Supporting Information

Atom-Efficient Iron-Catalyzed Cascade Synthesis of Pyrroles from Nitroarenes under Low-Pressure Conditions

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S1. General Information

Chemicals Availability

All chemicals were purchased from commercial suppliers (Sigma-Aldrich, TCI, BLDpharm, abcr or Enamine) and used without further purification. Ph-tetraphos ligand was synthesized following a previously reported procedure.[1] Anhydrous and oxygen-free solvents were either received from an Innovative Technology PS-MD-6 solvent purification system (THF, toluene, *i*-PrOH) or prepared using the freeze-pump-thaw technique. All anhydrous solvents were stored over 3 Å or 4 Å molecular sieves under an argon atmosphere. Unless otherwise stated, reactions were carried out under an inert atmosphere using standard Schlenk and glovebox techniques to exclude air and moisture.

Column Chromatography

Flash column chromatography was performed with a Combi Flash Rf + from Teledyne ISCO using HPLC grade solvents.

Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded on a Bruker Fourier 300 (300 MHz), Bruker Avance 300 (300 MHz), or Bruker Avance 400 (400 MHz) NMR spectrometer. The chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) in hertz (Hz). All chemical shifts (δ) are given relative to solvent: references for $CDCl_3$ 7.26 ppm (^1H) and 77.16 ppm (^{13}C). Multiplets of NMR were assigned as s (singlet), br (broad), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), and m (multiplet). All NMR measurements were carried out at room temperature.

Gas Chromatography

GC-MS measurements were performed using an Agilent 8890 chromatograph equipped with a HP-5 column (30 m × 250 µm × 0.25 µm) connected to an Agilent 5977B GC/MSD.

S2. Reaction Optimization

S2.1. Acid Screening

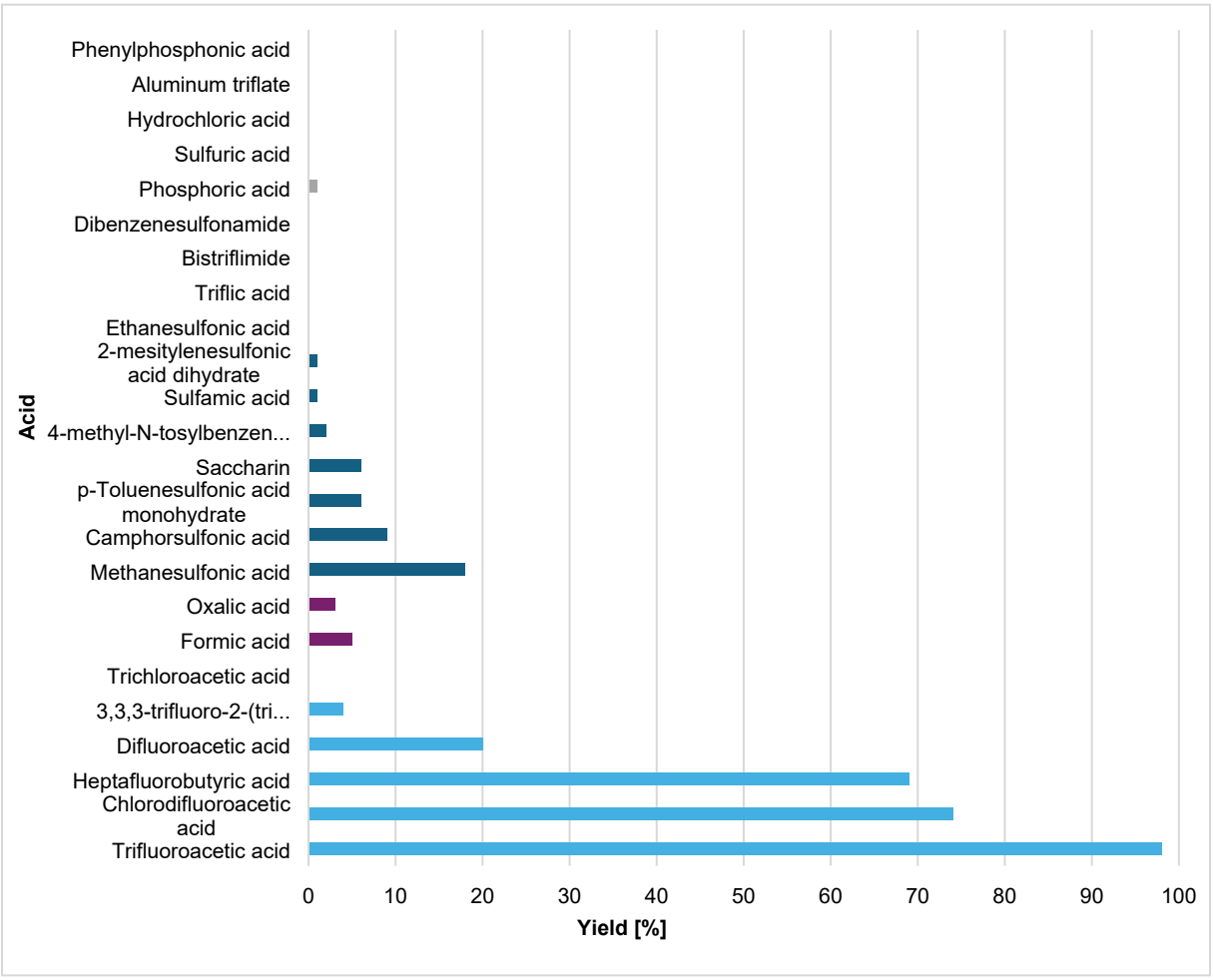


Figure S1. Screening of acids in the cascade synthesis of pyrroles from nitroarenes. Reaction conditions: $Fe(BF_4)_2 \cdot 6H_2O$ (3.4 mg, 2 mol%), **L1** (8.2 mg, 2 mol%), acid (0.25 mmol, 0.5 equiv.), nitrobenzene (0.5 mmol, 1.0 equiv.), 2,5-hexanedione (0.6 mmol, 1.2 equiv.), THF (1.5 mL), H_2 (20 bar), 120 °C, 2 h. Yields were determined by GC-FID analysis using hexadecane as internal standard. Grey: strong mineral acids / Lewis acids; green: sulfonic acids / sulfonamides / sulfonyl-imide derivatives; violet: non-halogenated carboxylic acids; light blue: halogenated carboxylic acids.

Table S1. Screening of acids in the cascade synthesis of pyrroles from nitroarenes.

Group	**Acid**	**Yield** [%]
Phosphonic acid	Phenylphosphonic acid	0
Mineral acid / Lewis acid	Aluminum triflate	0
	Hydrochloric acid	0
	Sulfuric acid	0
	Phosphoric acid	1
Sulfonic acid / sulfonamide / sulfonyl-imide derivative	Dibenzenesulfonamide	0
	Bistriflimide	0
	Triflic acid	0
	Ethanesulfonic acid	0
	2-mesitylenesulfonic acid dihydrate	1
	Sulfamic acid	1
	4-methyl-N-tosylbenzenesulfonamide	2
	Saccharin	6
	p-Toluenesulfonic acid	6
	Camphorsulfonic acid	9
	Methanesulfonic acid	18
Non-halogenated carboxylic acid	Oxalic acid	3
	Formic acid	5
Halogenated carboxylic acid	Trichloroacetic acid	0
	3,3,3-trifluoro-2-(trifluoromethyl)propionic acid	4
	Difluoroacetic acid	20
	Heptafluorobutyric acid	69
	Chlorodifluoroacetic acid	74
	Trifluoroacetic acid	98

Reaction conditions: $Fe(BF_4)_2 \cdot 6H_2O$ (0.01 mmol, 2 mol%), **L1** (0.01 mmol, 2 mol%), acid (0.25 mmol, 0.5 equiv.), nitrobenzene (0.5 mmol, 1.0 equiv.), 2,5-hexanedione (0.6 mmol, 1.2 equiv.), THF (1.5 mL), H_2 (20 bar), 120 °C, 2 h. Yields were determined by GC-FID analysis using hexadecane as internal standard.

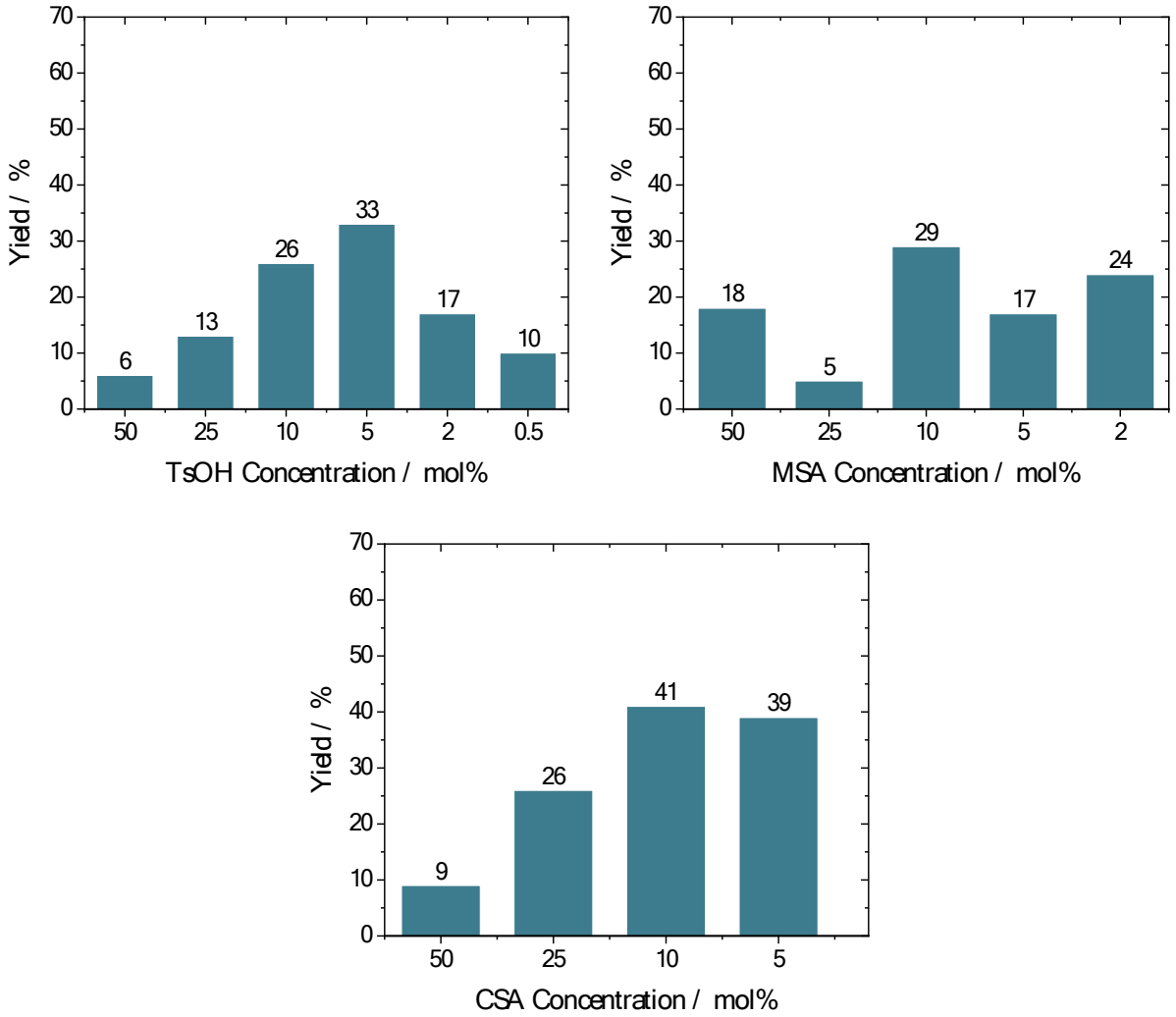


Figure S2. Screening of sulfonic acids in the cascade synthesis of pyrroles from nitroarenes: effect of acid concentration. Reaction conditions: $Fe(BF_4)_2 \cdot 6H_2O$ (3.4 mg, 2 mol%), Ph-tetraphos (8.2 mg, 2 mol%), nitrobenzene (0.5 mmol, 1.0 equiv.), 2,5-hexanedione (0.6 mmol, 1.2 equiv.), THF (1.5 mL), H_2 (20 bar), 120 °C, 2 h. Yields were determined by GC-FID analysis using hexadecane as internal standard. TsOH: *p*-Toluenesulfonic acid; MSA: methanesulfonic acid; CSA: camphorsulfonic acid.

S2.2. Solvent Screening

Table S2. Screening of solvents in the cascade synthesis of pyrroles from nitroarenes.

Solvent	**Yield** [%]
2-pentanol	72
THF	71
2-butanol	66
i-PrOH	65
2-methyl-2-butanol	58
t-BuOH	51
1,2-dimethoxyethane	51
1-butanol	47
1-pentanol	45
EtOH	38
Cyclohexanol	37
1,4-dioxane	19
MeOH	12
Cyclohexane	<5
Toluene	<5
Dibutyl ether	<5
1,2-propanediol	<5
Ethylen glycol	<5
Diethylene glycol	<5

Reaction conditions: $Fe(BF_4)_2 \cdot 6H_2O$ (0.01 mmol, 2 mol%), **L1** (0.01 mmol, 2 mol%), TFA (0.25 mmol, 0.5 equiv.), nitrobenzene (0.5 mmol, 1.0 equiv.), 2,5-hexanedione (0.6 mmol, 1.2 equiv.), solvent (1.5 mL), H_2 (20 bar), 100 °C, 1 h. Yields were determined by GC-FID analysis using hexadecane as internal standard.

S2.3. Fe Precursor Screening

Table S3. Screening of Fe precursors in the cascade synthesis of pyrroles from nitroarenes.

Precursor	**Yield** [%]
$Fe(BF_4)_2 \cdot 6H_2O$	55
$Fe(OAc)_2$	55
$Fe(acac)_2$	52
$Fe(OTf)_2$	18
$FeBr_2$	<5
$FeCl_2$	<5

Reaction conditions: Fe precursor (0.01 mmol, 2 mol%), **L1** (0.01 mmol, 2 mol%), TFA (0.5 mmol, 1.0 equiv.), nitrobenzene (0.5 mmol, 1.0 equiv.), 2,5-hexanedione (0.6 mmol, 1.2 equiv.), THF (1.5 mL), H_2 (20 bar), 100 °C, 1 h. Yields were determined by NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

S2.4. Pressure Optimization

Table S4. Pressure optimization in the cascade synthesis of pyrroles from nitroarenes.

H_2 Pressure [bar]	**Yield** [%]
20	83
5	84
1	13

Reaction conditions: $Fe(BF_4)_2 \cdot 6H_2O$ (0.01 mmol, 2 mol%), **L1** (0.01 mmol, 2 mol%), TFA (0.5 mmol, 1.0 equiv.), nitrobenzene (0.5 mmol, 1.0 equiv.), 2,5-hexanedione (0.6 mmol, 1.2 equiv.), THF (1.5 mL), 80 °C, 18 h. Yields were determined by NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

S2.5. TFA Concentration Optimization

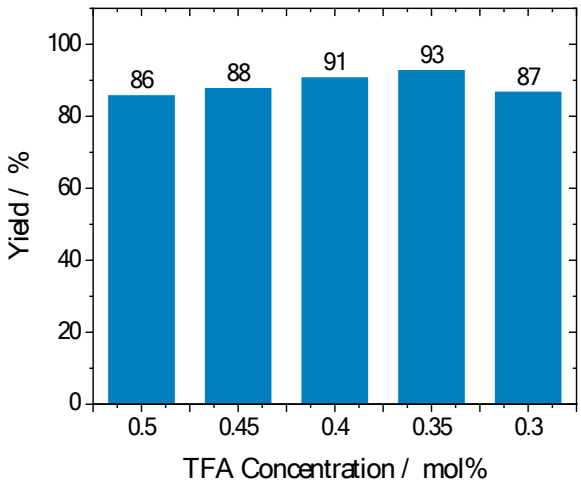


Figure S3. Optimization of the TFA concentration in the cascade synthesis of pyrroles from nitroarenes. Reaction conditions: $Fe(BF_4)_2 \cdot 6H_2O$ (3.4 mg, 2 mol%), **L1** (8.2 mg, 2 mol%), nitrobenzene (0.5 mmol, 1.0 equiv.), 2,5-hexanedione (0.6 mmol, 1.2 equiv.), THF (1.5 mL), H_2 (5 bar), 80 °C, 18 h. Yields were determined by NMR analysis using 1,3,5-trimethoxybenzene as internal standard. TFA: trifluoroacetic acid.

S2.6. Control Experiments

Table S5. Control experiments.

Entry	Fe Source	Ligand	TFA	Yield [%]
1	X	✓	✓	<5
2	✓	x	✓	<5
3	✓	✓	x	8
4	x	x	✓	<5
5	x	✓	x	<5
6	✓	x	x	<5
7	x	x	x	<5

Reaction conditions: $Fe(BF_4)_2 \cdot 6H_2O$(0.01 mmol, 2 mol%), **L1** (0.01 mmol, 2 mol%), TFA (0.5 mmol, 1.0 equiv.), nitrobenzene (0.5 mmol, 1.0 equiv.), 2,5-hexanedione (0.6 mmol, 1.2 equiv.), THF (1.5 mL), H_2 (20 bar), 80 °C, 18 h. Yields were determined by NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

S3. Synthesis and Characterization of Products

S3.1. Synthesis: General Procedures

General Procedure 1 (GP1): 3.4 mg of $Fe(BF_4)\cdot 6H_2O$ (2.0 mol%, 0.01 mmol) were added to an 8 mL glass vial under ambient conditions. Inside a glovebox, 8.2 mg of **L1** (2.0 mol%, 0.01 mmol) were added, followed by a stirring bar. The vial was capped with a septum cap and removed from the glovebox. Under argon flow, 1.5 mL of THF, 70 µL of 2,5-hexanedione (1.2 equiv., 0.6 mmol), 14 µL / 40 µL of TFA (0.35 equiv. / 1.00 equiv., 0.175 mmol / 0.5 mmol), and substrate (1.0 equiv., 0.5 mmol) were added in sequence. Note: substrate was added with no special precautions (*e.g.*, degassing). In the case of solid substrates, these were weighed together with the iron precursor outside the glovebox.

After the additions, the vial was placed into an alloy plate and transferred to an argon-flushed 300 mL autoclave. The septum cap of the vial was pierced with a syringe needle to allow free gas flow before closing the autoclave. Once tightly closed, the autoclave was sequentially flushed with hydrogen (3 x 15 bar) and pressurized to the desired pressure (5 bar). The autoclave was then placed into an aluminum heating block and left to stir for 18 hours at 80 °C. After the reaction time had elapsed, the autoclave was removed from the heating block and cooled to room temperature. Pressure was carefully released, and the autoclave was opened. NEt_3 were added in stoichiometric amounts to neutralize the excess of TFA. The solution was then transferred to a round-bottom flask, diluted with ethyl acetate, and silica was added. The solvent was removed under reduced pressure using a rotary evaporator, and the product was purified by flash chromatography.

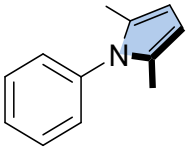
General Procedure 2 (GP2): 3.4 mg of $Fe(BF_4)\cdot 6H_2O$ (2.0 mol%, 0.01 mmol) were added to an 8 mL glass vial under ambient conditions. Inside a glovebox, 8.2 mg of **L1** (2.0 mol%, 0.01 mmol) were added, followed by a stirring bar. The vial was capped with a septum cap and removed from the glovebox. Under argon flow, 1.5 mL of THF, 70 µL of 2,5-hexanedione (1.2

equiv., 0.6 mmol), 40 µL of TFA (1.00 equiv., 0.5 mmol), and substrate (1.0 equiv., 0.5 mmol) were added in sequence. Note**:** substrate was added with no special precautions (*e.g.*, degassing). In the case of solid substrates, these were weighed together with the iron precursor outside the glovebox.

After the additions, the vial was placed into an alloy plate and transferred to an argon-flushed 300 mL autoclave. The septum cap of the vial was pierced with a syringe needle to allow free gas flow before closing the autoclave. Once tightly closed, the autoclave was sequentially flushed with hydrogen (3 x 15 bar) and pressurized to the desired pressure (5 bar). The autoclave was then placed into an aluminum heating block and left to stir for 18 hours at 80 °C. After the reaction time had elapsed, the autoclave was removed from the heating block and cooled to room temperature. Pressure was carefully released, and the autoclave was opened. The reaction mixture was diluted with ethyl acetate and transferred to an extraction funnel, together with 15 mL of a saturated Na_2CO_3 solution. The phases were separated, and the aqueous phase was extracted with ethyl acetate (or dichloromethane, for substrate **21a**) (3 x 10 mL). The combined organic extracts were washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The product was purified by flash chromatography on silica.

S.3.2. Characterization of Products

S.3.2.1. 2,5-dimethyl-1-phenyl-1*H*-pyrrole (1b)



Known compound.[2] Prepared according to **GP1** starting from nitrobenzene (60.1 mg, 0.488 mmol).

Chemical Formula: $C_{12}H_{13}N$.

Molecular Weight: 171.2430 g mol^{-1}.

Appearance: off-white solid.

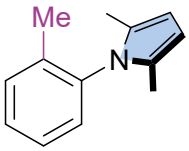
Yield: 92% (77.1 mg, 0.450 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.36 (m, 3H), 7.27 – 7.19 (m, 2H), 5.91 (s, 2H), 2.04 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 129.2, 128.9, 128.4, 127.8, 105.8, 13.1.

GC-MS: *m/z* (%) 171.14 (M^+, 100), 170.15 ($[M-H]^+$, 100), 156.08 (21), 154.07 (22), 129.07 (14), 128.06 (14), 115.05 (9), 77.06 (27), 51.06 (15).

S.3.2.2. 2,5-dimethyl-1-(*o*-tolyl)-1*H*-pyrrole (2b)



Known compound.[3] Prepared according to **GP2** starting from 1-methyl-2-nitrobenzene (67.3 mg, 0.491 mmol).

Chemical Formula: $C_{13}H_{15}N$.

Molecular Weight: 185.2700 g mol^{-1}.

Appearance: yellow oil.

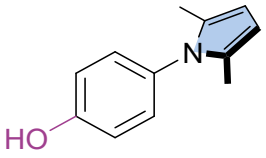
Yield: 62% (56.7 mg, 0.306 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 3H), 7.21 – 7.16 (m, 1H), 5.94 (s, 2H), 1.96 (s, 3H), 1.94 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 137.2, 130.8, 129.0, 128.5, 128.3, 126.8, 105.3, 17.2, 12.7.

