Chapter five: Experimental

5.1 Experimental Techniques

Melting Points: Melting points were recorded on a Griffin melting point apparatus, and are uncorrected.

Infra-red spectra: Infra-red spectra were recorded on a Bruker Tensor 27 Fourier Transform spectrometer, as a thin film between NaCl plates or pressed into a KBr disk. Absorption maxima (ν_{max}) are quoted in wave numbers (cm^{-1}).

NMR Spectra: Proton (^{1}H) and Carbon (^{13}C) NMR spectra were recorded using either Bruker AC200 (200 MHz), Bruker AMX400 (400 MHz), or Bruker AVII500 (500 MHz) spectrometers. Chemical shifts are quoted in parts per million (ppm) downfield of tetramethylsilane with residual solvent as the internal standard. Assignments were made on the basis of chemical shifts, coupling constants, COSY, HMQC and n.O.e data, comparison with spectra of related compounds, and comparison with spectra predicted by ACD/NMR predictor v8.08 or later. Resonances are described as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), se (sextet), hep (heptet), oct (octet), app (apparent), and br (broad). Coupling constants (*J*) are given in Hz and are rounded to the nearest 0.1 Hz. Where two coupling constants were recorded for a single interaction, the average was recorded. Multiplets structures were confirmed using the J-coupler function on ACD NMR SpecManager v8.08 or later.

Mass spectra: Mass spectra were recorded on a VG Platform spectrometer using atmospheric pressure chemical ionisation from the solvent system 40:40:20 CH_3OH:CH_3CN:H_2O in positive (APCI+) or negative (APCI–) scan mode as indicated. GC mass spectra were recorded on an Agilent 6890 Series GC System spectrometer. Other mass spectra were recorded on VG Micromass ZAB IF or Masslab 20-250 spectrometers. *m/z* values are reported with their percentage abundances, although peaks with a relative intensity less than 10% are not reported. High resolution mass spectra were recorded by the author, Mr. Robin Procter, or Dr. James McCullagh at the Chemistry Research Laboratory, and are calculated to four decimal places from the molecular formula.

Nomenclature: All compounds were named and numbered using the ChemDraw Ultra 12.0 software package.

Chromatography techniques: Thin layer chromatography was performed on Merck DC-Alufolien 60 F_{254} 0.2 mm precoated plates, and Fluka Alufolien aluminium oxide plates. Product spots were visualised by quenching of UV fluorescence (ν_{max}=254 nm), then stained and heated using acidic vanillin solution, basic potassium permanganate solution, *p*-anisaldehyde, Dragondorff's reagent, iodine on silica, or ninhydrin as appropriate. Flash column chromatography was carried out on silica gel (ICN Silica 32-63 60 Å), or alumina gel (Fluka aluminium oxide for chromatography), and the solvent system used is quoted in parentheses.

Solvents and reagents: CH_2Cl_2, pentane, toluene, THF and Et_2O were dried by filtration through an activated alumina purification column. Triethylamine, pyridine, and diisopropylamine were dried by distilling over calcium hydride, and stored over calcium hydride or 3 Å molecular sieves. HMPA was dried over 3 Å molecular sieves for 1 month prior to use. Reagents obtained from Acros, Aldrich, Avocado, Fluka and Lancaster fine chemicals suppliers were used directly as supplied or following purification according to procedures described by Perrin and Armarego.[206] All non-aqueous reactions were carried out under an atmosphere of argon using flame dried glassware. All reactions were carried out at room temperature unless otherwise stated. 'Petrol' refers to the fraction of light petroleum ether boiling in the range 40-60 °C.

5.2 Experimental procedures for section 2.2

5.2.1 General procedures

General Procedure A: Acylation of amine 253with α-alkoxyacrylic acids.

Triphenylphosphine (300 mol%) was added portion-wise to a solution of the corresponding acid (200 mol %) and trichloroacetonitrile (0.30 mL/mmol) in CH_2Cl_2 (0.90 mL/mmol) at 0 ºC. After 30 minutes a solution of amine **8a** (100 mol%) and Et_3N (400 mol%) in CH_2Cl_2 (3 mL/mmol) was added dropwise. The mixture was stirred at 0 °C for one hour and then at room temperature overnight. The mixture was diluted with CH_2Cl_2 (10 mL/mmol) and washed with saturated aqueous $NaHCO_3$ (5 mL/mmol). The organic portion was dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by flash column chromatography, under the conditions noted, afforded the corresponding amide.

General Procedure B: Ring-closing metathesis of acrylamides and allylic alcohols.

Catalyst HG-II (0.5-10 mol%) was added to a solution of the corresponding amide (100 mol%) in the specified, argon sparged, solvent (20 mL/mmol). The mixture was then heated at the specified temperature until TLC analysis indicated that starting material was fully consumed. The reaction mixture was concentrated in vacuo. Purification of the residue by flash column chromatography, under the conditions noted, afforded the corresponding α,β-unsaturated lactam.

General Procedure C: Aromatisation of α,β-unsaturated lactams.

DBU (500 mol%) was added to a solution of the corresponding α,β-unsaturated lactam (100 mol%) in THF (2 mL/mmol) and the reaction was stirred at the indicated temperature until TLC analysis indicated that starting material was fully consumed. The reaction mixture was

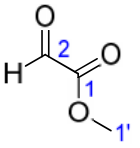
then concentrated *in vacuo*. Purification of the residue by flash column chromatography, under the conditions noted, afforded the corresponding pyridone.

General Procedure D: Triflation of pyridones.

KHMDS (0.5 M in PhMe, 200 mol%) was added dropwise to a solution of the corresponding pyridone (100 mol%) and Comins' reagent[184] (200 mol%) in THF (10 mL/mmol) at -78 °C. The resulting brown mixture was stirred at -78 °C for 1 hour and then warmed to room temperature over 3 hours. The solution was then diluted with hexane (20 mL/mmol) and washed with saturated aqueous Na_2CO_3 (10 mL/mmol). The organic portion was dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by flash column chromatography, under the conditions noted, afforded the corresponding pyridine triflated.

5.2.2 Experimental Procedures

Methyl 2-oxoacetate (251)



Ozone was bubbled through a solution of **250** (15.0 mL, 0.12 mol) in DCM (130 mL) at -78ºC for 5 hours and then the solution was purged with oxygen for 5 minutes. Dimethyl sulfide (9.80 mL, 0.13 mol) was added drop-wise and the reaction mixture was allowed to warm up to room temperature. Stirring continue for 16h then the reaction mixture was concentrated under reduced pressure and purified by distillation (b.p. 50ºC, 30 mmHg) to give the title compound **251** (9.57 g, 91%).

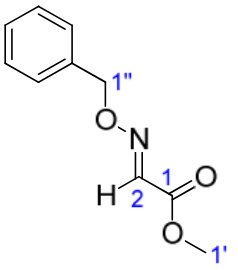
^{1}H NMR (400 MHz, $CDCl_3$) 9.43 (1H, s, C(2)H), 3.96 (3H, s, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 183.4 (C(2)), 159.8 (C(1)), 53.2 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the

literature.[185]

(E)-Methyl 2-(benzyloxyimino)acetate (252)



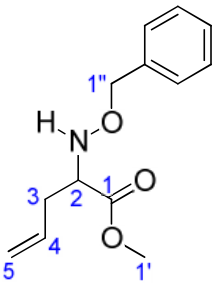
Methyl ester **251** was immediately added to a suspension of *O*-benzylhydroxylamine hydrochloride (9.71 g, 60.8 mmol) in methanol (250 mL). Pyridine (5.30 mL, 65.7 mmol) was added drop-wise and the reaction mixture heated at reflux for 4 hours. The solvent was removed and the crude product dissolved in DCM (200 mL) and washed with water (150 mL × 2). The aqueous layer was extracted with DCM (50 mL) and the combined organic layer was dried (Na_2SO_4), concentrated *in vacuo*. Purification by flash column chromatography (9:1 petrol:EtOAc) to give the title compound **252** as a colourless oil (11.6 g, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) 7.57 (1H, s, C(2)H), 7.38 (5H, s, Ph), 5.31 (2H, s, C(1")H_2), 3.87 (3H, s, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 162.4 (C(1)), 140.8 (C(2)), 135.8 (*i*-Ph), 128.6 (Ph), 128.6 (Ph), 128.5 (Ph), 78.1 (C(1")), 52.6 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[186]

Methyl 2-(benzyloxyamino)pent-4-enoate (253)



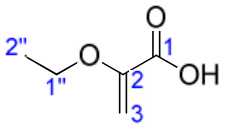
Zinc dust (7.23 g, 111 mmol) was added portion-wise to a biphasic solution of oxime **252** (11.6 g, 60.0 mmol) and allylbromide (5.20 mL, 60.1mmol) in THF (50 mL) and aqueous saturated NH_4Cl (260 mL). The reaction mixture was stirred for 3 hours and the aqueous layer was extracted with EtOAc (200 mL × 2). The combined organic layer was dried (Na_2SO_4) concentrated *in vacuo*. Purification by flash column chromatography (10:1 petrol:EtOAc) to give the title compound **253** as a colourless oil (10.2 g, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) 7.39-7.28 (5H, m, Ph), 5.96 (1H, br.s., NH), 5.72 (1H, ddt, *J* 17.0, 10.1, 7.0, C(4)H), 5.14-5.04 (2H, m, C(5)H_2),4.72 (2H, s, C(1")H_2),3.75 (3H, s, C(1')H_3),3.70 (1H, t, *J* 6.8, C(2)H),2.38-2.31 (2H, m, C(3)H_2).

^{13}C NMR (100 MHz, $CDCl_3$) 173.6 (C(1)), 137.6 (*i*-Ph), 133.0 (C(4)),128.4 (Ph),128.3 (Ph),127.8 (Ph),118.2 (C(5)),76.2 (C(1")),63.2 (C(2)),52.0 (C(1')),33.8 (C(3)).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[75]

2-Ethoxyacrylic acid (256)



Concentrated sulfuric acid (0.25 mL, 4.5 mmol) was added drop-wise to a mixture of pyruvic acid (3.50 mL, 50.0 mmol) in triethylorthoformate (20.0 mL) at 0 °C. The mixture

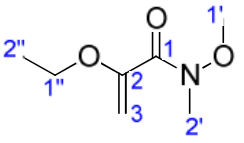
was stirred for 30 minutes and then diluted with CH_2Cl_2 (50 mL) and washed with water (2 × 25 mL) and brine (2 × 25 mL). The organic layer was dried (Na_2SO_4) concentrated *in vacuo*. Crude material was distilled at 1.5 mmHg to give a white crystalline solid. Trituration from pentane afforded the title compound **256** as a white crystalline solid (2.75 g, 47%).

^{1}H NMR (400 MHz, $CDCl_3$) 9,91 (1H, br. s., OH), 5.49 (1H, d, *J* = 2.5 Hz, C(3)H_2), 4.72 (1H, d, *J* = 2.5 Hz, C(3)H_2), 3.86 (2H, q, *J* = 7.0 Hz, C(1")H_2), 1.41 (3H, t, *J* = 7.0 Hz, C(2")H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 167.4 (C(1)), 150.0 (C(2)), 95.8 (C(3)), 64.4 (C(1")), 14.1 (C(2")).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[122]

2-Ethoxy-*N*-methoxy-*N*-methylacrylamide (265)



Triethylamine (140µL, 1.00 mmol) was added drop-wise to a mixture of 1,4-dimethylamino pyridine (1.8 mg, 0.01 mmol), amine **253** (41 mg, 0.43 mmol), acid **256** (35 mg, 0.30 mmol) in CH_2Cl_2 (5.00 mL). Then *N*-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (74 mg, 0.39 mmol) was added in one portion and the mixture was stirred under Argon at room temperature. Stirring was continued for 16 hours. The solution was diluted with CH_2Cl_2 (20 mL), and the organic layer was washed with saturated aqueous NH_4Cl solution (25 mL) and saturated aqueous $NaHCO_3$ solution (25 mL). The organic layer was dried (Na_2SO_4) concentrated *in vacuo*. Purification by flash column chromatography (4:1 petrol:EtOAc) to give the title compound **265** as a colourless oil (25 mg, 56%).

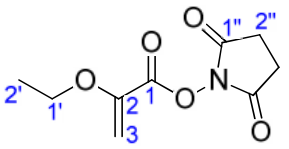
^{1}H NMR (400MHz, $CDCl_3$) 4.58 (1H, d, *J* = 3.0 Hz, C(3)H_2), 4.30 (1H, d, *J* = 3.0 Hz, C(3)H_2), 3.79 (2H, q, *J* = 7.0 Hz, C(1")H_2), 3.68 (3H, s, C(1')H_3), 3.18 (3H, s, C(2')H_3), 1.31 (t, *J* = 7.0 Hz, C(2")H_3).

^{13}C NMR (100MHz, $CDCl_3$) 166.0 (C(1)), 155.5 (C(2)), 88.2 (C(3)), 63.4 (C(1")), 61.2 (C(1')), 45.7 (C(2')), 14.1 (C(2")).

MS (ESI^+) Calculated for $C_7H_{13}NNaO_3$ $[M+Na]^+$ requires 182.0788. Found: 182.0789.

FTIR 3448, 1703, 1643, 1612, 1571, 1427 cm^{-1}.

2,5-Dioxopyrrolidin-1-yl 2-ethoxyacrylate (267)



A mixture of *N*-hydroxysuccinamide (254 mg, 2.20 mmol), acid **256** (195 mg, 1.67 mmol) in DMF (2.50 mL) was cooled at -10 °C and then *N*-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (388 mg, 2.05 mmol) was added in one portion. The reaction mixture was stirred under Argon at room temperature for 16 hours. The solution was diluted with CH_2Cl_2 (50 mL), and the organic layer was washed with saturated aqueous NH_4Cl solution (2 × 15 mL), saturated aqueous $NaHCO_3$ solution (2 × 15 mL) and brine (15 mL). The organic layer was dried (Na_2SO_4) concentrated *in vacuo*. Purification by flash column chromatography (1:1 petrol:EtOAc) to give the title compound **267** as a colourless oil (240 mg, 68%).

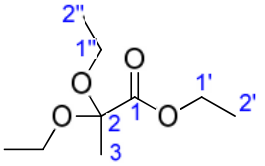
^{1}H NMR (400MHz, $CDCl_3$) 5.52 (1H, d, *J* = 3.5 Hz, C(3)H_2), 4.84 (1H, d, *J* = 3.3 Hz, C(3)H_2), 3.83 (2H, d, *J* = 6.8 Hz, C(1')H_2), 2.80 (4H, s, C(2")H_2), 1.34 (3H, t, *J* = 6.9 Hz, C(2')H_3).

^{13}C NMR (100MHz, $CDCl_3$) 168.9 (C(1")), 158.3 (C(1)), 147.4 (C(2)), 98.1 (C(3)), 64.5 (C(1')), 25.4 (C(2")), 13.9 (C(2')).

MS (ESI^+) Calculated for $C_9H_{11}NNaO_4$ 236.0529. Found 236.0529.

FTIR: 3451, 1705, 1687, 1663, 1643, 1610, 1583, 1432 cm^{-1}.

Ethyl 2,2-diethoxypropanoate (269)



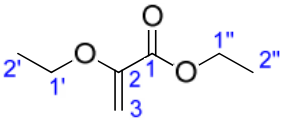
Concentrated sulfuric acid (0.10 mL, 0.19 mmol) was added drop-wise to a mixture of ethyl pyruvic acid (10.03 g, 87.8 mmol), triethylorthoformate (25.0 mL) and ethanol (25.0 mL) at 0 °C. The mixture was stirred for 16 hours at room temperature and then reflux for 8 hours. The organic layer was diluted with Et_2O (50 mL) and washed with water (2 × 25 mL) and brine (2 × 25 mL). The organic layer was dried (Na_2SO_4) concentrated *in vacuo*. Distillation at 67 °C (1.5 mmHg) afforded the title compound **269** as clear oil (10.35, 62%).

^{1}H NMR (400MHz, $CDCl_3$) 4.25 (2H, q, *J* = 7.0 Hz, C(1')H_2), 3.58 (2H, qd, *J* = 7.0, 9.0 Hz, C(1")H_2), 3.47 (2H, qd, *J* = 7.0, 9.0 Hz, C(1")H_2), 1.53 (3H, s, C(3)H_3), 1.30 (3H, t, *J* = 7.0 Hz, C(2")H_3), 1.23 (6H, t, *J* = 7.0 Hz, C(2")H_3).

^{13}C NMR (100MHz, $CDCl_3$)170.1 (C(1)), 99.5 (C(2)), 61.4 (C(1')), 57.9 (C(1")), 22.0 (C(3)), 15.2 (C(2")), 14.1 (C(2')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[187]

Ethyl 2-ethoxyacrylate (270)



Acetal **269** (1.04 g, 5.46 mmol) was dissolved in DMF (5.0 mL) and then P_2O_5 (0.40 g, 2.81 mmol) was added. The reaction mixture was heated at 100 °C for one hour and then cooled

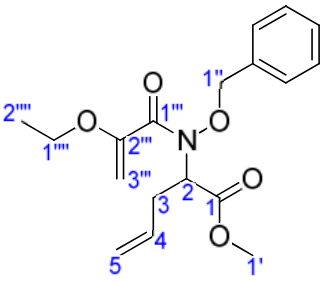
down to room temperature. The organic layer was added to aqueous saturated $NaHCO_3$ (100 mL) and extracted with Et_2O (3 × 50 mL). The organic layer was dried (Na_2SO_4) concentrated *in vacuo*. Distillation at 110 °C (6 mmHg) afforded the title compound **270** as clear oil (559 mg, 71%).

^{1}H NMR (200MHz, $CDCl_3$)5.33 (1H, d, *J* = 2.5 Hz, C(3)H_2), 4.59 (1H, d, *J* = 2.5 Hz, C(3)H_2), 4.27 (2H, q, *J* = 7.0 Hz, C(1')H_2, C(1")H_2), 3.83 (2H, q, *J* = 7.0 Hz, C(1')H_2, C(1")H_2), 1.40 (3H, t, *J* = 7.0 Hz, C(2')H_3, C(2")H_3), 1.33 (3H, t, *J* = 6.8 Hz, C(2')H_3, C(2")H_3).

^{13}C NMR (50MHz, $CDCl_3$)165.2 (C(1)), 150.7 (C(2)), 92.8 (C(3)), 64.4 and 61.9 (C(1'), C(1")), 14.1 and 14.0 (C(2'), C(2")).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[188]

Methyl 2-(*N*-(benzyloxy)-2-ethoxyacrylamido)pent-4-enoate (260)



Amine **253** (0.83 g, 3.53 mmol) and acid **256** (0.78 g, 6.72 mmol) were subjected to General Procedure A. Purification by FCC (5:1 petrol-EtOAc) afforded the title compound **260** as a pale brown oil (0.97 g, 82%).

^{1}H NMR (500 MHz, $CDCl_3$) 7.40-7.30 (5H, m, Ph), 5.83 (1H, ddt, *J* 17.1, 10.3, 6.9, C(4)H), 5.18 (1H, dd, *J* 17.2, 1.4, C(5)H), 5.12 (1H, dd, *J* 10.4, 0.9, C(5)H), 5.07 (1H, d, *J* 9.8, C(1")H), 5.02 (1H, d, *J* 9.8, C(1")H), 4.88 -4.81 (2H, m, C(3"')H, C(2)H), 4.44 (1H, d, *J* 2.8,

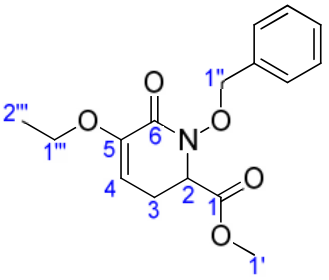
C(3”’)H), 3.83 (2H, q, *J* 6.9, C(1””)H_2), 3.76 (3H, s, C(1’)H_3), 2.81-2.75 (2H, m, C(3)H_2),1.33 (3H, t, *J* 6.9, C(2””)H_3).

^{13}C NMR (125 MHz, $CDCl_3$) 170.0 (C(1)),167.0 (C(2”’)), 154.9 (C(1”’)), 135.1 (*i*-Ph),133.6 (C(4)), 128.8 (Ph),128.4 (two signals Ph),118.4 (C(5)), 90.1 (C(3”’)), 77.7 (C(1”)),63.8 (C(1””)), 62.4 (C(2)),52.5 (C(1’)), 32.6 (C(3)), 14.1 (C(2””)).

MS (ESI$^+$) Calculated for $C_{23}H_{25}NNaO_5$ $[M+Na]^+$ requires 418.1625. Found 418.1624.

FTIR 3450, 2883, 1967, 1930, 1711, 1639, 1608, 1581, 1488, 1418, 1219 cm^{-1}.

Methyl 1-(benzyloxy)-5-ethoxy-6-oxo-1,2,3,6-tetrahydropyridine-2-carboxylate (284)



Diene **260** (267 mg, 0.80 mmol) and catalyst HG-II (23 mg, 5 mol%) were subjected to General Procedure B using CH_2Cl_2 (20 mL) at reflux for 16 hours. Purification by FCC (5:1 to 1:1 petrol-EtOAc) afforded the title compound **284** (222 mg, 91%) as a pale brown solid.

^{1}H NMR (500 MHz, $CDCl_3$)7.45-7.41 (2H, m, Ph), 7.39-7.34 (3H, m, Ph),5.17 (1H, dd, *J* 6.0, 3.0, C(4)H),5.04 (1H, d, *J* 11.0, C(1’)H),4.98 (1H, d, *J* 11.0, C(1’)H),3.91 (1H, dd, *J*7.0, 3.0, C(2)H),3.77 (2H, q, *J* 7.0, C(1”’)H_2),3.72 (3H, s, C(2”)H_3),2.60 (1H, ddd, *J* 17.0, 7.0, 3.0, C(3)H),2.54 (1H, ddd, *J* 17.0, 6.0, 3.0, C(3)H),1.39 (3H, t, *J* 7.0, C(2”’)H_3).

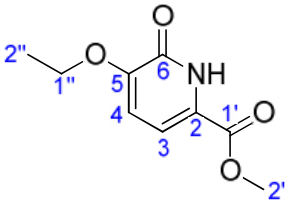
^{13}C NMR (125 MHz, $CDCl_3$) 170.8 (C(1”)), 162.8 (C(6)),146.5 (C(5)),135.6 (*i*-Ph),129.8 (Ph),128.7 (Ph),128.4 (Ph),102.1 (C(4)),77.5 (C(1”)),64.1 (C(1”’)),62.4 (C(2)),52.8 (C(1’)),25.4 (C(3)), 14.2 (C(2”’)).

HRMS (ESI$^+$) Calculated for $C_{16}H_{20}NO_5$ $[M+H]^+$: 306.1332. Found: 306.1336.

FTIR 2983, 1742, 1692, 1637, 1257 cm^{-1}.

M.P. 107-108 ºC (CH_2Cl_2-petrol).

Methyl 5-ethoxy-6-oxo-1,6-dihydropyridine-2-carboxylate (285)



α,β-Unsaturated lactam **284** (204 mg, 0.67 mmol) was subjected to General Procedure C and the reaction mixture was heated at 50 °C for 16 hours. Purification by FCC (1:1:0 to 0:10:1 petrol-EtOAc-MeOH) afforded the title compound **285** (115 mg, 87%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) 10.46 (1H, br. s, NH), 6.90 (1H, d, *J* = 7.5 Hz, C(3)H, C(4)H), 6.55 (1H, d, *J* = 7.5 Hz, C(3)H, C(4)H), 3.97 (2H, q, *J* = 7.0 Hz, C(1")), 3.81 (3H, s, C(2')H_3), 1.38 (3H, t, *J* = 7.0 Hz)

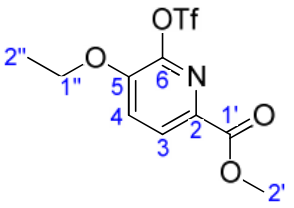
^{13}C NMR (100 MHz, $CDCl_3$): 161.1 (C(2')), 157.1 and 153.7 (C(5), C(6)), 124.1 (C(2)), 110.7 and 111.6 (C(3), C(4)), 64.5 (C(1")), 52.6 (C(2')), 13.9 (C(2")).

HRMS (ESI^+) Calculated for $C_9H_{11}NNaO_4$ $[M+Na]^+$: 220.0580, Found: 220.0583.

FTIR 2983, 1726, 1646, 1620, 1303, 1277 cm^{-1}.

M.P. 146-147 (CH_2Cl_2-petrol).

5-Ethoxy-6-trifluoromethanesulfonyloxypyridine-2-carboxylic acid methyl ester (289)



Pyridone **285** (84 mg, 0.42 mmol) was subjected to General Procedure D. Purification by FCC (10:1 to 1:1 petrol-EtOAc) afforded the title compound **289** (123 mg, 89%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) 8.17 (1H, d, *J* = 8.0 Hz, C(4)H), 7.43 (1H, d, *J* = 8.0 Hz, C(3)H), 4.24 (2 H, q, *J* = 7.0 Hz, C(1")H_2), 3.96 (3H, s, C(2')H_3), 1.52 (3H, t, *J* = 7.0 Hz, C(2")H_3).

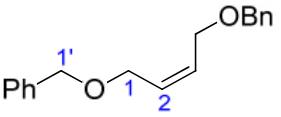
^{13}C NMR (125 MHz, $CDCl_3$) 163.9 (C(1')), 149.3, and 144.1 (C(5), C(6)), 136.7 (C(2)), 127.7 (C(4)), 121.8 (C(3)), 118.5 (q, *J* = 320 Hz, CF_3), 65.8 (C(1")), 52.9 (C(2')), 14.1 (C(2")).

HRMS (ESI^+) Calculated for $C_{10}H_{11}NF_3O_6S$ $[M+H]^+$: 330.0254, Found: 330.0249.

FTIR 3086, 1736, 1563, 1215 cm^{-1}.

M.P. 62-63 ºC (CH_2Cl_2-petrol).

(Z)-1,4-Bis(benzyloxy)but-2-ene (291)



Sodium hydride (60% dispersion in mineral oil, 5.9 g, 0.15 mol) was added portion-wise to a stirred mixture of diol **290** (5.8 mL, 70 mmol) in THF (200 mL) at 0ºC. The reaction mixture was stirred for 1 h at room temperature. Benzyl bromide (26 mL, 0.22 mol) was added drop-

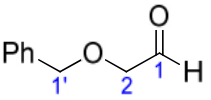
wise and the reaction mixture was heated at reflux overnight. Reaction mixture was cooled to room temperature and water (250 mL) was added. The aqueous layer was extracted with EtOAc (200 mL × 3). The combined organic layer was dried over Na_2SO_4, concentrated under reduced pressure and purified by flash column chromatography (10:2 petrol:EtOAc) to give the title compound **291** as a colourless oil (16 g, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) 7.41-7.25 (10H, m, Ph), 5.81 (2H, t, *J* = 4.5 Hz, C(2)H), 4.51 (4H, s, C(1')H_2), 4.08 (4 H, d, *J* = 4.5 Hz, C(1')H_2).

^{13}C NMR (100 MHz, $CDCl_3$) 138.1 (i-Ph), 129.5 (C(2)), 128.4 (Ph), 127.8 (Ph), 127.6 (Ph), 72.2 (C(1')), 65.7 (C(1)).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[189]

2-(Benzyloxy)acetaldehyde (292)



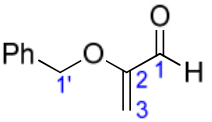
Ozone was bubbled through a solution of **291** (11 g, 41 mmol) in a mixture of methanol and CH_2Cl_2 (1:3, 100 mL) at -78 ºC for 2 h, then the solution was purged with oxygen for 5 min. Dimethyl sulfide (4.1 mL, 6.0 mL, 55 mmol) was added drop-wise and the reaction mixture was allowed to warm up to room temperature. Stirring continue for 16 h then the reaction mixture was concentrated under reduced pressure and purified flash column chromatography (10:2 petrol:EtOAc) to give the title compound **292** as a colourless oil (10 g, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) 9.74 (1H, s, C(2)H), 7.46-7.28 (5H, Ph), 4.65 (2H, s, C(1')H_2), 4.12 (2H, s, C(1)H_2).

^{13}C NMR (100 MHz, $CDCl_3$) 200.5 (C(2)), 136.7 (*i*-Ph), 128.6 (Ph), 128.2 (Ph), 128.0 (Ph), 75.2 and 73.6 (C(1') and C(1)).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[190]

2-(Benzyloxy)acrylaldehyde (293)



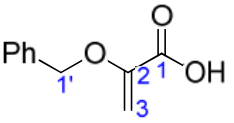
To a mixture of formaldehyde solution (37% in water, 5.80 mL, 78 mmol) and **292** (9.46 g, 63.0 mol) in *i*-PrOH (6.70 mL) was added propionic acid (0.47 mL, 6.3 mmol) and pyrrolidine (0.53 mL, 6.3 mL). The reaction mixture was stirred at 45 ºC for 16 h. $NaHCO_{3(sat)}$ (50 mL) was added and the reaction mixture extracted with CH_2Cl_2 (100 mL × 2). The combined organic layers were washed with brine (50 mL) dried over Na_2SO_4, concentrated under reduced pressure and purified by flash column chromatography (10:2 petrol:EtOAc) to give the title compound **293** as a colourless oil (9.4 g, 87%).

^{1}H NMR (200 MHz, $CDCl_3$)9.33 (1H, s, C(1)H), 7.45-7.29 (5H, m, Ph),5.27 (1H, *J*= 3.0, C(3)H),5.16 (1H, d, *J*= 3.0, C(3)H),4.95 (2H, s, C(1')H_2).

^{13}C NMR (100 MHz, $CDCl_3$)188.1 (C(1)), 158.1 (C(2)), 135.5 (*i*-Ph), 128.6 (Ph), 128.2 (Ph), 127.4 (Ph), 104.0 (C(3)), 70.2 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[135]

2-(Benzyloxy)acrylic acid (294)



Sodium chlorite (19.0 g, 0.21 mol) was added to a stirred phosphate buffer of pH 7 (0.75M, 300 mL) until all solids were dissolved. The oxidizing solution was added to a stirred

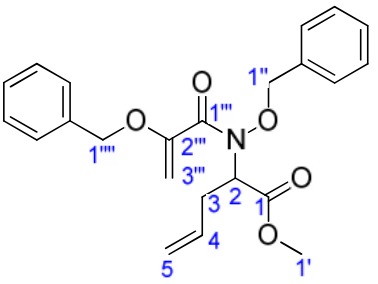
solution of **293** (6.0 g, 37 mmol), *tert*-butanol (150 mL) and 2-methyl-2-butene (30 mL, 0.28 mol) at 0 ºC and stirring continue for 24 h at room temperature. The organic layer was separated off then dried over Na_2SO_4, concentrated under reduced pressure and purified by recrystallisation (petrol:EtOAc) to give the title compound **294** as a white solid (4.4 g, 67%).

^{1}H NMR (400 MHz, $CDCl_3$)7.45-7.32 (5H, m, Ph), 5.59 (1H, *J*= 3.0, C(3)H), 4.91 (2H, s, C(1')H_2), 4.82 (1H, d, *J*= 3.0, C(3)H).

^{13}C NMR (100 MHz, $CDCl_3$) 167.5 (C(1)), 149.8 (C(2)), 135.4 (*i*-Ph), 128.5 (Ph), 128.1 (Ph), 127.3 (Ph), 97.1 (C(3)), 70.4 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[191]

Methyl 2-(*N*, 2-bis(benzyloxy)acrylamido)pent-4-enoate (295)



Amine **253** (270 mg, 1.14 mmol) and acid **294** (598 mg, 3.35 mmol) were subjected to General Procedure A. Purification by FCC (5:1 petrol-EtOAc) afforded the title compound **295** (363 mg, 80%) as a colourless oil.

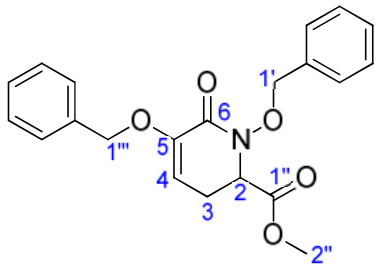
^{1}H NMR (500 MHz, $CDCl_3$) 7.34 (10H, m, Ph), 5.76 (1H, m C(4)H), 5.14 (1H, dd, *J* = 16.5 Hz, C(3"')H), 5.07 (1H, d, *J* = 10.0 Hz, C(3"')H, C(5)H_2, C(1")H_2), 5.04 (1H, m, C(3"')H, C(5)H_2, C(1")H_2), 4.99 (1H, m, C(3"')H, C(5)H_2, C(1")H_2), 4.94 (1H, m, C(3"')H, C(5)H_2, C(1")H_2), 4.88 (1H, m, C(3"')H, C(5)H_2, C(1")H_2), 4.91-4.82 (2H, m, C(1"")H_2), 4.60 (1H, d, *J* = 3.0 Hz), 3.69 (3H, s), 2.78 (2H, m).

^{13}C NMR (125 MHz, $CDCl_3$) 169.9 (C(1)), 166.7 (C(1”’)),154.7 (C(2”’)),133.4 (C(4)), 134.9 and 135.5 (*i*-Ph), 128.8 (Ph), 128.4 (two signals Ph), 128.3 (Ph),128.1 (Ph),127.7 (Ph),118.4 (C(5)),91.2 (C(3”’)),77.7 (C(1”)),70.2 (C(1””)),62.3 (C(2)),52.4 (C(1’)),32.6 (C(3)).

HRMS (ESI^+) Calculated for $C_{23}H_{25}NNaO_5$ $[M+Na]^+$: 418.1625, Found: 418.1624.

FTIR 2883, 1746, 1673, 1621, 1262, 1212 cm^{-1}.

Methyl 1,5-bis(benzyloxy)-6-oxo-1,2,3,6-tetrahydropyridine-2-carboxylate (296)



Diene **295** (397 mg, 1.00 mmol) and catalyst HG-II (30 mg, 5 mol%) were subjected to General Procedure B using CH_2Cl_2 (20 mL) at reflux for 16 hours. Purification by FCC (7:3 petrol-EtOAc) afforded the title compound **296** (312 mg, 85%) as a pale brown oil.

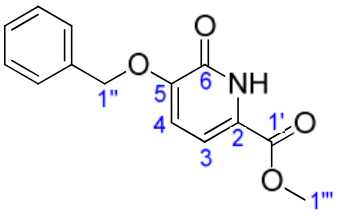
^{1}H NMR (500 MHz, $CDCl_3$) 7.47-7.42 (2H, m, Ph), 7.40-7.28 (8H, m, Ph), 5.25 (1H, dd, *J* = 6.5, 3.0 Hz, C(4)H), 5.07 (1H, d, *J* = 11.0 Hz, C(1’)H_2), 5.00 (1H, d, *J* = 11.0 Hz, C(1’)H_2), 4.92 (1H, d, *J* = 12.5 Hz, C(1”’)H_2), 4.87 (1H, d, *J* = 12.5 Hz, C(1”’)H_2), 3.92 (1H, dd, *J* = 6.5, 3.0 Hz, C(2)H), 3.71 (3H, s, C(2”)H_3), 2.58 (1H, ddd, *J* = 17.0, 6.5, 3.0 Hz, C(3)H_2), 2.51 (1H, ddd, *J* = 17.0, 6.5, 3.0 Hz, C(3)H_2).

^{13}C NMR (125 MHz, $CDCl_3$) 170.7 (C(1”)), 162.8 (C(6)), 146.1 (C(5)), 136.0 (*i*-Ph), 135.5 (*i*-Ph), 129.8 (Ph), 128.8 (Ph), 128.5 (two signals, (Ph)), 127.9 (Ph), 127.2 (Ph), 104.6 (C(4)), 77.6 (C(1’)), 70.5 (C(1”’)), 62.4 (C(2)), 52.8 (C(2”)), 25.4 (C(3)).

HRMS (ESI^+) Calculated for $C_{21}H_{21}NNaO_5$ $[M+Na]^+$: 390.1312, Found: 390.1309.

FITR 2956, 1750, 1700, 1645, 1259 cm^{-1}.

Methyl 5-(benzyloxy)-6-oxo-1,6-dihydropyridine-2-carboxylate (297):



α,β-Unsaturated lactam **296** (116 mg, 0.31 mmol) was subjected to General Procedure C and the reaction mixture was heated at 50 °C for 16 hours. Purification by FCC (1:1:0 to 0:10:1 to petrol-EtOAc-MeOH) afforded the title compound **297** (80 mg, 98%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) 9.54 (1H, br. s., NH), 7.45-7.41 (2H, m, Ph), 7.41-7.38 (3H, m, Ph), 6.94 (1H, d, *J* = 7.5 Hz, C(3)H, C(4H)), 6.67 (1H, d, *J* = 7.5 Hz, C(3)H, C(4)H), 5.20 (2H, s, C(1")H_2), 3.92 (3H, s, C(1"')H_3).

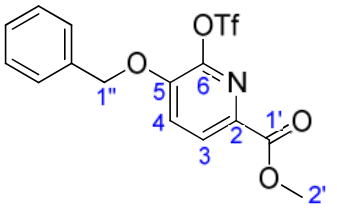
^{13}C NMR (125 MHz, $CDCl_3$) 161.3 (C(1"')), 157.0 and 153.8 (C(5), C(6)), 135.1 (*i*-Ph), 128.8 (Ph), 128.4 (Ph), 127.4 (Ph), 124.6 (C2)), 113.4 and 110.6 (C(3), C(4)), 71.0 (C(1")), 53.0 (C(2")).

HRMS (ESI^+) Calculated for $C_{14}H_{13}NNaO_4$ $[M+Na]^+$: 282.0737, Found: 282.0735.

FTIR 3041, 1730, 1662, 1624, 1258 cm^{-1}.

M.P. 170-171 ºC(CH_2Cl_2-petrol).

5-Benzyloxy-6-trifluoromethanesulfonyloxypyridine-2-carboxylic acid methyl ester (298)



Pyridone **297** (35 mg, 0.14 mmol) was subjected to General Procedure D. Purification by FCC (10:1 to 1:1 petrol-EtOAc) afforded the title compound **298** (46 mg, 87%) as a colourless solid.

^{1}H NMR (500 MHz, $CDCl_3$) 8.15 (1H, d, *J* = 8.0 Hz, C(4)H), 7.47 (1H, d, *J* = 8.0 Hz, C(3)H), 7.46-7.35 (5H, m, Ph), 5.29 (2H, s, C(1")H_2), 3.96 (3H, s, C(2')H_3).

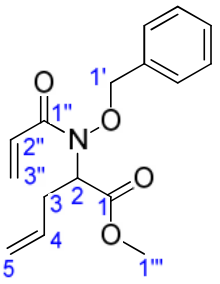
^{13}C NMR (125 MHz, $CDCl_3$) 163.8 (C(1')), 148.9 and 144.3 (C(5), C(6)), 137.1 (C(2)), 134.0 (*i*-Ph), 128.9 (Ph), 128.8 (Ph), 127.6 (C(4)), 127.2 (Ph), 122.7 (C(3)), 118.5 (q, *J* = 320 Hz, CF_3), 71.6 (C(1")), 52.9 (C(2')).

HRMS (ESI^+) Calculated for $C_{15}H_{12}F_3NNaO_6S$ $[M+Na]^+$: 414.0230, Found: 414.0222.

FTIR 3435, 1738, 1424, 1213 cm^{-1}.

M.P. 83-84 ºC (CH_2Cl_2-petrol).

Methyl 2-(*N*-(benzyloxy)acrylamido)pent-4-enoate (301)



Acryloyl chloride (2.00 mL, 24.73 mmol) was added drop-wise to a stirred solution of the amine **253** (3.83 g, 16.28 mmol) and triethylamine (5.30 mL, 38.03 mmol) in CH_2Cl_2 (100 mL) at 0 °C. The reaction mixture was left to warm up to room temperature and stirring was continued until TLC analysis indicated that the starting material was consumed. The mixture

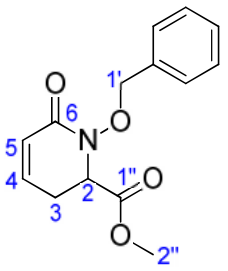
was diluted with CH_2Cl_2 (50 mL), washed with 1.0 M aq. HCl solution (50 mL) and saturated aqueous $NaHCO_3$ solution (50 mL). The organic portion was dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by flash column chromatography (8:1 to 1:1 petrol:EtOAc) to give the title compound **301** as a colourless oil (3.18 g, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) 7.43-7.40 (2H, m, Ph), 7.40-7.38 (3H, m, Ph), 6.71 (1H, dd, *J* = 17.0, 10.5, C(2")H), 6.43 (1H, dd, *J* = 17.0, 2.0, C(3")H_2), 5.80 (1H, ddt, *J* = 17.0, 10.5, 7.0, C(4)H), 5.76 (1H, dd, *J* = 10.5, 2.0, C(3")H_2),5.16 (1H, dd, *J* = 17.0, 1.0, C(5)H_2), 5.11 (1H, dd, *J* = 10.5, 1.0, C(5)H_2), 5.05-5.02 (1H, m, C(2)H),5.00 (1H, d, *J* = 10.5, C(1')H_2),4.93 (1H, d, *J* = 10.5, C(1')H_2),3.77 (3H, s, C(1"')H_3), 2.87-2.73 (2H, m, C(3)H_2).

^{13}C NMR (100 MHz, $CDCl_3$)170.1 (C(1)), 168.1 (C(1")), 134.1 (*i*-Ph),133.3 (C(4)),130.0 (C(3")),128.7 (two signals Ph),128.5 (Ph),125.9 (C(2")),118.2 (C(5)),78.8 (C(1')),60.5 (C(2)),52.4 (C(1"')),32.4 (C(3)).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[75]

Methyl 1-(benzyloxy)-6-oxo-1,2,3,6-tetrahydropyridine-2-carboxylate (302)



Diene **301** (3.18 g, 11.03 mmol) and catalyst HG-II (37 mg, 0.5 mol%) were subjected to General Procedure B using CH_2Cl_2 (110 mL) at reflux for 16 hours. Purification by FCC (1:1 to 0:1 petrol-EtOAc) afforded the title compound **302** (2.58 g, 90%) as a pale brown oil.

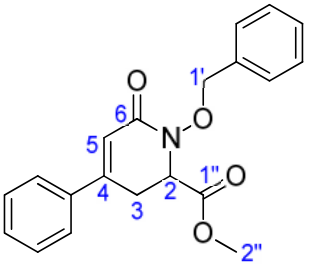
^{1}H NMR (400MHz, $CDCl_3$) 7.48-7.42 (2H, m, Ph), 7.42-7.35 (3H, m, Ph), 6.40 (1H, ddd, *J* = 3.5, 5.0, 10.0 Hz, C(4)H), 5.94 (1H, dd, *J* = 2.0, 10.0 Hz, C(5)H), 5.05 (1H, d, *J* = 11.0 Hz,

C(1')H_2), 4.97 (1H, d, *J* = 11.0 Hz, C(1')H_2), 4.03 (1H, dd, *J* = 3.5, 7.0 Hz, C(2)H_2), 3.73 (3H, s, C(2")H_3), 2.77-2.58 (2H, m, C(3)H_2).

^{13}C NMR (100MHz, $CDCl_3$) 170.4 (C(1")), 164.8 (C(6)), 137.0 (C(4)), 135.2 (*i*-Ph), 129.4 (Ph), 128.4 (Ph), 128.1 (Ph), 124.8 (C(5)), 77.1 (C(1')), 61.8 (C(2)), 52.4 (C(2")), 29.1 (C(3)).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[75]

Methyl 1-(benzyloxy)-6-oxo-4-phenyl-1,2,3,6-tetrahydropyridine-2-carboxylate (308)



A solution of $Pd(OAc)_2$ (13 mg, 0.06 mmol) and 1,10-phenanthroline (17 mg, 0.09 mmol) in DMF (2.65 mL) was stirred at room temperature for 30 minutes. α,β-Unsaturated lactam **302** (139 mg, 0.53 mmol) and phenyl boronic acid (138 mg, 1.13 mmol) were added and the reaction mixture was placed under an oxygen atmosphere oxygen (balloon pressure) and heated at 50 °C. After 14 hours the reaction mixture was diluted with EtOAc (50 mL) and washed with saturated aqueous NH_4Cl (35 mL) and brine (35 mL). The organic portion was dried ($MgSO_4$) and concentrated *in vacuo*. Purification by FCC (7:3 petrol-EtOAc) afforded the title compound **308** (164 mg, 92%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) 7.42 (10H, m, Ph), 6.30 (1H, d, *J* = 2.5 Hz, C(5)H), 5.09 (1H, d, *J* = 11.5 Hz, C(1')H_2), 5.02 (1H, d, *J* = 11.5 Hz, C(1')H_2), 4.07 (1H, dd, *J* = 7.0, 3.0 Hz,

C(2)H), 3.73 (3H, s), 3.10 (1H, dd, *J* = 17.5, 3.0 Hz, C(3)H_2), 3.00 (1H, ddd, *J* = 17.5, 7.0, 2.0 Hz, C(3)H_2).

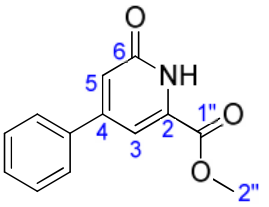
^{13}C NMR (100 MHz, $CDCl_3$) 170.6 (C(1")), 165.5 (C(6)), 147.1 (*i*-Ph, C(4)), 136.1 (*i*-Ph, C(4)), 135.6 (*i*-Ph, C(4)), 129.9 (Ph), 129.7 (Ph), 128.7 (Ph), 128.7 (Ph), 128.4 (Ph), 125.7 (Ph), 119.3 (C(5)), 77.5 (C(1')), 61.9 (C(2)), 52.8 (C(2")), 31.2 (C(3)).

HRMS (ESI^+) Calculated for $C_{20}H_{20}NO_4$ $[M+H]^+$: 338.1387, Found: 338.1380.

FTIR 3439, 3004, 2953, 1743, 1669, 1614, 1447, 1234, 1077 cm^{-1}.

M.P. 149-150 ºC (CH_2Cl_2-petrol).

Methyl 6-oxo-4-phenyl-1,6-dihydropyridine-2-carboxylate (309)



α,β-Unsaturated lactam **308** (169 mg, 0.27 mmol) was subjected to General Procedure C and the reaction mixture was stirred at 20 °C for 16 hours. Purification by FCC (1:1:0 to 10:10:1 CH_2Cl_2-EtOAc-MeOH) afforded the title compound **309** (101 mg, 88%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) 9.60 (1H, br. s. NH), 7.65-7.58 (2H, m, Ph), 7.53-7.46 (3H, m, Ph), 7.29 (1H, d, *J* = 2.0 Hz, C(3)H), 7.00 (1H, d, *J* = 2.0 Hz, C(5)H), 4.01 (3H, s, C(2")H_3).

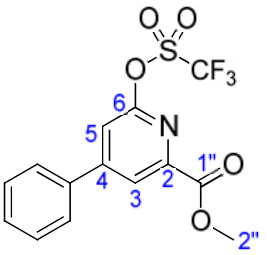
^{13}C NMR (100 MHz, $CDCl_3$) 163.6 and 161.4 (C(2"), C(6)), 152.0 (C(4)), 136.6 and 133.9 (C(2), *i*-Ph), 129.8 (Ph), 129.0 (Ph), 126.7 (Ph), 122.4 (C(3)), 109.5 (C(5)), 53.2 (C(2")).

FTIR 3266, 2959, 1735, 1645, 1447, 1288, 1139 cm^{-1}.

M.P. 181-183 ºC (CH_2Cl_2-petrol).

HRMS (ESI^+) Calculated for $C_{13}H_{11}NKO_3$ $[M+K]^+$: 268.0371, Found: 268.0361.

Phenyl-6-trifluoromethanesulfonyloxypyridine-2-carboxylic acid methyl ester (310)



Pyridone **309** (71 mg, 0.31 mmol) was subjected to General Procedure D. Purification by FCC (10:1 to 1:1 petrol-EtOAc) afforded the title compound **310** (60 mg, 57%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) 8.44 (1H, d, *J* = 1.5 Hz, C(3)H), 7.70 (2H, m, Ph), 7.56 (4H, m, Ph, C(5)H), 4.04 (3H, s, C(2")H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 164.1 (C(1")), 156.0 and 155.3 (C(6), C(4)), 147.5 and 135.4 (C(2), *i*-Ph), 130.7 (Ph), 129.6 (Ph), 127.2 (Ph), 123.6 (C(3)), 118.6 (q, *J* = 320 Hz, CF_3), 116.1 (C(5)), 53.3 (C(2")).

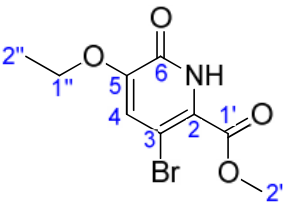
^{19}FNMR (377MHz, $CDCl_3$) -72.6 (CF_3).

HRMS (ESI^+) Calculated for $C_{14}H_{10}F_3KNO_5S$ $[M+K]^+$: 399.9863, Found: 399.9861.

FTIR 3441, 1727, 1609, 1437, 1219, 1073 cm^{-1}.

M.P. 61-62 ºC (CH_2Cl_2-petrol).

Methyl 3-bromo-5-ethoxy-6-oxo-1,6-dihydropyridine-2-carboxylate (311)



N-Bromosuccinimide (109 mg, 0.61 mmol) and pyridone **285** (0.12 g, 0.61 mmol) were dissolved in CH_2Cl_2 (15 mL) and the mixture was heated at reflux overnight with exclusion

of light. The reaction mixture was then cooled to room temperature and concentrated *in vacuo*. The residue was purified by FCC (9:1 EtOAc-MeOH) to afford pyridone **311** (90 mg, 74%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) 10.26 (1H, br. s, NH), 6.76 (1H, s, C(4)H), 4.06 (2H, q, *J* = 7.0 Hz, C(1")H_2), 3.94 (3H, s, C(2')H_3), 1.49 (3H, t, *J* = 7.0, C(2")H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 160.2 (C(1')), 156.0 and 152.9 (C(6), C(5)), 122.4 (C(2)), 118.9 (C(4)), 104.4 (C(3)), 65.4 (C(1")), 53.1 (C(2')), 14.0 (C(2")).

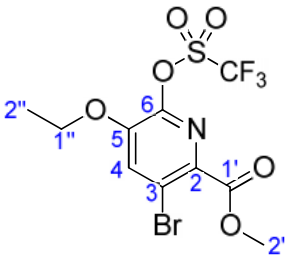
HRMS (ESI^+) Calculated for $C_9H_{10}{}^{79}BrNNaO_4$ $[M+Na]^+$: 297.9685, Found: 297.9685.

FTIR 2983, 1727, 1664, 1319 cm^{-1}.

M.P. 194-197 ºC (CH_2Cl_2-petrol).

The structure of this compound was confirmed by X-ray crystallographic analysis (Appendix III).

3-Bromo-5-ethoxy-6-trifluoromethanesulfonyloxypyridine-2-carboxylic acid methyl ester (312)



Pyridone **311** (86 mg, 0.31 mmol) was subjected to General Procedure D. Purification by FCC (1:0 to 3:2 petrol-CH_2Cl_2) afforded the title compound **312** (106 mg, 84%) as a colourless clear oil.

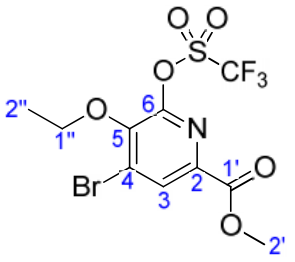
^{1}H NMR (400 MHz, $CDCl_3$) 7.60 (1H, s, C(4)H), 4.23 (2H, q, *J* = 7.0 Hz, C(1")H_2), 3.97 (3H, s, C(2')H_3), 1.53 (3H, t, *J* = 7.0 Hz, C(2")H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 163.3 (C(1')), 148.0 and 142.4 (C(6), C(5)), 136.1 (C(2)), 127.5 (C(4)), 120.8 (C(3)), 118.5 (q, *J*= 320 Hz, CF_3), 66.3 (C(1")), 53.0 (C(2')), 14.0 (C(2")).

HRMS (ESI^+) Calculated for $C_{10}H_9{}^{79}BrF_3NNaO_6S$ $[M+Na]^+$: 429.9178, Found: 429.9184.

FTIR 2905, 1738, 1592, 1460, 1260, 1145 cm^{-1}.

4-Bromo-5-ethoxy-6-trifluoromethanesulfonyloxypyridine-2-carboxylic acid methyl ester (321)



Bromine (320 µl, 6.24 mmol) was added to a solution of α,β-unsaturated lactam **284** (230 mg, 0.75 mmol) and Et_3N (0.51 mL, 3.73 mmol) in CH_2Cl_2 (20 mL) at 0 ºC. After stirring for 2 hours at this temperature, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with aq. 10% $Na_2S_2O_3$ (2 × 30 mL) and then brine (30 mL). The organic portion was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dissolved in THF (12 mL) and DBU (0.57 mL, 3.81 mmol) was added. After stirring at room temperature for 16 hours the reaction mixture was concentrated *in vacuo*. The residue was filtered through a short plug of SiO_2 (9:1 EtOAc-MeOH) and concentrated *in vacuo*. The resulting crude material was dissolved in THF (8 mL) and cooled to -78 ºC. Comins' reagent(295 mg, 0.75 mmol) and KHMDS (0.5M in PhMe, 1.40 mL, 0.70 mmol) were then added sequentially and the mixture was stirred at -78 ºC for 1 hour and then at room temperature for 3 hours. The mixture was then diluted with EtOAc (40 mL) and washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and then brine (30 mL). The organic portion was dried ($MgSO_4$) and

concentrated *in vacuo*. Purification by FCC (1:0 to 1:1 petrol-EtOAc) afforded the title compound **321** (135 mg, 44%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) 8.36 (1H, s, C(3)H), 4.30 (2H, q, *J* = 7.0 Hz, C(1")H_2), 3.97 (3H, s, C(2')H_3), 1.50 (3H, t, *J* = 7.0 Hz, C(2")H_3).

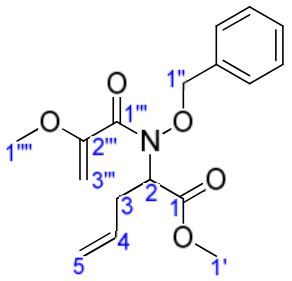
^{13}C NMR (100 MHz, $CDCl_3$) 162.7 (C(1')), 148.4 (C(6), C(5), C(4)), 147.5 (C(6), C(5), C(4)), C(5)), 140.5 (C(6), C(5), C(4)), 131.3 (C(3)), 130.2 (C(2)), 118.5 (q, *J* = 320 Hz, CF_3), 71.6 (C(1"), 53.3 (C(2')), 15.4 (C(2")).

HRMS (ESI^+) Calculated for $C_{10}H_9{}^{79}BrF_3NNaO_6S$ $[M+Na]^+$: 429.9178, Found: 429.9184.

FTIR 2990, 1747, 1378, 1245 cm^{-1}.

M.P. 55-56 ºC (CH_2Cl_2-petrol).

Methyl 2-(*N*-(benzyloxy)-2-methoxyacrylamido)pent-4-enoate (348)



Amine **253** (1.15 g, 4.88 mmol) and acid **352** (0.98 g, 9.64 mmol) were subjected to General Procedure A. Purification by FCC (1:0 to 5:1 petrol-EtOAc) afforded the title compound **348** (1.18 g, 76%) as a pale brown oil.

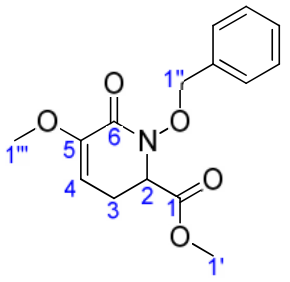
^{1}H NMR (500MHz, $CDCl_3$) 7.43-7.29 (5H, m, Ph), 5.82 (1H, ddt, *J* = 7.0, 10.0, 17.0 Hz, C(4)H), 5.18 (1H, dd, *J* = 1.5, 17.0 Hz, C(5)H_2), 5.13 (1H, d, *J* = 10.0 Hz, C(5)H_2), 5.13 (1H, d, *J* = 10.0 Hz, C(1")H_2), 5.04 (1H, d, *J* = 10.0 Hz, C(1")H_2), 4.88-4.82 (2H, m, C(3"')H, C(2)H), 4.47 (1H, d, *J* = 3.0 Hz, C(3"')H_2), 3.76 (3H, s, C(1')H_3), 3.64 (3H, s, C(1"")H_3), 2.87-2.67 (2H, m, C(3)H_2).

^{13}C NMR (125MHz, $CDCl_3$) 170.0 (C(1')), 166.9 (C(2"')), 155.6 (C(1"')), 134.9 (*i*-Ph), 133.5 (C(4)), 128.9 (Ph), 128.5 (Ph), 128.4 (Ph), 118.4 (C(5)), 89.7 (C(3"')), 77.9 (C(1")), 62.2 (C(2)), 55.2 and 52.5 (C(1') and C(1""), 32.6 (C(3)).

HRMS (ESI^+) Calculated for $C_{170}H_{21}NNaO_5$ $[M+Na]^+$: 342.1312, Found: 342.1312.

FTIR 3449, 2885, 1708, 1635, 1612, 1586, 1441, 1222 cm^{-1}.

Methyl 1-(benzyloxy)-5-methoxy-6-oxo-1,2,3,6-tetrahydropyridine-2-carboxylate(347)



Diene **348** (1.23 g, 3.84 mmol) and catalyst HG-II (120 mg, 5 mol%) were subjected to General Procedure B using CH_2Cl_2 (20 mL) at reflux for 16 hours. Purification by FCC (1:0 to 1:1 petrol-EtOAc) afforded the title compound **347** (0.91 g, 81%) as a pale brown solid.

^{1}H NMR (400MHz, $CDCl_3$) 7.57 -7.43 (2H, m, Ph), 7.44-7.34 (3H, m, Ph), 5.28 (1H, dd, *J* = 2.5, 6.0 Hz, C(4)H), 5.06 (1H, d, *J* = 11.0 Hz, C(1")H_2), 5.00 (1H, d, *J* = 11.0 Hz, C(1")H_2), 4.05 (1H, dd, *J* = 2.5, 7.0 Hz, C(2)H), 3.73 (3H, s, C(1')H_3), 3.63 (3H, s, C(1"')H_3), 2.72 (1H, ddd, *J* = 2.5, 7.0, 17.0 Hz, C(3)H_2), 2.62 (ddd, *J* = 2.5, 6.0, 17.0 Hz, C(3)H_2).

