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Ruthenium-Catalyzed Synthesis of Highly Substituted Pyrroles from 1-Vinylpropargyl Alcohols and Amines

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Ruthenium-catalyzed atom-economic transformations of 1-vinylpropargyl alcohols with amines leading to highly substituted pyrroles in a one-pot cascade process are reported. The allylation/cycloisomerization sequence is catalyzed by a single ruthenium(0) complex that contains a redox-coupled dienone ligand and can be extended by an additional [3,3] rearrangement. The environmentally benign reactions allow the metal-catalyzed conversion of inexpensive and readily accessible materials to highly functionalized pyrroles with water as the only waste product.

Introduction

Clean and sustainable organic synthesis requires atom-economic catalytic processes to obtain important core structures from readily and widely accessible starting materials.[1] In this context, ruthenium-catalyzed transformations of various unsaturated compounds, in particular, have been reported.[2] Because the pyrrole core is an important heteroaromatic system found in many natural products,[3] drugs[4] and functional materials,[5] several metal-catalyzed methods have been developed for its synthesis.[6,7] These catalytic processes include carbonylation reactions,[6d,6o] the rearrangement of diazo compounds,[6e,6h] the activation of C–H bonds,[6f,6i–6k] redox isomerization[6r] and cycloisomerization processes[6a–6c,6g,6l–6n,6p,6q,6s–6x] or the "borrowing-hydrogen" method.[7] Metal-free multi-component reactions for flexible pyrrole synthesis from easily accessible substrates have also been developed.[6c,8] The most effective methods for the metal-catalyzed conversion of inexpensive and readily accessible materials to highly functionalized pyrroles in one pot are based on the "borrowing-hydrogen" strategy,[7] many other synthetic protocols requiring multiple steps or pre-functionalized substrates. Nevertheless, alternatives to these generally superior methods are required in several cases. Herein, we report a ruthenium-catalyzed synthesis of highly substituted pyrroles directly from aromatic or aliphatic amines and various 1-en-4-yn-3-ols as an extension of our previous work on ruthenium-catalyzed transformations of propargyl alcohols (Scheme 1).[9]

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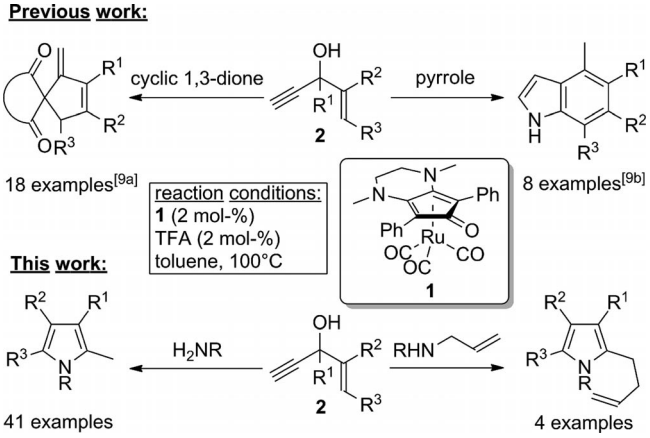
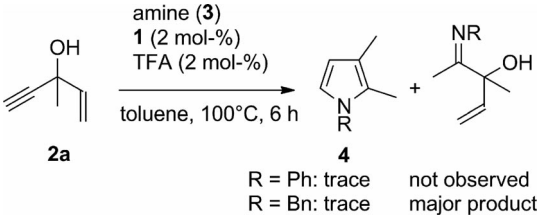
Results and Discussion

Recently we discovered that ruthenium cyclopentadienone complexes like **1** catalyze the allylation/cycloisomerization of heteroaromatics or 1,3-dicarbonyl compounds with 1-en-4-yn-3-ols **2**, readily available from α,β-unsaturated ketones (Scheme 1).[9a,9b]



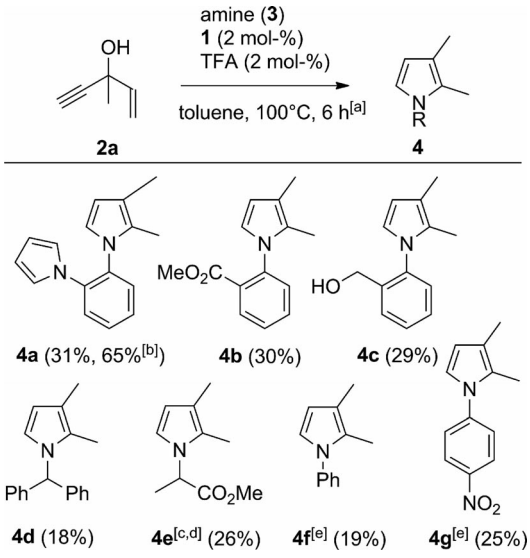
Scheme 1. Transformations of 1-en-4-yn-3-ols **2** catalyzed by complex **1**.

We envisioned that highly substituted pyrroles could be accessible in a related cascade transformation of 1-en-4-yn-3-ols with primary amines (Scheme 1). The first attempts to convert 3-methylpent-1-en-4-yn-3-ol (**2a**) with amines **3** into pyrroles in the presence of catalyst **1** and a catalytic amount of trifluoroacetic acid (TFA) as co-catalyst yielded only traces of the desired pyrroles **4**. At 100 °C, aniline barely reacted, whereas the more nucleophilic benzylamine formed the corresponding imine by Markovnikov addition as the major product (Scheme 2).



Scheme 2. Conversion of **2a** with aniline or benzylamine.

Moderate yields of substituted pyrroles **4** were obtained from amines **3** containing an additional coordinating group or at higher temperatures under microwave conditions (Scheme 3). The pyrroles were accompanied by unconverted starting materials and small amounts of the corresponding imines (see Scheme 2) as the sole detectable byproducts.

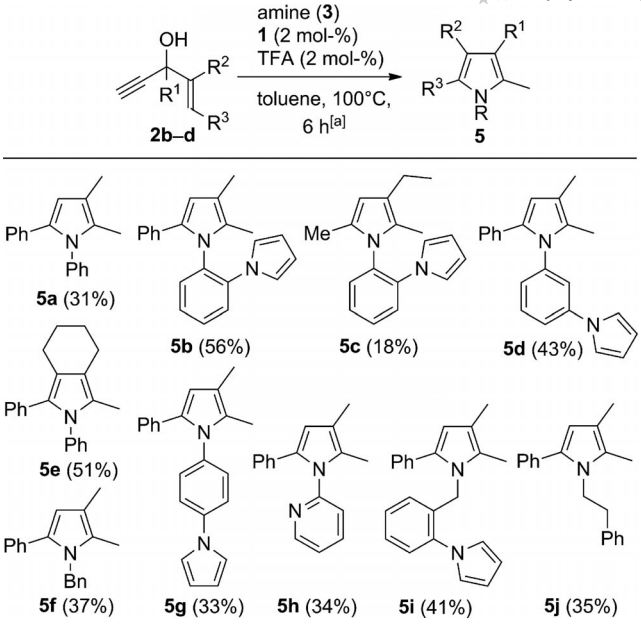


Scheme 3. Formation of pyrroles from the reaction of **2a** with various amines. [a] The reaction was stopped after 6 h, unconverted starting materials were recovered. [b] The reaction time was 48 h with full conversion of **2a**. [c] The amine was generated in situ from RNH_3Cl and Et_3N. [d] Racemization took place during the reaction. [e] The reaction was carried out at 200 °C in 5 min by using microwave irradiation.

A phenyl substituent at the distal end of the double bond led to a slight increase in the reactivity of the alcohol. Considering the amine, increasing yields were obtained in the order aniline < *p*- < *m*- < *o*-pyrrolylaniline (**5a** < **5g** < **5d** < **5b**). This shows that the reactivity of the amine depends on coordinative rather than electronic effects (Scheme 4).

Enhanced yields were obtained with biallylic substrates **2e**,**f** derived from dibenzylidene ketones due to their increased electrophilicity (Scheme 5).

In the case of aniline as the amine component, smaller amounts of pyrroles were obtained from substrates **2e** or **2f** in the absence of the ruthenium catalyst under acidic conditions. In this case, the pyrroles were accompanied by *ortho*- and *para*-allylated anilines, which were not formed in the presence of the catalyst (Scheme 6). This spontaneous allylation/cyclization reaction was not observed with less



Scheme 4. Formation of pyrroles from higher substituted enynols. [a] The reaction was stopped after 6 h, unconverted starting materials were recovered.

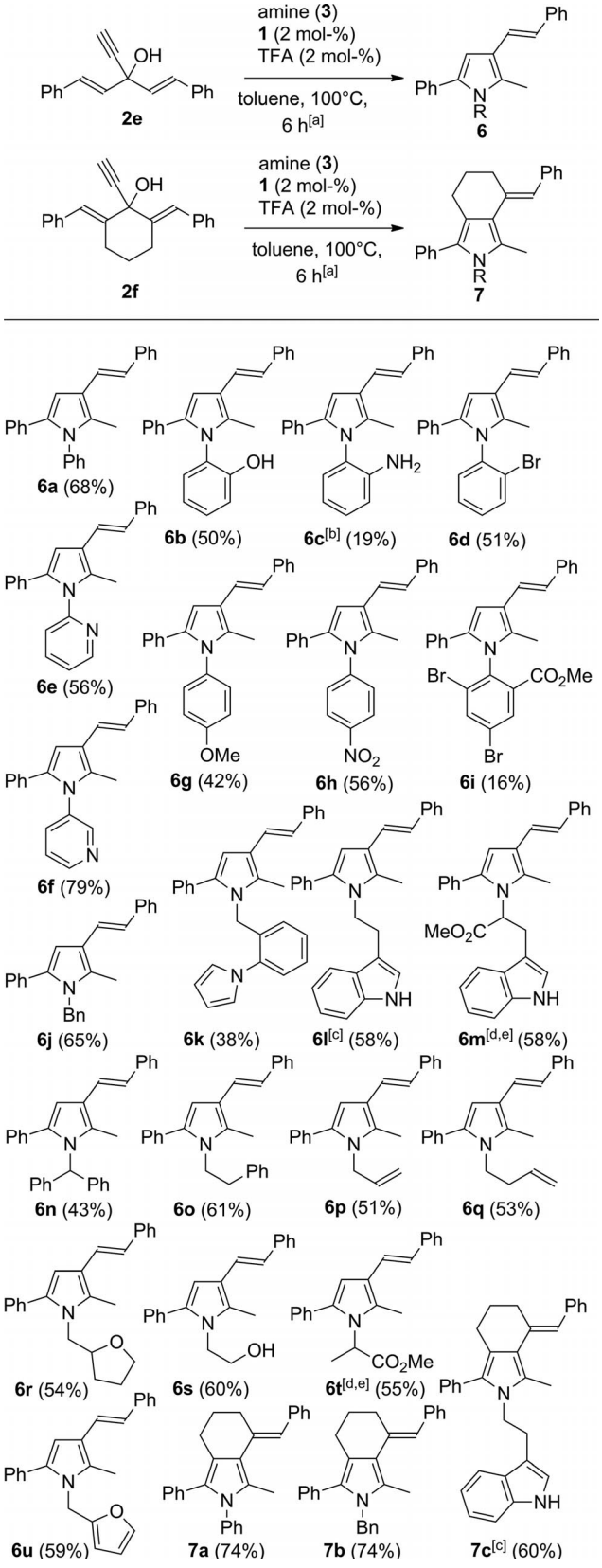
activated enynols or more basic amines. In general, no transformation was observed in the absence of catalyst **1**, whereas lower yields were obtained in the absence of the co-catalyst TFA.

Extension of the catalytic cascade transformation by a [3,3] rearrangement allowed the functionalization of the 2-methyl group of the initially formed pyrroles (Scheme 7). This sequence is limited to basic secondary allylamines. Pyrroles formed from primary allylamines did not rearrange (see **6p**, Scheme 5) and pyrrole formation from *N*-allylanilines was not observed. A related gold-catalyzed conversion has previously been published.[6p]

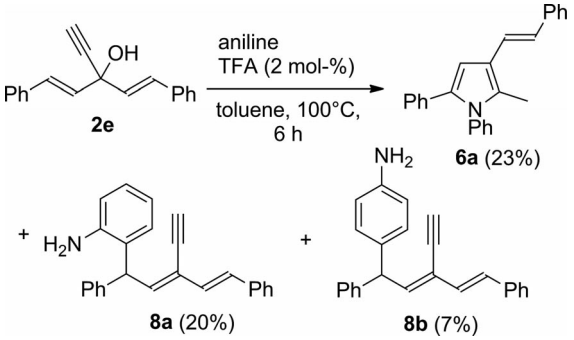
In contrast, the allylation of secondary allylamines with acyclic biallylic propargyl alcohols like **2e** was followed by a [4+2] cycloaddition rather than by a cycloisomerization process (Scheme 8). The coupling constants in the NMR spectra of products **10a** and **10b** indicate that *syn* cycloaddition occurs from the less hindered side with respect to the phenyl substituent at C-1 with the *endo* isomer formed as the major product. The assignments were made by comparison of the ^3J(H,H) coupling constants with the corresponding dihedral H–C–C–H angles generated from energy-minimized models (MM2 force field) and were confirmed by NOESY experiments (see the Supporting Information).

Similar cycloaddition products were obtained from *N*-propargylanilines or sterically hindered primary propargylamines. In contrast, *N*-propargylbenzylamine led to pyrrole **6j** and *N*,*N*-dipropargylbenzylamine by propargyl substitution (Scheme 9).

