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Synthesis of Polysubstituted Pyrroles via Pd-Catalyzed Oxidative Alkene C−H Bond Arylation and Amination

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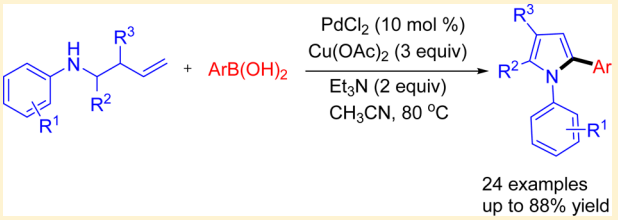
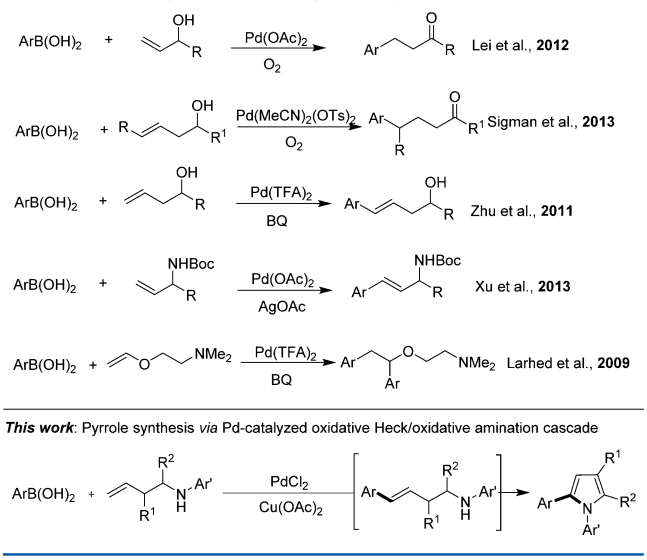
Supporting Information

ABSTRACT: A novel Pd(II)-catalyzed oxidative approach to construct polysubstituted pyrroles from *N*-homoallylicamines and arylboronic acids was developed. This transformation is supposed to proceed through cascade formation of C−C and C−N bonds via oxidative arylation of unactive alkenes, followed by intramolecular aza-Wacker cyclization.



Transition metal-catalyzed oxidative coupling reactions have emerged as one of the most powerful tools for the efficient construction of C−C and C−heteroatom bonds.[1,2] Among them, the Pd-catalyzed oxidative Heck reactions have drawn increasing attention of synthetic chemists due to the easy accessibility of starting materials such as arylboronic acids, alkenes and the utility of various products.[2] In 1975, Richard F. Heck reported the first example of oxidative Heck reaction of organoboron reagents with alkenes bearing an electron-withdrawing group.[3] Subsequently, the groups of Larhed, Gaunt, Sigman, Hou et al. reported various carbon nucleophile−metal species can undergo oxidative coupling with activated alkenes, such as styrenes, 1,3-dienes, strained cyclic olefins.[4−6] However, there are only limited examples about the oxidative Heck reactions with corresponding nonactivated olefins.[7−9] Two strategies are usually employed to increase the propensity of coordination of nonactivated olefins to Pd center and induce reactivity, thus removing the requirement of activated olefins for oxidative Heck reactions. One pathway is utilizing ligands to adjust the steric and electronic property of metal catalysts.[8] The other pathway is incorporating a functional group to nonactivated olefin, such as OH, NHBoc, etc., which can coordinate to the Pd center (Scheme 1).[9] Lei and Sigman recently reported respectively an oxidative Heck reaction between arylboronic acids and allylic alcohols to afford aryl ketones and aldehydes through selective *β*-H elimination.[9a,b] In 2011, Zhu et al. found that arylated homoallylic alcohols were obtained via a hydroxyl group assisted Pd-catalyzed oxidative Heck reactions of boronic acids with homoallylic alcohols.[9c] A corresponding oxidative arylation of protected-allylamines was reported by Xu and co-workers in 2013.[9d] The group of Larhed reported a Heck/Suzuki domino diarylation reaction by using chelating vinyl ethers.[9e] Herein, we report an oxidative cascade reaction that was initiated by the Pd-catalyzed oxidative Heck reactions with homoallylic amines and phenylboronic acids, followed by the oxidative amination processes.

Scheme 1. Pd-Catalyzed Oxidative Coupling between *N*-Homoallylic Amines and Aromatic Boronic Acids



Pyrrole skeleton frequently occurs in naturally and synthetically bioactive products as well as top-sold marketing medicines.[10] For example, COX-2 isoenzyme inhibitors, Zomepirac and Fludioxonil are used extensively in pharmaceuticals (Figure 1). Therefore, the development of efficient methods to access these privileged molecules is of significant importance.[11] As our persistent attention on Pd-catalyzed oxidative functionalization of electronically unbiased alkyl olefins,[12] various polysubstituted pyrroles were synthesized in good to excellent yields from easily prepared homoallylic amines and commercially available arylboronic acids in one-pot transformations, using Pd(II) catalyst system.

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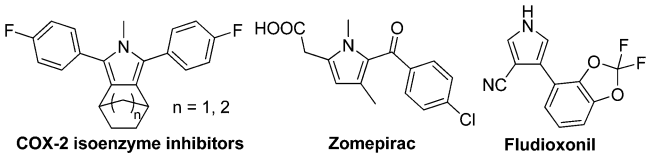
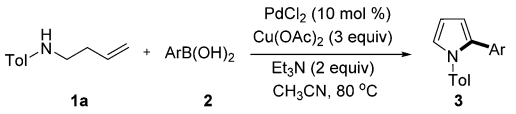


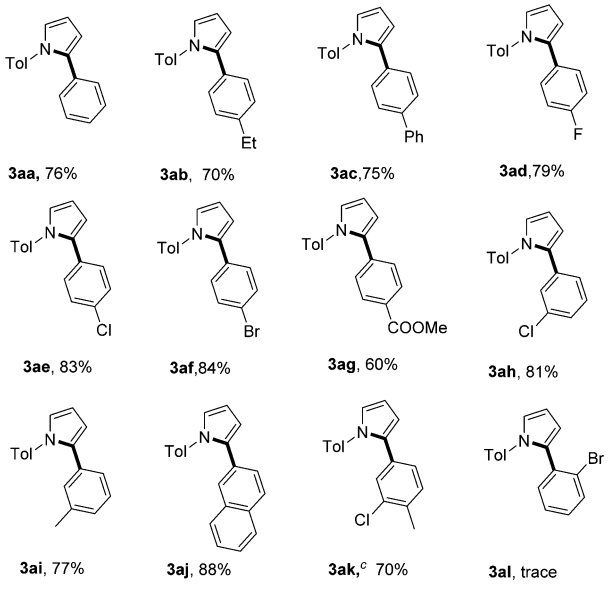
Figure 1. Examples of bioactive pyrroles.

Initially, using $PdCl_2$ as the catalyst, *N*-(but-3-en-1-yl)-4-methylaniline (**1a**) and phenylboronic acid (**2a**) were selected as model substrates to optimize the reaction conditions. As show in Table 1, decomposition was observed when $CuCl_2$, DDQ or BQ were used, only $Cu(OAc)_2$ gave 33% yield (Table 1, entries 1−4). As for the selection of solvent, no desired product was detected when DMSO, DMF was selected as the solvent. Toluene and 1,4-dioxane gave relatively lower yields than that of CH_3CN (Table 1, entries 5−8). Further investigation showed that Et_3N was the best additives in comparison with *t*-BuOLi, PivOH, HOAc, DABCO and DBU (Table 1, entries 9−17). Compared with $Pd(OAc)_2$ and $Pd(TFA)_2$, $PdCl_2$ exhibited better reactivity (Table 1, entries 18−19). When this reaction proceeded at 50 °C, only 42% of product was obtained (Table 1, entry 20). Thus, the standard conditions were obtained as $PdCl_2$ (10 mol %), $Cu(OAc)_2$ (3 equiv), Et_3N (2 equiv), in CH_3CN at 80 °C.

