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Supporting information

New synthesis of unsymmetrically-substituted 2,5-diarylpyrroles from homopropargylic sulfonamides

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1. General experimental methods

NMR spectra were acquired using a JEOL 300 MHz spectrometer operating at 300.01 MHz and 75 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (^{1}H) or relative to the internal (NMR) solvent signals (for ^{13}C spectra). High resolution mass spectroscopic measurements were made on a Shimadzu LCMS-IT-TOF instrument (in ESI mode). Melting points were determined using a Linkam THMS600 apparatus. MPLC flash chromatography was performed using an YFLC W-Prep 2XY apparatus (Yamazen). Chemicals received from commercial sources (specify) were used without further purification. Reaction solvents (*N,N*-dimethylformamide, tetrahydrofuran, and toluene; anhydrous, +99.5%) were used as purchased.

2. Experimental and characterization data

***N*-(4-Methoxybenzylidene)-4-methylbenzenesulfonamide 2.** A flame-dried flask was charged with 4-anisaldehyde (7.10 mL, 58.4 mmol, 1 equiv), *p*-toluenesulfonamide (10.00 g, 58.4 mmol, 1 equiv), DOWEX (1.0 g) and toluene (200 mL). The reaction mixture was stirred overnight at 150 °C with azeotropic water removal (Dean-Stark). The reaction mixture was cooled to room temperature and partially evaporated under reduced pressure. Heptane was added and the precipitate was filtered. Compound **2** was obtained as a white solid (15.01 g, 89%). This compound has been prepared before by M. Barbarotto *et al*.[1] Material identity was confirmed by mp, MS, ^{1}H and ^{13}C NMR.

Activation of zinc. Zinc powder (27 g) was dispersed in water (40 mL) with ultrasonification. 3M aqueous HCl (100 mL) was added to the resulting suspension with vigorous stirring and the mixture was stirred for 1 h (until gas evolution halted). The resulting activated Zn was filtered, washed with water and acetone, and subsequently dried overnight at 40 °C under vacuum.

***N*-[1-(4-Methoxyphenyl)-3-butyn-1-yl]-4-methylbenzenesulfonamide 3.** Activated Zn (17.00 g, 257.5 mmol, 5 equiv) in dry THF (400 mL) was stirred and cooled to 0 °C under N_2 atmosphere. Propargyl bromide (5.85 mL, 77.2 mmol, 1.5 equiv) was added dropwise and the reaction mixture was stirred for 1 h at rt. *N*-tosylimine **2** (14.90 g, 51.5 mmol, 1 equiv) was dispersed in 100 mL of dry THF and added portion wise to the reaction mixture. After 3 h, a saturated NH_4Cl solution (200 mL) was added and the mixture was left to stir for another 15 min. The reaction mixture was filtered, diluted with EtOAc (200 mL) and washed with saturated NH_4Cl solution (1×) and H_2O (3×). The organic fraction was dried over Na_2SO_4, solvents evaporated and the white solid dried overnight at 40°C under vacuum. Yield: 16.84 g, 99%). M.pt. 104.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.4 Hz, 2H; Ar-H), 7.20 (d, J = 8.1 Hz, 2H; Ar-H), 7.07 (d, J = 8.7 Hz, 2H; Ar-H), 6.74 (d, J = 9.0 Hz, 2H; Ar-H), 5.07 (d, J = 6.6 Hz, 1H; NH), 4.44 (q, J = 12.9 Hz, J = 6.3 Hz, 1H; benzyl), 3.76 (s, 3H; OMe), 2.62 (dd, J = 6.0 Hz, J = 2.7 Hz, 2H; CH_2), 2.39 (s, 3H; Me), 1.98 (t, J = 2.4 Hz, 1H; acetylene) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3 (C), 143.4 (C), 137.3 (C), 131.3 (C), 129.5 (CH; Ar-CH), 127.8 (CH; Ar-CH), 127.2 (CH; Ar-CH), 113.8 (CH; Ar-CH), 79.2 (C), 72.0 (CH), 55.2 (OCH_3), 55.1 (CH), 27.1 (CH_2), 21.4 (CH_3) ppm. HRMS (ESI+): calc'd for $C_{18}H_{19}NO_3S$ $[M+H]^+$: *m/z* 328.0768; found *m/z* 328.0641.

[1] M. Barbarotto, J. Geist, S. Choppin and F. Colobert, *Tetrahedron-Asymmetr.* 2009, **20**, 2780.

4-(3,5-Bis(trifluoromethyl)phenyl)-1-(4-methoxyphenyl)-*N*-tosylbut-3-yn-1-amine 4a. General method 1: A flame-dried Schlenk flask was charged with 1,3-bis(trifluoromethyl)-5-bromobenzene (100 µL, 0.57 mmol, 1 equiv), sulfonamide **3** (200 mg, 0.61 mmol, 1.05 equiv), $Pd(PPh_3)_2Cl_2$ (40 mg, 0.057 mmol, 10 mol%), CuI (22 mg, 0.114 mmol, 20 mol%), dry DMF (2 mL) and piperidine (172 µL, 3 equiv). The mixture was degassed by applying three freeze-pump-thaw cycles then stirred at 80 °C for 20 h. Saturated NH_4Cl solution was added and the mixture was extracted with EtOAc (3×). The combined organic fractions were washed with water (2×), dried over Na_2SO_4 and solvents removed under reduced pressure. The residue was purified by column chromatography (silica, MPLC: hexane–ethyl acetate, gradient 85:15 to 75:25) to obtain compound **4a** as a yellowish solid (216 mg, 78%). M.pt. 123.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (s, 1H; Ar-H), 7.68–7.63 (m, 4H; Ar-H), 7.19 (d, J = 7.5 Hz, 2H; Ar-H), 7.09 (d, J = 8.1 Hz, 2H; Ar-H), 6.78 (d, J = 8.1 Hz, 2H; Ar-H), 5.03 (d, J = 3.0 Hz, 1H; NH), 4.55-4.51 (m, 1H; benzyl), 3.77 (s, 3H; OMe), 2.91 (d, J = 5.7 Hz, 2H; CH_2), 2.36 (s, 3H; Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.5, 143.5, 137.3, 132.1 (t, J = 1.2 Hz; CF_3), 129.6, 127.7, 127.2, 125.3, 124.7, 121.5, 114.0, 89.2, 81.0 (C), 55.7 (CH), 55.2 (OCH_3), 28.2 (CH_2), 21.3 (CH_3) ppm. HRMS (ESI-): calc'd for $C_{26}H_{21}NO_3S$ $[M+H]^-$: *m/z* 541.1152; found *m/z* 541.1101.

