Electronic Supplementary Material (ESI) for Chemical Communications

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1. Experimental Details

General procedures. Anhydrous $MgSO_4$ was used to dry all organic extracts, all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by colour and TLC using commercial glass backed thin layer chromatography (TLC) plates (Kieselgel 60 F254). The plates were observed under UV light at 254 and 365 nm. The technique of flash column chromatography was used throughout for all separations using silica gel (LC60A35-70 μM).

Instrumentation.

UV spectra were obtained on a Jasco V-670 spectrophotometer, and fluorescence measurements were carried out on a Varian cary eclipse fluorescence spectrometer. The lifetimes were measured on a Fluotime 100 machine using a 450 nm pulsed laser source. ^{1}H and ^{13}C NMR spectra were recorded either at 400 and 100 MHz, respectively or at 600 and 150 MHz, respectively. Deuterated solvents were used for homonuclear lock, and the signals are referenced to the deuterated solvent peaks. CHN analysis was carried out in Chemistry and Chemical Biology Microanalytical Laboratory, University College Dublin. Resonance Raman spectra were acquired with a 100 X (N.A. = 0.90) Olympus objective on a confocal Labram HR spectrometers from Jobin-Yvon/Dilor coupled to diode laser sources at 532 nm and 473 nm. Laser power at the spot was approximately 100 W.

Computation

DFT methods were used in all calculations presented here. . The hydrid functional B3LYP was used along with the 6-311G(d) basis set.[1,2,3,4] Structural parameters were optimised without symmetry or other constraints. The calculations were performed using the Gaussian 09 package,[5] running on Ireland's High-Performance Computing Facility (http://www.ichec.ie/). The initial structures were obtained from molecular modeling calculations and the structures were optimized to tight convergence criteria. Partial, total density of state and charge decomposition analysis derived from accurate self consistent field calculations were obtained by using the AOMix software package.[6,7]

2. Synthesis and Structural Characterisation

General synthesis of naphthyridine (1) + compound data

Ethyl 4-bromo-6-methoxy-1,5-naphthyridine-3-carboxylate (310 mg, 1 mmol), K_2CO_3 (279 mg, 2 equiv), Pd(dppf)Cl_2·DCM (33 mg, 0.04 mmol) and 2-fluoro-4-formylphenylboronic acid (252 mg, 1.5 mmol) were dissolved in dioxane/H_2O (3:1) (2 mL). The stirred mixture was heated to reflux (preheated oil bath) and refluxed for 45 min until the reaction was finished (TLC), before it was allowed to cool to *ca.* 18 °C. It was diluted (DCM, 5 mL), dried ($MgSO_4$), and purified on silica gel using flash chromatography (hexane/EtOAc, 4:1) gave the *title compound* **1** (279 mg, 79%), R_f 0.36 (hexane/EtOAc, 3:1); (found: C, 64.3; H, 4.2; N, 7.7%. $C_{19}H_{15}FN_2O_4$ requires C, 64.4; H, 4.3; N, 7.9%). ^{1}H NMR ($CDCl_3$) δ 10.02 (s, 1H, C*H*O), 9.29 (s, 1H, Naph *H*-2), 8.23 (d, *J* = 9.2 Hz, 1H, Naph *H*-7), 7.71 (dd, *J* = 1.2, 8.0 Hz, 1H, Ar *H*), 7.63 (dd, *J* = 1.2, 8.0 Hz, 1H, Ar *H*), 7.45 (m,1H, Ar *H*), 7.14 (d, *J* = 9.2 Hz, 1H, Naph *H*-8), 4.16 (q, *J* = 6.8 Hz, 2H, OCH_2), 3.65 (s, 3H, OCH_3), and 1.07 (t, *J* = 6.8 Hz, 3H, CH_3) ppm; ^{13}C NMR ($CDCl_3$) *δ* 190.9 (*C*HO), 165.3, 162.6, 160.8 (d, *J* = 248.0 Hz), 147.9, 143.7, 141.3, 139.8, 139.4, 137.9 (d, *J* = 6.3 Hz), 132.2 (d, *J* = 3.3 Hz), 130.9 (d, *J* = 17.1 Hz), 125.8, 124.9 (d, J_{CF} = 3.0 Hz), 118.7, 114.9 (d, *J* = 22.5 Hz), 61.8, 53.8, and 13.8 ppm.

General synthesis of BODIPY (2) + compound data

Ethyl 4-(2-fluoro-4-formylphenyl)-6-methoxy-1,5-naphthyridine-3-carboxylate **(1)** (105 mg, 0.5 mmol), 2,4-dimethyl-1*H*-pyrrole (104 mg, 1.1 mmol) and TFA (cat) were dissolved in N_2-purged DCM (35 mL) and stirred for 4 h under N_2 atmosphere until the aldehyde was fully consumed (TLC). At this point a solution of tetrachlorobenzoquinone (123 mg, 0.5 mmol) in N_2-purged DCM (10 mL) was added and allowed to stir for 30 min. Following this Et_3N (1.31 mL) and BF_3.OEt_2 (1.31 mL) were added and the reaction allowed to stir at r.t over night. The crude mixture was then washed with water (2 x 50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified on silica

gel (20% EtOAc:Hex) which gave the *title compound* **2** (163 mg, 58%) as an bright red powder, R_f 0.2 (hexane/EtOAc 8:2); (found: C, 64.7; H, 5.9; N, 9.5. $C_{31}H_{28}BF_3N_4O_3$ requires C, 65.0; H, 4.9; N, 9.8%). %). ^{1}H NMR (DMSO) δ 9.16 (s, 1H, Naph *H*-2), 8.36 (d, J = 9.0 Hz, 1H, Naph *H*-7), 7.52 (t, J = 7.5 Hz, 1H, Ar *H*), 7.45 (dd, J = 8.6, 1.5 Hz, 1H, Naph *H*-8), 7.35 (d, J = 9.0 Hz, 1H, Ar *H*), 7.28 (dd, J = 6.4, 1.5 Hz, 1H, Ar *H*), 6.18 (s, 1H, Ar *H* pyr), 6.16 (s, 1H, Ar *H* pyr), 4.12 (m, 2H, OCH_2), 3.65 (s, 3H, OCH_3), 2.41 (2 x s, 6H, CH_3), 1.54 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), and 1.17 (t, 3H, J = 6.7 Hz, CH_3) ppm^{13}C NMR (DMSO) δ 164.9, 162.1, 160.4 (d, J_{CF} = 246.3 Hz), 155.3, 155.2, 147.2, 143.0, 142.9, 140.4, 140.4, 139.9, 138.8, 135.9 (d, J_{CF} = 8.8 Hz), 132.7 (d J_{CF} = 4.0 Hz), 130.4 (d J_{CF} = 20.8 Hz) , 126.7, 123.4, 121.6, 121.5, 118.5, 115.0 (d, J_{CF} = 23.1 Hz), 61.5, 53.3, 14.2, 14.0, 13.9 ppm; λ_{max} (ε [M^{-1} cm^{-1}]) = 501 nm (79000 ± 1800); λ_{em} = 520 nm (λ_{ex} = 499 nm), Φ_f = 0.61 (± 0.04), τ_f = 4.1 ns.

Synthesis of BODIPY (3) + compound data

1,3,5,7-tetramethyl-8-[(2-fluorophenyl)-6-methoxy-1,5-naphthyridine-3-ethyl carboxylate]-4,4'-difluoroboradiazaindacene **(2)** (90 mg, 0.16 mmol), ACHN (85.4 mg, 0.35 mmol), NBS (57 mg, 0.35 mmol), were added to anhydrous CCl_4 (5 ml) and refluxed until the reaction was finished (TLC). The residue was purified on silica gel (30% EtOAc:Hex) which gave the *title compound* **(3)** (25 mg, 22%), as a dark red crystalline solid, R_f 0.7 (hexane/EtOAc 2:1); (found: C, 50.9; H, 3.6; N,7.4. $C_{31}H_{26}BBr_2F_3N_4O_3$ requires C, 50.9; H, 3.6; N, 7.6%). ^{1}H NMR ($CDCl_3$) δ 9.26 (s, 1H, Naph *H*-2), 8.25 (d, J = 8.8 Hz, 1H, Naph *H*-7), 7.44 (t, J = 7.2 Hz, 1H, Ar *H*), 7.16 (d, J = 9.2 Hz, 1H, Naph *H*-8), 7.13 (dd, J = 6.4, 1.6 Hz, 1H, Ar *H*), 7.08 (dd, J = 9.2, 1.6 Hz, 1H, Ar *H*), 4.24 (m, 2H, OCH_2), 3.70 (s, 3H, OCH_3), 2.57 (s, 6H, CH_3), 1.59 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), and 1.29 (t, 3H, J = 7.2 Hz, CH_3) ppm; ^{13}C NMR ($CDCl_3$) δ 163.9, 161.6, 160.1 (d, J_{CF} = 248.7 Hz), 153.9, 153.2, 146.6, 142.5, 140.5, 140.0, 138.9, 138.7, 138.6, 134.9 (d, J = 7.9 Hz), 131.9 (d, J_{CF} = 3.9 Hz), 129.3, 128.9, 125.5, 124.3, 124.2, 121.9 (d, J_{CF} = 3.0 Hz), 117.6, 114.2 (d, J_{CF} = 23.2 Hz), 111.3, 110.8, 60.7, 52.6, 13.2, 13.1, 12.8, and 12.7 ppm; λ_{max} (ε [M^{-1} cm^{-1}]) = 534 nm (8800 ± 300); λ_{em} = 551 nm (λ_{ex} = 530 nm), Φ_f = 0.24 (± 0.005), τ_f = 1.6 ns.

