New Journal of Chemistry

Supplementary Information for

Luminescent Bi-Metallic Fluoroborates derivatives of bulky Salen ligands

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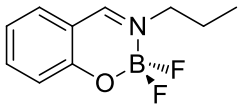
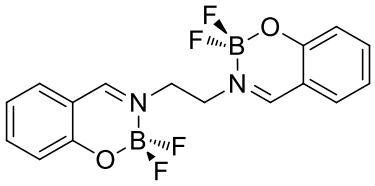
Synthesis and characterization

2,2-Difluoro-3-propyl-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide ***1***



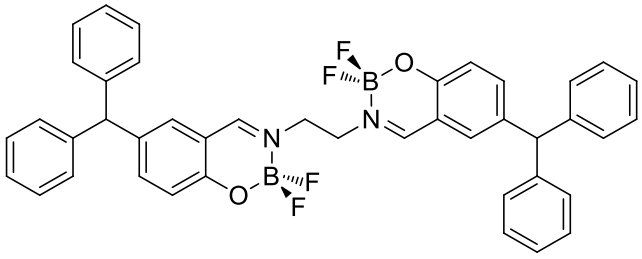
Schiff base ligand **5** (1 equiv., 1 mmol, 163 mg) was dissolved in dry 1,2-dichloroethane (2.5 mL) under nitrogen atmosphere. Dry Et_3N (10 equiv., 10 mmol, 1.22 mL) and BF_3-OEt_2 (10 equiv., 10 mmol, 1.40 mL) were successively added, and the resulting solution was stirred at 90ºC for one hour. At room temperature, water (5 mL) was added and the organic phase was extracted with dichloromethane (3 X 5 mL). The organic phases were combined, dried over sodium sulfate and concentrated under reduced pressure. Silica gel flash column chromatography of the residue (eluent: dichloromethane) gave the product as a white solid (126 mg, 60%). mp 109-111 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 8.22 (d, $^3J_{H\text{-}B}$ 3.6 Hz, 1H, C*H*N), 7.59 (dd, $^3J_{H\text{-}H}$ 7.2, $^3J_{H\text{-}H}$ 8.5 Hz, 1H, aromatic C*H*), 7.40 (d, $^3J_{H\text{-}H}$ 7.5 Hz, 1H, aromatic C*H*), 7.10 (dd, $^3J_{H\text{-}H}$ 8.5 Hz, 1H, aromatic C*H*), 6.98 (dd, $^3J_{H\text{-}H}$ 7.2, $^3J_{H\text{-}H}$ 7.5 Hz, 1H, aromatic C*H*), 3.75 (t, $^3J_{H\text{-}H}$ 6.8 Hz, 2H, N-CH_2), 2.00-1.88 (m, 2H, N-CH_2-CH_2), 1.02 (t, $^3J_{H\text{-}H}$ 7.4 Hz, 3H, CH_3).^{13}C NMR (75 MHz, $CDCl_3$, 25ºC): δ = 164.0 (C-O), 159.0 (*C*=N), 138.0 (*C*-H), 131.3 (*C*-H), 120.0 (*C*-H), 119.2 (*C*-H), 115.2 (*C*quat), 36.0 (*C*H_2), 23.2 (*C*H_2), 11.1 (*C*H_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ -161.48 (q, *J* = 15.5 Hz). ESI(+)-MS: 192.1 $[M\text{-}F]^+$, 234.1 $[M+Na]^+$.

3,3'-(Ethane-1,2-diyl)bis(2,2-difluoro-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide) ***2***



2,2'-{(1E,1'E)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)}bisphenol **6** (20 mg, 0.074 mmol) was dissolved in dry 1,2-dichloroethane (1.2 mL). *N*,*N*-Diisopropylethylamine (0.74 mmol; 129 μL) was added, and the resulting mixture stayed under magnetic stirring for 10 min at 80ºC after which boron trifluoride diethyl etherate (1.34 mmol; 165 μL) was added dropwise. The final mixture was stirred for 30 min. at 80ºC under nitrogen atmosphere and then cooled until room temperature. CH_2Cl_2 (4 mL) was added and the crude mixture was washed with water (3 x 2 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography [petroleum ether:EtOAc (7:3)] to afford the compound as a white solid (10 mg, 37%). mp 263-265 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ = 8.38 (s, 2H, C*H*N), 7.60 (t, $^3J_{H\text{-}H}$ 7.6 Hz, 2H, aromatic C*H*), 7.34 (d, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, aromatic C*H*), 7.09 (d, $^3J_{H\text{-}H}$ 7.6 Hz, 2H, aromatic C*H*), 6.94 (t, $^3J_{H\text{-}H}$ 7.6 Hz, 2H, aromatic C*H*), 4.37 (s, 4H, CH_2). ^{13}C NMR (75 MHz, DMSO, 25ºC): δ 168.5 (*C*=N), 157.8 (*C*-O), 151.3 (*C*quat), 138.4 (*C*-H), 132.6 (*C*-H), 120.1 (*C*-H), 118.1 (*C*-H), 52.2 (*C*-H_2). ^{19}F NMR (282 MHz, DMSO) δ -158.15 (q, *J* = 14.1 Hz). ESI(+)-MS: 387.1 $[M+Na]^+$.

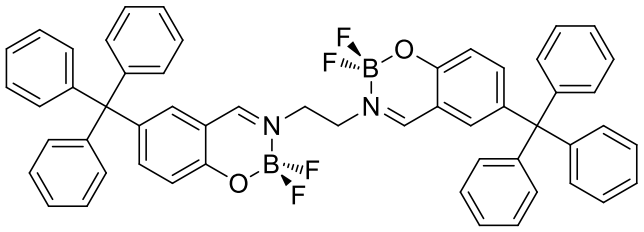
3,3'-(Ethane-1,2-diyl)bis(6-benzhydryl-2,2-difluoro-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide) ***3***



2,2'-{(1E,1'E)-[Ethane-1,2-diylbis(azanylylidene]bis(methanylylidene)}bis(4-benzylphenol) **7** (20 mg; 0.03 mmol) was dissolved in dry 1,2 dichloroethane (1.2 mL). *N*,*N*-diisopropylethylamine (0.3 mmol; 52 μL) was added, and the resulting mixture stayed under magnetic stirring for 10 min at 80 ºC after which boron trifluoride diethyl etherate (0.54 mmol; 67 μL) was added dropwise. The final mixture was stirred for 30 min. at 80 ºC under nitrogen atmosphere and then cooled until room temperature. CH_2Cl_2 (4 mL) was added and

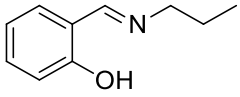
the crude mixture was washed with water (3 x 2 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography [petroleum ether:EtOAc (8:2)] to afford the product as a green pale solid (42 mg, quant.). mp 185-187 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 8.25 (s, 2H, C*H*N), 7.40 (dd, $^3J_{H\text{-}H}$ 8.7, $^4J_{H\text{-}H}$ 2.1 Hz, 2H, aromatic C*H*), 7.34-7.16 (m, 12H, aromatic C*H*), 7.12-6.90 (m, 12H, aromatic C*H*), 5.45 (s, 2H, C*H*), 4.29 (s, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5 (*C*=N), 158.0 (*C*-OH), 142.3 (2 X *C*-H), 140.5 (*C*-H), 136.4 (*C*-H), 132.0 (*C*-H), 129.2 (4 X *C*-H), 128.6 (4 X *C*-H), 126.8 (2 X *C*-H), 119.3 (*C*quat), 114.9 (*C*quat), 55.6 (*C*-H), 54.1 (*C*-H_2). ^{19}F NMR (282 MHz) δ -158.56 (bs). ESI(+)-MS: 677.3 $[M\text{-}F]^+$, 719.2 $[M+Na]^+$.

3,3'-(Ethane-1,2-diyl)bis(2,2-difluoro-6-trityl-2H-benzo[e][1,3,2]oxazaborinin-3-ium-2-uide) **4**



2,2'-{(1E,1'E)-(Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)}bis(4-tritylphenol) **8** (20 mg, 0.026 mmol) was dissolved in dry 1,2 dichloroethane (1.2 mL). N,N-diisopropylethylamine (0.26 mmol, 45 μL) was added, and the resulting mixture stayed under magnetic stirring for 10 min at 80 ºC after which boron trifluoride diethyl etherate (0.48 mmol, 59 μL) was added dropwise. The final mixture was stirred for 30 min at 80 ºC under nitrogen atmosphere and then cooled until room temperature. CH_2Cl_2 (4 mL) was added and the crude mixture was washed with water (3 x 2 mL). The organic layer was separated, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography [petroleum ether:EtOAc (8:2)] to afford the product as a white solid (21 mg, 95%). mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 8.23 (s, 2H, C*H*N), 7.40 (dd, $^3J_{H\text{-}H}$ 8.9, $^4J_{H\text{-}H}$ 2.2 Hz, 2H, aromatic C*H*), 7.33-7.15 (m, 20H, aromatic C*H*), 7.16-7.06 (m, 12H, aromatic C*H*), 6.97 (d, $^3J_{H\text{-}H}$ 8.9 Hz, 2H, aromatic C*H*), 4.29 (s, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25ºC): δ 167.5 (*C*=N), 157.9 (*C*-OH), 145.8 (3 X *C*quat), 143.5 (*C*-H), 139.4 (*C*-H), 132.3 (*C*-H), 130.8 (6 X *C*-H), 127.8 (6 X *C*-H), 126.4 (3 X *C*-H), 118.4 (*C*quat), 114.0 (*C*quat), 64.0 (*C*quat), 54.13 (*C*-H_2). ^{19}F NMR (282 MHz, $CDCl_3$) δ -158.10 (bs). ESI(+)-MS: 829.3 $[M\text{-}F]^+$, 871.3 $[M+Na]^+$.

