Direct coupling of carbenium ions with indoles and anilines for the synthesis of cationic π-conjugated dyes

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Supporting Information

1. General remarks

CH_2Cl_2 and Et_2O employed for purification were technical grade. Acetonitrile and *N*-methyl-2-pyrollidinone (NMP) were analytical grade. Bis(*para*-methoxyphenyl)phenylmethyl chloride (PMP_2PhCCl) was purchased from Aldrich® and used without any further purification. *tris*-(2,6-Dimethoxyphenyl)carbenium tetrafluoroborate **1** was prepared on gram scale using previously reported conditions.[1] 5-(*tert*-Butylcarbamate)indole, 1-methylindole and 1,2-dimethylindole were prepared according to described procedures respectively from 5-aminoindole[2], indole[3] and 2-methylindole.[4]

NMR spectra were recorded on Brucker AMX-500 or AMX-400 or ARX-300 at room temperature. For ^{1}H NMR, Chemical shifts are given in ppm relative to Me_4Si with solvent resonances used as internal standards (7.26 ppm for $CDCl_3$, 5.32 ppm for CD_2Cl_2, 2.50 ppm for DMSO-d_6 and 1.94 for CD_3CN). Following abbreviations were employed for multiplicity: s = singulet, br = broad singulet, d = doublet, t = triplet, q = quintuplet, dd = doublet of doublet; dt = doublet of triplet, m = multiplet; J = coupling constant (Hz). For ^{13}C NMR, chemicals shifts were given in ppm relative to Me_4Si with solvent resonances used as internal standards (77.1 ppm for $CDCl_3$, 53.8 ppm for CD_2Cl_2, 39.5 for DMSO-d_6 and 118.2 for CD_3CN). IR spectra were recorded with a Perkin-Elmer 1650. FT-IR spectrometer using a diamond ATR Golden Gate sampling. Melting points (M.P.) were measured in open capillary tubes with a Buchi Melting Point M-565 apparatus (5 °C/min grade) and are uncorrected. R*f* were measured on TLC Silica gel 60 F254 plates purchased from Merck. Electrospray mass spectra were obtained on a Finnigan SSQ 7000 spectrometer by the Department of Mass Spectroscopy of the University of Geneva. UV/Visible spectra were obtained using a Cary 50 spectrophotometer.

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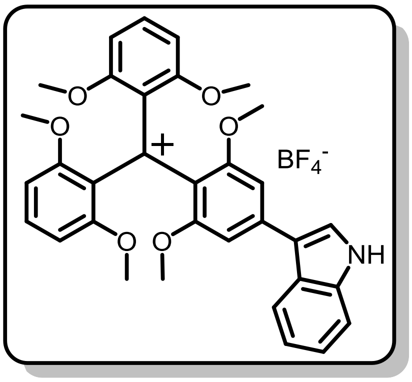
[2] J. M. Frost, M. J. Dart, K. R. Tietje, T. R. Garrison, G. K. Grayson, A. V. Daza, O. F. El-Kouhen, L. N. Miller, L. Li , B. B. Yao , G. C. Hsieh ,M. Pai , C. Z. Zhu , P. Chandran, M. D. Meyer, *J. Med. Chem.* **2008**, *51*, 1904-1912.
[3] L. Zhang, C. Peng, D. Zhao, Y. Wang, H.-J. Fu, Q. Shen, J.-X. Li, *Chem. Comm.* **2012**, *48*, 5928-2930.
[4] H. Zhang, D. Liu, C. Chen, C. Liu, A. Lei, *Chem. Eur. J.* **2011**, *17*, 9581-9585.

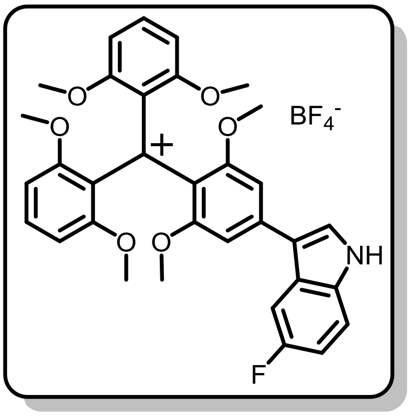
2. Synthesis and characterization of compounds 4, 6 and 7

General procedure for the oxidative cross-deshydrogenative coupling: To a solution of *tris*(2,6-dimethoxyphenyl)carbenium tetrafluoroborate **1** in NMP were added PMP_2PhCCl and either an indole or an aniline. The mixture was then stirred for the indicated period, conversion of starting material being monitored by TLC and MS-ESI. Aqueous $NaBF_4$ (0.2 M) was then added and resulting suspension was filtered. Unless otherwise stated, the collected solid was purified by a dissolution in CH_2Cl_2 and a selective precipitation upon addition of Et_2O.



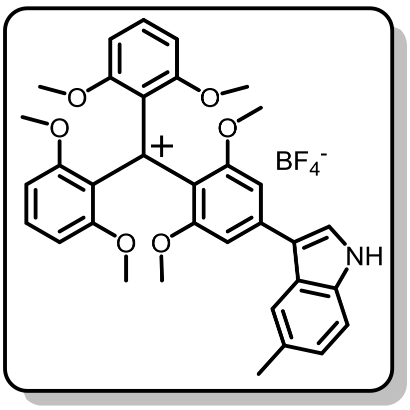
(4-(1H-Indol-3-yl)-2,6-dimethoxyphenyl)bis(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4a: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP_2PhCCl (0.55 mmol) and 64 mg of indole (0.55 mmol) were stirred for 5 h in 1.5 mL of NMP to yield, after purification, 242 mg of wanted compound **4a** as a deep blue solid (77 %).

R_f = 0.48 (CH_2Cl_2/MeOH 90:10). **^{1}H NMR (400 MHz, CD_3CN) δ (ppm):** 11.55 (s, 1H), 8.52 (s, 1H), 8.27 – 7.95 (m, 1H), 7.82 – 7.59 (m, 1H), 7.43 – 7.38 (m, 2H), 7.35 (t, J = 8.7 Hz, 2H), 6.95 (s, 2H), 6.61 (d, J = 8.4 Hz, 4H), 3.68 (s, 6H), 3.52 (s, 12H). **^{13}C NMR (100 MHz, DMSO-*d6*) δ (ppm):** 167.07 (C), 164.71 (C), 159.70 (C), 158.55 (C), 139.22 (C), 139.16 (CH), 132.83 (CH), 127.32 (C), 125.16 (C), 125.02 (CH), 124.33 (CH), 123.48 (C), 122.26 (CH), 117.70 (C), 114.46 (CH), 105.12 (CH), 100.60 (CH), 57.50 (CH_3), 56.60 (CH_3). **^{19}F NMR (282 MHz, CD_3CN) δ (ppm):** -151.76, -151.81. **UV/VIS (CH_3CN, 5.10^{-5} M), λ_{max} (ε):** 576 (32530). **MS (ESI$^+$), *m/z* (%):** 538.3 (M^+, 44), 266.4 (100). **M.P. =** 245 °C (decomposition). **IR (ATR) υ (cm^{-1}):** 3269, 2175, 1605, 1585, 1531, 1470, 1417, 1363, 1287, 1238, 1193, 1167, 1102, 1063, 1004, 932, 874, 824, 790, 766, 732, 657, 621. **HRMS (ESI$^+$)** calc. for $C_{33}H_{32}O_6N^+$ [M^+]: 538.2224. Found: 538.2232.



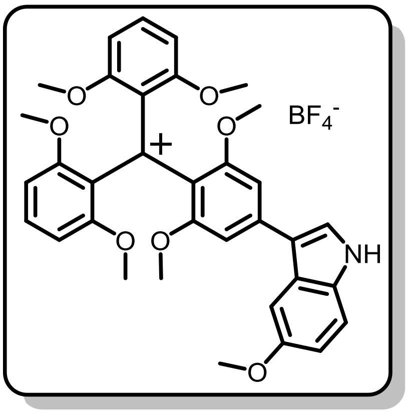
Bis(2,6-dimethoxyphenyl)(4-(5-fluoro-1H-indol-3-yl)-2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4b: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP_2PhCCl (0.55 mmol) and 95 mg of 5-fluoroindole (0.70 mmol) were stirred for 26.5 h in 1.5 mL of NMP to yield, after purification, 231 mg of wanted compound **4b** as a deep blue solid (72 %).

R_f = 0.42 (CH_2Cl_2/MeOH 90:10). **^{1}H NMR (400 MHz, CD_3CN) δ (ppm):** 10.69 (s, 1H), 8.46 (s, 1H), 7.79 (dd, *J* = 10.2, 2.4 Hz, 1H), 7.64 (dd, *J* = 9.0, 4.6 Hz, 1H), 7.37 (t, *J* = 8.4 Hz, 2H), 7.18 (td, *J* = 9.1, 2.4 Hz, 1H), 6.86 (s, 2H), 6.61 (d, *J* = 8.4 Hz, 4H), 3.69 (s, 6H), 3.52 (s, 12H). **^{13}C NMR (100 MHz, DMSO-*d6*) δ (ppm):** 166.79 (C), 165.52 (C), 160.57 (C), 159.07 (C), 158.20 (d, *J* = 2.7 Hz, C), 139.37 (CH), 135.25 (C), 132.67 (CH), 126.84 (C), 125.28 (d, *J* = 10.2 Hz, C), 123.06 (C), 116.97 (C), 115.16 (d, *J* = 10.1 Hz, CH), 112.39 (d, *J* = 25.9 Hz, CH), 107.44 (d, *J* = 25.4 Hz, CH), 104.69 (CH), 100.19 (CH), 57.14 (CH_3), 56.17 (CH_3). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -120.50, -151.93, -151.99. **UV/VIS (CH_3CN, 5.10^{-5} M), λ_{max} (ε):** 596 (30270). **MS (ESI^+, *m/z*):** 556.3 (M^+, 50), 284.4 (100). **M.P. =** 228 °C (decomposition). **IR (ATR) υ (cm^{-1}):** 3256, 2982, 2960, 1773, 1704, 1607, 1587, 1532, 1470, 1405, 1360, 1290, 1247, 1224, 1173, 1104, 989, 933, 839, 789, 620, 604. **HRMS (ESI^+)** calc. for $C_{33}H_{31}O_6N^+$ [M^+-F]: 556.2130. Found: 556.2130.



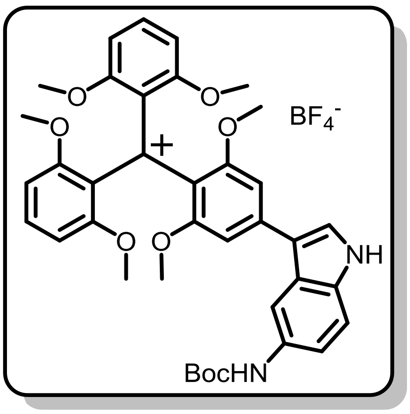
(2,6-dimethoxy-4-(5-methyl-1H-indol-3-yl)phenyl)bis(2,6-dimethoxyphenyl)methylium tetrafluoroborate 4c: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP_2PhCCl (0.55 mmol) and 79 mg of 5-methylindole (0.60 mmol) were stirred for 2 h in 2 mL of NMP to yield, after purification, 269 mg of wanted compound **4c** as a deep blue solid (84 %).

R_f = 0.56 (CH_2Cl_2/MeOH 90:10). **^{1}H NMR (400 MHz, CD_3CN) δ (ppm):** 10.76 (bs, 1H), 8.44 (s, 1H), 7.88 (s, 2H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.34 (t, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 1H), 6.92 (s, 2H), 6.61 (d, *J* = 8.4 Hz, 4H), 3.68 (s, 6H), 3.52 (s, 12H), 2.51 (s, 3H). **^{13}C NMR (100 MHz, CD_3CN) δ (ppm):** 168.02 (C), 166.90 (C), 161.01 (C), 159.68 (C), 137.79 (C), 137.15 (CH), 134.72 (C), 133.88 (CH), 128.38 (C), 127.10 (CH), 126.13 (C), 124.41 (C), 122.34 (CH), 118.22 (C), 114.49 (CH), 105.61 (CH), 101.52 (CH), 57.72 (CH_3), 56.86 (CH_3), 21.90 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm): -151.61, -151.67. **UV/VIS (CH_3CN, 5.10^{-5} M), λ_{max} (ε):** 606 (27970). **MS (ESI^+, *m/z*):** 552.5 (M+, 36), 280.5 (100). **M.P. =** 231 °C (decomposition). **IR (ATR) υ (cm^{-1}):** 1608, 1587, 1533, 1470, 1411, 1363, 1328, 1287, 1246, 1229, 1166, 1102, 1041, 1025, 1010, 932, 847, 824, 786, 579. **HRMS (ESI⁺)** calc. for $C_{34}H_{34}O_6N^+$ [M^+]: 552.2381. Found: 552.2381.



(2,6-Dimethoxy-4-(5-methoxy-1H-indol-3-yl)phenyl)bis(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4d: following general procedure, 255 mg of starting material (0.5 mmol), 186 mg of PMP_2PhCCl (0.55 mmol) and 81 mg of 5-methoxyindole (0.55 mmol) were stirred for 1.5 h in 1.5 mL of NMP to yield after purification, 295 mg of wanted compound **4d** as a deep blue solid (90 %).

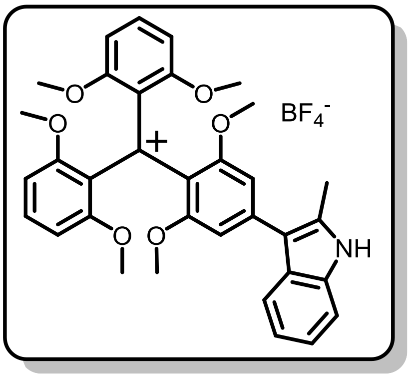
R_f = 0.48 (CH_2Cl_2/MeOH 90:10). **^{1}H NMR (400 MHz, CD_3CN) δ (ppm):** 10.80 (s, 1H), 8.42 (s, 1H), 7.55 (d, *J* = 8.9 Hz, 1H), 7.51 (s, 1H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.02 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.89 (s, 2H), 6.60 (d, *J* = 8.4 Hz, 4H), 3.88 (s, 3H), 3.67 (s, 6H), 3.52 (s, 12H). **^{13}C NMR (100 MHz, CD_3CN) δ (ppm):** 167.95 (C), 166.90 (C), 160.80 (C), 159.62 (C), 157.99 (C), 137.04 (CH), 134.08 (C), 133.83 (CH), 128.26 (C), 126.71 (C), 124.33 (C), 115.55 (CH), 114.47 (CH), 105.54 (CH), 105.25 (CH), 101.34 (CH), 57.62 (CH_3), 56.79 (CH_3), 56.32 (CH_3) (one signal is missing possibly hidden under the solvent signal at 118 ppm). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -151.76, -151.82. **UV/VIS (CH_3CN, 5.10^{-5} M), λ_{max} (ε):** 616 (33670). **MS (ESI⁺, *m/z*):** 568.3 (M^+, 56), 296.3 (100). **M.P. =** 228 °C (decomposition). **IR (ATR) υ (cm^{-1}):** 3287, 2932, 2837, 1610, 1585, 1538, 1468, 1434, 1409, 1368, 1338, 1289, 1251, 1217, 1169, 1152, 1100, 1029, 933, 907, 841, 781, 746, 666, 617. **HRMS (ESI⁺)** calc. for $C_{34}H_{34}O_7N^+$ [M^+]: 568.2330. Found: 568.2318.



(4-(5-((tert-butoxycarbonyl)amino)-1H-indol-3-yl)-2,6-dimethoxyphenyl)bis(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4e: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP_2PhCCl (0.55 mmol) and 139 mg of 5-(*tert*-butylcarbamate)indole (0.60 mmol) were stirred for 3 h in 1.5 mL of NMP, to yield, after purification, 255 mg of wanted compound **4e** as a deep blue solid (69 %).

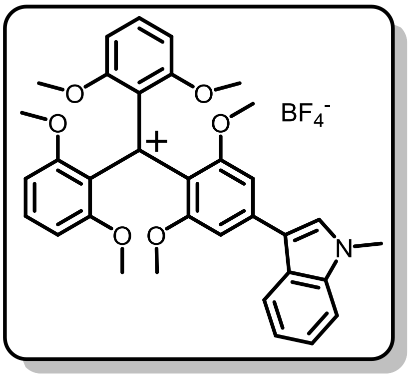
R_f = 0.50 (CH_2Cl_2/MeOH 90:10). **^{1}H NMR (400 MHz, CD_3CN) δ (ppm):** 10.89 (s, 1H), 8.32 (s, 1H), 7.73 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.39 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.34 (t, *J* = 8.4 Hz, 1H), 6.93 (s, 2H), 6.61 (d, *J* = 8.4 Hz, 4H), 3.69 (s, 6H), 3.52 (s, 12H), 1.49 (s, 9H). **^{13}C NMR (100 MHz, CD_3CN) δ (ppm):** 168.05 (C), 166.58 (C), 160.71 (C), 159.66 (C), 154.34 (C), 137.25 (CH), 136.88 (C), 135.30 (C), 133.82 (CH), 128.38 (C), 126.28 (C), 124.37 (C), 117.41

(CH), 114.95 (CH), 111.75 (CH), 105.62 (CH), 101.34 (CH), 80.66 (C), 57.72 (CH_3), 56.87 (CH_3), 28.54 (CH_3). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -151.82, -151.87. **UV/VIS (CH_3CN, 5.10^{-5} M), λ_{max} (ε):** 626 (47200). **MS (ESI$^+$, *m/z*):** 653.5 (M^+, 34), 697.5 (M^+-$(CH_3)_3C$, 100), 553.3 (M^+-$(CH_3)_3C$-CO_2, 34), 325.3 (82). **M.P. =** 216 °C (decomposition). **IR (ATR) υ (cm^{-1}):** 3317, 2931, 2838, 1714, 1610, 1588, 1529, 1473, 1409, 1366, 1338, 1290, 1233, 1159, 1101, 1060, 1005, 932, 889, 850, 793, 739, 716, 615. **HRMS (ESI$^+$)** calc. for $C_{38}H_{41}O_8N_2^+$ [M^+]: 653.2857. Found: 653.2844.



(2,6-dimethoxy-4-(2-methyl-1H-indol-3-yl)phenyl)bis(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4f: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP_2PhCCl (0.55 mmol) and 72 mg of 2-methylindole (0.55 mmol) were stirred for 4 h in 1.5 mL of NMP to yield, after purification, 226 mg of wanted compound **4f** as a deep blue solid (70 %).

