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Supporting Information

Negishi reaction in BODIPY dyes. Unprecedented alkylation by palladium-catalyzed C–C coupling in boron dipyrromethene derivatives

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General

Synthesis: Starting materials and reagents used in the preparation of BODIPYs are commercially available unless synthesis is described. The solvents were dried and distilled before use. Flash column chromatography was performed using silica gel Merck 60 (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-DPX-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) and Avance III (700 MHz for ^{1}H and 176 MHz for ^{13}C) spectrometers. All spectra were recorded in $CDCl_3$. ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane (δ = 0.00 ppm), using the residual solvent signal as the internal reference. ^{13}C chemical shifts are reported in ppm with $CDCl_3$ (δ = 77.67 ppm) as the internal standard. Chemical shift multiplicities are reported as s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, dd = double doublet and m = multiplet. IR spectra (in cm^{-1}) were recorded a Bruker Tensor-27-FTIR spectrophotometer. Gas chromatographic analysis was performed on an Agilent GC/MS system (gas chromatograph: 6890N Network; column: DB-5ms; quadrupole mass detector: 5973 MSD). High resolution mass spectra were determined by EI a Thermofisher MAT 95 XP.

BODIPY derivatives **1**,[1] **2**,[1] and **3**,[2] were synthesized by the methods previously described.

Photophysical properties: The photophysical properties were registered in diluted solutions (around 1×10^{-5} M), prepared by diluting a concentrated stock solution in ethyl acetate. UV-Vis absorption and fluorescence spectra were recorded on a Bio-Tek spectrophotometer (model UVIKON XL) and a Sim-Aminco spectrofluorimeter (model Aminco Bowman Series 2), respectively. The fluorescence spectra were corrected from the wavelength dependence of the detector sensibility. A Commercial BODIPY PM546 (4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-*s*-indacene) was used as the reference dye (Φ = 0.85 in AcOEt).[3]

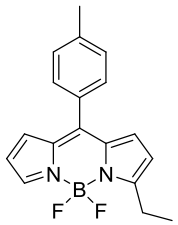
[1] M. R. Rao, K. V. Pavan Kumar and M. Ravikanth, *J. Orgamometallic Chem*., 2010, **695**, 863-869.
[2] T. Rohand, M. Baruah, W. Qin, N. Boens and W. Dehaen, *Chem. Commun.*, 2006, 266-268.
[3] F. López Arbeloa, J. Bañuelos, V. Martinez, T. Arbeloa and I. López Arbeloa, *Int. Rev. Phys. Chem.*, 2005, **24**, 339-374.

Synthesis and Characterization of BODIPYs

General procedure for Negishi cross-coupling reactions: Method A. To a flame-dried 100 mL two-neck flask were added the halogenated BODIPY (1 equiv), $Pd(PPh_3)_2Cl_2$ (10 mol %) and dry toluene (10 mL) under argon atmosphere. To the reaction mixture was added dropwise R_2Zn or RZnBr (1.1-20 equiv) and the mixture was stirred at room temperature for 5-120 min. The reaction was monitored by TLC. EtOAc was then added, and the solution was washed with 10% aq HCl, saturated aq $NaHCO_3$ solution and H_2O, dried over $MgSO_4$, filtered and concentrated to dryness. The compounds were purified by flash chromatography on silica gel.

General procedure for Negishi cross-coupling reactions: Method B. To a flame-dried 100 mL two-neck flask were added (trimethylsilyl)acetylene or phenylacetylene (5-10 equiv) and dry THF (5 mL). Then, BuLi (5-10 equiv) was added dropwise under argon atmosphere at -78ºC and the mixture was stirred for 30 min. After this time period, a solution of $ZnBr_2$ (5-10 equiv) in dry THF (2 mL) was added at -78ºC and 5 min later the reaction was allowed to reach room temperature. Then, halogenated BODIPY (1 equiv), $Pd(PPh_3)_2Cl_2$ (10 mol %) and dry toluene (10 mL) were added at room temperature and the reaction mixture was stirred for 20-60 min. EtOAc was then added, and the solution was washed with 10% aq HCl, saturated aq $NaHCO_3$ solution and H_2O, dried over $MgSO_4$, filtered and concentrated to dryness. The compounds were purified by flash chromatography on silica gel.

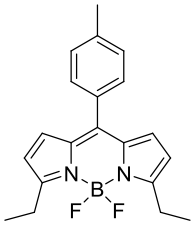
Synthesis of 3-ethyl-4,4-difluoro-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (4a).



According to the general procedure A, BODIPY **1** (42 mg, 0.117 mmol), $Pd(PPh_3)_2Cl_2$ (8 mg, 0.012 mmol) in dry toluene (10 mL) and $ZnEt_2$ (0.14 mL, 1 M in hexane, 0.14 mmol) were reacted for 60 min. Flash chromatography using hexane/EtOAc (98:2) afforded **4a** (24 mg, 64%, as a brown solid), and **1** (6 mg, 15%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (broad s, 1H, CH), 7.36 (d, *J* = 8.1 Hz, 2H, phenyl), 7.23 (d, *J* = 8.1 Hz,

2H, phenyl), 6.85 (d, *J* = 4.2 Hz, 1H, CH), 6.72 (d, *J* = 3.9 Hz, 1H, CH), 6.39 (dd, *J* = 3.9 and 1.8 Hz, 1H, CH), 6.36 (d, *J* = 4.2 Hz, 1H, CH), 3.18 (q, *J* = 7.8 Hz, 2H, CH_2), 2.39 (s, 3H, CH_3), 1.29 (t, *J* = 7.8 Hz, 3H, CH_3CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8 (C), 145.3 (C), 140.8 (C), 140.4 (CH), 135.5 (C), 133.8 (C), 133.1 (CH), 131.2 (C), 130.5 (CH), 129.1 (CH), 128.6 (CH), 118.8 (CH), 117.0 (CH), 22.3 (CH_2), 21.5 (CH_3), 12.5 (CH_3); IR (neat): 2971, 2924, 1536, 1398, 1351, 1268, 1252, 1121, 1030, 979, 825, 735 cm^{-1}; HRMS-EI: calcd for ($C_{18}H_{17}BF_2N_2$) 310.1450, found 310.1443.

Synthesis of 3,5-diethyl-4,4-difluoro-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (5a).



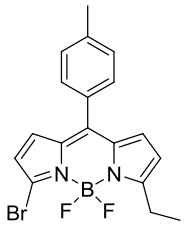
According to the general procedure A, BODIPY **2** (50 mg, 0.114 mmol), $Pd(PPh_3)_2Cl_2$ (8 mg, 0.011 mmol) in dry toluene (10 mL) and $ZnEt_2$ (0.46 mL, 1 M in hexane, 0.456 mmol) were reacted for 20 min. Flash chromatography using hexane/EtOAc (98:2) afforded **5a**[4] (33 mg, 86%) as a brown solid.

According to the general procedure A, BODIPY **3** (50 mg, 0.142 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) and $ZnEt_2$ (0.57 mL, 1 M in hexane, 0.568 mmol) were reacted for 120 min. Flash chromatography using hexane/EtOAc (98:2) afforded, by order of elution, **5a**[4] (35 mg, 73%) and **4c** (5 mg, 10%).

*Compound **5a***: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (d, *J* = 7.8 Hz, 2H, phenyl), 7.19 (d, *J* = 7.8 Hz, 2H, phenyl), 6.68 (d, *J* = 4.2 Hz, 2H, 2CH), 6.26 (d, *J* = 4.2 Hz, 2H, 2CH), 3.00 (q, *J* = 7.5 Hz, 4H, $2CH_2$), 2.36 (s, 3H, CH_3), 1.26 (t, *J* = 7.5 Hz, 6H, $2CH_3CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.2 (C), 142.2 (C), 139.2 (C), 133.2 (C), 130.3 (C), 129.4 (CH), 127.8 (CH), 116.0 (CH), 21.0 (CH_2), 20.4 (CH_3), 11.8 (CH_3); IR (neat): 2953, 2925, 2860, 1553, 1140, 1001 cm^{-1}; HRMS-EI: calcd for ($C_{20}H_{21}BF_2N_2$) 338.1764, found 338.1759.

[4] M. Pintado, Ph.D. Thesis, Universidad Complutense de Madrid (Spain), 2009.

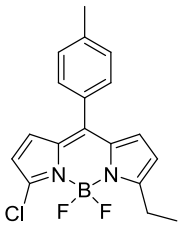
Synthesis of 3-bromo-5-ethyl-4,4-difluoro-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (4b).



According to the general procedure A, BODIPY **2** (50 mg, 0.114 mmol), $Pd(PPh_3)_2Cl_2$ (8 mg, 0.011 mmol) in dry toluene (10 mL) and $ZnEt_2$ (0.13 mL, 1 M in hexane, 0.125 mmol) were reacted for 120 min. Flash chromatography using hexane/EtOAc (98:2) afforded, by order of elution, **5a**[4] (7 mg, 18%), and **4b** (27 mg, 61%, as a brown solid).

*Compound **4b***: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.1 Hz, 2H, phenyl), 7.22 (d, *J* = 8.1 Hz, 2H, phenyl), 6.82 (d, *J* = 4.5 Hz, 1H, CH), 6.59 (d, *J* = 3.9 Hz, 1H, CH), 6.39-6.36 (m, 2H, 2CH), 3.03 (q, *J* = 7.5 Hz, 2H, CH_2), 2.38 (s, 3H, CH_3), 1.28 (t, *J* = 7.5 Hz, 3H, CH_3CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.7 (C), 143.1 (C), 140.9 (C), 135.4 (C), 134.7 (C), 133.1 (CH), 130.5 (CH), 129.1 (CH), 128.8 (CH), 126.9 (C), 120.4 (CH), 119.6 (CH), 22.4 (CH_2), 21.5 (CH_3), 12.7 (CH_3); IR (neat): 2970, 2930, 2878, 1547, 1436, 1319, 1136, 1033, 980 cm^{-1}; HRMS-EI: calcd for ($C_{18}H_{16}BBrF_2N_2$) 388.0556, found 388.0550.

Synthesis of 3-chloro-5-ethyl-4,4-difluoro-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (4c).



According to the general procedure A, BODIPY **3** (50 mg, 0.142 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) and $ZnEt_2$ (0.16 mL, 1 M in hexane, 0.156 mmol) were reacted for 40 min. Flash chromatography using hexane/EtOAc (98:2) afforded, by order of elution, **5a**[4] (4 mg, 8%) and **4c** (37 mg, 75%, as a brown solid).

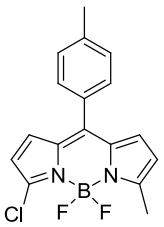
*Compound **4c**:* ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.1 Hz, 2H, phenyl), 7.22 (d, *J* = 8.1 Hz, 2H, phenyl), 6.81 (d, *J* = 4.5 Hz, 1H, CH), 6.64 (d, *J* = 4.2 Hz, 1H, CH), 6.37 (d, *J* = 4.5 Hz, 1H, CH), 6.26 (d, *J* = 4.2 Hz, 1H, CH), 3.04 (q, *J* = 7.5 Hz, 2H, CH_2), 2.38 (s, 3H, CH_3), 1.28 (t, *J* = 7.5 Hz, 3H, CH_3CH_2); ^{13}C NMR (75 MHz, $CDCl_3$):

δ 167.4 (C), 143.5 (C), 140.9 (C), 140.1 (C), 135.3 (C), 133.0 (CH), 133.5 (CH), 129.1 (CH), 128.8 (CH), 119.4 (CH), 116.7 (CH), 22.4 (CH_2), 21.5 (CH_3), 12.7 (CH_3); IR (neat): 2925, 1549, 1438, 1320, 1138, 1034, 984 cm^{-1}; HRMS-EI: calcd for ($C_{18}H_{16}BClF_2N_2$) 344.1061, found 344.1055.

Synthesis of 3,5-dimethyl-4,4-difluoro-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (5b).

According to the general procedure A, BODIPY **3** (50 mg, 0.142 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) and $ZnMe_2$ (2 mL, 1.2 M in toluene, 2.84 mmol) were reacted for 90 min. Flash chromatography using hexane/EtOAc (99:1) afforded **5b**[5] (35 mg, 80%). Characterization data are in agreement with literature.

