Supporting Information

Carbazole-Based BODIPYs: Facile Synthesis, Structures, and Fine-Tunable Optical Properties

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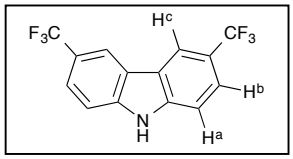
Instrumentation and Materials

^{1}H and ^{13}C NMR spectra were measured on a JEOL ECA-400 spectrometer, and chemical shifts were reported as the delta scale in ppm as internal reference (δ = 7.260 for ^{1}H NMR, 77.00 for ^{13}C NMR, for $CDCl_3$, and δ = 2.50 for ^{1}H NMR, 39.52 for ^{13}C NMR, for DMSO-d_6). UV/vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5300 spectrometer or on JASCO FP-750. Relative fluorescence quantum yields were determined with the reference value of Zn(II) tetraphenylporphyrin (0.033 in toluene). HR mass spectra were taken on a Bruker microTOF. Redox potentials were measured by the cyclic voltammetry method on an ALS electrochemical analyzer model CHI-600B. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Dry CH_2Cl_2 was distilled from CaH_2. 3,6-Dimethoxycarbazole[S1], 3,6-diphenylcarbazole[S2], dibenzocarbazole[S3] were prepared by the literature method.

Experimental Procedures and Compound Data

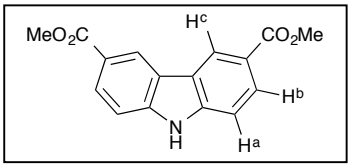
3,6-bis(trifluoromethyl)carbazole



A suspension of bis(4-trifluoromethylphenyl)amine[S4] (2.39 g, 7.84 mmol), $Pd(OAc)_2$ (614 mg, 2.73 mmol), and $Cu(OAc)_2 \cdot H_2O$ (15.6 g, 78.0 mmol) in AcOH (10 mL) was heated at 100 ˚C for 18 h under air. The mixture was passed through a silica gel column with $CHCl_3$. The solution was washed with $NaHCO_3$ aq, passed through a silica gel column with $CHCl_3$, and evaporated. Recrystallization from $CHCl_3$/hexane gave the product as a white solid (1.18 g, 3.87 mmol, 49%).

^{1}H NMR ($CDCl_3$) δ = 8.50 (s, 1H, NH), 8.39 (d, J = 0.8 Hz, 2H, H^c), 7.73 (dd, J = 0.6, 8.6 Hz, 2H, H^b), and 7.56 ppm (d, J = 8.4 Hz, 2H, H^a); ^{13}C NMR ($CDCl_3$) δ = 141.33, 124.93 (q, J = 271 Hz), 123.63 (q, J = 3.8 Hz), 122.63 (q, J = 32.5 Hz), 122.44, 118.16 (q, J = 3.8 Hz), and 111.10 ppm; HRMS (APCI): m/z = 304.0559. calcd for $C_{14}H_8NF_6$: 304.0555 $[M + H]^+$.

3,6-bis(methoxycarbonyl)carbazole[S5]

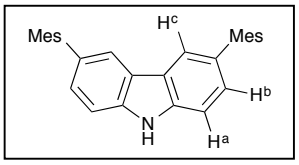


To a solution of 3,6-dibromocarbazole (1.32 g, 4.06 mmol) in dehydrated THF (22 mL) was added *n*-BuLi (1.6 M in hexane, 16 mL, 26 mmol) at –80 ˚C. The cool bath was removed for 1 h, and then the vessel was cooled again to –80 ˚C. Methyl chloroformate (2.4 mL, 31 mmol) was added, and the mixture was warmed to rt, and the reaction was quenched with water. Organic solvents were evaporated, and organic compounds were extracted with $CHCl_3$. The organic layer was washed with water, dried over Na_2SO_4, and evaporated. The residue was treated with NaOMe (5 M in MeOH, 0.40 mL) in DMF (5 mL) at 70 ˚C for 12 h. Water was added, and organic compounds were extracted with $CHCl_3$. The organic layer was washed with water, and evaporated. The residue was

purified by silica gel chromatography with $CHCl_3$ to give the product as a pale yellow solid (358 mg, 1.16 mmol, 29%).

^{1}H NMR ($CDCl_3$) δ = 8.85 (s, 2H, H^c), 8.42 (s, 1H, NH), 8.17 (dd, J = 1.4, 8.4 Hz, 2H, H^b), 7.56 (d, J = 8.8 Hz, 2H, H^a), and 3.99 ppm (s, 6H, CO_2Me); ^{13}C NMR ($CDCl_3$) δ = 167.45, 142.86, 128.28, 123.40, 123.16, 122.86, 110.50, and 51.90 ppm; HRMS (APCI): m/z = 282.0784. calcd for $C_{16}H_{12}NO_4$: 282.0772 $[M - H]^-$.

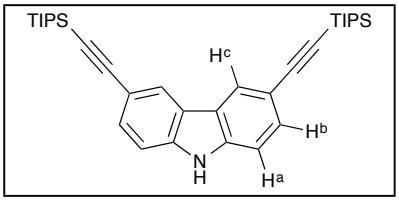
3,6-bis(2,4,6-trimethylphenyl)carbazole



A solution of 3,6-dibromocarbazole (1.28 g, 3.94 mmol), 2,4,6-trimethylphenylboronic acid (1.92 g, 11.7 mmol), $Pd(PPh_3)_4$ (114 mg, 98.6 μmol), and Cs_2CO_3 (4.17 g, 12.8 mmol) in toluene/EtOH/H_2O (15/10/10 mL) was heated at 100 ˚C for 12 h under Ar. The organic layer was extracted with EtOAc and evaporated. The residue was separated over a silica gel column with EtOAc/hexane as an eluent to give the product as a white solid (1.33 g, 3.29 mmol, 84%)

^{1}H NMR ($CDCl_3$) δ = 8.09 (s, 1H, NH), 7.83 (d, J = 0.8 Hz, 2H, H^c), 7.51 (d, J = 8.0 Hz, 2H, H^a), 7.23 (dd, J = 1.8, 8.4 Hz, 2H, H^b), 7.03 (s, 4H, Mes), 2.40 (s, 6H, *p*Mes), and 2.10 ppm (s, 12H, *o*Mes); ^{13}C NMR ($CDCl_3$) δ = 139.62, 138.55, 136.66, 136.34, 132.24, 128.00, 127.37, 123.44, 120.73, 110.54, 21.04, and 21.00 ppm; HRMS (APCI): m/z = 402.2214. calcd for $C_{30}H_{28}N$: 402.2227 $[M - H]^-$.

3,6-bis(triisopropylsilylethynyl)carbazole



A flask containing 3,6-diiodocarbazole (838 mg, 2.00 mmol), CuI (19.2 mg 101 μmol), and $PdCl_2(PPh_3)_2$ (70.5 mg, 100 μmol) was purged with N_2, charged with

dehydrated THF (20 mL) and Et_3N (17 mL), and degassed. Triisopropylsilylacetylene (1.2 mL, 5.4 mmol) was then added, and the resulting mixture was stirred at room temperature for 12 h. After the solvents were evaporated, the residue was purified by silica gel chromatography with EtOAc/hexane to give the product as a pale orange solid (931 mg, 1.76 mmol, 88%).

^{1}H NMR ($CDCl_3$) δ = 8.21 (d, J = 0.8 Hz, 2H, H^c), 8.13 (s, 1H, NH), 7.55 (dd, J = 1.6, 8.4 Hz, 2H, H^b), 7.33 (d, J = 8.4 Hz, 2H, H^a), and 1.17 ppm (s, 42H, TIPS); ^{13}C NMR ($CDCl_3$) δ = 139.31, 130.34, 124.53, 122.68, 114.88, 110.58, 108.09, 88.26, 18.75, and 11.41 ppm; HRMS (APCI): m/z = 526.3351. calcd for $C_{34}H_{48}NSi_2$: 526.3331 $[M - H]^-$.

General procedures for the synthesis of carbazole-based BODIPYs

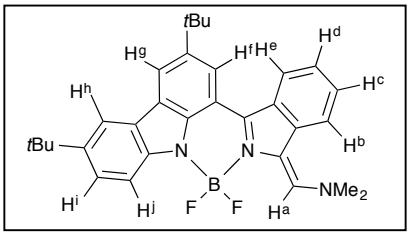
A solution of carbazole **1a**–**1h** (1.0 mmol), $(Bpin)_2$ (165 mg, 0.65 mmol), $[Ir(OMe)(cod)]_2$ (6.6 mg, 10 μmol), and dtbpy (5.4 mg, 20 μmol) in dry THF (1 mL) was heated at reflux for 16 h under N_2. After cooling to rt, the mixture was passed through a pad of silica gel with $CHCl_3$, and evaporated to dryness. The crude product was analyzed by ^{1}H NMR and used for the subsequent Suzuki–Miyaura coupling reaction.

A solution of the borylated carbazole, (3-chloro-1*H*-isoindol-1-ylidene)-*N*,*N*-dimethylmethanamine [S6] (**4**) (0.8–1.2 mmol), $Pd(OAc)_2$ (11 mg, 50 μmol), XPhos (47 mg, 100 μmol), and K_3PO_4 (320 mg, 1.5 mmol) in THF/H_2O (4 mL/0.20 mL) was heated at reflux for 48 h under N_2. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$ to give a crude coupling product.

The crude product was dissolved in dry CH_2Cl_2 (20 mL). Et_3N (0.40 mL) and then $BF_3{\cdot}OEt_2$ (0.63 mL) were added, and the mixture was stirred for 2 h. After the solvents were removed, the residue was

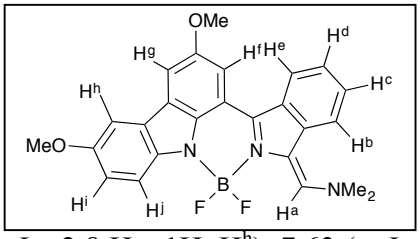
purified by silica gel chromatography with $CHCl_3$. The crude product was recrystallized from $CHCl_3$/MeOH to give carbazole-based BODIPYs in 6–28% yield in 3 steps.

Compound data for 5a



Orange solid, 120 mg, 241 μmol, 24%; ^{1}H NMR ($CDCl_3$) δ = 8.86 (s, 1H, H^a), 8.57 (d, J = 8.0 Hz, 1H, H^e), 8.46 (d, J = 1.2 Hz, 1H, H^f), 8.26 (s, 1H, H^g), 8.14 (d, J = 2.0 Hz, 1H, H^h), 7.85 (d, J = 8.4 Hz, 1H, H^j), 7.66 (d, J = 8.0 Hz, 1H, H^b), 7.58 (dd, J = 2.0, 8.0 Hz, 1H, H^i), 7.55 (t, J = 8.0 Hz, 1H, H^c), 7.45 (t, J = 7.6 Hz, 1H, H^d), 3.50 (s, 6H, Me), 1.58 (s, 9H, *t*-Bu), and 1.49 ppm (s, 9H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 150.16, 145.52, 142.38, 141.20, 138.67, 132.75, 128.26, 124.51, 124.43, 124.22, 123.84, 121.25, 119.82, 118.92, 117.11, 116.39, 113.09, 111.57, 45.96, 35.02, 34.73, 32.28, and 32.06 ppm; HRMS (APCI): m/z = 497.2833. calcd for $C_{31}H_{34}N_3BF_2$: 497.2814 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 292 (18300), 398 (14500), and 493 nm (25300 $mol^{-1}dm^3cm^{-1}$); Fluorescence (CH_2Cl_2, λ_{ex} = 440 nm); λ_{max} = 561 nm, Φ_F = 0.00036.

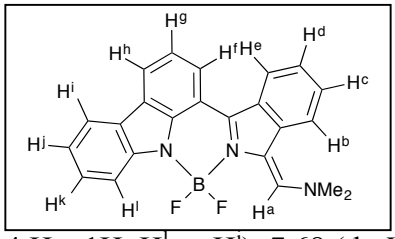
Compound data for 5b



Red solid, 55.4 mg, 124 μmol, 12%; ^{1}H NMR (DMSO-d_6) δ = 8.95 (s, 1H, H^a), 8.64 (d, J = 8.8 Hz, 1H, H^e), 8.02 (d, J = 2.0 Hz, 1H, H^f), 7.90 (d, J = 6.8 Hz, 1H, H^b), 7.89 (d, J = 2.4 Hz, 1H, H^g), 7.76 (d, J = 2.8 Hz, 1H, H^h), 7.63 (t, J = 7.6 Hz, 1H, H^c), 7.62 (d, J = 8.8 Hz, 1H, H^j), 7.50 (t, J = 8.0 Hz, 1H, H^d), 7.09 (dd, J = 2.4, 8.8 Hz, 1H, H^i), 4.00 (s, 3H, OMe), 3.89 (s, 3H, OMe), and 3.66 ppm (s, 6H, Me); ^{13}C NMR (DMSO-d_6) δ = 153.25, 152.86, 152.47, 139.62, 137.25, 134.33, 131.41, 127.82, 125.96, 124.33, 124.21, 123.19,

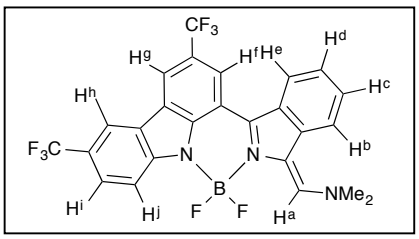
122.82, 121.40, 115.32, 114.85, 113.53, 112.25, 109.17, 106.86, 103.69, 56.23, 55.56, and 45.94 ppm; HRMS (APCI): m/z = 445.1790. calcd for $C_{25}H_{22}N_3O_2BF_2$: 445.1772 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 304 (19900), 409 (19600), and 509 nm (22200 $mol^{-1}dm^3cm^{-1}$); Fluorescence (CH_2Cl_2, λ_{ex} = 500 nm); λ_{max} = 650 nm, Φ_F = 0.0026.

Compound data for 5c



Yellow solid, 106 mg, 275 μmol, 28%; ^{1}H NMR ($CDCl_3$) δ = 8.90 (s, 1H, H^a), 8.60 (d, J = 8.4 Hz, 1H, H^e), 8.41 (d, J = 7.6 Hz, 1H, H^f), 8.18 (d, J = 7.6 Hz, 1H, H^h), 8.13 (d, J = 8.0 Hz, 1H, H^i or H^l), 7.95 (d, J = 8.4 Hz, 1H, H^l or H^i), 7.68 (d, J = 8.8 Hz, 1H, H^b), 7.57 (t, J = 7.6 Hz, 1H, H^c), 7.51 (t, J = 7.4 Hz, 1H, H^j or H^k), 7.46 (t, J = 7.6 Hz, 1H, H^d), 7.33 (t, J = 8.0 Hz, 1H, H^g), 7.29 (t, J = 7.4 Hz, 1H, H^k or H^j), and 3.55 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$) δ = 150.54, 145.49, 142.79, 139.89, 132.88, 128.56, 128.50, 126.88, 126.05, 124.65, 124.47, 124.02, 122.95, 121.84, 121.27, 120.46, 119.69, 118.43, 117.27, 113.85, 112.35, and 46.21 ppm; HRMS (APCI): m/z = 386.1640. calcd for $C_{23}H_{19}N_3BF_2$: 386.1639 $[M + H]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 292 (34900), 390 (18600), and 482 nm (29400 $mol^{-1}dm^3cm^{-1}$); Fluorescence (CH_2Cl_2, λ_{ex} = 460 nm); λ_{max} = 528 nm, Φ_F = 0.00022.

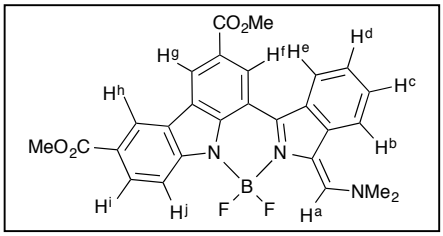
Compound data for 5d



Yellow solid, 108 mg, 207 μmol, 21%; ^{1}H NMR (DMSO-d_6) δ = 9.04 (s, 1H, H^a), 8.87 (s, 2H, H^f and H^h), 8.66 (s, 1H, H^g), 8.63 (d, J = 8.4 Hz, 1H, H^e), 7.98 (d, J = 8.8 Hz, 1H, H^j), 7.94 (d, J = 8.4 Hz, 1H, H^b), 7.87 (d, J = 8.4 Hz, 1H, H^i), 7.66 (t, J = 7.6 Hz, 1H, H^c), 7.56 (t, J = 7.6 Hz, 1H, H^d), and 3.73 ppm (s, 6H, Me); ^{13}C NMR

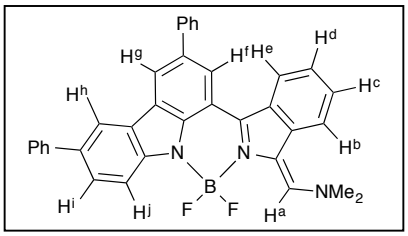
(DMSO-d_6) δ = 153.95, 144.25, 140.19, 136.90, 131.11, 127.91, 125.51, 125.09 (q, J = 271 Hz), 125.02 (q, J = 272 Hz), 124,64, 123.58, 123.14 (q, J = 3.8 Hz), 122.70, 122.13, 121.47, 120.95 (q, J = 31.5 Hz), 120.66 (q, J = 31.5 Hz), 119.45 (q, J = 3.8 Hz), 119.25 (q, J = 3.8 Hz), 117.61 (q, J = 3.8 Hz), 115.43, 113.81, 113.39, and 46.05 ppm; HRMS (APCI): m/z = 522.1382. calcd for $C_{25}H_{17}N_3BF_8$: 522.1387 $[M + H]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 292 (25800), 375 (10500), 448 (24200), and 471 nm (36300 $mol^{-1}dm^3cm^{-1}$) ; Fluorescence (CH_2Cl_2, λ_{ex} = 440 nm); λ_{max} = 508 nm, Φ_F = 0.00054.

