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Supporting Information

Rhodium-catalyzed annulation of pyrrole substituted BODIPYs with alkynes to access π-extended polycyclic heteroaromatic molecules and NIR absorption

Bixiang Zhou, Mengjie Guo, Qingjie Pan, Mingbo Zhou,* Ling Xu, Yutao Rao, Kaisheng Wang, Bangshao Yin, Jie Zhou, and Jianxin Song*

College of Chemistry and Chemical Engineering, Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research, Ministry of Education of China, Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, Hunan Normal University, Changsha, Hunan 410081, P. R. China

E-mail: zhoumingbo@hunnu.edu.cn, and jxsong@hunnu.edu.cn

Table of Contents

1 Instrumentation and Materials 2

2 General Procedure for the Rh-catalyzed Cyclization Reaction of 3-pyrrolyl BODIPY with Alkynes 2

3 General Procedure for the Rh-catalyzed Cyclization Reaction of 3,5-dipyrrolyl BODIPY with Alkynes 7

4 Synthesis of Dimer **6**.....13

5 NMR Spectra 14

6 Photophysical Data 34

7 Electrochemical Data 38

8 X-Ray Crystal Data.....41

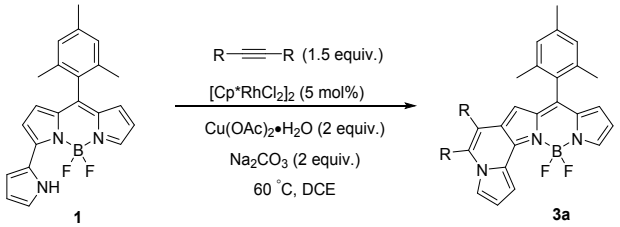
9 DFT/Calculation 48

10 References.....54

1 Instrumentation and Materials

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Bruker AVANCE-500 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ as internal reference for ^{1}H NMR (δ = 7.26 ppm), ^{13}C NMR (δ = 77.00 ppm) or CD_2Cl_2 as internal reference for ^{1}H NMR (δ = 5.30 ppm). UV/Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Photoluminescence spectra were recorded on a Thermo Scientific Lumina. The fluorescent quantum yields were measured in CH_2Cl_2 using an integrating sphere by an Edinburgh FLS1000 machine. MALDI-TOF mass spectra were obtained with a Bruker ultrafleXtreme MALDI-TOF/TOF spectrometer with matrix. Redox potentials were measured by cyclic voltammetry on a CHi-730D scanning electrochemical microscope. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. 3-pyrrolyl-8-mesityl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (3-pyrrolyl-BODIPY) and 8-mesityl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (3,5-dipyrrolyl-BODIPY) were prepared according to the related literatures.[1] Anhydrous dichloromethane (CH_2Cl_2) was distilled from CaH_2 and nitromethane CH_3NO_2 was distilled from P_2O_5.

2 General Procedure for the Rh-catalyzed Cyclization Reaction of 3-pyrrolyl BODIPY with Alkynes

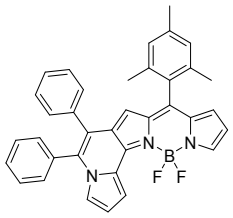


To a 10 mL Schlenk tube was added 3-pyrrolyl BODIPY **1** (0.15 mmol), alkyne (0.225 mmol), $[Cp^*RhCl_2]_2$ (4.6 mg, 7.5 μmol), Na_2CO_3 (31.8 mg, 0.30 mmol), $Cu(OAc)_2 \cdot H_2O$ (59.9 mg, 0.30 mmol in 1,2-dichloroethane (3.0 mL) under air. The tube was sealed with a teflon-coated screw cap and the reaction solution was heated at 60 °C for 8 h. The mixture was then cooled to ambient temperature, diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2. The solvent was removed under reduced pressure and the residue was

purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide the desired product.

Following the general procedure, the mixture of 3-pyrrolyl BODIPY **1** (56.3 mg, 0.15 mmol), diphenylacetylene (40.1 mg, 0.225 mmol), $[Cp^*RhCl_2]_2$ (4.64 mg, 7.50 μmol), $Cu(OAc)_2 \cdot H_2O$ (59.9 mg, 0.30 mmol), Na_2CO_3 (31.8 mg, 0.30 mmol) in 1,2-dichloroethane (3.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **3a** (70.1 mg) as red solid in 85% yield.

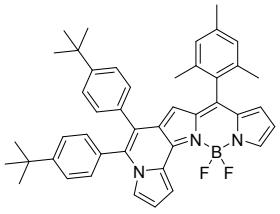
3a: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (br, 1H), 7.83 (s, 1H), 7.31 (br, 3H), 7.22 (br, 2H), 7.18 - 7.12 (m, 3H),



7.08- 7.05 (m, 2H), 6.99 - 6.96(m, 1H), 6.90 (s, 2H), 6.68 - 6.65 (m, 1H), 6.47-6.43 (m, 3H), 2.32 (s, 3H), 2.10 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 144.1, 142.2, 140.9, 138.4, 137.9, 136.6, 135.9, 135.7, 133.1, 132.6, 130.9, 130.4, 130.3, 128.8, 128.7, 128.6, 128.1, 128.0, 126.9, 126.6, 122.9, 122.8, 122.4, 118.5, 117.7, 114.8, 114.7, 114.6, 113.8, 21.1, 20.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 416 (9487), 502 (11380), 623 (42557), 674 (43551) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{36}H_{28}BF_2N_3$ 551.2344; Found 551.2319.

Following the general procedure, the mixture of 3-pyrrolyl BODIPY **1** (56.3 mg, 0.15 mmol), 1,2-bis(4-(*tert*-butyl)phenyl)acetylene (63.4 mg, 0.225 mmol), $[Cp^*RhCl_2]_2$ (4.64 mg, 7.50 μmol), $Cu(OAc)_2 \cdot H_2O$ (59.9 mg, 0.30 mmol), Na_2CO_3 (31.8 mg, 0.30 mmol) in 1,2-dichloroethane (3.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **3b** (86.2 mg) as purple solid in 87% yield.

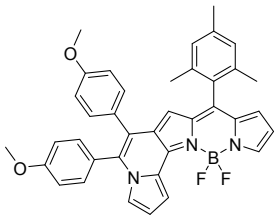
3b: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (br, 1H), 7.81 (s, 1H), 7.27 (s, 2H), 7.15 - 7.05 (m, 5H), 6.96 - 6.90 (m,



4H), 6.67 - 6.63 (m, 1H), 6.54 (s, 1H), 6.45 - 6.41 (m, 2H), 2.32 (s, 3H), 2.12 (s, 6H), 1.27 (s, 9H), 1.22 (s, 9H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 151.7, 149.6, 144.5, 141.8, 140.4, 138.3, 137.9, 136.8, 135.6, 132.9, 132.9, 130.6, 130.5, 130.2, 130.1, 128.9, 128.1, 126.2, 125.2, 124.6, 123.0, 122.8, 122.7, 118.5, 117.4, 115.0, 114.9, 114.9, 113.7, 34.6, 34.4, 31.2, 31.2, 21.1, 20.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 417 (6914), 508 (9455), 628 (29417), 679 (28541) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{44}H_{44}BF_2N_3$ 663.3596; Found 663.3594.

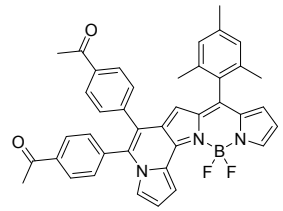
Following the general procedure, the mixture of 3-pyrrolyl BODIPY **1** (56.3 mg, 0.15 mmol), 1,2-bis(4-methoxyphenyl)acetylene (53.6 mg, 0.225 mmol), $[Cp^*RhCl_2]_2$ (4.64 mg, 7.50 μmol), $Cu(OAc)_2 \cdot H_2O$ (59.9 mg, 0.30 mmol), Na_2CO_3 (31.8 mg, 0.30 mmol) in 1,2-dichloroethane (3.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **3c** (79.4 mg) as red solid in 86% yield.

3c: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (br, 1H), 7.81 (s, 1H), 7.15 - 7.12 (m, 2H), 7.01 - 6.96 (m, 3H), 6.91 (s, 2H), 6.86 - 6.82 (m, 2H), 6.72 - 6.68 (m, 2H), 6.65 (m, 1H), 6.46 - 6.42 (m, 3H), 3.80 (s, 3H), 3.73 (s, 3H), 2.33 (s, 3H), 2.10 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 159.6, 158.2, 144.3, 141.9, 140.5, 138.3, 137.9, 136.7, 135.6, 132.4, 132.1, 131.4, 130.4, 129.2, 128.2, 128.1, 126.3, 125.4, 122.8, 122.8, 122.5, 118.2, 117.5, 114.9, 114.8, 114.8, 114.1, 113.7, 113.5, 55.2, 55.0, 21.1, 20.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 417 (8545), 502 (11694), 628 (35627), 677 (34605) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{38}H_{32}BF_2N_3O_2$ 611.2556; Found 611.2553.



Following the general procedure, the mixture of 3-pyrrolyl BODIPY **1** (56.3 mg, 0.15 mmol), 1,2-bis(4-carboxymethyl)acetylene (59.0 mg, 0.225 mmol), $[Cp^*RhCl_2]_2$ (4.64 mg, 7.50 μmol), $Cu(OAc)_2 \cdot H_2O$ (59.9 mg, 0.30 mmol), Na_2CO_3 (31.8 mg, 0.30 mmol) in 1,2-dichloroethane (3.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **3d** (53.9 mg) as red solid in 56% yield.

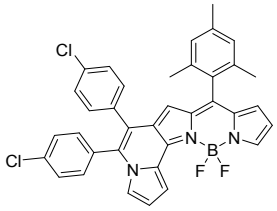
3d: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (br, 4H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.94 - 6.89 (m, 3H), 6.72 - 6.68 (m, 1H), 6.52 (d, *J* = 4.0 Hz, 1H), 6.50 - 6.46 (m, 1H), 6.37 (s, 1H), 2.59 (s, 3H), 2.52 (s, 3H), 2.32 (s, 3H), 2.10 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.6, 197.2, 143.5, 143.1, 142.2, 140.6, 138.6, 137.7, 137.6, 137.3, 136.6, 136.0, 135.9, 131.3, 131.2, 130.6, 130.0, 128.8, 128.3, 128.2, 127.7, 127.4, 123.1, 122.4, 121.6, 118.4, 118.0, 114.3, 26.6, 26.5, 21.1, 20.0 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 415 (10025), 492 (10069), 617 (46537), 667 (51050) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{40}H_{32}BF_2N_3O_2$ 635.2556; Found



635.2543.

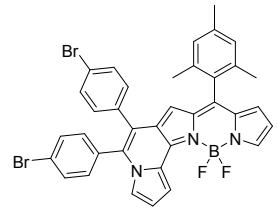
Following the general procedure, the mixture of 3-pyrrolyl BODIPY **1** (56.3 mg, 0.15 mmol), 1,2-bis(4-chlorophenyl)acetylene (55.6 mg, 0.225 mmol), $[Cp^*RhCl_2]_2$ (4.64 mg, 7.50 μmol), $Cu(OAc)_2 \cdot H_2O$ (59.9 mg, 0.30 mmol), Na_2CO_3 (31.8 mg, 0.30 mmol) in 1,2-dichloroethane (3.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **3e** (78.7 mg) as red solid in 84% yield.

3e: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (br, 1H), 7.86 (s, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.18 - 7.14 (m, 4H), 6.99 - 6.97 (m, 2H), 6.94 - 6.92 (m, 3H), 6.70 - 6.67 (m, 1H), 6.51 (d, *J* = 4.0 Hz, 1H), 6.47 - 6.45 (m, 1H), 6.36 (s, 1H), 2.34 (s, 3H), 2.09 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 143.6, 142.8, 141.8, 138.5, 137.7, 136.6, 135.9, 135.1, 134.1, 133.1, 132.2, 131.8, 131.6, 131.3, 131.3, 130.1, 129.2, 128.5, 128.3, 128.2, 127.9, 127.3, 123.0, 122.4, 121.7, 118.1, 118.1, 117.8, 114.5, 114.4, 114.4, 114.1, 21.1, 20.0 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 415 (12472), 494 (13360), 618 (57882), 668 (63348) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{36}H_{26}BF_2N_3Cl_2$ 619.1565; Found 619.1561.



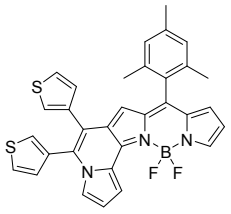
Following the general procedure, the mixture of 3-pyrrolyl BODIPY **1** (56.3 mg, 0.15 mmol), 1,2-bis(4-bromophenyl)acetylene (75.6 mg, 0.225 mmol), $[Cp^*RhCl_2]_2$ (4.64 mg, 7.50 μmol), $Cu(OAc)_2 \cdot H_2O$ (59.9 mg, 0.30 mmol), Na_2CO_3 (31.8 mg, 0.30 mmol) in 1,2-dichloroethane (3.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **3f** (77.3 mg) as red solid in 73% yield.

3f: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (br, 1H), 7.87 (s, 1H), 7.51 - 7.47 (m, 2H), 7.34 - 7.29 (m, 2H), 7.12 - 7.07 (m, 2H), 6.95 - 6.91 (m, 5H), 6.70 - 6.67 (m, 1H), 6.51 (d, *J* = 4.0 Hz, 1H), 6.47 (br, 1H), 6.37 (s, 1H), 2.34 (s, 3H), 2.10 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 143.6, 142.9, 141.8, 138.5, 137.7, 136.6, 135.9, 134.6, 132.4, 132.2, 131.9, 131.8, 131.5, 131.2, 130.1, 128.2, 127.8, 127.4, 123.4, 123.0, 122.4, 121.7, 121.4, 118.2, 117.7, 114.4, 114.4, 114.1, 21.1, 20.0 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 416 (9804), 495 (11380), 623 (42557), 674 (43551) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{36}H_{26}BF_2N_3Br_2$ 707.0555; Found 707.0540.



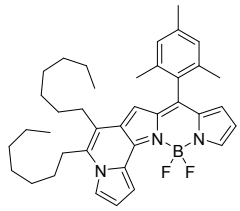
Following the general procedure, the mixture of 3-pyrrolyl BODIPY **1** (56.3 mg, 0.15 mmol), 1,2-bis(thiophen-3-yl)acetylene (42.8 mg, 0.225 mmol), $[Cp^*RhCl_2]_2$ (4.64 mg, 7.50 μmol), $Cu(OAc)_2 \cdot H_2O$ (59.9 mg, 0.30 mmol), Na_2CO_3 (31.8 mg, 0.30 mmol) in 1,2-dichloroethane (3.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **3g** (72.7 mg) as brown solid in 86% yield.

3g: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 (br, 1H), 7.84 (s, 1H), 7.39 - 7.36 (m, 1H), 7.2 (br, 1H), 7.16 - 7.10 (m, 2H), 7.05 - 7.01 (m, 1H), 6.96 - 6.90 (m, 3H), 6.74 - 6.71 (m, 1H), 6.70 - 6.66 (m, 1H), 6.57 (s, 1H), 6.50 - 6.47 (m, 1H), 6.46 - 6.43 (m, 1H), 2.34 (s, 3H), 2.12 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 144.0, 142.3, 141.1, 138.4, 137.8, 136.6, 135.8, 135.7, 133.0, 130.2, 128.9, 128.2, 128.1, 128.1, 127.9, 127.4, 126.8, 126.3, 124.8, 124.4, 122.8, 122.8, 122.1, 117.8, 114.7, 114.7, 114.6, 114.4, 113.9, 21.1, 20.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 417 (11589), 507 (14547), 624 (49719), 674 (50948) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{32}H_{24}BF_2N_3S_2$ 563.1473; Found 563.1464.

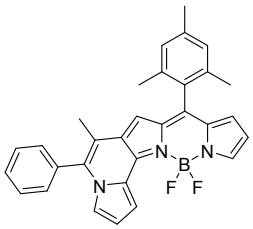


Following the general procedure, the mixture of 3-pyrrolyl BODIPY **1** (56.3 mg, 0.15 mmol), 8-hexadecyne (50.0 mg, 0.225 mmol), $[Cp^*RhCl_2]_2$ (4.64 mg, 7.50 μmol), $Cu(OAc)_2 \cdot H_2O$ (59.9 mg, 0.30 mmol), Na_2CO_3 (31.8 mg, 0.30 mmol) in 1,2-dichloroethane (3.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **3h** (57.5 mg) as red solid in 64% yield.

3h: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.84 (br, 1H), 7.78 (s, 1H), 7.39 - 7.36 (m, 1H), 7.00 (s, 2H), 6.74 - 6.70 (m, 1H), 6.59 (s, 1H), 6.47 - 6.40 (m, 2H), 2.82 (t, J = 8.0 Hz, 2H), 2.55 (t, J = 8.0 Hz, 2H), 2.40 (s, 3H), 2.14 (s, 6H), 1.69 - 1.63 (m, 2H), 1.52 - 1.45 (m, 4H), 1.35 - 1.20 (m, 14H), 0.93 - 0.92 (m, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 144.5, 141.1, 139.9, 138.3, 137.9, 136.9, 135.3, 131.9, 130.6, 128.9, 128.1, 125.7, 122.6, 121.0, 120.3, 117.1, 115.2, 114.7, 114.7, 114.6, 113.8, 31.7, 31.6, 30.2, 29.7, 29.4, 29.1, 29.0, 28.3, 28.0, 27.7, 22.6, 22.6, 21.1, 20.1, 14.0 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 417 (9183), 513 (13443), 633 (35866), 685 (31527) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{38}H_{48}BF_2N_3$ 595.3909; Found 595.3943.

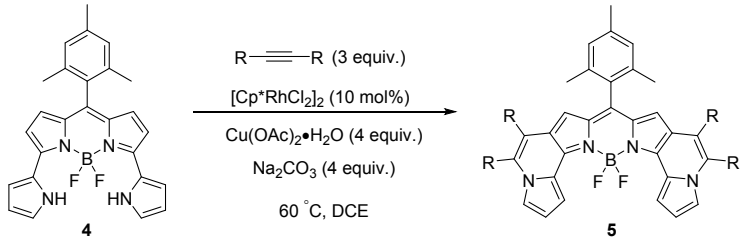


Following the general procedure, the mixture of 3-pyrrolyl BODIPY **1** (56.3 mg, 0.15 mmol), 1-phenyl-1-propyne (26.1 mg, 0.225 mmol), $[Cp^*RhCl_2]_2$ (4.64 mg, 7.50 μmol), $Cu(OAc)_2 \cdot H_2O$ (59.9 mg, 0.30 mmol), Na_2CO_3 (31.8 mg, 0.30 mmol) in 1,2-dichloroethane (3.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **3i** (60.4 mg) as red solid in 82% yield.



3i: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 - 7.79 (m, 2H), 7.52 (m, 3H), 7.37 - 7.33 (m, 2H), 7.00 (s, 2H), 6.80 - 6.77 (m, 1H), 6.66 (s, 1H), 6.59 - 6.55 (m, 1H), 6.46 - 6.51 (m, 1H), 6.44 (br, 1H), 2.39 (s, 3H), 2.17 (s, 6H), 1.95 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 144.4, 141.4, 140.3, 138.4, 137.9, 136.9, 135.4, 133.3, 132.0, 130.9, 130.5, 130.3, 129.4, 129.3, 129.2, 129.2, 128.8, 128.1, 126.0, 122.6, 122.4, 121.5, 117.4, 114.8, 114.7, 113.3, 111.8, 21.2, 20.1, 14.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 416 (8244), 504 (10053), 625 (36453), 676 (35222) nm, HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{31}H_{26}BF_2N_3$ 489.2188; Found 489.2171.

3 General Procedure for the Rh-catalyzed Cyclization Reaction of 3,5-dipyrrolyl BODIPY with Alkynes

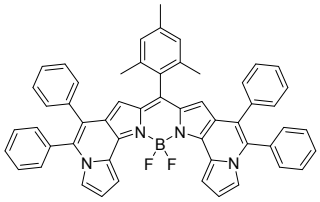


To a 10 mL Schlenk tube was added 3,5-dipyrroly BODIPY **4** (0.10 mmol), alkyne (0.30 mmol), $[Cp^*RhCl_2]_2$ (6.18 mg, 10.0 μmol), $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.40 mmol), Na_2CO_3 (42.4 mg, 0.40 mmol) in 1,2-dicholorethane (3.0 mL) under air. The tube was sealed with a teflon-coated screw cap and the reaction solution was heated at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide the desired product.

Following the general procedure, the mixture of 3,5-dipyrroly BODIPY **4** (44.0 mg, 0.10 mmol), diphenylacetylene (53.5mg, 0.30 mmol), $[Cp^*RhCl_2]_2$ (6.18 mg, 10.0 μmol), Na_2CO_3 (42.40 mg, 0.40 mmol), $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.40 mmol) in 1,2-dichloroethane (4.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column

chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **5a** (56.1 mg) as black solid in 70% yield.

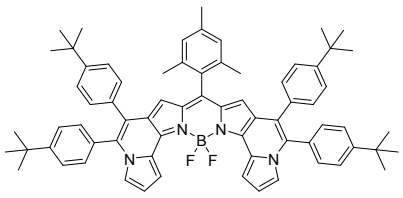
5a: ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 7.98 (br, 2H), 7.38 - 7.34 (m, 6H), 7.33 - 7.29 (m, 4H), 7.19 - 7.12 (m, 10H),



7.01 - 6.98 (m, 2H), 6.89 (s, 2H), 6.73 - 6.70 (m, 2H), 6.20 (s, 2H), 2.28 (s, 3H), 2.14 (s, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.2, 138.5, 138.0, 137.9, 136.8, 136.2, 133.5, 132.1, 131.0, 130.6, 130.5, 128.6, 128.6, 128.3, 128.2, 127.9, 126.7, 123.4, 121.2, 120.0, 118.5, 113.5, 113.1, 113.0, 113.0, 21.1, 20.1 ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 366 (33260), 541 (28540), 717 (57220), 794 (178160) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{54}H_{39}BF_2N_4$ 792.3236; Found 792.3255.

Following the general procedure, the mixture of 3,5-dipyrroly BODIPY **4** (44.0 mg, 0.10 mmol), 1,2-bis(4-(*tert*-butyl)phenyl)acetylene (87.1 mg, 0.30 mmol), $[Cp^*RhCl_2]_2$ (6.18 mg, 10.0 μmol), Na_2CO_3 (42.40 mg, 0.40 mmol), $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.40 mmol) in 1,2-dichloroethane (4.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **5b** (76.7 mg) as black solid in 75% yield.

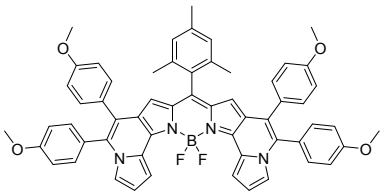
5b: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.05 (br, 2H), 7.28 - 7.26 (m, 4H), 7.13 - 7.08 (m, 8H), 7.06-7.04 (m, 2H), 6.98



- 6.94 (m, 4H), 6.87 (s, 2H), 6.69 - 6.66 (m, 2H), 6.34 (s, 2H), 2.27 (s, 3H), 2.14 (s, 6H), 1.27 (s, 18H), 1.22 (s, 18H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 151.5, 149.4, 142.3, 138.5, 137.9, 137.5, 137.1, 133.4, 132.3, 131.0, 130.7, 130.7, 130.2, 128.2, 128.1, 125.2, 124.5, 123.3, 121.3, 119.9, 118.5, 113.4, 112.9, 34.6, 34.4, 31.2, 21.0, 20.2 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 368 (29200), 543 (26000), 727 (53340), 801 (151720) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{70}H_{71}BF_2N_4$ 1016.5740; Found 1016.5723.

Following the general procedure, the mixture of 3,5-dipyrroly BODIPY **4** (44.0 mg, 0.10 mmol), 1,2-bis(4-methoxyphenyl (71.49 mg, 0.30 mmol), $[Cp^*RhCl_2]_2$ (6.18 mg, 10.0 μmol), Na_2CO_3 (42.40 mg, 0.40 mmol), $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.40 mmol) in 1,2-dichloroethane (4.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **5c** (64.3 mg) as black solid in 70% yield.

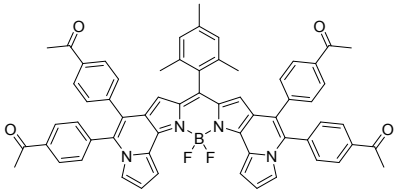
5c: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.03 (br, 2H), 7.15 - 7.12 (m, 4H), 7.00 - 6.97 (m, 4H), 6.98 - 6.97 (m, 2H),



6.86 - 6.84 (m, 4H), 6.85 - 6.82 (br, 2H), 6.70 - 6.68 (m, 4H), 6.67 - 6.65(m, 2H), 6.22 (s, 2H), 3.80 (s, 6H), 3.73 (s, 6H), 2.28 (s, 3H), 2.10 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 159.2, 157.8, 141.9, 138.2, 137.7, 137.3, 136.7, 132.0, 131.6, 131.3, 130.5, 128.5, 128.4, 127.9, 125.6, 123.1, 120.9, 119.6, 118.0, 113.8, 113.1, 54.9, 54.8, 31.3, 22.4, 20.8, 19.9, 13.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 367 (19505), 542 (17617), 725 (35701), 800 (105860) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{58}H_{47}BF_2N_4O_4$ 912.3658; Found 912.3689.

Following the general procedure, the mixture of 3,5-dipyrroly BODIPY **4** (44.0 mg, 0.10 mmol), 1,2-bis(4-carboxymethyl)acetylene (78.7 mg, 0.30 mmol), $[Cp^*RhCl_2]_2$ (6.18 mg, 10.0 μmol), Na_2CO_3 (42.40 mg, 0.40 mmol), $Cu(OAc)_2{\cdot}H_2O$ (79.9 mg, 0.40 mmol) in 1,2-dichloroethane (4.0 mL) under air at 85 °C for 20 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **5d** (39.0 mg) as red solid in 41% yield.

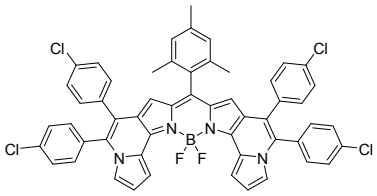
5d: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.08 (br, 2H), 7.92 (d, *J* = 8.0 Hz, 4H), 7.75 (d, *J* = 8.0 Hz, 4H), 7.36 (d, *J* =



8.0 Hz, 4H), 7.17 (d, *J* = 8.0 Hz, 4H), 6.95 -6.90 (m, 2H), 6.86 (s, 2H), 6.75 - 6.70 (m, 2H), 6.20 (s, 2H), 2.60 (s, 6H), 2.52 (s, 6H), 2.28 (s, 3H), 2.09 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.7, 197.3, 142.3, 140.9, 138.7, 138.4, 137.8, 137.2, 136.8, 135.8, 131.3, 131.1, 130.6, 130.2, 128.8, 128.3, 128.2, 127.6, 123.5, 121.1, 120.0, 118.1, 114.2, 113.5, 26.6, 26.5, 21.1, 20.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 347 (27327), 365 (30808), 539 (28038), 714 (54692), 789 (175038) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{62}H_{47}BF_2N_4O_4$ 960.3658; Found 960.3658.