GC-MS: *m/z* (%) 185.10 (M^+, 100), 184.08 ([M-H]$^+$, 93), 170.07 (100), 154.01 (30), 128.00 (10), 114.99 (4), 91.06 (14), 65.01 (9).

S.3.2.3. 4-(2,5-dimethyl-1*H*-pyrrol-1-yl)phenol (3b)



Known compound.[2] Prepared according to **GP1** starting from 4-nitrophenol (69.0 mg, 0.496 mmol).

Chemical Formula: $C_{12}H_{13}NO$.

Molecular Weight: 187.2420 g mol^{-1}.

Appearance: off-white solid.

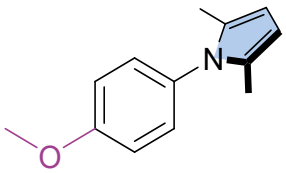
Yield: 88% (82.0 mg, 0.438 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 – 7.04 (m, 2H), 6.93 – 6.85 (m, 2H), 5.90 (s, 2H), 4.97 (s, 1H), 2.02 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 132.1, 129.6, 129.2, 115.9, 105.4, 13.1.

GC-MS: *m/z* (%): 187.11 (M^+, 100), 186.10 ([M-H]$^+$, 86), 172.05 (15), 145.05 (19), 131.03 (19), 115.04 (8), 93.87 (6), 65.04 (14).

S.3.2.4. 1-(4-methoxyphenyl)-2,5-dimethyl-1*H*-pyrrole (4b)



Known compound.[2] Prepared according to **GP1** starting from 1-methoxy-4-nitrobenzene (74.7 mg, 0.488 mmol).

Chemical Formula: $C_{13}H_{15}NO$.

Molecular Weight: 201.2690 g mol^{-1}.

Appearance: colorless solid.

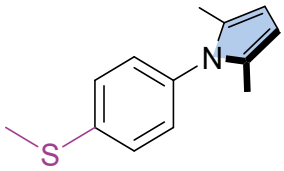
Yield: 59% (57.8 mg, 0.287 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 – 7.10 (m, 2H), 7.03 – 6.95 (m, 2H), 5.90 (s, 2H), 3.38 (s, 3H), 2.04 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 131.9, 129.3, 129.2, 114.3, 105.4, 55.6, 13.1, 13.1.

GC-MS: *m/z* (%): 201.18 (M^+, 100), 200.19 ($[M-H]^+$, 71), 186.14 (31), 159.13 (8), 145.10 (24), 129.10 (4), 117.09 (7).

S.3.2.5. 2,5-dimethyl-1-(4-(methylthio)phenyl)-1*H*-pyrrole (5b)



Known compound.[2] Prepared according to **GP1** starting from methyl(4-nitrophenyl)sulfane (84.3 mg, 0.498 mmol).

Chemical Formula: $C_{13}H_{15}NS$.

Molecular Weight: 217.3300 g mol^{-1}.

Appearance: light-yellow solid.

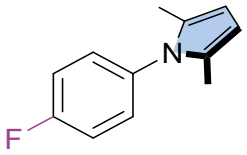
Yield: 77% (83.4 mg, 0.384 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 2H), 7.19 – 7.08 (m, 2H), 5.90 (s, 2H), 2.54 (s, 3H), 2.03 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 136.1, 129.0, 128.7, 126.9, 105.8, 15.9, 13.1.

GC-MS: *m/z* (%) 217.10 (M^+, 100), 216.09 ($[M-H]^+$, 44), 202.05 (28), 169.07 (15), 154.05 (16), 129.05 (31), 108.25 (7).

S.3.2.6. 1-(4-fluorophenyl)-2,5-dimethyl-1*H*-pyrrole (6b)



Known compound.[2] Prepared according to **GP1** starting from 1-fluoro-4-nitrobenzene (70.4 mg, 0.499 mmol).

Chemical Formula: $C_{12}H_{12}FN$.

Molecular Weight: 189.2334 g mol^{-1}.

Appearance: colorless solid.

Yield: 78% (74 mg, 0.391 mmol).

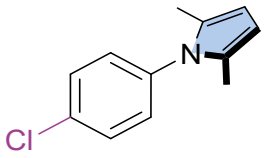
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.10 (m, 4H), 5.90 (s, 2H), 2.02 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 160.3, 135.1, 135.1, 130.0, 129.9, 129.0, 116.2, 115.9, 105.9, 13.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ -114.1.

GC-MS: *m/z* (%): 189.08 (M^+, 96), 188.07 ($[M-H]^+$, 100), 174.03 (14), 172.02 (12), 147.02 (12), 146.01 (9), 133.01 (9), 94.98 (20), 75.00 (13).

S.3.2.7. 1-(4-chlorophenyl)-2,5-dimethyl-1*H*-pyrrole (7b)



Known compound.[2] Prepared according to **GP2** starting from 1-chloro-4-nitrobenzene (77.7 mg, 0.493 mmol).

Chemical Formula: $C_{12}H_{12}ClN$.

Molecular Weight: 205.6850 g mol^{-1}.

Appearance: off-white solid.

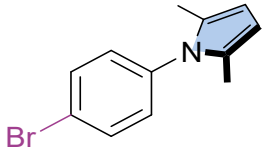
Yield: 81% (81.9 mg, 0.398 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 2H), 7.21 – 7.12 (m, 2H), 5.92 (s, 2H), 2.04 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 133.7, 129.6, 129.4, 128.9, 106.2, 13.1.

GC-MS: *m/z* (%) 207.02 ($[M+2]^+$, 45), 206.03 (63), 205.05 (M^+, 100), 204.05 ($[M-H]^+$, 100), 189.97 (15), 169.02 (31), 154.00 (37), 129.00 (27), 83.53 (11).

S.3.2.8. 1-(4-bromophenyl)-2,5-dimethyl-1*H*-pyrrole (8b)



Known compound.[2] Prepared according to **GP2** starting from 1-bromo-4-nitrobenzene (100.7 mg, 0.498 mmol).

Chemical Formula: $C_{12}H_{12}BrN$.

Molecular Weight: 250.1390 g mol^{-1}.

Appearance: colorless solid.

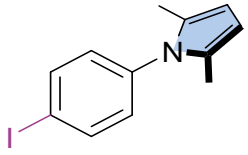
Yield: 77% (96.0 mg, 0.384 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 2H), 7.15 – 7.05 (m, 2H), 5.92 (s, 2H), 2.04 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 132.4, 130.0, 128.8, 121.6, 106.2, 13.1.

GC-MS: *m/z* (%) 250.99 ($[M+2]^+$, 99), 250.00 (99), 249.01 (M^+, 100), 248.01 ($[M-H]^+$, 91), 169.02 (34), 154.01 (49), 129.01 (27), 83.53 (11).

S.3.2.9. 1-(4-iodophenyl)-2,5-dimethyl-1*H*-pyrrole (9b)



Known compound.[2] Prepared according to **GP2** starting from 1-iodo-4-nitrobenzene (123.6 mg, 0.496 mmol).

Chemical Formula: $C_{12}H_{12}IN$.

Molecular Weight: 297.1395 g mol^{-1}.

Appearance: off-white solid.

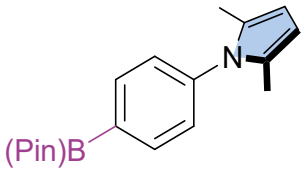
Yield: 70% (103.5 mg, 0.348 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 2H), 7.00 – 6.94 (m, 2H), 5.91 (s, 2H), 2.04 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.4, 130.3, 128.8, 106.3, 93.0, 13.1.

GC-MS: *m/z* (%) 297.01 (M^+, 100), 296.00 ($[M-H]^+$, 93), 169.02 (30), 154.00 (35), 129.00 (14), 75.99 (9).

S.3.2.10. 2,5-dimethyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)-1*H*-pyrrole (10b)



Known compound.[2] Prepared according to **GP1** starting from 4,4,5,5-tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane (124.5 mg, 0.500 mmol).

Chemical Formula: $C_{18}H_{24}BNO_2$.

Molecular Weight: 297.2050 g mol^{-1}.

Appearance: off-white solid.

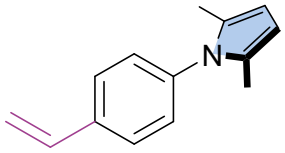
Yield: 71% (106.1 mg, 0.357 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 – 7.85 (m, 2H), 7.25 – 7.18 (m, 2H), 5.91 (s, 2H), 2.04 (s, 6H), 1.37 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7, 135.7, 128.8, 127.7, 106.0, 84.2, 25.1, 13.2. B-bound carbon was not detected.

GC-MS: *m/z* (%) 297.32 (M^+, 100), 296.32 ($[M-H]^+$, 100), 282.22 (9), 238.20 (14), 215.15 (4), 196.15 (50), 170.13 (14), 154.10 (9), 141.10 (12), 128.09 (5), 103.08 (4), 83.12 (5).

S.3.2.11. 2,5-dimethyl-1-(4-vinylphenyl)-1*H*-pyrrole (11b)



Known compound.[2] Prepared according to **GP2** starting from 1-nitro-4-vinylbenzene (74.4 mg, 0.499 mmol).

Chemical Formula: $C_{14}H_{15}N$.

Molecular Weight: 197.2810 g mol^{-1}.

Appearance: colorless solid.

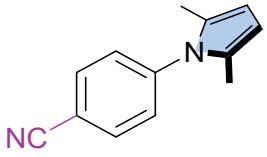
Yield: 50% (49.4 mg, 0.250 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.22 – 7.16 (m, 2H), 6.79 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.92 (s, 2H), 5.82 (dd, *J* = 17.5, 0.8 Hz, 1H), 5.34 (dd, *J* = 10.9, 0.8 Hz, 1H), 2.06 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 137.0, 136.1, 128.9, 128.4, 126.9, 114.9, 105.9, 13.2.

GC-MS: *m/z* (%) 197.07 (M^+, 100), 196.08 ($[M-H]^+$, 100), 180.01 (16), 167.00 (9), 155.01 (10), 140.99 (23), 127.99 (6), 114.98 (6), 76.99 (9).

S.3.2.12. 4-(2,5-dimethyl-1*H*-pyrrol-1-yl)benzonitrile (12b)



Known compound.[3] Prepared according to **GP1** starting from 4-nitrobenzonitrile (72.4 mg, 0.489 mmol).

Chemical Formula: $C_{13}H_{12}N_2$.

Molecular Weight: 196.2530 g mol^{-1}.

Appearance: colorless solid.

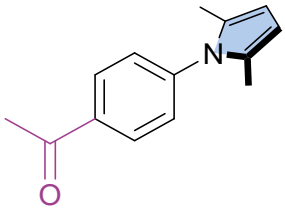
Yield: 21% (20.2 mg, 0.103 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 2H), 7.38 – 7.30 (m, 2H), 5.94 (s, 2H), 3.96 (s, 3H), 2.05 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 133.2, 129.1, 128.7, 118.4, 111.6, 107.3, 13.2.

GC-MS: *m/z* (%): 196.05 (77), 195.06 ([M-H]$^+$, 100), 181.03 (12), 179.02 (8), 154.02 (5), 101.99 (7).

S.3.2.13. 1-(4-(2,5-dimethyl-1*H*-pyrrol-1-yl)phenyl)ethan-1-one (13b)



Known Compound.[2] Prepared according to **GP1** starting from 1-(4-nitrophenyl)ethan-1-one (82.1 mg, 0.497 mmol).

Chemical Formula: $C_{14}H_{15}NO$.

Molecular Weight: 213.2800 g mol^{-1}.

Appearance: colorless solid.

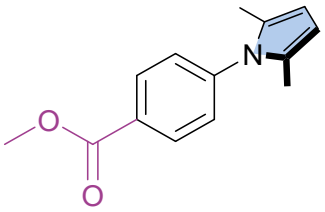
Yield: 40% (42.9 mg, 0.201 mmol) [2.0 mol%], or 66% (70.1 mg, 0.328 mmol) [5.0 mol%]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 – 8.01 (m, 2H), 7.37 – 7.27 (m, 2H), 5.94 (s, 2H), 2.66 (s, 3H), 2.06 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.3, 143.3, 136.2, 129.4, 128.7, 128.6, 128.4, 106.7, 26.8, 13.2.

GC-MS: *m/z* (%): 213.14 (M$^+$, 100), 212.14 ([M-H]$^+$, 100), 198.05 (15), 170.05 (51), 154.02 (25), 128.02 (10), 98.66 (14).

S.3.12.14. Methyl 4-(2,5-dimethyl-1*H*-pyrrol-1-yl)benzoate (14b)



Known compound.[2] Prepared according to **GP1** starting from methyl 4-nitrobenzoate (89.9 mg, 0.496 mmol).

Chemical Formula: $C_{14}H_{15}NO_2$.

Molecular Weight: 229.2790 g mol^{-1}.

Appearance: colorless solid.

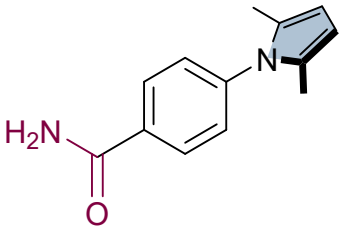
Yield: 60% (67.7 mg, 0.295 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 – 8.10 (m, 2H), 7.33 – 7.27 (m, 2H), 5.93 (s, 2H), 3.96 (s, 3H), 2.06 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 143.3, 130.6, 129.4, 128.7, 128.2, 106.6, 52.4, 13.2.

GC-MS: *m/z* (%): 229.06 (M^+, 100) 228.07 ([M-H]$^+$, 99), 198.03 (7), 168.03 (12), 154.01 (16), 129.02 (6), 98.62 (8), 83.53 (3).

S.3.12.15. 4-(2,5-dimethyl-1*H*-pyrrol-1-yl)benzamide (15b)



Known Compound.[2] Prepared according to **GP1** starting from 4-nitrobenzamide (83.1 mg, 0.500 mmol).

Chemical Formula: $C_{13}H_{14}N_2O$.

Molecular Weight: 214.2680 g mol^{-1}.

Appearance: off-white solid.

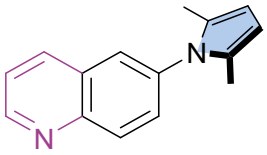
Yield: 56% (60.0 mg, 0.280 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.34 – 7.27 (m, 2H), 6.39 (br, 2H), 5.93 (s, 2H), 2.04 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 142.5, 132.6, 128.7, 128.5, 128.4, 106.6, 13.2.

GC-MS: *m/z* (%) 214.12 (M^+, 100), 213.12 ([M-H]$^+$, 100), 170.03 (44), 154.01 (22), 129.02 (11), 98.64 (16).

S.3.12.16. 6-(2,5-dimethyl-1H-pyrrol-1-yl)quinoline (16b)



Known Compound.[2] Prepared according to **GP2** starting from 6-nitroquinoline (86.6 mg, 0.497 mmol).

Chemical Formula: $C_{15}H_{14}N_2$.

Molecular Weight: 222.2910 g mol^{-1}.

Appearance: colorless solid.

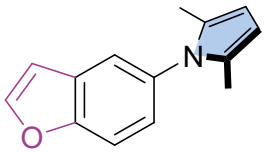
Yield: 18% (19.8 mg, 0.089 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.31 – 8.16 (m, 2H), 7.70 (d, *J* = 2.2 Hz, 1H), 7.58 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.50 (dd, *J* = 8.4, 4.3 Hz, 1H), 5.96 (s, 2H), 2.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 146.9, 137.4, 136.7, 130.4, 129.1, 128.4, 126.6, 121.9, 106.4, 13.3.

GC-MS: *m/z* (%) 222.12 (M^+, 100), 221.13 ($[M-H]^+$, 91), 206.08 (20), 180.07 (21), 166.05 (7), 128.03 (7), 111.05 (6), 101.03 (6).

S.3.12.17. 1-(benzofuran-5-yl)-2,5-dimethyl-1*H*-pyrrole (17b)



Known Compound.[2] Prepared according to **GP1** starting from 5-nitrobenzofuran (78.8 mg, 0.483 mmol).

Chemical Formula: $C_{14}H_{13}NO$.

Molecular Weight: 211.2640 g mol^{-1}.

Appearance: colorless solid.

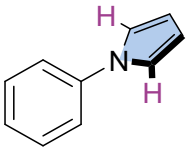
Yield: 78% (79.6 mg, 0.377 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 2.2 Hz, 1H), 7.59 (dt, *J* = 8.6, 0.8 Hz, 1H), 7.47 (dd, *J* = 2.1, 0.6 Hz, 1H), 7.15 (m,1H), 6.84 (dd, *J* = 2.2, 1.0 Hz, 1H), 5.94 (s, 2H), 2.06 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 146.4, 134.2, 129.3, 128.1, 124.7, 121.0, 111.8, 106.9, 105.5, 13.1.

GC-MS: *m/z* (%) 211.09 (M^+, 100), 210.10 ($[M-H]^+$, 100), 196.01 (19), 167.01 (16), 154.98 (15), 141.01 (11), 114.99 (5), 89.01 (10).

S.3.12.18. 1-phenyl-1*H*-pyrrole (19b)



Known Compound.[2] Prepared according to **GP2** starting from nitrobenzene (60.8 mg, 0.494 mmol) and 2,5-dimethoxytetrahydrofuran (*cis*/*trans*-mixture) as the 1,4-dicarbonyl source.

Chemical Formula: $C_{10}H_9N$.

Molecular Weight: 143.1890 g mol^{-1}.

Appearance: colorless solid.

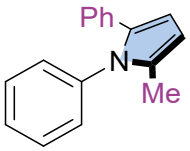
Yield: 50% (35.7 mg, 0.249 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 4H), 7.29 – 7.22 (m, 1H), 7.13 – 7.07 (m, 2H), 6.40 – 6.32 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9, 129.7, 125.8, 120.7, 119.5, 110.5.

GC-MS: *m/z* (%) 143.05 (M^+, 100), 117.04 (9), 116.04 (27), 115.04 (54), 77.03 (11), 51.02 (9).

S.3.12.19. 2-methyl-1,5-diphenyl-1*H*-pyrrole (20b)



Known Compound.[2] Prepared according to **GP2** starting from nitrobenzene (61.0 mg, 0.495 mmol) and 1-phenylpentane-1,4-dione as the 2,5-dicarbonyl source.

Chemical Formula: $C_{17}H_{15}N$.

Molecular Weight: 233.3140 g mol^{-1}.

Appearance: pale orange solid.

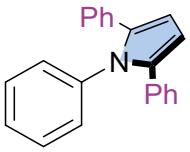
Yield: 80% (92.2 mg, 0.396 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 3H), 7.25 – 7.06 (m, 7H), 6.41 (d, *J* = 3.4 Hz, 1H), 6.15 (dd, *J* = 3.4, 1.1 Hz, 1H), 2.19 (d, *J* = 0.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 134.3, 133.6, 131.8, 129.1, 128.6, 128.0, 128.0, 127.9, 127.9, 127.5, 125.8, 108.8, 107.6, 13.5.

GC-MS: *m/z* (%) 233.15 (M^+, 100), 232.15 ($[M-H]^+$, 69), 217.09 (11), 191.08 (10), 128.05 (6), 115.07 (14), 108.58 (9), 77.04 (9).

S.3.12.20. 1,2,5-triphenyl-1*H*-pyrrole (21b)



Known Compound.[2] Prepared according to **GP2** starting from nitrobenzene (60.9 mg, 0.495 mmol) and 1,4-diphenylbutane-1,4-dione as the 2,5-dicarbonyl source.

Chemical Formula: $C_{22}H_{17}N$.

Molecular Weight: 295.3850 g mol^{-1}.

Appearance: white solid.

Yield: 56% (81.3 mg, 0.275 mmol).

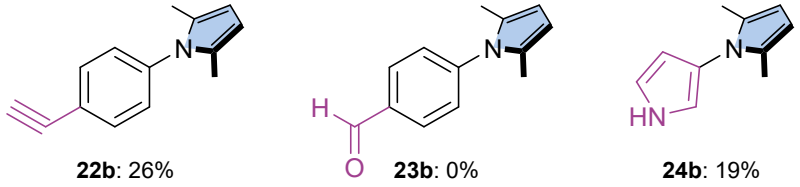
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 – 7.00 (m, 15H), 6.49 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 136.0, 133.4, 129.0, 128.9, 128.9, 128.0, 127.4, 126.4, 110.1.

GC-MS: *m/z* (%) 295.13 (M^+, 100), 294.16 ($[M-H]^+$, 14), 217.08 (5), 191.08 (27), 165.05 (7), 139.39 (10), 115.03 (4), 77.04 (5).

S.3.3. Unsuccessful Substrates

In addition to the examples described in the main manuscript, three more substrates were tested, showing low or no conversion (**Figure S4**). For substrate **22b**, a GC-FID chromatogram revealed the formation of both alkyne reduction and hydration products (**Figure S5**). The main products were as follows: unreacted 1-ethynyl-4-nitrobenzene (49%), 1-nitro-4-vinylbenzene (7%), 1-(4-ethynylphenyl)-2,5-dimethyl-1*H*-pyrrole (26%), 2,5-dimethyl-1-(4-vinylphenyl)-1*H*-pyrrole (5%), and the hydration product 1-(4-(2,5-dimethyl-1*H*-pyrrol-1-yl)phenyl)ethan-1-one (13%).



22b: 26% **23b**: 0% **24b**: 19%

Figure S4. Obtained yields for unsuccessful substrates. Reaction conditions: $Fe(BF_4)_2{\cdot}6H_2O$ (0.01 mmol, 2.0 mol%), **L2** (0.01 mmol, 2.0 mol%), TFA (0.5 mmol, 1.0 equiv), nitrobenzene (0.5 mmol, 1.0 equiv), 2,5-hexanedione (0.6 mmol, 1.2 equiv), THF (1.5 mL), H_2 (5 bar), 80 °C, 18 h. Substrates: **22b** from 1-ethynyl-4-nitrobenzene; **23b** from 1-(4-nitrophenyl)ethan-1-one; **24b** from 3-nitro-1*H*-pyrrole. Yields were determined by GC-FID analysis.

