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A novel synthetic methodology for pyrroles from nitrodienes

Mohamed A. EL-Atawy,[a,b] Francesco Ferretti,[a] and Fabio Ragaini*[a]

Abstract: Palladium complexes with 4,7-dimethoxy-1,10-phenanthroline as ligand catalyze the reductive cyclization of nitrodienes using carbon monoxide as the reductant to give pyrroles. Carbon dioxide is the only stoichiometric byproduct. Yields are good and the starting materials can be easily synthesized in two steps by a cross-aldol condensation followed by a Henry reaction. Different substitution patterns are possible with this novel synthetic strategy.

Introduction

The pyrrole nucleus is one of the most important heterocyclic moieties, abundantly found in bioactive natural molecules, forming the characteristic subunit of heme,[1] chlorophyll,[2] vitamin B12[3] as well as in melanin pigments.[4] 1,2,5-Trisubstituted pyrroles display interesting biological properties, such as anti-inflammatory,[5] antipsychotic,[6] spasmolytic,[7] and radioprotective.[8] Two clinical examples of pyrroles displaying this pattern of substitution are amtolmetin and tolmetin.[9](nonsteroidal anti-inflammatory agents) (Chart 1). Generally pharmaceuticals containing pyrroles are of high value as biological agents such as sunitinib [10] (anti-tumour), keterolac [11] (analgesic) and the highly successful cholesterol-lowering drug atorvastatin calcium (Lipitor), which is notable as the first

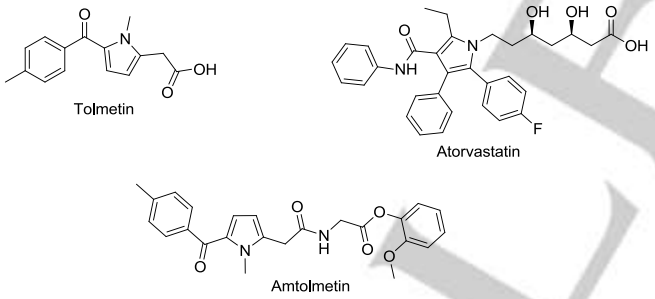
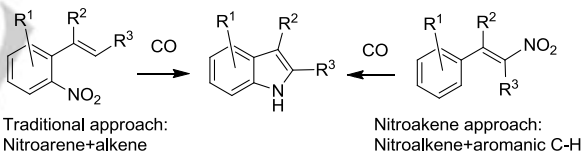


Figure 1: Important pharmaceutical drugs containing the pyrrole nucleus.

drug to earn in excess of $1 billion of sales in its first year.[12]

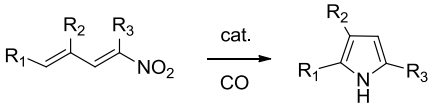
The electronic properties of pyrrole are important in the context of conducting polymers, where polypyrroles have found many useful applications.[13]

Consequently, many new synthetic methods have been developed for the construction of pyrroles and their derivatives. Classical methods for the synthesis of substituted pyrroles include the Knorr reaction,[14] the Hantzsch reaction,[15] and the Paal-Knorr condensation.[16] However, these methods have some limitations with respect to the regioselectivity, the substitution patterns that can be introduced, multistep synthetic operations and harsh reaction conditions. Despite recent advances, particularly in transition metal-catalyzed,[17] multicomponent processes[18] and domino reactions,[19] still novel and highly efficient chemical reaction that can be used to construct the skeleton of pyrroles with readily accessible substrates and in few steps remains an attractive goal. Over the past several years, metal catalyzed reductive condensation of a nitro and an olefin group for the construction of heterocyclic rings has been shown to be an effective, promising, extremely powerful method.[20],[21] Nitroarenes have exclusively been used as substrates for many years, but recently the use of nitroalkenes bearing in the beta position an aryl[22] or thienyl[23] moiety has been reported as an alternative strategy to construct nitrogen heterocycles in which the pyrrole nucleus is fused with the originally present aromatic ring (Scheme 1).



Scheme 1: Traditional and more recent approaches to the synthesis of N-heterocycles by reduction of organic nitro compounds.

Inspired by the importance of pyrrole derivatives and as an extension of our previous work, we report here our results on the developed of a new, facile and efficient synthesis for some pyrrole derivatives by reductive cyclization of nitrodienes, using palladium/phenanthroline as the catalyst and carbon monoxide as the reductant. The reaction proceeds through the activation of a diene C-H bond in the delta position relative to the nitro group and no aryl ring is directly involved in the reaction (Scheme 2).



Scheme 2. Synthesis of pyrroles from nitrodienes.

We are not aware of previous report of transition metal catalyzed reduction of nitrodienes by carbon monoxide to give

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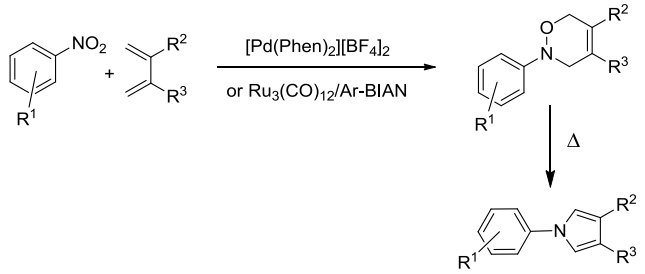
pyrroles. To our knowledge, only a single reaction has been mentioned in which this cyclization was effected by use of a stoichiometric amount of $P(OEt)_3$ (a Cadogan-type reaction).[24]

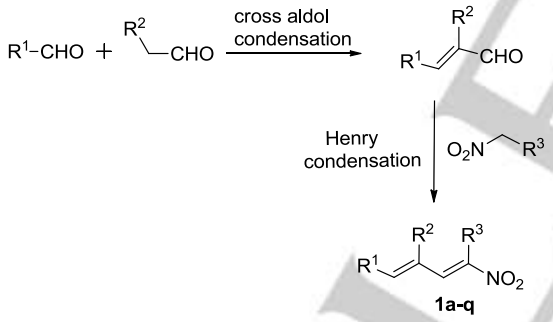
It should be recalled that we previously reported a synthesis of pyrroles by reduction of nitroarenes by CO in the presence of a conjugated diene. Oxazines are formed as intermediates in this case (Scheme 3, Ar-BIAN = *bis*-(arylimino)acenaphthene).[25] However, that strategy only affords N-arylpyrroles, whereas the presently described reaction gives N-unsubstituted compounds.



Scheme 3. N-Arylpyrrole synthesis from nitroarenes and dienes.

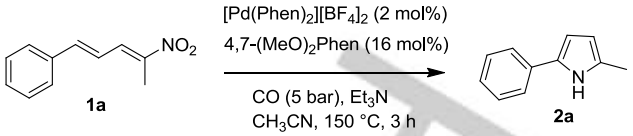
Results and Discussion

The starting nitrodienes were prepared by Henry condensation of a nitroalkane with an α-β-unsaturated aldehyde. The latter was in turn obtained by cross-aldol condensation (Scheme 4. See the experimental part for details).



Scheme 4. Synthesis of the starting nitrodienes

Recently we reported an extensive work on the optimization of a palladium catalytic system for the reductive cyclization of 1-(thien-2-yl)-2-nitropropene to 4*H*-5-methyl-thieno[3,2-b]pyrrole.[23] The best experimental conditions were $[Pd(Phen)_2][BF_4]_2$ (2 mol%) as catalyst, 4,7-dimethoxy-1,10-phenanthroline (16 mol%) as ligand, under 5 bar of CO and at 150 °C for 3 h, in the presence of Et_3N (400 µl) and in acetonitrile as the solvent. We tested the same conditions to cyclize (*1E,3E*)-4-nitro-1-phenylpenta-1,3-diene (**1a**) into 2-methyl-5-phenyl-1H-pyrrole (**2b**) and we were pleased to observe that **1a** was completely consumed, affording **2a** in a 76% isolated yield (Scheme 5).