The scope of this reaction was explored as the optimized conditions identified. A range of substituted phenylboronic acids were initially surveyed (Table 2). Both electron-donating and -withdrawing groups were tolerated in this cascade reaction. A variety of *para*-substituted functional groups, such as alkyl, phenyl, halogen and ester were compatible to obtain desired pyrroles **3ab**−**3ag** in moderate to good yields. The *meta*- and *para*-substituted substrates led to good yields of the corresponding products (**3ah**, **3ai**). The naphthylboronic acid also proceeded smoothly with **1a** to afford 88% yield of product

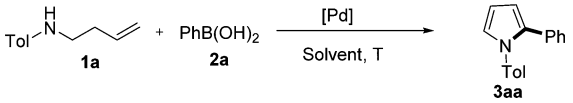
Table 2. Substrate Scope of Phenylboronic Acids[a,b]





[a]Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol), $PdCl_2$ (10 mol %), Et_3N (2 equiv) and $Cu(OAc)_2$ (3 equiv) in 1 mL CH_3CN at 80 °C for 12 h. [b]Isolated yield. [c]The reaction was stirred for 24 h.

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	oxidant	additive	solvent	yield (%)[b]
1	$PdCl_2$	$Cu(OAc)_2$	−	CH_3CN	33
2	$PdCl_2$	$CuCl_2$	−	CH_3CN	N.D.
3	$PdCl_2$	DDQ	−	CH_3CN	N.D.
4	$PdCl_2$	BQ	−	CH_3CN	N.D.
5	$PdCl_2$	$Cu(OAc)_2$	−	DMSO	N.D.
6	$PdCl_2$	$Cu(OAc)_2$	−	DMF	18
7	$PdCl_2$	$Cu(OAc)_2$	−	toluene	12
8	$PdCl_2$	$Cu(OAc)_2$	−	1,4-dioxane	21
9	$PdCl_2$	$Cu(OAc)_2$	*t*-BuOLi	CH_3CN	44
10	$PdCl_2$	$Cu(OAc)_2$	PivOH	CH_3CN	39
11	$PdCl_2$	$Cu(OAc)_2$	HOAc	CH_3CN	N.D.
12	$PdCl_2$	$Cu(OAc)_2$	Et_3N	CH_3CN	80 (76)[c]
13	$PdCl_2$	$Cu(OAc)_2$	DBU	CH_3CN	N.D.
14	$PdCl_2$	$Cu(OAc)_2$	pyridine	CH_3CN	N.D.
15	$PdCl_2$	$Cu(OAc)_2$	DABCO	CH_3CN	72
16	$PdCl_2$	$Cu(OAc)_2$	*N*-methylmorpholine	CH_3CN	N.D.
17	$PdCl_2$	$Cu(OAc)_2$	Bu_3N	CH_3CN	69
18	$Pd(OAc)_2$	$Cu(OAc)_2$	Et_3N	CH_3CN	67
19	$Pd(TFA)_2$	$Cu(OAc)_2$	Et_3N	CH_3CN	44
20[d]	$PdCl_2$	$Cu(OAc)_2$	Et_3N	CH_3CN	42

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst (10 mol %), oxidant (3 equiv) and additive (2 equiv) in 1 mL of solvent under at 80 °C for 12 h. [b]Determined by GC. [c]Isolated yield. [d]At 50 °C.

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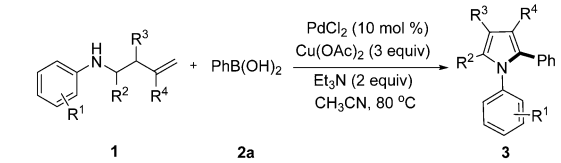
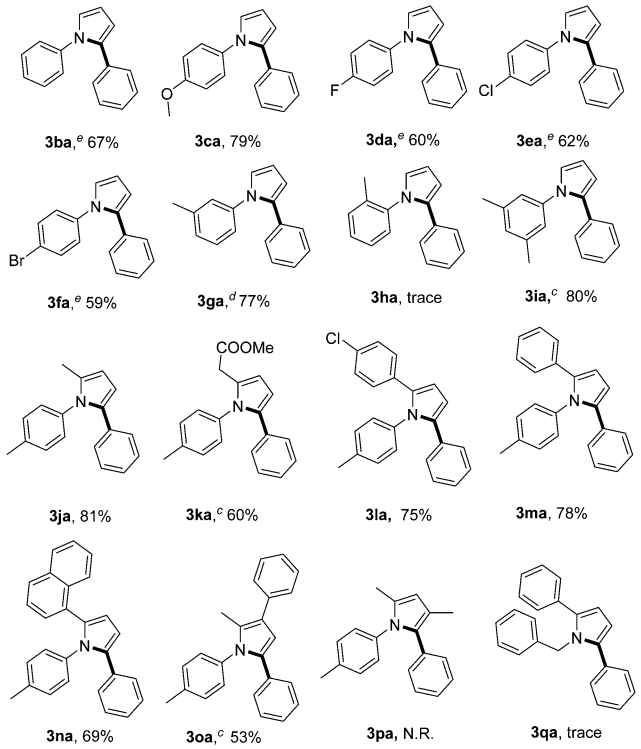
3aj. In addition, disubstituted phenylboronic acid could be employed as substrate to give moderate yield of the corresponding product (**3ak**). Unfortunately, *ortho*-halogen phenylboronic acids gave no desired product in this transformation (**3al**).

In view of the forementioned results, we turned our attention to the scope of substituted homoallylic amines (Table 3).

Table 3. Substrate Scope of *N*-Homoallyliamines[a,b]



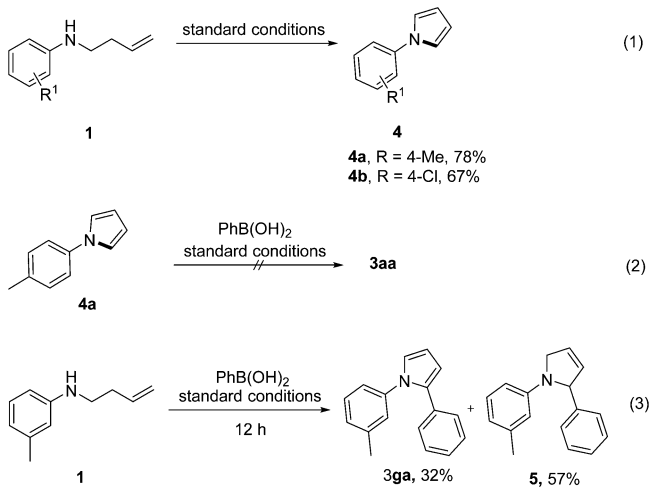


[a]Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol), $PdCl_2$ (10 mol %), Et_3N (2 equiv) and $Cu(OAc)_2$ (3 equiv) in 1 mL CH_3CN at 80 °C for 12 h. [b]Isolated yield. [c]The reaction was stirred for 24 h. [d]The reaction was stirred for 36 h. [e]The reaction was stirred for 48 h.

