Supporting Information: Gaywood and McNab

3-Hydroxypyrrolo[2,3-*b*]pyridine and related compounds – indoxyl analogues with fused electron deficient rings.

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Supporting Information

Experimental

3-Acetylpyridine-1-oxide

A solution of 3-acetylpyridine (20 g, 0.165 mol) in glacial acetic acid was treated with aqueous hydrogen peroxide (30%, 20 cm^3) and heated at 80 °C for 3 h. A further portion of hydrogen peroxide (30%, 20 cm^3) was added, and the reaction mixture heated at 80 °C for a further 23 h. The solution was cooled to room temperature, and concentrated to *ca.* 20 cm^3. Water (20 cm^3) was added, and the solution again concentrated by rotary evaporation. The solution was taken up in dichloromethane, and shaken with solid potassium carbonate (5 g). The potassium carbonate was filtered off, the filtrate extracted with dichloromethane (3×50 cm^3), the organic extracts dried (MgSO$_4$) and the solvent removed by rotary evaporation. The product was recrystallised from ethyl acetate, to yield pure 3-acetylpyridine-1-oxide (11.1 g, 50%); mp 146-147 °C (from ethyl acetate) (lit.,[1] 145-147 °C); δ_H (200 MHz) 2.68 (3H, s, CH$_3$), 7.48 (1H, m), 7.71 (1H, m), 8.42 (1H, m) and 8.79 (1H, m).

3-Acetyl-2-chloropyridine 4

Method 1

A mixture of 3-acetylpyridine-1-oxide (1 g, 7.3 mmol) and phosphorus oxychloride (20 g, 0.13 mol) was heated under reflux for at 100 °C for 1 h under a nitrogen atmosphere. The solution was cooled to room temperature, and the excess phosphorus oxychloride removed by Kugelrohr distillation. Ice was added, and the solution allowed to stand for 4 h. Ether (50 cm^3) was added and the organic layer was washed with water, dried (MgSO$_4$) and the solvent removed by rotary evaporation to leave 3-acetyl-2-chloropyridine **4** as a thick brown oil (0.74 g, 66%); δ_H (200 MHz) 2.63 (3H, s, CH$_3$), 7.30 (1H, dd, $J_{5,4}$ 7.6 and $J_{5,6}$ 4.7, H(5)], 7.85 [(1H, dd, $J_{5,6}$ 7.6 and J$_{4,6}$ 1.9, H(4)] and 8.43 [1H, dd, $J_{6,5}$ 4.7 $J_{6,4}$ 1.9 H(6)]. ^{1}H NMR spectrum consistent with reported data.[2]

Method 2

A solution of 2-chloronicotinonitrile (1.03 g, 7.46 mmol) in dry THF (10 cm^3) was added slowly to a solution of methyl magnesium chloride in THF (1.33 M, 24 cm^3, 24 mmol) under nitrogen, keeping the temperature below 10 °C. This was stirred at room temperature for 30 min, and heated under reflux for 1 h. The solution was cooled to room temperature and sulfuric acid (6.66%, 24 cm^3) was added dropwise. The mixture was stirred for 30 min, extracted with ether, the organic extracts washed with

brine, dried (MgSO$_4$) and the solvent removed by rotary evaporation to give 3-acetyl-2-chloropyridine **4** (750 mg, 65%); NMR data as quoted above.

Temperature profile of the FVP of 4-acetyltetrazolo[1,5-*a*]pyridine 5

The pyrolyses were carried out (typical conditions: 30 mg, 0.18 mmol, T_i 45 °C, P 1.9×10^{-2} Torr, t 5 min) at the temperatures described in Table 1, with the following peaks in the ^{1}H NMR spectrum of the product mixture used to calculate the product ratio: 4-acetyltetrazolo[1,5-*a*]pyridine **5** [3.15 (3H, s, CH$_3$) and 9.11 (1H, dd)], 3-methylisoxazolo[3,4-*b*]pyridine **6** [2.82 (3H, s, CH$_3$) and 8.73 (1H, dd)] and 1,2-dihydropyrrolo[2,3-*b*]pyridin-3-one **8** [3.90 (2H, s, CH$_2$) and 6.72 (1H, dd).

Table 1. Temperature profile of the FVP of 4-acetyltetrazolo[1,5-*a*]pyridine **5**

Temperature/°C	200	250	300	350	400	500	600	650	680
4-Acetyltetrazolo[1,5-*a*]pyridine **5**/%	100	96	25	3	0	0	0	0	0
3-Methylisoxazolo[3,4-*b*]pyridine **6**/%	0	4	75	97	100	93	55	5	0
1,2-Dihydropyrrolo[2,3-*b*]pyridin-3-one **8**/%	0	0	0	0	0	7	45	95	100

