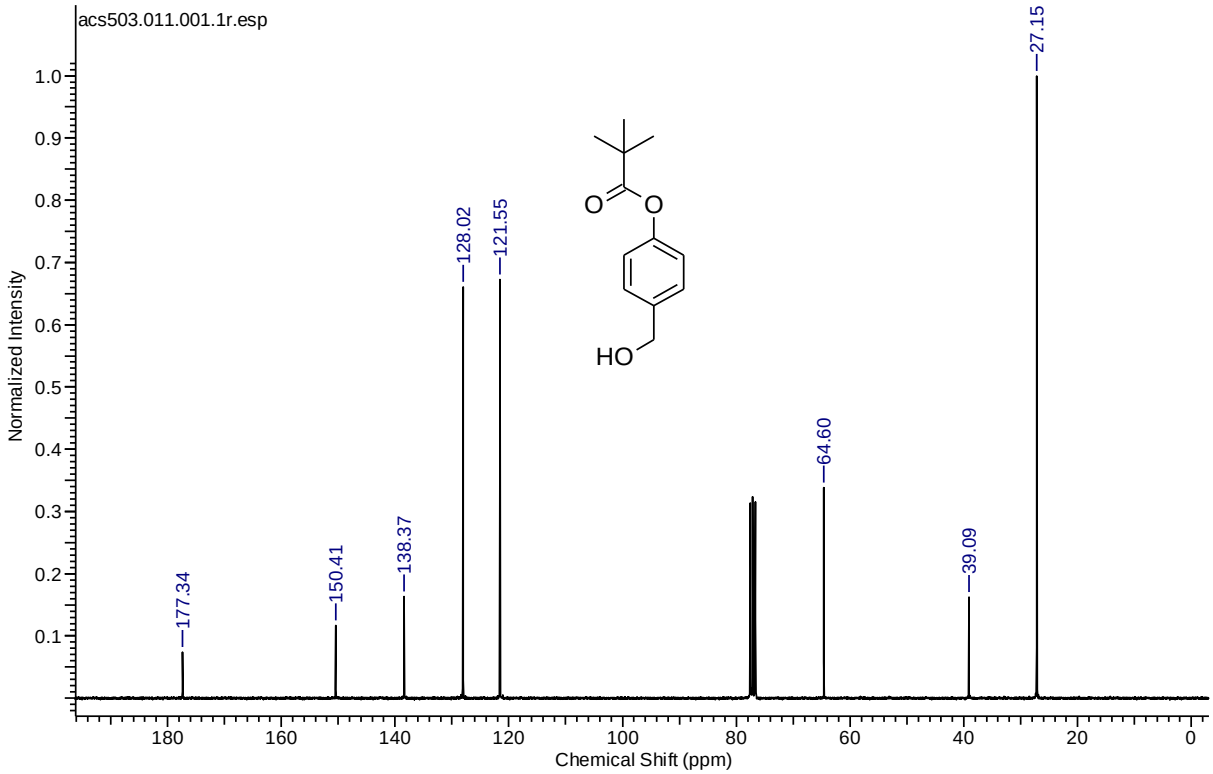
10-benzyl-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazine (Pinkment-Bn) (75.5 MHz, $CDCl_3$)



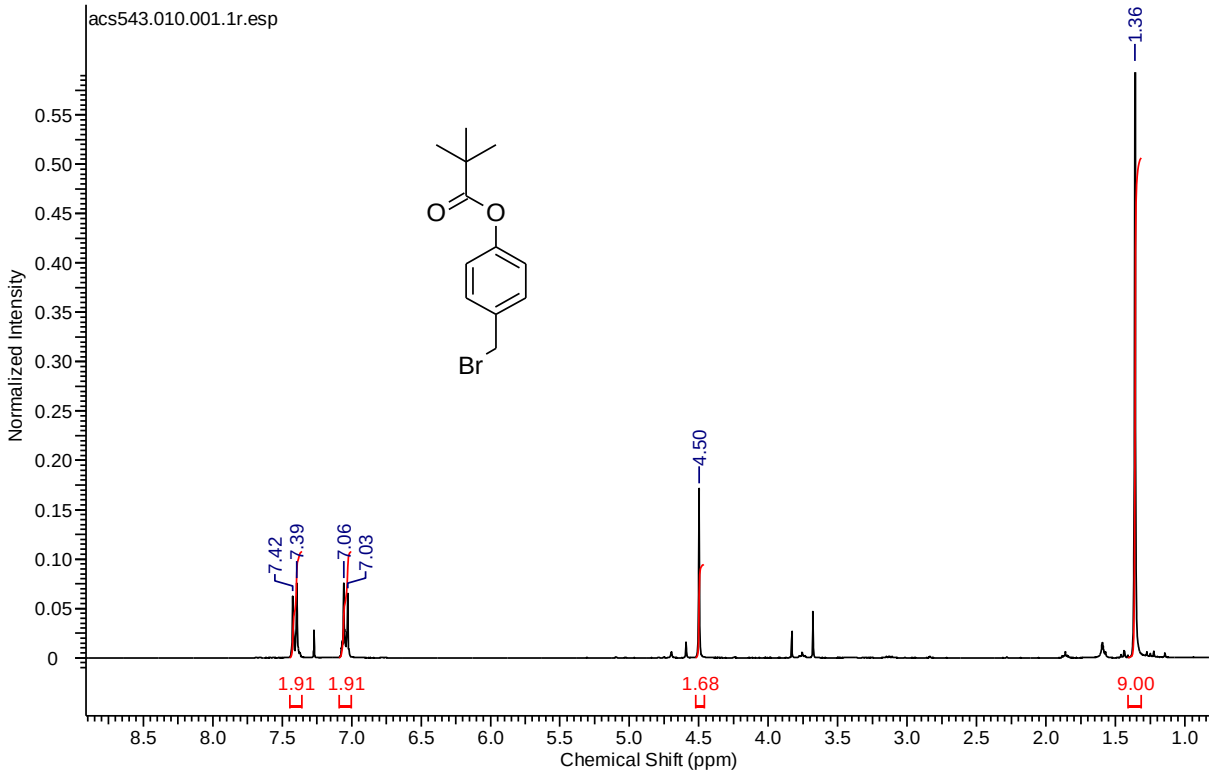
4-(Hydroxymethyl)phenyl pivalate (5) (300 MHz, $CDCl_3$)



