Supporting Information

for

Multicomponent Synthesis of Stereogenic-at-Boron Fluorophores (BOSPYR) from Boronic Acids, Salicylaldehydes, and 2-Formylpyrrole Hydrazones

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General

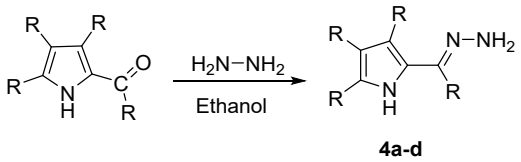
1D NMR spectra were recorded on a Bruker Spectrospin Avance DPX 400 spectrometer using $CDCl_3$, d_6-DMSO, and d_6-Acetone as the solvent. 2D and ^{11}B NMR spectra recorded on Bruker AVANCE III 400 MHz NMR spectrometer. Chemical shift values are reported in ppm from tetramethylsilane as an internal standard. Spin multiplicities are reported as the following: s (singlet), d (doublet), dd (doublet of doublet), m (multiplet). HRMS data were acquired on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. HPLC analyses were conducted on the Agilent HPLC system using Daicel Chiralpak OD-H, IA columns at room temperatures. Different n-Hexane/Isopropanol systems were used as mobile phases for the analyses. Chiral HPLC analytical resolutions were done using the same Agilent HPLC system. UV-Vis absorption spectra were taken on a Shimadzu UV-2450 UV–VIS spectrophotometer. Fluorescence measurements were recorded on a Perkin–Elmer (Model LS 55) spectrofluorometer. A 1.0 cm path length quartz cell was used for all absorption and emission spectra recordings. The fluorescence lifetime measurements were performed using a LaserStrobe Model TM-3 lifetime fluorophotometer from Photon Technology International (PTI). Polarimetry measurements were recorded on a Rudoph Scientific Autopole III polarimeter. Electrochemical measurements were performed by using a Gamry PCI4 potentiostat–galvanostat at room temperature. Electronic Circular Dichroism spectra were acquired on a JASCO J-1500 CD Spectrometer. X-ray data were collected on a four-circle Rigaku R-AXIS RAPID-S Diffractometer. Flash grade silica gel (SiliaFlash Irregular Silica Gels, F60, 40–63 μm, 60 Å) was used for flash column chromatography (FCC) purifications. Reactions were monitored by thin layer chromatography (TLC) using precoated silica gel plates (Merck Silica Gel PF-254), visualized by a handheld UV-Vis lamp.

Acknowledgement

We are grateful to Prof. Ahmet Önal and Elif Demir Arabacı (Middle East Technical University) for DPV analysis and helpful scientific discussions. We would like to thank Prof. Akın Akdağ and Aslınur Gökpınar (Middle East Technical University) for their assistance with quantum yield calculation and CD measurement. We are also grateful to Prof. Yavuz Onganer and Dr. Murat Acar (Atatürk University) for fluorescence lifetime measurements and to Prof. Cavit Kazaz and Prof. Yasin Çetinkaya (Atatürk University) for NMR (^{11}B, ^{13}C, ^{1}H) measurements. We also thank Assistant Professor Selbi Keskin (Giresun University) for ^{11}B NMR and 2D NMR measurements. Finally, the authors extend their gratitude to all members of the Tanyeli Group, in particular Dr. Esra Dündar, Zeynep Selçuk, and Itır Sezen.

1. Procedure for Synthesis of 2-formylpyrrole hydrazones (4a-d)

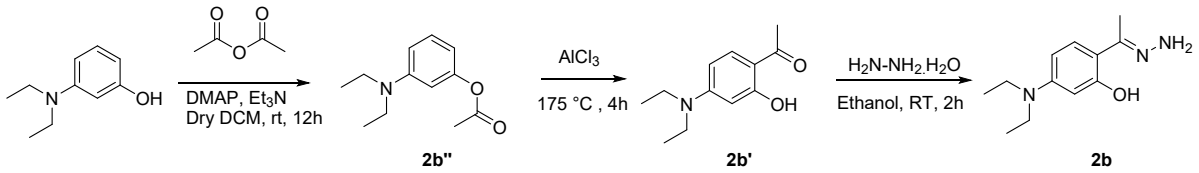
The compound 2-formylpyrrole hydrazones (**4a-d**) was synthesized by adapting a literature procedure.[i] Before use, absolute ethanol was treated with Argon for 15 minutes. In a container, 310 µL hydrazine (80%) (8 eq.) was slowly added to 1 mL absolute ethanol. Then, the 2-formylpyrroles (1mmol, 1 eq.) dissolved in sufficient ethanol (2 ml) was added dropwise to the first solution. The reaction mixture was stirred for 4 hours at room temperature. If sufficient conversion was achieved after TLC control, the solvent was removed under reduced pressure, and compounds **(4a-d)** were obtained as a yellow solid in quantitative yield.



Scheme S 1. *Sy*nthesis of compound **4a-d**

2. Procedure for Synthesis of 5-(diethylamino)-2-(1-hydrazonoethyl)phenol 2b

Compound **2b** was prepared by adapting a protocol from the literature.[ii]



Scheme S 2. Synthesis of compound **2b** and its precursors **2b′** and **2b″**

3-(diethylamino)phenol (0.85 g; 5.16 mmol) was dissolved in 10 mL of dry dichloromethane in a flame-dried round-bottom flask. The reaction mixture was stirred at room temperature for 12 hours after adding acetic anhydride (0.780 mL; 8.25 mmol), DMAP (0.032 g; 0.26 mmol), and triethylamine (0.86 mL; 6.19 mmol). The reaction was then treated with dichloromethane (100 mL), washed with a saturated $NaHCO_3$ (2x30 mL) solution and brine (2x30 mL), and dried with anhydrous $MgSO_4$. After filtration, dichloromethane was eliminated under reduced pressure, and column chromatography with silica gel (hexane/ethyl acetate = 90/10) was used to purify the crude product. Compound **2b"** was isolated as a yellow oil with a 68% yield.

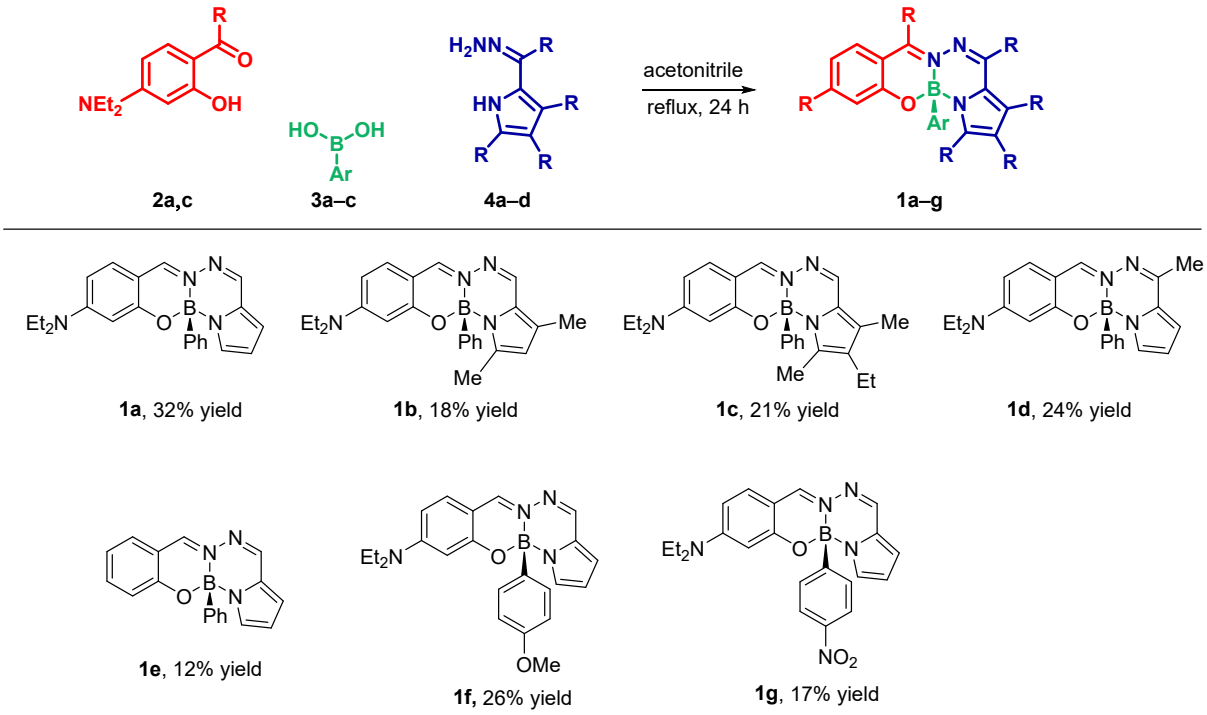
Aluminum trichloride (1.384 g; 10.38 mmol) and **2b"** (696 mg; 3.46 mmol) were combined in a round-bottom flask and heated to 175 °C for 4 hours. (It liquefies as it warms up and does not burn, therefore, there is no need for a solvent in the reaction.) $AlCl_3$ is a very fine powder; avoid breathing. After cooling, 14 mL of a 1 M cold HCl

solution was added to the reaction mixture. After one hour of stirring at room temperature, 50 milliliters of ethyl acetate were added to the mixture. Then, the organic phase was separated, and 2 × 25 mL of ethyl acetate was used to extract the aqueous phase. The mixed organic phase was dried over Na_2SO_4. The volatiles were eliminated under reduced pressure after filtration. The crude was purified using silica gel column chromatography (hexane/ethyl acetate = 95/5). Compound **2b'** was synthesized as an orange oil with a 37% yield.

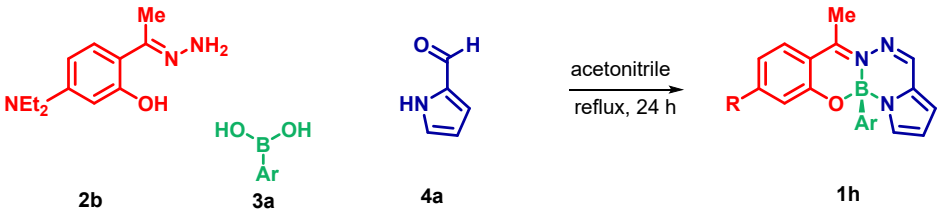
A solution of **2b'** (268 mg; 1.29 mmol) in 5 mL of ethanol was added dropwise to a solution of hydrazine hydrate (1.62 mL; 41.28 mmol) that had been dissolved in 5 mL of ethanol. At room temperature, the reaction mixture was stirred for six hours. After TLC control, the volatiles were evaporated. Compound **2b** was synthesized in nearly quantitative yield as a brown solid.

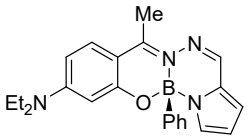
3. Procedure for Synthesis of BOSPYR Dyes through MCR Approach.

Among the MCR protocols, Procedure B led to competitive aldazine formation[i] when the hydrazone of 4-(diethylamino)salicylaldehyde was employed for the synthesis of model compound **1a**. Gratifyingly, switching to the hydrazone of pyrrole-2-carbaldehydes (**4a–d**) suppressed azine formation and improved overall yields in Procedure A. To further enhance product yields, we also explored linear synthetic approaches, but these attempts were unsuccessful (*vide infra*).



Scheme S 3. Synthesis of BOSPYR dyes with Procedure A





1h, 16% yield

Scheme S 4. Synthesis of BOSPYR dyes with Procedure B

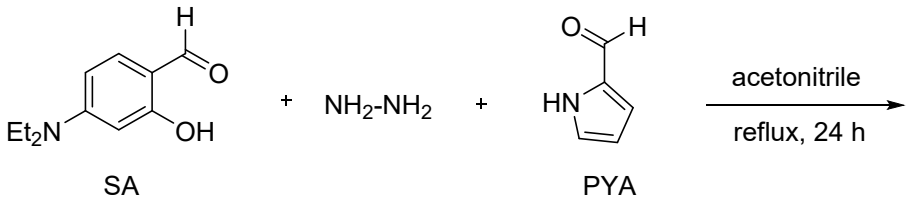
Procedure A. After mixing salicylaldehyde derivatives (**2a–d**) (0.5 mmol, 1 equiv.), arylboronic acids (**3a-c**) (0.5 mmol, 1 equiv.), and formylpyrrole hydrazones (**3a–d**) (0.5 mmol, 1 equiv.) in a round-bottom flask, 8 mL of degassed acetonitrile was introduced. The resulting mixture underwent refluxing for a duration of 24 hours. Subsequently, purification was accomplished via column chromatography, utilizing a solvent system consisting of hexane/ethyl acetate (5:1).

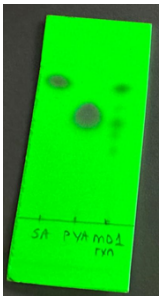
Procedure B. After mixing 1H-pyrrole-2-carbaldehyde **4a** (0.37 mmol, 1 equiv.), arylboronic acids **3a** (0.37 mmol, 1 equiv.), and compound **2b** (0.37 mmol, 1 equiv.) in a round-bottom flask, 6 mL of degassed acetonitrile was introduced. The resulting mixture underwent refluxing for a duration of 24 hours. Subsequently, purification was accomplished via column chromatography with hexane as solvent.

Unsuccessful efforts toward synthesis of 1a:

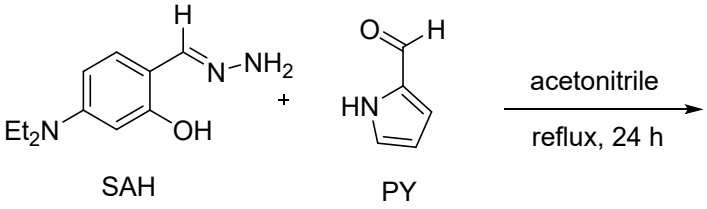
Alternatively, we explored three distinct synthetic pathways to access compound **1a**. These linear approaches involved the condensation of hydrazones with aldehydes to generate imines (Rxn 2 & 3) or the direct condensation of two aldehydes and hydrazine (Rxn 1) followed by complexation with arylboronic acid. Despite optimization efforts, none of these pathways yielded trace of the desired product. For condensation reactions, we have used solvents acetonitrile and toluene. Consequently, the multicomponent reaction described in Procedures A and B emerged as the most efficient route for the synthesis of **1a**. The corresponding TLC profiles are provided below.

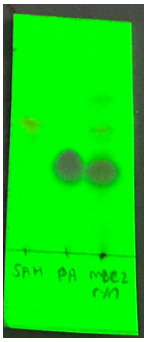
Rxn 1



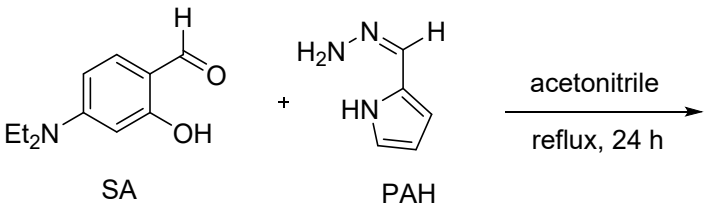


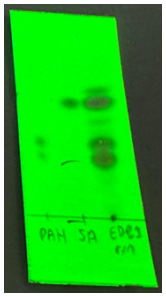
Rxn 2





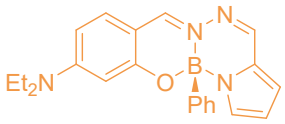
Rxn 3





Scheme S 5. Optimization studies

3.1 BOSPYR 1a



Compound **1a** was isolated as an orange solid in 32% yield (59.2 mg). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.75 (s, 1H), 7.30 (s, 1H), 7.21 – 7.07 (m, 6H), 6.65 (d, *J* = 3.6 Hz, 1H), 6.34 (t, *J* = 3.0 Hz, 1H), 6.30 – 6.23 (m, 2H), 3.43 (qd, *J* = 7.0, 4.4 Hz, 4H), 1.24 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 161.4, 156.0, 153.6, 146.2, 134.1, 130.6, 127.8, 127.5, 127.2, 125.6, 115.3, 112.3, 106.7, 106.1, 98.7, 45.1, 12.9 ppm. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 3.02 (bs). **HRMS** (APCI+) calculated for $C_{22}H_{24}BN_4O$ ^{10}B $[M+H]^+$, 370.2079; found, 370.2074. **HPLC analysis** (OD-H, n-Hexane/Isopropanol, 98:2, 1 mL/min, 474 nm) t_1 = 12.87 min and t_2 = 16.49 min. **mp** = 175 °C. $[\alpha]_D^{25}$ = − 2054.79 (c 3.65 x 10^{-5}, $CHCl_3$) for fast-eluting enantiomer, $[\alpha]_D^{25}$ = + 2082.19 (c 3.65 x 10^{-5}, $CHCl_3$) for slow-eluting enantiomer.

