

SUPPORTING INFORMATION

Heck Functionalization of Asymmetric Aza-Bodipy Core: Synthesis of Far-Red Infrared Probes for Bioimaging Applications

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General Content

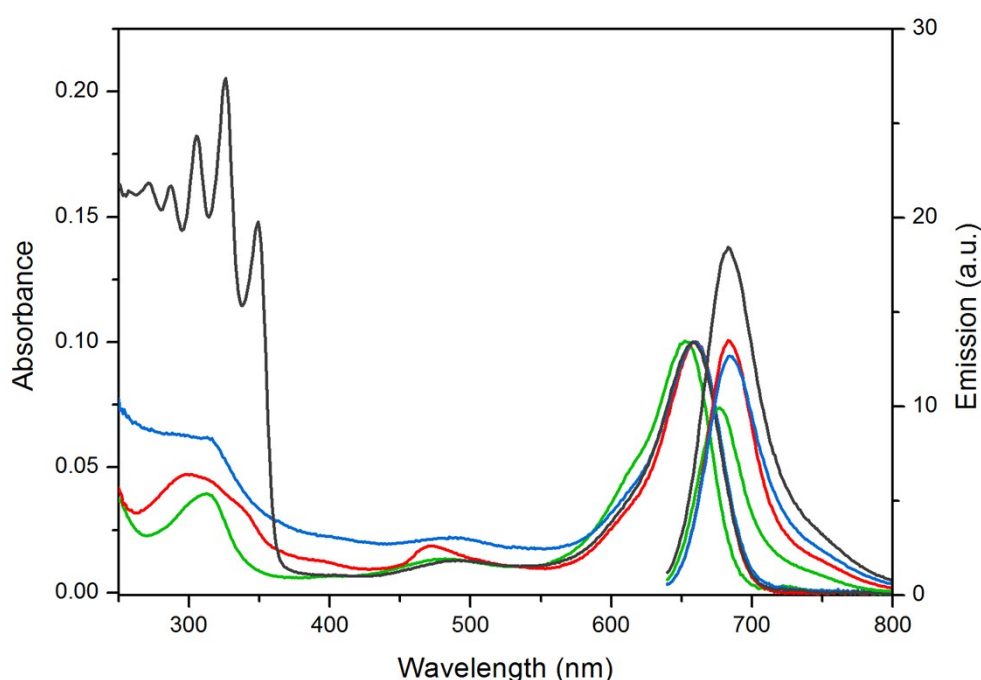
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General Details. Flasks and all equipment used for the generation and reaction of moisture-sensitive compounds were dried by electric heat gun under nitrogen. All reactions involving air-sensitive reagents were performed under a dry nitrogen atmosphere. DMF was purchased from Sigma Aldrich. Anhydrous CH_2Cl_2 was obtained by distillation from CaH_2 . Reagents were used as received if not otherwise specified, or prepared according to the literature procedures.

Reactions were monitored by TLC using silica-gel on TLC-PET foils Fluka, 2-25 μm , layer thickness 0.2 mm, medium pore diameter 60 Å. ^1H NMR spectra were recorded at 200 MHz, ^{13}C NMR spectra at 50.2 MHz, in CDCl_3 . Data were reported as follows: chemical shifts in ppm from Me_4Si as an internal standard, multiplicity, integration, coupling constants (Hz), and assignment. ^{13}C NMR spectra were measured with complete proton decoupling. Chemical shifts were reported in ppm from the residual pick solvent as an internal standard. Infrared spectra were acquired using a Perkin Elmer Spectrum Two ATR-FTIR spectrometer.

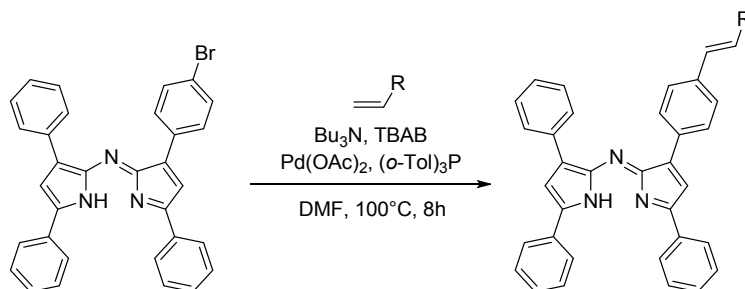
Photochemical Characterization of Fluorescent Derivatives. UV-Vis absorption and photoemission spectra, together with luminescence lifetimes and quantum yields, were recorded in chloroform solution at room temperature.

Absorption spectra were acquired on an Agilent Cary 60 UV-Vis spectrometer, while photoemission spectra, luminescence lifetimes and quantum yields were obtained on a HORIBA Jobin Yvon IBH Fluorolog-TCSPC spectrofluorometer equipped with a Quanta- ϕ integrating sphere. The luminescence lifetimes were determined by time-correlated single-photon counting; excitation was achieved with nanosecond pulses of 636 nm light generated by a NanoLED pulsed diode. Emission-decay data were collected in 2048 channels to 10000 counts in the peak channel and analysed with the software DAS6 (TCSPC decay-analysis software).

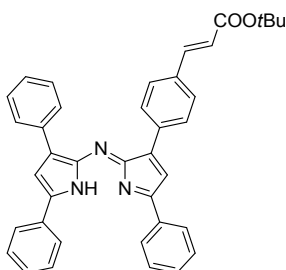


Experimental electronic absorption (left) and emission (right) spectra of **1** (green), **2** (red), **3** (blue) and **4** (black) in CHCl_3 solution.

Synthetic Procedures

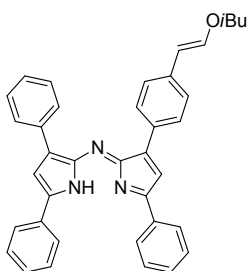


Typical Heck procedure: In a reaction tube, 4 mL of DMF are thoroughly degassed for 30 minutes by bubbling nitrogen. Then the aryl bromide (53.0 mg, 0.10 mmol, 1.0 eq), a suitable alkene (0.20 mmol, 2.0 eq), tributylamine (48 μ L mg, 0.3 mmol, 2.0 eq), TBAB (12.8 mg, 0.040 mmol, 0.4 eq), Pd(OAc)₂ (2.2 mg, 0.01 mmol, 0.10 eq) and (o-Tol)₃P (6.1 mg, 0.02 mmol, 0.20 eq) are added all in once. The tube is sealed and the dark blue solution is stirred at 100°C for 8 hours. After cooling down, the reaction mixture is diluted with ethyl acetate, washed with saturated ammonium chloride (1x15 mL) and brine (1x15 mL). The organic phase is dried over Na₂SO₄, filtered and the solvent is removed under reduced pressure to afford a dark solid that is purified by column.



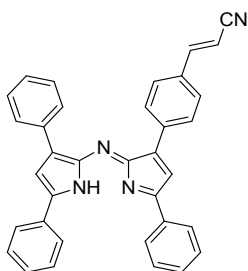
(E)-tert-butyl 3-(4-((Z)-2-((3,5-diphenyl-1H-pyrrol-2-yl)imino)-5-phenyl-2H-pyrrol-3-yl)phenyl)acrylate (8a)

Dark blue metallic solid (yield 90%), m.p. 225–227 °C, TLC R_f = 0.45 (EP/CH₂Cl₂ 1/1, v/v). ¹H NMR (200 MHz, CDCl₃) δ (ppm): 7.75–8.10 (m, 8H, Ar-H), 7.62 (d, 1H, J = 16.0 Hz, COCH=CH), 7.30–7.55 (m, 11H, Ar-H), 7.14 (s, 1H, Pyrr-H), 7.08 (s, 1H, Pyrr-H), 6.41 (d, 1H, J = 16.0 Hz, COCH=CH), 1.60 (s, 9H, CH₃), (NH not observed). ¹³C NMR (50.2 MHz, CDCl₃) δ (ppm): 166.3 (Cq), 156.9 (Cq), 152.7 (Cq), 150.8 (Cq), 148.1 (Cq), 143.3 (Cq), 143.2 (CH), 140 (Cq), 135.2 (Cq), 133.6 (Cq), 133.3 (Cq), 131.9 (Cq), 131.6 (Cq), 130.1 (CH), 129.6 (CH), 128.9 (CH), 128.0 (CH), 127.7 (CH), 126.5 (CH), 126.1 (CH), 119.6 (CH), 115.6 (CH), 113.7 (CH), 80.3 (Cq), 28.1 (CH₃). IR cm⁻¹: 2962, 1705, 1635, 1005, 902, 579, 680. m/z (HR, ESI) for C₃₉H₃₄N₃O₂⁺ Calcd 576.2646 [M + H]⁺. Found 576.2664 [M + H]⁺.



(Z)-N-(3-(4-((E)-2-isobutoxyvinyl)phenyl)-5-phenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine (8b)

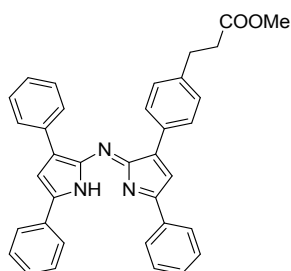
Dark blue metallic solid, (yield 75 %), m.p. 214–216 °C, TLC R_f = 0.69 (EP/CH₂Cl₂ 1/1, v/v). ¹H NMR (200 MHz, CDCl₃) δ (ppm): 7.85–8.15 (m, 8H, Ar–H), 7.35–7.60 (m, 9H, Ar–H), 7.26 (d, 1H, J = 10.0 Hz, Ar–H), 7.17 (s, 1H, Pyrr–H), 7.16 (s, 1H, Pyrr–H), 7.13 (d, 1H, J = 13.0 Hz, COCH=CH), 5.90 (d, 1H, J = 13.0 Hz, COCH=CH), 3.67 (d, 2H, J = 8.0 Hz, CH₂), 2.06 (m, 1H, J = 8.0 Hz, CHCH₃), 1.06 (d, 6H, J = 8.0 Hz, CH₃), (NH not observed). ¹³C NMR (50.2 MHz, CDCl₃) δ (ppm): 156.1 (Cq), 153.3 (Cq), 150.4 (Cq), 148.6 (CH), 148.5 (Cq), 142.8 (Cq), 141.1 (Cq), 136.4 (Cq), 133.7 (Cq), 132.1 (Cq), 131.9 (Cq), 130.8 (Cq), 129.8 (CH), 129.6 (CH), 129.1 (CH), 128.9 (CH), 128.0 (CH), 127.6 (CH), 126.4 (CH), 126.2 (CH), 124.6 (CH), 114.2 (CH), 114.0 (CH), 105.4 (CH), 76.4 (CH₂), 28.2 (CH), 19.0 (CH₃). IR cm⁻¹: 3045, 2924, 1633, 1543, 1350, 1239, 1133, 957, 902, 757, 685. m/z (HR, ESI) for C₃₈H₃₄N₃O⁺ Calcd 548.2696 [M + H]⁺. Found 548.2684 [M + H]⁺.



(E)-3-(4-((Z)-2-((3,5-diphenyl-1H-pyrrol-2-yl)imino)-5-phenyl-2H-pyrrol-3-yl)phenyl)acrylonitrile (8c)

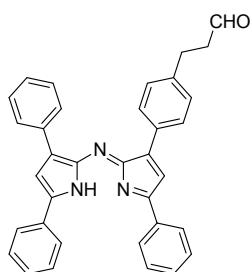
Dark blue metallic solid, (yield 88 %), m.p. 253–255 °C, TLC R_f = 0.55 (EP/CH₂Cl₂ 3/7, v/v). ¹H NMR (200 MHz, CDCl₃) δ (ppm): 8.10 (d, 2H, J = 8.0 Hz, Ar–H), 7.98 (m, 4H, Ar–H), 7.87 (m, 2H, Ar–H), 7.37–7.60 (m, 12H, Ar–H and CNCH=CH), 7.23 (s, 1H, Pyrr–H), 7.15 (s, 1H, Pyrr–H), 5.90 (d, 1H, J = 16.6 Hz, CNCH=CH), (NH not observed). ¹³C NMR (50.2 MHz, CDCl₃) δ (ppm): 158.5 (Cq), 151.8 (Cq), 151.5 (Cq), 150.0 (CH), 147.0 (Cq), 144.0 (Cq), 138.5 (Cq), 133.0 (Cq), 132.5

(Cq), 132.0 (CH), 131.9 (Cq), 131.7 (Cq), 130.5 (CH), 129.7 (CH), 129.2 (CH), 129.0 (CH), 127.6 (CH), 127.4 (CH), 127.1 (CH), 126.8 (CH), 126.1 (CH), 124.4 (CH), 121.5 (Cq), 118.0 (Cq), 116.6 (CH), 113.5 (CH), 95.6 (CH). IR cm^{-1} : 3445, 2924, 2215, 1596, 1536, 1261, 1242, 964, 902, 762, 685. m/z (HR, ESI) for $\text{C}_{35}\text{H}_{25}\text{N}_4^+$ Calcd 501.2074 [M + H]⁺. Found 501.2068 [M + H]⁺.



(Z)-methyl 3-(4-(2-((3,5-diphenyl-1H-pyrrol-2-yl)imino)-5-phenyl-2H-pyrrol-3-yl)phenyl)propanoate (8d)

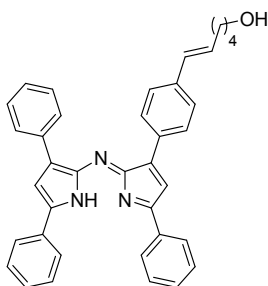
Dark blue metallic solid, (yield 69%), m.p. 188–190 °C, TLC R_f = 0.52 (EP/ CH_2Cl_2 35/65, v/v). ^1H NMR (200 MHz, CDCl_3) δ (ppm): 7.92–8.08 (m, 8H, Ar-*H*), 7.38–7.58 (m, 9H, Ar-*H*), 7.26 (d, 2H, J = 8.0 Hz, Ar-*H*), 7.19 (s, 1H, Pyrr-*H*), 7.18 (s, 1H, Pyrr-*H*), 3.72 (s, 3H, OCH_3), 3.04 (t, 2H, J = 7.5, 2.0 Hz, COCH_2), 2.85 (tm, 2H, J = 7.5 Hz, COCH_2CH_2), (*NH* not observed). ^{13}C NMR (50.2 MHz, CDCl_3) δ (ppm): 173.1 (Cq), 155.3 (Cq), 154.2 (Cq), 149.7 (Cq), 149.0 (Cq), 142.3 (Cq), 142.1 (Cq), 140.2 (Cq), 133.6 (Cq), 132.0 (Cq), 131.9 (Cq), 131.6 (Cq), 129.8 (CH), 129.7 (CH), 129.0 (CH), 128.9 (CH), 128.0 (CH), 127.7 (CH), 126.4 (CH), 126.3 (CH), 126.2 (CH), 114.4 (CH), 51.5 (CH_3), 35.5 (CH_2), 30.6 (CH_2). IR cm^{-1} : 3262, 3055, 2924, 1719, 1551, 1242, 957, 904, 759, 685. m/z (HR, ESI) for $\text{C}_{36}\text{H}_{30}\text{N}_3\text{O}_2^+$ Calcd 536.2333 [M + H]⁺. Found 536.2350 [M + H]⁺.



(Z)-3-(4-(2-((3,5-diphenyl-1H-pyrrol-2-yl)imino)-5-phenyl-2H-pyrrol-3-yl)phenyl)propanal (8e)

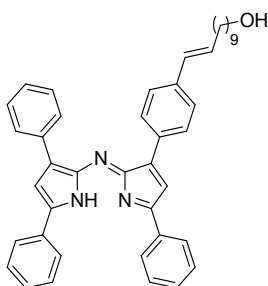
Dark blue metallic solid, (yield 70%), m.p. 175–177 °C, TLC R_f = 0.57 (EP/ CH_2Cl_2 3/7, v/v). ^1H NMR (200 MHz, CDCl_3) δ (ppm): 9.89 (t, 1H, J = 2.0 Hz, *CHO*), 7.92–8.07 (m, 8H, Ar-*H*), 7.37–7.58 (m,

9H, Ar-*H*), 7.25 (d, 2H, *J* = 8.0 Hz, Ar-*H*), 7.18 (s, 1H, Pyrr-*H*), 7.17 (s, 1H, Pyrr-*H*), 3.03 (td, 2H, *J* = 7.5, 2.0 Hz, CHOCH₂), 2.85 (tm, 2H, *J* = 7.5 Hz, CHOCH₂CH₂), (*NH* not observed). ¹³C NMR (50.2 MHz, CDCl₃) δ (ppm): 201.3 (Cq), 155.2 (Cq), 154.4 (Cq), 149.7 (Cq), 149.1 (Cq), 142.1 (Cq), 140.0 (Cq), 133.8 (Cq), 131.9 (Cq), 139.1 (Cq), 131.6 (Cq), 129.8 (CH), 129.7 (CH), 129.0 (CH), 128.9 (CH), 128.0 (CH), 127.7 (CH), 126.3 (CH), 126.2 (CH), 114.4 (CH), 45.1 (CH₂), 27.8 (CH₂). IR cm⁻¹: 3262, 3055, 2924, 1719, 1551, 1242, 957, 904, 759, 685. *m/z* (HR, ESI) for C₃₅H₂₈N₃O⁺ Calcd 506.2227 [M + H]⁺. Found 506.2216 [M + H]⁺.



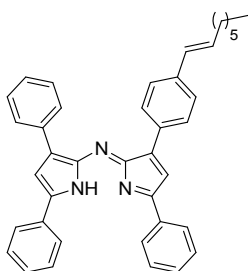
(E)-6-(4-((Z)-2-((3,5-diphenyl-1H-pyrrol-2-yl)imino)-5-phenyl-2H-pyrrol-3-yl)phenyl)hex-5-en-1-ol (8f)

Dark blue metallic solid, (yield 64%), m.p. 164–162 °C, TLC *R_f* = 0.45 (EP/CH₂Cl₂, 85/15 v/v). ¹H NMR (200 MHz, CDCl₃) δ (ppm): 7.89–8.09 (m, 8H, Ar-*H*), 7.30–7.60 (m, 11H, Ar-*H*), 7.20 (s, 2H, Pyrr-*H*), 6.35 (m, 2H, CH=CH) 3.70 (t, 2H, *J* = 7.0 Hz, CH₂OH), 2.35 (m, 2H, CH=CHCH₂), 1.65 (bs, 4H, 2XCH₂), (*NH*, *OH* not observed). ¹³C NMR (50.2 MHz, CDCl₃) δ (ppm): 155.3 (Cq), 154.3 (Cq), 149.8 (Cq), 149.1 (Cq), 142.3 (Cq), 142.2 (Cq), 137.3 (Cq), 135.0 (Cq), 133.6 (Cq), 132.1 (Cq), 132.0 (Cq), 131.9 (Cq), 130.8 (CH), 129.8 (CH), 129.7 (CH), 128.9 (CH), 128.7 (CH), 128.0 (CH), 127.7 (CH), 126.4 (CH), 126.3 (CH), 125.6 (CH), 125.2 (CH), 114.5 (CH), 114.4 (CH), 62.7 (CH₂), 32.7 (CH₂), 32.1 (CH₂), 25.3 (CH₂). IR cm⁻¹ 3344, 2987, 2852, 1451, 1276, 1251, 754, 749. *m/z* (HR, ESI) for C₃₈H₃₄N₃O⁺ Calcd 548.2696 [M + H]⁺. Found 548.2709 [M + H]⁺.