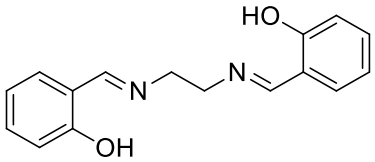
*(E)-2-[(Propylimino)methyl]phenol **5***



; Reference of the compound: Hiroaki Oie, Atsushi Sudo, Takeshi Endo, J. Polymer Sci. A: Polymer Chem., 2011, **49**, 3174-3183.

Salicylaldehyde (1 equiv., 2 mmol, 244 mg) and propylamine (1 equiv., 2 mmol, 118 mg) were dissolved in methanol (10 mL) and the resulting solution was refluxed for one hour, after which the solvent was removed under reduced pressure to yield the product **5** as a yellow oil (360 mg, quant.). It was used in the following step without purification.

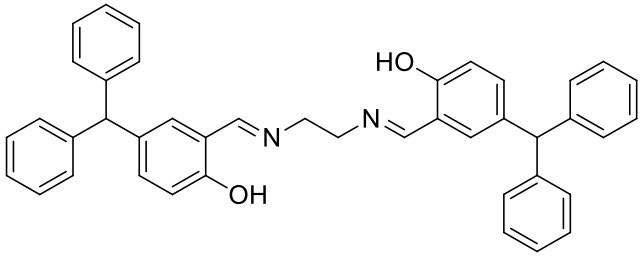
*2,2'-{(1E,1'E)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)}diphenol **6***



Reference of the compound: N. Bresciani Pahor, M. Calligaris, G. Nardin and L. Randaccio, *Acta Cryst.*, 1978, **B34**, 1360-1363.

Salicylaldehyde (2 equiv., 2 mmol, 244 mg) and ethylenediamine (1 equiv., 1 mmol, 60 mg) were dissolved in ethanol (10 mL) and the resulting solution was refluxed for one hour. After three days at room temperature, the yellow crystals that formed were collected by filtration, washed with petroleum ether (10 mL) and dried in air. The product was obtained as pale yellow crystals (260 mg, 97%). mp 105-107 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 ºC): δ = 13.23 (s, 2H, O*H*), 8.36 (s, 2H, C*H*N), 7.32-7.21 (m, 4H, aromatic C*H*), 6.94 (d, $^{3}J_{H\text{-}H}$ 7.5 Hz, 2H, aromatic C*H*), 6.85 (ddd, $^{3}J_{H\text{-}H}$ 0.9, $^{3}J_{H\text{-}H}$ 7.5, $^{3}J_{H\text{-}H}$ 7.5 Hz, 2H, aromatic C*H*), 3.95 (s, 4H, CH_2).

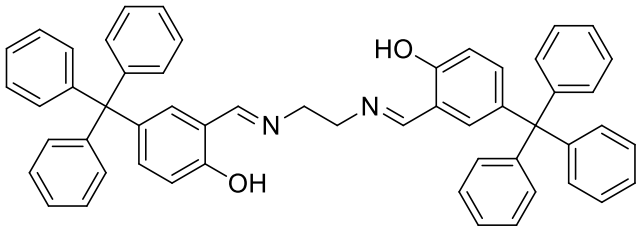
*2,2'-{(1E,1'E)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)}bis(4-benzhydrylphenol **7***



5-Benzhydryl-2-hydroxybenzaldehyde (2 equiv., 2 mmol, 576 mg) and ethylenediamine (1 equiv., 1 mmol, 60 mg) were dissolved in ethanol (10 mL) and the resulting solution was refluxed for two hour. After 12 h at room temperature, the yellow crystals that formed were collected by filtration, washed with ethanol (10 mL) and dried in air. The product was obtained as pale yellow crystals (485

mg, 81%). mp 225-227 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 13.11 (s, 2H, O*H*), 8.25 (s, 2H, C*H*N), 7.31-7.18 (m, 14H, aromatic C*H*), 7.11-7.05 (m, 8H, aromatic C*H*), 6.93 (d, $^{4}J_{H-H}$ 2.1 Hz, 2H, aromatic C*H*), 6.87 (d, $^{3}J_{H-H}$ 8.4 Hz, 2H, aromatic C*H*), 5.48 (s, 2H, C*H*), 3.86 (s, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25ºC): δ = 166.5 (*C*=N), 159.5 (*C*-OH), 143.8 (*C*-H), 134.1 (*C*-H), 133.5 (2 X *C*quat), 129.3 (4 X *C*-H), 128.3 (4 X *C*-H), 126.3 (2 X *C*-H), 118.2 (*C*quat), 116.9 (*C*quat), 59.8 (*C*-H), 55.8 (*C*-H_2). ESI(+)-MS: 601.3 $[M+H]^+$, 623.3 $[M+Na]^+$. Anal. Calcd for $C_{42}H_{36}N_2O_2$: C 83.97, H 6.04, N 4.66. Found: C 84.13, H 5.97, N 4.61%.

2,2'-{(1E,1'E)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)}bis(4-tritylphenol ***8***



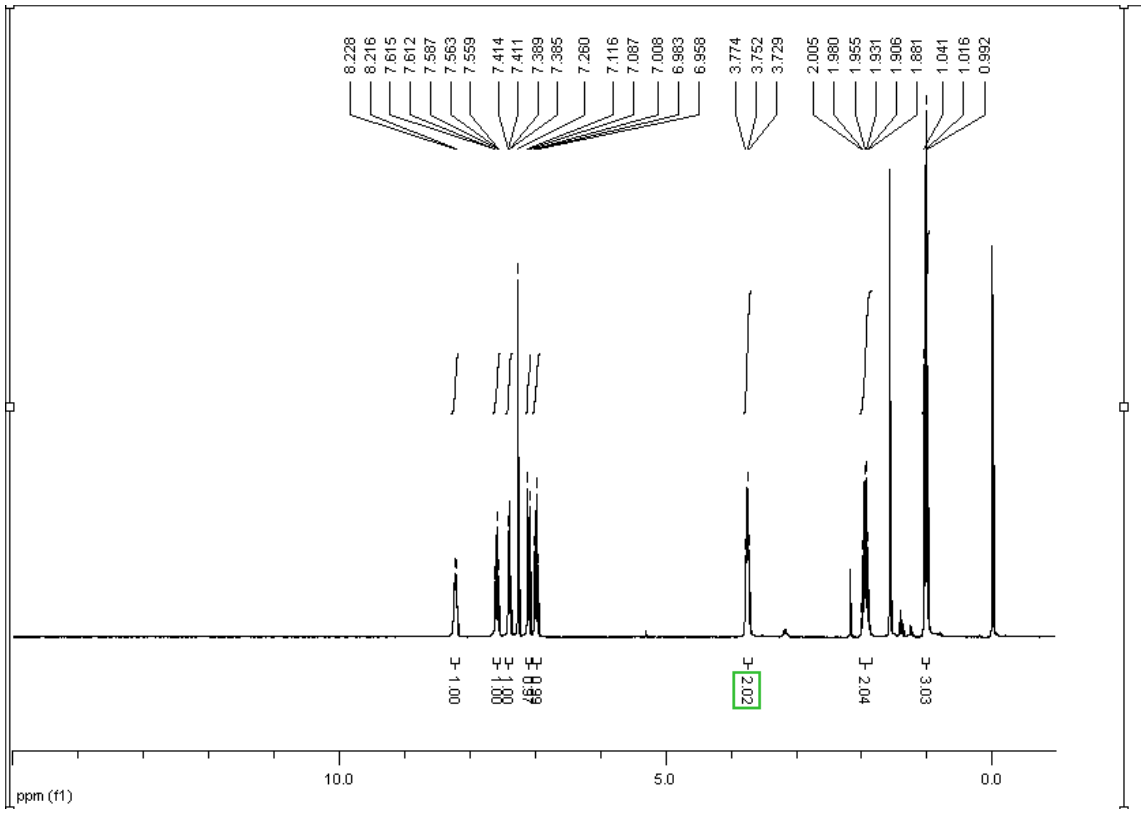
5-Trityl-2-hydroxybenzaldehyde (2 equiv., 0.25 mmol, 91 mg) and ethylenediamine (1 equiv., 0.12 mmol, 7.2 mg) were dissolved in ethanol (10 mL) and the resulting solution was refluxed for one hour. At room temperature, the yellow solid that formed was collected by filtration, washed with ethanol (10 mL) and dried in air. The product was obtained as a pale yellow solid (90 mg, quant.). mp 282-284 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 13.18 (s, 2H, O*H*), 8.21 (s, 2H, C*H*N), 7.27-7.09 (m, 34H, aromatic C*H*), 6.84 (d, $^{3}J_{H-H}$ 8.4 Hz, 2H, aromatic C*H*), 3.84 (s, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25ºC): δ = 166.7 (*CH*=N), 159.2 (*C*-OH), 146.6 (3 X *C*quat), 137.1 (*C*-H), 135.8 (*C*-H), 133.2 (*C*-H), 131.0 (6 X *C*-H), 127.5 (6 X *C*-H), 126.0 (3 X *C*-H), 117.4 (*C*quat), 116.1 (*C*quat), 64.1 (*C*quat), 59.7 (*C*-H_2).

ESI (+)-MS: 753.3 $[M+H]^+$. Anal. Calcd for $C_{54}H_{44}N_2O_2$ H_2O: C 84.13, H 6.01, N 3.63. Found: C 84.39, H 5.73, N 3.60%.