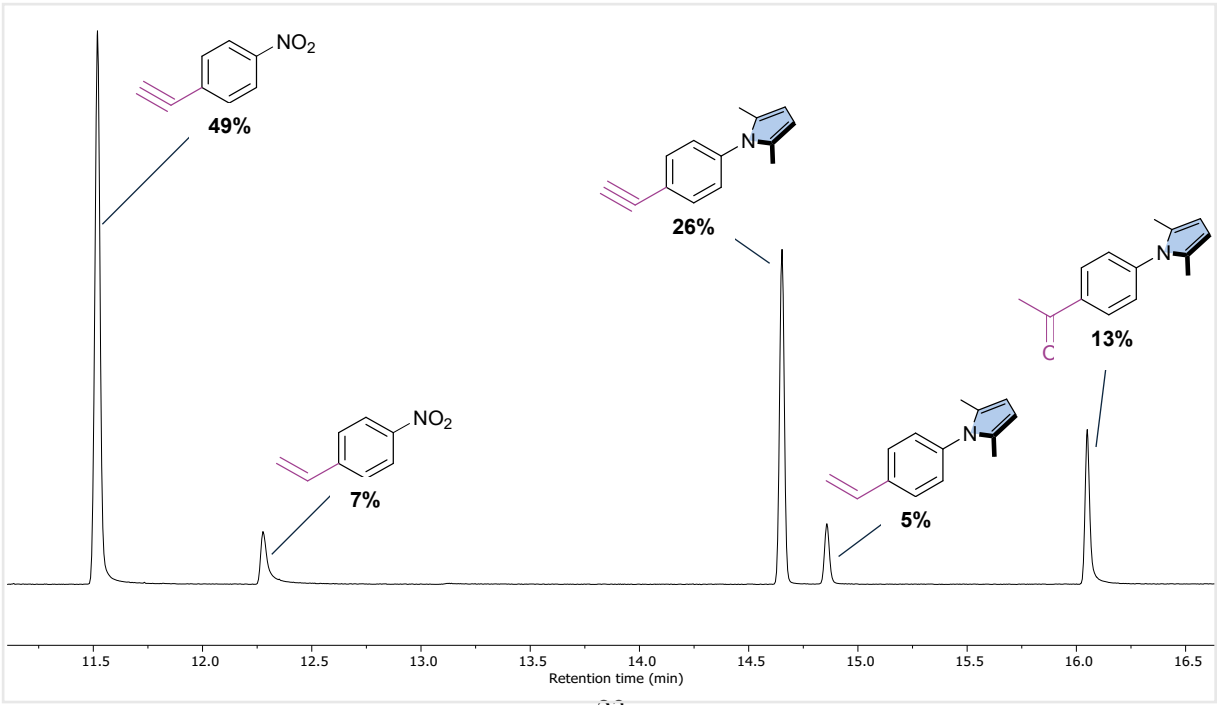


Figure S5. GC-FID chromatogram of substrate **22b**. Product identities were confirmed by GC-MS analysis.

S4. NMR Spectral Data

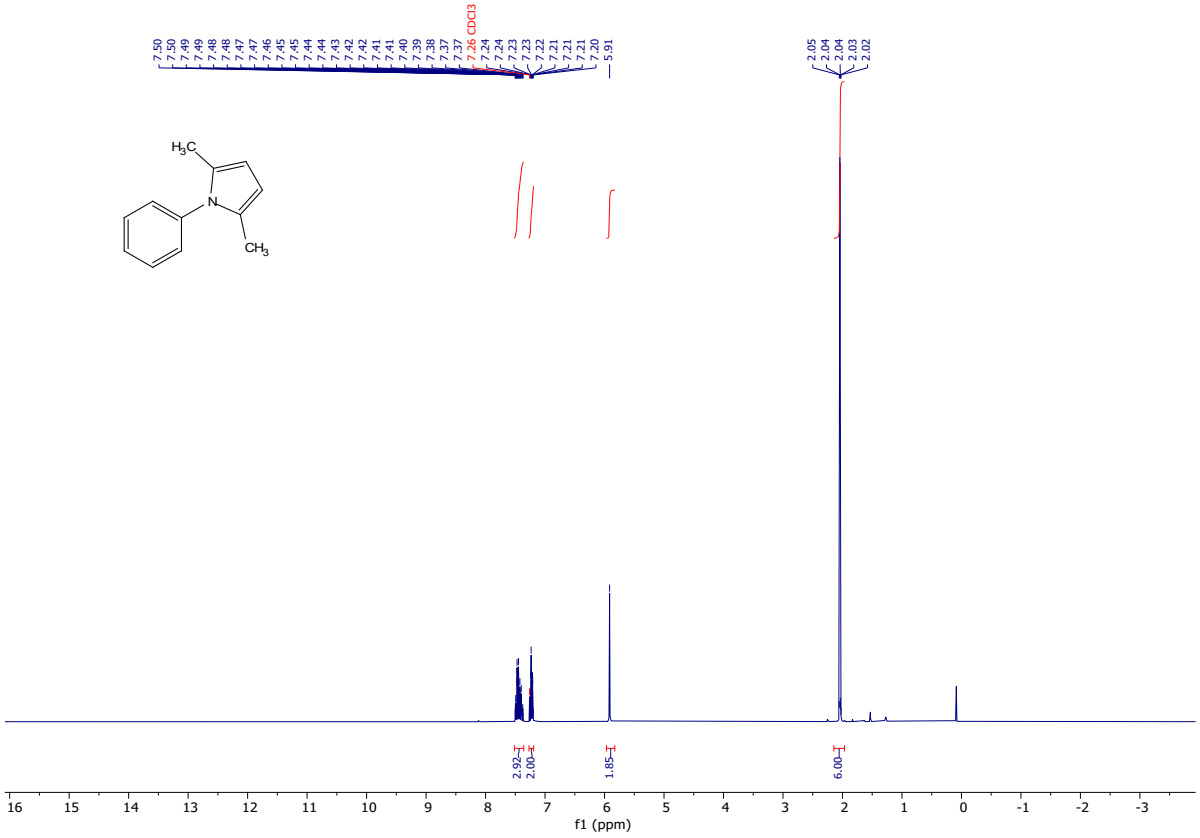


Figure S6. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **1b**.

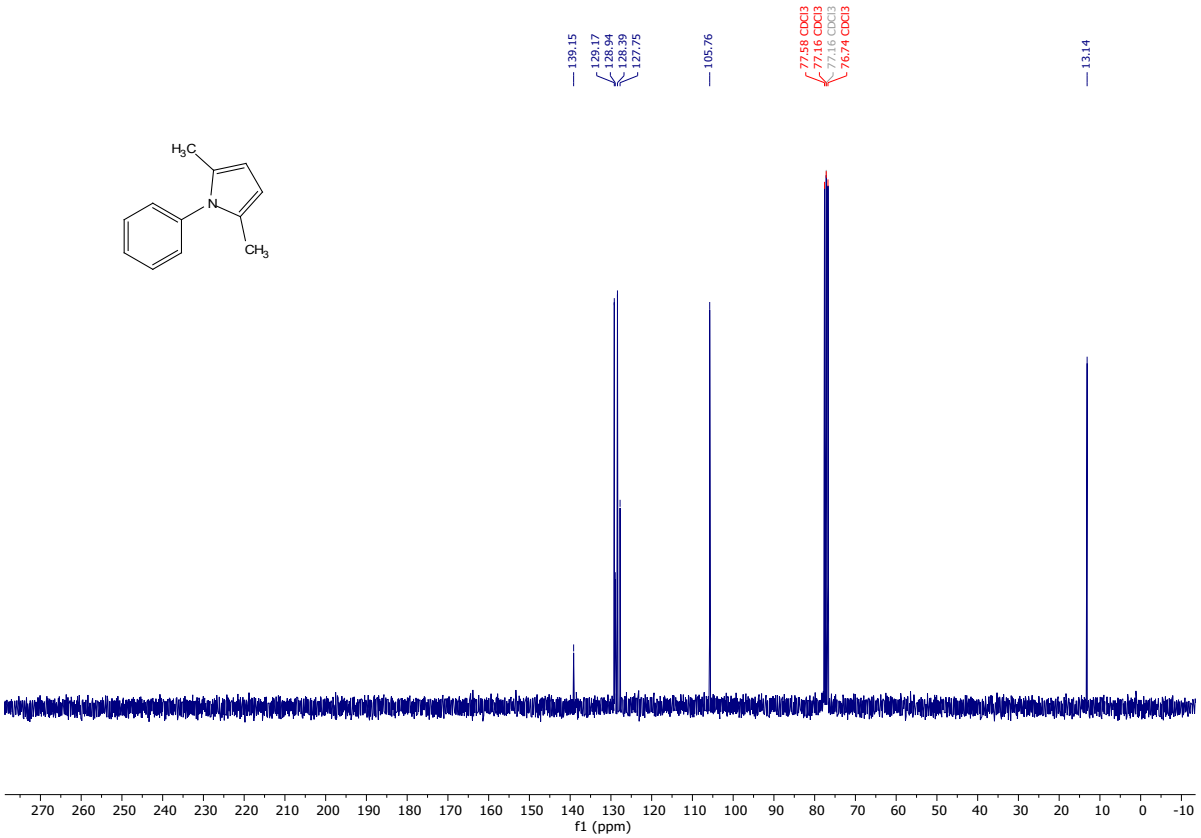


Figure S7. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **1b**.

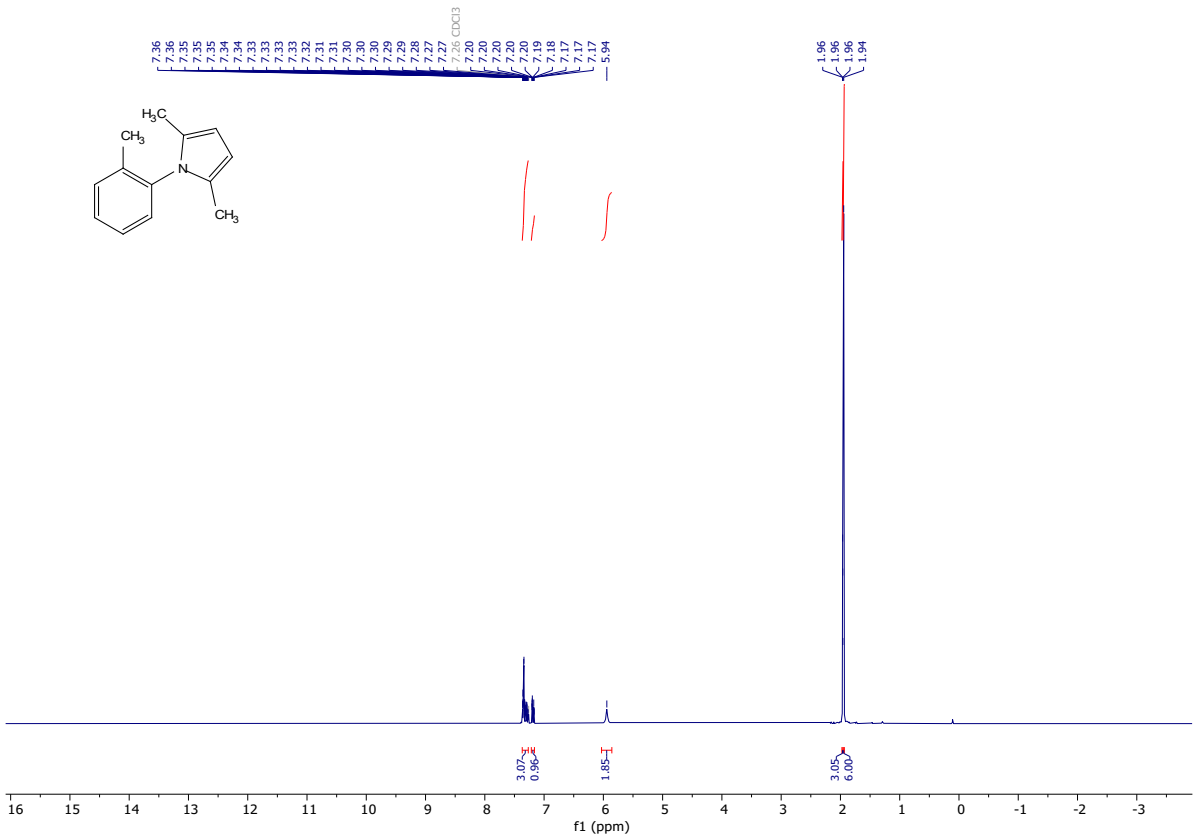


Figure S8. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2b**.

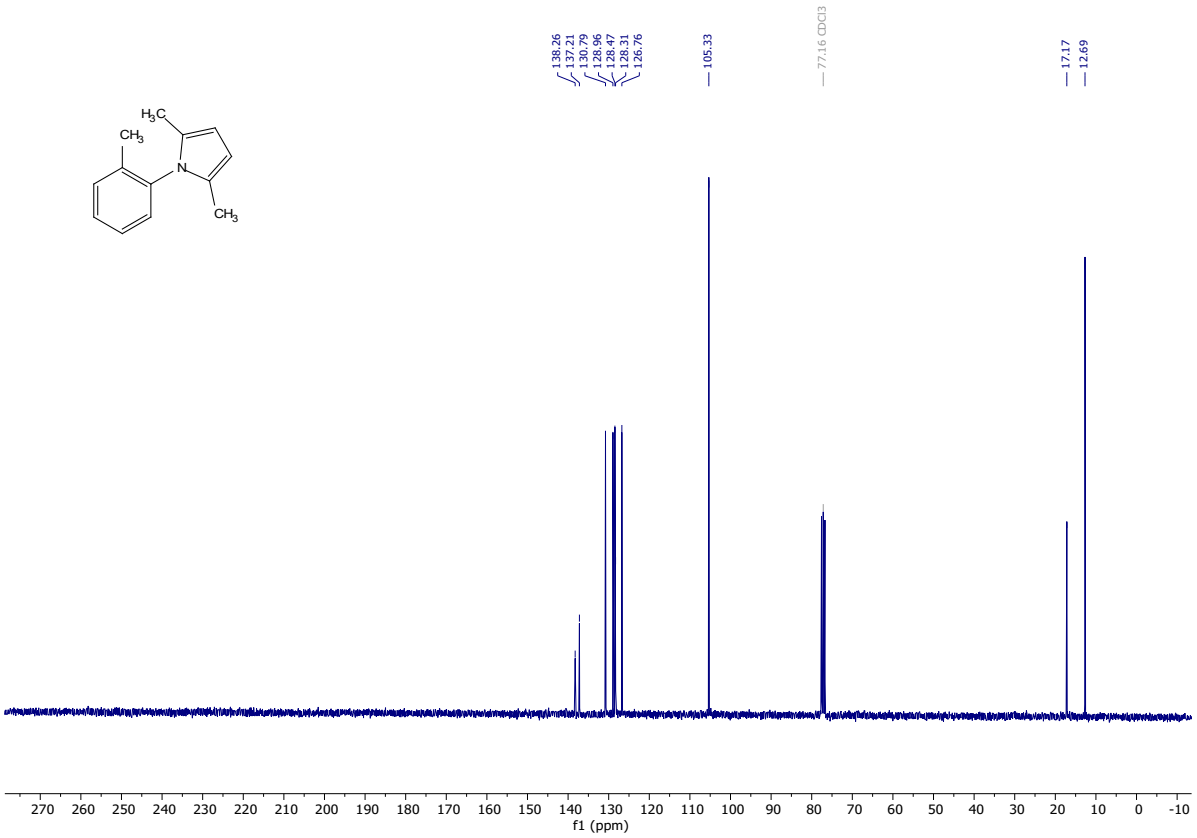


Figure S9. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **2b**.

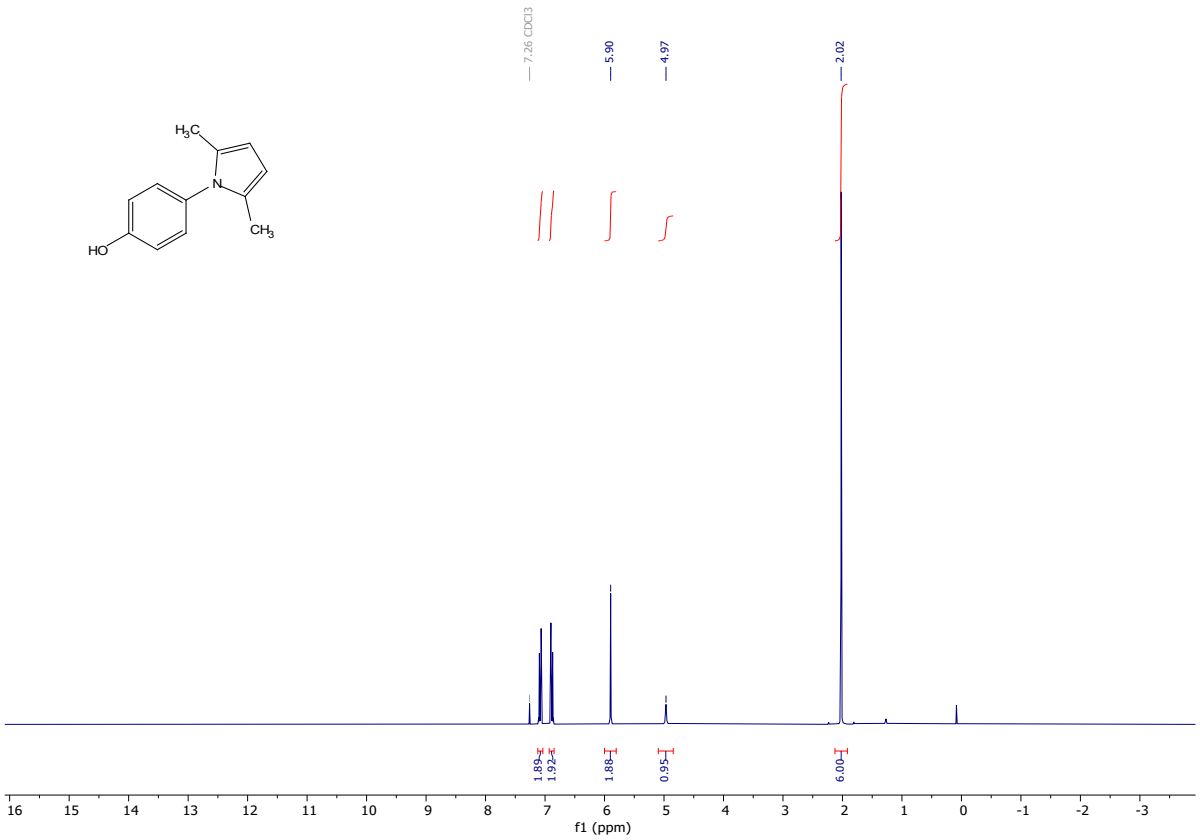


Figure S10. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **3b**.

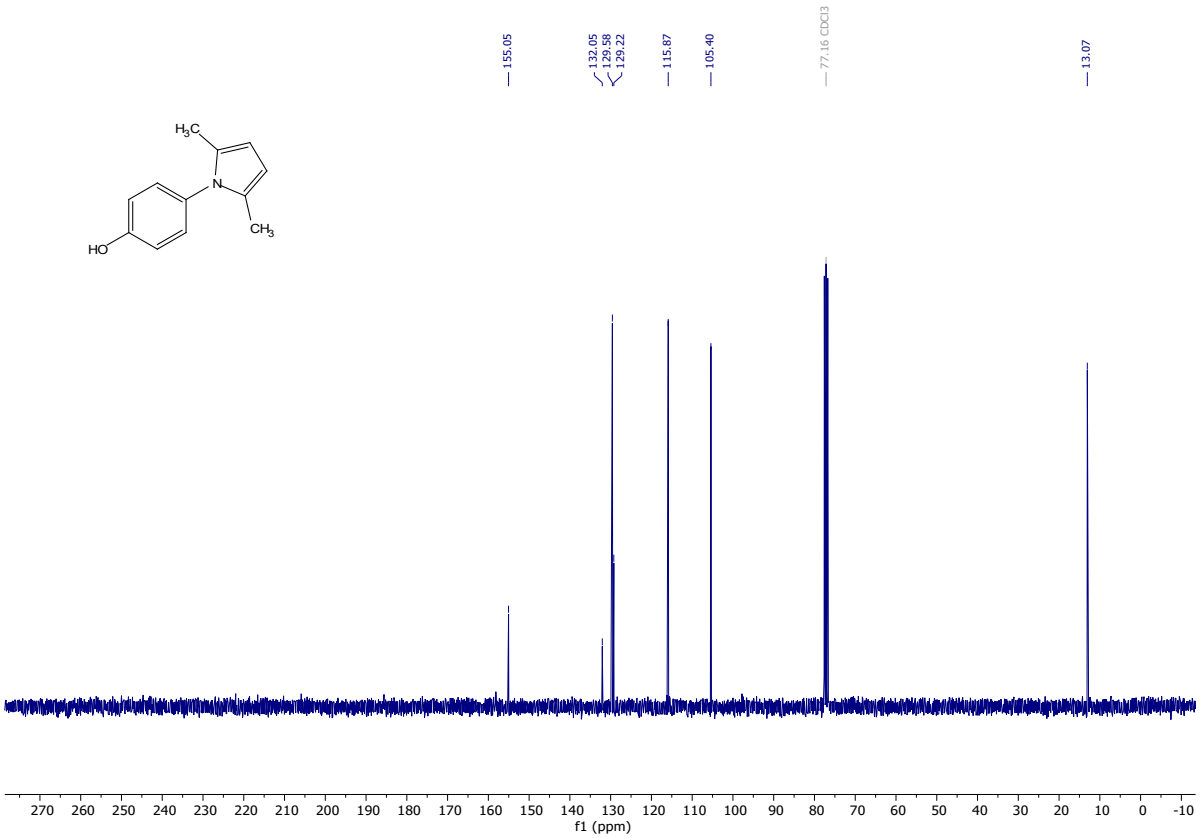


Figure S11. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **3b**.

