Gold(III)-oxo complexes as catalysts in intramolecular hydroamination

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Supporting Information

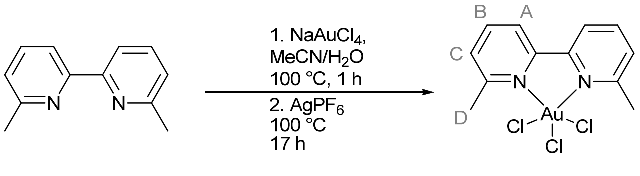
1. General Experimental Section

^{1}H NMR spectra were recorded on Bruker AV 300 and AV 400 spectrometers at 200 and 400 MHz respectively and referenced to residual solvent. ^{13}C NMR spectra were recorded using the same spectrometers at 75 and 100 MHz respectively. Chemical shifts (δ in ppm) were referenced to tetramethylsilane (TMS) or to residual solvent peaks ($CDCl_3$ at δ_H 7.26 and CD_3CN at 1.94). *J* values are given in Hz and s, d, dd, t, q, quint and m abbreviations correspond to singlet, doublet, doublet of doublet, triplet, quartet, quintet and multiplet. Mass spectra were obtained at the EPSRC National Mass Spectrometry Service Centre in Swansea. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat to a diamond/ZnSe plate. Flash column chromatography was carried out using Matrix silica gel 60 from Fisher Chemicals and TLC was performed using Merck silica gel 60 F254 pre-coated sheets and visualised by UV (254 nm) or stained by the use of aqueous acidic $KMnO_4$ or aqueous acidic ammonium molybdate as appropriate. Unless otherwise stated, solvents were purchased from commercial sources and used with no further purification. Pet. ether refers to petroleum ether which boils in the range 40 – 60 °C. Sodium tetrachloroaurate was kindly loaned by Johnson Matthey and used without further purification. Gold(III)-catalysed reactions were carried out in Fisherbrand^{TM} one dram screw cap micro vials without the requirement for an inert atmosphere. All other reactions were carried out under an atmosphere of N_2.

2. Catalyst Synthesis

Catalysts **8**,[1,2] **9**,[3] **10**,[1] and **11**[1] were synthesised in accordance with literature procedures.

Synthesis of [Au(bipy^{2Me})Cl$_3$] 4



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Method A

To a stirring solution of sodium tetrachloroaurate (1.00 g, 2.76 mmol) in 25 mL of distilled water was added dropwise a solution of 6,6'-dimethyl-2,2'-bipyridine (509 mg, 2.76 mmol) in acetonitrile (40 mL). The resulting orange mixture was heated at reflux (100 °C) for 1 hour. The reaction was then cooled briefly to facilitate the rapid addition of silver hexafluorophosphate (699 mg, 2.76 mmol) and then subsequently returned to reflux for a further 15 hours. The resulting off-white precipitate was removed by passage over a short plug of Celite™ and the filtrate concentrated *in vacuo*. The residue was then reconstituted in DCM, washed thrice with 100 mL distilled water and twice with brine (50 mL), before drying the organics over Na_2SO_4. Concentration *in vacuo* afforded a crude yellow-orange solid which was washed with cold MeOH (5 mL) to afford the target compound **4** as an orange solid (942 mg, 70%). Crystals were obtained by slow evaporation of a saturated acetonitrile solution of the product.

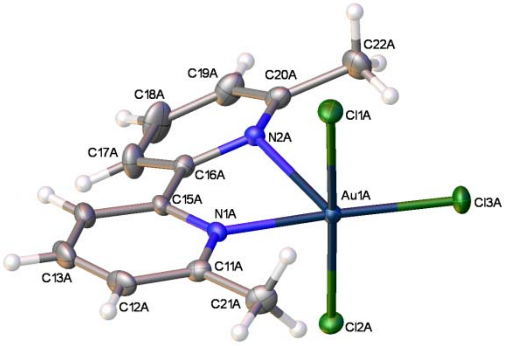
Method B

To a stirring solution of sodium tetrachloroaurate (1.00 g, 2.76 mmol) in 25 mL of distilled water and acetonitrile (40 mL) was added 6,6'-dimethyl-2,2'-bipyridine (509 mg, 2.76 mmol) and silver hexafluorophosphate (699 mg, 2.76 mmol). The resulting suspension was heated at 100 °C for 16 hours. The resulting off-white precipitate was removed by passage over a short plug of Celite^{TM} and the filtrate concentrated *in vacuo*. The residue was then reconstituted in DCM, washed thrice with 100 mL distilled water and twice with brine (50 mL), before drying the organics over Na_2SO_4. Concentration *in vacuo* afforded a crude yellow-orange solid which was recrystallised from acetonitrile/diethyl ether to give the title compound **4** (780 mg, 58%).

Method C

To a stirring solution of sodium tetrachloroaurate (1.00 g, 2.76 mmol) in 25 mL of distilled water and acetonitrile (40 mL) was added 6,6'-dimethyl-2,2'-bipyridine (509 mg, 2.76 mmol) and potassium hexafluorophosphate (508 mg, 2.76 mmol). The resulting suspension was heated at 100 °C for 16 hours. The reaction mixture was then concentrated *in vacuo* before being reconstituted in acetonitrile (50 mL). The resulting suspension was then passed over a short plug of Celite^{TM} and the residue washed with acetonitrile (50 mL) until the eluent was colourless. The resulting solution was then re-concentrated and the residue reconstituted in DCM, washed thrice with 100 mL distilled water and twice with brine (50 mL), before drying the organics over Na_2SO_4. Concentration *in vacuo* afforded a crude yellow-orange solid which was recrystallised from acetonitrile/diethyl ether to give the title compound **4** (474 mg, 35%).

Mp 188 ^{o}C (decomposes); ν_{max} /cm^{-1} 3096 (C-H), 1588 (Ar C=C), 1571 (Ar C=C), 1456 (Ar C=C); δ_H (300 MHz, CD_3CN) 8.04 - 8.15 (4 H, m, H_A, H_B), 7.65 (2 H, dd, J=7.7, 1.8 Hz, H_C), 3.05 (6 H, s, H_D); δ_C (75 MHz, CD_3CN) 160.4 (C), 152.5 (C), 142.0 (C-H), 128.7 (C-H), 124.7 (C-H), 26.2 (CH_3); Found (EI+): $[M-H]^+$ 484.9651, $C_{12} H_{11}N_2AuCl_3$ requires 484.9648.