Compound data for 5e



Yellow solid, 28.7 mg, 57.3 μmol, 6%; ^{1}H NMR ($CDCl_3$) δ = 9.16 (d, J = 0.8 Hz, 1H, H^f), 8.91 (s, 2H, H^a and H^g), 8.90 (d, J = 1.2 Hz, 1H, H^h), 8.69 (d, J = 8.0 Hz, 1H, H^e), 8.24 (dd, J = 1.6, 8.4 Hz, 1H, H^i), 7.95 (d, J = 8.8 Hz, 1H, H^j), 7.70 (d, J = 8.4 Hz, 1H, H^b), 7.61 (t, J = 7.6 Hz, 1H, H^c), 7.52 (t, J = 7.2 Hz, 1H, H^d), 4.06 (s, 3H, CO_2Me), 4.00 (s, 3H, CO_2Me), and 3.61 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$) δ = 167.83, 167.61, 151.49, 146.54, 144.37, 143.12, 132.87, 128.93, 128.39, 128.20, 125.15, 124.79, 124.71, 124.53, 124.31, 123.90, 123.22, 122.69, 121.70, 121.18, 117.62, 113.88, 112.59, 52.07, 51.80, and 46.26 ppm; HRMS (APCI): m/z = 501.1668. calcd for $C_{27}H_{22}N_3O_4BF_2$: 501.1682 $[M]^-$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 278 (33900), 296 (33100), 381 (12900), and 472 nm (50500 $mol^{-1}dm^3cm^{-1}$); Fluorescence (CH_2Cl_2, λ_{ex} = 460 nm); λ_{max} = 519 nm, Φ_F = 0.00029.

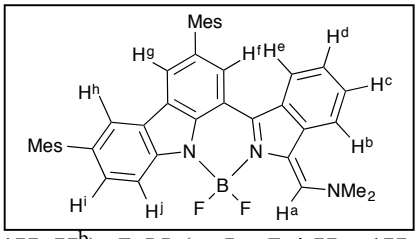
Compound data for 5f



Orange solid, 66.6 mg, 124 μmol, 12%; ^{1}H NMR (DMSO-d_6) δ = 9.00 (s, 1H, H^a), 8.76 (d, J = 8.0 Hz, 1H, H^e), 8.72 (s, 1H, H^f or H^g),

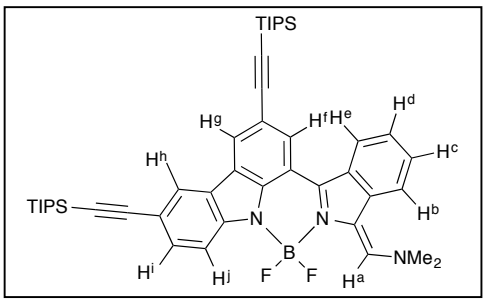
8.69 (s, 2H for H^g or H^f, and H^h), 7.97 (d, J = 7.6 Hz, 2H, *o*Ph), 7.92 (d, J = 8.4 Hz, 1H, H^b), 7.85 (s, 2H, H^i and H^j), 7.84 (d, J = 7.6 Hz, 2H, *o*Ph), 7.65 (t, J = 7.6 Hz, 1H, H^c), 7.58 (t, J = 7.6 Hz, 2H, *m*Ph), 7.53 (t, J = 7.6 Hz, 1H, H^d), 7.52 (t, J = 7.2 Hz, 2H, *m*Ph), 7.42 (t, J = 7.4 Hz, 1H, *p*Ph), 7.38 (t, J = 7.2 Hz, 1H, *p*Ph), and 3.36 ppm (s, 6H, Me); ^{13}C NMR (DMSO-d_6) δ = 152.88, 141.97, 141.26, 141.18, 139.58, 138.48, 132.09, 131.94, 131.60, 129.02, 128.92, 128.12, 127.16, 126.72, 126.58, 126.04, 125.14, 125.11, 124.53, 123.68, 123.64, 121.66, 120.99, 119.97, 119.36, 115.35, 113.65, 113.09, and 46.22 ppm; HRMS (APCI): m/z = 537.2194. calcd for $C_{35}H_{26}N_3BF_2$: 537.2188 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 287 (36100), 401 (16400), and 495 nm (27300 $mol^{-1}dm^3cm^{-1}$); Fluorescence (CH_2Cl_2, λ_{ex} = 490 nm); λ_{max} = 559 nm, Φ_F = 0.00063.

Compound data for 5g



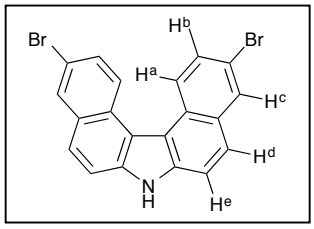
Orange solid, 93.0 mg, 150 μmol, 15%; ^{1}H NMR ($CDCl_3$) δ = 8.94 (s, 1H, H^a), 8.52 (d, J = 8.0 Hz, 1H, H^e), 8.19 (s, 1H, H^f), 8.03 (d, J = 8.4 Hz, 1H, H^j), 7.91 (s, 1H, H^g), 7.86 (s, 1H, H^h), 7.69 (d, J = 8.0 Hz, 1H, H^b), 7.55 (t, J = 7.4 Hz, 1H, H^c), 7.39 (t, J = 7.6 Hz, 1H, H^d), 7.31 (dd, J = 1.6, 8.4 Hz, 1H, H^i), 7.07 (s, 2H, Mes), 7.01 (s, 2H, Mes), 3.56 (s, 6H, Me), 2.42 (s, 3H, *p*Mes), 2.38 (s, 3H, *p*Mes), 2.16 (s, 6H, *o*Mes), and 2.12 ppm (s, 6H, *o*Mes); ^{13}C NMR ($CDCl_3$) δ = 150.58, 145.29, 141.79, 140.00, 139.75, 139.11, 137.03, 136.77, 136.68, 136.18, 132.77, 132.47, 131.20, 128.53, 128.41, 128.12, 127.94, 127.70, 124.81, 124.58, 124.56, 124.26, 123.77, 122.79, 121.20, 120.90, 117.29, 113.74, 112.41, 46.19, 21.44, 21.10, and 21.05 ppm; HRMS (APCI): m/z = 622.3214. calcd for $C_{41}H_{39}N_3BF_2$: 622.3207 $[M + H]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 295 (31500), 398 (16100), and 492 nm (23100 $mol^{-1}dm^3cm^{-1}$); Fluorescence (CH_2Cl_2, λ_{ex} = 490 nm); λ_{max} = 555 nm, Φ_F = 0.00024.

Compound data for 5h



Orange solid, 80.9 mg, 108 μmol, 11%; ^{1}H NMR ($CDCl_3$) δ = 8.83 (s, 1H, H^a), 8.48 (d, J = 8.4 Hz, 1H, H^e), 8.43 (s, 1H, H^f), 8.27 (s, 1H, H^g), 8.26 (d, J = 0.8 Hz, 1H, H^h), 7.83 (d, J = 8.8 Hz, 1H, H^j), 7.64 (dd, J = 1.6, 8.4 Hz, 1H, H^i), 7.56 (d, J = 8.0 Hz, 1H, H^b), 7.51 (t, J = 7.4 Hz, 1H, H^c), 7.45 (t, J = 7.4 Hz, 1H, H^d), 3.48 (s, 6H, Me), 1.24 (s, 21H, TIPS), and 1.19 ppm (s, 21H, TIPS); ^{13}C NMR ($CDCl_3$) δ = 151.18, 143.19, 142.79, 139.64, 132.35, 130.39, 128.48, 127.80, 126.74, 125.76, 124.78, 124.69, 124.09, 123.92, 123.20, 120.99, 116.97, 114.97, 113.80, 113.77, 112.50, 108.63, 108.46, 88.06, 87.95, 46.12, 18.83, 18.78, 11.49, and 11.45 ppm; HRMS (APCI): m/z = 745.4261. calcd for $C_{45}H_{58}N_3BF_2Si_2$: 745.4244 $[M]^-$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 289 (35100), 400 (14400), and 492 nm (26000 $mol^{-1}dm^3cm^{-1}$); Fluorescence (CH_2Cl_2, λ_{ex} = 490 nm); λ_{max} = 571 nm, Φ_F = 0.0013.

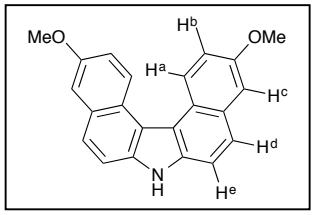
3,11-dibromodibenzocarbazole



A solution of 6,6'-dibromo-1,1'-binaphthyl-2,2'-diamine[S7] (1.83 g, 4.14 mmol) in 2-methoxyethanol (20 mL) was heated in the presence of conc. HCl (2.0 mL) at reflux for 41 h under N_2. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with $NaHCO_3$ aq and water, and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$, which gave the product as a white solid (983 mg, 2.31 mmol, 56%).

^{1}H NMR ($CDCl_3$) δ = 8.97 (d, J = 8.8 Hz, 2H, H^a), 8.76 (s, 1H, NH), 8.18 (d, J = 2.0 Hz, 2H, H^c), 7.78 (d, J = 8.8 Hz, 2H, H^d), 7.75 (dd, J = 2.4, 9.2 Hz, 2H, H^b), and 7.69 ppm (d, J = 8.4 Hz, 2H, H^e); ^{13}C NMR ($CDCl_3$) δ = 136.52, 131.61, 131.25, 128.76, 127.79, 126.55, 126.27, 117.72, 116.90, and 113.64 ppm; HRMS (APCI): m/z = 423.9164. calcd for $C_{20}H_{10}NBr_2$: 423.9166 $[M - H]^-$.

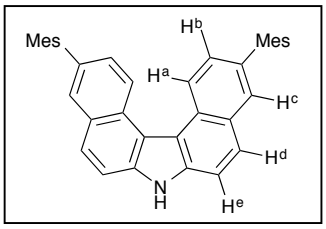
3,11-dimethoxydibenzocarbazole (6b)



A flask containing 3,11-dibromodibenzocarbazole (803 mg, 1.89 mmol) and CuI (846 mg, 4.45 mmol) was purged with N_2, charged with dehydrated DMF (1.0 mL) and NaOMe (5 M in MeOH, 2.5 mL), and heated at 80 ˚C for 19 h. The mixture was passed through a pad of Celite with $CHCl_3$. The solution was washed with water and evaporated. The residue was purified by silica gel chromatography with $CHCl_3$ to give the product as a white solid (370 mg, 1.13 mmol, 60%).

^{1}H NMR ($CDCl_3$) δ = 9.10 (d, J = 9.2 Hz, 2H, H^a), 8.54 (s, 1H, NH), 7.76 (d, J = 8.8 Hz, 2H, H^d), 7.61 (d, J = 8.4 Hz, 2H, H^e), 7.41 (d, J = 2.8 Hz, 2H, H^c), 7.37 (dd, J = 2.6, 9.0 Hz, 2H, H^b), and 4.01 ppm (s, 6H, OMe); ^{13}C NMR ($CDCl_3$) δ = 155.89, 135.41, 131.37, 126.56, 125.92, 124.45, 118.00, 116.60, 113.07, 109.18, and 55.53 ppm; HRMS (APCI): m/z = 326.1204. calcd for $C_{22}H_{16}NO_2$: 326.1187 $[M - H]^-$.

3,11-bis(2,4,6-trimethylphenyl)dibenzocarbazole (6c)

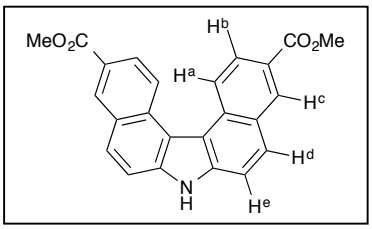


A solution of 3,11-dibromodibenzocarbazole (1.12 g, 2.64 mmol), 2,4,6-trimethylphenylboronic acid (1.32 g, 11.7 mmol), $Pd(PPh_3)_4$ (180 mg, 156 μmol), and Cs_2CO_3 (2.6 g, 8.0 mmol) in toluene/EtOH/H_2O (18/12/12 mL) was heated at 100 ˚C for 14 h under N_2. The organic layer was extracted with EtOAc and evaporated. The residue was separated over a silica gel column with $CHCl_3$/hexane as an eluent to give the product as a white solid (1.21 g, 2.40 mmol, 91%)

^{1}H NMR ($CDCl_3$) δ = 9.35 (d, J = 8.8 Hz, 2H, H^a), 8.74 (s, 1H, NH), 7.88 (d, J = 8.8 Hz, 2H, H^d), 7.83 (d, J = 2.0 Hz, 2H, H^c), 7.70 (d, J = 8.8 Hz, 2H, H^e), 7.54 (dd, J = 1.2, 8.8 Hz, 2H, H^b), 7.05 (s, 4H,

Mes), 2.41 (s, 6H, *p*Mes), and 2.14 ppm (s, 12H, *o*Mes); ^{13}C NMR ($CDCl_3$) δ = 138.99, 136.55, 136.43, 136.16, 135.94, 130.12, 129.33, 128.10, 127.92, 127.37, 126.92, 125.21, 117.74, 112.68, 21.08, and 20.98 ppm; HRMS (APCI): *m*/*z* = 502.2530. calcd for $C_{38}H_{32}N$: 502.2540 $[M - H]^-$.

3,11-bis(methoxycarbonyl)dibenzocarbazole (6d)



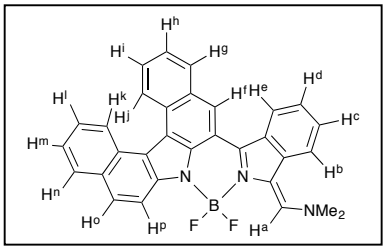
6d was prepared from 3,11-dibromodibenzocarbazole by a similar method to the synthesis of 3,6-bis(methoxycarbonyl)carbazole.

Yellow solid, 190 mg, 496 μmol, 38%; ^{1}H NMR ($CDCl_3$) δ = 9.18 (d, *J* = 8.8 Hz, 2H, H^a), 8.91 (s, 1H, NH), 8.80 (d, *J* = 2.0 Hz, 2H, H^c), 8.30 (dd, *J* = 2.0, 8.8 Hz, 2H, H^b), 8.01 (d, *J* = 8.8 Hz, 2H, H^d), 7.75 (d, *J* = 8.8 Hz, 2H, H^e), and 4.04 ppm (s, 6H, CO_2Me); ^{13}C NMR ($CDCl_3$) δ = 167.35. 137.84, 132.20, 131.80, 129.43, 128.51, 125.56, 125.37, 125.15, 117.95, 113.31, and 52.03 ppm; HRMS (APCI): *m*/*z* = 383.1151. calcd for $C_{24}H_{17}NO_4$: 383.1152 $[M]^+$.

General procedures for the synthesis of dibenzocarbazole-based BODIPYs

7a–**7d** were synthesized by a similar method to the synthesis of **5a**–**5f**. 1.0 mmol (1 eq) of $(Bpin)_2$, 50 μmol (0.05 eq) of $[Ir(OMe)(cod)]_2$, and 100 μmol (0.10 eq) of dtbpy were used.