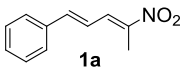
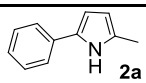
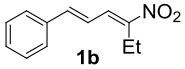
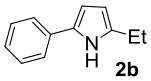
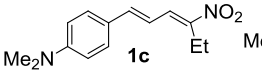
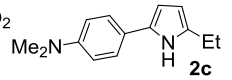
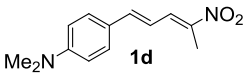
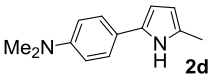
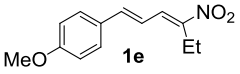
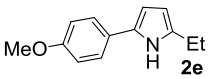
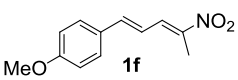
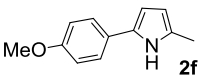
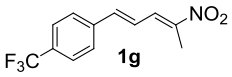
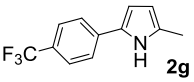
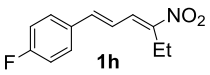
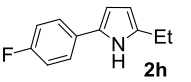
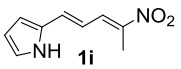
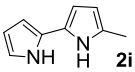
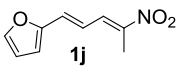
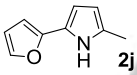
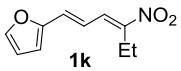
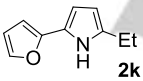
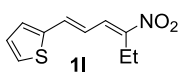
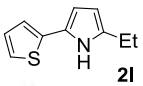
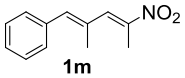
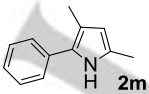
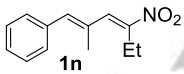
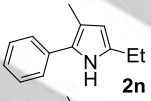
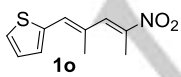
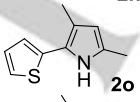
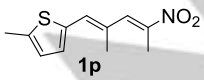
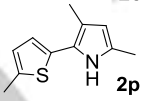
Scheme 5. Synthesis of 2-methyl-5-phenyl-1H-pyrrole (**2a**)

Encouraged by this result, we explored the scope of this reaction by applying it to a variety of differently substituted 1-nitro-1,3-butadienes (**1a**-**1q**, Table 1 and Scheme 6). Although this screening is not to be considered exhaustive and other substitution patterns are surely compatible with our protocol, it is evident that 2,5-disubstituted or 2,3,5-trisubstituted pyrroles can be obtained in moderate to good isolated yields (34-83%). Both strongly electronwithdrawing (-CF_3, **1g**) and strongly electrondonating (-NMe_2, **1c**, **1d**) substituents are well tolerated. The best result was obtained for the reductive cyclization of **1d** to **2d** (Table 1). Reductive cyclization of compounds **1a**-**1l** afforded disubstituted pyrrole in a good yield, whereas cyclization to trisubstituted pyrrole **2m**, **2n**, **2o** and **2p** gave lower and moderate yields. This can be correlated to the steric hindrance of the three substituents in the latter case, which hinders the cyclization step. Worth of note, the reaction is compatible with the presence of a second pyrrole, furan, or thiophene ring in the molecule (**2i-2l**, **2o**, **2p**). Such products belong to compound classes that can find applications for their optoelectronic properties.

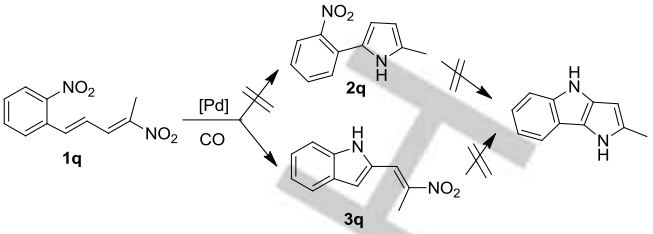
To test the relative ease of the present cyclization reaction with respect to the classical cyclization of an *o*-nitrostyrene to give an indole, we prepared (*1E,3E*)-4-nitro-1-(2-nitrophenyl)penta-1,3-diene (**1q**). This compound bears both a nitro group on the diene moiety and one on the aryl group. Thus, it may cyclize either by reduction of the former (to give pyrrole **2q**) or by reduction of the latter (to give indole **3q**). Both may further cyclize to 2-methyl-1,4-dihydropyrrolo[3,2-b]indole (Scheme 6). However, from the reaction mixture after the end of the reaction, only indole **3q** could be isolated (56% yield). Since the slow step of this kind of reductive cyclization has been shown to be the initial nitro group reduction in all the cases in which the kinetic has been investigated,[21e, 26] this indicates that the reduction of the nitro group bound to the aryl ring is faster than that of nitrodiene. Moreover, no 1,4-dihydropyrrolo[3,2-b]indole could be obtained even if isolated **3q** was employed as reagent for a second reaction under the same experimental conditions of the first. The electron-rich nature of the indole moiety is likely responsible for the lack of reactivity of **3q**. Indeed the initial reduction step of nitroarenes by metal complexes has been shown to be an electron transfer from the metal complex to the nitro group in all the cases in which this step has been experimentally analyzed[27] and electrondonating substituents are well known to make this reduction more difficult.

In this light, it should also be noted that the high yields obtained in the case of substrates having a strongly electrondonating substituent on the aryl ring (**1c**-**1f**) were initially not expected. Indeed, for all reactions of this kind we previously investigated employing nitroarenes as substrates, very poor

Table 1. Substrate scope.[a]

Entry	Substrate	Product	Yield (%)[b]
1	 **1a**	 **2a**	76
2	 **1b**	 **2b**	69
3	 **1c**	 **2c**	76
4	 **1d**	 **2d**	83
5	 **1e**	 **2e**	72
6	 **1f**	 **2f**	69
7	 **1g**	 **2g**	79
8	 **1h**	 **2h**	68
9	 **1i**	 **2i**	34
10	 **1j**	 **2j**	62
11	 **1k**	 **2k**	49
12	 **1l**	 **2l**	48
13	 **1m**	 **2m**	52
14	 **1n**	 **2n**	43
15	 **1o**	 **2o**	46
16	 **1p**	 **2p**	53

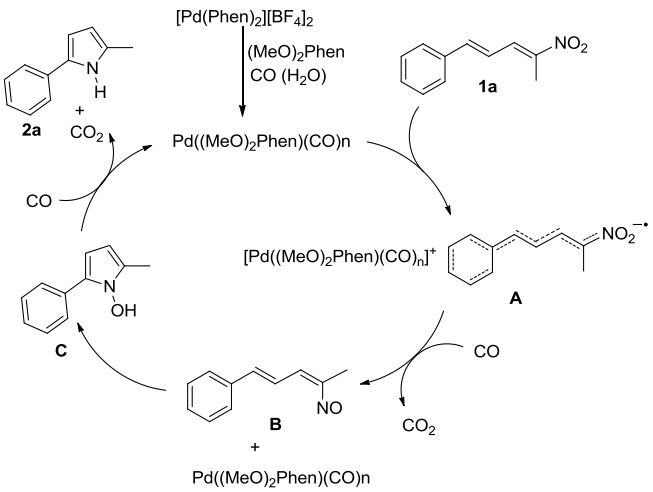
[a] Reaction conditions: **1** (0.5 mmol), $[Pd(Phen)_2][BF_4]_2$ (0.01 mmol), $(MeO)_2Phen$ (0.08 mmol), CH_3CN (15 mL), Et_3N (400 µl, 2.9 mmol), 150 °C, P_{CO} = 5 bar, for 3h. [b] Isolated yield.