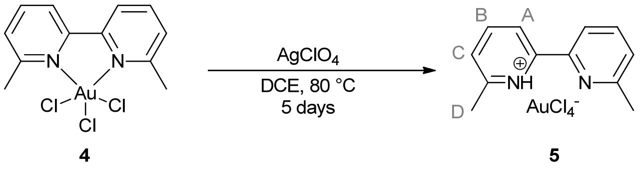


Empirical formula	$C_{24}H_{24}N_4Cl_6Au_2$
Formula weight	487.56
Temperature/K	100.15
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	18.1080(10)
b/Å	9.5124(5)
c/Å	18.3546(12)
α/°	90.00
β/°	113.590(8)
γ/°	90.00
Volume/Å^3	2897.4(3)
Z	4
ρ_{calc}mg/mm^3	2.235
m/mm^{-1}	10.691
F(000)	1824
Crystal size/mm^3	0.08 × 0.03 × 0.02
2Θ range for data collection	6.2 to 54.96°
Index ranges	$-23 \leq h \leq 23$, $-11 \leq k \leq 12$, $-13 \leq l \leq 23$
Reflections collected	13122

Independent reflections	6581[R(int) = 0.0217]
Data/restraints/parameters	6581/0/329
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	$R_1 = 0.0175$, $wR_2 = 0.0437$
Final R indexes [all data]	$R_1 = 0.0199$, $wR_2 = 0.0447$
Largest diff. peak/hole / e $Å^{-3}$	0.898/-0.777
Flack Parameter	N/A

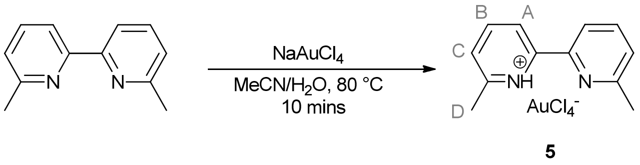
Synthesis of 6,6'-dimethyl-[2,2'-bipyridin]-1-ium tetrachloroaurate$^{(III)}$ 5

Method A:



To a stirring solution of [Au(bipy^{2Me})Cl$_3$] **4** (100 mg, 0.21 mmol) in 4 mL of DCE was added AgClO$_4$ (47 mg, 0.23 mmol) and the resulting orange mixture heated to 80 °C for 5 days, during which a grey precipitate formed. The reaction was then cooled to room temperature and the precipitate removed by vacuum filtration. The filter cake was washed thoroughly with DCE (5 mL) and the yellow filtrate concentrated *in vacuo* to afford a yellow-orange solid. The residue was then recrystallised by vapour diffusion (MeCN/Et$_2$O) to afford the target complex **5** as a bright yellow solid (81 mg, 75%).

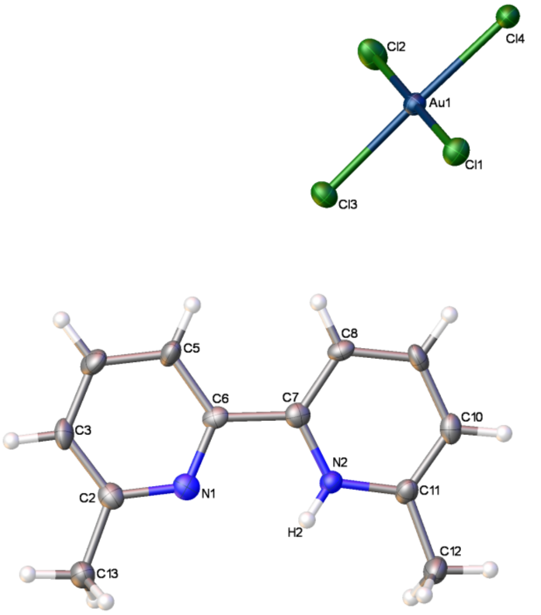
Method B:



To a stirring solution of NaAuCl$_4$ (100 mg, 0.276 mmol) in H$_2$O (1 mL) was added 6,6'-dimethyl-2,2'-bipyridine (51 mg, 0.276 mmol) in acetonitrile (1 mL) at the resulting mixture heated to 80 °C for 10 minutes during which time a bright yellow precipitated formed. The precipitate was removed by vacuum filtration and washed consecutively with H$_2$O (5 mL), EtOH (5 mL) and Et$_2$O (5 mL). The crude yellow product was then recrystallised from acetonitrile/Et$_2$O to afford the title compound **5** as a bright yellow solid (41 mg, 28%).

Mp 114-116 °C (decomposes); ν_{max} /cm^{-1} 3096 (N-H), 2924 (C-H), 1615 (Ar C=C) , 1595 (Ar C=C), 1520 (Ar C=C), 1446 (Ar C=C); δ_H (300 MHz, CD$_3$CN) 7.94 - 8.29 (4 H, m, H$_A$, H$_B$), 7.65 (2 H, dd, *J*=7.7, 1.8 Hz, H$_C$), 3.05 ppm (6 H, s, H$_D$); δ_C (75 MHz, CD$_3$CN) 158.8 (C), 147.1 (C), 144.6 (C-H), 129.1 (C-H), 121.9 (C-H), 22.7 (CH_3). Found (ESI): $[M]^+$ 185.1070, $C_{12}H_{13}N_2^+$ requires 185.1073. Found (ESI): $[M]^-$ 336.8424, $AuCl_4^-$ requires 336.8425.

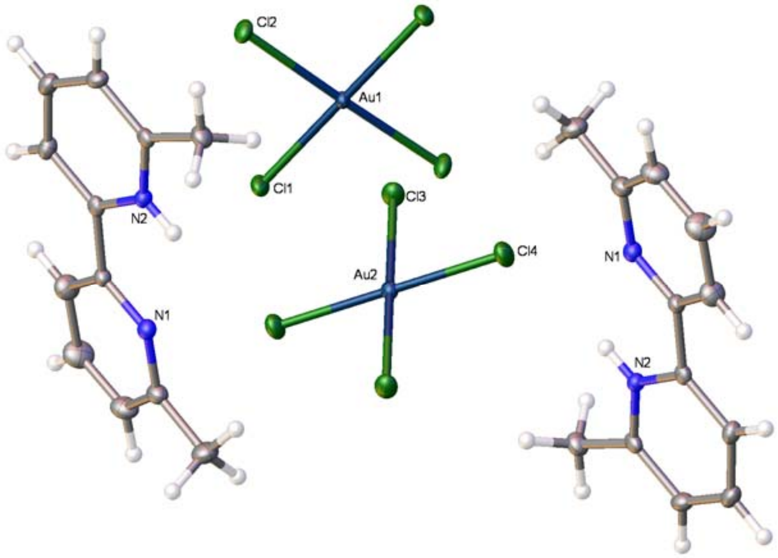
Polymorph using Method A:



Empirical formula	$C_{12}H_{13}N_2{\cdot}AuCl_4$
Formula weight	524.01
Temperature/K	100.15
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.8712(6)
b/Å	11.7030(7)
c/Å	12.3206(7)
α/°	90.00

β/°	95.806(3)
γ/°	90.00
Volume/$Å^3$	1559.46(15)
Z	4
$\rho_{calc}mg/mm^3$	2.232
m/mm^{-1}	10.11
F(000)	984
Crystal size/mm^3	0.38 × 0.24 × 0.08
2Θ range for data collection	5.2 to 53.4°
Index ranges	$-13 \leq h \leq 13, 0 \leq k \leq 14, 0 \leq l \leq 15$
Reflections collected	63730
Independent reflections	3289[R(int) = 0.059]
Data/restraints/parameters	3289/1/178
Goodness-of-fit on F^2	1.30
Final R indexes [I>=2σ (I)]	$R_1 = 0.041$, $wR_2 = 0.106$
Final R indexes [all data]	$R_1 = 0.0526$, $wR_2 = 0.1056$
Largest diff. peak/hole / e $Å^{-3}$	2.99/-1.02
Flack Parameter	N/A

