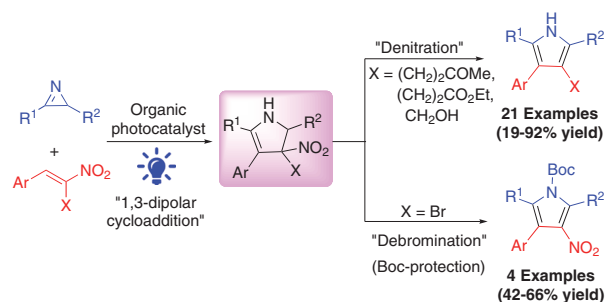


Organo-photocatalytic Synthesis of Functionalized Pyrroles from 2*H*-Azirines and α -Substituted Nitroalkenes

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Abstract An efficient organo-photocatalytic method for the synthesis of tetrasubstituted pyrroles bearing a ketone, ester, alcohol, or nitro group at the 3-position has been developed. The reaction involves visible-light-mediated formal [3+2] dipolar cycloaddition between 2*H*-azirines and α -substituted nitroalkenes followed by a denitration or debromination sequence. The notable features of the protocol are excellent regioselectivity, wide substrate scope, and high yields of the products.

Key words 2*H*-azirines, α -substituted nitroalkenes, organophotocatalysis, dipolar cycloaddition, functionalized pyrroles

The pyrrole moiety is present in natural heme and chlorophyll pigments, several medicinally valuable natural products, such as pyrrolostatin, pyrrolomycins, marinopyrroles, prodigiosin, and lamellarins, and some synthetic drugs and agrochemicals (Figure 1).¹ Consequently, there are several elegant classical and contemporary synthetic protocols for accessing pyrrole derivatives.² Recent progress in the field of visible-light-mediated heterocycle synthesis³ has inspired the discovery of several elegant protocols for the synthesis of pyrrole derivatives, including organometallic photocatalyst-mediated protocols such as the Hantzsch synthesis of 2,5-diaryl-substituted pyrroles,⁴ the Paal-Knorr type synthesis of 1,3,4-trisubstituted pyrroles via condensation of aryl azides with aldehydes,⁵ and the synthesis of the 2,3-fused pyrrole motif via coupling of naphthols and naphthoquinones with 2*H*-azirines.⁶ Moreover, strategies employing organic dyes as photocatalysts for the synthesis of thio-functionalized pyrroles⁷ and tetra-/trisub-

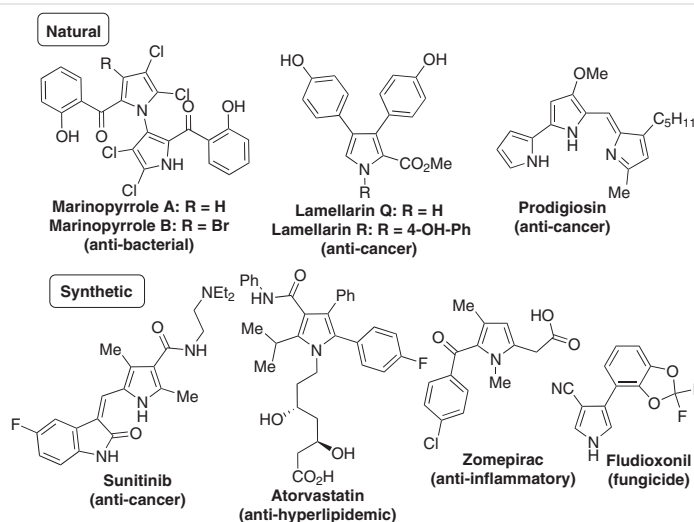
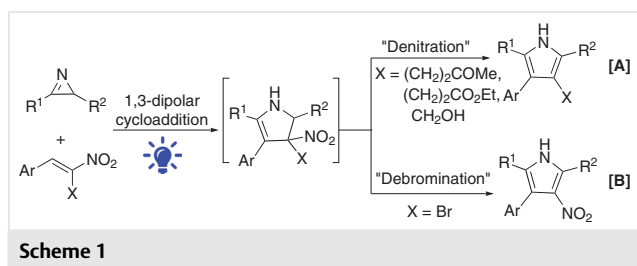


Figure 1 Pyrrole scaffolds in natural and synthetic medicinal compounds

stituted pyrroles through formal [3+2] cycloaddition of 2*H*-azirines with alkynes⁸ or nitroalkenes⁹ have been reported. Our group recently employed pyrylium salts in a dual role as a photosensitizer and dipolarophile in the dipolar cycloaddition with 2*H*-azirines for accessing chalcone-bearing tetrasubstituted pyrroles.¹⁰

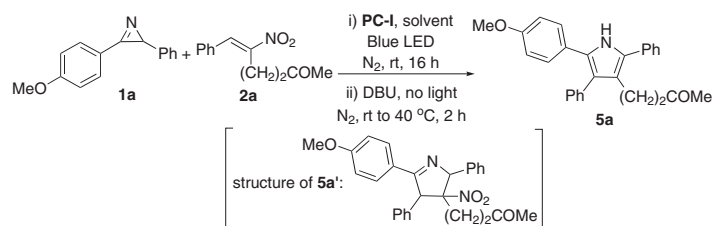
Herein we present an extension of our previous work⁹ utilizing α -substituted nitroalkenes as dipolarophiles in organo-photocatalytic formal [3+2] cycloadditions with azirines to prepare tetrasubstituted pyrroles (Scheme 1).



α -Substituted nitroalkenes can be prepared through the Rauhut–Currier (RC) or Morita–Baylis–Hillman (MBH) reaction of ethyl acrylate, methyl vinyl ketone, or formaldehyde with nitroalkenes.¹¹ We anticipated that the photocatalytic denitrative cycloaddition of these α -substituted nitroalkenes with 2*H*-azirines would lead to the installation of ester, ketone, or alcohol functionalities in the tetrasubstituted pyrrole products (Scheme 1, pathway A). On the other hand, α -bromo nitroalkene substrates would allow direct access to nitro-substituted pyrroles upon dipolar cycloaddition followed by debromination instead of the denitration sequence (Scheme 1, pathway B).

For preliminary investigations, 3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine (**1a**) and (*E*)-5-nitro-6-phenylhex-5-en-2-one (**2a**) were selected as the model substrates. 9-Mesityl-10-methylacridinium tetrafluoroborate (Mes-Acr⁺BF₄⁻; **PC-I**) was employed as the photocatalyst after consideration of the thermodynamic feasibility of the single-electron transfer between **PC-I** and **1a**, owing to their compatible redox potentials (Table 1).^{8,9}

Table 1 Optimization of Reaction Conditions^{a,b}



Entry	Ratio 1a / 2a	PC-I (mol%)	Solvent	Step (ii) DBU (equiv); temp.	Yield of 5a (%) ^c
1 ^d	2:1	3	CH ₂ Cl ₂	2; rt	complex mixture
2	2:1	3	CH ₂ Cl ₂	2; rt	19 (5a' : 14%)
3 ^e	2:1	3	CH ₂ Cl ₂	2; rt	32
4	2:1	3	CH ₂ Cl ₂	2; 40 °C	46
5	2:1	3	CH ₂ Cl ₂	3; 40 °C	41
6	2:1	3	DCE	2; 40 °C	35
7	2:1	3	MeOH	2; 40 °C	no reaction
8	2:1	3	MeCN	2; 40 °C	70
9	1:1	3	MeCN	2; 40 °C	61
10	1:2	3	MeCN	2; 40 °C	25
11	3:1	3	MeCN	2; 40 °C	92
12	3:1	2	MeCN	2; 40 °C	68
13	3:1	5	MeCN	2; 40 °C	25

^a All reactions were carried out with 0.2 mmol of **2a** in 4 mL of solvent.