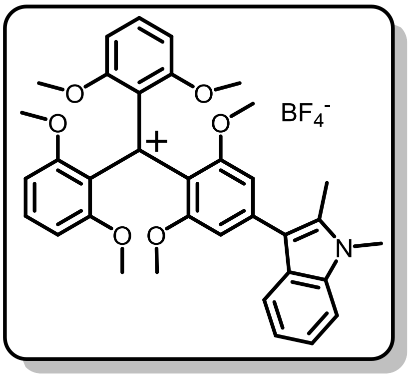
R_f = 0.44 (CH_2Cl_2/MeOH 90:10). **^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm):** 10.77 (s, 1H), 8.00 – 7.74 (m, 1H), 7.69 – 7.49 (m, 1H), 7.49 – 7.09 (m, 4H), 6.72 (s, 2H), 6.55 (d, *J* = 8.4 Hz, 4H), 3.64 (s, 6H), 3.56 (s, 12H), 2.87 (s, 3H). **^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm):** 167.01 (C), 165.96 (C), 161.04 (C), 159.25 (C), 148.01 (C), 137.57 (C), 133.53 (CH), 127.66 (C), 126.91 (C), 124.79 (CH), 123.98 (C), 123.72 (CH), 120.67 (CH), 116.69 (C), 114.00 (CH), 105.06 (CH), 102.70 (CH), 57.08 (CH_3), 56.77 (CH_3), 16.48 (CH_3). **^{19}F NMR (282 MHz, CD_3CN) δ (ppm):** -149.02, -149.08. **MS (ESI$^+$, *m/z*):** 552.3 (M^+, 34), 280.5 (100), 220.1 (28). **UV/VIS (CH_3CN, 5.10^{-5} M) λ_{max} (ε):** 636 (29670). **M.P. =** 195 °C (decomposition). **IR (ATR) υ (cm^{-1}):** 3297, 2937, 2838, 1606, 1586, 1470, 1386, 1341, 1286, 1236, 1168, 1104, 995, 930, 825, 788, 733, 601. **HRMS (ESI$^+$)** calc. for $C_{34}H_{34}O_6N^+$ [M^+]: 552.2381. Found: 552.2374.



(2,6-Dimethoxy-4-(1-methyl-1H-indol-3-yl)phenyl)bis(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4g: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP_2PhCCl (0.55 mmol) and 107 mg of 1-methylindole (107 mg, 0.83 mmol) were stirred for 5.5 h in 1.5 mL of NMP to yield, after purification, 247 mg of wanted compound **4g** as a deep blue solid (77 %).

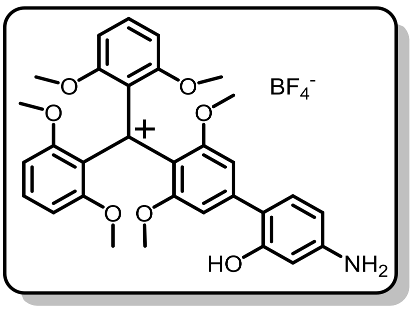
R_f = 0.52 (CH_2Cl_2/MeOH 90:10). **^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm):** 8.63 (s, 1H), 8.09 – 7.91 (m, 1H), 7.57 – 7.48 (m, 1H), 7.47 – 7.39 (m, 2H), 7.30 (t, *J* = 8.4

Hz, 2H), 6.93 (s, 2H), 6.54 (d, *J* = 8.4 Hz, 4H), 4.02 (s, 3H), 3.70 (s, 6H), 3.55 (s, 12H). **^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm):** 167.52 (C), 164.93 (C), 160.04 (C), 159.13 (C), 140.97 (CH), 140.25 (C), 133.12 (CH), 128.11 (C), 126.38 (C), 125.13 (CH), 124.60 (CH), 123.97 (C), 121.88 (CH), 117.28 (C), 112.47 (CH), 105.03 (CH), 100.77 (CH), 57.33 (CH_3), 56.76 (CH_3), 34.75 (CH_3). **^{19}F NMR (282 MHz, CD_3CN) δ (ppm):** -151.80, -151.85. **MS (ESI$^+$, *m/z*):** 552.3 (M^+, 44), 280.5 (100). **UV/VIS (CH_3CN, 5.10^{-5} M), λ_{max} (ε):** 630 (56270). **M.P. =** 217 °C (decomposition). **IR (ATR) υ (cm^{-1}):** 2941, 2835, 1615, 1587, 1541, 1519, 1773, 1447, 1437, 1409, 1381, 1357, 1287, 1254, 1227, 1186, 1140, 1114, 1089, 1060, 1021, 933, 881, 832, 781, 766, 732, 618. **HRMS (ESI$^+$)** calc. for $C_{34}H_{34}O_6N^+$ [M^+]: 552.2381. Found: 552.2391.



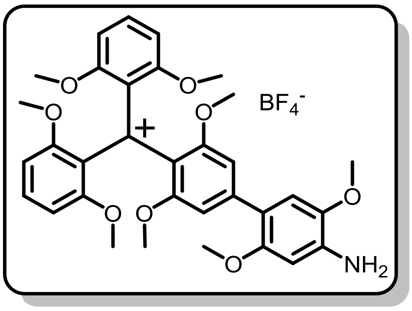
Bis(2,6-dimethoxyphenyl)(4-(1,2-dimethyl-1H-indol-3-yl)-2,6-dimethoxyphenyl)carbenium tetrafluoroborate 4h: following procedure I, 255 mg of starting material (0.50 mmol), 186 mg of PMP_2PhCCl (0.55 mmol) and 80 mg of 1,2-dimethylindole (0.55 mmol) were stirred for 6 h in 1.5 mL of NMP to yield, after purification, 243 mg of wanted **4h** compound as a deep blue solid (74 %).

R_f = 0.60 (CH_2Cl_2/MeOH 90:10). **^{1}H NMR (400 MHz, CD_3CN) δ (ppm):** 7.97 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.23 (m, 4H), 6.73 (s, 2H), 6.61 (d, *J* = 8.4 Hz, 4H), 3.83 (s, 3H), 3.64 (s, 6H), 3.54 (s, 12H), 2.79 (s, 3H). **^{13}C NMR (100 MHz, CD_3CN) δ (ppm):** 168.25 (C), 167.50 (C), 161.02 (C), 159.85 (C), 147.96 (CH), 139.39 (C), 134.37 (C), 128.05 (CH), 126.66 (C), 124.74 (CH), 124.46 (CH), 124.14 (C), 121.38 (CH), 116.60 (C), 112.07 (CH), 105.60 (CH), 104.02 (CH), 57.56 (CH_3), 56.83 (CH_3), 31.45 (CH_3), 14.23 (CH_3). **^{19}F NMR (282 MHz, CD_2Cl_2) δ (ppm):** -154.90, -154.95. **UV/VIS (CH_3CN, 5.10^{-5} M), λ_{max} (ε):** 656 (42260). **MS (ESI$^+$, *m/z*):** 566.3 (M^+, 31), 294.5 (100). **M.P. =** 208 °C (decomposition). **IR (ATR) υ (cm^{-1}):** 2924, 2844, 1583, 1470, 1428, 1380, 1339, 1287, 1241, 1154, 1104, 1031, 975, 932, 839, 791, 737, 615. **HRMS (ESI$^+$)** calc. for $C_{34}H_{36}O_6N^+$ [M^+]: 566.2530. Found: 566.2552.



4-amino-4'-(bis(2,6-dimethoxyphenyl)methyl)-3',5'-dimethoxy-[1,1'-biphenyl]-2-ol tetrefluoroborate 6: following modified procedure I, 255 mg of starting material (0.50 mmol) and 65 mg of 3-aminophenol (0.60 mmol) were stirred for 6 h in 1.5 mL of NMP (no additive was added) to yield, after purification, 120 mg of wanted compound **6** as a deep green solid (39 %).

R_f = 0.32 (CH_2Cl_2/MeOH 90:10). **^{1}H NMR (400 MHz, CD_3CN) δ (ppm):** 7.69 (d, *J* = 9.0 Hz, 1H), 7.33 (t, *J* = 8.4 Hz, 2H), 7.03 (s, 2H), 6.59 (d, *J* = 8.4 Hz, 4H), 6.39 (dd, *J* = 9.0, 2.2 Hz, 1H), 6.28 (d, *J* = 2.1 Hz, 1H), 5.51 (bs, 2H), 3.55 (s, 6H), 3.50 (s, 12H). **^{13}C NMR (100 MHz, CD_3CN) δ (ppm):** 167.09 (C), 166.60 (C), 163.19 (C), 162.63 (C), 159.69 (C), 157.62 (C), 134.69 (CH), 133.85 (CH), 128.28 (C), 124.52 (C), 115.15 (C), 110.24 (CH), 105.61 (CH), 103.61 (CH), 101.38 (CH), 57.32 (CH_3), 56.84 (CH_3). **^{19}F NMR (282 MHz, CD_3CN) δ (ppm):** -151.75, -151.80. **UV/VIS (CH_3CN, 5.10^{-5} M), λ_{max} (ε):** 655 (44600). **MS (ESI$^+$) m/z (%):** 530.3 (M^+, 21), 258.4 (100), 505.5 (33). **M.P. =** 258.1 °C. **IR (ATR) υ (cm^{-1}):** 3352, 1642, 1580, 1471, 1420, 1402, 1340, 1278, 1236, 1218, 1184, 1109, 1027, 933, 854, 808, 779, 731, 672, 622, 578, 555. **HRMS (ESI$^+$)** calc. for $C_{31}H_{32}O_7N^+$ [M^+]: 530.2173. Found: 530.2161.



(4'-Amino-2',3,5,5'-tetramethoxy-[1,1'-biphenyl]-4-yl)bis(2,6-dimethoxyphenyl)carbenium tetrafluoroborate 7: following modified procedure I, 357 mg of starting material (0.70 mmol) and 129 mg of 2,5-dimethoxyaniline (0.84 mmol) were stirred for 14 h in 2.5 mL of NMP (no additive was added) to yield, after purification, 212 mg of wanted compound **7** as a deep green solid (46 %).

R_f = 0.46 (CH_2Cl_2/MeOH 90:10). **^{1}H NMR (400 MHz, CD_3CN) δ (ppm):** 7.32 (t, *J* = 8.4 Hz, 2H), 7.15 (s, 1H), 6.96 (s, 2H), 6.59 (d, *J* = 8.4 Hz, 4H), 6.49 (s, 1H), 5.72 (bs, 2H), 3.92 (s, 3H), 3.90 (s, 3H), 3.57 (s, 6H), 3.51 (s, 12H). **^{13}C NMR (100 MHz, CD_3CN) δ (ppm):** 166.71 (C), 165.18 (C), 162.20 (C), 160.58 (C), 159.65 (C), 149.14 (C), 142.74 (C), 133.62 (CH), 128.37 (C), 124.56 (C), 115.72 (C), 112.72 (CH), 105.60 (CH), 104.14 (CH), 98.05 (CH), 57.31 (CH_3), 57.04 (CH_3), 57.02 (CH_3), 56.84 (CH_3). **^{19}F NMR (282 MHz, CD_2Cl_2) δ (ppm):** -152.71, -152.76. **UV/VIS (CH_3CN, 5.10^{-5} M), λ_{max} (ε):** 474 (9940), 700 (37090). **MS (ESI$^+$, *m/z*):** 574.3 (M^+, 42), 302.1 (100). **M.P. =** 240 °C (decomposition). **IR (ATR) υ (cm^{-1}):** 3342, 2922, 2840, 1647, 1610, 1587, 1545, 1471, 1147, 1428, 1402, 1374, 1353, 1333, 1244, 1231, 1202, 1108, 1063, 1019, 935, 843, 775, 748, 725, 711. **HRMS (ESI$^+$)** calc. for $C_{33}H_{36}O_8N^+$ [M^+]: 574.2435. Found: 574.2440.

3. NMR evidence for the presence of compound 5 in crude mixtures

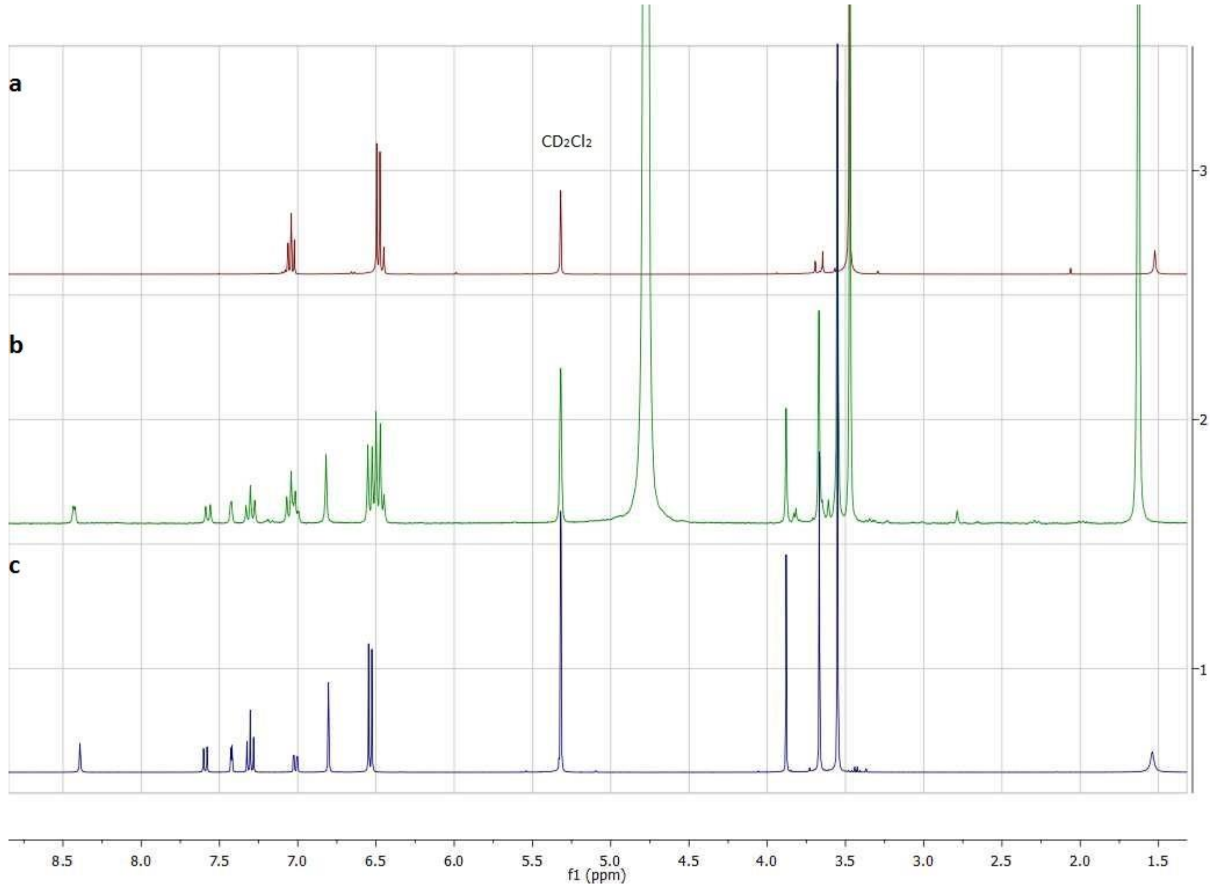
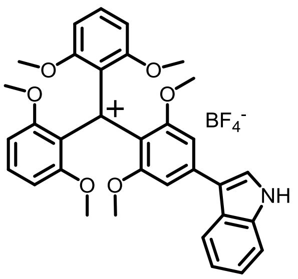


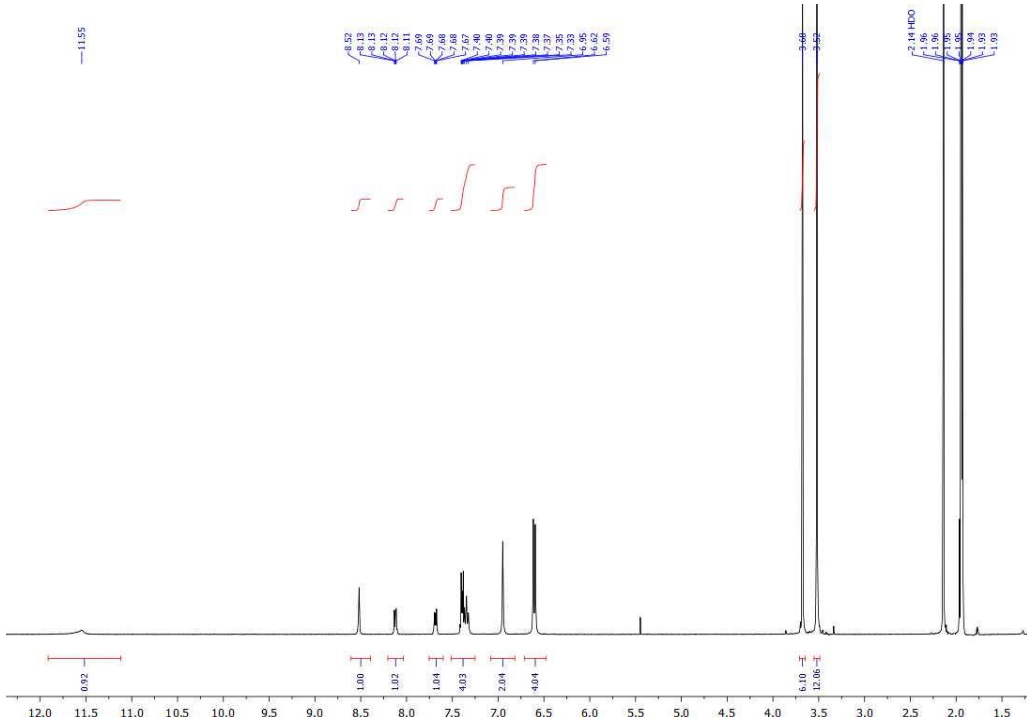
Figure S1. NMR Spectra in CD_2Cl_2 of a) reduced product **5** formed according to a previously reported procedure;[1] b) crude mixture of the reaction of **1** with 5-methoxyindole (**2d**); c) Salt [**4d**][BF_4].

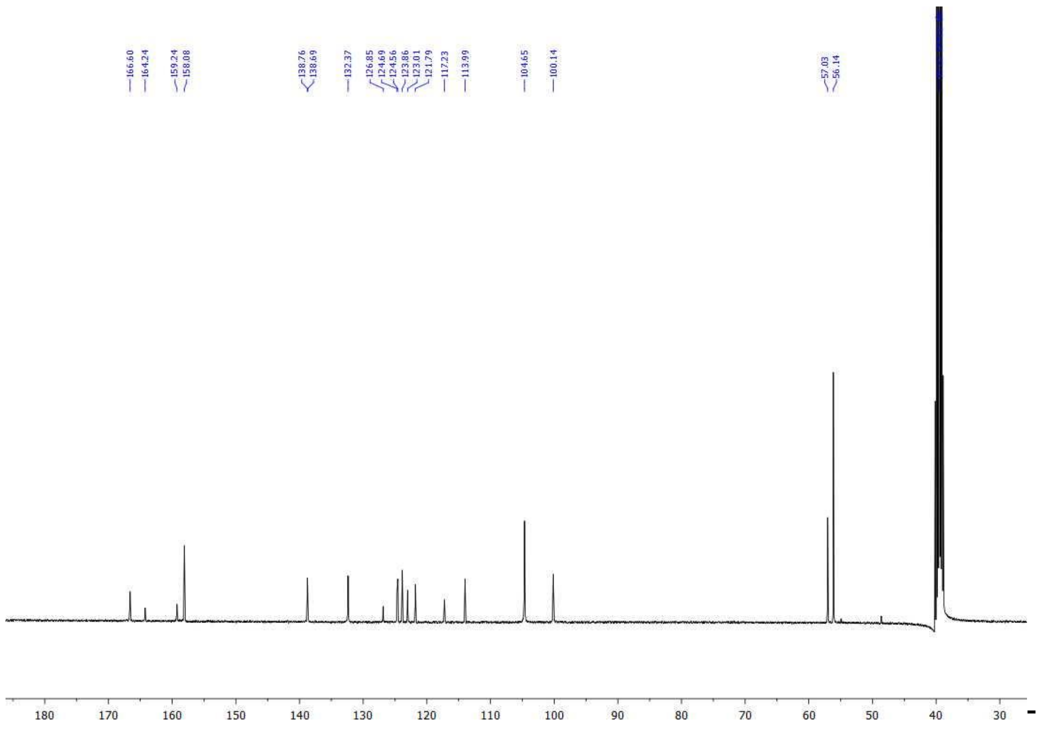
Note that the broad signal around 4.77 ppm in spectrum b) is attributed to the acid present in crude mixture.

