

Supporting information for

Fe(III)-catalyzed synthesis of pyrrolo[3,2-*b*]pyrroles: formation of new dyes and photophysical studies

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Experimental

General information

All chemicals were used as received, unless otherwise noted. All reported NMR spectra were recorded on a 500 MHz spectrometer unless otherwise noted. Chemical shifts (δ ; ppm) for ^1H and ^{13}C NMR were determined with TMS as the internal reference. J values are given in Hz. The absorption and fluorescence spectra were recorded in toluene or in CH_2Cl_2 . Mass spectra were obtained with EI ion source and the EBE double focusing geometry mass analyzer or spectrometer equipped with electro-spray ion source with Q-TOF type mass analyzer. The analysis of compounds **3a**, **3b**, **3c**, **3g**, **3h**, **3i**, **3j**, **3k**, **3l**, **3m**, **3n** and **3t** have been described previously.

General Procedure for the Synthesis of Pyrrolo[3,2-*b*]pyrrole

Glacial acetic acid (1,5 mL), toluene (1,5 mL), aldehyde (2 mmol) and aniline (2 mmol) were placed in a 50 mL round-bottom flask equipped with a magnetic stir bar. The mixture was stirred at 90°C for 30 min. After that time, $\text{Fe}(\text{ClO}_4)_3$ (20 mg) was added and subsequently diacetyl (88 μL , 1 mmol). The resulting mixture left stirring at 90°C for 3 h. The reaction mixture was then cooled to room temperature. The precipitate of the obtained dye was filtered and washed with CH_3CN . Recrystallization from AcOEt and drying under vacuum afforded pure product.

2,5-Bis(4-cyanophenyl)-1,4-bis(naphth-1-yl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (**3d**)

Yellow solid. Yield: 180 mg (32%). ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, $J = 8.2$ Hz, 1H), 8.03 (d, $J = 7.9$ Hz, 1H), 8.00 (d, $J = 8.1$ Hz, 1H), 7.97 - 7.92 (m, 2H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.64 - 7.55 (m, 3H), 7.51 (t, $J = 7.83$ Hz, 2H), 7.46 (t, $J = 7.74$ Hz, 1H), 7.39 (d, $J = 7.3$, 1H), 7.26 - 7.31 (m, 4H), 7.21 (d, $J = 7.3$ Hz, 1H), 7.15 - 7.06 (m, 4H), 6.29 (s, 1H), 6.27 (s, 1H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 137.4, 137.4, 137.2, 137.2, 136.1, 135.9, 135.1, 135.0, 134.7, 134.6, 131.9 (2), 130.0, 129.9, 128.6, 128.5, 128.4, 128.3, 127.3, 127.2, 127.0, 126.9, 126.8, 125.8, 125.7, 125.6 (2), 123.5, 123.5, 119.0, 108.9, 108.9, 96.2, 95.7 ppm. HRMS (EI): m/z calculated for $\text{C}_{40}\text{H}_{24}\text{N}_4$: 560.2001 [M^+]; found: 560.1998.

2,5-Bis(4-cyanophenyl)-1,4-bis[3,5-bis(trifluoromethyl)phenyl]-1,4-dihydropyrrolo[3,2-*b*]pyrrole (**3e**)

Yellow solid. Yield: 352 mg (48%). ^1H NMR (500 MHz, CDCl_3) δ 7.83 (s, 2H), 7.66 (s, 4H), 7.60, 7.29 (d, $J = 8.5$ Hz, AA'BB', 8H), 6.55 (s, 2H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 140.4, 136.0, 135.5, 133.3 (q, $J = 34.0$ Hz), 132.6, 132.5, 128.4, 124.8 (m), 123.7, 121.5, 120.1 (m), 118.4, 110.9, 97.8 ppm. HRMS (EI): m/z calculated for $\text{C}_{36}\text{H}_{16}\text{F}_{12}\text{N}_4$: 732.1183 [M^+], found: 732.1185.

2,5-Bis(4-cyanophenyl)-1,4-bis(4-pentafluorosulfanylphenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (**3f**)

Yellow solid. Yield: 311 mg (44%). ^1H NMR (500 MHz, CDCl_3) δ 7.82 (d, $J = 9.1$ Hz, 4H), 7.57 (d, $J = 8.5$ Hz, 4H), 7.33–7.26 (m, 8H), 6.56 (s, 2H) ppm; ^{13}C NMR (126 MHz, CDCl_3): δ 151.4, 141.5, 136.7, 135.3, 132.9, 132.4, 128.2, 127.6, 124.6, 118.6, 110.4, 97.9 ppm. HRMS (ESI): m/z calculated for $\text{C}_{32}\text{H}_{17}\text{N}_4\text{F}_{10}\text{S}_2$: 711.0735 [$\text{M}-\text{H}^+$]; found: 711.0717.

2,5-Bis(2-chlorobenzo[*h*]quinolin-3-yl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (**3o**)

Beige solid. Yield: 484 mg (68%). ¹H NMR (500 MHz, THF-*d*₈) δ 9.09 - 9.17 (m, 2H), 8.33 (s, 2H), 7.93 - 8.03 (m, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.62 - 7.79 (m, 6H), 7.13, 7.24 (dd, *J* = 8.1 Hz, AA'BB', 8H), 6.65 (s, 2H), 2.29 ppm (s, 6H); ¹³C NMR (126 MHz, THF-*d*₈) δ 150.2, 145.9, 141.0, 138.5, 136.1, 135.0, 132.0, 131.8, 131.3, 130.6, 129.5, 129.1 (2), 128.7, 128.0, 126.0, 125.5, 125.3, 124.9, 98.1, 20.9 ppm. HRMS (EI): *m/z* calculated for C₄₆H₃₀Cl₂N₄: 708.1848 [M⁺], found: 708.1850.

2,5-Bis[4-(acridin-9-yl)phenyl]-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (3p)

Yellow solid. Yield: 254 mg (32%). ¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, *J* = 9.2 Hz, 4H), 7.78 (d, *J* = 8.5 Hz, 8H), 7.50 (d, *J* = 7.9 Hz, 4H), 7.46 (t, *J* = 7.7 Hz, 4H), 7.37 (d, *J* = 8.2 Hz, 4H), 7.33 (d, *J* = 7.8 Hz, 4H), 7.28 (d, *J* = 8.1 Hz, 4H), 6.61 (s, 2H), 2.43 (s, 6H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 148.9, 147.1, 137.5, 135.8, 135.5, 133.9, 133.4, 132.3, 130.5, 130.0, 129.9, 129.7, 127.9, 126.9, 125.6, 125.2, 125.1, 95.0, 77.3, 77.0, 76.8, 21.1 ppm. HRMS (ESI): *m/z* calculated for C₅₈H₄₁N₄: 793.3331 [M+H⁺], found: 793.3345.

1,4-Bis(4-methylphenyl)-2,5-bis(thien-2-yl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (3q)

Beige solid. Yield: 54 mg (12%). ¹H NMR (500 MHz, CDCl₃) δ 7.21, 7.27 (AA'BB', *J* = 8.2 Hz, 8H), 7.09 (d, *J* = 4.9 Hz, 2H), 6.85 (dd, *J*₂ = 5.1 Hz, *J*₁ = 3.7 Hz, 2H), 6.62 (d, *J* = 3.1 Hz, 2H), 6.32 (s, 2H), 2.41 (s, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 136.9, 136.4, 135.9, 131.7, 129.7, 129.6, 127.1, 126.1, 124.7, 123.8, 93.9, 21.1 ppm. HRMS (EI): *m/z* calculated for C₂₈H₂₂N₂S₂: 450.1224 [M⁺], found: 450.1222.

1,4-Bis(4-methylphenyl)-2,5-bis(5-nitrofur-2-yl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (3r)

Purple solid. Yield: 173 mg (13%). ¹H NMR (500 MHz, THF-*d*₈) δ 7.40 (s, 8H), 7.28 (d, *J* = 4.0 Hz, 2H), 6.70 (s, 2H), 5.81 (d, *J* = 4.0 Hz, 2H), 2.47 (s, 6H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 150.6, 138.9, 135.6, 135.0, 130.5, 127.9, 126.6, 114.4, 107.9, 95.0, 21.3 ppm. HRMS (EI): *m/z* calculated for C₂₈H₂₀N₂O₆: 508.1383 [M⁺], found: 508.1361.

2,5-Bis(benzothiazol-2-yl)-1,4-bis(3,5-di-*tert*-butylphenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (3s)

Yellow solid. Yield: 113 mg (15%). ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 1.8 Hz, 2H), 7.41 - 7.36 (m, 2H), 7.36 (d, *J* = 1.8 Hz, 4H), 7.20 - 7.27 (m, 2H), 6.99 (s, 2H), 1.35 (s, 36H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 159.4, 153.1, 152.1, 137.5, 135.0, 134.7, 132.9, 126.0, 124.3, 122.4, 122.0, 121.9, 120.9, 96.5, 35.1, 31.4 ppm. HRMS (ESI): *m/z* calculated for C₄₈H₅₃N₄S₂: 749.3712 [M+H⁺], found: 749.3694.

1,4-Bis(3,5-di-*tert*-butylphenyl)-2,5-bis(thiazol-2-yl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (3u)

Beige solid. Yield: 55 mg (8%). ¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, *J* = 3.2 Hz, 2H), 7.45 (t, *J* = 1.6 Hz, 2H), 7.25 (d, *J* = 1.7 Hz, 4H), 7.07 (d, *J* = 3.2 Hz, 2H), 6.79 (s, 2H), 1.32 (s, 36H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 160.0, 152.1, 142.3, 137.7, 133.3, 132.0, 121.6, 121.4, 117.7, 95.0, 35.0, 31.4 ppm. HRMS (EI): *m/z* calculated for C₄₀H₄₈N₄S₂: 648.3320 [M⁺], found: 648.3314.

2,5-Bis(benzo[*b*]thien-2-yl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (3v)

Orange solid. Yield: 255 mg (46%). ¹H NMR (500 MHz, CDCl₃) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 4H), 7.25 (d, *J* = 8.1 Hz, 4H), 7.26 - 7.17 (m, 4H), 6.77 (s, 2H), 6.45 (s, 2H), 2.44 (s, 6H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 140.3, 139.0, 136.9,

136.8, 135.8, 132.8, 130.2, 130.0, 126.1, 124.2, 123.7, 123.1, 121.8, 120.2, 95.0, 21.2 ppm. HRMS (EI): m/z calculated for $C_{36}H_{26}N_2S_2$: 550.1537 [M^+], found: 550.1542.

2,5-Bis(benzo[b]thien-2-yl)-1,4-bis(3,5-di-*tert*-butylphenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (3w)

Yellow solid. Yield: 87 mg (12%). 1H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, $J = 7.5$ Hz, 2H), 7.50 (d, $J = 7.2$ Hz, 2H), 7.40 (bs, 2H), 7.31 (d, $J = 1.6$ Hz, 4H), 7.26 – 7.18 (m, 4H), 6.72 (s, 2H), 6.51 (s, 2H), 1.29 (s, 36H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 140.3, 139.0, 138.4, 135.8, 132.3, 130.0, 124.2, 123.7, 122.9, 121.6, 120.6, 120.5, 120.4, 94.9, 35.0, 31.3 ppm. HRMS (EI): m/z calculated for $C_{50}H_{54}N_2S_2$: 746.3728 [M^+], found: 746.3734.

2,5-Bis(benzo[b]fur-2-yl)-1,4-bis(3,5-di-*tert*-butylphenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (3x)

Yellow solid. Yield: 150 mg (21%). 1H NMR (500 MHz, $CDCl_3$) δ 7.49 (b s, 2H), 7.40 – 7.35 (m, 6H), 7.32 (d, $J = 7.3$ Hz, 2H), 7.21 – 7.14 (m, 2H), 7.14 – 7.08 (m, 2H), 6.70 (s, 2H), 5.95 (s, 2H), 1.36 (s, 36H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.9, 152.1, 149.9, 138.7, 133.2, 129.3, 127.9, 123.5, 122.7, 121.1, 120.9, 120.2, 110.6, 101.3, 93.7, 35.1, 31.5 ppm. HRMS (EI): m/z calculated for $C_{50}H_{54}N_2O_2$: 714.4185 [M^+], found: 714.4178.

1,4-Bis(4-methylphenyl)-2,5-bis(quinoxalin-2-yl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (3y)

Brown solid. Yield: 214 mg (39%). 1H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 2H), 7.96 (d, $J = 8.1$ Hz, 2H), 7.84 (d, $J = 8.2$ Hz, 2H), 7.70 – 7.59 (m, 4H), 7.31, 7.25 (AA'BB', $J = 8.1$, 8H), 7.00 (s, 2H), 2.42 ppm (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 144.6, 142.3, 140.2, 137.3, 136.8, 135.3, 134.9, 130.1 (2), 129.0 (2), 128.8, 125.6, 97.7, 21.1 ppm. HRMS (EI): m/z calculated for $C_{36}H_{26}N_6$: 542.2219 [M^+], found: 542.2233.

1,4-Bis(3,5-di-*tert*-butylphenyl)-2,5-bis(quinoxalin-2-yl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (3z)

Orange solid. Yield: 125 mg (17%). 1H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 2H), 7.97 – 7.92 (m, 2H), 7.88 (d, $J = 8.2$ Hz, 2H), 7.70 – 7.65 (m, 2H), 7.63 (td, $J_1 = 7.3$ Hz, $J_2 = 1.3$ Hz, 2H), 7.39 (t, $J = 1.5$ Hz, 2H), 7.22 (d, $J = 1.6$ Hz, 4H), 7.01 (s, 2H), 1.25 (s, 36H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.36, 147.01, 144.83, 142.18, 140.05, 139.01, 135.19, 134.53, 129.94, 129.01, 128.88, 128.76, 120.57, 120.05, 97.48, 34.94, 31.32 ppm. HRMS (EI): m/z calculated for $C_{50}H_{54}N_6$: 738.4410 [M^+], found: 738.4415.

2,5-Bis(4-cyanophenyl)-1,4-bis(4-methylphenyl)-3,6-dimethyl-1,4-dihydropyrrolo[3,2-*b*]pyrrole (3ab)

Yellow solid. Yield 19 mg (4%). 1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, $J = 8.2$ Hz, 4H), 7.17 (d, $J = 8.2$ Hz, 4H), 7.08–7.14 (m, 8H), 2.36 (s, 6H), 1.99 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 137.4, 136.8, 136.2, 133.3, 131.5, 131.1, 130.6, 129.4, 128.2, 127.6, 109.1, 103.4, 21.1, 10.6$ ppm. HRMS (EI): m/z calculated for $C_{36}H_{28}N_4$: 516.2314 [M^+]; found 516.2321.