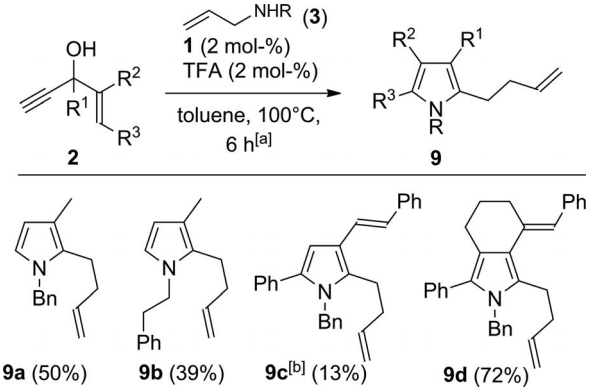
Tertiary enynols containing internal alkyne moieties allylated the nucleophile and led selectively to (*Z*)-enynes (Scheme 10). Subsequent cycloisomerization was not ob-



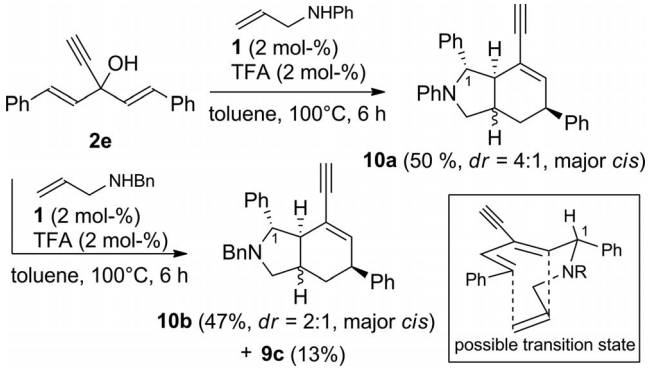
Scheme 5. Formation of pyrroles from biallylic substrates. [a] The reaction was stopped after 6 h, unconverted starting materials were recovered. [b] Side-product. [c] The reaction was carried out at 200 °C for 5 min under microwave irradiation. [d] The amine was generated in situ from RNH_3Cl and Et_3N. [e] Racemization took place during the reaction.



Scheme 6. Spontaneous allylation/cyclization reaction.



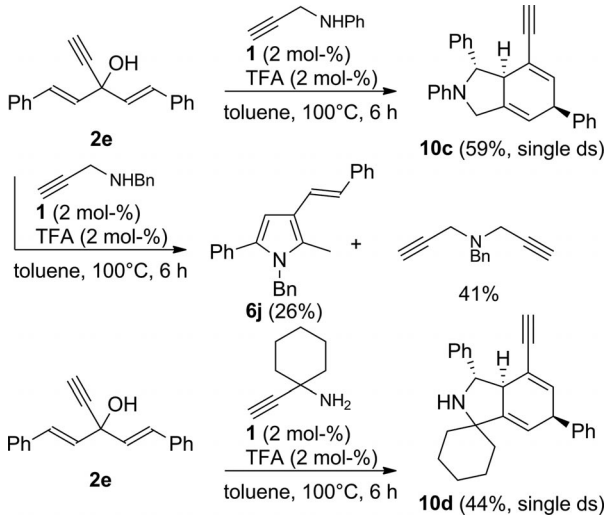
Scheme 7. Allylation/cyclization/rearrangement sequence. [a] The reaction was stopped after 6 h, unconverted starting materials were recovered. [b] Side-product, see Scheme 8.



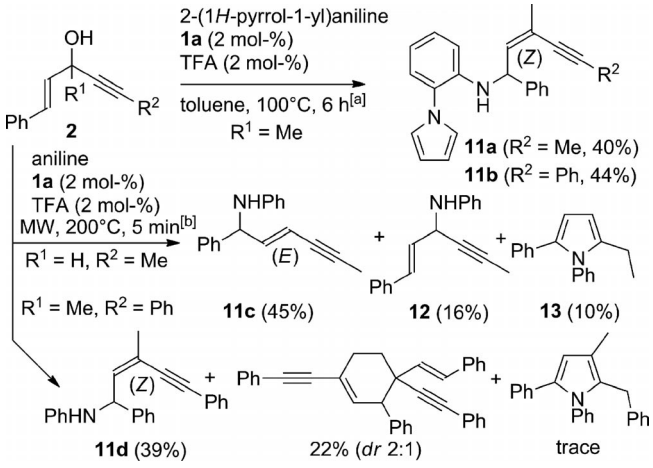
Scheme 8. Allylation/cycloaddition sequence of biallylic propargyl alcohol **2e** with allylamines.

served under standard conditions. As a consequence, all accessible pyrroles are methyl-substituted at C-2 with the exception of the rearranged products **9**. Secondary enynols were not transformed at 100 °C. At higher temperatures under microwave conditions enynes **11** were formed accompanied by small amounts of pyrroles from enynols containing an internal alkyne moiety. In addition, secondary substrates propargylated the nucleophile, whereas tertiary derivatives formed Diels–Alder adducts after initial dehydration (Scheme 10).

This reported pyrrole formation was not observed by using different ruthenium catalysts such as $[Ru_3(CO)_{12}]$,



Scheme 9. Allylation/cycloaddition sequence with propargylamines.



Scheme 10. Conversion of internal substrates. [a] The reaction was stopped after 6 h, unconverted starting materials were recovered. [b] The rreaction was carried out at 200 °C for 5 min by using microwave irradiation.

$[CpRuCl(PPh_3)_2]$, $[RuCl_2(PPh_3)_3]$, the tetracyclone complex **14a**,[9e,10a] its methyl derivative **14b**[9e] or the ethylated complex **14c**[10b] (Figure 1).

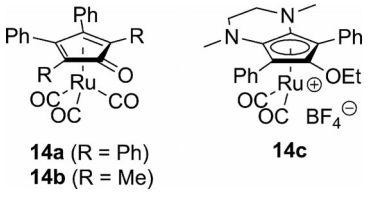
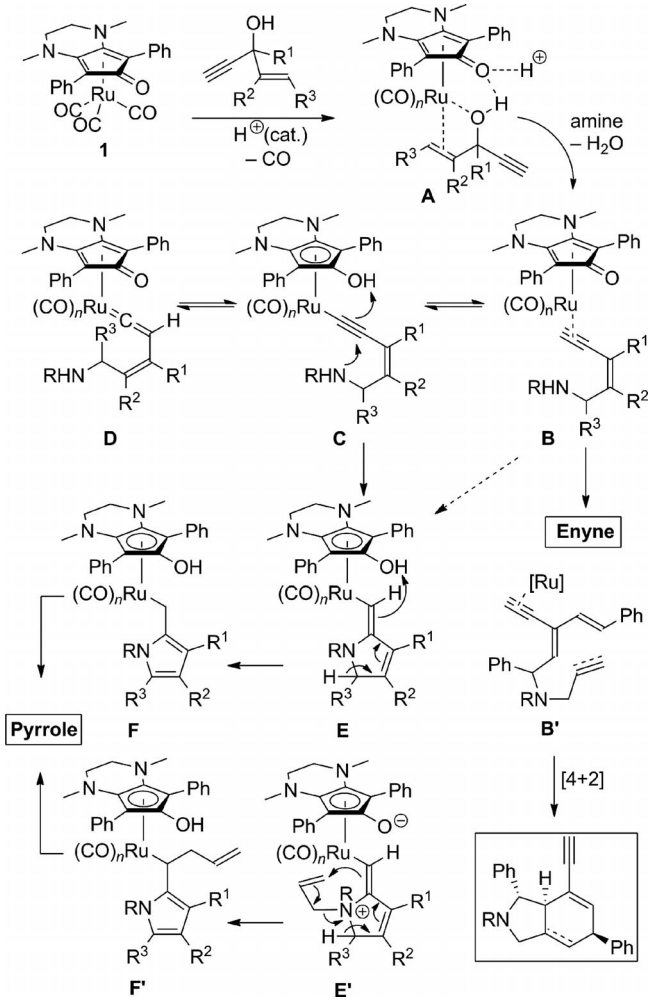


Figure 1. Inactive complex derivatives **14a**–**c**.

In agreement with our previously reported studies,[9a,9b] we assumed that the initially formed π complex **A** leads to the allylation of the nucleophile to yield the corresponding enynes (Scheme 11). Related gold-catalyzed conversions of 1-en-4-yn-3-ols have previously been published.[6n,11a,11b] Internal substrates are not further converted under standard conditions. The chelating substrate coordination in **A**, which involves the basic coordination site of the electronically coupled ligand, is crucial for this initial transformation. Derivatives containing weaker hydrogen-bond acceptors like **14a**–**c** remain inactive. In the case of terminal substrates, the resulting π complex **B** is in equilibrium with alkynyl species **C** and vinylidene complex **D**. Similar equilibria have been reported previously.[2,9b,11c] The subsequent cyclization leads to alkenyl complex **E** and may be derived from π complex **B** or from alkynyl species **C** by intramolecular protonation of the triple bond. A formal 1,5-hydrogen shift followed by reductive elimination of the product from complex **F** regenerated the active catalytic species. The analogous transformation of secondary allylamines leads to zwitterionic complex **E′**, which forms **F′** in a formal [3,3] rearrangement sequence. Enyne complex **B′**, derived from alcohol **2e** and secondary allyl- or propargylamines, forms the corresponding Diels–Alder product instead (Scheme 11). The use of an acidic additive is not crucial but accelerates the reaction. This effect may result from proton-



Scheme 11. Proposed mechanisms.

ation of the ligand's carbonyl group in **A**, thereby increasing the electrophilicity of the ruthenium centre and promoting the dehydration step.

Conclusions

We have described the ruthenium-catalyzed reactions of 1-en-4-yn-3-ols with primary amines to yield substituted pyrroles in an allylation/cycloisomerization cascade process with water as the only waste product. The sequence can be extended by a [3,3] rearrangement by using secondary allylamines. A different reaction pathway takes place with acyclic biallylic propargyl alcohols and propargyl or secondary allylamines. In this case, Diels–Alder adducts are obtained from the initially formed 1,3-dienes. The presented transformations depend on the basic coordination site of the electronically coupled cyclopentadienone ligand in **1**. Analogous ruthenium complexes containing weaker hydrogen-bond acceptors were catalytically inactive in this transformation. Further investigations with particular regard to detailed reaction mechanisms and applications in drug synthesis are currently under investigation.

Experimental Section

General: All reactions were carried out under dry argon using standard Schlenk techniques. Chemicals were dried and purified according to common procedures. Products were identified by spectroscopic analysis (^{1}H and ^{13}C NMR, IR, MS, HRMS). Multiplicity was determined by DEPT spectra for all compounds. Correlations and assignments were determined by ^{1}H-^{1}H COSY, HSQC, HMBC and ^{1}H-^{1}H NOESY spectra if necessary. IR spectra were obtained with a Perkin–Elmer FT-IR 2000 spectrometer. NMR spectra were recorded with a Bruker DPX 400 or Avance 600 spectrometer. MS and HRMS data were obtained with a Finnigan MAT 95 spectrometer. Reactions using microwave irradiation were performed in an Anton Paar Monowave 300 reactor. Catalyst **1** has previously been published in ref.[9e] and its crystal structure in ref.[9b]

General Catalytic Procedure: Catalyst **1** (0.02 mmol) was dissolved in toluene (1 mL) and TFA diluted in toluene (0.02 mmol, 1 M), the propargyl alcohol (1 mmol) and amine (1 mmol) were subsequently added. The mixture was stirred at 100 °C for 6 h under argon (standard conditions) or heated at 200 °C for 5 min by using microwave irradiation (microwave conditions). Evaporation of the solvent and flash chromatography on silica gel furnished the purified products as colourless or yellow oils or foams.

Characterization Data of Catalysis Products

2,3-Dimethyl-1-[2-(1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (4a): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68 (s, 3 H), 2.02 (s, 3 H), 6.09 (d, J = 2.6 Hz, 1 H), 6.19 (t, J = 1.9 Hz, 2 H), 6.48 (t, J = 1.9 Hz, 2 H), 6.52 (d, J = 2.7 Hz, 1 H), 7.35–7.37 (m, 2 H), 7.45–7.47 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.1 (CH_3), 11.4 (CH_3), 110.0 (CH), 110.6 (CH), 115.5 (C), 119.4 (CH), 120.4 (CH), 124.9 (CH), 126.3 (C), 126.4 (CH), 128.6 (CH), 129.6 (CH), 133.3 (C), 137.6 (C) ppm. IR: $\tilde{\nu}$ = 3102 (m), 3070 (m), 2921 (s), 2860 (s), 1737 (m), 1602 (s), 1587 (m), 1511 (s), 1483 (s), 1387 (m), 1351 (s), 1333 (s), 1265 (m), 1245 (m), 1229 (m), 1180 (s), 1160 (m), 1142 (m), 1125 (m), 1105 (s), 1069 (s), 1044 (m), 1015 (s), 986 (m), 946 (m), 921 (m), 870 (m), 828 (m), 764 (m), 727 (s), 703 (s), 659 (m), 636 (s) cm^{-1}. HRMS: calcd. for $C_{16}H_{16}N_2$ 236.1313 $[M]^+$; found 236.1314.

Methyl 2-(2,3-Dimethyl-1*H*-pyrrol-1-yl)benzoate (4b): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.94 (s, 3 H), 2.10 (s, 3 H), 3.71 (s, 3 H), 6.08 (d, J = 2.4 Hz, 1 H), 6.56 (d, J = 2.4 Hz, 1 H), 7.32 (dd, J = 8.4, 0.9 Hz, 1 H), 7.46 (td, J = 7.8, 1.2 Hz, 1 H), 7.58 (td, J = 7.2, 1.8 Hz, 1 H), 7.90 (dd, J = 7.8, 1.2 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 10.0 (CH_3), 11.6 (CH_3), 52.4 (CH_3), 109.9 (CH), 115.3 (C), 120.2 (CH), 126.3 (C), 127.7 (CH), 129.3 (CH), 129.8 (C), 130.6 (CH), 132.3 (CH), 140.1 (C), 166.8 (C) ppm. MS (EI): m/z (%) = 229 (100) $[M]^+$, 228 (62), 214 (28), 170 (25), 154 (26). HRMS: calcd. for $C_{14}H_{15}NO_2$ 229.1103 $[M]^+$; found 229.1104.