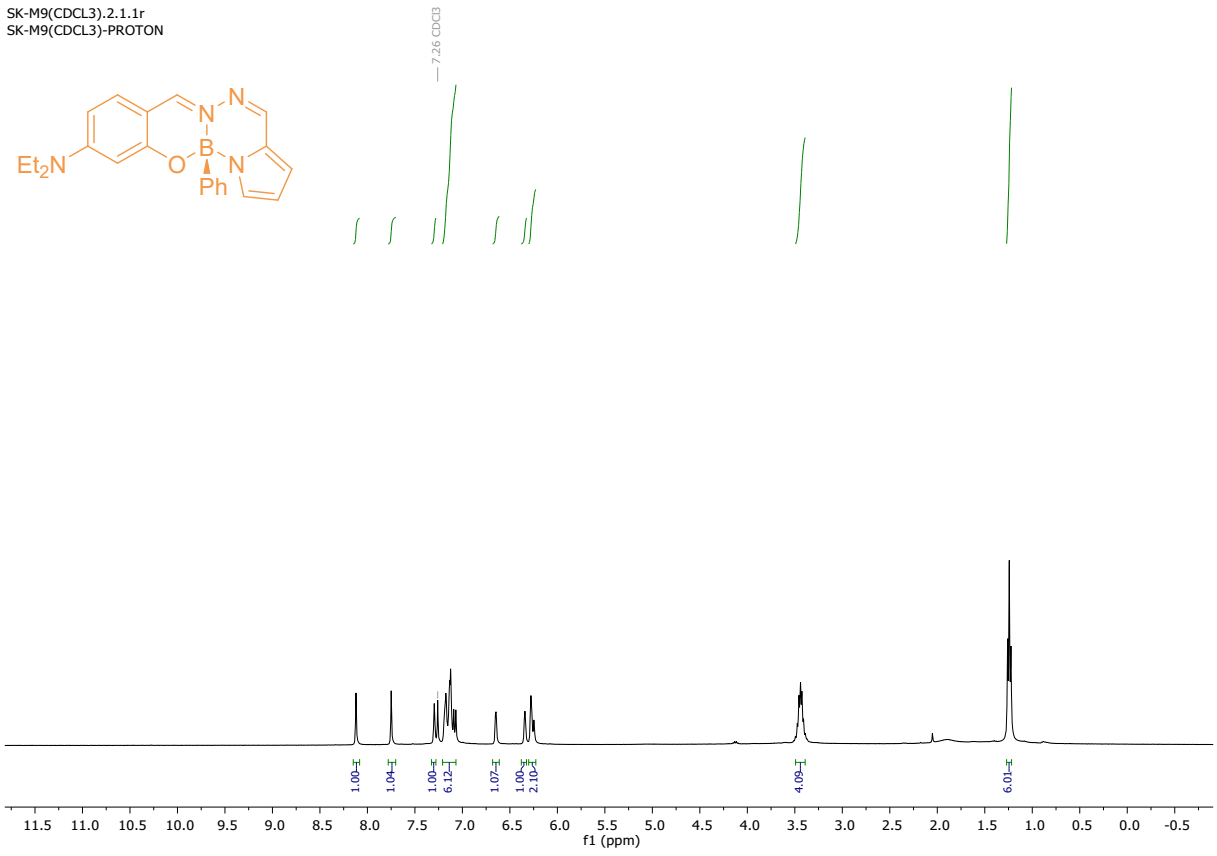


Figure S 1. ^{1}H NMR spectrum of **1a**

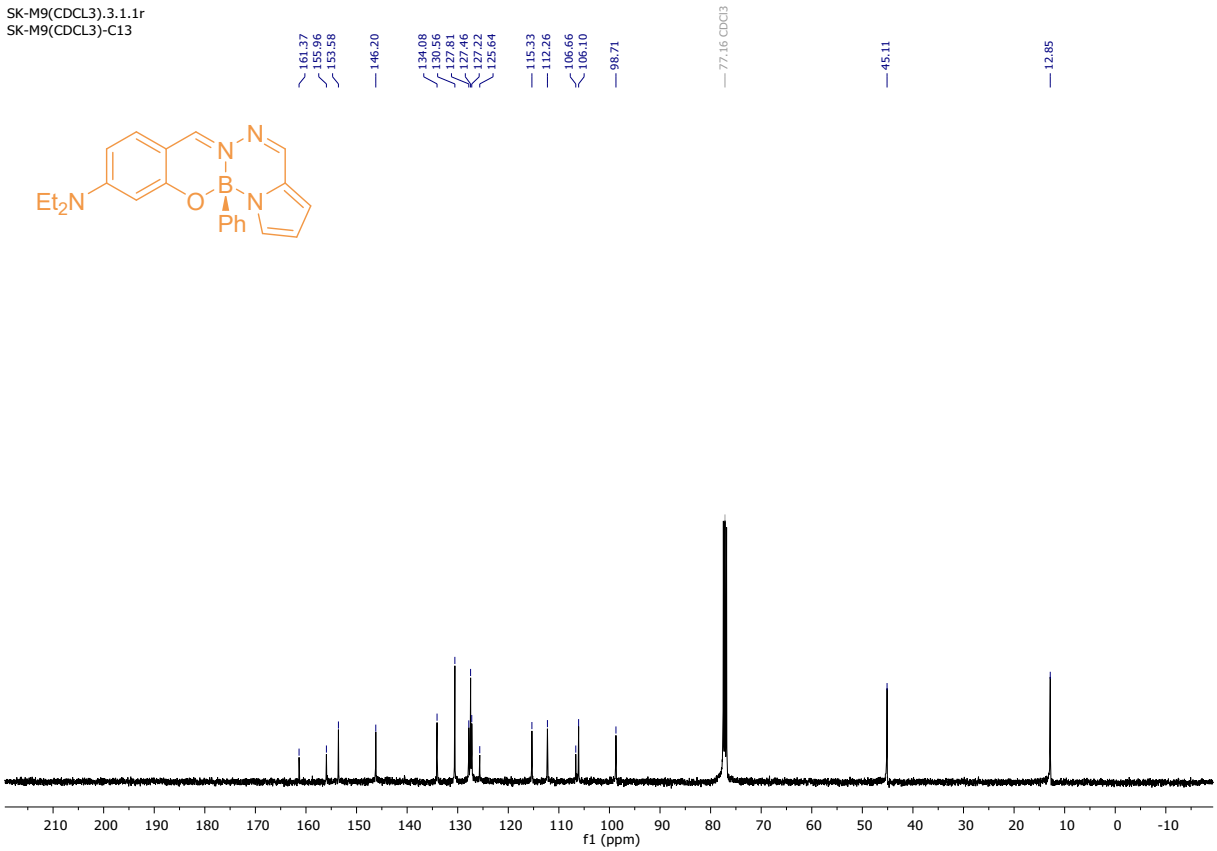


Figure S 2. ^{13}C NMR spectrum of **1a**

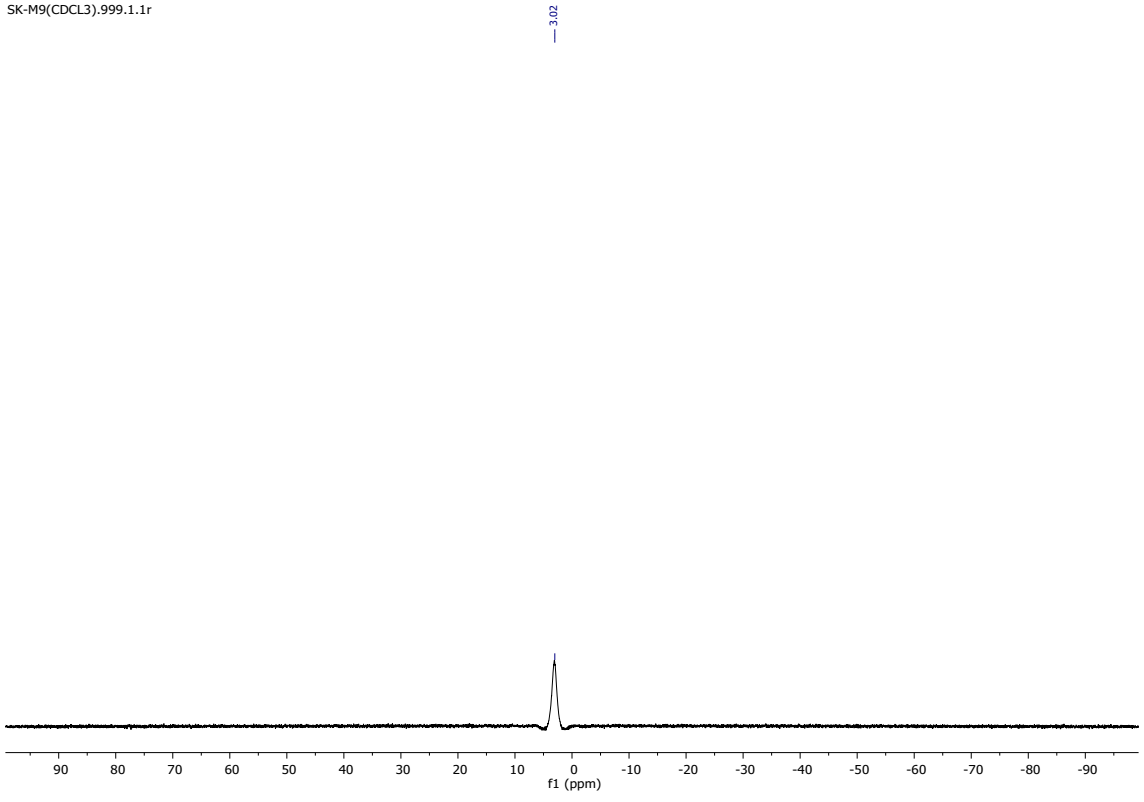


Figure S 3. ^{11}B NMR spectrum (128 MHz) of **1a** in $CDCl_3$

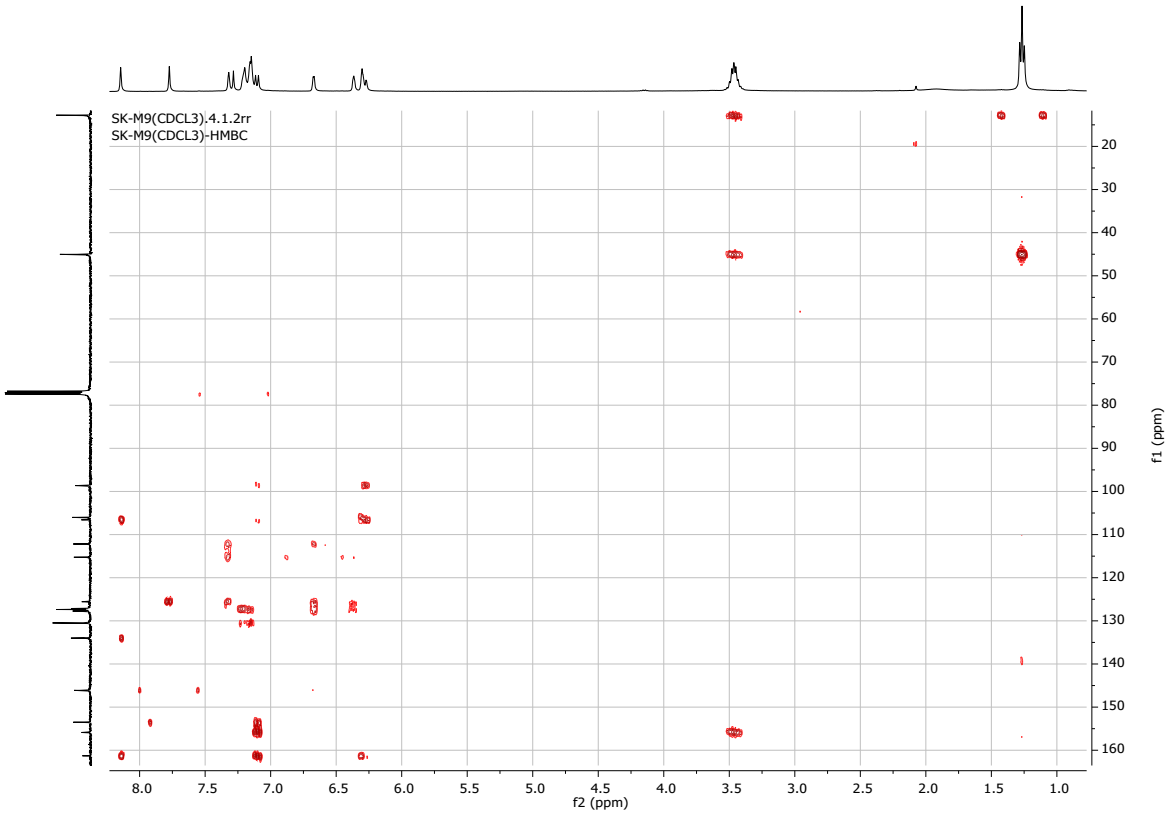


Figure S 4. HMBC NMR spectrum (400 MHz) of **1a** in $CDCl_3$.

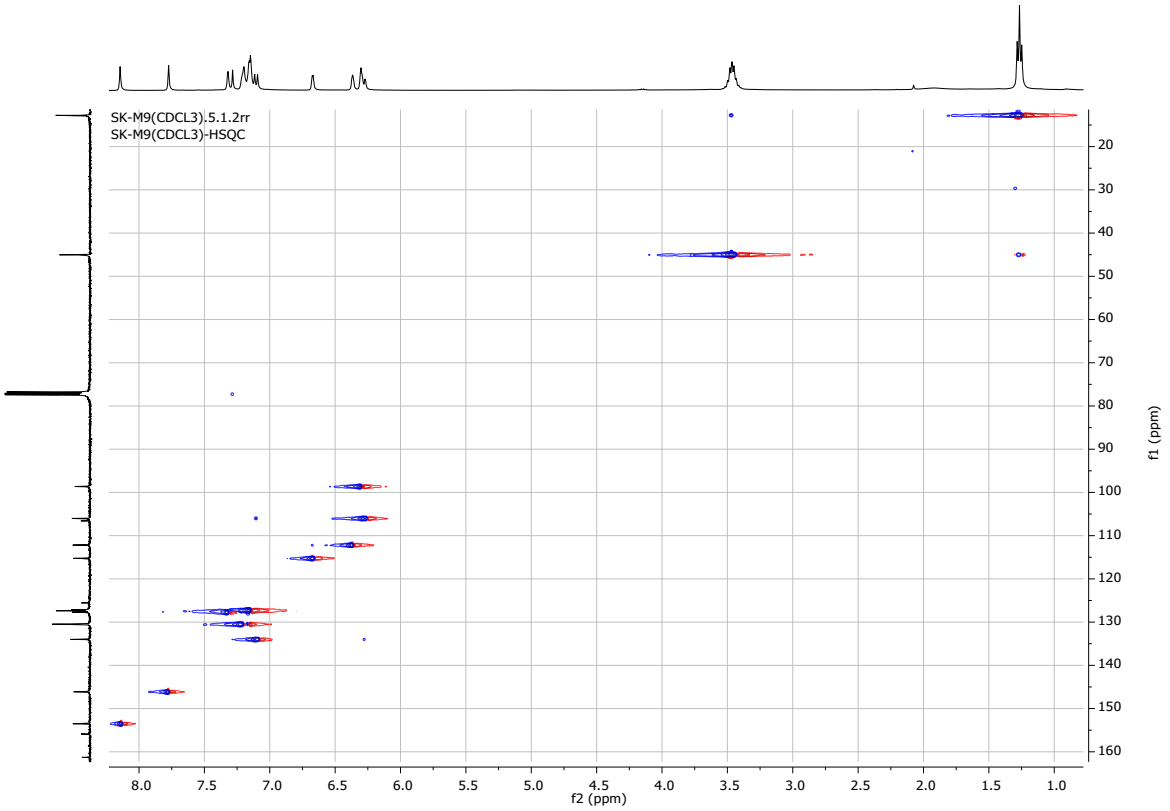
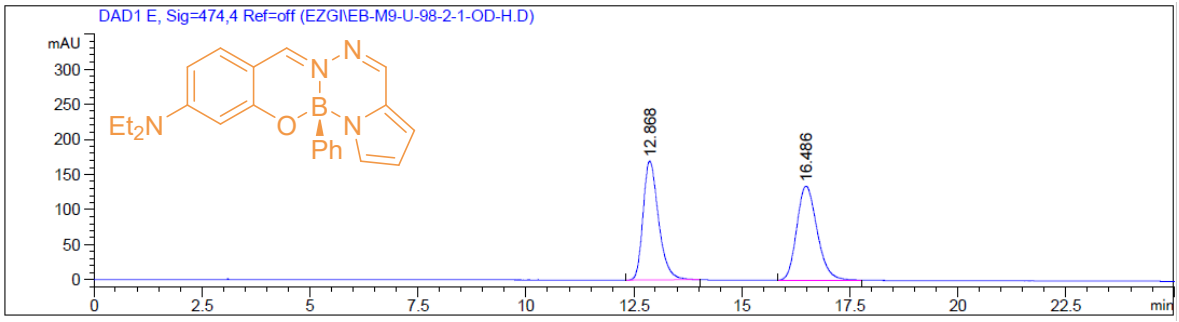


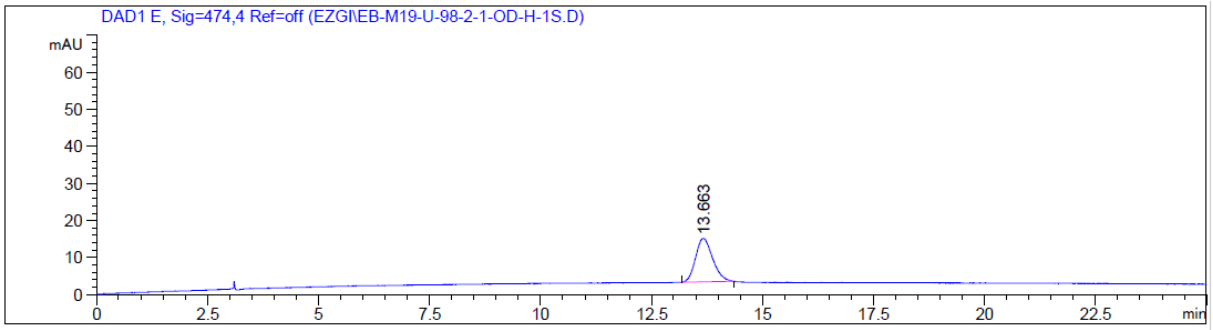
Figure S 5. HSQC NMR spectrum (400 MHz) of **1a** in $CDCl_3$.



Signal 5: DAD1 E, Sig=474,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.868	BB	0.3721	4210.91553	169.34698	49.0553
2	16.486	BB	0.4670	4373.09668	133.89679	50.9447
Totals :				8584.01221	303.24377	

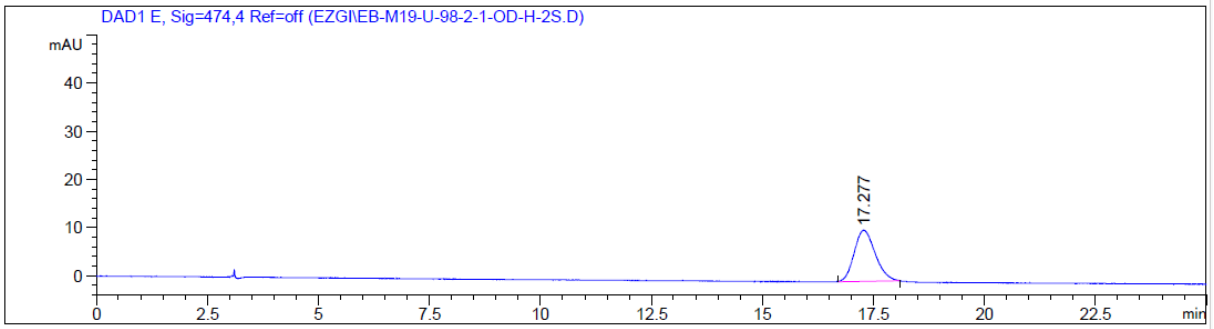
Figure S 6. HPLC chromatogram of **1a**



Signal 5: DAD1 E, Sig=474,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.663	BB	0.3151	313.11560	11.70368	100.0000
Totals :				313.11560	11.70368	

Figure S 7. HPLC chromatogram of (−)-**1a**



Signal 5: DAD1 E, Sig=474,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.277	BB	0.3863	348.62738	10.61120	100.0000
Totals :				348.62738	10.61120	

Figure S 8. HPLC chromatogram of (+)-**1a**

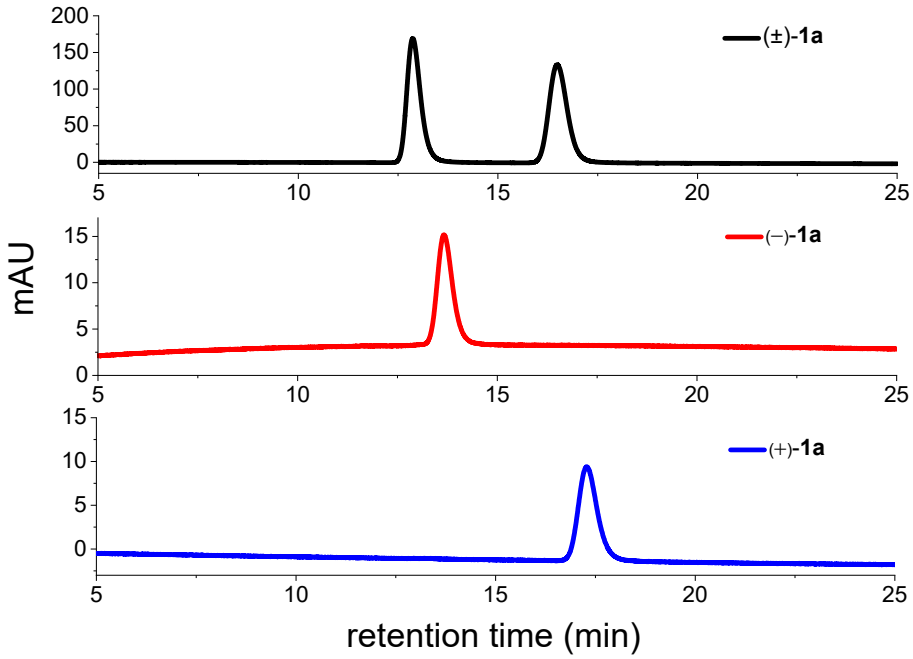


Figure S 9. Chiral HPLC separation of racemic **1a** on a Chiralcel® OD-H column. (top) Racemic mixture (±)-**1a**. (middle) Resolved fast-eluting enantiomer, (−)-**1a** (>99.9% ee). (bottom) Resolved slow-eluting enantiomer, (+)-**1a** (>99.9% ee).

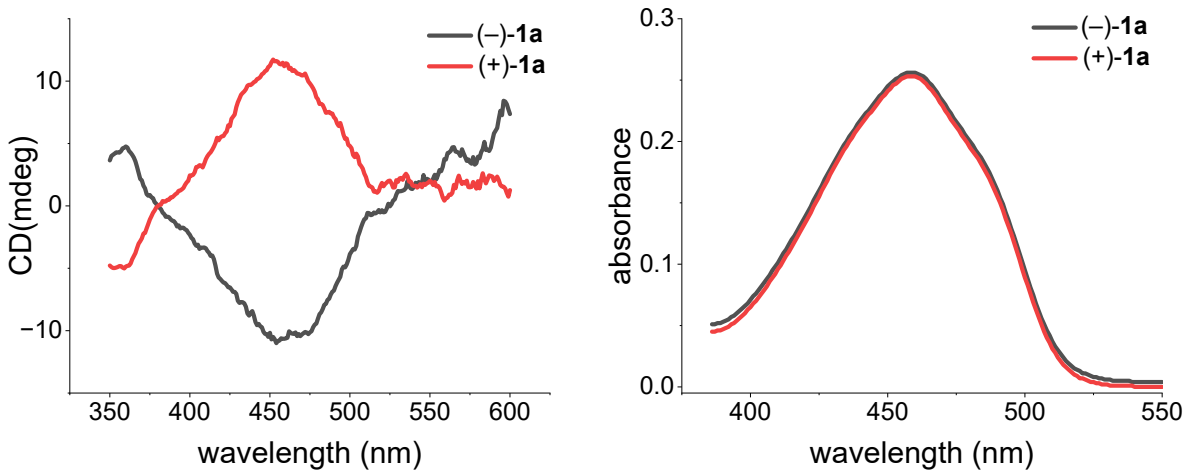
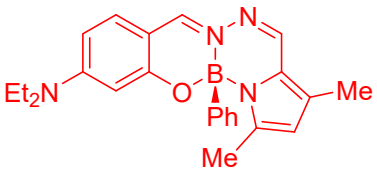


Figure S 10. Electronic circular dichroism (left) and UV-vis absorption (right) spectra of enantiomers of **1a** (each 10 μM) in toluene.

3.2 BOSPYR 1b



Compound **1b** was isolated as an orange solid in 18% yield (35.9 mg). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.71 (s, 1H), 7.18 – 7.10 (m, 5H), 7.05 (d, *J* = 9.5 Hz, 1H), 6.30 – 6.21 (m, 2H), 5.91 (s, 1H), 3.45 (qd, *J* = 7.2, 3.5 Hz, 4H), 2.37 (s, 3H), 2.26 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 161.1, 155.6, 152.2, 142.7, 142.0, 133.7, 130.8, 129.1, 127.4, 127.1, 123.0, 114.0, 106.7, 105.9, 98.5, 45.0, 14.5, 12.9, 10.8 ppm. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 3.25 (bs). **HRMS** (APCI) calculated for $C_{24}H_{28}BN_4O$ ^{10}B $[M+H]^+$, 398.2392; found, 398.2387. **HPLC analysis** (OD-H, n-Hexane/Isopropanol, 98:2, 0.7 mL/min, 254 nm) t_1 = 13.33 min and t_2 = 19.50 min.

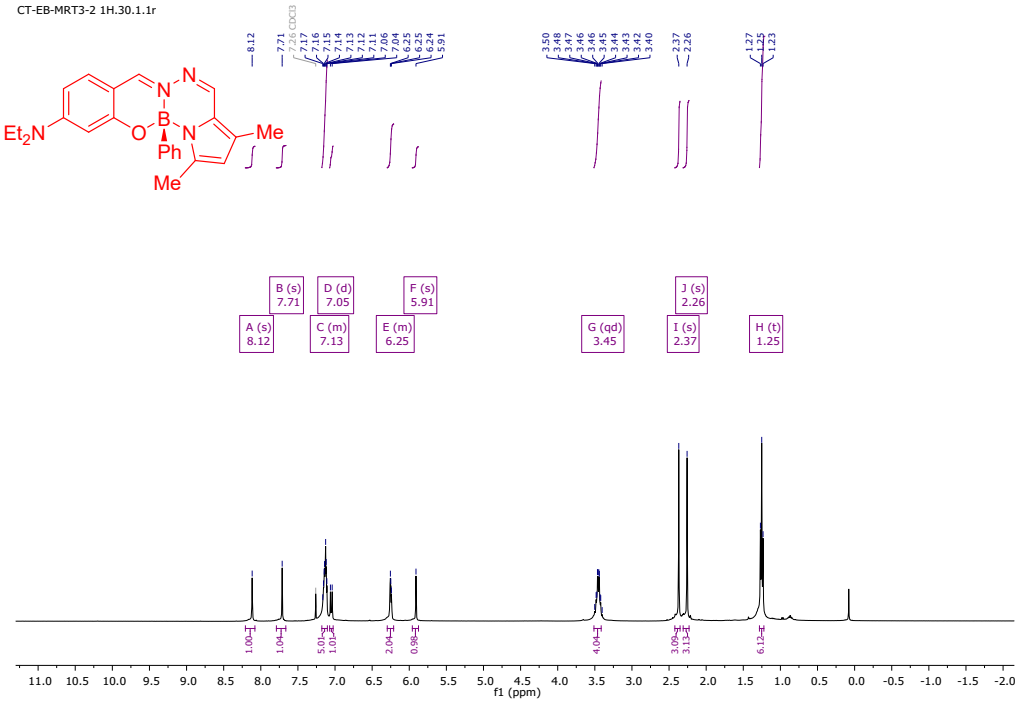


Figure S 11. ^{1}H NMR spectrum of **1b**

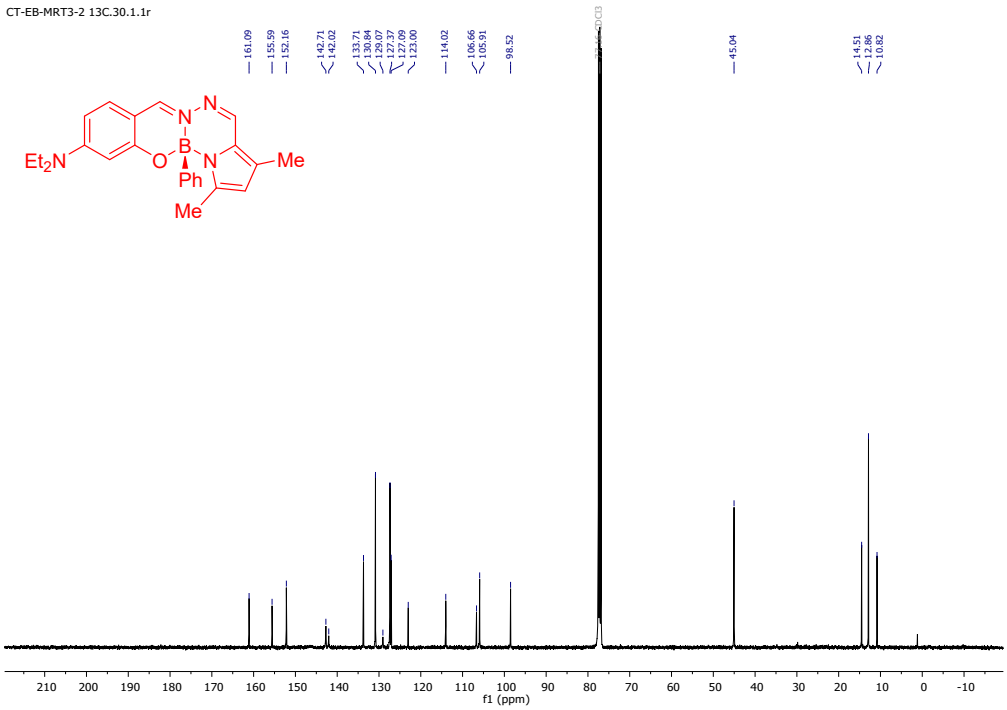


Figure S 12. ^{13}C NMR spectrum of **1b**

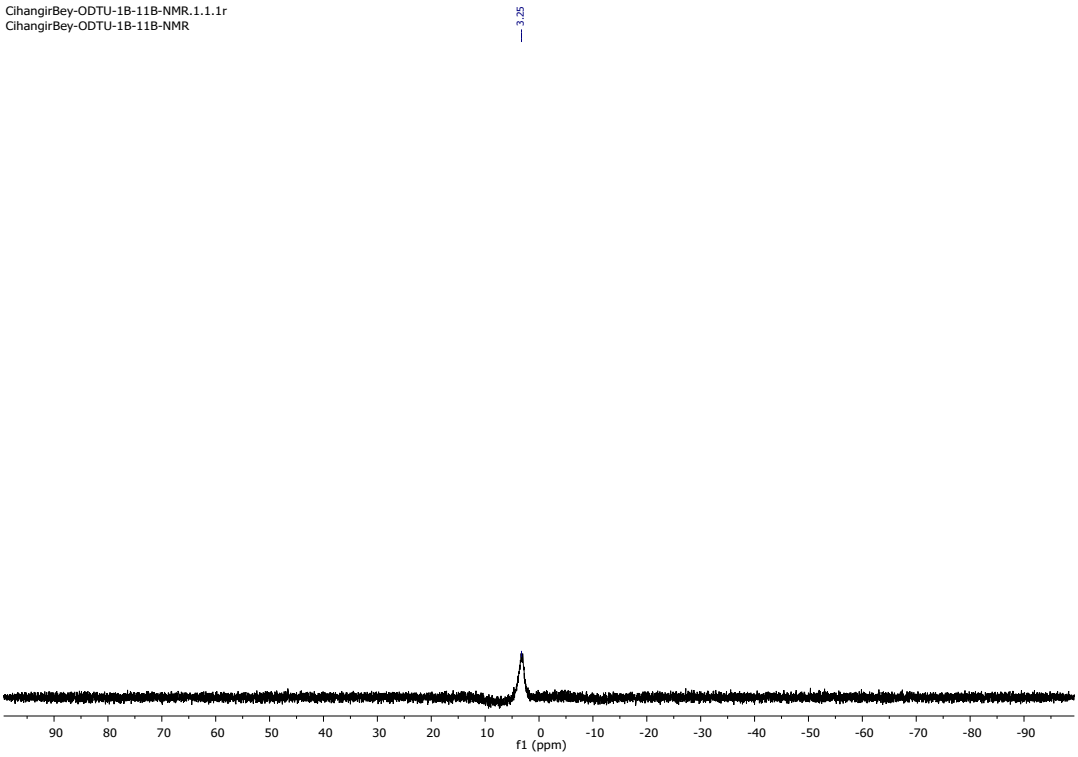
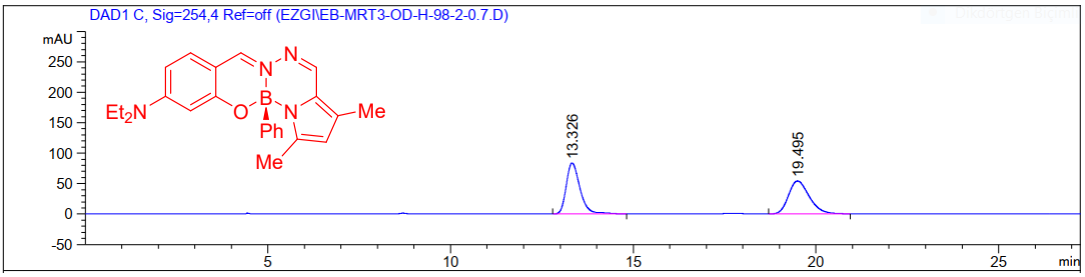


Figure S 13. ^{11}B NMR spectrum (128 MHz) of **1b** in $CDCl_3$

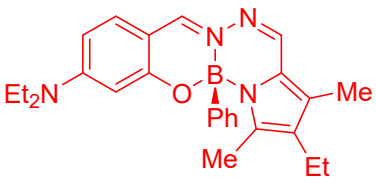


Signal 3: DAD1 C, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.326	BB	0.3870	2192.72803	83.87321	50.6470
2	19.495	BB	0.5206	2136.70654	54.06291	49.3530
Totals :				4329.43457	137.93612	

Figure S 14. HPLC chromatogram of **1b**

3.3 BOSPYR 1c



Compound **1c** was isolated as an orange solid in 21% yield (44.8 mg). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 8.23 (s, 1H), 7.72 (s, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.15 – 7.07 (m, 2H), 7.02 – 6.96 (m, 3H), 6.36 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.32 (d, *J* = 2.5 Hz, 1H), 3.50 (q, *J* = 7.0 Hz, 4H), 2.31 (q, *J* = 7.5 Hz, 2H), 2.24 (s, 3H), 2.13 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 6H), 0.95 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 161.0, 155.3, 152.1, 143.6, 138.1, 133.4, 130.9, 127.3, 126.9, 126.2, 125.7, 121.9, 106.8, 105.6, 98.5, 45.0, 17.5, 15.5, 12.9, 12.2, 9.1 ppm. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 3.37 (bs). **HRMS** (APCI) calculated for $C_{26}H_{32}BN_4O$ ^{10}B $[M+H]^+$, 426.2705; found, 426.2700. **HPLC analysis** (OD-H, n-Hexane/Isopropanol, 90:10, 1 mL/min, 500 nm) t_1 = 5.91 min and t_2 = 7.20 min.

