Supplementary materials

1-Methylimidazole as Organic Catalyst for [3+3]-Cyclodimerization of Acylethynylpyrroles to Bis(acylmethylidene)dipyrrolo[1,2-*a*:1',2'-*d*]pyrazines

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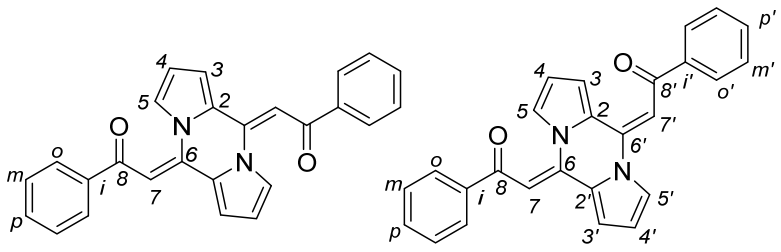
Contents

General Experiment

NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.1 MHz for ^{1}H and 100.6 MHz for ^{13}C) in $CDCl_3$ or CD_3CN (for monitoring). The internal standards were HMDS (for ^{1}H) and the residual solvents signal (for ^{13}C). Coupling constants (*J*) were measured from one-dimensional spectra, and multiplicities were abbreviated as follows: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), m (multiplet). IR spectra were recorded on a two-beam Bruker Vertex 70 spectrometer, in a microlyaer from chloroform. Mass spectra were recorded on an Agilent 6210 HRMS-TOF-ESI Mass spectrometer. Electrostatic sputtering, registration of positive ions. Sample Solvent - MeCN with the addition of 0.1% heptafluorobutanoic acid and with the addition of calibration mixture for mass spectrometer. Melting points (uncorrected) were measured on a Kofler micro hot-stage apparatus. 1-Methylimidazole was a commercial reagent. Acylethynylpyrroles **1a-f** were obtained according to methods [1]. Column and thin-layer chromatography for isolation and purification of compounds **2** were carried out on silica gel (0.06-0.2 mm) with chloroform/ethanol (20 : 1) mixture as eluent.

Experimental Procedures, Spectral and Analytical data

*2,2'-(5H,10H-dipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-diylidene)bis(1-phenylethan-1-one) (**2a**).*



A mixture of benzoylethynylpyrrole (**1a**) (90 mg, 0.5 mmol) and 1-methylimidazole (41 mg, 0.5 mmol) was stirred at 40-45 ºC for 24 h. After cooling reaction mixture to room temperature it

was passed through chromatography column affording to dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine **2a** (99 mg, 51%), as an orange gum.

IR (microlayer): 1568 (C=C), 1647 (C=O) cm^{-1}.

E,*E*:*E*,*Z*-isomer ratio = 70:30 (^{1}H NMR). *E*,*E*-isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.18 (m, 2H, 2 H-3), 7.96 (m, 4H, 2 H_o from 2 Ph), 7.53 (m, 2H, 2 H_p from 2 Ph), 7.45 (m, 6H, 2 H-5, 2 H_m from 2 Ph), 6.92 (s, 2H, 2 H-7), 6.46 (m, 2H, 2 H-4) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 188.5 (2 C-8), 139.9 (2 C_i from 2 Ph), 136.3 (2 C-2), 132.6 (2 C_p from 2 Ph), 128.7 (4 C_o from 2 Ph), 128.3 (4 C_m from 2 Ph), 123.6 (2 C-6), 120.9 (2 C-5), 120.5 (2 C-3), 113.7 (2 C-4), 105.4 (2 C-7) ppm.

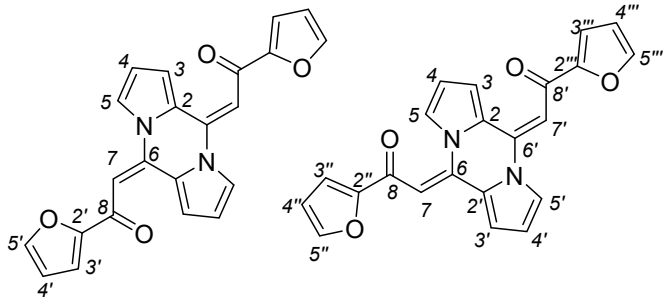
E,*Z*-isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.15 (m, 1H, H-3), 7.96 (m, 4H, $H_{o,o'}$ from 2 Ph), 7.53 (m, 2H, $H_{p,p'}$ from 2 Ph), 7.45 (m, 6H, H-5, H-5', $H_{m,m'}$ from 2 Ph), 6.94 (m, 1H, H-3'), 6.88 (s, 1H, H-7), 6.85 (s, 1H, H-7'), 6.46 (m, 1H, H-4), 6.34 (m, 1H, H-4') ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 188.8 (C-8'), 188.7 (C-8), 139.9 (C_i from Ph), 139.7 ($C_{i'}$ from Ph), 135.8 (C-2), 135.0 (C-2'), 132.8 ($C_{p'}$ from Ph), 132.6 (C_p from Ph), 128.7 ($C_{o,o'}$ from 2 Ph), 128.3 ($C_{m,m'}$ from 2 Ph), 123.6 (C-6), 123.0 (C-6'), 121.1 (C-5'), 120.9 (C-5), 119.7 (C-3), 114.0 (C-3'), 112.4 (C-4), 111.6 (C-4'), 104.3 (C-7), 101.8 (C-7') ppm.

HRMS (ESI-TOF) calcd for $[C_{26}H_{18}N_2O_2+H]^+$ 391.14465; found 391.1446.

Elemental analysis for $C_{26}H_{18}N_2O_2$ (390.44): calcd. C, 79.98; H, 4.65; N, 7.17; found: C, 79.67; H, 4.64; N, 7.10.

*2,2'-(5H,10H-dipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-diylidene)bis(1-(furan-2-yl)ethan-1-one) (**2b**)*.



Analogously from (furoyl-2)-ethynylpyrrole (**1b**) (93 mg, 0.5 mmol) and 1-methylimidazole (41 mg, 0.5 mmol), (40-45 ºC, 6 h) dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine **2b** was obtained (48 mg, 26%) as a red powder, mp 193-195 °C (MeCN).

IR (microlayer): 1575 (C=C), 1641 (C=O) cm^{-1}.

E,*E*:*E*,*Z*-isomer ratio = 75:25 (^{1}H NMR).

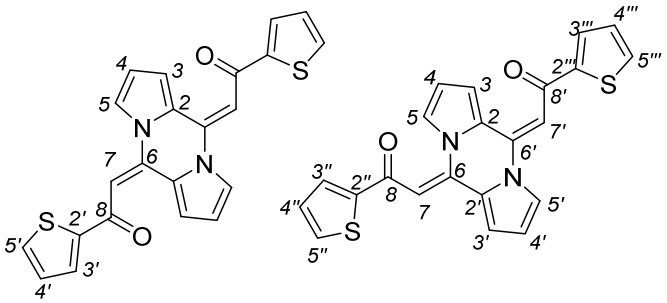
E,*E*-isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.51 (m, 2H, 2 H-3), 7.58 (m, 4H, 2 H-5, 2 H-5'), 7.23 (m, 2H, 2 H-3'), 7.01 (s, 2H, 2 H-7), 6.55 (m, 2H, 2 H-4'), 6.49 (m, 2H, 2 H-4) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 175.7 (2 C-8), 155.1 (2 C-2'), 146.7 (2 C-5'), 137.0 (2 C-2), 123.7 (2 C-6), 122.1 (2 C-5), 121.6 (2 C-3), 116.1 (2 C-3'), 113.9 (2 C-4), 112.8 (2 C-4'), 105.4 (2 C-7) ppm.

E,*Z*-isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.85 (m, 1H, H-5), 8.57 (m, 1H, H-3), 7.03 (s, 1H, H-7), 6.48 (m, 1H, H-4), 6.44 (m, 1H, H-4') ppm, signals of H-3', H-5', H-3'', H-4'', H-5'', H-3''', H-4''', H-5''', H-7' are overlapped by corresponding signals of the major isomer.

Elemental analysis for $C_{22}H_{14}N_2O_4$ (370.36): calcd. C, 71.35; H, 3.81; N, 7.56; found: C, 71.47; H, 3.64; N, 7.21.

*2,2'-(5H,10H-dipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-diylidene)bis(1-(thiophen-2-yl)ethan-1-one) (**2c**)*



Analogously from (thenoyl-2)-ethynylpyrrole (**1c**) (101 mg, 0.5 mmol) and 1-methylimidazole (41 mg, 0.5 mmol), (40-45 °C, 24 h) dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine **2c** was obtained (46 mg, 23%) as a brown gum.

IR (microlayer): 1568 (C=C), 1629, 1699 (C=O) cm^{-1}.

E,*E*:*E*,*Z*-isomer ratio = 80:20 (^{1}H NMR).

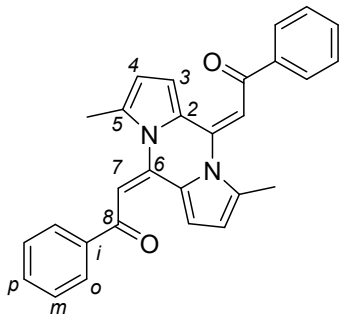
E,*E*-isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.31 (m, 2H, 2 H-3), 7.73 (m, 2H, 2 H-5'), 7.60 (m, 2H, 2 H-5), 7.50 (m, 2H, 2 H-4'), 7.12 (m, 2H, 2 H-3'), 6.89 (s, 2H, 2 H-7), 6.50 (m, 2H, 2 H-4) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 180.1 (2 C-8), 147.5 (2 C-2'), 136.5 (2 C-2), 133.3 (2 C-5'), 130.9 (2 C-5), 128.4 (2 C-3), 123.7 (2 C-6), 121.5 (2 C-3'), 121.1 (2 C-4), 113.8 (2 C-4'), 104.5 (2 C-7) ppm.

E,*Z*-isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.75 (m, 1H, H-5), 8.58 (m, 1H, H-3), 7.77 (m, 1H, H-5''), 6.98 (m, 1H, H-3''), 6.91 (s, 1H, H-7), 6.39 (m, 1H, H-4') ppm, signals of H-3', H-5', H-3'', H-4'', H-5'', H-3''', H-4''', H-5''', H-7' are overlapped by corresponding signals of the major isomer.

Elemental analysis for $C_{22}H_{14}N_2O_2S_2$ (402.49): calcd. C, 65.65; H, 3.51; N, 6.96; S, 15.93; found: C, 65.84; H, 3.68; N, 6.56; S, 15.76.

(2E,2'E)-2,2'-(3,8-dimethyl-5H,10H-dipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-diylidene)bis(1-phenylethan-1-one) ***(2d)***



Analogously from benzoylethynylpyrrole **1d** (105 mg, 0.5 mmol) and 1-methylimidazole (41 mg, 0.5 mmol), (40-45 °C, 32 h) dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine **2d** was obtained (48 mg, 23%) as a dark-yellow oil.

