Efficient Regio- and Stereoselective Synthesis of 5-Alkyl(aryl)idene- and 5-[Iodoalkyl(aryl)idene]-1*H*-pyrrol-2(5*H*)-ones via Electrophilic Cyclization

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Abstract: A variety of substituted 5-alkyl(aryl)idene- and 5-[iodoalkyl(aryl)idene]-1*H*-pyrrol-2(5*H*)-ones were readily prepared with good yields under very mild reaction conditions by the iodocyclization of (2*Z*,4*E*)-dienamides and (*Z*)-alk-2-en-4-ynamides with iodine monochloride. 3-Ylidene-isoindolin-1-ones were also synthesized in moderate to good yields under the same conditions. The methodology proceeded with total regioselectivity in all cases and was applied to the synthesis of new unsaturated lactam compounds.

Key words: alkylidene-pyrrolones, electrophilic cyclization, dienamides, regioselectivity, iodocyclization

The iodocyclization of heteroatoms such as oxygen, nitrogen, and sulfur with tethered alkynes has proved to be an effective method for the preparation of a wide variety of heterocyclic ring systems.[1–7] Important heterocycles such as furans,[1] pyrroles,[2] thiophenes,[3] indoles,[4] quinolines,[8] and others[5–7] have been accessed using this protocol.

Our success in employing this process for the synthesis of 5-alkyl(aryl)idenefuran-2(5*H*)-ones[9] led us to explore the possibility of preparing 5-ylidene-1*H*-pyrrol-2(5*H*)-ones (1,5-dihydro-2*H*-pyrrol-2-ones) and derivatives thereof by the same approach. The 5-ylidene-1*H*-pyrrol-2(5*H*)-one structural unit **4** (Figure 1) is found in a range of biologically important natural products including holomycin,[10] pukeleimide,[11] isoampullicin,[12] and the bile pigment bilirubin.[13] Although extensive methodology has been developed for the construction of 5-ylidene-furan-2(5*H*)-ones and 4-ylidene-tetronic acids,[14] few synthetic studies have been published involving 5-ylidene-1*H*-pyrrol-2(5*H*)-ones **4**.[15] In particular, 5-ylidene-1*H*-pyrrol-2(5*H*)-ones have been obtained through the reaction of transition-metal-coordinated bis(imidoyl) chlorides with carbon nucleophiles[16] maleimides and from 1*H*-pyrrol-2(5*H*)-ones.[17] The isoindolin-1-one (2,3-dihydro-1*H*-indol-1-one) ring system represents a key structural subunit in numerous natural and synthetic products exhibiting a wide range of biological activity, including antihypertensive,[18] anti-inflammatory,[19] antiulcer,[20] and antileukemic[21] properties.

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Isoindolinones have previously been prepared via Grignard[22] or lithiation[23] procedures, as well as by Wittig,[24] Diels–Alder,[21,25] rearrangement[26] and photochemical reactions.[27] The reduction of N-substituted phthalimides[28] and the condensation of phthalaldehyde[29] also affords isoindolinones. Besides the classical methods, metal-catalyzed synthesis of isoindolinones has also been reported. Cobalt, rhodium, and palladium complexes can be used as catalysts for the synthesis of isoindolinones.[30,31]

We recently reported the regioselective synthesis of α-pyrones, α-pyridones, and isoquinolinones under palladium complex catalysis by coupling (tributylstannyl)allenes with (*Z*)-iodovinylic acid or (*Z*)-iodovinylic amide derivatives.[32,33] We have also described the synthesis of dienoic acids and enynoic acids from β-iodovinylic acids and vinyltins and alkynylzinc reagents, respectively.[34] This methodology was then applied to the synthesis of 5-alkyl(aryl)idene-substituted furan-2(5*H*)-ones.[9] In addition, we have also described our first results for the regioselective synthesis of 5-alkyl(aryl)idene- and 5-[iodoalkyl(aryl)idene)]-1*H*-pyrrol-2(5*H*)-ones by iodolactamization of (2*Z*,4*E*)-dienamides and (*Z*)-alk-2-en-4-ynamides, respectively.[35] In continuation of these studies, we report here full details of a successful electrophilic cyclization strategy as a convenient and general regioselective method for the synthesis of 5-ylidene- or 5-(iodoylidene)-substituted 1*H*-pyrrol-2(5*H*)-ones **4** and the extension of this method to the synthesis of 3-ylidene-substituted isoindolin-1-ones **5** (Figure 1).

4 5-ylidene pyrrol-2(*5H*)-ones

5 3-ylidene isoindolin-1-ones

Figure 1

Synthesis of 5-Ylidene-1*H*-pyrrol-2(5*H*)-ones 4 and 3-Ylidene-isoindolin-1-ones 5

We began by examining the halolactamization of (2*Z*,4*E*)-dienamides **3** using several electrophilic halogen sources

(ICl, I_2, I_2/KI, NBS, etc.);[36] for the synthesis of **3** see Schemes 1 and 2. Iodine monochloride was found to be the best reagent to obtain fair to good yields of 5-alkylidene-1*H*-pyrrol-2(5*H*)-ones **4a–h** as the sole product (Scheme 3, Table 1, entries 1–9). In all cases, the five-membered ring products were obtained without any trace of the six-membered ring lactam, giving a regioselective character to the electrophilic cyclization strategy where only 5-*exo* mode cyclization was observed (Scheme 3). The use of other sources (NIS, NBS, I_2/KI, etc.) as the electrophilic reagents led to lower yields (<50%).

The influence of the reaction solvents were examined at room temperature using diethyl ether, tetrahydrofuran, acetonitrile, toluene, and dichloromethane. The latter gave the best results, which we believe may be due to a greater ability to solubilize iodine monochloride. Diethyl ether, tetrahydrofuran, and toluene were found to be ineffective, and acetonitrile afforded a poor yield (<40%) of cyclized product. Similar regioselectivity was also observed in all cases, and only the five-membered ring products were obtained.

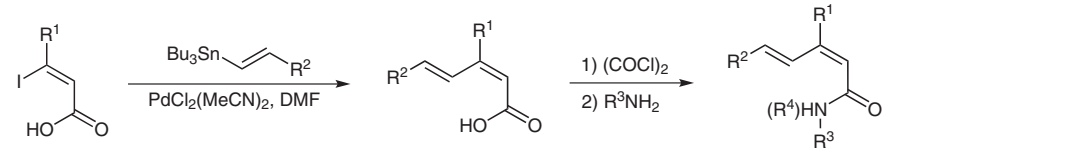
Interestingly, the cyclization reaction was followed by a spontaneous in situ dehydrohalogenation reaction providing 5-ylidene-1*H*-pyrrol-2(5*H*)-ones **4a–h**. This took place without the necessity for a base (Scheme 3, Table 1), in contrast to our previously reported results in the 5-alkylidenefuran-2(5*H*)-ones series (DBU induced dehydrohalogenation to form the exocyclic double bond).[9] The addition of sodium hydrogen carbonate improved the yield in this reaction (Table 1, cf. entries 1 and 2), although it was only a marginal effect.

A wide variety of unsaturated amides **3** were examined in this cyclization process. Excellent yields of amides **3a–k** were obtained by treatment of the corresponding (2*Z*,4*E*)-dienoic acids **2a–i** with oxalyl chloride followed by the addition of a primary or secondary amine (Scheme 1).[37]

The results varied according to the degree of substitution on the nitrogen. Attempts to cyclize unsubstituted (Table 1, entry 10) or disubstituted amides (Table 1, entry 11) under our conditions proved unsuccessful. Moreover, the reaction of pentadienamide **3k** in the presence of iodine monochloride afforded only trace amounts of the product **4k**, with the recovery of significant amounts of the starting material and polymerization of the product (Table 1, entry 12).

Other halogen sources used did not affect the *exo* selectivity of these iodocyclization reactions. After experimenting with a variety of conditions and methods, it was found that the best result of the final electrophilic cyclization step was obtained by using iodine monochloride as electrophilic halogen source in dichloromethane at room temperature, providing good yields of 5-alkyl(aryl)idene-1*H*-pyrrol-2(5*H*)-ones **4a–h** (Scheme 3, Table 1).

This method was then applied to the synthesis of 3-ylidene-isoindolin-1-ones **5**. Indeed, (*E*)-2-alk-1-enyl-*N*-benzylbenzamides **3l–n** reacted with iodine monochloride to produce the corresponding 3-alkyl(aryl)idene-2-benzylisoindolin-1-ones **5a–c** as the sole products in fair to good yields (Scheme 3, Table 1). Good yields of (*E*)-2-alk-1-enyl-*N*-benzylbenzamides **3l–n** were obtained by treatment of the corresponding (*E*)-2-alk-1-enylbenzoic acids **2j–l** with oxalyl chloride followed by addition of benzylamine (Scheme 2). Acids **2j–l** were prepared by

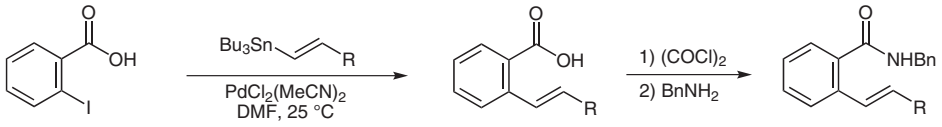


1a R^1 = Ph
1b R^1 = H
1c R^1 = CH_2OMe
1d R^1 = Me

2a R^1 = R^2 = Ph
2b R^1 = Ph, R^2 = $SiMe_3$
2c R^1 = H, R^2 = $SiMe_3$
2d R^1 = CH_2OMe, R^2 = $SiMe_3$
2e R^1 = Me, R^2 = $SiMe_3$
2f R^1 = Me, R^2 = $(CH_2)_4Me$
2g R^1 = Me, R^2 = *i*-Pr
2h R^1 = Me, R^2 = Ph
2i R^1 = Me, R^2 = H

3a R^1 = R^2 = Ph, R^3 = Bn
3b R^1 = Ph, R^2 = $SiMe_3$, R^3 = Bn
3c R^1 = Ph, R^2 = $SiMe_3$, R^3 = CH(*i*-Pr)Me
3d R^1 = H, R^2 = $SiMe_3$, R^3 = CH(Ph)Me
3e R^1 = CH_2OMe, R^2 = $SiMe_3$, R^3 = *m*-$MeOC_6H_4$
3f R^1 = Me, R^2 = $SiMe_3$, R^3 = Bn
3g R^1 = Me, R^2 = $SiMe_3$, R^3 = *m*-$MeOC_6H_4$
3h R^1 = Me, R^2 = Ph, R^3 = Bn
3i R^1 = Me, R^2 = *i*-Pr, R^3 = H
3j R^1 = Me, R^2 = Ph, R^3 = R^4 = *i*-Pr
3k R^1 = Me, R^2 = H, R^3 = Bn