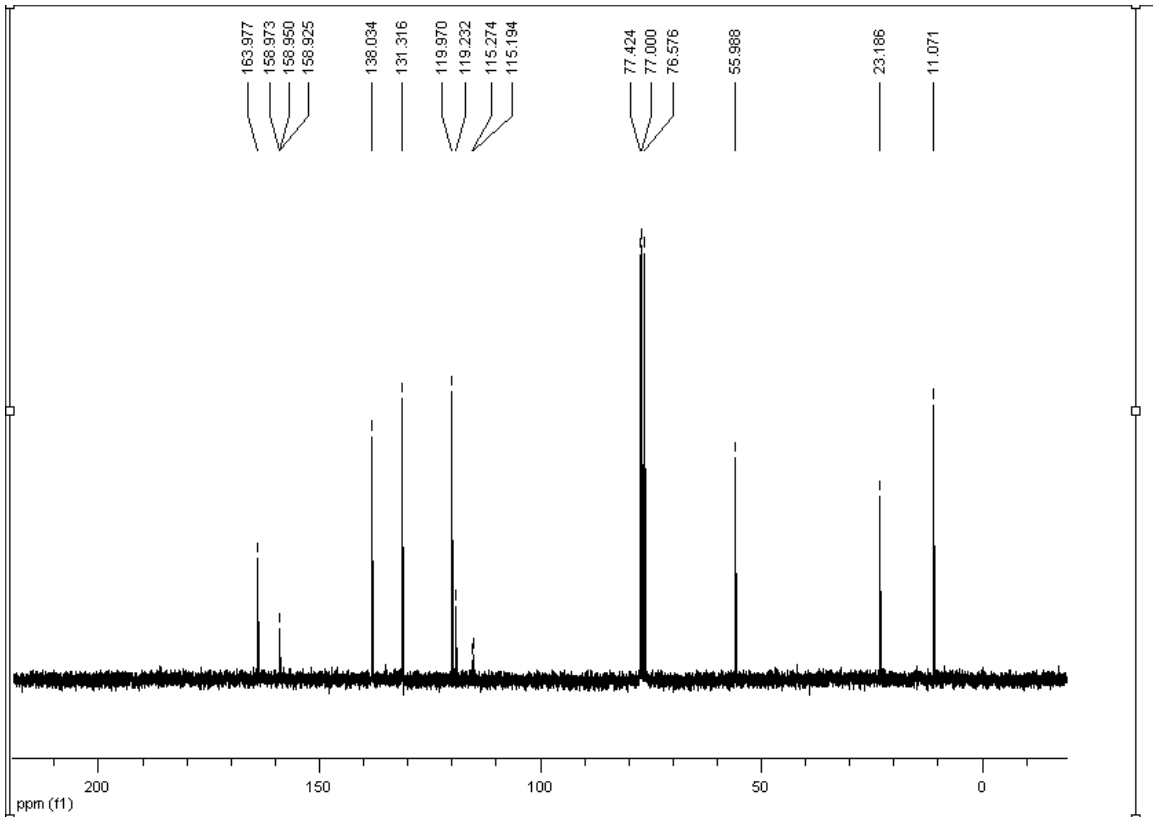
NMR spectra

2,2-Difluoro-3-propyl-2*H*-benzo[*e*][1,3,2]oxazaborinin-3-ium-2-uide 1

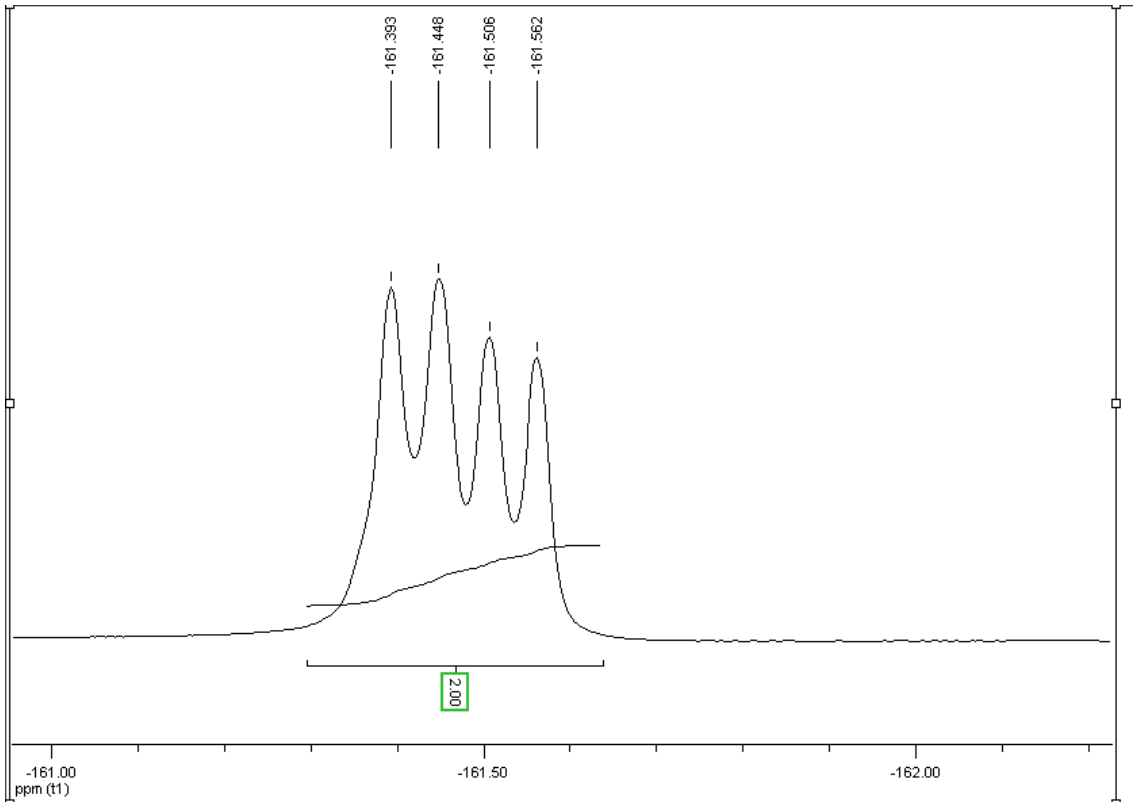
^{1}H NMR spectrum



^{13}C NMR spectrum

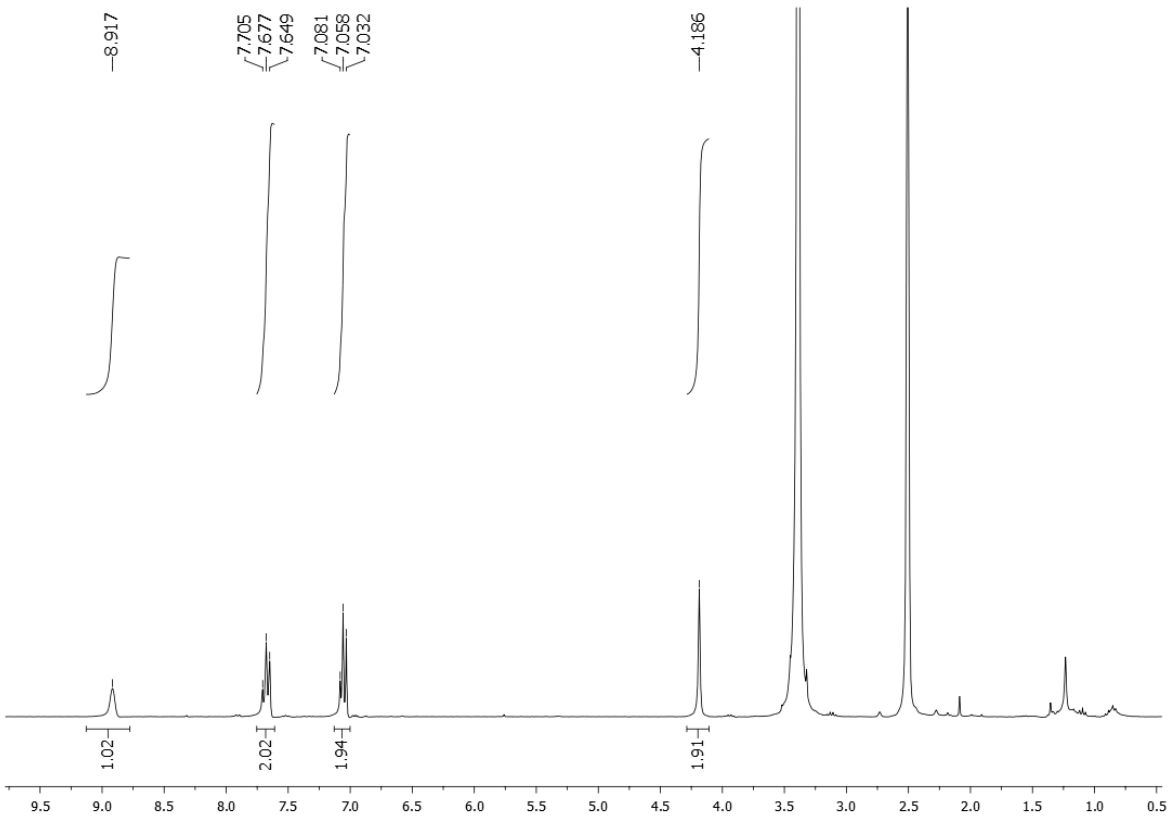


^{19}F NMR spectrum



3,3'-(Ethane-1,2-diyl)bis(2,2-difluoro-2*H*-benzo[*e*][1,3,2]oxazaborinin-3-ium-2-uide) 2