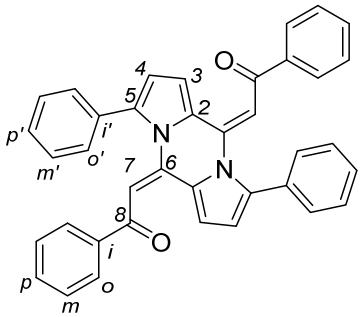
IR (microlayer): 1578 (C=C), 1652 (C=O) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.91 (m, 4H, H_o from 2 Ph), 7.80 (d, $^{3}J_{3,4}$ = 3.6 Hz, 2H, 2 H-3), 7.51 (m, 2H, H_p from 2 Ph), 7.43 (m, 4H, H_m from 2 Ph), 6.80 (s, 2H, 2 H-7), 6.21 (d, $^{3}J_{3,4}$ = 3.6 Hz, 2H, 2 H-4), 2.56 (s, 6H, 2 CH_3) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 187.9 (2 C-8), 139.6 (2 C_i from Ph), 137.3 (2 C-2), 132.5 (2 C_p from 2 Ph, 2 C-5), 128.7 (4 C_m from 2 Ph), 128.3 (4 C_o from 2 Ph), 125.1 (2 C-6), 118.1 (2 C-3), 113.5 (2 C-4), 110.2 (2 C-7), 15.8 (2 CH_3) ppm.

Elemental analysis for $C_{28}H_{22}N_2O_2$ (418.50): calcd. C, 80.36; H, 5.30; N, 6.69; found: C, 79.88; H, 5.79; N, 6.21.

(E,E)-2,2'-(5H,10H-dipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-diylidene)bis(1-(phenyl)ethan-1-one) ***(3e)***



Analogously from benzoylethynylpyrrole **1e** (136 mg, 0.5 mmol) and 1-methylimidazole (41 mg, 0.5 mmol), (40-45 °C, 48 h) dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine **2e** was obtained (68 mg, 25%) as a brown gum.

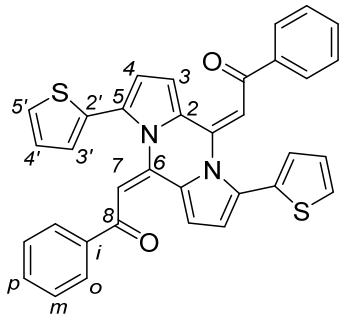
IR (microlayer): 1543, 1579, 1597 (C=C), 1652 (C=O) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.94 (d, $^{3}J_{3,4}$ = 3.6 Hz, 2H, 2 H-3), 7.56 (m, 4H, H_o from 2 Ph), 7.46 (m, 6H, $H_{p,m'}$ from 2 Ph), 7.40 (m, 4H, H_m from 2 Ph), 7.34 (m, 4H, $H_{o'}$ from 2 Ph), 7.25 (m, 2H, $H_{p'}$ from 2 Ph), 6.54 (d, 2H, 2 H-4), 6.52 (s, 2H, 2 H-7) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 187.7 (2 C-8), 139.5 (2 C_i from 2 Ph), 136.8 (2 C-2), 135.9 (2 $C_{i'}$ from 2 Ph), 132.9 (2 C-5), 132.4 (2 C_p from 2 Ph), 129.3 (4 C_m from 2 Ph), 128.9 (4 $C_{o'}$ from 2 Ph), 128.4 (4 $C_{m'}$ from 2 Ph), 128.2 (2 $C_{p'}$ from 2 Ph), 127.9 (4 C_o from 2 Ph), 127.6 (2 C-6), 118.6 (2 C-3), 115.5 (2 C-4), 114.0 (2 C-7) ppm.

Elemental analysis for $C_{38}H_{26}N_2O_2$ (542.64): calcd. C, 84.11; H, 4.83; N, 5.16; found: C, 84.04; H, 4.89; N, 5.10.

*(2E,2'E)-2,2'-(3,8-di(thiophen-2-yl)-5H,10H-dipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-diylidene)bis(1-phenylethan-1-one) (**2f**)*



Analogously from benzoylethynylpyrrole **1f** (139 mg, 0.5 mmol) and 1-methylimidazole (41 mg, 0.5 mmol), (40-45 °C, 24 h) dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine **2f** was obtained (130 mg, 47%) as a dark-red gum.

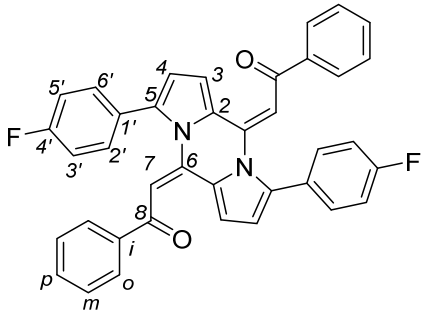
IR (microlayer): 1552, 1582, 1596 (C=C), 1653 (C=O) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.85 (d, $^{3}J_{3,4}$ = 4.0 Hz, 2H, 2 H-3), 7.53 (m, 4H, H_o from 2 Ph), 7.43 (m, 2H, H_p from 2 Ph), 7.38 (d, $^{3}J_{4',5'}$ = 5.1 Hz, 2H, H-5'), 7.31 (m, 4H, H_m from 2 Ph), 7.22 (d, $^{3}J_{3',5'}$ = 3.6 Hz, 2H, H-3'), 7.09 (dd, $^{3}J_{3',5'}$ = 3.6 Hz, $^{3}J_{4',5'}$ = 5.1 Hz, 2H, 2 H-4'), 6.79 (s, 2H, 2 H-7), 6.56 (d, $^{3}J_{3,4}$ = 4.0 Hz, 2H, 2 H-4) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 187.8 (2 C-8), 139.3 (2 C_i from 2 Ph), 135.4 (2 C-2), 133.9 (2 C-2'), 132.6 (2 C_p from 2 Ph), 129.1 (2 C-5), 128.5 (4 C_m from 2 Ph), 128.1 (4 C_o from 2 Ph), 128.0 (2 C-4'), 127.8 (2 C-6), 127.7 (2 C-3'), 127.2 (2 C-5'), 118.2 (2 C-3), 116.5 (2 C-4), 113.8 (2 C-7) ppm.

Elemental analysis for $C_{34}H_{22}N_2O_2S_2$ (554.68): calcd. C, 73.62; H, 4.00; N, 5.05; S, 11.56; found: C, 73.58; H, 3.89; N, 5.16; S, 11.73.

*(2E,2'E)-2,2'-(3,8-bis(4-fluorophenyl)-5H,10H-dipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-diylidene)bis(1-phenylethan-1-one) (**2g**)*



Analogously from benzoylethynylpyrrole **1g** (145 mg, 0.5 mmol) and 1-methylimidazole (41 mg, 0.5 mmol), (40-45 °C, 144 h) dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine **2g** was obtained (30 mg, 21%) as a dark-orange gum.

IR (microlayer): 1544, 1579, 1599 (C=C), 1653 (C=O) cm^{-1}.

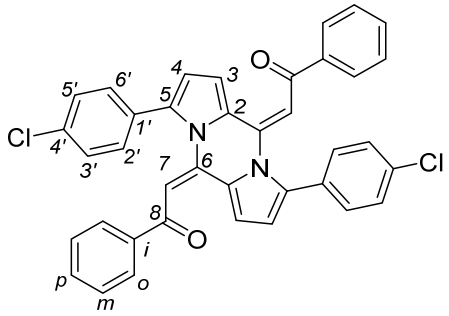
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.89 (d, $^{3}J_{3,4}$ = 3.6 Hz, 2H, 2 H-3), 7.52 (m, 4H, 2 H_o from 2 Ph), 7.42 (m, 6H, H_p, 2 H-2',6' from 2 Ph), 7.29 (m, 4H, 2 H_m from 2 Ph), 7.15 (m, 4H, 2 H-3',5' from 2 Ph), 6.49 (d, $^{3}J_{3,4}$ = 3.6 Hz, 2H, 2 H-4), 6.47 (s, 2H, 2 H-7) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 187.6 (2 C-8), 162.8 (d, $^{1}J_{CF}$ = 247.5 Hz, 2 C-4'), 139.2 (2 C_i from 2 Ph), 135.72 (2 C-2), 135.67 (2 C-5), 132.6 (2 C_p from 2 Ph), 130.6 (d, $^{3}J_{CF}$ = 8.1 Hz, 4 C-2'), 128.8 (d, $^{4}J_{CF}$ = 3.1 Hz, 2 C-1'), 128.6 (4 C_m from 2 Ph), 128.0 (4 C_o from 2 Ph), 127.5 (2 C-6), 118.6 (2 C-3), 116.4 (d, $^{2}J_{CF}$ = 21.57 Hz, 4 C-3'), 115.4 (2 C-4), 114.3 (2 C-7) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -122.5 ppm.

Elemental analysis for $C_{38}H_{24}F_2N_2O_2$ (578.62): calcd. C, 78.88; H, 4.18; F, 6.57; N, 4.84; found: C, 78.74; H, 4.39; N, 5.13.

*(2E,2'E)-2,2'-(3,8-bis(4-chlorophenyl)-5H,10H-dipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-diylidene)bis(1-phenylethan-1-one) (**2h**)*



Analogously from benzoylethynylpyrrole **1h** (153 mg, 0.5 mmol) and 1-methylimidazole (41 mg, 0.5 mmol), (40-45 °C, 72 h) dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine **2h** was obtained (28 mg, 18%) as a brown gum.

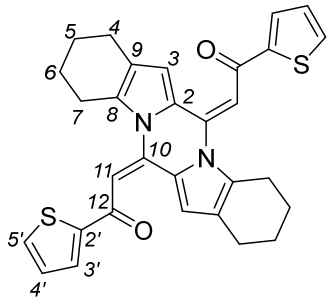
IR (microlayer): 1541, 1579, 1597 (C=C), 1652 (C=O) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.88 (d, $^{3}J_{3,4}$ = 4.0 Hz, 2H, 2 H-3), 7.49-7.39 (m, 12H, 2 $H_{o,m}$, 2 H-3',5' from 2 Ph), 7.33-7.29 (m, 6H, 2 H_p, 2 H-2',6' from 4 Ph), 6.53 (d, $^{3}J_{3,4}$ = 4.0 Hz, 2H, 2 H-4), 6.46 (s, 2H, 2 H-7) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 187.7 (2 C-8), 139.2 (2 C_i from 2 Ph), 135.5 (2 C-2), 135.4 (2 C-1'), 134.4 (2 C-4'), 132.7 (2 C_p from 2 Ph), 131.2 (2 C-5), 130.0 (2 C-2',6' from 2 Ar), 129.6 (2 C_m from 2 Ph), 128.6 (2 C-3',5' from 2 Ar), 128.0 (2 C_o from 2 Ph), 127.8 (2 C-6), 118.5 (2 C-3), 115.7 (2 C-4), 114.5 (2 C-7) ppm.

Elemental analysis for $C_{38}H_{24}Cl_2N_2O_2$ (611.52): calcd. C, 74.64; H, 3.96; Cl, 11.59; N, 4.58; found: C, 74.85; H, 4.03; Cl, 11.62; N, 4.43.

(2E,2'E)-2,2'-(1,2,3,4,8,9,10,11-octahydro-6H,13H-pyrazino[1,2-a:4,5-a']diindole-6,13-diylidene)bis(1-(thiophen-2-yl)ethan-1-one) ***(2i)***



Analogously from benzoylethynyltetrahydroindole **1i** (128 mg, 0.5 mmol) and 1-methylimidazole (41 mg, 0.5 mmol), (40-45 ºC, 144 h) dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine **2i** was obtained (18 mg, 14%) as an orange powder, mp 213-215 ºC.