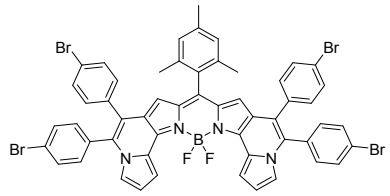
Following the general procedure, the mixture of 3,5-dipyrroly BODIPY **4** (44.0 mg, 0.10 mmol), 1,2-bis(4-chlorophenyl)acetylene (74.1 mg, 0.30 mmol), $[Cp^*RhCl_2]_2$ (6.18 mg, 10.0 μmol), Na_2CO_3 (42.40 mg, 0.40 mmol), $Cu(OAc)_2{\cdot}H_2O$ (79.9 mg, 0.40 mmol) in 1,2-dichloroethane (4.0 mL) under air at 60 °C for 8 h. Purified by silica-

gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **5e** (39.7 mg) as black solid in 42% yield.



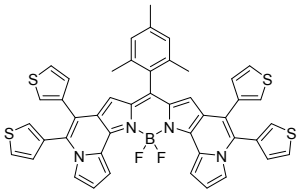
5e: ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.94 (br, 2H), 7.34 (d, *J* = 8.5 Hz, 4H), 7.21 (d, *J* = 8.0 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 4H), 7.02 (d, *J* = 8.5 Hz, 4H), 6.96 - 6.93 (d, *J* = 3.0 Hz, 2H), 6.87 (s, 2H), 6.72 - 6.69 (m, 2H), 6.17 (s, 2H), 2.27 (s, 3H), 2.09 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 136.8, 135.1, 132.3, 131.7, 131.0, 129.2, 128.5, 128.4, 121.1, 119.9, 113.9, 21.2, 20.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 366 (20485), 539 (18059), 714 (36554), 789 (110525) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{54}H_{35}BF_2N_4Cl_4$ 928.1677; Found 928.1677.

Following the general procedure, the mixture of 3,5-dipyrroly BODIPY **4** (44.0 mg, 0.10 mmol), 1,2-bis(4-bromophenyl)acetylene (100.8 mg, 0.30 mmol), $[Cp^*RhCl_2]_2$ (6.18 mg, 10.0 μmol), Na_2CO_3 (42.40 mg, 0.40 mmol), $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.40 mmol) in 1,2-dichloroethane (4.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **5f** (49.5 mg) as red solid in 44% yield.



5f: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.04 (s, 2H), 7.49 (d, *J* = 8.0 Hz, 4H), 7.31 (d, *J* = 8.0 Hz, 4H), 7.10 (d, *J* = 8.0 Hz, 4H), 6.95 - 6.85 (m, 8H), 6.71 (s, 2H), 6.18 (s, 2H), 2.32 (s, 3H), 2.09 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.2, 138.6, 136.8, 134.8, 132.5, 132.2, 132.0, 131.9, 131.4, 130.9, 130.3, 128.3, 127.8, 123.4, 123.3, 121.3, 121.1, 119.9, 117.7, 114.0, 113.4, 21.2, 20.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 366 (22623), 539 (20312), 600 (3974), 714 (40825), 789 (124195) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{54}H_{35}BF_2N_4Br_4$ 1103.9656; Found 1103.9685.

Following the general procedure, the mixture of 3,5-dipyrroly BODIPY **4** (44.0 mg, 0.10 mmol), 1,2-bis(thiophen-3-yl)acetylene (57.1 mg, 0.30 mmol), $[Cp^*RhCl_2]_2$ (6.18 mg, 10.0 μmol), Na_2CO_3 (42.40 mg, 0.40 mmol), $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.40 mmol) in 1,2-dichloroethane (4.0 mL) under air at 85 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **5g** (31.2 mg) as black solid in 38% yield.

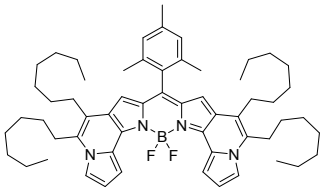


5g: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.04 (br, 2H), 7.40 - 7.35 (m, 2H), 7.21-7.18 (m, 2H), 7.14 - 7.11 (m, 2H), 7.11

- 7.08 (m, 2H), 7.05 (d, J = 5.0 Hz, 2H), 6.96 - 6.93 (m, 2H), 6.90 (s, 2H), 6.74 (d, J = 5.0 Hz, 2H), 6.70 (t, J = 3.5 Hz, 2H), 6.39 (s, 2H), 2.32 (s, 3H), 2.14 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.3, 138.5, 138.2, 138.0, 136.9, 136.3, 133.5, 130.6, 129.1, 128.3, 127.8, 127.4, 127.3, 126.2, 124.6, 124.3, 123.3, 121.1, 120.1, 114.4, 113.7, 113.2, 21.1, 20.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 368 (30620), 541 (27700), 720 (55480), 796 (165440) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{46}H_{31}BF_2N_4S_4$ 816.1493; Found 816.1527.

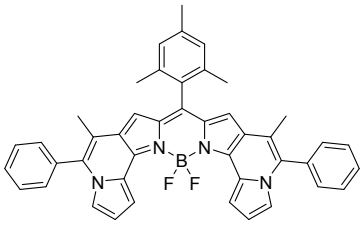
Following the general procedure, the mixture of 3,5-dipyrroly BODIPY **4** (44.0 mg, 0.10 mmol), 8-hexadecyne (66.7 mg, 0.30 mmol), $[Cp^*RhCl_2]_2$ (6.18 mg, 10.0 μmol), Na_2CO_3 (42.40 mg, 0.40 mmol), $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.40 mmol) in 1,2-dichloroethane (4.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **5h** (27.7 mg) as red solid in 31% yield.

5h: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.90 (br, 2H), 7.34 - 7.30 (m, 2H), 7.02 (s, 2H), 6.74 - 6.71 (m, 2H), 6.37 (s, 2H), 2.84 - 2.79 (m, 4H), 2.54 (t, J = 8.0 Hz, 4H), 2.43 (s, 3H), 2.17 (s, 6H), 1.69 - 1.61 (m, 4H), 1.52 - 1.42 (m, 9H), 1.35 - 1.23 (m, 26H), 0.92 - 6.84 (m, 13H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.1, 138.2, 138.0, 137.4, 136.5, 131.2, 131.0, 128.1, 123.2, 118.6, 117.7, 115.1, 113.3, 112.4, 31.8, 31.7, 30.2, 29.8, 29.5, 29.1, 29.0, 28.4, 28.1, 27.6, 22.6, 22.6, 21.2, 20.1, 14.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 367 (31028), 547 (29732), 728 (53676), 803 (152789) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{58}H_{79}BF_2N_4$ 880.6366; Found 880.6351.



Following the general procedure, the mixture of 3,5-dipyrroly BODIPY **4** (44.0 mg, 0.10 mmol), 1-phenyl-1-propyne (34.9 mg, 0.30 mmol), $[Cp^*RhCl_2]_2$ (6.18 mg, 10.0 μmol), Na_2CO_3 (42.40 mg, 0.40 mmol), $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.40 mmol) in 1,2-dichloroethane (4.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **5i** (46.1 mg) as black solid in 69% yield.

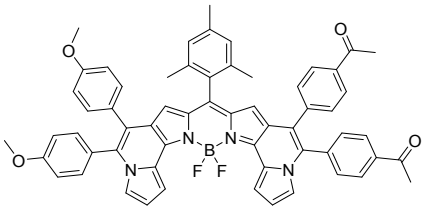
5i: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.95 (br, 2H), 7.58 - 7.46 (m, 6H), 7.36 (d, J = 7.0 Hz, 4H), 7.04 (s, 2H), 6.76 (s, 2H), 6.62 - 6.59 (m, 2H), 6.50 (s, 2H), 2.42 (s, 3H), 2.23 (s, 6H), 1.97 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 142.2, 138.3, 138.2, 137.4, 136.8, 133.8,



131.4, 131.2, 130.4, 129.1, 129.0, 128.7, 128.1, 123.3, 121.0, 118.3, 112.9, 112.7, 111.8, 21.2, 20.1, 14.6 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 366 (34965), 541 (28281), 720 (58842), 794 (172684) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{44}H_{35}BF_2N_4$, 668.2923; Found 667.2924.

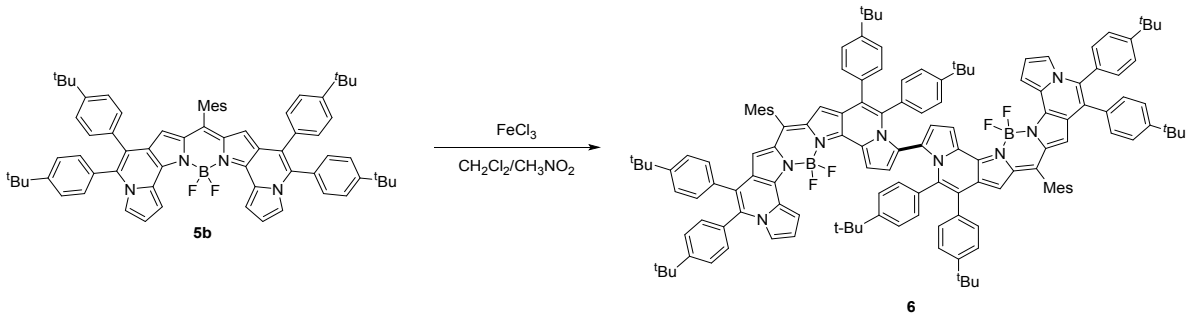
Following the general procedure, the mixture of 3,5-dipyrroly BODIPY **4** (44.0 mg, 0.10 mmol), 1,2-bis(4-methoxyphenyl (35.8 mg, 0.15 mmol), 1,2-bis(4-carboxymethyl)acetylene (39.4 mg, 0.15 mmol), $[Cp^*RhCl_2]_2$ (6.18 mg, 10.0 μmol), Na_2CO_3 (42.40 mg, 0.40 mmol), $Cu(OAc)_2 \cdot H_2O$ (79.9 mg, 0.40 mmol) in 1,2-dichloroethane (4.0 mL) under air at 60 °C for 8 h. Purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **5c** (27.1 mg), **5d** (5.0 mg) and **5k** (14.6 mg) as red solid in 30%, 6%, 15% yields, respectively.

5k: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.09 (br, 1H), 8.03 (br, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H),



7.36 (d, *J* = 8.0 Hz, 2H), 7.19 - 7.12 (m, 4H), 7.00 - 6.96 (m, 3H), 6.90 (br, 1H), 6.87 - 6.82 (m, 4H), 6.74 - 6.70 (m, 2H), 6.70 - 6.65 (m, 2H), 6.26 (s, 1H), 6.16 (s, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 2.60 (s, 3H), 2.52 (s, 3H), 2.28 (s, 3H), 2.10 (s, 6H). ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 197.7, 197.3, 159.6, 158.2, 143.3, 141.3, 139.0, 138.3, 138.2, 138.1, 138.0, 137.2, 136.9, 135.7, 132.4, 132.2, 131.5, 131.4, 130.7, 130.5, 129.6, 128.7, 128.4, 128.3, 128.2, 126.7, 125.6, 123.8, 123.2, 122.2, 120.8, 120.1, 118.9, 118.3, 118.1, 114.1, 113.9, 113.7, 113.5, 112.2, 55.2, 55.1, 26.6, 26.5, 21.1, 20.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 349 (25620), 366 (28580), 531 (26140), 719 (51500), 793 (149180) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{60}H_{47}BF_2N_4O_4$ 936.3658; Found 936.3680.

4 Synthesis of Dimer **6**



5b (102.8 mg, 0.10 mmol) was dissolved in degassed anhydrous DCM (20 mL), and a solution of $FeCl_3$ (56.77 mg, 0.35 mmol) in dry nitromethane (2.0 mL) was added dropwise to the ice bath-cooled solution under the nitrogen atmosphere. The reaction was carried out at room temperature for 1.5 h and then quenched by CH_3OH. The organic layer was washed with saturated brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by silica-gel column chromatography (CH_2Cl_2/*n*-hexane as an eluent) to provide **6** (33.3 mg) as red solid in 33% yield.

6: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.01 (br, 2H), 7.94 (br, 2H), 7.29 -7.26 (m, 4H), 7.25-7.23 (m, 4H), 7.13 - 7.03 (m, 12H), 6.97 - 6.93 (m, 4H), 6.87 (s, 2H), 6.84 - 6.76 (m, 6H), 6.72 (d, *J* = 4.5 Hz, 2H), 6.70 - 6.64 (m, 6H), 6.49 - 6.45 (m, 2H), 6.24 (s, 2H), 6.04 (s, 2H), 2.25 (s, 6H), 2.14 (s, 6H), 1.96 (s, 6H), 1.27 (s, 18H), 1.21 (d, *J* = 3.5 Hz, 36H), 0.98 (s, 18H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ = 151.4, 150.2, 149.3, 149.0, 141.9, 141.5, 139.0, 138.5, 137.7, 137.3, 137.0, 136.3, 134.2, 133.5, 132.8, 132.2, 131.1, 130.8, 130.7, 130.2, 129.6, 128.6, 128.4, 128.2, 128.0, 127.9, 127.2, 125.6, 125.2, 125.1, 124.5, 123.5, 122.1, 122.0, 121.0, 120.4, 119.3, 119.2, 118.5, 113.3, 112.7, 34.6, 34.4, 34.3, 34.1, 31.4, 31.2, 31.2, 31.1, 30.8, 29.7, 21.0, 20.1, 20.1 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 375 (24597), 561 (25875), 770 (37139), 947 (133014) nm; HRMS (MALDI-TOF) *m/z*: $[M]^+$ Calcd for $C_{140}H_{140}B_2F_4N_8$ 2031.1323; Found 2031.1294.

5 NMR Spectra

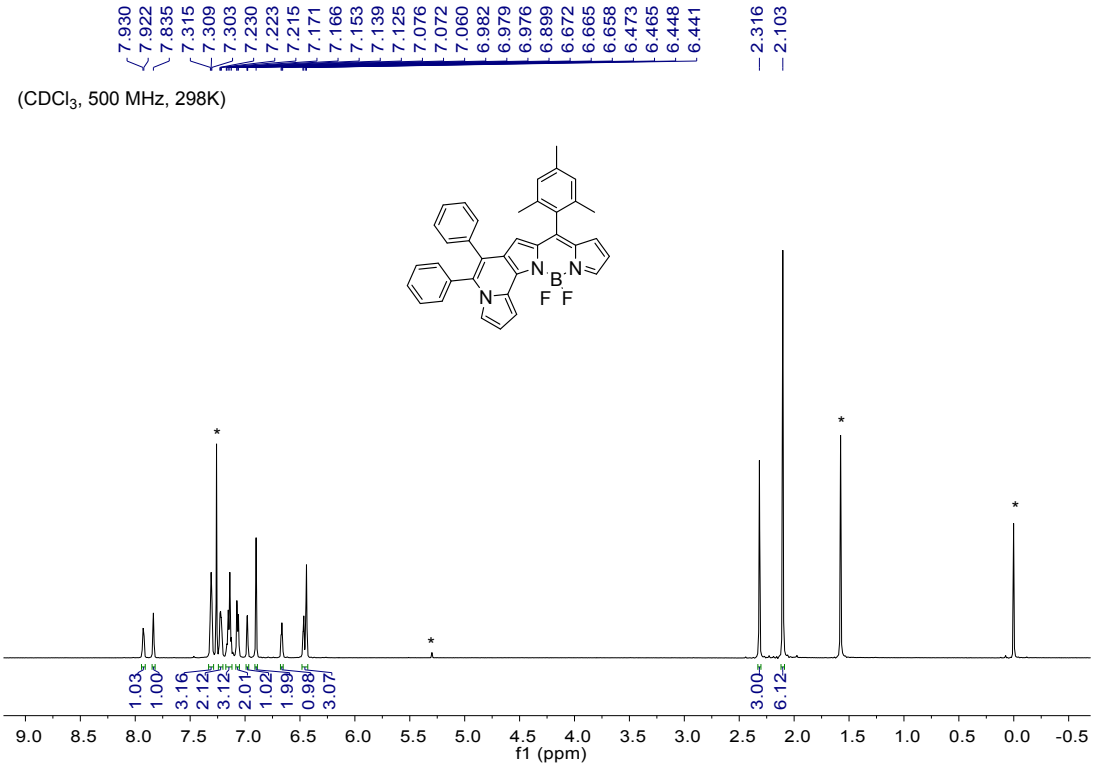


Figure S1. [1]H NMR spectrum of **3a** in $CDCl_3$ at 298 K (*Solvent peaks).

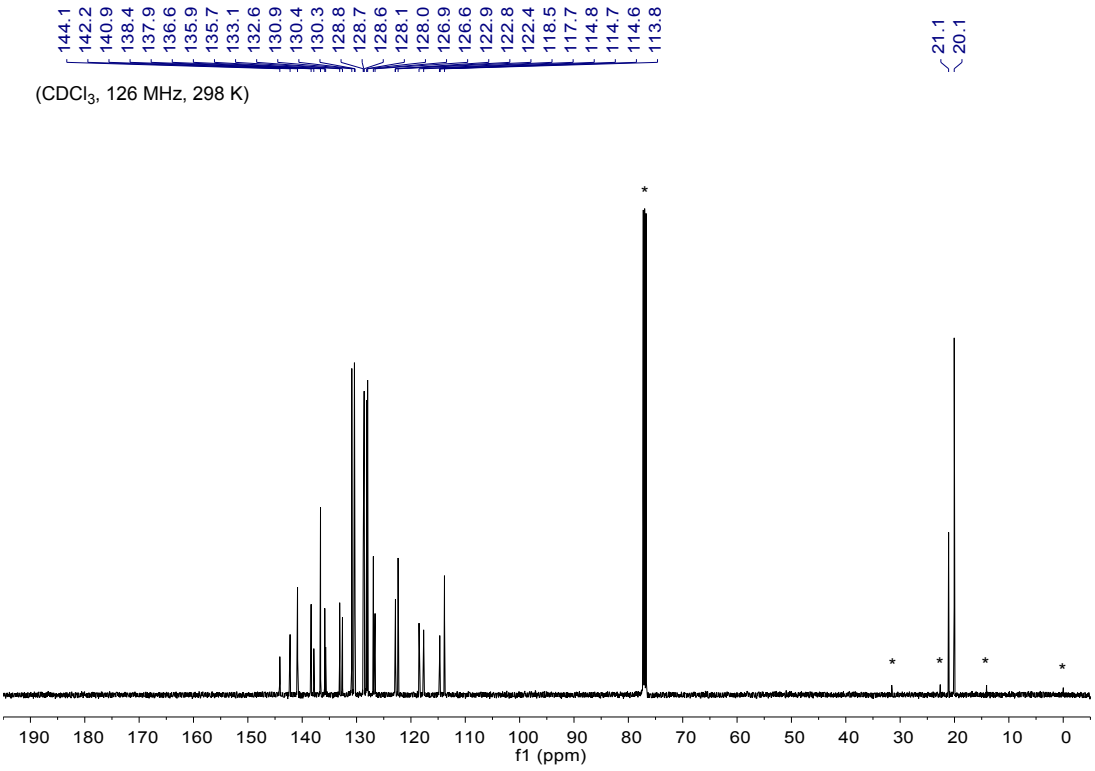


Figure S2. [13]C NMR spectrum of **3a** in $CDCl_3$ at 298 K (*Solvent peaks).

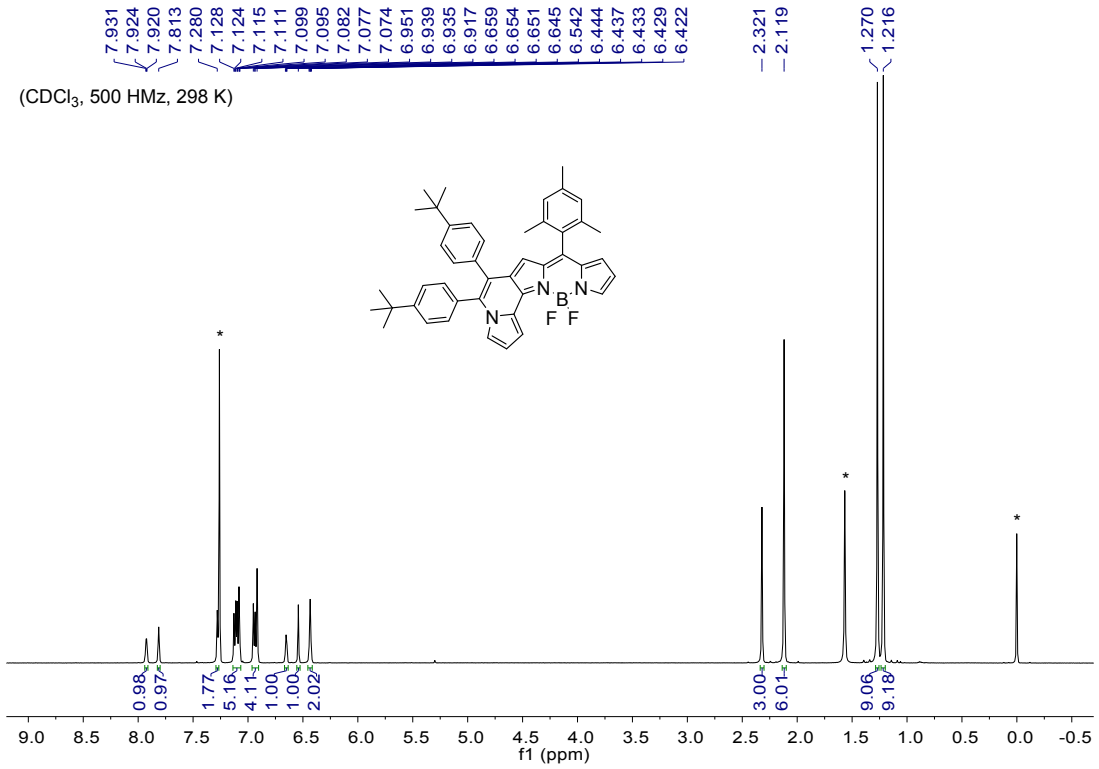


Figure S3. ^{1}H NMR spectrum of **3b** in $CDCl_3$ at 298 K (*Solvent peaks).

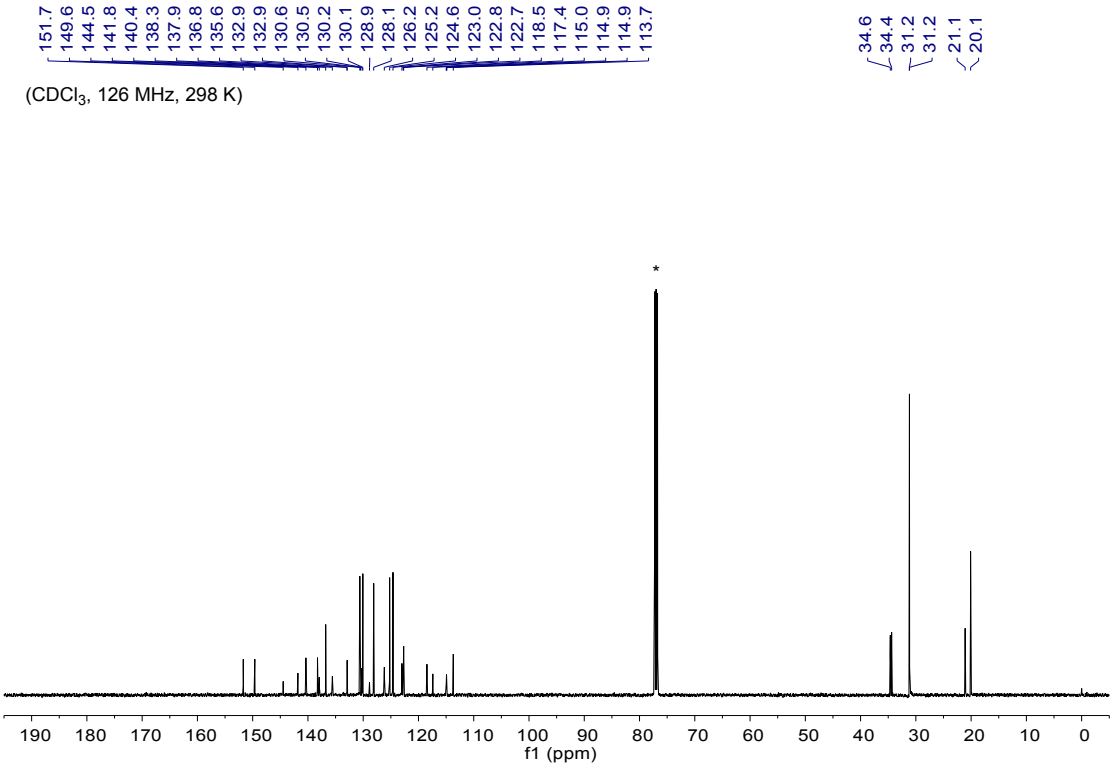


Figure S4. ^{13}C NMR spectrum of **3b** in $CDCl_3$ at 298 K (*Solvent peaks).

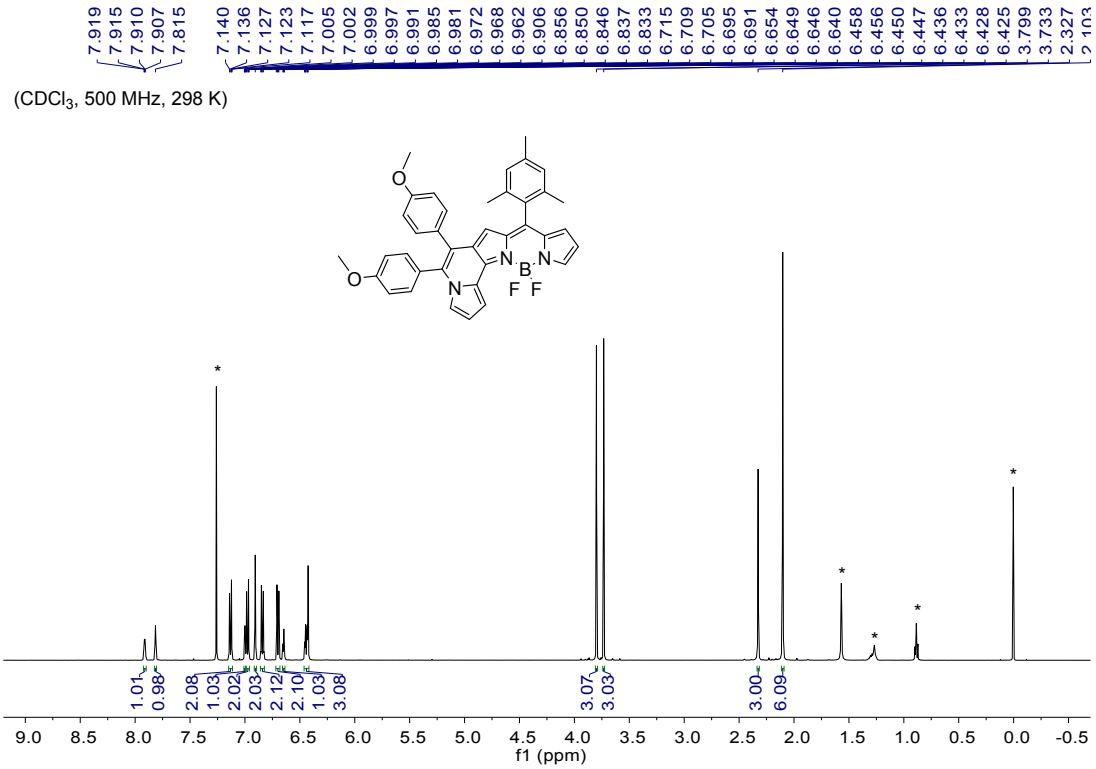


Figure S5. ^{1}H NMR spectrum of **3c** in $CDCl_3$ at 298 K (*Solvent peaks).