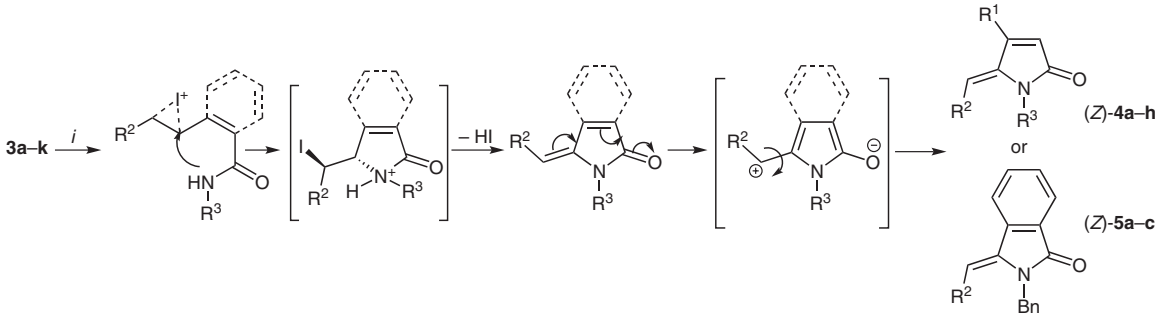
Scheme 1



2j R = Ph (77%)
2k R = $(CH_2)_4Me$ (75%)
2l R = $SiMe_3$ (79%)

3l R = Ph (85%)
3m R = $(CH_2)_4Me$ (82%)
3n R = $SiMe_3$ (84%)

Scheme 2



Scheme 3 *Reagents and conditions*: (i) ICl, CH_2Cl_2, 0 to 25 °C, 12 h.

Stille coupling of the 2-iodobenzoic acid with tributyl(vinyl)tins.[34]

The isoindolinones were distinguishable from the isoquinolinones on the basis of their IR spectra. The five-membered ring products generally exhibited a carbonyl absorption band at 1710–1690 cm^{-1}, while in the six-membered ring products the carbonyl absorption was observed at 1640–1650 cm^{-1}.[23b,33,38] The results are summarized in Table 1.

The reactions of a range of unsaturated amides **3a**–**n** with iodine monochloride in dichloromethane under regio- and stereo control provided fair to good yields of 5-alkyl(aryl)idene-1*H*-pyrrol-2(5*H*)-ones **4a**–**h** or 3-ylidene-isoindolin-1-ones **5a**–**c** as the sole products (Table 1, entries 1–9 and 13–15). The selectivity observed was largely in favor of *E* stereochemistry of the exocyclic double bond. Nevertheless, selectivity was highly dependent on temperature and the nature of the substituent. For the first time, (silylmethylene)-1*H*-pyrrol-2(5*H*)-ones **4b**–**g** were obtained with mainly *E* stereochemistry for the exocyclic double bond, which was confirmed by NOESY experiments. It should be noted that **4b**–**g** isomerized rapidly at 25 °C, largely in favor of *Z* stereochemistry during chromatography on silica gel. In the case of the formation of **4a** and **4h**, the desired 5-benzylidene-1*H*-pyrrol-2(5*H*)-ones were obtained with only *Z* configuration of the exocyclic double bond (Table 1, entries 1 and 9). This can be explained by the greater thermodynamic stability of the *Z*-isomers of **4a** and **4h** compared to the *E*-isomers, in which

Table 1 Synthesis of 5-Alkyl(aryl)idene-1*H*-pyrrol-2(5*H*)-ones **4** and 3-Ylidene-isoindolin-1-ones **5**

Entry	R^1	R^2	R^3	Product	Yield (%)	Ratio[a] *Z*/*E*	Ratio[b] *Z*/*E*
1	Ph	Ph	Bn	**4a**	55	100:0	100:0
2[c]	Ph	Ph	Bn	**4a**	56	100:0	100:0
3	Ph	$SiMe_3$	Bn	**4b**	80	10:90	100:0
4	Ph	$SiMe_3$	CH*(*i*-Pr)Me (*S*)	**4c**	77	5:95	100:0[d]
5	H	$SiMe_3$	CH(Ph)Me	**4d**	58	6:94	78:22
6	Me	$SiMe_3$	Bn	**4e**	78	3:97	100:0
7	Me	$SiMe_3$	3-$MeOC_6H_4$	**4f**	50	5:95	100:0
8	CH_2OMe	$SiMe_3$	3-$MeOC_6H_4$	**4g**	51	7:93	100:0
9	Me	Ph	Bn	**4h**	70	100:0	100:0
10	Me	*i*-Pr	H	**4i**	0	–	–
11[e]	Me	Ph	*i*-Pr	**4j**	0	–	–
12	Me	H	Bn	**4k**	trace	–	–
13	Me	Ph	Bn	**5a**	50	11:89	100:0
14	Me	$(CH_2)_4Me$	Bn	**5b**	60	23:77	100:0
15	Me	$SiMe_3$	Bn	**5c**	60	17:83	100:0

[a] Before isomerization reaction.
[b] After spontaneous isomerization.
[c] Using 2 equiv of $NaHCO_3$.
[d] $[\alpha]_D^{25}$ +29 (*c* 1.82, CH_2Cl_2).
[e] (2*Z*,4*E*)-*N*,*N*-Diisopropyl-3-methyl-5-phenylpenta-2,4-dienamide was used in this case.

the extensive interaction of the *ortho* hydrogens of the phenyl group and the substituent group prevent conjugation. As shown in Table 1, we obtained enantiomerically pure (silylmethylene)-1*H*-pyrrol-2(5*H*)-one **4c** from the available optically active dienamide **3c** (Table 1, entry 4), and in all cases the 5-ylidene-1*H*-pyrrol-2(5*H*)-ones **4** and 3-ylidene-isoindolin-1-ones **5** were obtained without any trace of 2-pyridones and isoquinolinones, respectively.

We believe that such 5-*exo-trig* cyclization proceeds by *anti* attack of the electrophile and the nitrogen atom on the alkene, resulting in a presumed intermediate product. Dehydrohalogenation of the presumed intermediate product to the 5-alkyl(aryl)idene-1*H*-pyrrol-2(5*H*)-ones and 3-ylidene-isoindolin-1-ones is evidently rapid, even in the absence of a base, since intermediates were not observed.

It should be noted that the 5-ylidene-1*H*-pyrrol-2(5*H*)-ones and 3-ylidene-isoindolin-1-ones were not stable and gradually decomposed upon heating or exposure to air. It was also necessary to neutralize the silica gel during chromatography using a base such as triethylamine to avoid their decomposition.

Synthesis and Reactivity of 5-[Iodoalkyl(aryl)idene]-1*H*-pyrrol-2(5*H*)-ones 7a–e

We next chose to extend our method by investigating similar cyclization of (*Z*)-alk-2-en-4-ynamides **6a–e**. Alk-2-en-4-ynamides **6a–e** were prepared via the Sonogashira cross-coupling reactions[39] of terminal alkynes with (*Z*)-*N*-benzyl-3-iodoalk-2-enamides (Table 2). The yields of this process ranged from 69% to 81%, and no polymerization or cyclized products were detected in this procedure.

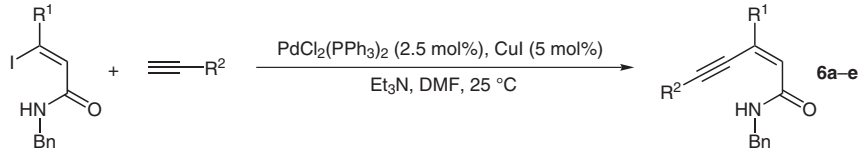
Indeed, good yields of 5-[iodoalkyl(aryl)idene]-1*H*-pyrrol-2(5*H*)-ones **7a–d** were easily prepared upon exposure of **6a**,**b** and **6d**,**e** to 3.1 equivalents of iodine monochloride in dichloromethane at room temperature for four hours in the presence of three equivalents of sodium hydrogen carbonate (Scheme 4, Table 3). A wide variety of alkynylcarboxamides were examined in this cyclization process. In all cases, this iodocyclization reaction proceeded via the 5-*exo-dig* process, and the corresponding six-membered ring lactams were not observed in any case. The exocyclic double bond formed had mainly the *E* configuration, except in the case of **7b** (Table 3, entry 2) where significant amounts of *Z*-isomer were observed. This stereochemistry of pyrrolones **7a–d** was assigned using a NOESY experiment. The *E*-isomer compounds exhibited a cross-peak between the CH_2 of the benzyl group and the protons of the substituent R^2 group. No products involving the simple addition of the electrophile iodine monochloride to the alkyne triple bond were observed with any of these alkynes. As shown in Table 3, the product **7d** was obtained after spontaneous deprotection on a silica gel column.

We propose the following mechanism to explain this electrophilic cyclization (Scheme 4): nucleophilic attack by the nitrogen of the amide group on the C≡C bond activated by coordination with I^+ is followed by deprotonation to yield the cyclized products.

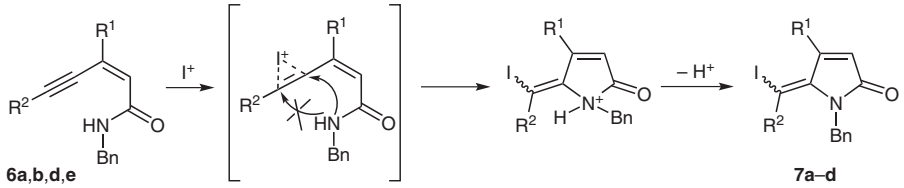
Reactivity of 1-Benzyl-5-(iodoarylidene)-1*H*-pyrrol-2(5*H*)-one 7b

The 5-(iodo-ylidene)-1*H*-pyrrol-2(5*H*)-ones produced by this method will be very valuable for the synthesis of a

Table 2 Synthesis of (*Z*)-Enynamides **6a–e**



Entry	R^1	R^2	Product	Yield (%)
1	H	Ph	**6a**	69
2	Me	Ph	**6b**	81
3	Ph	Ph	**6c**	70
4	Me	$SiMe_3$	**6d**	73
5	Me	$C(OTHP)Me_2$	**6e**	75



Scheme 4

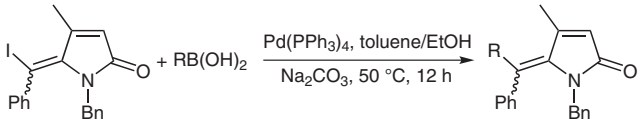
Table 3 Synthesis of 5-[Iodoalkyl(aryl)idene]-1*H*-pyrrol-2(5*H*)-ones **7a–d**

Entry	R^1	R^2	Product	Ratio *E*/*Z*	Yield[a] (%)
1	H	Ph	**7a**	90:10	65
2	Me	Ph	**7b**	65:35	79
3	Me	$SiMe_3$	**7c**	85:15	75
4	Me	$C(OH)Me_2$	**7d**	90:10	70[b]

[a] Isolated yield.
[b] After subsequent deprotection on silica gel.

wide variety of 5-ylidene-1*H*-pyrrol-2(5*H*)-ones. For example, the 1-benzyl-5-(iodoarylidene)-1*H*-pyrrol-2(5*H*)-one **7b** produced by this strategy can be further functionalized by applying palladium-catalyzed coupling reactions. Suzuki cross coupling[40] of **7b** with vinyl- or arylboronic acids, using toluene as solvent, ethanol as co-solvent and 3 mol% of tetrakis(triphenylphosphine)palladium(0) as catalyst provided good yields of stereoselective synthesis of the desired products **8a–f** (Table 4).

