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Regioselective Transition-Metal-Free Synthesis of 2-(Trimethylsilylmethylene)pyrrol-3-ones by Thermal Cyclization of Acetylenic Enamines

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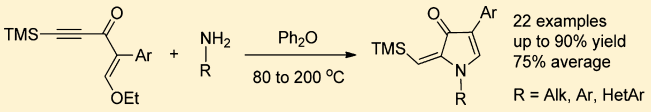
Supporting Information

ABSTRACT: Acetylenic enamines generated *in situ* from readily available enynones and primary amines undergo thermal cyclization in diphenyl ether providing easy access to 4-aryl-2-(trimethylsilylmethylene)-1,2-dihydro-3*H*-pyrrol-3-ones. This reaction is inherently versatile, allowing for variations of substituents in both enynone and amine. Full regioselectivity along with short reaction time (1−2 h) and simple workup afford single products in good to excellent isolated yields. Fluorescent properties of the obtained compounds were studied.



INTRODUCTION

The 3-pyrrolone core represents a valuable subclass of azaheterocycles which can be found in some pharmaceuticals and biologically active compounds. For example, *β*-pyrrolone derivatives were reported to possess antimalarial activity[1] as well as HIV-1 protease inhibitory[2] activity. In addition, 3,5-linked polypyrroline-4-ones were studied as nonpeptide peptidomimetics with promising pharmacological properties.[3]

Several synthetic strategies toward a pyrrolone core have been developed, mostly via cyclization of corresponding open-chain precursors. Among these, substituted 1-aminobut-3-yn-2-ones are the most commonly used starting material. It was shown that such compounds undergo gold-[4] or platinum-catalyzed[5] cyclization or can be transformed into pyrrolones by treatment with I_2 in PEG under microwave irradiation.[6] On the other hand, several enaminones were reported to undergo cyclization upon treatment with phenyliodine(III) bis(trifluoroacetate) and TFA to form polysubstituted pyrrolones.[7] Similar substrates can be converted into diacetylpyrrolones by $Cu(TFA)_2$-catalyzed oxidative cyclization.[8] Other known methods include gold-catalyzed oxidative rearrangement of homopropargyl azides,[9] flash-vacuum pyrolysis of Meldrum's acid aminomethylene derivatives,[10] cyclization of amino-acetylmalononitriles under acidic conditions,[11] and a three-component reaction of primary amines with 1,3-diketones in aqueous H_2O_2.[12] *N*-Aminopyrrolones can be obtained by a $PtCl_2$-catalyzed cyclization of tosylhydrazones of unsaturated hydroxyketones,[13] and a NIS-promoted coupling/cyclization of symmetrical diynones with primary amines was explored for the synthesis of iodinated products.[14] Nevertheless, development of rapid and efficient methodologies for direct construction of a pyrrolone core compatible with various functional groups is still of interest.

We have designed a straightforward method for the synthesis of 2-(trimethylsilylmethylene)pyrrol-3-ones bearing various substituents at 1- and 4-positions of the pyrrole core. The key starting compounds are cross-conjugated TMS-protected enynones **1**, readily available from bis(trimethylsilyl)acetylene and arylacetyl chlorides.[15] Previously we thoroughly investigated the reactions of compounds **1** with binucleophiles,[15] and herein we report the results obtained by employment of amines in reactions with enynones **1**.

RESULTS AND DISCUSSION

We first used enynone **1a** bearing a *p*-nitrophenyl group and *p*-anisidine (**2a**) to optimize reaction conditions, and an excellent result was obtained immediately: corresponding enamine **3aa** was isolated in nearly quantitative yield after an equimolar mixture of initial compounds was stirred in ethanol for 1 h at room temperature (Table 1). Nevertheless, we performed a few more experiments in other solvents, which revealed that ethanol was in fact the least effective one, and the reaction time could be reduced to 30 min by using THF. In general, the reaction could be successfully performed in any conventional solvent (benzene, CH_2Cl_2, THF, CH_3CN, etc.). Even in the presence of excess amine the only isolated product was the corresponding enamine **3aa**, and no products of addition to the carbonyl group or triple bond were observed. Enamine **3aa** exists in solution as a mixture of (*E*)- and (*Z*)-isomers, and distinction between two forms can be easily made on the basis of the difference in NH proton signal positions: 12.5 ppm due to intramolecular hydrogen bonding in (*Z*)-form and ∼8.5 ppm in (*E*)-form (^{1}H NMR spectrum in $CDCl_3$). The structure of the (*Z*)-isomer was also obtained from the X-ray analysis.[16] We have found that ratio of (*E*)- to (*Z*)-isomers depends on the solvent polarity but not on the temperature. Thus, in nonpolar $CDCl_3$ the (*Z*)-isomer is preferable due to its stabilization by an intramolecular hydrogen bond, and the (*E*)/(*Z*) ratio is ∼1:10

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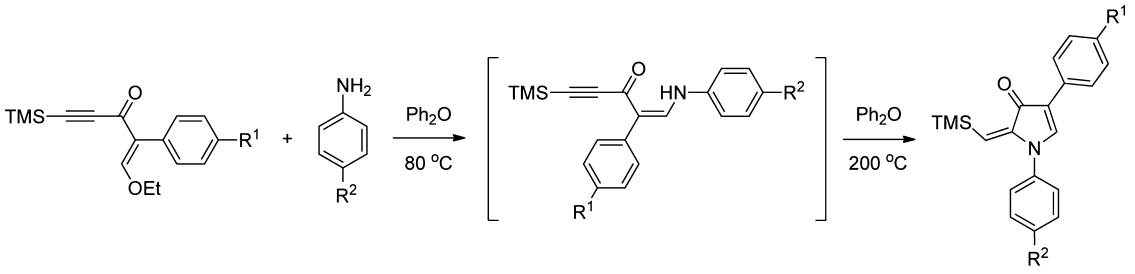
Table 1. Reaction of Ketones 1a–c with Anilines 2a–c[a]



1a-c **2a-c** **3aa-cb**, not isolated **4aa-cb**

entry	ketone	R^1	aniline	R^2	pyrrolone	isolated yield, %
1	**1a**	NO_2	**2a**	OCH_3	**4aa**[b]	90 (70)[c]
2	**1a**	NO_2	**2b**	H	**4ab**	88
3	**1a**	NO_2	**2c**	NO_2	**4ac**	trace
4	**1b**	H	**2a**	OCH_3	**4ba**	66
5	**1b**	H	**2b**	H	**4bb**	65
6	**1c**	OCH_3	**2a**	OCH_3	**4ca**	74
7	**1c**	OCH_3	**2b**	H	**4cb**	70

[a]Reactions were performed on a 0.35 mmol scale. [b]Enamine **3aa** was isolated in 95% yield. [c]Reaction was performed on a 5 mmol scale.

at 20–60 °C. On the other hand, when the ^{1}H NMR spectrum was registered in DMSO-d_6, the (*E*)-isomer was determined as the major one (ratio (*E*)/(*Z*) ~3:1), since intramolecular hydrogen bonding was suppressed by interaction with polar solvent. No imine form of compound **3aa** was detected in the NMR spectra, since it would possess an upfield signal from the Ar–CH proton.

