A Case of Radical Chain Propagation: a-Aminoalkyl Radicals as Initiators for Aryl Radical Chemistry

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1 General Experimental Details

All required fine chemicals were used directly without purification unless stated otherwise. *N*-Methylpyrrole was distilled from KOH under reduced pressure, degassed by bubbling nitrogen and stored in the dark at 4°C. All air and moisture sensitive reactions were carried out under nitrogen atmosphere using standard Schlenk manifold technique. All solvents were bought from Acros as 99.8% purity. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were acquired at various field strengths as indicated and were referenced to $CHCl_3$ (7.27 and 77.0 ppm for ^{1}H and ^{13}C respectively). ^{1}H NMR coupling constants are reported in Hertz and refer to apparent multiplicities and not true coupling constants. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, qi = quintet, sx = sextet, sp = septet, m = multiplet, dd = doublet of doublets, etc.), proton assignment (determined by 2D NMR experiments: COSY, HSQC and HMBC) where possible. High-resolution mass spectra were obtained using a JEOL JMS-700 spectrometer or a Fissions VG Trio 2000 quadrupole mass spectrometer. Spectra were obtained using electron impact ionization (EI) and chemical ionization (CI) techniques, or positive electrospray (ES). Analytical TLC: aluminum backed plates pre-coated (0.25 mm) with Merck Silica Gel 60 F254. Compounds were visualized by exposure to UV-light or by dipping the plates in permanganate ($KMnO_4$) stain followed by heating. Flash column chromatography was performed using Merck Silica Gel 60 (40–63 μm). All mixed solvent eluents are reported as v/v solutions. Absorption and emission spectra were obtained using an Horiba Duetta spectrometer and 1 mm High Precision Cell made of quartz from Hellma Analytics. The LEDs used are Kessil PR 160 440 nm. All the reactions were conducted in CEM 10 mL glass microwave tubes.

2 Pictures of Reaction Set-Up

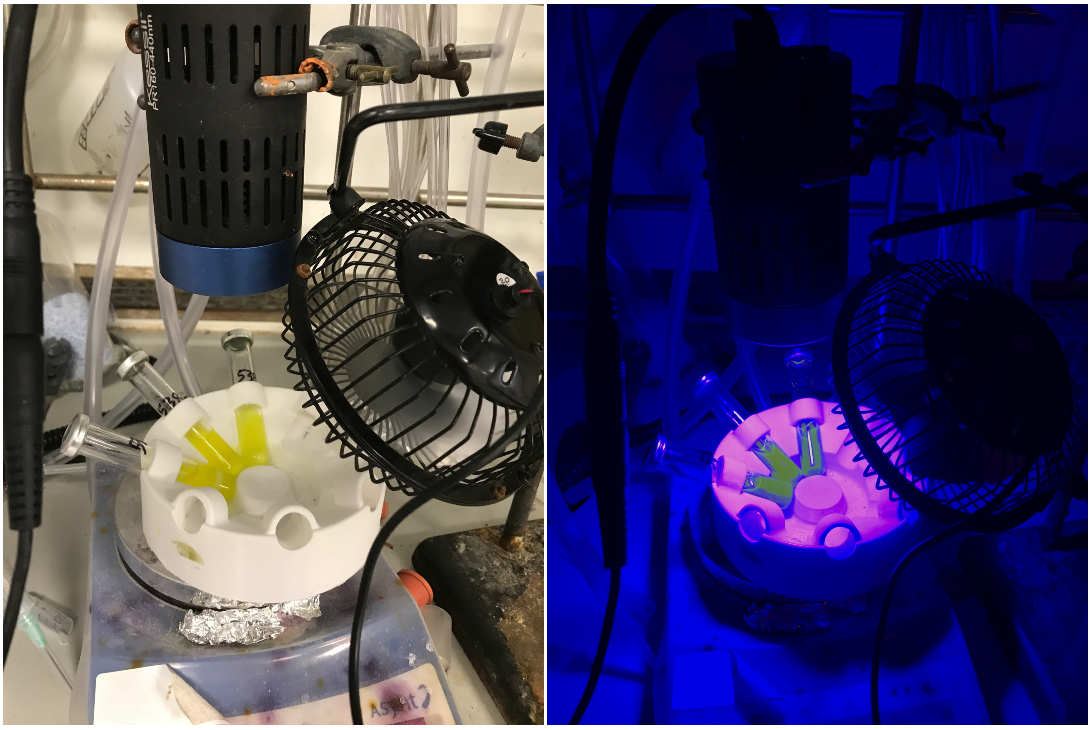
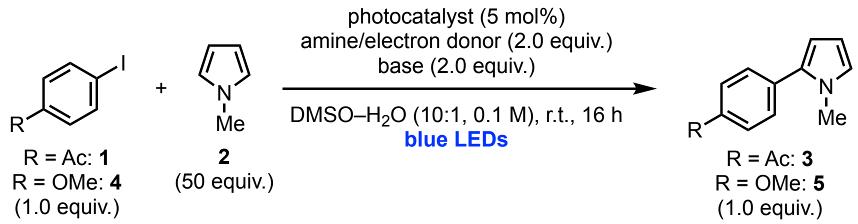


Figure S1.

3 Studies on the Arylation of *N*-Methylpyrrole with *p*-Acetyl-iodobenzene and *p*-Methoxy-iodobenzene

3.1 Screening of Reaction Parameters

General Procedure for the Arylation – GP1



A dry tube equipped with a stirring bar was charged with the aryl iodide (0.10 mmol, 1.0 equiv.), 4CzIPN (4 mg, 5 µmol, 5 mol%), the amine/electron donor (if solid) (0.20 mmol, 2.0 equiv.) and the base (if solid) (0.20 mmol, 2.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (x 3). Degassed DMSO–H_2O (10:1) (1.0 mL, 0.1 M), the amine/electron donor (if liquid) (0.20 mmol, 2.0 equiv.), the base (if liquid) (0.20 mmol, 2.0 equiv.) and **2** (440 µL, 5.0 mmol, 50.0 equiv.) were sequentially added. The blue LEDs were turned on and the mixture was stirred under irradiation for 16 h at room temperature. 1,3-dinitrobenzene (8.4 mg, 0.05 mmol, 0.5 equiv.) was added as the internal standard. Brine (5 mL) and EtOAc (5 mL) were added and the mixture was shaken vigorously. The layers were separated and the aqueous layer was extracted with EtOAc (10 mL x 2). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. The crude was solubilised in $CDCl_3$ (0.6 mL) and analysed by ^1H NMR spectroscopy to determine the ^1H NMR yield.

The results are detailed in Scheme 2D of the article.

3.2 Control Experiments

These experiments were performed according to GP1.

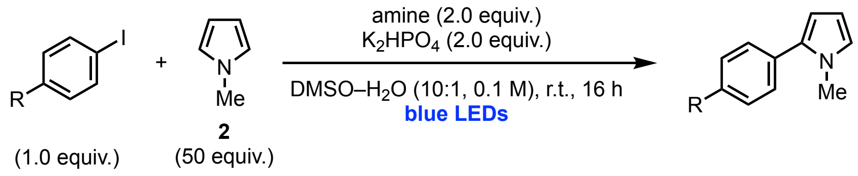
Table S1.

Entry	Variations	Base	Yield (%)
1	none	TMG	64
2	no light		–
3	no 4CzIPN		–
4	no *n*-Bu_3N		24
5	none	K_2HPO_4	58
6	no light		–
7	no 4CzIPN		–
8	no *n*-Bu_3N		–

Control experiments confirm that light and photocatalyst are crucial components of the reaction. However, in the absence of *n*-Bu_3N (entry 4), 24% of **5** was observed. We have rationalised this outcome on the basis that TMG can potentially generate α-aminoalkyl radicals and therefore initiate the reactivity. Indeed, when the base was changed for K_2HPO_4, no product was formed in the absence of *n*-Bu_3N (entry 8).

3.3 EDA Complex Formation

Electron poor arenes are known to form electron donor-acceptor (EDA) complexes with electron rich partners[1,2] which undergo SET upon irradiation at the charge-transfer λ_{max}. We therefore considered that, in the case of electron poor aryl iodides, the alkylamine could be involved in an additional productive reactivity pathway initiated by the formation and the following SET of an EDA complex.



These experiments were performed according to **GP1** but without the addition of 4CzIPN.

Table S2.

Entry	R	amine	Yield (%)
1	Ac	TMG	15
2		*n*-Bu_3N	73
3		*i*-Pr_2NH	56
4		Ph_2NPMP	83
5	CN	TMG	6
6		*n*-Bu_3N	6
7		*i*-Pr_2NH	27
8		Ph_2NPMP	81
9	H	TMG	–
10		*n*-Bu_3N	–
11		*i*-Pr_2NH	–
12		Ph_2NPMP	–
13	OMe	TMG	–
14		*n*-Bu_3N	–
15		*i*-Pr_2NH	–
16		Ph_2NPMP	–

In the cases of electron poor aryl iodides, *p*-acetyl-iodobenzene (entries 1–4) and *p*-cyano-iodobenzene (entries 5–8), product formation in the absence of 4CzIPN was observed, while electron neutral iodobenzene (entries 9–12) and electron rich *p*-methoxy-iodobenzene (entries 13–16) remain unreacted.

The successful reactivity in the presence of Ph_2NPMP, which cannot generate an α-aminoalkyl radical, supports the feasibility of an EDA-initiated process.

UV/Vis Absorption Spectroscopy Studies

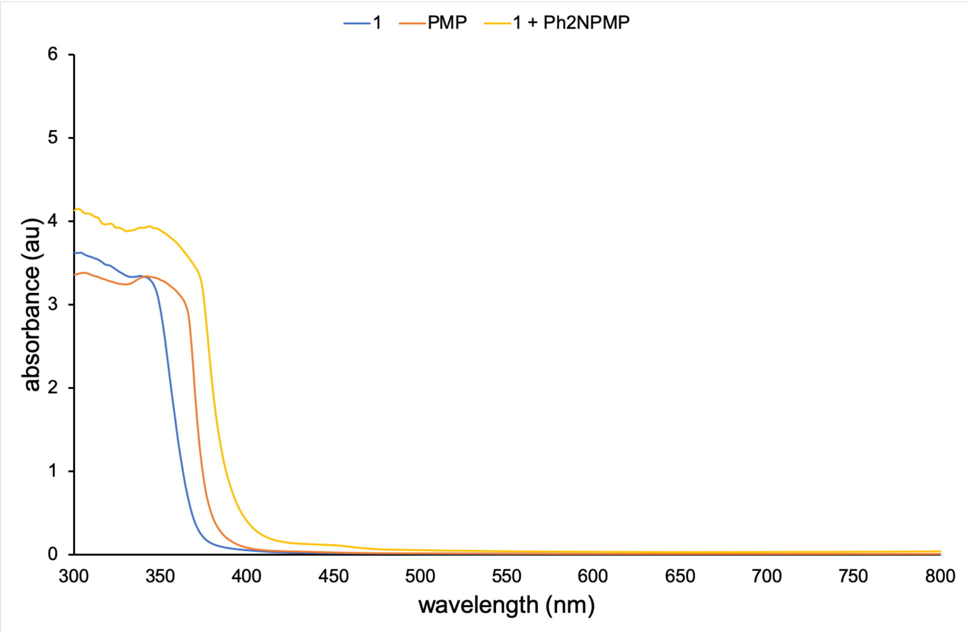
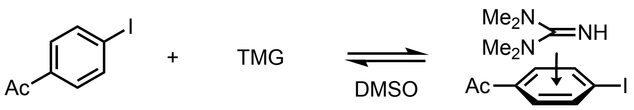


Figure S2.



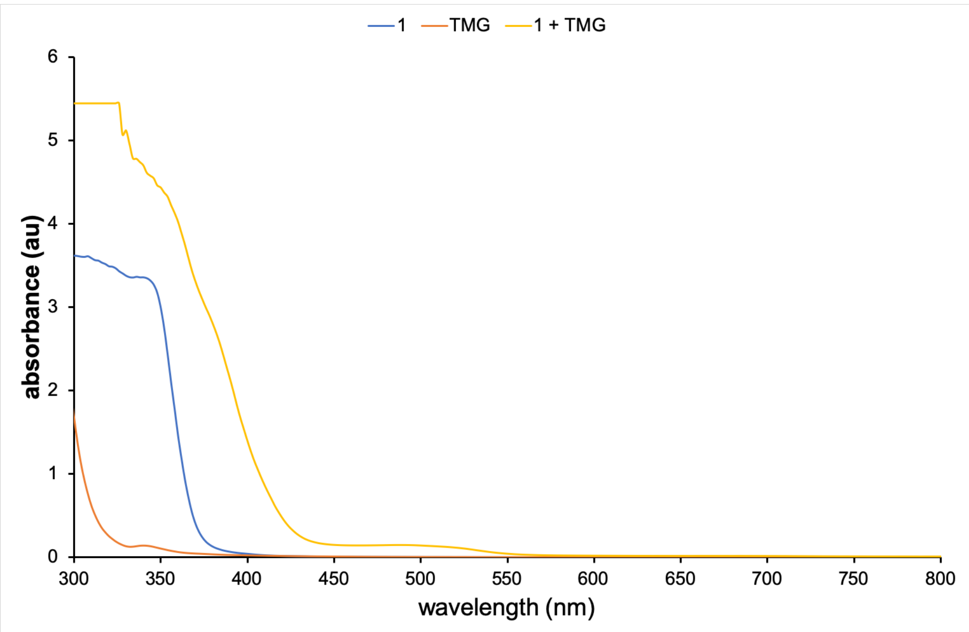


Figure S3.

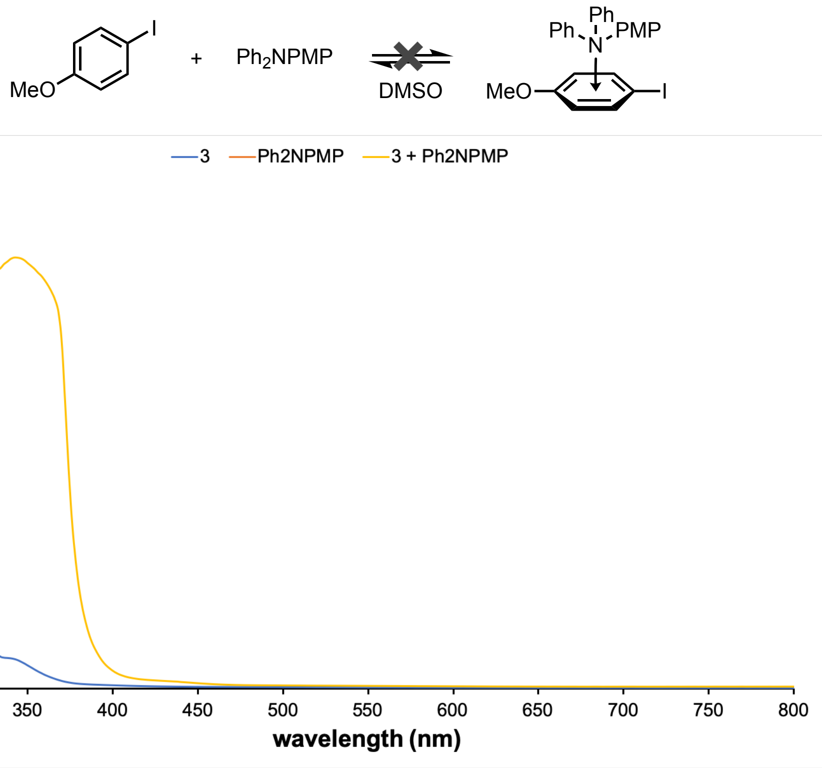
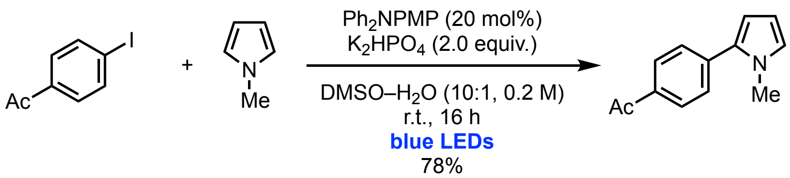


Figure S4.

EDA-Based Arylation of Pyrrole Using Catalytic Amine

In order to validate the ability of transient EDA complexes to initiate the radical reactivity we have identified conditions to enable the arylation of *N*-Me-pyrrole. In order to exclude the intermediacy of a purely photochemical EDA-based reactivity, the experiments were run with 20 mol% of Ph_2NPMP.