^b The first step was always carried out at rt under 450 nm blue LED irradiation for 16 h, and the light source was removed for the second step.

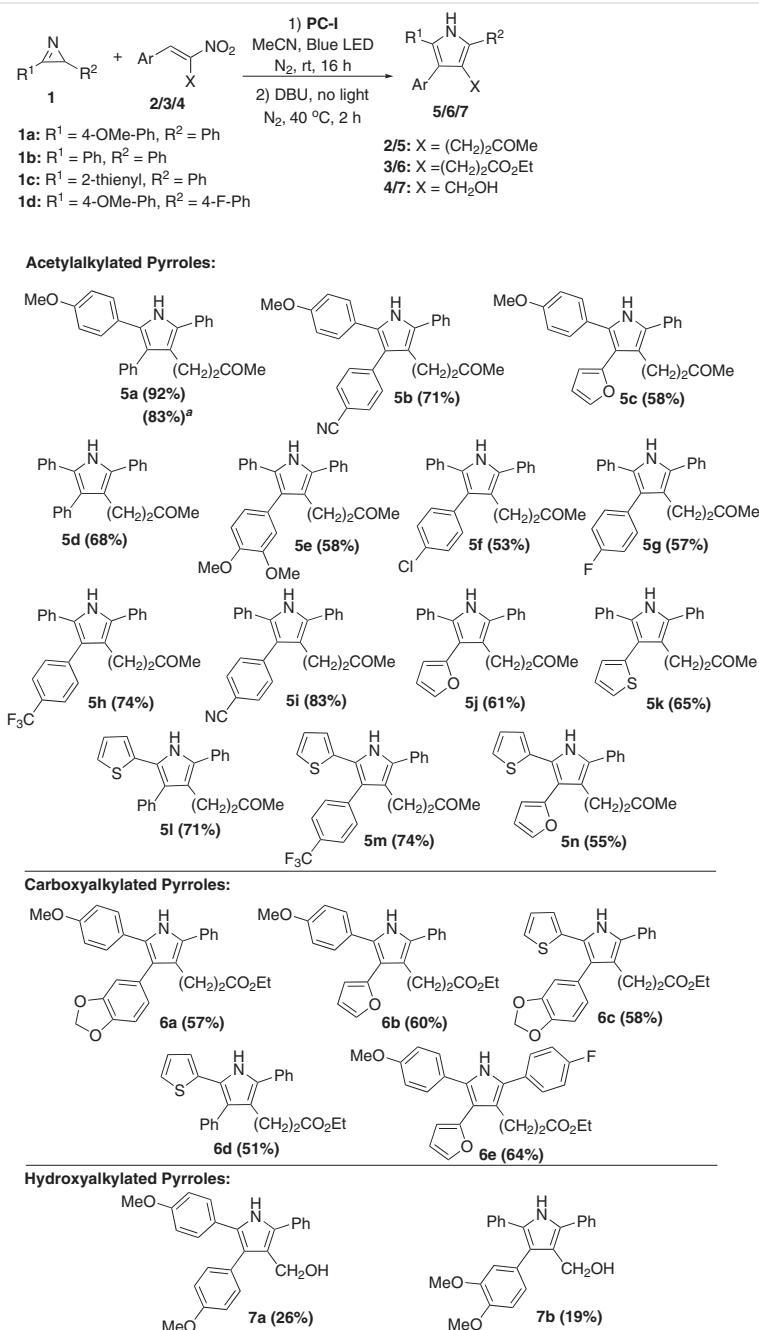
^c Yields of isolated product.

^d Single step reaction.

^e Both steps were continued for 48 h.

Initially, a 2:1 mixture of **1a** and **2a** in CH₂Cl₂ was irradiated with 450 nm blue LED in the presence of **PC-I** (3 mol%) and DBU (2 equiv), but this led to the formation of a complex mixture of products (Table 1, entry 1). Therefore, DBU was added into the reaction mixture after it had been irradiated with blue LED for 16 h (disappearance of **2a** evidenced by TLC) and the light source was then removed. In

this case, product **5a** was isolated in 19% yield along with 14% of **5a'** (identified by HRMS; see figure S-1 in the Supporting Information) after the reaction mixture had been stirred at room temperature for 2 h (Table 1, entry 2). The yield of **5a** increased to 32% when the reaction time for both the steps was increased to 48 h (Table 1, entry 3). However, heating of the reaction mixture to 40 °C after DBU

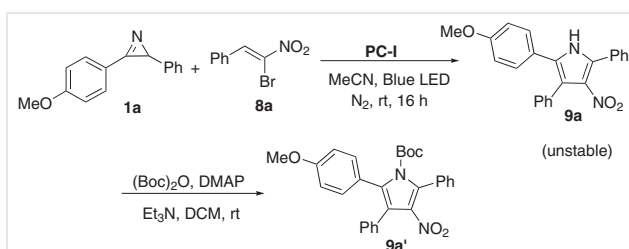


Scheme 2 Scope of the reaction: variation of RC/MBH adducts of nitroalkenes. *Reagents and conditions:* Unless otherwise noted, a mixture of **1** (0.6 mmol), **2/3/4** (0.2 mmol), and **PC-I** (0.006 mmol) in MeCN (4 mL) was irradiated with a 450 nm blue LED for 16 h at rt, followed by removal of the light source, addition of DBU (0.4 mmol), and heating at 40 °C. Isolated yields are given in parentheses. ^a Yield of the reaction at 5 mmol scale of **2a**.

addition led to a significant increase in the yield of **5a** (Table 1, entry 4). Further changes in the reaction parameters, such as increasing the amount of DBU to 3 equivalents (Table 1, entry 5) or changing the reaction solvent to DCE (Table 1, entry 6) or MeOH (Table 1, entry 7) did not improve the yield. However, performing the reaction in MeCN provided **5a** in 70% yield (Table 1, entry 8). We varied the substrate ratio of **1a:2a** to 1:1, 1:2, and 3:1 (Table 1, entries 9–11) and isolated **5a** in 61%, 25%, and 92% yield, respectively. The conditions employed in Table 1, entry 11 were finally selected as the optimal conditions because varying the catalyst loading to 2 mol% (Table 1, entry 12) and 5 mol% (Table 1, entry 13) led to reduced yields of **5a**. After establishing the optimal conditions, we investigated the scope of various RC and MBH adducts of nitroalkenes in the reaction with 2*H*-azirines (Scheme 2).

