

Deep Blue Asymmetrical Streptocyanine Dyes. Synthesis, Spectroscopic Characterizations and Ion-Specific Cooperative Adsorption at the Surface of TiO₂ Anatase Nanoparticles

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Supplementary Information

Detailed synthesis of all compounds

*3,6-Dibromo-9H-carbazole (4)*¹

Into a white suspension of carbazole **3** (2.00 g, 12.0 mmol, 1.00 eq.) in 120 mL of dry CH₂Cl₂ was poured dropwise, over a period of 1.5h, a solution of N-bromosuccinimide (NBS) (4.26 g, 23.9 mmol, 2.00 eq.) in dry DMF (30 mL), affording a yellow solution that was stirred at room temperature for 6 h. The solution was washed with deionized water (3 x 20 mL), dried onto MgSO₄ and the solvent was evaporated under reduced pressure and vacuum. The crude greenish oil was diluted in 10 mL acetone, and 200 mL of hexane were added and the system was placed in the refrigerator overnight for crystallization (3.55 g, 11.0 mmol, 93%).

¹H NMR (400 MHz, DMSO) δ: 11.61 (s, 1H), 8.44 (d, 2H, *J* = 1.72 Hz), 7.54 (dd, 2H, *J*₁ = 1.96 Hz, *J*₂ = 8.76 Hz), 7.48 (d, 2H, *J* = 8.80 Hz).

*3,6-Dimethoxy-9H-carbazole (5)*²

All glasswares were dried in an oven prior to any manipulation. Into a suspension of 3,6-dibromocarbazole (0.73 g, 2.26 mmol, 1.00 eq.) and CuI (1.70 g, 8.93 mmol, 3.95 eq.) in super dehydrated DMF (2.0 mL) was poured dropwise a solution of MeONa/MeOH (Na_(s)

(1.43 g, 28.3 eq.) was poured at 0 °C in dry MeOH in a 25.00 mL volumetric flask, and the volume of dry MeOH was completed to 25.00 mL afterwards) previously prepared, and the suspension turned yellow. The mixture was heated to reflux for 22 h, cooled to room temperature and poured in 100 mL of ethyl acetate. The suspension was filtered over a 2 cm high silica gel plug. The yellow filtrate was recovered and the solvent was removed under reduced pressure. Purification of the crude and silica gel column chromatography in CH₂Cl₂/Hexane (2:1, v/v) (*R_f* = 0.18) afforded **5** as a white solid (0.299 g, 1.32 mmol, 59%).

¹H NMR (400 MHz, DMSO) δ: 10.84 (s, 1H), 7.70 (s, 2H), 7.37 (dd, 2H, *J*₁ = 0.96 Hz, *J*₂ = 8.52 Hz), 7.02 (ddd, 2H, *J*₁ = 0.96 Hz, *J*₂ = 1.44 Hz, *J*₃ = 8.76 Hz), 3.88 (s, 6H).

*3,6-Dihydroxy-9H-carbazole (6)*³

A solid mixture of 3,6-dimethoxy-9H-carbazole **5** (0.22 g, 0.97 mmol) and pyridinium chloride (1.72 g, 14.9 mmol) was heated to 160 °C for 1 h, and the system was cooled down to room temperature. 50 mL of deionized water were added, and the aqueous phase was extracted thrice with 3 x 50 mL of ethyl acetate. The combined organic layers were dried onto Na₂SO₄, and the solvent was removed under reduced pressure. Purification of the light-pink crude by silica gel column chromatography with EtOAc/Hexane (1:1, v/v) as eluent (*R_f* = 0.31) afforded **6** as a white powder (0.17 g, 89%).

¹H NMR (400 MHz, DMSO) δ: 10.43 (s, 1H), 8.80 (s, 2H), 7.27 (d, 2H, *J* = 0.76 Hz), 7.19 (dd, 2H, *J*₁ = 0.76 Hz, *J*₂ = 8.76 Hz), 6.82 (ddd, 2H, *J*₁ = 1.44 Hz, *J*₂ = 2.20 Hz, *J*₃ = 8.76 Hz).

*4-(bis(4-(hexyloxy)phenyl)amino)benzaldehyde (7b)*⁴

Into a solution of 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-phenylaniline (0.40 g, 0.90 mmol) in 4.0 mL of anhydrous DMF was added dropwise and at 0 °C POCl₃ (0.80 mL, 8.57 mmol), the resulting mixture was stirred for 1 h, and heated to 95 °C for 2h. The mixture was poured into 100 mL of ice-water, neutralized with 25 wt% aqueous NaOH solution, and the aqueous phase was extracted with ethyl acetate (3 x 100 mL). The combined organic layers were back-extracted with deionized water (3 x 100 mL), dried over anhydrous MgSO₄ and the solvent was evacuated under reduced pressure. The dark brown crude was purified by silica gel column chromatography with CH₂Cl₂/Hexane (1:1 to 1:0, v/v) as eluent (*R_f* (CH₂Cl₂) = 0.34), affording the pure **7b** as a flickering yellow oil (0.38 g, 90%).

¹H NMR (400 MHz, CDCl₃) δ: 9.75 (s, 1H), 7.62 (d, 2H, *J* = 8.88 Hz), 7.11 (d, 4H, *J* = 8.96 Hz), 6.87 (d, 4H, *J* = 8.96 Hz), 6.84 (d, 2H, *J* = 8.84 Hz), 3.95 (t, 4H, *J* = 6.52 Hz), 1.78 (m,

4H), 1.47 (m, 4H), 1.35 (m, 8H), 0.91 (t, 6H, $J = 7.00$ Hz). ^{13}C NMR (400 MHz, CDCl_3) δ : 190.51, 157.18, 154.38, 138.83, 131.60, 128.23, 127.90, 116.87, 115.76, 68.40, 31.65, 29.32, 25.80, 22.66, 14.08. HRMS[FAB⁺, matrix: 3-nitrobenzyl alcohol, $\text{C}_{31}\text{H}_{39}\text{NO}_3^+$] Found 473.2937, Calcd 473.2930.

N,N-Diphenyl-4-vinylaniline (**8a**)⁵

N,N-(diphenylamino)benzaldehyde **7a** (2.00 g, 7.32 mmol) and methyltriphenylphosphonium iodide (3.36 g, 8.32 mmol, 1.14 eq.) were dissolved in DMF (20 mL) and the solution was stirred at room temperature for 30 min. Then potassium tertbutoxide (0.97 g, 8.66 mmol, 1.18 eq.) was dissolved in DMF (30 mL) and added dropwise to the solution. The reaction mixture was stirred for 1 h at room temperature and then heated to 95 °C for 13 h. After cooling down to room temperature, the reaction mixture was extracted with dichloromethane and washed with 1 M aqueous HCl solution. The organic phase was dried over MgSO_4 and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column chromatography with CH_2Cl_2 /Hexane (1:4 to 1:1, v/v) as eluent (R_f (1:1, v/v) = 0.88) to give a colorless oil that crystallizes on standing (1.70 g, 86%).

^1H NMR (400 MHz, DMSO) δ : 7.37 (d, 2H, $J = 8.80$ Hz), 7.30 (m, 6H), 7.05 (t, 2H, $J = 6.36$ Hz), 7.00 (d, 4H, $J = 8.32$ Hz), 6.91 (d, 2H, $J = 8.80$ Hz), 6.65 (dd, 1H, $J_1 = 17.60$ Hz, $J_2 = 10.76$ Hz), 5.68 (d, 1H, $J = 17.56$ Hz), 5.15 (d, 1H, $J = 10.76$ Hz). ^{13}C NMR (400 MHz, CDCl_3) δ : 147.85, 147.72, 136.45, 132.10, 129.45, 127.26, 124.58, 123.82, 123.12, 112.32.

4-(Hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-vinylphenyl)aniline (**8b**)⁶

Into a yellow suspension of compound **7b** (0.76 g, 1.59 mmol) and methyltriphenylphosphonium iodide (0.84 g, 2.07 mmol) in 13 mL THF was added a suspension of *t*-BuOK (0.48 g, 4.28 mmol) in 6 mL THF, and the system was stirred at room temperature for 5 h. Deionized water (100 mL) was poured inside the system, and the whole was extracted with ethyl acetate (4 x 100 mL). Drying of the combined organic layers with Na_2SO_4 and purification by silica gel chromatography with CH_2Cl_2 /Hexane (1:1, v:v) as eluent ($R_f = 0.77$) gave the light sensitive product as a clear oil (0.45 g, 60%).

^1H NMR (400 MHz, CDCl_3) δ : 7.24 (d, 2H, $J = 8.52$ Hz), 7.02 (d, 4H, $J = 8.56$ Hz), 6.87 (d, 2H, $J = 8.52$ Hz), 6.81 (d, 4H, $J = 8.56$ Hz), 6.62 (dd, 1H, $J_1 = 17.72$ Hz, $J_2 = 11.00$ Hz), 5.57 (dd, 1H, $J_1 = 17.72$ Hz, $J_3 = 1.24$ Hz), 5.08 (dd, 1H, $J_2 = 11.00$ Hz, $J_3 = 1.24$ Hz), 3.92 (t, 4H, $J = 6.72$ Hz), 1.77 (m, 4H), 1.47 (m, 4H), 1.35 (m, 8H), 0.91 (t, 6H, $J = 6.72$ Hz). ^{13}C NMR

(400 MHz, CDCl₃) δ : 155.70, 148.74, 140.89, 136.58, 130.02, 127.04, 126.74, 120.55, 115.43, 111.14, 68.38, 31.69, 30.41, 29.42, 25.84, 22.69, 14.10.

(E)-3-(4-(diphenylamino)phenyl)acrylaldehyde (**9a**)⁷

N,N-Diphenyl-4-vinylaniline **8a** (0.16 g, 0.57 mmol) was dissolved in 2.50 mL of dry DMF and Vilsmeier reagent that was prepared from 1.00 mL of dry DMF and 0.27 mL of phosphorus oxychloride, and then the mixture was kept at 60 °C for 24 h. The mixture was cooled down and poured into a 100 mL of dichloromethane and 100 mL of deionized water. The biphasic solution was neutralized using 25 wt% aqueous NaOH solution. Both layers were separated and the organic phase was extracted with deionized water and dried over anhydrous MgSO₄, and concentrated. Purification by silica gel column chromatography with CH₂Cl₂/Hexane (1:3 to 1:1, v/v) as eluent (R_f (1:1) = 0.17) yielded the product as a yellow viscous solid (83 mg, 49%).

¹H NMR (400 MHz, DMSO) δ : 9.59 (d, 1H, J = 7.84 Hz), 7.62 (d, 1H, J = 15.60 Hz), 7.61 (d, 2H, J = 8.80 Hz), 7.38 (dd, 4H, J_1 = 7.80 Hz, J_2 = 7.80 Hz), 7.17 (dd, 2H, J_1 = 1.24 Hz, J_2 = 7.80 Hz), 7.13 (dd, 4H, J_1 = 1.24 Hz, J_2 = 7.32 Hz), 6.88 (d, 2H, J = 8.80 Hz), 6.67 (dd, 1H, J_1 = 7.80 Hz, J_2 = 15.60 Hz). ¹³C NMR (400 MHz, CDCl₃) δ : 193.86, 152.78, 150.99, 146.77, 129.99, 129.76, 126.84, 126.19, 125.88, 124.63, 121.19.

(E)-3-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)acrylaldehyde (**9b**)

Into a solution of **8b** (0.45g, 0.947 mmol) in 4 mL dry DMF was poured dropwise a brown solution of Vilsmeier-Haack reagent made of POCl₃ (0.44 mL) in 1.7 mL dry DMF, and the system turned dark red. After heating to 60 °C for 23 h the system was allowed to cool down to room temperature and deionized water (100 mL) was added, and the pH was adjusted to 7 with a few drops of 25 wt% aqueous NaOH solution. The organic layer was extracted with another 3 x 100 mL deionized water. Removal of the solvent and purification by silica gel chromatography with CH₂Cl₂ as eluent (R_f = 0.33) afforded the pure product as an orange viscous oil (0.45g, 95%).

¹H NMR (400 MHz, CDCl₃) δ : 9.60 (d, 1H, J = 7.96 Hz), 7.36 (d, 1H, J = 15.88 Hz), 7.33 (d, 2H, J = 9.16 Hz), 7.09 (d, 4H, J = 8.52 Hz), 6.86 (d, 2H, J = 9.16 Hz), 6.84 (m, 4H), 6.54 (dd, 1H, J_1 = 15.88 Hz, J_2 = 7.96 Hz), 3.94 (t, 4H, J = 6.72 Hz), 1.78 (m, 4H), 1.46 (m, 4H), 1.34 (m, 8H), 0.91 (t, 6H, J = 6.72 Hz). ¹³C NMR (400 MHz, CDCl₃) δ : 193.93, 156.79, 153.28, 151.94, 139.32, 130.09, 127.82, 125.22, 125.02, 118.25, 115.67, 68.39, 31.66, 29.34, 25.80,

22.66, 14.08. **HRMS**[FAB⁺, matrix: 3-nitrobenzyl alcohol, C₃₃H₄₁NO₃⁺] Found 499.3081, Calcd 499.3086. **FTIR** (KBr, cm⁻¹): ν = 3326, 3182, 3038, 2953, 2919, 2869, 2850, 2732, 2516, 2359, 2238, 2015, 1889, 1673, 1593, 1560, 1504, 1469, 1434, 1390, 1366, 1327, 1293, 1240, 1190, 1167, 1128, 1115, 1059, 1028, 1010, 969, 938, 828, 814, 720, 677, 640, 607, 582, 525, 482, 456, 445, 419. melting point: 32.3(4) °C.

Example syntheses of a carbazolium dye: (R₁ = R₂ = H)

(E)-9-(3-(4-(diphenylamino)phenyl)allylidene)-9*H*-carbazol-9-ium tetrafluoroborate (**1H-BF₄**). Into a solution of carbazole **3** (18.6 mg, 0.111 mmol) and **9a** (36.6 mg, 0.122 mmol) in 4 mL of dry, freeze-pump-thawed acetonitrile was injected 42 wt% aqueous tetrafluoroboric acid (332 μL, 0.222 mmol), and the solution instantly turned dark blue. The system was stirred a further 15 min, and the acetonitrile was removed under reduced pressure and vacuum. The crude was taken with CH₂Cl₂ and recrystallized by slow elution with hexane as non-solvent, affording **1H-BF₄** as brilliant green spines (32.6 mg, 54.6%).