A dry tube equipped with a stirring bar was charged with **1** (25 mg, 0.10 mmol, 1.0 equiv.), Ph_2NPMP (5.5 mg, 0.02 mmol, 20 mol%) and K_2HPO_4 (35 mg, 0.2 mmol, 2.0 equiv.). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (x 3). Degassed DMSO–H_2O (10:1) (0.5 mL, 0.2 M) and **2** (0.45 mL, 5.0 mmol, 50.0 equiv.) were sequentially added. The blue LEDs were turned on and the mixture was stirred under irradiation for 16 h at room temperature. 1,3-Dinitrobenzene (8.4 mg, 0.05 mmol, 0.5 equiv.) was added as the internal standard. Brine (5 mL) and EtOAc (5 mL) were added and the mixture was shaken vigorously. The layers were separated and the aqueous layer was extracted with EtOAc (10 mL x 2). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. The crude was solubilised in $CDCl_3$ (0.6 mL) and analysed by ^1H NMR spectroscopy to determine the ^1H NMR yield.

3.4 Emission Quenching (Stern-Volmer) Studies

Stern-Volmer experiments were carried out monitoring the emission intensity of argon-degassed solutions of 4CzIPN (2 x 10^{-5} M) containing variable amounts of the quencher in dry DMSO. The k_q are reported in Scheme 2D of the article.

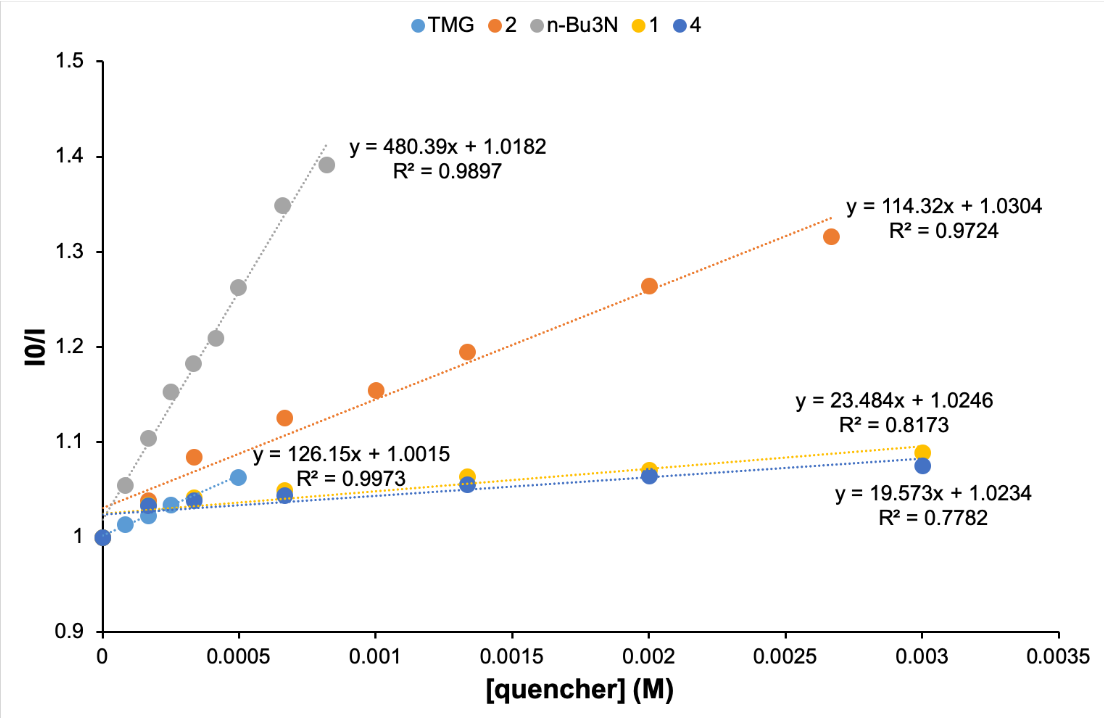
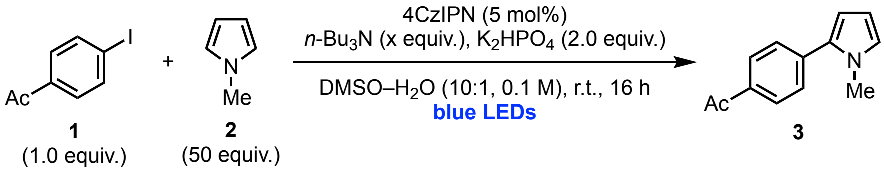


Figure S5.

3.5 Experiments with Sub-stoichiometric Amounts of *n*-Bu_3N

To gain insights on the α-aminoalkyl radical-initiated radical-chain process, we run reactions with sub-stoichiometric amounts of *n*-Bu_3N. The reactions were run using K_2HPO_4 in place of TMG as the base to avoid the presence of the EDA reactivity (see section 3.3).



These experiments were performed according to **GP1**.

Table S3.

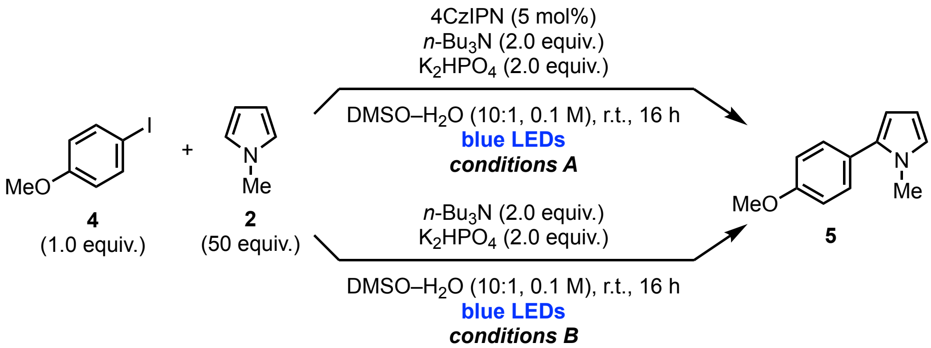
Entry	*n*–Bu_3N (equiv.)	Yield (%)
1	2.0	60
2	0.2	65
3	0.05	43
4	–	–

In theory, every molecule of *n*-Bu_3N could lead to the XAT-activation of up to 3 molecules of aryl iodide, which give a maximum yield of 15%. The good reaction performance in the presence of 5 mol% *n*-Bu_3N (entry 3) supports the presence of a radical-chain process initiated by the α-aminoalkyl radicals.

3.6 Evaluating the Presence of Photoactive Poly-pyrroles

Recently, Zheng and co-workers[3] reported the activation of aryl halides via photoinduced disproportionation of pyrroles. They described that commercial samples of *N*-methylpyrrole contain visible light-absorbing oligomers that, upon irradiation, are responsible for the formation of highly reducing [*N*-methylpyrrole]$^{\bullet-}$, which can reduce aryl halides. This means that under blue light irradiation C–H arylation can occur in the absence of an external photocatalyst.

To exclude this pathway under our reaction conditions we have run all reactions with distilled *N*-methylpyrrole. Furthermore, we have performed two reactions in parallel with and without photocatalyst and monitored them every h for a total of 4 hours. *p*-Methoxy-iodobenze **4** and K_2HPO_4 were used to exclude the intermediacy of the EDA initiated radical-chain propagation in the photocatalyst-free reaction.



These experiments were performed according to **GP1**.

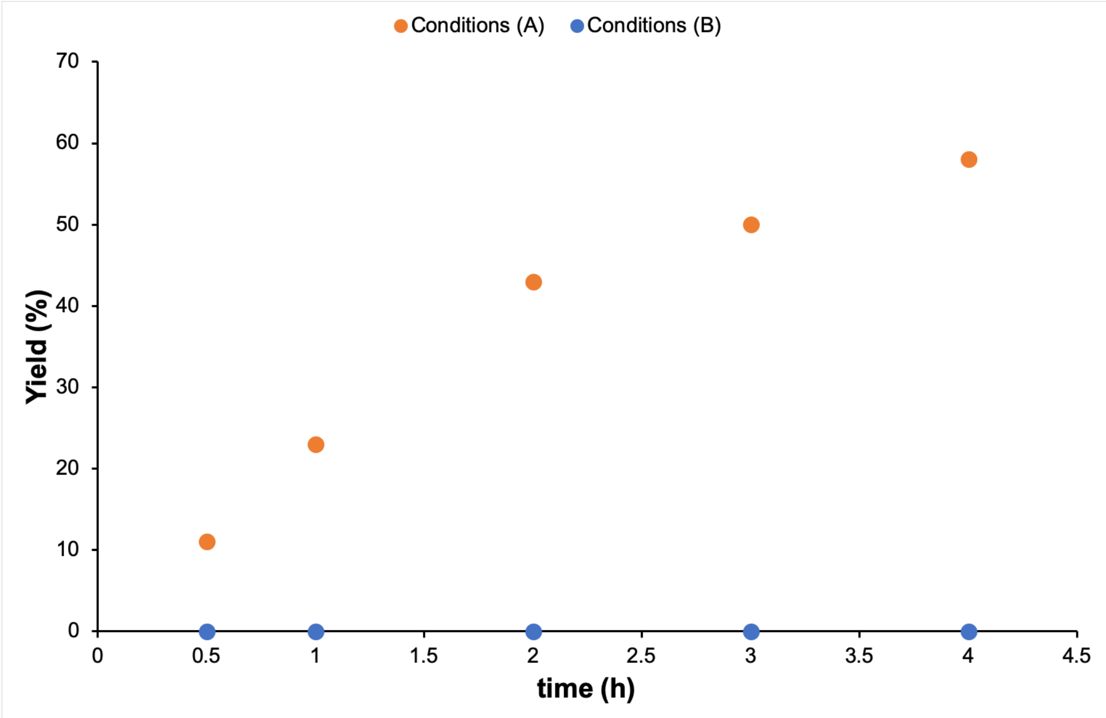
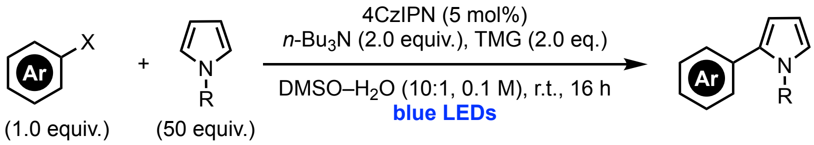


Figure S6.

No product formation was observed in the absence of 4CzIPN which rules out the presence of a poly-pyrrole-based photochemical reactivity under our conditions.

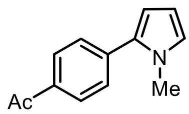
4 Substrate Scope for the Radical C–H Arylation

General Procedure for Radical C–H Arylation – GP2



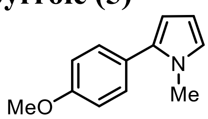
A dry tube equipped with a stirring bar was charged with the aryl halide (0.10 mmol, 1.0 equiv.) and 4CzIPN (4 mg, 5 µmol, 5 mol%). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (x 3). Degassed DMSO–H_2O (10:1) (1.0 mL, 0.1 M), *n*-Bu_3N (48 µL, 0.2 mmol, 2.0 equiv.), 1,1,3,3-tetramethylguanidine (25 µL, 0.2 mmol, 2.0 equiv.) and the pyrrole (5.0 mmol, 50.0 equiv.) were sequentially added. The blue LEDs were turned on and the mixture was stirred under irradiation for 16 h at room temperature. Brine (5 mL) and EtOAc (5 mL) were added and the mixture was shaken vigorously. The layers were separated and the aqueous layer was extracted with EtOAc (10 mL x 2). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. Purification by flash column chromatography on silica gel gave the products.

1-(4-(1-Methyl-1H-pyrrol-2-yl)phenyl)ethan-1-one (3)



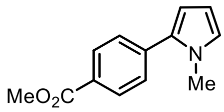
Following **GP2**, 4-iodoacetophenone (25 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **3** (15 mg, 73%) as a solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09–7.88 (2H, m), 7.61–7.42 (2H, m), 6.85–6.71 (1H, m), 6.36 (1H, dd, J = 3.7, 1.8 Hz), 6.24 (1H, dd, J = 3.6, 2.7 Hz), 3.73 (3H, s), 2.63 (3H, s). Data in accordance with the literature.[4]

1-Methyl-2-(4-nitrophenyl)-1H-pyrrole (5)



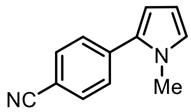
Following **GP2**, 4-iodoanisole (24 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **5** (11 mg, 58%) as a solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (2H, d, J = 8.8 Hz), 6.93 (2H, d, J = 8.8 Hz), 6.68 (1H, m), 6.20–6.12 (1H, m), 3.83 (3H, s), 3.62 (s, 3H). Data in accordance with the literature.[5]

Methyl 4-(1-methyl-1H-pyrrol-2-yl)benzoate (7)



Following **GP2**, methyl 4-iodobenzoate (26 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **7** (9 mg, 42%) as a solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (2H, d, J = 8.0 Hz), 7.48 (2H, d, J = 8.0 Hz), 6.76 (1H, s), 6.35–6.33 (1H, m), 6.23–6.22 (1H, m), 3.93 (3H, s), 3.71 (3H, s). Data in accordance with the literature.[6]

4-(1-Methyl-1H-pyrrol-2-yl)benzonitrile (8)

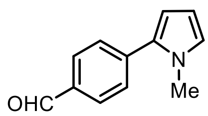


Following **GP2**, 4-iodobenzonitrile (23 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **8** (13 mg, 71%) as a solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (2H, d, J = 8.2 Hz), 7.53 (2H, d, J = 8.2 Hz), 6.81 (1H, s), 6.41–6.34 (1H, m), 6.26 (1H, t, J = 3.1 Hz), 3.74 (3H, s). Data in accordance with the literature.[7]

Following **GP2**, 4-bromobenzonitrile (18.2 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **8** (10 mg, 54%) as a solid.

Following **GP2**, 4-chlorobenzonitrile (13.7 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **8** (6 mg, 33%) as a solid.

4-(1-Methyl-1H-pyrrol-2-yl)benzaldehyde (9)

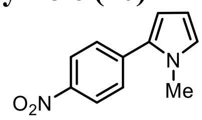


Following **GP2**, 4-iodobenzaldehyde (23 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **9** (13 mg, 67%) as a solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.01 (1H, s), 7.94–7.85 (2H, m), 7.62–7.53 (2H, m), 6.83–6.76 (1H, m), 6.40 (1H, dd, J = 3.7, 1.8 Hz), 6.25 (1H, dd, J = 3.7, 2.7 Hz), 3.74 (3H, s). Data in accordance with the literature.[8]

Following **GP2**, 4-bromobenzaldehyde (18 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **9** (8 mg, 42%) as a solid.

Following **GP2**, 4-chlorobenzaldehyde (14 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **9** (8 mg, 42%) as a solid.

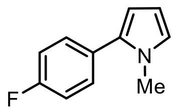
1-Methyl-2-(4-nitrophenyl)-1H-pyrrole (10)



Following **GP2**, 1-iodo-4-nitrobenzene (25 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **10** (15 mg, 70%) as a solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (2H, d, *J* = 8.6 Hz), 7.55 (2H, d, *J* = 8.6 Hz), 6.82 (1H, m), 6.42 (1H, dd, *J* = 3.4, 1.7 Hz), 6.25 (1H, t, *J* = 3.4 Hz), 3.75 (3H, s). Data in accordance with the literature.[9]

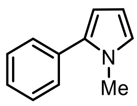
Following **GP2**, 1-bromo-4-nitrobenzene (20 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **10** (3 mg, 14%) as a solid.