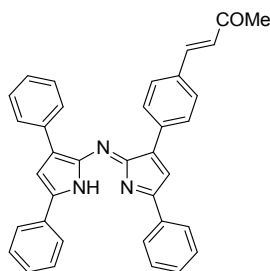
(E)-11-(4-((Z)-2-((3,5-diphenyl-1H-pyrrol-2-yl)imino)-5-phenyl-2H-pyrrol-3-yl)phenyl)undec-10-en-1-ol (8g)

Dark blue metallic solid, (58 %), m.p. 183–186 °C, TLC R_f = 0.60 (EP/CH₂Cl₂ 0/100, v/v). ¹H NMR (200 MHz, CDCl₃) δ (ppm): 7.90–8.09 (m, 8H, Ar-H), 7.40–7.52 (m, 11H, Ar-H), 7.17 (s, 1H, Pyrr-H), 7.16 (s, 1H, Pyrr-H), 6.35 (m, 2H, CH=CH), 3.66 (td, 2H, J = 6.0, 2.0 Hz, CH₂OH), 2.27 (q, 2H, J = 6.0 Hz, CH=CHCH₂), 2.10 (bs, 1H, OH), 1.56 (m, 4H, CH=CHCH₂ and CH₂CH₂OH), 1.36 (bs, 10H, 5XCH₂), (NH not observed). ¹³C NMR (50.2 MHz, CDCl₃) δ (ppm): 155.4 (Cq), 154.1 (Cq), 149.9 (Cq), 149.0 (Cq), 142.3 (Cq), 142.0 (Cq), 137.5 (Cq), 133.6 (Cq), 132.0 (Cq), 131.9 (Cq), 131.5 (CH), 129.9 (CH), 129.7 (CH), 129.4 (CH), 128.9 (CH), 128.0 (CH), 127.7 (CH), 126.3 (CH), 125.6 (CH), 125.2 (CH), 114.4 (CH), 114.3 (CH), 62.9 (CH₂), 33.0 (CH₂), 32.6 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 25.6 (CH₂). IR cm⁻¹ 3310, 2929, 2852, 1543, 1273, 1251, 751, 747. m/z (HR, ESI) for C₄₃H₄₄N₃O⁺ Calcd 618.3479 [M + H]⁺. Found 618.3499 [M + H]⁺.



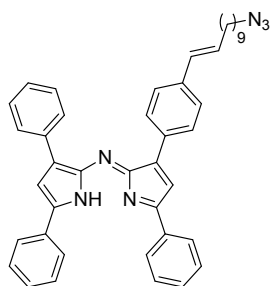
(Z)-N-(3-(4-((E)-oct-1-en-1-yl)phenyl)-5-phenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine (8h)

Dark blue metallic solid, (yield 83%), m.p. 174–x177 °C, TLC R_f = 0.67 (EP/CH₂Cl₂ 65/35, v/v). ¹H NMR (200 MHz, CDCl₃) δ (ppm): 7.92–8.08 (m, 8H, Ar-H), 7.36–7.58 (m, 11H, Ar-H), 7.18 (s, 1H, Pyrr-H), 7.17 (s, 1H, Pyrr-H), 6.37 (m, 2H, CH=CH), 2.27 (q, 2H, J = 6.0 Hz, CH=CHCH₂), 1.35–1.53 (m, 8H, 4xCH₂), 0.93 (t, 3H, J = 6.0 Hz, CH₃), (NH not observed). ¹³C NMR (50.2 MHz, CDCl₃) δ (ppm): 154.4 (Cq), 154.0 (Cq), 149.9 (Cq), 149.0 (Cq), 142.3 (Cq), 141.9 (Cq), 137.4 (Cq), 133.6 (Cq), 132.8 (Cq), 131.9 (Cq), 131.7 (Cq), 131.5 (CH), 129.8 (CH), 129.6 (CH), 129.4 (CH), 128.8 (CH), 128.6 (CH), 128.0 (CH), 127.6 (CH), 126.4 (CH), 126.2 (CH), 125.6 (CH), 125.2 (CH), 114.3 (CH), 114.2 (CH), 33.1 (CH₂), 31.6 (CH₂), 29.2 (CH₂), 28.8 (CH₂), 22.5 (CH₂), 14.0 (CH₃). IR cm⁻¹: 2924, 2852, 1733, 1455, 1276, 1251, 754, 750. m/z (HR, ESI) for C₄₀H₃₈N₃⁺ Calcd 560.3060 [M + H]⁺. Found 560.2696 [M + H]⁺.



(E)-4-(4-((Z)-2-((3,5-diphenyl-1H-pyrrol-2-yl)imino)-5-phenyl-2H-pyrrol-3-yl)phenyl)but-3-en-2-one (8i)

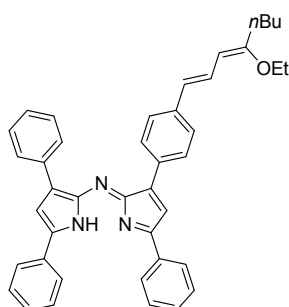
Dark blue metallic solid, (yield 79%), m.p. 249–252 °C, TLC R_f = 0.36 (EP/CH₂Cl₂ 8/92, v/v). ¹H NMR (200 MHz, CDCl₃) δ (ppm): 7.86–8.13 (m, 8H, Ar–H), 7.42–7.60 (m, 12H, Ar–H and COCH=CH), 7.22 (s, 1H, Pyrr–H), 7.16 (s, 1H, Pyrr–H), 6.77 (d, 1H, J = 16.0 Hz, COCH=CH), 2.44 (s, 3H, CH₃), (NH not observed). ¹³C NMR (50.2 MHz, CDCl₃) δ (ppm): 198.3 (Cq), 156.9 (Cq), 152.7 (Cq), 150.8 (Cq), 148.1 (Cq), 143.3 (Cq), 143.2 (CH), 140 (Cq), 135.2 (Cq), 133.6 (Cq), 133.3 (Cq), 131.9 (Cq), 131.6 (Cq), 130.1 (CH), 129.6 (CH), 128.9 (CH), 128.0 (CH), 127.7 (CH), 126.5 (CH), 126.1 (CH), 119.6 (CH), 115.6 (CH), 113.7 (CH), 27.2 (CH₃). IR cm⁻¹: 3059, 1559, 1546, 1352, 1261, 1242, 1172, 962, 796, 685. m/z (HR, ESI) for C₃₆H₂₈N₃O⁺ Calcd 518.2227 [M + H]⁺. Found 518.2229 [M + H]⁺.



(Z)-N-(3-(4-((E)-11-azidoundec-1-en-1-yl)phenyl)-5-phenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine (8j)

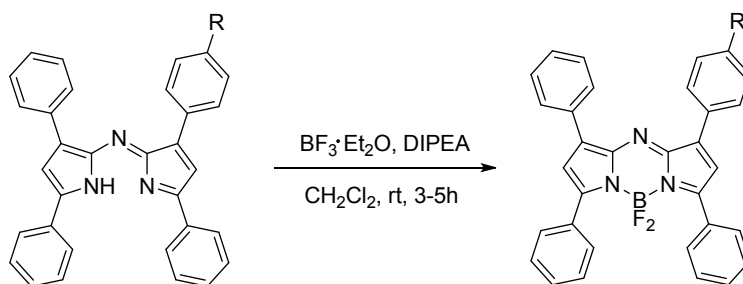
Dark blue metallic solid, (yield 63%), m.p. 164–166 °C, TLC R_f = 0.50 (EP/CH₂Cl₂ 55/45, v/v). ¹H NMR (200 MHz, CDCl₃) δ (ppm): 12.65 (bs, 1H, NH), 7.93–8.06 (m, 8H, Ar–H), 7.41–7.54 (m, 11H, Ar–H), 7.19 (s, 1H, Pyrr–H), 7.18 (s, 1H, Pyrr–H), 6.33 (m, 2H, CH=CH), 3.26 (t, 2H, J = 8.0 Hz, CH₂N₃), 2.27 (q, 2H, J = 6.0 Hz, CH=CHCH₂), 1.49–1.66 (m, 4H, CH=CHCH₂ and CH₂CH₂N₃), 1.35 (bs, 10H, 5XCH₂). ¹³C NMR (50.2 MHz, CDCl₃) δ (ppm): 155.4 (Cq), 154.1 (Cq), 149.8 (Cq), 149.0 (Cq), 142.2 (Cq), 141.9 (Cq), 137.4 (Cq), 133.6 (Cq), 131.9 (Cq), 131.4 (CH), 129.8 (CH), 129.7 (CH), 129.5 (CH), 128.9 (CH), 128.6 (CH), 128.0 (CH), 127.7 (CH), 126.4 (CH), 126.2 (CH), 125.6 (CH), 114.3 (CH), 114.2 (CH), 51.3 (CH₂), 33.0 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 28.7 (CH₂), 26.5 (CH₂). IR cm⁻¹: 3055, 2924, 2852, 2094, 1540, 1347, 1259,

1242, 960, 904, 759 m/z (HR, ESI) for $C_{43}H_{43}N_6^+$ Calcd 643.3544 $[M + H]^+$. Found 643.3546 $[M + H]^+$.

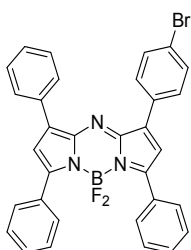


(Z)-N-(3-(4-((1E,3E)-4-ethoxyocta-1,3-dien-1-yl)phenyl)-5-phenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine (8h)

Dark blue metallic solid, (yield 43%), m.p. 198–200 °C, TLC R_f = 0.80 (EP/CH₂Cl₂ 1/1, v/v). ¹H NMR (200 MHz, CDCl₃) δ (ppm): 8.00–8.11 (m, 4H, Ar-H), 7.90–7.99 (m, 4H, Ar-H), 7.35–7.60 (m, 11H, Ar-H), 7.19 (s, 2H, Pyrr-H), 7.00 (dd, 1H, J = 16.0, 10.0 Hz, ArCH=CH), 6.40 (d, 1H, J = 16.0 Hz, ArCH=CH), 5.48 (d, 1H, J = 10.0 Hz, ArCH=CH-CH), 3.85 (q, 2H, J = 8.0 Hz, OCH₂CH₃), 2.43 (t, 3H, J = 8.0 Hz, COCH₂), 1.30–1.65 (m, 4H, COCH₂CH₂), 1.36 (t, 3H, J = 8.0 Hz, OCH₂CH₃), 0.99 (t, 3H, J = 8.0 Hz, OCH₂CH₂CH₂CH₃), (NH not observed). ¹³C NMR (50.2 MHz, CDCl₃) δ (ppm): 161.5 (Cq), 155.9 (Cq), 153.6 (Cq), 150.2 (Cq), 148.7 (Cq), 142.6 (Cq), 141.8 (Cq), 138.3 (Cq), 133.7 (Cq), 132.0 (Cq), 131.9 (Cq), 131.4 (Cq), 129.8 (CH), 129.6 (CH), 129.0 (CH), 128.9 (CH), 128.0 (CH), 127.6 (CH), 126.4 (CH), 126.2 (CH), , 126.0 (CH), 125.6 (CH), 125.2 (CH), 114.2 (CH), 114.1 (CH), 100.4 (CH), 62.4 (CH₂), 30.7 (CH₂), 30.0 (CH₂), 22.2 (CH₂), 14.4 (CH₃), 13.8 (CH₃). IR cm⁻¹: 3045, 2924, 1633, 1536, 1350, 1621, 1169, 962, 904, 757, 687. m/z (HR, ESI) for $C_{42}H_{40}N_3O$ Calcd 602.3166 $[M + H]^+$. Found 602.3170 $[M + H]^+$.

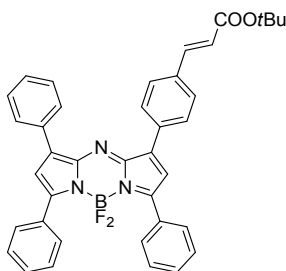


Synthesis of the fluorescent complexes: In a flame dried Schlenk flask a solution of the azadipyrromethene (0.10 mmol, 1.0 eq) and DIPEA (0.174 mL, 1.0 mmol, 10.0 eq) in anhydrous CH_2Cl_2 (10 mL) is stirred at room temperature for five minutes under a N_2 atmosphere. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.18 mL, 1.4 mmol, 14.0 eq) is added dropwise. The reaction is monitored by TLC and the mixture is reacted until disappearance of the blue spot. The dark green solution is washed with distilled water (1x15 mL) and brine (1x15 mL). The organic phase is dried over Na_2SO_4 , filtered and the solvent is removed under reduced pressure to afford a dark solid which is purified by column chromatography on silica gel. Eluents: petroleum ether/ CH_2Cl_2 .



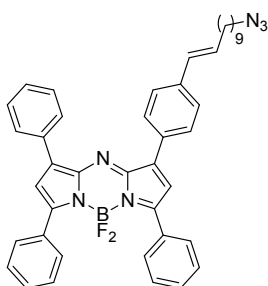
1-(4-bromophenyl)-5,5-difluoro-3,7,9-triphenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,5,2] triazaborinin-4-ium-5-uide (7)

Dark green metallic solid, (yield 83%), TLC, $R_f = 0.70$ (EP/ CH_2Cl_2 7/3, v/v). ^1H NMR (200 MHz, CDCl_3) δ (ppm): 7.99–8.10 (m, 6H, Ar-H), 7.96 (d, 2H, $J = 8.8$ Hz, Ar-H), 7.59 (d, 2H, $J = 8.8$ Hz, Ar-H), 7.44–7.53 (m, 9H, Ar-H). ^{13}C NMR (50.2 MHz, CDCl_3) δ (ppm): 160.1 (Cq), 158.9 (Cq), 145.6 (Cq), 145.1 (Cq), 144.5 (Cq); 142.1 (Cq), 132.0 (Cq), 131.6 (CH), 131.2 (Cq), 131.0 (CH), 130.9 (CH), 130.7 (Cq), 130.5 (CH), 129.5 (CH), 129.4 (CH), 129.3 (CH), 129.2 (CH), 128.5 (CH), 128.4 (CH), 123.8 (Cq), 119.3 (CH), 118.6 (CH). IR cm^{-1} : 1510, 1470, 1452, 1391, 1034, 1022, 810, 755, 687. m/z (HR, ESI) for $\text{C}_{32}\text{H}_{21}\text{BBrF}_2\text{N}_3^-$ Calcd 575.0980 [M] $^-$. Found 575.1011 [M] $^-$.



(E)-1-(4-(3-(tert-butoxy)-3-oxoprop-1-en-1-yl)phenyl)-5,5-difluoro-3,7,9-triphenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-4-ium-5-uide (8a')

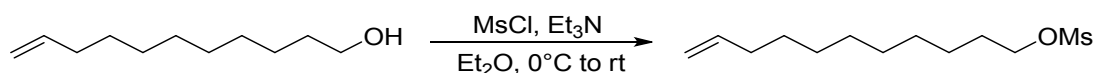
Dark green metallic solid, (yield 99%), TLC, $R_f = 0.40$ (EP/CH₂Cl₂ 1/1, v/v). ¹H NMR (200 MHz, CDCl₃) δ (ppm): 8.02–8.13 (m, 8H, Ar-H), 7.64 (d, 1H, $J = 16.0$ Hz, COCH=CH), 7.60 (d, 2H, $J = 8.0$ Hz, Ar-H), 7.48–7.52 (m, 9H, Ar-H), 7.06 (s, 2H, Pyrr-H), 6.48 (d, 1H, $J = 16.0$ Hz, COCH=CH), 1.58 (s, 9H, CH₃). ¹³C NMR (50.2 MHz, CDCl₃) δ (ppm): 166.0 (Cq), 160.0 (Cq), 158.9 (Cq), 145.6 (Cq), 145.3 (Cq), 144.4 (Cq), 142.5 (CH), 142.4 (Cq), 135.7 (Cq), 133.7 (Cq), 132.0 (Cq), 131.3 (Cq), 131.2 (Cq), 130.9 (CH), 130.7 (CH), 130.2 (CH), 129.4 (CH), 129.2 (CH), 128.4 (CH), 128.0 (CH), 120.8 (CH), 119.3 (CH), 118.7 (CH), 80.5 (Cq), 28.1 (CH₃). IR cm⁻¹: 2973, 1702, 1633, 1514, 1475, 1454, 1394, 1143, 1097, 1034, 764, 591. m/z (HR, ESI) for C₃₉H₃₁BF₂N₃O₂⁻ Calcd 623.2556 [M]⁻. Found 623.2593 [M]⁻.



(E)-1-(4-(11-azidoundec-1-en-1-yl)phenyl)-5,5-difluoro-3,7,9-triphenyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,5,2]triazaborinin-4-ium-5-uide (8j')

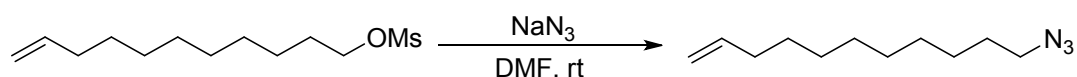
Dark green metallic solid, (yield 91%), TLC $R_f = 0.51$ (EP/CH₂Cl₂ 40/60, v/v). ¹H NMR (200 MHz, CDCl₃) δ (ppm): 8.00–8.12 (m, 8H, Ar-H), 7.40–7.56 (m, 11H, Ar-H), 7.03 (s, 1H, Pyrr-H), 7.01 (s, 1H, Pyrr-H), 6.43 (m, 2H, CH=CH), 3.28 (t, 2H, $J = 7.0$ Hz, CH₂N₃), 2.26 (q, 2H, $J = 6.0$ Hz, CH=CHCH₂), 1.32–1.70 (bs, 14H, 7xCH₂). ¹³C NMR (50.2 MHz, CDCl₃) δ (ppm): 159.8 (Cq), 158.8 (Cq), 145.6 (Cq), 145.2 (Cq), 145.0 (Cq), 143.9 (Cq), 143.6 (Cq), 139.1 (Cq), 133.9 (CH), 132.8 (Cq), 132.3 (Cq), 131.5 (Cq), 131.4 (Cq), 130.7 (CH), 130.6 (CH), 12.4 (CH), 129.2 (CH), 128.4 (CH), 126.0 (CH), 125.6 (CH), 118.8 (CH), 118.2 (CH), 51.3 (CH₂), 33.1 (CH₂), 29.2 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 28.7 (CH₂), 28.5 (CH₂). IR cm⁻¹: 3055, 2926, 2851, 2092, 1515, 1475, 1754,

1273, 1127, 762, 748 m/z (HR, ESI) for $C_{58}H_{54}BF_2N_7O_2S^+$ Calcd 643.3544 [M + H]⁺. Found 643.3546 [M + H]⁺.



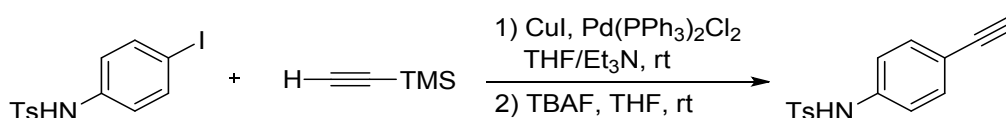
Undec-10-en-1-yl methanesulfonate^[1]: In a flame dried round bottomed flask, a solution of undec-10-en-1-ol (0.85 g, 5.0 mmol) and trimethylamine (1.1 mL, 7.5 mmol) in 20 mL of dry diethyl ether is cooled to 0°C. Methanesulfonyl chloride (0.86 g, 7.5 mmol) is added dropwise and the resulting suspension is stirred at room temperature. After three hours, water is added to quench the reaction and the aqueous phase is extracted with diethyl ether (3x20 mL). The collected ethereal phase is washed with brine (2x30 mL) and dried over Na₂SO₄. Removal of the solvent affords 1.3 g of the protected alcohol as a pale yellow oil that is used with no further purification (yield 100%).