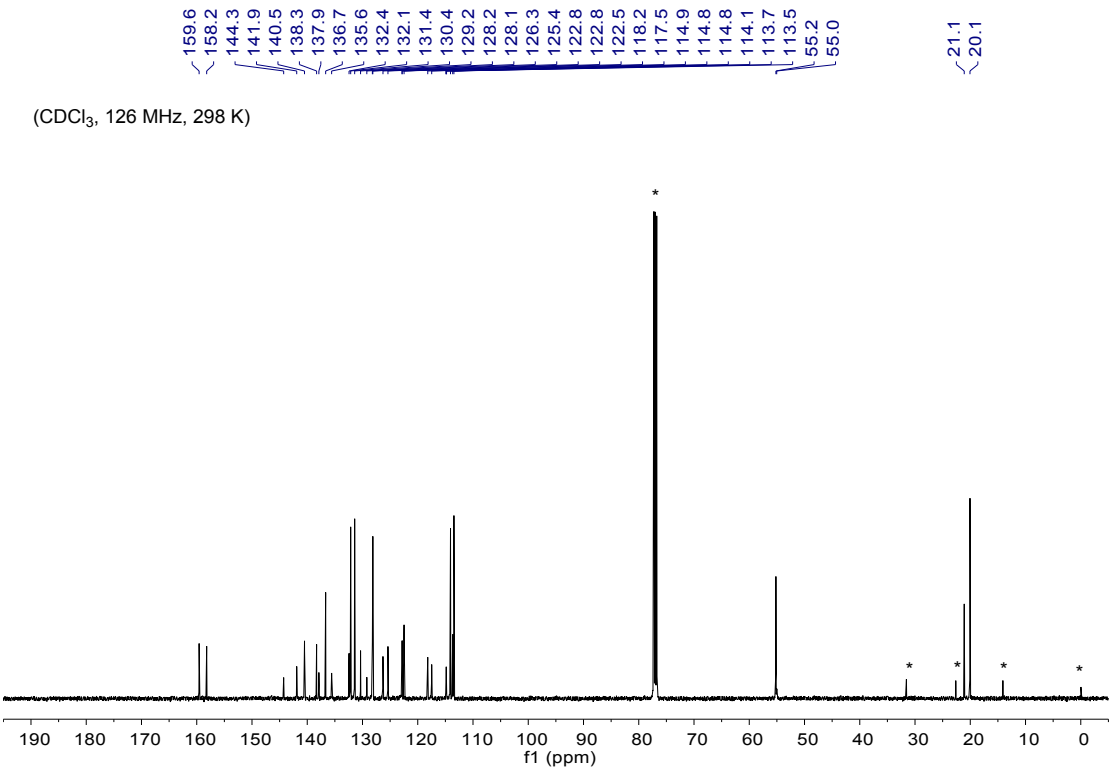


Figure S6. ^{13}C NMR spectrum of **3c** in $CDCl_3$ at 298 K (*Solvent peaks).

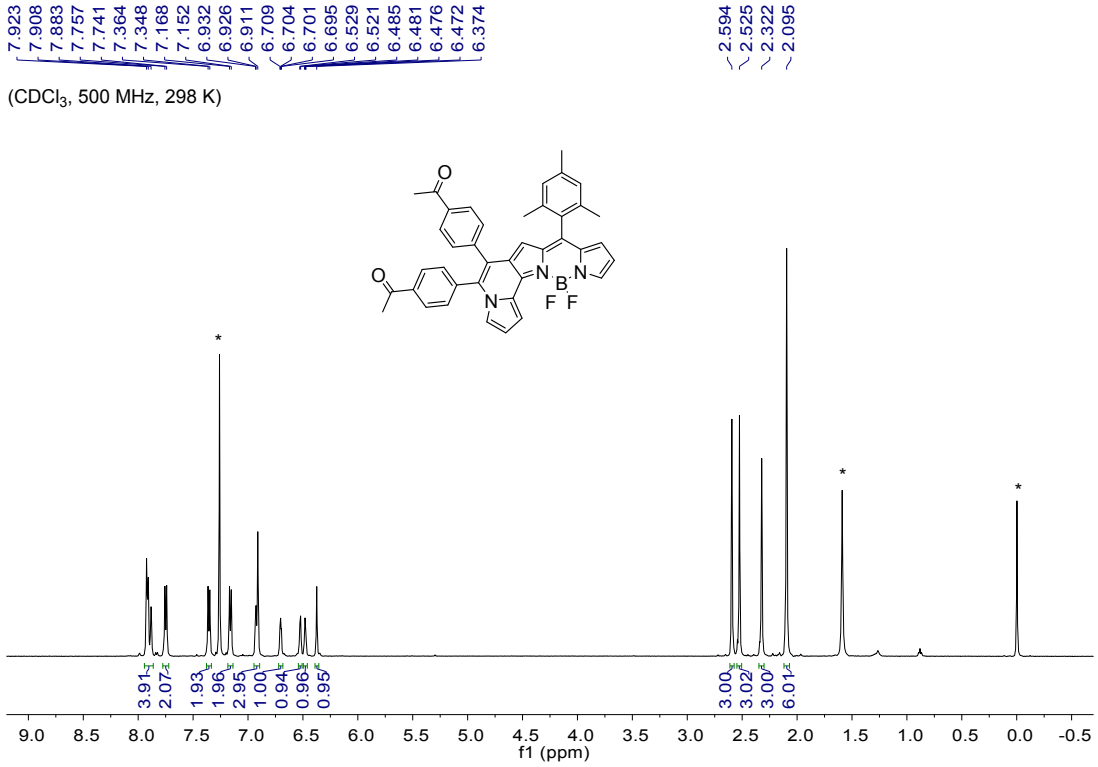


Figure S7. ^{1}H NMR spectrum of **3d** in $CDCl_3$ at 298K (*Solvent peaks).

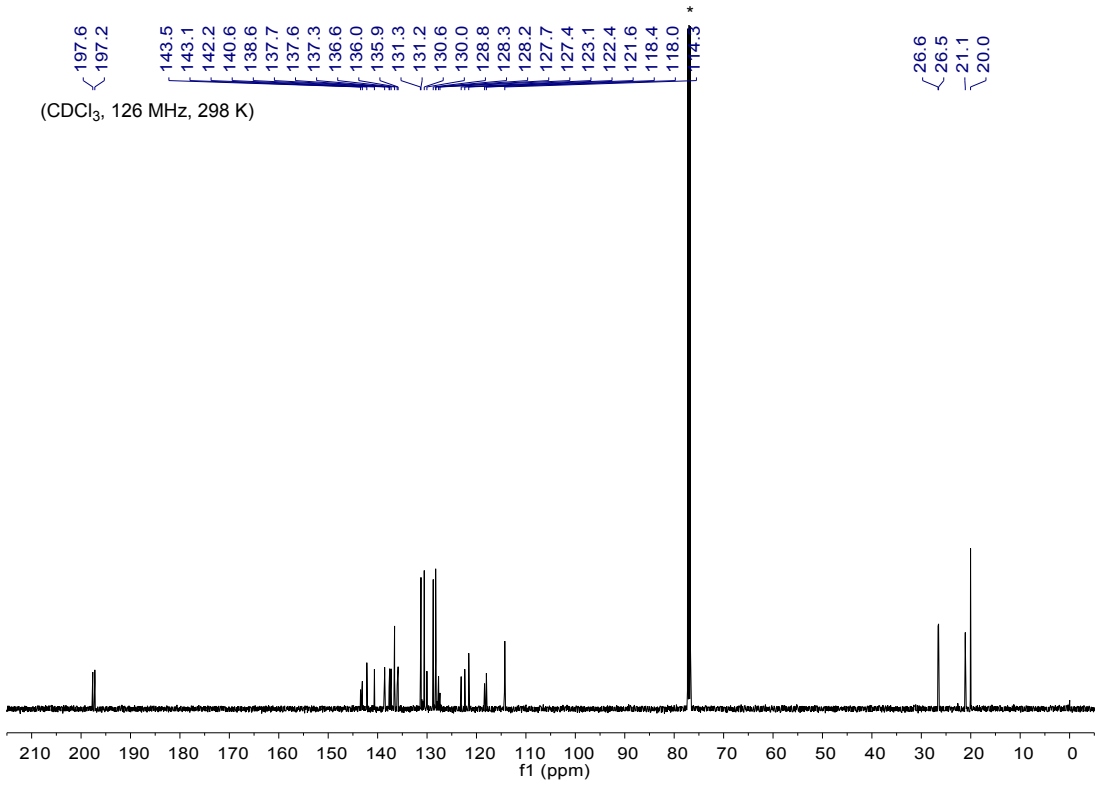


Figure S8. ^{13}C NMR spectrum of **3d** in $CDCl_3$ at 298 K (*Solvent peaks).

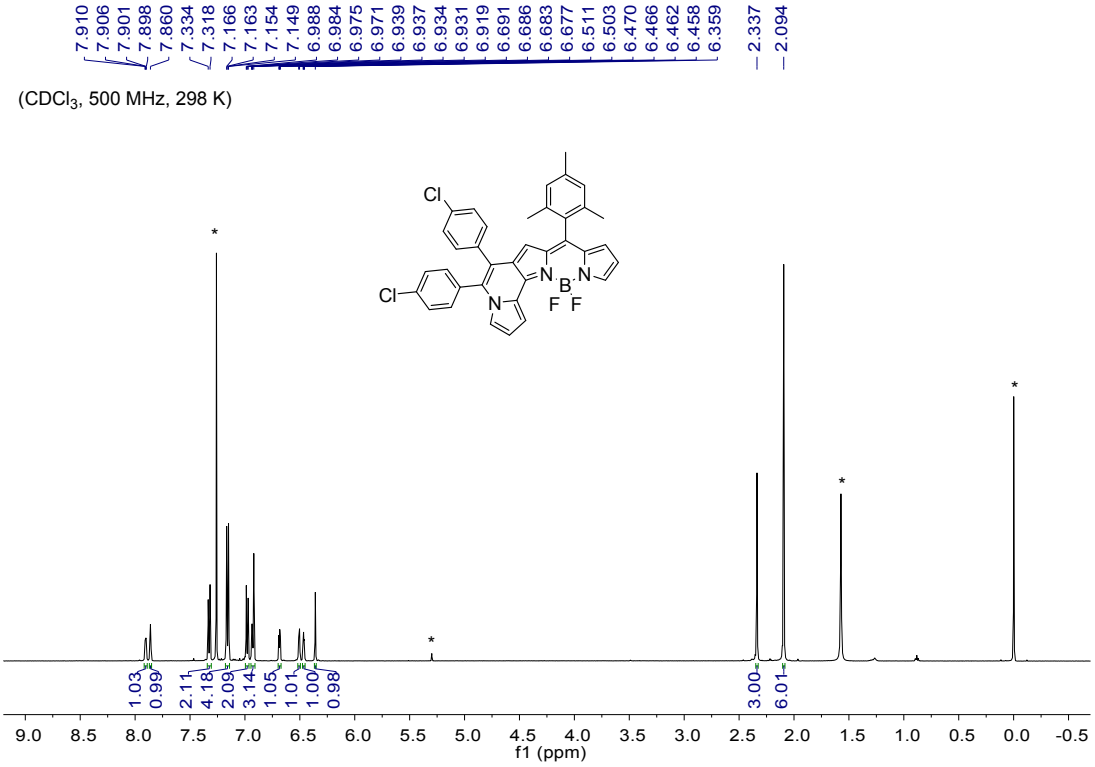


Figure S9. ^{1}H NMR spectrum of **3e** in $CDCl_3$ at 298 K (*Solvent peaks).

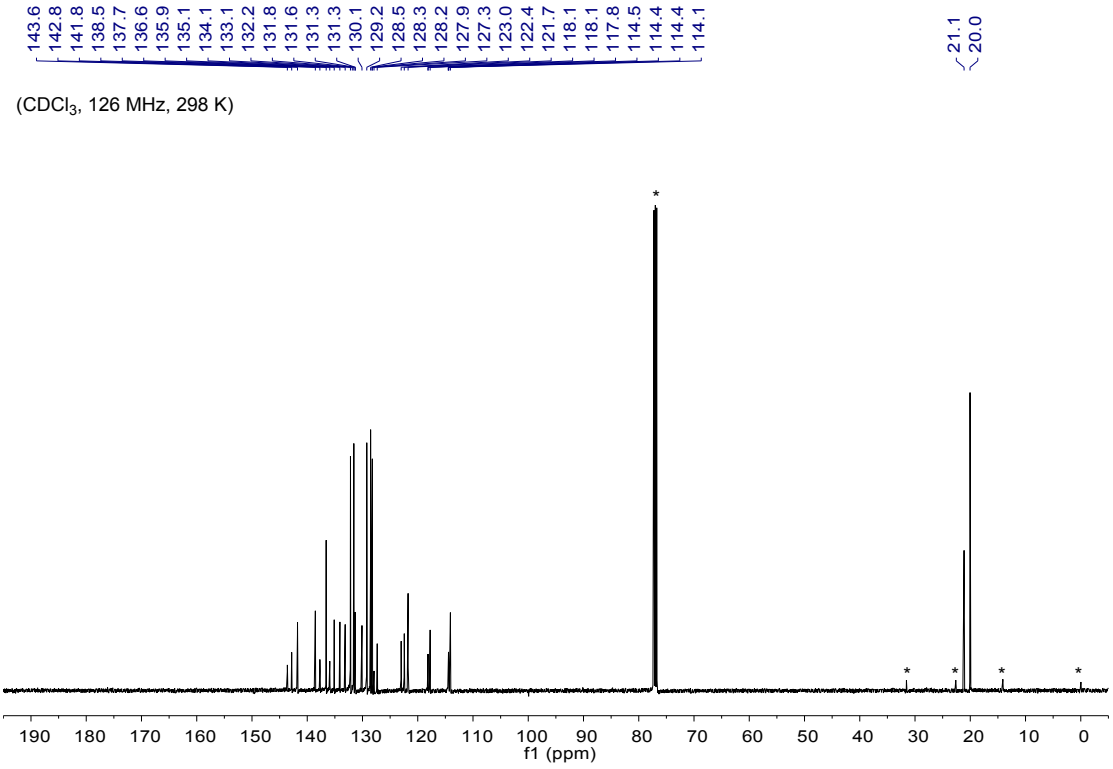


Figure S10. ^{13}C NMR spectrum of **3e** in $CDCl_3$ at 298 K (*Solvent peaks).

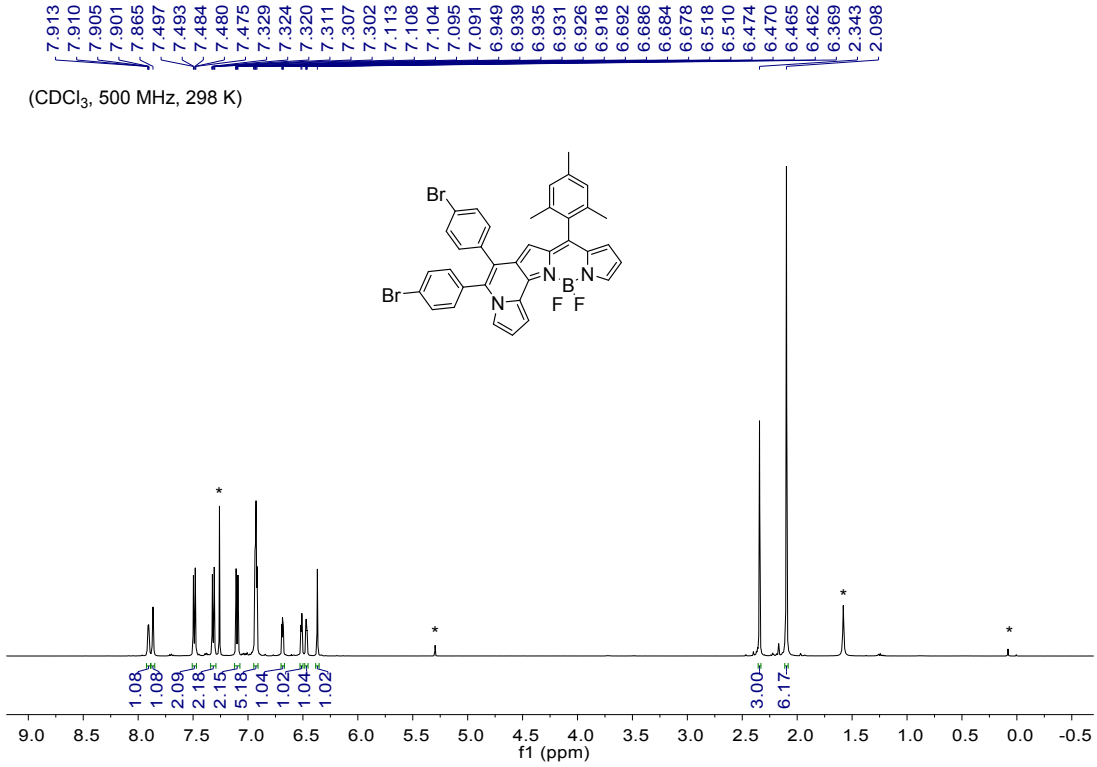


Figure S11. ^{1}H NMR spectrum of **3f** in $CDCl_3$ at 298 K (*Solvent peaks).

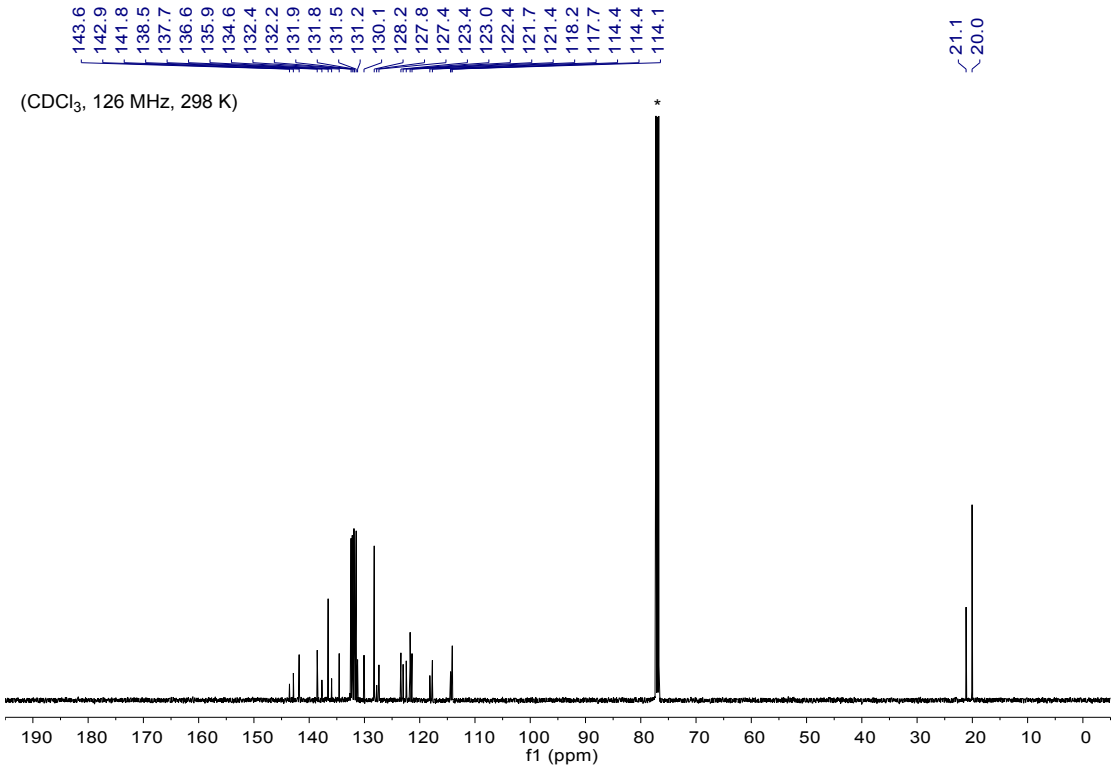


Figure S12. ^{13}C NMR spectrum of **3f** in $CDCl_3$ at 298 K (*Solvent peaks).

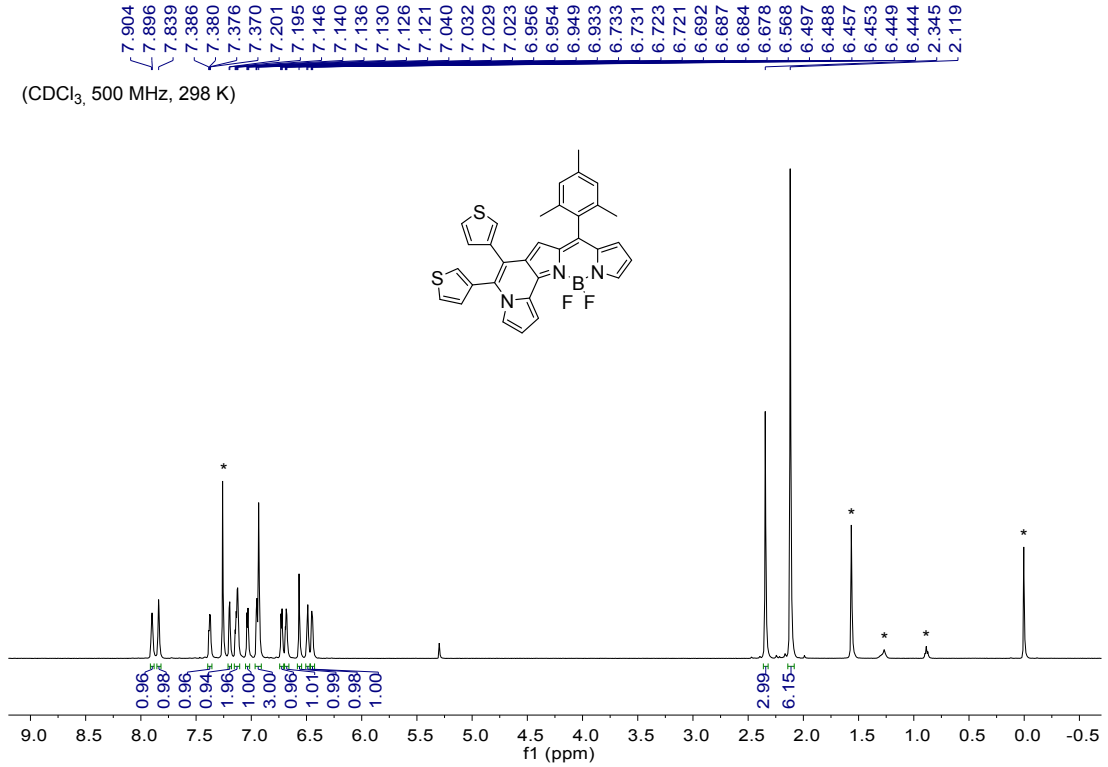


Figure S13. ^{1}H NMR spectrum of **3g** in $CDCl_3$ at 298 K (*Solvent peaks).

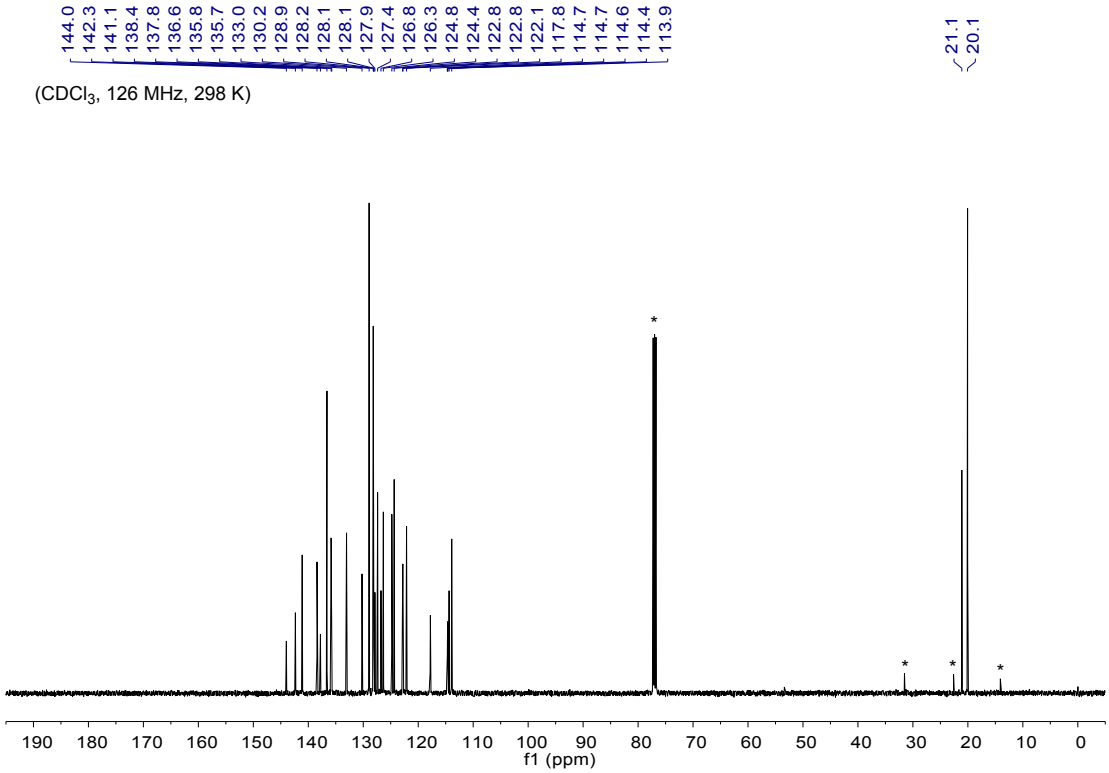


Figure S14. ^{13}C NMR spectrum of **3g** in $CDCl_3$ at 298 K (*Solvent peaks).