3-Acetyl-2-chloroquinoline 18

(a) 1-(2-Chloroquinolin-3-yl)ethanol

A solution of 2-chloroquinoline-3-carboxaldehyde (500 mg, 2.6 mmol) in anhydrous THF (10 cm^3) was added dropwise at room temperature under a nitrogen atmosphere to a solution of methyl magnesium chloride (7.8 mmol) in anhydrous THF (5.5 cm^3), and the mixture was stirred for 30 min. The reaction was quenched with an aqueous solution of ammonium chloride (10%, 10 cm^3), extracted with ethyl acetate (2×20 cm^3 portions), the organic extracts dried (MgSO$_4$) and the solvent removed by rotary evaporation to yield 1-(2-chloroquinolin-3-yl)ethanol (444 mg, 82%); mp 74–75 °C (lit.,[3] 72–73 °C); δ_H 1.59 (3H, d, *J* 6.5, CH$_3$), 2.84 (1H, br, OH), 5.27 (1H, q, *J* 6.5, CH), 7.55 (1H, ddd, *J* 1.5, 7.0 and 8.1, Ar-H), 7.69 (1H, ddd, *J* 1.5, 7.0 and 8.1, Ar-H), 7.79 (1H, dd, *J* 1.5 and 8.1, Ar-H), 7.98 (1H, m, *J* 1.5 and 8.1, Ar-H) and 8.36 [1H, s, H(4)]; δ_C 23.76 (CH$_3$), 66.53, 126.98, 127.34 (quat), 127.50, 127.88, 130.09, 134.93, 137.83 (quat), 146.64 (quat) and 148.55 (quat); *m/z* 209 (M$^+$, 20%), 207 (M$^+$, 69), 194 (65), 192 (100), 156 (95), 128 (94) and 101 (60).

(b) 3-Acetyl-2-chloroquinoline **18**

To a solution of 1-(2-chloroquinolin-3-yl)-ethanol (2.21 g, 10.7 mmol) in dichloromethane (35 cm^3) was added pyridinium chlorochromate (4.74 g, 21.6 mmol) and the mixture was stirred for 16 h at room temperature. Water (70 cm^3) was added, and the mixture was extracted with ether (3×150 cm^3), the organic extracts dried (MgSO$_4$) and the solvent removed by rotary evaporation. The resulting solid was passed through a thin band of silica using a solution of chloroform (10%) in ethyl acetate as eluent, and the solvent removed by rotary evaporation to yield 3-acetyl-2-chloroquinoline **18** (1.61 g, 73%); mp 65–67 °C (lit.,[3] 75–76 °C); δ_H 2.77 (3H, s, acetyl), 7.63 (1H, m, Ar-H), 7.79-7.92 (2H, m, 2Ar-H), 8.05 (1H, m, Ar-H) and 8.39 [1H, s, H(4)]; δ_C 30.47 (CH$_3$), 126.04 (quat), 127.77, 128.29, 128.34, 132.22, 132.94 (quat), 139.25, 145.87 (quat), 147.98 (quat) and 195.51 (quat); m/z 207 (M$^+$, 21%), 205 (M$^+$, 57), 192 (49), 190 (100), 164 (21), 162 (58) and 101 (22).

4-Chloroquinoline-3-carboxaldehyde 20

To a solution of o-aminoacetophenone (7.7 g, 57 mmol) in DMF (37 cm^3, 390 mmol) was added phosphoryl chloride (22 cm^3, 220 mmol) over 30 min at 0 °C. The solution was stirred for 30 min at room temperature and heated under reflux for 4.5 h. The mixture was cooled to room temperature, ice added and neutralised with solid sodium acetate. The resulting precipitate was collected, washed repeatedly with water and dried to yield 4-chloroquinoline-3-carboxaldehyde **20** (4.2 g, 40%); mp 138–140 °C (from ethyl acetate); δ_H 7.75 (1H, m, Ar-H), 7.92 (1H, m, Ar-H), 8.17 (1H, m, Ar-H), 8.39 (1H, m, Ar-H), 9.26 [1H, s, H(2)] and 10.70 (1H, s, aldehyde) (compatible with literature data[4] δ_C 124.19 (quat), 124.93, 125.49 (quat), 128.52, 130.02, 133.10, 148.02 (quat), 148.43, 150.65 (quat) and 188.90 (quat); m/z 193 (M$^+$, 81%), 192 (87), 191 (M$^+$, 98), 190 (100), 162 (87), 128 (71), 101 (79) and 75 (77).

3-Acetylquinolin-4-one 23

To a suspension of 3-acetyl-4-chloroquinoline **22** (98 mg, 0.48 mmol) in ethanol (6.5 cm^3) and conc. hydrochloric acid (0.5 cm^3) was added sodium azide (311 mg, 4.78 mmol) in water (3 cm^3) and the mixture was heated at 95 °C for 24 h. The solvent was removed, water (10 cm^3) was added, the mixture was extracted with ethyl acetate (3×20 cm^3), the organic extracts were dried (MgSO$_4$) and the solvent removed. Purification by dry flash chromatography (25% ethyl acetate in hexane) as eluent

yielded 3-acetylquinolin-4-one **23** (37 mg, 50%); mp 243-245 °C (from acetone) (lit.,[5] 240-244 °C); δ_H ([^{2}H$_6$]DMSO) 2.62 (3H, s, acetyl), 7.44 (1H, m, Ar-H), 7.63 (1H, m, Ar-H), 7.73 (1H, m, Ar-H), 8.23 (1H, m, Ar-H) and 8.52 [1H, s, H(2)]; δ_C ([^{2}H$_6$]DMSO) 30.20 (CH$_3$), 117.45 (quat), 118.65, 124.68, 125.51, 127.60 (quat), 132.30, 138.81 (quat), 143.92, 175.04 (quat) and 196.14 (quat); m/z 187 (M$^+$, 73%), 172 (100), 170 (25), 104 (19) and 61 (20).