The combination of an activated triple bond and a disubstituted amine nitrogen atom in the structure of enamine **3aa** creates an opportunity for a ring closure, and therefore we have examined its thermal transformations and started with heating at 110 °C in toluene. No reaction was observed under these conditions, and further experiments in xylene, DMF, and DMSO were performed at 140, 150, and 180 °C, respectively. Very slow formation of a new product occurred in the first two cases, while heating in DMSO led to decomposition of starting material. From these experiments it was clear that the desired transformation could be executed effectively only at temperature higher than 180 °C in inert medium. For this reason we decided to try diphenyl ether as reaction solvent. Upon being heated in Ph_2O for 0.5 h at 200 °C, enamine **3aa** smoothly underwent cyclization, and a single product was obtained in 95% yield (estimated by ^{1}H NMR spectrum of a crude reaction mixture after removal of Ph_2O). Finally, we attempted to perform both reactions without isolation of enamine **3aa**, but poor yield of cyclization product was obtained when an equimolar mixture of enynone **1a** and anisidine **2a** in Ph_2O was heated at 200 °C. Nevertheless, we managed to obtain the final product in 90% yield, when the reaction mixture was stirred at 80 °C for 0.5 h (at this point the full conversion of starting compounds was observed) and then at 200 °C for an additional 0.5 h. This stepwise approach was taken as the optimal one for further experiments.

Having found the optimal conditions, we carried out a series of experiments with various combinations of substituents in aromatic cores of both starting compounds to study the influence of electronic factors on the reaction course (Table 1). In line with our previous studies,[15] enynone **1a** was slightly more active than two other ketones and provided better yields of products. When *p*-anisidine (**2a**) or parent aniline (**2b**) was used, the reaction proceeded smoothly, and targeted products were formed in good to excellent yields. Not surprisingly, *p*-nitroaniline (**2c**) did not react even with ketone **1a**, and neither full conversion to enamine nor formation of cyclized product was achieved even after several hours of heating at 200 °C. For this reason reactions of enynones **1b,c** with nitroaniline **2c** were not performed.

For compound **4ab** we managed to obtain X-ray analysis data to unambiguously determine its structure as substituted 2-(trimethylsilylmethylene)pyrrol-3-one.[17] The same structure was ascribed to other obtained products due to the similarity of their NMR spectra, since a very consistent set of signals referring to the core of the molecule was observed in all cases. Thus, ^{1}H NMR spectra contain two characteristic singlets at ~5.8 and ~8.1 ppm assigned to the =CH—Si fragment and H^5 proton of the pyrrole core, respectively, and carbon atoms of 2-methylenepyrrol-3-one also feature signals at constant positions [$\delta \approx$ 112 (C^4), 121 (=CH—Si), 146 (C^2), 152 (C^5), and 184 (C^3) ppm] in ^{13}C NMR spectra.

The substrate scope of the presented two-step transformation was successfully extended to other anilines, including those with electron-withdrawing substituents, as well as to alkylamines and some aminoheterocycles (Scheme 1).

In the first reaction series we used ketone **1a** to test various anilines. *p*-Fluoroaniline (**2d**) provided high yield of pyrrolinone **4ad**, and even anilines with stronger electron-withdrawing groups [e.g., methyl 4-aminobenzoate (**2e**) and *p*-trifluoromethylaniline (**2f**)] furnished the corresponding pyrrolinones **4ae** and **4af** in 68% yield. In addition, *ortho*-substituted anilines **2g–i** were tested, and despite longer reaction times as compared to those of 4-substituted analogues (**2c** vs **2i**; **2f** vs **2g**), targeted products were obtained in all cases. Mesitylamine **2j** reacted smoothly as well, and even sterically crowded 2,6-diisopropylaniline (**2k**) provided a surprisingly high 80% yield of corresponding product **4ak** demonstrating reaction tolerance to steric hindrances in the aniline core. Next, several aminoheterocycles were explored to obtain *N*-heteroarylpyrrolinones. In this series we failed to obtain desired products when 2-, 3-, and 4-aminopyridines were used; in addition, 2-amino-1,3,4-oxa- and thiadiazoles were

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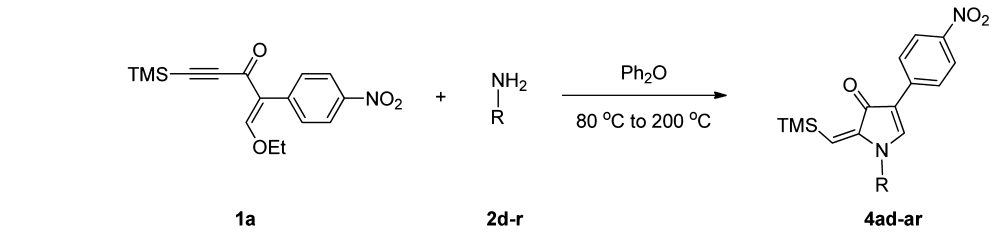
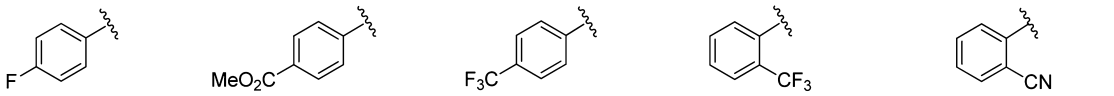
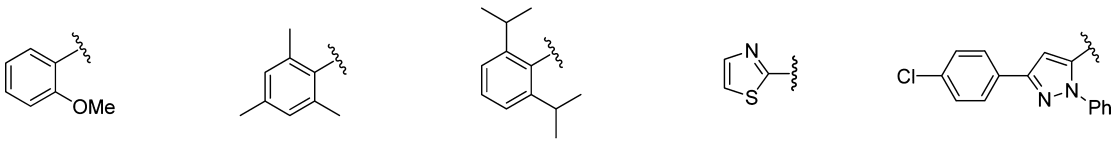
Scheme 1. Study of Amine Scope for the Synthesis of Pyrrolinones[a]



1a **2d-r** **4ad-ar**



90% (**ad**) 68% (**ae**) 68% (**af**) 62% (**ag**) 65% (**ah**)

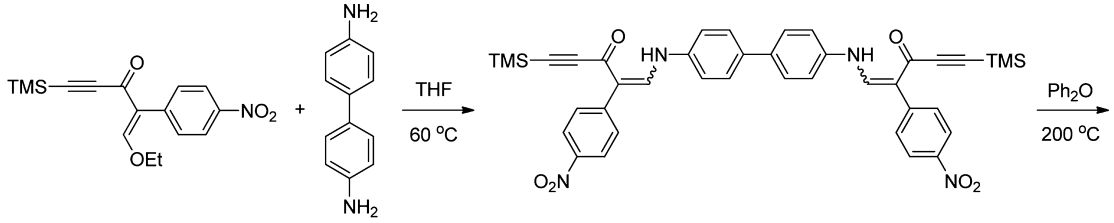


84% (**ai**) 84% (**aj**) 80% (**ak**) 45% (**al**) 75% (**am**)

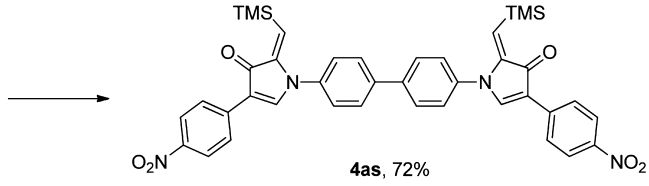
90% (**an**) 77% (**ao**) 73% (**ap**) 90% (**aq**) 80% (**ar**)

[a]Reactions were performed on 0.35 mmol scale. Isolated yields of pyrrolinones **4ad**−**ar** are given.