For this purpose, diaryl or heteroaryl-aryl 2*H*-azirines **1a–1d** bearing electron-releasing and electron-withdrawing groups were selected as reaction partners. Initially, we screened various (*E*)-5-nitro-6-arylhex-5-en-2-ones **2** (RC adducts of methyl vinyl ketone with aryl nitroalkenes) as dipolarophiles to access acetylkylated pyrroles **5**. 3-(4-Methoxyphenyl)-2-phenyl-2*H*-azirine (**1a**) reacted efficiently not only with (*E*)-5-nitro-6-phenylhex-5-en-2-one (**2a**) and (*E*)-4-(2-nitro-5-oxohex-1-en-1-yl) benzonitrile (**2b**) but also with heteroaryl substrate **2c** to afford the corresponding pyrroles **5a–5c** in good yields. Satisfyingly, a 5 mmol scale reaction of **1a** and **2a** furnished product **5a** in 83% yield. Furthermore, 2,3-diphenyl-2*H*-azirine (**1b**) reacted efficiently with various RC adducts **2** featuring aryl groups bearing electron-releasing and -withdrawing substituents or heteroaryl groups under the optimized reaction conditions to yield the corresponding acetylkylated products **5d–5k** in 53–83% yields. Similarly, the heteroaryl-aryl 2*H*-azirine **1c** provided tetrasubstituted acetylkylated pyrrole products **5l–5n** in good yields upon reaction with the respective α -acetylkylated nitroalkenes. After confirming the suitability of RC adducts of methyl vinyl ketone and (hetero)aryl nitroalkenes as substrates in this photocatalytic denitrative dipolar cycloaddition reaction with 2*H*-azirines, we employed the RC adducts of nitroalkenes with ethyl acrylate **3** and MBH adducts of (hetero)aryl nitroalkenes with formaldehyde **4** in the reaction, intending to synthesize carboxyalkylated and hydroxyalkylated pyrrole products **6** and **7**, respectively. In this case, various carboxyalkylated (hetero)aryl nitroalkenes **3** reacted efficiently with electron-releasing OMe-bearing **1a**, 2-thienyl-substituted **1c**, and electron-withdrawing fluoro-bearing **1d** to furnish the corresponding products **6a–6e** in 51–64% yields. However, the reactions between hydroxyalkylated MBH adducts of nitroalkenes **4** and 2*H*-azirines **1a** and **1b** under the standard conditions led to complex mixtures and products **7a** and **7b** were isolated in low yields (Scheme 2).

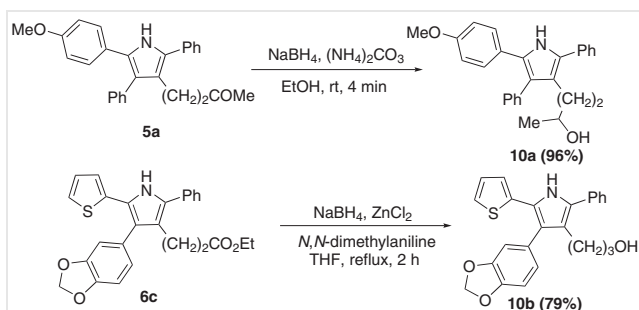
In addition, we planned to synthesize nitro-substituted pyrroles by using α -bromo nitroalkenes **8** as dipolarophiles in the reaction; we anticipated debromination to occur instead of denitration owing to the better leaving group ability of the bromo substituent. Consequently, when a mixture of 3-(4-methoxyphenyl)-2-phenyl-2*H*-azirine (**1a**), (*Z*)-(2-bromo-2-nitrovinyl)benzene (**8a**), and **PC-I** in acetonitrile was irradiated with blue LED for 16 h, the expected nitrated pyrrole product **9a** was formed. However, the desired product could not be purified because of its unstable nature. Therefore, crude **9a** was subjected to Boc protection, affording Boc-protected nitropyrrole **9a'** in 56% yield over two steps (Scheme 3).



Scheme 3 Synthesis of a nitro-substituted pyrrole

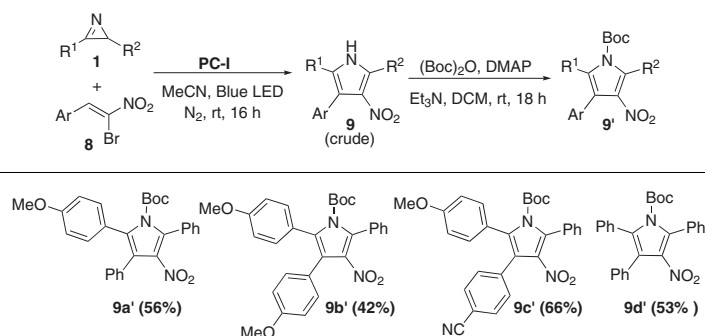
Following the same protocol, nitro-substituted pyrroles **9b**, **9c**, and **9d** were also isolated in crude form and immediately subjected to Boc protection, providing the corresponding Boc-protected nitropyrroles **9b'**, **9c'**, and **9d'** in good yields (Table 2).

Thus far, we had prepared tetrasubstituted pyrrole products bearing ketone, ester, and nitro functionalities in good to excellent yields, whereas the alcohol-group-bearing pyrroles **7a** and **7b** were isolated in low yields. We could however gain access to pyrroles bearing secondary and primary alcohol functionalities by the reduction of the ketone and ester groups in the representative pyrrole derivatives **5a** and **6c** (Scheme 4).^{12,13}



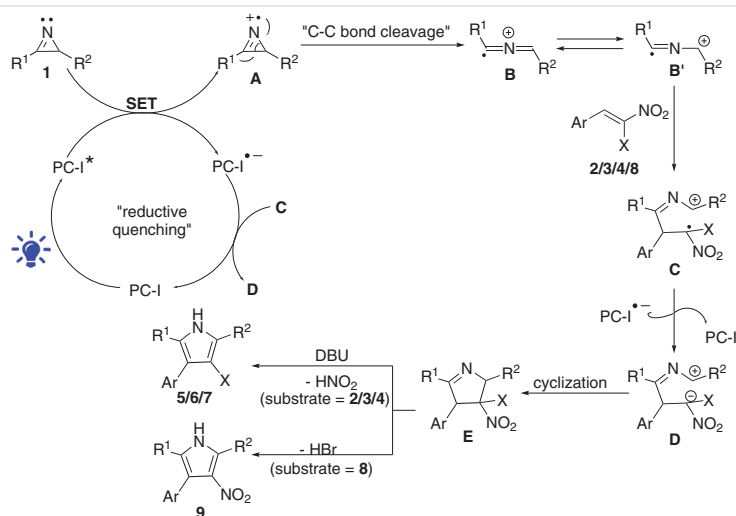
Scheme 4

The mechanism proposed on the basis of literature reports and our previous work is illustrated in Scheme 5.

Table 2 Synthesis of Boc-Protected Nitropyrroles^{a,b}

^a Reaction conditions for first step: A mixture of **1** (0.6 mmol), **8** (0.2 mmol), and **PC-I** (0.006 mmol) in MeCN (4 mL) was irradiated with a 450 nm blue LED for 16 h at rt.

^b Reaction conditions for second step: Crude **9** (0.1 mmol), (Boc)₂O (0.11 mmol), Et₃N (0.11 mmol), and DMAP (0.001) in CH₂Cl₂ (2 mL) for 18 h at rt.

**Scheme 5** Plausible mechanism

Single-electron reduction of the excited photocatalyst **PC-I*** by the strongly reducing 2*H*-azirine **1** results in the generation of 2*H*-azirinyl radical cation **A**. The radical cation **A** undergoes C–C bond homolysis to form 2-aza-allenyl radical cation **B** and its electroisomer **B'**, which adds onto the β-position of nitroalkenes **2/3/4/8**, furnishing intermediate **C**. The reduced photocatalyst transfers a single electron to intermediate **C**, generating intermediate **D** and completing the catalytic cycle. Intermediate **D**, upon intramolecular cyclization followed by DBU-mediated denitration or by debromination, is converted into the tetrasubstituted pyrroles **5/6/7** or **9**.

In summary, we have developed a simple method for direct access to tetrasubstituted pyrroles possessing ketone, ester, alcohol, and nitro functional groups under photocatalytic conditions. The reaction employs the organic dye Mes-Acr⁺BF₄⁻ as a photocatalyst in the formal [3+2] dipolar cycloaddition reaction between 2*H*-azirines and α-substituted

nitroalkenes. The reaction proceeds in a highly regioselective manner because initial attack of the photocatalytically generated radical species takes place exclusively on the β-position of the nitroalkene substrate. Furthermore, the leaving group ability of the nitro or bromo group was exploited for installing various functionalities at the 3-position in the tetrasubstituted pyrrole products. In addition, reduction of the ester and ketone groups in the pyrrole derivatives provided pyrroles substituted with primary and secondary alcohols.