Temperature profile of the FVP of 4-acetyltetrazolo[1,5-a]quinoline 19

Pyrolyses of 4-acetyltetrazolo[1,5-a]quinoline **19** were carried out (typical conditions: 20 mg, 0.09 mmol, T_i 85 °C, P 2.6×10^{-2} Torr, t 8 min) at the temperatures described in Table 2, with the following peaks in the ^{1}H NMR spectra of the product mixtures used to calculate the ratio of products formed: 4-acetyltetrazolo[1,5-a]quinoline **19** [3.12 (3H, s, CH$_3$)], 3-methyl-2-oxa-1,9-diaza-cyclopenta[b]naphthalene **26** [3.04 (3H, s, CH$_3$)], 1,2-dihydropyrrolo[2,3-b]quinolin-3-one **28** [4.04 (2H, s, CH$_2$)] and 2-(cyanophenyl)acetonitrile **30** [4.01 (2H, s, CH$_2$)].

Table 2. Temperature profile of the FVP of 4-acetyltetrazolo[1,5-a]pyridine **5**

Temperature/°C	300	350	400	450	500	600	700	750
4-Acetyltetrazolo[1,5-a]quinoline **19**/%	100	97	32	1	0	0	0	0
3-Methyl-2-oxa-1,9-diaza-cyclopenta[b]naphthalene **26**/%	0	3	50	1	0	0	0	0
1,2-Dihydropyrrolo[2,3-b]quinolin-3-one **28**/%	0	0	6	45	13	7	6	4
2-(Cyanophenyl)-acetonitrile **30**/%	0	0	8	53	87	93	94	96

Effect of inlet temperature on FVP of 4-acetyltetrazolo[1,5-a]quinoline 19

Pyrolyses of 4-acetyltetrazolo[1,5-a]quinoline **19** were carried out (30 mg, 0.14 mmol; T_f 450 °C, P 2.4×10^{-2} Torr) with the inlet temperature (T_i) varied as stated in Table 3. The ratio of 2-(cyanophenyl)-acetonitrile **30** and 3-acetyl-2-aminoquinoline **31** formed was measured by ^{1}H NMR spectroscopy, and the time of pyrolysis (t) and increase in pressure (ΔP) were noted.

Table 3. Effect of inlet temperature on FVP of 4-acetyltetrazolo[1,5-a]quinoline **19**

Inlet temperature T_i/°C	65	75	90	115
Time of pyrolysis t/min	180	35	10	5
Pressure change ΔP/×10^{-2} Torr	1	2.9	7.7	25.7
Ratio 2-(cyanophenyl)-acetonitrile **30** to 3-acetyl-2-aminoquinoline **31**	1 : 0.27	1 : 0.40	1 : 0.71	1 : 1.25

## Temperature profile of the FVP of 3-acetyl-4-azidoquinoline 24

The pyrolyses were carried out (typically m 20 mg, 0.09 mmol, T_i 75 °C, P 3.0×10^{-2} Torr, t 6 min) at the temperatures described in Table 4, with the following peaks in the ^{1}H NMR spectrum of the product mixture used to calculate the product ratio: 3-acetyl-4-azidoquinoline **24** [2.80 (3H, s, acetyl) and 9.17 (1H, s)] and 3-methylisoxazolo[4,3-*c*]quinoline **33** [2.91 (3H, s, CH$_3$) and 8.97 (1H, s)].

At higher temperatures unidentified thermal decomposition products began to appear in the product mixture which could not be isolated.

Table 4. Temperature profile of the FVP of 3-acetyl-4-azidoquinoline **24**

Temperature/°C	200	300	400	500
3-Acetyl 4-azidoquinoline **24**/%	74	2	0	0
3-Methylisoxazolo[4,3-*c*]quinoline **33**/%	26	98	100	100

NMR analysis of 3-hydroxypyrrolo[2,3-*b*]pyridine 8E

8E
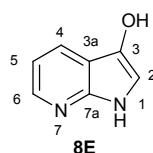
A full NMR analysis of the enol 3-hydroxypyrrolo[2,3-*b*]pyridine **8E** was carried out using HMBC, HSQC and COSY experiments. From the coupling patterns of the pyridine protons, the three proton signals could be identified; for 2,3-disubstituted pyridines the largest coupling constant would be expected to be between H(4) and H(5). HMBC data showed the quaternary peak at δ 114.31 to be the only carbon atom to show long range coupling to H(5), indicating it to be C(3a). The COSY experiment showed that of the two broad peaks corresponding to the NH and OH peaks, the signal at δ 10.60 corresponded to the NH, as it showed a coupling to the signal from H(2). The HMBC experiment then differentiated the two remaining quaternaries; although both coupled to H(2) and H(4), the signal at δ 132.16 also showed coupling to the OH, indicating it to be C(3), and therefore the signal at δ 146.13 must be C(7a). Full characterisation details are shown in Table 5. Similar analysis of the keto form was not possible due to the instability of the compound in CDCl$_3$.