1,4-Bis(4-*tert*-butylphenyl)-2,5-bis(2,6-dichlorophenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (3aa)

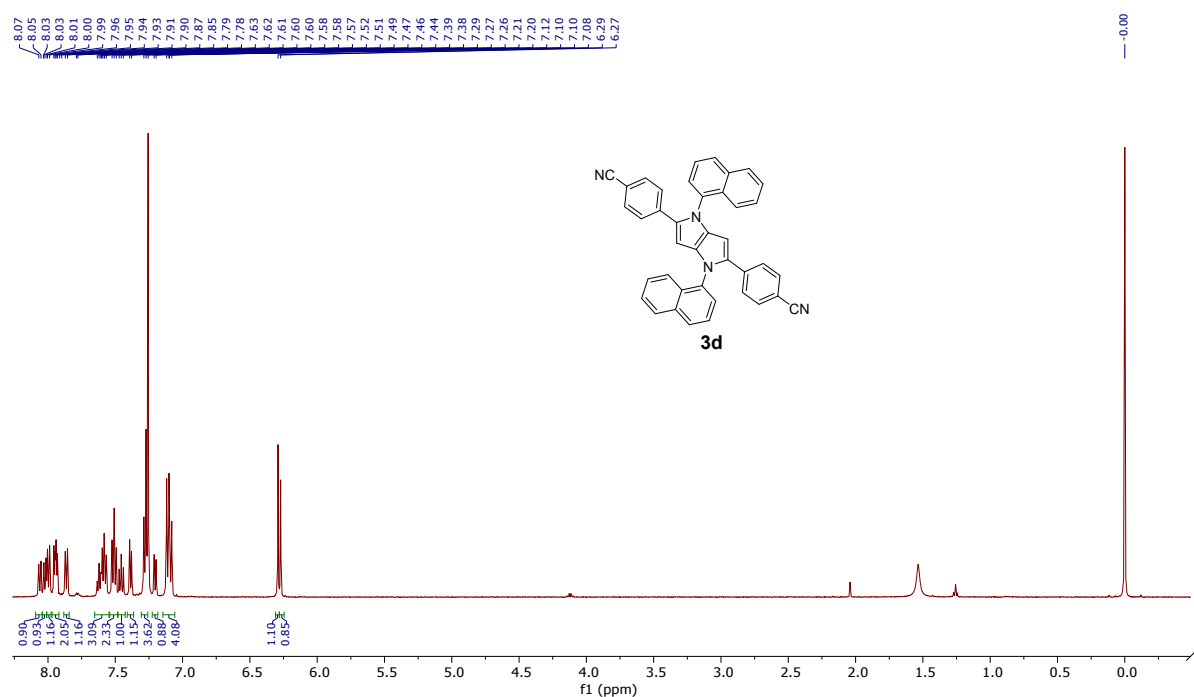
White solid. Yield: 453 mg (69%). 1H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, $J = 8.1$ Hz, 4H), 7.23 – 7.26 (m, 4H), 7.14 – 7.20 (m, 6H), 6.33 (s, 2H), 1.28 (s, 18H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 137.6, 137.2, 132.9, 129.5 (2), 128.3, 127.8, 125.6, 122.9, 96.2, 34.4, 31.4 ppm. HRMS (EI): m/z calculated for $C_{38}H_{34}N_2Cl_4$: 658.1476 [M^+], found: 658.1461.

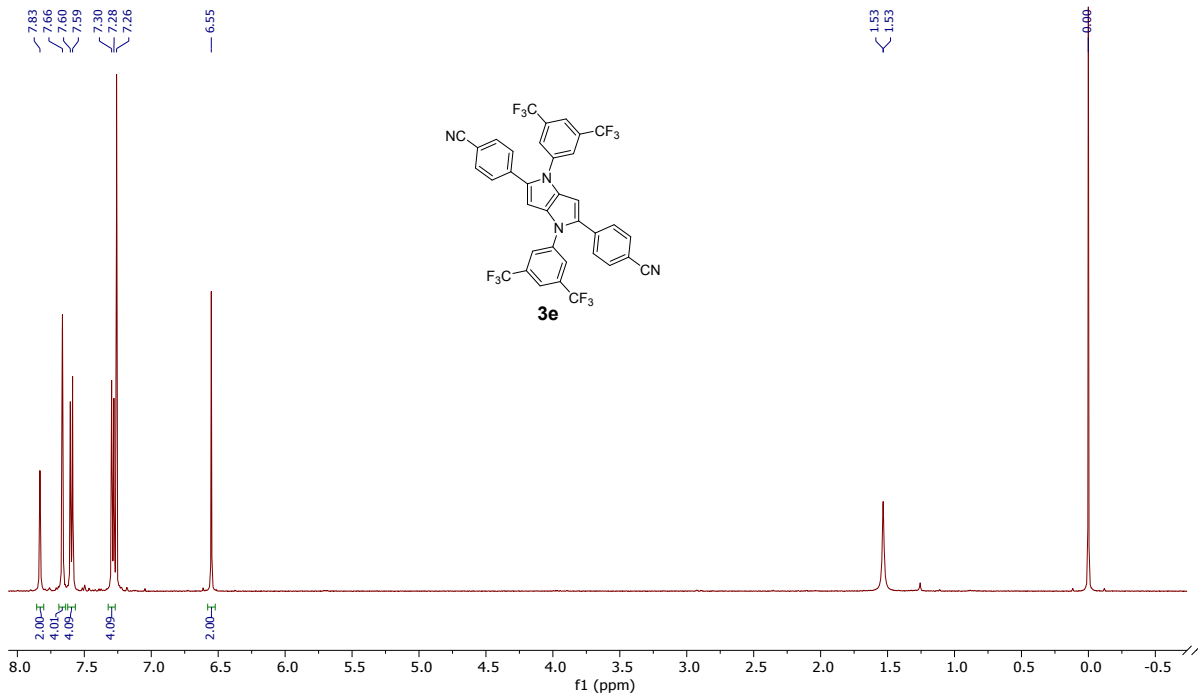
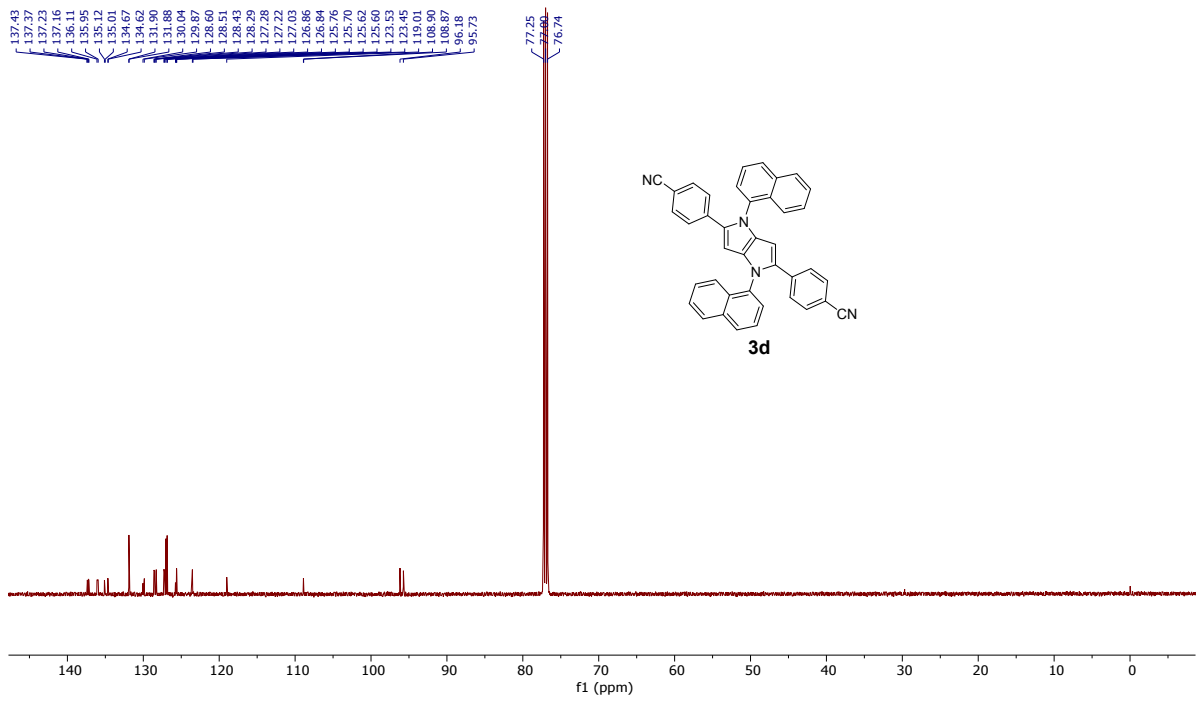
1,4-Bis(4-*tert*-butylphenyl)-2,5-bis(2,6-dichlorophenyl)-1,2,3,4-tetrahydropyrrolo[3,2-*b*]pyrrole (4aa)

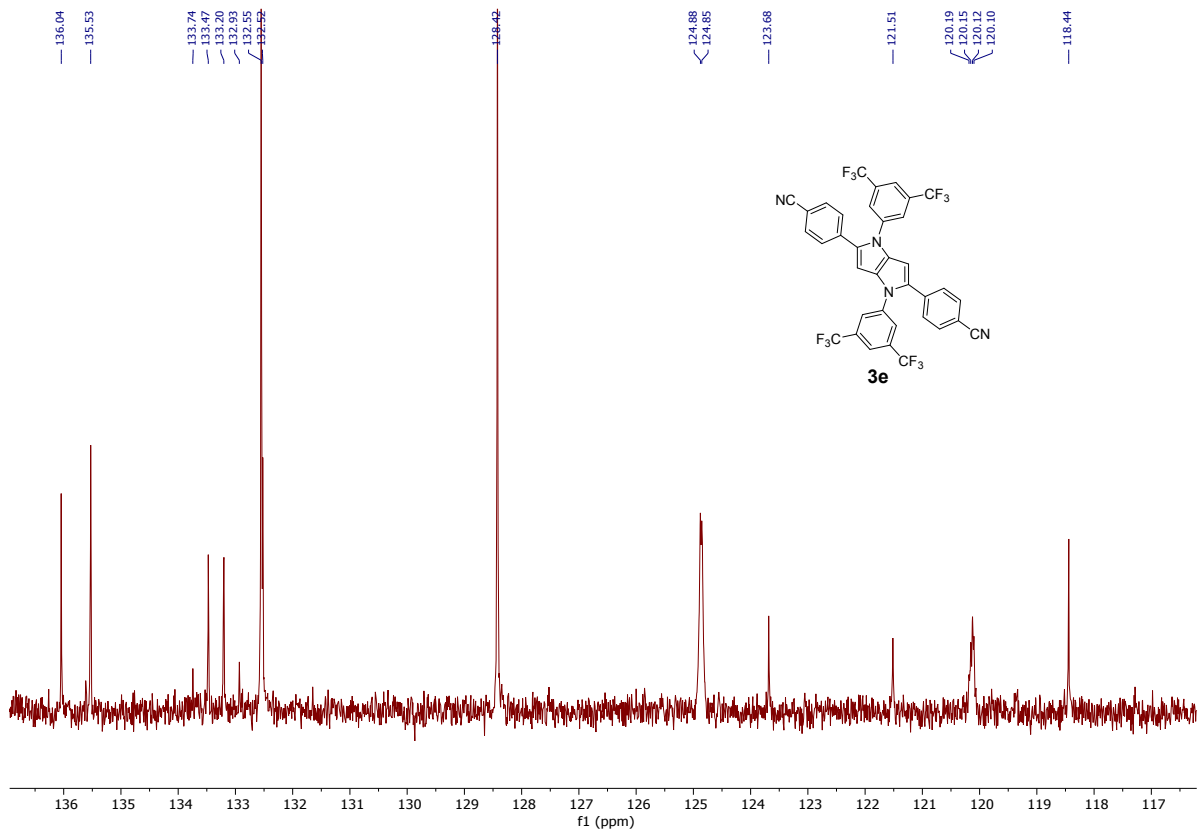
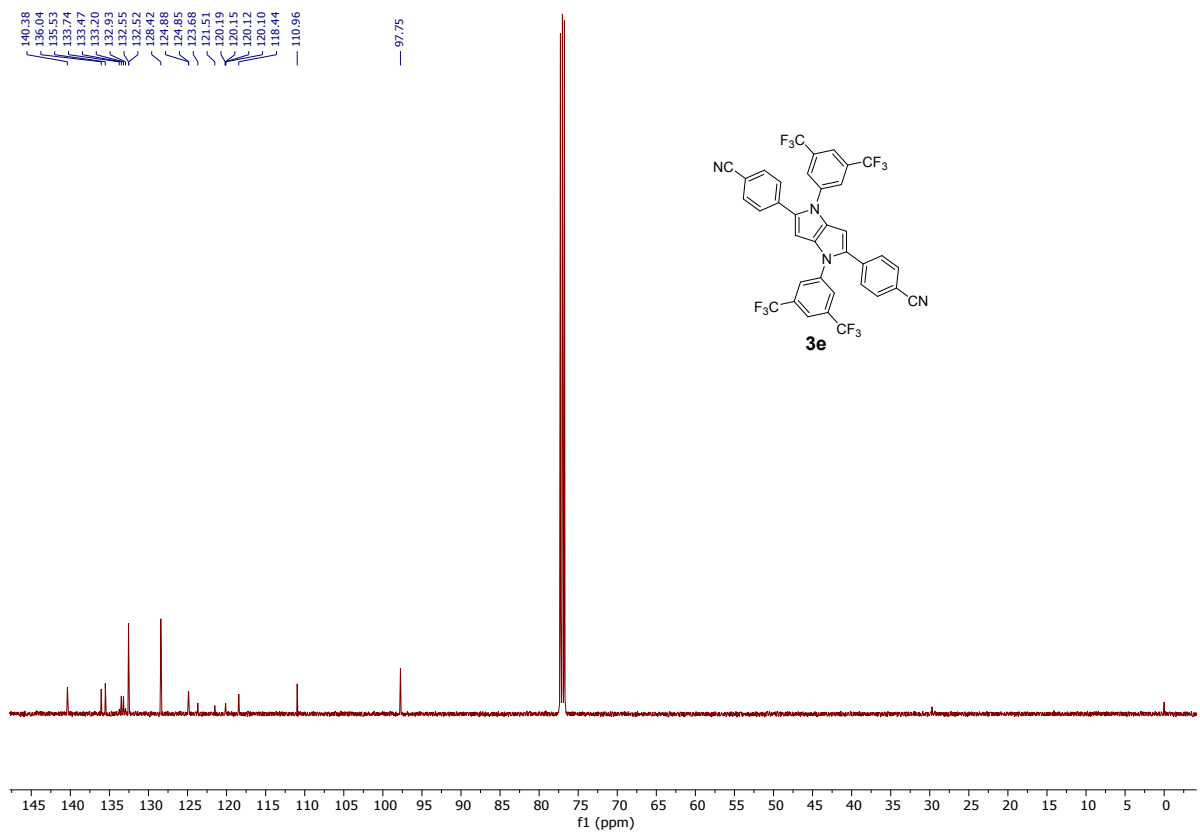
In a 25 mL round-bottom flask equipped with a reflux condenser and magnetic stir bar, glacial acid (2mL) was placed followed by 4-*tert*-butylaniline (**2k**, 2 mmol, 314 μ L), 2,6-dichlorobenzaldehyde (**1r**, 2 mmol, 350 mg), and TsOH (0.2 mmol, 34 mg). The mixture was stirred at 90°C for 30 min. After that time, butane-2,3-dione (1 mmol, 88 μ L) was slowly added via syringe and the resulting mixture was stirred at 90°C for 3 h. After cooling the precipitate of the product were filtered off and washed with CH₃CN, to afford 530 mg (80% yield) of the title compound contaminated with the compound **3aa** (yellowish solid). ¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.28 (m, 2H), 7.25 – 7.13 (m, 7H), 7.13 – 7.08 (t, *J*=8.0, 1H), 7.03 (d, *J*= 8.6, 2H), 6.86 (d, *J*= 8.2, 2H), 6.39 (bs, 1H), 6.26 (s, 1H), 3.74 (t, *J*= 12.8, 1H), 3.14 – 2.94 (m, 1H), 1.24 (s, 9H), 1.24 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 148.9, 147.9, 143.7, 140.3, 138.0, 137.8, 137.8, 137.6, 137.5, 137.2, 136.2, 136.1, 134.3, 132.9, 132.6, 130.8, 129.6, 129.5, 128.7, 128.3, 128.1, 127.8, 127.7, 127.7, 127.0, 125.8, 125.6, 125.6, 123.7, 123.0, 122.0, 113.0, 100.3, 96.2, 67.4, 34.4, 34.4, 33.9, 32.7, 31.5, 31.4, 31.3 ppm. HRMS (EI): *m/z* calculated for C₃₈H₃₆N₂Cl₄: 660.1633 [*M*⁺], found: 660.1621.