Scheme 2. Reaction of Ketone 1a with Benzidine 2s



1a **2s** **3as**, 92%



4as, 72%

found to be inert under reaction conditions, too. However, reactions with 2-aminothiazole **2l** and 5-aminopyrazole **2m** were successful, indicating that aminoheterocycles with π-donating core seem to be the only ones suitable for this transformation. Finally, reactions with alkylamines were studied. *n*-Propylamine (**2n**) allowed lower temperature for the second step, and the corresponding enamine already underwent cyclization at 175 °C. Good yields were obtained in reactions with cyclopentyl- and *tert*-butylamines (**2o**,**p**), as well as with benzylamine (**2q**) and its heteroaromatic analogue, 2-furylmethylamine (**2r**), which provided 90% and 80% yields of products, respectively.

The reaction between ketone **1a** and benzidine **2s** was attempted to demonstrate the applicability of diamines for the synthesis of linked bis-pyrrolones (Scheme 2). We were unable to obtain enamine **3as** in Ph_2O (most likely due to poor solubility of benzidine), but it was isolated in excellent yield after the reaction mixture was heated in THF. Compound **3as**, in theory, can exist in 3 forms, (*E*,*E*), (*Z*,*Z*), and (*E*,*Z*), and it is interesting to notice that only symmetrical (*E*,*E*)- and (*Z*,*Z*)-forms were seen in the ^{1}H NMR spectrum. As expected, enamine **3as** smoothly underwent cyclization upon heating in standard conditions leading to the bis-pyrrolone derivative **4as** in 72% yield.

It is worth mentioning the full regioselectivity in all reactions, where no isomeric 4-pyridones **5** were detected (Scheme 3). Well-known aza-Michael-type addition of nitrogen nucleophiles to activated multiple bonds usually occurs on the β-carbon

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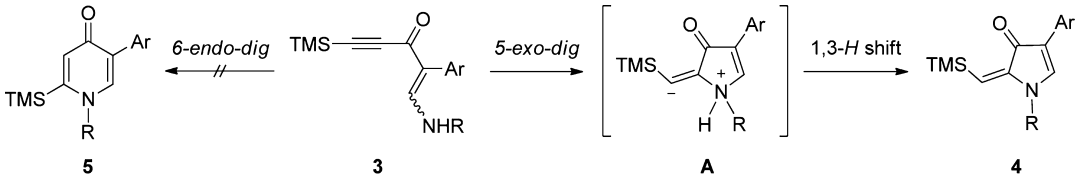
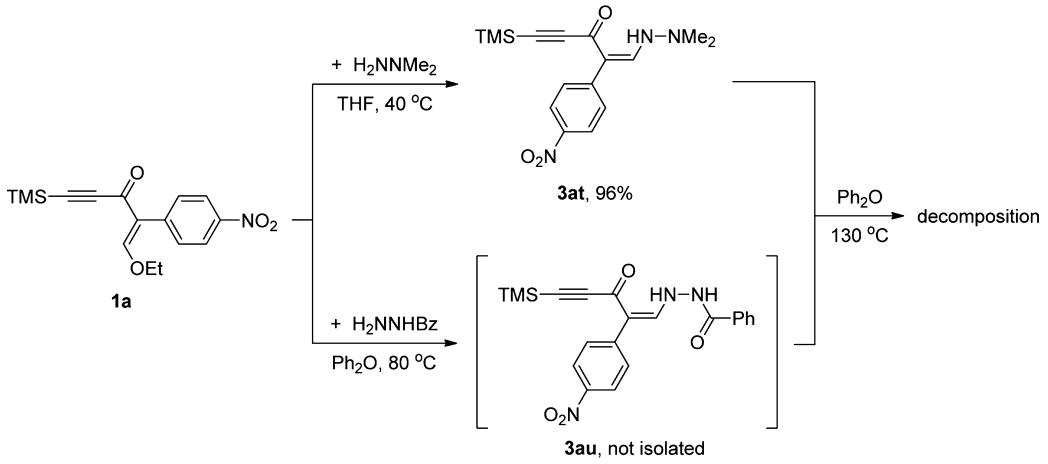
Scheme 3. Plausible Mechanism for the Thermal Cyclization of Enamines 3



Scheme 4. Reactions of Ketone 1a with Hydrazines



atom to an electron-withdrawing group, and according to literature data,[18] intramolecular addition to a triple bond attached to a carbonyl group mainly proceeds in the same manner. Intramolecular addition to silylated acetylenes has not been previously investigated, but inverse regioselectivity in the case of enamines **3** is obviously powered by the TMS group at the terminal position of a triple bond. It is well-known that the Me_3Si group creates no real steric hindrance, but on the other hand, a silicon atom in α-position effectively stabilizes the anion center of intermediate **A**.[19] For this reason, instead of *6-endo-dig*-type cyclization leading to 4-pyridones **5**, reaction occurs exclusively as a 5-*exo-dig*-process providing 2-methylenepyrrol-3-ones **4** as single products.

Finally, we expected to obtain *N*-amino-substituted pyrrolones using the reaction of ketone **1a** with *N,N*-dimethylhydrazine and benzhydrazide (Scheme 4). Initially, both reactions were executed in a standard one-pot fashion, and formation of new compounds, which were presumably identified as enhydrazines **3at** and **3au** by analogy with previous results, was observed by TLC when the reaction mixtures were heated at 40 or 80 °C, respectively. However, further increase of temperature led to full destruction of these compounds even under inert atmosphere, most likely due to the breach of a weak N−N bond under conditions of thermolysis. After this, the adduct with dimethylhydrazine **3at** was prepared individually, and its structure was confirmed by HRMS and NMR spectroscopic data.

Pyrrolones **4** appear as brightly colored solids (bright orange to deep red) and demonstrate distinctive fluorescence under a conventional UV lamp; therefore, their UV−vis spectra were studied. In Figure 1 the absorption and emission spectra of compound **4ab** are shown as a representative example. In all cases two or three bands were observed in the absorption spectra of pyrrolones: the one at 432−479 nm is characteristic; the emission wavelengths are ∼550 nm. We have found that the presence of a *p*-nitrophenyl ring at the C^4 position of the pyrrolone core is crucial for the molecule to exhibit fluorescence under UV irradiation, since very weak emission was observed for compounds **4bb** and **4cb**, while none was registered for compounds **4ba** and **4ca**. On the other hand, the substituent at the nitrogen atom also has a profound effect, and fluorescence increases in the following sequence: alkyl < C_6H_4-EDG < C_6H_4-EWG < heteroaryl. Thus, the best one was the 2-thiazolyl-substituted pyrrolone **4al**. For this compound we have estimated the quantum yield of fluorescence following a reported procedure,[20] and a calculated Φ value of 6 ± 1% was obtained. To the best of our knowledge it is the first mention of fluorescence properties for a 2-methylenepyrrolin-3-one scaffold, and we believe that these data may serve as a good start for development of novel fluorescent materials.

■ CONCLUSIONS

We have developed a rapid, general, and efficient method for the synthesis of previously unknown 2-(trimethylsilylmethylene)-1,2-dihydro-3*H*-pyrrol-3-one derivatives from easily accessible starting material. The described procedure is atom-efficient, since only 1 molecule of TMSCl and 3 molecules of EtOH are liberated during the whole sequence starting from bis(trimethylsilyl)acetylene. The key thermal cyclization of acetylenic enamines occurs in a regioselective manner via a 5-*exo-dig*-process providing single products in high yields. Moreover, most of the obtained compounds display fluorescence under UV irradiation.