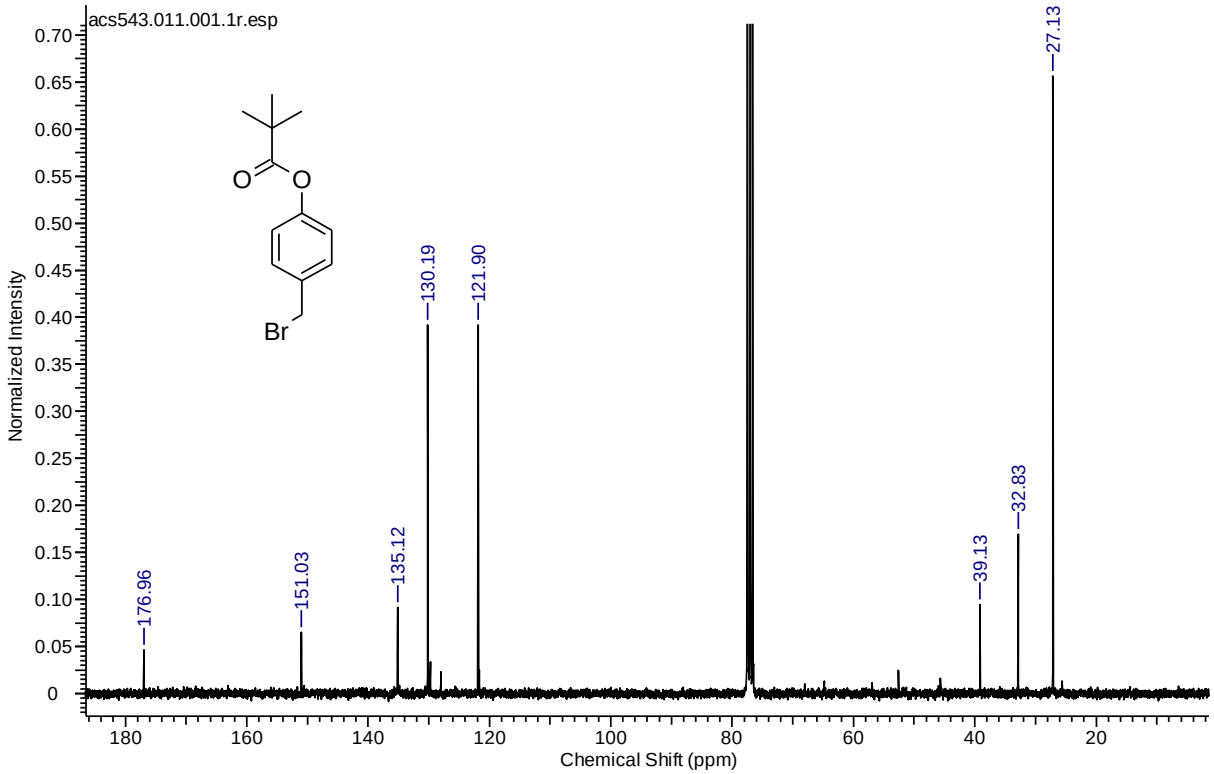
4-(Hydroxymethyl)phenyl pivalate (5) (75.5 MHz, $CDCl_3$)



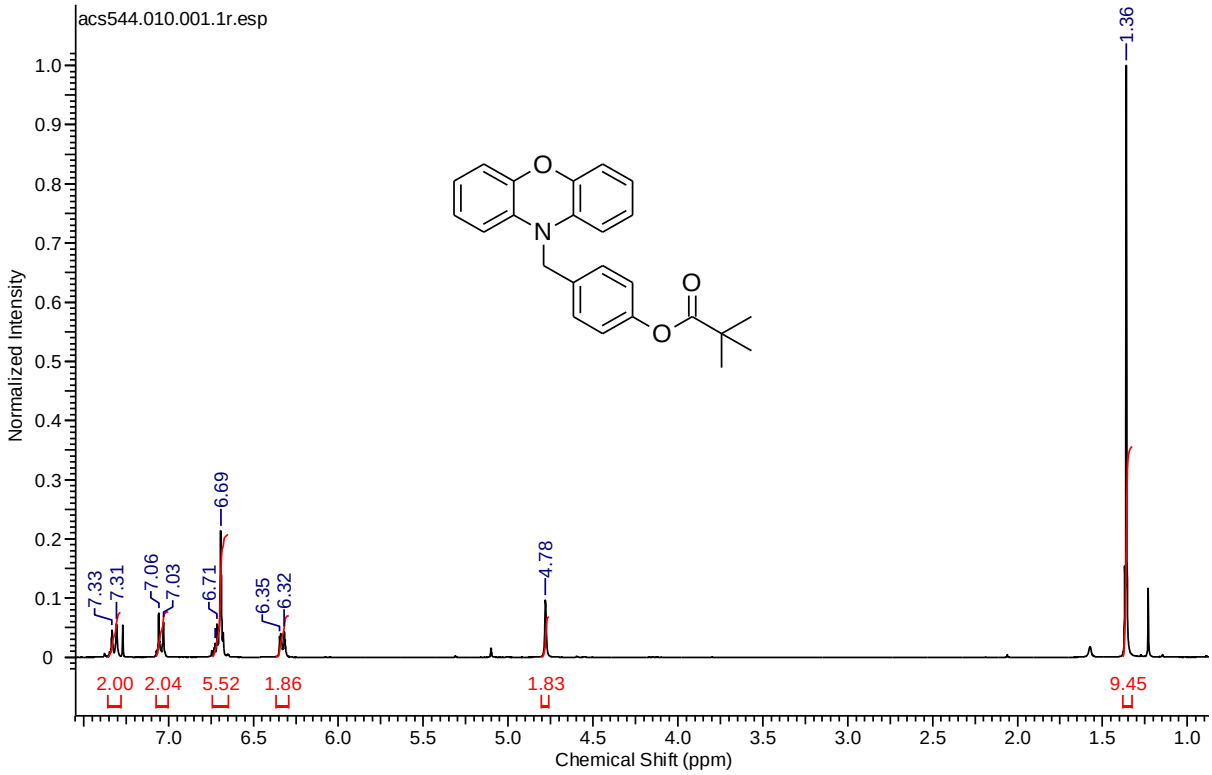
4-(Bromomethyl)phenyl pivalate (6) (300 MHz, $CDCl_3$)