2-(4-Fluorophenyl)-1-methyl-1H-pyrrole (11)



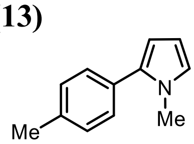
Following **GP2**, 4-fluoroiodobenzene (12 µL, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **11** (10 mg, 54%) as a solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (2H, dd, *J* = 8.8, 5.4 Hz), 7.11 (2H, dd, *J* = 8.7, 8.7 Hz), 6.73 (1H, t, *J* = 4.5 Hz), 6.20–6.17 (m, 2H), 3.62 (3H, s). Data in accordance with the literature.[5]

1-Methyl-2-phenyl-1H-pyrrole (12)



Following **GP2**, iodobenzene (11 µL, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **12** (9 mg, 55%) as a solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42–7.3 (4H, m), 7.32–7.26 (1H, m), 6.73 (1H, t, *J* = 4.5 Hz), 6.24 (1H, dd, *J* = 3.6, 1.8 Hz), 6.18 (1H, dd, *J* = 3.6, 2.7 Hz), 3.03 (3 H, s). Data in accordance with the literature.[5]

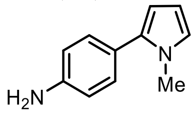
1-Methyl-2-(*p*-tolyl)-1H-pyrrole (13)



Following **GP2**, 4-iodotoluene (22 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **13** (9 mg, 48%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32

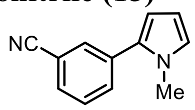
(2H, d, J = 8.0 Hz), 7.23 (2H, d, J = 8.0 Hz), 6.72 (1H, t, J = 2.0 Hz), 6.21 (2H, d, J = 2.4 Hz), 3.67 (3H, s), 2.40 (3H, s). Data in accordance with the literature.[6]

4-(1-Methylpyrrol-2-yl)phenylamine (14)



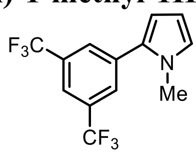
Following **GP2**, 4-iodoaniline (22 mg, 0.10 mmol) and *N*-Me-pyrrole (444 μL, 5.0 mmol, 50.0 equiv.) gave **14** (11 mg, 63%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (2H, d, J = 8.1 Hz), 6.73 (, 2Hd, J = 8.1 Hz), 6.69 (1H, m), 6.19 (1H, m), 6.14 (1H, m), 3.75 (2H, br s), 3.63 (3H, s). Data in accordance with the literature.[10]

3-(1-Methyl-1H-pyrrol-2-yl)benzonitrile (15)



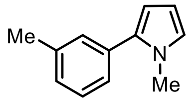
Following **GP2**, 3-iodobenzonitrile (23 mg, 0.10 mmol) and *N*-Me-pyrrole (444 μL, 5.0 mmol, 50.0 equiv.) gave **15** (14 mg, 77%) as a solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (1H, td, J = 1.7, 0.6 Hz), 7.62 (1H, ddd, J = 7.8, 1.8, 1.3 Hz), 7.56 (1H, dt, J = 7.7, 1.3 Hz), 7.50 (1H, td, J = 7.8, 0.6 Hz), 6.76 (1H, dd, J = 2.5, 1.9 Hz), 6.28 (1H, dd, J = 3.6,1.7 Hz), 6.22 (1H, J = 3.6, 2.7 Hz), 3.68 (3H, s). Data in accordance with the literature.[11]

2-(3,5-Bis(trifluoromethyl)phenyl)-1-methyl-1H-pyrrole (16)



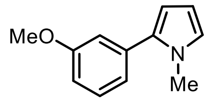
Following **GP2**, 1-iodo-3,5-bis(trifluoromethyl)benzene (18 μL, 0.10 mmol) and *N*-Me-pyrrole (444 μL, 5.0 mmol, 50.0 equiv.) gave **16** (20 mg, 67%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (2H, s), 7.81 (1H, s), 6.82 (1H, dd, J = 2.4, 2.0 Hz), 6.39 (1H, dd, J = 3.7, 1.8 Hz), 6.27 (1H, dd, J = 3.7, 2.7 Hz), 3.73 (3H, s). Data in accordance with the literature.[8]

1-Methyl-2-(*m*-tolyl)-1H-pyrrole (17)



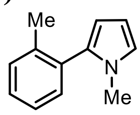
Following **GP2**, 3-iodotoluene (14 µL, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **17** (9 mg, 48%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.29 (1H, m), 7.25–7.22 (2H, m), 7.14 (1H, d, *J* = 8.0 Hz), 6.73 (1H, t, *J* = 2.0 Hz), 6.24–6.21 (2H, m), 3.68 (3H, s), 2.41 (3H, s). Data in accordance with the literature.[6]

2-(3-Methoxyphenyl)-1-methyl-1H-pyrrole (18)



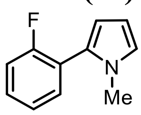
Following **GP2**, 3-iodoanisole (12 µL, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **18** (9 mg, 49%) as an oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (1H, m), 6.98 (1H, ddd, *J* = 7.6, 1.6, 1.0 Hz), 6.94 (1H, dd, *J* = 2.5, 1.5 Hz), 6.84 (1H, ddd, *J* = 8.3, 2.6, 1.0 Hz), 6.70 (1H, t, *J* = 4.5 Hz), 6.22 (1H, d, *J* = 3.6 Hz), 6.19 (1H, d, *J* = 3.4 Hz), 3.83 (3H, s), 3.66 (3H, s). Data in accordance with the literature.[5]

1-Methyl-2-(*o*-tolyl)-1H-pyrrole (19)



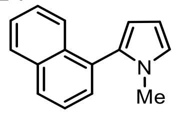
Following **GP2**, 2-iodotoluene (13 µL, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **19** (15 mg, 38%) as an oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.31–7.18 (4H, m), 6.80 (1H, s), 6.06 (s, 1H), 5.95 (s, 1H), 3.35 (s, 3H), 2.13 (s, 3H). Data in accordance with the literature.[12]

2-(2-Fluorophenyl)-1-methyl-1H-pyrrole (20)



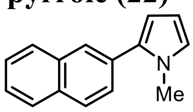
Following **GP2**, 2-fluoroiodobenzene (12 µL, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **20** (14 mg, 80%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.32 (2H, m), 7.19–7.12 (2H, m), 6.78 (1H, t, *J* = 2.0 Hz), 6.25 (2H, d, *J* = 2.0 Hz), 3.58 (3H, s). Data in accordance with the literature.[6]

1-Methyl-2-(naphthalen-1-yl)-1H-pyrrole (21)



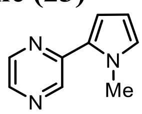
Following **GP2**, 1-iodonaphtalene (15 μL, 0.10 mmol) and *N*-Me-pyrrole (444 μL, 5.0 mmol, 50.0 equiv.) gave **21** (9 mg, 40%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.85 (2H, m), 7.76–7.70 (1H, m), 7.55–7.42 (4H, m), 6.86–6.80 (1H, m), 6.34–6.30 (1H, m), 6.27 (1H, dd, J = 3.5, 1.8 Hz), 3.40 (3H, s). Data in accordance with the literature.[13]

1-Methyl-2-(naphthalen-2-yl)-1H-pyrrole (22)



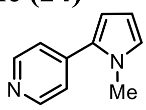
Following **GP2**, 2-iodonaphtalene (25 mg, 0.10 mmol) and *N*-Me-pyrrole (444 μL, 5.0 mmol, 50.0 equiv.) gave **22** (12 mg, 57%) as a solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.00 (4H, m), 7.77 (1H, d, J = 7.8 Hz), 7.71–7.62 (2H, m), 6.94 (1H, m), 6.61 (1H, m), 6.50 (1H, m), 3.86 (3H, s). Data in accordance with the literature.[14]

2-(1-Methyl-1H-pyrrol-2-yl)pyrazine (23)



Following **GP2**, iodopyrazine (9.9 μL, 0.10 mmol) and *N*-Me-pyrrole (444 μL, 5.0 mmol, 50.0 equiv.) gave **23** (10 mg, 65%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (1H, br s), 8.45 (1H, br s), 8.29 (1H, br), 6.80 (1H, m), 6.72 (1H, d, J = 4.3 Hz), 6.22 (1H, t, J = 3.6 Hz), 4.00 (3H, s). Data in accordance with the literature.[15]

4-(1-Methyl-1H-pyrrol-2-yl)pyridine (24)

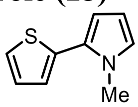


Following **GP2**, 4-iodopyridine (20.5 mg, 0.10 mmol) and *N*-Me-pyrrole (444 μL, 5.0 mmol, 50.0 equiv.) gave **24** (12 mg, 73%) as an oil. ^{1}H NMR (200 MHz, CDCl3) δ 8.56 (2H, d, J = 4.7 Hz), 7.39 (2H, d, J = 4.7 Hz, 2H), 6.78 (1H, dd, J = 3.2, 1.7 Hz), 6.43 (1H, dd, J =3.6, 1.7 Hz), 6.22 (1H, dd, J = 3.6, 3.2 Hz), 3.75 (3H, s). Data in accordance with the literature.[16]

Following **GP2** but with 3.0 equiv. of TMG (38 μL, 0.30 mmol), 4-bromopyridine hydrochloride (19 mg, 0.10 mmol) and *N*-Me-pyrrole (444 μL, 5.0 mmol, 50.0 equiv.) gave **24** (6 mg, 37%) as an oil.

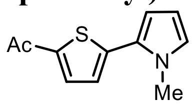
Following **GP2** but with 3 equiv. of TMG (38 μL, 0.30 mmol), 4-chloropyridine hydrochloride (15 mg, 0.10 mmol) and *N*-Me-pyrrole (444 μL, 5.0 mmol, 50.0 equiv.) gave **24** (4 mg, 24%) as an oil.

1-Methyl-2-(thiophen-2-yl)-1H-pyrrole (25)



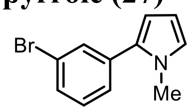
Following **GP2**, 2-iodothiophene (11 μL, 0.10 mmol) and *N*-Me-pyrrole (444 μL, 5.0 mmol, 50.0 equiv.) gave **25** (11 mg, 67%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (2H, d, J = 8.4 Hz), 7.28 (2H, d, J = 8.4 Hz), 6.74 (1H, t, J = 2.4 Hz), 6.25–6.21(1H, m), 6.21–6.20 (1H, m), 3.66 (3H, s). Data in accordance with the literature.[6]

1-(5-(1-Methyl-1H-pyrrol-2-yl)thiophen-2-yl)ethan-1-one (26)



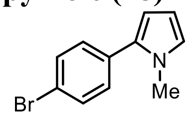
Following **GP2**, 2-acetyl-5-iodothiophene (25 mg, 0.10 mmol) and *N*-Me-pyrrole (444 μL, 5.0 mmol, 50.0 equiv.) gave **26** (14 mg, 64%) as a solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, d, J = 4.0 Hz), 7.06 (1H, d, J = 4.0 Hz), 6.77–6.72 (1H, m), 6.51 (1H, dd, J = 3.8, 1.8 Hz), 6.18 (1H, dd, J = 3.8, 2.7 Hz, 1H), 3.81 (3H, s), 2.55 (3H, s). Data in accordance with the literature.[13]

2-(3-Bromophenyl)-1-methyl-1H-pyrrole (27)



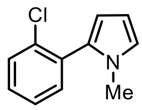
Following **GP2**, 3-bromoiodobenzene (13 μL, 0.10 mmol) and *N*-Me-pyrrole (444 μL, 5.0 mmol, 50.0 equiv.) gave **27** (18 mg, 75%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (1H, d, J = 1.6 Hz), 7.42 (1H, d, J = 1.6 Hz), 7.40–7.31(1H, m), 7.24–7.22 (1H, m), 6.71 (1H, t, J = 2.0 Hz), 6.24–6.18 (2H, m), 3.65 (3H, s). Data in accordance with the literature.[6]

2-(4-Bromophenyl)-1-methyl-1H-pyrrole (28)



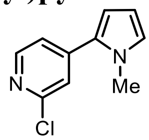
Following **GP2**, 4-bromoiodobenzene (28 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **28** (16 mg, 65%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (2H, d, *J* = 8.4 Hz), 7.28 (2H, d, *J* = 8.4 Hz), 6.74 (1H, t, *J* = 2.4 Hz), 6.25–6.21(1H, m), 6.21–6.20 (1H, m), 3.66 (3H, s). Data in accordance with the literature.[6]

2-(2-Chlorophenyl)-1-methyl-1H-pyrrole (29)



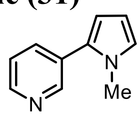
Following **GP2**, 1-chloro-2-iodobenzene (12 µL, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **29** (9 mg, 70%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.46 (1H, m), 7.37–7.30 (3H, m), 6.75 (1H, m), 6.25-6.17 (2H, m), 3.49 (3H, s). Data in accordance with the literature. [6]

2-Chloro-4-(1-methyl-1H-pyrrol-2-yl)pyridine (30)



Following **GP2**, 4-bromo-2-chloropyridine (11 µL, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **30** (9 mg, 44%) as a solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (1H, d, *J* = 5.1 Hz), 7.26 (1H, s), 7.18 (1H, d, *J* = 5.1 Hz), 6.72 (1H, s), 6.38 (1H, s), 6.15 (1H, s), 3.68 (3H, s). Data in accordance with the literature.[17]

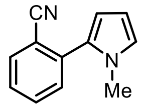
3-(1-Methyl-1H-pyrrol-2-yl)pyridine (31)



Following **GP2**, 3-bromopyridine (9.7 µL, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **31** (6 mg, 38%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (1H, d, *J* = 1.8 Hz), 8.53 (1H, dd, *J* = 4.8, 1.5 Hz), 7.74–7.66 (1H, m), 7.36–7.28 (1H, m), 6.81–6.72 (1H, m), 6.30 (1H, dd, *J* = 3.6, 1.8 Hz), 6.25-6.18 (1H, m), 3.68 (3H, s). Data in accordance with the literature.[13]

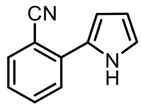
Following **GP2**, 3-chloropyridine (9.6 µL, 0.10 mmol) gave **31** (3 mg, 15%) as an oil.

2-(1-Methyl-1H-pyrrol-2-yl)benzonitrile (32)



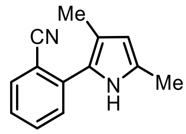
Following **GP2**, 2-iodobenzonitrile (23 mg, 0.10 mmol) and *N*-Me-pyrrole (444 µL, 5.0 mmol, 50.0 equiv.) gave **32** (12 mg, 65%) as a solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (1H, d, *J* = 7.7 Hz), 7.63 (1H, t, *J* = 7.7 Hz), 7.49–7.42 (2H, m), 6.82 (1H, m), 6.50–6.36 (1H, m), 6.28 (1H t, *J* = 2.9 Hz), 3.64 (3H, s). Data in accordance with the literature.[7]

2-(1H-Pyrrol-2-yl)benzonitrile (33)



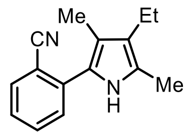
Following **GP2**, 2-iodobenzonitrile (22.9 mg, 0.10 mmol) and pyrrole (345 µL, 50.0 equiv., 5.0 mmol) gave **33** (12 mg, 71%) as a solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (1H, br s), 7.70–7.59 (2H, m), 7.59–7.49 (1H, m), 7.31–7.18 (1H, m), 7.01–6.93 (1H, m), 6.89–6.80 (1H, m), 6.40–6.31 (1H, m). Data in accordance with the literature.[8]

2-(3,5-Dimethyl-1H-pyrrol-2-yl)benzonitrile (34)



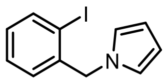
Following **GP2**, 2-iodobenzonitrile (23 mg, 0.1 mmol) and 2,4-dimethylpyrrole (515 µL, 50.0 equiv., 5.0 mmol) gave **34** (15 mg, 75%) as a solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.76 (1H, s), 7.83 (1H, dd, *J* = 7.8, 0.9 Hz), 7.69 (1H, td, *J* = 7.8, 1.4 Hz), 7.52–7.35 (2H, m), 5.74 (1H, d, *J* = 2.2 Hz), 2.19 (3H, s), 2.00 (3H, s). Data in accordance with the literature.[4]

2-(4-Ethyl-3,5-dimethyl-1H-pyrrol-2-yl)benzonitrile (35)



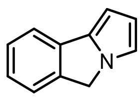
Following **GP2**, 2-iodobenzonitrile (23 mg, 0.10 mmol) and 3-ethyl-2,4-dimethylpyrrole (675 µL, 50.0 equiv., 5.0 mmol) gave **35** (17 mg, 76%) as a solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.58 (1H, s), 7.82 (1H, dd, *J* = 7.8, 1.2 Hz), 7.67 (1H, td, *J* = 7.7, 1.4 Hz), 7.44 (1H, d, *J* = 7.9 Hz), 7.39 (1H, td, *J* = 7.6, 1.1 Hz), 2.35 (2H, q, J = 7.5 Hz), 2.16 (3H, s), 1.96 (3H, s), 1.03 (3H, t, J = 7.5 Hz). Data in accordance with the literature.[4]

1-(2-Iodobenzyl)-1H-pyrrole (36)



