Synthesis of Pentafluorophenyl- and Pyridinyl-3 Allenes

Ramazan Erenler[†]* and Jean-François Biellmann*
Institute of Chemistry, Academia Sinica, Nankang 115, Taipei, Taiwan, R.O.C.

The allenes 1,2,3,4,5-pentafluoro-6-(3-phenylpropa-1,2-dienyl)benzene **4**, 3-(3-phenylpropa-1,2-dienyl)pyridine **11** and 3-(3-(pyridine-3-yl)propa-1,2-dienyl)pyridine **17** and the acetylenes **5**, **12** and **16** were obtained by reduction of the corresponding propargylic acetates **3**, **10** and **15** by Samarium(II) iodide in the presence of Pd(0). Base-promoted isomerisation of acetylene **12** provided allene **11** in a yield of 80%. 1-(Pentafluorophenyl)-3-phenylprop-2-yn-1-ol **2** was prepared from phenylacetylene and pentafluorobenzaldehyde. The condensation of nicotinaldehyde with trimethylsilylacetylene gave the 3-(trimethylsilyl)-1-(pyridine-3-yl)prop-2-yn-1-ol **7**. The removal of the silyl group of **7** to acetylene **8** was done in basic conditions. The Pd catalysed condensation of the acetylene **8** with iodobenzene gave 3-phenyl-1-(pyridine-3-yl)prop-2-yn-1-ol **9**. The Pd catalysed condensation of **8** with 3-bromopyridine gave the 1,3-dipyridin-3-yl-prop-2-yn-1-ol **14**. The propargylic alcohols **2**, **9** and **14** were converted to the acetates **3**, **10** and **15** with acetic anhydride-pyridine.

Key words: Isomerisation reaction; Heterocyclic allene; Pyridinyl allene; Tetrafluorophenyl allene; Samarium diiodide.

INTRODUCTION

Allenes present in some natural products is an interesting function whose reactivity is useful in synthesis. The activatation of allenes in biological reactions may lead to inhibition. The versatility of the allene acting as nucleophile as well as electrophile makes the preparation of some allenes a difficult task, for instance heterocyclic allenes whose number are limited. Indeed the presence of an electron attracting ring increases the reactivity of the allene toward nucleophilic addition so that the allenic function may not survive the reaction and/or purification conditions.[1-4] Among the most commonly used methods is the reduction of propargylic alcohols and esters to allenes. In another method, the mild conditions of the reduction of propargylic acetates into mono-, di-, and trisubstituted allenes by SmI_2 in the presence of Pd^0 opens the way to reactive allenes.[5]

For several reasons we became interested in pyridinic allenes and in allenes containing electron attracting groups. We found in the literature only one mention of an allenic pyridine: 2,4-(4-pyridinyl)penta-2,3-diene prepared by reaction of a Meldrum's acid derivative with methyl-lithium in THF-HMPA.[6] 5-(1,3-Butadienyl)-3-methyl-4-(1,2-propadienyl)isoxazole is described as polymerizing in the solid state.[7]

Herein we report the synthesis of some novel allenes: 1,2,3,4,5-pentafluoro-6-(3-phenylpropa-1,2-dienyl)benzene **4**, 3-(3-phenylpropa-1,2-dienyl)pyridine **11** and 3-(3-(pyridine-3-yl)propa-1,2-dienyl)pyridine **17**.