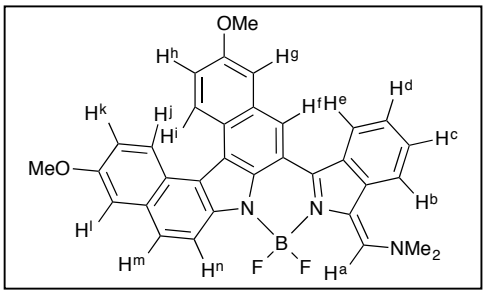
Compound data for 7a



Orange solid, 71.7 mg, 148 μmol, 15%; ^{1}H NMR (DMSO-d_6) δ = 9.17 (s, 1H, H^f), 9.16 (d, *J* = 8.0 Hz, 1H, H^k), 9.14 (d, *J* = 7.6 Hz, 1H, H^j), 9.06 (s, 1H, H^a), 9.03 (d, *J* = 8.0 Hz, 1H, H^e), 8.49 (d, *J* = 7.6 Hz, 1H, H^g), 8.17 (d, *J* = 9.2 Hz, 1H, H^p), 8.14 (d, *J* = 7.2 Hz, 1H, H^n), 8.00 (d, *J* = 9.2 Hz, 1H, H^o), 7.97 (d, *J* = 8.0 Hz, 1H, H^b), 7.79 (dt, *J* = 1.6, 8.0 Hz, 1H, H^i), 7.75 (dt, *J* = 1.2, 8.0 Hz, 1H, H^l), 7.69 (t, *J* = 7.2

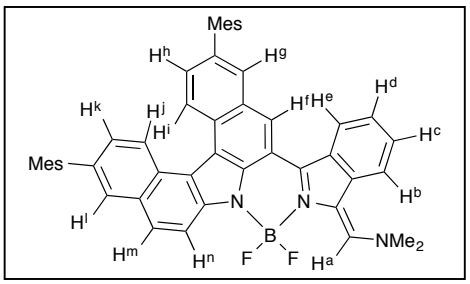
Hz, 1H, H^c), 7.593 (t, J = 7.6 Hz, 1H, H^d), 7.585 (t, J = 6.8 Hz, 1H, H^h), 7.55 (t, J = 7.4 Hz, 1H, H^m), and 3.73 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$) δ = 153.37, 138.86, 138.63, 134.63, 131.38, 130.66, 129.69, 129.50, 129.02, 129.00, 128.64, 127.91, 126.57, 126.27, 125.96, 125.17, 124.44, 124.23, 123.81, 123.62, 122.99, 122.92, 122.81, 121.50, 118.12, 116.21, 115.48, 115.10, 114.89, and 46.15 ppm; HRMS (APCI): m/z = 485.1866. calcd for $C_{31}H_{22}N_3BF_2$: 485.1875 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 279 (31600), 291 (29300), 344 (11700), and 482 nm (39900 $mol^{-1}dm^3cm^{-1}$)

Compound data for 7b



Orange solid, 183 mg, 336 μmol, 34%; ^{1}H NMR (DMSO-d_6) δ = 9.10 (s, 1H, H^f), 9.08–8.99 (m, 4H, H^a, H^e, H^i, H^j), 8.11 (d, J = 8.8 Hz, 1H, H^n), 8.00 (s, 1H, H^g), 7.96 (d, J = 8.4 Hz, 1H, H^b), 7.90 (d, J = 8.8 Hz, 1H, H^m), 7.68 (t, J = 7.2 Hz, 1H, H^c), 7.58 (t, J = 7.2 Hz, 1H, H^d, and s, 1H, H^l), 7.45 (dd, J = 2.0, 9.2 Hz, 1H, H^h), 7.41 (dd, J = 2.0, 9.2 Hz, 1H, H^k), 4.02 (s, 3H, OMe), 3.97 (s, 3H, OMe), and 3.72 ppm (s, 6H, Me); ^{13}C NMR (DMSO-d_6) δ = 154.98, 154.96, 153.23, 138.92, 137.72, 133.60, 131.41, 130.89, 130.74, 127.87, 126.32, 125.52, 125.06, 124.33, 124.13, 123.62, 123.53, 121.87, 121.50, 118.08, 117.86, 116.17, 115.99, 115.51, 115.09, 110.11, 109.00, 55.12, 55.07, and 46.12 ppm; HRMS (APCI): m/z = 545.2097. calcd for $C_{33}H_{26}N_3O_2BF_2$: 545.2086 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 277 (41200), 302 (26000), 358 (14100), and 460 nm (32700 $mol^{-1}dm^3cm^{-1}$)

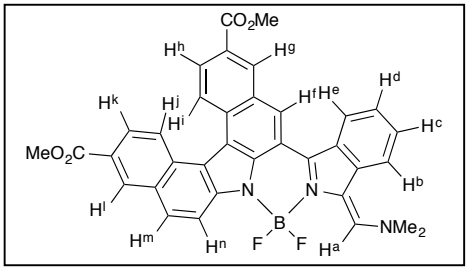
Compound data for 7c



Orange solid, 101 mg, 140 μmol, 14%; ^{1}H NMR ($CDCl_3$) δ = 9.39 (d, J = 8.8 Hz, 1H, H^i), 9.36 (d, J = 8.8 Hz, 1H, H^j), 9.01 (s,

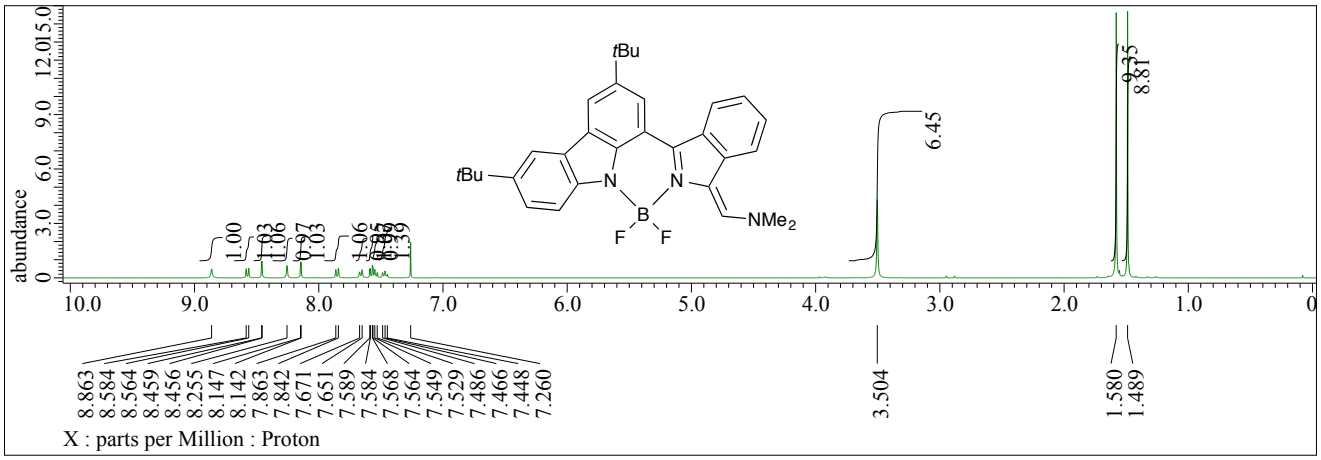
1H, H^a), 8.91 (s, 1H, H^f), 8.76 (d, J = 8.4 Hz, 1H, H^e), 8.31 (d, J = 8.8 Hz, 1H, H^n), 7.98 (s, 1H, H^g), 7.94 (d, J = 8.8 Hz, 1H, H^m), 7.84 (s, 1H, H^l), 7.72 (d, J = 8.0 Hz, 1H, H^b), 7.56 (m, 2H, H^c and H^h), 7.52 (m, 2H, H^d and H^k), 7.04 (s, 2H, Mes), 7.03 (s, 2H, Mes), 3.60 ppm (s, 6H, Me), 2.40 (s, 3H, *p*Mes), 2.39 (s, 3H, *p*Mes), 2.17 (s, 6H, *o*Mes), and 2.14 ppm (s, 6H, *o*Mes); ^{13}C NMR ($CDCl_3$) δ = 151.56, 143.70, 139.85, 139.27, 138.82, 136.57, 136.51, 136.42, 135.77, 135.64, 135.56, 132.50, 130.52, 130.29, 129.84, 129.33, 129.32, 128.85, 128.39, 128.20, 128.13, 128.06, 126.87, 126.46, 125.21, 125.12, 124.81, 124.15, 123.92, 121.19, 119.18, 117.69, 117.22, 115.83, 115.18, 46.19, 21.12, 21.10, 21.04, and 21.01 ppm; HRMS (APCI): m/z = 722.3499. calcd for $C_{49}H_{43}N_3BF_2$: 722.3521 $[M + H]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 293 (45000), 351 (13100), and 469 nm (43500 $mol^{-1}dm^3cm^{-1}$)

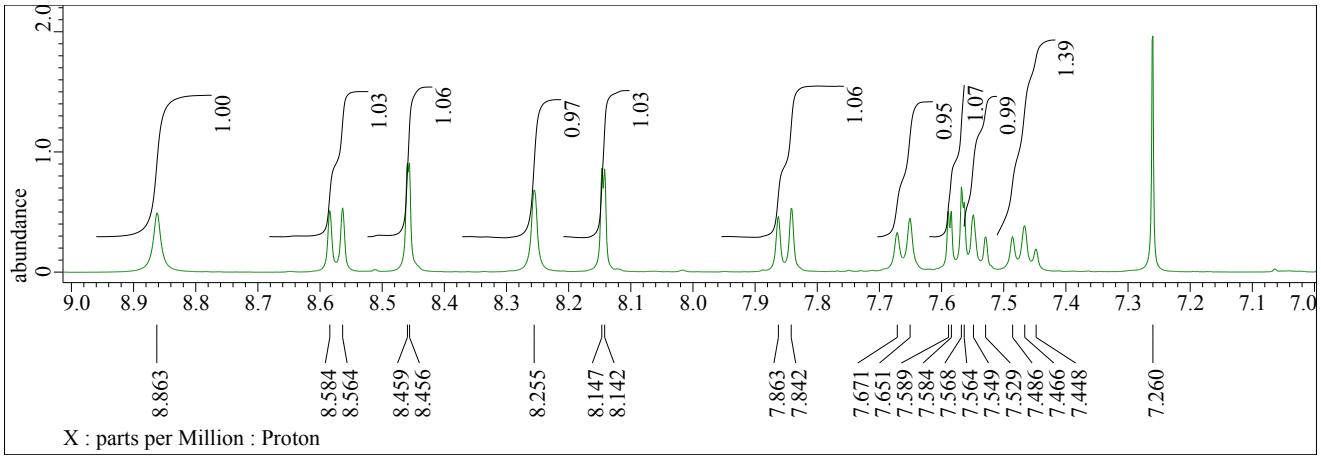
Compound data for 7d



Yellow solid, 74.5 mg, 124 μmol, 13%; ^{1}H NMR ($CDCl_3$) δ = 9.13 (d, J = 9.2 Hz, 1H, H^i or H^j), 9.09 (d, J = 8.0 Hz, 1H, H^j or H^i), 8.89 (s, 1H, H^a), 8.83–8.79 (m, 3H, H^f, H^g, H^l), 8.60 (d, J = 8.4 Hz, 1H, H^e), 8.27 (dd, J = 1.2, 9.2 Hz, 1H, H^h or H^k), 8.26 (d, J = 7.2 Hz, 1H, H^n), 8.21 (dd, J = 1.8, 8.6 Hz, 1H, H^k or H^h), 8.00 (d, J = 9.2 Hz, 1H, H^m), 7.58 (d, J = 8.0 Hz, 1H, H^b), 7.47 (t, J = 7.6 Hz, 1H, H^c), 7.39 (t, J = 7.4 Hz, 1H, H^d), 4.04 (s, 3H, CO_2Me), 4.02 (s, 3H, CO_2Me), and 3.58 ppm (s, 6H, Me); ^{13}C NMR ($CDCl_3$) δ = 167.63, 167.20, 151.97, 141.60, 137.12, 133.46, 132.60, 132.11, 131.99, 129.44, 128.80, 128.61, 128.52, 127.76, 126.34, 125.13, 125.08, 124.87, 124.68, 124.19, 121.09, 119.21, 117.66, 116.63, 115.70, 51.96, 51.92, and 46.28 ppm; HRMS (APCI): m/z = 601.1973. calcd for $C_{35}H_{26}N_3O_4BF_2$: 601.1985 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 278 (33700), 314 (46500), and 470 nm (44600 $mol^{-1}dm^3cm^{-1}$).

Figure S1. ^{1}H and ^{13}C NMR spectra of **5a** in $CDCl_3$





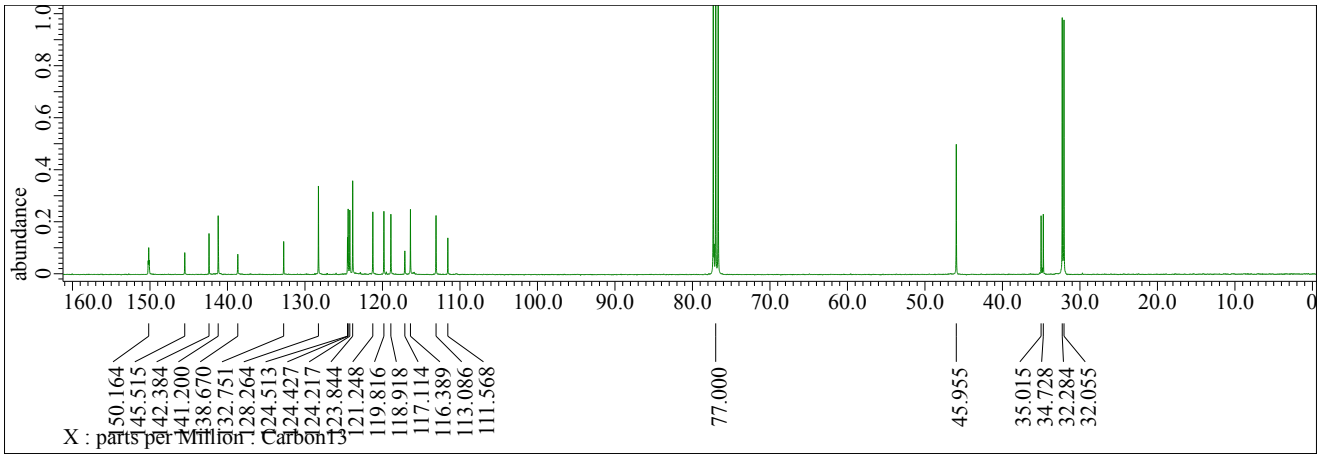


Figure S2. $^{1}H–^{1}H$ NOESY spectrum of **5a** in $CDCl_3$

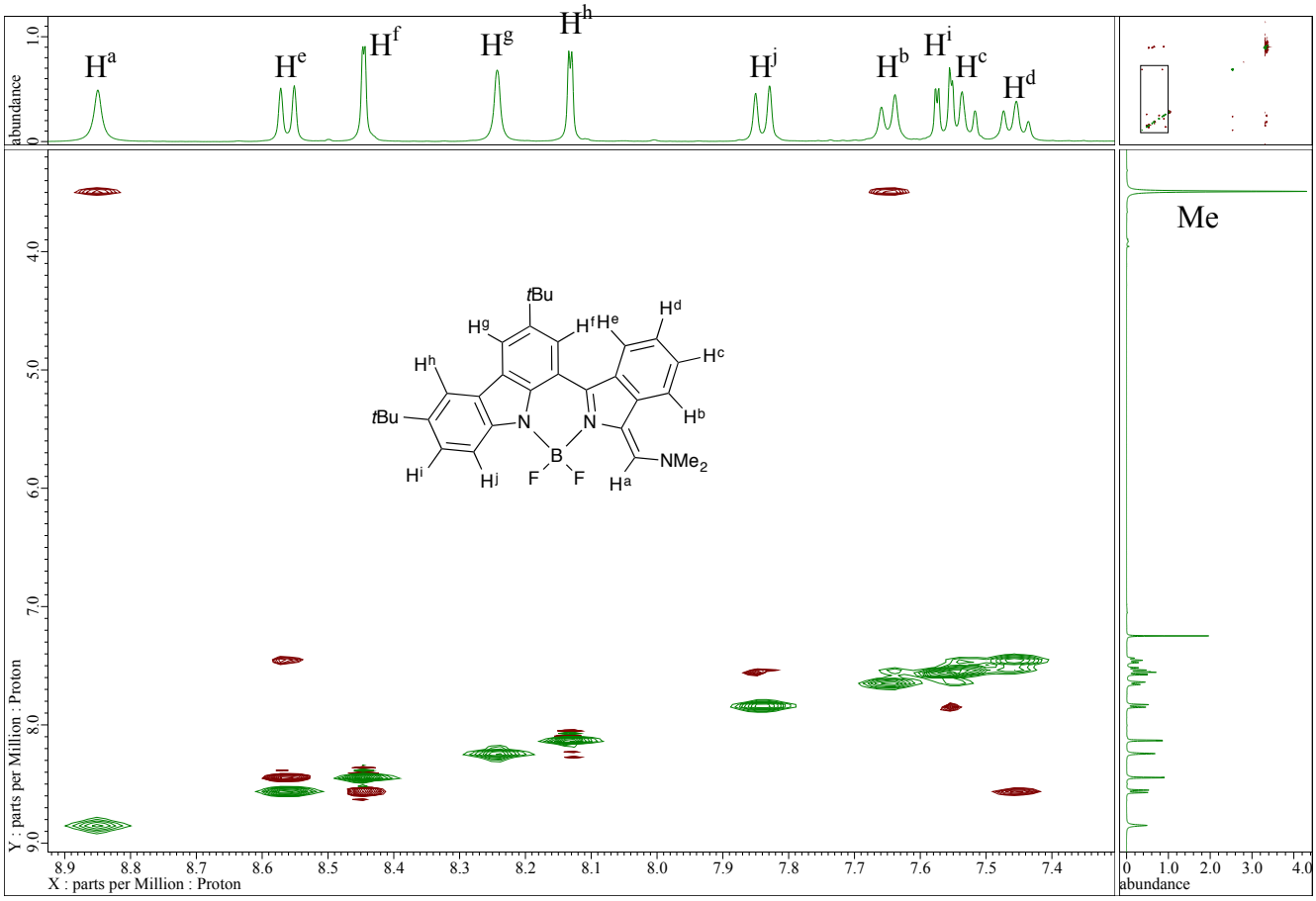
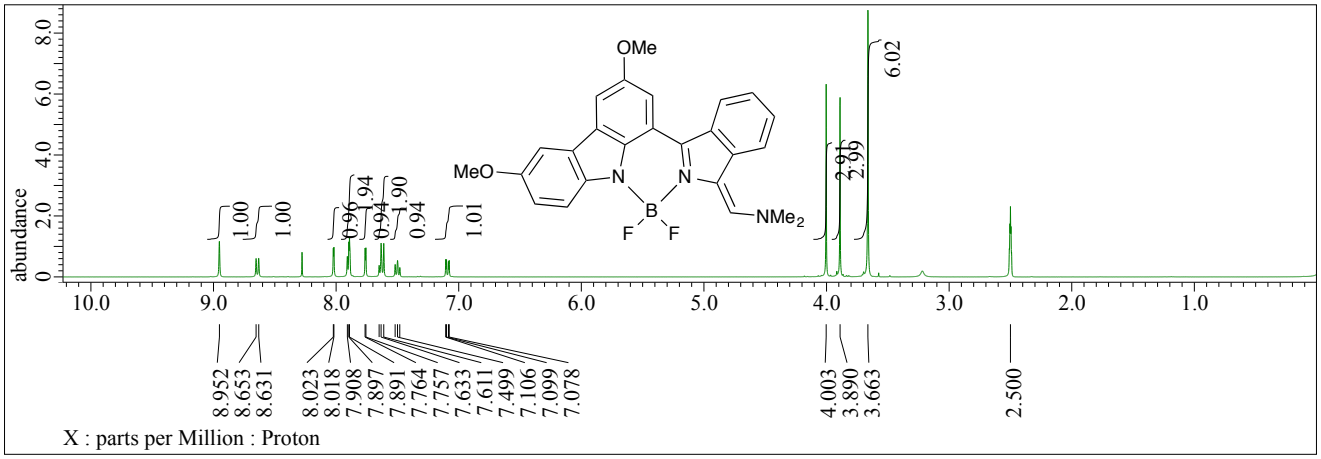
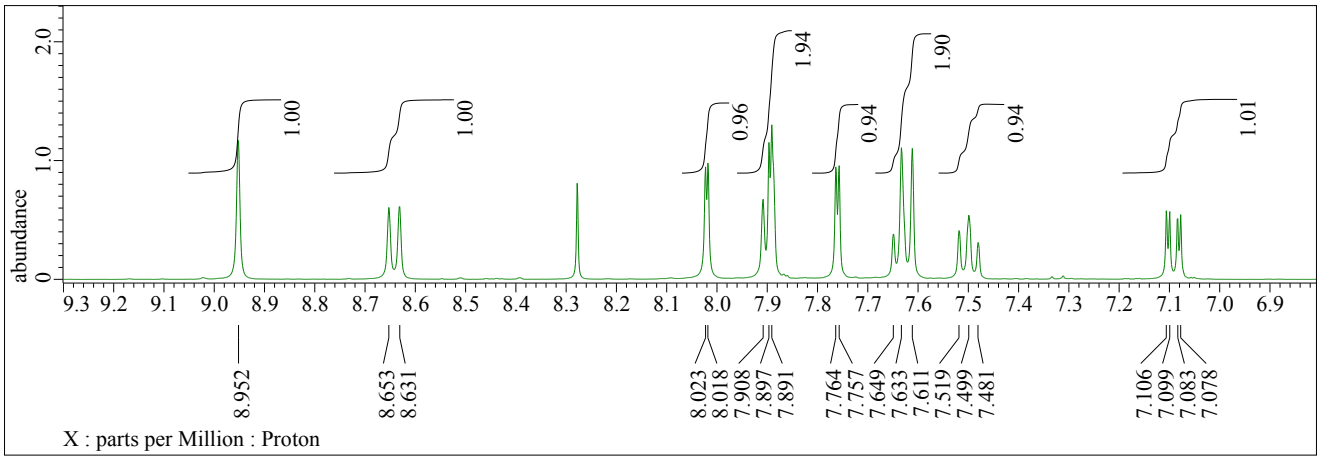