To a solution of pyrrole (94 µL, 1.35 mmol) in DMF (7 mL) was added NaOH (218 mg, 5.45 mmol, 4.0 equiv.) at 0 °C. The mixture was stirred for 10 min then 2-iodobenzyl bromide (400 mg, 1.35 mmol, 1.0 equiv.) was added and the reaction was allowed to stir at room temperature for 36 h. The mixture was diluted with Et_2O (10 mL) and NH_4Cl sat. (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic layers were washed with NH_4Cl sat. and brine, dried ($MgSO_4$), filtered and evaporated. The crude material was purified by flash column chromatography eluting with petrol–Et_2O (0% → 10%) to give **36** (342 mg, 90%) as an oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.84 (1H, dd, J = 7.9, 1.2 Hz), 7.29–7.23 (2H, m), 6.97 (1H, td, J = 7.6, 1.7 Hz), 6.71 (2H, t, J = 2.1 Hz), 6.64 (1H, dd, J = 7.8, 1.7 Hz), 6.23 (2H, t, J = 2.1 Hz), 5.08 (2H, s). Data in accordance with the literature.[18]

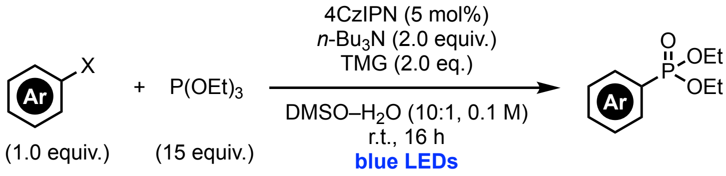
5H-Pyrrolo[2,1-a]isoindole (37)



Following **GP2**, 1-(2-iodobenzyl)-1H-pyrrole (28 mg, 0.10 mmol) gave **37** (6 mg, 36%) as a solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (1H, d, J = 7.6 Hz), 7.38–7.29 (2H, m), 7.15 (1H, t, J = 7.5 Hz), 6.99–6.93 (1H, m), 6.38–6.33 (1H, m), 6.32–6.27 (1H, m), 4.93 (2H, s). Data in accordance with the literature.[19]

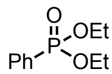
5 Substrate Scope for the Radical Phosphonylation

General Procedure – GP3



A dry tube equipped with a stirring bar was charged with the aryl halide (0.10 mmol, 1.0 equiv.) and 4CzIPN (4 mg, 5.0 µmol, 5 mol%). The tube was capped with a Supelco aluminium crimp seal with septum (PTFE/butyl), evacuated and refilled with N_2 (x 3). Degassed DMSO–H_2O (10:1) (1.0 mL, 0.1 M), *n*-Bu_3N (48 µL, 0.20 mmol, 2.0 equiv.), 1,1,3,3-tetramethylguanidine (25 µL, 0.20 mmol, 2.0 equiv.) and $P(OEt)_3$ (257 µL, 1.5 mmol, 15.0 equiv.) were sequentially added and the mixture was stirred in front of blue LEDs for 16 h at room temperature. Brine (5 mL) and EtOAc (5 mL) were added and the mixture was shaken. The aqueous layer was extracted with EtOAc (x 2), the combined organic layers were dried ($MgSO_4$), filtered and evaporated. Purification by flash column chromatography on silica gel gave the products.

Diethyl Phenylphosphonate (40)

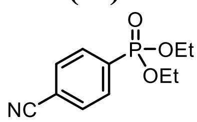


Following **GP3**, iodobenzene (11.7 µL, 0.1 mmol) and $P(OEt)_3$ (258 µL, 15.0 equiv., 1.5 mmol) gave **40** (21 mg, 99%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (2H, dd, J = 13.3, 6.9 Hz), 7.48 (1H, t, J = 7.3 Hz), 7.39 (2H, td, J = 7.6, 4.2 Hz), 4.15–3.99 (4H, m), 1.25 (6H, t, J = 7.1 Hz). Data in accordance with the literature.[20]

Following **GP3**, bromobenzene (10.7 µL, 0.1 mmol) and $P(OEt)_3$ (258 µL, 15 equiv. 1.5 mmol) gave **40** (13 mg, 60%) as an oil.

Following **GP3**, chlorobenzene (10.1 µL, 0.1 mmol) and $P(OEt)_3$ (258 µL, 15 equiv. 1.5 mmol) gave **40** (3 mg, 12%) as an oil.

Diethyl (4-Cyanophenyl)phosphonate (41)



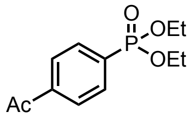
Following **GP3**, 4-iodobenzonitrile (22.9 mg, 0.1 mmol) and $P(OEt)_3$ (258 µL, 15.0 equiv., 1.5 mmol) gave **41** (12 mg, 49%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.95–7.87 (2H, m), 7.77–7.72 (2H, m), 4.24–4.05 (4H, m), 1.33 (6H, t, J = 7.1 Hz). Data in accordance with the literature.[8]

Following **GP3**, 4-bromobenzonitrile (18.2 mg, 0.1 mmol) and $P(OEt)_3$ (258 µL, 15.0 equiv., 1.5 mmol) gave **41** (9 mg, 35%) as an oil.

Following **GP3**, 4-chlorobenzonitrile (13.8 mg, 0.1 mmol) and $P(OEt)_3$ (258 µL, 15.0 equiv., 1.5 mmol) gave **41** (9 mg, 36%) as an oil.

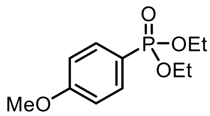
Diethyl (4-Acetylphenyl)phosphonate (42)



Following **GP3**, 4-iodoacetophenone (22.9 mg, 0.1 mmol) and $P(OEt)_3$ (258 µL, 15.0 equiv., 1.5 mmol) gave **42** (24 mg, 98%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.86 (2H, m), 7.91–7.87 (2H, m), 4.18–4.04 (4H, m), 2.61 (3H, s), 1.30 (6H, t, *J* = 7.0 Hz). Data in accordance with the literature.[21]

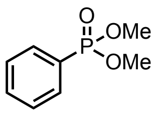
Following **GP3**, 4-bromoacetophenone (19.9 mg, 0.1 mmol) and triethyl phosphite (258 µL, 15.0 equiv., 1.5 mmol) gave **43** (8 mg, 30%) as an oil.

Diethyl (4-Methoxyphenyl)phosphonate (43)



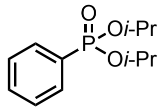
Following **GP3**, 4-iodoanisole (23.4 mg, 0.1 mmol) and $P(OEt)_3$ (258 µL, 15.0 equiv., 1.5 mmol) gave **43** (9 mg, 35%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (2H, dd, *J* = 12.8, 8.7 Hz), 6.89 (2H, dd, *J* = 8.6, 3.3 Hz), 4.14–4.00 (4H, m), 3.77 (3H, s), 1.24 (6H, t, *J* = 7.1 Hz). Data in accordance with the literature.[20]

Dimethyl Phenylphosphonate (44)



Following **GP3**, iodobenzene (11.7 µL, 0.1 mmol) and $P(OMe)_3$ (177 µL, 15.0 equiv., 1.5 mmol) gave **44** (20 mg, 90%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.74 (2H, m), 7.56–7.52 (1H, m), 7.47–7.42 (2H, m), 3.73 (6H, d, *J* = 11.1 Hz). Data in accordance with the literature.[22]

Diisopropyl Phenylphosphonate (45)



Following **GP3**, iodobenzene (11.7 μL, 0.1 mmol) and P(O*i*-Pr)$_3$ (370 μL, 15.0 equiv., 1.5 mmol) gave **45** (23 mg, 95%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (2H, m), 7.52–7.48 (1H, m), 7.44–7.40 (2H, m), 4.70–4.62 (2H, m), 1.34 (6H, d, *J* = 6.2 Hz), 1.20 (6H, d, *J* = 6.2 Hz). Data in accordance with the literature.[22]

6 Cyclic Voltammetry

6.1 General Experimental Details

Cyclic voltammetry was conducted on an EmStat (PalmSens) potentiostat using a 3-electrode cell configuration. A glassy carbon working electrode was employed alongside a platinum wire counter electrode and a Ag/AgCl reference electrode. All the solutions were degassed by bubbling N_2 prior to measurements. 10 mM solutions of the desired compounds were freshly prepared in dry acetonitrile along with 0.1 M of (n-Bu_4N)(PF_6) as supporting electrolyte and were examined at a scan rate of 0.1 V s^{-1}. Ferrocene ($E_{1/2}$ = +0.42 V vs SCE)[23] was added at the end of the measurements as an internal standard to determine the precise potential scale. Potential values are given versus the saturated calomel electrode (SCE). Irreversible waves were obtained in all cases; therefore, the potentials were estimated at half the maximum current.[24]

6.2 Redox Potentials

Table S4.

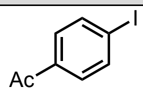
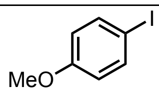
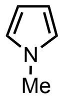
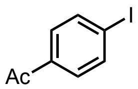
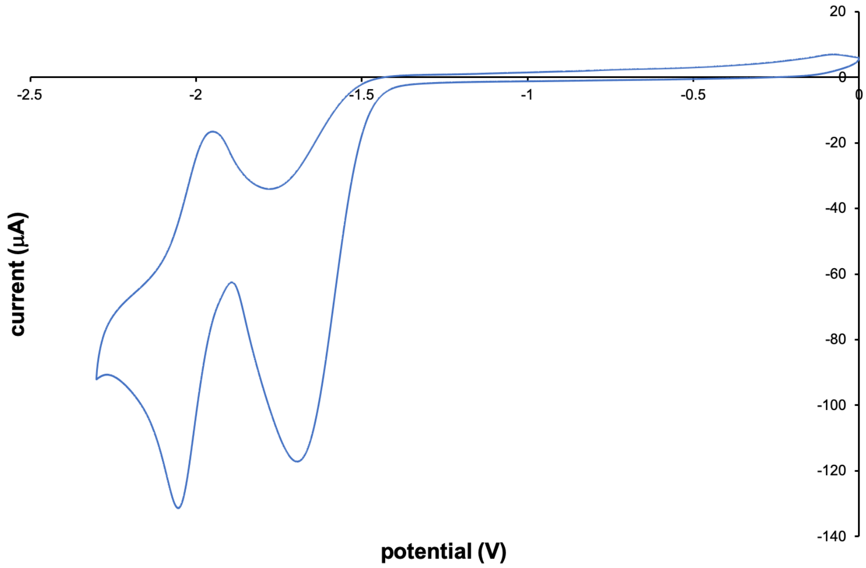
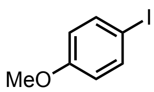
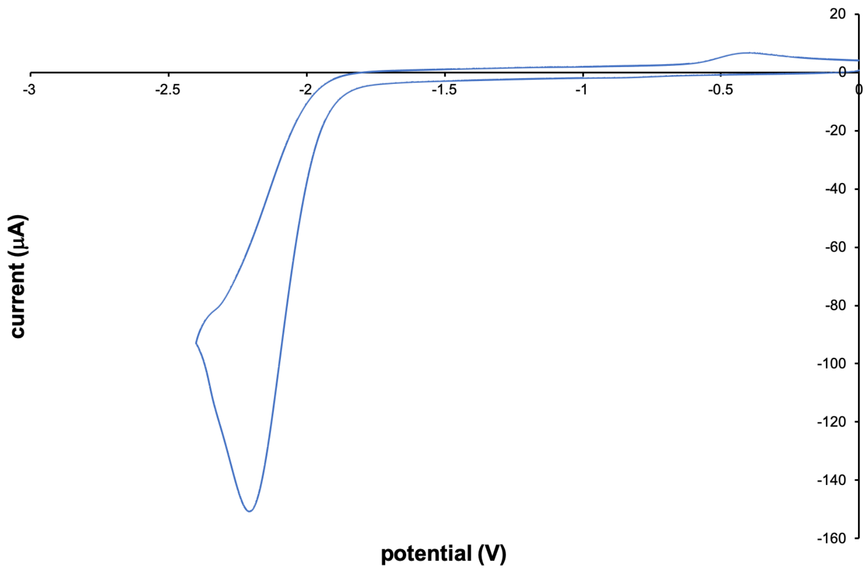
Entry	Substrate	E_{red} (V vs SCE)
1	 **1**	–1.64
2	 **4**	–2.17

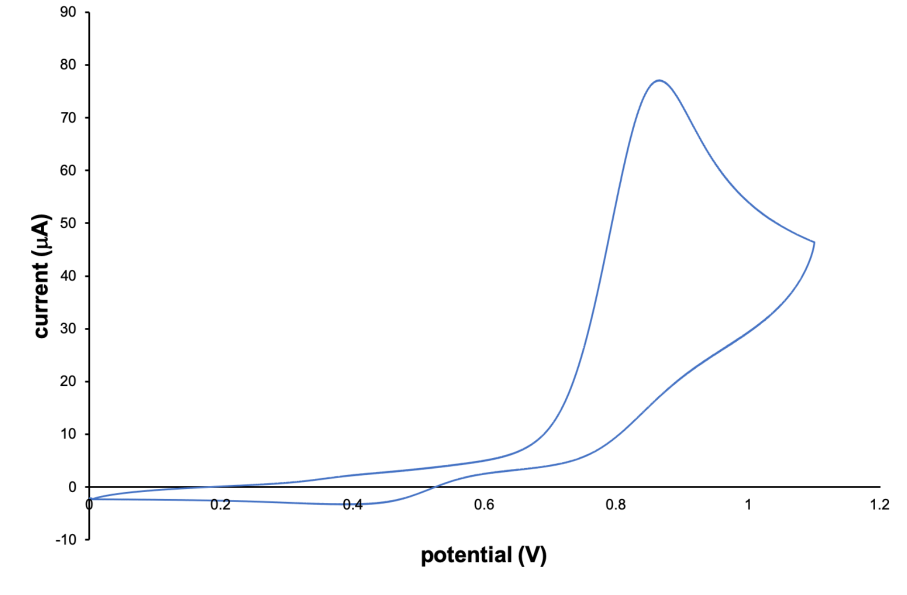
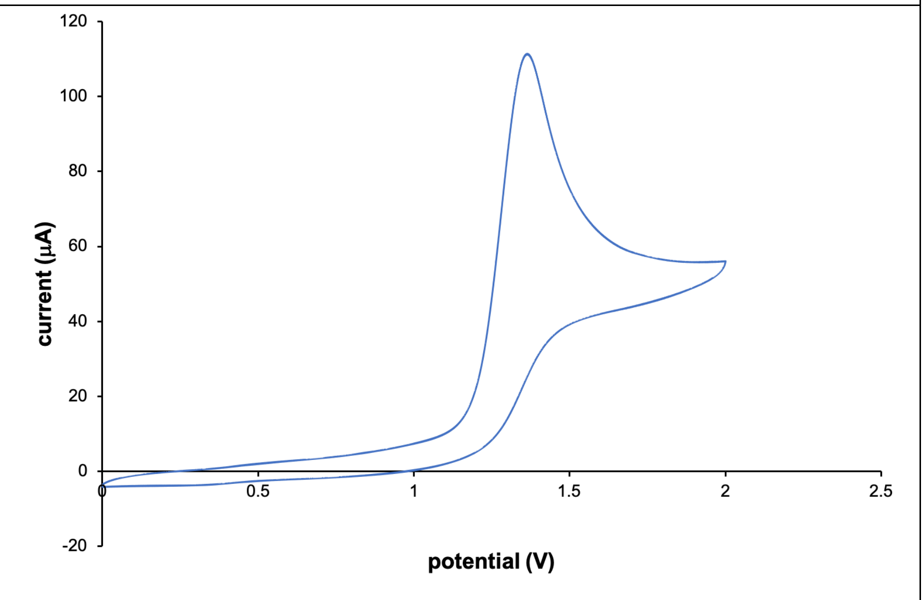
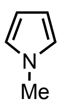
Table S5.

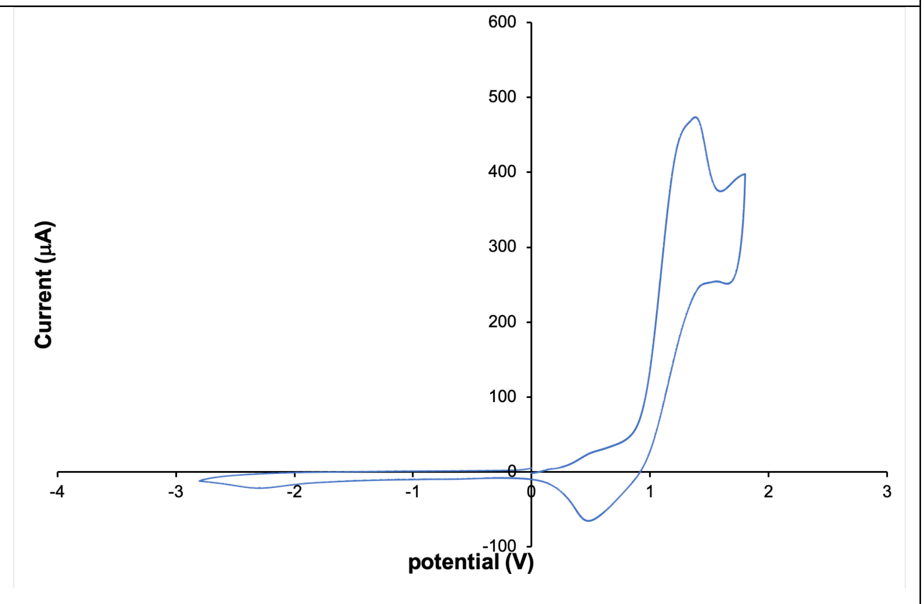
Entry	Substrate	E_{ox} (V vs SCE)
1	n-Bu_3N	0.71
2	TMG	1.07
3	 **2**	1.03

6.3 Cyclic Voltammograms

Table S6.