All reactions were monitored by TLC; visualization was effected with UV and/or by developing in iodine. Melting points are uncorrected. NMR spectra were recorded on a Bruker Avance spectrometer at 300/400 MHz (¹H), 75/100/125 MHz (¹³C), and 376 MHz (¹⁹F). Chemical shifts are reported in δ (ppm) relative to TMS as the internal standard for ¹H and ¹³C or TFA as the internal standard for ¹⁹F. Abbrevia-

tions s, d, t, q, m, dd refer to singlet, doublet, triplet, quartet, multiplet, and doublet of doublet, respectively. ESI-HRMS spectra were recorded on an Agilent 6520-Q-ToF LC/MS system.

The 2*H*-azirines **1a–1d** were synthesized from the corresponding ketones by following the standard procedure reported in literature.¹⁰ RC adducts **2** and **3** of nitroalkenes with methyl vinyl ketone and ethyl acrylate, respectively, and MBH adducts **4** of nitroalkenes with formaldehyde were synthesized by following standard protocols reported in the literature.¹⁴ All other chemicals, catalysts, and anhydrous solvents were used as received from commercial sources.

Synthesis of 5, 6, and 7: General Procedure

2*H*-Azirine **1** (0.6 mmol), α -substituted nitroalkene **2**, **3**, or **4** (0.2 mmol), and photocatalyst Mes-Acr⁺BF₄⁻ (2.4 mg, 0.006 mmol, 3 mol%) were dissolved in anhydrous acetonitrile (4 mL) in a 5 mL vial equipped with a magnetic bar. The resulting reaction mixture was degassed by three freeze–pump–thaw cycles by using a syringe needle. The vial was irradiated with a 450 nm blue LED, and the reaction temperature was maintained at around 25 °C by water circulation through an attached cooling device. After 16 h of irradiation (TLC monitoring for reaction completion), the light source was removed and DBU (0.06 mL, 0.4 mmol) was added to the reaction mixture, which was then stirred at 40 °C for an additional 2 h (TLC monitoring for reaction completion). The solvent was evaporated and the residue was dissolved in ethyl acetate (10 mL) and washed with water (3 × 10 mL) and brine (3 × 10 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. Purification of the crude product by column silica gel chromatography (60–120 mesh) with hexane/ethyl acetate as the eluent afforded pure product **5**, **6**, or **7**.

Synthesis of 9': General Procedure

2*H*-Azirine **1** (0.6 mmol), α -bromo nitroalkene **8** (0.2 mmol), and photocatalyst Mes-Acr⁺BF₄⁻ (2.4 mg, 0.006 mmol, 3 mol%) were dissolved in anhydrous acetonitrile (4 mL) in a 5 mL vial equipped with a magnetic bar. The resulting reaction mixture was degassed by three freeze–pump–thaw cycles by using a syringe needle. The vial was irradiated with a 450 nm blue LED, and the reaction temperature was maintained at around 25 °C for 16 h (TLC monitoring for reaction completion) by water circulation through an attached cooling device. The solvent was evaporated, and the residue was dissolved in ethyl acetate (10 mL) and washed with water (3 × 10 mL) and brine (3 × 10 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to obtain crude **9** that was used in the next step without purification.

Di-*tert*-butylcarbonate (24 mg, 0.025 mL, 0.11 mmol), triethylamine (0.015 mL, 0.11 mmol), and DMAP (1.2 mg, 0.01 mmol) were added to crude **9** (0.1 mmol) in CH₂Cl₂ (2 mL). The reaction mixture was stirred at room temperature for 18 h (TLC monitoring), concentrated under reduced pressure, and subjected to purification by silica gel column chromatography with hexane/ethyl acetate as the eluent to afford pure **9a'**.

Synthesis of 4-(5-(4-methoxyphenyl)-2,4-diphenyl-1*H*-pyrrol-3-yl)butan-2-ol (**10a**)¹²

NaBH₄ (4 mg, 0.1 mmol) and (NH₄)₂CO₃ (10 mg, 0.1 mmol) were added to a solution of 4-(5-(4-methoxyphenyl)-2,4-diphenyl-1*H*-pyrrol-3-yl)butan-2-one (**5a**; 40 mg, 0.1 mmol) in EtOH (2 mL), and the reaction mixture was stirred at room temperature for 4 min (TLC moni-

toring). After completion of the reaction, the mixture was filtered through a pad of Celite®, and the filtrate was concentrated under reduced pressure to give pure **10a**.

Synthesis of 3-(4-(benzo[*d*][1,3]dioxol-5-yl)-2-phenyl-5-(thiophen-2-yl)-1*H*-pyrrol-3-yl)propan-1-ol (**10b**)¹³

NaBH₄ (8 mg, 0.2 mmol), ZnCl₂ (13.6 mg, 0.1 mmol), and *N,N*-dimethylaniline (12 mg, 0.1 mmol) were added to a solution of ethyl 3-(4-(benzo[*d*][1,3]dioxol-5-yl)-2-phenyl-5-(thiophen-2-yl)-1*H*-pyrrol-3-yl)propanoate (**6c**; 45 mg, 0.1 mmol) in anhydrous THF (5 mL). The reaction mixture was heated to reflux for 2 h (TLC monitoring) under nitrogen. Upon completion of the reaction, ice cold 10% NH₄Cl solution (5 mL) was added, and the reaction mixture was extracted with chloroform (3 × 10 mL). The organic layer was washed with water (3 × 10 mL) and brine (3 × 10 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. Purification of the crude product was achieved by silica gel column chromatography with hexane/ethyl acetate as the eluent to afford pure **10b**.

4-(5-(4-Methoxyphenyl)-2,4-diphenyl-1*H*-pyrrol-3-yl)butan-2-one (**5a**)

White solid; isolated yield 92% (73 mg); *R*_f = 0.50 (20% EtOAc/hexane); mp 183–184 °C.

¹H NMR (300 MHz, CDCl₃): δ = 8.13 (s, 1 H), 7.40–7.50 (m, 4 H), 7.25–7.34 (m, 6 H, merged with solvent peak), 7.13 (d, *J* = 7.9 Hz, 2 H), 6.77 (d, *J* = 8.4 Hz, 2 H), 3.76 (s, 3 H), 2.94 (t, *J* = 8.0 Hz, 2 H), 2.35 (t, *J* = 8.0 Hz, 2 H), 1.86 (s, 3 H).

¹³C NMR (125 MHz, CDCl₃): δ = 208.8, 158.3, 136.2, 133.3, 130.5, 128.9, 128.8, 128.7, 128.5, 128.0, 127.1, 126.7, 126.4, 125.4, 122.9, 119.7, 114.0, 55.2, 44.5, 29.6, 19.2.

HRMS: *m/z* calcd for C₂₇H₂₅NO₂ [M + H]⁺: 396.1958; found: 396.1960.

4-(2-(4-Methoxyphenyl)-4-(3-oxobutyl)-5-phenyl-1*H*-pyrrol-3-yl)benzoxonitrile (**5b**)

White solid; isolated yield 71% (60 mg); *R*_f = 0.50 (25% EtOAc/hexane); mp 182–183 °C.

¹H NMR (300 MHz, CDCl₃): δ = 8.28 (s, 1 H), 7.60 (d, *J* = 8.2 Hz, 2 H), 7.29–7.49 (m, 7 H), 7.08 (d, *J* = 8.7 Hz, 2 H), 6.80 (d, *J* = 8.7 Hz, 2 H), 3.78 (s, 3 H), 2.95 (t, *J* = 8.2 Hz, 2 H), 2.32 (t, *J* = 8.2 Hz, 2 H), 1.88 (s, 3 H).