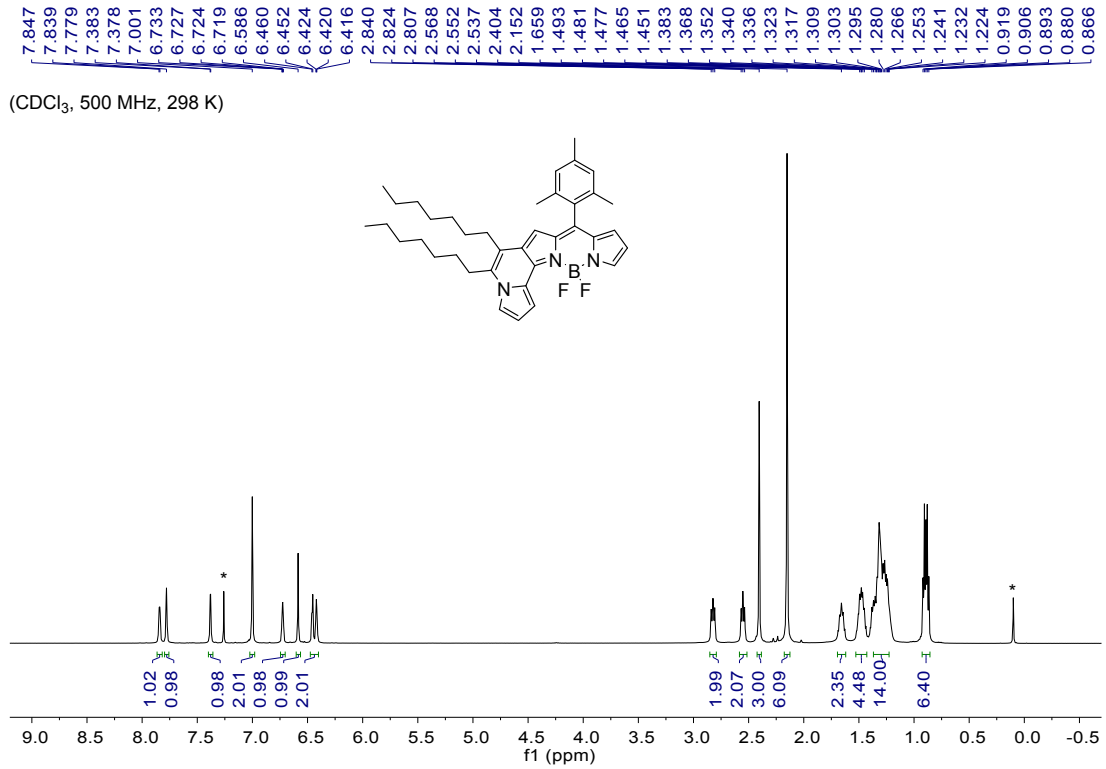


Figure S15. ^{1}H NMR spectrum of **3h** in $CDCl_3$ at 298 K (*Solvent peaks).

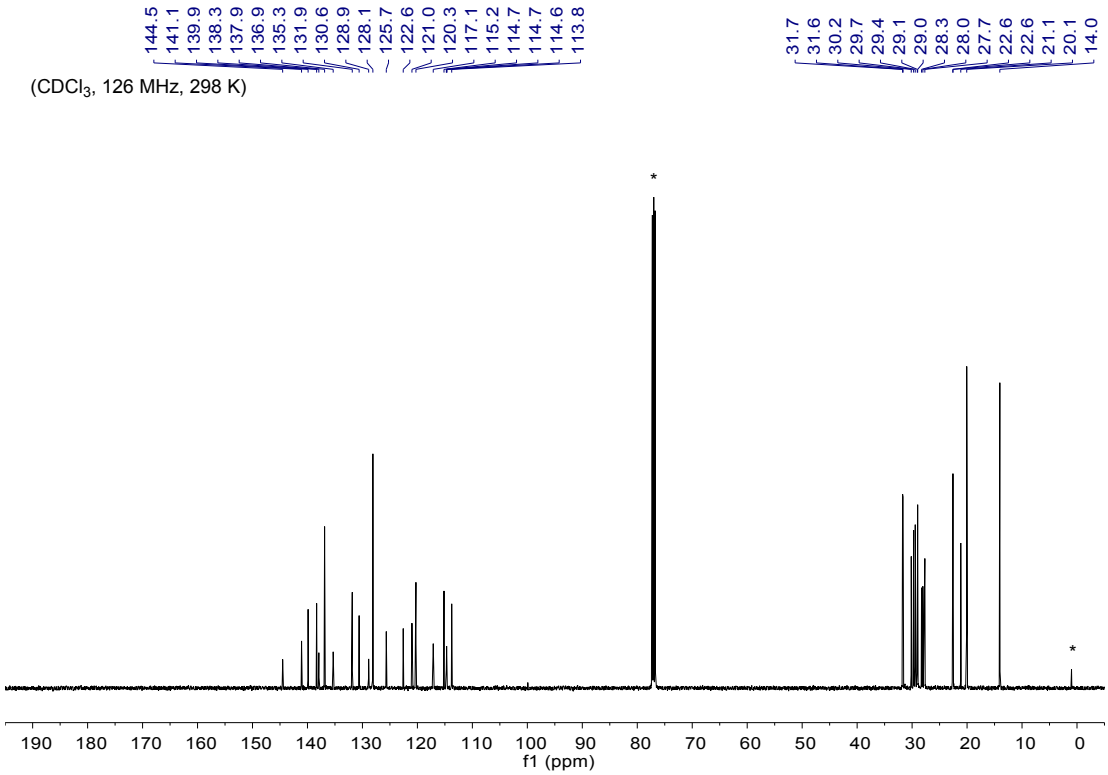


Figure S16. ^{13}C NMR spectrum of **3h** in $CDCl_3$ at 298 K (*Solvent peaks).

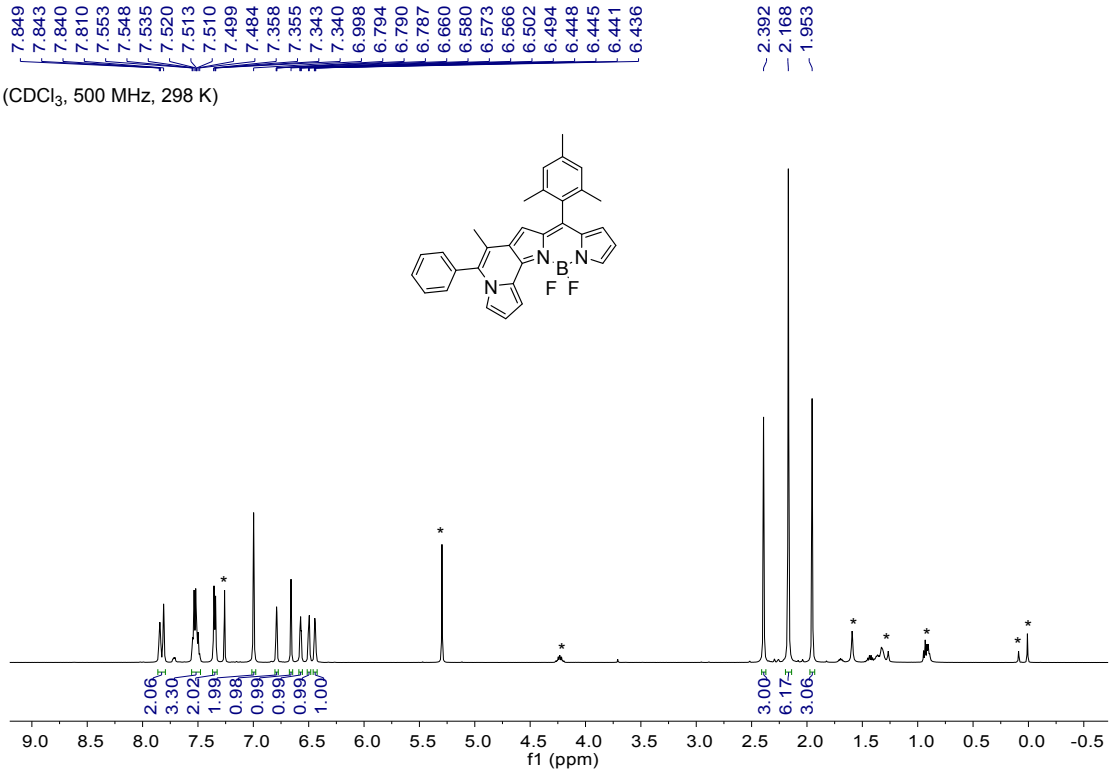


Figure S17. ^{1}H NMR spectrum of **3i** in $CDCl_3$ at 298 K (*Solvent peaks).

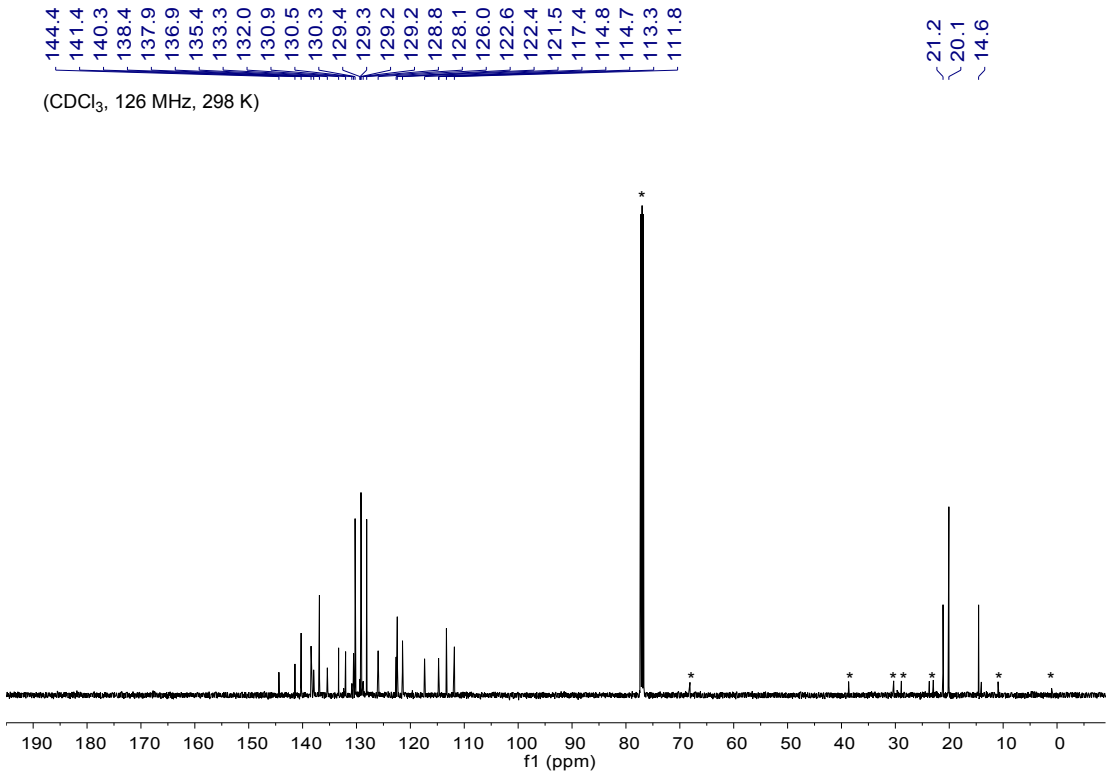


Figure S18. ^{13}C NMR spectrum of **3i** in $CDCl_3$ at 298 K (*Solvent peaks).

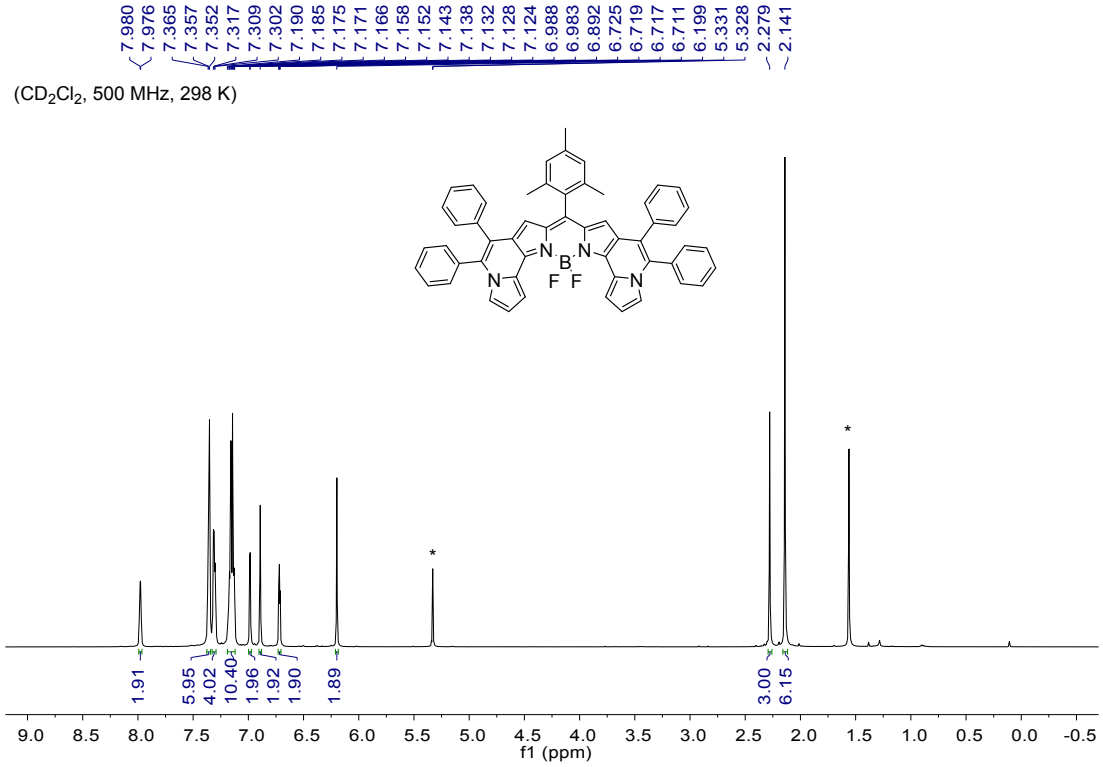


Figure S19. ^{1}H NMR spectrum of **5a** in CD_2Cl_2 at 298 K (*Solvent peaks).

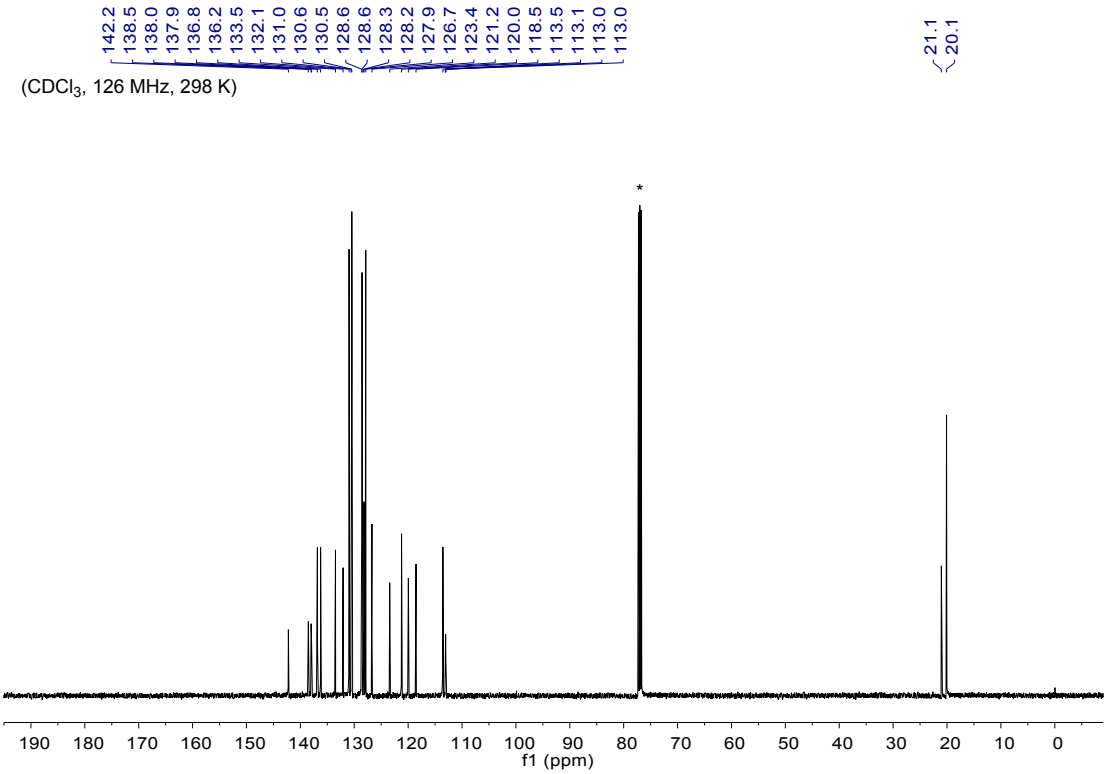


Figure S20. ^{13}C NMR spectrum of **5a** in $CDCl_3$ at 298 K (*Solvent peaks).

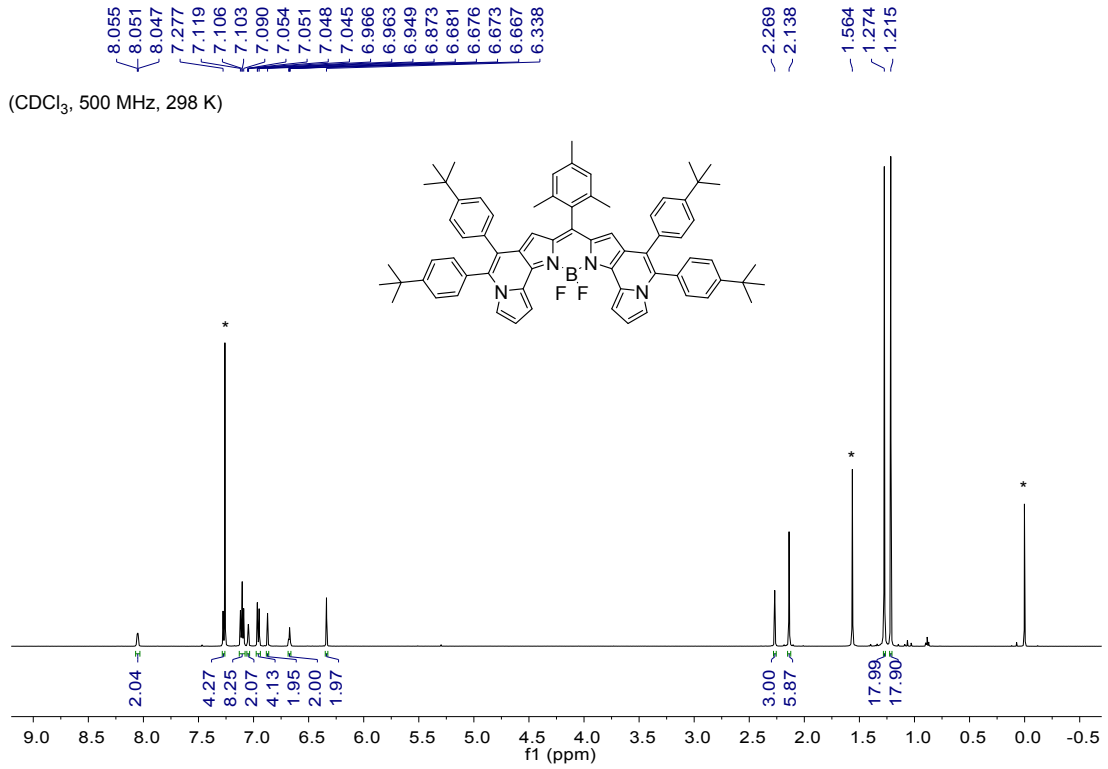


Figure S21. ^{1}H NMR spectrum of **5b** in $CDCl_3$ at 298 K (*Solvent peaks).

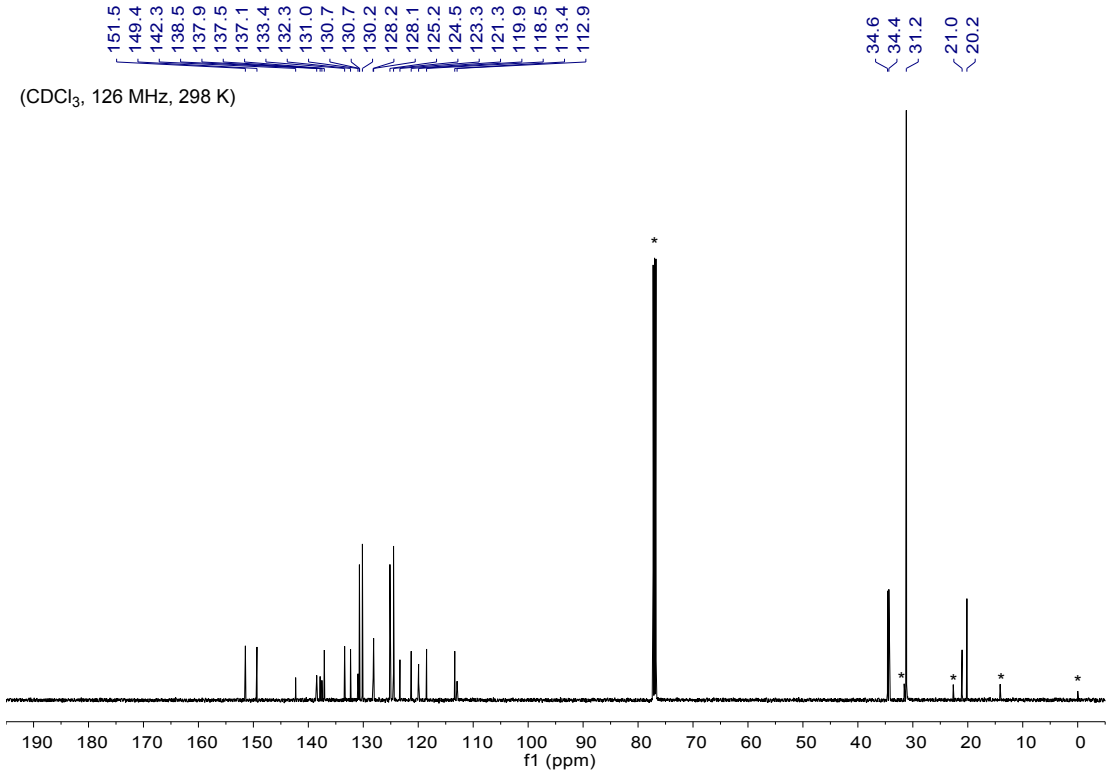


Figure S22. ^{13}C NMR spectrum of **5b** in $CDCl_3$ at 298 K (*Solvent peaks).

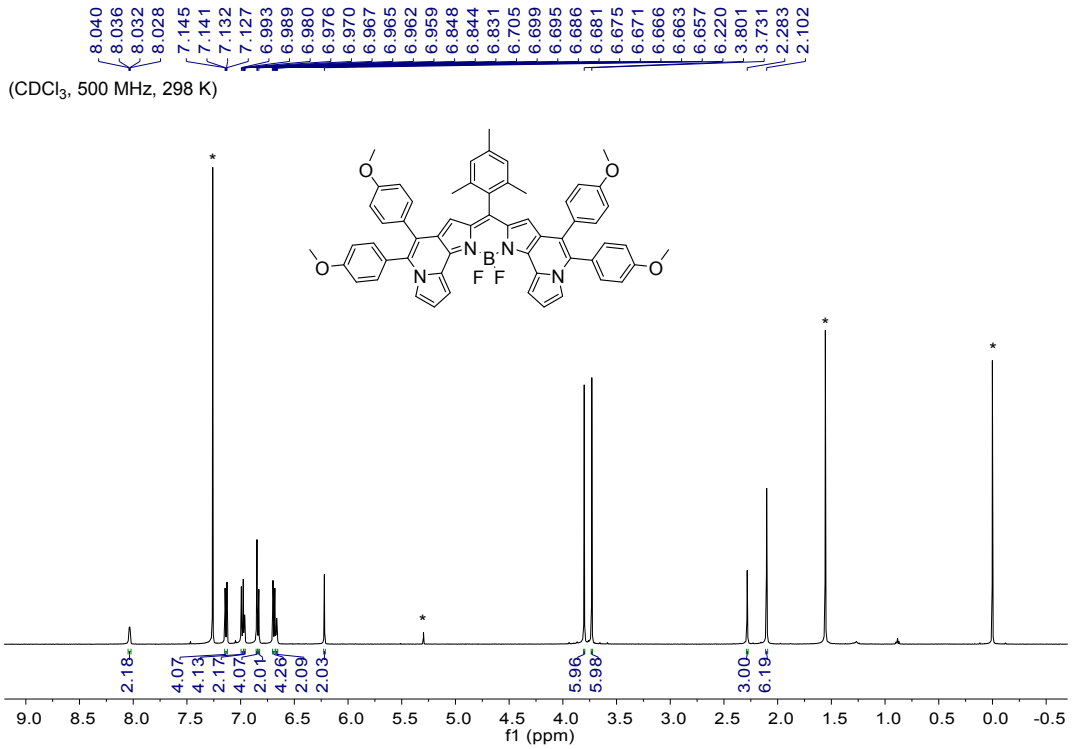


Figure S23. ^{1}H NMR spectrum of **5c** in $CDCl_3$ at 298 K (*Solvent peaks).

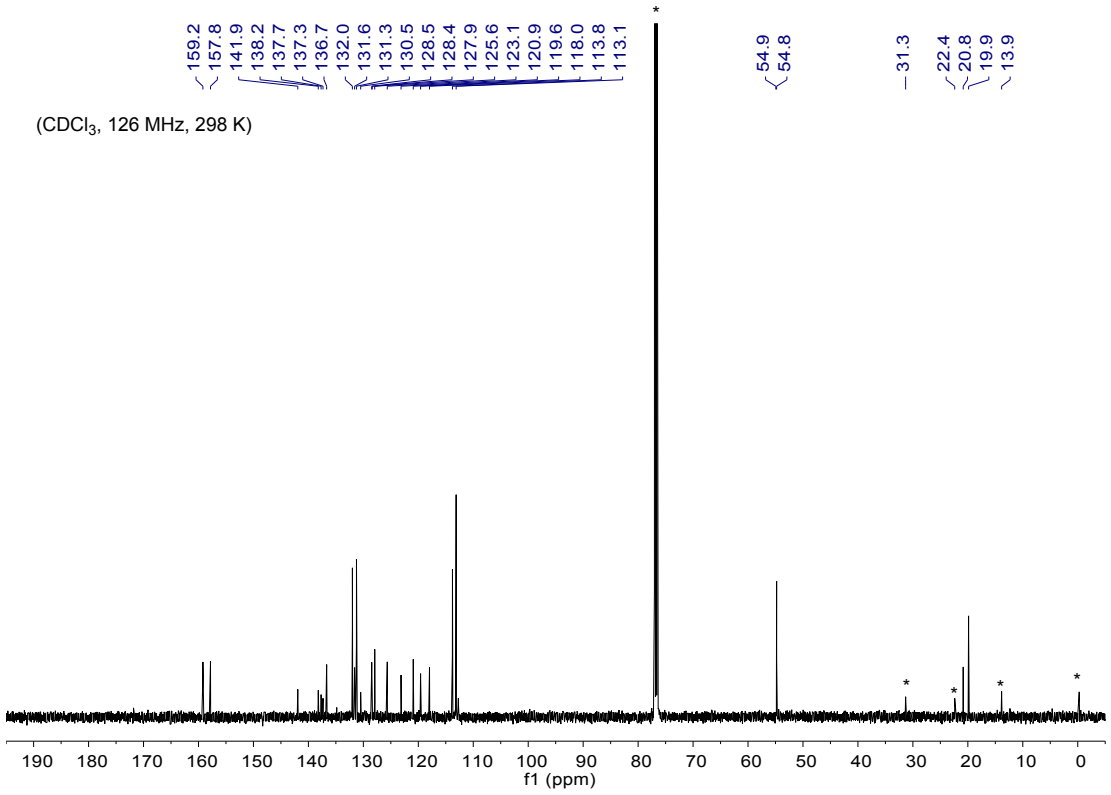


Figure S24. ^{13}C NMR spectrum of **5c** in $CDCl_3$ at 298 K (*Solvent peaks).