IR (microlayer): 1555, 1580 (C=C), 1627 (C=O) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.88 (s, 2H, 2 H-3), 7.62 (d, ^{3}J = 3.6 Hz, 2H, 2 H-3' from 2 thienyl), 7.54 (d, ^{3}J = 4.9 Hz, 2H, 2 H-5' from 2 thienyl), 7.08 (m, 2H, 2 H-4' from 2 thienyl), 6.68 (s, 2H, 2 H-11), 2.90 (m, 4H, 2 H-7), 2.60 (m, 4H, 2 H-4), 1.80 (m, 8H, 2 H-5, 2 H-6) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 179.5 (2 C-12), 147.8 (2 C-2'), 137.3 (2 C-8), 132.7 (2 C-5' from thienyl), 132.5 (2 C-2), 130.5 (2 C-3' from thienyl), 128.3 (2 C-4' from thienyl), 124.0 (2 C-10), 123.8 (2 C-9), 119.3 (2 C-3), 107.0 (2 C-11), 26.9 (2 C-7), 24.1 (2 C-6), 23.2 (2 C-5), 22.8 (2 C-4) ppm.

Elemental analysis for $C_{30}H_{26}N_2O_2S_2$ (510.67): calcd. C, 70.56; H, 5.13; N, 5.49; S, 12.56; found: C, 70.44; H, 5.03; N, 5.33; S, 12.37.

References

1. B. A. Trofimov, Z. V. Stepanova, L. N. Sobenina, A. I. Mikhaleva, I. A. Ushakov, Ethynylation of pyrroles with 1-acyl-2-bromoacetylenes on alumina: a formal inverse Sonogashira coupling. *Tetrahedron Lett*., 2004, **45**, 6513-6516.

Copies of NMR Spectra

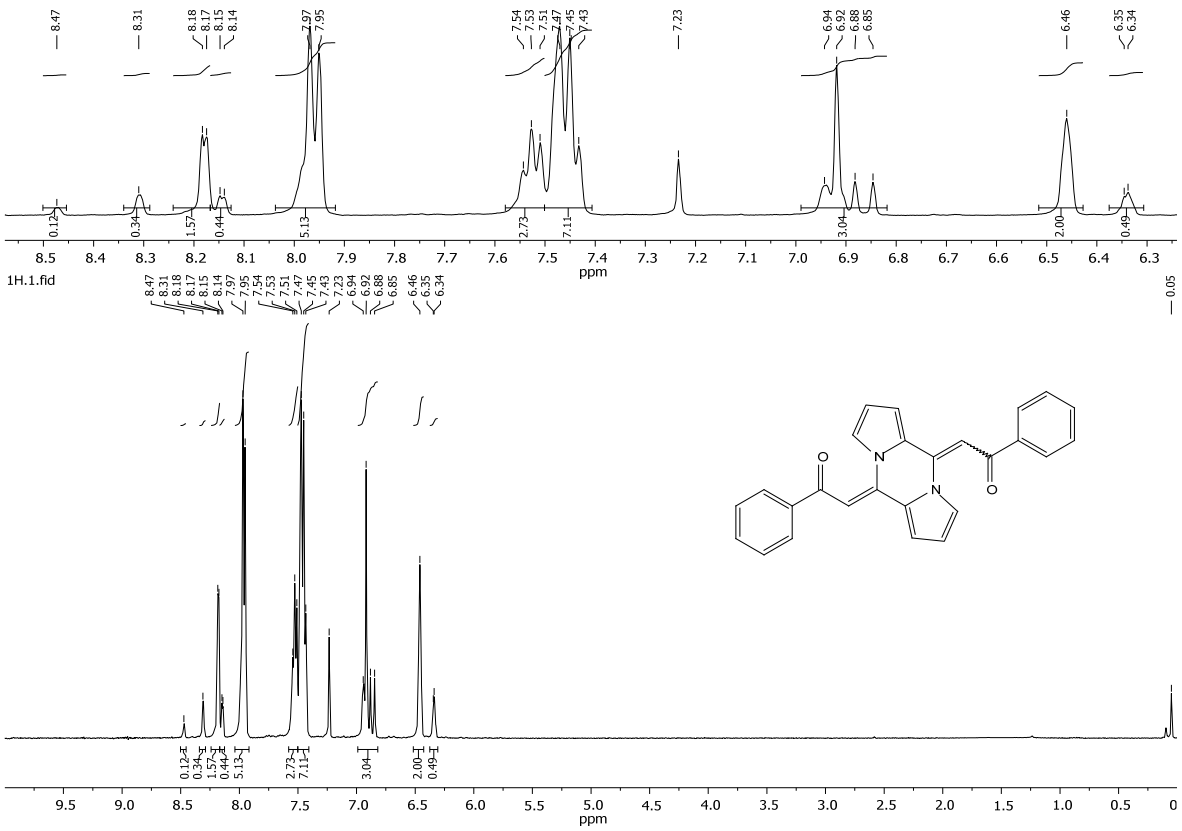


Figure S1. ^{1}H NMR spectrum of compound **2a** (400.13 MHz, $CDCl_3$).

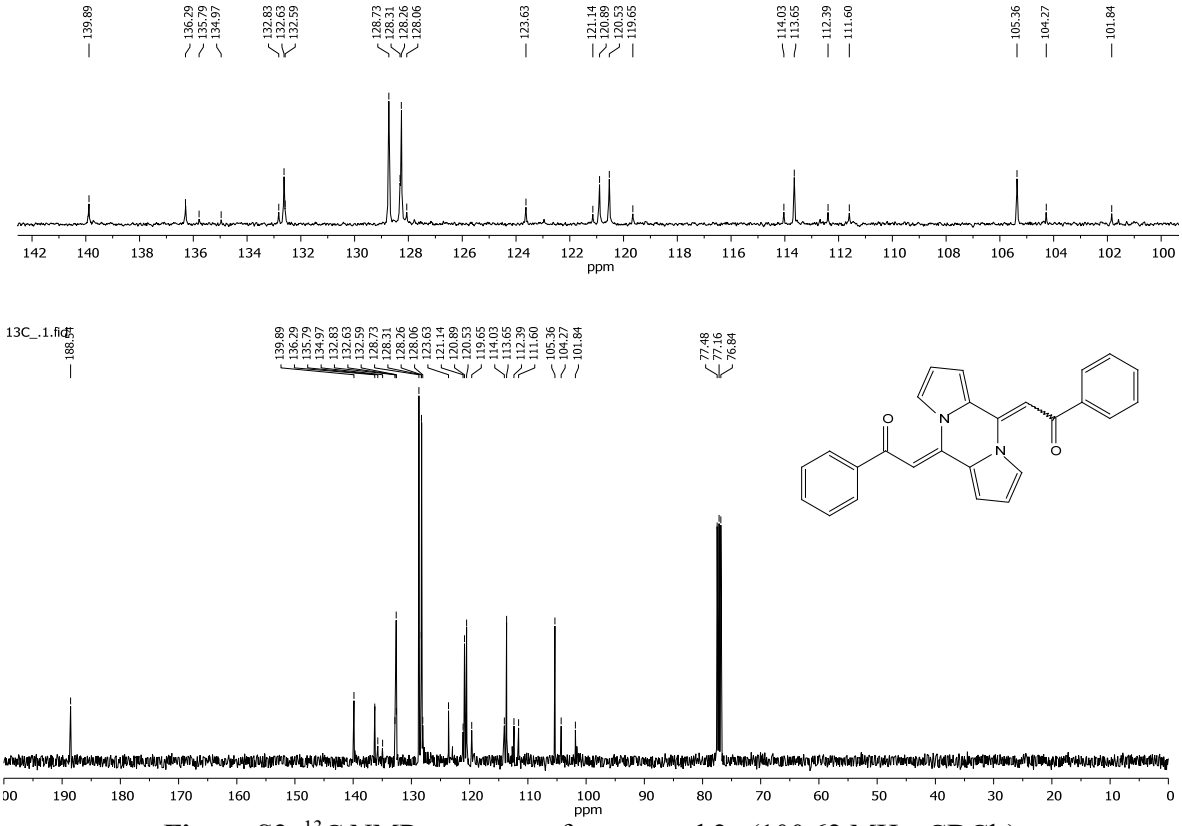


Figure S2. ^{13}C NMR spectrum of compound **2a** (100.62 MHz, $CDCl_3$).

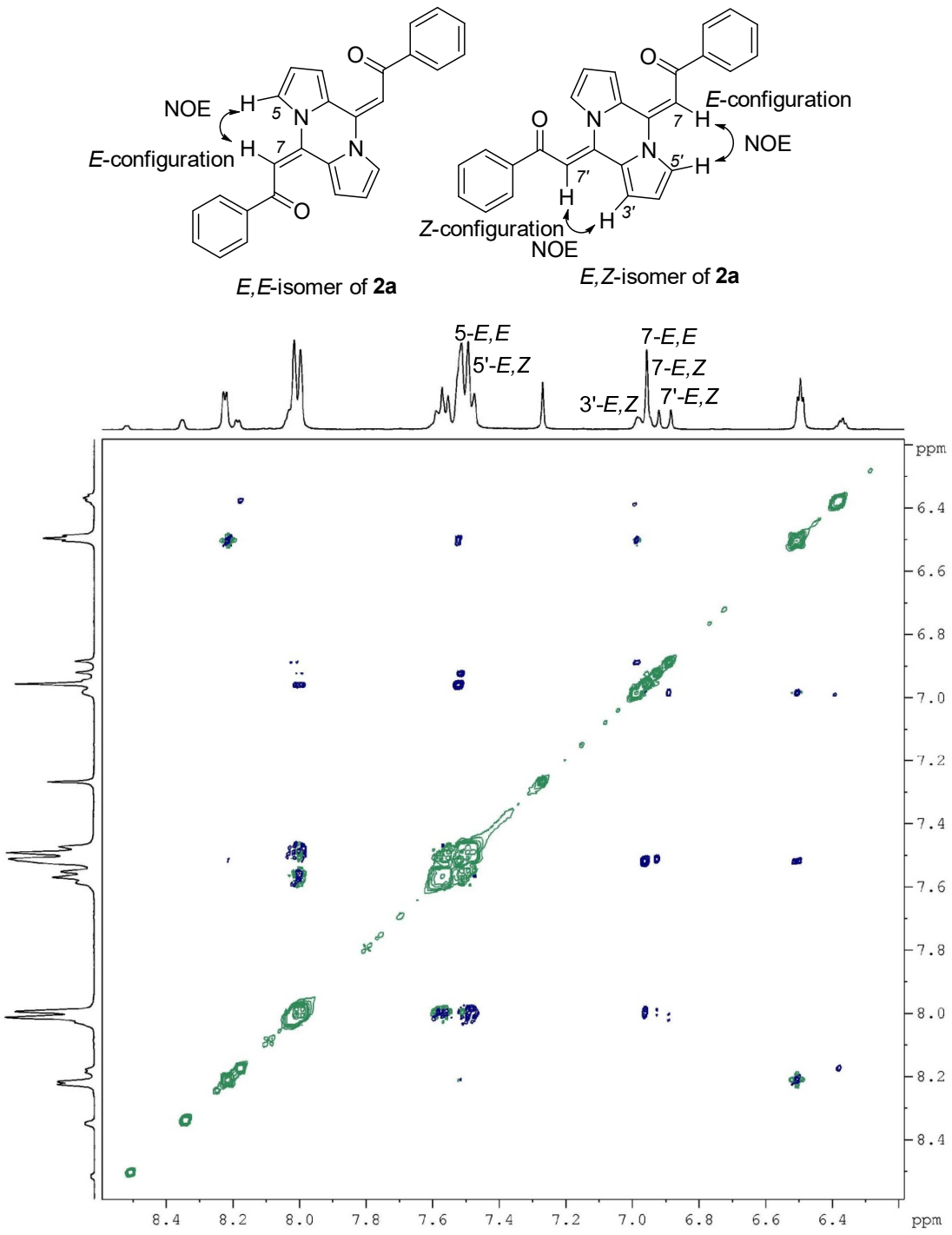


Figure S3. 2D NMR NOESY spectrum of compound **2a** (400.13 MHz, $CDCl_3$).

