

Supporting Information

Red-Edge Wavelength-Finely Tunable Laser Action from New Bodipy Dyes

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Synthesis of BODIPY 1-4.

Synthesis of 4,4-Difluoro-3,5-bis(*p*-formylphenyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (2). Compound **2** was synthesized from **1**¹ in Suzuki cross-coupling reaction under both microwave and ultrasonic irradiation conditions.

Suzuki cross-coupling reaction under microwave irradiation: Compound **1** (87 mg, 0.25 mmol) was dissolved in DME (20 mL). *p*-Formylphenyl boronic acid (95 mg, 0.63 mmol) and Na₂CO₃ (79 mg, 0.75 mmol) were added in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium (8.6 mg, 0.008 mmol). The reaction mixture was stirred under microwave irradiation for 30 min at 150 °C with a power of 200 W and 20 atm. After addition of H₂O (50 mL), the organic layer was extracted with EtOAc, dried over MgSO₄, filtered and concentrated to dryness. Flash chromatography using hexane/EtOAc (8:2) afforded compound **2** (57 mg, 46% yield) as dark red crystals. M.p. 142.8-143.3 °C; ¹H NMR (300 MHz, CDCl₃): δ 9.97 (2 H, s, CHO), 7.95 (4 H, d, *J* = 8.4 Hz, aromatic), 7.85 (4 H, d, *J* = 8.4 Hz, aromatic), 7.43 (2 H, d, *J* = 8.1 Hz, aromatic), 7.30 (2 H, d, *J* = 8.1 Hz, aromatic), 6.93 (2 H, d, *J* = 4.2 Hz, pyrrole), 6.63 (2 H, d, *J* = 4.2 Hz, pyrrole), 2.43 (3 H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 191.8 (CHO), 157.2 (C=N), 141.3, 138.2, 137.1, 136.5, 131.7, 131.1, 130.8, 130.1, 129.6, 129.3, 125.6, 121.3 (aromatic and C=C), 21.6 (CH₃); IR (neat): 2853, 2734 (CHO), 1699 (C=O), 1540 cm⁻¹; MS *m/z* (%): 490 (M⁺, 61), 283 (100), 255 (95), 157 (47); HR-MS-ESI⁺: calcd for (C₃₀H₂₁BF₂N₂O₂+H⁺) 491.1700 found 491.1733; HPLC (reverse phase C₁₈ column, CH₃CN-H₂O 9:1, flow rate 2 mL min⁻¹, λ_{anal} 550 nm): R_t = 1.94 min (98% purity).

Suzuki cross-coupling reaction under ultrasound irradiation: Compound **1** (48 mg, 0.14 mmol), 4-formylphenyl boronic acid (126 mg, 0.84 mmol), Na₂CO₃ (89 mg, 0.84 mmol) and a catalytic amount of tetrakis(triphenylphosphine)palladium (10 mg, 0.009 mmol) were stirred under ultrasound irradiation for 15 h at 75 °C with a power of 720 W. Flash chromatography using hexane/EtOAc (8:2) afforded compound **2** (44 mg, 50% yield).

Synthesis of 4,4-Difluoro-3,5-bis(*p*-2,2-dimethoxycarbonylvinylphenyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (3). To a solution of TiCl₄ (1.0 M in CH₂Cl₂) (0.8 mL, 0.8 mmol) in 30 mL of dry THF at 0 °C and under an argon atmosphere, were added

dropwise a solution of compound **2** (46 mg, 0.09 mmol) and dimethyl malonate (29 mg, 0.22 mmol) in dry THF. The reaction mixture was stirred at 0 °C for 30 min and then, a solution of pyridine (0.12 mL, 1.4 mmol) in dry THF was added. The reaction was stirred at RT for 24 h before being quenched with H₂O and extracted with ether. The combined organic phases were washed with H₂O, saturated NaHCO₃ solution and brine. The extract was dried over MgSO₄, filtered and concentrated to dryness. Flash chromatography using hexane/EtOAc (8:2) afforded compound **3** (34 mg, 47%) as dark blue crystals. M.p. 135.0-135.5 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.93 (4 H, d, *J* = 8.4 Hz, aromatic), 7.79 (2 H, s, 2 CH=C), 7.50 (6 H, m, aromatic), 7.37 (2 H, d, *J* = 6.8 Hz, aromatic), 6.97 (2 H, d, *J* = 4.3 Hz, pyrrole), 6.69 (2 H, d, *J* = 4.3 Hz, pyrrole), 3.88 (12 H, s, 4 CH₃O), 2.53 (3 H, s, CH₃); ¹³C NMR (75 MHz, CDCl₃): 167.0 (COO), 164.5 (COO), 157.6 (C=N), 142.1, 134.6, 133.7, 131.3, 130.7, 129.9, 129.4, 129.1, 126.1, 121.1 (aromatic and CH=C), 52.8 (CH₃O), 52.7 (CH₃O), 21.5 (CH₃); IR (neat): 1732, 1682 (C=O), 1597 (C=C) cm⁻¹; MS *m/z* (%): 718 (M⁺, 100), 59 (32); HR-MS-ESI⁺: calcd for C₄₀H₃₃BF₂N₂O₈ (M+NH₄)⁺ 736.2643 found 736.2642; HPLC (reverse phase C₁₈ column, CH₃CN-H₂O 9:1, flow rate 2 mL min⁻¹, λ_{anal} 500 nm): *R*_t = 2.53 min (99% purity).

