Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013

Supporting Information for

NIR-fluorescent coumarin-fused BODIPY dyes with large Stokes shifts

Andrei Y. Bochkov,*[a] Igor O. Akchurin,[a] Oleg A. Dyachenko[b] and Valery F. Traven[a]

[a] *Department of Organic Chemistry, Mendeleev University of Chemical Technology, 125047, Miusskaya square 9, Moscow, Russian Federation. E-mail: a.y.bochkov@gmail.com; Fax: +7 495 609 2964.*

[b] *Institute of Problems of Chemical Physics, 142432, Academician Semenov avenue 1, Chernogolovka, Moscow Region, Russian Federation*

Table of Contents

1. GENERAL INFORMATION

4,7-Dihydroxycoumarin **2b**[1], 4-chloro-3-formylcoumarin **3a**[2] and benzoylmethylenetriphenylphosphorane[3] were prepared according to procedures reported in literature. All other reagents were purchased from Sigma-Aldrich, Acros Organics, ABCR, Merck and Alfa Aesar and used as received. Anhydrous toluene and dichloromethane (DCM) were obtained by distillation over P_2O_5. Dry DMF was prepared by vacuum distillation over P_2O_5. Solvents used for UV-vis and fluorescence spectroscopy experiments were spectrophotometric grade.

Column chromatography was carried out using Macherey-Nagel Kieselgel 60 H silica gel. Analytical thin layer chromatography was carried out using aluminium-backed plates coated with Macherey-Nagel Alugram SILG/UV_{254} that were visualized under UV light (at 254 or 365 nm).

Melting points were measured on a Stuart melting point apparatus SMP30 and are uncorrected.

^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300, JEOL JNM ECX-400, Bruker 500 MHz NMR spectrometers in solvents as indicate. Chemical shifts (δ) are given in parts per million (ppm) downfield of tetramethylsilane, using the solvent signal as an internal reference ($CDCl_3$: δ_H = 7.27 ppm, δ_C = 77.16 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.52 ppm). Abbreviations used in the description of resonances: s (singlet), d (doublet), t (triplet), q (quartet), br (broad). Coupling constants (J) are reported in Hertz (Hz) and quoted to the nearest 0.1 Hz.

HRMS spectra were obtained on Bruker Daltonics MicroTof instrument operating in positive ionization mode.

UV-vis absorption spectrometry was performed using an SF-104 spectrophotometer (Interphotophysics LLC, Moscow, Russia). Fluorescence measurements were conducted using a Cary Eclipse (Varian) spectrofluorimeter. Absorption and fluorescence spectra were recorded in 1 cm-length quartz cuvettes.

Fluorescence quantum yields were determined following the reported procedure using serial dilutions.[4] Rhodamine 6G in ethanol (ϕ_F 0.95)[5] and Cresyl violet in methanol (ϕ_F 0.54)[6] were used as standards and excited at 488 and 530 nm respectively. The excitation wavelengths (λ_{ex}) of the BODIPYs were chosen such that the complete emission spectrum could be collected.

2. SYNTHETIC PROCEDURES AND CHARACTERIZATION DATA

Preparation of 7-(diethylamino)-4-hydroxycoumarin (2c)

Diphenyl malonate

To a stirred mixture of malonic acid (31.2 g, 0.3 mol) and phenol (56.4 g, 0.6 mol) in dry toluene (300 mL) were added thionyl chloride (46 mL, 0.63 mol) and finally DMF (0.5 mL). The reaction mixture was heated to 90 °C and stirred at this temperature for 12 h. The solution formed was washed with water (2×300 mL) and saturated aq. $NaHCO_3$ (300 mL). The organic phase was separated and filtered through a Silica gel column (15 cm-length, Ø 30 mm). Solvent was removed in vacuo to give brownish-yellow oil. This oil was mixed with equal volume of ethanol and the solution was stored in a refrigerator (-18 °C) overnight. The crystals formed were filtered-off and washed with cold ethanol to give title compound as beige crystals.
Yield: 51.9 g (68 %), m.p. 49–50 °C (lit.[7], 50 °C)

7-(Diethylamino)-4-hydroxy-2H-chromen-2-one (2c)[8]

Solution of diphenyl malonate (25.6 g, 0.1 mol) and 3-(*N,N*-diethylamino)phenol (16.5 g, 0.1 mol) in dry toluene (300 mL) was refluxed for 8 h. The reaction mixture was cooled and crystals formed were filtered off and washed with petroleum ether. The crude product was recrystallized from ethanol to give greenish-grey crystals.
Yield: 12.8 g (55 %). M.p. 240–241 ºC (lit.[9], 238 ºC). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.11 (t, 6H), 3.40 (q, 4H), 5.25 (s, 1H), 6.45 (d, J = 2.4 Hz, 1H), 6.65 (dd, J = 2.4 Hz, J = 9.2 Hz, 1H), 7.55 (d, J = 9 Hz, 1H), 11.86 (br.s., 1H).

Preparation of 4-chloro-3-formylcoumarins 3 by Vilsmeier reaction

4-chloro-3-formyl-7-hydroxy-2H-chromen-2-one (3b)

Phosphorus oxychloride (14.5 mmol, 2.22 g) was added to a stirred warm (40 °C) solution of 4,7-dihydroxycoumarin **2b** (5.79 mmol, 1030 mg) in DMF (5 mL). Stirring continued at this temperature until TLC showed full conversion of starting material (~ 30 min). Then reaction mixture was cooled, poured into water (100 mL) and stirred for 1 h. The precipitate formed was filtered off and washed with water to give crude aldehyde which was used without further purification.
Yield: 890 mg (68 %). Yellowish solid. M.p. 215–216 °C. R_f (Petr. ether / acetone 2:1) 0.40.

^{1}H NMR (500 MHz, acetone-d_6): δ 6.86 (s, 1H), 7.05 (d, J = 9.9 Hz, 1H), 8.05 (d, J = 9.1 Hz, 1H), 10.24 (s, 1H).

^{13}C NMR (125 MHz, acetone-d_6): δ 103.9, 112.7, 116.2, 128.3, 130.9, 153.8, 157.2, 160.1, 166.1, 187.8

HRMS (ESI-TOF): calcd. for $C_{10}H_5ClO_4$ $[M+Na]^+$: 246.9769; found: 246.9775.

4-chloro-7-(diethylamino)-3-formyl-2H-chromen-2-one (3c)

Phosphorus oxychloride (27 mmol, 2.50 mL) was added to a solution of 7-diethylamino-4-hydroxycoumarin **2c** (20 mmol, 4.66 g) in DMF (15 mL) and stirred at room temperature for 24 h. Then the reaction mixture was cooled, poured into aqueous sodium acetate (15 g in 300 mL) and stirred for 1 h. The precipitate formed was filtered off and washed with water to give crude aldehyde which was recrystallized from ethanol.

Yield: 4.70 g (84 %). Orange crystals.

General procedure for Wittig reaction of 4-chloro-3-formylcoumarins 3 and BzCH=PPh$_3$:

Aldehyde **3** (4 mmol) and benzoylmethylenetriphenylphosphorane (4.2 mmol, 1600 mg) were dissolved in CH_2Cl_2 (25 mL) and stirred at RT for 24 h, after which TLC showed completion of reaction.

(E)-4-chloro-3-(3-oxo-3-phenylprop-1-en-1-yl)-2H-chromen-2-one (4a)

Prepared according to general procedure and purified by column chromatography on silica using CH_2Cl_2 as eluent.

Yield: 1.16 g (93%). Yellow crystals. M.p. 142.2–144.3 °C (EtOH). R_f (Petr. ether / ethyl acetate 3:1) 0.59.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.42 (m, 2H), 7.49–7.68 (m, 4H), 8.00 (d, J = 7.8 Hz, 1H), 8.09–8.14 (m, 3H), 8.60 (d, J = 15.4 Hz, 1H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 116.8, 118.6, 120.2, 125.2, 126.6, 128.7, 128.8, 129.8, 133.3, 133.8, 133.9, 137.8, 150.3, 151.7, 157.7, 190.3

HRMS (ESI-TOF): calcd. for $C_{18}H_{12}ClO_3$ $[M+H]^+$: 311.0469; found: 311.0465.

(E)-4-chloro-7-hydroxy-3-(3-oxo-3-phenylprop-1-en-1-yl)-2H-chromen-2-one (4b)

Prepared according to general procedure. The solvent was evaporated at reduced pressure and oily residue was treated with ethanol to give yellow crystals, which were filtered-off and recrystallized from ethanol/acetone.

Yield: 525 mg (55%). Yellow crystals. M.p. 224.6–226.4 °C (EtOH/acetone). R_f (Petr. ether / acetone 2:1) 0.48.

^{1}H NMR (400 MHz, DMSO-d_6): δ 6.82 (s, 1H), 6.94 (d, J = 8.7 Hz, 1H), 7.60 (t, J = 7.5 Hz, 2H), 7.69 (t, J = 7.3 Hz, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.94 (d, J = 15.1 Hz, 1H), 7.99 (d, J = 6.9 Hz, 2H), 8.36 (d, J = 15.1 Hz, 1H), 11.25 (br. s, 1H).

^{13}C NMR (75 MHz, DMSO-d_6): δ 102.2, 114.6, 115.1, 127.1, 127.8, 128.3, 128.3, 132.7, 134.4, 137.7, 150.9, 153.5, 163.7, 190.2.