Figure S3. ^{1}H and ^{13}C NMR spectra of **5b** in DMSO-d_6





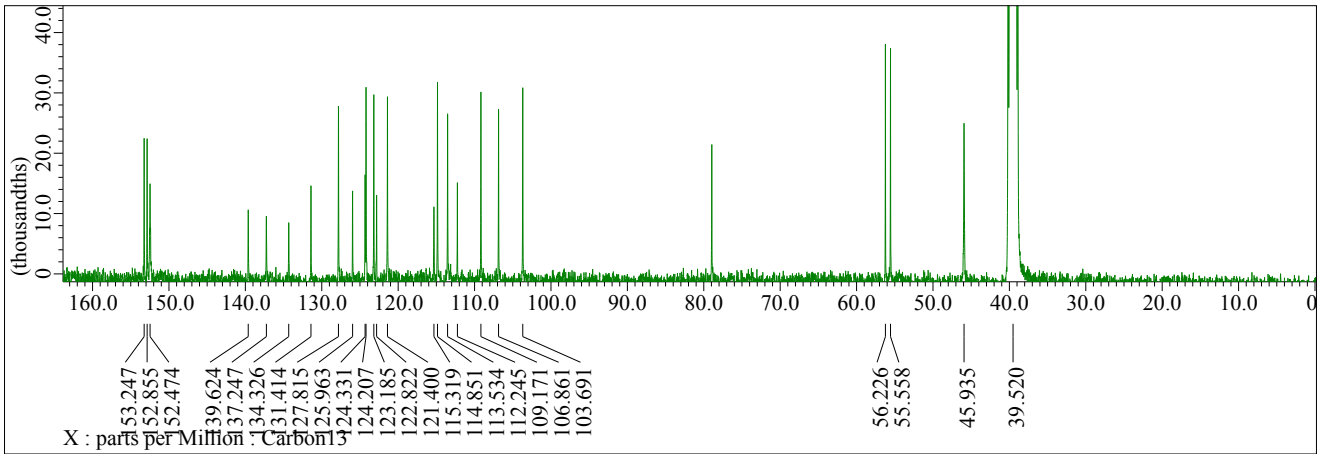
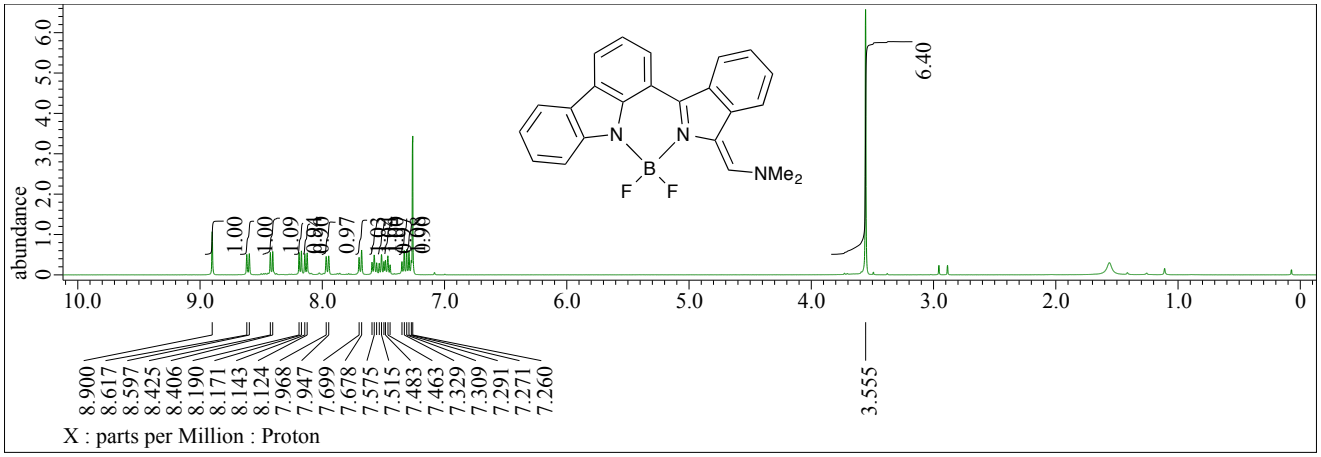
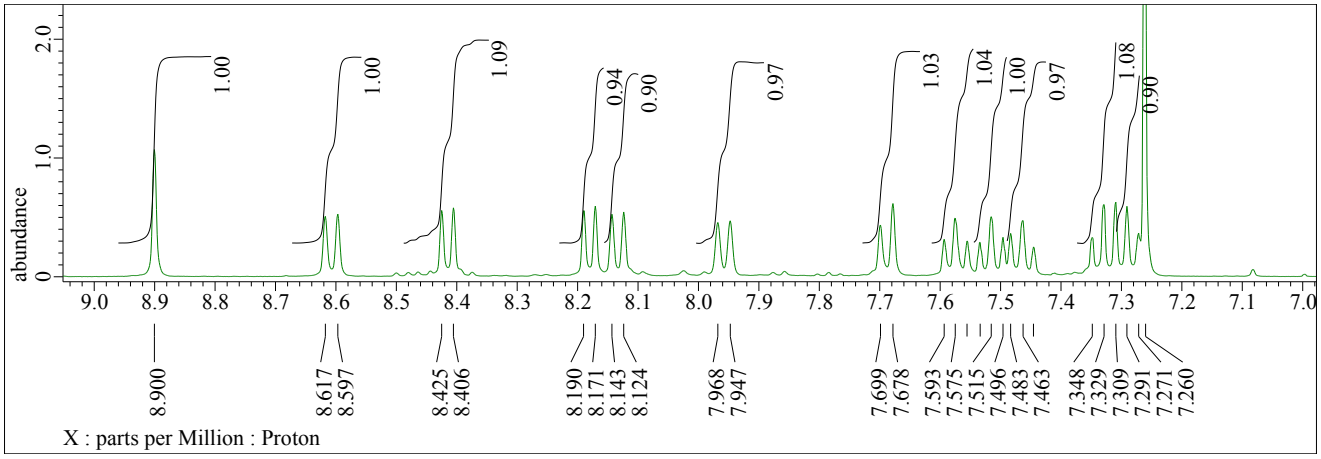


Figure S4. ^{1}H and ^{13}C NMR spectra of **5c** in $CDCl_3$





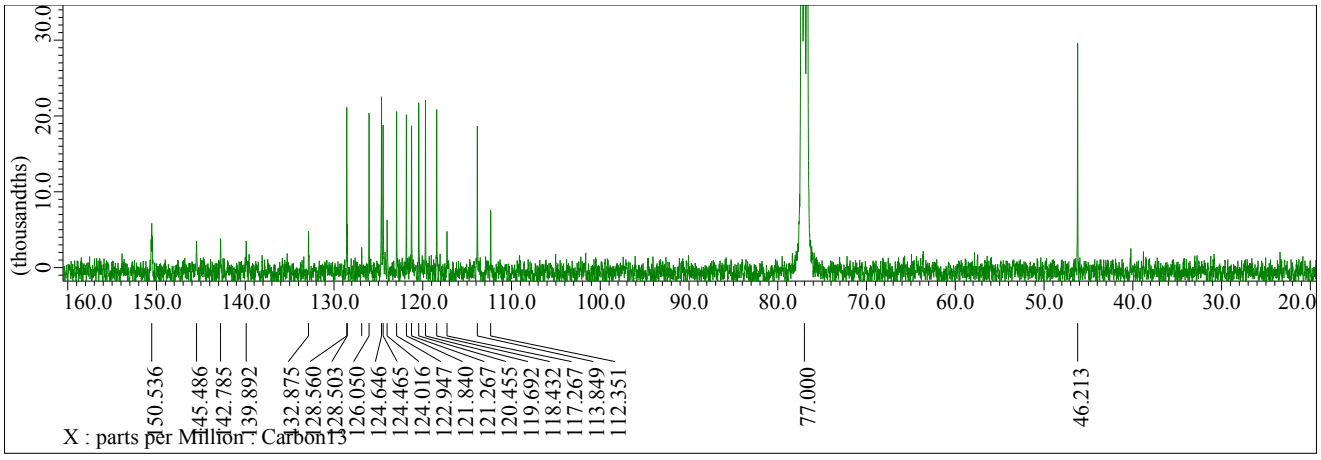
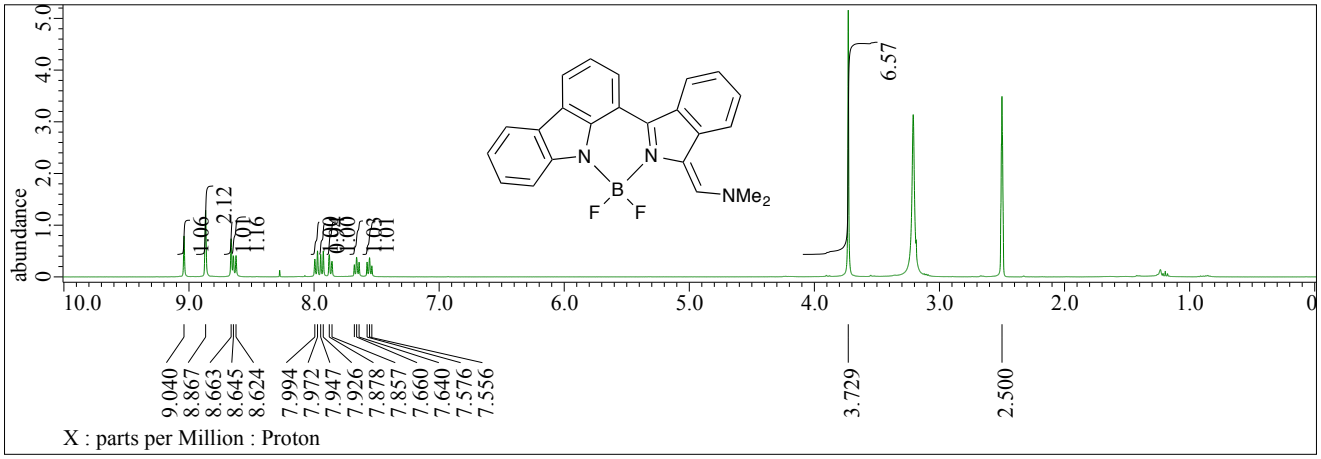
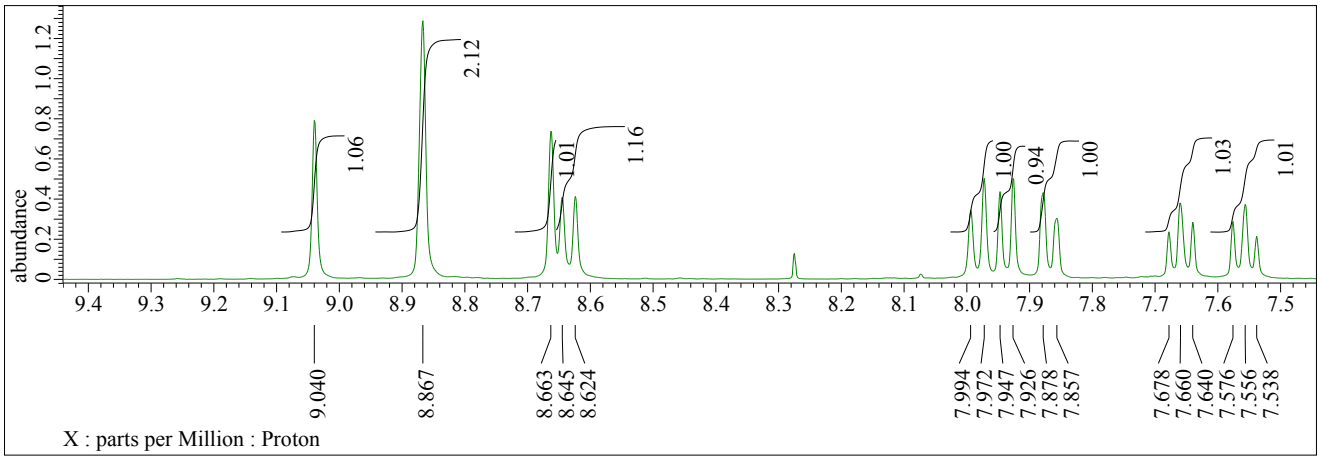