¹H NMR (400 MHz, CD₃CN) δ: 8.97 (d, 1H, *J* = 12.44 Hz), 8.36 (d, 1H, *J* = 13.40 Hz), 8.12 (d, 2H, *J* = 7.32 Hz), 8.11 (d, 2H, *J* = 8.04 Hz), 7.93 (dd, 1H, *J*₁ = 13.40 Hz, *J*₂ = 12.44 Hz), 7.60 (m, 6H), 7.53 (tt, 4H, *J*₁ = 7.80 Hz, *J*₂ = 2.44 Hz), 7.44 (tt, 2H, *J*₁ = 7.56 Hz, *J*₂ = 1.24 Hz), 7.39 (dt, 4H, *J*₁ = 8.52 Hz, *J*₂ = 1.24 Hz), 6.91 (d, 2H, *J* = 9.04 Hz). **¹³C NMR** (400 MHz, CD₃CN) δ: 170.27, 159.67, 154.60, 144.98, 131.85, 131.12, 129.90, 129.75, 129.12, 128.77, 128.37, 127.17, 122.78, 119.29, 113.59, 79.49, 66.60. **HRMS**[FAB⁺, matrix: 3-nitrobenzyl alcohol, **1H**⁺: C₃₃H₂₅N₂⁺] Found 449.2029, Calcd 449.2018. **HRMS**[FAB⁻, matrix: 3-nitrobenzyl alcohol, **BF₄**⁻] Found 87.0023, Calcd 87.0029. **FTIR** (KBr, cm⁻¹): ν = 3421, 3215, 3139, 3065, 3041, 2869, 2697, 2584, 2484, 2363, 2263, 1992, 1966, 1934, 1717, 1707, 1689, 1663, 1625, 1611, 1602, 1542, 1501, 1484, 1458, 1440, 1415, 1357, 1320, 1300, 1280, 1254, 1236, 1222, 1180, 1140, 1122, 1088, 1051, 992, 966, 944, 934, 914, 899, 859, 846, 835, 819, 784, 770, 761, 734, 718, 704, 696, 662, 640, 633, 622, 617, 588, 576, 542, 521, 483, 464, 449, 441, 428, 413, 406. thermal decomposition point: 221(3) °C.

(E)-9-(3-(4-(diphenylamino)phenyl)allylidene)-9*H*-carbazol-9-ium perchlorate (**1H-ClO₄**).

9a (35.9 mg, 0.120 mmol), carbazole **3** (18 mg, 0.108 mmol) and 60 wt% aqueous HClO₄ (21.6 μL, 0.215 mmol) in 4 mL of dry freeze-pump-thawed CH₃CN afforded **1H-ClO₄** (14.6 mg, 24.7%) as brown flickering spines.

¹H NMR (400 MHz, CD₃CN) δ: 8.98 (d, 1H, *J* = 12.52 Hz), 8.37 (d, 1H, *J* = 13.56 Hz), 8.14 (s, 1H), 8.13 (dd, 2H, *J*₁ = 7.28 Hz, *J*₂ = 1.60 Hz), 7.94 (dd, 1H, *J*₁ = 13.24 Hz, *J*₂ = 12.40 Hz), 7.63 (m, 6H), 7.55 (tt, 4H, *J*₁ = 8.00 Hz, *J*₂ = 1.68 Hz), 7.45 (tt, 2H, *J*₁ = 7.32 Hz, *J*₂ = 1.68 Hz), 7.40 (dt, 4H, *J*₁ = 7.20 Hz, *J*₂ = 1.56 Hz), 6.93 (d, 2H, *J* = 8.96 Hz). **HRMS**[FAB⁺, matrix: 3-nitrobenzyl alcohol, **1H**⁺: C₃₃H₂₅N₂⁺] Found 449.2022, Calcd 449.2018. **HRMS**[FAB⁻, matrix: 3-nitrobenzyl alcohol, **ClO₄**⁻] Found 98.9443, Calcd 98.9485. **FTIR** (KBr, cm⁻¹): ν = 3133, 3065, 2868, 2697, 2583, 2483, 2353, 2017, 1991, 1800, 1706, 1661, 1625, 1611, 1602, 1540, 1503, 1484, 1458, 1440, 1415, 1358, 1320, 1300, 1279, 1254, 1235, 1221, 1178, 1141, 1121, 1088, 1035, 1026, 991, 965, 934, 913, 898, 859, 845, 834, 816, 784, 761, 735, 718, 704, 664, 639, 623, 587, 576, 542, 527, 510, 498, 483, 449, 428, 419. thermal decomposition point: 268(3) °C.

Example synthesis of a 3,6-dimethoxy-carbazolium dye: (**R**₁ = H, **R**₂ = OMe)

(*E*)-9-(3-(4-(diphenylamino)phenyl)allylidene)-3,6-dimethoxy-9*H*-carbazol-9-ium tetrafluoroborate (**1OMe-BF₄**). Into a solution of 3,6-dimethoxy-9*H*-carbazole **5** (0.020 mg, 88.0 μmol) and **9a** (31.7 mg, 106 μmol) in 4 mL of dry benzonitrile was injected 42 wt% aqueous tetrafluoroboric acid (26.3 μL, 176 μmol), and the system turned instantly dark blue. The solution was stirred a further 15 min at room temperature, and the solvent was evacuated under reduced pressure and vacuum. The crude was diluted in CH₂Cl₂ and recrystallized by slow elution with hexane as non-solvent, affording **1OMe-BF₄** as brown flickering spines (31.5 mg, 60.0%).

¹H NMR (400 MHz, CD₃CN) δ: 8.76 (d, 1H, *J* = 11.96 Hz), 8.20 (d, 1H, *J* = 13.68 Hz), 8.12 (s, 2H), 7.89 (m, 2H), 7.75 (dd, 1H, *J*₁ = 13.68 Hz, *J*₂ = 12.20 Hz), 7.55 (m, 2H), 7.50 (d, 4H, *J* = 8.08 Hz), 7.40 (tt, 2H, *J*₁ = 7.56 Hz, *J*₂ = 1.24 Hz), 7.34 (dd, 4H, *J*₁ = 8.56 Hz, *J*₂ = 1.24 Hz), 7.11 (d, 2H, *J* = 9.04 Hz), 6.89 (d, 2H, *J* = 9.28 Hz), 3.93 (s, 6H). **¹³C NMR** (400 MHz, CD₃CN) δ: 168.34, 161.71, 158.17, 153.56, 145.52, 131.75, 131.12, 129.15, 128.74, 127.87, 127.17, 126.01, 121.98, 119.13, 113.37, 79.49, 66.60, 57.17. **HRMS**[FAB⁺, matrix: 3-nitrobenzyl alcohol, **1OMe**⁺: C₃₅H₂₉N₂O₂⁺] Found 509.2230, Calcd 509.2229. **HRMS**[FAB⁻, matrix: 3-nitrobenzyl alcohol, **BF₄**⁻] Found 87.0025, Calcd 87.0029. **FTIR** (KBr, cm⁻¹): ν = 3448, 3065, 3036, 2962, 2844, 2693, 2590, 2503, 2474, 2381, 2361, 2348, 2310, 2060, 1994, 1821, 1772, 1707, 1688, 1630, 1608, 1536, 1504, 1491, 1468, 1441, 1417, 1350, 1328, 1302, 1256, 1239, 1208, 1184, 1156, 1133, 1108, 1063, 1032, 1021, 1011, 997, 965, 927, 912, 904,

861, 822, 804, 773, 757, 748, 715, 703, 693, 664, 638, 611, 603, 574, 544, 532, 520, 504, 486, 457, 446, 420. thermal decomposition point: 202(3) °C.

(*E*)-9-(3-(4-(diphenylamino)phenyl)allylidene)-3,6-dimethoxy-9*H*-carbazol-9-ium perchlorate (**1OMe-ClO₄**). **9a** (19.3 mg, 64.5 μmol), 3,6-dimethoxy-9*H*-carbazole **5** (12.3 mg, 54.1 μmol) and 60 wt% aqueous perchloric acid (HClO₄) (11.9 μL, 0.108 mmol) in 5 mL of dry benzonitrile afforded **1OMe-ClO₄** (15.7 mg, 48%) as a glittering solid. ¹H NMR (400 MHz, CD₃CN) δ: 8.83 (d, 1H, *J* = 11.60 Hz), 8.23 (d, 1H, *J* = 13.44 Hz), 8.17 (s, 2H), 7.92 (s, 2H), 7.82 (dd, 1H, *J*₁ = 13.44 Hz, *J*₂ = 12.20 Hz), 7.62 (s, 2H), 7.50 (d, 4H, *J* = 7.92 Hz), 7.37 (m, 6H), 7.15 (d, 2H, *J* = 9.16 Hz), 6.91 (d, 2H, *J* = 8.56 Hz), 3.95 (s, 6H). HRMS[FAB⁺, matrix: 3-nitrobenzyl alcohol, **1OMe**⁺: C₃₅H₂₉N₂O₂⁺] Found 509.2235, Calcd 509.2229. HRMS[FAB⁻, matrix: 3-nitrobenzyl alcohol, **ClO₄**⁻] Found 98.9432, Calcd 98.9485. FTIR (KBr, cm⁻¹): ν = 3364, 3211, 3140, 3064, 3036, 3013, 2974, 2944, 2915, 2838, 2694, 2576, 2502, 2474, 2382, 2360, 2349, 2342, 2327, 2309, 2299, 2215, 2164, 2100, 2036, 2002, 1958, 1924, 1896, 1867, 1847, 1828, 1797, 1759, 1744, 1711, 1688, 1632, 1614, 1603, 1550, 1503, 1490, 1469, 1455, 1438, 1415, 1350, 1326, 1292, 1252, 1232, 1205, 1167, 1150, 1091, 1029, 999, 970, 932, 924, 899, 851, 826, 806, 795, 758, 749, 727, 715, 703, 664, 656, 638, 620, 599, 581, 563, 535, 518, 493, 483, 456, 450, 429, 419. thermal decomposition point: 184(2) °C.

Example synthesis of a 3,6-hydroxy-carbazolium dye: (R₁ = H, R₂ = OH)

(*E*)-9-(3-(4-(diphenylamino)phenyl)allylidene)-3,6-dihydroxy-9*H*-carbazol-9-ium perchlorate (**1OH-ClO₄**). Into a solution of 9*H*-carbazole-3,6-diol **6** (15.7 mg, 0.079 mmol) and **9a** (24.3 mg, 0.081 mmol) in 5 mL of dry benzonitrile was injected 60 μL of 60 wt% aqueous perchloric acid, and the solution instantly turned blue. The system was stirred for a further 5 min, and recrystallized by slow elution with benzene as non-solvent, affording the product as green flickering crystals in 20.3% yield.

¹H NMR (400 MHz, CD₃CN) δ: 8.80 (d, 1H, *J* = 12.20 Hz), 8.22 (d, 1H, *J* = 14.04 Hz), 8.13 (s, large, 1H), 7.91 (m, 2H), 7.78 (dd, 1H, *J*₁ = 13.44 Hz, *J*₂ = 12.24 Hz), 7.74 (s, 1H), 7.50 (m, 6H), 7.37 (m, 6H), 7.03 (d, 2H, *J* = 7.96 Hz), 6.90 (d, 2H, *J* = 9.16 Hz). HRMS[FAB⁺, matrix: 3-nitrobenzyl alcohol, **1OH**⁺: C₃₃H₂₅N₂O₂⁺] Found 481.1909, Calcd 481.1916. HRMS[FAB⁻, matrix: 3-nitrobenzyl alcohol, **ClO₄**⁻] Found 98.9456, Calcd 98.9485. FTIR (KBr, cm⁻¹): ν = 3408, 3127, 3071, 3041, 2865, 2769, 2689, 2575, 2470, 2380, 2364, 2349, 2328, 2045, 1991, 1930, 1874, 1627, 1606, 1536, 1504, 1491, 1465, 1449, 1415, 1387, 1361,

1344, 1322, 1301, 1289, 1265, 1253, 1234, 1163, 1142, 1118, 1025, 1002, 936, 916, 896, 886, 863, 828, 819, 812, 769, 753, 718, 697, 662, 637, 621, 611, 603, 570, 534, 516, 499, 478, 453, 441, 422, 409, 402. thermal decomposition point: 278(4) °C.

(E)-9-(3-(4-(diphenylamino)phenyl)allylidene)-3,6-dihydroxy-9*H*-carbazol-9-ium

tetrafluoroborate (**1OH-BF₄**). **9a** (54.1 mg, 0.181 mmol), 9*H*-carbazole-3,6-diol **6** (35.5 mg, 0.178 mmol) and 42 wt% aqueous tetrafluoroboric acid (HBF₄) (55.9 µL, 0.374 mmol) in 5 mL of dry benzonitrile afforded **1OH-BF₄** (97.5 mg, 96.2%) as green glittering platelets.

¹H NMR (400 MHz, CD₃CN) δ: 8.81 (d, 1H, *J* = 12.04 Hz), 8.23 (d, 1H, *J* = 13.76 Hz), 8.13 (s, 1H), 7.90 (d, 2H, *J* = 8.40 Hz), 7.82 (dd, 1H, *J*₁ = 13.76 Hz, *J*₂ = 12.08 Hz), 7.74 (s, 1H), 7.51 (m, 4H), 7.36 (m, 7H), 7.04 (d, 2H, *J* = 8.12 Hz), 6.91 (d, 2H, *J* = 9.24 Hz).

HRMS[FAB⁺, matrix: 3-nitrobenzyl alcohol, **1OH**⁺: C₃₃H₂₅N₂O₂⁺] Found 481.1913, Calcd 481.1916. HRMS[FAB⁻, matrix: 3-nitrobenzyl alcohol, **BF₄**⁻] Found 87.0014, Calcd 87.0029.

FTIR (solid state, KBr) ν = 3451, 3078, 2871, 2703, 2577, 2468, 1992, 1930, 1875, 1799, 1628, 1606, 1537, 1505, 1492, 1466, 1450, 1417, 1362, 1346, 1323, 1304, 1292, 1269, 1254, 1236, 1214, 1166, 1144, 1081, 1025, 1003, 937, 919, 895, 886, 863, 829, 813, 770, 753, 718, 698, 663, 638, 604, 571, 534, 523, 499, 481, 441, 424, 410. thermal decomposition point: 202(4) °C.

(E)-9-(3-(4-(diphenylamino)phenyl)allylidene)-3,6-dihydroxy-9*H*-carbazol-9-ium triflate

(**1OH-TfO**). **9a** (23.8 mg, 0.080 mmol), 9*H*-carbazole-3,6-diol **6** (14.4 mg, 0.072 mmol) and trifluoromethanesulfonic acid (TfOH) (12.7 µL, 0.144 mmol) in 5 mL of dry benzonitrile afforded **1OH-TfO** (31.0 mg, 68.0%) as green glittering platelets.

¹H NMR (400 MHz, CD₃CN) δ: 8.80 (d, 1H, *J* = 12.20 Hz), 8.22 (d, 1H, *J* = 14.04 Hz), 8.12 (s, 1H), 7.89 (d, 2H, *J* = 7.92 Hz), 7.80 (dd, 1H, *J*₁ = 12.20 Hz, *J*₂ = 11.60 Hz), 7.74 (s, 1H), 7.50 (m, 6H), 7.39 (m, 6H), 7.03 (d, 2H, *J* = 9.16 Hz), 6.90 (d, *J* = 9.16 Hz).