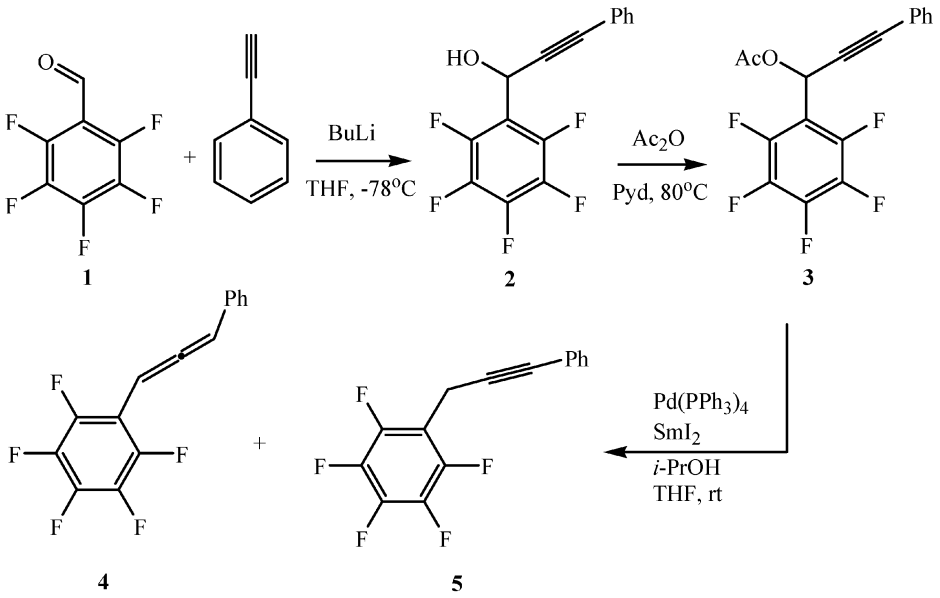
RESULTS AND DISCUSSION

Propargyl alcohol **2** was prepared by the treating of the lithium salt of phenylacetylene with pentafluorobenzaldehyde **1** in THF (yield 96%). This alcohol **2** was converted to propargylic acetate **3** by acetic anhydride with a catalytic amount of pyridine at reflux for 30 min. The reduction of propargylic acetate **3** with SmI_2 in the presence of catalytic Pd(0) yielded allene **4** (30%) and acetylene **5** (11%) (Scheme I). The ^{13}C-NMR signal observed at δ: 210.9 ppm in compound **4** is in agreement with the allenic structure, whereas the ^{13}C-NMR signals at δ: 81.6 and 83.6 ppm for compound **5** are typical of acetylene. All others' spectroscopic data confirm these structures.

3-(Trimethylsilyl)-1-(pyridine-3-yl)prop-2-yn-1-ol **7**

* Corresponding author. E-mail: rerenler@gop.edu.tr, jfb@chem.sinica.edu.tw
[†] Present address: Department of Chemistry, Faculty of Art and Science, Gaziosmanpasa University, 60240 Tokat-Turkey