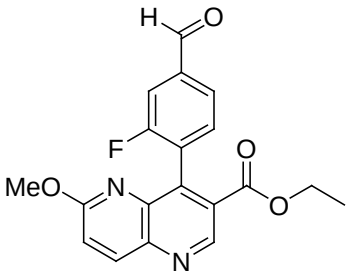
Synthesis of BODIPYs (4 & 5) + compound data

1,3,5,7-tetramethyl-2,6-dibromo-8-[(2-fluorophenyl)-6-methoxy-1,5-naphthyridine-3-ethylcarboxylate]-4,4' difluoroboradiazaindacene **(3).** (70 mg, 0.1 mmol), K_2CO_3 (55 mg, 4 equiv), Pd(dppf)Cl_2·DCM (10 mg, 0.01 mmol) and 4-dimethylaminophenylboronic acid (48 mg, 3.0 mmol) were dissolved in dioxane/H_2O (3:1) (2 mL). The stirred mixture was heated to reflux (preheated oil bath) and refluxed for 45 min until the reaction was finished (TLC), before it was allowed to cool to *ca.* 18 ^{o}C. It was diluted (DCM, 5 mL), dried ($MgSO_4$), and purified on silica gel using flash

chromatography (hexane/EtOAc, 4:1) gave the *title compound* **4** (25 mg, 30%), as a dark blue solid, R_f 0.6 (hexane/EtOAc 2:1); (found: C, 69.3; H, 5.4; N, 10.1. $C_{47}H_{46}BF_3N_6O_3$ requires C, 69.6; H, 5.7; N, 10.4%); ^{1}H NMR ($CDCl_3$) δ 9.20 (s, 1H, Naph *H*-2), 8.20 (d, *J* = 9.0 Hz, 1H, Naph *H*-7), 7.40 (t, *J* = 7.2 Hz, 1H, Ar *H*), 7.21 (dd, *J* = 1.8, 9.6 Hz, 1H, Ar *H*), 7.17 (d (J obscured), 1H, Ar *H*), 7.10 (d, *J* = 9.0 Hz, 1H, Naph *H*-8), 7.01 (d, *J* = 9.0 Hz, 2H, Ar *H*), 6.99 (d, *J* = 8.4 Hz, 2H, Ar *H*), 6.71-6.69 (m, 4H, Ar *H*), 4.11 (m, 2H, OCH_2), 3.61 (s, 3H, OCH_3), 2.92 (s, 12H, NCH_3), 2.49 (s, 6H, CH_3), 1.52 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), and 1.21 (t, *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR ($CDCl_3$) δ 164.2, 161.4, 160.1 (d, J_{CF} = 247.6 Hz), 154.2, 153.7, 148.4, 146.7, 142.6, 140.4, 138.9, 138.6, 138.1, 137.9, 136.7, 136.4 (d, J_{CF} = 7.8 Hz), 133.2, 132.9, 131.6 (d, J_{CF} = 4.0 Hz), 130.1, 129.9, 129.8, 129.7, 125.7, 123.5, 123.4, 122.4, 120.2, 120.1, 117.2, 114.5 (d, J_{CF} = 19.1 Hz), 111.1, 60.5, 52.7, 39.4, 13.1, 12.4, 12.2, and 11.9 ppm; ^{19}F NMR ($CDCl_3$) δ -112.5 and -146.0 ppm; λ_{max} (ε [M^{-1} cm^{-1}]) = 554 nm (3000 ± 180); λ_{em} = 740 nm (λ_{ex} = 570 nm) Φ_f = 0.06 (± 0.003), τ_f = 0.5 ns.

Title compound **5** (18 mg, 24%), as a dark red solid, R_f 0.4 (hexane/EtOAc 2:1); (found: C, 60.9; H, 4.5; N, 9.3. $C_{39}H_{36}BBrF_3N_5O_3$ requires C, 60.8; H, 4.7; N, 9.1%); ^{1}H NMR ($CDCl_3$) 9.23 (s, 1H, Naph *H*-2, rotamer A), 9.21 (s, 1H, Naph *H*-2, rotamer B), 8.23 (d, *J* = 7.2 Hz, 1H, Naph *H*-7, rotamer A), 8.21 (d, *J* = 9.0 Hz, 1H, Naph *H*-7, rotamer B), 7.44-7.37 (m, 2H, Ar *H*), 7.17-7.10 (m, 2H, Ar *H*), 6.99-6.95 (m, 2H, Ar *H*), 6.70-6.68 (m, 2H, Ar *H*), 4.22-4.16 (m, 2H, OCH_2, rotamer A), 4.15-4.08 (m, 2H, OCH_2, rotamer B), 3.71 (s, 3H, OCH_3, rotamer A), 3.59 (s, 3H, OCH_3, rotamer B), 2.92 (s, 6H, NCH_3), 2.56 (s, 6H, CH_3, rotamer A), 2.49 (s, 6H, CH_3, rotamer B), 1.58 (s, 3H, CH_3, rotamer A), 1.54 (s, 3H, CH_3, rotamer B), 1.53 (s, 3H, CH_3, rotamer A), 1.49 (s, 3H, CH_3, rotamer B), 1.29 (t, 3H, *J* = 7.2 Hz, 3H, CH_3, rotamer A), 1.22 (t, 3H, *J* = 7.2 Hz, 3H, CH_3, rotamer B) ppm; ^{13}C NMR ($CDCl_3$) δ 164.2 (rotamer A), 164.1 (rotamer B), 161.5 (rotamer A), 161.4 (rotamer B), 160.0 (Ar C_q-F, d, J_{CF} = 247.4 Hz), 158.1 (rotamer A), 157.5 (rotamer B), 150.2 (rotamer A), 149.7 (rotamer B), 148.6, 146.8 (rotamer A), 146.7 (rotamer B), 142.6 (d, J_{CF} = 4.3 Hz, rotamer A), 140.3 (d, J_{CF} = 4.3 Hz, rotamer B), 140.0, 138.9 (rotamer A), 138.8 (rotamer B), 138.5 (rotamer A), 138.6 (rotamer B), 138.3 (d, J_{CF} = 12.5 Hz), 137.3, 136.1, 135.7 (d, J_{CF} = 7.9 Hz), 134.6 (d, J_{CF} = 51.8 Hz), 131.7, 130.9, 130.5, 129.8, 129.7, 128.2, 128.6, 127.6, 126.7, 126.0, 125.6 (rotamer A), 125.5 (rotamer B), 125.2, 123.9 (d, J_{CF} = 19.6 Hz), 122.2 (rotamer A), 122.1 (rotamer B), 119.3, 117.4 (roatmer A), 117.2 (rotamer B), 114.3 (d, J_{CF} = 19.2 Hz), 111.1, 60.6 (rotamer A), 60.5 (rotamer B), 52.7 (rotamer A), 52.6 (rotamer B), 39.4, 13.2 (rotamer A), 13.1 (rotamer B), 12.8 (rotamer A), 12.5 (rotamer B), 12.4, 12.3 and 12.1 ppm; ^{19}F NMR ($CDCl_3$) δ -112.1 (rotamer A), -112.2 (rotamer B) and -146.0 ppm; λ_{max} (ε [M^{-1} cm^{-1}]) = 534 (71,000 ± 4800); λ_{em} = 565 nm (λ_{ex} = 513 nm), Φ_f = 0.14 (± 0.008), τ_f = 1.9 ns.

4. NMR Data for **1**,**2**,**3**, **4** and **5**



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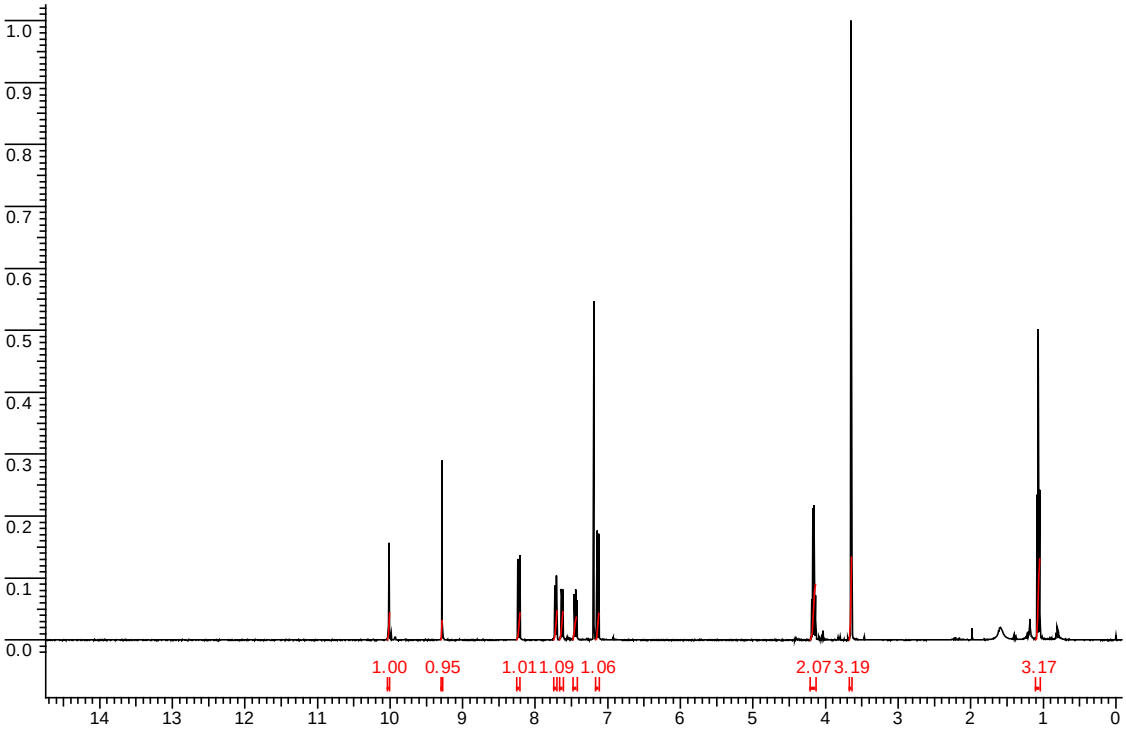