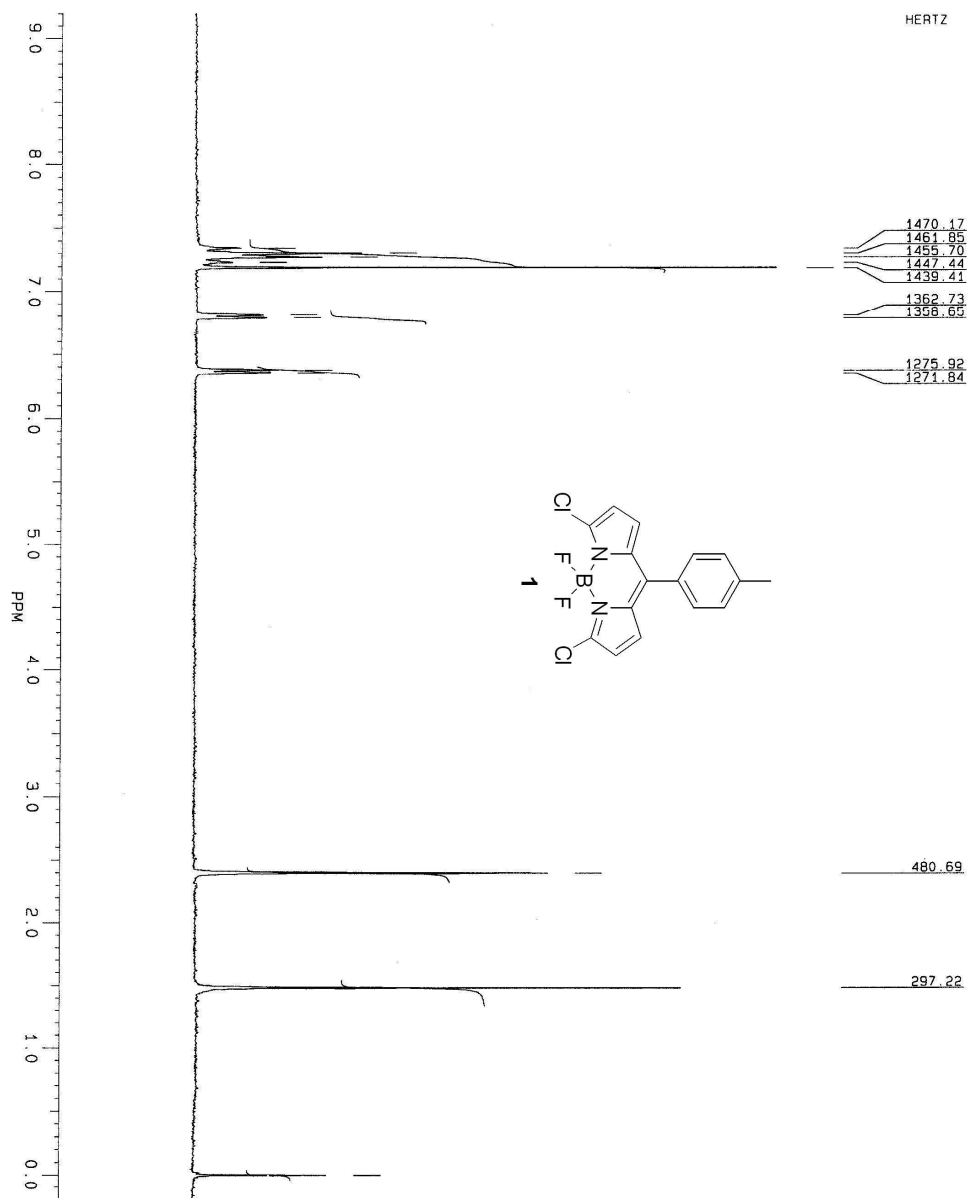
Synthesis of 4,4-Difluoro-3,5-bis(*p*-2,2-dicyanovinylphenyl)-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (4**).** A mixture of compound **2** (52 mg, 0.09 mmol), malononitrile (14.5 mg, 0.22 mmol), β-alanine (6 mg, 0.06 mmol) and 6 mL acetic acid in 30 mL of toluene was refluxed for 24 h. The H₂O generated during the condensation was azeotropically removed by using a Dean Stark trap. The mixture was then cooled, diluted with EtOAc, and washed with H₂O. The organic layer was dried over MgSO₄, filtered and concentrated to dryness. Flash chromatography using hexane/EtOAc (8:2) afforded compound **4** (13 mg, 21%) as dark blue crystals. M.p. 140.2-140.7 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.98 (4 H, d, *J* = 8.5 Hz, aromatic), 7.91 (4 H, d, *J* = 8.5 Hz, aromatic), 7.70 (2 H, s, 2 CH=C), 7.44 (2 H, d, *J* = 8.0 Hz, aromatic), 7.31 (2 H, d, *J* = 8.0 Hz, aromatic), 6.96 (2 H, d, *J* = 4.2 Hz, pyrrole), 6.68 (2 H, d, *J* = 4.2 Hz, pyrrole), 2.44 (3 H, s, CH₃); ¹³C NMR (125 MHz, CDCl₃): 159.1 (CH=C(CN)₂), 159.0 (CH=C(CN)₂), 156.8 (C=N), 145.1, 141.9, 138.5, 137.9, 132.4, 131.9, 131.8, 131.5, 131.3, 131.1, 131.0, 130.8, 129.7, 128.7, 121.9 (aromatic), 114.1 (CN), 113.0 (CN), 83.6 (2 (CN)₂C=CH), 21.5 (CH₃); IR (neat): 2229 (CN), 1538 cm⁻¹; MS *m/z* (%): 586