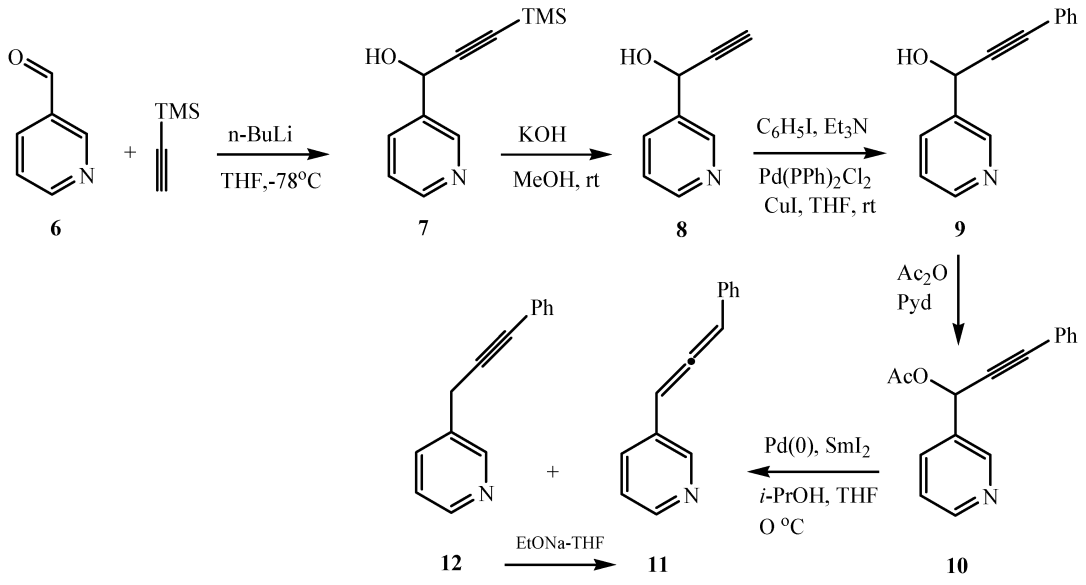
Scheme I



was prepared by the treating of nicotinaldehyde **6** with trimetylsilylacetylene and butyllithium in THF (yield 97%), and its spectral data are consistent with those of the literature.[8] Removal of the silyl group was performed with potassium hydroxide in methanol to give propargylic alcohol **8**. Sonogashira coupling of alkyne **8** with iodobenzene afforded the phenyl derivative of pyridine **9** converted to acetate **10** with acetic anhydride in the presence of pyridine at room temperature.[9,10] Reduction of acetate **10** with SmI_2 in the presence of palladium afforded allene **11** (16%) and acetylene **12** (40%). Moreover acetylene **12** was isomerised with sodium ethoxide to allene **11** in a yield of 80% (Scheme II). The signals in ^{1}H-NMR spectrum at δ: 6.57 and 6.64 ppm and in ^{13}C-NMR at δ: 208.1 ppm agree with the allenic structure of compound **11**.

The Pd-catalyzed cross-coupling reaction between 3-bromopyridine **13** with terminal alkyne **8** afforded dipyridine **14**. Treatment of this alcohol **14** with acetic anhydride in the presence of pyridine gave the acetate **15**. The treatment of acetate **15** with SmI_2 in the presence of palladium

Scheme II



gave acetylene **16** and allene **17** (Scheme III). ^{1}H and ^{13}C-NMR spectra of allene **17** agree with its symmetry. The signals at δ: 6.64 ppm in the ^{1}H-NMR spectrum and at δ: 208.2 ppm in the ^{13}C-NMR spectrum agree with the allenic structure for compound **17**.

CONCLUSION

The allenes **4**, **11** and **17** were prepared from the corresponding propargylic acetates by SmI_2 reduction in the presence of Pd(0). The acetylenes **5**, **12** and **16** were also produced. Acetylene **12** was isomerised to allene **11** by sodium ethoxide in THF. The allenes **4**, **11** and **17** were stable under the reaction conditions and could be chromatographed without loss. So the prejudice regarding their instability is not founded.

EXPERIMENTAL

General Procedures

Commercial reagents were purchased from standard chemical suppliers and purified to match the reported physical and spectroscopic data. 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. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AMX400 and 500 MHz instruments. Chemical shifts are in ppm from Me_4Si, generated from the $CDCl_3$. IR spectra were taken with a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analyses were measured with a Perkin-Elmer 2400CHN instrument. Mass spectra were obtained with a FAB JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan).

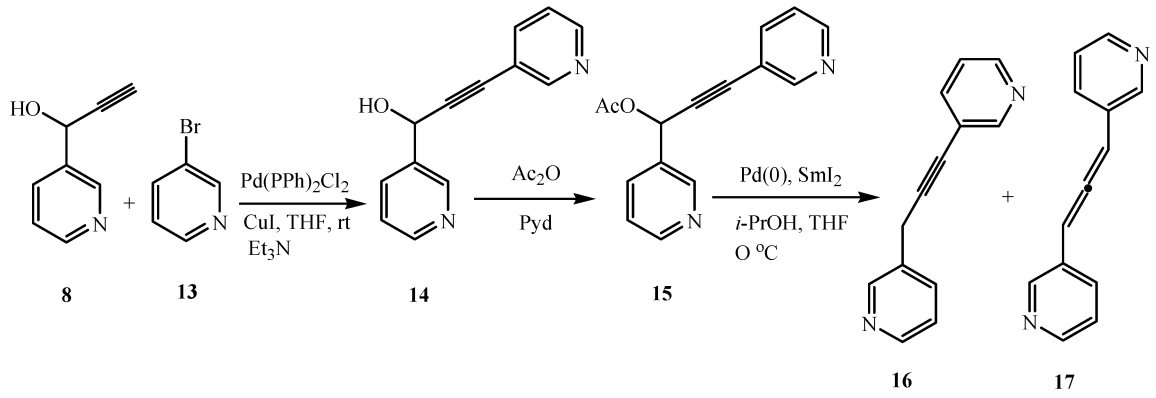
1-(Pentafluorophenyl)-3-phenylprop-2-yn-1-ol 2