■ EXPERIMENTAL SECTION

General Methods. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, DMSO-d_6, or acetone-d_6 and were referenced to the solvent residual proton (δ_H = 7.26, 2.50, and 2.05 ppm, respectively) and carbon signals (δ_C = 77.0, 39.5, and 29.8 ppm, respectively). DEPT spectra were used for the assignment of carbon signals. ^{19}F NMR spectra were recorded in $CDCl_3$ and referenced to an internal standard (fluorobenzene, δ_F = −113.2 ppm). UV−vis spectra were recorded for

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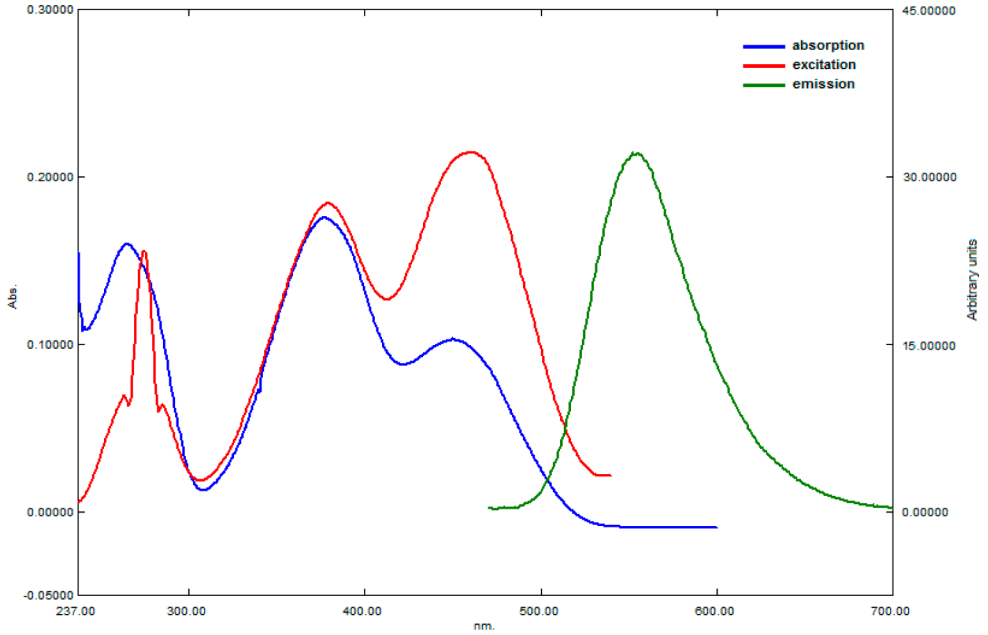
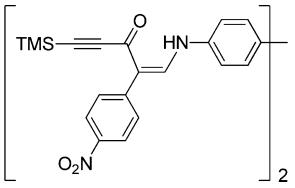


Figure 1. Overlay of UV−vis spectra for 10^{-5} M solution of pyrrolone **4ab** in $CHCl_3$: blue, absorption spectrum; red, excitation spectrum; green, emission spectrum. Left *y*-axis refers to the absorption spectrum, and the right one refers to emission and excitation spectra.

10^{-5} M solutions in $CHCl_3$; extinction coefficients are given in parentheses. Preparation of enynones **1a−c** was described earlier.[15a]

General Procedure for the Preparation of Enamines 3. A mixture of enynone **1a** (100 mg, 0.32 mmol) and corresponding amine (0.32 mmol, 1 equiv for **3aa**, **3at** or 0.16 mmol, 1 equiv for **3as**) in THF (2 mL) was heated at 60 °C (enamines **3aa**, **3as**) or 40 °C (**3at**) until TLC indicated the full conversion of starting material (0.5−2 h). Upon completion, solvent was removed by evaporation, and the residue was subjected to flash chromatography on silica (*n*-hexane/ethyl acetate 1:0 to 8:1) to afford enamine **3**. For TLC analysis, 1 drop of solution was taken from the reaction mixture, diluted by CH_2Cl_2 (0.1 mL), and used without additional workup.

*1-[(4-Methoxyphenyl)amino]-2-(4-nitrophenyl)-5-(trimethylsilyl)-pent-1-en-4-yn-3-one (**3aa**).* Bright orange crystals; yield 120 mg (95%); mp 63−65 °C. Mixture of (*E*)- and (*Z*)-isomers in ratio 3:1 (DMSO-d_6) or 1:10 ($CDCl_3$), respectively. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.09 (s, 2.25 H$^{(Z)}$), 0.26 (s, 6.75 H$^{(E)}$), 3.74 (s, 2.25 H$^{(E)}$), 3.75 (s, 0.75 H$^{(Z)}$), 6.94−6.97 (m, 2 H$^{(Z),(E)}$), 7.19 (d, *J* = 9.0 Hz, 1.5 H$^{(E)}$), 7.43 (d, *J* = 9.0 Hz, 0.5 H$^{(Z)}$), 7.53 (d, *J* = 8.7 Hz, 1.5 H$^{(E)}$), 7.78 (d, *J* = 8.8 Hz, 0.5 H$^{(Z)}$), 8.04 (d, *J* = 12.9 Hz, 0.25 H$^{(Z)}$), 8.19 (d, *J* = 8.8 Hz, 0.5 H$^{(Z)}$), 8.25 (d, *J* = 8.7 Hz, 1.5 H$^{(E)}$), 8.39 (br. d, *J* = 9.3 Hz, 0.75 H$^{(E)}$), 9.70 (br. d, *J* = 9.3 Hz, 0.75 H$^{(E)}$), 12.45 (d, *J* = 12.9 Hz, 0.25 H$^{(Z)}$) ppm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.11 (s, 8.2 H$^{(Z)}$), 0.29 (s, 0.8 H$^{(E)}$), 3.81 (s, 3 H$^{(Z),(E)}$), 6.90−6.93 (m, 2 H$^{(Z),(E)}$), 6.99 (d, *J* = 9.0 Hz, 0.18 H$^{(E)}$), 7.07−7.10 (m, 1.82 H$^{(Z)}$), 7.50 (d, *J* = 8.8 Hz, 0.18 H$^{(E)}$), 7.54 (d, *J* = 12.7 Hz, 0.91 H$^{(Z)}$), 7.59−7.62 (m, 1.82 H$^{(Z)}$), 7.96 (br. s, 0.09 H$^{(E)}$), 8.17−8.21 (m, 1.82 H$^{(Z)}$), 8.27 (d, *J* = 8.8 Hz, 0.18 H$^{(E)}$), 8.47 (d, *J* = 14.3 Hz, 0.09 H$^{(E)}$), 12.52 (br. d, *J* = 12.7 Hz, 0.91 H$^{(Z)}$) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = −1.1 (CH$^{(Z)}$), −0.7 (CH$^{(E)}$), 55.37 (CH$^{(E)}$), 55.41 (CH$^{(Z)}$), 95.4 (C), 98.1 (C), 101.5 (C), 103.3 (C), 111.9 (C), 114.8 (CH$^{(E)}$), 114.9 (CH$^{(Z)}$), 115.3 (C), 118.8 (CH$^{(E)}$), 119.4 (CH$^{(Z)}$), 122.8 (CH$^{(Z)}$), 123.4 (CH$^{(E)}$), 130.6 (CH$^{(Z)}$), 132.0 (CH$^{(E)}$), 132.4 (C$^{(Z)}$), 134.3 (C$^{(E)}$), 140.7 (C$^{(E)}$), 145.2 (C$^{(Z)}$), 145.4 (C$^{(Z)}$), 146.2 (C$^{(E)}$), 149.0 (br, CH$^{(E)}$), 149.2 (br, CH$^{(Z)}$), 156.2 (C$^{(E)}$), 157.0 (C$^{(Z)}$), 172.2 (C$^{(E)}$), 172.4 (C$^{(Z)}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.9 (CH$^{(Z)}$), −0.6 (CH$^{(E)}$), 55.57 (CH$^{(Z)}$), 55.60 (CH$^{(E)}$), 100.0 (C$^{(Z)}$), 102.7 (C$^{(Z)}$), 104.2 (C$^{(E)}$), 106.7 (C$^{(E)}$), 112.7 (C$^{(Z)}$), 115.1 (CH$^{(Z)}$), 118.1 (CH$^{(E)}$), 118.9 (CH$^{(Z)}$), 123.1 (CH$^{(Z)}$), 124.1 (CH$^{(E)}$), 130.2 (CH$^{(Z)}$), 131.3 (CH$^{(E)}$), 132.5 (CH$^{(Z)}$), 145.2 (C$^{(Z)}$), 146.2 (C$^{(Z)}$), 147.7 (CH$^{(Z)}$), 157.5 (C$^{(Z)}$), 173.9 (C$^{(Z)}$) ppm. Not all carbon signals of the minor (*E*)-form are clearly seen. HRMS (ESI-TOF) *m*/*z*: [M − H]$^-$ calcd for $C_{21}H_{22}N_2O_4Si$ 393.1276; found 393.1268.