Table 4 Suzuki Cross-Coupling of **7b**



7b (*E*/*Z* = 65:35) **8a–f**

Entry	R	Product	Ratio *E*/*Z*	Yield (%)
1	$4\text{-}MeC_6H_4$	**8a**	90:10	71
2	3-thienyl	**8b**	75:25	65
3	CH=CH*t*-Bu	**8c**	10:90	62
4	$4\text{-}BrC_6H_4$	**8d**	88:12	67
5	$3\text{-}ClC_6H_4$	**8e**	85:15	60
6	Ph	**8f**	–	75

The use of (*E*)-*tert*-butylvinylboronic acid reagent permitted the transfer of a vinyl group with retention of the configuration of the double bond, and no polymerization products were observed (Table 4, entry 3). As shown in Table 4, the selectivity of products **8** observed was largely in favor of *E* stereochemistry of the exocyclic double bond, except in the case of **8c**, which was obtained with mainly *Z* configuration. It should be possible to prepare many other substituted pyrrolones using these iodo substrates and other known palladium methodology.

The aim of this research was to develop an efficient and inexpensive method for the synthesis of a library of (*Z*)-5-ylidene-1*H*-pyrrol-2(5*H*)-ones under mild and sample conditions.

Efficient, regio- and stereoselective synthesis of 5-alkyl(aryl)idene-1*H*-pyrrol-2(5*H*)-ones from (2*Z*,4*E*)-dienamides or (*Z*)-enynamides was developed under very mild experimental conditions. A wide range of dienamides and enynamides readily underwent cyclization using iodine monochloride. The resulting iodine-containing products can be readily developed to more complex products using the Suzuki cross-coupling reaction. This methodology was general and was extended to the regioselective synthesis of 3-alkyl(aryl)idene-isoindolin-1-ones with good yields. Investigations into synthetic applications for biologically active natural products are currently in progress.

All reactions were carried out under inert atmosphere (Ar or N_2). THF and Et_2O were dried and freshly distilled from Na/benzophenone. DMF and CH_2Cl_2 were dried by distillation over CaH_2. The petroleum ether (PE) used was the fraction boiling in the range 60–90 °C. Flash chromatography was carried out with Merck silica gel (silica gel, 230–400 mesh). ^1H NMR spectra were recorded at 200 or 300 MHz using $CDCl_3$ as solvent. Findings, reported using the residual solvent proton resonance of $CDCl_3$ (δ_H = 7.25) as internal reference. ^{13}C NMR was recorded at 50.3 MHz using the $CDCl_3$ solvent peak at δ_C = 77.0 as reference. Mass spectra were obtained in the GC/MS (70 eV) mode. Melting points were uncorrected. The acids **2a–i** were prepared via the Stille cross-coupling reaction of vinyltin reagents with (*Z*)-3-iodoalk-2-enoic acids.[41] (*Z*)-*N*-Benzyl-3-iodoalk-2-enamides were prepared from (*Z*)-3-iodoalkenoic acids by a previously described procedure.[42]

Dienoic Acids 2a–l; General Procedure

(*Z*)-3-Iodoalk-2-enoic acid (10 mmol) diluted in DMF (5 mL) was added dropwise soln of the vinyltin reagent (12 mmol) in DMF. At the end of the addition, $PdCl_2(MeCN)_2$ (129 mg, 0.5 mmol) was added. The mixture was stirred at 25 °C for 3 h then hydrolyzed with 1 M KF soln and filtered. The organic layer was washed with sat. NH_4Cl soln and treated with 1 M NaOH soln. After washing with Et_2O, the aqueous layer was acidified with 1 M HCl soln and extracted with Et_2O and the combined extracts were dried ($MgSO_4$). The solvent was removed and the crude products were purified using column chromatography (silica gel, PE–Et_2O, 70:30) or by crystallization (Et_2O).

(2*E*,4*E*)-3,5-Diphenylpenta-2,4-dienoic Acid (2a)[43]

Mp 142 °C (Lit. 140–142 °C).

IR (KBr): 3444, 3057, 1681, 1613, 1585, 1409, 1265 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 5.91 (s, 1 H), 6.71 (d, *J* = 16.2 Hz, 1 H), 7.42 (m, 10 H), 8.54 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 116.9, 125.7, 127.6, 128.3, 128.7, 128.8, 128.9, 129.0, 136, 139, 140.8, 159, 171.9.

MS (EI): *m*/*z* (%) = 250 [M^+, 16], 205 (100), 190 (13), 178 (6), 165 (6), 127 (13), 101 (17), 77 (15).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{14}O_2$: 250.0994; found: 250.0991.

(2*E*,4*E*)-3-Phenyl-5-(trimethylsilyl)penta-2,4-dienoic Acid (2b)

Mp 160 °C.

IR (KBr): 3400, 3025, 2978, 2868, 1697, 1616, 1595, 1550, 1415, 1250 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.07 (s, 9 H), 5.89 (d, *J* = 18.6 Hz, 1 H), 5.95 (s, 1 H), 6.76 (d, *J* = 18.6 Hz, 1 H), 7.08–7.10 (m, 2 H), 7.35–7.40 (m, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –1.6, 119.6, 127.6 (3 C), 128.4 (2 C), 135.9, 142.9, 145.7, 157.2, 171.6.

MS (EI): *m*/*z* (%) = 246 [M$^+$, 3], 231 (7), 173 (100), 156 (14), 128 (24), 75 (56).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{14}H_{18}O_2Si$: 246.1076; found: 246.1081.

(2*Z*,4*E*)-5-(Trimethylsilyl)penta-2,4-dienoic Acid (2c)[44,45]
Mp 102 °C.

IR (KBr): 3430, 3049, 2957, 2856, 1680, 1618, 1244 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.18 (s, 9 H), 5.73 (d, *J* = 11.4 Hz, 1 H), 6.38 (d, *J* = 18.4 Hz, 1 H), 6.69 (dd, *J* = 11.4, 11 Hz, 1 H), 7.79 (dd, *J* = 18.4, 11 Hz, 1 H), 11.1 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –1.71 (d, J_{Si-C} = 53 Hz), 116.6, 139.1, 147.3, 148.8, 171.6.

MS (EI): *m*/*z* (%) = 97 [M$^+$ – ($SiMe_3$), 12], 75 (56), 71 (100), 43 (79), 42 (82).

(2*Z*,4*E*)-3-(Methoxymethyl)-5-(trimethylsilyl)penta-2,4-dienoic Acid (2d)[44,46]
Mp 83 °C.

IR (KBr): 3400, 3081, 3024, 1685, 1622, 1288 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.17 (s, 9 H), 3.45 (s, 3 H), 4.29 (s, 2 H), 6.05 (s, 1 H), 6.34 (d, *J* = 19.7 Hz, 1 H), 7.87 (d, *J* = 19.7 Hz, 1 H), 9.80 (br s, 1 H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = –1.20 (d, J_{Si-C} = 57 Hz), 59.0, 72.2, 116.0, 138.3, 138.4, 152.4, 172.3.

MS (EI): *m*/*z* (%) = 199 [M$^+$ – Me, 5], 110 (83), 75 (100), 73 (47), 45 (78).

(2*Z*,4*E*)-3-Methyl-5-(trimethylsilyl)penta-2,4-dienoic Acid (2e)[46]
Mp 110 °C.

IR (KBr): 3427, 3061, 3024, 2924, 2760, 1685, 1614, 1213 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.18 (s, 9 H), 2.08 (s, 3 H), 5.81 (s, 1 H), 6.43 (d, *J* = 19.2 Hz, 1 H), 8.02 (d, *J* = 19.2 Hz, 1 H), 9.56 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –1.62 (d, J_{Si-C} = 53 Hz), 20.7, 116.7, 139.1, 140.1, 154.0, 171.5.

MS (EI): *m*/*z* (%) = 184 (M$^+$, 8), 111 (47), 75 (45), 45 (60), 31 (100).

(2*Z*,4*E*)-3-Methyldeca-2,4-dienoic Acid (2f)[44,47]
IR (neat): 3415, 3052, 2930, 1690, 1618 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 6.5 Hz, 3 H), 1.32–1.37 (m, 6 H), 2.05 (s, 3 H), 2.23–2.27 (m, 2 H), 5.65 (s, 1 H), 6.22 (dt, *J* = 15.8, 7 Hz, 1 H), 7.59 (d, *J* = 15.8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.4, 21.7, 22.9, 29.1, 31.9, 33.8, 115.5, 128.0, 140.7, 154.3, 172.3.

MS (EI): *m*/*z* (%) = 182 (M$^+$, 6), 111 (100), 55 (10), 41 (12).

(2*Z*,4*E*)-3,6-Dimethylhepta-2,4-dienoic Acid (2g)[48]
Mp 90–92 °C.

IR (KBr): 3380–2500, 3081, 3024, 1688, 1620, 1288 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.60 (d, *J* = 8 Hz, 6 H), 2.06 (s, 3 H), 2.48–2.62 (m, 1 H), 5.67 (s, 1 H), 6.16 (dd, *J* = 16, 8 Hz, 1 H), 7.56 (d, *J* = 16 Hz, 1 H), 10.3 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.8, 22.6 (2 C), 32.4, 115.7, 125.3, 147.2, 154.5, 172.4.

MS (EI): *m*/*z* (%) = 154 (M$^+$, 5), 111 (100), 55 (17), 43 (17), 41 (23).

(2*Z*,4*E*)-3-Methyl-5-phenylpenta-2,4-dienoic Acid (2h)[46]
Mp 151–153 °C.