To a solution of phenylacetylene (1.14 g) in anhydrous THF (10 mL) was added a solution of n-BuLi (7.0 mL) at -78 °C under argon. The reaction mixture was allowed to warm to -50 °C, then a solution of pentafluorobenzaldehyde (2.0 g) in THF (5.0 mL) was slowly added via syringe. After 1 h of stirring, the mixture was washed with saturated NH_4Cl, extracted with CH_2Cl_2 (2 × 10 mL), dried over $MgSO_4$, concentrated under vacuum to yield the product as an oil (2.92 g, 96%). UV/Vis (CH_2Cl_2); λ_{max} (ε) = 246 (17200); IR (CH_2Cl_2), υ = 905, 997, 1118, 1502, 1653, 2228, 3055, 3571, 3675; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 3.0 (brs, 1H), 5.98 (s, 1H), 7.29-7.37 (m, 3H), 7.42-7.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 55.3, 85.4, 86.6, 114.7 (m), 121.5, 128.3 (2C), 129.1, 131.8 (2C), 136.4 (m), 138.9 (m), 140.0 (m), 142.5 (m), 143.4 (m), 145.9 (m); Ms (FAB^+), *m/z*, 299 $[M+H]^+$; Anal. Calcd for $C_{15}H_7F_5O$ (298.2), C 60.41; H 2.37. Found, C 60.52; H 2.31.

1-(Pentafluorophenyl)-3-phenylprop-2-ynyl-1-acetate 3

A solution of 1-(pentafluorophenyl)-3-phenylprop-2-yn-1-ol (1.0 g) in acetic anhydride (2 mL) and pyridine (2 drops) was heated at 80 °C for 30 min. After 30 min at rt, the reaction mixture was quenched with water (10 mL), and the product was extracted with CH_2Cl_2 (3 × 15 mL) and

Scheme III



dried over $MgSO_4$. After filtration and evaporation of the solvent the crude material was chromatographed on silica gel (hexane/EtOAc, 4/1) to give the acetate **3** as a solid (0.93 g, 82%), mp 45-46 °C. UV/Vis (CH_2Cl_2), λ_{max} (ε) = 250 (30800); IR (CH_2Cl_2), υ = 919, 997, 1126, 1214, 1370, 1426, 1440, 1508, 1652, 1749, 2233, 2857, 2953; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 2.14 (s, 3H), 6.93 (s, 1H), 7.29-7.35 (m, 3H), 7.44-7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 20.5, 55.9, 82.3, 87.0, 111.6 (m), 121.3, 128.3 (2C), 129.2, 131.9 (2C), 136.4 (m), 138.8 (m), 140.6 (m), 143.1 (m), 143.7 (m), 146.3 (m), 169.2; Ms (FAB^+), *m/z*, 340 $[M+H]^+$; Anal. Calcd for $C_{17}H_9F_5O_2$ (340.2), C 60.01; H 2.67. Found, C 60.11; H 2.59.