Table 5. NMR characterization of 3-hydroxypyrrolo[2,3-*b*]pyridine **8E**

| Position	δ_H	δ_C
2	6.62	107.49
3		132.16
3a		114.31
4	7.97	126.09
5	6.80	116.56
6	7.76	142.82
7a		146.43

Tautomerism of 8K/8E in various solvents

The ratio of tautomers present in various solvents was measured by ^{1}H NMR spectroscopy, having allowed equilibrium to become established, by recording spectra over several hours until the ratio of tautomers became constant. The results of this study are shown in Table 6, along with the ratios for indoxyl **2**. For the solvents of intermediate polarity 1,2-dihydropyrrolo[2,3-*b*]pyridin-3-one **8** shows a greater tendency to adopt the enol form than indoxyl **2**. This difference is may be due to the enol tautomer being an electron rich system which can be better stabilized by a fused electron deficient pyridine ring than a corresponding benzene ring.

Table 6. Ratio of keto to enol tautomers for 1,2-dihydropyrrolo[2,3-*b*]pyridin-3-one **8K/8E** and indoxyl **2K/2E**.

Solvent	Ratio of Keto:Enol for 8	Ratio of Keto:Enol for 2
CDCl$_3$	>95:5	>95:5
[^{2}H$_6$]-Acetone	33:67	>95:5
[^{2}H$_4$]-Methanol	5:95	92:8
[^{2}H$_6$]-DMSO	<5:95	<5:95

Protonation of 8 in TFA
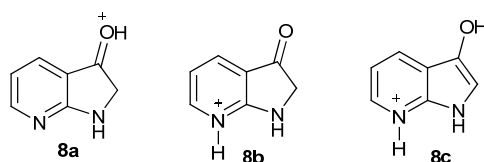
The carbonyl position and the nitrogen atom of the six-membered ring of **8** are both potential protonation sites under acid conditions. Whilst protonation at the *O*-position gives only one possible tautomer **8a**, protonation at the *N*-position leads to the possibility of the two tautomeric forms **8b** and **8c**. ^{1}H NMR spectroscopy of a solution of 1,2-dihydropyrrolo[2,3-*b*]pyridin-3-one **8** in TFA showed that two isomers were

present, which were identified as a keto and enol tautomer, present in a respective ratio of approximately 3:1. [1]H Chemical shifts are shown for these two species in Table 7, along with the chemical shifts for 1,2-dihydropyrrolo[2,3-*b*]pyridin-3-one **8** in CDCl$_3$ and [^{2}H$_6$]DMSO, which respectively showed the keto and enol tautomers. Table 8 shows the coupling constants observed for these solutions.

Table 7. ^{1}H NMR shifts for protonated keto and enol tautomers of 1,2-dihydropyrrolo[2,3-*b*]pyridin-3-one **8** in TFA, and the neutral keto and enol tautomers of **8** in CDCl$_3$ and [^{2}H$_6$]DMSO respectively, with differences upon protonation shown in parentheses.

Solvent	δ_H H(2)	δ_H H(4)	δ_H H(5)	δ_H H(6)
CDCl$_3$ (Keto Tautomer)	3.90	7.83	6.72	8.32
TFA (Keto Tautomer)	4.47 (+0.57)	8.58 (+0.75)	7.25 (+0.43)	8.30 (-0.02)
[^{2}H$_6$]-DMSO (Enol Tautomer)	6.62	7.97	6.80	7.76
TFA (Enol Tautomer)	7.34 (+0.72)	8.79 (+0.82)	7.60 (+0.80)	8.34 (+0.58)

Table 8. Coupling constants between pyridine protons for protonated and neutral forms of 1,2-dihydropyrrolo[2,3-*b*]pyridin-3-one **8**

Solvent	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$
CDCl$_3$ (Keto Tautomer)	7.3	1.5	5.1
TFA (Keto Tautomer)	7.3	1.3	6.4
[^{2}H$_6$]-DMSO (Enol Tautomer)	7.9	1.6	4.7
TFA (Enol Tautomer)	7.9	1.6	6.0

Similarities exist between the two tautomers, *e.g.* considerably larger shielding effects occur at the H(4) and H(5)-positions relative to the H(6) upon protonation. The only major change in coupling constants upon protonation for both tautomers is that between H(5) and H(6), which shows an increase of 1.3 Hz in both cases. These similarities suggest that protonation occurs at the same position for both of the tautomers of 1,2-dihydropyrrolo[2,3-*b*]pyridin-3-one **8** in TFA, *i.e.* forming the tautomers **8b** and **8c**. In [^{2}H]TFA *ca* 50% exchange at the H(2)-position was observed by ^{1}H NMR spectroscopy after 30 min.

Electron impact mass spectra of the heteroindigotin 9 and indigotin 1

The mass spectra of **1** and **9** show close similarities (Table 9). The molecular ion is the base peak in both cases, followed initially by sequential loss of two CO fragments.

Lower mass fragments appear to be derived from cleavage of the C(2)=C(2′) double bond.

Table 9. EI-Mass spectra of **9** and indigotin **1**

| *m/z* of heteroindigotin 9	*m/z* of indigotin 1	Fragment
265 (45)	263 (25)	$(M+1)^+$
264 (100)	262 (100)	M^+
236 (30)	234 (24)	$(M-28)^+$
208 (30)	206 (24)	$(M-56)^+$
104 (39)	104 (31)	$[(M-160/158]^+$
78 (56)	76 (21)	$(M-186)^+$

X-Ray crystallography.