Overall, the desired products were generated in moderate to good yields for various substituted homoallylic amines. When R^1 equaled to H, 67% yield of product **3ba** was obtained. Functional groups such as OMe, F, Cl and Br on the aryl ring were also tolerated in this transformation and gave pyrrole derivatives in 59−79% yields (**3ca**−**3fa**). Yield remained good when R^1 switched from *para*-position to *meta*-position (**3ga**). However, when R^1 was *ortho*-substituent, only trace of desired product could be detected (**3ha**). For the component with disubstitutents on the aryl ring, the reactions proceeded well to generate **3ia** in 80% yield. To our delight, substrates bearing different R^2, including alkyl, alkyl ester, phenyl, naphthyl, all allowed the formation of corresponding products (**3ja**−**3na**). In addition, a slightly lower yield was observed when R^3 was phenyl group (**3oa**). When 4-methyl-*N*-(4-methylpent-4-en-2-yl)aniline (**1p**) was used as the substrate, no reaction occurred. Only trace amount of product was obtained when *N*-phenyl was changed to *N*-benzyl group (**3qa**), which suggested that *N*-phenyl was crucial to this transformation.

Both oxidative arylation and aminopalladation start with palladium(II) catalyst, which means they might be competitive in one process. To gain further insight into the mechanistic information, we carried out several experiments under the standard conditions. The transformation still proceeded well to construct pyrroles when we only used homoallylic amines as the substrates. As shown in Scheme 2, **4a** and **4b** were obtained

Scheme 2. Control Experiments



in 75 and 64% yields, respectively (eq 1). In addition, no desired product was afforded between **4a** and phenylboronic acid under the standard conditions (eq 2). Then we shorten the time of the reaction between **1g** and **2a** from 36 to 12 h and successfully isolated intermediate **5** (eq 3), which indicated that the oxidative Heck reaction occurred first, followed by the intramolecular aminopalladation.

On the basis of the above information and previous reports,[9] a putative reaction pathway for this transformation is shown in Scheme 3. Arylpalladium(II) species was first formed by transmetalation of arylboronic acid, followed by migratory insertion of the olefin and β-hydride elimination to produce intermediate **B**. Then, intramolecular aminopalladation gave palladium(II)-alkyl complex **C**, and subsequently a second β-hydride elimination generated intermediate **5**. Finally, oxidative dehydrogenation afforded the desired product **3**. The Pd(0) species obtained in two β-hydride elimination process was oxidized by $Cu(OAc)_2$ to regenerate the Pd(II) species.

In summary, we have elaborated the Pd(II)-catalyzed oxidative arylative cyclization of *N*-homoallylic amines. Four hydrogen atoms were removed to forge C−N and C−C bonds in this protocol via sequential unreactive alkene oxidative arylation and intramolecular aza-Wacker-type cyclization. The present reaction allowed simple conversion of accessible starting materials to various polysubstituted pyrroles.

EXPERIMENTAL SECTION

General Method. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Mass spectra were obtained with gas chromatography mass spectrometer. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a spectrometer. GC−MS was obtained using electron

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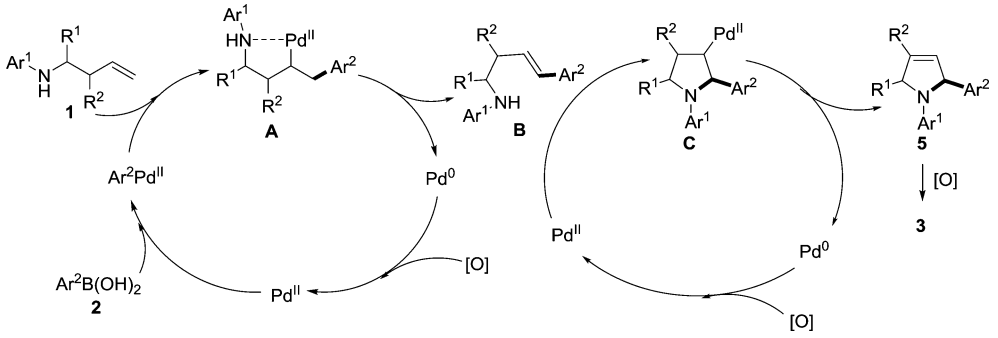
Scheme 3. Proposed Mechanism



ionization. HRMS was obtained with a LCMS-IT-TOF mass spectrometer.

General Procedure for Synthesis of Homoallylic Amines 1a–1i.[13a] Arylamine (1.2 mmol) and K_2CO_3 (2 mmol) were added to 3 mL of DMF. Allyl bromide (1 mmol) was slowly added to the mixture, which was stirred at 80 °C overnight. After that, water was added, and the mixture was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtered, concentrated and eventually purified by column chromatography on a silica gel to give **1a–1i** with petroleum ether/ethyl acetate as the eluent.

General Procedure for Synthesis of Homoallylic Amines 1j, 1k, 1o, 1p.[13b] A suspension of indium (2 mmol) and allyl bromide (3 mmol) in THF (2 mL) was stirred at room temperature under N_2 for 1 h. Then aniline (1 mmol) and ethyl vinyl ether (2 mmol) were added to the reaction mixture, which was stirred for another 2 h. The solution was quenched by saturated aqueous NH_4Cl (5 mL) and extracted with ethyl acetate. The organic layer was washed with water, dried over Na_2SO_4, filtered and concentrated. The residue was separated by column chromatography on a silica gel to afford the corresponding homoallylic amines with petroleum ether/ethyl acetate as the eluent.

General Procedure for Synthesis of Homoallylic Amines 1l–1n, 1q.[13c] A suspension of allylmagnesium bromide (1.0 M in THF, 1.0 mL, 1.3 mmol) and $ZnCl_2$ (0.1 mmol) was stirred at room temperature under N_2 for 1 h. Then, imine (1 mmol) was added to the mixture, which was stirred at room temperature for 2 h. The solution was quenched by saturated aqueous NH_4Cl (5 mL) and extracted with ethyl acetate. The organic layer was washed with water, dried over Na_2SO_4, filtered and concentrated. The residue was further purified by column chromatography on a silica gel to give corresponding compounds with petroleum ether/ethyl acetate as the eluent.

General Procedure for Synthesis of Pyrrole Derivatives. Homoallylic amine (0.1 mmol), arylboronic acid (0.15 mmol), $PdCl_2$ (10 mol %), $Cu(OAc)_2$ (3 equiv) and Et_3N (2 equiv) were added to 1 mL of CH_3CN. The mixture was stirred under air at 80 °C for the desired reaction time. After that, water was added and extracted with ethyl acetate twice. The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was eventually purified by flash column chromatography on a silica gel to afford the product with petroleum ether/ethyl acetate as the eluent.

*N-(But-3-en-1-yl)-4-methylaniline (**1a**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05 (d, J = 7.9 Hz, 2H), 6.60 (d, J = 7.9 Hz, 2H), 5.97–5.78 (m, 1H), 5.18 (t, J = 14.0 Hz, 2H), 3.84(s, 1H), 3.22 (t, J = 6.6 Hz, 2H), 2.43 (dd, J = 13.4, 6.7 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.1, 135.9, 129.8, 126.6, 117.0, 113.2, 43.3, 33.7, 20.4 ppm; MS (EI, 70 eV) m/z 91, 120, 261; HRMS (ESI) m/z calcd for $C_{11}H_{16}N$ $[M + H]^+$, 162.1277, found 162.1278; IR (KBr) 3407, 2919, 2861, 1616, 1519, 1479, 1323, 808 cm^{-1}.

