Supporting information for

KO^{t}Bu-Mediated annulation of acetonitrile with aldehyde: synthesis of substituted dihydropyridin-2(1*H*)-ones, pyridin-2(1*H*)-ones, and thiopyridin-2(1*H*)-ones

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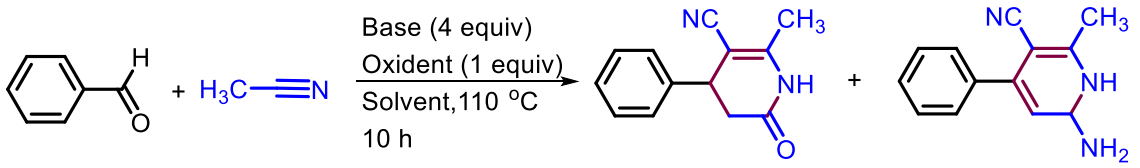
Crystal structure description for compounds

1038678 (**1**), 1038680 (**5**), 1057417 (**16**), 1057418 (**41**), 1038679 (**42**) S32-S77

General Experimental Details

All NMR experiments were carried out on Bruker 400/500/700 MHz spectrometer in $CDCl_3$ and NMR chemical shifts are reported in ppm referenced to the solvent peaks of $CDCl_3$ 7.26 ppm for ^1H and 77 (± 0.07) ppm for ^{13}C, DMSO-d6 3.31 ppm for H_2O, 2.47 ppm for DMSO 39.9 for carbon respectively. The following abbreviations were used to indicate multiplicity: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets) td (triplet of doublet) and m (multiplet). Infrared spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrophotometer and reported in frequency of absorption (cm^{-1}). High resolution mass analysis was performed on quadrupole-time of flight Bruker MicroTOF-Q II mass spectrometer equipped with an ESI and APCI source. Single crystal X-ray data for compounds **1**, **5**, **16**, **41**, and **42** were collected on a Bruker D8 VENTURE diffractometer equipped with CMOS Photon 100 detector and Mo-Kα (λ = 0.71073 Å) radiation was used. Various aldehydes were purchased from Sigma Aldrich co. India, Alfa Aser, and Spectrochem Pvt. Ltd. India. HPLC grade acetonitrile was used for reaction and purchased from Merck. Silica gel (100-200 mesh size) was used for column chromatography purchased from RANKEM Pvt. Ltd. India. TLC analysis of reaction mixtures was performed using Merck silica gel (60 F_{254}) plates.

Table 1. Optimization of reaction condition [#]



1 **2**

Entry	Base	Solvent	Peroxide	Yield 1 (%)
1	K_2CO_3	CH_3CN	-	ND
2	Cs_2CO_3	CH_3CN	-	ND
3	NaOH	CH_3CN	-	ND
4	KOH	CH_3CN	-	ND

5	LiO^tBu	CH_3CN	-	ND
6	NaO^tBu	CH_3CN	-[a]	ND
7	KO^tBu	CH_3CN	-[a]	42
8	KO^tBu	CH_3CN	DTBP	58
9	**KO^tBu**	**CH_3CN**	**30% H_2O_2 in H_2O**	**70**
10[b]	KO^tBu	CH_3CN	30% H_2O_2 in H_2O	50
11[c]	KO^tBu	CH_3CN	30% H_2O_2 in H_2O	ND
12	**LiO^tBu**	CH_3CN	30% H_2O_2 in H_2O	ND
13	**NaO^tBu**	CH_3CN	**30% H_2O_2 in H_2O**	ND
14	KO^tBu	CH_3CN	**TBHP in nonane**	35
15	KO^tBu	CH_3CN	**AIBN**	ND
16	KO^tBu	CH_3CN	**$K_2S_2O_8$**	ND[e]
17	KO^tBu	CH_3CN	**$NH_4S_2O_8$**	ND[e]
18	KO^tBu	CH_3CN	**PIDA**	ND
19	KO^tBu	**DMSO**	30% H_2O_2 in H_2O	ND
20	KO^tBu	**DMSO + CH_3CN (1:1)**	30% H_2O_2 in H_2O	28
21	KO^tBu	**CH_3CN + H_2O (1:1)**	30% H_2O_2 in H_2O	ND
22[d]	KO^tBu	**CH_3CN**	30% H_2O_2 in H_2O	20
23	KO^tBu	**DMF**	30% H_2O_2 in H_2O	ND
24	KO^tBu	**DME**	30% H_2O_2 in H_2O	ND
25	KO^tBu	**toluene**	30% H_2O_2 in H_2O	ND
26	KOH	CH_3CN	30% H_2O_2 in H_2O	ND
27	KOH	CH_3CN + ^tBuOH	-[a]	ND[e]
28	KOH	CH_3CN	-[a]	ND[e]