¹H NMR (200 MHz, CDCl₃) δ (ppm): 5.80 (m, 1H), 4.96 (m, 2H), 4.21 (t, 2H, *J* = 6.6 Hz), 3.00 (s, 3H), 2.05 (m, 2H), 1.75 (m, 2H) and 1.46-1.22 (m, 12H).



11-azidoundec-1-ene^[1]: undec-10-en-1-yl methanesulfonate (1.3 g, 5.0 mmol) is dissolved in 5 mL of DMF, NaN₃ (0.81 g, 12.5 mmol) is added and the suspension is strongly stirred overnight at room temperature. After reaction completion, the resulting mixture is diluted with 50 mL of diethyl ether, washed with brine (7x20 mL) and dried over Na₂SO₄. Evaporation of the solvent affords a pale yellow oil that is filtered through a short silica pad using CH₂Cl₂. 11-azidoundec-1-ene is obtained as a colorless oil (0.98 g, yield 99.5%).

¹H NMR (200 MHz, CDCl₃) δ (ppm): 5.81 (m, 1H), 5.00 (m, 2H), 3.25 (t, 2H, *J* = 7.0 Hz), 2.05 (m, 2H), 1.59 (m, 2H) and 1.44-1.22 (m, 12H).



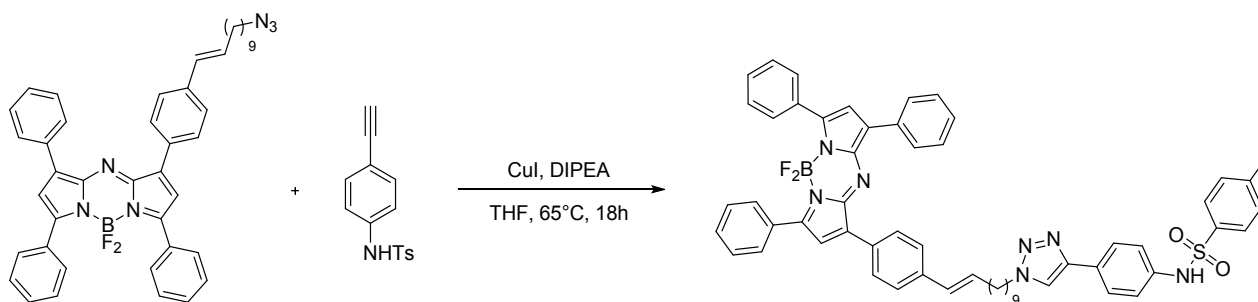
N-(4-ethynylphenyl)-4-methylbenzenesulfonamide^[2]: In a reaction tube, 3 mL of THF/Et₃N (1:1) are degassed for by bubbling nitrogen. Then *N*-(4-iodophenyl)-4-methylbenzenesulfonamide (75.0

¹ Salma, Y.; Ballereau, S.; Maalik, C.; Ladeira, S.; Andrieu-Abadie, N.; Génisson, Y. *Org. Biomol. Chem.*, **2010**, *8*, 3227–3243

² Sakai, R.; Barasa, E. B.; Sakai, N.; Sato, S.; Satoh, T.; Kakuchi, T. *Macromolecules*, **2012**, *45*, 8221–8227

mg, 0.2 mmol), CuI (4.0 mg, 10 mol%), Pd(PPh₃)₂Cl₂ (8 mg, 5 mol%) are charged. After 5 minutes, ethynyltrimethylsilane (39 mg, 0.4 mmol) is added dropwise. The tube is sealed and the black solution is stirred at room temperature for 4 hours. The resulting mixture is diluted with ethyl acetate and filtered through a silica pad to remove all the catalysts. Evaporation of the solvents affords a brown oil that is dissolved in anhydrous THF. TBAF is added (0.2 mL 1.1 M in THF, 0.22 mmol) and the reaction is stirred to completion. Removal of the solvents afford a brown oil that is purified by silica gel chromatography using pure dichloromethane as eluent. *N*-(4-ethynylphenyl)-4-methylbenzenesulfonamide is obtained as off white solid (54.0 mg, yield 99% starting from the aryl iodide).

¹H NMR (200 MHz, CDCl₃) δ (ppm): 7.70 (d, 2H, *J* = 8.6 Hz), 7.35 (dm, 2H, *J* = 8.6 Hz), 7.24 (d, 2H, *J* = 8.6 Hz), 7.17 (bs, 1H), 7.05 (d, 2H, *J* = 8.6 Hz), 3.04 (s, 1H), 2.39 (s, 1H).



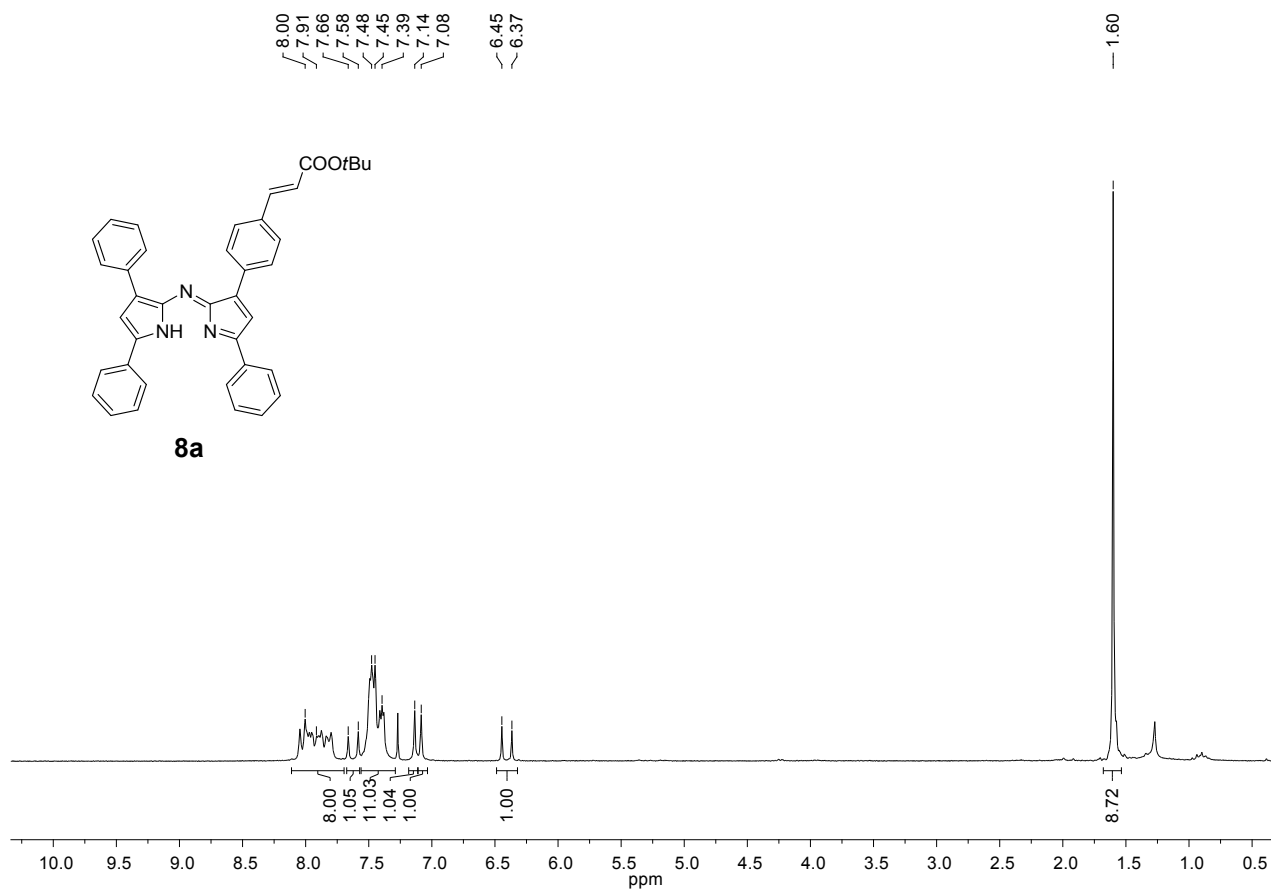
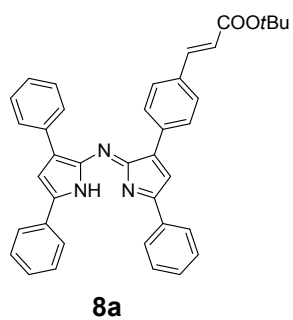
Click procedure: Synthesis of (*E*)-5,5-difluoro-1-(4-(11-(4-(4-(4-methylphenylsulfonamido)phenyl)-1*H*-1,2,3-triazol-1-yl)undec-1-en-1-yl)phenyl)-3,7,9-triphenyl-5*H*-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,5,2]triazaborinin-4-ium-5-uide (10): Following the reported procedure,³ a solution of *N*-(4-ethynylphenyl)-4-methylbenzene sulfonamide (71 mg, 0.26 mmol) in THF (2 mL) is treated with azido-azaBODIPY (138 mg, 0.20 mmol), CuI (7.0 mg, 0.037mmol) and DIPEA (64.0 mg, 0.73 mmol) in a sealed tube. The reaction mixture is heated up to 65 °C till completion. Solvent evaporation followed by purification of the crude residue by flash column chromatography (CHCl₃) affords 192 mg of the triazole.

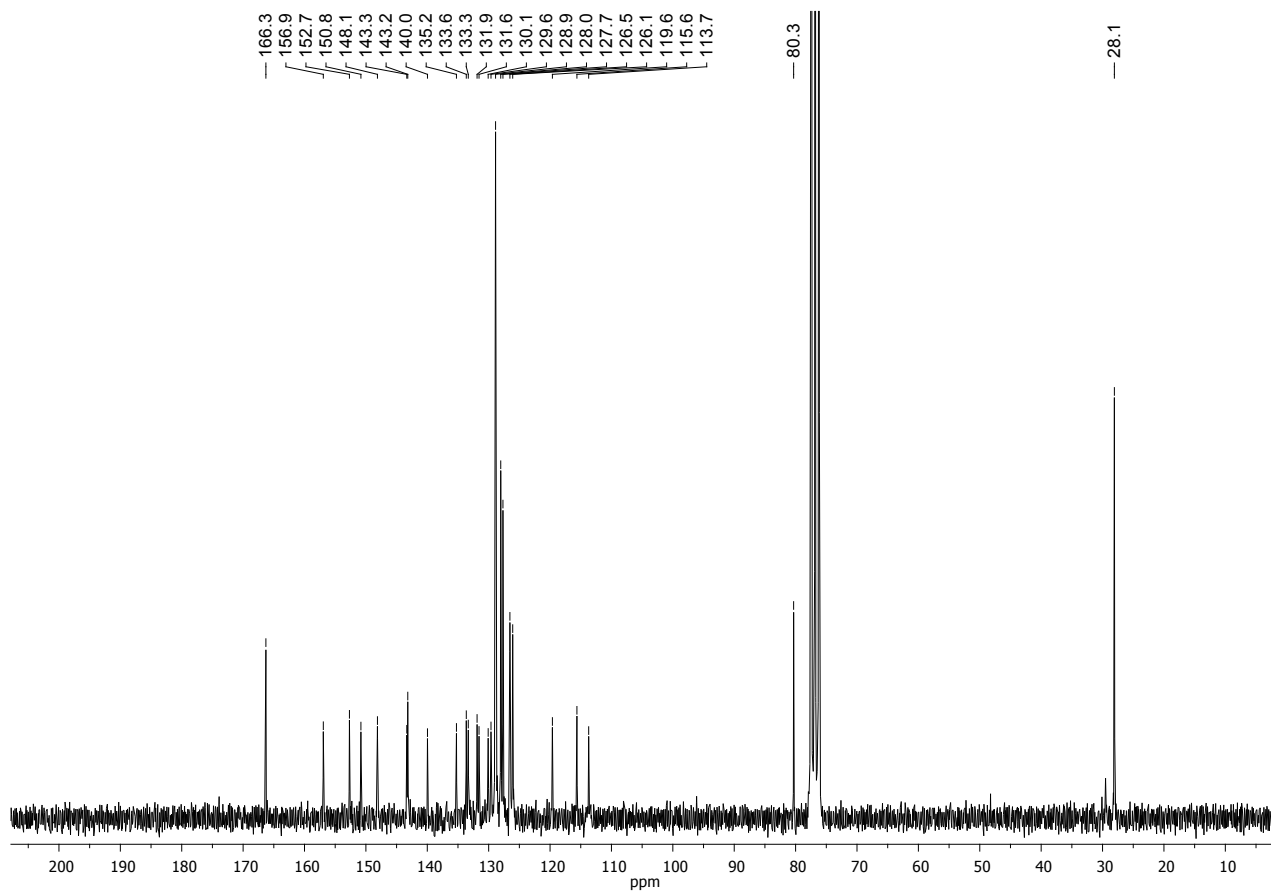
Dark green metallic solid, (yield 99%), TLC *R*_f = 0.11 (CHCl₃). ¹H NMR (200 MHz, CDCl₃) δ (ppm): 8.00–8.11 (m, 8H, Ar-*H*), 7.70 (s, 1H, Ar-*H*, triazole), 7.62 (d, 2H, *J* = 7.5 Hz, Ar-*H*), 7.40–7.58 (m, 12H, Ar-*H*), 7.20 (d, 2H, *J* = 7.5 Hz, Ar-*H*), 7.12 (d, 2H, *J* = 7.5 Hz, Ar-*H*), 7.05 (s, 1H, Pyrr-*H*), 7.00 (s, 1H, Pyrr-*H*), , 6.40 (m, 2H, CH=CH), 4.36 (t, 1H, *J* = 7.0 Hz, Triazole-CH₂), 2.36 (s, 3H,

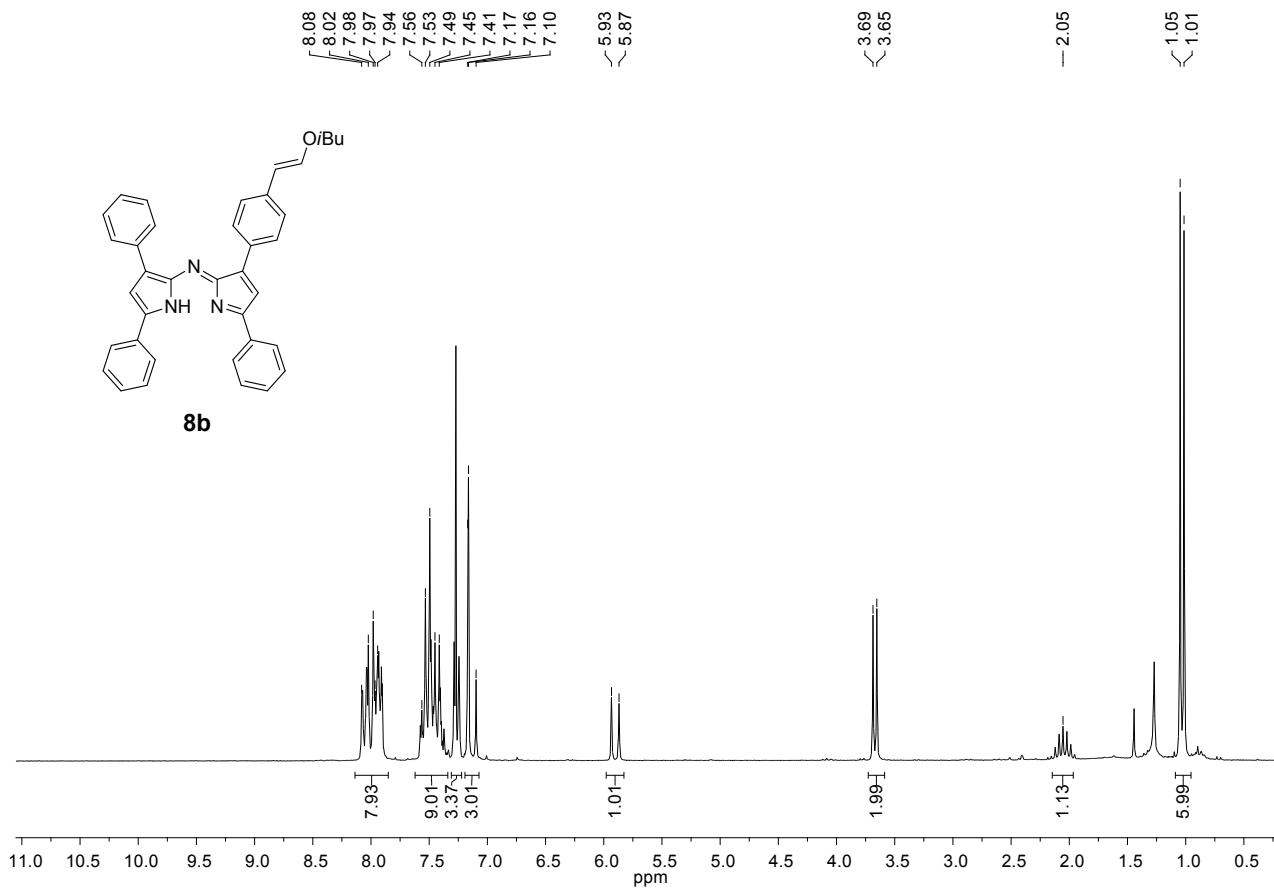
³ Mette Hansen, A.; Sewell, A. L.; Pedersen, R. H.; Long, D.; Gadegaard, N.; Marquez, R. *Tetrahedron*, **2013**, *69*, 8527–8533

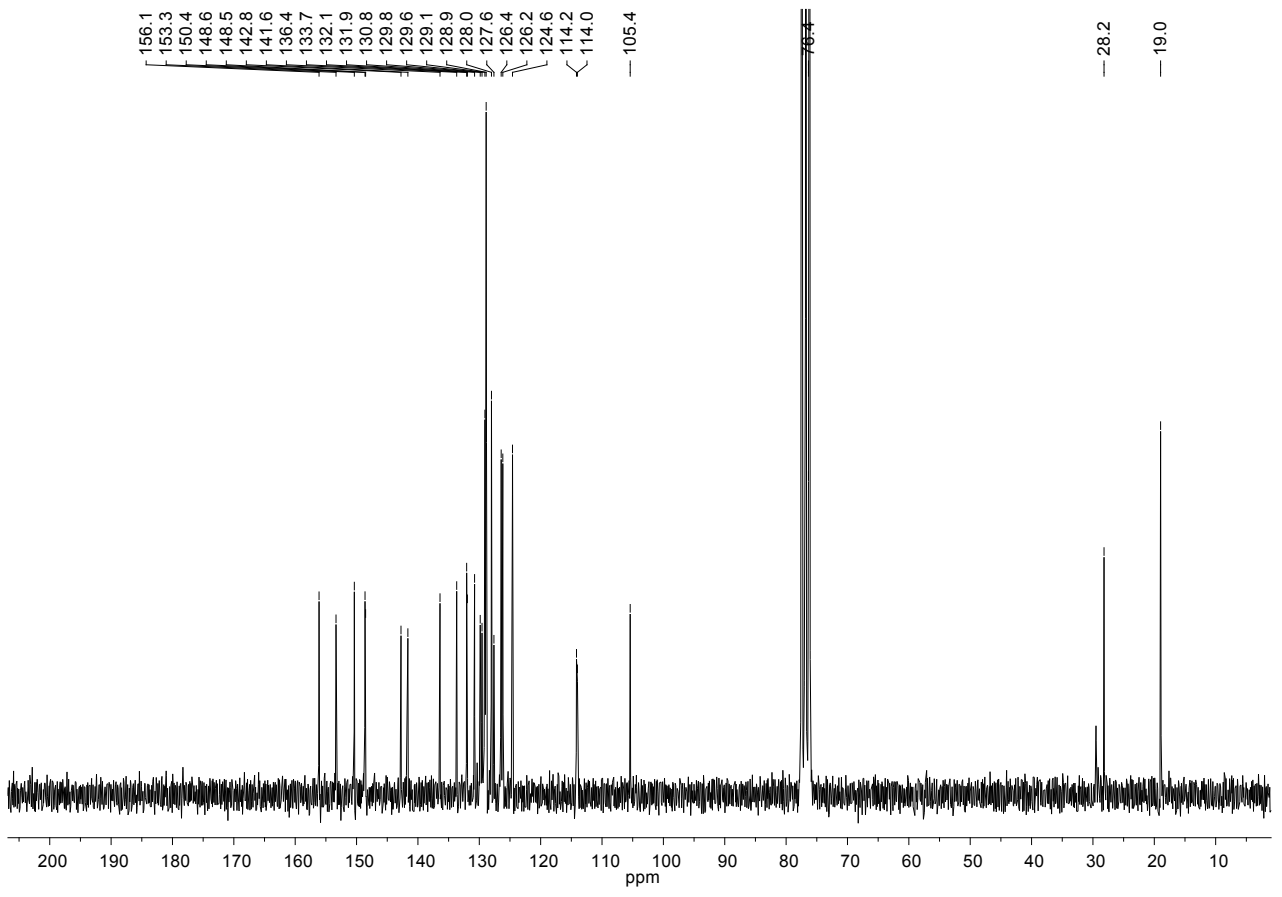
CH_3 tolyl), 2.25 (q, 2H, $J = 7.0$ Hz, $\text{CH}=\text{CHCH}_2$), 1.93 (m, 2H, Triazole- CH_2CH_2), 1.25–1.55 (m, 12H, $6\times\text{CH}_2$).