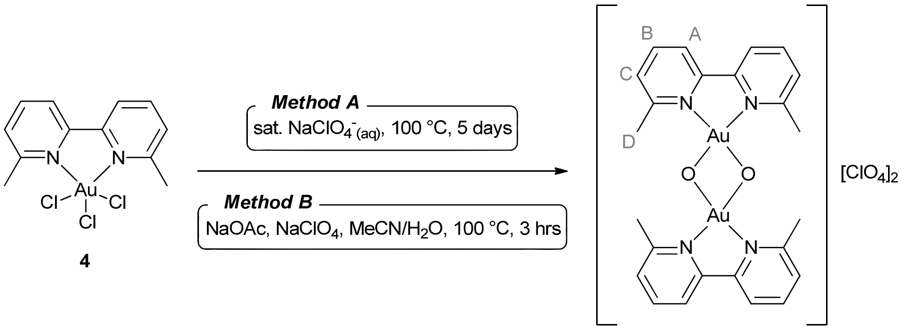
Polymorph using Method B:



Empirical formula	$C_{12}H_{13}N_2 \cdot AuCl_4$
Formula weight	524.01
Temperature/K	100.15
Crystal system	Monoclinic
Space group	C2/c
a/Å	22.1175(10)
b/Å	14.7910(7)
c/Å	9.5257(4)
α/°	90.00
β/°	99.676(2)
γ/°	90.00

Volume/Å^3	3071.9(2)
Z	8
ρ_{calc}mg/mm^3	2.266
m/mm^{-1}	10.260
F(000)	1968
Crystal size/mm^3	0.24 × 0.12 × 0.08
2Θ range for data collection	5.5 to 65.68°
Index ranges	$-33 \leq h \leq 33$, $-22 \leq k \leq 22$, $-14 \leq l \leq 14$
Reflections collected	40918
Independent reflections	5667[R(int) = 0.0574]
Completeness to Θ = 25.00°	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4941 and 0.1921
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5667/0/179
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0275, wR_2 = 0.0615
Final R indexes [all data]	R_1 = 0.0356, wR_2 = 0.0649
Largest diff. peak/hole / e Å^{-3}	2.160/-3.005

Synthesis of $[Au(bipy^{2Me})(\mu\text{-}O)]_2[ClO_4]_2$ 7



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Method A

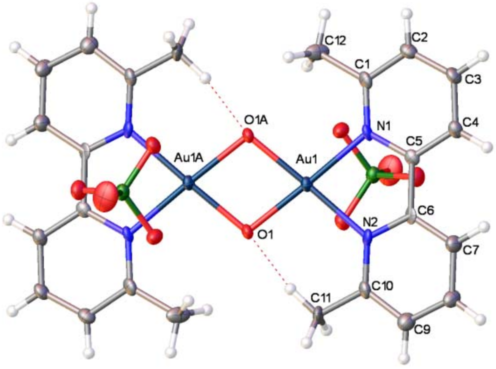
A saturated aqueous solution of $NaClO_4$ (30 mL) was added to [Au(bipy^{2Me})Cl_3] **4** (200 mg, 0.41 mmol) and the resulting suspension heated at 100 °C for 5 days. The reaction was then cooled to room temperature and the precipitate removed by vacuum filtration. The filter cake was washed thoroughly with distilled water (50 mL), ice-cold MeCN (3 mL) followed by Et_2O (10 mL). The crude residue was then recrystallised by vapour diffusion (MeCN/Et_2O) to afford the target complex **7** as a yellow solid (90 mg, 22%).

Method B

To a stirring suspension of [Au(bipy^{2Me})Cl_3] **4** (170 mg, 0.35 mmol) in CH_3CN (1 mL) were added an aqueous solution of NaOAc (95 mg, 0.70 mmol, 60 mL) and $NaClO_4$ (128 mg, 1.05 mmol). The resulting suspension was refluxed for 3 hours which corresponded with a lightening of the suspension colour. The reaction was then cooled to room temperature, the precipitate collected by vacuum filtration and the filter cake washed with H_2O (25 mL) then Et_2O (25 mL). Recrystallisation of the crude product from MeCN/Et_2O gave the target compound **7** as a pale yellow solid (145 mg, 42%).

Mp. 203-206 °C (decomposes); ν_{max} /cm^{-1} 3085 (C-H), 1603 (Ar C=C), 1570 (Ar C=C), 1471 (Ar C=C); δ_H (300 MHz, CD_3CN) 8.37 - 8.24 (4 H, m, H_A, H_B), 7.70 (2 H, dd, J =1.8, 7.3 Hz, H_C), 2.96 (6 H, s, H_D); δ_C (75 MHz, C_2D_6SO) 162.2 (C), 155.0 (C), 143.3 (C-H), 131.9 (C-

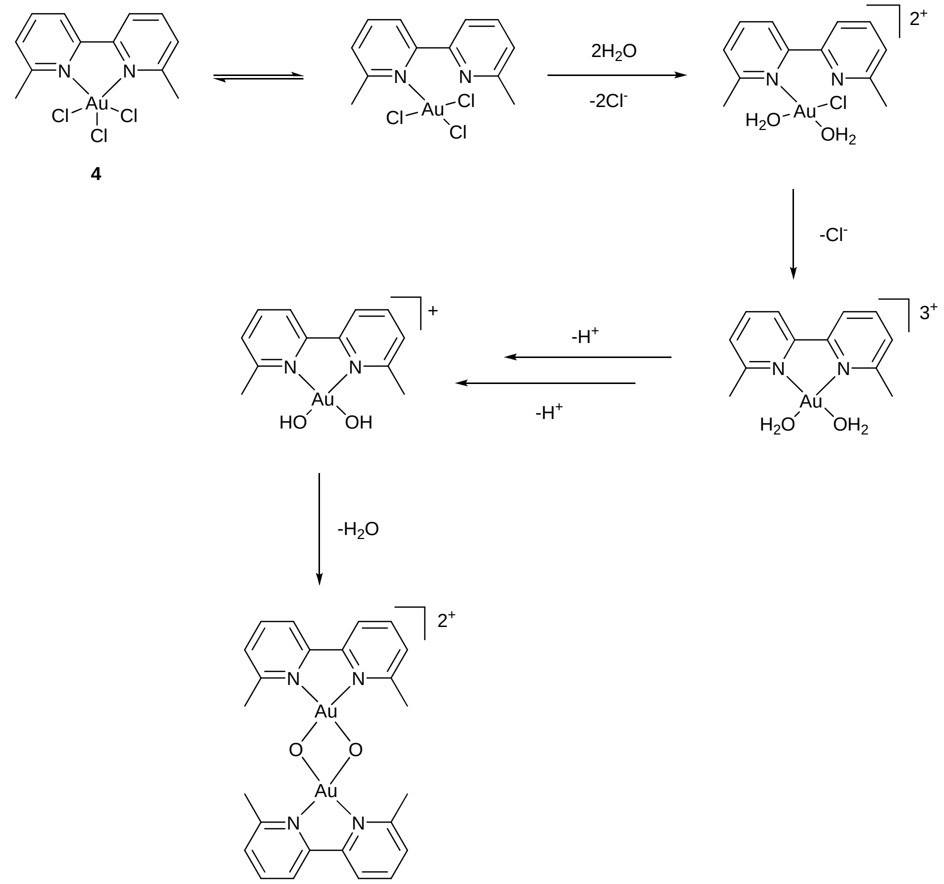
H), 123.1(C-H), 20.4 (CH_3); Found (ESI): $[M-ClO_4]^+$ 893.0687, $C_{24}H_{24}Au_2N_4O_6Cl$ requires 893.0710.