IR (KBr): 3160, 1675, 1615, 1595, 1090 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = (s, 3 H), 5.75 (br s, 1 H), 6.89 (d, *J* = 17.0 Hz, 1 H), 7.15–7.39 (m, 3 H_{Ar}), 7.42–7.44 (m, 2 H_{Ar}), 8.29 (d, *J* = 17.0 Hz, 1 H), 11.46 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.2, 117.3, 126.0, 127.6, 128.8, 129.0, 136.3, 136.7, 153.2, 171.8.

MS (EI): *m*/*z* (%) = 188 (M$^+$, 24), 143 (100), 142 (37), 141 (30), 77 (24).

(*Z*)-3-Methylpenta-2,4-dienoic Acid (2i)[46]
Mp 78–80 °C.

IR (neat): 3140, 1686, 1610, 1264, 1190 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.04 (s, 3 H), 5.49 (d, *J* = 10.8 Hz, 1 H), 5.64 (d, *J* = 17.5 Hz, 1 H), 5.76 (s, 1 H), 7.80 (dd, *J* = 17.5, 10.8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.6, 117.6, 121.5, 134.0, 153.4, 172.0.

MS (EI): *m*/*z* (%) = 112 (M$^+$, 8), 41 (18), 39 (18), 18 (100), 17 (38).

(*E*)-2-Styrylbenzoic Acid (2j)[49]
Mp 159 °C.

IR (KBr): 3430, 1684, 1565, 1481, 1447, 1405, 1300, 1275, 1250 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.05 (d, *J* = 16 Hz, 1 H), 7.29–7.51 (m, 4 H), 7.57–7.59 (m, 3 H), 7.77 (d, *J* = 8 Hz, 1 H), 8.05–8.14 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 126.9, 127.3, 127.4, 127.5, 127.9, 128.7, 131.7, 131.8, 133.2, 137.3, 140.2, 141.9, 173.1.

2-[(*E*)-Hept-1-enyl]benzoic Acid (2k)
IR (neat): 3400–3300, 1637, 1577, 1464, 1376, 1338 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7 Hz, 3 H), 1.30–1.47 (m, 6 H), 2.20 (q, *J* = 6.5 Hz, 2 H), 6.11 (dt, *J* = 16, 7 Hz, 1 H), 7.15–7.37 (m, 3 H), 7.50 (d, *J* = 7.7 Hz, 1 H), 7.83 (dd, *J* = 7.6, 2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0, 22.5, 29.0, 31.5, 33.2, 126.3, 126.5, 129.0, 130.6, 130.8, 132.8, 138.7, 140.7, 173.0.

MS (EI): *m*/*z* (%) = 218 (M$^+$, 2), 175 (28), 147 (11), 75 (100).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{14}H_{18}O_2$: 218.1307; found: 218.1310.

2-[(*E*)-2-(Trimethylsilyl)vinyl]benzoic Acid (2l)
IR (neat): 3400–3300, 2955–2855, 1692, 1635, 1563, 1464, 1336, 1247 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.24 (s, 9 H), 6.44 (d, *J* = 19 Hz, 1 H), 7.31 (td, *J* = 7.4, 1.3 Hz, 1 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 7.66 (d, *J* = 6.9 Hz, 1 H), 7.80 (d, *J* = 19 Hz, 1 H), 7.96 (d, *J* = 7.2 Hz, 1 H), 11.7 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –1.3, 126.7, 127.2, 130.6, 131.3, 131.9, 132.0, 139.9, 142.9, 173.2.

MS (EI): *m*/*z* (%) = 220 (M$^+$, 7), 205 (10), 147 (33), 75 (100).

HRMS (EI): *m*/*z* [M]$^+$ calcd for $C_{12}H_{16}O_2Si$: 220.0920; found: 220.0922.

Dienamides 3a–n; General Procedure
Oxalyl chloride (3 mmol) was added dropwise, at 0 °C, to acid **2** (1 mmol) dissolved in a minimum amount of CH_2Cl_2. The mixture was stirred at r.t. for 3 h and then the excess of oxalyl chloride and the solvent were removed under reduced pressure. The acyl chlorides were sufficiently pure to be used without further purification. At

–60 °C, amine (1.2 mmol) (freshly distilled over CaH_2) were added dropwise to the acyl chloride (1 mmol) diluted in Et_2O (10 mL). The temperature was slowly allowed to rise to 10 °C. After 1 h at 10 °C, the mixture was quenched with sat. NH_4Cl and extracted with Et_2O (3 × 25 mL) and the combined extracts were washed with brine and dried ($MgSO_4$). The crude amides **3** were purified by crystallization (hexane–Et_2O, 90:10) or by chromatography (silica gel, PE–Et_2O, 70:30).

(2*E*,4*E*)-*N*-Benzyl-3,5-diphenylpenta-2,4-dienamide (3a)
White solid; mp 152 °C.

IR (KBr): 3276, 3020, 2954, 1640, 1619, 1573 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.56 (d, *J* = 5.7 Hz, 2 H), 5.71 (s, 1 H), 6.09 (br s, NH), 6.55 (d, *J* = 16.3 Hz, 1 H), 7.28–7.48 (m, 15 H_{Ar}), 8.64 (d, *J* = 16.3 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.5, 120.6, 126.1, 127.3, 127.5, 127.8, 128.2, 128.5, 128.7, 128.9, 136.6, 138.3, 140.2, 152.4, 165.9.

MS (EI): *m*/*z* (%) = 339 (M^+, 8), 262 (31), 248 (76), 205 (89), 106 (79), 91 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{21}NO$: 339.1623; found: 339.1619.

(2*E*,4*E*)-*N*-Benzyl-3-phenyl-5-(trimethylsilyl)penta-2,4-dienamide (3b)
White solid; mp 118 °C.

IR (KBr): 3276, 3020, 2954, 1640, 1619, 1573 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.14 (s, 9 H), 4.59 (d, *J* = 5.7 Hz, 2 H), 5.76 (s, 1 H), 5.85 (br s, NH), 6.05 (d, *J* = 19.2 Hz, 1 H), 7.27–7.41 (m, 10 H_{Ar}), 8.15 (d, *J* = 19.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.95, 44.1, 121.5, 128.0, 128.4 (2 C), 128.5 (3 C), 129.2 (2 C), 129.5 (2 C), 138.7, 140.6, 140.7, 142.1, 153.1, 166.4.

MS (EI): *m*/*z* (%) = 335 (M^+, 2), 262 (10), 91 (39), 73 (17).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{25}NOSi$: 335.1705; found: 335.1708.

(2*E*,4*E*)-*N*-(1,2-Dimethylpropyl)-3-phenyl-5-(trimethylsilyl)penta-2,4-dienamide (3c)
White solid; mp 172 °C.

IR (KBr): 3275, 3023, 2957, 1645, 1620, 1570, 1524 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.14 (s, 9 H), 0.97 (d, *J* = 6.8 Hz, 3 H), 0.98 (d, *J* = 6.8 Hz, 3 H), 1.17 (d, *J* = 6.7 Hz, 3 H), 1.70–1.83 (m, 1 H), 3.99–4.09 (m, 1 H), 5.45 (br s, NH), 5.74 (s, 1 H), 6.03 (d, *J* = 19.2 Hz, 1 H), 7.32–7.41 (m, 5 H_{Ar}), 8.06 (d, *J* = 19.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.9, 18.1, 18.9, 19.1, 33.4, 50.3, 122.5, 128.4, 128.5 (2 C), 129.5 (2 C), 140.5, 140.6, 140.8, 152.1, 165.9.

MS (EI): *m*/*z* (%) = 315 (M^+, 2), 242 (100), 229 (23), 172 (49), 73 (17).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{29}NOSi$: 315.2018; found: 315.2021.

(2*Z*,4*E*)-*N*-(1-Phenylethyl)-5-(trimethylsilyl)penta-2,4-dienamide (3d)
White solid; mp 94–96 °C.

IR (KBr): 3268, 3034, 2958, 1635, 1615, 1562, 1538, 1265, 1243 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.07 (s, 9 H), 1.49 (d, *J* = 7 Hz, 3 H), 5.18 (dq, *J* = 7.1, 7 Hz, 1 H), 5.53 (d, *J* = 11.3 Hz, 1 H), 5.78 (br s, 1 H), 6.13 (d, *J* = 18.4 Hz, 1 H), 6.35 (dd, *J* = 11.3, 10.7 Hz, 1 H), 7.25–7.32 (m, 5 H_{Ar}), 7.80 (dd, *J* = 18.4, 10.7 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.0, 22.2, 49.1, 121.0, 126.7 (2 C), 128.1, 129.1 (2 C), 140.0, 143.6, 143.9, 144.4, 165.6.

MS (EI): *m*/*z* (%) = 273 (M^+, 4), 200 (60), 154 (22), 120 (16), 105 (56), 96 (100), 79 (24), 77 (23).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{23}NOSi$: 273.1549; found: 273.1547.

(2*E*,4*E*)-3-(Methoxymethyl)-*N*-(3-methoxyphenyl)-5-(trimethylsilyl)penta-2,4-dienamide (3e)
White solid; mp 188–190 °C.

IR (KBr): 3283, 3097, 2963, 2836, 1664, 1604, 1524, 1484, 1214 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.09 (s, 9 H), 3.40 (s, 3 H), 3.73 (s, 3 H), 4.22 (s, 2 H), 6.00 (s, 1 H), 6.16 (d, *J* = 19.7 Hz, 1 H), 6.63 (br s, 1 H), 6.96–7.37 (m, 4 H_{Ar}), 7.86 (d, *J* = 19.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.10, 54.1, 59.1, 72.2, 119.3, 128.0, 128.3 (2 C), 129.2 (2 C), 135.8, 138.6, 138.8, 146.2, 166.6.

MS (EI): *m*/*z* (%) = 246 ($M^+ - SiMe_3$, 3), 244 (71), 151 (9), 73 (100), 45 (12).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{25}NO_3Si$: 319.1614; found: 319.1619.

(2*Z*,4*E*)-*N*-Benzyl-3-methyl-5-(trimethylsilyl)pent-2,4-dienamide (3f)
White solid; mp 116–118 °C.

IR (KBr): 3271, 3025, 2955, 1642, 1618, 1569, 1522 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.08 (s, 9 H), 1.91 (s, 3 H), 4.46 (d, *J* = 5.7 Hz, 2 H), 5.64 (s, 1 H), 5.80 (br s, 1 H), 6.20 (d, *J* = 19.2 Hz, 1 H), 7.26–7.29 (m, 5 H), 7.94 (d, *J* = 19.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.9, 20.9, 43.9, 121.1, 127.9, 128.3, 129.2 (2 C), 137.0 (2 C), 138.7, 141.1, 147.3, 166.6.

MS (EI): *m*/*z* (%) = 273 (M^+, 3), 201 (13), 200 (92), 91 (100), 75 (13).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{23}NOSi$: 273.1549; found: 273.1546.

