Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information for

Visible-Light Induced Disproportionation of Pyrrole Derivatives for Photocatalyst-Free Aryl Halides Reduction

Zhi-Jun Li,[a] Shuya Li,[b] Elan Hofman,[a] Andrew Hunter Davis,[a] Gyu Leem,[b,c] Weiwei Zheng[a]*

[a] Department of Chemistry, Syracuse University, Syracuse, New York 13244, United States

[b] Department of Chemistry, State University of New York College of Environmental Science and Forestry, Syracuse, New York 13210, United States.

[c] The Michael M. Szwarc Polymer Research Institute, Syracuse, NY 13210, United States, Syracuse, NY 13210, United States.

Corresponding Author

*wzhen104@syr.edu

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Experimental Procedures

A. Materials and methods

Aryl halides, heteroaryl halides, pyrrole derivatives (*N*-methylpyrrole, pyrrole, 1-phenylpyrrole, 3-methylindole), and other reagents were purchased from Alfa Aesar or Sigma-Aldrich and used as received unless otherwise stated. Reaction progress was monitored by thin-layer chromatography (TLC), which was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm). The TLC plates were visualized by either ultraviolet light (λ = 254 nm) or iodine staining. Purification of products was accomplished by flash column chromatography using Silicycle Silia*Flash*® P60 Academic Silica gel (particle size 40–63 μm, 230-400 mesh).

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE nuclear magnetic resonance spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) in $CDCl_3$ or DMSO-d_6 solutions with internal solvent signals (for ^{1}H and ^{13}C) as reference (7.26 ppm and 77.16 ppm for $CDCl_3$, 2.50 ppm and 39.5 ppm for DMSO-d_6, respectively). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration of protons). Multiplicities are reported as follows: s =singlet, br. s. = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, hept = heptet, dd = doublet of doublets, ddd = doublet of doublets of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet. Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm) and no special nomenclature is used for equivalent carbons. High-resolution mass spectra (HR-MS) were obtained on an Agilent 6200 Series TOF LC/MS mass spectrometer and are reported as m/z. Fourier transform infrared spectra (FTIR) were recorded on a Nicolet IR200 FTIR spectrometer, in the range of 4000–500 cm^{-1}. The UV-Visible (UV-Vis) spectra were collected on an Agilent Cary 60 spectrophotometer. Steady-state photoluminescence (PL) spectra were recorded using an Edinburgh FLS-980 spectrometer. Unless otherwise specified, a quartz cell cuvette with a 10-mm path length was used for fluorescence measurements of liquid samples. GC-MS analyses were obtained on a Clarus 580 Gas Chromatograph and Clarus SQ 8S Mass spectrometer. Electrochemical experiments were performed on a Pine Wave Now Potentiostat under argon atmosphere. The measurements were performed in DMSO containing substrates or products (5-10 mM) and 0.1 M tetra-*n*-butylammonium tetrafluoroborate using ferrocene/ferrocenium (Fc/Fc^{+}) as an internal reference. A glassy carbon electrode (working electrode), platinum wire counter electrode, and Ag/Ag^{+} (in 0.01 M $AgNO_3$) reference electrode were employed. The scan rate is 100 mV s^{-1}. It should be noted, for the convenience of comparison with reported potential value in literature, we converted the potential value based on Ag/Ag^{+} (in 0.01 M $AgNO_3$) reference electrode into the potential value based on saturated calomel electrode (SCE) in the related descriptions and Figures. The photochemical reactions were performed with 455 nm LEDs (blue, λ_{max} = 455 ± 15 nm, 3.0 W) or 405 nm LEDs (purple, λ_{max} = 405 ± 15 nm, 2.5 W).

B. Photopolymerization mechanism of pyrrole.

Among the numerous conducting polymers prepared to date, polypyrrole (PPy) has been extensively studied in a variety of applications in the industry and new technology, because the pyrrole monomer (Py) is easily oxidized, environmentally stable, commercially available, and has good redox properties.[1-4] Although chemical and electrochemical polymerization has mostly been used in the synthesis of PPy,[1-4] photochemical polymerization should have great advantages for the fine fabrication of PPy with general mechanisms similar to chemical and electrochemical polymerizations.[4-7] The most widely accepted polymerization mechanism of PPy is the coupling between radical cations.[1-6] The process involves the following steps:[1-6] In the initiation step, the pyrrole monomers absorb a photon giving rise to photoexcited pyrrole molecules, which are immediately

quenched by unexcited pyrrole molecules to give both cation and anion pyrrole radicals (Step 1, note the cation radical has several resonance forms, *i.e.*, 1-3). This radical cation, which has a greater unpaired electron density in the α-position, dimerizes *via* the resonance form 1 to afford a dihydromer dication. Then, the di-cation generates a neutral pyrrole dimer with disproportionation (Step 2), as this dimer, on account of its greater conjugation, more easily absorbs longer wavelengths of light than the monomer. It is immediately be photoexcited and quenched by unexcited pyrrole molecules again to give both cation and anion pyrrole radicals (Step 3). The new cation radical centers undergo a coupling step with a monomeric radical cation, and then eliminate protons from the resulting charged trimer. (Step 4), The process continues until linear polypyrrole molecules (Step 5) with a degree of polymerization of **n** are generated.

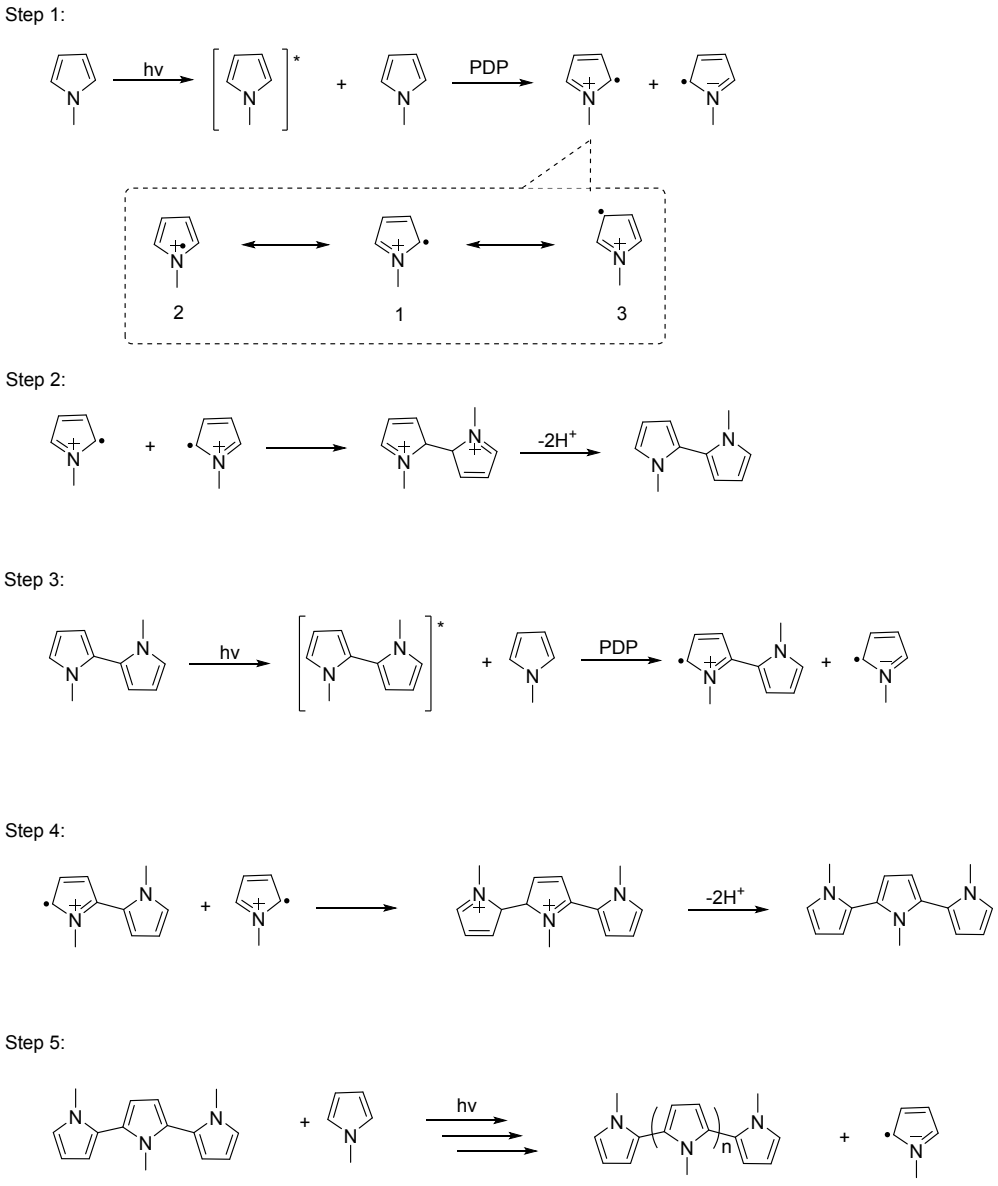
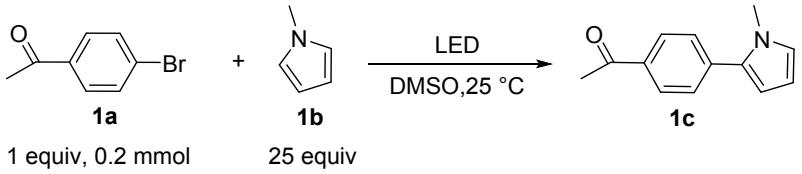


Figure S1. Accepted mechanism for the photochemical polymerization of pyrrole and their derivatives (Polymerization of N-methylpyrrole is demonstrated as an example).

C. General procedure for the C–H arylation reactions of aryl halides

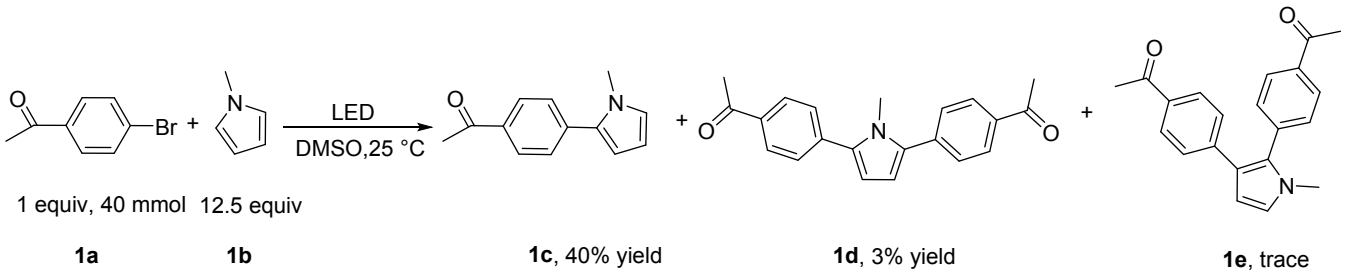
C.1. Procedure for the Model Reaction:



1a 1 equiv, 0.2 mmol + **1b** 25 equiv → **1c**

Aryl halides **1a** (0.2 mmol, 1 equiv) and pyrrole derivatives **1b** (5.0 mmol, 25 equiv) were dissolved in DMSO (total volume of the solution ~ 4 mL) using a 10 mL Pyrex tube equipped with a rubber septum and magnetic stir bar. The resulting mixture was kept under air conditions (or degassed using argon *via* a syringe needle if needed). The reaction mixture was irradiated through the side of the Pyrex tube using 455 (24 hours) or 405 (6 hours) nm LED light setup, which are equipped with water-cooling systems to keep the reaction solution at room temperature. The reaction mixture was transferred into a separating funnel where 10 mL of distilled water and 2 mL of brine were added after the reaction. The resulting mixture was extracted with ethyl acetate (AcOEt, 3 x 10 mL), and then the combined organic layers were dried using anhydrous $MgSO_4$. Purification of the crude product was achieved by flash column chromatography using hexane/ethyl acetate as eluents on a silica gel column.

C.2. Procedure for the gram-scale reaction:



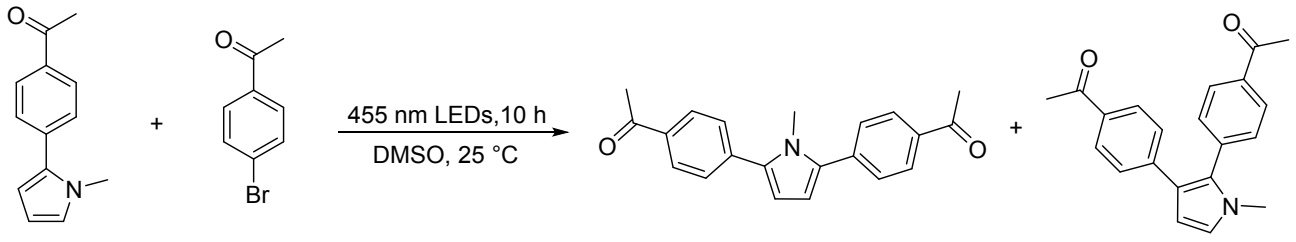
1 equiv, 40 mmol **1a** + 12.5 equiv **1b** → **1c**, 40% yield + **1d**, 3% yield + **1e**, trace

In a 500 mL capacity Schlenk tube, 4′-bromoacetophenone **1a** (8.0 g, 40 mmol, 1.0 equiv.) and N-methylpyrrole **1b** (500 mmol, 12.5 equiv) were dissolved in DMSO (total volume of the solution ~ 300 mL). The reaction mixture was irradiated using a high-power LED light setup, *i.e.,* 455 (~ 16 W, 120 hours) or 405 (~ 12 W, 30 hours) nm, which were equipped with water-cooling systems to keep the reaction solution at room temperature. The reaction mixture was transferred into a separating funnel and 500 mL of distilled water and 100 mL of brine were added after the reaction. The resulting mixture was extracted with ethyl acetate (AcOEt, 3 × 500 mL), and the combined organic layers were dried by anhydrous $MgSO_4$. Purification of the crude product was achieved by flash column chromatography using hexane/ethyl acetate as eluents on silica gel column. The products analysis showed ~ 40% and ~ 3% yields of product **1c** and **1d** with trace amount of **1e**, respectively, after the reaction. The conversion was greatly decreased because of the reduced efficiency of irradiation during the gram-scale reaction. The reaction mixture displayed a dark color after few hours of irradiation as a result of polymerization of the *N*-methylpyrrole **1b**. This effect further hindered the efficient irradiation of the solution, especially in larger volume reactions, where the conversion stalled with little to no further conversion was observed after conversion over the ~ 40% point.

C.3. Procedure for the TEMPO and norbornene trapping experiments.

4′-bromoacetophenone **1a** (0.2 mmol, 1 equiv) and N-methylpyrrole **1b** (5.0 mmol, 25 equiv) were dissolved in DMSO (total volume of the solution ~ 4 mL) using a 10 mL Pyrex tube equipped with a rubber septum and magnetic stir bar. The TEMPO (or norbornene, 0.2 mmol, 1 equiv) was added at the beginning of the reaction. The resulting mixture was degassed using argon *via* a syringe needle. The reaction mixture was irradiated using a 455 nm LED (24 h), which was equipped with a water-cooling system to keep the reaction solution at room temperature. After the irradiation time, 10 µL of the crude solution were taken with a syringe, diluted with MeOH (1/50) and analyzed by direct injection into the GC and GC-MS. A control experiment in which samples were tested under aphotic conditions showed no production of the trapping product.

C.4. Procedure for replacement of 1a with 1c or 1d in Model Reaction.



1.5 equiv. 1 equiv, 0.4 mmol

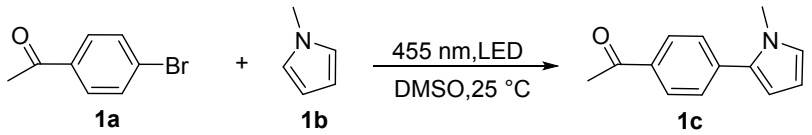
1c **1a** **1d**, 42% yield **1e**, 15% yield

4′-bromoacetophenone **1a** (0.4 mmol, 1 equiv) and **1c** (or **1d**, 0.6 mmol, 1.5 equiv) were dissolved in DMSO (total volume of the solution ~ 4 mL) using a 10 mL Pyrex tube equipped with a rubber septum and magnetic stir bar. The resulting mixture was kept under air conditions and irradiated through the side of the Pyrex tube using a 455 nm LED light setup (10 hours), which is equipped with a water-cooling system to keep the reaction solution at room temperature. The reaction mixture was transferred into a separating funnel and 10 mL of distilled water and 2 mL of brine were added after the reaction. The resulting mixture was extracted with ethyl acetate (AcOEt, 3 x 10 mL), and then the combined organic layers were dried by anhydrous $MgSO_4$. Purification of the crude product was achieved by flash column chromatography using hexane/ethyl acetate as eluents on a silica gel column.

D. Procedure for time course reaction monitoring by ^{1}H NMR.[8]

All time course monitoring reactions proceeded in NMR tubes charged with 4'-bromoacetophenone **1a** (0.03 mmol, 1 equiv) and N-methylpyrrole **1b** (0.75 mmol, 25 equiv) dissolved in DMSO-d_6 with a total volume of ~0.6 mL. The NMR tubes were capped with a corresponding Teflon plug and the system was irradiated through the side of the tube using a 455 nm LED light setup. ^{1}H NMR analysis was performed at certain time intervals over the course of the reaction. The reaction method provided above was followed without any alterations or the incorporation of any additional materials. Representative kinetic profiles are shown in **Fig. 3a**.

D.1. Procedure for the Model Reaction:



1a 1 equiv, 0.2 mmol **1b** 25 equiv **1c**

D.2. Procedure for the Model Reaction in the presence of TEMPO.

The given model reaction was followed apart from that the resulting mixture was degassed using argon *via* a syringe needle and TEMPO (0.003 mmol, 0.1 equiv) was added at the beginning of the reaction or at 8 h into the reaction at the ~40% conversion point. Representative kinetic profiles are shown in **Fig. 3b**.

D.3. Procedure for the Model Reaction in the presence of 1c or 1d.

The given model reaction was followed except that **1c** (or **1d**, 0.015 mmol, 0.5 equiv) was added to the NMR tube at the beginning of the reaction. Representative kinetic profiles are shown in **Fig. 3a**.

D.4. Procedure for light on (off) time course reaction monitoring by ^{1}H NMR.

The above model reaction was followed as given except that the irradiation was ceased after 8 h and the samples were kept in the dark for two hours before the reaction system was again exposed to light showing a continued reaction. Representative kinetic profiles are shown in **Figure S15**.

D.5. Procedure for the monitoring of photochemical polymerization of N-methylpyrrole.

The photochemical polymerization of N-methylpyrrole was confirmed by ^{1}H NMR monitoring method developed by Ghandi *et al.*[9] Poly(N-methylpyrrole) is insoluble and therefore did not affect the measurements of the other peaks when monitored. N-methylpyrrole proton NMR peaks are the only important peaks to be detected, where the concentration of remaining N-methylpyrrole in the solution can be obtained by the NMR integral of aromatic N-methylpyrrole protons. We measured the ratio of concentration of remained N-methylpyrrole to the initial concentration of N-methylpyrrole as a function of time, to investigate the polymerization rate. DMSO-d_6 was chosen to be the reference solvent, which do not affect the kinetics of polymerization. Some oligomers may still be soluble in DMSO-d_6 and therefore cannot be identified by this method. This suggests that the actual amount of polymerization is larger than the results given by this method. However, this method can give an approximate polymerization kinetic process, which is convenient for us to analyze and confirm the specific polymerization process.

E. Synthesis and late-stage preparation of a marketed drug intermediate and biorelevant compounds.

E.1. General procedure for marketed drug intermediate.

E.1.1. In DMSO:

Chloroacetonitrile (0.2 mmol, 1 equiv) and *N*-methylpyrrole (5.0 mmol, 25 equiv) were dissolved in DMSO (total volume of the solution ~ 4 mL) using a 10 mL Pyrex tube equipped with a rubber septum and magnetic stir bar. The reaction mixture was irradiated through the side of the Pyrex tube using a 455 (48 hours) or 405 (20 hours) nm LED light setup, which is equipped with a water-cooling system to keep the reaction solution at room temperature. The reaction mixture was transferred into a separating funnel and 10 mL of distilled water and 2 mL of brine were added after the reaction. The resulting mixture was extracted with ethyl acetate (AcOEt, 3 x 10 mL), and then the combined organic layers were dried by anhydrous $MgSO_4$. Purification of the crude product was achieved by flash column chromatography using hexane/ethyl acetate as eluents on a silica gel column (~35% yield).

E.1.2. In DCE:

Considering the low product conversion in DMSO, we modified the procedure by replacing the solvent with DCE according to reference method and added an appropriate amount of sodium acetate.[10] The optimized procedure is as follows: chloroacetonitrile (0.2 mmol, 1 equiv), *N*-methylpyrrole (5.0 mmol, 25 equiv), and sodium acetate (0.2 mmol, 1 equiv) were dissolved in 1,2-dichloroethane (DCE, total volume of the solution ~ 4 mL) using a 10 mL Pyrex tube equipped with a rubber septum and magnetic stir bar. The reaction mixture was irradiated through the side of the Pyrex tube using a 455 (36 hours) or 405 (10 hours) nm LED light setup, which was equipped with a water-cooling system to keep the reaction solution at room temperature. After the reaction, the reaction mixture was evaporated, and the residue was purified by flash column chromatography using hexane/ethyl acetate as eluents on a silica gel column. The product analysis affords the corresponding product with ~85% yield. Note: addition of sodium acetate in the reaction using DMSO as the solvent didn't increase the yield of product, therefore, DCE was utilized in the late-stage preparation of a marketed drug intermediate and biologically relevant compounds. Performing the multigram-scale preparation of adduct **20** required the use of a large reaction vessel as described in **Section C.2**. At a 0.1 mol scale (chloroacetonitrile, 7.55 g), the conversion stalled after 120 hours of irradiation (455 nm, 30 hours for 405 nm), and gave an ~ 36% isolated yield of product **20**.

E.2. Synthesis of biorelevant compounds of adduct (22).

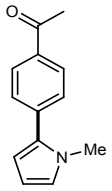
(1). cortisone analogues (21). Synthesized according to a procedure adapted by Melchiorre *et. al.* as follows:[10] In a round-bottomed flask, cortisone (500 mg, 1.39 mmol, 1.0 equiv.) and pyridine (5 mL) were added, cooled in an ice bath, followed by the addition of methanesulfonyl chloride (113 μL, 1.46 mmol, 1.05 equiv.). The reaction was naturally warmed to ambient temperature as the reaction proceeded for a total reaction time of 1 h. The crude product was concentrated to remove excess pyridine, then the residue was dissolved in CH_2Cl_2 and washed with 1 M HCl twice. The combined organic layers were dried by anhydrous $MgSO_4$. Purification of the crude product was achieved by flash column chromatography using *n*-hexane/ethyl acetate as eluents on a silica gel column (~ 50% yield).

(2). adduct (22). With cortisone analogues (**21**) in hand, we then synthesized adduct **22** according to the general procedure: cortisone mesylate **21** (87.5 mg, 0.2 mmol, 1 equiv.), *N*-methylpyrrole (5.0 mmol, 25 equiv), and sodium acetate (0.2 mmol, 1 equiv) were dissolved in 1,2-dichloroethane (DCE, total volume of the solution ~ 4 mL) using a 10 mL Pyrex tube equipped

with a rubber septum and magnetic stir bar. The reaction mixture was irradiated through the side of the Pyrex tube using a 455 (36 hours) or 405 (10 hours) nm LED light setup, which was equipped with a water-cooling system to keep the reaction solution at room temperature. After the reaction, the reaction mixture was evaporated and the residue was purified by flash column chromatography using hexane/ethyl acetate as eluents on a silica gel column. The products analysis affords the corresponding product with ~ 24% yield.

F. Characterization of the isolated products:

1-(4-(1-Methyl-1*H*-pyrrol-2-yl)phenyl)ethan-1-one (1c):



The compound was synthesized according to the general procedure (**Section C.1**) using 39.8 mg of 4′-Bromoacetophenone (0.2 mmol, 1.0 equiv), and 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 2% to 5% AcOEt in hexanes as eluent): 30.3 mg, 76% yield (455 nm); 29.1 mg, 73% yield (405 nm).

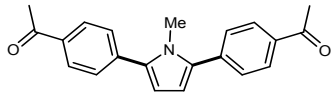
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 – 7.90 (m, 2H), 7.60 – 7.42 (m, 2H), 6.86 – 6.70 (m, 1H), 6.35 (dd, J = 3.7, 1.8 Hz, 1H), 6.23 (dd, J = 3.7, 2.7 Hz, 1H), 3.72 (s, 3H), 2.62 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.57, 137.93, 134.96, 133.43, 128.60, 127.97, 125.31, 110.23, 108.37, 35.45, 26.58.

HRMS: calculated for $C_{13}H_{13}NO^+$ $[M]^+$ 199.0992; found 199.0993.

1,1'-((1-methyl-1*H*-pyrrole-2,5-diyl)bis(4,1-phenylene))bis(ethan-1-one) (1d)



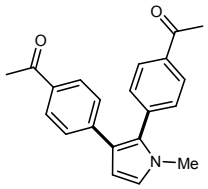
The compound was synthesized according to the general procedure (**Section C.4**) using 79.6 mg of 4′-Bromoacetophenone (0.4 mmol, 1.0 equiv), and 119.4 mg of 1-(4-(1-Methyl-1*H*-pyrrol-2-yl)phenyl)ethan-1-one **(1c)** (0.6 mmol, 1.5 equiv). Chromatography on silica gel (gradient from 4% to 10% AcOEt in hexanes as eluent): 53.3 mg, 42% yield (455 nm).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 – 8.00 (m, 4H), 7.63 – 7.54 (m, 4H), 6.46 (s, 2H), 3.68 (s, 3H), 2.64 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.49, 141.40, 137.55, 137.35, 135.34, 128.75, 128.69, 128.52, 128.26, 110.76, 34.99, 26.63, 26.47.

HRMS: calculated for $C_{21}H_{19}NO_2^+$ $[M]^+$ 317.1411; found 317.1416.

1,1'-((1-methyl-1*H*-pyrrole-2,3-diyl)bis(4,1-phenylene))bis(ethan-1-one) (1e)



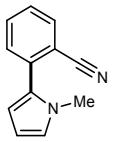
Compound **1e** was obtained along with **1d** in the same reaction mixture (**Section C.4**). Chromatography on silica gel (gradient from 10% to 20% AcOEt in hexanes as eluent): 19.0 mg, 15% yield (455 nm).

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.01 (d, J = 8.4 Hz, 2H), 7.92 – 7.82 (m, 2H), 7.64 – 7.53 (m, 2H), 7.42 – 7.31 (m, 2H), 6.40 (d, J = 3.9 Hz, 1H), 6.33 (d, J = 3.9 Hz, 1H), 3.63 (s, 3H), 2.54 (s, 6H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 197.74, 197.32, 145.86, 137.36, 135.46, 134.76, 133.55, 129.14, 129.09 (d, J = 7.5 Hz), 128.25, 125.31, 111.29, 110.95, 105.92, 34.50, 27.17, 26.96.

HRMS: calculated for $C_{21}H_{19}NO_2^+$ $[M]^+$ 317.1411; found 317.1413.

2-(1-Methyl-1*H*-pyrrol-2-yl)benzonitrile (2)



(1). The compound was synthesized according to the general procedure (**Section C.1**) using 36.4 mg of 2-bromobenzonitrile (0.2 mmol, 1.0 equiv), and 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 4% to 10% AcOEt in hexanes as eluent): 29.8 mg, 82% yield (455 nm); 28.4 mg, 78% yield (405 nm).

(2). The compound was also synthesized according to the general procedure (**Section C.1**) using 27.2 mg of 2-chlorobenzonitrile (0.2 mmol, 1.0 equiv), and 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 4% to 10% AcOEt in hexanes as eluent): 29.1 mg, 80% yield (455 nm); 26.9 mg, 74% yield (405 nm).

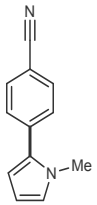
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (ddd, J = 7.8, 1.4, 0.6 Hz, 1H), 7.61 (td, J = 7.7, 1.4 Hz, 1H), 7.49 – 7.37 (m, 2H), 6.79 (dd, J = 2.7, 1.8 Hz, 1H), 6.40 (dd, J = 3.7, 1.7 Hz, 1H), 6.25 (dd, J = 3.7, 2.7 Hz, 1H), 3.61 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.95, 133.52, 132.33, 130.88, 129.94, 127.40, 124.82, 118.61, 112.89, 111.47, 108.33, 34.82.

HRMS: calculated for $C_{12}H_{10}N_2^+$ $[M]^+$ 182.0838; found 182.0840.