[2-(2,3-Dimethyl-1*H*-pyrrol-1-yl)phenyl]methanol (4c): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.83 (s, 3 H), 2.01 (s, 3 H), 4.32 (s, 2 H), 6.02 (d, J = 2.8 Hz, 1 H), 6.49 (d, J = 2.8 Hz, 1 H), 7.13 (dd, J = 7.6, 1.2 Hz, 1 H), 7.29 (td, J = 7.6, 1.6 Hz, 1 H), 7.36 (td, J = 7.6, 1.6 Hz, 1 H), 7.49 (dd, J = 7.6, 1.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.0 (CH_3), 11.6 (CH_3), 61.6 (CH_2), 109.9 (CH), 115.4 (C), 120.2 (CH), 126.2 (C), 128.3 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 138.7 (C), 138.8 (C) ppm. IR: $\tilde{\nu}$ = 3366 (s), 3067 (m), 3009 (m), 2925 (s), 2858 (s), 1680 (s), 1606 (s), 1590 (s), 1495 (s), 1458 (s), 1378 (s), 1349 (s), 1314 (m), 1260 (m), 947 (w), 928 (w), 849 (w), 755 (s), 667 (m), 639 (m) cm^{-1}. MS (EI): m/z (%) = 201 (80) $[M]^+$, 200 (60), 184 (76), 169 (100), 168 (61). HRMS: calcd. for $C_{13}H_{15}NO$ 201.1154 $[M]^+$; found 201.1152.

1-Benzhydryl-2,3-dimethyl-1*H*-pyrrole (4d): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.08 (s, 6 H), 5.96 (br. s, 1 H), 6.20 (br. s, 1 H), 6.43 (br. s, 1 H), 7.05 (d, J = 7.4 Hz, 4 H), 7.31 (t, J = 7.2 Hz, 2 H), 7.34 (t, J = 7.2 Hz, 4 H) ppm. ^{13}C NMR (150 MHz, DEPT, $CDCl_3$): δ = 9.9 (CH_3), 11.6 (CH_3), 64.0 (CH), 108.3 (CH), 115.4 (C), 118.3 (CH), 125.7 (C), 127.7 (CH), 128.5 (CH), 128.6 (CH), 140.7 (C) ppm. IR: $\tilde{\nu}$ = 3088 (w), 3063 (m), 3029 (m), 2991 (m), 2919 (s), 2861 (m), 1705 (w), 1603 (m), 1585 (w), 1528 (w), 1496 (s), 1481 (m), 1450 (s), 1387 (m), 1314 (s), 1279 (w), 1216 (s), 869 (w), 833 (w), 753 (s), 734 (s), 699 (s), 667 (m) cm^{-1}. MS (EI): m/z (%) = 261 (30) $[M]^+$, 167 (100), 165 (27), 152 (16). HRMS: calcd. for $C_{19}H_{19}N$ 261.1517 $[M]^+$; found 261.1518.

Methyl 2-(2,3-Dimethyl-1*H*-pyrrol-1-yl)propanoate (4e): The amine was generated in situ from L-alanine methyl ester and Et_3N (1 equiv.). Polarimetric analysis and ^{1}H NMR experiments in the presence of a chiral shift reagent (Eu[tfc]$_3$, 1.1 equiv.) revealed that the product was racemic. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 (d, J = 7.3 Hz, 3 H), 1.66 (s, 3 H), 1.74 (s, 3 H), 3.38 (s, 3 H), 4.40 (q, J = 7.3 Hz, 1 H), 5.61 (d, J = 2.9 Hz, 1 H), 6.28 (d, J = 2.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.9 (CH_3), 10.9 (CH_3), 17.4 (CH_3), 52.0 (CH), 53.0 (CH_3), 108.6 (CH), 114.2 (C), 115.2 (CH), 124.2 (C), 171.5 (C) ppm. HRMS: calcd. for $C_{10}H_{15}NO_2$ 181.1103 $[M]^+$; found 181.1103.

2,3-Dimethyl-1-phenyl-1*H*-pyrrole (4f): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.00 (s, 3 H), 2.02 (s, 3 H), 5.99 (d, J = 2.8 Hz, 1 H), 6.60 (d, J = 2.8 Hz, 1 H), 7.17–7.34 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.6 (CH_3), 11.5 (CH_3), 109.8 (CH), 116.2 (C), 119.8 (CH), 125.2 (C), 125.6 (CH), 126.5 (CH), 129.0 (CH), 140.7 (C) ppm. HRMS: calcd. for $C_{12}H_{13}N$ 171.1048 $[M]^+$; found 171.1048.

2,3-Dimethyl-1-(4-nitrophenyl)-1*H*-pyrrole (4g): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02 (s, 3 H), 2.13 (s, 3 H), 6.09 (d, J = 2.9 Hz, 1 H), 6.67 (d, J = 2.9 Hz, 1 H), 7.35 (d, J = 9.1 Hz, 2 H), 8.23 (d, J = 9.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =

10.9 (CH_3), 11.4 (CH_3), 111.9 (CH), 118.6 (C), 119.6 (CH), 124.8 (CH), 124.8 (CH), 124.8 (C), 145.3 (C), 145.9 (C) ppm. HRMS: calcd. for $C_{12}H_{12}N_2O_2$ 216.0899 $[M]^+$; found 216.0898.

2,3-Dimethyl-1,5-diphenyl-1*H*-pyrrole (5a):[12a] ^1H NMR (400 MHz, $CDCl_3$): δ = 1.98 (s, 3 H), 2.06 (s, 3 H), 6.19 (s, 1 H), 6.97–7.27 (m, 10 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.9 (CH_3), 11.3 (CH_3), 110.6 (CH), 115.6 (C), 125.4 (CH), 126.0 (C), 126.5 (CH), 127.6 (CH), 127.9 (CH), 128.4 (CH), 128.9 (CH), 131.7 (C), 133.4 (C), 139.7 (C) ppm. IR: $\tilde{\nu}$ = 3059 (m), 3026 (m), 2925 (s), 2856 (m), 1667 (m), 1599 (s), 1495 (s), 1379 (m), 1369 (m), 1261 (m), 1155 (m), 1073 (m), 1029 (m), 968 (w), 757 (s), 697 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 247 (100) $[M]^+$, 246 (52), 205 (19), 154 (20), 144 (29), 129 (54), 128 (35), 105 (30). HRMS: calcd. for $C_{18}H_{17}N$ 247.1361 $[M]^+$; found 247.1361.

2,3-Dimethyl-5-phenyl-1-[2-(1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (5b): ^1H NMR (400 MHz, $CDCl_3$): δ = 1.93 (s, 3 H), 2.13 (s, 3 H), 6.13 (t, *J* = 2.1 Hz, 2 H), 6.23 (s, 1 H), 6.28 (t, *J* = 2.1 Hz, 2 H), 6.88–6.90 (m, 2 H), 7.06–7.10 (m, 3 H), 7.33 (ddd, *J* = 7.9, 6.7, 1.5 Hz, 1 H), 7.36–7.40 (m, 2 H), 7.46 (ddd, *J* = 8.1, 6.8, 2.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.1 (CH_3), 11.3 (CH_3), 109.8 (CH), 110.8 (CH), 116.2 (C), 120.2 (CH), 124.9 (CH), 125.6 (CH), 126.3 (CH), 127.1 (CH), 127.4 (C), 127.7 (CH), 128.9 (CH), 131.2 (CH), 132.1 (C), 132.6 (C), 132.7 (C), 138.3 (C) ppm. IR: $\tilde{\nu}$ = 3062 (s), 3028 (s), 2920 (s), 2860 (s), 1706 (m), 1603 (s), 1505 (s), 1478 (s), 1455 (s), 1379 (s), 1368 (s), 1333 (s), 1284 (s), 1264 (s), 1182 (s), 1159 (s), 1107 (s), 1070 (s), 1070 (s), 1045 (s), 1028 (s), 1016 (s), 1000 (s), 966 (s), 946 (s), 921 (s), 909 (s), 871 (m), 794 (s), 760 (s), 726 (s), 696 (s), 649 (s), 635 (s) cm^{-1}. HRMS: calcd. for $C_{22}H_{20}N_2$ 312.1626 $[M]^+$; found 312.1626.

3-Ethyl-2,5-dimethyl-1-[2-(1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (5c): ^1H NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.6 Hz, 3 H), 1.74 (s, 3 H), 1.83 (s, 3 H), 2.37 (q, *J* = 7.6 Hz, 2 H), 5.81 (s, 1 H), 6.16 (t, *J* = 2.1 Hz, 2 H), 6.40 (t, *J* = 2.1 Hz, 2 H), 7.32–7.34 (m, 2 H), 7.46–7.48 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.8 (CH_3), 12.1 (CH_3), 15.7 (CH_3), 19.3 (CH_2), 106.7 (CH), 110.1 (CH), 120.3 (CH), 121.8 (C), 123.9 (C), 124.4 (CH), 126.1 (CH), 127.3 (C), 129.0 (CH), 131.0 (CH), 138.7 (C), 139.2 (C) ppm. IR: $\tilde{\nu}$ = 3104 (s), 2824 (s), 2854 (s), 1739 (s), 1712 (s), 1605 (s), 1508 (s), 1462 (s), 1377 (s), 1334 (s), 1162 (s), 1107 (s), 1069 (s), 1045 (s), 1015 (s), 967 (s), 922 (s), 887 (m), 861 (m), 760 (s), 726 (s), 704 (s), 635 (s) cm^{-1}. HRMS: calcd. for $C_{18}H_{20}N_2$ 264.1626 $[M]^+$; found 264.1626.

2,3-Dimethyl-5-phenyl-1-[3-(1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (5d): ^1H NMR (400 MHz, $CDCl_3$): δ = 2.14 (s, 3 H), 2.18 (s, 3 H), 6.31 (s, 1 H), 6.35 (t, *J* = 2.2 Hz, 2 H), 6.98 (t, *J* = 2.2 Hz, 2 H), 7.10–7.44 (m, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.7 (CH_3), 11.0 (CH_3), 110.6 (CH), 110.7 (CH), 115.8 (C), 118.8 (CH), 120.0 (CH), 125.0 (CH), 125.1 (CH), 125.5 (CH), 127.5 (C), 127.5 (CH), 127.8 (CH), 129.6 (CH), 132.7 (C), 133.0 (C), 140.6 (C), 140.8 (C) ppm. IR: $\tilde{\nu}$ = 3059 (m), 3026 (s), 2921 (s), 2853 (s), 1702 (s), 1604 (s), 1499 (s), 1451 (s), 1379 (s), 1341 (s), 1312 (s), 1258 (s), 1167 (s), 1069 (s), 1029 (s), 966 (m), 928 (m), 873 (m), 799 (m), 752 (m), 726 (s), 698 (s) cm^{-1}. HRMS: calcd. for $C_{22}H_{20}N_2$ 312.1626 $[M]^+$; found 312.1627.

1-Methyl-2,3-diphenyl-4,5,6,7-tetrahydro-2*H*-isoindole (5e): ^1H NMR (600 MHz, $CDCl_3$): δ = 1.88–1.91 (m, 2 H), 1.95–1.98 (m, 2 H), 2.18 (s, 3 H), 2.71 (t, *J* = 6.0 Hz, 2 H), 2.81 (t, *J* = 6.0 Hz, 2 H), 7.13 (d, *J* = 7.6 Hz, 2 H), 7.17 (t, *J* = 7.4 Hz, 1 H), 7.23 (d, *J* = 7.8 Hz, 2 H), 7.26 (t, *J* = 7.8 Hz, 2 H), 7.36 (t, *J* = 7.4 Hz, 1 H), 7.42 (t, *J* = 7.8 Hz, 2 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 10.8 (CH_3), 21.8 (CH_2), 23.2 (CH_2), 24.0 (CH_2), 24.3 (CH_2), 117.0 (C), 119.0 (C), 125.1 (CH), 125.3 (C), 126.6 (CH), 127.5 (C), 127.6 (CH), 128.4 (CH), 128.7 (CH), 129.1 (CH), 133.1 (C), 139.5 (C) ppm. IR: $\tilde{\nu}$ = 3060 (m), 3034 (m), 2923 (s), 2853 (m), 2834 (m), 1689 (m), 1657 (m), 1598 (s), 1523 (m), 1497 (s), 1442 (s), 1427 (m), 1372 (s), 1341 (m), 1329 (m), 1242 (m), 1156 (m), 1075 (m), 1029 (m), 910 (m), 756 (s), 731 (m), 699 (s), 646 (m) cm^{-1}. HRMS: calcd. for $C_{21}H_{21}N$ 287.1674 $[M]^+$; found 287.1674.

1-Benzyl-2,3-dimethyl-5-phenyl-1*H*-pyrrole (5f): ^1H NMR (400 MHz, $CDCl_3$): δ = 2.02 (s, 3 H), 2.08 (s, 3 H), 5.08 (s, 2 H), 6.10 (s, 1 H), 6.92 (d, *J* = 7.5 Hz, 2 H), 7.20–7.29 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.1 (CH_3), 11.3 (CH_3), 47.8 (CH_2), 109.7 (CH), 115.3 (C), 125.7 (CH), 126.4 (CH), 126.6 (C), 126.9 (CH), 128.3 (CH), 128.5 (CH), 128.7 (CH), 133.3 (C), 133.7 (C), 139.2 (C) ppm. IR: $\tilde{\nu}$ = 3059 (m), 3031 (m), 2914 (s), 2862 (s), 1768 (m), 1734 (m), 1649 (m), 1599 (s), 1510 (s), 1495 (s), 1471 (s), 1452 (s), 1395 (s), 1342 (s), 1180 (m), 1158 (m), 1073 (m), 1027 (m), 968 (m), 803 (m), 814 (m), 762 (s), 744 (s), 721 (s), 700 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 261 (83) $[M]^+$, 170 (100), 128 (7). HRMS: calcd. for $C_{19}H_{19}N$ 261.1517 $[M]^+$; found 261.1517.

2,3-Dimethyl-5-phenyl-1-[4-(1*H*-pyrrol-1-yl)phenyl]-1*H*-pyrrole (5g): ^1H NMR (400 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 2.17 (s, 3 H), 6.29 (br. s, 1 H), 6.38 (t, *J* = 2.2 Hz, 2 H), 7.08–7.22 (m, 9 H), 7.39 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.6 (CH_3), 11.0 (CH_3), 109.1 (CH), 110.6 (CH), 115.6 (C), 118.9 (CH), 120.1 (CH), 125.0 (C), 125.4 (CH), 127.5 (CH), 127.7 (CH), 129.3 (CH), 132.7 (C), 133.0 (C), 136.7 (C), 139.1 (C) ppm. IR: $\tilde{\nu}$ = 3059 (m), 3028 (m), 2922 (s), 2854 (m), 1712 (s), 1602 (s), 1519 (s), 1494 (s), 1450 (s), 1402 (m), 1380 (s), 1327 (s), 1291 (m), 1259 (m), 1181 (m), 1157 (m), 1118 (m), 1071 (s), 1021 (m), 964 (m), 921 (s), 909 (s), 844 (s), 760 (s), 729 (s), 699 (s) cm^{-1}. HRMS: calcd. for $C_{22}H_{20}N_2$ 312.1626 $[M]^+$; found 312.1626.