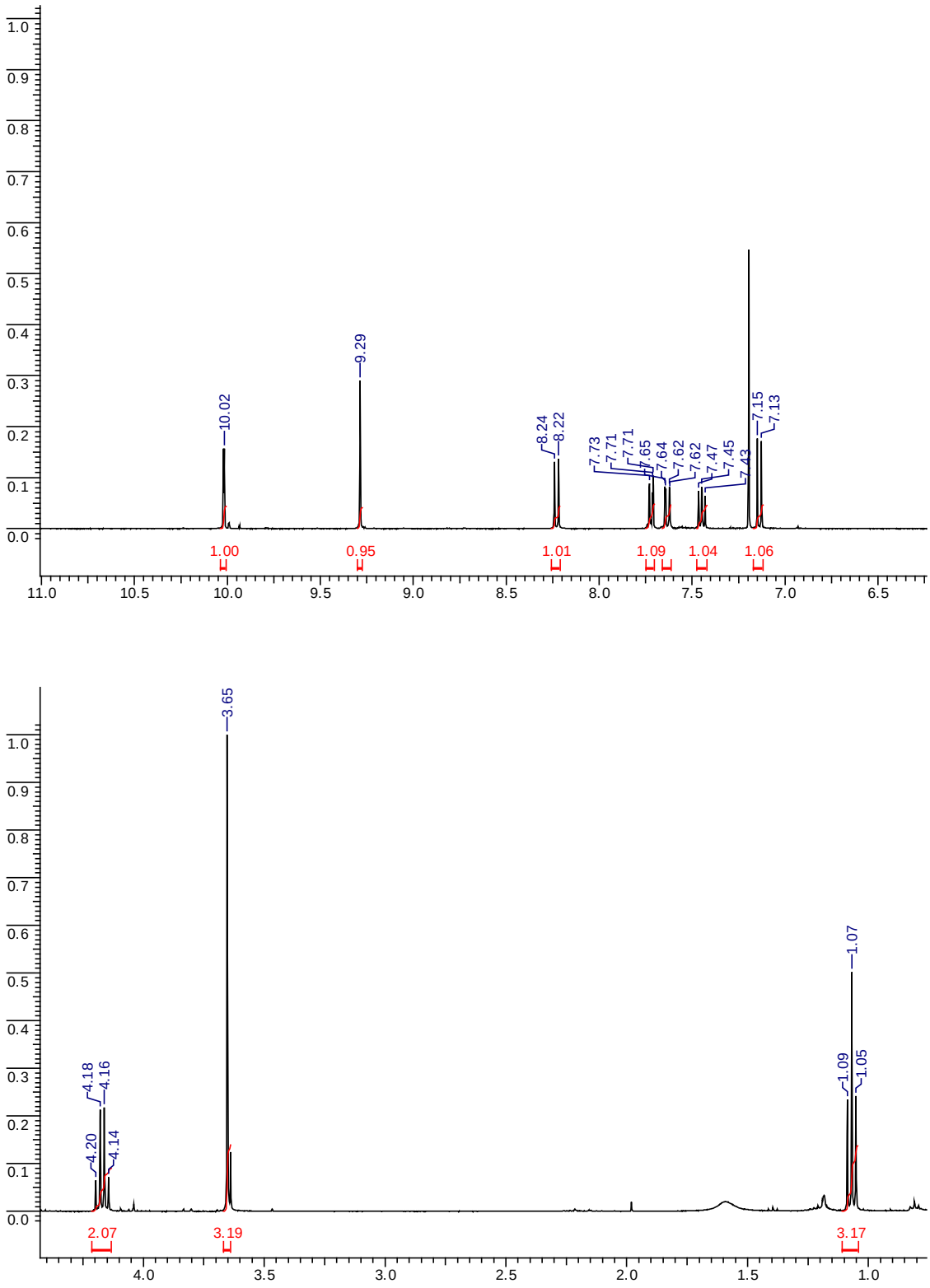


***Figure S1*:** ^{1}H NMR spectrum of **1** in $CDCl_3$

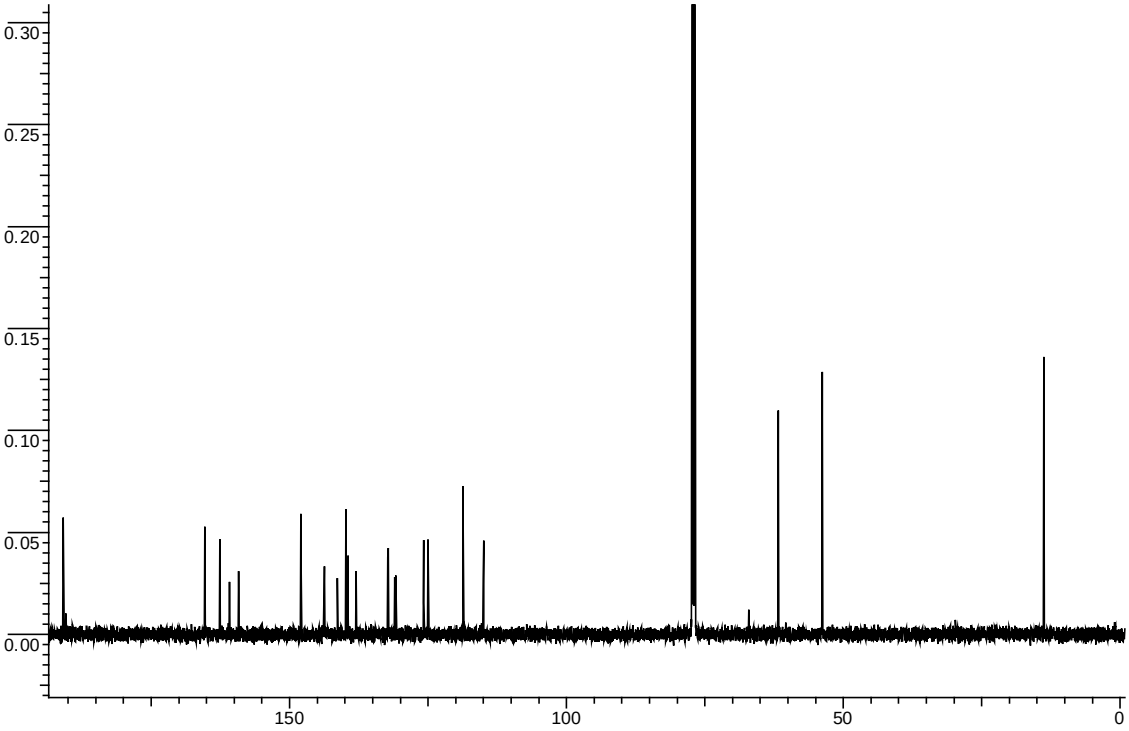
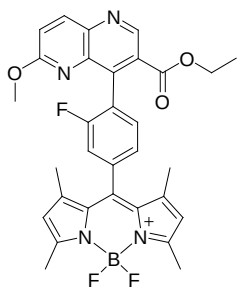


Figure S2: ^{13}C NMR spectrum of **1** in $CDCl_3$



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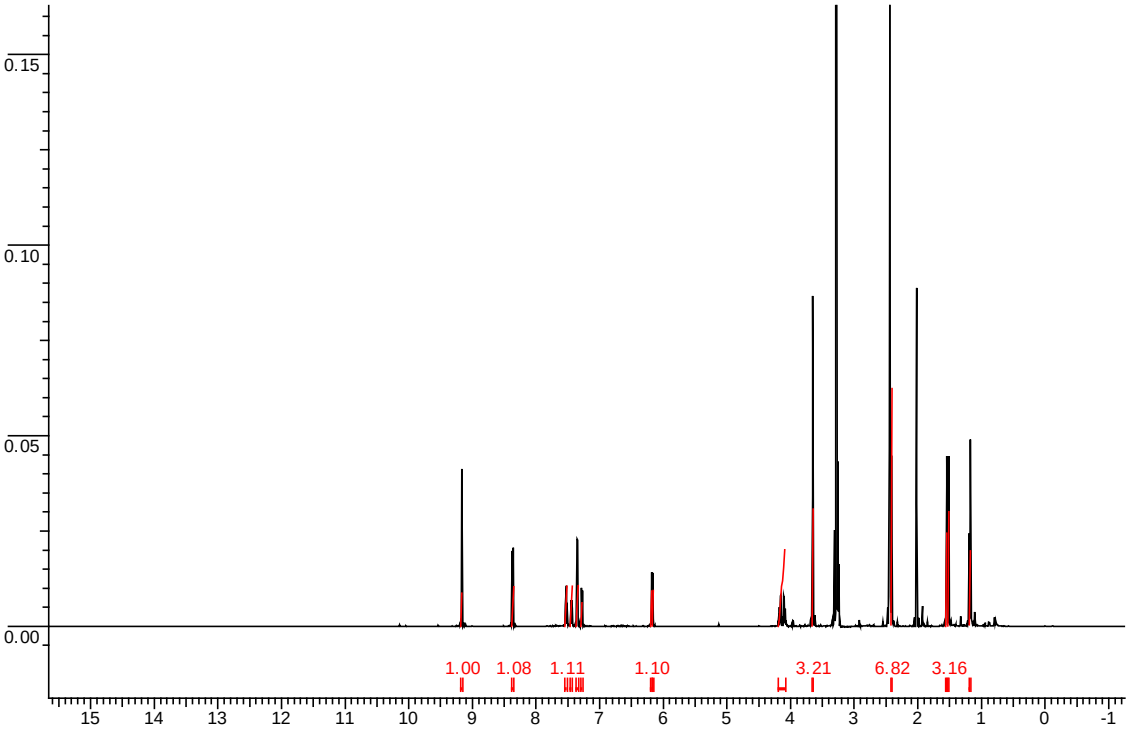
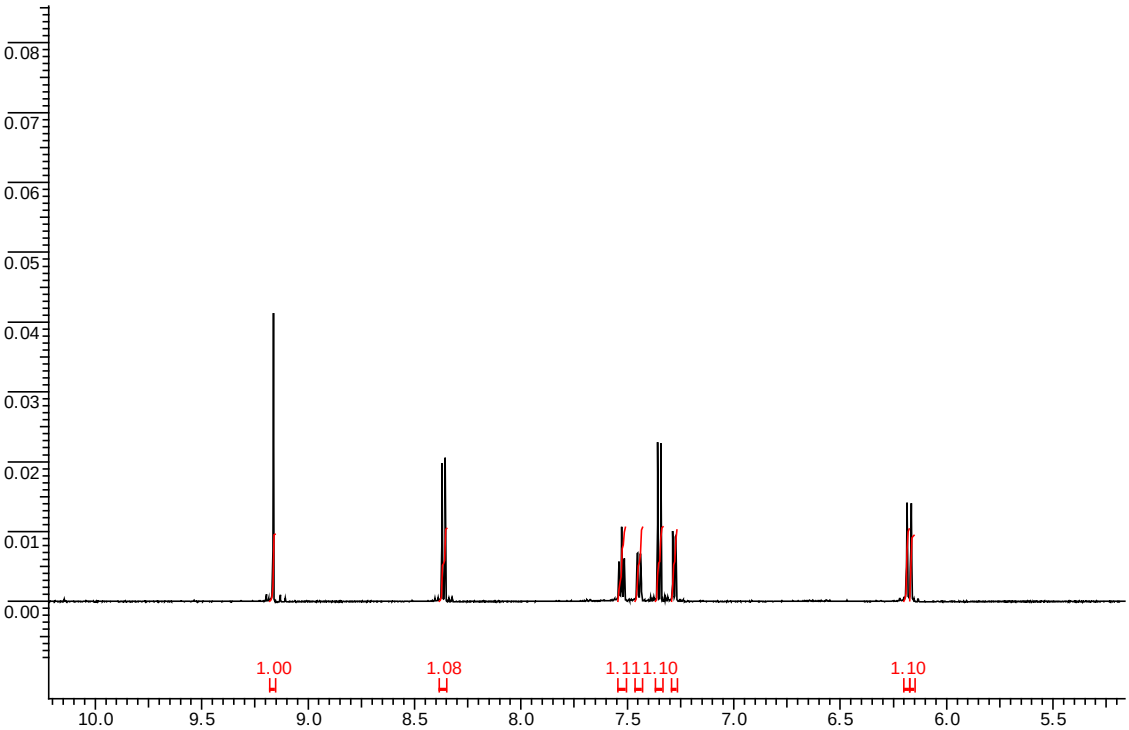