HRMS[FAB⁺, matrix: 3-nitrobenzyl alcohol, **1OH**⁺: C₃₃H₂₅N₂O₂⁺] Found 481.1929, Calcd 481.1916.

HRMS[FAB⁻, matrix: 3-nitrobenzyl alcohol, **TfO**⁻: CF₃SO₄⁻] Found 148.9525, Calcd 148.9520. FTIR (solid state, KBr) ν = 3418, 3129, 3060, 3039, 2859, 2759, 2691, 2563, 2510, 2453, 2380, 2308, 2010, 1970, 1885, 1810, 1742, 1666, 1630, 1607, 1577, 1538, 1489, 1466, 1449, 1440, 1413, 1383, 1334, 1318, 1288, 1264, 1254, 1234, 1168, 1024, 995, 973, 932, 922, 904, 873, 863, 834, 814, 758, 728, 719, 699, 664, 638, 609, 571, 534, 526, 516, 500, 476, 440. thermal decomposition point: 268(3) °C.

Example synthesis of a 3,6-dihydroxy-carbazolium dye: (R_1 = OHex, R_2 = OH)

(*E*)-9-(3-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)allylidene)-3,6-dihydroxy-9*H*-carbazol-9-ium triflate (**2OH-TfO**). Into a solution of 9*H*-carbazole-3,6-diol **6** (18.5 mg, 0.093 mmol) and **9b** (52.0 mg, 0.104 mmol) in 5 mL of dry acetonitrile was injected trifluoromethanesulfonic acid (16.3 μ L, 0.186 mmol), and the solution instantly turned dark blue. The system was stirred at r. t. for a further 15 min, and the solvent was evacuated under reduced pressure and vacuum. The crude product was solubilized in CH_2Cl_2 and recrystallized by slow elution with hexane as non-solvent, yielding the pure **2OH-TfO** as glittering green crystals (60.0 mg, 77.8%).

^1H NMR (400 MHz, CD_3CN) δ : 8.69 (d, 1H, J = 12.20 Hz), 8.12 (d, 1H, J = 13.92 Hz), 7.84 ~ 7.66 (m, 4H), 7.69 (dd, J_1 = 12.92 Hz, J_2 = 12.44 Hz), 7.36 (m, 2H), 7.23 (d, 4H, J = 8.80 Hz), 7.02 (m, 2H), 7.00 (d, 4H, J = 8.76 Hz), 6.79 (d, 2H, J = 9.00 Hz), 4.00 (t, 4H, J = 6.60 Hz), 1.76 (m, 4H), 1.45 (m, 4H), 1.34 (m, 8H), 0.91 (t, 6H, J = 6.84 Hz). **HRMS**[FAB⁺, matrix: 3-nitrobenzyl alcohol, **2OH**⁺: $\text{C}_{45}\text{H}_{49}\text{N}_2\text{O}_4^+$] Found 681.3687, Calcd 681.3687. **HRMS**[FAB⁻, matrix: 3-nitrobenzyl alcohol, **TfO**⁻: CF_3SO_4^-] Found 148.9525, Calcd 148.9520. **FTIR** (solid state, KBr) ν = 3332, 3071, 3046, 2954, 2932, 2869, 2699, 2577, 2476, 2379, 2349, 2326, 1982, 1766, 1628, 1607, 1547, 1504, 1469, 1448, 1415, 1364, 1351, 1321, 1304, 1271, 1242, 1173, 1161, 1144, 1032, 1011, 999, 959, 939, 907, 894, 863, 829, 813, 752, 734, 724, 712, 670, 664, 638, 608, 574, 544, 516, 482, 459, 442, 426, 418. thermal decomposition point: 192(3) °C.

Details of X-ray data collection and reduction for the single crystalline sample of **1H-ClO₄**, **1OH-BF₄** and **1OMe-ClO₄**

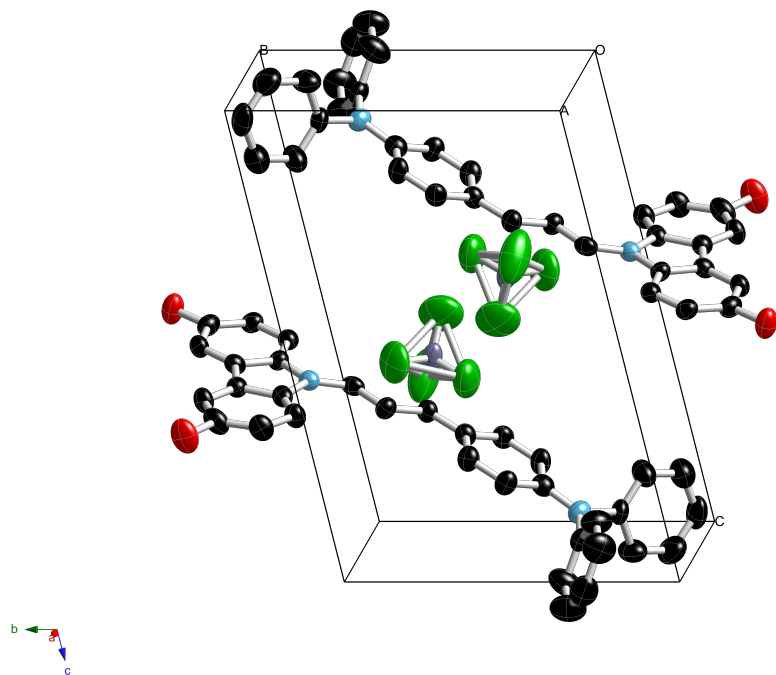
X-Ray diffraction data were collected for a dark green single crystal of **1H-ClO₄** and **1OMe-ClO₄** on a Rigaku AFC-7 Mercury CCD diffractometer with a graphite monochromated Mo-K α radiation ($\lambda = 0.71075 \text{ \AA}$) and a rotating anode generator (6.9 kW), and for a dark green single crystal of **1OH-BF₄** on a Rigaku AFC-8 Mercury CCD diffractometer with confocal X-ray mirror system [Mo-K α radiation ($\lambda = 0.71075 \text{ \AA}$)] and a rotating anode generator (0.8 kW). Lorentz and polarization corrections were applied. The structures of these compounds were solved by a direct method (SIR92),⁸ expanded by DIRDIF94,⁹ and refined on F with a full-matrix least squares analysis. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model [$d(\text{C-H}) = 0.95 \text{ \AA}$]. All the calculations were performed using the CrystalStructure crystallographic software package of the Molecular Structure Corporation.¹⁰ Crystal data and structure refinement parameters are given in Table S1.

Table S1 Crystallographic data for **1H-ClO₄**, **1OH-BF₄** and **1OMe-ClO₄**.

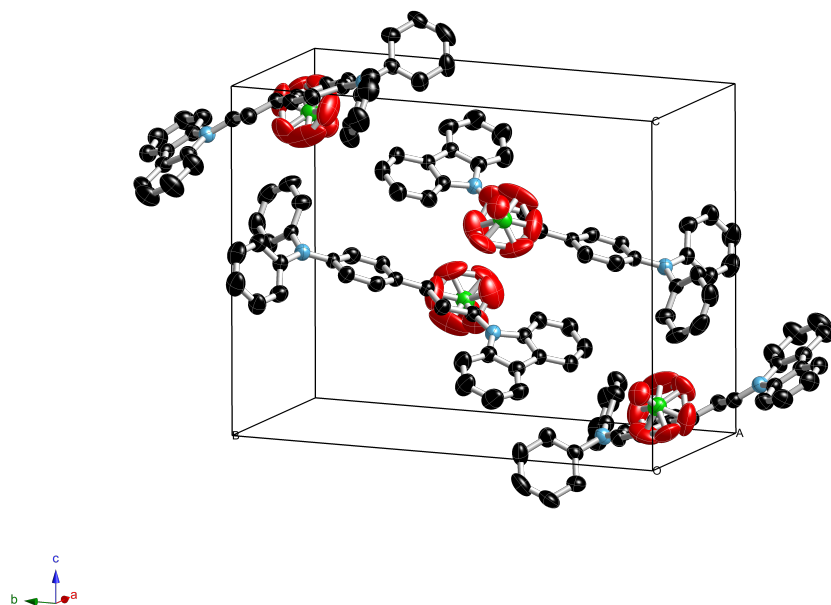
	1H-ClO₄	1OH-BF₄	1OMe-ClO₄
Temperature / K	293	293	293
Chemical Formula	C ₃₃ H ₂₅ ClN ₂ O ₄	C ₃₃ H ₂₅ BF ₄ N ₂ O ₂	C ₇₀ H ₅₈ Cl ₂ N ₄ O ₁₂
Formula weight	549.02	568.38	1218.15
Crystal colour, habit	dark green, platelet	dark green, platelet	dark green, platelet
Dimensions, mm	0.40 X 0.40 X 0.05	0.10×0.10×0.02	0.60 X 0.50 X 0.15
Crystal system	monoclinic	triclinic	monoclinic
<i>a</i> / Å	8.906(6)	9.469(4)	15.576(4)
<i>b</i> / Å	19.873(13)	10.302(6)	13.620(3)
<i>c</i> / Å	15.385(10)	14.831(7)	30.334(8)
α / °	90	100.015(12)	90
β / °	89.763(11)	93.889(10)	92.976(6)
γ / °	90	98.216(16)	90
<i>V</i> / Å ³	2723(3)	1403.6(11)	6427(3)
Space group, <i>Z</i>	<i>P</i> 2 ₁ / <i>c</i> , 4	<i>P</i> -1, 2	<i>P</i> 2 ₁ / <i>c</i> , 4
$\rho_{\text{calc.}}$ / g cm ⁻³	1.339	1.345	1.259
μ / cm ⁻¹	1.822	1.013	1.657
<i>F</i> ₀₀₀	1144.00	588.00	2544.00
2 θ_{max} / °	61.7	60.7	61.8
Range of Data	-11 ≤ <i>h</i> ≤ 11	-12 ≤ <i>h</i> ≤ 11	-12 ≤ <i>h</i> ≤ 22
	-26 ≤ <i>k</i> ≤ 28	-13 ≤ <i>k</i> ≤ 14	-18 ≤ <i>k</i> ≤ 18
	-12 ≤ <i>l</i> ≤ 22	-17 ≤ <i>l</i> ≤ 20	-43 ≤ <i>l</i> ≤ 36
Reflections collected	24021	15695	53990
Independent reflections	7629 (<i>R</i> _{int} = 0.059)	6914 (<i>R</i> _{int} = 0.080)	17926 (<i>R</i> _{int} = 0.034)
Reflections used [<i>I</i> > 2σ(<i>I</i>)]	3195	2616	7818
Number of variables	413	404	851

GOF on F	1.047	1.064	1.021
R_1	0.0933 [$I > 2\sigma(I)$]	0.1255 [$I > 2\sigma(I)$]	0.0941 [$I > 3\sigma(I)$]
wR_2	0.1107 [$I > 2\sigma(I)$]	0.1194 [$I > 2\sigma(I)$]	0.1188 [$I > 3\sigma(I)$]

(a)



(b)



(c)

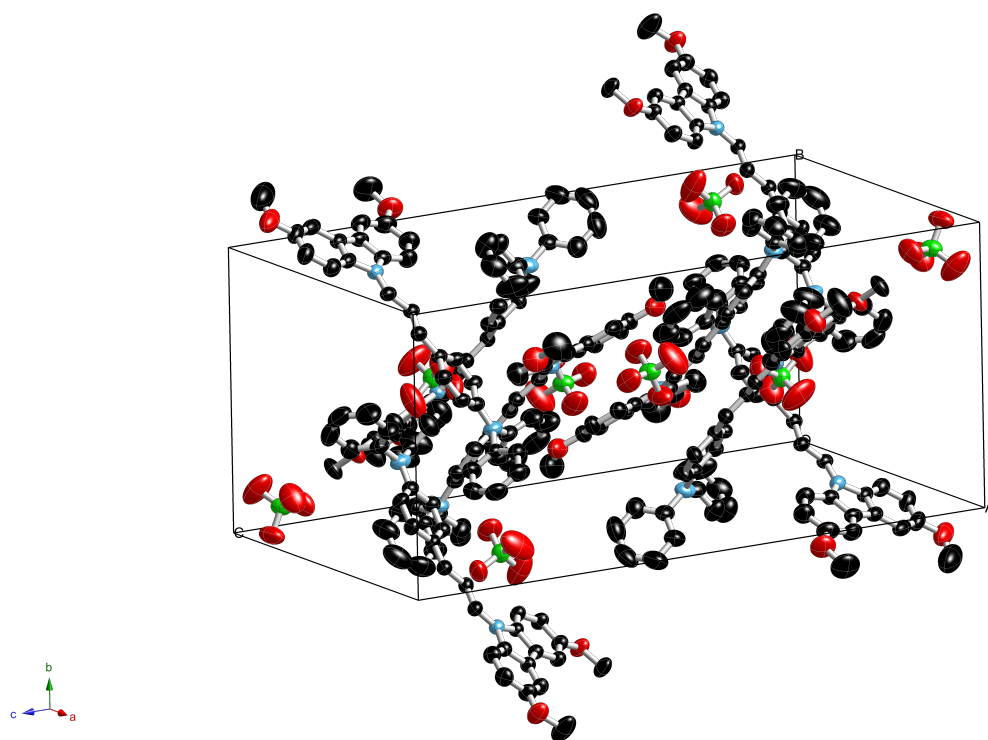


Figure S1. Crystal structures of dyes **1H-ClO₄** (a), **1OH-BF₄** (b) and **1OMe-ClO₄** (c). Hydrogen atoms are omitted for clarity.

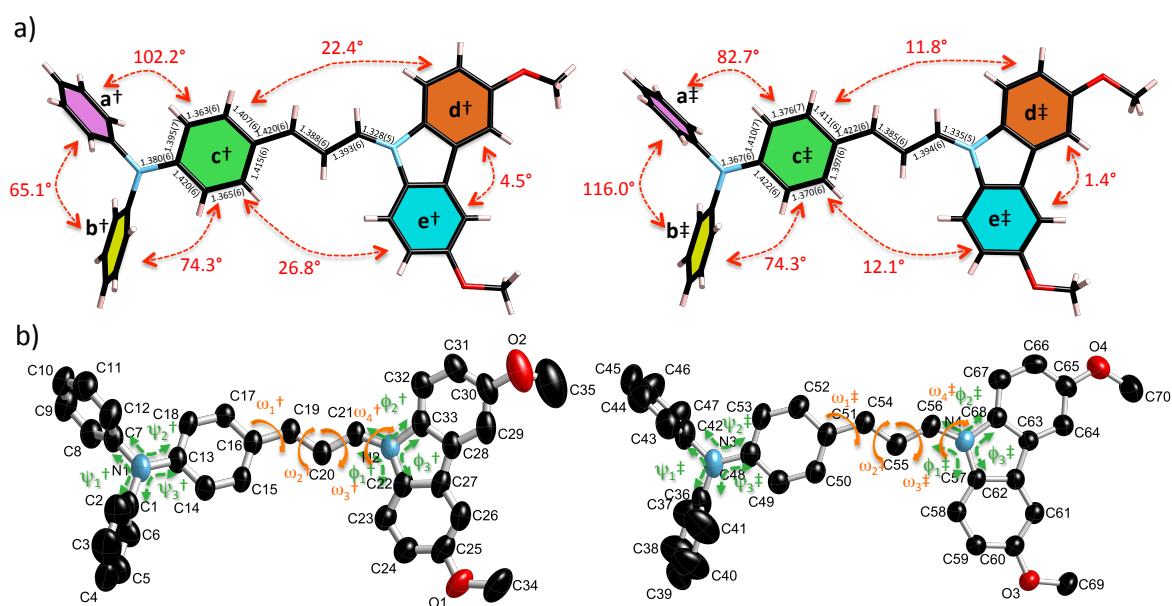


Figure S2. a) Single-crystal XRD-resolved coordinates of the two wireframe structures of the cationic chromophore **1OMe-ClO₄** present in the crystal (without counterions). Dihedral angle values between the colored molecular planes are written in degrees. Bond length of the bonds belonging to the $N_1 \leftrightarrow N_2$ π -conjugated chain are in Angstroms (Å). The number in brackets represents the error on the last digit. b) ORTEP drawings of the molecular structures represented thereabove. Hydrogen atoms were omitted for clarity. Black = Carbon, Blue = Nitrogen, Red = Oxygen.