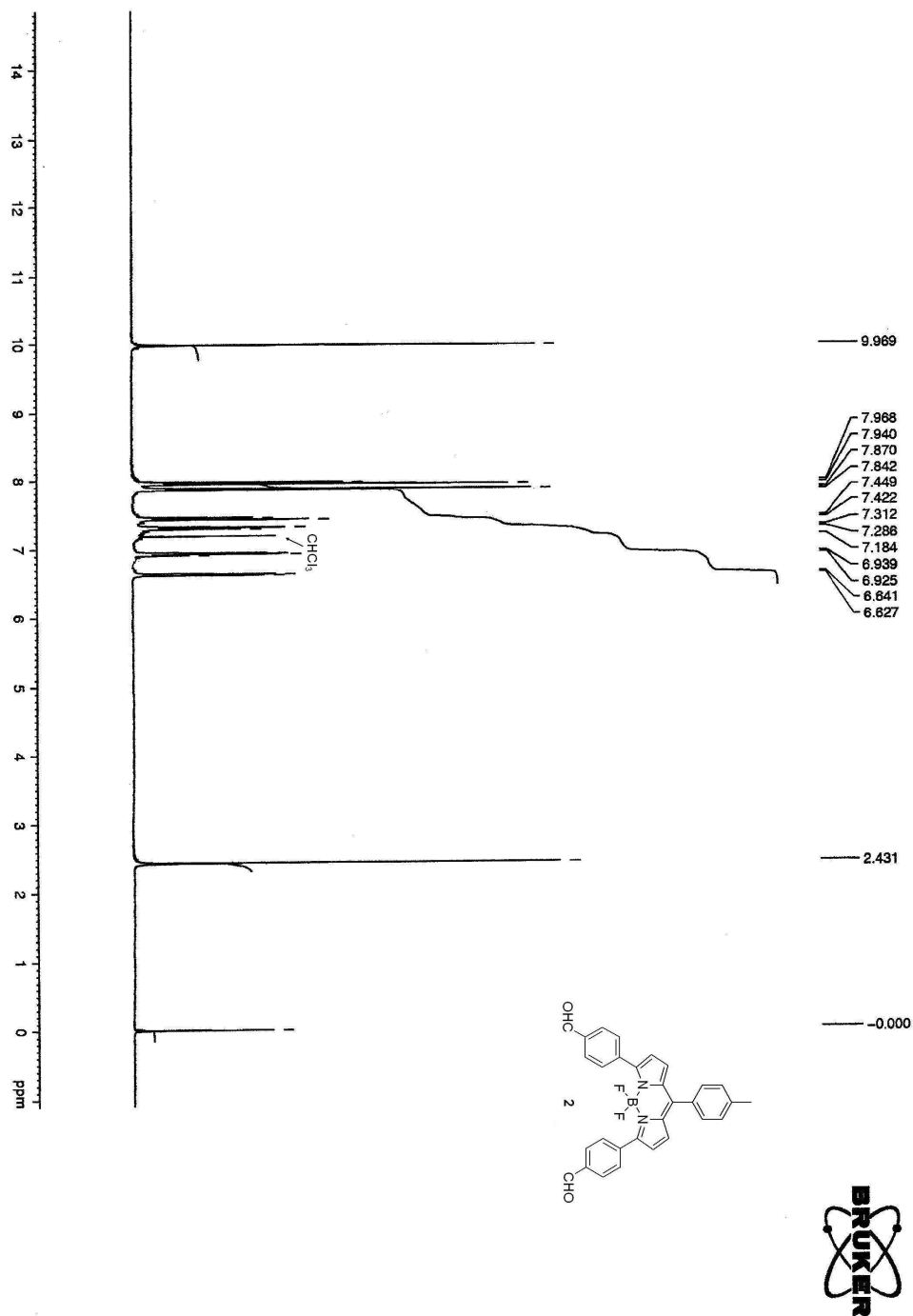
(M^+ , 100), 306 (40), 219 (28), 131 (41), 69 (79), 55 (51); HPLC (reverse phase C_{18} column, CH_3CN-H_2O 9:1, flow rate 2 mL min^{-1} , λ_{anal} 570 nm): $R_t = 2.57\text{ min}$ (98% purity).