Reduction of 1-(pentafluorophenyl)-3-phenylprop-2-ynyl-1-acetate 3 with SmI_2

To a solution of 1-(pentafluorophenyl)-3-phenylprop-2-ynylacetate **3** (0.50 g) in THF (10 mL) was added 2-propanol (88 mg), tetrakis(triphenylphosphine)-palladium(0) (84 mg) and 0.1 M solution of SmI_2 in THF (36.8 mL). After completion of the reaction (2 h), water was added (10 mL); the product was extracted with CH_2Cl_2 (2 × 15 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent the crude material was chromatographed on silica gel (hexane) to give the products **4** and **5**:

1,2,3,4,5-pentafluoro-6-(3-phenylpropa-1,2-dienyl)-benzene **4** as an oil (0.123 g, 30%), UV/Vis (CH_2Cl_2), λ_{max} (ε) = 252 (28300); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.61 (s, 1H), 6.62 (s, 1H), 7.29 (m, 1H), 7.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 83.4, 97.8, 110.0 (m), 126.6 (m), 127.5 (2C), 127.9, 128.3 (m), 128.9 (2C), 129.7 (m), 132.5, 136.6 (m), 139.0 (m), 141.3 (m), 143.3 (m), 145.8 (m), 210.9; Ms (FAB^+), *m/z*, 282 $[M]^+$; Anal. Calcd for $C_{15}H_7F_5$ (282.2), C 63.84; H 2.50. Found: C 63.79; H 2.55.

1,2,3,4,5-pentafluoro-6-(3-phenylprop-2-ynyl)benzene **5** as a solid (45 mg, 11%). mp 56-57 °C; UV/Vis (CH_2Cl_2), λ_{max} (ε) = 245 (11300); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 3.84 (s, 2H), 7.28-7.31 (m, 3H), 7.32-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 13.2, 81.6, 83.6, 110.9 (m), 122.9, 128.3 (3C), 131.8 (2C), 136.4 (m), 139.2 (m), 143.8 (m), 146.5 (m); IR (CH_2Cl_2), υ = 901, 1002, 1125, 1509, 1658, 2303, 2362; Ms (FAB^+), *m/z*, 282 $[M]^+$; Anal. Calcd for $C_{15}H_7F_5$ (282.2), C 63.84; H 2.50. Found, C 63.86; H 2.46.

1-(Pyridin-3-yl)prop-2-yn-1-ol 8

A solution of 3-(trimethylsilyl)-1-(pyridin-3-yl)prop-2-yn-1-ol **7** (1.30 g) in MeOH (5.0 mL) was added finely powdered KOH (0.53 g) in methanol (3.0 mL). After the completion of the reaction for 15 min at rt, the mixture was acidified with 1.0 N HCl. The aqueous solution was separated and neutralized with aqueous K_2CO_3 and extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under vacuum. The crude product was purified by column chromatography (silica, hexane/EtOAc, 1/1) to yield the product **8** as an oil (0.48 g, 57%). UV/Vis ($CHCl_3$), λ_{max} (ε) = 261 (2900); ^{1}H NMR (500 MHz, $CDCl_3$), δ: 2.62 (d, J = 2.2 Hz, 1H), 5.47 (d, J = 2.2 Hz, 1H), 6.0 (brs, 1H), 7.23 (dd, J = 7.8 Hz, J = 4.2 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 8.37 (d, J = 4.2 Hz, 1H), 8.62 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ: 61.4, 74.9, 83.2, 123.6, 135.0, 136.9, 147.6, 148.4; IR ($CHCl_3$), υ = 905, 1041, 1424, 1590, 2110, 2250, 3163; Ms (FAB^+), *m/z*, 134 $[M+H]^+$ (100); HRMS (FAB^+); Calcd for C_8H_7NO: *m/z* 133.0528; Found *m/z* 133.0525.