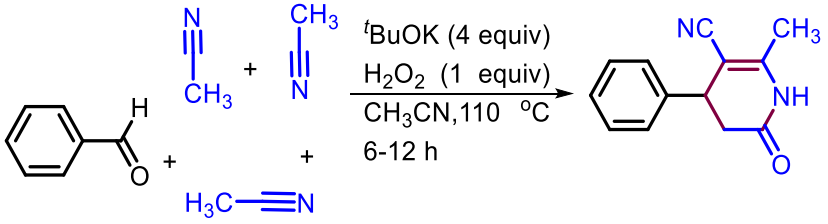
[#] Reaction carried using 1 mmol of benzaldehyde, 4 equiv KO^tBu, 4 mL solvent and 1equiv of 30% H_2O_2 in water. [a] 100 µL of water was added. [b] At 80 ^oC temperature. [c] At room temperature [d] 20 mol % of Cu(OTzf) was used. [e] Instead of **1**, formation of **2** was realized as study by GC Mass.

Optimization of reaction conditions were carried out by heating benzaldehyde (1 mmol) in acetonitrile (4 mL) at 110 ^oC in sealed tube by screening various bases and peroxides.

Bases KOH and NaOH and carbonate bases of Na, K, and Cs noticed to be ineffective for the formation of **1** (entries 1-4). Similarly, Lithium and sodium *tert*-butoxides failed to form any of **1** or **2** (entries 5-6). Interestingly, use of KO^{t}Bu gave 42% yield of dihydropyridin-2(1*H*)-one **1**. Addition of peroxides to the reaction mixture gave better yield of **1** (entry 9). Among the various peroxides screened (entries 8, 9, 14-18), H_2O_2 (30% aqueous solution) noticed to be effective. In many of the cases, self coupling of acetonitrile was also realized (please see pages S29, S30), however, did not interefere in the isolation of **1**. We also carried out reaction in other solvents (entries 19-25). DMSO provided **1**, albeit in low yield and solvents such as DME, benzene and EtOH were not effective for the formation of dihydropyridin-2(1*H*)-one **1**.

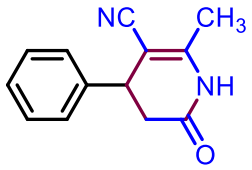
We have also screened KOH in the presence of hydrogen peroxide. Surprisengly, reaction failed to provide **1** presumably cleavage of amide bond of **1** by too strong KOH base. When reaction was performed in the absence of peroxide using KOH, reaction provide **2** as moniotered by GC analysis and complete conversion of benzaldehyde was observed. Isolation of **2** was unsuccessful despite several attempt and decomposes during column chromatography. After various screening, we used four equiv of KO^{t}Bu, one equiv of H_2O_2 with regard to aldehyde and 4 mL of acetonitrile.

Typical Procedure for the Synthesis of Dihydropyridinones

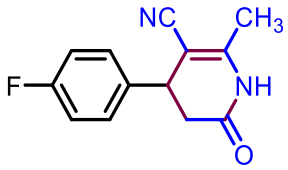


To the stirring solution of benzaldehyde (1 equiv, 1 mmol, 106 mg) in acetonitrile (4 mL) in a sealed tube, KO^{t}Bu (4 equiv, 4 mmol, 450 mg) was added followed by the immediate addition of

H_2O_2 (30% in H_2O) (1 equiv, 1 mmol, 100 µL), reaction vessel was placed in a pre-heated oil bath at 110 ^oC. Progress of the reaction was monitored by TLC. After completion of the reaction, reaction mixture was poured into water (15 mL), extracted with ethyl acetate (3 x 25 mL). Combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Obtained crude product was purified by column chromatography (silica gel, ethyl acetate/hexane 4:6 mL).

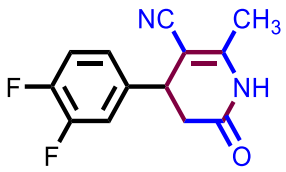


2-Methyl-6-oxo-4-phenyl-1,4,5,6-tetrahydropyridine-3-carbonitrile (1)[1] Pale yellow solid, yield 148 mg (70%); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.24 (s, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.27-7.21 (m, 1H), 7.18 (d, *J* = 7.67 Hz, 2H), 3.88 (t, *J* = 6.5 Hz, 1H), 3.31 (H_2O), 2.85 (dd, *J* = 16.4,7.6 Hz 1H), 2.48 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.80 (s,3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 169.2, 150.9, 141.5, 129.3, 127.8, 127.3, 119.5, 86.7, 38.7, 38.1, 18.6; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{12}N_2O$ $[M+H]^+$ 213.1022, found 213.1015.