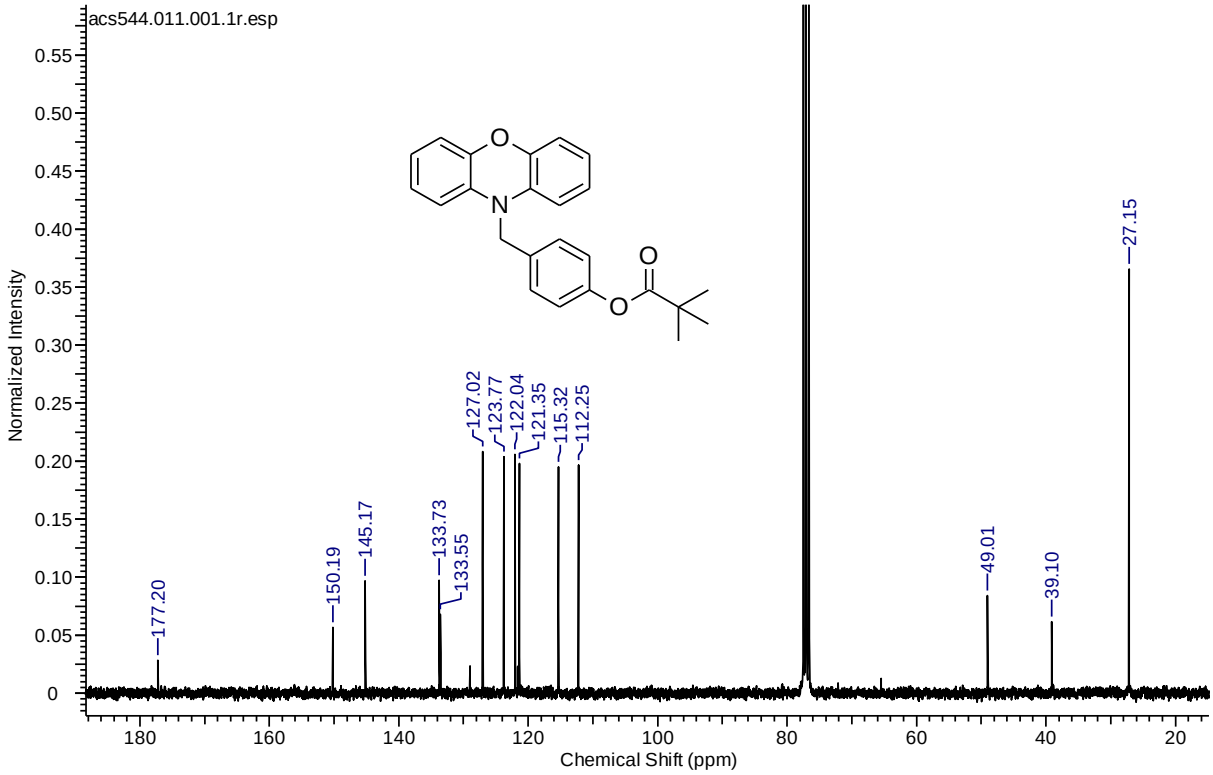
4-(bromomethyl)phenyl pivalate (6) (75.5 MHz, $CDCl_3$)