Crystal data for **6** have been previously deposited with the Cambridge Crystallographic Data Centre, and are available as refcode PELGET. For reference, bond lengths and angles of 3-methylisoxazolo[3,4-*b*]pyridine **6** (Table 10) and 4-acetyltetrazolo[1,5-*a*]quinoline **19** (Table 11) are reproduced below.

Table 10. Bond lengths [Å] and angles (deg) for 3-methylisoxazolo[3,4-*b*]pyridine **6**
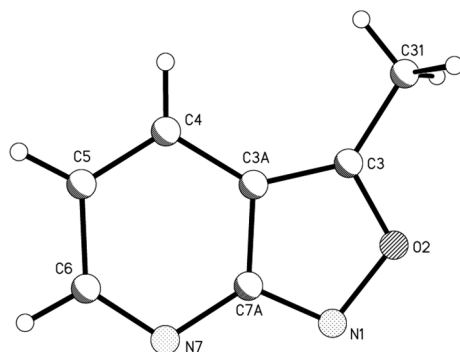
Bond lengths/Å		Bond angles/°	
N(1)-O(2)	1.405(3)	N(1)-O(2)-C(3)	111.46(15)
N(1)-C(7a)	1.329(3)	N(1)-C(7a)-C(3a)	112.41(19)
O(2)-C(3)	1.348(2)	N(1)-C(7a)-N(7)	122.87(18)
C(3)-C(31)	1.470(3)	O(2)-N(1)-C(7a)	103.48(16)
C(3)-C(3a)	1.371(3)	O(2)-C(3)-C(31)	117.90(19)
C(3a)-C(4)	1.416(3)	O(2)-C(3)-C(3a)	107.89(18)
C(3a)-C(7a)	1.418(3)	C(3)-C(3a)-C(4)	136.29(19)
C(4)-C(5)	1.352(3)	C(3)-C(3a)-C(7a)	104.76(19)
C(5)-C(6)	1.431(3)	C(31)-C(3)-C(3a)	134.2(2)
C(6)-N(7)	1.311(3)	C(3a)-C(4)-C(5)	116.56(19)
N(7)-C(7a)	1.373(3)	C(3a)-C(7a)-N(7)	124.72(19)
		C(4)-C(3a)-C(7a)	118.94 (19)
		C(4)-C(5)-C(6)	120.0(2)
		C(5)-C(6)-N(7)	126.4(2)
		C(6)-N(7)-C(7a)	113.37(17)

Table 11. Bond lengths [Å] and angles (deg) for 4-acetyltetrazolo[1,5-*a*]quinoline **19**
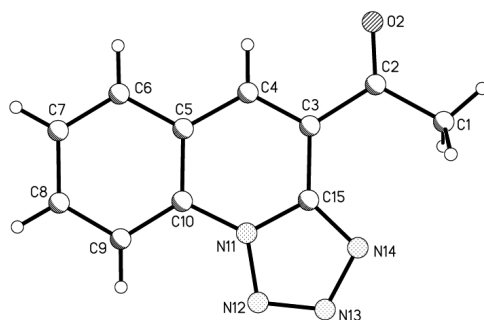
Bond lengths/Å	Bond angles/°
C1 C2 1.498(2)	O2 C2 C1 121.54(14)
C2 O2 1.2137(18)	O2 C2 C3 119.42(13)
C2 C3 1.502(2)	C1 C2 C3 119.03(13)
C3 C4 1.361(2)	C4 C3 C15 117.21(13)
C3 C15 1.4395(19)	C4 C3 C2 119.59(13)
C4 C5 1.435(2)	C15 C3 C2 123.18(12)
C5 C10 1.406(2)	C3 C4 C5 122.70(13)
C5 C6 1.409(2)	C10 C5 C6 117.79(13)
C6 C7 1.377(2)	C10 C5 C4 119.89(13)
C7 C8 1.397(2)	C6 C5 C4 122.32(13)
C8 C9 1.380(2)	C7 C6 C5 120.19(14)
C9 C10 1.395(2)	C6 C7 C8 120.54(14)
C10 N11 1.3942(17)	C8 C9 C10 117.93(14)
N11 N12 1.3564(16)	N11 C10 C9 122.08(13)
N11 C15 1.3584(18)	N11 C10 C5 115.54(12)
N12 N13 1.3016(17)	C9 C10 C5 122.38(13)
N13 N14 1.3527(18)	N12 N11 C15 108.74(11)
N14 C15 1.3284(18)	N12 N11 C10 125.69(12)
	C15 N11 C10 125.57(12)
	N13 N12 N11 105.39(11)
	N12 N13 N14 112.15(12)
	C15 N14 N13 105.81(12)
	N14 C15 N11 107.90(12)
	N14 C15 C3 133.00(13)
	N11 C15 C3 119.08(12)