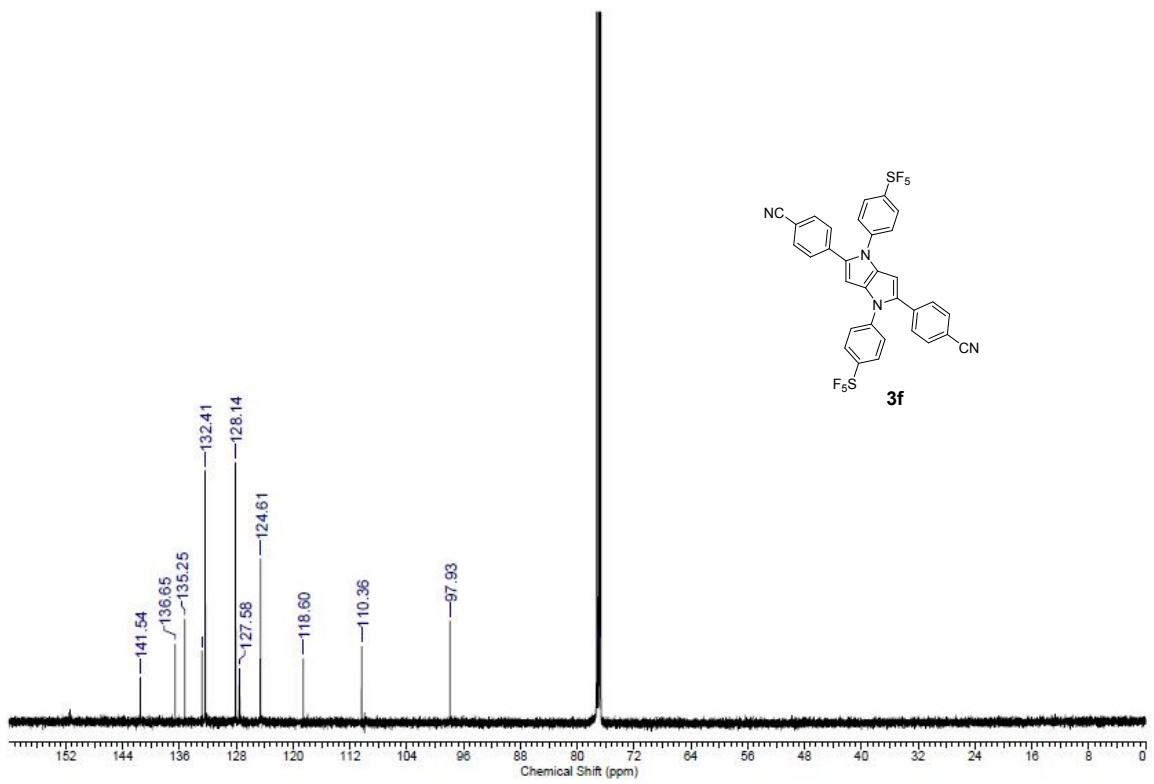
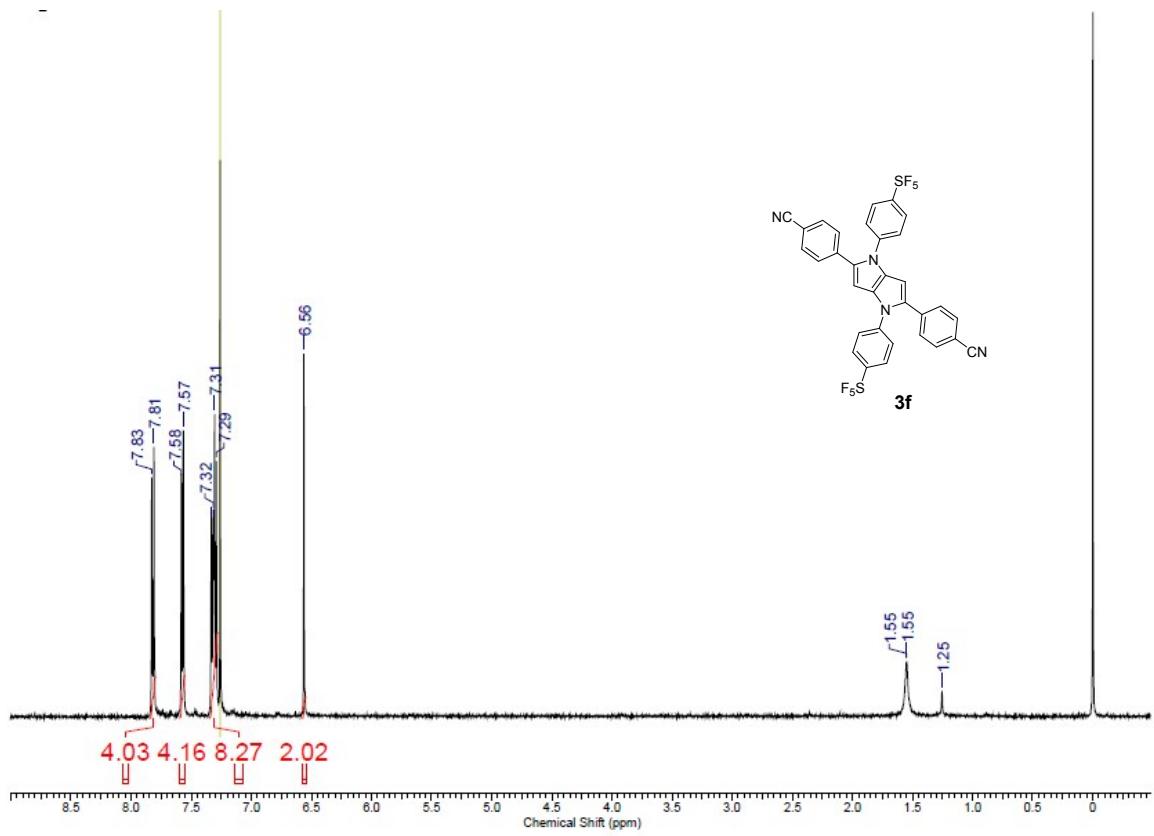
1,4-Bis(4-*tert*-butylphenyl)-2,5-bis(2,6-dichlorophenyl)-1,4-dihydropyrrolo[3,2-*b*]pyrrole (**3aa**)

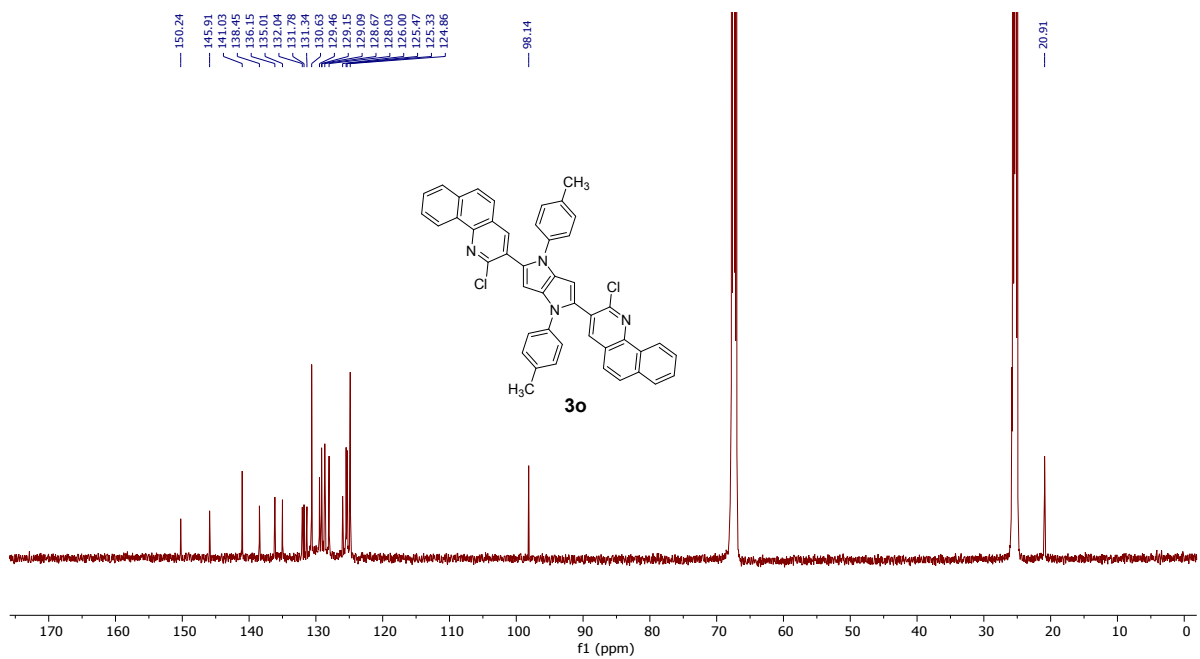
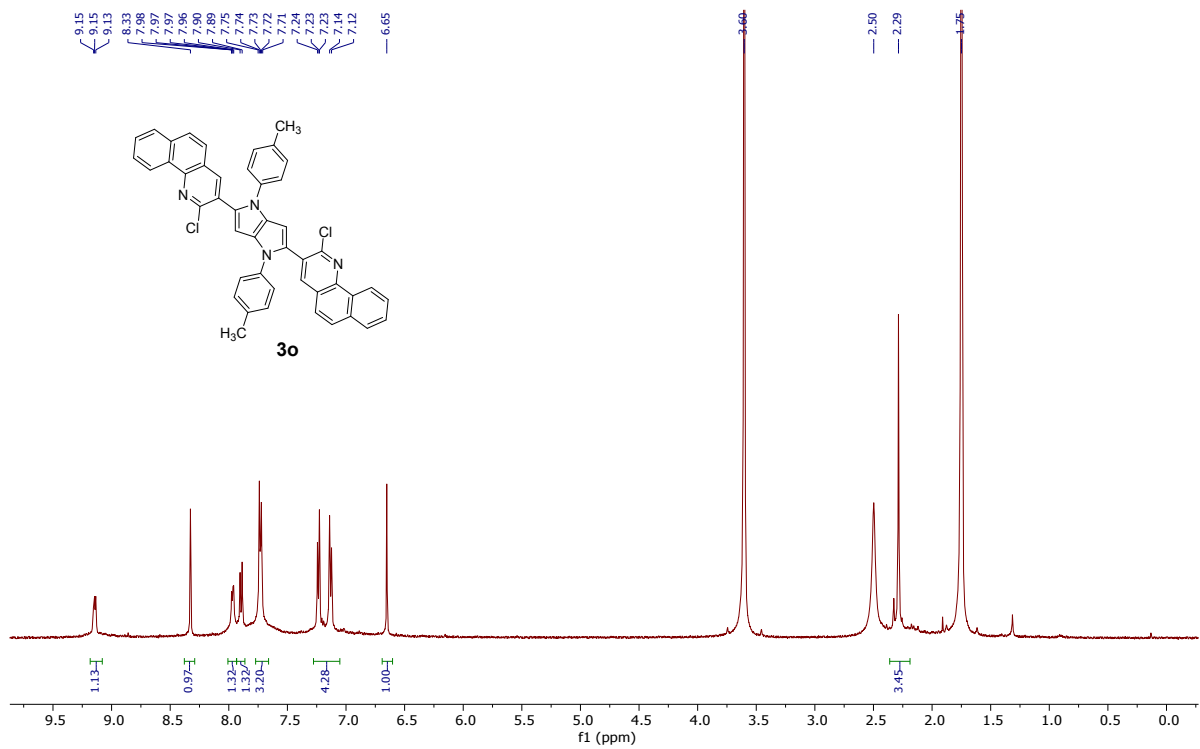
Compound **4aa** (0.8 mmol, 530 mg) was dissolved in toluene (7 mL) and DDQ (1.6 mmol, 363 mg) was added. The resulting mixture was stirred at 80 °C for 16 hours. The mixture was cooled to room temperature, evaporated and suspended in CH₃CN. The precipitate was filtered, washed with AcOEt to give 497 mg (94% yield) of the desired product.

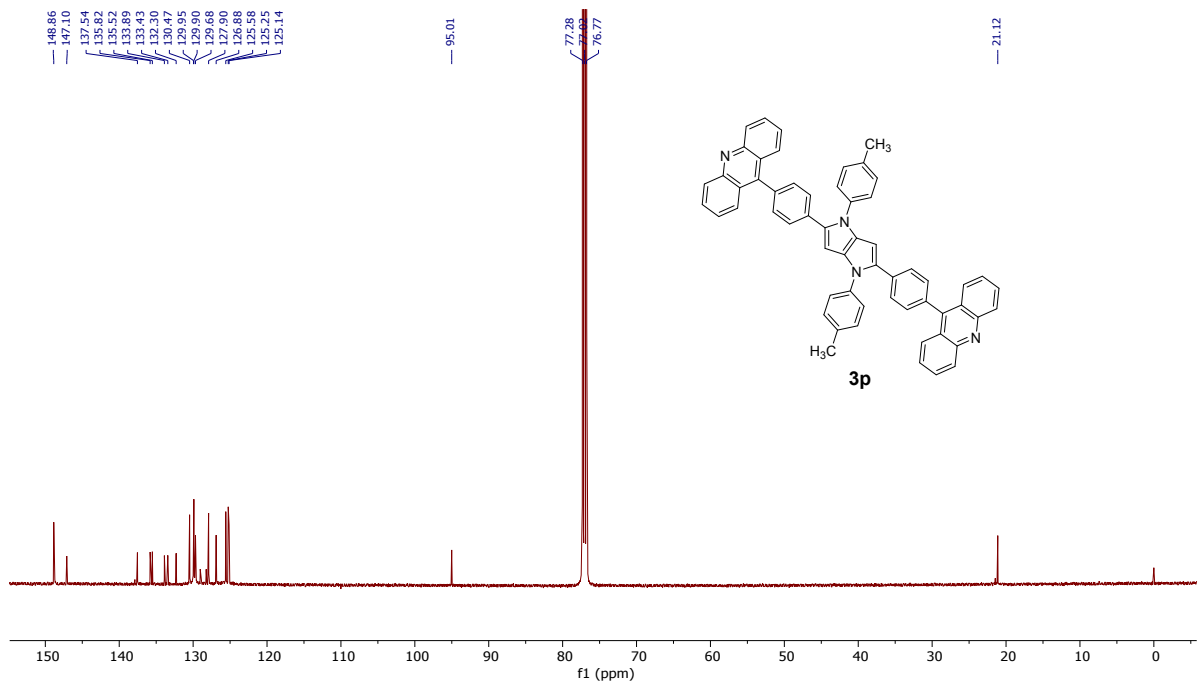
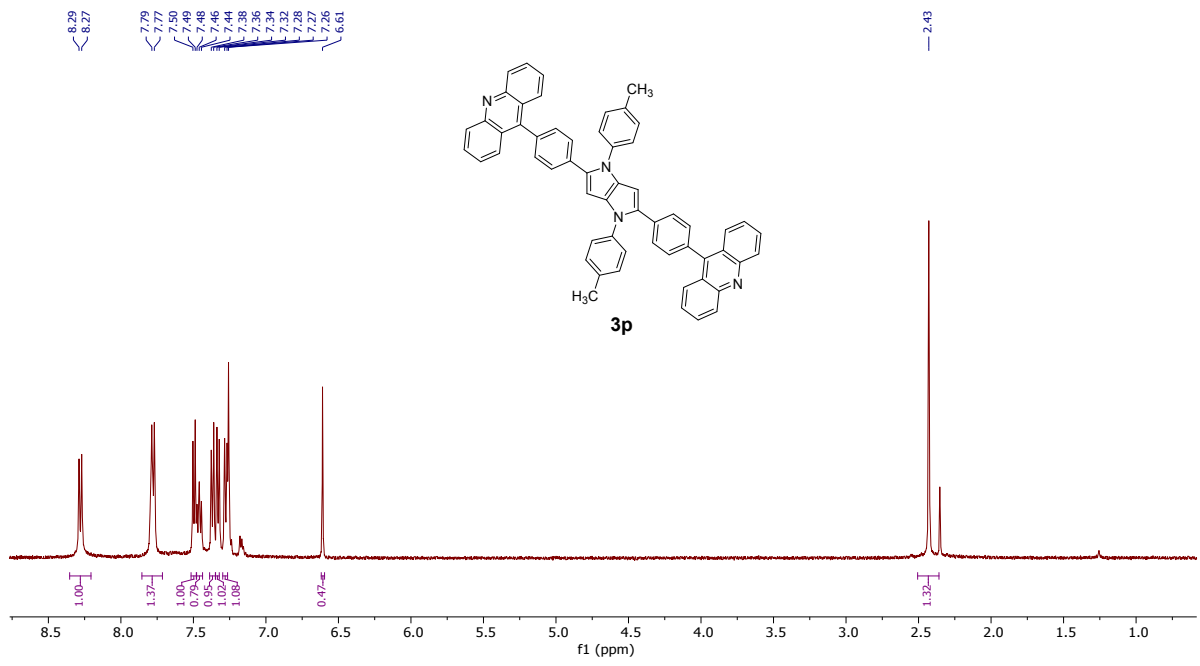