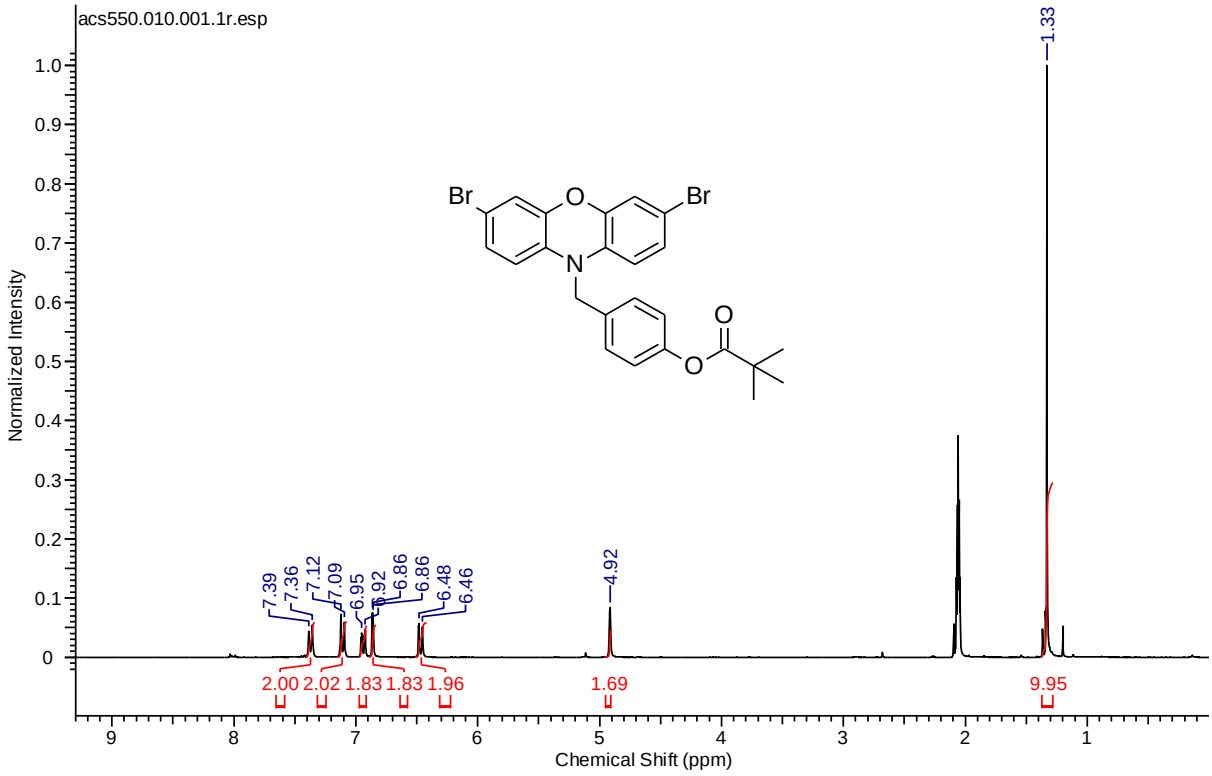
4-((10H-phenoxazin-10-yl)methyl)phenyl pivalate (7) (300 MHz, $CDCl_3$)



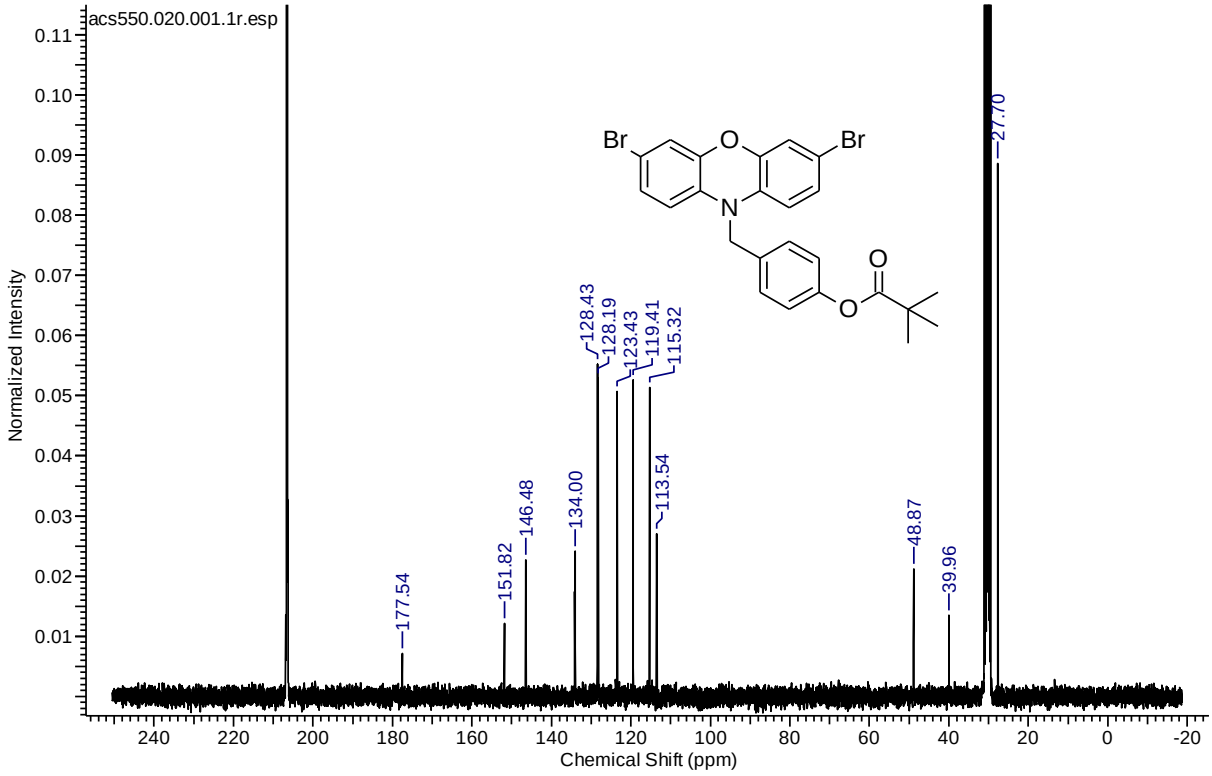
4-((10H-phenoxazin-10-yl)methyl)phenyl pivalate (7) (75.5 MHz, $CDCl_3$)