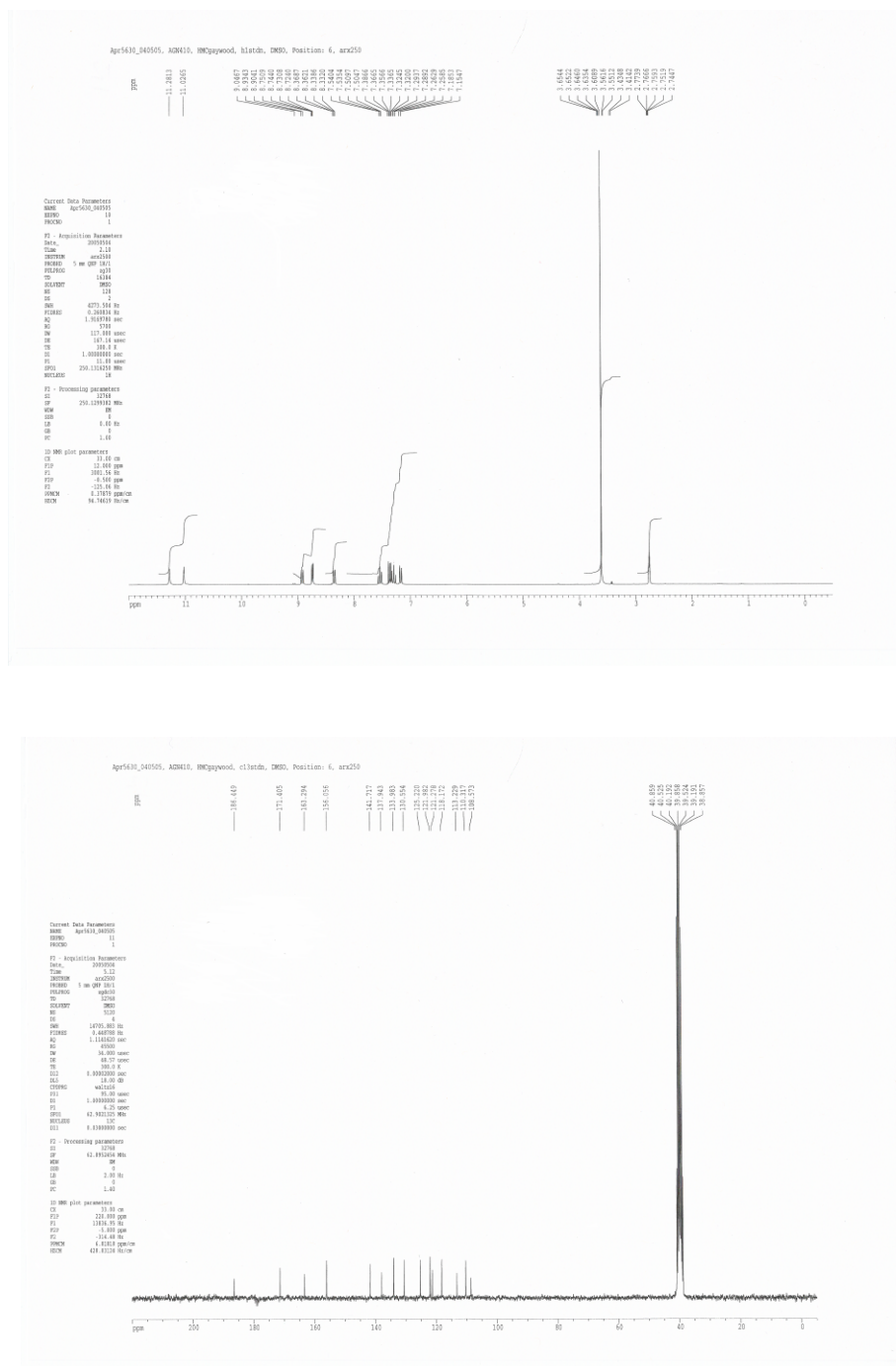## Selected ^{1}H and ^{13}C NMR spectra of new compounds.

Figure S1. ^{1}H and ^{13}C NMR spectra of **12** (^{1}H spectrum subsequently re-referenced to residual DMSO signal at δ_H 2.50)
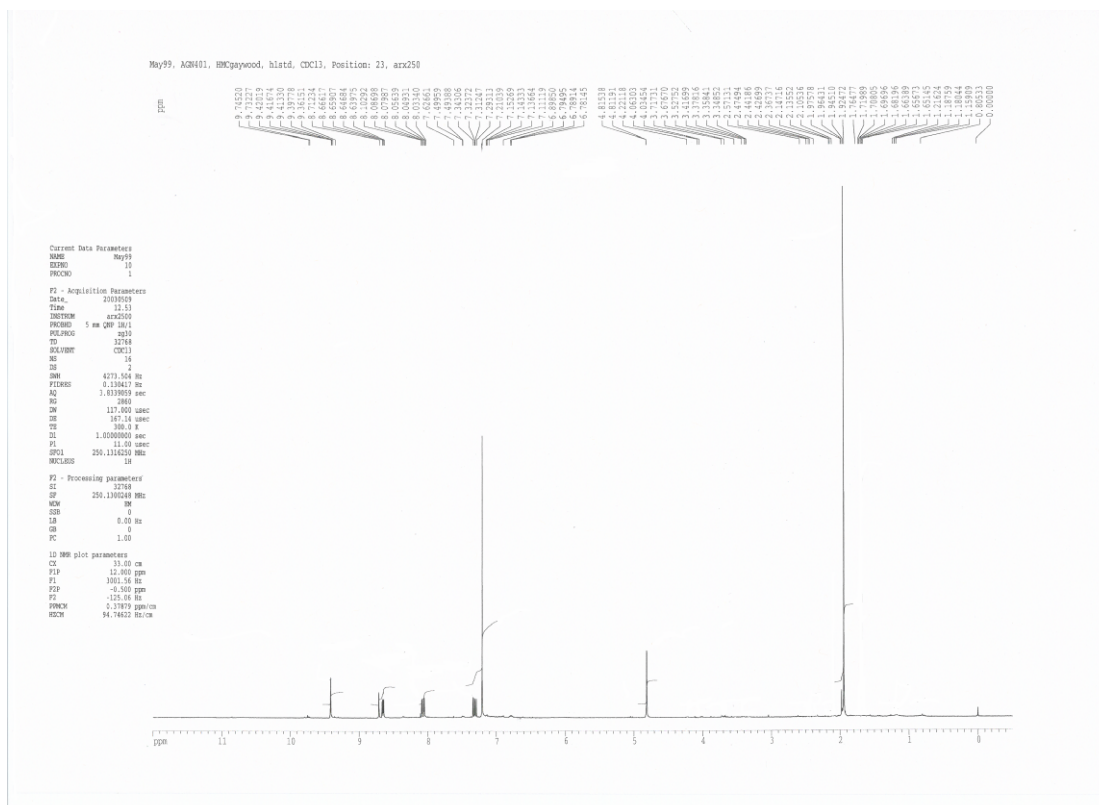
Figure S2. ^{1}H and ^{13}C NMR spectra of **14**