Synthesis of 3-chloro-5-methyl-4,4-difluoro-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (**4d**).

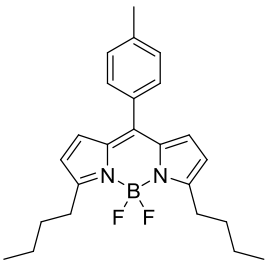


According to the general procedure A, BODIPY **3** (50 mg, 0.142 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) and $ZnMe_2$ (0.18 mL, 1.2 M in toluene, 0.213 mmol) were reacted for 60 min. Flash chromatography using hexane/EtOAc (99:1) afforded, by order of elution, **4d** (36 mg, 77%, as a brown solid) and **3** (7 mg, 14%).

*Compound **4d***: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.1 Hz, 2H, phenyl), 7.22 (d, *J* = 8.1 Hz, 2H, phenyl), 6.78 (d, *J* = 4.2 Hz, 1H, CH), 6.64 (d, *J* = 4.2 Hz, 1H, CH), 6.28 (d, *J* = 4.2 Hz, 1H, CH), 6.26 (d, *J* = 4.2 Hz, 1H, CH), 2.61 (s, 3H, CH_3), 2.38 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.4 (C), 143.3 (C), 140.9 (C), 140.3 (C), 135.5 (C), 133.0 (C), 132.8 (CH), 130.5 (CH), 130.4 (C), 129.1 (CH), 128.8 (CH), 121.4 (CH), 116.7 (CH), 21.4 (CH_3), 15.2 (CH_3); IR (neat): 2958, 2927, 2866, 1550, 1436, 1268, 1081, 1054, 1007, 984 m^{-1}; HRMS-EI: calcd for ($C_{17}H_{14}BClF_2N_2$) 330.0905, found 330.0899.

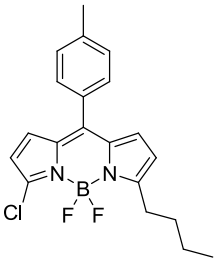
[5] (*a*) Q. Miao, J.-Y. Shin, B. O. Patrick and D. Dolphin, *Chem. Commun*., 2009, 2541-2543; (*b*) Y. Chen, L. Wan, D. Zhang, Y. Bian and J. Jiang, *Photochem. Photobiol. Sci*., 2011, **10**, 1030-1038.

Synthesis of 3,5-dibutyl-4,4-difluoro-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (5c).



According to the general procedure A, BODIPY **3** (50 mg, 0.142 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) and BuZnBr (5.7 mL, 0.5 M in THF, 2.84 mmol) were reacted for 30 min. Flash chromatography using hexane/EtOAc (98:2) afforded **5c** (29 mg, 52%, as a brown solid). ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.7 Hz, 2H, phenyl), 7.21 (d, *J* = 7.7 Hz, 2H, phenyl), 6.68 (d, *J* = 4.2 Hz, 1H), 6.25 (d, *J* = 4.2 Hz, 1H), 2.97 (t, *J* = 7.7 Hz, 4H, $2CH_2$), 2.38 (s, 3H, CH_3), 1.67 (quint, *J* = 7.7 Hz, 4H, $2CH_2$), 1.40 (sext, *J* = 7.7 Hz, 4H, $2CH_2$), 0.90 (t, *J* = 7.7 Hz, 6H, $2CH_3CH_2$); ^{13}C NMR (176 MHz, $CDCl_3$): δ 162.1 (C), 142.9 (C), 140.1 (C), 134.1 (C), 131.4 (C), 130.4 (CH), 130.2 (CH), 128.9 (CH), 117.6 (CH), 30.7 (CH_2), 28.5 (CH_2), 22.7 (CH_2), 21.4 (CH_3), 14.0 (CH_3); IR (neat): 2957, 2924, 2856, 1573, 1551, 1414, 1336, 1270, 1127, 976, 762 cm^{-1}; HRMS-EI: calcd for ($C_{24}H_{29}BF_2N_2$) 394.2390, found 394.2385.

Synthesis of 3-butyl-5-chloro-4,4-difluoro-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (4e).

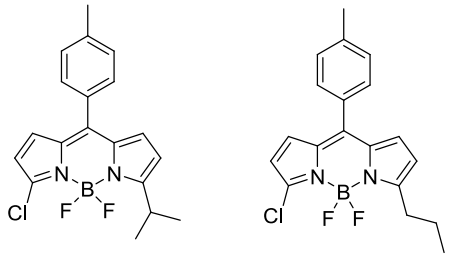


According to the general procedure A, BODIPY **3** (50 mg, 0.142 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) and BuZnBr (5.7 mL, 0.5 M in THF, 2.84 mmol) were reacted for 10 min. Flash chromatography using hexane/EtOAc (99.5:0.5) afforded, by order of elution, **5c** (9 mg, 9%) and **4e** (33 mg, 62%, as a brown solid).

*Compound **4e***: ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.7 Hz, 2H, phenyl), 7.23 (d, *J* = 7.7 Hz, 2H, phenyl), 6.81 (d, *J* = 4.2 Hz, 1H, CH), 6.64 (d, *J* = 4.2 Hz, 1H, CH), 6.36 (d, *J* = 4.2 Hz, 1H, CH), 6.26 (d, *J* = 4.2 Hz, 1H, CH), 3.01 (t, *J* = 7.7 Hz, 4H, $2CH_2$), 2.39 (s, 3H, CH_3), 1.68 (quint, *J* = 7.7 Hz, 4H, $2CH_2$), 1.41 (sext, *J* = 7.7 Hz,

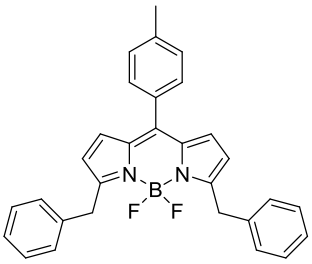
4H, $2CH_2$), 0.90 (t, *J* = 7.7 Hz, 6H, $2CH_3CH_2$); ^{13}C NMR (176 MHz, $CDCl_3$): δ 165.5 (C), 142.2 (C), 139.8 (C), 138.9 (C), 134.2 (C), 131.9 (C), 131.8 (CH), 129.4 (C and CH), 128.0 (CH), 127.5 (CH), 118.9 (CH), 115.5 (CH), 29.6 (CH_2), 27.8 (CH_2), 21.7 (CH_2), 20.4 (CH_3), 12.9 (CH_3); IR (neat): 2973, 2927, 1571, 1435, 1390, 1327, 1269, 1170, 1044, 989, 735 cm^{-1}; HRMS-EI: calcd for ($C_{20}H_{20}BClF_2N_2$) 372.1373, found 372.1368.

Synthesis of 3-chloro-4,4-difluoro-5-isopropyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (4f) and 3-chloro-4,4-difluoro-5-propyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (4g).



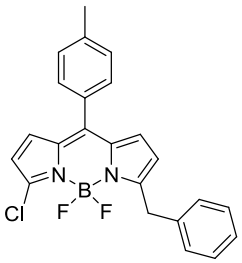
According to the general procedure A, BODIPY **3** (50 mg, 0.142 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) and $Zn(iPr)_2$ (1.4 mL, 1 M in toluene, 1.4 mmol) were reacted for 50 min. Flash chromatography using hexane/EtOAc (99:1) afforded a 2:1 mixture of **4f** and **4g** (35 mg, 70%, as a brown solid). ^1H NMR (700 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.7 Hz, 2H, phenyl-**4f** and **4g**), 7.23 (d, *J* = 7.7 Hz, 2H, phenyl-**4f** and **4g**), 6.83-6.81 (m, 1H, CH-**4f** and **4g**), 6.64 (broad s, 1H, CH-**4f** and **4g**), 6.42 (d, *J* = 4.2 Hz, 0.66H, CH-**4f**), 6.36 (d, *J* = 4.2 Hz, 0.33H, CH-**4g**), 6.27 (m, 1H, CH-**4f** and **4g**), 3.63 (m, 0.66H, CH-**4f**), 2.98 (t, *J* = 7.7 Hz, 0.66H, CH_2-**4g**), 2.39 (s, 3H, CH_3-**4f** and **4g**), 1.73 (sext, *J* = 7.7 Hz, 0.66H, CH_2-**4g**), 1.28 (d, *J* = 6.3 Hz, 4H, $2CH_3$-**4f**), 0.99 (t, *J* = 7.7 Hz, 1H, CH_3CH_2-**4g**); ^{13}C NMR (176 MHz, $CDCl_3$): δ 172.3 (C), 166.3 (C), 143.5 (C), 143.3 (C), 140.8 (C), 140.7 (C), 140.0 (C), 139.8 (C), 134.7 (C), 133.1 (CH), 132.8 (CH), 130.5 (C), 130.4 (CH), 129.1 (CH), 128.6 (CH), 128.5 (CH), 119.9 (CH), 117.3 (CH), 116.6 (CH), 116.5 (CH), 31.0 (CH_2), 28.3 (CH), 22.5 (CH_3), 21.9 (CH_2), 21.5 (CH_3), 14.1 (CH_3); GC-MS *m/z* (%) **4f**: 358.2 (M^+, 62), 343.2 (92), 323.1 (100); **4g**: 358.2 (M^+, 54), 329.2 (100).

Synthesis of 3,5-dibenzyl-4,4-difluoro-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (5d).



According to the general procedure A, BODIPY **3** (50 mg, 0.142 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) and BnZnBr (5.7 mL, 0.5 M in THF, 2.85 mmol) were reacted for 30 min. Flash chromatography using hexane/EtOAc (98:2) afforded **5d** (13 mg, 20%) as a brown solid. ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.32-7.19 (m, 14H, phenyl), 6.65 (d, *J* = 4.2 Hz, 2H, 2CH), 6.00 (d, *J* = 4.2 Hz, 2H, 2CH), 4.36 (s, 4H, $2CH_2$), 2.36 (s, 3H, CH_3); ^{13}C NMR (176 MHz, $CDCl_3$): δ 160.2 (C), 144.2 (C), 140.4 (C), 137.8 (C), 134.4 (C), 131.2 (C), 130.4 (CH), 129.5 (CH), 128.9 (CH), 128.6 (CH), 126.7 (CH), 118.7 (CH), 35.1 (CH_2), 21.4 (CH_3); IR (neat): 2924, 1572, 1543, 1482, 1431, 1302, 1260, 1112, 981, 885 cm^{-1}; HRMS-EI: calcd for ($C_{30}H_{25}BF_2N_2$) 462.2075, found 462.2072.

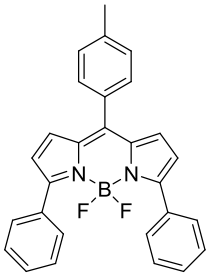
Synthesis of 3-benzyl-5-chloro-4,4-difluoro-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (4h).



According to the general procedure A, BODIPY **3** (50 mg, 0.142 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) and BnZnBr (1.14 mL, 0.5 M in THF, 0.57 mmol) were reacted for 25 min. Flash chromatography using hexane/EtOAc (99:1) afforded **4h** (10 mg, 18%) as a brown solid. ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.31-7.22 (m, 9H, phenyl), 6.74 (d, *J* = 4.2 Hz, 1H, CH), 6.68 (d, *J* = 4.2 Hz, 1H, CH), 6.30 (d, *J* = 4.2 Hz, 1H, CH), 6.09 (d, *J* = 4.2 Hz, 1H, CH), 4.36 (s, 2H, CH_2), 2.38 (s, 3H, CH_3); ^{13}C NMR (176 MHz, $CDCl_3$): δ 163.6 (C), 144.0 (C), 141.0 (C), 140.8 (C), 137.0 (C), 135.3 (C), 133.1 (C), 132.5 (CH), 130.5 (CH), 130.4 (C), 129.5 (CH), 129.3 (CH), 129.1

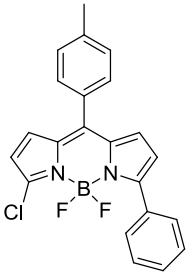
(CH), 128.8 (CH), 126.9 (CH), 120.5 (CH), 117.0 (CH), 35.3 (CH_2), 21.5 (CH_3); IR (neat): 2923, 2854, 1571, 1545, 1532, 1394, 1329, 1216, 1072, 971, 881 cm^{-1}; HRMS-EI: calcd for ($C_{23}H_{18}BClF_2N_2$) 406.1218, found 406.1211.