2-(2,3-Dimethyl-5-phenyl-1*H*-pyrrol-1-yl)pyridine (5h): ^1H NMR (600 MHz, $CDCl_3$): δ = 2.04 (s, 3 H), 2.07 (s, 3 H), 6.16 (s, 1 H), 6.82 (d, *J* = 7.8 Hz, 1 H), 6.93 (d, *J* = 7.4 Hz, 2 H), 7.00 (t, *J* = 7.2 Hz, 1 H), 7.05 (t, *J* = 7.4 Hz, 2 H), 7.14 (ddd, *J* = 7.2, 4.8, 1.2 Hz, 1 H), 7.51 (td, *J* = 7.8, 1.8 Hz, 1 H), 8.51 (dd, *J* = 4.8, 1.8 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 11.0 (CH_3), 11.3 (CH_3), 111.9 (CH), 116.5 (C), 122.2 (CH), 123.3 (CH), 125.8 (C), 127.8 (CH), 128.1 (CH), 129.1 (CH), 132.6 (C), 133.6 (C), 137.8 (CH), 149.2 (CH), 152.9 (C) ppm. IR: $\tilde{\nu}$ = 3059 (m), 3029 (m), 2981 (m), 2926 (m), 1714 (s), 1658 (s), 1635 (s), 1604 (s), 1491 (s), 1470 (s), 1436 (s), 1388 (s), 1359 (s), 1327 (m), 1254 (s), 1182 (m), 1150 (m), 1096 (m), 1073 (m), 1027 (m), 970 (m), 922 (m), 756 (s), 699 (s), 637 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 248 (38) $[M]^+$, 221 (20), 157 (59), 146 (75), 145 (60), 131 (100). HRMS: calcd. for $C_{17}H_{16}N_2$ 248.1313 $[M]^+$; found 248.1315.

2,3-Dimethyl-5-phenyl-1-[2-(1*H*-pyrrol-1-yl)benzyl]-1*H*-pyrrole (5i): ^1H NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, 3 H), 2.11 (s, 3 H), 4.92 (s, 2 H), 6.14 (s, 1 H), 6.33 (t, *J* = 2.1 Hz, 2 H), 6.71 (t, *J* = 2.1 Hz, 2 H), 7.24–7.34 (m, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.6 (CH_3), 11.0 (CH_3), 43.6 (CH_2), 109.1 (CH), 109.7 (CH), 115.2 (C), 121.7 (CH), 126.2 (C), 126.3 (CH), 126.5 (CH), 126.7 (CH), 127.3 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 133.1 (C), 133.3 (C), 135.4 (C), 138.3 (C) ppm. IR: $\tilde{\nu}$ = 3101 (m), 3062 (s), 3028 (s), 2921 (s), 2860 (s), 1713 (s), 1639 (s), 1602 (s), 1583 (s), 1500 (s), 1478 (s), 1453 (s), 1396 (s), 1273 (m), 1176 (s), 1158 (s), 1093 (s), 1071 (s), 1044 (m), 1029 (m), 1016 (s), 968 (m), 925 (s), 910 (s), 871 (m), 799 (m), 762 (s), 729 (s), 700 (s), 633 (s) cm^{-1}. HRMS: calcd. for $C_{23}H_{22}N_2$ 326.1783 $[M]^+$; found 326.1782.

2,3-Dimethyl-1-phenethyl-5-phenyl-1*H*-pyrrole (5j): ^1H NMR (400 MHz, $CDCl_3$): δ = 1.97 (s, 3 H), 2.08 (s, 3 H), 2.65 (t, *J* = 8.0 Hz, 2 H), 3.94 (t, *J* = 8.0 Hz, 2 H), 5.90 (s, 1 H), 6.84 (d, *J* = 7.8 Hz, 2 H), 7.07–7.27 (m, 8 H) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 10.0 (CH_3), 11.2 (CH_3), 37.7 (CH_2), 45.9 (CH_2), 109.8 (CH), 114.9 (C), 125.9 (C), 126.4 (CH), 126.6 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 129.0 (CH), 132.5 (C), 134.2 (C), 138.4 (C) ppm. IR: $\tilde{\nu}$ = 3062 (m), 3026 (s), 2919 (s), 2861 (s), 1649 (m), 1603 (s), 1515 (m), 1496 (m), 1453 (s), 1393 (m), 1344 (s), 1229 (m), 1176 (m), 1114 (w), 1072 (w), 1029 (w), 755 (s), 699 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 275 (70) $[M]^+$, 184 (100), 105 (18). HRMS: calcd. for $C_{20}H_{21}N$ 275.1674 $[M]^+$; found 275.1674.

(*E*)-2-Methyl-1,5-diphenyl-3-styryl-1*H*-pyrrole (6a): ^1H NMR (600 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 6.60 (s, 1 H), 6.78 (d, *J* = 16.1 Hz, 1 H), 6.99–7.11 (m, 9 H), 7.22–7.26 (m, 5 H), 7.40 (d, *J* = 7.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1 (CH_3), 105.7 (CH), 119.7 (C), 121.3 (CH), 124.4 (CH), 125.7 (CH), 126.1 (CH), 126.3 (CH), 127.6 (CH), 127.9 (CH), 127.8 (CH), 128.4 (CH), 128.5 (CH), 128.9 (CH), 130.6 (C), 132.9 (C), 134.8 (C), 138.6 (C), 138.9 (C) ppm. IR: $\tilde{\nu}$ = 3056 (m), 3025 (m), 2915 (m), 1722 (w), 1635 (m), 1595 (s), 1497 (s), 1448 (m), 1419 (m), 1375 (m), 1181 (m), 1071 (m), 1028 (m), 951 (m), 767 (m), 756 (s), 694 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 335 (100) $[M]^+$, 261 (15), 193 (12), 149 (12),105 (20). HRMS: calcd. for $C_{25}H_{21}N$ 335.1674 $[M]^+$; found 335.1675.

(*E*)-2-(2-Methyl-5-phenyl-3-styryl-1*H*-pyrrol-1-yl)phenol (6b): ^1H NMR (600 MHz, $CDCl_3$): δ = 2.04 (s, 3 H), 5.26 (br. s, 1 H, OH), 6.67 (s, 1 H), 6.78–6.84 (m, 2 H), 6.92–6.99 (m, 3 H), 7.03–7.16 (m, 6 H), 7.20 (dt, *J* = 8.1, 1.6 Hz, 1 H), 7.26 (t, *J* = 7.6 Hz, 2 H), 7.41 (d, *J* = 7.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.3 (CH_3), 106.3 (CH), 116.4 (CH), 120.6 (C), 120.8 (CH), 120.9 (CH), 124.9 (CH), 125.5 (C), 125.8 (CH), 126.5 (CH), 126.6 (CH), 127.3 (CH), 128.2 (CH), 128.6 (CH), 129.5 (CH), 130.1 (CH), 131.1 (C), 132.0 (C), 134.9 (C), 138.4 (C), 152.3 (C) ppm. IR: $\tilde{\nu}$ = 3421 (m), 3026 (m), 2991 (m), 2918 (m), 1720 (m), 1636 (m), 1597 (s), 1497 (s), 1447 (s), 1374 (s), 1236 (s), 1203 (s), 1072 (m), 1029 (m), 953 (m), 908 (m), 757 (s), 694 (s) cm^{-1}. HRMS: calcd. for $C_{25}H_{21}NO$ 351.1623 $[M]^+$; found 351.1623.

(*E*)-2-(2-Methyl-5-phenyl-3-styryl-1*H*-pyrrol-1-yl)aniline (6c): ^1H NMR (600 MHz, $CDCl_3$): δ = 2.06 (s, 3 H), 3.50 (br. s, 2 H, NH), 6.65–6.69 (m, 3 H), 6.79 (d, *J* = 16.1 Hz, 1 H), 6.93 (dd, *J* = 7.7, 1.2 Hz, 1 H), 7.02–7.06 (m, 2 H), 7.09–7.17 (m, 6 H), 7.25 (t, *J* = 7.76 Hz, 2 H), 7.40 (d, *J* = 7.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.2 (CH_3), 105.5 (CH), 115.8 (CH), 118.5 (CH), 119.9 (C), 121.2 (CH), 124.2 (CH), 124.6 (C), 125.7 (CH), 126.2 (CH), 126.3 (CH), 127.1 (CH), 128.0 (CH), 128.5 (CH), 129.5 (CH), 129.7 (CH), 130.9 (C), 132.5 (C), 134.3 (C), 138.5 (C), 143.7 (C) ppm. IR: $\tilde{\nu}$ = 3461 (m), 3380 (m), 3057 (m), 3026 (m), 2922 (m), 2853 (m), 1633 (s), 1616 (s), 1597 (s), 1501 (s), 1462 (s), 1448 (s), 1419 (s), 1372 (s), 1311 (m), 1264 (m), 1184 (m), 1156 (m), 1073 (m), 1028 (m), 952 (s), 908 (m), 751 (s), 694 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 350 (100) $[M]^+$, 335 (10), 273 (9), 269 (12), 246 (9), 187 (9). HRMS: calcd. for $C_{25}H_{22}N_2$ 350.1783 $[M]^+$; found 350.1783.

(*E*)-1-(2-Bromophenyl)-2-methyl-5-phenyl-3-styryl-1*H*-pyrrole (6d): ^1H NMR (600 MHz, $CDCl_3$): δ = 2.05 (s, 3 H), 6.63 (s, 1 H), 6.80 (d, *J* = 16.1 Hz, 1 H), 7.02–7.09 (m, 6 H), 7.10 (t, *J* = 7.3 Hz, 1 H), 7.13–7.17 (m, 2 H), 7.22 (td, *J* = 7.6, 1.4 Hz, 1 H), 7.24 (t, *J* = 7.6 Hz, 2 H), 7.40 (d, *J* = 7.3 Hz, 2 H), 7.56 (dd, *J* = 7.9, 1.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.6 (CH_3), 105.5 (CH), 119.8 (C), 121.2 (CH), 124.3 (C), 124.5 (CH), 125.7 (CH), 126.3 (CH), 126.4 (CH), 127.7 (CH), 128.0 (CH), 128.2 (CH), 128.5 (CH), 129.8 (CH), 130.7 (C), 131.1 (CH), 132.7 (C), 133.3 (CH), 134.9 (C), 138.5 (C), 138.6 (C) ppm. IR: $\tilde{\nu}$ = 3056 (m), 3026 (m), 2920 (m), 1635 (m), 1596 (m), 1481 (s), 1447 (m), 1419 (m), 1373 (m), 1073 (m), 1028 (m), 953 (m), 757 (s), 731 (m), 695 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 415 (98) [$C_{25}H_{20}{}^{81}BrN$], 413 (100) $[M]^+$, 293 (32), 260 (16), 167 (13), 129 (58), 112 (18). HRMS: calcd. for $C_{25}H_{20}BrN$ 413.0779 $[M]^+$; found 413.0780.

(*E*)-2-(2-Methyl-5-phenyl-3-styryl-1*H*-pyrrol-1-yl)pyridine (6e): ^1H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 6.67 (s, 1 H), 6.86 (d, *J* = 16.2 Hz, 1 H), 6.90 (d, *J* = 8.0 Hz, 1 H), 7.06–7.23 (m, 8 H, 7-H or 8-H), 7.31 (t, *J* = 7.6 Hz, 2 H), 7.48 (d, *J* = 7.9 Hz, 2 H), 7.58 (td, *J* = 7.8, 1.2 Hz, 1 H), 8.59 (dd, *J* = 4.9, 1.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.0 (CH_3), 106.6 (CH), 120.3 (C), 121.0 (CH), 122.4 (CH), 123.1 (CH), 124.7 (CH), 125.7 (CH), 126.2 (CH), 126.4 (CH), 127.8 (CH), 128.1 (CH), 128.5 (CH), 130.8 (C), 132.9 (C), 134.4 (C), 137.8 (CH), 138.5 (C), 149.1 (CH), 152.1 (C) ppm. IR: $\tilde{\nu}$ = 3052 (m), 3028 (m), 2922 (m), 2854 (m), 1633 (m), 1596 (s), 1585 (s), 1471 (s), 1435 (s), 1376 (m), 1027 (m), 953 (m), 757 (s), 696 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 336 (100) $[M]^+$, 278 (25). HRMS: calcd. for $C_{24}H_{20}N_2$ 336.1626 $[M]^+$; found 336.1626.

(*E*)-3-(2-Methyl-5-phenyl-3-styryl-1*H*-pyrrol-1-yl)pyridine (6f): ^1H NMR (600 MHz, $CDCl_3$): δ = 2.14 (s, 3 H), 6.61 (s, 1 H), 6.80 (d, *J* = 16.1 Hz, 1 H), 6.97–7.00 (m, 2 H), 7.04–7.15 (m, 5 H, 7-H or 8-H), 7.20 (ddd, *J* = 8.0, 4.8, 0.6 Hz, 1 H), 7.25 (t, *J* = 7.5 Hz, 2 H), 7.33 (ddd, *J* = 8.0, 2.4, 1.6 Hz, 1 H), 7.41 (d, *J* = 7.2 Hz, 2 H), 8.40 (d, *J* = 2.5 Hz, 1 H), 8.48 (dd, *J* = 4.8, 1.5 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1 (CH_3), 106.6 (CH), 120.5 (C), 120.8 (CH), 123.5 (CH), 125.2 (CH), 125.8 (CH), 126.5 (CH), 126.6 (CH), 128.2 (CH), 128.3 (CH), 128.6 (CH), 130.3 (C), 132.2 (C), 135.1 (C), 135.6 (C), 138.4 (C), 138.7 (CH), 148.5 (CH), 149.3 (CH) ppm. MS (EI): *m*/*z* (%) = 336 (100) $[M]^+$, 276 (24), 262 (12), 233 (16). HRMS: calcd. for $C_{24}H_{20}N_2$ 336.1626 $[M]^+$; found 336.1627.