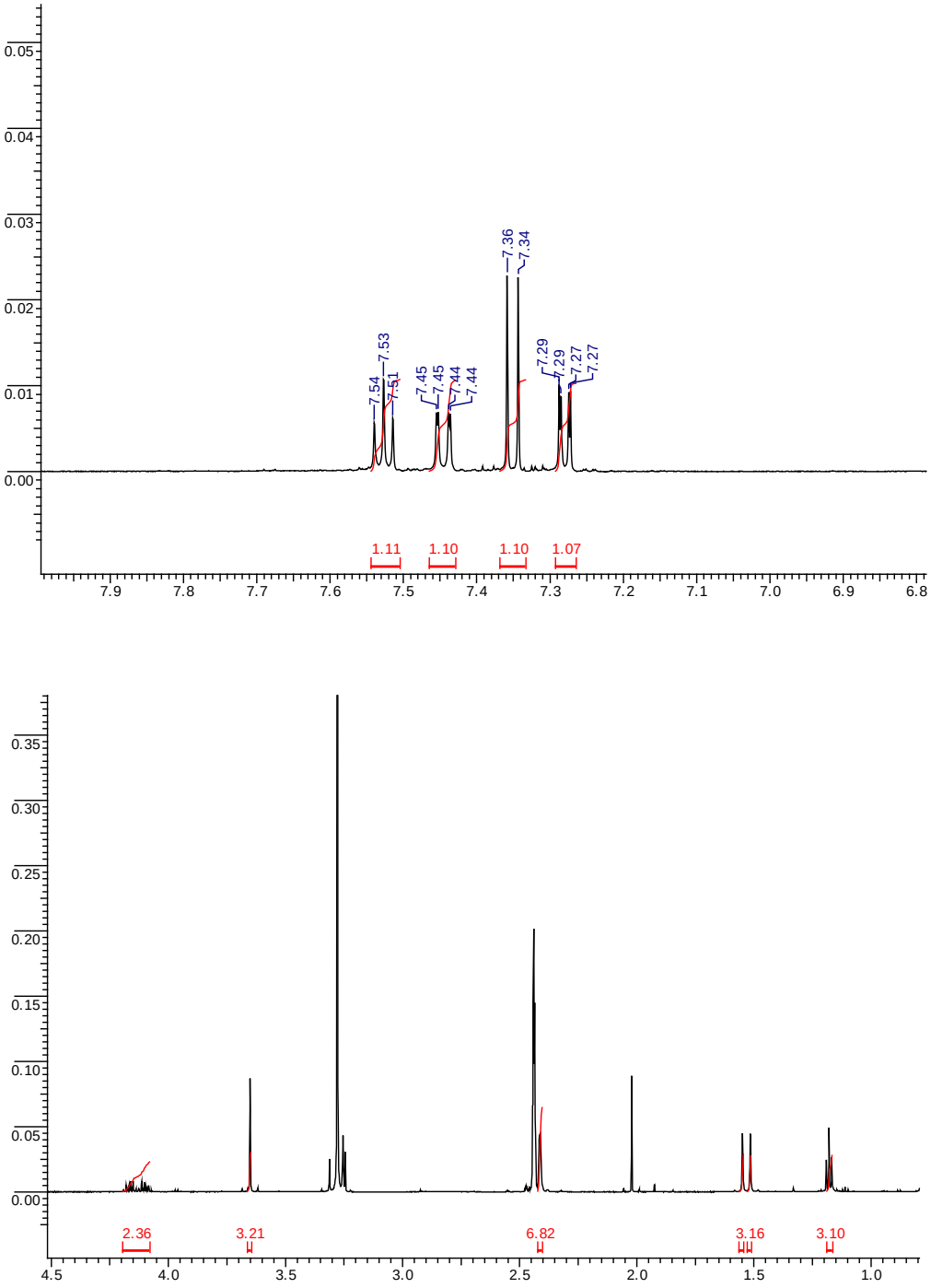
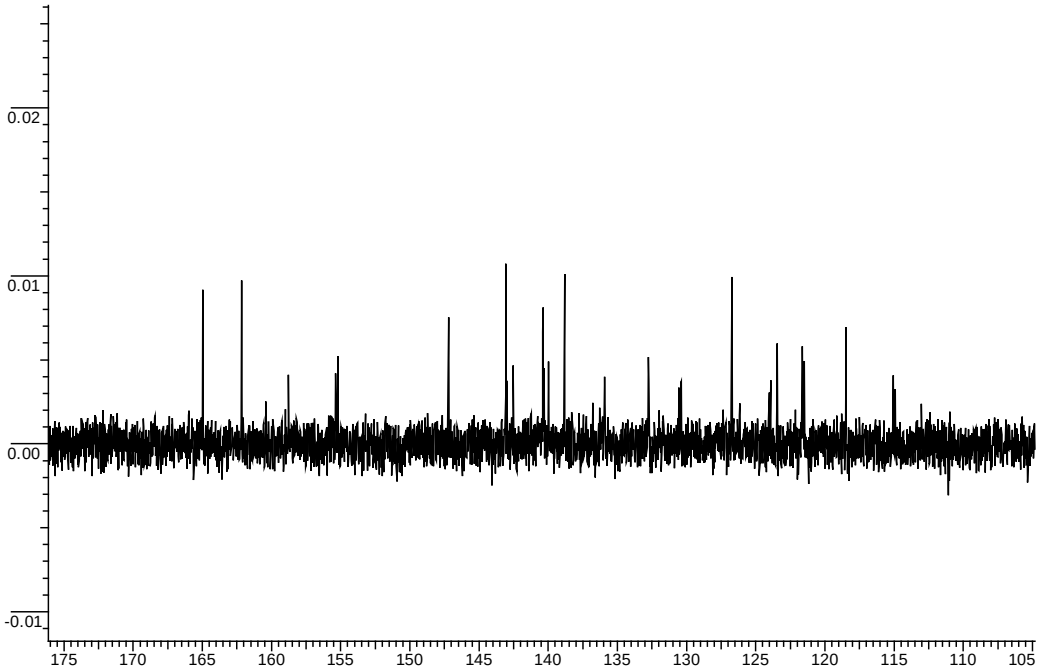


Figure S3: ^{1}H NMR spectrum of **2** in DMSO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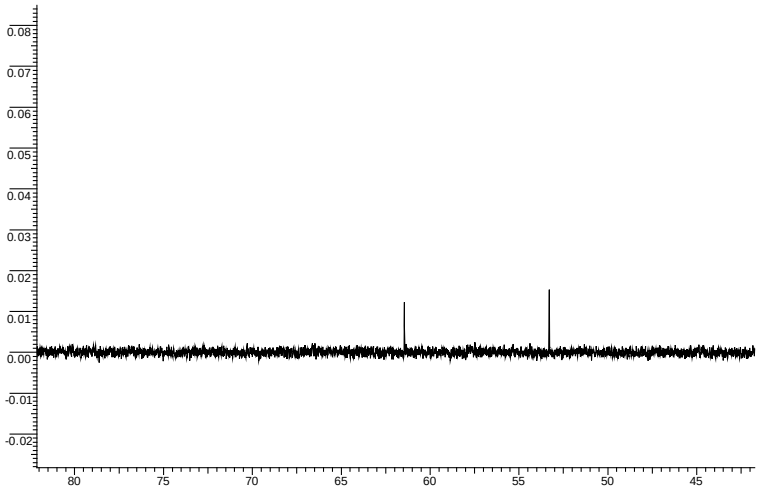
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55
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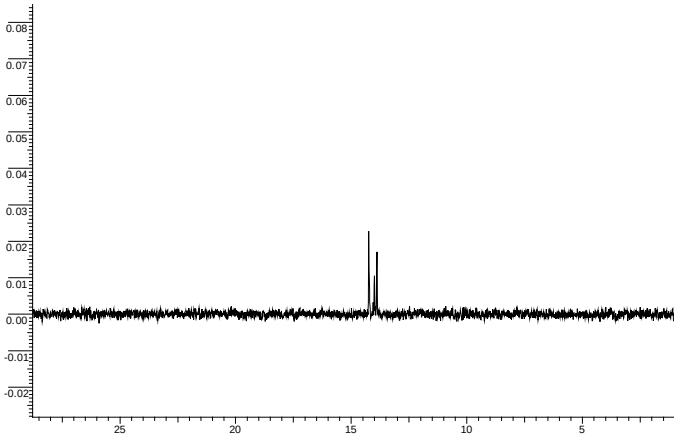
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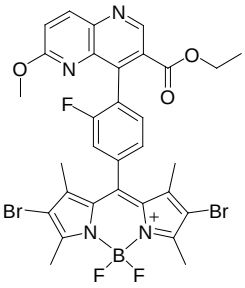
20
15
10
5

Figure S4: ^{13}C NMR spectrum of **2** in DMSO.



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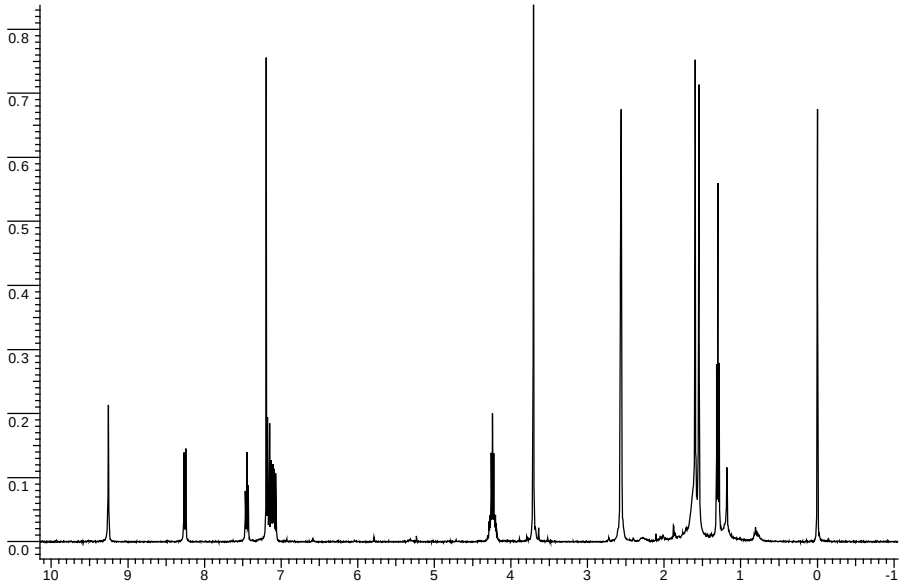