Table S2. Values of the bond angles ψ_i , ϕ_i , dihedral angles between least-squares planes a, b, c, d, e and deviation from planarity of the torsion angles ω_i .

Dye	1H-ClO ₄	1OH-BF ₄ (')	1OMe-ClO ₄ (†)	1OMe-ClO ₄ (‡)
ϕ_1	130.2(5)	122.6(5)	130.4(4)	130.8(3)
ϕ_2	122.0(5)	130.0(6)	121.9(4)	121.3(3)
ϕ_3	107.8(4)	107.2(5)	107.4(4)	107.9(3)
ψ_1	116.8(4)	117.3(6)	118.1(4)	117.2(4)
ψ_2	119.1(5)	120.8(5)	119.2(4)	120.7(4)
ψ_3	124.0(5)	121.8(5)	122.7(4)	122.1(4)
ω_1	11.3(8)	2.7(10)	0.6(4)	2.6(4)
ω_2	5.6(5)	5.3(5)	7.6(4)	4.6(4)
ω_3	5.9(9)	5.8(5)	4.3(4)	5.4(4)
ω_4	4.7(4)	7.0(5)	13.0(4)	3.6(4)
a $\wedge$ b	84.1	69.3	65.1	116.0
a $\wedge$ c	72.1	68.3	102.2	82.7
b $\wedge$ c	52.0	89.5	74.3	74.3
c $\wedge$ d	18.9	18.0	22.4	11.8
c $\wedge$ e	22.3	17.5	26.8	12.1
d $\wedge$ e	4.7	3.7	4.5	1.4

All values are written in °. The number in brackets represents the experimental error on the last digit.

Cyclic voltammetry of the chromophores

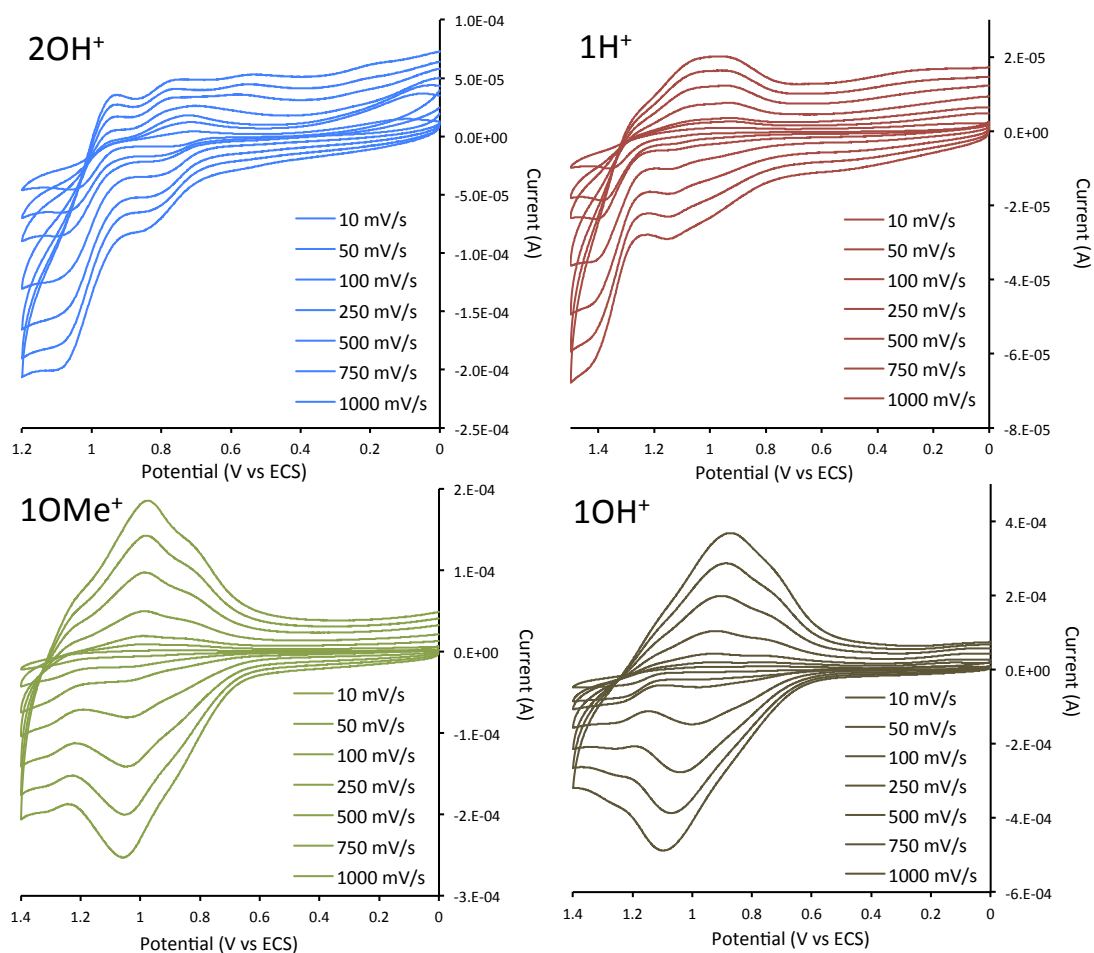


Figure S3: Cyclic voltammograms of the **2OH⁺**, **1OH⁺**, **1OMe⁺** and **1H⁺** chromophores. Conditions for the experiments were as described in Table 1. Redox potentials were extracted from the above displayed curves drawn, from the least sensitive to the most at 10, 50, 100, 250, 500, 750 and 1000 mV sec⁻¹.

FTIR spectroscopy of the dyes in solid state and dyes@TiO₂

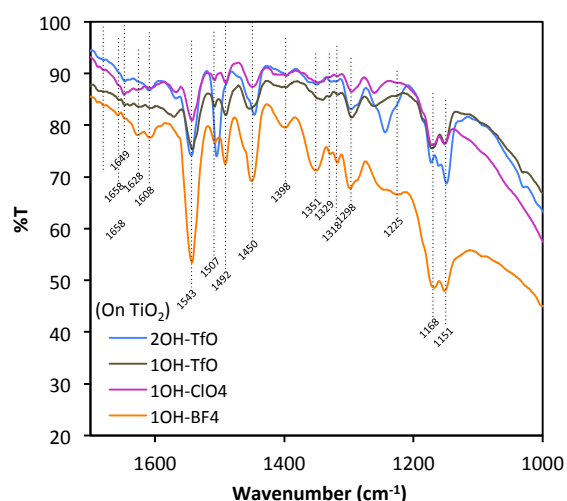


Figure S4. Highlight of the FTIR spectra of the dyes **2OH-TfO** (blue), **1OH-TfO** (gray), **1OH-CfO₄** (purple) and **1OH-BF₄** (orange) adsorbed on nanocrystalline TiO₂ on KBr.

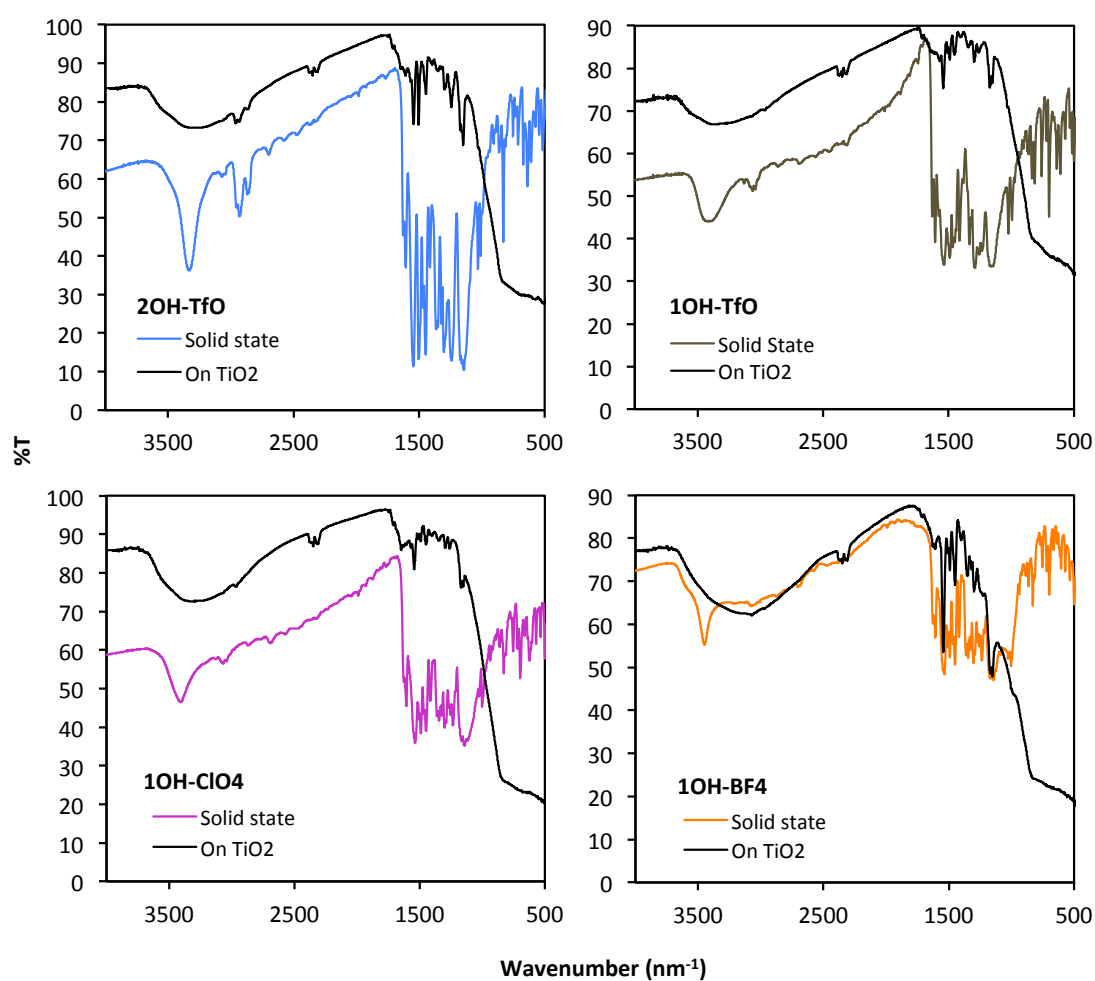


Figure S5. FTIR spectra of the dyes **2OH-TfO**, **1OH-TfO**, **1OH-CfO₄** and **1OH-BF₄** powdered in KBr (colored spectra) and adsorbed on nanocrystalline TiO₂ on KBr (black).

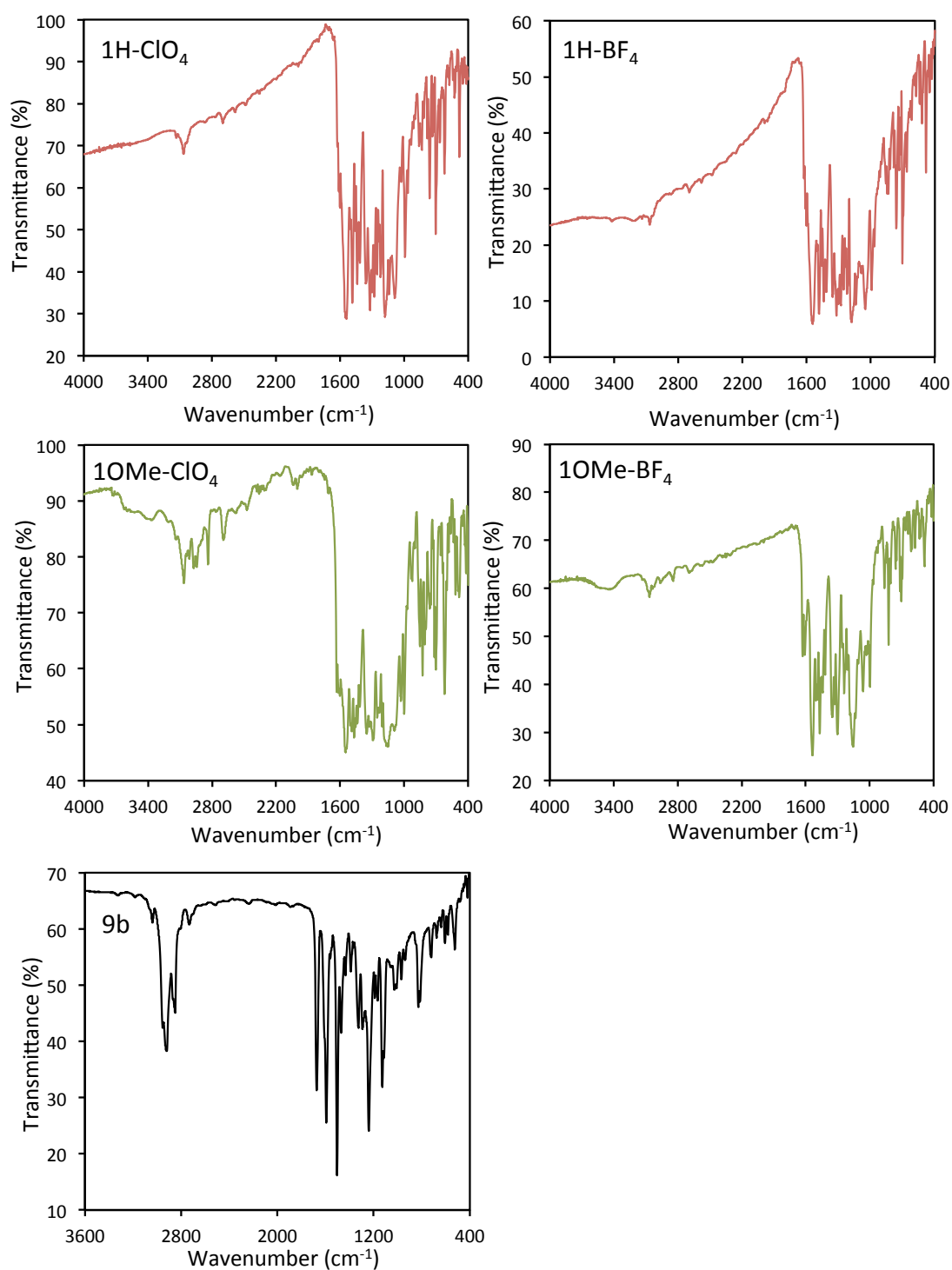


Figure S6. FTIR spectra of the dyes **1H-ClO₄**, **1H-BF₄**, **1OMe-ClO₄**, **1OMe-BF₄** and **9b** powdered in KBr.