Substrate	Cyclic Voltammogram
 **1**	
 **4**	

<table>
<tr><td>n-Bu_3N</td><td>
</td></tr>
<tr><td>TMG</td><td>
</td></tr>
<tr><td>

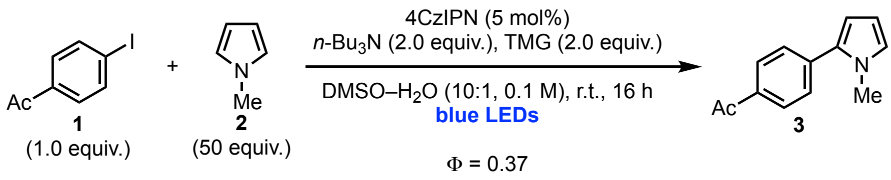
2</td><td>
</td></tr>
</table>

7 Quantum Yield Determination

7.1 General Experimental Details

The quantum yield of the photochemical reactions was determined at 298 K following procedures described in literature.[25] Degassed reaction tubes were irradiated using as the light source Blue LEDs plates (λ_{max} = 444 nm) for 1 min. The yield of products was determined by ^{1}H NMR spectroscopy; in all cases the conversion was lower than 10%. The photon flux of the blue LEDs used was determined by standard ferrioxalate actinometry.[26]

7.2 Quantum Yield Determination

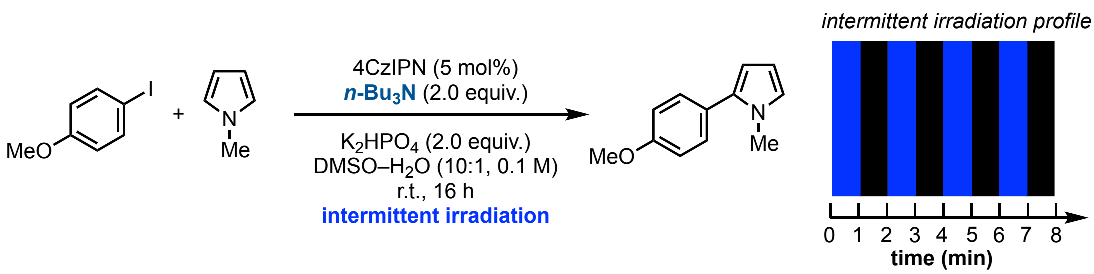


We believe the low quantum yield obtained for this reaction suggests the presence of a short-lived radical chain-propagation[27] or alternatively an inefficient initiation of the radical chain.[28]

Intermittent Irradiation Experiments

To obtain evidences supporting an inefficient initiation process as the likely explanation for the low quantum yield observed we have run some intermittent irradiation experiments.[28]

The reaction shown below was subjected to short “light on–off” cycles (1 min each) and periodically monitored by ^{1}H NMR spectroscopy.



After 5 on–off cycles, 3% product formation was observed and the signals for 4CzIPN disappeared suggesting a decomposition process (at the moment we do not know how 4CzIPN might decompose under these conditions) (Figure S7). After another 10 on–off cycles, only 2% more of product was observed. The intermittent illumination was continued for other 50 cycles without any change in the reaction profile.
A control reaction under continuous irradiation was also performed and delivered 11% and 36% of product after 20 min and 60 min of irradiation respectively.

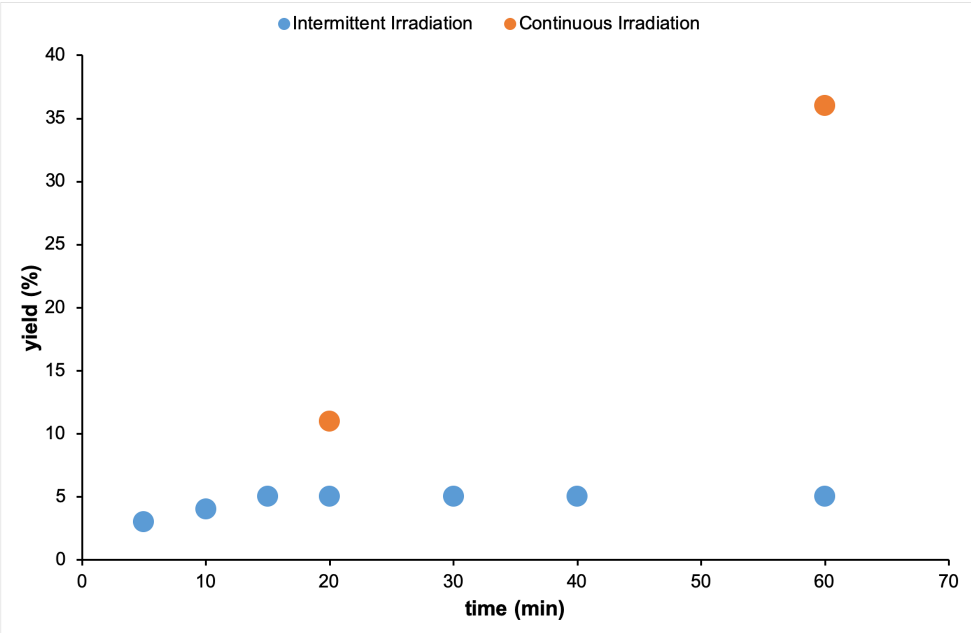


Figure S7.

These results support the possibility of an inefficient initiation step being responsible for the low quantum yield.

8 Comparison of XAT Reactions Energy Profiles

We have not been able to locate the transition state for the XAT reactions on Ph–I with the various α-N, α-O and α-S-alkyl radicals arising from the addition to *N*-Me-pyrrole, furan and thiophene.

However, we have conducted determined the ΔGº for the individual XAT reactions. As shown in Figure S8, the one with pyrrole is by far the easiest which agrees with our proposed mechanistic analysis.

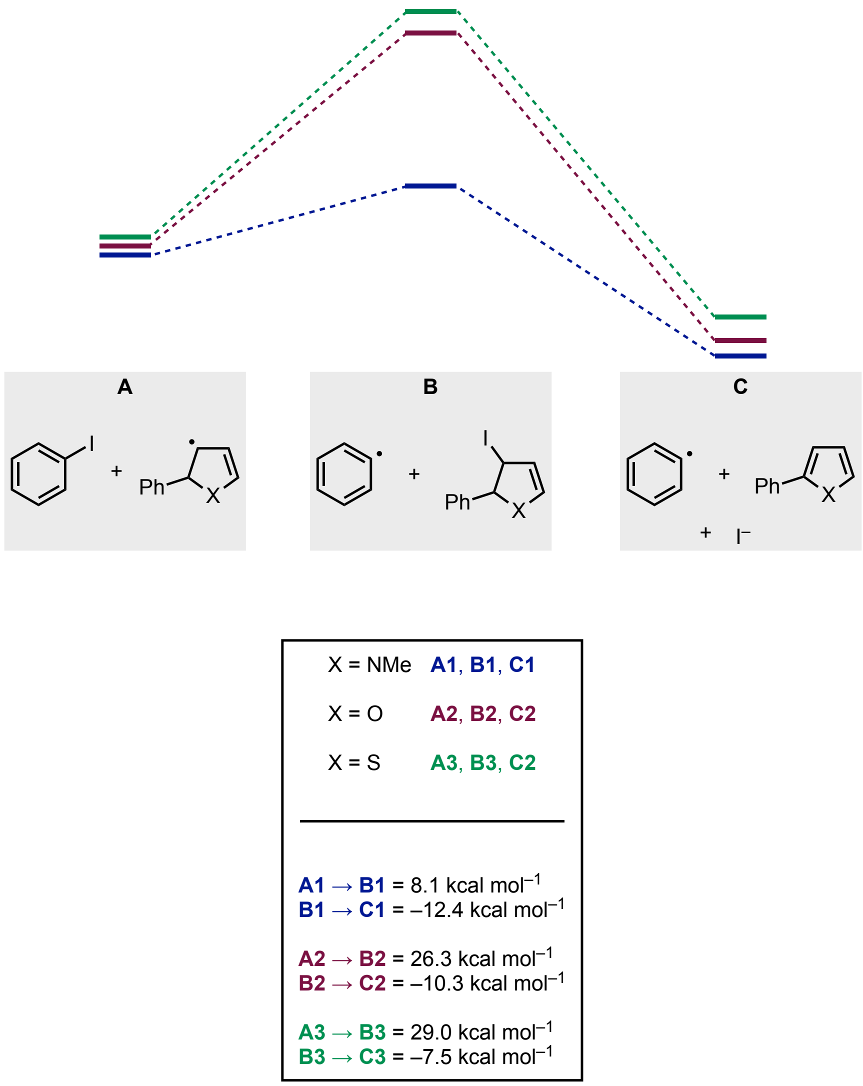


Figure S8.

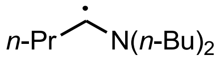
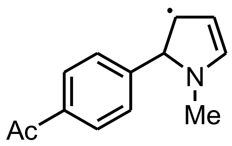
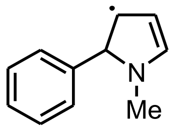
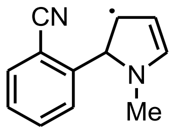
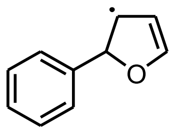
9 Computational Studies

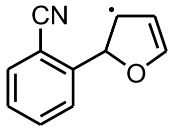
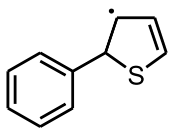
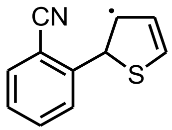
9.1 Computational Methods

Density functional theory (DFT)[29] calculations were performed using Gaussian 09 (revision E.01)[30] and the Gaussview[31] was used to generate input geometries and visualize output structures. Geometry optimizations and frequency calculations for the calculation of reaction energies were performed using the B3LYP functional[32–35] and an atom-pairwise dispersion correction (D3)[36,37] with a flexible triplet zeta basis set (def2-TZVP).[38] For comparative purpose and to model solvation effect, the calculations were carried out in DMSO as solvent at the same level of theory, by applying the most commonly used integral equation formalism (IEF) version of polarized continuum model (PCM).[39,40] For calculation of electronic properties of radicals, global and local electrophilicity index, B3LYP functional[32–35] was used and the geometries of studied radicals were optimized at the UB3LYP/6-311+G(d,p) level of theory, followed by frequency calculations at the same level.[41] The computed Hirshfeld charges on the radicals were also calculated at the same level of theory.[42] All stationary points were characterized as minima based on normal vibrational mode analysis. Thermal corrections were computed from unscaled frequencies, assuming a standard state of 298.15 K and 1 atm.

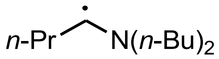
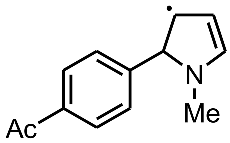
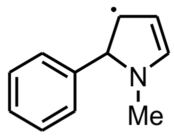
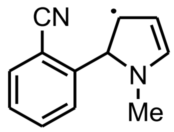
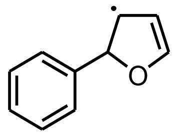
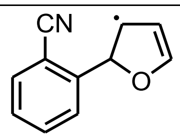
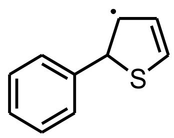
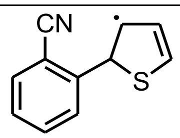
9.2 Electronic Properties of Radicals

DFT Method: UB3LYP/6-311+G(d,p)

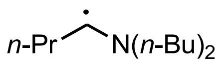
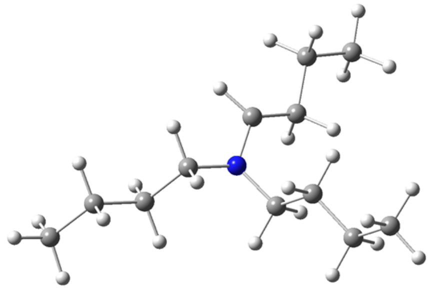
Entry	Radical	Ionization Potential (IP, eV)	Electron affinity (EA, eV)	Electronegativity (χ, eV)	Electronic Chemical Potential (μ, eV)	Chemical Hardness (η, eV)	Chemical Softness (S, meV)	Global Electrophilicity Index (ω, eV)	Local Electrophilicity Index (ω^{+}_{rc}, eV)	Hirshfeld Charge
1		5.41	-0.95	2.23	-2.23	6.36	157.30	0.39	0.13	-0.0432
2		5.89	0.27	3.08	-3.08	5.62	177.87	0.84	0.15	-0.0368
3		5.73	-0.15	2.79	-2.79	5.88	170.01	0.66	0.16	-0.0389
4		5.99	0.24	3.12	-3.12	5.75	173.92	0.85	0.17	-0.0302
5		6.51	-0.01	3.25	-3.25	6.52	153.31	0.81	0.26	-0.0213

6		6.81	0.40	3.60	-3.60	6.40	156.15	1.01	0.26	-0.0120
7		6.55	0.32	3.43	-3.43	6.23	160.45	0.94	0.30	-0.0119
8		6.65	0.49	3.57	-3.57	6.15	162.51	1.04	0.32	-0.0121

Computed Energies [values are in Hartree]

Entry	Species	Total Electronic Energy	Sum of Electronic and Zero-point Energies	Sum of Electronic and Thermal Enthalpies	Gibbs Free Energy
1		-527.7944891	-527.433485	-527.414559	-527.482521
2		-633.9035981	-633.667107	-633.652006	-633.709951
3		-481.2127423	-481.013307	-481.001826	-481.050913
4		-573.478742	-573.280569	-573.267290	-573.320746
5		-461.7612287	-461.601850	-461.592112	-461.637664
6		-554.0267894	-553.868680	-553.857213	-553.906494
7		-784.7472348	-784.590794	-784.580572	-784.627214
8		-877.0091731	-876.854098	-876.842152	-876.892366

Optimized Structures and Cartesian Coordinates

Entry	Species	Optimized Structure
1		

Cartesian Coordinates

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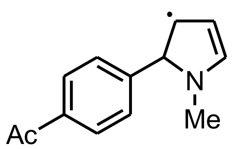
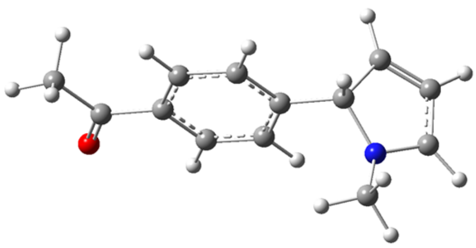
N	-0.27220500	-0.27531300	0.00205700
C	-1.56932100	-0.15119400	-0.65966200
H	-1.57261500	-0.80440200	-1.53695700
H	-1.69830200	0.87065600	-1.04191200
C	-2.74948800	-0.51109400	0.25234500
H	-2.72875500	0.12550600	1.14523200
H	-2.61695700	-1.54036000	0.60475800
C	0.22497500	0.92046500	0.67809500
H	-0.62480600	1.40061400	1.17415600
H	0.90897700	0.61515300	1.47541400
C	1.87778900	-1.55619800	0.27486000
H	1.64264200	-1.90348600	1.29895300
H	2.50562200	-0.66427900	0.40961200
C	0.92877900	1.93608100	-0.23916900
H	0.24098000	2.24900700	-1.03393200
H	1.76727000	1.43885900	-0.73891400
H	0.15777500	-2.02473600	-1.04565000
C	-4.10638500	-0.36778400	-0.44608000
H	-4.11982700	-0.99796600	-1.34399600
H	-4.22695200	0.66406400	-0.79866200
C	-5.28940200	-0.73962200	0.45253200
H	-6.24121000	-0.63028800	-0.07470500
H	-5.21555200	-1.77696900	0.79348600
H	-5.32692500	-0.10205600	1.34146900
C	1.42780000	3.16918100	0.52099400
H	0.58117500	3.65581600	1.02167100
H	2.10924700	2.85085500	1.31975500
C	2.13913000	4.18619700	-0.37640300
H	2.48269600	5.05234000	0.19615800
H	3.01273600	3.74093900	-0.86244100
H	1.47370300	4.55175600	-1.16484400
C	2.71336100	-2.63634400	-0.42655700
H	2.10294100	-3.53928800	-0.54719600
H	2.95872600	-2.29521200	-1.43832500
C	3.99874100	-2.98742000	0.32712200
H	4.57013400	-3.75846800	-0.19736900
H	4.64629500	-2.11123000	0.43467400
H	3.78084200	-3.36222300	1.33231000