3-Phenyl-1-(pyridin-3-yl)prop-2-yn-1-ol 9

To a solution of 1-(pyridin-3-yl)prop-2-yn-1-ol **8** (1.20 g) and of iodobenzene (2.2 g) in THF (10.0 mL) was added bis(triphenylphosphine)palladium chloride (0.126 g), copper(I)iodide (69 mg) and triethylamine (5.0 mL). After being stirred for 15 h at rt, the reaction mixture was neutralized with 2 M HCl and the product was extracted with CH_2Cl_2 (2 × 10 mL). After adding $NaHCO_3$ to the solution, it was dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude material was chromatographed on silica gel (hexane/EtOAc, 3/2) to yield the product **9** as an oil (1.50 g, 80%).[11] UV/Vis ($CHCl_3$), λ_{max} (ε) = 244 (13700), 254 (13100); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 5.27 (brs, 1H), 5.71 (s, 1H), 7.25-7.30 (m, 4H), 7.39 (dd, J = 1.5 Hz, J = 7.9 Hz, 2H), 7.95 (d, J = 7.9 Hz, 1H), 8.44 (s, 1H), 8.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 62.2, 86.7, 88.4, 122.1, 123.6, 128.3 (2C), 128.6, 131.7 (2C), 134.9, 137.3, 147.7, 148.6; IR ($CHCl_3$), υ = 1040, 1432, 1485, 1737, 2232, 2359, 2394, 3014; Ms (FAB^+), *m/z*, 210 $[M+H]^+$ (100), HRMS (FAB^+); Calcd for $C_{14}H_{11}NO$: *m/z* 209.0841; Found *m/z* 209.0845.

1-(3-Phenyl-1-(pyridin-3-yl)prop-2-ynyl)-1-acetate 10

To a solution of 3-phenyl-1-(pyridin-3-yl)prop-2-yn-1-ol **9** (1.50 g) in acetic anhydride (3.0 mL) was added four drops of pyridine. After completion of the reaction for 2 h at rt, the reaction mixture was washed with water (5.0 mL) and the product was extracted with CH_2Cl_2 (3 × 10

mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude material was chromatographed on silica gel (hexane/EtOAc, 3/2) to give the product **10** as an oil (1.30 g, 72%). UV/Vis ($CHCl_3$) λ_{max} (ε) = 243 (15800); ^{1}H NMR (500 MHz, $CDCl_3$), δ: 2.10 (s, 3H), 6.69 (s, 1H), 7.27 (m, 3H), 7.32 (dd, *J* = 4.0 Hz, *J* = 7.9 Hz, 1H), 7.44 (dd, *J* = 1.6 Hz, *J* = 7.9 Hz, 2H), 7.92 (d, *J* = 7.9 Hz, 1H), 8.60 (d, *J* = 4.0 Hz, 1H), 8.81 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ: 20.9, 63.9, 84.3, 87.8, 121.5, 123.7, 128.3 (2C), 129.1, 131.9 (2C), 133.3, 135.8, 148.7, 149.6, 169.6; IR ($CHCl_3$), υ = 1380, 1461, 1494, 1797, 1856, 1941, 2944, 3003, 3055; Ms (FAB^+), *m/z*, 252 $[M+H]^+$ (30), 235 (30), 221 (32), 119 (93); HRMS (FAB^+) Calcd for $C_{16}H_{13}NO_2$: *m/z* 251.0946; Found *m/z* 251.0941.

Reduction of propargylic acetate 10 with SmI_2

To a solution of 3-phenyl-1-(pyridin-3-yl)prop-2-ynyl acetate **10** (0.98 g) in THF (2.0 mL) was added 2-propanol (0.23 g), $Pd(PPh_3)_4$ (0.23 g) and a 0.1 M solution of SmI_2 in THF (98 mL). After completion of the reaction (10 h), the mixture was concentrated under vacuum. Water was added to the reaction mixture; it was extracted with CH_2Cl_2 (2 × 15 mL) and dried over $MgSO_4$, After filtration and evaporation of the solvent the crude material was chromatographed on silica gel (hexane/EtOAc, 9/1) to give the products **11** and **12**.

3-(3-phenylpropa-1,2-dienyl)pyridine **11** as an oil (0.12 g, 16%). UV/Vis ($CHCl_3$), λ_{max} (ε) = 250 (24800); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.57 (d, *J* = 6.5 Hz, 1H), 6.64 (d, *J* = 6.5 Hz, 1H), 7.20-7.26 (m, 2H), 7.29-7.35 (m, 4H), 7.66 (d, *J* = 7.9 Hz, 1H), 8.45 (d, *J* = 4.3 Hz, 1H), 8.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 95.2, 99.0, 123.6, 127.0 (2C), 127.6, 128.9 (2C), 129.7, 132.8, 133.7, 148.2, 148.3, 208.1; IR ($CHCl_3$), υ = 905, 1023, 1214, 1421, 1520, 1601, 1941, 2398, 3025, 3623, 3690; HRMS (FAB^+); Calcd for $C_{14}H_{12}N$: *m/z* 194.0970; Found *m/z* 194.0967.