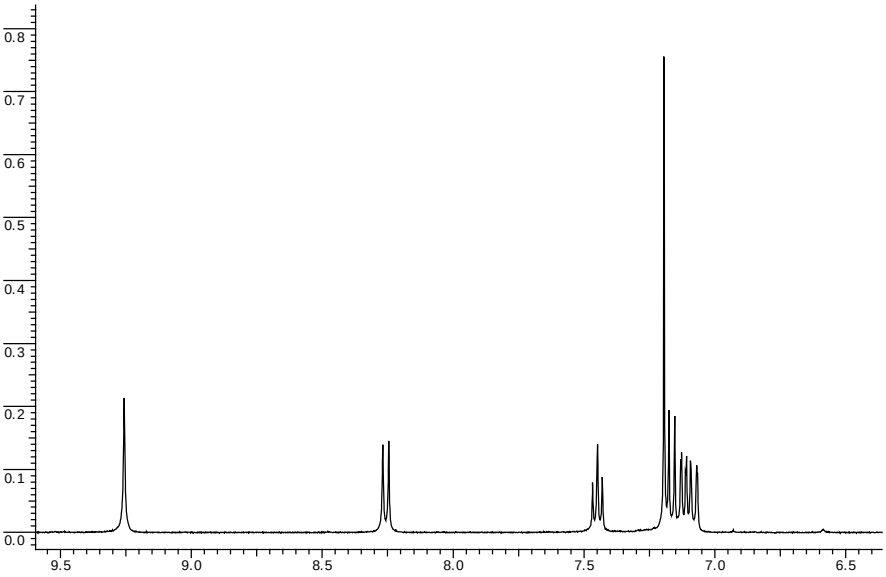


Figure S5: ^{1}H NMR spectrum of **3** in $CDCl_3$

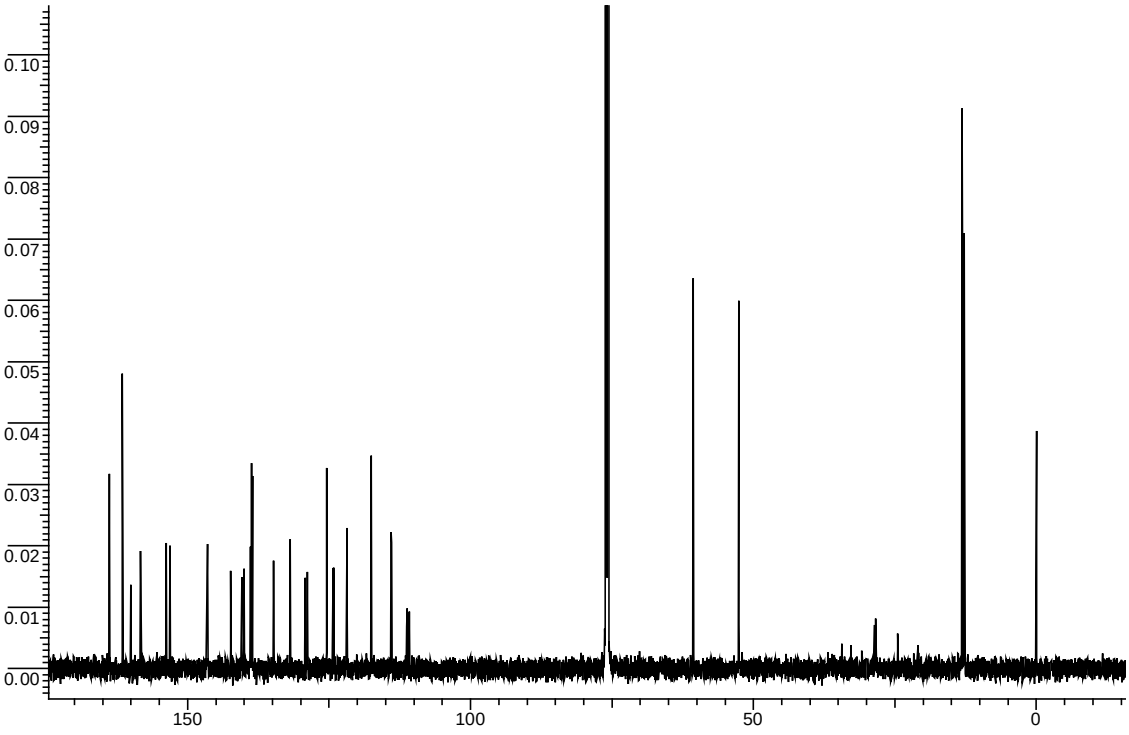
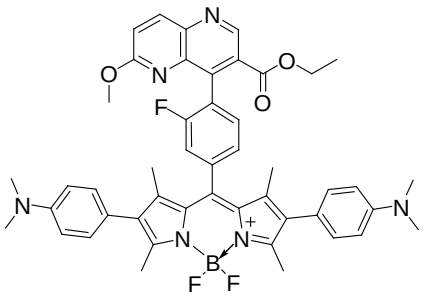


Figure S6: ^{13}C NMR spectrum of **3** in $CDCl_3$.



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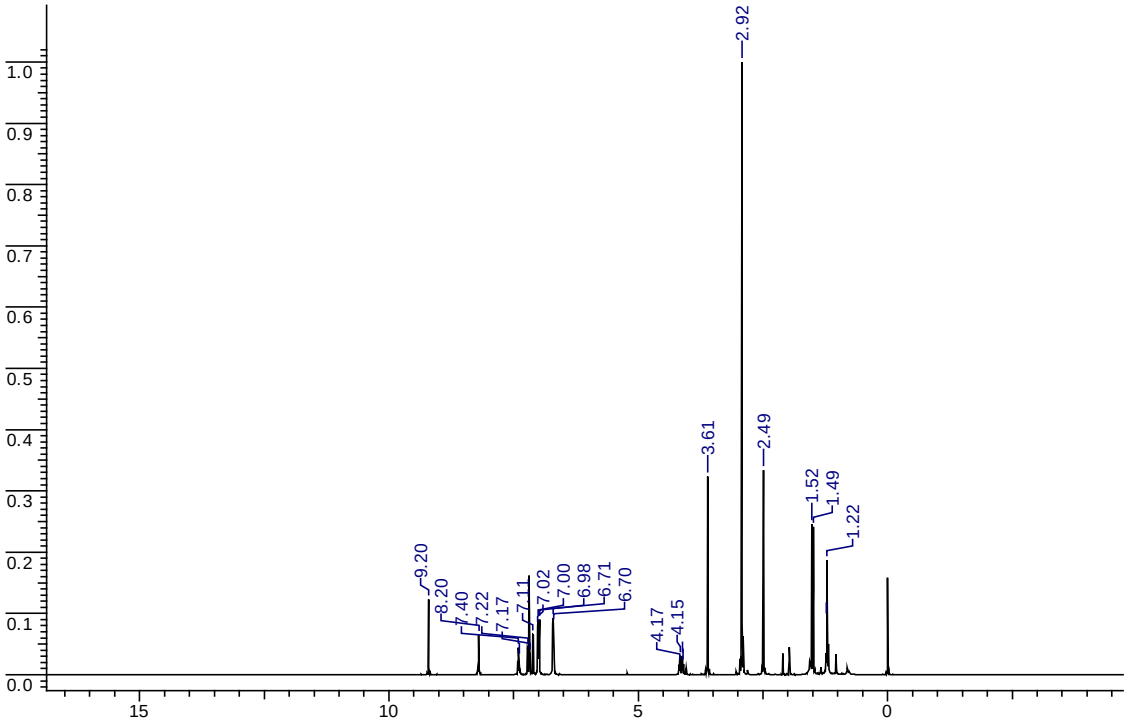

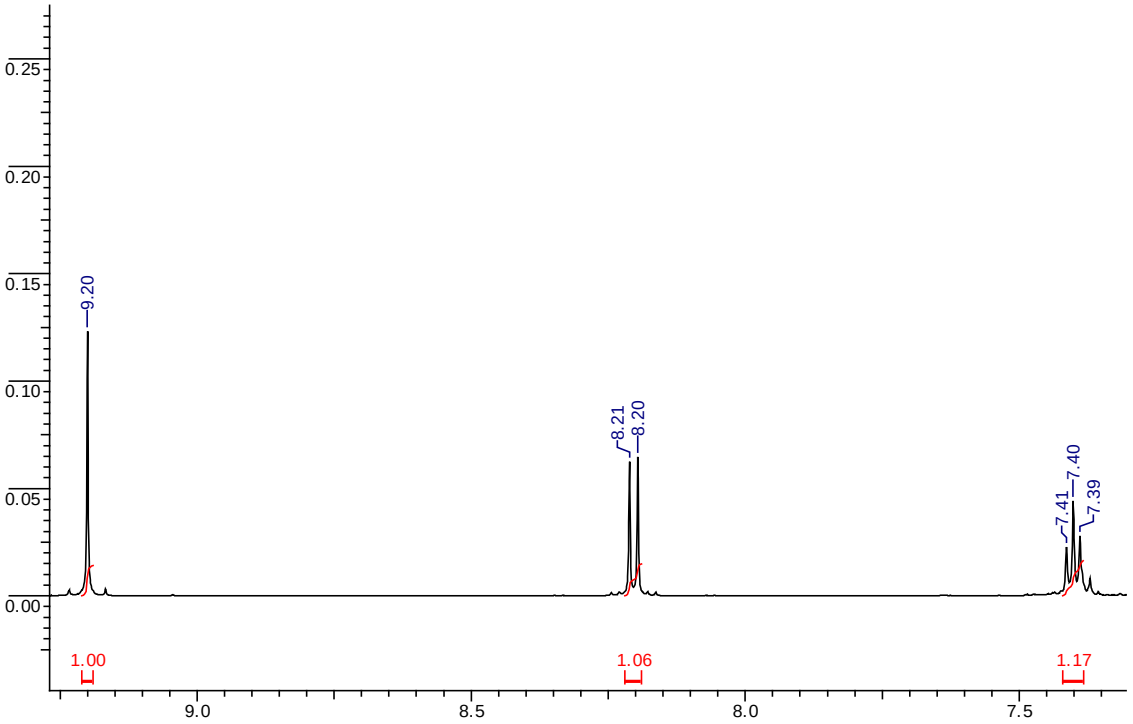
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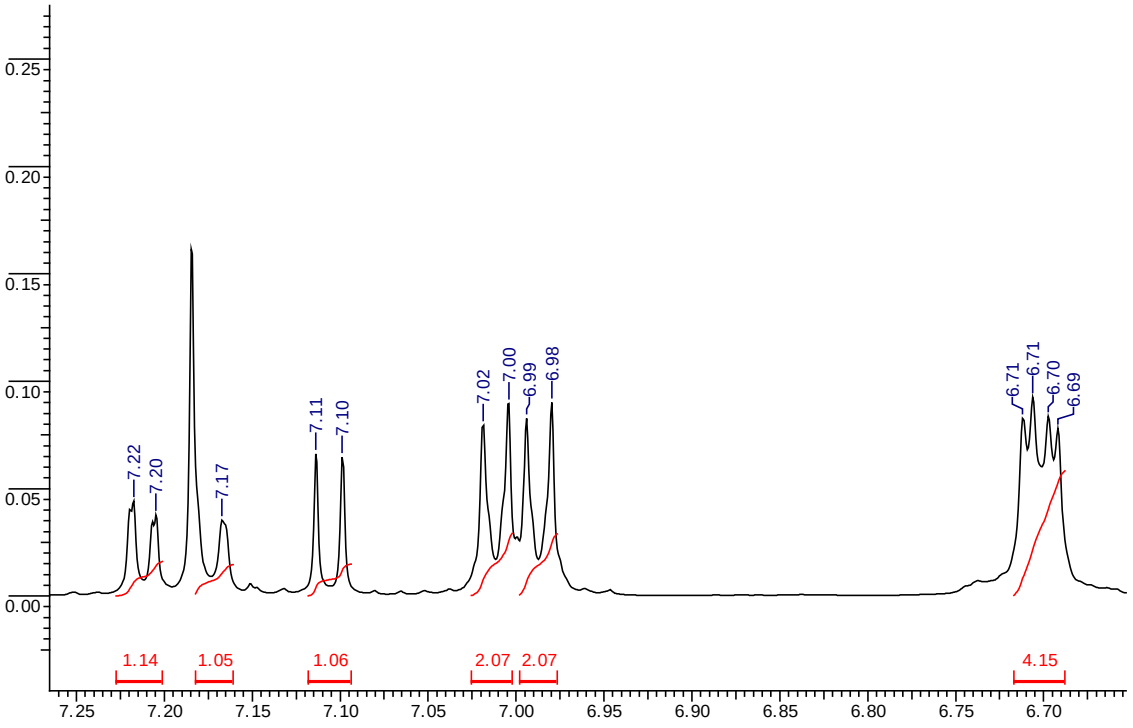
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6.98
6.71
6.71
6.70
6.69
1.14
1.05
1.06
2.07
2.07
4.15
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7.10
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6.70