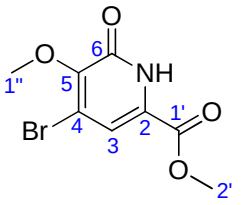
^{13}C NMR (100MHz, $CDCl_3$) 169.8 (C(1)), 162.1 (C(6)), 146.3 (C(5)), 134.7 (*i*-Ph), 128.9 (Ph), 128.0 (Ph), 127.7 (Ph), 100.8 (C(4)), 76.6 (C(1")), 61.5 (C(2)), 54.9 (C(1"')), 52.0 (C(1')), 24.5 (C(3)).

HRMS (ESI^+) Calculated for $C_{15}H_{17}NNaO_5$ $[M+Na]^+$: 314.0999. Found: 314.0999.

FTIR 2987, 1740, 1689, 1642, 1238 cm^{-1}.

M.P.74-75 ºC (CH_2Cl_2-petrol).

Methyl 4-bromo-5-methoxy-6-oxo-1,6-dihydropyridine-2-carboxylate (346)



Bromine (350 µl, 6.85 mmol) was added to a solution of α,β-unsaturated lactam**347** (230 mg, 0.75 mmol) in CH_2Cl_2 (20 mL) at -90 ºC. After stirring for 2 hours at this temperature, Et_3N (0.91 mL, 6.65 mmol) and 2-methyl-2-butene (0.70 mL, 6.61 mmol) were added and the reaction monitored by TLC analysis. Bromine (200 µl, 3.91 mmol) and the reaction mixture were stirred for further 15 minutes. Et_3N (0.46 mL, 3.33 mmol) and 2-methyl-2-butene (0.35 mL, 3.30 mmol) were added. The reaction mixture was allowed to warm up to room temperature diluted with CH_2Cl_2 (30 mL) and washed with aq. 10% $Na_2S_2O_3$ (2 × 20 ml) and then brine (50 mL). The organic portion was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was dissolved in THF (30 mL) and DBU (0.56 mL, 3.75 mmol) was added. After stirring at room temperature for 16 hours the reaction mixture was concentrated *in vacuo*. Purification by FCC was filtered through a short plug of SiO_2 (9:1 EtOAc-MeOH) afforded the title compound **346** (119 mg, 61%) as a white solid.

^{1}H NMR (500MHz, $CDCl_3$) 9.45 (1H, br. s., NH), 7.18 (1H, s, C(3)H), 4.14 (3H, s, C(1")H_3), 3.96 (3H, s, C(2')H_3).

^{13}C NMR (125MHz, $CDCl_3$) 160.5 (C(1')), 156.6 and 152.2 (C(5) and C(6)), 126.5 and 122.2 (C(2) and C(4)), 114.9 (C(3)), 60.1 (C(1")), 53.5 (C(2')).

HRMS (ESI^+) Calculated for $C_8H_8{}^{79}BrNNaO_4$ $[M+Na]^+$: 283.9529, Found: 293.9830.

FTIR 2987, 1735, 1661, 1320 cm^{-1}.

M.P. 171-172 ºC (CH_2Cl_2-petrol).

5.3 Experimental procedures for section 3.2

5.3.1 General procedures

General procedure A: for allylic amination under Mitsunobu conditions.

To a solution of the corresponding allylic alcohol (200 mol%), PPh_3 (300 mol%), and sulfonamide **11** (1 mmol) in THF (10 mL/mmol) was added dropwise DIAD (260 mol%). After 16 hours the reaction mixture concentrated *in vacuo*. Purification of the residue by FCC, under the conditions noted, afforded the corresponding product.

General procedure B: for acetal deprotection.

To a solution of the corresponding acetal (100 mol%) in acetone (15 mL/mmol) was added 6 M aq. HCl (3 mL/mmol) at 0 ºC and the reaction mixture was stirred for 4 hours at room temperature. The reaction mixture was then diluted with EtOAc (70 mL/mmol) and washed with saturated aq. $NaHCO_3$ (50 mL/mmol) and brine (50 mL/mmol). The organic portion was then dried ($MgSO_4$) and concentrated *in vacuo* to afford the corresponding aldehyde which was used without further purification.

General procedure C: for the formation of allylic alcohols using vinylmagnesium bromide.

To a solution of the corresponding aldehyde (100 mol%) in THF (20 mL/mmol) at -78 ºC, was added dropwise vinylmagnesium bromide (1.0 M in THF, 150 mol%). After 30 minutes the reaction mixture was warmed to 0 ºC. After 2 hours saturated aq. NH_4Cl (20 mL/mmol). The mixture was then extracted with EtOAc (2 × 50 mL/mmol). The organic extracts were combined, washed with brine (50 mL/mmol), dried ($MgSO_4$) and concentrated *in vacuo* to afford the product which was used without further purification.

General procedure D: for ring-closing metathesis.

Catalyst HG-II (1.5-10 mol%) was added to a stirred solution of α,β-unsaturated amide (100 mol%) in argon sparged CH_2Cl_2 or toluene (25 mL/mmol), and the mixture was heated at the specified temperature until TLC analysis indicated that the starting material was consumed. The mixture was then concentrated *in vacuo* and purified by FCC, under the conditions noted, to afford the corresponding product.

General Procedure E: for the oxidation of allylic alcohols with Jones reagent.

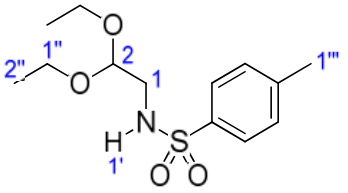
To a solution of the corresponding cyclic alcohol (100 mol%) in acetone (10 mL/mmol) at 0 ^oC, was added dropwise Jones reagent (100 mol%). After 30 minutes 2-propanol (0.3 mL/mmol) was added. After a further 15 minutes the reaction mixture was diluted with EtOAc (50 mL/mmol) and washed with saturated aq. $NaHCO_3$ (50 mL/mmol). The aqueous layer was then back extracted with EtOAc (25 mL/mmol). The organic extracts were combined, washed with brine (30 mL/mmol), dried ($MgSO_4$) and concentrated *in vacuo* to afford the product which was used without further purification.

General procedure F: for one-pot aromatisation and triflation.

A solution of the corresponding enone (100 mol%) in THF (20 mL/mmol) was treated with DBU (500 mol%) and stirred until all the starting material was consumed (TLC monitoring). *N*-Phenyltriflimide (150 mol%) was added and the reaction mixture was stirred for 6 hours. The reaction mixture was then concentrated *in vacuo* and the residue was purified by FCC, under the conditions noted, to afford the corresponding pyridine triflate.

5.3.2 Experimental Procedures

N-(2,2-Diethoxyethyl)-4-methylbenzenesulfonamide (412)



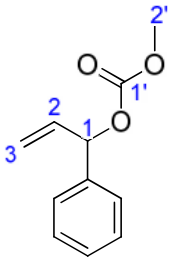
To a stirred solution of amino acetaldehyde diethyl acetal (7.26 mL, 50.0 mmol) and anhydrous Et_3N (14.0 mL, 100 mmol) in CH_2Cl_2 (100 mL) was added dropwise a solution of *p*-toluenesulfonyl chloride (10.5 g, 55.0 mmol) in CH_2Cl_2 (100 mL) over 30 min at 0 ºC. After 1 hour the reaction mixture was diluted with water (200 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (100 mL). The organic extracts were combined, washed with 1 M aq. HCl (50 mL), water (100 mL), and saturated aq. $NaHCO_3$ (100 mL), dried ($MgSO_4$), and concentrated *in vacuo*. Purification of the residue by FCC (4:1 petrol-EtOAc) afforded the title compound **412**(13.7 g, 94%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.74 (2H, d, *J* = 8.0 Hz, Ph), 7.30 (2H, d, *J* = 8.0 Hz, Ph), 4.77 (1H, t, *J* = 6.0 Hz, C(2)H, C(1')H), 4.45 (1H, t, *J* = 6.0 Hz, C(2)H, C(1')H), 3.62 (2H, dq, *J* = 9.0, 7.0 Hz, C(1")H_2), 3.45 (2H, dq, *J* = 9.0, 7.0 Hz, C(1")H_2), 3.02 (2H, t, *J* = 6.0 Hz, C(1)H_2), 2.41 (3H, s, C(1"')H_3), 1.15 (6H, t, *J* = 7.0 Hz, C(2")H_3).

^{13}C NMR (100 MHz, $CDCl_3$): 143.4 (*i*-Ph), 136.7 (*i*-Ph), 129.6 (Ph), 127.0 (Ph), 100.6 (C(2)), 63.0 (C(1")), 45.4 (C(1)), 21.4 (C(1"')), 15.1 (C(2")).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[192]

Methyl (1-phenylallyl) carbonate (419)



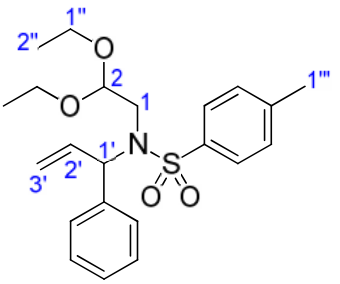
A mixture of 1-phenylprop-2-en-1-ol (310 mg, 2.31 mmol) and THF (10.0 mL) was cooled to -78 ºC. *N*-Butyl lithium (1.6 M in hexanes, 2.00 mL, 3.20 mmol) was added dropwise and the reaction mixture stirred for 30 minutes. Methyl chloroformate (0.22 mL, 2.82 mmol) was added and the reaction mixture stirred at this temperature for 4 hours. The reaction mixture was diluted with saturated aqueous NH_4Cl (25.0 mL) and extracted with Et_2O (3 × 25.0 mL). The combined organic layer was washed with brine (30.0 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by FCC (1:0 to 4:1 petrol-Et_2O) afforded to title compound (307 mg, 69%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.50-7.20 (5H, m, Ph), 6.21-5.94 (2H, m, C(2)H, C(1)H), 5.47-5.23 (2H, m, C(3)H_2), 3.79 (3H, s, C(2')H_3).

^{13}C NMR (101 MHz, $CDCl_3$) 154.9 (C(1')), 138.2 (*i*-Ph), 135.7 (C(2)), 128.5 (Ph), 128.3 (Ph), 127.0 (Ph), 117.4 (C(3)), 80.1 (C(1)), 54.7 (C(2')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[193]

_N_-(2,2-Diethoxyethyl)-4-methyl-_N_-(1-phenylprop-2-en-1-yl)benzenesulfonamide (411)



Trimethylphosphite (0.17 mL, 1.44 mmol) was added to a solution of Wilkinson's catalyst **416** (332 mg, 0.36 mmol) in THF (10 mL) at 30 ºC, under argon. In a separate vessel, sulfonamide **412** (3.00 g, 10.4 mmol) in THF (30 mL) was treated with LiHMDS (1.0 M in THF, 10.4 mmol) at room temperature. After 30 minutes this solution was added *via* cannula to the catalyst solution. Carbonate **419** (1.06 g, 5.53 mmol) was then added and the mixture was heated at 30 ºC for 16 hours. The reaction mixture was then cooled and diluted with EtOAc (200 mL). The organic layer was washed with a saturated aq. NH_4Cl (50 mL), brine (50 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by FCC (9:1, petrol-EtOAc) afforded the title compound **411** (1.72 g, 77%) as a clear oil.

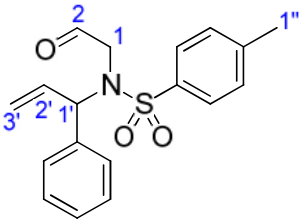
^{1}H NMR (400 MHz, $CDCl_3$): 7.68 (2H, d, *J* = 8.0 Hz, Ph), 7.22 (7H, m, Ph), 6.21 (1H, ddd, *J* = 17.0, 10.0, 7.5 Hz, C(2')H), 5.54 (1H, d, *J* = 7.5 Hz, C(3')H_2), 5.26 (1H, d, *J* = 10.0 Hz, C(3')H_2), 5.07 (1H, dd, *J* = 17.0, (C(1')H, C(2)H), 4.51 (1H, t, *J* = 5.0 Hz, (C(1')H, C(2)H), 3.64 (1H, app quintet, *J* = 7.0 Hz, C(1")H_2), 3.54 (1H, app quintet, *J* = 7.0 Hz, C(1")H_2), 3.39 (1H, app quintet, *J* = 7.0 Hz, C(1")H_2), 3.30 (2H, m, C(1")H_2, C(1)H_2), 3.19 (1H, dd, *J* = 15.0, 5.0 Hz, C(1)H_2), 2.43 (3H, s, C(1"')H_3), 1.17 (3H, t, *J* = 7.0 Hz, C(2")H_3), 1.04 (3H, t, *J* = 6.5 Hz, C(2")H_3).

^{13}C NMR (100 MHz, $CDCl_3$): 143.0 (*i*-Ph), 138.4 (*i*-Ph), 137.4 (*i*-Ph), 135.2 (C(2')), 129.2 (Ph), 128.1 (two signals, Ph), 127.4 (Ph), 127.3 (Ph), 118.8 (C(3')), 102.0 (C(2)), 64.2 (C(1"), 63.3 (C(1")), 62.9 (C(1')), 48.4 (C(1)), 21.3 (C(1"'), 15.0 (two signals, (C(2")).

MS (ESI$^+$) Calculated for $C_{22}H_{29}NNaO_4S$ $[M+Na]^+$: 426.1710, Found: 426.1710.

FTIR 3529, 3063, 3031, 2976, 2929, 1917, 1599, 1495, 1451, 1342, 1161, 1092, 1020 cm^{-1}.

4-Methyl-*N*-(2-oxoethyl)-*N*-(1-phenylprop-2-en-1-yl)benzenesulfonamide (420)



Acetal **411** (619 mg, 1.53 mmol) was subjected to General Procedure B. Purification by FCC (4:1 petrol-EtOAc) afforded the title compound **420** (391 mg, 78%) as a clear oil.

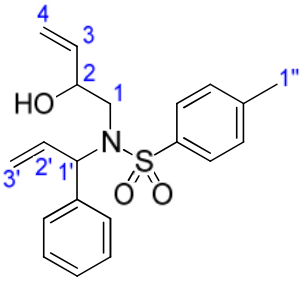
^{1}H NMR (500 MHz, $CDCl_3$): 9.13 (1H, dd, *J* = 2.0, 2.0 Hz, C(2)H), 7.72 (2H, d, *J* = 8.5 Hz, Ph), 7.30 (7H, m, Ph), 5.86 (2H, m, C(3')H_2), 5.27 (1H, d, *J* = 8.5 Hz, C(1')H), 5.10 (1H, m, C(2')H), 3.75 (1H, dd, *J* = 18.5, 2.0 Hz, C(1)H_2), 3.61 (1H, dd, *J* = 18.5, 2.0 Hz, C(1)H_2), 2.45 (3H, s, C(1")H_3).

^{13}C NMR (125 MHz, $CDCl_3$): 199.2, 143.9, 137.4, 136.5, 133.0, 129.7, 128.9, 128.5, 128.3, 127.6, 119.6, 62.9, 53.0, 21.6.

MS (ESI$^+$) Calculated for $C_{19}H_{23}NNaO_4S$ $[M+CH_3OH+Na]^+$: 384.1240, Found: 384.1224.

FTIR 3661, 3447, 3088, 3063, 3031, 2828, 2723, 2586, 1734, 1643, 1598, 1494, 1452, 1340, 1155, 1095, 1019, 942 cm^{-1}.

_N_-(2-Hydroxybut-3-en-1-yl)-4-methyl-_N_-(1-phenylprop-2-en-1-yl)benzenesulfonamide (421)



Aldehyde **420** (358 mg, 1.08 mmol) was subjected to the General Procedure C. Purification by FCC (9:1 to 8:1 petrol-EtOAc) gave the title compound **421** (295 g, 77%, 1:0.7 *dr*) as a clear oil.

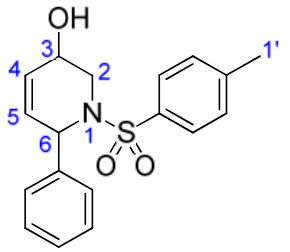
^{1}H NMR (500 MHz, $CDCl_3$): 7.75 (2H, d, *J* = 8.5 Hz, Ph), 7.69 (1.4H, d, *J* = 8.5 Hz, Ph), 7.31 (10H, m, Ph), 7.15 (1.7H, m, Ph), 6.08 (0.7H, ddd, *J* = 17.0, 10.5, 6.5 Hz, C(2')H), 5.92 (1H, ddd, *J* = 17.0, 10.5, 6.5 Hz, C(2')H), 5.78 (1H, d, *J* = 6.5 Hz, $C(4)H_2$), 5.64 (1.4H, m, $C(4)H_2$, C(3)H), 5.47 (1H, ddd, *J* = 17.0, 10.5, 6.0 Hz, C(3)H), 5.33 (0.7H, d, *J* = 10.5 Hz, $C(3')H_2$), 5.23 (2.4H, m, $C(3')H_2$), 5.03 (3.7H, m, C(1')H, $C(3')H_2$, $C(4)H_2$), 4.28 (0.7H, m, C(2)H), 3.50 (1H, m, C(2)H), 3.33 (1H, d, *J* = 3.0 Hz, OH), 3.15 (3.4H, m, $C(1)H_2$), 2.62 (0.7H, d, *J* = 4.0 Hz, OH), 2.45 (3H, s, $C(1'')H_3$), 2.44 (2.1H, s, $C(1'')H_3$).

^{13}C NMR (125 MHz, $CDCl_3$): 143.7 (*i*-Ph), 143.6 (*i*-Ph), 138.4 (*i*-Ph), 137.9 (*i*-Ph), 137.3 (two signals, C(2')), 136.7 (*i*-Ph), 136.5 (*i*-Ph), 134.7 (C(3)), 133.0 (C(3)), 129.6 (Ph), 129.5 (Ph), 128.7 (two signals, Ph), 128.5 (Ph), 128.4 (Ph), 128.3 (Ph), 128.1 (Ph), 127.8 (Ph), 127.6 (Ph), 119.8 (C(4)), 119.5 (C(4)), 116.1 (C(3')), 116.0 (C(3')), 71.9 (C(2)), 71.6 (C(2)), 64.0 (C(1')), 63.6 (C(1')), 51.6 (C(1)), 51.5 (C(1)), 21.5 (two signals, C(1")).

MS (ESI^+) Calculated for $C_{20}H_{23}NNaO_3S$ $[M+Na]^+$: 380.1291, Found: 380.1291.

FTIR 3500, 3071, 3054, 3021, 1604, 1406, 1330, 1158 cm^{-1}.

1-[(4-Methylphenyl)sulfonyl]-6-phenyl-1,2,3,6-tetrahydropyridin-3-ol (422)



Alcohol **421** (515 mg, 1.44 mmol), catalyst HG-II (44 mg, 5 mol%) and CH_2Cl_2 were subjected to the General Procedure D, and the reaction mixture was stirred at room temperature for 16 hours. Purification by FCC (4:1 to 1:1 petrol-EtOAc) afforded the title compound **422**(440 mg, 91%, 1:0.5 *dr*) as a pale brown oil.

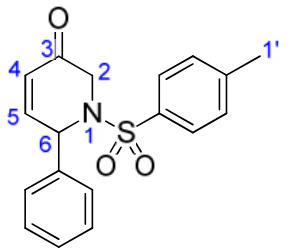
^{1}H NMR (400 MHz, $CDCl_3$): 7.62 (1H, d, *J* = 8.5 Hz, Ph), 7.57 (2H, d, *J* = 8.0 Hz, Ph), 7.38 (3H, m, Ph), 7.31 (4.5H, m, Ph), 7.21 (3H, m, Ph), 6.18 (0.5H, dd, *J* = 10.5, 4.5 Hz, C(5)H, C(4)H), 6.11 (0.5H, dd, *J* = 10.0, 4.5 Hz, C(5)H, C(4)H), 5.89 (2H, m, C(5)H, C(4)H), 5.67 (0.5H, d, *J* = 4.0 Hz, C(6)H), 5.52 (1H, br s, C(6)H), 4.11 (1H, m, (C(3)H), 4.02 (0.5H, m, C(3)H), 3.92 (1H, dd, *J* = 13.5, 6.0 Hz, (C(2)H_2), 3.70 (0.5H, d, *J* = 15.0 Hz, C(2)H_2), 3.24 (0.5H, m, C(2)H_2), 2.86 (1H, dd, *J* = 14.0, 10.0 Hz, C(2)H_2), 2.44 (0.5H, s, OH), 2.39 (4.5H, s, C(1')H_3), 1.71 (1H, d, *J* = 7.0 Hz, OH).

^{13}C NMR (125 MHz, $CDCl_3$): 143.6 (*i*-Ph), 143.3 (*i*-Ph), 138.2 (*i*-Ph), 137.5 (*i*-Ph), 137.3 (*i*-Ph), 136.4 (*i*-Ph), 130.7 (C(5)), 130.2 (C(5)), 129.5 (two signals, Ph), 128.5 (two signals, Ph), 128.2 (Ph), 128.1 (3 signals, Ph), 128.0 (C(4)), 127.9 (C(4)), 127.6 (Ph), 127.0 (Ph), 62.4 (C(3)), 62.0 (C(3)), 56.0 (C(6)), 55.1 (C(6)), 46.3 (C(2)), 44.8 (C(2)), 21.5 (two signals, C(1')).

MS (ESI^+) Calculated for $C_{18}H_{19}NNaO_3S$ $[M+Na]^+$: 352.0978, Found: 352.0972.

FTIR 3497, 3061, 3032, 2922, 2873, 1653, 1493, 1371, 1183 cm^{-1}.

1-[(4-Methylphenyl)sulfonyl]-6-phenyl-1,6-dihydropyridin-3(2*H*)-one (423)



Alcohol **422** (426 mg, 1.29 mmol) was subjected to the General procedure E. The title compound **423** (358 mg, 85%) was obtained as an analytically pure colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.59 (2H, d, *J* = 8.0 Hz, Ph), 7.38 (5H, s, Ph), 7.25 (2H, m, *J* = 8.0 Hz, Ph), 6.97 (1H, dd, *J* = 10.5, 5.0 Hz, C(5)H), 5.99 (1H, d, *J* = 10.0 Hz, C(4)H), 5.82 (1H, d, *J* = 5.0 Hz, C(6)H), 4.32 (1H, d, *J* = 18.5 Hz, $C(2)H_2$), 3.70 (1H, d, *J* = 18.5 Hz, $C(2)H_2$), 2.40 (3H, s, $C(1')H_3$).

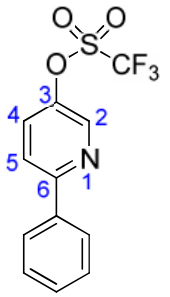
^{13}C NMR (100 MHz, $CDCl_3$): 191.4 (C(3)), 146.6 (C(4)), 143.9 (*i*-Ph), 135.7 (*i*-Ph), 134.5 (*i*-Ph), 129.9 (Ph), 128.9 (Ph), 128.8 (C(5), Ph), 128.2 (Ph), 127.9 (C(5), Ph), 127.1 (Ph), 56.2 (C(6)), 49.4 (C(2)), 21.5 (C(1')).

HRMS (EI) Calculated for $C_{18}H_{17}NO_3S$ $[M]^+$: 327.0929, Found: 327.0929.

FTIR 3441, 3062, 3032, 2967, 1917, 1687, 1375, 1289, 1163, 925 cm^{-1}.

M.P. 159-160 ºC (CH_2Cl_2-pentane).

6-Phenylpyridin-3-yl trifluoromethanesulfonate (424)



Enone **423** (275 mg, 0.84 mmol) was subjected to the General Procedure F. Purification by FCC (4:1 to 1:1 petrol-EtOAc) afforded the title compound **424** (220 mg, 86%) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): 8.66 (1H, d, *J* = 3.0 Hz, C(2)H), 8.00 (2H, dd, *J* = 8.0, 1.5 Hz, Ph), 7.84 (1H, d, *J* = 9.0 Hz, C(5)H, C(4)H), 7.70 (1H, dd, *J* = 9.0, 3.0 Hz, C(5)H, C(4)H), 7.44-7.55 (3H, m, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): 157.4 (C(6)), 145.6 (C(3)), 142.4 (C(2)), 137.4 (*i*-Ph), 129.8 (Ph), 129.6 (C(4)), 128.9 (Ph), 127.0 (Ph), 121.2 (C(5)), 118.7 (q, *J* = 321.0 Hz, CF_3).

^{19}F NMR (377 MHz, $CDCl_3$): -72.5 (s).

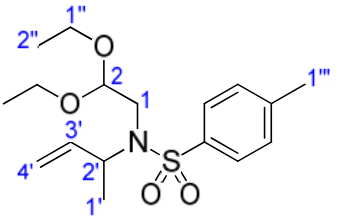
HRMS (CI) Calculated for $C_{12}H_9NO_3F_3S$ $[M+H]^+$: 304.0255, Found: 304.0255.

FTIR 3080, 1964, 1590, 1579, 1471, 1450, 1426, 1250, 1226, 1168, 1135, 1074, 1016, 938 cm^{-1}.

M.P. 88-89 ºC (CH_2Cl_2-pentane).

The structure of this compound was confirmed by X-ray crystallographic analysis (Appendix III).

N-(But-3-en-2-yl)-*N*-(2,2-diethoxyethyl)-4-methylbenzenesulfonamide (426)



Sulfonamide **412** (1.48 g, 5.16 mmol) and 3-buten-2-ol (0.77 g, 8.9 mmol) were subjected to the General Procedure A. Purification by FCC (1:0 to 9:1 petrol-EtOAc) afforded the title compound **426** (1.54 g, 88%) as a colourless oil.

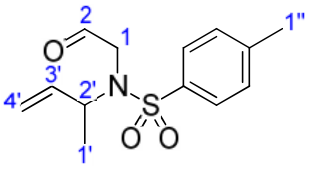
^{1}H NMR (500 MHz, $CDCl_3$) 7.74 (2H, d, *J* = 8.0 Hz, Ph), 7.30 (2H, d, *J* = 8.0 Hz, Ph), 5.52 (1H, ddd, *J* = 17.5, 11.0, 4.5 Hz, C(3')H), 5.04 (2H, m, C(4')H_2), 4.80 (1H, dd, *J* = 6.5, 4.0 Hz, C(2)H), 4.44 (1H, dq, *J* = 6.5, 4.5 Hz, C(2')H), 3.76 (2H, m, C(1")H_2), 3.59 (2H, m, C(1")H_2), 3.17 (1H, dd, *J* = 15.0, 4.5 Hz, C(1)H_2), 3.04 (1H, dd, *J* = 15.0, 6.5 Hz, C(1)H_2), 2.43 (3H, s, C(1"')H_3), 1.22 (9H, m, C(2")H_3, C(1')H_3).

^{13}C NMR (125 MHz, $CDCl_3$) 143.3 (*i*-Ph), 137.6 (C(3')), 137.4 (*i*-Ph), 129.6 (Ph), 127.3 (Ph), 116.8 (C(4')), 102.9 (C(2)), 64.4 (C(1")), 63.6 (C(1")), 55.6 (C(2')), 47.5 (C(1)), 21.5 (C(1"')), 17.7 (C(1')), 15.3 (C(2")), 15.2 (C(2")).

MS (ESI^+) Calculated for $C_{17}H_{27}NNaO_4S$ $[M+Na]^+$: 364.1553, Found: 364.1551.

FTIR 2977, 2931, 2879, 1922, 1758, 1639, 1598, 1493, 1453, 1375, 1339, 1305, 1230, 1156, 1129, 1063 cm^{-1}.

N-(But-3-en-2-yl)-4-methyl-*N*-(2-oxoethyl)benzenesulfonamide (428)



Acetal **426** (1.28 g, 4.1 mmol) was subjected to the General Procedure B. Purification by FCC (10:0 to 7.5:2.5 petrol-EtOAc) afforded the title compound **428** (1.10 g, 95%) as a clear oil.

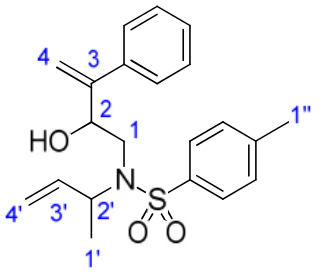
^{1}H NMR (400 MHz, $CDCl_3$) 9.61 (1H, dd, *J* = 2.0, 2.0 Hz, C(2)H), 7.74 (2H, dt, *J* = 8.5, 2.0 Hz, Ph), 7.32 (2H, dd, *J* = 8.5, 1.0 Hz, Ph), 5.57 (1H, ddd, *J* = 17.5, 10.5, 4.5 Hz, C(3')H), 5.16 (1H, ddd, *J* = 10.5, 2.0, 1.0 Hz, C(4')H_2), 5.09 (1H, ddd, *J* = 17.5, 2.0, 1.0 Hz, C(4')H_2), 4.63 (1H, dddq, *J* = 7.0, 4.5, 2.0, 2.0 Hz, C(2')H), 3.71 (1H, dd, *J* = 18.5, 1.5 Hz, C(1)H_2), 3.62 (1H, dd, *J* = 18.5, 1.5 Hz, C(1)H_2), 2.44 (3H, s, C(1")H_3), 1.13 (3H, d, *J* = 7.0 Hz, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 199.6 (C(2)), 143.9 (*i*-Ph), 136.7 (*i*-Ph), 136.6 (C(3')), 129.9 (Ph), 127.3 (Ph), 118.0 (C(4')), 54.1 (C(2')), 51.7 (C(1)), 21.5 (C(1")), 16.4 (C(1')).

MS (ESI^-) Calculated for $C_{13}H_{16}NO_3S$ $[M-H]^-$: 266.0856, Found: 266.0861.

FTIR 3089, 2979, 2945, 2722, 1785, 1735, 1378, 1154, 1020 cm^{-1}.

_N_-(But-3-en-2-yl)-_N_-(2-hydroxy-3-phenylbut-3-enyl)-4-methylbenzenesulfonamide (429)



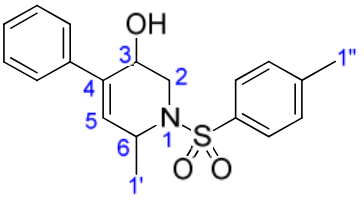
A solution of 1-phenylvinyl bromide (0.36 mL, 2.8 mmol) in THF (4 mL) was added dropwise to a mixture of magnesium turnings (0.14 g, 5.6 mmol), iodine (1 crystal) and THF (1 mL) and the reaction was stirred at room temperature for 30 min. The resulting Grignard was added to a solution of aldehyde **428** (369 mg, 1.38 mmol) in THF at -78 ºC. After 1 hour the reaction mixture was warmed to 0 ºC. After a further 3 hours the reaction mixture was diluted with saturated aq. NH_4Cl (60 mL) and EtOAc (100 mL). The aqueous layer was extracted with EtOAc (2 × 30 mL). The organic extracts were combined, washed with brine (30 mL), then dried ($MgSO_4$), and concentrated *in vacuo*. Purification by FCC (1:0 to 5:1 petrol-EtOAc) afforded the title compound **429** (444 mg, 68%, 1:1 *dr*) as a colourless oil. This material was contaminated with *ca.* 22% of starting aldehyde.

^{1}H NMR (400 MHz, $CDCl_3$) 7.68 (2H, dt, *J* = 8.5, 2.0 Hz, Ph), 7.65 (2H, dt, *J* = 8.5, 2.0 Hz, Ph), 7.32 (14H, m, Ph), 5.68 (1H, ddd, *J* = 17.5, 10.5, 4.5 Hz, C(3')H), 5.57 (2H, m, C(4')H_2), 5.37 (3H, m, C(4)H_2, C(3')H), 5.08 (2H, m, C(4)H_2), 4.99 (2H, m, C(4')H_2), 4.87 (2H, m, C(2)H), 4.54 (2H, m, C(2')H), 3.81 (1H, d, *J* = 3.0 Hz, OH), 3.38 (1H, d, *J* = 3.0 Hz, OH), 3.01 (4H, m, C(1)H_2), 2.41 (6H, m, C(1")H_3), 1.16 (3H, d, *J* = 7.0 Hz, C(1')H_3), 1.04 (3H, d, *J* = 7.0 Hz, C(1')H_3).

^{13}C NMR (101 MHz, $CDCl_3$) 148.8 (*i*-Ph, *i*-Ar), 148.7 (*i*-Ph), 143.6 (two signals, *i*-Ph), 139.6 (C(3)), 139.3 (C(3)), 138.0 (C(3')), 136.5 (C(3')), 129.7 (two signals, Ph), 128.4 (two signals, Ph), 127.8 (Ph), 127.3 (two signals, Ph), 126.9 (Ph), 126.8 (Ph), 117.7 (C(4)), 116.9

(C(4')), 113.8 (C(4)), 113.6 (C(4')), 73.7 (C(2)), 72.2 (C(2)), 55.6 (C(2')), 54.9 (C(2')), 50.0 (C(1)), 49.6 (C(1)), 21.4 (two signals, C(1")), 17.9 (C(1')), 15.8 (C(1')). Only 31 signals were observed.

6-Methyl-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (430)



Alcohol **429** (418 mg, 78% purity, 0.88 mmol), catalyst HG-II (25 mg, 5 mol%) and CH_2Cl_2 were subjected to the General procedure D and the reaction mixture was heated at 70 ºC, in a sealed tube for 3 hours. Purification by FCC (4:1 to 3:2 petrol-EtOAc) afforded the title compound **430** (240 mg, 80%, 1:1 *dr*) as pale brown solid. *N.B.* Yield is based on a purity of 78% for alcohol **430** as judged by ^{1}H NMR (*vide supra*). The overall yield from aldehyde **428** is 54%.

^{1}H NMR (400 MHz, $CDCl_3$): 7.81 (2H, dt, *J* = 8.5, 2.0 Hz, Ph), 7.75 (2H, dt, *J* = 8.5, 2.0 Hz, Ph), 7.50 (2H, m, Ph), 7.32 (8H, m, Ph), 7.20 (4H, m, Ph), 6.10 (1H, d, *J* = 4.5 Hz, C(5)H), 5.81 (1H, dd, *J* = 4.0, 1.0 Hz, C(5)H), 4.69 (1H, qd, *J* = 7.0, 4.5 Hz, C(3)H, C(6)H), 4.48 (3H, m, C(3)H, C(6)H), 4.00 (2H, m, $C(2)H_2$), 3.34 (1H, dd, *J* = 14.0, 2.5 Hz, $C(2)H_2$), 3.18 (1H, dd, *J* = 13.5, 9.0 Hz, $C(2)H_2$), 2.43 (3H, s, $C(1")H_3$), 2.42 (3H, s, $C(1")H_3$), 2.05 (1H, d, *J* = 10.0 Hz, OH), 1.74 (1H, d, *J* = 5.5 Hz, OH), 1.37 (3H, d, *J* = 7.0 Hz, $C(1')H_3$), 1.22 (3H, d, *J* = 7.0 Hz, $C(1')H_3$).

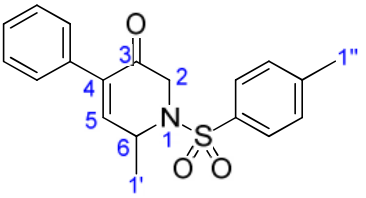
^{13}C NMR (100 MHz, $CDCl_3$): 143.5 (*i*-Ph), 143.4 (*i*-Ph), 139.4 (*i*-Ph), 138.2 (*i*-Ph), 137.4 (*i*-Ph), 137.3 (*i*-Ph), 136.5 (C(4)), 129.7 (two signals, Ph), 128.9 (C(5)), 128.7 (C(5)), 128.6 (two signals, Ph), 127.9 (Ph), 127.7 (Ph), 127.3 (Ph), 127.0 (Ph), 126.4 (Ph), 125.6 (Ph), 64.3 (C(3)), 63.1 (C(3)), 50.3 (C(6)), 49.7 (C(6)), 45.8 (C(2)), 45.0 (C(2)), 21.5 (two signals, C(1")), 19.6 (C(1')), 17.6 (C(1')). Only 29 signals were observed.

MS (ESI^+) Calculated for $C_{19}H_{21}NKO_3S$ $[M+K]^+$: 382.0874, Found: 382.0874.

FTIR 3566, 3538, 3064, 2979, 2901, 1598, 1494, 1446, 1370, 1329, 1280, 1193, 1019 cm^{-1}.

M.P. 102-103ºC (CH_2Cl_2).

6-Methyl-4-phenyl-1-tosyl-1,2-dihydropyridin-3(6H)-one (431)



To a solution of alcohol **430** (212 mg, 0.62 mmol) in CH_2Cl_2 at 0 ºC was added $NaHCO_3$ (262 mg, 3.12 mmol) and then DMP (406 mg, 0.96 mmol). After 3 hours further DMP (200 mg, 0.47 mmol) was added. After 5 hours the mixture was concentrated *in vacuo* (at 20 ºC). Purification of the residue by FCC (7:3 petrol-EtOAc) afforded the title compound **431** (142 mg, 67%) as a white solid.

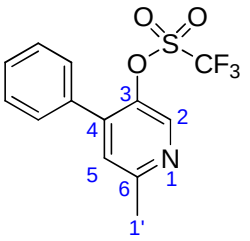
^{1}H NMR (400 MHz, $CDCl_3$) 7.69 (2H, d, *J* = 8.5 Hz, Ph), 7.28 (5H, m, Ph), 6.94 (2H, m, Ph), 6.72 (1H, d, *J* = 5.0 Hz, C(5)H), 4.92 (1H, qd, *J* = 7.0, 5.0 Hz, C(6)H), 4.53 (1H, d, *J* = 18.5 Hz, C(2)H_2), 4.08 (1H, d, *J* = 18.5 Hz, C(2)H_2), 2.38 (3H, s, C(1")H_3), 1.52 (3H, d, *J* = 7.0 Hz, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 190.2 (C(3)), 146.5 (C(5)), 144.0 (*i*-Ph), 137.2 (*i*-Ph), 135.9 (C(4)), 133.7 (*i*-Ph), 130.0 (Ph), 128.2 (Ph), 128.0 (two signals, Ph), 127.2 (Ph), 50.4 (C(6)), 49.2 (C(2)), 21.4 (C(1")), 17.7 (C(1')).

FTIR 3442, 2982, 1744, 1676, 1344, 1186, 1017 cm^{-1}.

M.P. 143-144 ºC (CH_2Cl_2).

6-Methyl-4-phenylpyridin-3-yl trifluoromethanesulfonate (432)



Enone **431** (42 mg, 0.12 mmol) was subjected to General Procedure F. Purification by FCC (1:0 to 1:20 petrol-EtOAc) afforded the title compound **432** (30 mg, 77%) as clear oil.

^{1}H NMR (500 MHz, $CDCl_3$) 8.53 (1H, s, C(2)H), 7.50 (5H, s, Ph), 7.29 (1H, s, C(5)H), 2.65 (3H, s, C(1')H_3).

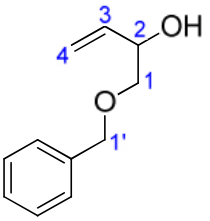
^{13}C NMR (125 MHz, $CDCl_3$) 159.0 (C(6)), 143.0 (C(4), C(3)), 142.8 (C(2)), 142.4 (C(4), C(3)), 133.3 (*i*-Ph), 129.6 (Ph), 128.9 (Ph), 128.8 (Ph), 125.2 (C(5)), 118.3 (q, J = 320.0 Hz, CF_3), 24.0 (C(1')).

^{19}F NMR (377 MHz, $CDCl_3$): -73.6 (s).

HRMS (CI) Calculated for $C_{13}H_{11}NO_3F_3S$ $[M+H]^+$: 318.0412, Found: 318.04089.

FTIR 3662, 3062, 1725, 1599, 1500, 1248, 1212, 1042 cm^{-1}.

1-(Benzyloxy)but-3-en-2-ol (434)



Aldehyde **292** (3.60 g, 24.00 mmol) was subjected to the General Procedure C. Purification by FCC (1:0 to 4:1 petrol-EtOAc) afforded the title compound **434** (4.02 g, 94%) as a clear oil.

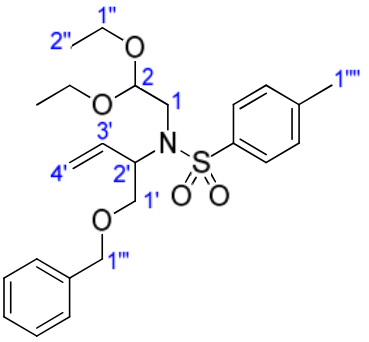
^{1}H NMR (400 MHz, $CDCl_3$) 7.28-7.43 (5H, m, Ph), 5.85 (1H, ddd, J = 17.0, 10.5, 6.0 Hz, C(3)H), 5.42-5.32 (1H, m, C(4)H_2), 5.21 (1H, dd, J = 10.5, 1.5 Hz, C(4)H_2), 4.59 (2H, m,

C(1')H_2), 4.40-4.32 (1H, m, C(2)H), 3.56 (1H, dd, *J*=9.5, 3.5 Hz, C(1)H_2), 3.39 (1H, dd, *J*=9.5, 8.0 Hz, C(1)H_2), 2.46 (1H, d, *J*=3.5 Hz, OH).

^{13}C NMR (100 MHz, $CDCl_3$) 137.7 (*i*-Ph), 136.5 (C(3)), 128.4 (Ph), 127.7 (Ph), 127.7 (Ph), 116.4 (C(4)), 73.9 (C(1)), 73.3 (C(1')), 71.4 (C(2)).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[194]

N-[1-(Benzyloxy)but-3-en-2-yl]-*N*-(2,2-diethoxyethyl)-4-methylbenzene-sulfonamide (435)



Sulfonamide **412** (302 mg, 1.05 mmol) and **434** (382 mg, 2.14 mmol) were subjected to General Procedure A. Purification by FCC (10:0:0 to 1:1:0 to 0:0:1 petrol-EtOAc- CH_2Cl_2) afforded the title compound **435** (355 g, 74%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$): 7.73 (2H, d, *J* = 8.5 Hz, Ph), 7.27 (7H, m, Ph), 5.64 (1H, ddd, *J* = 17.0, 11.0, 6.0 Hz, C(3')H), 5.15 (1H, d, *J* = 11.0 Hz, C(4')H_2), 5.08 (1H, d, *J* = 17.0 Hz, C(4')H_2), 4.70 (1H, dd, *J* = 6.0, 4.5 Hz, C(2')H, C(2)H), 4.53 (1H, m, C(2')H, C(2)H), 4.46 (2H, s, C(1"')H_3), 3.69 (4H, m, C(1")H_2), 3.53 (2H, dd, *J* = 9.5, 2.5 Hz, C(1)H_2), 3.27 (1H, dd, *J* = 15.5, 4.5 Hz, C(1')H_2), 3.13 (1H, dd, *J* = 15.5, 6.0 Hz, C(1')H_2), 2.40 (3H, s, C(1"")H_3), 1.20 (3H, t, *J* = 7.0 Hz, C(2")H_3), 1.17 (3H, t, *J* = 7.0 Hz, C(2")H_3).

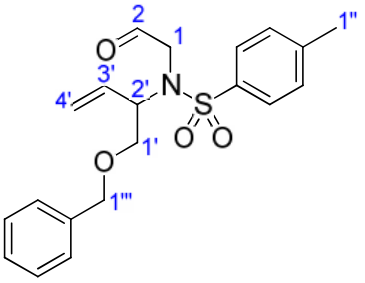
^{13}C NMR (125 MHz, $CDCl_3$): 143.2 (*i*-Ph), 138.0 (*i*-Ph), 137.2 (*i*-Ph), 134.0 (C(3')), 129.4 (Ph), 128.2 (Ph), 127.5 (two signals, Ph), 127.4 (Ph), 118.8 (C(4')), 102.9 (C(2)), 72.9

(C(1”’)), 70.8 (C(1’)), 64.0 (C(1”)), 63.4 (C(1”)), 59.6 (C(2’)), 48.4 (C(1)), 21.5 (C(1””)), 15.3 (C(2”)), 15.2 (C(2”)).

MS (ESI^+) Calculated for $C_{24}H_{33}NNaO_5S$ $[M+Na]^+$: 470.1972, Found: 470.1983.

FTIR 3306, 3031, 2979, 2873, 1808, 1751, 1599, 1496, 1376, 1340, 1110, 1027 cm^{-1}.

N-[1-(Benzyloxy)but-3-en-2-yl]-4-methyl-*N*-(2-oxoethyl)benzenesulfonamide (436)



Acetal **435** (1.00 g, 2.23 mmol) was subjected to General Procedure B. Purification by FCC (1:0 to 3:1 petrol-EtOAc) afforded the title compound **436** (715 mg, 86%) as a clear oil.

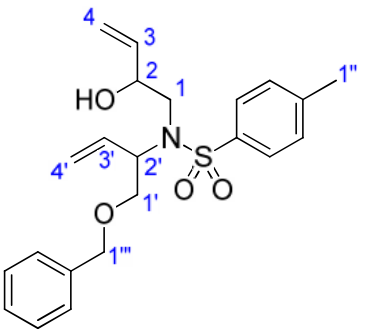
^{1}H NMR (500 MHz, $CDCl_3$): 9.54 (1H, d, *J* = 1.5 Hz, C(2)H), 7.72 (2H, d, *J* = 8.0 Hz, Ph), 7.31 (5H, m, Ph), 7.21 (2H, d, *J* = 6.0 Hz, Ph), 5.58 (1H, ddd, *J* = 17.0, 11.0, 5.5 Hz, C(3’)H), 5.19 (1H, d, *J* = 11.0 Hz, C(4’)H_2), 5.08 (1H, d, *J* = 17.0 Hz, C(4’)H_2), 4.71 (1H, m, C(2’)H), 4.44 (1H, d, *J* = 12.0 Hz, C(1”’)H_2), 4.35 (1H, d, *J* = 12.0 Hz, C(1”’)H_2), 3.86 (1H, dd, *J* = 19.0, 1.5 Hz, C(1)H_2), 3.79 (1H, dd, *J* = 19.0, 1.5 Hz, C(1)H_2), 3.66 (1H, dd, *J* = 10.0, 4.5 Hz, C(1’)H_2), 3.56 (1H, dd, *J* = 10.0, 4.5 Hz, C(1’)H_2), 2.42 (3H, s, C(1”)H_3).

^{13}C NMR (125 MHz, $CDCl_3$): 200.0 (C(2)), 143.8 (*i*-Ph), 137.1 (*i*-Ph), 136.8 (*i*-Ph), 132.5 (C(3’)), 129.7 (Ph), 128.4 (Ph), 127.9 (Ph), 127.8 (Ph), 127.4 (Ph), 119.5 (C(4’)), 73.3 (C(1”’)), 71.0 (C(2’)), 58.4 (C(1’)), 53.3 (C(1)), 21.5 (C(1”)).

MS (ESI^+) Calculated for $C_{21}H_{27}NNaO_5S$ $[M+CH_3OH+Na]^+$: 428.1502, Found: 428.1496.

FTIR 3444, 3088, 3054, 2919, 2862, 2721, 1733, 1641, 1598, 1341, 1157, 1099 cm^{-1}.

_N_-[1-(Benzyloxy)but-3-en-2-yl]-_N_-(2-hydroxybut-3-en-1-yl)-4-methylbenzene-sulfonamide (437)



Aldehyde **436** (300 mg, 0.80 mmol) was subjected to the General Procedure C. The title compound **437** (297 mg, 92%, 1:1 *dr*) was afforded as analytically pure clear oil.

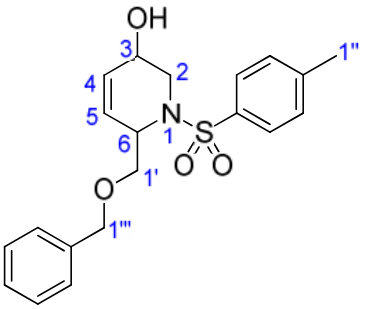
^{1}H NMR (400 MHz, $CDCl_3$) 7.73 (4H, d, *J* = 8.0 Hz, Ph), 7.29 (12H, m, Ph), 7.17 (2H, d, *J* = 8.0 Hz, Ph), 5.74 (3H, m, C(3)H, C(3')H), 5.57 (1H, ddd, *J* = 17.5, 11.0, 5.5 Hz, C(3)H, C(3')H), 5.37 (1H, dt, *J* = 17.0, 1.5 Hz, C(4)H_2, C(4')H_2), 5.28 (1H, dt, *J* = 17.0, 1.5 Hz, C(4)H_2, C(4')H_2), 5.14 (6H, m, C(4)H_2, C(4')H_2), 4.71 (1H, m, C(2)H), 4.51 (6H, m, C(2')H, C(1"')H_2), 4.29 (1H, dddd, *J* = 6.0, 4.5, 2.5, 1.5 Hz, C(2)H), 3.93 (1H, d, *J* = 1.5 Hz, OH), 3.83 (1H, m, C(1')H_2), 3.73 (1H, d, *J* = 3.0 Hz, OH), 3.65 (3H, m, C(1')H_2), 3.41 (1H, dd, *J* = 15.0, 2.5 Hz, C(1)H_2), 3.23 (1H, m, C(1)H_2), 3.12 (1H, m, C(1)H_2), 2.84 (1H, dd, *J* = 15.0, 10.0 Hz, C(1)H_2), 2.41 (3H, s, C(1")H_3), 2.38 (3H, s, C(1")H_3).

^{13}C NMR (125 MHz, $CDCl_3$) 143.5 (*i*-Ph), 143.4 (*i*-Ph), 137.3 and 137.2 (C(3'), C(3)), 137.1 (*i*-Ph), 137.0 (*i*-Ph), 137.0 (*i*-Ph), 136.9 (*i*-Ph), 133.0 and 132.6 (C(3'), C(3)), 129.5 (Ph), 129.5 (Ph), 128.4 (two signals, Ph), 128.0 (Ph), 127.9 (two signals, Ph), 127.8 (Ph), 127.6 (Ph), 127.5 (Ph), 119.5 and 119.2 (C(4'), C(4)), 116.3 and 116.0 (C(4'), C(4)), 73.3 and 72.7 (C(1"')), 72.0 (C(2)), 71.3 and 71.2 (C(1')), 69.1 (C(2)), 61.4 and 58.9 (C(2')), 52.4 and 50.9 (C(1)), 21.5 (two signals, C(1")).

MS (ESI^+) Calculated for $C_{22}H_{27}NNaO_4S$ $[M+Na]^+$: 424.1553, Found: 424.1556.

FTIR 3468, 3087, 3064, 3031, 2982, 2923, 2866, 1875, 1805, 1643, 1495, 1336, 1156 cm^{-1}.

6-[(Benzyloxy)methyl]-1-[(4-methylphenyl)sulfonyl]-1,2,3,6-tetrahydropyridin-3-ol (438)



Alcohol **437** (297 mg, 0.74 mmol), catalyst HG-II (23 mg, 5 mol%) and CH_2Cl_2 (15 mL) were subjected to the General Procedure D and the reaction mixture was stirred at room temperature for 24 hours. Purification by FCC (4:1 to 1:1 petrol-EtOAc) afforded the title compound **438** (258 mg, 93%, 1:1 *dr*) as a pale brown oil.

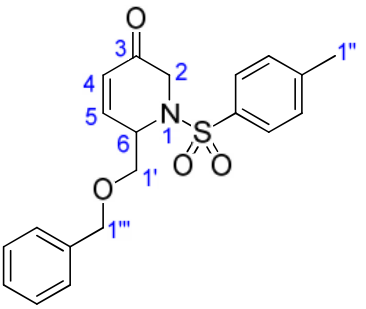
^{1}H NMR (400 MHz, $CDCl_3$): 7.78 (2H, d, *J* = 8.5 Hz, Ph), 7.70 (2H, d, *J* = 8.5 Hz, Ph), 7.33 (8H, m, Ph), 7.23 (6H, m, Ph), 6.06 (1H, ddt, *J* = 10.0, 5.5, 1.5 Hz, C(4)H, C(5)H), 5.94 (1H, dd, *J* = 10.0, 4.5 Hz, C(4)H, C(5)H), 5.84 (1H, m, C(4)H, C(5)H), 5.78 (1H, ddt, *J* = 10.5, 4.0, 1.5 Hz, C(4)H, C(5)H), 4.65 (1H, m, C(6)H), 4.47 (5H, m, C(6)H, C(1"')), 3.95 (2H, m, C(3)H), 3.86 (2H, m, $C(2)H_2$), 3.63 (2H, m, $C(1')H_2$), 3.54 (2H, m, $C(1')H_2$), 3.43 (1H, dd, *J* = 14.5, 3.0 Hz, $C(2)H_2$), 3.02 (1H, dd, *J* = 13.0, 9.0 Hz, $C(2)H_2$), 2.40 (6H, m, $C(1")H_3$), 2.18 (1H, d, *J* = 10.0 Hz, OH), 1.76 (1 H, d, *J* = 8.0 Hz, OH).

^{13}C NMR (125 MHz, $CDCl_3$): 143.5 (*i*-Ph), 143.4 (*i*-Ph), 137.7 (two signals, *i*-Ph), 137.5 (*i*-Ph), 137.2 (*i*-Ph), 131.4and 129.7 (C(4)), 129.6 (Ph), 129.1 (Ph), 128.4 (three signals, Ph), 127.7 (Ph), 127.6 (three signals, Ph), 127.0 (two signals, C(5)), 73.3 and 73.2 (C(1"')), 71.7 and 70.5 (C(1')), 62.2 and 61.9 (C(3)), 52.8 and 52.3 (C(6)), 47.2 and 46.5 (C(2)), 21.5 (two signals, C(1")). Only 31 signals were observed.

MS (ESI^+) Calculated for $C_{20}H_{23}NNaO_4S$ $[M+Na]^+$: 396.1240, Found: 396.1229.

FTIR 3496, 3032, 2923, 2864, 1723, 1597, 1495, 1454, 1212, 1194, 1068 cm^{-1}.

6-[(Benzyloxy)methyl]-1-[(4-methylphenyl)sulfonyl]-1,6-dihydropyridin-3(2*H*)-one (439)



Alcohol **438** (264 mg, 0.70 mmol) was subjected to the General Procedure E. Purification by FCC (4:1 to 1:1 petrol-EtOAc) afforded the title compound **439** (219 mg, 84%) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.62 (2H, d, *J* = 8.0 Hz, Ph), 7.34 (3H, m, Ph), 7.24 (4H, m, Ph), 6.79 (1H, dd, *J* = 10.5, 5.0 Hz, C(5)H), 5.92 (1H, dd, *J* = 10.5, 2.0 Hz, C(4)H), 4.75 (1H, dddd, *J* = 5.0, 5.0, 4.0, 2.0 Hz, C(6)H), 4.53 (1H, d, *J* = 12.0 Hz, $C(2)H_2$, $C(1'''')H_2$), 4.46 (1H, d, *J* = 12.0 Hz, $C(2)H_2$, $C(1'''')H_2$), 4.36 (1H, d, *J* = 18.5 Hz, $C(2)H_2$, $C(1'''')H_2$), 4.09 (1H, d, *J* = 18.5 Hz, $C(2)H_2$, $C(1'''')H_2$), 3.84 (1H, dd, *J* = 10.0, 4.5 Hz, $C(1')H_2$), 3.74 (1H, dd, *J* = 10.0, 4.5 Hz, $C(1')H_2$), 2.40 (3H, s, $C(1'')H_3$).

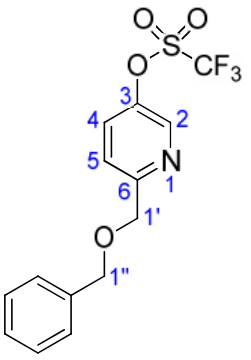
^{13}C NMR (100 MHz, $CDCl_3$): 191.5 (C(3)), 146.2 (C(4)), 143.8 (*i*-Ph), 137.1 (*i*-Ph), 135.7 (*i*-Ph), 129.7 (Ph), 128.2 (Ph), 128.0 and 127.6 (Ph, C(5)), 127.2 (Ph), 126.8 (Ph), 73.1 and 70.7 (C(1'), C(1''')), 53.3 (C(6)), 50.8 (C(2)), 21.3 (C(1'')).

FTIR 3357, 3026, 2921, 2867, 1683, 1598, 1495, 1421, 1260, 1167, 1092 cm^{-1}.

MS (ESI^+) Calculated for $C_{20}H_{21}NKO_4S$ $[M+K]^+$: 410.0823, Found: 410.0819.

M.P. 78-79 ºC (CH_2Cl_2-pentane).

6-[(Benzyloxy)methyl]pyridin-3-yl trifluoromethanesulfonate (440)



Enone **439** (239 mg, 0.64 mmol) was subjected to the General Procedure F. Purification by FCC (1:1 to 0:1 petrol-CH_2Cl_2) afforded the title compound **440** (98 mg, 44%) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.53 (1H, br. s., C(2)H), 7.65 (1H, d, *J* = 10.0 Hz, C(4)H), 7.63 (1H, d, *J* = 10.0 Hz, C(5)H), 7.44-7.26 (5H, m, Ph), 4.73 (2H, s, C(1')H_2), 4.69 (2H, s, C(1")H_2).

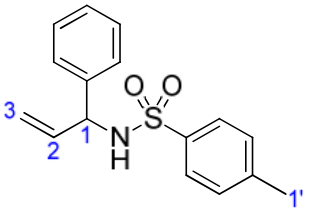
^{13}C NMR (125 MHz, $CDCl_3$): 159.2 (C(3)), 145.6 (C(6)), 141.9 (C(2)), 137.5 (*i*-Ph), 129.5 (Ph), 128.5 (Ph), 128.0 (C(4)), 127.8 (Ph), 122.3 (C(5)), 118.6 (q, *J* = 320.0 Hz, CF_3), 73.1 (C(1")), 72.1 (C(1')).

^{19}F NMR (377 MHz, $CDCl_3$): -72.5 (s).

HRMS (CI) Calculated for $C_{14}H_{13}NO_4F_3S$ $[M+H]^+$: 348.0517, Found: 348.0505.

FTIR 3066, 3033, 2862, 1812, 1481, 1454, 1428, 1215, 1161, 1140, 1103, 1019 cm^{-1}.