*N-(But-3-en-1-yl)aniline (**1b**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (t, J = 7.2 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.66 (d, J = 7.8 Hz, 2H), 5.88 (td, J = 16.5, 7.3 Hz, 1H), 5.18 (t, J = 14.3 Hz, 2H), 3.70 (s, 1H), 3.23 (t, J = 6.6 Hz, 2H), 2.43 (q, J = 6.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.3, 135.8, 129.2, 117.4, 117.1, 112.9, 42.9, 33.7 ppm; MS (EI, 70 eV) m/z 77, 106, 147; HRMS (ESI) m/z calcd for $C_{10}H_{14}N$ $[M + H]^+$, 148.1121, found 148.1121; IR (KBr) 3411, 3079, 2926, 2833, 1732, 1600, 1510, 1434, 1321, 918 cm^{-1}.

*N-(But-3-en-1-yl)-4-methoxyaniline (**1c**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.77 (d, J = 7.9 Hz, 2H), 6.58 (d, J = 7.7 Hz, 2H), 5.99–5.66 (m, 1H), 5.11 (t, J = 13.6 Hz, 2H), 3.71 (d, J = 15.8 Hz, 3H), 3.15 (dd, J = 19.2, 12.6 Hz, 2H), 2.36 (q, J = 6.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.2, 142.7, 135.9, 117.0, 114.9, 114.3, 55.8, 43.9, 33.7 ppm; MS (EI, 70 eV) m/z 108, 121, 136, 177; HRMS (ESI) m/z calcd for $C_{11}H_{16}NO$ $[M + H]^+$, 178.1226, found 178.1226; IR (KBr) 3392, 2929, 2830, 1513, 1468, 1237, 819 cm^{-1}.

*N-(But-3-en-1-yl)-4-fluoroaniline (**1d**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.93 (t, J = 8.0 Hz, 2H), 6.58 (dd, J = 6.9, 4.4 Hz, 2H), 5.97–5.78 (m, 1H), 5.18 (t, J = 12.4 Hz, 2H), 3.49 (s, 1H), 3.18 (t, J = 6.5 Hz, 2H), 2.41 (q, J = 6.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.9 (d, J = 233.0 Hz), 144.7, 135.7, 117.2, 115.6 (d, J = 18.0 Hz), 113.73 (d, J = 7.4 Hz, 15H), 43.5, 33.6. ppm; MS (EI, 70 eV) m/z 75, 95, 124, 165; HRMS (ESI) m/z calcd for $C_{10}H_{13}FN$ $[M + H]^+$, 166.1027, found 166.1025; IR (KBr) 3409, 3079, 2928, 2852, 1612, 1514, 1317, 1219, 820 cm^{-1}.

*N-(But-3-en-1-yl)-4-chloroaniline (**1e**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.15 (d, J = 8.2 Hz, 2H), 6.56 (d, J = 7.8 Hz, 2H), 5.85 (td, J = 16.8, 7.1 Hz, 1H), 5.24–5.07 (m, 2H), 3.69 (s, 1H), 3.18 (t, J = 6.5 Hz, 2H), 2.41 (q, J = 6.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.8, 135.5, 129.0, 121.9, 117.3, 113.9, 42.9, 33.5 ppm; MS (EI, 70 eV) m/z 77, 105, 140, 181; HRMS (ESI) m/z calcd for $C_{10}H_{13}ClN$ $[M + H]^+$, 182.0731, found 182.0729; IR (KBr) 3412, 3078, 2925, 2851, 1601, 1503, 1318, 815 cm^{-1}.

*4-Bromo-N-(but-3-en-1-yl)aniline (**1f**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (d, J = 7.7 Hz, 2H), 6.51 (d, J = 7.8 Hz, 2H), 5.85 (td, J = 16.8, 7.2 Hz, 1H), 5.26–5.09 (m, 2H), 3.69 (s, 1H), 3.18 (t, J = 6.5 Hz, 2H), 2.41 (q, J = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.3, 135.5, 131.9, 117.3, 114.4, 108.9, 42.8, 33.5 ppm; MS (EI, 70 eV) m/z 91, 118, 132, 160, 192, 233; HRMS (ESI) m/z calcd for $C_{10}H_{13}BrN$ $[M + H]^+$, 226.0226, found 226.0226; IR (KBr) 3411, 3076, 2925, 2849, 1595, 1502, 1320, 812 cm^{-1}.

*N-(But-3-en-1-yl)-3-methylaniline (**1g**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.15 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 7.0 Hz, 1H), 6.51 (d, J = 7.7 Hz, 2H), 5.91 (td, J = 16.2, 7.3 Hz, 1H), 5.21 (t, J = 14.5 Hz, 2H), 3.61 (s, 1H), 3.25 (t, J = 6.6 Hz, 2H), 2.44 (dd, J = 13.6, 7.7 Hz, 2H), 2.35 (d, J = 14.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ =148.4, 139.0, 135.9, 129.2, 118.4, 117.0, 113.8, 110.1, 42.9, 33.7, 21.7 ppm; MS (EI, 70 eV) m/z 91, 120, 261; HRMS (ESI) m/z calcd for $C_{11}H_{16}N$ $[M + H]^+$, 162.1277, found 162.1278; IR (KBr) 3410, 3043, 2919, 2847, 1609, 1514, 1424, 1328, 769 cm^{-1}.

*N-(But-3-en-1-yl)-2-methylaniline (**1h**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 6.74 (dd, J = 19.0, 7.7 Hz, 2H), 5.95 (td, J = 16.8, 7.1 Hz, 1H), 5.24 (t, J = 14.9 Hz, 2H), 3.61 (s, 1H), 3.32 (t, J = 6.6 Hz, 2H), 2.53 (q, J = 6.5 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.2, 136.0, 130.1, 127.2, 122.0, 117.1, 116.9, 109.9, 42.7, 33.7, 17.39 ppm; MS (EI, 70 eV) m/z 91, 120, 261; HRMS (ESI) m/z calcd for $C_{11}H_{16}N$ $[M + H]^+$, 162.1277, found 162.1278; IR (KBr) 3421, 3076, 2920, 2851, 1607, 1512, 1443, 1316, 745 cm^{-1}.

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*N-(But-3-en-1-yl)-3,5-dimethylaniline (**1i**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.44 (s, 1H), 6.33 (s, 2H), 5.89 (tt, J = 8.8, 7.1 Hz, 1H), 5.19 (t, J = 14.9 Hz, 2H), 3.56 (s, 1H), 3.23 (t, J = 6.4 Hz, 2H), 2.44 (dd, J = 13.0, 6.4 Hz, 2H), 2.33 (d, J = 14.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.4, 138.9 135.9, 119.5, 117.0, 110.9, 42.9, 33.7, 21.5 ppm; MS (EI, 70 eV) m/z 77, 134, 175; HRMS (ESI) m/z calcd for $C_{12}H_{18}N$ $[M + H]^+$, 176.1434, found 176.1434; IR (KBr) 3408, 2916, 2853, 1603, 1513, 1472, 1302, 1178, 821 cm^{-1}.

*4-Methyl-N-(pent-4-en-2-yl)aniline (**1j**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.97 (d, J = 7.9 Hz, 2H), 6.51 (d, J = 7.9 Hz, 2H), 5.82 (dt, J = 16.6, 7.3 Hz, 1H), 5.15−4.97 (m, 2H), 3.51 (dd, J = 12.3, 6.1 Hz, 1H), 2.38−2.29 (m, 1H), 2.28−2.13 (m, 4H), 1.17 (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.1, 135.1, 129.8, 126.4, 117.5, 113.7, 48.4, 40.9, 20.5, 20.4 ppm; MS (EI, 70 eV) m/z 91, 119, 134, 175; HRMS (ESI) m/z calcd for $C_{12}H_{18}N$ $[M + H]^+$, 176.1434, found 176.1434; IR (KBr) 3404, 2970, 2922, 2865, 1617, 1518, 1302, 807 cm^{-1}.