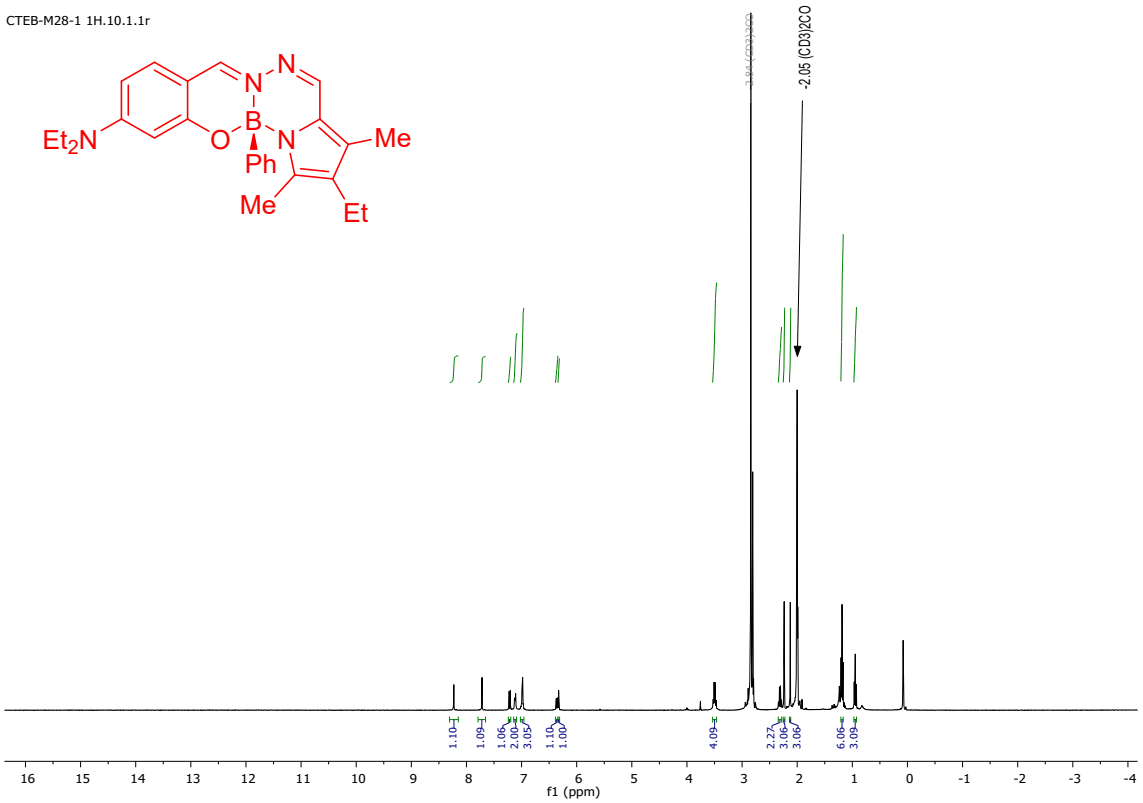


Figure S 15. ^{1}H NMR spectrum of **1c**

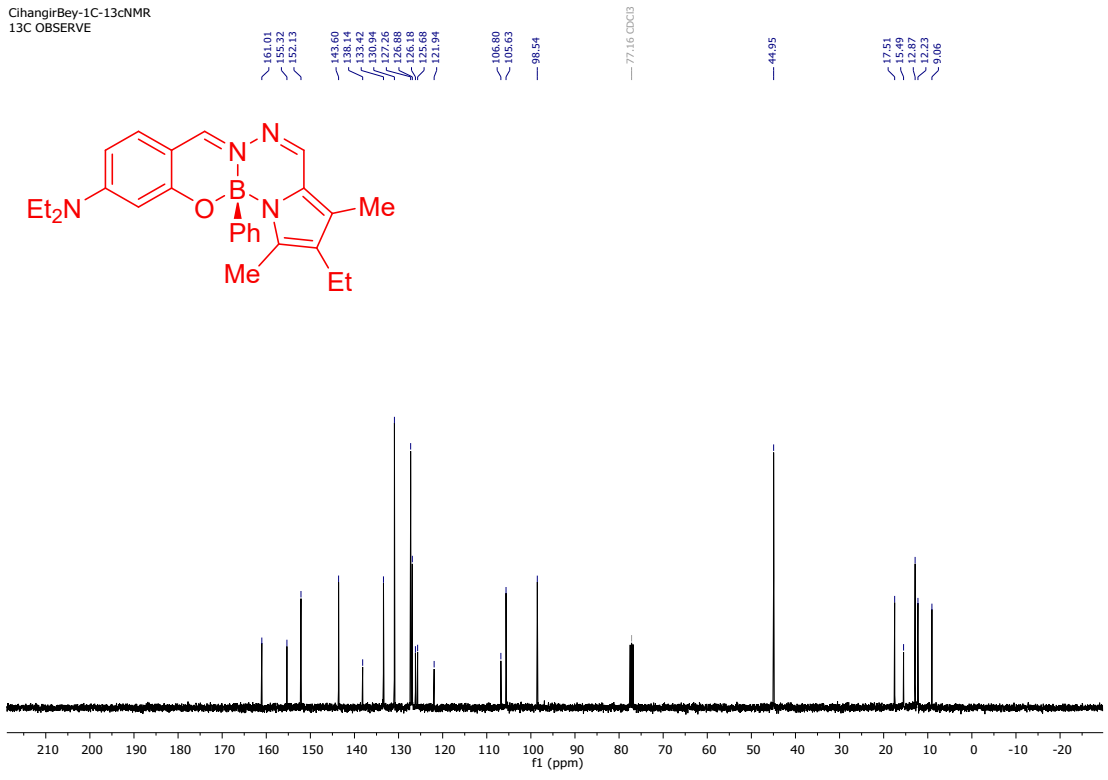


Figure S 16. ^{13}C NMR spectrum of **1c**

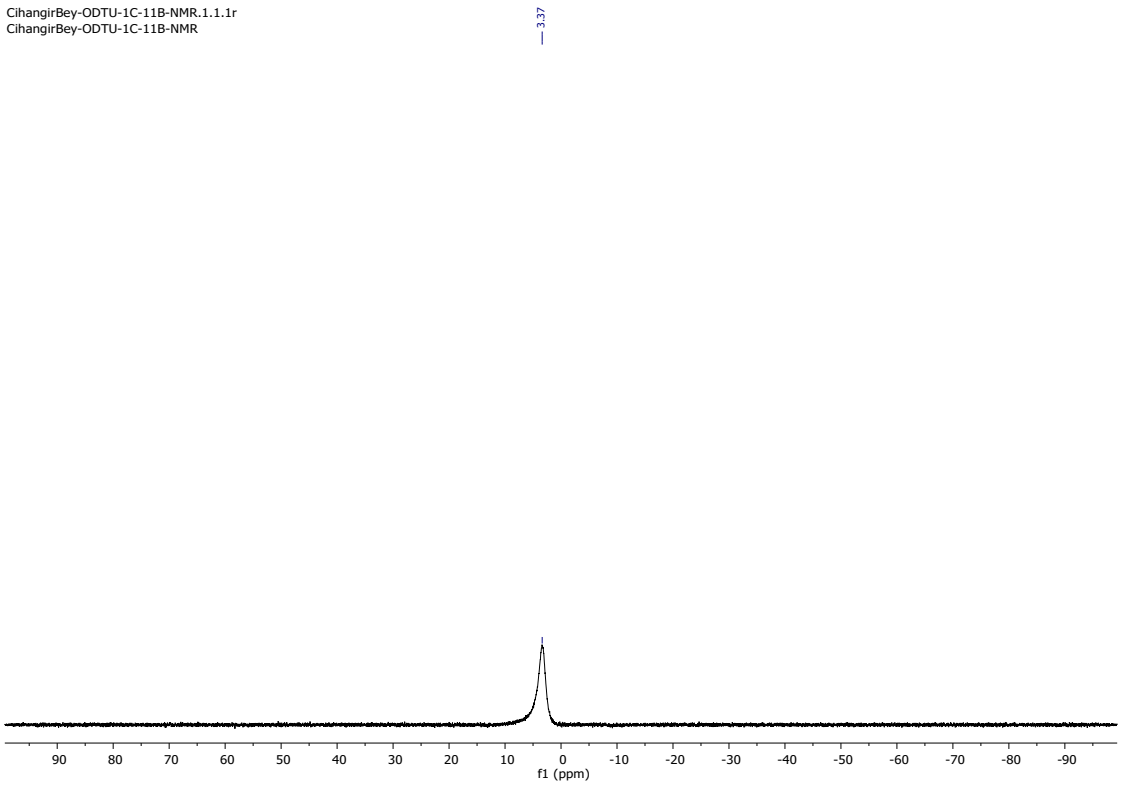
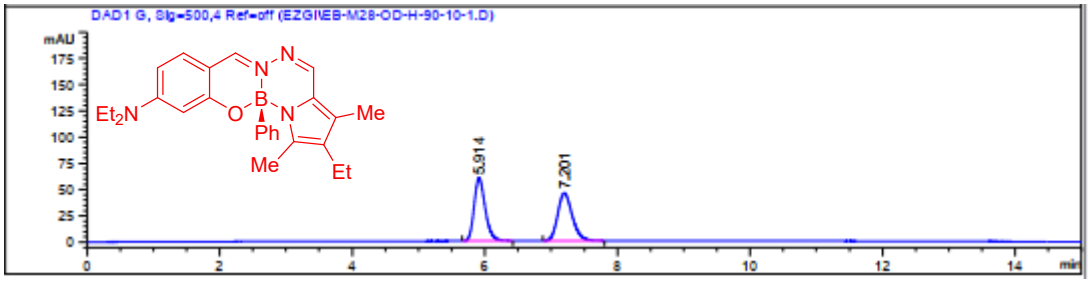


Figure S 17. ^{11}B NMR spectrum (128 MHz) of **1c** in $CDCl_3$

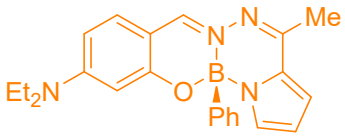


Signal 7: DAD1 G, Sig=500,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.914	BB	0.1776	695.83942	59.66790	50.0903
2	7.201	BB	0.2330	693.33124	45.31171	49.9097
Totals :				1389.17065	104.97962	

Figure S 18. HPLC chromatogram of **1c**

3.4 BOSPYR 1d



Compound **1d** was isolated as an orange solid in 24% yield (46.1 mg). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 8.30 (s, 1H), 7.25 (d, J = 9.0 Hz, 1H), 7.16 – 7.14 (m, 1H), 7.12 – 7.07 (m, 2H), 7.03 – 6.96 (m, 3H), 6.61 (dd, J = 3.7, 1.2 Hz, 1H), 6.35 (dd, J = 9.0, 2.5 Hz, 1H), 6.23 – 6.16 (m, 2H), 3.47 (qd, J = 7.2, 2.2 Hz, 4H), 2.27 (s, 3H), 1.16 (t, J = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, Acetone-d_6) δ 161.9, 156.7, 154.7, 154.2, 135.0, 131.3, 127.9, 127.5, 126.9, 126.8, 113.9, 111.9, 107.5, 106.8, 98.9, 45.4, 19.4, 12.9 ppm. **^{11}B NMR** (128 MHz, Chloroform-d) δ 2.83 (bs). **HRMS** (APCI) calculated for $C_{23}H_{26}BN_4O$ ^{10}B [M+H]$^+$, 384.2236; found, 384.2231. **HPLC analysis** (OD-H, n-Hexane/Isopropanol, 98:2, 1 mL/min, 474 nm) t_1 = 11.65 min and t_2 = 13.16 min.

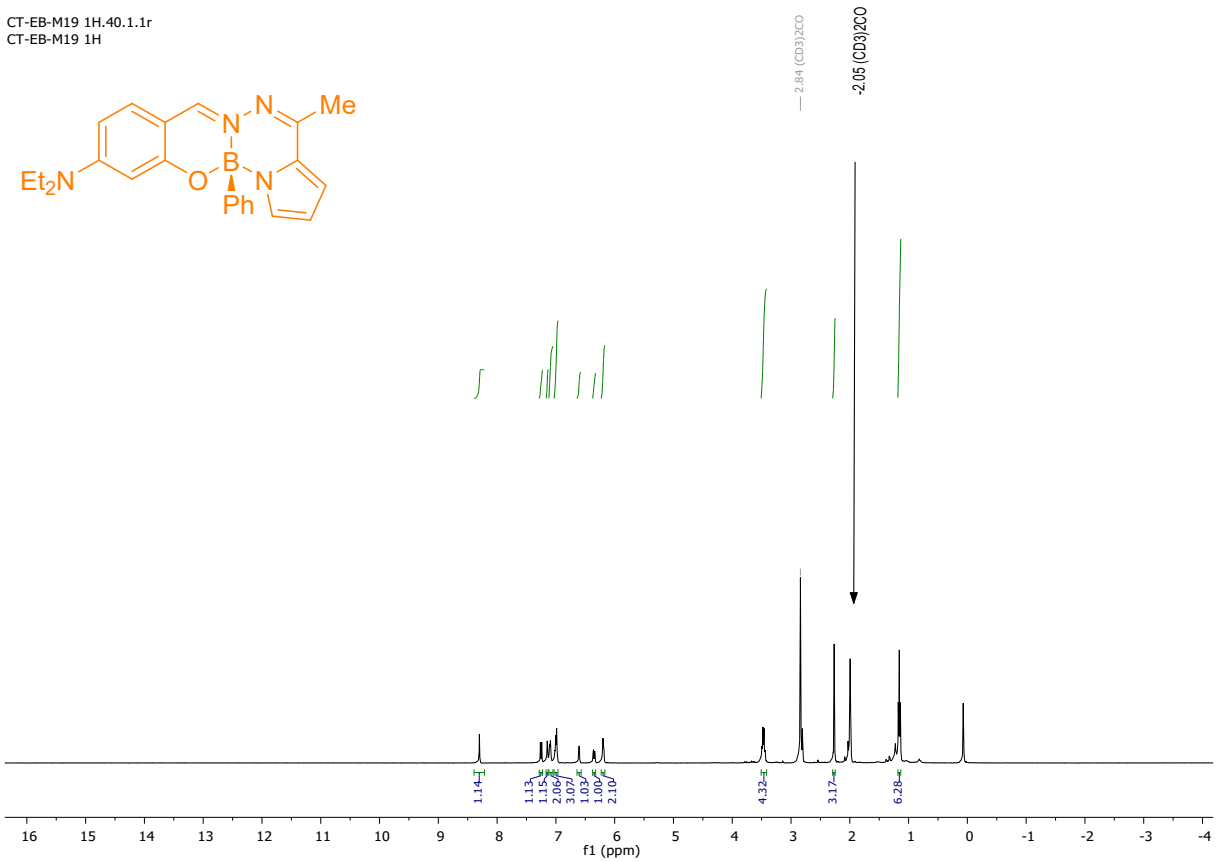


Figure S 19. ^{1}H NMR spectrum of **1d**

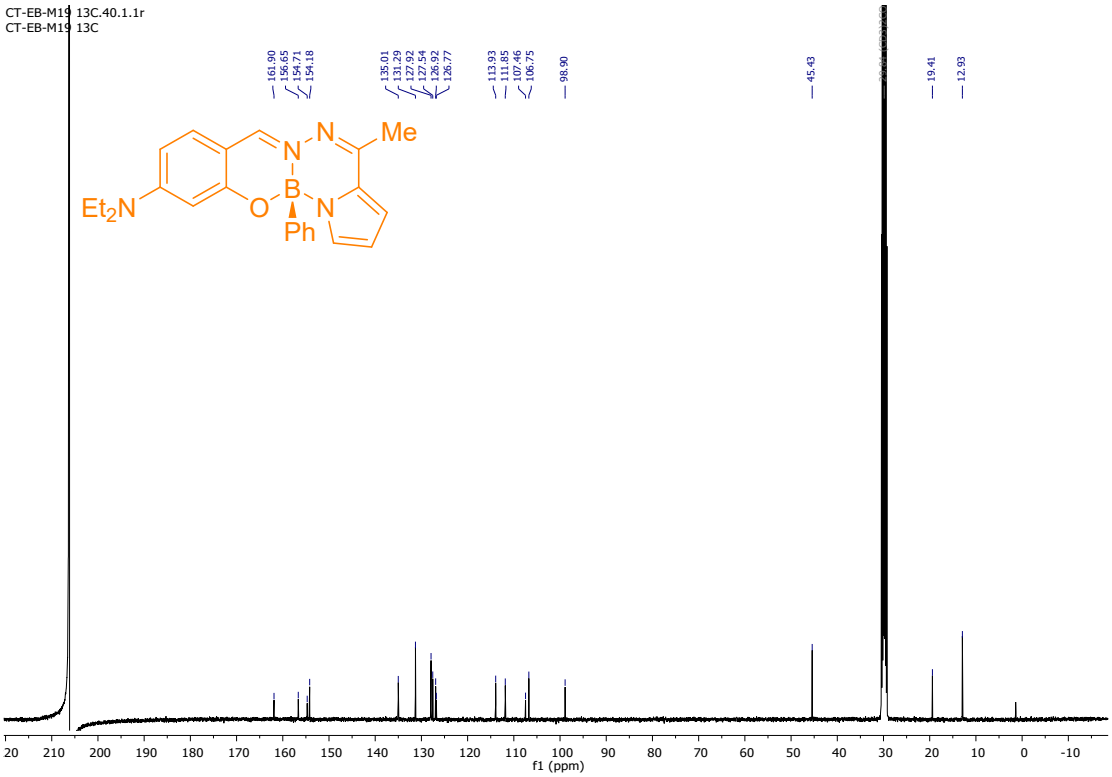


Figure S 20. ^{13}C NMR spectrum of **1d**

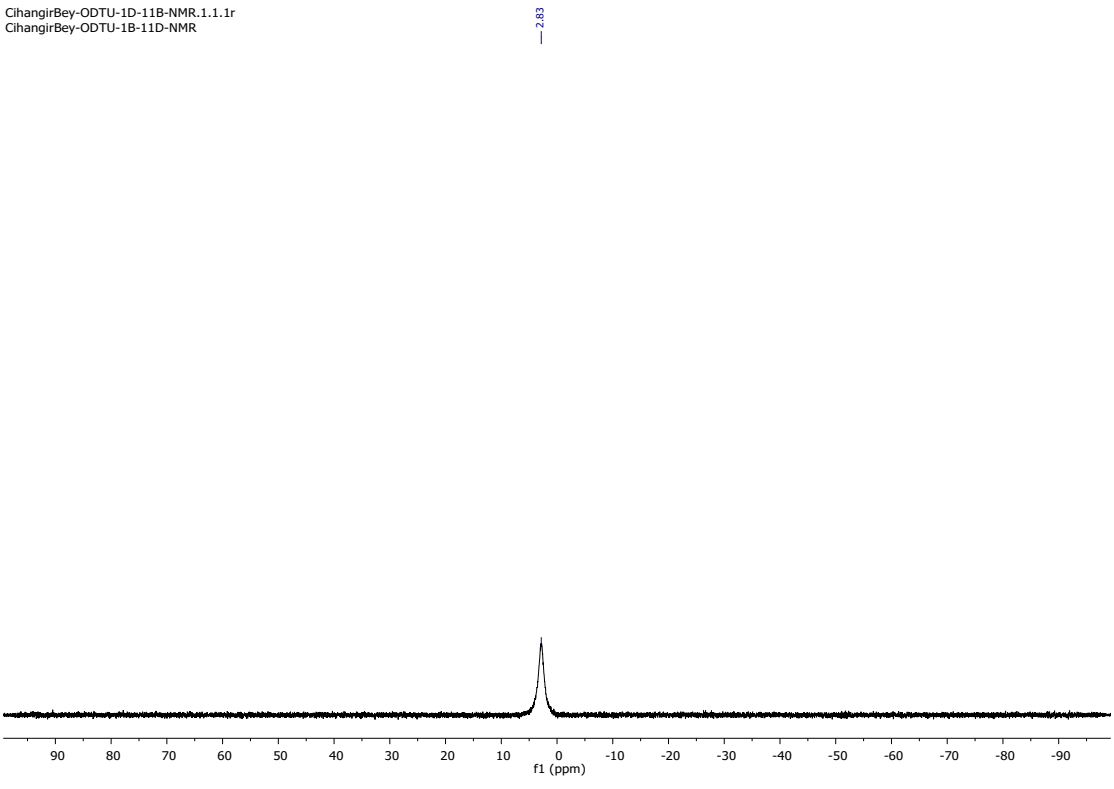
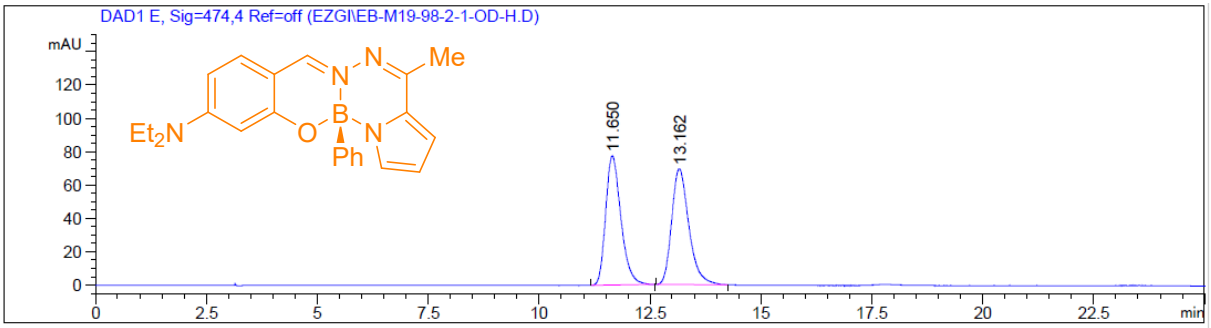


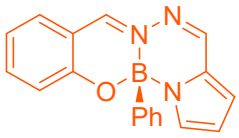
Figure S 21. ^{11}B NMR spectrum (128 MHz) of **1d** in $CDCl_3$



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.650	BB	0.3410	1855.27441	77.29108	49.8066
2	13.162	BB	0.3833	1869.68591	69.29373	50.1934
Totals :				3724.96033	146.58482	

Figure S 22. HPLC chromatogram of **1d**

3.5 BOSPYR 1e



Compound **1e** was isolated as an orange solid in 12% yield (18.0 mg). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 8.76 (s, 1H), 7.96 (s, 1H), 7.54 (d, J = 7.8 Hz, 2H), 7.25 (s, 1H), 7.10 – 6.95 (m, 6H), 6.90 (t, J = 7.5 Hz, 1H), 6.68 (d, J = 3.6 Hz, 1H), 6.26 – 6.20 (m, 1H). **^{13}C NMR** (100 MHz, Acetone-d_6) δ 159.7, 158.2, 150.3, 139.1, 133.8, 131.2, 129.8, 128.2, 128.1, 126.3, 121.2, 119.6, 118.2, 118.1, 113.3 ppm. **^{11}B NMR** (128 MHz, Chloroform-d) δ 3.96 (bs). **HRMS** (APCI) calculated for $C_{18}H_{15}BN_3O$ ^{10}B $[M+H]^+$, 299.1344; found, 229.1339. **HPLC analysis** (IA, n-Hexane/Isopropanol, 90:10, 1 mL/min, 500 nm) t_1 = 14.21 min and t_2 = 21.24 min.