4-Methyl-*N*-(1-phenylallyl)benzenesulfonamide (405)



A mixture of benzaldehyde **403** (2.10 mL, 20.6 mmol), *p*-toluenesulfonamide (3.51 g, 20.5 mmol)and tetraethyl orthosilicate (5.00 mL, 22.4 mmol) was heated at 160 ºC and ethanol

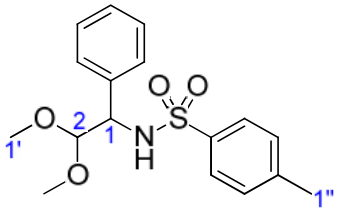
was collected into a separate flask. After 5 hours the reaction mixture was cooled to room temperature and the crude material was washed with petrol (30 mL). THF (20 mL) and Et_2O (20 mL) were added to the crude solid and the reaction mixture was cooled to -78ºC. Vinyl magnesium bromide (1.0M in THF, 26.0 mL, 26.0 mmol) was added and the reaction mixture was left to warm up to room temperature. After 16 hours saturated aqueous NH_4Cl (30 ml) was added and the reaction mixture was extracted with EtOAc(3 × 50mL). The combined organic layer was washed with brine (30 ml), dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by FCC (1:0 to 1:1 petrol-EtOAc) afforded the title compound **405** (4.49 g, 76%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.66-7.61 (2H, m, Ph), 7.22-7.10 (7H, m, Ph), 5.86 (1H, ddd, *J* = 17.0, 10.0, 6.0 Hz, C(2)H), 5.61 (1H, d, *J* = 6.0 Hz, NH) 5.14-5.07 (2H, m, C(3)H_2), 4.96 (1H, t, *J* = 6.0, C(1)H), 2.38 (3H, s, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 143.2 (*i*-Ph), 140.1 (*i*-Ph), 137.7 (*i*-Ph), 137.2 (C(2)), 129.3 (Ph), 128.5 (Ph), 127.7 (Ph), 127.2 (Ph), 127.0 (Ph), 116.7 (C(3)), 59.9 (C(1)), 21.6 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[195]

N-(2,2-Dimethoxy-1-phenylethyl)-4-methylbenzenesulfonamide (458)



Allylic sulfonamide **405** (4.49 g, 15.6 mmol) was dissolved in CH_2Cl_2 (150 mL) and cooled to -78ºC. Ozone was bubbled through the reaction mixture until a blue colour persisted then dimethylsulfide (5.0 mL, 68.1 mmol) was added and the reaction mixture left to warm up to room temperature. After 16 hours the reaction mixture was dried by passing a stream of

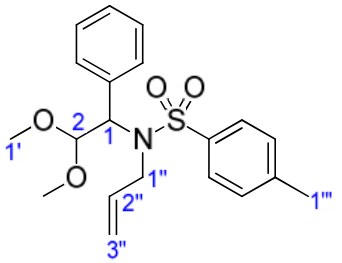
nitrogen and the crude material was dissolved in methanol (50.0 mL). Triethylorthoformate (5.0 mL, 46.1 mmol) and *p*-toluensulfonic acid (0.10 g, 0.6 mmol) were added sequentially and the reaction mixture heated at reflux. After 6 hours saturated aqueous $NaHCO_3$ (30 mL) and EtOAc (200 mL) were added. The aqueous layer was extracted with EtOAc (3 × 50 mL) and the combined organic layer was washed with brine (40 mL), dried ($MgSO_4$) and concentrated in vacuo. Purification by FCC (1:0 to 1:1 petrol-EtOAc) afforded the title compound **458** (4.89 g, 93%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) 7.51 (2H, d, *J* = 8.0 Hz, Ph), 7.23-7.05 (7H, Ph), 5.30 (1H, d, *J* = 6.0 Hz, NH), 4.40 (1H, dd, *J* = 6.0, 5.0 Hz, C(1)H), 4.34 (1 H, d, *J*= 5.0 Hz, C(2)H), 3.31 (3 H, s, C(1')H_3), 3.25 (3 H, s, C(1')H_3), 2.35 (3 H, s, C(1")H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 142.8 (*i*-Ph), 137.2 (*i*-Ph), 136.4 (*i*-Ph), 129.0 (Ph), 127.8 (Ph), 127.4 (Ph), 127.0 (Ph), 106.0 (C(2)), 59.0 (C(1)), 55.8 (C(1')), 54.9 (C(1')), 21.3 (C(1")). Only 12 signals were observed.

The spectroscopic properties of this compound were consistent with the data reported in the literature.[196]

N-Allyl-*N*-(2,2-dimethoxy-1-phenylethyl)-4-methylbenzenesulfonamide (459)



Sulfonamide **458** (1.68 g, 5.02 mmol) was dissolved in DMF (15.0 mL) and cooled to 0ºC. Sodium hydride (60% dispersion in mineral oil, 0.22g, 5.50 mmol) was added and the reaction mixture was stirred at room temperature. After 1 hour allyl bromide (0.65 mL, 7.51 mmol) was added and the reaction mixture stirred at room temperature. After 16 hours the

saturated aqueous NH_4Cl (50 mL) was added and the mixture was extracted with EtOAc (3 × 50 mL). The organic layer was washed with brine (30 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by FCC (1:0 to 4:1 petrol-EtOAc) afforded the title compound **459** (1.59 g, 84%) as a clear oil.

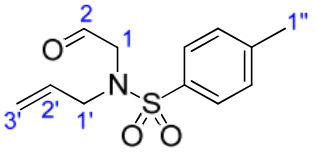
^{1}H NMR (500 MHz, $CDCl_3$) 7.65 (2H, d, *J* = 8. 0 Hz, Ph), 7.37-7.32 (2H, m, Ph), 7.31-7.25 (3H, m, Ph), 7.22 (2H, d, *J* = 8.0 Hz, Ph), 5.52 (1H, dddd, *J* = 17.0, 10.0, 7.2, 5.5 Hz, C(2")H), 5.11 (1H, d, *J* = 7.0 Hz, C(1)H), 5.04 (1H, dd, *J* = 17.0, 1.5 Hz, C(3")H_2), 5.01-4.95 (2H, m, C(2)H, C(3")H_2), 3.96-3.87 (1H, m, C(1")H_2), 3.71 (1H, dd, *J*= 17.0, 7.0 Hz, C(1")H_2), 3.42 (3H, s, C(1')H_3), 3.33 (3H, s, C(1')H_3), 2.41 (3H, s, C(1"')H_3).

^{13}C NMR (125 MHz, $CDCl_3$) 142.8 (*i*-Ph), 138.3 (*i*-Ph), 135.7 (*i*-Ph), 135.3 (C(2")), 129.6 (Ph), 129.1 (Ph), 128.2 (Ph), 127.8 (Ph), 127.7 (Ph), 117.2 (C(3")), 104.6 (C(2)), 61.5 (C(1)), 55.5 (C(1')), 54.3 (C(1')), 48.7 (C(1")), 21.5 (C(1"')).

MS (ESI^+) Calculated for $C_{20}H_{25}NNaO_4S$ $[M+Na]^+$: 398.1397, Found: 398.1386.

FTIR 3031, 2934, 1419, 1159, 1089 cm^{-1}.

N-Allyl-4-methyl-*N*-(2-oxoethyl)benzenesulfonamide (449)



Sulfonamide **412** (1.89 g, 6.58 mmol) was dissolved in DMF (12.0 mL) and cooled to 0 ºC. Sodium hydride (60% dispersion in mineral oil, 310 mg, 7.75 mmol) was added and the reaction mixture stirred for 15 minutes at this temperature. Allyl bromide (0.85 mL, 9.82 mmol) was added and the reaction mixture stirred at room temperature. After 16 hours the reaction mixture was diluted with saturated aq. NH_4Cl (50 mL) and EtOAc (100 mL). The aqueous layer was extracted with EtOAc (2 × 40 mL). The organic extracts were combined, washed with brine (30 mL), then dried ($MgSO_4$), and concentrated *in vacuo*. The crude

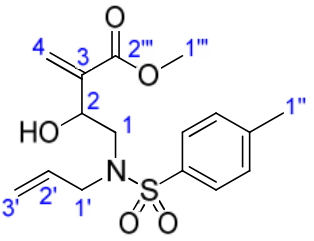
material was then subjected to the General Procedure B. Purification by FCC (1:0 to 4:1 petrol-EtOAc) afforded the title compound **449** (889 mg, 90%) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) 9.60 (1H, t, *J* = 1.0 Hz, C(2)H), 7.71 (2H, d, *J* = 8.0 Hz, Ph), 7.34 (2H, d, *J* = 8.0 Hz, Ph), 5.69 (1 H, ddt, *J* = 17.0, 10.0, 6.5, C(2')H), 5.23 (1H, dd, *J* = 10.0, 1.0 Hz, C(3')H_2), 5.18 (1H, dd, *J* = 17.0, 1.0 Hz, C(3')H_2), 3.82 (2 H, d, *J*=6.57 Hz, C(1')H_2), 3.79 (2H, d, *J* = 1.0 Hz, C(1)H_2), 2.45 (3 H, s).

^{13}C NMR (100 MHz, $CDCl_3$) 198.2 (C(2)), 144.1 (*i*-Ph), 135.4 (*i*-Ph), 131.9 (C(2')), 129.9 (Ph), 127.4 (Ph), 120.8 (C(3')), 55.9 (C(1)), 52.3 (C(1')), 21.6 (C(1").

The spectroscopic properties of this compound were consistent with the data reported in the literature.[197]

Methyl 4-(N-allyl-4-methylphenylsulfonamido)-3-hydroxy-2-methylene-butanoate (450)



Quinuclidine (81 mg, 0.68 mmol) was added to a solution of methyl acrylate (290 µl, 3.22 mmol), aldehyde **449** (689 mg, 2.72 mmol) and MeOH (90 µl, 2.20 mmol) at room temperature. The mixture was stirred at room temperature for 16 hours and then concentrated *in vacuo*. Purification of the residue by FCC (1:0 to 1:1 petrol-EtOAc) afforded the title compound **450** (580 mg, 63%) as a brown oil.

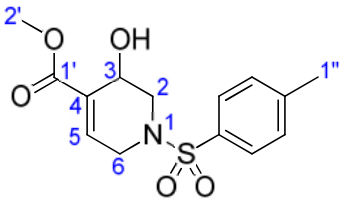
^{1}H NMR (400 MHz, $CDCl_3$) 7.71 (2H, d, *J* = 8.5 Hz, Ph), 7.31 (2H, d, *J* = 8.5 Hz, Ph), 6.38 (1H, t, *J* = 1.5 Hz, C(4)H_2), 6.10 (1H, t, *J* = 1.5 Hz, C(4)H_2), 5.62 (1 H, ddt, *J* = 17.0, 10.0, 7.0 Hz, C(2')H), 5.19 (2H, m, C(3')H_2), 4.67 (1H, m, C(2)H), 3.89 (2H, t, *J* = 6.5 Hz,

C(1')H_2), 3.75 (3H, s, C(1"')H_3), 3.48 (1H, d, *J* = 5.0 Hz, OH), 3.32 (1H, dd, *J* = 14.5, 4.0 Hz, C(1)H_2), 3.22 (1H, dd, *J* = 14.5, 8.0 Hz, C(1)H_2), 2.43 (3H, s, C(1")H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 166.3 (C(2"')), 143.7 (C(3), *i*-Ph), 139.2 (C(3), *i*-Ph), 136.2 (C(3), *i*-Ph), 132.4 (C(2')), 129.8 (Ph), 127.5 (C(4)), 127.3 (Ph), 119.8 (C(3')), 69.4 (C(2)), 52.8 (C(1)), 52.3 (C(1')), 51.8 (C(1"')), 21.5 (C(1")).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[198]

Methyl 3-hydroxy-1-tosyl-1,2,3,6-tetrahydropyridine-4-carboxylate (451):



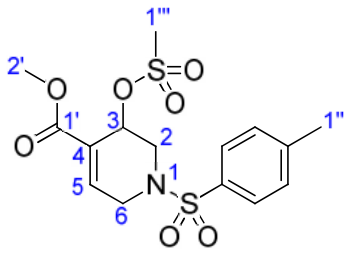
Allylic alcohol **450** (420 mg, 1.24 mmol) and catalyst HG-II (40 mg, 5 mol%) were subjected to General Procedure B using CH_2Cl_2 (25 mL) at reflux for 24 hours. Purification by FCC (1:0 to 1:1 petrol-EtOAc) afforded the title compound **451** (253 mg, 65%) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.64 (2H, d, *J* = 8.5 Hz, Ph), 7.30 (2H, d, *J* = 8.5 Hz, Ph), 6.89 (1H, t, *J* = 3.5 Hz, C(5)H), 4.57 (1H, dt, *J* = 6.0, 4.0 Hz, C(3)H), 3.93 (1H, dd, *J* = 19.0, 4.0 Hz, C(6)H_2), 3.72 (3H, s, C(2')H_3), 3.46 (2H, m, C(6)H_2, C(2)H_2), 3.18 (1H, d, *J* = 6.5 Hz, OH), 2.96 (1H, dd, *J* = 12.0, 4.0 Hz, C(2)H_2), 2.38 (3H, s, C(1")H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 165.5 (C(1')), 144.0 (C(4), *i*-Ph), 136.2 (C(5)), 132.4 and 130.9 (C(4), *i*-Ph), 129.7 (Ph), 127.5 (Ph), 62.1 (C(3)), 52.0 (C(2')), 49.1 (C(2)), 45.0 (C(6)), 21.3 (C(1")).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[198]

Methyl 3-(methylsulfonyloxy)-1-tosyl-1,2,3,6-tetrahydropyridine-4-carboxylate (457)



Ms_2O (369 mg, 2.12 mmol) was added to a solution of cyclic alcohol **451** (321 mg, 1.03 mmol) and Et_3N (0.35 ml, 2.51 mmol) in CH_2Cl_2 (30 ml) at 0ºC. The reaction mixture was then stirred at room temperature for 5 hours. The mixture was diluted with CH_2Cl_2 (50 ml) and washed sequentially with saturated aqueous NH_4Cl (30 ml), saturated aqueous $NaHCO_3$ (30 ml) and then brine (30 ml). The organic portion was dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by FCC (1:1 petrol-EtOAc) afforded the title compound **457** (381 mg, 95%) as an opaque oil.

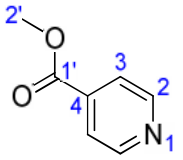
^{1}H NMR (400 MHz, $CDCl_3$) 7.70 (2H, d, *J* = 8.5 Hz, Ph), 7.34 (2 H, d, *J* = 8.5 Hz, Ph), 7.19 (1H, dd, *J* = 4.5, 2.5 Hz, C(5)H), 5.47 (1H, m, C(3)H), 4.26 (2H, m, $C(2)H_2$, $C(6)H_2$), 3.79 (3H, s, $C(2')H_3$), 3.46 (1H, d, *J* = 19.5 Hz, $C(6)H_2$), 3.15 (3H, s, $C(1''')H_3$), 2.82 (1H, dd, *J* = 13.5, 1.5 Hz, $C(2)H_2$), 2.43 (3H, s, $C(1'')H_3$).

^{13}C NMR (100 MHz, $CDCl_3$) 164.1 (C(1')), 144.3 (C(4), *i*-Ph), 141.3 (C(5)), 133.0 (C(4), *i*-Ph), 129.9 (Ph), 127.6 (Ph), 125.8 (C(4), *i*-Ph), 70.4 (C(3)), 52.4 (C(2')), 47.6 (C(2)), 44.5 (C(6)), 39.0 (C(1''')), 21.5 (C(1'')).

MS (ESI^+) Calculated for $C_{15}H_{19}NNaO_7S_2$ $[M+Na]^+$: 412.0495, Found: 412.0501.

FTIR 3422, 2955,1719, 1665, 1597, 1494, 1352, 1272, 1174 cm^{-1}.

Methyl isonicotinate (456):



KHMDS (0.5M in PhMe, 3.60 ml, 1.80 mmol) was added to a solution of mesylate **457** (330 mg, 0.85 mmol) in THF (15 ml) at -78 ºC. After 1 hour the reaction mixture was warmed to 0 ºC and stirring was continued for a further 3 hours. The mixture was then diluted with EtOAc (60 ml) and washed with saturated aqueous $NaHCO_3$ (30 ml) and brine (30 ml). The organic portion was dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by FCC (9:1 CH_2Cl_2-EtOAc) afforded the title compound **456** (61 mg, 53%) as a clear oil.

^{1}H NMR (500 MHz, $CDCl_3$) 8.80 (2H, d, *J*=4.5 Hz, C(2)H_2), 7.86 (2 H, dd, *J*= 4.5 Hz, C(3)H_2), 3.97 (3 H, s, C(2')H_3).

^{13}C NMR (125 MHz, $CDCl_3$) 165.6 (C(1')), 150.6 (C(2)), 137.3 (C(4)), 122.9 (C(3)), 52.7 (C(2')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[199]

5.4 Experimental procedures for section 4.3

5.4.1 General procedures

Procedure A: for the cross-metathesis of β,γ-unsaturated ketones.

A resealable reaction tube, fitted with a magnetic follower, was charged with catalyst Z-1B (3 - 8 mol%). The tube was then sealed with a rubber septum and purged with argon. Argon sparged CH_2Cl_2 (0.10 M with respect to the β,γ-unsaturated ketone employed), the appropriate α,β-enone (500 mol%), and the corresponding β,γ-unsaturated ketone (100 mol%) were added sequentially *via* syringe. The rubber septum was then replaced with a

screw cap and the tube was heated at 55 °C (oil bath temperature) for 48 hours. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification of the residue by flash column chromatography (FCC), under the conditions noted, afforded the corresponding α,β-unsaturated 1,5-dicarbonyl.

Procedure B: for the cross-metathesis of homoallylic alcohols.

A resealable reaction tube, fitted with a magnetic follower, was charged with catalyst Z-1B (2 - 5 mol%). The tube was then sealed with a rubber septum and purged with argon. Argon sparged CH_2Cl_2 (0.10 M or 0.25 M with respect to the homoallylic alcohol), the corresponding α,β-enone (500 mol%) and the corresponding homoallylic alcohol (100 mol%) were added sequentially *via* syringe. The rubber septum was then replaced with a screw cap and the tube was heated at 55 °C (oil bath temperature) for between 24 and 48 hours. After cooling to 0 ºC, the reaction mixture was diluted with CH_2Cl_2 (0.10 M with respect to the homoallylic alcohol), water (100 μL/mmol of homoallylic alcohol) and Dess-Martin periodinane (150 mol%) were added and the reaction was monitored by TLC until the cross-metathesis product was consumed. The reaction mixture was filtered through a cartridge of SiO_2 (eluting with Et_2O) and solvent was removed in vacuo. Purification of the residue by FCC, under the conditions noted, afforded the corresponding α,β-unsaturated 1,5-dicarbonyl.

Procedure C: for the cross-metathesis of homoallylic alcohols.

A reaction tube, fitted with a magnetic follower, was charged with catalyst Z-1B (2.5 -5 mol%). The tube was then sealed with a rubber septum and purged with argon. Argon sparged CH_2Cl_2 (0.10 M or 0.25 M with respect to the homoallylic alcohol), the corresponding α,β-enone (500 mol%) and the corresponding homoallylic alcohol (100 mol%) were added sequentially *via* syringe. The reaction mixture was heated at reflux under argon for between 24 and 48 hours. After cooling to room temperature the reaction mixture

was filtered through a cartridge of SiO2 (under the conditions noted). The fractions containing the target CM product were combined and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (0.10 M with respect to the homoallylic alcohol) and then cooled to 0 ºC. Water (100 μL/mmol of homoallylic alcohol) and Dess-Martin periodinane (200 - 300 mol%) were added sequentially and the reaction was monitored by TLC until the cross-metathesis product was consumed. The reaction mixture was filtered through a cartridge of SiO_2 (eluting with Et_2O) and solvent was removed in vacuo. Purification of the residue by FCC, under the conditions noted, afforded the corresponding α,β-unsaturated 1,5-dicarbonyl.

Procedure D: for the synthesis of polysubstituted pyridines.

The corresponding α,β-unsaturated 1,5-dicarbonyl (100 mol%) was dissolved in a solution of NH_4OAc (1000 mol%) and AcOH (1000 mol%) in EtOH (0.10 M with respect to α,β-unsaturated 1,5-dicarbonyl). The reaction mixture was heated at 55 °C for24 hours and then cooled to room temperature. The reaction mixture was diluted with EtOAc (20 mL/mmol), washed with saturated aqueous $NaHCO_3$ (20 mL/mmol) and then brine (20 mL/mmol). The organic portion was dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by FCC, under the conditions noted, afforded the corresponding pyridine.

Procedure E: for the arylation of α,β-unsaturated 1,5-dicarbonyl intermediates.

A reaction tube, fitted with magnetic follower, was charged with Pd_2dba_3 (5 mol%), P(*t*-Bu_3)HBF_4 (20 mol%), and (if solid) the corresponding aryl bromide (300 mol%). The tube was sealed with a septum and purged with argon. Argon sparged, anhydrous toluene (0.10 M with respect to the enone component), the requisite α,β-unsaturated 1,5-dicarbonyl (100 mol%), the corresponding aryl bromide (if liquid) (300 mol %) andCy_2NMe (300 mol%) were added sequentially *via* syringe. The mixture was then heated at 55 °C for 16 hours. The mixture was cooled to room temperature, diluted with EtOAc (20 mL/mmol) and then filtered through Celite. Solvent was removed in vacuo, the residue was filtered through a

cartridge of SiO_2 (under the conditions noted) and solvent was removed in vacuo to afford a crude product which was directly subjected to General Procedure D.

Procedure F: for the allylation of aldehydes.

To a mixture of the corresponding aldehyde (100 mol%) in THF (2 mL/mmol) and saturated aqueous NH_4Cl (4 mL/mmol) was added zinc powder (300 mol%) and the corresponding allylic halide (150 - 200 mol%) and the mixture was vigorously stirred at room temperature and monitored by TLC. After all of the aldehyde was consumed the reaction mixture was extracted with EtOAc (3 × 20 mL/mmol). The organic extracts were combined and extracted with brine (20 mL/mmol), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by flash column chromatography (FCC), under the conditions noted, afforded the corresponding allyl alcohol.

General Procedure G: for the oxime formation from the corresponding dienone.

A mixture of the corresponding dienone (100 mol%), $NaOAc{\cdot}3H_2O$ (110 mol%) and $NH_2OR{\cdot}HCl$ (125 mol%, OR = OH or OMe) was dissolved in EtOH (0.14 M with respect to the dienone) and H_2O (1.18 M with respect to the dienone). The mixture stirred at 60 ^oC for 16 hours. The mixture was then diluted with H_2O (*ca.* 20 mL/mmol) and extracted with EtOAc (3 × 20 mL/mmol). The organic extracts were combined, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC under the conditions noted, to afford the corresponding oxime.

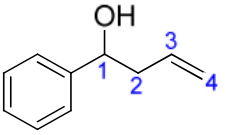
General Procedure H: for one pot oxime formation followed by the 6-π-electrocyclisation.

A re-sealable reaction tube, fitted with a magnetic follower, was charged with the corresponding ketone (100 mol%), $NH_2OR{\cdot}HCl$ (115 mol%, OR = OH or OMe), $NaOAc{\cdot}3H_2O$ (105 mol%) and 1,2-dichlorobenzene (0.10 M with respect to the

dienone).The tube was then sealed with a rubber septum and heated under Argon at 55 ^{o}C (oil bath temperature) for the time stated. After cooling to room temperature, concentrated aqueous HCl (200 mol%) was added. The tube was sealed and heated at 180 ^{o}C (oil bath temperature) for the time stated. After cooling to room temperature, $NaHCO_3$ (1000 mol %) was added and the mixture was stirred for 1 hour. The reaction mixture was diluted Et_2O (*ca.* 20 mL/mmol) and then filtered off. The organic layer was concentrated *in vacuo*. Purification of the residue by FCC under the conditions noted afforded the corresponding pyridine.

5.4.2 Experimental procedures

1-Phenylbut-3-en-1-ol (485)



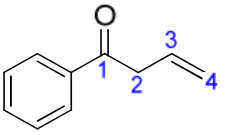
Aldehyde**403** (500 μL, 4.93 mmol) and allylbromide (200 mol%) were subjected to General Procedure F. Purification by FCC (petrol-Et_2O 4:1) afforded the homoallylic alcohol **485** (548 mg, 75%) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.45-7.33 (3H, m, Ph), 7.32-7.22 (2H, m, Ph),5.90-5.75 (1H, m, C(3)H), 5.23-5.10 (2H, m, C(4)H_2), 4.84-4.73 (1H, m, C(1)H), 2.61-2.45 (2H, m, C(2)H_2), 2.24-2.13 (1H, s, OH).

^{13}C NMR (100 MHz, $CDCl_3$) 143.9 (*i*-Ph), 134.5 (C(3)), 128.4 (Ph), 127.6 (Ph), 125.8 (Ph), 118.4 (C(4)), 73.3 (C(1)), 43.8 (C(2)).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[210]

1-Phenylbut-3-en-1-one (486)



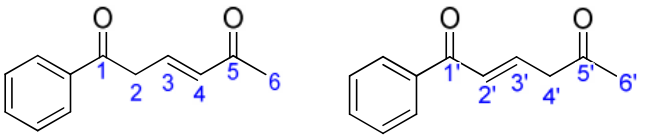
A solution of allyl alcohol **485** (1.54 g, 10.38 mmol) in CH_2Cl_2 (50.0 mL) was added to a mixture of Dess-Martin periodinane (13.4 g, 31.6 mmol, $NaHCO_3$ (13.3 g, 158.3 mmol) and CH_2Cl_2 (50.0 mL) previously stirred for 5 minutes, and the reaction mixture was stirred for 1 hour. The reaction mixture was filtered through a cartridge of SiO_2 (eluting with Et_2O) and solvent was removed *in vacuo*. Purification of the residue by FCC (petrol-EtOAc 1:0 to 7:3) afforded the β,γ-unsaturated ketone **486** (1.23 g, 81%) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.03-7.96 (2H, m, Ph), 7.62-7.55 (1H, m, Ph), 7.52-7.45 (2H, m, Ph), 6.11 (1H, ddt, *J* = 17.0, 10.5, 7.0, C(3)H), 5.33-5.19 (2H, m, C(4)H_2), 3.78 (2H, dt, *J* = 7.0, 1.5 Hz, C(2)H_2).

^{13}C NMR (100 MHz, $CDCl_3$) 198.0 (C(1)), 136.5 (*i*-Ph), 133.2 and 131.0 (C(3)H and Ph), 128.6 (Ph), 128.3 (Ph), 118.7 (C(4)), 43.4 (C(2)).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[200]

1-Phenylhex-2-ene-1,5-dione (487) and 1-phenylhex-3-ene-1,5-dione (488)



1 : 0.3

487 **488**

***Via* CM of β,γ-unsaturated ketone.**

A solution of ketone **486** (87 mg, 0.60 mmol), catalyst Z-1B (8 mol%) and 3-butene-2-one were subjected to General Procedure A. In a modification to the general procedure, the

reaction was run for 96 hours. Purification by FCC (petrol-EtOAc 9:1 to 7:3) afforded the inseparable mixture of regioisomers **487** and **488** (71 mg, 63%, 1:0.3 *rr*) as a red oil.

***Via* CM/oxidation of homoallylic alcohol.**

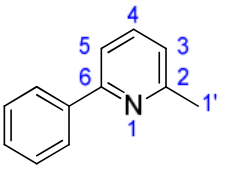
A solution of alcohol **485** (76 mg, 0.51 mmol), CH_2Cl_2 (0.10 M), catalyst Z-1B (2 mol%) and 3-butene-2-one were subjected to General Procedure B. The reaction mixture was heated for 24 hours. Purification by FCC (petrol-EtOAc 7:3 to 6:4) afforded the inseparable mixture of regioisomers **487** and **488** (73 mg, 75%, 1:0.3 *rr*) as a red oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.02-7.89 (2.6H, m, Ph), 7.66-7.54 (1.3H, m, Ph), 7.53-7.42 (2.6H, m, Ph), 7.08 (1.3H, dt, *J* = 16.0, 7.0 Hz, C(3)H, C(3')H), 6.93 (0.3H, dt, *J* = 15.5, 1.5, C(2')H), 6.19 (1H, dt, *J* = 16.0, 1.5 Hz, C(4)H), 3.94 (2H, dt, *J* = 7.0, 1.5 Hz, C(2)H_2), 3.46 (0.6H, d, *J* = 7.5 Hz, C(4')H_2), 2.31 (3H, s, C(6)H_3), 2.24 (0.9H, s, C(6')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 198.2 and 196.1 (C(1) and C(5)), 139.9 (C(3)), 136.0 (*i*-Ph), 134.3 (C(4)), 133.7 (Ph), 132.9 and 129.2 (C(2') and Ph), 128.8 (Ph), 128.6 (2 signals, Ph), 128.2 (Ph), 47.0 (C(4')), 41.6 (C(2)), 30.0 (C(6')), 26.6 (C(6)) (only 16 signals were observed).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[164]

2-Methyl-6-phenylpyridine (490)



***Via* condensation with NH_4OAc of unsaturated 1,5-diketone.**

Mixture of ketones **487** and **488** (60 mg, 0.32 mmol) were subjected to General Procedure D. Purification by FCC (petrol-EtOAc 1:0 to 9:1) afforded pyridine **10** (47 mg, 88%) as a colourless oil.

***Via* 6-π-electrocyclisation of the *O*-methyl oxime.**

A re-sealable reaction tube, fitted with a magnetic follower, was charged with **537** (20 mg, 0.10 mmol), 1,2-dichlorobenzene (1.00 mL) and concentrated aqueous HCl (16 μL, 0.20 mmol). The tube was sealed and heated at 165 ^oC (oil bath temperature) for 24 hours. After cooling to room temperature, $NaHCO_3$ (84 mg, 1.00 mmol) was added and the mixture was stirred for 1 hour. The reaction mixture was diluted Et_2O (*ca.* 20 mL/mmol) and then filtered off. The organic layer was concentrated *in vacuo*. Purification of the residue by FCC (1:0 to 9:1 petrol-Et_2O) afforded pyridine **490** (14 mg, 80%) as a clear oil.

***Via* cascade condensation/6-π-electrocyclisation of dienone with NH_2OH.**

Dienone **536** (61 mg, 0.35 mmol) and $NH_2OH{\cdot}HCl$ were subjected to the General Procedure H. The reaction mixture was heated at 55^oC (oil bath temperature) for 6 hours at. After addition of HCl the tube was sealed and heated at 180 ^oC (oil bath temperature) for 12 hours. Purification by FCC (1:0 to 9:1 petrol-EtOAc) afforded pyridine **490** (42 mg, 70%) as a clear oil.

***Via* cascade condensation/6-π-electrocyclisation of dienone with NH_2OMe.**

Dienone **536** (63 mg, 0.36 mmol) and $NH_2OMe{\cdot}HCl$ were subjected to the General Procedure H. The reaction mixture was heated at 55 ^oC (oil bath temperature) for 6 hours. After addition of HCl the tube was sealed and heated at 180 ^oC (oil bath temperature) for 12 hours. Purification of the residue by FCC (1:0 to 9:1 petrol-EtOAc) afforded pyridine **490** (49 mg, 80%) as a clear oil.

***Via* cascade condensation/6-π-electrocyclisation of δ-hydroxy enone with NH_2OMe.**

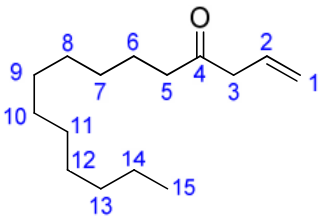
δ-Hydroxy enone **527** (57 mg, 0.36 mmol) and $NH_2OMe{\cdot}HCl$ were subjected to the General Procedure H. The reaction mixture was heated at 55 ^oC (oil bath temperature) for 9.5 hours. After addition of HCl the tube was sealed and heated at 180 ^oC (oil bath temperature) for 4 hours. Purification of the residue by FCC (1:0 to 19:1 petrol-EtOAc) pyridine **490** (41 mg, 81%) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.03-7.95 (2H, m, Ph), 7.64 (1H, t, *J* = 7.5 Hz, C(4)H), 7.53 (1H, d, *J* = 7.5 Hz, C(5)H), 7.51-7.45 (2H, m, Ph), 7.44-7.38 (1H, m, Ph), 7.11 (1H, d, *J* = 7.5 Hz, C(3)H), 2.65 (3H, s, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 158.3 (C(6)), 156.9 (C(2)), 139.8 (*i*-Ph), 136.8 (C(4)), 128.6 (2 signals, Ph), 127.0 (Ph), 121.6 (C(3)), 117.6 (C(5)), 24.7 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[166]

Pentadec-1-en-4-one (492)



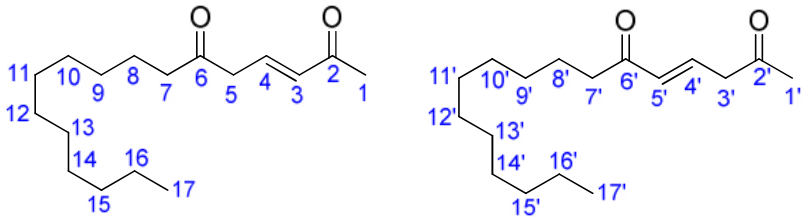
n-Butyl lithium (1.6M in hexanes, 6.50 mL, 10.40 mmol) was added to a mixture of dodecanoic acid **491** (2.02 g, 10.10 mmol) and THF (60.0 mL) previously cooled at -78 ºC and the reaction mixture was stirred at this temperature for 1 hour. Allyl magnesium bromide (1.0M in THF, 11.0 mL, 11.00 mmol) was added and the reaction mixture was left to warm up to room temperature and stirred for 16 hours. The reaction mixture was diluted with EtOAc (50.0 mL) and washed with saturated aqueous NH_4Cl (50 mL). The organic layer was washed with brine (40 mL), dried (Na_2SO_4), and concentrated *in vacuo*. Purification by FCC (petrol-EtOAc 1:0 to 9:1) afforded the title compound **492** (1.88 g, 83%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) 6.01-5.77 (1H, m, C(2)H), 5.25-4.98 (2H, m, C(1)H_2), 3.15 (2H, t, J = 7.5 Hz, C(3)H_2), 2.42 (2H, q, J = 8.0 Hz, C(5)H_2), 1.55 (2H, m, C(6)H_2), 1.25 (16 H, br. s., C(7)H_2, C(8)H_2, C(9)H_2, C(10)H_2, C(11)H_2, C(12)H_2, C(13)H_2, C(14)H_2) 0.94-0.77 (3 H, C(15)H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 208.8 (C(4)), 130.7 (C(2)), 118.5 (C(1)), 47.6 (C(3)), 42.3 (C(5)), 31.8, 29.5, 29.4, 29.3 (two signals), 29.1, 23.6 and 22.6 (C(6), C(7),C(8),C(9),C(10),C(11),C(12),C(13),C(14), 14.0 (C(15)) (only 14 signals were observed).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[201]

Heptadec-3-ene-2,6-dione (493) and heptadec-4-ene-2,6-dione(494)



1 : 1

493 **494**

Ketone **492** (222 mg, 1.00 mmol), catalyst Z-1B (22 mg, 0.03 mmol, 3 mol%) and 3-butene-2-one were subjected to General Procedure A. The reaction mixture was heated for 48 hours. Purification by FCC (petrol-EtOAc 9:1 to 7:3) afforded the inseparable mixture of regioisomers **493** and **494** (193 mg, 73%, 1:1 *rr*) as a red oil.

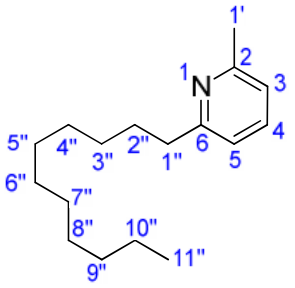
^{1}H NMR (400 MHz, $CDCl_3$) 6.89 (2H, m, C(4)H and C(4')H), 6.11 (2H, m, C(3)H, C(5')H), 3.40-3.32 (4H, m, C(3')H_2, C(5)H_2), 2.56 (2H, t, *J* = 7.5 Hz, C(7)H_2 and C(7')H_2), 2.46 (2H, t, *J* = 7.5 Hz, C(7)H_2 and C(7')H_2), 2.28 (3H, s, C(1)H_3 and C(1')H_3), 2.21 (3H, s, C(1)H_3 and C(1')H_3), 1.65-1.52 (4H, m, C(8)H_2 and C(8')H_2), 1.35-1.18 (32H, m, C(9)H_2, C(9')H_2,C(10)H_2,C(10')H_2, C(11)H_2,C(11')H_2, C(12)H_2,C(12')H_2, C(13)H_2,C(13')H_2, C(14)H_2,C(14')H_2, C(15)H_2,C(15')H_2, C(16)H_2,C(16')H_2), 0.87 (6H, t, *J* = 6.5 Hz, C(17)H_3C(17')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 206.8, 204.4, 200.3 and 198.1 (C(6), C(6'), C(2) and C(2')), 139.4 and 137.5 (C(4) and C(4')), 134.1 and 133.4 (C(5') and C(3)), 46.5 and 45.6 (C(5) and C(3')), 43.0 and 39.9 (C(7) and C(7')), 30.0 and 26.7 (C(1) and C(1')), 31.8 29.6, 29.5, 29.4 (two signals), 29.3 (two signals), 29.2, 29.1, 24.0, 23.4 and 22.6 (C(8), C(8'), C(9),C(9'), C(10),C(10'), C(11),C(11'), C(12),C(12'), C(13),C(13'), C(14),C(14'), C(15),C(15'), C(16), C(16'), 14.1 (C(17) and C(17')) (only 27 signals were observed).

MS (ESI^+) Calculated for $C_{17}H_{30}NaO_2$ $[M+Na]^+$: 289.2138. Found: 289.2140.

FTIR 2956, 2917, 2851, 1708, 1688, 1630, 1468, 1184 cm^{-1}.

2-Methyl-6-undecylpyridine (495)



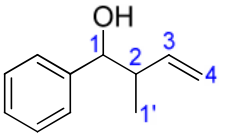
Mixture of 1,5-diketones **493** and **494** (64 mg, 0.24 mmol) were subjected to General Procedure D. Purification by FCC (petrol-EtOAc 1:0 to 9:1) afforded pyridine **495** (54 mg, 91%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.52 (1H, t, *J* = 7.5 Hz, C(4)H), 6.99 (2H, m, C(3)H, C(5)H), 2.78 (2H, t, *J* = 8.0 Hz, C(1")H_2), 2.57 (3H, s, C(1')H_3), 1.77-1.63 (2H, m, C(2")H_2), 1.44-1.16 (16H, m, C(3")H_2, C(4")H_2,C(5")H_2,C(6")H_2,C(7")H_2,C(8")H_2,C(9")H_2,C(10")H_2), 0.93-0.83 (3H, m, C(11")H_2).

^{13}C NMR (100 MHz, $CDCl_3$) 161.9 and 157.6 (C(1') and C(1")), 136.5 (C(4)), 120.3 and 119.4 (C(3) and C(5)), 38.5 (C(7)), 31.9 (C(9")), 30.2 (C(2")), 29.6 (two signals), 29.5 (two signals) and 29.3 (C(3"), C(4"),C(5"),C(6"),C(7"),C(8")), 24.4 (C(1')), 22.7 (C(10")), 14.1 (C(11"))(only 16 signals were observed).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[202]

2-Methyl-1-phenylbut-3-en-1-ol (503)



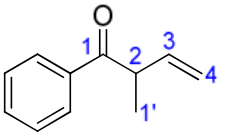
Aldehyde **403** (1.25 g, 11.83 mmol) and crotonylbromide (200 mol%) were subjected to General Procedure F. Purification by FCC (petrol-EtOAc 19:1) afforded the homoallylic alcohol **503** (1.61 g, 84%,1:1 *dr*) as a clear oil.

^{1}H NMR (400MHz ,$CDCl_3$) 7.45-7.21 (10H, m, Ph), 5.91-5.69 (2H, m, C(3)H), 5.27-5.16 (2H, m, C(4)H_2), 5.13-5.00 (2H, m, C(4)H_2), 4.60 (1H, d, *J* = 5.5 Hz, C(1)H), 4.37 (1H, d, *J* = 8.0 Hz, C(1)H), 2.66-2.55 (1H, m, C(2)H), 2.55-2.45 (1H, m, C(2)H), 2.17 (2H, br. s., OH), 1.03 (3H, d, *J* = 7.0 Hz, C(1')H_3), 0.89 (3H, d, *J* = 7.0 Hz, C(1')H_3).

^{13}C NMR (100MHz, $CDCl_3$) 142.5 (*i*-Ph), 142.4 (*i*-Ph), 140.6 (C(3)), 140.2 (C(3)), 128.2 (Ph), 128.0 (Ph), 127.6 (Ph), 127.2 (Ph), 126.8 (Ph), 126.5 (Ph), 116.7 (C(4)), 115.4 (C(4)), 77.8 (C(1)), 77.2 (C(1)), 46.2 (C(2)), 44.5 (C(2)), 16.4 (C(1')), 14.0 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[203]

2-Methyl-1-phenylbut-3-en-1-one (504)



A solution of homoallylic alcohol **503** (196 mg, 1.21 mmol) in CH_2Cl_2 (6.0 mL) was added to a mixture of Dess-Martin periodinane (1.56 g, 3.68 mmol), $NaHCO_3$ (1.55 g, 18.45 mmol) and CH_2Cl_2 (12.3 mL) previously stirred for 5 minutes, and the reaction mixture was stirred for 1 hour. The reaction mixture was filtered through a cartridge of SiO_2 (eluting with Et_2O)

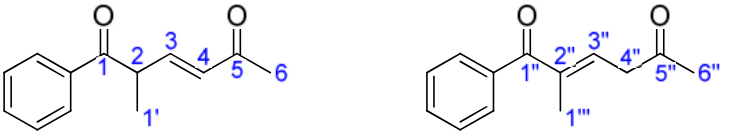
and solvent was removed *in vacuo*. Purification of the residue by FCC (petrol-Et2O 19:1 to 9:1) afforded the β,γ-unsaturated ketone **504** (171 mg, 88%) as a clear oil.

^{1}H NMR (400MHz, $CDCl_3$) 7.99 (2H, d, *J* = 7.5 Hz, Ph), 7.61-7.53 (1H, m, Ph), 7.53-7.43 (2H, m, Ph), 6.01 (1H, ddd, *J* = 7.5, 10.0, 17.5 Hz, C(3)H), 5.19 (1H, d, *J* = 17.5 Hz, C(4)H_2), 5.15 (1H, d, *J* = 10.0 Hz, C(4)H_2), 4.18 (1H, dq, *J* = 7.5, 7.0 Hz, C(2)H), 1.35 (3H, d, *J* = 7.0, C(1')H_3).

^{13}C NMR (100MHz, $CDCl_3$) 201.2 (C(1)), 138.1 (C(3)), 136.3 (*i*-Ph), 132.9 (Ph), 128.6 (Ph), 128.5 (Ph), 116.5 (C(4)), 45.5 (C(2)), 17.0 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[204]

2-Methyl-1-phenylhex-3-ene-1,5-dione (505) and 2-methyl-1-phenylhex-2-ene-1,5dione (506)



0.2 : 1

505 **506**

***Via* CM α,β-unsaturated ketone.**

Ketone **504** (62 mg, 0.39 mmol), catalyst Z-1B (8 mol%) and 3-buten-2-one were subjected to the General Procedure A. The reaction mixture was heated for 48 hours. Purification by FCC (petrol-EtOAc 9:1 to 7:3) afforded the inseparable mixture of regioisomers **505** and **506** (11 mg, 14%, 1:0.2 *rr*) as a yellow oil.

***Via* CM/oxidation homnoallylic alcohol**

Homoallylic alcohol **503** (53 mg, 0.32 mmol), CH_2Cl_2 (0.10 M), catalyst Z-1B (5 mol%) and 3-buten-2-one were subjected to the General Procedure B. The reaction mixture was heated

for 48 hours. Purification by FCC (petrol-EtOAc 1:0 to 4:1) afforded the inseparable mixture of regioisomers **505** and **506** (55 mg, 83%, 1:0.2 *rr*) as a yellow oil.

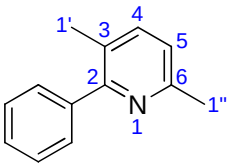
^{1}H NMR (400 MHz, $CDCl_3$) 7.90 (0.4H, d, *J* = 0.8 Hz, Ph), 7.63 (2H, d, *J* = 8.0 Hz, Ph), 7.55-7.48 (0.2H, m, Ph), 7.49-7.40 (1H, m, Ph), 7.39-7.32 (2.4H, m, Ph), 6.91 (0.2H, dd, *J* = 16.0, 8.0 Hz, C(3)H), 6.40 (1H, t, *J* = 7.0 Hz, C(3")H), 6.11 (0.2H, d, *J* = 16.0 Hz, C(4)H), 4.29 (0.2H, quintet, *J* = 7.0 Hz, C(2)H), 3.39 (2H, d, *J* = 7.0 Hz, C(4")H_2), 2.18 (0.6H, s, C(6)H_3), 2.14 (3H, s, C(6")H_3), 1.90 (3H, s, C(1'")H_3), 1.34 (0.6H, d, *J* = 7.0 Hz, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 204.1 (C(5")), 199.4 (C(1)), 198.0 (two signals, C(1"), C(5)), 146.1 (C(3)), 138.4 and 137.7 (*i*-Ph, C(2")), 135.9 (C(3")), 135.4 (*i*-Ph), 133.3 (Ph), 131.7 (C(4)), 131.6 (Ph), 129.2 (Ph), 128.6 (Ph), 128.3 (Ph), 127.9 (Ph), 43.9 (C(2)), 43.1 (C(4")), 29.8 (C(6")), 26.6 (C(6)), 17.0 (C(1'), 12.8 (C(1"')).

MS (ESI^+) Calculated for $C_{13}H_{14}NaO_2$ $[M+Na]^+$: 225.0886, Found: 225.0886.

FTIR 1760, 1717, 1685, 1630, 1489, 1397, 1293, 1195 cm^{-1}.

3,6-Dimethyl-2-phenylpyridine (507)



***Via* condensation with NH_4OAc of unsaturated 1,5-diketone.**

Mixture of 1,5-diketones **505** and **506** (52 mg, 0.26 mmol) were subjected to the General Procedure D. Purification by FCC (petrol-Et_2O 1:0 to 9:1) afforded pyridine **507** (34 mg, 72%) as a colourless oil.

***Via* cascade condensation/6-π-electrocyclisationof dienone with NH_2OMe.**

Dienone **552** (71mg, 0.38 mmol) and $NH_2OMe{\cdot}HCl$ were subjected to the General Procedure H. The reaction mixture was heated at 55^{o}C (oil bath temperature) for 6 hours at. After

addition of HCl the tube was sealed and heated at 180 ^{o}C (oil bath temperature) for 12 hours. Purification of the residue by FCC (1:0 to 7:3 petrol-Et_2O) afforded pyridine **507** (33 mg, 48%) as a clear oil.

***Via* cascade condensation/6-π-electrocyclisation of δ-hydroxy enone with NH_2OMe.**

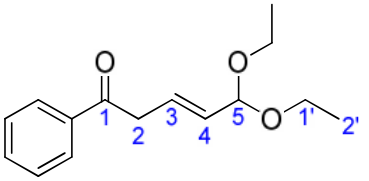
δ-Hydroxy enone **528** (63 mg, 0.31 mmol) and $NH_2OMe{\cdot}HCl$ were subjected to the General Procedure H. The reaction mixture was heated at 55^{o}C (oil bath temperature) for 16 hours at. After addition of HCl the tube was sealed and heated at 180 ^{o}C (oil bath temperature) for 24 hours. Purification of the residue by FCC (petrol-EtOAc 1:0 to 9:1) afforded pyridine **507** (22 mg, 38%) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.55-7.48 (2H, m, Ph), 7.48-7.41 (3H, m, Ph and C(4)H), 7.41-7.33 (1H, m, Ph), 7.03 (1H, d, *J* = 7.5 Hz, C(5)H), 2.59 (3H, s, C(1")H_3), 2.29 (3H, s, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 157.8 (C(2)), 155.1 (C(6)), 140.7 (C(3)), 138.5 (C(4)), 128.8 (Ph), 127.9 (Ph), 127.5 (Ph), 127.2 (*i*-Ph), 121.5 (C(5)), 24.0 (C(1")), 19.3 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[205]

5,5-Diethoxy-1-phenylpent-3-en-1-one (513)



Ketone **486** (76 mg, 0.52 mmol), CH_2Cl_2 (0.10 M), and catalyst Z-1B (5 mol%) were subjected to the General Procedure A. In a modification to the general procedure, acrolein diethylacetal (1000 mol%) was used and the reaction was heated at reflux under argon for 48

hours. Purification by FCC (petrol-Et_2O 1:0 to 7:3) afforded unsaturated carbonyl **513** (64 mg, 50%) as a yellow oil.

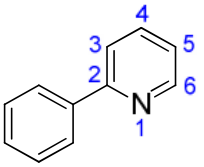
^{1}H NMR (400 MHz, $CDCl_3$) 7.96 (2H, d, *J* = 7.5 Hz, Ph), 7.61-7.53 (1H, m, Ph), 7.50-7.42 (2H, m, Ph), 6.13 (1H, dt, *J* = 16.0, 6.5 Hz, C(3)H), 5.67 (1H, dd, *J* = 16.0, 5.5 Hz, C(4)H), 4.90 (1H, d, *J* = 5.5 Hz, C(5)H), 3.78 (2H, d, *J* = 6.5 Hz, C(2)H_2), 3.71-3.58 (2H, m, C(1')H_2), 3.57-3.42 (2H, m, C(1')H_2), 1.21 (6H, t, *J* = 6.5 Hz, C(2')H_2).

^{13}C NMR (100 MHz, $CDCl_3$) 197.5 (C(1)), 136.4 (*i*-Ph), 133.2 (Ph), 131.5 (C(4)), 128.6 (Ph), 128.2 (Ph), 126.9 (C(3)), 101.3 (C(5)), 61.2 (C(1')), 41.6 (C(2)), 15.2 (C(2')).

MS (ESI^+) Calculated for $C_{15}H_{20}NaO_3$ $[M+Na]^+$: 271.1305, Found: 271.1305.

FTIR 2975, 2879, 1688, 1597, 1448 cm^{-1}.

2-Phenylpyridine (514)



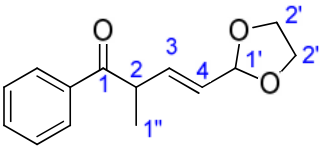
Unsaturated carbonyl **513** (56 mg, 0.23 mmol) was subjected to the General Procedure D. In a modification of the general procedure, water (1000 mol%) was added. Purification by FCC (petrol-Et_2O 1:0 to 9:1) afforded pyridine **514** (21 mg, 60%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.71 (1H, d, *J* = 5.0 Hz, C(6)H), 8.00 (2H, d, *J* = 7.0 Hz, Ph), 7.82-7.70 (2H, m, C(3)H and C(4)H), 7.54-7.46 (2H, m, Ph), 7.46-7.40 (1H, m, Ph), 7.29-7.21 (1H, m, C(5)H).

^{13}C NMR (100 MHz, $CDCl_3$) 157.5 (C(2)), 149.6 (C(6)), 139.4 (*i*-Ph), 136.7 (C(4)), 128.9 (Ph), 128.7 (Ph), 126.9 (Ph), 122.1 (C(5)), 120.6 (C(3)).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[166]

4-(1,3-Dioxolan-2-yl)-2-methyl-1-phenylbut-3-en-1-one (515)



Ketone **504** (83 mg, 0.57 mmol), CH_2Cl_2 (0.10 M) and catalyst Z-1B (5 mol%) were subjected to the General Procedure A. In a modification to the general procedure, 2-vinyl-1,3-dioxolane (1000 mol%) was used and the reaction mixture was heated at reflux under argon for 48 hours. Purification by FCC (petrol-Et_2O 1:0 to 7:3) afforded unsaturated carbonyl **515** (81 mg, 68%) as a yellow oil.

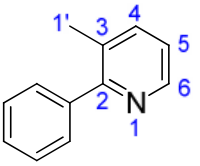
^{1}H NMR (400 MHz, $CDCl_3$) 7.96 (2H, d, *J* = 7.5 Hz, Ph), 7.60-7.53 (1H, m, (Ph)), 7.51-7.42 (2H, m, Ph), 6.15 (1H, dd, *J* = 15.5, 8.0 Hz, C(3)H), 5.64 (1H, dd, *J* = 15.5, 6.0 Hz, C(4)H), 5.22 (1H, d, *J* = 6.0 Hz, C(1')H), 4.22 (1H, quintet, *J* = 7.0 Hz, C(2)H), 4.04-3.92 (2H, m, C(2')H_2), 3.92-3.81 (2H, m, C(2')H_2), 1.36 (3H, d, *J* = 7.0 Hz, C(1")H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 200.5 (C(1)), 136.2 (C(4)), 136.1 (*i*-Ph), 133.1 (Ph), 128.7 (Ph), 128.5 (Ph), 128.1 (C(3)), 103.4 (C(1')), 64.9 (two signals, C(2')), 43.9 (C(2)), 17.3 (C(1")).

MS (ESI^+) Calculated for $C_{14}H_{16}NaO_3$ $[M+Na]^+$: 255.0992, Found: 255.0992.

FTIR 2977, 2855, 1685, 1596, 1449, 1399 cm^{-1}.

3-Methyl-2-phenylpyridine (516)



Unsaturated carbonyl **515** (81 mg, 0.35 mmol) was subjected to the General Procedure D. In a modification of the general procedure, water (1000 mol%) was added and the reaction

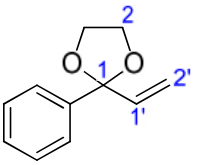
mixture was heated in a sealed tube at 90 ºC for 48 hours. Purification by FCC (petrol-Et_2O 1:0 to 8:2) afforded pyridine **516** (52 mg, 87%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.54 (1H, d, *J* = 5.0 Hz, C(6)H), 7.58 (1H, d, *J* = 7.5 Hz, C(4)H), 7.56-7.51 (2H, m, Ph), 7.46 (2H, t, *J* = 7.5 Hz, Ph), 7.42-7.36 (1H, m, Ph), 7.18 (1H, dd, *J* = 7.5, 5.0 Hz, C(5)H), 2.36 (3H, s, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 158.6 (C(2)), 146.9 (C(6)), 140.5 (*i*-Ph), 138.4 (C(4)), 130.7 (C(3)), 128.9 (Ph), 128.1 (Ph), 127.8 (Ph), 122.0 (C(5)), 20.0 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[206]

2-Phenyl-2-vinyl-1,3-dioxolane (518)



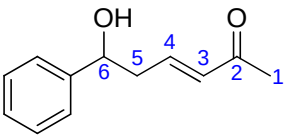
A mixture of ketone **517** (3.38 g, 20.0 mmol), toluene (50.0 mL), ethylene glycol (4.0 mL) and pyridinium p-toluenesulfonate (0.20 g, 0.80 mmol) were refluxed under Dean-Stark conditions overnight. The solvent was removed *in vacuo*, and Et_2O (50 mL) added. The solution was then washed with saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed *in vacuo*. The crude product was dissolved in 1,2-dichloroethane (54.0 mL), and Et_3N (6.0 mL, 44.1 mmol) was added dropwise. The reaction was then refluxed for 8 hours before cooling to room temperature and quenching with water (50.0 mL).The aqueous layer was separated, extracted with CH_2Cl_2 (2 × 20.0 mL) and the organic layers were combined, dried ($MgSO_4$) and solvent was removed *in vacuo*. Purification by FCC (petrol-Et_2O 1:0 - 9:1) affordedthe title compound **518** (1.88 g, 53%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.52 (2H, d, *J*=7.5 Hz, Ph), 7.41-7.29 (3H, m, Ph), 6.04 (1H, dd, *J*=17.0, 10.5 Hz, C(1')H), 5.36 (1H, d, *J*=17.0 Hz, C(2')H_2), 5.26 (1H, d, *J*=10.5 Hz, C(2')H_2), 4.05-3.99 (2H, m, C(2)H_2), 3.99-3.93 (2H, m, C(2)H_2).

^{13}C NMR (100 MHz, $CDCl_3$) 141.5 (1 C, s), 138.1 (1 C, s), 128.1 (2 C, s), 126.0 (2 C, s), 125.5 (1 C, s), 116.4 (1 C, s), 108.9 (1 C, s), 64.7 (2 C, s).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[207]

6-Hydroxy-6-phenylhex-3-en-2-one (527)



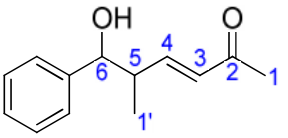
A resealable reaction tube, fitted with a magnetic follower, was charged with catalyst HG-II (23 mg, 0.04 mmol). The tube was then sealed with a rubber septum and purged with argon. Argon sparged CH_2Cl_2 (0.10 M with respect to the β,γ-unsaturated ketone employed), MVK (0.58 mL, 7.20 mmol), and homoallylic alcohol **485** (213 mg, 1.44 mmol) were added sequentially *via* syringe. The rubber septum was then replaced with a screw cap and the tube was heated at 55 °C (oil bath temperature) for 24 hours. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification of the residue by FCC (1:0 to 4:1 CH_2Cl_2-EtOAc) afforded δ-hydroxyl enone **527** (264 mg, 97%) as a pale brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.41-7.28 (5H, m), 6.82 (1H, dt, *J* = 16.0, 7.0 Hz, C(4)H), 6.14 (1H, dd, *J* = 16.0, 1.0 Hz, C(11)H), 4.92-4.80 (1H, m, C(6)H), 2.81-2.57 (2H, m, C(5)H_2), 2.24 (3H, s, C(1)H_3), 2.13 (1H, br. s., OH).

^{13}C NMR (100MHz, $CDCl_3$) 198.5 (C(2)), 143.8 (C(4)), 143.4 (*i*-Ph), 133.6 (C(11)), 128.7 (Ph), 128.0 (Ph), 125.6 (Ph), 73.2 (C(6)), 42.0 (C(5)), 26.9 (C(1)).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[208]

6-Hydroxy-5-methyl-6-phenylhex-3-en-2-one (528)



A resealable reaction tube, fitted with a magnetic follower, was charged with catalyst Z-1B (11 mg, 0.02 mmol). The tube was then sealed with a rubber septum and purged with argon. Argon sparged CH_2Cl_2 (0.10 M with respect to the β,γ-unsaturated ketone employed), MVK (0.16 mL, 1.55 mmol), and homoallylic alcohol **503** (51 mg, 0.31 mmol, 1:1.2 *dr*) were added sequentially *via* syringe. The rubber septum was then replaced with a screw cap and the tube was heated at 55 °C (oil bath temperature) for 48 hours. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification of the residue by FCC (CH_2Cl_2-Et_2O 1:0 to 20:3) then FCC (4:1 to 3:2 petrol-EtOAc) afforded δ-hydroxyl enone **528** (52 mg, 1:1.2 *dr*, 82%) as a pale brown oil.