3-(3-phenylprop-2-ynyl)pyridine **12** as an oil (0.30 g, 40%). UV/Vis (CH_2Cl_2), λ_{max} (ε) = 240 (17500); ^{1}H NMR (500 MHz, $CDCl_3$), δ: 3.79 (s, 2H), 7.23 (dd, *J* = 4.3 Hz, *J* = 7.8 Hz, 1H), 7.27 (m, 3H), 7.42 (m, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 8.48 (d, *J* = 4.3 Hz, 1H), 8.62 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ: 23.2, 83.3, 85.9, 123.2, 123.4, 128.1, 128.3 (2C), 131.6 (2C), 132.4, 135.5, 148.1, 149.3; IR ($C2Cl_2$), υ = 1026, 1166, 1214, 1295, 1421, 1487, 1579, 1601, 2302, 3040, 3682; HRMS (FAB^+); Calcd for $C_{14}H_{12}N$: *m/z* 194.0970; Found *m/z* 194.0975.

Isomerisation of 3-(3-phenylprop-2-ynyl)pyridine 12

To a solution of 3-(3-phenylprop-2-ynyl)pyridine **12** (0.21 g) in THF (5.0 mL) was added sodium ethoxide (90 mg) in THF (3.0 mL). After completion of the reaction (4 h at rt), water was added to the mixture; it was extracted with CH_2Cl_2 (3 × 10 mL), dried over $MgSO_4$, and concentrated under vacuum to yield the product, 3-(3-phenylpropa-1,2-dienyl)pyridine **11** (0.168 g, 80%).

1,3-Bis-pyridin-3-yl-prop-2-yn-1-ol 14

To a solution of 1-(pyridine-3-yl)prop-2-yn-1-ol **8** (1.56 g) in THF (10.0 mL) was added 3-bromopyridine **10** (2.0 g), bis(triphenylphosphine)palladium(II)dichloride (164 mg), copper(I)iodide (89 mg) and triethylamine (4.0 mL). The mixture was stirred for 15 h at rt. The reaction mixture was washed with water (5.0 mL), and the product was extracted with dichloromethane (2 × 10 mL). The organic layer was dried over magnesium sulphate. After filtration and evaporation of the solvent, the crude material was chromatographed on silica gel (hexane/EtOAc, 3/2) to yield the product **14** as an oil (0.51 g, 21%). UV/Vis (CH_2Cl_2), λ_{max} (ε) = 244 (23400); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 5.50 (brs, 1H), 5.37 (s, 1H), 7.20 (dd, *J* = 4.9 Hz, *J* = 7.9 Hz, 1H), 7.29 (dd, *J* = 4.9 Hz, *J* = 7.9 Hz, 1H), 7.69 (dt, *J* = 1.8 Hz, *J* = 3.7 Hz, *J* = 7.9 Hz, 1H), 7.94 (dd, *J* = 1.5 Hz, *J* = 7.9 Hz, 1H), 8.42 (d, *J* = 4.0 Hz, 1H), 8.48 (s, 1H), 8.66 (s, 1H), 8.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 62.0, 82.8, 92.6, 119.7, 123.3, 123.6, 134.7, 136.9, 139.0, 147.8, 148.4, 148.8, 151.8; IR ($CHCl_3$), υ = 960, 1023, 1045, 1365, 1406, 1424, 1476, 1579, 1730, 2981, 3195; HRMS (FAB^+); Calcd for $C_{13}H_{10}N_2O$: *m/z* 211.0871 $[M+H]^+$; Found *m/z* 211.0871.