^{1}H NMR spectrum



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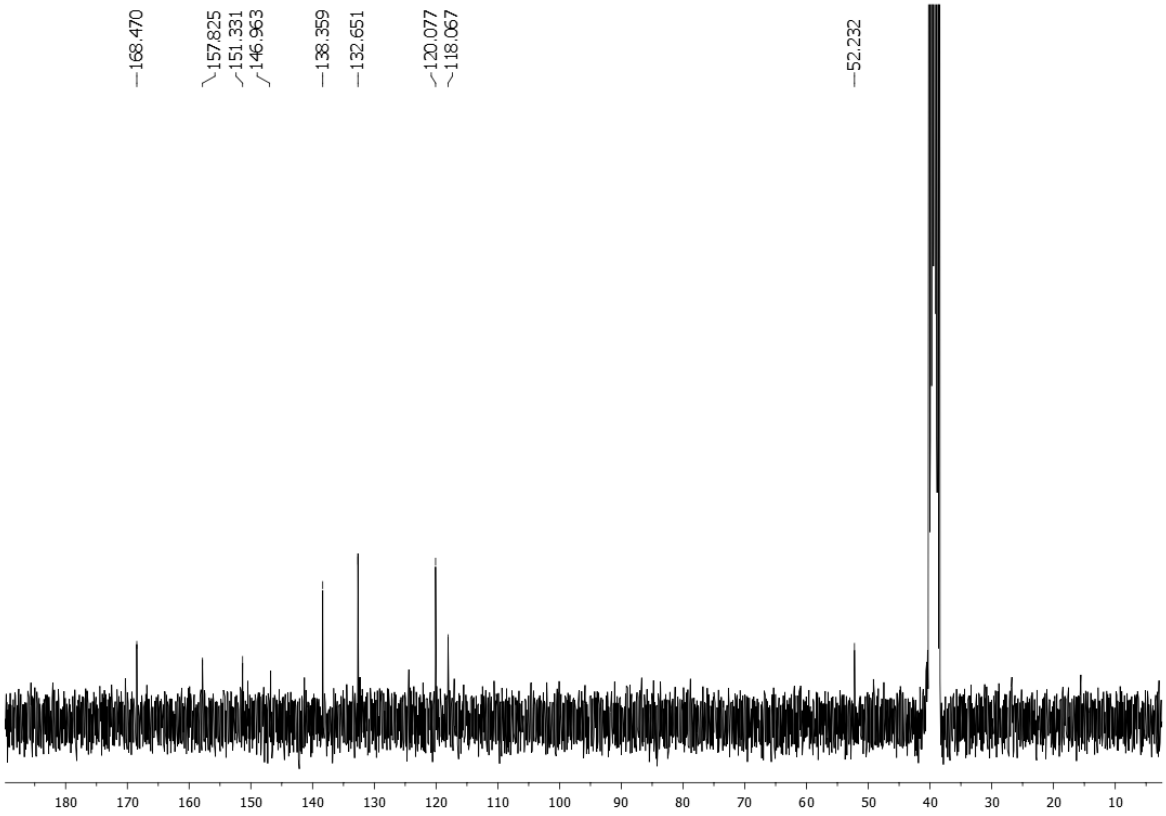

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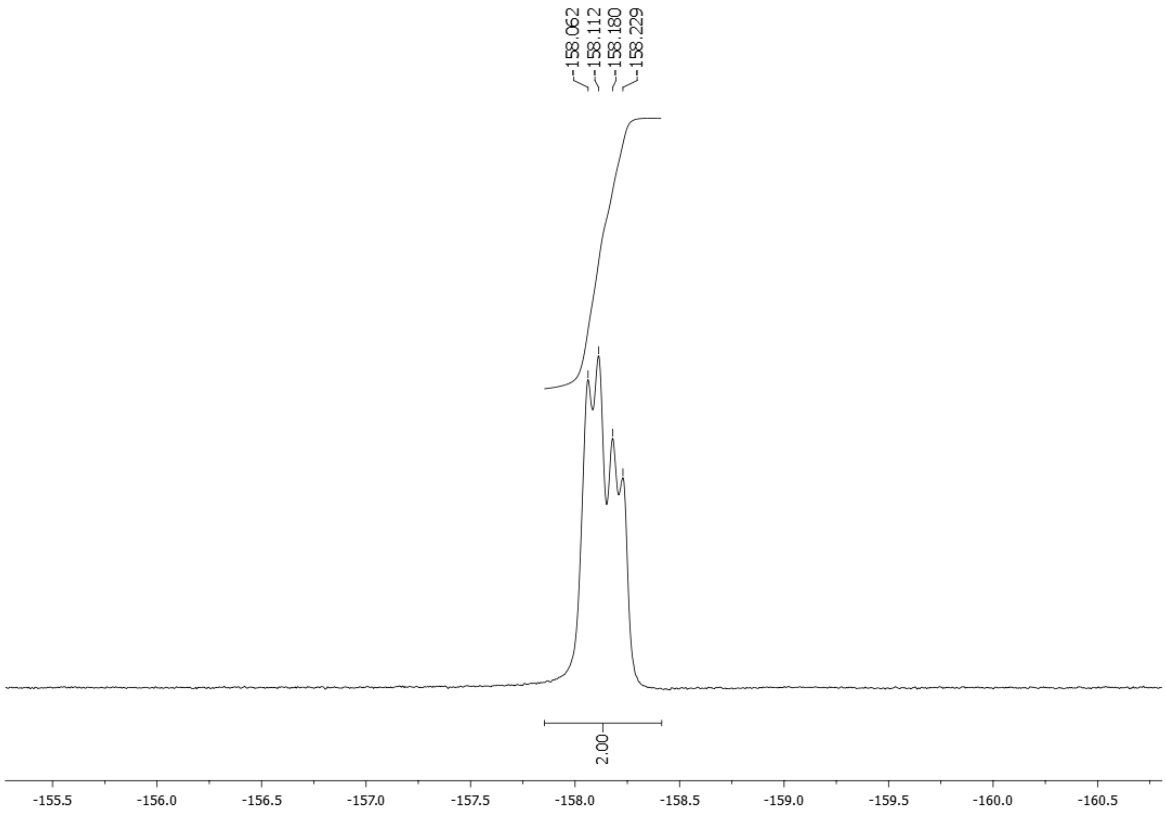
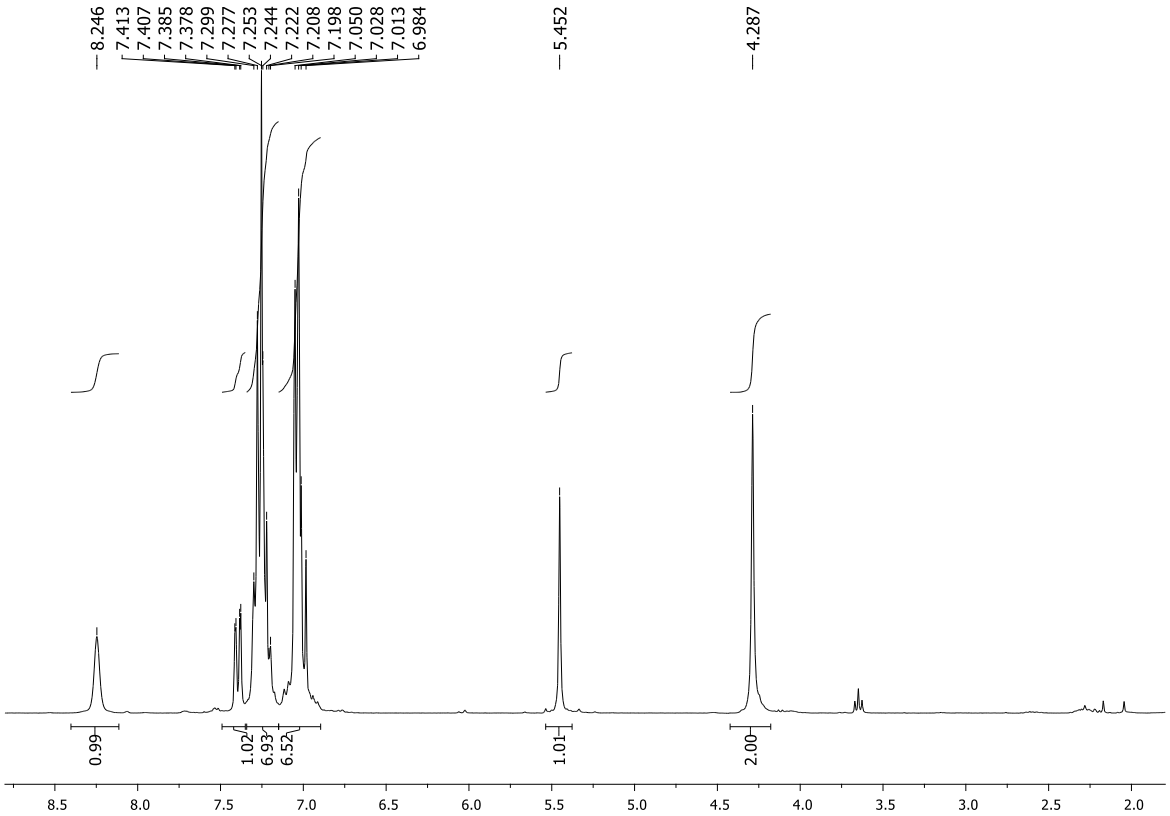
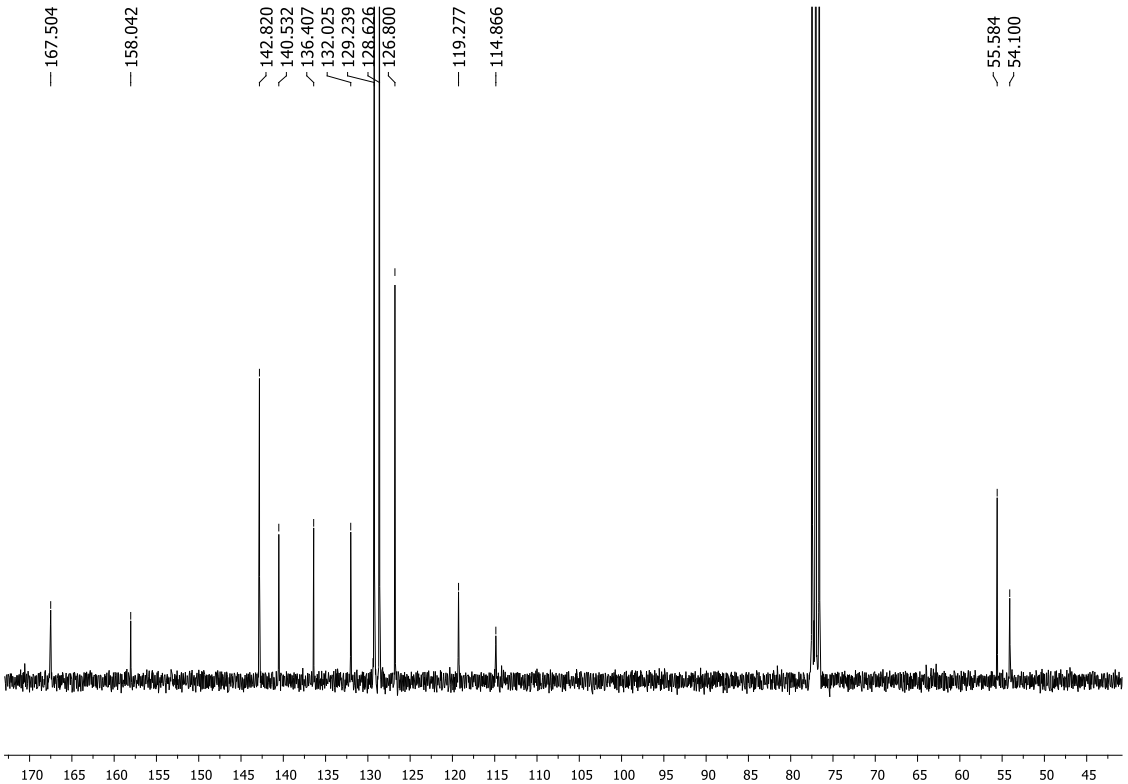