Figure S3. ^{1}H NMR spectrum of **16**

Figure S4. ^{1}H and ^{13}C NMR spectra of **17**

Figure S5. ^{1}H and ^{13}C NMR spectra of **19** (^{1}H spectrum subsequently re-referenced to residual chloroform signal at δ_H 7.25)

Figure S6. ^{1}H and ^{13}C NMR spectra of **21** (^{1}H spectrum subsequently re-referenced to residual chloroform signal at δ_H 7.25)

Figure S7. ^{1}H and ^{13}C NMR spectra of **22** (^{1}H spectrum subsequently re-referenced to residual chloroform signal at δ_H 7.25)

/archive/HMC/gaywood_AGN809_230804_1H-13C-D135-D90_arx250/10/pdata/1/: gaywood , AGN809, 1H
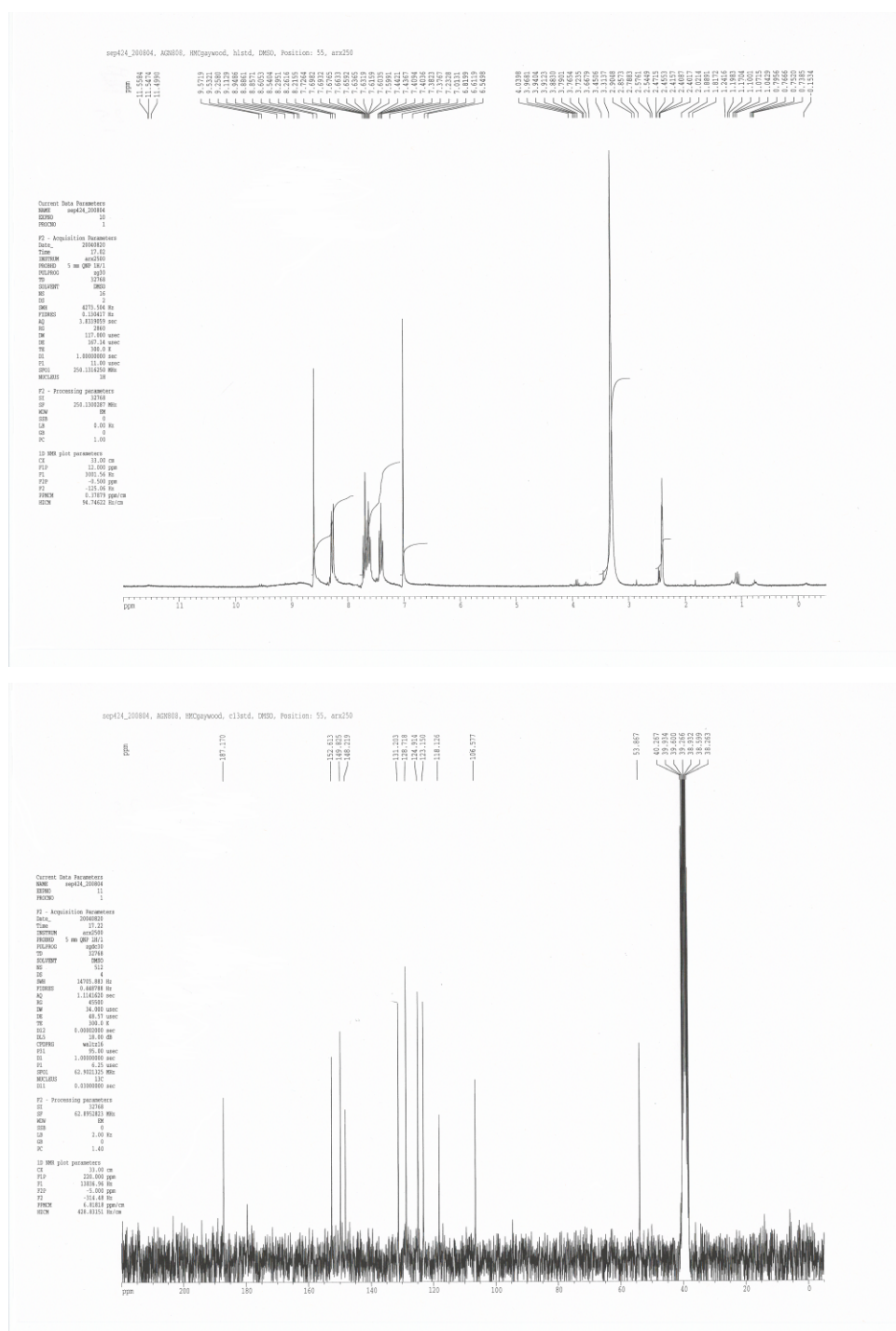
Figure S8. ^{1}H NMR spectrum of **24**