*Methyl 3-(p-tolylamino)hex-5-enoate (**1k**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.99 (d, J = 7.6 Hz, 2H), 6.57 (d, J = 7.6 Hz, 2H), 5.81 (dt, J = 16.0, 7.5 Hz, 1H), 5.11 (d, J = 13.0 Hz, 2H), 3.92−3.83 (m, 1H), 3.66 (s, 3H), 2.54 (ddd, J = 32.9, 15.3, 6.1 Hz, 2H), 2.44−2.31 (m, 2H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.3, 134.1, 129.9, 127.2, 118.3, 114.1, 51.6, 50.4, 38.5, 38.4, 20.4 ppm; MS (EI, 70 eV) m/z 91, 118, 160, 192, 233; HRMS (ESI) m/z calcd for $C_{14}H_{20}NO_2$ $[M + H]^+$, 234.1489, found 234.1491; IR (KBr) 3414, 3018, 2918, 2862, 1616, 1518, 1484, 1300, 1089, 919, 809 cm^{-1}.

*N-(1-(4-Chlorophenyl)but-3-en-1-yl)-4-methylaniline (**1l**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (d, J = 2.2 Hz, 4H), 7.03 (d, J = 4.7 Hz, 2H), 6.63−6.49 (m, 2H), 5.96−5.69 (m, 1H), 5.38−5.13 (m, 2H), 4.55−4.33 (m, 1H), 4.11 (s, 1H), 2.81−2.45 (m, 2H), 2.32 (d, J = 2.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.9, 142.5, 134.4, 132.6, 129.7, 128.8, 127.9, 126.9, 118.7, 113.8, 57.0, 43.3, 20.5 ppm; MS (EI, 70 eV) m/z 91, 118, 230, 271; HRMS (ESI) m/z calcd for $C_{17}H_{19}ClN$ $[M + H]^+$, 272.1201, found 272.1200; IR (KBr) 3403, 2919, 2862, 1735, 1617, 1519, 1437, 1297, 1202, 810 cm^{-1}.

*4-Methyl-N-(1-phenylbut-3-en-1-yl)aniline (**1m**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57−7.31 (m, 5H), 7.03 (s, 2H), 6.57 (s, 2H), 6.00−5.83 (m, 1H), 5.29 (t, J = 14.2 Hz, 2H), 4.55−4.40 (m, 1H), 3.99 (s, 1H), 2.67 (dd, J = 38.2, 5.1 Hz, 2H), 2.32 (d, J = 3.0 Hz, 3H) ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.2, 143.9, 134.9, 129.7, 128.7, 127.0, 126.6, 126.4, 118.3, 113.7, 57.5, 43.4, 20.5 ppm; MS (EI, 70 eV) m/z 90, 118, 196, 237; HRMS (ESI) m/z calcd for $C_{17}H_{20}N$ $[M + H]^+$, 238.1590, found 238.1592; IR (KBr) 3413, 3024, 2919, 2860, 1616, 1518, 1301, 807 cm^{-1}.

*4-Methyl-N-(1-(naphthalen-1-yl)but-3-en-1-yl)aniline (**1n**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.51 (d, J = 5.1 Hz, 1H), 8.25−8.16 (m, 1H), 8.01 (dd, J = 16.3, 7.1 Hz, 2H), 7.94−7.75 (m, 2H), 7.69 (dd, J = 8.6, 6.3 Hz, 1H), 7.18 (d, J = 4.1 Hz, 2H), 6.74 (s, 2H), 6.29−6.00 (m, 1H), 5.53 (dd, J = 16.8, 8.9 Hz, 2H), 4.64−4.33 (m, 1H), 3.14 (d, J = 13.4 Hz, 1H), 2.86 (d, J = 7.2 Hz, 1H), 2.50 (d, J = 2.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.3, 138.7, 135.3, 134.6, 131.1, 129.9, 129.6, 127.8, 126.7, 126.4, 126.1, 125.7, 123.6, 122.7, 118.5, 113.9, 53.6, 41.9, 20.7 ppm; MS (EI, 70 eV) m/z 91, 118, 246, 287; HRMS (ESI) m/z calcd for $C_{21}H_{22}N$ $[M + H]^+$, 288.1747, found 288.1745; IR (KBr) 3416, 3070, 2916, 2861, 1616, 1517, 1302, 1261, 918, 808 cm^{-1}.

*4-Methyl-N-(3-phenylpent-4-en-2-yl)aniline (**1o**).* According to ref 23, **1o** has enantiomers, dr = 67:33. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27−7.06 (m, 5H), 6.90 (s, 2H), 6.45 (d, J = 6.1 Hz, 2H), 6.18−5.99 (m, 1H), 5.18−4.99 (m, 2H), 3.71−3. 66 (m, 1H), 3.49−3.47 (m, 1H), 2.15 (d, 3H), 1.03 (d, 3H), 0.93 (d, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.0, 144.9, 141.8, 141.0, 139.4, 136.9, 130.0, 129.9, 128.6, 128.4, 128.1, 126.6, 126.5, 117.9, 116.6, 114.2, 113.8, 54.9, 54.4, 52.8, 52.7, 20.5, 18.3, 17.2 ppm; MS (EI, 70 eV) m/z 91, 134, 251; HRMS (ESI) m/z calcd for $C_{18}H_{22}N$ $[M + H]^+$, 252.1747, found 252.1750; IR (KBr) 3405, 3025, 2971, 2921, 2865, 1616, 1517, 1450, 1299, 807, 701 cm^{-1}.

*4-Methyl-N-(4-methylpent-4-en-2-yl)aniline (**1p**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.04 (d, J = 7.9 Hz, 2H), 6.59 (d, J = 7.9 Hz, 2H), 4.85 (d, J = 24.7 Hz, 2H), 3.63 (dd, J = 12.9, 6.4 Hz, 1H), 3.22 (s, 1H), 2.39 (dd, J = 13.8, 6.7 Hz, 1H), 2.29 (s, 3H), 2.16 (dd, J = 13.9, 7.1 Hz, 1H), 1.80 (s, 3H), 1.24 (d, J = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.3, 143.1, 129.8, 126.4, 113.5, 112.9, 46.8, 45.6, 22.4, 20.9, 20.4 ppm; MS (EI, 70 eV) m/z 91, 119, 134, 189; HRMS (ESI) m/z calcd for $C_{13}H_{20}N$ $[M + H]^+$, 190.1590, found 190.1591.IR (KBr) 3403, 2968, 2923, 2862, 1650, 1518, 1451, 807 cm^{-1}.

*N-Benzyl-1-phenylbut-3-en-1-amine (**1q**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43−7.18 (m, 10H), 5.70 (td, J = 16.9, 8.1 Hz, 1H), 5.04 (t, J = 13.9 Hz, 2H), 3.68 (dd, J = 13.4, 6.2 Hz, 2H), 3.52 (d, J = 13.3 Hz, 1H), 2.40 (d, J = 8.7 Hz, 2H), 1.93 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.8, 140.6, 135.5, 128.5, 128.4, 128.2, 127.4, 127.1, 126.9, 117.6, 61.7, 51.5, 43.1 ppm; MS (EI, 70 eV) m/z 91, 196, 236; HRMS (ESI) m/z calcd for $C_{17}H_{20}N$ $[M + H]^+$, 238.1590, found 238.1595; IR (KBr) 3324, 3080, 3062, 2927, 2836, 1603, 1493, 1455, 915, 699 cm^{-1}.

