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# The fluoride ion-induced intramolecular conjugate addition of propargylsilanes to dihydropyridones. A novel method for the stereoselective construction of azabicyclic ring systems

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**Abstract**—The fluoride ion-induced intramolecular conjugate addition of propargylsilanes to dihydropyridones is reported. Our results revealed that tetrabutylammonium triphenyldifluorosilicate (TBAT), an air-stable, non-hygroscopic fluoride ion source, catalyzes cyclocondensation to provide the corresponding 1-vinylidene indolizidines in a high yield as single isomers, while Lewis acid catalysts were ineffective. The scope of this method was further investigated in the reactions leading to compounds with larger ring size. In these cases dihydropyridones with the propargylsilane located in the side-chain underwent cyclization to give 9-vinylidene quinolizidines with significantly lower yields.
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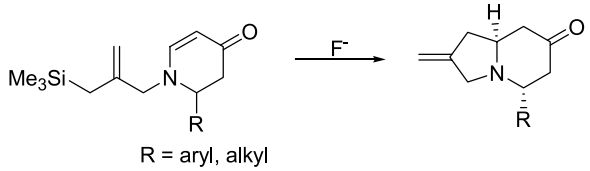
## 1. Introduction

The chemistry of propargylsilanes continues to be widely exploited in organic synthesis. The main interest in propargylsilanes relates to their ability to react with various electrophiles activated by a Lewis acid to form a new C–C bond.[1] With propargylsilanes, the addition of an electrophile provides a quite general route to allenes, which are emerging as versatile building blocks in organic synthesis.[2] The intramolecular cyclizations, involving a terminal propargylsilane function have been successfully employed in the stereospecific synthesis of polycyclic compounds.[3] The proper choice of Lewis acid can, in some cases, enable control of the stereoselectivity and prevent protodesilylation, which is a common drawback of such a reaction.

The fluoride ion is generally known to be a good activating reagent for organosilicon reagents, which readily generates reactive pentacoordinate silicates. In 1978, Hosomi and Sakurai[4] found that a fluoride ion source—tetrabutylammonium fluoride (TBAF) catalyzed the allylation of carbonyl compounds with allylsilanes to give the corresponding homoallyl alcohols. Recently, Wang et al.,[5] have found that TBAF (1 mol%) in the presence of 4 Å MS is an effective catalyst for the allylation of aromatic imines. Majetich et al.,[6] reported that the fluoride ion-catalyst is effective in the conjugate allylation of α,β-unsaturated esters, nitriles, and amides, a reaction, which cannot be achieved by the $TiCl_4$-promoted procedure. Occasionally, intramolecular conjugate allylation of α,β-unsaturated ketones is also catalyzed efficiently by TBAF.[7] In contrast to the reaction of allylsilanes, little is known about the reaction of propargylsilanes with electrophiles under fluoride ion catalysis. To our knowledge, the fluoride ion-promoted 1,4-addition of propargylsilanes to the α,β-unsaturated compounds has never been reported.

Recently,[8] we reported that the intramolecular fluoride-promoted allylation of the appropriate dihydropyridones proceeds in a conjugate fashion in good yield (Scheme 1). The Lewis acid catalyzed allylation fails, in marked contrast to the known efficiency of this method in the intermolecular allylation of dihydropyridones.[9]




**Scheme 1.**

*Keywords*: Conjugate addition; Fluoride ions; Propargylsilanes; Dihydropyridones.
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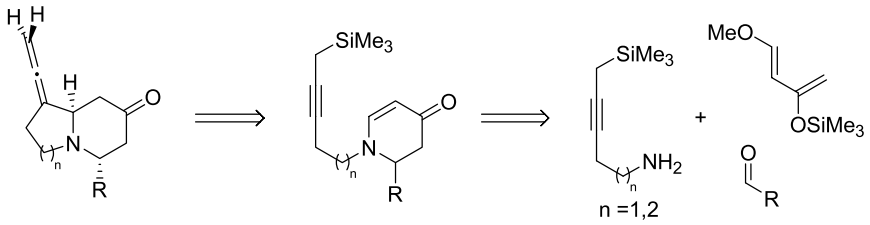



**Scheme 2.** Synthetic strategy.

We now report that the similar cyclocondensation of dihydropyridones with propargylsilanes located in the side-chain provides a concise protocol for the highly stereoselective construction of the vinylidene azabicyclic skeleton. The proposed reaction sequence consists of the Lewis acid-mediated addition of an imine to the silyloxy-diene followed by the fluoride ion-initiated intramolecular 1,4-addition of propargylsilanes to dihydropyridones (Scheme 2).

## 2. Results and discussion

The two amines **1**[10] and **2**[11] were employed for the construction of the desired dihydropyridones (Fig. 1).

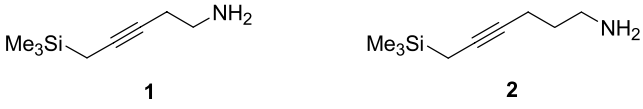



**Figure 1.**

These substrates were easily prepared in five steps using literature methods from 3-butyn-1-ol and 4-butyn-1-ol in 52 and 35% overall yield, respectively.

The propargylamine **1** was converted into the required Schiff bases **3** by treatment with series of different aldehydes in $CH_2Cl_2$ in the presence of molecular sieves (4 Å). These intermediates were not isolated. After exchange of the solvent, they were immediately subjected to the Lewis acid-mediated reaction with Danishefsky's diene **4**. We found that for aromatic and aliphatic imines of the type **3** the highest yield of dihydropyridones **5** were attained using $Yb(OTf)_3$ (0.1 equiv) as a Lewis acid with $CH_3CN$ as a solvent (Table 1).

The reactions of the imines **3** with dienes **4** shown in Table 1 take place smoothly to afford the corresponding adducts **5** in good yield. The aliphatic imines worked well, however, the dihydropyridones **5h** and **5i** were obtained in a slightly decreased yield.