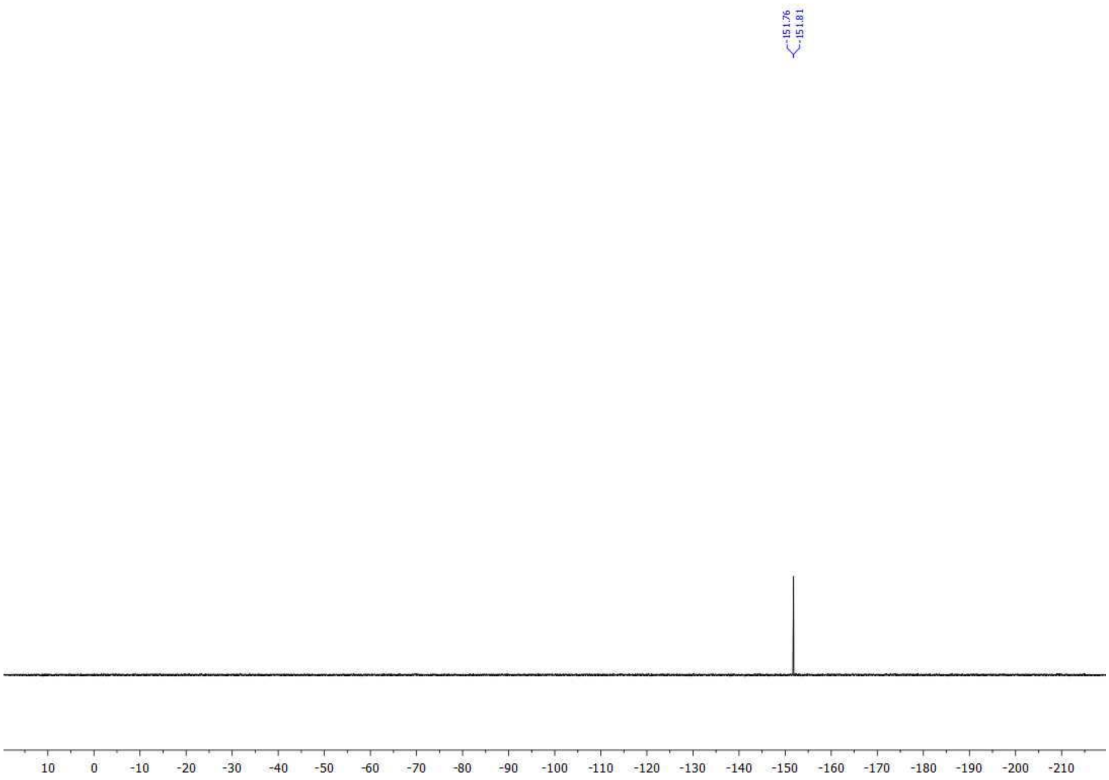
[1] P. Huszthy, K. Lempert, G. Simig, *J. Chem. Soc., Perkin Trans. 2* **1985**, *0*, 1351-1354.

4. NMR (^{1}H, ^{13}C and ^{19}F) and absorption (UV-Vis) spectra





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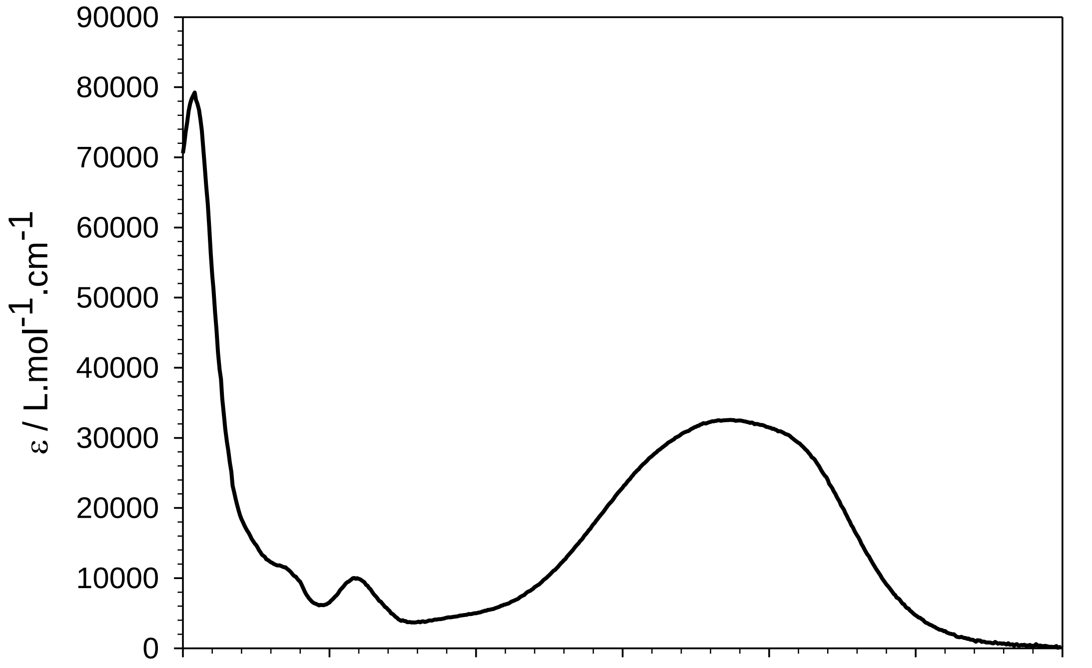
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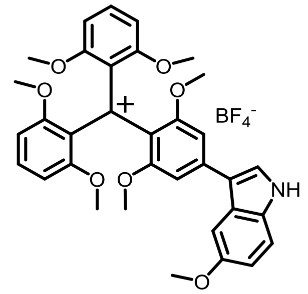
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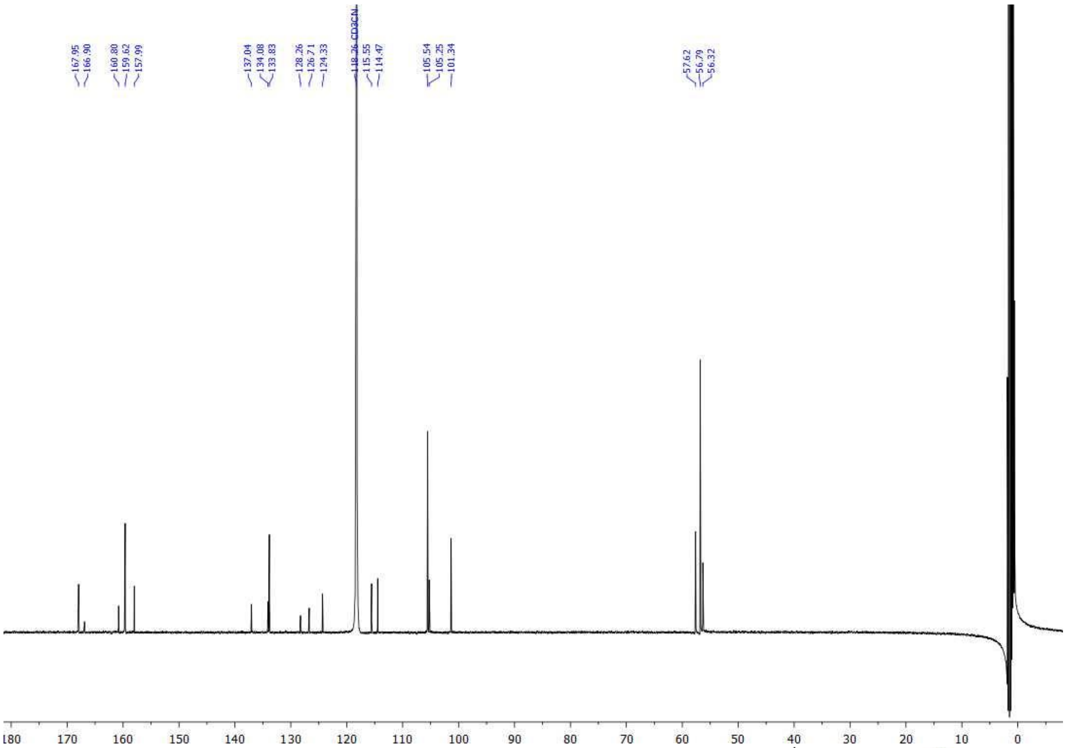
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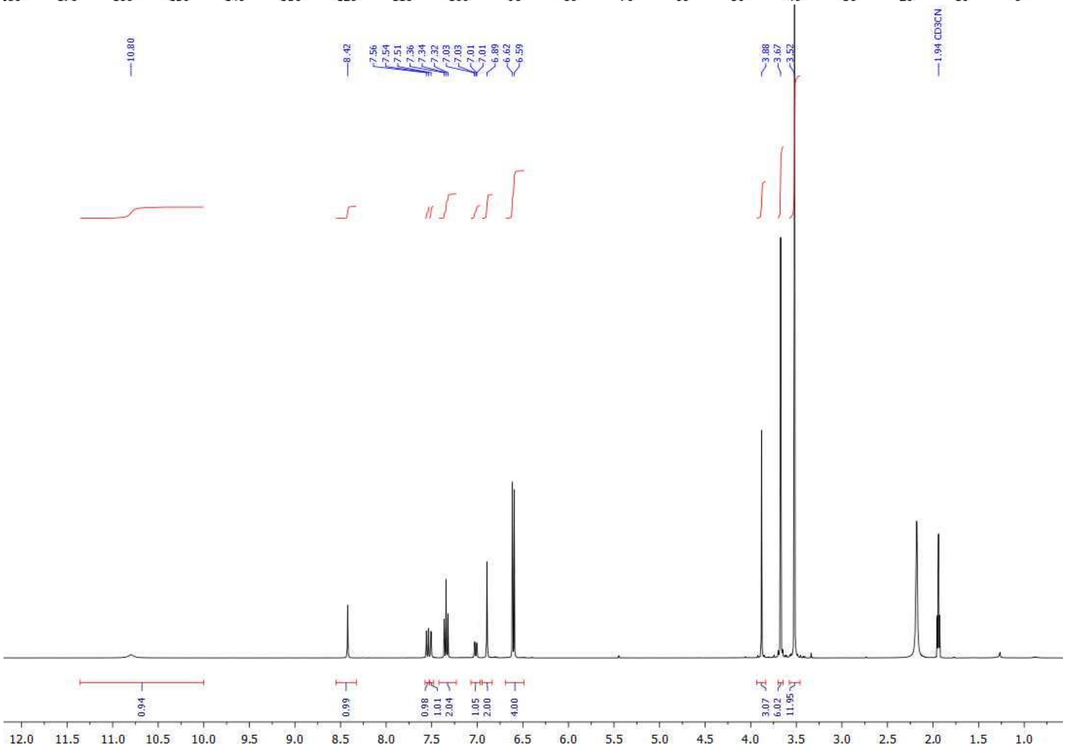
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11.95
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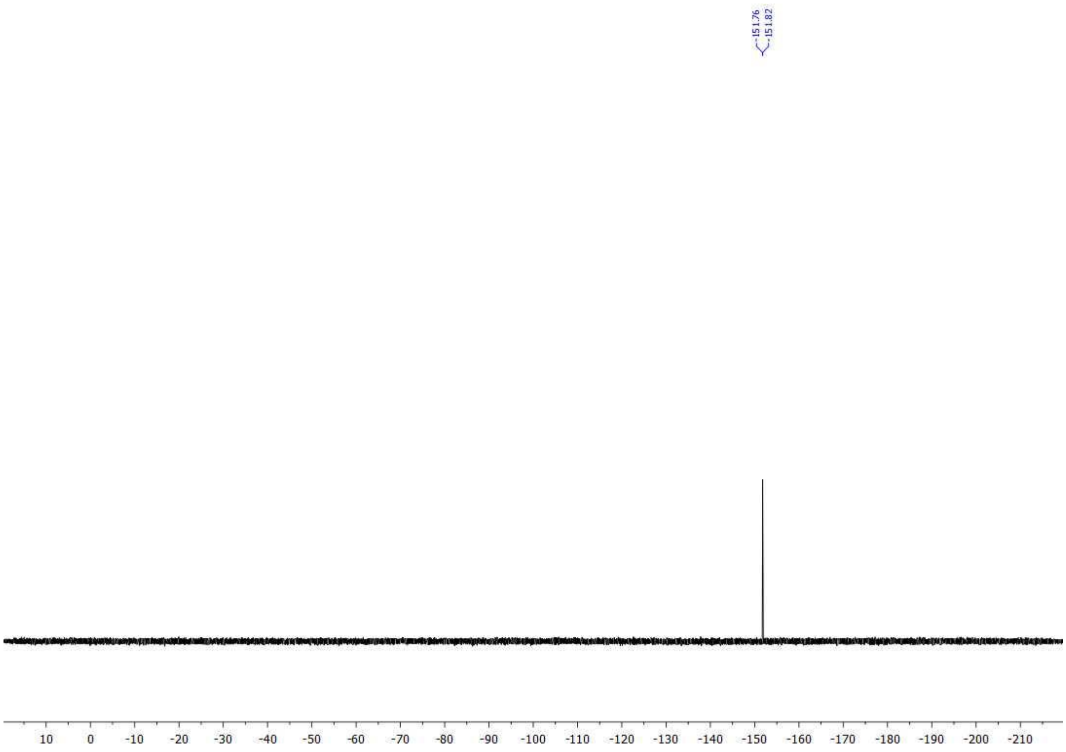
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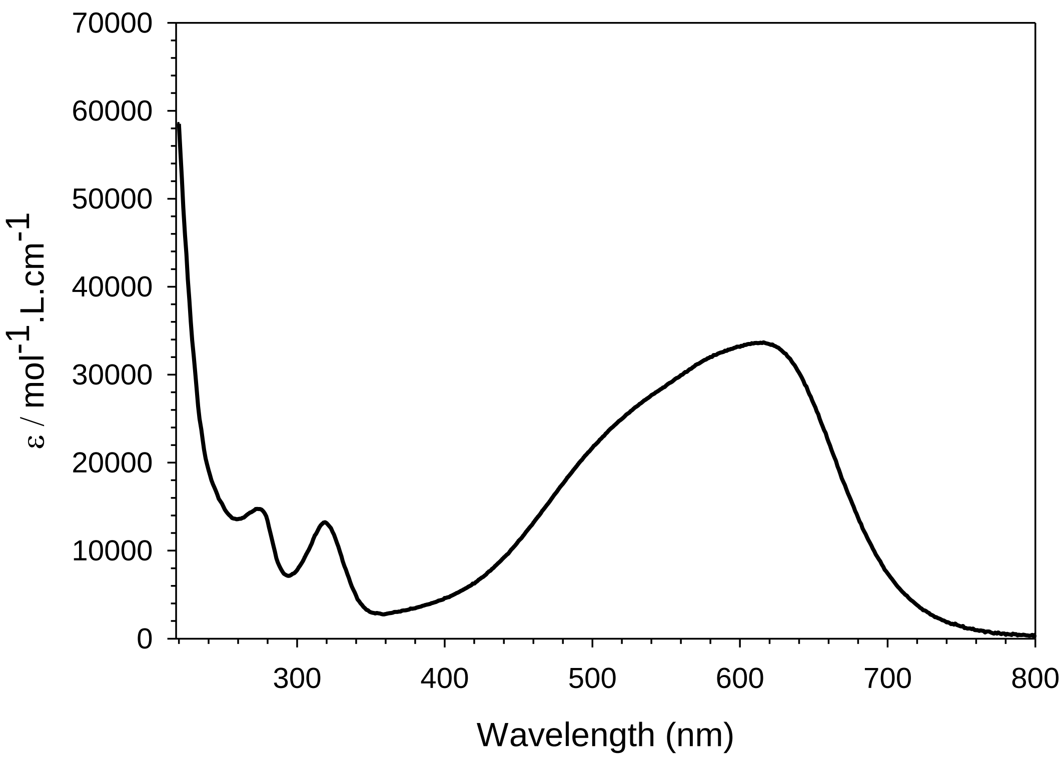
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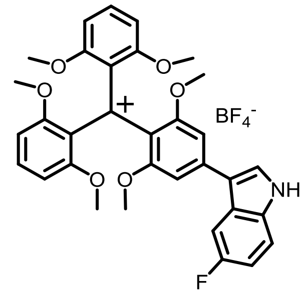
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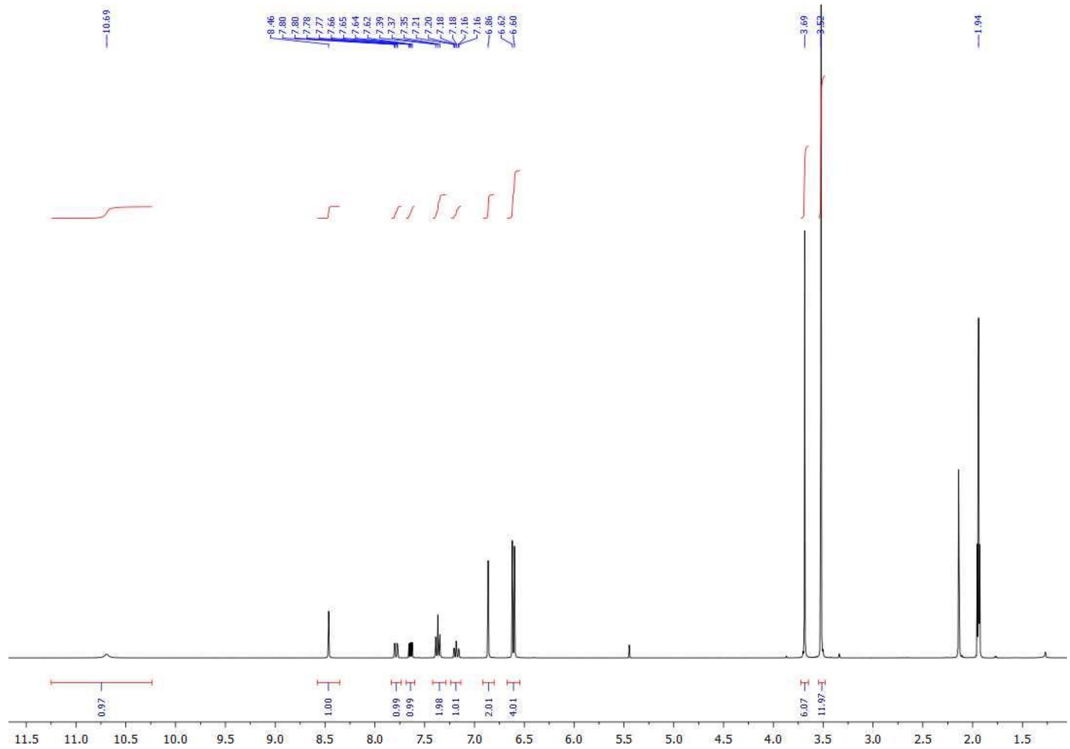
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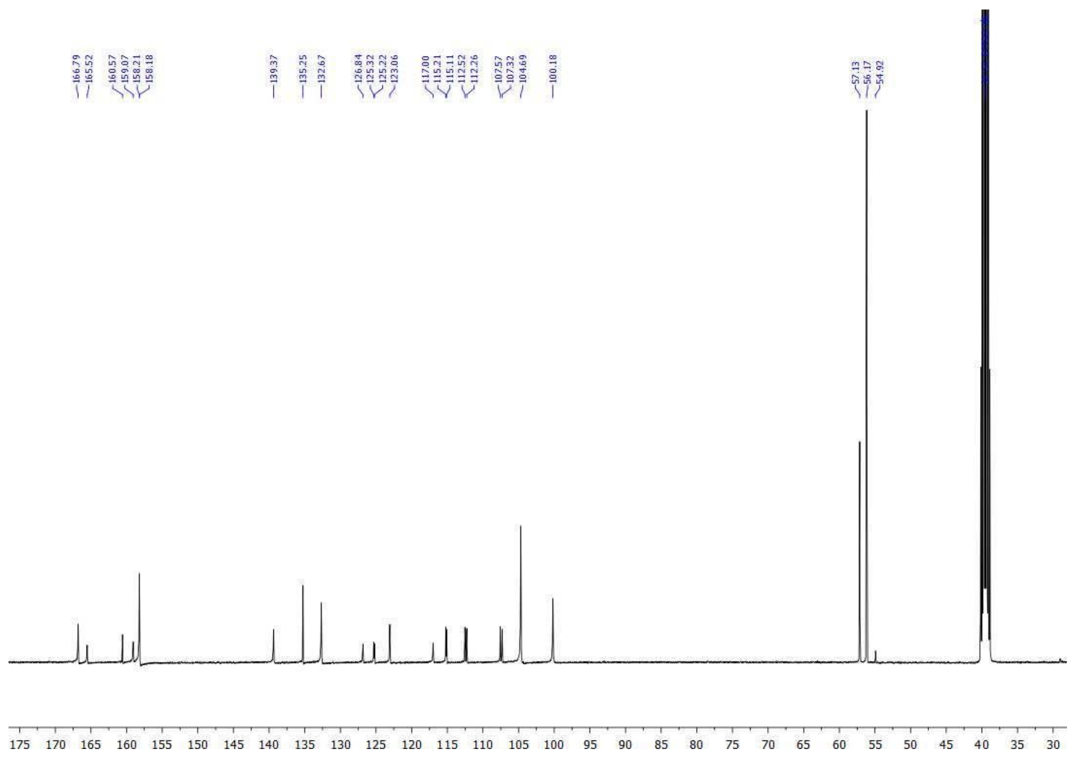
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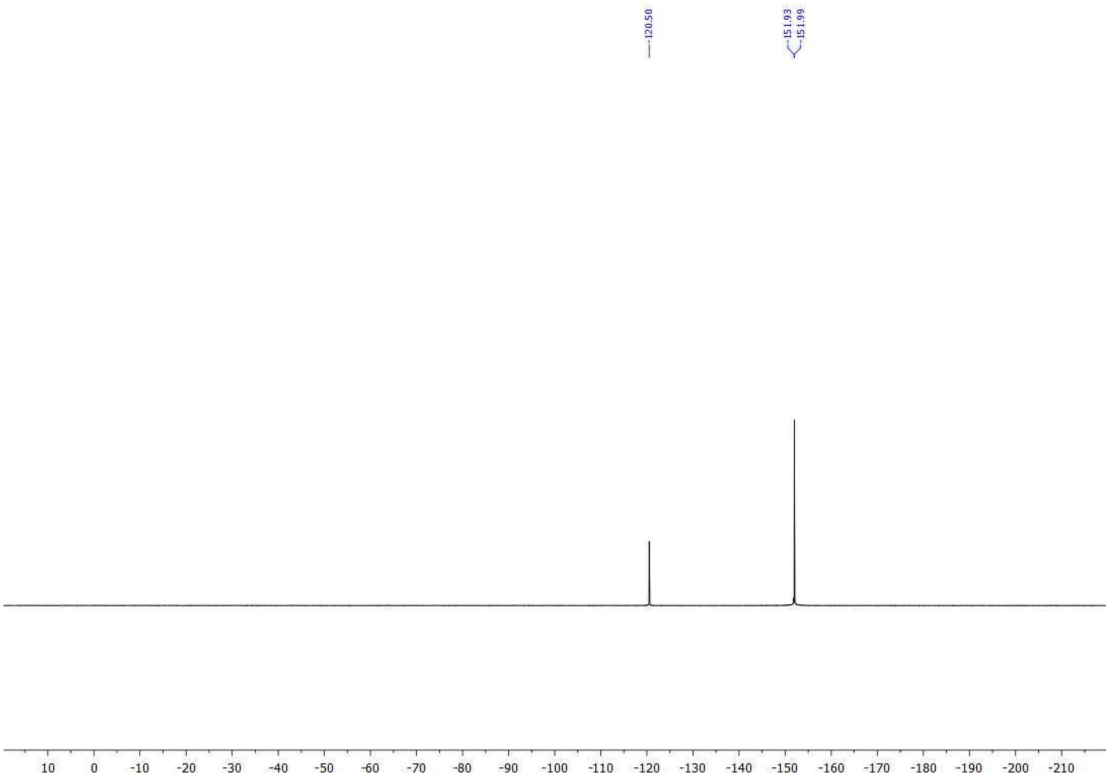
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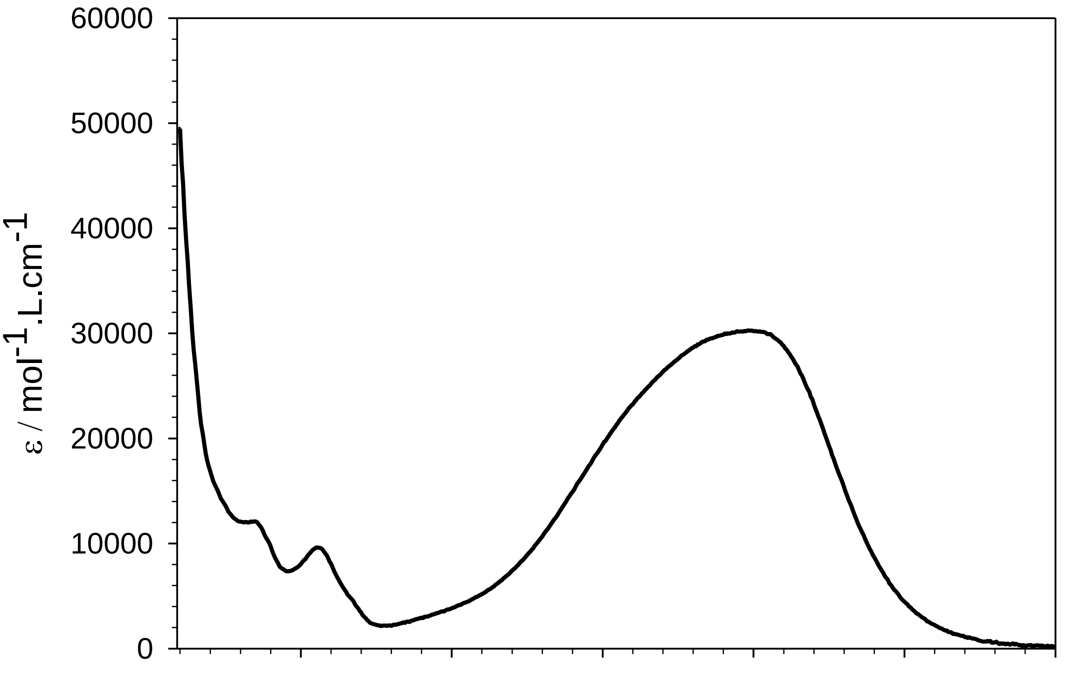
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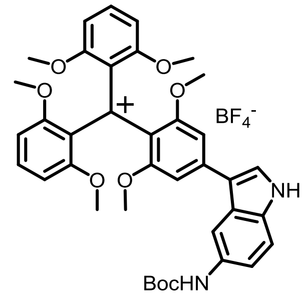