Figure S5. ^{1}H and ^{13}C NMR spectra of **5d** in DMSO-d_6





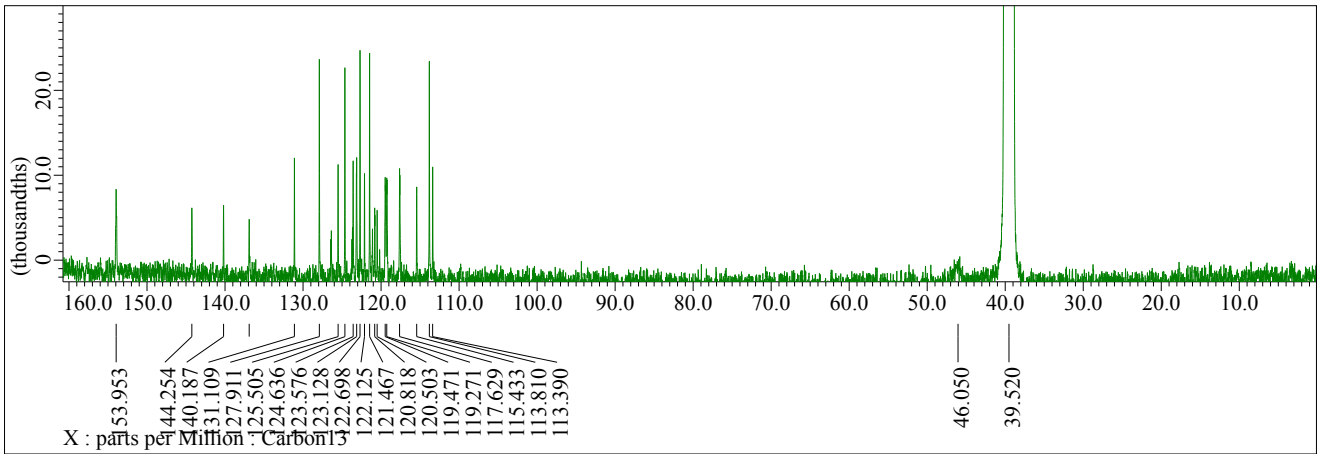


Figure S6. ^{1}H and ^{13}C NMR spectra of **5e** in $CDCl_3$

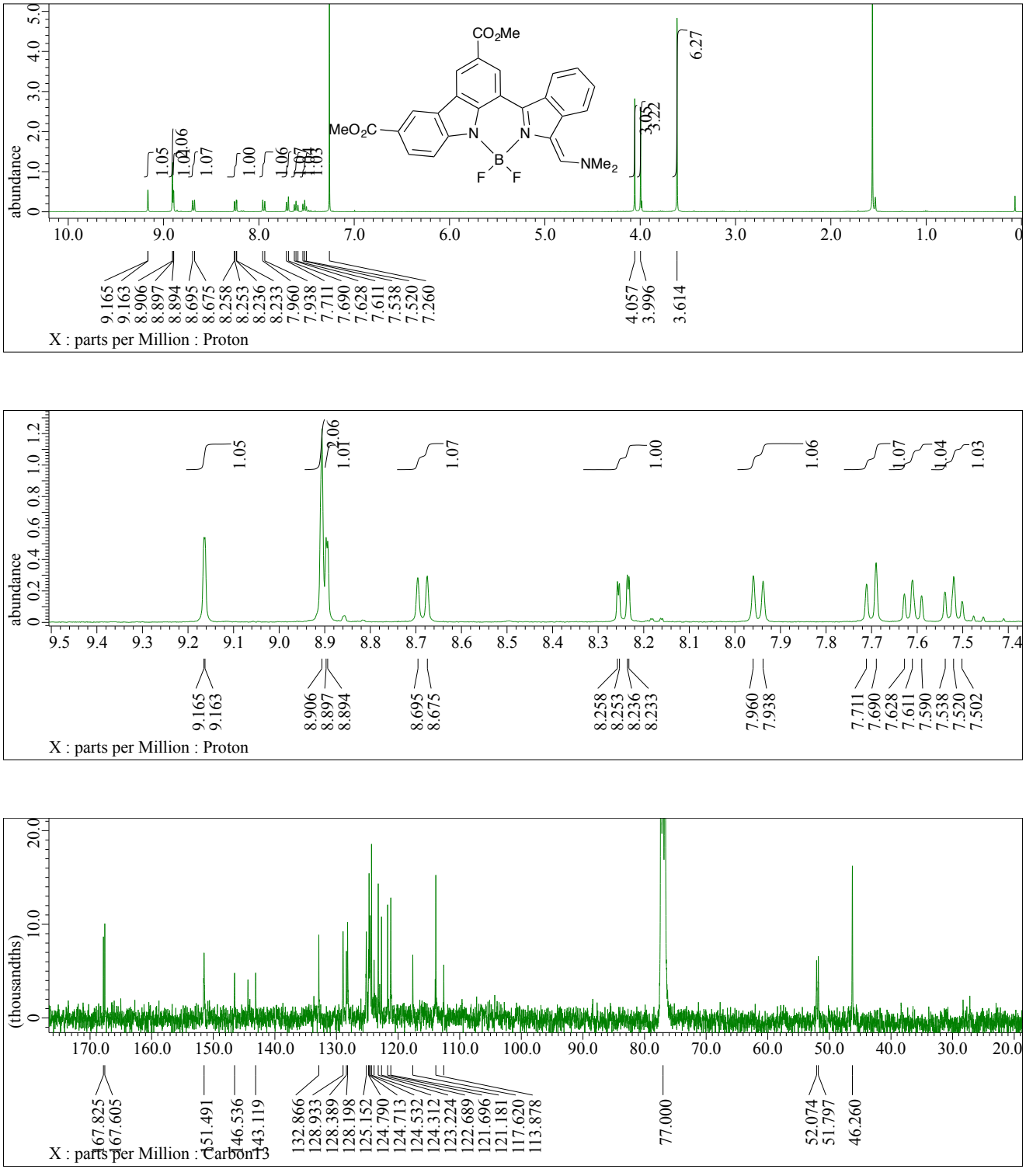


Figure S7. ^{1}H and ^{13}C NMR spectra of **5f** in DMSO-d_6

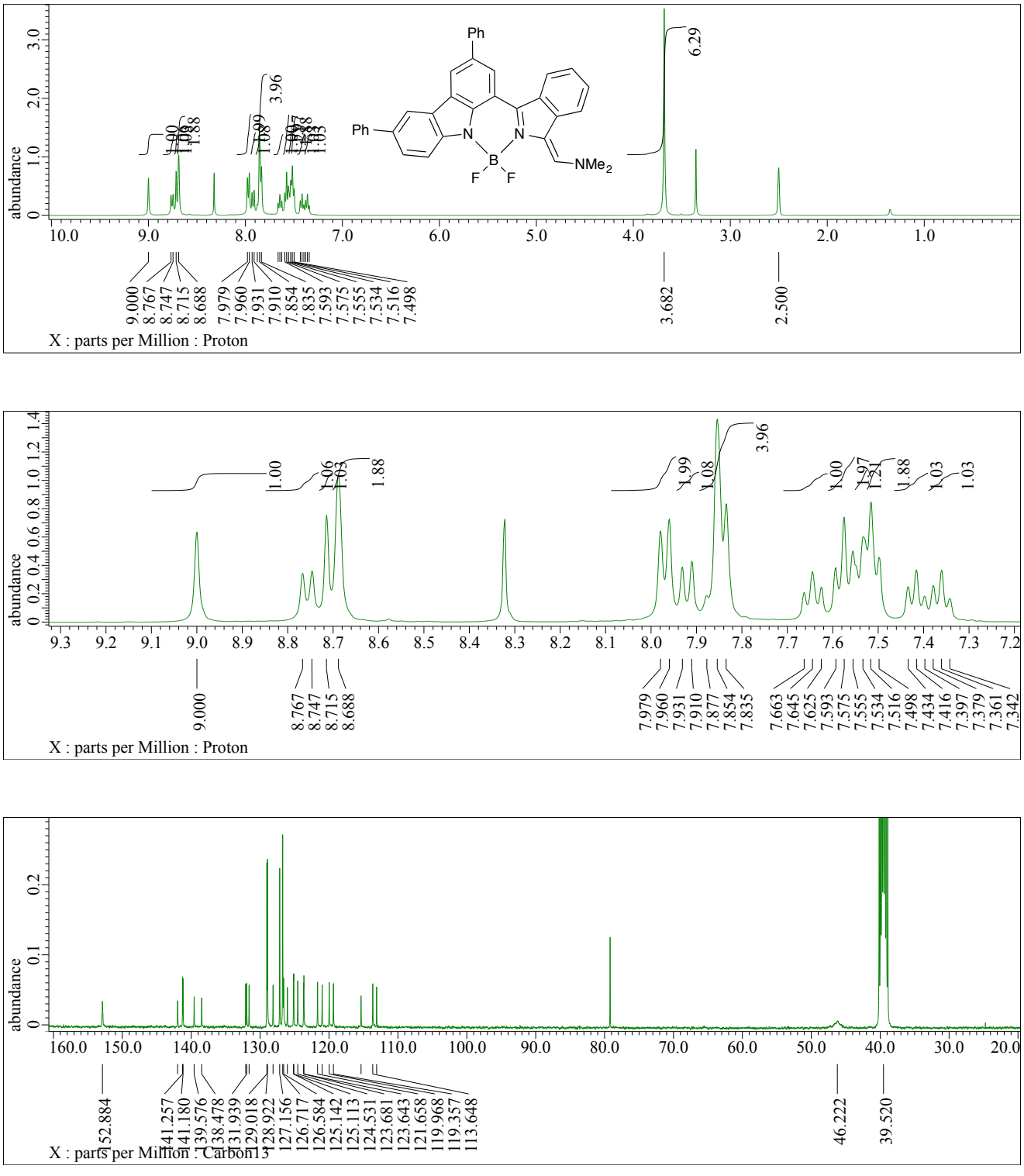


Figure S8. ^{1}H and ^{13}C NMR spectra of **5g** in $CDCl_3$

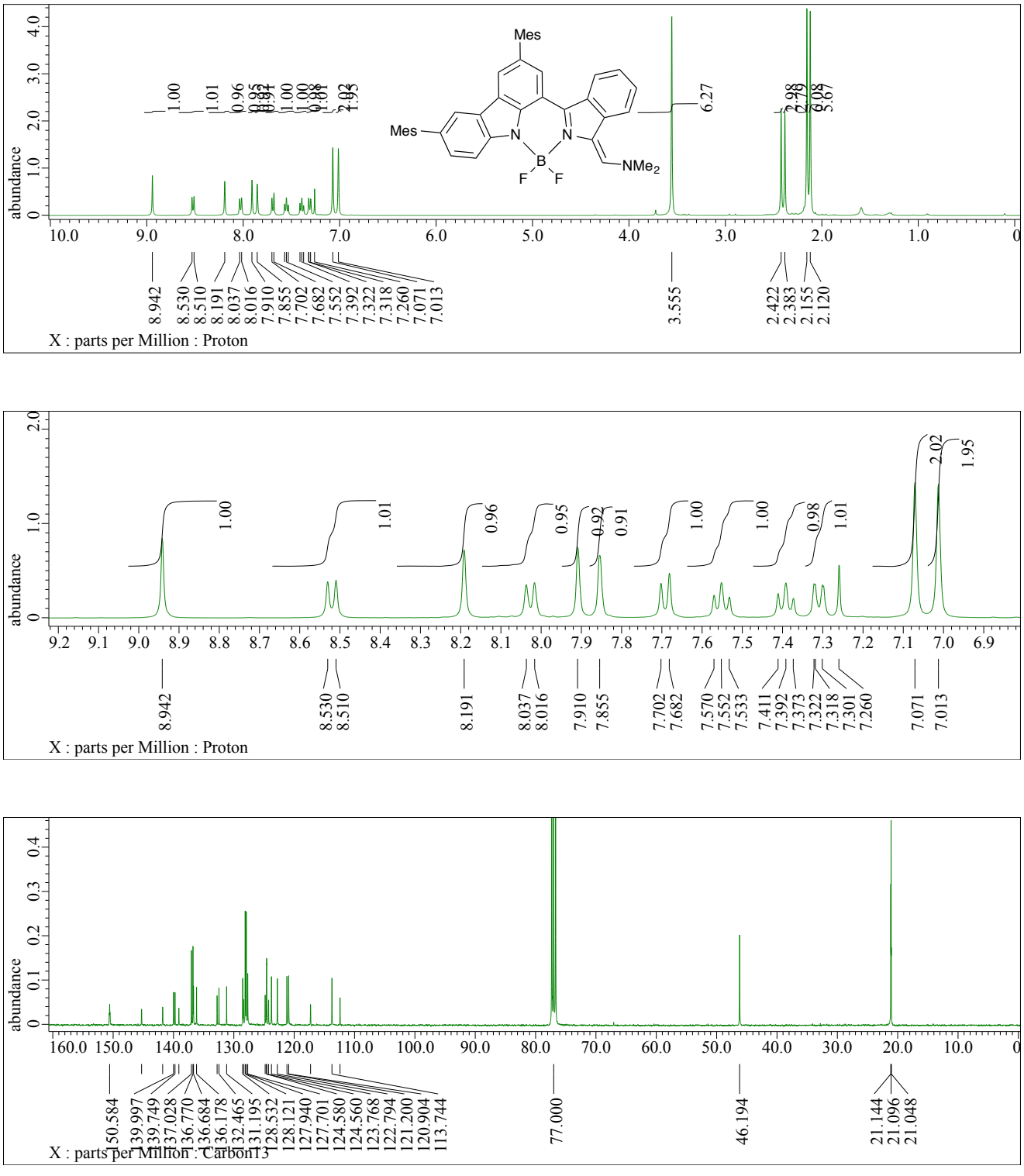
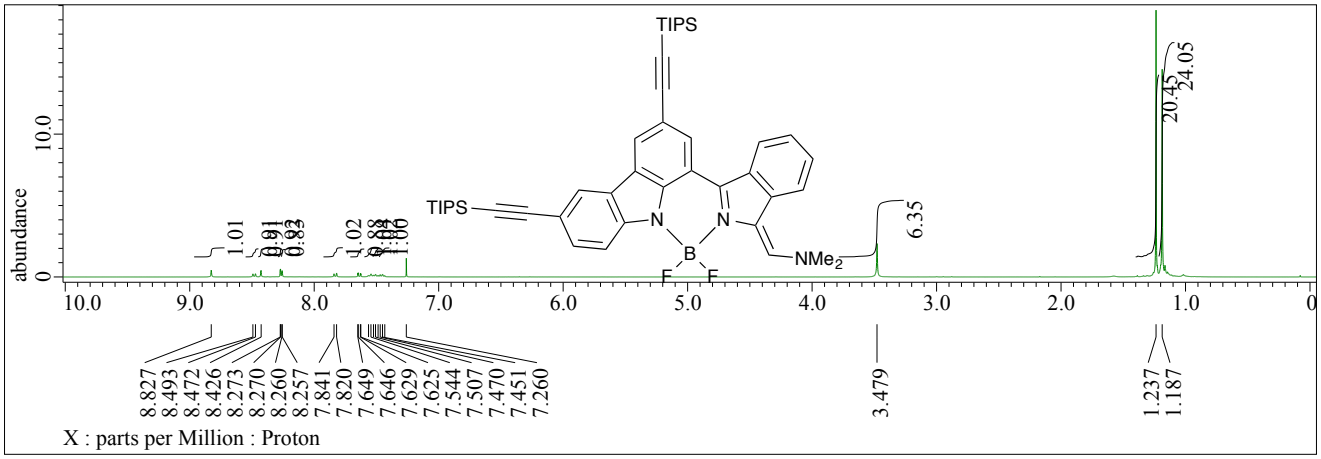
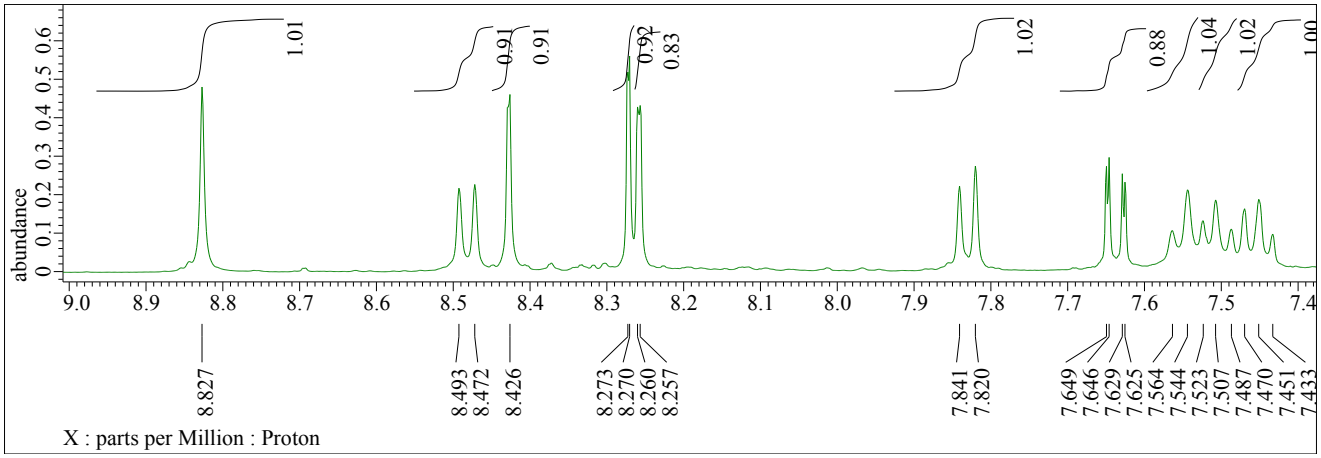