(2*Z*,4*E*)-*N*-(3-Methoxyphenyl)-3-methyl-5-(trimethylsilyl)penta-2,4-dienamide (3g)
White solid; mp 84–86 °C.

IR (KBr): 3252, 3097, 2953, 1645, 1609, 1496, 1211 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.08 (s, 9 H), 1.95 (s, 3 H), 3.74 (s, 3 H), 5.75 (s, 1 H), 6.26 (d, *J* = 19.2 Hz, 1 H), 6.61 (br s, 1 H), 7.00–7.27 (m, 3 H_{Ar}), 7.41–7.46 (m, 1 H_{Ar}), 7.98 (d, *J* = 19.2 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.50, 21.1, 55.7, 106.1, 110.7, 112.8, 121.5, 130.0, 138.0, 139.9, 141.1, 149.1, 160.6, 166.8.

MS (EI): *m*/*z* (%) = 289 (M^+, 5), 216 (70), 123 (14), 75 (11), 73 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{23}NO_2Si$: 289.1498; found: 289.1492.

(2*Z*,4*E*)-*N*-Benzyl-3-methylpenta-2,4-dienamide (3h)
White solid; mp 104–106 °C.

IR (KBr): 3305, 3064, 3031, 2927, 2857, 1644, 1602, 1538, 1454, 1378, 1268 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.13 (s, 3 H), 4.57 (d, *J* = 5.7 Hz, 2 H), 5.70 (s, 1 H), 6.88 (d, *J* = 16.4 Hz, 1 H), 7.31–7.58 (m, 10 H), 8.51 (d, *J* = 16.4 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.3, 43.9, 121.0, 126.7, 127.7, 128.0, 128.3, 128.8, 129.0, 129.2, 134.5, 137.3, 139.0, 147.2, 166.7.

MS (EI): *m*/*z* (%) = 277 (M^+, 12), 128 (58), 91 (100), 65 (30).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{19}NO$: 277.36; found: 277. 35.

(2*Z*,4*E*)-3,6-Dimethylhepta-2,4-dienamide (3i)
White solid; mp 100–102 °C.

IR (KBr): 3310, 3097, 2965, 2833, 1658, 1612, 1214 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.07 (d, *J* = 6 Hz, 6 H), 1.99 (s, 3 H), 2.45–2.55 (m, 1 H), 5.55 (br s, 2 H), 5.60 (s, 1 H), 6.03 (dd, *J* = 16, 6 Hz, 1 H), 7.53 (d, *J* = 16 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.5, 22.8 (2 C), 32.3, 118.4, 125.3, 145.2, 148.7, 169.4.

MS (EI): *m*/*z* (%) = 153 (M^+, 2), 110 (100), 109 (3), 95 (7), 67 (14).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_9H_{15}NO$: 153.1154; found: 153.1158.

(2*Z*,4*E*)-*N*,*N*-Diisopropyl-3-methyl-5-phenylpenta-2,4-dienamide (3j)
White solid; mp 78–80 °C.

IR (KBr): 3024, 2972, 1616, 1444, 1379, 1324 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.01 (d, *J* = 6.4 Hz, 6 H), 1.39 (d, *J* = 6.4 Hz, 6 H), 1.92 (s, 3 H), 3.39–3.43 (m, 1 H), 3.95–3.99 (m, 1 H), 5.82 (s, 1 H), 6.56 (d, *J* = 16.2 Hz, 1 H), 7.05–7.33 (m, 6 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.0, 19.9, 45.1, 49.2, 124.2, 125.9, 126.1 (2 C), 127.1, 127.9 (2 C), 130.7, 136.3, 138.2, 166.7.

MS (EI): *m*/*z* (%) = 271 (M^+, 8), 256 (18), 228 (19), 171 (100), 128 (84).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{25}NO$: 271.1936; found: 271.1933.

(2*Z*)-*N*-Benzyl-3-methylpenta-2,4-dienamide (3k)
White solid; mp 80–82 °C.

IR (KBr): 3275, 3019, 2949, 1647, 1612, 1558 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.92 (s, 3 H), 4.42 (d, *J* = 5.6 Hz, 2 H), 5.33 (d, *J* = 11 Hz, 1 H), 5.47 (d, *J* = 17.5 Hz, 1 H), 5.61 (s, 1 H), 5.90 (br s, NH), 7.19–7.33 (m, 5 HAr), 7.81 (dd, *J* = 11, 17.5 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.0, 44.0, 119.7, 121.2, 128.0, 129.3 (2 C), 129.3 (2 C), 134.8, 138.5, 147.0, 166.5.

MS (EI): *m*/*z* (%) = 201 (M^+, 9), 186 (23), 106 (89), 95 (92), 91 (100), 77 (78).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{15}NO$: 201.1154; found: 201.1160.

(*E*)-*N*-Benzyl-2-styrylbenzamide (3l)[10]
White solid; mp 126 °C.

IR (KBr): 3309, 3057, 2924, 1644, 1531, 1422, 1304 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.64 (d, *J* = 5.7 Hz, 2 H), 6.2 (br s, 1 H), 7.03 (d, *J* = 16 Hz, 1 H), 7.26–7.55 (m, 14 H_{Ar}), 7.69 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 44.7, 126.5, 126.8, 127.4, 128.1, 128.2, 128.3, 128.5, 128.6, 129.3, 129.4, 130.8, 132.1, 136.0, 136.1, 137.5, 138.8, 171.0.

MS (EI): *m*/*z* (%) = 313 (M^+, 27), 222 (82), 208 (32), 178 (72), 91 (100), 77 (30).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{22}H_{19}NO$: 313.1467; found: 313.1471.

***N*-Benzyl-2-[(*E*)-hept-1-enyl]benzamide (3m)**
White liquid.

IR (neat): 3305, 3027, 1648, 1560 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.0 Hz, 3 H), 1.23–1.27 (m, 6 H), 2.09–2.13 (m, 2 H), 4.44 (d, *J* = 6 Hz, 2 H), 6.10 (dt, *J* = 16.6, 7.6 Hz, 1 H), 6.66 (d, *J* = 16.6 Hz, 1 H), 6.75–6.78 (m, 1 H), 7.05–7.45 (m, 9 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7, 22.2, 28.5, 31.1, 32.7, 43.4, 125.8, 126.2, 126.8, 126.9, 127.1, 127.4, 128.1, 129.5, 133.6, 134.3, 135.5, 138.0, 169.2.

MS (EI): *m*/*z* (%) = 307 (M^+, 5), 236 (15), 216 (15), 115 (15), 91 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{25}NO$: 307.1936; found: 307.1939.

***N*-Benzyl-2-[(*E*)-2-(trimethylsilyl)vinyl]benzamide (3n)**
White solid; mp 107 °C.

IR (KBr): 3285, 3064, 2954, 2870, 1638, 1528, 1455, 1247 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.12 (s, 9 H), 4.35 (d, *J* = 6 Hz, 2 H), 6.36 (d, *J* = 19 Hz, 1 H), 7.07–7.31 (m, 9 H_{Ar}), 7.49 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –1.7, 43.2, 125.4, 127.7, 126.8, 126.9, 127.2, 128.0, 129.2, 132.0, 134.8, 136.0, 138.0, 140.6, 169.0.

MS (EI): *m*/*z* (%) = 309 (M^+, 3), 236 (54), 222, 178, 91 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{23}NOSi$: 309.1549; found: 309.1553.

Enynamides 6a–e; General Procedure
$PdCl_2(PPh_3)_2$ (0.1 mmol) was added to a stirred DMF soln (10 mL) of alkyne (2.4 mmol) and Et_3N (4.8 mmol) then after 5 min (*Z*)-*N*-benzyl-3-iodoalk-2-enamide (2 mmol) and CuI (0.2 mmol) were added to the soln. The mixture was stirred at r.t. for 4 h then hydrolyzed with sat. NH_4Cl (20 mL). After the usual workup the crude product was purified by column chromatography (silica gel, PE–Et_2O, 60:40).

(*Z*)-*N*-Benzyl-5-phenylpent-2-en-4-ynamide (6a)
White solid; mp 108–110 °C.

IR (KBr): 3490, 3045, 2245, 1670, 1620 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.62 (d, *J* = 5.3 Hz, 2 H), 6.27 (s, 2 H), 7.04–7.41 (m, 10 H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 44.6, 85.6, 101.2, 116.1, 122.0, 128.3, 128.9, 129.1 (2 C), 129.5, 130.1 (2 C), 132.3 (2 C), 134.1 (2 C), 138.3, 165.1.

MS (EI): *m*/*z* (%) = 261 (M^+, 100), 260 (66), 91 (90), 77 (55), 65 (25).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{15}NO$: 261.1154; found: 261.1159.

(*Z*)-*N*-Benzyl-3-methyl-5-phenylpent-2-en-4-ynamide (6b)
White solid; mp 116–118 °C.

IR (KBr): 3485, 3045, 2240, 1665, 1615 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.16 (d, *J* = 1.4 Hz, 3 H), 4.61 (d, *J* = 5.6 Hz, 2 H), 6.15 (d, *J* = 1.4 Hz, 1 H), 7.06–7.39 (m, 10 H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.4, 44.4, 87.5, 100.3, 121.8 126.8, 128.0, 128.6 (2 C), 128.9 (2 C), 129.2 (2 C), 129.7, 130.2, 132.0 (2 C), 138.5, 165.3.

MS (EI): *m*/*z* (%) = 275 (M^+, 64), 274 (44), 115 (92), 91 (100), 51 (17).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{17}NO$: 275.1310; found: 275.1317.

(*Z*)-*N*-Benzyl-3,5-diphenylpent-2-en-4-ynamide (6c)
Colorless prisms; mp 128–130 °C.

IR (KBr): 3487, 3045, 2245, 1670, 1615 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.68 (d, *J* = 5.8 Hz, 2 H), 6.72 (s, 1 H), 7.14–7.75 (m, 15 H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 44.6, 86.3, 102.0, 121.7, 127.3, 128.0, 128.2, 128.7 (2 C), 128.9 (2 C), 129.1 (2 C), 129.3 (2 C), 129.5 (2 C), 130.0 (2 C), 132.0, 137.5, 138.4, 165.4.

MS (EI): *m*/*z* (%) = 337 (M^+, 21), 246 (73), 202 (100), 201 (26), 91 (72).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{19}NO$: 337.1467; found: 337.1470.

(*Z*)-*N*-Benzyl-3-methyl-5-(trimethylsilyl)pent-2-en-4-ynamide (6d)
White solid; mp 131–133 °C.