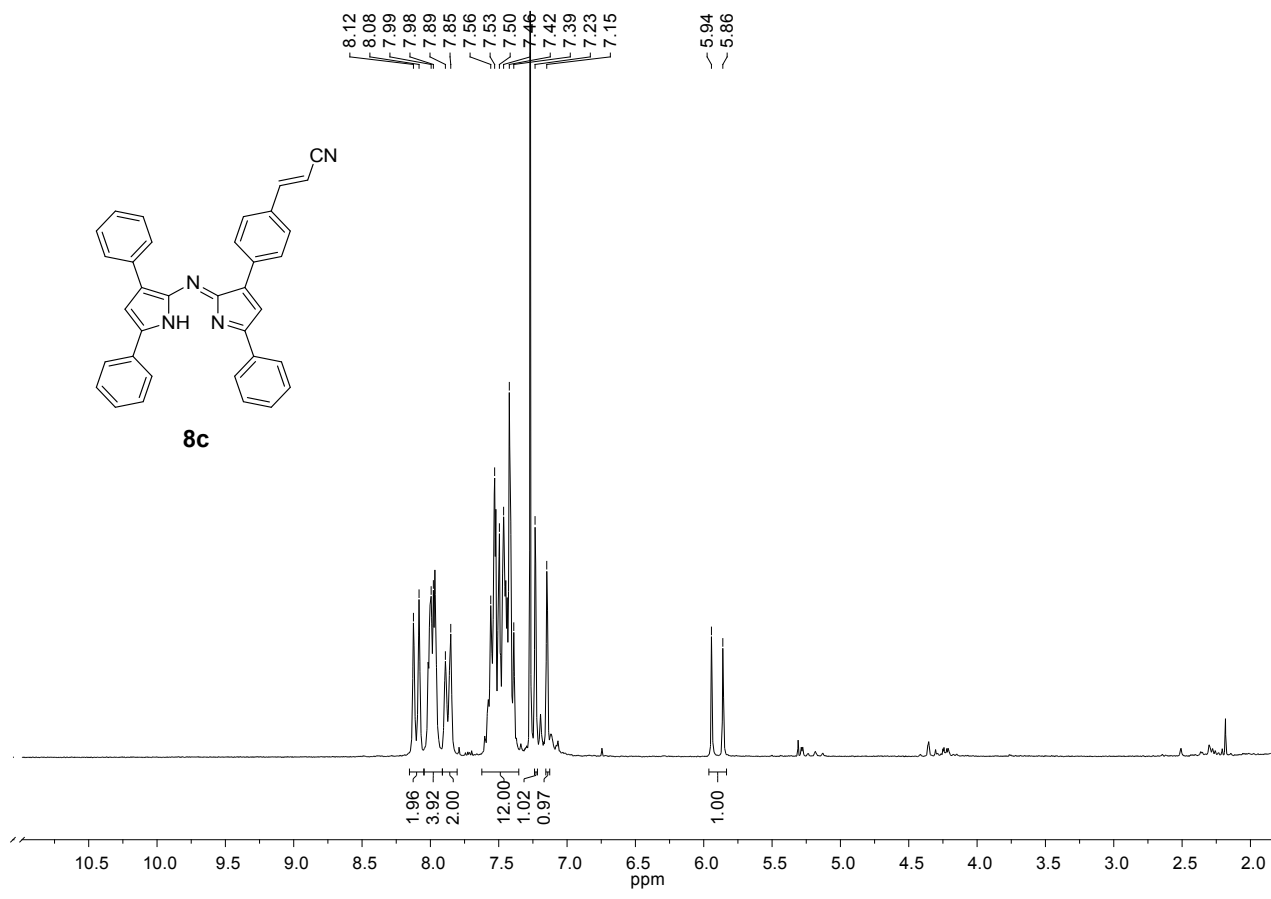
^{13}C NMR (50.2 MHz, CDCl_3) δ (ppm): 159.6 (Cq), 158.7 (Cq), 148.8 (Cq), 145.6 (Cq), 145.2 (Cq), 143.7 (Cq), 143.5 (Cq), 139.1 (Cq), 136.5 (Cq), 135.9 (Cq), 132.8 (CH), 132.2 (Cq), 131.5 (Cq), 131.4 (Cq), 130.7 (CH), 130.5 (CH), 129.5 (CH), 129.4 (CH), 129.2 (CH), 128.4 (CH), 127.4 (Cq), 127.1 (CH), 126.4 (CH), 126.0 (CH), 121.6 (CH), 119.4 (CH), 118.8 (CH), 118.3 (CH), 50.2 (CH_2), 33.1 (CH_2), 30.1 (CH_2), 29.2 ($2\times\text{CH}_2$), 29.1 ($2\times\text{CH}_2$), 28.8 (CH_2), 26.3(CH_2), 21.3 (CH_3). IR cm^{-1} : 2926, 2850, 1658, 1604, 1503, 1151, 1092, 914 $\text{C}_{58}\text{H}_{54}\text{BF}_2\text{N}_7\text{O}_2\text{S}^+$ Calcd 961.9766 $[\text{M} + \text{H}]^+$. Found 961.9755 $[\text{M} + \text{H}]^+$.