(*E*)-1-(4-Methoxyphenyl)-2-methyl-5-phenyl-3-styryl-1*H*-pyrrole (6g): ^1H NMR (600 MHz, $CDCl_3$): δ = 2.11 (s, 3 H), 3.72 (s, 3 H), 6.59 (s, 1 H), 6.77–6.80 (m, 3 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 7.02–7.14 (m, 7 H, 7-H or 8-H), 7.24 (t, *J* = 7.6 Hz, 2 H), 7.40 (d, *J* = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.0 (CH_3), 55.4 (CH_3), 105.3 (CH), 114.2 (CH), 119.4 (C), 121.3 (CH), 124.2 (CH), 125.7 (CH), 126.0 (CH), 126.3 (CH), 127.9 (CH), 128.0 (CH), 128.5 (CH), 129.4 (CH), 131.0 (C), 131.7 (C), 132.9 (C), 134.9 (C); 138.7 (C), 158.7 (C) ppm. IR: $\tilde{\nu}$ = 3024 (m), 2911 (w), 1633 (m), 1599 (m), 1512 (s), 1448 (m), 1293 (m), 1247 (s), 1182 (m), 1167 (m), 1029 (m), 951 (m), 838 (m), 758 (m), 695 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 365 (100) $[M]^+$, 350 (8), 288 (6), 215 (6). HRMS: calcd. for $C_{26}H_{23}NO$ 365.1779 $[M]^+$; found 365.1778.

(*E*)-2-Methyl-1-(4-nitrophenyl)-5-phenyl-3-styryl-1*H*-pyrrole (6h): ^1H NMR (600 MHz, $CDCl_3$): δ = 2.18 (s, 3 H), 6.62 (s, 1 H), 6.80 (d, *J* = 16.1 Hz, 1 H), 6.97 (d, *J* = 6.7 Hz, 2 H), 7.01 (d, *J* = 16.1 Hz, 1 H), 7.07–7.16 (m, 4 H), 7.19 (d, *J* = 8.9 Hz, 2 H), 7.26 (t, *J* = 7.5 Hz, 2 H), 7.41 (d, *J* = 7.5 Hz, 2 H), 8.14 (d, *J* = 8.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.3 (CH_3), 107.3 (CH), 120.5 (CH), 121.0 (C), 124.4 (CH), 125.6 (CH), 125.8 (CH), 126.7 (CH), 126.8 (CH), 128.1 (CH), 128.3 (CH), 128.6 (CH), 128.9 (CH), 129.8 (C), 132.2 (C), 134.9 (C), 138.2 (C), 144.5 (C), 146.3 (C) ppm. IR: $\tilde{\nu}$ = 3070 (w), 3055 (w), 3030 (w), 2924 (w), 1592 (s), 1514 (s), 1498 (s), 1369 (m), 1335 (s), 965 (m), 856 (m), 765 (m), 757 (m), 753 (m), 706 (m), 697 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 380 (100) $[M]^+$, 334 (8). HRMS: calcd. for $C_{25}H_{20}N_2O_2$ 380.1524 $[M]^+$; found 380.1524.

Methyl (*E*)-3,5-Dibromo-2-(2-methyl-5-phenyl-3-styryl-1*H*-pyrrol-1-yl)benzoate (6i): ^1H NMR (600 MHz, $CDCl_3$): δ = 2.01 (s, 3 H), 3.54 (s, 3 H), 6.59 (s, 1 H), 6.75 (d, *J* = 16.1 Hz, 1 H), 6.98–7.25 (m, 9 H), 7.37 (d, *J* = 7.4 Hz, 2 H), 7.78 (d, *J* = 2.2 Hz, 1 H), 7.87 (d, *J* = 2.2 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 10.4 (CH_3), 52.9 (CH_3), 106.0 (CH), 120.2 (C), 121.1 (CH), 122.6 (C), 124.5 (CH), 125.7 (CH), 126.3 (CH), 126.7 (CH), 127.3 (C), 127.6

(CH), 128.1 (CH), 128.5 (CH), 130.5 (C), 132.3 (C), 132.7 (CH), 134.2 (C), 134.8 (C), 136.8 (C), 138.5 (C), 138.7 (CH), 163.8 (C) ppm. MS (EI): *m*/*z* (%) = 553 (55) [$C_{27}H_{21}{}^{81}Br_2NO_2$], 551 (100) [$C_{27}H_{21}Br^{81}BrNO_2$], 549 (51) $[M]^+$, 479 (20), 477 (35), 475 (19). HRMS: calcd. for $C_{27}H_{21}Br_2NO_2$ 548.9934 $[M]^+$; found 548.9934.

(*E*)-1-Benzyl-2-methyl-5-phenyl-3-styryl-1*H*-pyrrole (6j): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.12 (d, *J* = 1.2 Hz, 3 H), 5.03 (s, 2 H), 6.49 (d, *J* = 1.7 Hz, 1 H), 6.76 (d, *J* = 16.0 Hz, 1 H), 6.87 (d, *J* = 7.6 Hz, 2 H), 7.02 (dd, *J* = 16.0, 1.6 Hz, 1 H), 7.06–7.11 (m, 1 H), 7.14–7.18 (m, 2 H), 7.20–7.25 (m, 8 H), 7.38 (d, *J* = 7.7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.3 (CH_3), 47.7 (CH_2), 105.0 (CH), 119.5 (C), 121.4 (CH), 123.8 (CH), 125.6 (CH), 125.7 (CH), 126.2 (CH), 127.0 (CH), 127.1 (CH), 128.4 (CH), 128.5 (CH), 128.7 (C), 128.8 (CH), 129.5 (C), 133.1 (C), 135.3 (C), 138.5 (C), 138.7 (C) ppm. IR: $\tilde{\nu}$ = 3058 (m), 3025 (m), 2912 (m), 1633 (s), 1598 (s), 1495 (s), 1452 (s), 1428 (s), 1350 (s), 1165 (m), 1072 (m), 1028 (m), 952 (s), 756 (s), 728 (s), 693 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 349 (100) $[M]^+$, 258 (28), 243 (40). HRMS: calcd. for $C_{26}H_{23}N$ 349.1831 $[M]^+$; found 349.1830.

(*E*)-2-Methyl-5-phenyl-1-[2-(1*H*-pyrrol-1-yl)benzyl]-3-styryl-1*H*-pyrrole (6k): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.04 (s, 3 H), 4.81 (s, 2 H), 6.22 (t, *J* = 1.9 Hz, 2 H), 6.46 (s, 1 H), 6.56 (t, *J* = 2.0 Hz, 2 H), 6.62–6.64 (m, 1 H), 6.73 (d, *J* = 16.1 Hz, 1 H), 6.98 (d, *J* = 16.1 Hz, 1 H), 7.06–7.09 (m, 2 H), 7.15–7.23 (m, 9 H), 7.36 (d, *J* = 8.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.1 (CH_3), 43.8 (CH_2), 105.3 (CH), 109.4 (CH), 119.6 (C), 121.3 (CH), 121.9 (CH), 123.9 (CH), 125.7 (CH), 126.3 (CH), 126.7 (CH), 126.9 (CH), 127.2 (CH), 127.8 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 129.3 (C), 132.9 (C), 134.9 (C), 135.3 (C), 138.5 (C), 138.6 (C) ppm. IR: $\tilde{\nu}$ = 3057 (m), 3025 (m), 2922 (m), 2853 (m), 1633 (m), 1599 (m), 1500 (s), 1479 (m), 1457 (m), 1428 (m), 1349 (m), 1326 (m), 1167 (m), 1092 (m), 1070 (m), 1015 (m), 952 (m), 925 (m), 758 (s), 728 (s), 693 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 414 (100) $[M]^+$, 258 (24), 243 (23),156 (48). HRMS: calcd. for $C_{30}H_{26}N_2$ 414.2095 $[M]^+$; found 414.2095.

(*E*)-3-[2-(2-Methyl-5-phenyl-3-styryl-1*H*-pyrrol-1-yl)ethyl]-1*H*-indole (6l): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.28 (s, 3 H), 2.82 (t, *J* = 7.9 Hz, 2 H), 4.06 (t, *J* = 7.9 Hz, 2 H), 6.39 (s, 1 H), 6.69 (d, *J* = 1.8 Hz, 1 H), 6.71 (d, *J* = 16.0 Hz, 1 H), 6.93 (t, *J* = 7.1 Hz, 1 H), 7.01–7.04 (m, 2 H, 7-H or 8-H), 7.06–7.10 (m, 2 H), 7.21–7.34 (m, 8 H), 7.39 (d, *J* = 7.5 Hz, 2 H), 7.82 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.3 (CH_3), 26.9 (CH_2), 44.9 (CH_2), 105.1 (CH), 111.1 (CH), 112.1 (C), 118.3 (CH), 119.0 (C), 119.3 (CH), 121.5 (CH), 121.8 (CH), 121.9 (CH), 123.5 (CH), 125.6 (CH), 126.1 (CH), 127.0 (C), 127.2 (CH), 128.4 (CH), 128.5 (CH), 128.9 (C), 129.3 (CH), 133.6 (C), 134.5 (C), 136.0 (C), 138.8 (C) ppm. IR: $\tilde{\nu}$ = 3420 (s), 3056 (m), 3027 (m), 2923 (m), 2854 (m), 1719 (m), 1632 (s), 1597 (s), 1456 (s), 1429 (s), 1353 (s), 1165 (m), 1092 (m), 1073 (m), 1029 (m), 1011 (m), 954 (s), 761 (s), 742 (s), 695 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 402 (100) $[M]^+$, 272 (72), 260 (22), 130 (21). HRMS: calcd. for $C_{29}H_{26}N_2$ 402.2095 $[M]^+$; found 402.2095.

Methyl (*E*)-3-(1*H*-Indol-3-yl)-2-(2-methyl-5-phenyl-3-styryl-1*H*-pyrrol-1-yl)propanoate (6m): The amine was generated in situ from L-tryptophan methyl ester and Et_3N (1 equiv.). Polarimetric analysis and ^{1}H NMR experiments in the presence of a chiral shift reagent (Eu[tfc]$_3$, 1.1 equiv.) revealed that the product was racemic. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 3.13 (dd, *J* = 15.0, 9.2 Hz, 1 H), 3.58 (dd, *J* = 15.0, 5.9 Hz, 1 H), 3.74 (s, 3 H), 5.05 (dd, *J* = 9.2, 5.9 Hz, 1 H), 6.23 (s, 1 H), 6.51 (d, *J* = 2.3 Hz, 1 H), 6.69 (d, *J* = 16.0 Hz, 1 H), 6.80 (d, *J* = 7.1 Hz, 2 H), 6.81 (t, *J* = 7.3 Hz, 1 H), 6.91 (d, *J* = 7.9 Hz, 1 H), 7.01–7.05 (m, 4 H), 7.09 (t, *J* = 7.4 Hz, 1 H), 7.12 (t, *J* = 7.3 Hz, 1 H), 7.22 (d, *J* = 8.1 Hz, 1 H), 7.26 (t, *J* = 7.7 Hz, 2 H), 7.39 (d, *J* = 7.6 Hz, 2 H), 7.82 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.2 (CH_3), 27.1 (CH_2), 52.7 (CH_3), 58.2 (CH), 104.9 (CH), 110.4 (C), 110.9 (CH), 117.9 (CH), 119.4 (CH), 120.3 (C), 121.2 (CH), 121.7 (CH), 123.0 (CH), 124.2 (CH), 125.7 (CH), 126.3 (CH), 127.0 (C), 127.2 (CH), 128.0 (CH), 128.1 (C), 128.5 (CH), 129.4 (CH), 132.7 (C), 135.8 (C), 136.5 (C), 138.6 (C), 171.5 (C) ppm. IR: $\tilde{\nu}$ = 3414 (m), 3055 (m), 3025 (m), 2949 (m), 2925 (m), 1738 (s), 1632 (m), 1597 (m), 1455 (s), 1429 (s), 1356 (s), 1727 (m), 1220 (s), 1172 (m), 1093 (m), 1071 (s), 1028 (m), 1010 (m), 986 (m), 954 (m), 792 (m), 762 (s), 742 (s), 695 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 460 (100) $[M]^+$, 331 (21), 272 (18), 260 (26), 130 (34). HRMS: calcd. for $C_{31}H_{28}N_2O_2$ 460.2146 $[M]^+$; found 460.2145.

(*E*)-1-Benzhydryl-2-methyl-5-phenyl-3-styryl-1*H*-pyrrole (6n): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.82 (d, *J* = 0.8 Hz, 3 H), 6.55 (s, 1 H), 6.78 (s, 1 H), 6.81 (d, *J* = 16.0 Hz, 1 H), 7.02 (dd, *J* = 16.0, 0.6 Hz, 1 H), 7.11–7.16 (m, 5 H), 7.24–7.33 (m, 13 H), 7.42 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7 (CH_3), 62.5 (CH), 105.2 (CH), 120.2 (C), 121.3 (CH), 123.9 (CH), 125.7 (CH), 126.2 (CH), 127.3 (CH), 127.4 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 129.4 (CH), 129.9 (C), 133.6 (C), 136.6 (C), 138.7 (C), 139.3 (C) ppm. IR: $\tilde{\nu}$ = 3057 (m), 3025 (m), 2920 (m), 1632 (m), 1598 (m), 1494 (m), 1446 (s), 1427 (m), 1352 (m), 1178 (m), 1153 (m), 1071 (m), 1028 (m), 952 (m), 761 (s), 749 (s), 721 (s), 697 (s), 603 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 425 (35) $[M]^+$, 167 (100). HRMS: calcd. for $C_{23}H_{27}N$ 425.2143 $[M]^+$; found 425.2146.