The 5-*E*,*E* and 5'-*E*,*Z* signals of *E*,*E*- and *E*,*Z*-isomers of compound **2a** are overlapped with the H_m and $H_{m'}$ signals.

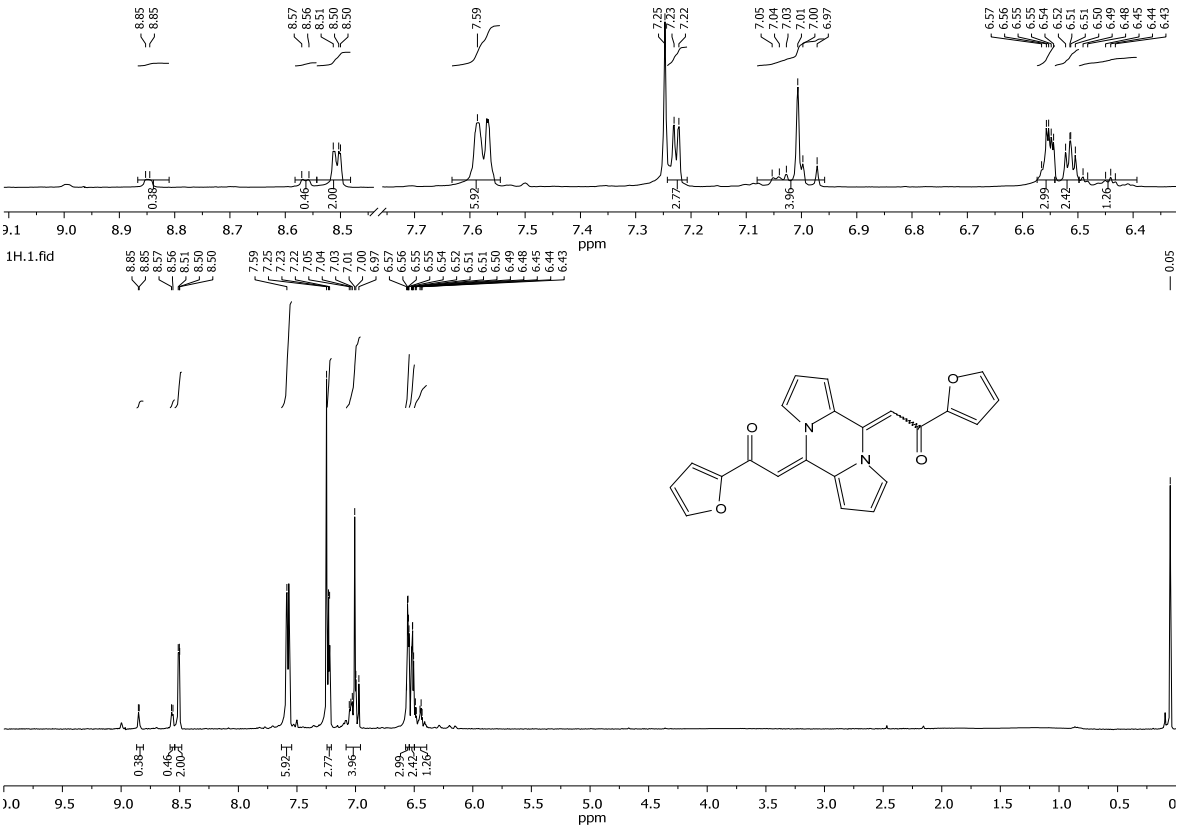


Figure S4. ^{1}H NMR spectrum of compound **2b** (400.13 MHz, $CDCl_3$).

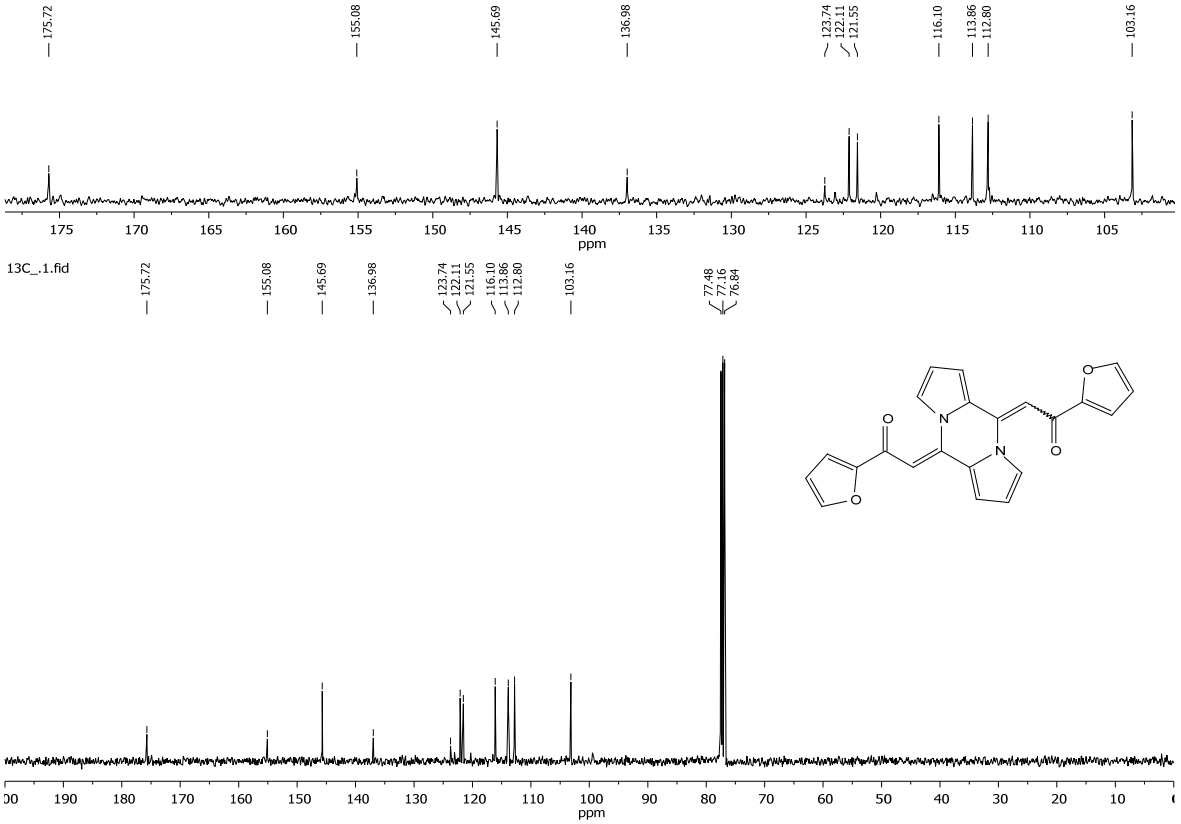


Figure S5. ^{13}C NMR spectrum of compound **2b** (100.62 MHz, $CDCl_3$).

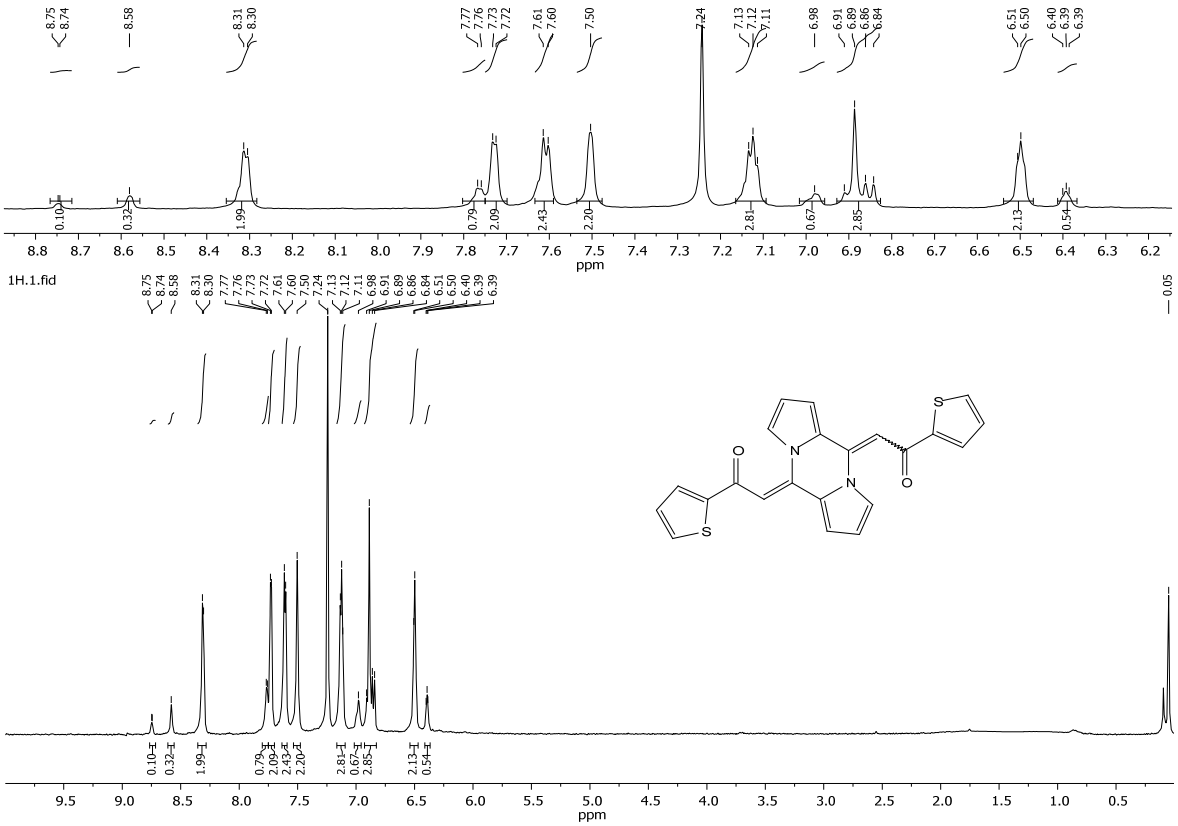


Figure S6. ^{1}H NMR spectrum of compound **2c** (400.13 MHz, $CDCl_3$).