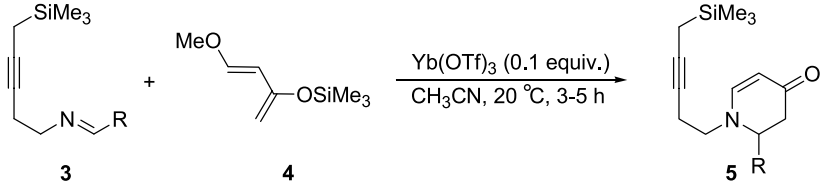
Since imines, particularly those derived from aliphatic aldehydes, are usually not stable, it is synthetically useful when they are generated in situ and allowed to react under one-pot reaction conditions. Recently, Kobayashi et al.[12] reported that $Yb(OTf)_3$ catalyzes the three-component coupling reaction between aldehydes, amines, and Danishefsky's diene to afford dihydropyridone derivatives.

Following this report, we studied the direct synthesis of dihydropyridones as one-pot reaction (Table 2).

As shown in Table 2, the modified procedure afforded the corresponding adducts in yields comparable to those obtained by the reaction of the pre-formed and isolated aldimines. The one-pot reaction can be carried out with various aldehydes, including aliphatic, aromatic, and heteroaromatic compounds.

Very recently we reported[8] that tetrabutylammonium triphenyldifluorosilicate (TBAT)[13] efficiently catalyzes the

**Table 1**. Lewis acid mediated synthesis of 2-substituted dihydropyridones[a]




| Entry | R | Product | Yield (%)[b] |
|---|---|---|---|
| 1 | Ph | **5a** | 82 |
| 2 | *p*-MePh | **5b** | 80 |
| 3 | *p*-MeOPh | **5c** | 78 |
| 4 | *p*-ClPh | **5d** | 86 |
| 5 | 2-Furyl | **5e** | 81 |
| 6 | 2-Pyridyl | **5f** | 76 |
| 7 | $PhCH_2OCH_2$ | **5g** | 89 |
| 8 | $CH_3(CH_2)_5$ | **5h** | 77 |
| 9 | *c*-$C_6H_{11}$ | **5i** | 70 |

[a] All reactions were conducted in $CH_3CN$ at 20 °C in the presence of 0.1 equiv $Yb(OTf)_3$.
[b] Isolated yield after chromatographic purification.

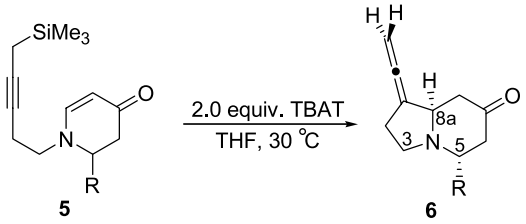
**Table 2**. Results of direct synthesis of 2-substituted dihydropyridones[a]

| Entry | R | Product | Time/h | Yield[b] (%) |
|---|---|---|---|---|
| 1 | Ph | **5a** | 5 | 80 |
| 2 | *p*-MePh | **5b** | 6 | 83 |
| 3 | *p*-MeOPh | **5c** | 4 | 81 |
| 4 | *p*-ClPh | **5d** | 5 | 79 |
| 5 | 2-Furyl | **5e** | 8 | 74 |
| 6 | 2-Pyridyl | **5f** | 9 | 72 |
| 7 | $PhCH_2OCH_2$ | **5g** | 2 | 88 |
| 8 | $CH_3(CH_2)_5$ | **5h** | 3 | 80 |
| 9 | *c*-$C_6H_{11}$ | **5i** | 3 | 77 |

[a] All reactions were conducted in $CH_3CN$ at 20 °C in the presence of 0.1 equiv $Yb(OTf)_3$.
[b] Isolated yield after chromatographic purification.

intramolecular conjugate allylation of various 2-substituted dihydropyridones with allylsilanes. To our satisfaction we found that the use of 2.0 equiv of TBAT resulted in a nearly quantitative formation of the corresponding vinylidene indolizidines (Table 3). Other fluoride ion sources such as CsF, KF or TBAF failed to promote the cyclization at all. It is important to note that none of the desired products could be obtained by treatment of respective dihydropyridones with Lewis acids such as $EtAlCl_2$, $TiCl_4$, $SnCl_4$, TMSOTf or $BF_3 \cdot Et_2O$.

**Table 3**. TBAT-initiated intramolecular conjugate addition of propargylsilane to dihydropyridones[a]




5 6

| Entry | R | Product | Time/h | Yield[b] (%) |
|---|---|---|---|---|
| 1 | Ph | **6a** | 1 | 95 |
| 2 | *p*-MePh | **6b** | 1 | 93 |
| 3 | *p*-MeOPh | **6c** | 2 | 97 |
| 4 | *p*-ClPh | **6d** | 2 | 98 |
| 5 | 2-Furyl | **6e** | 5 | 89 |
| 6 | 2-Pyridyl | **6f** | 5 | 92 |
| 7 | $PhCH_2OCH_2$ | **6g** | 2 | 89 |
| 8 | $CH_3(CH_2)_5$ | **6h** | 2 | 83 |
| 9 | *c*-$C_6H_{11}$ | **6i** | 2 | 86 |

[a] All reactions were conducted in THF at 30 °C in the presence of 2.0 equiv of TBAT.
[b] Isolated yield after chromatographic purification.

For all entries in Table 3, treatment of the 2-substituted dihydropyridones with 2.0 equiv of TBAT in THF at 30 °C led to the desired indolizidines (single diastereomer), as estimated from the $^1H$ and $^{13}C$ NMR data. It was observed that, in the case of the reaction of dihydropyridones **6e** and **6f** (R = furyl or pyridyl), longer reaction times (4–5 h) were needed to afford products in a high yield. When we used compounds containing aliphatic substituents **6h** and **6i** the yield was slightly decreased, compared to other dihydropyridones.