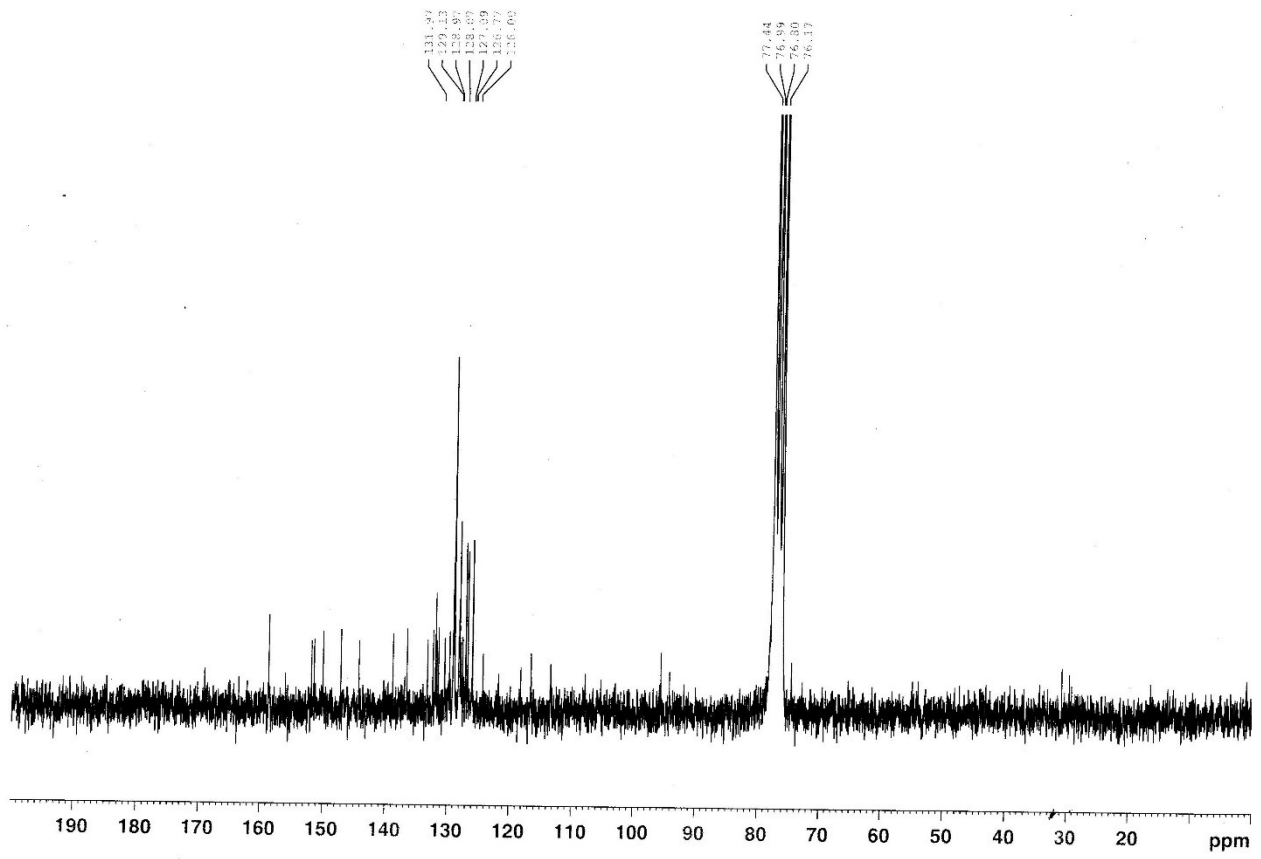


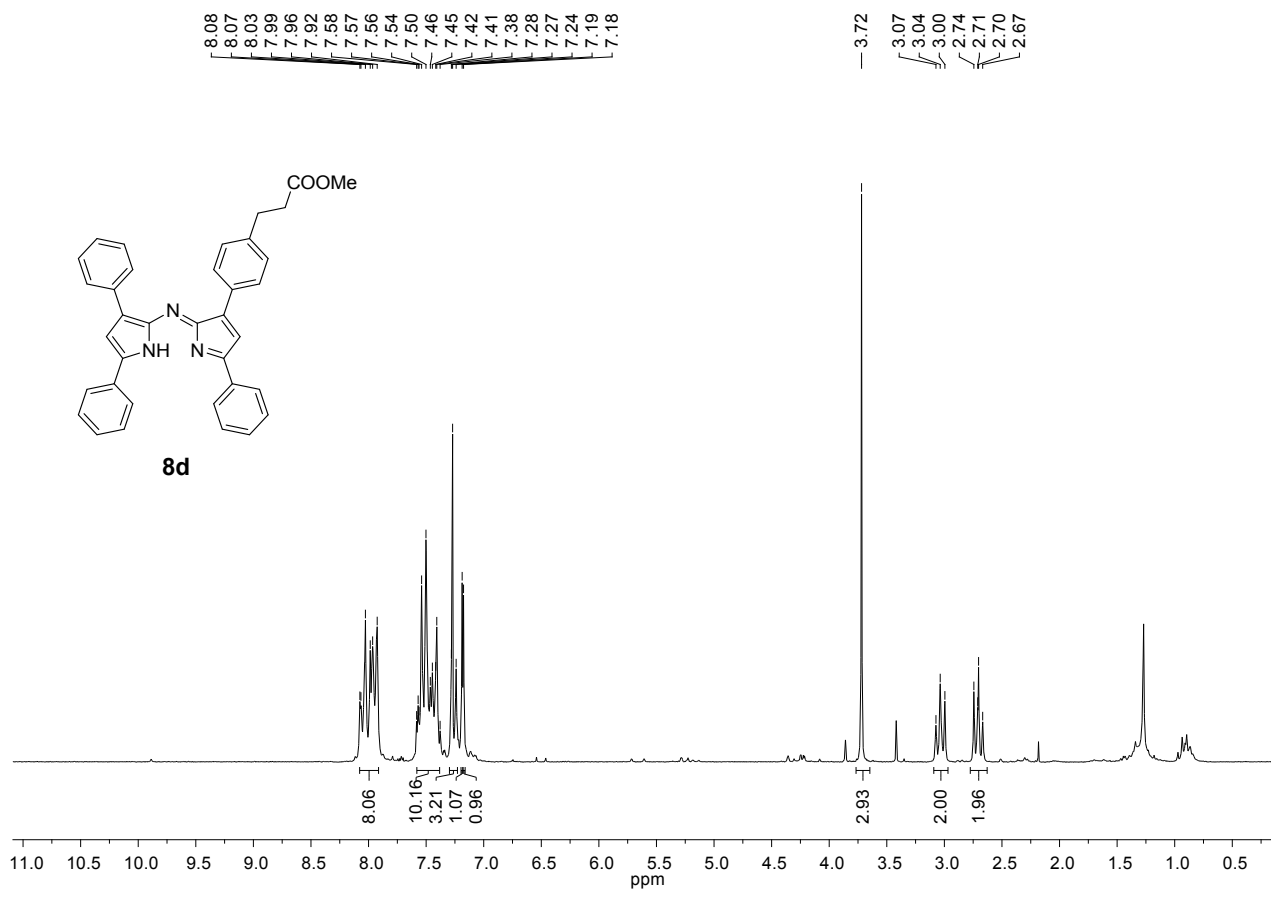


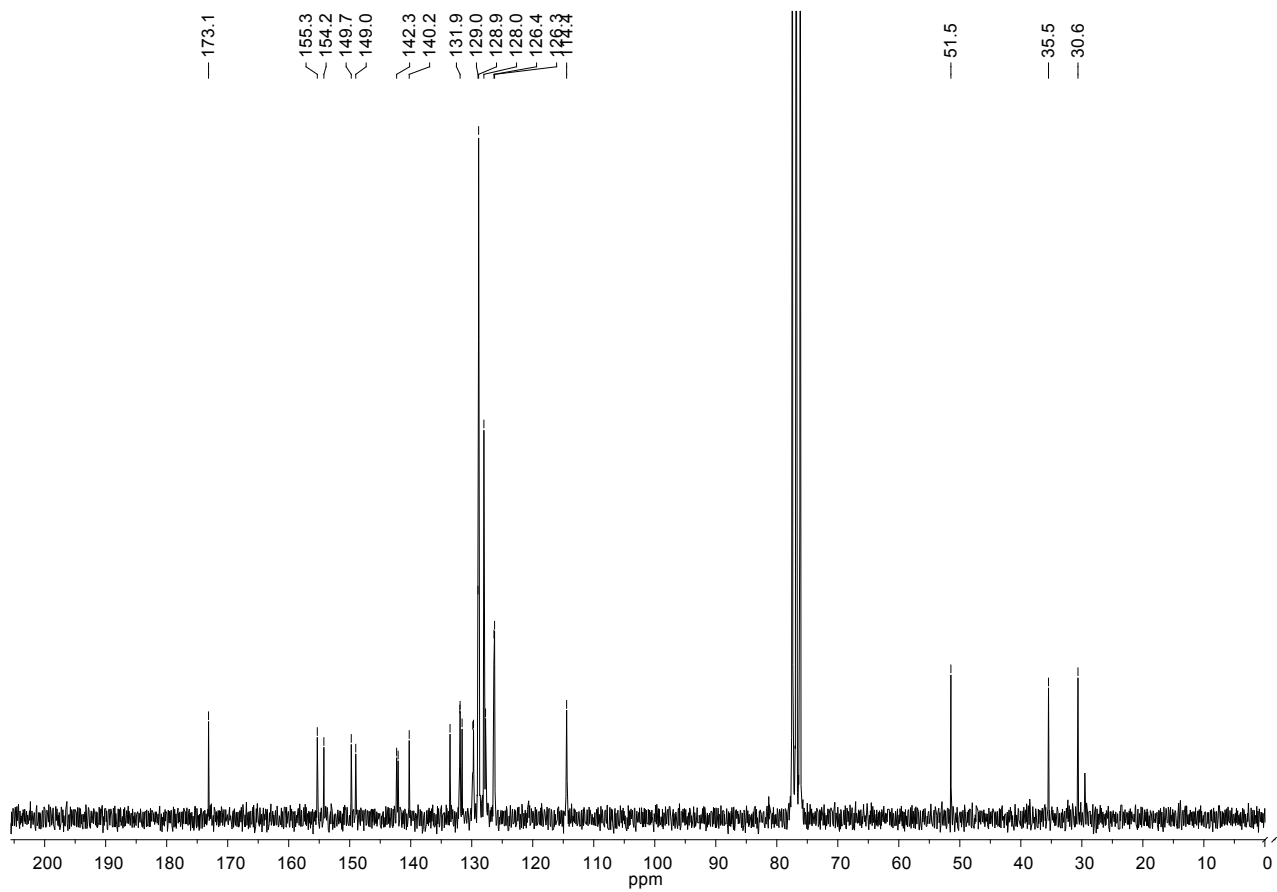


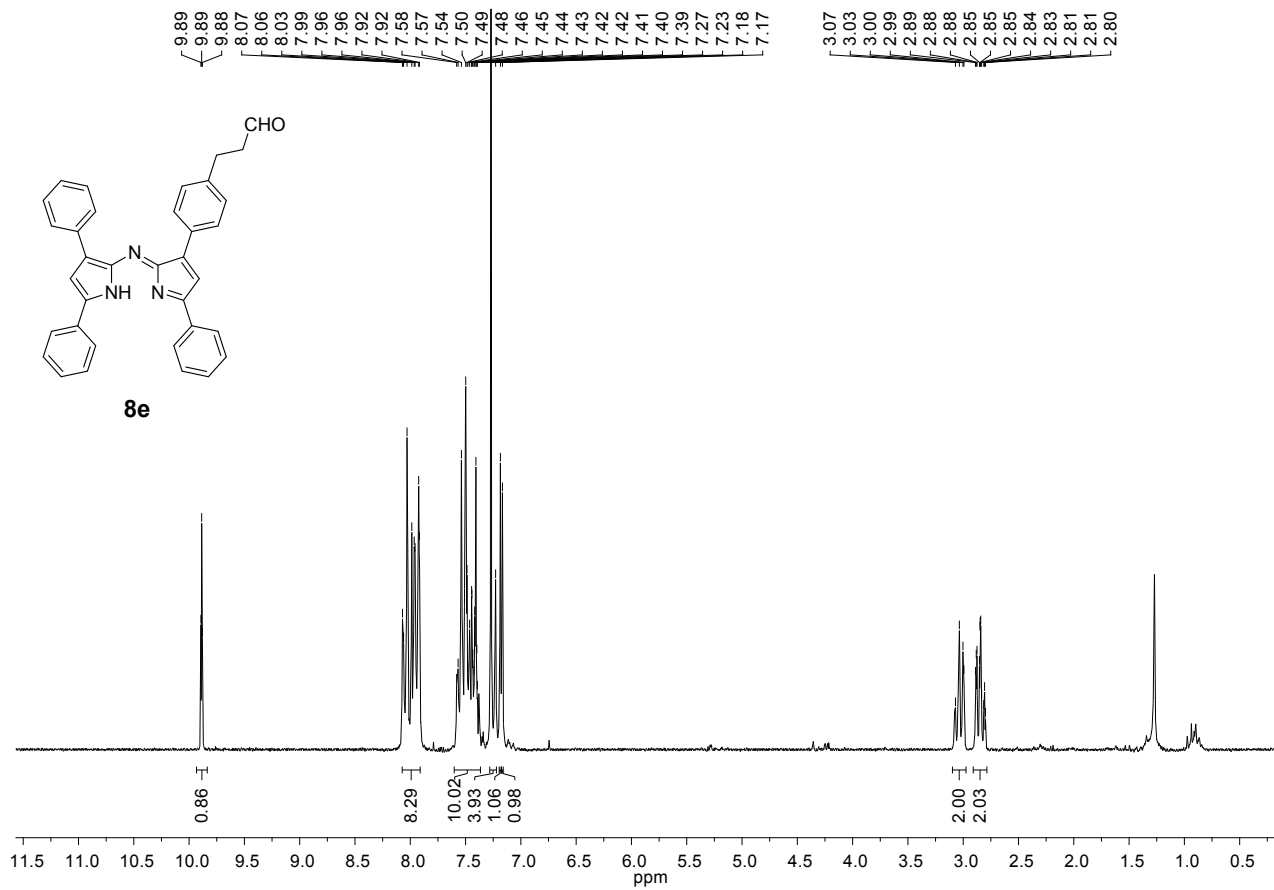


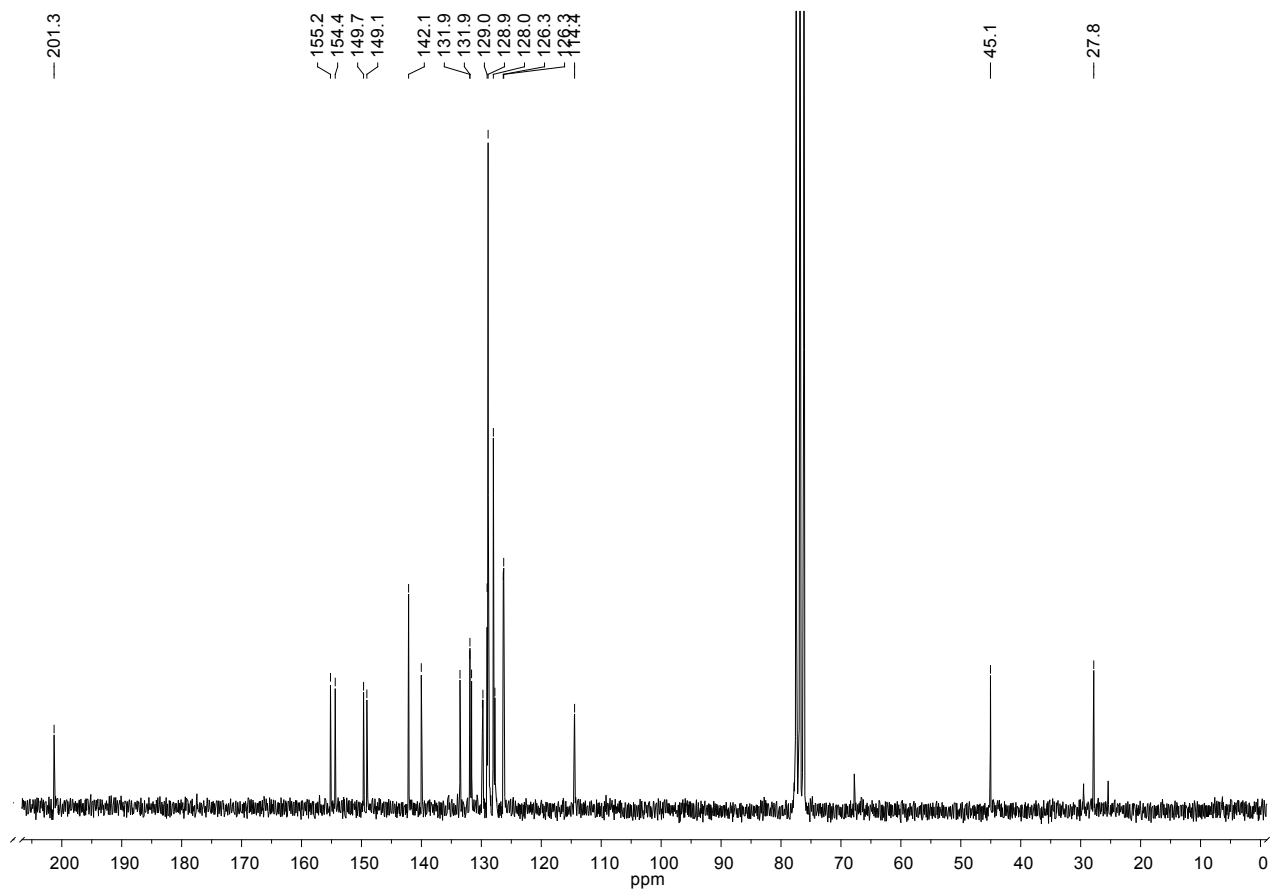


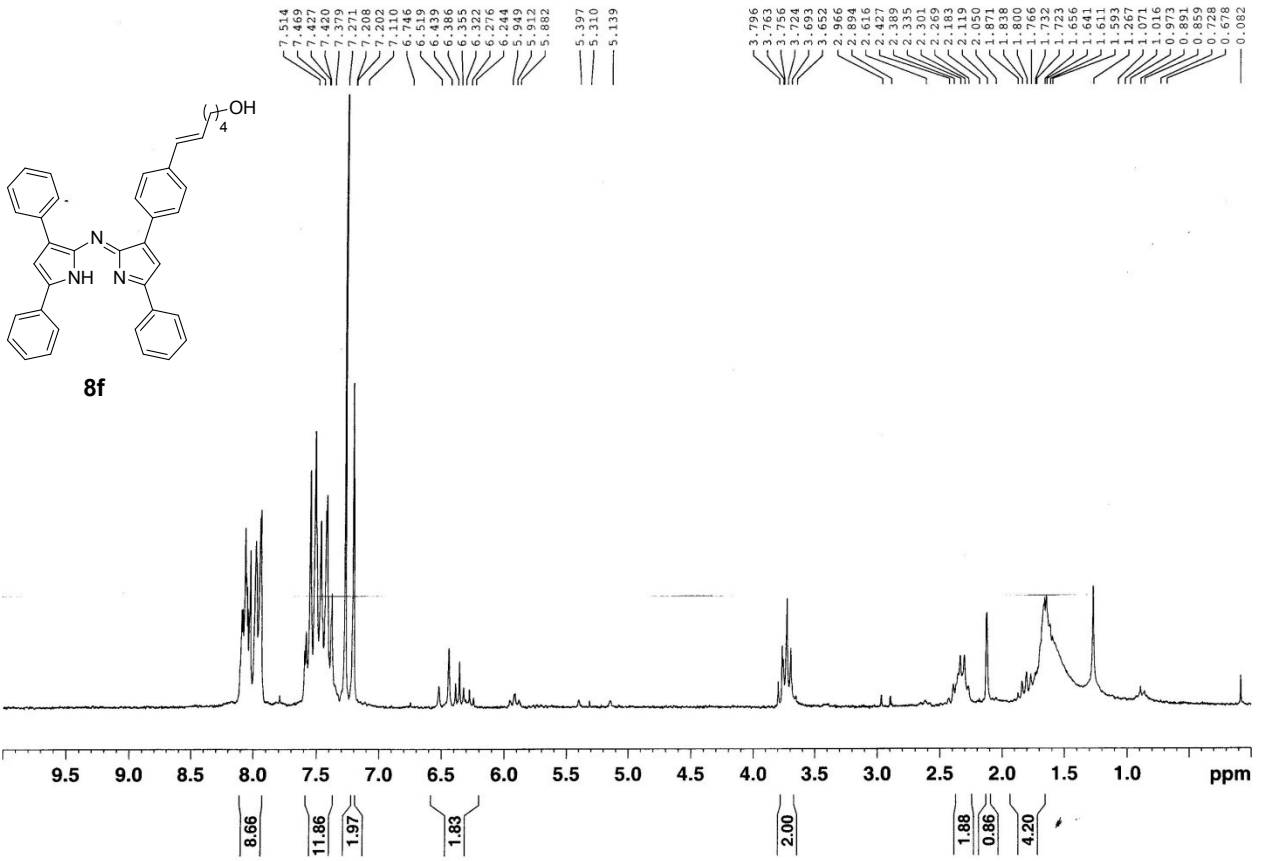


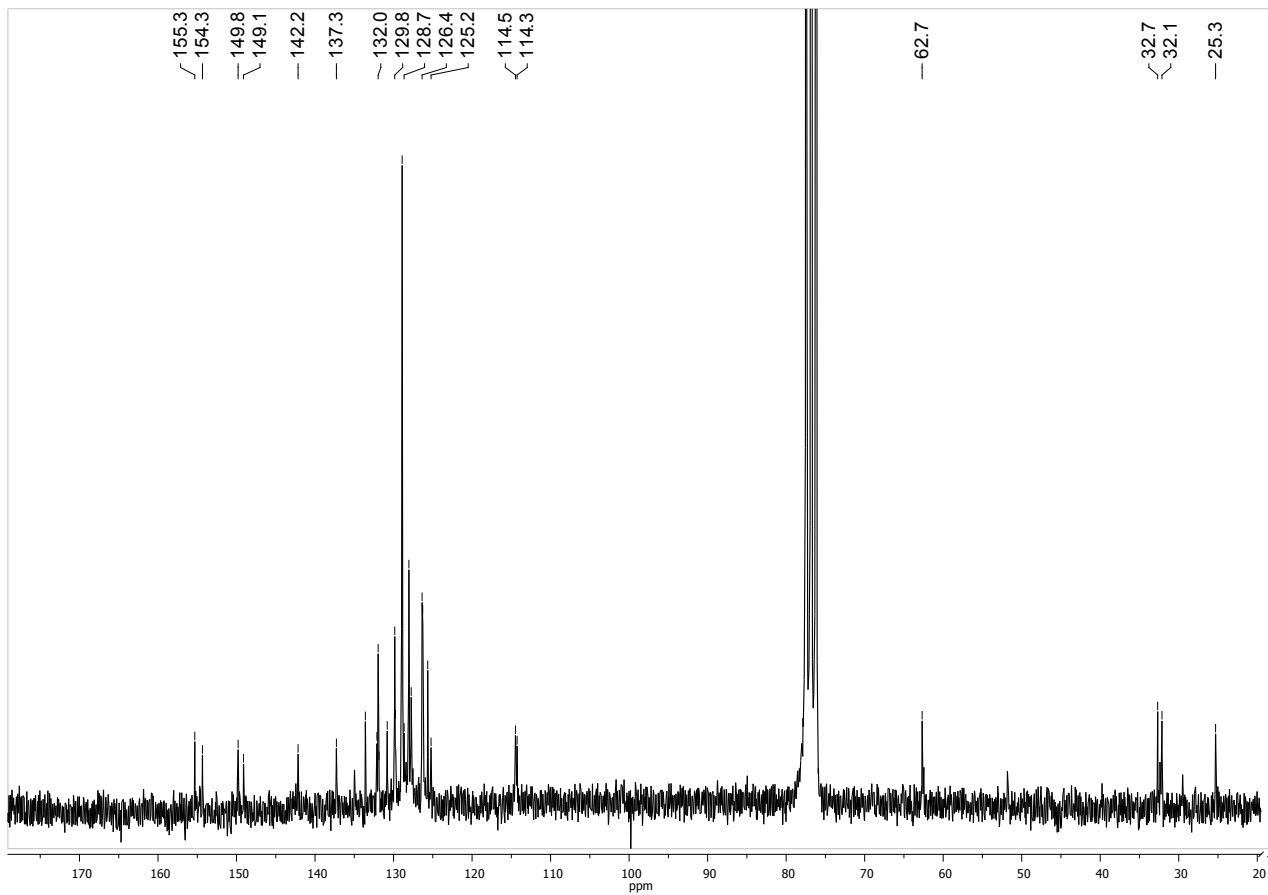


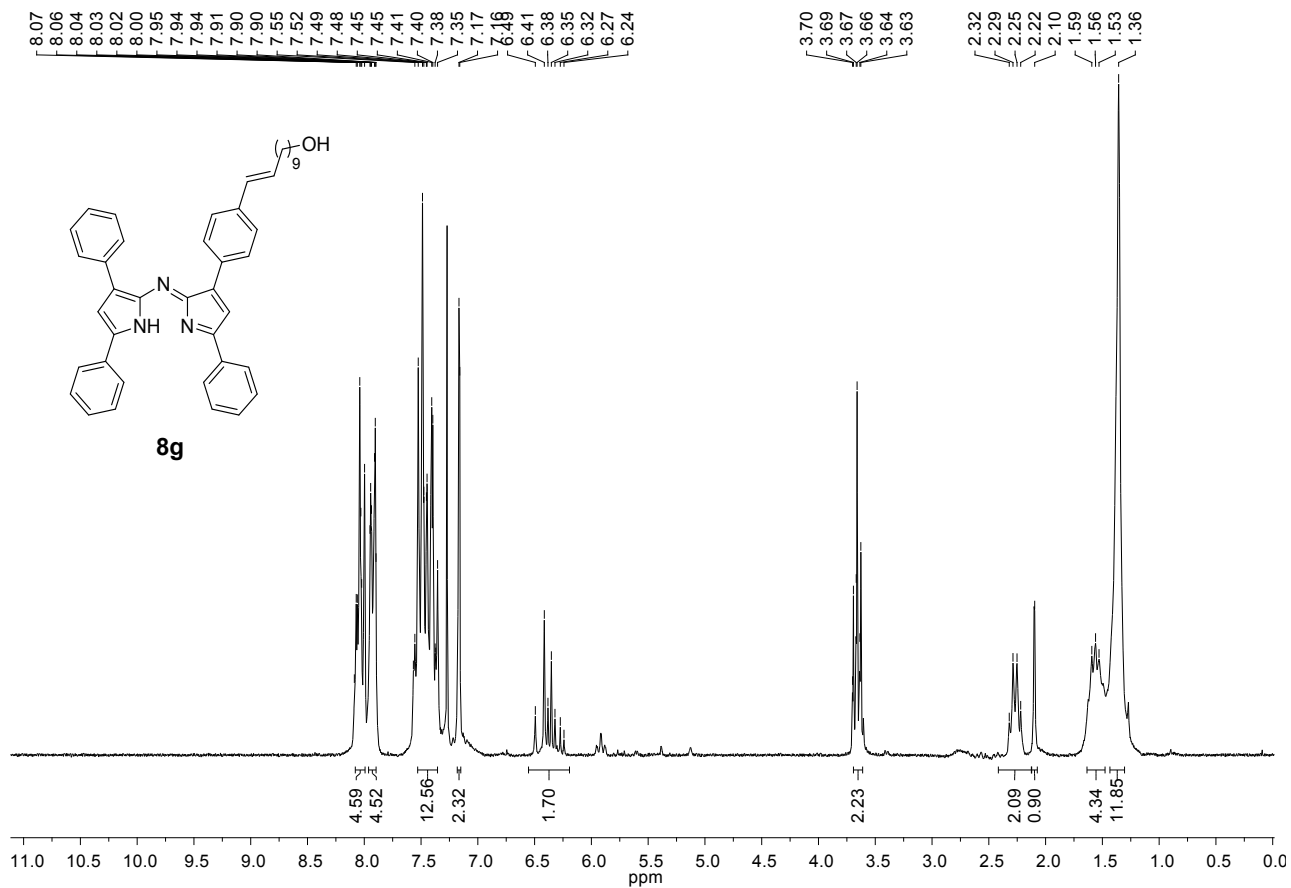


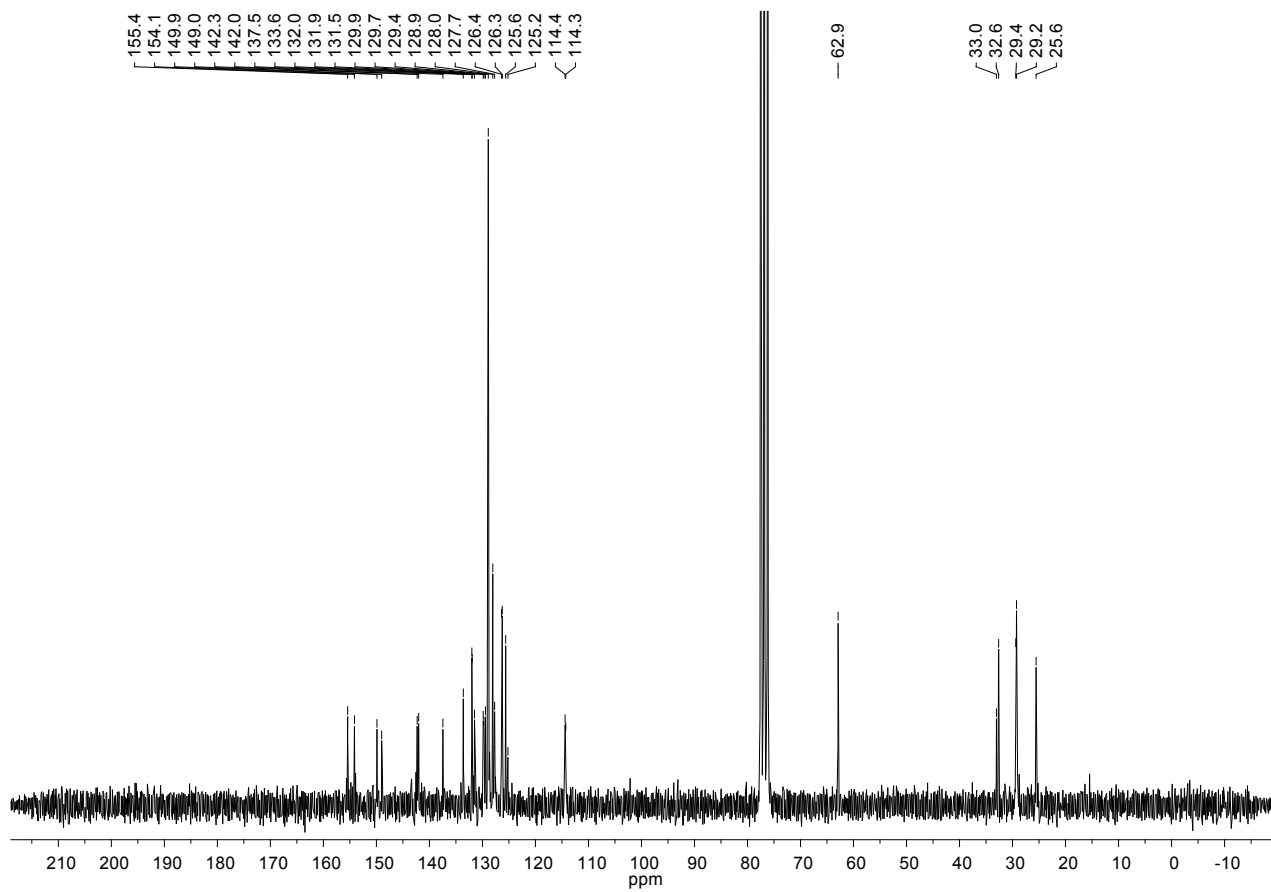


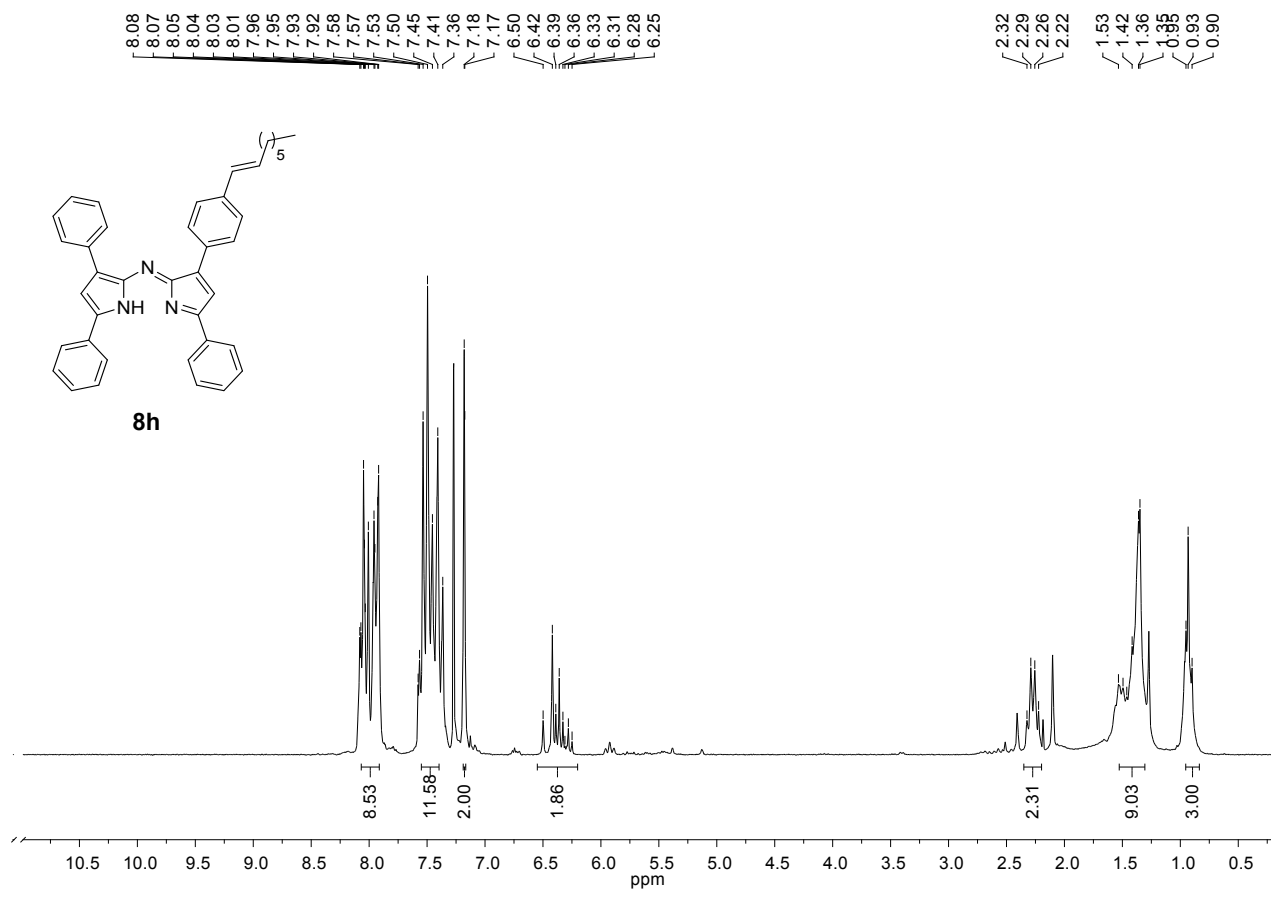


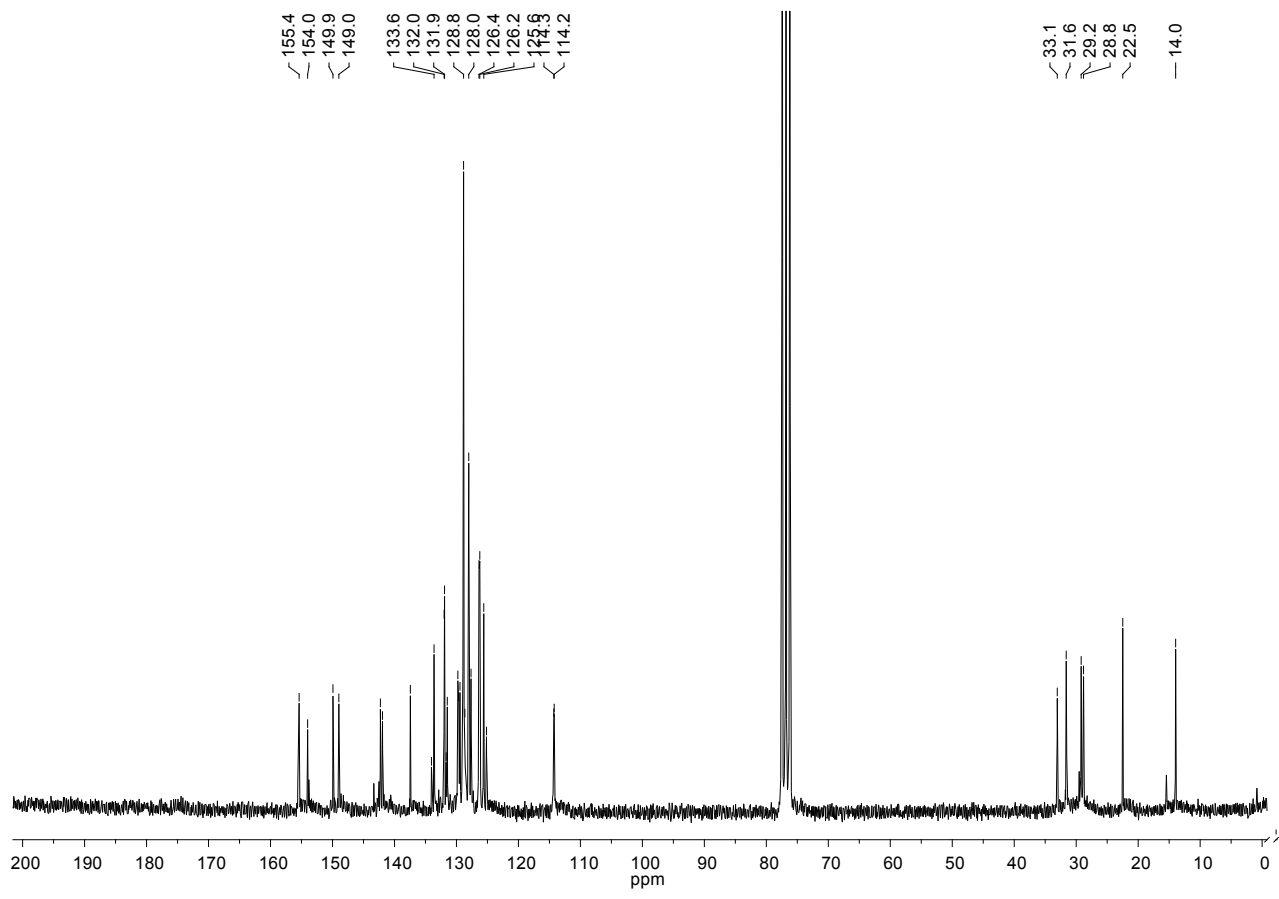


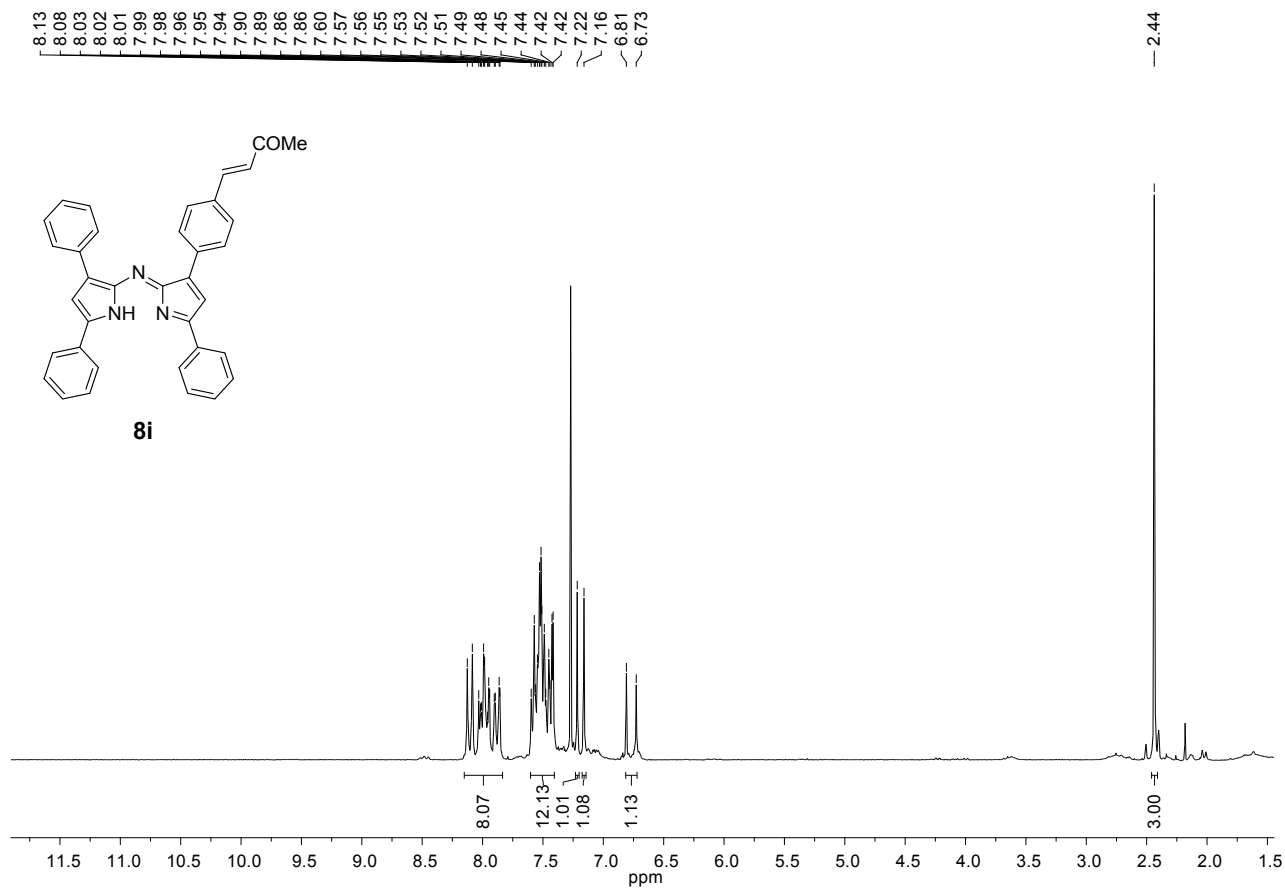


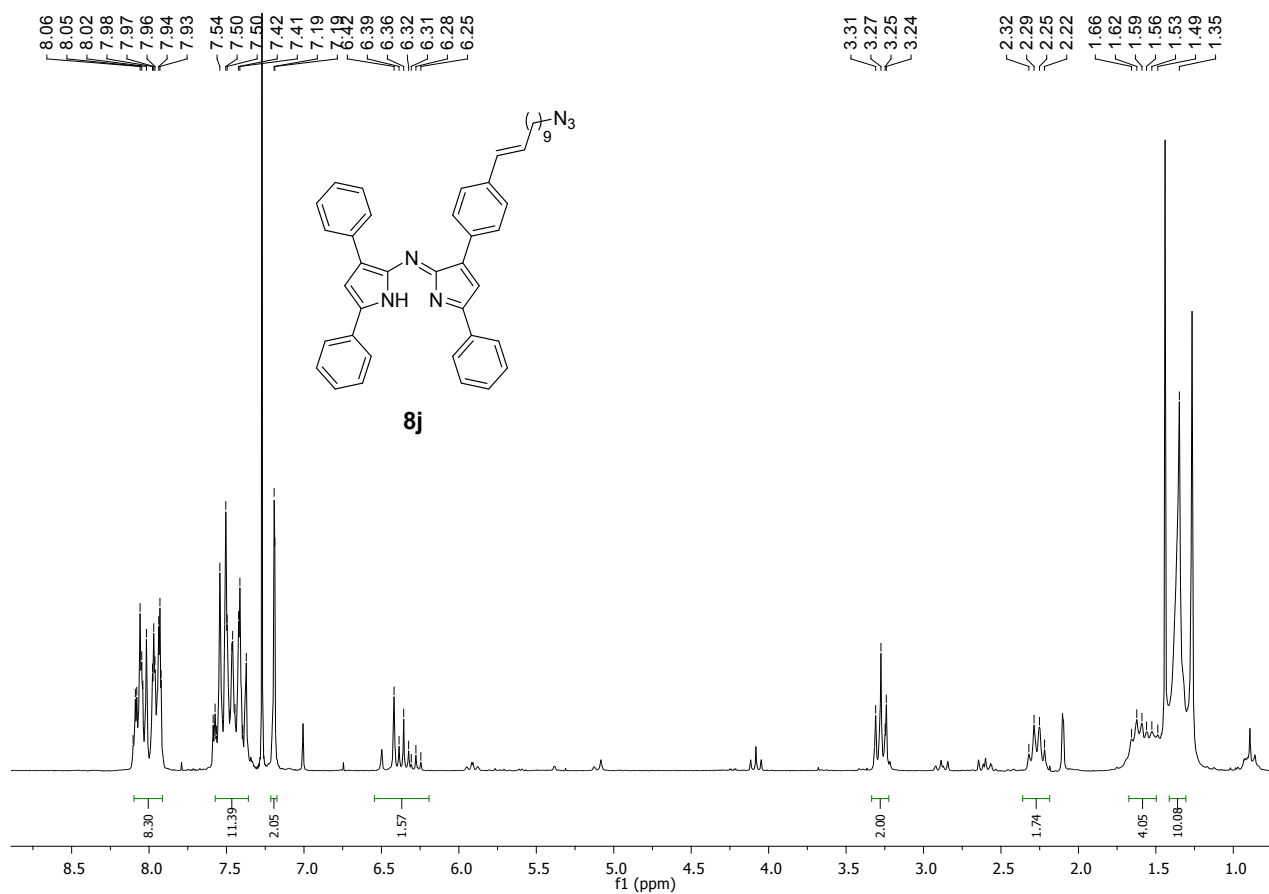


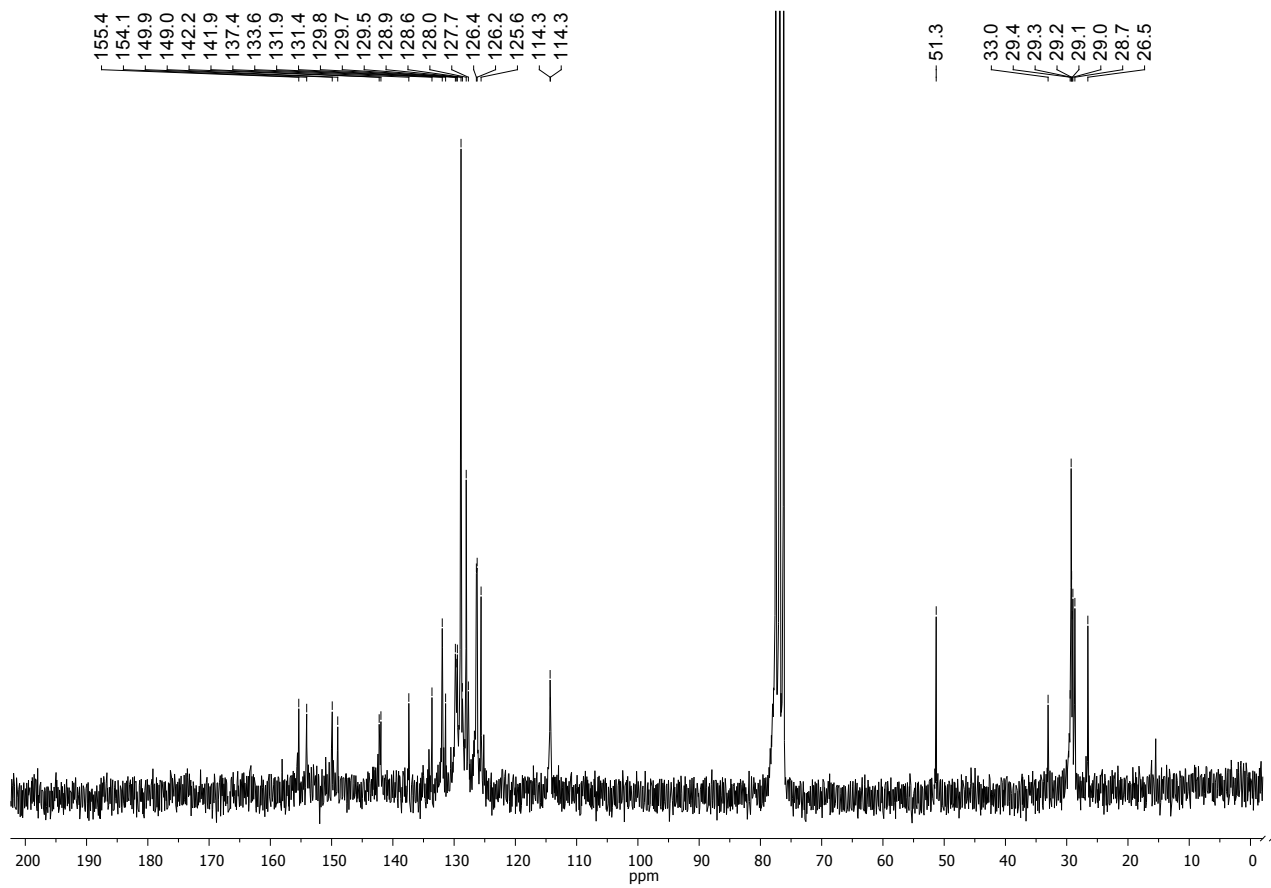


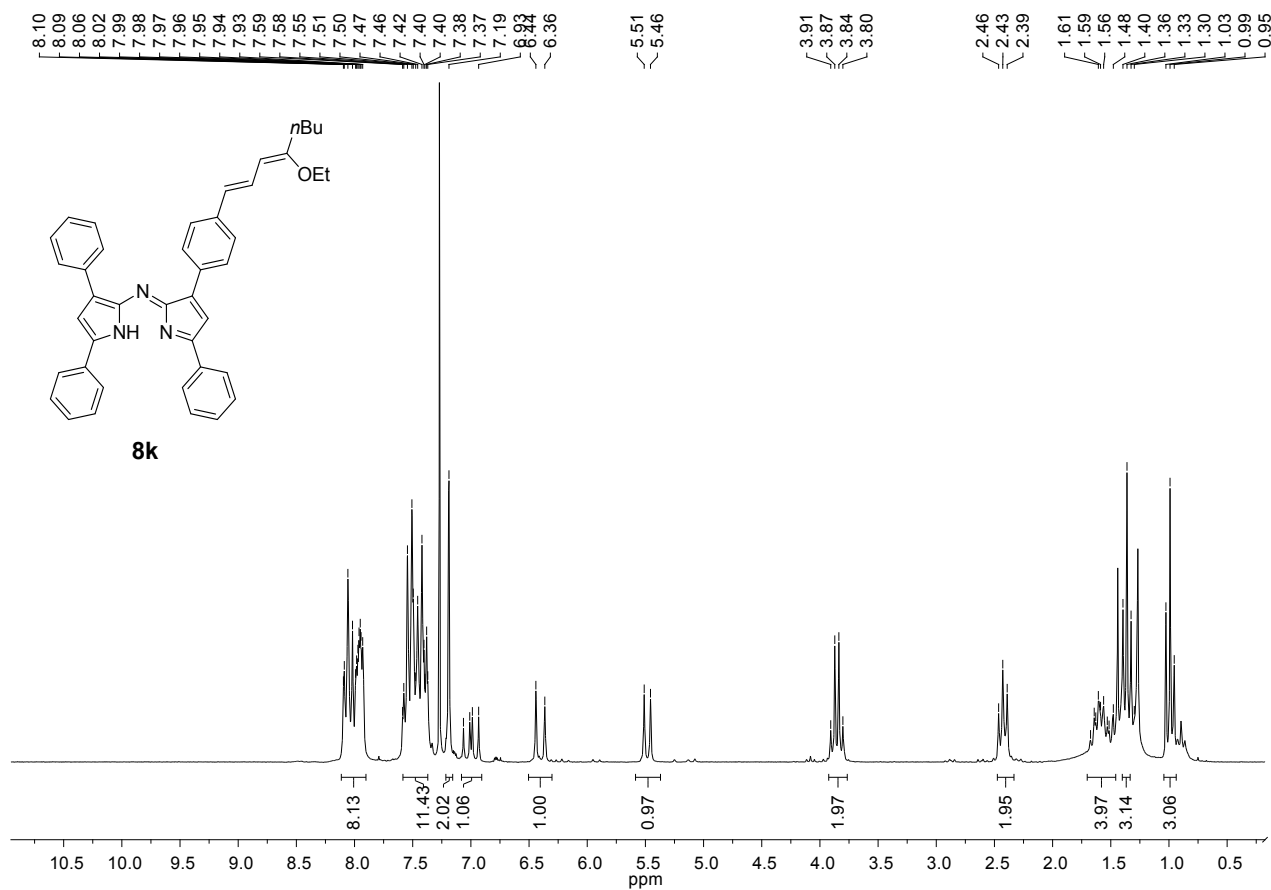


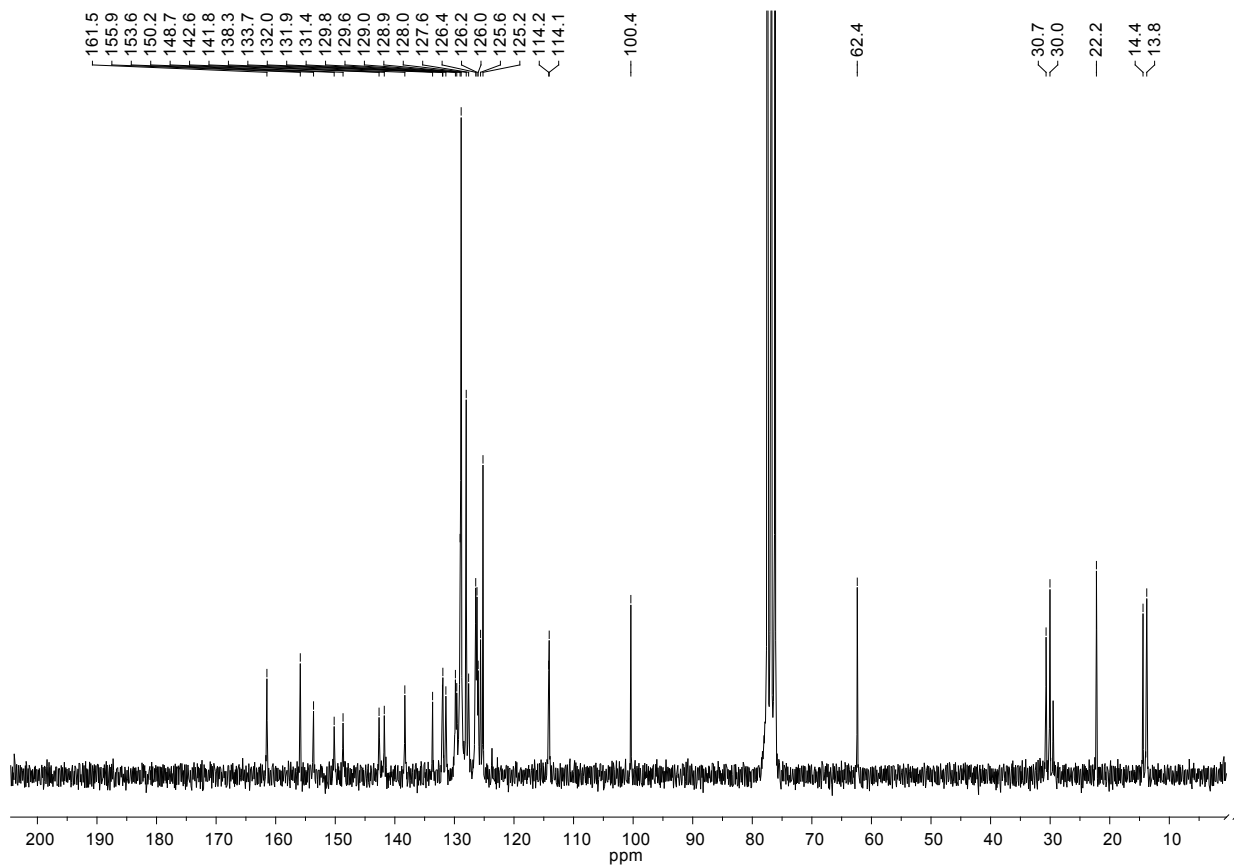


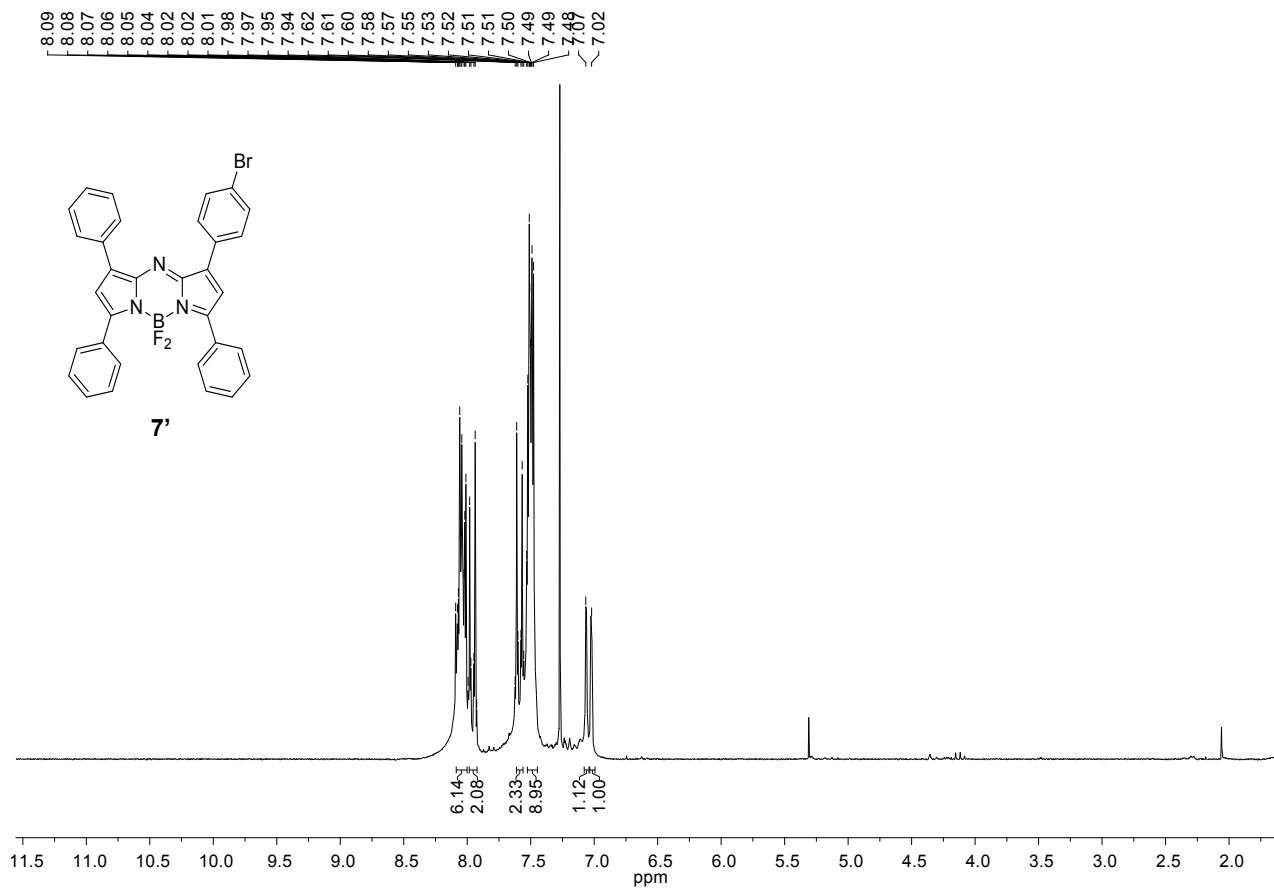




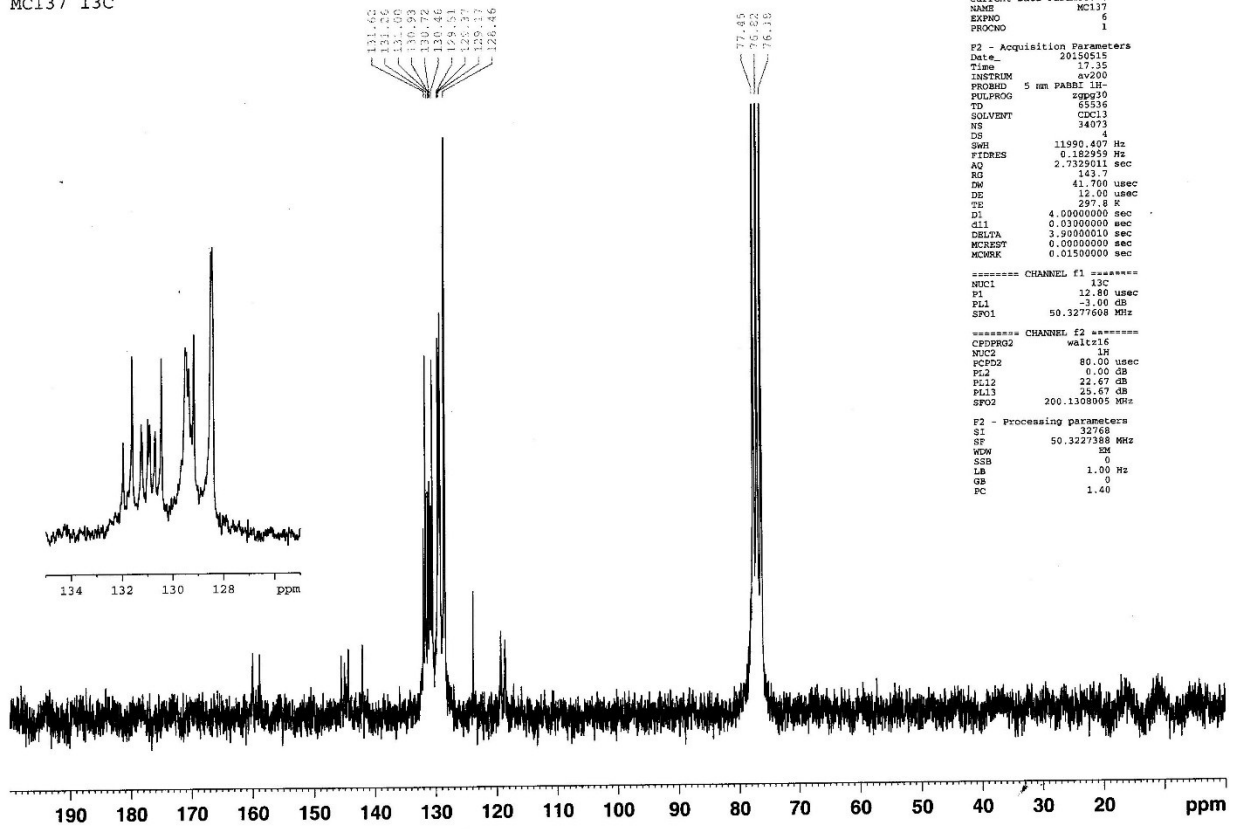


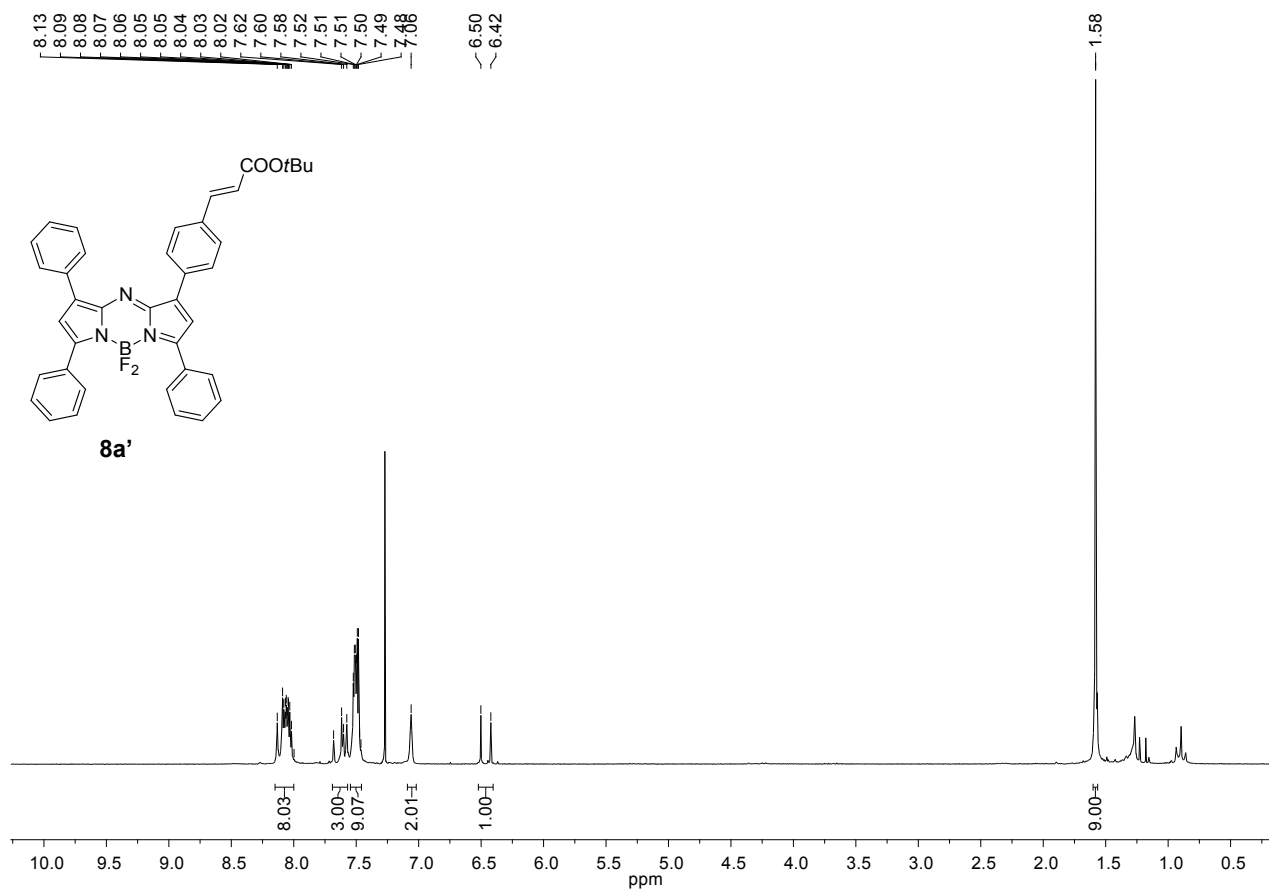


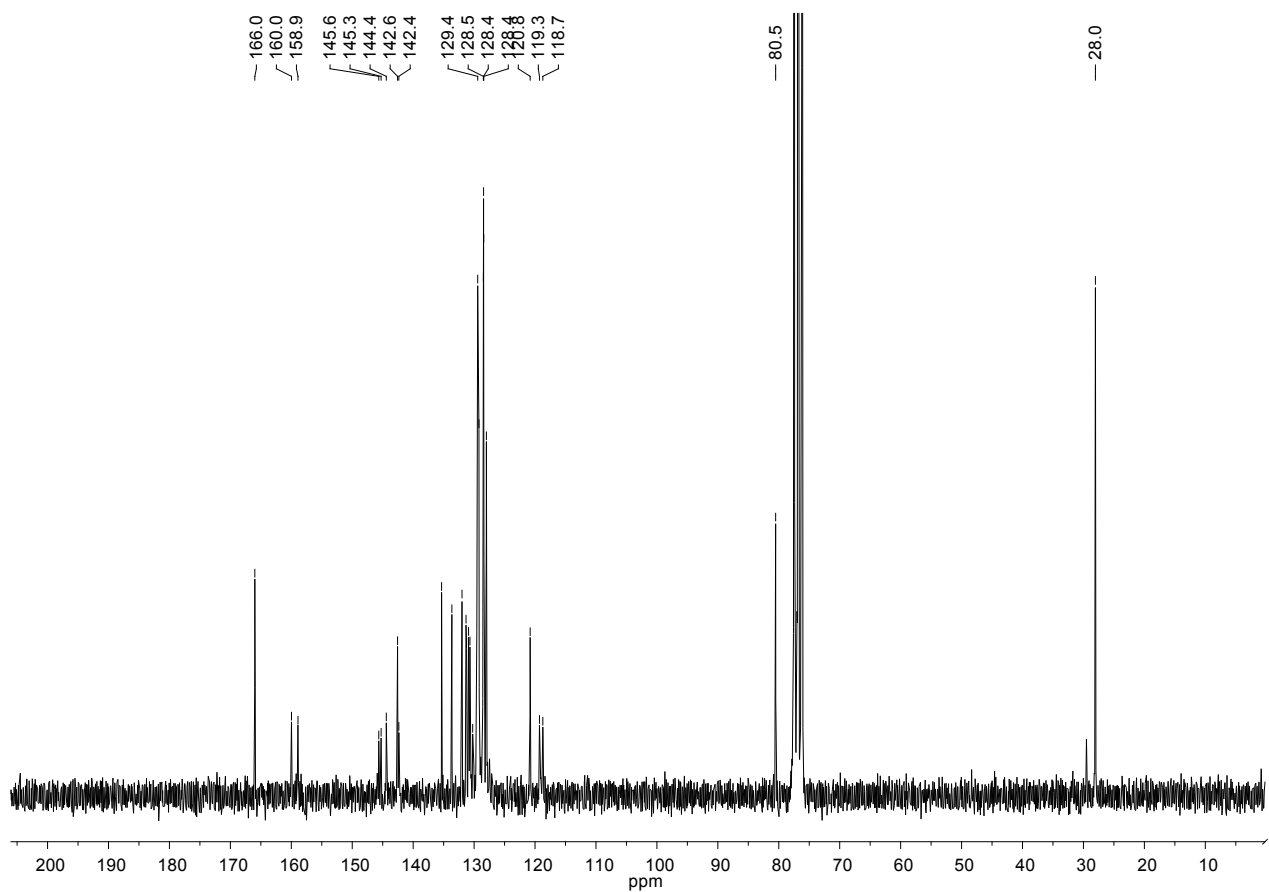


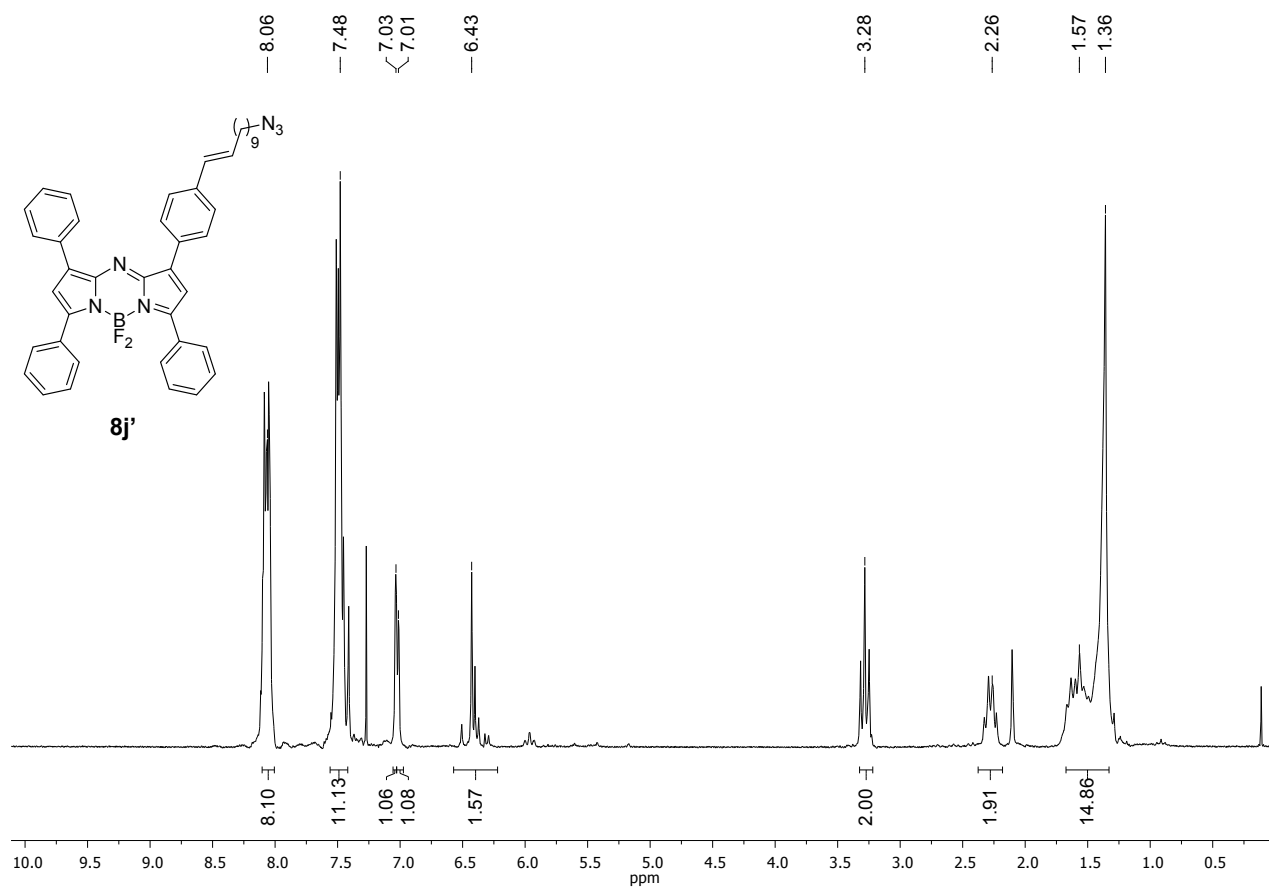


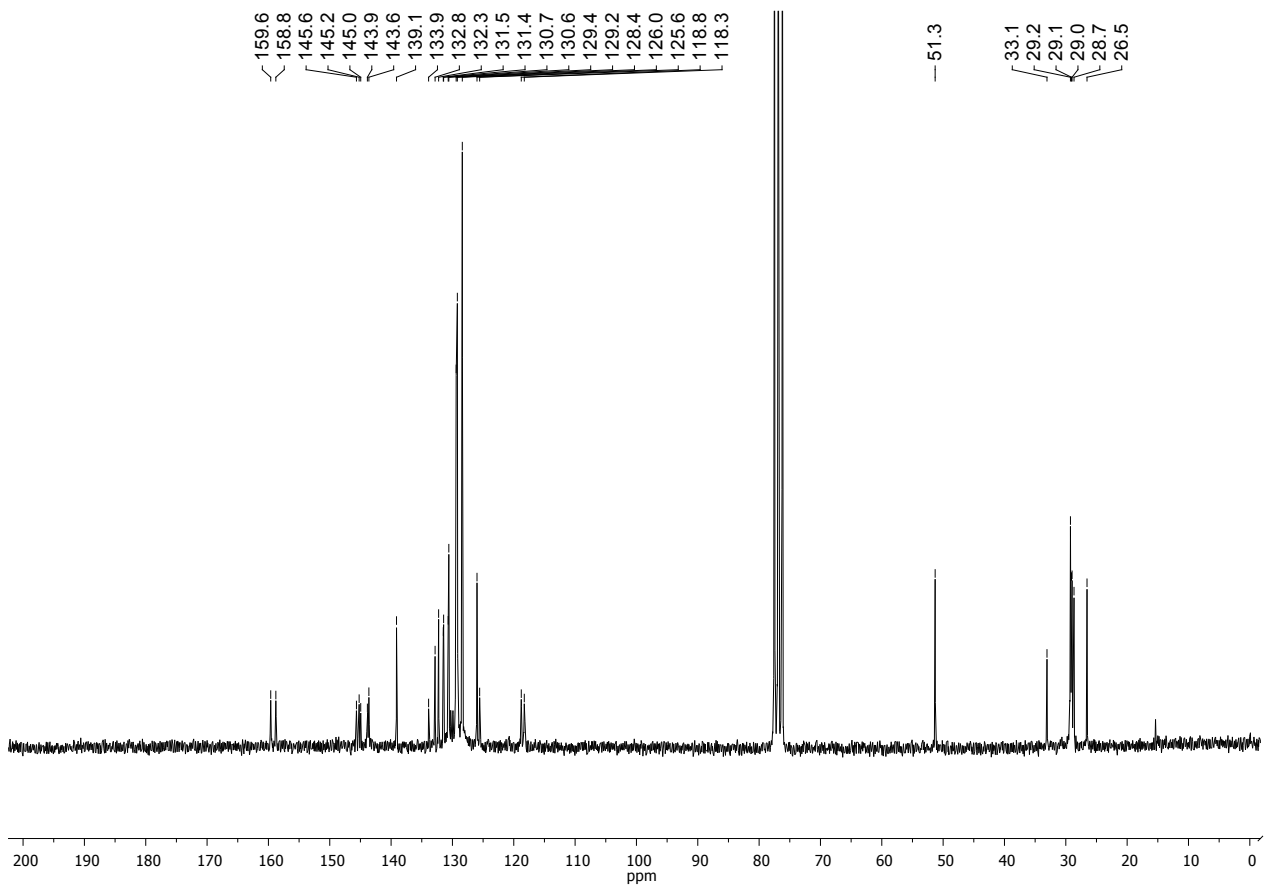
MC137 13C

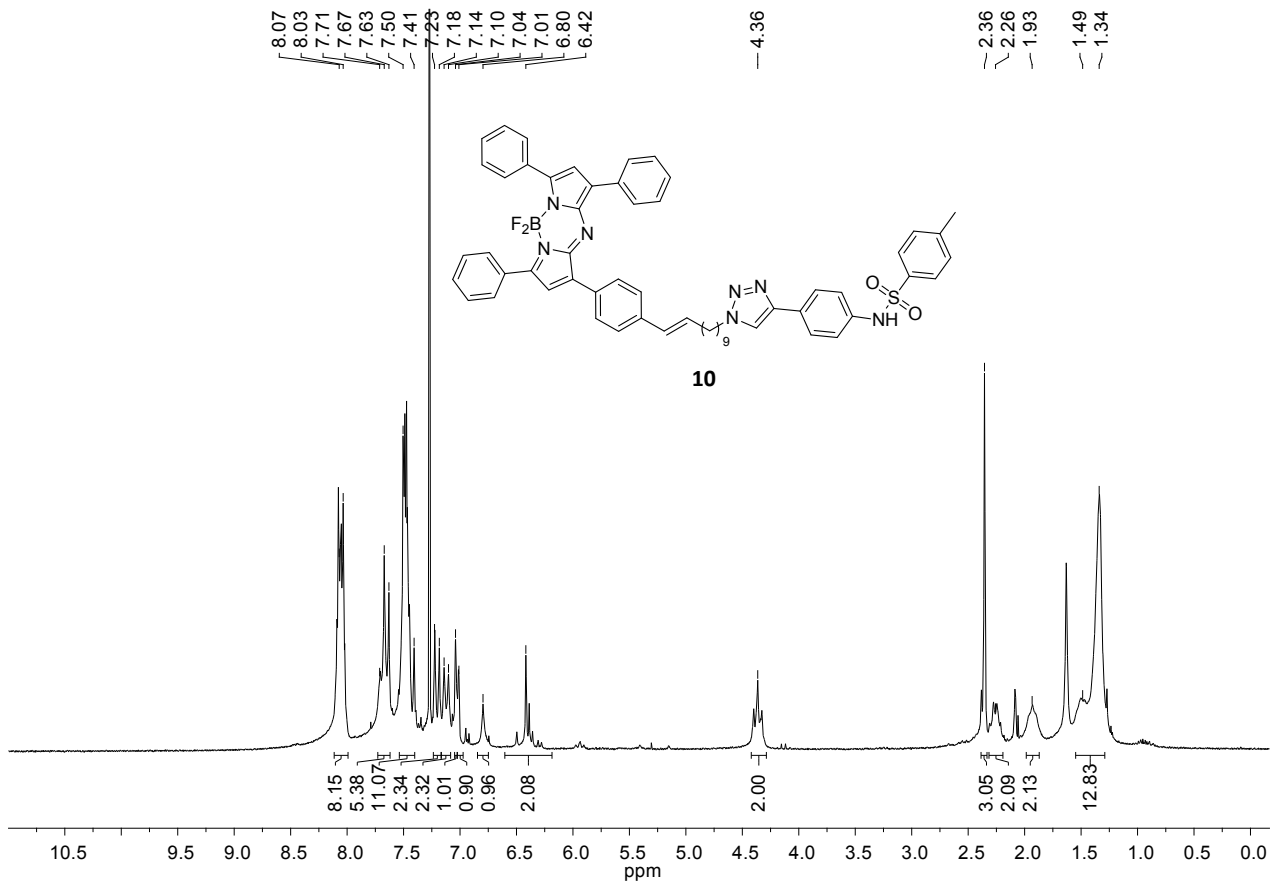


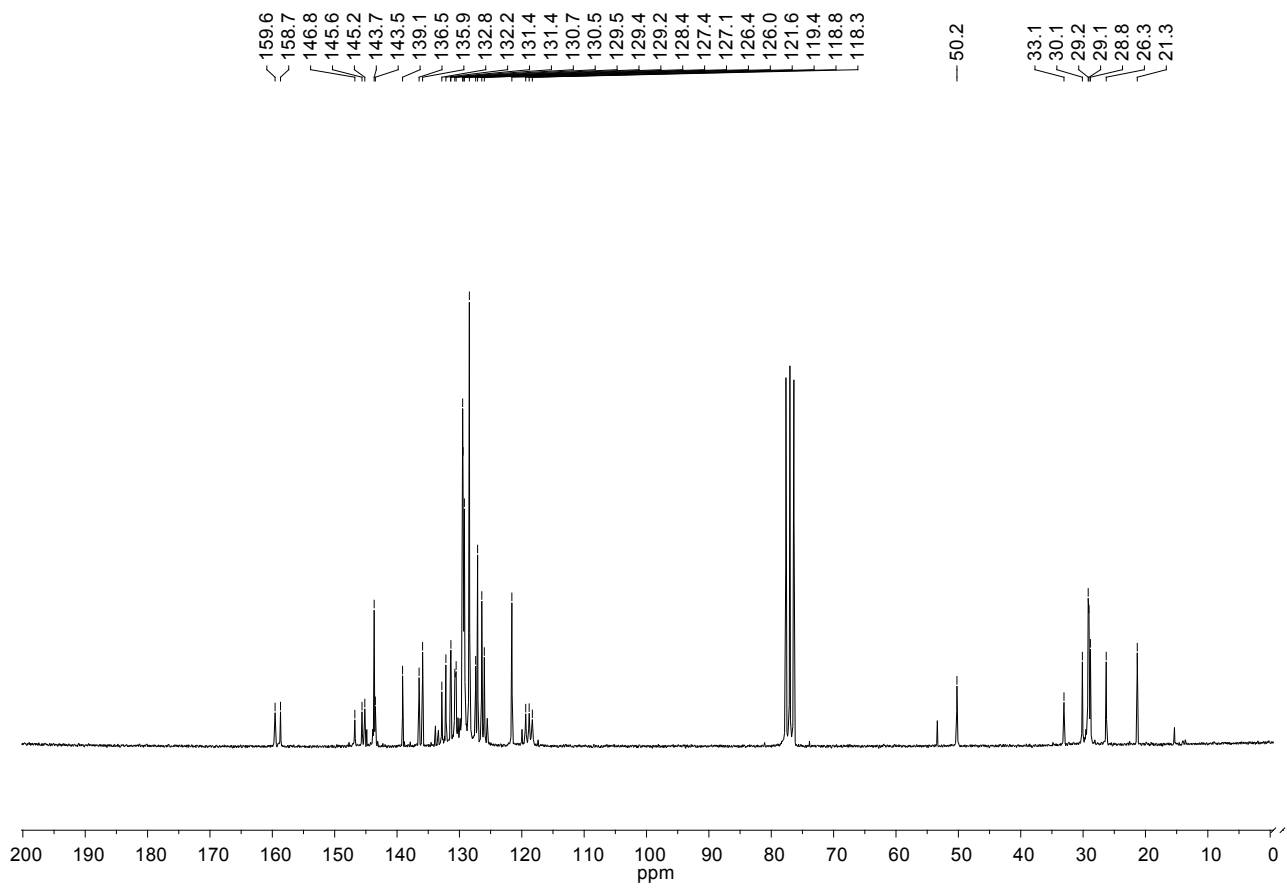












Biological tests