HRMS (ESI-TOF): calcd. for $C_{18}H_{11}ClNaO_4$ $[M+Na]^+$: 349.0238; found: 349.0225.

(E)-4-chloro-7-(diethylamino)-3-(3-oxo-3-phenylprop-1-en-1-yl)-2H-chromen-2-one (4c)

Prepared according to general procedure and purified by column chromatography on silica using CH_2Cl_2 as eluent and further recrystallization from ethanol (50 mL) / acetonitrile (20 mL) mixture.

Yield: 1.21 g (79%). Orange crystals. M.p. 166.3–168.3 °C (EtOH/acetonitrile). R_f (Petr. ether / ethyl acetate 3:1) 0.36.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (t, J = 5.8 Hz, 6H, Me), 3.42 (q, J = 7.0 Hz, 4H), 6.44 (s, 1H), 6.63 (d, J = 9.3 Hz, 1H), 7.49–7.55 (m, 3H), 7.69 (d, J = 9.2 Hz, 1H), 8.10 (d, J = 6.7 Hz, 2H), 8.14 (d, J = 15.4 Hz, 1H), 8.46 (d, J = 15.2 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 12.5, 45.2, 96.5, 107.9, 110.1, 112.6, 125.5, 128.0, 128.6, 128.7, 132.8, 135.6, 138.4, 151.3, 152.3, 154.6, 158.9, 190.7

HRMS (ESI-TOF): calcd. for $C_{22}H_{21}ClNO_3$ $[M+H]^+$: 382.1204; found: 382.1200.

Preparation of 4-azido-3-(2-benzoylvinyl)coumarins 5

(E)-4-azido-3-(3-oxo-3-phenylprop-1-en-1-yl)-2H-chromen-2-one (5a)

To a solution of **4a** (2.75 mmol, 850 mg) in acetone (40 mL) was added NaN_3 (5 mmol, 325 mg) and resulting suspension was vigorously stirred at RT for 2 h. The reaction mixture was poured into water and the precipitate was filtered-off and dried to afford title compound, which was used without purification.

Yield: 770 mg (88%). Yellow crystals. M.p. 141.0–142.3 °C. R_f (Petr. ether / ethyl acetate 3:1) 0.45.

(E)-4-azido-7-hydroxy-3-(3-oxo-3-phenylprop-1-en-1-yl)-2H-chromen-2-one (5b)

To a suspension of **4b** (1.5 mmol, 500 mg) in acetone (40 mL) and ethanol (20 mL) was added NaN_3 (2.5 mmol, 160 mg) and reaction mixture was vigorously stirred at 40 °C for 2 h gradually changing color from yellow to orange-red. After completion of the reaction solvent was evaporated at reduced pressure and the residue was treated with water to give precipitate. Crystals were filtered-off and dried to afford title compound, which was used without purification.

Yield: 440 mg (87%). Orange crystals. Decomposes at 150–151 °C. R_f (Petr. ether / acetone 2:1) 0.42.

(E)-4-azido-7-(diethylamino)-3-(3-oxo-3-phenylprop-1-en-1-yl)-2H-chromen-2-one (5c)

To a suspension of **4c** (1.88 mmol, 720 mg) in acetone (50 mL) was added NaN_3 (3 mmol, 200 mg) and the reaction mixture was vigorously stirred at 40 °C for 2 h. After completion of the reaction solvent was removed at reduced pressure and the residue was treated with water to give precipitate. Crystals were filtered-off and dried to afford title compound, which was used without purification.

Yield: 620 mg (85 %). Orange crystals. Decomposes at 170 °C. R_f (Petr. ether / ethyl acetate 3:1) 0.31.

Preparation of 2-benzoylchromeno[4,3-b]pyrrol-4(1H)-ones 6

2-benzoylchromeno[4,3-b]pyrrol-4(1H)-one (6a)

Suspension of **5a** (710 mg, 2.23 mmol) in dry toluene (12 mL) was refluxed for 1 h. Reaction mixture was cooled, the precipitate was filtered off, washed with toluene and dried to give pure title compound.

Yield: 435 mg (67 %). White solid. M.p. 326.2–328.3 °C. R_f (Petr. ether / ethyl acetate 3:1) 0.37.

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.26–7.93 (m, 9H), 8.47 (s, 1H), 13.51 (s, 1H, br, NH)

^{13}C NMR (75 MHz, DMSO-d_6): δ 109.5, 112.9, 117.0, 117.1, 123.3, 124.5, 128.7, 128.9, 130.7, 132.7, 134.1, 137.3, 139.1, 152.4, 157.7, 184.8

HRMS (ESI-TOF): calcd. for $C_{18}H_{12}NO_3$ $[M+H]^+$: 290.0812; found: 290.0814.

2-benzoyl-7-hydroxychromeno[4,3-b]pyrrol-4(1H)-one (6b)

Suspension of **5b** (430 mg, 1.29 mmol) in dry toluene (20 mL) was refluxed for 1 h. Reaction mixture was cooled, the precipitate was filtered off, washed with toluene and dried to give pure title compound.

Yield: 373 mg (95 %). Yellow solid. M.p. 322–325 °C (dec.). R_f (Petr. ether / acetone 2:1) 0.36.

^{1}H NMR (400 MHz, DMSO-d_6): δ 6.71 (s, 1H), 6.77 (d, J = 8.4 Hz, 1H), 7.16 (s, 1H), 7.51–7.62 (m, 3H), 7.84 (d, J = 6.8 Hz, 2H), 8.21 (d, J = 8.3 Hz, 2H), 13.22 (s, 1H, br, NH)

^{13}C NMR (100 MHz, DMSO-d_6): δ 103.6, 105.2, 108.0, 113.6, 118.0, 125.1, 129.2, 129.4, 133.0, 133.8, 138.0, 140.6, 154.8, 158.4, 160.7, 184.7

HRMS (ESI-TOF): calcd. for $C_{18}H_{11}NNaO_4$ $[M+Na]^+$: 328.0580; found: 328.0557.

2-benzoyl-7-(diethylamino)chromeno[4,3-b]pyrrol-4(1H)-one (6c)

Suspension of **5c** (1086 mg, 2.8 mmol) in dry toluene (15 mL) was refluxed for 1 h. Reaction mixture was cooled, the precipitate was filtered off, washed with toluene and dried to give pure title compound.

Yield: 965 mg (96 %). Orange solid. M.p. 308.4–310.8 °C. R_f (Petr. ether / ethyl acetate 3:1) 0.32.

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.16 (t, J = 5.8 Hz, 6H, Me), 3.42 (q, J = 7.0 Hz, 4H), 6.57 (s, 1H), 6.75 (d, J = 8.5 Hz, 1H), 7.18 (s, 1H), 7.58–7.67 (m, 3H), 7.90 (d, J = 6.7 Hz, 2H), 8.23 (d, J = 8.4 Hz, 2H), 13.04 (s, 1H, br, NH)

^{13}C NMR (75 MHz, DMSO-d_6): δ 12.4, 44.0, 97.6, 100.4, 106.8, 108.8, 117.7, 124.4, 128.6, 128.7, 132.3, 132.9, 137.8, 141.0, 149.7, 154.9, 158.3, 184.3

HRMS (ESI-TOF): calcd. for $C_{22}H_{21}N_2O_3$ $[M+H]^+$: 361.1547; found: 361.1533.

General procedure for synthesis of BODIPY dyes 1

To a stirred suspension of 2-benzoylchromeno[4,3-b]pyrrol-4(1H)-one **6** (1–1.5 mmol) in DCM (50 mL) were added di-(tri-)alkylpyrrole (1 eq.) and phosphoryl chloride (1 eq.). The reaction mixture was stirred at RT until TLC analysis indicated complete consumption of **6**. Then triethylamine (10 eq.) was added and stirring continued for 15 min, then $BF_3{\cdot}Et_2O$ (11 equiv) was added and reaction mixture was further stirred at RT for 6 h. The reaction mixture was quenched with water. Organic layer was separated, evaporated at reduced pressure and the residue was chromatographed on silica gel column using an appropriate eluent.

BODIPY 1a

Prepared using general procedure from **6a** (1.55 mmol, 450 mg) and 3-ethyl-2,4-dimethylpyrrole. 1st step reaction time: 5 days. Chromatographic column elution: petr. ether/DCM 3:2, then DCM.

Yield: 280 mg (41%). Pink-red crystals. M.p. 345–347 °C (dec.).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (t, J = 7.6 Hz, 3H), 1.54 (s, 3H), 2.44 (q, J = 7.6 Hz, 2H), 2.80 (s, 3H), 6.94 (s, 1H), 7.37–7.41 (m, 4H), 7.48–7.59 (m, 4H), 8.79 (d, J = 8.2 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 12.49, 13.92, 17.27, 29.68, 114.23, 117.62, 123.71, 124.45, 126.14, 126.27, 126.41, 128.78, 128.83, 129.83, 130.72, 133.21, 137.71, 139.18, 139.24, 140.86, 143.59, 153.53, 158.9, 168.3.

HRMS (ESI-TOF): calcd. for $C_{26}H_{21}BF_2N_2NaO_2$ $[M+Na]^+$: 465.1561; found: 465.1563.