Raw plotting of the intensity of the zeta potential values

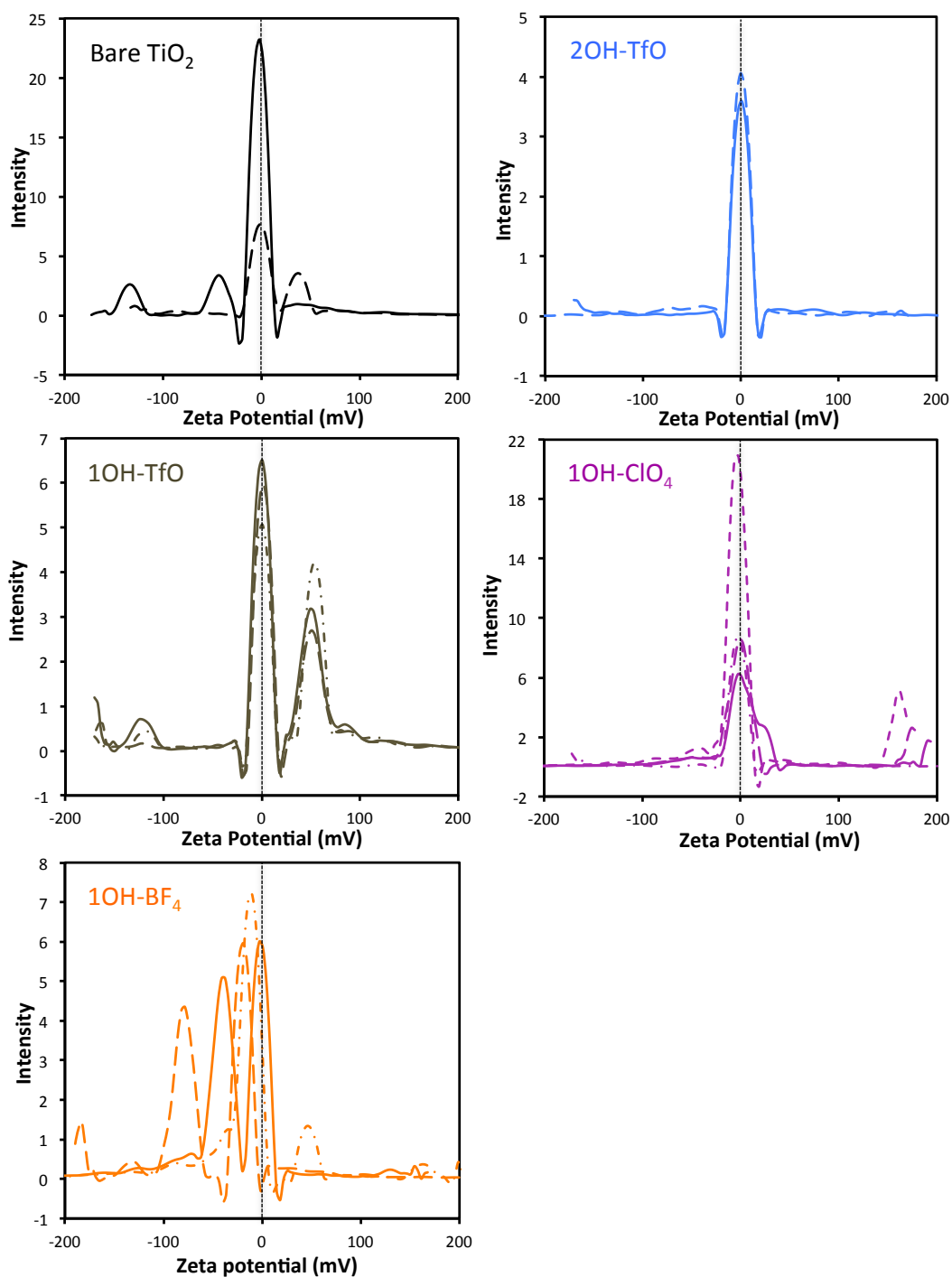


Figure S7. Raw plotting of the intensity of the ζ potential values for each sample. The plots outline the dispersity of the measures for determination of the ζ potential values for each sample. All measurements were performed on highly diluted colloidal suspensions in anhydrous conditions, and the ζ potential values displayed in **Table 3** were determined by the average of at least two consistent measurements.

Data on the radii of counterions

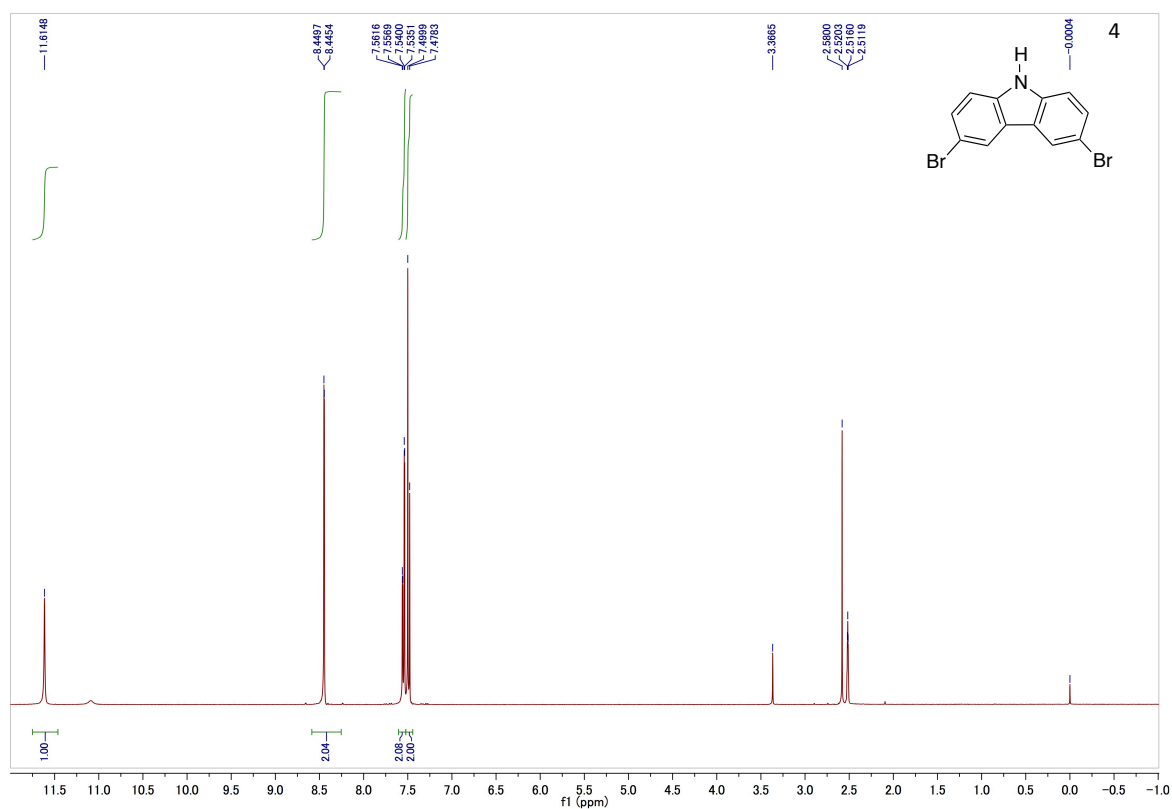
Table S3. Effective and thermochemical radii of counterions.

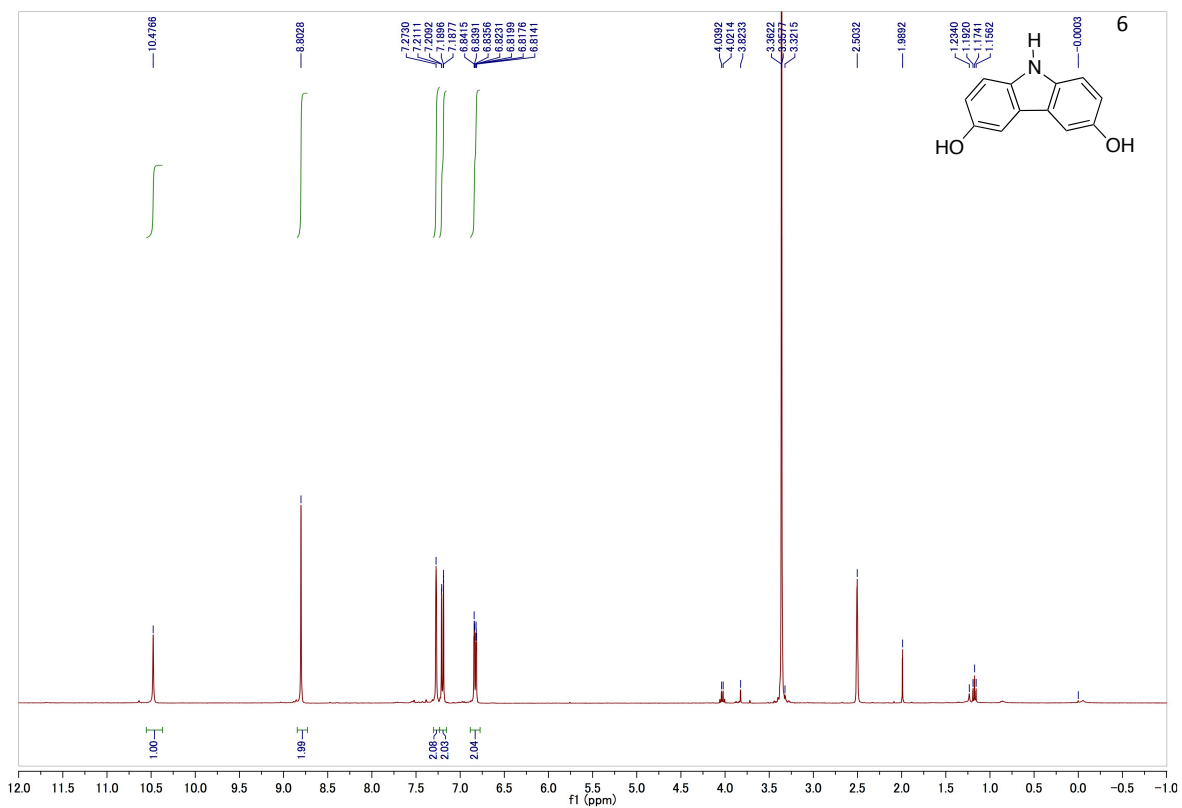
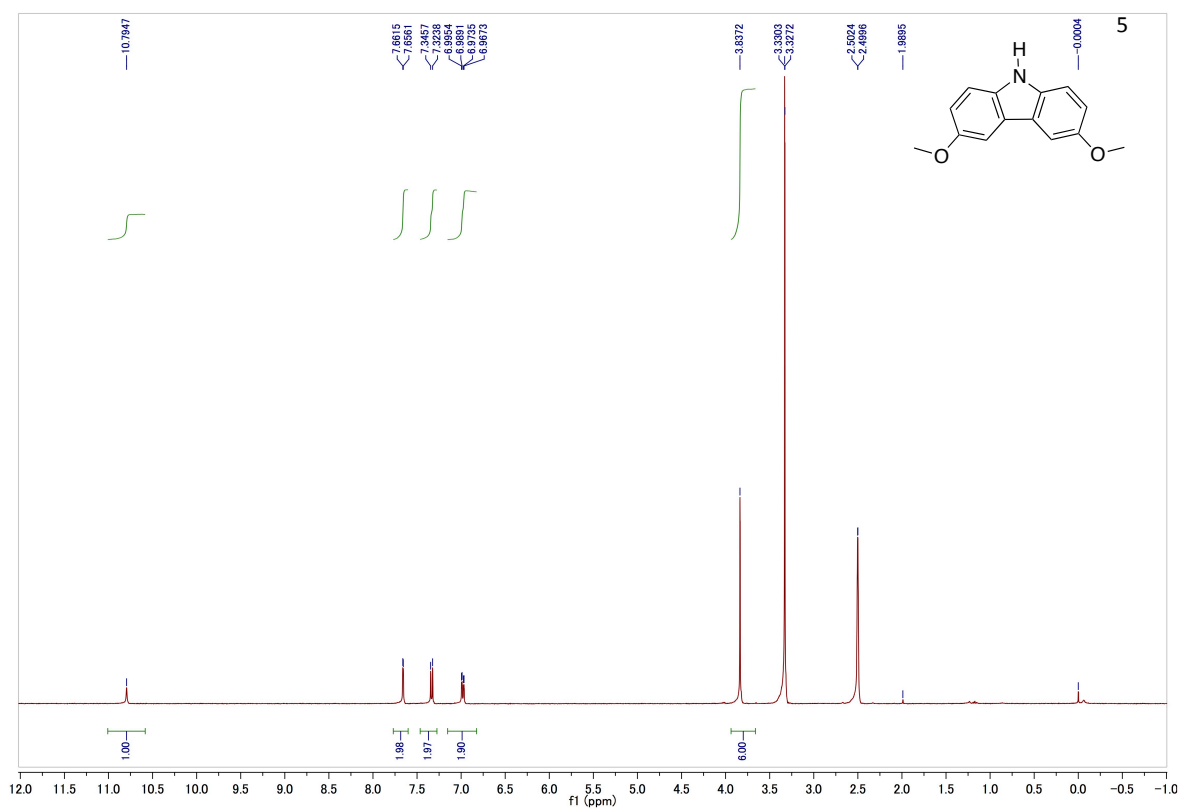
Anion	$r_{\text{eff}} (\text{\AA})^i$	$r_{\text{T}} (\text{\AA})^j$
TfO ⁻	3.07	-
ClO ₄ ⁻	2.31	2.25
BF ₄ ⁻	-	2.05