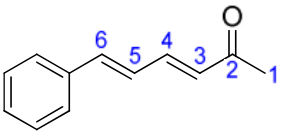
^{1}H NMR (400 MHz, $CDCl_3$) 7.42-7.19 (11H, m, Ph), 6.87 (1H, dd, *J* = 16.0, 8.0 Hz, C(4)H), 6.73 (1.2H, dd, *J* = 16.0, 7.0 Hz, C(4)H), 6.06 (1H, d, *J* = 16.0 Hz, C(3)H), 5.97 (1.2H, d, *J* = 16.0 Hz, C(3)H), 4.65 (1.2H, d, *J* = 5.5 Hz, C(6)H), 4.50 (1H, d, *J* = 7.0 Hz, C(6)H), 2.86 (2.2H, br. s., OH), 2.76-2.60 (2.2H, m, C(5)H), 2.22 (3H, s, C(1)H_3), 2.15 (3.6H, s, C(1)H_3), 1.06 (3.6H, d, *J* = 7.0 Hz, C(1')H_3), 0.94 (3H, d, *J* = 7.0 Hz, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 198.9 (C(2)), 150.0 and 149.8 (C(4)), 142.3 and 142.0 (*i*-Ph), 131.5 and 131.1 (C(3)), 128.3 (Ph), 128.2 (Ph), 127.8 (Ph), 127.6 (Ph), 126.4 (Ph), 126.2 (Ph), 77.8 and 76.9 (C(6)), 44.3 and 43.8 (C(5)), 26.8 and 26.7 (C(1)), 16.1 and 14.1 (C(1)) (only 21 signals were observed).

MS (ESI^+) Calculated for $C_{13}H_{16}NaO_2$ $[M+Na]^+$: 227.1043. Found: 227.1044.

FTIR 3430, 3030, 2360, 2341, 1671, 1672, 1182 cm^{-1}.

6-Phenylhexa-3,5-dien-2-one (536)



***Via* elimination of δ-hydroxy enone**

A solution of **527** (810 mg, 4.26 mmol) in CH_2Cl_2 (42.60 mL) was cooled at 0 ^oC and then methanesulfonyl chloride (0.49 mL, 6.39 mmol) and triethylamine (1.78 mL, 12.78 mmol) were added sequentially and the mixture stirred at room temperature for 16 hours. The mixture was then diluted with brine (50 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic extracts were combined, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC (CH_2Cl_2) afforded dienone **536** (671 mg, 91%) as a yellow solid.

***Via* one pot CM/elimination of homoallylic alcohol.**

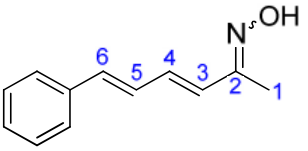
A re-sealable reaction tube, fitted with a magnetic follower, was charged with catalyst HG-II (50 mg, 0.08 mmol, 3 mol%). The tube was then sealed with a rubber septum and purged with argon. Argon sparged CH_2Cl_2 (26.80 mL), alcohol **485** (397 mg, 2.68 mmol) and MVK (1.10 mL, 13.40 mmol) were then added sequentially *via* syringe. The rubber septum was then replaced with a screw cap and the tube was heated at 55 ^oC (oil bath temperature) for 24 hours. After cooling to 0 ^oC methanesulfonyl chloride (1.24 mL, 16.08 mmol) and triethylamine (4.48 mL, 32.16 mmol) were added sequentially and the mixture stirred at room temperature for 16 hours. The mixture was then diluted with brine (50 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic extracts were combined, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC (1:0 to 7:3 petrol-EtOAc) afforded dienone **536** (365 mg, 79%) as a yellow solid.

^{1}H NMR (400MHz, $CDCl_3$) 7.49 (2H, d, *J* = 7.5 Hz, Ph), 7.43 - 7.28 (4H, m, Ph, C(4)H), 7.03-6.83 (2H, m, C(6)H, C(5)H), 6.27 (1H, d, *J* = 15.5 Hz, C(3)H), 2.33 (3H, s, C(1)H_3).

^{13}C NMR (100MHz, $CDCl_3$) 198.6 (C(2)), 143.6 (C(4)), 141.3 (C(6)), 135.9 (*i*-Ph), 130.4 (C(3)), 129.2 (Ph), 128.8 (Ph), 127.2 (Ph), 126.6 (C(5)), 27.3 (C(1)).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[209]

6-Phenylhexa-3,5-dien-2-one oxime (537)



Dienone **536** (118 mg, 0.67 mmol) and $NH_2OH{\cdot}HCl$ were subjected to the General Procedure G. Purification of the residue by FCC (4:1 to 1:1 petrol-EtOAc) afforded oxime **537** (123 mg, 95%, 1:0.3*dr*) as a clear oil.

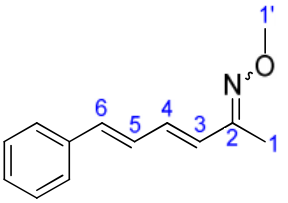
^{1}H NMR (400MHz, $CDCl_3$) 9.46 (1.3H, br. s., OH), 7.50-7.43 (2.6H, m, Ph), 7.40-7.32 (2.6H, m, Ph), 7.32-7.23 (1.3H, m, Ph), 7.17 (0.3H, d, *J* = 16.0 Hz, C(3)H), 6.98-6.87 (1.3H, m, C(5)H, C(6)H), 6.84-6.68 (2.6H, m, C(6)H, C(5)H, C(4)H), 6.46 (1H, d, *J* = 15.5 Hz, C(3)H), 2.13 (3H, s, C(1)H_3), 2.12 (0.9H, s, C(1)H_3).

^{13}C NMR (100MHz,$CDCl_3$) 156.7 and 153.2 (C(2)), 137.0 and 136.9 (C(6) and C(4)), 136.8 and 136.5 (*i*-Ph), 134.9 and 133.8 (C(6) and C(4)), 129.3 (C(3)), 128.7 (two signals, Ph), 128.6 and 128.3 (C(5)), 128.0 (Ph), 126.8 (Ph), 126.6 (Ph), 120.5 (C(3)), 16.7 (C(1)), 9.8 (C(1))(only 19 signals were observed).

MS (ESI^+) Calculated for $C_{12}H_{13}NNaO$ $[M+Na]^+$: 210.0889. Found: 210.0887.

FTIR 3410, 2889, 1223, 1104 cm^{-1}.

6-Phenylhexa-3,5-dien-2-one *O*-methyl oxime (538)



Dienone **536** (671 mg, 3.89 mmol) and $NH_2OMe{\cdot}HCl$ were subjected to the General Procedure G. Purification of the residue by FCC (1:1petrol-CH_2Cl_2) afforded oxime **538** (645 mg, 82%, 1:0.1*dr*) as a clear oil.

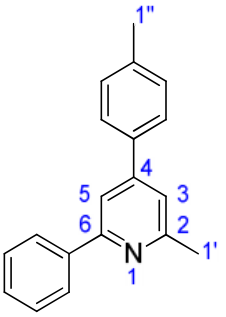
^{1}H NMR (400MHz, $CDCl_3$) 7.45 (2.2H, d, *J* = 7.5 Hz, Ph), 7.36 (2.2H, t, *J* = 7.5 Hz, Ph), 7.32-7.25 (1.1H, m, Ph), 7.02 (1H, d, *J* = 15.5 Hz, C(6)H), 6.97-6.85 (1.2H, m, C(5)H, C(4)H), 6.82-6.64 (2.3H, m, C(5)H, C(4)H, C(3)H), 6.42 (0.1H, d, *J* = 15.5 Hz, C(3)H), 3.97 (0.3H, s, C(1')H_3), 3.94 (3H, s, C(1')H_3), 2.08 (3H, s, C(1)H_3), 2.03 (0.3H, s, C(1)H_3).

^{13}C NMR (100MHz,$CDCl_3$) 155.5 and 152.3 (C(2)), 136.7 (C(6), C(4)), 136.5 (*i*-Ph), 136.4, 134.5 and 133.2 (C(6), C(4)), 129.6 (C(3)), 128.6 (two signals, Ph), 128.5, 128.4, 128.2 and 127.9 (Ph, C(5)), 126.6 (Ph), 126.5 (Ph), 120.8 (C(3)), 61.7 and 61.5 (C(1')), 16.7 and 10.1 (C(1))(only 21 signals were observed).

MS (ESI^+) Calculated for $C_{13}H_{15}NNaO$ $[M+Na]^+$: 224.1046. Found: 224.1044.

FTIR 2935, 1491, 1059 cm^{-1}.

2-Methyl-6-phenyl-4-(p-tolyl) pyridine (551)



A reaction tube, fitted with magnetic follower, was charged with **527** (103 mg, 0.54 mmol), Pd_2dba_3 (24 mg, 0.03 mmol, 5 mol%), *t*-$Bu_3P{\cdot}HBF_4$ (31.3 mg, 0.11 mmol), and 4-Br-Tol (231 mg, 1.35 mmol). The tube was sealed with a septum and purged with argon. Anhydrous PhMe (0.1 M with respect to the δ-hydroxy enone) and then Cy_2NMe (0.26 mL, 1.35 mmol) were added sequentially *via* syringe. The mixture was then heated at 55 ^oC (oil bath temperature) for 16 hour. The reaction mixture was filtered through a short cartridge of SiO_2 (eluting with 3:1 petrol-EtOAc) and the solvent was concentrated *in vacuo* and the residue was subjected to General Procedure G: $NH_2OMe{\cdot}HCl$ was used. The reaction mixture was heated at 55 ^oC (oil bath temperature) for 24 hours at. After addition of HCl the tube was sealed and heated at 180 ^oC (oil bath temperature) for 24 hours. Purification of the residue by FCC (two columns: firstly petrol-EtOAc 1:0 to 24:1 and secondly PhMe:CH_2Cl_2 7:3) afforded the title compound **551** (76 mg, 54%) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): 8.04 (2H, d, *J* = 7.5 Hz, Ph), 7.72 (1H, s, C(5)H), 7.60 (2H, d, *J* = 8.0 Hz, Ph), 7.50 (2H, m, Ph), 7.43 (1H, m, Ph), 7.34-7.30 (3H, m, Ph, C(3)H), 2.70 (3H, s, C(1')H_3), 2.44 (3H, s, C(1")H_3).

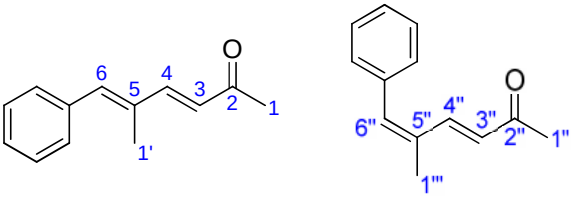
^{13}C NMR (100 MHz, $CDCl_3$): 158.8 and 157.6 (C(6) and C(2)), 149.3 (C(4)), 140.0, 138.9 and 135.9 (i-Ph), 129.8 (Ph), 128.7 (two signals, Ph), 127.2 (Ph), 126.9 (Ph), 119.6 (C(3)), 115.9 (C(5)), 24.9 (C(1')), 21.2 (C(1")).

MS (ESI^+) Calculated for $C_{19}H_{18}N$ $[M+H]^+$: 260.1434. Found: 260.1433.

FTIR 3032, 2920, 1599, 1547, 1515, 1448 cm^{-1}.

MP 54-56 ^{o}C (Et_2O-petrol).

(3E, 5E)-5-Methyl-6-phenylhexa-3,5-dien-2-one (552) dienes and (3*E*, 5*Z*)-5-Methyl-6-phenylhexa-3,5-dien-2-one (553)



1 0.6

552 **553**

A solution of **503** (206 mg, 1.01 mmol) in CH_2Cl_2 (10.10 mL) was cooled at 0 ^{o}C and then methanesulfonyl chloride (117 µL, 1.51 mmol) and triethylamine (210 µL, 1.51 mmol) were added sequentially and the mixture stirred at room temperature for 16 hours, then DBU (452 µl, 3.03 mmol) was added and the mixture was stirred at room temperature for 4 hours. The mixture was then diluted with brine (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The organic extracts were combined, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC (9:1 to 1:1 petrol-EtOAc) afforded the inseparable mixture of diasteroisomers **552** and **553** (160 mg, 85%, 1:0.6 *dr*) as a clear oil.

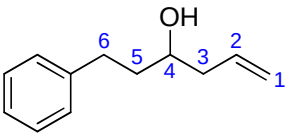
^{1}H NMR (400MHz, $CDCl_3$) 7.62 (0.6H, d, *J* = 16.0 Hz, C(4")H), 7.37-7.29 (6.2H, m, Ph, C(4)H), 7.29-7.17 (3.6H, m, Ph), 6.84 (1H, s, C(6)H), 6.81 (0.6H, s, C(6")H), 6.24 (0.6H, d, *J* = 16.0 Hz, C(3")H), 6.22 (1H, d, *J* = 16.0 Hz, C(3)H), 2.29 (3H, s, $C(1)H_3$), 2.19 (1.8H, s, $C(1")H_3$), 2.00 (3H, s, $C(1')H_3$), 2.00 (1.8H, s, $C(1"')H_3$).

^{13}C NMR (100MHz ,$CDCl_3$) 198.5 (C(2")), 198.1 (C(2)), 148.3 (C(4)), 141.1 (C(4")), 139.4 (C(6)), 137.5 (C(6")), 136.3 (C(5) and (*i*-Ph)), 136.2 (C(5") and (*i*-Ph)), 134.0 (C(5) and (*i*-Ph)), 132.8 (C(5") and (*i*-Ph)), 129.2 (Ph), 129.1 (Ph), 128.7 (C(3")), 128.1 (Ph), 128.0 (Ph), 127.5 (Ph), 127.4 (Ph), 126.4 (C(3)), 27.2 (C(1)), 26.9 (C(1")), 20.3 (C(1"')), 13.4 (C(1')).

MS (ESI^{+}) Calculated for $C_{13}H_{14}NaO$ $[M+Na]^{+}$: 209.0937. Found: 209.0937.

FTIR 3022, 2949, 1668, 1588, 1360, 1256, 1024 cm^{-1}.

1-Phenylhex-5-en-3-ol (556)



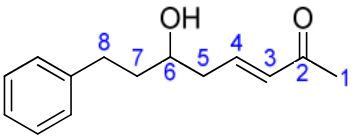
Aldehyde **555** (2.60 g, 19.3 mmol) and allylbromide (150 mol%) were subjected to the General Procedure F. Purification by FCC (petrol-Et_2O 9:1 to 4:1) afforded the homoallylic alcohol **556** (3.03 g, 89%) as a clear oil.

^{1}H NMR (400MHz ,$CDCl_3$) 7.37-7.28 (2H, m, Ph), 7.28-7.17 (3H, m, Ph), 5.92-5.77 (1H, m, C(2)H), 5.17 (2H, m, C(1)H_2), 3.79-3.63 (1H, m, C(4)H), 2.92-2.78 (1H, m, C(6)H_2), 2.79-2.64 (1H, m, C(6)H_2), 2.43-2.28 (1H, m, C(3)H_2), 2.28-2.14 (1H, m, C(3)H_2), 1.91-1.68 (3H, m, C(5)H_2, OH).

^{13}C NMR (100MHz, $CDCl_3$) 142.0 (*i*-Ph), 134.6 (C(2)), 128.4 (Ph), 128.3 (Ph), 125.8 (Ph), 118.3 (C(1)), 69.9 (C(4)), 42.0 (C(3)), 38.4 (C(5)), 32.0 (C(6)).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[177]

6-Hydroxy-8-phenyloct-3-en-2-one (557)



A resealable reaction tube, fitted with a magnetic follower, was charged with catalyst HG-II (93 mg, 0.13 mmol). The tube was then sealed with a rubber septum and purged with argon. Argon sparged CH_2Cl_2 (0.10 M with respect to the β,γ-unsaturated ketone employed), MVK (0.16 mL, 1.55 mmol), and homoallylic alcohol **556** (896 mg, 5.09 mmol) were added sequentially *via* syringe. The rubber septum was then replaced with a screw cap and the tube

was heated at 55 °C (oil bath temperature) for 24 hours. After cooling to room temperature, the reaction mixture was concentrated in vacuo. Purification of the residue by FCC (1:0 to 4:1 CH_2Cl_2-Et_2O) afforded δ-hydroxyl enone **557** (934 mg, 84%) as a pale brown oil.

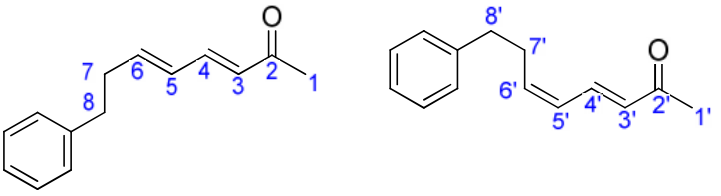
^{1}H NMR (400MHz, $CDCl_3$) 7.34-7.26 (2H, m, Ph), 7.24-7.17 (3H, m, Ph), 6.84 (1H, dt, *J* = 16.0, 7.5 Hz, C(4)H), 6.14 (1H, d, *J* = 16.0 Hz, C(3)H), 3.89-3.69 (1H, m, C(6)H), 2.87-2.77 (1H, m, C(8)H_2), 2.75-2.65 (1H, m, C(8)H_2), 2.51-2.33 (2H, m, C(5)H_2), 2.25 (3H, s, C(1)H_3), 2.10-2.03 (1H, m, OH), 1.86-1.77 (2H, m, C(7)H_2).

^{13}C NMR (100, $CDCl_3$) 198.6 (C(2)), 144.3 (C(4)), 141.5 (*i*-Ph), 133.4 (C(3)), 128.4 (Ph), 128.3 (Ph), 125.9 (Ph), 69.8 (C(6)), 40.5 (C(5)), 38.8 (C(7)), 31.9 (C(8)), 26.9 (C(1)).

MS (CI^+) Calculated for $C_{14}H_{22}NO_2$ $[M+NH_4]^+$: 236.1651. Found: 236.1655.

FTIR 3424, 2929, 1671, 1626, 1529, 1029 cm^{-1}.

(3*E*, 5*E*)-8-Phenylocta-3,5-dien-2-one (559) and (3*E*, 5*Z*)-8-Phenylocta-3,5-dien-2-one (560)



1 0.3

559 **560**

A solution of **557** (173 mg, 4.26 mmol) in CH_2Cl_2 (42.6 mL) was cooled at 0 ^oC and then methanesulfonyl chloride (0.49 mL, 6.39 mmol) and triethylamine (1.78 mL, 12.78 mmol) were added sequentially and the mixture stirred at 55 ^oC for 16 hours. The mixture was then diluted with brine (50.0 mL) and extracted with CH_2Cl_2 (3 × 20.0 mL). The organic extracts were combined, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC (1:0 to 7:3 petrol-EtOAc) afforded an inseparable mixture of diasteroisomers **559** and **560** (138 mg, 87%, 1:0.3 *dr*) as a clear oil.

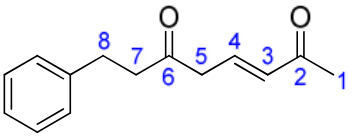
^{1}H NMR (400MHz, $CDCl_3$) 7.36-7.25 (2.6H, m, Ph, C(4')H), 7.25-7.14 (3H, m, Ph), 7.14-7.04 (1H, m, C(4)H), 6.27-6.18 (2.3H, m, C(6)H, C(5)H, C(5')H), 6.14 (0.3H, d, *J*=10.5 Hz, C(3')H), 6.06 (1H, d, *J* = 15.5 Hz, C(3)H), 5.94 (0.3H, td, *J* = 7.5, 11.0 Hz, C(6')H), 2.82-2.73 (2.6H, m, $C(8)H_2$, $C(8')H_2$), 2.69-2.63 (0.6H, m, $C(7')H_2$), 2.57-2.48 (2H, m, $C(7)H_2$), 2.27 (3H, s, $C(1)H_3$), 2.25 (0.9H, s, $C(1')H_3$).

^{13}C NMR (100MHz ,$CDCl_3$) 198.5 (C(2)), 144.0 (C(6)), 143.5 (C(4)), 140.8 (*i*-Ph), 140.7 (*i*-Ph), 140.6 (C(6')), 137.5 (C(4')), 130.5 (C(5')), 129.3 (C(5)), 129.0 (C(3)), 128.4 (Ph), 128.3 (Ph), 128.2 (Ph), 127.5 (C(3')), 126.0 (two signals, Ph), 35.2 (C(8')), 34.9 (C(8)), 34.6 (C(7)), 30.0 (C(7')), 27.3 (C(1')), 27.1 (C(1)) (only 22 signals were observed).

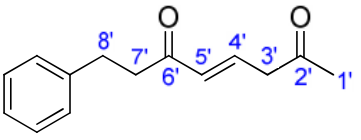
MS (ESI^+) Calculated for $C_{14}H_{16}NaO$ $[M+Na]^+$: 223.1093. Found: 223.1093.

FTIR 3053, 1686, 1295, 1024 cm^{-1}.

8-Phenyloct-3-ene-2,6-dione (563) and 8-phenyloct-4-ene-2,6-dione (564)



563



564

Homoallylic alcohol **556** (112 mg, 0.63 mmol), CH_2Cl_2 (0.10 M), catalyst Z-1B (2.5 mol%) and 3-butene-2-one were subjected to the General Procedure C. The reaction mixture was heated for 24 hours and then filtered using CH_2Cl_2-Et_2O (4:1). Dess-Martin periodinane (200 mol%) was used for the oxidation step. Purification by FCC (petrol-EtOAc 7:3) afforded the inseparable mixture of regioisomers **563** and **564** (97 mg, 71%, 1:0.9 *rr*) as a yellow oil.

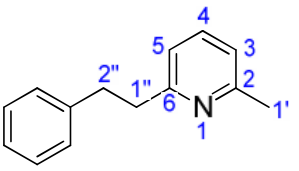
^{1}H NMR (400 MHz, $CDCl_3$) 7.36-7.25 (3.8H, m, Ph), 7.25-7.13 (5.6H, m, Ph), 6.97-6.80 (1.9H, m, C(4)H, C(4')H), 6.14 (0.9H, d, *J* = 16.0 Hz, C(5')H and C(3)H), 6.07 (1H, d, *J* = 16.0 Hz, C(5')H and C(3)H), 3.35 (3.8H, dd, *J* = 12.0, 7.5 Hz, $C(5)H_2$ and $C(3')H_2$), 3.00-2.88 (5.6H, m, $C(8)H_2$, $C(8')H_2$, $C(7)H_2$, $C(7')H_2$), 2.86-2.78 (2H, m, $C(8)H_2$, $C(8')H_2$), 2.27 (3H, s, $C(1)H_3$, $C(1')H_3$), 2.21 (2.7H, s, $C(1)H_3$, $C(1')H_3$).

^{13}C NMR (50 MHz, $CDCl_3$) 205.6, 204.2, 198.8 and 197.9 (C(6), C(6'), C(2) and (C(2')), 141.0 and 140.4 (*i*-Ph), 138.8 and 138.0 (C(4) and C(4')), 134.1 and 133.2 (C(5') and C(3)), 128.5 (Ph), 128.4 (Ph), 128.3 (Ph), 128.2 (Ph), 126.2 (Ph), 126.0 (Ph), 46.4, 45.8, 44.3 and 41.4 (C(7), C(7'), C(5) and C(3')), 29.9 and 29.8 (C(8) and C(8')), 29.5 and 26.6 (C(1) and C(1')).

MS (ESI^+) Calculated for $C_{14}H_{16}NaO_2$ $[M+Na]^+$: 239.1043, Found: 239.1042.

FTIR 3083, 3059, 3012, 2965, 1726, 1668, 1417, 1285 cm^{-1}.

2-Methyl-6-phenethylpyridine (558)



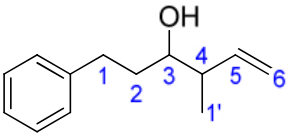
Mixture of 1,5-diketone **563** and **564** (94 mg, 0.44 mmol) were subjected to the General Procedure D. Purification by FCC (petrol-Et_2O 1:0 to 6:4) afforded pyridine **558** (70 mg, 81%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.46 (1H, t, *J* = 8.0 Hz, C(4)H), 7.33-7.25 (2H, m, Ph), 7.25-7.16 (3H, m), 6.98 (1H, d, *J* = 8.0 Hz, C(3)H, C(5)H), 6.89 (1H, d, *J* = 8.0 Hz, C(3)H, C(5)H), 3.13-3.01 (4H, m, C(1")H_2, C(2")H_2), 2.57 (3H, s, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 160.6 and 157.8 (C(2) and C(6)), 141.6 (*i*-Ph), 136.4 (C(4)), 128.4 (Ph), 128.2 (Ph), 125.8 (Ph), 120.6 and 119.7 (C(5) and C(3)), 40.2 and 36.2 (C(1") and C(2")), 24.5 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[179]

4-Methyl-1-phenylhex-5-en-3-ol (565)



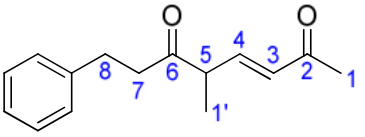
Aldehyde **555** (2.60 mL, 19.8 mmol) and crotonylbromide (200 mol%) were subjected to the General Procedure F. Purification by FCC (petrol-EtOAc 19:1) afforded the homoallylic alcohol **565** (2.85 g, 76 %, 1:1 *dr*) as a clear oil.

^{1}H NMR (400MHz ,$CDCl_3$) 7.34-7.25 (5H, m, Ph), 7.26-7.16 (5H, m, Ph), 5.86-5.67 (2H, m, C(5)H), 5.18-5.05 (4H, m, C(6)H_2), 3.54 (1H, ddd, *J* = 8.5, 5.5, 3 Hz, C(3)H), 3.43 (1H, ddd, *J* = 9.0, 6.0, 3.0 Hz, , C(3)H), 2.93-2.80 (2H, m, C(1)H_2), 2.73-2.60 (2H, m, , C(1)H_2), 2.38-2.19 (2H, m, C(4)H), 1.92-1.75 (2H, m, C(2)H_2), 1.77-1.64 (4H, m, C(2)H_2, OH), 1.04 (6H, d, *J* = 7.0 Hz, C(1')H_3).

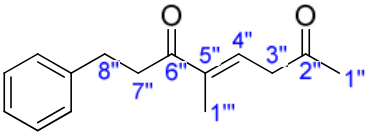
^{13}C NMR (100MHz, $CDCl_3$) 142.2 (two signals, *i*-Ph), 140.7 and 140.1 (C(5)), 128.4 (Ph), 128.3 (Ph), 125.7 (two signals, Ph), 116.4 and 115.4 (C(6)), 74.0 and 73.9 (C(3)), 44.2 and 43.6 (C(4)), 36.0 and 35.8 (C(2)),32.4 and 32.1 (C(7)), 16.1 and 14.3 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[210]

5-Methyl-8-phenyloct-3-ene-2,6-dione (566) and 5-methyl-8-phenyloct-4-ene-2,6-dione (567)



566



567

Homoallylic alcohol **565** (190 mg, 1.00 mmol), CH_2Cl_2 (0.25 M), catalyst Z-1B (2 mol%) and 3-butene-2-one were subjected to the General Procedure B. The reaction mixture was

heated for 48 hours. Purification by FCC (petrol-EtOAc 1:0 to 4:1) afforded the inseparable mixture of regioisomers **566** and **567** (168 mg, 73%, 1:1 *rr*) as a yellow oil.

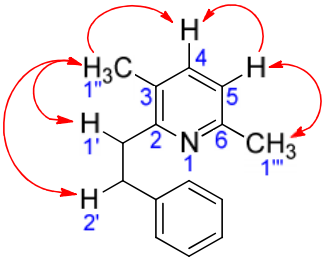
^{1}H NMR (400 MHz, $CDCl_3$) 7.28-7.20 (4H, m, Ph), 7.20-7.09 (6H, m, Ph), 6.81 (1H, t, *J* = 6.5 Hz, C(4")H), 6.68 (1H, dd, *J* = 16.0, 8.0 Hz, C(4)H), 6.04 (1H, d, *J* = 16.0 Hz, C(3)H), 3.34 (2H, d, *J* = 7.0 Hz, C(3")H_2), 3.25-3.33 (1H, m, C(5)H), 3.03-2.95 (2H, m, C(7")H_2), 2.93-2.81 (4H, m, C(8)H_2, C(8")H_2), 2.81-2.73 (2H, m, C(7)H_2), 2.17 (3H, s, C(1)H_3, C(1")H_3), 2.16 (3H, s, C(1)H_3, C(1")H_3), 1.75 (3H, s, C(1'")H_3), 1.19 (3H, d, *J* = 7.0 Hz, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 208.2, 204.0, 200.0 and 197.6 (C(6), C(6"), C(2) and C(2")), 144.8 (C(4)), 141.1, 140.4 and 138.8 (*i*-Ph, C(5)), 132.7 (C(4")), 131.8 (C(3)), 128.2 (Ph), 128.1 (two signals, Ph), 128.0 (Ph), 125.9 (Ph), 125.7 (Ph), 49.6 (C(5)), 42.9 (C(3")), 42.6 (C(7)), 38.8 (C(7")), 30.2 (C(8) and C(8")), 29.7 (C(1")), 29.3 (C(8) and C(8")), 26.7 (C(1)), 15.4 (C(1')), 11.6 (C(1'")).

MS (ESI^+) Calculated for $C_{15}H_{18}NaO_2$ $[M+Na]^+$: 253.1199, Found: 253.1200.

FTIR 3085, 3062, 3002, 2975, 1718, 1674, 1419, 1286 cm^{-1}.

3,6-Dimethyl-2-phenethylpyridine (568)



Mixture of 1,5-diketones **566** and **567** (64 mg, 0.28 mmol) were subjected to the General Procedure D. Purification by FCC (petrol-Et_2O 9:1 to 4:1) afforded pyridine **568** (48 mg, 82%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.33-7.26 (3H, m, Ph, C(4)H), 7.26-7.17 (3H, m, Ph, C(4)H), 6.92 (1H, d, *J* = 7.5 Hz, C(5)H), 3.10-3.04 (2H, m, C(1')H_2, C(2')H_2), 3.04-2.96 (2H, m, C(1')H_2, C(2')H_2), 2.54 (3H, s, C(1"')H_3), 2.19 (3H, s, C(1")H_3).

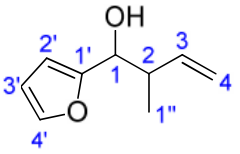
^{13}C NMR (100 MHz, $CDCl_3$) 158.7 and 155.0 (C(2) and C(6)), 142.0 (*i*-Ph), 138.0 (C(4)), 128.4 (Ph), 128.3 (Ph), 127.6 (C(3)), 125.8 (Ph), 120.7 (C(5)), 37.5 and 35.3 (C(1') and C(2')), 24.0 (C(1"')), 18.2 (C(1")).

MS (ESI^+) Calculated for $C_{15}H_{18}N$ $[M+H]^+$: 212.1434, Found: 212.1433.

FTIR 3061, 2958, 1594, 1576, 1496, 714 cm^{-1}.

*Characteristic n.O.e enhancements associated with pyridine **568** are represented by red arrows on the compound structure (for n.O.e spectrum see appendix II).*

1-(Furan-2-yl)-2-methylbut-3-en-1-ol (570)



A solution of aldehyde **569** (976 mg, 10.17 mmol) in THF (50 mL) was cooled to -78 °C and the reaction mixture was treated with a 0.5M solution of 1-methyl-2-propenylmagnesium bromide (25 mL, 12.25 mmol) in THF. The reaction mixture was left to warm-up to room temperature and stirred for further 2 hours. The reaction mixture was diluted with saturated aqueous NH_4Cl (50 mL) and the aqueous layer was extracted with EtOAc (3 × 20 mL). The organic extracts were combined and extracted with brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification by FCC (petrol-EtOAc 19:1 to 9:1) afforded the homoallylic alcohol **570** (1.52 g, 98%, 1:1 *dr*) as a clear oil.

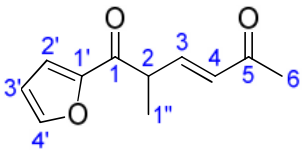
^{1}H NMR (400MHz ,$CDCl_3$) 7.37 (2H, d, *J* = 8.0 Hz, C(4')H), 6.33 (2H, br. s., C(3')H), 6.27 (1H, d, *J* = 3.0 Hz, C(2')H), 6.23 (1H, d, *J* = 3.0 Hz, C(2')H), 5.89-5.65 (2 H, m, C(3)H), 5.26-5.14 (2H, m, C(4)H_2), 5.14-5.01 (2 H, m, , C(4)H_2), 4.56 (1H, t, *J* = 6.0 Hz, C(1)H),

4.42 (1H, dd, *J* = 7.5, 4.0 Hz, C(1)H), 2.80-2.57 (2 H, m, C(2)H), 2.22 (1H, d, *J* = 4.0 Hz, OH), 2.17 (1H, d, *J* = 6.0 Hz, OH), 1.07 (3H, d, *J* = 7.0 Hz, C(1")H_3), 0.95 (3H, d, *J* = 7.0 Hz, C(1")H_3).

^{13}C NMR (100MHz, $CDCl_3$) 155.3 and 155.0 (C(5)), 141.9 and 141.6 (C(4')), 139.9 and 139.6 (C(3)), 116.9 and 115.8 (C(4)), 110.0 (two signals, (C(3'))), 107.2 and 106.8 (C(2')), 71.3 (C(1)), 43.5 and 43.0 (C(2)), 16.2 and 15.0 (C(1")) (only 17 signals were observed).

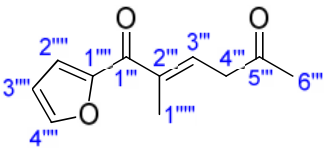
The spectroscopic properties of this compound were consistent with the data reported in the literature.[211]

1-(Furan-2-yl)-2-methylhex-3-ene-1,5-dione (571) and 1-(furan-2-yl)-2-methylhex-2-ene-1,5-dione (572)



1

571



0.5

572

Homoallylic alcohol **570** (79 mg, 0.52 mmol), CH_2Cl_2 (0.25 M), catalyst Z-1B (5 mol%) and 3-butene-2-one were subjected to the General Procedure C. The reaction mixture was heated for 48 hours and then filtered using CH_2Cl_2-Et_2O (9:1). Dess-Martin periodinane (300 mol%) was used for the oxidation step. Purification by FCC (petrol-Et_2O 7:3 to 1:1) afforded the inseparable mixture of regioisomers **571** and **572** (70 mg, 71%, 1:0.5 *rr*) as a yellow oil.

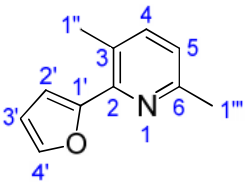
^{1}H NMR (400 MHz, $CDCl_3$) 7.59 (1.5H, m, C(4')H, C(4"")H), 7.22 (1H, d, *J* = 4.0 Hz, C(2')H), 7.13 (0.5H, d, *J* = 3.5 Hz, C(2"")H), 6.86 (1H, dd, *J* = 16.0, 8.0 Hz, C(3)H), 6.74 (0.5H, t, *J* = 7.0 Hz, C(3"')H), 6.55-6.50 (1H, m, C(3')H), 6.50-6.45 (0.5H, m, C(3"")H), 6.13 (1H, d, *J* = 16.0 Hz, C(4)H), 4.09 (1H, t, *J* = 7.0 Hz, C(2)H), 3.42 (1H, d, *J* = 7.0 Hz, C(4"')H_2), 2.20 (4.5H, s, C(6)H_3, C(6"')H_3), 1.88 (1.5H, s, C(1""')H_3), 1.34 (3H, d, *J* = 7.0 Hz, C(1")H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 204.5, 198.2, 188.1 and 184.1 (C(5), C(5"'), C(1) and C(1"')), 151.5 (two signals, C(1') and C(1""")), 146.9 (C(4')), 146.8 (C(4""")), 145.5 (C(3)), 137.9 (C(2"')), 133.1 (C(3"')), 132.0 (C(4)), 119.9 (C(2""")), 118.2 (C(2')), 112.5 (C(3""")), 111.8 (C(3')), 44.7 (C(2)), 43.0 (C(4"')), 30.0 (C(6)), 26.7 (C(6"')), 16.4 (C(1")), 13.0 (C(1""")).

MS (ESI^+) Calculated for $C_{11}H_{12}NaO_3$ $[M+Na]^+$: 215.0679, Found: 215.0680.

FTIR 3131, 2980, 2935, 1716, 1674, 1639, 1465, 1257 cm^{-1}.

2-(Furan-2-yl)-3,6-dimethylpyridine (573)



Mixture of 1,5-diketones **571** and **572** (72 mg, 0.38 mmol) were subjected to the General Procedure D. Purification by FCC (petrol-Et_2O 1:0 to 4:1) afforded pyridine **573** (45 mg, 70%) as a colourless oil.

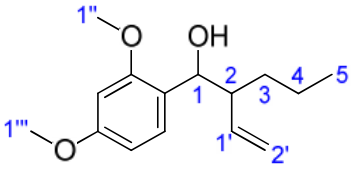
^{1}H NMR (400 MHz, $CDCl_3$) 7.59 (1H, s, C(4')H), 7.41 (1H, d, *J* = 8.0 Hz, C(4)H), 6.97 (1H, d, *J* = 8.0 Hz, C(5)H), 6.89 (1H, d, *J* = 3.0 Hz, C(2')H, C(3')H), 6.53 (1H, m, C(2')H, C(3')H), 2.58 (3H, s, C(1"')H_3), 2.49 (3H, s, C(1")H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 155.5 and 153.5 (C(2) and C(6)), 147.1 (C(1')), 142.9 (C(4')), 139.5 (C(4)), 126.6 (C(3)), 121.6 (C(5)), 111.3 and 110.9 (C(3') and C(2')), 24.2 (C(1"')), 20.3 (C(1")).

MS (ESI^+) Calculated for $C_{11}H_{12}NO$ $[M+H]^+$: 174.0913, Found: 174.0913.

FTIR 3115, 3056, 2965, 2927, 2864, 1578, 1492, 1467 cm^{-1}.

1-(2,4-dimethoxyphenyl)-2-vinylpentan-1-ol (575)



Aldehyde **574** (0.85 g, 5.13 mmol) and 1-bromohex-2-ene (150 mol%) were subjected to the General Procedure F. Purification by FCC (petrol-Et_2O 9:1 to 4:1) afforded the homoallylic alcohol **575** (1.11 g, 86%, 1:1 *dr*) as a clear oil.

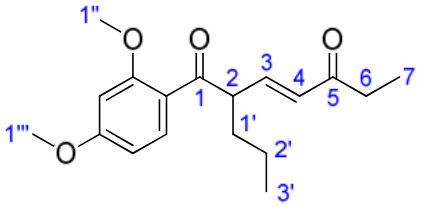
^{1}H NMR (400MHz, $CDCl_3$) 7.21 (1H, d, *J* = 8.0 Hz, Ph), 7.13 (1H, d, *J* = 8.0 Hz, Ph), 6.54-6.41 (4H, m, Ph), 5.71 (1H, dt, *J* = 10.0, 17.0 Hz, C(1')H), 5.52 (1H, dt, *J* = 10.0, 17.0 Hz, C(1')H), 5.18 (1H, dd, *J* = 2.0, 10.0 Hz, C(2')H_2), 5.10 (1H, dd, *J* = 1.5, 17.0 Hz, C(2')H_2), 4.95 (1H, dd, *J* = 2.0, 10.0 Hz, C(2')H_2), 4.90 (1H, dd, *J* = 1.5, 17.0 Hz, C(2')H_2), 4.71 (2H, d, *J* = 7.0 Hz, C(1)H), 3.84-3.78 (12H, m, C(1")H_3, C(1"')H_3), 2.61-2.33 (4H, m, C(2)H, OH), 1.72-1.60 (1 H, m, C(3)H_2), 1.46-1.28 (3 H, m, C(3)H_2), 1.29-1.09 (4 H, m, C(4)H_2), 0.88 (3H, t, *J*=7. 0 Hz, C(5)H_3), 0.81 (3H, t, *J*=7.0 Hz, C(5)H_3).

^{13}C NMR (100MHz, $CDCl_3$) 159.9, 159.8, 157.8 and 157.7 (*i*-Ar), 140.0 and 139.6 (C(1')), 128.9 (Ar), 128.4 (Ar), 123.5 (*i*-Ar), 117.4 and 115.9 (C(2')), 104.2 (Ar), 103.8 (Ar), 98.5 (Ar), 98.4 (Ar), 73.5 and 71.6 (C(1)), 55.3 and 55.2 (C(1") and C(1"')), 55.2 and 51.1 and 50.4 (C(2)), 32.8 and 32.0 (C(3)), 20.4 and 20.2 (C(4)), 14.1 and 13.9 (C(5)) (only 27 signals were observed).

MS (ESI^+) Calculated for $C_{15}H_{22}NaO_3$ $[M+Na]^+$: 273.1461, Found: 273.1461.

FTIR 3468, 2951, 1632, 1434, 1185, 1057 cm^{-1}.

1-(2,4-Dimethoxyphenyl)-2-propylhept-3-ene-1,5-dione (576)



Homoallylic alcohol **575** (86 mg, 0.28 mmol) and 1-pentene-3-one were subjected to the General Procedure C. In a modification to the general procedure, PhMe (0.20M) and catalyst HG-II (10 mol%) were employed and the reaction mixture was heated at 80 ºC for 48 hours, then filtered using CH_2Cl_2-Et_2O (9:1). Dess-Martin periodinane (200 mol%) was used for the oxidation step. Purification by FCC (petrol-EtOAc 17:3) afforded unsaturated dicarbonyl **576** (45 mg, 52%) as a yellow oil.

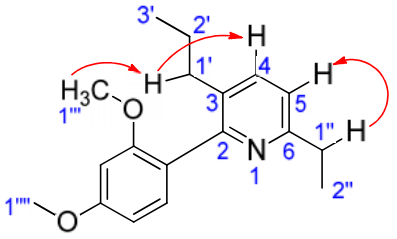
^{1}H NMR (400 MHz, $CDCl_3$) 7.69 (1H, d, *J* = 8.5 Hz, Ph), 6.91 (1H, dd, *J* = 16.0, 9.0 Hz, C(3)H), 6.52 (1H, dd, *J* = 9.0, 2.5 Hz, Ph), 6.45 (1H, d, *J* = 2.0 Hz, Ph), 6.08 (1H, d, *J* = 16.0 Hz, C(4)H), 4.35-4.19 (1H, m, C(2)H), 3.88 (3H, s, C(1")H_3, C(1"')H_3), 3.84 (3H , s, C(1")H_3, C(1"')H_3), 2.59 (2H, q, *J* = 7.5 Hz, C(6)H_2), 1.95-1.80 (1H, m, C(1')H_2), 1.63-1.49 (1H, m, C(1')H_2), 1.40-1.21 (2H, m, C(2')H_2), 1.07 (3H, t, *J* = 7.5 Hz, C(7)H_3), 0.88 (3H, t, *J* = 7.5 Hz, C(3')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 201.2 and 200.3 (C(1) and C(5)), 164.6 (*i*-Ar), 160.3 (*i*-Ar), 145.8 (C(3)), 133.0 (Ar), 131.4 (C(4)), 120.8 (*i*-Ar), 105.4 (Ar), 98.4 (Ar), 55.5 and 55.4 (C(1") and (C(1"')), 54.0 (C(2)), 34.3 (C(6)), 32.6 (C(1')), 20.4 (C(2')), 13.9 (C(3')), 8.1 (C(7)).

MS (ESI^+) Calculated for $C_{18}H_{24}NaO_4$ $[M+Na]^+$: 327.1567, Found: 327.1567.

FTIR 3130, 2977, 2936, 1723, 1678, 1641, 1465 cm^{-1}.

2-(2,4-Dimethoxyphenyl)-6-ethyl-3-propylpyridine (577)



Unsaturated 1,5-dicarbonyl **577** (37 mg, 0.12 mmol) was subjected to the General Procedure D. Purification by FCC (two columns: firstly petrol-Et_2O 4:1 to 3:2 and secondly CH_2Cl_2-Et_2O 1:0 to 19:1) afforded pyridine **577** (24 mg, 69%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.48 (1H, d, *J* = 8.0 Hz, C(4)H), 7.16 (1H, d, *J* = 8.5 Hz, Ph), 7.08 (1H, d, *J* = 8.0 Hz, C(5)H), 6.57 (1H, dd, *J* = 8.5, 2.5 Hz, Ph), 6.52 (1H, d, *J* = 2.5 Hz, Ph), 3.84 (3H, s, C(1’’’’)H_3), 3.71 (3H, s, C(1’’’)H_3), 2.84 (2H, q, *J* = 7.5 Hz, C(1’’)H_2), 2.39 (2H, t, *J* = 7.5 Hz, C(1’)H_2), 1.55-1.39 (2H, m, C(2’)H_2), 1.30 (3H, t, *J* = 7.5 Hz, C(2’’)H_2), 0.80 (3H, t, *J* = 7.5 Hz, C(3’)H_3).

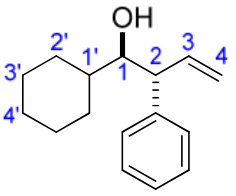
^{13}C NMR (100 MHz, $CDCl_3$) 160.6 (*i*-Ar), 160.1 (*i*-Ar), 157.5 (C(6)), 155.6 (C(2)), 136.5 (C(4)), 133.9 (C(3)), 131.2 (Ar), 123.2 (*i*-Ar), 120.0 (C(5)), 104.5 (Ar), 98.5 (Ar), 55.3 and 55.2 (C(1’’’) and C(1’’’’)), 33.8 (C(1’)), 31.0 (C(1’’)), 23.3 (C(2’)), 14.1 (C(3’)), 13.9 (C(2’’)).

MS (ESI^+) Calculated for $C_{18}H_{24}NO_2$ $[M+H]^+$: 286.1802, Found: 286.1801.

FTIR 3049, 2999, 1612, 1585, 1509, 1463 cm^{-1}.

n.O.e enhancements associated with pyridine **577** *are represented by red arrows on the compound structure (for n.O.e spectrum see appendix II).*

1-cyclohexyl-2-phenylbut-3-en-1-one (581)



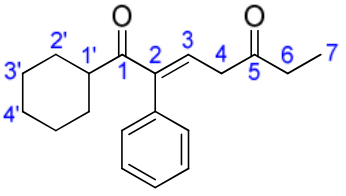
Aldehyde **579** (1.22 g, 10.89 mmol) and bromide **580** (150 mol%) were subjected to the General Procedure F. Purification by FCC (petrol-Et_2O 9:1 to 4:1) afforded the homoallylic alcohol **581** (1.32 g, 53%) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.34 (2H, t, *J* = 7.5 Hz, Ph), 7.24 (3H, t, *J* = 7.5 Hz, Ph), 6.17 (1H, dt, *J* = 17.0, 9.5 Hz, C(3)H), 5.28-5.15 (2H, m, C(4)H_2), 3.65-3.54 (1H, m, C(1)H), 3.48 (1 H, t, *J* = 8.0 Hz, C(2)H), 1.93-1.81 (1H, m, C(2')H_2, C(3')H_2,C(4')H_2), 1.81-1.56 (5H, m, C(2')H_2, C(3')H_2,C(4')H_2), 1.36-1.01 (6H, m, C(1')H, C(2')H_2, C(3')H_2,C(4')H_2, OH).

^{13}C NMR (100 MHz, $CDCl_3$) 142.1 (*i*-Ph), 138.4 (C(3)H), 128.7 (Ph), 127.9 (Ph), 126.5 (Ph), 117.6 (C(4)), 78.0 (C(1)), 53.6 (C(2)), 39.5 (C(1')), 30.1 (C(2'), 26.5, 26.4, 26.3 and 26.0 (C(2'), C(3'), C(4')).

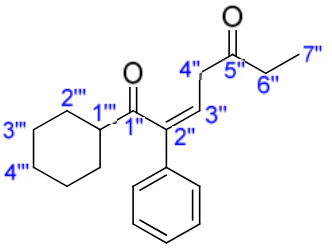
The spectroscopic properties of this compound were consistent with the data reported in the literature.[180]

(*E*)-1-Cyclohexyl-2-phenylhept-2-ene-1,5-dione (582) and (*Z*)-1-Cyclohexyl-2-phenylhept-2-ene-1,5-dione (583)



1

582



0.2

583

A reaction tube, fitted with a magnetic follower, was charged with catalyst HG-II (50 mg, 0.08 mmol, 10 mol%). The tube was then sealed with a rubber septum and purged with

argon. Argon sparged PhMe (3.20 mL), homoallylic alcohol **581** (184 mg, 0.80 mmol) and enone **578** (328 μL, 4.00 mmol). Tube was heated at 80 ^{o}C (oil bath temperature) for 48 hours. After cooling to room temperature, the reaction mixture was filtered through a short cartridge of SiO_2 (eluting with 19:1 petrol-Et_2O) and the solvent was concentrated *in vacuo* and the residue was dissolved in wet CH_2Cl_2 (8.00 mL). Dess-Martin Periodinane (678 mg, 1.60 mmol) was added and the reaction mixture was stirred for 0.5 hours and then the reaction mixture was filtered through a small plug of SiO_2 (eluting with Et_2O). The organic layer was concentrated *in vacuo*. Purification by FCC (1:0 to 9:1 petrol-EtOAc) afforded an inseparable mixture of diasteroisomers **582** and **583** (75 mg, 33%, 1:0.2 *dr*) as a clear oil.

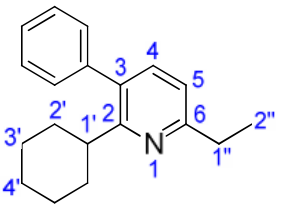
^{1}H NMR (400MHz, $CDCl_3$) 7.44-7.29 (3H, m, Ph), 7.27-7.20 (1H, m, Ph), 7.08 (2H, d, *J* = 7.5 Hz, Ph), 6.96 (1H, t, *J* = 7.5 Hz, C(3)H), 6.19 (0.2H, t, *J* = 7.5 Hz, C(3")H), 3.39 (0.4H, d, *J* = 7.5 Hz, C(4")H_2), 3.21 (2H, d, *J* = 7.5 Hz, , C(4)H_2), 2.97-2.82 (1.2H, m, C(1')H and C(1'")H), 2.52 (0.4H, q, *J* = 7.5 Hz, C(6")H_2), 2.38 (2H, q, *J* = 7.5 Hz, C(6)H_2), 1.90-1.48 (4.8H, m, C(2')H_2 and C(2"')H_2), 1.48-1.31 (2.4H, m, C(3')H_2, C(3"')H_2), 1.31-1.06 (7.2H, m, C(4')H_2, C(4"')H_2, C(3')H_2, C(3'")H_2), 1.03 (3.6H, t, *J* = 7.5 Hz, C(7)H_3, C(7")H_3).

^{13}C NMR (100MHz, $CDCl_3$) (data presented for major isomer only) 207.7 and 204.3 (C(1), C(5)), 144.4 (C(2)), 135.6 (*i*-Ph), 133.0 (C(3)), 129.2 (Ph), 128.4 (Ph), 127.7 (Ph), 45.8 (C(1')), 42.8 (C(4)), 36.2 (C(6)), 29.2 (C(2')), 25.8 (C(4')), 25.7 (C(3')), 7.6 (C(7)).

MS (ESI^+) Calculated for $C_{19}H_{24}NaO_2$ $[M+Na]^+$: 307.1669. Found: 307.1661.

FTIR 2977, 2934, 2855, 1716, 1684, 1494, 1030 cm^{-1}.

2-Cyclohexyl-6-ethyl-3-phenylpyridine (584)



Mixture of 1,5-diketones diasteroisomers **582** and **583** (74 mg, 0.26 mmol) were subjected to the General Procedure D. Purification of the residue by FCC (1:0 to 19:1 petrol-Et_2O) afforded pyridine **584** (44 mg, 64%) as a clear oil.

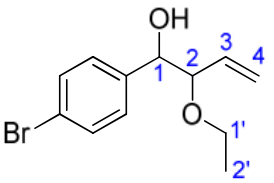
^{1}H NMR (400MHz, $CDCl_3$) 7.48-7.35 (4H, m, Ph, C(4)H), 7.33-7.28 (2H, m, Ph), 7.00 (1H, d, *J* = 8.0 Hz, C(5)H), 2.86 (2H, q, *J* = 7.0 Hz, C(1")H_2), 2.81 (1H, m, C(1')H), 1.90-1.60 (7H, m, C(2')H_2, C(3')H_2, C(4')H_2), 1.36 (3H, t, *J* = 7.5 Hz, C(2")H_3), 1.32 (1H, m, C(2')H_2, C(3')H_2, C(4')H_2), 1.19 (2H, m, C(2')H_2, C(3')H_2, C(4')H_2).

^{13}C NMR (100MHz, $CDCl_3$) 162.4 and 161.7 (C(2) and C(6)), 140.6 (*i*-Ph, C(3)), 137.6 (C(4)), 133.0 (*i*-Ph, C(3)), 129.2 (Ph), 128.2 (Ph), 126.9 (Ph), 118.5 (C(5)), 41.9 (C(1')), 32.5 (C(2')), 31.2 (C(1")), 26.4 (C(3')), 25.9 (C(4')), 13.8 (C(2")).

MS (ESI^+) Calculated for $C_{19}H_{24}N$ $[M+H]^+$: 266.1903. Found: 266.1903.

FTIR 3025, 2924, 1590, 1571, 1463, 1208 cm^{-1}.

1-(4-bromophenyl)-2-ethoxybut-3-en-1-one (587)



s-Butyl lithium (1.3 M solution in hexanes, 4.60 mL, 5.98 mmol) was added to a stirred solution of allyl ethyl ether (0.68 mL, 6.00 mmol) in THF (20.0 mL) at -78 ^oC. After stirring for 1 hour, a solution of $InCl_3$ (0.44 g, 2.02 mmol) in THF (6.00 mL) was added. Stirring was continued for a further 30 minutes then aldehyde **585** (0.37 g, 2.01 mmol) was added. After 1 hour, the reaction mixture was allowed to warm to room temperature and aqueous

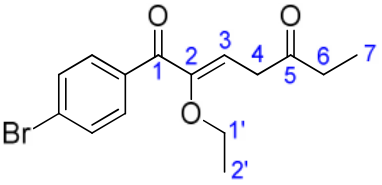
HCl solution (1M, 10.0 mL) was added. The aqueous layer was extracted with Et_2O (20.0 mL ×2) and the combined organic layers were washed with water (20.0 mL) and brine (20.0 mL) and then dried (Na_2SO_4).The organic layer was concentrated *in vacuo*. Purification by FCC (1:0 to 9:1 petrol-Et_2O) afforded homoallylic alcohol 587 (0.28 g, 52%, 1:0.2 *dr*) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.45 (2.4H, d, *J* = 8.5 Hz, Ar), 7.22 (2.4H, d, *J* = 8.5 Hz, Ar), 5.63 (0.2H, ddd, *J* = 17.5, 10.5, 8.0 Hz, C(3)H), 5.55 (1H, ddd, *J* = 17.5, 10.0, 7.5 Hz, C(3)H), 5.23 (0.2H, d, *J* = 10.0 Hz, C(4)H_2), 5.17 (1.2H, d, *J* = 10.0 Hz, C(4)H), 5.05 (1H, d, *J* = 17.5 Hz, C(4)H), 4.76 (0.2H, br. s., C(1)H), 4.45 (1H, d, *J* = 7.5 Hz, C(1)H), 3.82 (0.2H, dd, *J* = 7.5, 4.5 Hz, C(2)H), 3.71-3.61 (2H, m, C(1')H_2, C(2)H), 3.61-3.53 (0.2H, m, C(1')H_2), 3.44-3.30 (2.2H, m, C(1')H_2, OH), 2.77 (0.2H, br. s, OH), 1.23 (3H, t, *J* = 7.0 Hz, C(2')H_3), 1.17 (0.6H, t, *J* = 7.0 Hz, C(2')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 139.3 (*i*-Ar), 138.8 (*i*-Ar), 134.3 and 133.9 (C(3)), 131.1 (Ar), 131.0 (Ar), 129.0 (Ar), 128.5 (Ar), 121.7 (*i*-Ar), 121.2 (*i*-Ar), 119.8 and 119.5 (C(4)), 85.6 and 84.5 (C(2)), 76.1 and 74.8 (C(1)), 64.5 and 64.3 (C(1')), 15.2 (C(2')) (only 19 signals were observed).

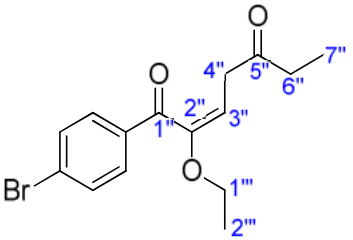
The spectroscopic properties of this compound were consistent with the data reported in the literature.[70]

(*E*)-1-(4-Bromophenyl)-2-ethoxyhept-2-ene-1,5-dione (588), (*Z*)-1-(4-Bromophenyl)-2-ethoxyhept-2-ene-1,5-dione (589) and 1-(4-Bromophenyl)-2-ethoxyhept-3-ene-1,5-dione (590)



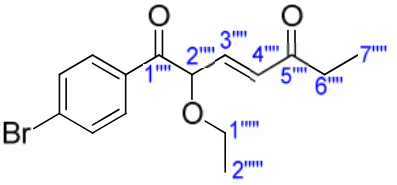
1

588



0.2

589



0.1

590

Homoallylic alcohol **587** (87 mg, 0.32 mmol), CH_2Cl_2 (0.10 M), catalyst Z-1B (5 mol%) and 1-pentene-3-one were subjected to the General Procedure B. The reaction mixture was heated for 48 hours. In a modification to the general procedure, after cooling to room

temperature the reaction mixture was filtered through a cartridge of SiO_2 (CH_2Cl_2-Et_2O 19:1). The fractions containing the target CM product were combined and concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (0.10 M with respect to the homoallylic alcohol) and subjected to the oxidation step. Purification by FCC (petrol-Et_2O 1:0 to 4:1) afforded the inseparable mixture of diasteroisomers and regioisomers **588**, **589** and **590** (46 mg, 44%, 1:0.2:0.1) as a yellow oil.