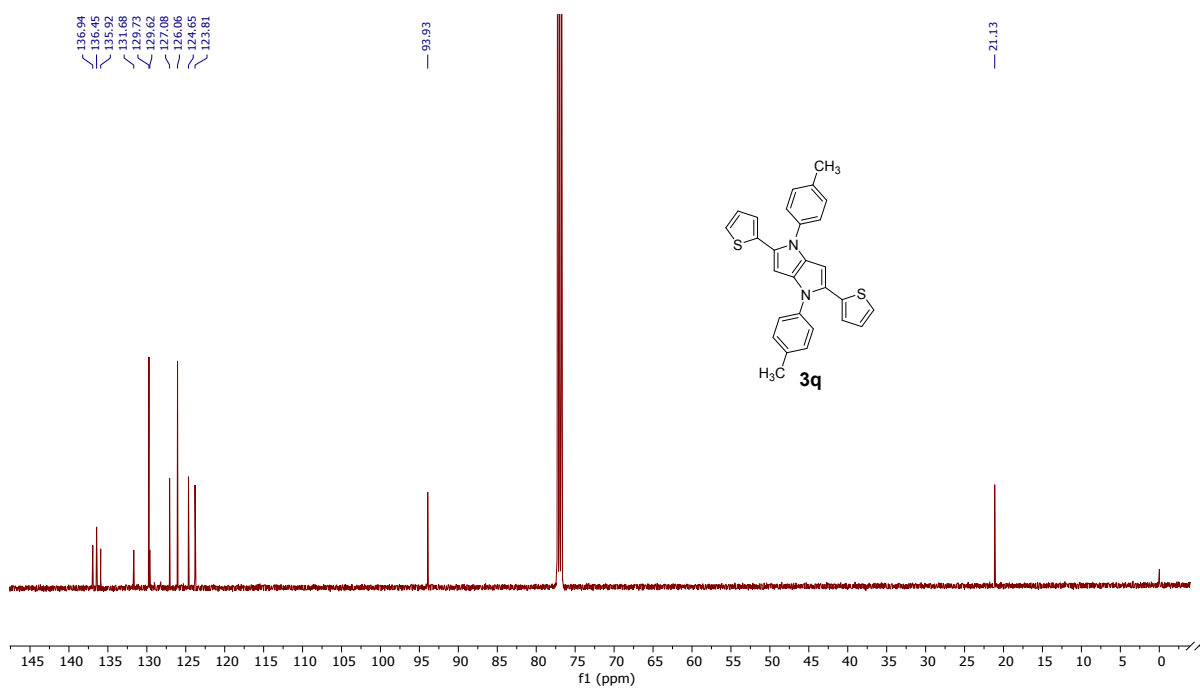
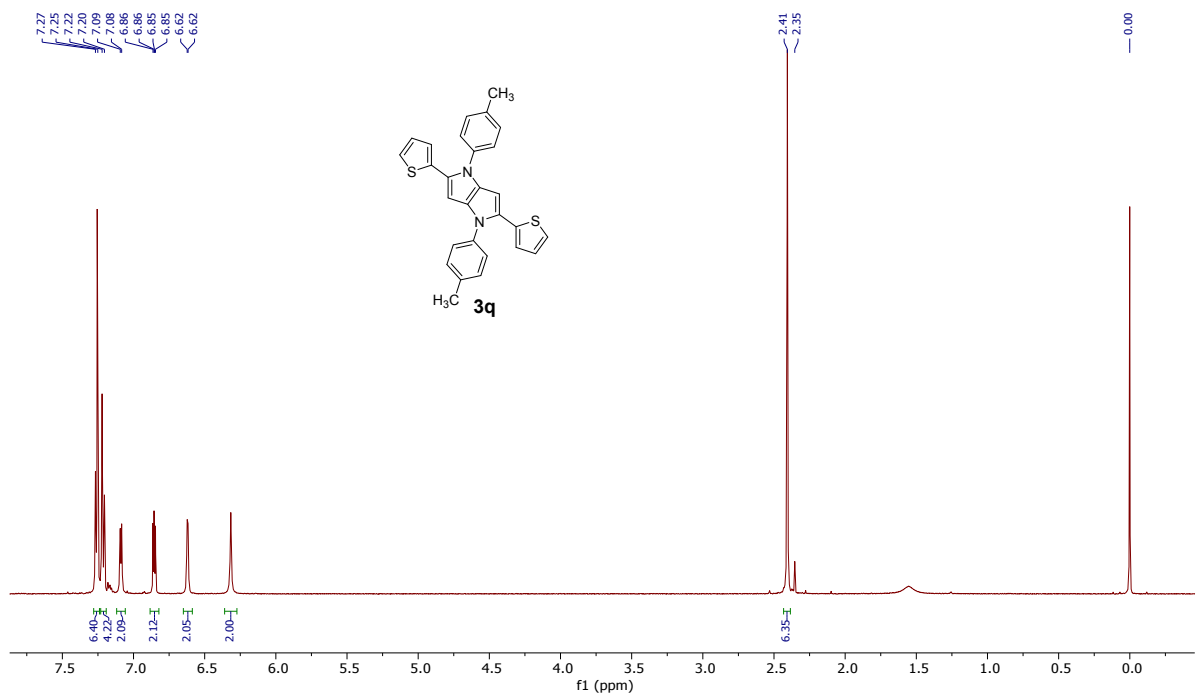


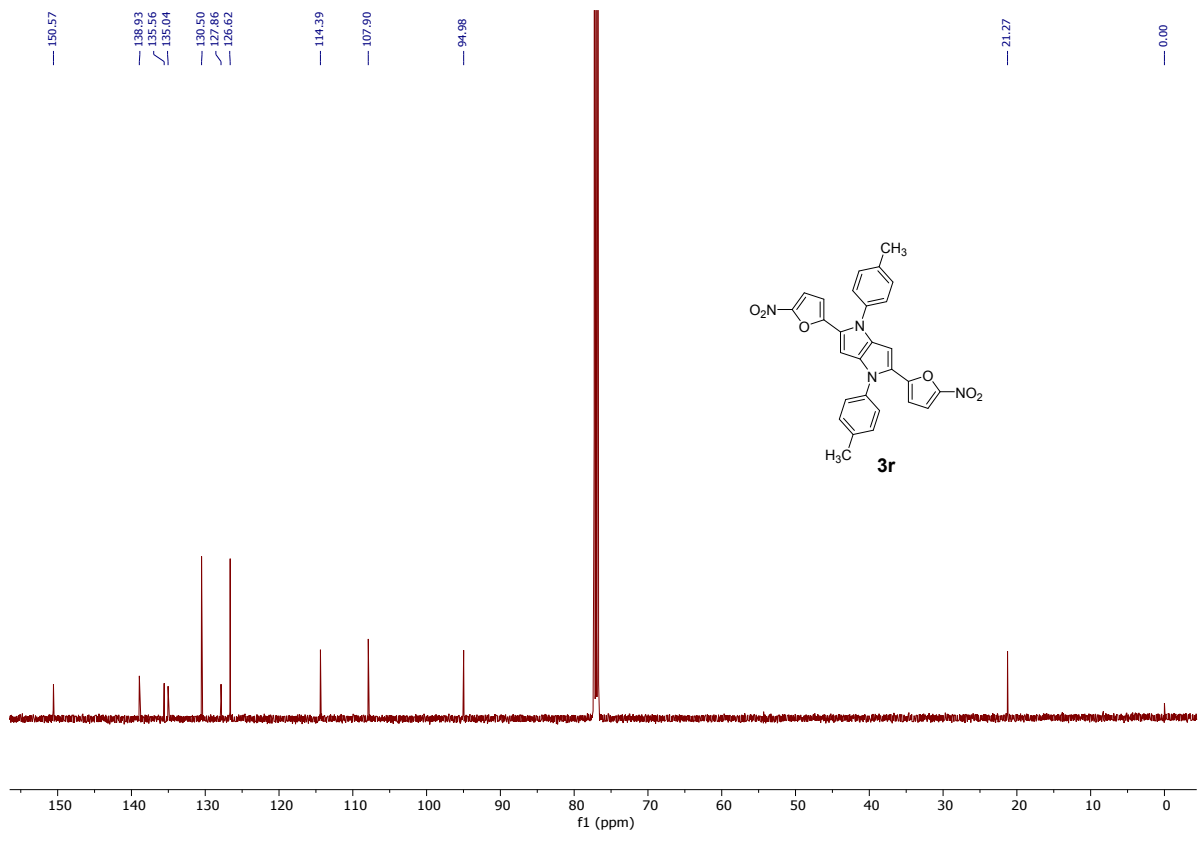
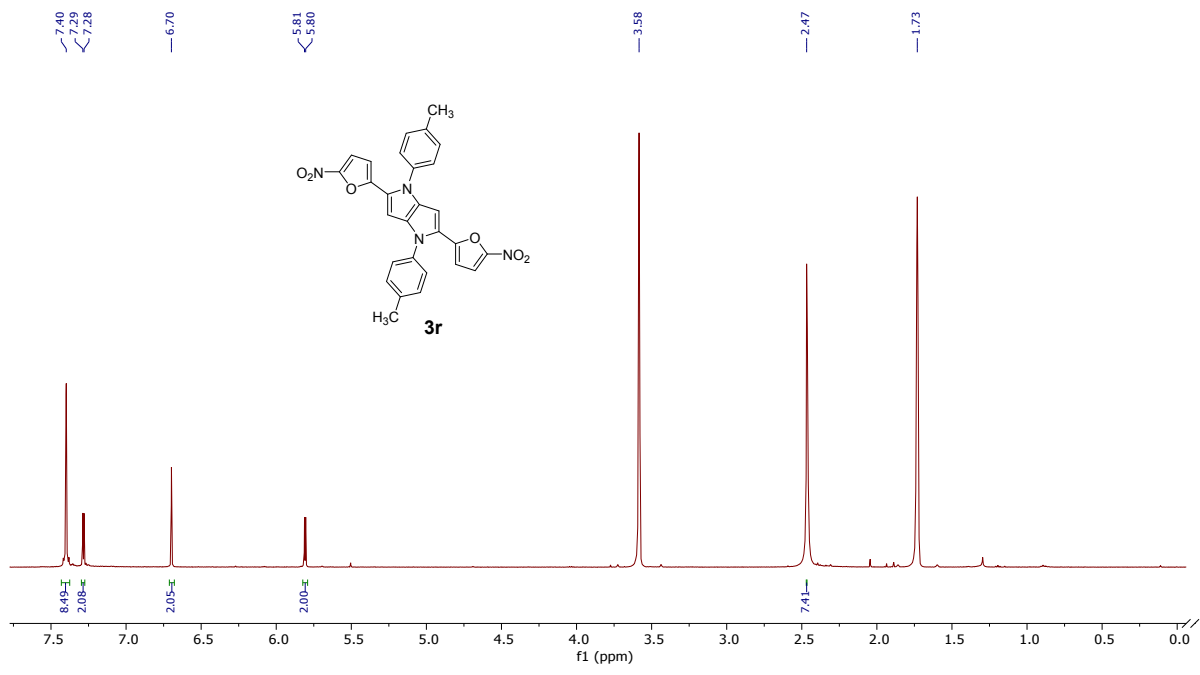


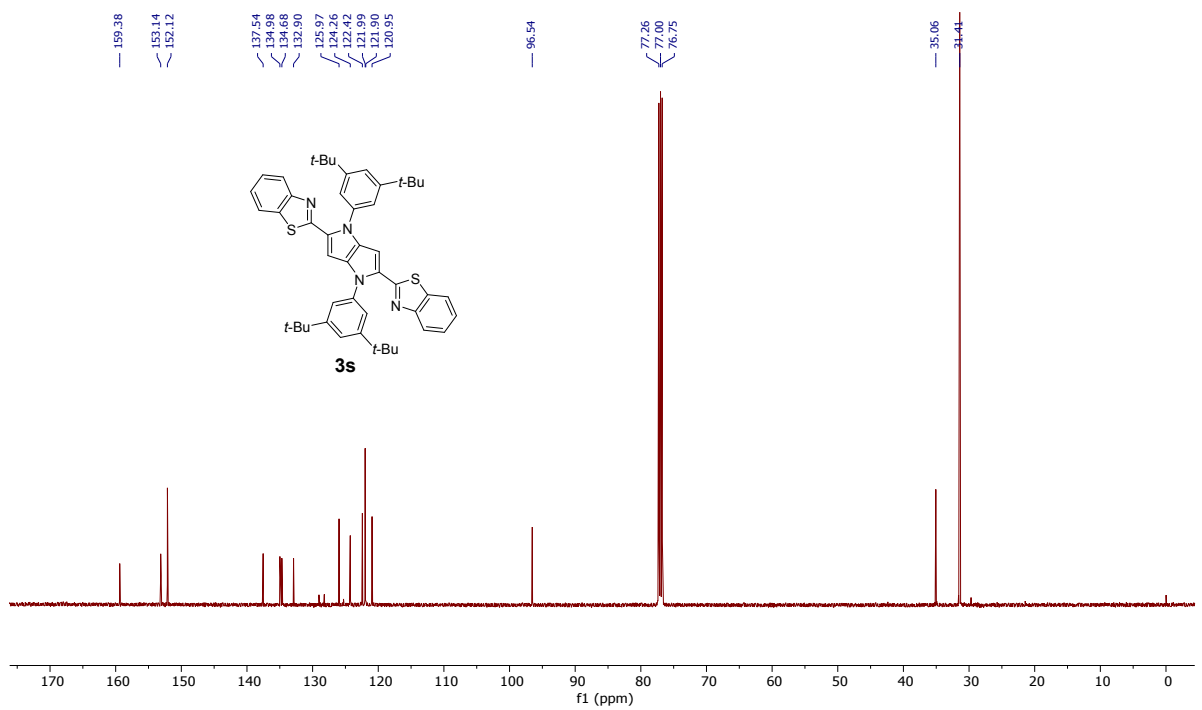
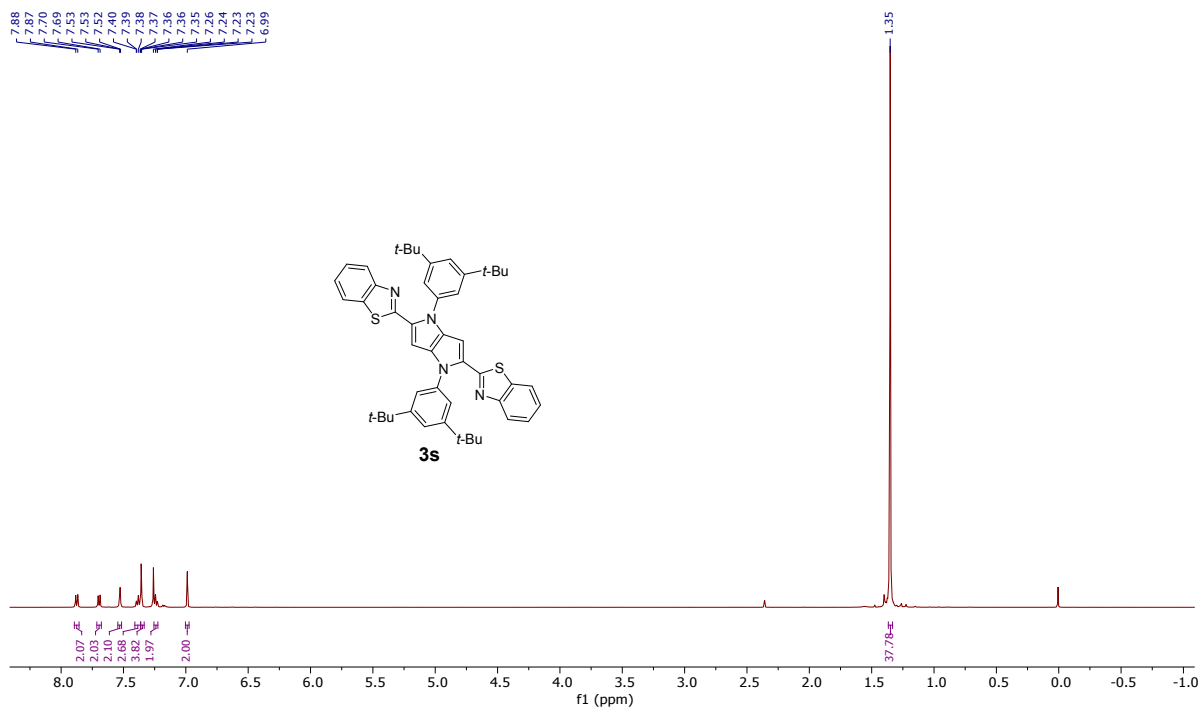