*2-Phenyl-1-(p-tolyl)-1H-pyrrole (**3aa**).*[14] (Yellow oil). Yield (17.5 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 (ddd, J = 19.2, 12.9, 8.1 Hz, 7H), 7.07 (d, J = 7.7 Hz, 2H), 6.92 (s, 1H), 6.44 (s, 1H), 6.36 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.1, 136.4, 133.8, 133.1, 129.6, 128.3, 128.0, 126.2, 125.6, 124.4, 110.4, 109.0, 21.0 ppm; MS (EI, 70 eV) m/z 115, 129, 233; IR (KBr) 3266, 3073, 2928, 2867, 1598, 1513, 1424, 1325, 1158, 1090 cm^{-1}.

*2-(4-Ethylphenyl)-1-(p-tolyl)-1H-pyrrole (**3ab**).* (Yellow oil). Yield (18.3 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20−7.01 (m, 8H), 6.91 (s, 1H), 6.41 (s, 1H), 6.36 (s, 1H), 2.62 (q, J = 7.6 Hz, 2H), 2.37 (s, 3H), 1.23 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.2, 138.2, 136.3, 133.9, 130.5, 129.6, 128.2, 127.5, 125.6, 124.1, 110.1, 108.9, 28.5, 21.0, 15.3 ppm; MS (EI, 70 eV) m/z 91, 115, 128, 246, 261; HRMS (ESI) m/z calcd for $C_{19}H_{20}N$ $[M + H]^+$, 262.1588, found 262.1590; IR (KBr) 3309, 3112, 2965, 1705, 1575, 1513, 1460, 1266, 754 cm^{-1}.

*2-([1,1′-Biphenyl]-4-yl)-1-(p-tolyl)-1H-pyrrole (**3ac**).* (White solid). Yield (23.2 mg, 75%). mp 127−128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (d, J = 7.7 Hz, 2H), 7.48−7.39 (m, 4H), 7.32 (t, J = 7.3 Hz, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.13 (q, J = 8.1 Hz, 4H), 6.94 (s, 1H), 6.49 (s, 1H), 6.38 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =140.7, 138.7, 138.1, 136.5, 133.4, 132.1, 129.7, 128.7, 128.5, 127.0, 126.7, 125.6, 124.7, 110.6, 109.1, 21.0 ppm; MS (EI, 70 eV) m/z 91, 115, 129, 191, 309; HRMS (ESI) m/z calcd for $C_{23}H_{20}N$ $[M + H]^+$, 310.1588, found310.1590; IR (KBr) 3302, 3114, 2923, 1712, 1579, 1514, 1266, 755 cm^{-1}.

*2-(4-Fluorophenyl)-1-(p-tolyl)-1H-pyrrole (**3ad**).* (Yellow oil). Yield (19.8 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.07 (m, 4H), 7.04 (d, J = 8.1 Hz, 2H), 6.90 (t, J = 8.6 Hz, 3H), 6.39−6.38 (m, 1H), 6.34 (t, J = 2.9 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =δ 160.5 (d, J = 244 Hz), 136.8, 135.5, 131.8, 128.86 (d, J = 7.9 Hz), 128.6, 128.2 (d, J = 4 Hz), 124.5, 123.3, 113.9 (d, J = 22 Hz), 109.2, 107.9, 20.0 ppm; MS (EI, 70 eV) m/z 91, 115, 133, 251; HRMS (ESI) m/z calcd for $C_{17}H_{15}FN$ $[M + H]^+$, 252.1177, found252.1183; IR (KBr) 2200, 2110, 2965, 1720, 1551, 1510, 1462, 1266, 754 cm^{-1}.

*2-(4-Chlorophenyl)-1-(p-tolyl)-1H-pyrrole (**3ae**).* (White solid). Yield (22.2 mg, 83%). mp 88−89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.15 (dd, J = 14.0, 8.2 Hz, 4H), 7.05 (t, J = 6.9 Hz, 4H), 6.91 (s, 1H), 6.42 (s, 1H), 6.35 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.8, 136.7, 132.6, 131.6, 129.7, 129.4, 128.2, 125.6, 124.8, 110.7, 109.1, 21.0 ppm; MS (EI, 70 eV) m/z 115, 129, 267; HRMS (ESI) m/z calcd for $C_{17}H_{15}ClN$ $[M + H]^+$, 268.0881, found 268.0888; IR (KBr) 3299, 3113, 1711, 1572, 1514, 826, 753 cm^{-1}.

*2-(4-Bromophenyl)-1-(p-tolyl)-1H-pyrrole (**3af**).* (White solid). Yield (26.1 mg, 84%). mp 100−101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 7.02 (dd, J = 18.4, 7.9 Hz, 4H), 6.92 (s, 1H), 6.43 (m, 1H), 6.35 (s, 1H), 2.37 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.8, 136.7, 132.6, 132.0, 131.2, 129.8, 129.7, 125.6, 124.9, 120.2, 110.7, 109.2, 21.0 ppm; MS (EI, 70 eV) m/z 115, 129, 311; HRMS (ESI) m/z calcd for $C_{17}H_{15}BrN$ $[M + H]^+$, 312.0377, found312.0382; IR (KBr) 3307, 3038, 2921, 1707, 1575, 1514. 1457, 1266, 823, 753 cm^{-1}.

*Methyl 4-(1-(p-tolyl)-1H-pyrrol-2-yl)benzoate (**3ag**).* (White solid.). Yield (17.4 mg, 60%). mp 86−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, J = 7.4 Hz, 2H), 7.16 (dd, J = 18.1, 7.6 Hz, 4H),

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7.05 (d, J = 7.6 Hz, 2H), 6.94 (s, 1H), 6.53 (s, 1H), 6.36 (s, 1H), 3.88 (s, 3H), 2.36 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 137.8, 137.5, 136.9, 132.7, 129.8, 129.4, 127.6, 127.4, 125.8, 125.6, 111.8, 109.4, 52.0, 21.0 ppm; MS (EI, 70 eV) m/z 91, 115, 130, 232, 260, 291; HRMS (ESI) m/z calcd for $C_{19}H_{18}NO_2$ $[M + H]^+$, 292.1337, found 292.1332; IR (KBr) 3300, 3114, 1719, 1600, 1568, 1515, 1277 cm^{-1}.

*2-(3-Chlorophenyl)-1-(p-tolyl)-1H-pyrrole (**3ah**).* (Yellow oil). Yield (21.6 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (s, 1H), 7.04−7.15 (m, 6H), 6.92 (s, 2H), 6.44 (s, 1H), 6.34 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.7, 136.8, 134.9, 133.9, 132.3, 129.7, 129.2, 128.0, 126.3, 126.1, 125.5, 125.1, 111.1, 109.2, 21.0. ppm; MS (EI, 70 eV) m/z 115, 129, 267; HRMS (ESI) m/z calcd for $C_{17}H_{15}ClN$ $[M + H]^+$, 268.0889, found 268.0888; IR (KBr) 3113, 1713, 1565, 1516, 1266, 751 cm^{-1}.

*2-(m-Tolyl)-1-(p-tolyl)-1H-pyrrole (**3ai**).* (Yellow oil). Yield (19.0 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.15−7.04 (m, 6H), 6.98 (d, J = 7.4 Hz, 1H), 6.91 (s, 1H), 6.87 (d, J = 7.6 Hz, 1H), 6.42 (s, 1H), 6.35 (t, J = 2.7 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) = 138.2, 137.6, 136.3, 133.9, 133.0, 129.5, 129.0, 127.8, 127.0, 125.5, 125.4, 124.3, 110.3, 108.9, 21.4, 21.0 ppm; MS (EI, 70 eV) m/z 91, 115, 129, 247; HRMS (ESI) m/z calcd for $C_{18}H_{18}N$ $[M + H]^+$, 248.1429, found248.1434; IR (KBr) 3035, 2922, 1700, 1599, 1514, 1466, 1334, 822, 775, 709 cm^{-1}.