4-(4-(Trifluoromethyl)phenyl)-1-(4-methoxyphenyl)-*N*-tosylbut-3-yn-1-amine 4b. Synthesis according to general method 1: 1-bromo-4-(trifluoromethyl)benzene (300 µL, 1.96 mmol, 1 equiv), sulfonamide **3** (677 mg, 2.06 mmol, 1.05 equiv), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.19 mmol, 10 mol%), CuI (76 mg, 0.40 mmol, 20 mol%), dry DMF (3 mL), piperidine (580 µL, 5.88 mmol, 3 equiv); purification by column chromatography (silica, MPLC: hexane–ethyl acetate, gradient 85:15 to 75:25). Yield: 67% (620 mg). M.pt 189.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.4 Hz, 2H; Ar-H), 7.52 (d, J = 8.4 Hz, 2H; Ar-H), 7.37 (d, J = 8.4 Hz, 4H; Ar-H), 7.15 (d, J = 8.4 Hz, 2H; Ar-H), 7.10 (d, J = 8.7 Hz, 2H; Ar-H), 6.76 (d, J = 8.4 Hz, 2H; Ar-H), 5.18 (d, J = 6.9 Hz, 1H; NH), 4.54 (q, J = 12.6 Hz, J = 6.3 Hz, 1H; benzyl), 3.77 (s, 3H; OMe), 2.87 (d, J = 6.0 Hz, 2H; CH_2), 2.35 (s, 3H; Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.4 (C), 143.4 (C), 137.4 (C), 131.9 (CH), 131.5, 130.1, 129.7, 129.5, 127.8, 127.2, 126.8 (t, J = 1.2 Hz; C), 125.7, 125.2 (q, J = 8.0 Hz, J = 4.2 Hz; CF_3), 122.1, 113.9, 87.6 (C), 82.6 (C), 55.7 (CH), 55.2 (OCH_3), 28.3 (CH_2), 21.3 (CH_3) ppm. HRMS (ESI-): calc'd for $C_{25}H_{22}NO_3SF_3$ $[M+H]^-$: *m/z* 472.1200; found *m/z* 472.1289.

1-(4-Methoxyphenyl)-4-(pyridin-2-yl)-*N*-tosylbut-3-yn-1-amine 4c. Synthesis according to general method 1: 2-bromopyridine (300 µL, 3.13 mmol, 1 equiv), sulfonamide **3** (1081 mg, 3.28 mmol, 1.05 equiv), $Pd(PPh_3)_2Cl_2$ (218 mg, 0.31 mmol, 10 mol%), CuI (119 mg, 0.62 mmol, 20 mol%), dry DMF (4 mL), piperidine (928 µL, 9.40 mmol, 3 equiv); stirred at 40 °C for 22 h; purification by column chromatography (silica, MPLC: hexane–ethyl acetate, gradient 50:50 to 40:60). Yield: 77% (987 mg). M.pt. 144.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.53 (d, J = 4.8 Hz, 1H; Pyr), 7.65 (d, J = 8.1 Hz, 2H; Ar-H), 7.60 (t, J = 7.8 Hz, 1H; Pyr), 7.26 (d, J = 7.8 Hz, 1H; Pyr), 7.23–7.17 (m, 1H; Pyr), 7.15 (d, J = 7.8 Hz, 2H; Ar-H), 7.13 (d, J = 8.7 Hz, 2H; Ar-H), 6.76 (d, J = 8.4 Hz, 2H; Ar-H), 5.29 (s_{br}, 1H; NH), 4.54 (q, J = 12.9 Hz, J = 6.3 Hz, 1H; benzyl), 3.75 (s, 3H; OMe), 2.87 (d, J = 6.3 Hz, 2H; CH_2), 2.35 (s, 3H; Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 149.9, 143.3, 143.1, 137.4, 136.1, 131.6, 129.5, 127.8, 127.2, 127.1, 122.8, 113.9, 85.3 (C), 83.4 (C), 55.5 (CH), 55.2 (OCH_3), 28.1 (CH_2), 21.3 (CH_3) ppm. HRMS (ESI+): calc'd for $C_{23}H_{22}N_2O_3S$ $[M+H]^+$: *m/z* 407.1424; found *m/z* 407.1371

1-(4-Methoxyphenyl)-4-phenyl-*N*-tosylbut-3-yn-1-amine 4d. Synthesis according to general method 1: iodobenzene (150 µL, 3.13 mmol, 1 equiv), sulfonamide **3** (1081 mg, 3.28 mmol, 1.05 equiv),

$Pd(PPh_3)_2Cl_2$ (218 mg, 0.31 mmol, 10 mol%), CuI (119 mg, 0.62 mmol, 20 mol%), dry DMF (4 mL), piperidine (928 µL, 9.40 mmol, 3 equiv); stirred at 40 °C for 22 h; purification by column chromatography (silica, MPLC: hexane–ethyl acetate, gradient 50:50 to 40:60). Yield: 86% (472 mg). M.pt 105.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.63 (d, J = 8.1 Hz, 2H; Ar-H), 7.31–7.26 (m, 5H; Ar-H), 7.16–7.11 (m, 4H; Ar-H), 6.76 (d, J = 8.4 Hz, 2H; Ar-H), 5.29 (d, J = 6.6 Hz, 1H; NH), 4.50 (q, J = 12.6 Hz, J = 6.0 Hz, 1H; benzyl), 3.76 (s, 3H; OMe), 2.81 (d, J = 6.3 Hz, 2H; CH_2), 2.35 (s, 3H; Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 143.3, 137.4, 131.8, 131.7, 129.5, 128.3, 128.2, 127.8, 127.2, 122.9, 113.8, 84.7 (C), 84.0 (C), 55.7 (CH), 55.2 (OCH_3), 28.3 (CH_2), 21.3 (CH_3) ppm. HRMS (ESI-): calc'd for $C_{24}H_{23}NO_3S$ $[M+H]^-$: *m/z* 405.1404; found *m/z* 405.1350.

Methyl 6-(4-(4-methoxyphenyl)-4-(tosylamine)but-1-ynyl)pyridine-2-carboxylate 4e. Synthesis according to general method 1: methyl 6-bromopyridine-2-carboxylate (300 mg, 3.13 mmol, 1 equiv), sulfonamide **3** (1081 mg, 3.28 mmol, 1.05 equiv), $Pd(PPh_3)_2Cl_2$ (218 mg, 0.31 mmol, 10 mol%), CuI (119 mg, 0.62 mmol, 20 mol%), dry DMF (4 mL), piperidine (928 µL, 9.40 mmol, 3 equiv); stirred at 40 °C for 22 h; purification by column chromatography (silica, MPLC: hexane–ethyl acetate, gradient 50:50 to 40:60). Yield: 77% (987 mg). M.pt. 136.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.1 Hz, 1H; pyr), 7.75 (t, J = 7.8 Hz, 1H; pyr), 7.65 (d, J = 8.1 Hz, 2H; Ar-H), 7.42 (d, J = 7.8 Hz, 1H; pyr), 7.16 (d, J = 8.1 Hz, 2H; Ar-H), 7.12 (d, J = 8.4 Hz, 2H; Ar-H), 6.75 (d, J = 8.7 Hz, 2H; Ar-H), 5.37 (d, J = 4.5 Hz, 1H; NH), 4.55 (q, J = 12.9 Hz, J = 6.3 Hz, 1H; benzyl), 3.99 (s, 3H; COOMe), 3.76 (s, 3H; OMe), 2.88 (d, J = 6.0 Hz, 2H; CH_2), 2.35 (s, 3H; Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 159.4, 148.2, 143.3, 137.4, 137.2, 131.5, 130.2, 129.5, 127.8, 127.2, 124.0, 113.9, 86.9 (C), 82.7 (C), 55.4 (CH), 55.2 (OCH_3), 52.9 (CH_3), 28.2 (CH_2), 21.3 (CH_3) ppm. HRMS (ESI+): calc'd for $C_{25}H_{24}N_2O_5S$ $[M+H]^+$: *m/z* 465.1479; found *m/z* 465.1413.