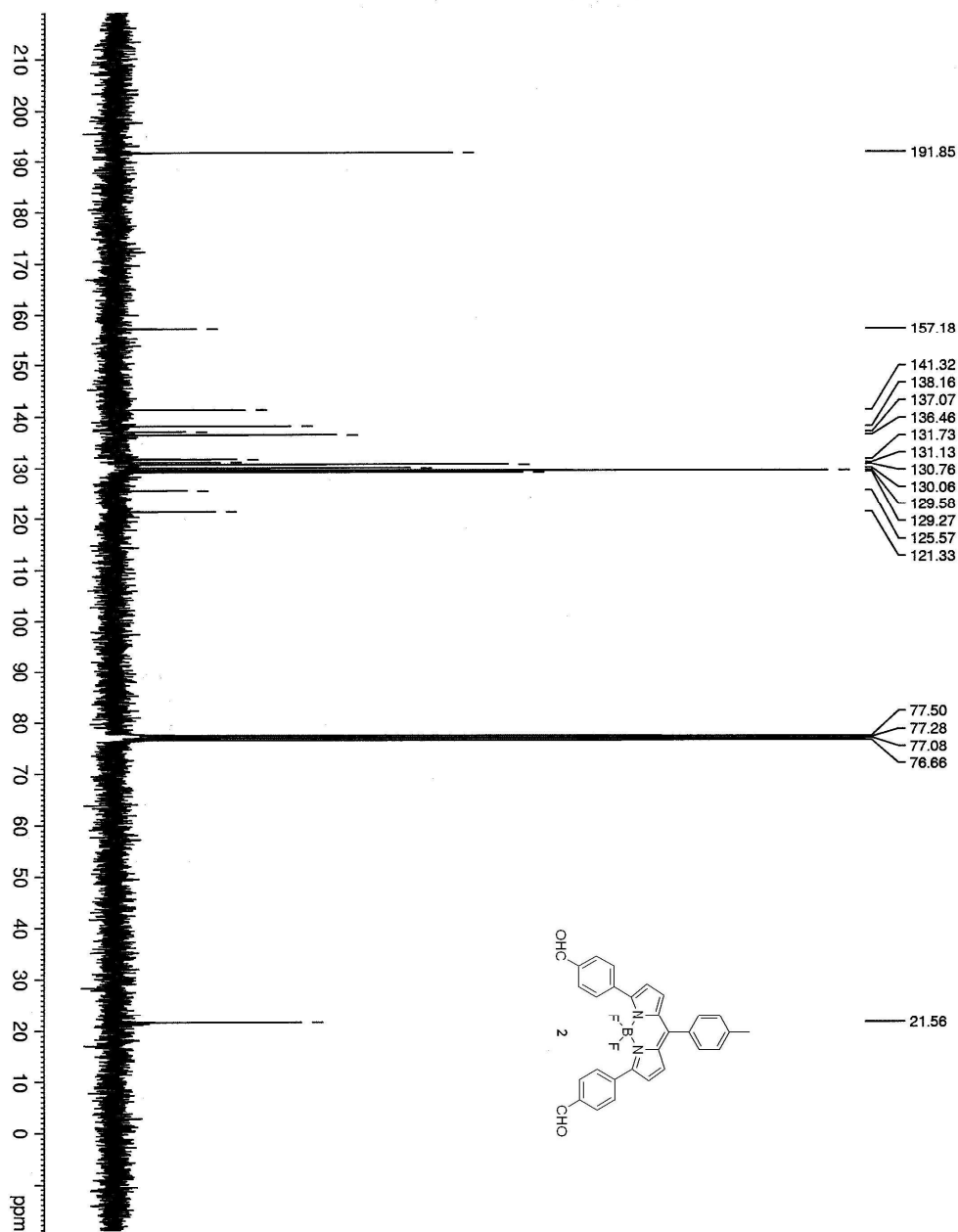
Combustion Analysis Data

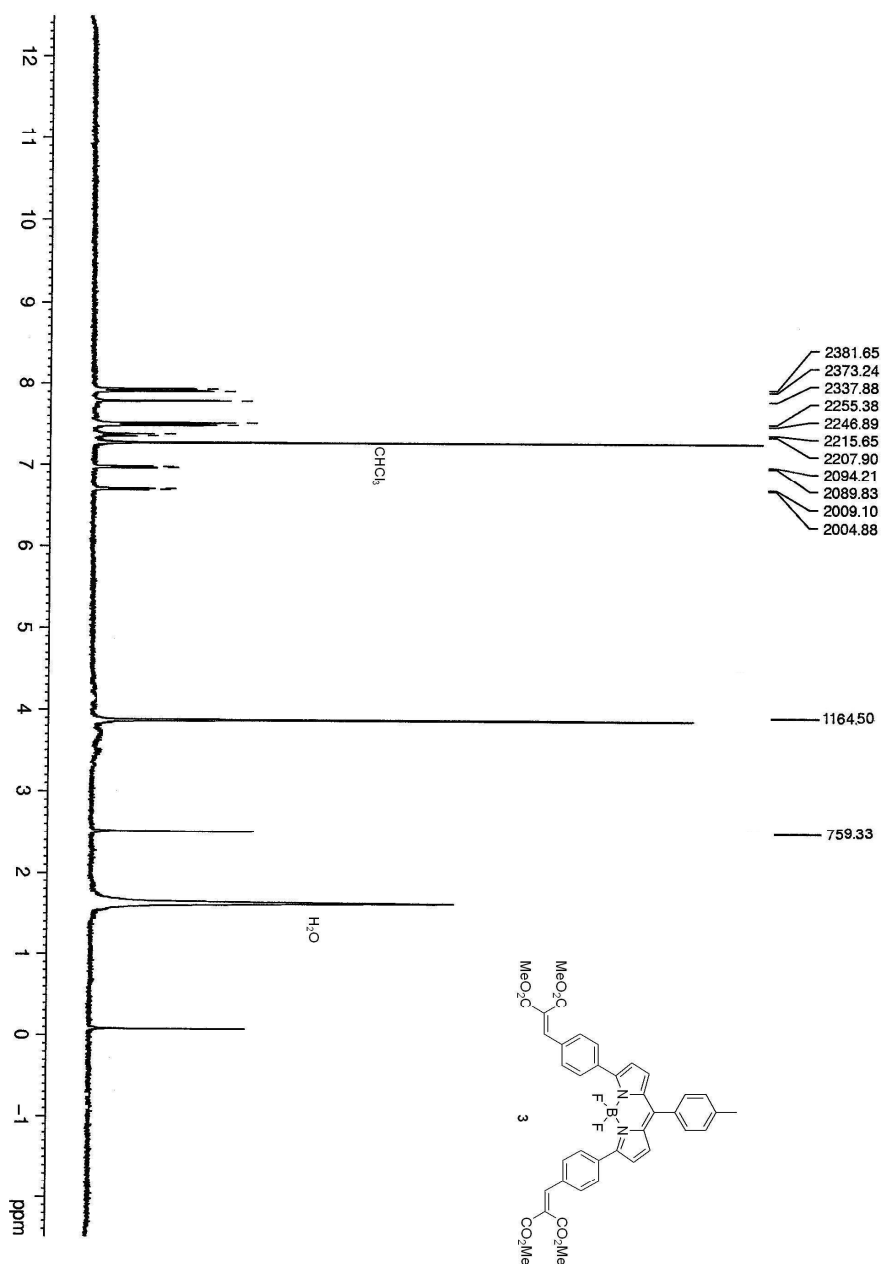
Compd	Molecular Formula	Calculated			Found		
		C	H	N	C	H	N
1	$C_{16}H_{11}BCl_2F_2N_2$	54.75	3.16	7.98	54.72	3.19	7.68
2	$C_{30}H_{21}BF_2N_2O_2$	73.49	4.32	5.71	73.18	4.59	5.52
3	$C_{40}H_{33}BF_2N_2O_8$	66.86	4.63	3.90	66.64	4.53	3.82
4	$C_{36}H_{21}BF_2N_6$	73.74	3.61	14.33	73.57	3.53	14.18