Synthesis of 4,4-difluoro-3,5-diphenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (5e).



According to the general procedure A, BODIPY **3** (50 mg, 0.142 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) and PhZnBr (5.7 mL, 0.5 M in THF, 2.85 mmol) were reacted for 60 min. Flash chromatography using hexane/CH_2Cl_2 (7:3) afforded **5e**[6] (34 mg, 56%). Characterization data are in agreement with literature.

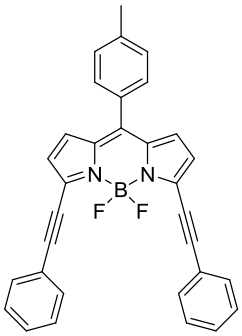
Synthesis of 3-chloro-4,4-difluoro-5-phenyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (4i).



According to the general procedure A, BODIPY **3** (50 mg, 0.142 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) and PhZnBr (5.7 mL, 0.5 M in THF, 2.85 mmol) were reacted for 5 min. Flash chromatography using hexane/EtOAc (98:2) afforded, by order of elution, **5e**[6] (4 mg, 6%), **4i**[6] (39 mg, 70%) and **3** (9 mg, 18%). Characterization data are in agreement with literature.

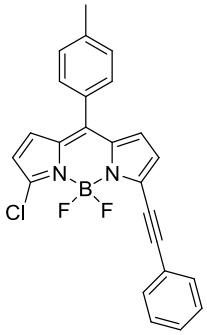
[6] T. Rohand, W. Qin, N. Boens and W. Dehaen, *Eur. J. Org. Chem*., 2006, 4658-4663.

Synthesis of 4,4-difluoro-3,5-bis(phenylethynyl)-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (5f).



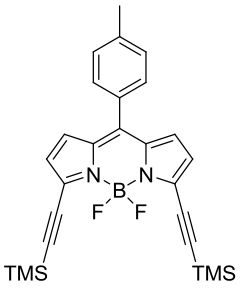
According to the general procedure B, phenylacetylene (0.16 mL, 1.42 mmol), BuLi (0.9 mL, 1.6 M hexano, 1.42 mmol), $ZnBr_2$ (320 mg, 1.42 mmol), BODIPY **3** (50 mg, 0.142 mmol) and $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) were reacted for 40 min. Flash chromatography using hexane/EtOAc (98:2) afforded **5f**[6] (37 mg, 54%). Characterization data are in agreement with literature.

Synthesis of 3-chloro-4,4-difluoro-5-(phenylethynyl)-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (4j).



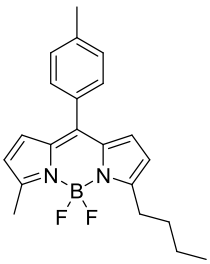
According to the general procedure B, phenylacetylene (0.08 mL, 0.71 mmol), BuLi (0.45 mL, 1.6 M hexano, 0.71 mmol), $ZnBr_2$ (160 mg, 0.71 mmol), BODIPY **3** (50 mg, 0.142 mmol) and $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) were reacted for 10 min. Flash chromatography using hexane/CH_2Cl_2 (6:4) afforded, by order of elution, **5f**[6] (11 mg, 12%) and **4j**[6] (47 mg, 71%). Characterization data are in agreement with literature.

Synthesis of 4,4-difluoro-8-(*p*-tolyl)-3,5-bis[(trimethylsilyl)ethynyl]-4-bora-3a,4a-diaza-*s*-indacene (5g).



According to the general procedure B, trimethylsilylacetylene (0.2 mL, 1.42 mmol), BuLi (0.9 mL, 1.6 M hexano, 1.42 mmol), $ZnBr_2$ (320 mg, 1.42 mmol), BODIPY **3** (50 mg, 0.142 mmol) and $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) were reacted for 60 min. Flash chromatography using hexane/EtOAc (98:2) afforded **5g**[7] (47 mg, 70%). Characterization data are in agreement with literature.

Synthesis of 3-butyl-4,4-difluoro-5-methyl-8-(*p*-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (5h).



According to the general procedure A, BODIPY **4d** (21 mg, 0.063 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 0.014 mmol) in dry toluene (10 mL) and BuZnBr (1 mL, 0.5 M in THF, 0.5 mmol) were reacted for 90 min. Flash chromatography using hexane/EtOAc (99.5:0.5) afforded **5h** (14.5 mg, 65%) as a brown solid. ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.4 Hz, 2H, phenyl), 7.21 (d, *J* = 8.4 Hz, 2H, phenyl), 6.69 (d, *J* = 4.2 Hz, 1H, CH), 6.66 (d, *J* = 4.2 Hz, 1H, CH), 6.26 (d, *J* = 4.2 Hz, 1H, CH), 6.18 (d, *J* = 4.2 Hz, 1H, CH), 2.98 (t, *J* = 7.7 Hz, 2H, CH_2), 2.58 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 1.67 (quint, *J* = 7.7 Hz, 2H, CH_2), 1.41 (sext, *J* = 7.7 Hz, 2H, CH_2), 0.91 (t, *J* = 7.7 Hz, 3H, CH_3CH_2) ; ^{13}C NMR (176 MHz, $CDCl_3$): δ 162.4 (C), 157.0 (C), 142.9 (C), 140.2 (C), 134.4 (C), 134.2 (C), 131.4 (C), 130.5 (CH), 130.4 (CH), 130.1 (CH), 128.9 (CH), 119.1 (CH), 117.7 (CH), 30.8 (CH_2), 28.5 (CH_2), 22.7 (CH_2), 21.4 (CH_3), 14.9 (CH_3), 14.2 (CH_3); IR

[7] M. R. Rao, S. M. Mobin and, M. Ravikanth, *Tetrahedron*, 2010, **66**, 1728-1734.

(neat): 2923, 2854, 1573, 1549, 1428, 1350, 1267, 1114, 988, 886 cm^{-1}; HRMS-EI: calcd for ($C_{21}H_{23}BF_2N_2$) 352.1920, found 352.1918.

Photophysical Properties

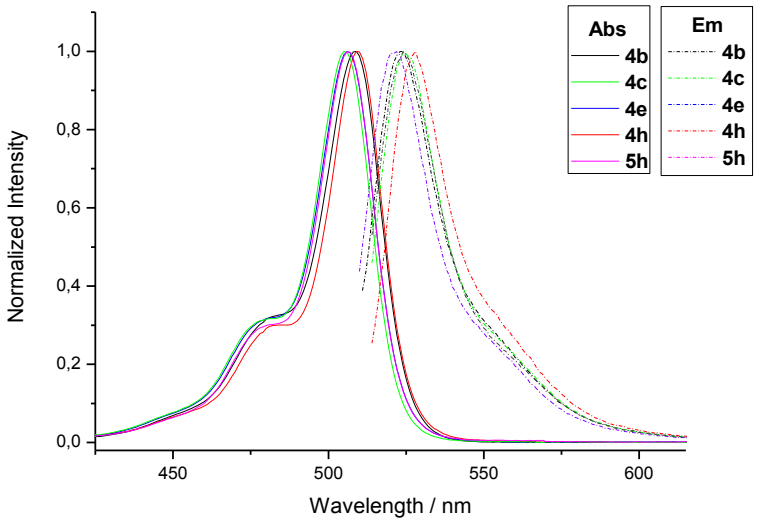
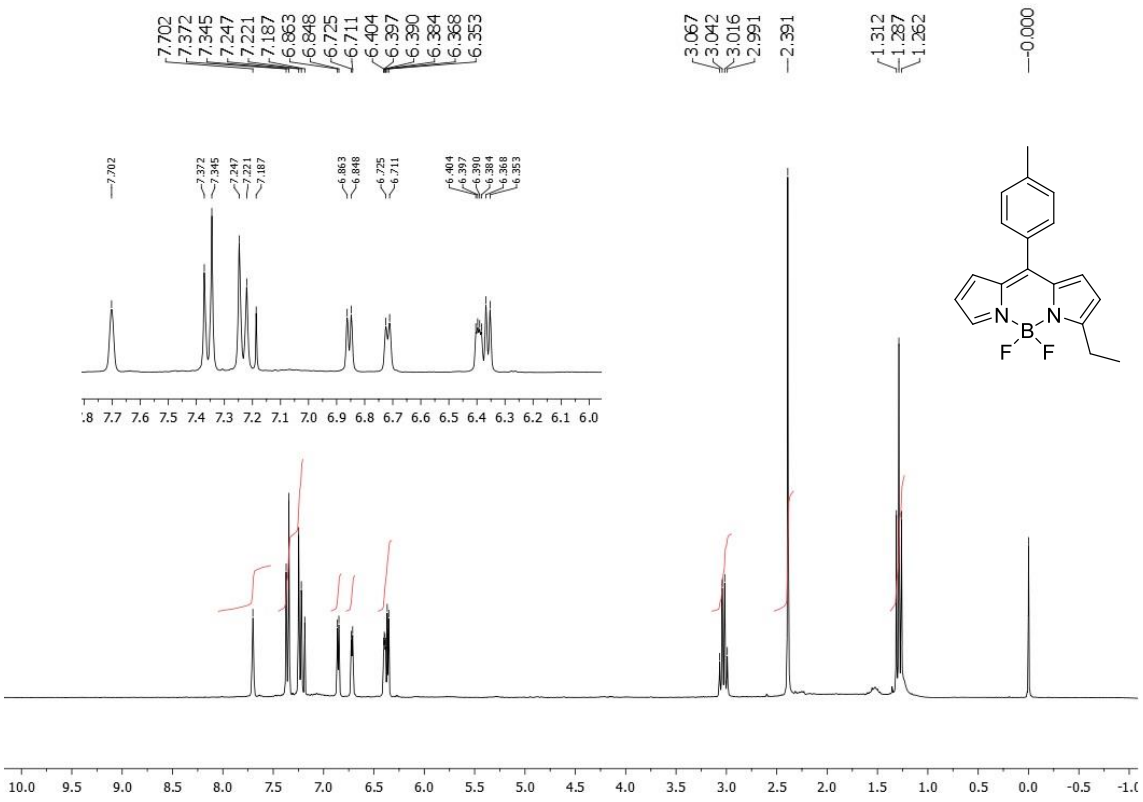
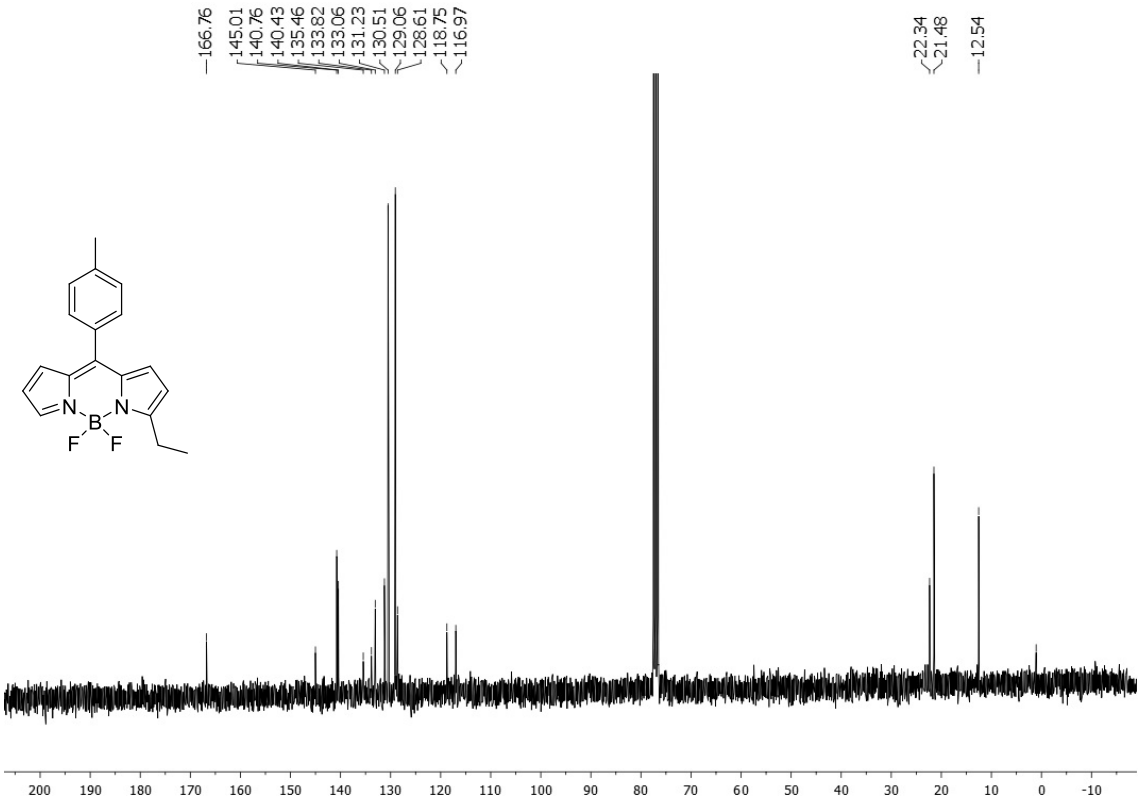


Figure S1 A selection of the normalized visible absorption spectra and corresponding fluorescence emission spectra of the new compounds in AcOEt.