Scheme 6. Alternative reaction pathways for the reductive cyclization of (*1E,3E*)-4-nitro-1-(2-nitrophenyl)penta-1,3-diene (**1q**)

yields or no reaction at all were observed when a methoxy or dimethylamino group was directly connected to the nitroarene.[20a] An intermediate outcome was observed when the cyclization of β-nitrostyrenes was investigated, where an olefinic bond is spacing the nitro and the aryl groups.[22b] Good results were obtained when a methoxy group was present, but the yield dropped in the presence of a dimethylamino substituent. In the present case, two double bonds keep the electron rich ring far from the nitro group. This is apparently enough to insulate the two groups to the point that negative effects are not detected, although it should also be considered that the use of the electron rich 4,7$(MeO)_2$Phen ligand surely plays a role in allowing the reaction to run smoothly. The same combination of spacing/electron rich ligand is responsible for the successful cyclization of substrates containing the very electron rich pyrrole, furan, and thiophene rings (substrates **1i**-**1l**, **1o**, **1p**). Note that in the case of the latter compounds, difficulties in isolating in a pure form the quite reactive products surely account in part for the lower isolated yields.

As far as the reaction mechanism is concerned, we propose it to proceed similarly to what it occurs in other related transition-metal catalyzed deoxygenation of organic nitro compounds by carbon monoxide, leading to heterocycles (Scheme 7).



Scheme 7. Proposed mechanism for the reductive cyclization of **1a** to **2a.**

The first step of this reaction pathway is the already mentioned initial electron transfer from the metal complex to the nitroarene. The formation of a delocalized radical anion and the easy cis/trans isomerization of such a type of compound explain why the cyclization occurs even if the orientation of the nitro group in the starting material would not allow it to approach the distal C=C double bond. The radical couple than collapses with liberation of CO_2 and formation of a nitrosodiene. The latter is involved in the cyclization step to give a N-hydroxypyrrole. That the cyclization reaction occurs at this stage and not from a nitrene intermediate (or imido complex) generated by further reduction of the nitroso compound, as often proposed in the older literature, is strongly indicated by the isolation of N-hydroxy derivatives (*e.g.* N-hydroxyindoles) during several similar reactions and by theoretical calculations.[21d, 26, 28]] Further deoxygenation of the N-hydroxypyrrole by carbon monoxide finally affords the product.

Conclusions

In this work, we have reported a novel palladium-catalyzed reductive cyclization of nitrodienes employing carbon monoxide as the reductant and affording carbon dioxide as the only stoichiometric byproduct. The method is versatile and moderate to good yields of the products can be obtained. Both strongly electronwithdrawing (-CF_3) and strongly electrondonating (-NMe_2) substituents are well tolerated. Because of our interests, we mainly focused our synthetic attempts to some model substrates and to compounds containing a second five-membered ring. However, the reaction never failed in any of our attempts and it is clear that it should work well even for a much broader class of compounds. Worth of note, the starting materials can be obtained in a simple way from cheap products and without the need for expensive reagents at any stage of the process. Thus, the synthesis is amenable to scale up even at the production scale in an economically competitive way.

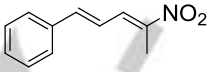
Experimental Section

Unless otherwise stated, all reactions were conducted under a dinitrogen atmosphere. All the solvents used in catalytic reactions, were dried by distillation over CaH_2 and stored under a dinitrogen atmosphere. All glassware and magnetic stirring bars were kept in an oven at 125 °C for at least two hours and let to cool under vacuum before use. 1,10-Phenanthroline (Phen), purchased as the hydrate, was dried over Na_2SO_4 after dissolution in CH_2Cl_2, followed by filtration under a dinitrogen atmosphere and evaporation of the solvent in vacuo. Then, it was stored under dinitrogen. 4,7-Dimethoxy-1,10-phenathroline ($(MeO)_2$Phen) was synthesized as reported in the literature.[29] Both phenanthrolines can be weighed in the air, but must be stored in an inert atmosphere to avoid water uptake. $[Pd(Phen)_2][BF_4]_2$, was synthesized following the procedure reported in the literature.[30] α,β-Unsaturated aldehydes were prepared by cross aldol condensation.[31] They are all known compounds and their spectroscopic characterization matched the published data ((*E*)-3-(4-(trifluoromethyl)phenyl)acrylaldehyde,[32] (*E*)-3-(4-fluorophenyl)acrylaldehyde,[33] (*E*)-3-(1H-pyrrol-2-yl)acrylaldehyde,[34] (*E*)-3-(fur-2-yl)acrylaldehyde,[35] (*E*)-3-(thiophen-2-yl)acrylaldehyde,[36] (*E*)-2-methyl-3-(thiophen-2-yl)acrylaldehyde,[37] (*E*)-2-methyl-3-(5-methylthiophen-2-yl)acrylaldehyde,[38] (*E*)-2-methyl-3-(thien-3-yl)acrylaldehyde.[39] If not otherwise stated, all the other reagents were purchased from Aldrich or Alfa-Aesar and used without further purification. ^{1}H, ^{13}C and 2D (COSY, NOESY) NMR spectra were recorded on a Bruker Avance DRX 300 or on a Bruker Avance DRX 400, operating at 300 and 400 MHz respectively.

Synthesis and characterization of substituted nitrodiene

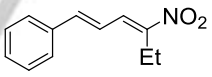
Nitrodienes were prepared by Henry condensation between the corresponding α,β-unsaturated aldehyde and the appropriate nitroalkane.

In a Schlenk flask, the aldehyde (10 mmol) and ammonium acetate (5 mmol) were dissolved in nitroethane (5 ml). The mixture was stirred at reflux for 5 hours and the conversion of the aldehyde checked by TLC on silica gel. The mixture was then allowed to cool to room temperature and the solvent was evaporated. The residue was taken up with CH_2Cl_2 and washed with water. The organic layer was dried (Na_2SO_4) and evaporated in vacuo. Finally, purification over a short silica column with EtOAc: hexane as the eluent afforded the olefin.[40]



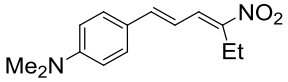
(*1E,3E*)-4-Nitro-1-phenylpenta-1, 3-diene (1a) [41]

Henry condensation between cinnamaldehyde and nitroethane. Yellow solid, yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.80 (d, *J* = 11.5 Hz, 1H, H_{diene}), 7.57 – 7.52 (m, 2H, H_{Ph}), 7.46 – 7.35 (m, 3H, H_{Ph}), 7.12 (d, *J* = 15.4 Hz, 1H, H_{diene}), 6.92 (dd, *J* = 15.4, 11.5 Hz, 1H, H_{diene}), 2.39 (s, 3H, C*H*$_3$) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ = 143.93 (*C*H), 135.64 (*C*), 133.64 (*C*H), 130.06 (*C*H), 129.05 (*C*H), 127.77 (*C*H), 121.48 (*C*H), 13.17 (*C*H$_3$) ppm. One quaternary carbon was not detected. Spectral data of the compound are in accordance with those reported in the literature. $C_{11}H_{11}NO_2$ requires: C, 69.83; H, 5.86; N, 7.40%. Found: C, 70.20; H, 6.00; N, 7.05%.