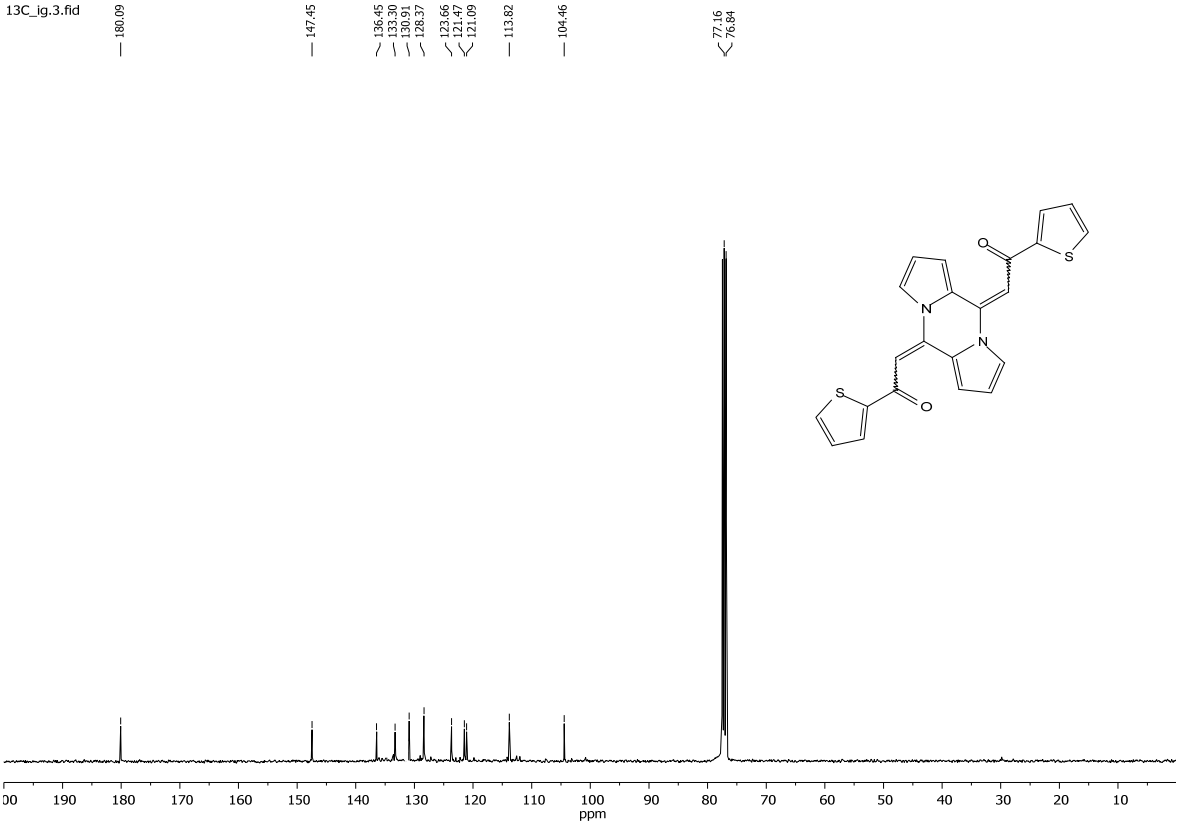


Figure S7. ^{13}C NMR spectrum of compound **2c** (100.62 MHz, $CDCl_3$).

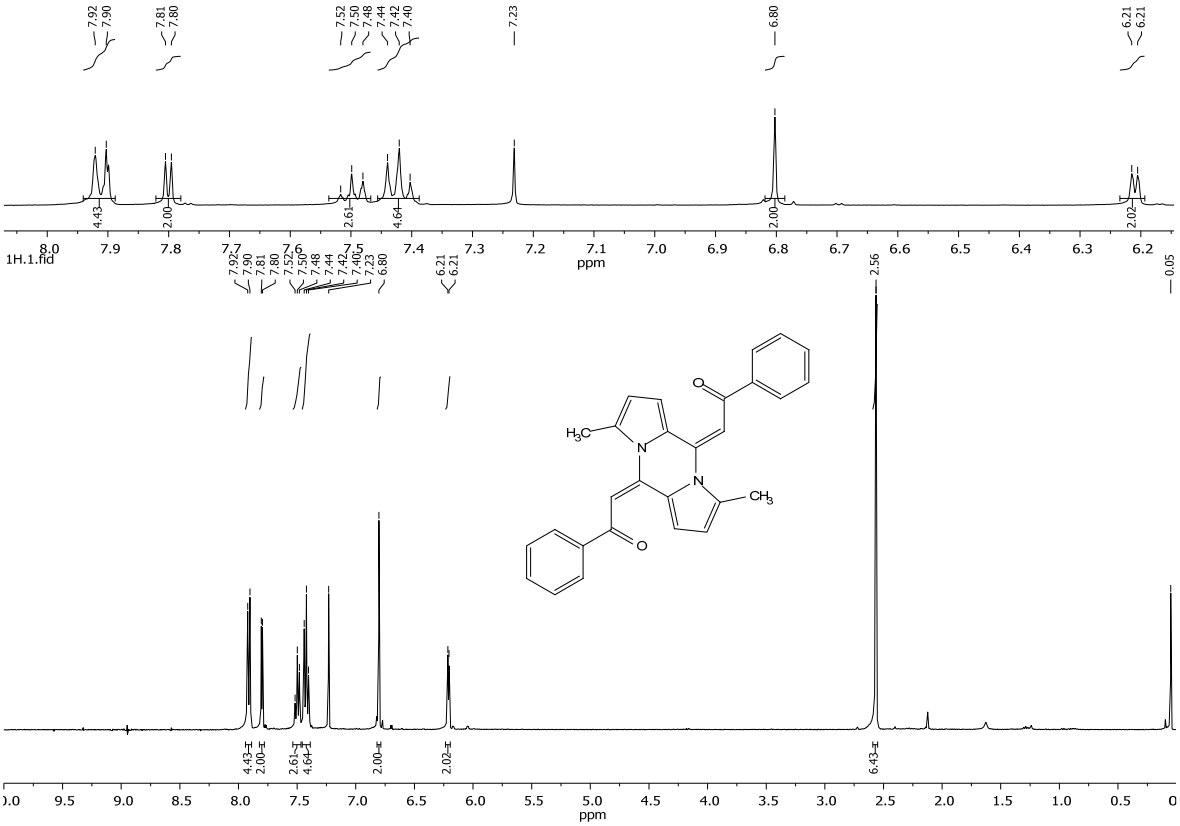


Figure S8. ^{1}H NMR spectrum of compound **2d** (400.13 MHz, $CDCl_3$).

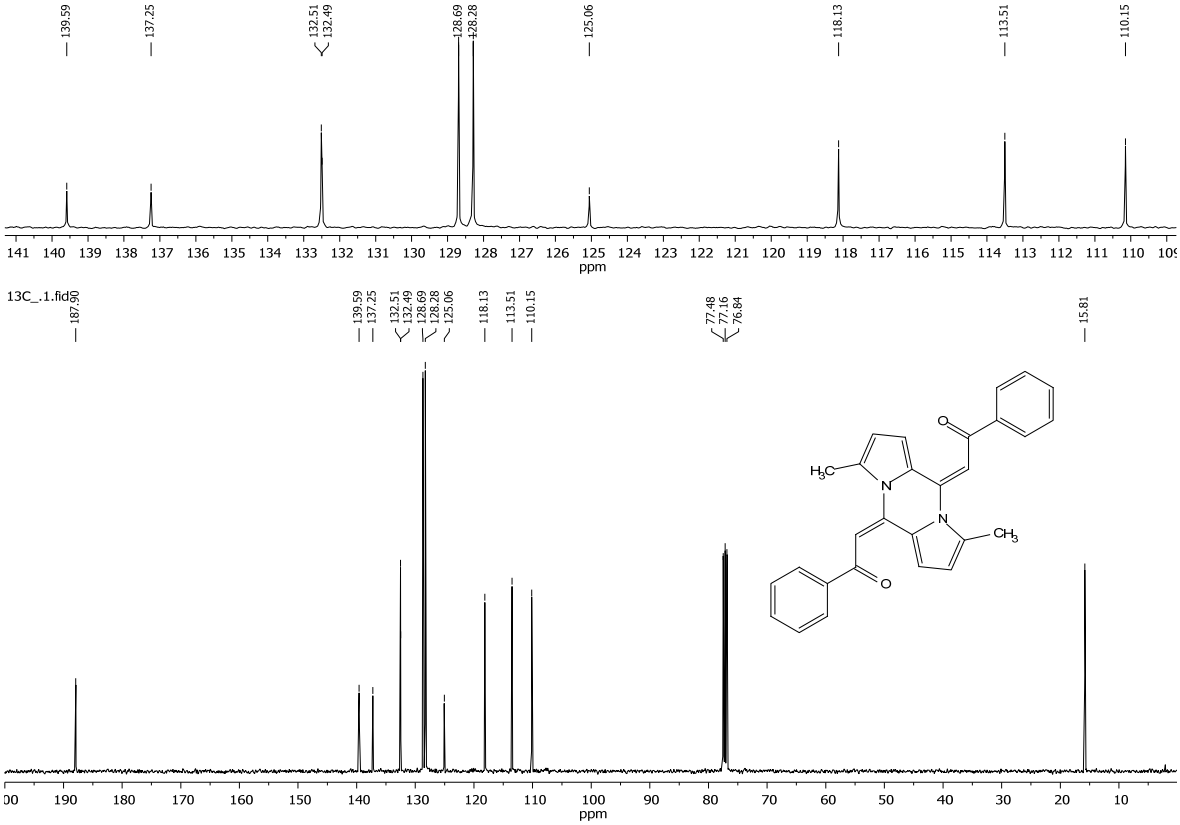


Figure S9. ^{13}C NMR spectrum of compound **2d** (100.62 MHz, $CDCl_3$).

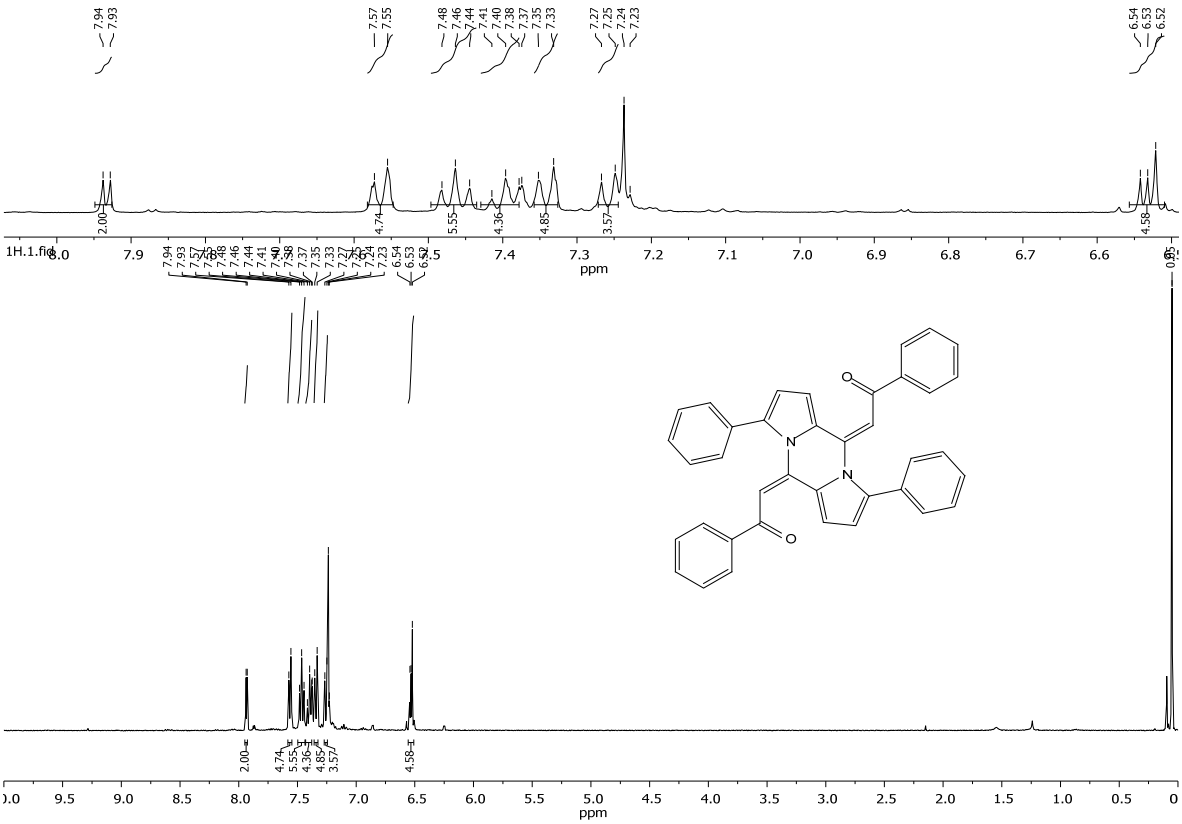


Figure S10. ^{1}H NMR spectrum of compound **2e** (400.13 MHz, $CDCl_3$).