4-(1-Methyl-1*H*-pyrrol-2-yl)benzonitrile (3)



(1). The compound was synthesized according to the general procedure (**Section C.1**) using 36.4 mg of 4-bromobenzonitrile (0.2 mmol, 1.0 equiv), and 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 3% to 8% AcOEt in hexanes as eluent): 27.3 mg, 75% yield (455 nm); 25.9 mg, 71% yield (405 nm).

(2). The compound was also synthesized according to the general procedure (**Section C.1**) using 27.2 mg of 4-chlorobenzonitrile (0.2 mmol, 1.0 equiv), and 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 3% to 8% AcOEt in hexanes as eluent): 26.2 mg, 72% yield (455 nm); 24.7 mg, 68% yield (405 nm).

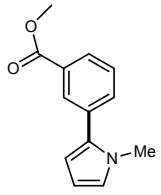
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.62 (m, 2H), 7.57 – 7.40 (m, 2H), 6.83 – 6.70 (m, 1H), 6.35 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.23 (dd, *J* = 3.7, 2.7 Hz, 1H), 3.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.72, 132.64, 132.27, 128.30, 125.85, 119.04, 110.77, 109.72, 108.60, 35.47.

HRMS: calculated for $C_{12}H_{10}N_2^+$ $[M]^+$ 182.0838; found 182.0836.

Methyl 3-(1-methyl-1*H*-pyrrol-2-yl)benzoate (4):



The compound was synthesized according to the general procedure (**Section C.1**) using 42.2 mg of methyl 3-bromobenzoate (0.2 mmol, 1.0 equiv), and 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 0% to 4% AcOEt in hexanes as eluent): 30.1 mg, 70% yield (455 nm); 29.2 mg, 68% yield (405 nm).

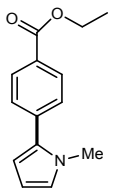
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (t, *J* = 1.7 Hz, 1H), 7.96 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.63 – 7.54 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 6.79 – 6.65 (m, 1H), 6.28 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.21 (dd, *J* = 3.5, 2.8 Hz, 1H), 3.93 (s, 3H), 3.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.00, 133.56 (d, *J* = 17.9 Hz), 132.86, 130.36, 129.50, 128.50, 127.73, 124.22, 109.27, 107.98, 52.21, 35.13.

HRMS: calculated for $C_{13}H_{14}NO_2^+$ $[M+H]^+$ 216.1025; found 216.1018.

Ethyl 4-(1-methyl-1*H*-pyrrol-2-yl)benzoate (5):



The compound was synthesized according to the general procedure (**Section C.1**) using 45.8 mg of Ethyl 4-bromobenzoate (0.2 mmol, 1.0 equiv), and 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 0% to 3% AcOEt in hexanes as eluent): 33.9 mg, 74% yield (455 nm); 33.0 mg, 72% yield (405 nm).

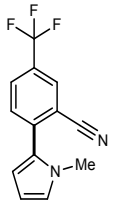
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 – 7.86 (m, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 6.80 – 6.66 (m, 1H), 6.33 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.22 (dd, *J* = 3.6, 2.7 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.49, 137.65, 133.58, 129.72, 128.33, 127.87, 125.07, 110.01, 108.28, 60.94, 35.39, 14.39.

HRMS: calculated for $C_{14}H_{15}NO_2^+$ $[M]^+$ 229.1097; found 229.1095.

2-(1-Methyl-1*H*-pyrrol-2-yl)-5-(trifluoromethyl)benzonitrile (6):



The compound was synthesized according to the general procedure (**Section C.1**) using 41.2 mg of 2-chloro-5-(trifluoromethyl)benzonitrile (0.2 mmol, 1.0 equiv), and 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 0% to 2% AcOEt in hexanes as eluent): 40.0 mg, 80% yield (455 nm); 38.5 mg, 77% yield (405 nm).

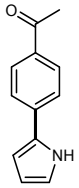
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 – 7.91 (m, 1H), 7.83 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 6.88 – 6.78 (m, 1H), 6.51 (dd, *J* = 3.8, 1.7 Hz, 1H), 6.26 (dd, *J* = 3.7, 2.7 Hz, 1H), 3.64 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.13 (d, *J* = 0.9 Hz), 131.04, 130.64 (q, *J* = 3.9 Hz), 129.71, 129.37, 129.01 (q, *J* = 3.4 Hz), 128.65, 126.31, 124.46 (s), 121.76, 117.50, 112.96 (d, *J* = 2.6 Hz), 108.89, 35.05.

HRMS: calculated for $C_{13}H_9F_3N_2^+$ $[M]^+$ 250.0712; found 250.0716.

1-(4-(1*H*-pyrrol-2-yl)phenyl)ethan-1-one (7)



The compound was synthesized according to the general procedure (**Section C.1**) using 39.8 mg of 4′-Bromoacetophenone (0.2 mmol, 1.0 equiv), and 350 μL of pyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 2% to 10% AcOEt in hexanes as eluent): 25.7 mg, 69% yield (455 nm); 24.9 mg, 67% yield (405 nm).

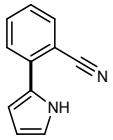
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.53 (s, 1H), 8.01 – 7.85 (m, 2H), 7.81 – 7.68 (m, 2H), 6.97 (td, J = 2.6, 1.5 Hz, 1H), 6.72 (ddd, J = 3.9, 2.6, 1.5 Hz, 1H), 6.18 (dt, J = 3.5, 2.4 Hz, 1H), 2.56 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 197.32, 137.67, 133.95, 130.53, 129.46, 123.31, 121.58, 110.23, 108.50, 26.98.

HRMS: calculated for $C_{12}H_{12}NO^+$ $[M+H]^+$ 186.0919; found 186.0915.

2-(1*H*-pyrrol-2-yl)benzonitrile (8)



(1). The compound was synthesized according to the general procedure (**Section C.1**) using 36.4 mg of 2-bromobenzonitrile (0.2 mmol, 1.0 equiv), and 350 μL of pyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 2% to 6% AcOEt in hexanes as eluent): 26.9 mg, 80% yield (455 nm); 25.6 mg, 76% yield (405 nm).

(2). The compound was also synthesized according to the general procedure (**Section C.1**) using 27.2 mg of 2-chlorobenzonitrile (0.2 mmol, 1.0 equiv), and 350 μL of pyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 2% to 6% AcOEt in hexanes as eluent): 25.9 mg, 77% yield (455 nm); 24.2 mg, 72% yield (405 nm).

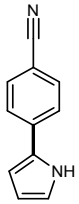
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.52 (s, 1H), 7.82 (dd, J = 7.8, 0.7 Hz, 1H), 7.77 – 7.65 (m, 2H), 7.35 (ddd, J = 7.8, 6.9, 1.7 Hz, 1H), 7.02 (td, J = 2.7, 1.5 Hz, 1H), 6.86 (ddd, J = 3.9, 2.7, 1.4 Hz, 1H), 6.24 (dt, J = 3.6, 2.5 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 136.09, 134.87, 133.83, 127.78, 126.91, 126.51, 121.71, 119.96, 110.04 (d, J = 14.1 Hz), 106.97.

HRMS: calculated for $C_{11}H_9N_2^+$ $[M+H]^+$ 169.0766; found 169.0764.

4-(1*H*-pyrrol-2-yl)benzonitrile (9)



(1). The compound was synthesized according to the general procedure (**Section C.1**) using 36.4 mg of 4-bromobenzonitrile (0.2 mmol, 1.0 equiv), and 350 μL of pyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 0% to 5% AcOEt in hexanes as eluent): 25.2 mg, 75% yield (455 nm); 23.9 mg, 71% yield (405 nm).

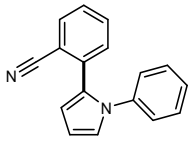
(2). The compound was also synthesized according to the general procedure (**Section C.1**) using 27.2 mg of 4-chlorobenzonitrile (0.2 mmol, 1.0 equiv), and 350 μL of pyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 0% to 5% AcOEt in hexanes as eluent): 24.2 mg, 72% yield (455 nm); 22.9 mg, 68% yield (405 nm).

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.58 (s, 1H), 7.83 – 7.72 (m, 4H), 6.99 (td, J = 2.7, 1.5 Hz, 1H), 6.76 (ddd, J = 3.9, 2.6, 1.5 Hz, 1H), 6.19 (dt, J = 3.5, 2.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 137.58, 133.18, 129.91, 123.92, 122.10, 119.79, 110.42, 109.18, 107.36.

HRMS: calculated for $C_{11}H_9N_2^+$ $[M+H]^+$ 169.0766; found 169.0762.

2-(1-Phenyl-1*H*-pyrrol-2-yl)benzonitrile (10)



(1). The compound was synthesized according to the general procedure (**Section C.1**) using 36.4 mg of 2-bromobenzonitrile (0.2 mmol, 1.0 equiv), and 716 mg of 1-phenylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 2% to 10% AcOEt in hexanes as eluent): 39.5 mg, 81% yield (455 nm); 38.6 mg, 79% yield (405 nm).

(2). The compound was also synthesized according to the general procedure (**Section C.1**) using 27.2 mg of 2-chlorobenzonitrile (0.2 mmol, 1.0 equiv), and 716 mg of 1-phenylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 2% to 10% AcOEt in hexanes as eluent): 39.1 mg, 80% yield (455 nm); 37.1 mg, 76% yield (405 nm).

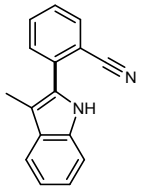
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.82 (dd, J = 7.8, 1.0 Hz, 1H), 7.55 (td, J = 7.7, 1.4 Hz, 1H), 7.42 (td, J = 7.7, 1.2 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.32 – 7.23 (m, 2H), 7.17 – 7.05 (m, 3H), 6.60 (dd, J = 3.6, 1.7 Hz, 1H), 6.41 (dd, J = 3.6, 2.9 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 139.69, 136.48, 134.01, 133.15, 131.34, 129.72, 129.04, 128.17, 127.29, 125.95, 125.57, 118.75, 113.87, 111.68, 110.04.

HRMS: calculated for $C_{17}H_{12}N_2^+$ $[M]^+$ 244.0995; found 244.0994.

2-(3-Methyl-1*H*-indol-2-yl)benzonitrile (11)



(1). The compound was synthesized according to the general procedure (**Section C.1**) using 36.4 mg of 2-bromobenzonitrile (0.2 mmol, 1.0 equiv), and 656 mg of 3-methylindole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 4% to 10% AcOEt in hexanes as eluent): 32.5 mg, 70% yield (455 nm); 31.1 mg, 67% yield (405 nm).

(2). The compound was also synthesized according to the general procedure (**Section C.1**) using 27.2 mg of 2-

chlorobenzonitrile (0.2 mmol, 1.0 equiv), and 656 mg of 3-methylindole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 4% to 10% AcOEt in hexanes as eluent): 31.6 mg, 68% yield (455 nm); 29.7 mg, 64% yield (405 nm).

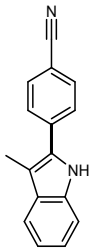
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.73 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.56 (ddd, *J* = 11.0, 8.8, 3.7 Hz, 3H), 7.41 – 7.31 (m, 2H), 7.23 – 7.12 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.74, 136.36, 133.84, 132.76, 130.92, 130.33, 129.22, 127.98, 123.29, 119.84, 119.52, 118.62, 112.13, 111.91, 111.17, 10.06.

HRMS: calculated for $C_{16}H_{12}N_2^+$ $[M]^+$ 232.0995; found 232.0998.

4-(3-Methyl-1*H*-indol-2-yl)benzonitrile (12)



(1). The compound was synthesized according to the general procedure (**Section C.1**) using 36.4 mg of 4-bromobenzonitrile (0.2 mmol, 1.0 equiv), and 656 mg of 3-methylindole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 2% to 5% AcOEt in hexanes as eluent): 30.2 mg, 65% yield (455 nm); 28.8 mg, 62% yield (405 nm).

(2). The compound was also synthesized according to the general procedure (**Section C.1**) using 27.2 mg of 4-chlorobenzonitrile (0.2 mmol, 1.0 equiv), and 656 mg of 3-methylindole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 2% to 5% AcOEt in hexanes as eluent): 29.2 mg, 63% yield (455 nm); 27.9 mg, 60% yield (405 nm).

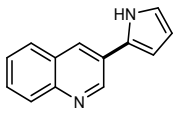
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.76 – 7.68 (m, 2H), 7.67 – 7.59 (m, 3H), 7.40 – 7.35 (m, 1H), 7.25 (ddd, *J* = 7.1, 4.7, 1.2 Hz, 1H), 7.17 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.79, 136.42, 132.60, 131.84, 129.87, 127.77, 123.55, 120.05, 119.47, 118.93, 111.45, 111.00, 110.28, 9.95.

HRMS: calculated for $C_{16}H_{12}N_2^+$ $[M]^+$ 232.0995; found 232.0991.

3-(1*H*-pyrrol-2-yl)quinoline (13)



The compound was synthesized according to the general procedure (**Section C.1**) using 41.6 mg of 3-bromoquinoline (0.2 mmol, 1.0 equiv), and 350 μL of pyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 10% to 33%

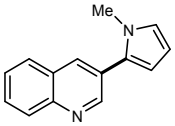
AcOEt in hexanes as eluent): 26.5 mg, 68% yield (455 nm); 25.8 mg, 66% yield (405 nm).

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.65 (s, 1H), 9.29 (d, J = 2.3 Hz, 1H), 8.46 (d, J = 2.2 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.89 (dd, J = 8.2, 1.1 Hz, 1H), 7.66 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.58 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.01 (td, J = 2.6, 1.5 Hz, 1H), 6.83 (ddd, J = 3.8, 2.6, 1.5 Hz, 1H), 6.23 (dt, J = 3.4, 2.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 148.40, 146.20, 129.24, 128.73, 128.40, 128.13, 127.47 (d, J = 6.7 Hz), 126.71, 121.24, 110.09, 107.87.

HRMS: calculated for $C_{13}H_{11}N_2^+$ $[M+H]^+$ 195.0922; found 195.0920.

3-(1-Methyl-1*H*-pyrrol-2-yl)quinolone (14)



The compound was synthesized according to the general procedure (**Section C.1**) using 41.6 mg of 3-bromoquinoline (0.2 mmol, 1.0 equiv), and 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 5% to 20% AcOEt in hexanes as eluent): 30.8 mg, 74% yield (455 nm); 29.6 mg, 71% yield (405 nm).

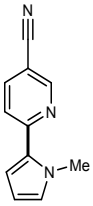
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (d, J = 2.2 Hz, 1H), 8.12 (s, 1H), 8.10 (d, J = 2.2 Hz, 1H), 7.82 (dd, J = 8.2, 1.1 Hz, 1H), 7.70 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.56 (dd, J = 11.1, 4.1 Hz, 1H), 6.86 – 6.73 (m, 1H), 6.41 (dd, J = 3.6, 1.8 Hz, 1H), 6.28 (dd, J = 3.5, 2.8 Hz, 1H), 3.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.00, 146.73, 133.75, 131.03, 129.28 (d, J = 5.3 Hz), 127.79, 127.06, 126.52, 124.98, 110.27, 108.45, 35.26.

HRMS: calculated for $C_{14}H_{12}N_2^+$ $[M]^+$ 208.0995; found 208.0992.

6-(1-Methyl-1*H*-pyrrol-2-yl)nicotinonitrile (15)



The compound was synthesized according to the general procedure (**Section C.1**) using 27.8 mg of 6-chloro-3-pyridinecarbonitrile (0.2 mmol, 1.0 equiv), and 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 0% to 3% AcOEt in hexanes as eluent): 24.5 mg, 67% yield (455 nm); 23.4 mg, 64% yield (405 nm).

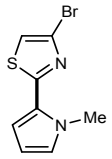
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (dd, J = 2.2, 0.8 Hz, 1H), 7.77 (dd, J = 8.5, 2.2 Hz, 1H), 7.57 (dd, J = 8.5, 0.8 Hz, 1H), 6.85 – 6.76 (m, 1H), 6.75 (dd, J = 4.0, 1.8 Hz, 1H), 6.20 (dd, J = 3.9, 2.6 Hz, 1H), 4.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.19, 151.73, 138.69, 130.32, 129.33, 119.90, 117.61, 114.01, 108.70, 104.78, 38.03.

HRMS: calculated for $C_{11}H_9N_3^+$ $[M]^+$ 183.0791; found 183.0786.

4-Bromo-2-(1-methyl-1*H*-pyrrol-2-yl)thiazole (16)



The compound was synthesized according to the general procedure (**Section C.1**) using 48.6 mg of 2,4-dibromothiazole (0.2 mmol, 1.0 equiv), and 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 0% to 3% AcOEt in hexanes as eluent): 31.5 mg, 65% yield (455 nm); 30.5 mg, 63% yield (405 nm).

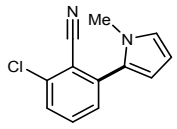
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (s, 1H), 6.77 – 6.71 (m, 1H), 6.67 (dd, J = 3.9, 1.7 Hz, 1H), 6.14 (dd, J = 3.8, 2.7 Hz, 1H), 4.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.79, 127.30, 125.91, 124.72, 113.76, 112.96, 108.56, 36.76.

HRMS: calculated for $C_8H_7BrN_2S^+$ $[M]^+$ 241.9508; found 241.9505.

2-Chloro-6-(1-methyl-1*H*-pyrrol-2-yl)benzonitrile (17)



The compound was synthesized according to the general procedure (**Section C.1**) using 34.4 mg of 2,6-dichlorobenzonitrile (0.2 mmol, 1.0 equiv), and 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv). Chromatography on silica gel (gradient from 0% to 3% AcOEt in hexanes as eluent): 24.2 mg, 56% yield (455 nm); 19.0 mg, 44% yield (405 nm).

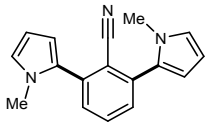
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.42 (m, 2H), 7.32 (dd, J = 7.7, 1.2 Hz, 1H), 6.83 – 6.74 (m, 1H), 6.42 (dd, J = 3.7, 1.7 Hz, 1H), 6.24 (dd, J = 3.7, 2.7 Hz, 1H), 3.61 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.22, 137.92, 132.84, 129.03 (d, J = 19.9 Hz), 128.22, 125.34, 115.67, 113.57, 112.07, 108.52, 34.91.

HRMS: calculated for $C_{12}H_9ClN_2^+$ $[M]^+$ 216.0449; found 216.0448.

2,6-Bis(1-methyl-1*H*-pyrrol-2-yl)benzonitrile (18)



Compound **18** was obtained along with **17** in the same reaction mixture (**Section C.1**). Chromatography on silica gel (gradient from 4% to 8% AcOEt in hexanes as eluent): 14.6 mg, 28% yield (455 nm); 19.8 mg, 38% yield (405 nm).

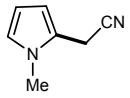
Matching reported data.[11, 12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.54 (m, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 6.84 – 6.72 (m, 2H), 6.40 (dd, *J* = 3.7, 1.7 Hz, 2H), 6.23 (dd, *J* = 3.6, 2.8 Hz, 2H), 3.62 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.13, 131.71, 130.15, 129.69, 124.72, 117.84, 113.46, 111.51, 108.31, 34.87.

HRMS: calculated for $C_{17}H_{15}N_3^+$ $[M]^+$ 261.1260; found 216.1258.

2-(1-Methyl-1*H*-pyrrol-2-yl)acetonitrile (20)



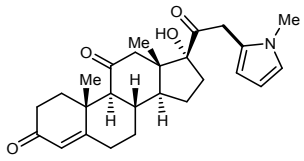
The compound was synthesized according to the procedure for marketed drug intermediate **20** (**Section E.1**) using 13 µL of chloroacetonitrile (0.2 mmol, 1 equiv), 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv), and 16.4 mg of sodium acetate (0.2 mmol, 1 equiv) in 1,2-dichloroethane (DCE). Chromatography on silica gel (gradient from 3% to 10% AcOEt in hexanes as eluent): 20.7 mg, 86% yield (455 nm); 19.9 mg, 83% yield (405 nm).

Matching reported data.[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.66 – 6.59 (m, 1H), 6.14 – 6.09 (m, 1H), 6.09 – 6.02 (m, 1H), 3.68 (s, 2H), 3.62 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 123.61, 119.93, 116.56, 109.24, 107.50, 33.84, 15.94.

(8*S*,9*S*,10*R*,13*S*,14*S*,17*R*)-17-hydroxy-10,13-dimethyl-17-(2-(1-methyl-1*H*-pyrrol-2-yl)acetyl)-1,6,7,8,9,10,12,13,14,15,16,17-dodecahydro-3*H*cyclopenta[*a*]phenanthrene-3,11(2*H*)-dione (22)



The compound was synthesized according to the procedure for biorelevant compounds of adduct **22** (**Section E.2**) using 87.5 mg of cortisone mesylate **21** (0.2 mmol, 1 equiv), 444 μL of *N*-methylpyrrole (5.0 mmol, 25 equiv), and 16.4 mg of sodium acetate (0.2 mmol, 1 equiv) in 1,2-dichloroethane (DCE). Chromatography on silica gel (gradient from 30% to 60% AcOEt in hexanes as eluent): 20.7 mg, 26% yield (455 nm); 19.9 mg, 22% yield (405 nm).

Matching reported data.[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 – 6.56 (m, 1H), 6.04 – 6.02 (m, 1H), 5.92 – 5.91 (m, 1H), 5.71 – 5.69 (m, 1H), 3.97 (d, *J* = 16.6 Hz, 1H), 3.64 (d, *J* = 16.6 Hz, 1H), 3.50 (s, 3H), 2.94 (br s, 1H), 2.86 – 2.75 (m, 3H), 2.49 – 2.24 (m, 5H), 1.99 – 1.93 (m, 5H), 1.73 – 1.66 (m, 1H), 1.65 – 1.57 (m, 1H), 1.49 – 1.43 (m, 1H), 1.41 (s, 3H), 1.28 – 1.26 (m, 1H), 0.67 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.02, 208.54, 200.10 (d, *J* = 27.1 Hz), 169.04 (d, *J* = 18.9 Hz), 124.72, 124.53 (d, *J* = 9.1 Hz), 123.52, 108.56, 107.21, 89.46, 62.49, 51.60, 50.39, 50.18, 38.54, 38.39 – 38.12 (m), 37.72, 36.79 (d, *J* = 8.9 Hz), 35.18, 34.68, 34.04, 32.77, 32.62, 23.79, 17.60, 16.56 (d, *J* = 2.6 Hz).

HRMS: calculated for $C_{26}H_{34}NO_4^+$ $[M+H]^+$ 424.5520; found 424.5525.

G. The feasibility analysis of photoinduced Electron Transfer.

The thermodynamically feasibility analysis and estimation of free energy for a photoinduced electron transfer (ΔG_{PET}) can be derived from the "Rehm-Weller Equation."[13-15] When a PET involves oxidation of the excited state **1b*** and reduction of the ground state sub **1a**, the ΔG_{PET} can be defined as:

$$\Delta G_{PET} = E^*_{ox}\left(1b^{\cdot+}/1b^*\right) - E_{red}\left(1a/1a^{\cdot-}\right)$$

where E^*_{ox} is the excited state oxidation potential of **1b** and can be calculated by:

$$E^*_{ox}\left(1b^{\cdot+}/1b^*\right) = E_{ox}\left(1b^{\cdot+}/1b\right) - E_{0,0}$$

The $E_{red}\left(1a/1a^{\cdot-}\right)$ and $E_{ox}\left(1b^{\cdot+}/1b\right)$ are ground state reduction and oxidation potentials of **1a** and **1b**, which can be obtained by electrochemical methods (cyclic voltammetry (CV)) for each species **1a** and **1b** undergoing reduction and oxidation, respectively. The excited state energy $E_{0,0}$ can be estimated at the intersection between the normalized absorbance and emission spectra of **1b** after converting the wavelength axis to an energy scale or by finding the midpoint between absorption and emission maxima (i.e., one-half the Stokes shift). *Note that we present $E_{0,0}$ in units of eV to allow for ease of combination with electrochemical potential (in units of V) used to estimate excited state redox potentials. This is commonplace when approaching a single electron transfer on a per molar basis.*

Electrochemical measurements show that **1a** has reduction potentials of -1.91 V vs SCE[16] (**Figure S2a**), while the **1b** has oxidation potentials of +1.2 V vs SCE (**Figure S2b**) which is consistent with previous reports.[17] The excited state energy $E_{0,0}$ is estimated to be 2.89 eV (**Figure S2c**). Rehm−Weller theory calculations show that the ΔG_{PET} is 0.22 eV, which indicates direct photoinduced electron transfer (PET) between excited-state **1b** to **1a** is thermodynamically unfeasible.

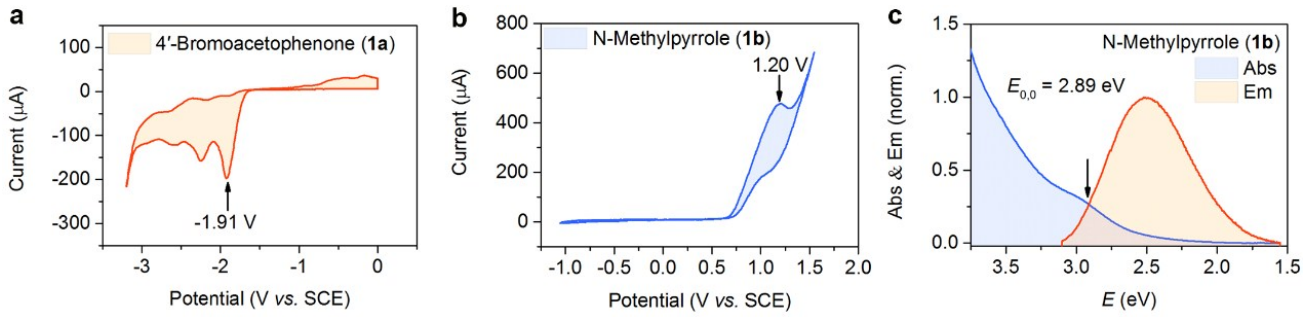


Figure S2. Cyclic voltammogram of (a) **1a** and (b) **1b** in DMSO, 100 mV s^{-1}. (c) Normalized absorbance and emission spectra of **1b** after converting the wavelength axis to an energy scale.

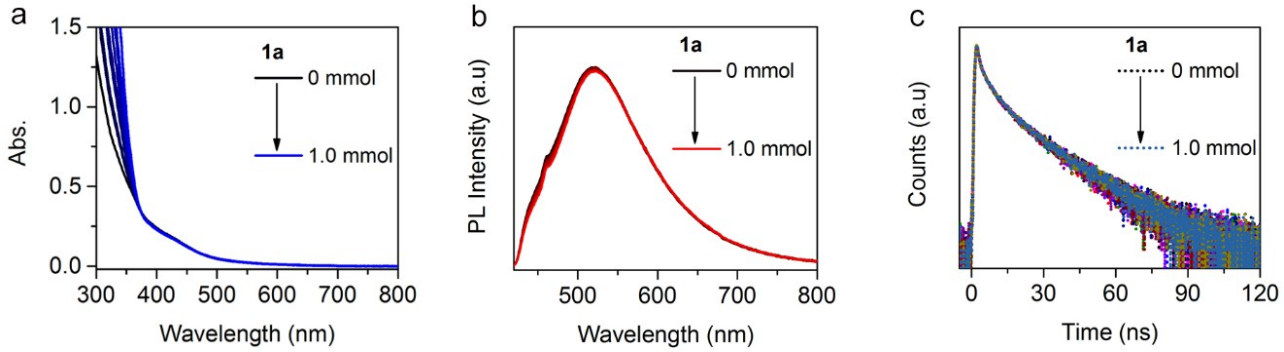


Figure S3. Stern-Volmer quenching experiments of the model system. (a) UV-Vis absorption, (b) photoluminescence spectra and (c) PL decay curves of **1b** after adding 0 to 1mmol of **1a** in DMSO.

H. The actual component for absorption of visible light in as-purchased N-methylpyrrole.

It is well known that pyrrole monomers are highly sensitive to sunlight and ambient condition, causing polymerization to occur, which results in a color change from colorless to yellow.[18, 19] This is why the as-purchased pyrrole is usually yellow in color instead of colorless, because of the existence of a small amount of oligomers.[18, 19] To collect enough experimental evidence and identify the actual component for absorption of visible light, in as-purchased N-methylpyrrole, we redistilled the purchased N-methylpyrrole. As shown in **Figure S4a and S5** (0 h samples), the pure N-methylpyrrole monomers have no absorption in the visible light range (colorless, plot A in **Figure S4a**, defined as **I** in **Figure S5** (0 h)) with respect to the as-purchased yellow N-methylpyrrole (yellow, plot B in **Figure S4a**, defined as **II** in **Figure S5** (0 h)). While the residue of distillation shows a clay bank color with an absorption onset increasing to 700 nm (plot C in **Figure S4a**, defined as **III** in **Figure S5** (0 h)), suggesting the existence of oligomers which are responsible for the visible light absorption. This result was confirmed by the GC-MS analysis of the distillation residue and as-purchased N-methylpyrrole. For example, GC-MS clearly displayed a signal with m/z that matches the tripolymer of the N-methylpyrrole (**Figure S6**). Most importantly, we also found that the distillation residue absorption spectrum was like the as-purchased N-methylpyrrole if we diluted the residue of

distillation (plot D in **Figure S4a**). This indicates that the distillation process does not change the basic components of the as-purchased N-methylpyrrole.