(*E*)-2-Methyl-1-phenethyl-5-phenyl-3-styryl-1*H*-pyrrole (6o): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.21 (d, *J* = 0.7 Hz, 3 H), 2.65 (t, *J* = 7.9 Hz, 2 H), 3.98 (t, *J* = 7.3 Hz, 2 H), 6.35 (s, 1 H), 6.68 (d, *J* = 16.0 Hz, 1 H), 6.82 (d, *J* = 7.4 Hz, 2 H), 6.99 (dd, *J* = 16.0, 0.7 Hz, 1 H), 7.06–7.14 (m, 4 H), 7.20–7.33 (m, 7 H), 7.37 (d, *J* = 7.7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.2 (CH_3), 37.4 (CH_2), 45.7 (CH_2), 105.2 (CH), 119.1 (C), 121.5 (CH), 123.6 (CH), 125.6 (CH), 126.1 (CH), 126.5 (CH), 127.2 (CH), 128.4 (CH), 128.5 (CH), 128.5 (CH), 128.6 (CH), 128.8 (C), 129.2 (CH), 133.6 (C), 134.5 (C), 138.0 (C), 138.8 (C) ppm. IR: $\tilde{\nu}$ = 3058 (m), 3025 (m), 2928 (m), 1633 (m), 1598 (m), 1448 (m), 1429 (m), 1352 (s), 1165 (m), 1072 (m), 1029 (m), 952 (m), 909 (m), 750 (s), 697 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 363 (100) $[M]^+$, 272 (64). HRMS: calcd. for $C_{27}H_{25}N$ 363.1981 $[M]^+$; found 363.1982.

(*E*)-1-Allyl-2-methyl-5-phenyl-3-styryl-1*H*-pyrrole (6p): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.25 (s, 3 H), 4.37–4.38 (m, 2 H), 4.83 (dd, *J* = 17.1, 0.8 Hz, 1 H), 5.13 (dd, *J* = 10.4, 0.9 Hz, 1 H), 5.82–5.87 (m, 1 H), 6.41 (s), 6.71 (d, *J* = 16.0 Hz, 1 H), 7.01 (d, *J* = 16.0 Hz, 1 H), 7.09 (t, *J* = 7.4 Hz, 1 H), 7.22–7–25 (m, 3 H), 7.30 (t, *J* = 7.6 Hz, 2 H), 7.34 (d, *J* = 7.2 Hz, 2 H), 7.38 (d, *J* = 7.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.0 (CH_3), 46.5 (CH_2), 104.7 (CH), 116.1 (CH_2), 119.1 (C), 121.4 (CH), 123.6 (CH), 125.6 (CH), 126.1 (CH), 127.1 (CH), 128.3 (CH), 128.5 (CH), 128.7 (CH), 129.5 (C), 133.2 (C), 134.5 (CH), 134.9 (C), 138.8 (C) ppm. IR: $\tilde{\nu}$ = 3057 (m), 3024 (m), 2923 (m), 2853 (m), 1633 (s), 1599 (s), 1447 (m), 1428 (s), 1364 (m), 1350 (s), 1166 (s), 1072 (s), 953 (s), 916 (m), 787 (m), 767 (s), 755 (s), 693 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 299 (100) $[M]^+$, 243 (41), 215 (16). HRMS: calcd. for $C_{22}H_{21}N$ 299.1674 $[M]^+$; found 299.1673.

(*E*)-1-(But-3-en-1-yl)-2-methyl-5-phenyl-3-styryl-1*H*-pyrrole (6q): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.17 (q, *J* = 7.5 Hz, 2 H), 2.30 (d, *J* = 1.0 Hz, 3 H), 3.83 (t, *J* = 7.5 Hz, 2 H), 4.87–4.90 (m, 2 H), 5.45–5.55 (m, 1 H), 6.34 (d, *J* = 1.7 Hz, 1 H), 6.68 (d, *J* = 16.1 Hz, 1 H), 7.00 (dd, *J* = 16.1, 1.5 Hz, 1 H), 7.07 (t, *J* = 7.3 Hz, 1 H),

7.20–7.25 (m, 3 H), 7.30–7.32 (m, 4 H), 7.35 (d, J = 7.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.4 (CH_3), 35.2 (CH_2), 43.6 (CH_2), 105.1 (CH), 117.1 (CH_2), 119.1 (C), 121.4 (CH), 123.6 (CH), 125.6 (CH), 126.1 (CH), 127.1 (CH), 128.4 (CH), 128.5 (CH), 128.8 (C), 129.1 (CH), 133.6 (C), 134.1 (CH), 134.5 (C), 138.8 (C) ppm. IR: $\tilde{\nu}$ = 3058 (m), 3027 (m), 2976 (m), 2905 (m), 1631 (s), 1594 (m), 1443 (m), 1428 (m), 1353 (s), 1169 (m), 1073 (m), 1021 (m), 994 (m), 950 (s), 923 (m), 799 (m), 749 (s), 696 (s) cm^{-1}. MS (EI): m/z (%) = 313 (100) $[M]^+$, 272 (80). HRMS: calcd. for $C_{23}H_{23}N$ 313.1826 $[M]^+$; found 313.1825.

(*E*)-2-Methyl-5-phenyl-3-styryl-1-[(tetrahydrofuran-2-yl)methyl]-1*H*-pyrrole (6r): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.15–1.21 (m, 1 H), 1.52–1.62 (m, 3 H), 2.34 (d, J = 1.2 Hz, 3 H), 3.50–3.59 (m, 2 H), 3.81 (quint., J = 6.1 Hz, 1 H), 3.92 (d, J = 6.4 Hz, 2 H), 6.36 (d, J = 1.4 Hz, 1 H), 6.68 (d, J = 16.0 Hz, 1 H), 7.02 (d, J = 16.0 Hz, 1 H), 7.07 (t, J = 7.3 Hz, 1 H), 7.17 (t, J = 7.5 Hz, 1 H), 7.22 (t, J = 7.4 Hz, 2 H), 7.29–7.34 (m, 4 H), 7.38 (d, J = 7.6 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.6 (CH_3), 25.1 (CH_2), 28.9 (CH_2), 47.8 (CH_2), 67.8 (CH_2), 78.3 (CH), 105.5 (CH), 119.1 (C), 121.5 (CH), 123.5 (CH), 125.6 (CH), 126.0 (CH), 126.9 (CH), 128.3 (CH), 128.4 (CH), 129.3 (CH), 129.6 (C), 133.8 (C), 134.7 (C), 138.8 (C) ppm. IR: $\tilde{\nu}$ = 3058 (m), 3025 (m), 2927 (m), 1632 (m), 1598 (m), 1448 (m), 1429 (m), 1352 (s), 1165 (m), 1027 (m), 1029 (m), 952 (m), 750 (s), 697 (s) cm^{-1}. MS (EI): m/z (%) = 343 (100) $[M]^+$, 272 (36), 259 (38), 169 (41). HRMS: calcd. for $C_{24}H_{25}NO$ 343.1931 $[M]^+$; found 343.1931.

(*E*)-2-(2-Methyl-5-phenyl-3-styryl-1*H*-pyrrol-1-yl)ethanol (6s): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.24 (s, 3 H), 3.43 (t, J = 6.1 Hz, 2 H), 3.90 (t, J = 6.1 Hz, 2 H), 6.29 (s, 1 H), 6.62 (d, J = 16.0 Hz, 1 H), 6.93 (d, J = 16.0 Hz, 1 H), 7.01–7.27 (m, 8 H), 7.32 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.5 (CH_3), 45.9 (CH_2), 62.0 (CH_2), 105.5 (CH), 119.2 (C), 121.2 (CH), 123.8 (CH), 125.6 (CH), 126.2 (CH), 127.2 (CH), 128.4 (CH), 128.5 (CH), 129.2 (CH), 129.5 (C), 133.4 (C), 134.7 (C), 138.7 (C) ppm. IR: $\tilde{\nu}$ = 3402 (m), 3057 (m), 3026 (m), 2935 (m), 1632 (s), 1598 (s), 1494 (m), 1448 (s), 1429 (m), 1357 (m), 1203 (m), 1167 (m), 1053 (m), 954 (m), 752 (s), 697 (s) cm^{-1}. MS (EI): m/z (%) = 303 (100) $[M]^+$, 272 (31), 260 (45), 127 (60), 118 (43), 105 (23). HRMS: calcd. for $C_{21}H_{21}NO$ 303.1618 $[M]^+$; found 303.1618.

Methyl (*E*)-2-(2-Methyl-5-phenyl-3-styryl-1*H*-pyrrol-1-yl)propanoate (6t): The amine was generated in situ from L-alanine methyl ester and Et_3N (1 equiv.). Polarimetric analysis and ^{1}H NMR experiments in the presence of a chiral shift reagent (Eu[tfc]$_3$, 1.1 equiv.) revealed that the product was racemic. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.62 (d, J = 7.3 Hz, 3 H), 2.32 (s, 3 H), 3.78 (s, 3 H), 5.03 (q, J = 7.3 Hz, 1 H), 6.47 (s, 1 H), 6.81 (d, J = 16.0 Hz, 1 H), 7.08 (d, J = 16.0 Hz, 1 H), 7.20 (t, J = 7.9 Hz, 1 H), 7.34 (t, J = 7.6 Hz, 2 H), 7.38–7.44 (m, 5 H), 7.48 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.9 (CH_3), 17.7 (CH_3), 52.7 (CH_3), 53.2 (CH), 105.4 (CH), 120.2 (C), 121.0 (CH), 124.4 (CH), 125.7 (CH), 126.3 (CH), 127.5 (CH), 128.3 (C), 128.5 (CH), 128.4 (CH), 129.4 (CH), 133.1 (C), 135.3 (C), 138.6 (C), 171.9 (C) ppm. IR: $\tilde{\nu}$ = 3056 (m), 3025 (m), 2996 (m), 2949 (m), 1742 (s), 1622 (m), 1597 (m), 1489 (m), 1431 (m), 1357 (m), 1297 (m), 1224 (s), 1172 (m), 1123 (m), 1089 (m), 1072 (m), 1028 (m), 953 (s), 910 (m), 761 (s), 695 (s) cm^{-1}. MS (EI): m/z (%) = 345 (100) $[M]^+$, 286 (38), 258 (48), 243 (30), 215 (61), 143 (23), 106 (26). HRMS: calcd. for $C_{23}H_{23}NO_2$ 345.1729 $[M]^+$; found 345.1729.

(*E*)-1-(Furan-2-ylmethyl)-2-methyl-5-phenyl-3-styryl-1*H*-pyrrole (6u): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 4.93 (s, 2 H), 5.89 (d, J = 1.3 Hz, 1 H), 6.22 (d, J = 1.4 Hz, 1 H), 6.43 (s, 1 H), 6.74 (d, J = 16.1 Hz, 1 H), 7.02 (d, J = 16.0 Hz, 1 H), 7.11 (t, J = 7.3 Hz, 1 H), 7.23–7.27 (m, 4 H), 7.30–7.37 (m, 4 H), 7.40 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.2 (CH_3), 41.8 (CH_2), 105.1 (C), 107.2 (CH), 110.3 (CH), 119.4 (C), 121.3 (CH), 123.4 (CH), 125.7 (CH), 126.2 (CH), 127.2 (CH), 128.5 (CH), 128.4 (CH), 129.1 (CH), 129.6 (C), 133.1 (C), 135.1 (C), 138.7 (C), 142.1 (CH), 151.3 (C) ppm. IR: $\tilde{\nu}$ = 3057 (m), 3025 (m), 2915 (m), 1633 (s), 1598 (s), 1447 (s), 1428 (s), 1338 (s), 1166 (m), 1146 (m), 1072 (m), 1010 (s), 751 (s), 693 (s) cm^{-1}. MS (EI): m/z (%) = 339 (46) $[M]^+$, 258 (54), 243 (100). HRMS: calcd. for $C_{24}H_{21}NO$ 339.1618 $[M]^+$; found 339.1618.

(*E*)-4-Benzylidene-3-methyl-1,2-diphenyl-4,5,6,7-tetrahydro-2*H*-isoindole (7a): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.73 (quint., J = 6.0 Hz, 2 H), 2.27 (s, 3 H), 2.68 (t, J = 6.2 Hz, 2 H), 2.73 (t, J = 6.0 Hz, 2 H), 6.62 (s, 1 H), 6.92 (d, J = 7.2 Hz, 2 H), 7.03–7.26 (m, 13 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 (CH_3), 23.4 (CH_2), 25.5 (CH_2), 29.1 (CH_2), 118.8 (C), 119.6 (C), 121.0 (CH), 125.6 (CH), 125.7 (CH), 126.2 (C), 127.3 (CH), 127.7 (CH), 127.9 (C), 128.0 (CH), 128.8 (CH), 128.9 (CH), 129.3 (CH), 129.4 (CH), 132.8 (C), 135.8 (C), 138.8 (C), 138.9 (C) ppm. IR: $\tilde{\nu}$ = 3057 (m), 3028 (m), 2924 (m), 1663 (m), 1597 (s), 1495 (s), 1448 (s), 1374 (s), 1316 (m), 1266 (m), 1177 (m), 1073 (m), 1028 (m), 910 (m), 761 (m), 731 (s), 698 (s) cm^{-1}. MS (EI): m/z (%) = 375 (20) $[M]^+$, 314 (38), 300 (21), 180 (45), 105 (100). HRMS: calcd. for $C_{28}H_{25}N$ 375.1987 $[M]^+$; found 375.1989.

(*E*)-2-Benzyl-4-benzylidene-3-methyl-1-phenyl-4,5,6,7-tetrahydro-2*H*-isoindole (7b): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.73 (quint., J = 6.0 Hz, 2 H), 2.29 (s, 3 H), 2.59 (t, J = 6.0 Hz, 2 H), 2.72 (t, J = 6.0 Hz, 2 H), 5.03 (s, 2 H), 6.56 (s, 1 H), 6.91 (d, J = 7.2 Hz, 2 H), 7.17–7.27 (m, 13 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.1 (CH_3), 22.8 (CH_2), 25.4 (CH_2), 29.2 (CH_2), 47.5 (CH_2), 118.3 (C), 118.7 (C), 120.4 (CH), 124.9 (C), 125.4 (CH), 125.7 (CH), 126.9 (CH), 127.0 (CH), 128.0 (CH), 128.2 (C), 128.3 (CH), 128.7 (CH), 129.2 (CH), 129.9 (CH), 132.8 (C), 136.0 (C), 138.3 (C), 139.0 (C) ppm. HRMS: calcd. for $C_{29}H_{27}N$ 389.2143 $[M]^+$; found 389.2143.