*1,1′-[1,1′-Biphenyl]-4,4′-diyldi(imino)]bis[2-(4-nitrophenyl)-5-(trimethylsilyl)pent-1-en-4-yn-3-one] (**3as**).* Orange solid; yield 93 mg (80%); mp 227−228 °C (dec). Mixture of (*E*,*E*)- and (*Z*,*Z*)-isomers in ratio 4:1 (DMSO-d_6). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.09 (s, 3.6 H$^{(Z)}$), 0.29 (s, 14.4 H$^{(E)}$), 7.32 (d, *J* = 8.7 Hz, 3.2 H$^{(E)}$), 7.55 (d, *J* = 8.7 Hz, 4 H$^{(E),(Z)}$), 7.70−7.74 (m, 4 H$^{(E),(Z)}$), 7.80 (d, *J* = 8.7 Hz, 0.8 H$^{(Z)}$), 8.16 (d, *J* = 12.7 Hz, 0.4 H$^{(Z)}$), 8.21 (d, *J* = 8.7 Hz, 0.8 H$^{(Z)}$), 8.28 (d, *J* = 8.7 Hz, 3.2 H$^{(E)}$), 8.53 (d, *J* = 13.6 Hz, 1.6 H$^{(E)}$), 9.80 (d, *J* = 13.6 Hz, 1.6 H$^{(E)}$), 12.38 (d, *J* = 12.7 Hz, 0.4 H$^{(Z)}$) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = −1.4 (CH$^{(Z)}$), −1.0 (CH$^{(E)}$), 95.7 (C$^{(E)}$), 101.3 (C$^{(E)}$), 116.2 (C$^{(E)}$), 117.3 (CH$^{(E)}$), 118.0 (CH$^{(Z)}$), 122.4 (CH$^{(Z)}$), 123.1 (CH$^{(E)}$), 127.0 (CH$^{(E)}$), 127.1 (CH$^{(Z)}$), 130.6 (CH$^{(Z)}$), 131.7 (CH$^{(E)}$), 134.5 (C$^{(E)}$), 139.8 (C$^{(E)}$), 140.2 (C$^{(E)}$), 146.3 (C$^{(E)}$), 147.1 (CH$^{(E)}$), 147.4 (CH$^{(Z)}$), 172.5 (C$^{(E)}$) ppm. Not all carbon signals of the minor (*Z*, *Z*)-form are clearly seen. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{40}H_{38}N_4O_6Si_2$ 727.2403; found 727.2412.

*1-(2,2-Dimethylhydrazino)-2-(4-nitrophenyl)-5-(trimethylsilyl)-pent-1-en-4-yn-3-one (**3at**).* Pale yellow solid; yield 100 mg (96%); mp 114−116 °C (dec). Mixture of (*Z*)- and (*E*)-isomers in ratio ~1:0.07 ($CDCl_3$). Not all signals of minor (*E*)-isomer are visible in the NMR spectra. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.1 (s, 9 H$^{(Z)}$), 0.27 (s, 0.63 H$^{(E)}$), 2.60 (s, 0.42 H$^{(E)}$), 2.73 (s, 6 H$^{(Z)}$), 7.32 (d, *J* = 8.0 Hz, 1 H$^{(Z)}$), 7.39 (d, *J* = 8.7 Hz, 0.14 H$^{(E)}$), 7.55 (d, *J* = 8.8 Hz, 2 H$^{(Z)}$), 8.15 (d, *J* = 8.8 Hz, 2 H$^{(Z)}$), 8.21 (d, *J* = 8.7 Hz, 0.14 H$^{(E)}$), 11.48 (d, *J* = 8.0 Hz, 1 H$^{(Z)}$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.9 (CH$^{(Z)}$), −0.6 (CH$^{(E)}$), 47.4 (CH$^{(Z)}$), 99.8 (C$^{(Z)}$), 101.9 (C$^{(Z)}$), 110.8 (C$^{(Z)}$), 123.1 (CH$^{(Z)}$), 129.8 (CH$^{(Z)}$), 131.0 (CH$^{(E)}$), 145.2 (C$^{(Z)}$), 146.0 (C$^{(Z)}$), 149.8 (CH$^{(Z)}$), 165.1 (C$^{(Z)}$) ppm. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{16}H_{21}N_3O_3Si$ 332.1425; found 332.1424.

General Procedure for the Preparation of Pyrrolones 4. A 3 mL screw-cap vial was charged with a solution of enynone **1a−c** (0.35 mmol) in diphenyl ether (1 mL). Then, the corresponding amine

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(0.35 mmol, 1 equiv) was added in one portion to the stirred solution, and the vial was sealed and heated at 80 °C (40 °C for **4an**) until TLC indicated the full conversion of starting material (15−60 min). The reaction mixture was then heated at 200 °C (175 °C for **4an**) in an oil bath for an additional 30−60 min. After cooling to room temperature the reaction mixture was subjected to flash chromatography on silica (*n*-hexane/ethyl acetate 1:0 to 10:1) to afford pyrrolones **4**.

*(2E)-1-(4-Methoxyphenyl)-4-(4-nitrophenyl)-2-[(trimethylsilyl)-methylene]-1,2-dihydro-3H-pyrrol-3-one (**4aa**).* Orange crystals; yield 124 mg (90%); mp 57−59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.27 (s, 9 H), 3.87 (s, 3 H), 5.81 (s, 1 H), 7.02 (d, J = 8.9 Hz, 2 H), 7.21 (d, J = 8.9 Hz, 2 H), 7.95 (d, J = 9.0 Hz, 2 H), 8.18 (d, J = 9.0 Hz, 2 H), 8.21 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −1.1 (CH), 55.6 (CH), 111.0 (C), 115.1 (CH), 123.2 (CH), 124.1 (CH), 124.2 (CH), 127.2 (CH), 130.3 (C), 138.8 (C), 145.1 (C), 146.8 (C), 153.9 (CH), 159.3 (C), 184.0 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{22}N_2O_4Si$ 395.1422; found 395.1422. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 262 (1.74), 382 (1.64), 456 (0.98) nm. Emission λ_{max} 567 nm.