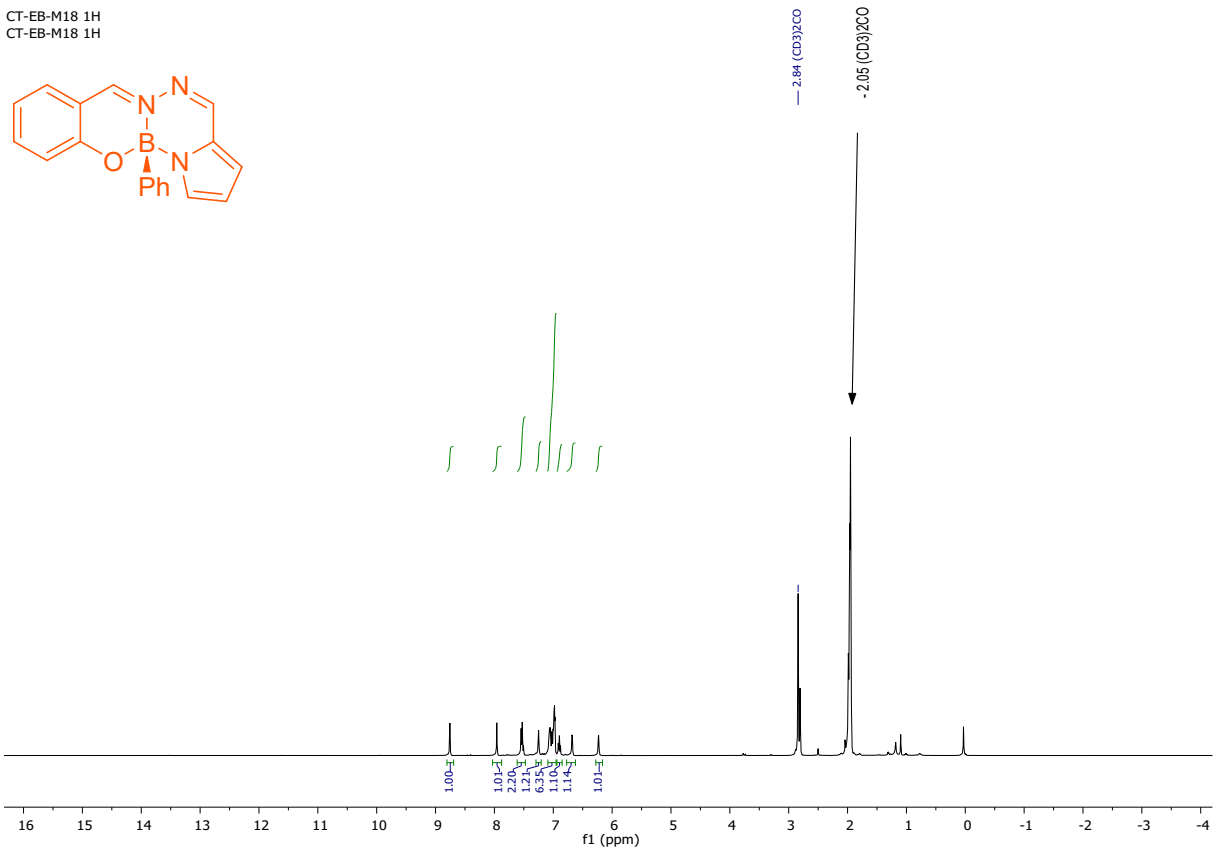


Figure S 23.[1]H NMR spectrum of **1e**

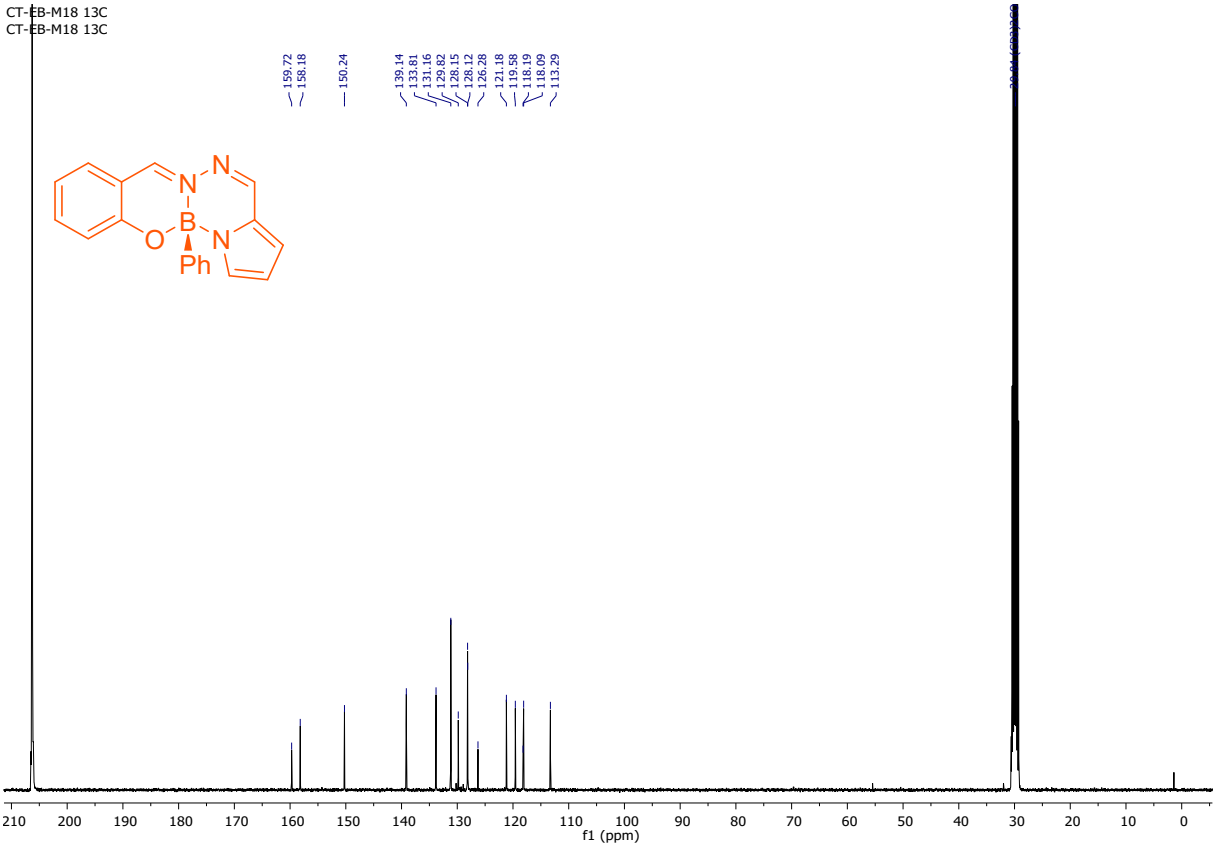


Figure S 24. [13]C NMR spectrum of **1e**

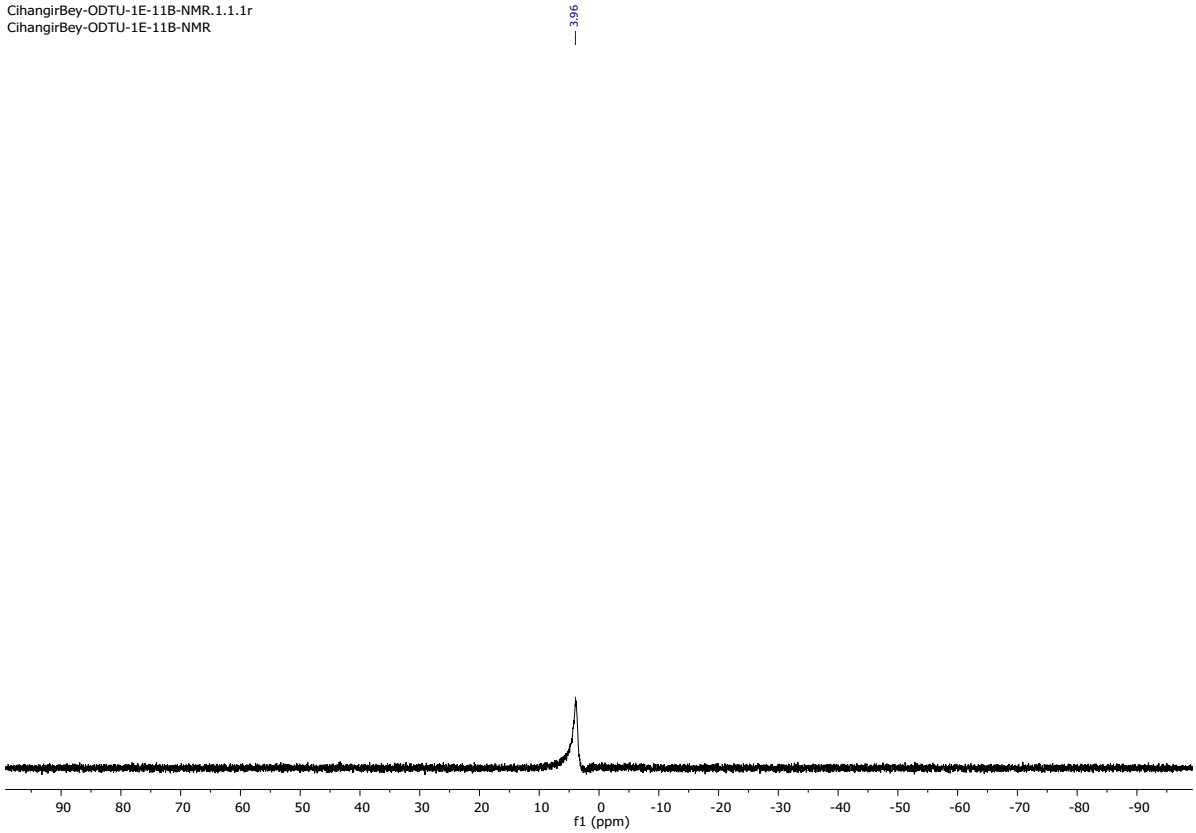
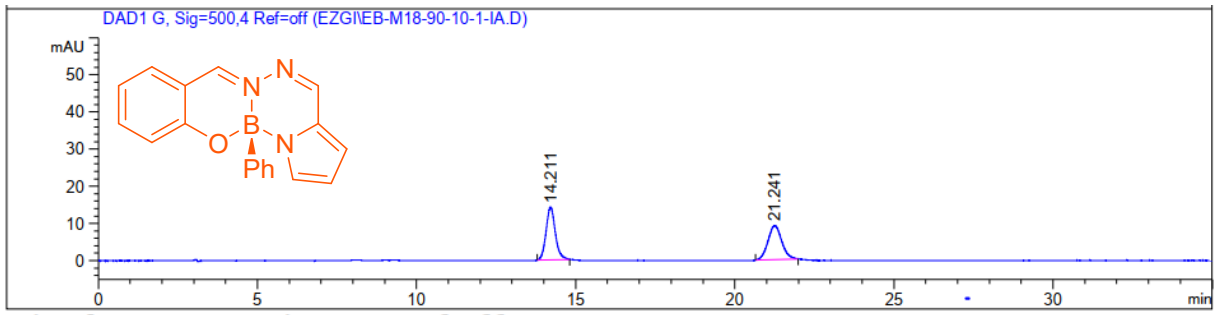


Figure S 25. ^{11}B NMR spectrum (128 MHz) of **1e** in $CDCl_3$

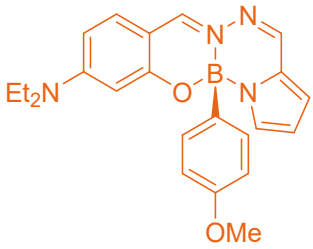


Signal 7: DAD1 G, Sig=500,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.211	BB	0.2449	287.75186	14.23140	51.1131
2	21.241	BB	0.3521	275.21890	9.17043	48.8869
Totals :				562.97076	23.40183	

Figure S 26. HPLC chromatogram of **1e**

3.6 BOSPYR 1f



Compound **1f** was isolated as an orange solid in 26% yield (52.0 mg). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 8.37 (s, 1H), 7.82 (s, 1H), 7.32 (d, J = 9.0 Hz, 1H), 7.20 (s, 1H), 7.06 (d, J = 8.0 Hz, 2H), 6.66 – 6.53 (m, 3H), 6.42 (dd, J = 9.0, 2.5 Hz, 1H), 6.27 – 6.22 (m, 2H), 3.64 (s, 3H), 3.53 (q, J = 6.8, 6.2 Hz, 4H), 1.22 (t, J = 7.0 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-d) δ 161.4, 159.0, 155.9, 153.5, 146.2, 134.0, 131.8, 127.7, 125.7, 115.2, 113.0, 112.2, 106.6, 106.0, 98.6, 55.0, 45.1, 12.9 ppm. **^{11}B NMR** (128 MHz, Chloroform-d) δ 3.24 (bs). **HRMS** (APCI) calculated for $C_{23}H_{26}BN_4O_2$ ^{10}B [M+H]$^+$, 400.2185; found, 400.2180. **HPLC analysis** (OD-H, n-Hexane/Isopropanol, 90:10, 1 mL/min, 500 nm) t_1 = 12.81 min and t_2 = 17.51 min.

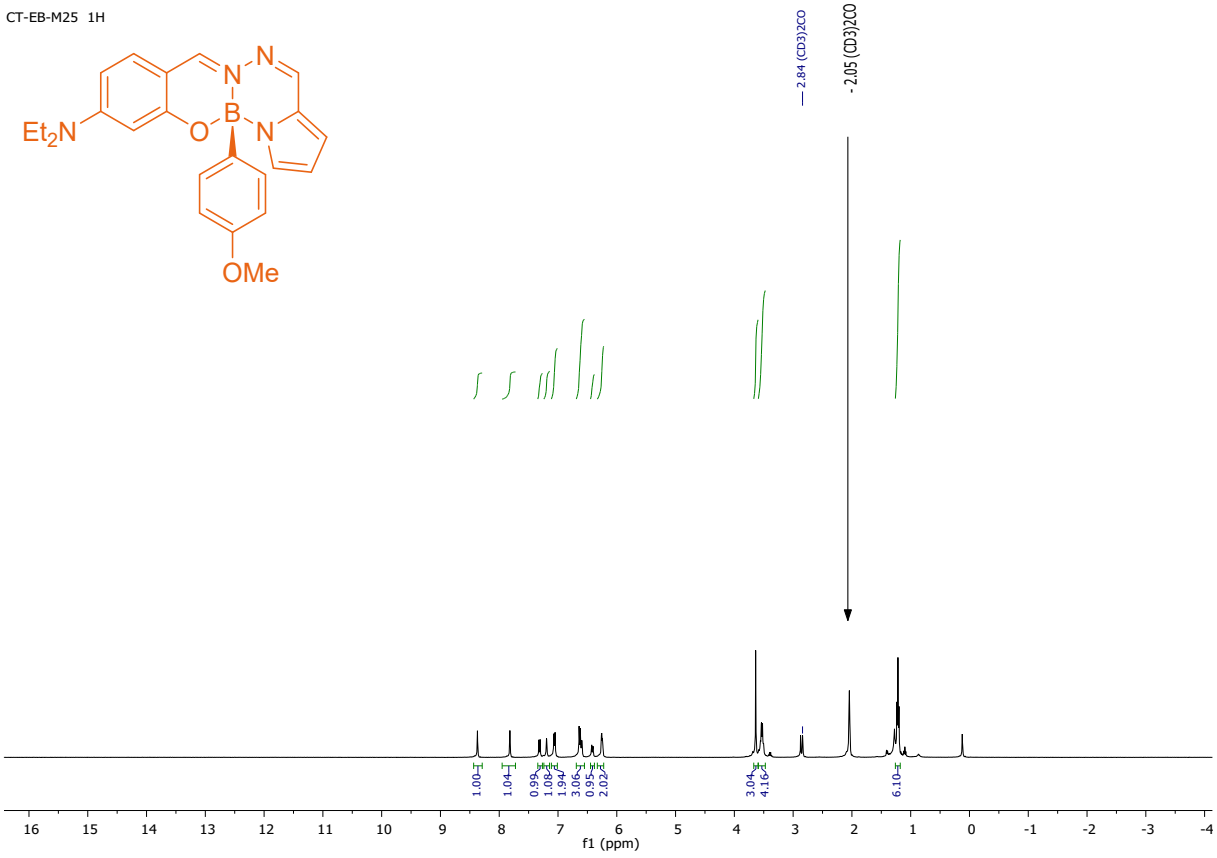


Figure S 27. ^{1}H NMR spectrum of **1f**

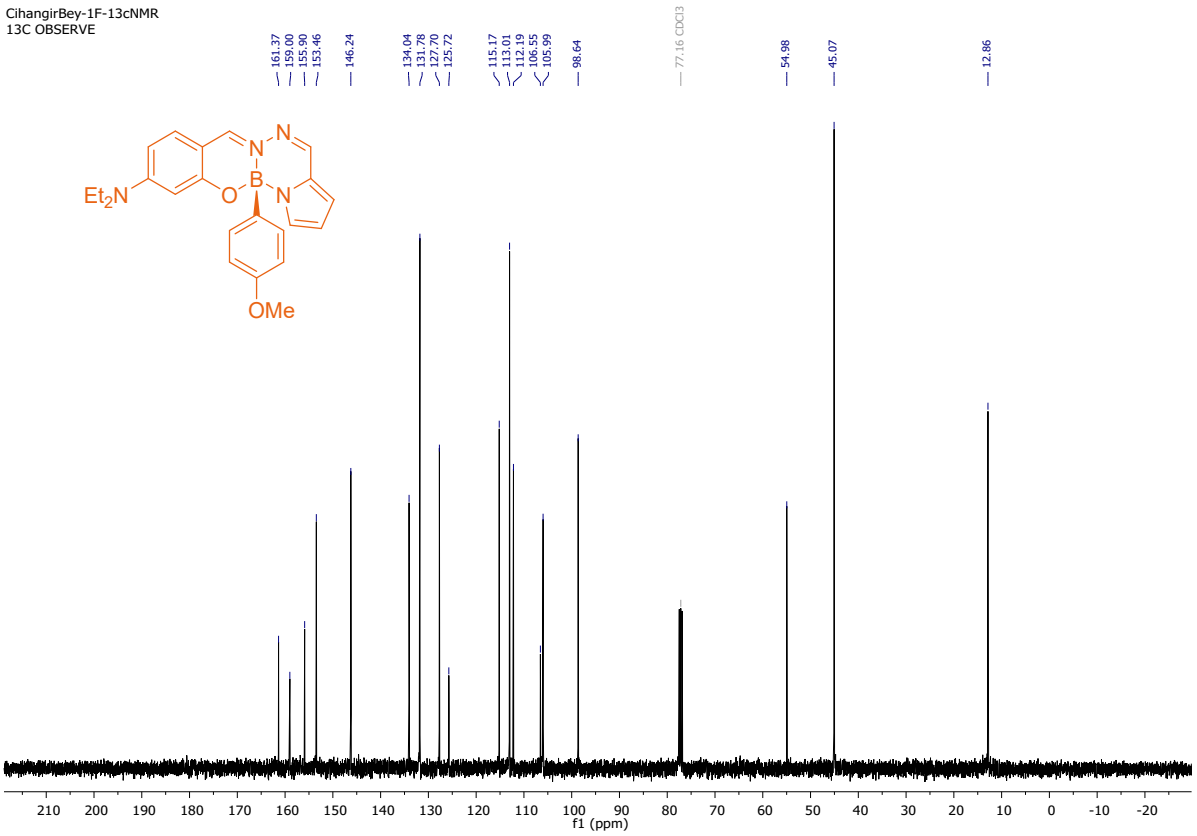


Figure S 28. ^{13}C NMR spectrum of **1f**

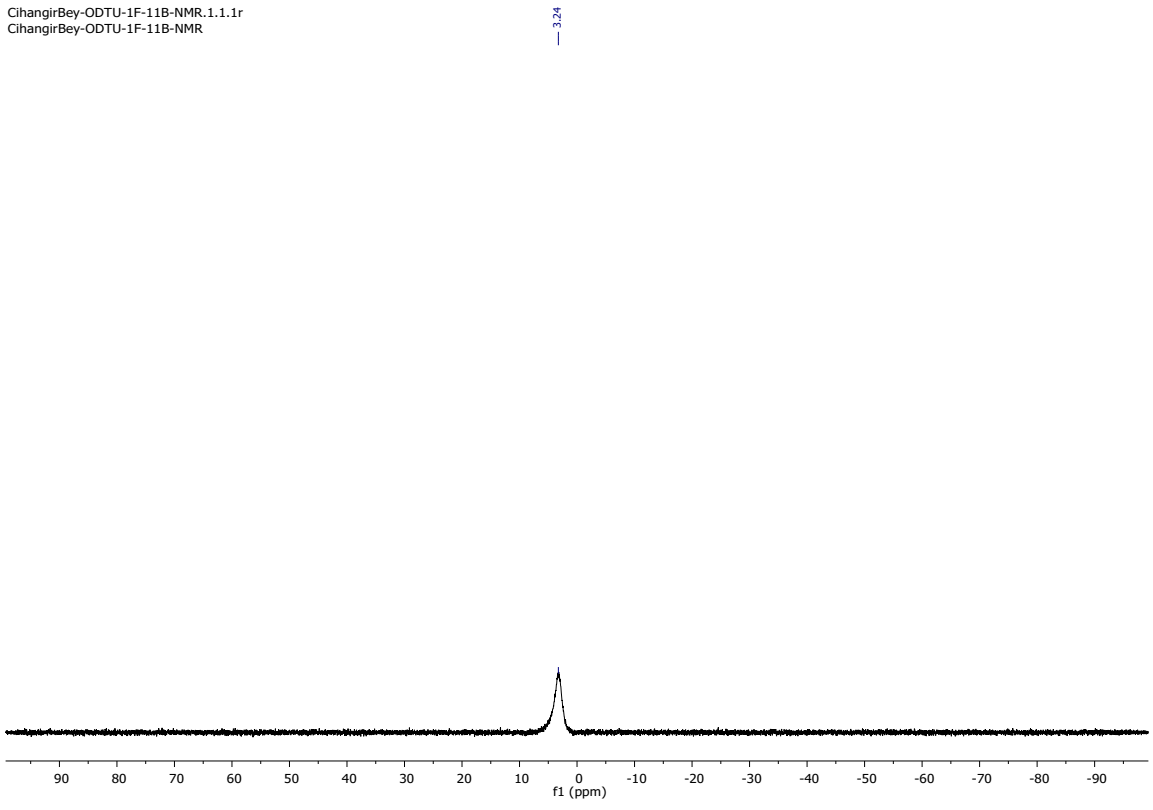
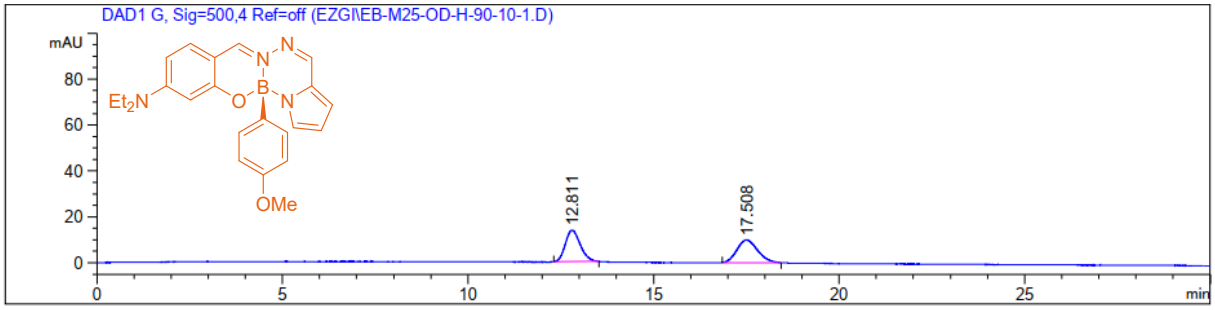


Figure S 29. ^{11}B NMR spectrum (128 MHz) of **1f** in $CDCl_3$

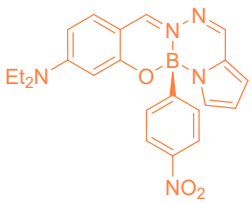


Signal 7: DAD1 G, Sig=500,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.811	BB	0.3300	382.37674	13.68368	50.1621
2	17.508	BB	0.4537	379.90616	9.85519	49.8379
Totals :				762.28290	23.53887	

Figure S 30. HPLC chromatogram of **1f**

3.7 BOSPYR 1g



Compound **1g** was isolated as an orange solid in 17% yield (35.3 mg). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.77 (s, 1H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.29 – 7.22 (m, 1H), 7.09 (d, *J* = 9.6 Hz, 1H), 6.66 (dd, *J* = 3.5, 1.3 Hz, 1H), 6.35 (dd, *J* = 3.5, 2.3 Hz, 1H), 6.28 (dd, *J* = 7.0, 2.3 Hz, 2H), 3.59 – 3.27 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ160.9, 156.3, 153.9, 147.4, 146.1, 134.3, 131.3, 127.4, 125.3, 122.4, 115.8, 112.7, 106.6, 106.4, 98.6, 45.2, 12.8 ppm. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 2.37 (bs). **HRMS** (APCI) calculated for $C_{22}H_{23}BN_5O_3$ ^{10}B $[M+H]^+$, 415.1930; found, 415.1925. **HPLC analysis** (OD-H, n-Hexane/Isopropanol, 90:10, 1 mL/min, 474 nm) t_1 = 18.67 min and t_2 = 26.24 min.