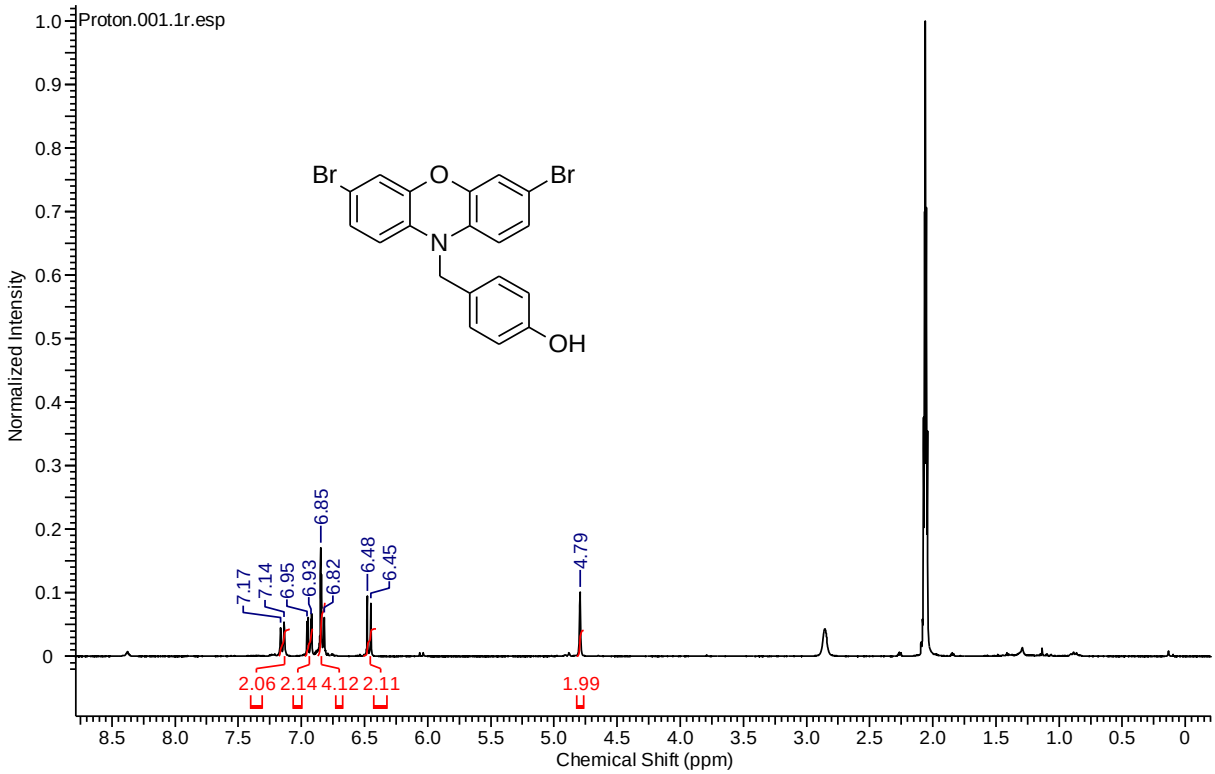
4-((3,7-dibromo-10H-phenoxazin-10-yl)methyl)phenyl pivalate (8) (300 MHz, Acetone-d6)



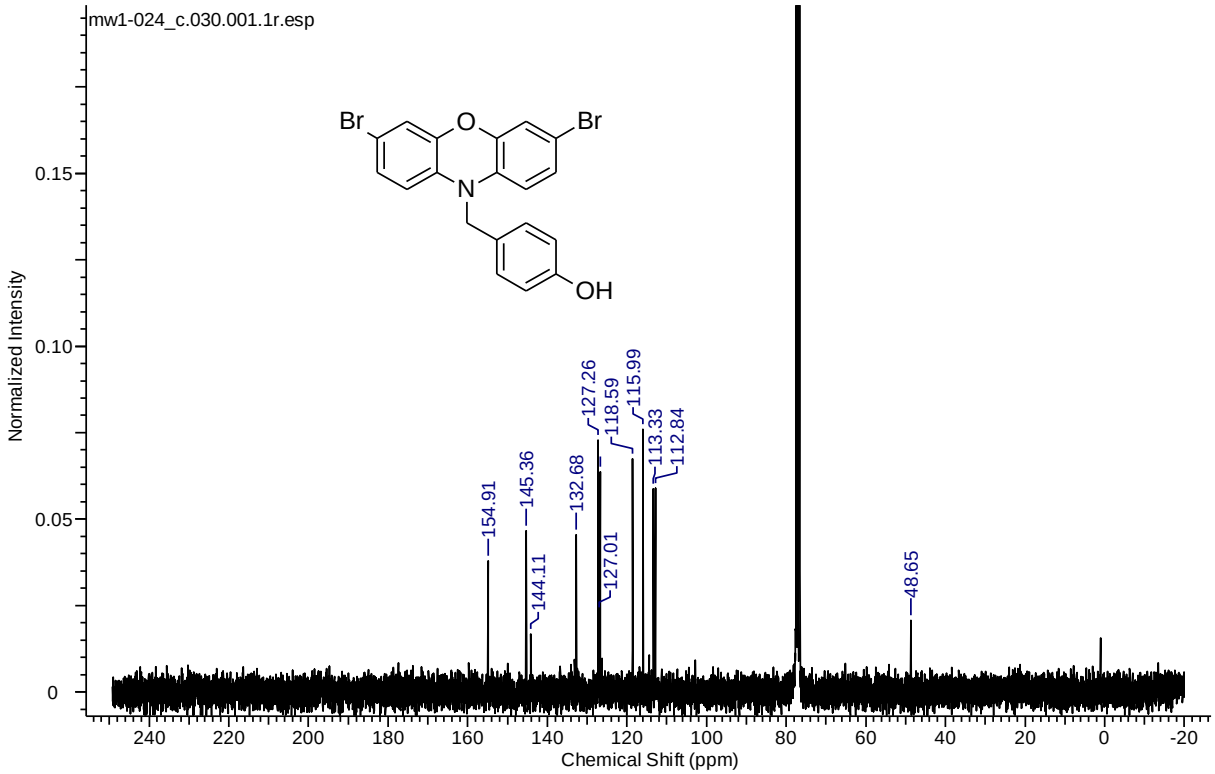
4-((3,7-Dibromo-10H-phenoxazin-10-yl)methyl)phenyl pivalate (8) (75.5 MHz, Acetone-d6)