IR (KBr): 3488, 3040, 2241, 1673, 1618 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.08 (s, 9 H), 2.05 (d, *J* = 1.2 Hz, 3 H), 4.57 (d, *J* = 5.4 Hz, 2 H), 6.11 (q, *J* = 1.2 Hz, 1 H), 7.26–7.37 (m, 5 H_{Ar}), 7.7 (br s, NH).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.2 (3 C), 25.2, 44.0, 103.1, 107.1, 126.4, 128.0, 128.3 (2 C), 129.1 (2 C), 131.4, 138.5, 165.1.

MS (EI): *m*/*z* (%) = 271 (M^+, 8), 180 (27), 106 (44), 91 (100), 77 (15).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{21}NOSi$: 271.1392; found: 271.1396.

(*Z*)-*N*-Benzyl-3,6-dimethyl-6-(tetrahydro-2*H*-pyran-2-yloxy)hept-2-en-4-ynamide (6e)
White solid; mp 71–73 °C.

IR (KBr): 3475, 3050, 2243, 1660, 1610 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.34–1.79 (m, 12 H), 2.04 (s, 3 H), 3.44–3.48 (m, 1 H), 3.87–3.91 (m, 1 H), 4.56 (d, *J* = 5.5 Hz, 2 H), 4.90–4.93 (m, 1 H), 6.07 (s, 1 H), 7.20–7.35 (m, 5 H_{Ar}), 7.57 (br s, NH).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.4, 25.5, 25.7, 29.6, 30.2, 32.1, 43.9, 63.3, 71.0, 82.1, 96.1, 103.4, 126.2, 127.8, 128.3 (2 C), 129.0 (2 C), 130.5, 139.0, 165.1.

MS (EI): *m*/*z* (%) = 341 (M^+, 4), 240 (28), 150 (27), 134 (33), 91 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{27}NO_3$: 341.1396; found: 341.1388.

5-Alkyl(aryl)idene-1,5-dihydro-2*H*-pyrrol-2-ones 4a–k, 5a–c and 5-[Iodoalkyl(aryl)idene]-1,5-dihydro-2*H*-pyrrol-2-ones 7a–d; General Procedure
ICl (1.7 g, 10.5 mmol) in anhyd CH_2Cl_2 (10 mL) was added dropwise at 0 °C to dienamide **3a**–**k** (or enynamide **6a**–**e**) (10 mmol). Stirring was then maintained at r.t. for 3 h in darkness, the mixture was hydrolyzed by dropwise addition of 5% $Na_2S_2O_3$ soln until the mixture became clear. The soln was then extracted with CH_2Cl_2 (3 × 15 mL) and dried ($MgSO_4$). After evaporation of the solvent, the products were obtained after purification by flash column chromatography (silica gel, PE–Et_2O–Et_3N, 80:19:1) or by crystallization (Et_2O) to yield **4a**–**k** or **7a**–**e**.

(*Z*)-1-Benzyl-5-benzylidene-4-phenyl-1,5-dihydro-2*H*-pyrrol-2-one (4a)
Colorless liquid; yield: 55%.

IR (neat): 2955, 1679, 1610 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.90 (s, 2 H), 7.39–7.88 (m, 16 H), 8.29 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 46.5, 105.6, 106.4, 126.4 (2 C), 127.9 (2 C), 128.3 (2 C), 129, 129.6 (2 C), 129.7, 130 (2 C), 130.3 (2 C), 133.1, 133.3, 133.6, 135.1, 156.4, 160, 165.

MS (EI): *m*/*z* (%) = 337 (M^+, 6), 220 (21), 91 (100), 77 (17), 65 (16).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{24}H_{19}NO$: 337.1467; found: 337.1471.

(*Z*)-1-Benzyl-4-phenyl-5-[(trimethylsilyl)methylene]-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-4b]
White liquid; yield: 80%.

IR (neat): 2957, 1680, 1613 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.3 (s, 9 H), 4.79 (s, 2 H), 5.15 (s, 1 H), 6.52 (s, 1 H), 7.33–7.49 (m, 9 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.2 (3 C), 53, 106, 124, 128.2, 129.5 (2 C), 129.8 (2 C), 130 (2 C), 130.2 (2 C), 131, 132.3, 140.7, 149.7, 159.8, 162.6.

MS (EI): *m*/*z* (%) = 333 (M^+, 10), 305 (52), 91 (100), 73 (26), 65 (16).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{23}NOSi$: 333.1549; found: 333.1544.

(*E*)-1-Benzyl-4-phenyl-5-[(trimethylsilyl)methylene]-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-4b]
^1H NMR (200 MHz, $CDCl_3$): δ = 0.34 (s, 9 H), 4.88 (s, 2 H), 6.29 (s, 1 H), 7.35–7.60 (m, 9 H), 7.72 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.1 (3 C), 50.8, 110.3, 119.8, 127.6, 128.5 (2 C), 129 (2 C), 129.2 (2 C), 129.5 (2 C), 130.7, 131, 137, 152.4, 161.6, 164.4.

(*Z*)-1-(1,2-Dimethylpropyl)-4-phenyl-5-[(trimethylsilyl)methylene]-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-4c]
White liquid; yield: 77%.

IR (neat): 2960, 1677, 1612 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.36 (s, 9 H), 1.10 (d, *J* = 6.7 Hz, 3 H), 1.12 (d, *J* = 6.7 Hz, 3 H), 1.55 (d, *J* = 6.7 Hz, 3 H), 2.10–2.27 (m, 1 H), 3.93–4.08 (m, 1 H), 6.27 (s, 1 H), 7.52–7.62 (m, 5 H), 7.75 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.03 (3 C), 17.2, 19.0, 19.6, 33.3, 59.0, 115.1, 125.5, 129, 129.3 (2 C), 130 (2 C), 132.3, 156.1, 160.1, 170.3.

MS (EI): *m*/*z* (%) = 313 (M^+, 2), 270 (60), 75 (48), 73 (75), 43 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{27}NOSi$: 313.1862; found: 313.1859.

(*E*)-1-(1,2-Dimethylpropyl)-4-phenyl-5-[(trimethylsilyl)methylene]-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-4c]
^1H NMR (200 MHz, $CDCl_3$): δ = 0.34 (s, 9 H), 0.95 (d, *J* = 6.7 Hz, 3 H), 0.96 (d, *J* = 6.7 Hz, 3 H), 1.46 (d, *J* = 6.7 Hz, 3 H), 2.10–2.27 (m, 1 H), 3.91–4.05 (m, 1 H), 5.8 (s, 1 H), 7.54–7.65 (m, 5 H), 7.35 (s, 1 H).

(*Z*)-1-(1-Phenylethyl)-5-[(trimethylsilyl)methylene]-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-4d]
White liquid; yield: 58%; mixture of isomers.

IR (neat): 2953, 2918, 1673, 1617, 1256 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.21 (s, 9 H), 1.52 (d, *J* = 6.7 Hz, 3 H), 4.84 (s, 1 H), 5.03 (q, *J* = 6.7 Hz, 1 H), 6.40 (d, *J* = 5.5 Hz, 1 H), 6.74 (d, *J* = 5.5 Hz, 1 H), 7.31–7.33 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.04 (3 C), 25, 57.4, 105.8, 126.9, 127, 127.2, 129, 137.1, 146, 160.2, 163.2.

MS (EI): *m*/*z* (%) = 271 (M^+, 6), 105 (100), 79 (13), 77 (11).

(*E*)-1-(1-Phenylethyl)-5-[(trimethylsilyl)methylene]-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-4d]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.17 (s, 9 H), 1.52 (d, *J* = 6.7 Hz, 3 H), 4.84 (s, 1 H), 5.03 (q, *J* = 6.7 Hz, 1 H), 6.49 (d, *J* = 5.7 Hz, 1 H), 6.96 (d, *J* = 5.7 Hz, 1 H), 7.31–7.51 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.03, 24.7, 57.0, 104.5, 126.8, 126.7 (2 C), 127, 129.2 (2 C), 135.2, 146, 159.4, 161.6.

(*Z*)-1-Benzyl-4-methyl-5-[(trimethylsilyl)methylene]-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-4e]

White liquid; yield: 78%.

IR (neat): 2954, 1672, 1611 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.21 (s, 9 H), 1.98 (s, 3 H), 4.64 (s, 2 H), 4.85 (s, 1 H), 6.18 (s, 1 H), 7.19–7.31 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.04 (3 C), 12.3, 52.2, 103.5, 117.8, 127.2, 128.4 (2 C), 129 (2 C), 139.8, 147.5, 161.6, 164.3.

MS (EI): *m*/*z* (%) = 271 (M^+, 4), 243 (22), 91 (100), 73 (16), 65 (20).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{21}NOSi$: 271.1392; found: 271.1397.

(*E*)-1-Benzyl-4-methyl-5-[(trimethylsilyl)methylene]-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-4e]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.20 (s, 9 H), 2.05 (s, 3 H), 4.65 (s, 2 H), 5.23 (s, 1 H), 6.56 (s, 1 H), 7.21–7.33 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.17 (3 C), 14.1, 51, 108.4, 121.1, 127.9, 128.4 (2 C), 129.1 (2 C), 138.2, 150, 163.8, 164.6.

(*Z*)-1-(3-Methoxyphenyl)-4-methyl-5-[(trimethylsilyl)methylene]-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-4f]

White liquid; yield: 50%.

IR (neat): 2941, 1670, 1614, 1589, 1476, 1310 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.10 (s, 9 H), 2.02 (s, 3 H), 3.75 (s, 3 H), 4.93 (s, 1 H), 6.25 (s, 1 H), 6.65 (dd, *J* = 8.2, 2.6 Hz, 1 H), 6.76 (dd, *J* = 2.6, 2.0 Hz, 1 H), 6.84 (dd, *J* = 8, 2.0 Hz, 1 H), 7.21 (dd, *J* = 8.2, 8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.10 (3 C), 12.3, 55.5, 103.5, 109.7, 111, 114.8, 116.7, 129.5, 147.0, 149.6, 158.6, 160.2, 164.5.

MS (EI): *m*/*z* (%) = 287 (M^+, 52), 272 (28), 258 (93), 77 (36), 73 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{21}NO_2Si$: 287.1342; found: 287.1338.

(*E*)-1-(3-Methoxyphenyl)-4-methyl-5-[(trimethylsilyl)methylene]-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-4f]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.28 (s, 9 H), 2.0 (s, 3 H), 3.75 (s, 3 H), 5.01 (s, 1 H), 6.25 (s, 1 H), 6.48–6.66 (m, 2 H), 7.11–7.22 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.10 (3 C), 12.3, 55.5, 104.6, 108.3, 111.0, 115.6, 123.5, 130.1, 147.8, 149.1, 160.6, 163.8, 164.5.