2-(4-Methoxyphenyl)-5-(1,3-bis(trifluoromethyl)phenyl)-1*H*-pyrrole 5a. General method 2: A flame-dried flask was charged with **4a** (200 mg, 0.37 mmol, 1 equiv), $TBAF.3H_2O$ (582 mg, 1.84 mmol, 5 equiv) and dry DMF (2 mL). The mixture was stirred at 80 °C for 48 h under a nitrogen atmosphere. Saturated NH_4Cl solution was added and the mixture was extracted with EtOAc (3×). The combined organic fractions were washed with water (2×), dried over Na_2SO_4 and solvents removed under reduced pressure. The residue was purified by column chromatography (silica, eluent MPLC: hexane–ethyl acetate, gradient 95:5 to 90:10) to obtain compound **5a** as a yellow solid (106 mg, 74%). M.pt 124.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (s, 1H; NH), 7.86 (s, 2H; Ar-H), 7.65 (s, 1H; Ar-H), 7.50 (d, J = 8.7 Hz, 2H; Ar-H), 6.97 (d, J = 9.0 Hz, 2H; Ar-H), 6.71 (t, J = 3.0 Hz, 1H; pyrrole), 6.50 (s, J = 2.7 Hz, 1H; pyrrole), 3.85 (s, 3H; Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.2, 135.5, 134.5, 132.4 (q, J = 65.6 Hz, J = 32.8 Hz, C; CF_3), 129.4, 125.7, 125.2, 124.8, 123.0, 121.6, 119.1–118.9 (m, C-CF_3), 114.6, 110.5, 107.7, 55.3 (OCH_3) ppm. HRMS (ESI-): calc'd for $C_{19}H_{14}NOF_6$ $[M+H]^-$: *m/z* 385.0861; found *m/z* 385.0749.

2-(4-Methoxyphenyl)-5-(4-trifluoromethylphenyl)-1*H*-pyrrole 5b. Synthesis according to general method 2: **4b** (200 mg, 0.42 mmol, 1 equiv), $TBAF.3H_2O$ (665 mg, 2.11 mmol, 5 equiv), dry DMF (2 mL); purification by column chromatography (silica, MPLC: hexane–ethyl acetate, gradient 85:15 to 80:20) to obtain compound **5b** as a yellow solid (92 mg, 68%). M.pt 197.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.51 (s, 1H; NH), 7.64–7.56 (m, 4H; Ar-H), 7.47 (d, J = 8.7 Hz, 2H; Ar-H), 6.98–6.93 (m, 2H; Ar-H), 6.66 (s_{br}, 1H; pyrrole), 6.49 (s_{br}, 1H; pyrrole), 3.84 (s, 3H; Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9, 135.8, 134.6, 130.9, 127.9, 127.5, 126.2–125.9 (m, C; CF_3), 125.5, 125.1, 123.3, 122.5,

114.5, 109.6, 107.4, 55.3 (OCH_3) ppm. HRMS (ESI+): calc'd for $C_{18}H_{15}NOF_3$ $[M+H]^+$: *m/z* 318.1100; found *m/z* 318.2368.

2-[5-(4-Methoxyphenyl)-1*H*-pyrrol-2-yl]-pyridine 5c. A flame-dried flask was charged with **4c** (200 mg, 0.49 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (34 mg, 0.05 mmol, 10 mol%), K_2CO_3 (340 mg, 2.46 mmol, 5 equiv) and dry DMF (2 mL). The mixture was stirred at 80 °C during 24 h under a nitrogen atmosphere. Subsequently, NaOH (393 mg, 9.84 mmol, 20 equiv) and 2 drops of water were added and the reaction mixture was stirred for another 3 h at 80 °C under a nitrogen atmosphere. Saturated NH_4Cl solution was added and the mixture was extracted with EtOAc (3×). The combined organic fractions were washed with water (2×), dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by column chromatography (silica, eluent MPLC: hexane–ethyl acetate, gradient 80:20 to 65:35) to obtain compound **5c** as a yellow solid (59 mg, 48%). M.pt. 122.5 °C. ^{1}H NMR (300 MHz, THF-d_8): δ = 10.62 (s, 1H; NH), 8.44 (d, J = 6.3 Hz, 1H; pyr), 7.64–7.61 (m, 4H; Ar-H, pyr), 7.01–6.95 (m, 1H; pyr), 6.91 (d, J = 8.7 Hz, 2H; Ar-H), 6.74 (t, J = 2.1 Hz, 1H; pyrrole), 6.43 (t, J = 2.3 Hz, 1H; pyrrole), 3.78 (s, 3H; Me) ppm. ^{13}C NMR (75 MHz, THF-d_8): δ = 159.9, 152.3, 149.8, 137.0, 135.7, 133.3, 126.8, 126.6, 120.8, 118.7, 114.9, 110.1, 107.7, 55.5 (OCH_3) ppm. HRMS (ESI+): calc'd for $C_{16}H_{14}N_2O$ $[M+H]^+$: *m/z* 250.1179; found *m/z* 250.1154.

2-(4-Methoxyphenyl)-5-(phenyl)-1*H*-pyrrole 5d. A flask was charged with compound **7d** (100 mg, 0.24 mmol, 1 equiv), NaOH (394 mg, 9.86 mmol, 40 equiv), DMF (2 mL) and 2 drops of water. The mixture was stirred at 80 °C during 72 h under a nitrogen atmosphere. Saturated NH_4Cl solution was added and the mixture was extracted with EtOAc (3×). The combined organic fases were washed with water (2×), dried over Na_2SO_4 and solvents were removed under reduced pressure. The residue was purified by column chromatography (silica, eluent MPLC: hexane–ethyl acetate, gradient 95:5 to 90:10) to obtain compound **5d** as a yellow solid (11 mg, 18%). M.pt. 158.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.46 (s, 1H; NH), 7.52–7.20 (m, 7H; Ar-H), 6.93 (d, J = 6.6 Hz, 2H; Ar-H), 6.55 (s_{br}, 1H; pyrrole), 6.45 (s_{br}, 1H; pyrrole), 3.82 (s, 3H; Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.6, 133.3, 132.7, 132.6, 129.0, 126.2, 125.7, 125.3, 123.7, 114.5, 107.8, 106.9, 55.3 (OCH_3). HRMS (ESI+): calc'd for $C_{17}H_{15}NO$ $[M+H]^+$: *m/z* 249.1148; found *m/z* 249.1125.

2,3-Dihydro-2-(4-methoxyphenyl)-*N*-tosylbut-3-yn-1-amine 6. Synthesis according to general method 2: *N*-tosylimine **3** (100 mg, 0.30 mmol, 1.0 equiv), TBAF.$3H_2O$ (478 mg, 1.51 mmol, 5 equiv), dry DMF (1 mL); purification by column chromatography (silica, MPLC: hexane–ethyl acetate, gradient 90:10 to 80:20) to obtain compound **6** as a yellow solid (69 mg, 69%). M.pt. 122.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.4, 2H; Ar-H), 7.28 (d, J = 8.7, 2H; Ar-H), 7.24 (d, J = 9.0, 2H; Ar-H), 6.51 (d, J = 9.0, 2H; Ar-H), 6.53–6.50 (m, 1H; Ar-H), 5.13–5.09 (m, 1H; CH), 4.68 (dd, J = Hz, J = Hz, 1H; benzyl), 3.79 (s, 3H; OCH_3), 2.94–2.84 (m, 1H), 2.51–2.47 (m, 1H), 2.42 (s, 3H; CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1, 143.6, 134.9, 134.3, 130.8, 129.5, 128.0, 127.6, 127.3, 113.9, 113.7, 109.9, 62.6 (CH), 55.2 (OCH_3), 40.5 (CH_2), 21.4 (CH_3) ppm. HRMS (ESI+): calc'd for $C_{18}H_{19}NO_3S$ $[M+H]^+$: *m/z* 330.1158; found *m/z* 330.1198;