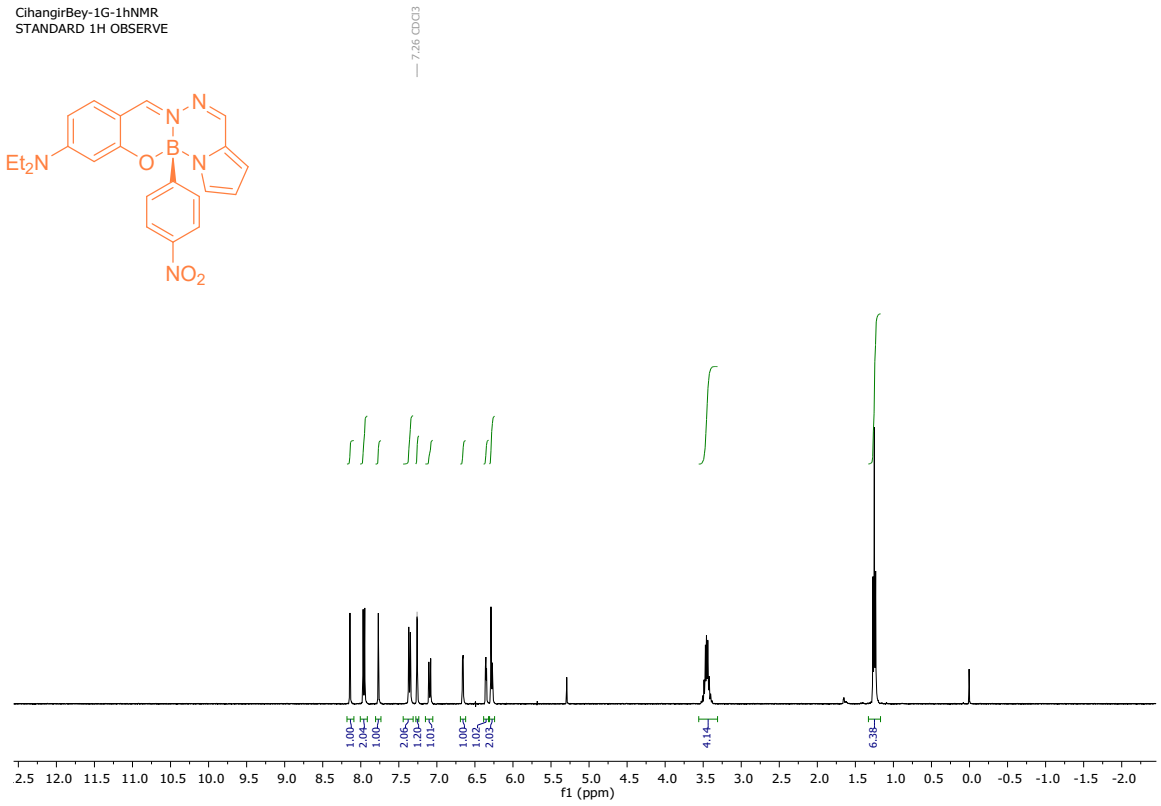


Figure S 31. ^{1}H NMR spectrum of **1g**

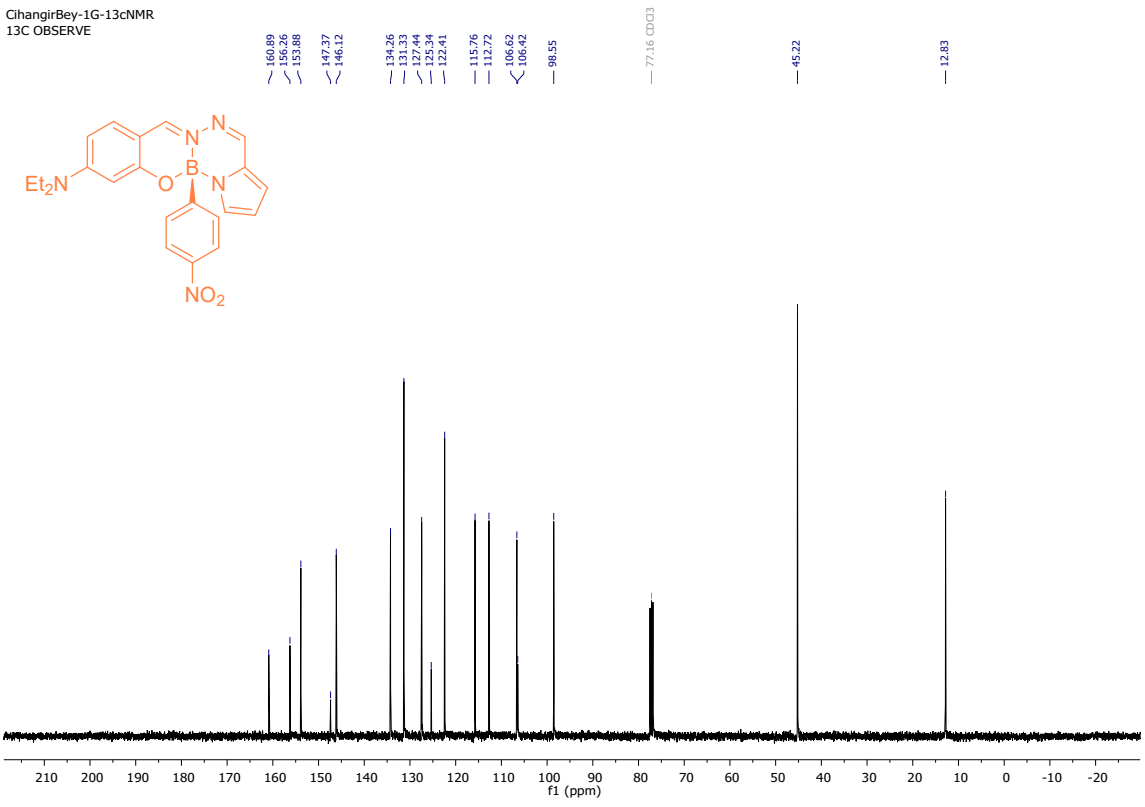


Figure S 32. ^{13}C NMR spectrum of **1g**

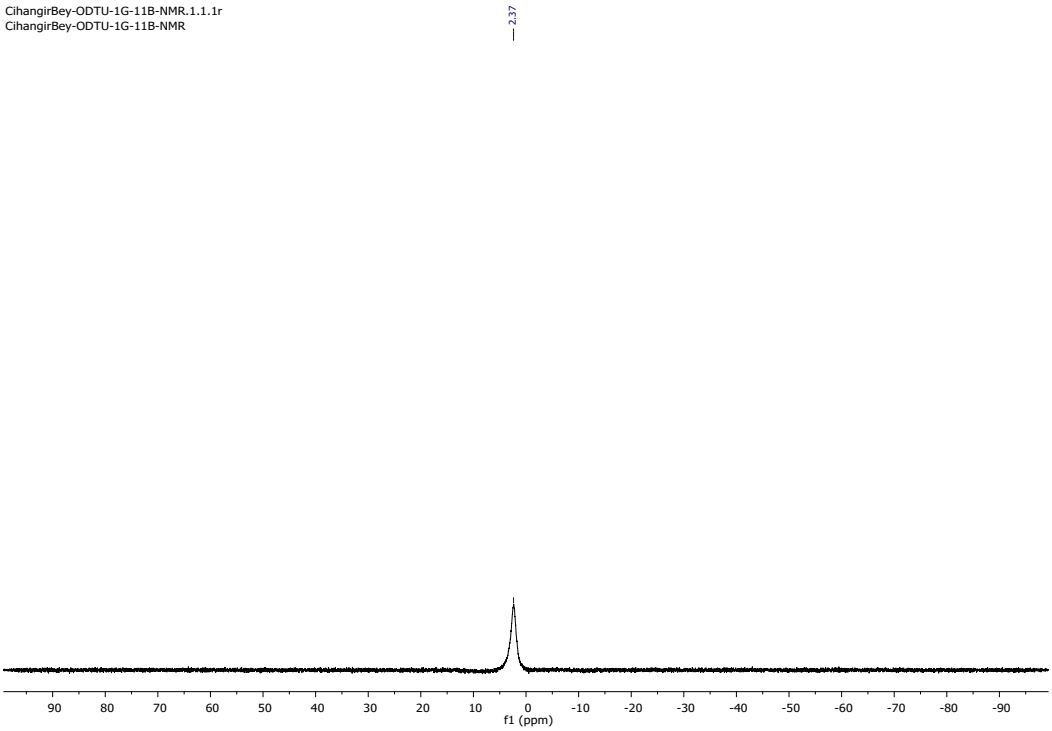
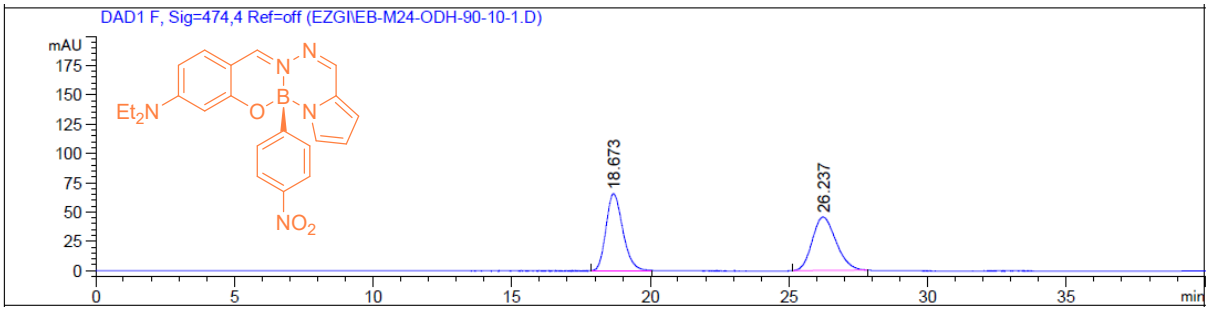


Figure S 33. ^{11}B NMR spectrum (128 MHz) of **1g** in $CDCl_3$

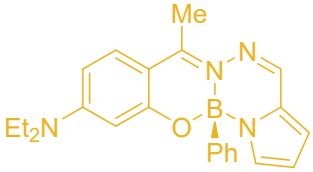


Signal 6: DAD1 F, Sig=474,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.673	BV R	0.5073	2756.71045	65.59792	50.3852
2	26.237	BB	0.6979	2714.56201	45.57777	49.6148
Totals :				5471.27246	111.17569	

Figure S 34. HPLC chromatogram of **1g**

3.8 BOSPYR 1h



1h was isolated as an orange solid in 16% yield (22.8 mg). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.35 (d, *J* = 8.9

Com

Hz, 1H), 7.32 (s, 1H), 7.20 – 7.08 (m, 5H), 6.64 (d, *J* = 3.3 Hz, 1H), 6.33 (s, 3H), 3.49 – 3.36 (m, 4H), 2.67 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.6, 160.3, 154.2, 145.3, 131.3, 130.7, 127.9, 127.4, 127.0, 125.4, 115.2, 112.3, 108.7, 106.2, 100.0, 45.4, 14.5, 12.8 ppm. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 2.61 (bs). **HRMS** (APCI) calculated for $C_{23}H_{26}BN_4O$ ^{10}B $[M+H]^+$, 384.2236; found, 384.2231. **HPLC analysis** (OD-H, n-Hexane/Isopropanol, 98:2, 1 mL/min, 474 nm) t_1 = 8.26 min and t_2 = 9.02 min.

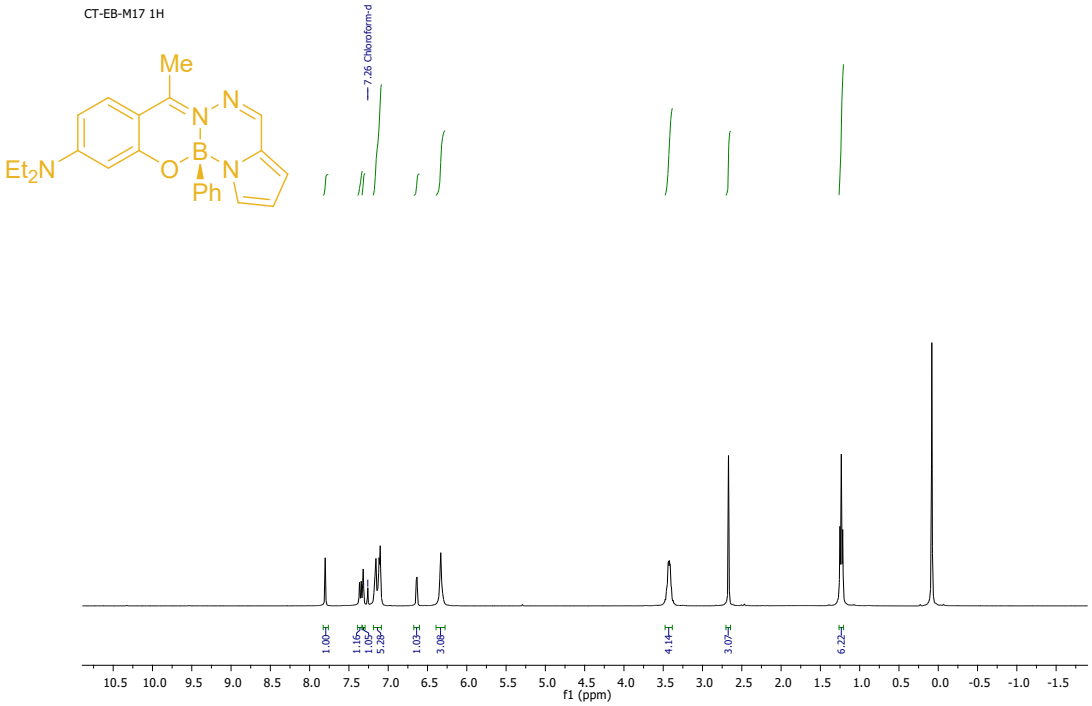


Figure S 35. ^{1}H NMR spectrum of **1h**

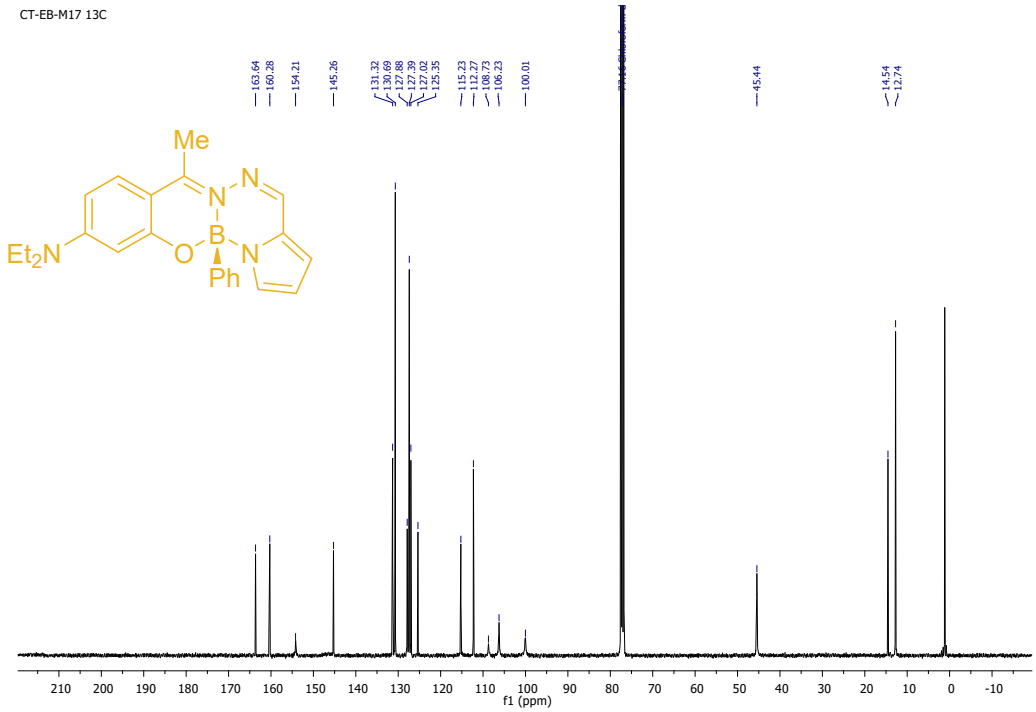


Figure S 36. ^{13}C NMR spectrum of **1h**

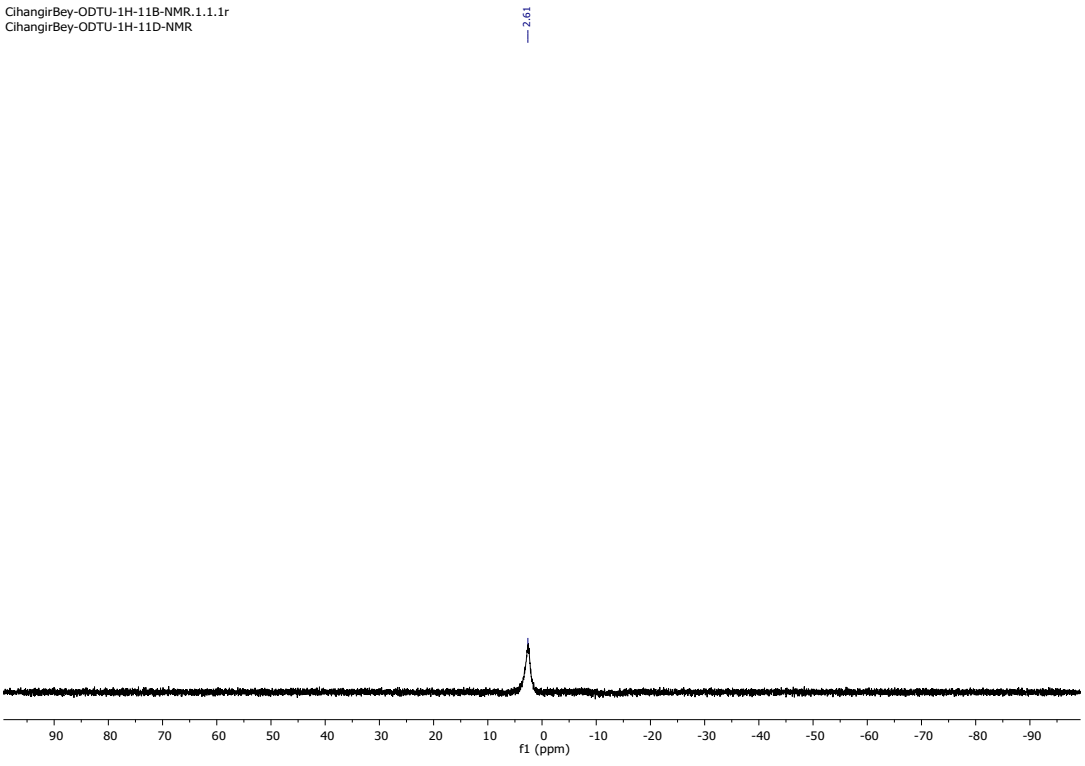
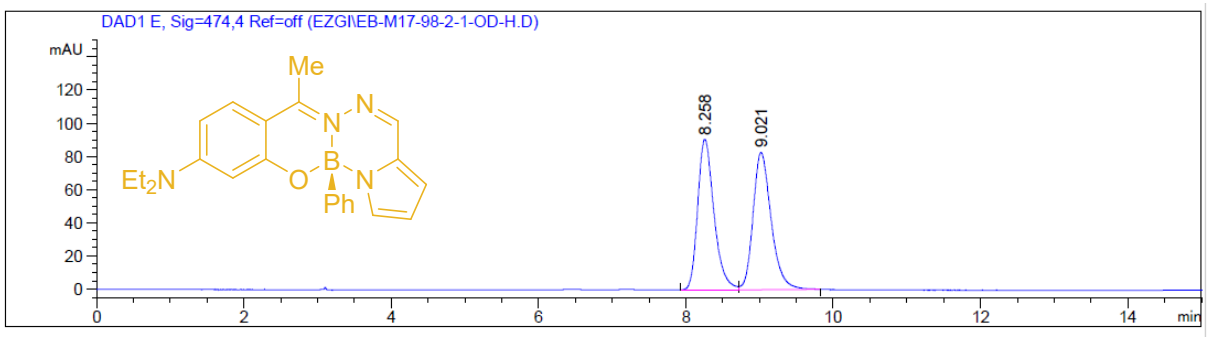


Figure S 37. ^{11}B NMR spectrum (128 MHz) of **1h** in $CDCl_3$



Signal 5: DAD1 E, Sig=474,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.258	BV	0.2271	1389.92542	90.54473	49.6381
2	9.021	VB	0.2531	1410.19214	82.43614	50.3619
Totals :				2800.11755	172.98087	

Figure S 38. HPLC chromatogram of **1h**

4. Optical Characterization of the Dyes 1a-h

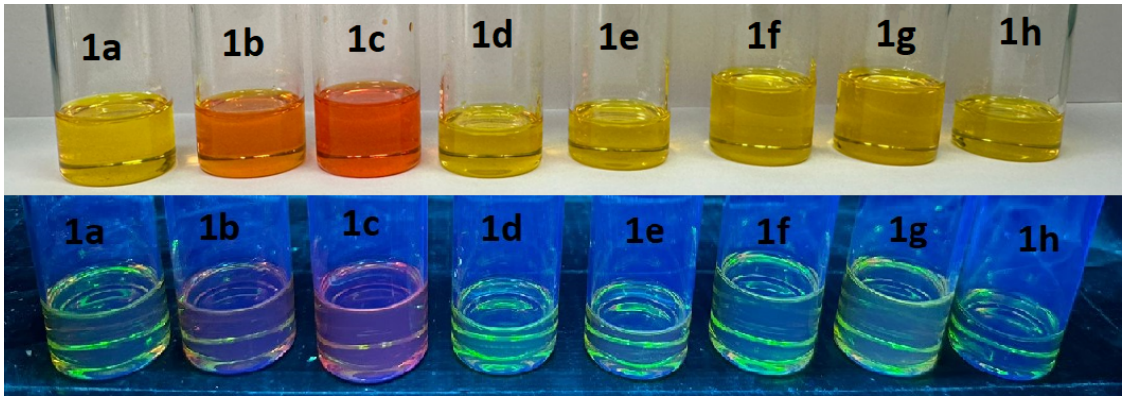


Figure S 39. Digital photographs of 1 mM DMSO solutions of each dye under daylight and 365 nm UV light irradiation (bottom).