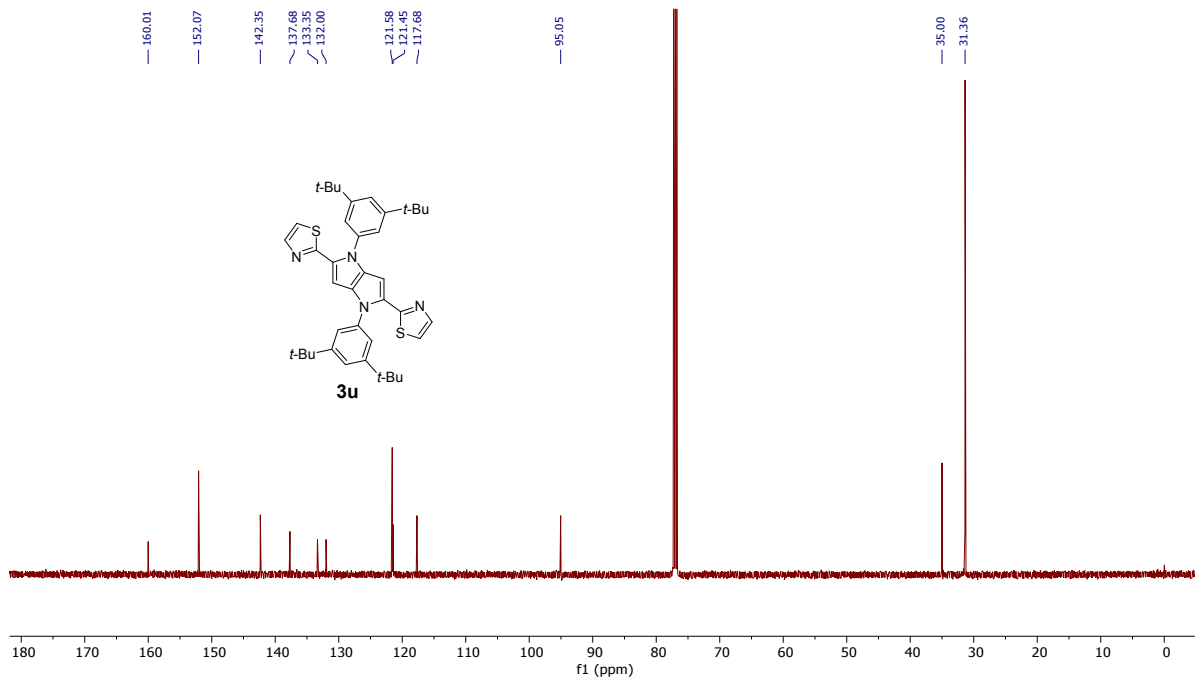
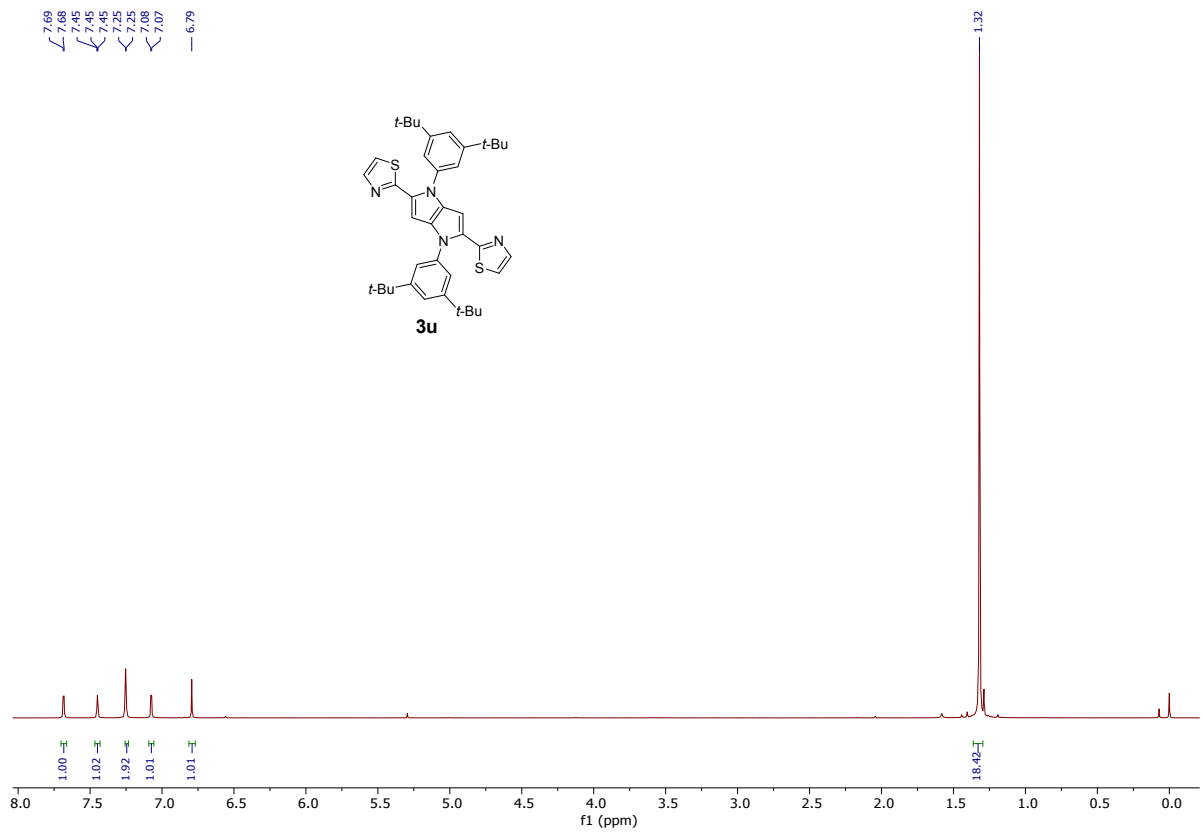


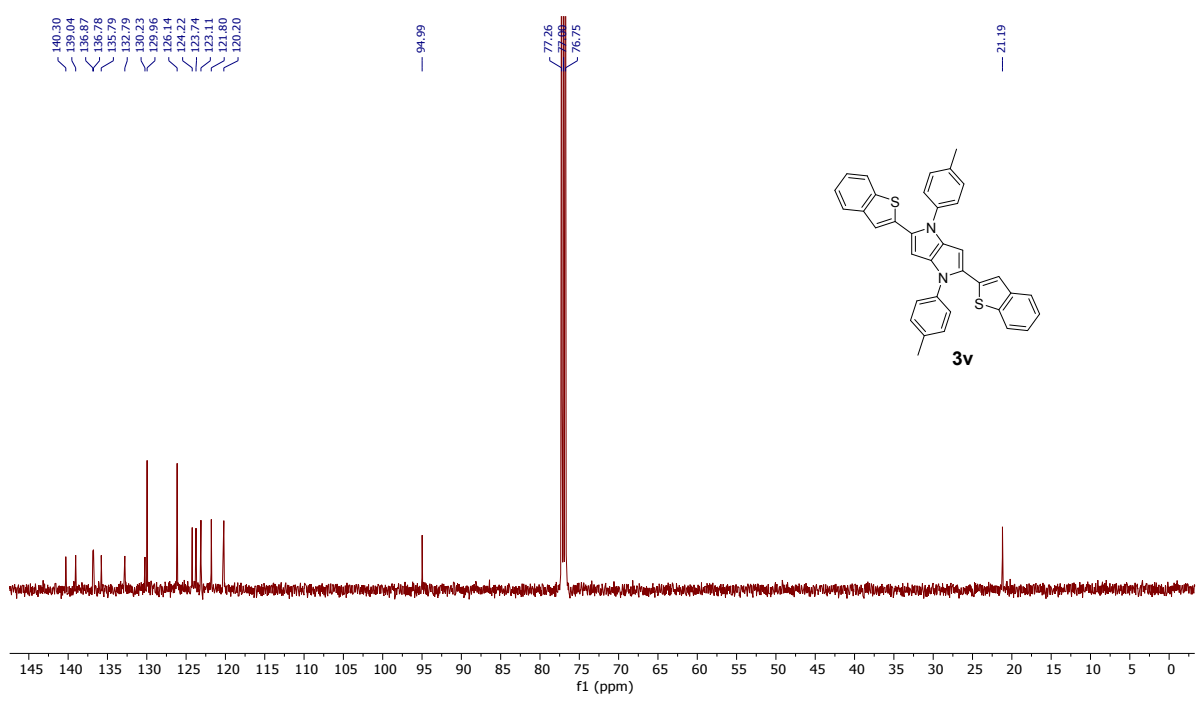
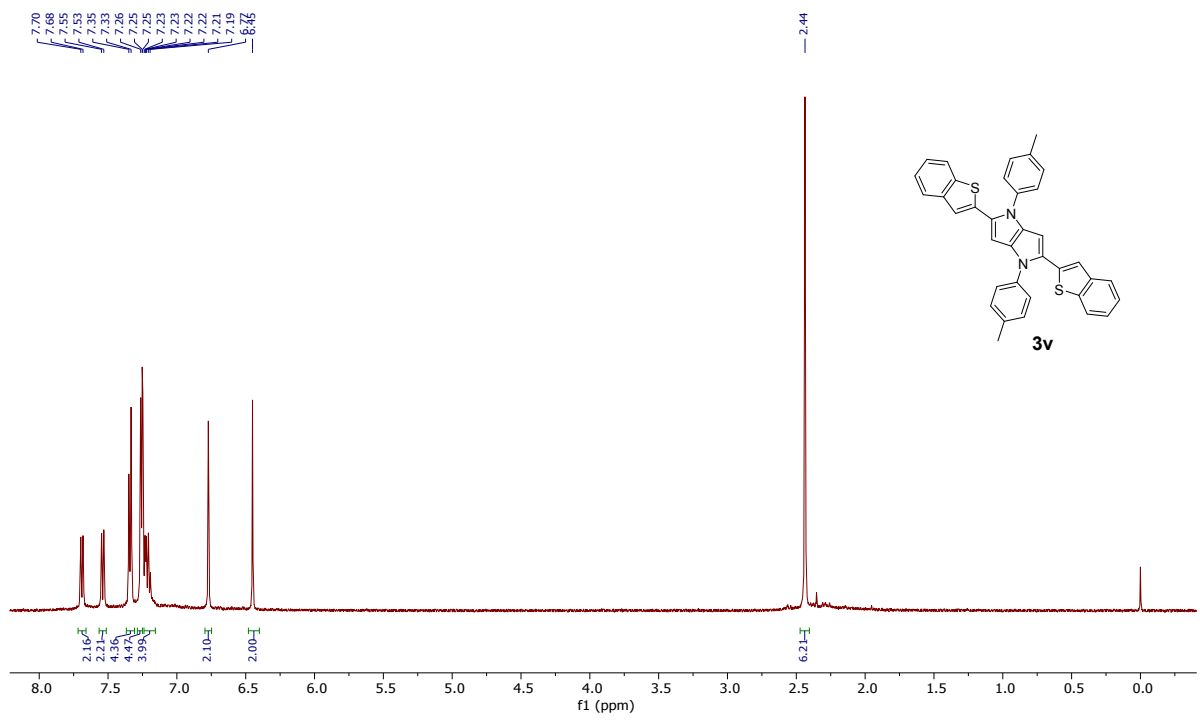


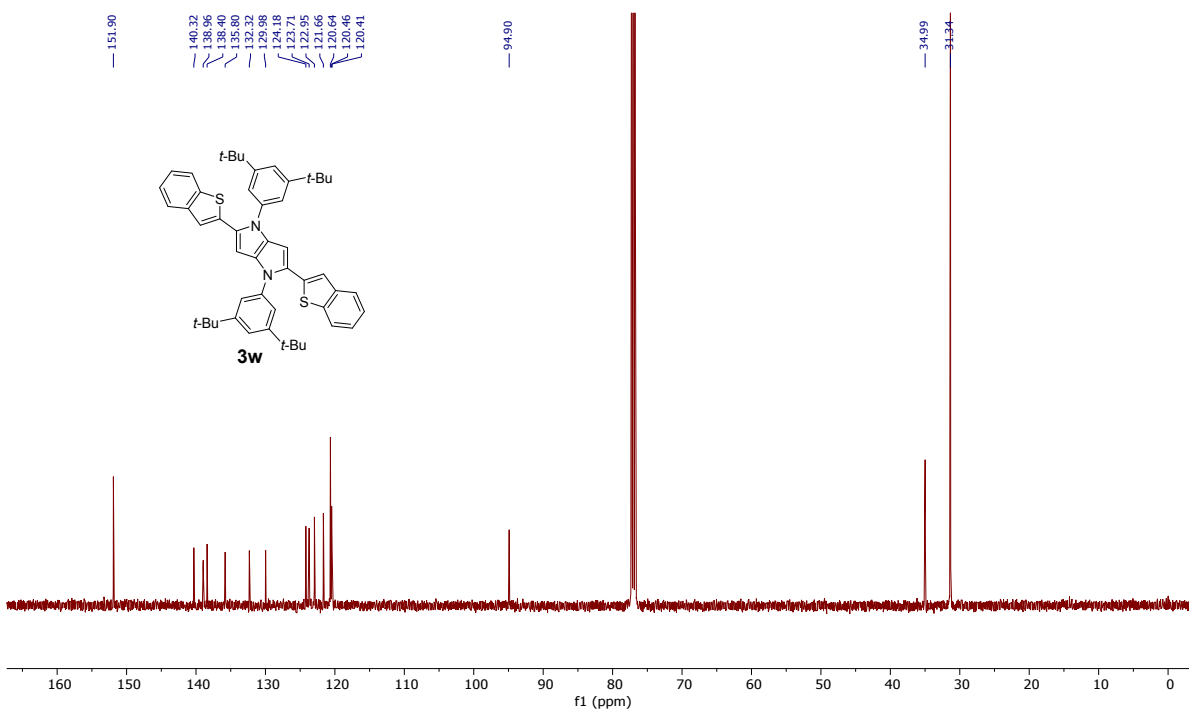
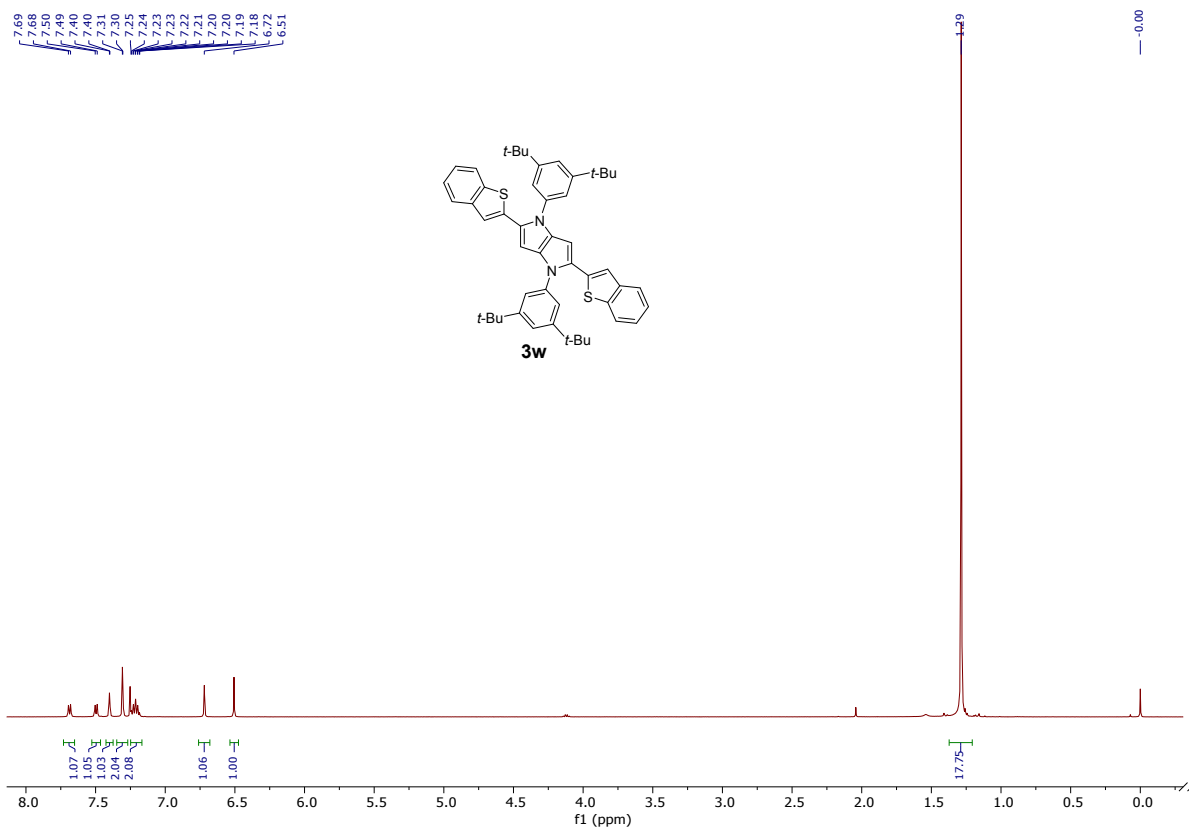