*(2E)-4-(4-Nitrophenyl)-1-phenyl-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4ab**).* Orange crystals; yield 108 mg (85%); mp 167−169 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.27 (s, 9 H), 5.96 (s, 1 H), 7.30−7.32 (m, 2 H), 7.41−7.45 (m, 1 H), 7.52−7.56 (m, 2 H), 7.96 (d, J = 9.0 Hz, 2 H), 8.18 (d, J = 9.0 Hz, 2 H), 8.29 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −1.1 (CH), 111.6 (C), 123.2 (CH), 124.1 (CH), 124.3 (CH), 125.4 (CH), 128.0 (CH), 130.0 (CH), 137.7 (C), 138.6 (C), 145.2 (C), 145.9 (C), 153.5 (CH), 184.1 (C) ppm. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{20}H_{20}N_2O_3Si$ 387.1135; found 387.1125. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 265 (1.58), 377 (1.73), 451 (1.1) nm. Emission λ_{max} 554 nm.

*(2E)-1-(4-Fluorophenyl)-4-(4-nitrophenyl)-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4ad**).* Orange crystals; yield 121 mg (90%); mp 187−188 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.28 (s, 9 H), 5.83 (s, 1 H), 7.21−7.25 (m, 2 H), 7.27−7.31 (m, 2 H), 7.93−7.97 (m, 2 H), 8.17−8.20 (m, 2 H), 8.23 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −1.1 (CH), 111.7 (C), 117.1 (d, J_{C-F} = 23.1 Hz, CH), 123.2 (CH), 124.1 (CH), 124.4 (CH), 127.6 (d, J_{C-F} = 8.6 Hz, CH), 133.7 (d, J_{C-F} = 3.3 Hz, C), 138.4 (C), 145.3 (C), 146.2 (C), 153.4 (CH), 161.9 (d, J_{C-F} = 249.2 Hz, C), 184.0 (C) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −112.2 ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{20}H_{19}FN_2O_3Si$ 383.1222; found 383.1225. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 263 (1.43), 374 (1.59), 450 (0.91) nm. Emission λ_{max} 553 nm.

*Methyl 4-{(2E)-4-(4-Nitrophenyl)-3-oxo-2-[(trimethylsilyl)methylene]-2,3-dihydro-1H-pyrrol-1-yl}benzoate (**4ae**).* Orange crystals; yield 100 mg (68%); mp 202−203 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.25 (s, 9 H), 3.89 (s, 3 H), 6.10 (s, 1 H), 7.65 (d, J = 8.6 Hz, 2 H), 8.12 (d, J = 8.6 Hz, 2 H), 8.17−8.23 (m, 4 H), 9.35 (s, 1 H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = −0.9 (CH), 52.3 (CH), 111.0 (C), 122.0 (CH), 123.9 (CH), 124.6 (CH), 124.7 (CH), 127.9 (C), 130.8 (CH), 138.8 (C), 141.1 (C), 144.5 (C), 144.6 (C), 156.6 (CH), 165.5 (C), 183.9 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{22}H_{22}N_2O_5Si$ 423.1371; found 423.1381. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 316 (0.90), 370 (1.83), 445 (0.99) nm. Emission λ_{max} 547 nm.

*(2E)-4-(4-Nitrophenyl)-1-(4-(trifluoromethyl)phenyl)-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4af**).* Dark orange crystals; yield 103 mg (68%); mp 192−193 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 0.29 (s, 9 H), 6.19 (s, 1 H), 7.79 (d, J = 8.4 Hz, 2 H), 7.93 (d, J = 8.4 Hz, 2 H), 8.23 (s, 4 H), 9.14 (s, 1 H) ppm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.30 (s, 9 H), 6.03 (s, 1 H), 7.45 (d, J = 8.4 Hz, 2 H), 7.81 (d, J = 8.4 Hz, 2 H), 7.96 (d, J = 8.9 Hz, 2 H), 8.18 (d, J = 8.9 Hz, 2 H), 8.32 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −1.1 (CH), 112.9 (C), 123.3 (CH), 123.6 (q, J_{C-F} = 272.1 Hz, CF_3), 124.1 (CH), 124.7 (CH), 125.2 (CH), 127.3 (q, J_{C-F} = 3.7 Hz, CH), 129.7 (q, J_{C-F} = 33.1 Hz, C), 138.0 (C), 140.8 (C), 145.0 (C), 145.6 (C), 152.5 (CH), 184.1 (C) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −62.6 ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{19}F_3N_2O_3Si$ 433.1190; found 433.1200. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 368 (1.49), 443 (0.84) nm. Emission λ_{max} 547 nm.

*(2E)-4-(4-Nitrophenyl)-1-[2-(trifluoromethyl)phenyl]-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4ag**).* Orange crystals; yield 94 mg (62%); mp 132−133 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 0.25 (s, 9 H), 5.45 (s, 1 H), 7.74 (d, J = 7.9 Hz, 1 H), 7.82−7.86 (m, 1 H), 7.93−7.97 (m, 1 H), 8.01 (d, J = 7.9 Hz, 1 H), 8.20−8.26 (m, 4 H), 8.91 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = −1.0 (CH), 111.9 (C), 122.7 (CH), 124.2 (q, J_{C-F} = 272.9 Hz, CF_3), 124.7 (CH), 125.3 (CH), 128.6 (q, J_{C-F} = 5.1 Hz, CH), 129.6 (q, J_{C-F} = 30.7 Hz, C), 131.1 (CH), 132.9 (CH), 135.1 (CH), 136.3 (C), 140.0 (C), 146.1 (C), 149.0 (C), 157.4 (CH), 184.8 (C) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −60.4 ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{19}F_3N_2O_3Si$ 433.1190; found 433.1180. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 366 (1.52), 432 (0.99) nm. Emission λ_{max} 538 nm.

*2-{(2E)-4-(4-Nitrophenyl)-3-oxo-2-[(trimethylsilyl)methylene]-2,3-dihydro-1H-pyrrol-1-yl}benzonitrile (**4ah**).* Dark orange crystals; yield 89 mg (65%); mp 194−195 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 0.27 (s, 9 H), 5.80 (s, 1 H), 7.71−7.74 (m, 1 H), 7.78 (d, J = 8.1 Hz, 1 H), 7.93−7.97 (m, 1 H), 8.03 (d, J = 7.7 Hz, 1 H), 8.20−8.26 (m, 4 H), 9.10 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = −1.0 (CH), 112.2 (C), 112.9 (C), 116.7 (C), 122.9 (CH), 124.7 (CH), 125.6 (CH), 129.8 (CH), 130.1 (CH), 135.3 (CH), 135.6 (CH), 139.6 (C), 140.8 (C), 146.3 (C), 146.4 (C), 156.4 (CH), 184.8 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{19}N_3O_3Si$ 390.1268; found 390.1271. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 362 (1.85), 432 (1.07) nm. Emission λ_{max} 537 nm.