(*1E,3E*)-4-Nitro-1-phenylhexa-1,3-diene (1b)

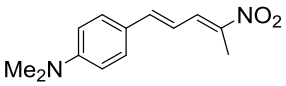
Henry condensation between cinnamaldehyde and nitropropane. Yellow solid, yield 53%. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.73 (d, *J* = 11.4 Hz, 1H, H_{diene}), 7.59 – 7.30 (m, 5H, H_{Ph}), 7.12 (d, *J* = 15.5 Hz, 1H, H_{diene}), 6.92 (dd, *J* = 15.5, 11.5 Hz, 1H, H_{diene}), 2.84 (q, *J* = 7.4 Hz, 2H, CH_2), 1.24 (t, *J* = 7.4 Hz, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 152.59 (*C*), 144.43 (*C*H), 136.12 (*C*), 133.55 (*C*H), 130.26 (*C*H), 129.38 (*C*H), 127.94 (*C*H), 121.36 (*C*H), 20.84 (CH_2), 13.41 (CH_3) ppm. $C_{12}H_{13}NO_2$ requires: C, 70.92; H, 6.45; N, 6.89%. Found: C 70.64; H 6.43; N 6.97 %



***N,N*-Dimethyl-4-((1*E*,3*E*)-4-nitrohexa-1,3-dienyl)aniline (1c)**

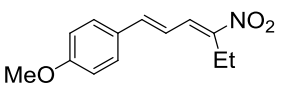
Henry condensation between 4-dimethylaminocinnamaldehyde and nitropropane. Dark purple solid, yield 85%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 11.2 Hz, 1H, H_{diene}), 7.44 (d, *J* = 8.8 Hz, 2H, H_{Ar}), 7.04 (d, *J* = 15.1 Hz, 1H, H_{diene}), 6.72 (m, 3H, H_{Ar} and H_{diene}), 3.06 (s, 6H, C*H*$_3$), 2.80 (q, *J* = 7.4 Hz, 2H, C*H*$_2$), 1.21 (t, *J* = 7.4 Hz, 3H, C*H*$_3$) ppm. ^{13}C

NMR (75 MHz, $CDCl_3$) δ 151.68 (*C*), 149.11 (*C*), 145.02 (*C*H), 135.29 (*C*H), 129.37 (*C*H), 124.21 (*C*), 116.30 (*C*H), 112.06 (*C*H), 40.20 (CH_3), 20.37 (CH_2), 12.92 (CH_3) ppm. $C_{14}H_{18}N_2O_2$ requires: C, 68.27; H, 7.37; N, 11.37%. Found: C, 68.43; H, 7.22; N, 11.20%.



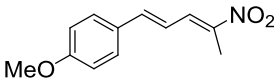
***N*,*N*-Dimethyl-4-((1*E*,3*E*)-4-nitropenta-1,3-dienyl)aniline (1d)**

Henry condensation between 4-dimethylaminocinnamaldehyde and nitroethane. Dark purple solid, yield 87%. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 11.7 Hz, 1H, H_{diene}), 7.44 (d, *J* = 8.7 Hz, 2H, H_{Ar}), 7.04 (d, *J* = 15.2 Hz, 1H, H_{diene}), 6.77 – 6.61 (m, 3H, H_{Ar} and H_{diene}), 3.06 (s, 6H, CH_3), 2.35 (s, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.37 (*C*), 145.29 (*C*H), 143.39 (*C*), 135.67 (*C*H), 129.54 (*C*H), 124.15 (*C*), 116.66 (*C*H), 112.20 (*C*H), 40.35 (CH_3), 12.88 (CH_3) ppm. $C_{13}H_{16}N_2O_2$ requires: C, 67.22; H, 6.94; N, 12.06%. Found: C, 67.25; H, 6.71; N, 11.79%.



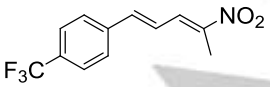
1-Methoxy-4-((1*E*,3*E*)-4-nitrohexa-1,3-dienyl)benzene (1e) [42]

Henry condensation between 4-methoxycinnamaldehyde and nitropropane. Orange solid, yield 89%. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 11.6 Hz, 1H, H_{diene}), 7.48 (d, *J* = 8.6 Hz, 2H, H_{Ar}), 7.04 (d, *J* = 15.3 Hz, 1H, H_{diene}), 6.91 (t, *J* = 9.5 Hz, 2H, H_{Ar}), 6.78 (dd, *J* = 15.2, 11.7 Hz, 1H, H_{diene}), 3.85 (s, 3H, CH_3), 2.80 (q, *J* = 7.4 Hz, 2H, CH_2), 1.21 (t, *J* = 7.4 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.05 (*C*), 150.79 (*C*), 144.04 (*C*H), 133.99 (*C*H), 129.24 (*C*H), 128.69 (*C*), 118.75 (*C*H), 114.46 (*C*H), 55.31 (CH_3), 20.38 (CH_2), 12.97 (CH_3) ppm. Spectral data of the compound are in accordance with those reported in the literature. $C_{13}H_{15}NO_3$ requires: C, 66.94; H, 6.48; N, 6.00%. Found: C, 67.09; H, 6.44; N, 5.96%.



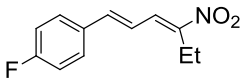
1-Methoxy-4-((1*E*,3*E*)-4-nitropenta-1,3-dienyl)benzene (1f) [42]

Henry condensation between 4-methoxycinnamaldehyde and nitroethane. Orange solid, yield 54%. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 11.6 Hz, 1H, H_{diene}), 7.49 (d, *J* = 8.7 Hz, 2H, H_{Ar}), 7.06 (d, *J* = 15.4 Hz, 1H, H_{diene}), 6.94 (d, *J* = 8.7 Hz, 2H, H_{Ar}), 6.78 (dd, *J* = 15.3, 11.6 Hz, 1H, H_{diene}), 3.87 (s, 1H, OCH_3), 2.37 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.09 (*C*), 145.26 (*C*), 143.83 (*C*H), 134.41 (*C*H), 129.19 (*C*H), 128.64 (*C*), 119.13 (*C*H), 114.41 (*C*H), 55.29 (OCH_3), 13.07 (CH_3) ppm. Spectral data of the compound are in accordance with those reported in the literature. $C_{12}H_{13}NO_3$ requires: C, 65.74; H, 5.98; N, 6.39%. Found: C, 65.70; H, 5.98; N, 6.31%.



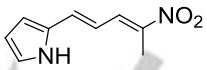
1-((1*E*,3*E*)-4-Nitropenta-1,3-dienyl)-4-(trifluoromethyl)benzene (1g)

Henry condensation between 4-trifluoromethylcinnamaldehyde and nitroethane. Yellow solid, yield 93%. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 11.5 Hz, 1H, H_{diene}), 7.67 (d, *J* = 8.5 Hz, 2H, H_{Ar}), 7.64 (d, *J* = 8.3 Hz, 2H, H_{Ar}), 7.12 (d, *J* = 15.5 Hz, 1H, H_{diene}), 6.99 (dd, *J* = 15.5, 11.4 Hz, 1H, H_{diene}), 2.41 (s, 3H, CH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 147.70 (*C*), 141.62 (*C*H), 139.00 (*C*), 132.58 (*C*H), 131.36 (q, $^2J_{C,F}$ = 31.71 Hz, *C*), 127.65 (*C*H), 125.88 (q,$^3J_{C,F}$ = 3.6 Hz, *C*H), 124.85 (q, $^1J_{C,F}$ = 270 Hz, *C*F_3), 123.58 (*C*H), 13.18 (CH_3) ppm. $C_{12}H_{10}F_3NO_2$ requires: C, 56.04; H, 3.92; N, 5.45%. Found: C, 56.11; H, 3.98; N, 5.26%.



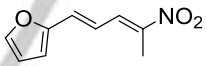
1-Fluoro-4-((1*E*,3*E*)-4-nitrohexa-1,3-dienyl)benzene (1h)

Henry condensation between 4-fluorocinnamaldehyde and nitropropane. Orange solid, yield 74%. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 11.6 Hz, 1H, H_{diene}), 7.53 (dd, *J* = 8.8, 5.4 Hz, 2H, H_{Ar}), 7.15 – 7.05 (m, 3H, H_{Ar} and H_{diene}), 6.84 (dd, *J* = 15.4, 11.6 Hz, 1H, H_{diene}), 2.83 (q, *J* = 7.4 Hz, 2H, CH_2), 1.23 (t, *J* = 7.5 Hz, 3H, CH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.81 (d, $^1J_{CF}$ = 237.1 Hz, *C*F), 152.42 (*C*), 142.61 (*C*H), 133.35 (*C*H), 132.23 (*C*), 129.43 (d, $^3J_{CF}$ = 8.2 Hz, *C*H), 120.73 (*C*H), 116.22 (d, $^2J_{CF}$ = 21.8 Hz, *C*H), 20.38 (CH_2), 12.94 (CH_3) ppm. $C_{12}H_{12}FNO_2$ requires: C, 65.15; H, 5.47; N, 6.33%. Found: C, 65.08; H, 5.42; N, 6.14%.