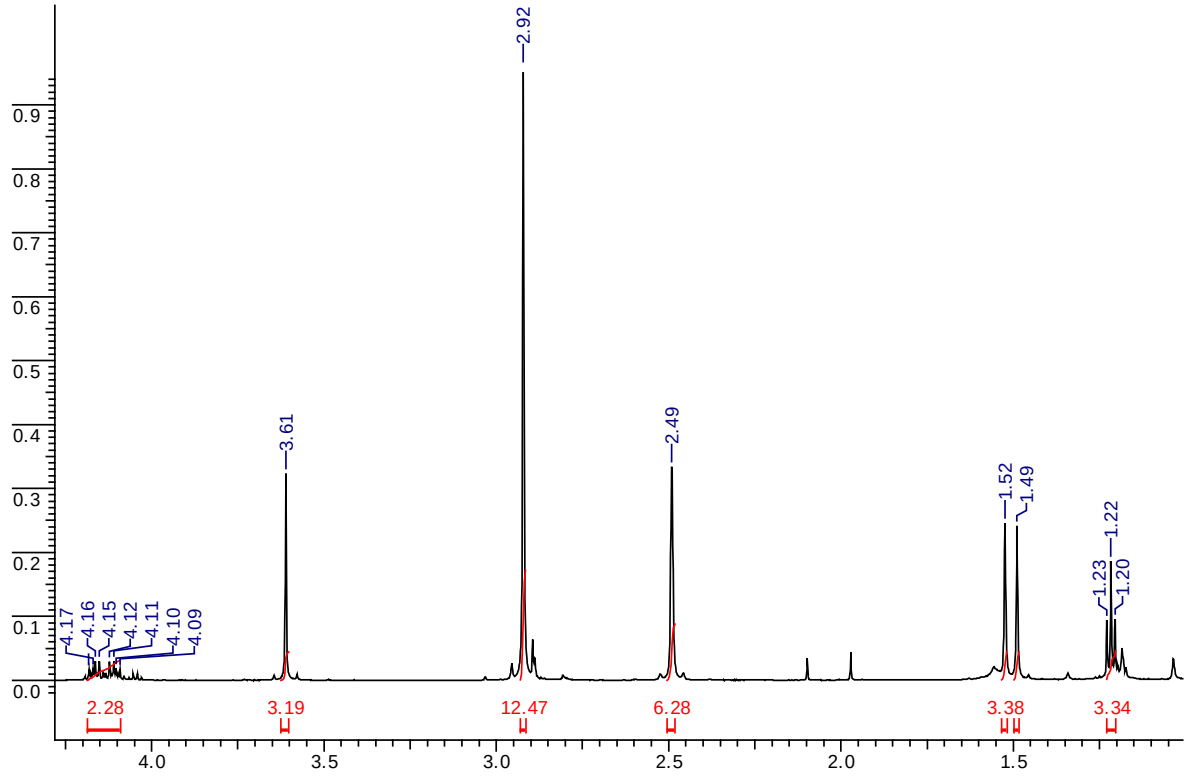


Figure S7: ^{1}H NMR spectrum of **4** in $CDCl_3$.

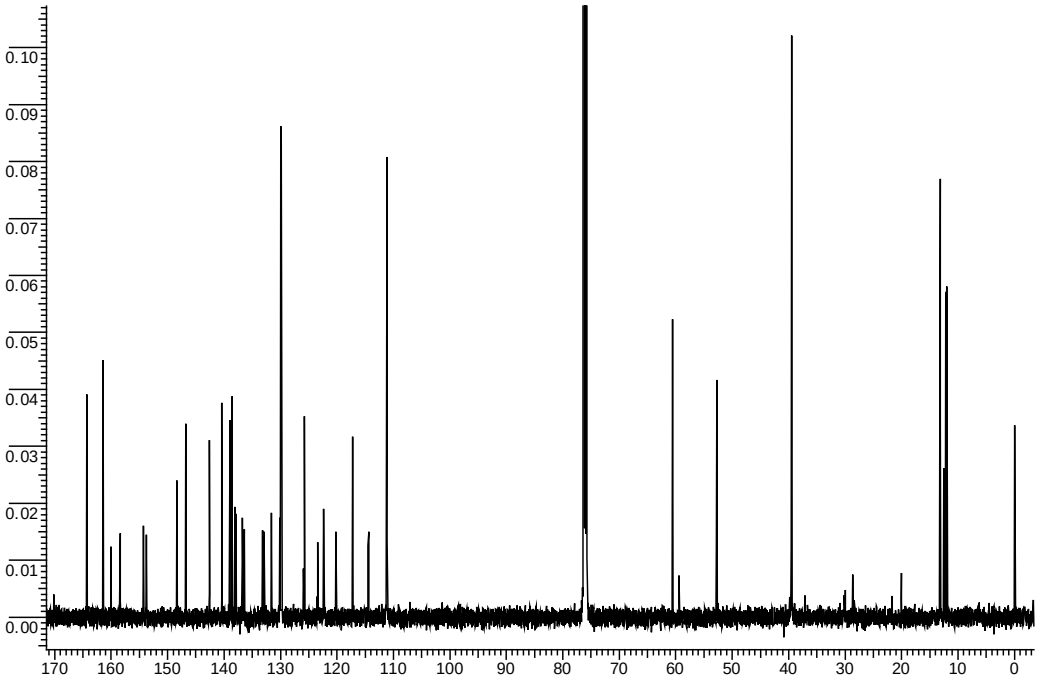


Figure S8: ^{13}C NMR spectrum of **4** in $CDCl_3$.

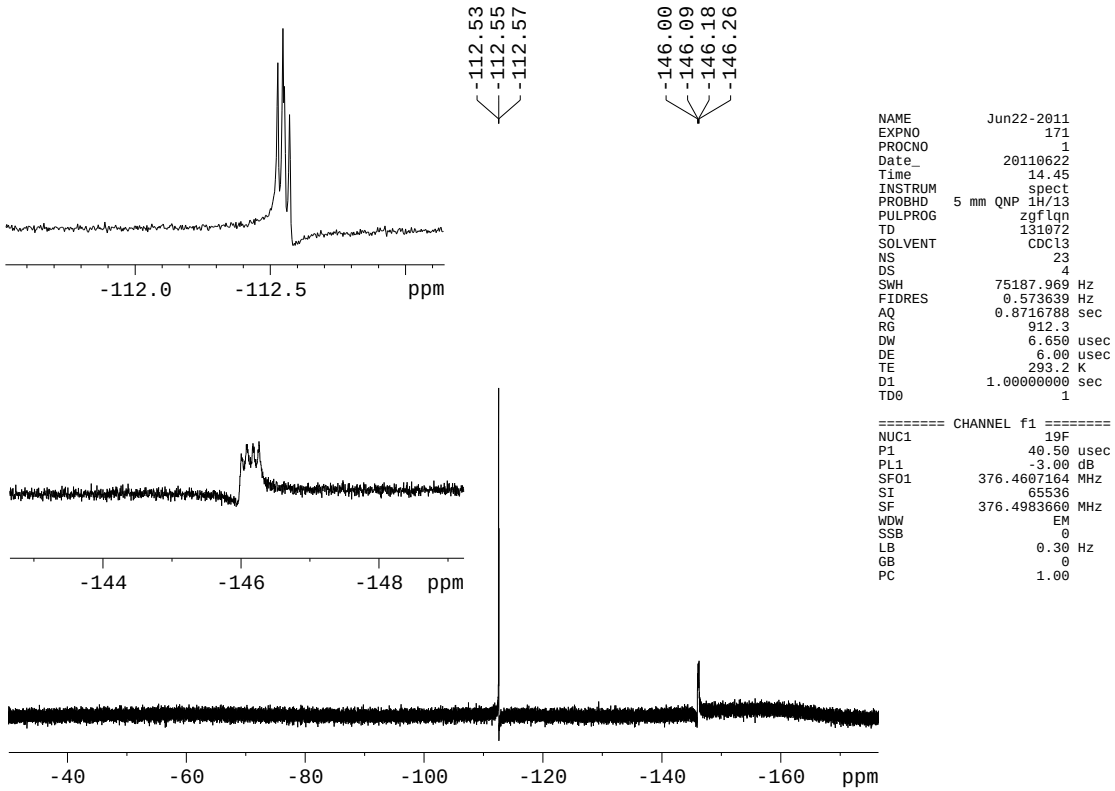
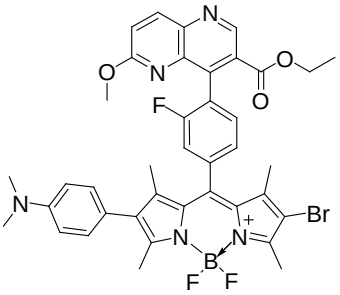


Figure S9: ^{19}F NMR spectrum of **4** in $CDCl_3$.