Germination activity

Seeds of *Phelipanche aegyptiaca* were collected from fieldgrown tomato in the West Galilee of Israel. The seeds were stored in glass vials in the dark at room temperature until use in germination tests. Preparation of test solutions: the compound to be tested was weighted out very accurately and dissolved in 1 ml of acetone and then diluted with sterile distilled water to reach the desired concentrations. All solutions were prepared just before use. Seeds were surface-sterilized and preconditioned according to Bhattacharya et al. (2009).¹Briefly, seeds were exposed for 5 min to 50% (v/v) aqueous solutions of commercial bleach (2% hypochlorite) and rinsed with sterile distilled water. For preconditioning, seeds were sown using a sterile toothpick on a glass fiber filter paper disc (approximately 20 seeds per disc); the glass fiber discs were placed on two filter paper discs, wetted with sterile distilled water, and incubated at 25°C in the dark for 6 d. The preconditioned seeds were then allowed to dry completely (under the hood) in the laminar flow, treated with compounds **10**, **8j'** and **CL-BP** at five different concentrations: 10⁻⁵ M, 10⁻⁶ M, 10⁻⁷ M, 10⁻⁸ M and 10⁻⁹ M, and the germination rate was evaluated under a stereomicroscope 7 d after treatment. For each concentration, at least 100 seeds were analyzed; synthetic strigolactone GR24 (10⁻⁷ M) was included as positive control, while an aqueous solution of 0.1% acetone and sterile distilled water were included as negative control. Seeds were considered to be germinated if the radicle protruded through the seed coat.

Confocal microscope

Seeds of *Arabidopsis thaliana* wild type (WT; Columbia; Col-0) were surface sterilized and germinated on half-strength Murashige and Skoog (MS) plates supplemented with 1.5% (w/v) sucrose and 1% agar (w/v). Plates were incubated vertically in the dark at 4 °C for 2 d to synchronize germination. Plates were then positioned in an upright 45° position, and incubated at 22 °C. Light intensity at plate level was 50–60 IE m₂ s₁ provided by white fluorescent tubes with a photoperiod of 16/8 h (light/dark) for 6 d.

For confocal observations, 6-d-old seedlings were incubated 10 minutes in 10⁻⁵ M aqueous solution of compounds **10**, **8j'**, **CL-BP** and **GR24-BP** (10mM acetone stock), quickly rinsed in water and then gently transferred to slides using forceps. Seedlings were covered with a coverslip and immediately imaged with a Leica TCS SP2 confocal microscope using a long-distance 40X water-immersion objective (HCX Apo 0.80).

The Ar/Kr laser was set at 488 nm to excite the fluorochromes of compounds **CL-BP** and **GR24-BP** and an emission window of 500 to 550 nm was used to visualize their fluorescence; the He/Ne laser (633 nm) was used for excitation of compounds **10** and **8j'** with an emission window of 645 to 700 nm.

1. C. Bhattacharya, P. Bonfante, A. Deagostino, Y. Kapulnik, P. Larini, E. G. Occhiato, C. Prandi and P. Venturello, A new class of conjugated strigolactone analogues with fluorescent properties: synthesis and biological activity, *Organic & Biomolecular Chemistry*, 2009, **7**, 3413-3420.