We then utilize these different distillation components to identify their effect on the PDP reaction process. The kinetic behavior of the product formation profile by ^{1}H NMR analysis (**Figure S4 and S5**) shows that pure **I** have a clear delay of the induction period (plot A in **Figure S4b**), in contrast to the as-purchased yellow N-methylpyrrole (plot B in **Figure S4b**). **Figure S5** confirmed that the pure N-methylpyrrole monomers **I** indeed turned yellow with continued exposed to blue LED irradiation, becoming darker with increased time. These results illustrate that the pyrrole monomers are sensitive to light and ambient condition. Meanwhile, the induction period was significantly shortened if the as-purchased yellow N-methylpyrrole (plot B in **Figure S4b**) was replaced by the distillation residue (plot C in **Figure S4b**). These results suggest that the oligomers in the as-purchased yellow N-methylpyrrole are responsible for the visible light absorption which drives the initial stages of the photoinduced disproportionation (PDP) process.

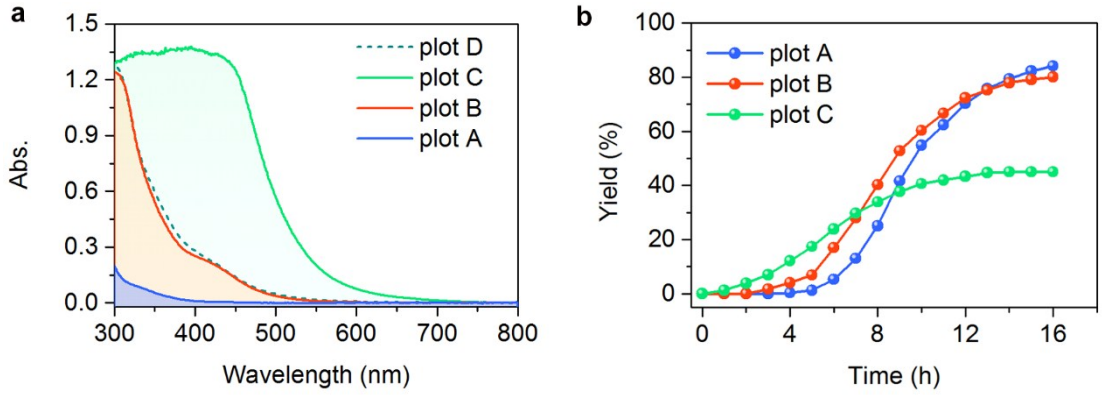


Figure S4. (a) UV-Vis absorption spectrum and (b) representative kinetic profiles of the model reaction monitored by ^{1}H NMR spectroscopy of the different distillation components after the distillation of as-purchased N-methylpyrrole, plot A: the pure N-methylpyrrole monomers; plot B: as-purchased N-methylpyrrole; plot C: the residue of distillation. Note: plot D in **Figure S4a** refer to the diluted solution of the residue of distillation.

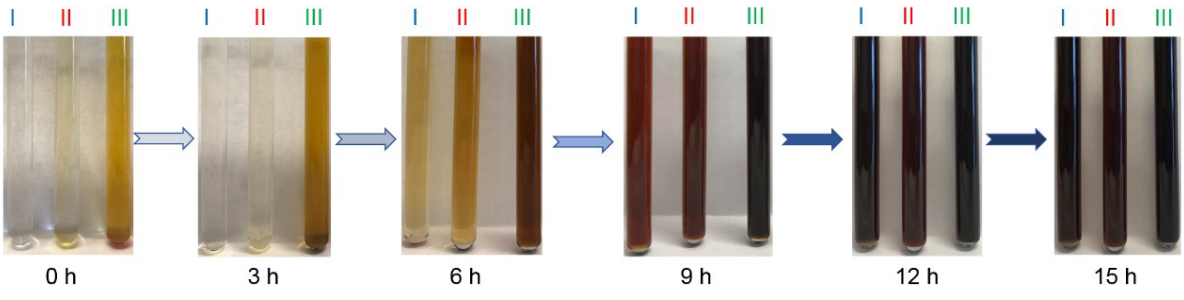


Figure S5. Images recorded of the different color changes for reactions monitored using ^{1}H NMR spectroscopy in **Figure S4a**.

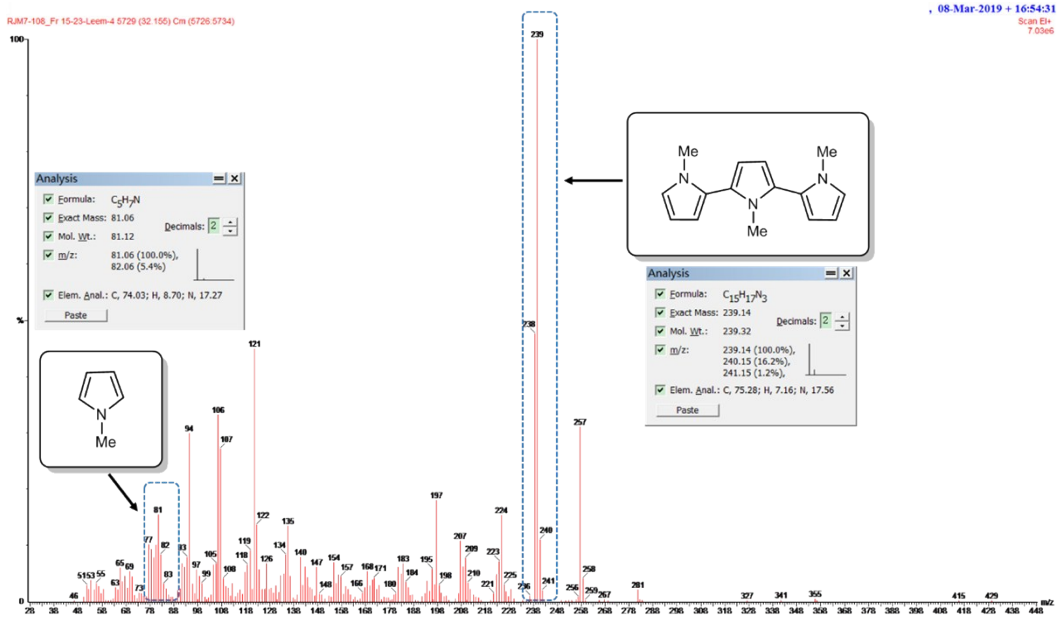


Figure S6. GC-MS analysis of the distillation residue and as-purchased N-methylpyrrole, which show a signal with m/z that matches the tripolymer of the N-methylpyrrole.

I. Spectral and ^{1}H NMR monitoring.

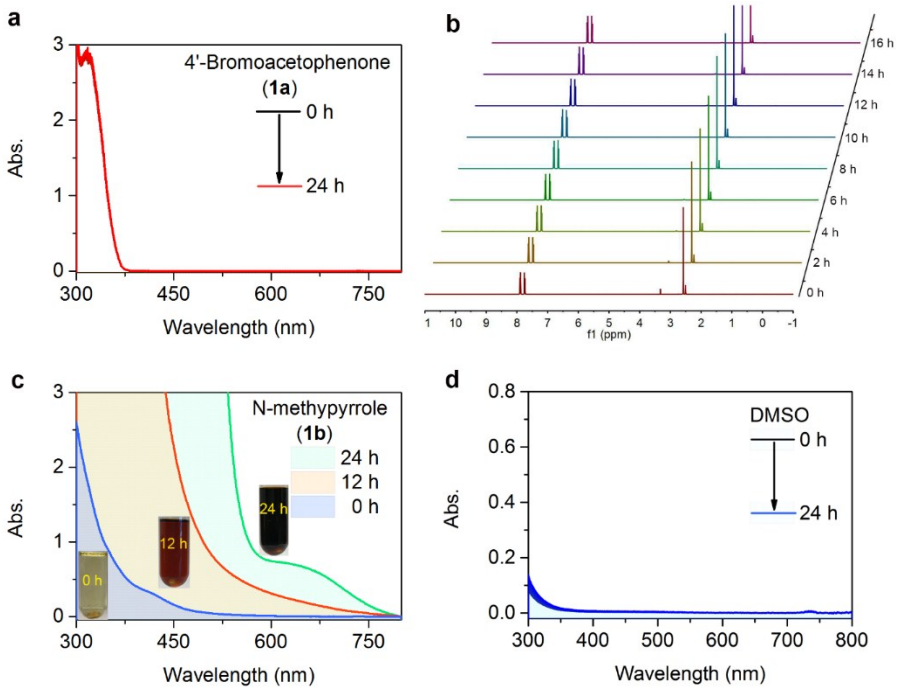


Figure S7. (a) UV-Vis absorption spectrum of the 4′-bromoacetophenone **1a** in DMSO monitored under blue LED irradiation within 24 h. (b) ^{1}H NMR of **1a** in DMSO-d_6 was monitored for stability under blue LED irradiation for up to 16 h. (c) UV-Vis absorption spectral monitoring of N-methylpyrrole **1b** in DMSO under blue LED irradiation within 24 h. (d) UV-Vis absorption spectral monitoring of the stability of DMSO under blue LED irradiation within 24 h.

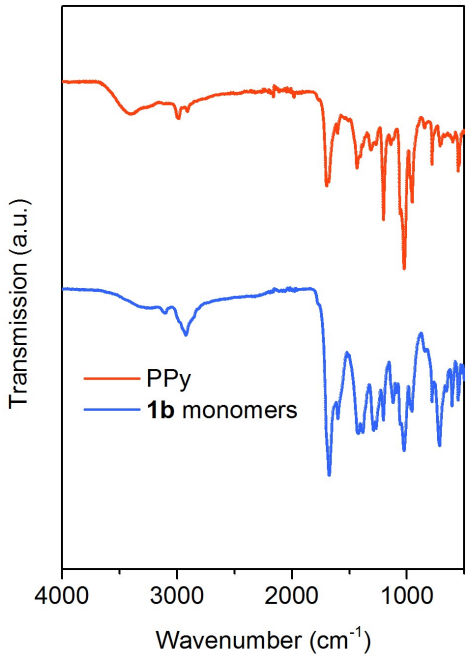
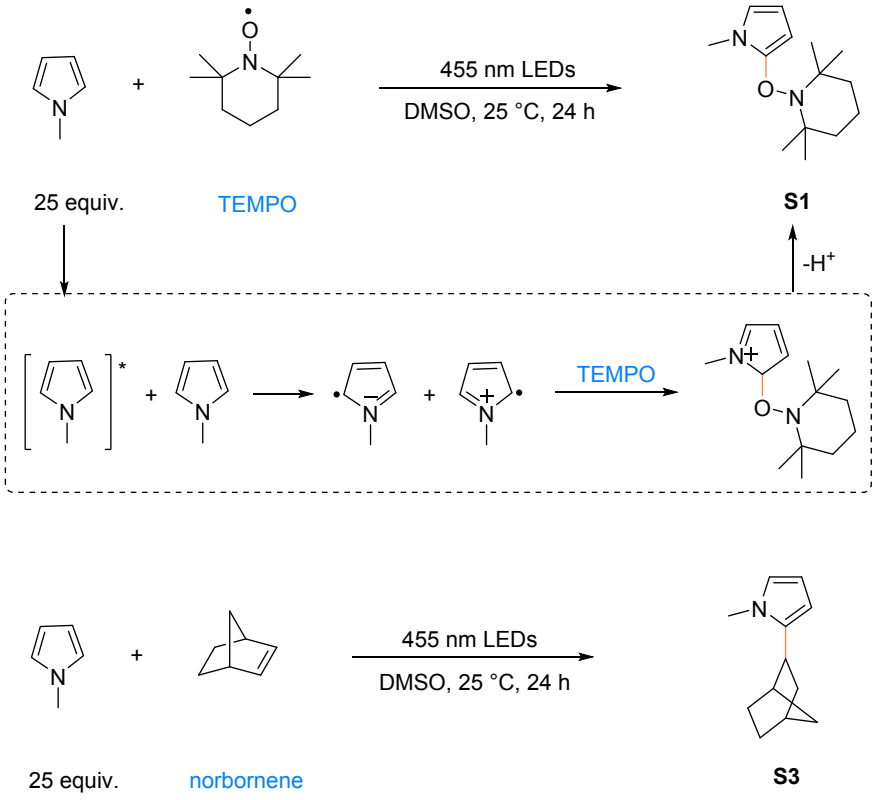


Figure S8. FTIR-ATR spectrum of N-methylpyrrole monomers (Py, blue line) and poly(N-methyl pyrrole) (PPy, red line). The N-methylpyrrole monomers were obtained from the distillation of the purchased N-methylpyrrole. On the hand, PPy was obtained from the black insoluble residue after the model reaction was irradiated by the blue LED.

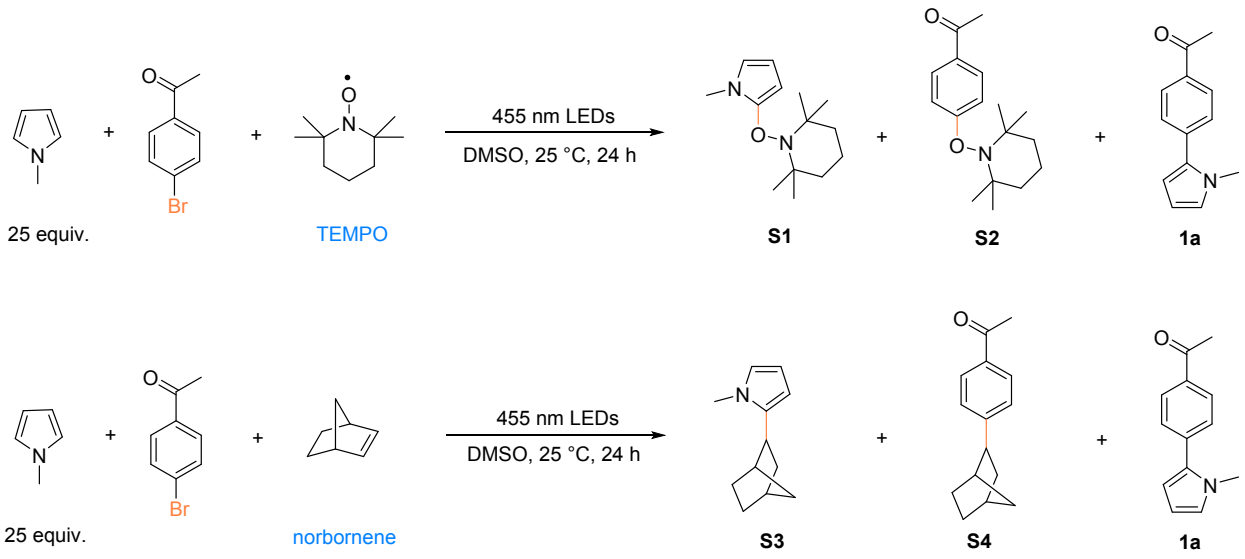
The FTIR spectrum of Py and PPy was presented in **Figure S8**. The weak peak at 2990 and 2912 cm^{-1} characterizes the CH_3 stretching of the Py units. Three weak peaks at 1421, 1389, and 1298 cm^{-1} result from the ring stretch of the Py units. The peak at 1032 cm^{-1} is attributed to the C-H out of plane deformation of the Py units. Thus, the FTIR spectrum confirms the formation of PPy during the reaction, which is in agreement with literature results.[20, 21]

J. TEMPO and norbornene trapping experiments.

The presence of N-methylpyrrole cation radicals and aryl halide aryl radicals was demonstrated by trapping reactions with TEMPO, to produce TEMPO adducts (**Scheme S1 and S2,** adducts **S1** and **S2**), and with norbornene to give norbornene adducts (**Scheme S1 and S2,** adducts **S3** and **S4**).[8, 22] The reaction was processed according to the procedure for the TEMPO and norbornene trapping experiments (see **Section C.3** in the SI for details). After irradiation, 10 µL of crude solution were taken with a syringe, diluted with MeOH (1/50), and analyzed by direct injection in a GC or GC-MS.



Scheme S1. Trappimg cation N-methylpyrrole radicals with TEMPO or norbornene in a system containing N-methylpyrrole (5.0 mmol, 25 equiv), TEMPO or norbornene (0.2 mmol, 1.0 equiv), and DMSO (3.5ml) under 455-nm blue LEDs irradiation (24 h).



Scheme S2. Trappimg of N-methylpyrrole cation radicals with TEMPO or norbornene, was performed in a system containing aryl halides (0.2 mmol, 1.0 equiv), N-methylpyrrole (5.0 mmol, 25 equiv), TEMPO or norbornene (0.2 mmol, 1.0 equiv), and DMSO (3.5 ml) under 455-nm blue LEDs irradiation (24 h).

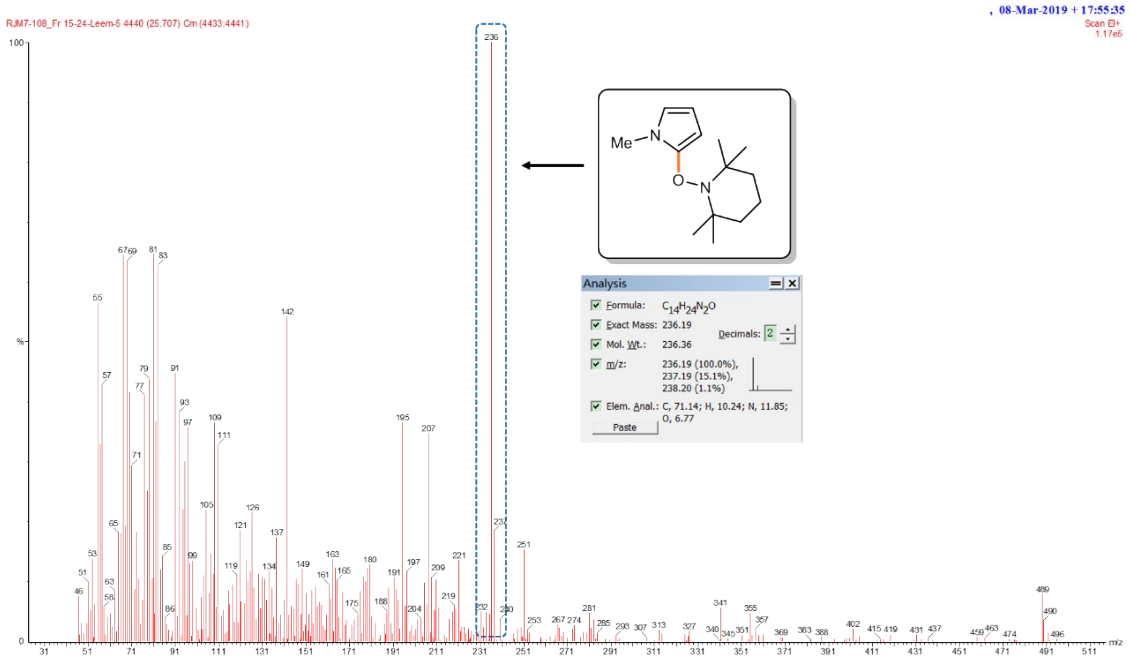


Figure S9. GC-MS analysis of the N-methylpyrrole mixture with stoichiometric TEMPO that displayed a signal with m/z that matches the expected mass of the TEMPO adducts (formed from the capture of cation N-methylpyrrole radicals) after blue LED irradiation.

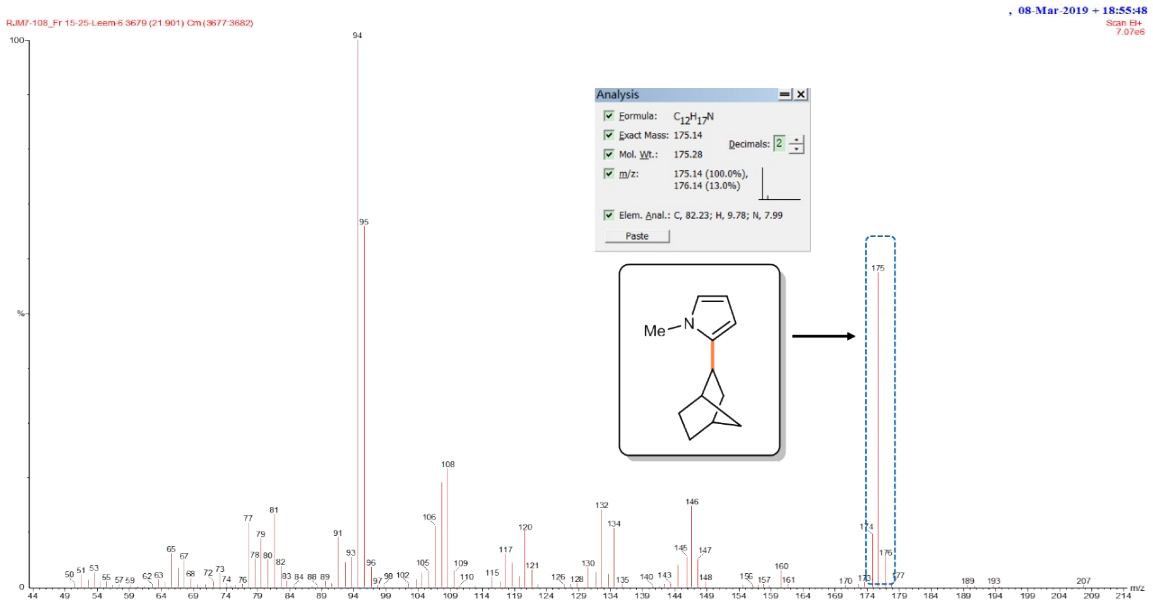


Figure S10. GC-MS analysis of the N-methylpyrrole mixture with stoichiometric norbornene that displayed a signal with m/z that matches the expected mass of the norbornene adducts (formed from the capture of cation N-methylpyrrole radicals) after blue LED irradiation.

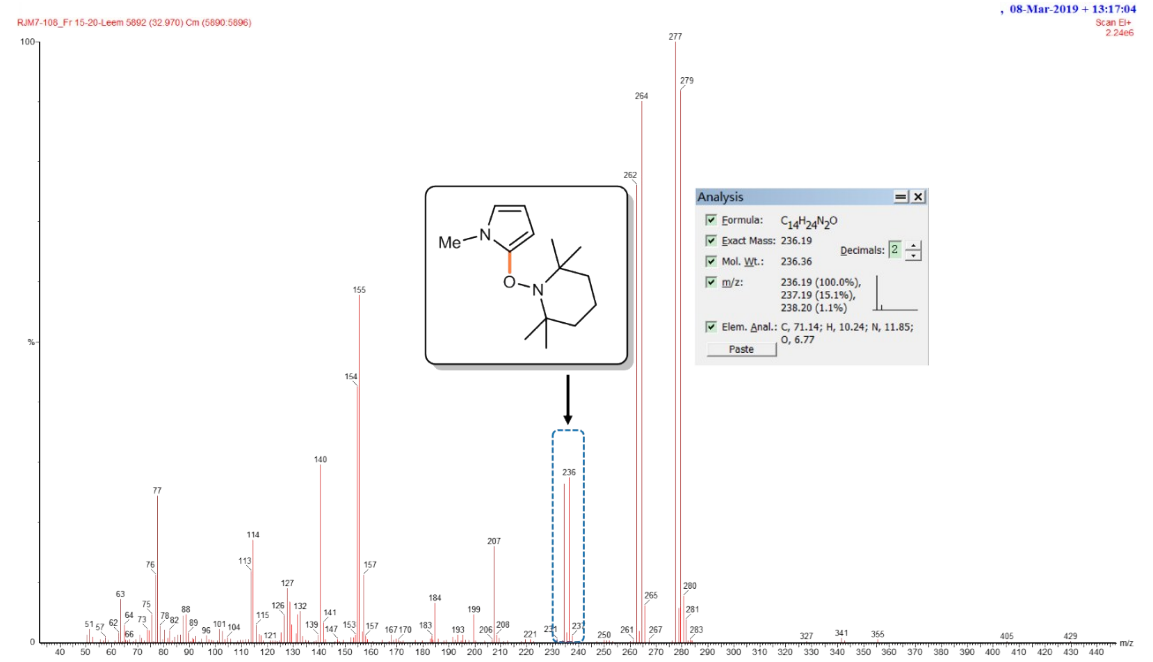


Figure S11. GC-MS analysis of the crude product (model reaction) mixture with stoichiometric TEMPO that displayed a signal with m/z that matches the expected mass of the TEMPO adducts (formed from the capture of the cation N-methylpyrrole radicals) after blue LED irradiation.

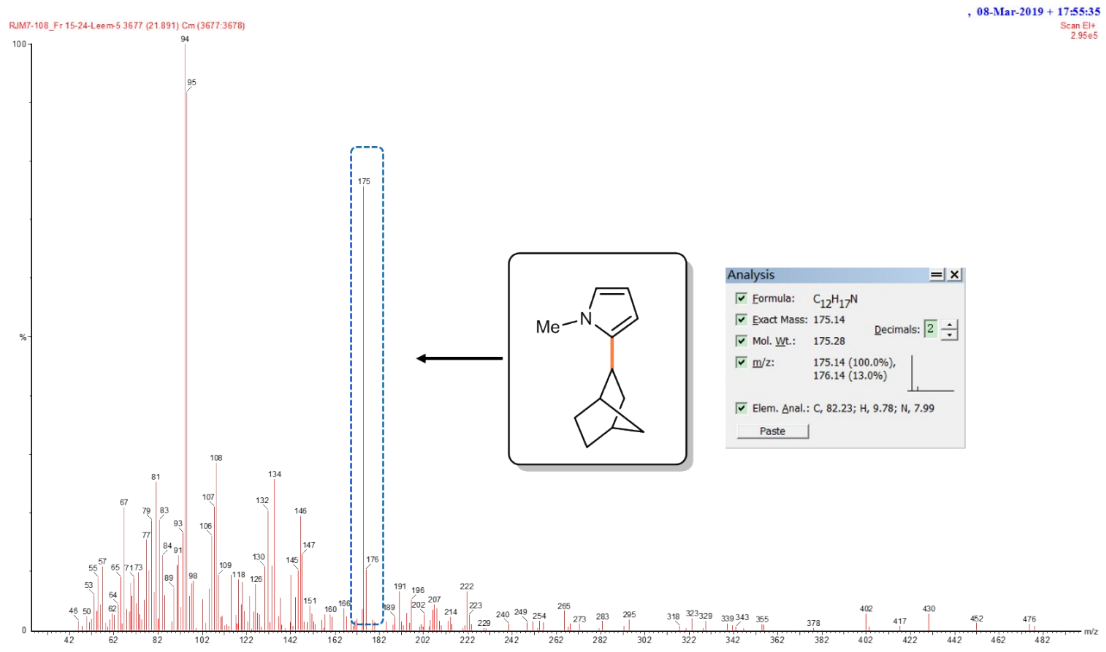


Figure S12. GC-MS analysis of the crude product (model reaction) mixture with stoichiometric norbornene that displayed a signal with m/z that matches the expected mass of the norbornene adducts (the cation N-methylpyrrole radicals) after the blue LED irradiation.