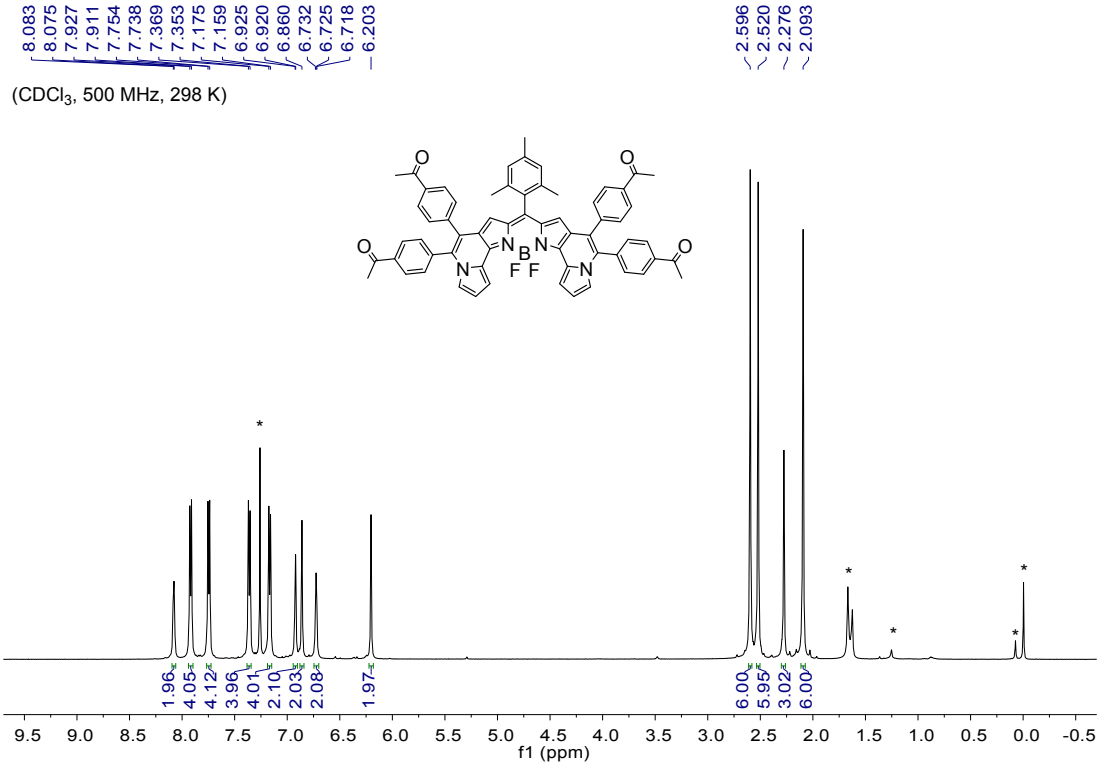


Figure S25. ^{1}H NMR spectrum of **5d** in $CDCl_3$ at 298 K (*Solvent peaks).

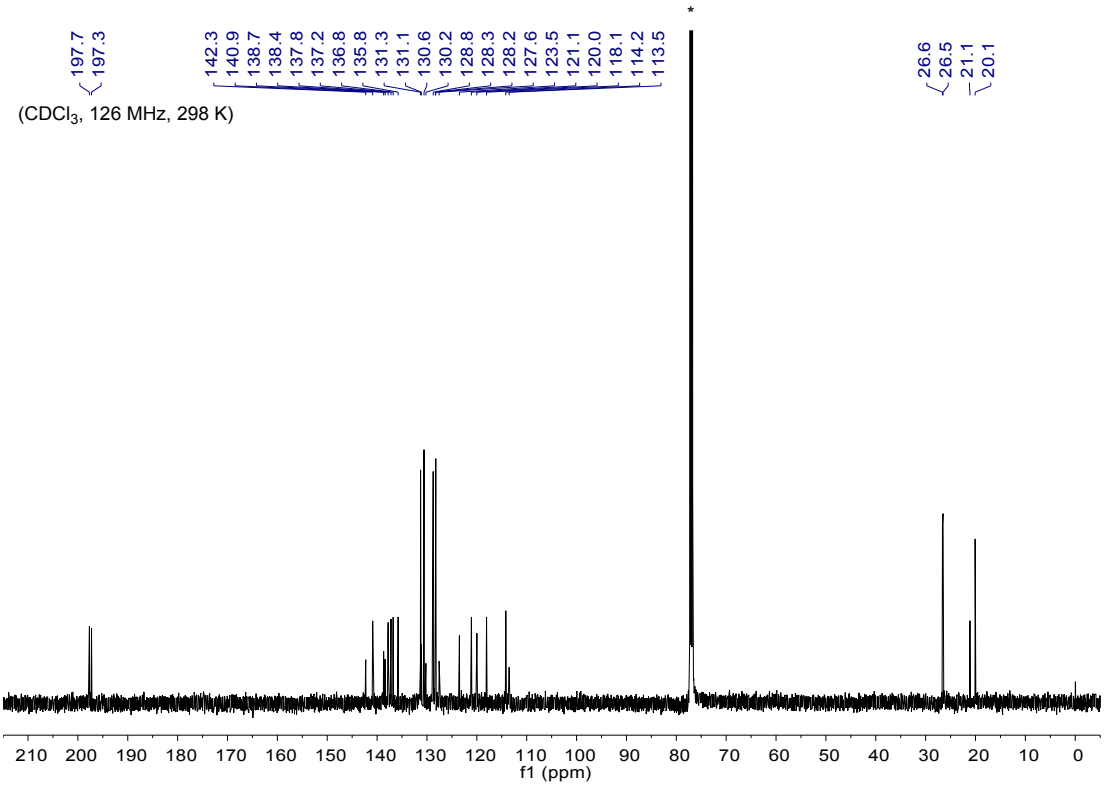


Figure S26. ^{13}C NMR spectrum of **5d** in $CDCl_3$ at 298 K (*Solvent peaks).

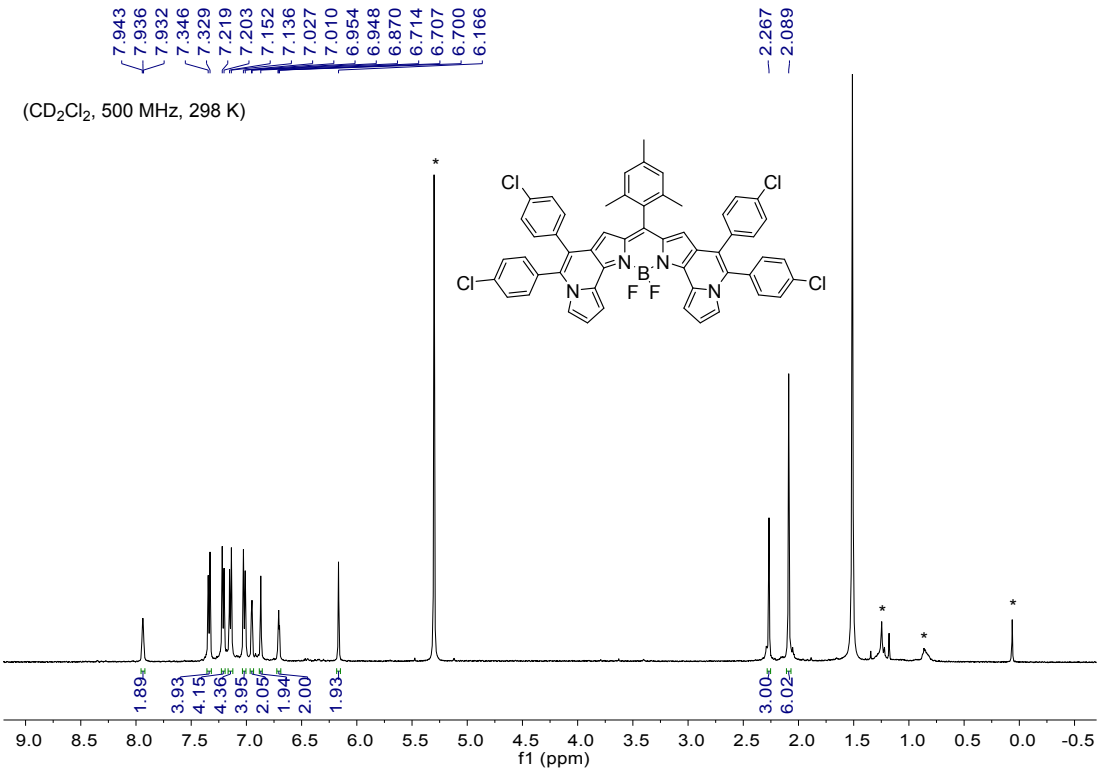


Figure S27. ^{1}H NMR spectrum of **5e** in CD_2Cl_2 at 298 K (*Solvent peaks).

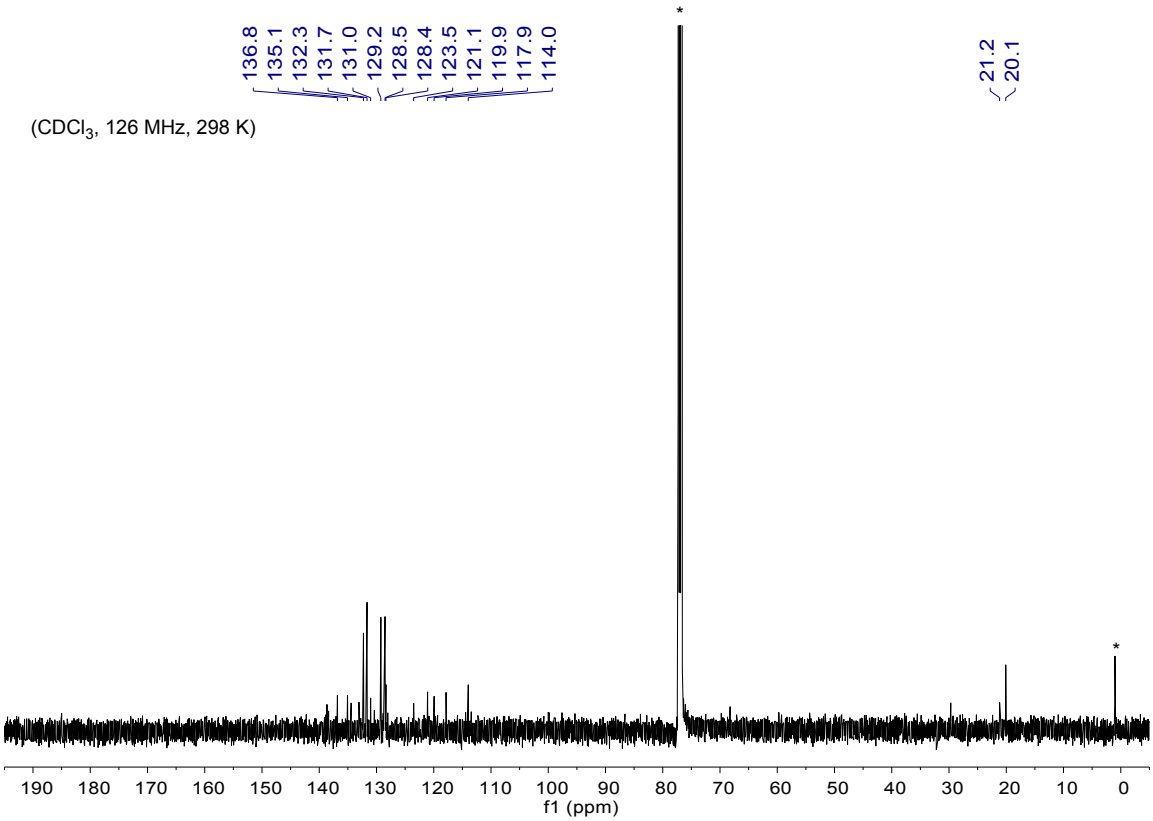


Figure S28. ^{13}C NMR spectrum of **5e** in $CDCl_3$ at 298 K (*Solvent peaks).

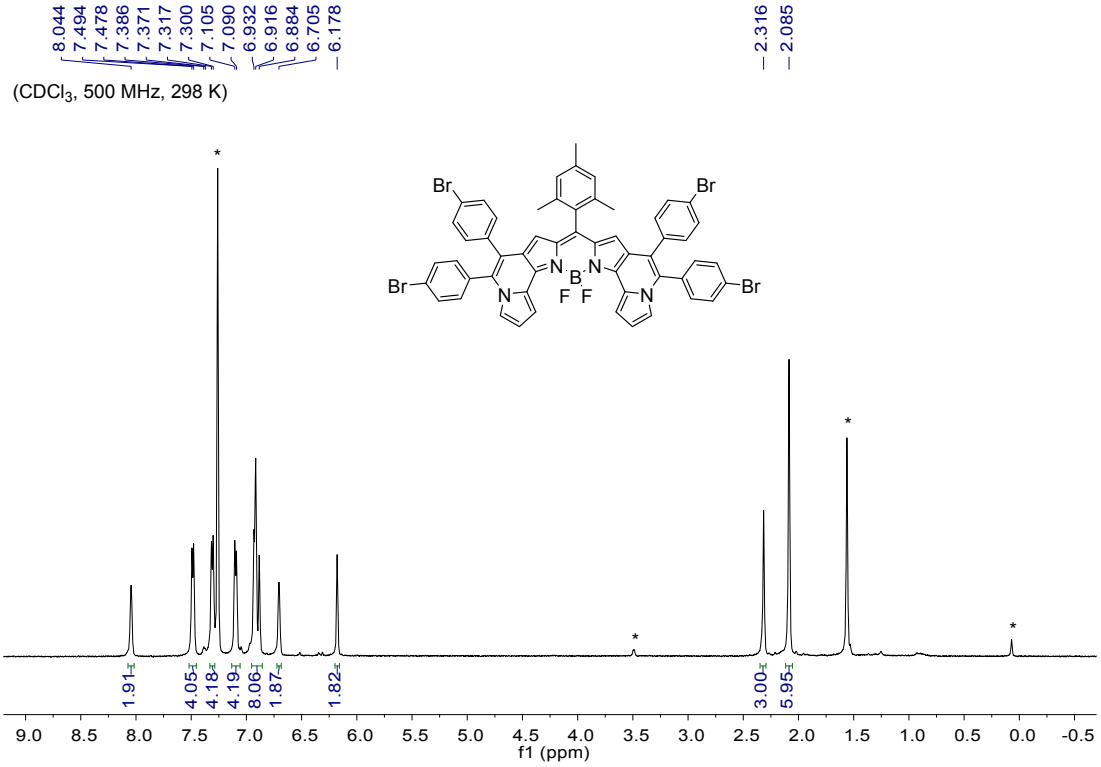


Figure S29. ^{1}H NMR spectrum of **5f** in $CDCl_3$ at 298 K (*Solvent peaks).

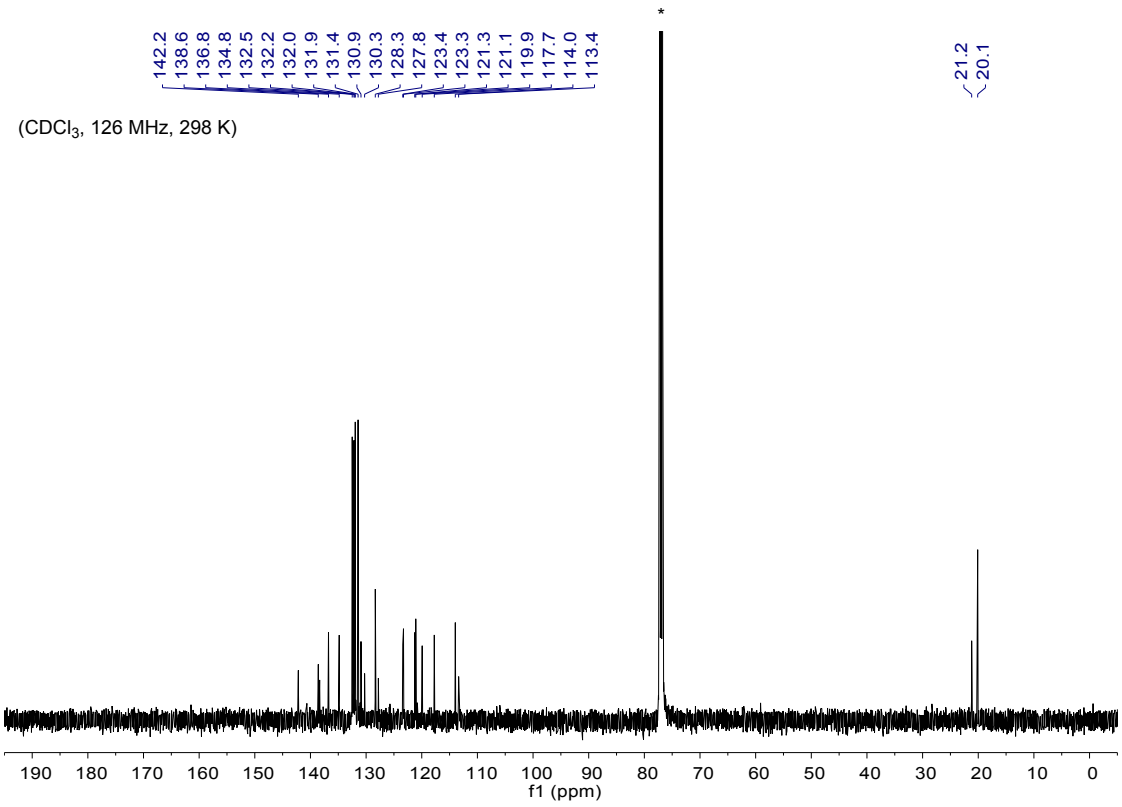


Figure S30. ^{13}C NMR spectrum of **5f** in $CDCl_3$ at 298 K (*Solvent peaks).

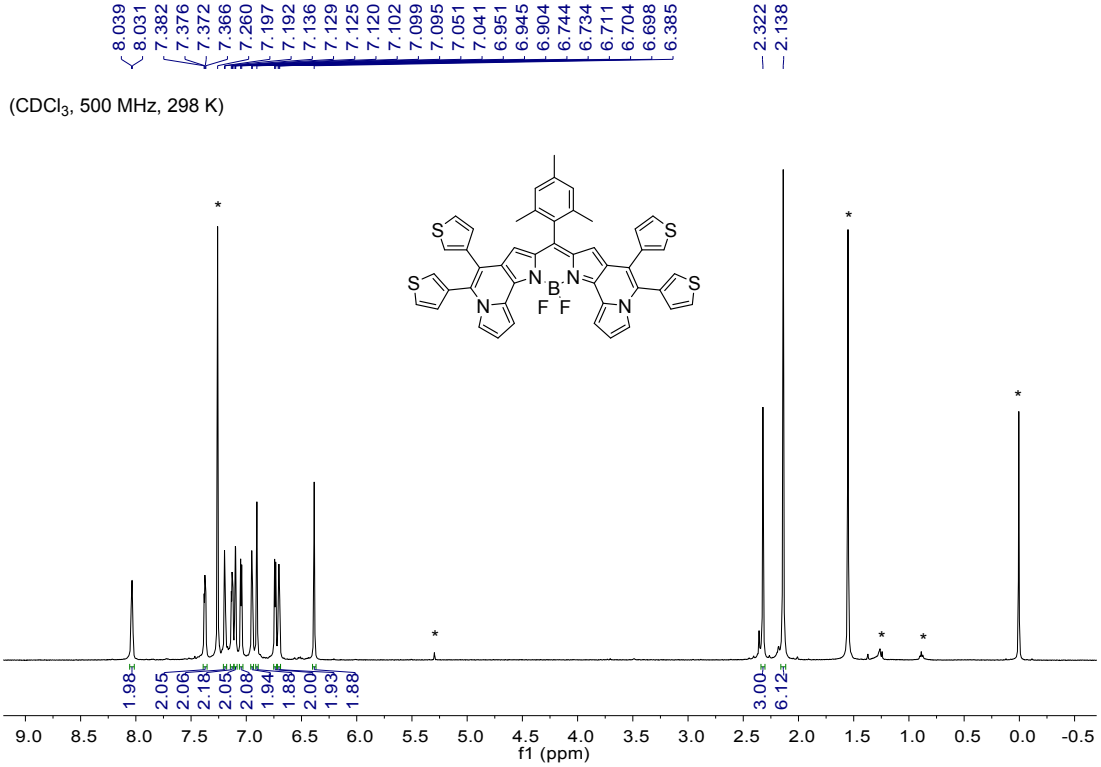


Figure S31. ^{1}H NMR spectrum of **5g** in $CDCl_3$ at 298 K (*Solvent peaks).

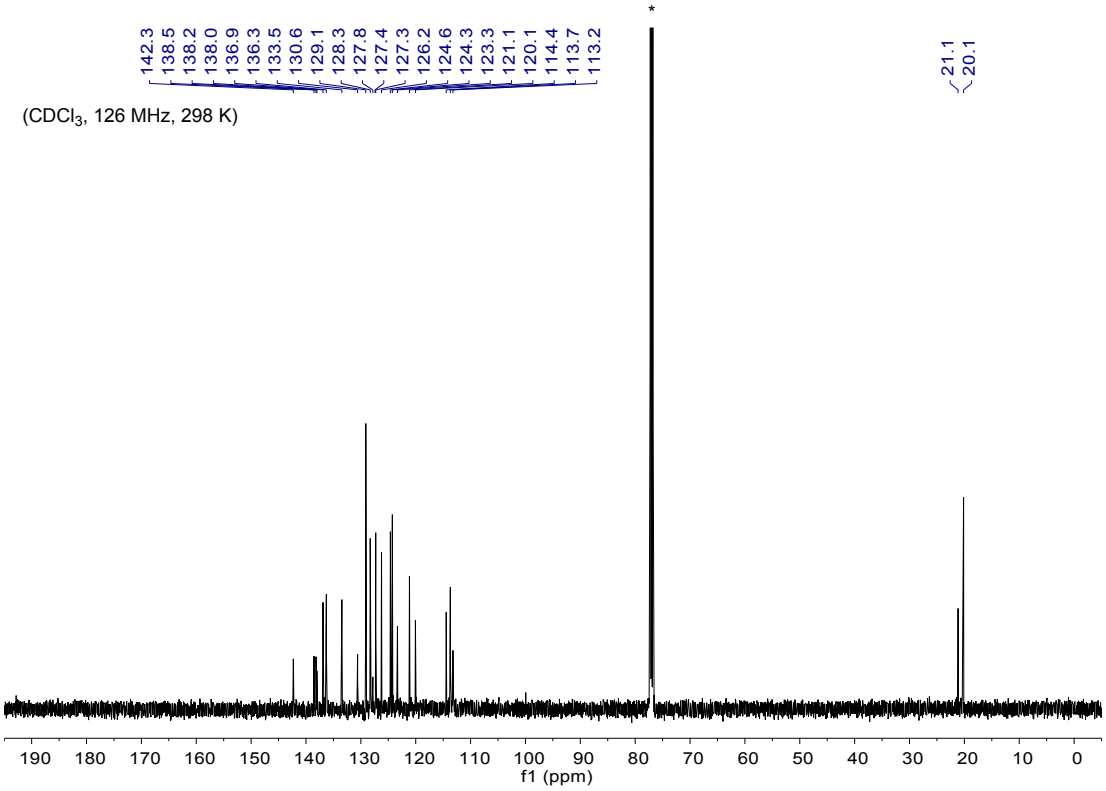


Figure S32. ^{13}C NMR spectrum of **5g** in $CDCl_3$ at 298 K (*Solvent peaks).

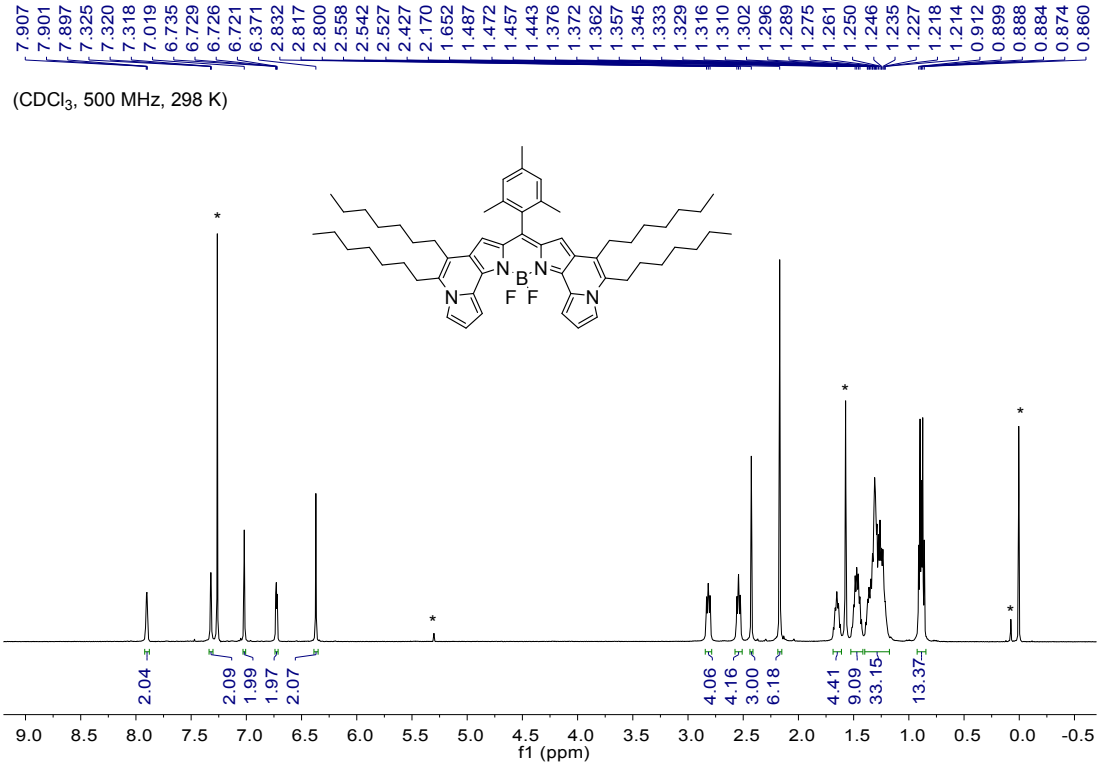


Figure S33. ^{1}H NMR spectrum of **5h** in $CDCl_3$ at 298 K (*Solvent peaks).