5

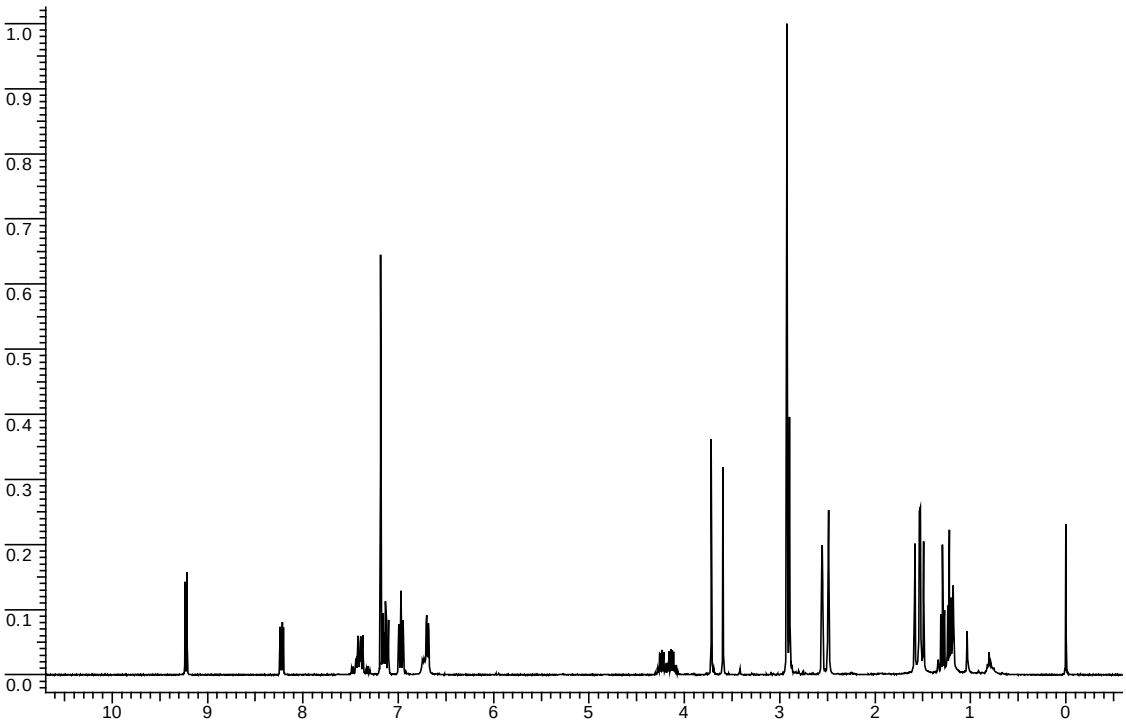


Figure S10: ^{1}H NMR spectrum of **5** in $CDCl_{3.}$

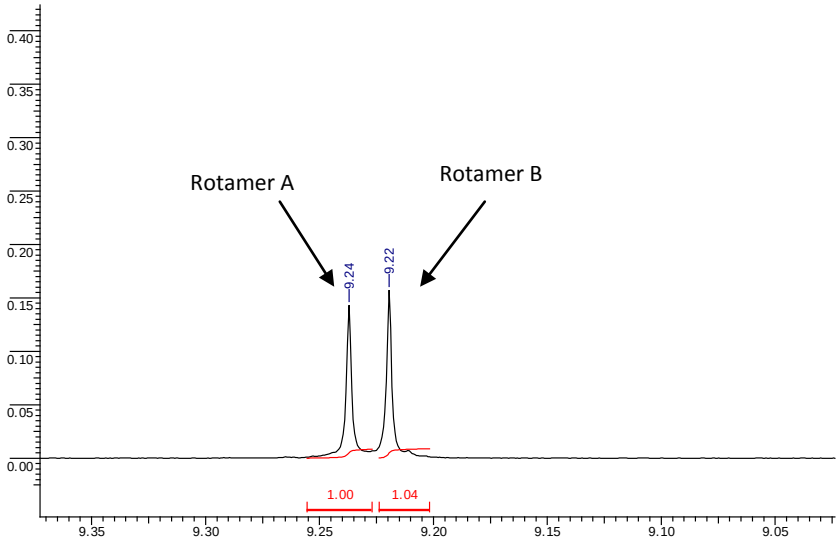


Figure S11: ^{1}H NMR spectrum of **5** in $CDCl_3$.

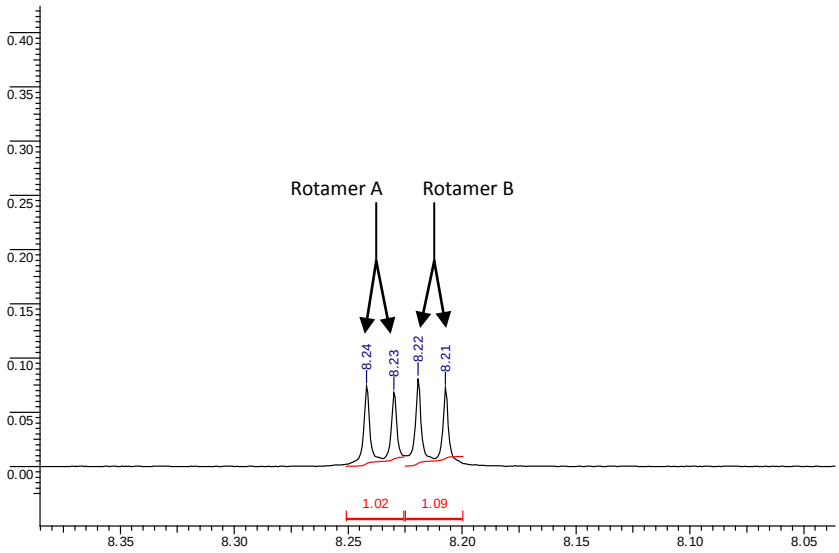


Figure S12: ^{1}H NMR spectrum of **5** in $CDCl_3$.

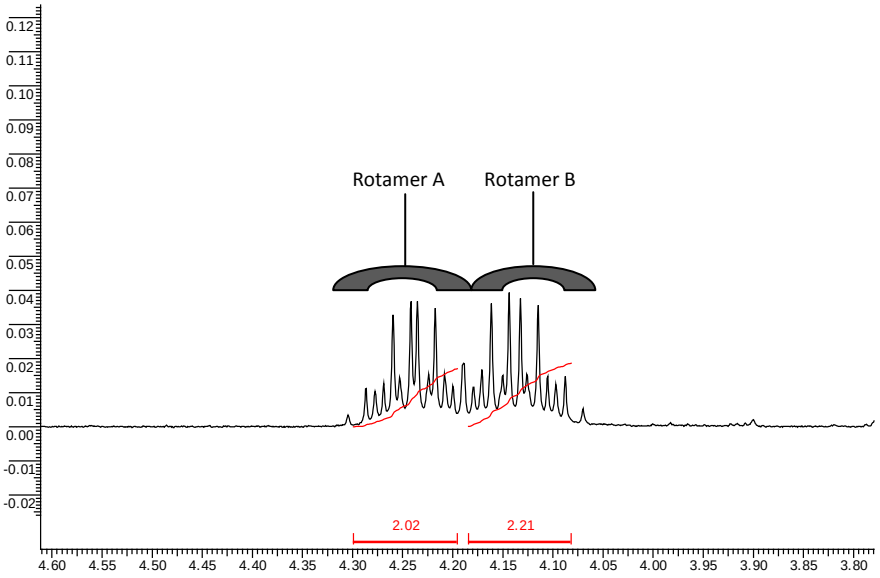


Figure S13: ^{1}H NMR spectrum of **5** in $CDCl_3$.

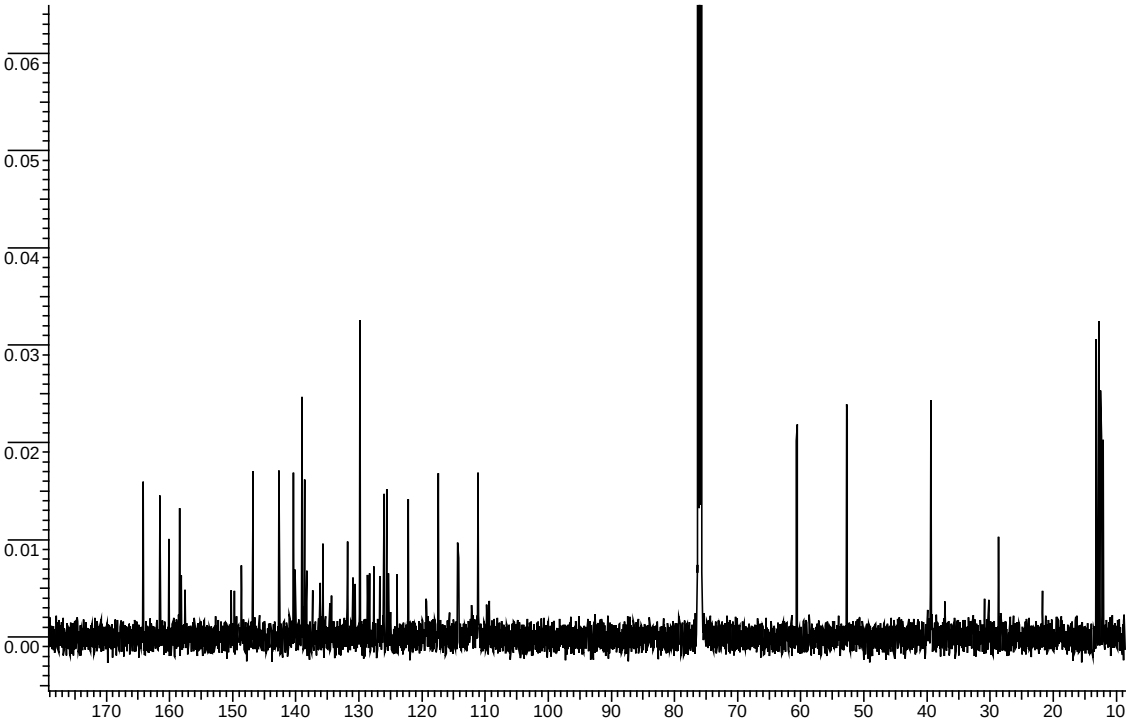


Figure S14: ^{13}C NMR spectrum of **5** in $CDCl_3$.