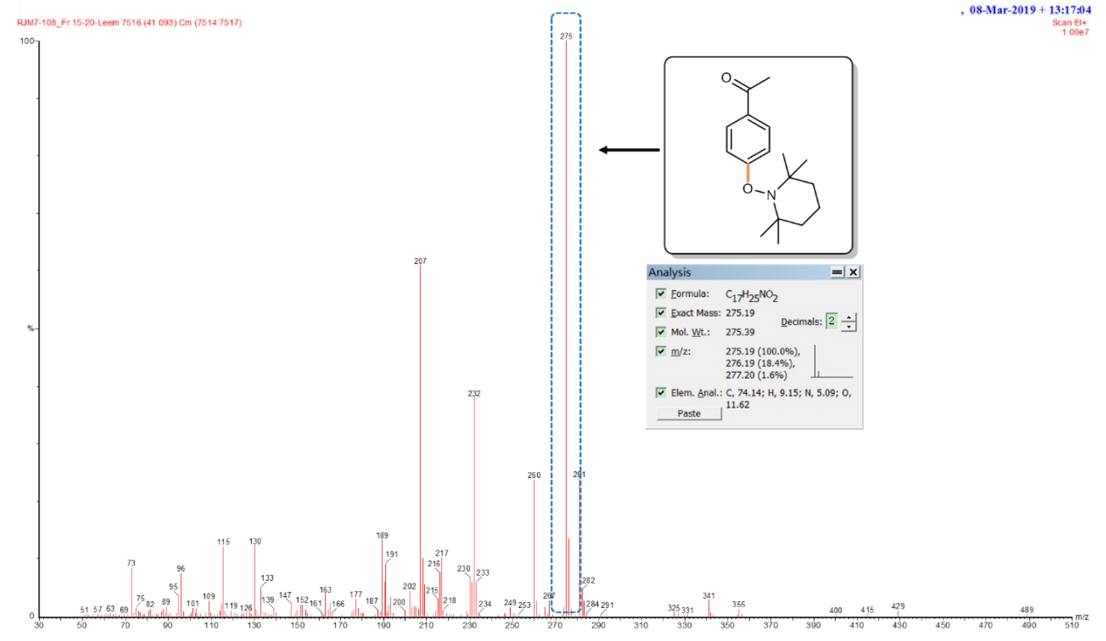


Figure S13. GC-MS analysis of the crude product (model reaction) mixture with stoichiometric TEMPO that displayed a signal with m/z that matches the expected mass of the TEMPO adducts (formed from the capture of the aryl radical) after blue LED irradiation.

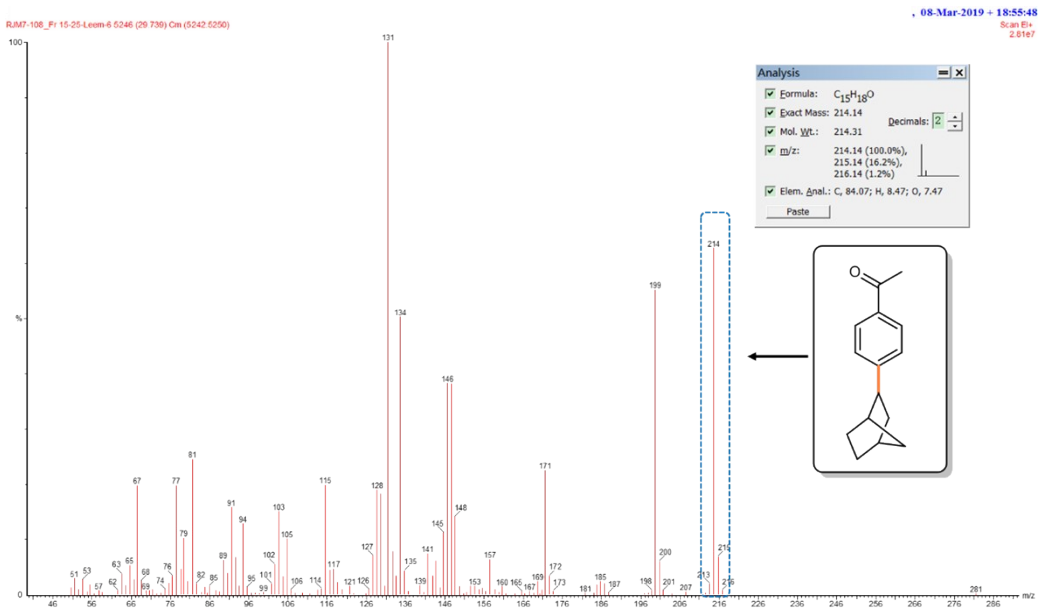


Figure S14. GC-MS analysis of the crude product (model reaction) mixture with stoichiometric norbornene that displayed a signal with m/z that matches the expected mass of the norbornene adducts (formed from the capture of the aryl radical) after blue LED irradiation.

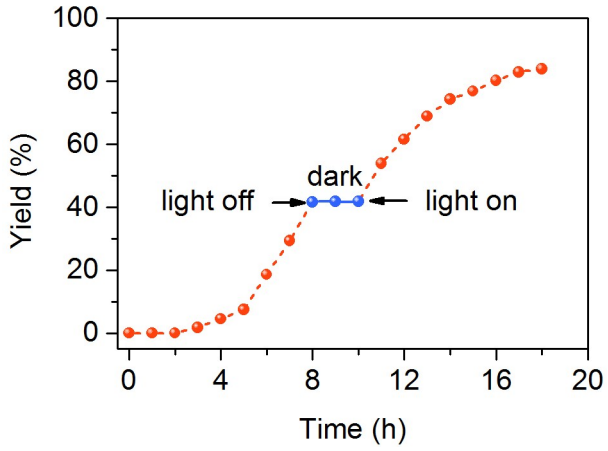


Figure S15. Light responsive control experiment of: product formation in the model reaction that ceased in aphotic conditions even after irradiation for 8 h with the product formation continuing upon re-exposure to light. The conversion ceases during dark periods, indicating that the radical chain mechanism can be excluded.[13, 23]

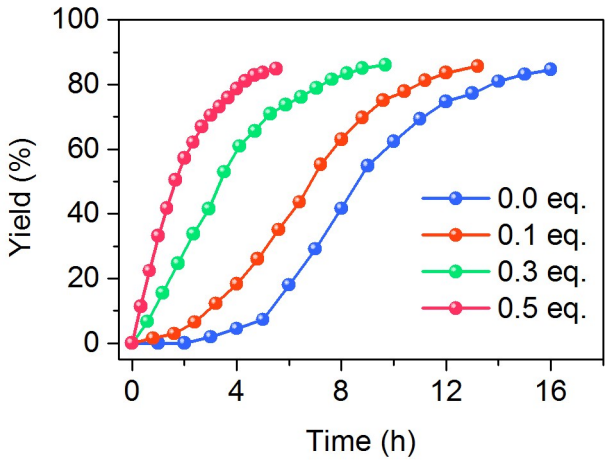


Figure S16. The kinetic profiles of the SSI-ET catalytic process performed by adding various amounts of reduction product **1c** (0 to 0.5 equiv, deducted when calculating yield) in the model reaction which was monitored by ^{1}H NMR spectroscopy undere blue LED irradiation.

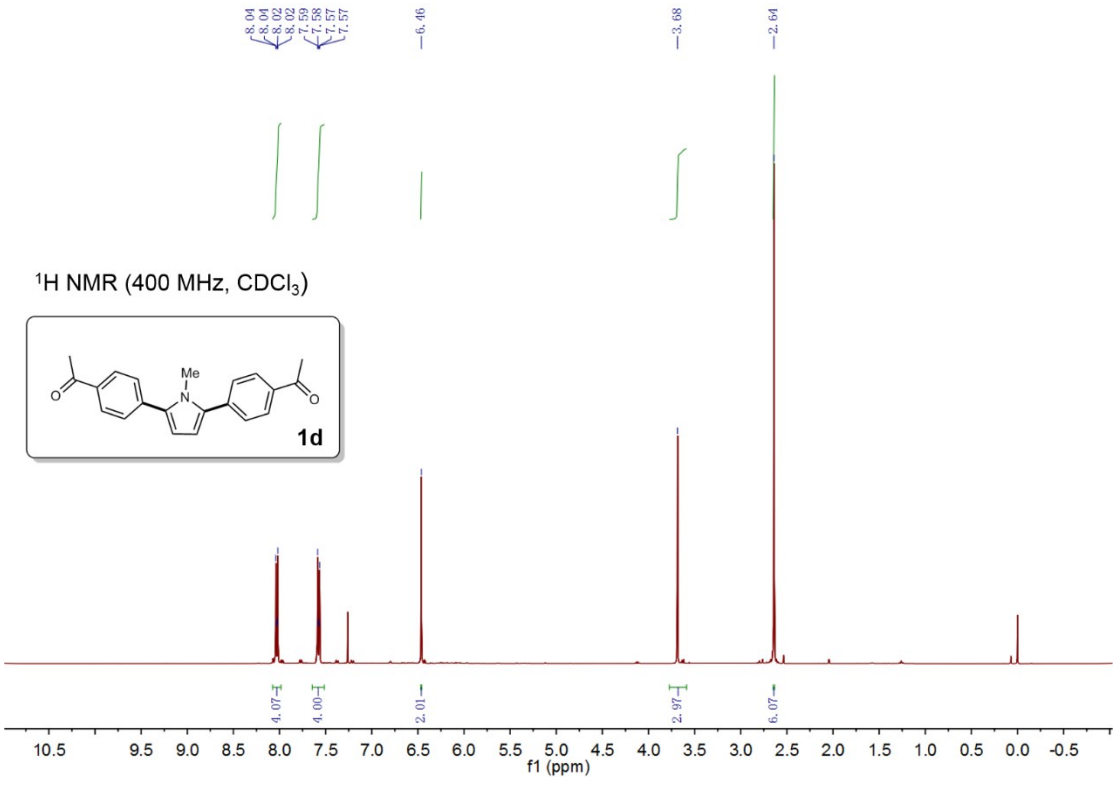


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) of isolated product **1d**.

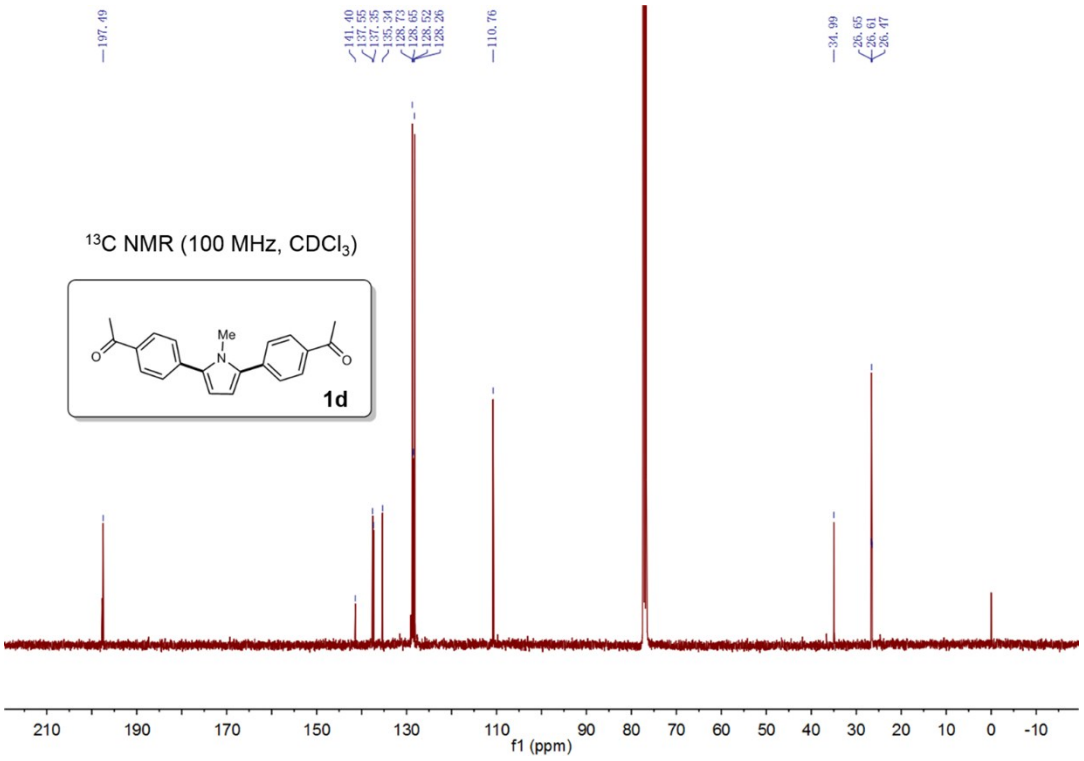


Figure S18. ^{13}C NMR (100 MHz, $CDCl_3$) of isolated product **1d**.

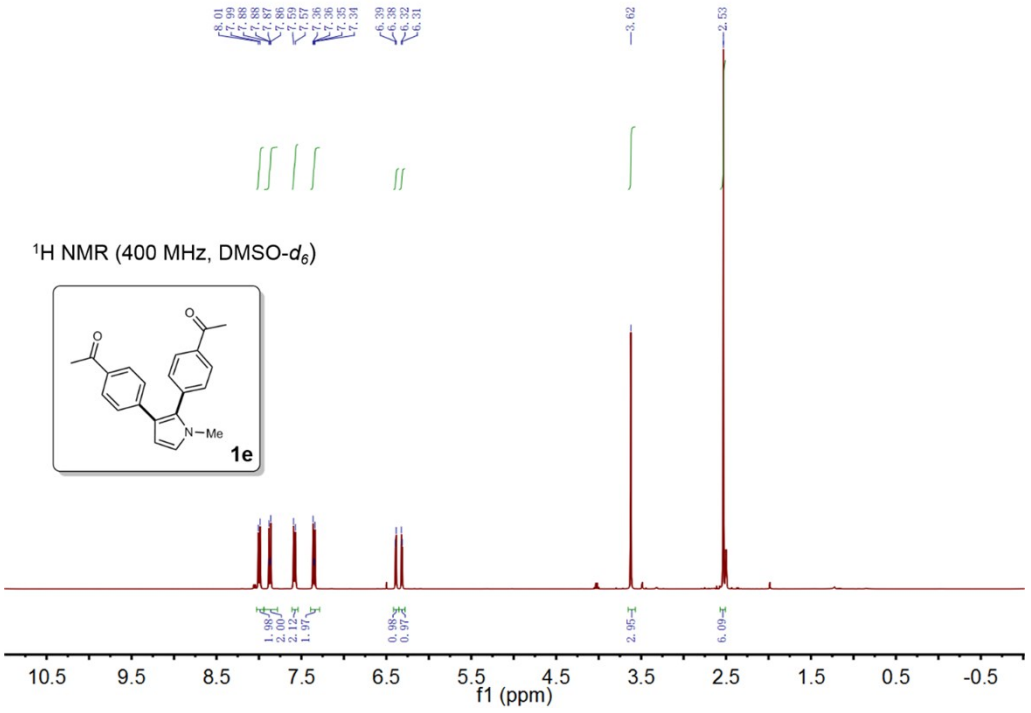


Figure S19. [1]H NMR (400 MHz, DMSO-d_6) of isolated product **1e**.

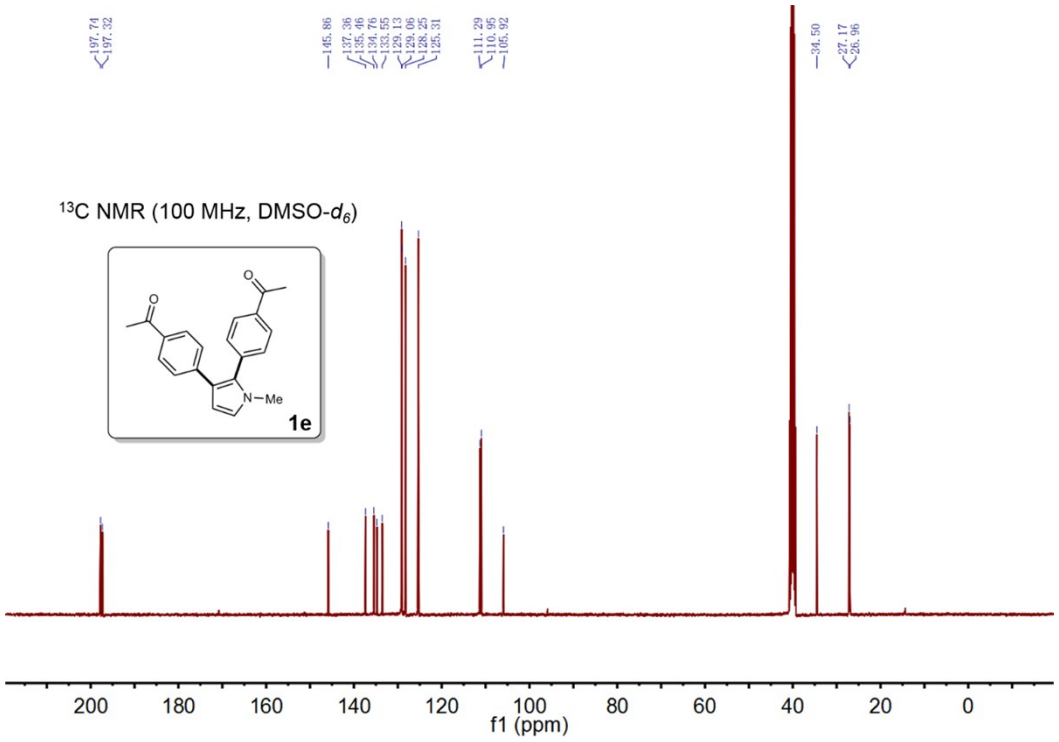


Figure S20. [13]C NMR (100 MHz, DMSO-d_6) of isolated product **1e**.

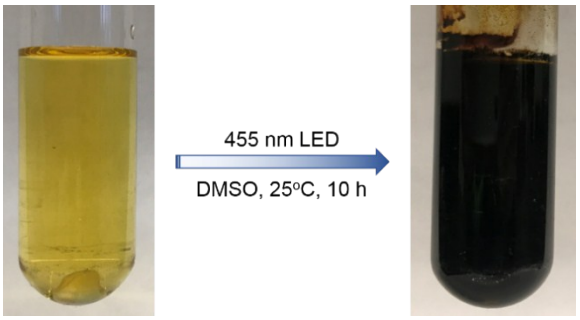


Figure S21. Images displaying the color change of the reaction in **Fig. 4a**.

K. Electrochemistry experiments analysis of substrates and products.

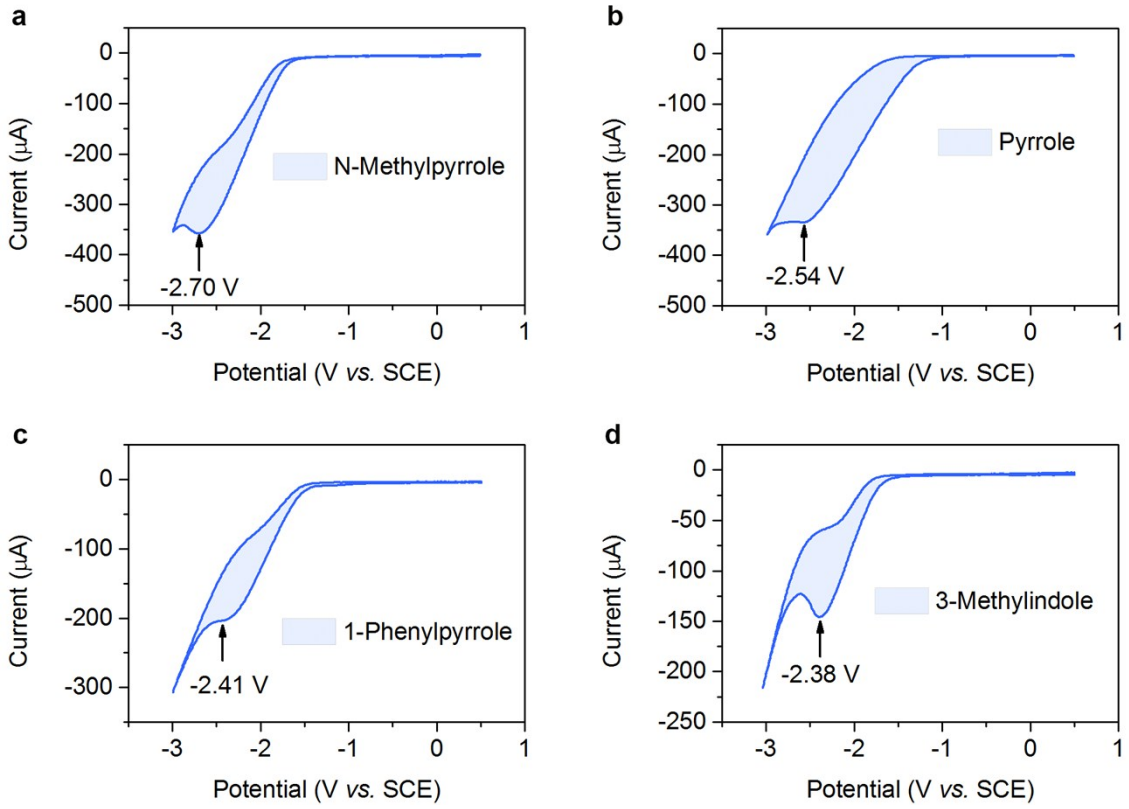


Figure S22. Cyclic voltammograms of N-Methylpyrrole, Pyrrole, 1-Phenylpyrrole, and 3-Methylindole recorded with a glassy carbon working electrode using a sweep rate of 100 mV s^{-1} in DMSO.

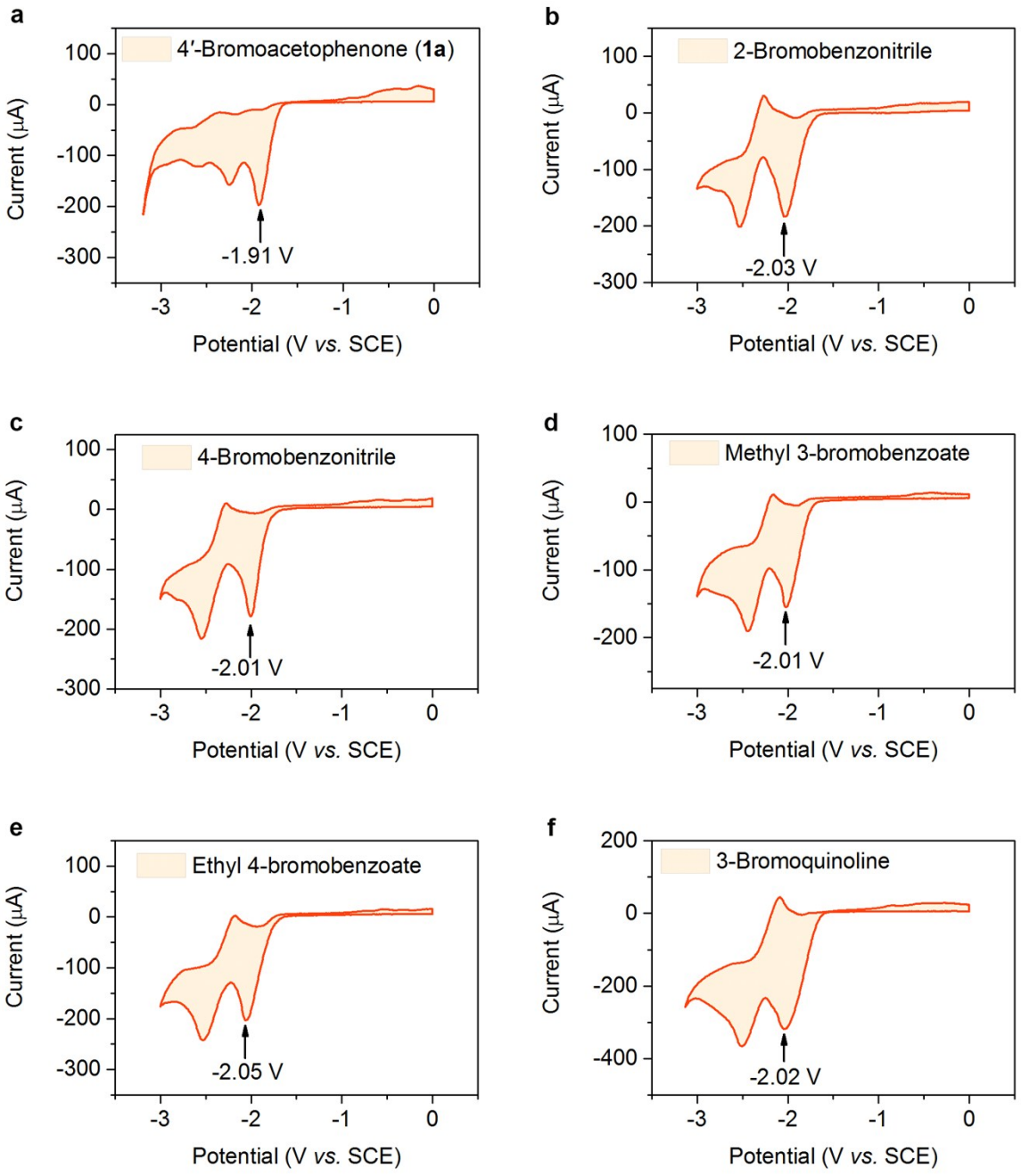


Figure S23. Cyclic voltammograms of various aryl halides substrates recorded with a glassy carbon working electrode using a sweep rate of 100 mV s^{-1} in DMSO.

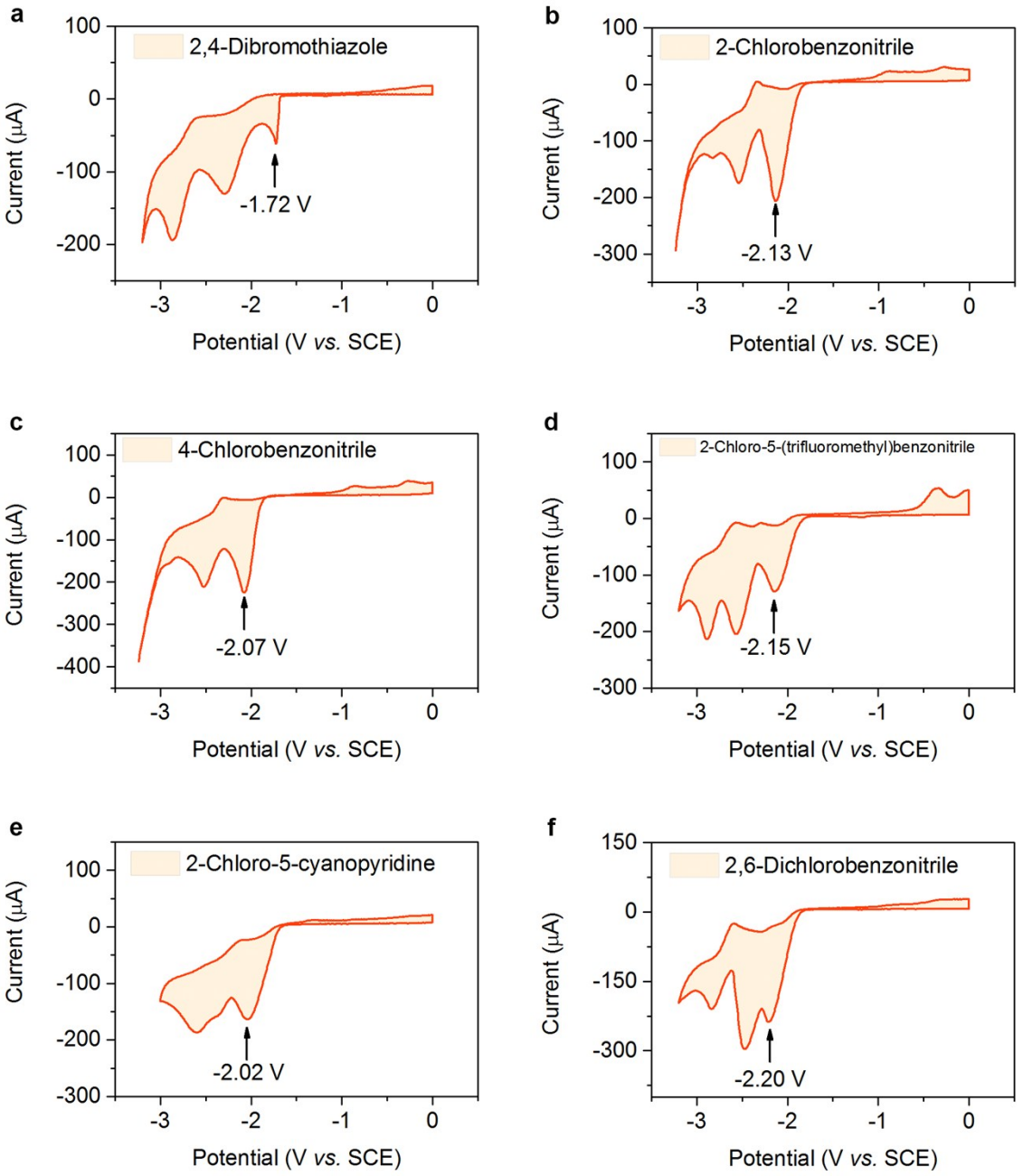


Figure S24. Cyclic voltammograms of various aryl halides substrates recorded with a glassy carbon working electrode using a sweep rate of 100 mV s^{-1} in DMSO.