*(2E)-1-(2-Methoxyphenyl)-4-(4-nitrophenyl)-2-[(trimethylsilyl)-methylene]-1,2-dihydro-3H-pyrrol-3-one (**4ai**).* Orange crystals; yield 116 mg (84%); mp 71−73 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 0.25 (s, 9 H), 3.88 (s, 3 H), 5.58 (s, 1 H), 7.11−7.15 (m, 1 H), 7.27 (d, J = 8.3 Hz, 1 H), 7.40−7.43 (m, 1 H), 7.46−7.51 (m, 1 H), 8.18−8.22 (m, 4 H), 8.85 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = −0.9 (CH), 56.3 (CH), 110.9 (C), 113.7 (CH), 121.4 (CH), 121.9 (CH), 124.6 (CH), 124.9 (CH), 126.6 (C), 129.6 (CH), 130.9 (CH), 140.5 (C), 145.7 (C), 147.4 (C), 156.0 (C), 158.2 (CH), 184.8 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{22}N_2O_4Si$ 395.1422; found 395.1431. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 380 (1.55), 448 (1.05) nm. Emission λ_{max} 551 nm.

*(2E)-1-Mesityl-4-(4-nitrophenyl)-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4aj**).* Orange crystals; yield 119 mg (84%); mp 178−180 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 0.24 (s, 9 H), 2.13 (s, 6 H), 2.34 (s, 3 H), 5.32 (s, 1 H), 7.07 (s, 2 H), 8.20 (s, 4 H), 8.82 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = −0.9 (CH), 17.6 (CH), 21.1 (CH), 110.9 (C), 121.4 (CH), 124.6 (CH), 124.9 (CH), 130.3 (CH), 133.2 (C), 137.8 (C), 140.1 (C), 140.6 (C), 145.7 (C), 146.9 (C), 158.0 (CH), 184.5 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{23}H_{26}N_2O_3Si$ 407.1785; found 407.1778. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 258 (1.33), 378 (1.72), 451 (1.12) nm. Emission λ_{max} 551 nm.

*(2E)-1-(2,6-Diisopropylphenyl)-4-(4-nitrophenyl)-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4ak**).* Bright orange crystals; yield 125 mg (80%); mp 73−75 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 0.24 (s, 9 H), 1.17 (d, J = 6.9 Hz, 6 H), 1.21 (d, J = 6.9 Hz, 6 H), 2.82 (sept, J = 6.9 Hz, 2 H), 5.32 (s, 1 H), 7.40 (d, J = 7.8 Hz, 2 H), 7.53 (t, J = 7.8 Hz, 1 H), 8.20−8.25 (m, 4 H), 8.94 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = −1.0 (CH), 24.3 (CH), 24.7 (CH), 29.5 (CH), 111.0 (C), 122.8 (CH), 124.7 (CH), 125.0 (CH), 125.4 (CH), 131.3 (CH), 133.0 (C), 140.5 (C), 145.8 (C), 148.9 (C), 149.2 (C), 158.2 (CH), 184.5 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{26}H_{32}N_2O_3Si$ 449.2255; found 449.2245. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 376 (1.67), 451 (1.03) nm. Emission λ_{max} 551 nm.

*(2E)-4-(4-Nitrophenyl)-1-(1,3-thiazol-2-yl)-2-[(trimethylsilyl)-methylene]-1,2-dihydro-3H-pyrrol-3-one (**4al**).* Red crystals; yield 59 mg (45%); mp 176−177 °C (dec). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.27 (s, 9 H), 7.16 (s, 1 H), 7.56 (s, 1 H), 7.68 (s, 1 H), 8.22 (s, 4 H), 9.38 (s, 1 H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = −0.9 (CH), 113.4 (C), 115.8 (CH), 123.8 (CH), 125.6 (CH), 125.7 (CH), 137.4 (C), 139.4 (CH), 142.3 (C), 145.3 (C), 153.5 (CH), 158.5 (C), 183.9 (C) ppm. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for

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$C_{17}H_{17}N_3O_3SSi$ 394.0652; found 394.0654. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 272 (1.10), 360 (1.39), 438 (0.85) nm. Emission λ_{max} 540 nm.

(2E)-1-[3-(4-Chlorophenyl)-1-phenyl-1H-pyrazol-5-yl]-4-(4-nitrophenyl)-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4am**). Orange crystals; yield 155 mg (82%); mp 205−207 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 (s, 9 H), 5.70 (s, 1 H), 6.77 (s, 1 H), 7.37−7.48 (m, 7 H), 7.84−7.86 (m, 4 H), 8.02 (s, 1 H), 8.17 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −1.4 (CH), 102.2 (CH), 114.0 (C), 123.1 (CH), 124.0 (CH), 125.0 (CH), 125.1 (CH), 126.9 (CH), 128.5 (CH), 129.0 (CH), 129.7 (CH), 130.7 (C), 134.6 (C), 136.1 (C), 137.4 (C), 138.1 (C), 144.5 (C), 145.9 (C), 150.9 (C), 151.9 (CH), 183.4 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{29}H_{25}ClN_4O_3Si$ 541.1457; found 541.1450.

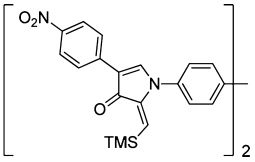
(2E)-4-(4-Nitrophenyl)-1-propyl-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4an**). Ruby crystals; yield 104 mg (90%); mp 129−131 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 0.28 (s, 9 H), 0.96 (t, J = 7.3 Hz, 3 H), 1.78 (sext, J = 7.3 Hz, 2 H), 3.76 (t, J = 7.3 Hz, 2 H), 5.98 (s, 1 H), 8.08−8.11 (m, 2 H), 8.14−8.17 (m, 2 H), 8.85 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = −0.8 (CH), 11.5 (CH), 22.7 (CH_2), 48.7 (CH_2), 109.0 (C), 120.7 (CH), 124.3 (CH), 124.6 (CH), 141.0 (C), 145.2 (C), 147.1 (C), 158.1 (CH), 184.9 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{17}H_{22}N_2O_3Si$ 331.1472; found 331.1470. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 382 (1.59), 459 (0.86) nm. Emission λ_{max} 558 nm.

(2E)-1-Cyclopentyl-4-(4-nitrophenyl)-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4ao**). Dark red crystals; yield 96 mg (77%); mp 162−164 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 0.28 (s, 9 H), 1.67−1.78 (m, 2 H), 1.83−1.94 (m, 4 H), 2.08−2.17 (m, 2 H), 4.42−4.49 (m, 1 H), 6.03 (s, 1 H), 8.14 (s, 4 H), 8.88 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = −0.8 (CH), 24.4 (CH_2), 31.8 (CH_2), 57.1 (CH), 109.5 (C), 121.1 (CH), 124.4 (CH), 124.5 (CH), 141.0 (C), 145.2 (C), 147.7 (C), 154.8 (CH), 185.1 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{19}H_{24}N_2O_3Si$ 357.1629; found 357.1634. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 387 (1.54), 462 (0.88) nm. Emission λ_{max} 562 nm.

(2E)-1-(tert-Butyl)-4-(4-nitrophenyl)-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4ap**). Orange crystals; yield 88 mg (73%); mp 180−182 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 0.29 (s, 9 H), 1.65 (s, 9 H), 6.20 (s, 1 H), 8.11−8.16 (m, 4 H), 8.88 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = −0.4 (CH), 29.3 (CH), 58.2 (C), 108.5 (C), 119.6 (CH), 124.50 (CH), 124.52 (CH), 141.1 (C), 145.2 (C), 146.0 (C), 156.8 (CH), 185.0 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{18}H_{24}N_2O_3Si$ 345.1629; found 345.1625. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 381 (1.41), 454 (0.71) nm. Emission λ_{max} 552 nm.