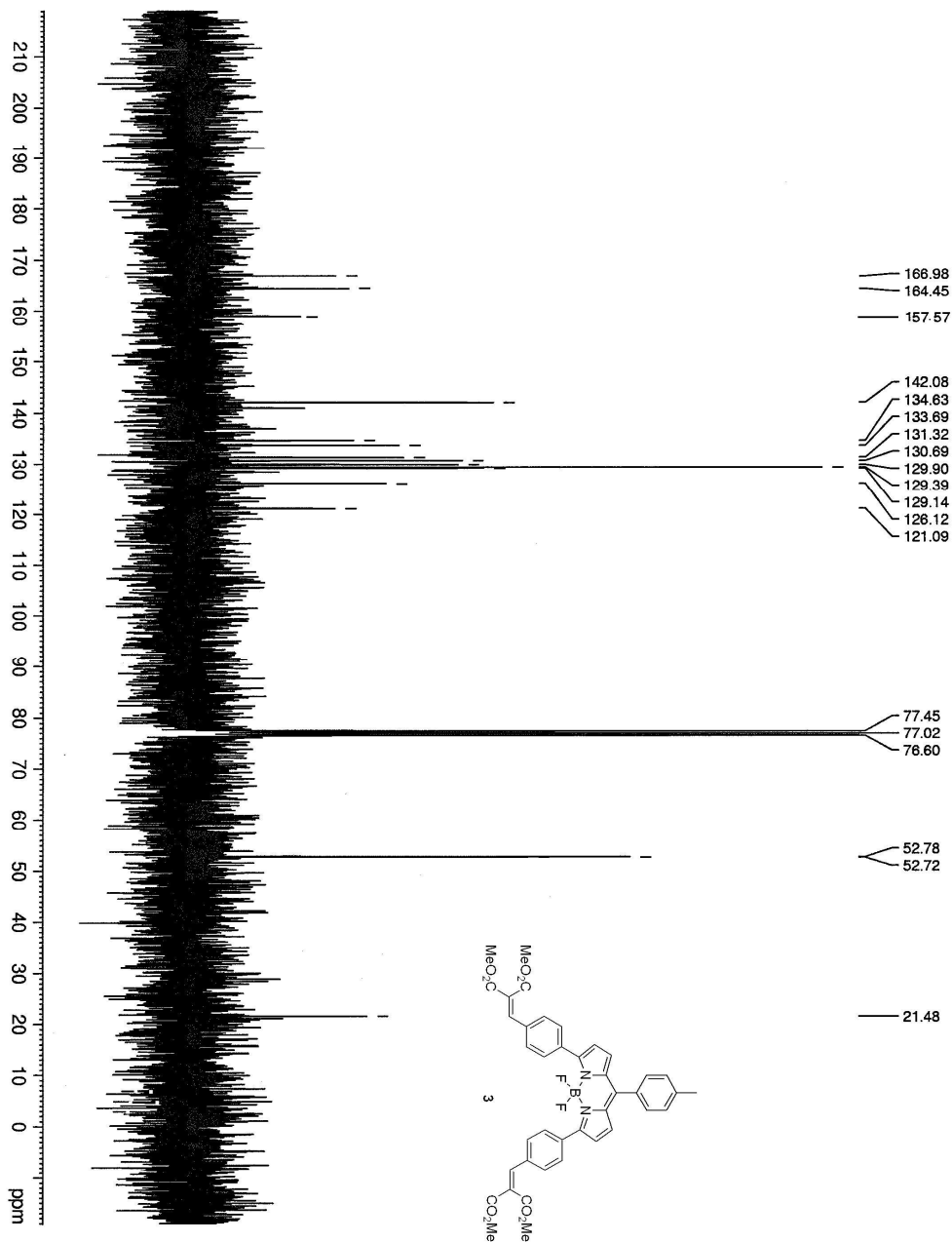
^1H and ^{13}C NMR spectra

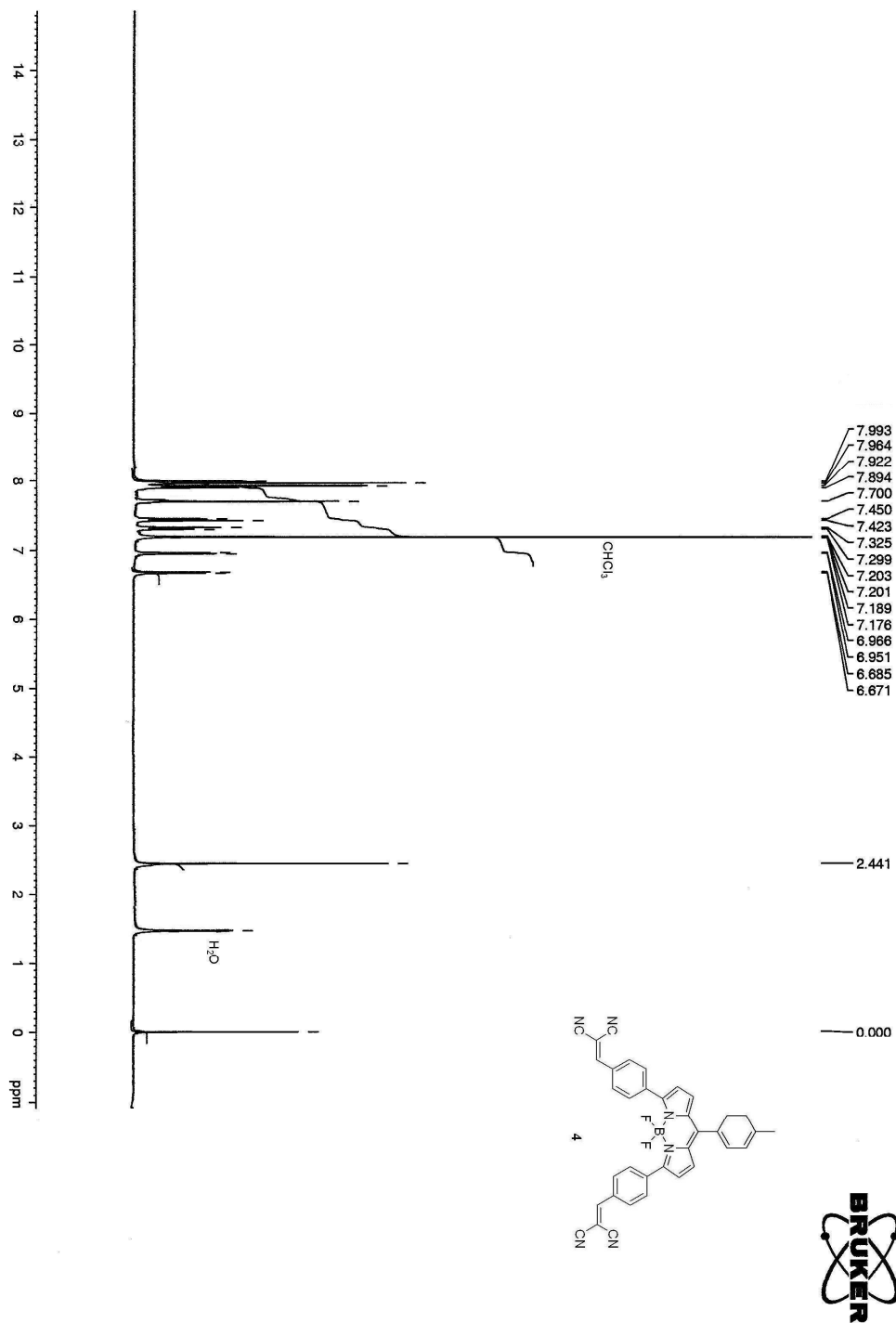


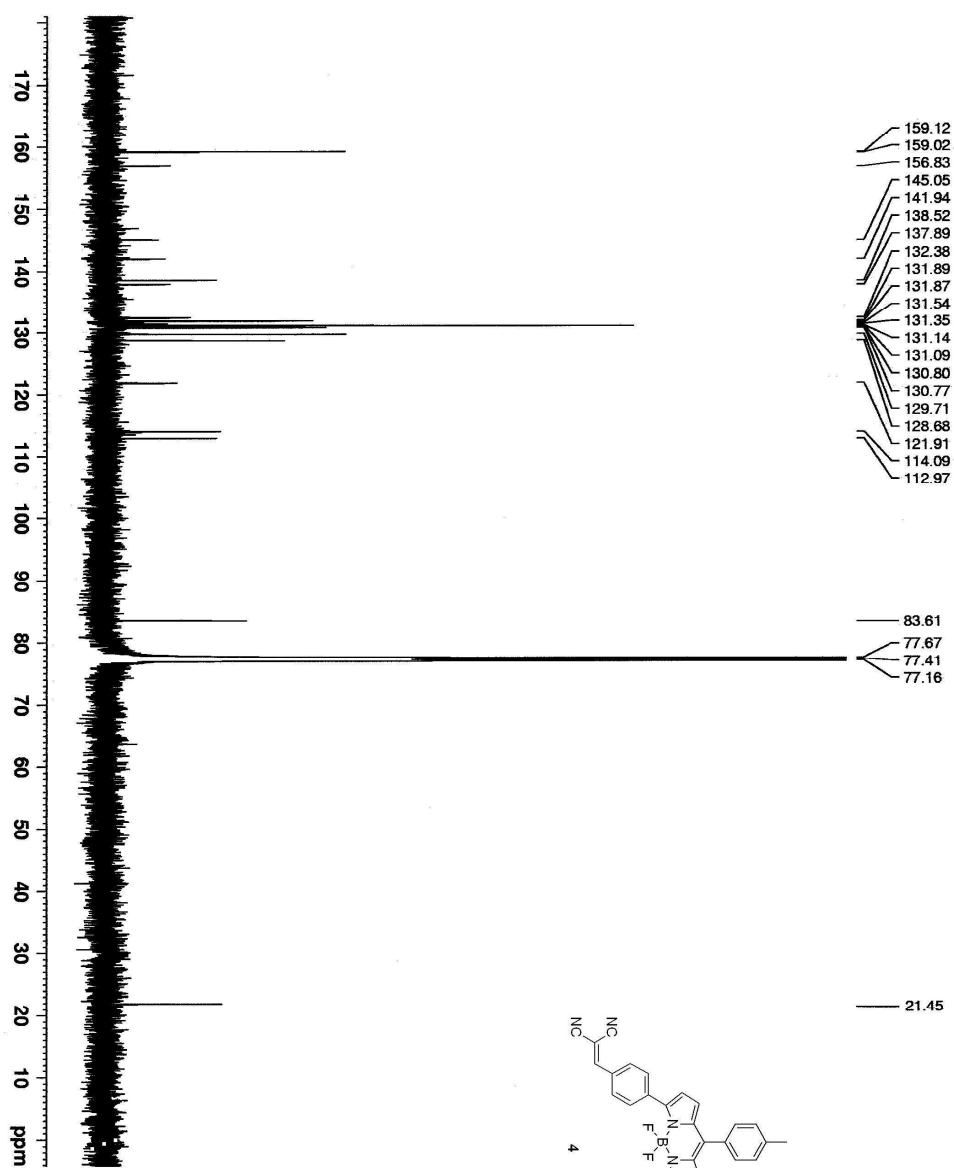