¹³C NMR (125 MHz, CDCl₃): δ = 208.2, 158.8, 141.7, 132.9, 132.3, 130.9, 129.8, 129.5, 129.0, 128.5, 127.2, 127.1, 124.6, 120.9, 119.2, 119.1, 114.3, 109.7, 55.3, 44.3, 29.6, 18.9.

HRMS: *m/z* calcd for C₂₈H₂₄N₂O₂ [M + H]⁺: 421.1911; found: 421.1903.

4-(4-(Furan-2-yl)-5-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrol-3-yl)butan-2-one (**5c**)

White solid; isolated yield 58 % (45 mg); *R*_f = 0.50 (20% EtOAc/hexane); mp 123–124 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.16 (s, 1 H), 7.40–7.47 (m, 5 H), 7.25–7.32 (m, 3 H, merged with solvent peak), 6.85–6.88 (m, 2 H), 6.41 (dd, *J* = 3.2, 1.9 Hz, 1 H), 6.19 (d, *J* = 3.2 Hz, 1 H), 3.81 (s, 3 H), 2.95–3.00 (m, 2 H), 2.54–2.58 (m, 2 H), 2.02 (s, 3 H).

¹³C NMR (75 MHz, CDCl₃): δ = 208.8, 158.9, 149.8, 141.3, 133.0, 130.8, 129.0, 128.9, 128.3, 127.2, 1227.0, 125.1, 120.3, 114.1, 112.2, 111.0, 107.8, 55.3, 44.9, 29.7, 19.6.

HRMS: *m/z* calcd for C₂₅H₂₃NO₃ [M + H]⁺: 386.1751; found: 386.1743.

4-(2,4,5-Triphenyl-1H-pyrrol-3-yl)butan-2-one (5d)

White solid; isolated yield 68% (50 mg); $R_f = 0.50$ (15% EtOAc/hexane); mp 171–172 °C.

^1H NMR (400 MHz, CDCl_3): $\delta = 8.21$ (s, 1 H), 7.51 (d, $J = 7.4$ Hz, 2 H), 7.45 (t, $J = 7.6$ Hz, 2 H), 7.29–7.38 (m, 6 H), 7.15–7.23 (m, 5 H), 2.94 (t, $J = 8.1$ Hz, 2 H), 2.35 (t, $J = 8.2$ Hz, 2 H), 1.88 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 208.7$, 136.1, 133.2, 132.7, 130.4, 129.3, 129.0, 128.8, 128.5, 128.2, 127.1, 126.9, 126.6, 126.5, 126.3, 123.8, 120.0, 44.4, 29.6, 19.1.

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{23}\text{NO}$ [M + H] $^+$: 366.1852; found: 366.1846.

4-(4-(3,4-Dimethoxyphenyl)-2,5-diphenyl-1H-pyrrol-3-yl)butan-2-one (5e)

White solid; isolated yield 58% (49 mg); $R_f = 0.50$ (25% EtOAc/hexane); mp 192–193 °C.

^1H NMR (400 MHz, CDCl_3): $\delta = 8.20$ (s, 1 H), 7.42–7.51 (m, 4 H), 7.29–7.33 (m, 1 H), 7.13–7.24 (m, 5 H), 6.88 (s, 2 H), 6.82 (s, 1 H), 3.92 (s, 3 H), 3.76 (s, 3 H), 2.96 (t, $J = 8.2$ Hz, 2 H), 2.39 (t, $J = 8.2$ Hz, 2 H), 1.91 (s, 3 H).

^{13}C NMR (125 MHz, CDCl_3): $\delta = 208.7$, 148.8, 147.7, 133.2, 132.7, 129.3, 129.0, 128.8, 128.6, 128.5, 127.1, 126.9, 126.5, 126.3, 123.5, 122.5, 120.0, 113.7, 111.4, 55.8, 55.8, 44.5, 29.7, 19.2.

HRMS: m/z calcd for $\text{C}_{28}\text{H}_{27}\text{NO}_3$ [M + H] $^+$: 426.2064; found: 426.2068.

4-(4-(4-Chlorophenyl)-2,5-diphenyl-1H-pyrrol-3-yl)butan-2-one (5f)

White solid; isolated yield 53% (42 mg); $R_f = 0.50$ (15% EtOAc/hexane); mp 158–159 °C.

^1H NMR (400 MHz, CDCl_3): $\delta = 8.19$ (s, 1 H), 7.42–7.50 (m, 4 H), 7.33 (d, $J = 8.2$ Hz, 4 H), 7.17–7.25 (m, 6 H, merged with solvent peak), 2.93 (t, $J = 8.1$ Hz, 2 H), 2.35 (t, $J = 8.2$ Hz, 2 H), 1.90 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 208.5$, 134.6, 133.1, 132.4, 132.3, 131.7, 129.5, 129.1, 129.0, 128.8, 128.7, 127.2, 127.1, 126.7, 126.6, 122.3, 119.8, 44.4, 29.6, 19.0.

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{22}\text{ClNO}$ [M + H] $^+$: 400.1463; found: 400.1461.

4-(4-(4-Fluorophenyl)-2,5-diphenyl-1H-pyrrol-3-yl)butan-2-one (5g)

White solid; isolated yield 57% (44 mg); $R_f = 0.50$ (15% EtOAc/hexane); mp 160–161 °C.

^1H NMR (400 MHz, CDCl_3): $\delta = 8.21$ (s, 1 H), 7.42–7.50 (m, 4 H), 7.17–7.33 (m, 8 H, merged with solvent peak), 7.05 (t, $J = 8.4$ Hz, 2 H), 2.92 (t, $J = 8.0$ Hz, 2 H), 2.35 (t, $J = 8.0$ Hz, 2 H), 1.89 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 208.5$, 161.8 (d, $J_{\text{C-F}} = 243.7$ Hz), 133.1, 132.5, 132.0, 131.9, 129.4, 129.0, 128.6, 127.1, 127.0, 126.6, 126.5, 122.6, 119.9, 115.5 (d, $J_{\text{C-F}} = 21.1$ Hz), 44.4, 29.6, 19.0.

^{19}F NMR (376 MHz, CDCl_3): $\delta = -116.1$ (s).

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{22}\text{FNO}$ [M + H] $^+$: 384.1758; found: 384.1750.

4-(2,5-Diphenyl-4-(4-(trifluoromethyl)phenyl)-1H-pyrrol-3-yl)butan-2-one (5h)

White solid; isolated yield 74% (64 mg); $R_f = 0.50$ (20% EtOAc/hexane); mp 158–159 °C.

^1H NMR (400 MHz, CDCl_3): $\delta = 8.24$ (s, 1 H), 7.60 (d, $J = 7.8$ Hz, 2 H), 7.41–7.51 (m, 6 H), 7.33 (t, $J = 7.2$ Hz, 1 H), 7.16–7.26 (m, 5 H, merged with solvent peak), 2.95 (t, $J = 8.2$ Hz, 2 H), 2.33 (t, $J = 8.0$ Hz, 2 H), 1.88 (s, 3 H).

^{13}C NMR (125 MHz, CDCl_3): $\delta = 208.4$, 140.1, 133.0, 132.2, 130.6, 129.8, 129.4, 129.0, 128.7, 128.5 (q, $J_{\text{C-F}} = 32.3$ Hz), 127.2, 127.1, 126.9, 126.8, 125.5 (q, $J_{\text{C-F}} = 3.6$ Hz), 123.3 (q, $J_{\text{C-F}} = 269.9$ Hz), 122.2, 119.6, 44.3, 29.6, 18.9.

^{19}F NMR (376.5 MHz, CDCl_3): $\delta = -62.3$ (s).