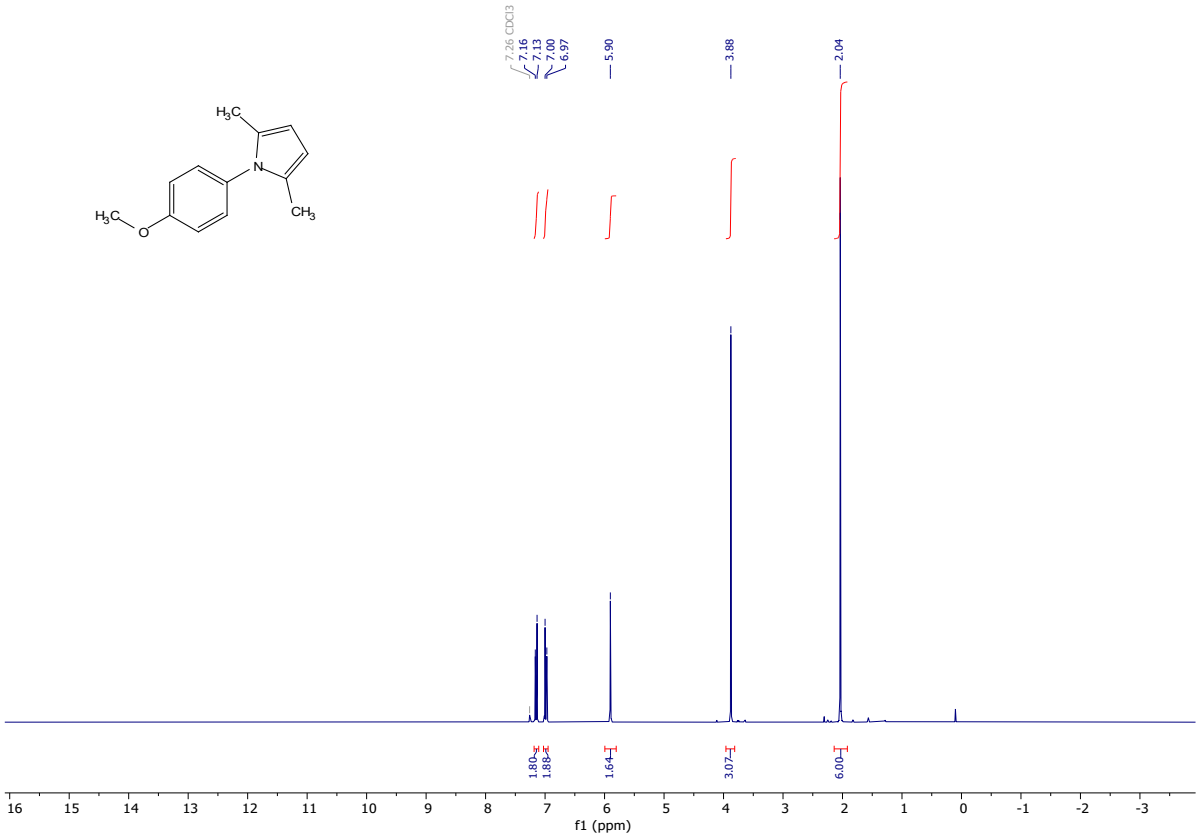


Figure S12. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **4b**.

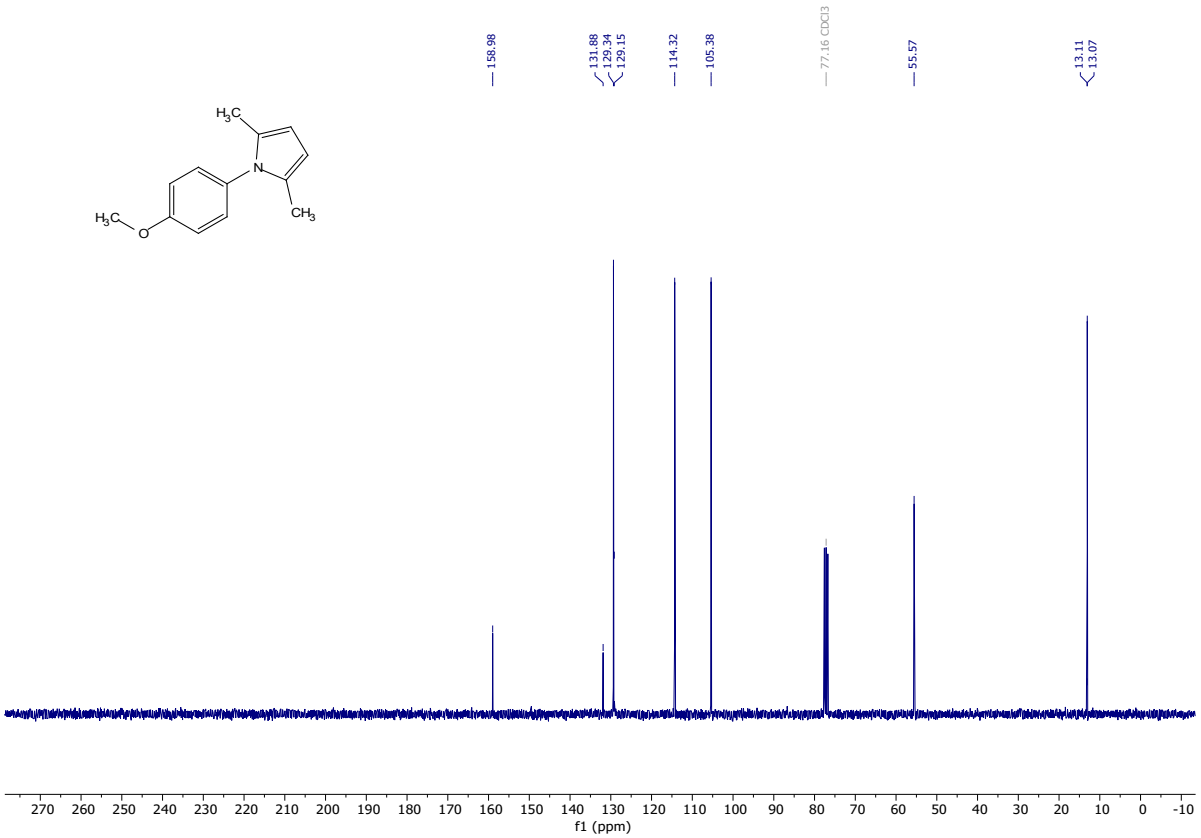


Figure S13. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **4b**.

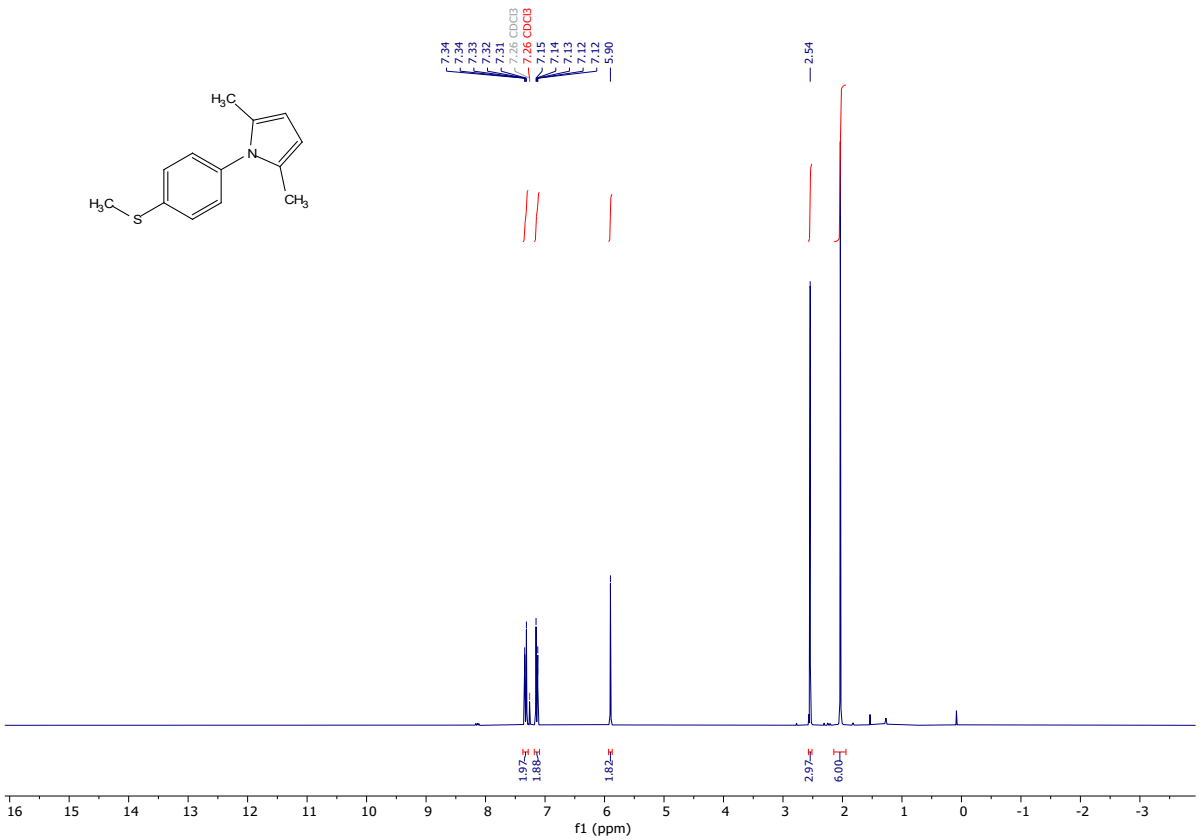


Figure S14. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **5b**.

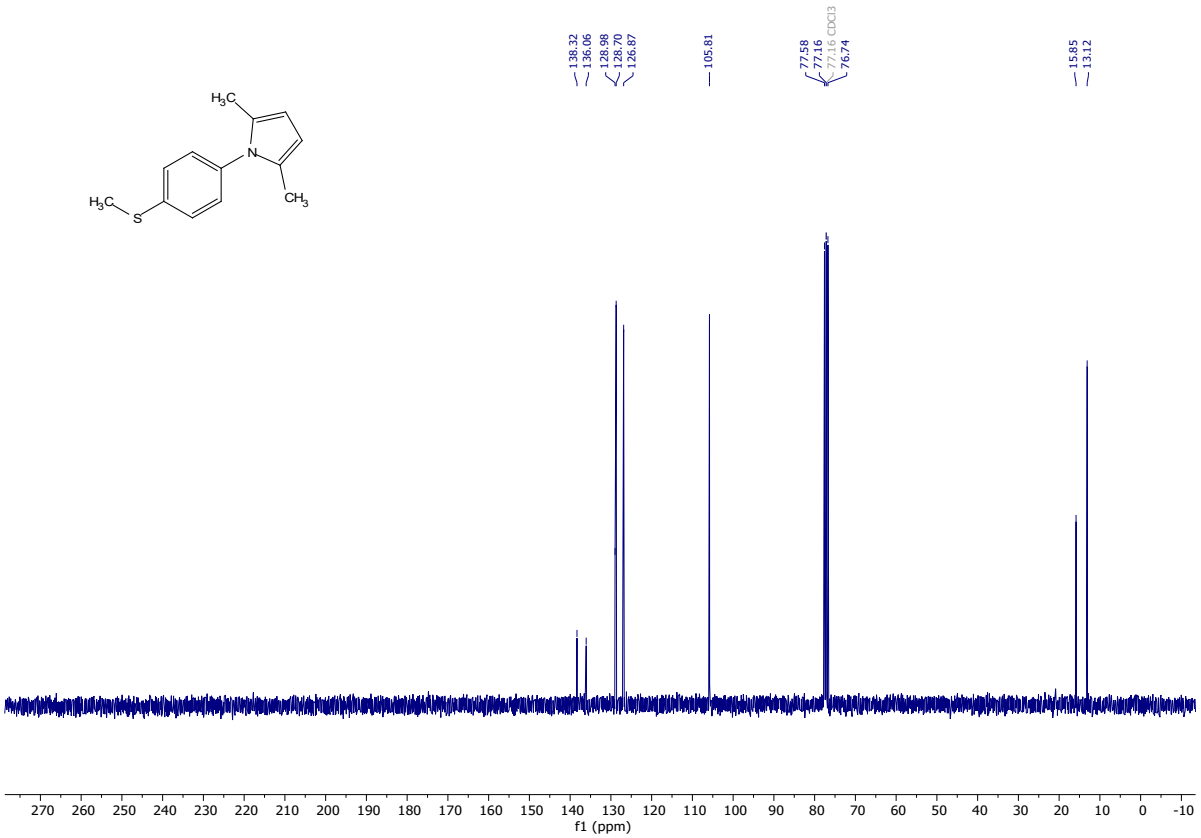


Figure S15. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **5b**.

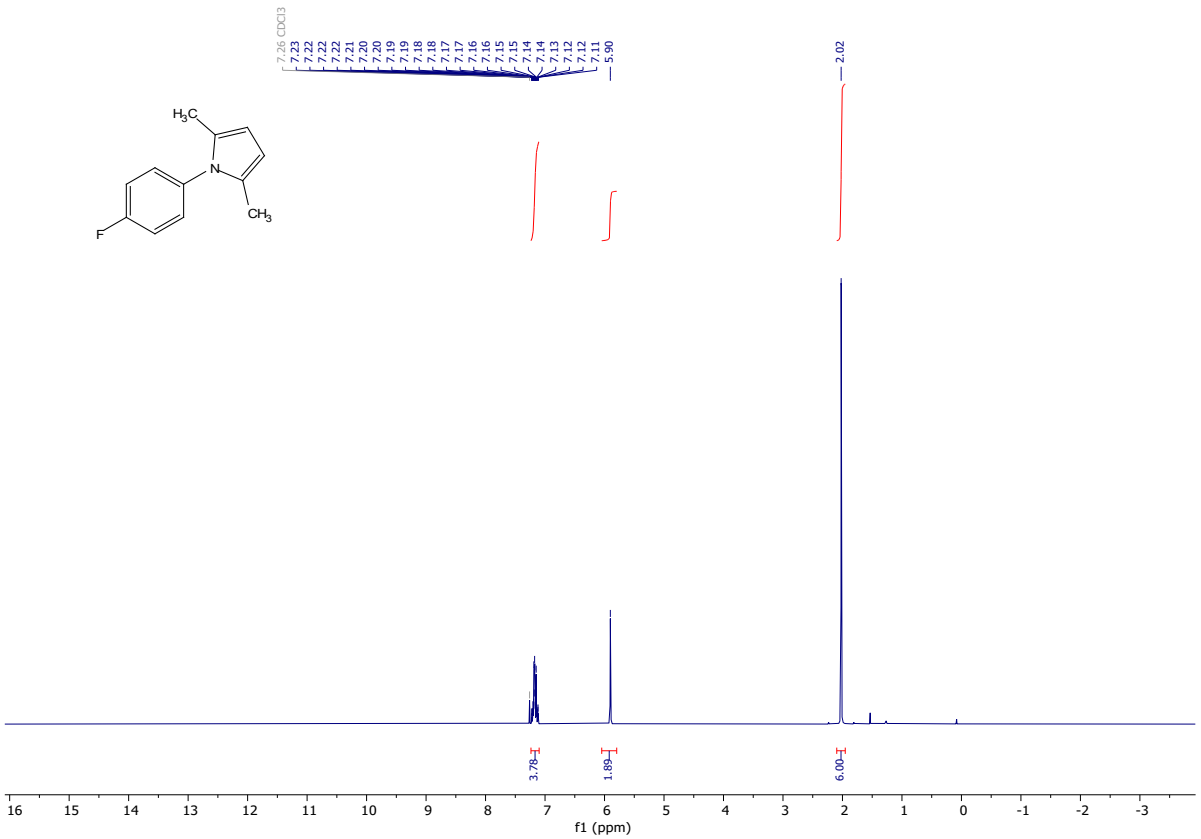


Figure S16. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **6b**.

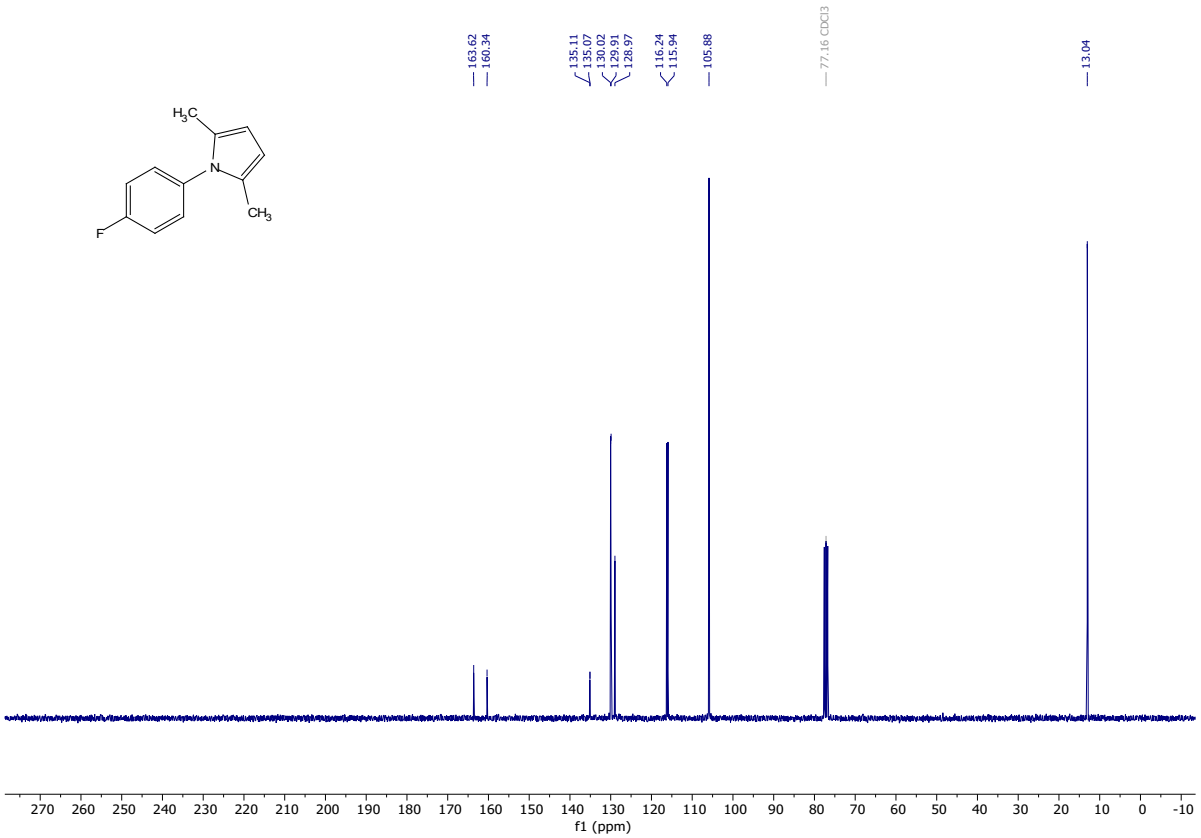


Figure S17. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **6b**.

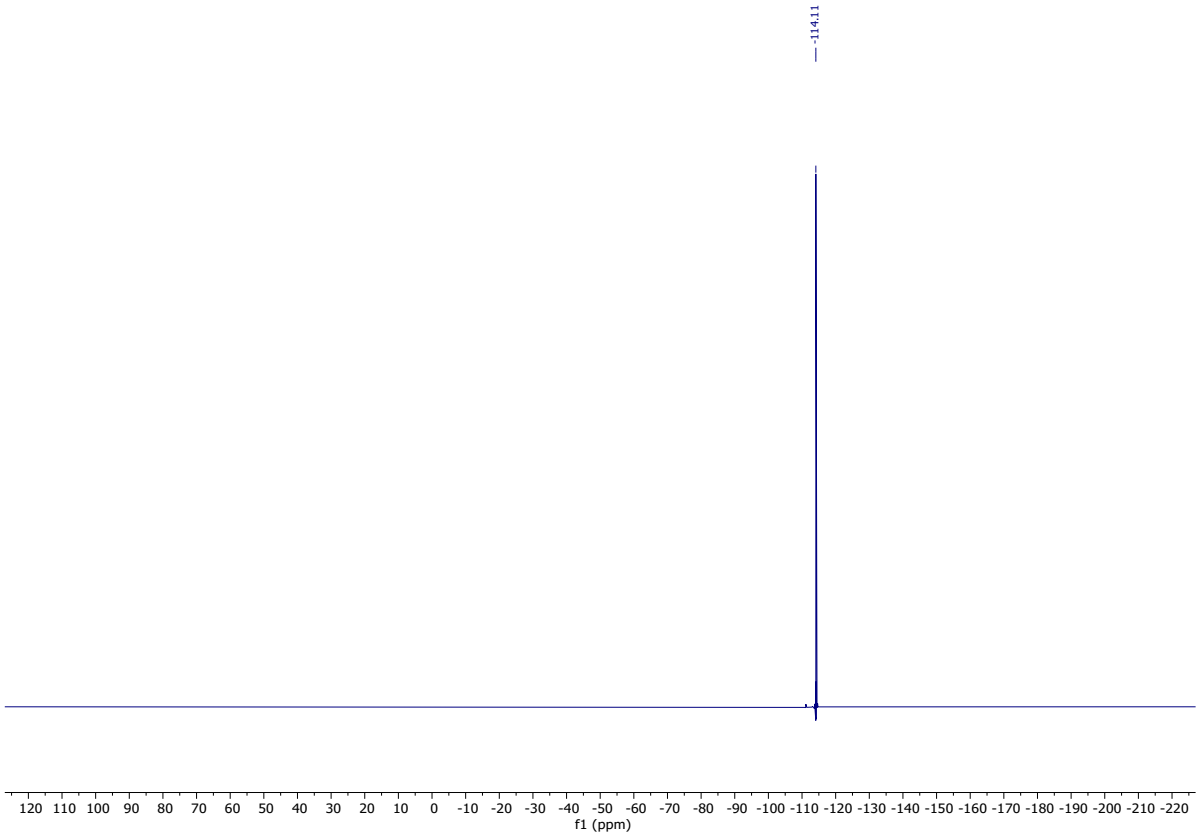


Figure S18. ^{19}F NMR spectrum (282 MHz, $CDCl_3$) of **6b**.