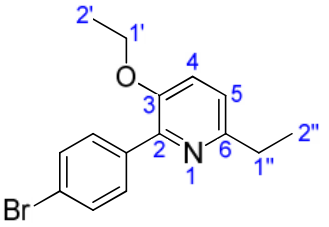
^{1}H NMR (400 MHz, $CDCl_3$) 8.04 (0.2H, d, *J* = 8.0 Hz, Ph), 7.94 (0.4H, d, *J* = 8.0 Hz, Ph), 7.81-7.69 (2H, m, Ph), 7.65-7.54 (2.6H, m, Ph), 6.86 (0.1H, dd, *J* = 16.0, 4.5 Hz, C(3””)H), 6.53 (0.1H, dd, *J* = 16.0, 1.5 Hz, C(4””)H), 5.91 (1H, t, *J* = 7.0 Hz, C(3)H), 5.34 (0.2H, t, *J* = 7.5 Hz, C(3”)H), 5.03 (0.1H, dd, *J* = 4.5, 1.5 Hz, C(2””)H), 3.90 (0.4H, q, *J* = 7.0 Hz, C(1”’)H_2), 3.84 (2H, q, *J* = 7.0 Hz, C(1’)H_2), 3.63-3.52 (0.2H, m, C(1””’)H_2), 3.45 (2H, d, *J* = 7.5 Hz, C(4)H_2), 3.37 (0.4H, d, *J* = 7.5 Hz, C(4”)H_2), 2.58 (0.2H, q, *J* = 7.0 Hz, C(6””)H_2), 2.53 (2H, q, *J* = 7.5 Hz, C(6)H_2), 2.45 (0.4H, q, *J* = 7.5 Hz, C(6”)H_2), 1.31 (0.9H, t, *J* = 7.0 Hz, C(2”’)H_3), 1.24 (3.3H, t, *J* = 7.0 Hz, C(2’)H_3, C(2””’)H_3), 1.09 (3H, t, *J* = 7.0 Hz, C(7)H_3), 1.04 (1.1H, t, *J* = 7.5 Hz, C(7”)H_3 , C(7””)H_3).

^{13}C NMR (100 MHz, $CDCl_3$) (data presented for major isomer only) 207.7 (C(5)), 191.1 (C(1)), 153.3 (C(2)), 135.9 (*i*-Ph), 131.6 (Ph), 131.0 (Ph), 127.9 (Ph), 120.5 (C(3)), 66.8 (C(1’)), 39.1 (C(4)), 36.0 (C(6)), 15.4 (C(2’)), 7.7 (C(7)).

MS (ESI^+) Calculated for $C_{15}H_{17}{}^{79}BrNaO_3$ $[M+Na]^+$: 347.0259, Found: 347.0248.

FTIR 2978, 2937, 2360, 1716, 1656, 1584, 1257, 1069 cm^{-1}.

2-(4-Bromophenyl)-3-ethoxy-6-ethylpyridine (591)



Mixture of 1,5-diketones **588**, **589** and **590** (43 mg, 0.13 mmol) were subjected to the General Procedure D. Purification by FCC (petrol-Et_2O 1:0 to 19:1) afforded pyridine **591** (31 mg, 78%) as a yellow oil.

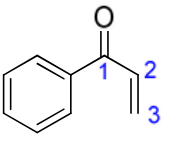
^{1}H NMR (400 MHz, $CDCl_3$) 7.90 (2H, d, *J* = 8.5 Hz, Ph), 7.56 (2H, d, *J* = 8.5 Hz, Ph), 7.21 (1H, d, *J* = 8.5 Hz, C(4)H, C(5)H), 7.08 (1H, d, *J* = 8.5 Hz, C(4)H, C(5)H), 4.05 (2H, q, *J* = 7.0 Hz, C(1')H_2), 2.83 (2H, q, *J* = 7.5 Hz, C(1")H_2), 1.41 (3H, t, *J* = 7.0 Hz, C(2')H_3), 1.33 (3H, t, *J* = 7.5, C(2")H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 154.9 and 150.9 (C(2) and C(6)), 145.5 (C(3)), 137.0 (*i*-Ph), 131.1 (Ph), 130.9 (Ph), 122.2 (*i*-Ph), 121.2 and 120.7 (C(4) and C(5)), 64.3 (C(1')), 30.5 (C(1")), 14.8 (C(2')), 14.1 (C(2")).

MS (ESI^+) Calculated for $C_{15}H_{17}{}^{79}BrNO$ $[M+H]^+$: 306.0488, Found: 306.0489.

FTIR 3074, 2974, 2931, 1653, 1573, 1455 cm^{-1}.

1-phenyl-2-propene-1-one (593)



To a solution of chloride **592** (2.47 g, 14.65 mmol) in chloroform (33.0 mL) was added triethylamine (5.0 mL, 35.84 mmol) over 5 minutes. The solution was stirred at 20 ºC for 16 hours under nitrogen. The reaction mixture was extracted with aqueous HCl (0.1M, 25.0 mL), aqueous saturated $NaHCO_3$ (20.0 mL), brine (20.0 mL). The organic layer was dried

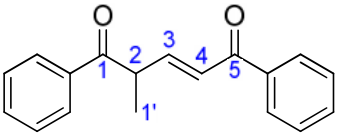
(Na_2SO_4) and concentrated in vacuo. Purification by Kugelrohr distillation at 80 ºC at 4 mbar afforded the title compound **593** (1.37 g, 71%) as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.93 (2H, d, *J* = 7.5 Hz, Ph), 7.60-7.50 (1H, m, Ph), 7.50-7.40 (2H, m, Ph), 7.14 (1H, dd, *J* = 17.0, 10.5 Hz, C(2)H), 6.42 (1H, dd, *J* = 17.0, 1.5 Hz, C(3)H_2), 5.89 (1H, dd, *J* = 10.5, 1.5 Hz, C(3)H).

^{13}C NMR (100 MHz, $CDCl_3$) 190.8 (C(1)), 137.1 (*i*-Ph), 132.8 (Ph), 132.2 (C(2)), 130.0 (C(3)), 128.5 (Ph), 128.4 (Ph).

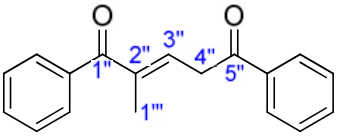
The spectroscopic properties of this compound were consistent with the data reported in the literature.[212]

2-Methyl-1,5-diphenylpent-3-ene-1,5-dione (594) and Methyl-1,5-diphenylpent-3-ene-1,5-dione (595).



1

594



0.1

595

Homoallylic alcohol **503** (84 mg, 0.52 mmol), CH_2Cl_2 (0.25 M), catalyst Z-1B (5 mol%) and PhVK were subjected to the General Procedure C. The reaction mixture was heated for 48 hours and then filtered using CH_2Cl_2-Et_2O (19:1). Dess-Martin periodinane (200 mol%) was used for the oxidation step. Purification by FCC (petrol-EtOAc 9:1 to 7:3) afforded the inseparable mixture of regioisomers **594** and **595** (74 mg, 54%, 1:0.1 *rr*) as a yellow oil.

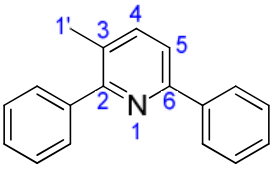
^{1}H NMR (400 MHz, $CDCl_3$) (data presented for major isomer only) 8.02-7.96 (2H, m), 7.77-7.71 (2H, m), 7.68-7.58 (1H, m), 7.55-7.47 (3H, m), 7.47-7.39 (2H, m), 6.67 (1H, m, C(3)H), 4.00 (2H, d, *J* = 7.0 Hz, C(4)H_2), 2.06 (3H, d, *J* = 1.5 Hz, C(1')H_3).

^{13}C NMR (50 MHz, $CDCl_3$) (data presented for major isomer only) 198.3 and 196.1 (C(1) and C(5)), 138.7, 138.0, 136.7 and 136.3 (*i*-Ph, Ph, C(2)), 133.5 (Ph), 131.8 (Ph), 129.5 (Ph), 128.8 (Ph), 128.1 (two signals, Ph), 38.6 (C(4)), 13.2 (C(1')).

MS (ESI^+) Calculated for $C_{18}H_{16}NaO_2$ $[M+Na]^+$: 287.1043, Found: 287.1046.

FTIR 3061, 2931, 1712, 1683, 1648, 1448, 1269 cm^{-1}.

3-Methyl-2,6-diphenylpyridine (596)



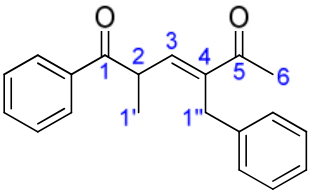
Mixture of 1,5-diketone **594** and **595** (56 mg, 0.21 mmol) were subjected to the General Procedure D. Purification by FCC (petrol-Et_2O 1:0 to 9:1) afforded pyridine **596** (44 mg, 86%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 8.08 (2H, d, *J*=7.3 Hz, Ph), 7.62-7.71 (4H, m, Ph, C(4)H, C(5)H), 7.35-7.55 (6H, m, Ph, C(4)H, C(5)H), 2.42 (3H, s, C(1')H_3)

^{13}C NMR (100 MHz, $CDCl_3$) 158.1 and 154.5 (C(2) and C(6)), 140.9 and 139.4 (*i*-Ph), 139.3 (C(4)), 129.2 (two signals, Ph), 128.6 (Ph), 128.5 (Ph), 128.0 (Ph), 127.9 (Ph), 126.8 (Ph), 118.6 (C(5)), 19.9 (C(1')).

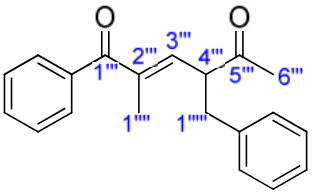
The spectroscopic properties of this compound were consistent with the data reported in the literature.[213]

4-benzyl-2-methyl-1-phenylhex-2-ene-1,5-dione (606) and 4-benzyl-2-methyl-1-phenylhex-3-ene-1,5-dione (607)



1

606



1

607

To a solution of unsaturated 1,5-diketones **505** and **506** (54 mg, 0.27 mmol) and benzyl bromide (100 μL, 0.84 mmol) in THF (3.0 mL) was added DBU (40 μL, 0.27 mmol) and the

mixture was stirred at room temperature for 1 hour. The mixture was diluted with EtOAc (25 mL) and extracted with saturated aq. NH_4Cl (2 × 15 mL). The aqueous layers were combined and extracted with EtOAc (2 × 10 mL). The organic extracts were combined and extracted with brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC (petrol-EtOAc 1:0 to 4:1) afforded the inseparable mixture of regioisomers **606** and **607** (66 mg, 85%, 1:1 *rr*) as a brown oil.

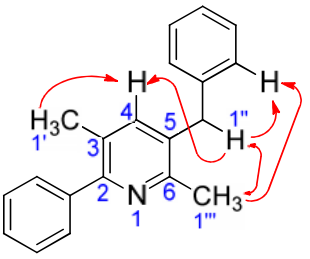
^{1}H NMR (400 MHz, $CDCl_3$) 7.77-7.70 (2H, m, Ph), 7.60-7.45 (4H, m, Ph), 7.45-7.36 (4H, m, Ph), 7.36-7.29 (2H, m, Ph), 7.29-7.20 (4H, m, Ph), 7.20-7.12 (4H, m, Ph), 6.97 (1H, d, *J* = 10.0 Hz, C(3)H), 6.14-6.05 (1H, m, C(3”’)H), 4.60-4.49 (1H, m, C(2)H), 3.99-3.91 (1H, m, C(4”’)H), 3.89 (1H, d, *J* = 15.0 Hz, C(1”)H_2), 3.75 (1H, m, *J* = 15.0 Hz, C(1”)H_2), 3.28-3.15 (1H, m, C(1””)H_2), 2.79 (1H, dd, *J* = 14.0, 9.0 Hz, C(1””)H_2), 2.38 (3H, s, C(6)H_3), 2.14 (3H, s, C(6”’)H_3), 1.89 (3H, s, C(1””)H_3), 1.33 (3H, d, *J* = 7.0 Hz, C(1’)H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 206.8, 200.5, 199.2 and 198.2 (C(6), C(6”’), C(1) and C(1”’)), 143.8 (C(3)), 140.8 (*i*-Ph, C(4), C(2”’)), 140.2 (C(3”’)), 139.4, 139.2, 138.2, 137.6 and 135.7 (*i*-Ph, C(4), C(2”’)), 133.4 (Ph), 131.9 (Ph), 129.4 (Ph), 128.9 (Ph), 128.7 (Ph), 128.6 (Ph), 128.5 (Ph), 128.3 (Ph), 128.2 (Ph), 128.1 (Ph), 126.7 (Ph), 126.1 (Ph), 55.3 (C(4”’)), 41.4 (C(2)), 37.2 (C(1””’)), 31.1 (C(1”)), 29.7 (C(6”’)), 25.8 (C(6)), 17.8 (C(1’)), 13.2 (C(1””)).

MS (ESI^+) Calculated for $C_{20}H_{20}NaO_2$ $[M+H]^+$: 315.1356, Found: 315.1356.

FTIR 3053, 2928, 1711, 1691, 1616 cm^{-1}.

3-Benzyl-2,5-dimethyl-6-phenylpyridine (609)



Mixture of 1,5-diketones **606** and **607** (43 mg, 0.15 mmol) was subjected to the General Procedure D. Purification by FCC (two columns: firstly petrol-Et_2O 1:0 to 4:1 and secondly CH_2Cl_2) afforded pyridine **609** (25 mg, 62%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.57-7.50 (2H, m, Ph), 7.45 (2H, t, *J* = 7.5 Hz, Ph), 7.41-7.31 (3H, m, Ph), 7.30-7.23 (2H, m, C(4)H, Ph), 7.20 (2H, d, *J* = 7.5 Hz, Ph), 4.02 (2H, s, C(1")H_2), 2.54 (3H, s, C(1"')H_3), 2.29 (3H, s, C(1')H_3).

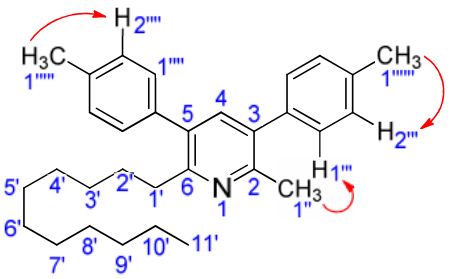
^{13}C NMR (100 MHz, $CDCl_3$) 155.9 (C(6)), 154.1 (C(2)), 140.7 (*i*-Ph), 139.8 (C(4)), 139.4 (*i*-Ph), 132.4 (C(5)), 129.0 (Ph), 128.7 (Ph), 128.6, 128.1, 128.0 (C(3)), 127.6 (Ph), 126.3 (Ph), 38.4 (C(1")), 22.2 (C(1"')), 19.4 (C(1')).

MS (ESI^+) Calculated for $C_{20}H_{20}N$ $[M+H]^+$: 274.1590, Found: 274.1587.

FTIR 3032, 2354, 1500, 1451, 1419 cm^{-1}.

Characteristic n.O.e enhancements associated with pyridine **609** *are represented by red arrows on the compound structure (for n.O.e spectrum see appendix II).*

2-Methyl-3,5-di-p-tolyl-6-undecylpyridine (612)



Mixture of 1,5-diketones **493** and **494** (75 mg, 0.28 mmol) and 4-Br-Tol were subjected to the General Procedure E. The crude material was filtered through a cartridge of SiO_2 (petrol-EtOAc 4:1) and then subjected to General Procedure D. Purification by FCC (petrol-EtOAc 1:0 to 24:1) afforded pyridine **612** (57 mg, 47%) as a colourless oil.

^{1}H NMR (500 MHz, C_6D_6) 7.40 (1H, s, C(4)H), 7.23 (2H, d, *J* = 8.0 Hz, C(1'''')H), 7.14 (2H, d, *J* = 8.0 Hz, C(1''')H), 7.05 (2H, d, *J* = 8.0 Hz, C(2'''')H), 7.00 (2H, d, *J* = 8.0 Hz, C(2''')H), 3.11-3.01 (2H, m, C(1')H_2), 2.70 (3H, s, C(1'')H_3), 2.16 (3 H, s, C(1''''')H_3, C(1''''')H_3), 2.15 (3H, s, C(1''''')H_3, C(1''''')H_3), 2.06-1.97 (2H, m, C(3')H_2), 1.41-1.17 (16 H, m, C(2')H_2, C(3')H_2, C(4')H_2, C(5')H_2, C(6')H_2, C(7')H_2, C(8')H_2, C(9')H_2, C(10')H_2), 0.91 (3H, t, *J*= 7.0 Hz, C(11')H_3).

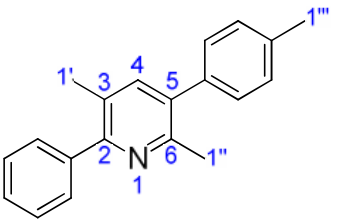
^{13}C NMR (100 MHz, C_6D_6) 158.4 (C(6)), 154.6 (C(2)), 139.2 (C(4)), 138.2 (*i*-Ar), 138.1 (*i*-Ar), 137.2 (*i*-Ar), 137.2 (*i*-Ar), 134.9 (C(5)), 134.6 (C(3)), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 36.0 (C(1')), 32.7 (C(9')), 30.7 (C(2')), 30.5 (two signals, 1 C, s), 30.4 (two signals,), 30.3 (C(3')), 30.2 (C(4')), 23.9 (C(1'')), 23.5 (C(10')), 21.5 (C(1''''') and C(1''''')), 14.7 (C(11')) (only 26 signals were observed).

MS (ESI^+) Calculated for $C_{31}H_{42}N$ $[M+H]^+$: 428.3312, Found: 428.3312.

FTIR 3054, 2959, 1584, 1581, 1483 cm^{-1}.

Characteristic n.O.e enhancements associated with pyridine **612** *are represented by red arrows on the compound structure (for n.O.e spectrum see appendix II).*

2,5-Dimethyl-6-phenyl-3-p-tolylpyridine (619)



Mixture of 1,5-diketones **505** and **506** (94 mg, 0.46 mmol) and 4-Br-Tol were subjected to the General Procedure E. The crude material was filtered through a cartridge of SiO_2 (petrol-EtOAc 9:1) and then subjected to General Procedure D. Purification by FCC (petrol-Et_2O 9:1 to 4:1) afforded pyridine **619** (57 mg, 48%) as a colourless solid.

^{1}H NMR (400 MHz, C_6D_6) 7.67 (2H, d, *J* = 8.0 Hz, Ph), 7.27-7.19 (2H, m, Ph), 7.15 (1H, s, C(4)H, Ph), 7.10 (3H, d, *J* = 8.0 Hz, C(4)H, Ph), 6.99 (2H, d, *J* = 8.0 Hz, Ph), 2.60 (3H, s, C(1")H_3), 2.12 (3H, s, C(1')H_3, C(1'")H_3), 2.07 (3H, s, C(1')H_3, C(1'")H_3).

^{13}C NMR (100 MHz, C_6D_6) 157.2 (C(6)), 153.5 (C(2)), 141.9 (*i*-Ph, C(3), C(5)), 140.3 (C(4)), 138.0, 137.3 and 135.8 (*i*-Ph, C(3), C(5)), 130.1 (Ph), 129.7 (two signals, Ph), 128.6 (Ph), 128.2 (Ph), 23.7 (C(1")), 21.5 and 19.9 (C(1') and C(1"'))(only 15 signals were observed).

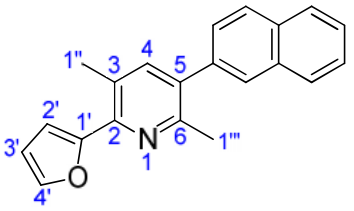
MS (ESI$^+$) Calculated for $C_{20}H_{20}N$ $[M+H]^+$: 274.1590, Found: 274.1591.

MP112-114 ºC (CH_2Cl_2)

FTIR 3055, 3028, 2963, 1950, 1925, 1426 cm^{-1}.

The structure of this compound was confirmed by X-ray crystallographic analysis (Appendix III).

2-(Furan-2-yl)-3,6-dimethyl-5-(naphthalen-2-yl)pyridine (623)



Mixture of 1,5-diketone **571** and **572** (29 mg, 0.15 mmol) and 2-bromonaphthalene were subjected to the General Procedure E. The crude material was filtered through a cartridge of SiO_2 (petrol-EtOAc 3:2) and then subjected to General Procedure D. Purification by FCC (petrol-Et_2O 1:0 to 9:1) afforded pyridine **623** (24 mg, 54%) as a colourless oil.

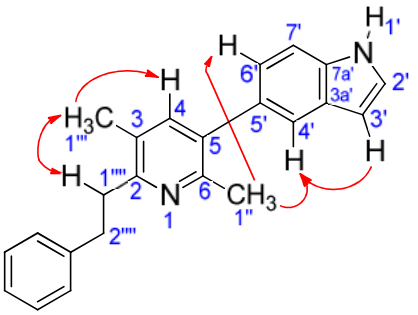
^{1}H NMR (500 MHz, $CDCl_3$) 7.92 (3H, m, Ph), 7.81 (1H, s, Ph), 7.64 (1H, d, *J* = 1.0 Hz, C(4')H), 7.57-7.53 (2H, m, Ph), 7.52-7.47 (2H, m, C(4)H, Ph), 7.00 (1H, d, *J* = 3.0 Hz, C(2')H), 6.58 (1H, dd, *J* = 3.0, 2.0 Hz, C(3')H), 2.61 (3H, s, C(1"')H_3, C(1")H_3), 2.59 (3H, s, C(1"')H_3, C(1")H_3).

^{13}C NMR (125 MHz, $CDCl_3$) 153.4 and 153.1 (C(2) and C(6)), 146.1 (C(1')), 143.1 (C(4')), 140.8 (C(4)), 137.2 (C(5), *i*-Ph), 135.2 (C(5), *i*-Ph), 133.2 (*i*-Ph), 132.4 (*i*-Ph), 128.0 (Ph), 127.9 (two signals, Ph), 127.7 (Ph), 127.1 (two signals, Ph), 126.4 (Ph), 126.2 (Ph), 111.4 (C(3')), 111.2 (C(2')), 23.2 and 20.2 (C(1") and C(1"')).

MS (ESI^+) Calculated for $C_{21}H_{18}NO$ $[M+H]^+$: 300.1383, Found: 300.1383.

FTIR 3113, 3041, 2970, 2963, 1728, 1578, 1588, 1492 cm^{-1}

5-(2,5-Dimethyl-6-phenethylpyridin-3-yl)-1*H*-indole (627)



Mixture of 1,5-diketones **566** and **567** (45 mg, 0.20 mmol) and 5-bromoindole were subjected to the General Procedure E. The crude product was filtered through a cartridge of SiO_2 (petrol-EtOAc 4:1) and subjected to General Procedure D. Purification by FCC (petrol-Et_2O 1:0 to 9:1) afforded pyridine **627** (31 mg, 49%) as colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) 8.46 (1H, br s, NH), 7.60 (1H, s, C(4')H), 7.45 (1H, d, *J* = 8.0 Hz, C(7')H), 7.35 (1H, s, C(4)H), 7.34-7.25 (5H, m, Ph),7.25-7.20 (1H, m, C(2')H), 7.17 (1H, dd, *J* = 8.5, 1.5 Hz, C(6')H), 6.63-6.58 (1H, m, C(3')H), 3.16-3.10 (2H, m, C(1'''')H_2, C(2'''')H_2), 3.10-3.03 (2H, m, C(1'''')H_2, C(2'''')H_2), 2.55 (3H, s, C(1'')H_3), 2.27 (3H, s, C(1''')H_3).

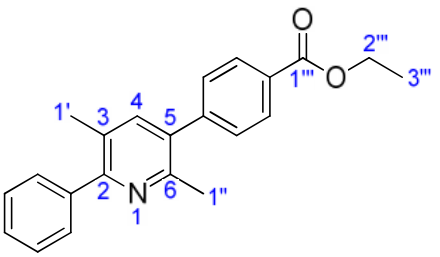
^{13}C NMR (125 MHz, $CDCl_3$) 157.0 and 152.7 (C(2) and C(6)), 142.2, 139.7 (C(4)), 135.6, 135.0 and 131.8 (*i*-Ph, C(3), C(5), C(5'), C(3a'), C(7a')), 128.5 (Ph), 128.3 (Ph), 127.9 (two signals, (*i*-Ph, C(3), C(5), C(5'), C(3a'), C(7a')), 125.9 (C(2')), 124.8 (*i*-Ph, C(3), C(5), C(5'), C(3a'), C(7a')), 123.5 (C(6')), 121.1 (C(4')), 110.7 (C(7')), 102.7 (C(3')), 37.3 and 35.5 (C(1'''') and C(2'''')), 22.9 (C(1'')), 18.1 (C(1''')).

MS (ESI$^+$) Calculated for $C_{23}H_{23}N_2$ $[M+H]^+$: 327.1856, Found: 327.1858.

FTIR 3420, 3130, 1495, 1454, 1428 cm^{-1}.

*Characteristic n.O.e enhancements associated with pyridine **627** are represented by red arrows on the compound structure (for n.O.e spectrum see appendix II).*

Ethyl 4-(2,5-dimethyl-6-phenylpyridin-3-yl)benzoate (630)



Mixture of 1,5-diketones **505** and **506** (67 mg, 0.33 mmol) and ethyl 4-bromobenzoate were subjected to the General Procedure E. The crude material was filtered through a cartridge of SiO_2 (petrol-EtOAc 4:1) and then subjected to General Procedure D. Purification by FCC (petrol-Et_2O 1:0 to 9:1) afforded pyridine **630** (75 mg, 69%) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$) 8.15 (2H, d, *J* = 8.5 Hz, Ph), 7.57 (2H, d, *J* = 7.5 Hz, Ph), 7.53-7.36 (6H, m, Ph, C(4)H), 4.43 (2H, q, *J* = 7.0 Hz, C(2”’)H_2), 2.53 (3H, s, C(1”)H_3), 2.36 (3H, s, C(1’)H_3), 1.44 (3H, t, *J* = 7.0 Hz, C(3’”)H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 166.3 (C(1”’)), 157.4 (C(2)), 152.4 (C(6)), 144.5 and 140.3 (*i*-Ph), 139.6 (C(4)), 134.4 (C(5)), 129.6 (Ph), 129.5 (*i*-Ph), 129.1 (Ph), 129.0 (Ph), 128.2 (Ph), 128.0 (C(5)), 127.9 (Ph), 61.0 (C(2”’)), 23.0 (C(1”)), 19.4 (C(1’)), 14.3 (C(3”’)).

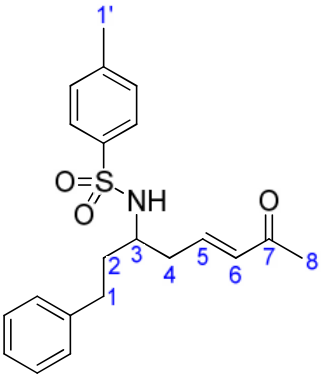
MS (ESI^+) Calculated for $C_{22}H_{22}NO_2$ $[M+H]^+$: 332.1645, Found: 332.1644.

MP 123-124ºC (CH_2Cl_2-Petrol)

FTIR 3070, 2993, 2927, 1707, 1607, 1288, 1277 cm^{-1}.

The structure of this compound was confirmed by X-ray crystallographic analysis (Appendix III).

4-Methyl-*N*-(7-oxo-1-phenyloct-5-en-3-yl)benzenesulfonamide (642)



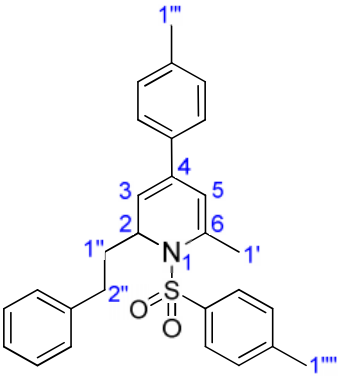
Homoallylic sulfonamide **641** (392 mg, 1.19 mmol) and MVK were subjected to the General procedure A. In a modification to the general procedure, catalyst HG-II (57 mg, 0.09 mmol, 8 mol%) and CH_2Cl_2 (4.80 mL) were used and the reaction mixture was heated at 55 ºC for 72 hours. Purification by FCC (9:1 to 1:1 petrol-EtOAc) afforded the title compound **642** (392 mg, 89%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.74 (2H, d, *J* = 8.0 Hz, Ar), 7.31 (2H, d, *J* = 8.0 Hz, Ar), 7.25 (2H, t, *J* = 7.0 Hz, Ph), 7.19 (1H, t, *J* = 7.0 Hz, Ph), 7.01 (2H, d, *J* = 7.0 Hz, Ph), 6.58 (1H, dt, *J* = 16.0, 7.5 Hz, C(5)H), 5.99 (1H, d, *J* = 16.0 Hz, C(6)H), 4.56 (1H, d, *J* = 8.5 Hz, NH), 3.48-3.37 (1H, m, C(3)H), 2.63-2.52 (1H, m, $C(4)H_2$, $C(1)H_2$), 2.52-2.37 (5H, m, $C(1')H_3$, $C(4)H_2$, $C(1)H_2$), 2.37-2.26 (1H, m, $C(4)H_2$, $C(1)H_2$), 2.17 (3H, s, $C(8)H_3$), 1.83-1.62 (2H, m, $C(2)H_2$).

^{13}C NMR (100 MHz, $CDCl_3$) 198.1 (C(7)), 143.7 (*i*-Ph), 142.3 (C(5)), 140.6 (*i*-Ar), 137.8 (*i*-Ar), 134.1 (C(6)), 129.8 (Ar), 128.5 (Ar, Ph), 128.2 (Ph), 127.0 (Ar, Ph), 126.2 (Ph), 52.8 (C(3)), 38.2 and 36.7 (C(4) and C(2)), 31.7 (C(1)), 27.0 (C(8)), 21.5 (C(1')).

The spectroscopic properties of this compound were consistent with the data obtained from an authentic sample of this compound.

6-Methyl-2-phenethyl-4-(p-tolyl)-1-tosyl-1,2-dihydropyridine (643)



A reaction tube, fitted with magnetic follower, was charged with Pd_2dba_3 (43 mg, 0.05 mmol, 5 mol%), *t*-$Bu_3P{\cdot}HBF_4$ (56 mg, 0.19 mmol), 5-amino enone **642** (362 mg, 0.97 mmol), and 4-Br-Tol (416 mg, 2.43 mmol). The tube was sealed with a septum and purged with argon. Anhydrous PhMe (10.0 mL) and then Cy_2NMe (0.31 mL, 1.46 mmol) were added sequentially *via* syringe. The mixture was then heated at 80 ^oC until TLC analysis indicated full consumption of the δ-amino enone (*ca.* 2-5 hours). TFA (0.10 mL, 1.30 mmol) was then added and heating was continued until complete condensation of the Heck product was observed by TLC analysis (*ca.* 1-4 hours). The reaction mixture was cooled to 20 ^oC and purification by FCC (first column: 1:0 to 9:1 petrol-EtOAc, second column: 1:1 to 1:3 petrol-CH_2Cl_2) afforded the title compound **643** (356 mg, 83%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.62 (2H, d, *J* = 8.0 Hz, Ar), 7.34-7.15 (5H, m, Ph), 7.11 (2H, d, *J* = 8.0 Hz, Ar), 7.05 (2H, d, *J* = 8.0 Hz, Ar), 6.85 (2H, d, *J* = 8.0 Hz, Ar), 5.91 (1H, s, C(5)H), 5.45 (1H, d, *J* = 6.0 Hz, C(3)H), 4.87 (1H, dt, *J* = 9.0, 6.0 Hz, C(2)H), 2.94-2.81 (1H, m, C(2")H_2), 2.81-2.70 (1H, m, C(2")H_2), 2.32 (3H, s, C(1')H_3, C(1"')H_3, C(1"")H_3), 2.28 (3H, s, C(1')H_3, C(1"')H_3, C(1"")H_3), 2.27 (3H, s, C(1')H_3, C(1"')H_3, C(1"")H_3), 1.91 (1 H, qd, *J* = 9.0, 5.0 Hz, C(1")H_2), 1.86-1.73 (1 H, m, C(1")H_2).

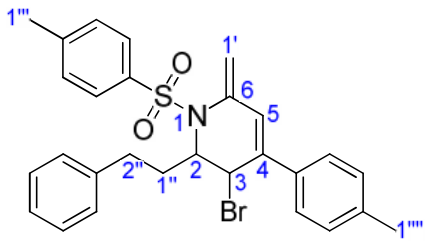
^{13}C NMR (125 MHz, $CDCl_3$) 143.3 (i-Ar), 141.9 (i-Ph), 137.2 (i-Ar), 136.3 (i-Ar), 135.4 (i-Ar), 134.1 and 134.0 (C(6) and C(4)), 129.0 (Ar), 128.9 (Ar), 128.5 (Ph), 128.4 (Ph), 127.1

(Ar), 125.8 (Ph), 125.5 (Ar), 118.8 (C(3)), 117.4 (C(5)), 55.8 (C(2)), 33.9 (C(1")), 31.2 (C(2")), 23.3 (C(1')), 21.4 and 21.0 (C(1"') and C(1"")).

The formation of dihydropyridine **643** was demonstrated by comparison of the ^{1}H and ^{13}C NMR spectra with the spectroscopic data of.

The spectroscopic properties of this compound were consistent with the data obtained from an authentic sample of this compound.

3-Bromo-6-methylene-2-phenethyl-4-(p-tolyl)-1-tosyl-1,2,3,6-tetrahydropyridine (644)



A solution of **643**(86 mg, 0.19 mmol) in CH_2Cl_2 (1.9 mL) was covered in aluminium foil and cooled at -78 ^{o}C. Triethylamine (130 μL, 0.94 mmol) and 1,3-dibromo-5,5-dimethyl hydantoin (62 mg, 0.22 mmol) were added sequentially and the reaction mixture was stirred for 10 minutes. The reaction mixture was warm up to room temperature and stirred over 16 hours. The mixture was then diluted with aqueous saturated $NaHCO_3$ (*ca.* 20 mL/mmol) and 5% aqueous $Na_2S_2O_3$ (*ca.* 20 mL/mmol) and extracted with CH_2Cl_2 (3 × 40 mL/mmol). The organic extracts were combined, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC (1:0 to 19:1 petrol-EtOAc) afforded the bromide **644** (77 mg, 76%, 1:0.2 *dr*) as yellow oil.

^{1}H NMR (500MHz, $CDCl_3$) (data for major diasteroisomer) 8.11 (2H, d, *J* = 8.0 Hz, Ar), 7.37 - 7.30 (7H, m, Ar, Ph), 7.29-7.24 (2H, m, Ar), 7.21 (2H, d, *J* = 8.0 Hz, Ar), 6.35 (1H, s, C(5)H), 5.67 (1H, s, C(1')H_2), 5.26 (1H, dd, *J* = 5.5, 9.0 Hz, C(2)H), 5.12 (1H, s, C(3)H), 4.90 (1H, s, C(1')H_2), 3.06 (1H, ddd, *J* = 5.5, 11.0, 13.5 Hz, C(2")H_2), 2.91 (1H, ddd, *J* =

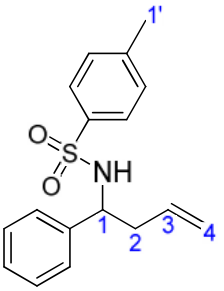
5.5, 11.0, 13.5 Hz, , C(2")H_2), 2.46 (3H, s, C(1"")H_3), 2.40 (3H, s, C(1"')H_3), 2.13-2.05 (1H, m, C(1")H_2), 2.00 - 1.90 (1H, m, C(1")H_2).

^{13}C NMR (125MHz, $CDCl_3$) (data for major diasteroisomer) 144.1 (*i*-Ar), 141.1 (C(6)), 138.8 (*i*-Ph), 135.8 (*i*-Ar), 135.7 (*i*-Ar), 134.1 and 133.1 (C(4) and *i*-Ar), 129.5 (Ar), 129.3 (Ar), 129.0 (Ar), 128.5 (Ph), 128.4 (Ar, Ph), 125.3 (Ph), 123.9 (C(5)), 107.2 (C(1')), 61.1 (C(2)), 47.4 (C(3)), 35.8 (C(1")), 32.9 (C(2")), 21.6 (C(1"")), 21.2 (C(1"')) (Only 21 signals were observed).

MS (ESI^+) Calculated for $C_{28}H_{29}{}^{79}BrNO_2S$ $[M+H]^+$: 522.1097. Found: 522.1105.

FTIR 3026, 2921, 1595, 1458, 1342, 1160 cm^{-1}.

4-Methyl-*N*-(1-phenylbut-3-en-1-yl)benzenesulfonamide (647)



A mixture of benzaldehyde **403** (1.20 mL, 11.8 mmol) 772.10 mL, 20.6 mmol), *p*-toluenesulfonamide (2.22 g, 13.0 mmol) and tetraethyl orthosilicate (2.90 mL, 13.0 mmol) was heated at 160 ºC and ethanol was collected into a separate flask. After 5 hours the reaction mixture was cooled to room temperature and the crude material was washed with petrol (25 mL). THF (100.0 mL) was added to the crude solid and the reaction mixture was cooled to -78ºC. Allyl magnesium bromide (1.0M in THF, 12.0 mL, 12.0 mmol) was added and the reaction mixture was left to warm up to room temperature. After 16 hours saturated aqueous NH_4Cl (50 ml) was added and the reaction mixture was extracted with EtOAc (3 × 50mL). The combined organic layer was washed with brine (50 ml), dried ($MgSO_4$) and

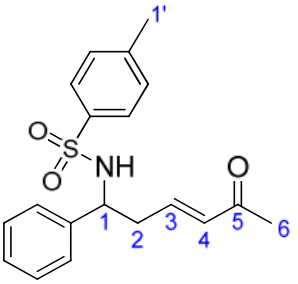
concentrated *in vacuo*. Purification of the residue by FCC (5:1 petrol-EtOAc) afforded the title compound **647** (2.53 g, 71%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) 7.56 (2H, d, *J* = 8.0 Hz, Ar), 7.23-7.11 (5H, m, Ar, Ph), 7.11-7.04 (2H, m, Ph), 5.58-5.45 (1H, m, C(3)H), 5.08 (1H, s, C(4)H_2), 5.05 (1H, d, *J* = 4.5 Hz, C(4)H_2), 4.97 (1H, d, *J* = 6.5 Hz, NH), 4.38 (1H, q, *J* = 6.5 Hz, C(1)H), 2.50-2.43 (2H, m, C(2)H_2), 2.37 (3H, s, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 143.1 (*i*-Ph), 140.3 (*i*-Ar), 137.4 (*i*-Ar), 133.0 (C(3)), 129.3 (Ph, Ar), 128.3 (Ph, Ar), 127.3 (Ph), 127.1 (Ph, Ar), 126.5 (Ph, Ar), 119.3 (C(4)), 57.1 (C(1)), 41.8 (C(2)), 21.4 (C(1')).

The spectroscopic properties of this compound were consistent with the data reported in the literature.[214]

4-Methyl-N-(5-oxo-1-phenylhex-3-en-1-yl)benzenesulfonamide (648)



Homoallylic sulfonamide **647** (1.21 g, 4.02 mmol) and MVK were subjected to the General procedure A. In a modification to the general procedure, catalyst HG-II (85 mg, 0.14 mmol, 3 mol%) and CH_2Cl_2 (14.0 mL) were used and the reaction mixture was heated at 55 ºC for 72 hours. Purification by FCC (4:1 to 6:4 petrol-EtOAc) afforded the title compound **648** (1.01 g, 73%) as a colourless solid.

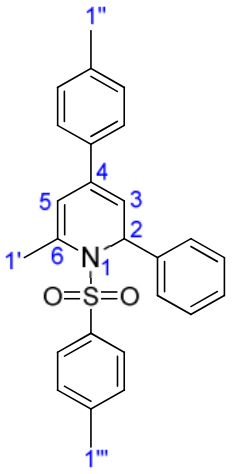
^{1}H NMR (400 MHz, $CDCl_3$) 7.58 (2H, d, *J* = 8.0 Hz, Ar), 7.25-7.13 (5H, m, Ar, Ph), 7.07-6.99 (2H, m, Ph), 6.53 (1H, dt, *J* = 16.0, 7.0 Hz, C(3)H), 6.01 (1H, d, *J* = 16.0 Hz, C(4)H),

4.98 (1H, d, *J* = 7.0 Hz, NH), 4.45 (1H, q, *J* = 7.0 Hz, C(1)H), 2.78-2.61 (2H, m, C(2)H_2), 2.38 (3H, s, C(1')H_3), 2.15 (3 H, s, C(6)H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 198.1 (C(5)), 143.7 (*i*-Ph), 142.0 (C(3)), 139.5 (*i*-Ar), 137.2 (*i*-Ar), 134.1 (C(4)), 129.5 (Ar), 128.8 (Ph), 128.0 (Ph), 127.1 (Ar), 126.3 (Ph), 57.1 (C(1)), 40.2 (C(2)), 26.9 (C(6)), 21.5 (C(1')).

The spectroscopic properties of this compound were consistent with the data obtained from an authentic sample of this compound.

6-Methyl-2-phenyl-4-(I-tolyl)-1-tosyl-1,2-dihydropyridine (649)



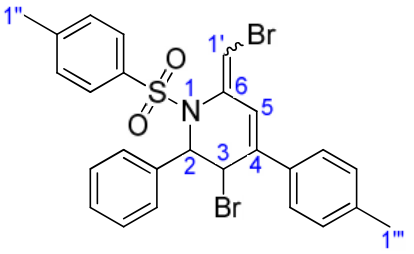
A reaction tube, fitted with magnetic follower, was charged with Pd_2dba_3 (70 mg, 0.08 mmol, 5 mol%), *t*-$Bu_3P{\cdot}HBF_4$ (90 mg, 0.31 mmol), 5-amino enone **648** (508 mg, 1.48 mmol), and 4-Br-Tol (630 mg, 3.68 mmol). The tube was sealed with a septum and purged with argon. Anhydrous PhMe (15.0 mL) and then Cy_2NMe (0.47 mL, 2.19 mmol) were added sequentially *via* syringe. The mixture was then heated at 80 ^{o}C until TLC analysis indicated full consumption of the δ-amino enone (*ca.* 2-5 hours). TFA (0.22 mL, 2.87 mmol) was then added and heating was continued until complete condensation of the Heck product was observed by TLC analysis (*ca.* 1-4 hours). The reaction mixture was cooled to 20 ^{o}C and purification by FCC (first column: 9:1 petrol-EtOAc, second column: PhMe) afforded the title compound **649** (514 mg, 84%) as a pale yellow foam.

^{1}H NMR (400 MHz, $CDCl_3$) 7.68 (2H, d, *J* = 8.0 Hz, Ar), 7.46 (2H, d, *J* = 7.0 Hz, Ph), 7.38-7.24 (3H, m, Ph), 7.15 (2H, d, *J* = 8.0 Hz, Ar), 7.10 (2H, d, *J* = 8.0 Hz, Ar), 6.99 (2H, d, *J* = 8.0 Hz, Ar), 6.02 (1H, d, *J* = 6.5 Hz, C(2)H), 5.89 (1H, s, C(5)H), 5.75 (1H, d, *J*=6.5 Hz, C(3)H), 2.35 (3H, s, C(1"')H_3), 2.30 (3H, s, C(1")H_3), 2.14 (3H, s, C(1')H_3).

^{13}C NMR (100 MHz, $CDCl_3$) 143.5 (*i*-Ph), 139.3 (*i*-Ar), 137.5, 136.3, 135.7, 135.2 and 135.0 (C(6), C(4) and *i*-Ar), 129.2 (Ar, Ph), 129.0 (Ar, Ph), 128.3 (Ar, Ph), 127.8 (Ph), 127.2 (two signals, Ar, Ph), 125.6 (Ar, Ph), 117.6 (C(5)), 116.4 (C(3)), 57.3 (C(2)), 23.3 (C(1')), 21.4 and 21.1 (C(1") and C(1"')).

The spectroscopic properties of this compound were consistent with the data obtained from an authentic sample of this compound.

3-Bromo-6-(bromomethylene)-2-phenyl-4-(p-tolyl)-1-tosyl-1,2,3,6-tetrahydropyridine (650)



A solution of **649** (49 mg, 0.12 mmol) in CH_2Cl_2 (1.3 mL) was covered in aluminium foil and cooled at -78 ^{o}C. Triethylamine (85µL, 0.61 mmol) and 1,3-dibromo-5,5-dimethyl hydantoin (68 mg, 0.24 mmol) were added sequentially and the reaction mixture was stirred for 1 hour. The reaction mixture was warm up to room temperature and stirred over 16 hours. The mixture was then diluted with aqueous saturated $NaHCO_3$ (*ca.* 20 mL/mmol) and 5% aqueous $Na_2S_2O_3$ (*ca.* 20 mL/mmol) and extracted with CH_2Cl_2 (3 × 40 mL/mmol). The organic extracts were combined, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of

the residue by FCC (1:0 to 0:1 petrol-toluene) afforded the dibromide **650** (50 mg, 75%, 1:0.1 *dr*) as yellow oil.

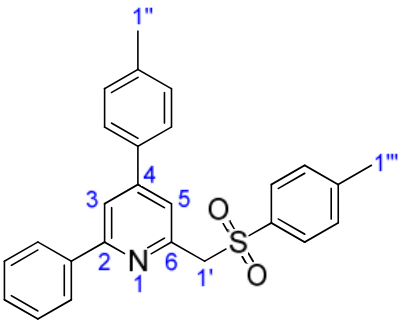
^{1}H NMR (400MHz, $CDCl_3$) (data for major diasteroisomer) 7.97 (2H, d, *J* = 8.0 Hz, Ar), 7.44-7.25 (9H, m, Ph),7.19 (2H, d, *J* = 8.0 Hz, Ar),7.04 (1H, s, C(5)H), 6.86 (1H, s, C(1')H), 6.32 (1H, d, *J* = 1.5 Hz, (C(2)H), 5.52 (1H, d, *J* = 1.5 Hz, C(3)H), 2.43 (3H, s, C(1")H_3, C(1"')H_3), 2.36 (3H, s, C(1")H_3, C(1"')H_3).

^{13}C NMR (100MHz, $CDCl_3$) (data for major diasteroisomer) 144.5 (*i*-Ar), 139.5 (C(6)), 138.3 (*i*-Ph, *i*-Ar), 137.4 (*i*-Ph, i-Ar), 135.7 (*i*-Ar), 132.9 and 132.7 (C(4), *i*-Ar), 129.6 (Ar), 129.4 (Ar), 129.0 (Ar), 128.9 (Ar), 128.3 (Ar), 126.5 (Ph), 125.6 (Ph), 119.3 (C(5)), 99.7 (C(1')), 63.8 (C(2)), 46.5 (C(3)), 21.6 (C(1"')), 21.2 (C(1")).

MS (ESI^+) Calculated for $C_{26}H_{23}{}^{79}Br_2NNaO_2S$ $[M+Na]^+$: 595.9689. Found: 595.9681.

FTIR 3424, 2921, 1545, 1337 cm^{-1}.

2-Phenyl-4-(*p*-tolyl)-6-(tosylmethyl)pyridine (651)



A solution of dibromide **650** (40 mg, 0.07 mmol) in toluene (2.0 mL) was treated with DBU (74 μL, 0.50 mmol) and then the reaction mixture was heated at 80 ^{o}C (oil bath temperature) for 13 hours. After cooling to room temperature, the reaction mixture purified directly by FCC (1:0 to 4:1 petrol-EtOAc) to afford the pyridine **651** (11 mg, 36%) as a white solid.

^{1}H NMR (400MHz, $CDCl_3$) 7.82 (1H, d, *J* = 1.0 Hz, C(3)H), 7.65-7.57 (7H, m, Ph, Ar, C(5)H), 7.42-7.36 (3H, m, Ph), 7.33 (2H, d, *J* = 8.0 Hz, Ar), 7.26 (2H, d, *J* = 8.5 Hz, Ar), 4.66 (2H, s, C(1')H_2), 2.45 (3H, s, C(1")H_3, C(1"')H_3), 2.40 (3H, s, C(1")H_3, C(1"')H_3).

^{13}C NMR (100MHz, $CDCl_3$) 157.7 (C(6)), 150.0 (C(2)), 149.5 (C(4)), 144.6 (i-Ar), 139.5 (i-Ar, i-Ph), 138.7 (i-Ar, i-Ph), 135.3 (i-Ar), 134.9 (i-Ar), 129.9 (Ar), 129.5 (Ar, Ph), 129.1 (Ph), 128.8 (Ar, Ph), 128.5 (Ar, Ph), 127.0 (Ar, Ph), 126.9 (Ar, Ph), 121.9 (C(3)), 117.8 (C(5)), 64.9 (C(1')), 21.5 and 21.3 (C(1") and C(1"')).

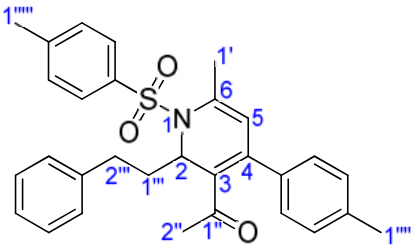
MS (ESI^+) Calculated for $C_{26}H_{24}NO_2S$ $[M+H]^+$: 414.1522. Found: 414.1533.

FTIR 2998, 2939, 1600, 1311, 1301, 1161 cm^{-1}.

MP 161-162 ^oC (CH_2Cl_2-petrol).

The structure of this compound was confirmed by X-ray crystallographic analysis (Appendix III).

1-(6-Methyl-2-phenethyl-4-(p-tolyl)-1-tosyl-1,2-dihydropyridin-3-yl)ethanone (652)



A solution of **643** (41 mg, 0.09 mmol) in CH_2Cl_2 (0.9 mL) was cooled at 0 ^oC. Aluminium trichloride (31 mg, 0.23 mmol) and acetyl chloride (14 μL, 0.18 mmol) were added sequentially at this temperature. The reaction mixture was warm up to room temperature and stirred over 16 hours. The mixture was then diluted with aqueous saturated $NaHCO_3$ (*ca.* 20 mL/mmol) and extracted with CH_2Cl_2 (3 × 40 mL/mmol). The organic extracts were combined, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by FCC (1:0 to 4:1 petrol-EtOAc) afforded ketone **652** (29 mg, 64%, 1:0.2 *rr*) as yellow oil.

^{1}H NMR (500MHz, $CDCl_3$) (data for major diasteroisomer) 7.68 (2H, d, *J* = 8.0 Hz, Ar), 7.33-7.25 (3H, m, Ph), 7.25-7.11 (4H, m, Ph, Ar), 7.06 (2H, d, *J* = 8.0 Hz, Ar), 6.50 (2H, d,

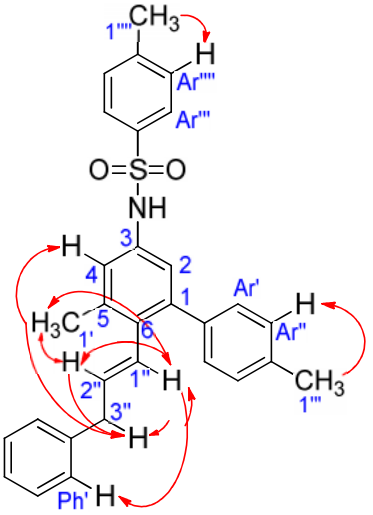
J= 8.0 Hz, Ar), 5.76 (1H, d, *J* = 1.5 Hz, C(5)H), 5.49 (1H, dd, *J* = 4.5, 10.0 Hz, C(2)H), 2.94 - 2.84 (1H, ddd, *J* = 14.0, 11.0, 5.0 Hz, C(2”’)H_2), 2.75 (1H, ddd, *J* = 14.0, 11.0, 6.0, C(2”’)H_2), 2.40 (3H, s, C(1””’)H_3), 2.33 (6H, s, C(1’)H_3, C(1””)H_3), 1.95-1.84 (1H, m, C(1”’)H_3), 1.77-1.65 (1H, m, C(1”’)H_3), 1.39 (3H, s, C(2”)H_3).

^{13}C NMR (125MHz, $CDCl_3$) 199.0 (C(1”)), 143.7 (*i*-Ar), 141.9 (*i*-Ph), 141.5 (C(4)), 138.6 (*i*-Ar), 137.9 (C(6)), 136.7 (*i*-Ar), 135.5 (*i*-Ar), 130.2 (C(3)), 129.2 (two signals, Ph, Ar), 128.4 (Ar), 128.3 (Ph), 127.4 (Ar), 126.9 (Ar), 125.7 (Ph), 120.4 (C(5)), 56.1 (C(2)), 33.1 (C(1”’)), 31.5 (C(2”’)), 29.9 (C(2”)), 23.1 (C(1’)), 21.4 and 21.2 (C(1””) and C(1””’)).

MS (ESI$^+$) Calculated for $C_{30}H_{32}NO_3S$ $[M+H]^+$: 486.2097. Found: 486.2100.

FTIR 2923, 1712, 1646, 1593, 1355, 1088 cm^{-1}.

(E)-*N*-(4',5-Dimethyl-6-(3-phenylprop-1-en-1-yl)-[1,1'-biphenyl]-3-yl)-4-methylbenzenesulfonamide (653)



A mixture of ketone **652** (98 mg, 0.26 mmol) and *tert*-butyl alcohol (2.0 mL) was treated with potassium *tert*-butoxide (46 mg, 0.41 mmol) and the reaction mixture was heated 135 ^oC (oil bath temperature) for 3 hours. After cooling to room temperature the mixture was then diluted with aqueous saturated $NaHCO_3$ (10.0 mL) and extracted with EtOAc (3 × 20 mL). The organic extracts were combined, dried (Na_2SO_4) and concentrated *in vacuo*.

Purification of the residue by FCC (1:0 to 0:1 petrol-CH_2Cl_2) afforded sulfonamide **653** (34 mg, 36%) as yellow oil.

^{1}H NMR (700 MHz, $CDCl_3$) 7.73 (2H, d, *J* = 8.5 Hz, Ar), 7.25 (4H, t, *J*= 8.0 Hz, Ar, Ph), 7.20 (1H, t, *J*=7.0 Hz, Ph), 7.13 (2H, d, *J*=7.5 Hz, Ar), 7.08 (2H, d, *J*= 7.5 Hz, Ar), 7.02 (2H, d, *J*=7.0 Hz, Ph), 6.98 (1H, d, *J*=2.0 Hz, C(4)H), 6.90 (1H, s, NH), 6.79 (1H, d, *J*=2.0 Hz, C(2)H), 6.22 (1H, d, *J* = 16.0 Hz, C(1")H), 5.55 (1H, dt, *J* = 16.0, 7.0 Hz, C(2")H), 3.37 (2H, d, *J* = 7.0 Hz, C(3")H_2), 2.41 (3H, s, C(1"')H_3, C(1"")H_3), 2.40 (3H, s, C(1"')H_3, C(1"")H_3), 2.32 (3H, s, C(1')H_3).

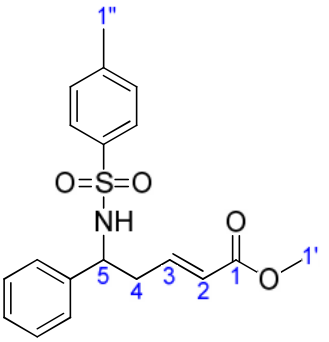
^{13}C NMR (125MHz, $CDCl_3$) 143.7 (*i*-Ar), 142.3 (C(1)), 140.1 (*i*-Ph), 138.6 (*i*-Ar), 137.6 (C(5)), 136.3 (*i*-Ar), 136.2 (*i*-Ar), 134.7 (C(2")), 134.4 (C(3)), 133.1 (C(6)), 129.6 (two signals, Ar), 128.5 (two signals, Ar), 128.3 (C(1")), 128.2 (Ph), 127.3 (Ph), 125.9 (Ph), 121.9 (C(4)), 120.5 (C(2)), 39.7 (C(3")), 21.5, 21.4 and 21.1 (C(1'), C(1"') and C(1"")).

MS (ESI^+) Calculated for $C_{30}H_{29}NNaO_2S$ $[M+Na]^+$: 490.1811. Found: 490.1814.

FTIR 3255, 3026, 2921, 1599, 1453, 1382, 1306, 1092 cm^{-1}.

*Characteristic n.O.e correlations associated with sulfonamide **653** are represented on the compound structure by red arrows (for n.O.e spectrum see appendix II).*

Methyl 5-(4-methylphenylsulfonamido)-5-phenylpent-2-enoate (668)



A re-sealable reaction tube, fitted with a magnetic follower, was charged with catalyst HG-II (75 mg, 0.12 mmol, 5 mol%) and **647** (742 mg, 2.48 mmol). The tube was then sealed with a

rubber septum and purged with argon. Argon sparged CH_2Cl_2 (24.80 mL) methyl acrylate 667 (1.12 mL, 12.40 mmol) were then added sequentially via syringe. The rubber septum was then replaced with a screw cap and the tube was heated at 55 ^oC (oil bath temperature) for 72 hours. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the residue was purified directly by FCC (1:0 to 7:3 petrol-EtOAc) to afford the sulfonamide **668** (634 mg, 71%) as a white solid.

^{1}H NMR (400MHz, $CDCl_3$) 7.56 (2H, d, *J* = 8.0 Hz, Ar), 7.18-7.08 (5H, m, Ar, Ph), 7.08-6.99 (2H, m, Ph), 6.68 (1H, dt, *J* = 16.0, 7.5 Hz, C(3)H), 5.76 (1H, dt, *J* = 16.0, 1.5 Hz, C(2)H), 5.73 (1H, d, *J* = 7.5 Hz, NH), 4.43 (1H, dt, *J* = 7.5, 7.0 Hz, C(5)H), 3.66 (3H, s, C(1')H_3), 2.73-2.64 (1H, m, C(4)H_2), 2.64-2.55 (1H, m, C(4)H_2), 2.35 (3H, s, C(1")H_3).