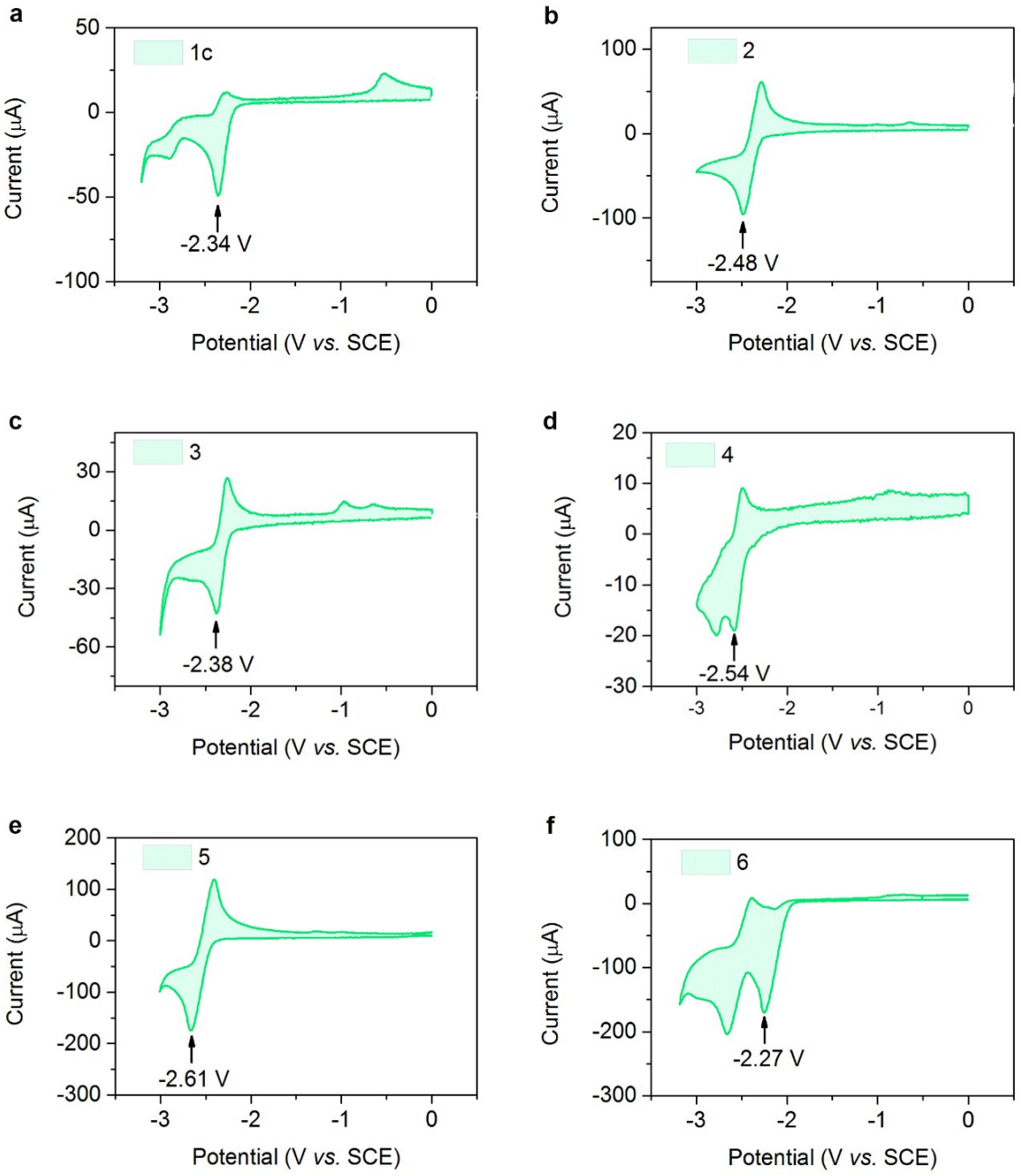


Figure S25. Cyclic voltammograms of various products (**1-6**) in **Fig. 5** recorded with a glassy carbon working electrode using a sweep rate of 100 mV s^{-1} in DMSO.

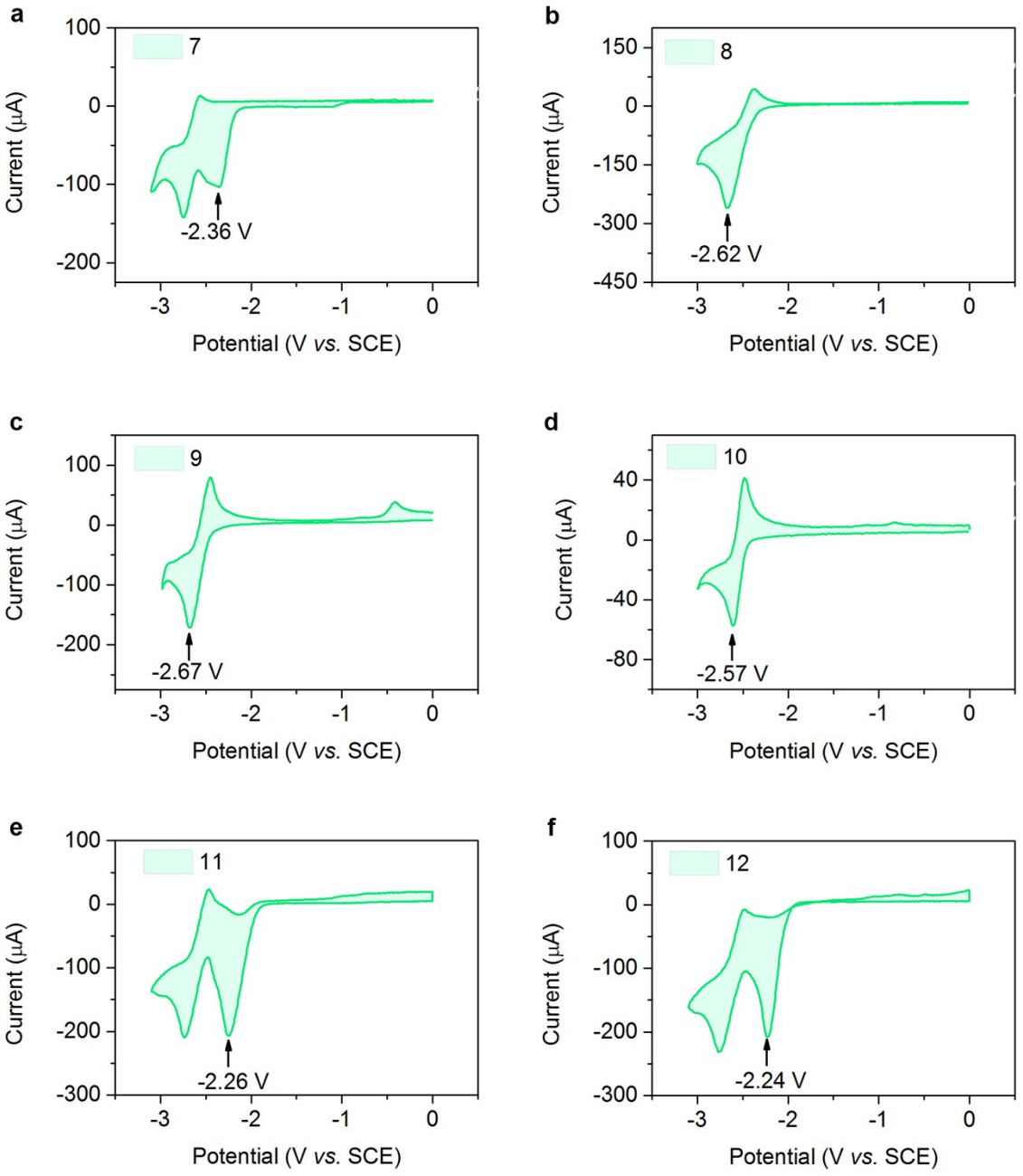


Figure S26. Cyclic voltammograms of various products (**7-12**) in **Fig. 5** recorded with a glassy carbon working electrode using a sweep rate of 100 mV s^{-1} in DMSO.

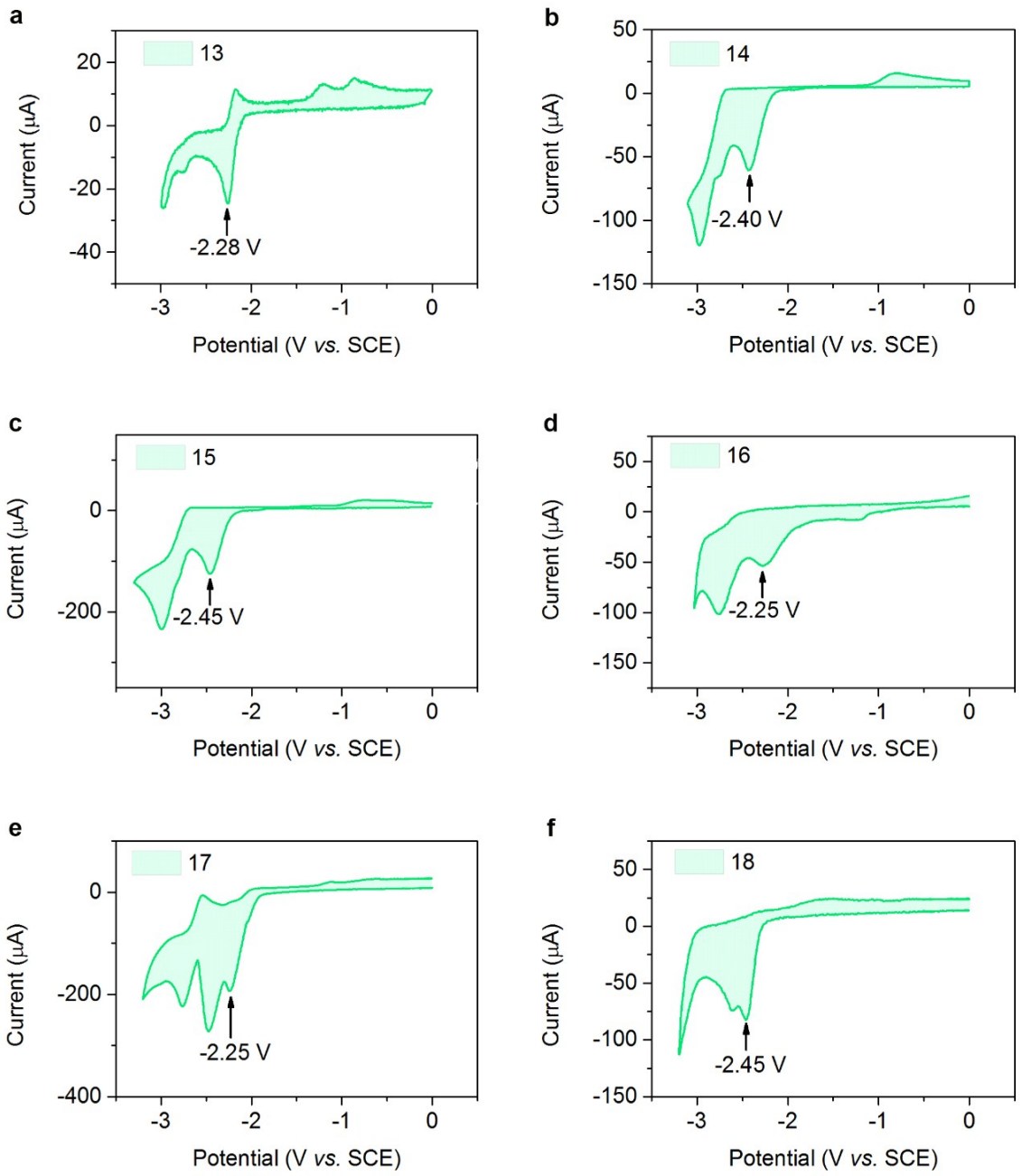


Figure S27. Cyclic voltammograms of various products (**13-18**) in **Fig. 5** recorded with a glassy carbon working electrode using a sweep rate of 100 mV s^{-1} in DMSO.

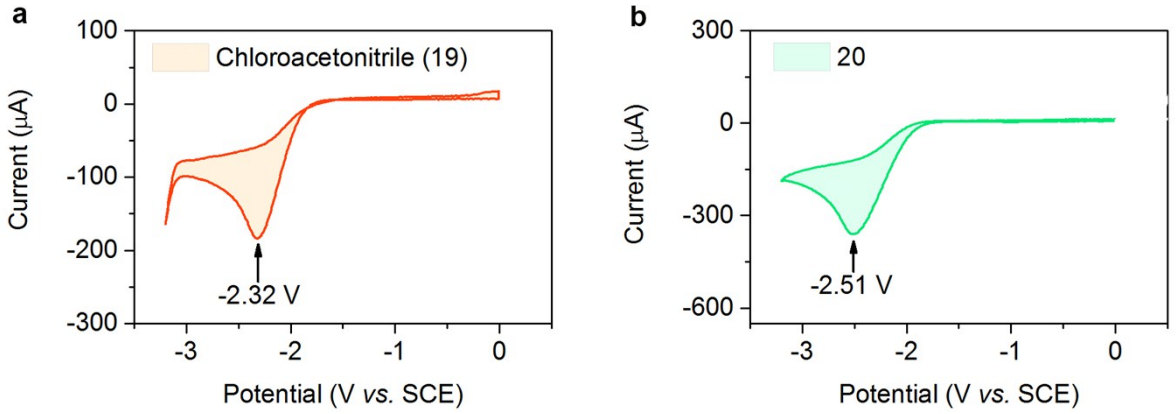


Figure S28. Cyclic voltammograms of Chloroacetonitrile (**substrate 19**) and corresponding products (**adduct 20**) in **Fig. 6** recorded with a glassy carbon working electrode using a sweep rate of 100 mV s^{-1} in DMSO.

L. References

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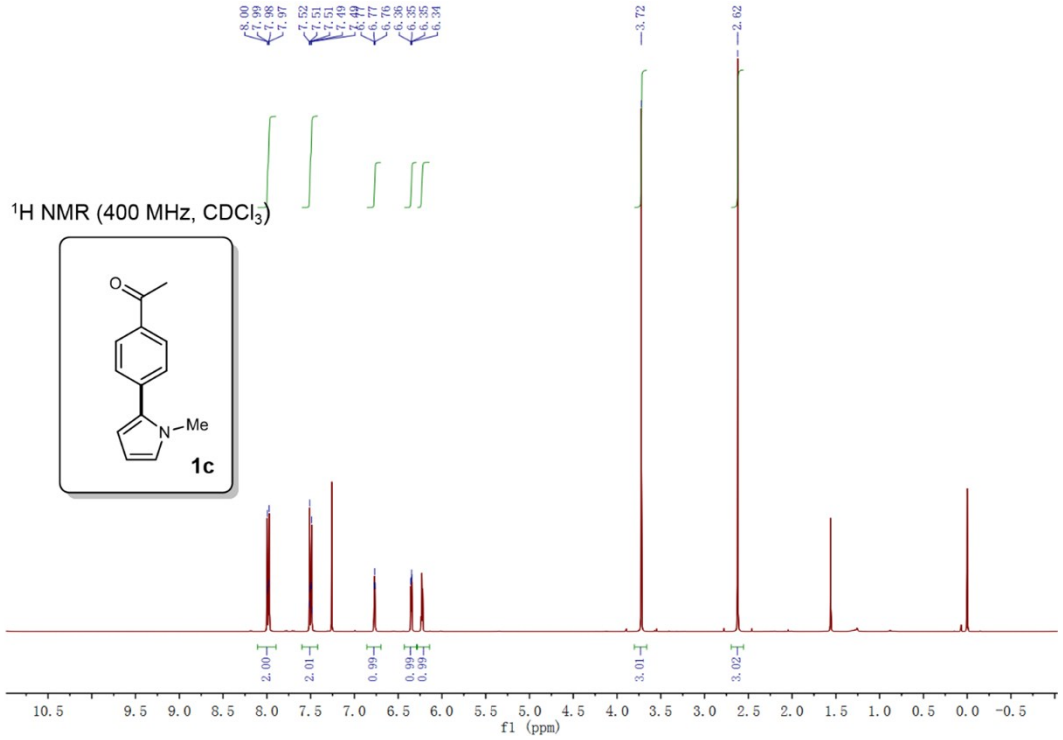
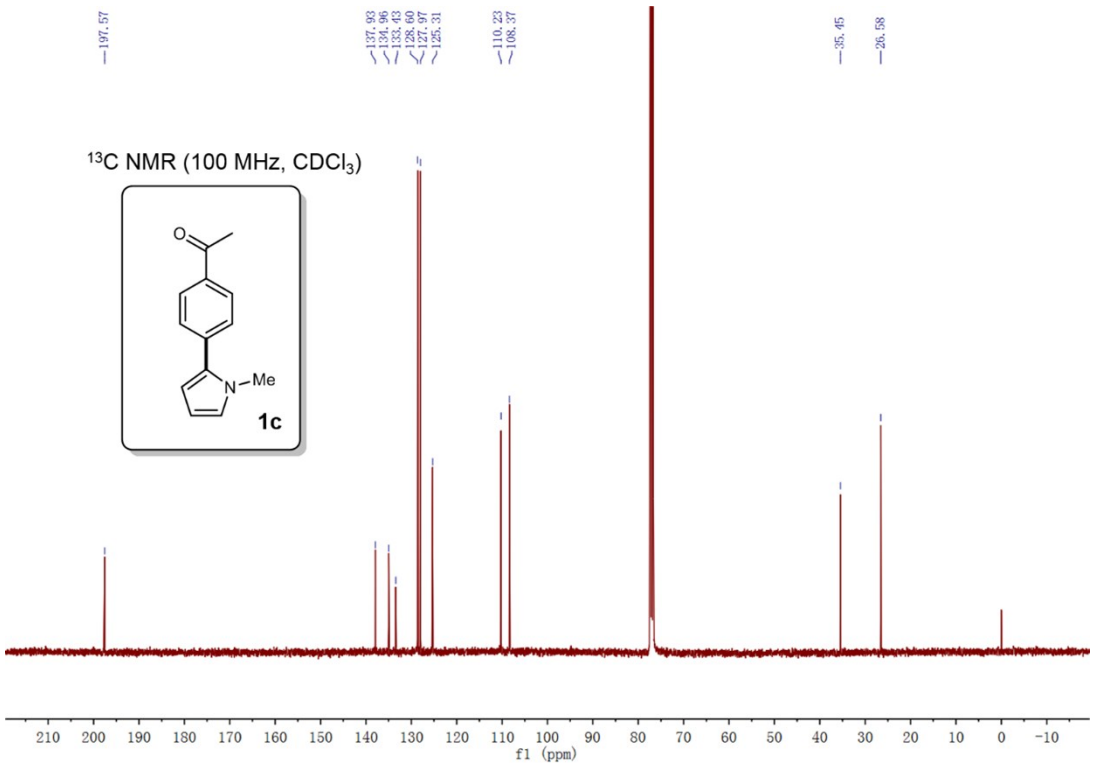
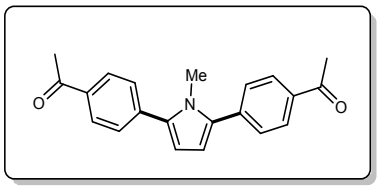
M. NMR Spectra (^{1}H and ^{13}C NMR)

1-(4-(1-Methyl-1*H*-pyrrol-2-yl)phenyl)ethan-1-one (1c):



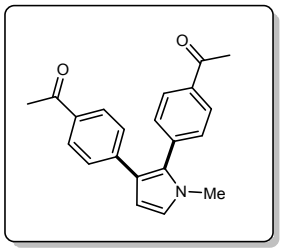


1,1'-((1-methyl-1*H*-pyrrole-2,5-diyl)bis(4,1-phenylene))bis(ethan-1-one) (1d)



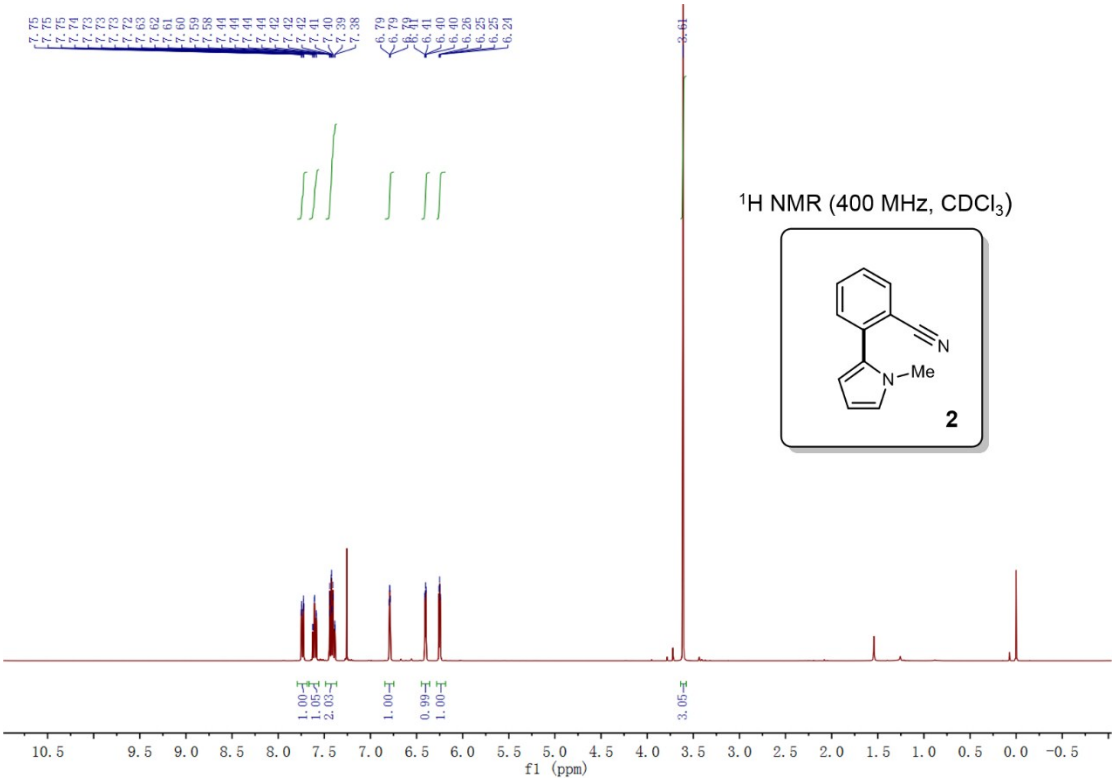
See the ^{1}H and ^{13}C NMR spectra of **1d** in **Figure S17 and S18.**

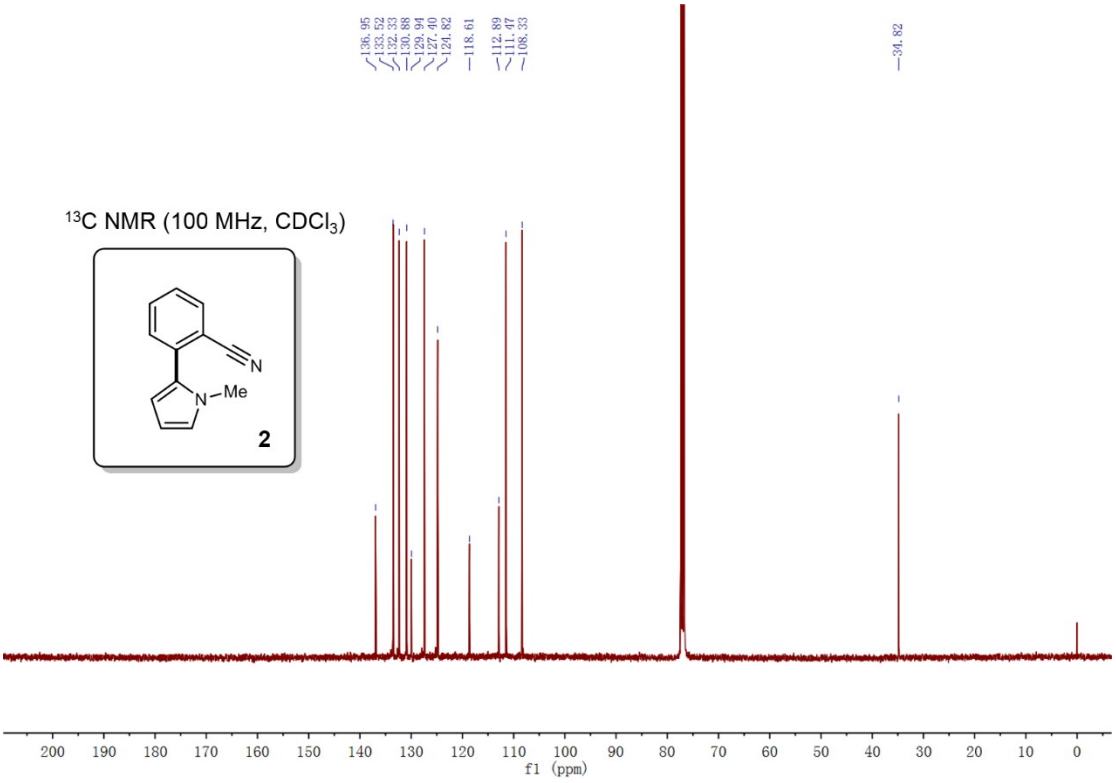
1,1'-((1-methyl-1*H*-pyrrole-2,3-diyl)bis(4,1-phenylene))bis(ethan-1-one) (1e)



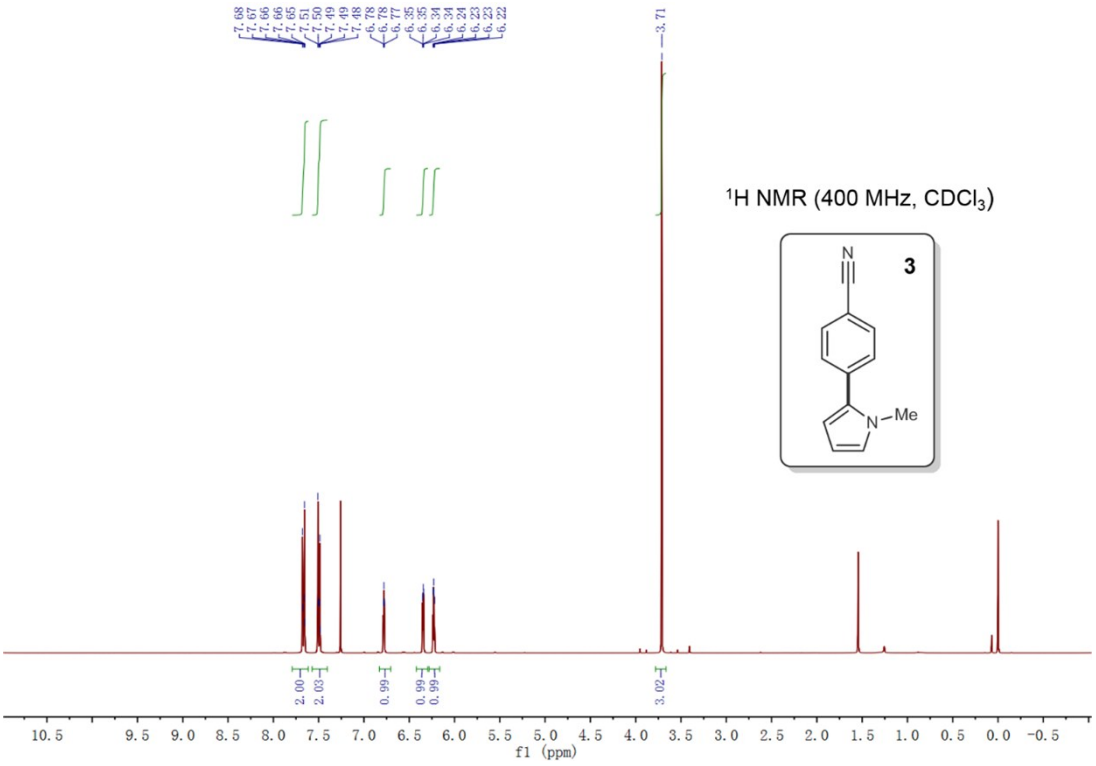
See the ^{1}H and ^{13}C NMR spectra of **1e** in **Figure S19 and S20.**