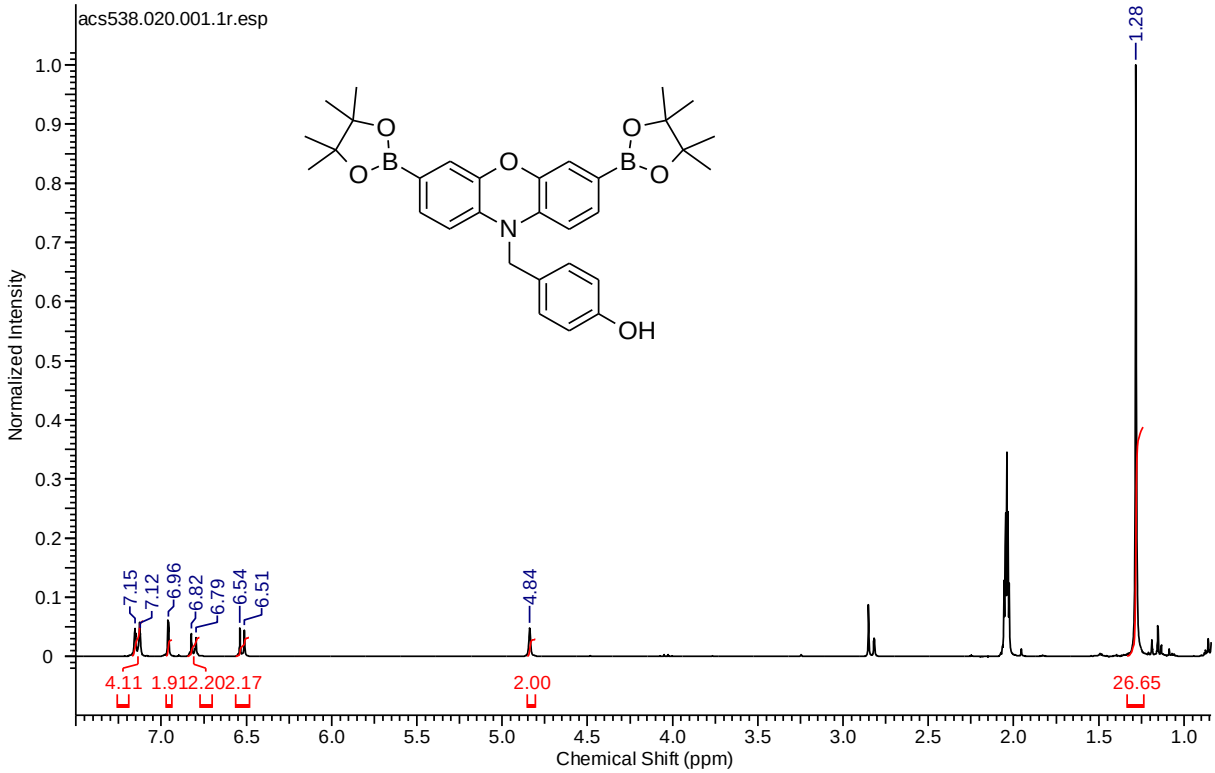
4-((3,7-Dibromo-10H-phenoxazin-10-yl)methyl)phenol (9) (300 MHz, Acetone-d6)



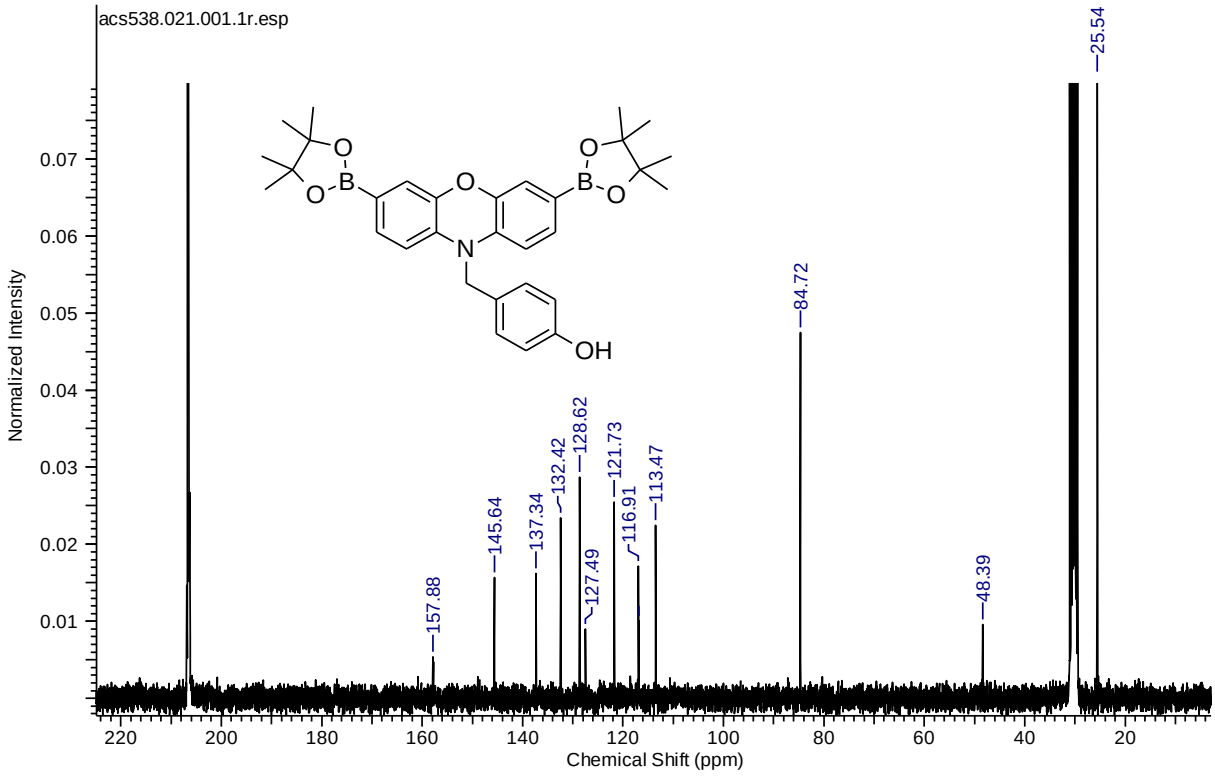
4-((3,7-Dibromo-10H-phenoxazin-10-yl)methyl)phenol (9) (75.5 MHz, $CDCl_3$)