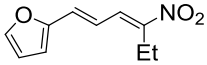
2-((1*E*,3*E*)-4-Nitropenta-1,3-dienyl)-1*H*-pyrrole (1i)

Henry condensation between (*E*)-3-(1*H*-pyrrol-2-yl)acrylaldehyde and nitroethane. Violet crystals, yield 83%. ^1H NMR (600 MHz, $CDCl_3$): δ = 8.74 (br s, 1H, N*H*), 7.80 (d, *J* = 11.7 Hz, 1H, H_{diene}), 6.96 (m, 2H, $H_{diene,}$ and $H_{pyrrole}$), 6.59 (s, 1H, $H_{pyrrole}$), 6.49 (dd, *J* = 15.3, 11.8 Hz, 1H, H_{diene}), 6.32 (br s, 1H, $H_{pyrrole}$), 2.34 (s, 3H, CH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 143.90 (*C*), 135.34 (*C*H), 133.79 (*C*H), 130.31 (*C*), 122.75 (*C*H), 115.89 (*C*H), 113.88 (*C*H), 111.53 (*C*H), 13.02 (CH_3) ppm. $C_9H_{10}N_2O_2$ requires: C, 60.66; H, 5.66; N, 15.72%. Found: C, 60.82; H, 5.64; N, 15.57%.



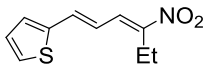
(1*E*,3*E*) 4-Nitro-1-fur-2-ylpenta-1,3-diene (1J)

Henry condensation between (*E*)-3-(fur-2-yl)acrylaldehyde and nitroethane. Yellow solid, yield 70%. ^1H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.72 (d, *J* = 9.8 Hz, 1H, H_{diene}), 7.50 (br s, 1H, H_{furan}), 6.91 – 6.71 (m, 2H, H_{diene}), 6.57 (d, *J* = 3.4 Hz, 1H, H_{furan}), 6.50 (dd, *J* = 3.4, 1.8 Hz, 1H, H_{furan}), 2.35 (s, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 152.42 (*C*), 146.61 (*C*), 144.89 (*C*H), 133.81 (*C*H), 130.31 (*C*H), 119.96 (*C*H), 113.92 (*C*H), 113.02 (*C*H), 13.42 (CH_3) ppm. $C_9H_9NO_3$ requires: C, 60.33; H, 5.06; N, 7.82%. Found: C, 60.56; H, 4.93; N, 7.86%.



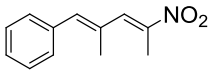
(1*E*,3*E*) 4-Nitro-1-fur-2-ylhexa-1,3-diene (1k)

Henry condensation between (*E*)-3-(fur-2-yl)acrylaldehyde and nitropropane. Orange solid, yield = 66 %. ^1H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, *J* = 9.6 Hz, 1H, H_{diene}), 7.50 (br s, 1H, H_{furan}), 6.93 – 6.68 (m, 2H, H_{diene}), 6.55 (d, *J* = 3.4 Hz, 1H, H_{furan}), 6.49 (dd, *J* = 3.2, 1.7 Hz, 1H, H_{furan}), 2.79 (q, J = 7.4 Hz, 2H, CH_2), 1.19 (t, J = 7.4 Hz, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.47 (*C*), 152.20 (*C*), 144.90 (*C*H), 133.34 (*C*H), 130.32 (*C*H), 119.60 (*C*H), 114.05 (*C*H), 112.94 (*C*H), 20.75 (CH_2), 13.32 (CH_3) ppm. $C_{10}H_{11}NO_3$ requires: C, 62.17; H, 5.74; N, 7.25%. Found: C, 62.03; H, 5.71; N, 7.11%.



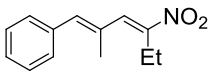
2-((1*E*,3*E*)-4-Nitrohexa-1,3-dienyl)thiophene (1l)

Henry condensation between (*E*)-3-(thien-2-yl)acrylaldehyde and nitropropane. Red oil, yield 88%. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 11.7 Hz, 1H, H_{diene}), 7.39 (d, *J* = 5.0 Hz, 1H, H_{thiop}), 7.23 – 7.19 (m, 2H, H_{thioph} and H_{diene}), 7.08 (dd, *J* =5.0, 3.4 Hz, 1H, H_{thioph}), 6.68 (dd, *J* =15.2, 11.7 Hz, 1H, H_{diene}), 2.79 (q, J = 7.4 Hz, 2H, C*H*$_2$), 1.22 (t, J = 7.4 Hz, 3H, C*H*$_3$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 151.68 (*C*), 141.33 (*C*), 136.39 (*C*H), 133.07 (*C*H), 129.85 (*C*H), 128.36 (*C*H), 128.07 (*C*H), 120.43 (*C*H), 20.52 (*C*H$_2$), 13.08 (*C*H$_3$) ppm. $C_{10}H_{11}NO_2S$ requires: C, 57.39; H, 5.30; N, 6.69%. Found: C, 57.68; H, 5.42; N, 6.39%.



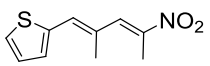
(1*E*,3*E*)-2-Methyl-4-nitro-1-phenylpenta-1,3-diene (1m)

Henry condensation between *trans*-α-methylcinnamaldehyde and nitroethane. Yellow solid, yield 52%. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.77 (s, 1H, H_{diene}), 7.49 – 7.31 (m, 5H, H_{Ar}), 6.85 (s, 1H, H_{diene}), 2.47 (s, 3H, C*H*$_3$), 2.20 (s, 3H, C*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 146.43 (*C*), 139.27 (*C*H), 138.34 (*C*H), 136.18 (*C*), 131.29 (*C*), 129.49 (*C*H), 128.48 (*C*H), 128.14 (*C*H), 17.80 (CH_3), 14.34 (CH_3) ppm. $C_{12}H_{13}NO_2$ requires: C, 70.92; H, 6.45; N, 6.89%. Found: C, 71.16; H, 6.33; N, 6.83%.



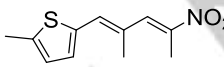
(1*E*,3*E*)-2-Methyl-4-nitro-1-phenylhexa-1,3-diene (1n)

Henry condensation between α-methylcinnamaldehyde and nitropropane. Yellow oil, yield 44%. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.71 (s, 1H, H_{diene}), 7.51 – 7.32 (m, 5H, H_{Ar}), 6.86 (s, 1H, H_{diene}), 2.92 (q, *J* = 7.4 Hz, 2H, C*H*$_2$), 2.18 (s, 3H, C*H*$_3$), 1.25 (t, *J* = 7.4 Hz, 3H, C*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 152.35 (*C*), 139.07 (*C*H), 138.27 (*C*H), 136.69 (*C*), 131.62 (*C*), 129.79 (*C*H), 128.84 (*C*H), 128.47 (*C*H), 21.55 (CH_2), 17.85 (CH_3), 13.71 (CH_3) ppm. $C_{13}H_{15}NO_2$ requires C, 71.87; H, 6.96; N, 6.45%. Found: C, 72.17; H, 7.15; N, 6.05%.