BODIPY 1b

Prepared using general procedure from **6b** (0.94 mmol, 123 mg) and 3-ethyl-2,4-dimethylpyrrole. 1st step reaction time: 8 days. Chromatographic column elution: DCM, then DCM/acetone 100:1.5.

Yield: 160 mg (37 %). Brown shiny crystals. M.p. 340–342 °C (dec.). R_f (Petr. ether / acetone 2:1) 0.41.

^{1}H NMR (300 MHz, DMSO-d_6): δ 1.02 (t, J = 7.1 Hz, 3H), 1.50 (s, 3H), 2.44 (q, J = 7.6 Hz, 2H), 2.73 (s, 3H), 6.59 (s, 1H), 6.79 (s, 1H), 6.91 (d, J = 9.2 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.59–7.65 (m, 3H), 8.46 (d, J = 9.2 Hz, 1H), 10.62 (s, 1H).

^{13}C NMR (75 MHz, DMSO-d_6): δ 12.15, 13.66, 13.73, 16.53, 103.29, 105.20, 112.29, 113.11, 122.41, 127.08, 128.76, 128.88, 129.90, 132.62, 134.95, 136.51, 139.14, 139.86, 143.29, 146.07, 154.84, 157.39, 160.64, 167.88.

HRMS (ESI-TOF): calcd. for $C_{26}H_{22}BF_2N_2O_3$ $[M+H]^+$: 459.1691; found: 459.1651.

BODIPY 1c

Prepared using general procedure from **6c** (1.1 mmol, 400 mg) and 3-ethyl-2,4-dimethylpyrrole. 1st step reaction time: 5 days. Chromatographic column elution: petroleum ether/DCM 3:2, then DCM.

Yield: 330 mg (58 %). Deep green crystals. M.p. 282.5–284.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.06 (t, J = 7.5 Hz, 3H), 1.23 (t, J = 7.0 Hz, 6H), 1.50 (s, 3H), 2.41 (q, J = 7.6 Hz, 2H), 2.74 (s, 3H), 3.45 (q, J = 7.0 Hz, 4H), 6.57 (s, 1H), 6.73 (d, J = 9.4 Hz, 1H), 6.92 (s, 1H), 7.36 (d, J = 7.2 Hz, 2H), 7.50–7.52 (m, 3H), 8.57 (d, J = 9.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 12.31, 12.52, 14.07, 17.16, 29.63, 44.69, 98.32, 101.94, 108.94, 112.93, 125.48, 127.63, 128.55, 128.87, 129.44, 133.62, 134.71, 137.09, 137.64, 139.99, 141.9, 148.44, 150.02, 156.08, 159.4, 164.21.

HRMS (ESI-TOF): calcd. for $C_{30}H_{30}BF_2N_3O_2$ $[M]^+$: 513.2399; found: 513.2374.

BODIPY 1d

Prepared using general procedure from **6c** (1.5 mmol, 540 mg) and 2,4-dimethylpyrrole. 1st step reaction time: 7 days. Chromatographic column elution: petroleum ether /DCM 1:1, then DCM.

Yield: 215 mg (30 %). Deep green crystals. M.p. 295–297 °C (dec.).

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23 (t, J = 7.0 Hz, 6H), 1.58 (s, 3H), 2.74 (s, 3H), 3.45 (q, J = 7.0 Hz, 4H), 6.26 (s, 1H), 6.57 (s, 1H), 6.73 (d, J = 9.5 Hz, 1H), 7.00 (s, 1H), 7.36 (d, J = 7.3 Hz, 2H), 7.49–7.53 (m, 3H), 8.58 (d, J = 9.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 12.58, 14.92, 15.45, 44.77, 98.4, 101.87, 109.11, 113.61, 124.77, 126.93, 127.93, 128.64, 128.86, 129.62, 133.35, 134.87, 137.21, 141.47, 146.99, 149.15, 150.37, 156.32, 159.23, 163.59.

HRMS (ESI-TOF): calcd. for $C_{28}H_{26}BF_2N_3O_2$ $[M]^+$: 485.2086; found: 485.2059.

This journal is © The Royal Society of Chemistry 2013

3. UV-VIS AND FLUORESCENCE SPECTRA OF BODIPYs 1a-d

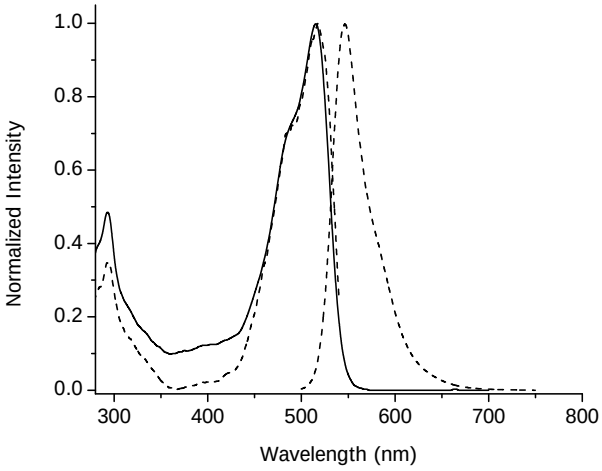


Fig. S1 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1a** in DCM.

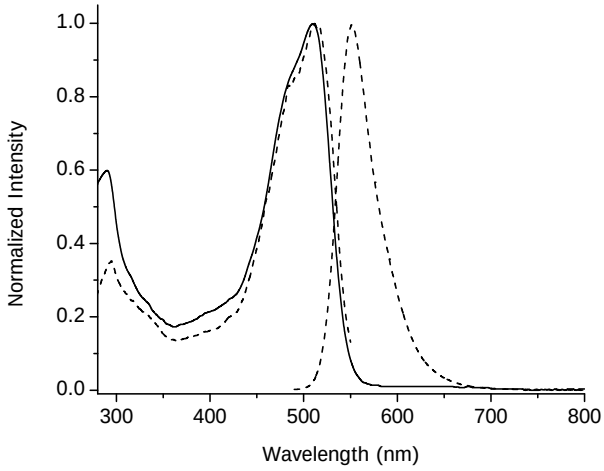


Fig. S2 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1a** in DMF.

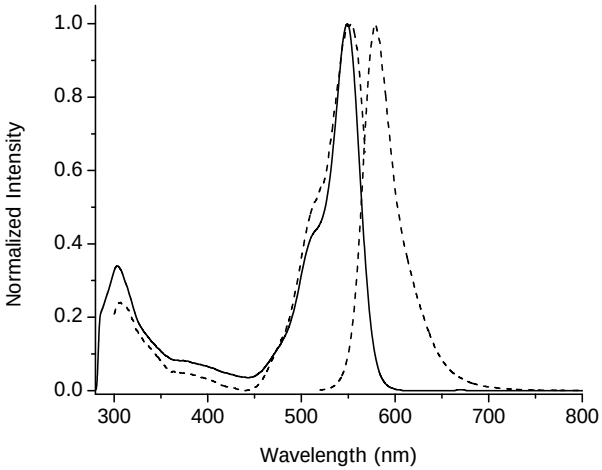


Fig. S3 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1b** in toluene.

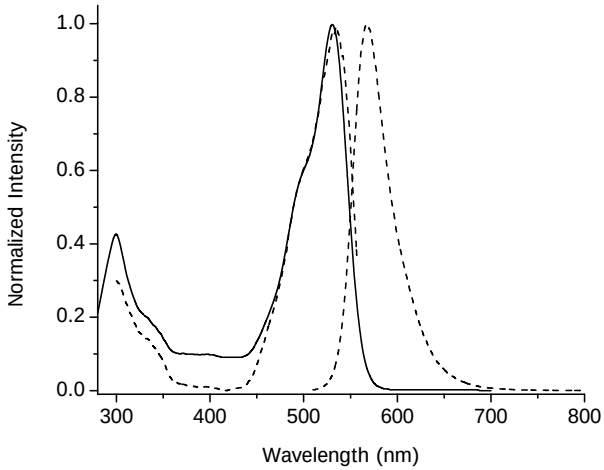


Fig. S4 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1b** in DCM.

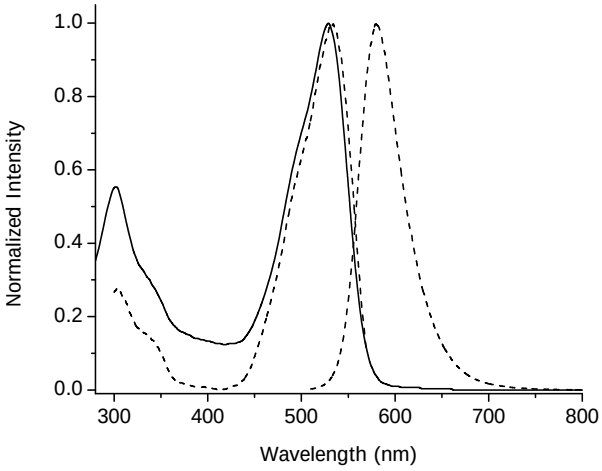


Fig. S5 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1b** in MeOH.