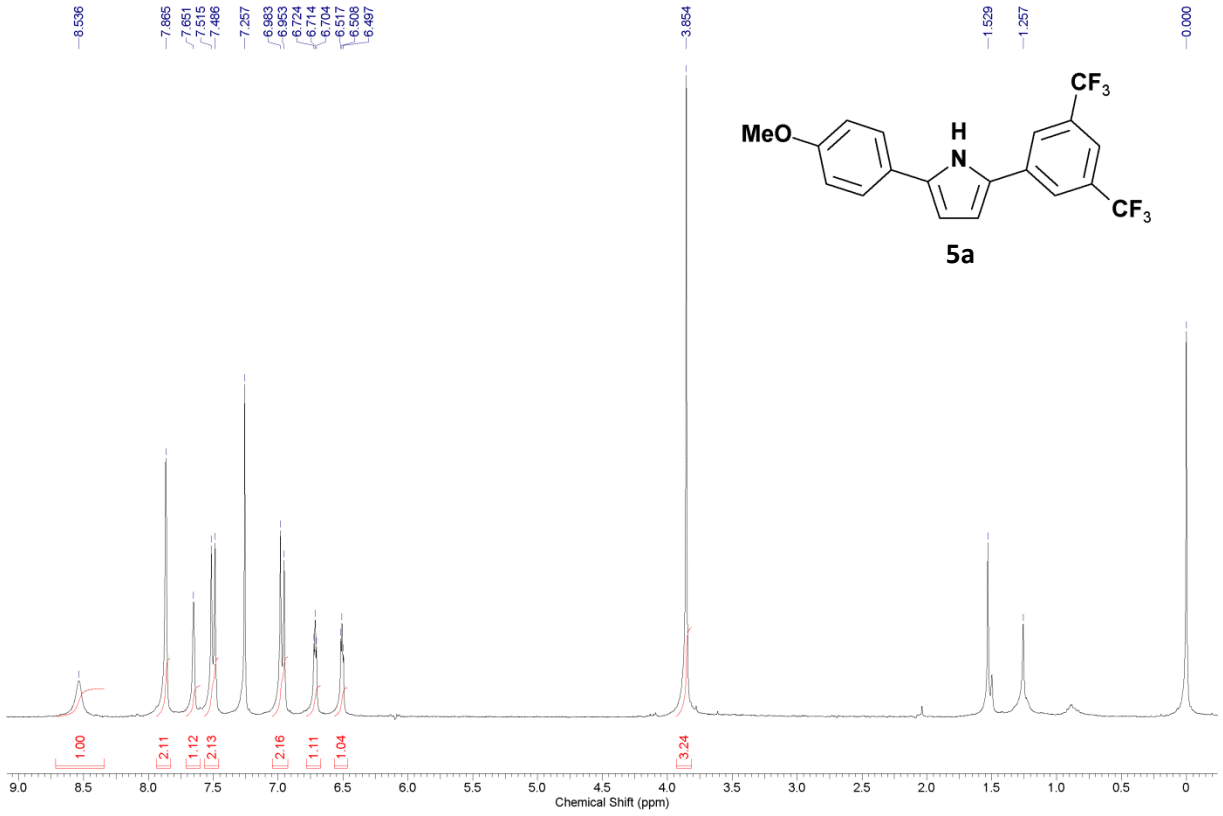
5-(4-(Trifluoromethyl)phenyl)-2,3-dihydro-2-(4-methoxyphenyl)-1-tosyl-1*H*-pyrrole 7b. General method 3: A flame-dried flask was charged with **4b** (120 mg, 0.25 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (18 mg, 0.02 mmol, 10 mol%), K_2CO_3 (175 mg, 1.26 mmol, 5 equiv) and dry DMF (2 mL). The mixture was stirred at 80 °C during 24 h. Saturated NH_4Cl solution was added and the mixture was extracted with

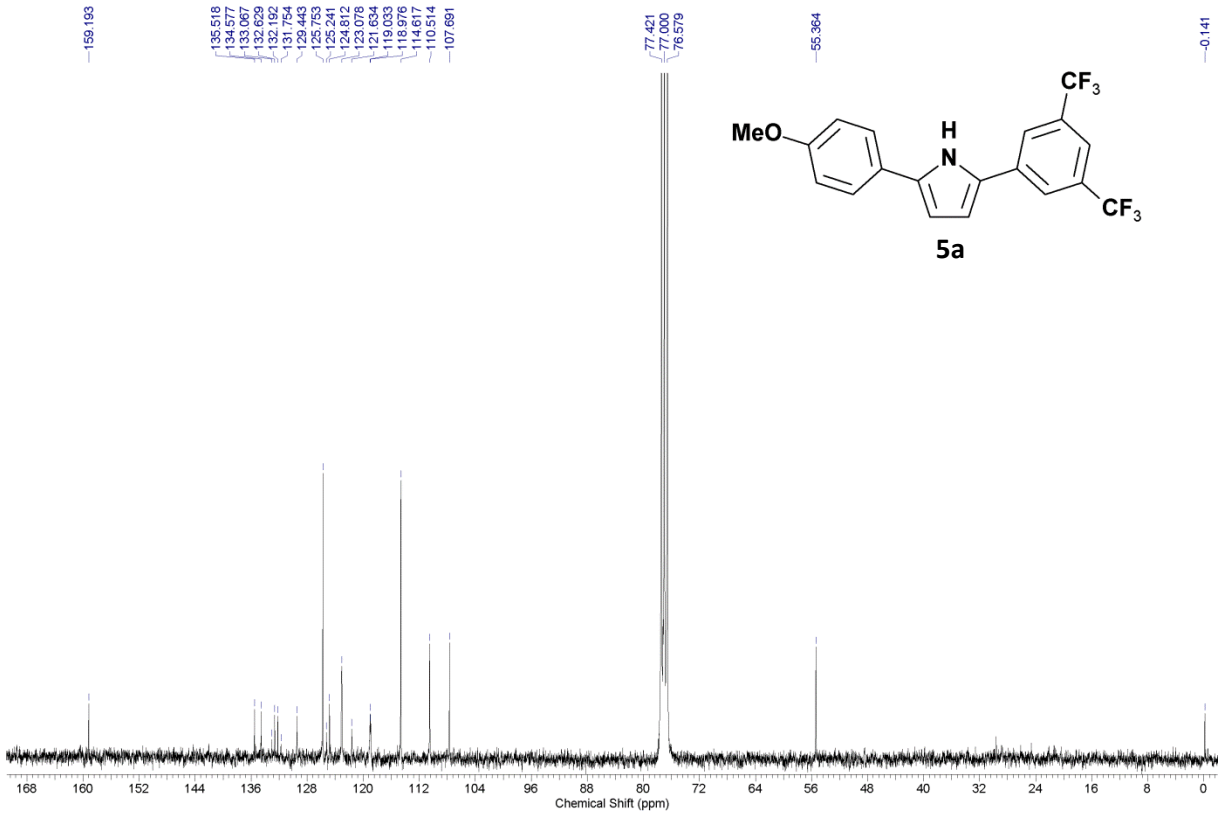
EtOAc (3×). The combined organic fractions were washed with water (2×), dried over Na_2SO_4 and solvents were removed under reduced pressure. The residue was purified by column chromatography (silica, MPLC: hexane–ethyl acetate, gradient 85:15 to 75:25) to obtain compound **7b** as a yellowish solid (33 mg, 27%). M.pt. 137.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.1 Hz, 2H; Ar-H), 7.63–7.58 (m, 4H; Ar-H), 7.35 (dt, J = 8.7 Hz, J = 2.7 Hz, 2H; Ar-H), 7.30 (d, J = 8.1 Hz, 2H; Ar-H), 6.89 (dt, J = 8.7 Hz, J = 3.0 Hz, 2H; Ar-H), 5.56 (dd, J = 3.9 Hz, J = 2.4 Hz, 1H; CH), 4.53 (dd, J = 9.0 Hz, J = 2.4 Hz, 1H; benzyl), 3.80 (s, 3H; O CH_3), 2.45 (s, 3H; CH_3), 2.45–2.30 (m, 2H; CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3 (C), 144.1 (C), 143.4 (C), 136.8 (C), 134.7 (C), 134.3 (C), 130.7, 130.3, 129.6 (CH; Ar-CH), 127.9 (CH; ; Ar-CH), 127.7 (CH; Ar-CH), 127.0 (CH; Ar-CH), 125.9, 125.1 (q, J = 7.4 Hz, J = 3.6 Hz; CF_3), 122.3, 118.5 (CH), 114.2 (CH; Ar-CH), 64.9 (CH), 55.2 (OCH_3), 36.7 (CH_2), 21.5 (CH_3) ppm. HRMS (ESI+): calc'd for $C_{25}H_{22}NO_3SF_3$ $[M+H]^+$: *m/z* 474.1345; found *m/z* 474.1285;