(2E)-1-Benzyl-4-(4-nitrophenyl)-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4aq**). Orange crystals; yield 119 mg (90%); mp 145−146 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 0.23 (s, 9 H), 5.04 (s, 2 H), 5.96 (s, 1 H), 7.30−7.36 (m, 1 H), 7.38−7.41 (m, 4 H), 8.10−8.12 (m, 2 H), 8.16−8.18 (m, 2 H), 8.94 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = −0.9 (CH), 50.8 (CH_2), 109.9 (C), 121.7 (CH), 124.60 (CH), 124.64 (CH), 128.0 (CH), 128.7 (CH), 129.7 (CH), 137.3 (C), 140.7 (C), 145.5 (C), 147.1 (C), 158.2 (CH), 185.0 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{22}N_2O_3Si$ 379.1472; found 379.1483. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 379 (1.55), 454 (0.91) nm. Emission λ_{max} 558 nm.

(2E)-1-(2-Furylmethyl)-4-(4-nitrophenyl)-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4ar**). Deep red crystals; yield 103 mg (80%); mp 117−118 °C. ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 0.26 (s, 9 H), 5.02 (s, 2 H), 6.10 (s, 1 H), 6.42 (dd, J = 3.2, 1.9 Hz, 1 H), 6.51 (d, J = 3.2 Hz, 1 H), 7.55 (d, J = 1.9 Hz, 1 H), 8.08−8.11 (m, 2 H), 8.16−8.18 (m, 2 H), 8.86 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = −0.9 (CH), 43.7 (CH_2), 109.9 (CH), 110.2 (C), 111.5 (CH), 121.4 (CH), 124.64 (CH), 124.65 (CH), 140.6 (C), 144.0 (CH), 145.6 (C), 146.7 (C), 150.2 (C), 157.6 (CH), 184.9 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{19}H_{20}N_2O_4Si$ 369.1265; found 369.1260. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 377 (1.45), 450 (0.89) nm. Emission λ_{max} 557 nm.



(2E,2′E)-1,1′-Biphenyl-4,4′-diylbis{4-(4-nitrophenyl)-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one} (**4as**). This material was obtained from enamine **3as** (0.16 mmol) after heating at 200 °C in Ph_2O for 1 h and was purified by flash chromatography under conditions that were the same as those for other compounds **4**. Red powder; yield 84 mg (72%); mp 260−261 °C (dec). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.26 (s, 18 H), 6.05 (s, 2 H), 7.63 (d, J = 8.3 Hz, 4 H), 7.95 (d, J = 8.3 Hz, 4 H), 8.19−8.24 (m, 8 H), 9.34 (s, 2 H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = −0.9 (CH), 110.2 (C), 121.7 (CH), 123.9 (CH), 124.3 (CH), 125.7 (CH), 128.0 (CH), 136.7 (C), 138.0 (C), 139.2 (C), 144.3 (C), 145.4 (C), 157.1 (CH), 183.8 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{40}H_{38}N_4O_6Si_2$ 727.2403; found 727.2397. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 312 (2.06), 376 (3.96), 454 (2.36) nm. Emission λ_{max} 556 nm.

(2E)-1-(4-Methoxyphenyl)-4-phenyl-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4ba**). Dark red crystals; yield 80 mg (66%); mp 119−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.27 (s, 9 H), 3.87 (s, 3 H), 5.71 (s, 1 H), 7.00−7.02 (m, 2 H), 7.17−7.21 (m, 3 H), 7.33−7.37 (m, 2 H), 7.75−7.76 (m, 2 H), 8.05 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.96 (CH), 55.6 (CH), 113.4 (C), 114.9 (CH), 120.2 (CH), 124.8 (CH), 125.9 (CH), 127.0 (CH), 128.5 (CH), 131.2 (C), 131.6 (C), 146.9 (C), 152.7 (CH), 158.7 (C), 185.0 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{23}NO_2Si$ 350.1571; found 350.1575. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 291 (2.64), 467 (0.37) nm.

(2E)-1,4-Diphenyl-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4bb**). Dark red crystals; yield 73 mg (65%); mp 133−134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.29 (s, 9 H), 5.87 (s, 1 H), 7.19−7.22 (m, 1 H), 7.28−7.30 (m, 2 H), 7.34−7.39 (m, 3 H), 7.49−7.53 (m, 2 H), 7.76−7.78 (m, 2 H), 8.13 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.78 (CH), 114.3 (C), 120.4 (CH), 125.1 (CH), 125.3 (CH), 126.3 (CH), 127.3 (CH), 128.7 (CH), 130.0 (CH), 131.5 (C), 138.6 (C), 146.2 (C), 152.4 (CH), 185.3 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{20}H_{21}NOSi$ 320.1465; found 320.1467. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 296 (3.89), 462 (0.64) nm. Emission λ_{max} 468 nm.

(2E)-1,4-Bis(4-methoxyphenyl)-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4ca**). Red crystals; yield 98 mg (74%); mp 88−89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.26 (s, 9 H), 3.81 (s, 3 H), 3.86 (s, 3 H), 5.68 (s, 1 H), 6.90 (d, J = 8.8 Hz, 2 H), 7.00 (d, J = 8.8 Hz, 2 H), 7.19 (d, J = 8.8 Hz, 2 H), 7.68 (d, J = 8.8 Hz, 2 H), 7.96 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.9 (CH), 55.3 (CH), 55.6 (CH), 113.4 (C), 114.0 (CH), 114.9 (CH), 119.6 (CH), 124.2 (C), 126.1 (CH), 126.9 (CH), 131.4 (C), 146.9 (C), 151.9 (CH), 158.0 (C), 158.6 (C), 185.2 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{22}H_{25}NO_3Si$ 380.1677; found 380.1682. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 290 (2.25), 479 (0.26) nm.

(2E)-4-(4-Methoxyphenyl)-1-phenyl-2-[(trimethylsilyl)methylene]-1,2-dihydro-3H-pyrrol-3-one (**4cb**). Red crystals; yield 86 mg (70%); mp 146−148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.27 (s, 9 H), 3.81 (s, 3 H), 5.85 (s, 1 H), 6.89−6.91 (m, 2 H), 7.26−7.28 (m, 2 H), 7.33−7.36 (m, 1 H), 7.47−7.51 (m, 2 H), 7.68−7.70 (m, 2 H), 8.04 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.9 (CH), 55.3 (CH), 114.0 (CH), 114.1 (C), 119.7 (CH), 124.0 (C), 125.0 (CH), 126.2 (CH), 126.9 (CH), 129.8 (CH), 138.6 (C), 146.0 (C), 151.3 (CH), 158.1 (C), 185.3 (C) ppm. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{23}NO_2Si$ 350.1571; found 350.1579. UV−vis λ_{max} ($\varepsilon \times 10^{-4}$): 298 (2.57), 473 (0.35) nm. Emission λ_{max} 502 nm.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General protocol for the synthesis of enynones **1**; copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra for compounds **3aa,as,at**, **4aa−as**, and **4ba−cb**; UV−vis spectra of pyrrolones **4aa−as** and **4ba−**

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cb; and X-ray diffraction data for compounds **3aa**, **4ab**, **4ar**. X-ray crystallographic data files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(16) CCDC 1045422 (for compound **3aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(17) CCDC 1046271 (for compound **4ab**) and 1050103 (for compound **4ar**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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