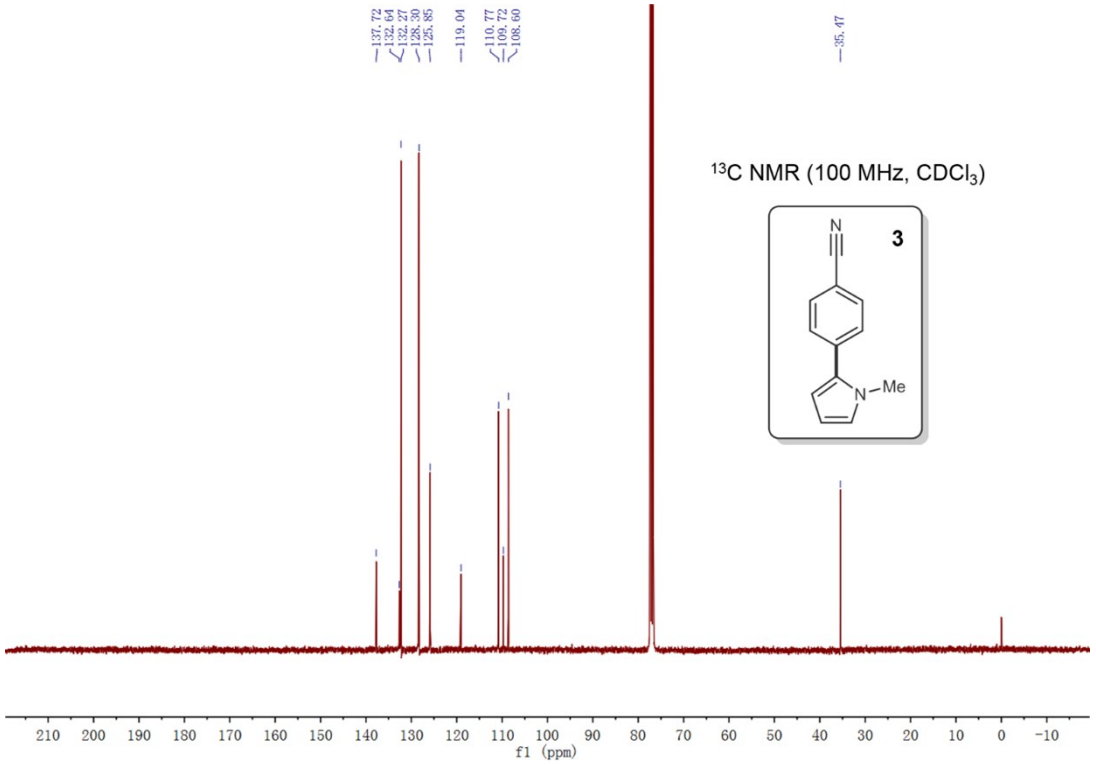
2-(1-Methyl-1*H*-pyrrol-2-yl)benzonitrile (2)



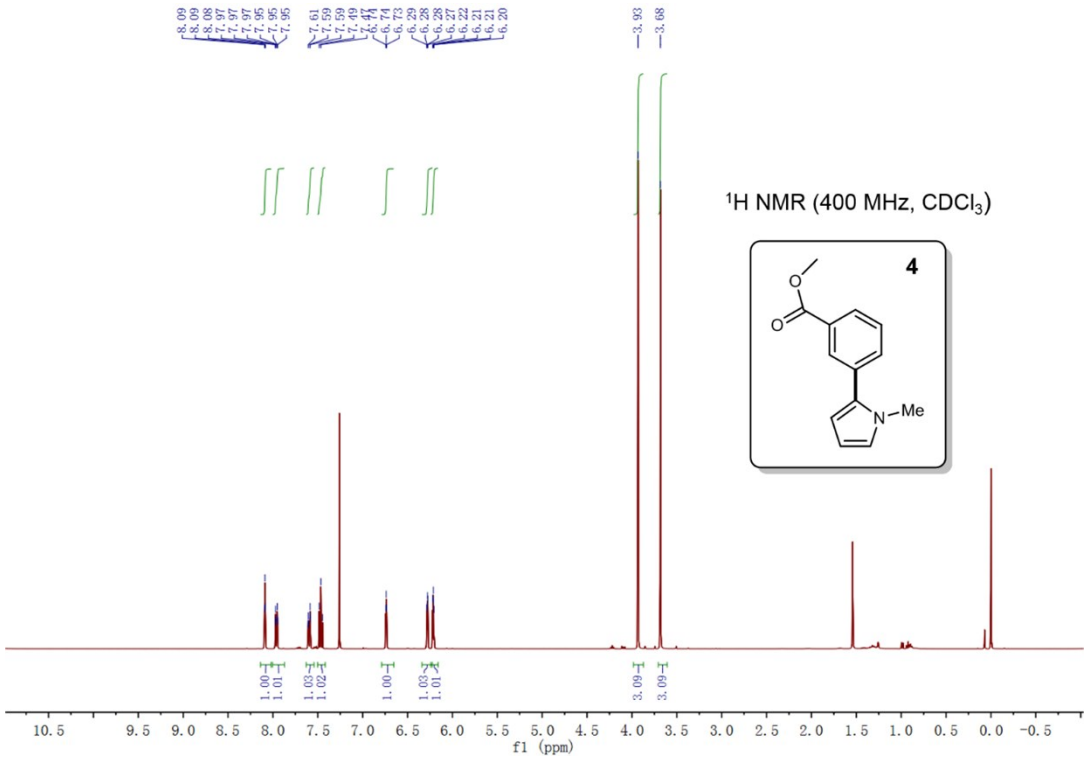


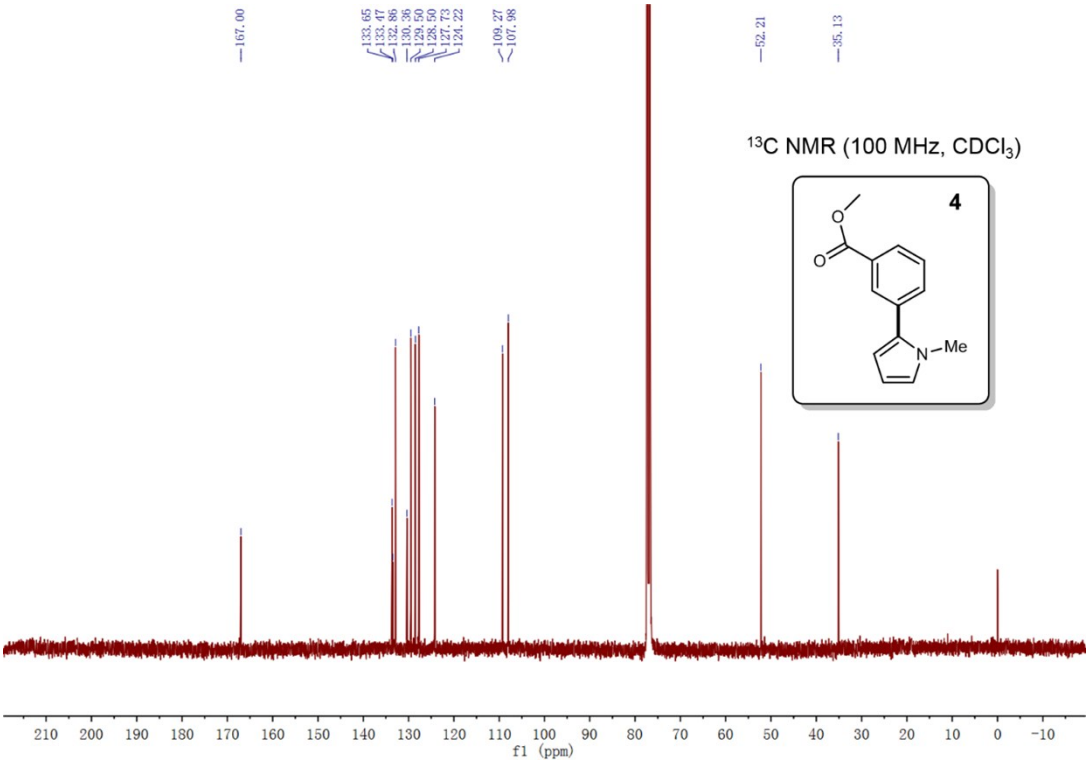
4-(1-Methyl-1*H*-pyrrol-2-yl)benzonitrile (3)



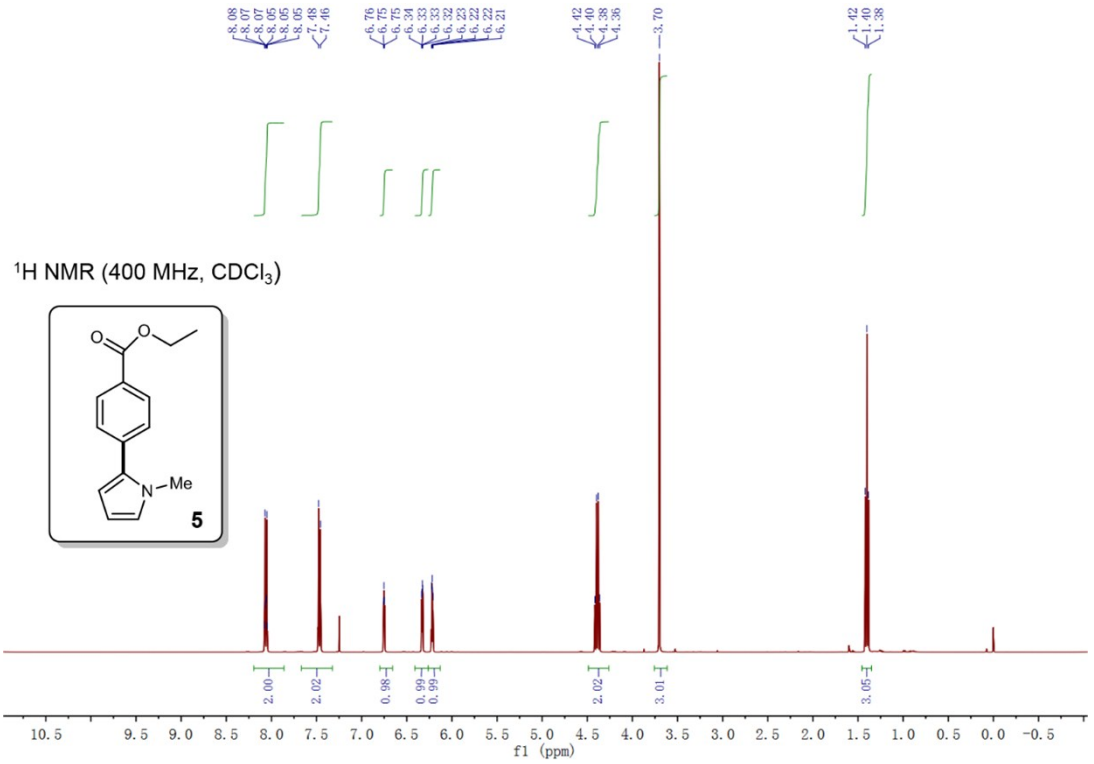


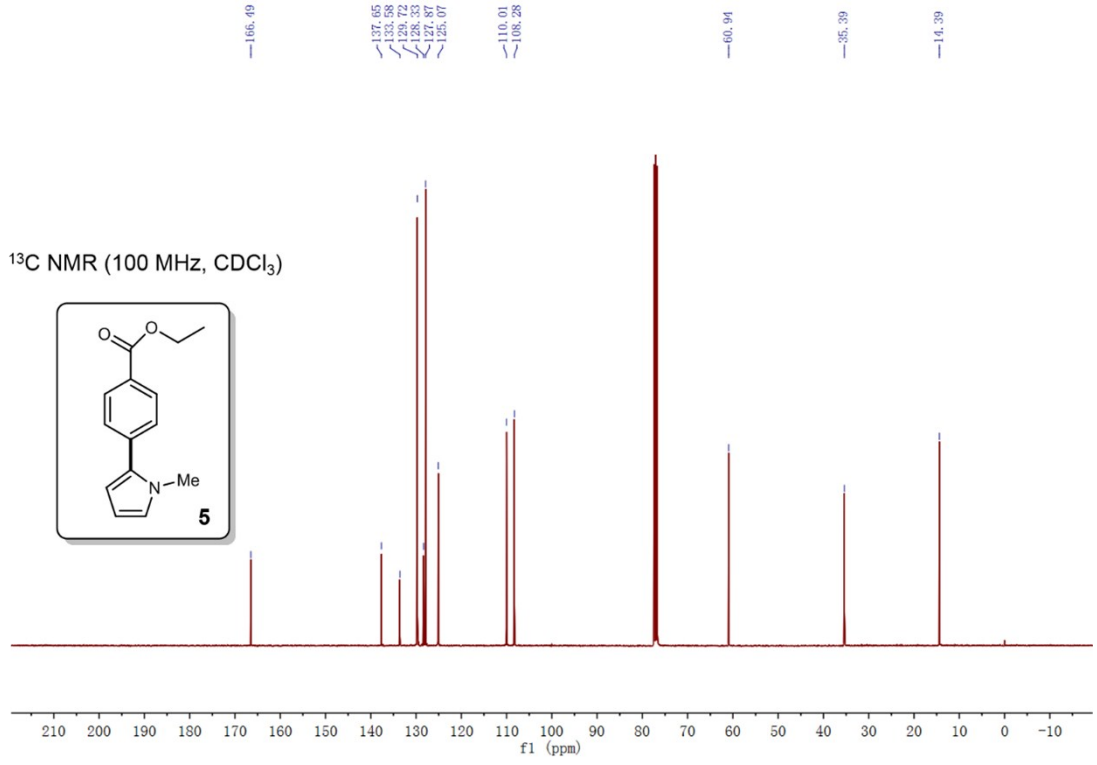
Methyl 3-(1-methyl-1*H*-pyrrol-2-yl)benzoate (4):



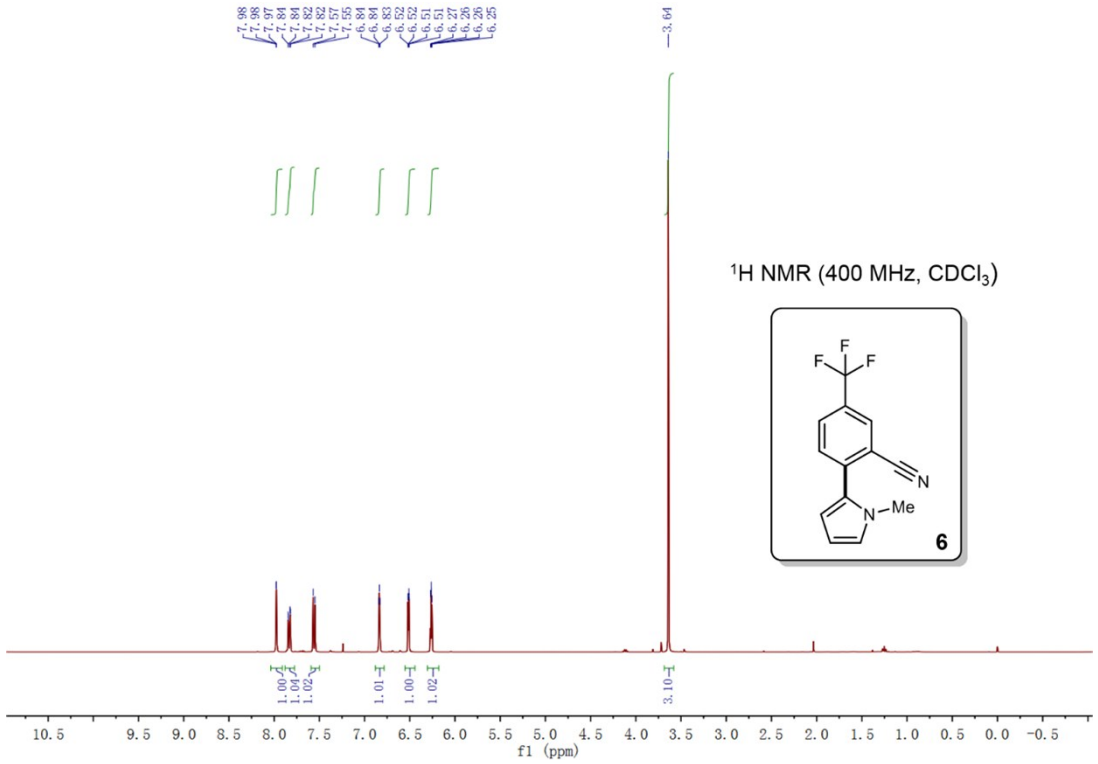


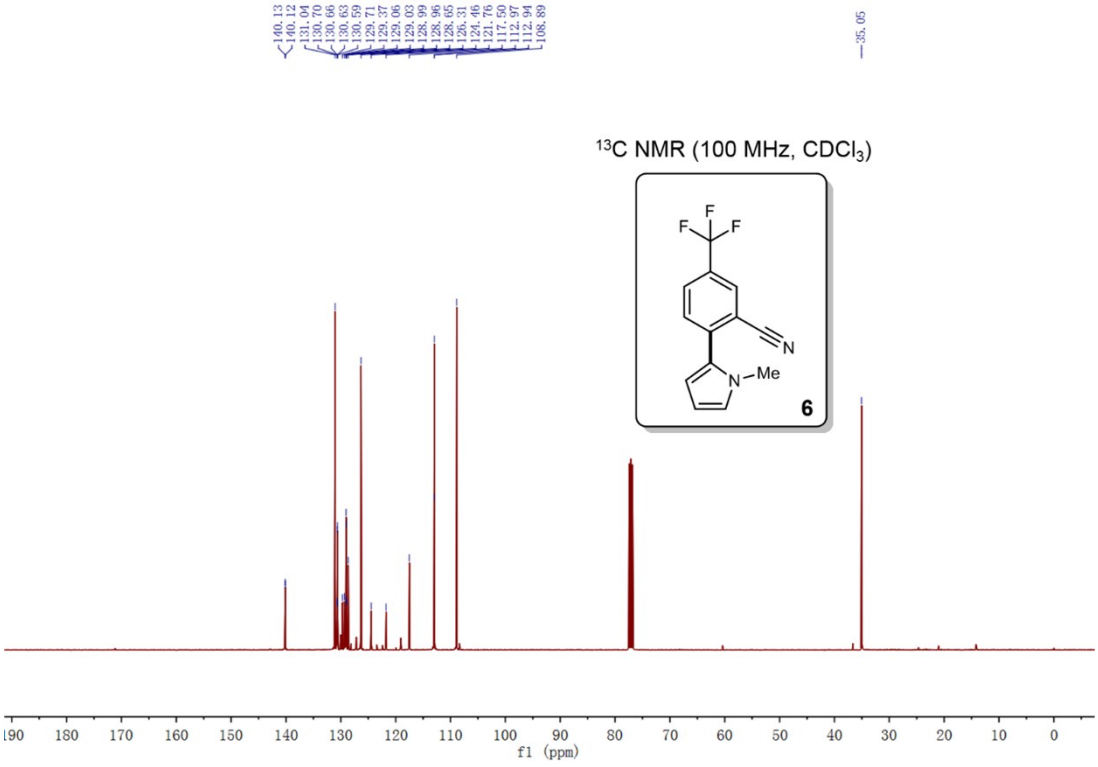
Ethyl 4-(1-methyl-1*H*-pyrrol-2-yl)benzoate (5):



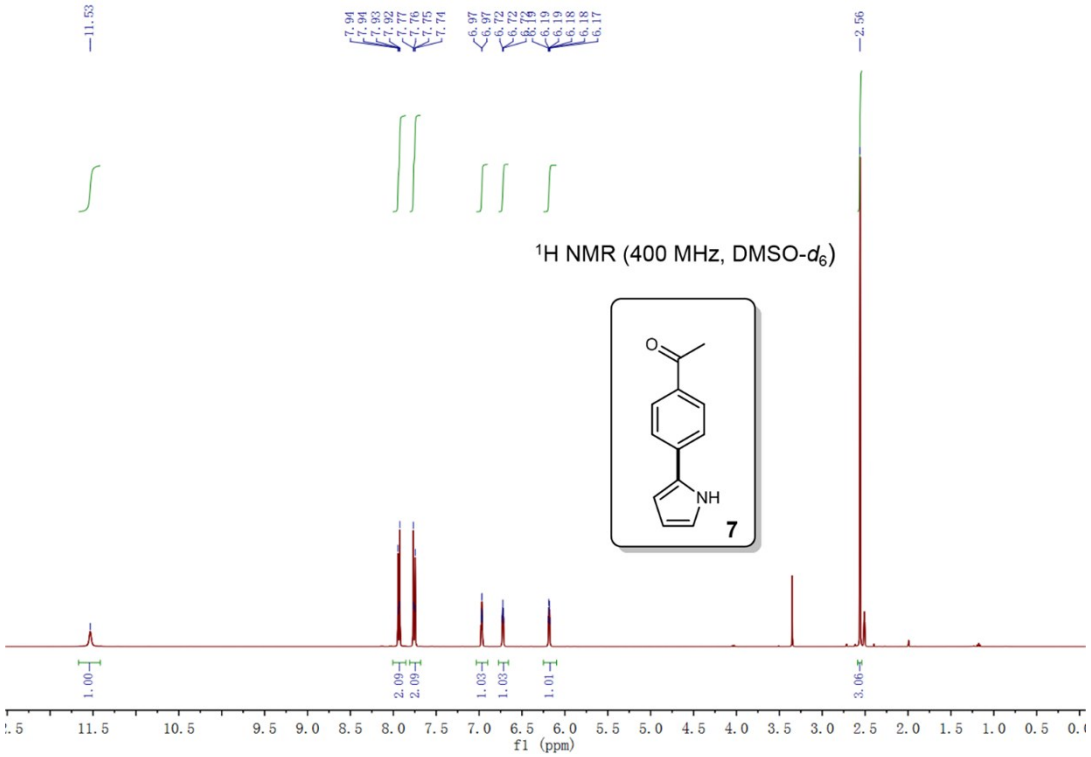


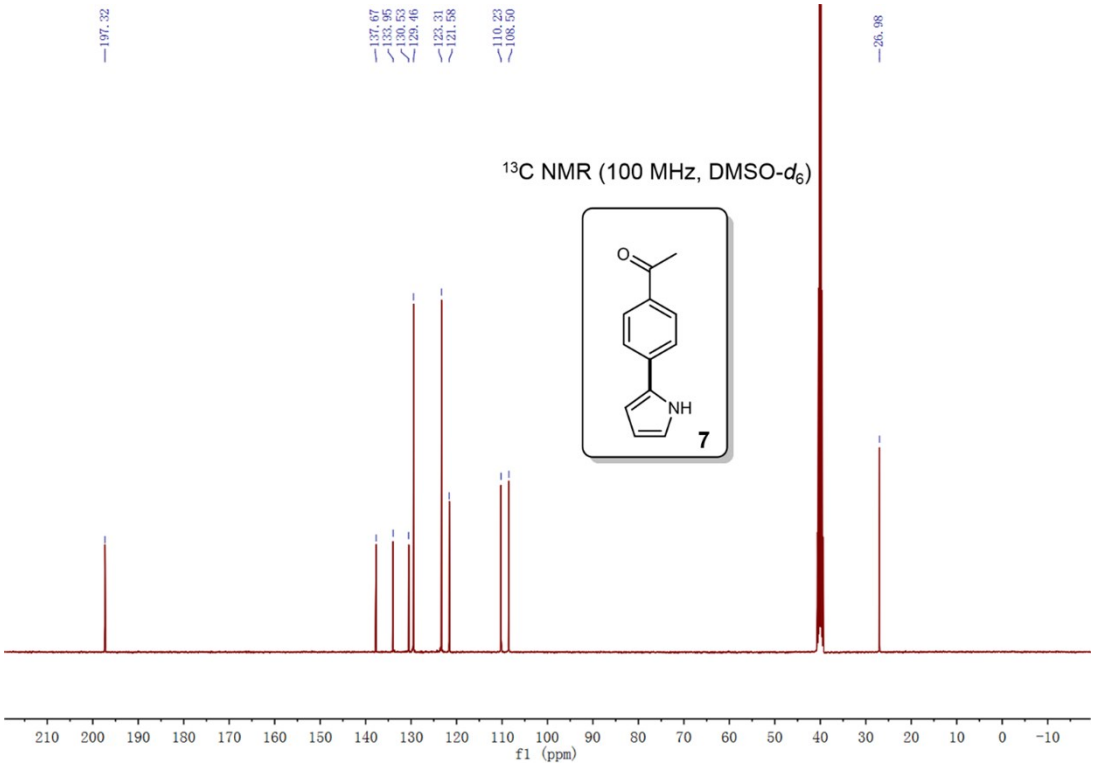
2-(1-Methyl-1*H*-pyrrol-2-yl)-5-(trifluoromethyl)benzonitrile (6):



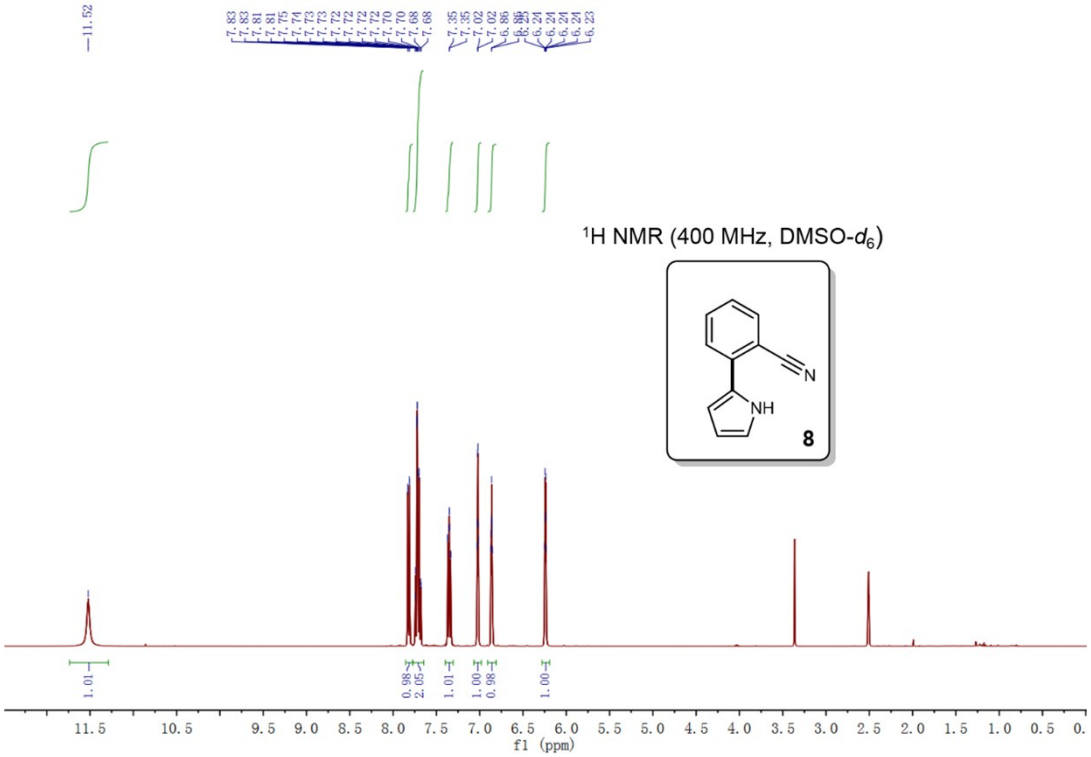


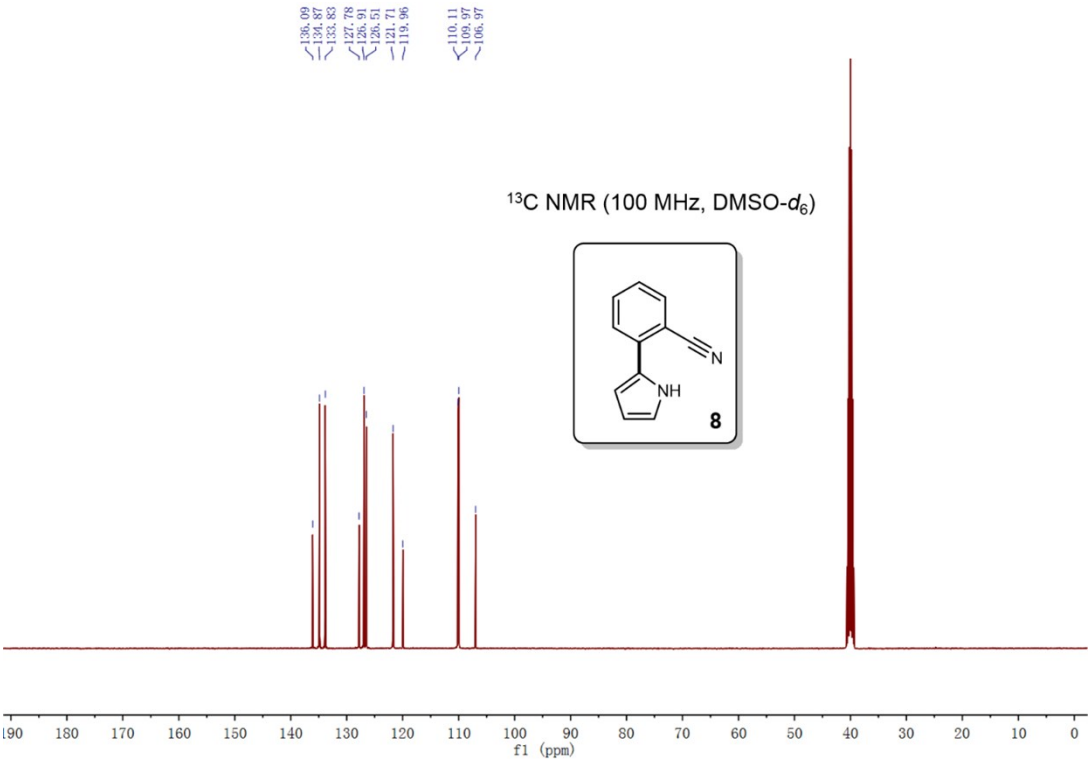
1-(4-(1*H*-pyrrol-2-yl)phenyl)ethan-1-one (7)