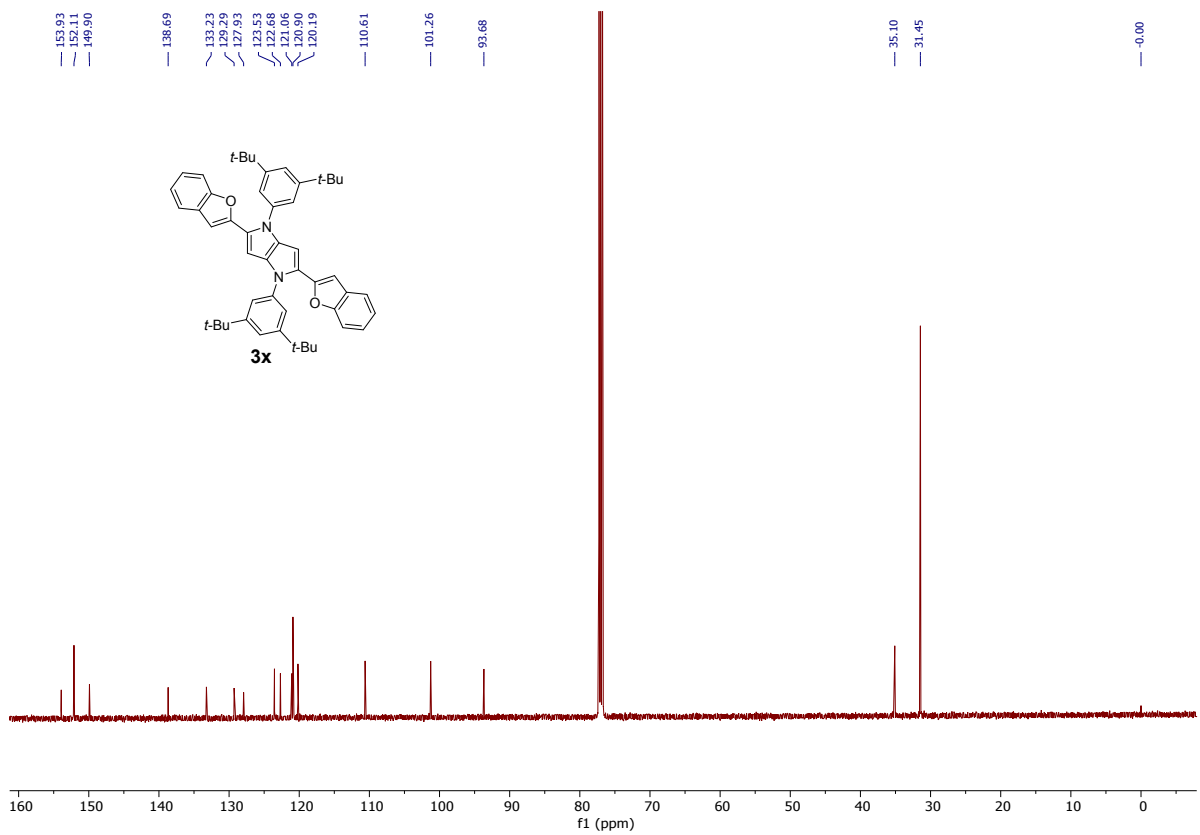
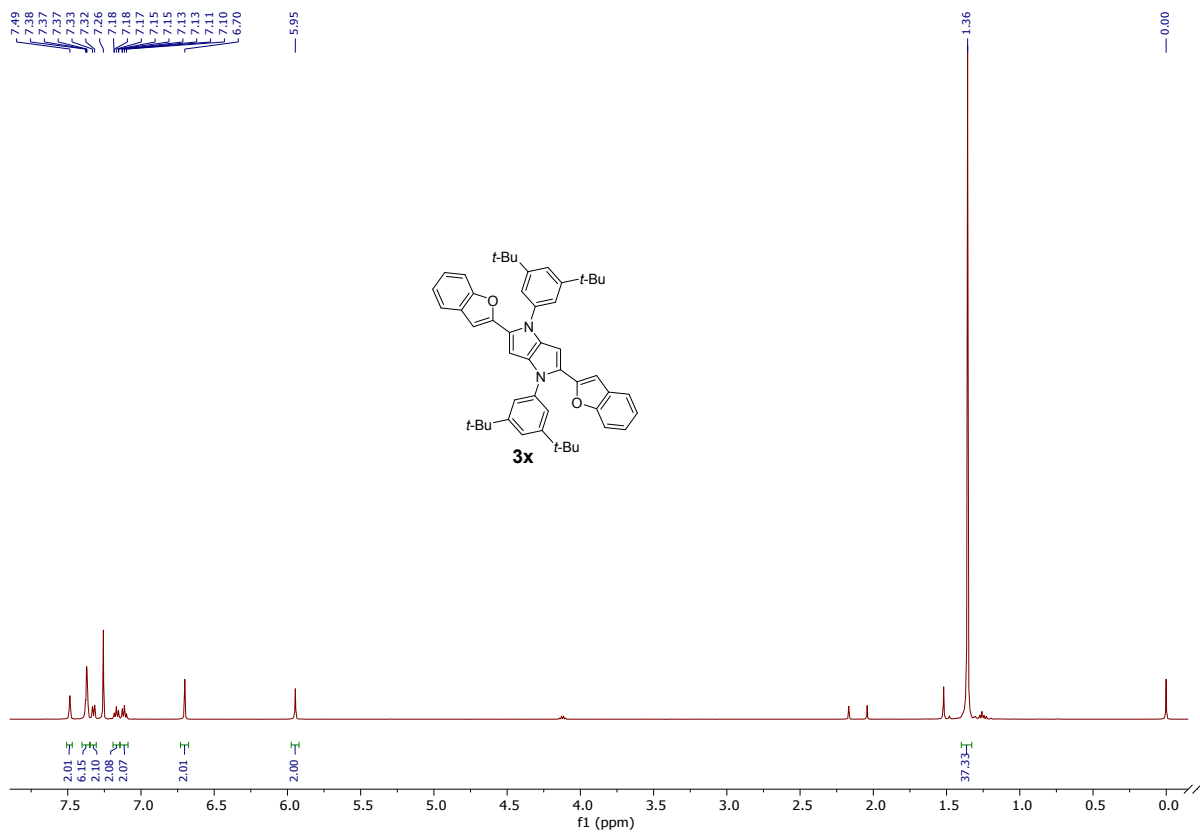


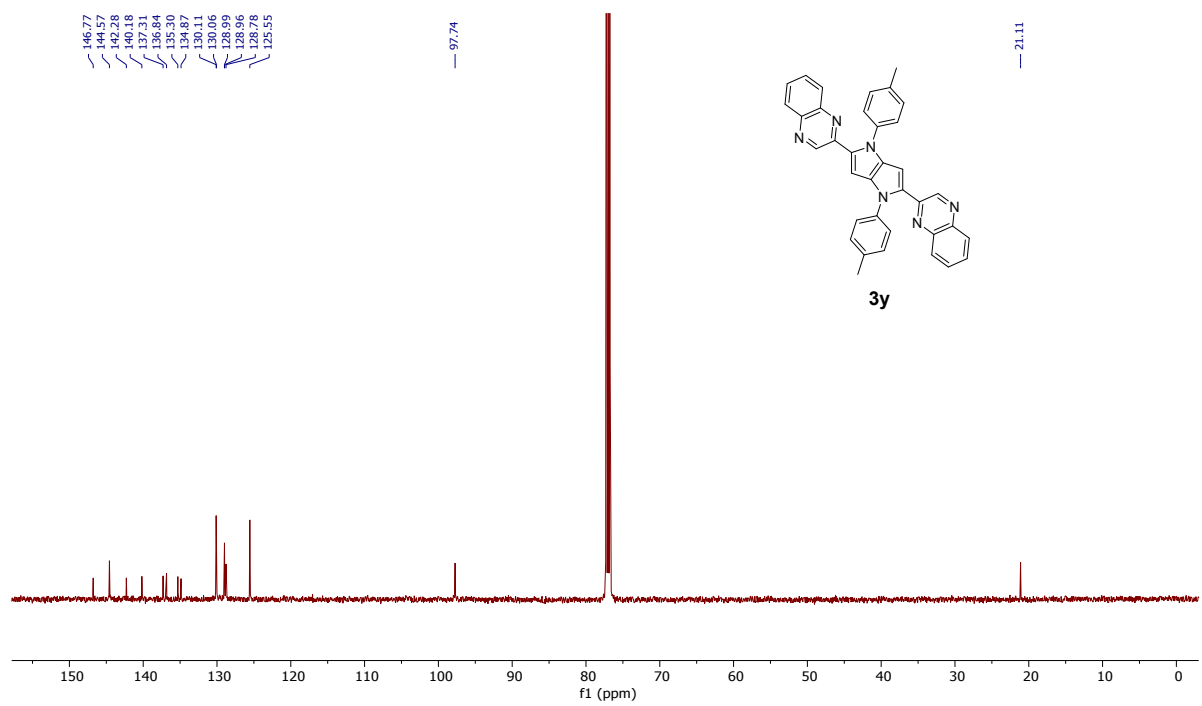
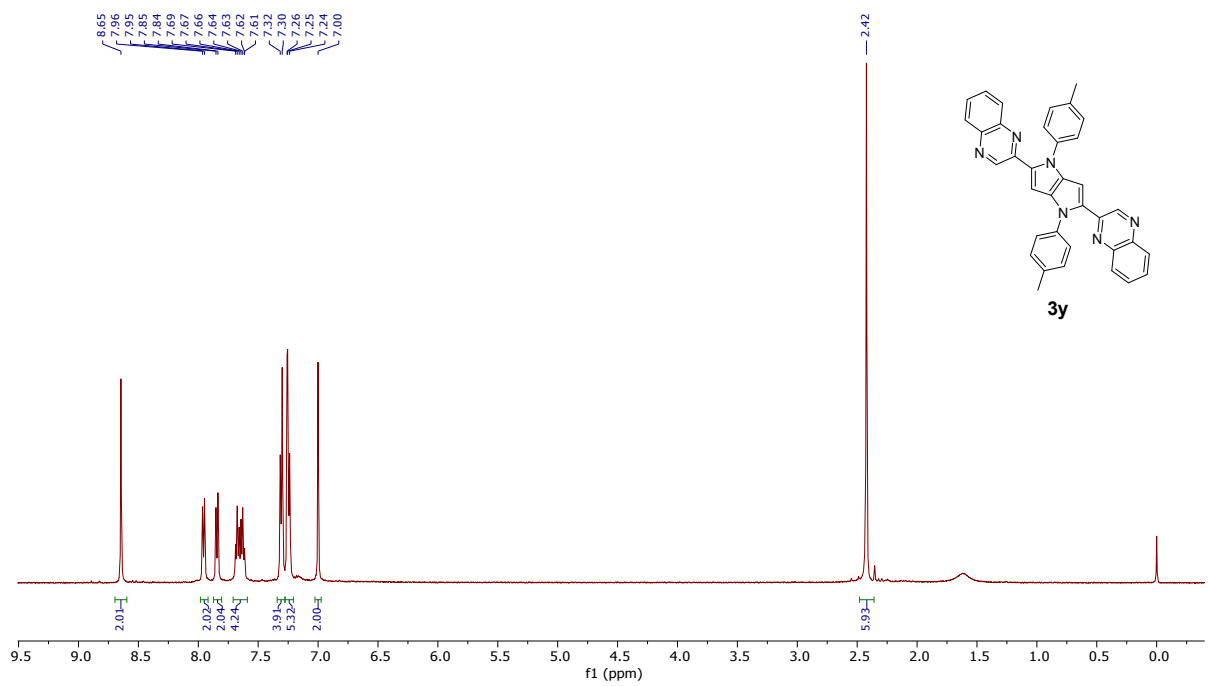