4.1 Optical characterization of 1a

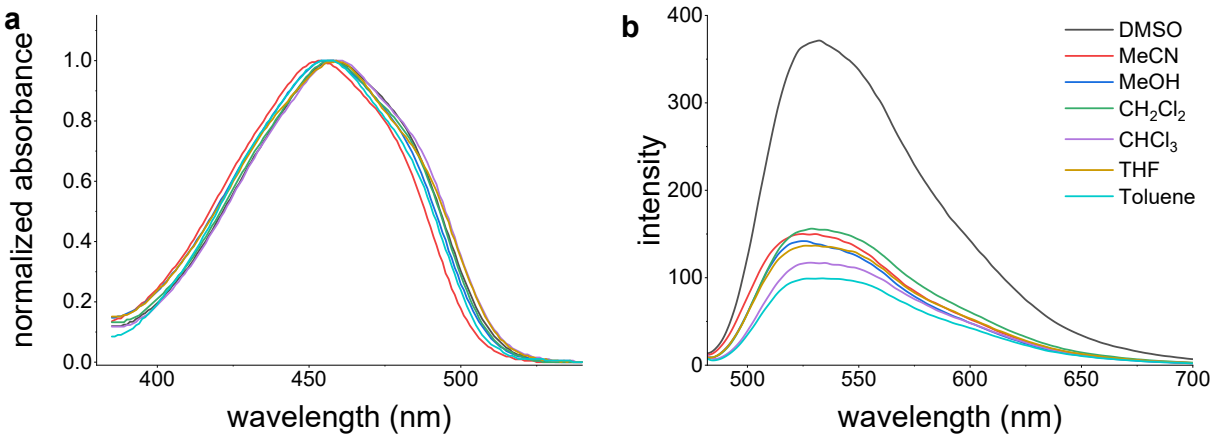
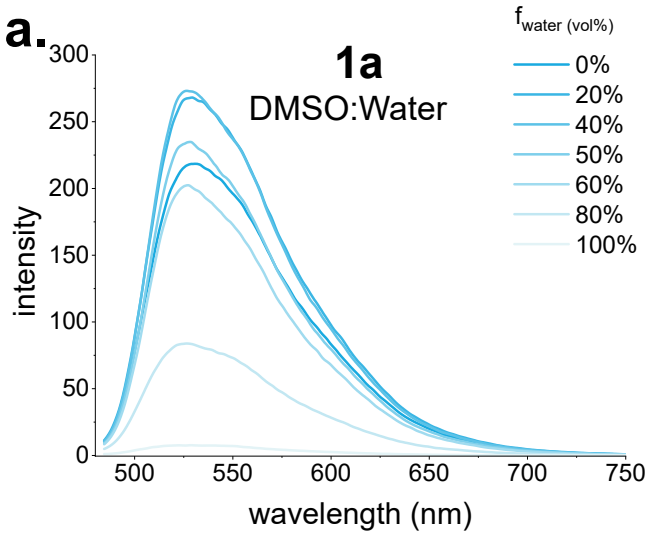


Figure S 40. **a.** Normalized UV-vis electronic absorption and **b.** fluorescence emission spectra of **1a** (2 μM) in various organic solvents.



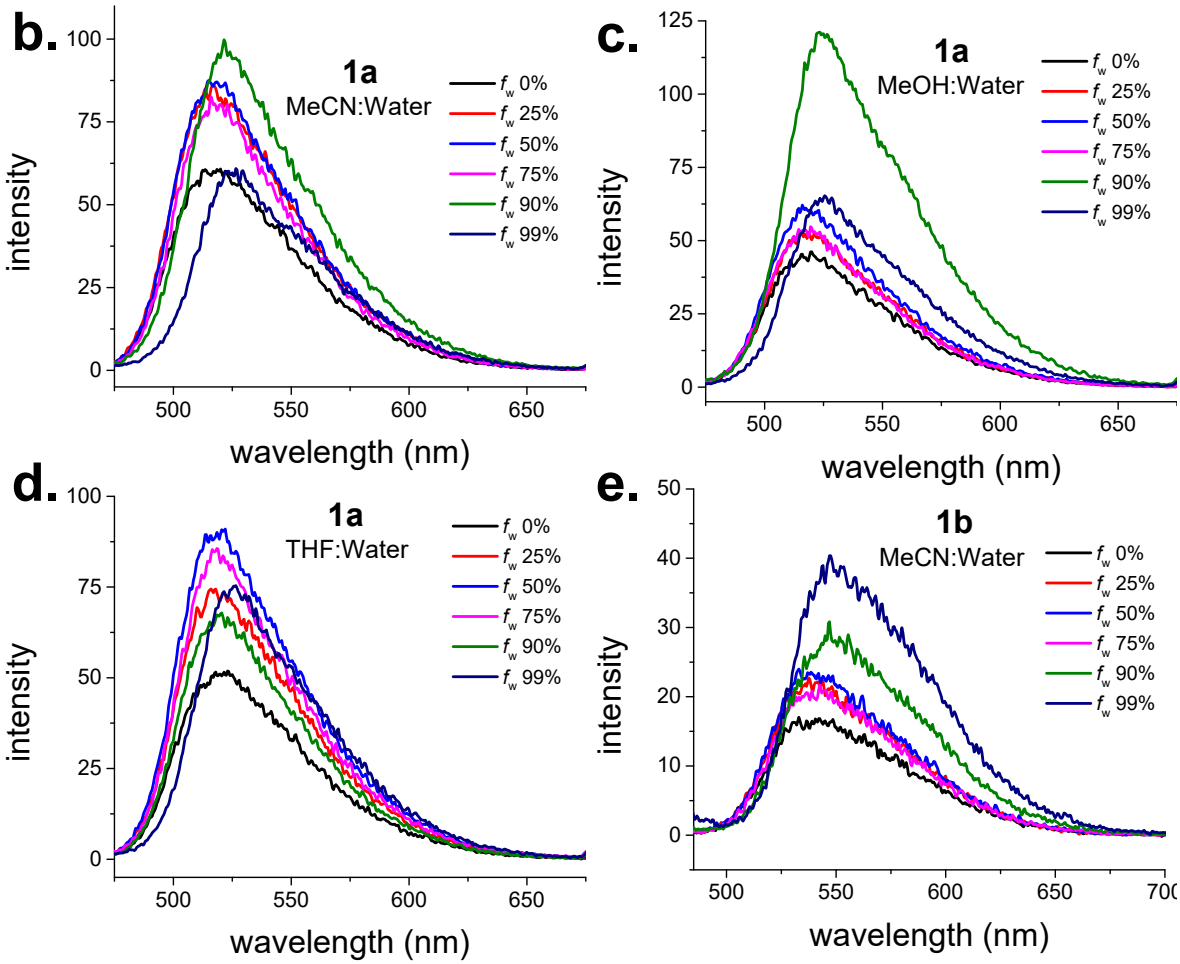


Figure S 41. Fluorescence emission spectra of **1a** and **1b** in water–DMSO/MeCN/MeOH/THF mixtures with varying water fractions [f_{water} (vol%): 0–100%] at 25 °C.

Table S 1. Optical characterization of the dyes **1a**–**h** in DMSO.[a]

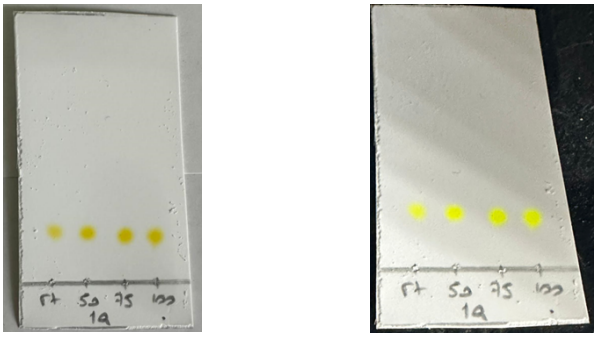
BOSPYR	λ_{abs} [nm]	ε_{max} [$M^{-1}cm^{-1}$]	λ_{ems} [nm]	$\Delta\lambda$ [nm; cm^{-1}]	Φ_{fl}[b]	τ_p[c] [ns]
1a	457	45600	530	73; 3014	0.034	0.94
1b	476	23000	555	79; 2990	0.020	1.09
1c	481	29600	573	92; 3338	0.042	0.71
1d	454	36900	521	67; 2833	0.091	1.21
1e	437	8800	557	120; 4930	0.040	2.00
1f	461	28500	528	67; 2753	0.058	1.37
1g	462	25700	526	64; 2633	0.023	0.47
1h	456	39900	524	68; 2846	0.015	1.49

[a]A concentration of 2 μM was used for all the dyes in the described investigations. [b]Relative fluorescence quantum yields were calculated using quinine sulphate as the reference (Φ_{fl} = 0.60 in 0.5 M H_2SO_4; see ref 21 of the paper). [c]Fluorescence lifetimes (prompt) were all characterized by a monoexponential fit.

5. Thermal, Configurational, (Photo)chemical Stability of 1a

5.1 Thermal stability test;

The thermal stability of racemic **1a** was evaluated by heating toluene solutions (0.1 mM) at 50, 75, and 100 °C for one hour in sealed vessels. Additionally, a solution was heated at 120 °C for one hour under an open atmosphere. TLC analysis of all samples indicated no detectable decomposition.



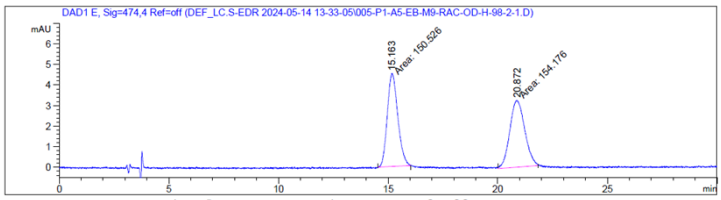
(a) daylight (b) UV (366 nm)

Figure S 41. TLC analysis of compound **1a** after heating at various temperatures for 1 hour.

5.2 Configurational stability test; chiral HPLC reports

The configurational stability of the first-eluting enantiomer (**(–)-1a**) was assessed by heating toluene solutions (0.1 mM) at 50, 75, and 100 °C for 1 h in sealed vessels, and at 120 °C for 1 h under an open atmosphere. Subsequent chiral HPLC analysis revealed no detectable epimerization, indicating high configurational stability. The HPLC chromatograms were obtained at a column temperature of 18 °C.

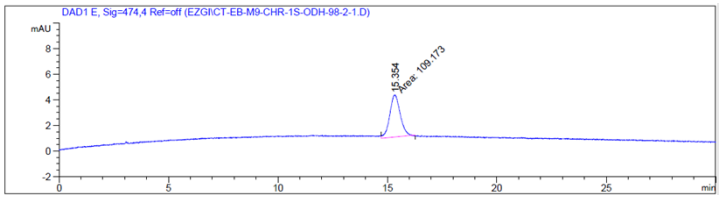
I. Rac-**1a**



Signal 5: DAD1 E, Sig=474,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.163	MM	0.5540	150.52641	4.52878	49.4012
2	20.872	MM	0.7872	154.17564	3.26424	50.5988
Totals :				304.70206	7.79302	

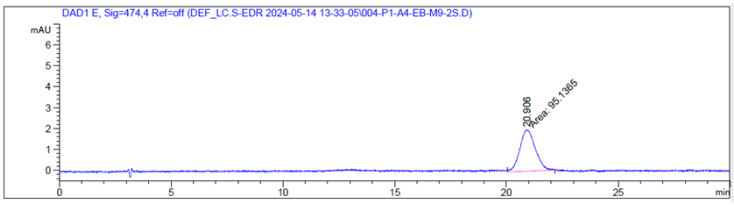
II. Fast-eluting enantiomer, (–)-**1a**



Signal 5: DAD1 E, Sig=474,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.354	MM	0.5504	109.17337	3.30573	100.0000
Totals :				109.17337	3.30573	

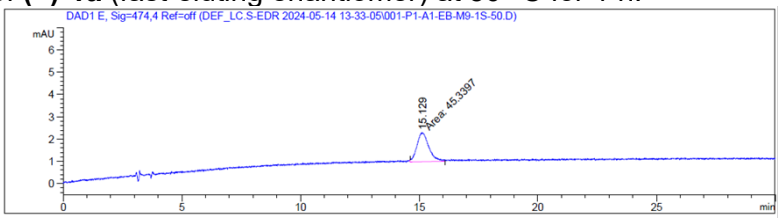
III. Slow-eluting enantiomer, (+)-**1a**



Signal 5: DAD1 E, Sig=474,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.906	MM	0.8025	95.13651	1.97591	100.0000
Totals :				95.13651	1.97591	

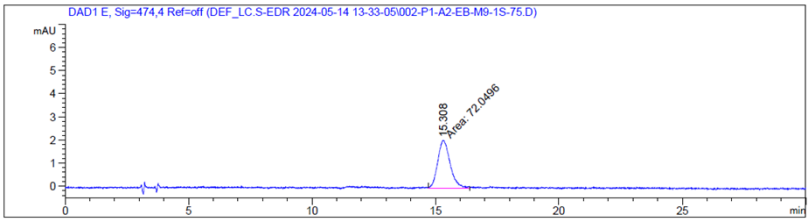
IV. Heating of **(−)-1a** (fast-eluting enantiomer) at 50 °C for 1 h.



Signal 5: DAD1 E, Sig=474,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.129	MM	0.5738	45.33974	1.31705	100.0000
Totals :				45.33974	1.31705	

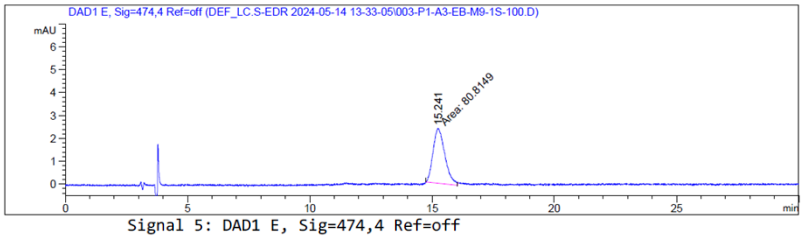
V. Heating of **(−)-1a** (fast-eluting enantiomer) at 75 °C for 1 h.



Signal 5: DAD1 E, Sig=474,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.308	MM	0.5774	72.04960	2.07960	100.0000
Totals :				72.04960	2.07960	

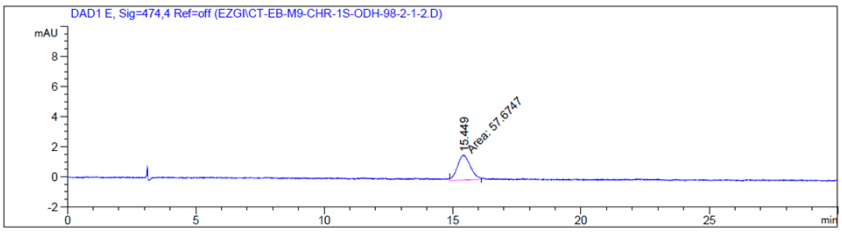
VI. Heating of **(−)-1a** (fast-eluting enantiomer) at 100 °C for 1 h.



Signal 5: DAD1 E, Sig=474,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.241	MM	0.5569	80.81493	2.41880	100.0000
Totals :				80.81493	2.41880	

VII. Heating of **(−)-1a** (fast-eluting enantiomer) at 120 °C for 1 h (open atm).

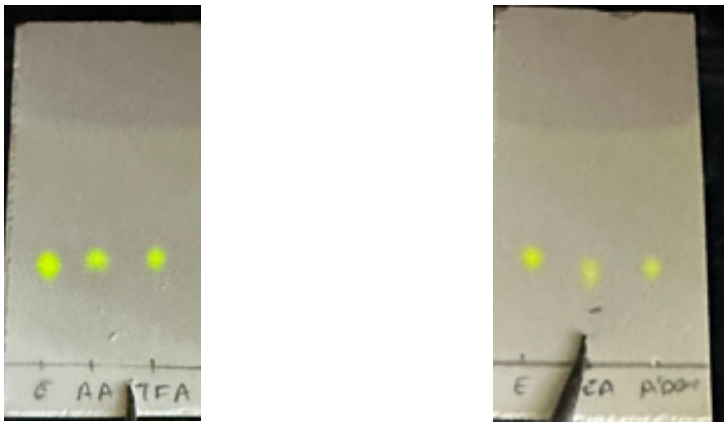


Signal 5: DAD1 E, Sig=474,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.449	MM	0.5810	57.67474	1.65442	100.0000
Totals :				57.67474	1.65442	

5.3 Chemical stability test

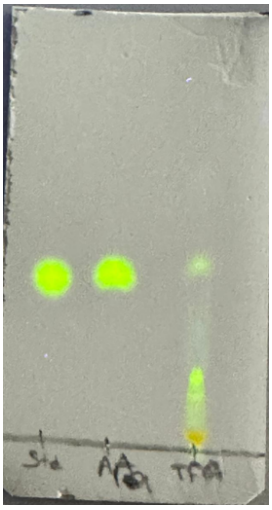
Motivated by the observed thermal stability, the acid-base stability of *rac*-**1a** was subsequently evaluated. Equimolar dichloromethane solutions (1 mM) of **1a** and either acetic acid (AA), trifluoroacetic acid (TFA), triethylamine (TEA), or piperidine were stirred at room temperature for 1 hour. No discernible decomposition was observed in any case.



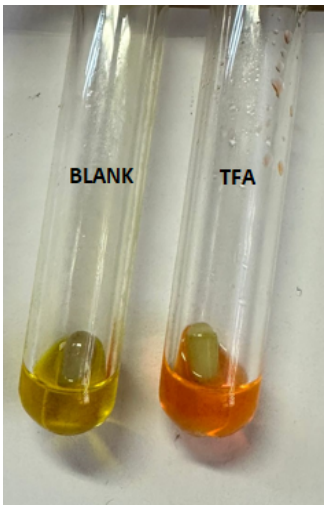
(a) TLC of acid-stability test at 366 nm (b) TLC of base-stability test at 366 nm

Figure S 42. TLC analysis of *rac*-**1a** after exposure to acids and bases**.**

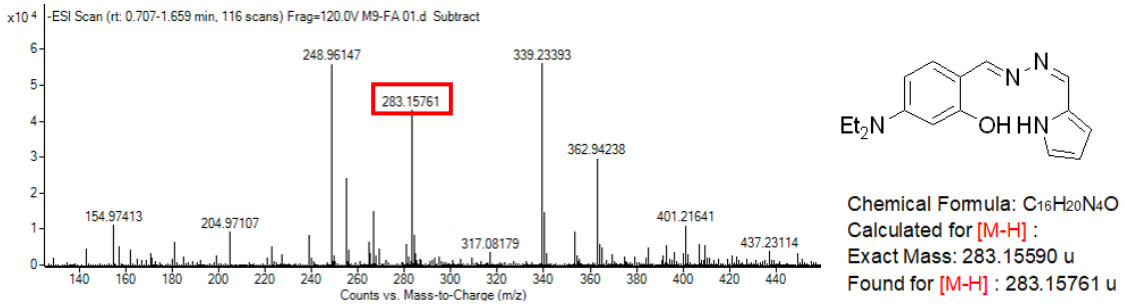
Only trifluoroacetic acid induced a color change from yellow to orange after 2 days, indicative of boron bridge cleavage (confirmed by HRMS, Figure S37). No discernible degradation was observed for the other tested conditions (acetic acid, triethylamine, piperidine).



(a) TLC plate of the reaction mixture after 2 days of exposure to TFA (*rac*-**1a** +TFA), visualized under UV light at 366 nm.



(b) Color of the solution after 2 days of exposure to TFA (*rac*-**1a** +TFA), visualized under daylight.



(c) HRMS result of chemical stability experiment: **1a** with TFA

Figure S 43. TLC plate, color change, and HRMS result of *rac*-**1a** treated with TFA.

5.4 Chemical stability of 1e

Compound **1e** exhibited gradual discoloration in DMSO solution over time, indicative of degradation. This observation was corroborated by TLC analysis and time-dependent fluorescence measurements. To assess photostability, compound **1e** in DMSO was subjected to intermittent light pulses (λex = 440 nm, pulse interval: 10 s, total exposure: 5400 s). As depicted in Figure S38, a progressive decrease in fluorescence intensity was observed, confirming the compound's photosensitivity.

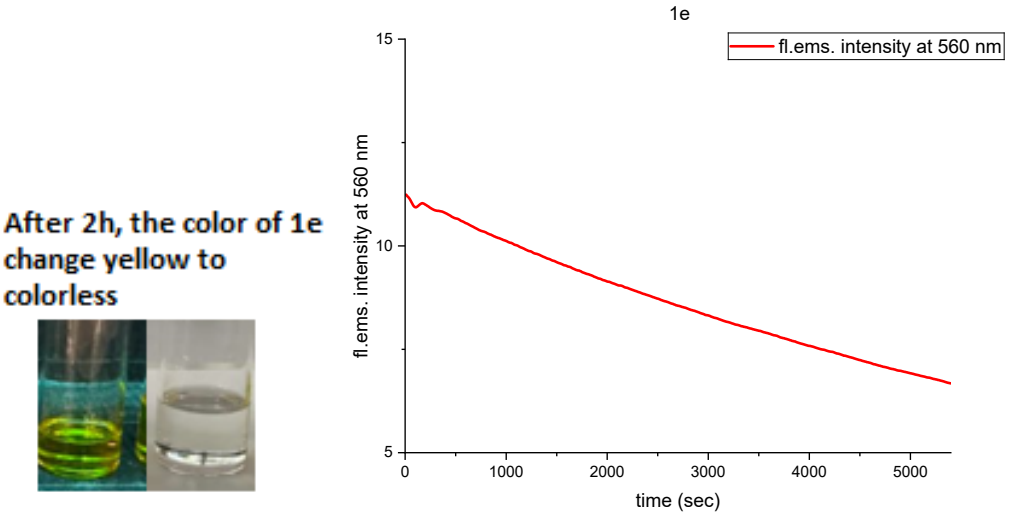


Figure S 44. Chemical stability of **1e**, time-dependent fluorescence intensity profile of **1e** (2 μM) in DMSO at 560 nm. A laser pulse of 440 nm is given for 5400 sec with 10-sec intervals.

The thermal stability of compound **1e** was investigated by heating a toluene solution (0.1 mM) at 100 °C for 1 hour (Figure S39, entry 1). As a control, a toluene solution of **1e** was stirred at room temperature for 1 hour (Figure S39, entry 2). To evaluate chemical stability, equimolar mixtures of **1e** (1 mM) with acetic acid, trifluoroacetic acid, triethylamine, and piperidine in dichloromethane were stirred at room temperature for 1 hour (Figure S39, entries 3-6, respectively). Additionally, the stability of **1e** in DMSO was assessed under identical conditions (Figure S39, entry 7). While **1e** demonstrated stability towards heat, acetic acid, and ambient conditions, exposure to trifluoroacetic acid, triethylamine, piperidine, and DMSO resulted in notable degradation.

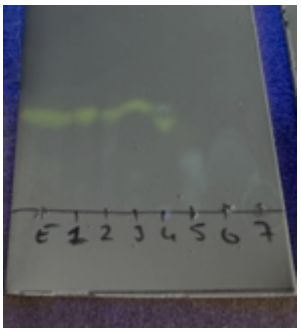


Figure S 45. TLC analysis of compound **1e** stability. TLC under UV illumination (366 nm).

5.5 Photostability test

The photostability of the racemic dye **1a** was evaluated in DMSO by exposing it to a light pulse (λ_{ex} 460 nm) for 5400 seconds, with intervals of 10 seconds between pulses, and measuring its fluorescence. As illustrated in Fig. S40, the dye demonstrated significant photostability, with its fluorescence remaining nearly unchanged throughout the testing period.

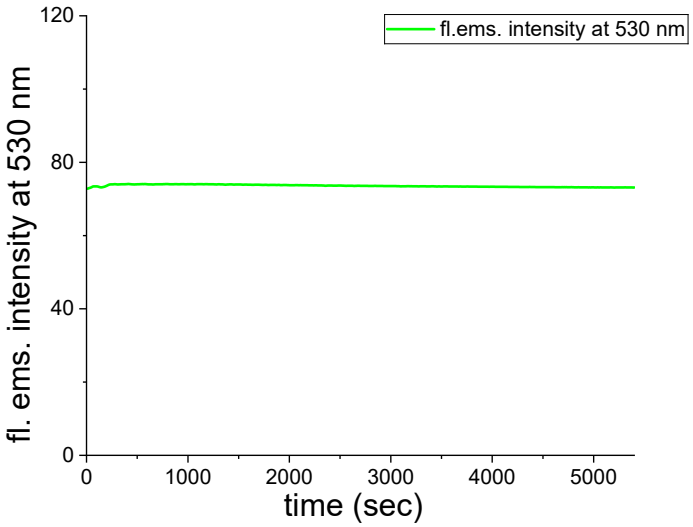


Figure S 46. Time-dependent fluorescence intensity profile of **1a** (2 μM) in DMSO at 530 nm. A laser pulse of 460 nm is given for 5400 sec with 10-sec intervals.

6. Electrochemical Properties

The electrochemical characteristics of compound **1a** were investigated using differential pulse voltammetry (DPV). The experiments were conducted relative to an Ag/AgCl reference electrode in a degassed, anhydrous acetonitrile solution, with $[Bu_4N^+][PF_6^-]$ (0.1 M) as the supporting electrolyte. The electrochemical measurement results, along with the calculated HOMO/LUMO energy levels, are presented in Table S2. There is a correlation between the results of the electrochemical measurements and the results of the computational studies.