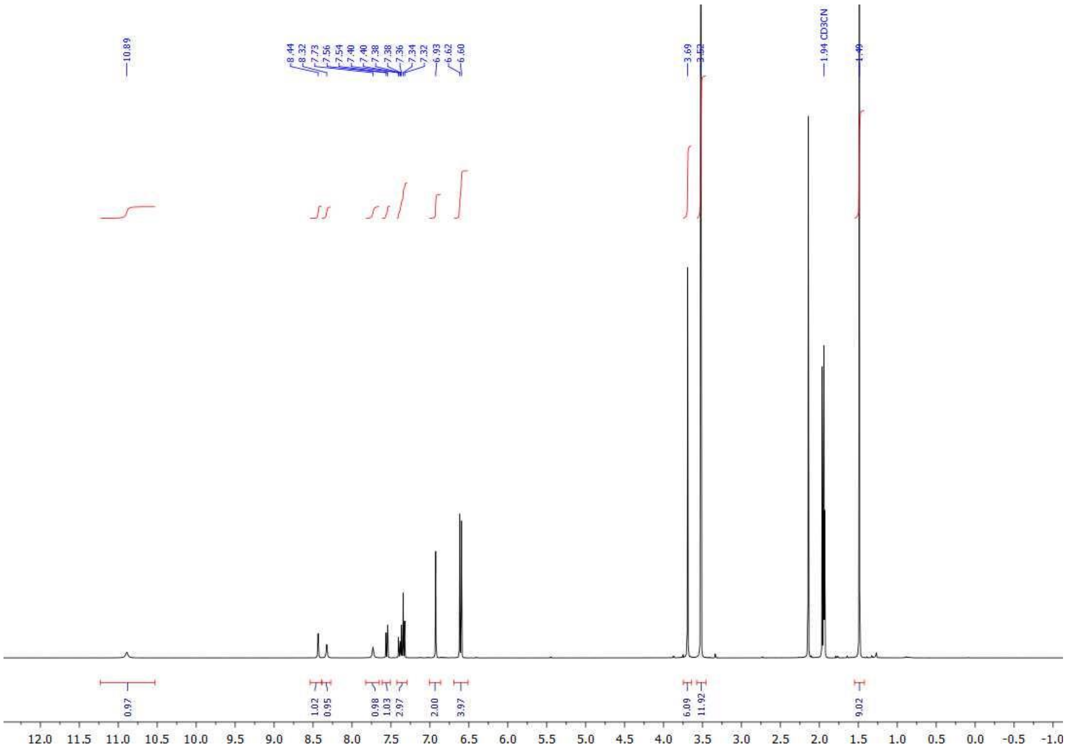

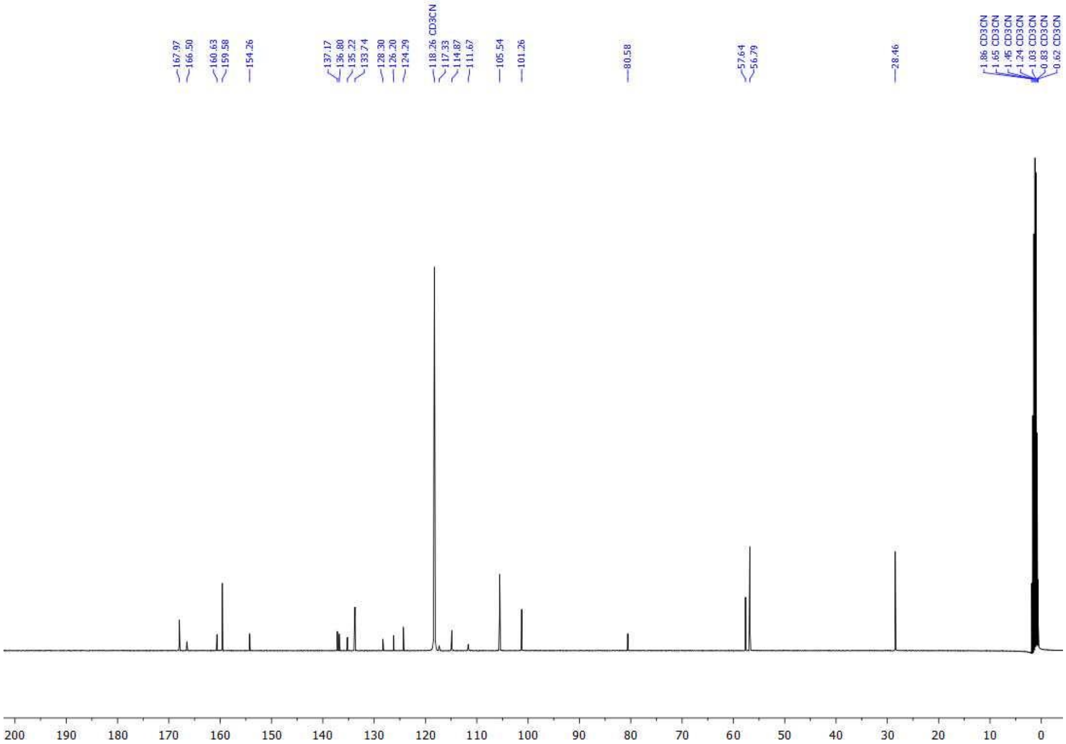

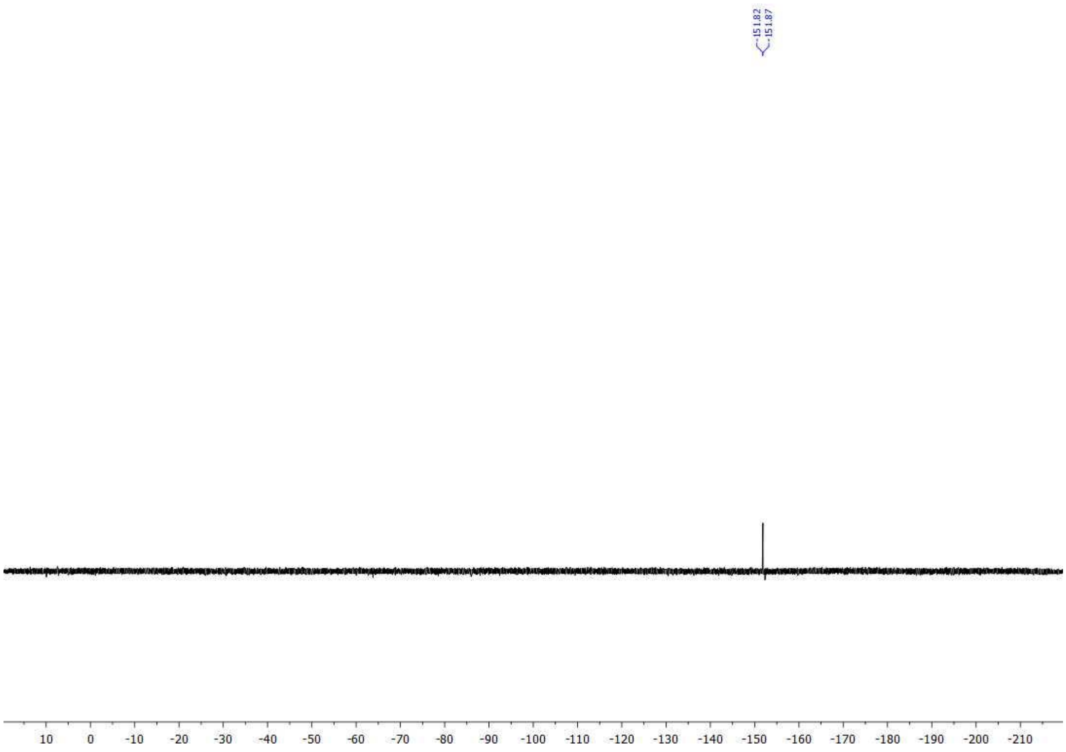
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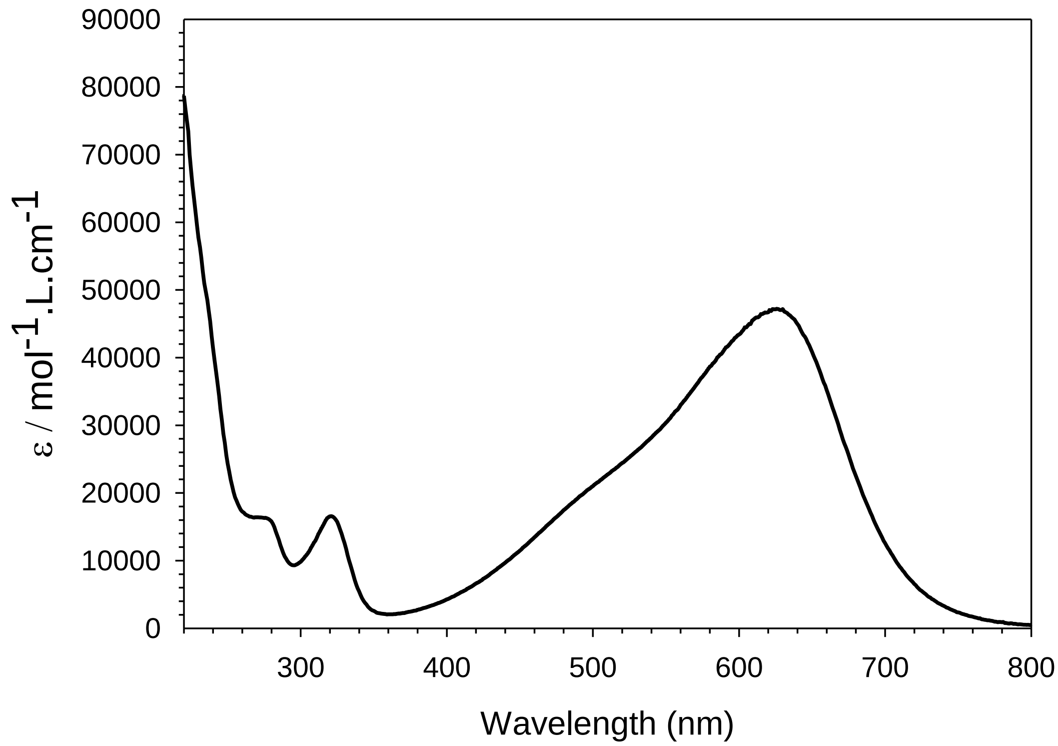
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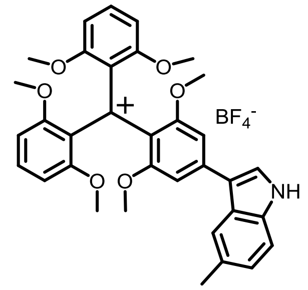
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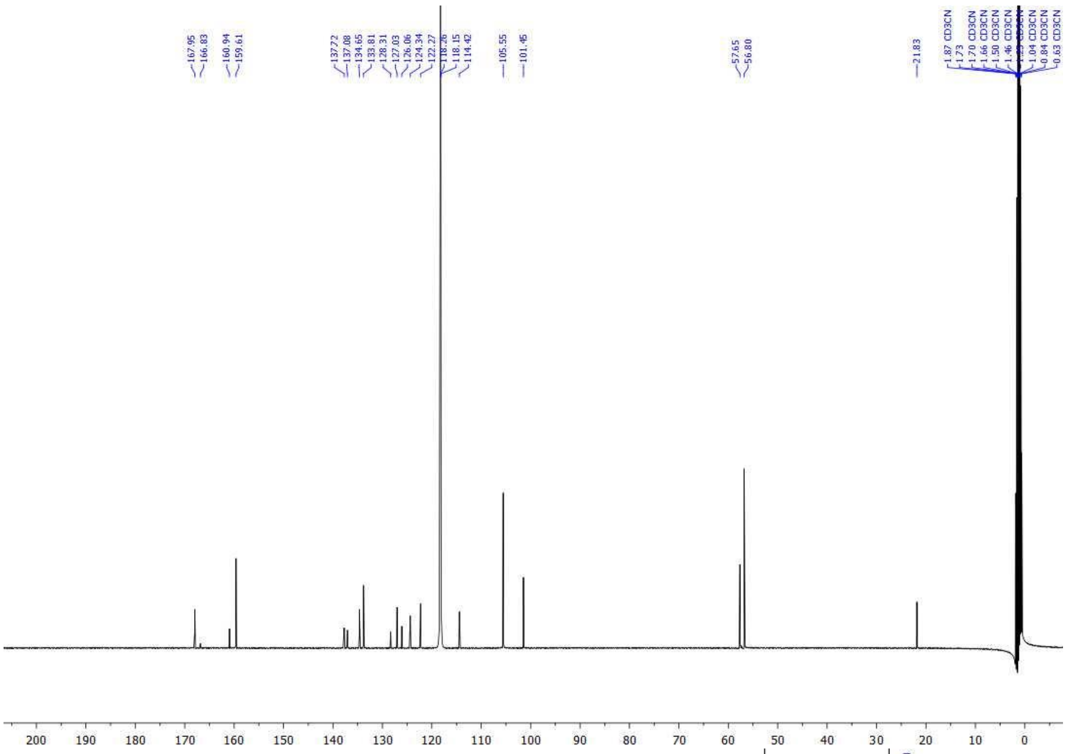
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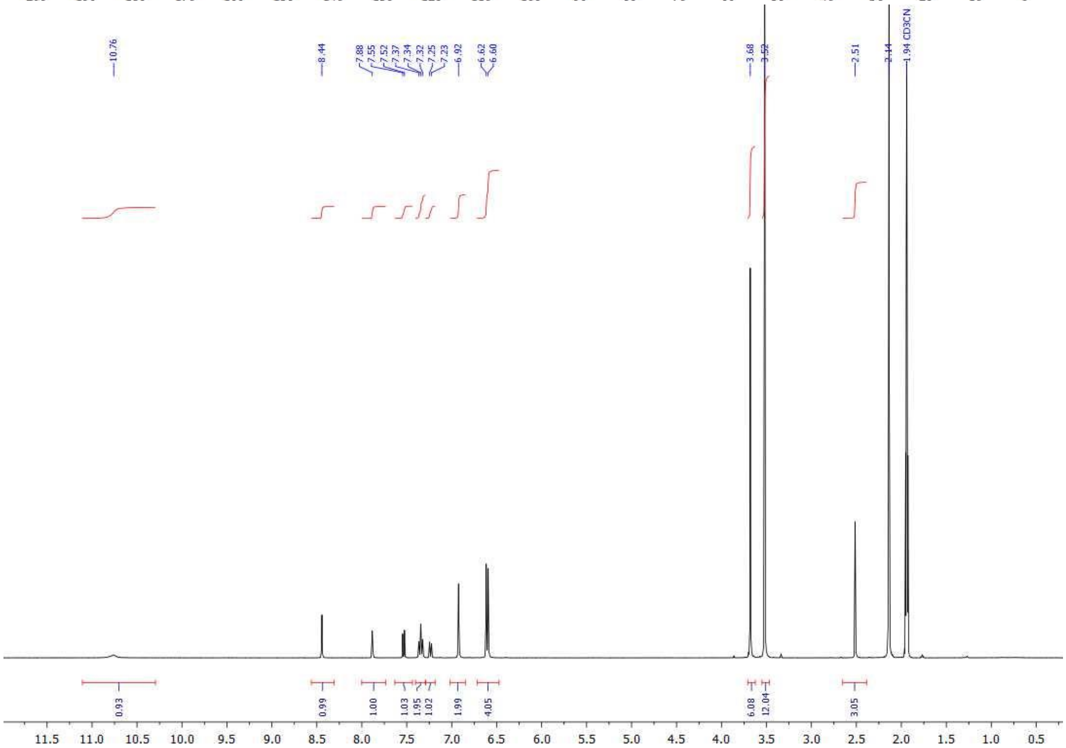
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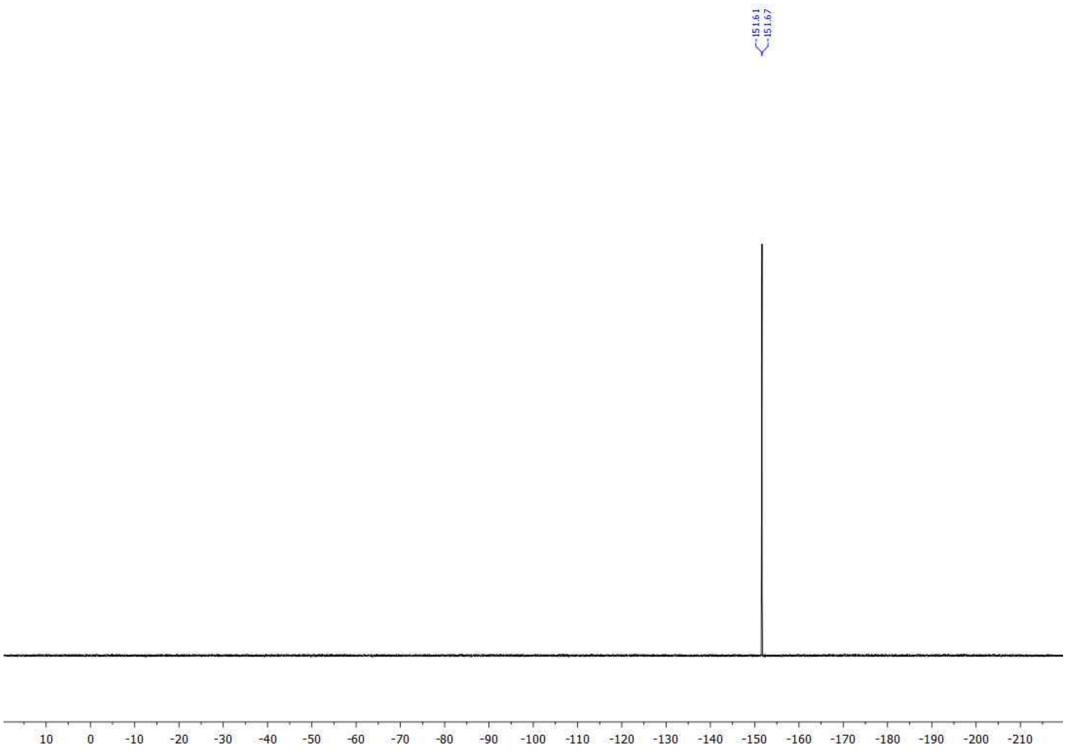