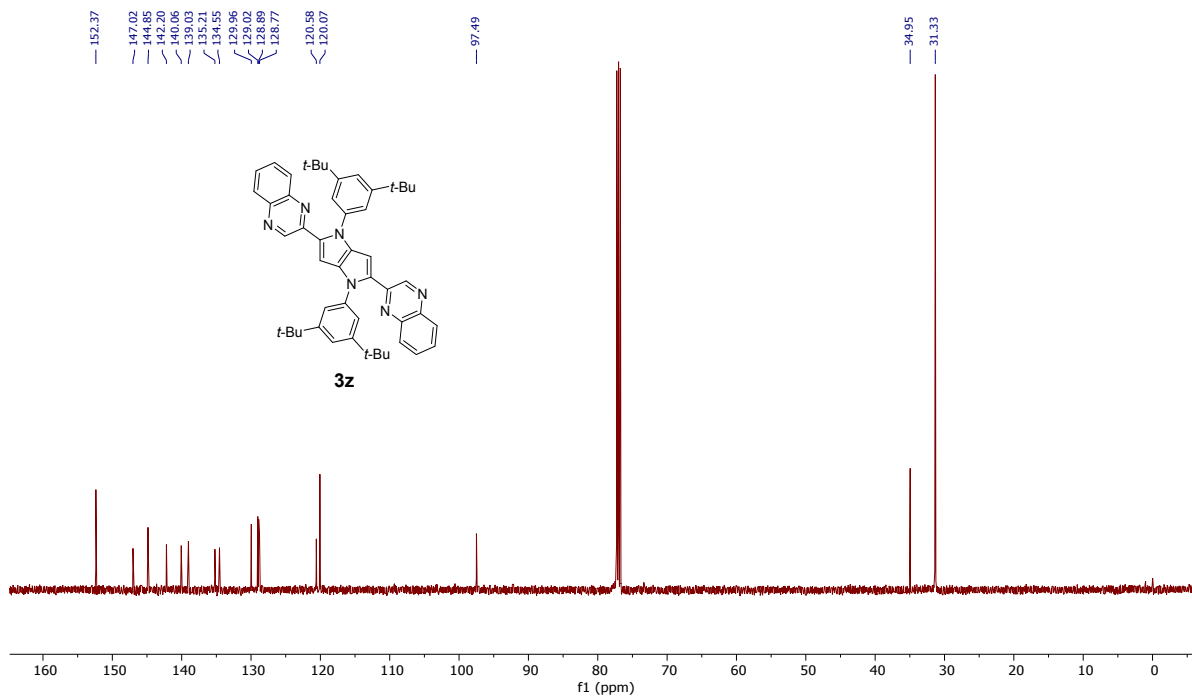
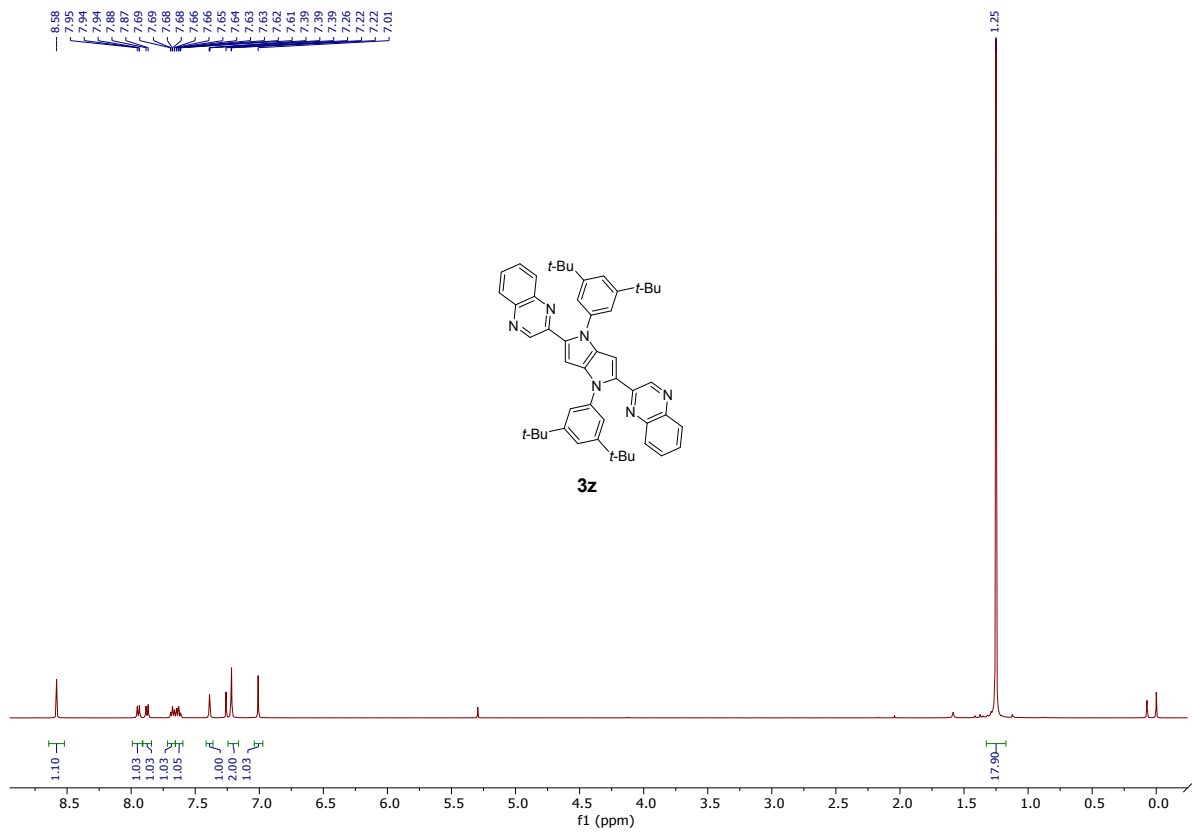


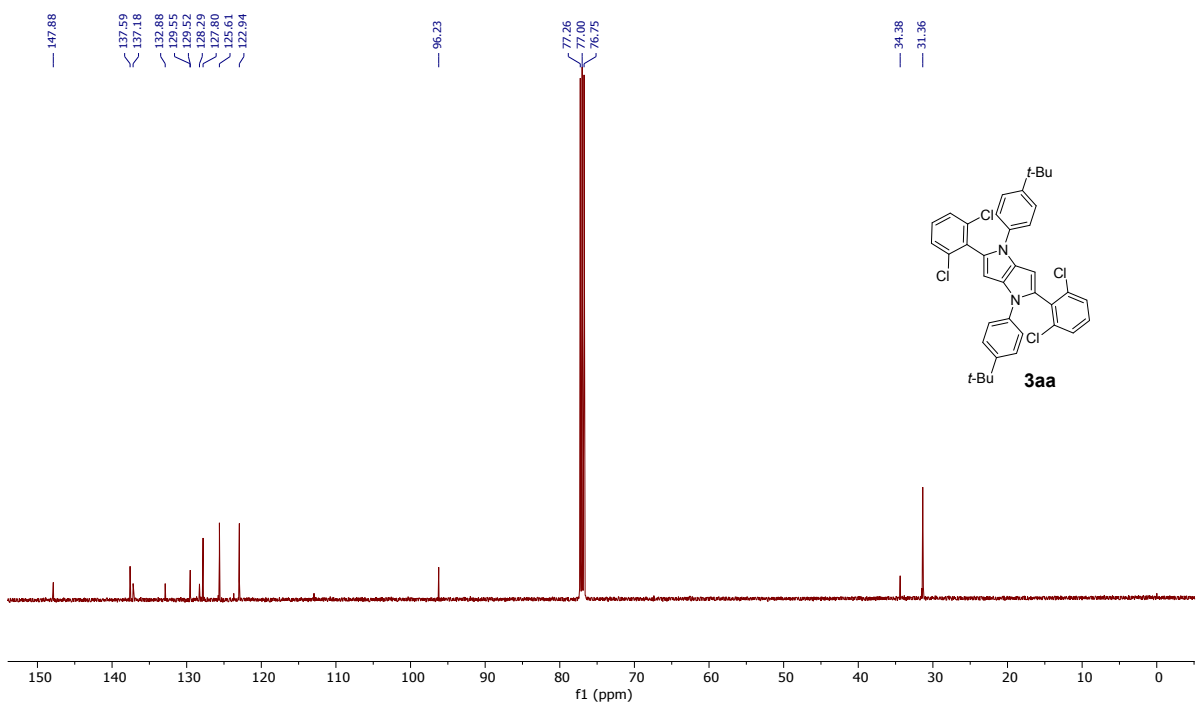
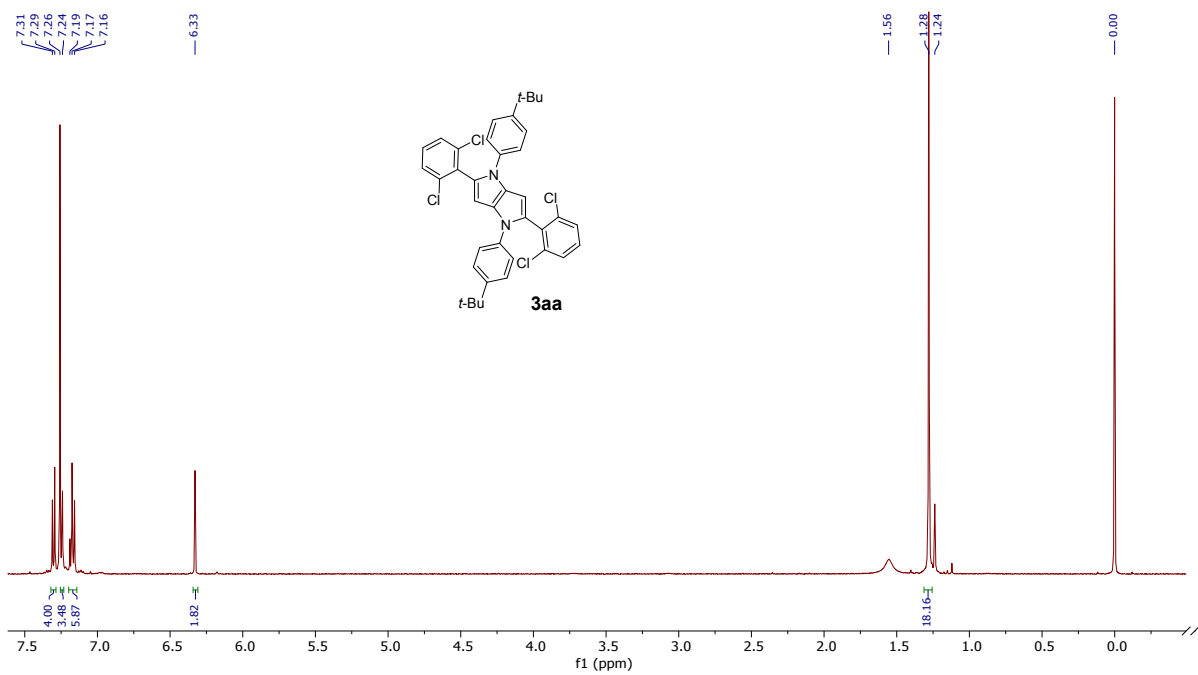


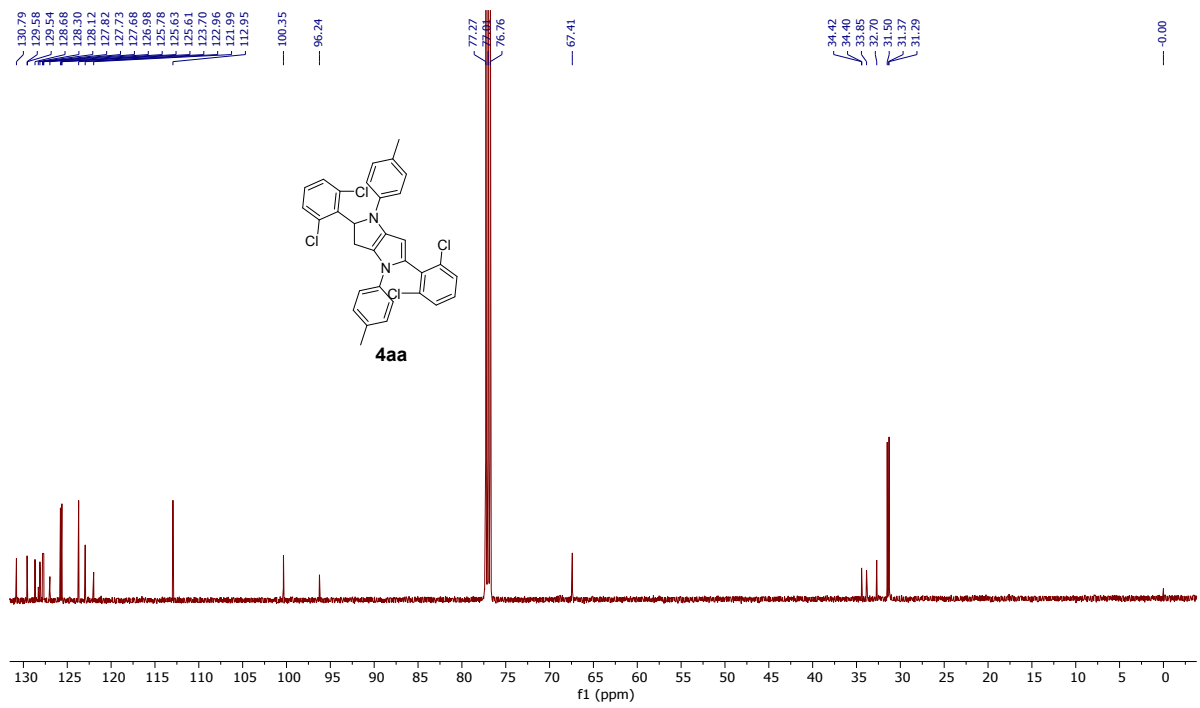
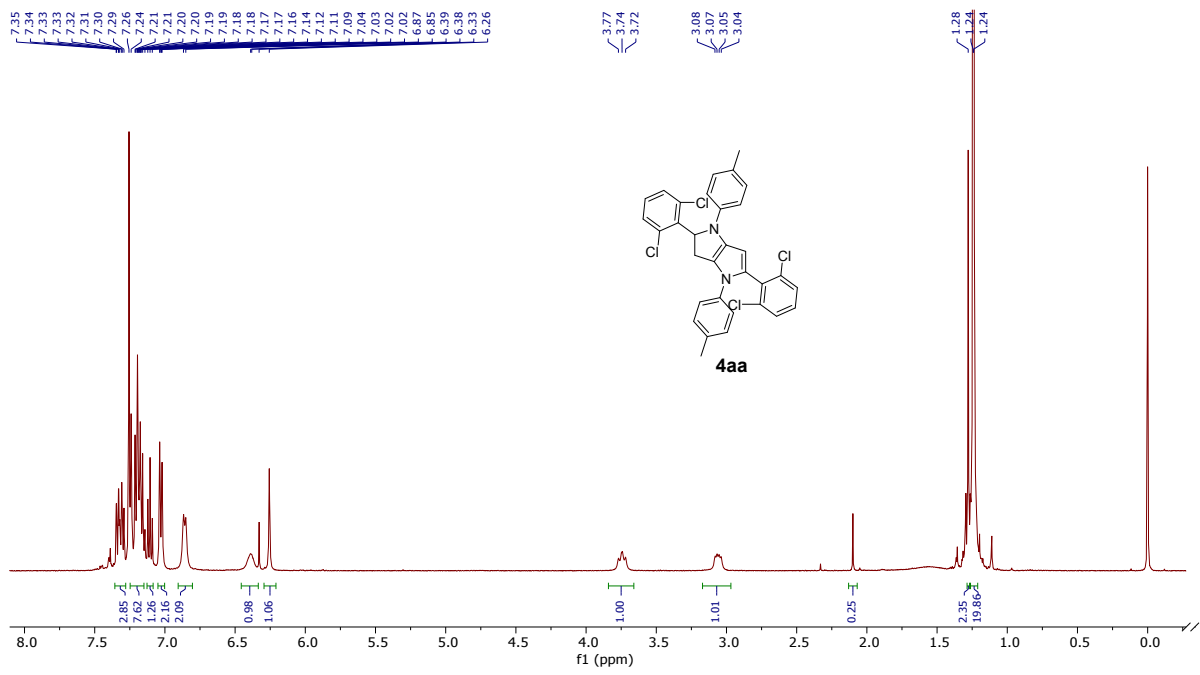