(*Z*)-4-(Methoxymethyl)-1-(3-methoxyphenyl)-5-[(trimethylsilyl)methylene]-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-4g]

White liquid; yield: 51%.

IR (neat): 2953, 1664, 1612, 1588, 1473, 1254 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.34 (s, 9 H), 3.41 (s, 3 H), 3.76 (s, 3 H), 4.30 (s, 2 H), 4.93 (s, 1 H), 6.14 (s, 1 H), 6.37–7.22 (m, 4 H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 1.7 (3 C), 55.7, 59.4, 67, 104.6, 109.7, 111.4 114.7, 116.7, 129.5, 147.2, 149.3, 158.3, 161.7, 164.1.

MS (EI): *m*/*z* (%) = 317 (M^+, 21), 288 (25), 92 (27), 77 (36), 73 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{23}NO_3Si$: 317.1447; found: 317.1454.

(*E*)-4-(Methoxymethyl)-1-(3-methoxyphenyl)-5-[(trimethylsilyl)methylene]-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-4g]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.10 (s, 9 H), 3.06 (s, 3 H), 3.36 (s, 3 H), 4.24 (s, 2 H), 4.97 (s, 1 H), 6.14 (s, 1 H), 6.37–7.22 (m, 4 H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.2, 55.7, 59.5, 67.1, 105.6, 108.2, 110.2, 115.5, 124.1, 130.1, 147.4, 149.5, 160.3, 160.6, 164.2.

(*Z*)-1-Benzyl-5-benzylidene-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-4h]

Yield: 70%.

IR (neat): 3063, 2929, 1668, 1531, 1455, 1261 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 4.80 (s, 2 H), 6.30 (s, 1 H), 7.20–7.55 (m, 9 H), 7.62–7.75 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.5, 51.7, 102.5, 116.35, 121.6, 125.2, 126.0, 126.8, 127.2, 129.8, 130.5, 132.8, 143.9, 147.5, 153.7, 156.1.

MS (EI): *m*/*z* (%) = 275 (M^+, 31), 91 (100), 65 (15).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{17}NO$: 275.1310; found: 275.1307.

(*Z*)-2-Benzyl-3-benzylidene-2,3-dihydro-1*H*-isoindol-1-one [(*Z*)-5a][50]

Colorless liquid; yield: 50%.

IR (neat): 3418, 3062, 1663, 1635, 1605, 1494, 1452, 1340 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.92 (s, 2 H), 6.67 (s, 1 H), 7.28–7.60 (m, 11 H), 7.79 (m, 2 H), 8.36 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 50.0, 100.8, 124.1, 124.6, 125.4, 126.4, 126.8, 127.6, 127.8, 128.3, 128.6, 129.3, 131.6, 132.9, 133.1, 142.0, 151.1, 154.0.

MS (EI): *m*/*z* (%) = 311 (M^+, 35), 147 (26), 105 (31), 91 (100).

(*E*)-2-Benzyl-3-benzylidene-2,3-dihydro-1*H*-isoindol-1-one [(*E*)-5a]

IR (neat): 3422, 3062, 1705, 1655, 1637, 1613, 1493, 1450, 1347 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.01 (s, 2 H), 6.22 (s, 1 H), 7.32–7.85 (m, 14 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.2, 102.2, 119.5, 123.3, 126.8, 127.3, 127.9, 128.4, 128.7, 129.0, 129.2, 129.5, 131.7, 134.1, 136.0, 140.3, 148.0, 156.0.

(*Z*)-2-Benzyl-3-hexylidene-2,3-dihydro-1*H*-isoindol-1-one [(*Z*)-5b][51]

White liquid; yield: 60%.

IR (neat): 3422, 3062, 2928, 2858, 1702, 1664, 1472, 1351, 1265 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.96 (m, 3 H), 1.38–1.47 (m, 6 H), 2.46–2.56 (m, 2 H), 4.86 (s, 2 H), 5.67 (t, *J* = 8 Hz, 1 H), 7.27–7.60 (m, 7 H), 7.75 (d, *J* = 7.6 Hz, 1 H), 7.95 (d, *J* = 7.1 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9, 22.4, 25.6, 29.5, 31.4, 51.3, 108.2, 122.6, 123.2, 126.4, 127.8, 128.2, 128.9, 131.4, 135.9, 140.5, 148.8, 155.5.

MS (EI): *m*/*z* (%) = 305 (M^+, 17), 238 (22), 160 (23), 91 (100).

(*E*)-2-Benzyl-3-hexylidene-2,3-dihydro-1*H*-isoindol-1-one [(*E*)-5b]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.96 (m, 3 H), 1.38–1.47 (m, 6 H), 2.46–2.56 (m, 2 H), 4.89 (s, 2 H), 5.38 (t, *J* = 8.2 Hz, 1 H), 7.27–7.60 (m, 7 H), 7.75 (d, *J* = 7.6 Hz, 1 H), 7.80 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9, 22.4, 25.4, 29.0, 31.4, 51.7, 103.5, 119.1, 123.0, 126.5, 127.9, 128.2, 128.8, 131.3, 135.9, 140.5, 148.8, 155.5.

(*Z*)-2-Benzyl-3-[(trimethylsilyl)methylene]-2,3-dihydro-1*H*-isoindol-1-one [(*Z*)-5c][52]

White liquid; yield: 60%.

IR (neat): 3426, 2955, 2898, 1780, 1701, 1623, 1495, 1472, 1347, 1250 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.35 (s, 9 H), 4.84 (s, 2 H), 5.47 (s, 1 H), 7.27–7.57 (m, 7 H), 7.73 (d, *J* = 8 Hz, 1 H), 7.92 (d, *J* = 7 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.5, 51.1, 99.8, 122.1, 122.8, 126.1, 127.4, 127.8, 129.3, 130.7, 133.0, 135.4, 139.8, 154.8, 157.4.

MS (EI): *m*/*z* (%) = 307 (M^+, 100), 279 (10), 219 (8), 147 (10), 91 (64).

(*E*)-2-Benzyl-3-[(trimethylsilyl)methylene]-2,3-dihydro-1*H*-isoindol-1-one [(*E*)-5c]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.35 (s, 9 H), 4.91 (s, 2 H), 5.99 (s, 1 H), 7.27–7.57 (m, 8 H), 7.70–7.75 (m, 1 H), 7.90–7.93 (m, 1 H).

1-Benzyl-5-(α-iodobenzylidene)-1,5-dihydro-2*H*-pyrrol-2-one (7a)

Colorless liquid; yield: 65%; mixture of isomers, *E*/*Z* (90:10).

(*E*)-1-Benzyl-5-(α-iodobenzylidene)-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-7a]

IR (neat): 3063, 2967, 1673, 1605 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.67 (s, 2 H), 6.60 (d, *J* = 5.6 Hz, 1 H), 7.28–7.46 (m, 8 H), 7.53 (d, *J* = 5.6 Hz, 1 H), 7.71–7.76 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 52.8, 79.8, 127.6, 128.4, 128.6 (2 C), 128.8 (2 C), 129.1 (2 C), 129.5 (2 C), 131.2, 141.0, 153.3, 161.4.

MS (EI): *m*/*z* (%) = 387 (M^+, 10), 260 (16), 91 (100), 65 (10), 77 (36).

(*Z*)-1-Benzyl-5-(α-iodobenzylidene)-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-7a]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.72 (s, 2 H), 6.80 (d, *J* = 5.6 Hz, 1 H), 7.28–7.46 (m, 8 H), 7.65 (d, *J* = 5.6 Hz, 1 H), 7.71–7.76 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 53.3, 77.4, 128, 128.3, 128.8 (2 C), 129.0 (2 C), 129.2 (2 C), 129.4 (2 C), 131.0, 142.0, 156.8, 159.4.

1-Benzyl-5-(α-iodobenzylidene)-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one (7b)

Colorless liquid; yield: 79%; mixture of isomers, *E*/*Z* (65:35).

(*E*)-1-Benzyl-5-(α-iodobenzylidene)-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-7b]

IR (neat): 3065, 2964, 1677, 1603 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.55 (s, 3 H), 4.46 (s, 2 H), 6.47 (s, 1 H), 7.22–7.56 (m, 10 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.0, 52.5, 74.3, 127.1, 127.2, 128.3 (2 C), 128.5 (2 C), 128.8 (2 C), 129.8, 130.3 (2 C), 140.5, 141.6, 147.2, 152.3, 157.7.

MS (EI): *m*/*z* (%) = 401 (M^+, 1), 91 (100), 65 (18), 64 (17).

(*Z*)-1-Benzyl-5-(α-iodobenzylidene)-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-7b]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.61 (s, 3 H), 4.51 (s, 2 H), 6.34 (s, 1 H), 7.22–7.56 (m, 10 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.1, 54.6, 74.2, 126.9, 127.3, 128.0 (2 C), 128.6 (2 C), 128.8 (2 C), 129.3, 130.5 (2 C), 140.4, 141.1, 146.1, 152, 157.6.

1-Benzyl-5-[iodo(trimethylsilyl)methylene]-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one (7c)

Colorless liquid; yield: 75%; mixture of isomers, *E*/*Z* (85:15).

(*E*)-1-Benzyl-5-[iodo(trimethylsilyl)methylene]-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-7c]

IR (neat): 3063, 2967, 1673, 1602 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.36 (s, 9 H), 2.42 (s, 3 H), 4.67 (s, 2 H), 6.43 (s, 1 H), 7.31–7.36 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.86, 17.0, 52.6, 118.5, 125.7, 127.2, 128.2 (2 C), 129.0 (2 C), 140.4, 147.0, 158.8, 159.3.

MS (EI): *m*/*z* (%) = 397 (M^+, 1), 277 (10), 91 (100), 65 (15).

(*Z*)-1-Benzyl-5-[iodo(trimethylsilyl)methylene]-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-7c]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.34 (s, 9 H), 2.37 (s, 3 H), 4.68 (s, 2 H), 6.15 (s, 1 H), 7.31–7.36 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.60, 17.5, 54.6, 116.3, 123.0, 127.8, 128.0 (2 C), 129.0 (2 C), 140.5, 148.3, 158.6, 160.1.

1-Benzyl-5-(2-hydroxy-1-iodo-2-methylpropylidene)-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one (7d)

Colorless liquid; yield: 70%; mixture of isomers, *E*/*Z* (90:10).

(*E*)-1-Benzyl-5-(2-hydroxy-1-iodo-2-methylpropylidene)-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-7d]

IR (neat): 3410, 3060, 2957, 2927, 1681, 1603 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.61 (s, 6 H), 2.38 (d, *J* = 1.3 Hz, 3 H), 3.36 (s, OH), 4.67 (s, 2 H), 6.27 (q, *J* = 1.3 Hz, 1 H), 7.31–7.38 (m, 5 H_{Ar}).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.6, 29.2, 52.4, 75, 115.2, 124.6, 127.3, 128.0 (2 C), 129 (2 C), 140.1, 148, 148.6, 157.7.