(*E*)-3-[2-(4-Benzylidene-3-methyl-1-phenyl-4,5,6,7-tetrahydro-2*H*-isoindol-2-yl)ethyl]-1*H*-indole (7c): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.69–1.71 (m, 2 H), 2.50 (s, 3 H), 2.51–2.53 (m, 2 H), 2.70 (t, J = 5.8 Hz, 2 H), 2.86 (t, J = 8.3 Hz, 2 H), 4.04 (t, J = 8.3 Hz, 2 H), 6.59 (s, 1 H), 6.72 (d, J = 2.0 Hz, 1 H), 6.91 (d, J = 4.0 Hz, 2 H), 7.05–7.08 (m, 1 H), 7.11–7.13 (m, 1 H), 7.15–7.20 (m, 2 H), 7.24–7.30 (m, 6 H), 7.34–7.37 (m, 2 H), 7.83 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9 (CH_3), 22.5 (CH_2), 25.4 (CH_2), 27.3 (CH_2), 29.1 (CH_2), 44.7 (CH_2), 111.0 (CH), 112.4 (C), 117.8 (C), 118.4 (CH), 118.6 (C), 119.3 (CH), 120.2 (CH), 121.7 (CH), 121.9 (CH), 124.1 (C), 125.3 (CH), 126.9 (CH), 127.0 (C), 127.5 (C), 128.0 (CH), 128.4 (CH), 129.2 (CH), 130.4 (CH), 133.2 (C), 136.1 (C), 139.0 (C), 140.7 (C) ppm. IR: $\tilde{\nu}$ = 3418 (s), 3054 (m), 2923 (s), 2854 (m), 1600 (s), 1566 (m), 1488 (m), 1456 (s), 1443 (m), 1420 (m), 1351 (m), 1164 (w), 1095 (m), 1074 (m), 1029 (m), 1011 (m), 909 (m), 740 (s), 700 (s) cm^{-1}. MS (EI): m/z (%) = 442 (100) $[M]^+$, 312 (65), 300 (22), 273 (20), 105 (21). HRMS: calcd. for $C_{32}H_{30}N_2$ 442.2409 $[M]^+$; found 442.2408.

2-[(2*Z*,4*E*)-3-Ethynyl-1,5-diphenylpenta-2,4-dien-1-yl]aniline (8a): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.35 (s, 1 H), 3.60 (br. s, 2 H, NH), 5.39 (d, J = 10.4 Hz, 1 H), 6.44 (d, J = 10.4 Hz, 1 H), 6.62 (d, J = 7.8 Hz, 1 H), 6.70 (t, J = 7.5 Hz, 1 H), 6.73 (d, J = 15.7 Hz, 1 H), 6.94 (d, J = 15.9 Hz, 1 H), 6.98 (d, J = 7.7 Hz, 1 H), 7.02 (t, J = 7.6 Hz, 1 H), 7.16–7.21 (m, 4 H), 7.23–7.28 (m, 4 H), 7.34 (d, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.6 (CH), 78.5 (C), 84.7 (CH), 116.5 (CH), 118.8 (CH), 122.6 (C), 126.6 (CH), 126.8 (CH), 127.2 (C), 127.7 (CH), 127.8 (CH), 128.0 (CH),

128.1 (CH), 128.6 (CH), 128.8 (CH), 129.0 (CH), 131.7 (CH), 136.8 (C), 141.9 (C), 142.2 (CH), 144.6 (C) ppm.

4-[(2*Z*,4*E*)-3-Ethynyl-1,5-diphenylpenta-2,4-dien-1-yl]aniline (8b): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.37 (s, 1 H), 3.61 (br. s, 2 H, NH), 5.38 (d, J = 10.4 Hz, 1 H), 6.49 (d, J = 10.4 Hz, 1 H), 6.64 (d, J = 8.5 Hz, 2 H), 6.78 (d, J = 15.7 Hz, 1 H), 7.00 (d, J = 15.7 Hz, 1 H), 7.02 (d, J = 8.1 Hz, 2 H), 7.21–7.25 (m, 4 H), 7.29–7.34 (m, 4 H), 7.41 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.8 (CH), 78.7 (C), 83.9 (CH), 115.3 (CH), 121.9 (C), 126.4 (CH), 126.6 (CH), 127.6 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 129.2 (CH), 131.3 (CH), 133.1 (C), 136.9 (C), 143.6 (C), 144.3 (CH), 144.9 (C) ppm.

1-Benzyl-2-(but-3-enyl)-3-methyl-1*H*-pyrrole (9a): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.05 (td, J = 8.0, 6.8 Hz, 2 H), 2.07 (s, 3 H), 2.56 (t, J = 8.0 Hz, 2 H), 4.91–4.97 (m, 2 H), 5.02 (s, 2 H), 5.77 (ddt, J = 16.8, 10.4, 6.8 Hz, 1 H), 6.00 (d, J = 1.4 Hz, 1 H), 6.53 (d, J = 1.8 Hz, 1 H), 7.01 (d, J = 7.2 Hz, 2 H), 7.24 (t, J = 7.2 Hz, 1 H), 7.31 (t, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.7 (CH_3), 24.2 (CH_2), 34.4 (CH_2), 50.7 (CH_2), 108.9 (CH), 115.0 (CH_2), 115.7 (C), 119.8 (CH), 126.5 (CH), 127.4 (CH), 128.8 (CH), 128.9 (C), 138.2 (CH), 139.0 (C) ppm. IR: $\tilde{\nu}$ = 3065 (m), 3030 (m), 2924 (s), 2860 (s), 1709 (s), 1693 (s), 1640 (s), 1606 (m), 1496 (s), 1489 (s), 1454 (s), 1414 (s), 1384 (s), 1354 (s), 1337 (s), 1259 (m), 1244 (w), 1207 (m), 1189 (w), 1162 (w), 1076 (w), 1050 (w), 1029 (m), 994 (m), 966 (w), 945 (w), 912 (s), 845 (w), 822 (w), 800 (w), 727 (s), 696 (s), 667 (m), 641 (m) cm^{-1}. MS (EI): *m*/*z* (%) = 225 (20) $[M]^+$, 185 (20), 184 (100), 91 (90). HRMS: calcd. for $C_{16}H_{19}N$ 225.1517 $[M]^+$; found 225.1517.

2-(But-3-enyl)-3-methyl-1-phenethyl-1*H*-pyrrole (9b): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.08 (s, 3 H), 2.22 (tdt, J = 8.1, 6.7, 1.2 Hz, 2 H), 2.61 (t, J = 8.1 Hz, 2 H), 3.03 (t, J = 7.8 Hz, 2 H), 4.02 (t, J = 7.8 Hz, 2 H), 5.03 (ddt, J = 10.2, 1.9, 1.1 Hz, 1 H), 5.08 (dq, J = 17.1, 1.7 Hz, 1 H), 5.88 (ddt, J = 17.1, 10.2, 6.7 Hz, 1 H), 5.99 (d, J = 2.7 Hz, 1 H), 6.54 (d, J = 2.7 Hz, 1 H), 7.18 (d, J = 6.9 Hz, 2 H), 7.28 (t, J = 7.3 Hz, 1 H), 7.35 (t, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4 (CH_3), 23.7 (CH_2), 34.3 (CH_2), 38.4 (CH_2), 48.1 (CH_2), 108.5 (CH), 114.6 (C), 114.8 (CH_2), 118.1 (CH), 126.4 (CH), 128.0 (C), 128.5 (CH), 128.6 (CH), 137.9 (CH), 138.4 (C) ppm. HRMS: calcd. for $C_{17}H_{21}N$ 239.1674 $[M]^+$; found 239.1674.

(*E*)-1-Benzyl-2-(but-3-en-1-yl)-5-phenyl-3-styryl-1*H*-pyrrole (9c): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.10 (q, J = 7.1 Hz, 2 H), 2.63 (t, J = 7.8 Hz, 2 H), 4.89 (d, J = 10.8 Hz, 1 H), 4.90 (d, J = 16.3 Hz, 1 H), 5.07 (s, 2 H), 5.67–5.77 (m, 1 H), 6.49 (s, 1 H), 6.76 (d, J = 16.0 Hz, 1 H), 6.85 (d, J = 7.2 Hz, 2 H), 7.00 (d, J = 16.0 Hz, 1 H), 7.10–7.31 (m, 11 H), 7.38 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5 (CH_2), 34.9 (CH_2), 47.7 (CH_2), 105.3 (CH), 115.4 (CH_2), 119.7 (C), 121.3 (CH), 123.9 (CH), 125.6 (CH), 125.7 (CH), 126.3 (CH), 127.1 (CH), 127.2 (CH), 128.4 (CH), 128.5 (CH), 128.7 (CH), 128.9 (CH), 133.1 (C), 133.2 (C), 135.3 (C), 137.5 (CH), 138.7 (C), 138.9 (C) ppm. IR: $\tilde{\nu}$ = 3059 (m), 3026 (m), 2924 (s), 2854 (m), 1633 (m), 1598 (m), 1495 (m), 1452 (m), 1353 (m), 1072 (m), 1028 (m), 954 (m), 911 (m), 752 (m), 730 (m), 696 (s) cm^{-1}. HRMS: calcd. for $C_{29}H_{27}N$ 389.2143 $[M]^+$; found 389.2143.

(*E*)-2-Benzyl-4-benzylidene-3-(but-3-enyl)-1-phenyl-4,5,6,7-tetrahydro-2*H*-isoindole (9d): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.72 (quint., J = 6.0 Hz, 2 H), 2.19–2.24 (m, 2 H), 2.56 (t, J = 6.1 Hz, 2 H), 2.71 (t, J = 6.0 Hz, 2 H), 2.77 (t, J = 8.2 Hz, 2 H), 4.87–4.95 (m, 2 H), 5.05 (s, 2 H), 5.74 (ddt, J = 17.0, 10.2, 6.6 Hz, 1 H), 6.60 (s, 1 H), 6.85 (d, J = 7.0 Hz, 2 H), 7.17–7.27 (m, 13 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.9 (CH_2), 25.1 (CH_2), 26.2 (CH_2), 29.3 (CH_2), 32.9 (CH_2), 47.4 (CH_2), 115.1 (CH_2), 118.1 (C), 119.2 (C), 119.6 (CH), 125.4 (CH), 125.7 (CH), 126.8 (CH), 127.0 (CH), 128.0 (CH), 128.2 (CH), 128.3 (C), 128.6 (CH), 128.8 (C), 129.3 (CH), 130.0 (CH), 132.8 (C), 135.6 (C), 137.7 (CH), 139.0 (C), 139.2 (C) ppm. IR: $\tilde{\nu}$ = 3060 (m), 3027 (m), 2927 (s), 1664 (m), 1640 (m), 1601 (s), 1495 (s), 1452 (s), 1354 (s), 1329 (m), 1265 (m), 1177 (m), 1074 (m), 1029 (m), 1001 (m), 916 (m), 754 (s), 733 (s), 700 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 429 (36) $[M]^+$, 389 (38), 388 (100), 338 (23), 296 (18). HRMS: calcd. for $C_{32}H_{31}N$ 429.2457 $[M]^+$; found 429.2456.

7-Ethynyl-1,2,5-triphenyl-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (10a): Major diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.72 (dt, J = 13.2, 10.6 Hz, 1 H), 2.08 (dt, J = 13.3, 5.0 Hz, 1 H), 2.67–2.71 (m, 1 H), 2.73 (s, 1 H), 2.96 (t, J = 7.4 Hz, 1 H), 3.47 (dd, J = 9.8, 2.1 Hz), 3.61 (m, 1 H), 3.99 (dd, J = 9.7, 7.4 Hz, 1 H), 4.80 (d, J = 7.3 Hz, 1 H), 6.46 (br. s, 1 H), 6.50 (d, J = 7.6 Hz, 2 H), 6.62 (t, J = 7.5 Hz, 1 H), 7.11 (t, J = 7.6 Hz, 2 H), 7.25–7.37 (m, 8 H), 7.46 (d, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.6 (CH_2), 36.2 (CH), 42.1 (CH), 51.4 (CH), 55.0 (CH_2), 68.3 (CH), 77.6 (CH), 83.9 (C), 112.8 (CH), 115.8 (CH), 121.2 (C), 126.6 (CH), 127.0 (CH), 127.3 (CH), 127.4 (CH), 128.2 (CH), 128.6 (CH), 128.7 (CH), 140.6 (CH), 143.8 (C), 144.4 (C), 146.8 (C) ppm. IR: $\tilde{\nu}$ = 3059 (m), 3026 (m), 2924 (m), 1598 (s), 1503 (s), 1452 (m), 1343 (m), 1076 (m), 1029 (m), 994 (m), 909 (m), 750 (s), 699 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 375 (88) $[M]^+$, 335 (19), 297 (20), 233 (26), 194 (100), 192 (25), 169 (23), 104 (21). HRMS: calcd. for $C_{28}H_{25}N$ 375.1981 $[M]^+$; found 375.1982.