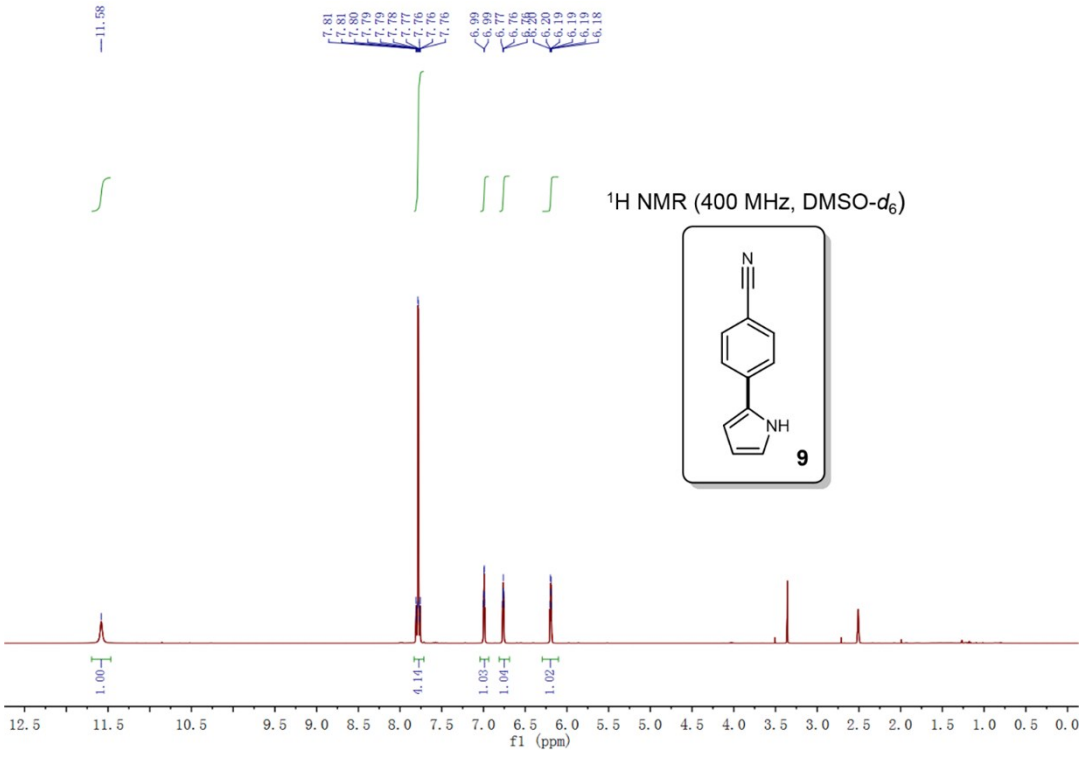


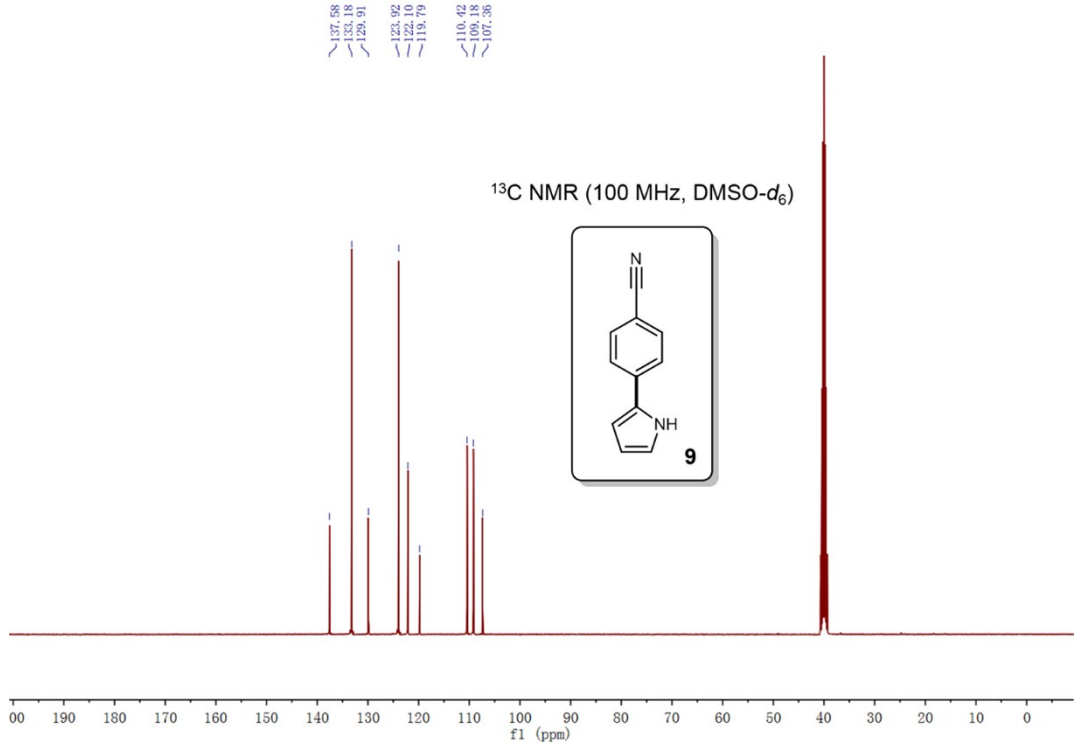
2-(1*H*-pyrrol-2-yl)benzonitrile (8)



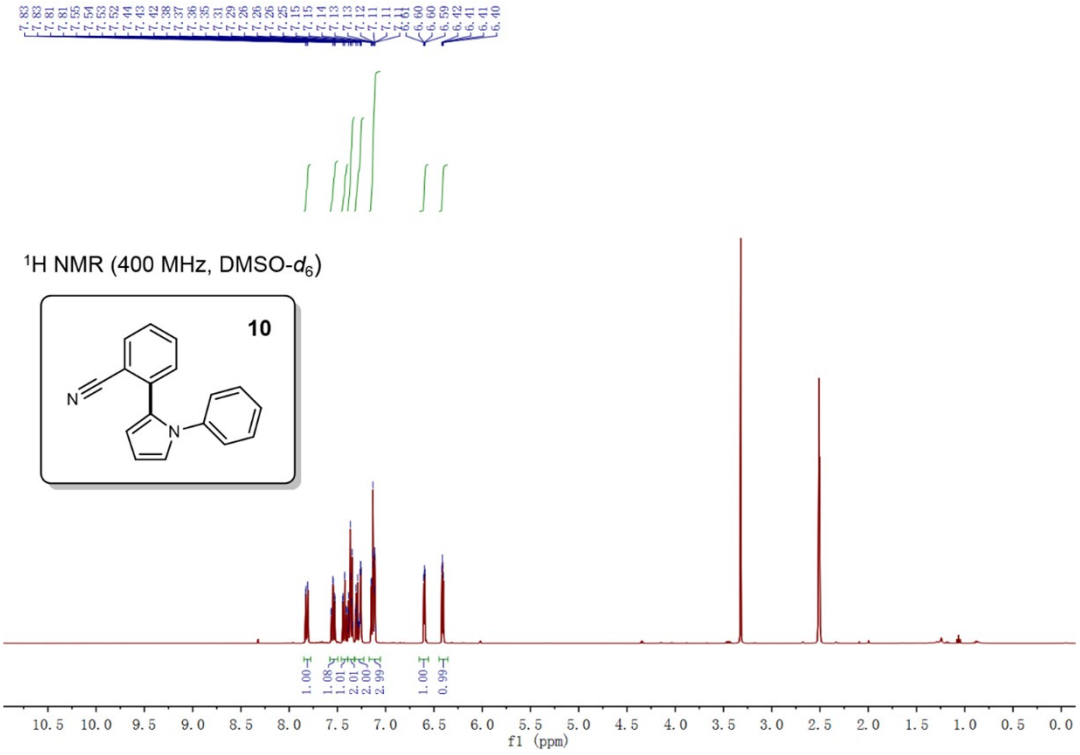


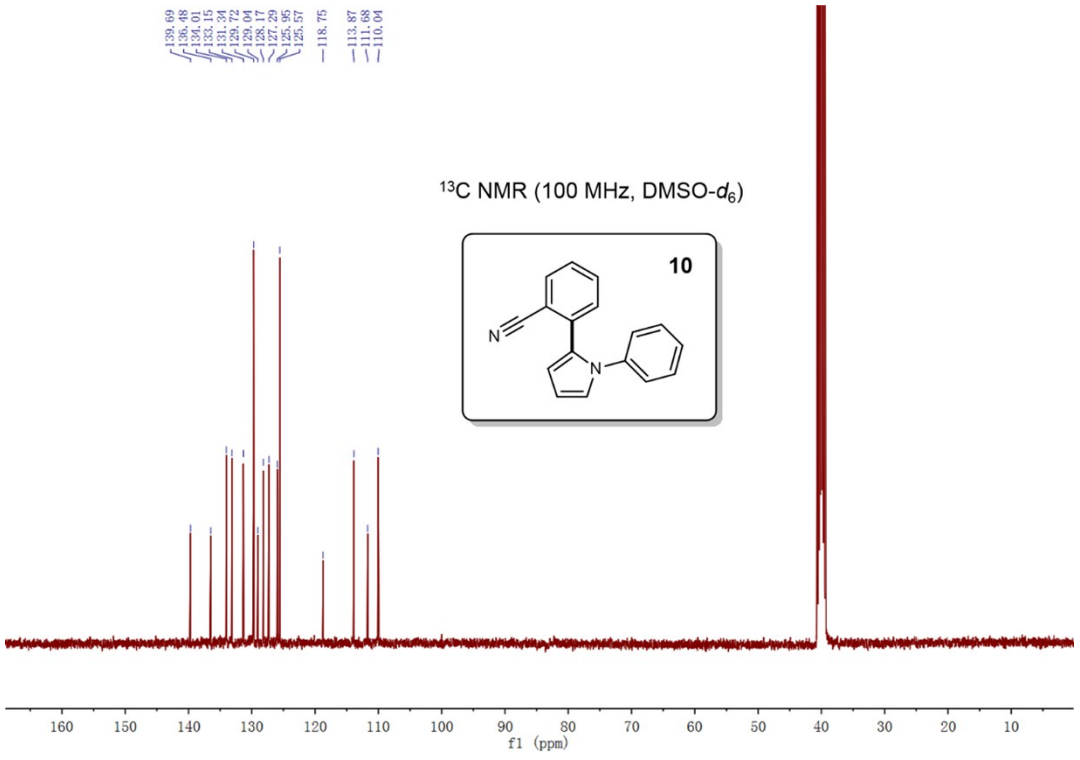
4-(1*H*-pyrrol-2-yl)benzonitrile (9)



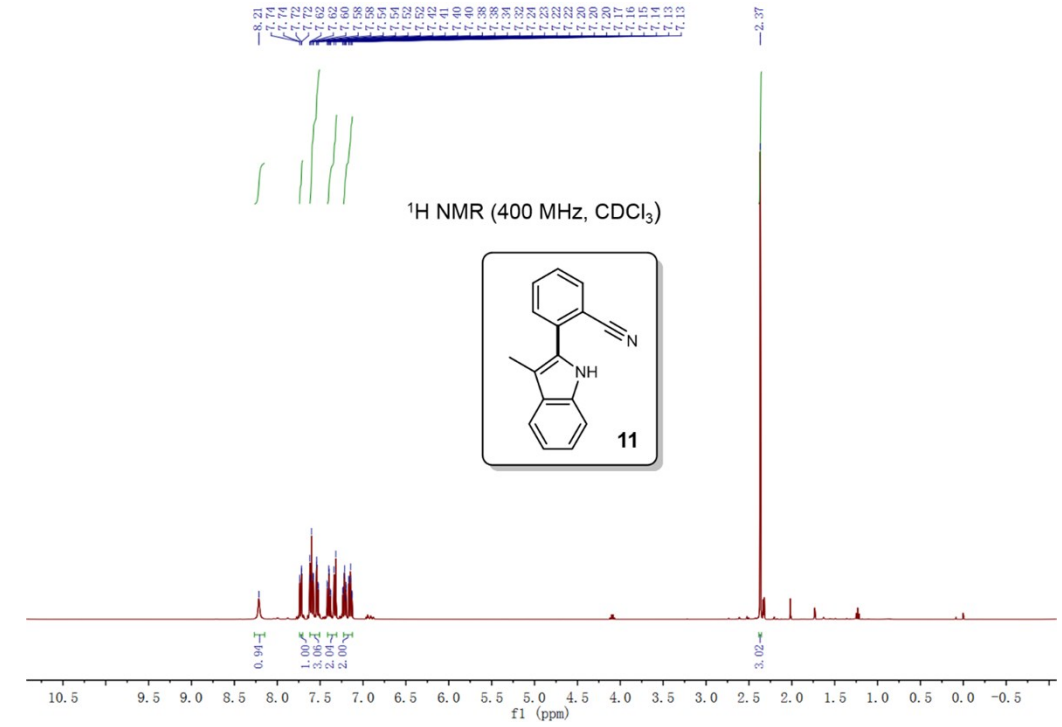


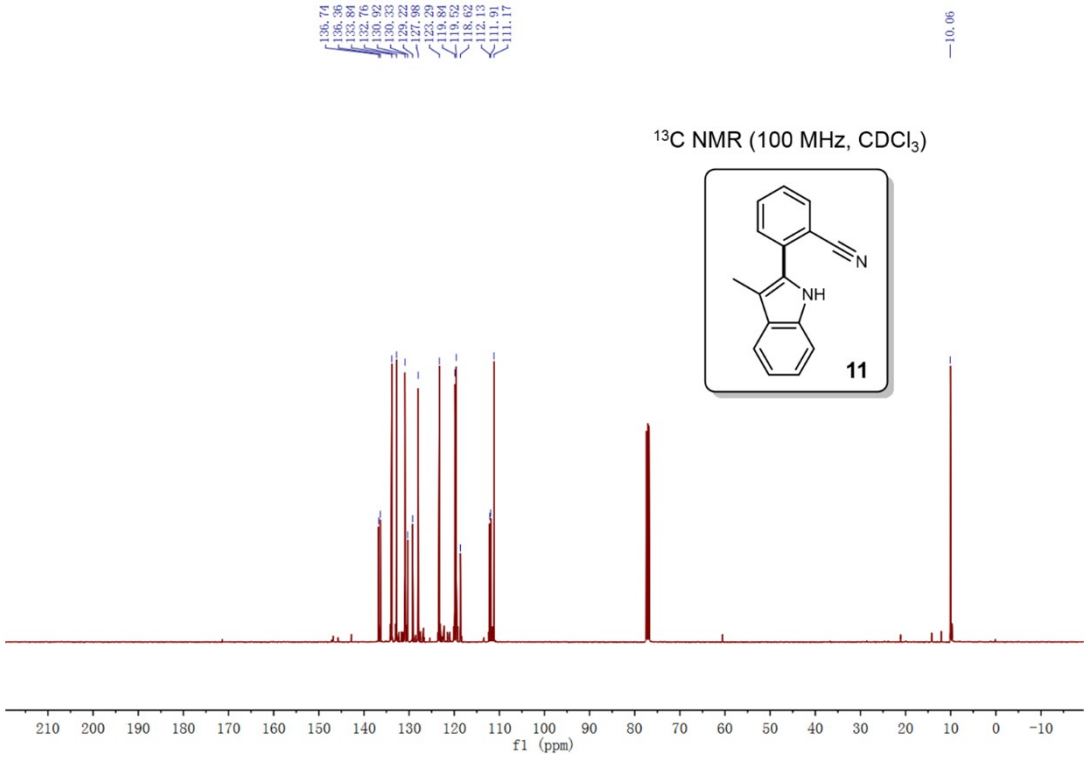
2-(1-Phenyl-1*H*-pyrrol-2-yl)benzonitrile (10)



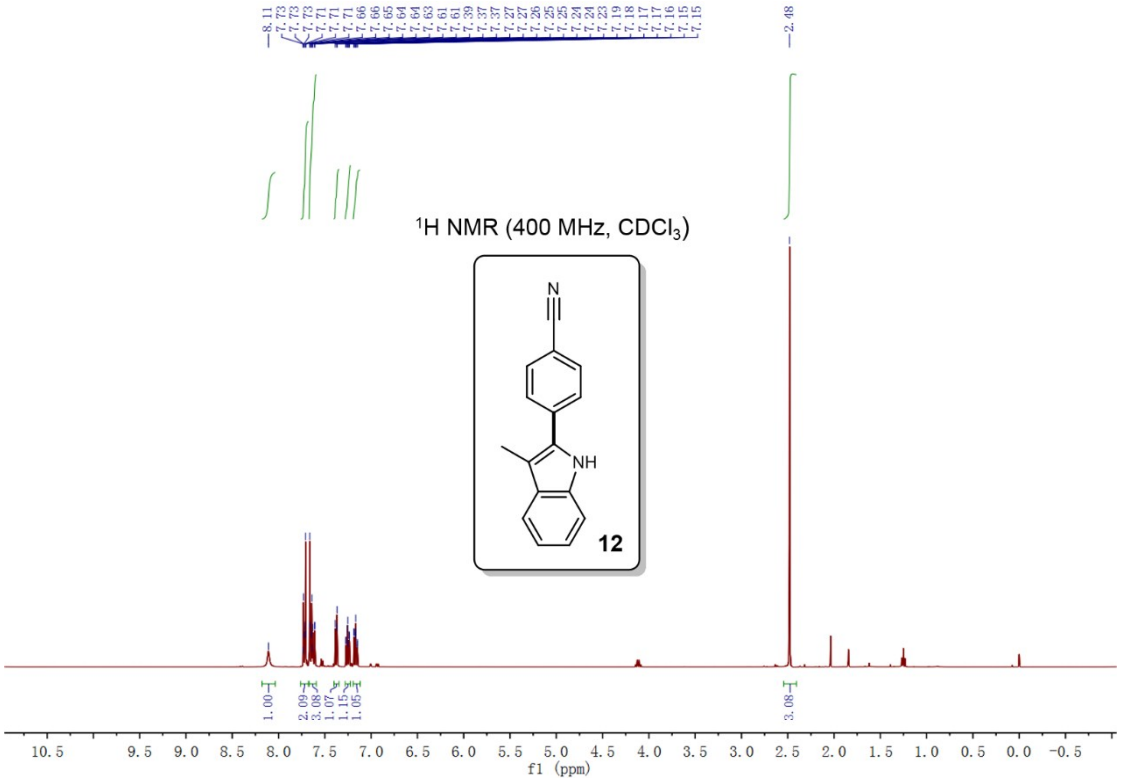


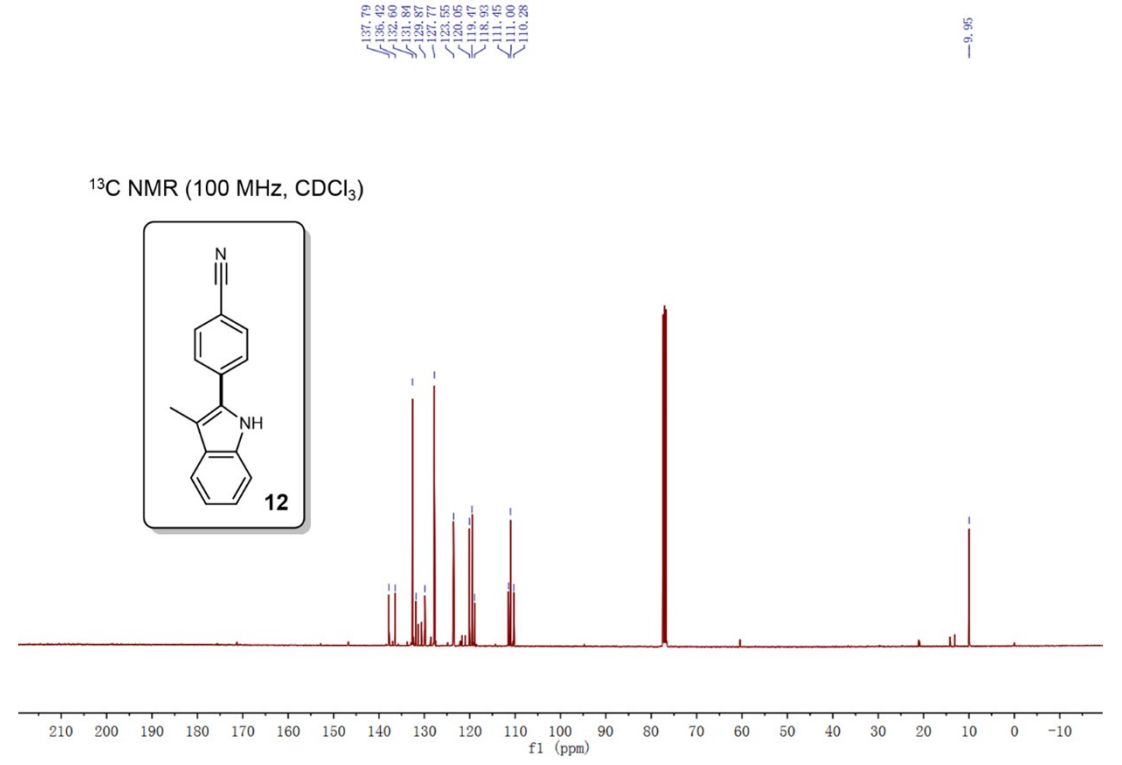
2-(3-Methyl-1*H*-indol-2-yl)benzonitrile (11)



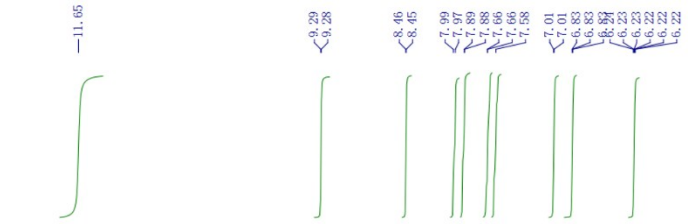


4-(3-Methyl-1*H*-indol-2-yl)benzonitrile (12)

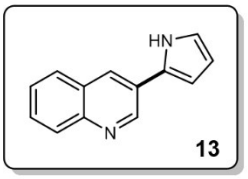


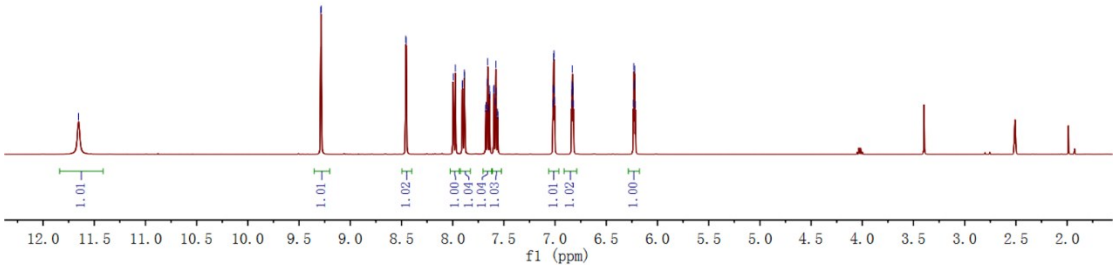


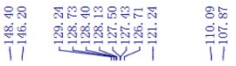
3-(1*H*-pyrrol-2-yl)quinoline (13)



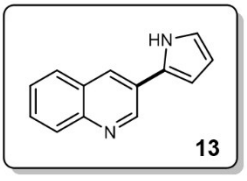
^{1}H NMR (400 MHz, DMSO-d_6)



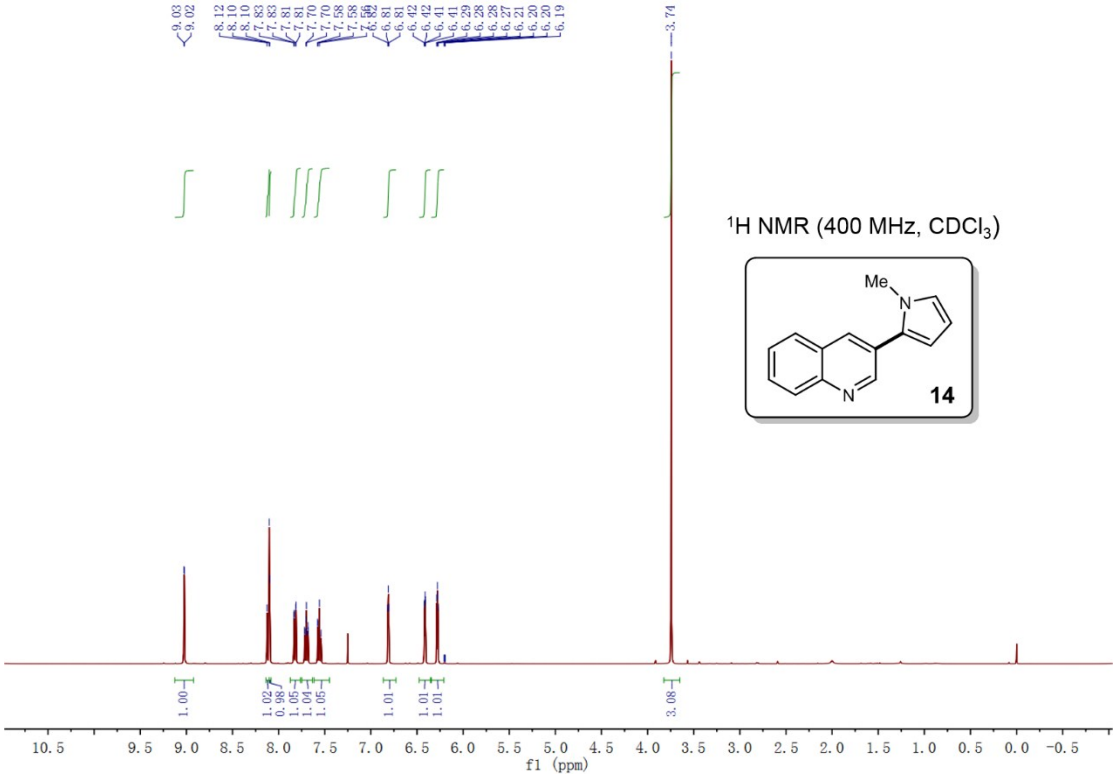


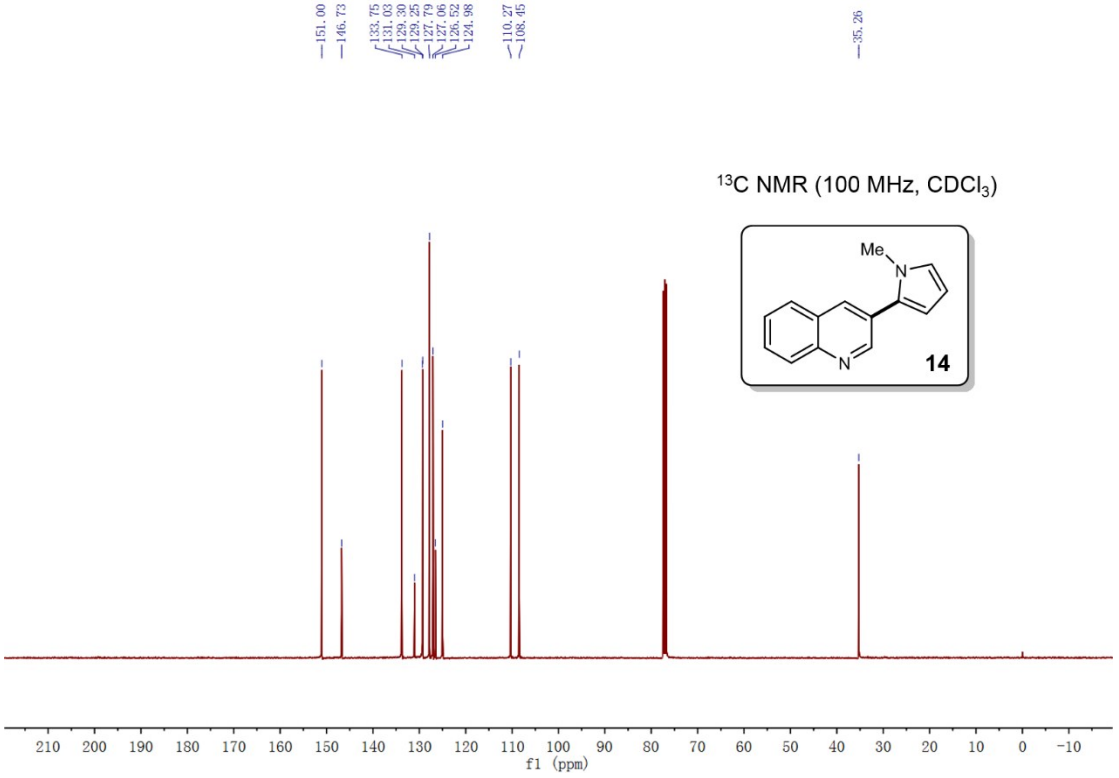


^{13}C NMR (100 MHz, DMSO-d_6)