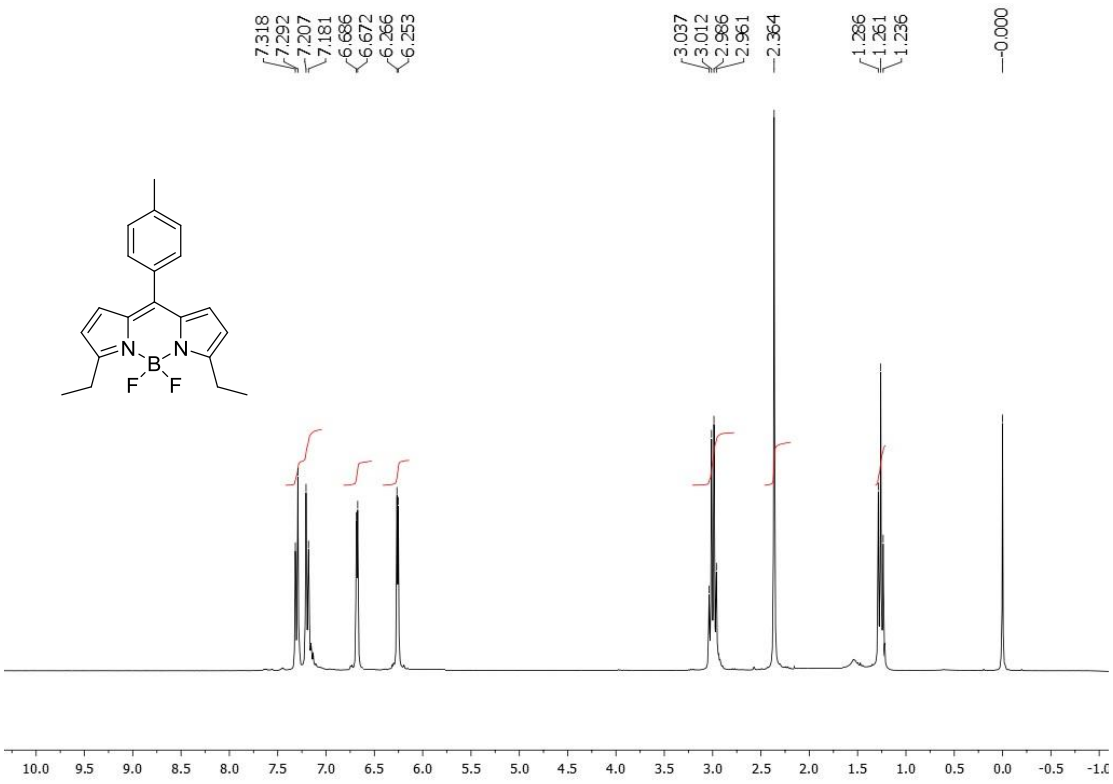
^{1}H NMR and ^{13}C NMR Spectra of Compounds

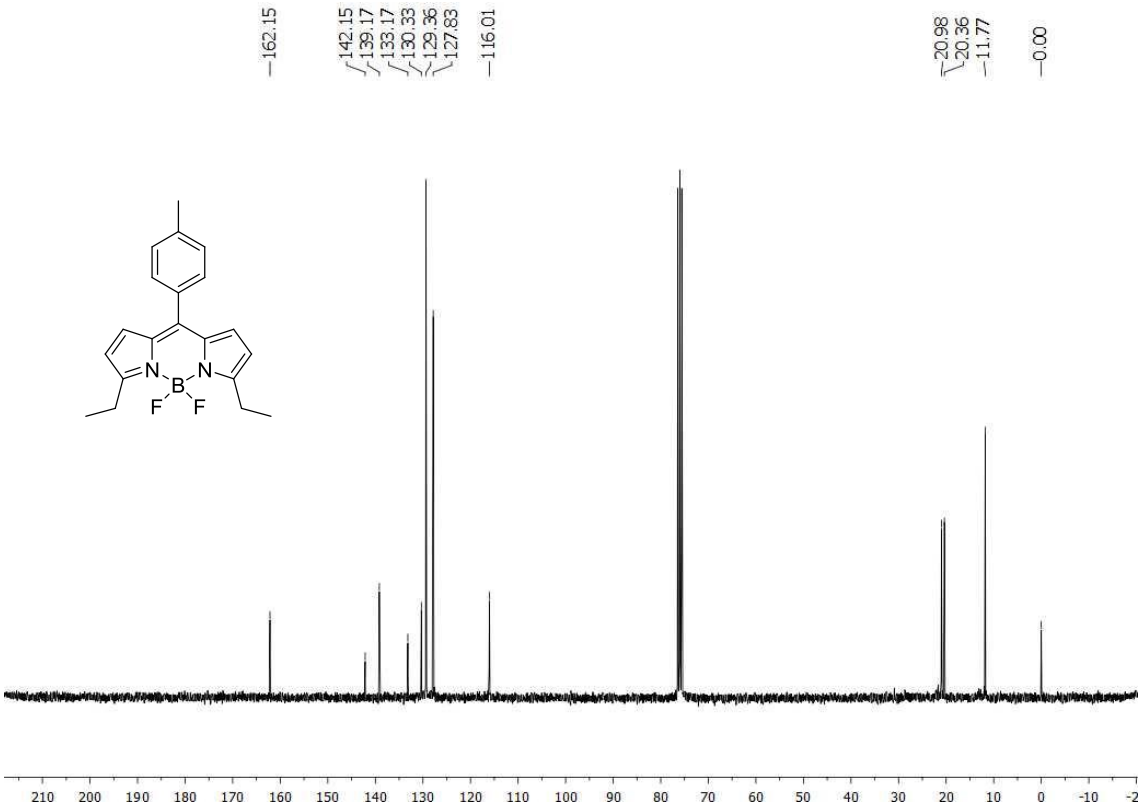
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of compound **4a**



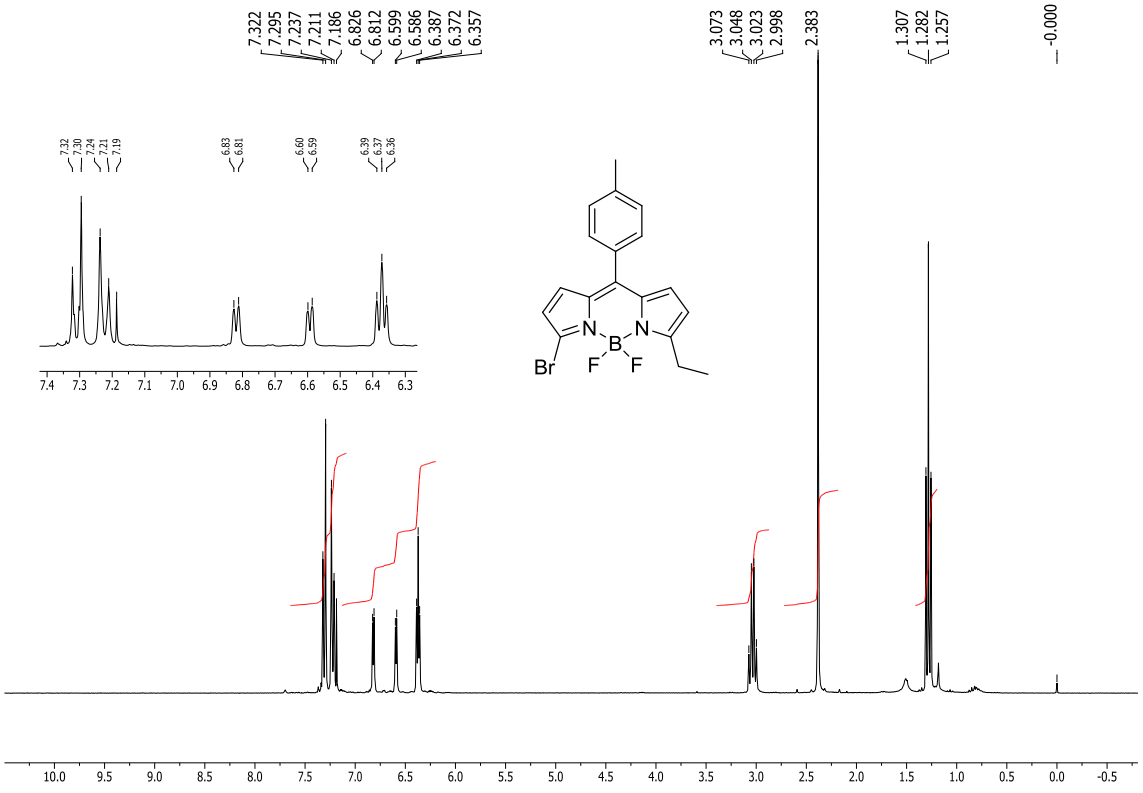


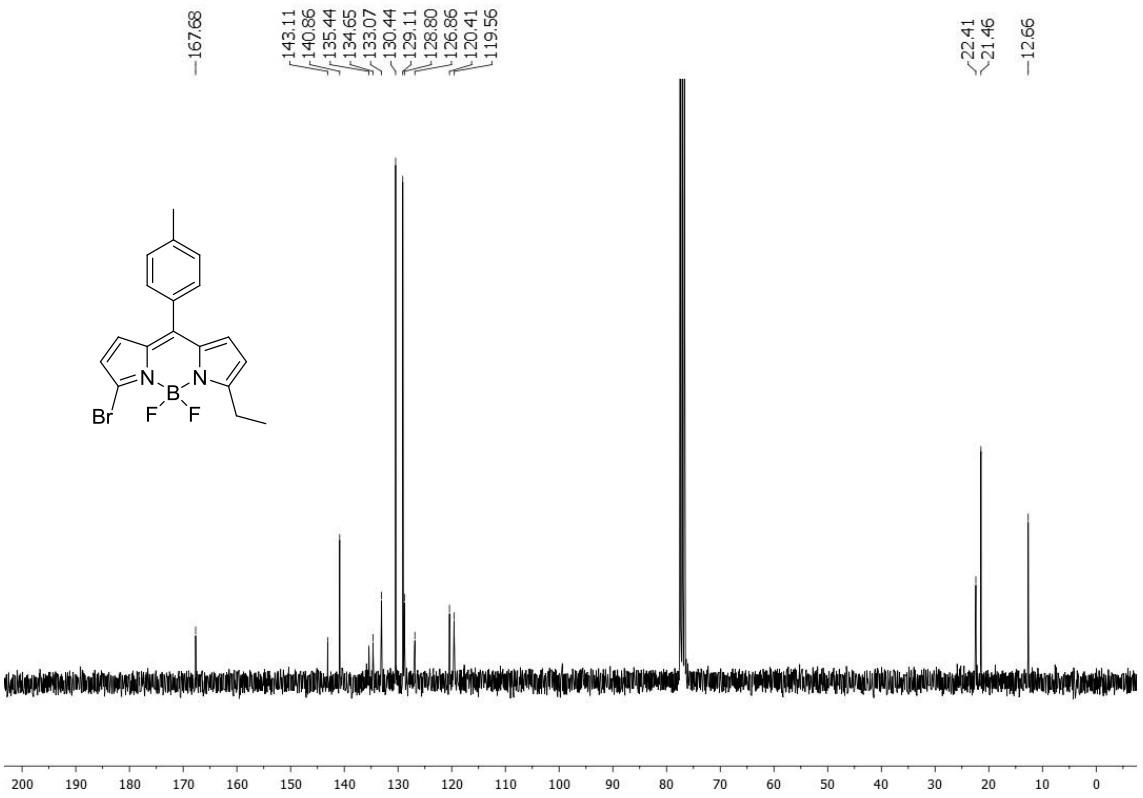
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of compound **5a**