The relative stereochemistry at C5 and C8a was established with the aid of NOE experiments. Furthermore, the structure and relative stereochemistry of the cyclized product was unambiguously established by the single-crystal X-ray analysis.[14] As revealed in Figure 2, compound **6a** possesses the indolizidine skeleton and two hydrogens at C5 and C8a are trans to each other.

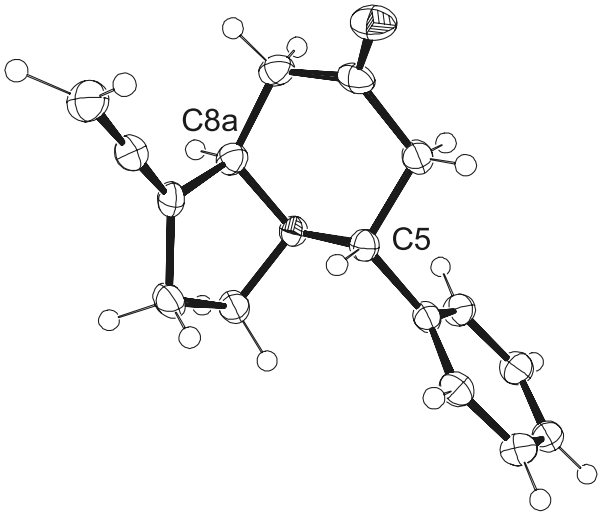



**Figure 2.** The X-ray structure of **6a**.

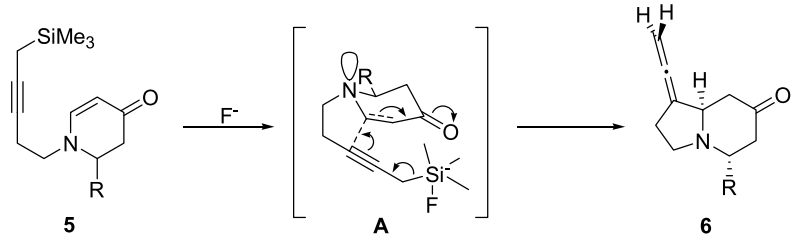
The stereochemical outcome of this cyclocondensation is rationalized in Scheme 3.

We propose that the cyclization proceeds through the transition state **A**, where the substituent R is located in the equatorial position while the nitrogen electron pair is in the axial orientation. The nucleophilic terminal of the double bond approaches exclusively anti to the R substituent leading to the compound **6** with trans-orientation between C5 and C8a protons.

The generality of this transformation was further tested with different ring size. The enaminones of the type **7** were prepared by the similar strategy as described earlier, starting from amine **2**.

For the compounds with a longer side chain the intramolecular 1,4-addition, under standard cyclization conditions (2.0 equiv TBAT in THF at 30 °C), led to the 9-vinylidene quinolizidines **8a** and **8b**, obtained as single diastereomers in 35 and 27% yield, respectively (Table 4). However, significant amounts of protodesilylation products were also observed. No cyclization occurred when compound containing an aliphatic substituent **7c** was used. Numerous attempts to affect the reaction outcome, such as applying alternative fluoride sources or selected Lewis acids, were unsuccessful and only protodesilylation products were observed.

The relative stereochemistry of **8a** was assigned by the NOE experiments. Upon irradiation of the proton at C4 no enhancement was observed for the proton at C9a. This clearly reveals that the two hydrogens at C4 and C9a are trans to each other. The 9-vinylidene quinolizidines have similar relative stereochemistry at bridgehead carbon atoms




**Scheme 3.** Fluoride ion-initiated intramolecular 1,4-addition of propargylsilane to dihydropyridones.

**Table 4**. TBAT-initiated synthesis of 9-vinylidene quinolizidines[a]


| Entry | R | Product | Time/h | Yield[b] (%) |
|---|---|---|---|---|
| 1 | (**7a**) Ph | **8a** | 2 | 35 |
| 2 | (**7b**) *p*-MeOPh | **8b** | 2 | 27 |
| 3 | (**7c**) $CH_3(CH_2)_5$ | **8c** | 2 | 0[c] |

[a] All reactions were conducted in THF at 30 °C in the presence of 2.0 equiv of TBAT.
[b] Isolated yield after chromatographic purification.
[c] Only protodesilylation products were observed.

as indolizidines discussed earlier. Thus, the similar rationalization for the stereochemical outcome observed in these cyclizations should be applicable as well.

## 3. Conclusions

A novel method for the stereoselective construction of vinylidene azabicyclic compounds has been described. It is based on the fluoride ion-induced intramolecular 1,4-addition of propargylsilanes to dihydropyridones. The structure and relative stereochemistry of the cyclization product, 1-vinylidene indolizidine, was confirmed by the NMR and X-ray analysis. The scope of this method was further investigated in the reactions leading to the compounds with larger ring size. However, the one carbon homologated compounds did not show the same cyclization behavior, and the expected 9-vinylidene quinolizidines were obtained in low yields.

## 4. Experimental

### 4.1. General

Column chromatography was performed on silica gel, Merck grade 60 (230–400 mesh). TLC plates were visualized with UV and staining with phosphomolybdic acid. $^1$H and $^{13}$C NMR spectra were recorded on Bruker AM500 (500 MHz) and Varian (400 MHz) spectrometers and the chemical shifts are reported in ppm from the solvent resonans ($CDCl_3$ 7.26 ppm). Infrared (IR) spectra were measured with a Perkin-Elmer FT-IR-1600 infrared spectrophotometer. High-resolution mass spectra were taken on a Mariner PerSeptive Biosystems mass spectrometer with time-of-flight (TOF) detector. Unless stated otherwise, all reagents and solvents were purchased from commercial sources and used without additional purification.

### 4.2. General procedure for the synthesis of imines

To a solution of amine **1** or **2** (0.5 mmol) in $CH_2Cl_2$ (5 mL) was added the corresponding aldehyde (0.5 mmol) and activated 4 Å molecular sieves (200 mg). The mixture was stirred for 12 h at ambient temperature, filtered through a Celite pad and the solvent was evaporated in vacuo. The resulting imines were used directly in the subsequent reactions without further purification.