Empirical formula	$C_{12}H_{12}AuClN_2O_5$
Formula weight	496.65
Temperature/K	200.15
Crystal system	Triclinic
Space group	P-1
a/Å	7.6032(6)
b/Å	7.6032(6)
c/Å	9.9600(9)
α/°	82.321(5)
β/°	85.907(5)
γ/°	88.085(5)

Volume/$Å^3$	690.65(10)
Z	2
ρ_{calc}mg/mm^3	2.388
m/mm^{-1}	10.867
F(000)	468.0
Crystal size/mm^3	0.34 × 0.12 × 0.04
2Θ range for data collection	4.14 to 61.16°
Index ranges	$-10 \leq h \leq 10$, $-12 \leq k \leq 13$, $-14 \leq l \leq 13$
Reflections collected	14381
Independent reflections	4058[R(int) = 0.0572]
Data/restraints/parameters	4058/421/192
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	$R_1 = 0.0724$, $wR_2 = 0.1982$
Final R indexes [all data]	$R_1 = 0.0821$, $wR_2 = 0.2089$
Largest diff. peak/hole / e $Å^{-3}$	13.15/-4.46
Flack Parameter	N/A

Proposed mechanism[2] for Scheme 3:



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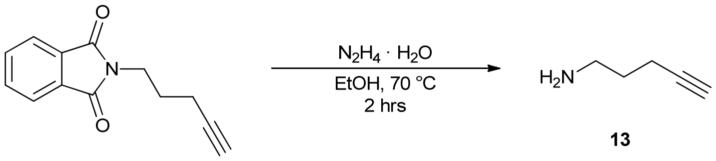
3. Hydroamination

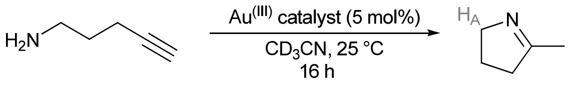
Synthesis of pent-4-yn-1-amine[4] 13



To a stirring suspension of *N*-(pent-4-yn-1-yl)phthalimide (4.00 g, 0.02 mmol) in EtOH (40 mL) was added hydrazine monohydrate (1.90 g, 0.04 mmol) and the reaction heated at 70 °C for 2 hours, during which time the initial suspension was replaced by a thick white precipitate. The precipitate was fully solvated by addition of distilled water (70 mL) and subsequently cooled to 0 °C. The pH of the solution was then carefully adjusted to pH 3.5 by dropwise addition of 2 M HCl (monitored with a calibrated Hanna Instruments^{TM} pH meter) and the resulting white suspension removed by vacuum filtration. The filtrate was concentrated *in vacuo* to remove the ethanol, before the solution was re-cooled to 0 °C and basified with 10 M NaOH (aq). The aqueous mixture was then extracted twice with DCM (150 ml) and the combined organic extracts washed with brine, before drying over Na_2SO_4. Evaporation of the solvent afforded the title amine **13** as a pale yellow oil (0.81 g, 52%) which was used without further purification.

ν_{max} /cm^{-1} 3369 (N-H), 3294 (≡C-H), 3214 (N-H), 2938 (C-H), 2863 (C-H), 2115 (C≡C); δ_H (300 MHz, $CDCl_3$) 2.76 (2H, t, *J*=7.0 Hz, $NC\underline{H_2}$), 2.22 (2H, td, *J*=2.8, 7.0 Hz, $C\underline{H_2}C{\equiv}$), 1.92 (1H, t, *J*=2.8 Hz, $\equiv C\text{-}\underline{H}$), 1.62 (2H, quint., *J*=7.0 Hz, $CH_2C\underline{H_2}CH_2$), 1.41 - 1.18 (2H, br. s, -NH_2); δ_C (75 MHz, $CDCl_3$) 83.9 (C), 68.5 (C-H), 41.0 (CH_2), 32.0 (CH_2), 15.8 (CH_2; Found (CI+): $[M+H]^+$ 84.0807, $C_5H_{10}N$ requires 84.0808.

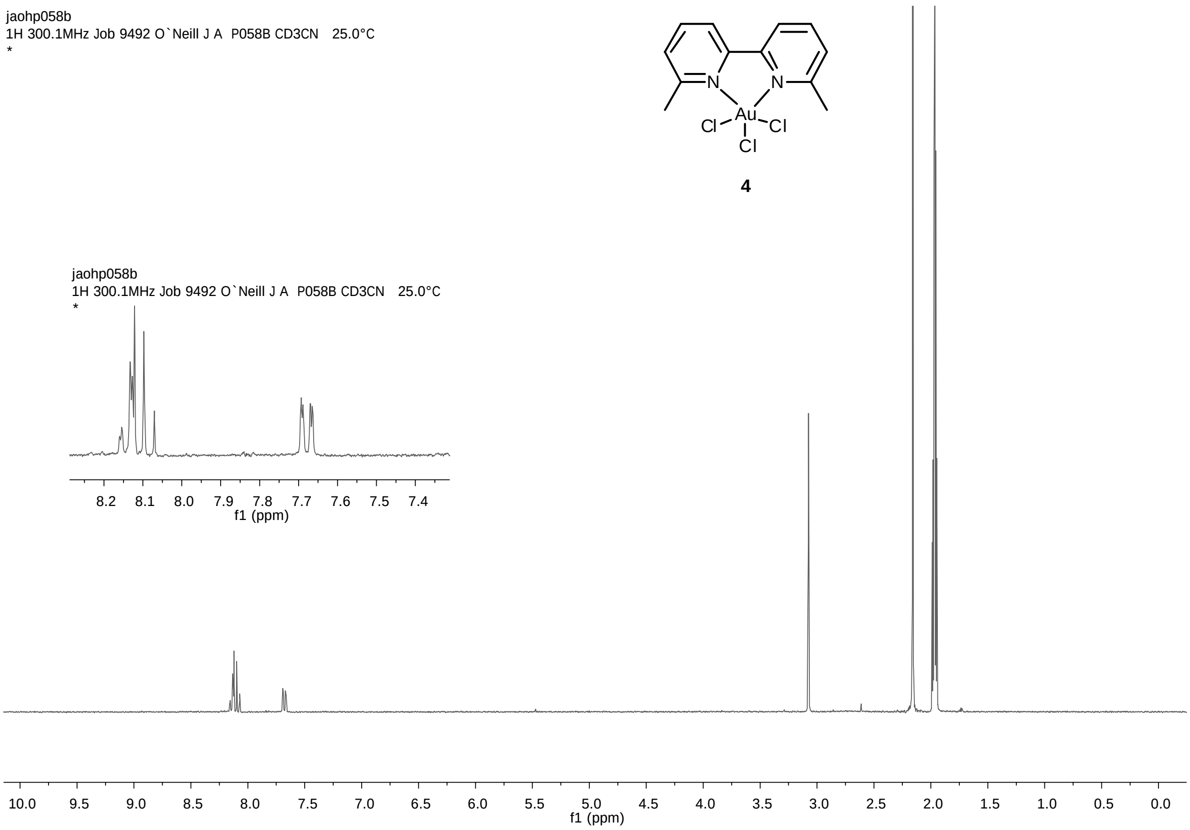
General experimental procedure for the Au$^{(III)}$ catalysed hydroamination reaction