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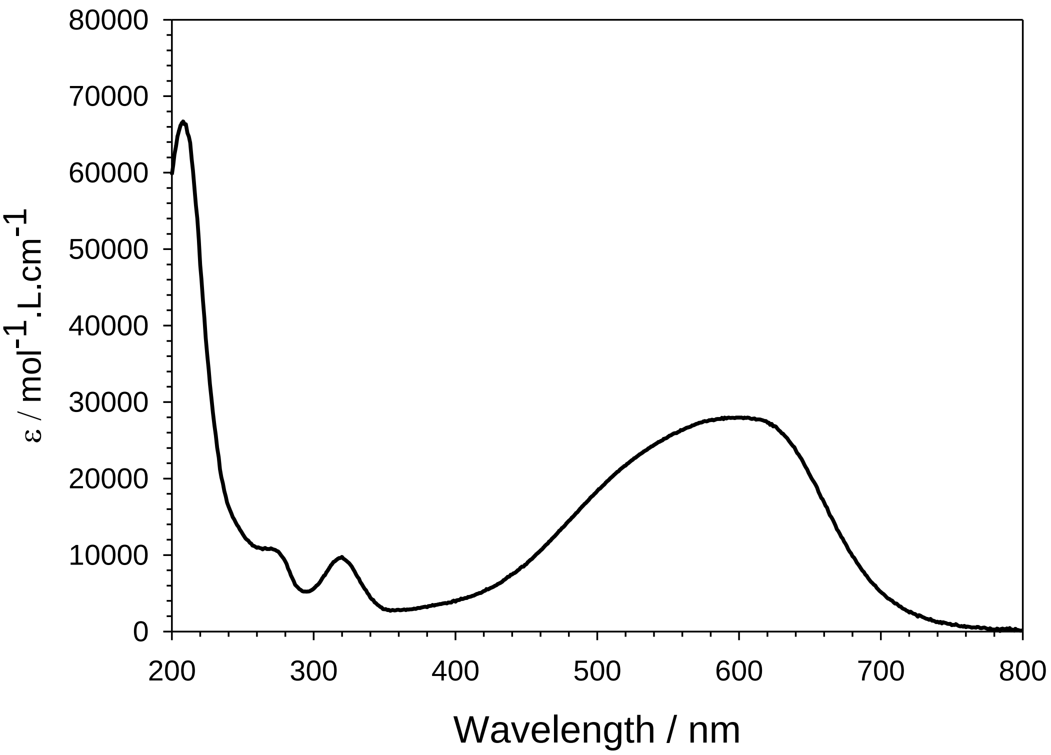
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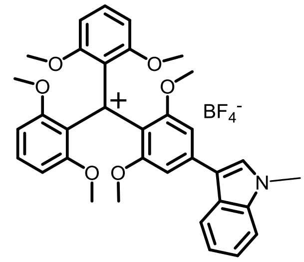

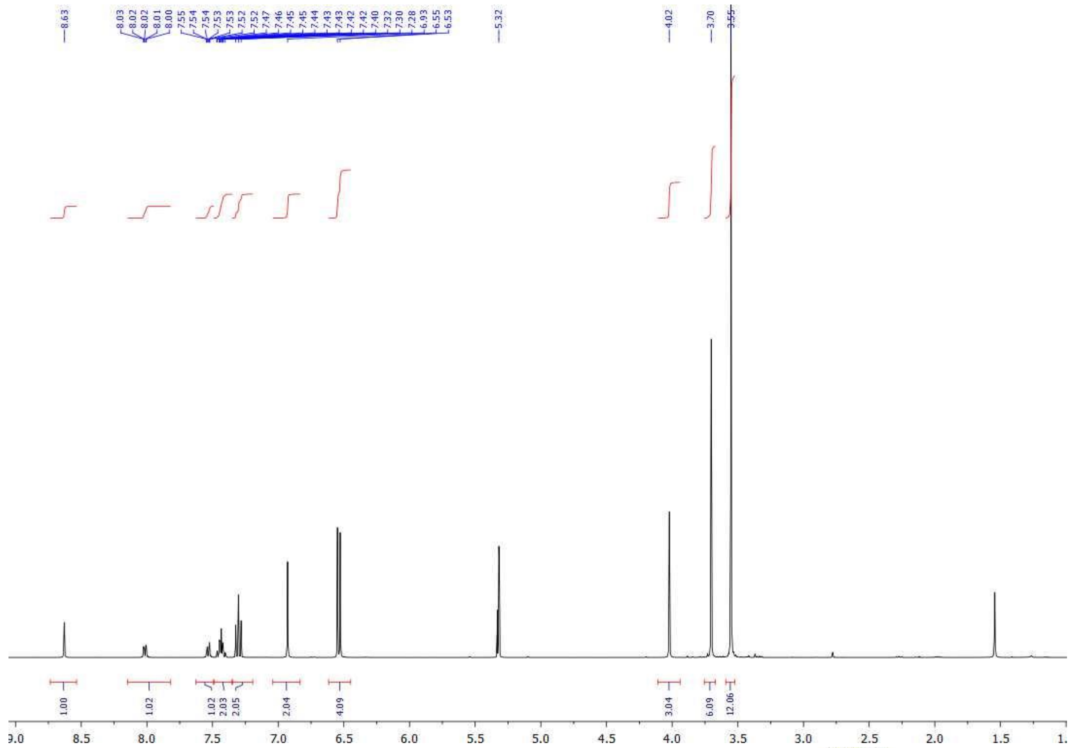

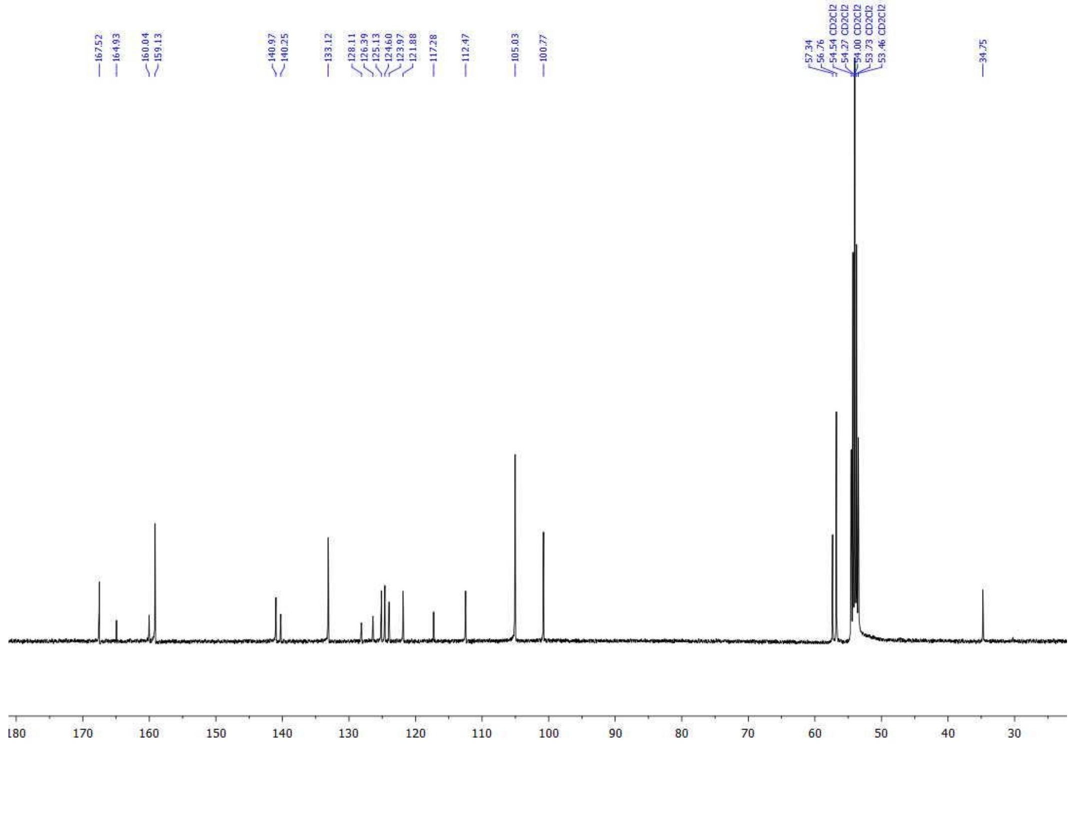

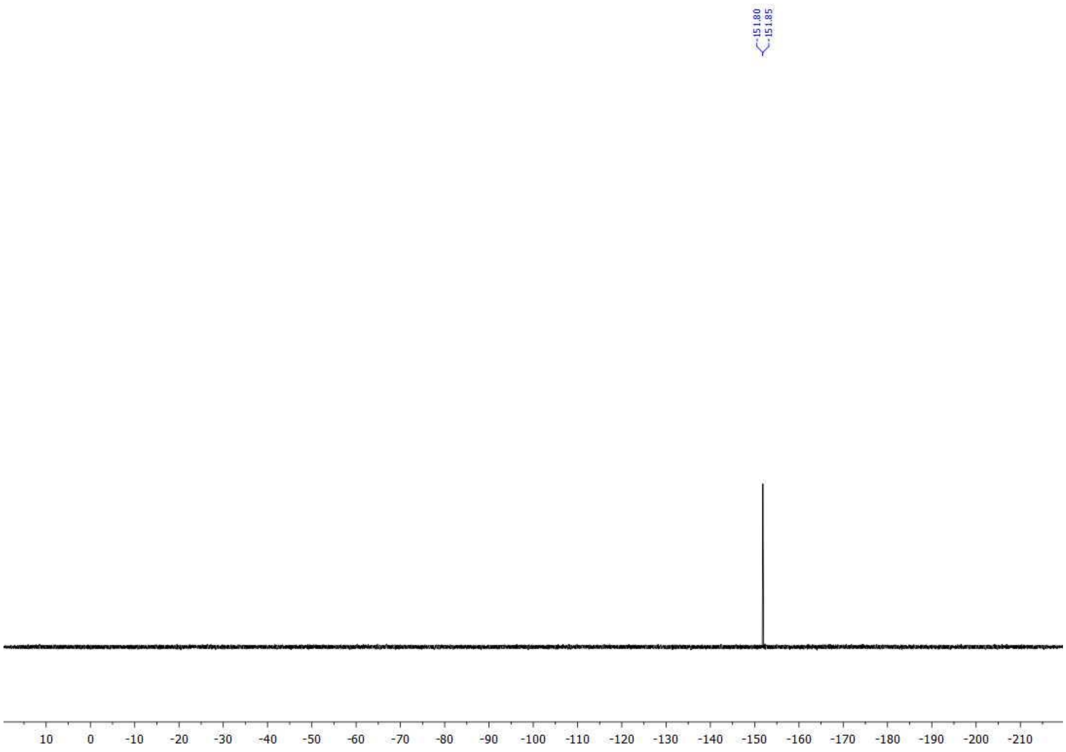
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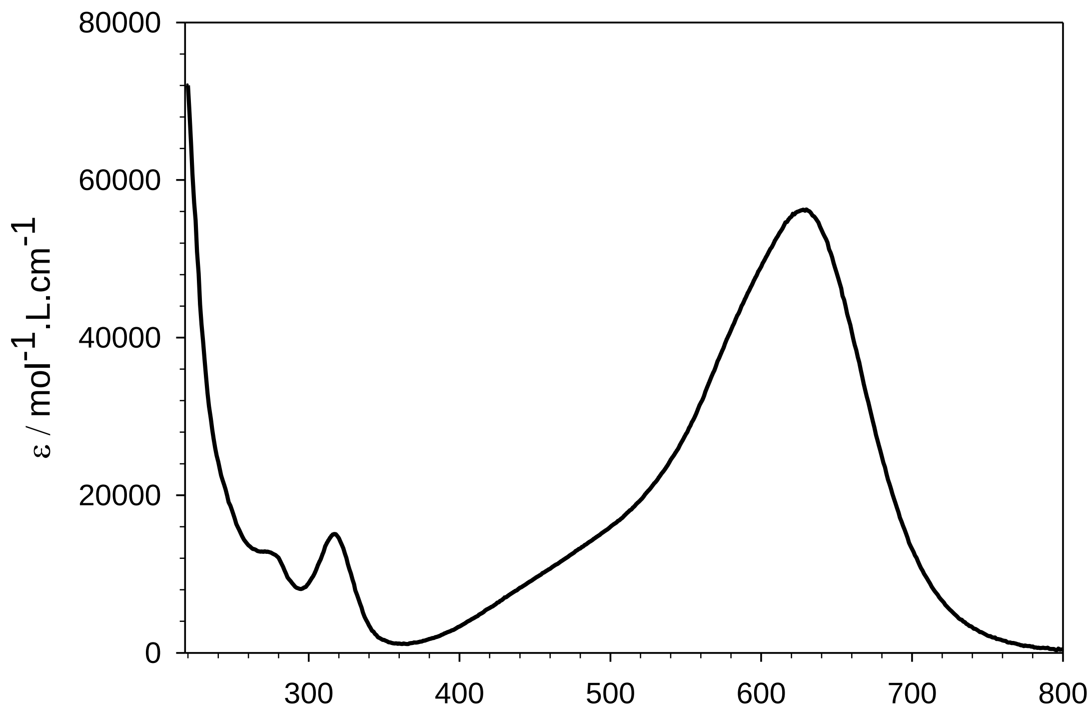
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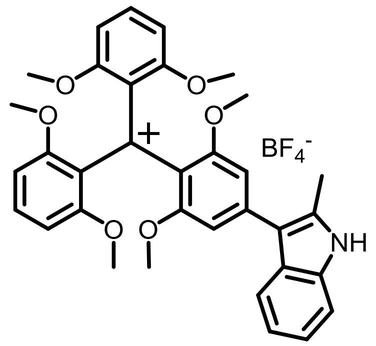