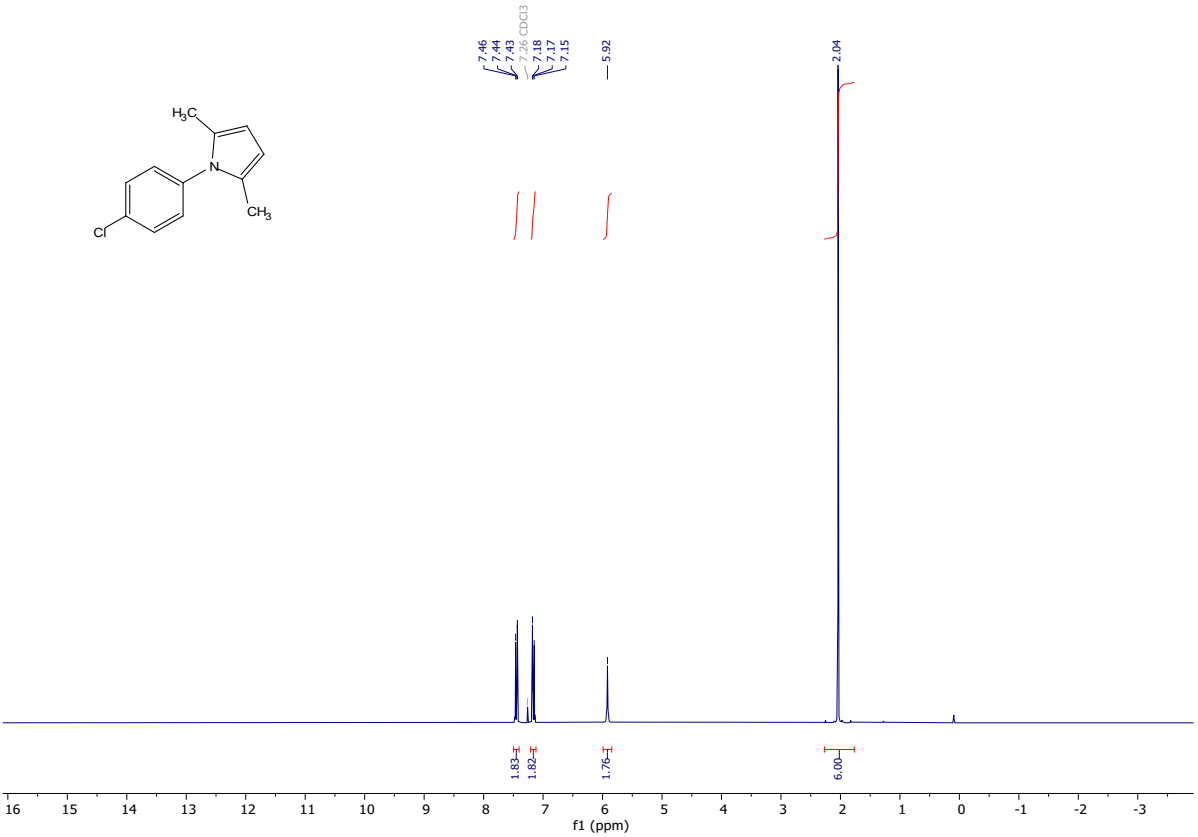


Figure S19. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **7b**.

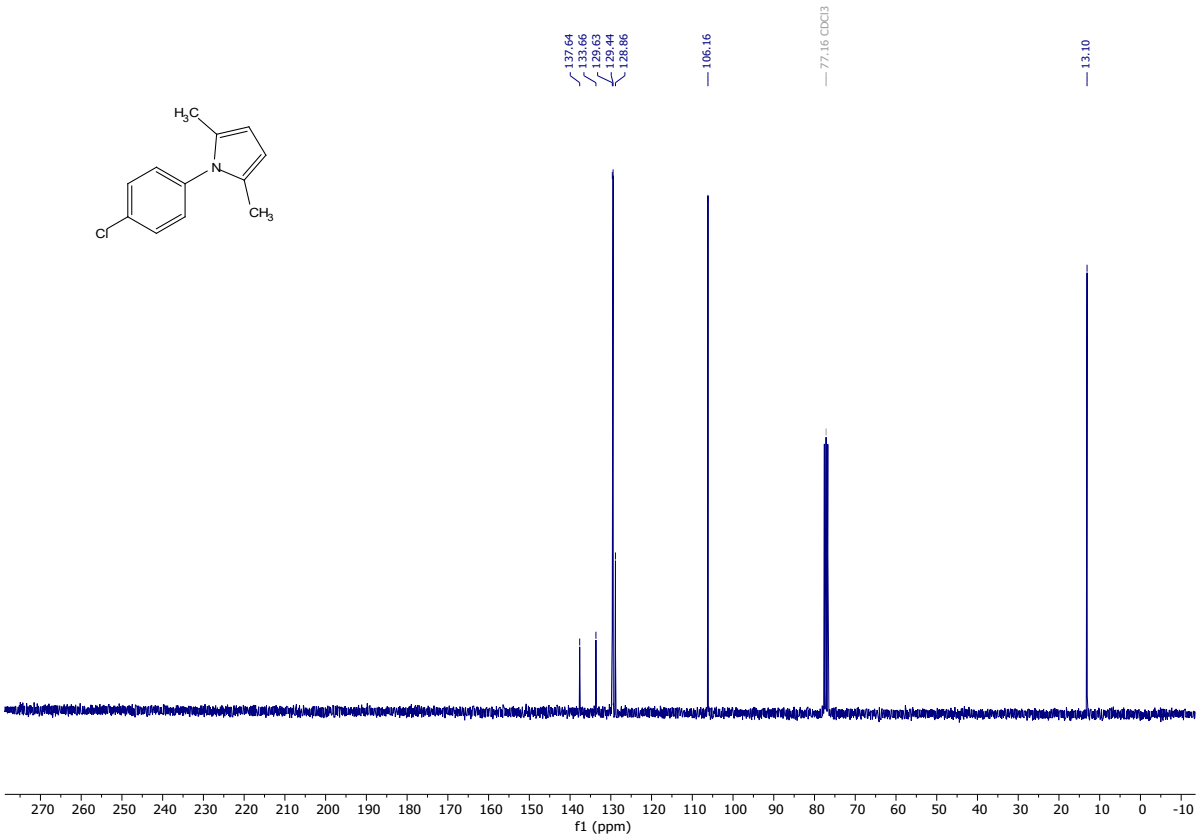


Figure S20. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **7b**.

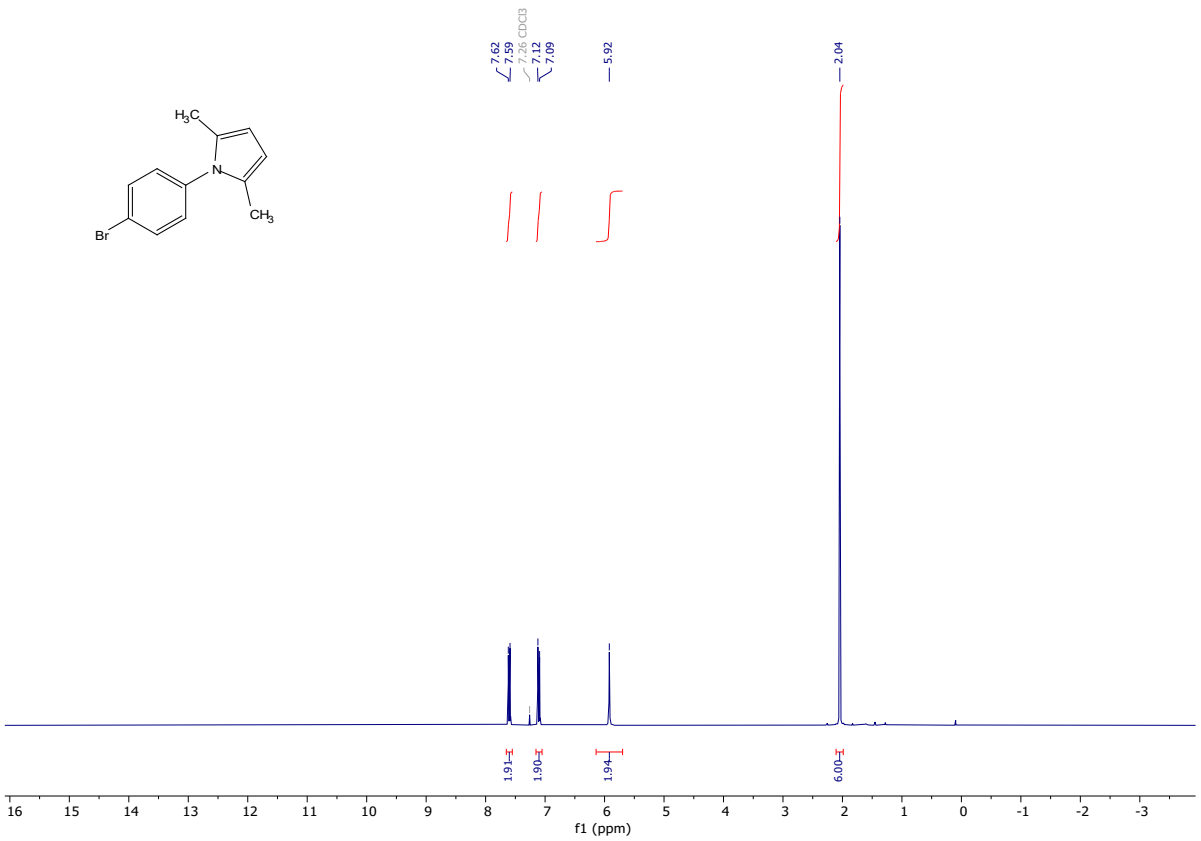


Figure S21. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **8b**.

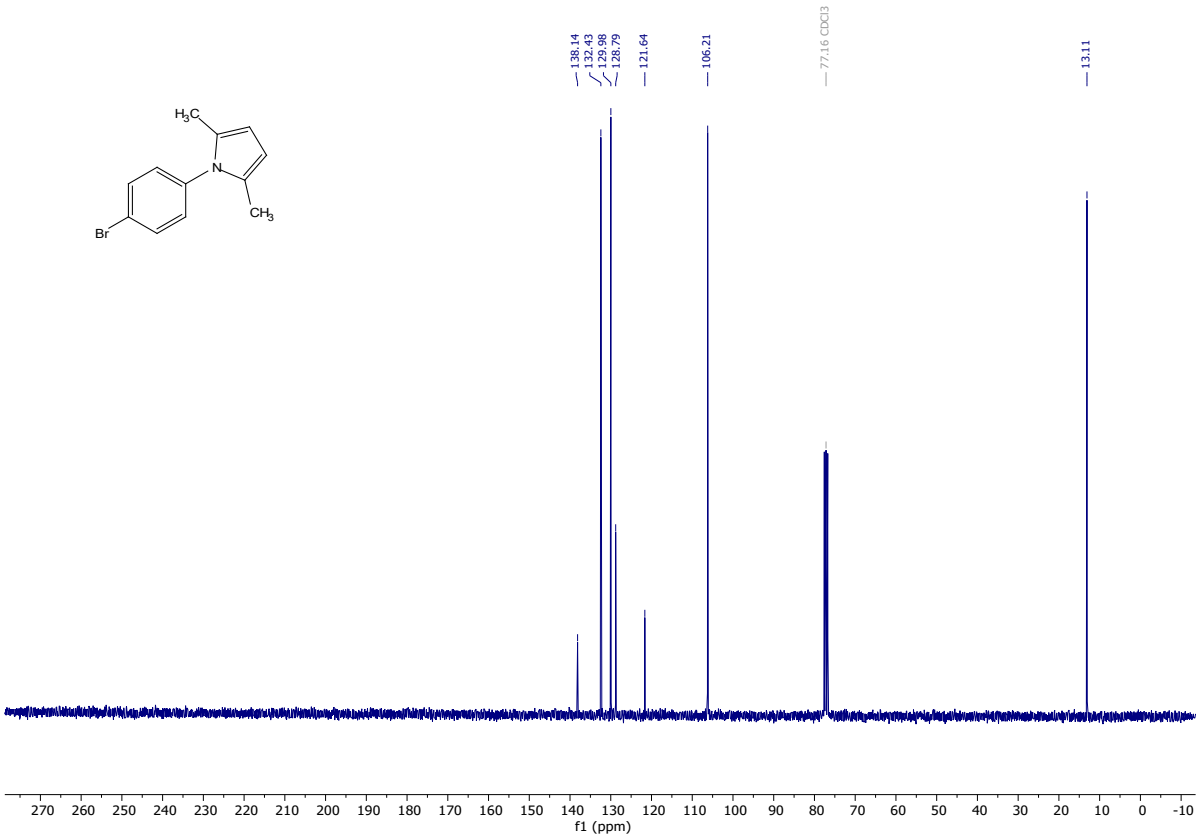


Figure S22. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **8b**.

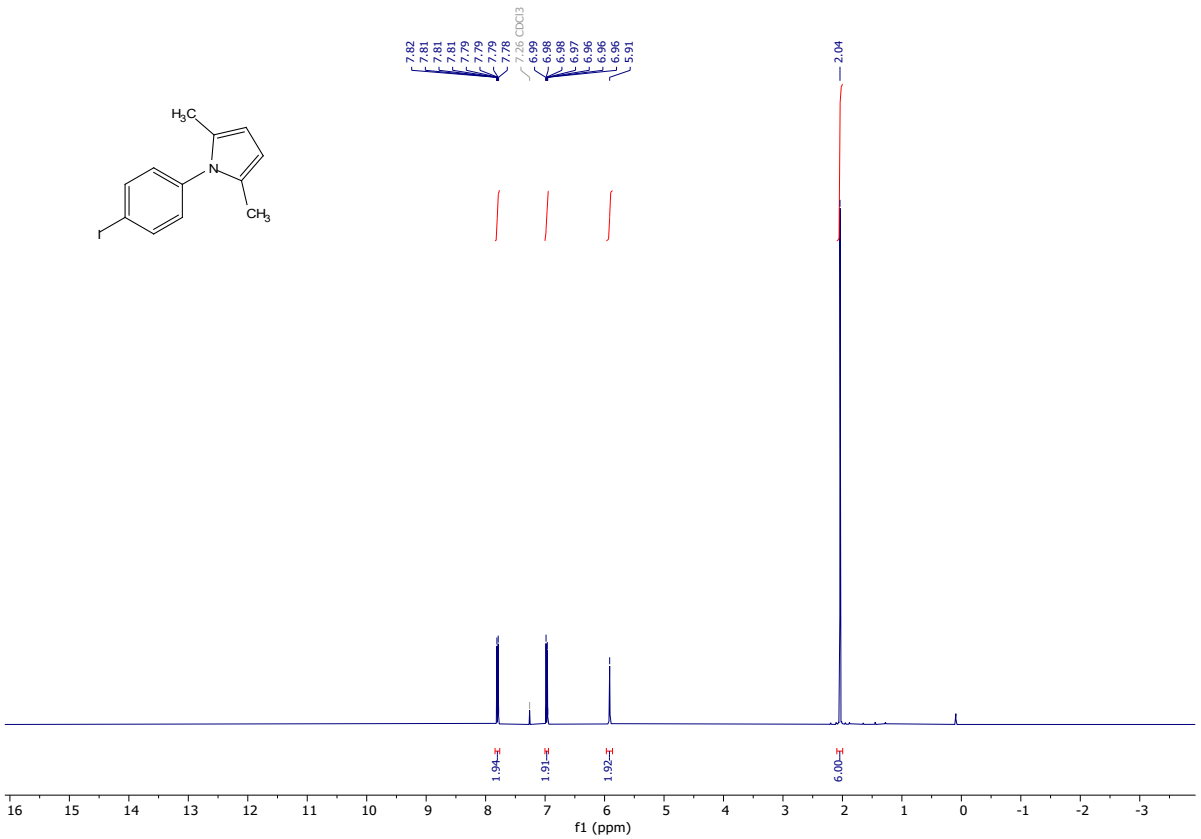


Figure S23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9b**.

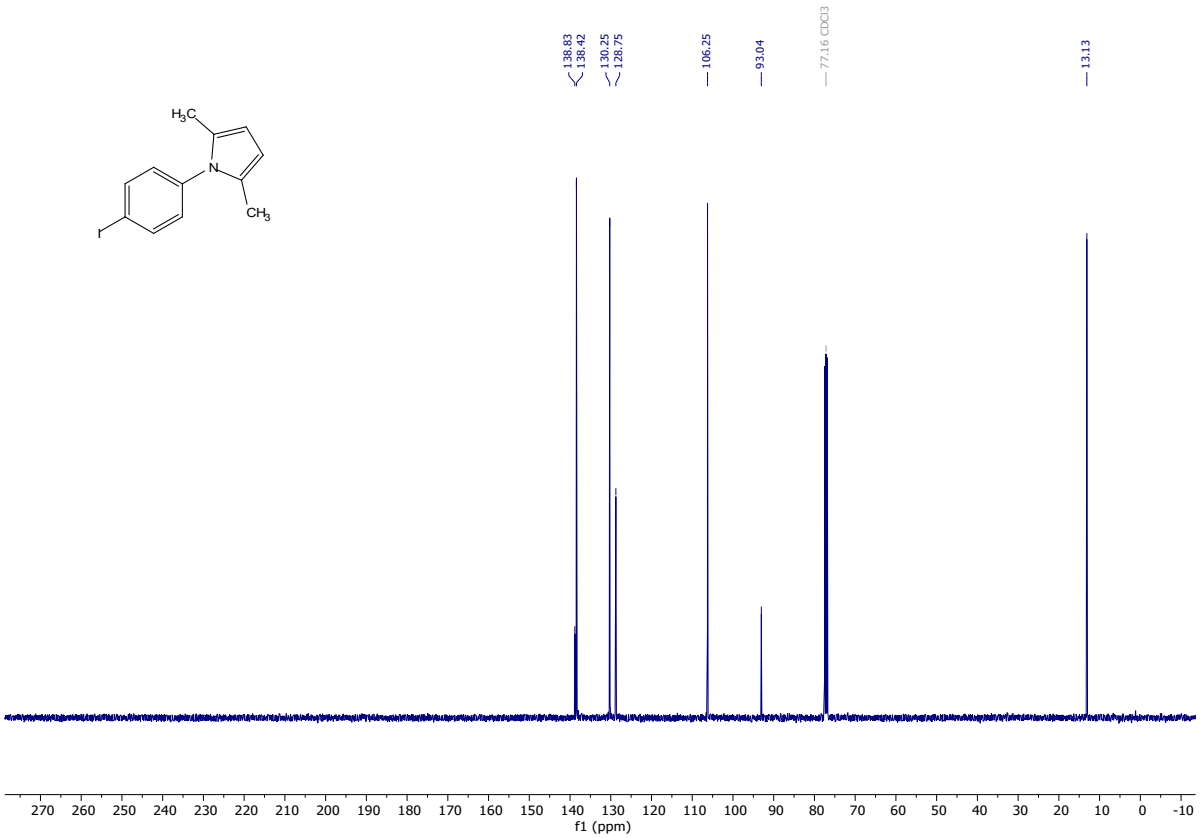


Figure S24. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **9b**.

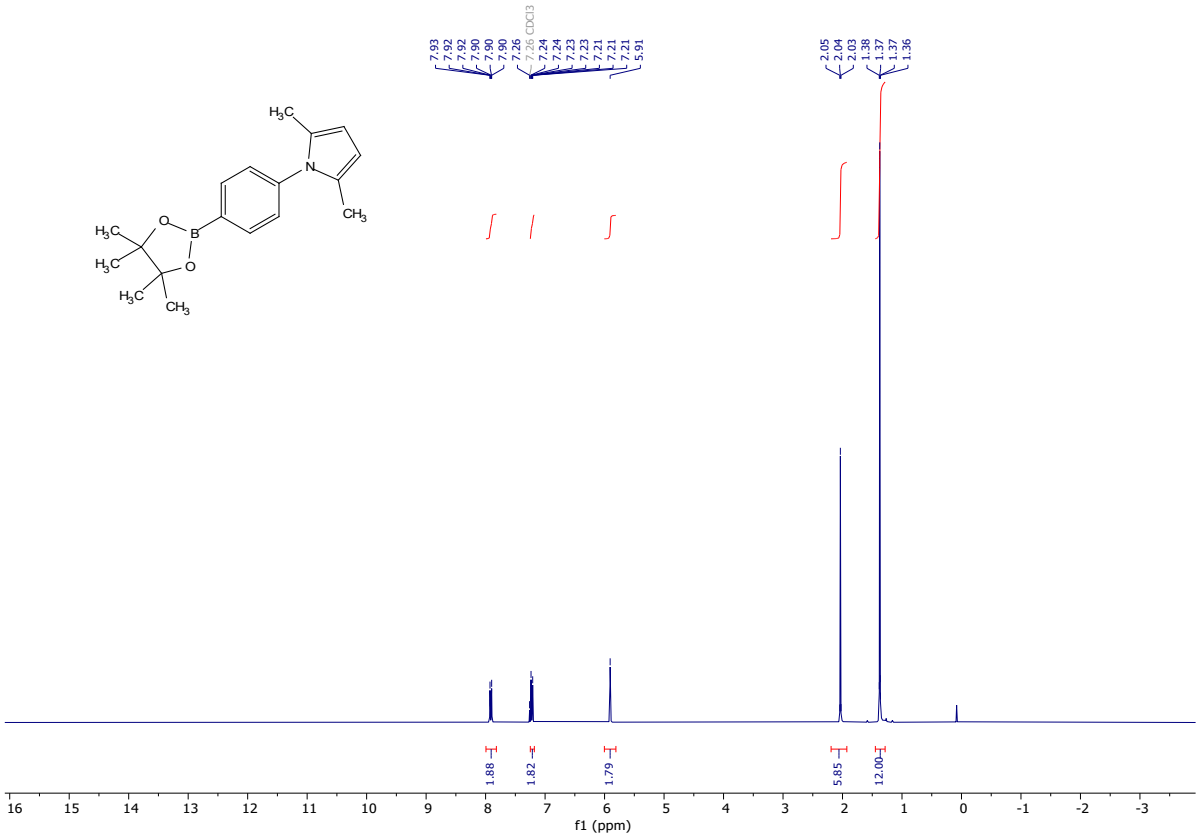


Figure S25. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **10b**.