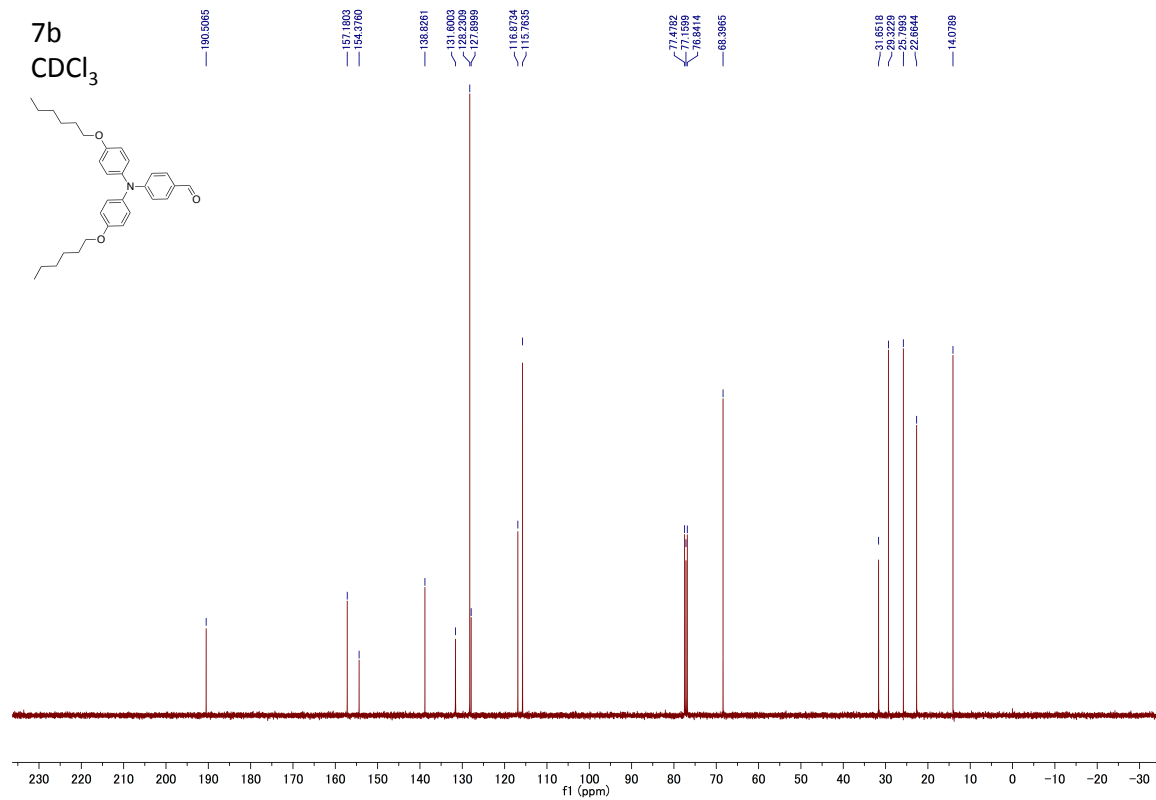
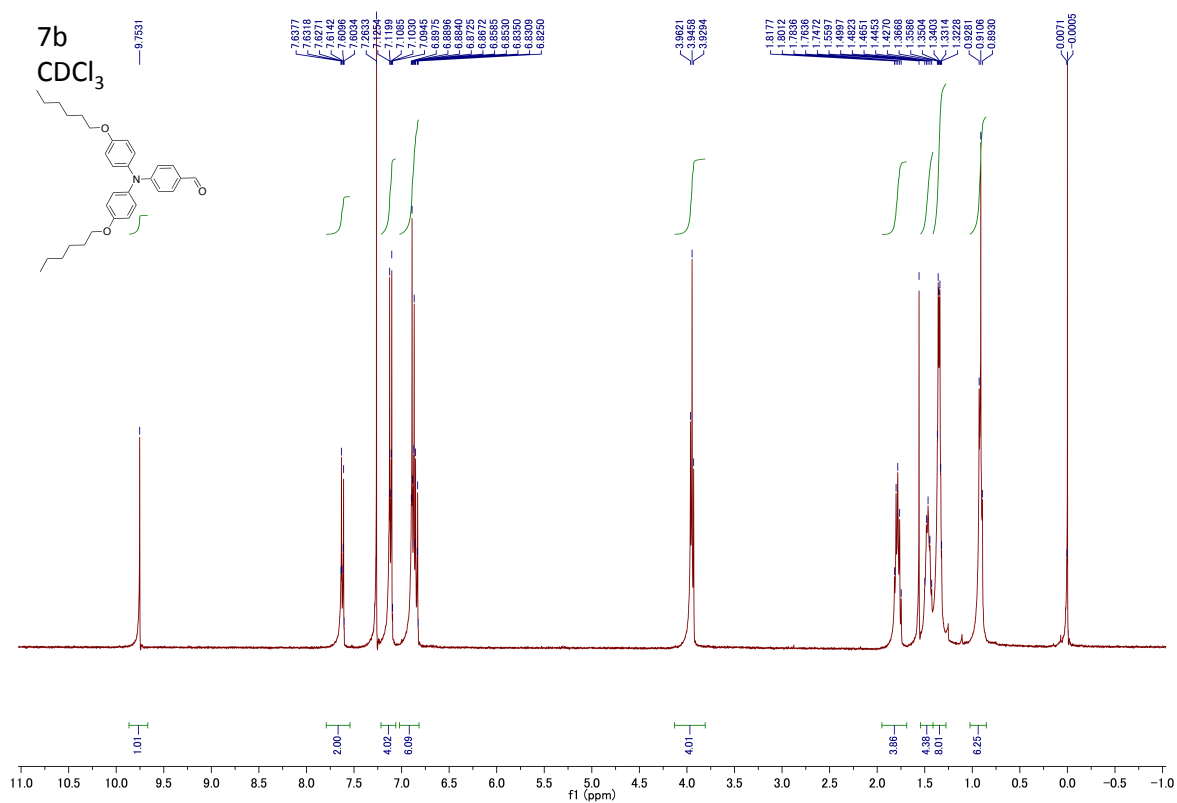
ⁱ Effective radii of anions reported in Å from the work of Champeney & al.¹¹

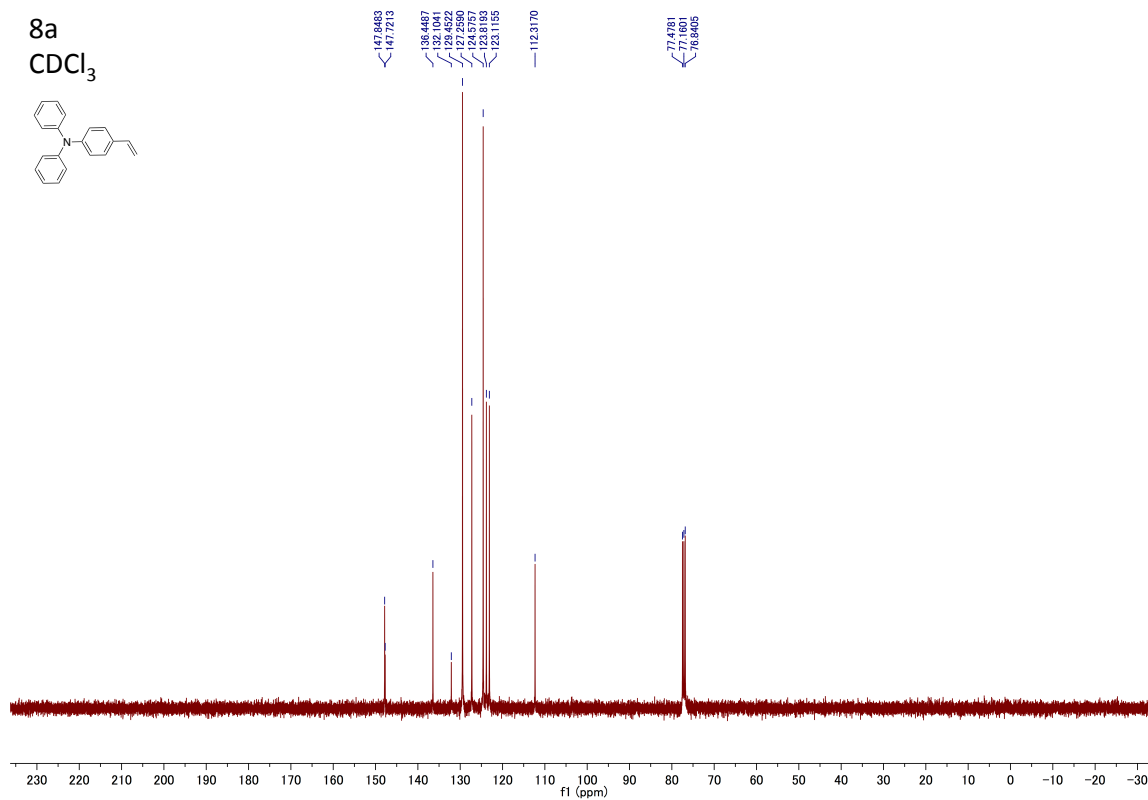
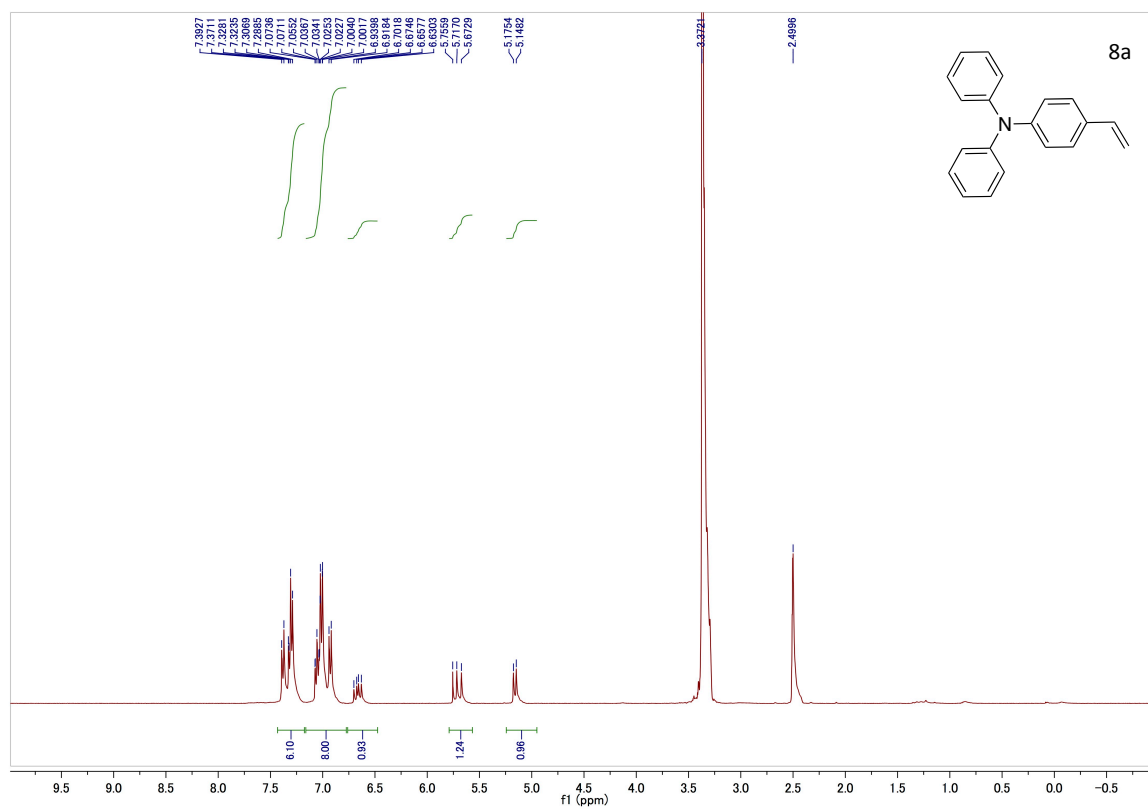
^j Thermochemical radius reported in Å from the work of Jenkins & al.¹²

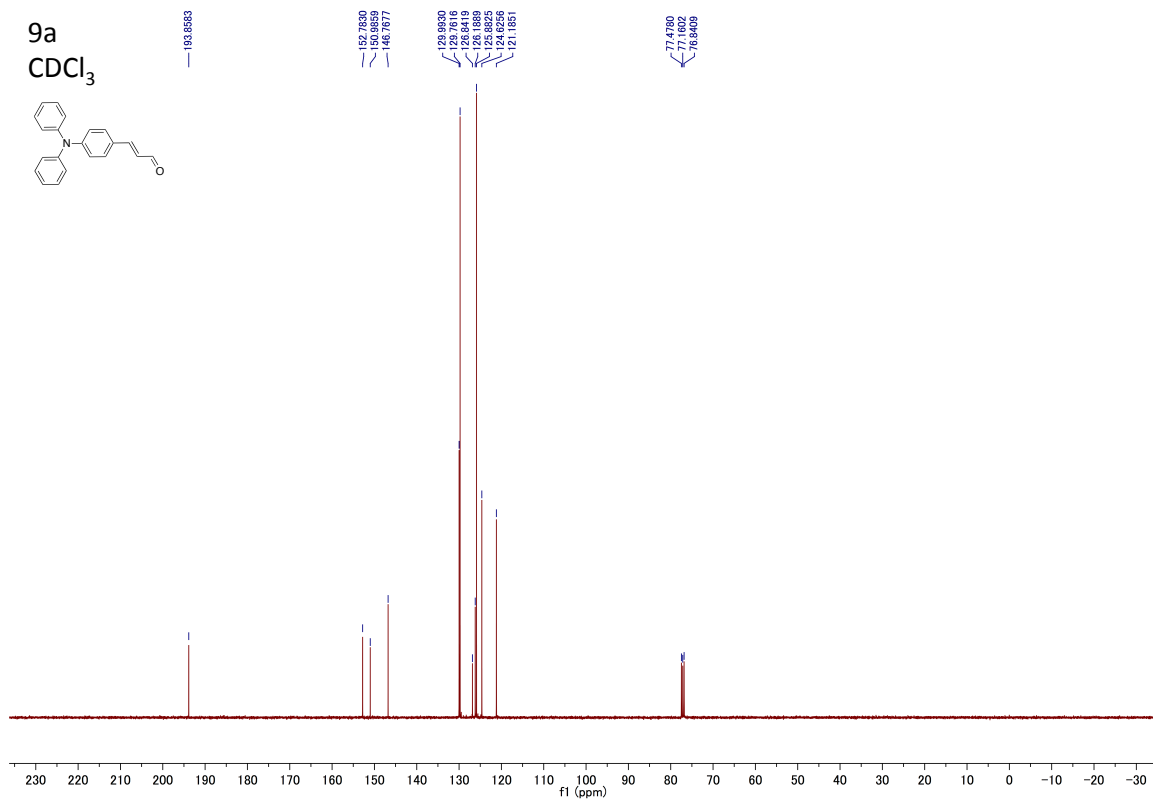
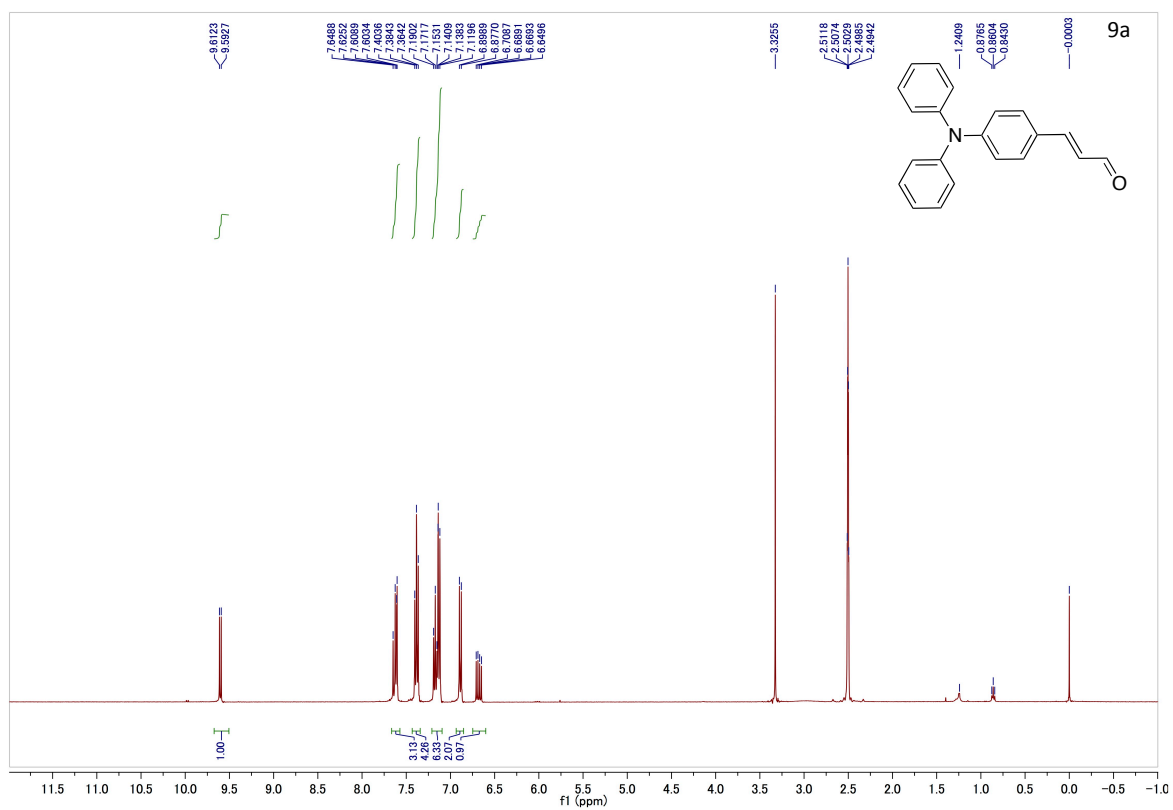
^1H NMR and ^{13}C NMR spectra of chromophores and synthesis intermediates