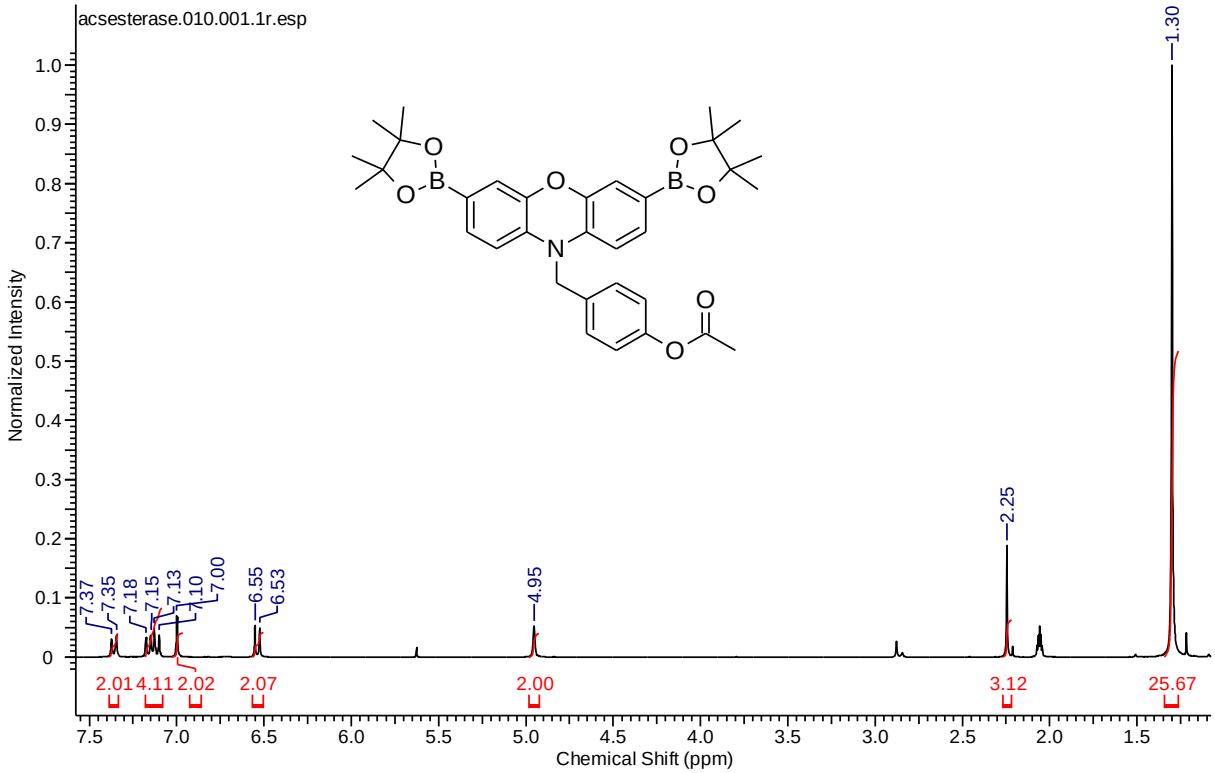
4-((3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazin-10-yl)methyl)phenol (Pinkment-OH) (300 MHz, Acetone-d6)



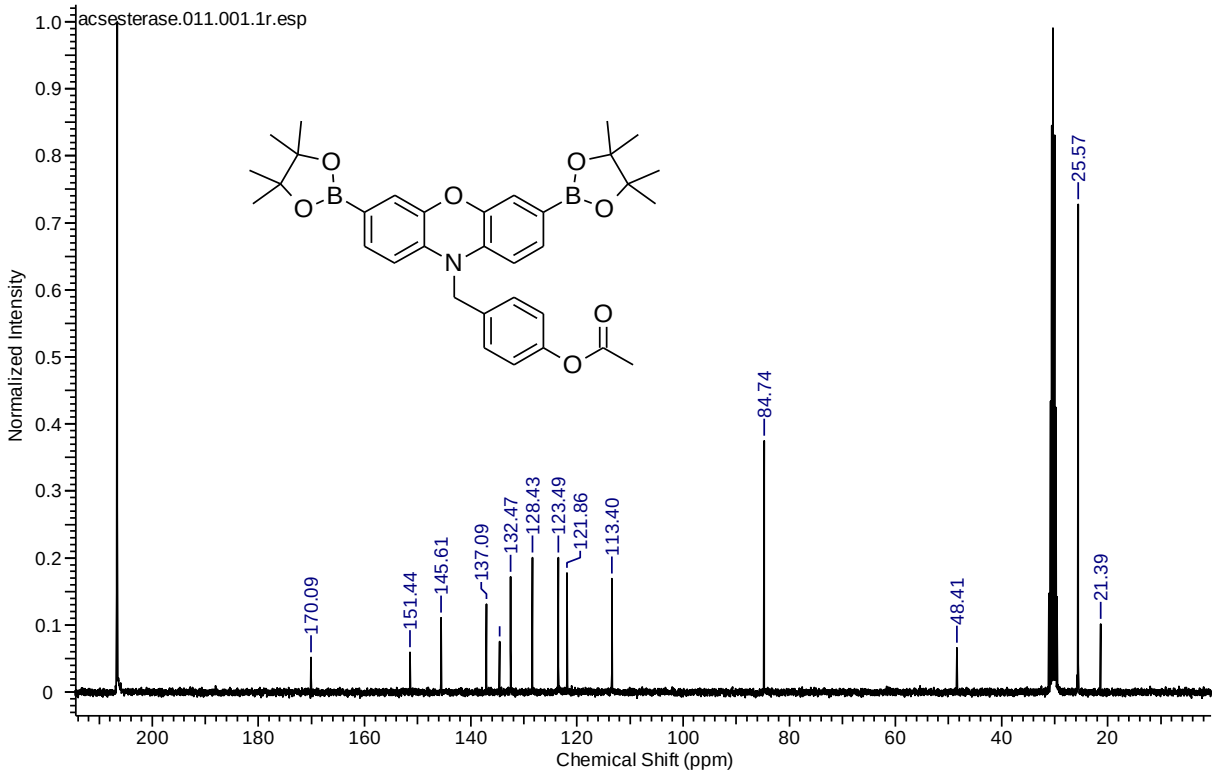
4-((3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazin-10-yl)methyl)phenol (Pinkment-OH) (75.5 MHz, Acetone-d6)