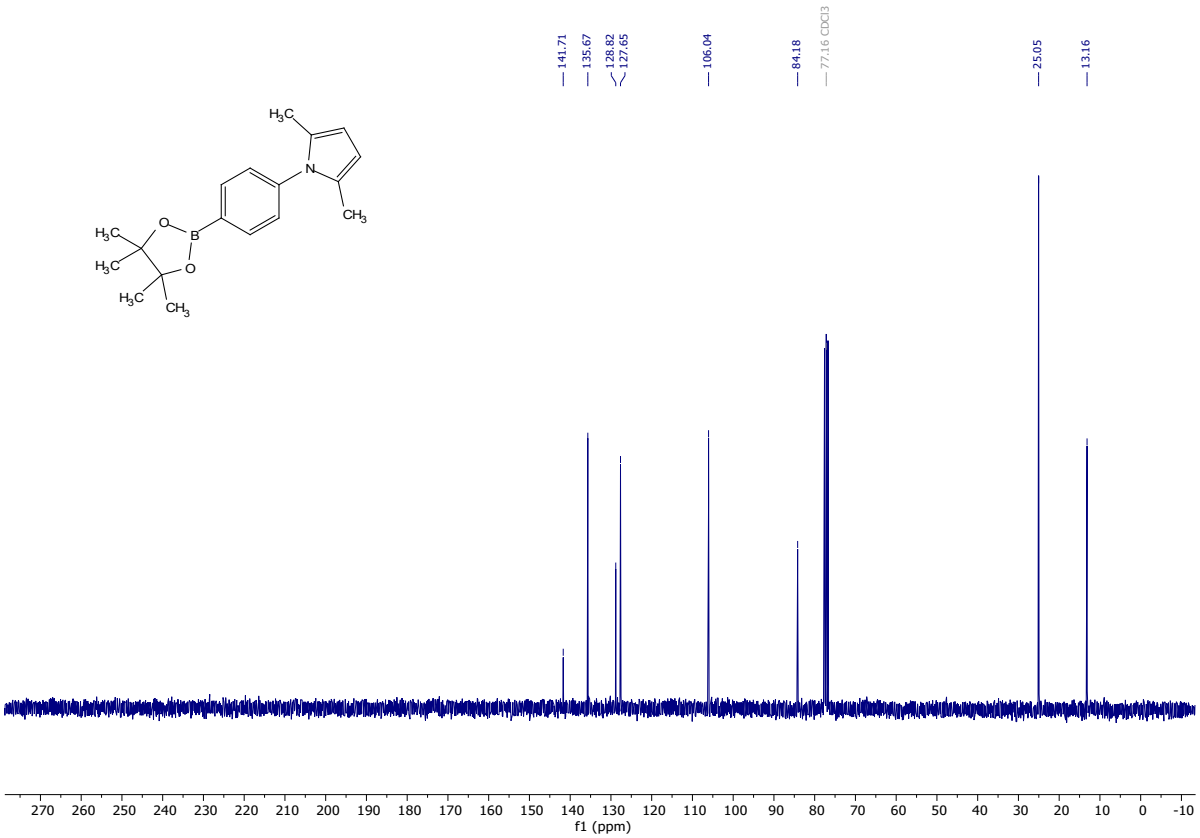


Figure S26. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **10b**.

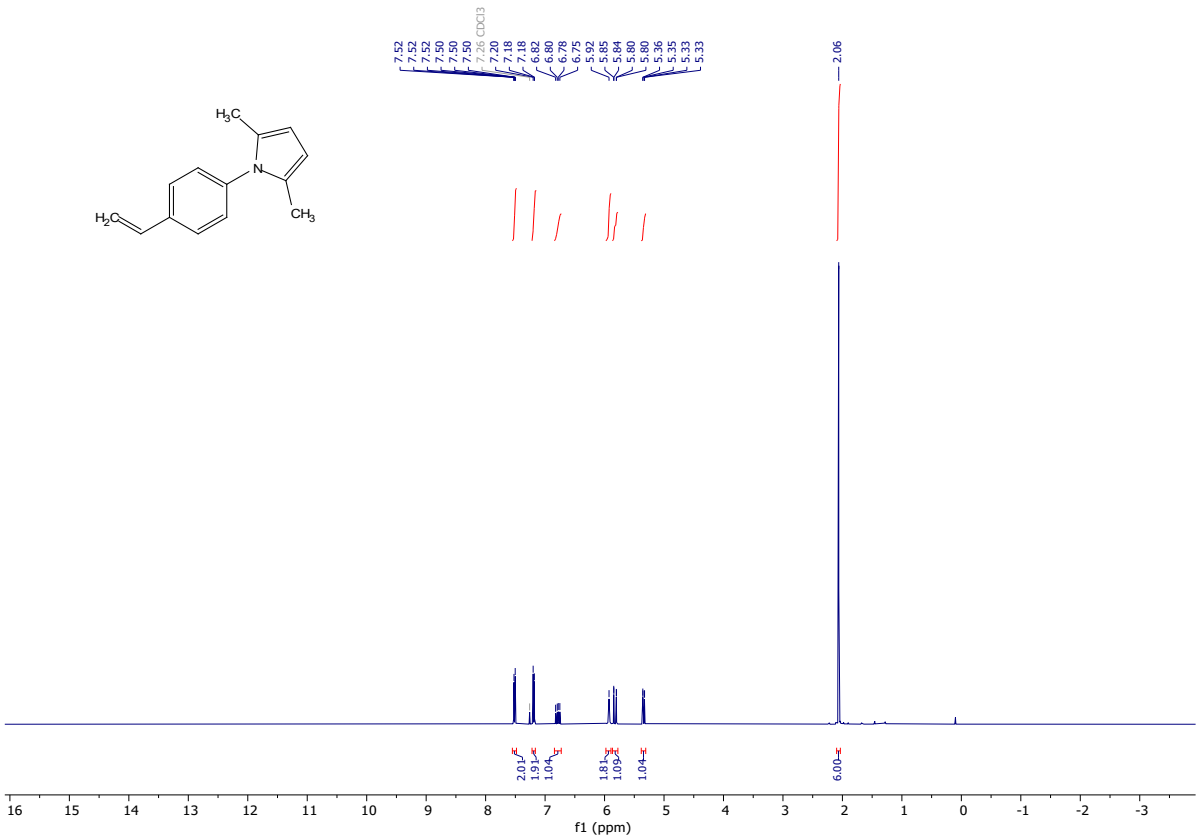


Figure S27. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **11b**.

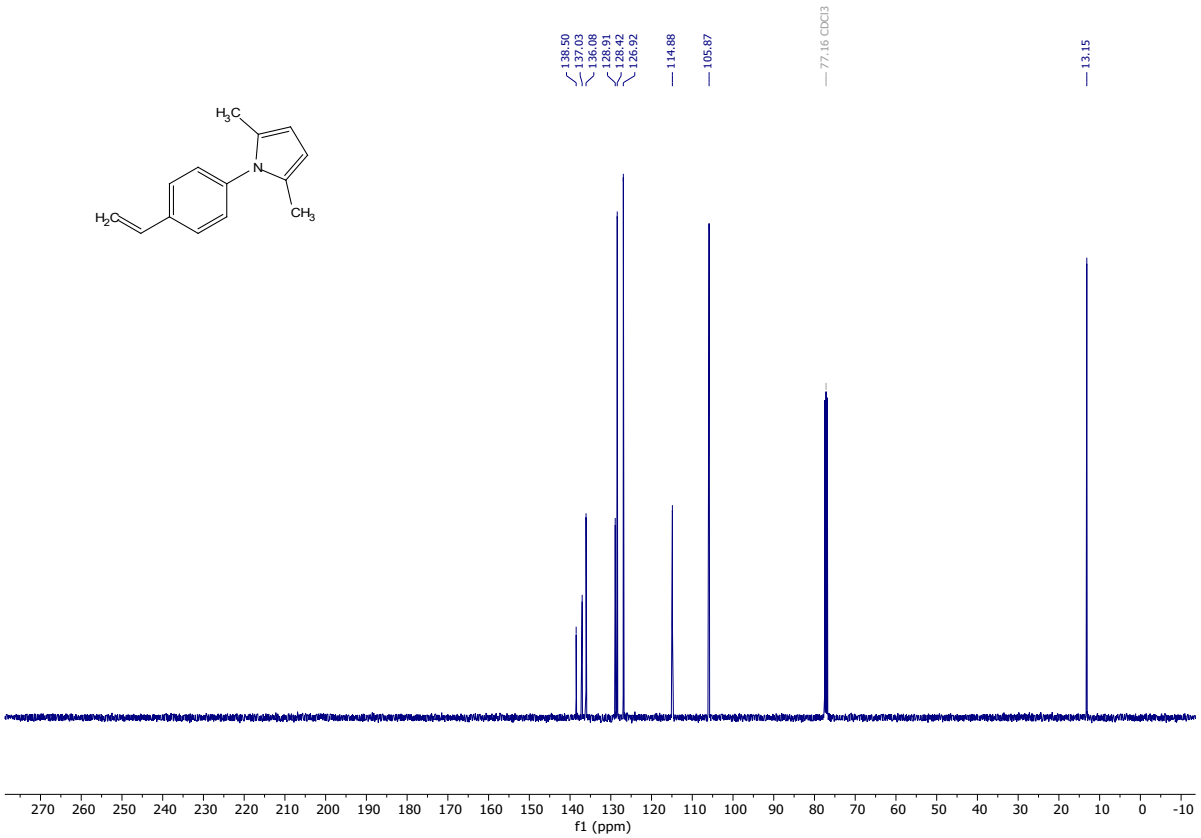


Figure S28. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **11b**.

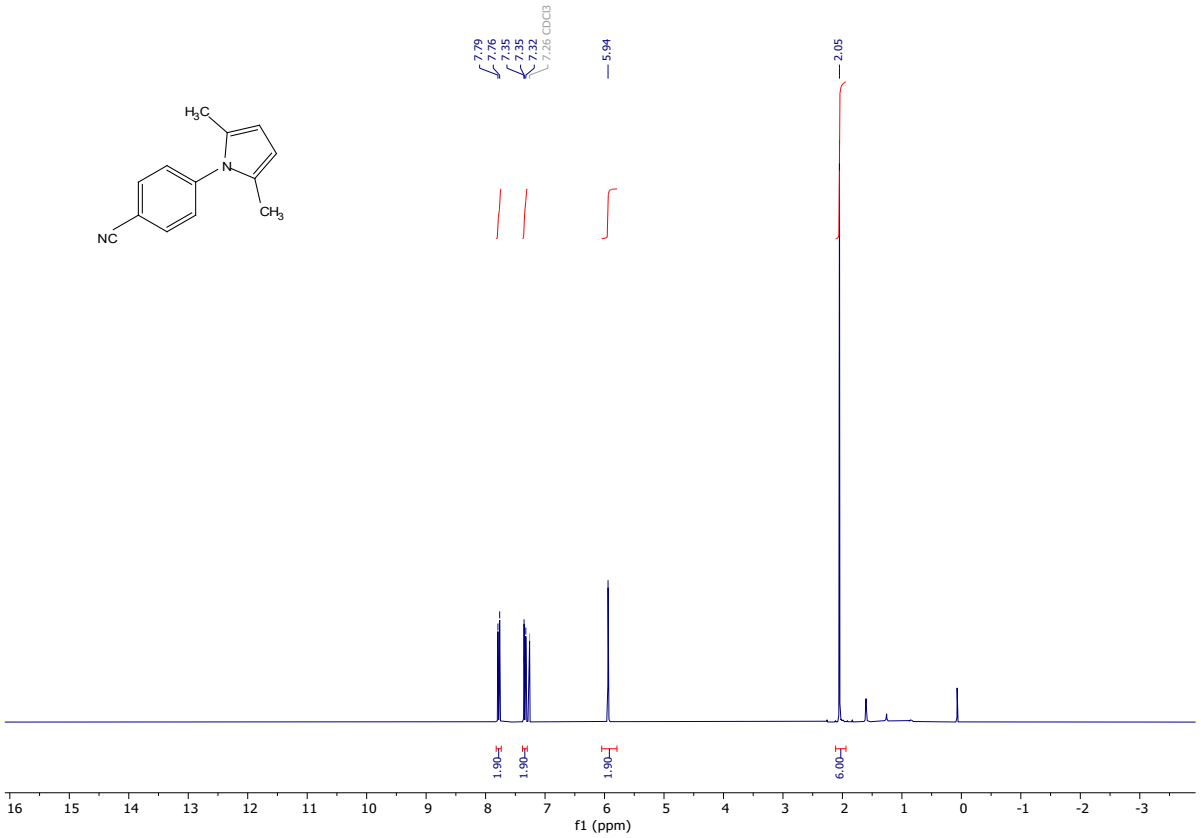


Figure S29. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **12b**.

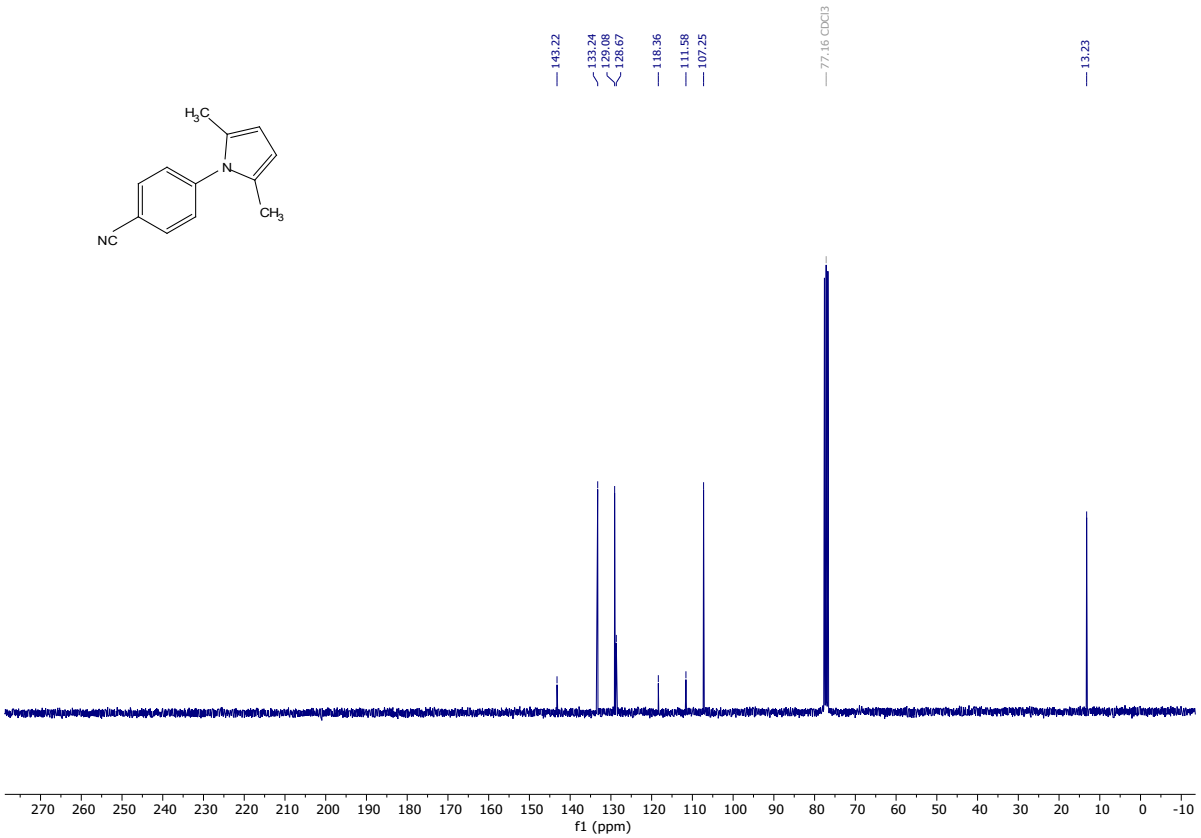


Figure S30. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **12b**.

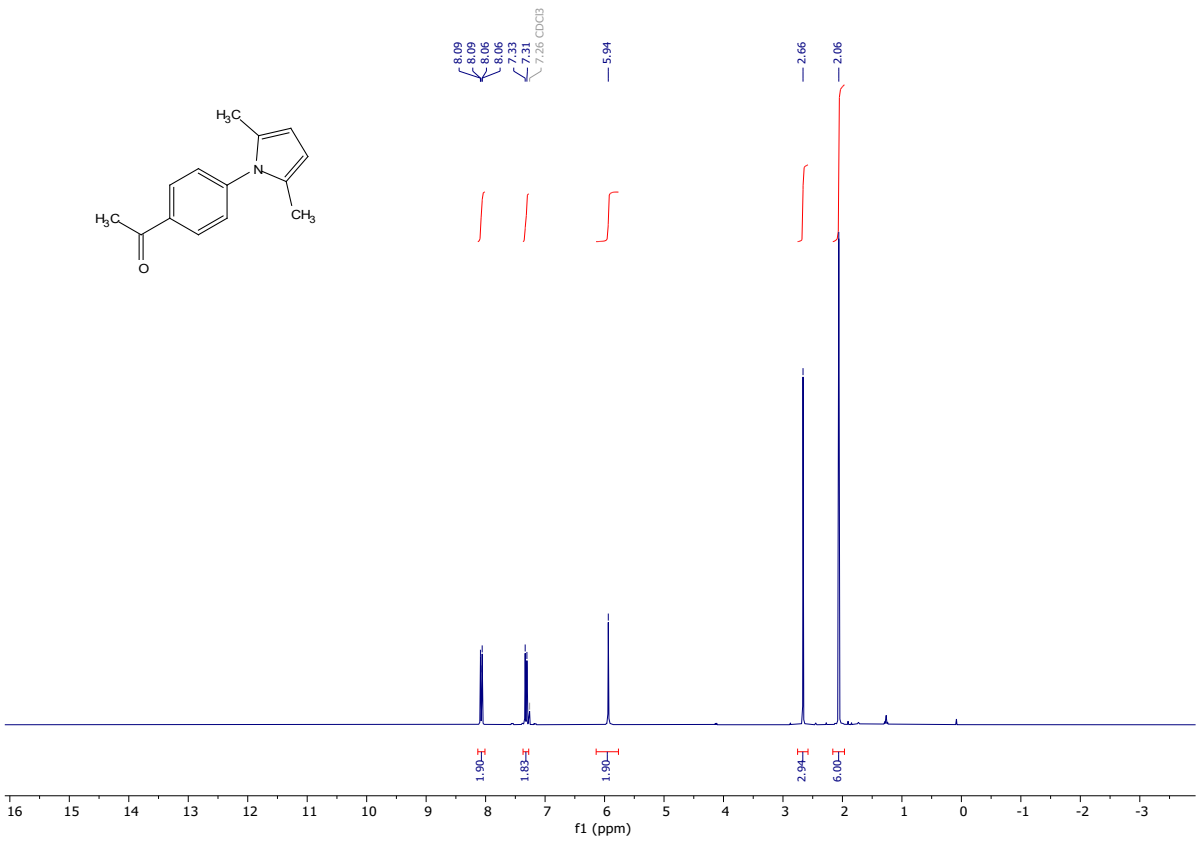


Figure S31. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **13b**.

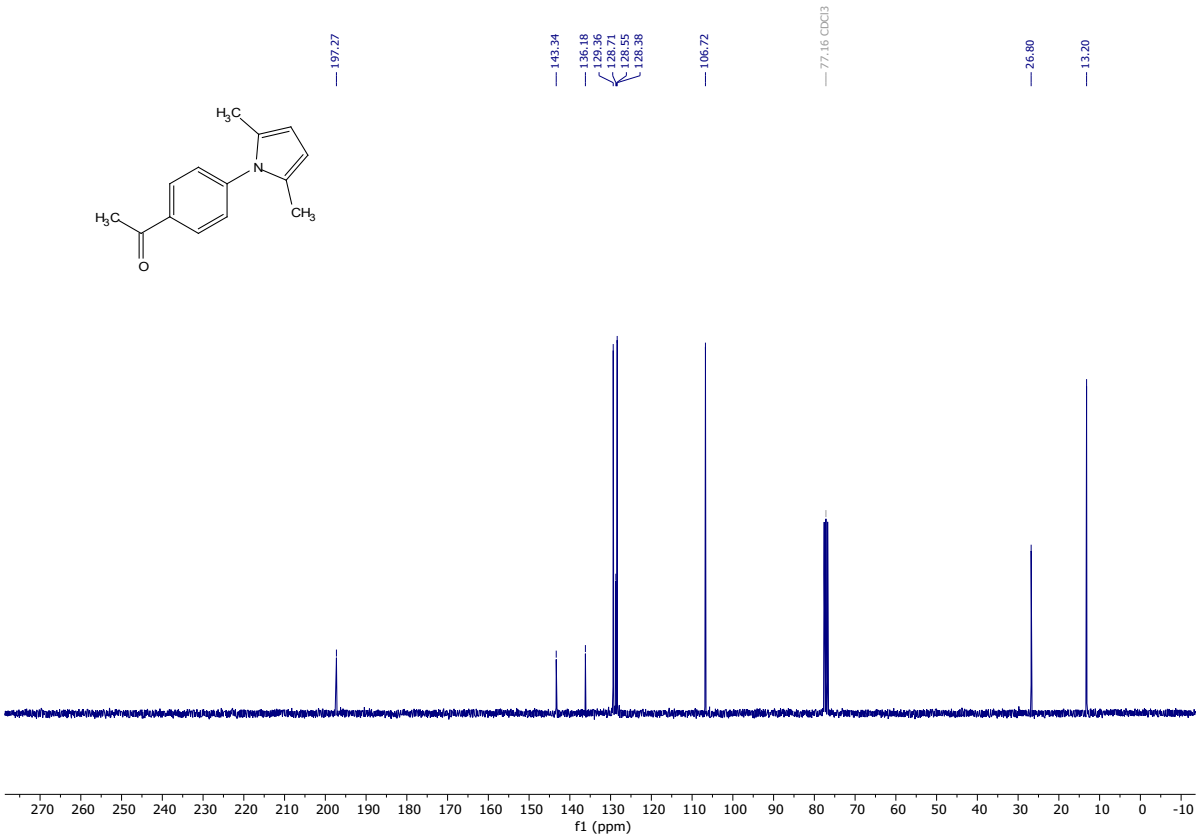


Figure S32. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **13b**.