Figure S9. ^{1}H and ^{13}C NMR spectra of **5h** in $CDCl_3$





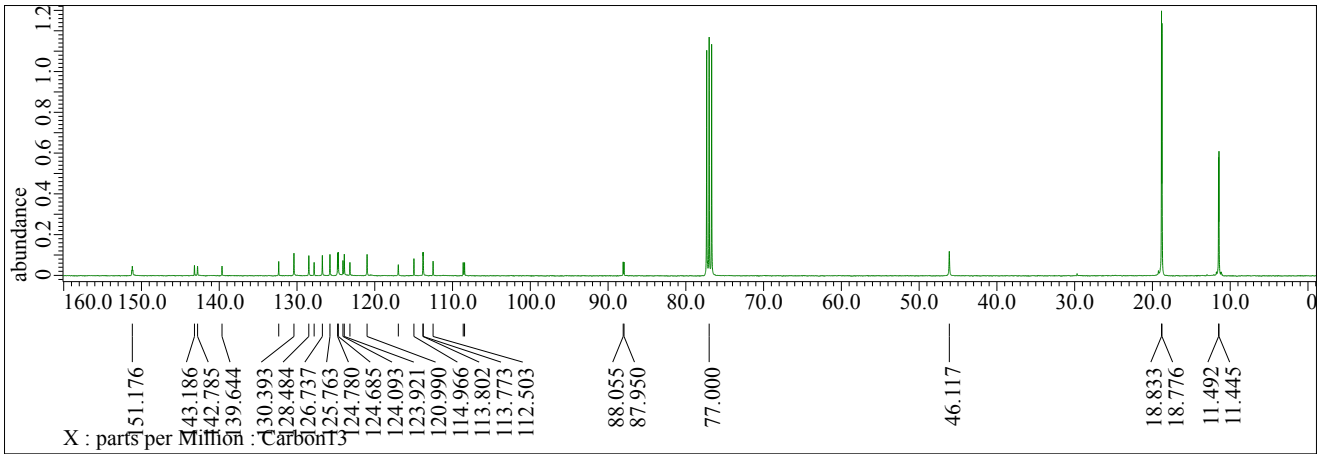


Figure S10. ^{1}H and ^{13}C NMR spectra of **7a** in DMSO-d_6

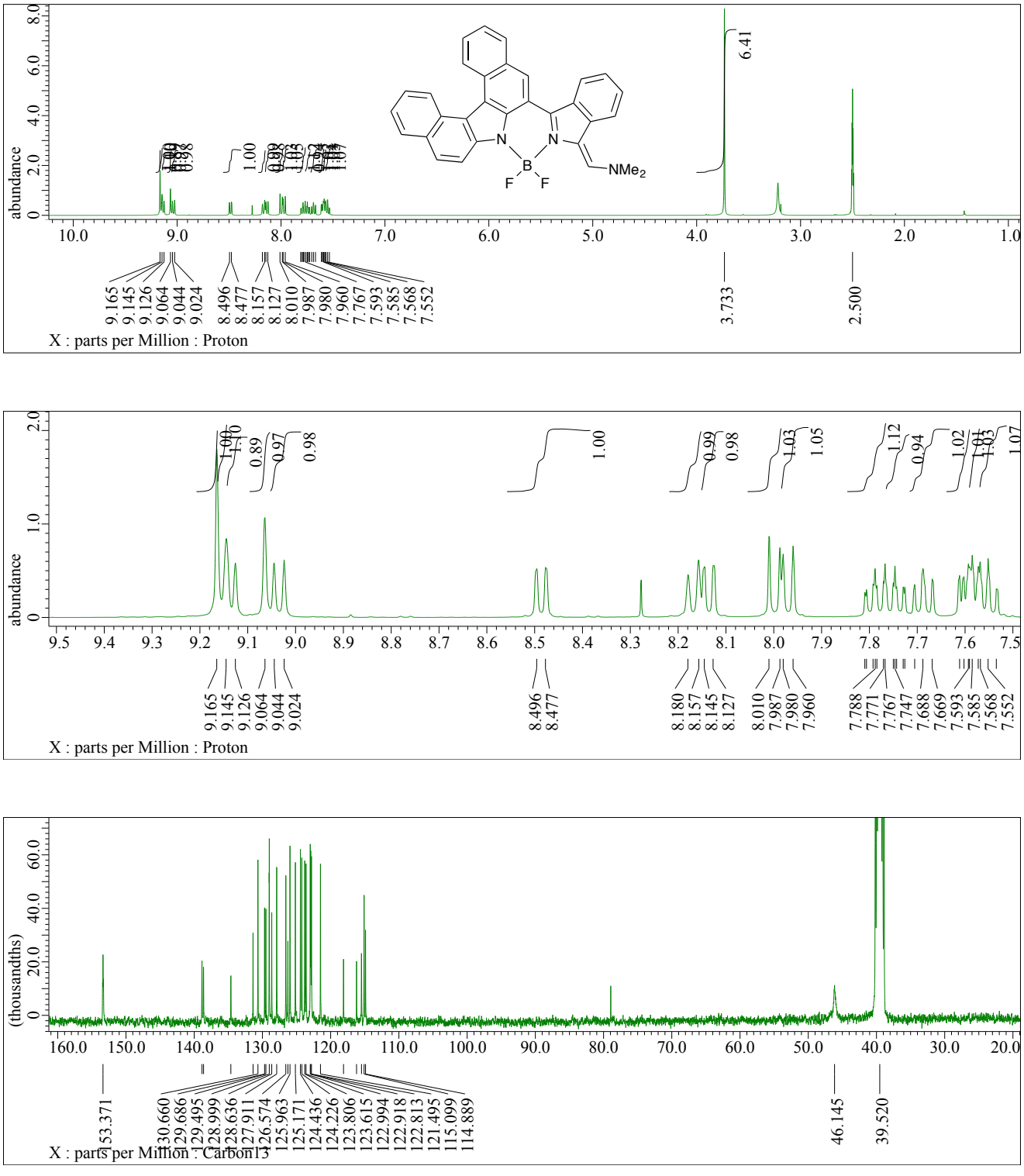


Figure S11. ^{1}H and ^{13}C NMR spectra of **7b** in DMSO-d_6

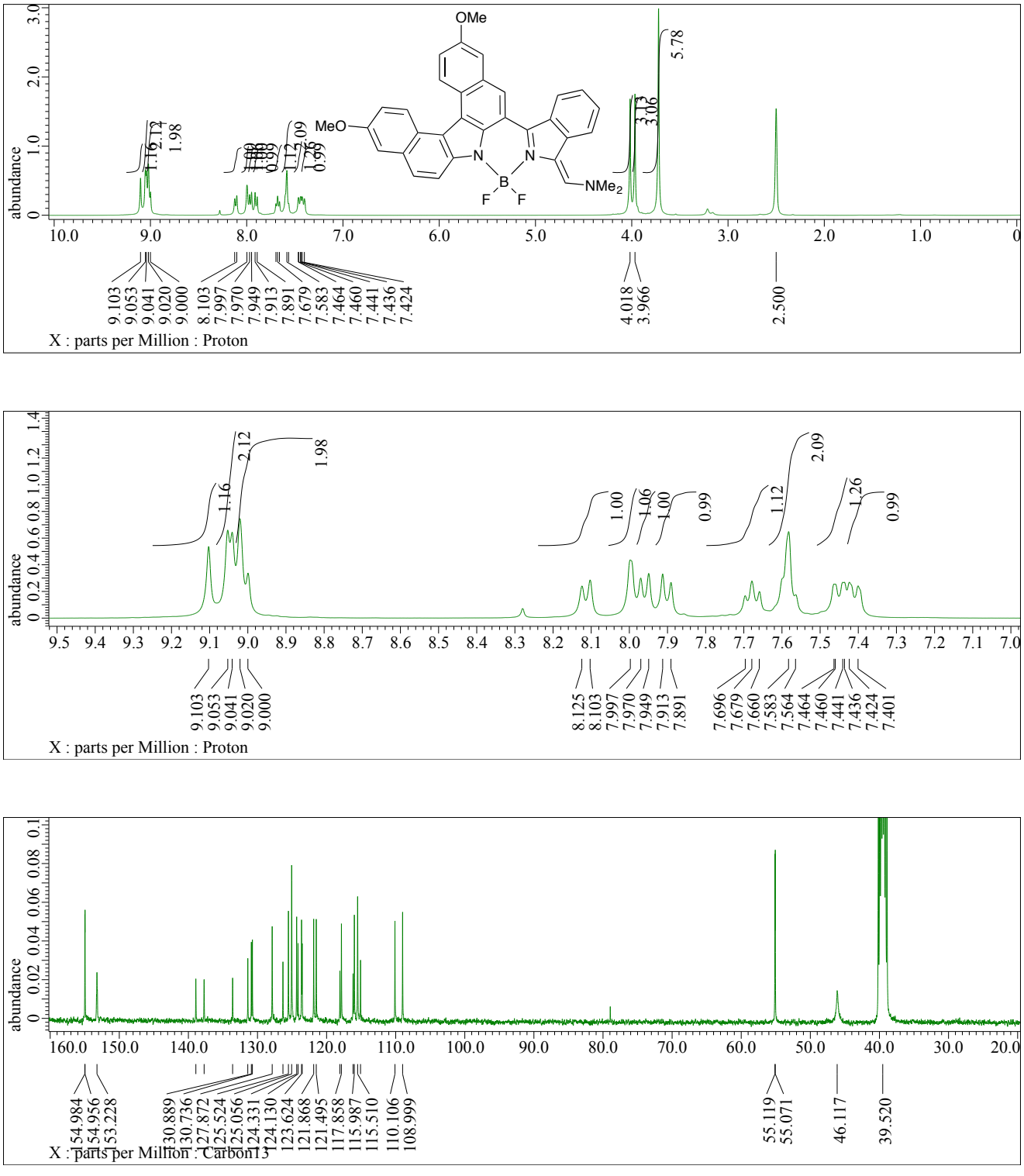


Figure S12. ^{1}H and ^{13}C NMR spectra of **7c** in $CDCl_3$

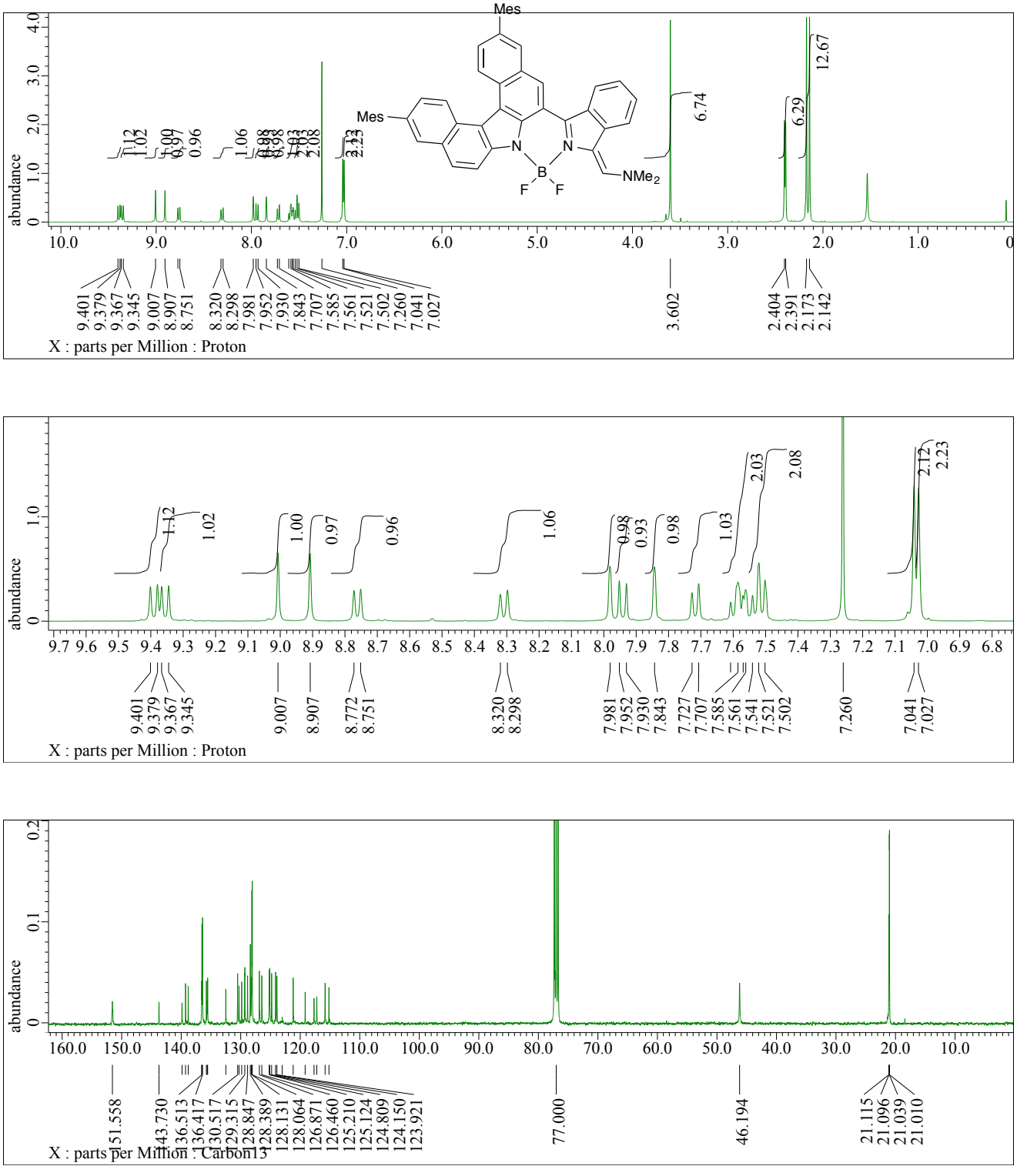


Figure S13. ^{1}H and ^{13}C NMR spectra of **7d** in $CDCl_3$

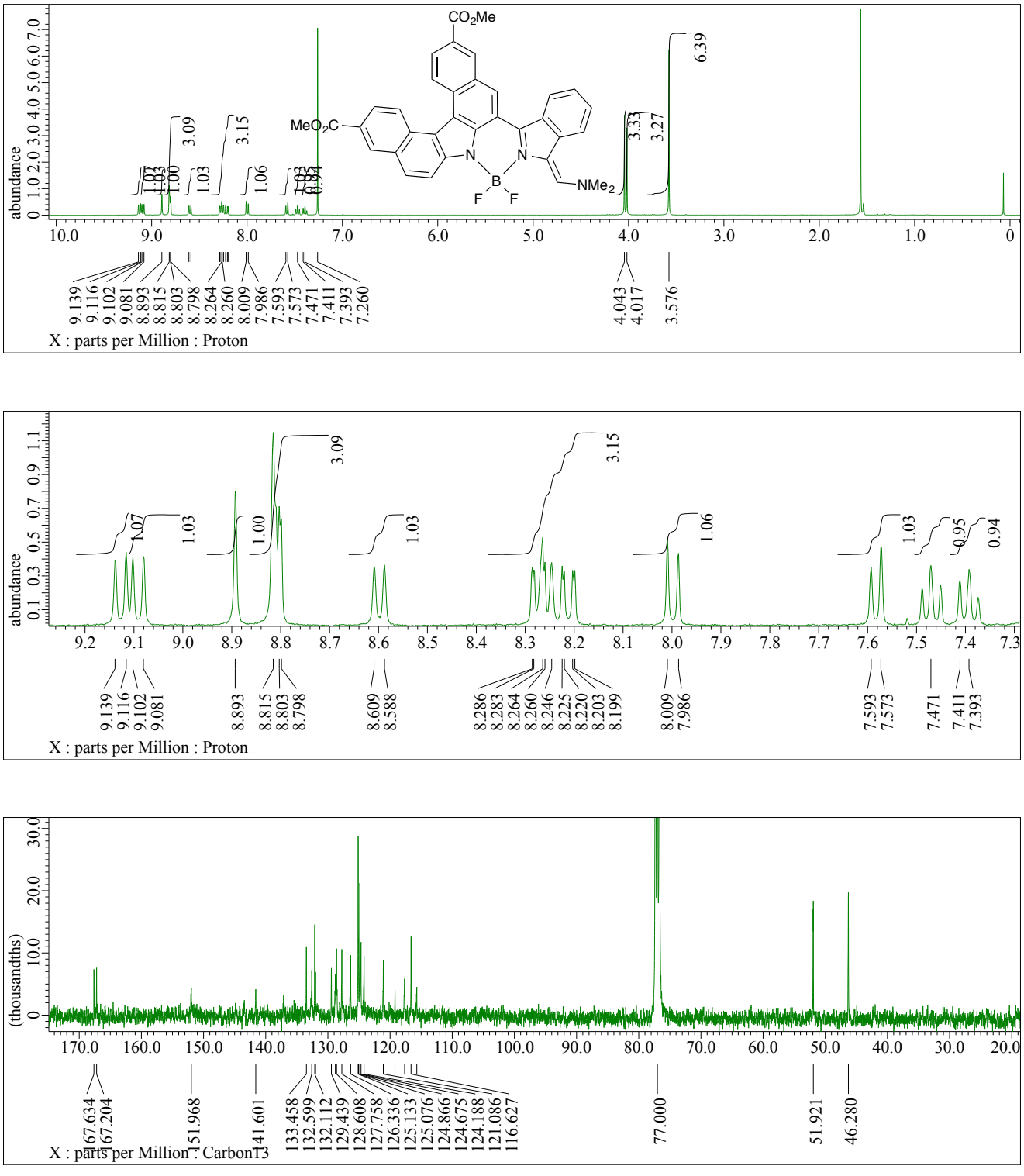


Figure S14. UV/vis absorption (left) and fluorescence (right) spectra of **5a**–**5h** in CH_2Cl_2. (b) UV/vis absorption spectra of **5b**, **5c**, and **5d** in CH_2Cl_2. Calculated oscillator strength were inserted in the spectra. (c) UV/vis absorption spectra of **5a**, **5b**, **5c** with TFA in CH_2Cl_2. (d) UV/vis absorption spectra of **7a**–**7d** in CH_2Cl_2.