*2-(Naphthalen-2-yl)-1-(p-tolyl)-1H-pyrrole (**3aj**).* (Yellow oil). Yield (24.9 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79−7.75 (m, 1H), 7.72−7.63 (m, 3H), 7.45−7.39 (m, 2H), 7.23 (d, J = 8.5 Hz, 1H), 7.11 (s, 4H), 6.98 (s, 1H), 6.57−6.56 (m, 1H), 6.41 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.1, 136.5, 133.8, 133.4, 131.9, 130.7, 129.7, 127.9, 127.6, 127.4, 126.8, 126.6, 126.0, 125.6, 125.5, 124.7, 110.9, 109.2, 21.0 ppm; MS (EI, 70 eV) m/z 91, 115, 133, 165, 283; HRMS (ESI) m/z calcd for $C_{21}H_{18}N$ $[M + H]^+$, 284.1033, found284.1034; IR (KBr) 3052, 2928, 1711, 1571, 1513, 1457, 1334, 820, 747, 714 cm^{-1}.

*2-(3-Chloro-4-methylphenyl)-1-(p-tolyl)-1H-pyrrole (**3ak**).* (Yellow oil). Yield (19.7 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (s, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 7.8 Hz, 2H), 7.01 (d, J = 7.9 Hz, 1H), 6.89 (s, 1H), 6.81 (d, J = 7.9 Hz, 1H), 6.41−6.40 (m, 1H), 6.33 (s, 1H), 2.36 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.8, 136.7, 134.0, 133.7, 132.3, 130.4, 129.7, 128.5, 126.4, 125.6, 124.7, 110.6, 110.1, 109.1, 21.0, 19.7 ppm; MS (EI, 70 eV) m/z 91, 115, 129, 281; HRMS (ESI) m/z calcd for $C_{18}H_{17}ClN$ $[M + H]^+$, 282.1044, found282.1044; IR (KBr) 3109, 2926, 1713, 1561, 1513, 1460, 1335, 822 cm^{-1}.

*1,2-Diphenyl-1H-pyrrole (**3ba**).*[15] (White solid). Yield (14.7 mg, 67%). mp 88−90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (m, 3H), 7.17 (td, J = 14.5, 7.2 Hz, 7H), 6.94 (s, 1H), 6.44 (s, 1H), 6.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.6, 133.8, 133.0, 129.0, 128.3, 128.1, 126.6, 126.3, 125.8, 124.4, 110.7, 109.2 ppm; MS (EI, 70 eV) m/z 77, 108, 115, 219; IR (KBr) 3055, 2924, 1715, 1591, 1396, 1461, 1329, 759, 697 cm^{-1}.

*1-(4-Methoxyphenyl)-2-phenyl-1H-pyrrole (**3ca**).*[16] (Yellow oil). Yield (19.7 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16 (ddd, J = 24.1, 15.4, 7.7 Hz, 7H), 6.89 (s, 1H), 6.85 (d, J = 8.6 Hz, 2H), 6.43 (s, 1H), 6.34 (t, J = 2.6 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2, 133.9, 133.8, 133.1, 128.2, 128.0, 126.9, 126.1, 124.5, 114.1, 110.1, 108.8, 55.4 ppm; MS (EI, 70 eV) m/z 77, 115, 234, 249; IR (KBr) 3054, 2923, 2845, 1712, 1595, 1511, 1462, 1248, 1034, 755 cm^{-1}.

*1-(4-Fluorophenyl)-2-phenyl-1H-pyrrole (**3da**).* (Yellow oil). Yield (14.0 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20−7.00 (m, 6H), 6.93 (t, J = 8.5 Hz, 2H), 6.82 (s, 1H), 6.35 (s, 1H), 6.28 (t, J = 2.7 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.1(d, J = 245 Hz), 135.6(d, J = 3 Hz), 132.9, 131.7, 127.2 (d, J = 19 Hz), 126.3 (d, J = 8.4 Hz), 125.3, 123.3, 114.9, 114.7, 109.6, 108.3 ppm; MS (EI, 70 eV) m/z 95, 115, 133, 237; HRMS (ESI) m/z calcd for $C_{16}H_{13}FN$ $[M + H]^+$, 238.1028, found 238.1027; IR (KBr) 3067, 2926, 1709, 1591, 1509, 1466, 1224, 838, 756 cm^{-1}.

*1-(4-Chlorophenyl)-2-phenyl-1H-pyrrole (**3ea**).*[17] (Yellow oil). Yield (15.7 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29−7.20 (m, 5H), 7.10 (dd, J = 12.2, 8.2 Hz, 4H), 6.90 (s, 1H), 6.42 (s, 1H), 6.36 ((t, J = 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.1, 133.8, 132.6, 132.2, 129.1, 128.3, 128.2, 126.8, 126.5, 124.2, 111.0, 109.6. ppm; MS (EI, 70 eV) m/z 95, 108, 115, 217, 253; IR (KBr) 3110, 1709, 1580, 1495, 1334 cm^{-1}.

*1-(4-Bromophenyl)-2-phenyl-1H-pyrrole (**3fa**).*[18] (Yellow oil). Yield (17.5 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (d, J = 8.2 Hz, 2H), 7.21 (dd, J = 12.5, 7.1 Hz, 3H), 7.12 (d, J = 7.6 Hz, 2H), 7.03 (d, J = 8.2 Hz, 2H), 6.90 (s, 1H), 6.42 (s, 1H), 6.36 (t, J = 2.7 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.6, 133.8, 132.7, 132.1, 128.3, 128.2, 127.1, 126.5, 124.1, 120.1, 111.1, 109.7 ppm; MS (EI, 70 eV) m/z 115, 143, 224, 299; IR (KBr) 3075, 2924, 1709, 1582, 1491, 1334, 755 cm^{-1}.

*2-Phenyl-1-(m-tolyl)-1H-pyrrole (**3ga**).* (Yellow oil). Yield (17.9 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24−7.12 (m, 6H), 7.08 (d, J = 7.6 Hz, 1H), 7.04 (s, 1H), 6.93 (d, J = 7.0 Hz, 2H), 6.44 (s, 1H), 6.36 ((t, J = 3.0 Hz, 1H), 2.32 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.5, 139.0, 133.8, 133.1, 128.7, 128.2, 128.0, 127.4, 126.3, 126.2, 124.4, 123.0, 110.5, 109.1, 21.3. ppm; MS (EI, 70 eV) m/z 115, 129, 233; HRMS (ESI) m/z calcd for $C_{17}H_{16}N$ $[M + H]^+$, 234.1276, found 234.1277.IR (KBr) 3106, 1710, 1588, 1493, 1336, 755, 701 cm^{-1}.

*1-(3,5-Dimethylphenyl)-2-phenyl-1H-pyrrole (**3ia**).* (Yellow oil). Yield (19.8 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22−7.12 (m, 5H), 6.93−6.86 (m, 2H), 6.81−6.74 (m, 2H), 6.42 (m, 1H), 6.33 (s, 1H), 2.24 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.4, 138.6, 133.7, 133.1, 128.3, 128.1, 127.9, 126.1, 124.4, 123.5, 110.4, 108.9, 21.2 ppm; MS (EI, 70 eV) m/z 77, 115, 129, 247; HRMS (ESI) m/z calcd for $C_{18}H_{18}N$ $[M + H]^+$, 248.1435, found 248.1434; IR (KBr) 3108, 1712, 1598, 1475, 1346, 756 cm^{-1}.