HRMS: m/z calcd for $\text{C}_{27}\text{H}_{22}\text{F}_3\text{NO}$ [M + H] $^+$: 434.1726; found: 434.178.

4-(4-(3-Oxobutyl)-2,5-diphenyl-1H-pyrrol-3-yl)benzotrile (5i)

White solid; isolated yield 83% (65 mg); $R_f = 0.50$ (20% EtOAc/hexane); mp 178–179 °C.

^1H NMR (400 MHz, CDCl_3): $\delta = 11.33$ (s, 1 H), 7.80 (d, $J = 7.9$ Hz, 2 H), 7.56 (d, $J = 7.5$ Hz, 2 H), 7.46 (t, $J = 7.7$ Hz, 2 H), 7.41 (d, $J = 7.9$ Hz, 2 H), 7.15–7.33 (m, 6 H), 2.76 (t, $J = 7.9$ Hz, 2 H), 2.32 (t, $J = 7.8$ Hz, 2 H), 1.86 (s, 3 H).

^{13}C NMR (125 MHz, CDCl_3): $\delta = 208.1$, 141.5, 132.8, 132.3, 132.0, 131.0, 130.1, 129.7, 129.1, 128.8, 127.3, 127.2, 127.1, 121.7, 119.4, 119.2, 110.0, 44.2, 29.7, 18.2.

HRMS: m/z calcd for $\text{C}_{27}\text{H}_{22}\text{N}_2\text{O}$ [M + H] $^+$: 391.1805; found: 391.1807.

4-(4-(Furan-2-yl)-2,5-diphenyl-1H-pyrrol-3-yl)butan-2-one (5j)

White solid; isolated yield 61% (43 mg); $R_f = 0.50$ (15% EtOAc/hexane); mp 150–152 °C.

^1H NMR (300 MHz, CDCl_3): $\delta = 8.21$ (s, 1 H), 7.41–7.48 (m, 5 H), 7.30–7.34 (m, 5 H), 7.24–7.27 (m, 1 H, merged with solvent peak), 6.42 (dd, $J = 3.2$, 1.9 Hz, 1 H), 6.22 (dd, $J = 3.2$, 0.5 Hz, 1 H), 2.95–3.01 (m, 2 H), 2.53–2.58 (m, 2 H), 2.03 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 208.8$, 149.5, 141.4, 132.8, 132.4, 130.8, 129.6, 129.0, 128.6, 127.2, 127.1, 126.8, 120.6, 112.8, 111.0, 108.1, 44.8, 29.7, 19.6.

HRMS: m/z calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_2$ [M + H] $^+$: 356.1645; found: 356.1649.

4-(2,5-Diphenyl-4-(thiophen-2-yl)-1H-pyrrol-3-yl)butan-2-one (5k)

White solid; isolated yield 65% (48 mg); $R_f = 0.50$ (15% EtOAc/hexane); mp 140–141 °C.

^1H NMR (300 MHz, CDCl_3): $\delta = 8.26$ (s, 1 H), 7.41–7.50 (m, 4 H), 7.20–7.34 (m, 7 H, merged with solvent peak), 7.04–7.06 (m, 1 H), 6.94 (d, $J = 2.8$ Hz, 1 H), 2.96 (t, $J = 8.3$ Hz, 2 H), 2.49 (t, $J = 8.3$ Hz, 2 H), 1.96 (s, 3 H).

^{13}C NMR (75 MHz, CDCl_3): $\delta = 208.6$, 137.0, 132.9, 132.2, 130.4, 129.3, 129.0, 128.6, 127.3, 127.2, 127.1, 127.0, 126.8, 126.7, 125.5, 121.0, 115.6, 44.7, 29.6, 19.2.

HRMS: m/z calcd for $\text{C}_{24}\text{H}_{21}\text{NOS}$ [M + H] $^+$: 372.1417; found: 372.1412.

4-(2,4-Diphenyl-5-(thiophen-2-yl)-1H-pyrrol-3-yl)butan-2-one (5l)

White solid; isolated yield 71% (53 mg); $R_f = 0.50$ (15% EtOAc/hexane); mp 164–165 °C.

^1H NMR (300 MHz, $\text{DMSO}-d_6$): $\delta = 11.19$ (s, 1 H), 7.53–7.56 (m, 2 H), 7.27–7.48 (m, 8 H), 7.19–7.22 (m, 2 H), 6.92–6.95 (m, 1 H), 2.61–2.66 (m, 2 H), 2.32–2.37 (m, 2 H), 1.84 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 208.6, 135.4, 135.0, 132.9, 130.7, 129.1, 129.0, 128.5, 127.2, 127.1, 127.1, 127.0, 124.4, 123.6, 123.4, 122.7, 120.1, 44.4, 29.6, 19.1.

HRMS: m/z calcd for $\text{C}_{24}\text{H}_{21}\text{NOS}$ $[\text{M} + \text{H}]^+$: 372.1417; found: 372.1412.

4-(2-Phenyl-5-(thiophen-2-yl)-4-(4-(trifluoromethyl)phenyl)-1H-pyrrol-3-yl)butan-2-one (5m)

White solid; isolated yield 74% (65 mg); R_f = 0.50 (20% EtOAc/hexane); mp 170–171 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.23 (s, 1 H), 7.65 (d, J = 8.0 Hz, 2 H), 7.43–7.49 (m, 6 H), 7.31–7.35 (m, 1 H), 7.11 (d, J = 4.5 Hz, 1 H), 6.91 (dd, J = 5.0, 3.6 Hz, 1 H), 6.78 (d, J = 2.9 Hz, 1 H), 2.88 (t, J = 8.2 Hz, 2 H), 2.34 (t, J = 8.2 Hz, 2 H), 1.89 (s, 3 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 208.2, 139.5, 134.4, 132.7, 131.0, 129.6, 129.1 (q, $^2J_{\text{C-F}}$ = 32.2 Hz), 129.0, 127.4, 127.3, 127.2, 125.4 (q, $^3J_{\text{C-F}}$ = 3.6 Hz), 124.3 (q, $^1J_{\text{C-F}}$ = 270.2 Hz), 124.0, 123.7, 123.5, 122.8, 119.8, 44.3, 29.6, 18.9.

^{19}F NMR (376 MHz, CDCl_3): δ = -62.3 (s).

HRMS: m/z calcd for $\text{C}_{25}\text{H}_{20}\text{F}_3\text{NOS}$ $[\text{M} + \text{H}]^+$: 440.1290; found: 440.1293.

4-(4-(Furan-2-yl)-2-phenyl-5-(thiophen-2-yl)-1H-pyrrol-3-yl)butan-2-one (5n)

White solid; isolated yield 55% (40 mg); R_f = 0.50 (15% EtOAc/hexane); mp 162–163 °C.

^1H NMR (300 MHz, CDCl_3): δ = 8.20 (s, 1 H), 6.51 (d, J = 1.1 Hz, 1 H), 7.41–7.46 (m, 4 H), 7.31–7.35 (m, 1 H), 7.19–7.21 (m, 1 H), 6.98–7.01 (m, 2 H), 6.47 (dd, J = 3.2, 1.9 Hz, 1 H), 6.35 (d, J = 3.1 Hz, 1 H), 2.91–2.97 (m, 2 H), 2.51–2.57 (m, 2 H), 2.02 (s, 3 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 208.7, 148.7, 141.8, 134.2, 132.6, 129.5, 129.0, 127.4, 127.3, 125.1, 124.4, 124.0, 120.8, 113.5, 111.1, 109.1, 44.7, 29.8, 19.5.

HRMS: m/z calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_2\text{S}$ $[\text{M} + \text{H}]^+$: 362.1209; found: 362.1208.