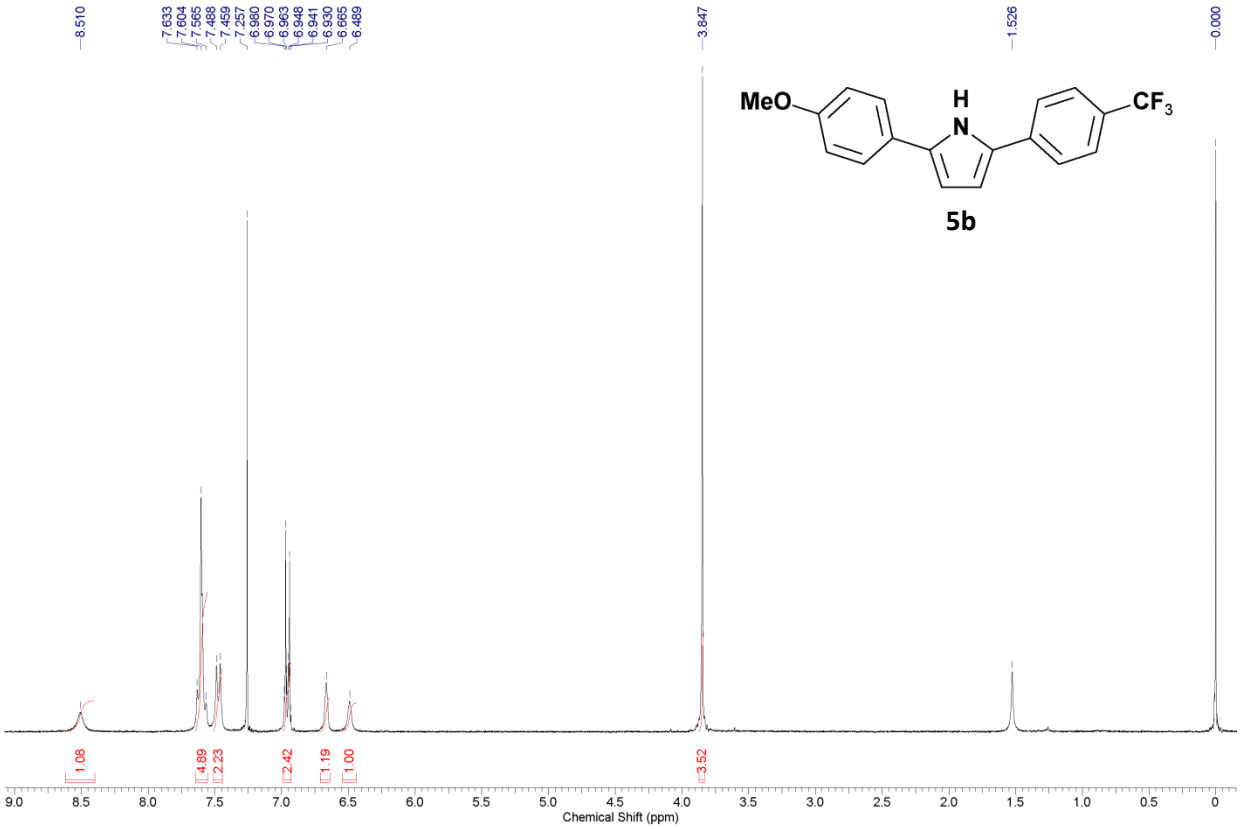
2-(4,5-Dihydro-5-(4-methoxyphenyl)-1-tosyl-1*H*-pyrrol-2-yl)pyridine 7c. Synthesis according to general method 3: **4c** (159 mg, 0.39 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (27 mg, 0.04 mmol, 10 mol%), K_2CO_3 (270 mg, 1.95 mmol, 5 equiv), dry DMF (2 mL); purification by column chromatography (silica, MPLC: hexane–ethyl acetate, gradient 85:15 to 75:25) to obtain compound **7c** as a yellowish solid (90 mg, 60%). M.pt. 57.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.60–8.57 (m, 1H; Ar-H), 7.80 (d, J = 8.1 Hz, 1H; Ar-H), 7.74–7.68 (m, 3H; Ar-H), 7.37–7.30 (m, 4H; Ar-H), 7.25–7.21 (m, 1H; Ar-H), 6.86 (dt, J = 8.7 Hz, J = 3.0 Hz, 2H; Ar-H), 5.98 (t, J = 3.0 Hz, 1H; CH), 5.24 (dd, J = 6.6 Hz, J = 3.9 Hz, 1H; benzyl), 3.79 (s, 3H; OCH_3), 2.43 (s, 3H; CH_3), 2.44–2.29 (m, 2H; CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.2, 151.8, 149.0, 144.0, 135.9, 134.6, 133.8, 133.3, 133.1, 129.6, 128.8, 128.6, 128.1, 127.1, 125.8, 123.5, 123.1, 120.6, 114.1, 65.2 (CH), 55.2 (OCH_3), 36.5 (CH_2), 21.5 (CH_3) ppm. HRMS (ESI+): calc'd for $C_{23}H_{22}N_2O_3S$ $[M+H]^+$: *m/z* 407.1424; found *m/z* 407.1404.