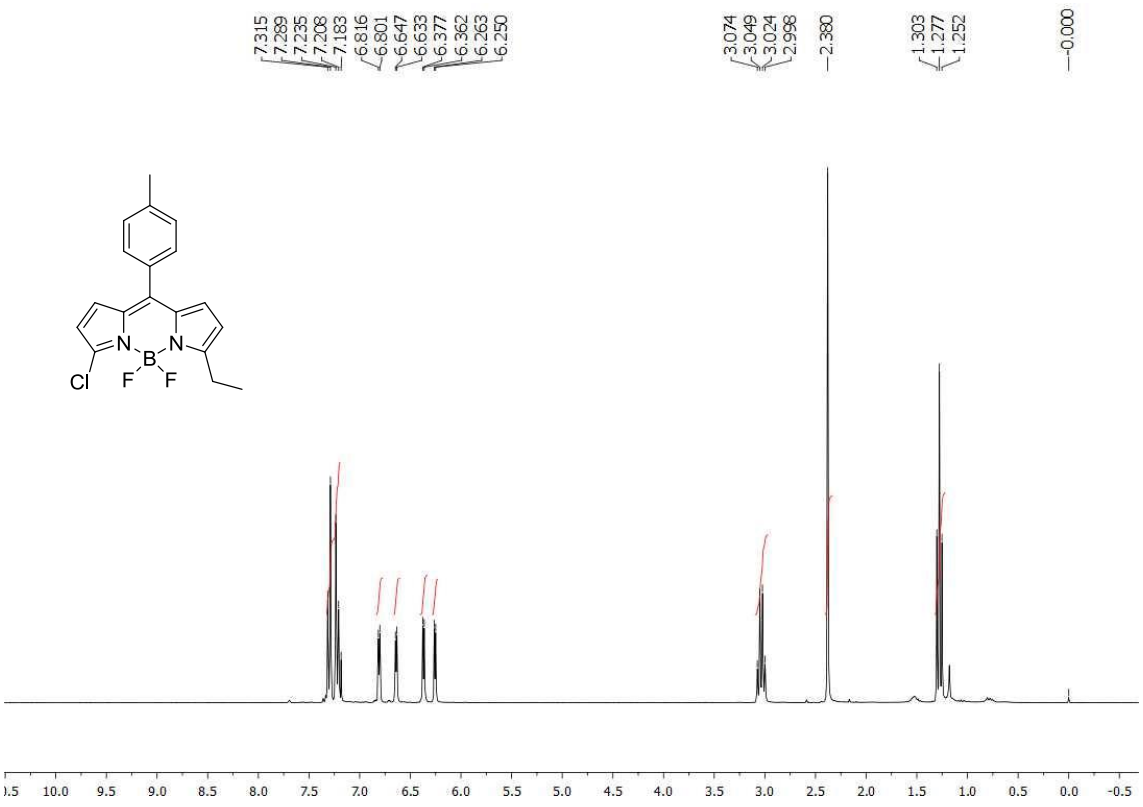


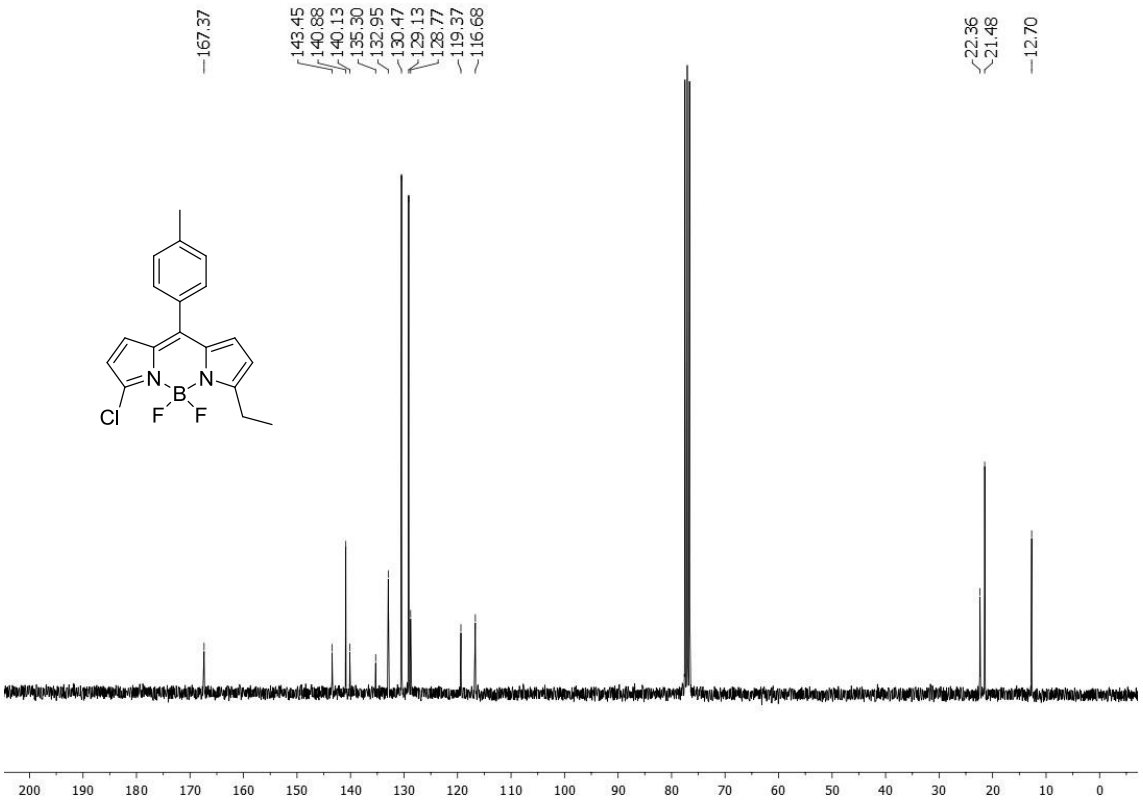
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of compound **4b**



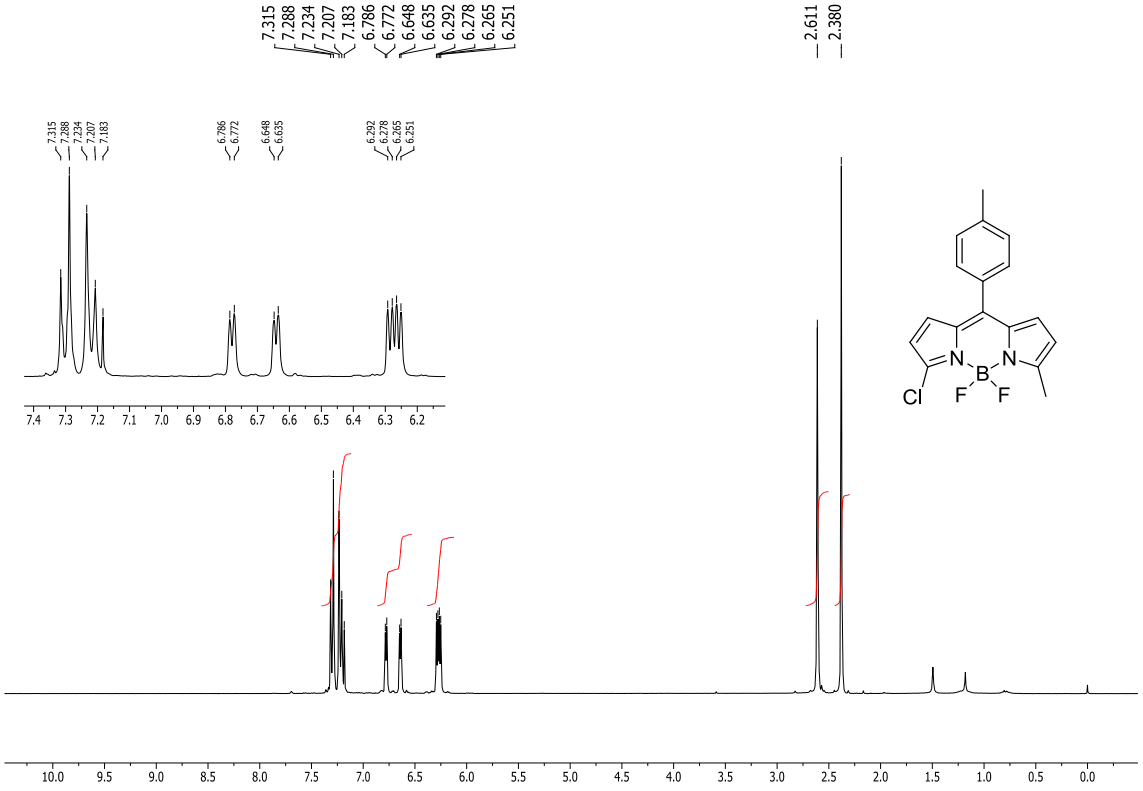


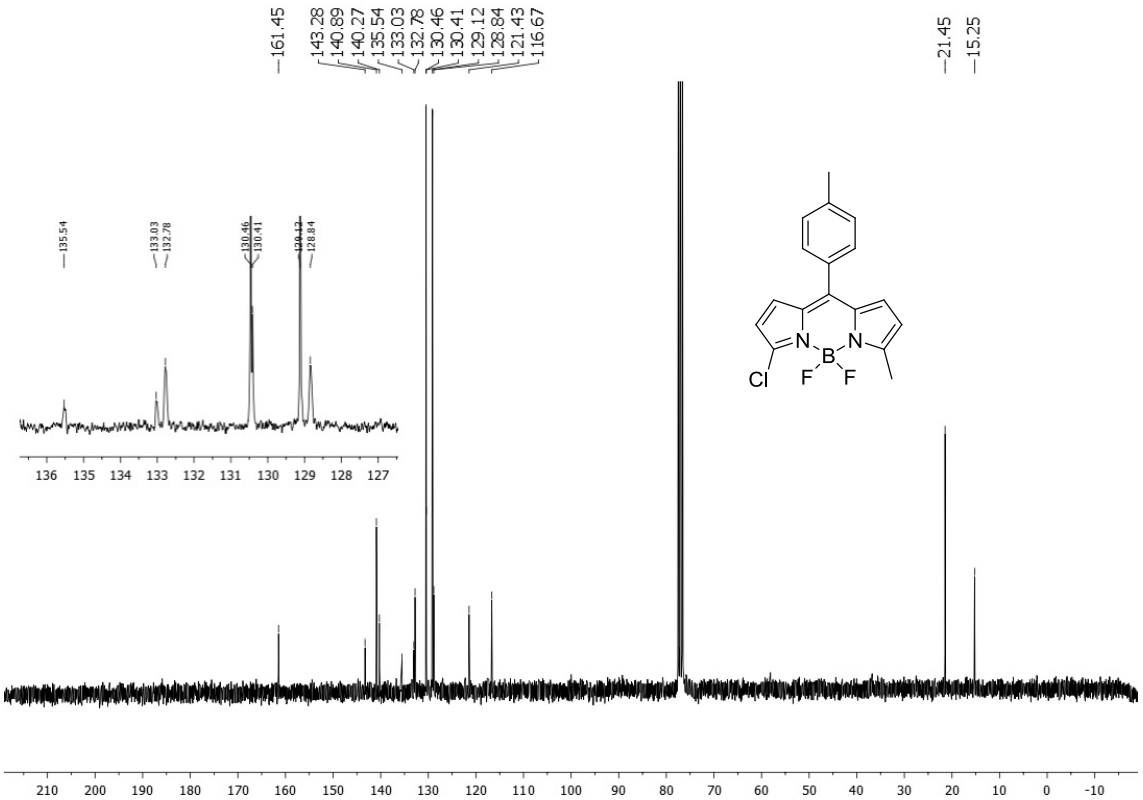
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of compound **4c**