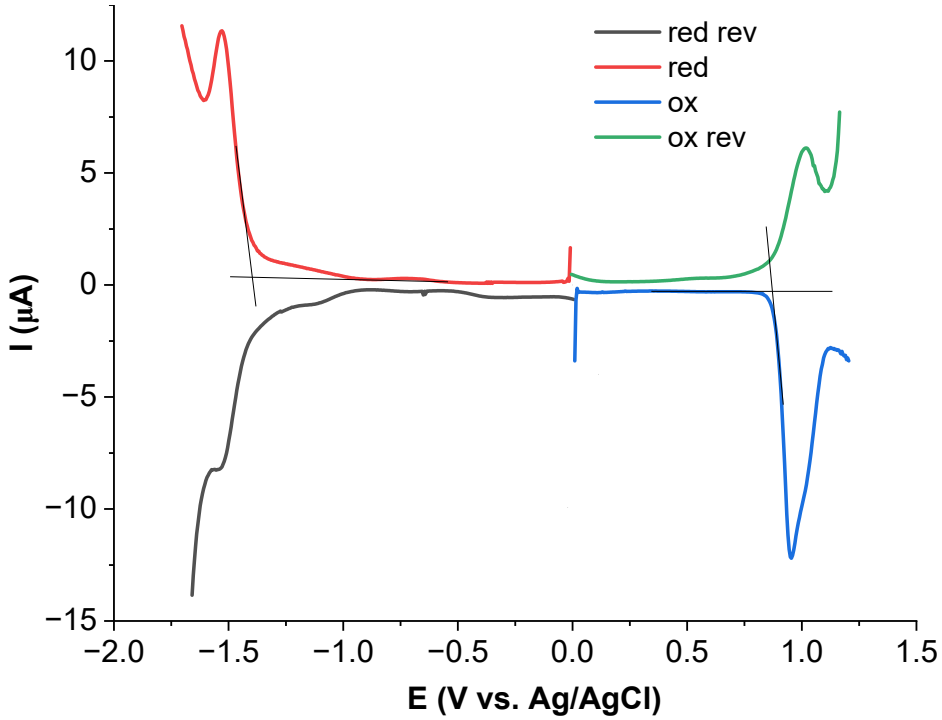


Figure S 47. DPV of **1a** in MeCN

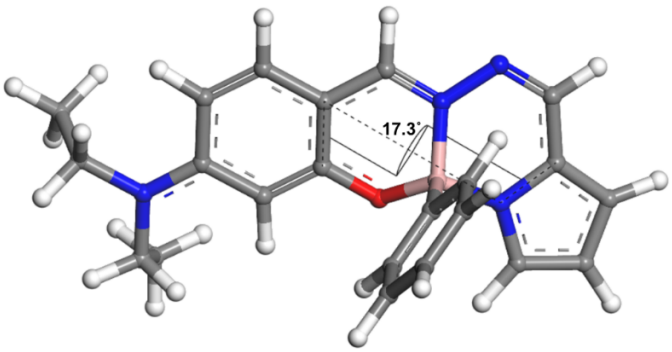
Table S 2. Electrochemical properties of **1a** in MeCN

	E_{ox}^{onset} (V)[a]	E_{red}^{onset} (V)[a]	E_{HOMO} (eV)[b]	E_{LUMO} (eV)[c]	$E_g^{electro}$ (eV)[d]	E_g^{opt} (eV)
1a	0.872	-1.40	- 5.58	- 3.31	2.27	2.3

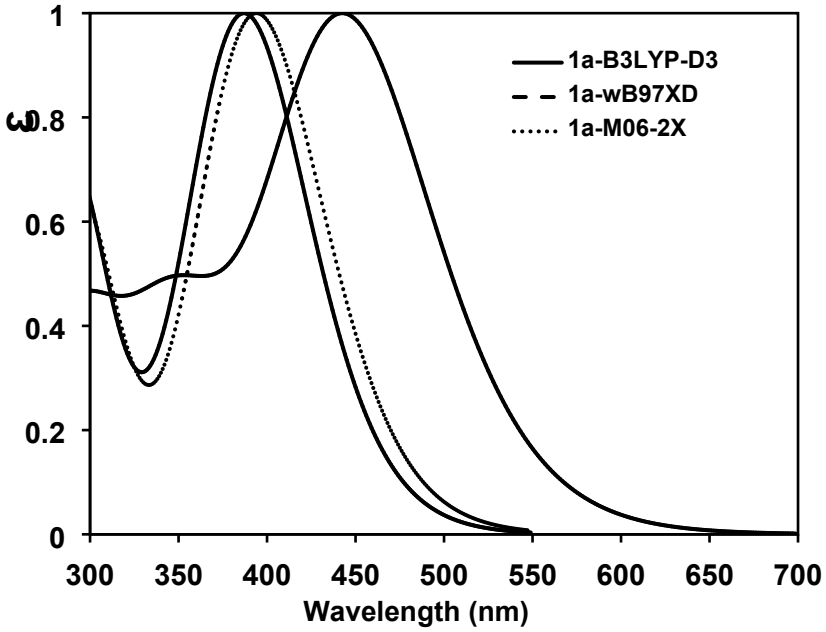
[a]Calculated from the DPV, [b]Calculated with E_{HOMO}: - (4.71 + E_{ox}^{onset})
[c]Calculated with E_{LUMO}: - (4.71 + E_{red}^{onset}t) [d]Calculated with E_{gap} : E_{LUMO} - E_{HOMO}

7. Computational Studies

Geometry optimization and excited state calculations were performed by Density Functional Theory (DFT) and TD-DFT using B3LYP-D3,[iii] wB97XD[iv] and M06-2X[v] functionals and 6-311+(d) basis sets. The UV-Vis adsorption spectra and comparison with the experimental structure were used as validation of the method (Figure S49). B3LYP with Grimme D3-dispersion correction provided the closest results with the experimental study both for dihedral angle between chelating mean planes and λ_{max} in the UV-Vis. The UV-vis spectra calculation was in agreement with all BOSPYR dyes (Figure S50).



a



b

Figure S 48. a) Geometry optimized structure, b) Calculated UV-Vis spectra for **1a** by different functionals.

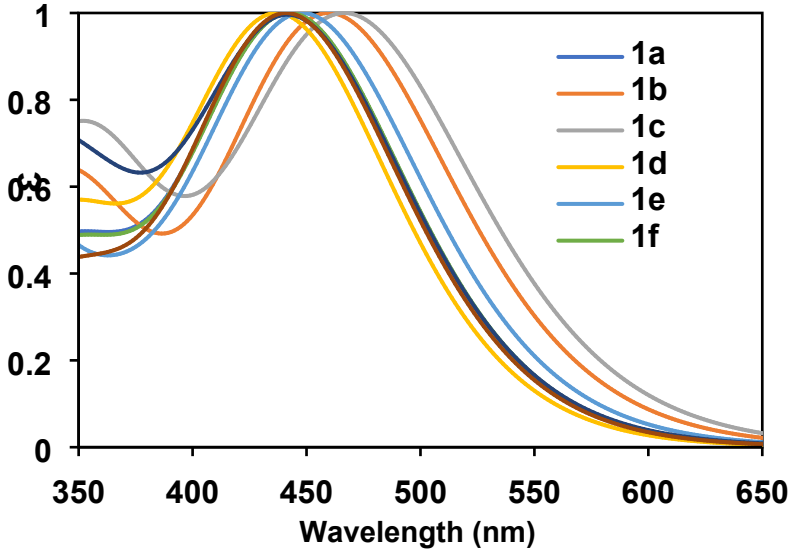


Figure S 49. Calculated UV-Vis for BOSPYR dyes (**1a–h**)

	μ	α	Δα	β
1a	9.53	494.84	340.75	10648.85
1b	8.60	535.08	369.98	9360.86
1c	8.25	570.40	373.48	9285.42
1d	6.44	360.68	248.22	2574.71
1e	3.34	376.85	212.31	5278.20
1f	8.36	518.56	325.06	10813.75
1g	12.88	526.95	306.78	11105.11
1h	8.98	510.71	327.12	12026.99

Table S 3. Dipole Moment (μ), polarizability (α), anisotropy in the polarizability (Δα), first order hyperpolarizability (β) calculated by DFT calculations.

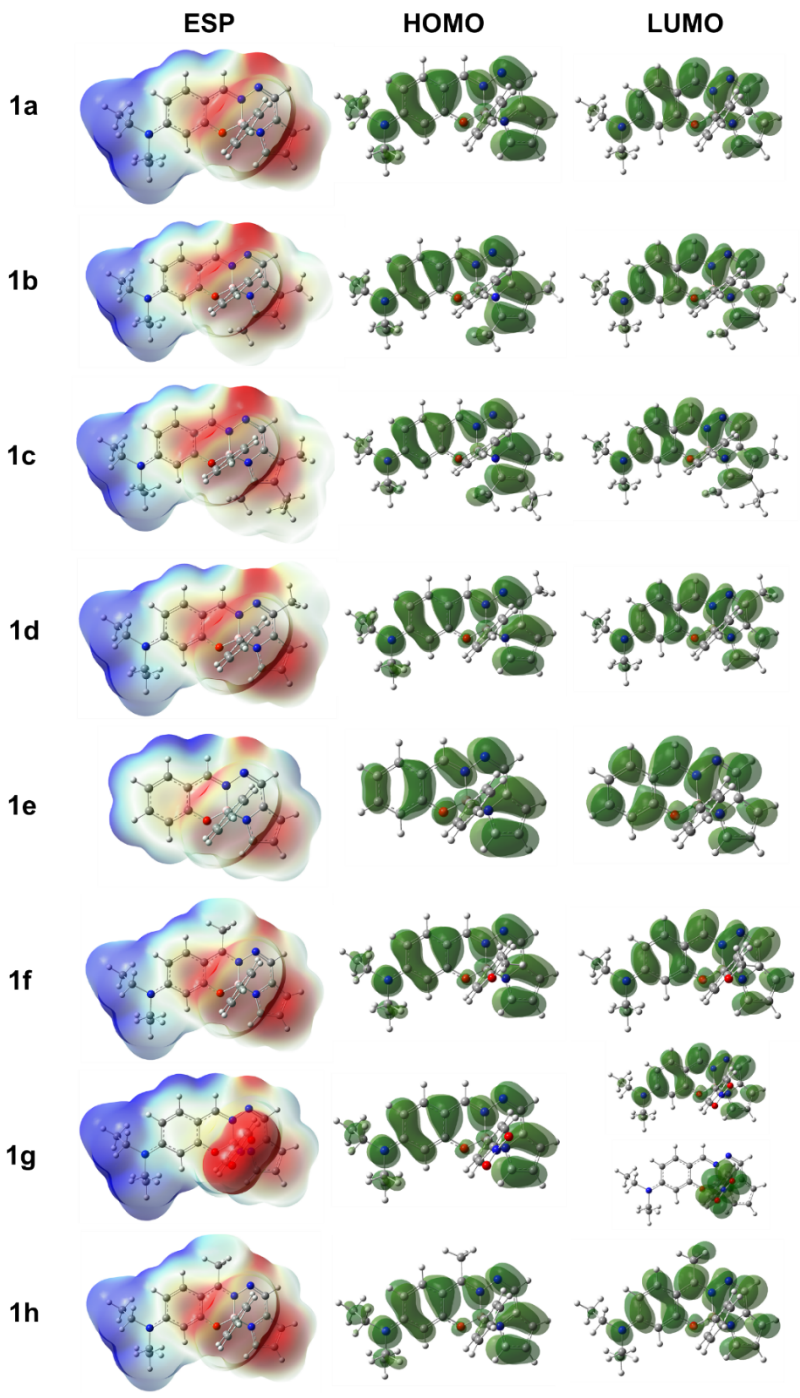


Figure S 50. ESP, HOMO and LUMO surfaces for 1a-1h structures at the ground state optimized geometries.

The most important singlet excited state transition energies, oscillatory frequencies and natural transition orbitals for singlet excitations with high oscillatory frequencies were determined for **1a-1h** (Table S 4, Figure S 52).

Table S 4. Frontier orbital energy levels, singlet excites state energy levels and their oscillatory frequencies.

	HOMO (GSOP)	LUMO	E_g	E_g^{opt} S_0-S_1	ESOP	S_0-S_2	S_0-S_3	S_0-S_4	S_0-S_5	S_0-S_6	S_0-S_7
1a	-5.58	-2.34	3.24	**2.79** ***f=0.60***	-2.79	3.49 *f=0.20*	3.63 *f=0.05*	3.72 *f=0.02*	4.02 *f=0.00*	4.08 *f=0.04*	4.14 *f=0.17*
1b	-5.40	-2.24	3.15	**2.69** ***f=0.57***	-2.71	3.51 *f=0.28*	3.53 *f=0.01*	3.69 *f=0.02*	4.00 *f=0.03*	4.01 *f=0.17*	4.11 *f=0.00*
1c	-5.33	-2.21	3.12	**2.65** ***f=0.53***	-2.69	3.43 *f=0.25*	3.52 *f=0.09*	3.61 *f=0.01*	3.97 *f=0.19*	3.99 *f=0.00*	4.13 *f=0.00*
1d	-5.56	-2.27	3.29	**2.82** ***f=0.61***	-2.74	3.53 *f=0.24*	3.63 *f=0.06*	3.77 *f=0.01*	4.08 *f=0.01*	4.10 *f=0.16*	4.13 *f=0.05*
1e	-6.03	-2.27	3.76	**2.75** ***f=0.24***	-3.29	3.36 *f=0.05*	3.42 *f=0.02*	3.67 *f=0.0.*	3.79 *f=0.04*	4.15 *f=0.20*	4.41 *f=0.09*
1f	-5.57	-2.33	3.24	**2.79** ***f=0.60***	-2.78	3.17 *f=0.00*	3.49 *f=0.20*	3.65 *f=0.07*	3.99 *f=0.02*	4.09 *f=0.00*	4.18 *f=0.22*
1g	-5.64	-2.99	2.65	2.21 *f=0.00*	-3.43	**2.79** ***f=0.61***	2.95 *f=0.01*	3.25 *f=0.01*	3.49 *f=0.09*	3.50 *f=0.20*	3.65 *f=0.05*
1h	-5.54	-2.29	3.25	**2.80** ***f=0.61***	-2.74	3.46 *f=0.15*	3.64 *f=0.07*	3.75 *f=0.04*	4.05 *f=0.00*	4.10 *f=0.01*	4.22 *f=0.19*

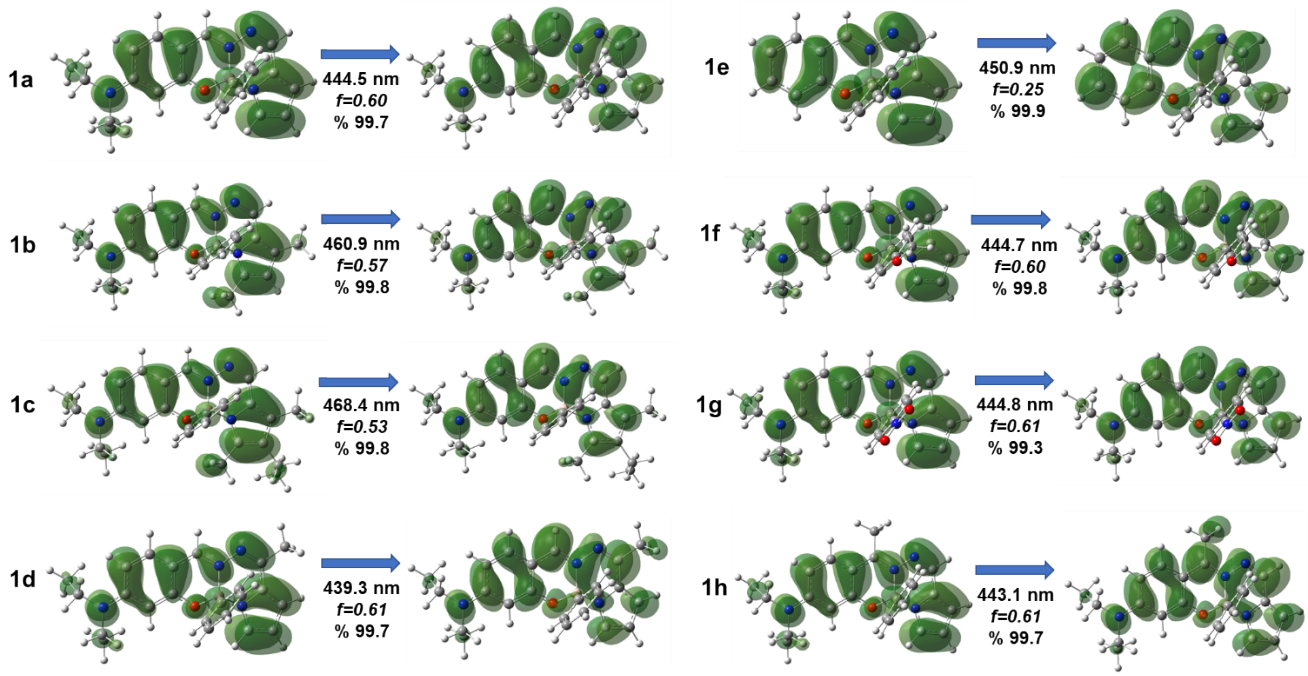


Figure S 51. Natural transition orbitals for singlet excitations with high oscillatory frequencies.

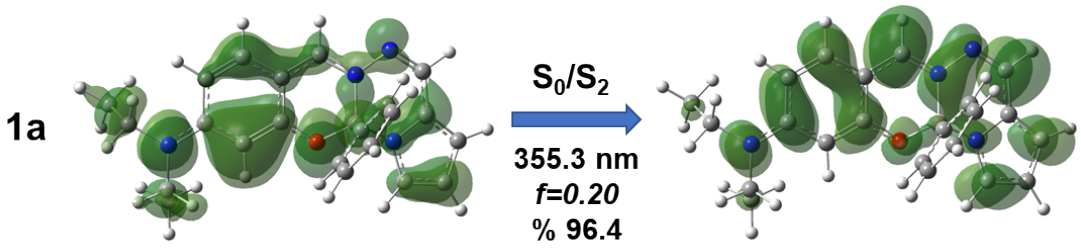


Figure S 52. Natural transition orbital for the $S_0 \rightarrow S_2$ excitation for 1a which has the second highest oscillatory frequencies.

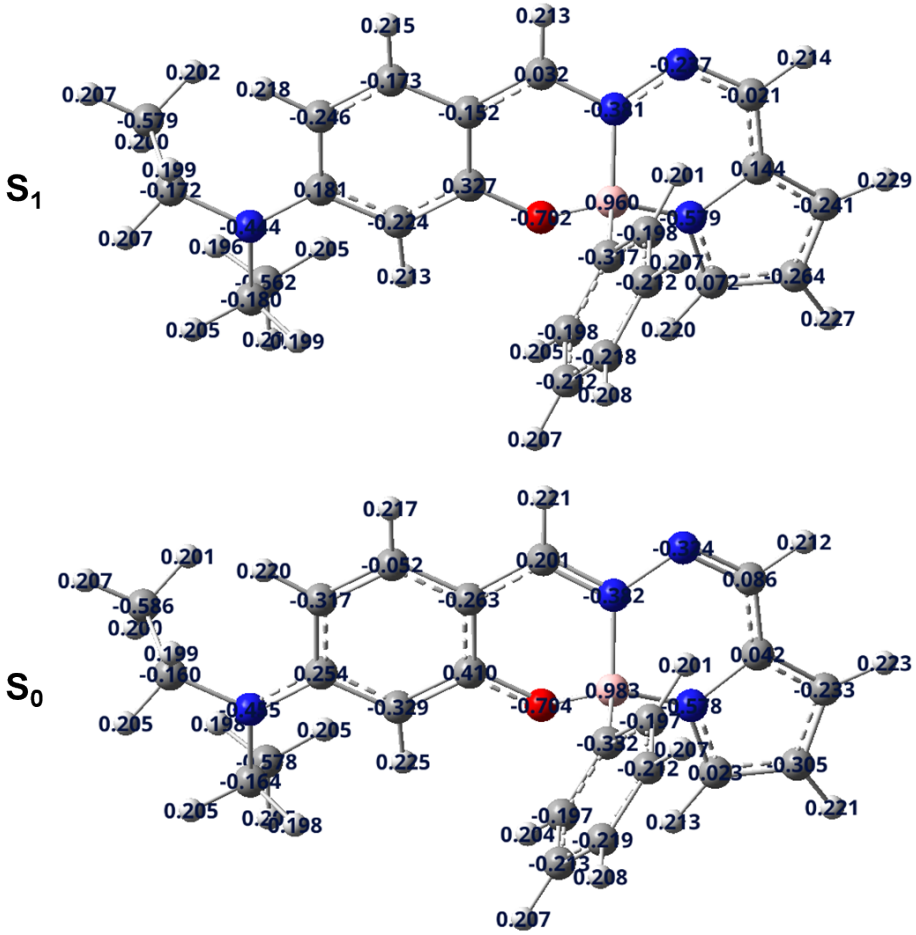


Figure S 53. Atomic charges calculated based on the natural population analysis for ground state and excited state geometries and electron densities for **1a**.

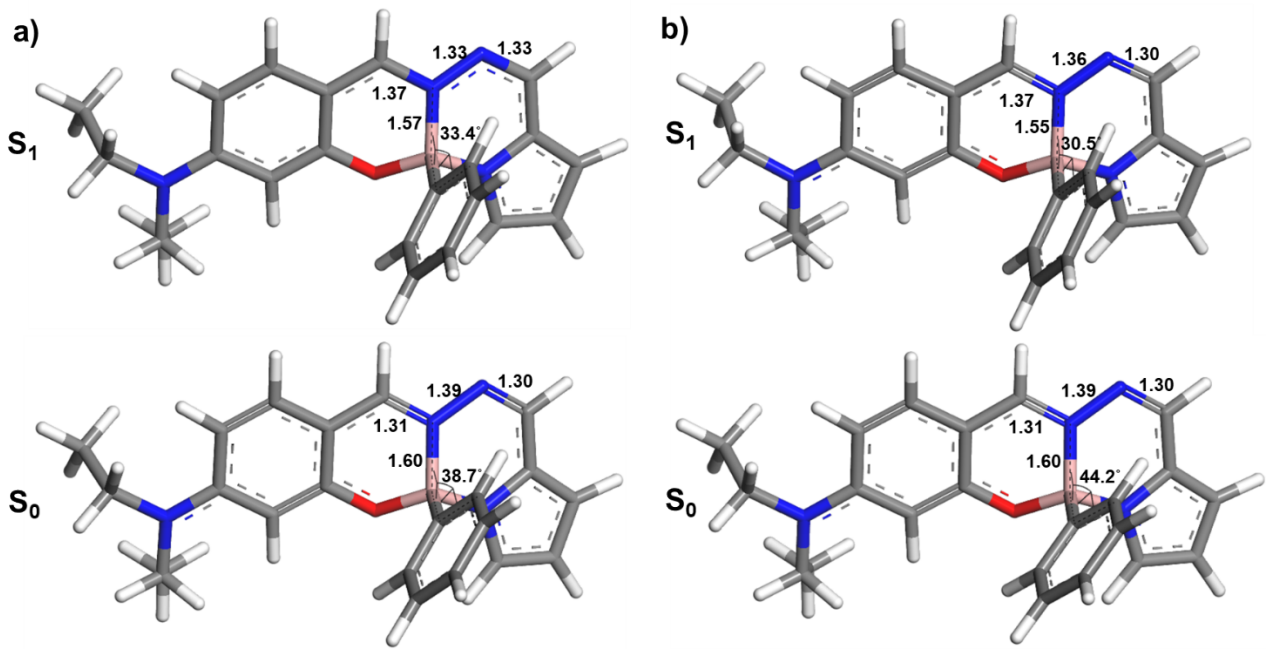
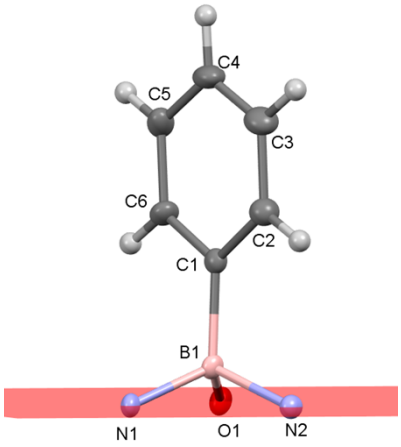


Figure S 54. Dihedral angles for B-Ph group and bond distances for the ground state and first excited of **1a** in a) DMSO and b) without solvent.