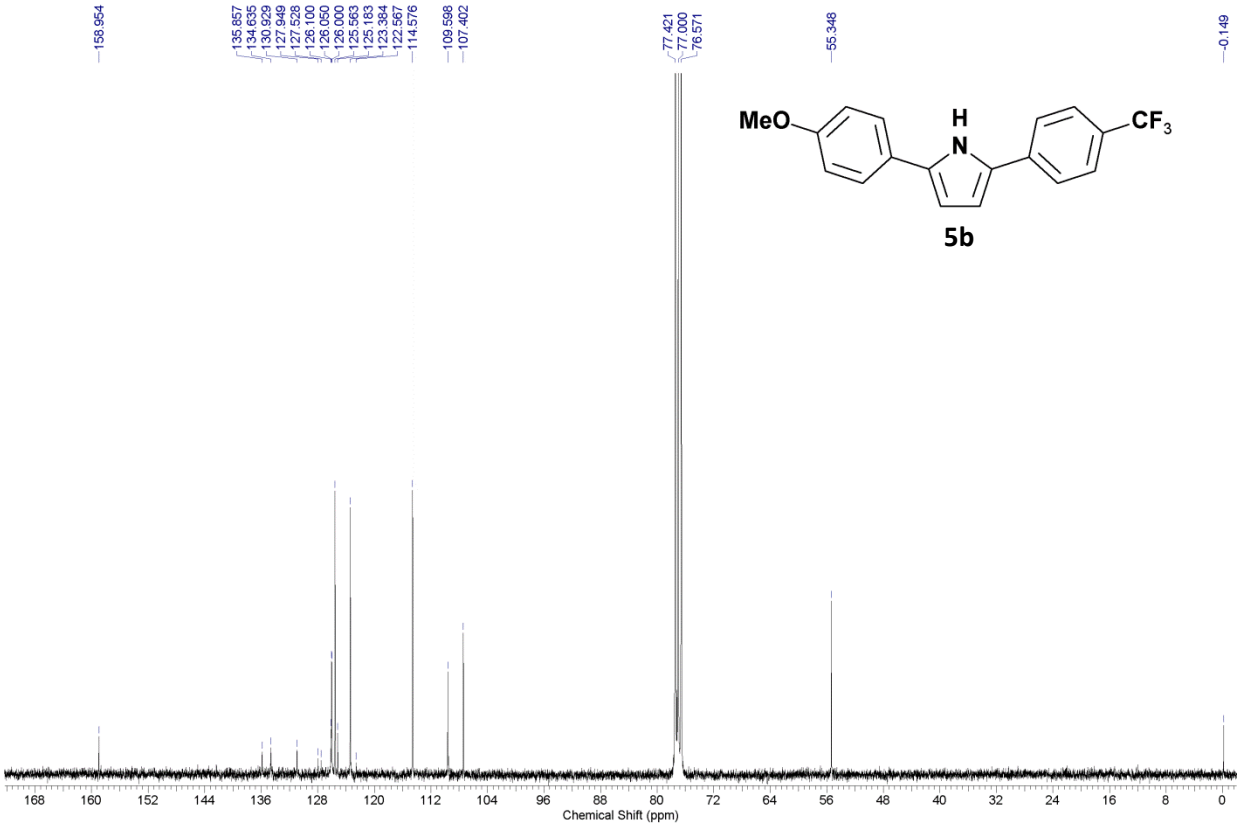
2,3-Dihydro-2-(4-methoxyphenyl)-5-phenyl-1-tosyl-1*H*-pyrrole 7d. Synthesis according to general method 3: **4d** (100 mg, 0.24 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (17 mg, 0.02 mmol, 10 mol%), K_2CO_3 (170 mg, 1.23 mmol, 5 equiv), dry DMF (2 mL); stirred at 100 °C for 48 h; purification by column chromatography (silica, MPLC: hexane–ethyl acetate, gradient 90:10 to 70:30) to obtain compound **7d** as a yellowish solid (33 mg, 33%). M.pt. 52.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.58 (m, 4H; Ar-H), 7.413–7.34 (m, 5H; Ar-H), 7.29 (d, J = 8.1 Hz, 2H; Ar-H), 6.88 (dt, J = 9.0 Hz, J = 3.0 Hz, 2H; Ar-H), 5.42 (q, J = 3.6 Hz, J = 2.1 Hz, 1H; Ar-H), 5.30 (dd, J = 8.7 Hz, J = 1.8 Hz, 1H; CH), 3.79 (s, 3H; OMe), 2.44 (s, 3H; Me), 2.41–2.26 (m, 2H; CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1 (C), 144.5 (C), 143.8, 135.2, 134.5, 133.3, 129.7, 129.4, 128.8, 128.7, 128.3, 128.0, 127.9, 127.6, 127.0, 116.1, 114.0, 64.8 (CH), 55.2 (OCH_3), 36.6 (CH_2), 21.5 (CH_3) ppm. HRMS (ESI+): calc'd for $C_{24}H_{23}NO_3S$ $[M+H]^+$: *m/z* 406.1471; found *m/z* 406.1438.

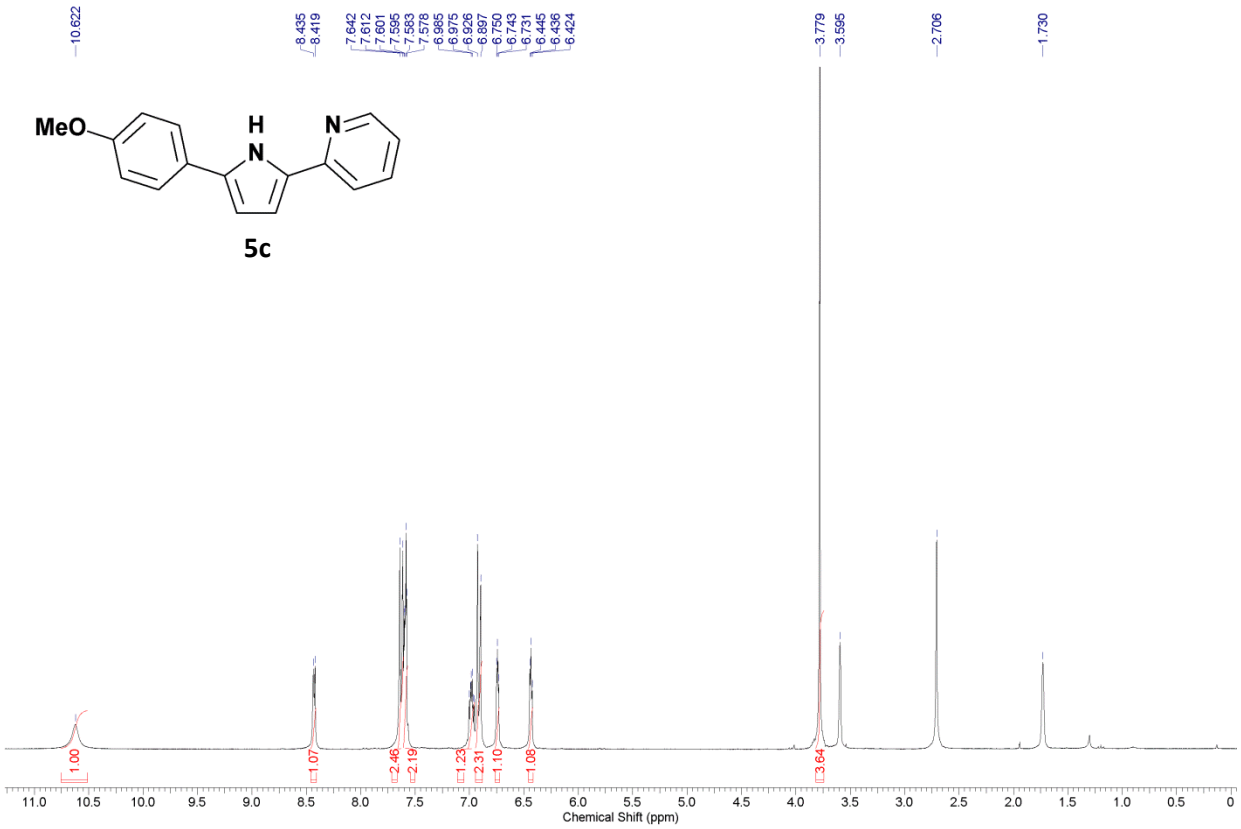
3. ^{1}H and ^{13}C NMR spectra of pyrroles 5a–d