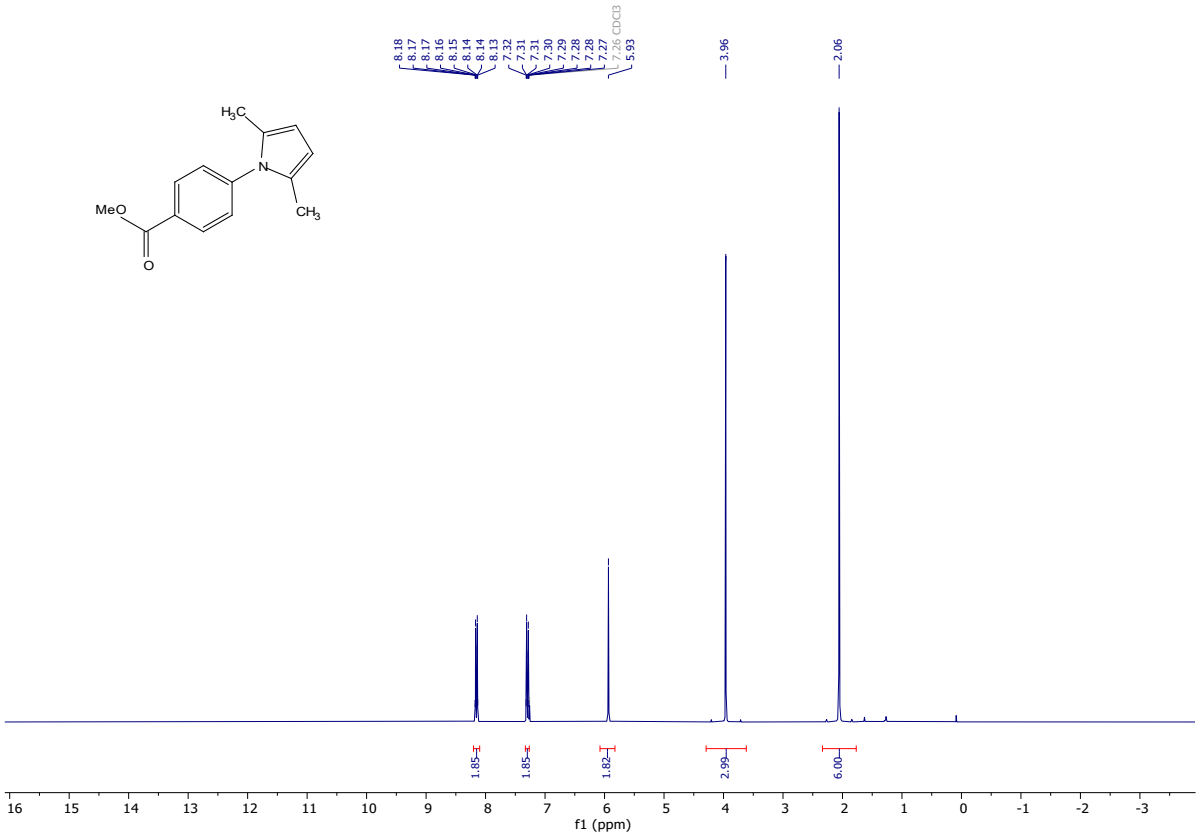


Figure S33. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **14b**.

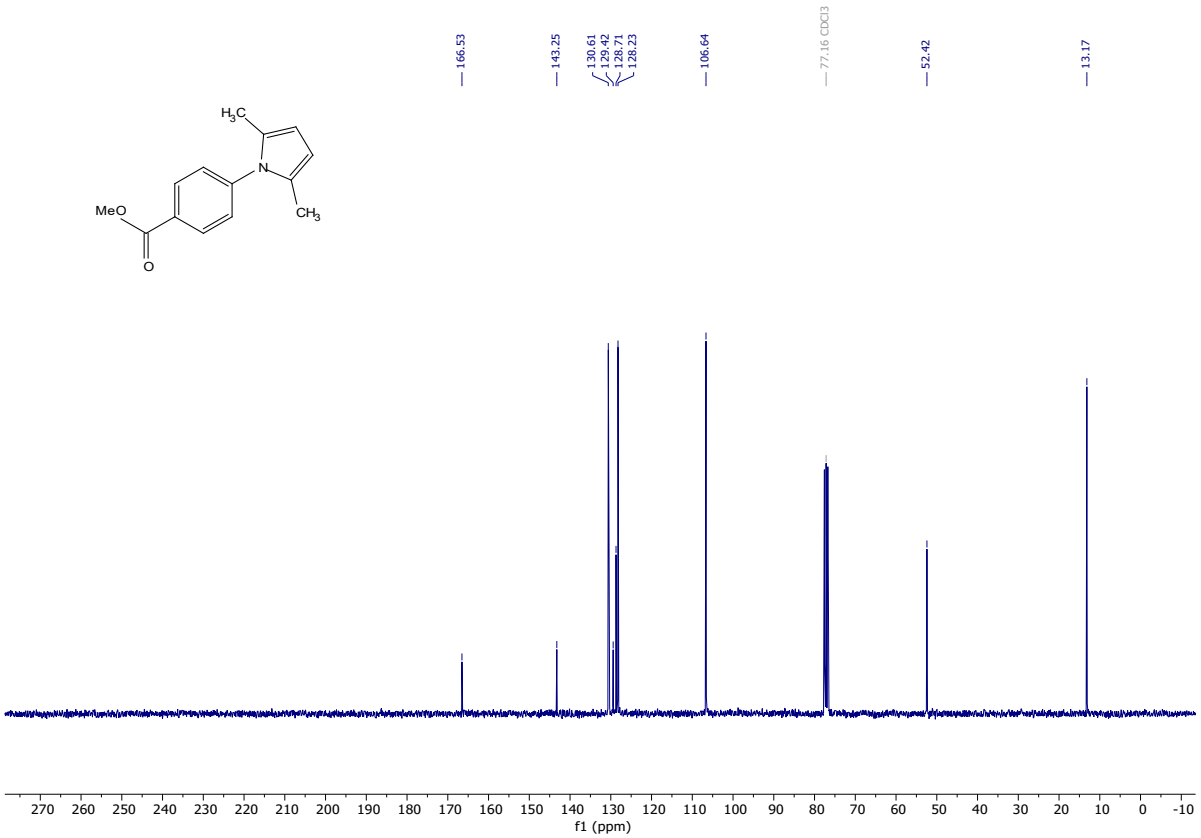


Figure S34. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **14b**.

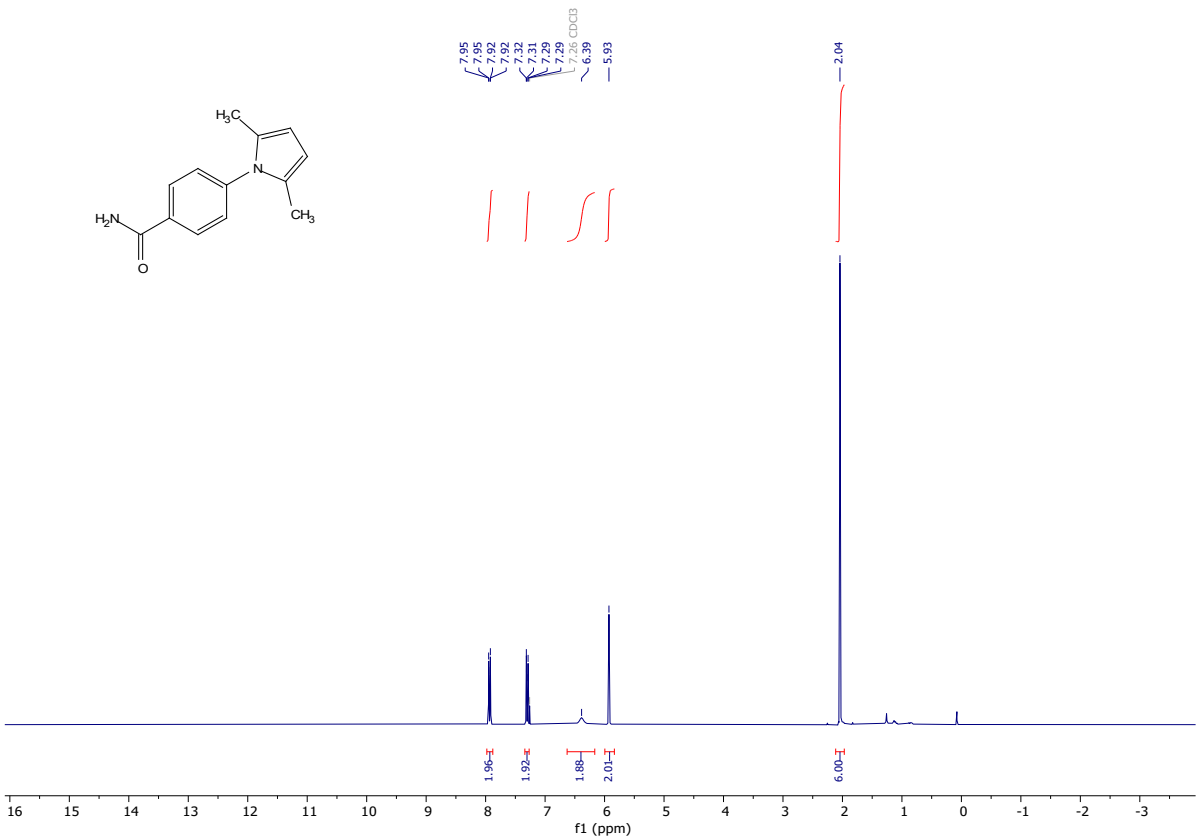


Figure S35. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **15b**.

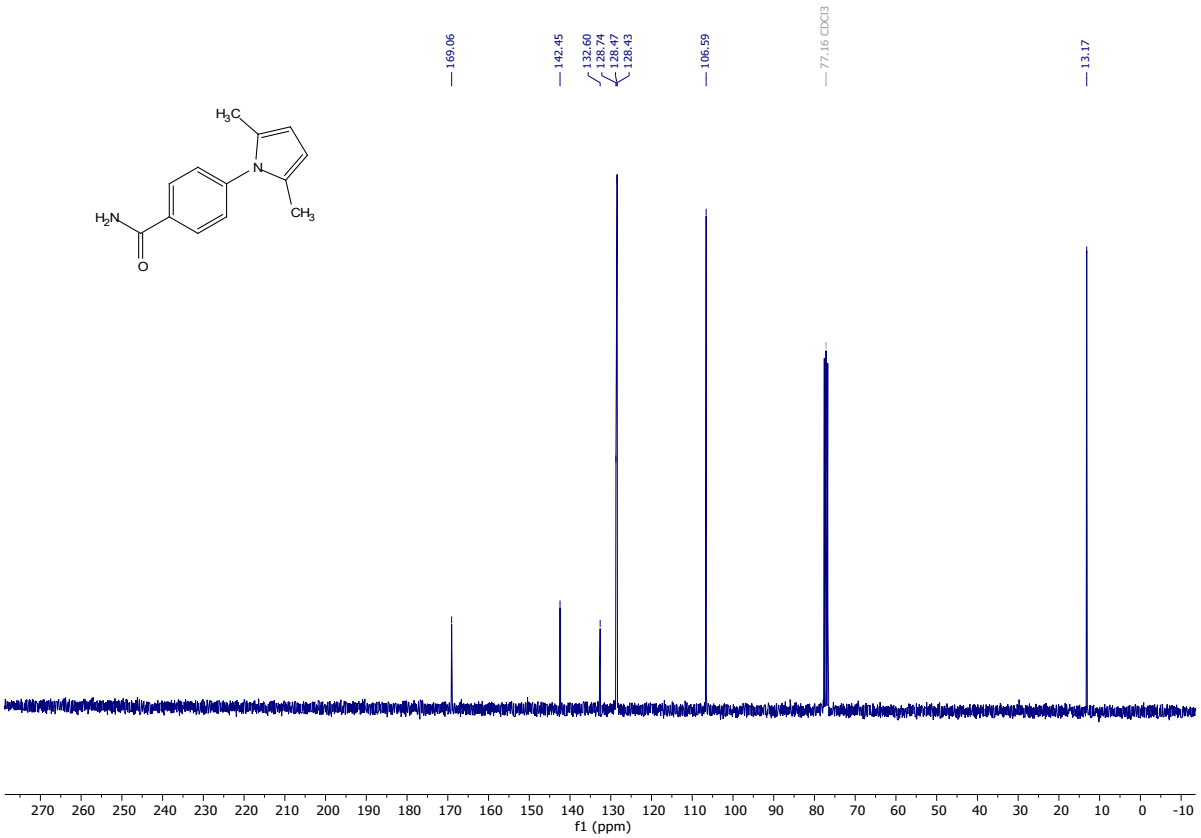


Figure S36. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **15b**.

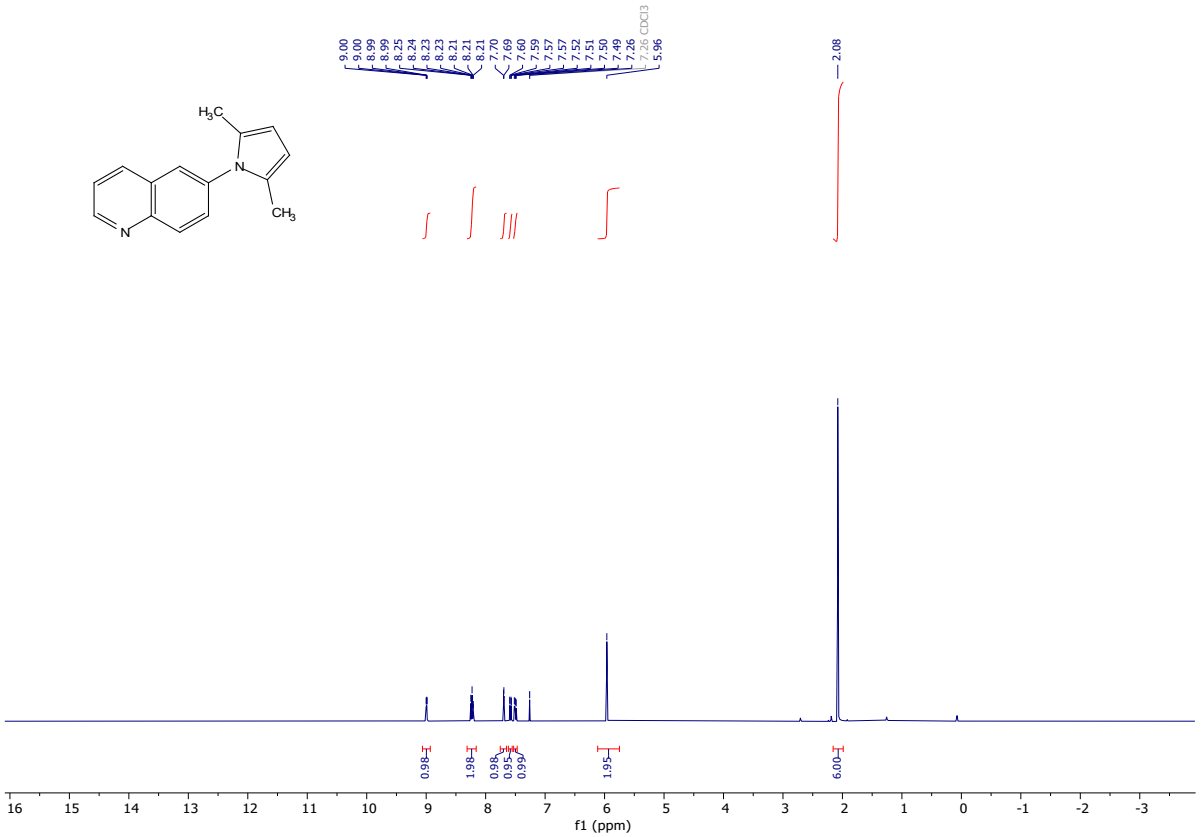


Figure S37. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **16b**.

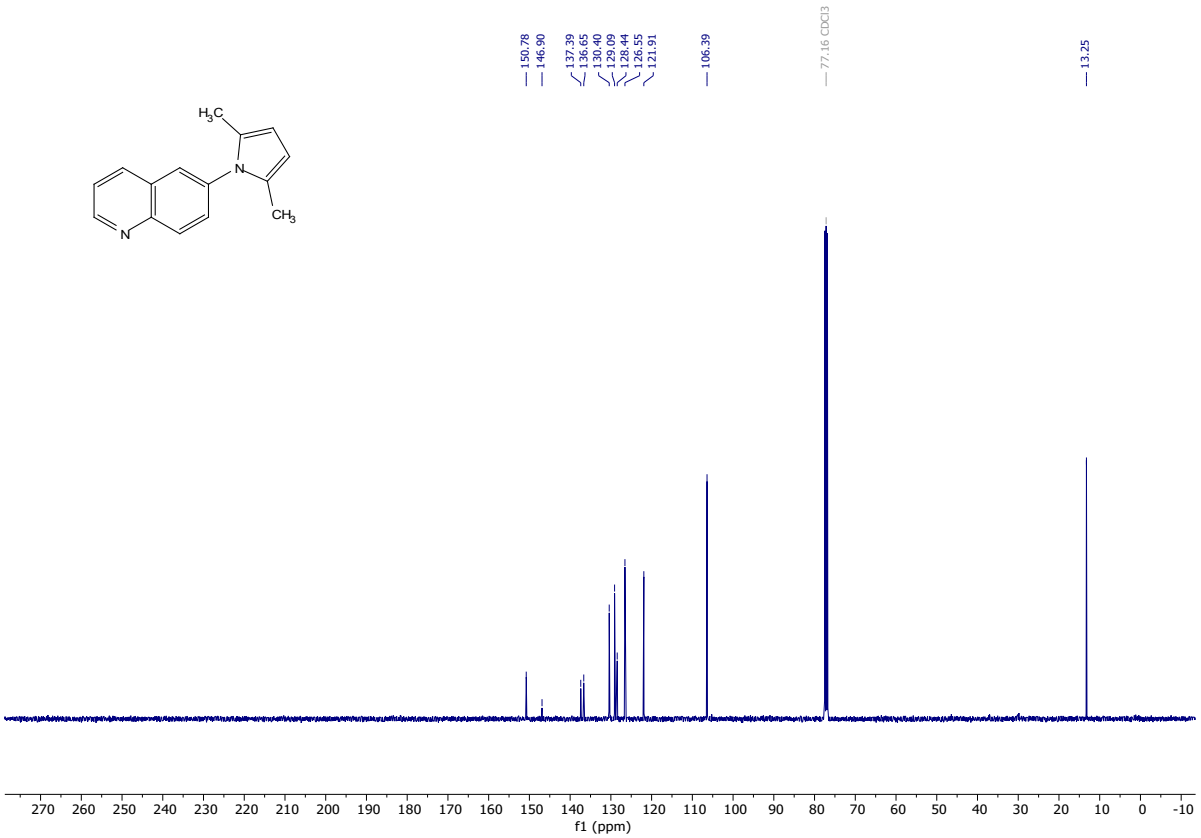


Figure S38. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **16b**.

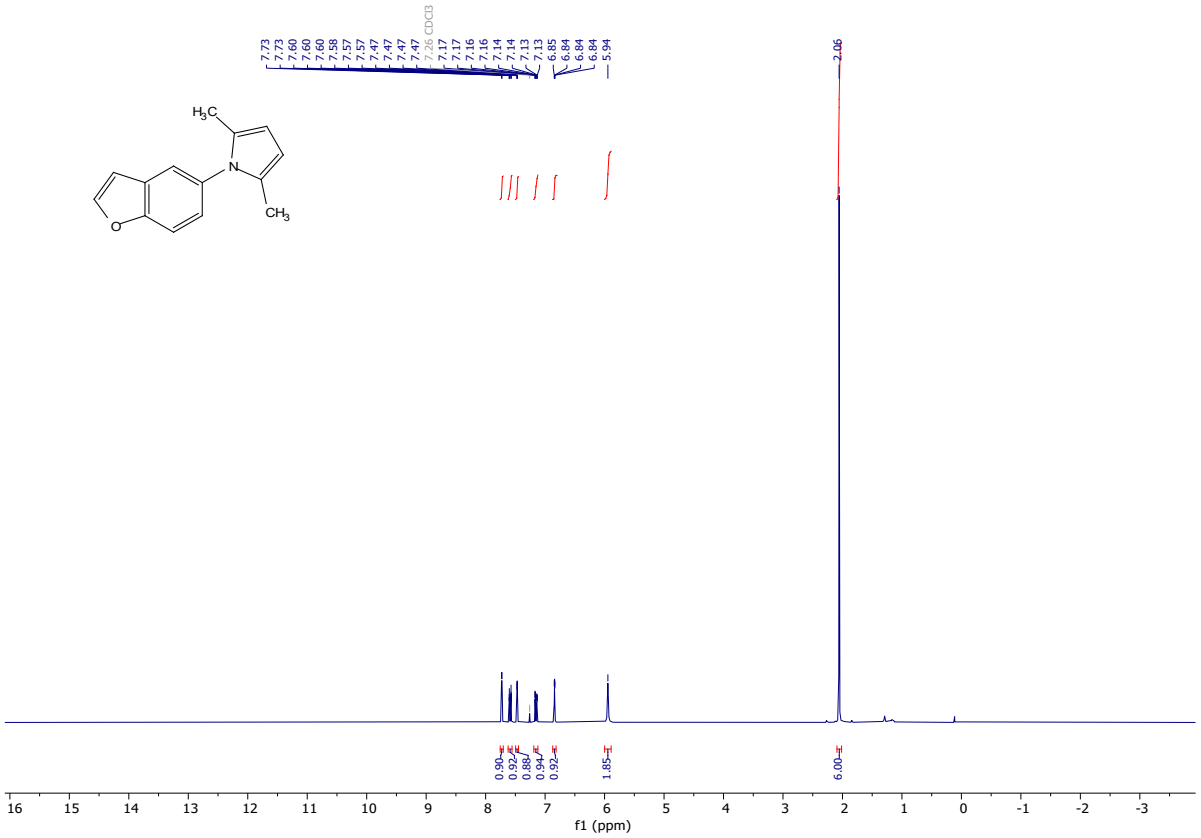


Figure S35. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **17b**.