3,3'-(Ethane-1,2-diyl)bis(6-benzhydryl-2,2-difluoro-2*H*-benzo[*e*][1,3,2]oxazaborinin-3-ium-2-uide) 3

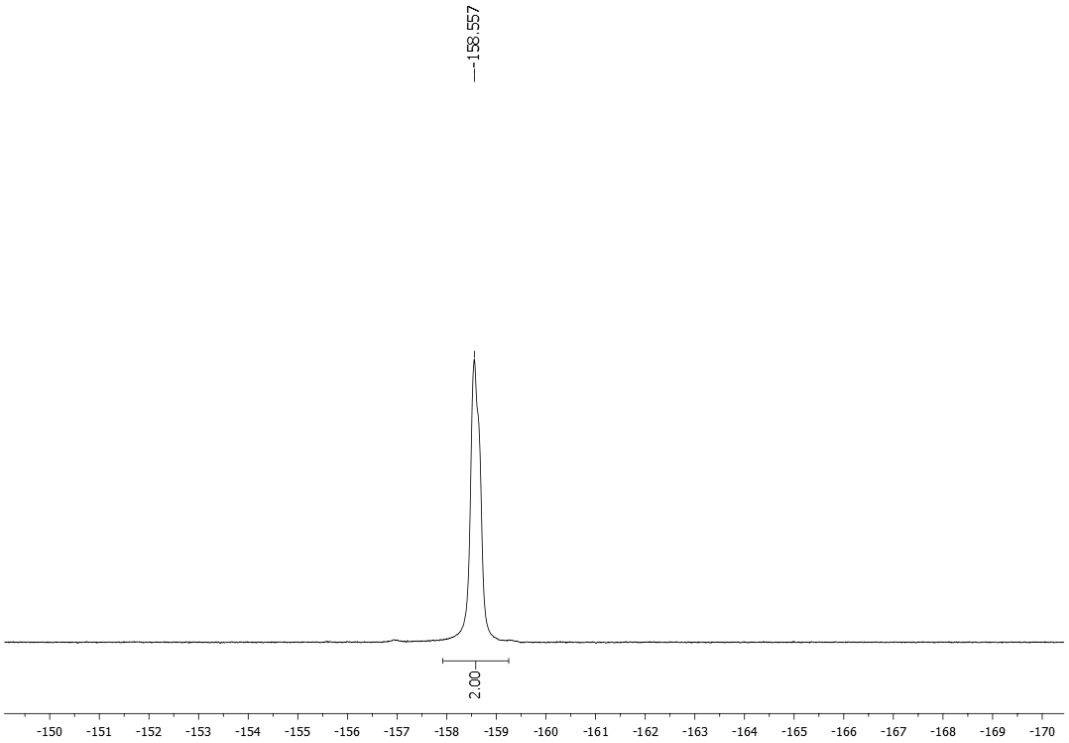
^{1}H NMR spectrum



^{13}C NMR spectrum

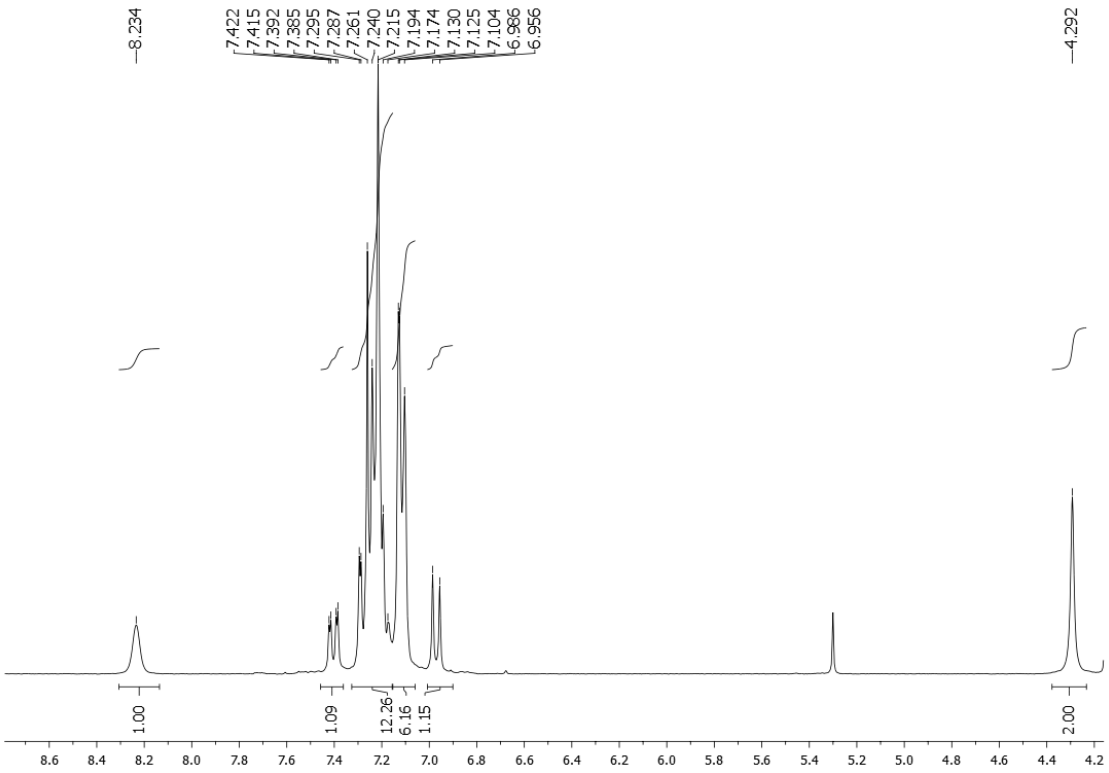


^{19}F NMR spectrum

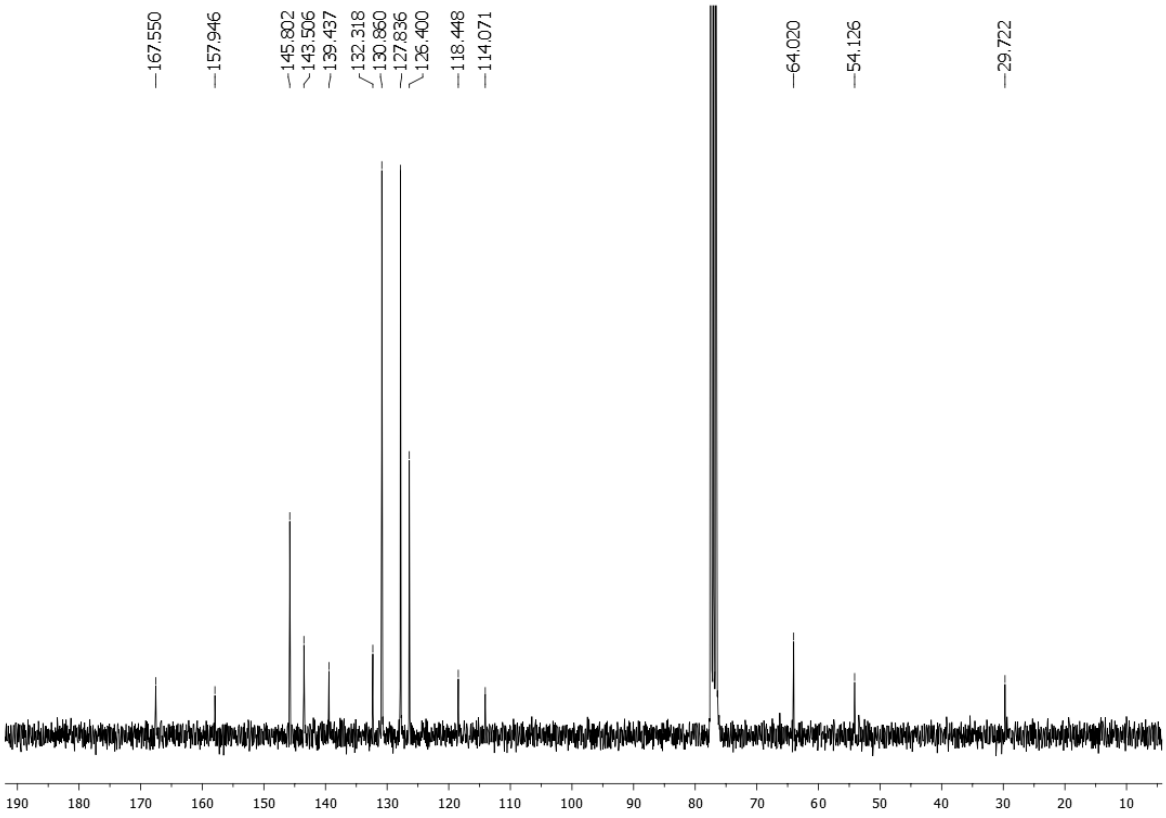


3,3'-(Ethane-1,2-diyl)bis(2,2-difluoro-6-trityl-2*H*-benzo[*e*][1,3,2]oxazaborinin-3-ium-2-uide) 4