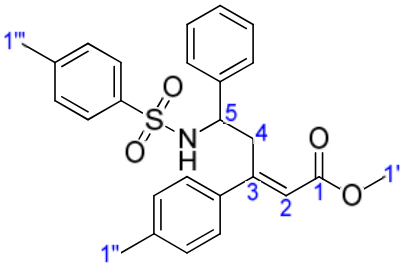
^{13}C NMR (100MHz, $CDCl_3$) 166.2 (C(1)), 143.3 (C(3)), 143.1 (*i*-Ar), 139.5 (*i*-Ph), 137.2 (*i*-Ar), 129.3 (Ar), 128.5 (Ph), 127.6 (Ph), 126.9 (Ar), 126.4 (Ph), 124.1 (C(2)), 57.0 (C(5)), 51.4 (C(1')), 39.8 (C(4)), 21.4 (C(1")).

MS (ESI^+) Calculated for $C_{19}H_{21}NNaO_4S$ $[M+Na]^+$: 382.1083. Found: 382.1084.

FTIR 3227, 1703, 1459, 1330, 1301, 1180 cm^{-1}.

MP 91-92 ^oC (CH_2Cl_2-petrol).

Methyl 5-(4-methylphenylsulfonamido)-5-phenyl-3-(p-tolyl)pent-2-enoate (669)



A reaction tube, fitted with magnetic follower, was charged with Pd_2dba_3 (23 mg, 0.02 mmol, 5 mol%), *t*-$Bu_3P{\cdot}HBF_4$ (30 mg, 0.10 mmol), ester **668** (183 mg, 0.51 mmol) and 4-Br-Tol (218 mg, 1.28 mmol). The tube was sealed with a septum and purged with argon.

Anhydrous PhMe (5.10 mL) and then Cy_2NMe (0.16 mL, 0.76 mmol) were added sequentially *via* syringe and the mixture was then heated at 100 ^oC for 2 hours. The mixture was cooled to room temperature, concentrated *in vacuo* and purified by FCC (1:0 to 7:3 petrol-EtOAc) to afford the sulfonamide **669** (149 mg, 65%) as a pale yellow foam.

^{1}H NMR (400MHz, $CDCl_3$) 7.40 (2H, d, *J* = 8.0 Hz, Ar), 7.24-7.10 (9H, m, Ar, Ph), 7.03 (2H, d, *J* = 8.0 Hz, Ar), 6.50 (1H, d, *J* = 6.5 Hz, NH), 6.08 (1H, s, C(2)H), 4.36 (1H, ddd, *J* = 11.0, 7.0, 4.0 Hz, C(5)H), 3.81 (3H, s, C(1')H_3), 3.76 (1H, dd, *J* = 13.5, 11.0 Hz, C(4)H_2), 2.94 (1H, dd, *J* = 13.5, 4.0 Hz, C(4)H_2), 2.40 (3H, s, C(1")H_3), 2.35 (3H, s, C(1"')H_3).

^{13}C NMR (100MHz, $CDCl_3$) 168.5 (C(1)), 155.6 (C(3)), 142.3 (*i*-Ar), 142.0 (*i*-Ar), 139.8 (*i*-Ph), 138.1 (*i*-Ar), 136.3 (*i*-Ar), 129.4 (Ar), 129.0 (Ar, Ph), 128.3 (Ar, Ph), 127.2 (Ph), 126.8 (Ar), 126.7 (Ar, Ph), 126.2 (Ar, Ph), 118.9 (C(2)), 57.2 (C(5)), 51.8 (C(1')), 38.8 (C(4)), 21.4 (C(1"')), 21.2 (C(1")).

MS (ESI^+) Calculated for $C_{26}H_{27}NNaO_4S$ $[M+Na]^+$: 472.1553. Found: 472.1539.

FTIR 3290, 2923, 1713, 1694, 1625, 1606, 1455, 1331, 1119 cm^{-1}.

Appendices

Appendix I: Tables of optimisation

Optimisation for the CM reaction of β,γ-unsaturated-ketone 486.

entry	catalyst	loading (mol %)	solvent	concentration (M)	enone (mol %)	temperature (ºC)	time (hours)	yield (%)
1	HG-II	10.00%	CH_2Cl_2	0.25	500	20	16	10%
2	HG-II	10.00%	CH_2Cl_2	0.25	500	55	24	46%
3	HG-II	5.00%	CH_2Cl_2	0.1	1000	55	13	57%
4	HG-II	5.00%	CH_2Cl_2	0.1	1000	100	16	0%
5	HG-II	5.00%	CH_2Cl_2	0.1	500	55	24	59%
6	HG-II	10.00%	CH_2Cl_2	0.1	500	20	48	0%
7	Z-1B	10.00%	CH_2Cl_2	0.1	500	20	48	47%
8	HG-II	10.00%	CH_2Cl_2	0.1	500	35	96	52%
9	HG-II	10.00%	PhMe	0.1	500	35	96	15%
10	Z-1B	10.00%	CH_2Cl_2	0.1	500	35	96	59%
11	Z-1B	**10.00%**	**CH_2Cl_2**	**0.1**	**500**	**55**	**96**	**63%**
12	HG-II	10.00%	CH_2Cl_2	0.1	70	35	48	21%
13	Z-1B	10.00%	CH_2Cl_2	0.1	2000	55	24	50%
14	Z-1B	5.00%	CH_2Cl_2	0.1	2000	55	24	45%
15	Z-1B	2.50%	CH_2Cl_2	0.1	2000	55	24	47%
16	HG-II	5.00%	CH_2Cl_2	0.1	100	55	24	22%
17	HG-II	2.50%	CH_2Cl_2	0.1	500	55	72	55%
18	HG-II	5.00%	CH_2Cl_2	0.1	500	65	72	48%
19	HG-II	5.00%	$ClCH_2CH_2Cl$	0.1	500	90	72	14%
20	HG-II	10.00%	CH_2Cl_2	0.05	500	55	24	41%

*Table I.1- Optimisations for the synthesis of α,β-unsaturated-1,5-diketones **489**.*

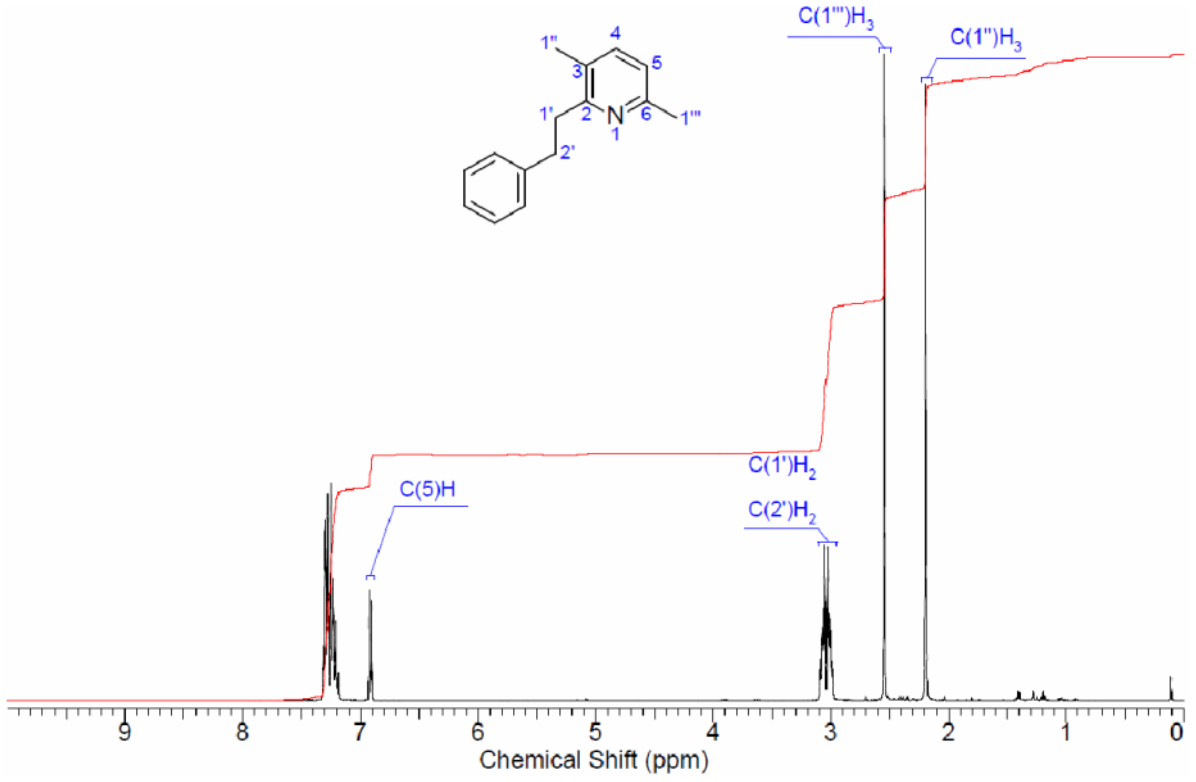
Optimisation for the 6π-electrocyclisation-aromatisation cascade of oxime 538

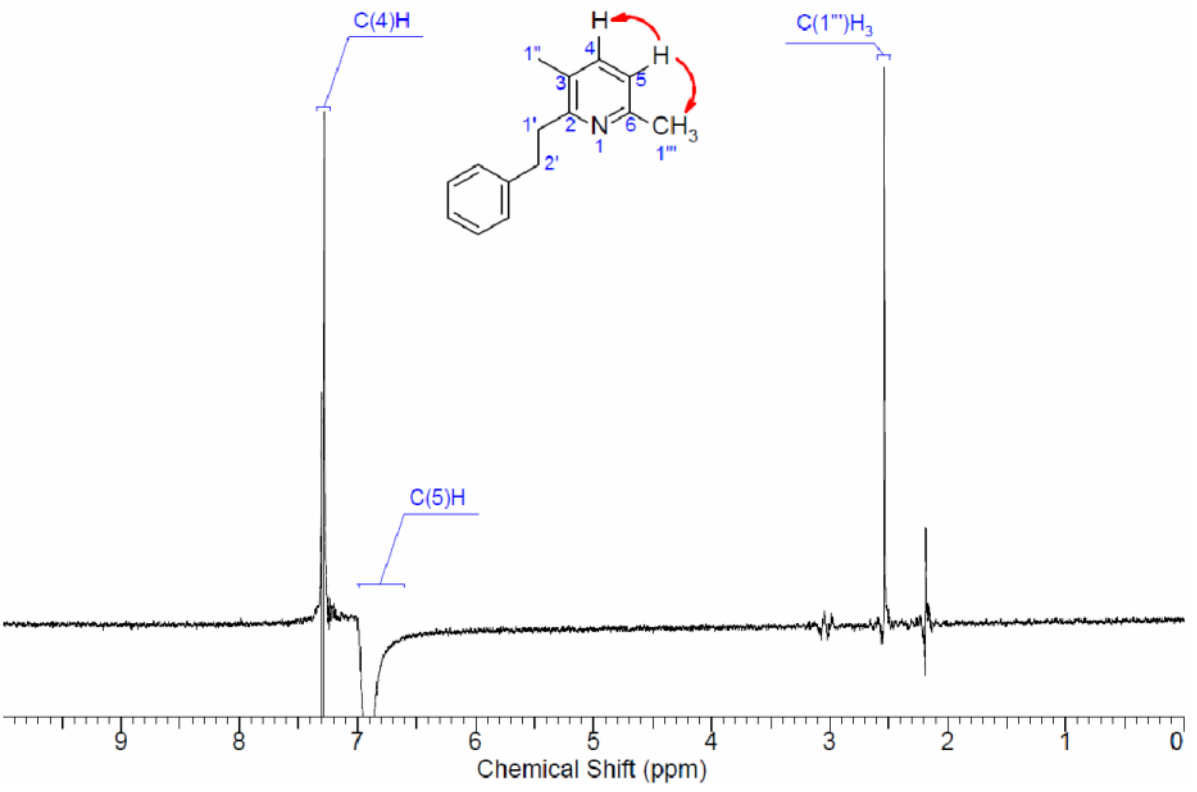
entry	solvent	concentration (M)	catalyst	temperature (ºC)	time (hours)	yield (%)
1	1,2-DCB	0.10	none	180 ºC	16 hours	0%
2	1,2-DCB	1.00	*p*-TsOH (5 mol%.)	180 ºC	16 hours	59%
3	PhMe	0.10	*p*-TsOH (5 mol%.)	120 ºC	24 hours	0%
4	PhMe	0.10	*p*-TsOH (5 mol%) $Cu(OTf)_2$ (20 mol%)	120 ºC	24 hours	0%
5	PhMe	0.10	*n*-Bu_3P (100 mol%)	120 ºC	24 hours	0%
6	*t*-BuOH	0.10	*n*-Bu_3P (100 mol%) $Sc(OTf)_3$ (20 mol%)	85 ºC	24 hours	0 %
7	1,2-DCB	0.10	PPTS (10 mol%.)	180 ºC	16 hours	0%
8	THF	0.10	DBU (100 mol%)	60 ºC	16 hours	0%
9	AcOH	1.00	Ac_2O (1 mL/mmol)	110 ºC	24 hours	0%
10	1,2-DCB	0.10	TFA (110 mol%.)	180 ºC	16 hours	0%
11	**1,2-DCB**	**0.10**	**HCl (200 mol%.)**	**165 ºC**	**24 hours**	**80%**
12	PhMe	0.10	$Ru(PPh_3)_3(CO)H_2$ (5 mol%.) TFA (5 mol%)	110 ºC	16 hours	0%
13	PhMe	0.10	$Ru(PPh_3)_3(CO)H_2$ (5 mol%.) Xantphos (5 mol%)	110 ºC	16 hours	5%
14	PhMe	0.10	$Ru(PPh_3)_3(CO)H_2$ (5 mol%.)	110 ºC	16 hours	0%

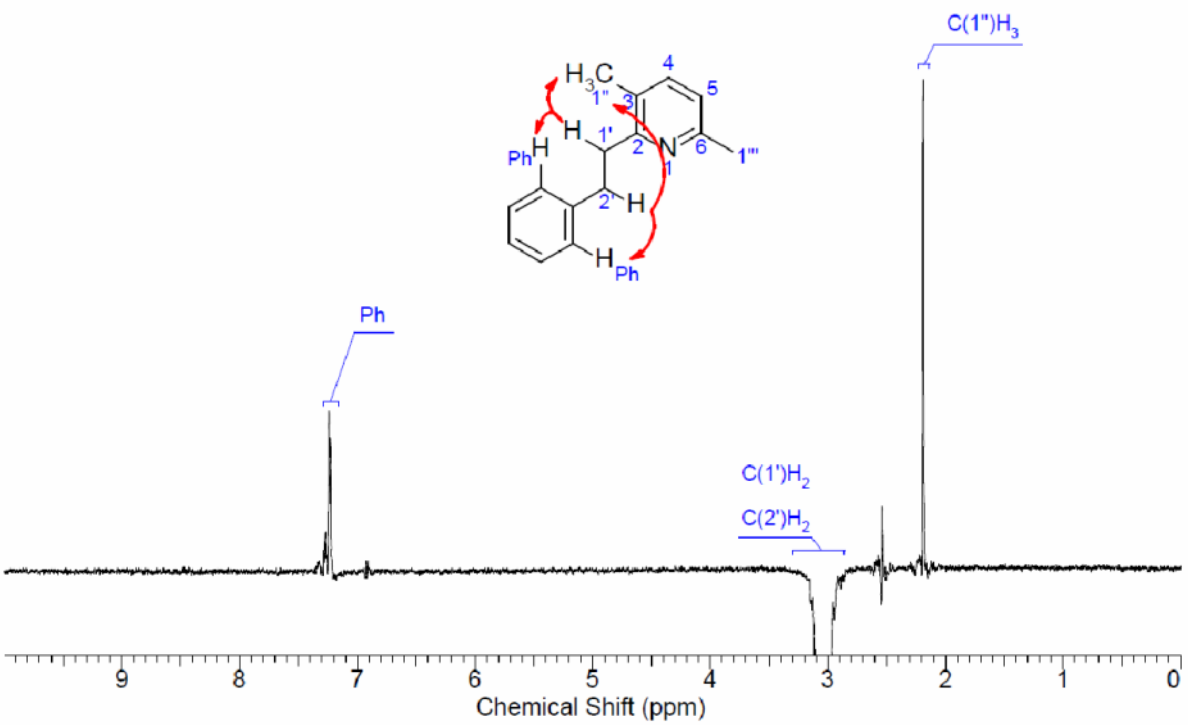
Table I.2*- Conditions for the synthesis of pyridine* ***490****.*

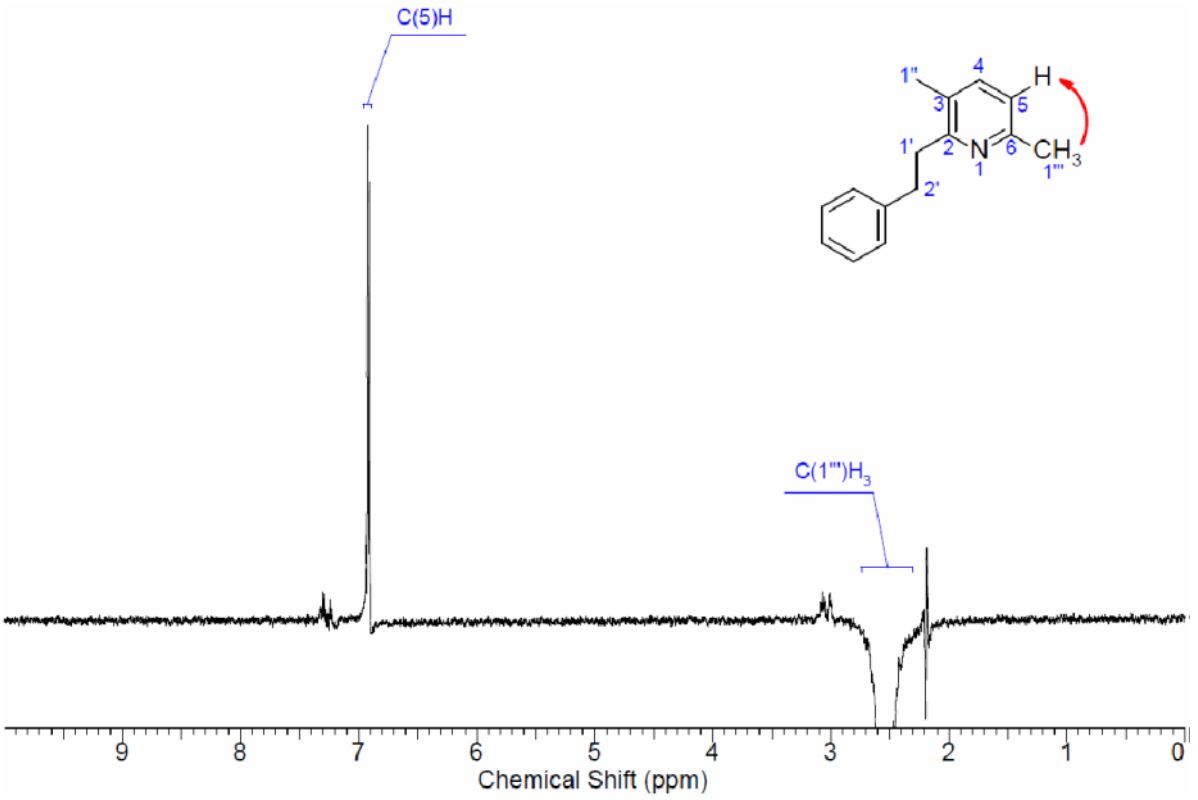
Appendix II: n.O.e spectra

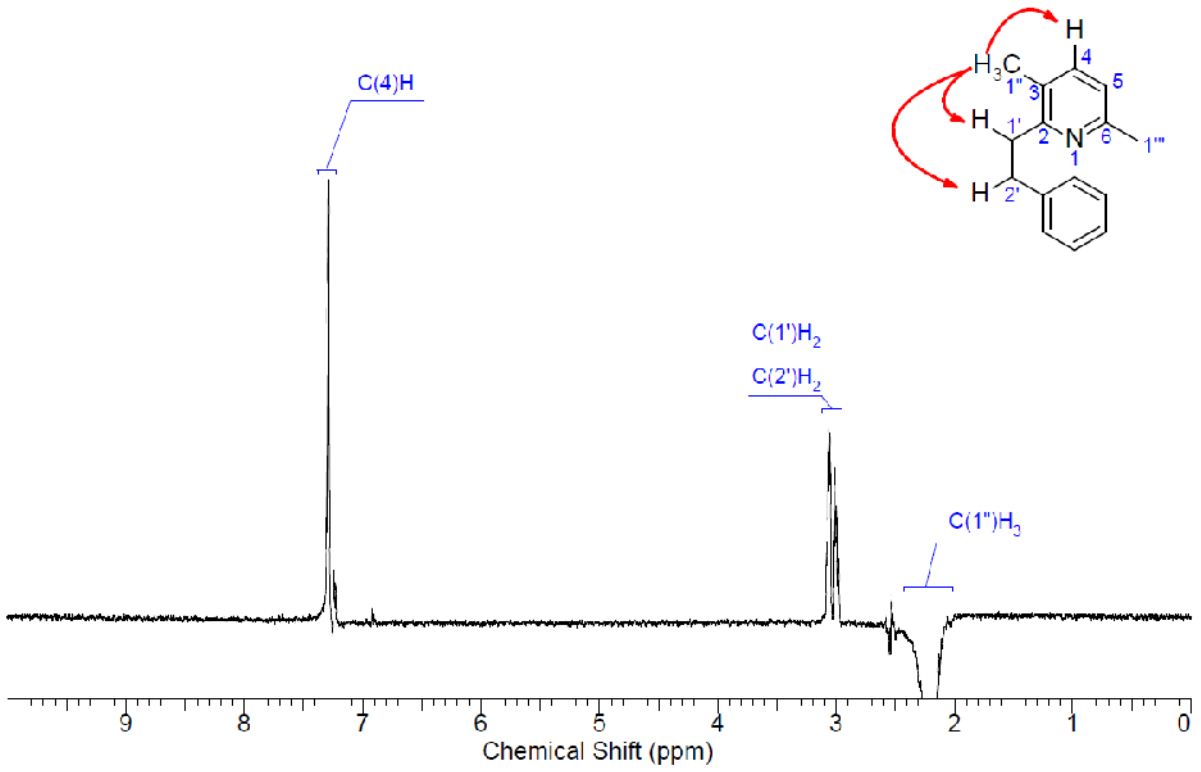
3,6-Dimethyl-2-phenethylpyridine (568)



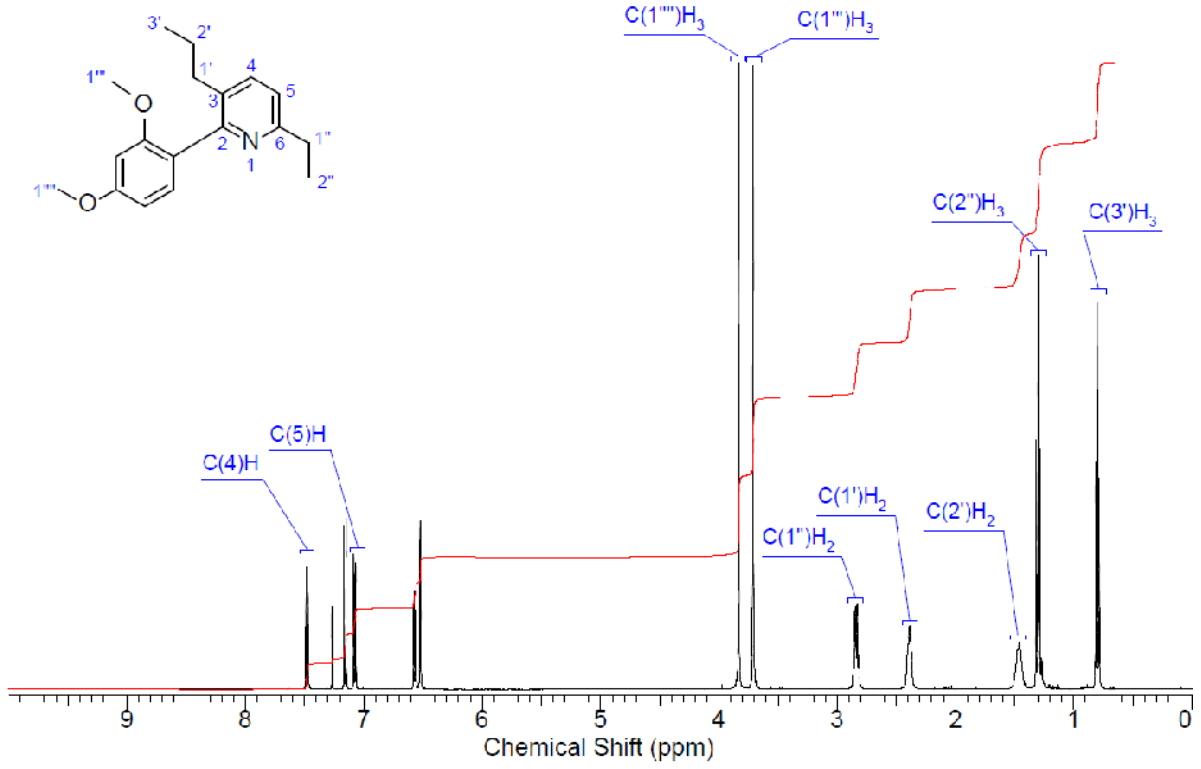


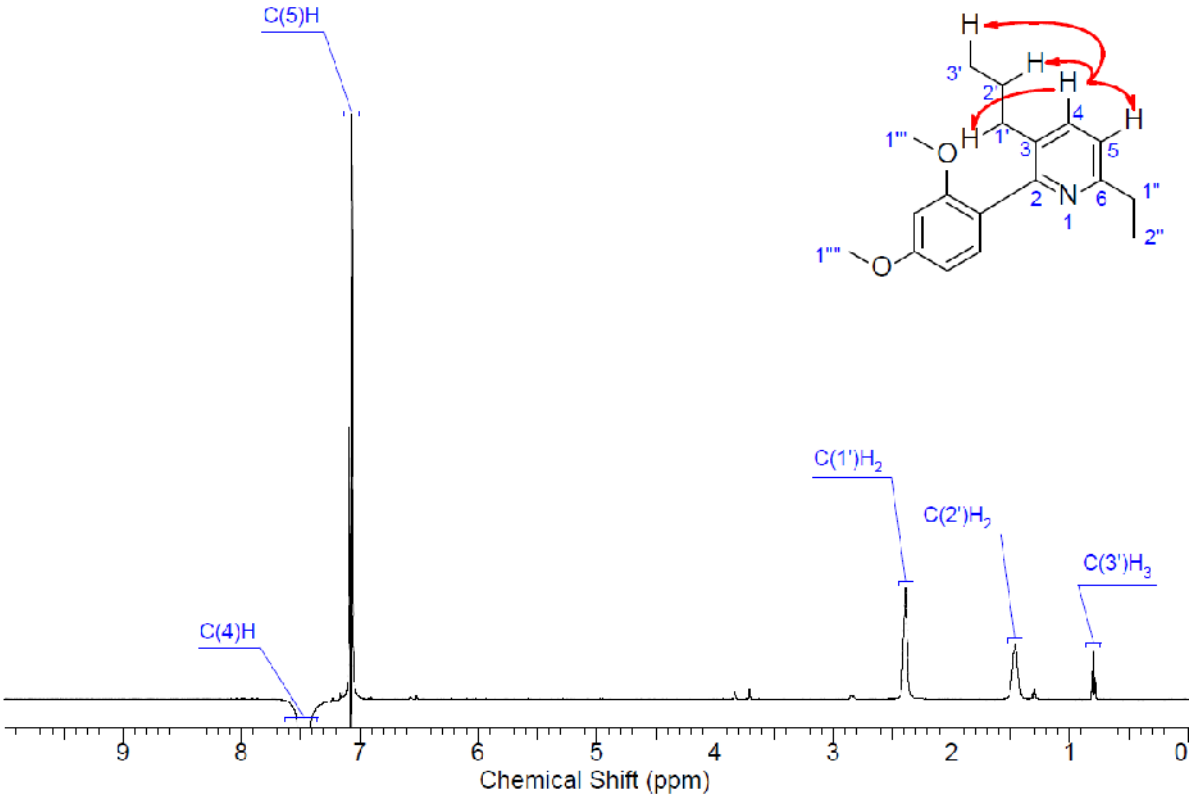

C(1")H3
Ph
C(1')H2
C(2')H2
Chemical Shift (ppm)

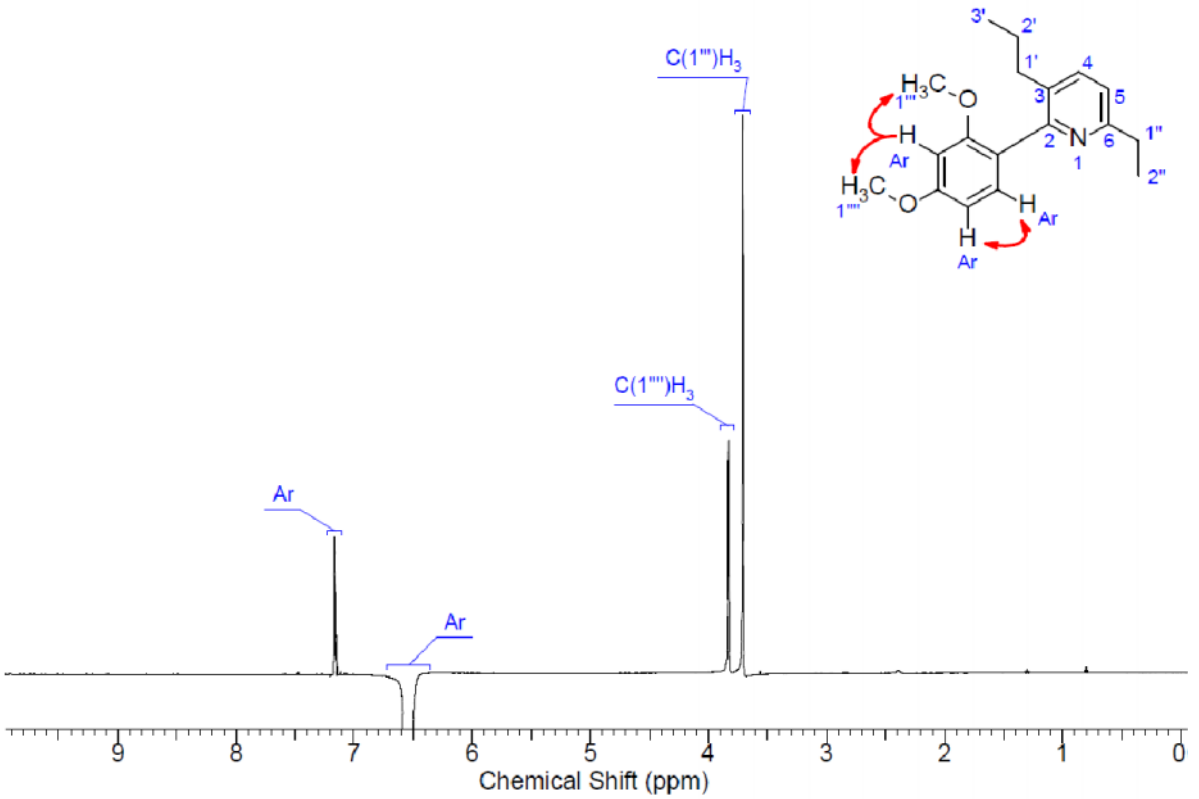

C(5)H
C(1"')H3
Chemical Shift (ppm)

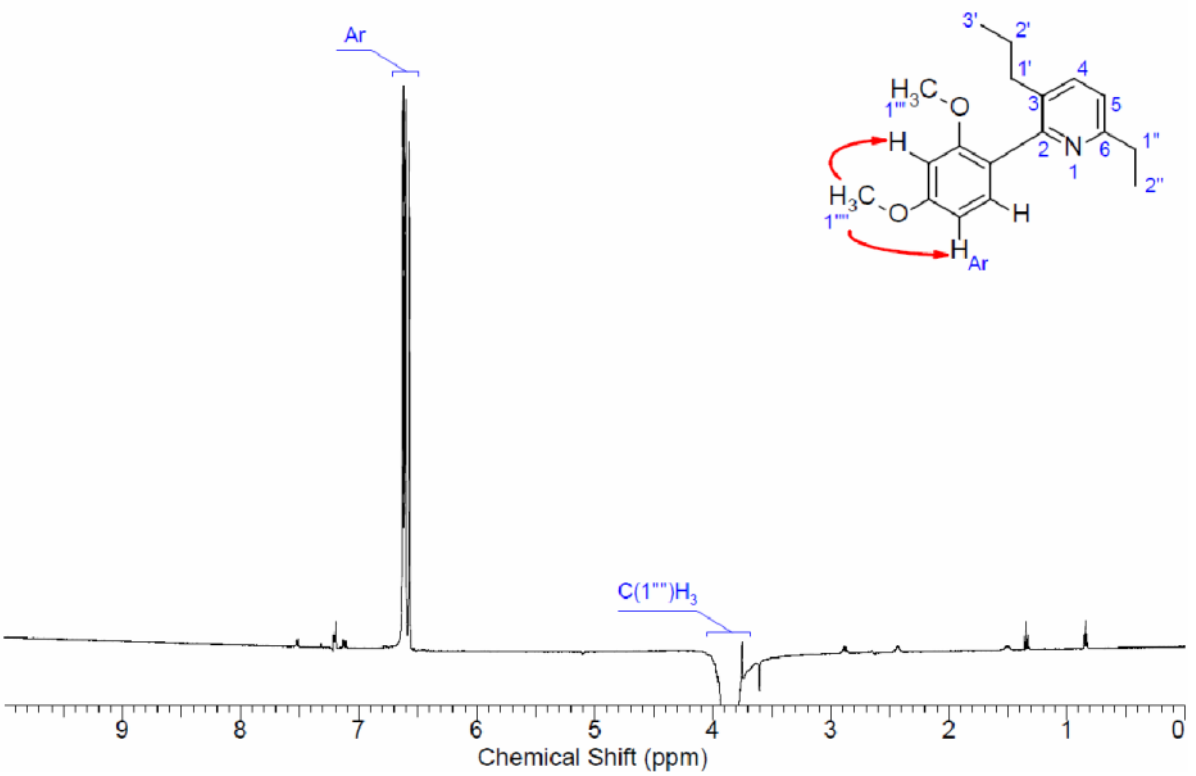


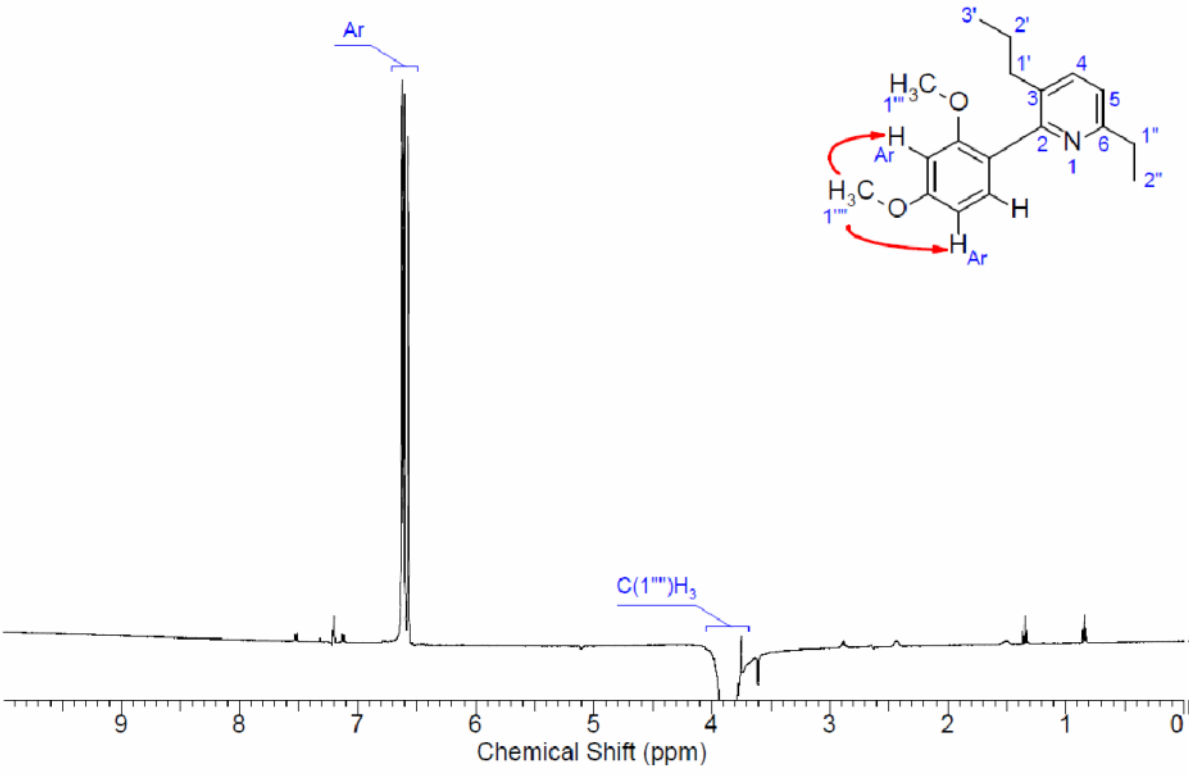
2-(2,4-Dimethoxyphenyl)-6-ethyl-3-propylpyridine (577)

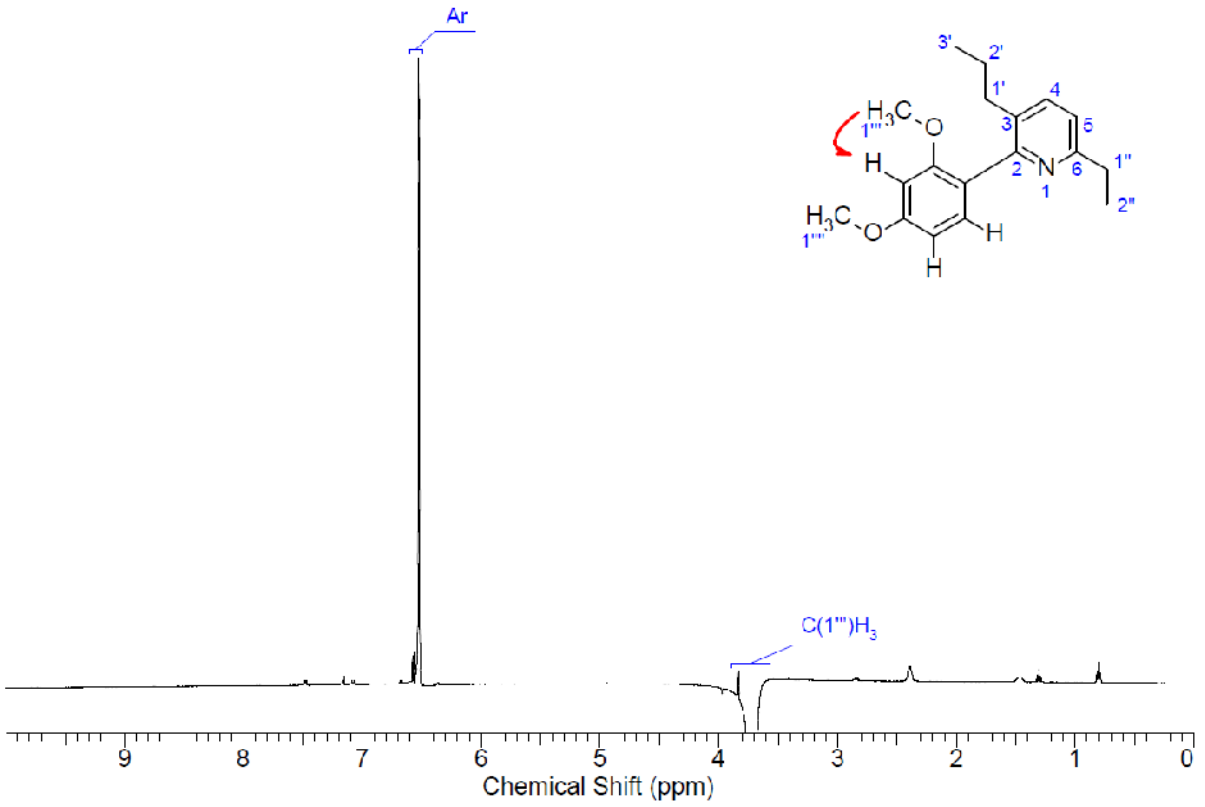


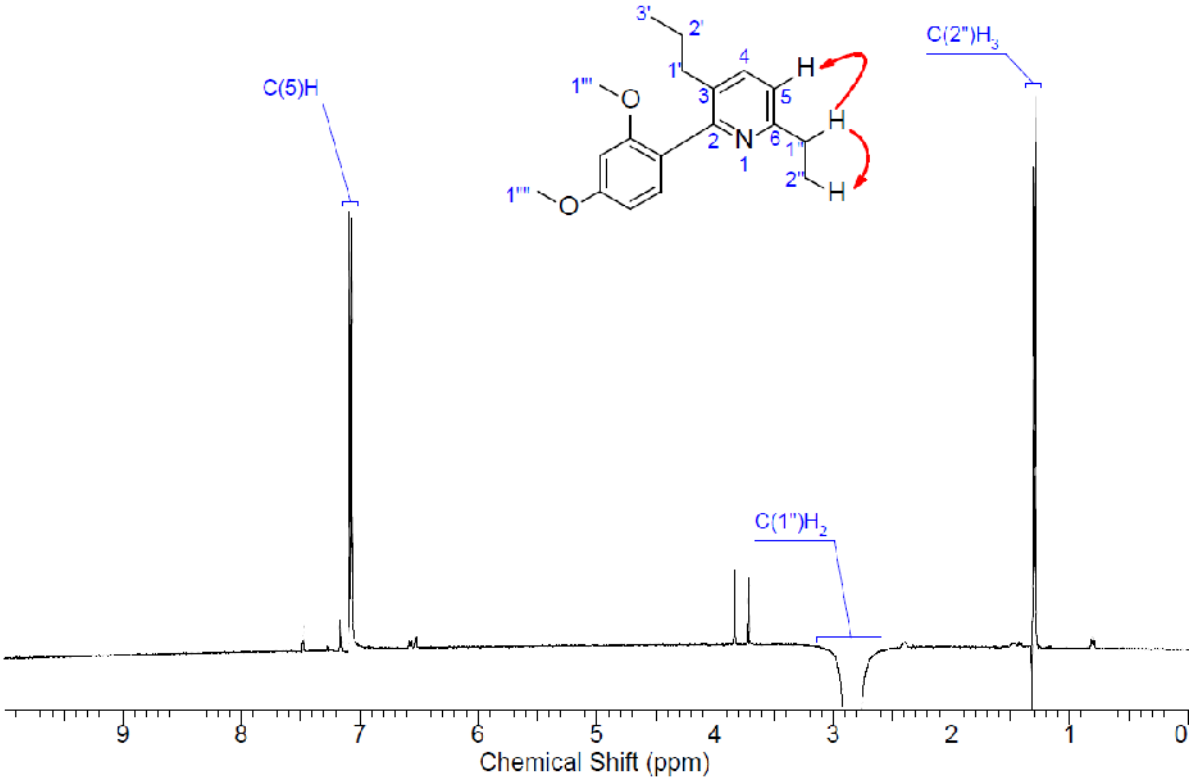

C(5)H
C(1')H2
C(2')H2
C(3')H3
C(4)H
Chemical Shift (ppm)

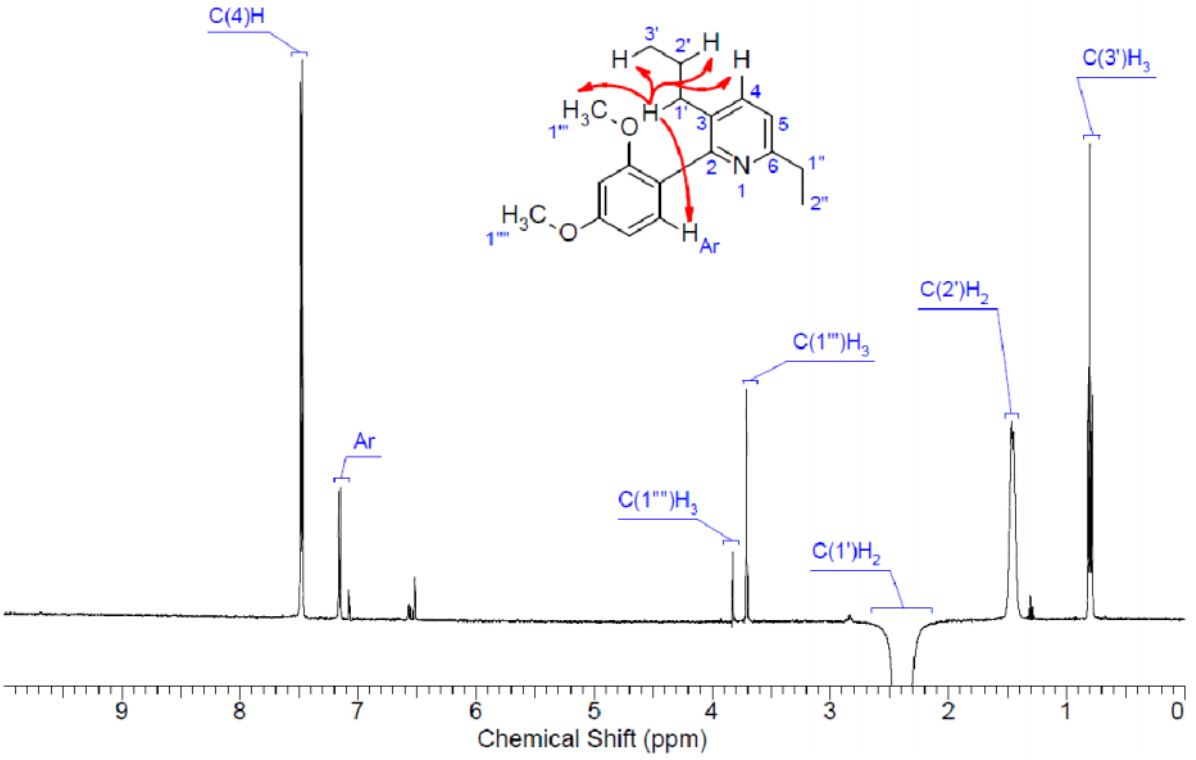

C(1"")H3
C(1"")H3
Ar
Ar
Chemical Shift (ppm)


Ar
C(1"")H3
Chemical Shift (ppm)

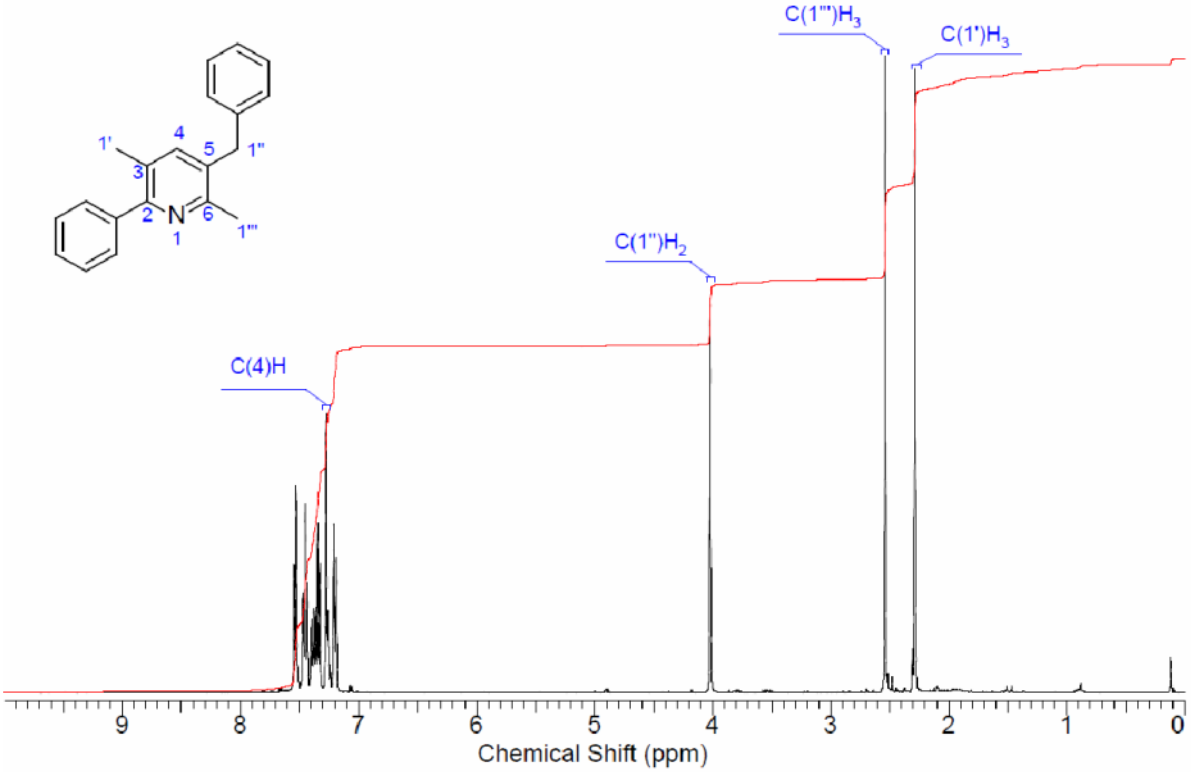

Ar
C(1"")H3
Chemical Shift (ppm)

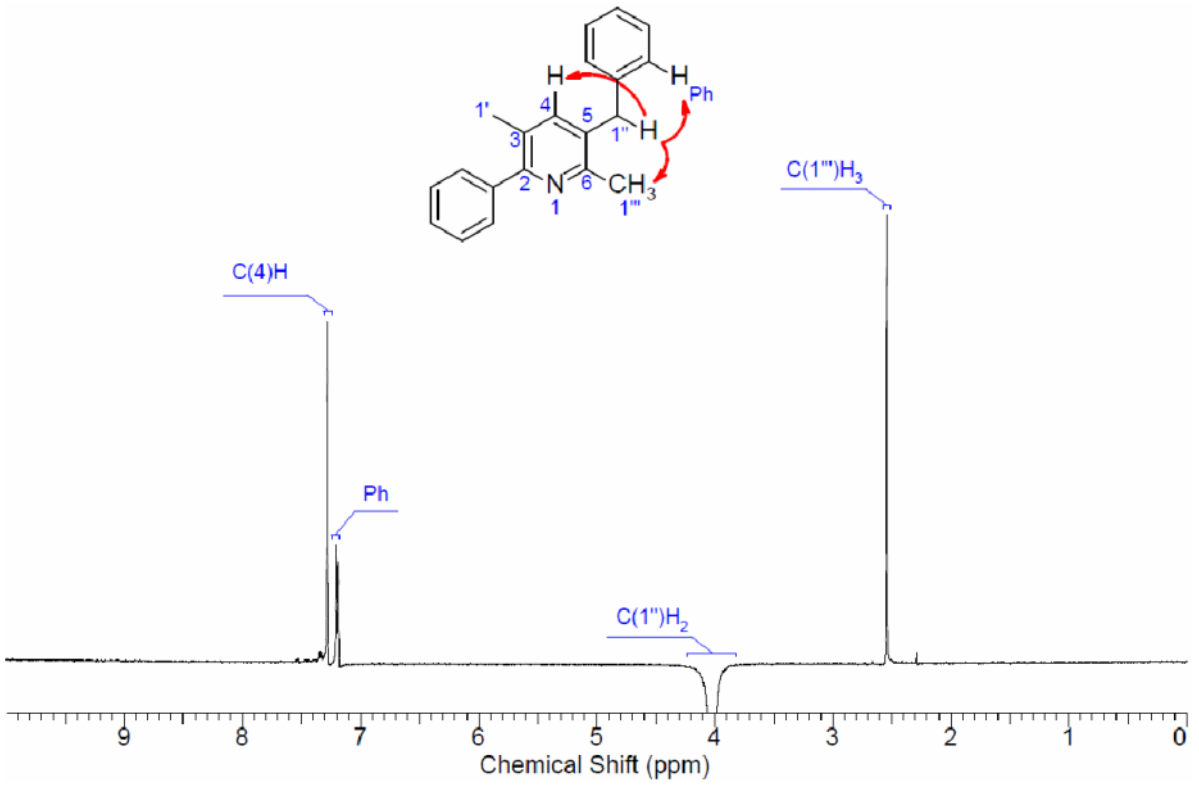

Ar
C(1''')H3
Chemical Shift (ppm)

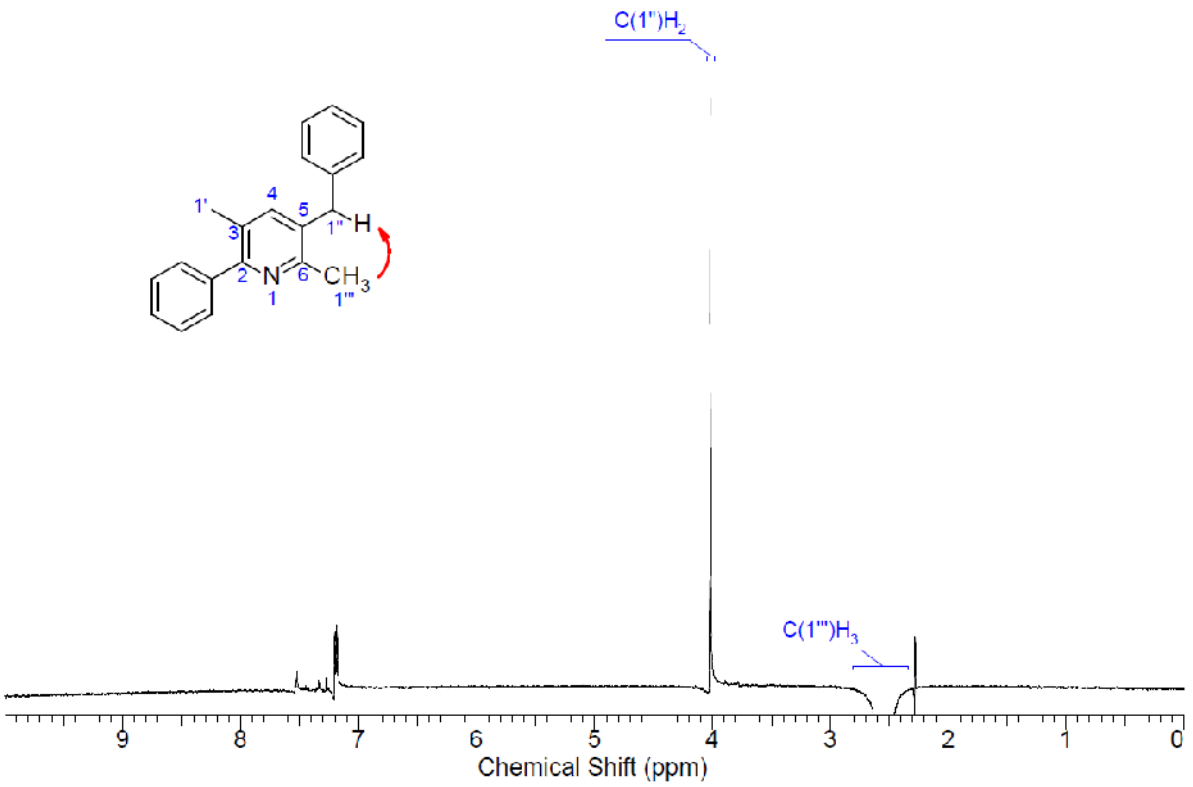

C(5)H
C(2")H3
C(1")H2
Chemical Shift (ppm)

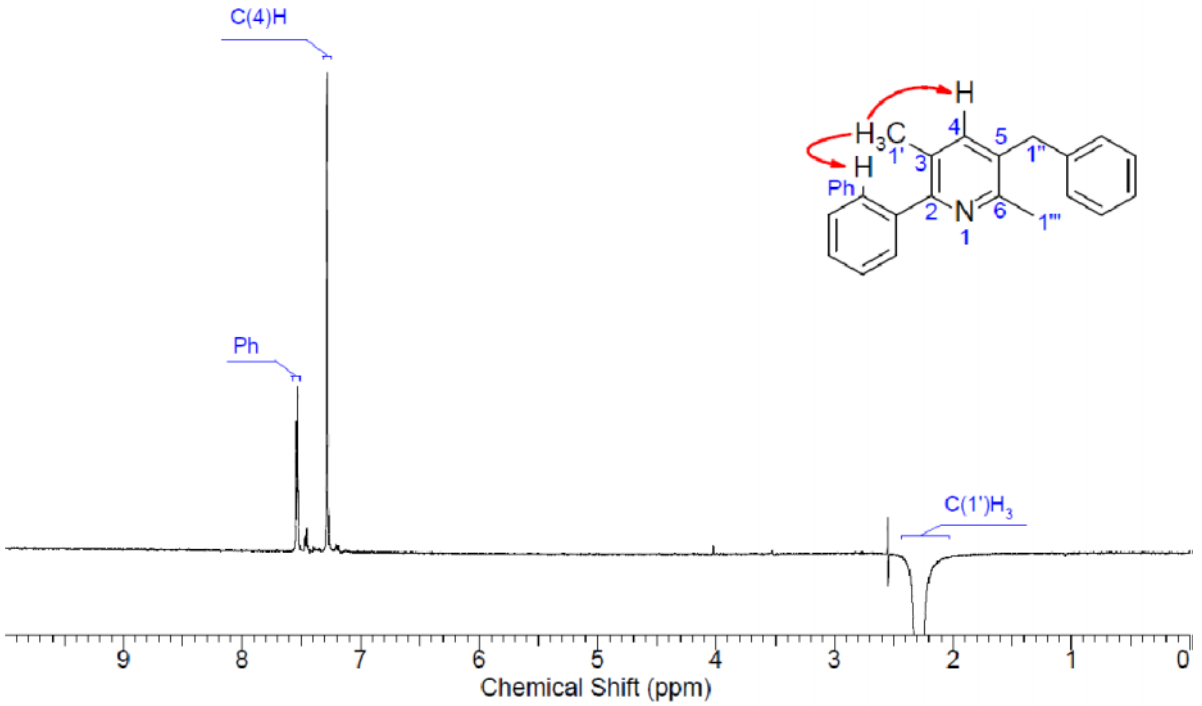


3-Benzyl-2,5-dimethyl-6-phenylpyridine (609)