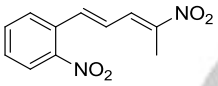
(1*E*,3*E*)-2-Methyl-4-nitro-1-thien-2-ylpenta-1,3-diene (1o)

Henry condensation between (*E*)-2-methyl-3-(thien-3-yl)acrylaldehyde and nitroethane. Yellow oil, yield = 53%. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.79 (s, 1H, H_{diene}), 7.48 (d, *J* = 5.0 Hz, 1H, H_{thioph}), 7.22 (d, *J* = 3.6 Hz, 1H, H_{thioph}), 7.12 (dd, *J* = 5.0, 3.6 Hz, 1H, H_{thioph}), 7.01 (s, 1H, H_{diene}), 2.47 (s, 3H, C*H*$_3$), 2.30 (s, 3H, C*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.30 (*C*), 140.04 (*C*), 138.92 (*C*H), 132.75 (*C*H), 131.09 (*C*H), 129.09 (*C*), 128.86 (*C*H), 127.99 (*C*H), 18.47 (CH_3), 14.93 (CH_3) ppm. $C_{10}H_{11}NO_2S$ requires: C, 57.39; H, 5.30; N, 6.69%. Found: C, 57.49; H, 5.35; N, 6.45;



(1*E*,3*E*)-2-Methyl-4-nitro-1-(5-methylthien-2-yl)penta-1,3-diene (1p)

Henry condensation between (*E*)-2-methyl-3-(5-methylthiophen-2-yl)acrylaldehyde and nitroethane. Orange solid, yield = 32%. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.79 (s, 1H, H_{diene}), 7.02 (d, *J* = 3.7 Hz, 1H, H_{thioph}), 6.94 (s, 1H, H_{diene}), 6.79 (dd, *J* = 3.7, Hz, 1H, H_{thioph}), 2.55 (s, 3H, C*H*$_3$), 2.45 (s, 3H, C*H*$_3$), 2.27 (s, 3H, C*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 145.66 (*C*), 144.44 (*C*), 139.48 (*C*H), 137.92 (*C*), 133.84 (*C*H), 131.69 (*C*H), 127.45 (*C*), 126.21 (*C*H), 18.16 (CH_3), 15.92 (CH_3), 14.75 (CH_3) ppm. $C_{11}H_{13}NO_2S$ requires: C, 59.17; H, 5.87; N, 6.27%. Found: C, 59.21; H, 5.86; N, 6.20%.



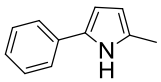
(1*E*,3*E*)-4-Nitro-1-(2-nitrophenyl)penta-1,3-diene

Henry condensation between *o*-nitrocinnamaldehyde and nitroethane. Yellow solid, yield = 92%. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 8.06 (d, *J* = 8.1 Hz, 1H, H_{diene}), 7.80 (d, *J* = 11.6 Hz, 1H, H_{diene}), 7.67 – 7.50 (m, 4H, H_{Ar}), 6.86 (dd, *J* = 15.2, 11.6 Hz, 1H, H_{diene}), 2.40 (s, 3H, C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 158.62 (*C*), 148.47 (*C*), 138.62 (*C*H), 133.80 (*C*H), 132.65 (*C*H), 131.85 (*C*), 130.15 (*C*H), 128.96 (*C*H), 126.36 (*C*H), 125.61 (*C*H), 13.60 (CH_3) ppm. $C_{11}H_{10}N_2O_4$ requires: C, 56.41; H, 4.30; N, 11.96%. Found: C, 56.52; H, 4.23; N, 12.00%.

Typical Catalytic Reaction

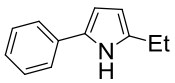
The catalyst, $[Pd(Phen)_2][BF_4]_2$ (0.01 mmol), the ligand, $(MeO)_2$Phen (0.08 mmol), and the nitrodiene (0.50 mmol) were weighed in the air in a glass liner and then placed inside a Schlenk tube with a wide mouth under a dinitrogen atmosphere. The solvent, CH_3CN (15 mL), and Et_3N (400 µl, 2.9 mmol), were added by volume and the liner was closed with a screw cap having a glass wool-filled open mouth that allows gaseous reagents to exchange. The resulting solution was stirred for 10 minutes and then the Schlenk tube was immersed in liquid nitrogen until the solvent froze and evacuated and filled with dinitrogen for three times. The liner was rapidly transferred to a 200 mL stainless steel autoclave equipped with magnetic stirring. The autoclave was then evacuated and filled with dinitrogen three times. CO, 5 bar, was charged at room temperature and the autoclave was immersed in an oil bath preheated at 150 °C and stirred at this temperature for 3h.. At the end of the reaction, the autoclave was quickly cooled with an ice bath, and vented. The substrate scope was investigated by isolating the products by column chromatography (gradient elution from hexane to hexane/AcOEt 9:1 with the addition of 1% Et_3N).

Characterization of pyrroles



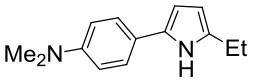
2-Methyl-5-phenyl-1*H*-pyrrole (2a) [43]

White solid, yield 76%. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 8.13 (br s, exchangeable, 1H, N*H*), 7.46 (d, *J* = 7.9 Hz, 2H, H_{Ar}), 7.37 (t, *J* = 7.7 Hz, 2H, H_{Ar}), 7.19 (t, *J* = 7.3 Hz, 1H, H_{Ar}), 6.43 (br s, 1H, $H_{pyrrole}$), 5.99 (br s, 1H, $H_{pyrrole}$), 2.37 (s, 3H, C*H*$_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 133. 53 (*C*), 131.20 (*C*), 129.42 (*C*), 129.21 (*C*H), 126.05 (*C*H), 123.74 (*C*H), 108.36 (*C*H), 106.61 (*C*H), 13.58 (CH_3) ppm. $C_{11}H_{11}N$ requires: C, 84.04; H, 7.05; N, 8.91%. Found: C, 84.18; H, 6.69; N, 8.60%. Spectral data of the compound are in accordance with those reported in the literature



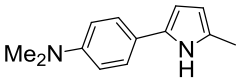
2-Ethyl-5-phenyl-1*H*-pyrrole (2b) [44]

White solid, yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 8.14 (br s, exchangeable, 1H, N*H*), 7.47 (d, *J* = 7.9 Hz, 2H, H_{Ar}), 7.37 (t, *J* = 7.7 Hz, 2H, H_{Ar}), 7.19 (t, *J* = 7.3 Hz, 1H, H_{Ar}), 6.45 (br s, 1H, $H_{pyrrole}$), 6.02 (br s, 1H, $H_{pyrrole}$). 2.72 (q, *J* = 7.6 Hz, 2H, CH_2), 1.33 (t, *J* = 7.6 Hz, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 135.62 (*C*), 133.21 (*C*), 130.70 (*C*), 128.82 (*C*H), 125.79 (*C*H), 123.34 (*C*H), 106.38 (*C*H), 106.00 (*C*H), 21.09 (*C*H_2), 13.71 (*C*H_3) ppm. $C_{12}H_{13}N$: requires: C, 84.17; H, 7.65; N, 8.18%. Found: C, 84.11; H, 7.76; N, 8.05%. Spectral data of the compound are in accordance with those reported in the literature



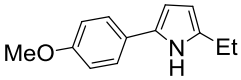
4-(5-Ethyl-1*H*-pyrrol-2-yl)-*N*,*N*-dimethylaniline (2c)

White solid, yield 76%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (br s, exchangeable, 1H, N*H*), 7.39 (d, *J* = 8.9 Hz, 2H, H_{Ar}), 6.80 (d, *J* = 8.9 Hz, 2H, H_{Ar}), 6.36 – 6.28 (m, 1H, $H_{pyrrole}$), 6.02 (m, 1H, $H_{pyrrole}$), 3.01 (s, 6H, N(CH_3)$_2$), 2.73 (q, *J* = 7.5 Hz, 2H, CH_2), 1.35 (t, *J* = 7.6 Hz, 3H, CH_3) ppm.^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.15 (*C*), 134.28 (*C*), 131.68 (*C*), 124.94 (*C*H), 122.31 (*C*), 113.19 (*C*H), 105.73 (*C*H), 104.15 (*C*H), 40.66 (*C*H_3), 21.04 (*C*H_2), 13.70 (*C*H_3) ppm. $C_{14}H_{18}N_2$ requires: C, 78.46; H, 8.47; N, 13.07%. Found: C, 78.84; H, 8.41; N, 12.90.