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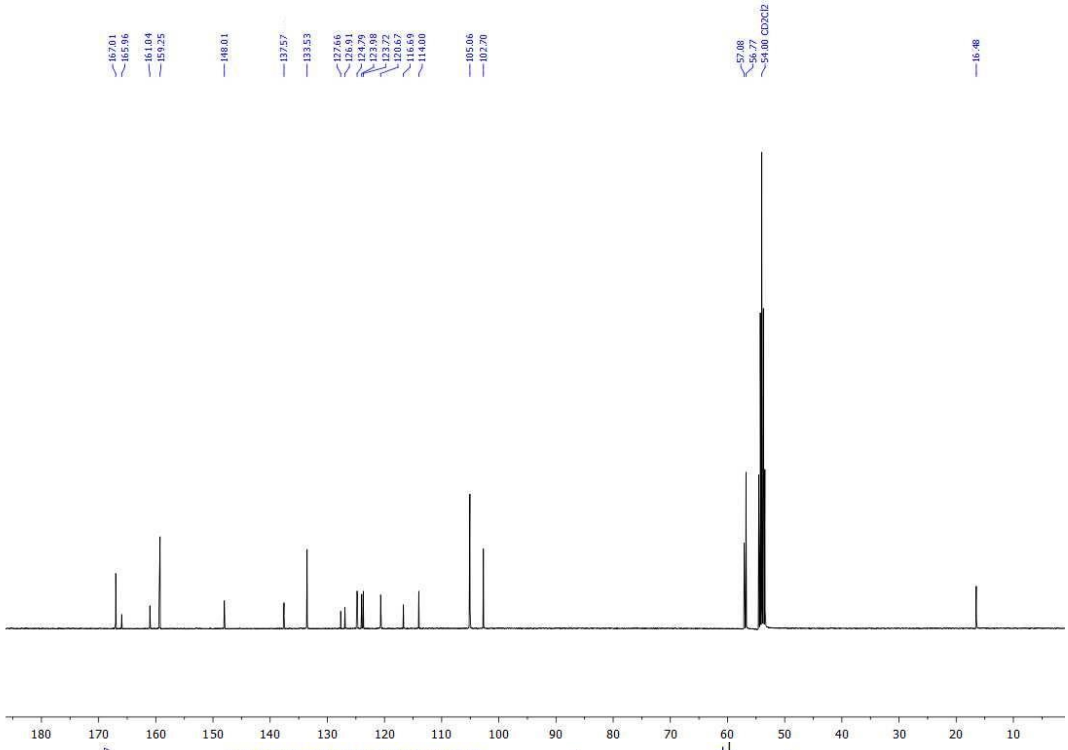

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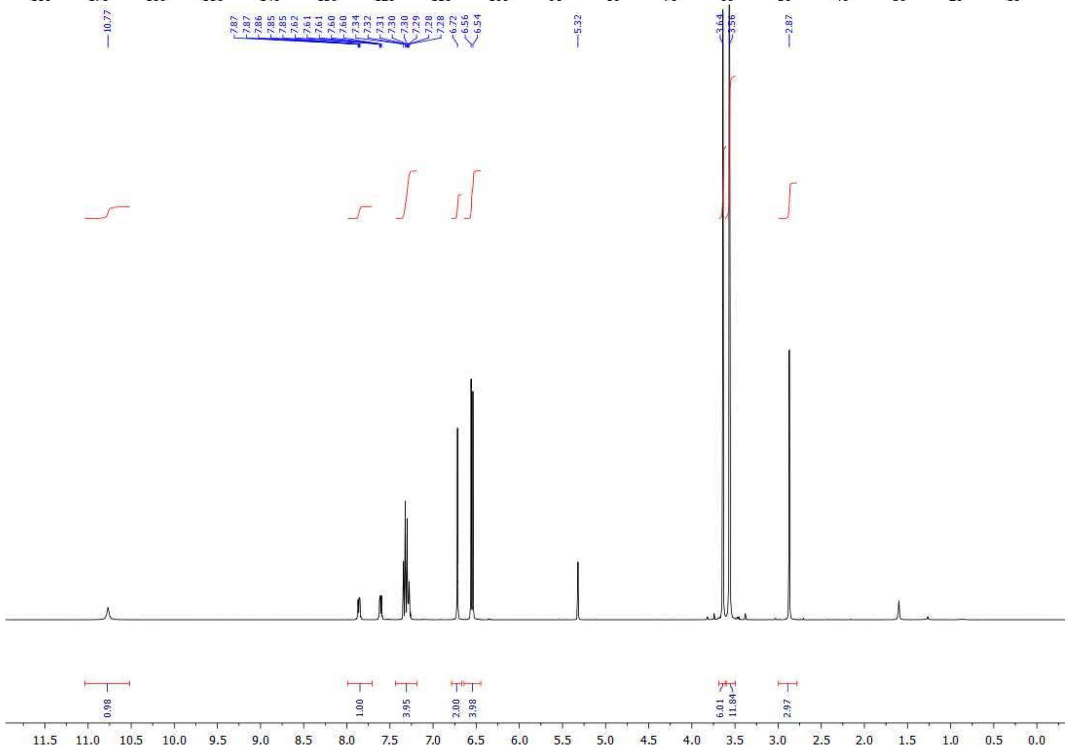

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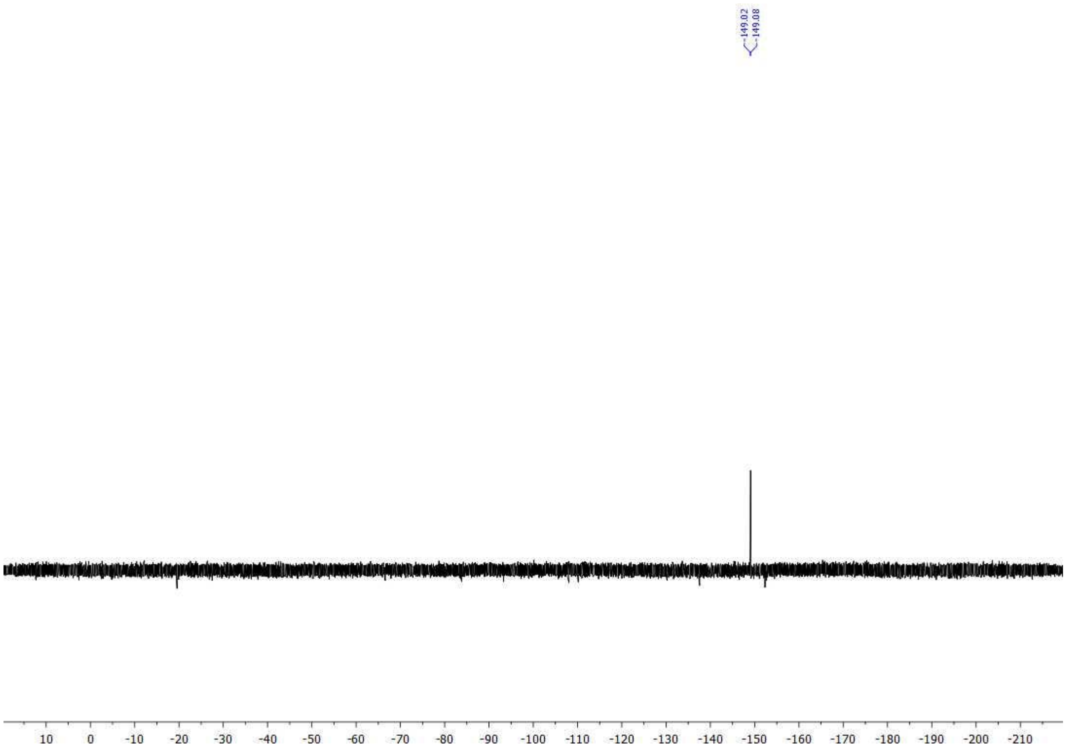
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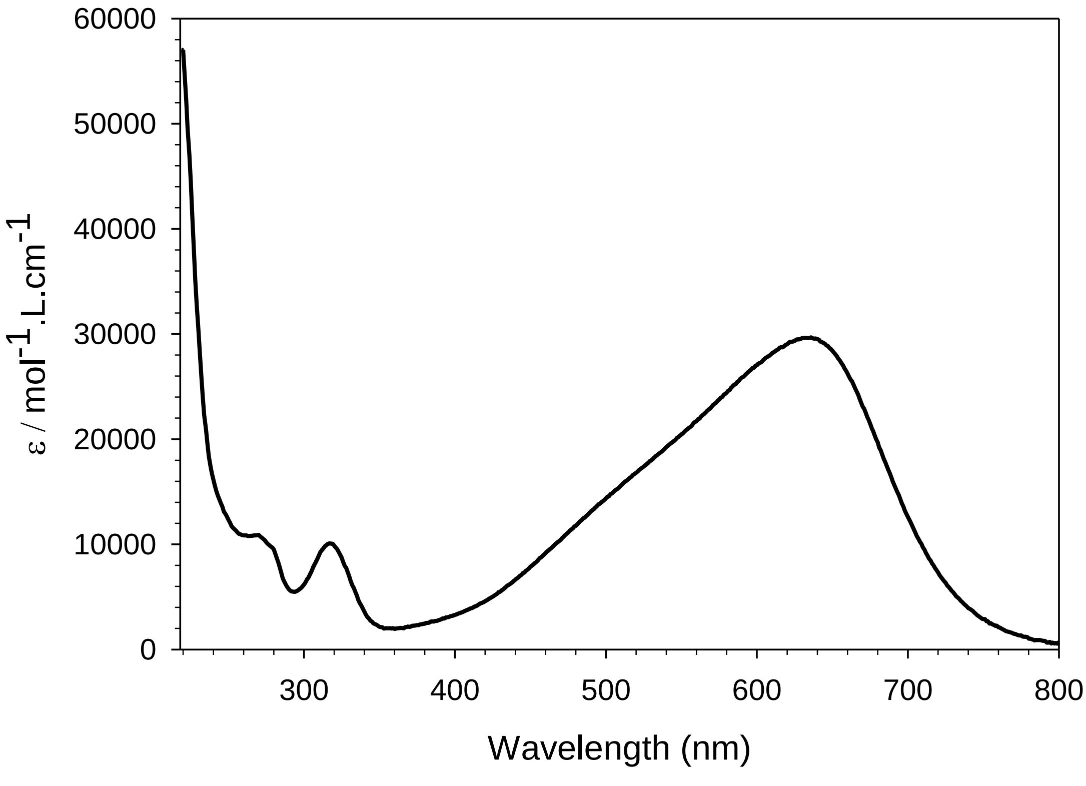
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ε / mol-1.L.cm-1
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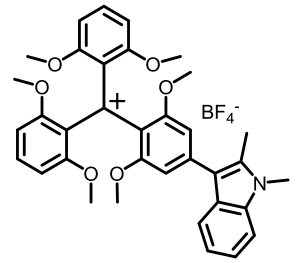
400
500
600
700
800
Wavelength (nm)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O
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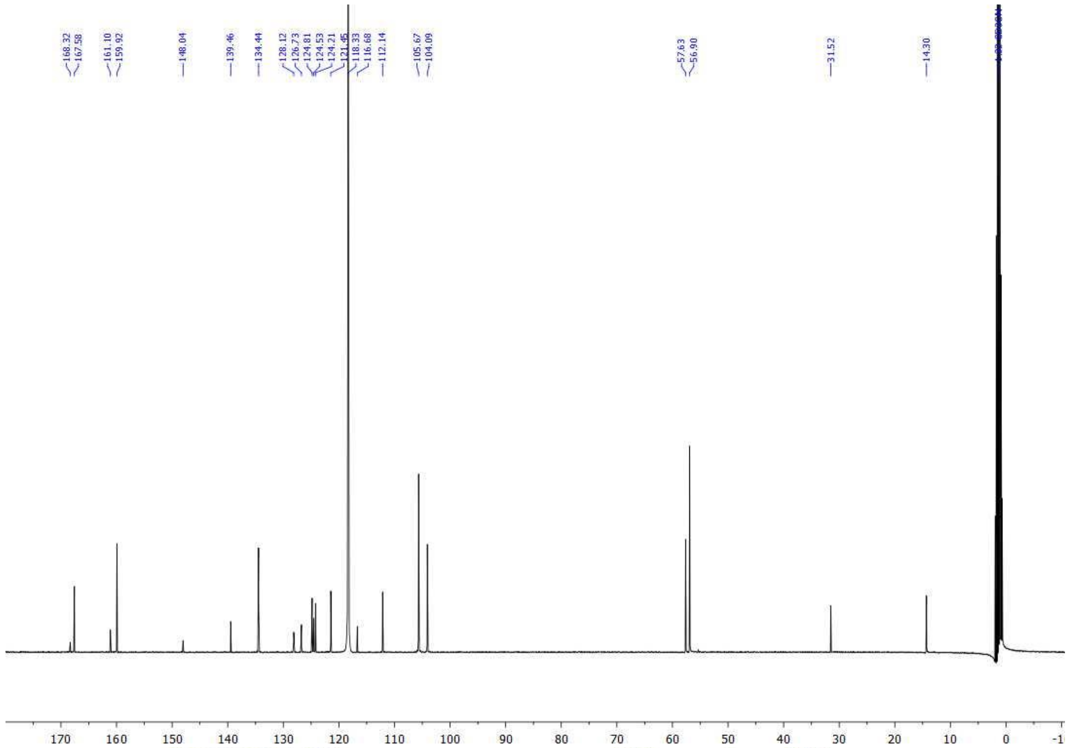
N
BF4-
+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31.52
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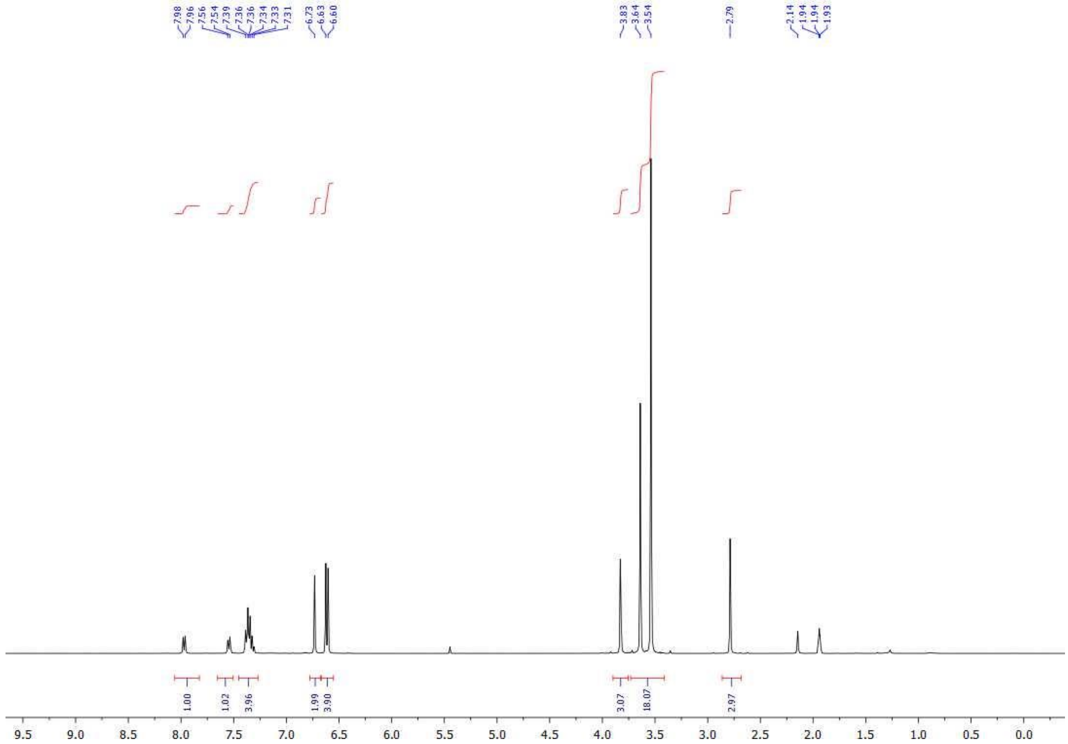
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2.79
2.14
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1.94
1.93
1.00
1.02
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1.99
3.90
3.07
18.07
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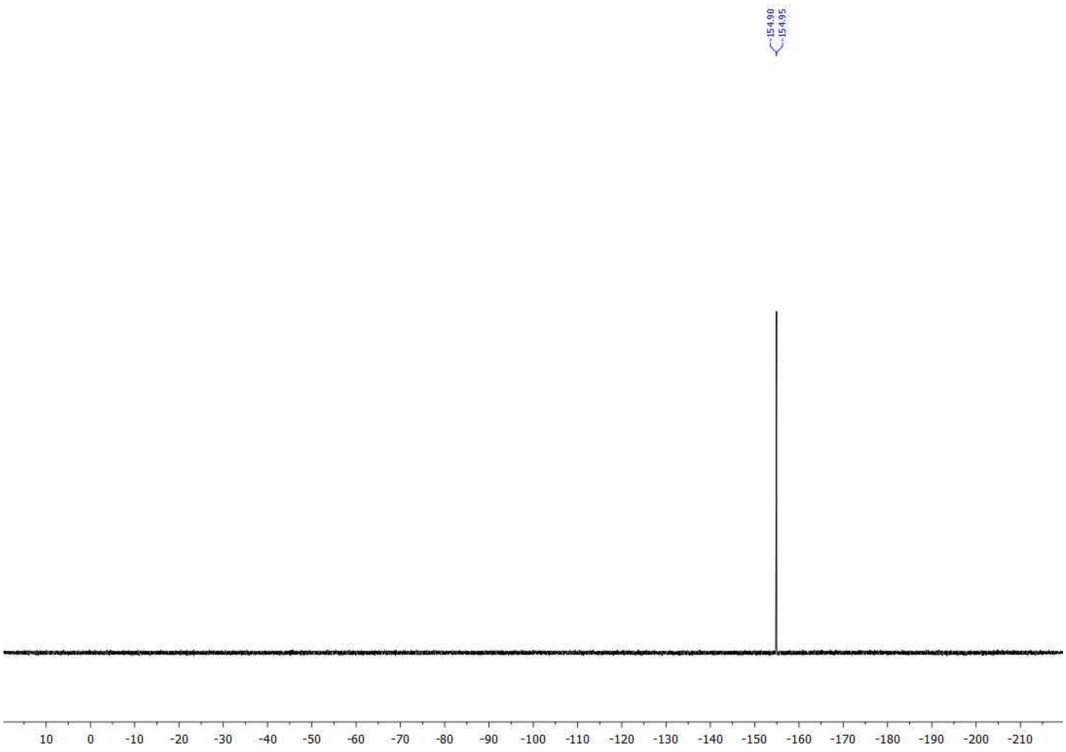