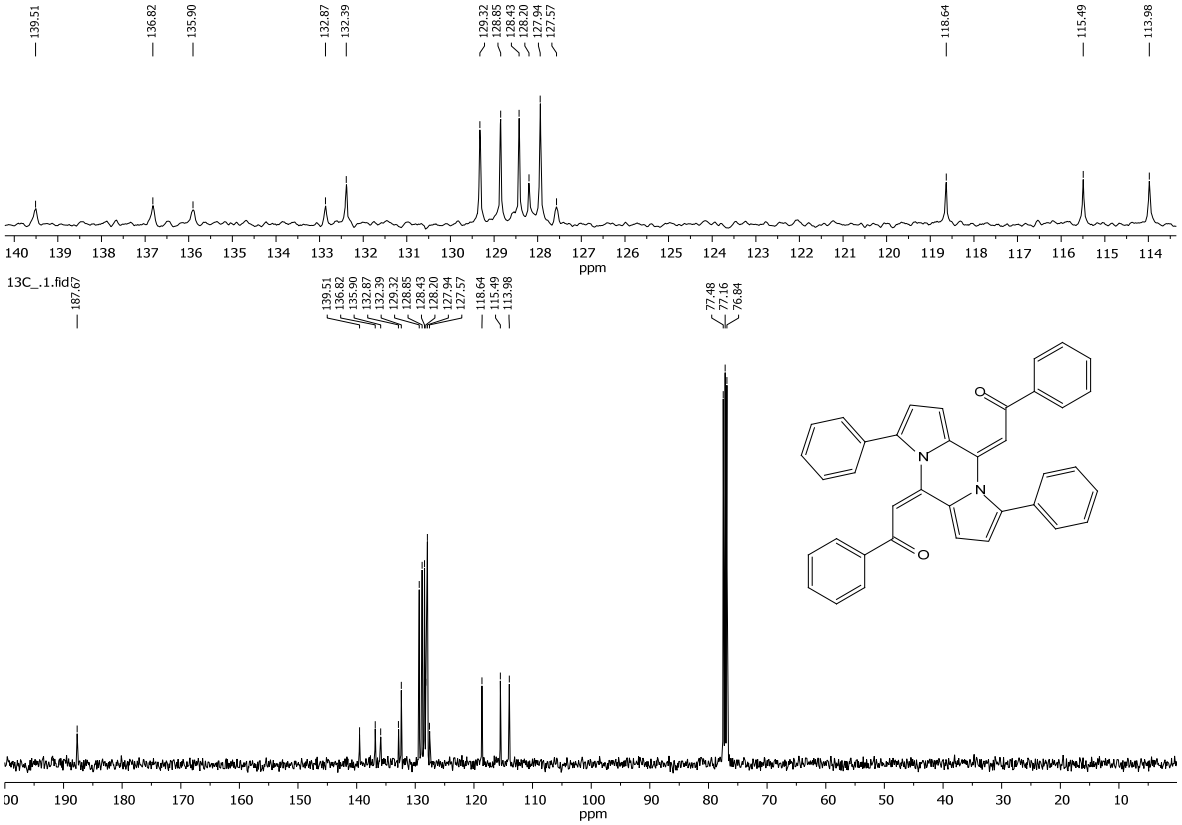


Figure S11. ^{13}C NMR spectrum of compound **2e** (100.62 MHz, $CDCl_3$).

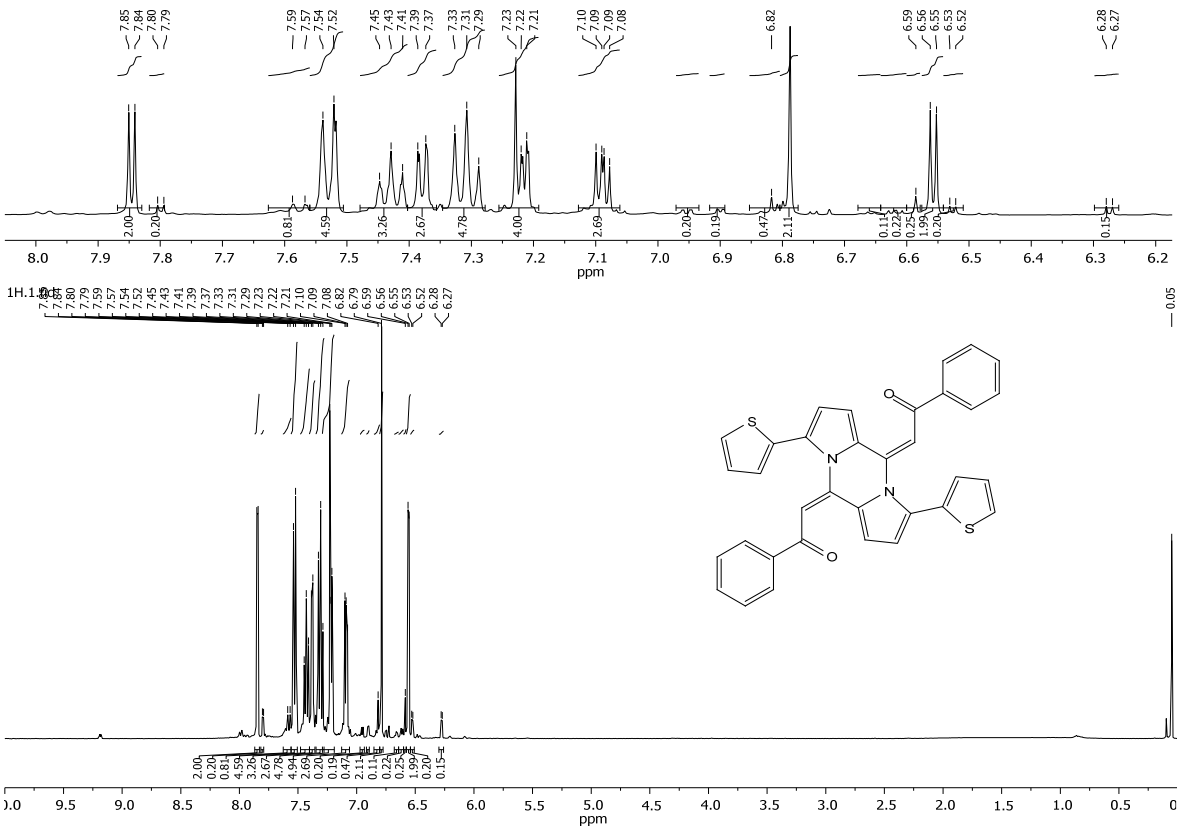


Figure S12. ^{1}H NMR spectrum of compound **2f** (400.13 MHz, $CDCl_3$).

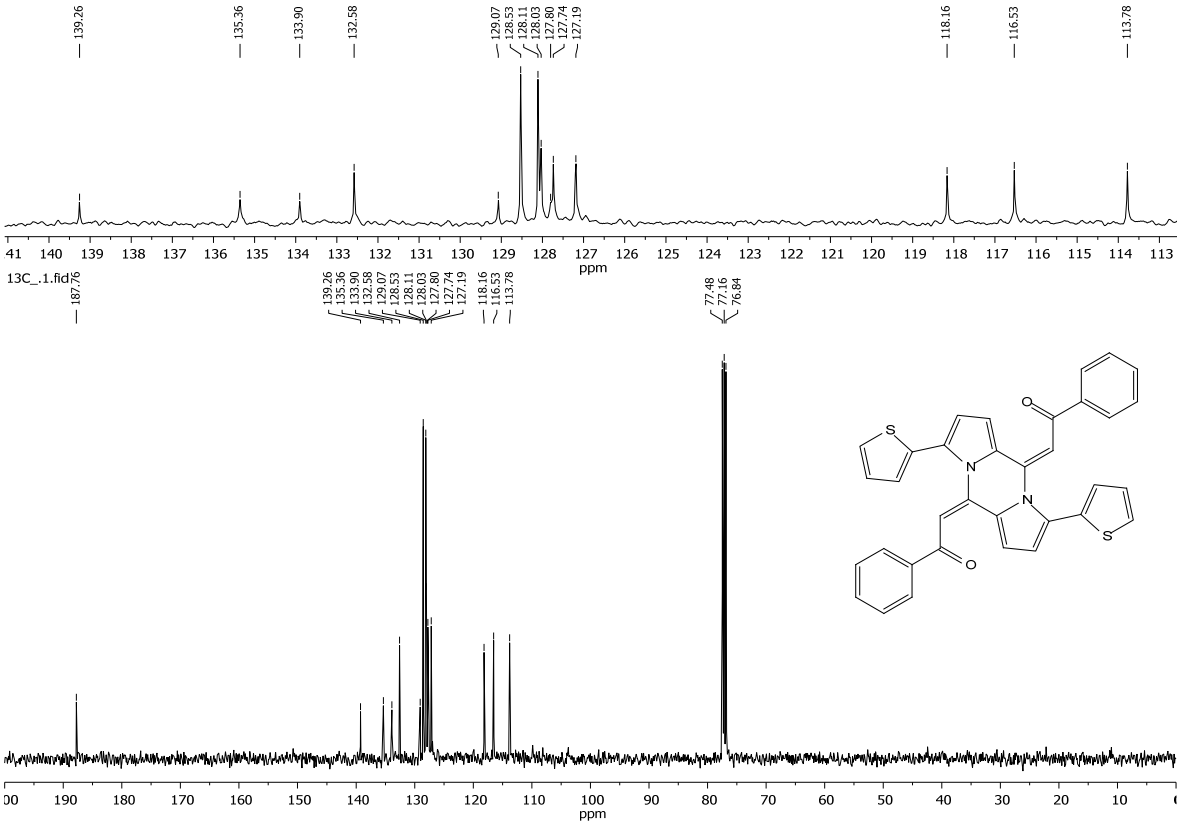


Figure S13. ^{13}C NMR spectrum of compound **2f** (100.62 MHz, $CDCl_3$).