2-Benzyl-7-ethynyl-1,5-diphenyl-2,3,3a,4,5,7a-hexahydro-1*H*-isoindole (10b): Major diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.51 (q, J = 12.8 Hz, 1 H), 2.00 (d, J = 12.8 Hz, 1 H), 2.10 (dd, J = 10.0, 4.5 Hz, 1 H), 2.32 (s, 1 H), 2.57–2.61 (m, 1 H), 2.85 (t, J = 10.0 Hz, 1 H), 3.07 (d, J = 13.0 Hz, 1 H), 3.42 (br. d, J = 12.8 Hz, 1 H), 3.48 (dd, J = 9.9, 7.9 Hz, 1 H), 3.53 (d, J = 9.9 Hz, 1 H), 3.82 (d, J = 13.0 Hz, 1 H), 6.36 (br. s, 1 H), 7.21–7.29 (m, 9 H), 7.35–7.37 (m, 4 H), 7.59 (d, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.1 (CH), 37.6 (CH_2), 42.8 (CH), 49.7 (CH), 57.6 (CH_2), 59.0 (CH_2), 73.5 (CH), 76.9 (CH), 83.3 (C), 120.7 (C), 126.5 (CH), 126.7 (CH), 127.3 (CH), 127.5 (CH), 127.9 (CH), 128.1 (CH), 128.5 (C), 128.6 (CH), 129.2 (CH), 139.5 (C), 141.8 (C), 142.0 (CH), 144.9 (C) ppm. IR: $\tilde{\nu}$ = 3060 (m), 3026 (m), 2921 (m), 2853 (m), 2789 (m), 1600 (m), 1492 (m), 1451 (m), 1077 (m), 1027 (m), 909 (m), 887 (m), 759 (s), 699 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 389 (80) $[M]^+$, 311 (100), 298 (22), 209 (40), 178 (17). HRMS: calcd. for $C_{29}H_{27}N$ 389.2143 $[M]^+$; found 389.2141. Minor diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.89 (br. d, J = 12.6 Hz, 1 H), 2.03 (td, J = 12.6, 7.6 Hz, 1 H), 2.11–2.21 (m, 1 H), 2.56 (s, 1 H), 2.56 (t, J = 10.5 Hz, 1 H), 2.64 (t, J = 9.1 Hz, 1 H), 2.89 (t, J = 8.9 Hz, 1 H), 3.42 (d, J = 13.5 Hz, 1 H), 3.76–3.78 (m, 2 H, 3-H_b), 3.82 (d, J = 13.5 Hz, 1 H), 6.19 (br. s, 1 H), 7.19–7.39 (m, 13 H), 7.59 (d, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.9 (CH_2), 36.9 (CH), 41.8 (CH), 51.2 (CH), 54.6 (CH_2), 57.4 (CH_2), 72.0 (CH), 78.7 (CH), 81.6 (C), 122.2 (C), 126.3 (CH), 126.5 (CH), 127.3 (CH), 127.6 (CH), 128.0 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 129.5 (CH), 139.5 (CH), 140.4 (C), 142.3 (C), 145.4 (C) ppm.

4-Ethynyl-2,3,6-triphenyl-2,3,3a,6-tetrahydro-1*H*-isoindole (10c): Single diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.72 (s, 1 H), 3.41 (br. t, J = 9.5 Hz, 1 H), 4.07 (br. d, J = 10.0 Hz, 1 H), 4.10 (d, J = 12.4 Hz, 1 H), 4.60 (d, J = 12.4 Hz, 1 H), 4.65 (d, J = 8.5 Hz, 1 H), 5.62 (br. s, 1 H), 6.27 (br. s, 1 H), 6.57 (d, J = 8.6 Hz, 2 H), 6.61 (t, J = 7.4 Hz, 1 H), 7.09 (t, J = 7.7 Hz, 2 H), 7.16–7.34 (m, 8 H), 7.55 (d, J = 7.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 44.0 (CH), 49.4 (CH), 54.3 (CH_2), 68.3 (CH), 78.9 (CH), 82.5 (C), 113.4 (CH), 116.5 (CH), 117.5 (C), 119.4 (CH), 126.9 (CH), 127.3 (CH), 128.0 (CH), 128.1 (CH), 128.3 (CH), 128.7 (CH), 128.8 (CH), 134.6 (C), 139.8 (CH), 143.3 (C), 143.5 (C), 146.8 (C) ppm. IR: $\tilde{\nu}$ = 3059 (m), 3028 (m), 2923 (m), 2851 (m), 1696 (s), 1598 (s), 1502 (s), 1469 (s), 1453 (s), 1362 (s), 1252 (m), 1178 (m), 1155 (m), 1075 (m), 1028 (m), 907 (m), 893 (m), 752 (s), 696 (s) cm^{-1}. HRMS: calcd. for $C_{28}H_{23}N$ 373.1830 $[M]^+$; found 373.1830.

4′-Ethynyl-3′,6′-diphenyl-2′,3′,3a′,6′-tetrahydrospiro[cyclohexane-1,1′-isoindole] (10d): Single diastereomer: ^1H NMR (600 MHz, $CDCl_3$): δ = 1.20–1.83 (m, 10 H), 2.38 (s, 1 H), 3.34 (tt, J = 10.8, 2.6 Hz, 1 H), 4.00 (d, J = 10.5 Hz, 1 H), 4.10 (br. d, J = 11.2 Hz, 1 H), 5.50 (dt, J = 2.5, 1.7 Hz, 1 H), 6.15 (td, J = 2.5, 1.7 Hz, 1 H), 7.19 (d, J = 7.9 Hz, 2 H), 7.25–7.36 (m, 6 H), 7.54 (d, J = 7.9 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3 (CH_2), 23.1 (CH_2), 25.6 (CH_2), 36.6 (CH_2), 40.5 (CH_2), 44.4 (CH), 47.2 (CH), 60.5 (C), 65.3 (CH), 78.3 (CH), 82.1 (C), 117.5 (CH), 118.2 (C), 126.7 (CH), 127.5 (CH), 127.9 (CH), 128.1 (CH), 128.6 (CH), 128.7 (CH), 139.5 (CH), 142.4 (C), 144.3 (C), 148.5 (C) ppm. HRMS: calcd. for $C_{27}H_{27}N$ 365.2143 $[M]^+$; found 365.2143.

(*Z*)-*N*-(3-Methyl-1-phenylhex-2-en-4-yn-1-yl)-2-(1*H*-pyrrol-1-yl)-aniline (11a): ^1H NMR (400 MHz, $CDCl_3$): δ = 1.91 (br. s, 3 H), 2.11 (br. s, 3 H), 4.28 (br. s, 1 H, NH), 5.57 (br. d, J = 9.0 Hz, 1 H), 5.64 (br. d, J = 9.0 Hz, 1 H), 6.47 (br. s, 2 H), 6.81–6.85 (m, 2 H), 6.98 (br. s, 2 H), 7.23–7.47 (m, 7 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 4.4 (CH_3), 23.3 (CH_3), 57.8 (CH), 78.5 (C), 91.4 (C), 109.4 (CH), 112.7 (CH), 116.7 (CH), 120.8 (C), 121.7 (CH), 126.0 (CH), 126.8 (CH), 127.2 (CH), 127.4 (C), 128.6 (CH), 128.7 (CH), 136.4 (CH), 142.2 (C), 142.7 (C) ppm; NOESY (600 MHz, $CDCl_3$) cross peak: 1.91/5.64, *Z* isomer. HRMS: calcd. for $C_{23}H_{22}N_2$ 326.1783 $[M]^+$; found 326.1783.

(*Z*)-*N*-(3-Methyl-1,5-diphenylpent-2-en-4-yn-1-yl)-2-(1*H*-pyrrol-1-yl)aniline (11b): ^1H NMR (400 MHz, $CDCl_3$): δ = 2.01 (br. s, 3 H), 4.31 (br. s, 1 H, NH), 5.61 (br. d, J = 8.8 Hz, 1 H), 5.76 (br. d, J = 9.0 Hz, 1 H), 6.42 (br. s, 2 H), 6.80 (t, J = 7.5 Hz, 1 H), 6.87 (d, J = 8.0 Hz, 1 H), 6.93 (br. s, 2 H), 7.20–7.50 (m, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.0 (CH_3), 58.2 (CH), 88.0 (C), 94.9 (C), 109.5 (CH), 112.7 (CH), 116.9 (CH), 120.5 (C), 121.9 (CH), 123.0 (C), 126.2 (CH), 127.0 (CH), 127.4 (CH), 127.5 (C), 128.3 (CH), 128.4 (CH), 128.7 (CH), 128.8 (CH), 131.5 (CH), 138.2 (CH), 142.0 (C), 142.8 (C) ppm; NOESY (600 MHz, $CDCl_3$) cross peak: 2.01/5.76, *Z* isomer. HRMS: calcd. for $C_{28}H_{24}N_2$ 388.1939 $[M]^+$; found 388.1939.

(*E*)-*N*-(1-Phenylhex-2-en-4-ynyl)aniline (11c): ^1H NMR (600 MHz, $CDCl_3$): δ = 1.84 (d, J = 2.0 Hz, 3 H), 3.90 (br. s, 1 H, NH), 4.86 (d, J = 5.9 Hz, 1 H), 5.61 (dq, J = 15.8, 1.9 Hz, 1 H), 6.13 (dd, J = 15.8, 5.9 Hz, 1 H), 6.49 (d, J = 8.0 Hz, 2 H), 6.62 (t, J = 7.3 Hz, 1 H), 7.05 (t, J = 7.5 Hz, 2 H), 7.22–7.26 (m, 5 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 4.2 (CH_3), 60.2 (CH), 77.6 (C), 87.3 (C), 111.8 (CH), 113.5 (CH), 117.8 (CH), 127.2 (CH), 127.7 (CH), 128.8 (CH), 129.1 (CH), 141.2 (C), 142.0 (CH), 146.9 (C) ppm. HRMS: calcd. for $C_{18}H_{17}N$ 247.1361 $[M]^+$; found 247.1361.

(*Z*)-*N*-(3-Methyl-1,5-diphenylpent-2-en-4-yn-1-yl)aniline (11d): ^1H NMR (400 MHz, $CDCl_3$): δ = 1.99 (br. s, 3 H), 4.11 (br. s, 1 H, NH), 5.54 (br. d, J = 8.9 Hz, 1 H), 5.88 (br. d, J = 8.9 Hz, 1 H), 6.71 (d, J = 8.3 Hz, 2 H), 6.73 (t, J = 7.5 Hz, 1 H), 7.17 (t, J = 8.0 Hz, 1 H), 7.29–7.44 (m, 8 H), 7.51 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.1 (CH_3), 58.7 (CH), 88.1 (C), 94.9 (C), 113.6 (CH), 117.7 (CH), 120.1 (C), 123.1 (C), 126.6 (CH), 127.4 (CH), 128.3 (CH), 128.4 (CH), 128.9 (CH), 129.2 (CH), 131.6 (CH), 138.9 (CH), 142.6 (C), 147.5 (C) ppm; NOESY (600 MHz, $CDCl_3$) cross peak: 1.99/5.88, *Z* isomer. HRMS: calcd. for $C_{24}H_{21}N$ 323.1674 $[M]^+$; found 323.1674.

(*E*)-*N*-(1-Phenylhex-1-en-4-yn-3-yl)aniline (12): ^1H NMR (400 MHz, $CDCl_3$): δ = 1.78 (d, J = 2.1 Hz, 3 H), 3.70 (br. s, 1 H, NH), 4.78 (br. s, 1 H), 6.22 (dd, J = 15.8, 5.4 Hz, 1 H), 6.66 (d, J = 8.0 Hz, 2 H), 6.69 (t, J = 7.3 Hz, 1 H), 6.78 (d, J = 15.8 Hz, 1 H), 7.11–7.33 (m, 7 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.6 (CH_3), 47.8 (CH), 77.5 (C), 80.8 (C), 114.1 (CH), 118.4 (CH), 126.6 (CH), 127.7 (CH), 127.8 (CH), 128.5 (CH), 129.1 (CH), 131.6 (CH), 136.4 (C), 146.4 (C) ppm. HRMS: calcd. for $C_{18}H_{17}N$ 247.1361 $[M]^+$; found 247.1362.

2-Ethyl-1,5-diphenyl-1*H*-pyrrole (13):[12b] ^1H NMR (400 MHz, $CDCl_3$): δ = 1.07 (t, J = 7.5 Hz, 3 H), 2.40 (q, J = 7.5 Hz, 2 H), 6.05 (d, J = 3.4 Hz, 1 H), 6.32 (d, J = 3.4 Hz, 1 H), 6.98–7.30 (m, 10 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0 (CH_3), 20.5 (CH_2), 105.6 (CH), 108.6 (CH), 123.5 (C), 125.6 (CH), 127.4 (CH), 127.9 (CH), 128.6 (CH), 128.9 (CH), 129.2 (CH), 134.5 (C), 138.1 (C), 139.3 (C) ppm. HRMS: calcd. for $C_{18}H_{17}N$ 247.1361 $[M]^+$; found 247.1362.

Complex 14c: A solution of $Et_3O{\cdot}BF_4$ in CH_2Cl_2 (0.2 mmol, 1 M) was added dropwise to a solution of catalyst **1** (0.2 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The mixture was stirred at room temp. for 1 h under argon. Evaporation of the solvent and flash chromatography on silica gel furnished complex **14c** as a pale-yellow foam. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.69 (t, J = 7.2 Hz, 3 H), 2.20 (s, 6 H), 2.62 (ddd, J = 16.6, 6.6, 3.8 Hz, 2 H), 3.29 (q, J = 7.2 Hz, 2 H), 3.60 (ddd, J = 16.6, 6.6, 3.4 Hz, 2 H), 7.40–7.42 (m, 6 H), 7.57–7.59 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.7 (CH_3), 41.6 (CH_3), 49.9 (CH_2), 72.0 (CH_2), 76.0 (C), 118.6 (C), 127.1 (CH), 129.1 (CH), 129.8 (C), 132.8 (CH), 139.7 (C), 192.6 (C, CO) ppm. IR: $\tilde{\nu}$ = 3060 (w), 2958 (m), 2928 (m), 2873 (m), 2857 (m), 2086 (s), 2017 (s), 1730 (w), 1673 (w), 1598 (s), 1501 (s), 1482 (s), 1444 (s), 1417 (s), 1365 (s), 1344 (s), 1316 (s), 1279 (s), 1205 (m), 1119 (m), 1050 (s), 1001 (s), 951 (s), 913 (s), 858 (s), 823 (m), 797 (w), 779 (m), 752 (s), 724 (s), 701 (s) cm^{-1}. MS (EI): *m/z* (%) = 506 (12), 505 (33), 504 (18), 503 (65) $[M]^+$, 502 (39), 501 (26), 500 (20), 497 (10), 481 (50), 445 (29), 417 (100), 389 (50). HRMS: calcd. for $C_{25}H_{25}N_2O_3Ru$ 503.0909 $[M]^+$; found 503.0902.

Supporting Information (see footnote on the first page of this article): Full characterization data, NMR assignments and ^1H and ^{13}C NMR spectra of all key intermediates and final products.

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