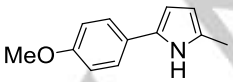
***N*,*N*-Dimethyl-4-(5-methyl-1*H*-pyrrol-2-yl)aniline (2d)**

White solid, yield 83%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (br s, exchangeable, 1H, N*H*), 7.36 (d, *J* = 8.9 Hz, 2H, H_{Ar}), 6.77 (d, *J* = 8.9 Hz, 2H, H_{Ar}), 6.27 (t, *J* = 3.0 Hz, 1H, $H_{pyrrole}$), 5.96 (t, *J* = 3.0 Hz, 1H, $H_{pyrrole}$), 2.99 (s, 6H, N(CH_3)$_2$), 2.36 (s, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.93 (*C*), 131.59 (*C*), 127.75 (*C*), 124.70 (*C*H), 122.28 (*C*), 113.04 (*C*H), 107.44 (*C*H), 104.05 (*C*H), 40.84 (*C*H_3), 13.17 (*C*H_3) ppm. $C_{13}H_{16}N_2$ requires: C, 77.96; H, 8.05; N, 13.99 %. Found: C, 77.93; H, 7.64; N, 13.56.



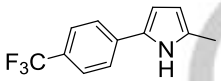
2-Ethyl-5-(4-methoxyphenyl)-1*H*-pyrrole (2e) [45]

White solid, yield 72%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 (br s, exchangeable, 1H, N*H*), 7.41 (d, *J* = 8.8 Hz, 2H, H_{Ar}), 6.94 (d, *J* = 8.8 Hz, 2H, H_{Ar}), 6.35 (t, *J* = 2.9 Hz, 1H, $H_{pyrrole}$), 6.01 (t, *J* = 2.9 Hz, 1H, $H_{pyrrole}$), 3.86 (s, 3H, CH_3), 2.72 (q, *J* = 7.6 Hz, 2H, CH_2), 1.33 (t, *J* = 7.6 Hz, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.78 (*C*), 135.01 (*C*), 130.83 (*C*), 126.39 (*C*), 125.00 (*C*H), 114.43 (*C*H), 106.11 (*C*H), 104.74 (*C*H), 55.33 (*C*H_3), 21.16 (*C*H_2), 13.66 (*C*H_3) ppm. $C_{13}H_{15}NO$ requires: C, 77.58; H, 7.51; N, 6.96%. Found: C, 77.41; H, 7.47; N, 6.92%. Spectral data of the compound are in accordance with those reported in the literature



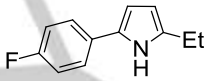
2-(4-Methoxyphenyl)-5-methyl-1*H*-pyrrole (2f) [46]

White solid, yield 69%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (br s, exchangeable, 1H, N*H*), 7.38 (d, *J* = 8.8 Hz, 2H, H_{Ar}), 6.92 (d, *J* = 8.8 Hz, 2H, H_{Ar}), 6.30 (t, *J* = 3.0 Hz, 1H, $H_{pyrrole}$), 5.98 - 5.94 (m, 1H, $H_{pyrrole}$), 3.84 (s, 3H, CH_3), 2.35 (s, 3H, CH_3) ppm.^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.10 (*C*), 130.83 (*C*), 128.36 (*C*), 126.30 (*C*), 124.80 (*C*H), 114.30 (*C*H), 107.66 (*C*H), 105.15 (*C*H), 55.45 (*C*H_3), 13.37 (*C*H_3) ppm. $C_{12}H_{13}NO$ requires: C, 76.98; H, 7.00; N, 7.48%. Found: C, 77.07; H, 6.73; N, 7.32%. Spectral data of the compound are in accordance with those reported in the literature



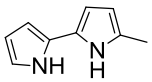
2-Methyl-5-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole (2g) [47]

White solid, yield 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (br s, exchangeable, 1H, N*H*), 7.60 (d, *J* = 8.2 Hz, 2H, H_{Ar}), 7.52 (d, *J* = 8.2 Hz, 2H, H_{Ar}), 6.54 (t, *J* = 3.0 Hz, 1H, $H_{pyrrole}$), 6.03 (m, 1H, $H_{pyrrole}$), 2.38 (s, 3H, CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.24. (s, CF_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 136.21 (*C*), 130. 69 (*C*), 129.40 (*C*), 127.29 (q, $^2J_{C,F}$ = 32.5 Hz, *C*), 126.00 (q, $^3J_{C,F}$ = 3.9 Hz, *C*H), 124.52 (q, $^1J_{C,F}$ = 270.8 Hz, *C*F_3), 123.08 (*C*H), 108.76 (*C*H), 108.27 (*C*H), 13.32 (*C*H_3) ppm. $C_{12}H_{10}F_3N$ requires: C, 64.00; H, 4.48; N, 6.22%. Found: C, 63.82; H, 4.45; N, 6.12%. Spectral data of the compound are in accordance with those reported in the literature



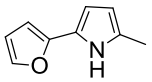
2-Ethyl-5-(4-fluorophenyl)-1*H*-pyrrole (2h)

White solid, yield 68%. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.06 (br s, exchangeable,1H, N*H*), 7.41 (dd, *J* = 8.8, 5.2 Hz, 2H, H_{Ar}), 7.07 (t, *J* = 8.7 Hz, 2H, H_{Ar}), 6.37 (t, *J* = 2.9 Hz, 1H, $H_{pyrrole}$), 6.01 (t, *J* = 2.9 Hz, 1H, $H_{pyrrole}$), 2.71 (q, *J* = 7.7 Hz, 2H, CH_2), 1.32 (q, *J* = 7.7 Hz, 3H, CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -117.01 (s, F) ppm. ^{13}C NMR (150 MHz, CDCl3): δ = 161.22 (d, $^1J_{C,F}$ = 244.9 Hz, *C*F), 135.62 (*C*), 129.81 (*C*), 129.45 (*C*), 125.02 (d, $^3J_{CF}$ = 7.5 Hz, *C*H), 115.71 (d, $^2J_{CF}$ = 22.5 Hz, *C*H), 106.27 (*C*H), 105.90 (*C*H), 20.98 (*C*H_2), 13.59 (*C*H_3) ppm. $C_{12}H_{12}FN$ requires: C, 76.17; H, 6.39; N, 7.40%. Found: C, 75.93; H, 6.26; N, 7.22%.



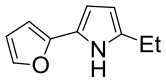
5-Methyl-1*H*,1'*H*-2,2'-bipyrrole (2i) [48]

White solid (it turns into greenish white immediately if exposed to the air), yield 34%. The low yield in this case is mainly due to the instability of the product and its difficult isolation from the silica gel of the column, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (br s, exchangeable, 1H, N*H*), 7.95 (br s, exchangeable, 1H, N*H*), 6.76 (d, *J* = 1.0 Hz, 1H, $H_{pyrrole}$), 6.25 (dd, *J* = 5.6, 2.8 Hz, 1H, $H_{pyrrole}$), 6.18 (s, 1H, $H_{pyrrole}$), 6.10 (t, *J* = 2.8 Hz, 1H, $H_{pyrrole}$), 5.91 (s, 1H, $H_{pyrrole}$), 2.32 (s, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 127.67 (*C*), 126.22 (*C*), 124.62 (*C*), 117.21 (*C*H), 109.30 (*C*H), 107.02 (*C*H), 103.60 (*C*H), 102.90 (*C*H), 13.02 (*C*H_3) ppm. $C_9H_{10}N_2$ requires: C, 73.94; H, 6.89; N, 19.16%. Found: C, 73.81; H, 6.73; N, 19.12%. Spectral data of the compound are in accordance with those reported in the literature



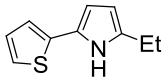
2-(Fur-2-yl)-5-methyl-1*H*-pyrrole (2j) [49]

Colorless oil, yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (br s, exchangeable, 1H, N*H*), 7.35 (d, *J* = 1.4 Hz, 1H, H_{furan}), 6.44 (dd, *J* = 3.3, 1.8 Hz, 1H, H_{furan}), 6.34 (t, *J* = 2.9 Hz, 1H, $H_{pyrrole}$), 6.30 (d, *J* = 3.3 Hz, 1H, H_{furan}), 5.95 (m, 1H, $H_{pyrrole}$), 2.34 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 148.57 (*C*), 139.91 (*C*H), 128.39 (*C*), 122.73 (*C*), 111.42 (*C*H), 107.55 (*C*H), 105.63 (*C*H), 101.32 (*C*H), 13.04 (*C*H_3) ppm. C_9H_9NO requires: C, 73.45; H, 6.16; N, 9.52%. Found: C, 73.17; H, 6.27; N, 9.35%. Spectral data of the compound are in accordance with those reported in the literature.