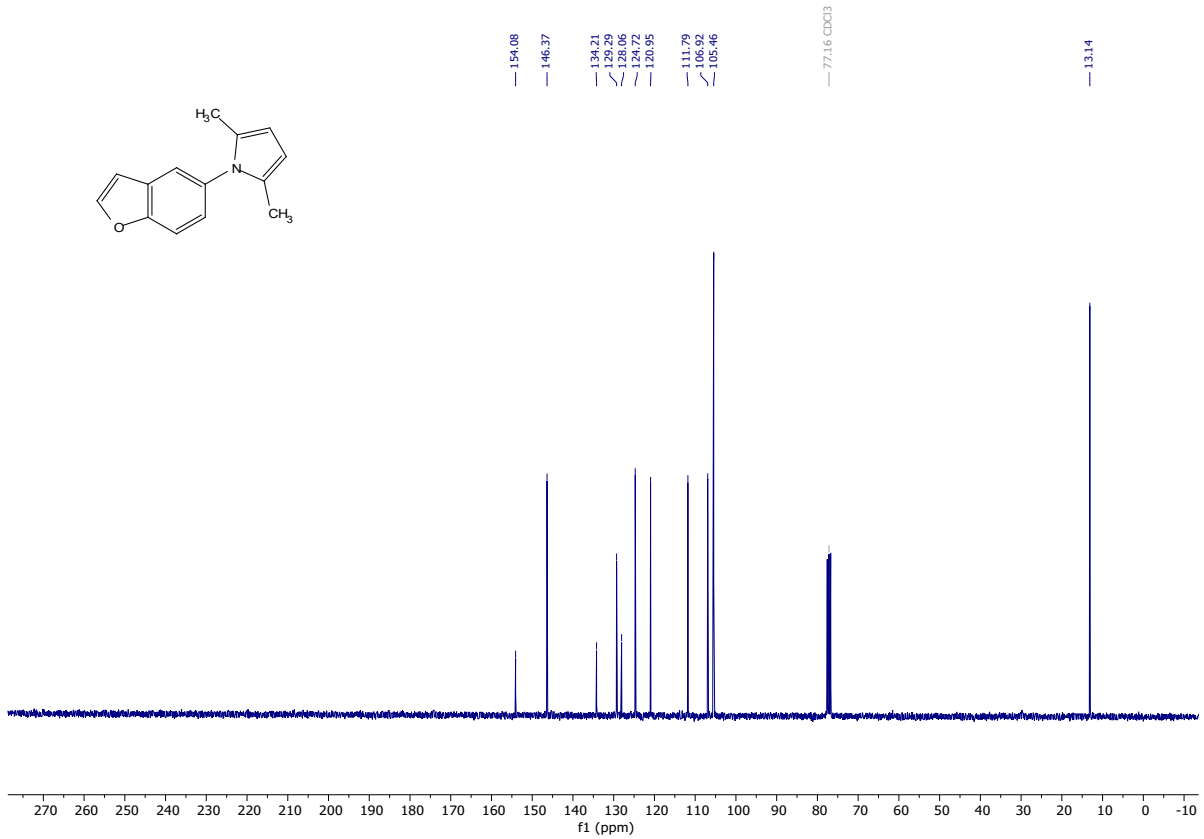


Figure S36. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **17b**.

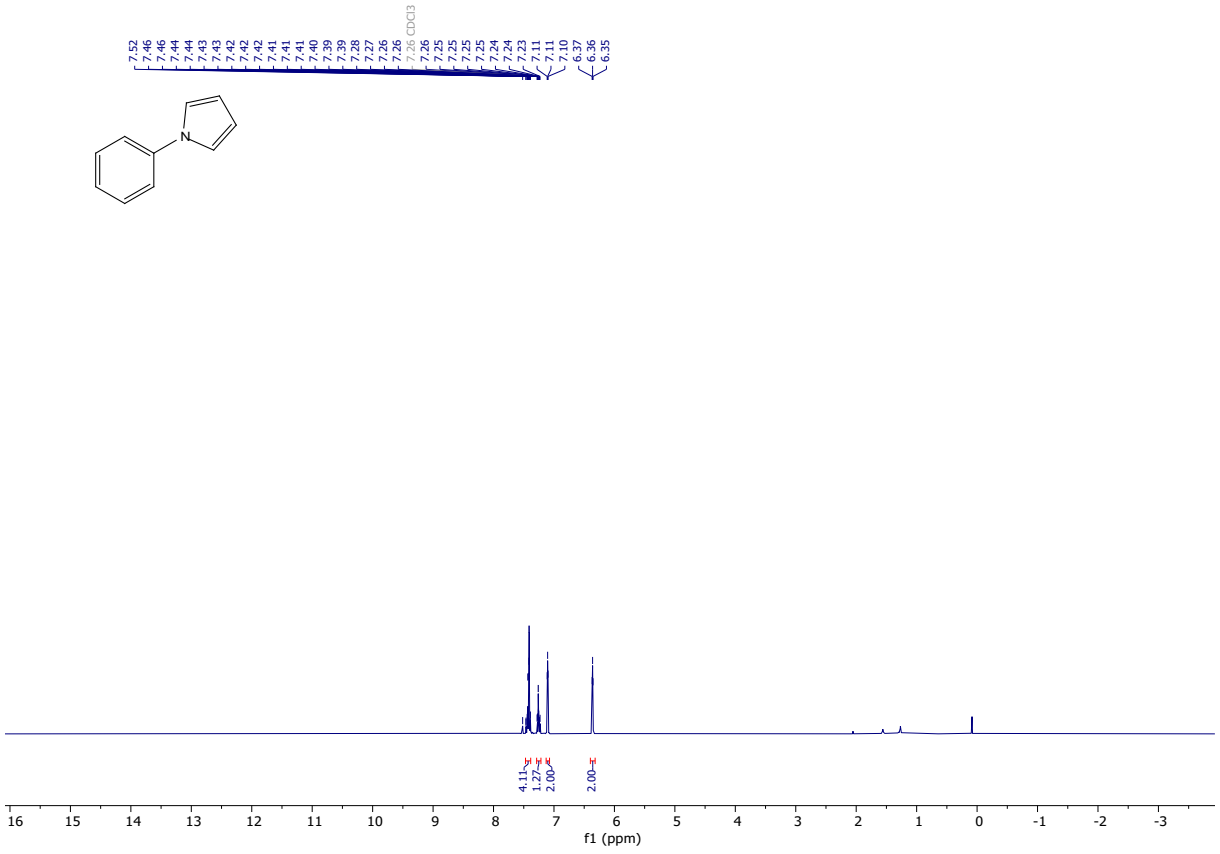


Figure S37. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **19b**.

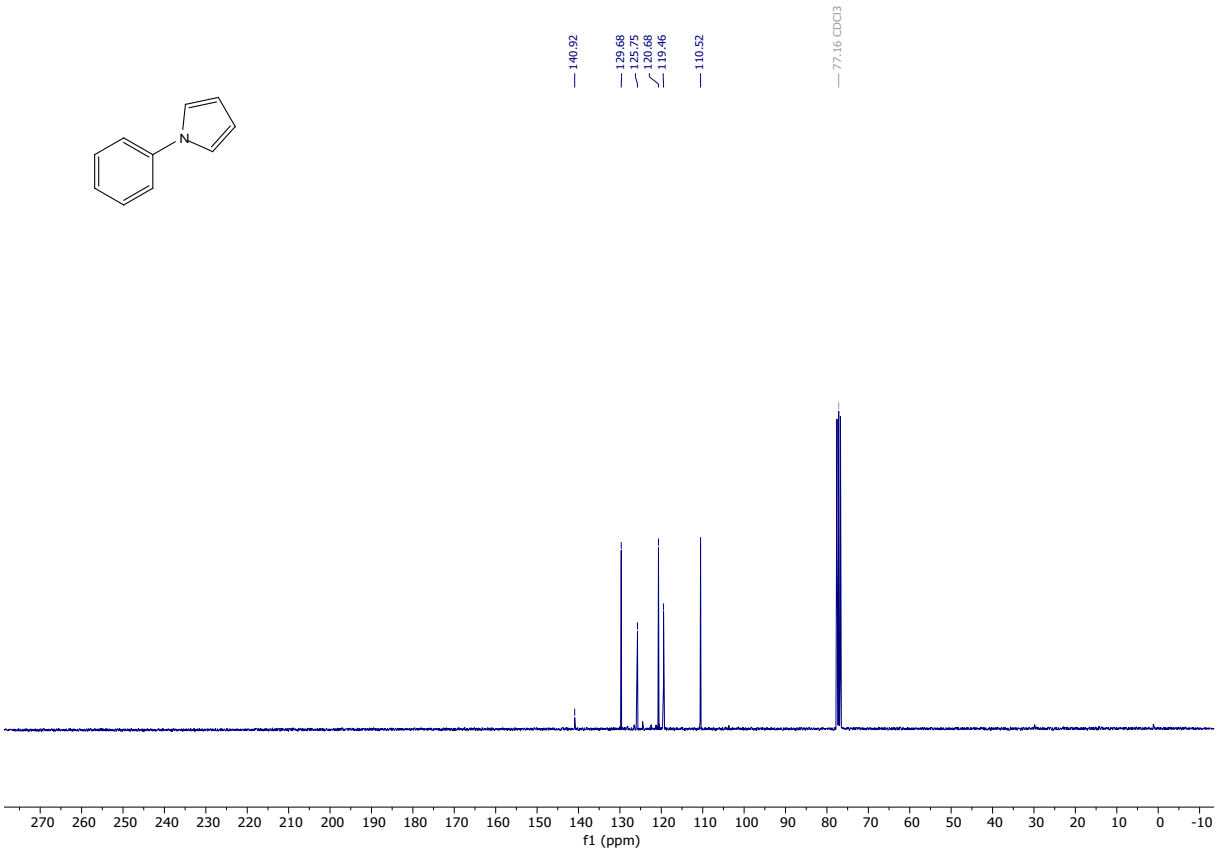


Figure S38. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **19b**.

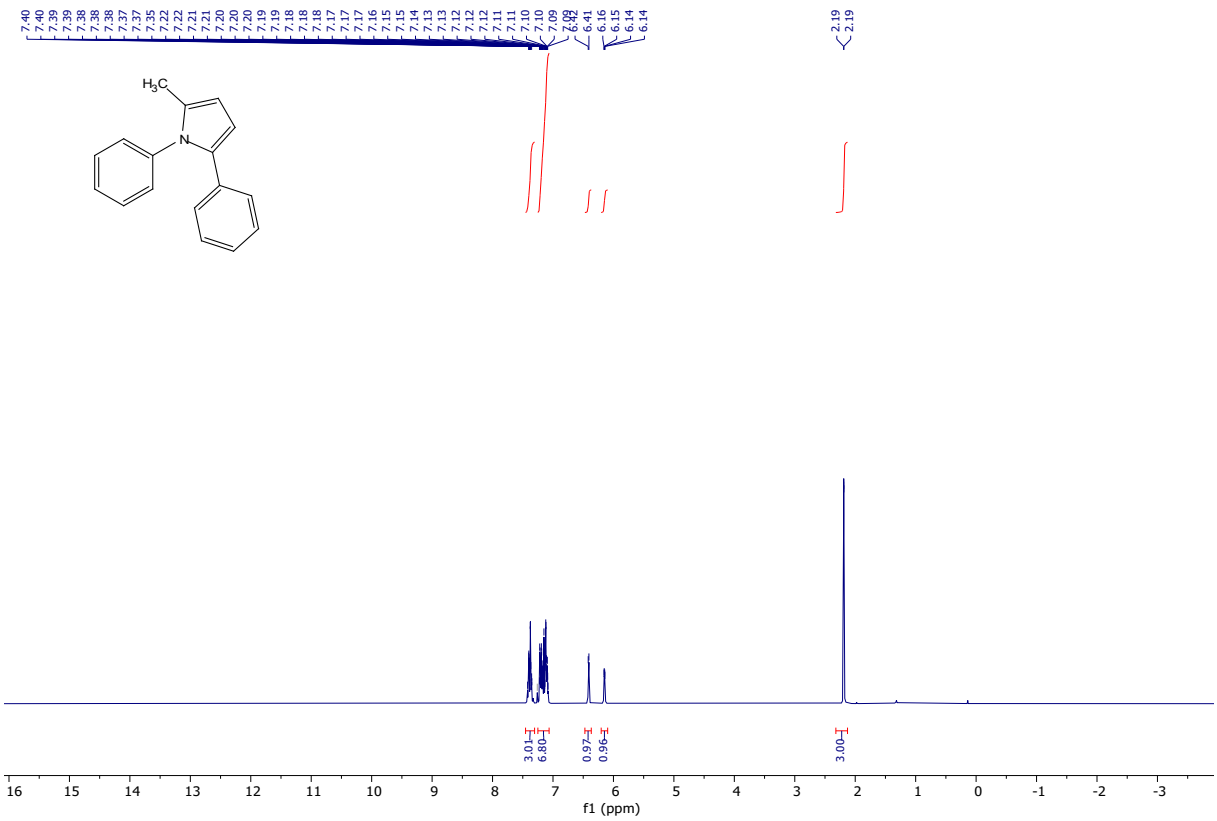


Figure S39. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **20b**.

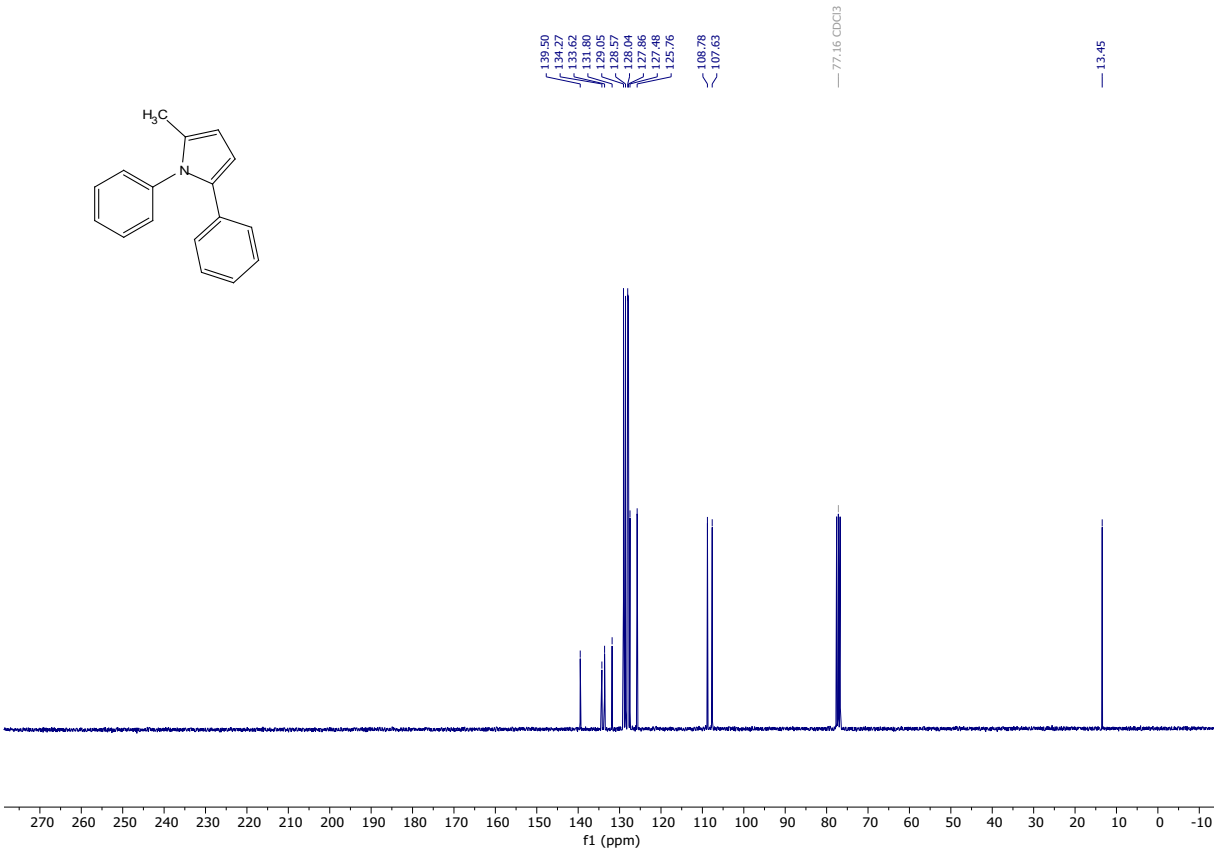


Figure S40. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **20b**.

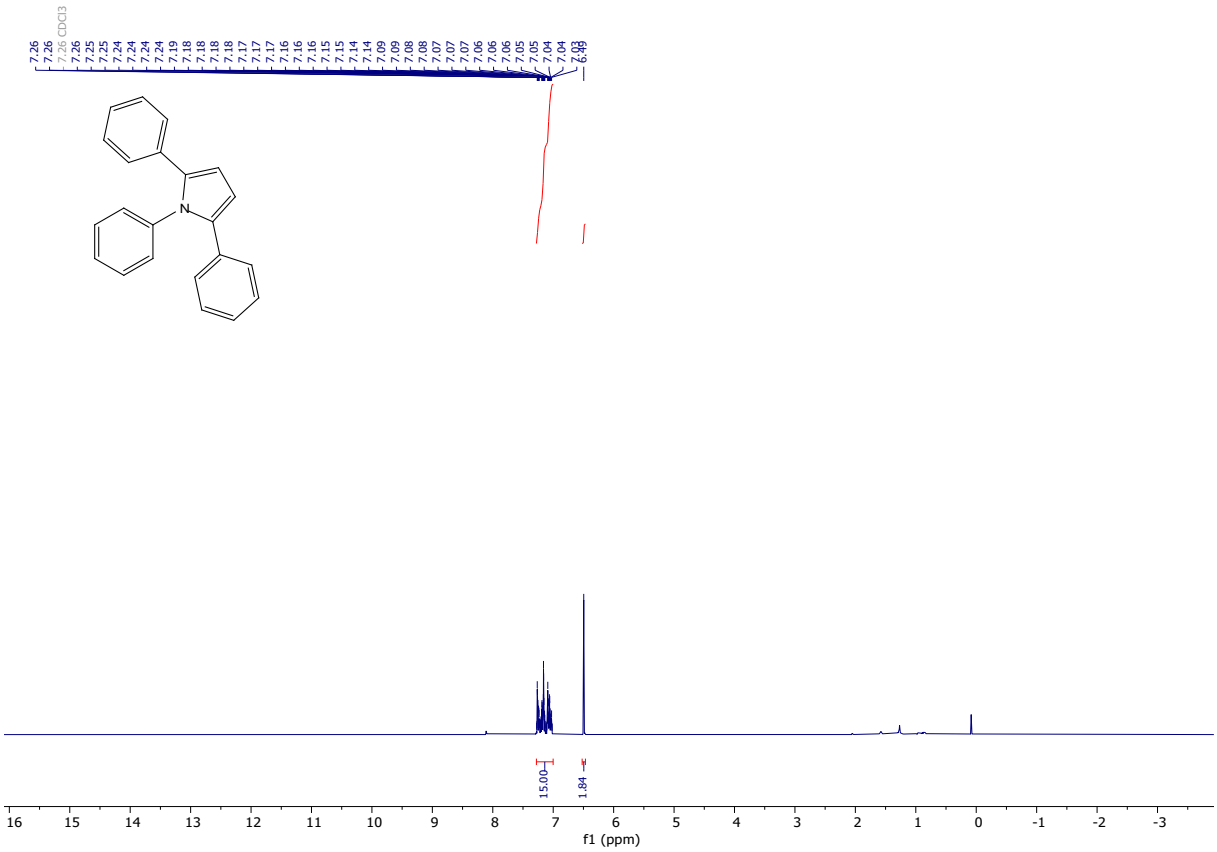


Figure S41. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **21b**.

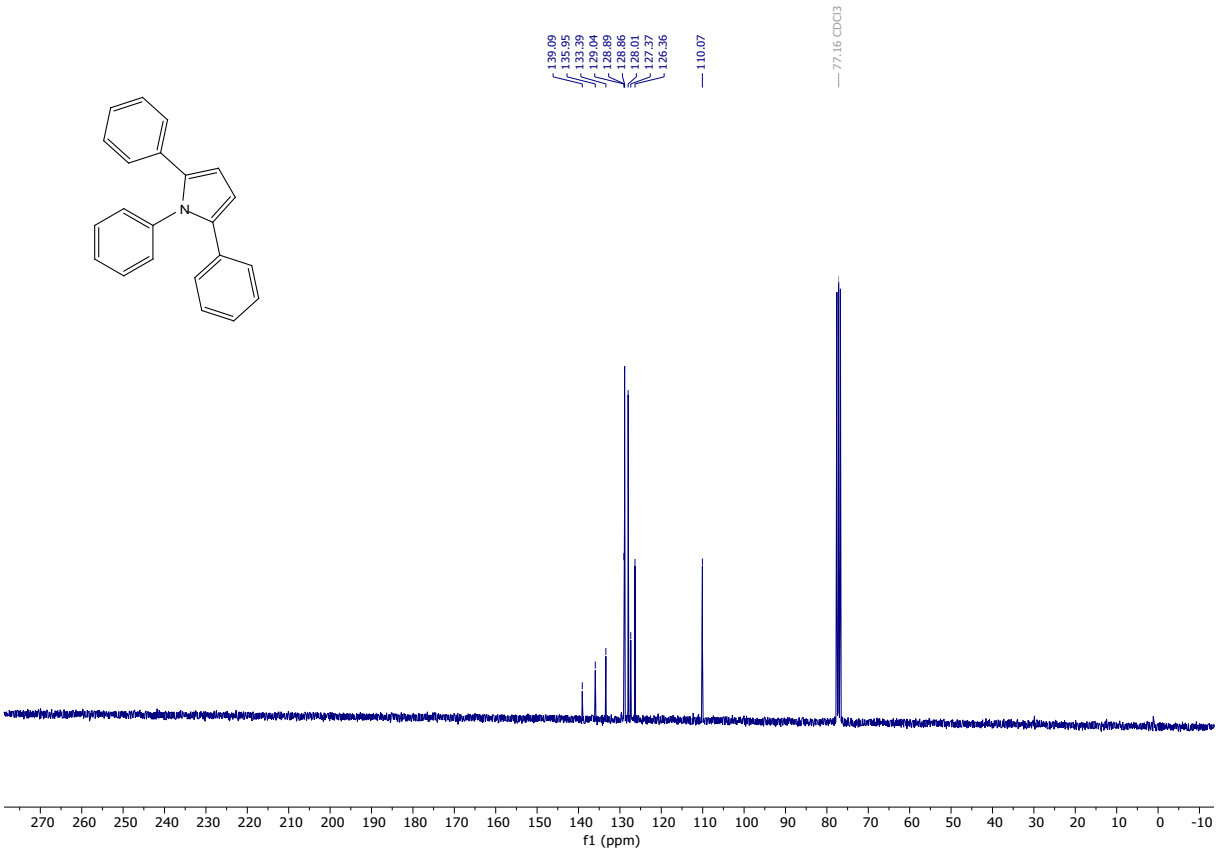


Figure S42. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **21b**.

S5. References

1. *Germany Pat.,* DE102011087302A1.
2. J. Fessler, K. Junge and M. Beller, *Chem. Sci.*, 2023, **14**, 11374-11380.
3. Z. Gong, Y. Lei, P. Zhou and Z. H. Zhang, *New. J. Chem.*, 2017, **41**, 10613-10618.