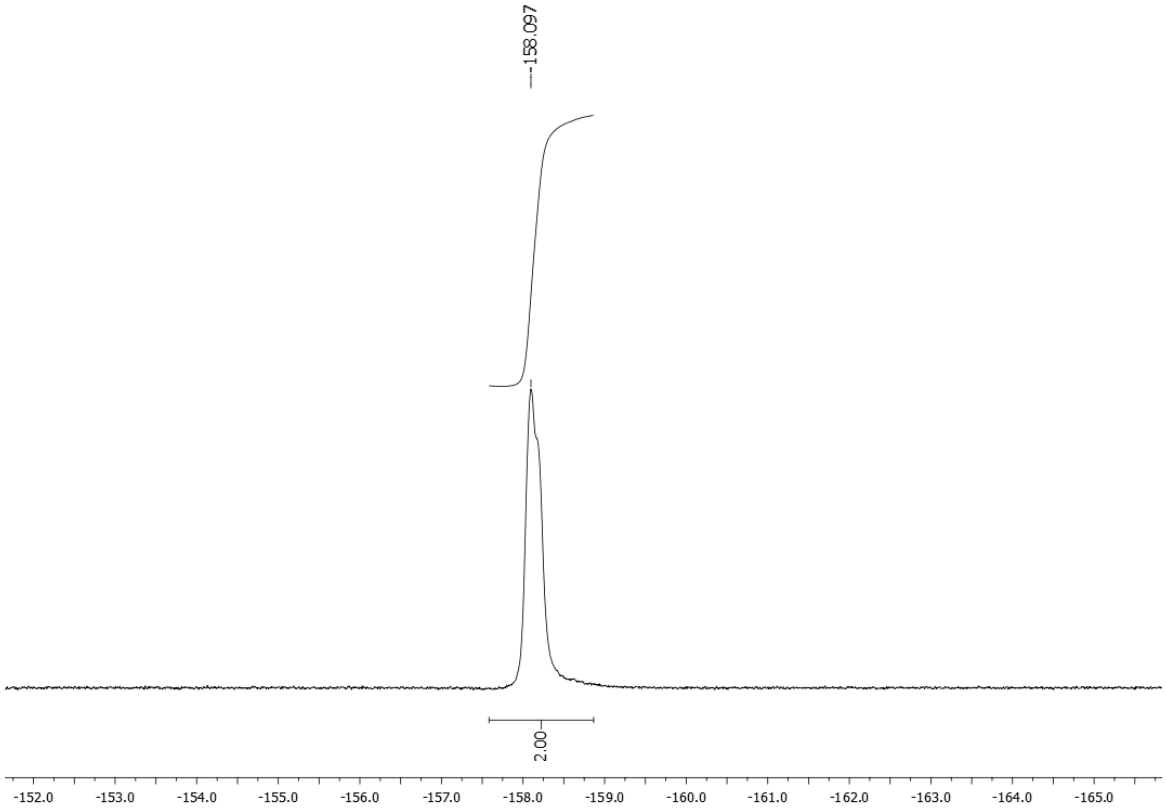
^{1}H NMR spectrum



^{13}C NMR spectrum



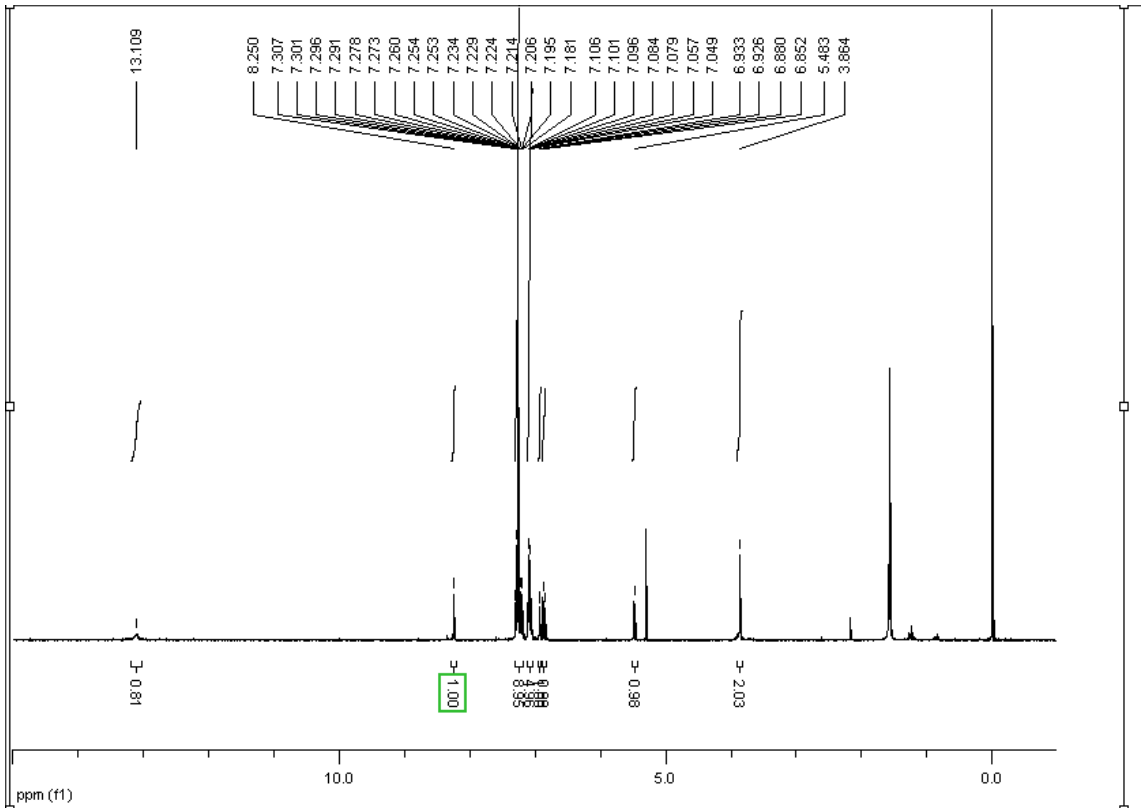
^{19}F NMR spectrum



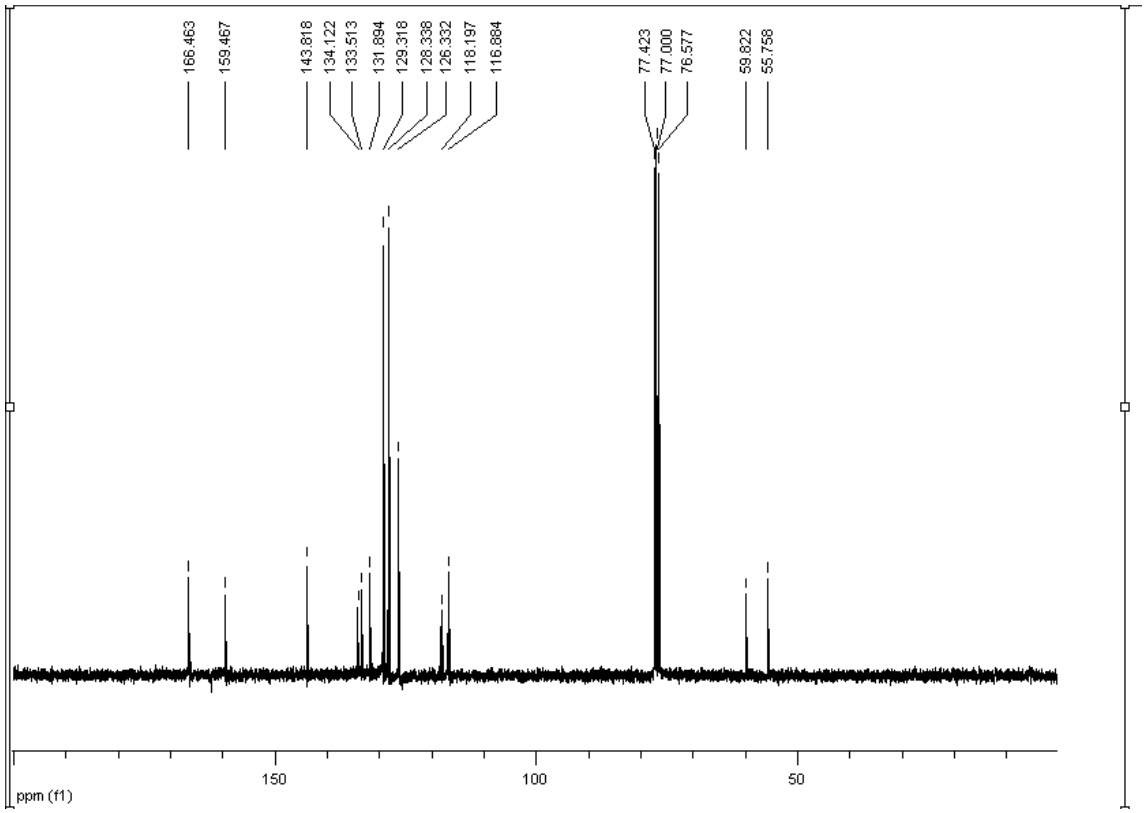
2,2'-{(1*E*,1'*E*)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)}bis(4-benzhydrylphenol