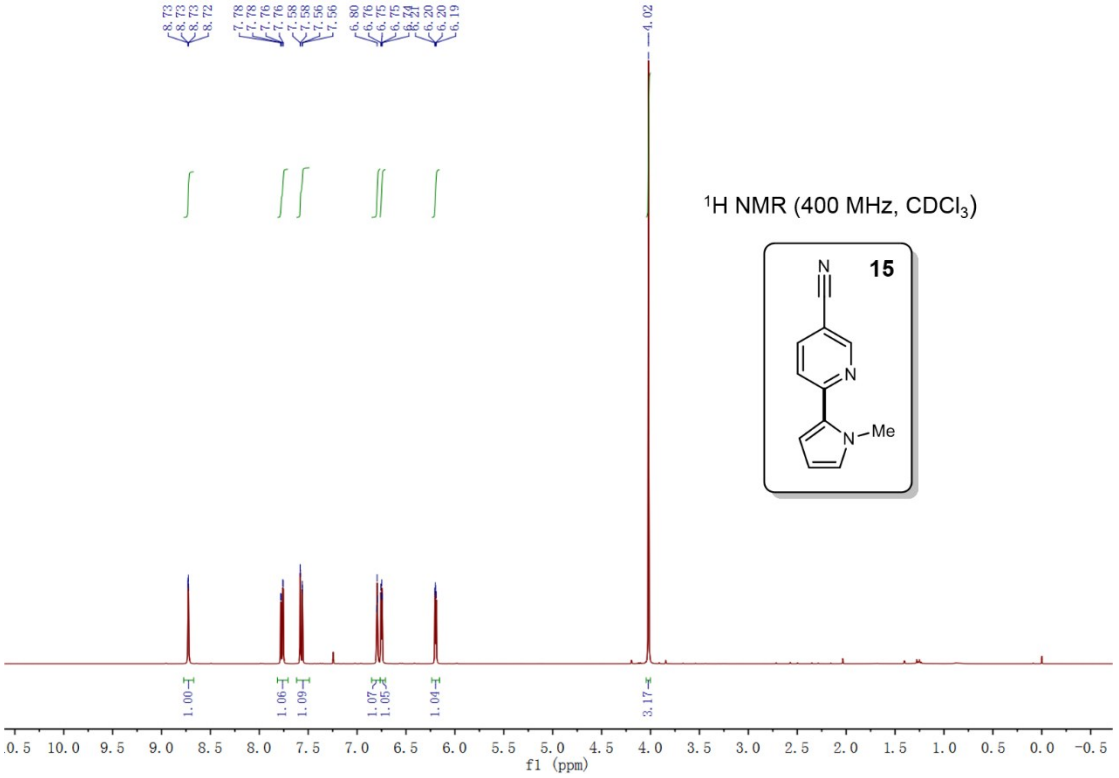


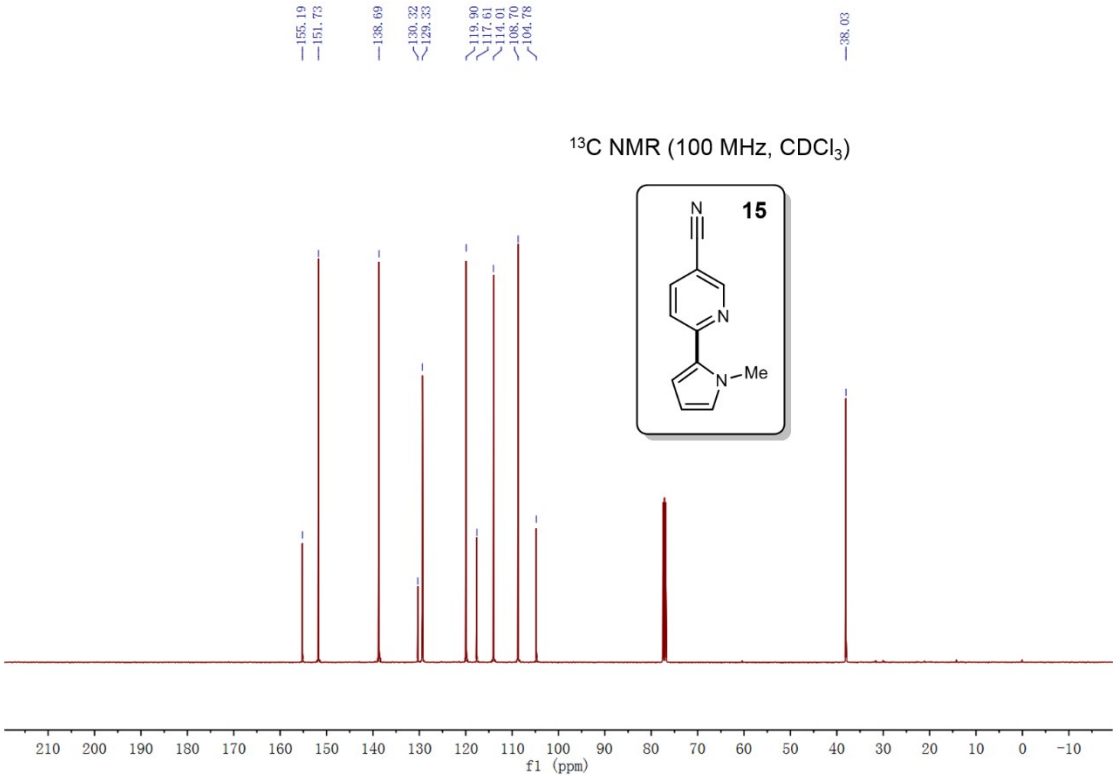
3-(1-Methyl-1*H*-pyrrol-2-yl)quinolone (14)



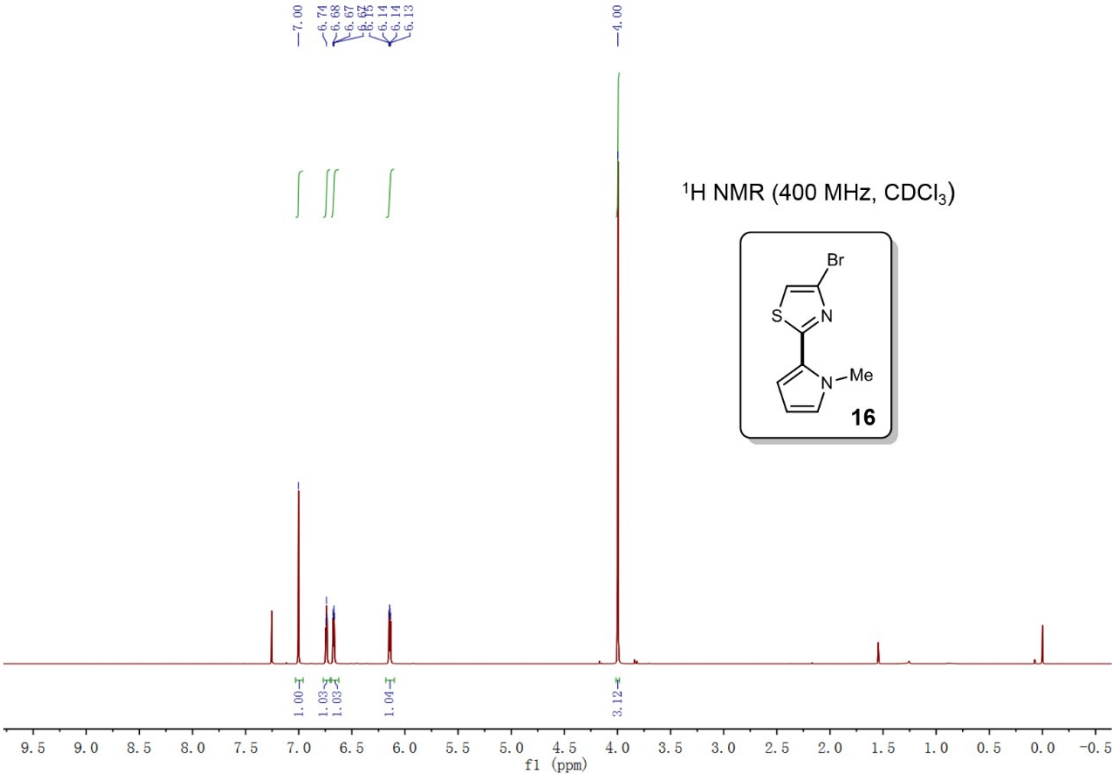


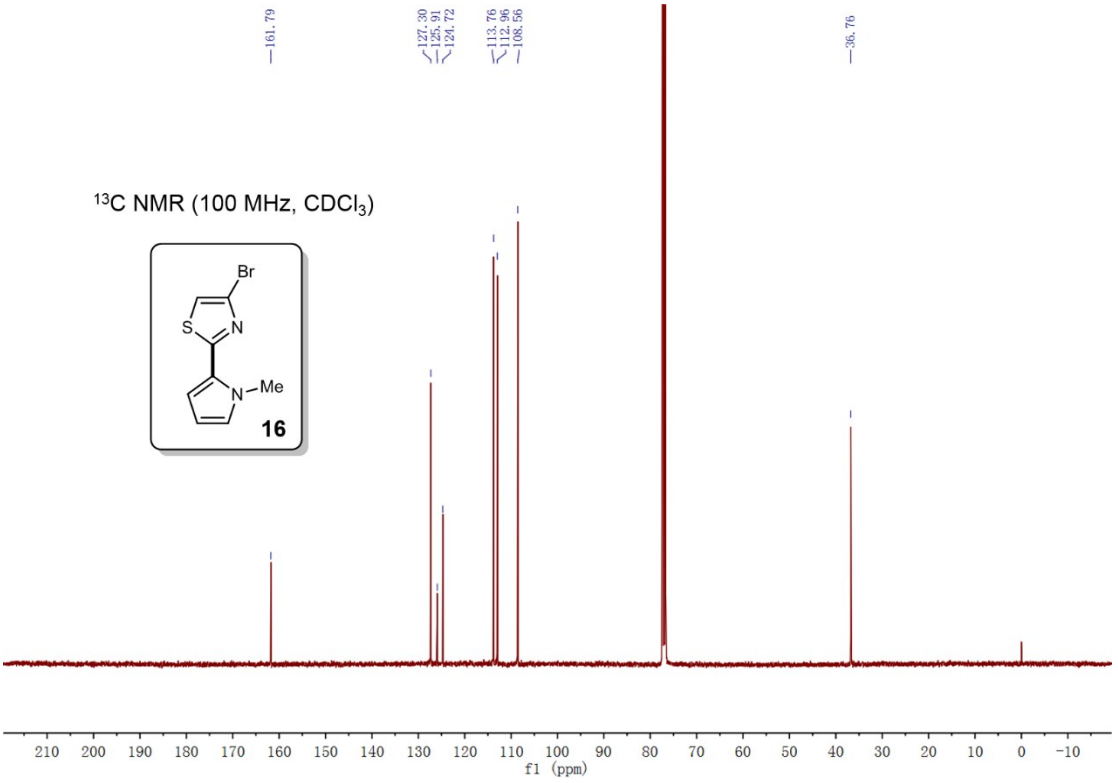
6-(1-Methyl-1*H*-pyrrol-2-yl)nicotinonitrile (15)



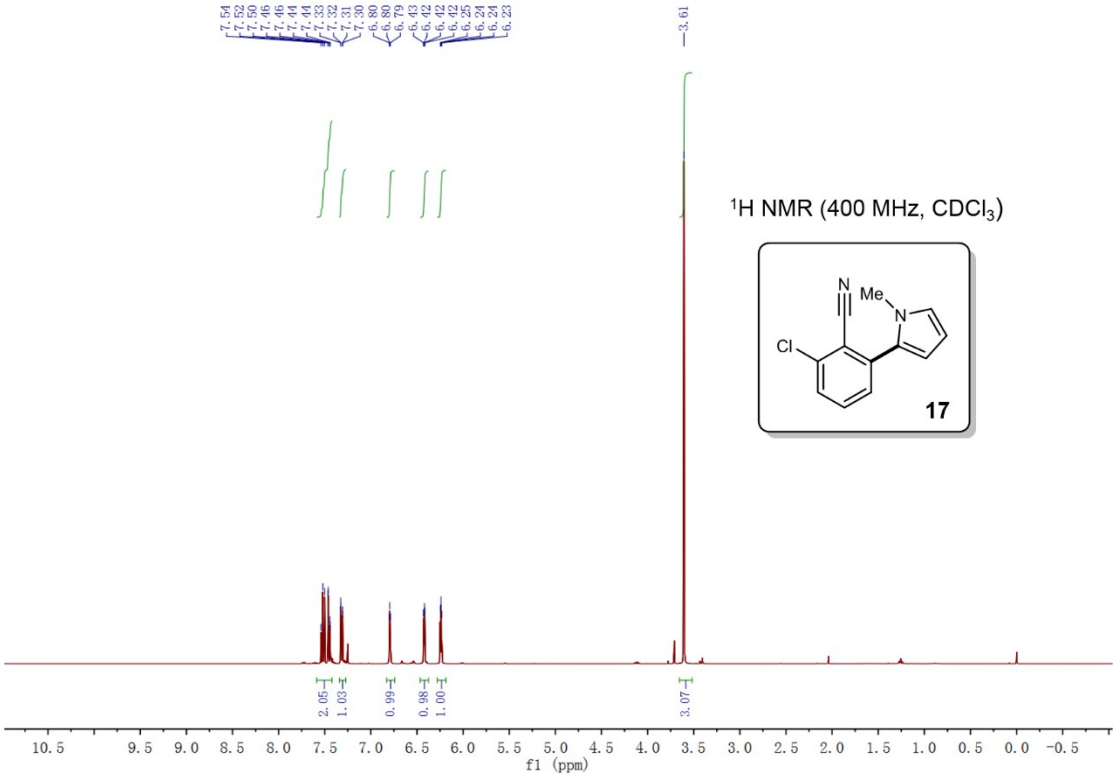


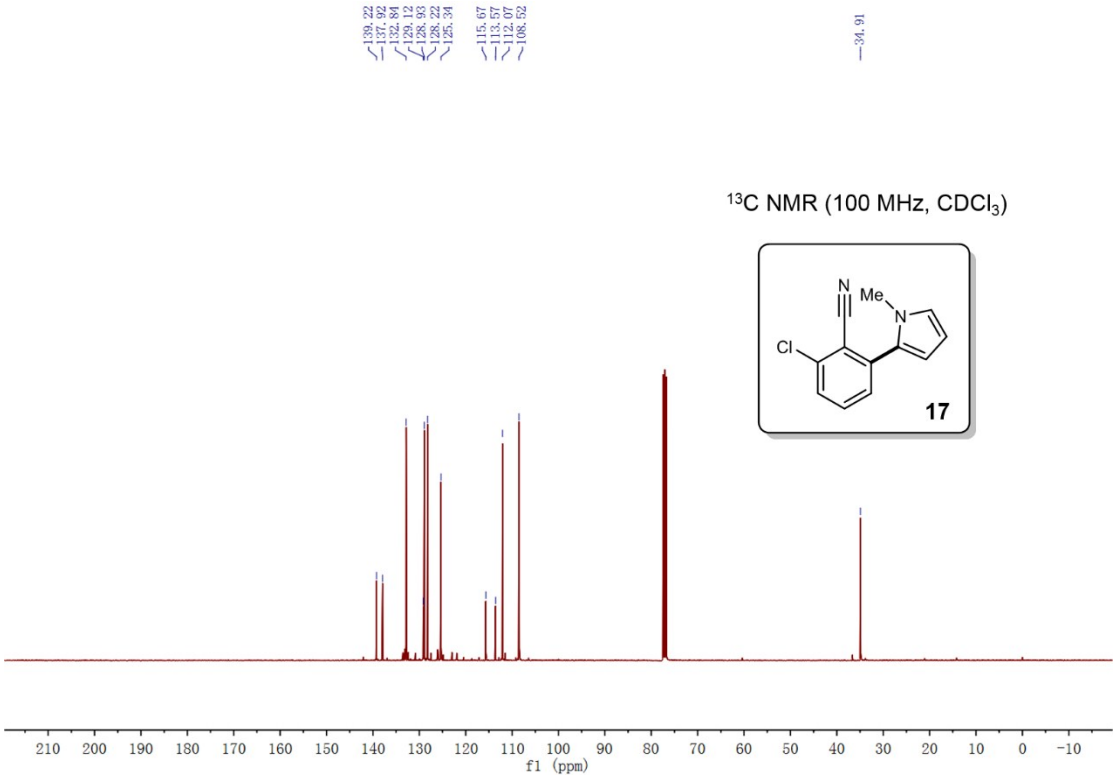
4-Bromo-2-(1-methyl-1*H*-pyrrol-2-yl)thiazole (16)



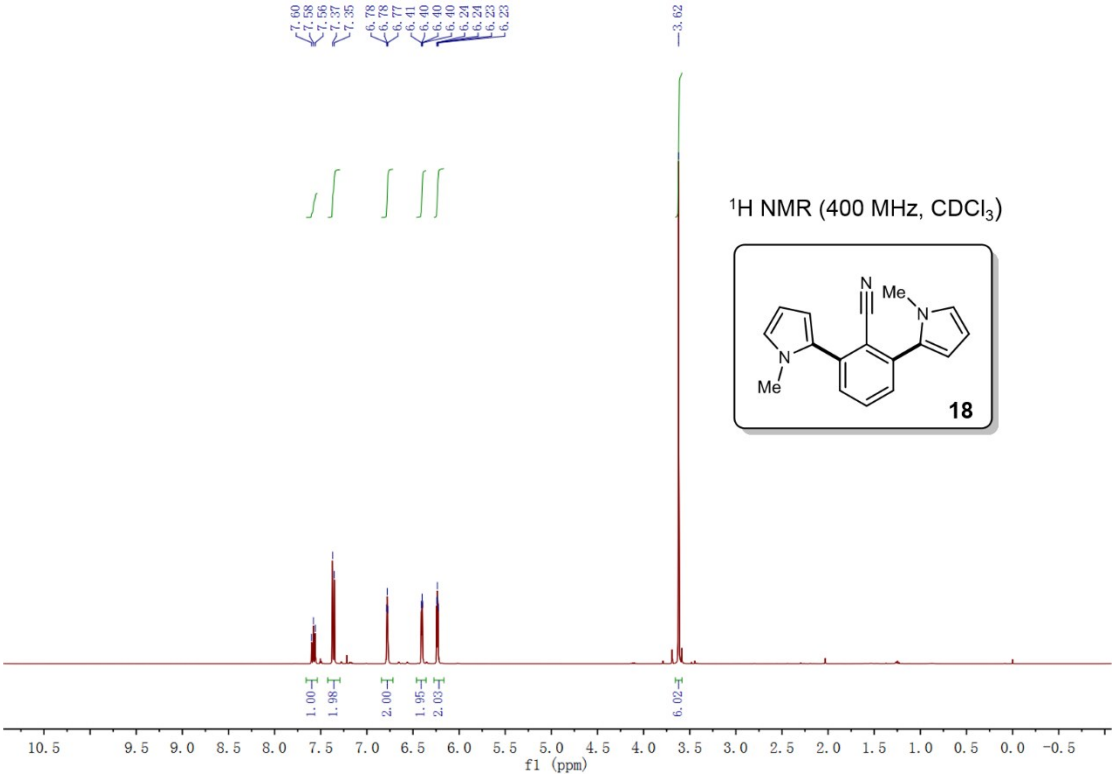


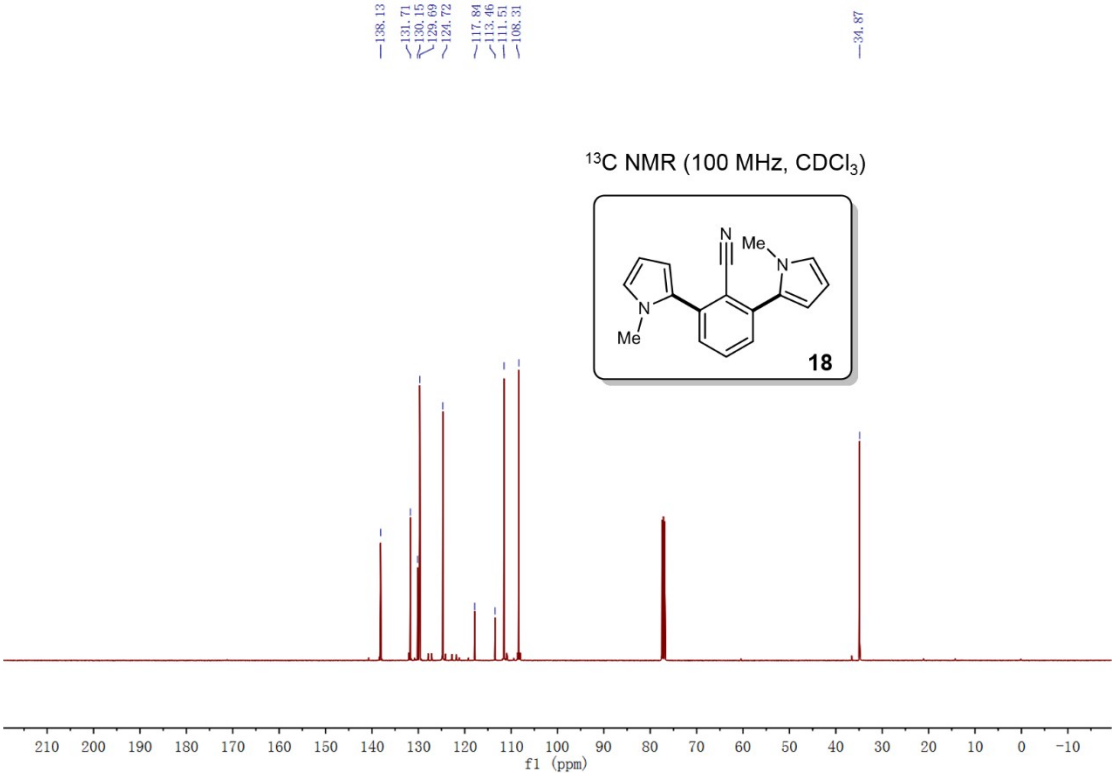
2-Chloro-6-(1-methyl-1*H*-pyrrol-2-yl)benzonitrile (17)



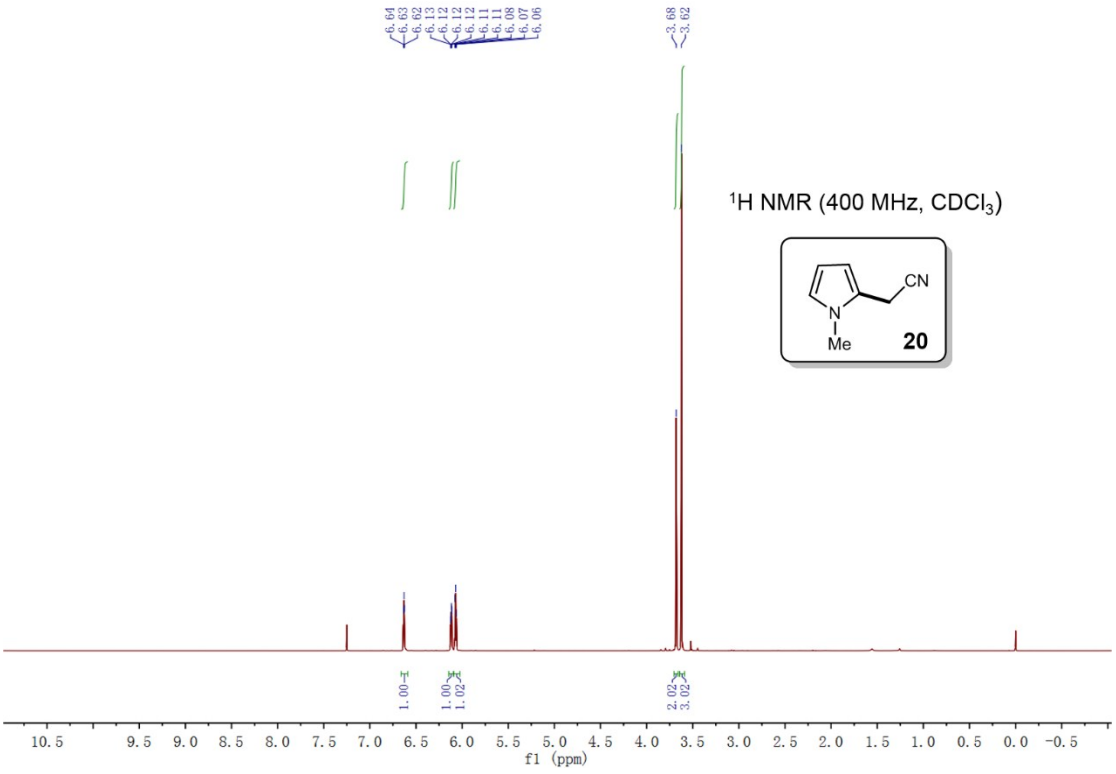


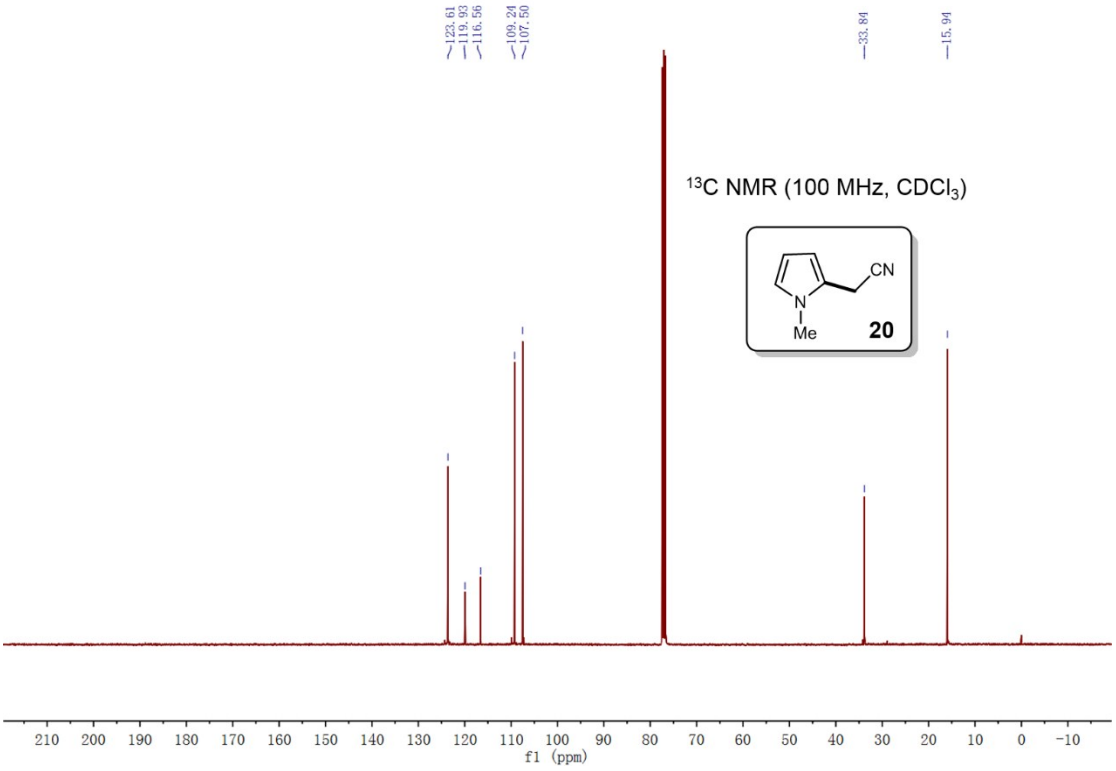
2,6-Bis(1-methyl-1*H*-pyrrol-2-yl)benzonitrile (18)





2-(1-Methyl-1*H*-pyrrol-2-yl)acetonitrile (20)





(8*S*,9*S*,10*R*,13*S*,14*S*,17*R*)-17-hydroxy-10,13-dimethyl-17-(2-(1-methyl-1*H*-pyrrol-2-yl)acetyl)-1,6,7,8,9,10,12,13,14,15,16,17-dodecahydro-3*H*cyclopenta[*a*]phenanthrene-3,11(2*H*)-dione (22)