Ethyl 3-(4-(Benzo[d][1,3]dioxol-5-yl)-5-(4-methoxyphenyl)-2-phenyl-1H-pyrrol-3-yl)propanoate (6a)

White solid; isolated yield 57% (53 mg); R_f = 0.50 (15% EtOAc/hexane); mp 127–128 °C.

^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 10.99 (s, 1 H), 7.56 (d, J = 7.6 Hz, 2 H), 7.44 (t, J = 7.5 Hz, 2 H), 7.28 (t, J = 7.2 Hz, 1 H), 7.22 (d, J = 8.5 Hz, 2 H), 6.92 (d, J = 7.8 Hz, 1 H), 6.83 (d, J = 8.5 Hz, 2 H), 6.76 (s, 1 H), 6.69 (d, J = 7.8 Hz, 1 H), 6.04 (s, 2 H), 3.98 (q, J = 7.1 Hz, 2 H), 3.72 (s, 3 H), 2.82 (t, J = 7.8 Hz, 2 H), 2.20 (t, J = 7.9 Hz, 2 H), 1.07 (t, J = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 172.7, 158.0, 147.6, 146.1, 133.7, 130.8, 128.9, 128.7, 128.6, 127.8, 126.6, 125.7, 124.1, 122.2, 119.1, 114.1, 111.1, 108.9, 101.3, 60.1, 55.5, 35.2, 20.6, 14.4.

HRMS: m/z calcd for $\text{C}_{29}\text{H}_{27}\text{NO}_5$ $[\text{M} + \text{H}]^+$: 470.1962; found: 470.1965.

Ethyl 3-(4-(Furan-2-yl)-5-(4-methoxyphenyl)-2-phenyl-1H-pyrrol-3-yl)propanoate (6b)

Yellow viscous liquid; isolated yield 60% (50 mg); R_f = 0.50 (15% EtOAc/hexane).

^1H NMR (300 MHz, CDCl_3): δ = 8.14 (s, 1 H), 7.41–7.49 (m, 5 H), 7.26–7.33 (m, 3 H, merged with solvent peak), 6.87 (d, J = 8.5 Hz, 2 H), 6.41 (br s, 1 H), 6.21 (d, J = 2.2 Hz, 1 H), 4.05 (q, J = 7.1 Hz, 2 H), 3.80 (s, 3 H), 3.01–3.07 (m, 2 H), 2.43–2.49 (m, 2 H), 1.19 (t, J = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 173.3, 158.8, 149.7, 141.3, 133.0, 130.7, 129.1, 128.9, 128.3, 127.2, 126.9, 125.2, 120.1, 114.1, 112.3, 110.9, 107.8, 60.2, 55.3, 35.6, 20.9, 14.2.

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_4$ $[\text{M} + \text{H}]^+$: 416.1856; found: 416.1858.

Ethyl 3-(4-(Benzo[d][1,3]dioxol-5-yl)-2-phenyl-5-(thiophen-2-yl)-1H-pyrrol-3-yl)propanoate (6c)

Yellow viscous liquid; isolated yield 58% (52 mg); R_f = 0.50 (20% EtOAc/hexane).

^1H NMR (400 MHz, CDCl_3): δ = 8.19 (s, 1 H), 7.48–7.50 (m, 2 H), 7.41–7.44 (m, 2 H), 7.28–7.32 (m, 1 H), 7.05 (dd, J = 5.1, 1.1 Hz, 1 H), 6.80–6.91 (m, 5 H), 5.99 (s, 2 H), 3.98 (q, J = 7.2 Hz, 2 H), 2.89–2.93 (m, 2 H), 2.26–2.31 (m, 2 H), 1.14 (t, J = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 173.1, 147.7, 146.8, 135.0, 133.0, 129.0, 129.0, 128.9, 127.2, 127.1, 127.0, 124.2, 124.0, 123.8, 123.3, 122.4, 120.1, 111.2, 108.5, 101.0, 60.2, 35.1, 20.3, 14.1.

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_4\text{S}$ $[\text{M} + \text{H}]^+$: 446.1421; found: 446.1425.

Ethyl 3-(2,4-Diphenyl-5-(thiophen-2-yl)-1H-pyrrol-3-yl)propanoate (6d)

Yellow viscous liquid; isolated yield 51% (41 mg); R_f = 0.50 (15% EtOAc/hexane).

^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 11.22 (s, 1 H), 7.56–7.57 (m, 2 H), 7.41–7.48 (m, 4 H), 7.29–7.38 (m, 4 H), 7.19–7.22 (m, 2 H), 6.93–6.95 (m, 1 H), 3.88 (q, J = 7.1 Hz, 2 H), 2.72–2.76 (m, 2 H), 2.15–2.19 (m, 2 H), 1.05 (t, J = 7.1 Hz, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 173.1, 135.4, 135.1, 133.0, 130.8, 129.2, 129.0, 128.5, 127.2, 127.1, 127.1, 127.0, 124.5, 123.6, 123.3, 122.6, 120.0, 60.1, 35.0, 20.3, 14.1.

HRMS: m/z calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_2\text{S}$ $[\text{M} + \text{H}]^+$: 402.1522; found: 402.1518.

Ethyl 3-(2-(4-Fluorophenyl)-4-(furan-2-yl)-5-(4-methoxyphenyl)-1H-pyrrol-3-yl)propanoate (6e)

Yellow viscous liquid; isolated yield 64% (55 mg); R_f = 0.50 (20% EtOAc/hexane).

^1H NMR (400 MHz, CDCl_3): δ = 8.06 (s, 1 H), 7.42–7.46 (m, 3 H), 7.27 (d, J = 7.5 Hz, 2 H, merged with solvent peak), 7.11–7.16 (m, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 6.40–6.42 (m, 1 H), 6.20 (d, J = 3.0 Hz, 1 H), 4.05 (q, J = 7.1 Hz, 2 H), 3.81 (s, 3 H), 2.97–3.01 (m, 2 H), 2.41–2.45 (m, 2 H), 1.19 (t, J = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 173.3, 161.9 (d, $J_{\text{C-F}}$ = 245.4 Hz), 158.9, 149.6, 141.3, 130.7, 129.0 (d, $J_{\text{C-F}}$ = 7.9 Hz), 128.3, 128.2, 125.1, 120.0, 115.9 (d, $J_{\text{C-F}}$ = 21.5 Hz), 114.1, 112.1, 110.9, 107.8, 60.2, 55.2, 35.4, 20.7, 14.1.

^{19}F NMR (376 MHz, CDCl_3): δ = -114.8 (s).

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{24}\text{FNO}_4$ $[\text{M} + \text{H}]^+$: 434.1762; found: 434.1762.

(4,5-Bis(4-methoxyphenyl)-2-phenyl-1H-pyrrol-3-yl)methanol (7a)

White solid; isolated yield 26% (20 mg); R_f = 0.50 (40% EtOAc/hexane); mp 179–180 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.26 (s, 1 H), 7.66 (d, J = 7.5 Hz, 2 H), 7.45 (t, J = 7.7 Hz, 2 H), 7.31–7.34 (m, 3 H), 7.20 (d, J = 8.6 Hz, 2 H), 6.90 (d, J = 8.5 Hz, 2 H), 6.81 (d, J = 8.6 Hz, 2 H), 4.54 (s, 2 H), 3.83 (s, 3 H), 3.78 (s, 3 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 158.4, 158.3, 132.4, 131.5, 131.2, 128.9, 128.8, 128.2, 127.6, 127.0, 126.9, 125.4, 122.8, 120.3, 114.1, 113.9, 56.1, 55.2, 55.1.

HRMS: m/z calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_3$ [$\text{M} + \text{Na}$] $^+$: 408.1576; found: 408.1571.