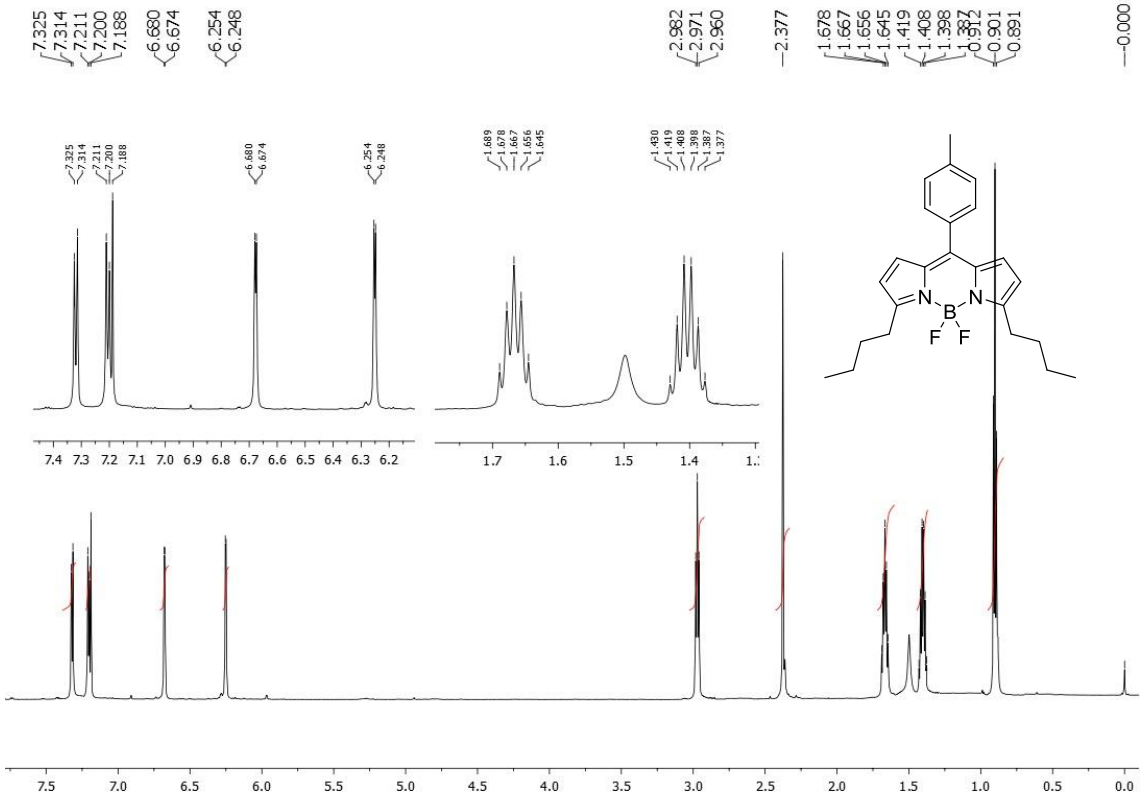


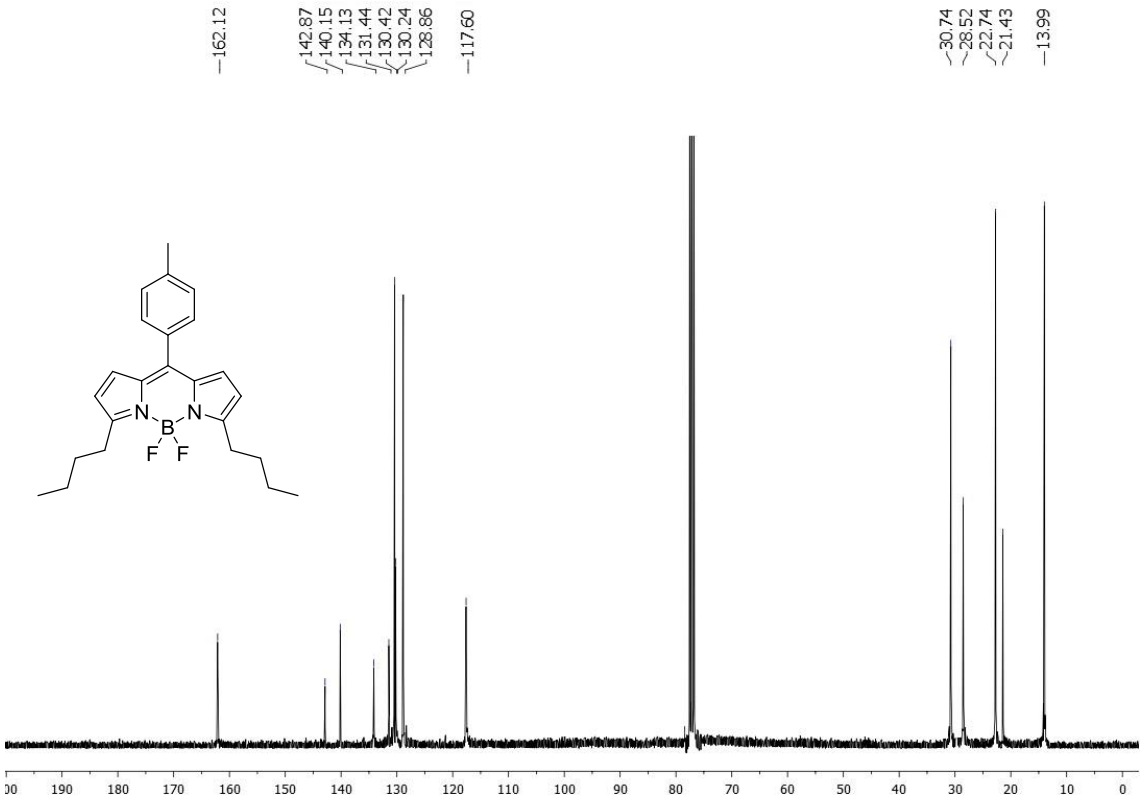
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of compound **4d**



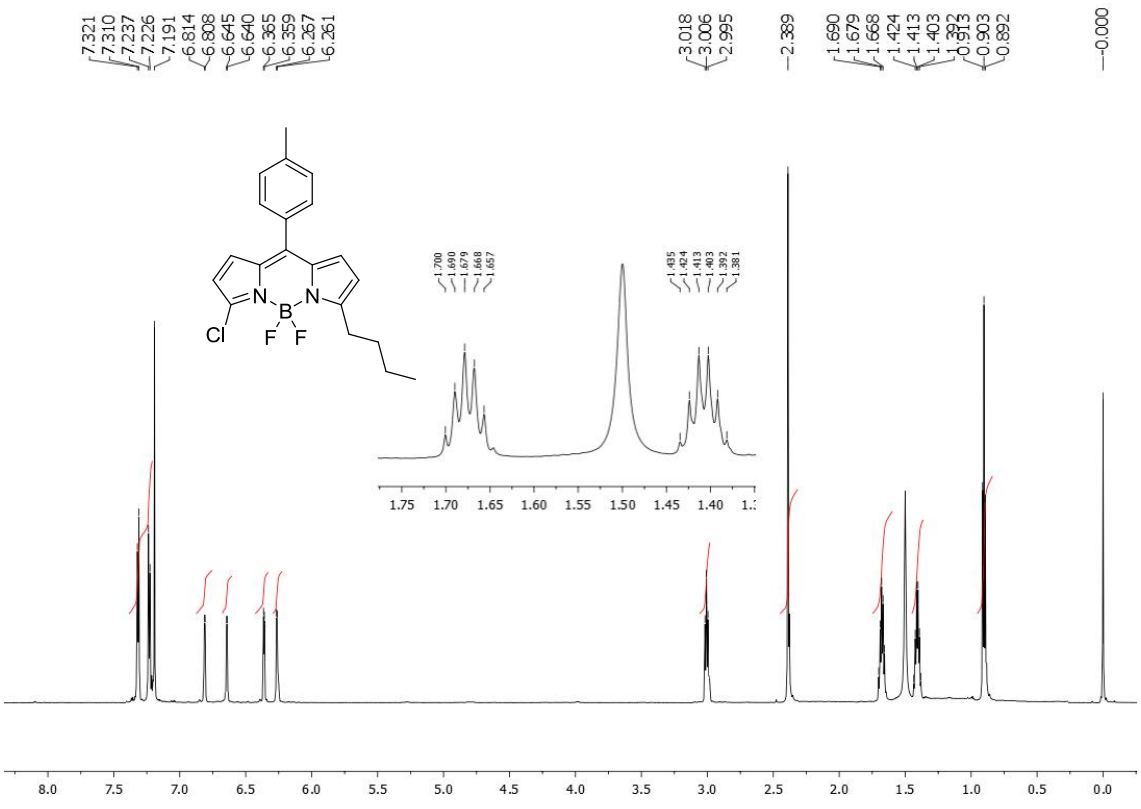


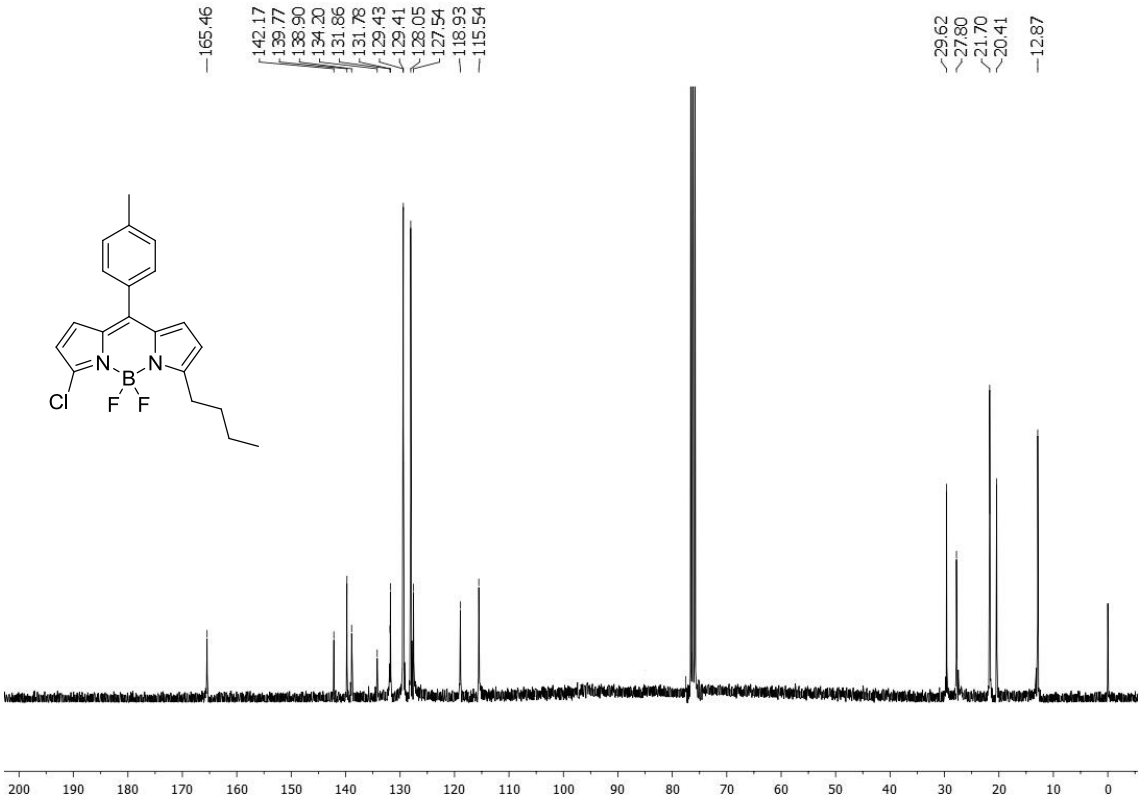
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of compound **5c**