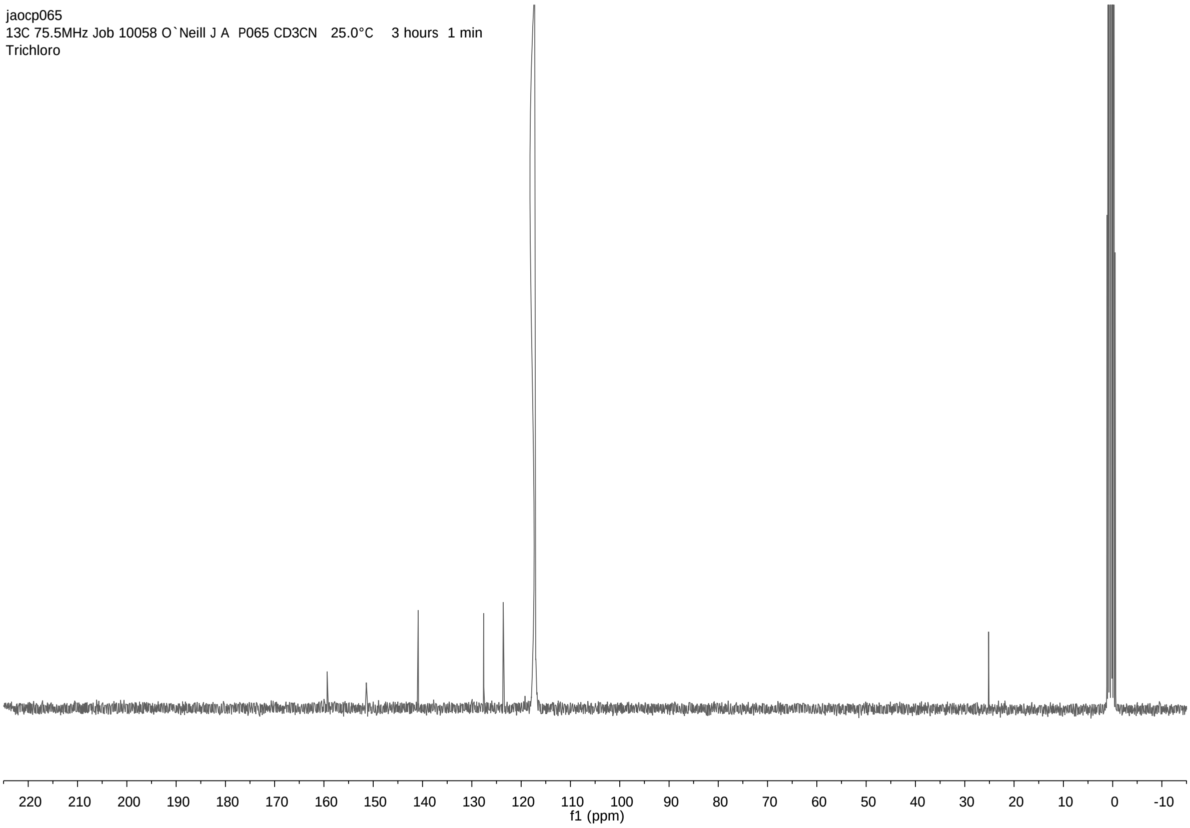


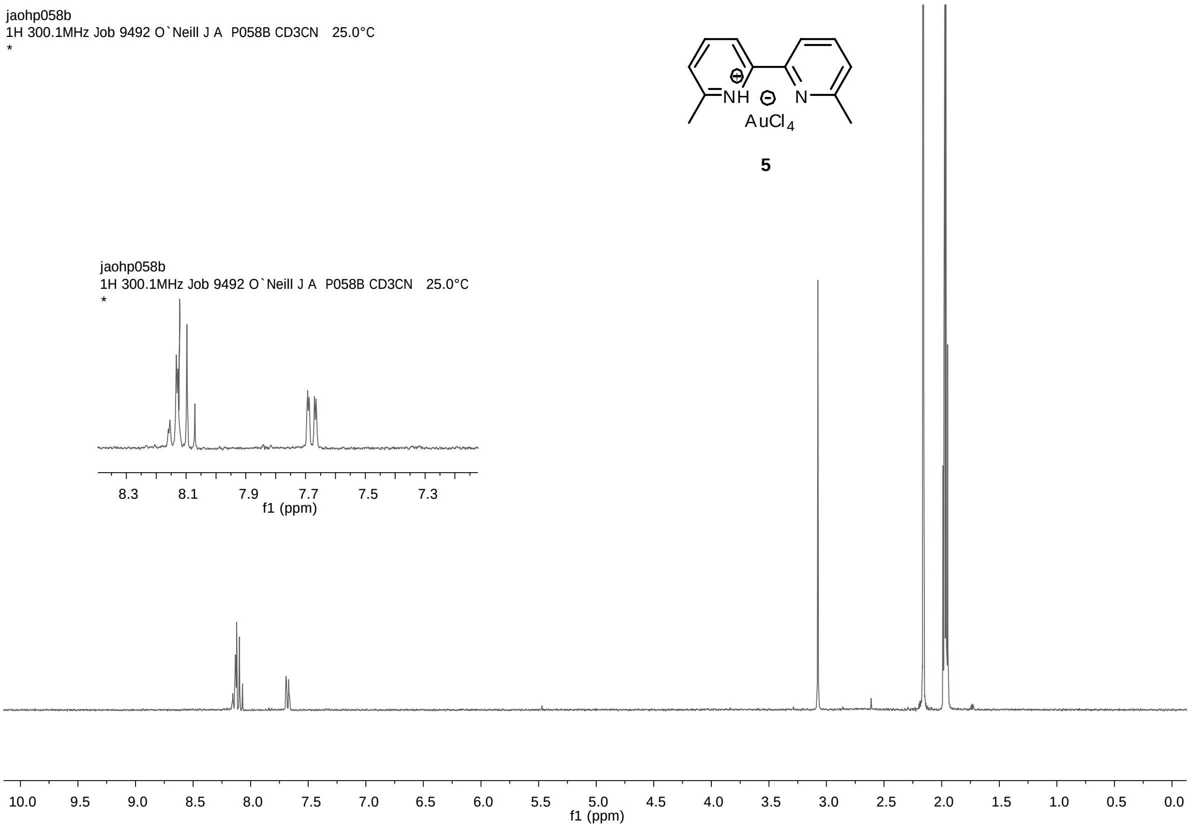
13 **14**

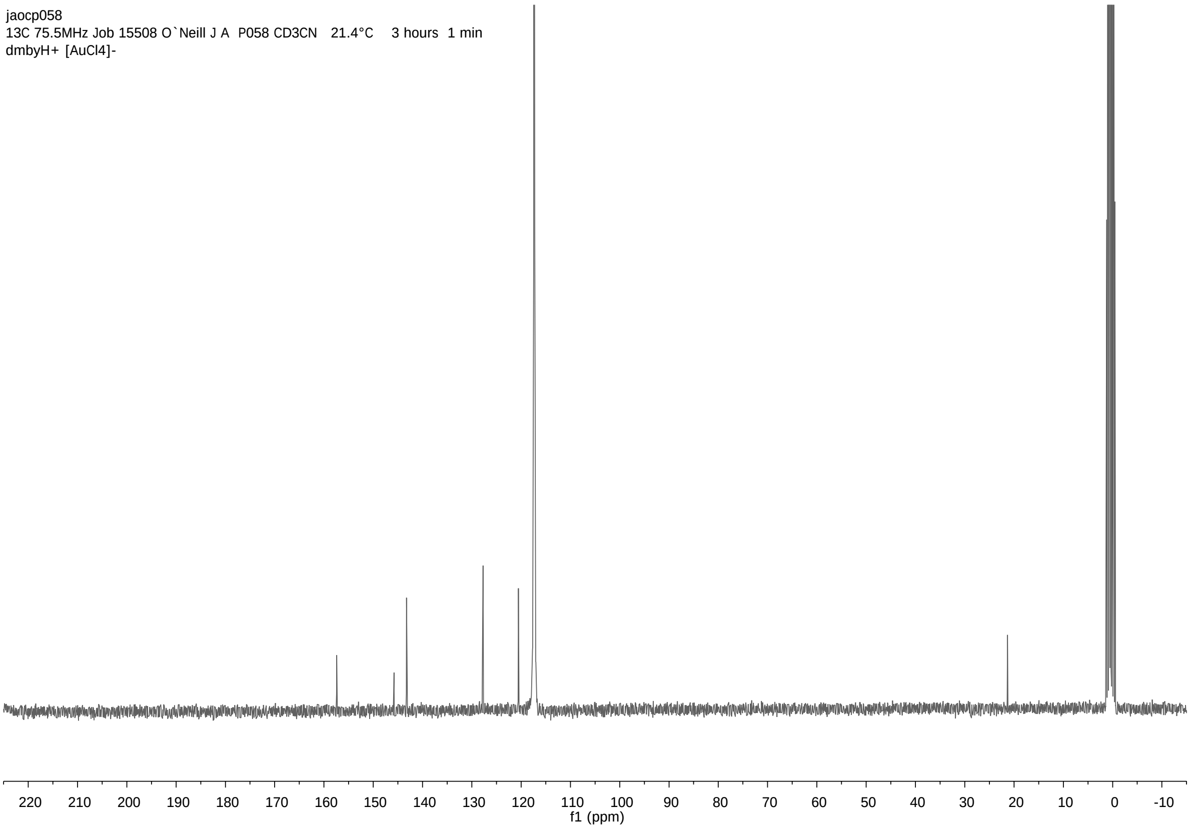
To a one dram micro-vial equipped with a micro stirrer bar, was added pent-4-yn-1-amine **13** (1 equiv) and dissolved in CD_3CN (0.5 M). The appropriate gold catalyst (5 mg, 5 mol%) was added to the vial and the lid screwed on. The reaction was stirred for 16 h at 25 °C before mesitylene (1 equiv.) was added. The reaction mixture was then further diluted with CD_3CN (0.5 mL) and an aliquot taken for crude ^1H NMR analysis. The yield of **14**[5] was measured by integration of the multiplet peak corresponding to H_A with respect to the mesitylene aromatic peak (*N.B.* **14** is not stable on silica or alumina). ^1H NMR (300 MHz, CD_3CN) δ 3.78 – 3.62 (2H, m, H_A), 2.44 (2H, app. t, *J* = 11.1 Hz, CH_2), 1.96 (3H, s, CH_3), 1.91 – 1.77 (2H, m, CH_2).