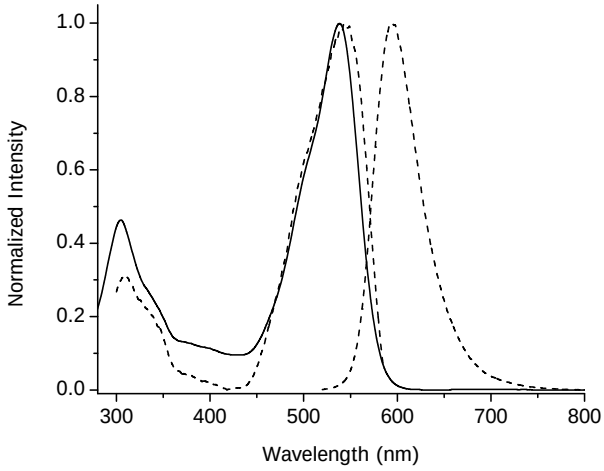


Fig. S6 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1b** in DMF.

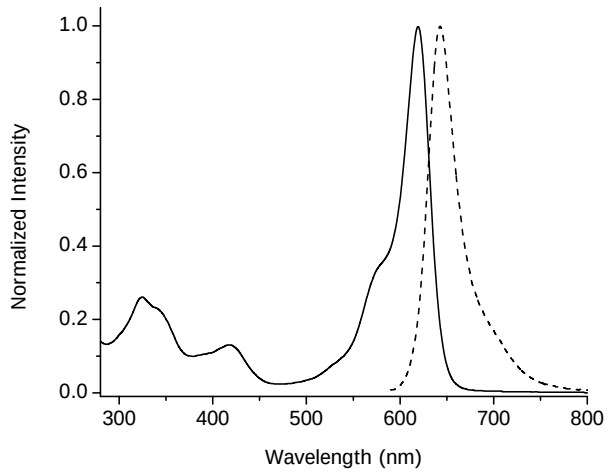


Fig. S7 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1c** in cyclohexane.

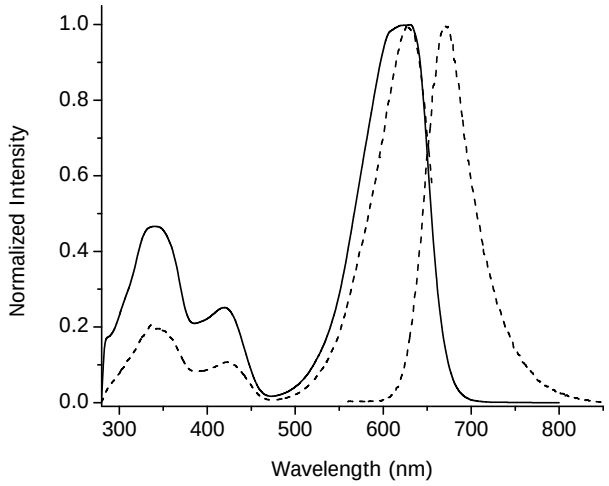


Fig. S8 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1c** in toluene.

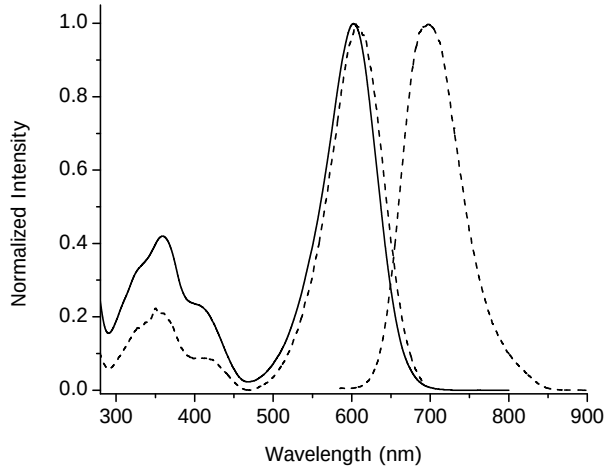


Fig. S9 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1c** in DCM.

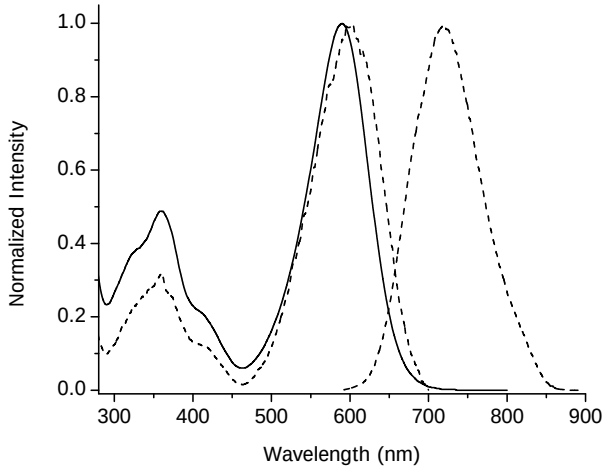


Fig. S10 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1c** in methanol.

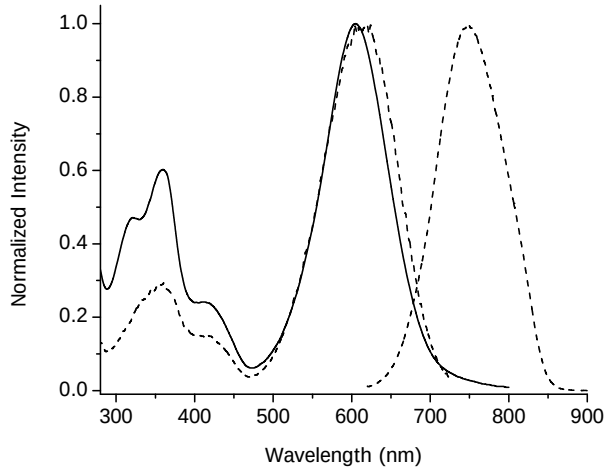


Fig. S11 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1c** in DMF.

This journal is © The Royal Society of Chemistry 2013

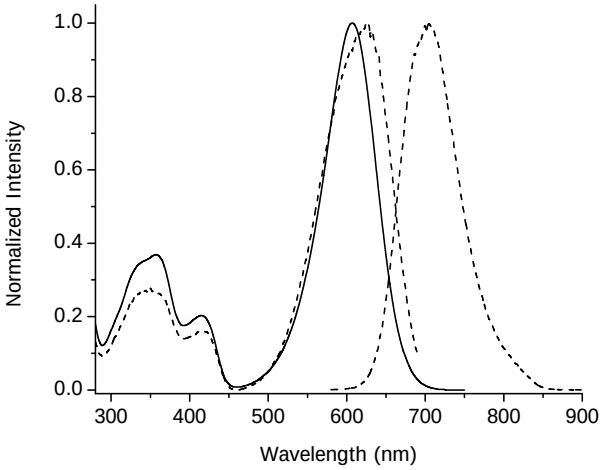


Fig. S12 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1d** in DCM.

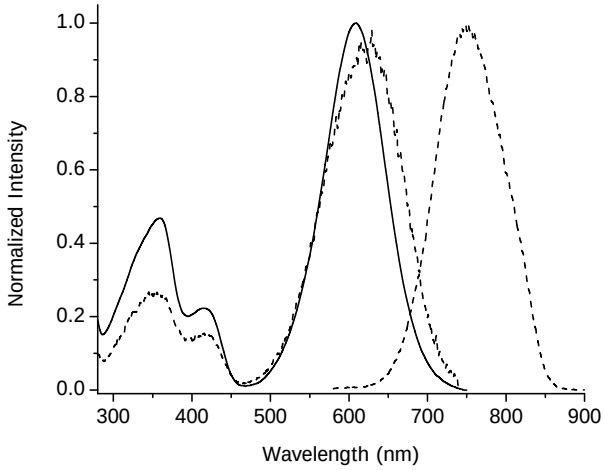


Fig. S13 Normalized UV-vis absorption (solid) and fluorescence excitation and emission (dashed) spectra of **1d** in DMF.

4. X-RAY DIFFRACTION ANALYSIS OF 1c

X-ray diffraction data were measured using a Bruker SMART APEX2 CCD diffractometer, with graphite monochromated Mo-K_α radiation at 150 K.

The structure was solved by direct methods using SHELXS-97 and developed by full least-squares refinement on F2 using SHELXL-97 [Sheldrick, G. M. (1997). SHELXS 97, University of Gottingen, Germany]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined using a riding model. The CIF file has been deposited at the Cambridge Crystallographic Data Centre as CCDC 956947.

Table S1 Crystallographic data for **1c**.