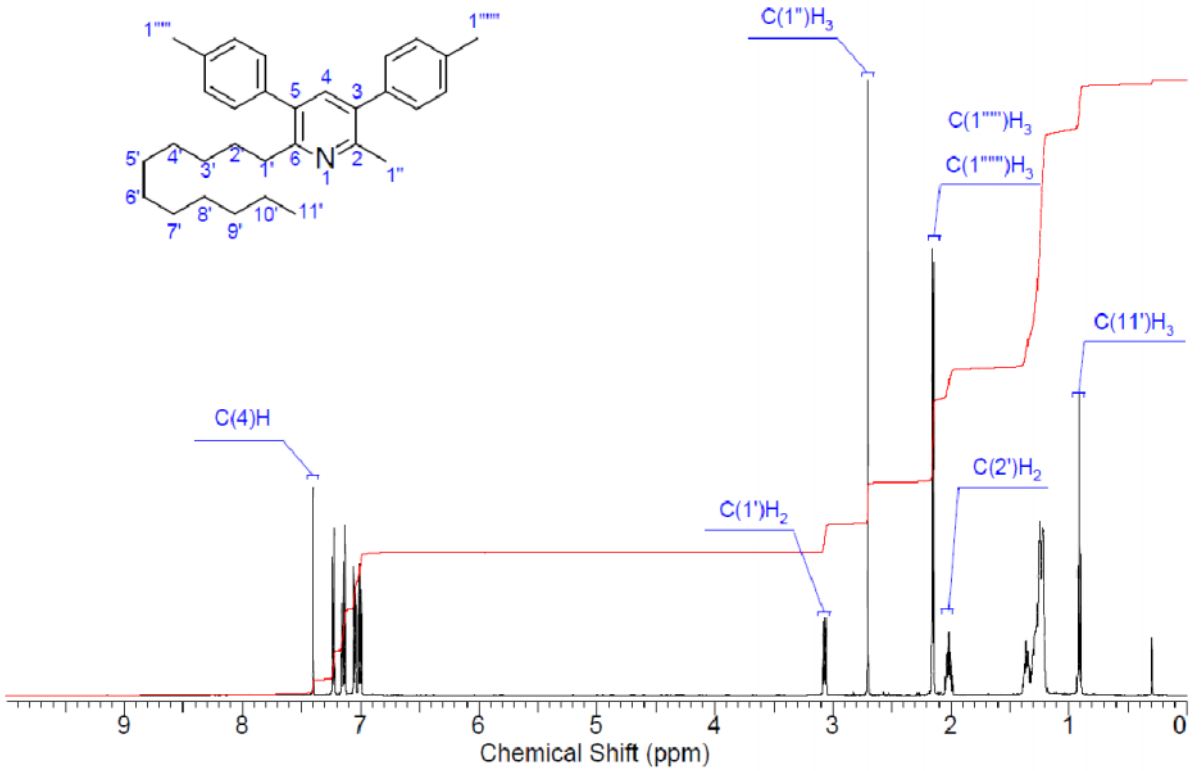


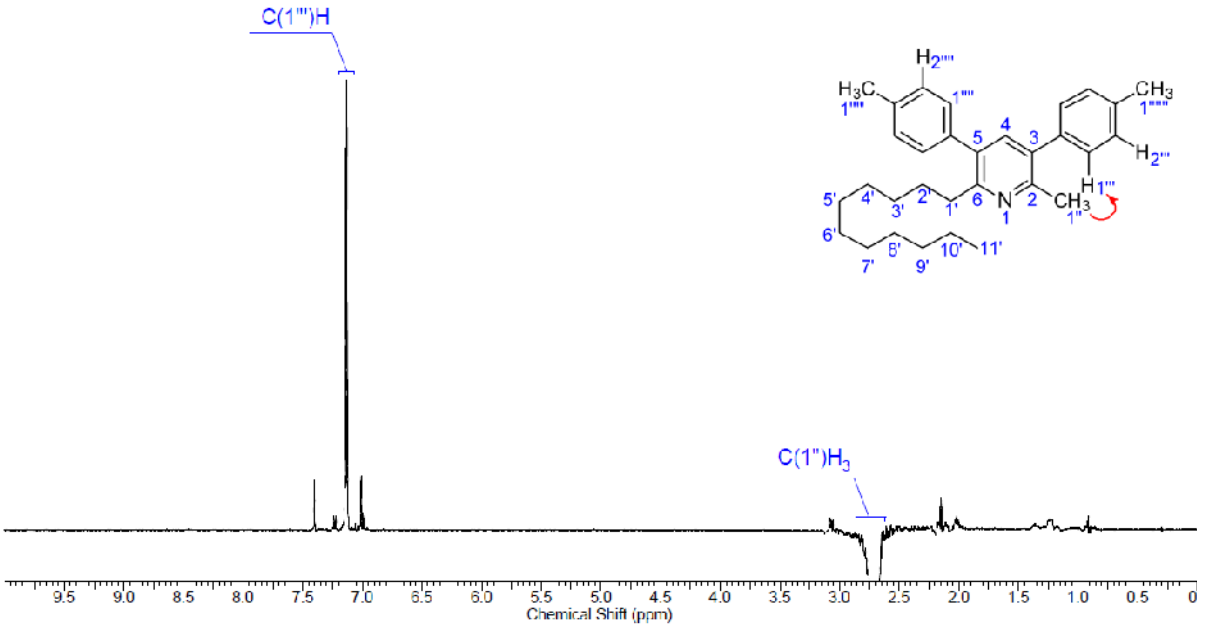

H
H
Ph
1'
4
5
3
1''
H
2
N
6
CH3
1
1'''
C(1''')H3
C(4)H
Ph
C(1'')H2
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

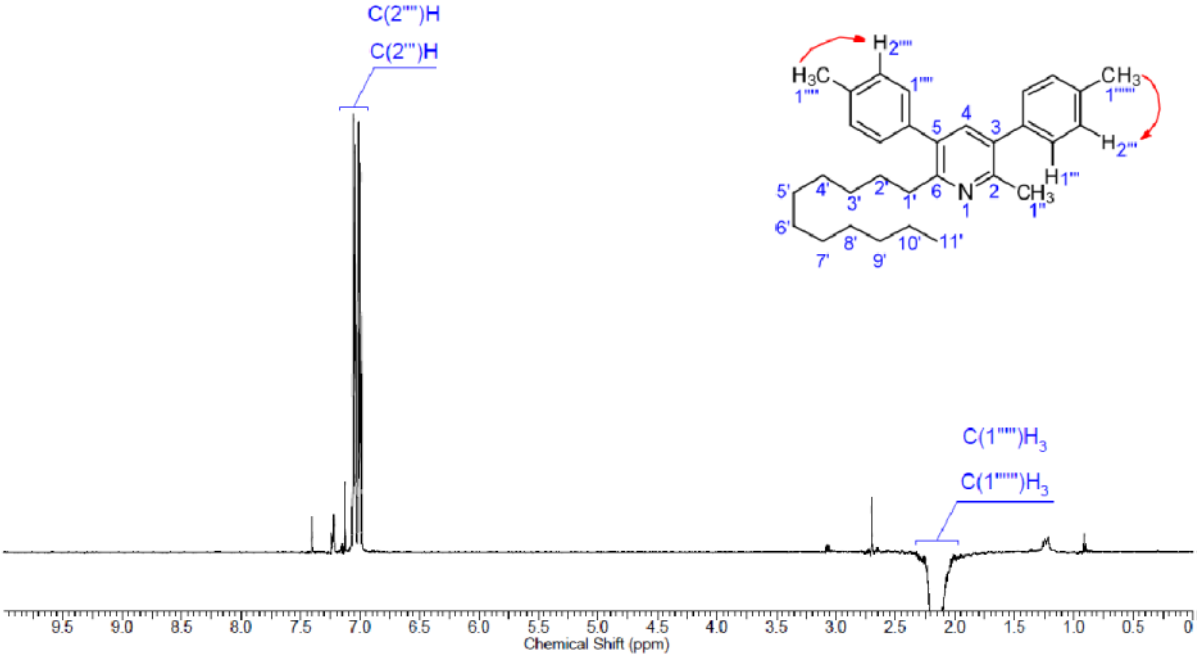

C(1'')H2
1'
4
5
3
1''
H
2
N
6
CH3
1
1'''
C(1''')H3
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)



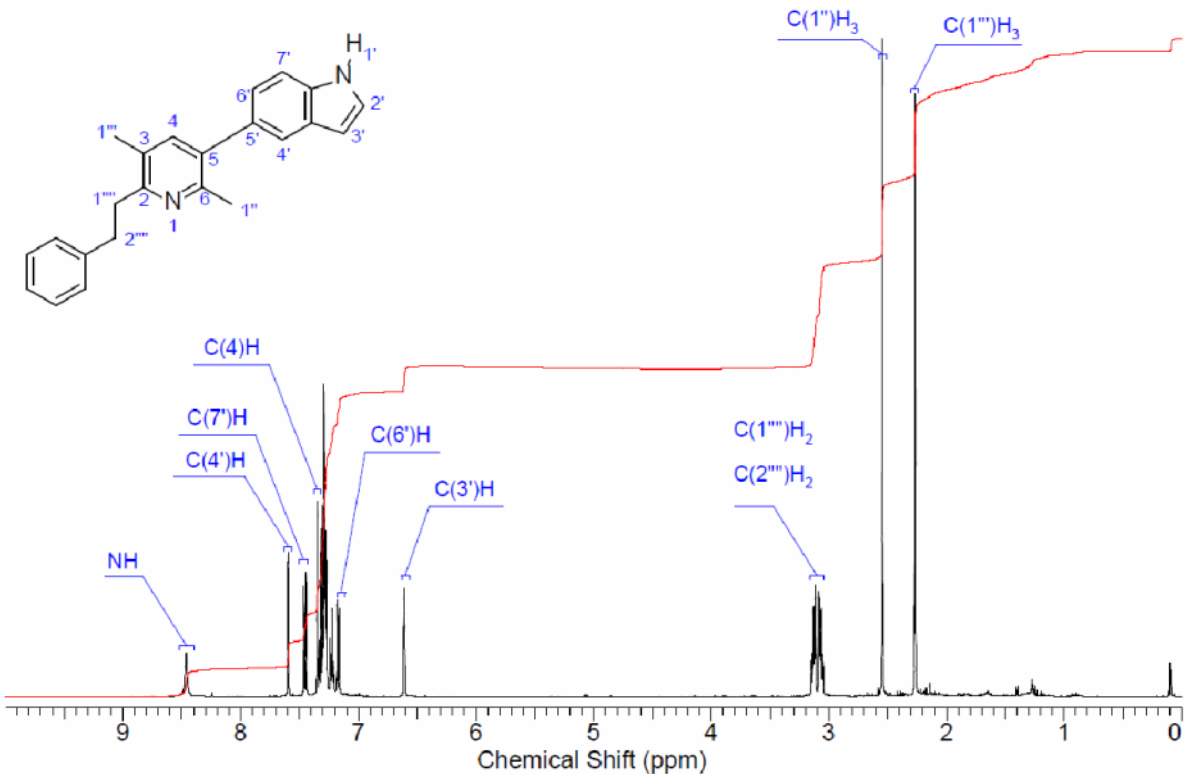
n.O.e specta of 2-methyl-3,5-di-p-tolyl-6-undecylpyridine (612)

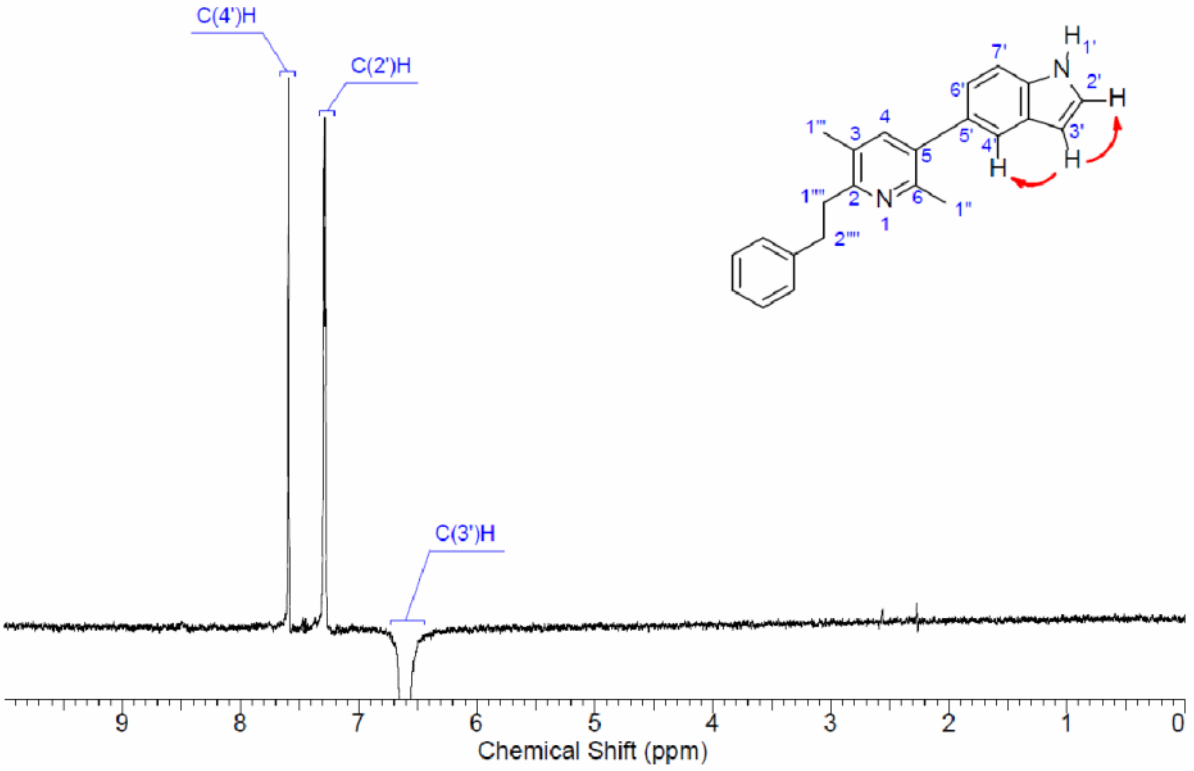


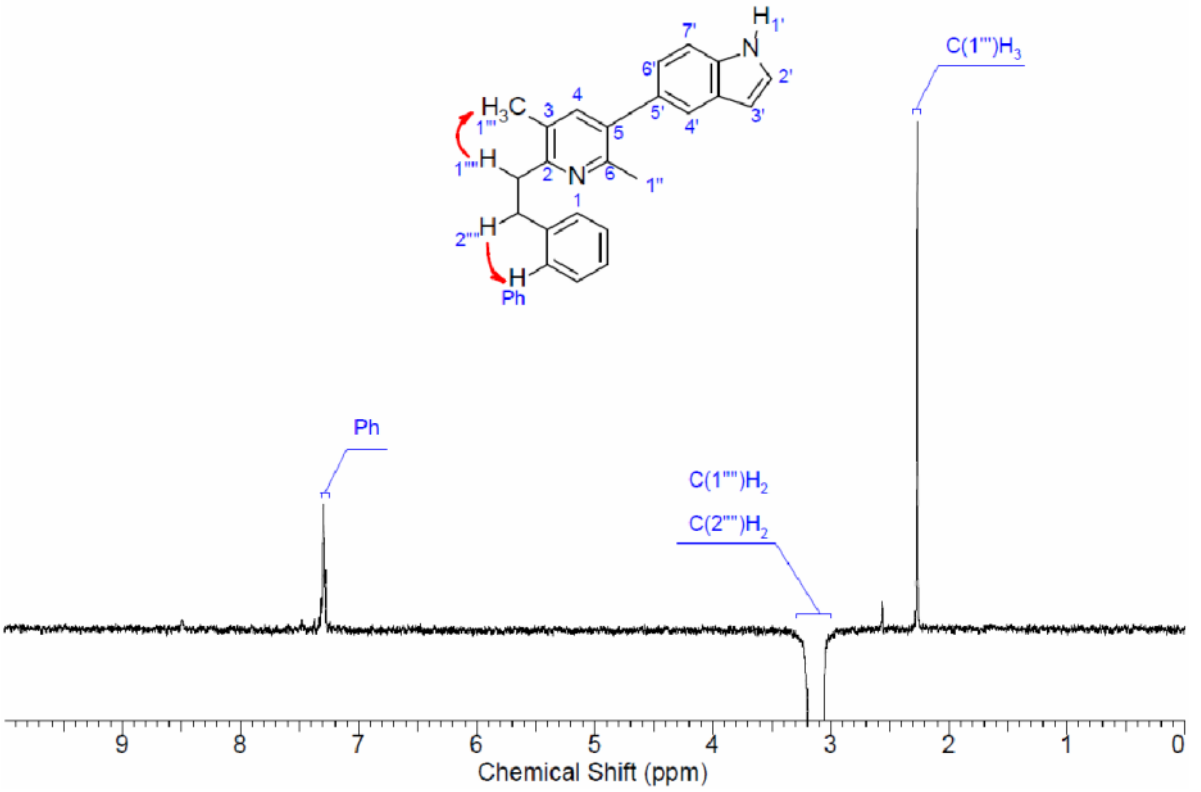

C(1''')H
C(1'')H3
Chemical Shift (ppm)

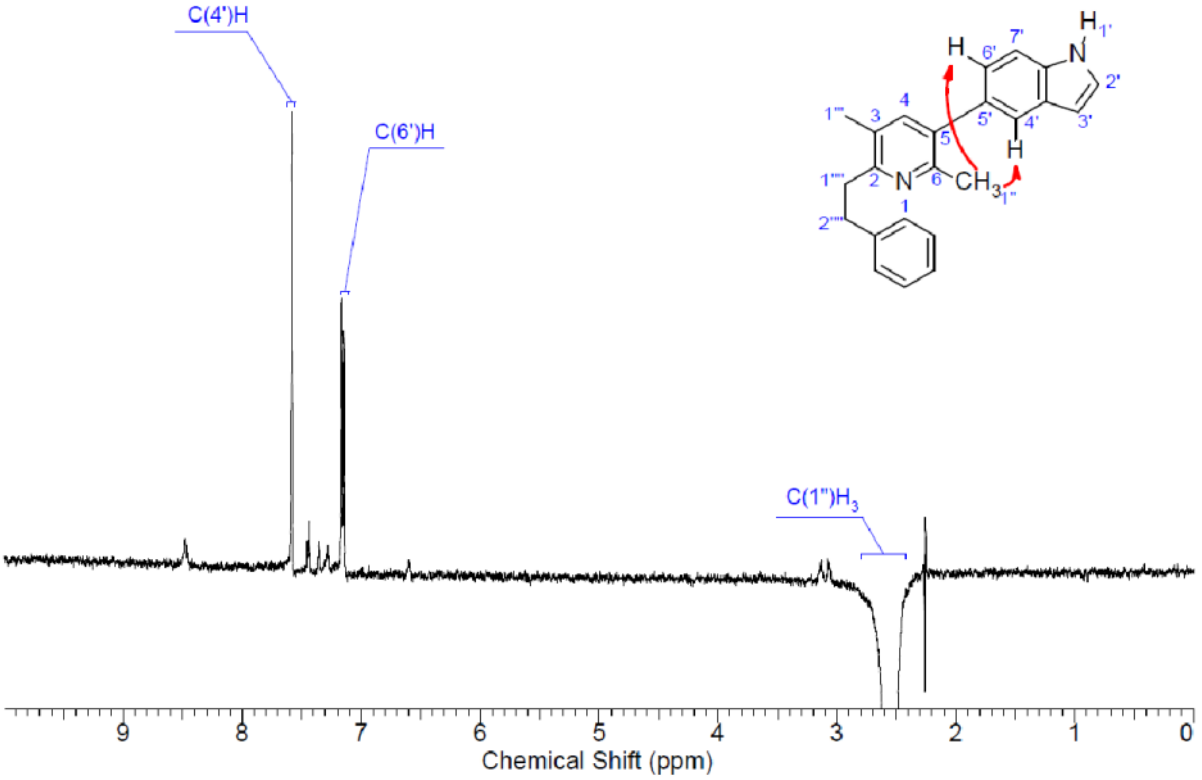

C(2'''')H
C(2''')H
C(1''''')H3
C(1'''''')H3
Chemical Shift (ppm)

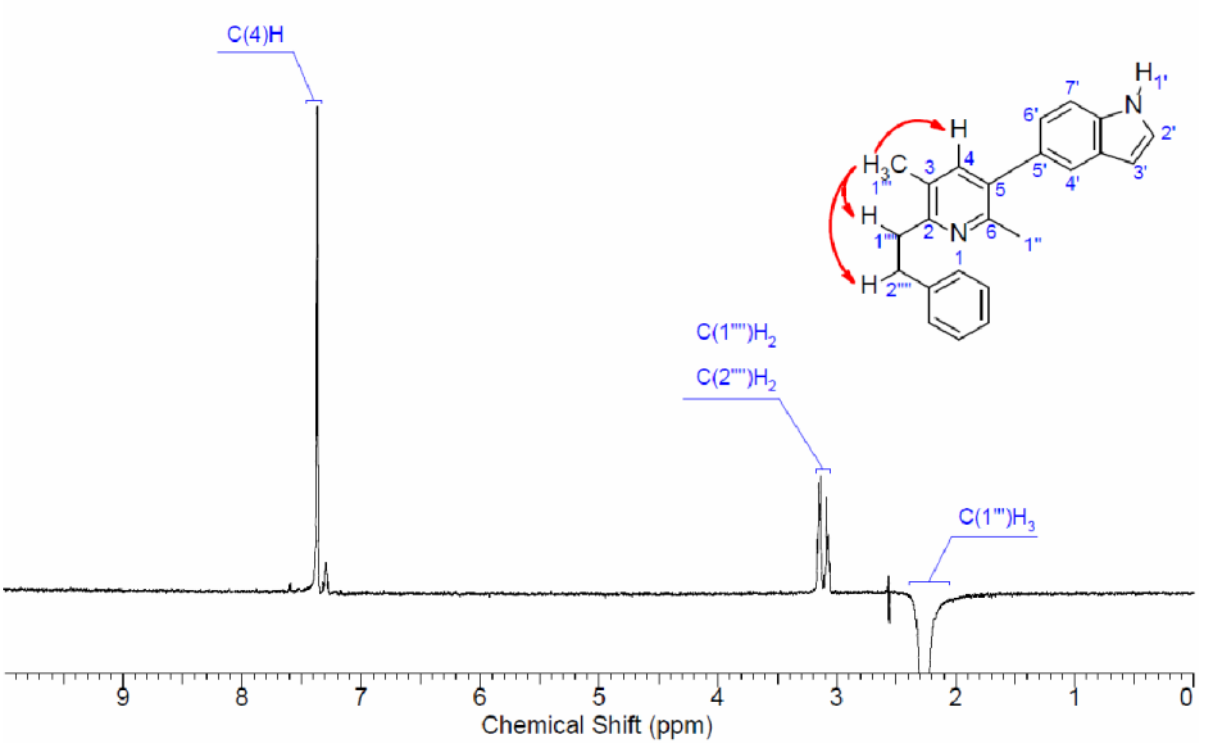
5-(2,5-Dimethyl-6-phenethylpyridin-3-yl)-1*H*-indole (627)



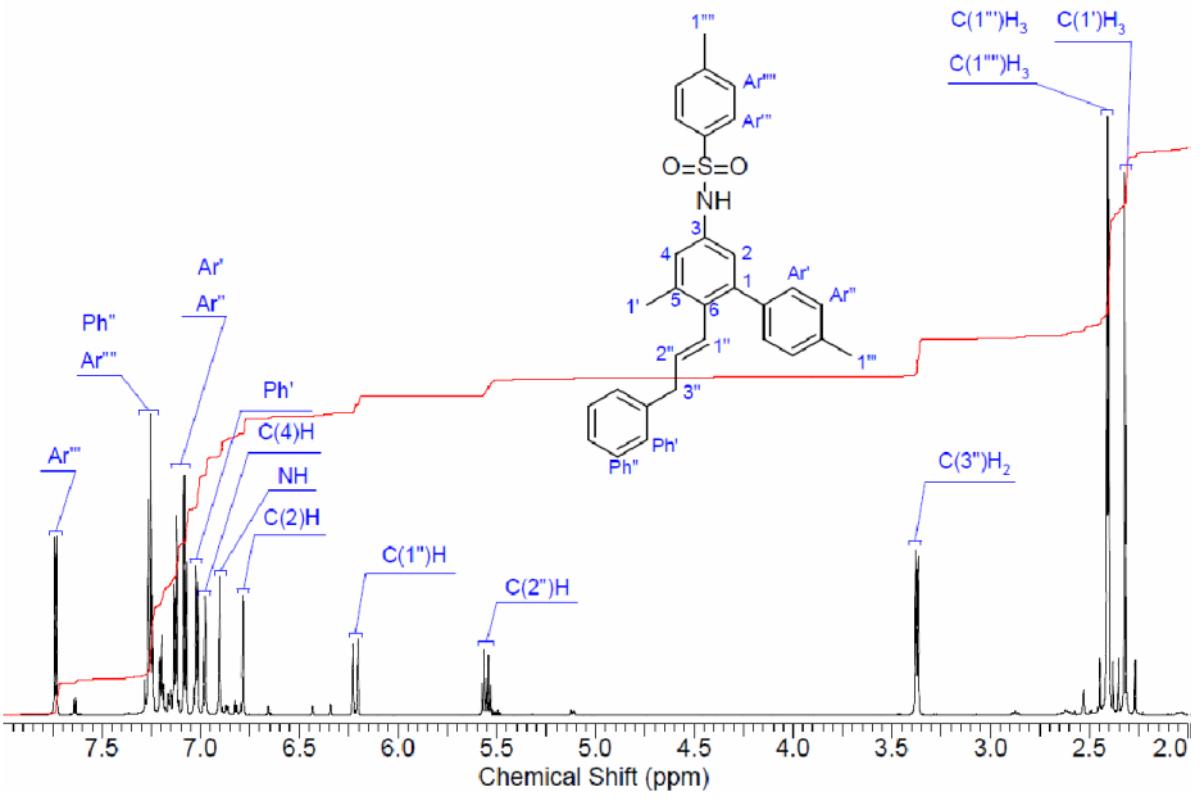


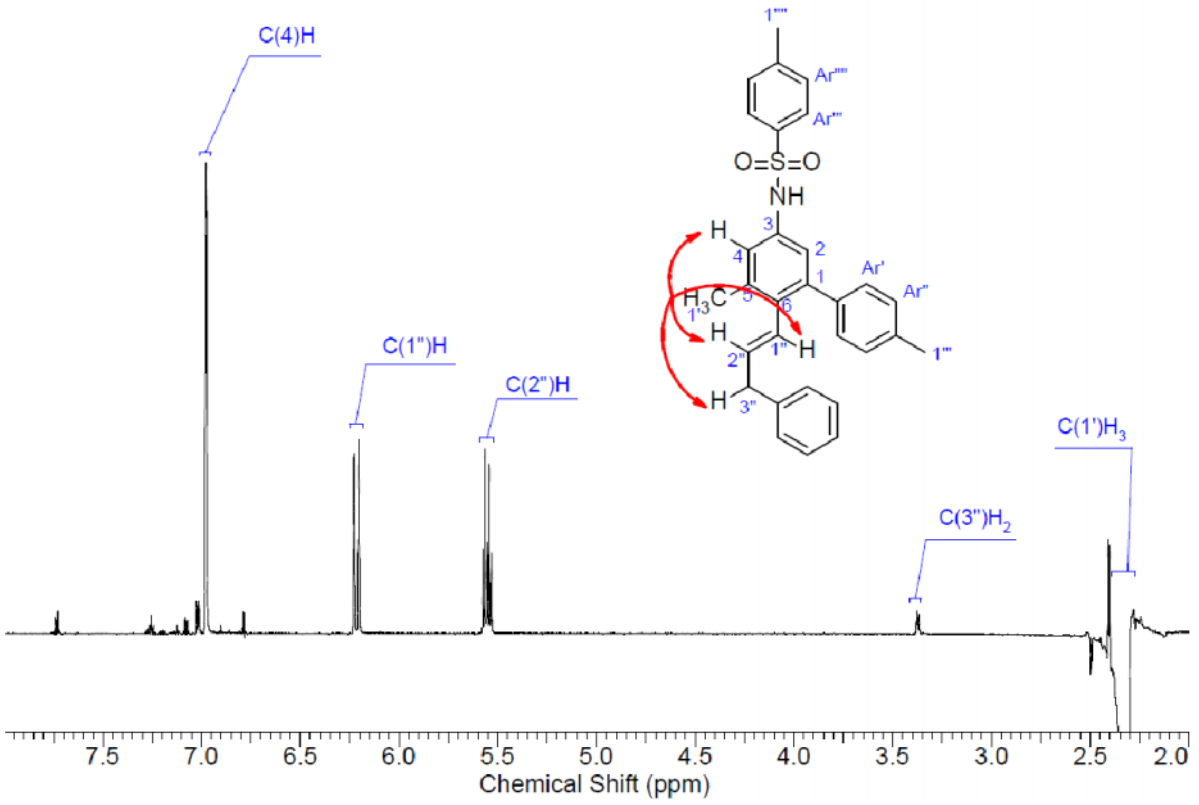

C(1"")H3
Ph
C(1"")H2
C(2"")H2
Chemical Shift (ppm)

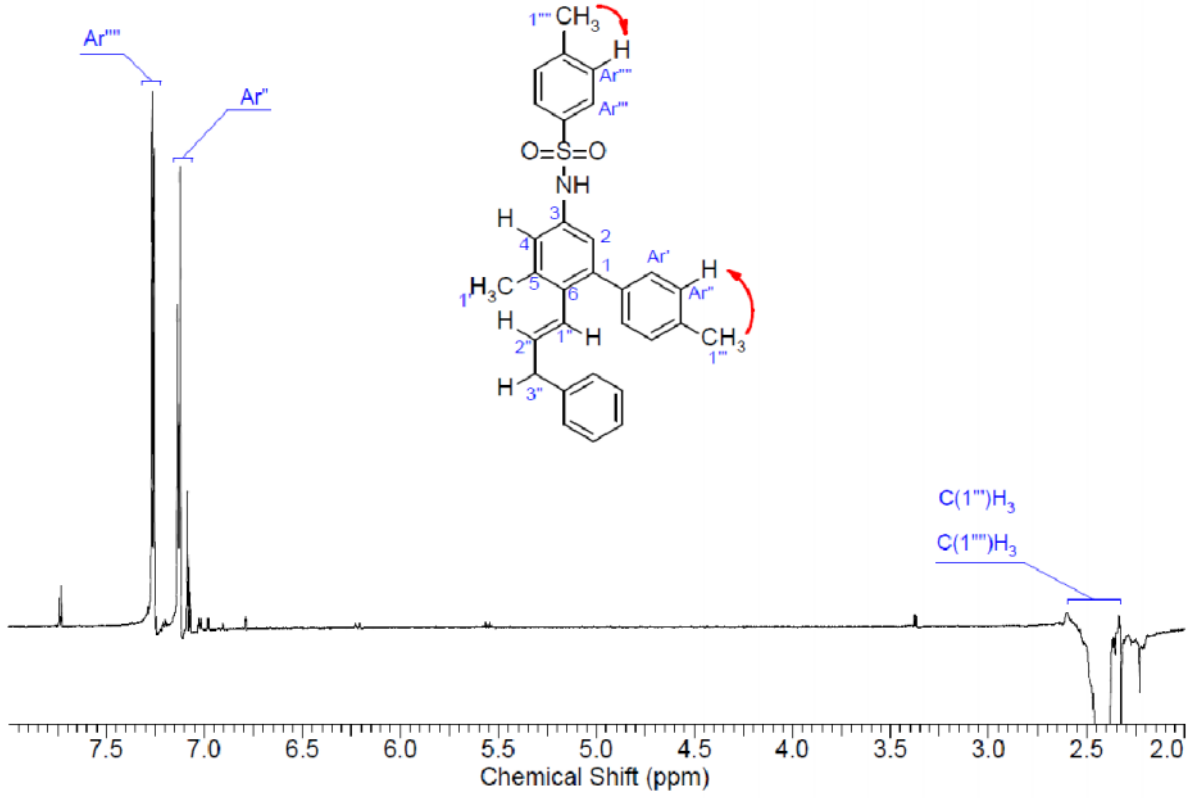

C(4')H
C(6')H
C(1")H3
Chemical Shift (ppm)

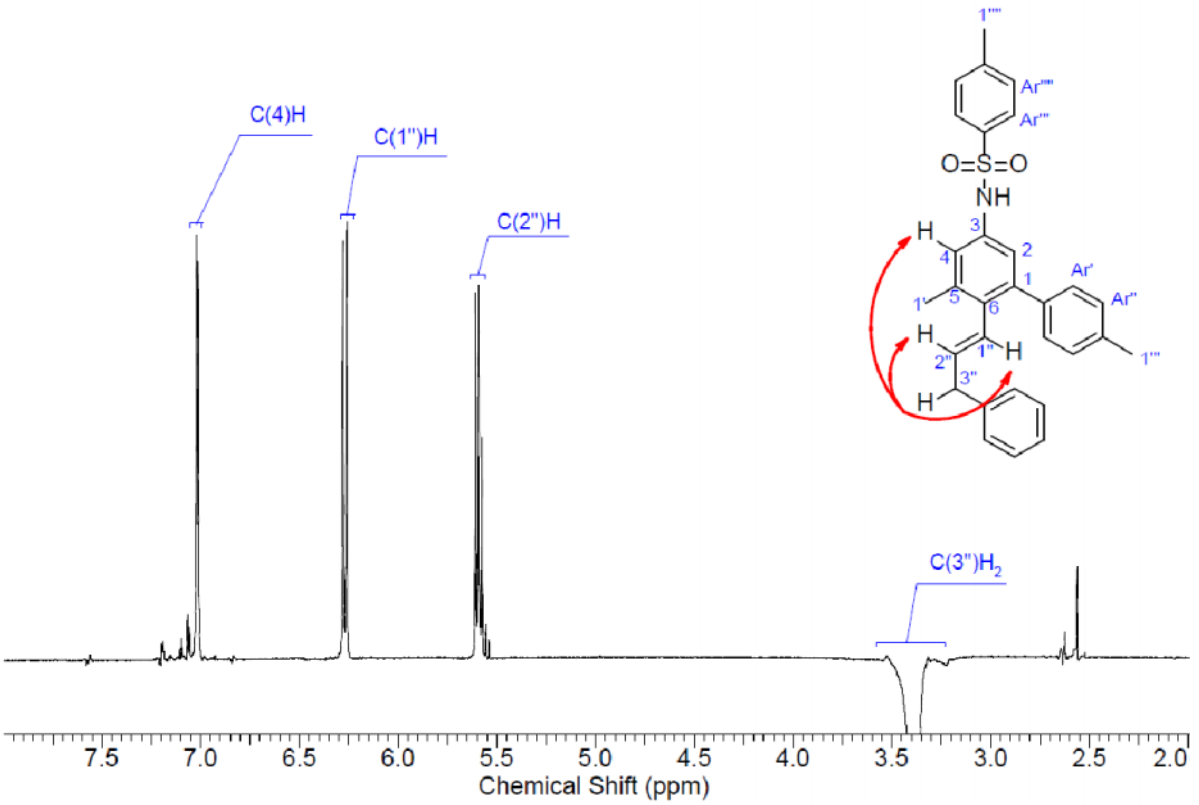


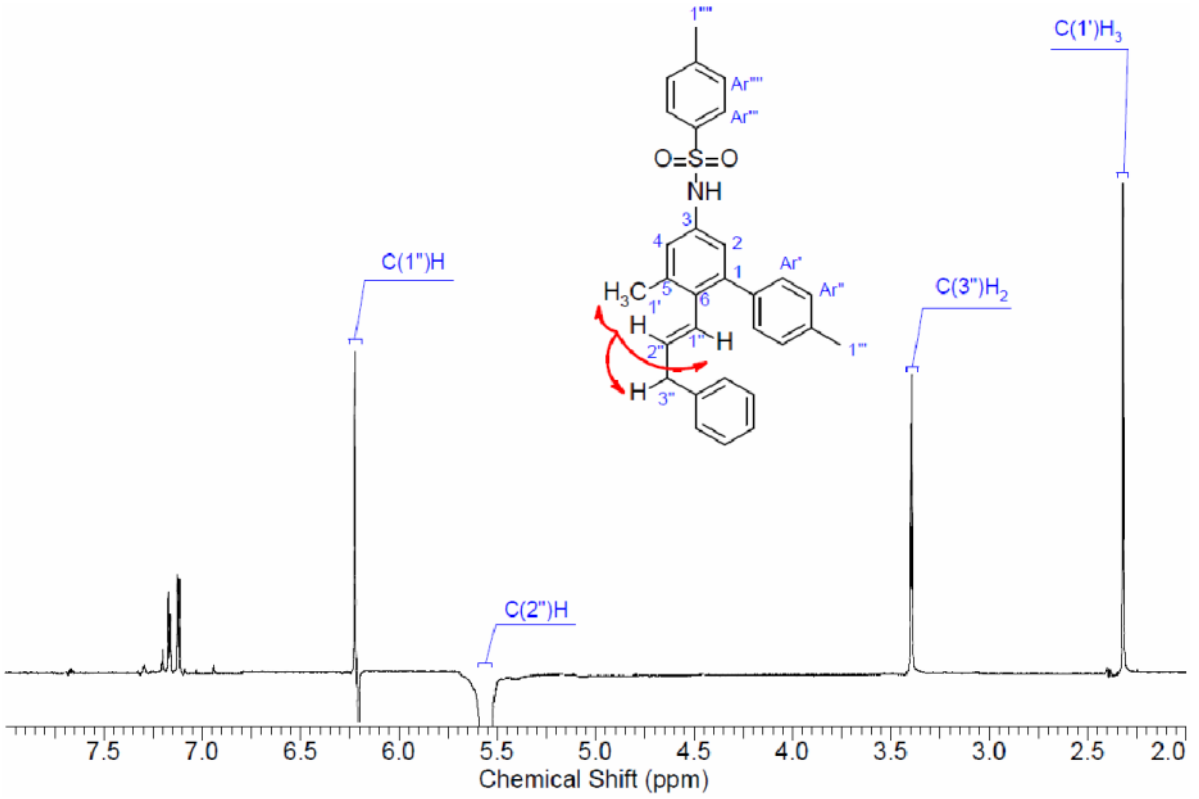
(*E*)-*N*-(4',5-Dimethyl-6-(3-phenylprop-1-en-1-yl)-[1,1'-biphenyl]-3-yl)-4-methylbenzenesulfonamide (653)

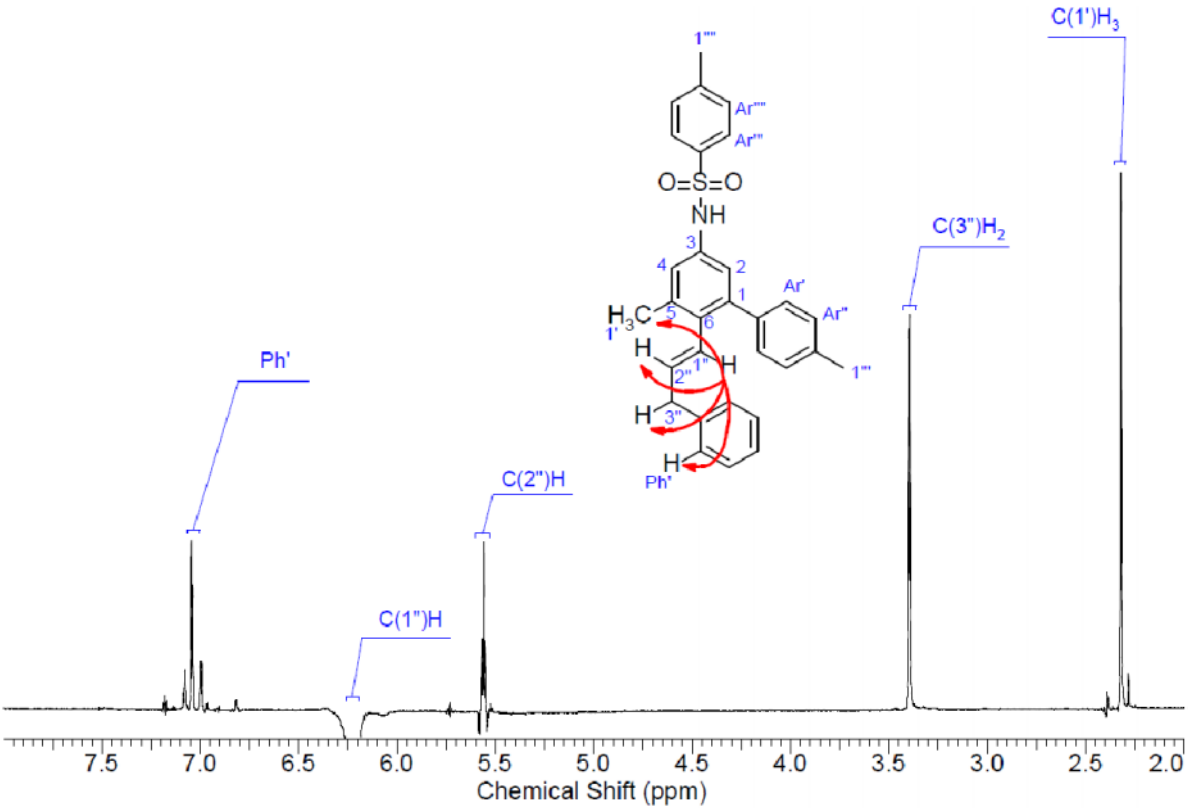



C(4)H
C(1")H
C(2")H
C(1')H3
C(3")H2
1""
Ar""
Ar'''
O=S=O
NH
H
3
4
2
1
Ar'
Ar"
H3C
5
6
1'
H
2"
1"
H
1'''
H
3"
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)


Ar""
Ar"
1"" CH3
H
Ar""
Ar'''
O=S=O
NH
H
3
4
2
1
Ar'
H
Ar"
1'
H3C
5
6
H
2"
1"
H
CH3
1'''
H
3"
C(1''')H3
C(1"")H3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)

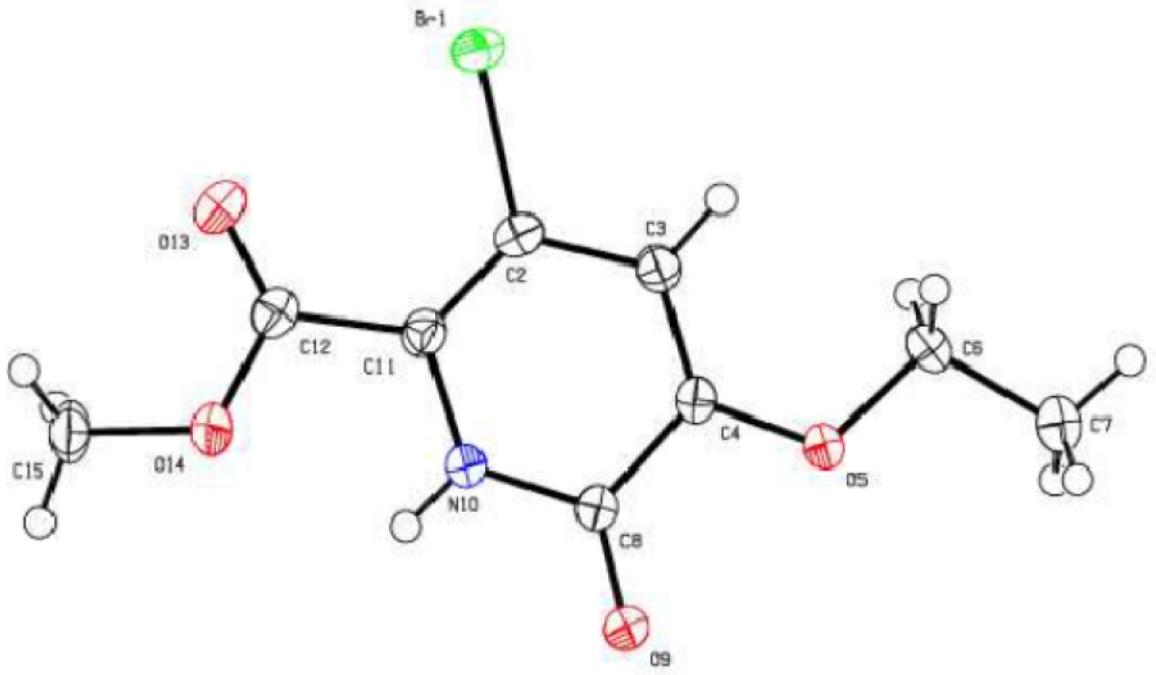

C(4)H
C(1")H
C(2")H
C(3")H2
1""
Ar""
Ar'''
O=S=O
NH
Ar'
Ar"
1'''
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)


C(1')H3
C(1")H
C(2")H
C(3")H2
1""
Ar""
Ar'''
O=S=O
NH
Ar'
Ar"
1'''
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)


C(1')H3
C(3")H2
Ph'
C(2")H
C(1")H
1""
Ar""
Ar'''
O=S=O
NH
3
4
2
1
Ar'
Ar"
H3C
5
6
1'
H
2"
1"
H
H
3"
H
Ph'
1'''
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)

Appendix III: Crystallographic data

Methyl 3-bromo-5-ethoxy-6-oxo-1,6-dihydropyridine-2-carboxylate (311)



A single crystal having dimensions approximately 0.02×0.13×0.35 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package.[1]

Examination of the systematic absences of the intensity data showed the space group to be *P 21/c*. The structure was solved in this space group using the direct-methods program SIR92,[2] which located all non-hydrogen atoms. The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. Subsequent full-matrix least-squares refinement was carried out against F^2 using the CRYSTALS program suite.[3] Coordinates and anisotropic thermal parameters were refined for all non-hydrogen atoms,

and the hydrogens were refined with riding constraints. A modified statistical weighting scheme was applied. Refinement converged satisfactorily to give R = 0.0524, wR = 0.1344. Attached is a thermal ellipsoid plot (CAMERON) at 50% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

References:

1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, **276**, Eds C. W. Carter and R. M. Sweet, Academic Press.

2 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi ,M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst*. 1994, **27**, 435.

3 CRYSTALS Issue 12, P. W. Betteridge, J. R. Cooper, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl.Cryst.*, 2003, **36**, 1487

Crystal data

Formula:	$C_9H_{10}BrNO_4$
Space group:	P1
Symmetrycellsetting:	Triclinic
Cell length a:	4.049
Cell length b:	15.74
Cell length c:	16.024
Cell angle alpha:	90
Cell angle beta:	93.32
Cell angle gamma:	90
Cell volume:	1019.52

Atomic coordinates and equivalent isotropic thermal parameters (Å^2) of non-hydrogen atoms.

Number	Label	Charge	SybylType	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD	Symm. op.
1	BR1	0	B	0.833396	0.569695	0.30218	x,y,z
2	C2	0	C.3	0.996601	0.576874	0.194223	x,y,z
3	C3	0	C.2	1.04155	0.660356	0.162967	x,y,z
4	C4	0	C.2	1.17983	0.67141	0.088516	x,y,z
5	O5	0	O.3	1.22979	0.746315	0.050009	x,y,z
6	C6	0	C.3	1.09929	0.82141	0.088391	x,y,z
7	C7	0	C.3	1.14712	0.894155	0.0298179	x,y,z
8	C8	0	C.2	1.29846	0.599111	0.041445	x,y,z
9	O9	0	O.2	1.44634	0.605909	-.0234417	x,y,z
10	N10	0	N.am	1.23033	0.52122	0.0750136	x,y,z
11	C11	0	C.2	1.08244	0.507751	0.14959	x,y,z
12	C12	0	C.2	1.02272	0.416773	0.171343	x,y,z
13	O13	0	O.2	0.868122	0.392757	0.228479	x,y,z
14	O14	0	O.3	1.15841	0.366773	0.116834	x,y,z
15	C15	0	C.3	1.08428	0.277446	0.120959	x,y,z

Atomic coordinates and isotropic thermal parameters (Å^2) of hydrogen atoms

Number	Label	Charge	SybylType	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD	Symm. op.
1	H31	0	H	0.972587	0.70648	0.193973	x,y,z
2	H61	0	H	0.868209	0.813088	0.0973926	x,y,z
3	H62	0	H	1.21312	0.831957	0.141088	x,y,z
4	H71	0	H	1.06363	0.944536	0.0545724	x,y,z
5	H72	0	H	1.02025	0.884689	-.0226291	x,y,z
6	H73	0	H	1.37617	0.901906	0.0195035	x,y,z
7	H15	0	H	1.20601	0.249873	0.0788268	x,y,z
8	H15	0	H	0.848485	0.269187	0.109395	x,y,z
9	H15	0	H	1.15255	0.255781	0.175282	x,y,z
10	H10	0	H	1.28502	0.477954	0.0474461	x,y,z

Bond lengths (Å).

Number	Atom1	Atom2	Length
1	BR1	C2	1.8906
2	C2	C3	1.4217
3	C2	C11	1.3582
4	C3	C4	1.3581
5	C3	H31	0.9316
6	C4	O5	1.3514

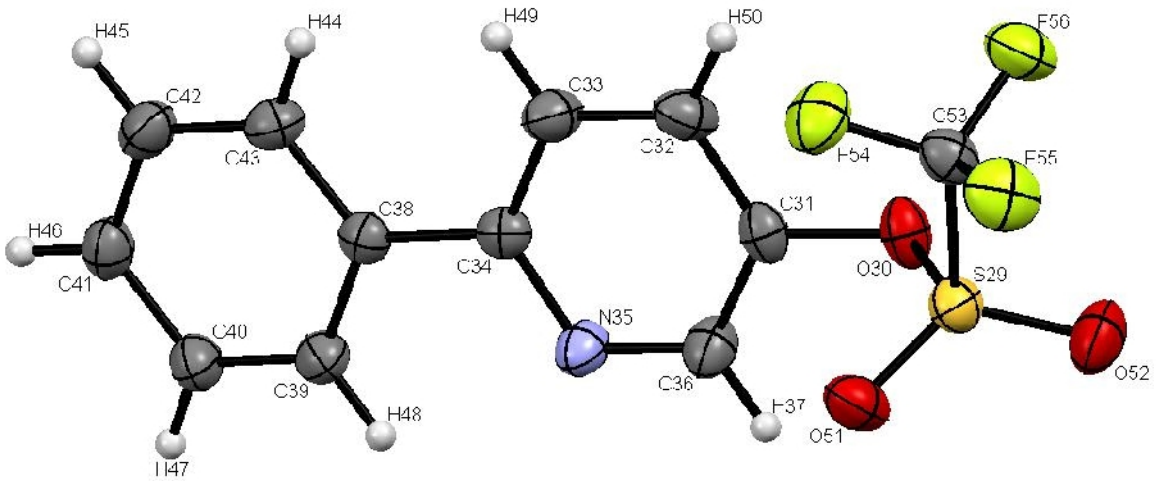
7	C4	C8	1.4617
8	O5	C6	1.4465
9	C6	C7	1.5002
10	C6	H61	0.9639
11	C6	H62	0.9529
12	C7	H71	0.9571
13	C7	H72	0.9708
14	C7	H73	0.9592
15	C8	O9	1.2342
16	C8	N10	1.3732
17	N10	C11	1.3836
18	N10	H10	0.8481
19	C11	C12	1.4968
20	C12	O13	1.1997
21	C12	O14	1.319
22	O14	C15	1.44
23	C15	H15	0.9621
24	C15	H15	0.9707
25	C15	H15	0.9605

Bond angles (°).

Number	Atom1	Atom2	Atom3	Angle
1	BR1	C2	C3	115.86
2	BR1	C2	C11	123.2
3	C3	C2	C11	120.86
4	C2	C3	C4	119.71
5	C2	C3	H31	118.94
6	C4	C3	H31	121.34
7	C3	C4	O5	126.38
8	C3	C4	C8	121.2
9	O5	C4	C8	112.41
10	C4	O5	C6	116.79
11	O5	C6	C7	107.1
12	O5	C6	H61	109.53
13	O5	C6	H62	110.45
14	C7	C6	H61	111.04
15	C7	C6	H62	110.37
16	H61	C6	H62	108.36
17	C6	C7	H71	108.16
18	C6	C7	H72	110.09
19	C6	C7	H73	111.47
20	H71	C7	H72	107.7
21	H71	C7	H73	109.53
22	H72	C7	H73	109.8
23	C4	C8	O9	123.86

24	C4	C8	N10	114.42
25	O9	C8	N10	121.71
26	C8	N10	C11	125.59
27	C8	N10	H10	116.64
28	C11	N10	H10	117.77
29	C2	C11	N10	117.96
30	C2	C11	C12	126.44
31	N10	C11	C12	115.57
32	C11	C12	O13	125.28
33	C11	C12	O14	109.73
34	O13	C12	O14	124.97
35	C12	O14	C15	117.15
36	O14	C15	H15	106.96
37	O14	C15	H15	109.11
38	O14	C15	H15	109.78
39	H15	C15	H15	110.11
40	H15	C15	H15	110.09
41	H15	C15	H15	110.71

6-Phenylpyridin-3-yl trifluoromethanesulfonate (424)



A single crystal having dimensions approximately 0.02×0.18×0.31 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold

N_2using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package.[1] Examination of the systematic absences of the intensity data showed the space group to be *P 21/c*. The structure was solved in this space group using the direct-methods program SIR92,[2] which located all non-hydrogen atoms. The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. Subsequent full-matrix least-squares refinement was carried out against F^2 using the CRYSTALS program suite.[3] Coordinates and anisotropic thermal parameters were refined for all non-hydrogen atoms, and the hydrogens were refined with riding constraints. A modified statistical weighting scheme was applied. Refinement converged satisfactorily to give R = 0.0524, wR = 0.1344. Attached is a thermal ellipsoid plot (CAMERON) at 50% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

References:

1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, **276**, Eds C. W. Carter and R. M. Sweet, Academic Press.

2 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi ,M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst*. 1994, **27**, 435.

3 CRYSTALS Issue 12, P. W. Betteridge, J. R. Cooper, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl.Cryst.*, 2003, **36**, 1487

Crystal data

Formula: $C_{12}H_8F_3NO_3S$

Space group: P-1

Symmetrycellsetting: Triclinic

Cell length a:	5.75160 (10)
Cell length b:	14.1435 (3)
Cell length c:	14.7981 (3)
Cell angle alpha:	85.5227 (9)
Cell angle beta:	89.9217 (9)
Cell angle gamma:	89.0555 (9)
Cell volume:	1199.96 (4)

Atomic coordinates and equivalent isotropic thermal parameters (Å^2) of non-hydrogen atoms.