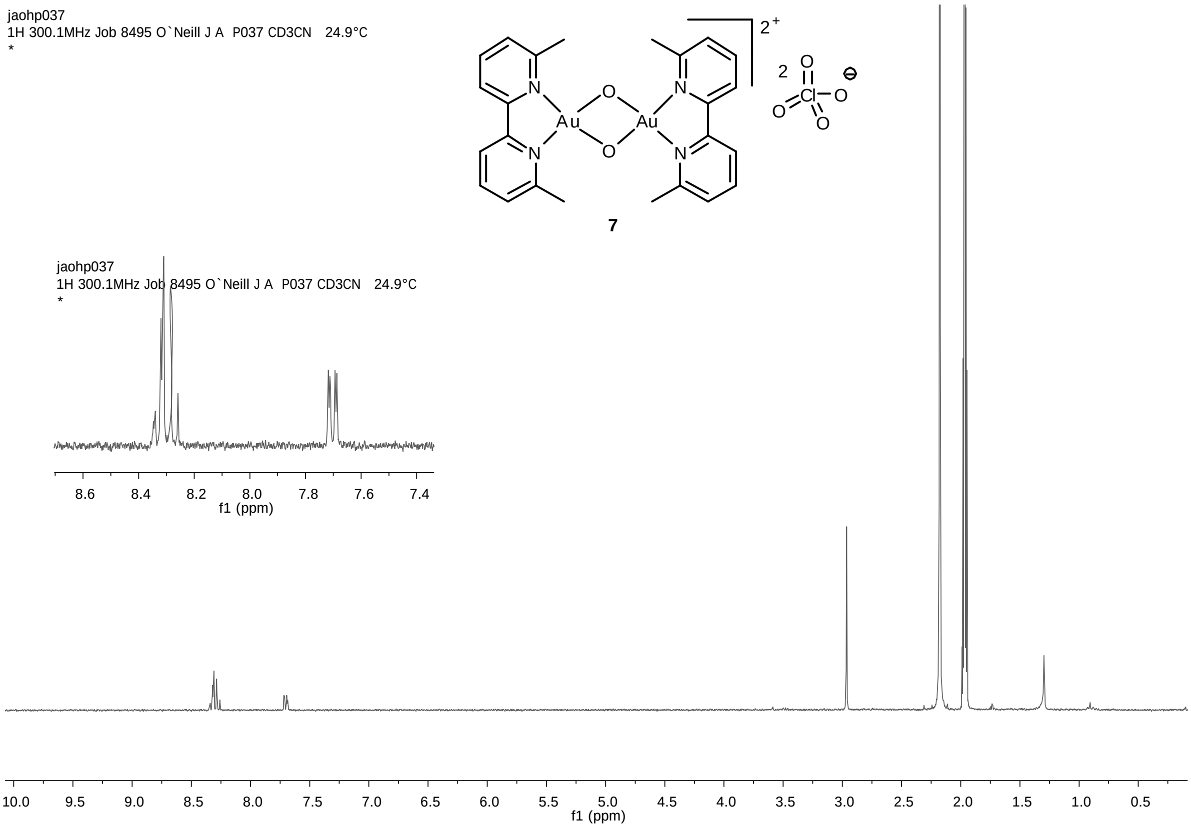
4. Spectra

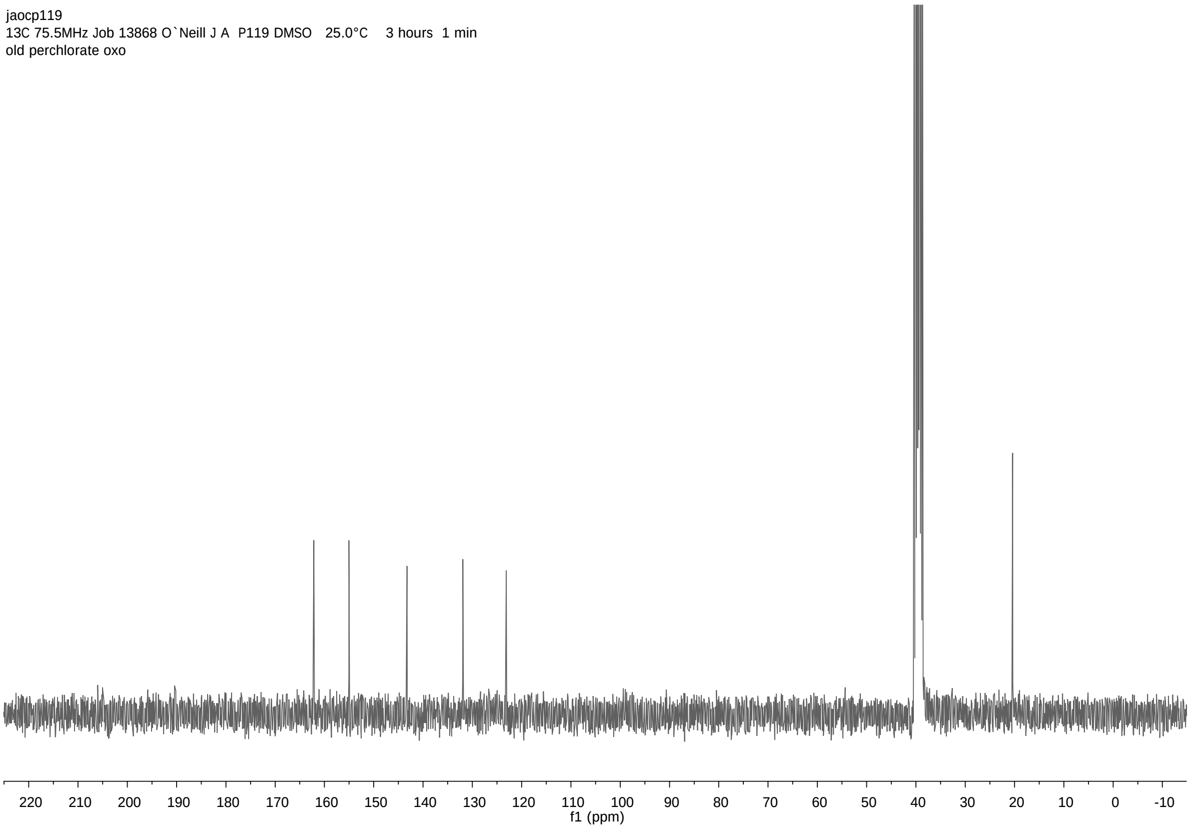

jaohp058b
1H 300.1MHz Job 9492 O`Neill J A P058B CD3CN 25.0°C
*
N
N
Au
Cl
Cl
Cl
4
jaohp058b
1H 300.1MHz Job 9492 O`Neill J A P058B CD3CN 25.0°C
*
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


jaocp065
13C 75.5MHz Job 10058 O`Neill J A P065 CD3CN 25.0°C 3 hours 1 min
Trichloro
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

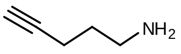

jaohp058b
1H 300.1MHz Job 9492 O`Neill J A P058B CD3CN 25.0°C
*
NH
N
AuCl4
5
jaohp058b
1H 300.1MHz Job 9492 O`Neill J A P058B CD3CN 25.0°C
*
8.3
8.1
7.9
7.7
7.5
7.3
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


jaocp058
13C 75.5MHz Job 15508 O`Neill J A P058 CD3CN 21.4°C 3 hours 1 min
dmbyH+ [AuCl4]-
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


jaohp037
1H 300.1MHz Job 8495 O`Neill J A P037 CD3CN 24.9°C
*
2+
2
O
O
O
Cl
O
N
N
Au
O
O
Au
N
N
7
jaohp037
1H 300.1MHz Job 8495 O`Neill J A P037 CD3CN 24.9°C
*
8.6
8.4
8.2
8.0
7.8
7.6
7.4
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

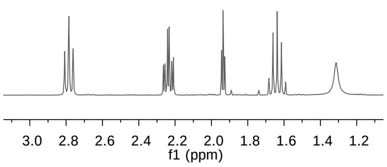

jaocp119
13C 75.5MHz Job 13868 O`Neill J A P119 DMSO 25.0°C 3 hours 1 min
old perchlorate oxo
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

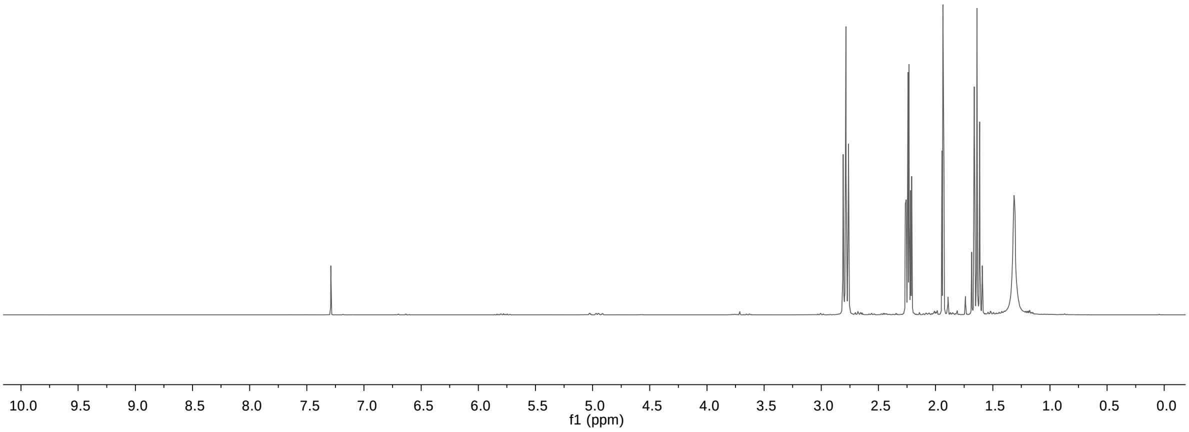
jaohp109
1H 300.1MHz Job 13120 O`Neill J A P109 CDCl3   25.1°C
Amino pentyne crude