Chemical formula	$C_{30}H_{30}BF_2N_3O_2$
Formula Mass	513.38
Crystal system	Triclinic
a/Å	10.508(6)
b/Å	10.783(6)
c/Å	11.982(6)
α/°	84.890(8)
β/°	69.760(7)
γ/°	81.743(9)
Unit cell volume/Å^3	1259.4(11)
Temperature/K	150(2)
Space group	$P\bar{1}$,
Z	2
D_{calc}/g×cm^{-3}	1.35
No. of reflections measured	9978
No. of independent reflections	5178
R_{int}	0.0503
Final R_1 values ($I > 2\sigma(I)$)	0.0664
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1608
Final R_1 values (all data)	0.1104
Final $wR(F^2)$ values (all data)	0.1851
Goodness of fit on F^2	1.017

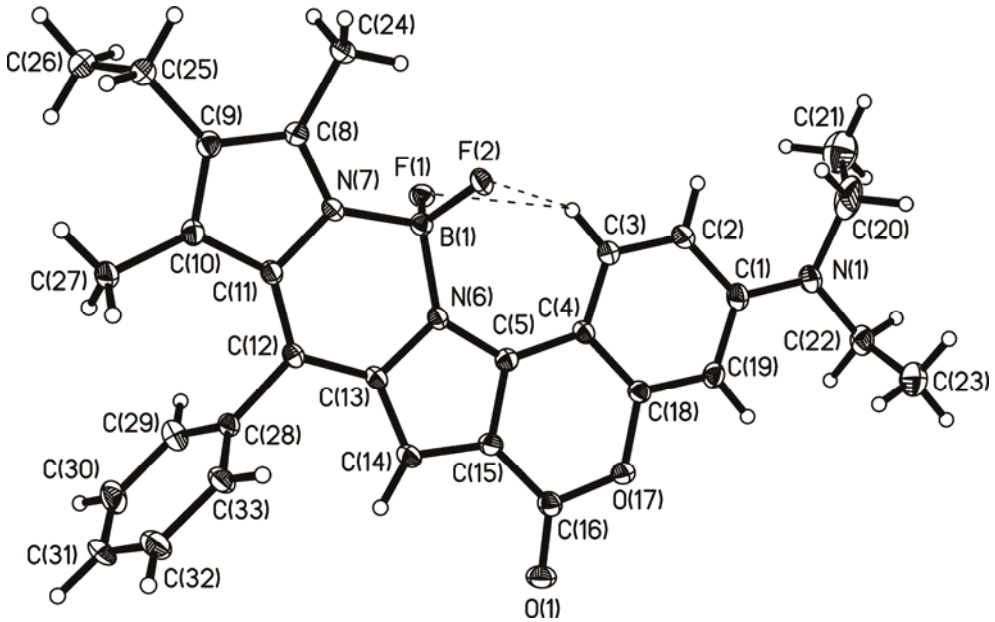


Fig. S14 Molecular structure of BODIPY **1c**.

This journal is © The Royal Society of Chemistry 2013

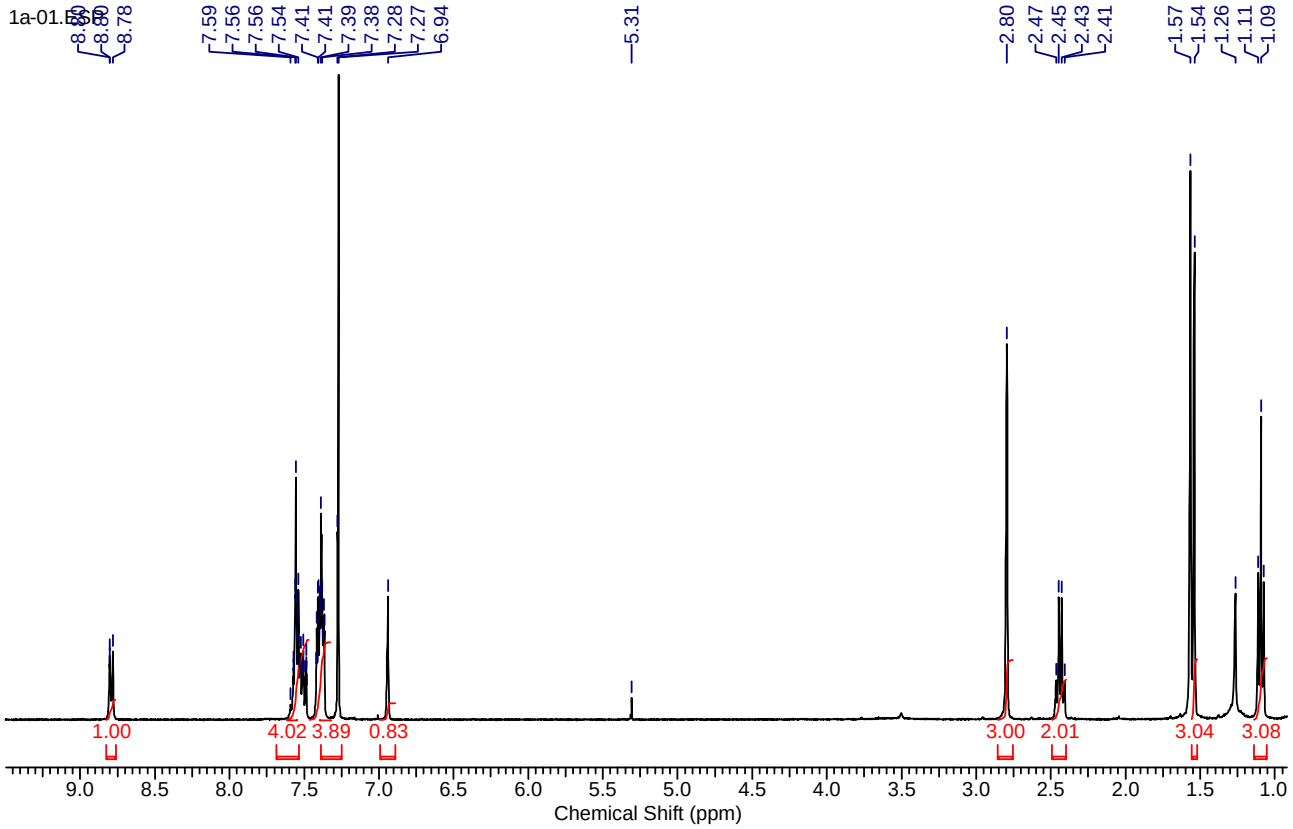
Table S2 Bond lengths (Å) and valence angles (°) of **1c**.