### 4.3. General procedure for the aza-Diels–Alder reaction of Danishefsky's diene with imines

To a solution of the respective imine (0.5 mmol) in MeCN (5 mL) was added $Yb(OTf)_3$ (0.05 mmol) followed by diene **4** (0.6 mmol, 1.2 equiv). The reaction mixture was stirred for 3–5 h at room temperature. After addition of saturated $NaHCO_3$ (10 mL), the aqueous phase was extracted with $CH_2Cl_2$ (3×10 mL), the combined organic phases were dried over $MgSO_4$, and the solvent was evaporated in vacuo. The crude material was purified by flash column chromatography on silica gel.

**4.3.1. 2-Phenyl-1-(5-trimethylsilanyl-pent-3-ynyl)-2,3-dihydro-1*H*-pyridin-4-one (5a).** Chromatography (80:20 $Et_2O$/hexane) afforded 0.127 g (82%) of a colorless oil: IR (neat) 2219, 1639, 1593, 1579, 849 $cm^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 0.08 (s, 9H), 1.42 (t, $J$=2.6 Hz, 2H), 2.24–2.42 (m, 2H), 2.69 (dd, $J$=16.4, 8.6 Hz, 1H), 2.86 (dd, $J$=16.4, 6.7 Hz, 1H), 3.21 (m, 2H), 4.69 (dd, $J$=8.6, 6.7 Hz, 1H), 5.04 (d, $J$=7.7 Hz, 1H), 7.23 (d, $J$=7.7 Hz, 1H), 7.30–7.39 (m, 5H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ −2.0, 6.9, 19.4, 43.9, 52.8, 60.9, 74.2, 81.3, 98.4, 126.9, 128.3, 129.1, 138.7, 154.5, 190.3; HRMS calcd for $C_{19}H_{25}NOSi$ ($M^+$) 311.1705, found 311.1716.

**4.3.2. 2-*p*-Tolyl-1-(5-trimethylsilanyl-pent-3-ynyl)-2,3-dihydro-1*H*-pyridin-4-one (5b).** Chromatography (80:20 $Et_2O$/hexane) afforded 0.130 g (80%) of a colorless oil: IR (neat) 2220, 1642, 1591, 849 $cm^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 0.08 (s, 9H), 1.42 (t, $J$=2.6 Hz, 2H), 2.24–2.33 (m, 2H), 2.34 (s, 3H), 2.68 (dd, $J$=16.4, 9.2 Hz, 1H), 2.81 (dd, $J$=16.4, 6.6 Hz, 1H), 3.18 (m, 2H), 4.69 (dd, $J$=9.2, 6.6 Hz, 1H), 5.03 (d, $J$=7.6 Hz, 1H), 7.15 (d, $J$=7.6 Hz,

1H), 7.18–7.23 (m, 4H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ −2.0, 6.9, 19.4, 21.1, 44.1, 52.7, 60.8, 74.3, 81.3, 98.3, 126.9, 129.7, 135.7, 138.1, 154.4, 190.5; HRMS calcd for $C_{20}H_{27}NOSi$ 325.1862, found 325.1870.

**4.3.3. 2-(4-Methoxyphenyl)-1-(5-trimethylsilanyl-pent-3-ynyl)-2,3-dihydro-1*H*-pyridin-4-one (5c).** Chromatography (80:20 $Et_2O$/hexane) afforded 0.133 g (78%) of a yellow oil: IR (neat) 2220, 1640, 1591, 848 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 0.08 (s, 9H), 1.42 (t, $J$=2.6 Hz, 2H), 2.22–2.40 (m, 2H), 2.69 (dd, $J$=16.4, 9.3 Hz, 1H), 2.80 (dd, $J$=16.4, 6.6 Hz, 1H), 3.18 (m, 2H), 3.81s, 3H), 4.62 (dd, $J$=9.3, 6.6 Hz, 1H), 5.02 (d, $J$=7.6 Hz, 1H), 6.88 (m, 2H), 7.21 (d, $J$=7.6 Hz, 1H), 7.24 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ −2.0, 6.9, 19.4, 30.3, 44.1, 52.6, 55.3, 81.3, 98.2, 114.4, 120.2, 128.2, 130.6, 154.5, 159.5, 190.7; HRMS calcd for $C_{20}H_{27}NNaO_2Si$ (M+Na) 364.1703, found 364.1698.

**4.3.4. 2-(4-Chlorophenyl)-1-(5-trimethylsilanyl-pent-3-ynyl)-2,3-dihydro-1*H*-pyridin-4-one (5d).** Chromatography (90:10 $Et_2O$/hexane) afforded 0.127 g (86%) of a colorless oil: IR (neat) 2220, 1639, 1589, 1574, 849 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 0.08 (s, 9H), 1.42 (t, $J$=2.6 Hz, 2H), 2.25–2.41 (m, 2H), 2.62 (dd, $J$=16.4, 8.0 Hz, 1H), 2.88 (dd, $J$=16.4, 6.9 Hz, 1H), 3.15–3.25 (m, 2H), 4.67 (dd, $J$=8.0, 6.9 Hz, 1H), 5.06 (d, $J$=7.7 Hz, 1H), 7.18 (d, $J$=7.7 Hz, 1H), 7.25 (m, 2H), 7.32 (m, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ −2.0, 7.0, 19.5, 43.7, 52.9, 60.4, 74.1, 81.5, 98.6, 128.3, 129.3, 134.2, 137.3, 154.1, 189.8; HRMS calcd for $C_{19}H_{24}$-ClNNaOSi (M+Na) 368.1208, found 368.1207.

**4.3.5. 2-Furan-2-yl-1-(5-trimethylsilanyl-pent-3-ynyl)-2,3-dihydro-1*H*-pyridin-4-one (5e).** Chromatography (70:30 EtOAc/hexane) afforded 0.120 g (81%) of a yellow oil: IR (neat) 2217, 1644, 1589, 848 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 0.08 (s, 9H), 1.42 (t, $J$=2.6 Hz, 2H), 2.35–2.51 (m, 2H), 2.78 (dd, $J$=16.4, 6.5 Hz, 1H), 2.85 (dd, $J$=16.4, 6.6 Hz, 1H), 3.27 (m, 1H), 3.38 (m, 1H), 4.76 (m, 1H), 4.99 (d, $J$=7.6 Hz, 1H), 6.30 (d, $J$=3.3 Hz, 1H), 6.33 (dd, $J$=3.3, 1.8 Hz, 1H), 7.03 (d, $J$=7.6 Hz, 1H), 7.39 (d, $J$=1.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ −2.0, 6.9, 20.0, 39.9, 53.5, 54.1, 74.4, 81.1, 98.0, 108.5, 110.4, 142.6, 151.2, 152.8, 190.3; HRMS calcd for $C_{17}H_{23}NO_2Si$ ($M^+$) 301.1498, found 301.1494.

**4.3.6. 1-(5-Trimethylsilanyl-pent-3-ynyl)-2,3-dihydro-1*H*-[2,2′]bipyridinyl-4-one (5f).** Chromatography (30:70 *i*-PrOH/hexane) afforded 0.118 g (76%) of a brown oil: IR (neat) 2219, 1640, 1594, 1584, 850 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 0.08 (s, 9H), 1.43 (t, $J$=2.6 Hz, 2H), 2.33–2.50 (m, 2H), 2.85 (dd, $J$=16.5, 5.6 Hz, 1H), 2.99 (dd, $J$=16.4, 7.5 Hz, 1H), 3.33 (m, 2H), 4.83 (dd, $J$=7.5, 5.5 Hz, 1H), 5.01 (d, $J$=7.6 Hz, 1H), 7.21 (d, $J$=7.6 Hz, 1H), 7.22 (ddd, $J$=7.7, 4.8, 1.1 Hz, 1H), 7.33 (d, $J$=7.7 Hz, 1H), 7.67 (m, 1H), 8.6 (m, 1H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ −2.0, 6.9, 19.8, 41.5, 53.8, 61.8, 74.2, 81.2, 98.3, 121.0, 122.9, 136.9, 150.0, 153.7, 157.9, 189.9; HRMS calcd for $C_{18}H_{24}N_2OSi$ ($M^+$) 312.1658, found 312.1652.

**4.3.7. 2-Benzyloxymethyl-1-(5-trimethylsilanyl-pent-3-ynyl)-2,3-dihydro-1*H*-pyridin-4-one (5g).** Chromatography (70:30 $Et_2O$/hexane) afforded 0.150 g (89%) of a yellow oil: IR (neat) 2220, 1642, 1580, 849 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 0.07 (s, 9H), 1.42 (t, $J$=2.6 Hz, 2H), 2.36 (dd, $J$=16.8, 2.3 Hz, 1H), 2.45 (m, 2H), 2.78 (dd, $J$=16.4, 6.8 Hz, 1H), 3.29 (m, 1H), 3.46 (m, 1H), 3.55 (dt, $J$=13.0, 6.0 Hz, 1H), 3.82 (m, 2H), 4.49 (s, 2H), 4.87 (d, $J$=7.4 Hz, 1H), 6.97 (d, $J$=7.4 Hz, 1H), 7.27–7.36 (m, 5H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ −2.0, 6.9, 20.6, 37.7, 54.5, 56.2, 68.7, 73.6, 74.4, 80.9, 96.8, 127.6, 127.8, 128.4, 137.6, 152.4, 190.1; HRMS calcd for $C_{21}H_{29}NO_2Si$ ($M^+$) 355.1968, found 355.1979.

**4.3.8. 2-Hexyl-1-(5-trimethylsilanyl-pent-3-ynyl)-2,3-dihydro-1*H*-pyridin-4-one (5h).** Chromatography (60:40 $Et_2O$/hexane) afforded 0.112 g (77%) of a colorless oil: IR (neat) 2220, 1640, 1588, 851 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 0.08 (s, 9H), 0.87 (t, $J$=7.1 Hz, 3H), 1.20–1.35 (m, 6H), 1.43 (t, $J$=2.6 Hz, 2H), 1.57–1.75 (m, 4H), 2.32 (ddd, $J$=16.3, 3.2, 1.0 Hz, 1H), 2.45 (m, 2H), 2.76 (dd, $J$=16.3, 6.8 Hz, 1H), 3.30 (m, 2H), 3.51 (m, 1H), 4.89 (dd, $J$=7.4, 1.1 Hz, 1H), 6.95 (dd, $J$=7.4, 1.0 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ −2.0, 6.9, 14.0, 20.7, 22.5, 25.6, 28.9, 29.2, 31.7, 39.5, 53.6, 56.6, 74.3, 81.0, 96.9, 152.2, 190.7; HRMS calcd for $C_{19}H_{34}NOSi$ (M+H) 320.2404, found 320.2400.

**4.3.9. 2-Cyclohexyl-1-(5-trimethylsilanyl-pent-3-ynyl)-2,3-dihydro-1*H*-pyridin-4-one (5i).** Chromatography (60:40 $Et_2O$/hexane) afforded 0.100 g (70%) of a colorless oil: IR (neat) 2220, 1638, 1586, 850 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 0.08 (s, 9H), 0.86–1.31 (m, 6H), 1.42 (t, $J$=2.7 Hz, 2H), 1.69–1.93 (m, 5H), 2.41–2.49 (m, 3H), 2.76 (dd, $J$=16.5, 7.4 Hz, 1H), 3.26–3.39 (m, 3H), 4.87 (dd, $J$=7.3, 1.1 Hz, 1H), 7.02 (dd, $J$=7.3, 1.0 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ −2.0, 6.9, 21.0, 26.1, 28.8, 30.1, 37.4, 38.7, 54.8, 61.4, 74.3, 80.7, 97.2, 152.8, 192.2; HRMS calcd for $C_{19}H_{32}NOSi$ (M+H) 318.2248, found 318.2239.

**4.3.10. 2-Phenyl-1-(6-trimethylsilanyl-hex-4-ynyl)-2,3-dihydro-1*H*-pyridin-4-one (7a).** Chromatography (70:30 $Et_2O$/hexane) afforded 0.123 g (78%) of a colorless oil: IR (neat) 2219, 1641, 1593, 1579, 850 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 0.06 (s, 9H), 1.39 (t, $J$=2.6 Hz, 2H), 1.60–1.72 (m, 2H), 2.12–2.23 (m, 2H), 2.67 (dd, $J$=16.4, 7.7 Hz, 1H), 2.88 (dd, $J$=16.4, 7.1 Hz, 1H), 3.18 (m, 1H), 3.27 (m, 1H), 4.61 (t, $J$=7.4 Hz, 1H), 5.01 (d, $J$=7.6 Hz, 1H), 7.20 (d, $J$=7.6 Hz, 1H), 7.28–7.37 (m, 5H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ −2.0, 6.9, 16.0, 28.1, 43.7, 52.3, 61.0, 76.5, 79.3, 98.3, 126.9, 128.2, 129.0, 138.7, 154.1, 190.0; HRMS calcd for $C_{20}H_{28}NOSi$ (M+H) 326.1935, found 326.1940.

**4.3.11. 2-(4-Methoxyphenyl)-1-(6-trimethylsilanyl-hex-4-ynyl)-2,3-dihydro-1*H*-pyridin-4-one (7b).** Chromatography (70:30 $Et_2O$/hexane) afforded 0.125 g (71%) of a colorless oil: IR (neat) 2219, 1641, 1593, 1579, 850 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 0.06 (s, 9H), 1.39 (t, $J$=2.6 Hz, 2H), 1.58–1.68 (m, 2H), 2.10–2.23 (m, 2H), 2.66 (dd, $J$=16.4, 8.3 Hz, 1H), 2.82 (dd, $J$=16.4, 6.8 Hz, 1H), 3.17 (m, 1H), 3.23 (m, 1H), 3.80 (s, 3H), 4.55 (dd, $J$=8.3, 6.8 Hz, 1H), 5.01 (d, $J$=7.6 Hz, 1H), 6.88 (m, 2H), 7.17 (d, $J$=7.6 Hz, 1H), 7.22 (m, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ −2.0, 6.9, 16.0, 28.1, 43.9, 52.0, 55.3, 60.5, 76.5, 79.2,

98.1, 114.4, 128.2, 130.8, 154.1, 159.5, 190.4; HRMS calcd for $C_{21}H_{29}NNaO_2Si$ (M+Na) 378.1860, found 378.1852.

**4.3.12. 2-Hexyl-1-(6-trimethylsilanyl-hex-4-ynyl)-2,3-dihydro-1*H*-pyridin-4-one (7c).** Chromatography (60:40 $Et_2O$/hexane) afforded 0.107 g (65%) of a colorless oil: IR (neat) 2220, 1641, 1587, 850 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 0.1 (s, 9H), 0.88 (t, $J$=7.0 Hz, 3H) 1.15–1.37 (m, 7H), 1.44 (t, $J$=2.6 Hz, 2H), 1.53–1.62 (m, 2H), 1.70–1.80 (m, 3H), 2.20–2.28 (m, 2H), 2.33 (dd, $J$=16.4, 3.0 Hz, 1H), 2.73 (dd, $J$=16.4, 6.8 Hz, 1H), 3.32 (m, 2H), 3.44 (m, 1H), 4.88 (d, $J$=7.4 Hz, 1H), 6.94 (d, $J$=7.4 Hz, 1H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ −2.0, 6.9, 14.0, 16.0, 22.5, 25.6, 28.6, 29.1, 29.2, 31.7, 39.4, 52.6, 56.7, 76.5, 79.3, 96.7, 152.3, 190.4; HRMS calcd for $C_{20}H_{36}NOSi$ (M+H) 334.2561, found 334.2575.

### 4.4. General procedure for the direct aza-Diels–Alder reaction

The aldehyde (0.1 mmol), amine **1** or **2** (0.1 mmol) and Danishefsky's diene (0.11 mmol) were dissolved in MeCN (5 mL) at room temperature and $Yb(OTf)_3$ (0.01 mmol) was added in one portion. The reaction mixture was stirred for 2–9 h. Then water was added and the mixture was extracted with $CH_2Cl_2$ (3×5 mL) and the combined organic layers were washed with brine and dried ($MgSO_4$). The residue was purified by flash column chromatography.

### 4.5. General procedure for the TBAT-mediated cyclocondensation

The dihydropyridones (0.1 mmol) and TBAT (0.2 mmol) were dissolved in THF (5 mL) at 30 °C. After 20 min, the reaction turned orange, and after 1–5 h the reaction was complete (TLC monitoring). The THF was removed under reduced pressure, the residue was redissolved in $Et_2O$ (10 mL), and filtered. The filtrate was concentrated, and the crude material obtained was purified by flash column chromatography.

**4.5.1. (5*R**,8a*R**)-5-Phenyl-1-vinylidene-hexahydro-indolizin-7-one (6a).** Chromatography (50:50 $Et_2O$/hexane) afforded 0.023 g (95%) of white needles. Recrystallisation from TBME/pentane afforded **6a** as white needles: mp 118–119 °C; IR (neat) 1966, 1718 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 2.52 (m, 1H), 2.57–2.75 (m, 6H), 2.88 (m, 1H), 3.85 (m, 1H), 4.12 (dd, $J$=7.1, 5.5 Hz, 1H), 4.81 (dq, $J$=9.9, 4.4 Hz, 1H), 4.89 (dq, $J$=10.0, 4.4 Hz, 1H), 7.23–7.36 (m, 5H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 28.3, 43.1, 47.0, 49.9, 58.3, 60.7, 79.1, 103.1, 127.7, 127.9, 128.4, 139.8, 201.4, 208.6; HRMS calcd for $C_{16}H_{17}NO$ ($M^+$) 239.1310, found 239.1320.

**4.5.2. (5*R**,8a*R**)-5-*p*-Tolyl-1-vinylidene-hexahydro-indolizin-7-one (6b).** Chromatography (50:50 $Et_2O$/hexane) afforded 0.023 g (93%) of a colorless oil: IR (neat) 1966, 1715 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 2.35 (s, 3H), 2.47–2.77 (m, 7H), 2.89 (m, 1H), 3.85 (m, 1H), 4.06 (t, $J$=6.1 Hz, 1H), 4.81 (dq, $J$=9.9, 4.4 Hz, 1H), 4.89 (dq, $J$=10.0, 4.4 Hz, 1H), 7.10–7.18 (m, 4H); $^{13}C$ NMR ($CDCl_3$, 100 MHz) $\delta$ 21.0, 28.2, 43.2, 46.9, 49.7, 58.1, 60.2, 79.1, 103.1, 127.9, 129.1, 136.4, 137.4, 201.4, 208.9; HRMS calcd for $C_{17}H_{19}NO$ ($M^+$) 253.1467, found 253.1468.

**4.5.3. (5*R**,8a*R**)-5-(4-Methoxyphenyl)-1-vinylidene-hexahydro-indolizin-7-one (6c).** Chromatography (40:60 $Et_2O$/hexane) afforded 0.025 g (97%) of a yellow oil: IR (neat) 1965, 1718, 1512, 1251 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 2.47–2.76 (m, 7H), 2.88 (ddd, $J$=10.9, 7.7, 3.3 Hz, 1H), 3.80 (s, 3H), 3.81 (m, 1H), 4.10 (t, $J$=6.1 Hz, 1H), 4.81 (dq, $J$=10.0, 4.5 Hz, 1H), 4.89 (dq, $J$=10.0, 4.4 Hz, 1H), 6.89 (m, 2H), 7.14 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 28.3, 43.3, 47.1, 49.8, 55.3, 58.1, 59.9, 79.1, 103.2, 113.8, 129.1, 131.7, 159.1, 201.4, 208.8; HRMS calcd for $C_{17}H_{20}NO_2$ (M+H) 270.1489, found 270.1501.

**4.5.4. (5*R**,8a*R**)-5-(4-Chlorophenyl)-1-vinylidene-hexahydro-indolizin-7-one (6d).** Chromatography (60:40 $Et_2O$/hexane) afforded 0.026 g (98%) of a yellow oil: IR (neat) 1965, 1719 $cm^{-1}$; $^1H$ NMR ($C_6D_6$, 500 MHz) $\delta$ 2.20–2.35 (m, 6H), 2.43 (dd, $J$=15.4, 8.5 Hz, 1H), 2.54 (dd, $J$=15.4, 4.8 Hz, 1H), 3.53 (t, $J$=6.5 Hz, 1H), 3.64 (m, 1H), 4.70 (m, 1H), 4.78 (m, 1H), 6.82 (m, 2H), 7.09 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 28.3, 42.8, 46.9, 50.1, 58.4, 60.3, 79.2, 102.9, 128.6, 129.1, 133.4, 138.6, 201.4, 208.2; HRMS calcd for $C_{16}H_{17}ClNO$ (M+H) 274.0993, found 274.1006.

**4.5.5. (5*R**,8a*R**)-5-Furan-2-yl-1-vinylidene-hexahydro-indolizin-7-one (6e).** Chromatography (40:60 *t*-BuOMe/hexane) afforded 0.020 g (89%) of a yellow oil: IR (neat) 1972, 1722 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 2.42 (m, 1H), 2.50–2.77 (m, 5H), 2.88 (dd, $J$=15.3, 6.9 Hz, 1H), 3.10 (m, 1H), 3.34 (m, 1H), 4.47 (dd, $J$=6.9, 2.3 Hz, 1H), 4.79 (dq, $J$=9.8, 4.8 Hz, 1H), 4.89 (dq, $J$=9.9, 4.6 Hz, 1H), 6.13 (d, $J$=3.2 Hz, 1H), 6.31 (dd, $J$=3.2, 1.8 Hz, 1H), 7.36 (d, $J$=1.8 Hz, 1H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 28.4, 44.0, 45.3, 49.1, 53.2, 57.3, 79.2, 103.5, 109.1, 109.9, 142.4, 152.1, 201.1, 207.5; HRMS calcd for $C_{14}H_{15}NO_2$ ($M^+$) 229.1103, found 229.1106.

**4.5.6. (5*R**,8a*R**)-5-Pyridin-2-yl-1-vinylidene-hexahydro-indolizin-7-one (6f).** Chromatography (50:50 *t*-BuOMe/hexane) afforded 0.022 g (92%) of a yellow oil: IR (neat) 1967, 1712 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 2.44–2.54 (m, 3H), 2.65–2.80 (m, 4H), 3.01 (m, 1H), 3.75 (m, 1H), 4.37 (t, $J$=4.8 Hz, 1H), 4.79 (dq, $J$=9.9, 4.7 Hz, 1H), 4.87 (dq, $J$=9.8, 4.6 Hz, 1H), 7.17 (ddd, $J$=1.1, 4.8, 7.7 Hz, 1H), 7.21 (d, $J$=7.7 Hz, 1H), 7.66 (m, 1H), 8.57 (m, 1H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 28.3, 44.0, 44.6, 49.3, 57.0, 61.1, 79.0, 103.3, 122.3, 122.8, 136.1, 149.2, 157.9, 201.1, 207.6; HRMS calcd for $C_{15}H_{16}N_2NaO$ (M+Na) 263.1155, found 263.1152.

**4.5.7. (5*R**,8a*R**)-5-Benzyloxymethyl-1-vinylidene-hexahydro-indolizin-7-one (6g).** Chromatography (40:60 *t*-BuOMe/hexane) afforded 0.025 g (89%) of a colorless oil: IR (neat) 1965, 1713 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 2.36 (m, 1H), 2.41–2.51 (m, 2H), 2.59–2.71 (m, 3H), 3.03 (m, 2H), 3.44 (m, 1H), 3.51 (dd, $J$=9.7, 4.6 Hz, 1H), 3.58 (dd, $J$=9.7, 4.6 Hz, 1H), 3.95 (m, 1H), 4.49 (d, $J$=2.2 Hz, 2H), 4.80 (m, 1H), 4.84 (m, 1H), 7.27–7.36 (m, 5H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 28.7, 42.2, 44.0, 49.6, 56.2, 58.4, 70.3, 73.4, 78.9, 103.9, 127.5, 127.6, 128.4, 137.9,

201.0, 208.3; HRMS calcd for $C_{18}H_{21}NO_2$ ($M^+$) 283.1572, found 283.1578.

**4.5.8. (5*S**,8a*R**)-5-Hexyl-1-vinylidene-hexahydro-indolizin-7-one (6h).** Chromatography (40:60 $Et_2O$/hexane) afforded 0.020 g (83%) of a colorless oil: IR (neat) 1967, 1715 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 0.87 (t, $J$= 7.1 Hz, 3H), 1.20–1.56 (m, 10H), 2.28 (ddd, $J$=14.2, 4.0, 1.5 Hz, 1H), 2.34–2.44 (m, 2H), 2.62 (dd, $J$=14.2, 5.6 Hz, 1H), 2.68 (m, 2H), 2.92–3.03 (m, 2H), 3.21 (m, 1H), 3.79 (m, 1H), 4.80 (m, 1H), 4.84 (m, 1H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 14.0, 22.6, 26.5, 28.8, 29.3, 29.8, 31.7, 43.6, 44.3, 48.9, 57.1, 57.9, 78.8, 103.9, 201.1, 209.3; HRMS calcd for $C_{16}H_{26}NO$ (M+H) 248.2009, found 248.2009.

**4.5.9. (5*R**,8a*R**)-5-Cyclohexyl-1-vinylidene-hexahydro-indolizin-7-one (6i).** Chromatography (40:60 $Et_2O$/hexane) afforded 0.021 g (86%) of a colorless oil: IR (neat) 1966, 1714 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 0.83–0.96 (m, 2H), 1.09–1.25 (m, 4H), 1.37 (m, 1H), 1.63–1.86 (m, 4H), 2.30 (ddd, $J$=15.0, 4.5, 1.5 Hz, 1H), 2.36–2.42 (m, 2H), 2.49 (dd, $J$=14.4, 5.1 Hz, 1H), 2.64 (m, 1H), 2.74 (m, 1H), 2.90 (m, 1H), 3.00 (m, 1H), 3.07 (m, 1H), 4.05 (m, 1H), 4.79–4.83 (m, 2H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 26.2, 26.5, 29.2, 30.4, 39.3, 40.2, 43.2, 50.5, 58.8, 63.2, 78.4, 104.3, 201.1, 209.9; HRMS calcd for $C_{16}H_{24}NO$ (M+H) 246.1852, found 246.1853.

**4.5.10. (4*R**,9a*R**)-4-Phenyl-9-vinylidene-octahydro-quinolizin-2-one (8a).** Chromatography (40:60 $Et_2O$/hexane) afforded 0.008 g (35%) of a colorless oil: IR (neat) 1968, 1720 $cm^{-1}$; $^1H$ NMR ($C_6D_6$, 500 MHz) $\delta$ 0.88–0.95 (m, 1H), 1.58–1.70 (m, 1H), 1.91 (m, 1H), 2.30–2.41 (m, 2H), 2.47 (dd, $J$=14.6, 9.5 Hz, 1H), 2.53–2.62 (m, 2H), 2.74 (ddd, $J$=14.8, 3.6, 2.1 Hz, 1H), 2.82 (m, 1H), 3.61 (m, 1H), 4.12 (dd, $J$=9.5, 4.2 Hz, 1H), 4.76 (dt, $J$=10.1, 4.1 Hz, 1H), 4.84 (dq, $J$=13.7, 3.5 Hz, 1H), 7.13–7.25 (m, 5H); $^{13}C$ NMR ($CDCl_3$, 125 MHz) $\delta$ 20.4, 29.9, 44.0, 49.0, 49.8, 57.7, 59.4, 77.5, 98.8, 127.8, 127.7, 140.8, 203.7, 207.4; HRMS calcd for $C_{17}H_{19}NO$ ($M^+$) 253.1467, found 253.1462.

**4.5.11. (4*R**,9a*R**)-4-(4-Methoxyphenyl)-9-vinylidene-octahydro-quinolizin-2-one (8b).** Chromatography (40:60 $Et_2O$/hexane) afforded 0.006 g (27%) of a brown oil: IR (neat) 1972, 1718 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 0.83–0.94 (m, 1H), 1.70–1.80 (m, 1H), 2.10–2.21 (m, 1H), 2.38–2.43 (m, 1H), 2.49–2.54 (m, 2H), 2.57–2.64 (m, 1H), 2.68 (dd, $J$=15.2, 3.8 Hz, 1H), 2.73 (dd, $J$=15.2, 6.0 Hz, 1H), 2.86–2.92 (m, 1H), 3.81 (s, 3H), 3.84–3.89 (m, 1H), 4.13–4.17 (m, 1H), 4.74–4.81 (m, 2H), 6.88 (d, $J$=8.7 Hz, 2H) 7.23 (d, $J$=8.7 Hz, 2H); HRMS calcd for $C_{18}H_{21}NO_2$ ($M^+$) 283.1573, found 283.1582.

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14. Crystallographic data for the structure **6a** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 270291. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].