MS (EI): *m*/*z* (%) = 383 (M^+, 3), 238 (11), 91 (100), 65 (14).

(*Z*)-1-Benzyl-5-(2-hydroxy-1-iodo-2-methylpropylidene)-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-7d]

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.61 (s, 6 H), 2.42 (d, *J* = 1.3 Hz, 3 H), 3.36 (s, OH), 4.63 (s, 2 H), 6.43 (q, *J* = 1.3 Hz, 1 H), 7.31–7.38 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.9, 29.3, 54.5, 75.2, 109.5, 123.3, 127.4, 128.3 (2 C), 129.2 (2 C), 140, 148.1, 149.5, 159.2.

Synthesis of 8a–f; General Procedure

An oven-dried Schlenk flask was evacuated and back-filled with argon and charged with EtOH (8 mL), toluene (10 mL), pyrrolone **7b** (5 mmol), and arylboronic acid (6 mmol). The flask was evacuated and back-filled with argon and then 1 M Na_2CO_3 (0.6 mL) and $Pd(PPh_3)_4$ (173 mg, 0.15 mmol, 3 mol%) were added. The mixture was stirred at 50 °C for 12 h, the soln was filtered through a Celite pad and the solvents were evaporated. The residue was extracted

with Et_2O and dried (anhyd $MgSO_4$). Products **8a–f** were obtained after purification by flash column chromatography (silica gel, PE–Et_2O–Et_3N, 80:19:1).

1-Benzyl-4-methyl-5-[α-(4-tolyl)benzylidene]-1,5-dihydro-2*H*-pyrrol-2-one (8a)
White liquid; yield: 71%; mixture of isomers, *E*/*Z* (90:10).

(*E*)-1-Benzyl-4-methyl-5-[α-(4-tolyl)benzylidene]-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-8a]
IR (neat): 3060, 3028, 2964, 1673, 1604 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.53 (d, *J* = 1.4 Hz, 3 H), 2.45 (s, 3 H), 4.74 (s, 2 H), 6.29 (q, *J* = 1.4 Hz, 1 H), 7.23–7.46 (m, 14 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.8, 21.8, 52.5, 115.8, 124.4, 127.1, 128.0, 128.3 (2 C), 128.4 (2 C), 128.8 (2 C), 129.5 (2 C), 130.6 (2 C), 131.6 (2 C), 135.3, 138.5, 139.3, 141.0, 148.0, 150.5, 160.1.

MS (EI): *m*/*z* (%) = 365 (M^+, 35), 275 (21), 274 (100), 105 (22), 65 (24).

(*Z*)-1-Benzyl-4-methyl-5-[α-(4-tolyl)benzylidene]-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-8a]
^1H NMR (200 MHz, $CDCl_3$): δ = 1.55 (d, *J* = 1.4 Hz, 3 H), 2.44 (s, 3 H), 4.73 (s, 2 H), 6.34 (q, *J* = 1.4 Hz, 1 H), 7.20–7.49 (m, 14 H).

1-Benzyl-4-methyl-5-[α-(3-thienyl)benzylidene]-1,5-dihydro-2*H*-pyrrol-2-one (8b)
Colorless liquid; yield: 65%; mixture of isomers, *E*/*Z* (75:25).

(*E*)-1-Benzyl-4-methyl-5-[α-(3-thienyl)benzylidene]-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-8b]
IR (neat): 3065, 3032, 2956, 1674, 1607 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.61 (d, *J* = 1.3 Hz, 3 H), 4.74 (s, 2 H), 6.29 (q, *J* = 1.3 Hz, 1 H), 7.01 (d, *J* = 5 Hz, 1 H), 7.24–7.53 (m, 12 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15, 52.6, 115.8, 124.8, 126.4, 126.7, 127.1, 128.1, 128.4, 129.0 (2 C), 130.2 (2 C), 130.5, 138, 138.5, 141.0, 147.8, 151.0, 159.6.

MS (EI): *m*/*z* (%) = 357 (M^+, 77), 266 (100), 234 (31), 91 (79), 65 (22).

(*Z*)-1-Benzyl-4-methyl-5-[α-(3-thienyl)benzylidene]-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-8b]
^1H NMR (200 MHz, $CDCl_3$): δ = 1.49 (d, *J* = 1.3 Hz, 3 H), 4.85 (s, 2 H), 6.24 (q, *J* = 1.3 Hz, 1 H), 7.22 (d, *J* = 5 Hz, 1 H), 7.32–7.48 (m, 12 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.5, 52.8, 116.5, 124, 125.2, 127, 127.2, 128.3 (2 C), 128.7, 128.8 (2 C), 129.0 (2 C), 129.4, 131.3 (2 C), 138.0, 140.3, 141.0, 148.1, 149.6, 159.7.

1-Benzyl-4-methyl-5-(4,4-dimethyl-1-phenylpent-2-enylidene)-1,5-dihydro-2*H*-pyrrol-2-one (8c)
White liquid; yield: 62%; mixture of isomers, *E*/*Z* (10:90).

(*Z*)-1-Benzyl-4-methyl-5-(4,4-dimethyl-1-phenylpent-2-enylidene)-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-8c]
IR (neat): 3061, 3029, 2967, 1678, 1601 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.08 (s, 9 H), 1.36 (d, *J* = 1.3 Hz, 3 H), 4.80 (s, 2 H), 5.37 (d, *J* = 16 Hz, 1 H), 6.14 (d, *J* = 1.3 Hz, 1 H), 6.96 (d, *J* = 16 Hz, 1 H), 7.21–7.51 (m, 10 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15, 30 (3 C), 34.3, 52.4, 121.3, 123.1, 124, 127, 128.3, 128.5 (2 C), 128.6 (2 C), 128.8 (2 C), 131.3 (2 C), 135.7, 141.2, 146.8, 148.6, 149.4, 159.5.

MS (EI): *m*/*z* (%) = 357 (M^+, 17), 300 (12), 266 (17), 91 (100), 65 (15).

(*E*)-1-Benzyl-4-methyl-5-(4,4-dimethyl-1-phenylpent-2-enylidene)-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-8c]
^1H NMR (200 MHz, $CDCl_3$): δ = 1.03 (s, 9 H), 1.39 (d, *J* = 1.3 Hz, 3 H), 4.65 (s, 2 H), 5.33 (d, *J* = 16 Hz, 1 H), 6.32 (d, *J* = 1.3 Hz, 1 H), 7.06 (d, *J* = 16 Hz, 1 H), 7.21–7.51 (m, 10 H).

1-Benzyl-5-[α-(4-bromophenyl)benzylidene]-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one (8d)
Colorless liquid: yield: 67%; mixture of isomers, *E*/*Z* (88:12).

(*E*)-1-Benzyl-5-[α-(4-bromophenyl)benzylidene]-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-8d]
IR (neat): 3061, 3029, 2967, 1678, 1601 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.56 (d, *J* = 1.3 Hz, 3 H), 4.77 (s, 2 H), 6.35 (q, *J* = 1.3 Hz, 1 H), 7.00–7.58 (m, 14 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.6, 52.5, 119.5, 120.0, 122.8, 125.2, 127.2, 128.5 (2 C), 128.6 (2 C), 129.0 (2 C), 130.3 (2 C), 130.4 (2 C), 130.6 (2 C), 131.8, 138.5, 140.4, 147.5, 151.0, 160.0.

MS (EI): *m*/*z* (%) = 429 (M^+, 13), 340 (14), 338 (14), 259 (16), 91 (100).

(*Z*)-1-Benzyl-5-[α-(4-bromophenyl)benzylidene]-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-8d]
^1H NMR (200 MHz, $CDCl_3$): δ = 1.50 (d, *J* = 1.3 Hz, 3 H), 4.71 (s, 2 H), 6.50 (q, *J* = 1.3 Hz, 1 H), 7.0–7.58 (m, 14 H).

1-Benzyl-5-[α-(3-chlorophenyl)benzylidene]-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one (8e)
Colorless liquid; yield: 60%; mixture of isomers, *E*/*Z*, (85:15).

(*E*)-1-Benzyl-5-[α-(3-chlorophenyl)benzylidene]-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one [(*E*)-8e]
IR (neat): 3064, 3031, 2965, 1673, 1604 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.55 (d, *J* = 1.3 Hz, 3 H), 4.76 (s, 2 H), 6.32 (q, *J* = 1.3 Hz, 1 H), 6.70 (d, *J* = 8.7 Hz, 1 H), 7.12 (d, *J* = 8.7 Hz, 1 H), 7.23–7.52 (m, 12 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0, 52.4, 120.6, 124.8, 127.2, 128.4 (2 C), 128.5 (2 C), 128.9 (2 C), 129.1 (2 C), 129.6, 130.6, 131.6, 132.0, 133.0, 135.0, 136.7, 138.6, 140.6, 147.8, 150.7, 156.5.

MS (EI): *m*/*z* (%) = 385 (M^+, 28), 296 (25), 294 (72), 91 (100), 65 (22).

(*Z*)-1-Benzyl-5-[α-(3-chlorophenyl)benzylidene]-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one [(*Z*)-8e]
^1H NMR (200 MHz, $CDCl_3$): δ = 1.59 (d, *J* = 1.3 Hz, 3 H), 4.70 (s, 2 H), 6.48 (q, *J* = 1.3 Hz, 1 H), 6.80 (d, *J* = 8.7 Hz, 1 H), 7.02 (d, *J* = 8.7 Hz, 1 H), 7.23–7.52 (m, 12 H).

1-Benzyl-5-(diphenylmethylene)-4-methyl-1,5-dihydro-2*H*-pyrrol-2-one (8f)
White liquid; yield: 75%; mixture of isomers, *E*/*Z* (88:12).

IR (neat): 3059, 3029, 2964, 1677, 1603 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.50 (d, *J* = 1.3 Hz, 3 H), 4.76 (s, 2 H), 6.29 (q, *J* = 1.3 Hz, 1 H), 7.26–7.48 (m, 15 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.7, 52.5, 115.3, 124.7, 127.1, 128.0, 128.4 (2 C), 128.6 (2 C), 128.8 (2 C), 129.9 (2 C), 130.6 (2 C), 131.7 (2 C), 138.3, 139.1, 141.1, 148.0, 150.6, 160.0.

MS (EI): *m*/*z* (%) = 351 (M^+, 24), 260 (91), 165 (29), 91 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{25}H_{21}NO$: 351.1623; found: 351.1621.

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