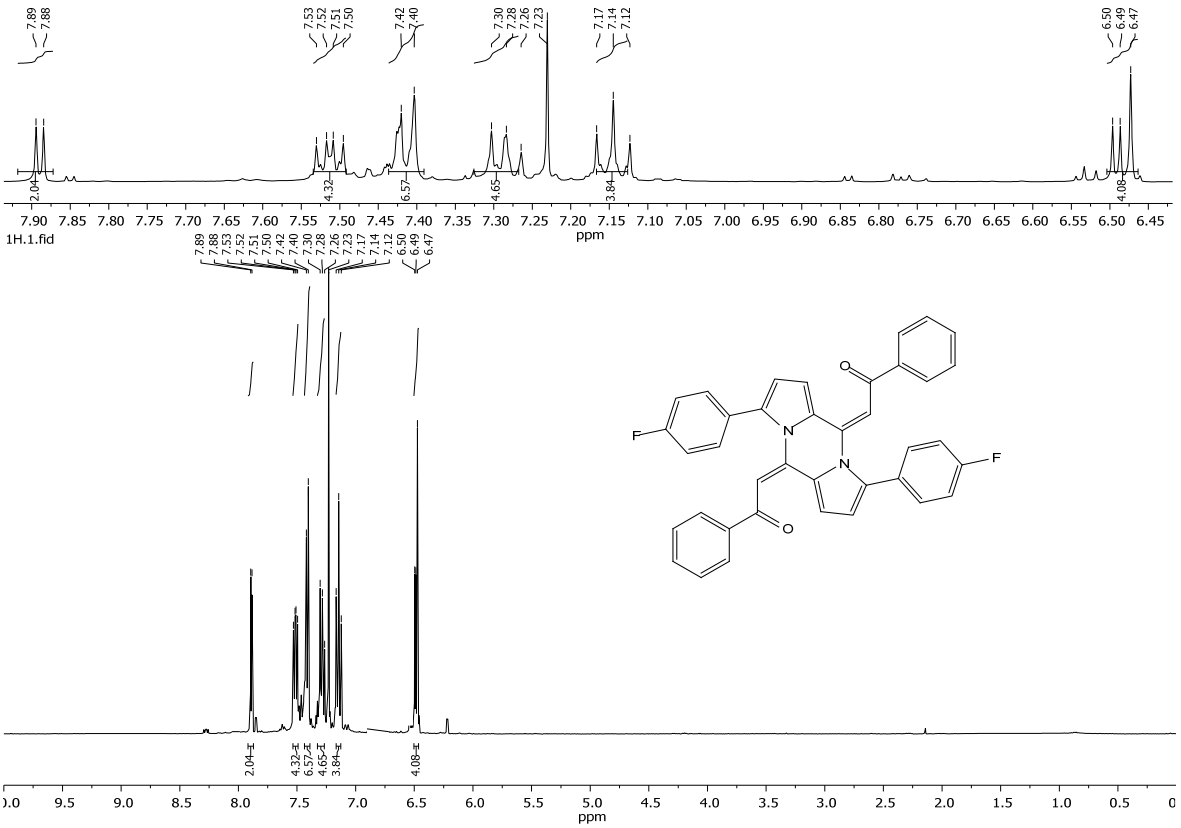


Figure S14. ^{1}H NMR spectrum of compound **2g** (400.13 MHz, $CDCl_3$).

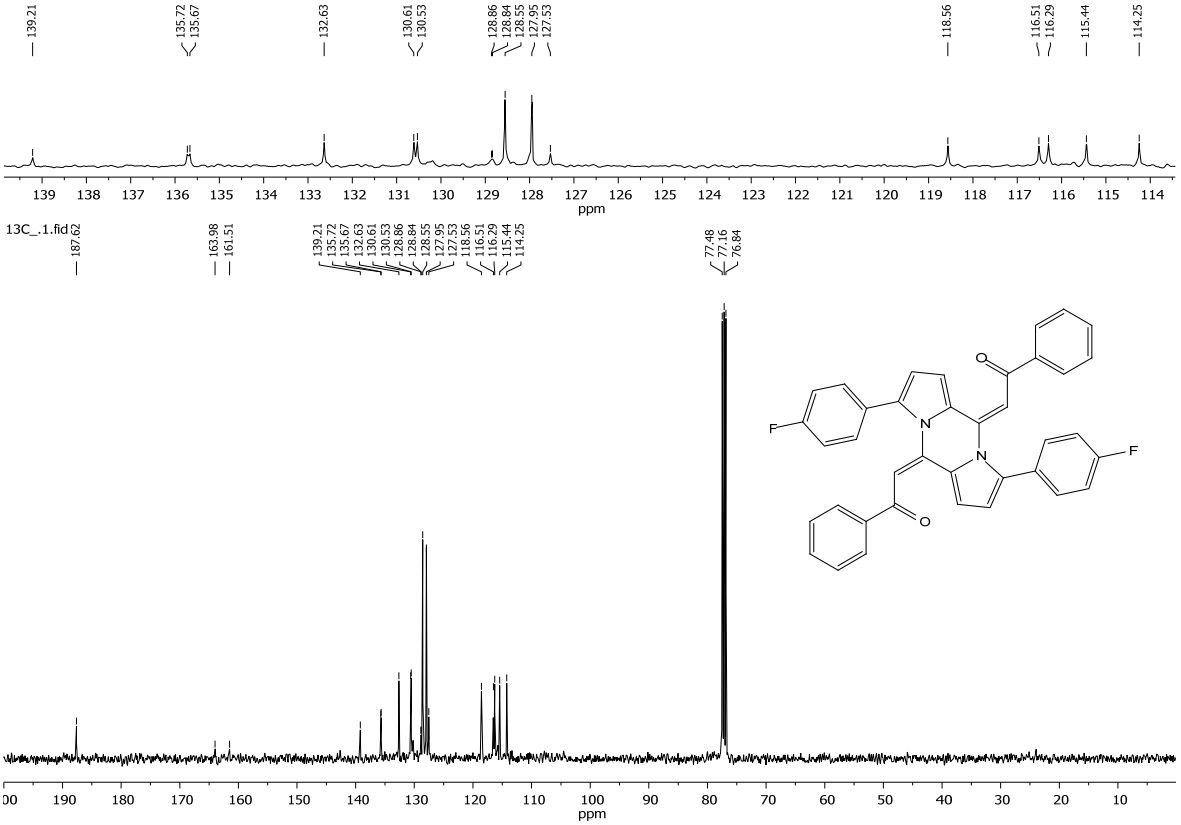


Figure S15. ^{13}C NMR spectrum of compound **2g** (100.62 MHz, $CDCl_3$).

Figure S16. ^{19}F NMR spectrum of compound **2g** (376.5 MHz, $CDCl_3$).

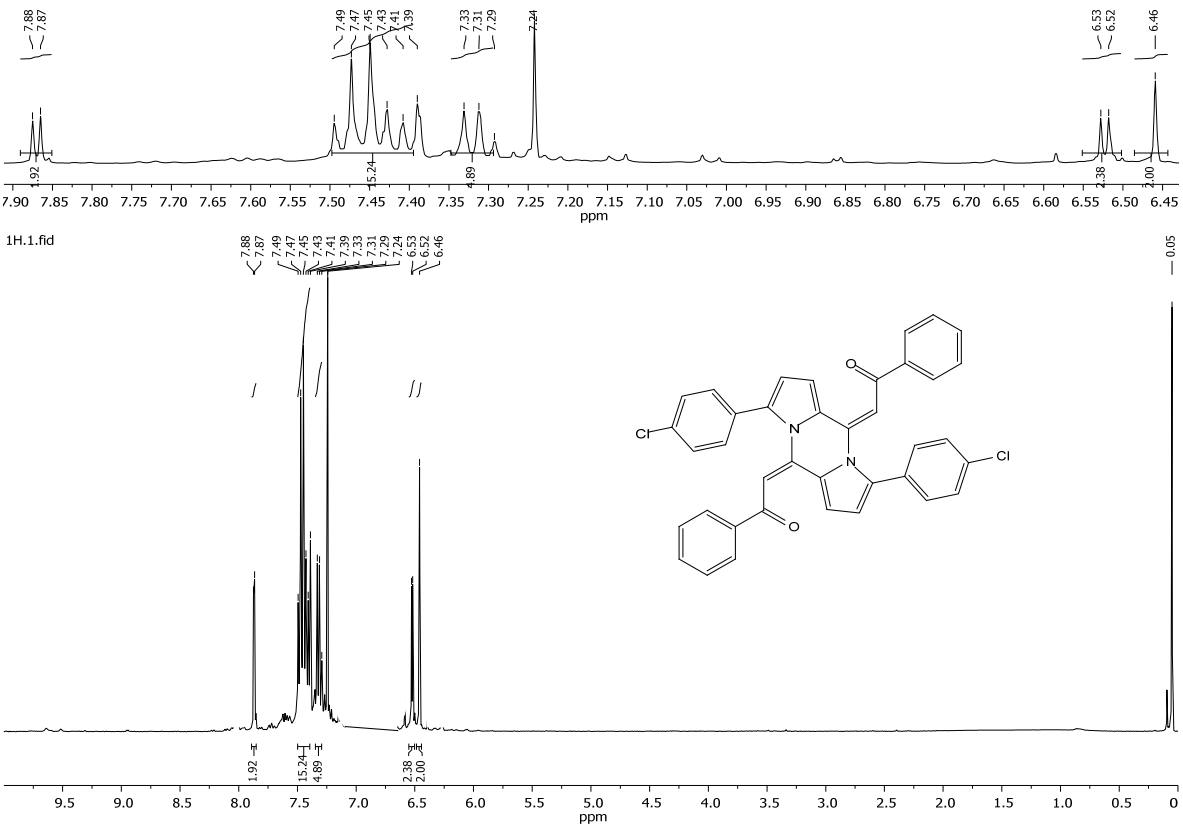


Figure S17. ^{1}H NMR spectrum of compound **2h** (400.13 MHz, $CDCl_3$).

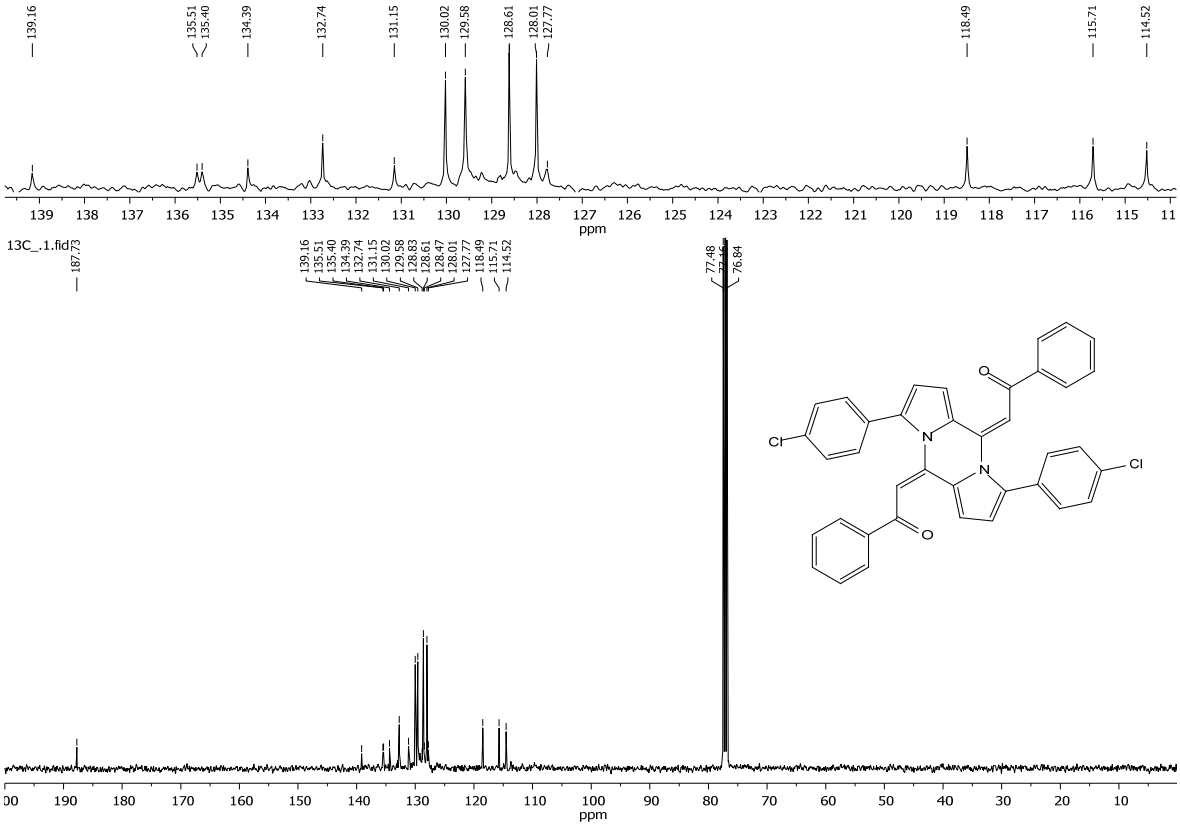


Figure S18. ^{13}C NMR spectrum of compound **2h** (100.62 MHz, $CDCl_3$).