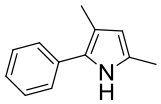
2-(Fur-2-yl)-5-ethyl-1*H*-pyrrole (2k)

Yellow oil, yield 49%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (br s, exchangeable, 1H, N*H*), 7.37 (dd, *J* = 1.8, 0.5 Hz 1H, H_{furan}), 6.45 (dd, *J* = 3.3, 1.8 Hz, 1H, H_{furan}), 6.38 (t, *J* = 3.0 Hz, 1H, $H_{pyrrole}$), 6.33 (d, *J* = 3.3 Hz, 1H, H_{furan}), 6.05 – 5.94 (m, 1H, $H_{pyrrole}$), 2.70 (q, *J* = 7.6 Hz, 2H, CH_2), 1.32 (t, *J* = 7.6 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.64 (*C*), 139.92 (*CH*), 134.96 (*C*), 122.67 (*C*), 111.60 (*CH*), 106.10 (*CH*), 105.49 (*CH*), 101.40 (*CH*), 21.08 (*CH$_2$*), 14.01(*CH$_3$*) ppm. $C_{10}H_{11}NO$ requires: C, 74.51; H, 6.88; N, 8.69%. Found: C, 74.73; H, 6.99; N, 8.48%.



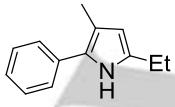
2-Ethyl-5-(thien-2-yl)-1H-pyrrole (2l) [44]

Yellow oil, yield 48%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (br s, exchangeable, 1H, N*H*), 7.20 – 7.07 (m, 1H, H_{thioph}), 7.03-6.97 (m, 2H, H_{thioph}), 6.43 (t, *J* = 3.0 Hz, 1H, $H_{pyrrole}$), 5.98 (t, *J* = 3.0 Hz, 1H, $H_{pyrrole}$), 2.69 (q, *J* = 7.6 Hz, 2H, CH_2), 1.31 (t, *J* = 7.6 Hz, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.68 (*C*), 135.33 (*C*), 127.56 (*C*H), 125.17 (*C*), 122.02 (*C*H), 120.11 (*C*H), 106.81 (*C*H), 106.13 (*C*H), 20.93 (CH_2), 13.58 (CH_3) ppm. $C_{10}H_{11}NS$ requires: C, 67.76; H, 6.25; N, 7.90%. Found: C, 68.10; H, 6.50; N, 7.68%. Spectral data of the compound are in accordance with those reported in the literature



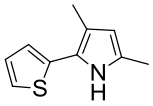
3,5-Dimethyl-2-phenyl-1H-pyrrole (2m) [50]

Colorless oil, yield 52%.^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.83 (br s, exchangeable, 1H, N*H*), 7.43 (s, 4H, H_{Ar}), 7.23 (m, 1H, H_{Ar}), 5.87 (s, 1H, $H_{pyrrole}$), 2.33 (s, 3H, CH_3), 2.28 (s, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ = 133.90 (*C*), 128.65 (*C*H), 127.49 (*C*), 126.75 (*C*), 125.92 (*C*H), 125.46 (*C*H), 116.49 (*C*), 110.30 (*C*H), 12.98 (CH_3), 12.49 (CH_3) ppm. $C_{12}H_{13}N$ requires: C, 84.17; H, 7.65; N, 8.18%. Found: C, 84.30; H, 7.55; N, 8.01%. Spectral data of the compound are in accordance with those reported in the literature.



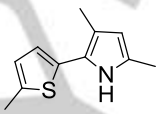
5-Ethyl-3-methyl-2-phenyl-1H-pyrrole (2n) [44]

Colorless oil, yield 43%. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.85 (br s, exchangeable, 1H, N*H*), 7.55 – 7.34 (m, 4H, H_{Ar}), 7.34 – 7.20 (m, 1H, H_{Ar}), 5.91 (s, 1H, $H_{pyrrole}$), 2.69 (q, *J* = 7.6 Hz, 2H, CH_2), 2.29 (s, 3H, CH_3), 1.32 (t, *J* = 7.6 Hz, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 134.59 (*C*), 134.46 (*C*), 129.04 (*C*H), 126.67 (*C*), 126.37 (*C*H), 125.87 (*C*H), 116.66 (*C*), 108.99 (*C*H), 21.26 (CH_2), 14.00 (CH_3), 12.95 (CH_3). $C_{13}H_{15}N$ requires: C, 84.28; H, 8.16; N, 7.56%. Found: C, 84.59; H, 8.40; N, 7.30%. Spectral data of the compound are in accordance with those reported in the literature.



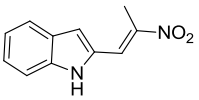
3,5-Dimethyl-2-(thien-2-yl)-1H-pyrrole (2o)

Colorless oil, yield 46%. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 7.79 (br s, exchangeable, 1H, N*H*), 7.17 (dd, *J* = 5.1, 1.1 Hz, 1H, $H_{thioph.}$), 7.05 (dd, *J* = 5.1, 3.6 Hz, 1H, H_{thioph}), 6.95 (dd, *J* = 3.6, 1.1 Hz, 1H, H_{thioph}).5.81 (s, 1H, $H_{pyrrole}$), 2.29 (s, 3H, CH_3), 2.21 (s, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ = 131.54 (*C*), 128.02 (*C*), 127.75 (*C*H), 122.48 (*C*H), 121.99 (*C*), 121.44 (*C*H), 117.66 (*C*), 110.54 (*C*H), 13.34 (CH_3), 12.76 (CH_3) ppm. $C_{10}H_{11}NS$ requires: C, 67.76; H, 6.25; N, 7.90%. Found: C, 68.01; H, 6.35; N, 7.63%.



3,5-Dimethyl-2-(5-methylthien-2-yl)-1H-pyrrole (2p)

Yellow oil, yield %. ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ = 7.73 (br s, exchangeable, 1H, N*H*), 6.74 (d, *J* = 3.5 Hz, 1H, $H_{thioph.}$), 6.70 (m, 1H, $H_{thioph.}$), 5.80 (br s, 1H, $H_{pyrrole}$), 2.51 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.22 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ = 136.86 (*C*), 134.14 (*C*), 127.60 (*C*), 125.79 (*C*H), 121.20 (*C*H), 119.90 (*C*), 116.56 (*C*), 110.10 (*C*H), 15.20 (CH_3), 13.09 (CH_3), 12.44 (CH_3) ppm. $C_{11}H_{13}NS$ requires: C, 69.07; H, 6.85; N, 7.32%. Found: C, 69.38; H, 7.12; N, 7.11%.



(E)-2-(2-Nitroprop-1-en-1-yl)-1H-indole[51]

Yellow solid, yield 56%. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ = 8.37 (br s, exchangeable, 1H, N*H*), 8.13 (s, 1H, alkenyl H), 7.71 (d, *J* = 8.0 Hz, 1H, H_{Ar}), 7.45 (d, *J* = 8.2 Hz, 1H, H_{Ar}), 7.34 (t, *J* = 7,6 Hz, 1H, H_{Ar}), 7.20 (t, *J* = 7.6 Hz, 1H, H_{Ar}), 6.99 (s, 1H, $H_{pyrrole}$), 2.66 (s, 3H, CH_3) ppm. Spectral data of the compound are in accordance with those reported in the literature.

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