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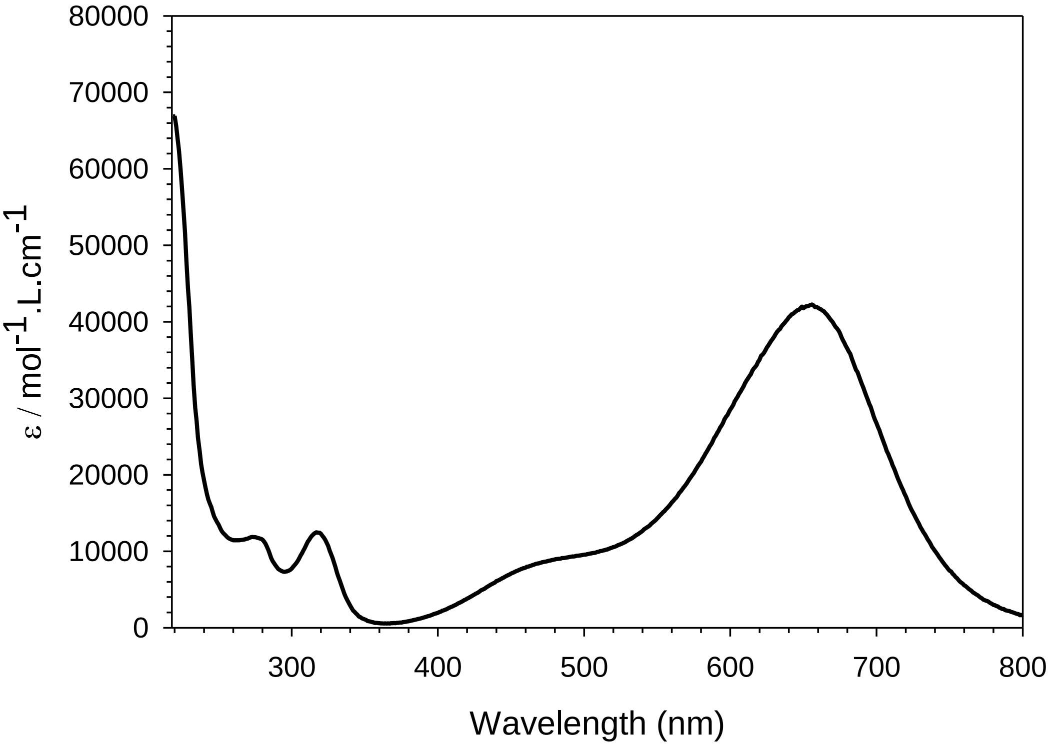

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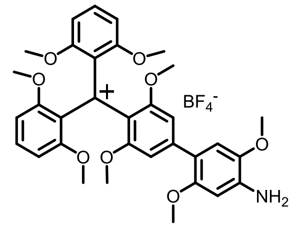
10000
0
300
400
500
600
700
800
Wavelength (nm)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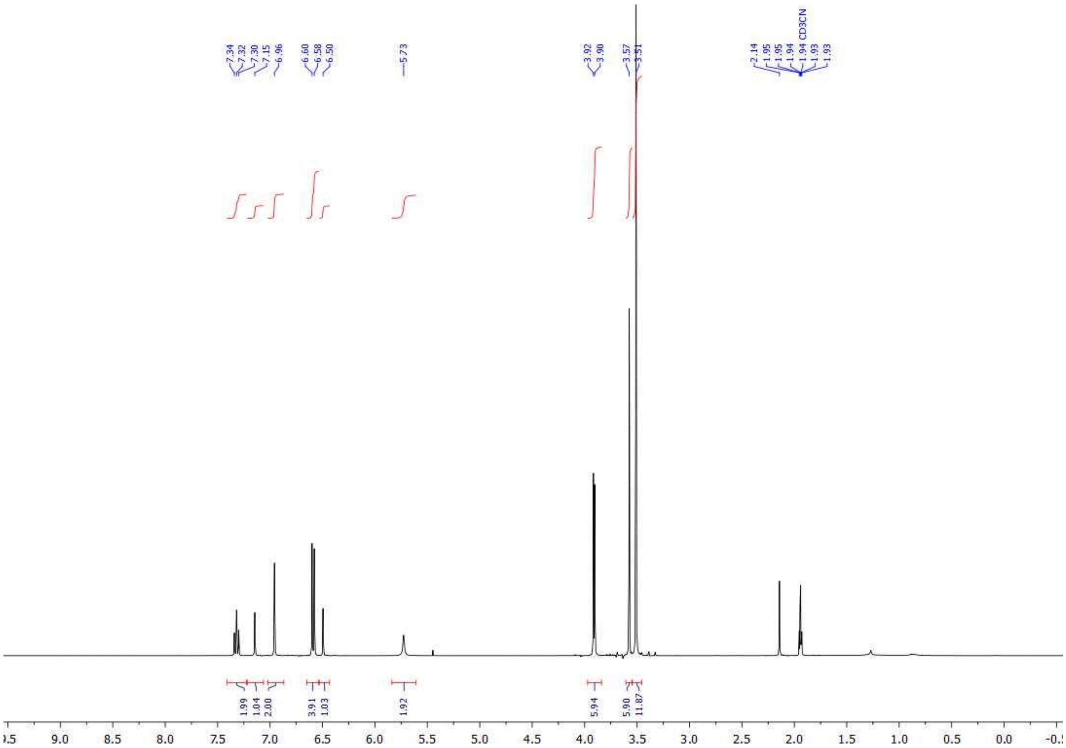

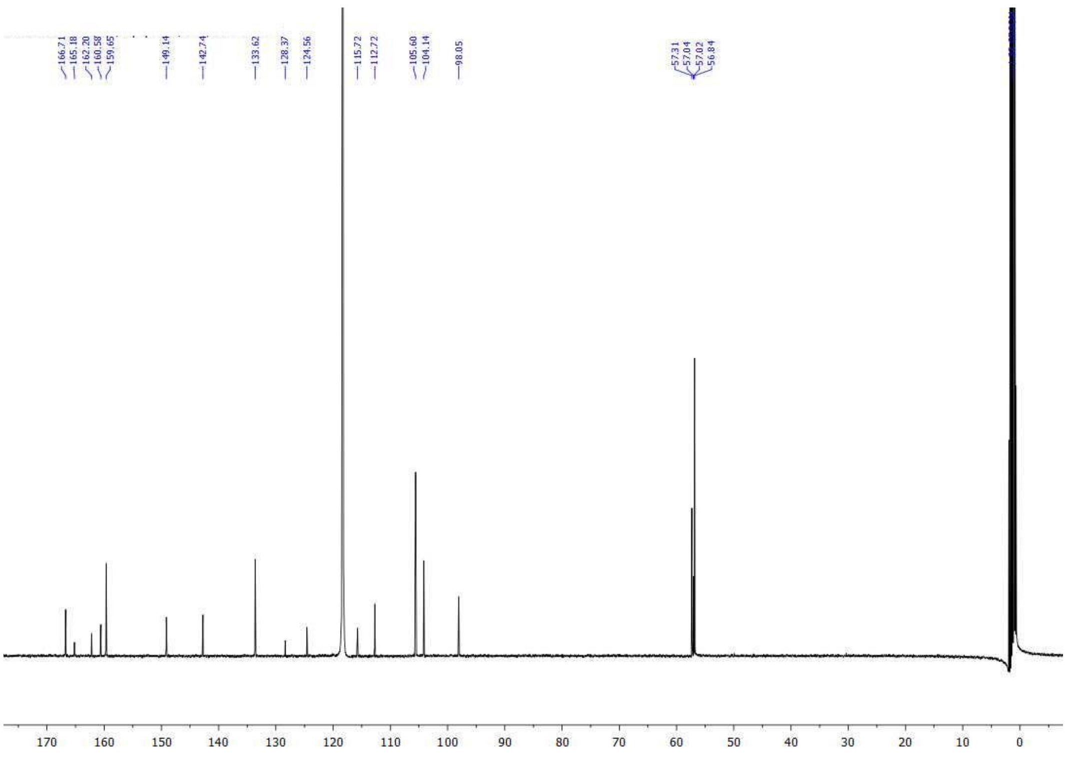

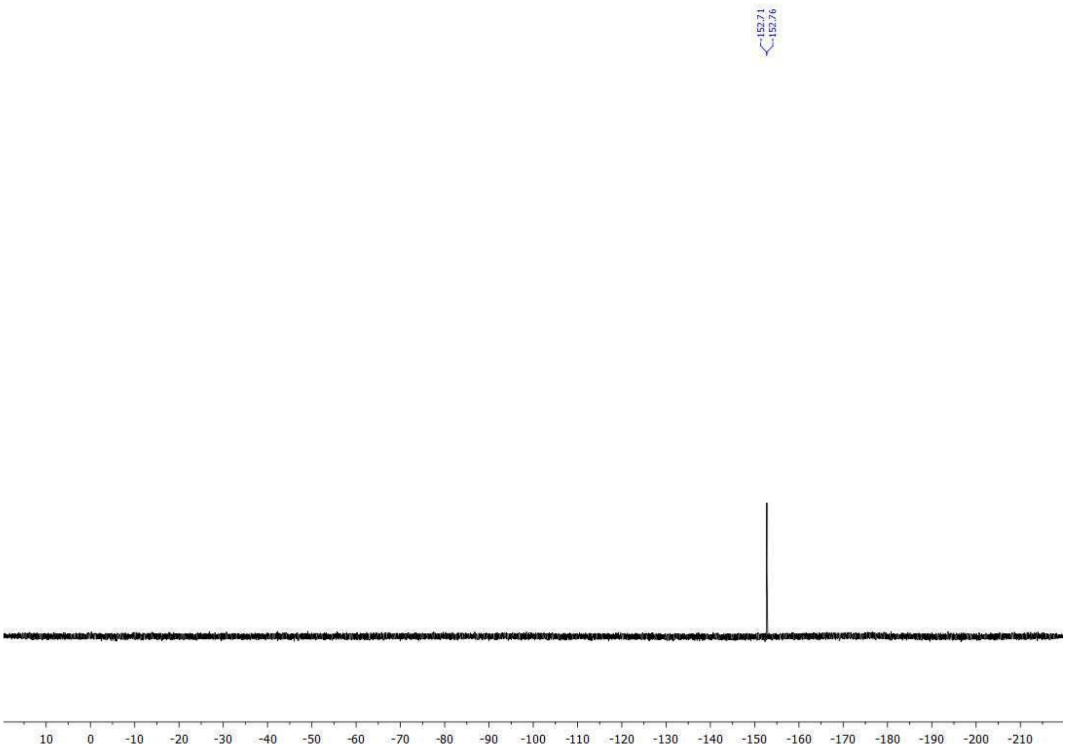
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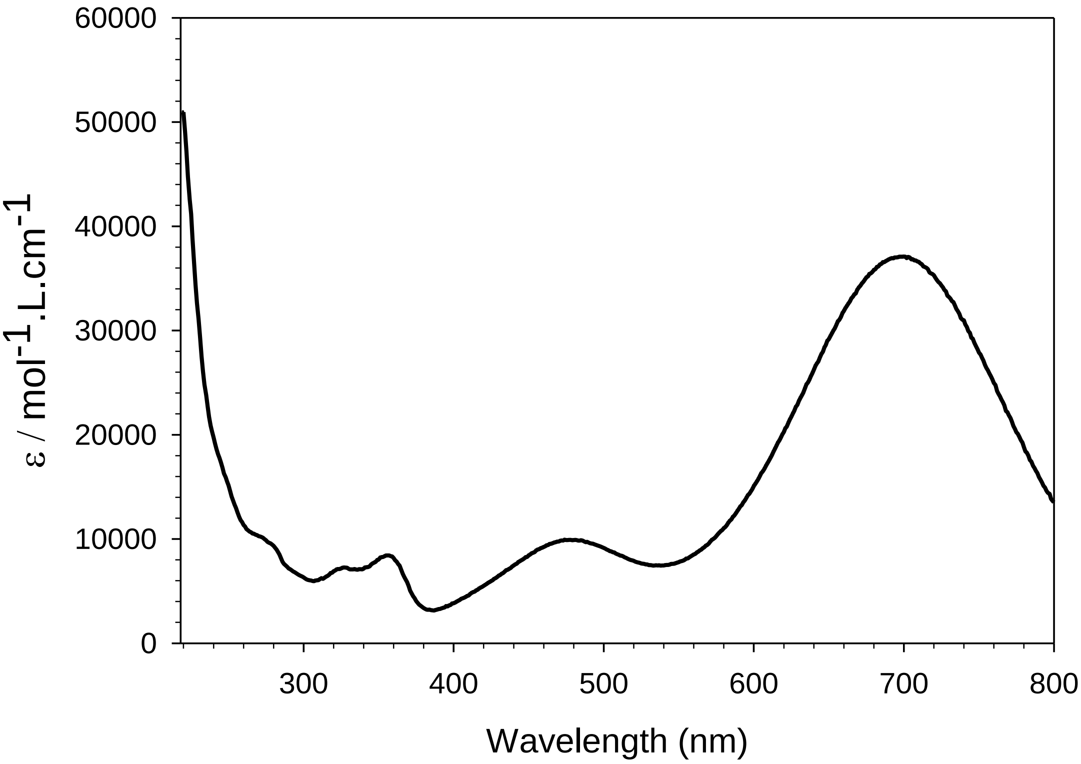
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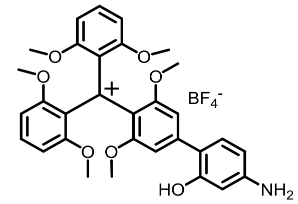
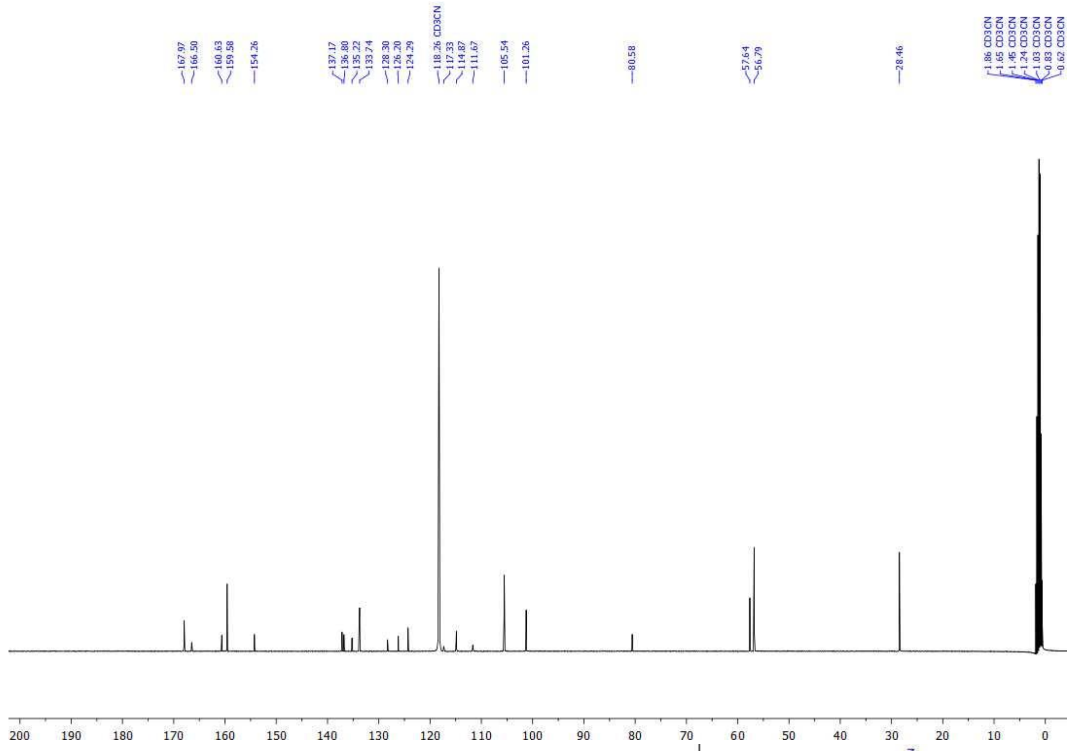
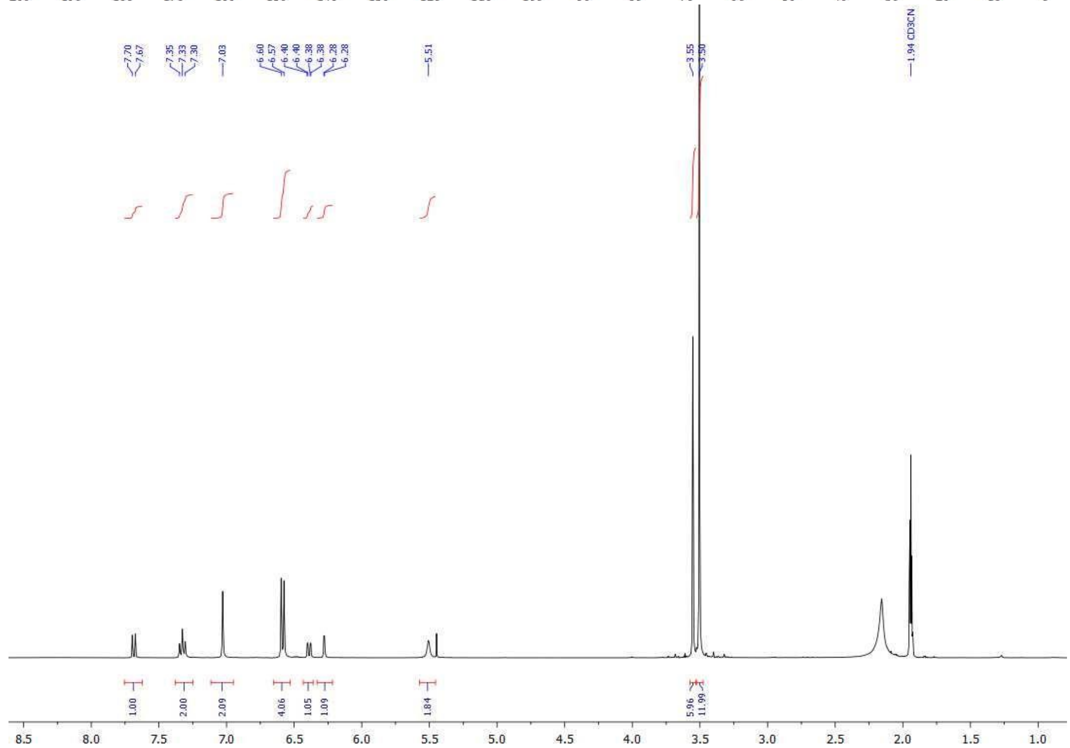
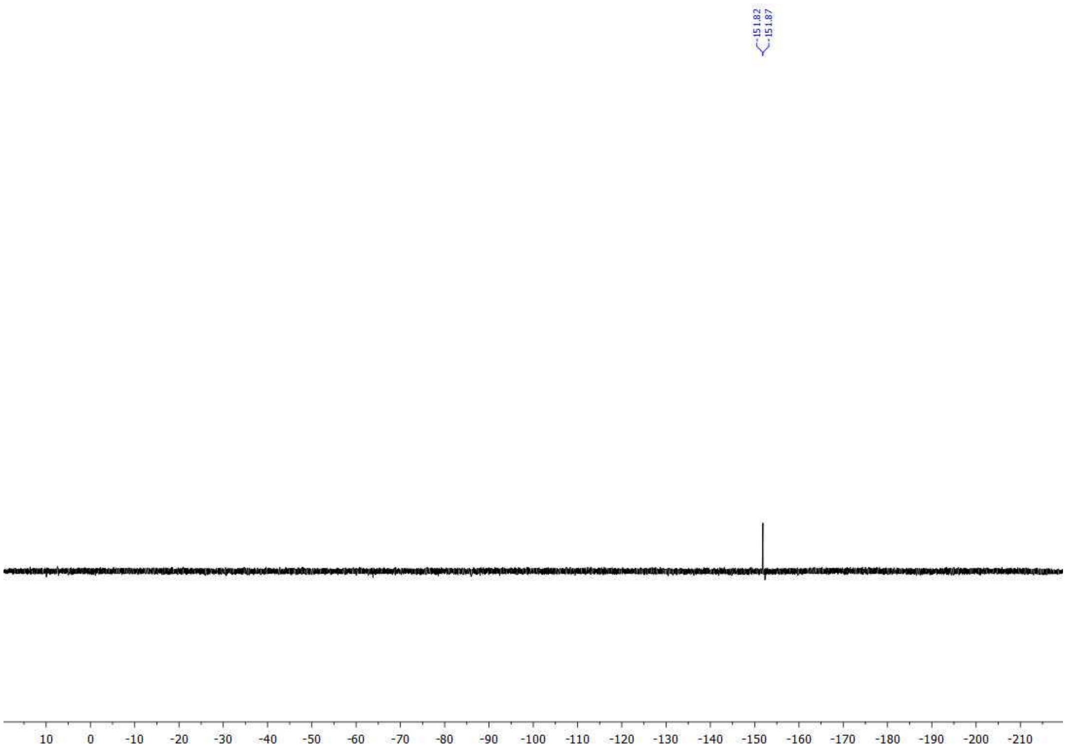
Wavelength (nm)