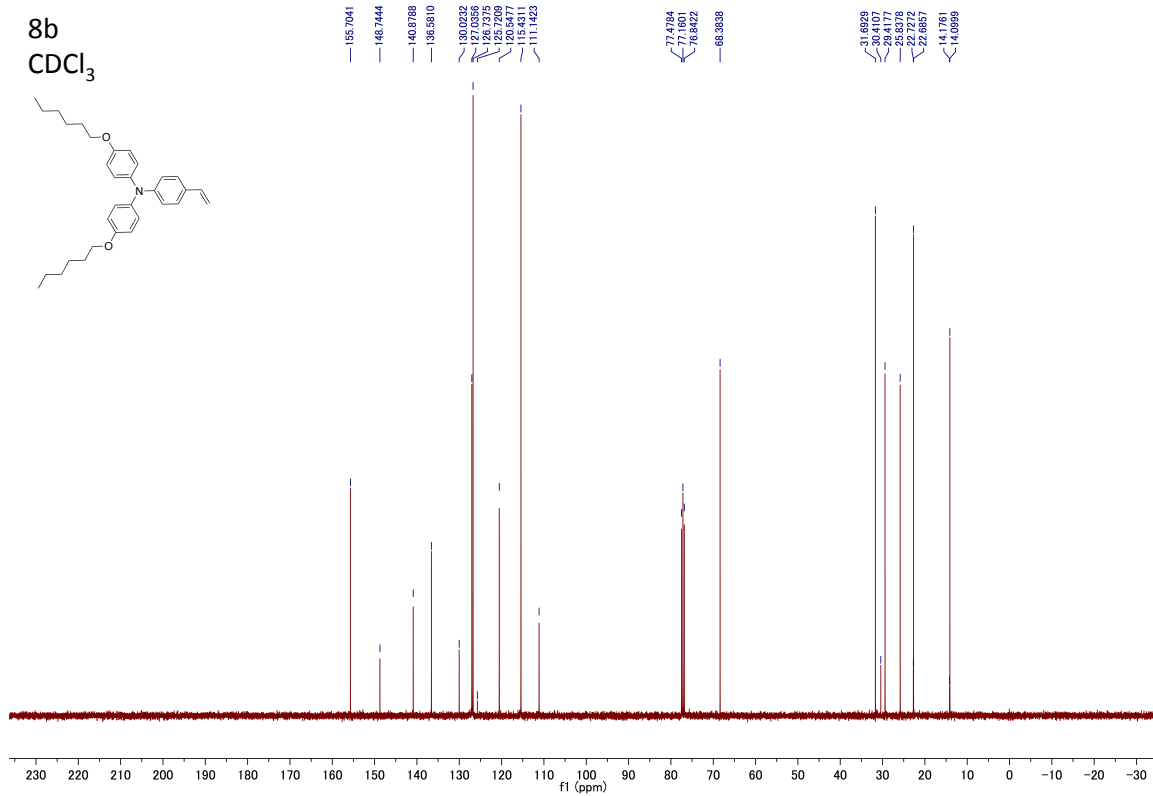
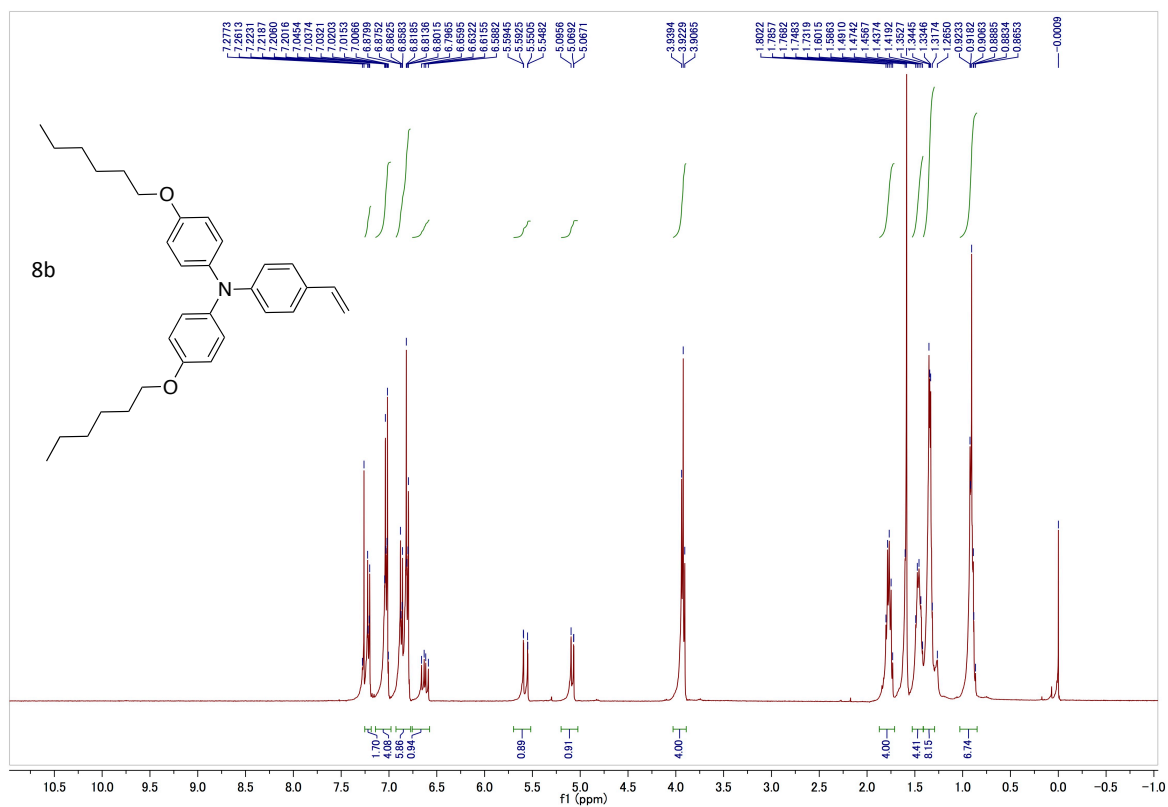


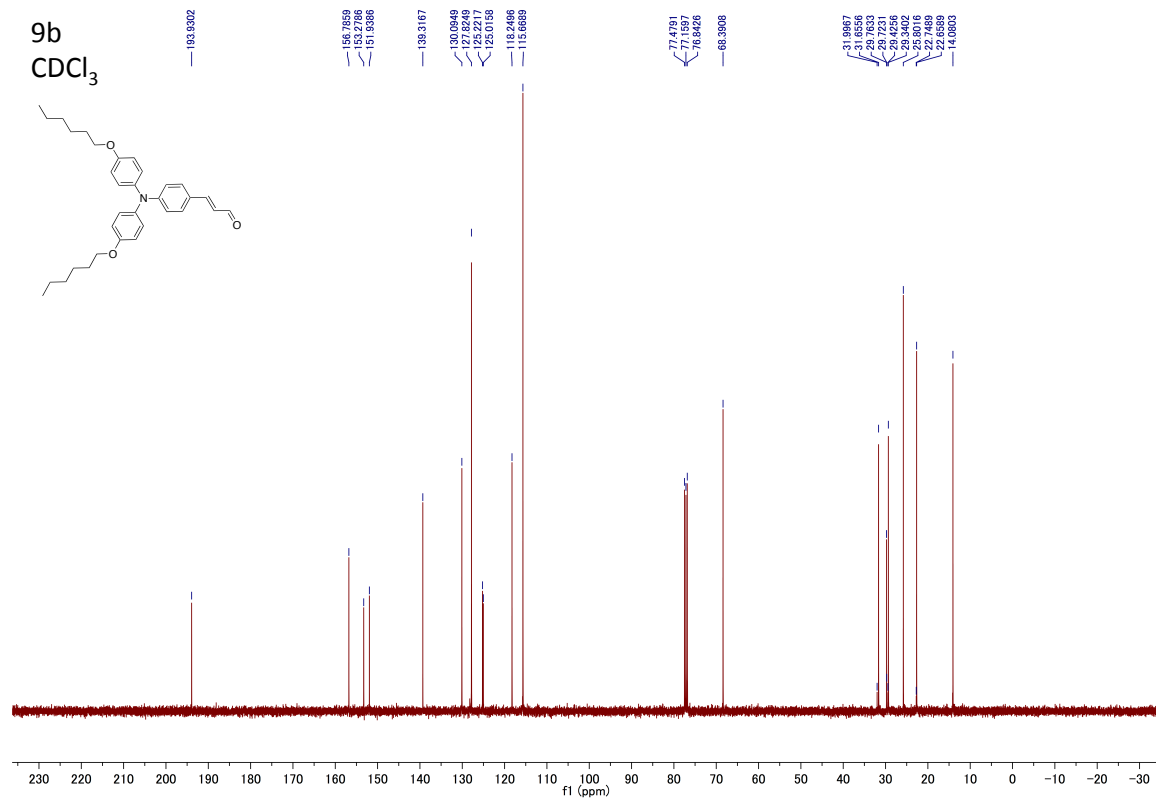
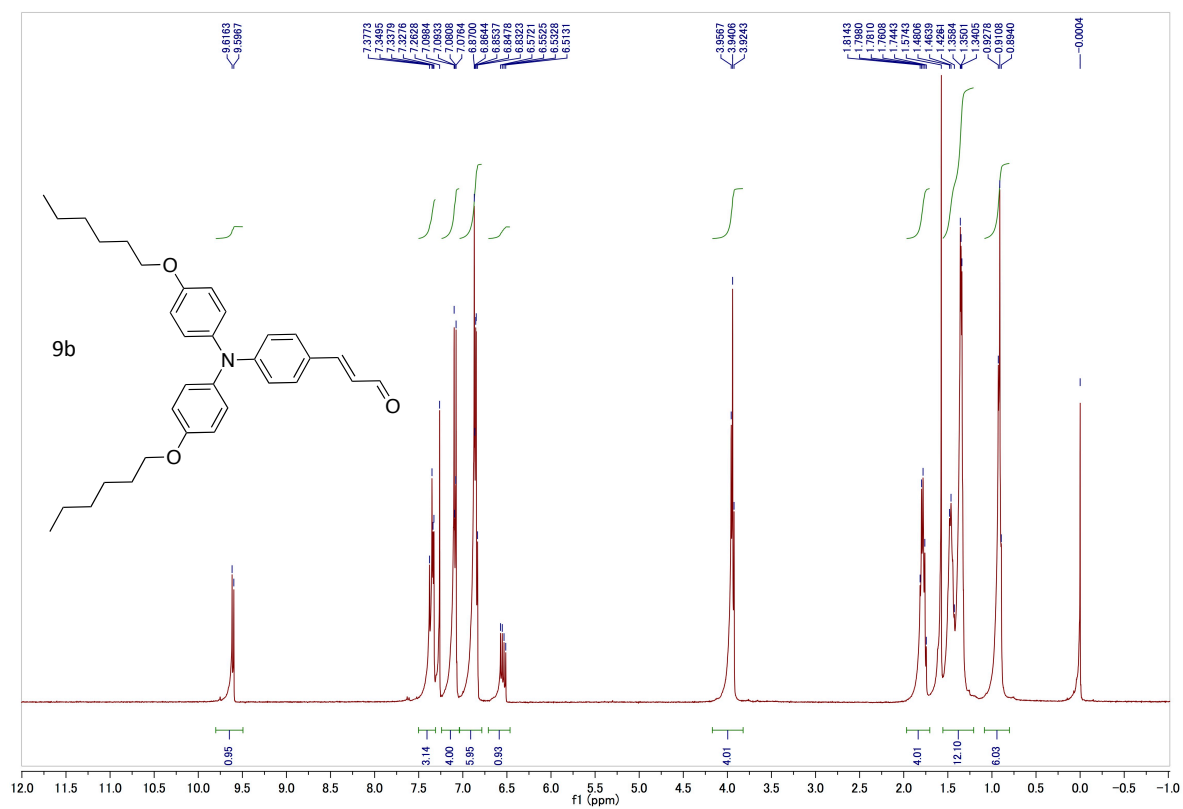