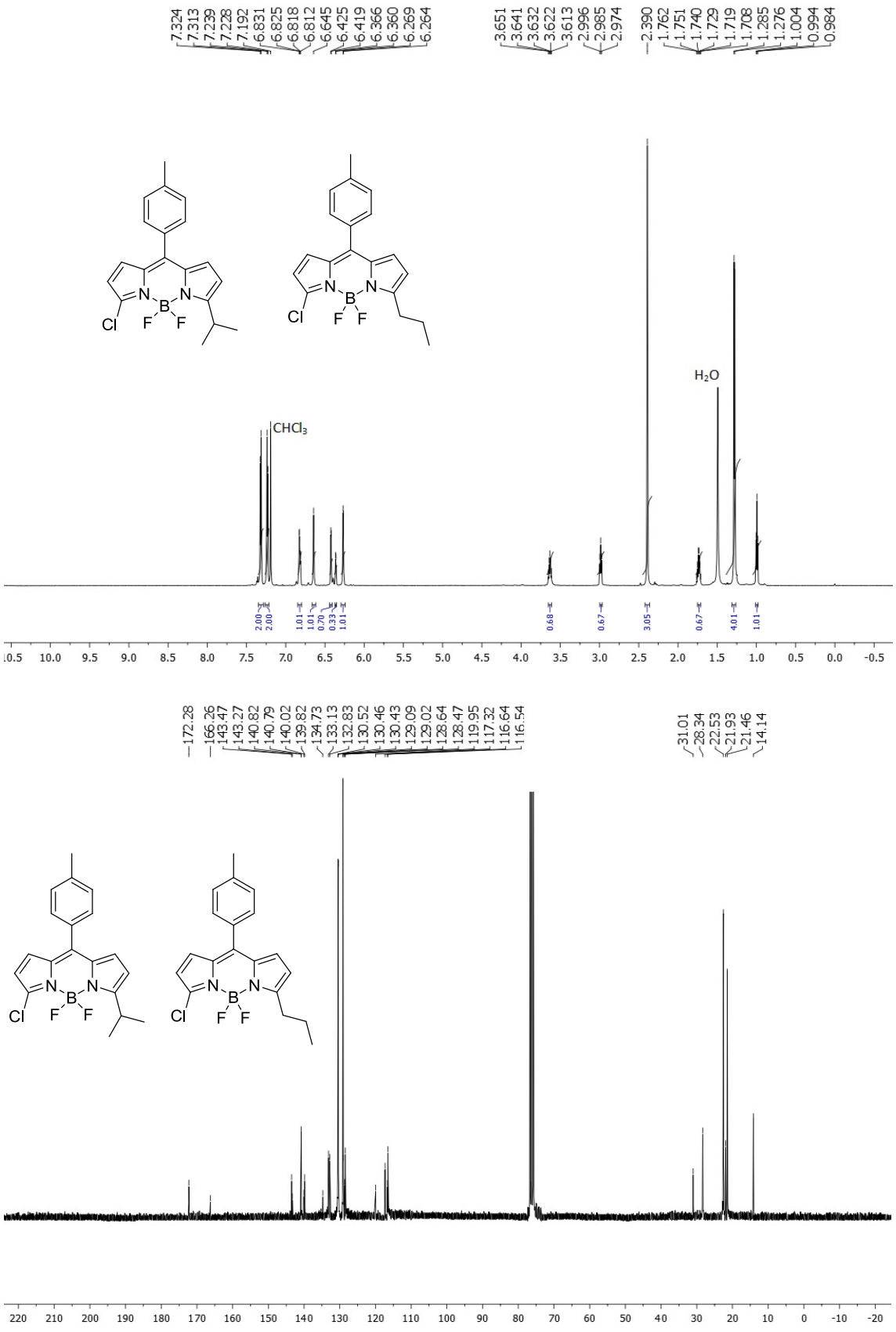


^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of compound **4e**

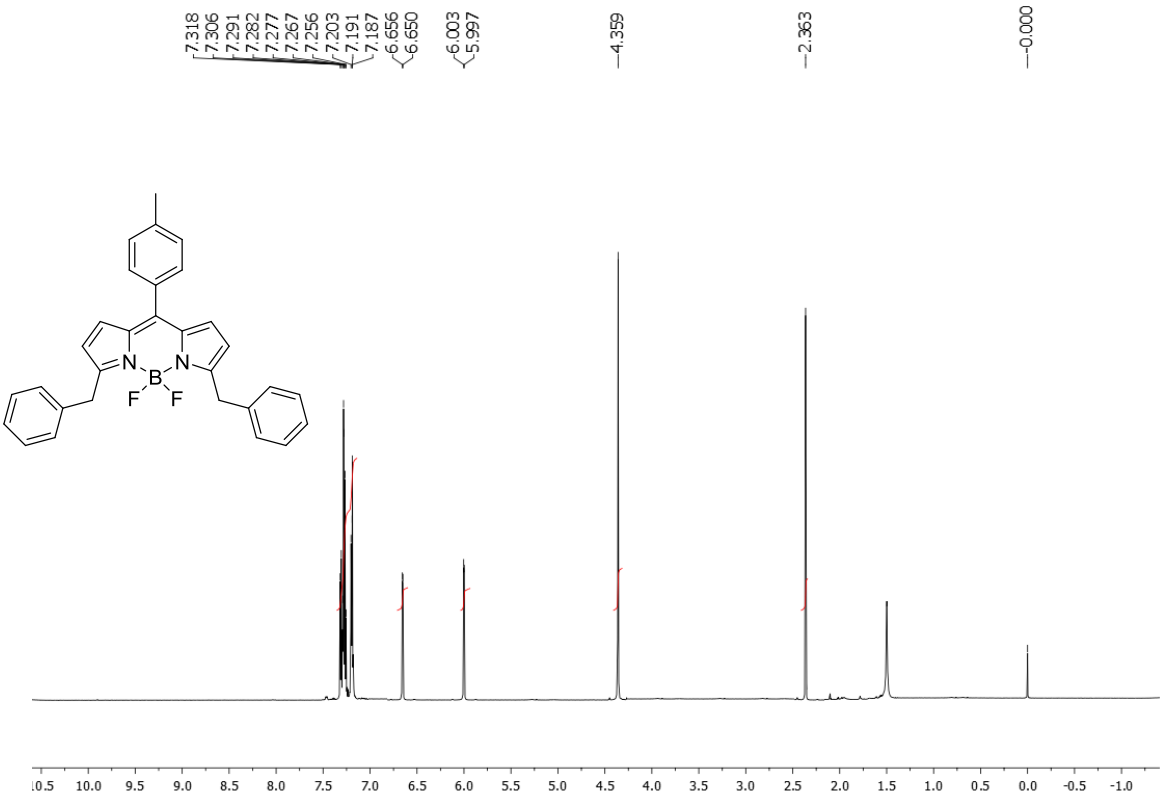


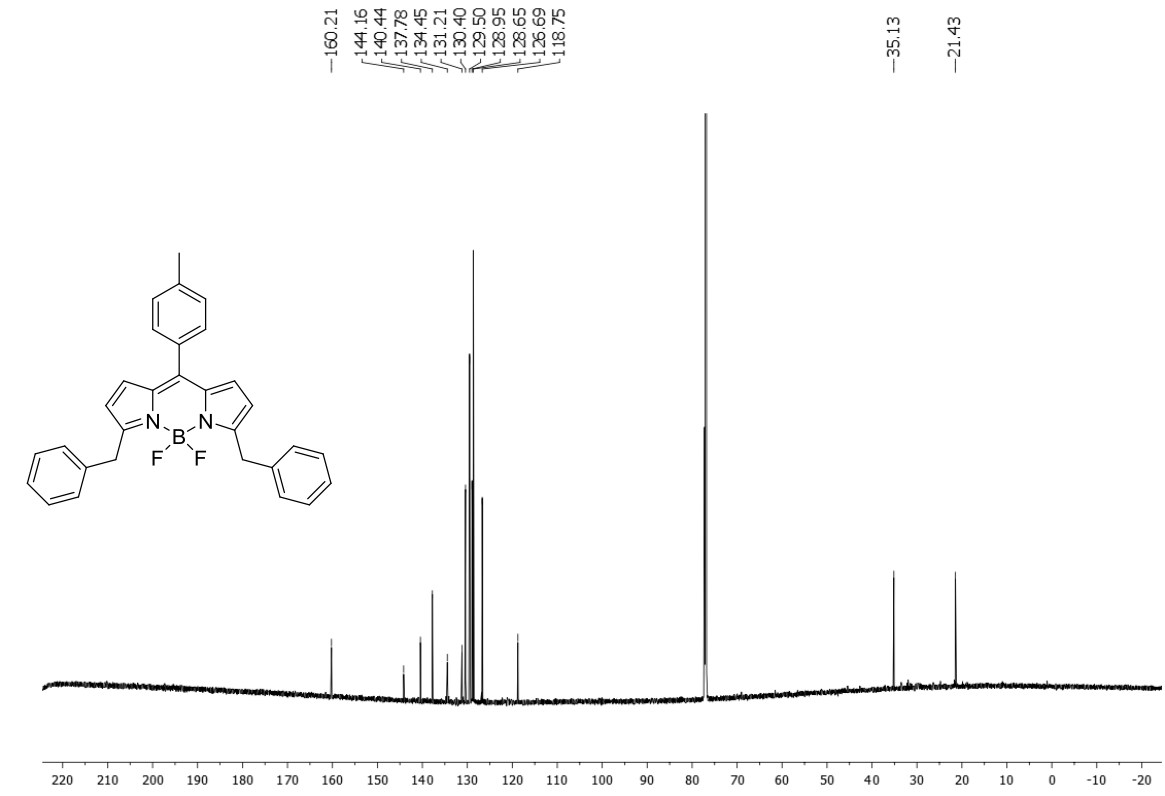


^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of compounds **4f** and **4g**