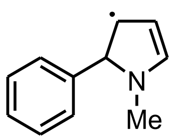
Entry	Species	Optimized Structure
2		

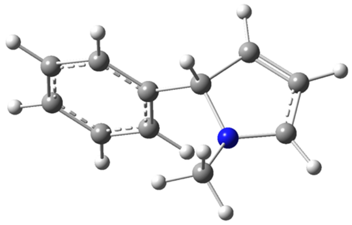
Cartesian Coordinates

C	2.01798900	0.70210000	-0.00061300
C	2.62720400	0.80502300	-1.38151900
N	2.82216800	-0.36977700	0.61441500
C	3.74699000	-0.00291400	-1.43396200
C	3.89032800	-0.66669000	-0.21452600
H	4.40237400	-0.13263500	-2.28326600
H	4.64137800	-1.37839500	0.09303500

C	2.89307700	-0.47457700	2.05695300
H	1.88677100	-0.55621300	2.47388500
H	3.44766800	-1.37404400	2.33030700
H	3.39130600	0.39477200	2.51351900
H	2.22880200	1.44029600	-2.15744600
H	2.18155800	1.64185200	0.56521900
C	0.52008200	0.42093700	0.01321900
C	-0.38590800	1.44271500	0.30089400
C	0.02526400	-0.85045500	-0.30474200
C	-1.75903300	1.20823200	0.26656300
H	-0.01598500	2.43061700	0.55726000
C	-1.34006500	-1.08931400	-0.33092800
H	0.72430500	-1.64889000	-0.52573800
C	-2.25420200	-0.06219200	-0.04820700
H	-2.43713300	2.02167200	0.49482700
H	-1.72953900	-2.07097600	-0.57182100
C	-3.71988900	-0.37362300	-0.09124100
O	-4.10943300	-1.49466300	-0.36266300
C	-4.71445900	0.73313700	0.21038400
H	-4.56351700	1.13019300	1.21852100
H	-4.60007000	1.56481900	-0.49092500
H	-5.72189200	0.32840700	0.12937400

3

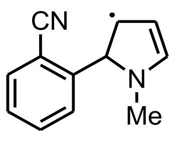


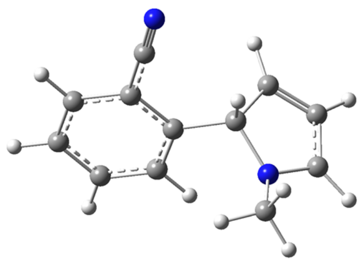


Cartesian Coordinates

C	-0.84282000	-0.17255200	0.67290100
C	-1.48478400	-1.53161700	0.50847700
N	-1.72077000	0.68367500	-0.14879000
C	-2.67831700	-1.38172800	-0.17128700
C	-2.84124500	-0.03902300	-0.51884400
H	-3.37250900	-2.16940500	-0.42736200
H	-3.64339900	0.43355700	-1.06538100
C	-1.74514000	2.11254700	0.07982800
H	-0.73350300	2.51720500	0.00324400
H	-2.36292900	2.59366400	-0.68084600
H	-2.14978300	2.36944500	1.07150800
H	-1.05556200	-2.43896900	0.90474900
H	-0.91506400	0.15846800	1.72953600
C	0.62744400	-0.09202700	0.27740800
C	1.61621600	0.03035700	1.25521700
C	1.01102700	-0.17596800	-1.06514100
C	2.96667300	0.06235200	0.90435200
H	1.32856700	0.10302200	2.29984700
C	2.35649400	-0.13561500	-1.41908300
H	0.24677200	-0.26884200	-1.82859200
C	3.33964700	-0.01898000	-0.43469200
H	3.72304800	0.15705400	1.67576600
H	2.64106500	-0.19785600	-2.46386400
H	4.38751100	0.01044900	-0.71189000

4

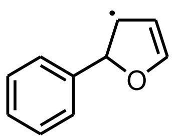
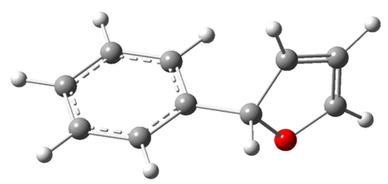




Cartesian Coordinates

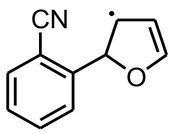
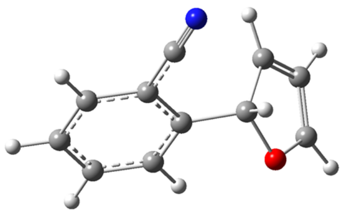
C	0.92943500	0.47018500	-0.06740100
C	1.51266900	0.62878900	-1.45540800
N	1.96147700	-0.32773900	0.61966600
C	2.79245000	0.10811400	-1.45824100
C	3.07795000	-0.41643000	-0.19748300
H	3.46959200	0.08458800	-2.30001900
H	3.97710400	-0.89776800	0.15606600

C	2.05889400	-0.26828800	2.06556400
H	1.10253800	-0.54550800	2.51481300
H	2.81351200	-0.97855800	2.40832300
H	2.33475200	0.73505200	2.42297400
H	0.98720300	1.10928700	-2.26602500
H	0.84184700	1.45358500	0.42972700
C	-0.44595100	-0.19111900	-0.05077500
C	-1.62486400	0.57469200	0.03100700
C	-0.56681100	-1.57689000	-0.16896400
C	-2.88605700	-0.04413900	-0.01215900
C	-1.81515000	-2.18976900	-0.20405500
H	0.33756900	-2.17031600	-0.22869500
C	-2.97936300	-1.42334100	-0.12840800
H	-3.77765700	0.56758100	0.05138400
H	-1.88202200	-3.26833400	-0.29257800
H	-3.95252500	-1.89886800	-0.15764300
C	-1.57074700	2.00088600	0.16027300
N	-1.55385600	3.15247100	0.26290200

5		

Cartesian Coordinates

C	1.01287300	-0.74597700	0.17440500
C	1.86242200	-0.05192000	1.20393600
O	1.70868100	-0.46310900	-1.08902500
C	2.94564300	0.51619300	0.55584700
H	1.63346000	-0.03726800	2.25818100
C	2.82939900	0.25223300	-0.79902800
H	3.74972400	1.07887000	1.00741700
H	3.44915700	0.52579500	-1.63796100
H	1.03765200	-1.83950200	0.29060700
C	-0.43813000	-0.31149400	0.08494700
C	-1.45819700	-1.26368700	0.09413100
C	-0.77356900	1.04354400	-0.00762700
C	-2.79563300	-0.87384600	0.01777200
H	-1.20581400	-2.31734800	0.15977600
C	-2.10590900	1.43479900	-0.09288300
H	0.01338200	1.78949500	-0.01122000
C	-3.12117600	0.47647900	-0.07744700
H	-3.57867100	-1.62378800	0.02864800
H	-2.35538400	2.48743900	-0.16785800
H	-4.15929700	0.78322600	-0.13971600

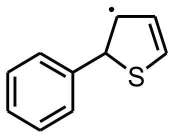
6		

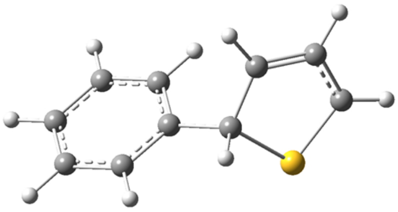
Cartesian Coordinates

C	-1.11038800	0.34382300	-0.43244800
C	-1.81393300	0.81214900	0.81760100
O	-2.00299600	-0.66185500	-0.98103400
C	-3.01277900	0.12768400	0.90453800
H	-1.42463600	1.57190400	1.47650000
C	-3.10577800	-0.73128300	-0.17642700
H	-3.76167800	0.23132400	1.67587900
H	-3.86958100	-1.42786100	-0.48141400
H	-1.03396300	1.14494000	-1.18199500
C	0.27510800	-0.24190800	-0.20017100
C	1.38855400	0.61079000	-0.06247400
C	0.47435700	-1.61692600	-0.09206600
C	2.66470200	0.08419800	0.18835800
C	1.74323900	-2.13707700	0.15304900
H	-0.37258500	-2.27870400	-0.21526600
C	2.84025400	-1.28891500	0.29635600
H	3.50476700	0.76006700	0.29108300
H	1.87528700	-3.21041500	0.22917200

H	3.82689700	-1.69419800	0.48617400
C	1.23625800	2.03037600	-0.17193300
N	1.11455600	3.17718800	-0.25402300

7

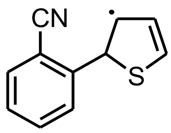


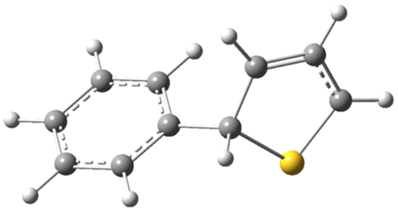


Cartesian Coordinates

C	0.76124500	-0.45898800	0.64647900
C	1.53475600	0.68180700	1.25293700
C	2.70726600	1.00932700	0.61264800
H	1.15563800	1.17842400	2.13667100
C	2.99636700	0.24515900	-0.51845500
H	3.36393700	1.80362200	0.94817900
H	3.85017400	0.34409100	-1.17189300
H	0.77979600	-1.33139800	1.31022400
C	-0.68489800	-0.16467800	0.29657000
C	-1.68867400	-1.07305800	0.64227700
C	-1.04103700	1.01173700	-0.37300500
C	-3.02310800	-0.81485500	0.32853000
H	-1.42564300	-1.98915100	1.16189600
C	-2.37125800	1.27219800	-0.68570000
H	-0.26919000	1.72194400	-0.64835400
C	-3.36759600	0.35893600	-0.33634800
H	-3.78988600	-1.53004500	0.60474300
H	-2.63303500	2.18833600	-1.20346500
H	-4.40387500	0.56312700	-0.58101800
S	1.77710700	-0.95965300	-0.85953700

8



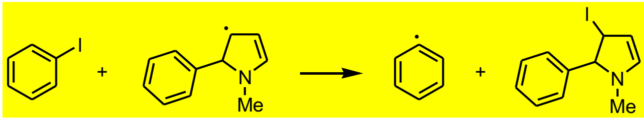
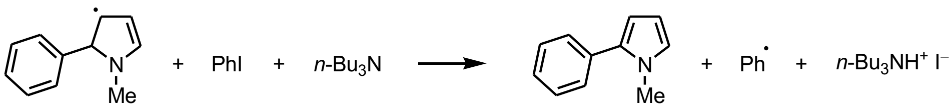
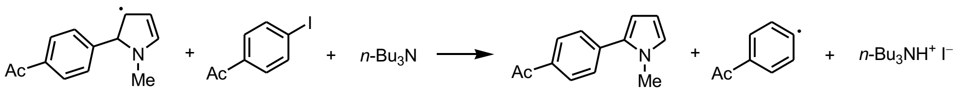
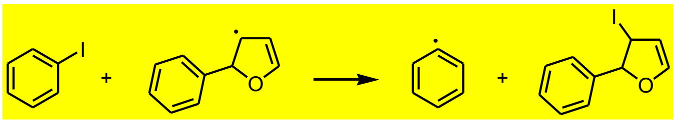
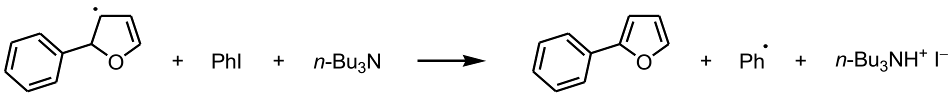
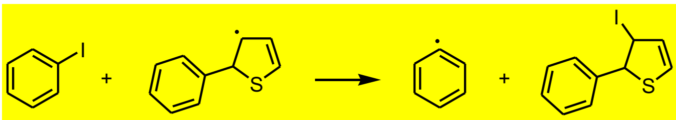
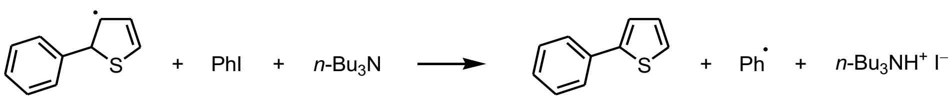
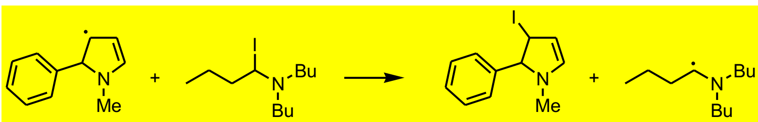


Cartesian Coordinates

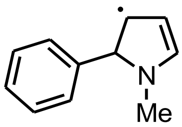
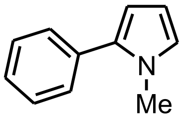
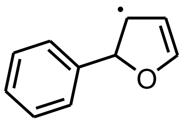
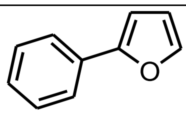
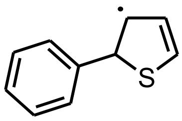
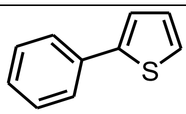
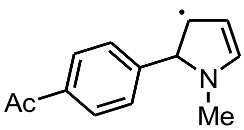
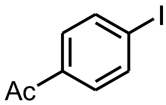
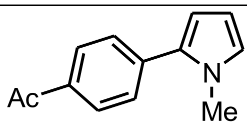
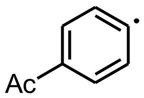
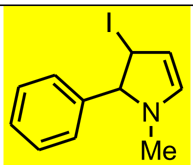
C	0.70518600	-0.99908900	0.39975700
C	1.50886400	-0.27506700	1.44733900
C	2.73913400	0.17783700	1.02981900
H	1.11827300	-0.16699000	2.45070700
C	3.02870200	-0.05174500	-0.31222500
H	3.43007900	0.69889300	1.68134100
H	3.91217700	0.25357100	-0.85216100
H	0.67191200	-2.07072600	0.62980500
C	-0.73070300	-0.54887100	0.20307000
C	-1.74645600	-1.50665300	0.24770500
C	-1.10152900	0.79512300	-0.01851300
C	-3.08650400	-1.16210900	0.08557000
H	-1.47845700	-2.54445100	0.41416300
C	-2.45179200	1.14045800	-0.17949900
C	-3.44186900	0.16668400	-0.12788200
H	-3.84887500	-1.93157900	0.12616400
H	-2.70978300	2.17886600	-0.34753400
H	-4.48109200	0.44543700	-0.25490400
S	1.73487400	-0.86260700	-1.16476000
C	-0.14236500	1.85692300	-0.09887700
N	0.56339600	2.76825000	-0.18128800

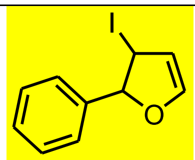
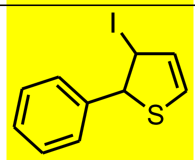
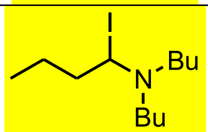
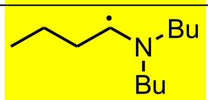
9.3 Reaction Energies (ΔG°)

DFT Method: B3LYP-D3/def2-TZVP [solvent: DMSO, values are in Kcal mol^{-1}]

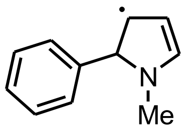
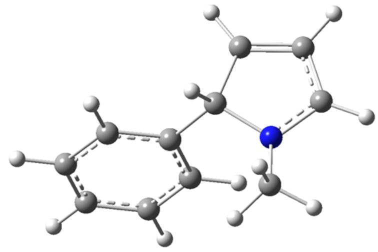
Entry	Reaction	ΔG
1		8.1
2		-12.4
3		-12.5
4		26.3
5		-10.3
6		29.0
7		-7.5
8		12.9

Computed Energies [values are in Hartree]