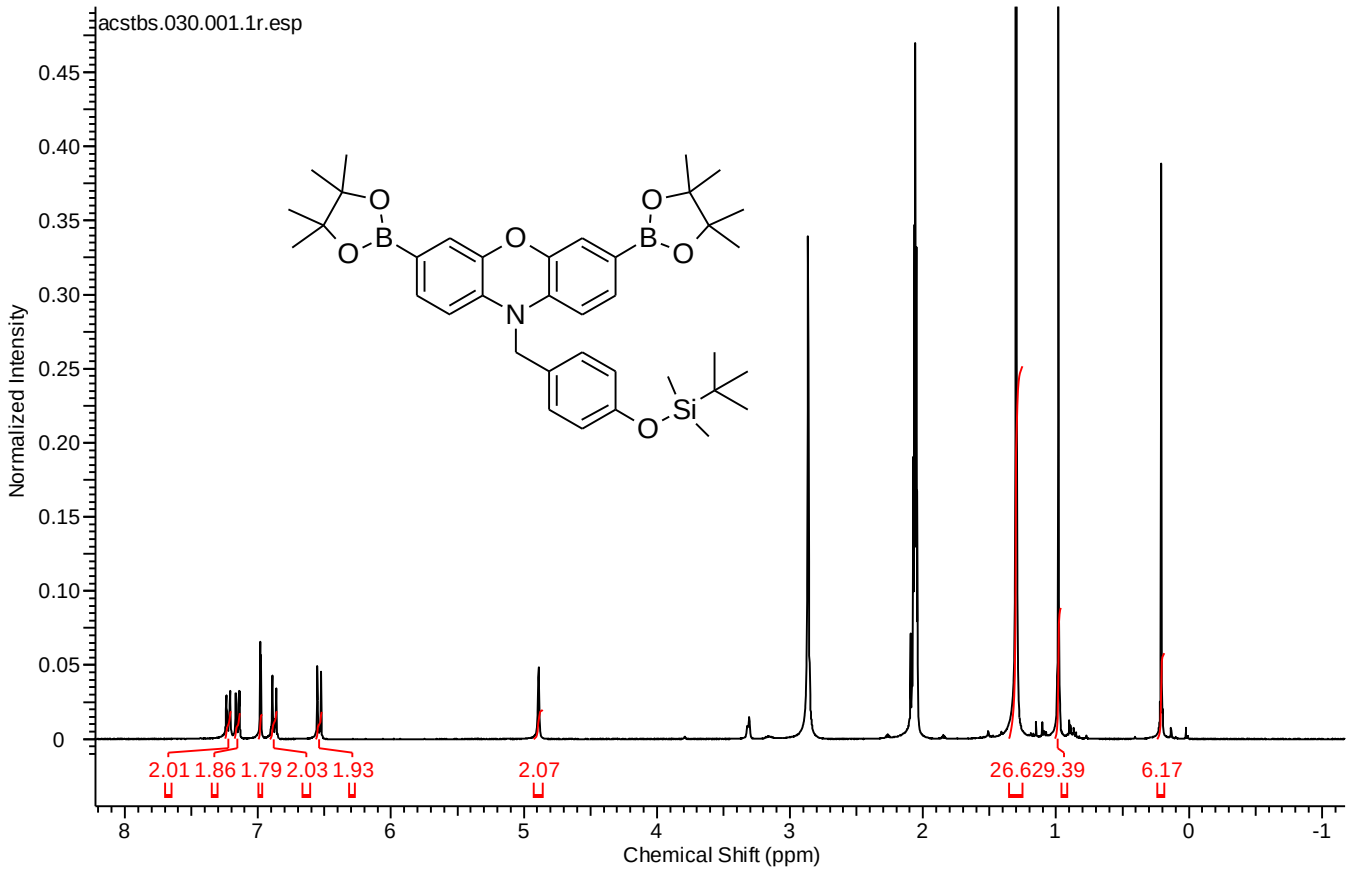
4-((3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazin-10-yl)methyl)phenyl acetate (Pinkment-OAc) (300 MHz, Acetone-d6)



4-((3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazin-10-yl)methyl)phenyl acetate (Pinkment-OAc) (75.5 MHz, Acetone-d6)



10-(4-((tert-butyldimethylsilyl)oxy)benzyl)-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazine (Pinkment-OTBS) (300 MHz, Acetone-d6)



10-(4-((tert-butyldimethylsilyl)oxy)benzyl)-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenoxazine (Pinkment-OTBS) (75.5 MHz, Acetone-d6)