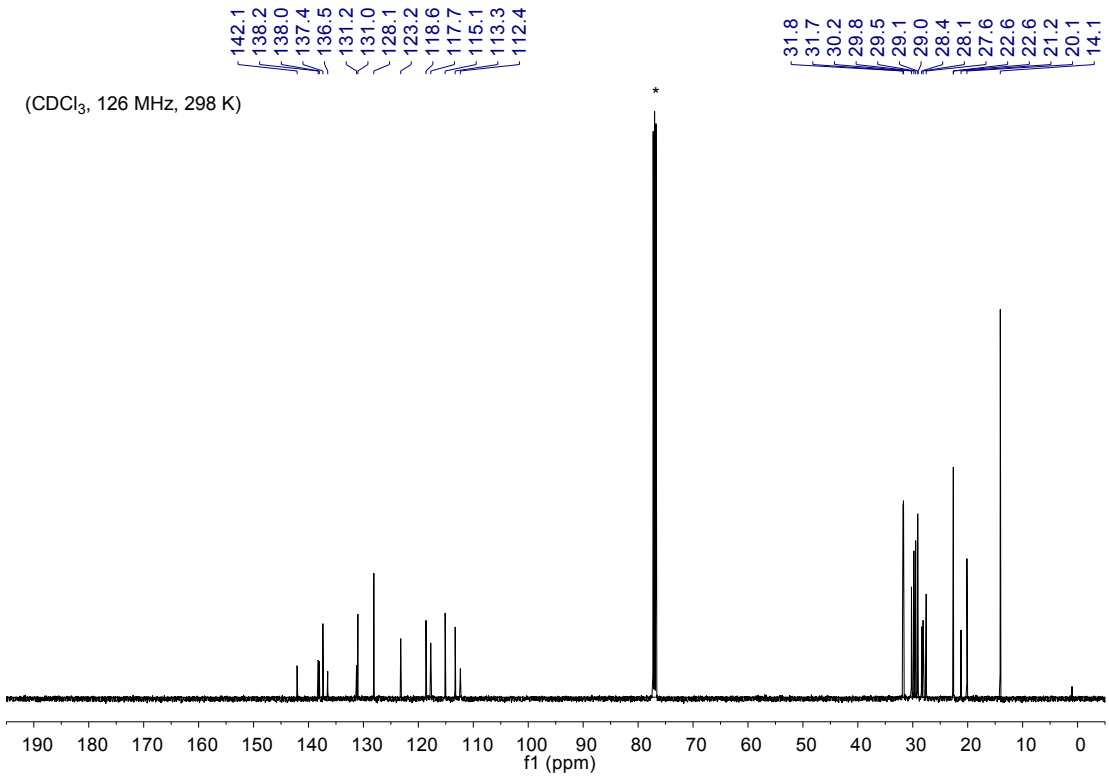


Figure S34. ^{13}C NMR spectrum of **5h** in $CDCl_3$ at 298 K (*Solvent peaks).

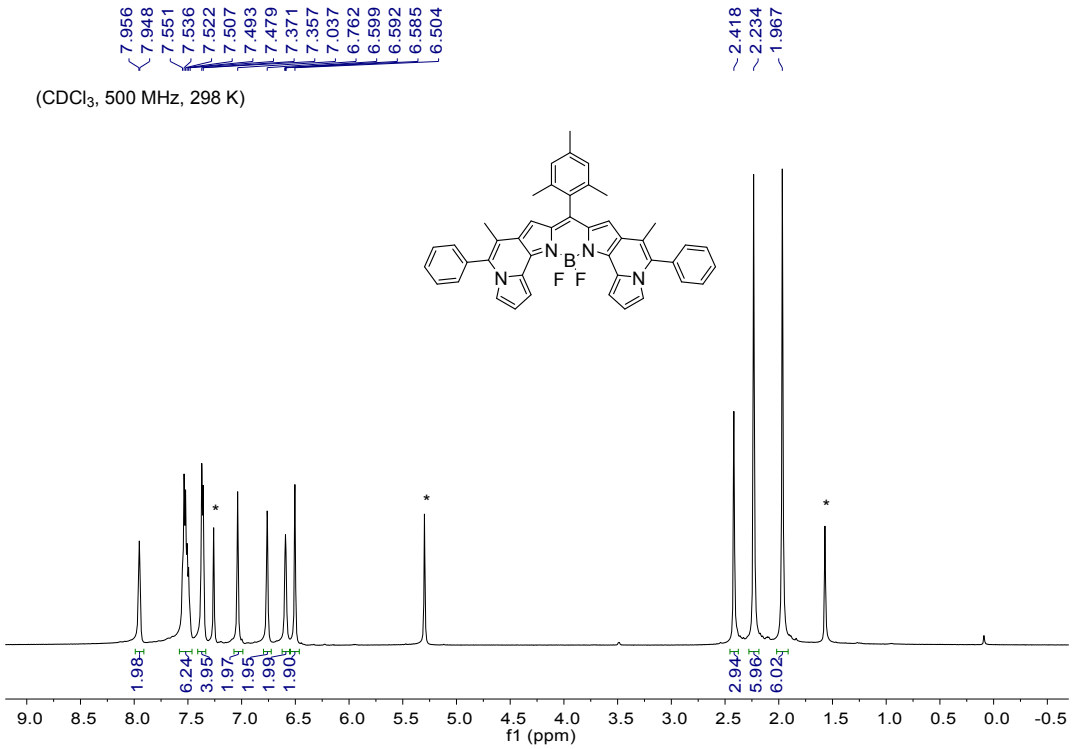


Figure S35. ^{1}H NMR spectrum of **5i** in $CDCl_3$ at 298 K (*Solvent peaks).

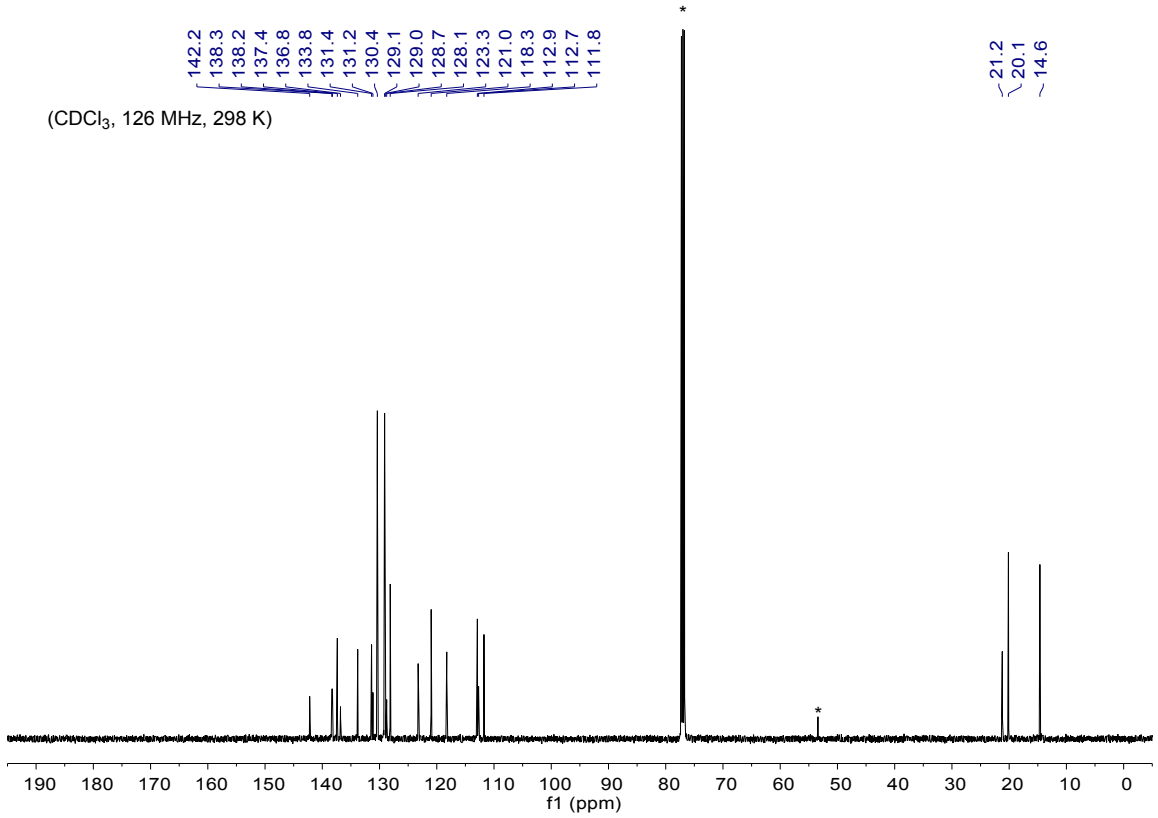


Figure S36. ^{13}C NMR spectrum of **5i** in $CDCl_3$ at 298 K (*Solvent peaks).

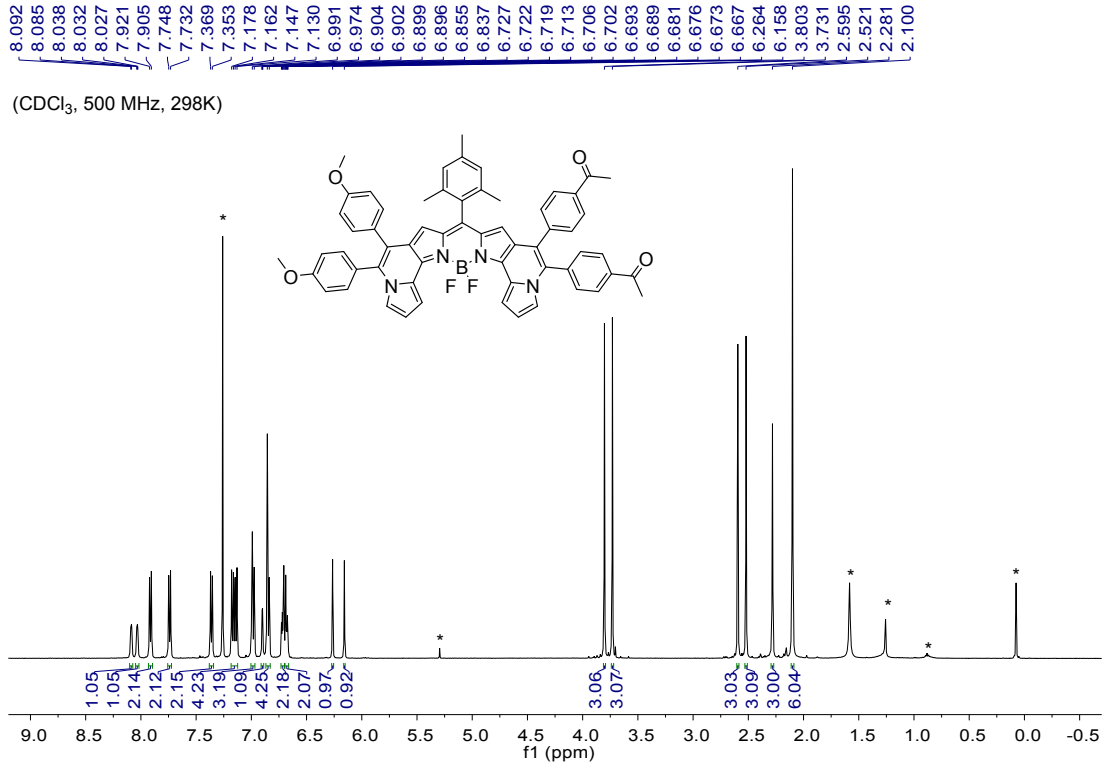


Figure S37. ^{1}H NMR spectrum of **5k** in $CDCl_3$ at 298 K (*Solvent peaks).

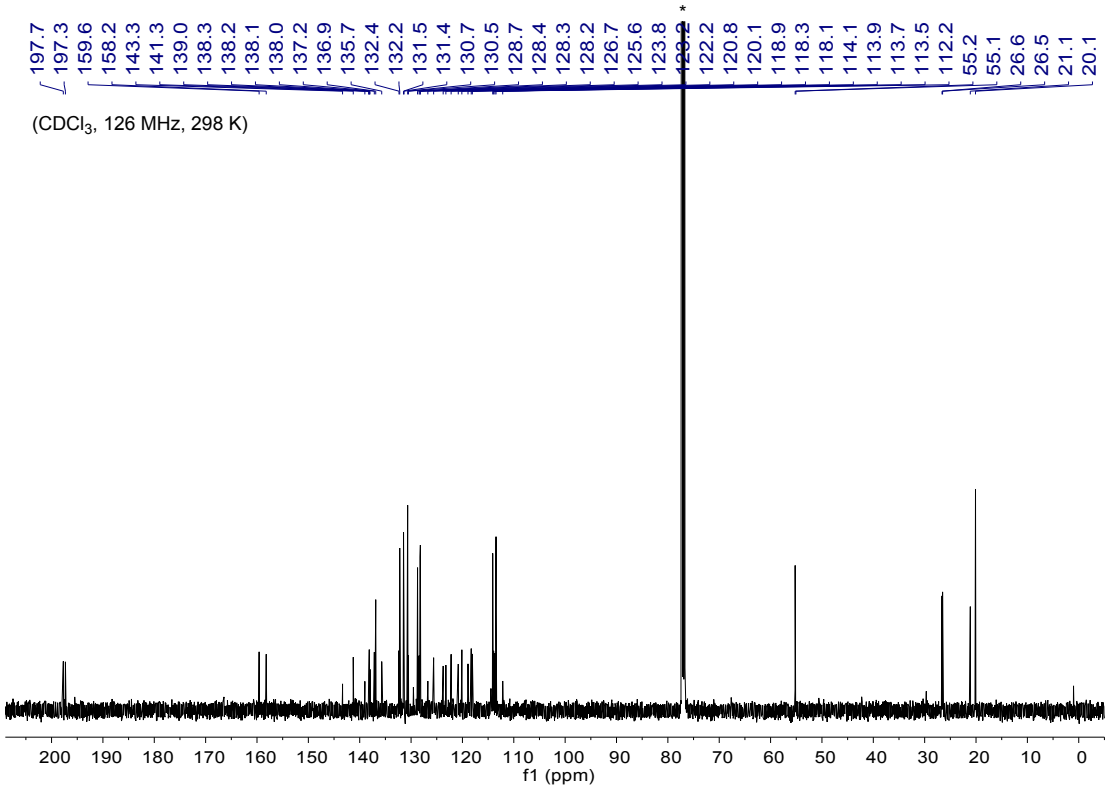


Figure S38. ^{13}C NMR spectrum of **5k** in $CDCl_3$ at 298 K (*Solvent peaks).

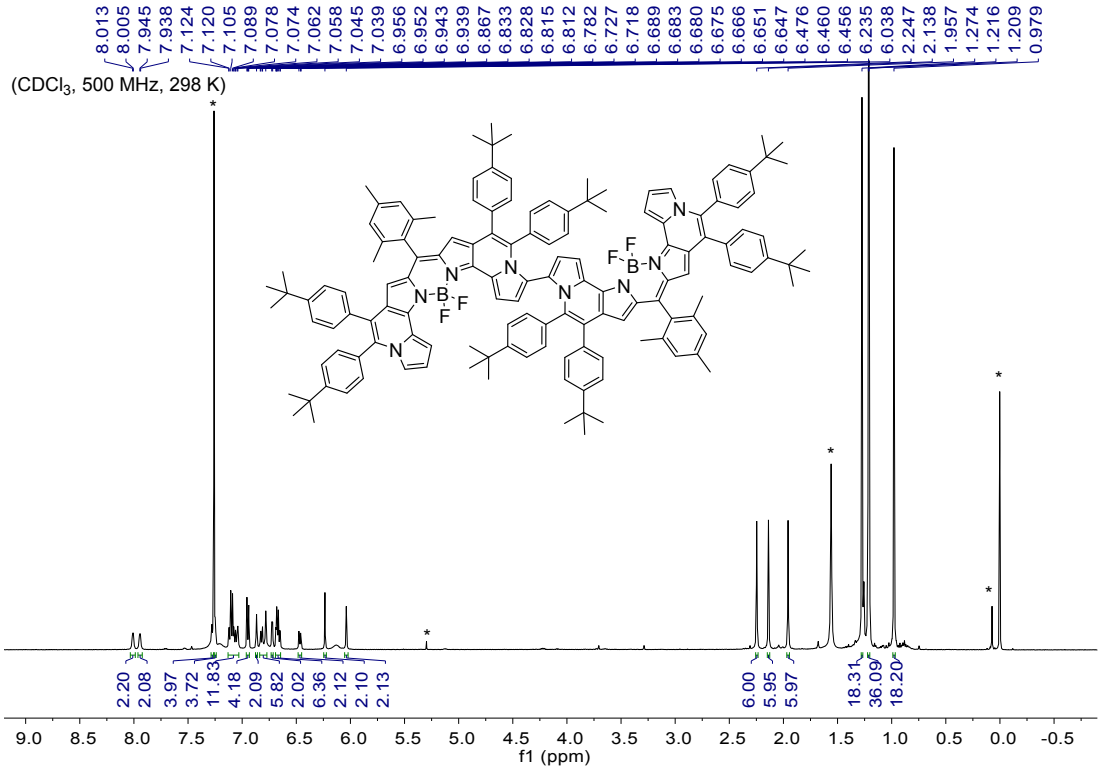


Figure S39. ^{1}H NMR spectrum of **6** in $CDCl_3$ at 298 K (*Solvent peaks).

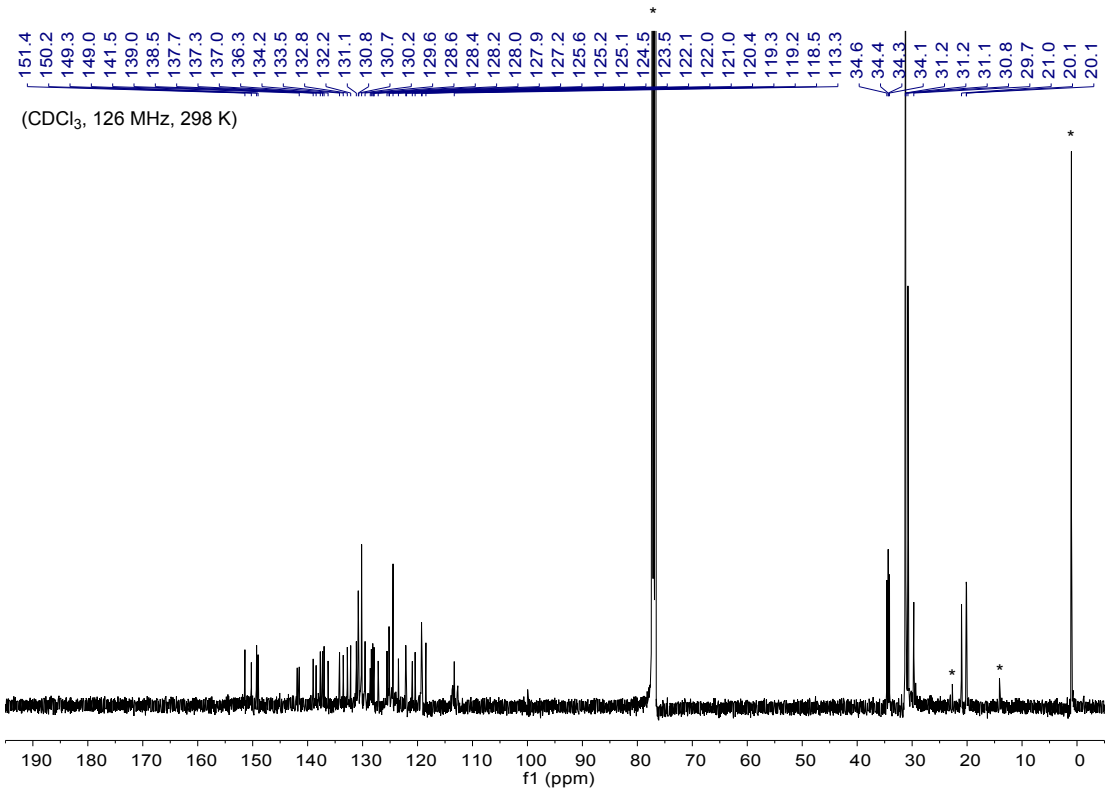


Figure S40. ^{13}C NMR spectrum of **6** in $CDCl_3$ at 298 K (*Solvent peaks).

6 Photophysical Data

Table S1. Spectroscopic data of BODIPYs measured in CH_2Cl_2.

Compounds	λ_{abs}^{max} (nm)	ε (10^5 $M^{-1}cm^{-1}$)	λ_{em}^{max} (nm)	Φ_{FL} (%)[f]	Stokes Shift (cm^{-1})[g]
1[a]	574	1.22	601	-	783 (27 nm)
3a[b]	674	0.44	712	1.84	792 (38 nm)
3b[b]	679	0.53	726	0.84	953 (47 nm)
3c[b]	677	0.35	732	0.34	1110 (55 nm)
3d[b]	667	0.51	701	4.88	727 (34 nm)
3e[b]	668	0.63	705	2.50	786 (37 nm)
3f[b]	668	0.50	704	2.78	766 (36 nm)
3g[b]	674	0.51	721	0.71	967 (47 nm)
3h[b]	685	0.32	726	0.59	824 (41 nm)
3i[b]	676	0.35	715	0.80	807 (39 nm)
4[c]	658	1.27	689	-	684 (31 nm)
5a[d]	794	1.78	922	4.06	1748 (128 nm)
5b[d]	801	1.52	930	5.80	1732 (129 nm)
5c[d]	800	1.06	931	5.18	1747 (131 nm)
5d[d]	789	1.75	914	7.13	1733 (125 nm)
5e[d]	789	1.11	919	4.99	1793 (130 nm)
5f[d]	789	1.24	918	7.92	1781 (129 nm)
5g[d]	796	1.65	925	8.83	1752 (129 nm)
5h[d]	803	1.53	931	4.58	1712 (128 nm)
5i[d]	794	1.73	924	7.94	1772 (130 nm)
5k[d]	793	1.49	924	6.06	1788 (131 nm)
6[e]	947	1.33	1060	2.09	1126 (113 nm)

[a] Excited at 400 nm; [b] Excited at 620 nm; [c] Excited at 450 nm; [d] Excited at 790 nm; [e] Excited at 850 nm; [f] Absolute quantum yields measured by an integrating sphere; [g] Stokes shift (cm^{-1}) = $10^7 \times (1/\lambda_{abs} - 1/\lambda_{em})$.

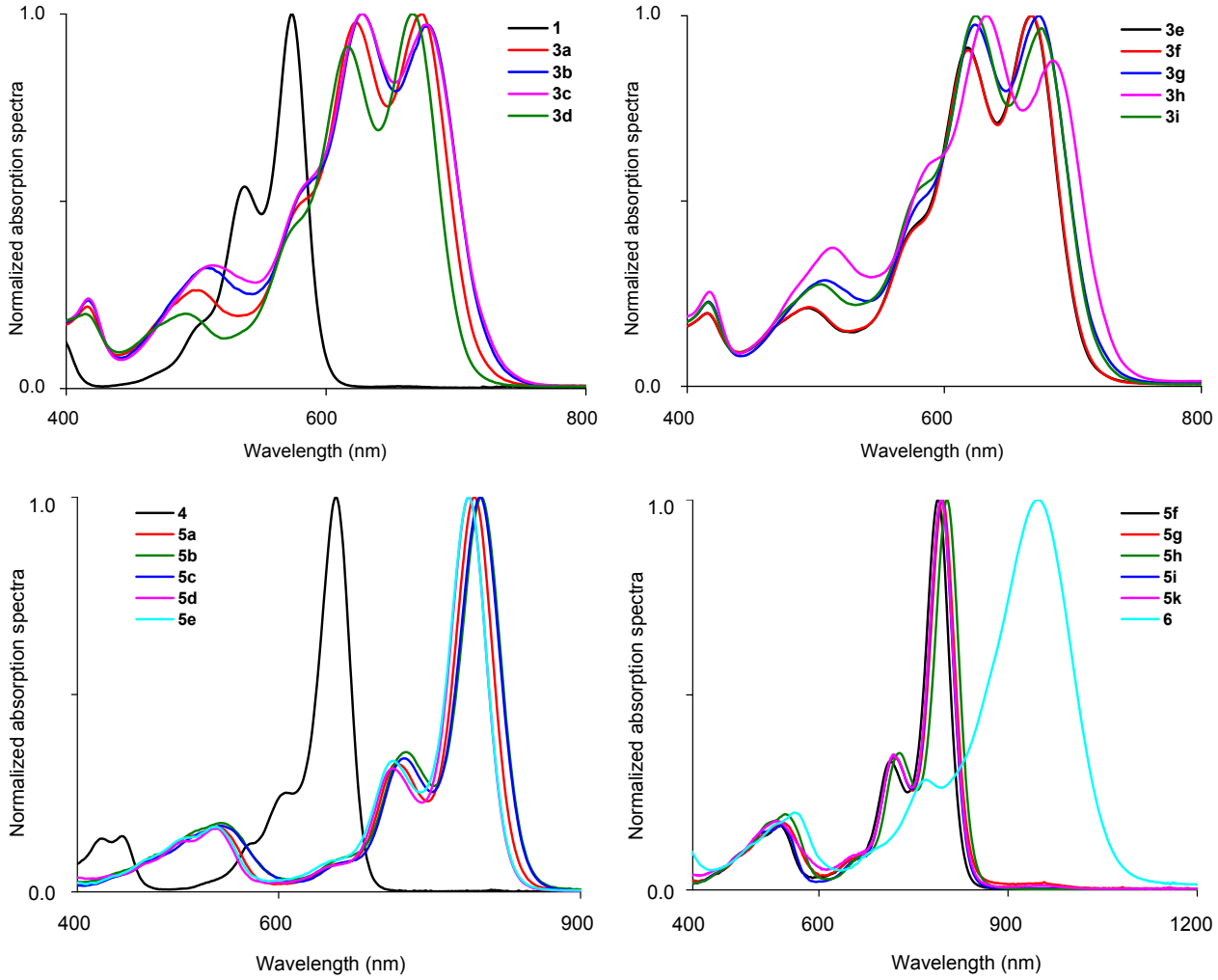


Figure S41. Normalized absorption spectra of BODIPYs in CH_2Cl_2.