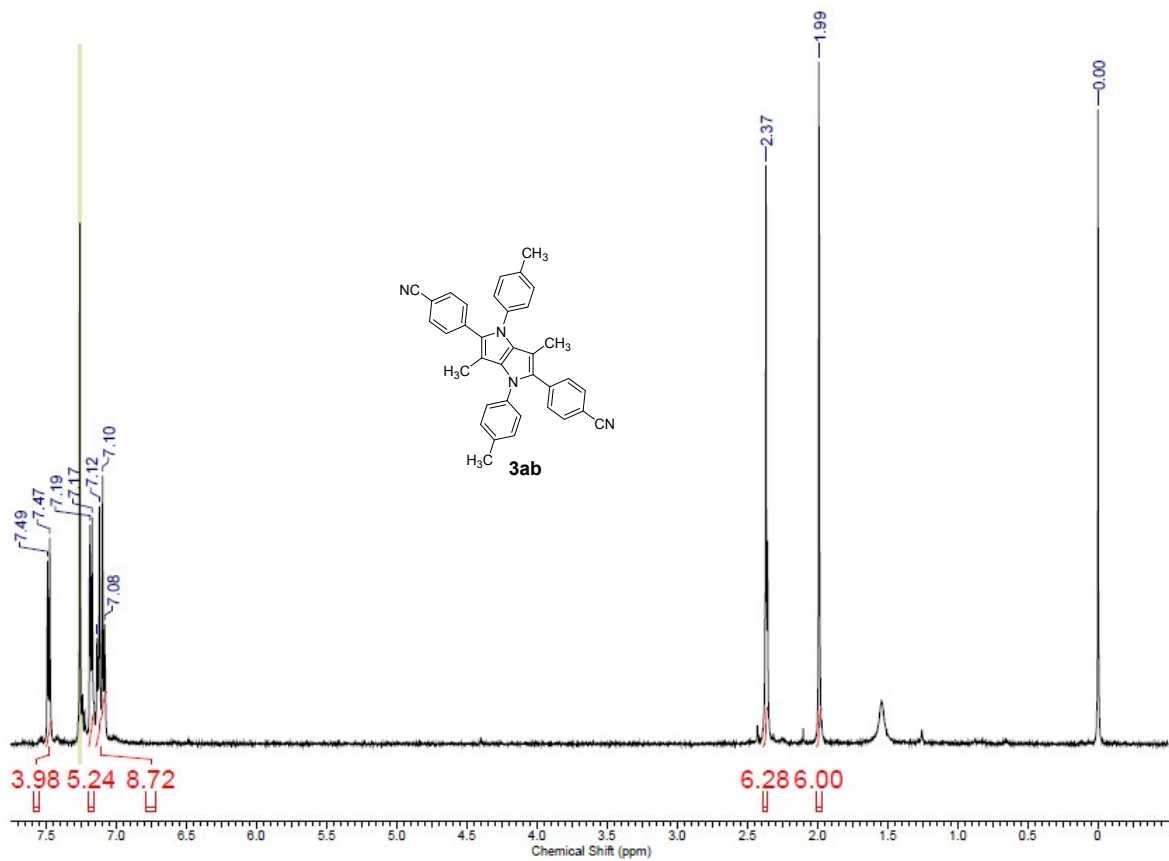




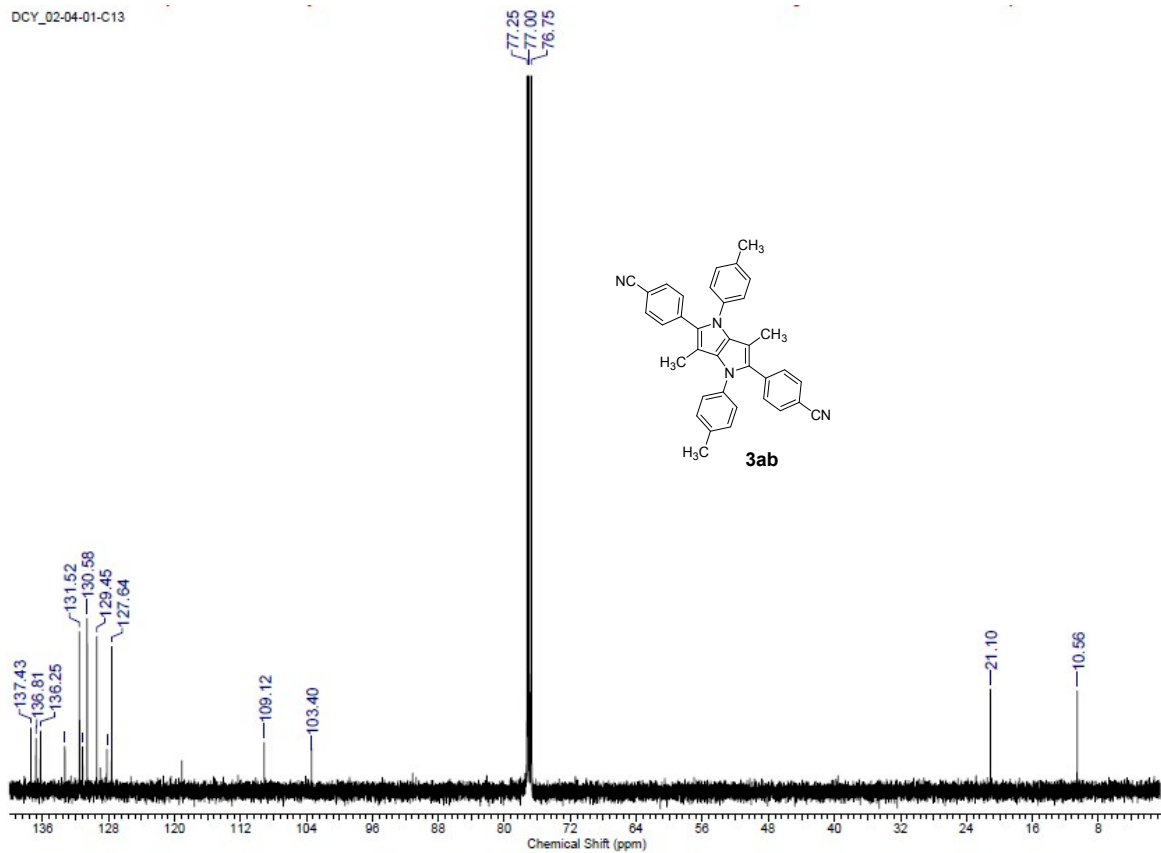






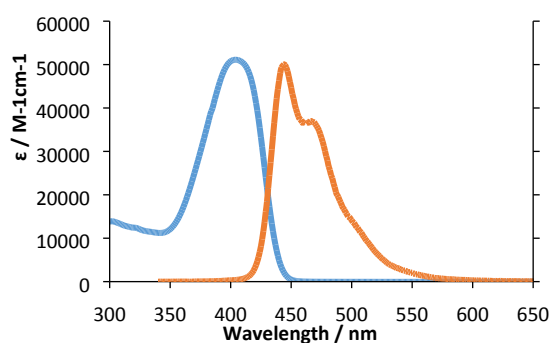


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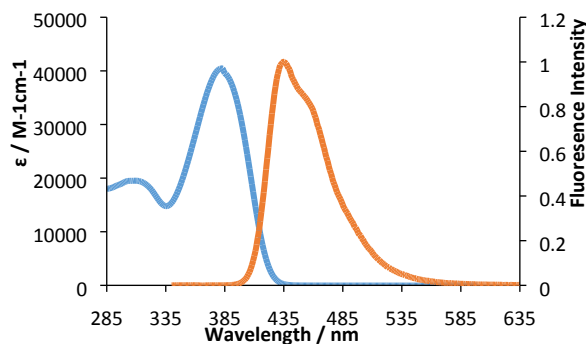


Spectra of compounds **3d**, **3e**, **3f**, **3h**, **3i**, **3k**, **3l**, **3m**, **3o**, **3p**, **3q**, **3r**, **3s**, **3v**, **3y**, **3aa** and **3ab**.

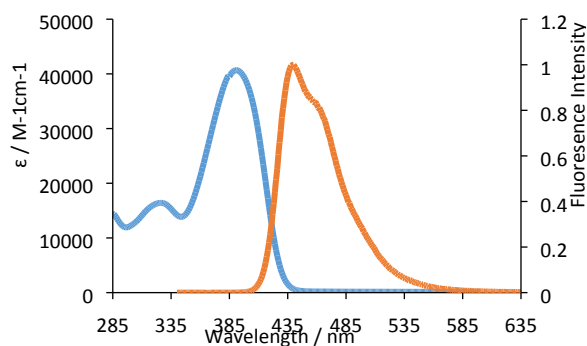
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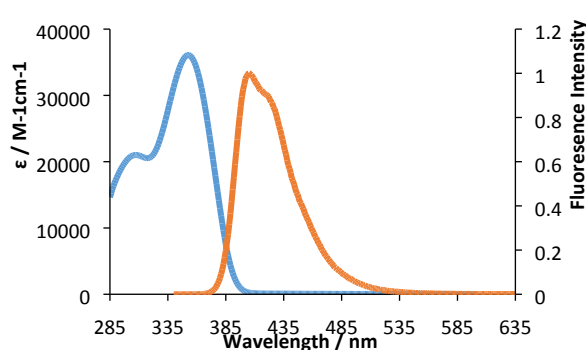
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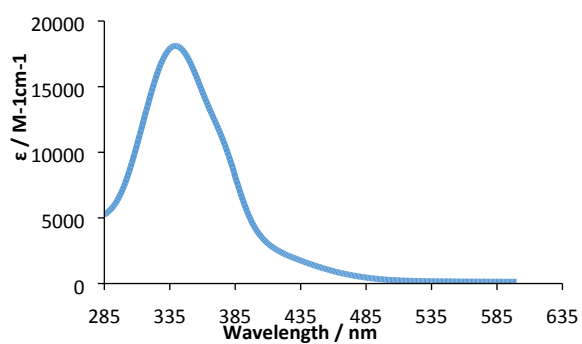
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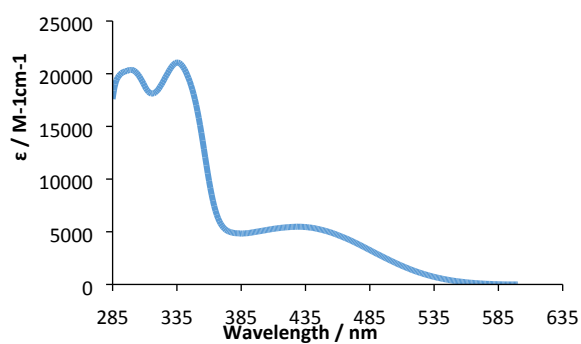
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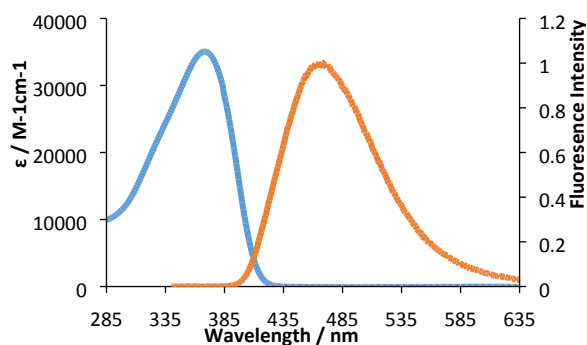
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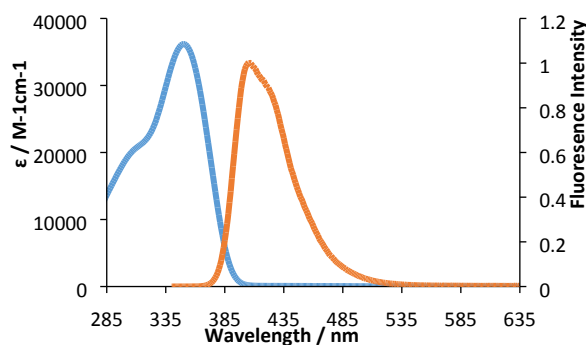
3k

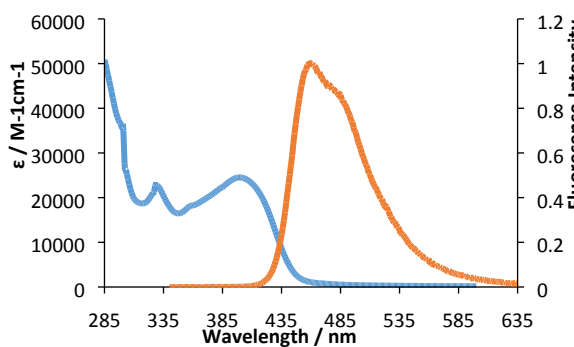
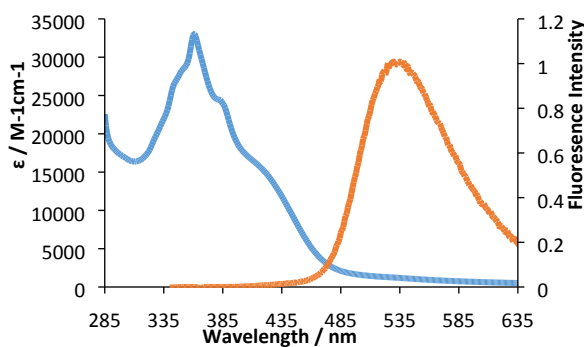
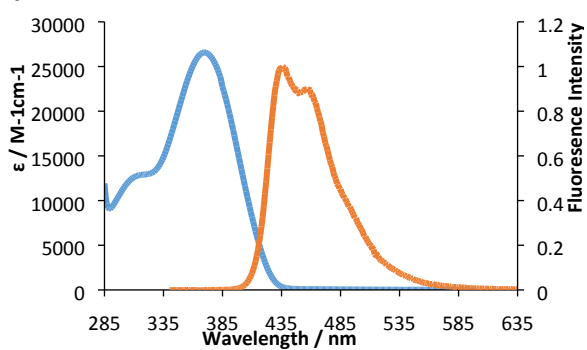
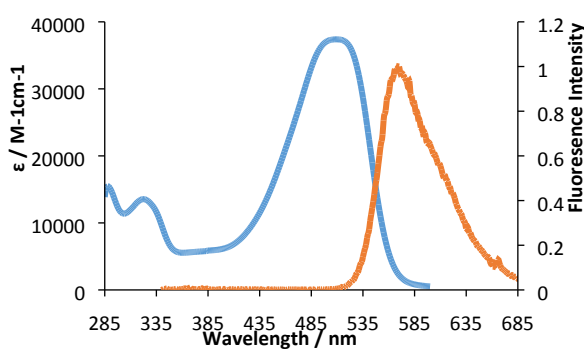
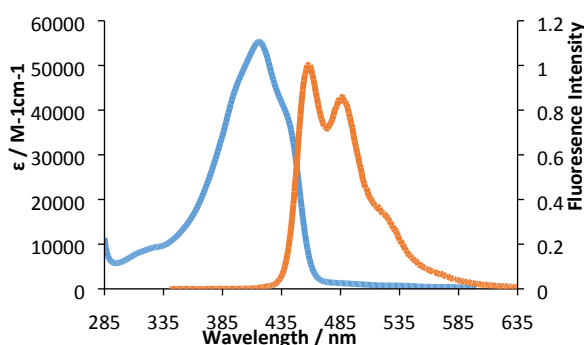
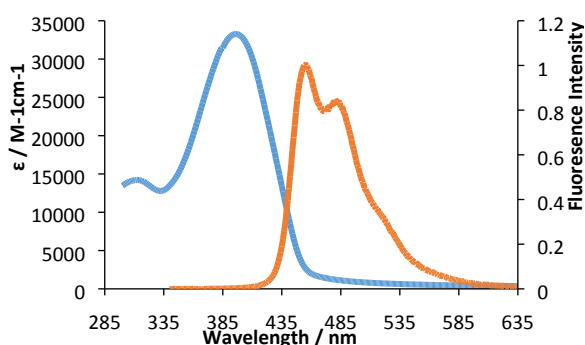
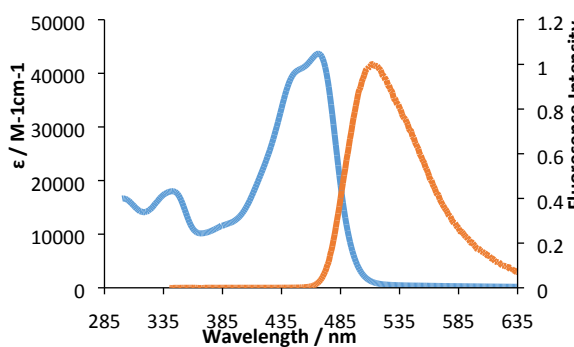
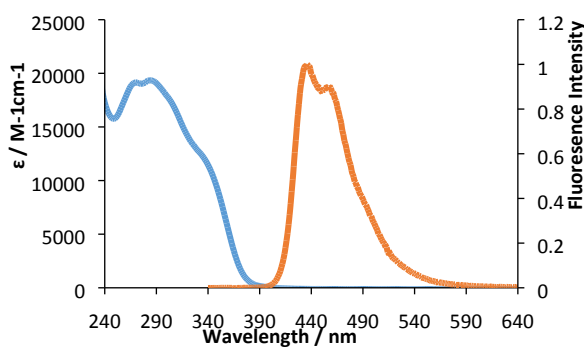


3l



3m



3o**3p****3q****3r****3s****3v****3y****3aa**

3ab