Entry	Species	Total Electronic Energy	Sum of Electronic and Zero-point Energies	Sum of Electronic and Thermal Enthalpies	Gibbs Free Energy
1		-481.2882338	-481.088470	-481.076992	-481.126063
2	PhI	-529.5451257	-529.455249	-529.448427	-529.486987
3	*n*-Bu_3N	-528.5313195	-528.155647	-528.137231	-528.202577
4		-480.7374963	-480.546020	-480.535277	-480.581465
5	$Ph^{\bullet}$	-231.6555749	-231.568454	-231.563134	-231.596490
6	*n*-Bu_3NH^+ I^-	-826.9963739	-826.603619	-826.582681	-826.657460
7		-461.8329	-461.673296	-461.663586	-461.708945
8		-461.2764966	-461.125862	-461.116685	-461.160939
9		-784.8150757	-784.658346	-784.648165	-784.694669
10		-784.2552308	-784.107650	-784.098105	-784.142310
11		-634.0065281	-633.769590	-633.754539	-633.812542
12		-682.2619762	-682.134991	-682.124607	-682.172056
13		-633.4565404	-633.227775	-633.213515	-633.268439
14		-384.3724134	-384.247903	-384.239205	-384.281257
15		-779.1643514	-778.960429	-778.946926	-779.003707

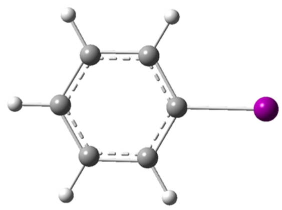
16		-759.6749764	-759.511434	-759.500247	-759.550608
17		-1082.658983	-1082.498824	-1082.487033	-1082.538952
18		-825.7770994	-825.409988	-825.389445	-825.462680
19		-527.8792386	-527.516855	-527.498354	-527.564408

Optimized Structures and Cartesian Coordinates

Entry	Species	Optimized Structure
1		

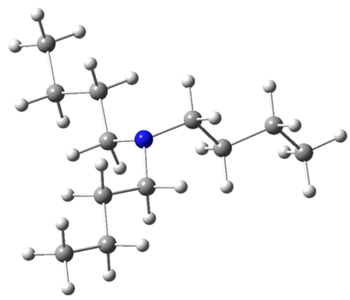
Cartesian Coordinates

C	-0.84208300	-0.36979900	0.60940000
C	-1.45487300	-1.62288900	0.03161900
N	-1.73112900	0.67528500	0.08515600
C	-2.63506000	-1.28750900	-0.60142700
C	-2.81836600	0.09225400	-0.52415000
H	-3.30682900	-1.96628100	-1.10502800
H	-3.62194400	0.69861800	-0.91020900
C	-1.75587400	1.97830100	0.70481900
H	-0.74818000	2.39591000	0.72590100
H	-2.39335900	2.64659100	0.12698300
H	-2.13441700	1.93610300	1.73508400
H	-1.01394100	-2.59983000	0.14475100
H	-0.91133400	-0.37588900	1.71402800
C	0.62105300	-0.15859300	0.25041000
C	1.62175300	-0.48867200	1.16193600
C	0.98543000	0.32354800	-1.00693500
C	2.96517500	-0.35033800	0.82281000
H	1.34916900	-0.85342300	2.14587900
C	2.32508800	0.47171400	-1.34582600
H	0.21071900	0.58936500	-1.71522000
C	3.32067500	0.13114200	-0.43261100
H	3.73188300	-0.61117900	1.54183800
H	2.59423300	0.85253100	-2.32340200
H	4.36440600	0.24552600	-0.69695900

Entry	Species	Optimized Structure
2	PhI	

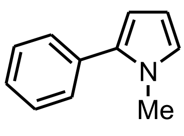
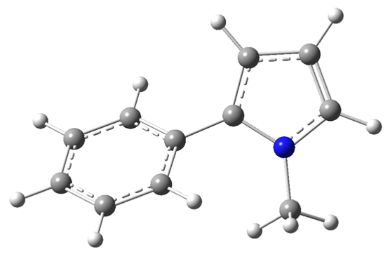
Cartesian Coordinates

I	2.92864432	0.37369519	-0.18216464
C	0.80776032	0.37367519	-0.18216464
C	0.12510832	1.58530619	-0.18215464
C	0.12510132	-0.83791681	-0.18217264
C	-1.26709768	1.57693719	-0.18217364
H	0.66201632	2.52364819	-0.18215864
C	-1.26713468	-0.82952981	-0.18215664
H	0.66195932	-1.77628781	-0.18217664
C	-1.96489968	0.37370019	-0.18216364
H	-1.80207268	2.51814219	-0.18217464
H	-1.80208768	-1.77074581	-0.18215564
H	-3.04706768	0.37372919	-0.18216764

Entry	Species	Optimized Structure
3	*n*-Bu_3N	

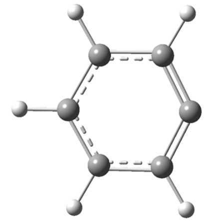
Cartesian Coordinates

C	-1.64115908	-0.36164684	-0.08815116
N	-0.46748508	0.32068616	0.46106484
C	0.59394692	-0.60565284	0.86415384
H	0.14483792	-1.32914784	1.55103084
H	1.33137192	-0.05240684	1.45098184
C	1.32063192	-1.36834284	-0.25232816
H	1.82184692	-0.66222784	-0.92181916
H	0.59376892	-1.91365984	-0.86283216
C	-0.02001708	1.41672116	-0.39972216
H	0.31576792	1.04736516	-1.38467316
H	-0.88525108	2.05261416	-0.59722216
C	-2.94726808	0.40274516	0.12375984
H	-2.89234808	1.38741816	-0.34942616
H	-3.07842508	0.57928316	1.19609084
C	1.07856592	2.28404316	0.20797284
H	2.00578392	1.71141816	0.30274984
H	0.78387192	2.57373816	1.22196284
H	-1.72826608	-1.33108684	0.40954984
H	-1.51949008	-0.57751884	-1.16344616
C	-4.15975408	-0.34492384	-0.43049516
H	-4.22127708	-1.33269184	0.03887384
H	-4.01552408	-0.52402584	-1.50122416
C	-5.47166708	0.40641116	-0.21195916
H	-5.44805108	1.38458516	-0.69939916
H	-6.32202508	-0.14734484	-0.61543516
H	-5.65513808	0.57189116	0.85283784
C	2.35417992	-2.34950484	0.29931284
H	1.85468892	-3.06549484	0.96077084
H	3.07061692	-1.80501484	0.92390584
C	3.10402492	-3.10455284	-0.79666516
H	3.83265292	-3.80177984	-0.37744416
H	2.41213092	-3.67773984	-1.41938616
H	3.64102792	-2.41237284	-1.45055616
C	1.35736492	3.53459616	-0.62528416
H	0.44234992	4.13152016	-0.69950116
H	1.61342092	3.23779816	-1.64789116
C	2.48136992	4.39202916	-0.04665516
H	3.41669092	3.82859016	0.00412684
H	2.65954992	5.28161816	-0.65433616
H	2.23895692	4.72236716	0.96681184

4		

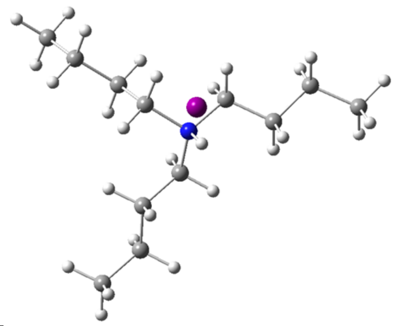
Cartesian Coordinates

C	0.60229400	-0.17962600	0.04723900
C	1.24225900	0.95041300	0.57544800
C	1.40283700	-1.19747300	-0.49259800
C	2.62736600	1.06288200	0.55187500
H	0.65781800	1.73694500	1.03246200
C	2.78714000	-1.08930100	-0.50409000
H	0.92778000	-2.07315500	-0.91591100
C	3.40766500	0.04487400	0.01287600
H	3.09807800	1.94495000	0.96793000
H	3.38273600	-1.88804600	-0.92841000
H	4.48644600	0.13315500	-0.00274600
C	-0.85224500	-0.35345500	0.08628100
C	-1.56452700	-1.50624400	0.37862000
N	-1.77473500	0.64659600	-0.16035400
C	-2.94292700	-1.19534800	0.31585400
H	-1.12267900	-2.45520800	0.63599100
C	-3.03824400	0.13550400	-0.02300700
H	-3.76985300	-1.86220200	0.49833100
H	-3.90080600	0.75815400	-0.19246600
C	-1.50625600	2.01066600	-0.58979700
H	-0.61577500	2.03707800	-1.21371400
H	-2.35238500	2.36802200	-1.17290700
H	-1.36039700	2.67678000	0.26172200

5	Ph$^{\bullet}$	

Cartesian Coordinates

C	-0.00001100	-1.39124300	-0.00000400
C	1.22327700	-0.77038400	0.00004400
C	-1.22327000	-0.77040100	-0.00003600
C	1.21064900	0.63037200	-0.00003100
H	2.15712100	-1.31877500	0.00001200
C	-1.21063600	0.63040000	0.00003300
H	-2.15714700	-1.31873400	-0.00003000
C	-0.00000700	1.31936900	0.00000000
H	2.14811300	1.17351100	-0.00005600
H	-2.14812600	1.17349200	0.00004300
H	0.00002400	2.40182100	-0.00000600

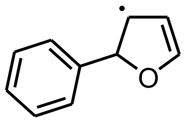
6	*n*-$Bu_3NH^+ I^-$	

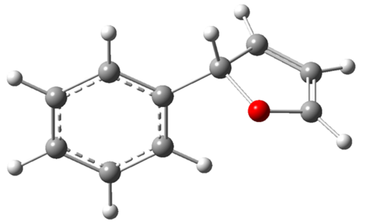
Cartesian Coordinates

C	-0.66222300	1.25516800	1.40377700
N	0.77120100	1.53163300	1.00067100
C	1.75090000	0.75840000	1.86099000
H	1.50757000	1.01659900	2.89083200
H	2.73808000	1.16041500	1.64493300
C	1.71708200	-0.74610100	1.65380700
H	1.93409900	-0.99338800	0.61270200
H	0.72211700	-1.13906400	1.86962700
C	0.98345500	1.35513400	-0.48810300
H	0.63905400	0.35236400	-0.73644300
H	0.31366700	2.06350700	-0.96926300
C	-1.66013800	2.23216000	0.80418600
H	-1.72135000	2.09803200	-0.27727500
H	-1.33504300	3.26150100	0.98867800
C	2.41214400	1.60427900	-0.94013300
H	3.08280200	0.84379000	-0.53528900
H	2.75952300	2.57313000	-0.56652700
H	-0.68285400	1.30970700	2.49151100
H	-0.88520800	0.23620700	1.09480600
H	0.94580400	2.51702100	1.20629200
I	-1.56915100	-1.84083300	-1.06485000
C	2.74202400	-1.43571500	2.55766900
H	2.53399500	-1.18119000	3.60134700
H	3.74033200	-1.04640300	2.33563500
C	2.73193900	-2.95285500	2.38627500
H	2.96583500	-3.23217400	1.35625300
H	3.46775900	-3.42664700	3.03820000
H	1.75077900	-3.36746300	2.62905700
C	2.50454600	1.58283200	-2.46793300
H	1.85241800	2.35794300	-2.88095000
H	2.12257000	0.62623300	-2.83698600
C	3.93301000	1.79194600	-2.96457200
H	4.59668700	1.00910600	-2.58975300
H	3.97615600	1.77428300	-4.05482800
H	4.32797700	2.75371100	-2.62835500
C	-3.05133700	2.01955000	1.40645900
H	-3.00377700	2.16873600	2.48926600
H	-3.35447200	0.98049200	1.24696800
C	-4.09290200	2.95715200	0.80075900

H	-4.18218100	2.79898000	-0.27661000
H	-5.07550300	2.79259700	1.24609900
H	-3.82122700	4.00300600	0.96332600

7

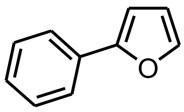


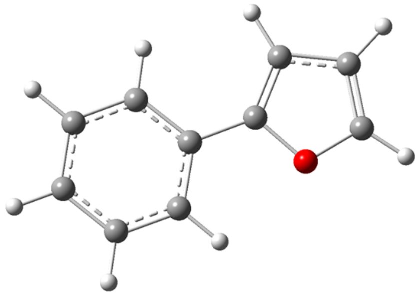


Cartesian Coordinates

C	1.01056000	-0.79126000	-0.10123400
C	1.81799500	-0.48364300	1.12719400
O	1.72990600	-0.08727800	-1.16790700
C	2.88599300	0.30713300	0.75323200
H	1.56092700	-0.83773700	2.11160000
C	2.81470400	0.52253100	-0.60993900
H	3.65360600	0.70565400	1.39830200
H	3.44447000	1.08545100	-1.27863700
H	1.03679300	-1.85792400	-0.35841900
C	-0.43309500	-0.33691400	-0.05726100
C	-1.46864300	-1.26570200	-0.10520600
C	-0.73801900	1.02054600	0.05663100
C	-2.79564300	-0.84770300	-0.03366600
H	-1.23917700	-2.32062500	-0.20035900
C	-2.06000100	1.44064900	0.11608400
H	0.06613000	1.74494000	0.09552500
C	-3.09336900	0.50567000	0.07439500
H	-3.59343200	-1.57887700	-0.06950600
H	-2.28740500	2.49609500	0.19883200
H	-4.12405300	0.83340000	0.12454400

8

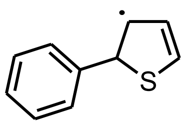


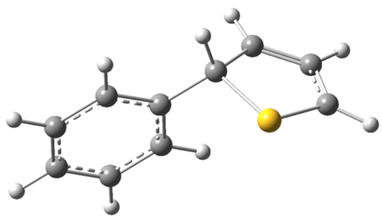


Cartesian Coordinates

C	0.43854900	0.05818500	0.00007900
C	1.10275200	-1.17624700	0.00010600
C	1.20696500	1.23187400	-0.00002700
C	2.49078300	-1.23188600	0.00006600
H	0.52734600	-2.09171000	0.00016200
C	2.59245400	1.17011600	-0.00006900
H	0.71755900	2.19705700	-0.00008100
C	3.24348700	-0.06181400	-0.00001700
H	2.98579200	-2.19493300	0.00009700
H	3.16765200	2.08742500	-0.00014100
H	4.32490600	-0.10759100	-0.00005300
C	-1.01432500	0.13027000	0.00010000
C	-1.90433700	1.16760200	0.00001100
O	-1.70718200	-1.05210500	-0.00032200
C	-3.21114200	0.59364000	0.00007300
H	-1.66263600	2.21673900	0.00002600
C	-3.03506700	-0.75127300	0.00007000
H	-4.15323100	1.11581200	0.00014100
H	-3.71063900	-1.58876300	0.00007700

9

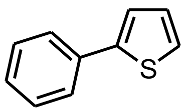


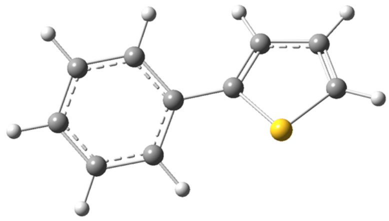


Cartesian Coordinates

C	0.76509900	-0.47190300	0.66871000
C	1.54147900	0.67320500	1.25482600
C	2.67972000	1.02296800	0.57521900
H	1.17803100	1.16542800	2.14551200
C	2.94803700	0.25748600	-0.55898600
H	3.32894100	1.83270400	0.88250100
H	3.77894800	0.37332100	-1.23707000
H	0.77970300	-1.33598500	1.33973300
C	-0.67550300	-0.16807800	0.31603100
C	-1.68194000	-1.08164200	0.62479000
C	-1.01729300	1.02072400	-0.33236700
C	-3.00775600	-0.81498400	0.29340500
H	-1.42824900	-2.00716400	1.12829300
C	-2.33868500	1.28929600	-0.66369000
H	-0.24038700	1.73473800	-0.57700800
C	-3.33949500	0.37096300	-0.35171600
H	-3.77892700	-1.53369200	0.54080900
H	-2.59032500	2.21566100	-1.16480300
H	-4.36982100	0.58091200	-0.60953900
S	1.75625700	-0.97588300	-0.83786000