1,3-Bis-pyridin-3-yl-prop-2-ynyl-1-acetate 15

To a solution of alcohol **14** (0.31 g) in acetic anhydride (3.0 mL) was added 5 drops of pyridine. After 3 h at rt, the reaction mixture was washed with water (5.0 mL) and the product was extracted with dichloromethane (3 × 10 mL); it was then dried over magnesium sulfate. After filtration and evaporation of the solvent the crude material was chromatographed on silica gel (hexane/EtOAc, 1/4) to yield the product **15** as an oil (0.27 g, 73%). UV/Vis ($CHCl_3$), λ_{max} (ε) = 243 (14700); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 2.11 (s, 3H), 6.67 (s, 1H), 7.23 (dd, *J* = 4.9 Hz, *J* = 7.7 Hz, 1H), 7.32 (dd, *J* = 4.9 Hz, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 8.53 (s, 1H), 8.60

(s, 1H), 8.67 (s, 1H), 8.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 20.8, 63.7, 84.3, 87.8, 118.8, 122.9, 123.6, 132.6, 135.3, 138.8, 149.0, 149.3, 150.1, 152.4, 169.4; IR ($CHCl_3$), υ = 1406, 1432, 1476, 1517, 1576, 1738, 2250, 2398, 2974; Ms (FAB), *m/z* (%) = 253 $[M+H]^+$ (60), 193 (30), 143 (35), 119 (85); HRMS (FAB^+); Calcd for $C_{15}H_{12}N_2O_2$: *m/z* 252.2680; Found *m/z* 252.2684.

Reduction of propargylic acetate 15 with SmI_2

To a solution of acetate **15** (0.26 g) in THF (2.0 mL) was added 2-propanol (62 mg), $Pd(PPh_3)_4$ (60 mg) and a 0.1 M SmI_2 solution in THF (25.8 mL). After completion of the reaction for 4 h, half of the solvent was evaporated. Water (8 mL) was added to the mixture and it was extracted with dichloromethane (2 × 15 mL). The organic layer was dried over magnesium sulfate and treated with silica gel chromatography (hexane/EtOAc, 1/4) to give products **16** and **17**:

3-(3-(pyridine-3-yl)prop-2-ynyl)pyridine **16** as an oil (51 mg, 20%), UV/Vis ($CHCl_3$), λ_{max} (ε) = 242 (22900); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 3.86 (s, 2H), 7.24 (dd, *J* = 4.9 Hz, *J* = 7.9 Hz, 1H), 7.31 (dd, *J* = 5.2 Hz, *J* = 7.6 Hz, 1H), 7.70 (dt, *J* = 1.8 Hz, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 8.53 (s, 2H), 8.68 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 23.3, 80.0, 89.5, 122.9, 135.8, 138.6 (2C), 147.9, 148.4 (2C), 149.0, 152.3 (2C); IR ($CHCl_3$), υ = 1096, 1380, 1421, 1476, 1520, 1598, 1797, 2243, 2405; HRMS (FAB^+); Calcd for $C_{13}H_{10}N_2$: *m/z* 194.0884 $[M]^+$; Found *m/z* 194.08473.

3-(3-(pyridine-3yl)propa-1,2-dienyl)pyridine **17** as an oil (59 mg, 23%) UV/Vis (CH_2Cl_2), λ_{max} (ε) = 251 (22100); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.64 (s, 2H), 7.25 (dd, *J* = 4.8 Hz, *J* = 7.9 Hz, 2H), 7.64 (dd, *J* = 1.7 Hz, *J* = 7.9 Hz, 2H), 8.47 (dd, *J* = 1.4 Hz, *J* = 4.8 Hz, 2H), 8.56 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 95.8, 123.7, 129.0, 133.8, 148.3, 148.6, 208.3; IR ($CHCl_3$), υ = 1026, 1093, 1376, 1421, 1472, 1520, 1605, 1793, 1944, 2250, 2391, 3151; HRMS (FAB^+); Calcd for $C_{13}H_{10}N_2$: *m/z* 195.0922 $[M+H]^+$; Found *m/z* 195.0923.

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11. Data close to those published.[10]