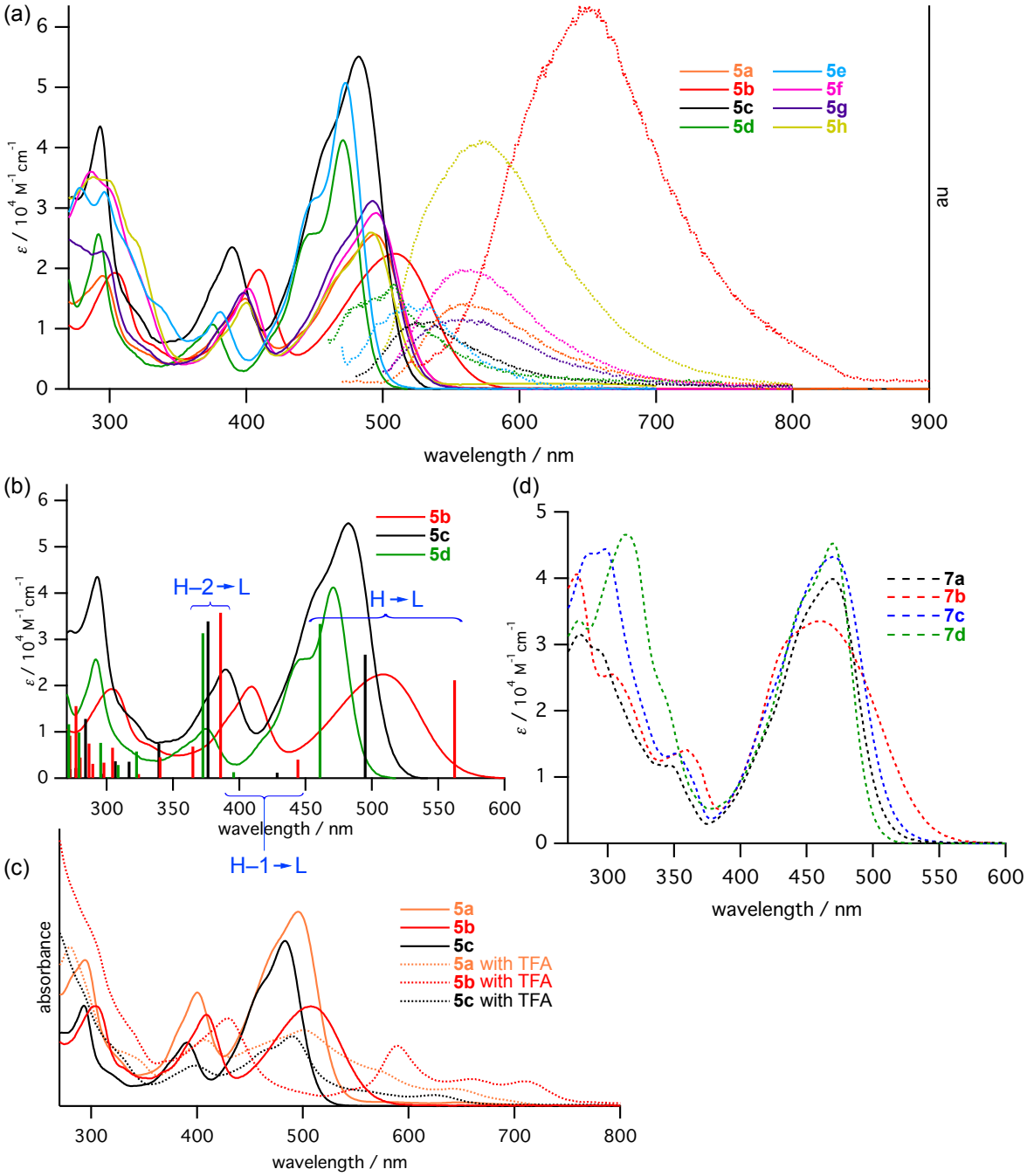
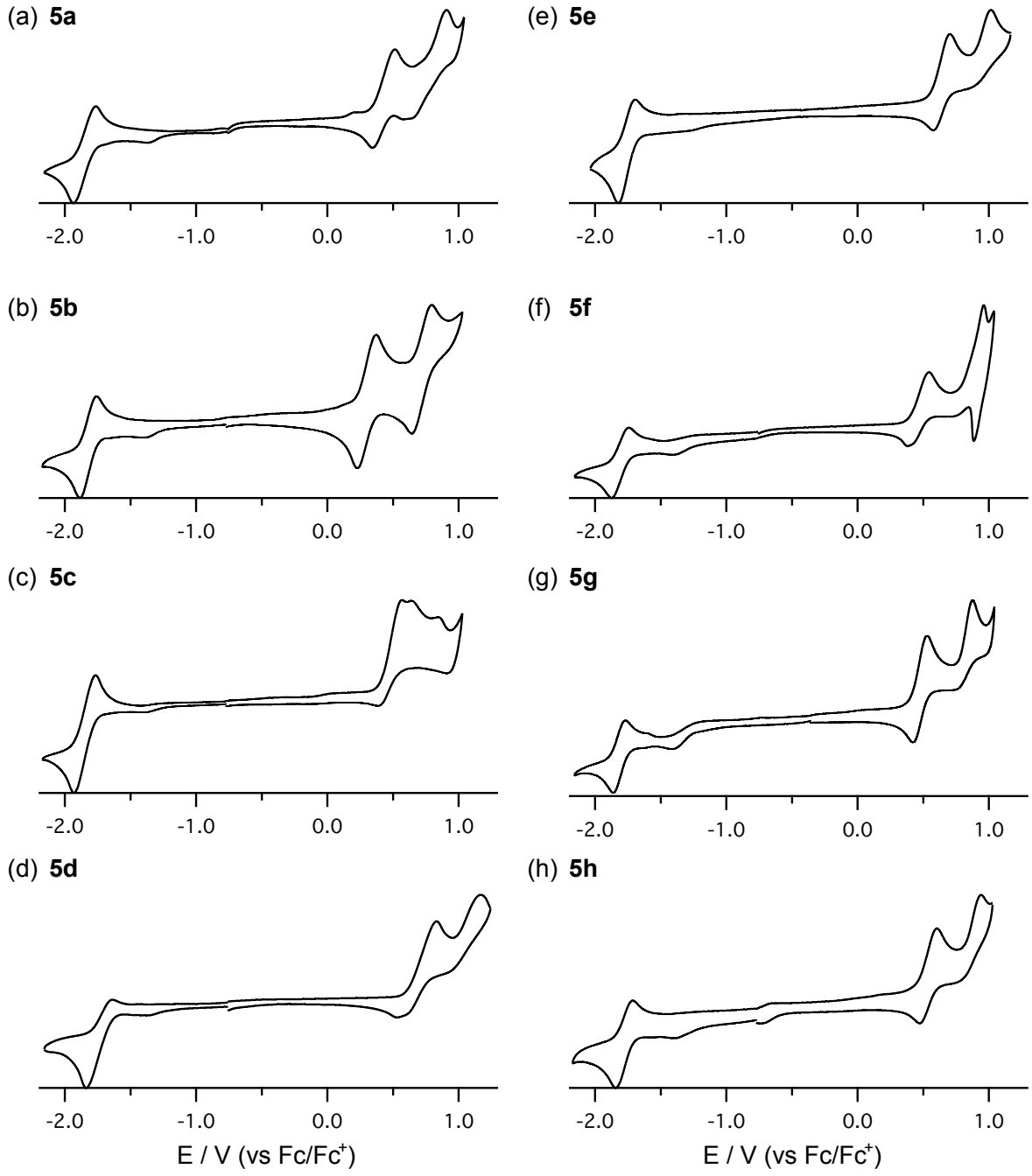
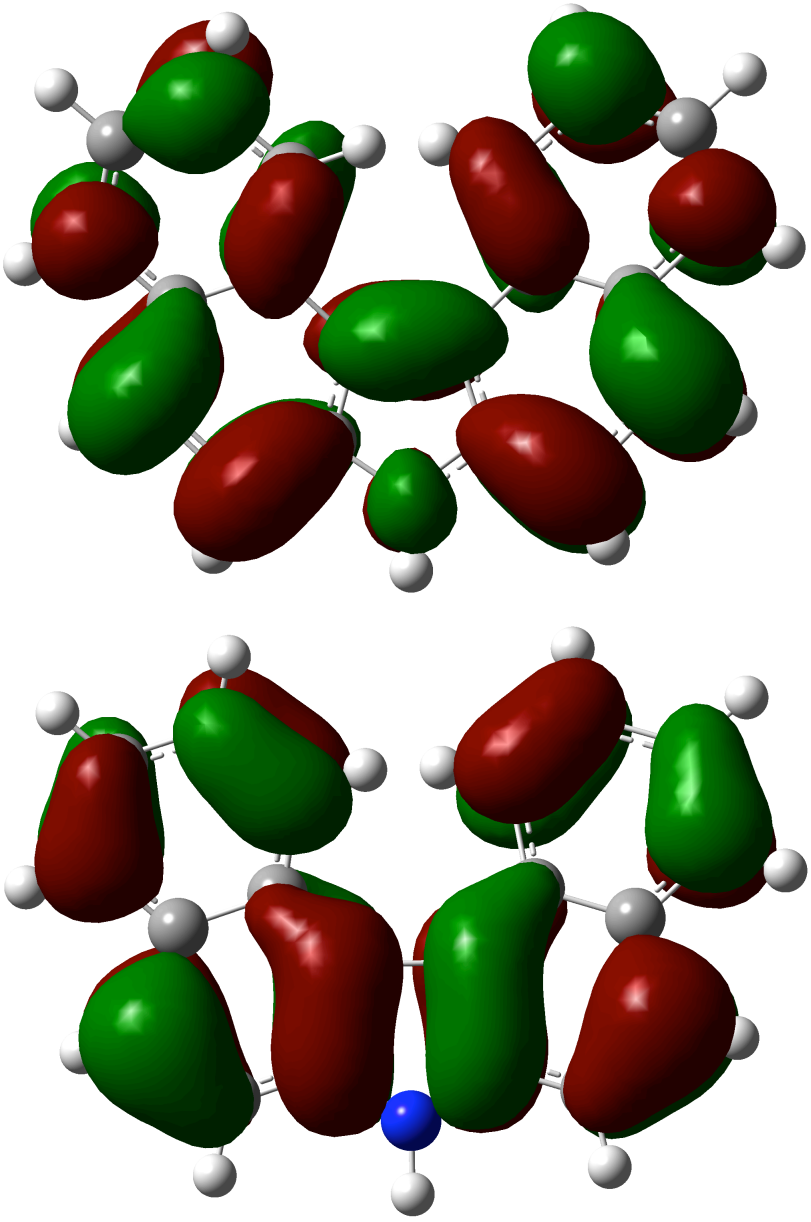


Figure S15. Cyclic voltammograms of **5a**–**5h** (solvent: CH_2Cl_2, supporting electrolyte: Bu_4NPF_6 (0.10 M), counter electrode: Pt, reference electrode: Ag/Ag^+, working electrode: glassy carbon, scan rate: 0.1 V/s, rt).



*The oxidation wave of **5c** was different from those of others probably because oxidation reaction occurred at the uncapped 3,6-posisions of the carbazole moiety.

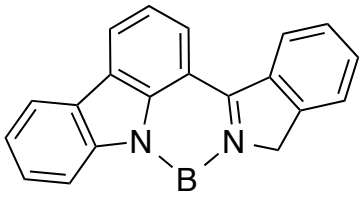
Figure S16. HOMO (bottom) and LUMO (top) of dibenzocarbazole, calculated at B3LYP/6-31G(d) level.[S8]



X-ray Crystal Structures

Single crystals of **5b**, **5c**, **5d**, **5f**, **7a**, and **7c** were obtained by slow diffusion of MeOH vapor into each dichloromethane solution, and that of **5g** was obtained by slow diffusion of MeOH vapor into a toluene solution of **5g**. X-ray data at 93 K were taken on a Rigaku-Raxis-RAPID imaging plate system with Cu-*K*α radiation (λ = 1.54187 Å), and structures were processed and refined by CrystalStructure and Yadokari. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were calculated in ideal positions.

The mean plane deviations in Figure S17–23 were calculated for the following 23 atoms for **5b**, **5c**, **5d**, **5f**, and **5g**, and 31 atoms for **7a** and **7c**.



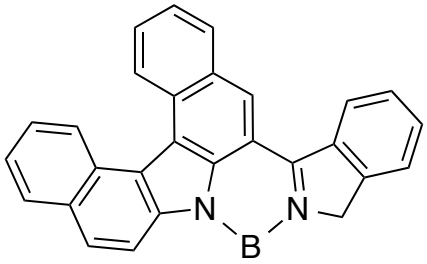
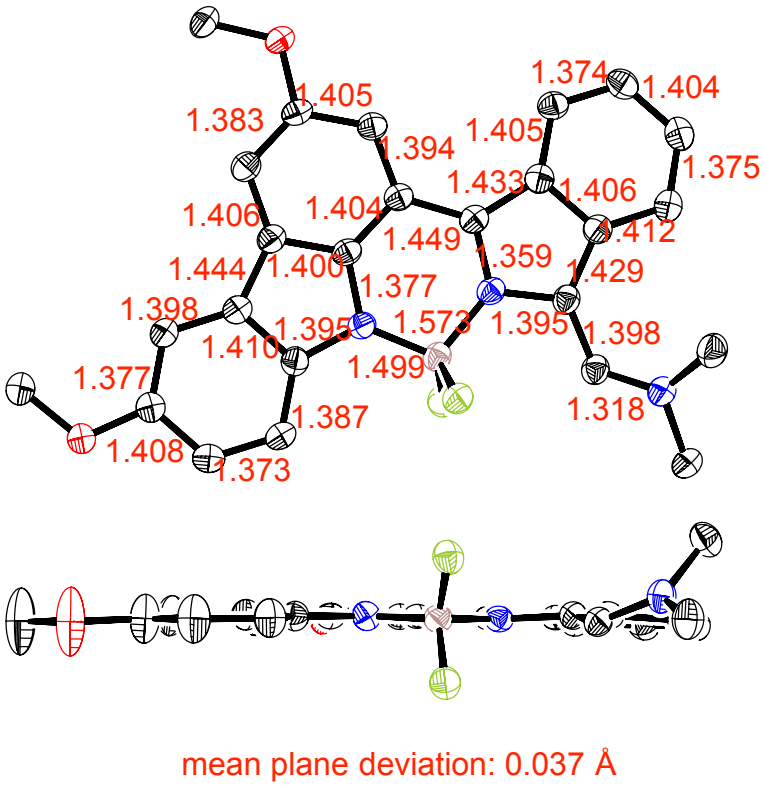
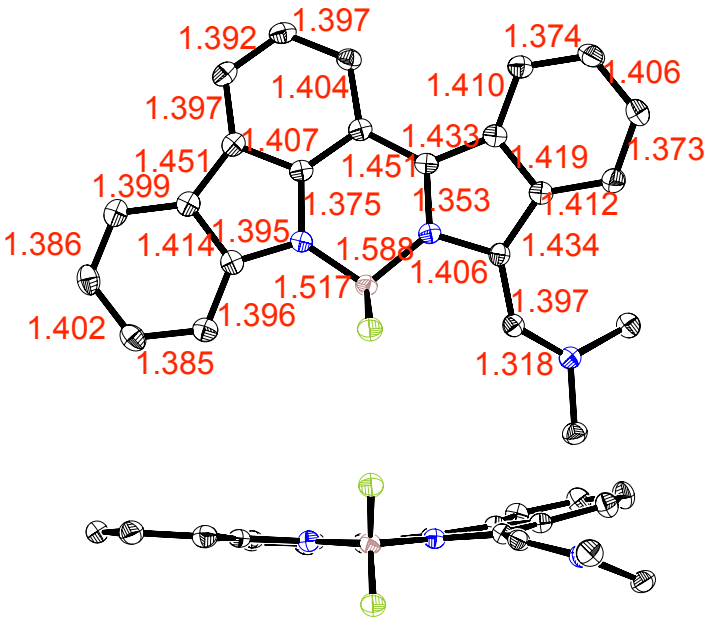


Figure S17. X-ray crystal structure of **5b**. Top view and side view. Hydrogen atoms are omitted for clarity. The selected bond distances (Å) and are shown. The thermal ellipsoids were at 50% probability level.



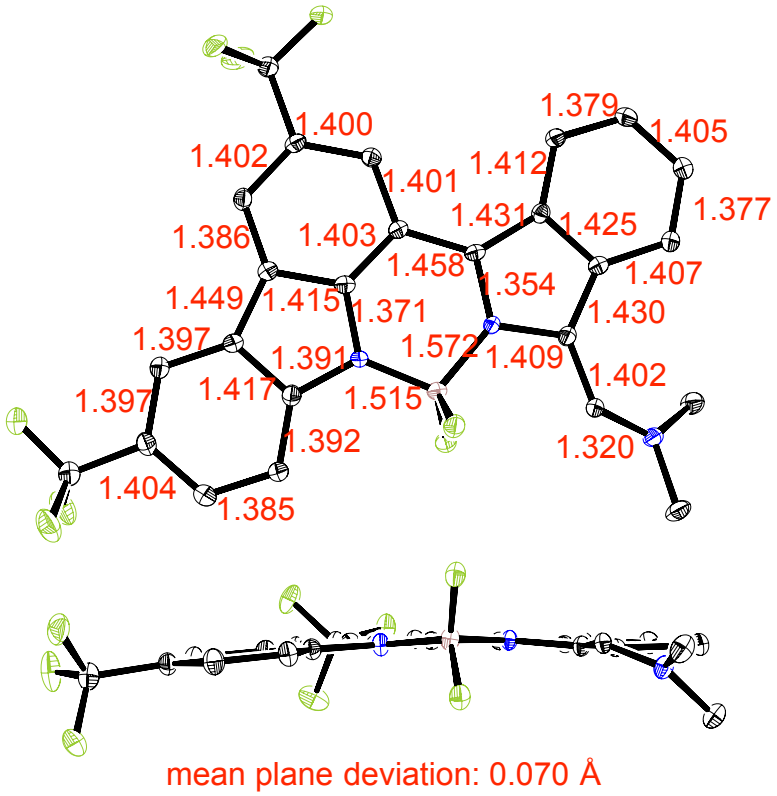
Crystallographic data: $C_{25}H_{22}N_3O_2BF_2 \cdot 0.4CH_2Cl_2 \cdot 0.6CO$, M_w = 507.76, monoclinic, space group $P2_1/c$, a = 13,159(5), b = 12.065(4), c = 15.082(6) Å, β = 98.075(14)°, V = 2370.7(15) Å^3, Z = 4, ρ_{calcd} = 1.423 gcm^{-3}, T = –180 °C, 15623 measured reflections, 4306 unique reflections (R_{int} = 0.0487), R_1 = 0.0577 ($I > 2\sigma(I)$), wR_2 = 0.1681 (all data), GOF = 1.049.

Figure S18. X-ray crystal structure of **5c**. Top view and side view. Hydrogen atoms are omitted for clarity. The selected bond distances (Å) and are shown. The thermal ellipsoids were at 50% probability level.