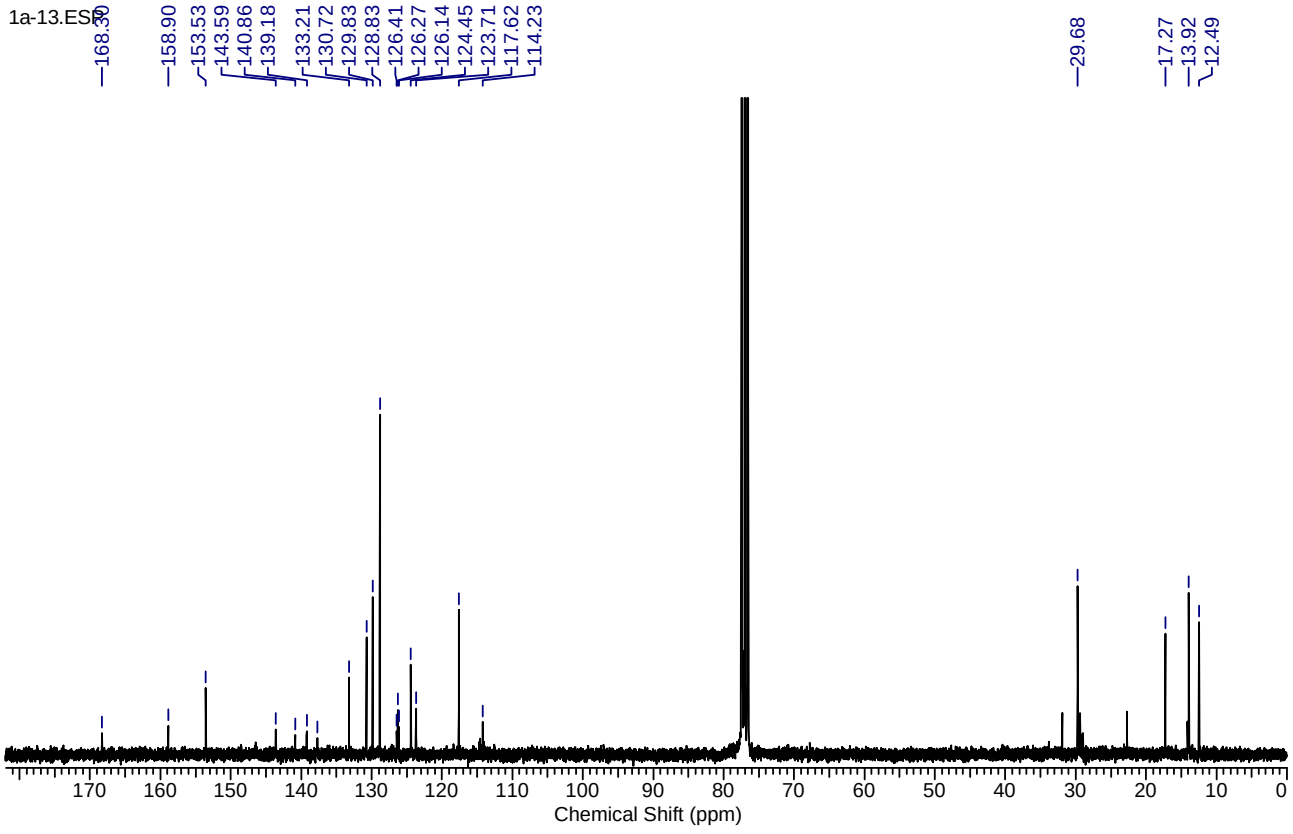
F(1)-B(1)	1.387(3)	C(1)-N(1)-C(22)	120.9(2)
F(2)-B(1)	1.385(3)	C(1)-N(1)-C(20)	119.5(3)
O(1)-C(16)	1.207(3)	C(22)-N(1)-C(20)	117.0(2)
N(1)-C(1)	1.372(3)	N(1)-C(1)-C(19)	121.6(3)
N(1)-C(22)	1.460(4)	N(1)-C(1)-C(2)	121.3(3)
N(1)-C(20)	1.552(5)	C(19)-C(1)-C(2)	117.1(2)
C(1)-C(19)	1.404(4)	C(3)-C(2)-C(1)	121.6(3)
C(1)-C(2)	1.410(4)	C(2)-C(3)-C(4)	121.8(2)
C(2)-C(3)	1.376(4)	C(18)-C(4)-C(3)	115.6(2)
C(3)-C(4)	1.405(4)	C(18)-C(4)-C(5)	116.5(2)
C(4)-C(18)	1.401(4)	C(3)-C(4)-C(5)	127.9(2)
C(4)-C(5)	1.438(4)	N(6)-C(5)-C(15)	108.7(2)
C(5)-N(6)	1.368(3)	N(6)-C(5)-C(4)	131.8(2)
C(5)-C(15)	1.407(4)	C(15)-C(5)-C(4)	119.5(2)
N(6)-C(13)	1.401(3)	C(5)-N(6)-C(13)	107.1(2)
N(6)-B(1)	1.549(4)	C(5)-N(6)-B(1)	129.9(2)
N(7)-C(8)	1.344(3)	C(13)-N(6)-B(1)	122.9(2)
N(7)-C(11)	1.408(3)	C(8)-N(7)-C(11)	107.6(2)
N(7)-B(1)	1.558(4)	C(8)-N(7)-B(1)	126.7(2)
C(8)-C(9)	1.426(4)	C(11)-N(7)-B(1)	125.5(2)
C(8)-C(24)	1.496(4)	N(7)-C(8)-C(9)	110.3(2)
C(9)-C(10)	1.386(4)	N(7)-C(8)-C(24)	123.4(2)
C(9)-C(25)	1.505(4)	C(9)-C(8)-C(24)	126.3(2)
C(10)-C(11)	1.432(4)	C(10)-C(9)-C(8)	107.0(2)
C(10)-C(27)	1.498(4)	C(10)-C(9)-C(25)	126.8(2)
C(11)-C(12)	1.374(4)	C(8)-C(9)-C(25)	126.1(2)
C(12)-C(13)	1.417(4)	C(9)-C(10)-C(11)	107.0(2)
C(12)-C(28)	1.499(4)	C(9)-C(10)-C(27)	125.2(2)
C(13)-C(14)	1.390(4)	C(11)-C(10)-C(27)	127.8(2)
C(14)-C(15)	1.395(4)	C(12)-C(11)-N(7)	119.5(2)
C(15)-C(16)	1.435(4)	C(12)-C(11)-C(10)	132.3(2)
C(16)-O(17)	1.380(3)	N(7)-C(11)-C(10)	108.1(2)
O(17)-C(18)	1.397(3)	C(11)-C(12)-C(13)	121.4(2)
C(18)-C(19)	1.377(4)	C(11)-C(12)-C(28)	121.1(2)
C(20)-C(21)	1.432(6)	C(13)-C(12)-C(28)	117.6(2)
C(22)-C(23)	1.509(5)	C(14)-C(13)-N(6)	109.5(2)
C(25)-C(26)	1.523(4)	C(14)-C(13)-C(12)	128.4(2)
C(28)-C(33)	1.389(4)	N(6)-C(13)-C(12)	122.0(2)
C(28)-C(29)	1.386(4)	C(13)-C(14)-C(15)	106.5(2)
C(29)-C(30)	1.390(4)	C(14)-C(15)-C(5)	108.1(2)
C(30)-C(31)	1.383(5)	C(14)-C(15)-C(16)	128.7(2)
C(31)-C(32)	1.380(4)	C(5)-C(15)-C(16)	123.1(3)
C(32)-C(33)	1.381(4)	O(1)-C(16)-O(17)	117.4(2)
		O(1)-C(16)-C(15)	127.2(3)
		O(17)-C(16)-C(15)	115.4(2)
		C(16)-O(17)-C(18)	122.8(2)
		C(19)-C(18)-O(17)	113.8(2)
		C(19)-C(18)-C(4)	123.6(2)
		O(17)-C(18)-C(4)	122.6(2)
		C(18)-C(19)-C(1)	120.1(2)
		C(21)-C(20)-N(1)	110.2(4)

N(1)-C(22)-C(23)	113.7(3)
C(9)-C(25)-C(26)	112.1(2)
C(33)-C(28)-C(29)	119.3(2)
C(33)-C(28)-C(12)	120.4(2)
C(29)-C(28)-C(12)	120.3(3)
C(28)-C(29)-C(30)	120.4(3)
C(31)-C(30)-C(29)	119.9(3)
C(32)-C(31)-C(30)	119.8(3)
C(31)-C(32)-C(33)	120.5(3)
C(32)-C(33)-C(28)	120.1(3)
F(2)-B(1)-F(1)	109.5(2)
F(2)-B(1)-N(6)	110.9(2)
F(1)-B(1)-N(6)	110.1(2)
F(2)-B(1)-N(7)	109.4(2)
F(1)-B(1)-N(7)	109.3(2)
N(6)-B(1)-N(7)	107.5(2)