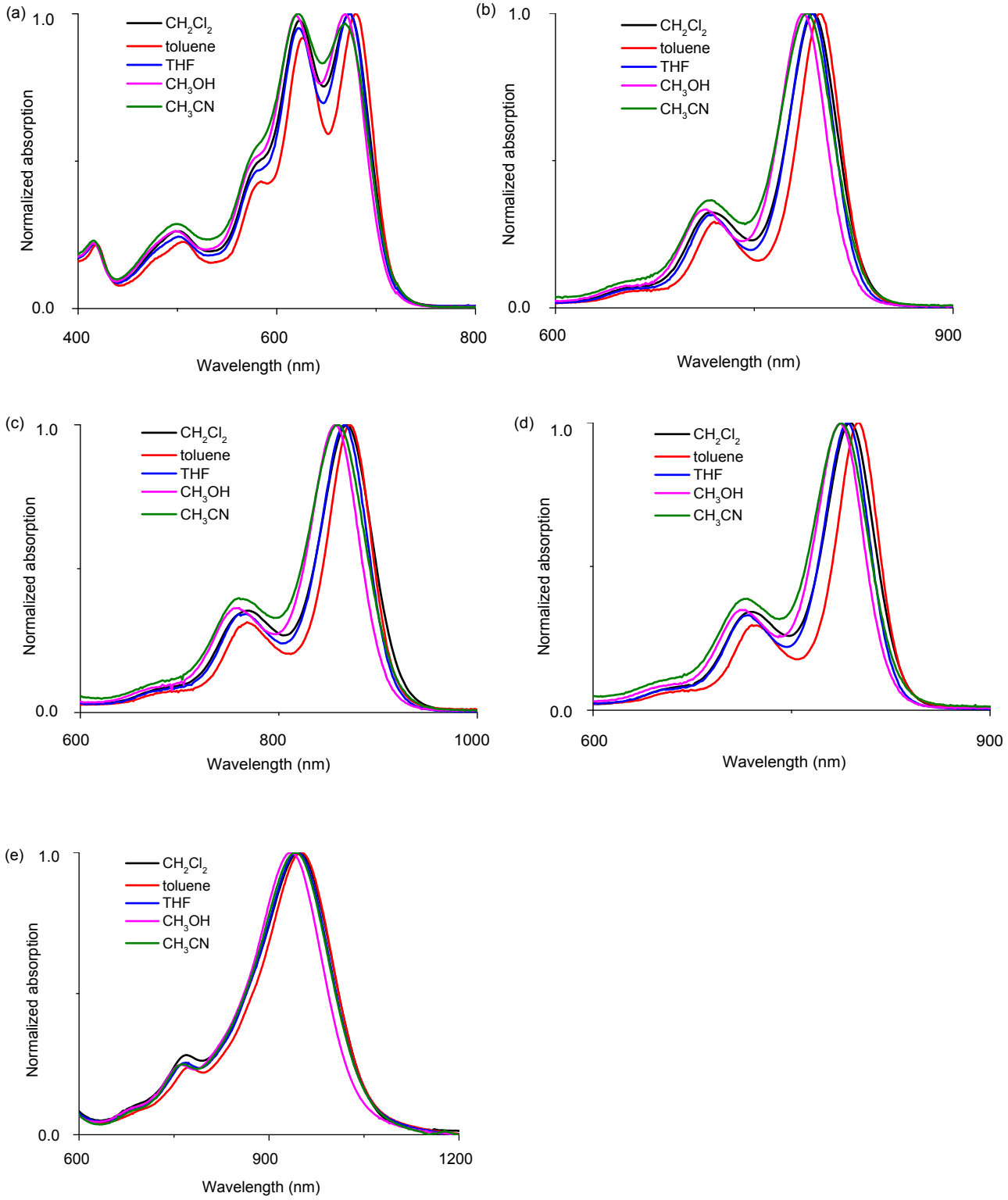


Figure 42. Normalized absorption spectra of **3a** (a), **5a** (b), **5b** (c), **5i** (d) and **6** (e) in different solvents.

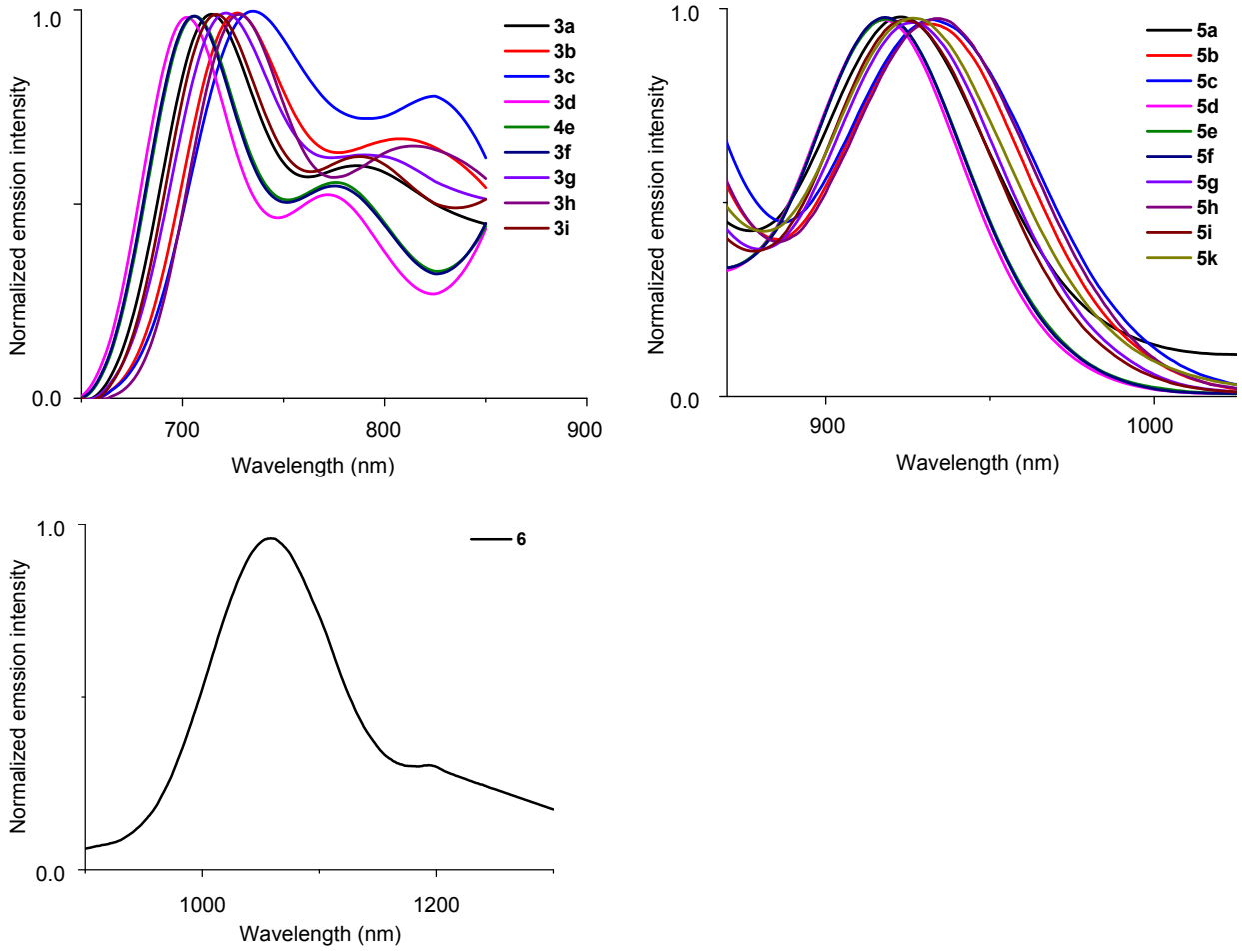


Figure S43. Normalized fluorescence emission spectra of **BODIPYs** in CH_2Cl_2.

7 Electrochemical Data

Table S2. Electrochemical properties of **3a**, **5a**, **5b**, **5g**, **5i** and **6** measured in CH_2Cl_2.[a]

Compounds	$E_{ox.1}$	$E_{red.1}$	ΔE_{HL}[b]
3a	0.47	-1.34	1.81
5a	0.14	-1.30	1.44
5b	0.10	-1.31	1.41
5g	0.16	-1.32	1.48
5i	0.06	-1.34	1.40
6	-0.06	-1.33	1.27

[a] Potentials were determined vs ferrocene/ferrocenium ion by differential pulse voltammograms; Scan rate: 0.05 V/s; working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: $Ag/AgNO_3$ supporting electrolyte: 0.1 M $n Bu_4NPF_6$ in CH_2Cl_2. [b] Electrochemical HOMO-LUMO gaps (ΔE_{HL} = e ($E_{ox.1} - E_{red.1}$) [eV]).

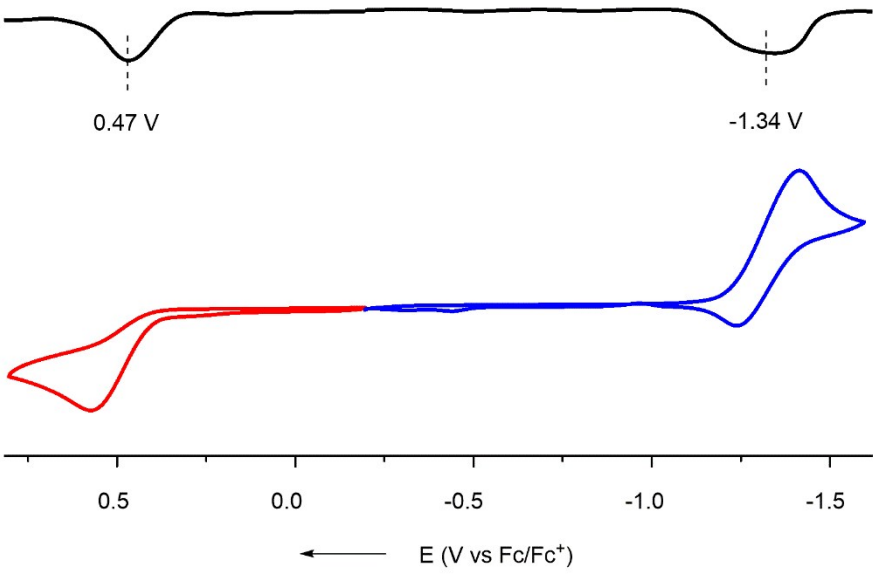


Figure S44. Cyclic voltammograms and differential pulse voltammograms of **3a**.

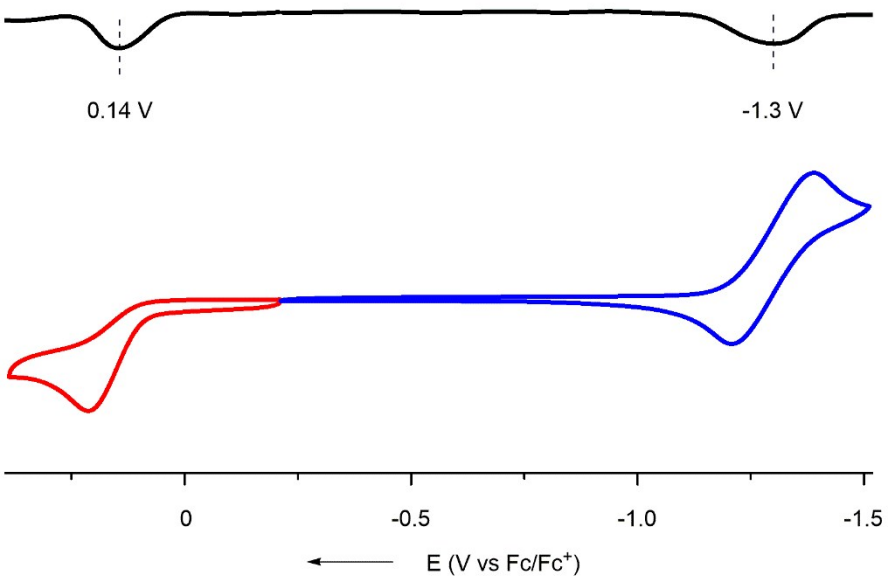


Figure S45. Cyclic voltammograms and differential pulse voltammograms of **5a**.

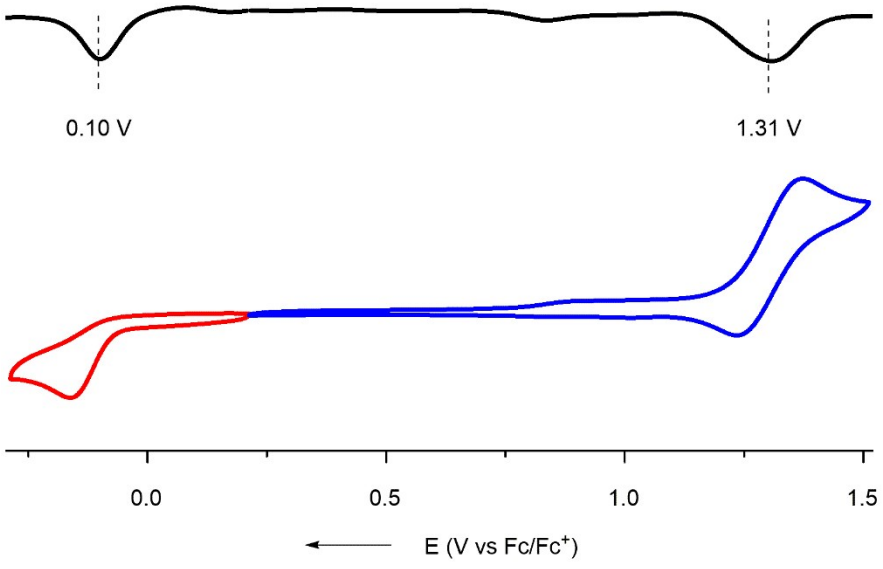


Figure S46. Cyclic voltammograms and differential pulse voltammograms of **5b**.

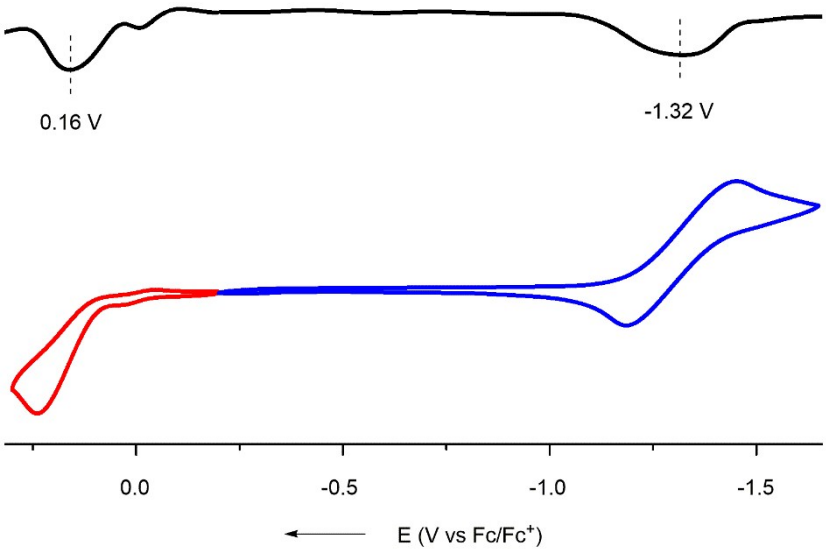


Figure S47. Cyclic voltammograms and differential pulse voltammograms of **5g**.

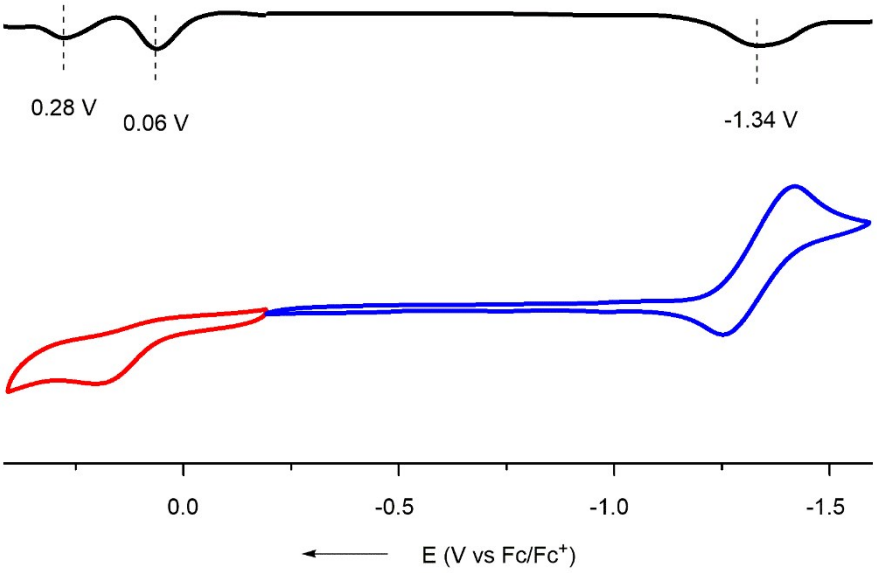


Figure S48. Cyclic voltammograms and differential pulse voltammograms of **5i**.

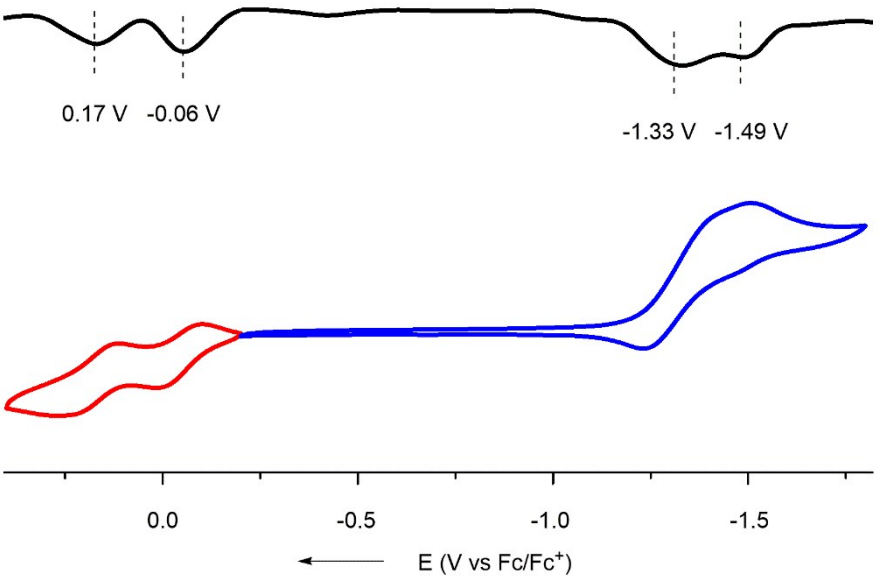


Figure S49. Cyclic voltammograms and differential pulse voltammograms of **6**.

8 X-Ray Crystal Data

Single crystal of **5a** was obtained by diffusion of methanol into $CHCl_3$ solution. Single crystal of **5i** and **6** were obtained by diffusion of methanol into toluene solution.

A suitable crystal of **5a** was selected and measured on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. The crystal was kept at 103(2) K during data collection. Using Olex[2], the structure was solved with the olex2.solve[3] structure solution program using Charge Flipping and refined with the ShelXL[4] refinement package using Least Squares minimisation.

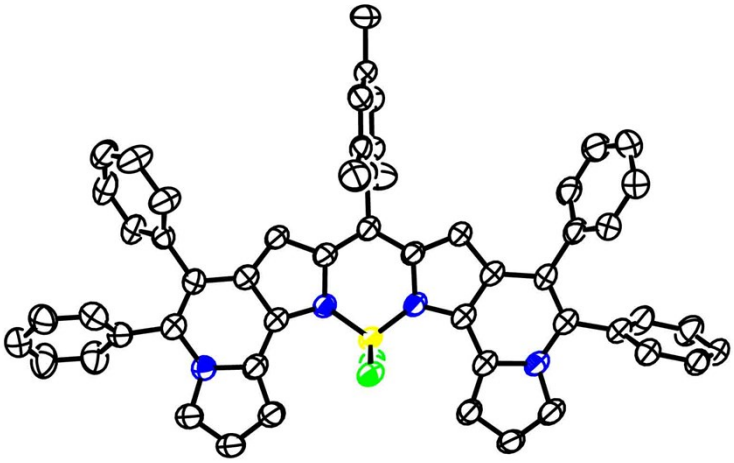
A suitable crystal of **5i** was selected and measured on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. The crystal was kept at 100.01(10) K during data collection. Using Olex[2], the structure was solved with the olex2.solve[3] structure solution program using Charge Flipping and refined with the ShelXL[4] refinement package using Least Squares minimisation.

A suitable crystal of **6** was selected and measured on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. The crystal was kept at 100.01(10) K during data collection. Using Olex[2], the structure was solved with the olex2.solve[3]

structure solution program using Charge Flipping and refined with the ShelXL[4] refinement package using Least Squares minimisation.

Crystallographic data for **5a**, **5i** and **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-20496302, 2049305 and 2049303, respectively.

a)



b)

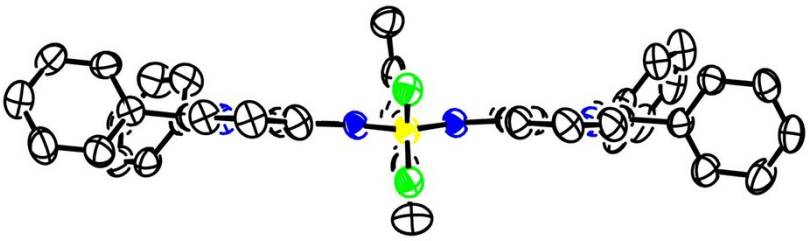


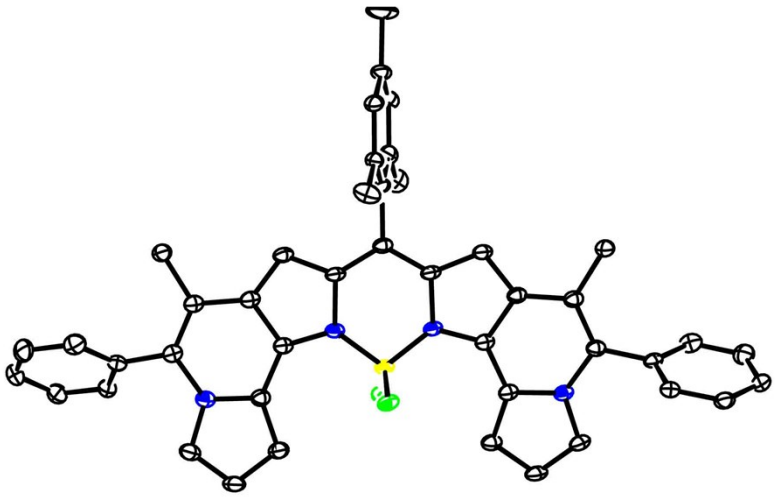
Figure S50. X-ray crystal structure of **5a**: (a) top view, (b) side view. The thermal ellipsoids are 50% probability level. H atom and solvent molecules are omitted for clarity.

Table S3. Crystal data and structure refinement for **5a**.

Identification code	exp_969
Empirical formula	$C_{55}H_{39}BF_2N_4$
Formula weight	792.32
Temperature	103(2) K

Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.8215(4) Å	α = 95.886(4)°.
	b = 16.5415(9) Å	β = 92.564(3)°.
	c = 24.4131(9) Å	γ = 99.903(4)°.
Volume	4668.5(4) $Å^3$	
Z	4	
Density (calculated)	1.298 Mg/m^3	
Absorption coefficient	2.178 mm^{-1}	
F(000)	1888	
Crystal size	0.3 x 0.1 x 0.02 mm^3	
Theta range for data collection	3.448 to 66.599°	
Index ranges	-8<=h<=14, -19<=k<=19, -29<=l<=24	
Reflections collected	30787	
Independent reflections	16467 [R(int) = 0.0471]	
Completeness to theta = 66.599°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.03581	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16467 / 0 / 1177	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0841, wR2 = 0.2381	
R indices (all data)	R1 = 0.1174, wR2 = 0.2780	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.149 and -0.702 $e.Å^{-3}$	

c)



d)

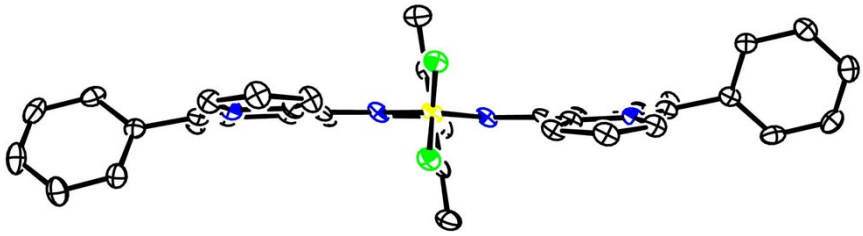


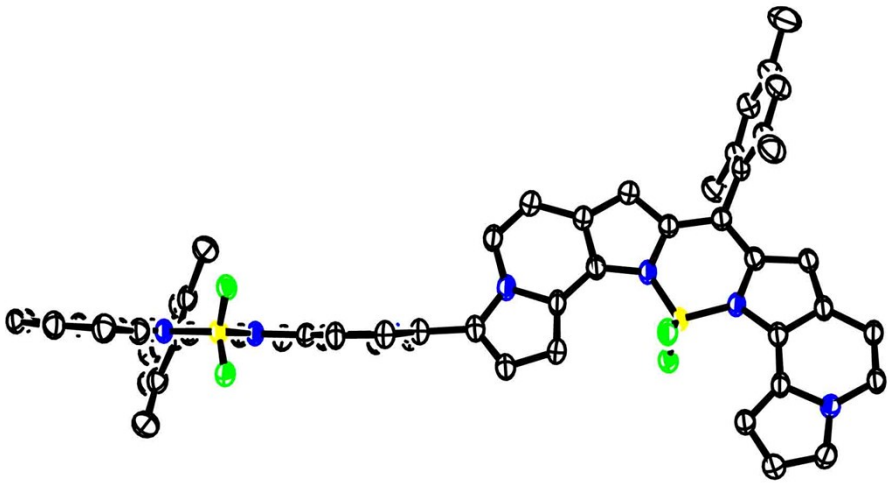
Figure S51. X-ray crystal structure of **5i**: (c) top view, (d) side view. The thermal ellipsoids are 50% probability level. H atom and solvent molecules are omitted for clarity.

Table S4. Crystal data and structure refinement for **5i**.

Identification code	exp_1201	
Empirical formula	$C_{44}H_{35}BF_2N_4$	
Formula weight	668.29	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.12882(13) Å	α = 90°.
	b = 14.06583(16) Å	β = 98.6568(11)°.
	c = 25.7320(3) Å	γ = 90°.