Figure S9. ^{1}H and ^{13}C NMR spectra of **25** (^{1}H spectrum subsequently re-referenced to residual DMSO signal at δ_H 2.50)
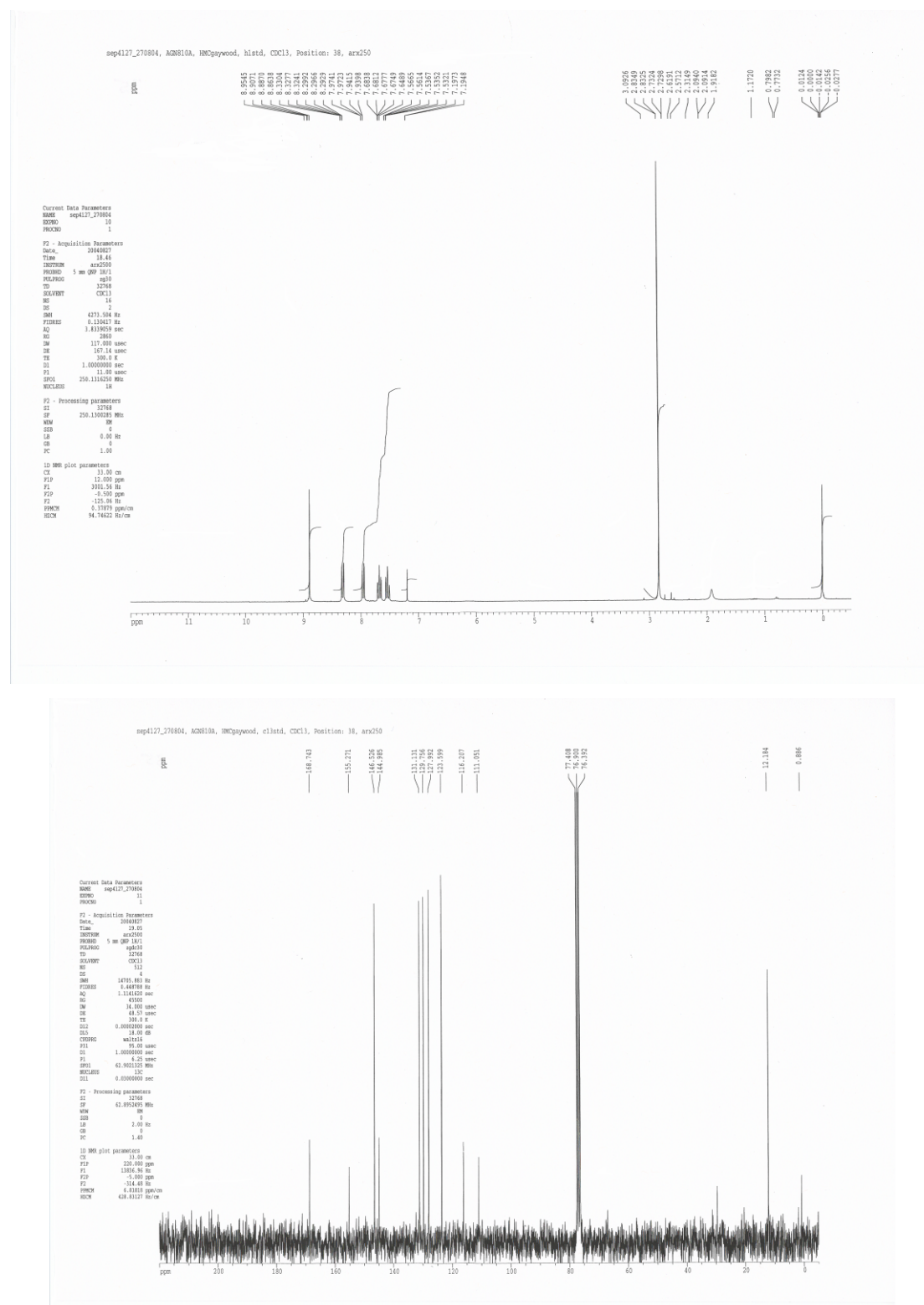
Figure S10. ^{1}H and ^{13}C NMR spectra of **35** (^{1}H spectrum subsequently re-referenced to residual chloroform signal at δ_H 7.25)

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