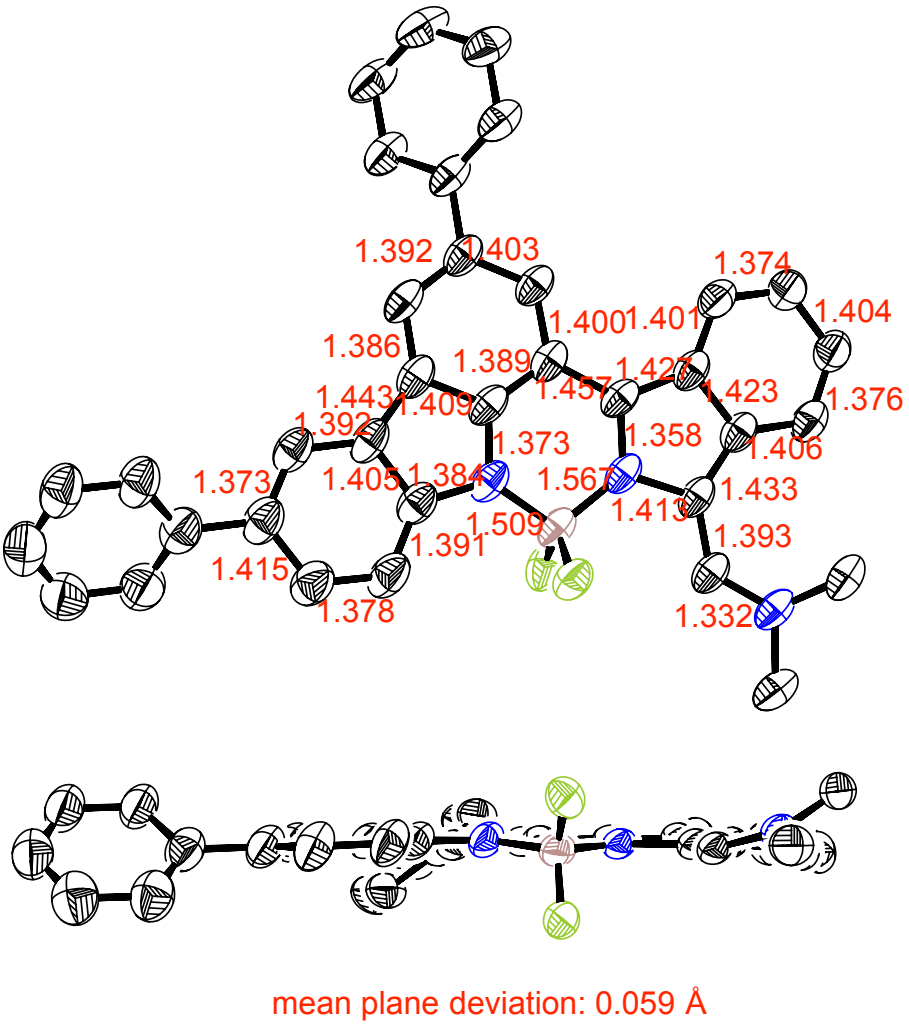
Crystallographic data: formula: $C_{23}H_{18}N_3BF_2$, M_w = 385.21, monoclinic, space group $P2_1/n$, a = 9.594(2), b = 8.7428(17), c = 21.526(6) Å, β = 100.795(8)°, V = 1773.5(7) Å^3, Z = 4, ρ_{calcd} = 1.443 gcm^{-3}, T = –180 °C, 17445 measured reflections, 3076 unique reflections (R_{int} = 0.0282), R_1 = 0.0314 ($I > 2\sigma(I)$), wR_2 = 0.0876 (all data), GOF = 1.000.

Figure S19. X-ray crystal structure of **5d**. Top view and side view. Hydrogen atoms are omitted for clarity. The selected bond distances (Å) and are shown. The thermal ellipsoids were at 50% probability level.



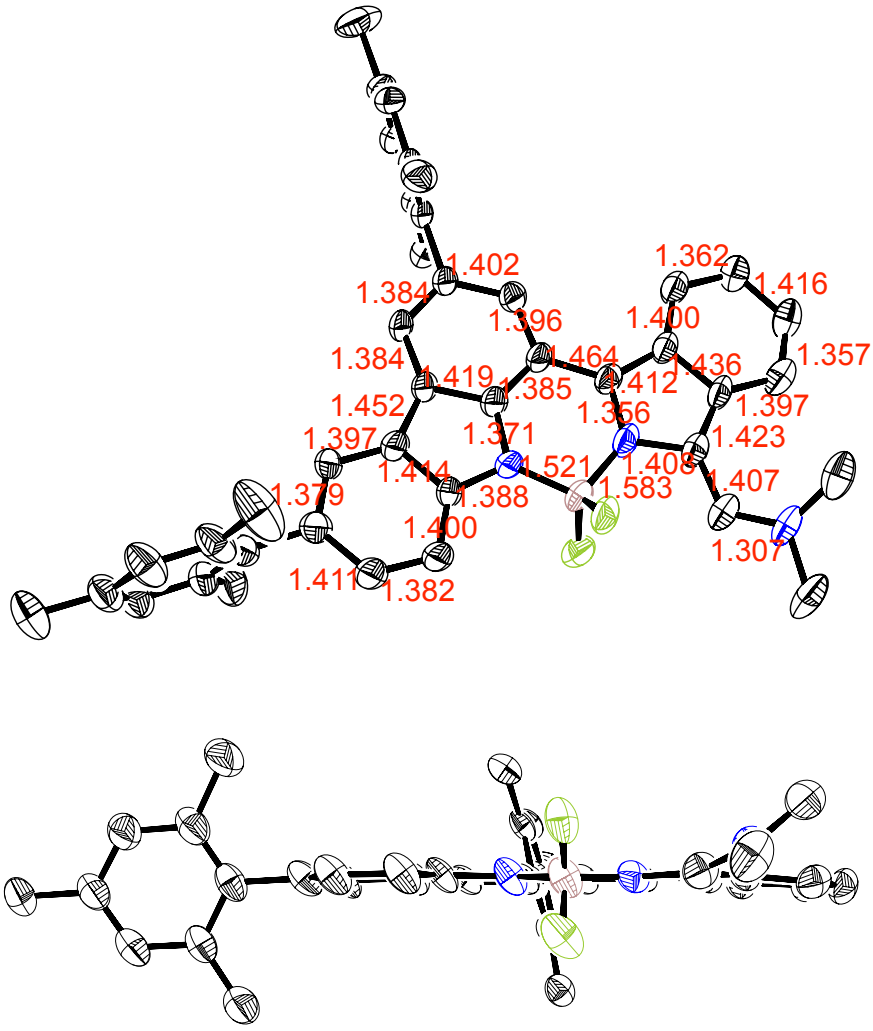
Crystallographic data: formula: $C_{25}H_{16}N_3BF_8 \cdot CH_2Cl_2$, M_w = 606.14, monoclinic, space group $P2_1/c$, a = 7.923(3), b = 11.039(4), c = 27.770(12) Å, β = 96.981(14)°, V = 2410.8(16) Å^3, Z = 4, ρ_{calcd} = 1.670 gcm^{-3}, T = –180 °C, 14876 measured reflections, 4181 unique reflections (R_{int} = 0.039), R_1 = 0.0549 ($I > 2\sigma(I)$), wR_2 = 0.1491 (all data), GOF = 1.019.

Figure S20. X-ray crystal structure of **5f**. Top view and side view. Hydrogen atoms are omitted for clarity. The selected bond distances (Å) and are shown. The thermal ellipsoids were at 50% probability level.



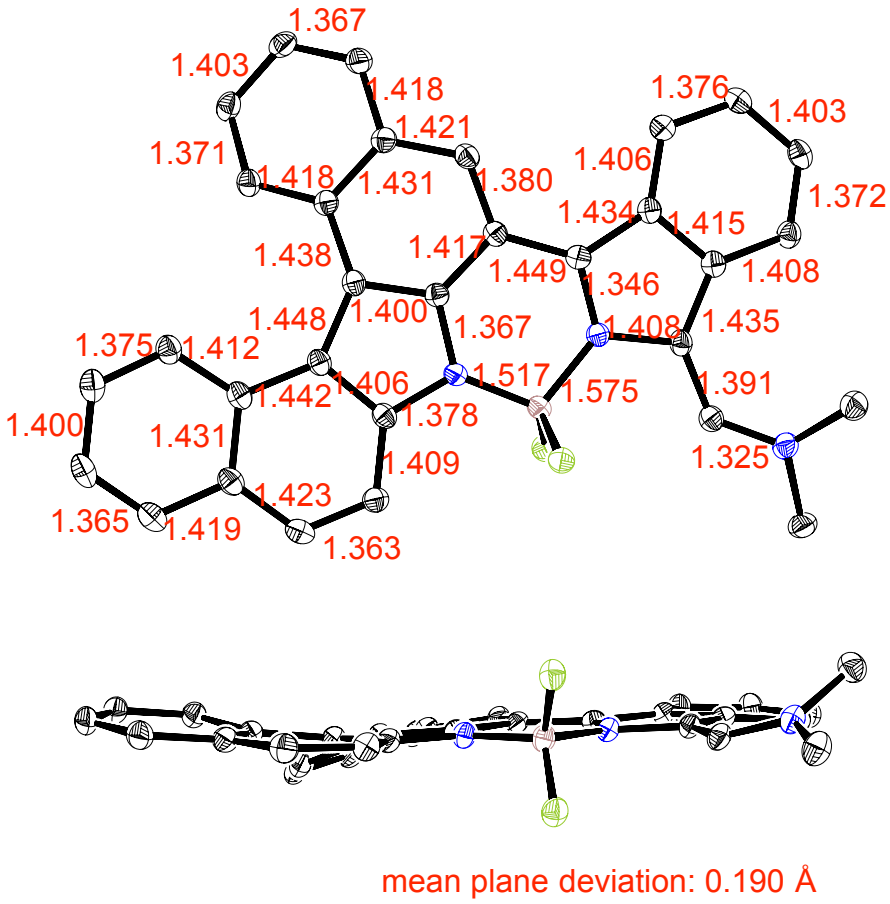
Crystallographic data: formula: $C_{35}H_{26}N_3BF_2 \cdot 0.78CH_2Cl_2$, M_w = 604.06, Monoclinic, space group *C*2/*c*, a = 33.021(12), b = 10.588(4), c = 23.034(8) Å, β = 132.890(5)°, V = 5900(4) Å^3, Z = 8, ρ_{calcd} = 1.360 gcm^{-3}, T = –180 °C, 19003 measured reflections, 5082 unique reflections (R_{int} = 0.0430), R_1 = 0.0610 ($I > 2\sigma(I)$), wR_2 = 0.1850 (all data), GOF = 1.039.

Figure S21. Preliminary X-ray crystal structure of **5g**. Top view, and side view. Hydrogen atoms are omitted for clarity. The selected bond distances (Å) and are shown. The thermal ellipsoids were at 50% probability level.



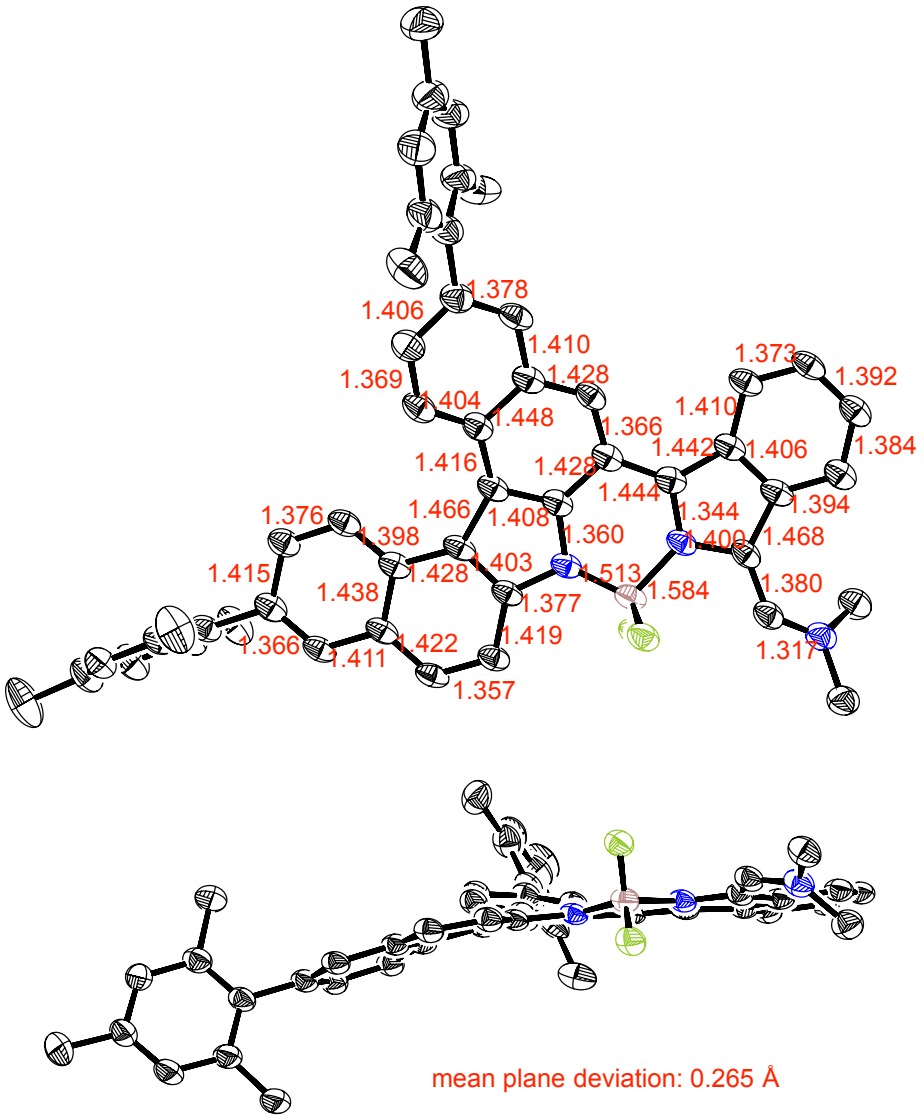
Crystallographic data: formula: $C_{707}H_{656}N_{48}O_9B_{16}F_{32}$, M_w = 10749.66, monoclinic, space group $P21/c$, a = 15.429(2), b = 41.602(7), c = 24.490(4) Å, β = 91.209(6)°, V = 15716(4) Å^3, Z = 1, ρ_{calcd} = 1.136 gcm^{-3}, T = –180 °C, 95813 measured reflections, 24939 unique reflections (R_{int} = 0.0917), R_1 = 0.1213 ($I > 2\sigma(I)$), wR_2 = 0.3481 (all data), GOF = 1.104. CCDC 1057357.

Figure S22. X-ray crystal structure of **7a**. Top view and side view. Hydrogen atoms are omitted for clarity. The selected bond distances (Å) and are shown. The thermal ellipsoids were at 50% probability level.



Crystallographic data: formula: $C_{31}H_{22}N_3BF_2\cdot(CH_2Cl_2)$, M_w = 570.25, triclinic, space group P–1, a = 7.3425(14), b = 11.0127(16), c = 15.884(3) Å, α = 94.772(4), β = 97.467(7), γ = 91.375(10)˚, V = 1268.3(4) Å^3, Z = 2, ρ_{calcd} = 1.493 gcm^{-3}, T = –180 °C, 16223 measured reflections, 4378 unique reflections (R_{int} = 0.0253), R_1 = 0.0294 ($I > 2\sigma(I)$), wR_2 = 0.0868 (all data), GOF = 1.093

Figure S23. X-ray crystal structure of **7c**. Top view and side view. Hydrogen atoms are omitted for clarity. The selected bond distances (Å) and are shown. The thermal ellipsoids were at 50% probability level.



Crystallographic data: formula: $C_{49}H_{42}N_3BF_2 \cdot 1.45(CH_2Cl_2)$, M_w = 844.81, monoclinic, space group $P21/c$, a = 8.0911(18), b = 21.853(5), c = 25.007(6) Å, β = 97.291(6)˚, V = 4385.9(18) Å^3, Z = 4 ρ_{calcd} = 1.279 gcm^{-3}, T = –180 °C, 35327 measured reflections, 7047 unique reflections (R_{int} = 0.0541), R_1 = 0.0935 ($I > 2\sigma(I)$), wR_2 = 0.2764 (all data), GOF = 1.026.

References

[S1] Louillat, M.-L.; Patureau, F. W. *Org. Lett.* **2013**, *15*, 164.

[S2] Inoue, M.; Suzuki, T.; Nakada, M. *J. Am. Chem. Soc.* **2003**, *125*, 1140.

[S3] Lim, B.-Y.; Choi, M.-K.; Cho, C.-G. *Tetrahedron Lett.* **2011**, *52*, 6015.

[S4] Tlili, A.; Monnier, F.; Taillefer, M. *Chem. Commun.* **2012**, *48*, 6408.

[S5] For the lithiation of 3,6-dibromocarbazole, see: Folmer-Andersen, J. F.; Buhler, E.; Candau, S.-J.; Joulie, S.; Schmutz, M.; Lehn, J.-M. *Polym. Int.* **2010**, *59*, 1477.

[S6] Diana, P.; Martorana, A.; Barraja, P.; Montalbano, A.; Carbone, A.; Cirrincione, G. *Tetrahedron* **2011**, *67*, 2072.

[S7] Sakakura, A.; Suzuki, K.; Ishihara, K. *Adv. Synth. Catal.* **2006**, *348*, 2457.

[S8] *Gaussian 09, Revision C.01*. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.