7

^{1}H NMR spectrum

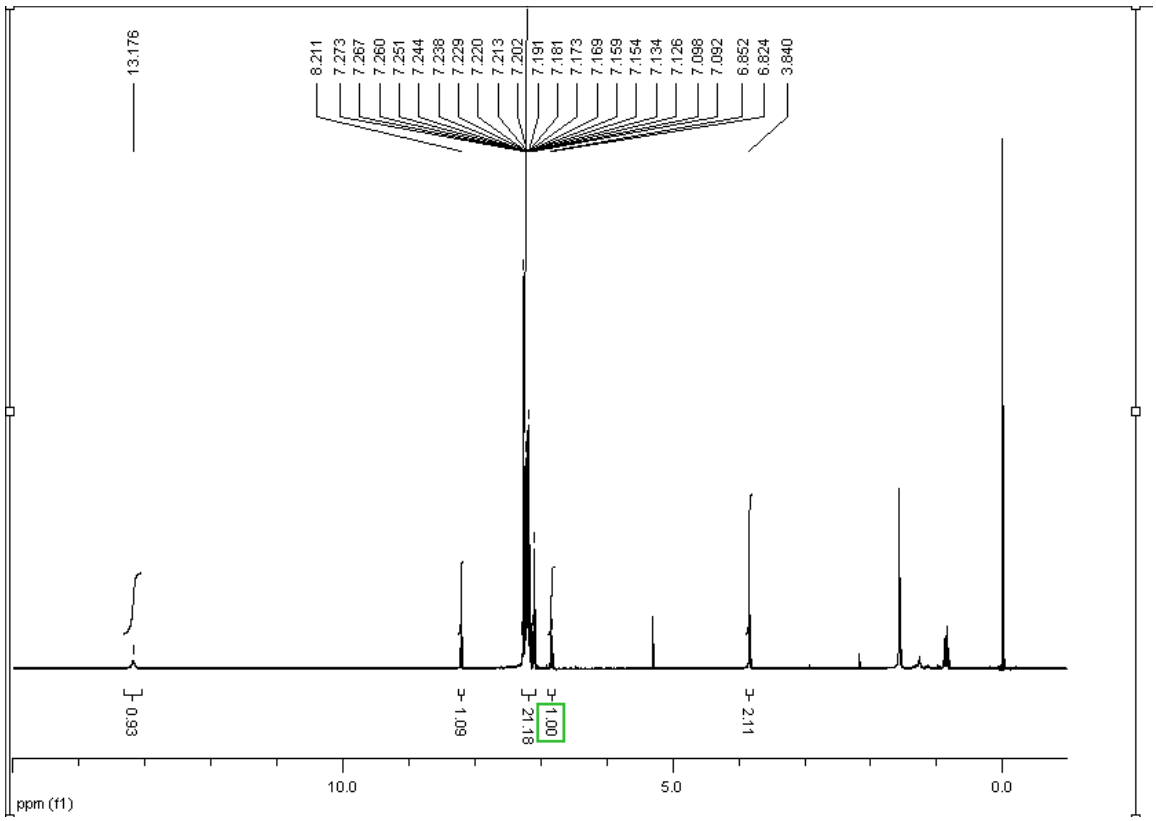


^{13}C NMR spectrum

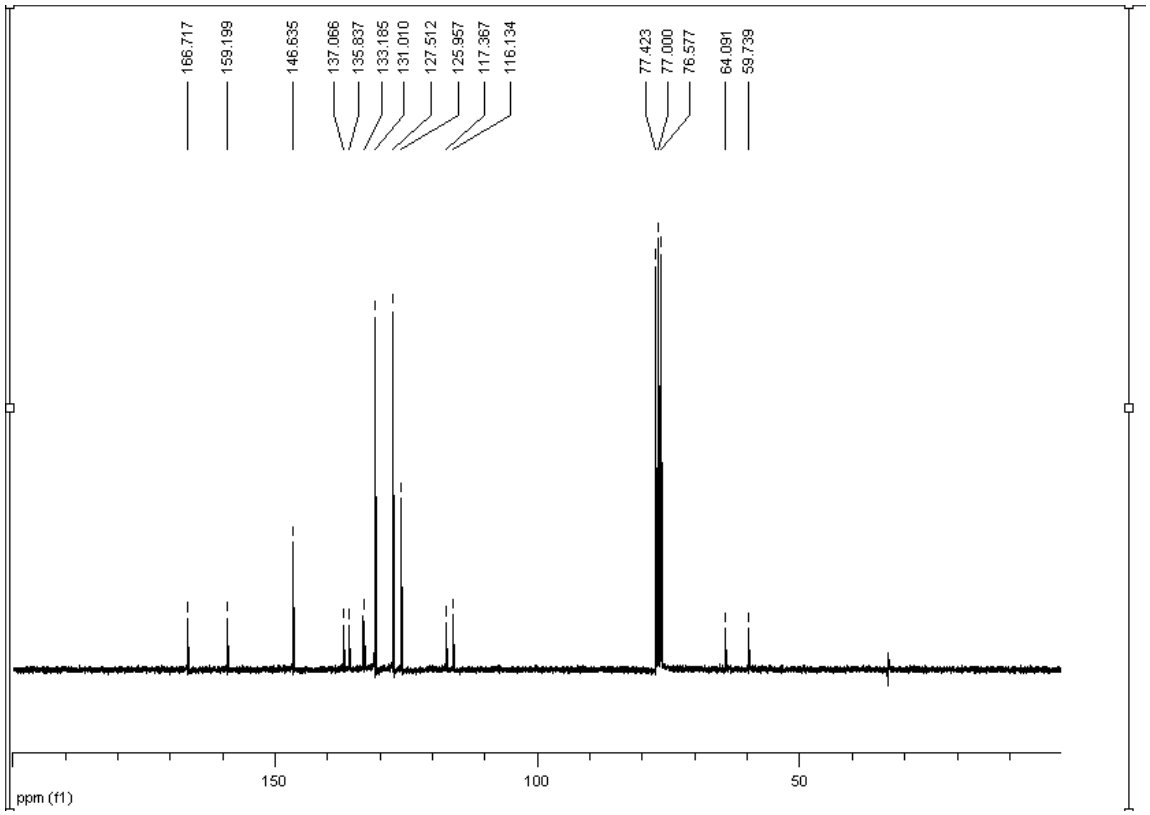


2,2'-{(1*E*,1'*E*)-[Ethane-1,2-diylbis(azanylylidene)]bis(methanylylidene)}bis(4-tritylphenol 8

^{1}H NMR spectrum



^{13}C NMR spectrum



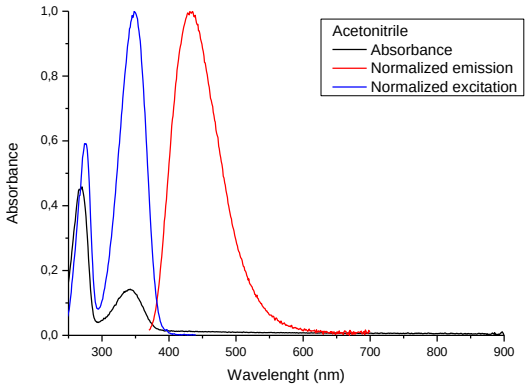
Absorption, excitation and emission results

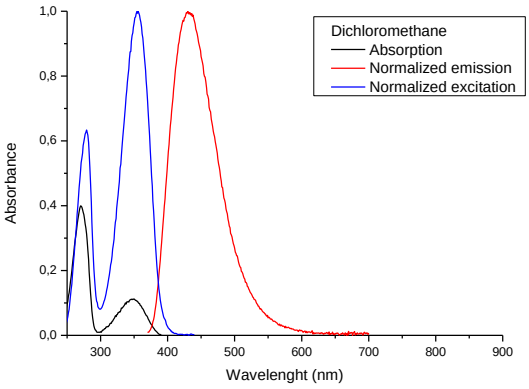
Dye	Solvent	Abs max (nm)	Molar extinction coefficient (M^{-1} cm^{-1})	Emission max (nm)	Stroke shift (nm)	Quantum yield [(a)]
1	Toluene	348	8 900	434	86	0.08
	Dichloromethane	349	5 300	430	81	0.10
	Acetonitrile	342	5 600	434	92	0.12
	Methanol	342	6 100	429	87	0.11
	Ethyleneglycol	342	6 300	432	90	0.12
2	Toluene	349	2 250	442	93	0.24
	Dichloromethane	354	32 700	442	88	0.17
	Acetonitrile	350	15 200	445	95	0.26
	Methanol	346	550	444	98	0.35
	Ethyleneglycol	341	950	449	108	0.09
3	Toluene	366	10 500	457	91	0.32
	Dichloromethane	365	9 500	464	99	0.34
	Acetonitrile	361	8 850	465	104	0.36
	Methanol	359	1 950	465	106	0.28
	Ethyleneglycol	349	2 000	468	119	0.10
4	Toluene	367	19 200	467	100	0.44
	Dichloromethane	365	12 100	473	108	0.35
	Acetonitrile	360	11 750	476	116	0.38
	Methanol	356	10 100	473	117	0.34
	Ethyleneglycol	360	6 700	435	75	0.10