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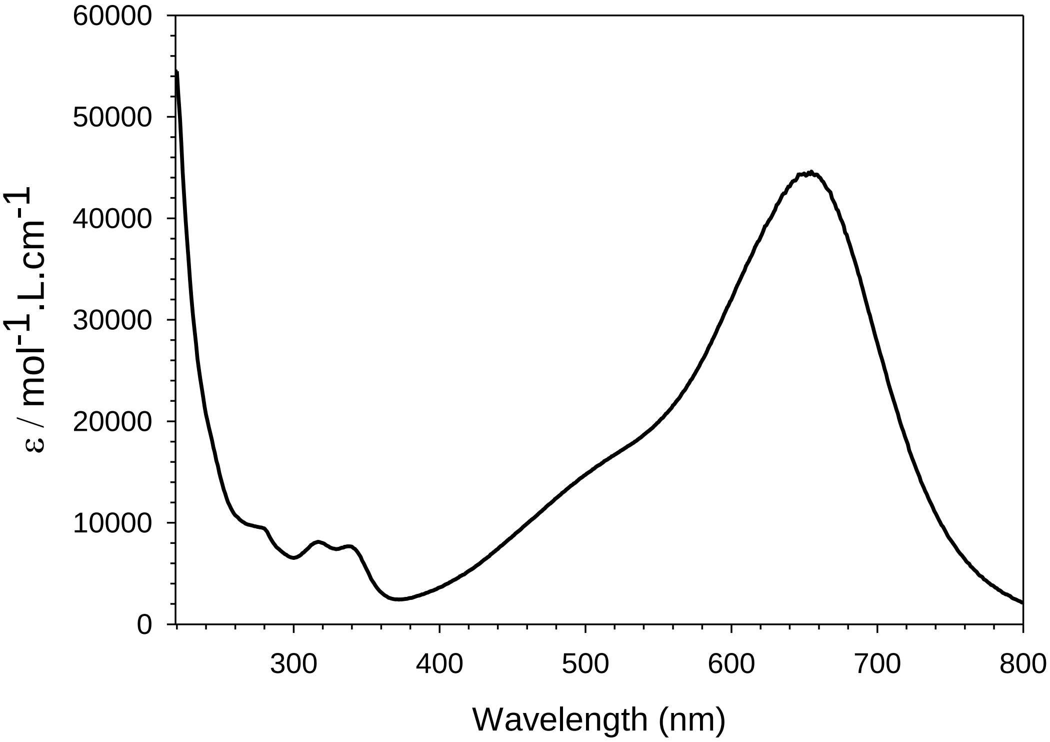
60000
50000
40000
30000
20000
10000
0
ε / mol-1.L.cm-1
300
400
500
600
700
800
Wavelength (nm)

5. Absorption properties

Entry	Product	λ_{abs} max (nm)	ε ($mol^{-1}.L.cm^{-1}$)
1	**1**	523	18400
2	**4a**	574	32500
3	**4b**	596	30200
4	**4c**	599	28000
5	**4d**	616	33700
6	**4e**	627	47200
7	**4f**	636	29700
8	**4g**	630	56300
9	**4h**	656	42300
10	**6**	655	44600
11	**7**	700	37100

Table S1: Absorption maximum wavelengths and extinction coefficient of hexamethoxycarbenium derivatives. All absorption spectra have been recorded in acetonitrile.

Entry	Product	λ_{abs} max (nm) in ACN	λ_{abs} max (nm) in THF	λ_{abs} max (nm) in $CHCl_3$	λ_{abs} max (nm) in DCM
1	**1**	523	525	526	526
2	**4a**	574	615	625	629
3	**4f**	636	633	645	653

Table S2: Absorption maxima of **1**, **4a** and **4f** in various solvents.

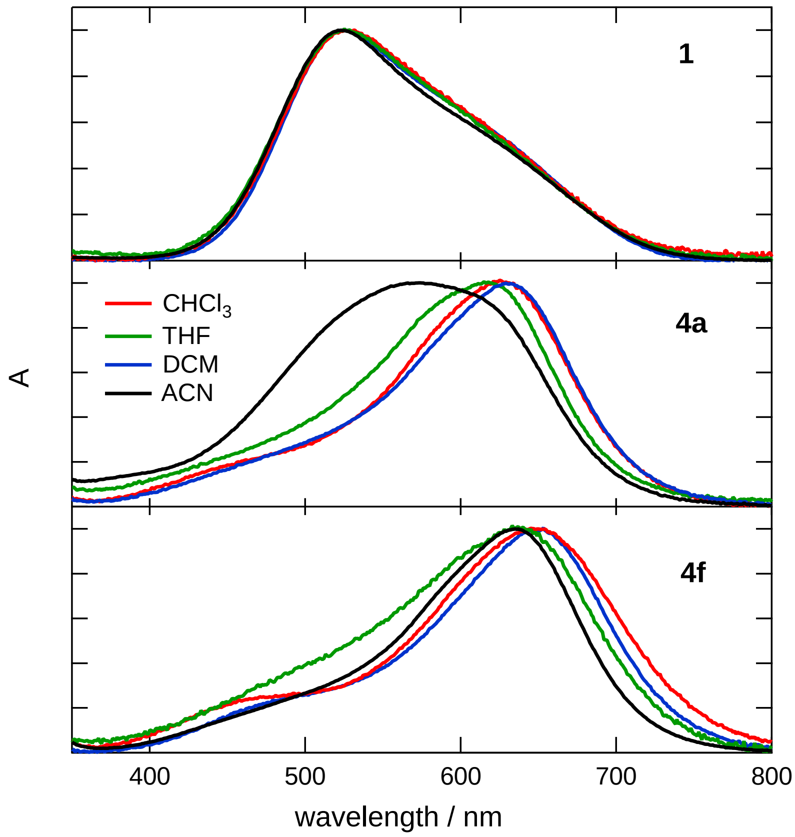

Figure S2. Electronic absorption spectra of **1**, **4a** and **4f** in various solvents.

6. Photophysics

Experimental details

Solvent. Acetonitrile (ACN, Fisher scientific, UK, > 99.9) and glycerol (Alfa Aesar, ultrapure, HPLC grade, stored under Ar) were used as received.

Steady-state spectroscopy. Electronic absorption spectra were obtained using a Cary 50 spectrophotometer. All the molar extinction coefficients were measured using 5.10^{-6} to 5.10^{-5} M solutions in acetonitrile. They are summarised with maximum absorption wavelengths in table S1.

Fluorescence spectra were measured with a Jobin-Yvon (Horiba) Fluoromax 4, using of 3 and 6 nm excitation and emission slits, respectively, 0.5 s accumulation time and taking the average of 10 spectra. The measurements were done with 1 to 5.10^{-5} M solutions. The fluorescence quantum yield of **4a** in glycerol has been measured upon 550 nm excitation with oxazine1 in ethanol ($\Phi_f = 0.11$)[1] as reference.

Fluorescence up-conversion. The fluorescence up-conversion set-up has been described in detail elsewhere.[2,3] Excitation was carried out at 450 nm using the frequency-doubled output of a Kerr-lens mode-locked Ti:Sapphire oscillator (Mai Tai HP, Spectra Physics). The polarization of pump pulses was at magic angle relative to that of the gate pulses at 900 nm. The pump intensity on the sample was 5μJ cm^{-2} and the full width at half maximum of the instrument response function was ca. 230 fs. All measurements were performed in a 0.4 mm rotating cell and the absorbance of the samples at 450 nm was between 0.2 and 0.5. No photodegradation of the samples was observed throughout the measurements.

Transient electronic absorption. The femtosecond transient electronic absorption set-up has been described in detail previously.[4,5] Excitation was performed at 400 nm using the frequency-doubled output of a standard 1-kHz Ti:Sapphire amplifier. The pump intensity on the sample was about 1 mJ/cm^2. All data were corrected for the chirp of the white light. The polarization of the pump pulse was at the magic angle relative to that of the probe pulse. The samples were located in a 1 mm quartz cell and stirred by nitrogen bubbling to avoid photodegradation. Their absorbance at 400 nm was 0.04. No noticeable photodegradation was observed throughout the measurements.

Quantum chemistry calculations. Ground-state gas-phase geometry optimization was performed at the density functional level of theory (DFT) using the CAM-B3LYP functionals,[6] and the 6-31G* basis set. The electronic transitions were computed with time-dependent DFT (TD-DFT) using the same functional and basis set. The calculations were carried out using Gaussian 09.[7]

Data

Quantum chemistry calculations

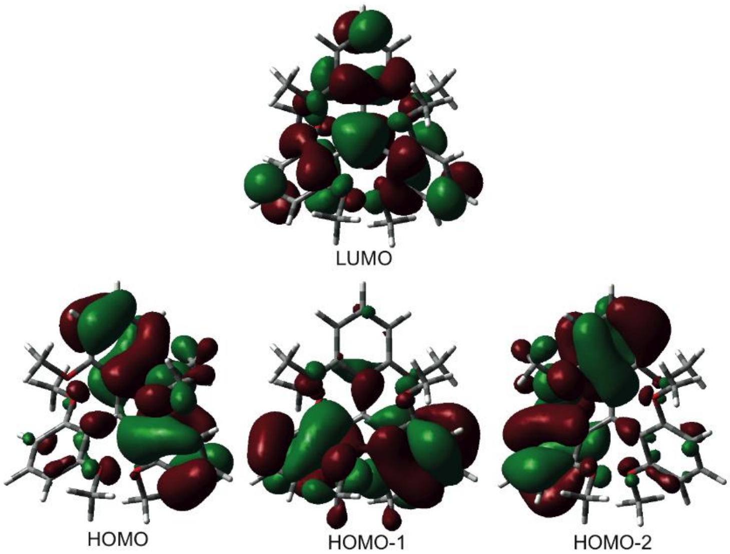

Figure S3. Frontier molecular orbitals of **1** calculated at the CAM-B3LYP/6-31G* level of theory. The energy of three HOMOs is within 6 meV.

Transient electronic absorption

Figure S4a-c depicts transient absorption (TA) spectra recorded at several time delays after 400 nm excitation of **4a** in ACN. The scaled steady-state absorption spectrum of **4a** in ACN is also shown for comparison. These spectra are dominated by a negative band coinciding with the steady-state absorption spectrum that can be ascribed to the bleach of the absorption due to the depletion of the ground-state population. Additionally, two positive bands can be observed, one around 430 nm and the other at about 700 nm. The time evolutions of these two band differ considerably. Whereas the 430 nm band decays almost completely within 5 ps, the 700 nm band rises during the first 3-4 ps and decays on a 10-15 ps timescale. On the other hand, the negative band exhibits a biphasic decay, and has totally vanished after about 20 ps, pointing to a full recovery of the ground-state population. The time evolution and spectral position of the 700 nm band, i.e. on the red side of the ground-state bleach, are typical of an unrelaxed/vibrationally hot ground state.[8] The temporal evolution of the TA spectra can be rationalized in terms of an A→B→C kinetic scheme, where A is the excited state of **4a**, characterised by the 430 nm TA band, B is the unrelaxed ground state populated upon internal conversion from A, and C is the thermally equilibrated ground state. Global target analysis of the TA data assuming this scheme resulted to time constants of 1 ps and 7.4 ps for the internal conversion (A→B) and the relaxation to the equilibrated ground state (B→C), respectively, and to the species associated difference absorption spectra depicted in Figure S4d.

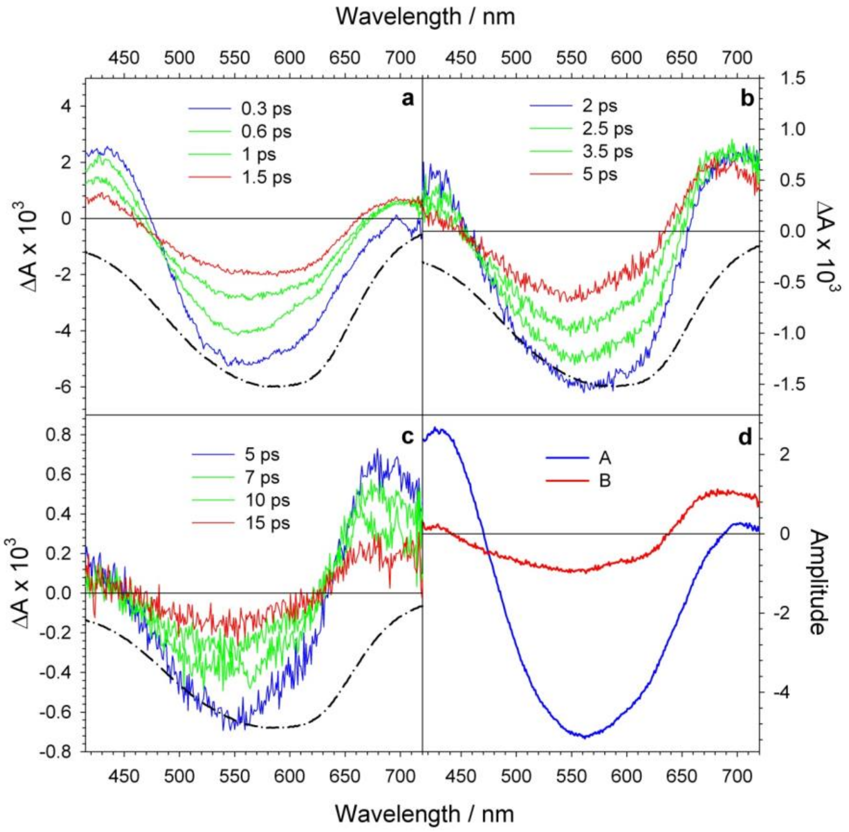

Figure S4. (a-c) Transient absorption spectra recorded at various time delays after 400 nm excitation of **4a** in acetonitrile; (d) species-associated difference absorption spectra resulting from a target global analysis assuming a A→B→C scheme. The dashed-dot line is the scaled steady-state absorption spectrum.

Time-resolved fluorescence

Time profiles of the fluorescence intensity measured at 720 nm with **4a** in ACN upon 450 nm excitation are shown in Figure S5. This profile could be analysed using the convolution of the instrument response function and the sum of two exponential functions with 0.2 and 1.05 ps time constants. The relative amplitude of the slow component was found to increase with the detection wavelength. From the comparison with the transient absorption measurements, the 1.05 ps component can be ascribed to the decay of the excited-state population, whereas the 0.2 ps can be assigned to relaxation processes (vibrational and solvent relaxation) from the initially populated Franck-Condon excited state.

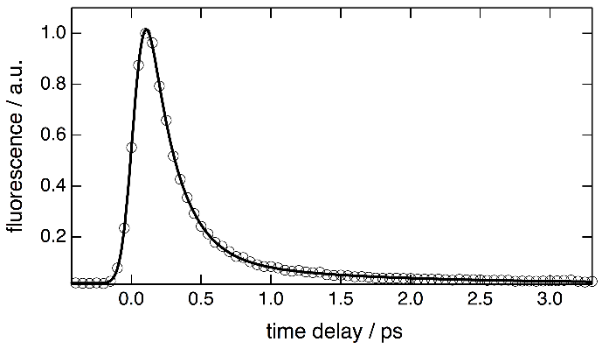

Figure S5. Fluorescence time profile measured with **4a** in acetonitrile upon 450 nm excitation.

A qualitatively similar result was obtained with **4g** in ACN wit, 0.17 ps and 0.95 ps time constants, the latter being assigned to the excited-state lifetime (Figure S6)

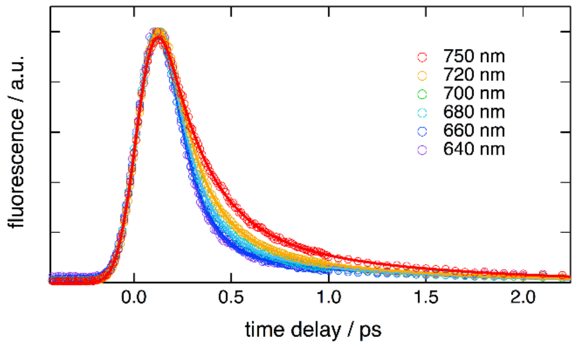

Figure S6. Fluorescence time profiles measured with **4g** in acetonitrile upon 450 nm excitation.

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