10

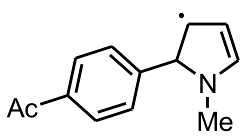


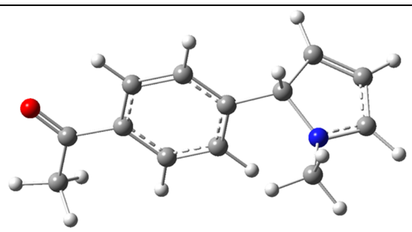


Cartesian Coordinates

C	1.07746083	0.12122117	0.00474500
C	1.73106283	-1.08982083	0.27180700
C	1.86281283	1.24666717	-0.28526000
C	3.11736483	-1.17237383	0.24994800
H	1.15154583	-1.97146583	0.51604300
C	3.24859083	1.16406717	-0.29611900
H	1.38319183	2.18773417	-0.52036400
C	3.88423083	-0.04576483	-0.03068300
H	3.59933283	-2.11857483	0.46135900
H	3.83400583	2.04609917	-0.52367100
H	4.96464583	-0.10973683	-0.04440300
C	-0.38489817	0.22979217	0.02874900
C	-1.14929317	1.34012017	0.29504300
C	-2.54588317	1.09788417	0.22997200
H	-0.72151317	2.29832417	0.55291800
C	-2.84207417	-0.19633783	-0.08951600
H	-3.29735317	1.85136917	0.41852600
H	-3.81246417	-0.65189383	-0.20535300
S	-1.41591717	-1.12918183	-0.31398300

11

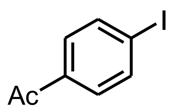
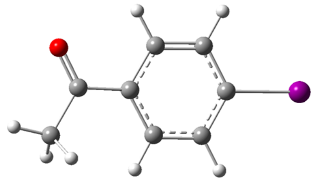




Cartesian Coordinates

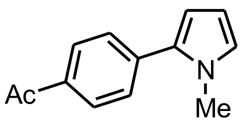
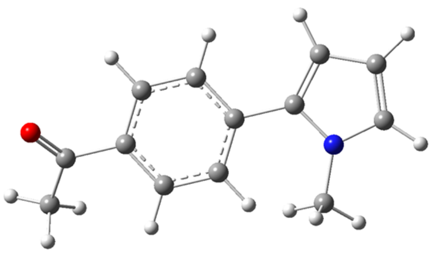
C	2.03167800	0.64048600	0.26967000
C	2.60590200	1.24456000	-0.99026000
N	2.80921100	-0.59634600	0.40147300
C	3.67972100	0.47759900	-1.39629200
C	3.82574000	-0.60095100	-0.52631100
H	4.30186600	0.65493900	-2.26049900
H	4.55364200	-1.39615300	-0.53738800
C	2.87681200	-1.27363500	1.67505700
H	1.86899600	-1.49021900	2.03214100
H	3.41043500	-2.21624600	1.55982000
H	3.39063500	-0.66946600	2.43451500
H	2.21493300	2.13989000	-1.44504000
H	2.23204300	1.28870600	1.14355800
C	0.53017200	0.41459000	0.20652000
C	-0.34169500	1.39073300	0.69323200

C	-0.00258700	-0.73372100	-0.37638300
C	-1.71281400	1.22674900	0.59105600
H	0.06071800	2.28298300	1.15860500
C	-1.37584300	-0.90585600	-0.47092900
H	0.66754300	-1.49693100	-0.74974000
C	-2.25228900	0.07444400	0.00840500
H	-2.38619100	1.98385800	0.96950200
H	-1.75803000	-1.81097400	-0.92213700
C	-3.73463900	-0.06943000	-0.07482400
C	-4.31130200	-1.32976400	-0.67522400
O	-4.47281800	0.81317900	0.33512800
H	-5.39677300	-1.27241000	-0.65372000
H	-3.97376400	-1.45536500	-1.70606500
H	-3.98112600	-2.20844000	-0.11719900

12		

Cartesian Coordinates

I	-0.59563195	0.05279575	1.17709436
C	1.51774005	0.09628675	1.17695936
C	2.17926505	1.32259075	1.17688436
C	2.22705205	-1.09941225	1.17698536
C	3.56460505	1.34108175	1.17693036
H	1.62474205	2.25046775	1.17679936
C	3.61595705	-1.06464225	1.17695536
H	1.71197505	-2.04945625	1.17703436
C	4.30203405	0.15259675	1.17696336
H	4.09247305	2.28493575	1.17692836
H	4.15276305	-2.00276925	1.17693836
C	5.79538005	0.22902775	1.17709136
C	6.58927705	-1.05414825	1.17707736
H	7.65051605	-0.81849125	1.17689736
H	6.34979705	-1.65550325	2.05667936
H	6.34949305	-1.65573925	0.29773836
O	6.35982405	1.31044175	1.17725936

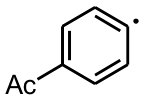
13		

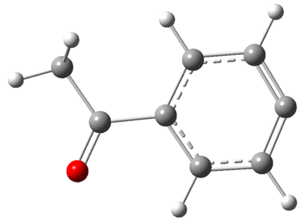
Cartesian Coordinates

C	4.47967953	6.04760489	-0.76846889
C	5.17720097	4.84008319	-0.72573001
C	5.17718514	7.25474990	-0.81130570
C	6.57191289	4.83982576	-0.72514984
H	4.62700792	3.88859162	-0.69118757
C	6.57232301	7.25463029	-0.81172682
H	4.62758785	8.20655072	-0.84517366
C	7.26974433	6.04745434	-0.76852084
H	7.12177576	3.88810652	-0.69083036
H	7.12200802	8.20655009	-0.84592229
C	2.93967953	6.04760489	-0.76846889
C	2.03648919	7.11904684	-0.80639138
N	2.21299831	4.86131322	-0.72645852
C	0.71496360	6.56045241	-0.78643276
H	2.28873909	8.17346190	-0.84373789
C	0.85513709	5.16660155	-0.73709460
H	-0.21780461	7.11398250	-0.80593264
H	0.09623867	4.38569742	-0.70943790
C	2.78543651	3.50820753	-0.67829725
H	3.72901529	3.53784143	-0.17462977
H	2.11963954	2.85784835	-0.15042669
H	2.92432741	3.14401914	-1.67477913
C	8.80974409	6.04681731	-0.76795050
C	9.57900348	5.05287186	0.12194412

O	9.42533542	6.84017403	-1.47825495
H	10.51401196	5.48426025	0.41274163
H	9.00031861	4.83399237	0.99493645
H	9.75716529	4.14976448	-0.42354231

14

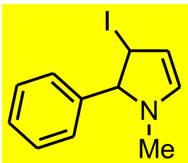


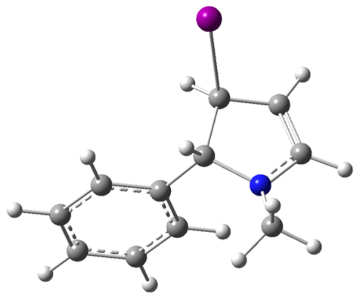


Cartesian Coordinates

C	2.57486800	0.13134700	0.00003000
C	2.03991800	-1.13369700	0.00001100
C	1.87078000	1.30730600	-0.00000400
C	0.64899200	-1.21690800	-0.00007500
H	2.65133700	-2.02705300	0.00000900
C	0.47742800	1.19881400	0.00001100
H	2.35082300	2.27746200	0.00001000
C	-0.13907100	-0.05819900	0.00001100
H	0.16078900	-2.18248500	-0.00009600
H	-0.11228400	2.10533600	-0.00001500
C	-1.62724600	-0.20856600	0.00000900
C	-2.48578100	1.03295900	-0.00002900
H	-3.53336100	0.74257000	0.00008800
H	-2.27754000	1.64567000	0.87949000
H	-2.27768800	1.64560000	-0.87961000
O	-2.14017500	-1.31568000	0.00004300

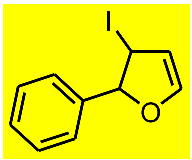
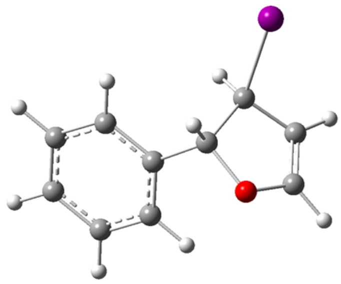
15





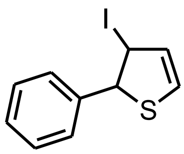
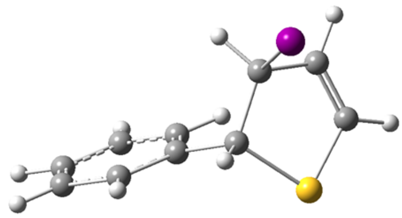
Cartesian Coordinates

C	-1.49291736	1.97368192	-0.69015833
C	-0.53584836	1.65146092	0.48242467
N	-1.54255636	3.43954792	-0.68595333
C	-0.33359936	2.92151092	1.16164467
C	-0.86736636	3.90626692	0.40133367
H	0.19934464	3.05188092	2.08744267
H	-0.83257336	4.97160592	0.58443467
C	-1.81928936	4.18683792	-1.88789833
H	-2.75077736	3.83531392	-2.33543833
H	-1.93765236	5.24174692	-1.63998633
H	-1.01762136	4.09226692	-2.63063933
H	-1.08982136	1.62719692	-1.64071033
C	-2.85513236	1.33550092	-0.47666733
C	-3.11794536	0.08588292	-1.03568233
C	-3.83010936	1.94634292	0.30933367
C	-4.33637436	-0.54518308	-0.81236633
H	-2.36461136	-0.39550108	-1.64849033
C	-5.04882736	1.31669492	0.53260467
H	-3.63117936	2.91787992	0.74258167
C	-5.30524636	0.06915892	-0.02688733
H	-4.53025536	-1.51351808	-1.25629833
H	-5.79945436	1.80076092	1.14487267
H	-6.25580336	-0.41946908	0.14566567
H	-0.81427836	0.78464792	1.06542467
I	1.50289464	0.79589292	-0.33320333

16		

Cartesian Coordinates

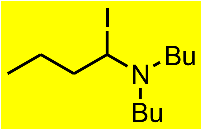
C	1.78018678	0.00261462	0.95982920
C	0.83740878	-0.12305038	-0.26045280
O	1.79110578	1.41664162	1.27790520
C	0.68266878	1.27231462	-0.69912180
C	1.22023478	2.06396262	0.23247820
H	0.17072178	1.59163662	-1.59050080
H	1.26360178	3.14172162	0.28233420
I	-1.16010422	-1.04660438	0.28681720
H	1.17730878	-0.83757938	-0.99964080
H	1.39942378	-0.51200538	1.83875120
C	3.17018978	-0.50200338	0.63013720
C	3.38060878	-1.88134538	0.59780020
C	4.22223478	0.35535962	0.32603720
C	4.62503178	-2.39564438	0.25973420
H	2.56599678	-2.55466438	0.83979420
C	5.46939778	-0.16095738	-0.01184780
H	4.06878978	1.42456562	0.36421520
C	5.67410378	-1.53476738	-0.04824380
H	4.77743778	-3.46737638	0.24172420
H	6.28265578	0.51461262	-0.24555080
H	6.64583678	-1.93383338	-0.30976980

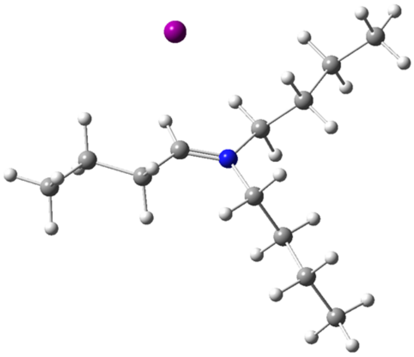
17		

Cartesian Coordinates

C	-0.03213101	1.36380457	-1.29332059
C	0.89366599	1.32195157	-0.06656559
C	1.10660199	2.67736057	0.44247241
H	0.59483099	0.57509357	0.65914441
C	0.76409999	3.64843857	-0.41638059
H	1.55383099	2.86075557	1.40839841
H	0.88489099	4.70947657	-0.25004759
H	0.32196599	0.71842757	-2.09045659
C	-1.45109401	0.96817957	-0.94193259
C	-2.02804801	-0.12736843	-1.58248359
C	-2.19017101	1.65164157	0.02748041
C	-3.32034401	-0.53605543	-1.26323559
H	-1.46536001	-0.66503343	-2.33611259
C	-3.47722801	1.24301157	0.34853941
H	-1.75732001	2.50768057	0.52882741
C	-4.04737501	0.14681557	-0.29590959
H	-3.75511401	-1.38689343	-1.77230959
H	-4.03842801	1.78078457	1.10222741
H	-5.05185201	-0.16938343	-0.04507459
S	0.08447799	3.10692157	-1.92653259
I	2.94788499	0.43811757	-0.64890059

18





Cartesian Coordinates

C	-0.05461300	1.11188300	0.83346800
N	0.95312000	0.37175500	0.53710000
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H	0.29241200	-1.05400600	1.89444800
H	2.04223100	-0.87743700	1.80996700
C	1.18941300	-2.11045800	0.24195500
H	2.08653100	-2.04831700	-0.37841800
H	0.32336100	-2.06597400	-0.42283700
C	1.93465800	0.73329000	-0.50543100
H	1.83846300	-0.00009500	-1.30640900
H	1.65617600	1.69798200	-0.91606700
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H	-0.56575100	2.31412800	-0.82087800
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H	3.67152900	-0.20545200	0.37834800
H	3.40688800	1.45785100	0.88274800
H	-0.70386300	0.73478300	1.61271100
C	1.19434400	-3.44140900	0.99499600
H	0.29016100	-3.51225400	1.60716200
H	2.04149600	-3.46505600	1.68764300
C	1.26829400	-4.63817100	0.04939900
H	2.18039600	-4.60758500	-0.55157700
H	1.26274800	-5.57880800	0.60285100
H	0.41761900	-4.64664800	-0.63610600
C	-1.57054800	3.10491100	0.92801100
H	-1.35716700	3.22553100	1.99371300
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C	-1.89928200	4.45905100	0.30788100
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C	5.78082200	1.28939400	-0.55835900
H	6.10984400	0.29917700	-0.23415400
H	6.45952300	1.62811400	-1.34292900
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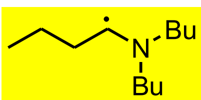
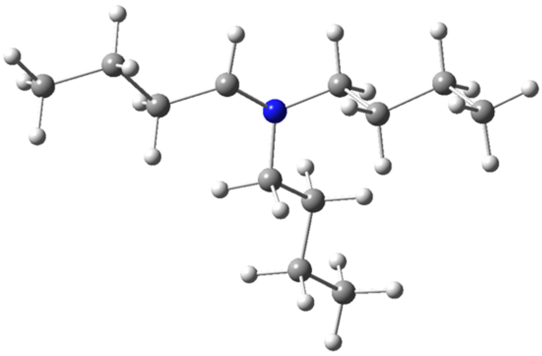
19





Cartesian Coordinates

C	-1.13730784	-0.89454655	0.46010264
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C	1.18762016	-1.15526955	1.06629464
H	0.78127816	-1.89177355	1.76342164
H	1.92588016	-0.57732655	1.62561964
C	1.87696416	-1.88039855	-0.09331236
H	2.29739216	-1.14717855	-0.78918836
H	1.12608916	-2.44814455	-0.65172536
C	0.43406916	0.88326945	-0.14817336
H	0.65403216	0.57057945	-1.18108836
H	-0.44357584	1.52686245	-0.20122936
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H	-2.23363384	0.37050945	-0.89219536
H	-2.53102484	0.71353745	0.79671164
C	1.60000616	1.70988245	0.38609264
H	2.52765016	1.13211645	0.35095164
H	1.41799416	1.95100545	1.43840264
H	-1.28492384	-1.78523055	1.06217164
C	2.98701716	-2.81358755	0.38508964
H	2.56643916	-3.54818855	1.08025864
H	3.72155216	-2.23677955	0.95736464
C	3.68934116	-3.53963655	-0.76071336
H	4.15089916	-2.82831055	-1.45046736
H	4.47352516	-4.20421455	-0.39197936
H	2.98060316	-4.14364455	-1.33311336
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H	-3.75869084	-1.45678855	1.01702064
H	-3.45061684	-1.80486855	-0.67223036
C	-4.86484884	-0.20699855	-0.34857236
H	-4.75393984	0.24805545	-1.33636436
H	-5.74479084	-0.85303955	-0.37581536
H	-5.06223484	0.59660745	0.36562764
C	1.79581916	2.99929445	-0.41160236
H	0.88270716	3.60109145	-0.35823936
H	1.93878616	2.75130245	-1.46857536
C	2.98210516	3.82390545	0.08364164
H	3.91238216	3.25496245	0.00886864
H	3.10223616	4.73939345	-0.49905436
H	2.85112916	4.10846545	1.13083264

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