Volume	3982.10(8) $Å^3$
Z	4
Density (calculated)	1.269 Mg/m^3
Absorption coefficient	0.637 mm^{-1}
F(000)	1600
Crystal size	0.3 x 0.1 x 0.1 mm^3
Theta range for data collection	3.475 to 66.598°.
Index ranges	-13<=h<=10, -16<=k<=16, -29<=l<=30
Reflections collected	13666
Independent reflections	7043 [R(int) = 0.0211]
Completeness to theta = 66.598°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.38444
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7043 / 0 / 529
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0968
R indices (all data)	R1 = 0.0429, wR2 = 0.1008
Extinction coefficient	n/a
Largest diff. peak and hole	0.208 and -0.251 $e.Å^{-3}$

e)



f)

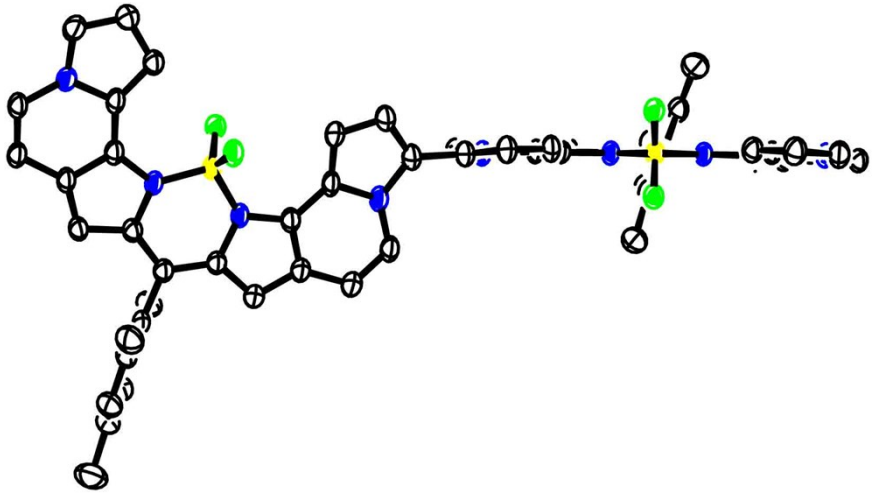


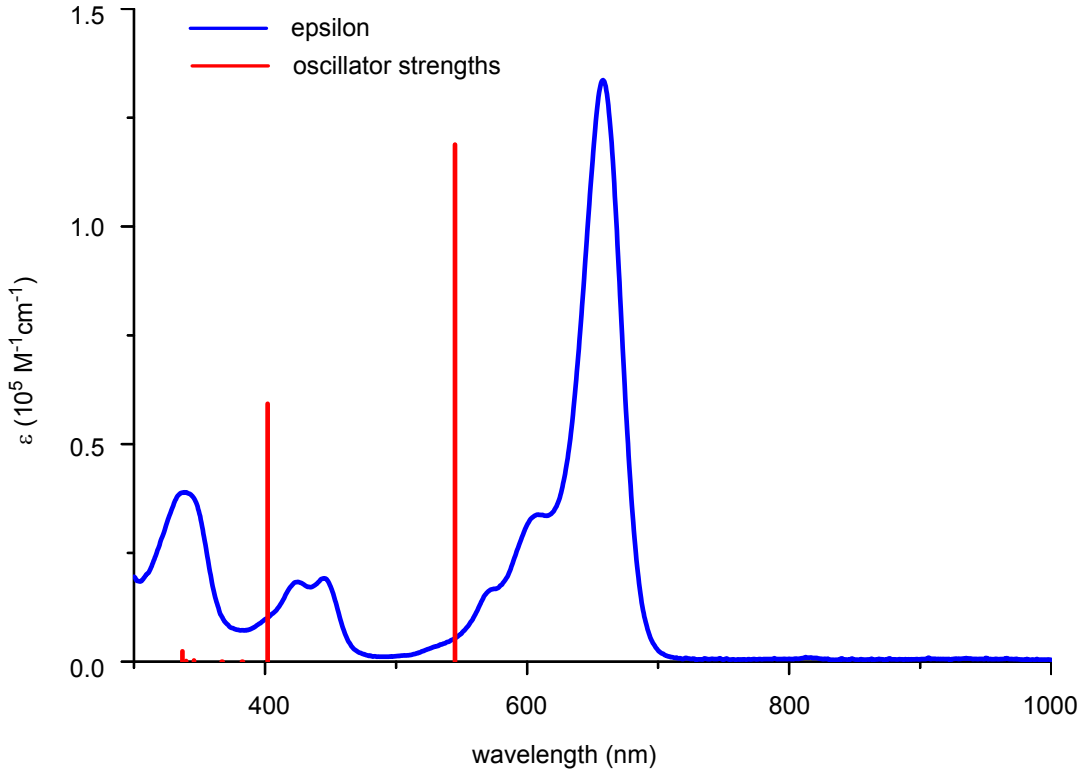
Figure S52. X-ray crystal structure of **6**: (e) top view, (f) side view. The thermal ellipsoids are 50% probability level. H atom, solvent molecules and 1-(*tert*-butyl)phenyl of are omitted for clarity;

Table S5. Crystal data and structure refinement for **6**.

Identification code	exp_1129_sq
Empirical formula	$C_{140}H_{140}B_2F_4N_8$
Formula weight	2030.14
Temperature	100.01(10) K
Wavelength	1.54184 Å

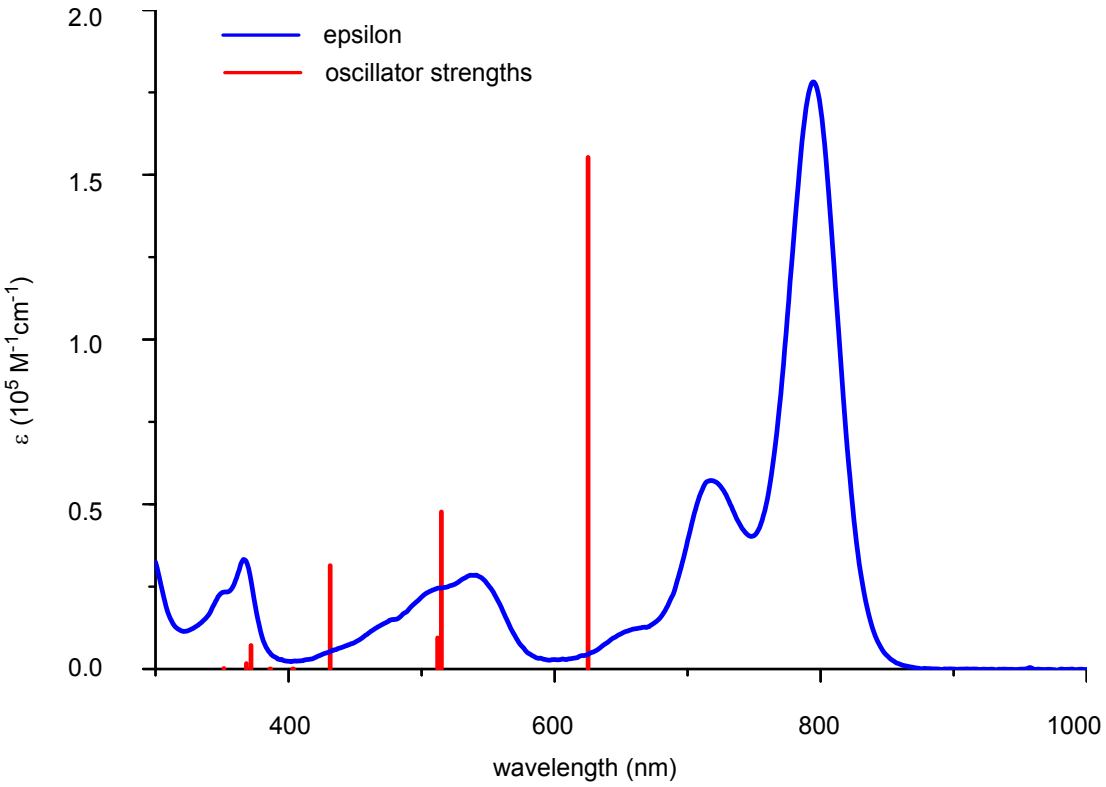
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 21.0519(3) Å	α = 90°.
	b = 37.6546(10) Å	β = 97.112(2)°.
	c = 19.1086(4) Å	γ = 90°.
Volume	15030.9(6) $Å^3$	
Z	4	
Density (calculated)	0.898 Mg/m^3	
Absorption coefficient	0.429 mm^{-1}	
F(000)	4328	
Crystal size	0.2 x 0.1 x 0.05 mm^3	
Theta range for data collection	2.419 to 66.594°	
Index ranges	-25<=h<=20, -44<=k<=42, -22<=l<=21	
Reflections collected	46028	
Independent reflections	13291 [R(int) = 0.0477]	
Completeness to theta = 66.594°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.76116	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13291 / 0 / 709	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0677, wR2 = 0.1841	
R indices (all data)	R1 = 0.0974, wR2 = 0.2047	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.301 and -0.237 $e.Å^{-3}$	

9 DFT/Calculation



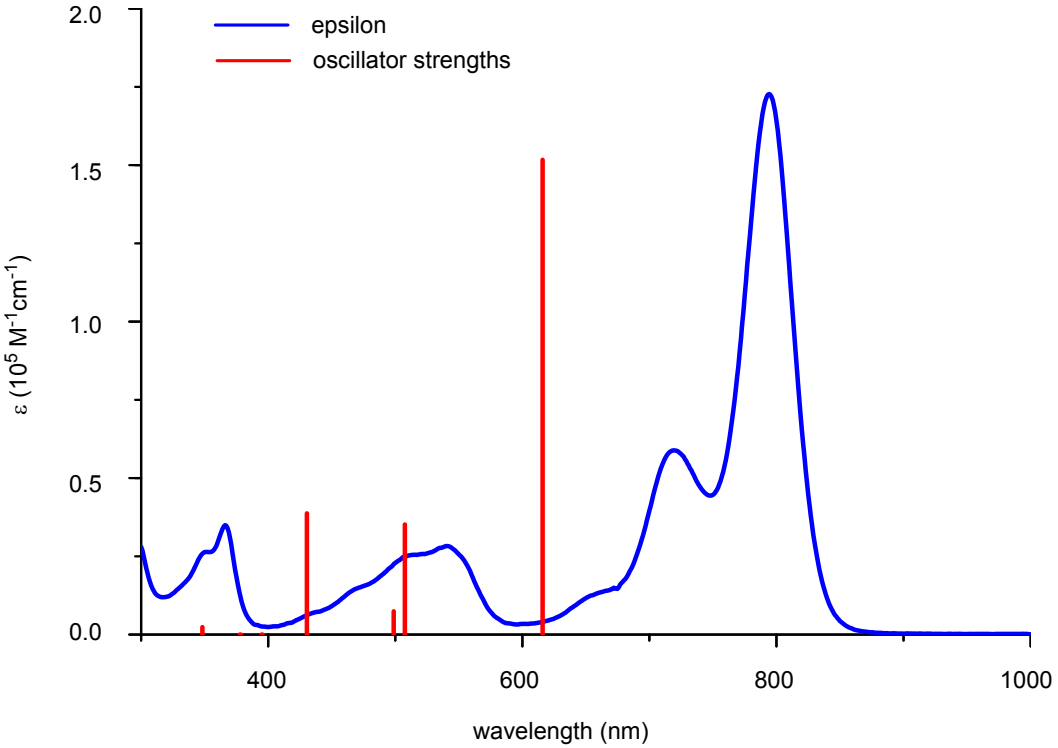
Wavelength(nm)	Oscillator Strengths	Major Transitions
545	0.5940	HOMO→LUMO (102%)
402	0.2963	HOMO-1→LUMO (93%)
382	0.0000	HOMO-2→LUMO (99%)
367	0.0000	HOMO-3→LUMO (100%)
346	0.0015	HOMO-6→LUMO (17%); HOMO-4→LUMO (74%)
340	0.0008	HOMO-5→LUMO (70%)
337	0.0119	HOMO-6→LUMO (73%); HOMO-4→LUMO (23%)
319	0.0169	HOMO-8→LUMO (97%)
308	0.0059	HOMO→LUMO+1 (91%)
307	0.0334	HOMO-7→LUMO (73%)

Figure S53. Calculated vertical transitions and major transitions of **4** calculated by TD-DFT using B3LYP employing the 6-31G(d) basis set.



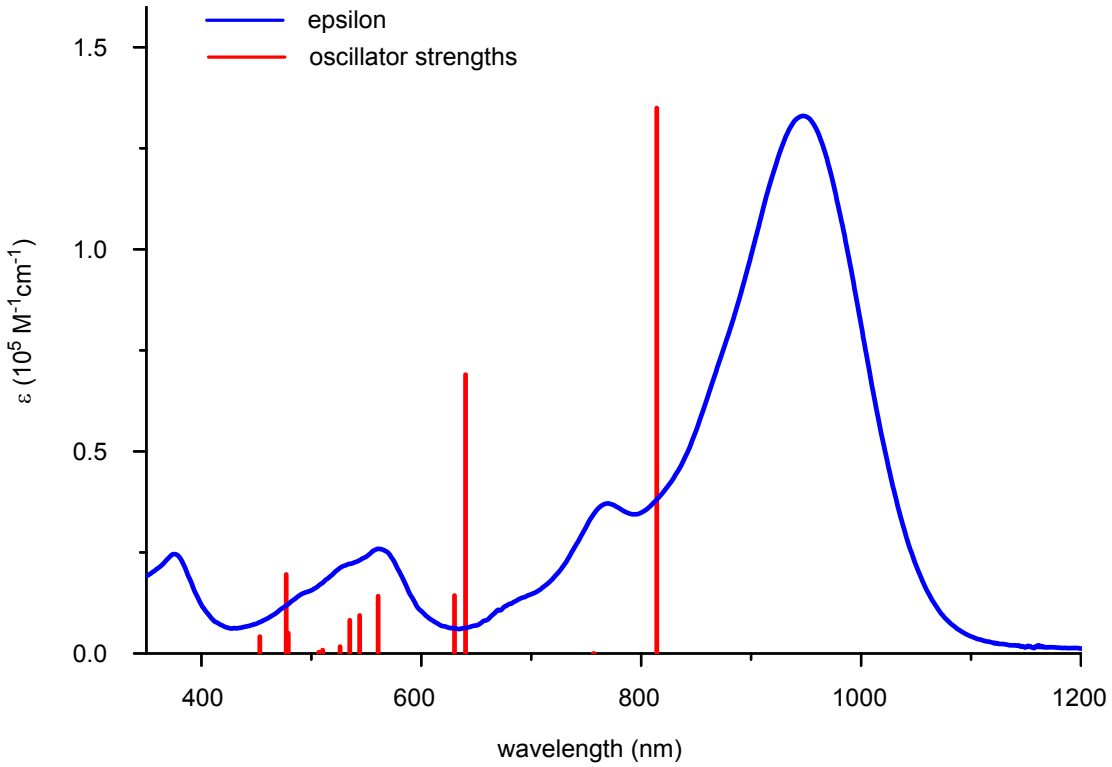
Wavelength(nm)	Oscillator Strengths	Major Transitions
625	0.7764	HOMO→LUMO (96%)
515	0.2384	HOMO-2→LUMO (91%)
512	0.0473	HOMO-3→LUMO (21%); HOMO-1→LUMO (76%)
431	0.1568	HOMO-3→LUMO (74%); HOMO-1→LUMO (19%)
403	0.0001	HOMO-4→LUMO (99%)
386	0.0000	HOMO-5→LUMO (100%)
372	0.0358	HOMO→LUMO+1 (95%)
368	0.0082	HOMO→LUMO+2 (94%)
351	0.0008	HOMO-6→LUMO (93%)
345	0.0010	HOMO-7→LUMO (95%)
332	0.0155	HOMO-8→LUMO (93%)
331	0.0002	HOMO-9→LUMO (96%)

Figure S54. Calculated vertical transitions and major transitions of **5a** calculated by TD-DFT using B3LYP employing the 6-31G(d) basis set.



Wavelength(nm)	Oscillator Strengths	Major Transitions
616	0.7585	HOMO→LUMO (97%)
508	0.1758	HOMO-2→LUMO (94%)
499	0.0373	HOMO-3→LUMO (33%); HOMO-1→LUMO (66%)
430	0.1936	HOMO-3→LUMO (64%); HOMO-1→LUMO (31%)
395	0.0000	HOMO-4→LUMO (99%)
378	0.0000	HOMO-5→LUMO (100%)
348	0.0120	HOMO→LUMO+1 (96%)
341	0.0013	HOMO→LUMO+2 (96%)
328	0.0088	HOMO-7→LUMO (80%)
324	0.0034	HOMO→LUMO+3 (96%)
323	0.0092	HOMO→LUMO+4 (95%)

Figure S55. Calculated vertical transitions and major transitions of **5i** calculated by TD-DFT using B3LYP employing the 6-31G(d) basis set.



Wavelength(nm)	Oscillator Strengths	Major Transitions
814	1.3498	HOMO→LUMO (99%)
757	0.0000	HOMO-1→LUMO (41%); HOMO→LUMO+1 (58%)
640	0.6901	HOMO-1→LUMO+1 (94%);
630	0.1436	HOMO-1→LUMO (51%); HOMO→LUMO+1 (38%)
561	0.1417	HOMO-4→LUMO (84%)
544	0.0942	HOMO-4→LUMO+1 (13%); HOMO-2→LUMO (76%)
535	0.0824	HOMO-6→LUMO+1 (15%); HOMO-5→LUMO+1 (11%); HOMO-3→LUMO (62%)
526	0.0169	HOMO-5→LUMO (38%); HOMO-4→LUMO+1 (35%)
510	0.0084	HOMO-5→LUMO (25%); HOMO-4→LUMO+1 (46%) HOMO-3→LUMO+1 (10%); HOMO-2→LUMO (12%)
507	0.0034	HOMO-2→LUMO+1 (81%)
479	0.0505	HOMO-5→LUMO (23%); HOMO-3→LUMO+1 (72%)
477	0.1957	HOMO-6→LUMO (29%); HOMO-5→LUMO+1 (40%); HOMO-3→LUMO (24%);

Figure S56. Calculated vertical transitions and major transitions of **6** calculated by TD-DFT using B3LYP employing the 6-31G(d) basis set.

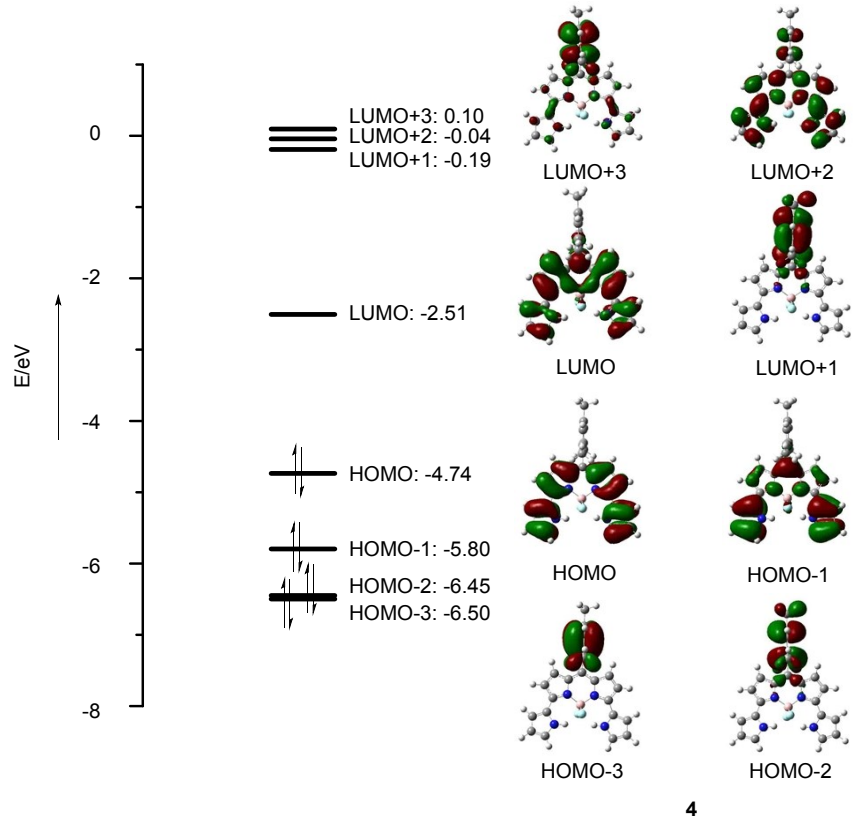


Figure S57. Energy diagram and selected Kohn–Sham orbitals of **4**.

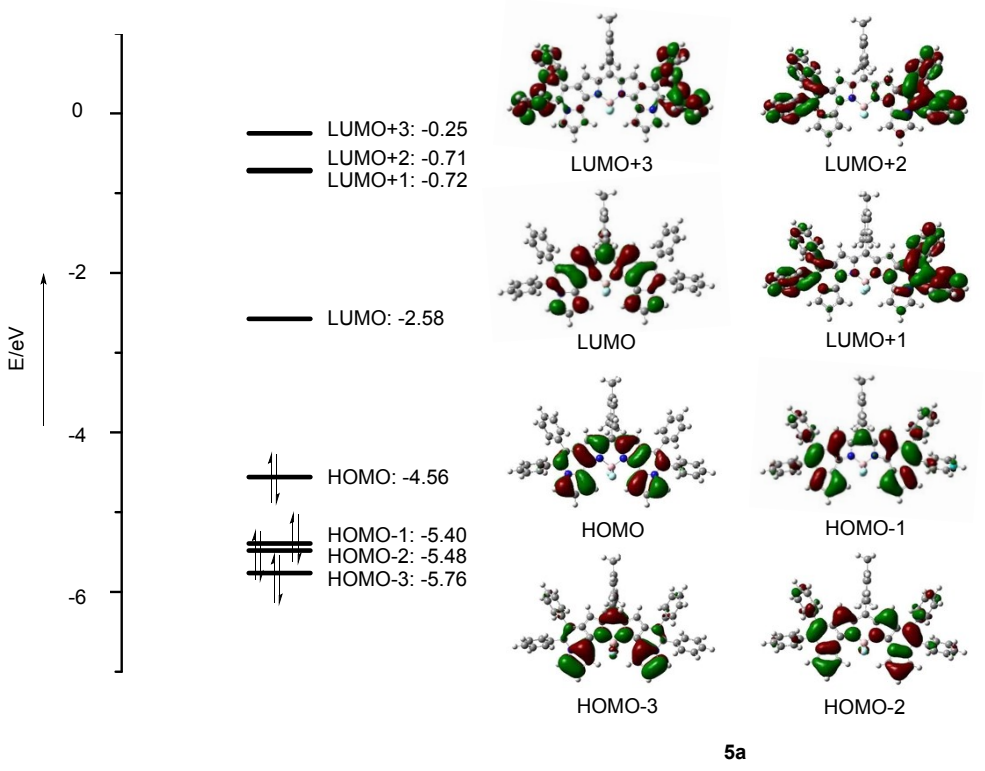


Figure S58. Energy diagram and selected Kohn–Sham orbitals of **5a**.

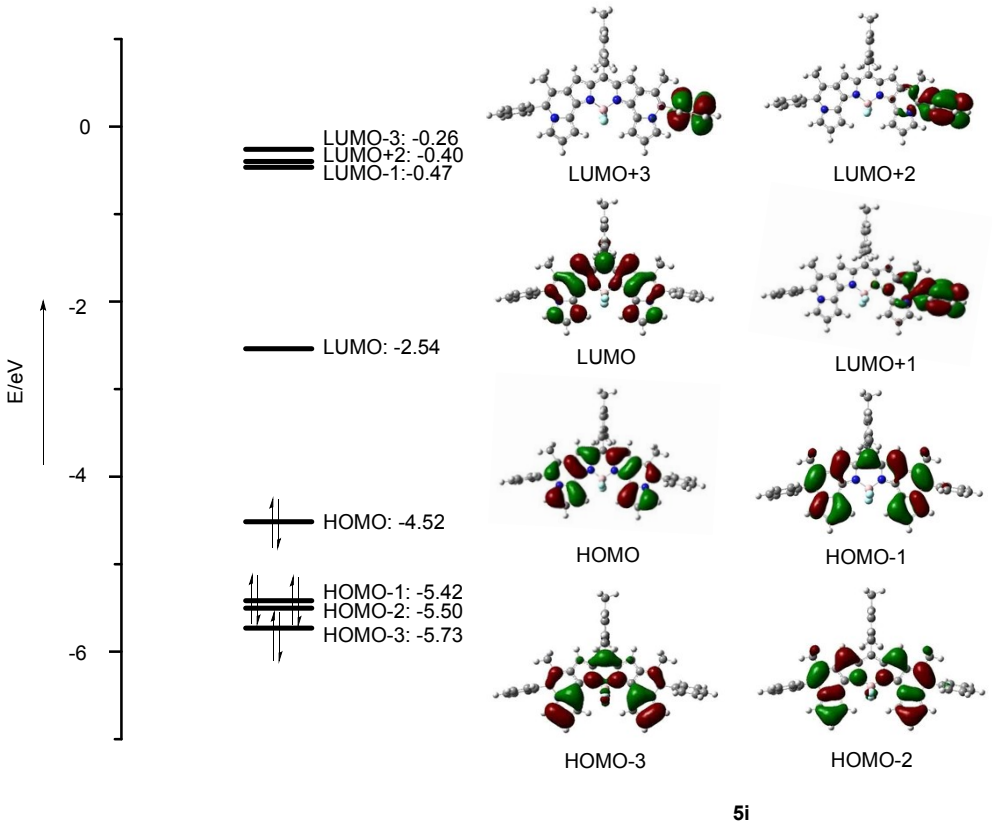


Figure S59. Energy diagram and selected Kohn–Sham orbitals of **5i**.

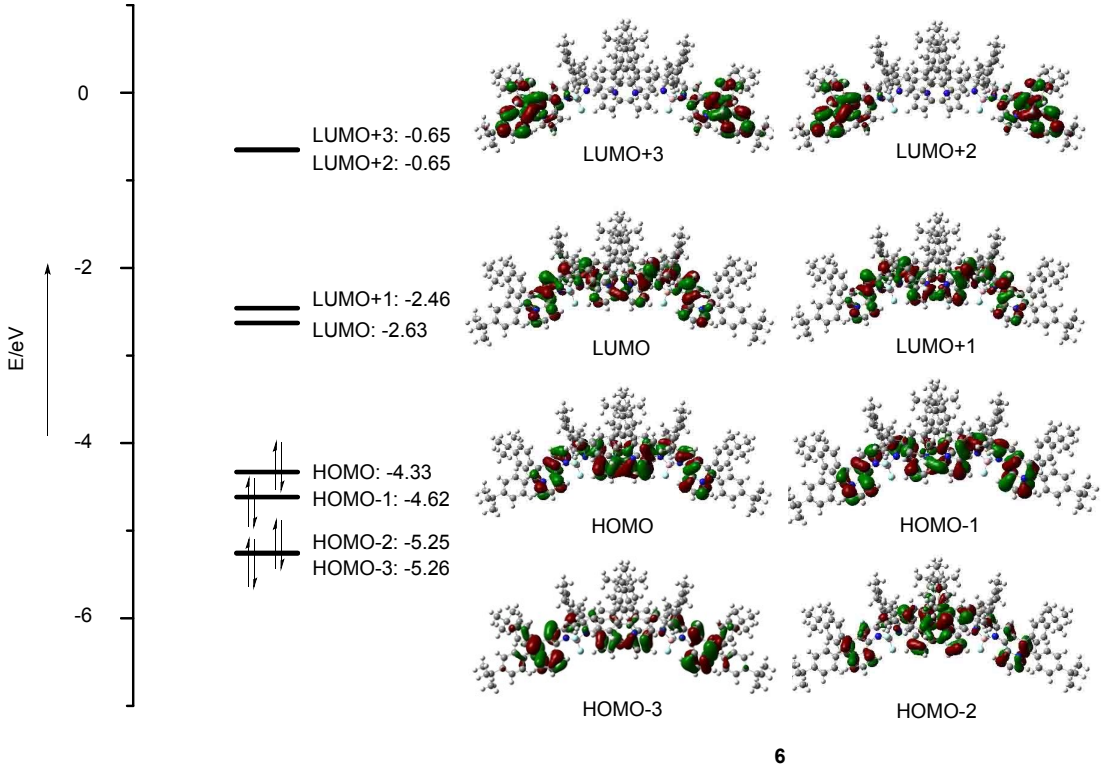


Figure S60. Energy diagram and selected Kohn–Sham orbitals of **6**.

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1 (*a*) W. Miao, E. Dai, W. Sheng, C. Yu, E. Hao, W. Liu, Y. Wei and L. Jiao, Direct synthesis of dipyrrolyldipyrrins from S_NAr reaction on 1,9-dihalodipyrrins with pyrroles and their NIR fluorescence "turn-on" response to Zn^{2+}, *Org. Lett.*, 2017, **19**, 6244-6247; (*b*) T. Jiang, P. Zhang, C. Yu, J. Yin, L. Jiao, E. Dai, J. Wang, Y. Wei, X. Mu and E. Hao, *Org. Lett.*, 2014, **16**, 1952-1955.

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