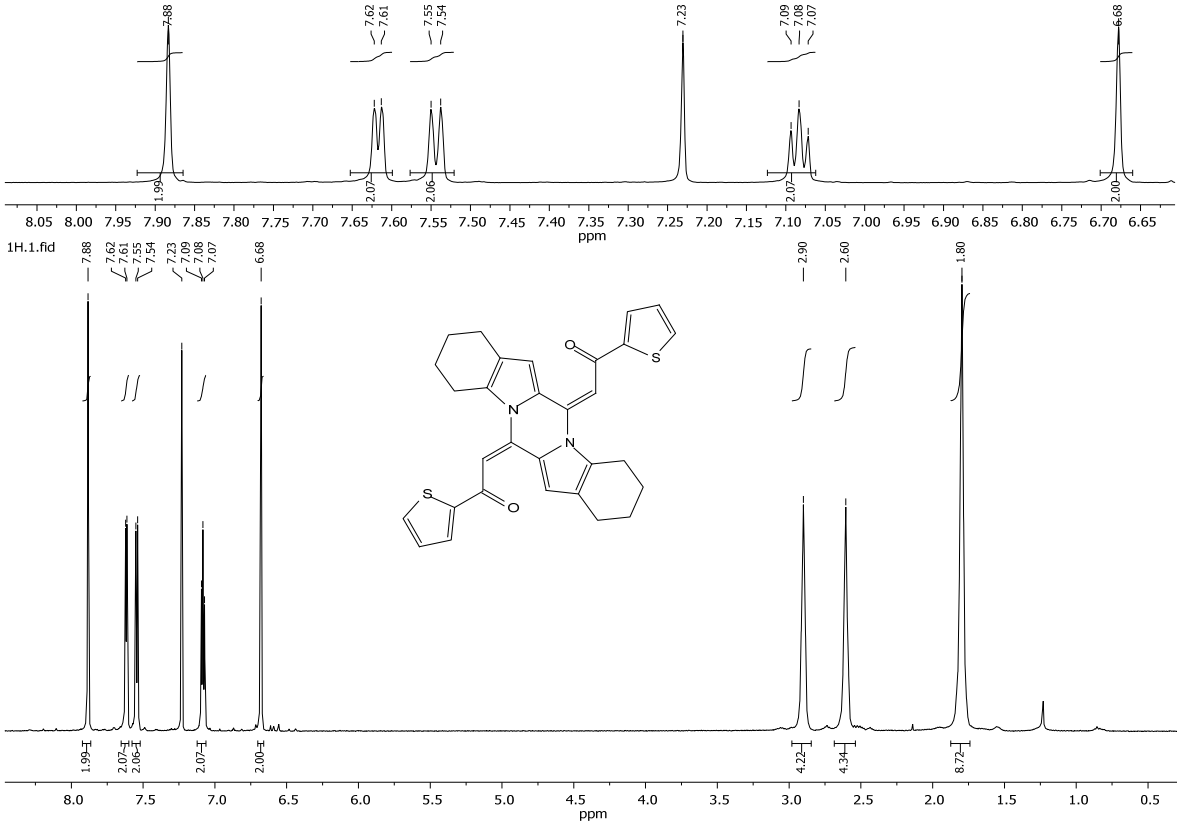


Figure S19. ^{1}H NMR spectrum of compound **2i** (400.13 MHz, $CDCl_3$).

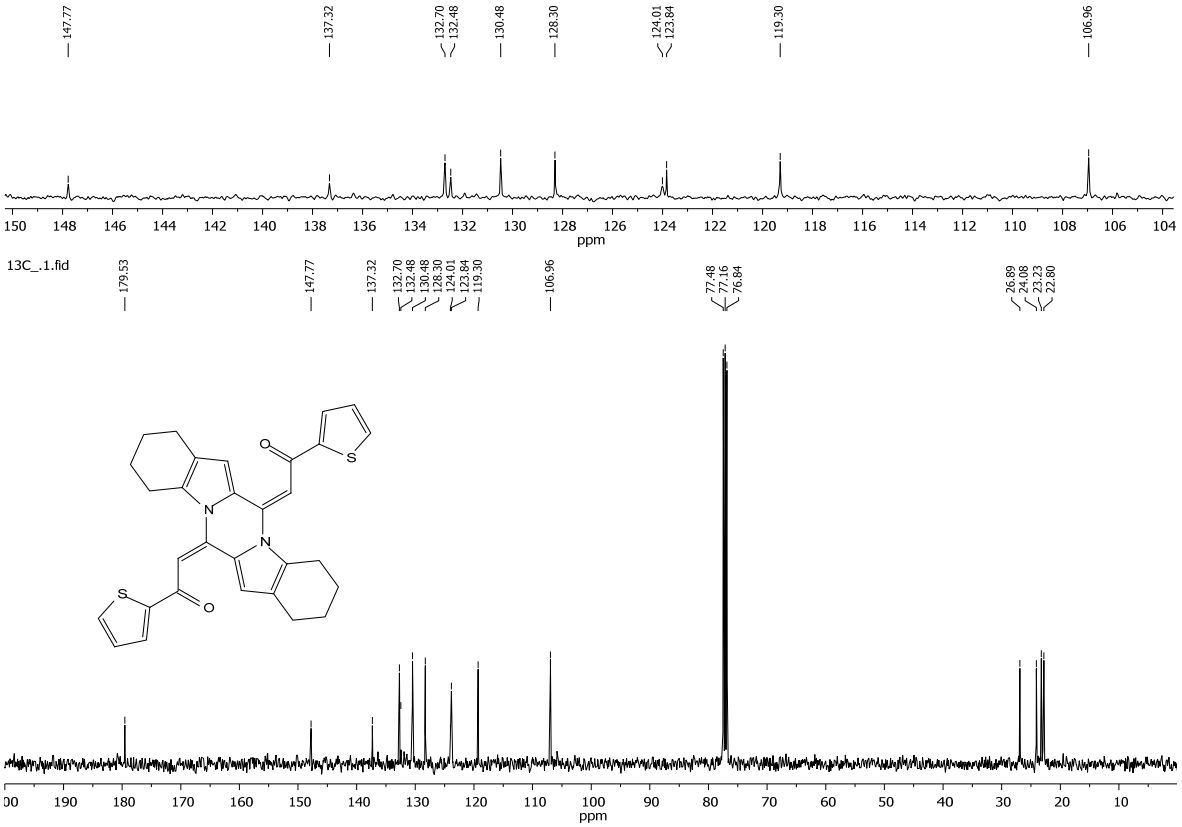


Figure S20. ^{13}C NMR spectrum of compound **2i** (100.62 MHz, $CDCl_3$).

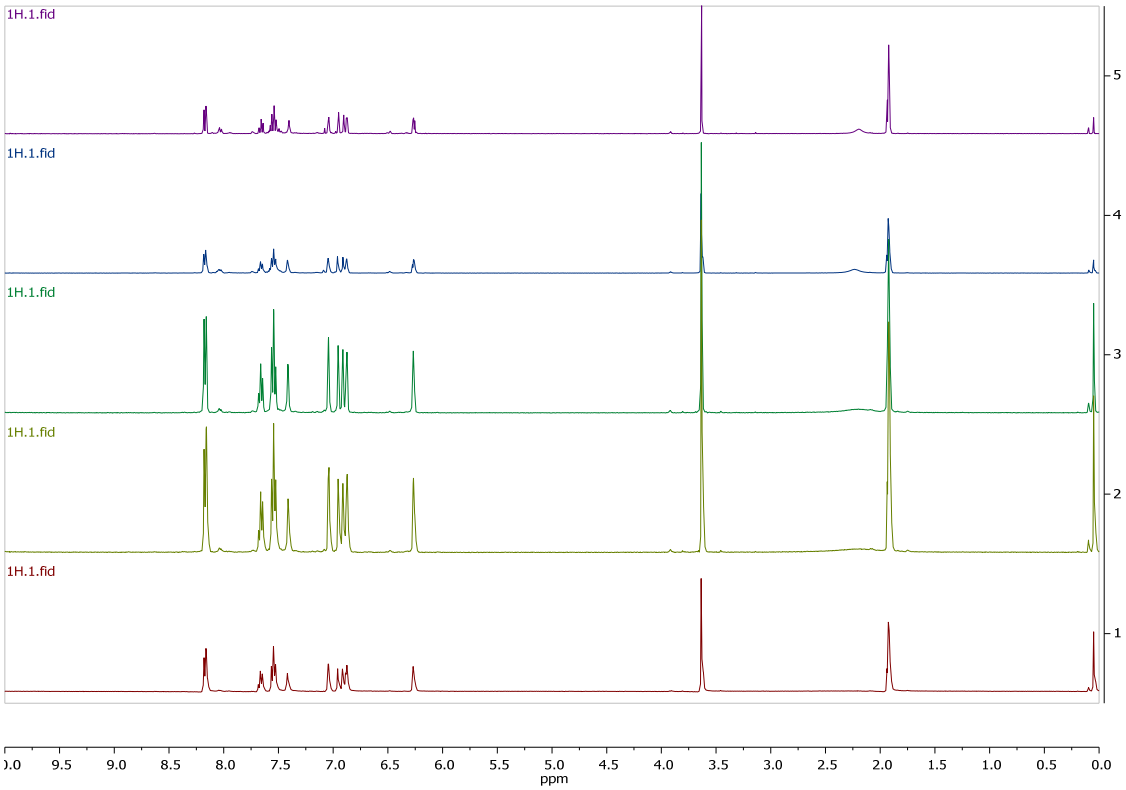


Figure S21. ^{1}H NMR monitoring of the reaction mixture between benzoylethynylpyrrole **1a** and 1-methylimidazole (1:1, 40 ^{o}C) (CD_3CN, 400.13 MHz).

1. Reaction mixture after 0.5 h
2. Reaction mixture after 2 h
3. Reaction mixture after 6 h
4. Reaction mixture after 96 h
5. Reaction mixture after 144 h