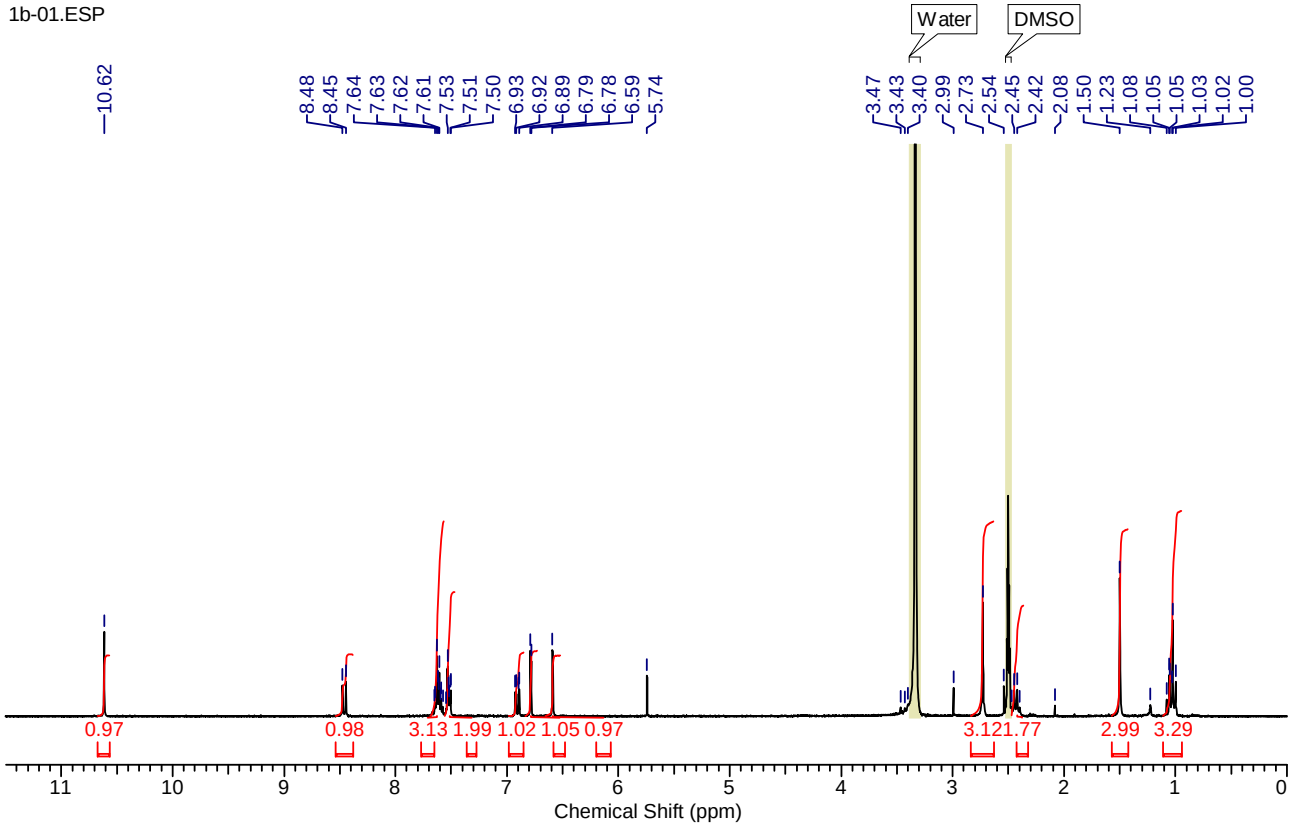
5. NMR SPECTRA OF BODIPYs 1a-d

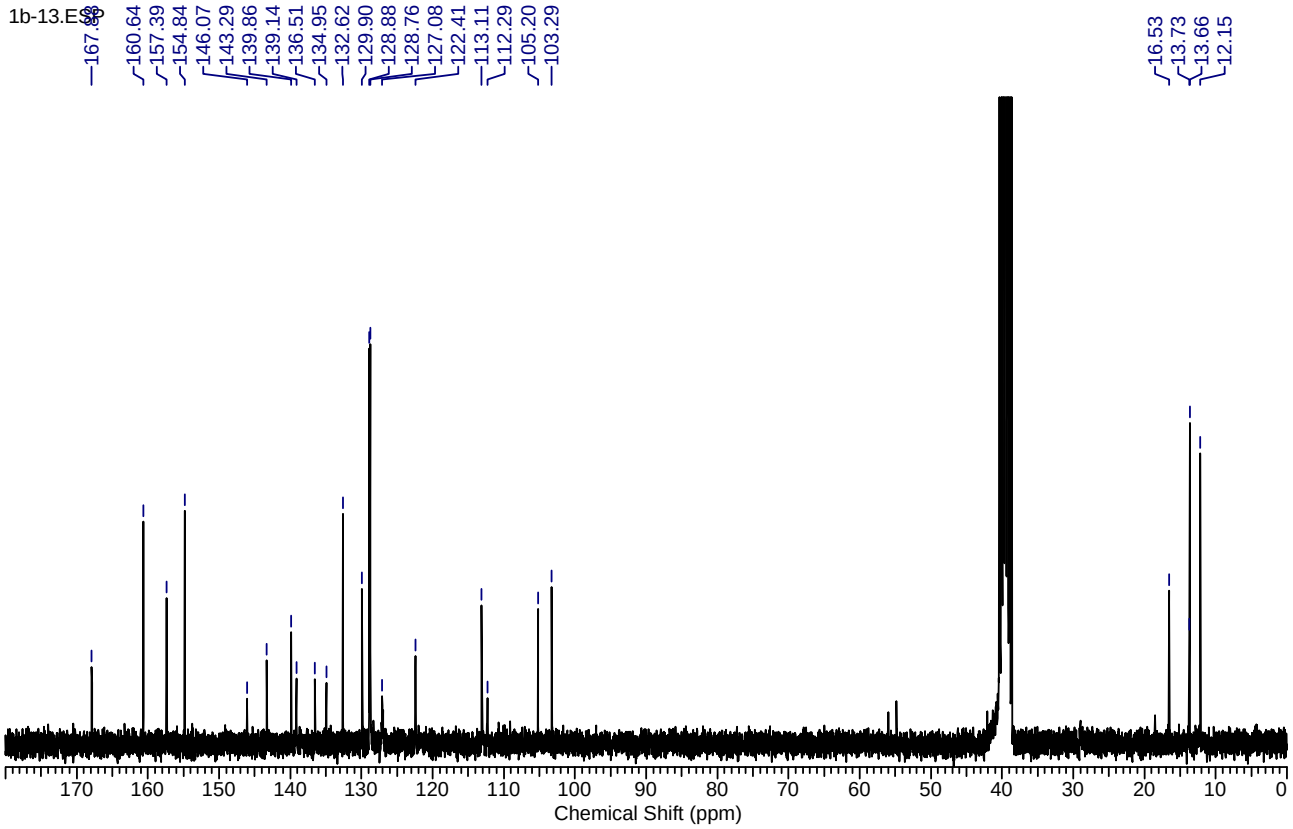
^{1}H and ^{13}C NMR spectra of BODIPY **1a**



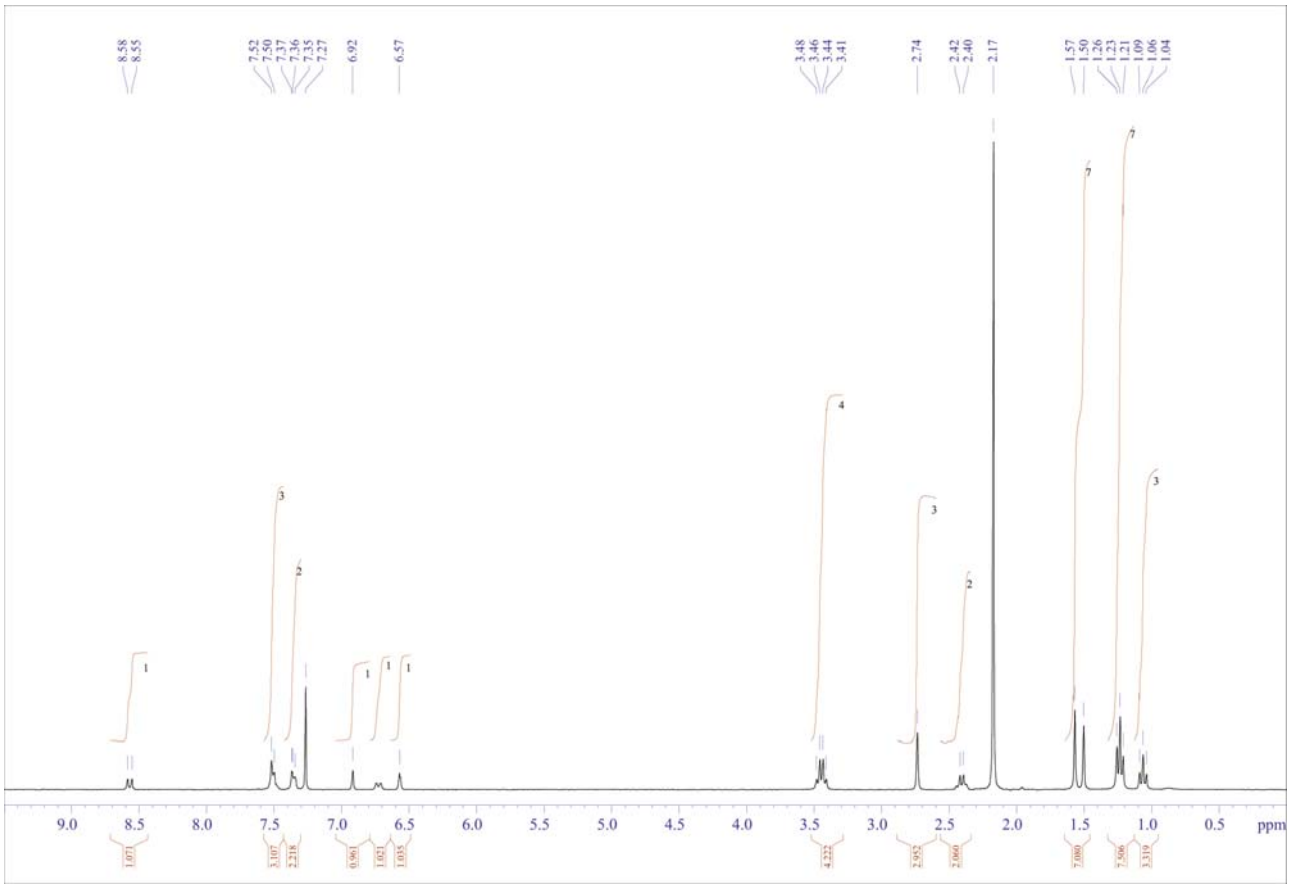


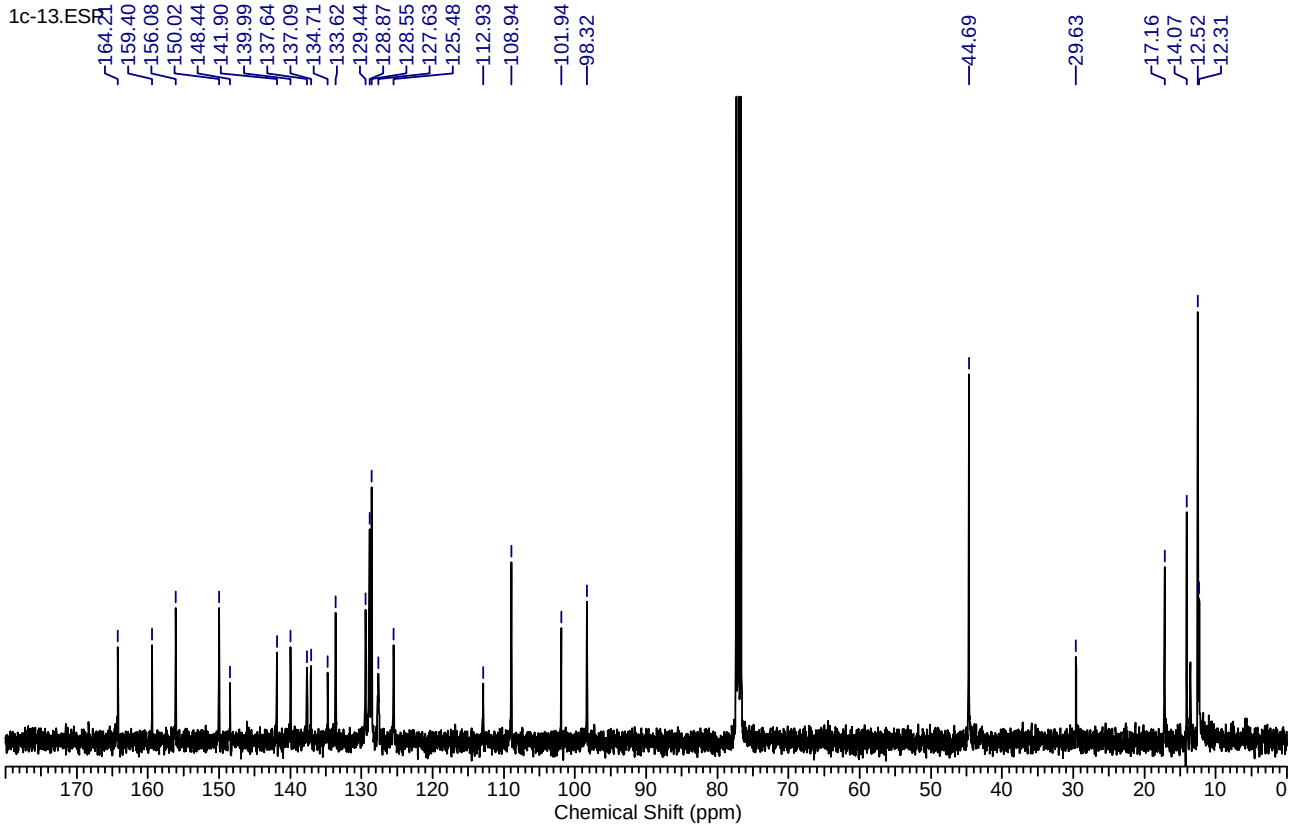
^{1}H and ^{13}C NMR spectra of BODIPY **1b**