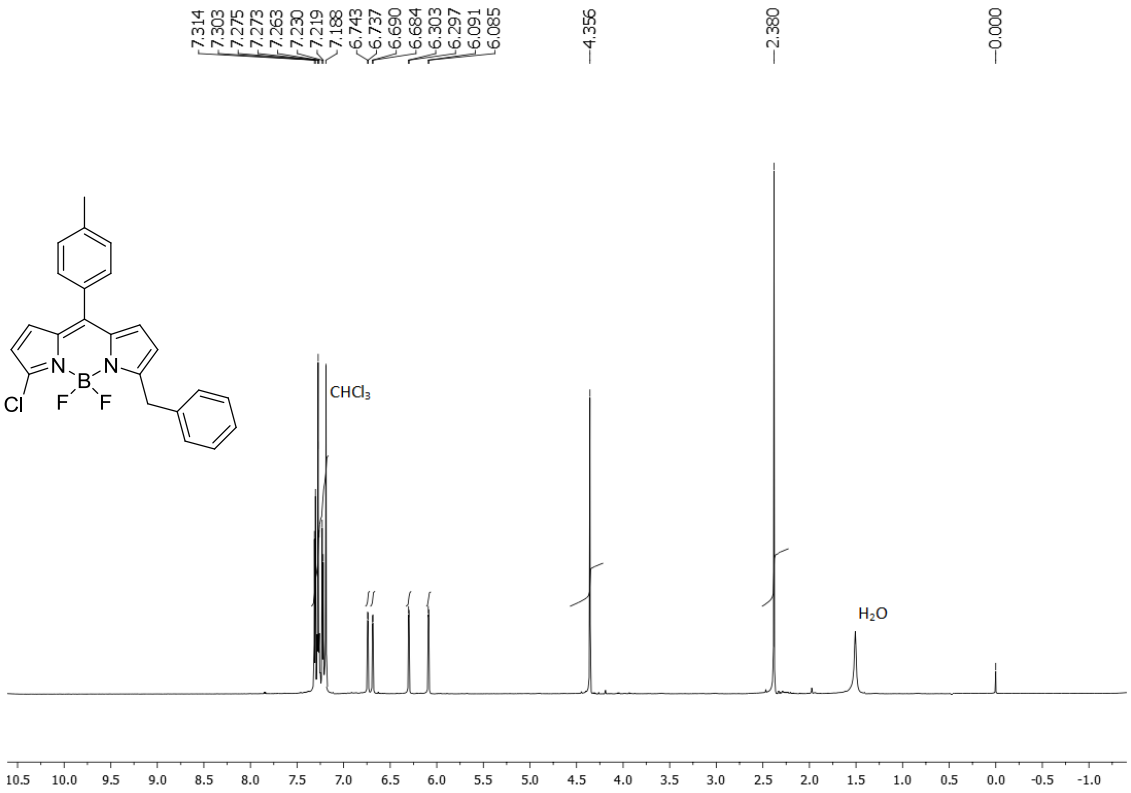


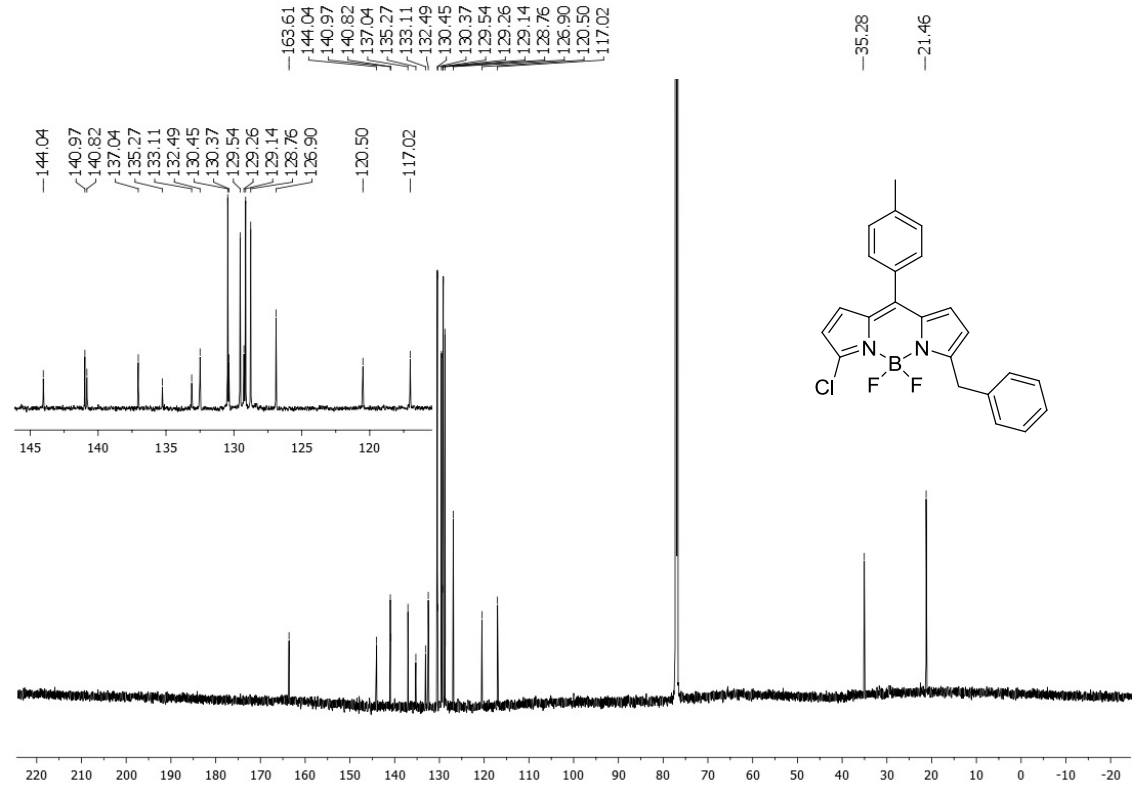
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of compound **5d**



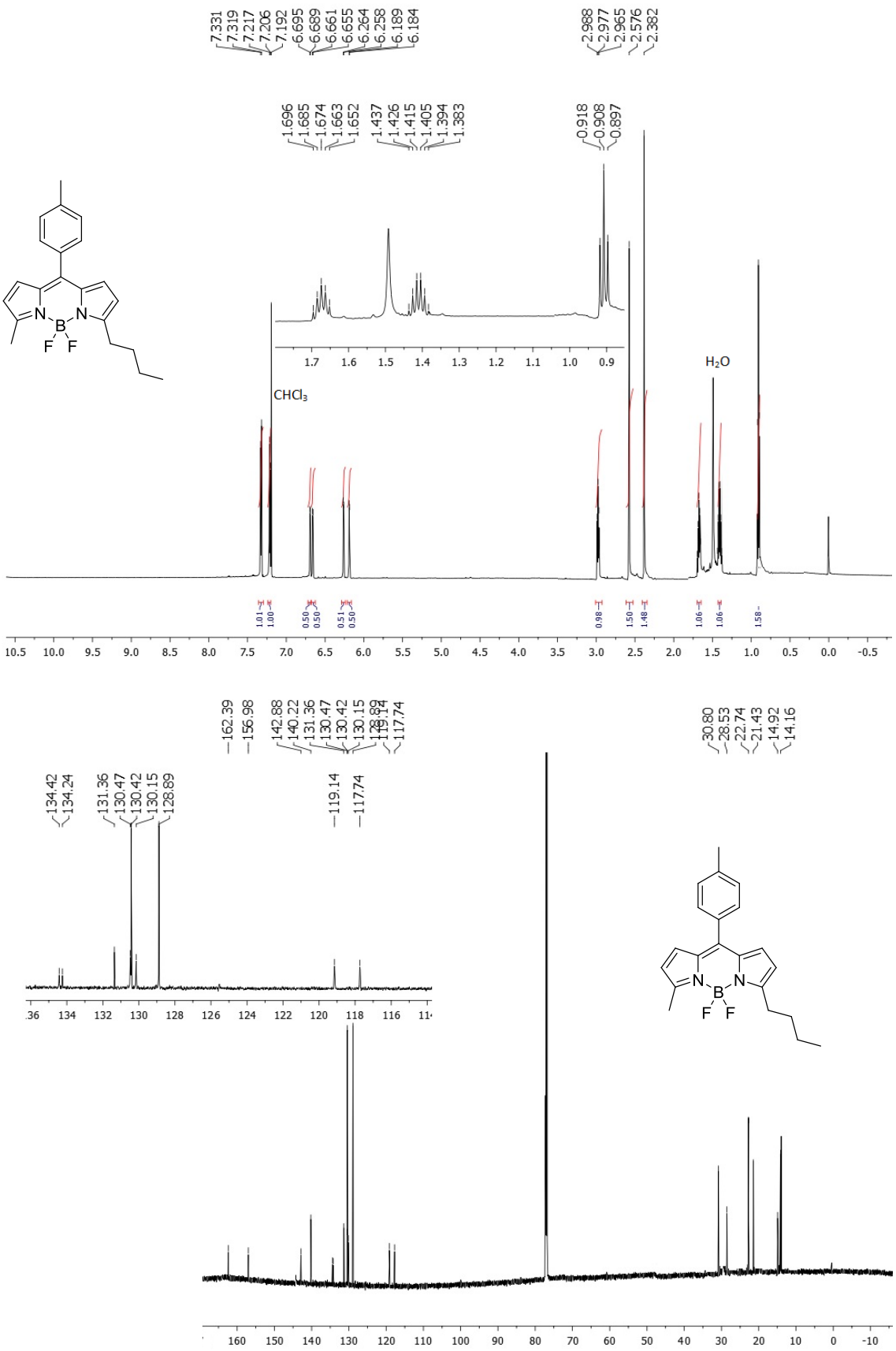


^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of compound **4h**



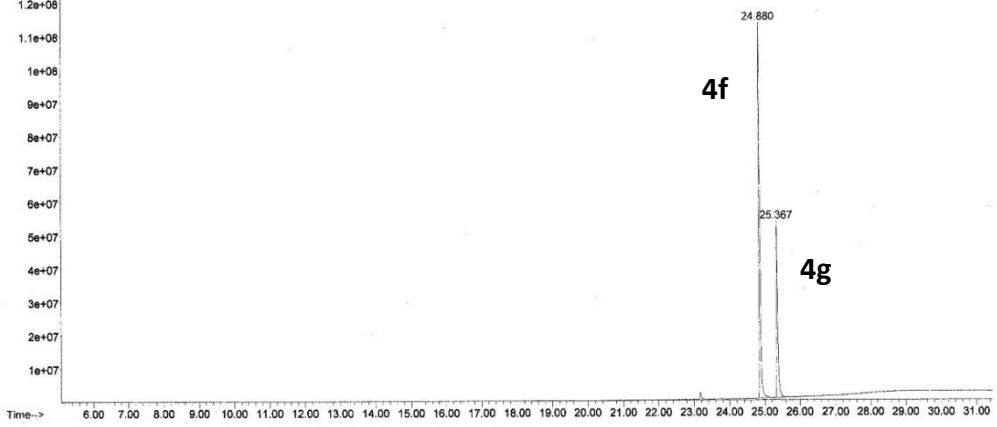


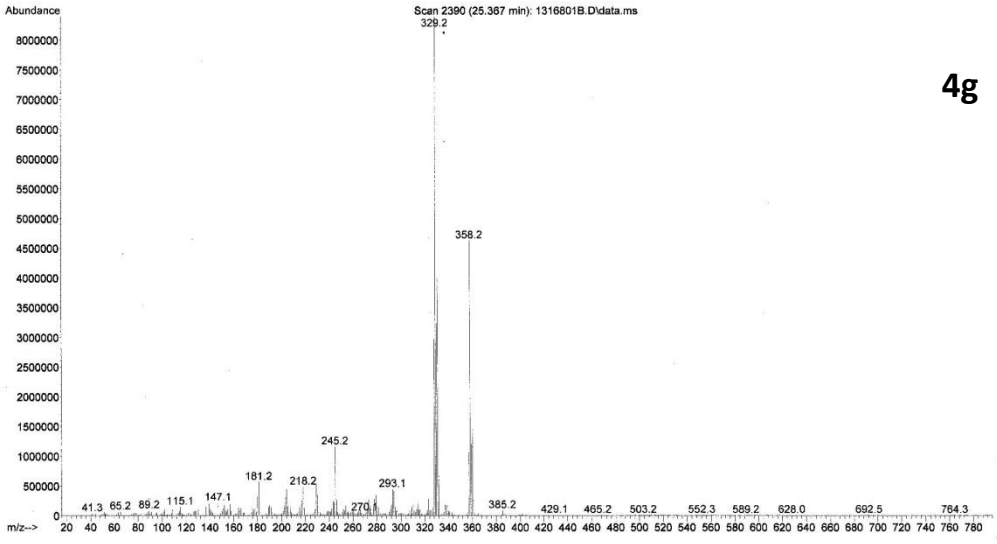
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of compound **5h**



GC/MS Chromatogram of 4f/4g, and Corresponding Mass Spectra

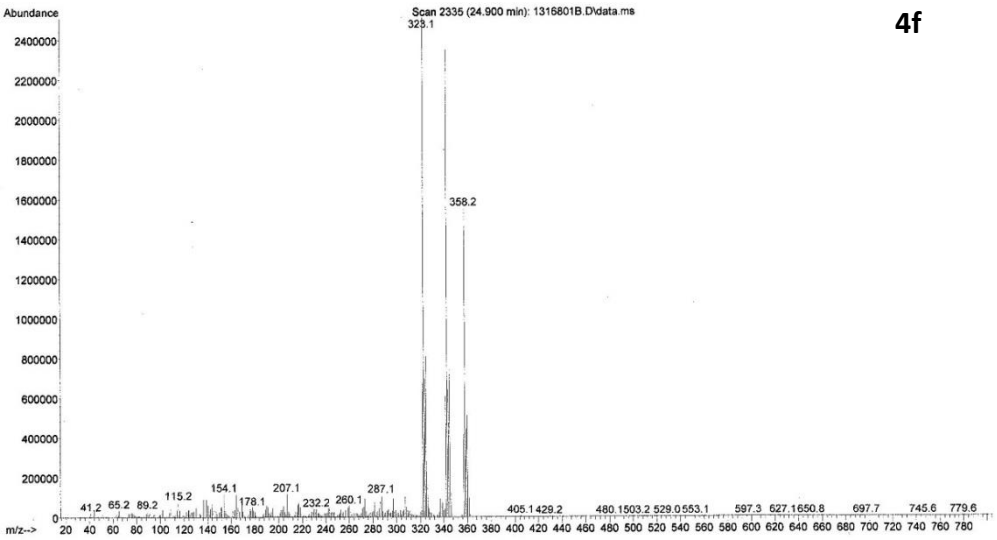
peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	24.880	2320	2333	2360	M	119129783	2497655370	100.00%	67.504%
2	25.367	2383	2390	2420	M	53045501	1202367487	48.14%	32.496%





4g

4f


Abundance
Scan 2335 (24.900 min): 1316801B.D\data.ms
323.1
358.2
m/z-->