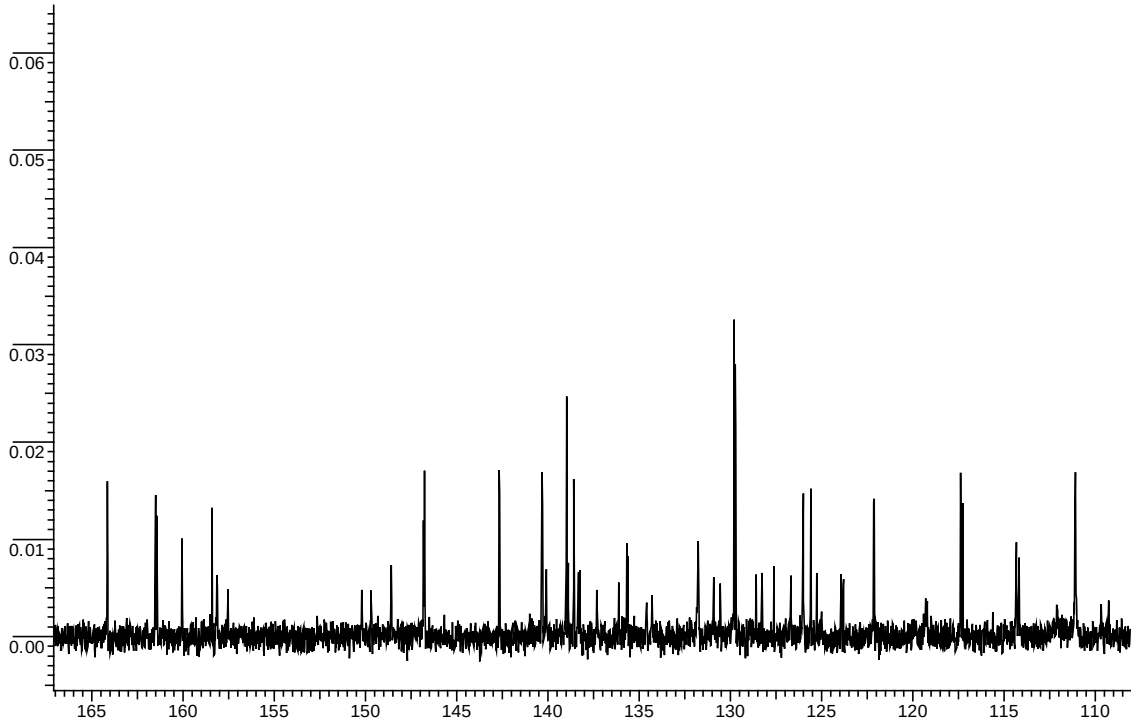


Figure S15: ^{13}C NMR spectrum of **5** in $CDCl_3$.

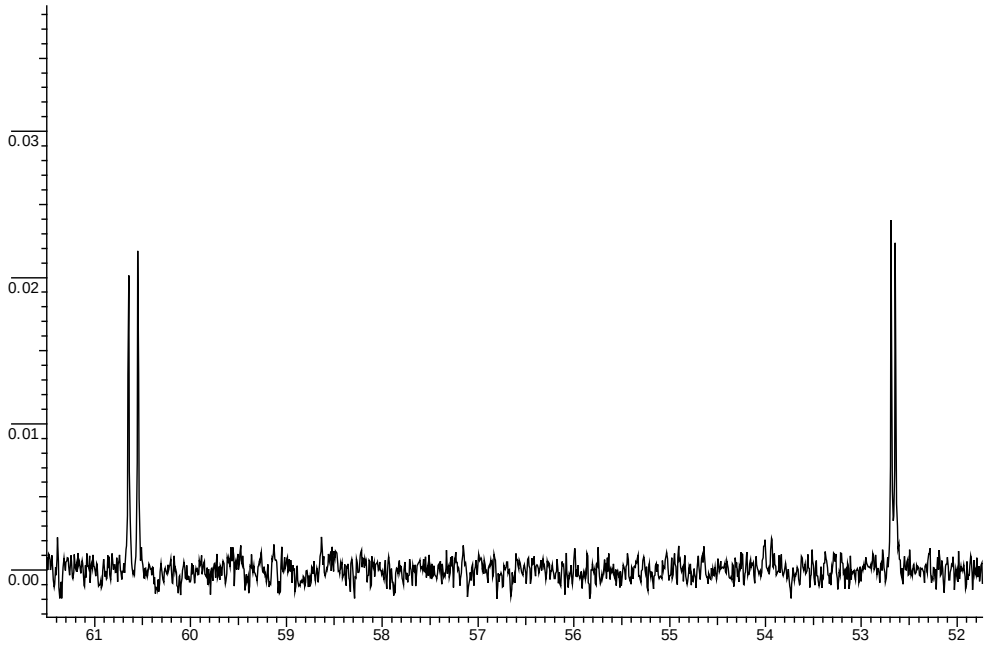


Figure S16: ^{13}C NMR spectrum of **5** in $CDCl_3$.

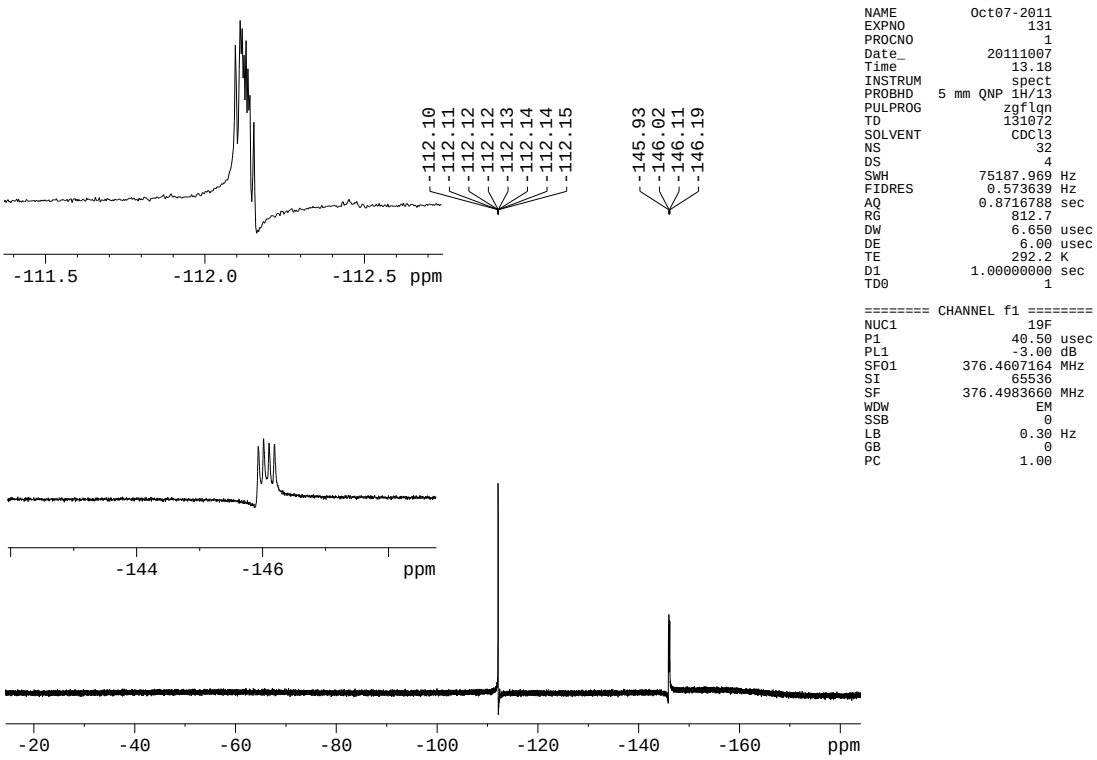
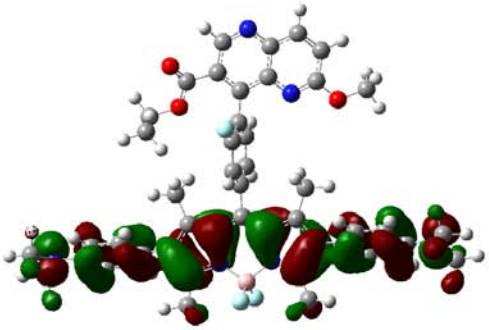
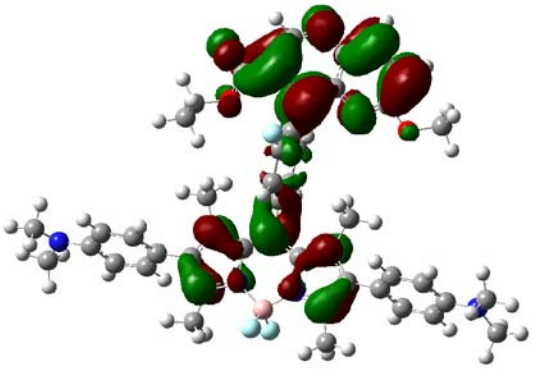


Figure S17: ^{19}F NMR spectrum of **5** in $CDCl_3$.

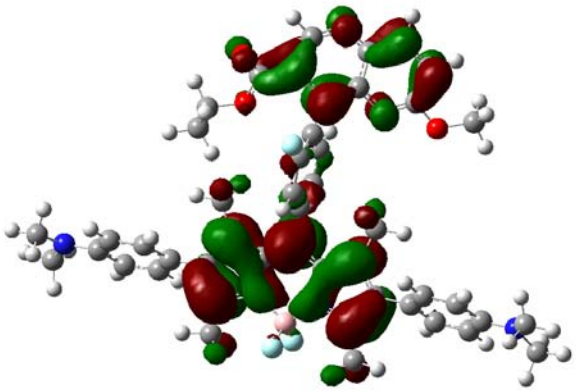
4. MO diagrams from DFT calculations



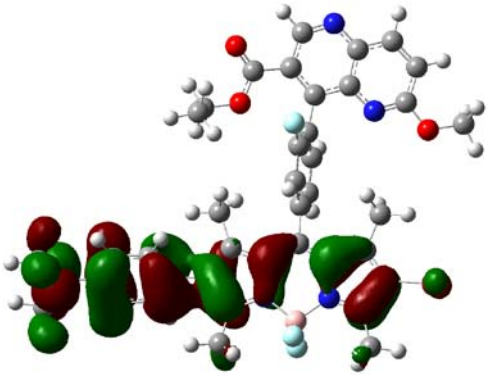
(a)



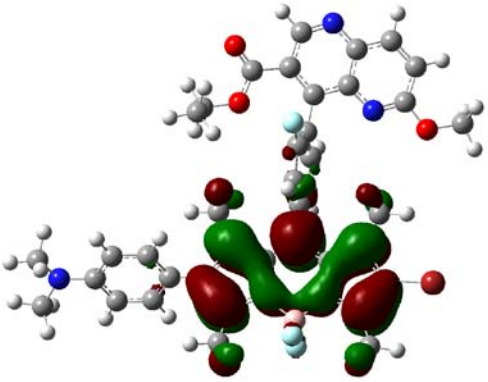
(b)



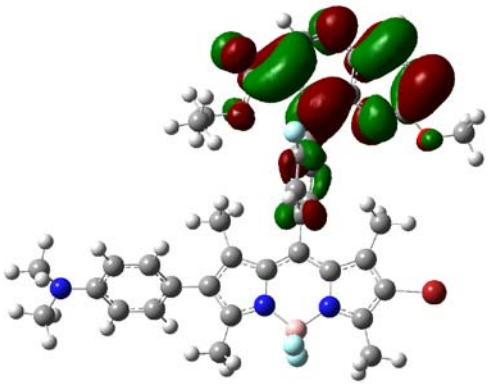
(c)



(d)



(e)



(f)

Figure S18. Frontier Molecular Orbital Calculated for **4** (a)HOMO, (b) LUMO, (c) LUMO+1 and **5** (d) HOMO, (e) LUMO, (f) LUMO+1

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