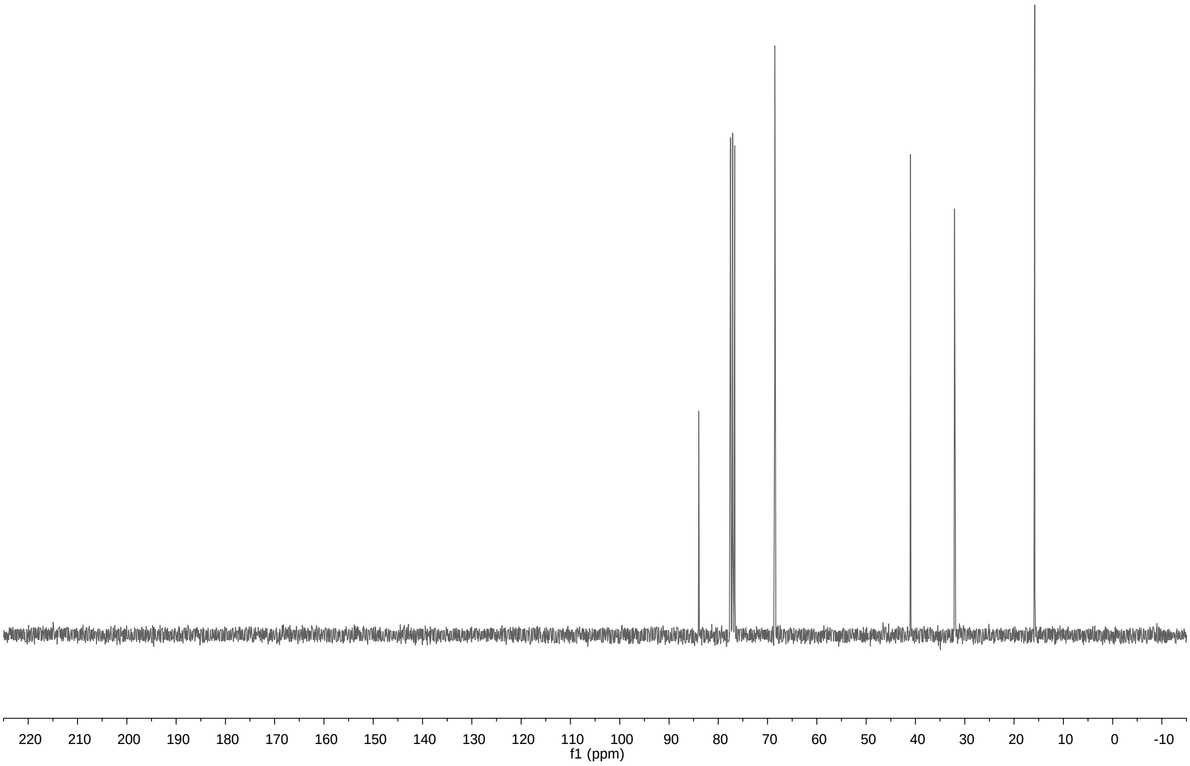
13

jaohp109
1H 300.1MHz Job 13120 O`Neill J A P109 CDCl3   25.1°C
Amino pentyne crude

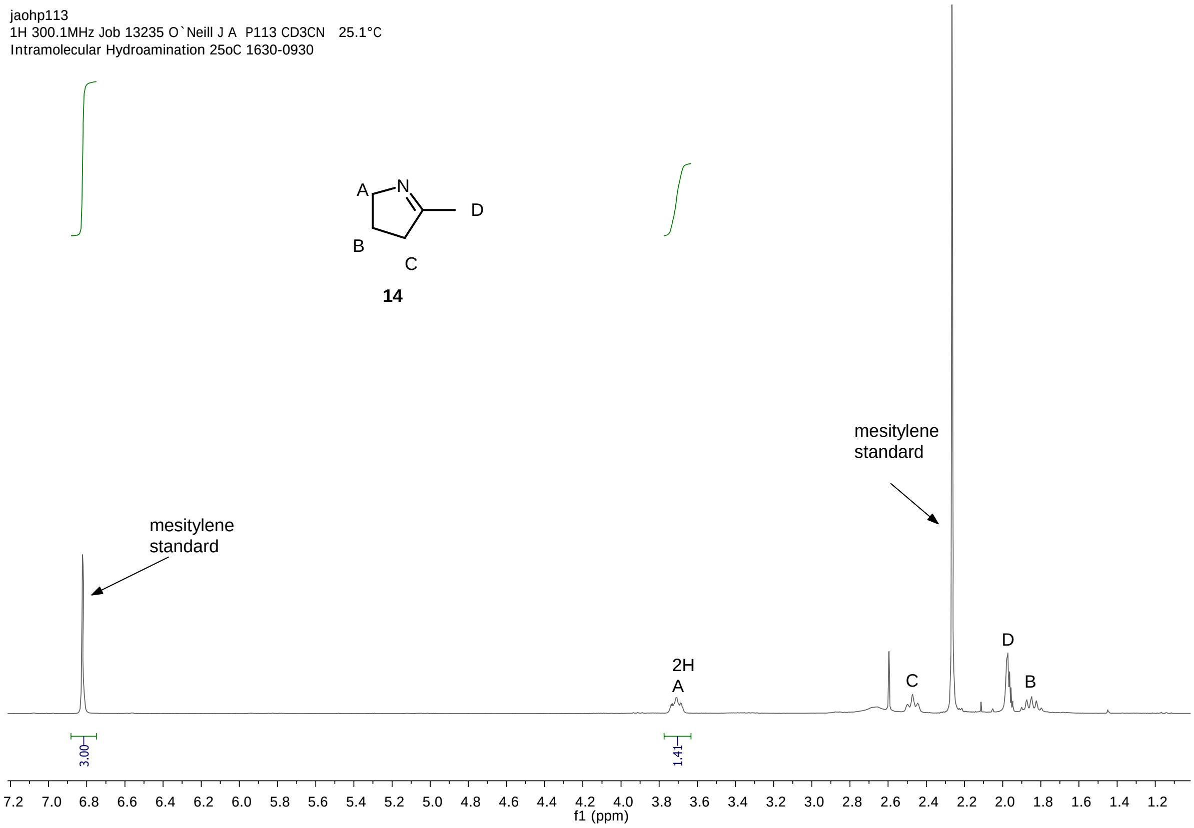




jaocp109
13C 75.5MHz Job 13121 O`Neill J A P109 CDCl3   25.0°C   0 hour 18 min
amino pentyne crude



Representative ^{1}H-NMR of reaction to form **14** (with internal standard, Table 1, Entry 2):



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