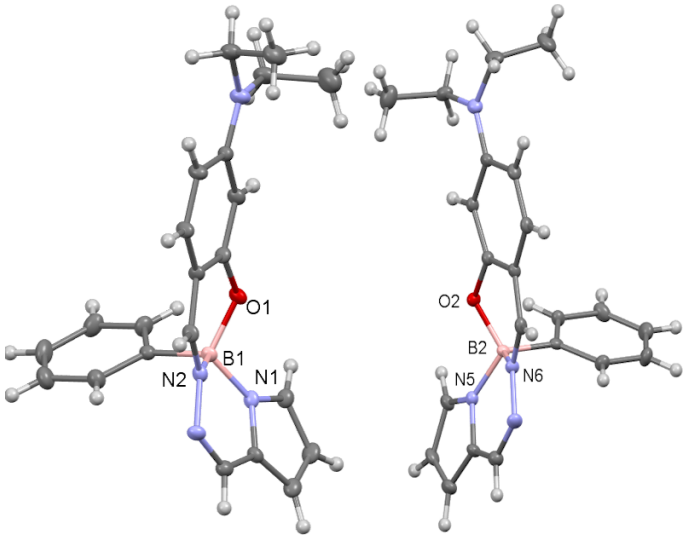
8. X-ray Diffraction Data

For the crystal structure determination, single-crystal of the molecule **1a** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). Graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and oscillation scans technique with Δw = 5º for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2>2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using CrystalClear (Rigaku/MSC Inc., 2005) software.[vi] The structures were solved by direct methods using SHELXS-2013,[vii] which allowed location of most of the heaviest atoms, with the remaining non-hydrogen atoms being located from difference Fourier maps calculated from successive full-matrix least squares refinement cycles on F^2 using SHELXL-2013.[iv] All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restrains. The final difference Fourier maps showed no peaks of chemical significance. Crystal data for **1a**: $C_{22}H_{23}ON_4B$, crystal system, space group: triclinic, *P*-1; (no:2); unit cell dimensions: a =11.2219(4), b=13.1963(6), c=15.947(2) Å, α= 72.800(5) *β*=70.920(4), γ=65.017(5)º; volume; 1988.4(5) $Å^3$; calculated density: 1.237 g/cm^3; absorption coefficient: 0.077 mm^{-1}; *F*(000): 784; *θ*-range for data collection 2.4-28.6º; refinement method: full matrix least-square on F^2; data/parameters: 5163/506; goodness-of-fit on

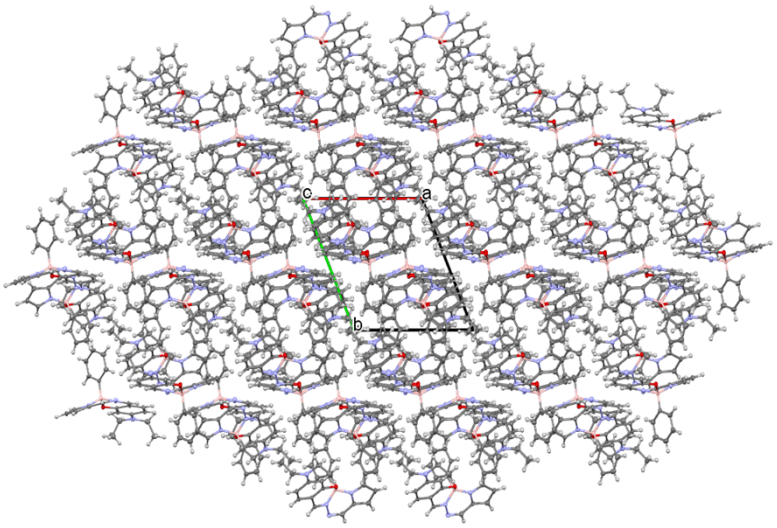
F^2: 1.015; Data completeness; 0.99, final R-indices [I>2σ(I)]: R_1 = 0.089, wR_2 = 0.183; largest diff. peak and hole: 0.793 and -0.734 eÅ^{-3}.
CCDC-2344453 (**1a**) number contains the supplementary crystallographic data for the structures. These data are provided free of charge via the joint CCDC/FIZ Karlsruhe deposition service www.ccdc.cam.ac.uk/structures



(a)



(b)



(c)

Figure S 55. (a) Boron coordination geometry with the O1/N1/N2 plane. (b) Depicting the mirror image of the enantiomers. (c) Stacking motif of the molecules viewed down along the *c*-axis.

9. Optimized coordinates for the ground state geometries

Gaussian16 Rev C.01[viii]
Method: B3LYP/6-311+g(d)
Solvent: DMSO, Solvation Method: IEFPCM
Dispersion correction: Grimme D3 [ix]

1a

C	3.07580000	0.15110000	1.62240000
C	3.17470000	0.05350000	0.19490000
C	1.99060000	-0.24560000	-0.52630000
C	0.77480000	-0.39500000	0.11670000
C	0.68440000	-0.29450000	1.53820000
C	1.87320000	-0.02660000	2.25630000
C	-0.53100000	-0.61600000	2.18030000
N	-1.64150000	-0.77210000	1.49770000
B	-1.63010000	-0.32430000	-0.03510000
O	-0.31580000	-0.70660000	-0.59880000
N	-2.74810000	-1.23170000	2.20490000
C	-3.73240000	-1.64720000	1.46330000
C	-3.76990000	-1.68960000	0.03860000
N	-2.73040000	-1.15980000	-0.70240000
H	3.95120000	0.34840000	2.22280000
N	4.36190000	0.25510000	-0.44490000
H	1.98980000	-0.35370000	-1.60090000
H	1.82900000	0.03430000	3.33940000
H	-0.57580000	-0.78340000	3.25270000
H	-4.59560000	-2.01180000	2.01170000
C	-3.01780000	-1.32550000	-2.01840000
C	-4.23900000	-1.98750000	-2.14520000
C	-4.72260000	-2.21340000	-0.84170000
H	-2.34610000	-0.96070000	-2.78130000
H	-4.71220000	-2.26980000	-3.07460000

H	-5.64000000	-2.70870000	-0.55600000
C	-1.89510000	1.26770000	-0.15330000
C	-1.24240000	2.03100000	-1.13320000
C	-1.49380000	3.39630000	-1.28540000
C	-2.41210000	4.03420000	-0.45050000
C	-3.07180000	3.29620000	0.53450000
C	-2.81250000	1.93230000	0.67640000
H	-0.51970000	1.54930000	-1.78540000
H	-0.97150000	3.96280000	-2.05110000
H	-2.60940000	5.09580000	-0.56300000
H	-3.78480000	3.78480000	1.19230000
H	-3.33260000	1.37980000	1.45470000
C	5.59430000	0.55300000	0.29830000
C	6.28980000	-0.68230000	0.87750000
C	4.48580000	0.05650000	-1.89570000
C	4.56930000	-1.41260000	-2.32100000
H	5.37090000	1.27400000	1.08680000
H	6.26700000	1.06650000	-0.38970000
H	7.16710000	-0.37940000	1.45580000
H	6.62390000	-1.35520000	0.08540000
H	5.62460000	-1.24250000	1.53830000
H	5.38490000	0.58350000	-2.21590000
H	3.65320000	0.55550000	-2.39760000
H	4.60700000	-1.48260000	-3.41150000
H	3.70350000	-1.98110000	-1.97530000
H	5.46660000	-1.88770000	-1.92000000

1b

C	3.47138400	0.28208200	1.62254800
C	3.51715600	-0.03393700	0.22516500
C	2.29163000	-0.34121900	-0.41776100
C	1.08844500	-0.29509900	0.26598500
C	1.05154500	0.02252900	1.65517500
C	2.27844700	0.29832100	2.30028600
C	-0.16729900	-0.10216200	2.36040100
N	-1.30644000	-0.27261500	1.73356800
B	-1.31831500	-0.06664800	0.14409200
O	-0.04432700	-0.61581500	-0.37495500
N	-2.41818800	-0.53367000	2.52825400
C	-3.45214800	-0.99060500	1.87631100
C	-3.54598800	-1.24170400	0.48395600
N	-2.49439100	-0.91046000	-0.36349700
H	4.37761400	0.49667400	2.16889900
N	4.69653800	-0.02355400	-0.46275500
H	2.24730300	-0.60703900	-1.46377600
H	2.27400100	0.52258200	3.36259500
H	-0.19117000	-0.10446000	3.44660700
H	-4.31661600	-1.20116600	2.49830200
C	-2.85737900	-1.21551300	-1.63855100
C	-4.13816400	-1.77651200	-1.61318900
C	-4.58827000	-1.79250300	-0.27901900
H	-4.68055400	-2.13103500	-2.47949400
C	-1.49313200	1.50500200	-0.20336300
C	-0.64567800	2.16131800	-1.10796300
C	-0.82352500	3.50852200	-1.43392600
C	-1.86369700	4.23539000	-0.85551700
C	-2.72182200	3.60396700	0.04854300
C	-2.53427500	2.25871600	0.36497400
H	0.16858100	1.61068900	-1.56856300
H	-0.15035200	3.98973000	-2.13763600
H	-2.00574100	5.28252100	-1.10472000
H	-3.53497900	4.16133000	0.50451900
H	-3.21384500	1.78817100	1.07063600
C	5.97204400	0.26637300	0.20592100
C	6.57319300	-0.92717100	0.95411700
C	4.75623800	-0.43417100	-1.87180000

C	4.72362800	-1.95074300	-2.08490000
H	5.83847300	1.11465300	0.88035600
H	6.66674700	0.60694400	-0.56291000
H	7.49127100	-0.62368600	1.46497300
H	6.82164900	-1.73898000	0.26760000
H	5.88172200	-1.31896100	1.70331400
H	5.67739100	-0.02426000	-2.28716700
H	3.94261500	0.04770000	-2.41942500
H	4.71508300	-2.17663900	-3.15482200
H	3.83466700	-2.39986900	-1.63713300
H	5.60106100	-2.42888900	-1.64524200
C	-5.89137000	-2.33388500	0.22604400
H	-6.67612300	-2.22387900	-0.52632200
H	-5.81868500	-3.40108800	0.46271700
H	-6.22651600	-1.82445500	1.13275100
C	-1.97997400	-0.93846500	-2.81426200
H	-1.74203600	0.12742300	-2.88761800
H	-1.02782800	-1.46900800	-2.73694100
H	-2.47612000	-1.24434700	-3.73634700

1c

C	-4.00196300	0.79086500	-1.21768600
C	-3.87576300	-0.16574900	-0.15793900
C	-2.56740300	-0.56935200	0.20836200
C	-1.44885700	-0.02854500	-0.40358700
C	-1.58323700	0.92285400	-1.45628500
C	-2.88983400	1.30072400	-1.83956100
C	-0.43304600	1.32712300	-2.17270900
N	0.77369800	1.03627600	-1.75094600
B	0.92363300	0.44556200	-0.26823500
O	-0.23131700	-0.45460800	-0.04046000
N	1.82286400	1.35013200	-2.60863100
C	2.95825500	0.78214400	-2.30252100
C	3.21445200	-0.09675900	-1.22073700
N	2.22286400	-0.36706300	-0.28692800
H	-4.97545600	1.11160900	-1.55753100
N	-4.97581100	-0.65843700	0.48431200
H	-2.39244700	-1.29795900	0.98643200
H	-3.01392300	2.00858900	-2.65350600
H	-0.51654300	1.85346500	-3.11950200
H	3.77272300	1.02440700	-2.97776000
C	2.74229700	-1.19263300	0.66364600
C	4.07408400	-1.48936000	0.33477300
C	4.37814400	-0.79349400	-0.85673900
C	0.97138900	1.66145200	0.80078700
C	0.12596300	1.70217400	1.91920900
C	0.19618700	2.73831700	2.85433200
C	1.12320300	3.76691800	2.68868600
C	1.97786000	3.74837200	1.58332000
C	1.89857100	2.70811700	0.65795600
H	-0.60032800	0.90891600	2.06607600
H	-0.47247500	2.74253700	3.71040200
H	1.18118900	4.57462400	3.41190200
H	2.70432200	4.54408700	1.44579500
H	2.57410900	2.71310300	-0.19339100
C	-6.33379800	-0.24705400	0.10530400
C	-6.90060700	-0.99500400	-1.10491600
C	-4.85273800	-1.71951700	1.49249400
C	-4.62300600	-3.11685900	0.90810700
H	-6.34509200	0.83058900	-0.06929000
H	-6.97356400	-0.41196400	0.97341300
H	-7.88942800	-0.60220100	-1.35772500
H	-7.00480700	-2.06164900	-0.89619200
H	-6.25699900	-0.88381300	-1.98041000
H	-5.77209200	-1.71379800	2.07868700

H	-4.05277800	-1.45970000	2.19049400
H	-4.49091200	-3.84143000	1.71643600
H	-3.73187600	-3.14752500	0.27783600
H	-5.47454900	-3.43549300	0.30376100
C	5.68442300	-0.82112200	-1.59028900
H	6.51298800	-0.53004600	-0.93679100
H	5.91429500	-1.82508600	-1.96213000
H	5.69134000	-0.14604100	-2.44791900
C	1.94055000	-1.65137100	1.83720800
H	1.50879200	-0.80399900	2.37790600
H	1.10590700	-2.28545400	1.52620200
H	2.56007300	-2.22055300	2.53078700
C	4.98964100	-2.42323500	1.07524100
H	6.02834900	-2.11406700	0.91823000
H	4.81658200	-2.34578800	2.15388600
C	4.82913600	-3.89053900	0.64252600
H	5.51676000	-4.54385400	1.18857700
H	3.80995800	-4.24199300	0.82813800
H	5.02953200	-4.00763400	-0.42650300

1d

C	-3.21617700	-0.33046800	-1.65919100
C	-3.37950800	-0.07607500	-0.25773900
C	-2.21900500	-0.11795100	0.55622000
C	-0.96737200	-0.35135200	0.01387000
C	-0.81312900	-0.60068700	-1.38244700
C	-1.97631100	-0.58914700	-2.18578300
C	0.44890300	-0.99469600	-1.88141300
N	1.52923900	-0.91286100	-1.14245600
B	1.42626200	-0.11500700	0.23285000
O	0.10073900	-0.40972600	0.82276800
N	2.69317000	-1.44786300	-1.68390800
C	3.67479700	-1.63827200	-0.84688800
C	3.62026800	-1.35387500	0.56133900
N	2.52077000	-0.72363500	1.11415400
H	-4.06940000	-0.33822700	-2.32079600
N	-4.60497100	0.21055800	0.26938800
H	-2.26543700	0.04316600	1.62322400
H	-1.88246800	-0.79628400	-3.24737500
H	0.55579400	-1.41288200	-2.87838500
C	2.73516800	-0.57317600	2.44615400
C	3.97007000	-1.12606100	2.77896600
C	4.53689200	-1.61558600	1.58476700
H	2.00448900	-0.08077400	3.07060100
H	4.39964800	-1.16869500	3.76956600
H	5.48853400	-2.11430300	1.47151900
C	1.63659300	1.46945200	-0.02344100
C	0.83604000	2.42101800	0.62578900
C	1.03705500	3.79192300	0.44699400
C	2.05307000	4.24449300	-0.39507000
C	2.86221900	3.31612800	-1.05430700
C	2.65207600	1.94967900	-0.86706400
H	0.03848100	2.08419700	1.28133200
H	0.39991600	4.50569400	0.96130500
H	2.21222500	5.30877100	-0.53905100
H	3.65393900	3.65860500	-1.71435400
H	3.29083600	1.24609600	-1.39466000
C	-5.81425900	0.22848200	-0.56510200
C	-6.40672400	-1.15694000	-0.83879200
C	-4.78669300	0.38461000	1.71690200
C	-4.83073600	-0.92804200	2.50518500
H	-5.59551300	0.74507100	-1.50176600
H	-6.54940100	0.84842000	-0.05048800
H	-7.27168000	-1.06845100	-1.50203600
H	-6.73778000	-1.63405200	0.08576300

H	-5.67872200	-1.81610100	-1.31680100
H	-5.71952100	0.93082300	1.85982500
H	-3.99807600	1.03657800	2.10043200
H	-4.91303700	-0.71726000	3.57500900
H	-3.92870500	-1.52252500	2.34595400
H	-5.69030700	-1.53419800	2.21270600
C	4.93907500	-2.21286800	-1.42110800
H	5.77439300	-1.52033900	-1.28433100
H	5.20637400	-3.14491400	-0.91574000
H	4.81686800	-2.41249600	-2.48513600

1e

C	4.56518500	-0.74099800	0.20310600
C	4.27344800	-0.57708200	-1.16093800
C	2.96311900	-0.56809600	-1.62260400
C	1.90613500	-0.70025500	-0.71689400
C	2.19015600	-0.88964400	0.66214800
C	3.52887800	-0.91134000	1.10362300
C	1.10965900	-1.19957600	1.54819700
N	-0.12920900	-1.05941300	1.17582800
B	-0.41605900	-0.29590700	-0.21369700
O	0.64260400	-0.70641500	-1.15712300
N	-1.09990500	-1.51735300	2.06392000
C	-2.28657400	-1.65244400	1.54263300
C	-2.66831400	-1.39497100	0.19864000
N	-1.76426900	-0.84629000	-0.69258700
H	5.59385500	-0.74611700	0.54380300
H	2.73628100	-0.44233200	-2.67504800
H	3.73442400	-1.06653100	2.15783300
H	1.29504500	-1.60994300	2.53651100
H	-3.04279700	-2.01901200	2.23004900
C	-2.38495000	-0.69690300	-1.88814200
C	-3.69492600	-1.17097300	-1.79368600
C	-3.88037200	-1.60702300	-0.46995700
H	-1.86775300	-0.25959000	-2.72927200
H	-4.41789500	-1.19416800	-2.59601600
H	-4.77085300	-2.04043600	-0.03726300
C	-0.43652200	1.29913100	0.03517500
C	0.15852400	2.17642900	-0.88375700
C	0.10858400	3.56130900	-0.70972800
C	-0.54339500	4.10238000	0.39847300
C	-1.14182900	3.24869600	1.32773200
C	-1.08633900	1.86706600	1.14330800
H	0.67228200	1.77049100	-1.75003000
H	0.58010700	4.21676500	-1.43606400
H	-0.58314200	5.17807000	0.53931500
H	-1.64891900	3.66053500	2.19528900
H	-1.55500800	1.22331900	1.88290200
H	5.08471200	-0.45305600	-1.87063700

1f

C	-3.30720700	0.32205200	-1.63273100
C	-3.41881100	0.27632400	-0.20373700
C	-2.31433200	-0.23464700	0.52468400
C	-1.15279500	-0.63200500	-0.11355900
C	-1.04867900	-0.58035600	-1.53661600
C	-2.16435900	-0.10071300	-2.26134100
C	0.08072700	-1.14251500	-2.17093400
N	1.14222300	-1.49505900	-1.48414400
B	1.22117700	-1.02195600	0.04111700
O	-0.14193300	-1.13531500	0.60968700
N	2.14010500	-2.16870500	-2.18143800
C	3.02764900	-2.75187900	-1.43046400
C	3.05692500	-2.77736000	-0.00521600
N	2.13849400	-2.04674400	0.72459200
H	-4.12837600	0.67525100	-2.23818400

N	-4.54091400	0.72229800	0.43038200
H	-2.33169300	-0.31896300	1.60134800
H	-2.11232100	-0.07212200	-3.34533200
H	0.08983600	-1.33573700	-3.24002900
H	3.80542900	-3.28335400	-1.97047800
C	2.38897200	-2.24446500	2.04343500
C	3.46105600	-3.12615700	2.18383800
C	3.89233500	-3.46031200	0.88539100
H	1.79995200	-1.74584600	2.79893900
H	3.87137800	-3.47966300	3.11882400
H	4.69762000	-4.12652400	0.60964000
C	1.78298500	0.48924000	0.12597600
C	1.28057600	1.39715400	1.07383100
C	1.78101200	2.68869000	1.19690700
C	2.81667300	3.12148100	0.36027500
C	3.33771000	2.24462500	-0.59618100
C	2.81621200	0.95117200	-0.69724900
H	0.47216200	1.08762500	1.72967800
H	1.37955200	3.37922200	1.93196800
H	4.13535300	2.55017500	-1.26176000
H	3.23659600	0.29442800	-1.45447600
C	-5.69557000	1.23457800	-0.32074000
C	-6.61569300	0.14346400	-0.87560100
C	-4.69306700	0.59164700	1.88607500
C	-5.07077900	-0.81774400	2.35202200
H	-5.34102000	1.88381900	-1.12371600
H	-6.25650200	1.88060100	0.35571300
H	-7.42214600	0.59687100	-1.45860300
H	-7.06773900	-0.43867400	-0.07015500
H	-6.07262600	-0.54554100	-1.52619800
H	-5.46355000	1.29940700	2.19294800
H	-3.77286300	0.92338200	2.37298900
H	-5.11318100	-0.84955200	3.44421500
H	-4.34119500	-1.55935900	2.02016300
H	-6.04923200	-1.11099600	1.96682100
O	3.24397500	4.40840200	0.55059700
C	4.29456100	4.90511500	-0.27692700
H	4.00556300	4.90034400	-1.33243800
H	4.46849400	5.93003900	0.04486800
H	5.21232900	4.32338000	-0.14718200

1g

C	-3.39360800	0.24960200	-1.64665100
C	-3.48183600	0.31869300	-0.21638900
C	-2.39417500	-0.19871000	0.53405300
C	-1.27162200	-0.71066900	-0.08889300
C	-1.18943500	-0.77361900	-1.51297000
C	-2.28941000	-0.28510700	-2.25715000
C	-0.10575600	-1.44462700	-2.11735300
N	0.94645200	-1.80774500	-1.41861500
B	1.07342300	-1.23792200	0.06084400
O	-0.27551500	-1.21518400	0.65778900
N	1.89390700	-2.58770900	-2.07490500
C	2.76673300	-3.15489100	-1.29519600
C	2.82683900	-3.06623000	0.12680000
N	1.95910100	-2.23446900	0.81042000
H	-4.20438900	0.60303800	-2.26576000
N	-4.56433600	0.87359800	0.39693900
H	-2.39639800	-0.20041100	1.61402500
H	-2.25564100	-0.34177600	-3.34061000
H	-0.12344500	-1.71524500	-3.16920600
H	3.50420100	-3.76770500	-1.80436100
C	2.22999800	-2.33312800	2.13795200
C	3.26196900	-3.25011500	2.33042300
C	3.64778300	-3.71177300	1.05628800

H	1.68044500	-1.74755500	2.85994700
H	3.67658500	-3.54457300	3.28365400
H	4.41446900	-4.43706200	0.82324800
C	1.73079200	0.24829600	0.02546500
C	1.30828800	1.23473800	0.93100200
C	1.88412900	2.49960000	0.95809500
C	2.90757400	2.78425200	0.05498900
C	3.35731300	1.83652400	-0.86485600
C	2.76287300	0.58091300	-0.86808800
H	0.50682300	1.01045000	1.62651300
H	1.55055600	3.25446600	1.65762400
H	4.15025900	2.08491700	-1.55756800
H	3.11044000	-0.15098400	-1.59011700
C	-5.70121500	1.39624000	-0.37497900
C	-6.69220000	0.32251700	-0.83278700
C	-4.69888600	0.85901500	1.86078300
C	-5.14403800	-0.48979100	2.43370100
H	-5.32392600	1.96175400	-1.22909700
H	-6.21110900	2.12270900	0.25869300
H	-7.48125100	0.77787300	-1.43756300
H	-7.16275200	-0.16981000	0.02046600
H	-6.20157800	-0.44410300	-1.43652100
H	-5.42499300	1.62856200	2.12354900
H	-3.75434800	1.17490100	2.31002700
H	-5.17140100	-0.43875100	3.52557400
H	-4.46040500	-1.29249700	2.14963100
H	-6.14245000	-0.75671900	2.08220300
N	3.52339700	4.11391600	0.06927800
O	4.42330200	4.35137500	-0.73563800
O	3.11607300	4.93938700	0.88587100

1h

C	-3.04361300	-0.63763800	-1.35419700
C	-3.16252400	0.00586100	-0.08208300
C	-1.98585600	0.11075100	0.69579000
C	-0.76696100	-0.36094700	0.23674800
C	-0.65281000	-1.03549200	-1.01817600
C	-1.84026400	-1.13818300	-1.78408100
C	0.57893100	-1.67547000	-1.37709800
N	1.66803500	-1.37691700	-0.68149300
B	1.60470800	-0.14567500	0.32539600
O	0.30832000	-0.21925300	1.02524600
N	2.81953700	-2.09731300	-0.97999400
C	3.80062300	-1.96300700	-0.13713800
C	3.80688900	-1.18005000	1.05218400
N	2.72431900	-0.37810500	1.34937300
H	-3.90362700	-0.75264300	-1.99721500
N	-4.35264700	0.51878500	0.34755200
H	-1.98298500	0.58527900	1.66629300
H	-1.81449700	-1.61738400	-2.75446400
H	4.69163700	-2.53387700	-0.38185800
C	2.97406000	0.25859800	2.52138000
C	4.21835500	-0.14318900	3.00875600
C	4.75338900	-1.05163000	2.07459900
H	2.26265300	0.95847600	2.93396400
H	4.67252500	0.18660100	3.93209000
H	5.69980500	-1.57104400	2.12764200
C	1.78265600	1.24715200	-0.48202100
C	1.14948400	2.41632600	-0.03303500
C	1.32626200	3.64003100	-0.68159100
C	2.14956800	3.72142200	-1.80593800
C	2.78767700	2.57109000	-2.27350900
C	2.60209300	1.35329000	-1.61655500
H	0.49807000	2.36580200	0.83502100
H	0.82006400	4.52817900	-0.31425900

H	2.28887100	4.67008000	-2.31527100
H	3.42584600	2.62327700	-3.15093100
H	3.10177900	0.46873400	-2.00312400
C	-5.57728700	0.38543500	-0.45246400
C	-6.26171900	-0.97904400	-0.32826400
C	-4.48487800	1.10270500	1.68862600
C	-4.59158500	0.06953100	2.81446400
H	-5.34885800	0.60619100	-1.49727700
H	-6.26018400	1.17119100	-0.12697100
H	-7.13344400	-1.02117600	-0.98727200
H	-6.60229100	-1.15832200	0.69354200
H	-5.58657300	-1.79131000	-0.60642500
H	-5.37636600	1.73061400	1.67945500
H	-3.64595100	1.77960000	1.86829800
H	-4.63239900	0.57601600	3.78278400
H	-3.73317500	-0.60541500	2.82159500
H	-5.49499200	-0.53459200	2.71029400
C	0.67161300	-2.70349200	-2.46403700
H	1.45804800	-2.43559900	-3.17212100
H	0.95253100	-3.66933300	-2.03795700
H	-0.26591600	-2.82638400	-2.99700200

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