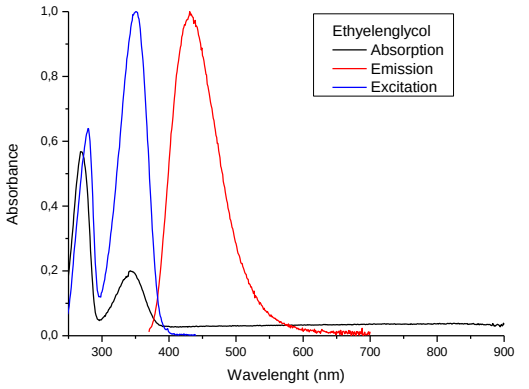
(a) Determined by comparison with fluorescein ($\varphi f = 0.90$ in water with NaOH 0.1 $mol.L^{-1}$)

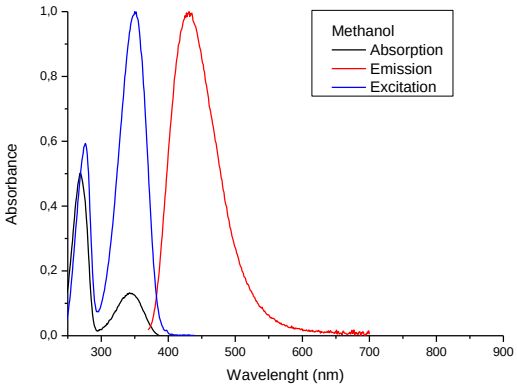
Absorption, excitation and emission spectra of boron fluorophores:

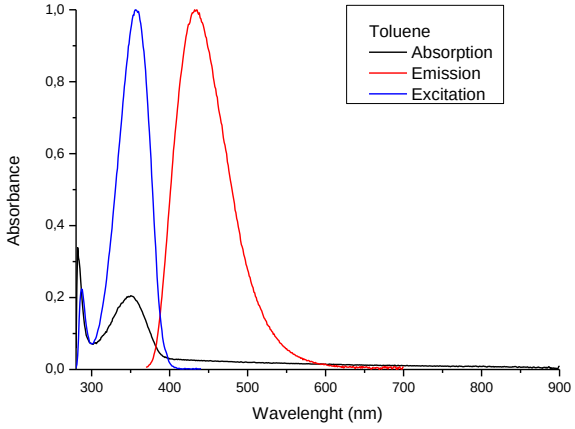
Fluorophore **1** at 2.19 10^{-5} M:



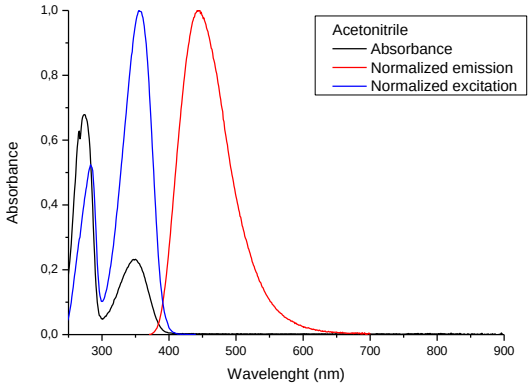


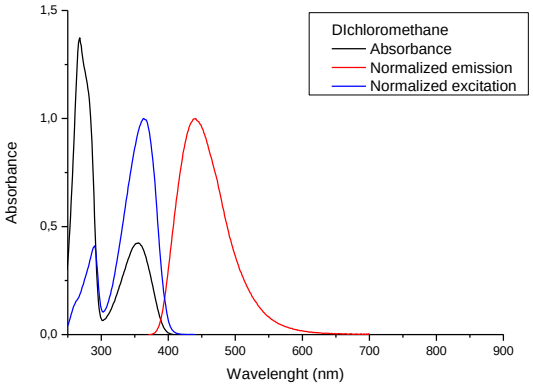


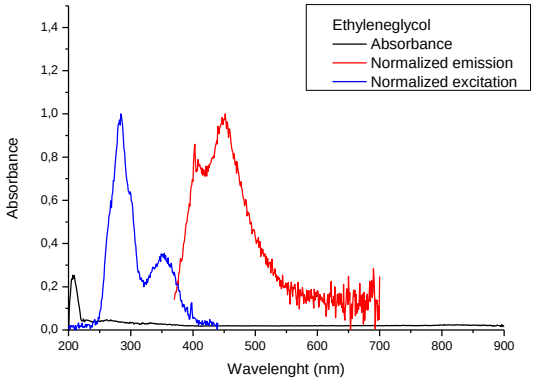


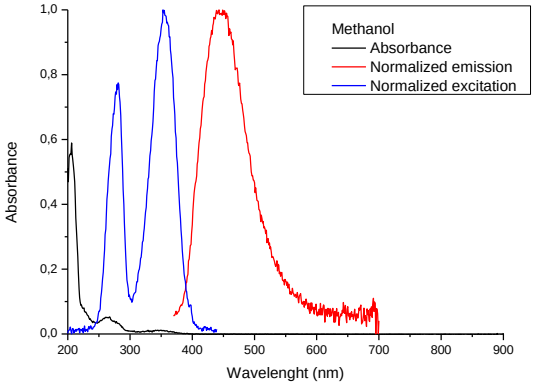


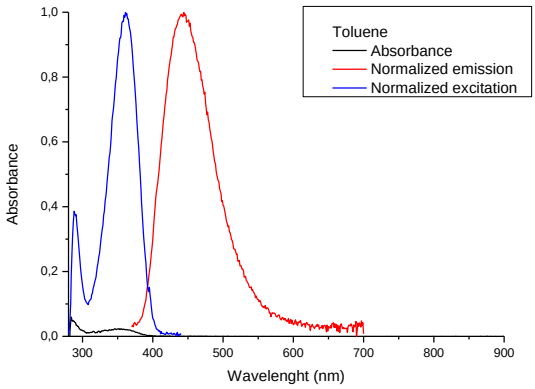
Fluorophore **2** at 1.53 10^{-5} M:



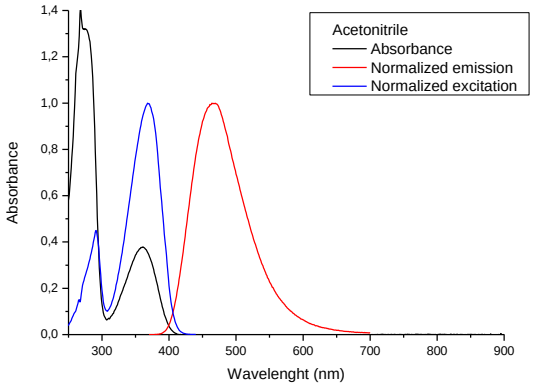


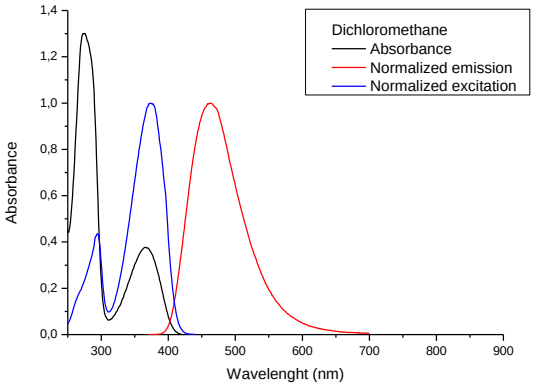


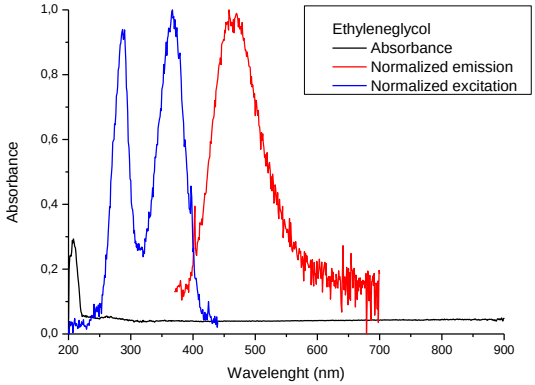


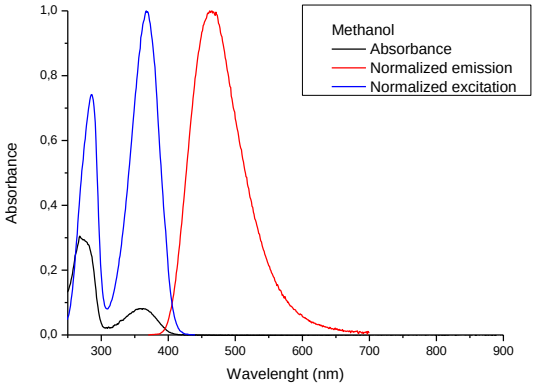


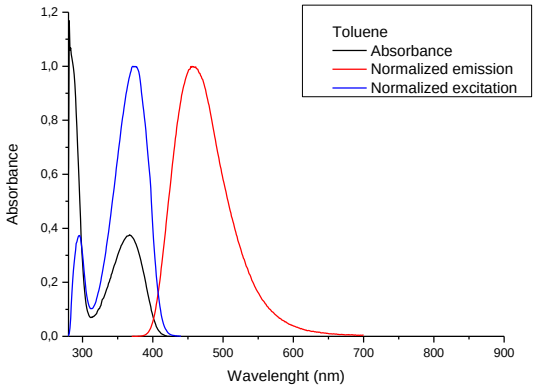
Fluorophore **3** at 3.99 10^{-5} M:











Fluorophore **4** at 3.27 10^{-5} M: