Preparation of some heterocyclic enones and ynones by isomerisation of the propargylic alcohols

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The propargylic alcohols were synthesised by treatment of aldehydes with substituted acetylenes. The conversion of propargylic alcohols to propynones and propenones takes place with pyridine hydrochloride in methanol at room temperature. In presence of pyridinium triflate and *p*-toluenesulfonate the propynone was the only product isolated in the isomerisation of alcohol. The silylated propenone undergoes with cyclopentadiene a Diels–Alder cycloaddition to give ketone whose skeleton is related to that of quinine.

Keywords: isomerisation, propargylic alcohol, enone; ynone, heterocyclic

The pyridine ring plays a key role in several biological processes.[1,2] The quinoline ring system is an important target in synthetic chemistry. It is found in a large number of natural products, many of which have important biological activities.[3-7] In addition, they are used as dyestuffs and photographic sensitisers.[8]

In a preliminary communication we reported the facile isomerisation of heterocyclic propargylic alcohols to propenones and propynones in the presence of pyridine hydrochloride.[9] We had shown that this isomerisation occurs when the propargylic hydrogen is activated at C-2 and C-4 in case of pyridine and that the ethylenic protons originated from protons of the solvent. An enolic allene was postulated as an intermediate and its protonation gives a (*Z*) enone subsequently isomerised to the (*E*) form. Related isomerisations have been reported on different systems under various conditions.[10-20] We now report more examples of this isomerisation and the results obtained with two other pyridinium salts as catalysts and the Diels–Alder reaction of one of these enones whose chemistry has not been explored.

Results and discussions

We prepared in good yields the proparglic alcohols **3** from aldehydes **1** and substituted acetylenes **2**. These alcohols **3** except **3a**, **3m** and **3n** are not too stable and their isomerisation was carried out without delay. Table 1 shows the results of the preparation of the propargylic alcohols **3** and their isomerisation with pyridine hydrochloride catalyst to ynones **4** and enones **5**. The structure of enone **5d** was elucidated by X-ray diffraction (Fig. 1).

We tried with the quinoline alcohol other pyridinium salts: trifluoromethanesulfonate, *p*-toluensulfonate, and compared the results with those obtained with pyridinium hydrochloride. (Table 2). The ynone **6** was the only product isolated in the presence of pyridinium triflate and pyridinium toluenesulfonate. Enone **7** was found only in the presence of pyridinium hydrochloride. The presence of air seemed to increase the yield of the ynone, but the ynone was also obtained under argon (Table 2). In addition to the ynone and enone, coloured and polar material was obtained.

Concerning the mechanism of the conversion of the propargylic alcohols, the protonation of the nitrogen is an essential step. So the first step is the protonation at the nitrogen to give the pyridinium or quinolinium cation. Now the hydrogen at the alpha position is activated and is abstracted by a base to give the anhydro base **8**. This base **8**

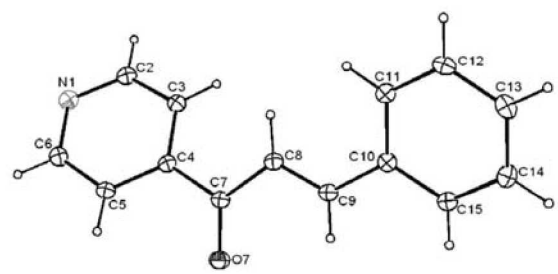

Fig. 1 ORTEP structure of **5d**.

Table 1 Preparation of propargylic alcohols (**3**) and their conversion to ynones (**4**) and enones (**5**) with pyridinium hydrochloride

Compound			**3**[a]	**4** (ynone)	**5** (enone)
	R^1	R^2	Yield/%	Yield/%	Yield/%
a	Phenyl	Me_3Si	100	–	–
b	4-Pyridyl	Me_3Si	83	26	52
c	4-Pyridyl	Me	82	15	49
d	4-Pyridyl	Phenyl	90	10	55
e	4-Pyridyl	*t*-Butyl	96	12	75
f	4-Quinolyl	Me_3Si	79	see Table 2	
g	4-Quinolyl	Me	83	30	36
h	4-Quinolyl	*t*-Butyl	80	26	37 (*E*)–18(*Z*)
i	4-Quinolyl	Phenyl	74	24	21
k	2-Pyridyl	Me_3Si	88	–	42
m	3-Pyridyl[21,22]	Me_3Si	97	Stable	
n	3-Pyridyl[21,22]	H		Stable	

[a]Except for **3n** prepared from **3m** by removal of the trimethylsilyl group by TBAF.

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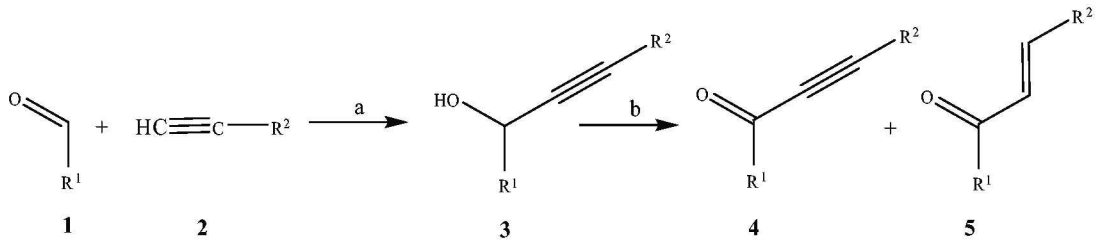
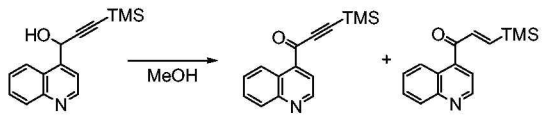


Scheme 1 Reagents and conditions: (a) n-BuLi, THF, –78 °C (b) C_5H_6NCl, MeOH.

Table 2 Conversion of **3f** using various pyridinium salts



3f **6** **7**

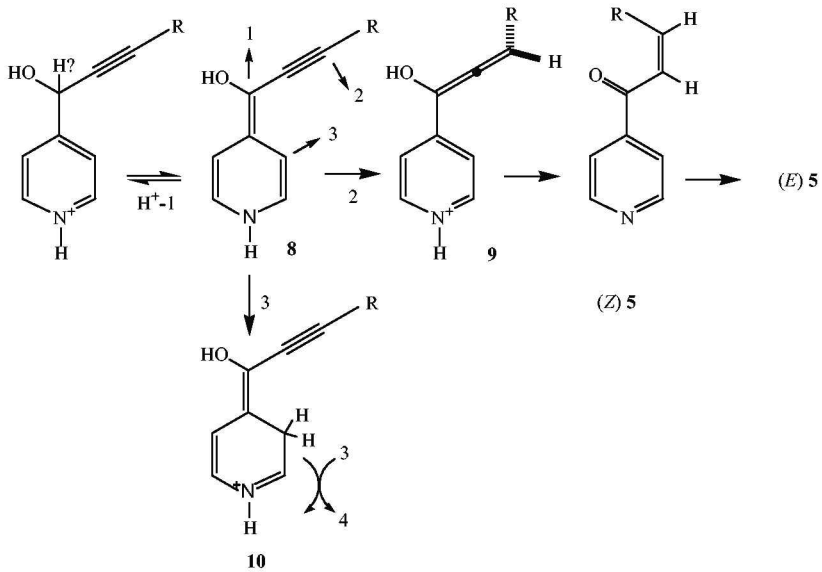
PyH+ salt	Atmosphere	Additive	6	7
CF_3SO^-	Air	–	36%	–
	Ar	–	32%	–
p-Me-C_6H_4-SO_3^-	Air	–	67%	–
	Ar	–	49%	–
	Ar	Na_2CO_3	33%	–
Cl^-	Air	–	40%	–
	Ar	–	40%	50%

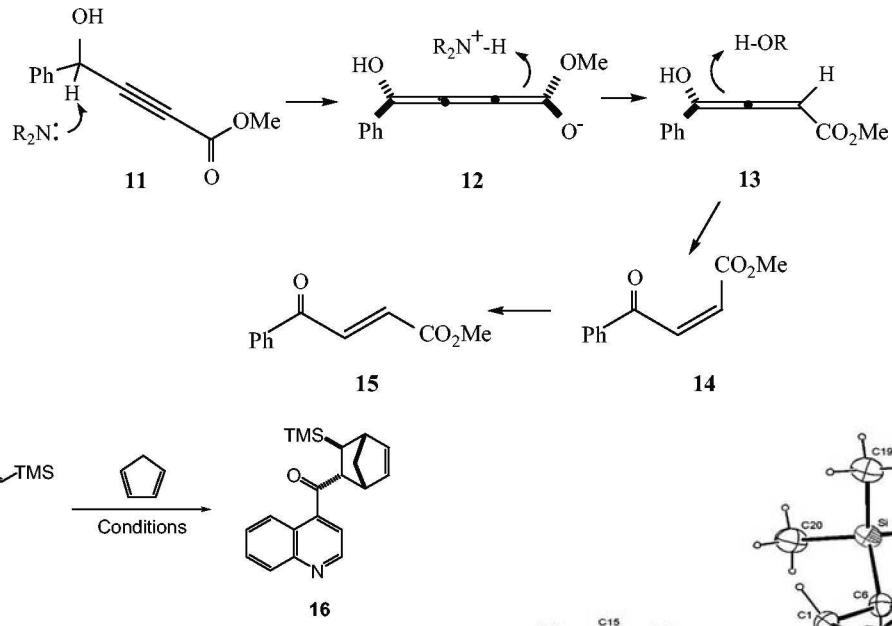
may be protonated at several positions: 1, 2 and 3. At position 1 to give back the pyridinium salt, resulting in the exchange of this hydrogen. With the protonation at position 2, the terminal carbon of the triple bond, the pyridinium allenol **9** is obtained. The deprotonation of the nitrogen and the ketonisation of the allenol gives at first the (*Z*) isomer of ketone later isomerised to the (*E*) isomer. The kinetic product of the protonation of the allenol **9** to (*Z*) isomer of ketone is documented in the cases where allenols are intermediates.[23-27] The protonation at C-3 (position 3) gives iminium salt **10** which could be involved in the oxidation of the alcohol to the ynones. We have not tried to isolate the reduced products resulting from this dismutation. If we follow the reaction by NMR using MeO^2H, the exchange of the alpha hydrogen of propargylic alcohol is observed and later the appearance of the (*Z*) enone is observed and its transformation to the (*E*) enone and both hydrogens at the ethylenic positions are exchanged with a deuteron as shown by ^1H NMR and mass spectrometry. A related intramolecular dismutation reaction has been observed in the reaction of vinylmagnesium bromide with isonicotinaldehyde.[28]

The isomerisation of γ-hydroxy-α,β-alkynoates **11** to γ-oxo-α,β-alkenoates with the organic base (DABCO) or sodium bicarbonate in DMSO-water has been studied.[29] The base removes the propargylic proton giving rise to a cumulene **12** which is protonated by the conjugated acid to an allenol **13** which in turn is protonated by an external proton. The protonation occurs to give first the (*Z*) isomer **14** later isomerised to the (*E*) isomer **15**. The propargylic proton is transferred to the vinylic position with little exchange and the other proton originates from solvent. In the propargylic alcohol, the ester group provides the acidity so that the proton can be removed. In the propargylic alcohols in Table 1, the protonation at the nitrogen lowers the p*K*a of the proton so that it can be removed by a base.

The easy preparation of heterocyclic enone induced us to try the Diels–Alder reaction with cyclopentadiene to prepare a cyclic system related to quinine. The Diels–Alder adduct **16** with cyclopentadiene was obtained at 120 °C (neat) in a yield of 25%.

In boron trifluoride etherate at –78 °C in toluene, no adduct was isolated. So, we turned to lithium chloride as a catalyst and obtained in THF at 25 °C the adduct **16** in a yield of 50%.[30] The *endo* cycloaddition product is obtained as expected.[31,32] This has been ascertained by the structure determination by X-ray diffraction (Fig. 2).





These enones and ynones not previously prepared should open a new strategy for the synthesis of some complex heterocyclic systems such as alkaloids. They also could be the precursors of synthetically and pharmaceutically valuable compounds.

Fig. 2 ORTEP structure of **16**.

Experimental

General procedures

Commercial reagents were purchased from standard chemical suppliers and purified if needed. Solvents were purified and dried by passing through activated aluminum oxide under argon pressure. Flash column chromatography was carried out on Silica Gel 60 (230–400 mesh, E. Merck). TLC was performed on pre-coated glass plates of Silica Gel 60 F254 (0.25 mm, E. Merck); detection was done by spraying with a solution of $Ce(NH_4)_2(NO_3)_6$, $(NH_4)_6Mo_7O_{24}$, and H_2SO_4 in water or ninhydrin and acetic acid solution in *n*-butanol and subsequent heating on a hot plate. Melting points were determined with a Büchi B-540 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded with Bruker AV400 and 500 MHz instruments. Chemical shifts are in ppm from TMS as internal standard, generated from the $CDCl_3$. IR spectra were taken with a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analysis was done with a Perkin-Elmer 2400CHN instrument. Mass spectra were obtained with a FAB JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan).

1-*Phenyl-3-trimethylsilanyl-prop-2-yn-1-ol* (**3a**)**:** Prepared according to the literature and its physical data were in agreement with those published.[21]

4-(1-Hydroxy-3-trimethylsilanyl-2-propynyl) pyridine (**3b**): To a solution of (trimethylsilyl) acetylene (1.7 mL) in THF (20 mL) at –78 °C was added a solution of n-BuLi (7 mL, 1.6 M in hexane). The reaction mixture was allowed to warm to –10 °C, then a solution of 4-pyridinecarboxaldehyde (1.0 g) in THF (3 mL) was added. After 1 h stirring, saturated NH_4Cl solution in water was added and the organic layer was washed with brine (2 × 30 mL), extracted with CH_2Cl_2 and dried over $MgSO_4$ and concentrated in *vacuo*. Product **3b** is a colourless solid (1.6 g, 83%), m.p. 94–95 °C. (lit. m.p. 83–85 °C).[24] ^1H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 9H), 4.60 (brs, 1H), 5.48 (s, 1H), 7.49 (d, *J* = 6.0 Hz 2H), 8.53 (d, *J* = 6.0 Hz 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.18, 63.2, 92.0, 104.2, 121.5, 149.4, 150.3. MS (EI): *m/z* 205 $[M]^+$.

4-(1-Hydroxy-2-butynyl) pyridine (**3c**)**:** To a solution of propyne (1.12 g) in THF (10 mL), was added a solution of n-BuLi (7.0 mL, 1.6 M in hexane) as for **3b**. A solution of 4-pyridinecarboxaldehyde (1.0 g) in THF (5 mL) was added. The product **3c** was isolated as for **3b**, and as a liquid (1.12 g, 82%). UV (CH_2Cl_2): λ_{max} (ε) 255 (3540 M^{-1} cm^{-1}). IR (CH_2Cl_2): 1230, 1414, 1564, 1602, 1716, 2232, 2874, 2959, 3018, 3026, 3061 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.76 (s, 3H), 5.37 (d, *J* = 1.6 Hz, 1H), 6.30 (brs, 1H), 7.41 (d *J* = 5.9 Hz, 2H), 8.36 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.8, 62.5, 78.8, 82.8, 121.6, 149.0, 151.1. MS (FAB^+): *m/z* 148 $(M + H^+)$. Anal. Calcd for C_9H_9NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.40; H, 6.12; N, 9.47%.

4-(1-Hydroxy-3-phenyl-2-propynyl)pyridine (**3d**)**:** Phenylacetylene (1.04 g) in THF (10 mL) was treated as for **3b** with n-BuLi (7.0 mL) and 4-pyridinecarboxaldehyde (1.0 g) in THF (5 mL) was added. The product (1.75 g, 90%) was a liquid. UV (CH_2Cl_2): λ_{max} (ε) 242 (5100), 309 (1300). IR (CH_2Cl_2): 1042, 1243, 1376, 1461, 1733, 2869, 2926, 2960, 3583. ^1H NMR (500 MHz, $CDCl_3$): δ 3.95 (brs, 1H), 5.68 (s, 1H), 7.27 (m, 3H), 7.40 (m, 2H), 7.53 (d, *J* = 6.0 Hz, 2H), 8.55 (d, *J* = 6.0 Hz 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 63.2, 86.7, 87.9, 121.4, 121.6, 128.2, 128.6, 131.7, 146.2, 149.4. MS (FAB^+): *m/z* 201 $[M+H]^+$. Anal. Calcd for $C_{14}H_{11}NO$ (209.2): C, 80.36; H, 5.30; N, 6.69. Found: C, 80.20; H, 5.34; N, 6.74%.

4-(1-Hydroxy-4,4-dimethyl-2-pentynyl)pyridine (**3e**)**:** 3, 3-Dimethyl-1-butyne (0.46 g) in THF (10 mL) was treated as for **3b** with n-BuLi (3.5 mL, 1.6 M in hexane) and 4-pyridinecarboxaldehyde (0.50 g) in THF (3.0 mL) was added. The product **3e** (0.85 g, 96%) was a solid, m.p. 85–88 °C. UV ($CHCl_3$): λ_{max} (ε) 257 (2000). IR (CH_2Cl_2): 1068, 1404, 1599, 2232, 2333, 2363, 2970, 3060, 3596, 3685 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.20 (s, 9H), 3.50 (brs, 1H), 5.42 (s, 1H), 7.44 (d, *J* = 4.7 Hz, 2H), 8.50 (d, *J* = 4.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.4, 30.7, 62.8, 77.6, 95.9, 121.4, 149.3, 151.0. MS (FAB^+): *m/z* 190 $[M + H]^+$. Anal. Calcd for $C_{12}H_{15}NO$ (189.3): C, 76.16; H, 7.99; N, 7.40. Found: C, 76.11; H, 8.03; N, 7.47%.

4-(1-Hydroxy-3-trimethylsilanyl-2-propynyl)quinoline (**3f**):Trimethylsilylacetylene (0.39 g) in THF (10 mL) was treated as for **3b** with n-BuLi (2.5 mL, 1.6 M, in hexane) and 4-quinolinecarboxaldehyde (0.5 g) in THF (2 mL) was added. The product **3f** was a solid (0.64 g, 78%), m.p. 95–96 °C; UV (CH_2Cl_2): λ_{max} (ε) 234 (13900), 281 (4800 M^{-1} cm^{-1}). IR (CH_2Cl_2): 1510, 1573, 1607, 1636, 1654, 1686, 1717, 1734, 1750, 1774, 1801, 1830, 1884, 1963, 2174, 2305, 2339, 2360 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 9H), 4.80 (brs, 1H), 6.10 (s, 1H), 7.55 (dd, *J* = 7.6 Hz, *J* = 15.6 Hz, 1H), 7.65 (dd, *J* = 7.6 Hz, *J* = 15.6 Hz, 1H), 7.69 (d, *J* = 4.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.72 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.4, 61.3, 92.4, 104.1, 118.2, 124.1, 125.6, 126.7, 129.3, 129.4, 146.1, 147.7, 149.8. MS (FAB^+): *m/e* (%): 256 $[M + H]^+$ (100), 180(5), 154 (6), 130 (10). Anal. Calcd for $C_{15}H_{17}NOSi$: C, 70.54; H, 6.71; N 5.48. Found: C, 70.50; H, 6.69; N, 5.52%.

4-(1-Hydroxy-2-butynyl)quinoline (**3g**): Propyne (0.38 g) in THF (10 mL) was treated as for **3b** with n-BuLi (2.5 mL, 1.6 M in hexane), and 4-quinolinecarboxaldehyde (0.50 g) in THF (2 mL). The product **3g** was a solid (0.52 g, 83%); m.p. 130°C. UV (MeOH): λ_{max} (ε) 210 (13400), 222 (13000), 283 (4400). IR (CH_2Cl_2): 556, 648, 698, 1035, 1049, 1109, 1379, 1414, 1432, 1453, 1475, 2808, 2878, 2900, 2978, 2992, 3056, 3092, 3184, 3432, 3567 cm^{-1}. ^1H NMR (400 MHz, DMSO-*d6*): δ 1.75 (s, 3H), 5.95 (brs, 1H), 6.35 (d, *J* = 4.4 Hz, 1H), 7.60 (t, *J* = 5.7 Hz, *J* = 12.2 Hz, 1H), 7.63 (d, *J* = 3.4 Hz, 1H), 7.72 (t, *J* = 5.7 Hz, *J* = 12.2 Hz, 1H), 8.01 (d, *J* = 6.6 Hz, 1H), 8.24 (d, *J* = 6.6 Hz, 1H), 8.84 (d, *J* = 3.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-*d6*): δ 3.6, 60.3, 80.1, 82.9, 118.4, 124.9, 125.4, 126.9, 129.7 (2C), 147.6, 148.1, 150.8. MS (EI): *m/e* (%): 197 $[M]^+$ (100), 182 (77), 130 (50), 129 (20). Anal. Calcd for $C_{13}H_{11}NO$ (197.2): C, 79.16; H, 5.62; N 7.10. Found: C, 79.27; H, 5.80; N 6.99%.

4-(1-Hydroxy-4,4-dimethyl-2-pentynyl)quinoline (**3h**): 3,3-Dimethyl-1-butyne (0.31 g) in THF (8 mL) was treated as for **3b** with n-BuLi (2.4 mL, 1.6 M in hexane), and 4-quinolinecarboxaldehyde (0.5 g) in THF (3 mL) was added. The product was liquid (0.61 g, 80%). UV (CH_2Cl_2): λ_{max}(ε) 283 (4900). IR (CH_2Cl_2): 3428 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.18 (s, 9H), 4.20 (brs, 1H), 6.08 (s, 1H), 7.55 (dd, *J* = 1.1 Hz, *J* = 8.2 Hz, 1H), 7.67 (m, 2H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 8.79 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.5, 30.7, 61.3, 77.5, 96.7, 118.0, 124.1, 125.7, 126.6, 129.2, 129.6, 146.5, 148.0, 150.0. MS (FAB^+): *m/z* 240 $[M+H]^+$. Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.19; H, 7.22; N, 5.91%.

4-(1-Hydroxy-3-phenyl-2-propynyl)quinoline (**3i**): Phenylacetylene (0.39 g) in THF (8 mL) was treated as for **3b** with n-BuLi (2.39 mL, 1.6 M in hexane) and 4-quinolinecarboxaldehyde (0.50 g) in THF (3 mL) was added. The product **3j** (0.610 g, 74%) was a liquid. UV (CH_2Cl_2): λ_{max} (ε) 225 (24000). IR (acetone): 3618 cm^{-1}. ^1H NMR (500 MHz, MeOD): δ 4.85 (brs, 1H), 6.33 (s, 1H), 7.30 (m, 3H), 7.39 (m, 2H), 7.67 (ddd, *J* = 0.9 Hz, *J* = 8.1 Hz, 1H), 7.78 (ddd, *J* = 0.9 Hz, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 4.5 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.88 (d, *J* = 4.5 Hz, 1H). ^{13}C NMR (125 MHz, MeOD): δ 60.7, 86.3, 87.8, 117.9, 122.2, 124.2, 125.6, 126.6, 128.1, 128.3, 128.4, 129.4, 131.1, 147.6, 149.8. MS (FAB^+): *m/z* 260 $[M+H]^+$. Anal. Calcd for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40.Found: C, 83.41; H, 5.11; N, 5.31%.

2-(1-Hydroxy-3-trimethylsilanyl-2-propynyl) pyridine (**3k**): The same experiment was carried out as above except that 2-pyridinecarboxaldehyde was added. The product **3k** was isolated as oil in a yield of 88% (1.69 g). UV (CH_2Cl_2): λ_{max} (ε) 260 (6060). IR (CH_2Cl_2): 894, 1262, 1421, 1590, 2302, 2405, 2678, 2981, 3062 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.13 (s, 9H), 4.40 (brs, 1H), 5.48 (s, 1H), 7.22 (m, 1H), 7.51 (m, 1H), 7.70 (m, 1H), 8.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -0.15, 64.0, 90.5, 104.5, 120.9, 123.3, 137.2, 148.1, 153.7. MS (FAB^+): *m/z* 206 $[M+H]^+$. Anal. Calcd for $C_{11}H_{15}NOSi$ (205.3): C, 64.34; H, 7.36; N, 6.82. Found: C, 64.29; H, 7.39; N, 6.89%.

General procedure for the reaction of propargylic alcohol (**3**) *with pyridinium hydrochloride*

To a solution of propargylic alcohol **3** (1 mmol) in MeOH (4 mL) was added pyridinium hydrochloride (0.04 mmol) at r.t. After stirring for 6 h, water (5 mL) was added, extraction with CH_2Cl_2 (2 × 10 mL) was performed. The organic layer was dried over $MgSO_4$ and concentrated under vacuum to yield the products **4b–i** and **5b–i** which were separated by column chromatography.

Reaction of 4-(1-hydroxy-3-trimethylsilanyl-2-propynyl) pyridine (**3b**) *with pyridinium hydrochloride*

4-(1-Hydroxy-3-trimethylsilanyl-2-propynyl) pyridine **3b** (0.20 g) in MeOH (4.0 mL), pyridinium hydrochloride (5.6 mg). yielded the two products separated by column chromatography (silica gel, hexane/EtOAc, 4/1).

1-Pyridin-4-yl-3-trimethylsilanyl-prop-2yn-1-one (**4b**): Yellow liquid (0.52 g, 26%). UV (CH_2Cl_2): λ_{max} (ε) 237 (6610). IR (CH_2Cl_2): 1408, 1558, 1650, 1737, 1943, 2154, 2856, 2909, 2927, 2963, 3052, 3055 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.30 (s, 9H), 7.87 (dd, *J* = 6.0 Hz, *J* = 3.0 Hz, 2 H), 8.81 (dd, *J* = 6.0 Hz, *J* = 3.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.7, 100.1, 103.2, 122.1, 142.1, 150.9, 176.7. MS (FAB^+): 204 $[M+H]^+$. Anal. Calcd for $C_{11}H_{13}NOSi$ (203.3): C, 64.98; H, 6.44; N, 6.89. Found: C, 64.95; H, 6.41; N, 6.85%.

(E)-*1-Pyridin-4-yl-3-trimethylsilanyl-prop-2-en-1-one* (**5b**): (0.105 g, 52%). UV (CH_2Cl_2): λ_{max} (ε) 195 (2900), 231 (4500), 277(2300).IR (CH_2Cl_2): 1409, 1557, 1652, 2294, 2316, 2351, 2854, 2863, 2923, 2954, 3055 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.11(s, 9H), 7.05 (d, *J* = 18.8 Hz, 1H), 7.25 (d, *J* = 18.8 Hz, 1H), 7.60 (dd, *J* = 6.0 Hz, *J* = 2.0 Hz, 2H), 8.70 (dd, *J* = 6.0 Hz, *J* = 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –1.8, 121.8, 137.4, 143.9, 150.7, 152.7, 189.9. MS (EI): 205 $[M]^+$. Anal. Calcd for $C_{11}H_{15}NOSi$ (205.3): C, 64.34; 7.36; N, 6.82. Found: C, 64.30; H, 7.34; N, 6.85%.

Reaction of 4-(1-hydroxy-2-butynyl) pyridine (**3c**) *with pyridinium hydrochloride*

4-(1-Hydroxy-2-butynyl) pyridine **3c** (0.18 g) in MeOH (8 mL), pyridinium hydrochloride (7 mg) yielded the two products separated by column chromatography (silica gel, $CHCl_3$/Hexane, 2/1).

1-Pyridin-4-yl-but-2-yn-1-one (**4c**): Yellow liquid (27 mg, 15%), UV (CH_2Cl_2): λ_{max} (ε) 247 (9050 M^{-1} cm^{-1}). IR (CH_2Cl_2): 1206, 1223, 1271, 1467, 1710, 2398, 2872, 2886, 2928, 2958, 3016, 3024 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.17 (s, 3H), 7.68 (d, *J* = 5.8 Hz, 2H), 8.81 (d, *J* = 5.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.7, 78.6, 94.7, 122.1, 142.4, 150.8, 177.0. MS (EI): *m/z* 145 $[M]^+$. HRMS Calcd for C_9H_9NO: 145.1580. Found: 145.1577.

(E)-*1-Pyridin-4-yl-but-2-en-1-one* (**5c**): Yellow liquid (88 mg, 49%), UV (CH_2Cl_2): λ_{max} (ε) 249 (9300 M^{-1} cm^{-1}). IR (CH_2Cl_2): 1228, 1296, 1336, 1441, 1555, 1595, 1625, 1676, 3018, 3024 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.04 (dd, *J* = 1.6 Hz, *J* = 6.9 Hz, 3H), 6.81 (dq, *J* = 1.6 Hz, *J* = 3.2 Hz, *J* = 15.4 Hz, 1H), 7.07–7.16 (m, 1H), 7. 69 (d, *J* = 5.8 Hz, 2H), 8.80 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.8, 121.7, 127.2, 144.3, 147.7, 150.7, 190.1. MS (EI): *m/z* 147 $[M]^+$. HRMS Calcd for C_9H_9NO: 147.1739. Found: 147.1735.

Reaction of 4-(1-hydroxy-3-phenyl-2-propynyl) pyridine (**3d**) *with pyridinium hydrochloride*

3-Phenyl-1-(pyridine-4-yl) prop-2-yn-1-ol (**3d**) (0.20 g) in MeOH (5 mL), pyridinium hydrochloride (5.5 mg) yielded two products separated by column chromatography (silica gel, hexane/EtOAc, 1/1).

1-Pyridin-4-yl-3-phenyl-prop-2-yn-1-one (**4d**): (20 mg, 10%), UV (CH_2Cl_2): λ_{max} (ε) 233 (9300), 301 (7200). IR (CH_2Cl_2): 1264, 1421, 1551, 1604, 1650, 1961 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 2H), 7.48 (m, 1H), 7.66 (m, 2H), 7.96 (d, *J* = 5.8 Hz, 2H), 8.83 (d, *J* = 5.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 86.2, 95.2, 119.3, 122.1, 128.8, 131.4, 133.3, 142.5, 150.6, 176.7. MS (FAB^+): *m/z* 208 $[M+H]^+$. Anal. Calcd for $C_{14}H_9NO$ (207.2): C, 81.14; H, 4.38; N, 6.76. Found: C, 81.02; H, 4.42; N, 6.69%.

(E)-*1-Pyridin-4-yl-3-phenyl-prop-2-en-1-one* (**5d**) (0.11 g, 55%). m.p. 75–76°C. UV (CH_2Cl_2): λ_{max} (ε) 235 (14800), 308 (14600). IR (CH_2Cl_2): 1149, 1261, 1416, 1541, 2291, 2397, 2516, 2675, 2980, 3046, 3682, 3755 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 15.7 Hz, 1H), 7.43 (m, 3H), 7.63 (m, 2H), 7.76 (d, *J* = 5.4 Hz, 2H), 7.81 (d, *J* = 15.7 Hz, 1H), 8.82 (d, *J* = 5.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 121.2, 121.5, 128.6, 129.1, 131.2, 134.3, 144.4, 146.8, 150.7, 189.8. MS (FAB^+): *m/z* 210 $[M+H]^+$. Anal. Calcd for $C_{14}H_{11}NO$ (209.2): C, 80.36; H, 5.30; N, 6.69. Found: C, 80.40; H, 5.29; N, 6.72%.

Reaction of 4-(1-hydroxy-4, 4-dimethyl-2-pentynyl) pyridine (**3e**) *with pyridinium hydrochloride*

4-(1-Hydroxy-4, 4-dimethyl-2-pentynyl) pyridine (**3e**) (0.57 g) in MeOH (10 mL) pyridinium hydrochloride (17 mg) yielded after column chromatography (silica gel, hexane/EtOAc, 9/1) two products.

1-Pyridin-4-yl-4,4-dimethyl-pent-2-yn-1-one (**4e**): (68 mg, liquid, 12%). UV ($CHCl_3$): λ_{max} (ε) 239 (13500). IR (CH_2Cl_2): 1062, 1209, 1257, 1324, 1365, 1407, 1457, 1560, 1652, 2212, 2975 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.35 (s, 9H), 7.84 (d, *J* = 5.2 Hz, 2H), 8.78 (d, *J* = 5.2 Hz, 2H). ^{13}C (125 MHz, $CDCl_3$): δ 28.1, 30.0, 77.6, 106.1, 121.9, 142.5, 150.7, 177.1. MS (FAB^+): *m/z* 188 $[M+H]^+$. Anal. Calcd for $C_{12}H_{13}NO$ (189.3): C, 76.98; H, 7.00; N, 7.48. Found: C, 76.94; H, 7.03; N, 7.51%.

(E)-*1-Pyridin-4-yl-4,-4-dimethyl-pent-2-en-1-one* (**5e**): (0.43 g, 75%). UV ($CHCl_3$): λ_{max} (ε) 235 (11300). IR (CH_2Cl_2); 1220, 1300, 1334, 1610, 1652, 1671, 2206, 2297, 2859, 2959, 3044 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.05 (s, 9H), 6.59 (d, *J* = 15.8 Hz, 1H), 7.01 (d, *J* = 15.8 Hz, 1H), 7.57 (d, *J* = 5.7 Hz, 2H), 8.68 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.5, 34.3, 120.4, 121.5, 114.5, 150.5, 161.7, 190.6. MS (FAB^+): *m/z* 190 $[M+H]^+$, Anal. Calcd for $C_{12}H_{15}NO$ (189.3): C, 76.16; H, 7.99; N, 7.40. Found: C, 76.13; H, 8.06; N, 7.35%.

(E)-*1-Quinolin-4-yl-3-trimethylsilanyl-prop-2-en-1-one* (**5f**): 4-(1-Hydroxy-3-trimethylsilanyl-2-propynyl) quinoline (**3f**) (0.42 g) in MeOH (8 mL) pyridinium hydrochloride (9.5 mg, For the *p*-toluenesulfonate and the triflate pyridinium salts the same molar amount was used), yielded after column chromatography (hexane/

EtOAc 4/1) one product **5f** (0.231 g, 55%), as a yellow liquid. UV (CH_2Cl_2): λ_{max} (ε) 232 (11200), 317 (2450 M^{-1} cm^{-1}). IR (CH_2Cl_2): 1463, 1509, 1579, 1603, 1658, 1726, 2332, 2862, 2932, 3374, 3610 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.14 (s, 9H), 6.95 (d, J = 15.3 Hz, 1H), 7.09 (d, J = 15.3 Hz, 1H), 7.39 (d, J = 3.4 Hz, 1H), 7.58 (t, J = 5.6 Hz, J = 12.2 Hz, 1H), 7.74 (t, J = 5.6 Hz, J = 12.2 Hz, 1H), 8.01 (d, J = 7.0 Hz, 1H), 8.15 (d, J = 7.0 Hz, 1H), 8.98 (d, J = 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –1.9, 119.4, 125.3, 127.7, 129.9 (2C), 141.7, 143.9, 148.7, 149.5, 154.0, 155.4, 194.6. MS (EI): *m/e* (%): 255 $[M]^+$(50), 240 (100), 183 (10),156 (15), 128 (20). Anal. Calcd for $C_{15}H_{17}NOSi$ (255.4): C, 70.54; H, 6.71; N, 5.48. Found: C, 70.51; H, 6.74; N, 5.50%.

Reaction of 4-(1-hydroxy-2-butynyl) quinoline (**3g**) *with pyridinium hydrochloride*

4-(1-Hydroxy-2-butynyl) quinoline (**3g**) (0.22 g) in MeOH (10 mL), pyridinium hydrochloride (6.4 mg) yielded after column chromatography (silica gel, hexane/EtOAc, 4/1) two products.

1-Quinolin-4-yl-but-2-yn-1-one (**4g**): Colourless liquid (65 mg, 30%). UV (MeOH): λ_{max} (ε) 230 (8700), 248 (8600), 329 (2500). IR (CH_2Cl_2): 725, 895, 1262, 1418, 1633, 2300, 2689, 2989, 3058, 3419, 3945 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 3H), 7.71 (t, J = 7.1 Hz, J = 15.4 Hz, 1H), 7.79 (t, J = 7.1 Hz, J = 15.4 Hz, 1H), 8.16 (d, J = 4.0 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 8.93 (d, J = 8.4 Hz, 1H), 9.12 (d, J = 4 Hz, 1H). 13C NMR (100 MHz, CDCl3): δ 29.8, 80.4, 93.4, 124.1, 124.3, 125.7, 129.1, 130.0 (2C), 139.6, 149.3, 149.9, 179.2. MS (EI): *m/z* 195 [M]+. Anal. Calcd for $C_{13}H_9NO$ (195.2): C, 79.98; H, 4.65; N, 7.17. Found: C, 79.95; H, 4.68; N, 7.15%.

(E)-*1-Quinolin-4-yl-but-2-en-1-one* (**5g**): Orange liquid (79 mg, 36%). UV ($CHCl_3$): λ_{max} (ε) 243 (9700), 306 (2800), 317(2900). IR (CH_2Cl_2): 1264, 1282, 1456, 1503, 1539, 1621, 1653, 1683, 1716, 1732, 1771, 1843, 2401, 2851, 2925 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.0 (dd, J = 1.1 Hz, J = 6.8 Hz, 3H), 6.62 (dd, J = 1.1 Hz, J = 15.7 Hz, 1H), 6.82 (septet, 1H), 7.41 (d, J = 3.6 Hz, 1H), 7.59 (t, J = 7.3 Hz, J = 15.3 Hz, 1H), 7.77 (t, J = 7.3 Hz, J = 15.3 Hz, 1H), 8.02 (d, J = 8.5 Hz, 1H), 8.18 (d, J = 8.5 Hz, 1H), 9.0 (d, J = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.2, 119.2, 124.7, 125.4 (2C), 127.8, 129.9, 130.1, 132.4, 144.8, 148.8, 149.6, 195.0. MS (EI): *m/z* 197 $[M]^+$. Anal. Calcd for $C_{13}H_{11}NO$ (197.2): C, 79.16; H, 5.62; N, 7.10. Found: C, 79.18; H, 5.59; N, 7.7%.

Reaction of 4-(1-hydroxy-4, 4-dimethyl-2-pentynyl) quinoline (**3h**) *with pyridinium hydrochloride*

4-(1-Hydroxy-4, 4-dimethyl-2-pentynyl) quinoline (**3h**) (0.40 g) in MeOH (10 mL), pyridiniym hydrochloride (9.6 mg) yielded after column chromatography (silica, hexane/EtOAc, 9/1) three products.

1-Quinolin-4-yl-4, 4-dimethyl-pent-2-yn-1-one (**4h**): (0.103 g, 26%). UV (CH_2Cl_2): λ_{max} (ε) 250 (12100), 328 (6400). IR (CH_2Cl_2): 1508, 1652, 2204, 2974 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.37 (s, 9H), 7.64 (ddd, J = 1.2 Hz, J = 6.8 Hz, 1H), 7.74 (ddd, J = 1.2 Hz, J = 6.8 Hz, 1H), 8.07 (d, J = 4.4 Hz, 1H), 8.15 (d, J = 8.1 Hz, 1H), 8.88 (d, J = 8.1 Hz, 1H), 9.08 (d, J = 4.4 Hz 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.1, 29.9, 79.5, 104.5, 123.9, 124.0, 125.5, 128.8, 129.8 (2C), 139.8, 149.2, 149.8, 179.3. MS (FAB^+): *m/z* 238 [M + H]$^+$. Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.85; H, 6.45; N, 6.01%.

(E)-*1-Quinolin-4-yl-4, 4-dimethyl-pent-2-en-1-one* (**5h**): (0.149 g, 37%). UV (CH_2Cl_2): λ_{max} (ε) 230 (13400), 307 (2940), 317 (2940). IR (CH_2Cl_2): 1651, 2303, 2955, 3060 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.06 (s, 9H), 6.48 (d, J = 16.1 Hz, 1H), 6.77 (d, J = 16.1 Hz, 1H), 7.38 (d, J = 4.3 Hz, 1H) 7.55 (ddd, J = 1.1 Hz, J = 7.0 Hz, 1H), 7.71 (ddd, J = 1.1 Hz, J = 7.0 Hz, 1H), 8.01 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 8.96 (d, J = 4.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.6, 34.5, 119.4, 124.7, 125.5, 125.9, 127.7, 129.9, 130.0, 144.7, 148.9, 149.7, 163.5, 195.6. MS (FAB^+): *m/z* 240 [M + H]$^+$. Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.41; H, 7.01; N, 6.05%.

(Z)-*1-Quinolin-4-yl-4, 4-dimethyl-pent-2-en-1-one* (**5h**): (18% evaluated from NMR spectrum) ^1H NMR (400 MHz, $CDCl_3$): δ 1.16 (s, 9H), 6.08 (d, J = 13.1 Hz, 1H), 6.27 (d, J = 13.1 Hz, 1H), 7.56–7.60 (m, 2H), 7.68 (ddd, J = 1.3 Hz, J = 6.9 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 8.50 (d, J = 8.4 Hz, 1H), 8.95 (d, J = 4.3 Hz, 1H).

Reaction of 4-(1-hydroxy-3-phenyl-2-propynyl) quinoline (**3i**) *with pyridinium hydrochloride*

4-(1-Hydroxy-3-phenyl-2-propynyl) quinoline (**3i**) (0.70 g) in MeOH (10 mL), pyridinium hydrochloride (16 mg) yielded after column chromatography (silica gel, hexane/EtOAc, 9/1) two products.

1-Quinolin-4-yl-3-phenyl-prop-2yn-1-one (**4i**): (0.17 g, 24%). UV (CH_2Cl_2): λ_{max} (ε) 230 (25200), 309 (13200). IR (CH_2Cl_2): 1605, 2354, 3679 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43–7.47 (m, 2H), 7.50 (m, 1H), 7.69–7.74 (m, 3H), 7.78–7.83 (m, 1H), 8.21 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 4.4 Hz, 1H), 8.98 (d, J = 8.5 Hz, 1H), 9.15 (d, J = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 88.2, 93.8, 119.7, 124.1, 125.7, 128.9, 129.2, 130.2, 131.4, 133.3, 139.7, 149.4, 150.1, 179.1. MS (FAB^+). *m/z* 258 [M + H]$^+$. Anal. Calcd for $C_{18}H_{11}NO$: C, 84.03; H, 4.31; N, 5.44. Found: C, 84.11; H, 4.23; N, 5.49%.

(E)-*1-Quinolin-4-yl-3-phenyl-prop-2-en-1-one* (**5i**): (0.15 g, 21%). UV (CH_2Cl_2): λ_{max} (ε) 230 (21300), 305 (17200). IR (CH_2Cl_2): 1599, 2156, 2191 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.18 (d, J = 16.1 Hz, 1H), 7.35–7.40 (m, 3H), 7.47–7.53 (m, 4H), 7.57 (t, J = 7.8 Hz, J = 15.2 Hz, 1H), 7.74 (t, J = 7.8 Hz, J = 15.2 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 9.01 (d, J = 4.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 119.2, 124.5, 126.2, 127.8, 129.1, 129.5, 129.9, 130.0, 131.3, 133.9, 144.6, 148.0, 148.7, 149.6, 194.7. MS (FAB^+): *m/z* 260 [M + H]$^+$. Anal. Calcd for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.31; H, 5.07; N, 5.49%.

(E)-*1-Pyridin-2-yl-3-trimethylsilanyl-prop-2-en-1-one* (**5k**): Obtained from 2-(1-hydroxy-3-trimethylsilanyl-2-propynyl)pyridine **3k** with pyridinium hydrochloride as above in a yield of 42%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.12 (s, 9H), 7.37 (ddd, J = 1.0 Hz, J = 4.7 Hz, 1H), 7.44 (d, J = 18.9 Hz, 1H), 7.83 (ddd, J = 2.0 Hz, 7.8 Hz, 1H), 8.01 (d, J = 18.9 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 8.70 (d, J = 4.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –1.76, 123.2, 126.7, 136.4, 136.9, 148.8, 150.2, 154.0, 188.4. IR (CH_2Cl_2): 1316, 1600, 1666, 2326, 2359, 2955, 3479 cm^{-1}. UV (CH_2Cl_2): λ_{max} (ε) 257 (11850). MS (FAB^+): *m/z* 206 [M + H]$^+$. Anal. Calcd for $C_{11}H_{15}NOSi$ (205.3): C, 64.34; H, 7.36; N, 6.82. Found: C, 64.37; H, 7.31; N, 6.90%.

Reaction of 4-(1-hydroxy-3-trimethylsilanyl-2-propynyl) pyridine (**3b**) *with pyridinium hydrochloride in MeO^{2}H*

To a solution of 4-(1-hydroxy-3-trimethylsilanyl-2-propynyl) pyridine (3b) (0.15 g) in d-MeO^{2}H (4.0 mL) was added pyridine hydrochloride (4.2 mg) at rt. After stirring for 6 h, water (5 mL) was added, extracted with CH_2Cl_2 (2 × 10 mL), dried over $MgSO_4$ and concentrated under vacuum to yield the product purified by column chromatography (silica gel, hexane/EtOAc, 4/1). (E)-1-pyridin-4-yl-3-trimethylsilanyl-prop-2-en-1-one **5b** was obtained in a yield of 51%. ^1H NMR (500 MHz, $CDCl_3$): δ 0.17(s, 9H), 7.64 (dd, J = 4.5 Hz, J = 1.6 Hz, 2H), 8.76 (dd, J = 4.5 Hz J = 1.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ –1.9, 121.7, 137.2, 143.7, 150.6, 152.4, 189.9. MS (FAB^+): 208 [M + H]$^+$. Anal. Calcd for $C_{11}H_{13}D_2NOSi$ (207.3): C, 63.72; H, 8.26; N, 6.76. Found: C, 63.69; H, 8.24; N, 6.79%.

Endo-*2-(quinolin-4-yl-carbonyl)*-exo-*3-trimethylsilanyl-bicyclo[2.2.1]hepte-5-ene* (**16**): A solution of the silylated enone **5f** (50 mg) and of cyclopentadiene (1 mL) in 0.1 M LiCl THF (1 mL) was left at 25 °C for 12 h. The reaction medium was chromatographed on a silica gel column (hexane–EtOAc, 9 : 1). The product **16** was isolated in a yield of 50%. Crystallised in MeOH:acetone (7 : 3) as a white solid, m.p. 87.4 °C. UV (MeOH) λ_{max}: 205 nm (0.7758), 232 (0.2188). IR (MeOH): 1679, 2974 cm^{-1}. ^1H NMR ($CDCl_3$ 400 MHz): δ 0.06 (s, 9H), 1.28–1.34 (m, 3H), 2.88 (s, 1H), 3.07 (s, 1H), 3.63 (q, J = 3.6 Hz, 1H), 5.63 (q, J = 3.2, 2.8 Hz, 1H), 6.41 (q, J = 3.2, 2.8 Hz, 1H), 7.54 (d, J = 4.4 Hz, 1H), 7.57 (m, 1H), 7.59 (t, J = 6.8 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 9.0 (d, J = 4.4 Hz, 1H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ –1.85, 27.88, 44.5, 48.2, 48.9, 54.2, 118.1, 125.1, 127.9, 128.6, 129.7, 130.0, 139.5, 141.1, 145.4, 148.4, 149.3, 204.2. MS (FABMS): *m/z* 322 [M + H]$^+$; Exact mass Calcd for $C_{20}H_{24}ONS$: 322.1627. Found: 322.1627.

Crystal structure determination

Diffraction measurements were made on an Enraf-Nonius CAD-4 diffratometer by use of graphite-monochromatised MoKα radiation (λ = 0.7107Å). Unit cell parameters were obtained by least squares fit to the automatically centred settings for 25 reflections. Intensity data were collected by use of ω-2θ scan mode. All intensity data were collected for Lorentz polarisation and absorption (empirical ψ corrections). Crystallographic data (excluding structure factors) for the structures of enone (**5d**) and of the Diels–Alder adduct (**16**) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 658185 for enone (**5d**) and CCDC 658184 for D7A adduct (**16**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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