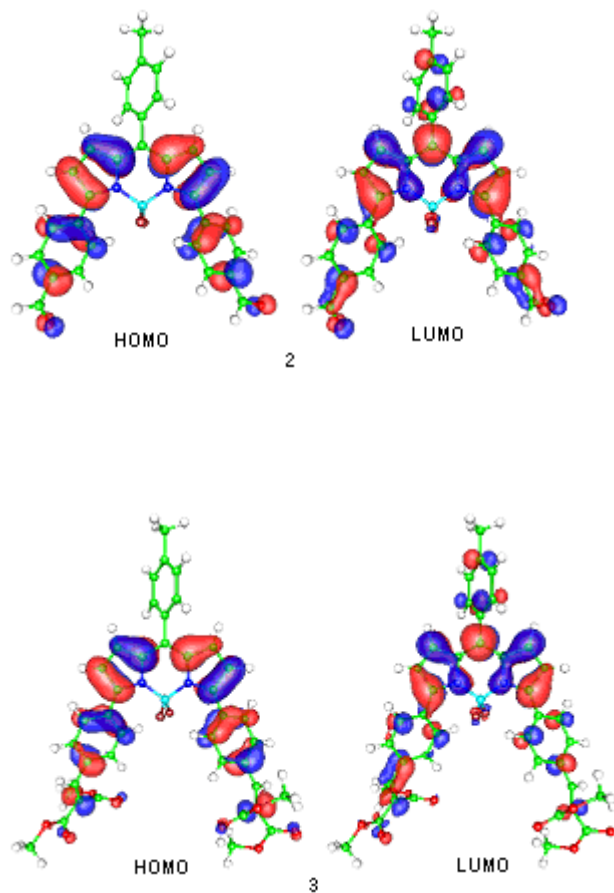








Electronic density maps of the HOMO and LUMO orbitals for dyes 2 and 3



References

- 1 W. Qin, T. Rohand, M. Baruah, A. Stefan, M. Van der Auweraer, W. Dehaen, N. Boens, *Chem. Phys. Lett.* 2006, **420**, 562-568.