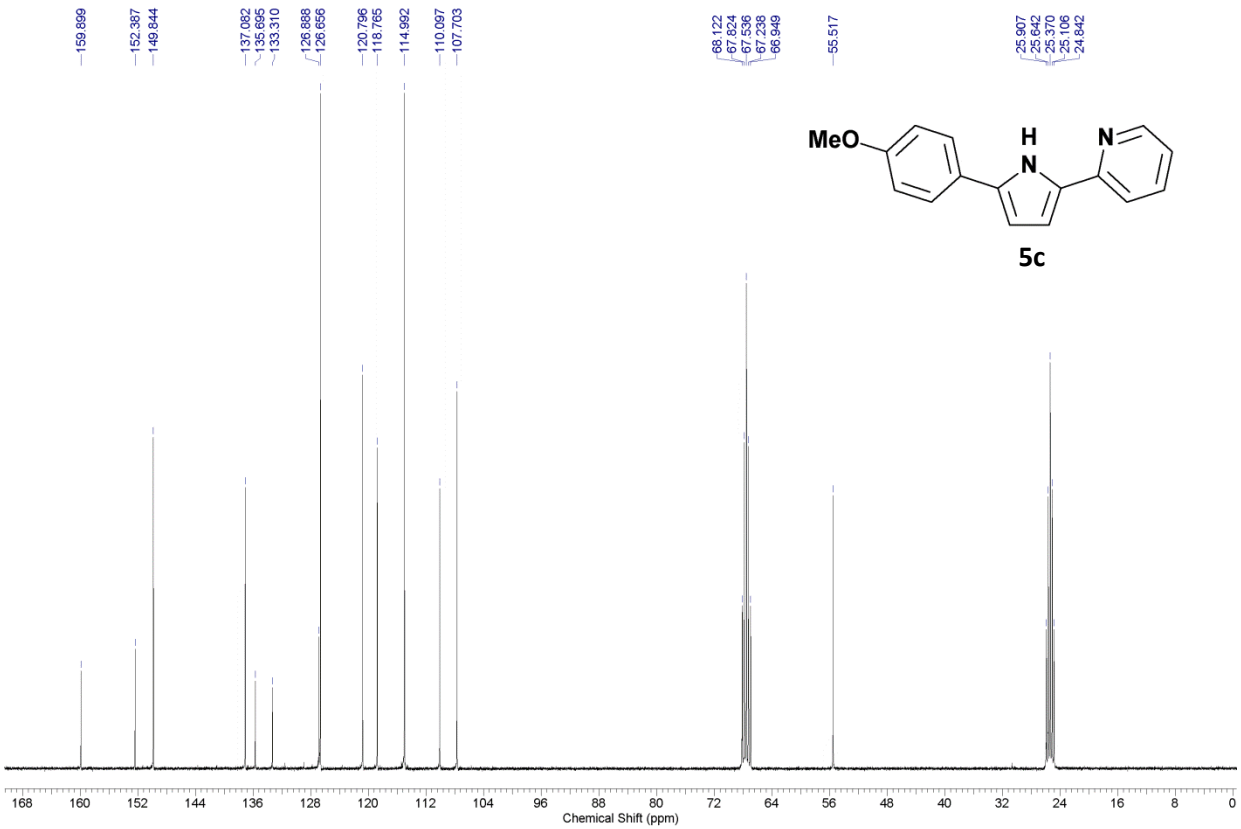


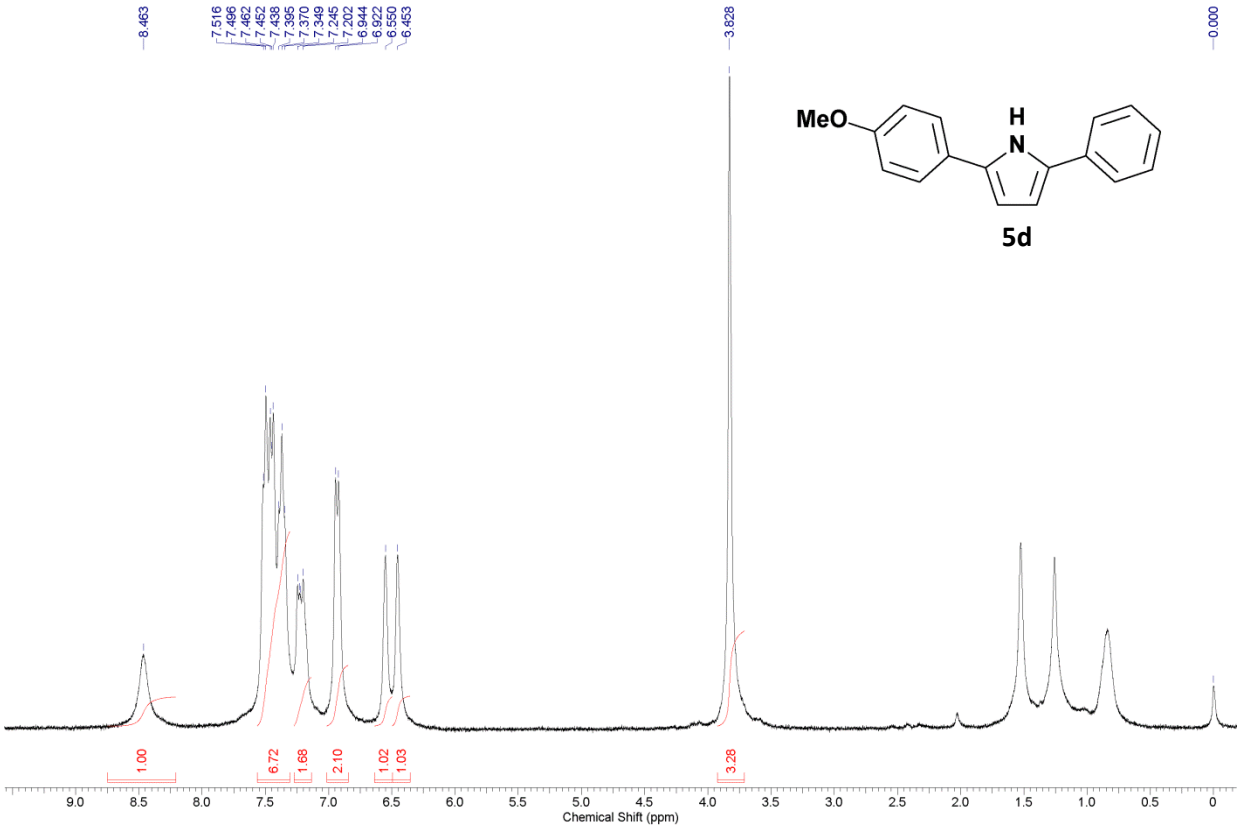


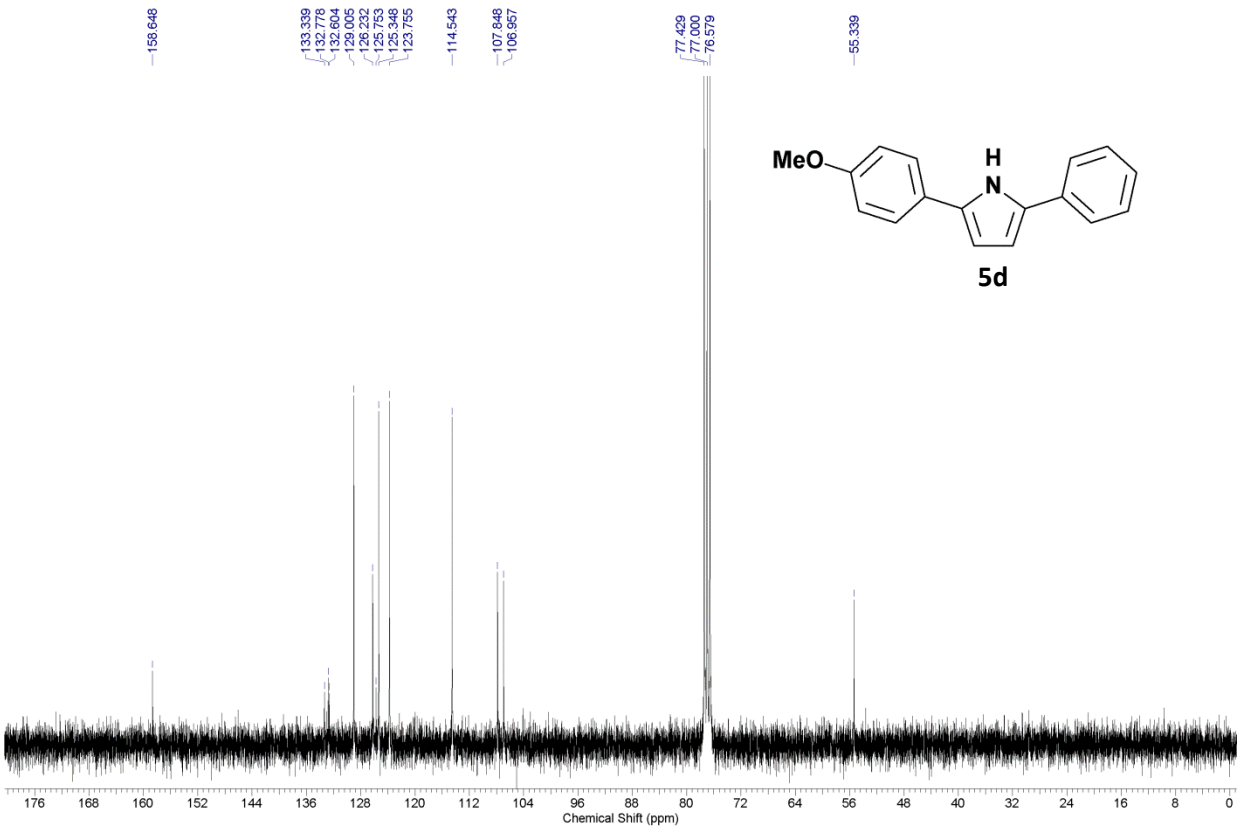









8.463
7.516
7.496
7.462
7.452
7.438
7.395
7.370
7.349
7.245
7.202
6.944
6.922
6.550
6.453
3.828
0.000
MeO
H
N
5d
1.00
6.72
1.68
2.10
1.02
1.03
3.28
Chemical Shift (ppm)


158.648
133.339
132.778
132.604
129.005
126.232
125.753
125.348
123.755
114.543
107.848
106.957
77.429
77.000
76.579
55.339
MeO
H
N
5d
Chemical Shift (ppm)

4. X-ray crystallographic structure and data for pyrrole 5c

Data collection was performed using MoKα radiation (λ = 0.71073 Å) on a RIGAKU VariMax Saturn diffractometer equipped with a CCD detector. Prior to the diffraction experiment the crystals were flash-cooled to 100 K in a cold N_2 gas flow. Cell refinement and data reduction were carried out by the program d*trek package in CrystalClear software suite.[2] The structures were solved by direct methods (SIR-92)[3] and refined by full-matrix least squares on F^2 using the SHELXL-97[4] in WinGX program package.[5] Nonhydrogen atoms were anisotropically refined and the hydrogen atoms were placed on calculated positions with temperature factors fixed at 1.2 times Ueq of the parent atoms and 1.5 times Ueq for methyl groups. The fundamental crystal data and experimental parameters for the structure determinations are summarized below. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 962821. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK:http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

formula	$C_{16}H_{14}N_2O_1$
M (g mol^{-1})	250.29
crystal dimensions (mm^3)	0.12 x 0.24 x 0.07
T (K)	100(2)
crystal system	Monoclinic
space group	$P\,2_1$
a (Å)	5.6181(4)
b (Å)	21.2320(19)
c (Å)	10.8628(9)
β (deg)	98.103(2)
V (Å^3)	1282.82(18)
Z	2
ρ_{calc} (g cm^{-3})	1.413
μ (mm^{-1})	0.082
F(000)	524
λ (Å)	0.71073 (Mo Kα)
θ_{max} (deg)	31.070
measured reflections	6030
unique reflections	3938
observed reflections (Io > 2σ(Io))	3256
parameters refined	354
R_1	0.0414
wR_2[a]	0.1013
R_1 (all data)	0.0579
wR_2 (all data)	0.1152
GOOF	1.031

[2] *CrystalClear,* Rigaku Corporation, Tokyo, Japan (2005).
[3] A. Altomare, G. Cascarano, C. Giacovazzo, and A. Guagliardi *J. Appl. Cryst.* 1993, **26**, 343.
[4] G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112.
[5] L. J. Farrugia, *J. Appl. Cryst.* 1999, **32**, 837.

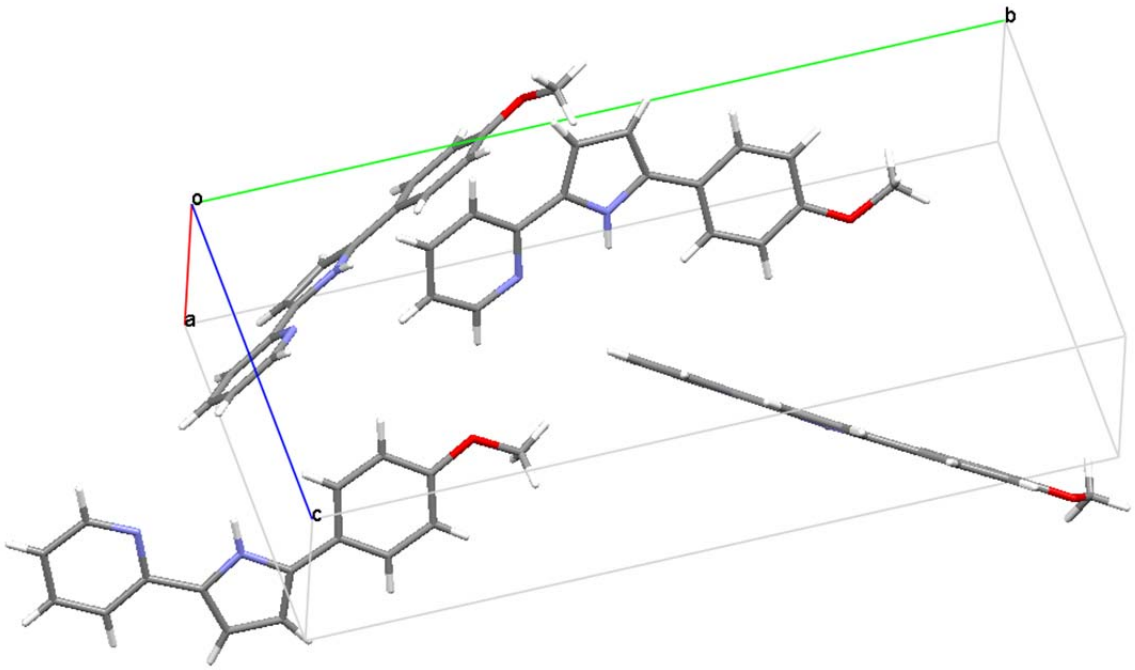


Figure S1. Unit cell for pyrrole **5c**.