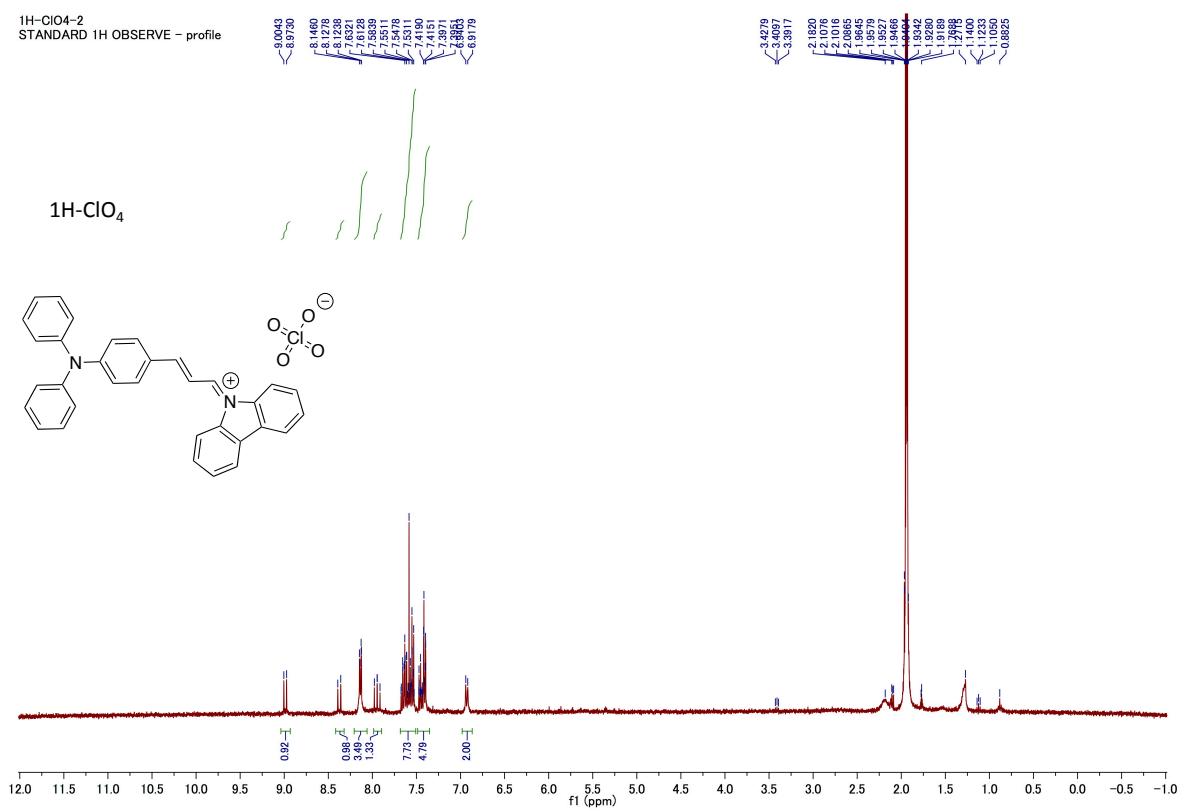


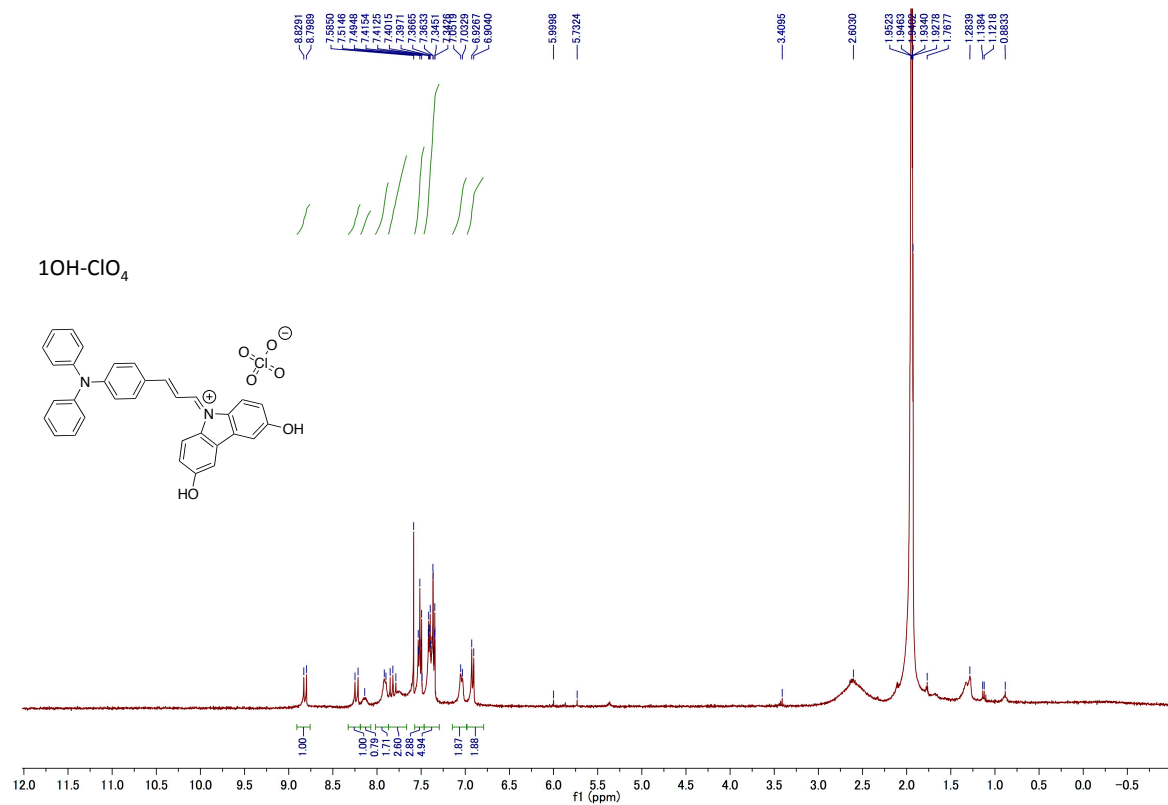
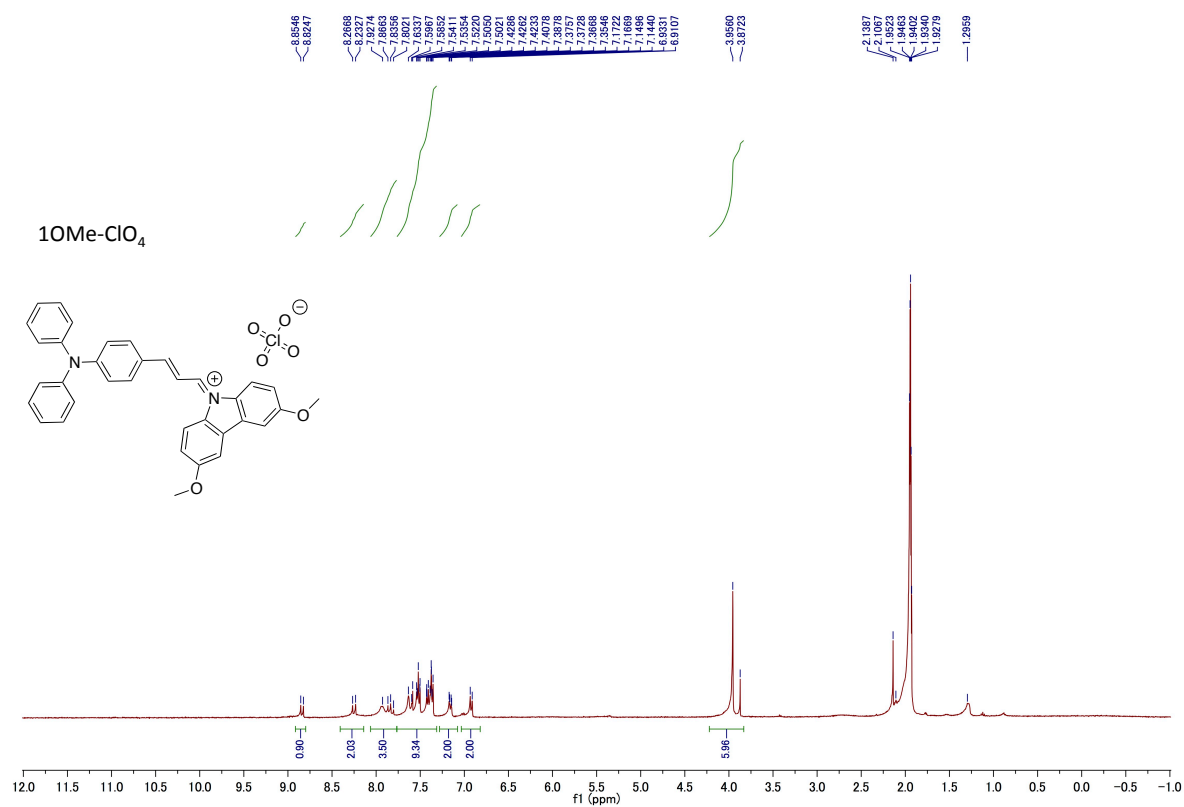




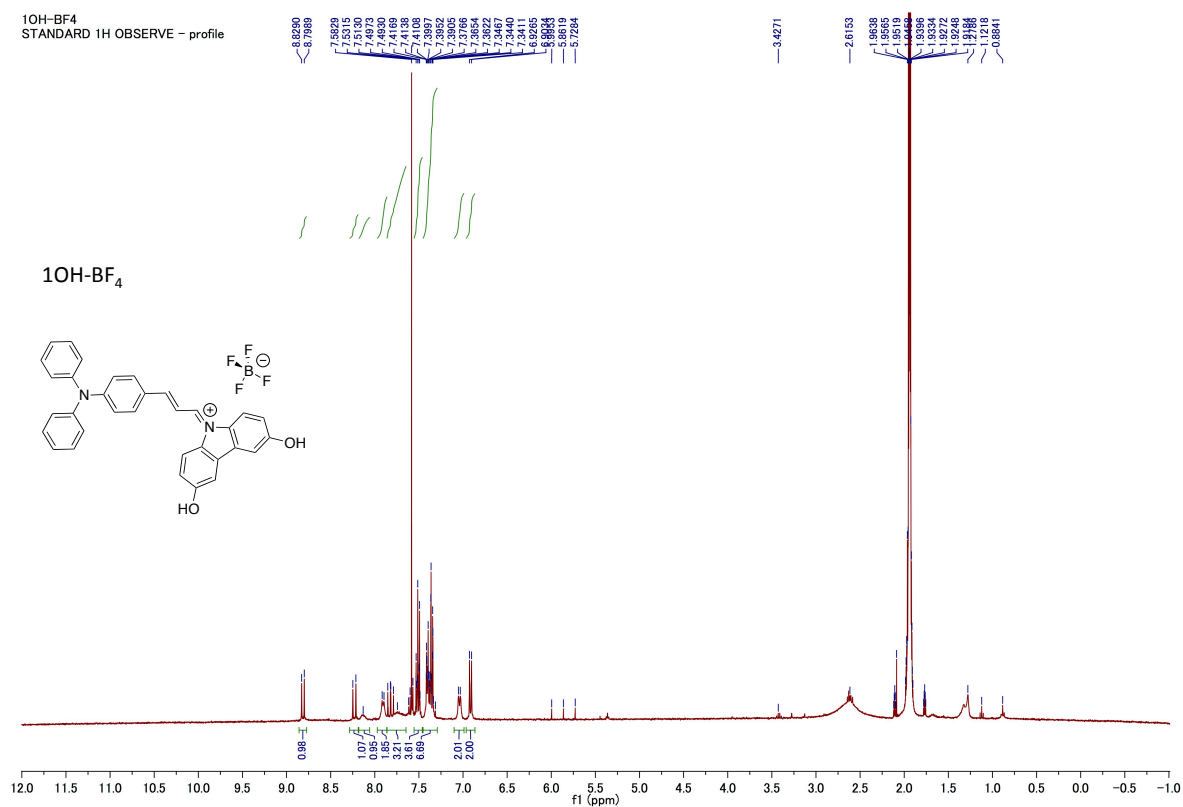


1H-ClO4-2
STANDARD 1H OBSERVE - profile

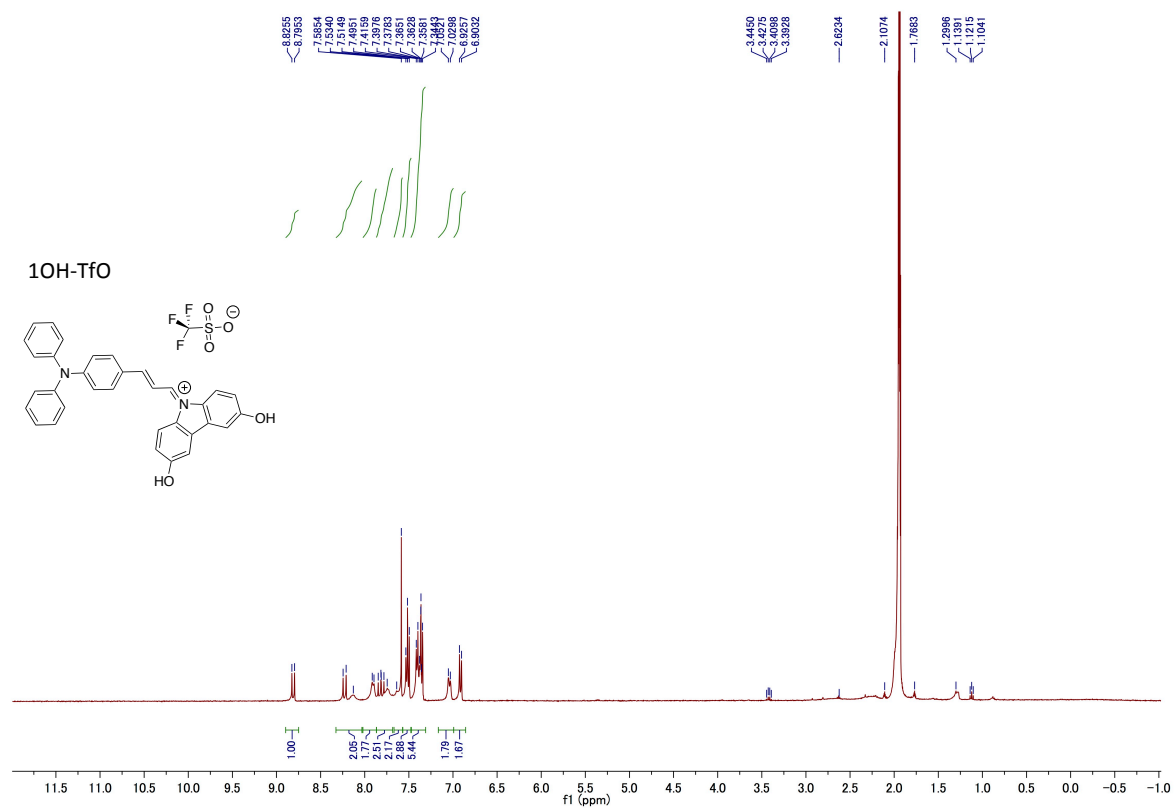




1OH-BF₄
STANDARD 1H OBSERVE - profile



1OH-TfO





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