*2-Methyl-5-phenyl-1-(p-tolyl)-1H-pyrrole (**3ja**).*[19] (Yellow oil). Yield (20.0 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (s, 1H), 7.17 (dd, J = 11.2, 7.4 Hz, 4H), 7.09 (dd, J = 13.9, 7.5 Hz, 5H), 6.38 (d, J = 3.1 Hz, 1H), 6.12 (d, J = 2.7 Hz, 1H), 2.41 (s, 3H), 2.16 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.2, 136.8, 134.2, 133.7, 131.8, 129.6, 128.2, 127.9, 127.8,125.6, 108.5, 107.3, 21.1, 13.3 ppm; MS (EI, 70 eV) m/z 91, 115, 129, 191, 247; IR (KBr) 3035, 2924, 1714, 1593, 1513, 1450, 1396, 754 cm^{-1}.

*Methyl 2-(5-phenyl-1-(p-tolyl)-1H-pyrrol-2-yl)acetate (**3ka**).* (Yellow oil). Yield (18.3 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.06 (t, J = 6.7 Hz, 4H), 6.99 (dd, J = 13.8, 7.7 Hz, 5H), 6.32 (d, J = 2.8 Hz, 1H), 6.19 (d, J = 2.8 Hz, 1H), 3.51 (s, 3H), 3.46 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.1, 137.8, 136.0, 135.2, 133.3, 129.7, 128.5, 128.0, 127.9, 127.8, 125.9, 109.2, 108.9, 52.0, 33.1, 21.1 ppm; MS (EI, 70 eV) m/z 115, 230, 246, 305; HRMS (ESI) m/z calcd for $C_{20}H_{20}NO_2$ $[M + H]^+$, 306.1495, found 306.1489; IR (KBr) 3069, 2923, 1738, 1572, 1513, 1447 cm^{-1}.

*2-(4-Chlorophenyl)-5-phenyl-1-(p-tolyl)-1H-pyrrole (**3la**).* (White solid). Yield (25.7 mg, 75%). mp 199−200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.15 (dd, J = 12.0, 8.1 Hz, 5H), 7.09−7.01 (m, 4H), 6.98 (d, J = 8.3 Hz, 2H), 6.89 (d, J = 7.9 Hz, 2H), 6.45 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.3, 136.2, 136.1,134.5, 133.2, 132.0, 131.9, 129.8, 129.6, 128.7, 128.5, 128.1, 127.9, 126.3, 110.0, 109.9, 21.1 ppm; MS (EI, 70 eV) m/z 91, 145, 191, 205, 343; HRMS (ESI) m/z calcd for $C_{23}H_{19}ClN$ $[M + H]^+$, 344.1203, found 344.1201; IR (KBr) 3115, 1712, 1567, 1515, 1482, 826, 754 cm^{-1}.

*2,5-Diphenyl-1-(p-tolyl)-1H-pyrrole (**3ma**).*[20] (White solid). Yield (24.1 mg, 78%). mp 193−194 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12−7.04 (m, 6H), 7.00 (d, J = 7.3 Hz, 4H), 6.95 (d, J = 7.7 Hz, 2H), 6.83 (d, J = 7.7 Hz, 2H), 6.39 (s, 2H), 2.24 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.0, 136.4, 135.9, 133.4, 129.4, 128.7, 128.6, 127.8, 126.1, 109.8, 21.1 ppm; MS (EI, 70 eV) m/z 91, 139, 191, 309; IR (KBr) 2991, 2924, 1764,1600, 1513, 1454, 1381, 1242, 1056, 753 cm^{-1}.

*2-(Naphthalen-1-yl)-5-phenyl-1-(p-tolyl)-1H-pyrrole (**3na**).* (Yellow solid). Yield (24.8 mg, 69%). mp 151−152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, J = 7.5 Hz, 1H), 7.72 (d, J = 6.1 Hz, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.38−7.32 (m, 2H), 7.23−7.16 (m, 2H), 7.12−7.06 (m, 6H), 6.72 (s, 3H), 6.51 (m, 1H), 6.40 (m, 1H), 2.09 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.34, 136.3, 134.9, 133.5,

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133.4,131.3 129.4, 129.0, 128.4, 128.0, 127.9, 127.6, 126.6, 126.0, 125.9, 125.6, 124.8, 111.7, 109.5, 21.0 ppm; MS (EI, 70 eV) *m/z* 91, 165, 207, 239, 359; HRMS (ESI) *m/z* calcd for $C_{27}H_{21}NNa$ [M + Na]$^+$, 382.1558, found 382.1566; IR (KBr) 2991, 1764, 1595, 1514, 1477, 1377, 1242, 1056, 753 cm^{-1}.

*2-Methyl-3,5-diphenyl-1-(p-tolyl)-1H-pyrrole (**3oa**).*[21] (Yellow solid). Yield (17.1 mg, 69%). mp 137−139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.16 (m, 10H), 6.57 (s, 1H), 2.39 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.4, 137.0, 136.6, 133.9, 133.3, 129.7, 128.4, 128.1, 128.0, 127.9, 125.8, 125.4, 122.6, 118.9, 116.9, 109.1, 21.2, 12.4 ppm; MS (EI, 70 eV) *m/z* 91, 117, 146, 161, 191, 323; IR (KBr) 3026, 2924, 1732, 1598, 1513, 1452, 1379, 754.698 cm^{-1}.

*1-(p-Tolyl)-1H-pyrrole (**4a**).*[22] (Yellow solid). Yield (12.3 mg, 78%). mp 84−85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.38−7.22 (m, 5H), 7.09 (s, 2H), 6.36 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.5, 134.3, 129.0, 119.5, 118.4, 109.0, 19.8 ppm; MS (EI, 70 eV) *m/z* 115, 129, 157; IR (KBr) 2919, 2851, 1652, 1588, 1467, 1262, 1092, 1022, 801, 753 cm^{-1}.

*1-(4-Chlorophenyl)-1H-pyrrole (**4b**).*[23] (Yellow solid). Yield (11.9 mg, 67%). mp 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.39 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.05 (s, 2H), 6.36 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.3, 131.1, 129.6, 121.6, 119.3, 110.8 ppm; MS (EI, 70 eV) *m/z* 115, 142, 177; IR (KBr) 2921, 2862, 1639, 1506, 1467, 1074, 826, 729 cm^{-1}.

*2-Phenyl-1-(m-tolyl)-2,5-dihydro-1H-pyrrole (**5**).* (Yellow oil). Yield (13.4 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32−7.26 (m, 4H), 7.22 (d, *J* = 6.4 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.47 (d, *J* = 7.3 Hz, 1H), 6.36 (s, 1H), 6.31 (d, *J* = 8.2 Hz, 1H), 5.96−5.91 (m, 1H), 5.85 (d, *J* = 6.0 Hz, 1H), 5.40 (s, 1H), 4.47 (dd, *J* = 14.0, 5.0 Hz, 1H), 4.25 (d, *J* = 13.9 Hz, 1H), 2.24 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.5, 142.8, 138.8, 132.5, 128.9, 128.8, 127.1, 126.2, 124.2, 117.1, 112.85, 109.5, 69.7, 56.2, 21.8 ppm; MS (EI, 70 eV) *m/z* 91, 118, 143, 158, 194, 235; HRMS (ESI) *m/z* calcd for $C_{17}H_{18}N$ [M + H]$^+$, 236.1433, found 236.1434; IR (KBr) 3055, 2925, 1708, 1594, 1494, 1357, 758, 699 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of all synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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