(4-(3,4-Dimethoxyphenyl)-2,5-diphenyl-1H-pyrrol-3-yl)methanol (7b)

White solid; isolated yield 19% (15 mg); R_f = 0.50 (40% EtOAc/hexane); mp 85–86 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.36 (s, 1 H), 7.64 (d, J = 7.2 Hz, 2 H), 7.44 (t, J = 7.4 Hz, 2 H), 7.16–7.33 (m, 6 H, merged with solvent peak), 6.85–6.97 (m, 3 H), 4.54 (s, 2 H), 3.88 (s, 3 H), 3.71 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 148.7, 147.8, 132.6, 132.3, 131.9, 129.0, 128.9, 128.6, 127.8, 127.3, 127.1, 126.9, 126.6, 124.0, 122.5, 120.4, 113.9, 111.3, 56.1, 55.8, 55.7.

HRMS: m/z calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_3$ [$\text{M} + \text{Na}$] $^+$: 408.1576; found: 408.1576.

tert-Butyl 2-(4-Methoxyphenyl)-4-nitro-3,5-diphenyl-1H-pyrrole-1-carboxylate (9a')

White solid; isolated yield 56% (53 mg); R_f = 0.50 (15% EtOAc/hexane); mp 154–155 °C.

^1H NMR (400 MHz, CDCl_3): δ = 7.51–7.53 (m, 2 H), 7.45–7.48 (m, 3 H), 7.22–7.26 (m, 3 H, merged with solvent peak), 7.18–7.21 (m, 2 H), 7.12–7.16 (m, 2 H), 6.78–6.81 (m, 2 H), 3.77 (s, 3 H), 1.10 (s, 9 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 159.6, 148.2, 134.8, 132.1, 131.7, 131.5, 130.9, 130.4, 130.2, 129.6, 129.3, 128.1, 127.9, 127.3, 122.6, 119.7, 113.5, 86.2, 55.2, 26.9.

HRMS: m/z calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_5$ [$\text{M} + \text{H}$] $^+$: 471.1914; found: 471.1918.

tert-Butyl 2,3-Bis(4-methoxyphenyl)-4-nitro-5-phenyl-1H-pyrrole-1-carboxylate (9b')

Yellow solid; isolated yield 42% (42 mg); R_f = 0.50 (20% EtOAc/hexane); mp 163–164 °C.

^1H NMR (400 MHz, CDCl_3): δ = 7.46–7.51 (m, 5 H), 7.13 (t, J = 9.0 Hz, 4 H), 6.78–6.82 (m, 4 H), 3.78 (s, 3 H), 3.77 (s, 3 H), 1.10 (s, 9 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 159.5, 158.7, 148.3, 134.9, 132.0, 131.6, 131.5, 130.8, 130.2, 129.7, 129.3, 128.1, 123.5, 122.7, 119.3, 113.5, 113.4, 86.1, 55.2, 55.1, 26.9.

HRMS: m/z calcd for $\text{C}_{29}\text{H}_{28}\text{N}_2\text{O}_6$ [$\text{M} + \text{H}$] $^+$: 501.2020; found: 501.2023.

tert-Butyl 3-(4-Cyanophenyl)-2-(4-methoxyphenyl)-4-nitro-5-phenyl-1H-pyrrole-1-carboxylate (9c')

White solid; isolated yield 66% (65 mg); R_f = 0.50 (20% EtOAc/hexane); mp 159–160 °C.

^1H NMR (400 MHz, CDCl_3): δ = 7.47–7.55 (m, 7 H), 7.30 (d, J = 8.2 Hz, 2 H), 7.11 (d, J = 8.7 Hz, 2 H), 6.82 (d, J = 8.7 Hz, 2 H), 3.79 (s, 3 H), 1.10 (s, 9 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 160.0, 147.8, 136.9, 133.9, 133.0, 131.7, 131.6, 131.5, 131.2, 130.1, 129.6, 129.2, 128.2, 121.6, 118.8, 118.0, 113.8, 111.0, 86.7, 55.2, 26.9.

HRMS: m/z calcd for $\text{C}_{29}\text{H}_{25}\text{N}_3\text{O}_5$ [$\text{M} + \text{H}$] $^+$: 496.1867; found: 496.1864.

tert-Butyl 3-Nitro-2,4,5-triphenyl-1H-pyrrole-1-carboxylate (9d')

White solid; isolated yield 53% (47 mg); R_f = 0.50 (10% EtOAc/hexane); mp 140–141 °C.

^1H NMR (400 MHz, CDCl_3): δ = 7.51–7.54 (m, 2 H), 7.46–7.48 (m, 3 H), 7.18–7.29 (m, 10 H, merged with solvent peak), 1.08 (s, 9 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 148.1, 134.9, 132.4, 131.3, 131.0, 130.5, 130.4, 130.3, 130.1, 129.5, 129.4, 128.4, 128.1, 128.0, 127.9, 127.4, 120.0, 86.3, 26.9.

HRMS: m/z calcd for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_4$ [$\text{M} + \text{H}$] $^+$: 441.1809; found: 441.1806.

4-(5-(4-Methoxyphenyl)-2,4-diphenyl-1H-pyrrol-3-yl)butan-2-ol (10a)

White solid; isolated yield 96% (38 mg); R_f = 0.50 (40% EtOAc/hexane); mp 172–173 °C.

^1H NMR (400 MHz, CDCl_3): δ = 8.11 (s, 1 H), 7.54 (d, J = 7.4 Hz, 2 H), 7.44 (t, J = 7.8 Hz, 2 H), 7.28–7.37 (m, 6 H), 7.14 (d, J = 8.8 Hz, 2 H), 6.77 (d, J = 8.8 Hz, 2 H), 3.77 (s, 3 H), 3.54–3.59 (m, 1 H), 2.66–2.82 (m, 2 H), 1.43–1.47 (m, 2 H), 0.96 (d, J = 6.2 Hz, 3 H).

^{13}C NMR (125 MHz, CDCl_3): δ = 158.2, 136.4, 133.5, 130.7, 128.9, 128.8, 128.5, 128.4, 127.9, 127.0, 126.6, 126.4, 125.5, 123.1, 121.1, 114.0, 67.6, 55.2, 40.2, 22.9, 20.7.

HRMS: m/z calcd for $\text{C}_{27}\text{H}_{27}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 398.2115; found: 398.2120.

3-(4-(Benzo[d][1,3]dioxol-5-yl)-2-phenyl-5-(thiophen-2-yl)-1H-pyrrol-3-yl)propan-1-ol (10b)

Yellow viscous liquid; isolated yield 79% (32 mg); R_f = 0.50 (40% EtOAc/hexane).

^1H NMR (400 MHz, CDCl_3): δ = 8.18 (s, 1 H), 7.51 (d, J = 7.3 Hz, 2 H), 7.43 (t, J = 7.8 Hz, 2 H), 7.30 (t, J = 7.3 Hz, 1 H), 7.07 (d, J = 4.8 Hz, 1 H), 6.90–6.92 (m, 1 H), 6.81–6.87 (m, 4 H), 6.00 (s, 2 H), 3.43 (t, J = 6.4 Hz, 2 H), 2.66 (t, J = 7.7 Hz, 2 H), 1.54–1.61 (m, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 147.6, 146.7, 135.1, 133.2, 129.2, 128.9, 128.8, 127.2, 127.0, 126.9, 124.3, 124.1, 123.7, 123.3, 122.4, 121.4, 111.3, 108.5, 101.0, 62.4, 33.7, 20.7.

HRMS: m/z calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_3\text{S}$ [$\text{M} + \text{H}$] $^+$: 404.1315; found: 404.1307.

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0042-1751360>. Included are copies of the ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra of the products.

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