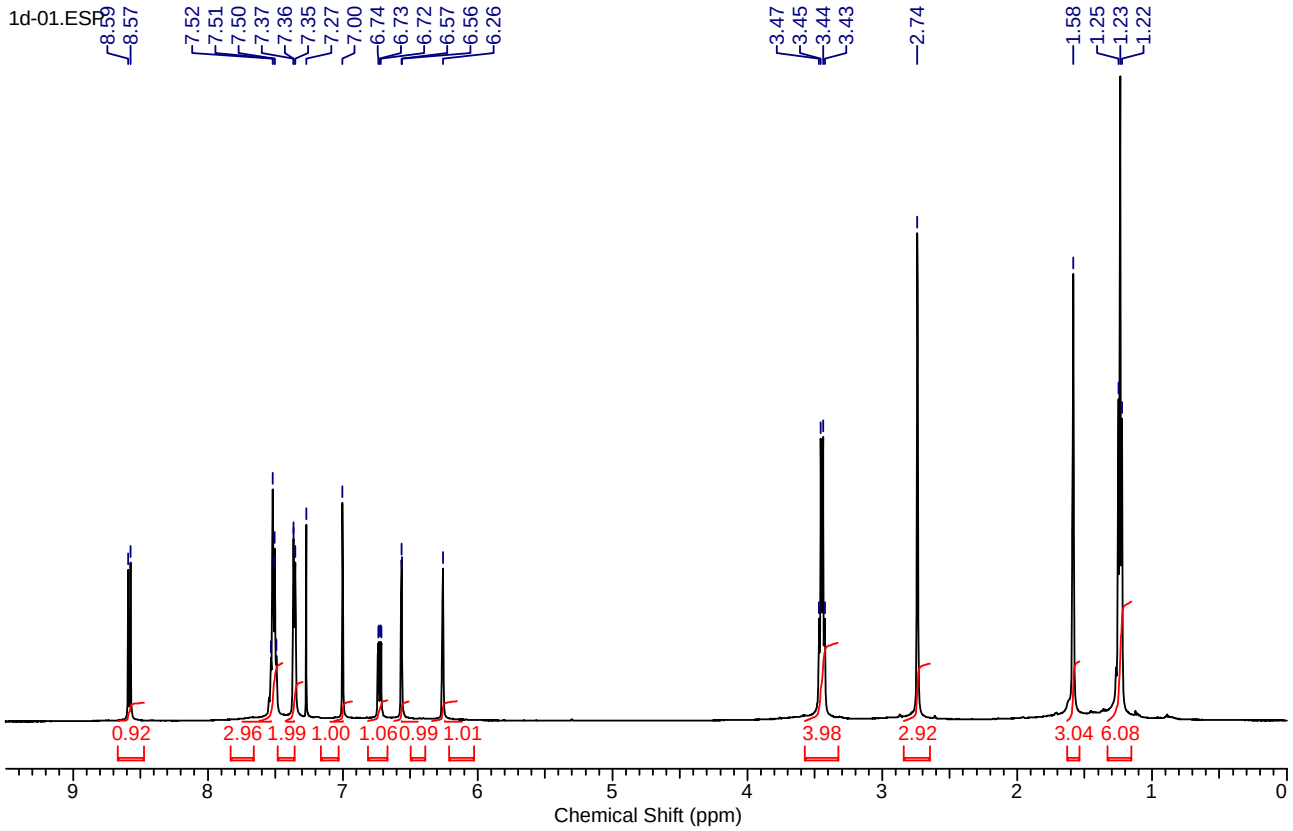


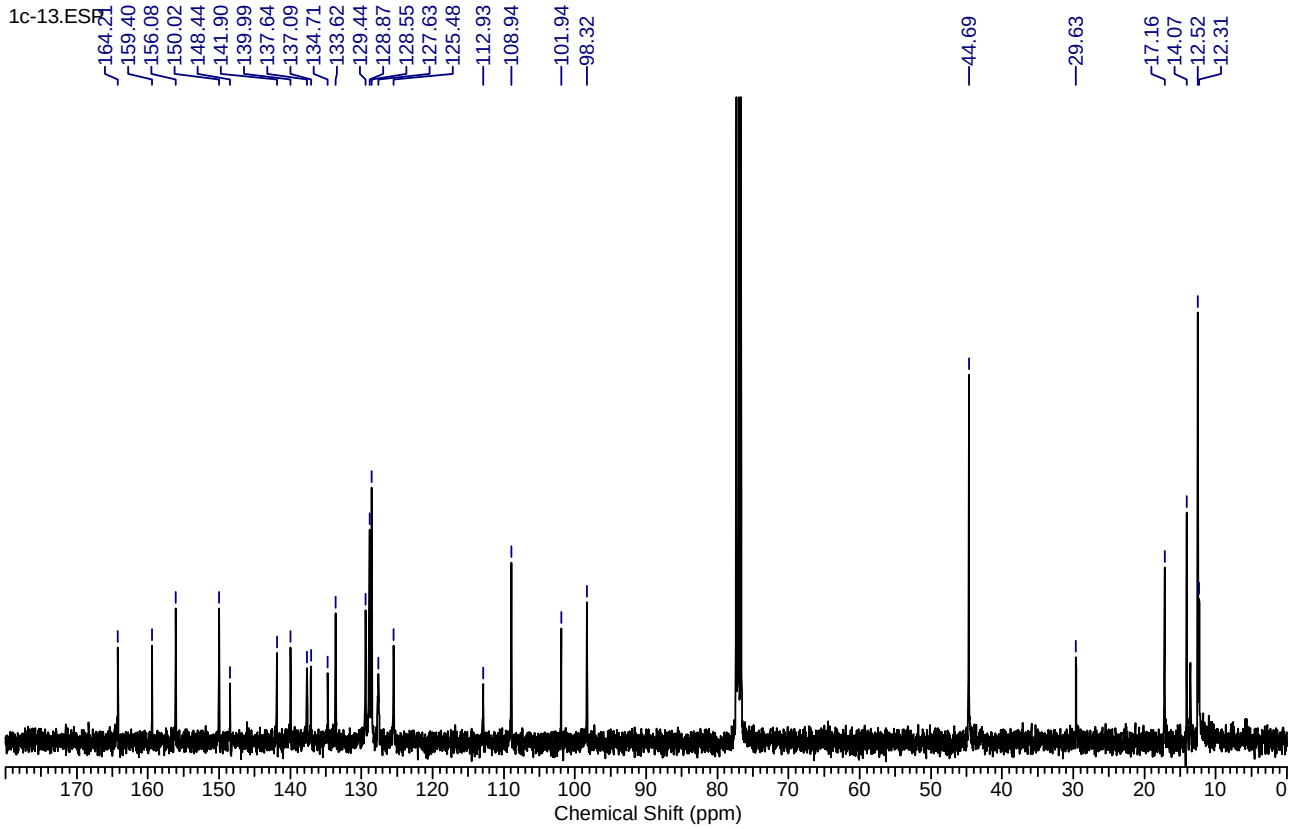
^{1}H and ^{13}C NMR spectra of BODIPY **1c**





^{1}H and ^{13}C NMR spectra of BODIPY **1d**





This journal is © The Royal Society of Chemistry 2013

6. REFERENCES

1. Q. Shen, J. Shao, Q. Peng, W. Zhang, L. Ma, A. S. C. Chan, L. Gu, *J. Med. Chem.*, 2010, **53**, 8252.
2. D. Heber, I. C. Ivanov, S. K. Karagiosov, *J. Heterocycl. Chem.*, 1995, **32**, 505.
3. H. Kuroda, E. Hanaki, H. Izawa, M. Kano, H. Itahashi, *Tetrahedron*, 2004, **60**, 1913.
4. W. Zhao, E. M. Carreira, *Angew. Chem. Int. Ed.*, 2005, **44**, 1677.
5. D. Magde, R. Wong, P. G. Seybold, *Photochem. Photobiol.*, 2002, **75**, 327.
6. D. Magde, J. H. Brannon, T. L. Cremers, J. J. Olmsted, *Phys. Chem.*, 1979, **83**, 696.
7. I. Jabin, G. Revial, N. Monnier-Benoit, P. Netchitailo, *J. Org. Chem.*, 2001, **66**, 256.
8. Y.-S. Chen, P.-Y. Kuo, T.-L. Shie, D.-Y. Yang, *Tetrahedron*, 2006, **62**, 9410.
9. A. Knierzinger, O. S. Wolfbeis, *J. Heterocycl. Chem.*, 1980, **17**, 225.