Number	Label	Charge	SybylType	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD	Symm. op.
1	S1	0	S.o2	0.23278(9)	0.44518(4)	0.90074(4)	x,y,z
2	O2	0	O.2	0.1577(3)	0.53895(11)	0.91366(11)	x,y,z
3	O3	0	O.3	0.3905(3)	0.41166(10)	0.98363(10)	x,y,z
4	C4	0	C.2	0.4146(4)	0.31362(14)	1.01434(14)	x,y,z
5	C5	0	C.2	0.6213(4)	0.26777(15)	0.99890(15)	x,y,z
6	N6	0	N.2	0.6640(3)	0.17837(12)	1.03170(12)	x,y,z
7	C7	0	C.2	0.4964(4)	0.13283(14)	1.08064(13)	x,y,z
8	C8	0	C.2	0.2841(4)	0.17695(15)	1.09829(15)	x,y,z
9	C9	0	C.2	0.2415(4)	0.26967(15)	1.06514(14)	x,y,z
10	C10	0	C.2	0.5531(4)	0.03290(14)	1.11515(14)	x,y,z
11	C11	0	C.2	0.4006(4)	-.02099(15)	1.17043(15)	x,y,z
12	C12	0	C.2	0.4573(4)	-.11358(16)	1.20139(16)	x,y,z
13	C13	0	C.2	0.6667(4)	-.15400(16)	1.17703(16)	x,y,z
14	C14	0	C.2	0.8196(4)	-.10175(16)	1.12199(16)	x,y,z
15	C15	0	C.2	0.7638(4)	-.00883(16)	1.09141(15)	x,y,z
16	O16	0	O.2	0.0777(3)	0.37362(11)	0.87870(11)	x,y,z
17	C17	0	C.3	0.4516(4)	0.45548(15)	0.81028(15)	x,y,z
18	F18	0	F	0.5568(2)	0.37299(9)	0.80215(10)	x,y,z
19	F19	0	F	0.3457(3)	0.48269(11)	0.73298(9)	x,y,z
20	F20	0	F	0.6078(3)	0.51877(10)	0.82717(10)	x,y,z
21	H51	0	H	0.7377	0.3002	0.964	x,y,z
22	H81	0	H	0.169	0.1433	1.1324	x,y,z
23	H91	0	H	0.1003	0.3012	1.0762	x,y,z
24	H111	0	H	0.2572	0.0052	1.1869	x,y,z
25	H121	0	H	0.3527	-0.1493	1.2395	x,y,z
26	H131	0	H	0.7038	-0.2172	1.1979	x,y,z
27	H141	0	H	0.9634	-0.1289	1.1046	x,y,z
28	H151	0	H	0.8673	0.0266	1.054	x,y,z

29	S21	0	S.o2	0.31459(10)	0.67473(4)	0.45658(4)	x,y,z
30	O22	0	O.3	0.1584(3)	0.75555(10)	0.49309(10)	x,y,z
31	C23	0	C.2	0.1323(4)	0.84599(15)	0.44445(14)	x,y,z
32	C24	0	C.2	-0.0685(4)	0.86848(16)	0.39717(17)	x,y,z
33	C25	0	C.2	-0.0953(4)	0.96049(16)	0.35922(17)	x,y,z
34	C26	0	C.2	0.0766(4)	1.02638(15)	0.37075(14)	x,y,z
35	N27	0	N.2	0.2745(3)	1.00204(13)	0.41586(13)	x,y,z
36	C28	0	C.2	0.3001(4)	0.91298(16)	0.45243(16)	x,y,z
37	C29	0	C.2	0.0538(4)	1.12755(15)	0.33552(14)	x,y,z
38	C30	0	C.2	0.2297(4)	1.19120(16)	0.35077(15)	x,y,z
39	C31	0	C.2	0.2079(4)	1.28653(16)	0.32266(16)	x,y,z
40	C32	0	C.2	0.0094(4)	1.32030(16)	0.27722(16)	x,y,z
41	C33	0	C.2	-0.1655(4)	1.25812(17)	0.25987(16)	x,y,z
42	C34	0	C.2	-0.1451(4)	1.16267(16)	0.28905(15)	x,y,z
43	O35	0	O.2	0.4757(3)	0.71240(12)	0.39126(12)	x,y,z
44	O36	0	O.2	0.3807(3)	0.61375(12)	0.53258(13)	x,y,z
45	C37	0	C.3	0.0957(4)	0.61199(16)	0.39551(16)	x,y,z
46	F38	0	F	0.0201(3)	0.66643(11)	0.32438(10)	x,y,z
47	F39	0	F	0.1921(3)	0.53407(10)	0.36706(11)	x,y,z
48	F40	0	F	-0.0809(3)	0.58875(11)	0.44867(11)	x,y,z
49	H241	0	H	-0.1809	0.8221	0.3908	x,y,z
50	H251	0	H	-0.2294	0.9779	0.3265	x,y,z
51	H281	0	H	0.4356	0.8969	0.4856	x,y,z
52	H301	0	H	0.3654	1.1693	0.3813	x,y,z
53	H311	0	H	0.3288	1.3278	0.3341	x,y,z
54	H321	0	H	-0.0069	1.3855	0.257	x,y,z
55	H331	0	H	-0.3	1.2805	0.228	x,y,z
56	H341	0	H	-0.2656	1.1214	0.2776	x,y,z

Atomic coordinates and isotropic thermal parameters (Å^2) of hydrogen atoms

Number	Label	Charge	SybylType	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD	Symm. op.
1	H241	0	H	-0.1809	0.8221	0.3908	x,y,z
2	H251	0	H	-0.2294	0.9779	0.3265	x,y,z
3	H281	0	H	0.4356	0.8969	0.4856	x,y,z
4	H301	0	H	0.3654	1.1693	0.3813	x,y,z
5	H311	0	H	0.3288	1.3278	0.3341	x,y,z
6	H321	0	H	-0.0069	1.3855	0.257	x,y,z
7	H331	0	H	-0.3	1.2805	0.228	x,y,z
8	H341	0	H	-0.2656	1.1214	0.2776	x,y,z

Anisotropic thermal parameters (Å2)

Number	Label	U11	U22	U33	U12	U13	U23
1	S1	0.0255	0.0244	0.0283	0.0008	-0.0001	0.0007
2	O2	0.037	0.026	0.0384	0.0097	0.0019	0.0007
3	O3	0.0339	0.021	0.0299	-0.0003	-0.0057	0.0022
4	C4	0.0285	0.0201	0.0265	-0.0002	-0.0054	-0.0003
5	C5	0.0243	0.0286	0.0341	-0.0016	-0.0004	0.0045
6	N6	0.0225	0.027	0.0321	0.0008	0.0013	0.0027
7	C7	0.0244	0.0234	0.0234	-0.0017	-0.0008	-0.0028
8	C8	0.0267	0.0259	0.029	-0.0006	0.0046	0.0024
9	C9	0.0268	0.0264	0.0288	0.0046	0.0025	-0.0014
10	C10	0.0265	0.0227	0.0235	-0.001	-0.0028	-0.0022
11	C11	0.0301	0.0284	0.0326	0.0001	0.0013	-0.0006
12	C12	0.0375	0.0284	0.0371	-0.0047	-0.0009	0.0036
13	C13	0.0428	0.0238	0.0363	0.0008	-0.0117	-0.002
14	C14	0.0324	0.0273	0.0408	0.0061	-0.0065	-0.0068
15	C15	0.0288	0.0291	0.0309	0.001	0.0007	-0.0049
16	O16	0.0283	0.0345	0.0338	-0.0067	-0.002	0.0015
17	C17	0.0305	0.0263	0.0306	-0.0005	-0.0008	-0.0007
18	F18	0.0397	0.034	0.0456	0.0092	0.0109	-0.0022
19	F19	0.0448	0.0563	0.0317	0.0081	0.0022	0.007
20	F20	0.0447	0.0451	0.0522	-0.0206	0.0131	-0.009
29	S21	0.0318	0.0249	0.0357	-0.0018	-0.0022	-0.0021
30	O22	0.0505	0.022	0.0309	-0.0001	0.0064	-0.0009
31	C23	0.0365	0.023	0.0258	-0.0009	0.0056	-0.0019
32	C24	0.0264	0.028	0.0503	-0.0043	0.0036	-0.0062
33	C25	0.0271	0.0304	0.0457	0.0004	-0.0052	-0.0045
34	C26	0.0252	0.0271	0.0228	-0.0003	0.0011	-0.0068
35	N27	0.0326	0.0263	0.035	-0.0016	-0.0093	-0.0012
36	C28	0.0404	0.0262	0.0342	-0.0009	-0.0107	-0.0022
37	C29	0.0263	0.027	0.0234	-0.0002	0.0017	-0.0035
38	C30	0.0297	0.0318	0.0287	-0.0025	-0.0032	-0.0003
39	C31	0.0342	0.0285	0.0359	-0.004	-0.0035	0.0029
40	C32	0.0375	0.0281	0.0343	0.0044	0.0019	0.0023
41	C33	0.0311	0.0393	0.034	0.0072	-0.0022	0.0006
42	C34	0.0263	0.0335	0.0335	-0.0001	-0.0036	-0.0049
43	O35	0.0316	0.0334	0.0543	-0.0051	0.0077	-0.0027
44	O36	0.0562	0.0355	0.0455	0.0031	-0.0156	0.0051
45	C37	0.0328	0.0282	0.0376	-0.0031	0.0037	-0.0054
46	F38	0.0539	0.0457	0.0396	-0.0011	-0.0134	-0.0037
47	F39	0.052	0.0316	0.0601	-0.0005	0.0034	-0.0177
48	F40	0.0341	0.0449	0.0611	-0.0094	0.0085	-0.0033

Bond lengths (Å).

Number	Atom1	Atom2	Length
1	S1	O2	1.415(2)
2	S1	O3	1.565(2)
3	S1	O16	1.417(2)
4	S1	C17	1.835(2)
5	O3	C4	1.430(2)
6	C4	C5	1.372(3)
7	C4	C9	1.374(3)
8	C5	N6	1.338(3)
9	C5	H51	0.947(2)
10	N6	C7	1.347(3)
11	C7	C8	1.396(3)
12	C7	C10	1.496(3)
13	C8	C9	1.382(3)
14	C8	H81	0.944(2)
15	C9	H91	0.940(2)
16	C10	C11	1.394(3)
17	C10	C15	1.396(3)
18	C11	C12	1.387(3)
19	C11	H111	0.938(2)
20	C12	C13	1.384(3)
21	C12	H121	0.949(2)
22	C13	C14	1.381(3)
23	C13	H131	0.944(2)
24	C14	C15	1.389(3)
25	C14	H141	0.950(2)
26	C15	H151	0.937(2)
27	C17	F18	1.319(3)
28	C17	F19	1.324(3)
29	C17	F20	1.316(3)
30	S21	O22	1.571(2)
31	S21	O35	1.418(2)
32	S21	O36	1.411(2)
33	S21	C37	1.831(2)
34	O22	C23	1.424(2)
35	C23	C24	1.371(3)
36	C23	C28	1.375(3)
37	C24	C25	1.383(3)
38	C24	H241	0.939(2)
39	C25	C26	1.390(3)
40	C25	H251	0.931(2)
41	C26	N27	1.346(3)
42	C26	C29	1.488(3)
43	N27	C28	1.337(3)
44	C28	H281	0.937(2)

45	C29	C30	1.395(3)
46	C29	C34	1.399(3)
47	C30	C31	1.383(3)
48	C30	H301	0.938(2)
49	C31	C32	1.385(3)
50	C31	H311	0.939(2)
51	C32	C33	1.384(3)
52	C32	H321	0.950(2)
53	C33	C34	1.388(3)
54	C33	H331	0.944(2)
55	C34	H341	0.937(2)
56	C37	F38	1.324(3)
57	C37	F39	1.323(3)
58	C37	F40	1.314(3)

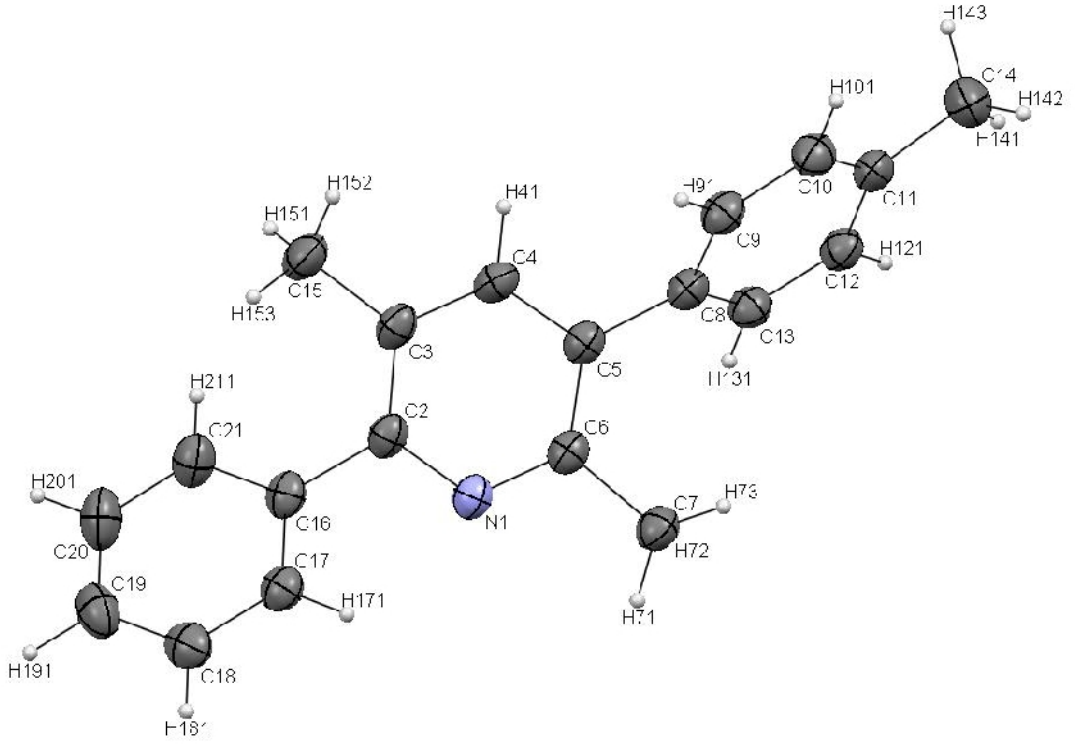
Bond angles (°).

Number	Atom1	Atom2	Atom3	Angle
1	O2	S1	O3	106.88(9)
2	O2	S1	O16	122.6(1)
3	O2	S1	C17	106.0(1)
4	O3	S1	O16	111.81(9)
5	O3	S1	C17	100.29(9)
6	O16	S1	C17	106.8(1)
7	S1	O3	C4	121.5(1)
8	O3	C4	C5	118.4(2)
9	O3	C4	C9	120.0(2)
10	C5	C4	C9	121.3(2)
11	C4	C5	N6	122.0(2)
12	C4	C5	H51	119.3(2)
13	N6	C5	H51	118.8(2)
14	C5	N6	C7	118.2(2)
15	N6	C7	C8	121.7(2)
16	N6	C7	C10	115.9(2)
17	C8	C7	C10	122.4(2)
18	C7	C8	C9	120.0(2)
19	C7	C8	H81	120.0(2)
20	C9	C8	H81	120.0(2)
21	C4	C9	C8	116.9(2)
22	C4	C9	H91	121.4(2)
23	C8	C9	H91	121.8(2)
24	C7	C10	C11	122.0(2)
25	C7	C10	C15	119.7(2)
26	C11	C10	C15	118.3(2)
27	C10	C11	C12	120.8(2)
28	C10	C11	H111	120.0(2)

29	C12	C11	H111	119.2(2)
30	C11	C12	C13	120.1(2)
31	C11	C12	H121	120.0(2)
32	C13	C12	H121	119.8(2)
33	C12	C13	C14	119.8(2)
34	C12	C13	H131	119.8(2)
35	C14	C13	H131	120.4(2)
36	C13	C14	C15	120.1(2)
37	C13	C14	H141	120.5(2)
38	C15	C14	H141	119.4(2)
39	C10	C15	C14	120.8(2)
40	C10	C15	H151	119.1(2)
41	C14	C15	H151	120.2(2)
42	S1	C17	F18	110.5(1)
43	S1	C17	F19	108.6(2)
44	S1	C17	F20	110.7(2)
45	F18	C17	F19	108.9(2)
46	F18	C17	F20	109.2(2)
47	F19	C17	F20	108.9(2)
48	O22	S21	O35	111.0(1)
49	O22	S21	O36	106.7(1)
50	O22	S21	C37	100.0(1)
51	O35	S21	O36	123.0(1)
52	O35	S21	C37	107.0(1)
53	O36	S21	C37	106.6(1)
54	S21	O22	C23	121.8(1)
55	O22	C23	C24	119.9(2)
56	O22	C23	C28	119.3(2)
57	C24	C23	C28	120.6(2)
58	C23	C24	C25	117.5(2)
59	C23	C24	H241	120.2(2)
60	C25	C24	H241	122.3(2)
61	C24	C25	C26	119.9(2)
62	C24	C25	H251	119.6(2)
63	C26	C25	H251	120.5(2)
64	C25	C26	N27	121.4(2)
65	C25	C26	C29	122.7(2)
66	N27	C26	C29	115.9(2)
67	C26	N27	C28	118.5(2)
68	C23	C28	N27	122.1(2)
69	C23	C28	H281	119.7(2)
70	N27	C28	H281	118.2(2)
71	C26	C29	C30	120.3(2)
72	C26	C29	C34	121.7(2)
73	C30	C29	C34	117.9(2)
74	C29	C30	C31	121.5(2)
75	C29	C30	H301	119.6(2)

76	C31	C30	H301	119.0(2)
77	C30	C31	C32	119.9(2)
78	C30	C31	H311	119.6(2)
79	C32	C31	H311	120.5(2)
80	C31	C32	C33	119.6(2)
81	C31	C32	H321	120.7(2)
82	C33	C32	H321	119.7(2)
83	C32	C33	C34	120.5(2)
84	C32	C33	H331	120.0(2)
85	C34	C33	H331	119.5(2)
86	C29	C34	C33	120.5(2)
87	C29	C34	H341	119.7(2)
88	C33	C34	H341	119.7(2)
89	S21	C37	F38	109.9(2)
90	S21	C37	F39	108.8(2)
91	S21	C37	F40	110.7(2)
92	F38	C37	F39	108.9(2)
93	F38	C37	F40	109.3(2)
94	F39	C37	F40	109.2(2)

2,5-Dimethyl-6-phenyl-3-p-tolylpyridine (619)



A single crystal having dimensions approximately 0.02×0.16×0.33 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package.[1]

Examination of the systematic absences of the intensity data showed the space group to be *P 21/c*. The structure was solved in this space group using the direct-methods program SIR92,[2] which located all non-hydrogen atoms. The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. Subsequent full-matrix least-squares refinement was carried out against F^2 using the CRYSTALS program suite.[3] Coordinates and anisotropic thermal parameters were refined for all non-hydrogen atoms, and the hydrogens were refined with riding constraints. A modified statistical weighting scheme was applied. Refinement converged satisfactorily to give R = 0.0524, wR = 0.1344. Attached is a thermal ellipsoid plot (CAMERON) at 50% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

References:

1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, **276**, Eds C. W. Carter and R. M. Sweet, Academic Press.

2 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi ,M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst*. 1994, **27**, 435.

3 CRYSTALS Issue 12, P. W. Betteridge, J. R. Cooper, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl.Cryst.*, 2003, **36**, 1487

Crystal data

Formula: $C_{20}H_{19}N$

Space group: P-1

Symmetrycellsetting: Triclinic

Cell length a: 9.3961(2)

Cell length b: 9.4690 (2)

Cell length c: 10.2833(2)

Cell angle alpha: 68.3797(10)

Cell angle beta: 81.4469(9)

Cell angle gamma: 62.3658(10)

Cell volume: 753.26(3)

Atomic coordinates and equivalent isotropic thermal parameters (Å^2) of non-hydrogen atoms.

Number	Label	Charge	SybylType	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD	Symm. op.
1	N1	0	N.2	0.48207(14)	0.23418(14)	0.80533(12)	x,y,z
2	C2	0	C.2	0.59732(16)	0.21234(18)	0.70877(14)	x,y,z
3	C3	0	C.2	0.63780(17)	0.09278(18)	0.64322(14)	x,y,z
4	C4	0	C.2	0.54776(17)	0.00269(18)	0.67738(14)	x,y,z
5	C5	0	C.2	0.42438(16)	0.02735(17)	0.77281(14)	x,y,z
6	C6	0	C.2	0.39720(16)	0.14498(17)	0.83724(14)	x,y,z
7	C7	0	C.3	0.27592(18)	0.17529(19)	0.94972(16)	x,y,z
8	C8	0	C.2	0.33092(17)	-0.07151(18)	0.80183(14)	x,y,z
9	C9	0	C.2	0.40977(17)	-0.24507(18)	0.82269(15)	x,y,z
10	C10	0	C.2	0.32560(18)	-0.33644(19)	0.83621(15)	x,y,z
11	C11	0	C.2	0.15836(18)	-0.25734(18)	0.82943(15)	x,y,z
12	C12	0	C.2	0.07925(17)	-0.08635(19)	0.81408(15)	x,y,z
13	C13	0	C.2	0.16341(17)	0.00574(18)	0.79936(15)	x,y,z
14	C14	0	C.3	0.0658(2)	-0.3525(2)	0.83301(19)	x,y,z
15	C15	0	C.3	0.77272(19)	0.0567(2)	0.54173(17)	x,y,z
16	C16	0	C.2	0.68040(16)	0.32167(18)	0.68109(15)	x,y,z
17	C17	0	C.2	0.73332(16)	0.33637(18)	0.79294(16)	x,y,z
18	C18	0	C.2	0.80774(18)	0.4399(2)	0.76945(18)	x,y,z
19	C19	0	C.2	0.82777(19)	0.5327(2)	0.63398(19)	x,y,z
20	C20	0	C.2	0.77411(19)	0.5206(2)	0.52225(19)	x,y,z
21	C21	0	C.2	0.70191(18)	0.4154(2)	0.54485(16)	x,y,z

Atomic coordinates and isotropic thermal parameters (Å^2) of hydrogen atoms

Number	Label	Charge	SybylType	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD	Symm. op.
1	H41	0	H	0.5716	-0.0786	0.6321	x,y,z
2	H73	0	H	0.2709	0.0689	1.011	x,y,z
3	H71	0	H	0.3042	0.2239	1.0064	x,y,z
4	H72	0	H	0.1684	0.2566	0.9059	x,y,z
5	H91	0	H	0.5275	-0.3029	0.8267	x,y,z

Anisotropic thermal parameters (Å2)

Number	Label	U11	U22	U33	U12	U13	U23
1	N1	0.0259	0.0298	0.0271	-0.0114	0.0012	-0.0077
2	C2	0.0245	0.0318	0.0231	-0.0112	-0.0002	-0.0061
3	C3	0.0266	0.0374	0.023	-0.0128	0.0008	-0.0086
4	C4	0.0301	0.0355	0.0254	-0.0114	0.0016	-0.0135
5	C5	0.0252	0.0284	0.0246	-0.0096	-0.0005	-0.0072
6	C6	0.0237	0.0266	0.0247	-0.0075	0.0003	-0.0066
7	C7	0.0309	0.0346	0.0328	-0.0128	0.0063	-0.0141
8	C8	0.0277	0.0303	0.0245	-0.0117	0.0026	-0.01
9	C9	0.0267	0.0321	0.0317	-0.0089	0.0031	-0.0117
10	C10	0.0369	0.0281	0.033	-0.0128	0.0042	-0.0106
11	C11	0.0361	0.0354	0.0268	-0.0196	0.0071	-0.0127
12	C12	0.0267	0.0375	0.0315	-0.0135	0.0047	-0.0148
13	C13	0.0285	0.0289	0.0311	-0.0101	0.0019	-0.0113
14	C14	0.0505	0.0452	0.0478	-0.029	0.0097	-0.0191
15	C15	0.0384	0.0534	0.0321	-0.0221	0.0103	-0.0196
16	C16	0.0208	0.031	0.0316	-0.0089	0.0017	-0.0083
17	C17	0.0254	0.0327	0.0341	-0.0099	0.0025	-0.012
18	C18	0.0272	0.0389	0.0477	-0.0125	0.0027	-0.0197
19	C19	0.0323	0.0386	0.0587	-0.0191	0.006	-0.0156
20	C20	0.038	0.0425	0.0432	-0.0215	0.004	-0.0022
21	C21	0.0329	0.0452	0.0325	-0.02	0.0003	-0.0063

Bond lengths (Å).

Number	Atom1	Atom2	Length
1	N1	C2	1.351(2)
2	N1	C6	1.342(2)
3	C2	C3	1.403(3)
4	C2	C16	1.493(3)
5	C3	C4	1.388(3)
6	C3	C15	1.510(2)

7	C4	C5	1.393(2)
8	C4	H41	0.966(2)
9	C5	C6	1.405(3)
10	C5	C8	1.488(3)
11	C6	C7	1.506(2)
12	C7	H73	0.991(2)
13	C7	H71	0.990(2)
14	C7	H72	0.987(1)
15	C8	C9	1.398(2)
16	C8	C13	1.394(2)
17	C9	C10	1.381(3)
18	C9	H91	0.980(1)
19	C10	C11	1.392(2)
20	C10	H101	0.986(2)
21	C11	C12	1.389(2)
22	C11	C14	1.504(3)
23	C12	C13	1.384(3)
24	C12	H121	0.978(1)
25	C13	H131	0.972(2)
26	C14	H141	0.999(2)
27	C14	H142	0.991(2)
28	C14	H143	0.983(2)
29	C15	H152	0.975(2)
30	C15	H153	0.998(2)
31	C15	H151	0.982(1)
32	C16	C17	1.394(3)
33	C16	C21	1.399(2)
34	C17	C18	1.385(3)
35	C17	H171	0.994(1)
36	C18	C19	1.386(2)
37	C18	H181	0.985(2)
38	C19	C20	1.382(3)
39	C19	H191	1.009(2)
40	C20	C21	1.384(3)
41	C20	H201	0.988(2)
42	C21	H211	0.972(2)

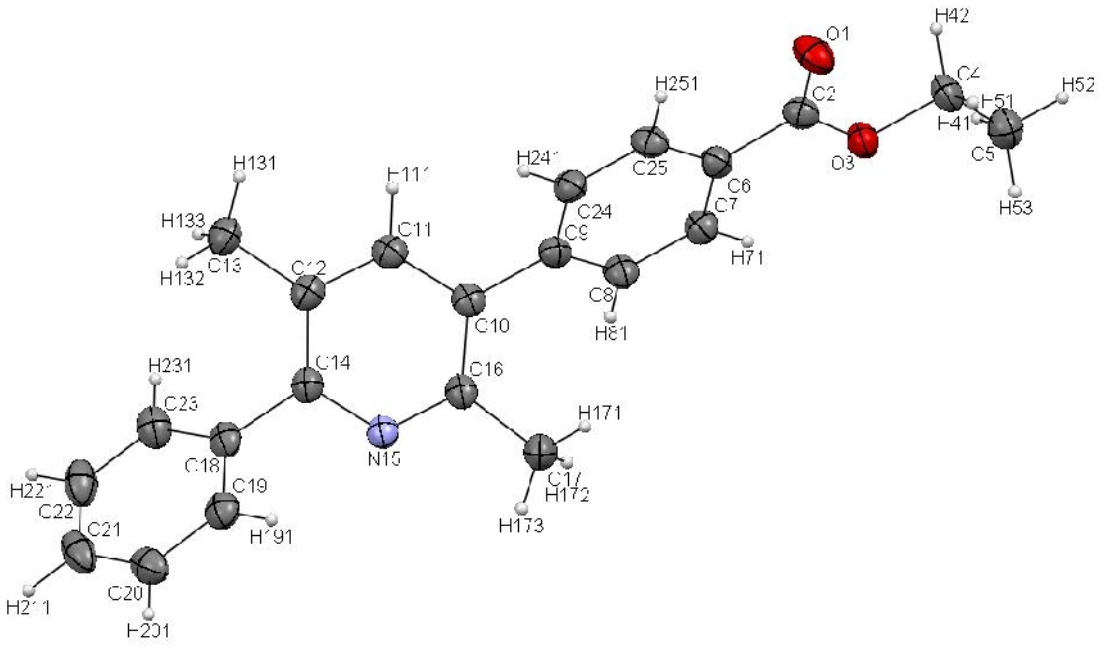
Bond angles (°).

Number	Atom1	Atom2	Atom3	Angle
1	C2	N1	C6	120.1(1)
2	N1	C2	C3	122.2(1)
3	N1	C2	C16	114.6(1)
4	C3	C2	C16	123.1(1)
5	C2	C3	C4	116.6(1)
6	C2	C3	C15	123.9(1)

7	C4	C3	C15	119.5(1)
8	C3	C4	C5	122.2(1)
9	C3	C4	H41	118.2(2)
10	C5	C4	H41	119.6(2)
11	C4	C5	C6	117.0(1)
12	C4	C5	C8	119.1(1)
13	C6	C5	C8	123.9(1)
14	N1	C6	C5	121.8(1)
15	N1	C6	C7	115.4(1)
16	C5	C6	C7	122.7(1)
17	C6	C7	H73	111.3(1)
18	C6	C7	H71	109.6(1)
19	C6	C7	H72	109.4(1)
20	H73	C7	H71	109.8(2)
21	H73	C7	H72	108.0(2)
22	H71	C7	H72	108.7(2)
23	C5	C8	C9	120.3(1)
24	C5	C8	C13	122.0(1)
25	C9	C8	C13	117.6(1)
26	C8	C9	C10	121.5(2)
27	C8	C9	H91	119.2(2)
28	C10	C9	H91	119.3(2)
29	C9	C10	C11	120.6(2)
30	C9	C10	H101	119.8(2)
31	C11	C10	H101	119.7(2)
32	C10	C11	C12	118.2(2)
33	C10	C11	C14	121.0(2)
34	C12	C11	C14	120.8(2)
35	C11	C12	C13	121.3(2)
36	C11	C12	H121	118.5(2)
37	C13	C12	H121	120.2(2)
38	C8	C13	C12	120.8(1)
39	C8	C13	H131	119.8(2)
40	C12	C13	H131	119.4(2)
41	C11	C14	H141	109.8(2)
42	C11	C14	H142	109.1(2)
43	C11	C14	H143	110.2(2)
44	H141	C14	H142	109.4(2)
45	H141	C14	H143	109.7(2)
46	H142	C14	H143	108.6(2)
47	C3	C15	H152	109.0(2)
48	C3	C15	H153	111.3(2)
49	C3	C15	H151	109.2(2)
50	H152	C15	H153	110.2(2)
51	H152	C15	H151	107.0(2)
52	H153	C15	H151	110.1(2)
53	C2	C16	C17	119.7(1)

54	C2	C16	C21	121.6(1)
55	C17	C16	C21	118.6(1)
56	C16	C17	C18	120.6(2)
57	C16	C17	H171	119.3(2)
58	C18	C17	H171	120.1(2)
59	C17	C18	C19	120.2(2)
60	C17	C18	H181	120.1(2)
61	C19	C18	H181	119.7(2)
62	C18	C19	C20	119.7(2)
63	C18	C19	H191	120.8(2)
64	C20	C19	H191	119.5(2)
65	C19	C20	C21	120.4(2)
66	C19	C20	H201	119.6(2)
67	C21	C20	H201	120.0(2)
68	C16	C21	C20	120.4(2)
69	C16	C21	H211	118.7(2)
70	C20	C21	H211	120.9(2)

Ethyl 4-(2,5-dimethyl-6-phenylpyridin-3-yl)benzoate (630)



A single crystal having dimensions approximately 0.02×0.15×0.34 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold

N_2using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package.[1] Examination of the systematic absences of the intensity data showed the space group to be *P 21/c*. The structure was solved in this space group using the direct-methods program SIR92,[2] which located all non-hydrogen atoms. The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. Subsequent full-matrix least-squares refinement was carried out against F^2 using the CRYSTALS program suite.[3] Coordinates and anisotropic thermal parameters were refined for all non-hydrogen atoms, and the hydrogens were refined with riding constraints. A modified statistical weighting scheme was applied. Refinement converged satisfactorily to give R = 0.0524, wR = 0.1344. Attached is a thermal ellipsoid plot (CAMERON) at 50% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

References:

1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol.*, 1997, **276**, Eds C. W. Carter and R. M. Sweet, Academic Press.

2 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi ,M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst*. 1994, **27**, 435.

3 CRYSTALS Issue 12, P. W. Betteridge, J. R. Cooper, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl.Cryst.*, 2003, **36**, 1487

Crystal data

Formula: $C_{22}H_{21}NO_2$

Space group: P 1 21/c 1

Symmetrycellsetting: Monoclinic

Cell length a: 9.6999(3)

Cell length b: 13.5546(5)

Cell length c: 13.8504(6)

Cell angle alpha: 90

Cell angle beta: 73.7676(16)

Cell angle gamma: 90

Cell volume: 1748.43(11)

Atomic coordinates and equivalent isotropic thermal parameters (Å^2) of non-hydrogen atoms.

Number	Label	Charge	SybylType	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD	Symm. op.
1	O1	0	O.2	0.20522(16)	-.06444(11)	0.35110(12)	x,y,z
2	C2	0	C.2	0.1137(2)	-.00104(15)	0.36368(15)	x,y,z
3	O3	0	O.3	-.02039(14)	-.01916(10)	0.35856(11)	x,y,z
4	C4	0	C.3	-0.0487(2)	-.12079(15)	0.33501(17)	x,y,z
5	C5	0	C.3	-0.1994(2)	-.12630(17)	0.32711(18)	x,y,z
6	C6	0	C.2	0.1375(2)	0.10358(14)	0.38611(15)	x,y,z
7	C7	0	C.2	0.0329(2)	0.17673(15)	0.39609(16)	x,y,z
8	C8	0	C.2	0.0615(2)	0.27262(15)	0.41896(16)	x,y,z
9	C9	0	C.2	0.1951(2)	0.29807(14)	0.43248(15)	x,y,z
10	C10	0	C.2	0.2286(2)	0.40022(14)	0.45892(15)	x,y,z
11	C11	0	C.2	0.3517(2)	0.44728(15)	0.40067(16)	x,y,z
12	C12	0	C.2	0.3906(2)	0.54133(15)	0.42341(15)	x,y,z
13	C13	0	C.3	0.5291(2)	0.58684(16)	0.36029(17)	x,y,z
14	C14	0	C.2	0.2993(2)	0.58703(14)	0.50870(15)	x,y,z
15	N15	0	N.2	0.18251(16)	0.54109(12)	0.56747(12)	x,y,z
16	C16	0	C.2	0.1467(2)	0.45037(14)	0.54417(15)	x,y,z
17	C17	0	C.3	0.0169(2)	0.40631(15)	0.61812(16)	x,y,z
18	C18	0	C.2	0.3235(2)	0.68758(15)	0.54435(16)	x,y,z
19	C19	0	C.2	0.3020(2)	0.70249(16)	0.64768(17)	x,y,z
20	C20	0	C.2	0.3159(2)	0.79566(17)	0.68483(18)	x,y,z
21	C21	0	C.2	0.3515(2)	0.87544(17)	0.6204(2)	x,y,z
22	C22	0	C.2	0.3720(2)	0.86235(16)	0.5185(2)	x,y,z
23	C23	0	C.2	0.3580(2)	0.76899(16)	0.48081(18)	x,y,z
24	C24	0	C.2	0.2993(2)	0.22496(15)	0.42036(15)	x,y,z
25	C25	0	C.2	0.2708(2)	0.12891(15)	0.39758(15)	x,y,z

Atomic coordinates and isotropic thermal parameters (Å^2) of hydrogen atoms

1	H41	0	H	-0.0347	-0.164	0.3897	x,y,z
2	H42	0	H	0.0203	-0.1404	0.2693	x,y,z
3	H52	0	H	-0.2198	-0.1952	0.3125	x,y,z
4	H53	0	H	-0.2663	-0.1065	0.3913	x,y,z
5	H51	0	H	-0.2089	-0.0826	0.2731	x,y,z
6	H71	0	H	-0.061	0.1601	0.3872	x,y,z
7	H81	0	H	-0.0105	0.3236	0.4259	x,y,z
8	H111	0	H	0.4119	0.4136	0.342	x,y,z
9	H132	0	H	0.5754	0.6227	0.4036	x,y,z
10	H131	0	H	0.5938	0.5347	0.3243	x,y,z
11	H133	0	H	0.508	0.6336	0.3116	x,y,z
12	H173	0	H	-0.0041	0.4423	0.6821	x,y,z
13	H171	0	H	0.0322	0.3371	0.6306	x,y,z
14	H172	0	H	-0.0662	0.411	0.5918	x,y,z
15	H191	0	H	0.2781	0.6465	0.6924	x,y,z
16	H201	0	H	0.3004	0.8046	0.756	x,y,z
17	H211	0	H	0.3619	0.9404	0.6457	x,y,z
18	H221	0	H	0.3948	0.9184	0.4739	x,y,z
19	H231	0	H	0.3712	0.7611	0.4085	x,y,z
20	H241	0	H	0.3938	0.2416	0.4279	x,y,z
21	H251	0	H	0.3427	0.0784	0.3898	x,y,z

Anisotropic thermal parameters (Å2)

Number	Label	U11	U22	U33	U12	U13	U23
1	O1	0.0388	0.0314	0.0508	0.009	-0.0208	-0.0107
2	C2	0.0294	0.0296	0.0254	0.003	-0.0092	-0.0029
3	O3	0.0298	0.0244	0.0375	-0.0015	-0.0109	-0.0019
4	C4	0.0384	0.0222	0.0392	-0.0014	-0.0127	-0.0043
5	C5	0.0386	0.0342	0.0397	-0.0042	-0.0133	-0.0022
6	C6	0.0277	0.0245	0.0242	0.0004	-0.0072	-0.0011
7	C7	0.0248	0.029	0.0314	0.0012	-0.0106	-0.001
8	C8	0.0237	0.0261	0.0359	0.0039	-0.0098	-0.0015
9	C9	0.0251	0.025	0.0234	0.0013	-0.0062	0.0001
10	C10	0.0231	0.0242	0.0294	0.0031	-0.0118	0.0005
11	C11	0.0245	0.0281	0.0296	0.0033	-0.0103	-0.0007
12	C12	0.0234	0.0279	0.0286	0.0011	-0.0092	0.0048
13	C13	0.0262	0.0349	0.0362	-0.0032	-0.0073	0.0029
14	C14	0.0237	0.0239	0.03	-0.0005	-0.0118	0.0029
15	N15	0.0227	0.0238	0.0303	0.0006	-0.0083	0.0003
16	C16	0.0224	0.0225	0.0319	0.0013	-0.0111	0.0014
17	C17	0.0303	0.0277	0.0339	-0.0031	-0.0055	-0.0007
18	C18	0.0202	0.0263	0.0378	0.0008	-0.0112	-0.0001
19	C19	0.0234	0.0314	0.038	0.0004	-0.0105	0.0003

20	C20	0.0275	0.0391	0.0436	0.0026	-0.0144	-0.0121
21	C21	0.0288	0.0293	0.0666	0.0027	-0.0209	-0.0117
22	C22	0.0336	0.0255	0.0613	-0.0014	-0.0183	0.0073
23	C23	0.0333	0.029	0.0449	-0.001	-0.0172	0.0025
24	C24	0.0212	0.0309	0.0308	0.0003	-0.0071	-0.0024
25	C25	0.0263	0.0284	0.0299	0.0068	-0.0094	-0.0027

Bond lengths (Å).

Number	Atom1	Atom2	Length
1	O1	C2	1.213(2)
2	C2	O3	1.345(3)
3	C2	C6	1.484(3)
4	O3	C4	1.459(3)
5	C4	C5	1.498(3)
6	C4	H41	0.996(2)
7	C4	H42	1.003(2)
8	C5	H52	0.987(2)
9	C5	H53	0.980(2)
10	C5	H51	0.979(2)
11	C6	C7	1.398(3)
12	C6	C25	1.389(3)
13	C7	C8	1.384(3)
14	C7	H71	0.979(2)
15	C8	C9	1.403(3)
16	C8	H81	0.968(2)
17	C9	C10	1.491(3)
18	C9	C24	1.392(3)
19	C10	C11	1.395(3)
20	C10	C16	1.401(3)
21	C11	C12	1.390(3)
22	C11	H111	0.972(2)
23	C12	C13	1.514(3)
24	C12	C14	1.407(3)
25	C13	H132	0.974(2)
26	C13	H131	0.983(2)
27	C13	H133	0.988(2)
28	C14	N15	1.348(2)
29	C14	C18	1.490(3)
30	N15	C16	1.341(3)
31	C16	C17	1.507(2)
32	C17	H173	0.982(2)
33	C17	H171	0.973(2)
34	C17	H172	0.975(2)
35	C18	C19	1.402(3)
36	C18	C23	1.393(3)

37	C19	C20	1.384(3)
38	C19	H191	0.966(2)
39	C20	C21	1.383(3)
40	C20	H201	0.962(2)
41	C21	C22	1.381(4)
42	C21	H211	0.963(2)
43	C22	C23	1.390(3)
44	C22	H221	0.965(2)
45	C23	H231	0.979(2)
46	C24	C25	1.386(3)
47	C24	H241	0.978(2)
48	C25	H251	0.962(2)

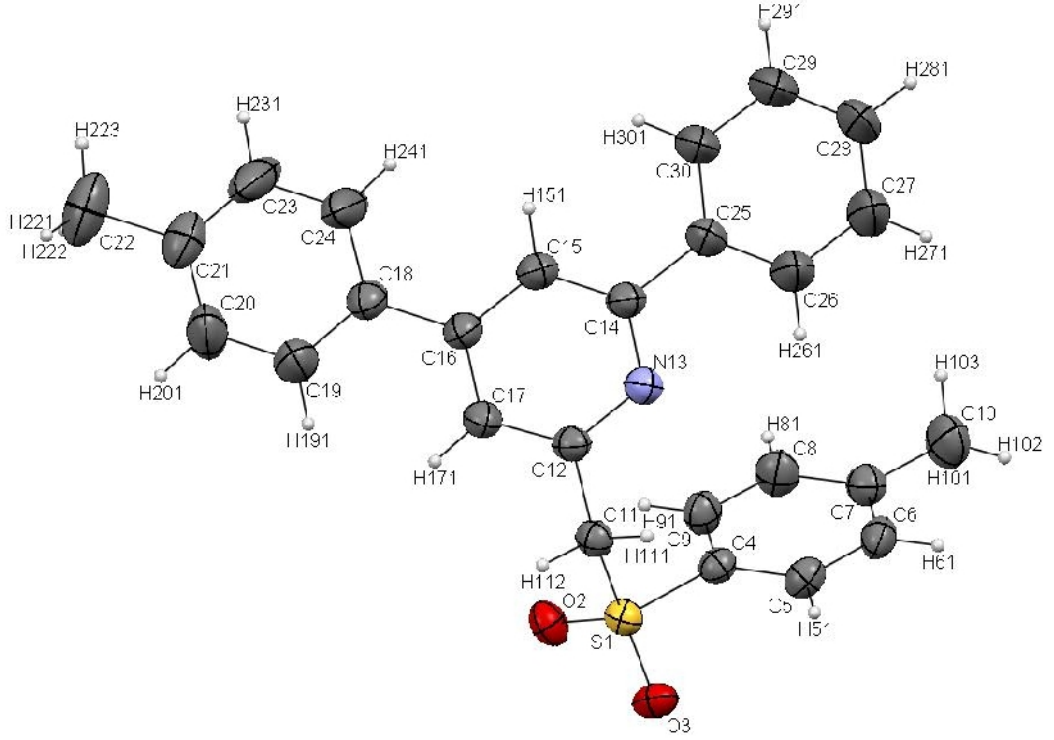
Bond angles (°).

Number	Atom1	Atom2	Atom3	Angle
1	O1	C2	O3	122.9(2)
2	O1	C2	C6	123.8(2)
3	O3	C2	C6	113.3(2)
4	C2	O3	C4	115.4(2)
5	O3	C4	C5	108.2(2)
6	O3	C4	H41	108.1(2)
7	O3	C4	H42	109.5(2)
8	C5	C4	H41	111.7(2)
9	C5	C4	H42	109.7(2)
10	H41	C4	H42	109.6(2)
11	C4	C5	H52	108.5(2)
12	C4	C5	H53	109.4(2)
13	C4	C5	H51	109.1(2)
14	H52	C5	H53	109.0(2)
15	H52	C5	H51	110.4(2)
16	H53	C5	H51	110.3(2)
17	C2	C6	C7	123.2(2)
18	C2	C6	C25	117.7(2)
19	C7	C6	C25	119.1(2)
20	C6	C7	C8	120.2(2)
21	C6	C7	H71	120.0(2)
22	C8	C7	H71	119.9(2)
23	C7	C8	C9	120.9(2)
24	C7	C8	H81	120.5(2)
25	C9	C8	H81	118.6(2)
26	C8	C9	C10	122.3(2)
27	C8	C9	C24	118.4(2)
28	C10	C9	C24	119.3(2)
29	C9	C10	C11	119.5(2)
30	C9	C10	C16	123.1(2)

31	C11	C10	C16	117.2(2)
32	C10	C11	C12	122.1(2)
33	C10	C11	H111	119.1(2)
34	C12	C11	H111	118.8(2)
35	C11	C12	C13	119.7(2)
36	C11	C12	C14	116.6(2)
37	C13	C12	C14	123.7(2)
38	C12	C13	H132	109.6(2)
39	C12	C13	H131	109.7(2)
40	C12	C13	H133	109.6(2)
41	H132	C13	H131	109.4(2)
42	H132	C13	H133	108.6(2)
43	H131	C13	H133	109.9(2)
44	C12	C14	N15	121.9(2)
45	C12	C14	C18	124.1(2)
46	N15	C14	C18	113.9(2)
47	C14	N15	C16	120.6(2)
48	C10	C16	N15	121.6(2)
49	C10	C16	C17	123.4(2)
50	N15	C16	C17	115.0(2)
51	C16	C17	H173	109.9(2)
52	C16	C17	H171	111.3(2)
53	C16	C17	H172	109.9(2)
54	H173	C17	H171	108.8(2)
55	H173	C17	H172	108.7(2)
56	H171	C17	H172	108.2(2)
57	C14	C18	C19	118.5(2)
58	C14	C18	C23	123.2(2)
59	C19	C18	C23	118.1(2)
60	C18	C19	C20	120.6(2)
61	C18	C19	H191	118.8(2)
62	C20	C19	H191	120.6(2)
63	C19	C20	C21	120.4(2)
64	C19	C20	H201	119.5(2)
65	C21	C20	H201	120.1(2)
66	C20	C21	C22	119.9(2)
67	C20	C21	H211	120.8(2)
68	C22	C21	H211	119.3(2)
69	C21	C22	C23	120.0(2)
70	C21	C22	H221	119.7(2)
71	C23	C22	H221	120.4(2)
72	C18	C23	C22	121.0(2)
73	C18	C23	H231	120.0(2)
74	C22	C23	H231	119.0(2)
75	C9	C24	C25	120.8(2)
76	C9	C24	H241	119.6(2)
77	C25	C24	H241	119.6(2)

78	C6	C25	C24	120.6(2)
79	C6	C25	H251	118.7(2)
80	C24	C25	H251	120.7(2)

2-Phenyl-4-(*p*-tolyl)-6-(tosylmethyl)pyridine (651)



A single crystal having dimensions approximately 0.02×0.14×0.32 mm was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated MoK_α radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package.[1]

Examination of the systematic absences of the intensity data showed the space group to be *P 21/c*. The structure was solved in this space group using the direct-methods program SIR92,[2] which located all non-hydrogen atoms. The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. Subsequent full-matrix least-squares refinement was carried out against F^2 using the CRYSTALS program

suite.[3]Coordinates and anisotropic thermal parameters were refined for all non-hydrogen atoms, and the hydrogens were refined with riding constraints. A modified statistical weighting scheme was applied. Refinement converged satisfactorily to give R = 0.0524, wR = 0.1344.

Attached is a thermal ellipsoid plot (CAMERON) at 50% probability. A summary of crystallographic data is given below, as are full lists of atomic coordinates, anisotropic thermal parameters and those bond lengths and angles not concerning H atoms.

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Crystal data

Formula:	$C_{26}H_{23}NO_2S$
Space group:	P 1 21/c 1
Symmetrycellsetting:	Monoclinic
Cell length a:	17.7852(5)
Cell length b:	5.3916(2)
Cell length c:	22.8137(7)
Cell angle alpha:	90
Cell angle beta:	101.2669(12)
Cell angle gamma:	90
Cell volume:	2145.46(12)

Atomic coordinates and equivalent isotropic thermal parameters (Å^2) of non-hydrogen atoms.

Number	Label	Charge	SybylType	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD	Symm. op.
1	S1	0	S.o2	0.97846(4)	0.81471(14)	0.57895(3)	x,y,z
2	O2	0	O.2	0.97023(12)	1.0770(4)	0.56771(9)	x,y,z
3	O3	0	O.2	1.05420(11)	0.7086(4)	0.58772(9)	x,y,z
4	C4	0	C.3	0.93870(16)	0.7475(5)	0.64235(12)	x,y,z
5	C5	0	C.2	0.96032(17)	0.5312(6)	0.67367(13)	x,y,z
6	C6	0	C.2	0.92957(17)	0.4794(6)	0.72353(13)	x,y,z
7	C7	0	C.2	0.87758(18)	0.6372(6)	0.74205(13)	x,y,z
8	C8	0	C.2	0.85667(19)	0.8520(6)	0.70918(14)	x,y,z
9	C9	0	C.2	0.88660(17)	0.9076(6)	0.65916(13)	x,y,z
10	C10	0	C.3	0.8446(2)	0.5767(8)	0.79656(16)	x,y,z
11	C11	0	C.3	0.91973(16)	0.6504(6)	0.51974(12)	x,y,z
12	C12	0	C.2	0.83659(16)	0.7187(6)	0.51054(13)	x,y,z
13	N13	0	N.2	0.79498(13)	0.5828(5)	0.54192(10)	x,y,z
14	C14	0	C.2	0.72003(16)	0.6356(6)	0.53451(13)	x,y,z
15	C15	0	C.2	0.68592(17)	0.8232(6)	0.49622(14)	x,y,z
16	C16	0	C.2	0.72860(17)	0.9611(6)	0.46293(13)	x,y,z
17	C17	0	C.2	0.80619(17)	0.9051(6)	0.47150(13)	x,y,z
18	C18	0	C.2	0.69275(18)	1.1517(6)	0.41901(14)	x,y,z
19	C19	0	C.2	0.7359(2)	1.3159(7)	0.39369(16)	x,y,z
20	C20	0	C.2	0.7023(2)	1.4855(8)	0.35153(19)	x,y,z
21	C21	0	C.2	0.6243(2)	1.5005(7)	0.33192(15)	x,y,z
22	C22	0	C.3	0.5884(3)	1.6860(8)	0.28494(18)	x,y,z
23	C23	0	C.2	0.5816(2)	1.3417(8)	0.3576(2)	x,y,z
24	C24	0	C.2	0.6147(2)	1.1683(9)	0.3998(2)	x,y,z
25	C25	0	C.2	0.67534(18)	0.4799(7)	0.56922(15)	x,y,z
26	C26	0	C.2	0.7091(2)	0.3855(9)	0.62409(18)	x,y,z
27	C27	0	C.2	0.6680(2)	0.2379(12)	0.6563(2)	x,y,z
28	C28	0	C.2	0.5937(2)	0.1762(13)	0.6327(3)	x,y,z
29	C29	0	C.2	0.5594(2)	0.2742(13)	0.5794(3)	x,y,z
30	C30	0	C.2	0.5999(2)	0.4235(10)	0.5472(2)	x,y,z

Atomic coordinates and isotropic thermal parameters (Å^2) of hydrogen atoms

Number	Label	Charge	SybylType	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD	Symm. op.
1	H51	0	H	0.9948	0.424	0.6617	x,y,z
2	H61	0	H	0.9437	0.3336	0.745	x,y,z
3	H81	0	H	0.821	0.9592	0.7208	x,y,z
4	H91	0	H	0.8726	1.0501	0.6379	x,y,z
5	H101	0	H	0.8546	0.7115	0.8243	x,y,z
6	H102	0	H	0.8658	0.4239	0.8149	x,y,z

7	H103	0	H	0.7899	0.5589	0.7854	x,y,z
8	H111	0	H	0.9265	0.4758	0.5292	x,y,z
9	H112	0	H	0.9399	0.6905	0.4849	x,y,z
10	H151	0	H	0.631	0.8618	0.494	x,y,z
11	H171	0	H	0.8369	0.9943	0.4507	x,y,z
12	H191	0	H	0.789	1.3112	0.4051	x,y,z
13	H201	0	H	0.7336	1.5958	0.3358	x,y,z
14	H223	0	H	0.5342	1.6589	0.2739	x,y,z
15	H222	0	H	0.5971	1.8535	0.3002	x,y,z
16	H221	0	H	0.6107	1.6693	0.2498	x,y,z
17	H231	0	H	0.5288	1.3452	0.3469	x,y,z
18	H241	0	H	0.5833	1.0607	0.4154	x,y,z
19	H261	0	H	0.7604	0.4244	0.6398	x,y,z
20	H271	0	H	0.6909	0.1804	0.694	x,y,z
21	H281	0	H	0.5666	0.067	0.6535	x,y,z
22	H291	0	H	0.5077	0.2427	0.564	x,y,z
23	H301	0	H	0.576	0.4876	0.5096	x,y,z

Anisotropic thermal parameters (Å2)

Number	Label	U11	U22	U33	U12	U13	U23
1	S1	0.0293	0.0312	0.0318	-0.0018	0.0067	-0.0016
2	O2	0.0472	0.0284	0.0435	-0.0034	0.0151	0.0015
3	O3	0.0262	0.0471	0.0386	0.0013	0.005	-0.0053
4	C4	0.0292	0.0299	0.0287	0.0001	0.0025	-0.0023
5	C5	0.0359	0.034	0.0319	0.0058	0.0037	-0.0032
6	C6	0.0417	0.037	0.032	0.0003	-0.0003	0.0059
7	C7	0.0385	0.046	0.0352	-0.002	0.0071	0.0021
8	C8	0.045	0.049	0.0429	0.0118	0.0184	0.0021
9	C9	0.0412	0.0332	0.0401	0.0062	0.0098	0.0051
10	C10	0.062	0.083	0.045	0.007	0.0213	0.015
11	C11	0.0312	0.0332	0.0291	-0.0006	0.0087	-0.0012
12	C12	0.0271	0.0375	0.0299	-0.0025	0.0049	-0.0016
13	N13	0.03	0.0386	0.0344	-0.0017	0.0064	0.0011
14	C14	0.0273	0.044	0.0352	-0.0013	0.0046	0.0011
15	C15	0.0284	0.045	0.0399	0.0012	0.0035	0.0028
16	C16	0.0309	0.0386	0.0365	-0.0018	-0.0003	0.0036
17	C17	0.0323	0.0403	0.036	-0.0064	0.0039	0.0038
18	C18	0.0368	0.04	0.0393	-0.0044	-0.0013	0.0022
19	C19	0.042	0.059	0.062	0.0063	0.0119	0.017
20	C20	0.064	0.075	0.072	0.015	0.025	0.037
21	C21	0.069	0.043	0.04	0.0072	-0.004	0.0005
22	C22	0.111	0.068	0.052	0.028	-0.001	0.013
23	C23	0.049	0.07	0.109	-0.008	-0.032	0.033
24	C24	0.04	0.082	0.121	-0.013	-0.016	0.056
25	C25	0.0323	0.056	0.047	0.0015	0.0115	0.014

26	C26	0.035	0.103	0.07	0.002	0.0081	0.041
27	C27	0.049	0.171	0.102	0.003	0.013	0.091
28	C28	0.043	0.186	0.126	-0.007	0.018	0.109
29	C29	0.039	0.204	0.136	-0.031	-0.004	0.112
30	C30	0.034	0.121	0.084	-0.015	0.002	0.055

Bond lengths (Å).

Number	Atom1	Atom2	Length
1	S1	O2	1.440(2)
2	S1	O3	1.441(2)
3	S1	C4	1.767(3)
4	S1	C11	1.775(3)
5	C4	C5	1.382(4)
6	C4	C9	1.375(4)
7	C5	C6	1.383(5)
8	C5	H51	0.922(3)
9	C6	C7	1.382(5)
10	C6	H61	0.934(3)
11	C7	C8	1.390(4)
12	C7	C10	1.511(5)
13	C8	C9	1.383(5)
14	C8	H81	0.934(3)
15	C9	H91	0.917(3)
16	C10	H101	0.957(4)
17	C10	H102	0.967(4)
18	C10	H103	0.961(3)
19	C11	C12	1.498(4)
20	C11	H111	0.968(3)
21	C11	H112	0.958(3)
22	C12	N13	1.343(4)
23	C12	C17	1.381(4)
24	N13	C14	1.341(4)
25	C14	C15	1.395(4)
26	C14	C25	1.486(5)
27	C15	C16	1.390(5)
28	C15	H151	0.990(3)
29	C16	C17	1.389(4)
30	C16	C18	1.489(4)
31	C17	H171	0.925(3)
32	C18	C19	1.371(5)
33	C18	C24	1.375(5)
34	C19	C20	1.376(5)
35	C19	H191	0.930(3)
36	C20	C21	1.374(5)
37	C20	H201	0.933(4)

38	C21	C22	1.513(5)
39	C21	C23	1.352(6)
40	C22	H223	0.959(5)
41	C22	H222	0.969(4)
42	C22	H221	0.966(5)
43	C23	C24	1.388(6)
44	C23	H231	0.923(3)
45	C24	H241	0.923(5)
46	C25	C26	1.376(5)
47	C25	C30	1.372(5)
48	C26	C27	1.385(7)
49	C26	H261	0.937(3)
50	C27	C28	1.367(5)
51	C27	H271	0.930(4)
52	C28	C29	1.356(9)
53	C28	H281	0.945(6)
54	C29	C30	1.383(8)
55	C29	H291	0.934(4)
56	C30	H301	0.945(4)

Bond angles (°).

Number	Atom1	Atom2	Atom3	Angle
1	O2	S1	O3	118.3(1)
2	O2	S1	C4	107.7(1)
3	O2	S1	C11	109.3(1)
4	O3	S1	C4	108.5(1)
5	O3	S1	C11	107.6(1)
6	C4	S1	C11	104.5(1)
7	S1	C4	C5	118.7(2)
8	S1	C4	C9	119.9(2)
9	C5	C4	C9	121.3(3)
10	C4	C5	C6	118.7(3)
11	C4	C5	H51	120.6(3)
12	C6	C5	H51	120.6(3)
13	C5	C6	C7	121.5(3)
14	C5	C6	H61	119.5(3)
15	C7	C6	H61	119.0(3)
16	C6	C7	C8	118.2(3)
17	C6	C7	C10	120.6(3)
18	C8	C7	C10	121.2(3)
19	C7	C8	C9	121.3(3)
20	C7	C8	H81	119.2(3)
21	C9	C8	H81	119.5(3)
22	C4	C9	C8	118.9(3)
23	C4	C9	H91	120.5(3)

24	C8	C9	H91	120.6(3)
25	C7	C10	H101	109.2(3)
26	C7	C10	H102	111.0(3)
27	C7	C10	H103	109.8(3)
28	H101	C10	H102	110.8(4)
29	H101	C10	H103	107.4(4)
30	H102	C10	H103	108.6(4)
31	S1	C11	C12	113.7(2)
32	S1	C11	H111	106.7(2)
33	S1	C11	H112	105.0(2)
34	C12	C11	H111	110.3(3)
35	C12	C11	H112	110.3(3)
36	H111	C11	H112	110.7(3)
37	C11	C12	N13	115.0(3)
38	C11	C12	C17	121.4(3)
39	N13	C12	C17	123.6(3)
40	C12	N13	C14	117.0(3)
41	N13	C14	C15	122.2(3)
42	N13	C14	C25	115.8(3)
43	C15	C14	C25	122.0(3)
44	C14	C15	C16	120.9(3)
45	C14	C15	H151	119.2(3)
46	C16	C15	H151	119.9(3)
47	C15	C16	C17	116.1(3)
48	C15	C16	C18	122.0(3)
49	C17	C16	C18	121.9(3)
50	C12	C17	C16	120.1(3)
51	C12	C17	H171	120.9(3)
52	C16	C17	H171	119.0(3)
53	C16	C18	C19	121.9(3)
54	C16	C18	C24	122.2(3)
55	C19	C18	C24	115.9(3)
56	C18	C19	C20	121.4(3)
57	C18	C19	H191	119.1(4)
58	C20	C19	H191	119.5(4)
59	C19	C20	C21	122.7(4)
60	C19	C20	H201	118.8(4)
61	C21	C20	H201	118.5(4)
62	C20	C21	C22	121.9(3)
63	C20	C21	C23	116.0(4)
64	C22	C21	C23	122.1(4)
65	C21	C22	H223	110.4(4)
66	C21	C22	H222	110.2(4)
67	C21	C22	H221	110.0(4)
68	H223	C22	H222	108.5(4)
69	H223	C22	H221	108.8(4)
70	H222	C22	H221	108.8(4)

71	C21	C23	C24	122.0(4)
72	C21	C23	H231	120.1(4)
73	C24	C23	H231	118.0(4)
74	C18	C24	C23	122.0(4)
75	C18	C24	H241	119.0(4)
76	C23	C24	H241	119.0(4)
77	C14	C25	C26	120.7(3)
78	C14	C25	C30	121.1(3)
79	C26	C25	C30	118.2(4)
80	C25	C26	C27	120.9(4)
81	C25	C26	H261	119.0(4)
82	C27	C26	H261	120.1(4)
83	C26	C27	C28	120.0(5)
84	C26	C27	H271	120.1(5)
85	C28	C27	H271	119.9(5)
86	C27	C28	C29	119.3(5)
87	C27	C28	H281	120.2(6)
88	C29	C28	H281	120.6(6)
89	C28	C29	C30	120.9(5)
90	C28	C29	H291	120.3(6)
91	C30	C29	H291	118.9(5)
92	C25	C30	C29	120.5(4)
93	C25	C30	H301	119.0(4)
94	C29	C30	H301	120.4(5)

Appendix IV: References and footnotes

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