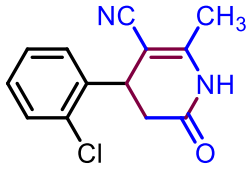
4-(4-Fluorophenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (3) Yellow solid, yield 129 mg (56%), mp 172 - 174 ^oC; **IR** (film): 3261, 2208, 1697, 1682, 1651, 1598, 1491 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (s, 1H), 7.19-7.15 (m, 2H), 7.05-7.01 (m, 2H), 3.86 (t, *J* = 6.7 Hz, 1H), 2.90 (dd, *J* = 16.8, 7.7 Hz 1H), 2.70 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.21 (d, *J* = 1.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.8, 163.5, 161.1, 184.5, 135.47, 135.44,

128.5, 118.0, 116.3, 116.0, 89.2, 38.5, 37.6, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{11}FN_2O$ [M-H]$^-$ 229.0772, found 229.0776.

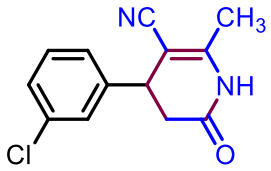


4-(3,4-Difluorophenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (4)[1]

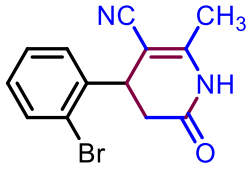
Yellow solid, yield 136 mg (55%); **IR** (film): 3440, 2208, 1693, 1651, 1644, 1491 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.92 (s, 1H), 7.17-7.12 (m, 1H), 7.04-7.00 (m, 1H), 6.96-6.93 (m, 1H), 3.85 (t, *J* = 6.9 Hz, 1H), 2.92 (dd, *J* = 16.8, 7.8 Hz 1H), 2.69 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.23 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.6, 151.5, 151.0, 150.9, 149.6, 149.5, 149.0, 148.9, 136.66, 136.63, 136.59, 123.1, 123.07, 123.04, 123.02, 118.2, 118.0, 117.8, 116.0, 115.8, 88.5, 38.4, 37.4, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{10}F_2N_2O$ [M-H]$^-$ 247.0677, found 247.0674.



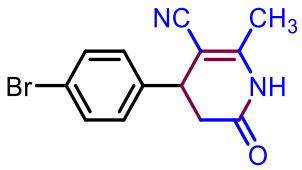
4-(2-Chlorophenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (5)[2] Pale yellow solid, yield 165 mg (67%); **^{1}H NMR (400 MHz, DMSO-d_6)** δ 10.35 (s, 1H), 7.7.48 (d, *J* = 7.3,1.8 Hz, 1H), 7.36-7.29 (m, 2H), 7.24 (dd, *J* = 7.3,2.23Hz, 1H), 4.27 (t, *J* = 6.7 Hz, 1H), 3.31 (H_2O), 2.93 (dd, *J* = 16.5,7.9 Hz 1H), 2.49 (dd, *J* = 16.5, 5.7 Hz, 1H), 2.14 (d, *J* = 0.8 Hz, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 173.5, 157.0, 142.5, 137.6, 135.3, 134.6, 133.5, 133.1, 123.7, 89.9, 41.2, 40.8,23.5; **GC-LRMS** *m/z* calcd for $C_{13}H_{11}ClN_2O$ [M]$^+$ 246.1, found 246.1.



4-(3-Chlorophenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (6) Pale yellow solid, yield 160 mg (65%), mp 174 - 176 ^{o}C; **IR** (film): 3098, 2207, 1713, 1698, 1644, 1597, 1491 cm^{-1}; **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 10.30 (s, 1H), 7.39-7.31 (m, 2H), 7.18 (d, *J* = 7.4,Hz, 1H), 3.95 (d, *J* = 6.6 Hz, 1H), 3.31 (H_2O), 2.86 (dd, *J* = 16.4, 7.5 Hz 1H), 2.55 (dd, *J* = 16.5, 6.3 Hz, 1H), 2.10 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 169.0, 151.5, 144.0, 133.9, 131.3, 127.9, 127.4, 126.2, 119.3, 86.1, 38.2, 37.8, 18.7; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{11}ClN_2O$ [M-H]$^-$ 245.0476, found 245.0479.

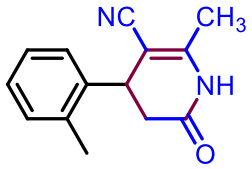


4-(2-Bromophenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (7) Pale yellow solid, yield 195 mg (67%), mp 132 - 134 ^{o}C; **IR** (film): 3236, 2206, 1698, 1643, 1598, 1491 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.74 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 2H), 4.40 (t, *J* = 7.0 Hz, 1H), 2.92 (dd, *J* = 16.9, 8.1 Hz 1H), 2.71 (dd, *J* = 16.9, 6.1 Hz, 1H), 2.27 (d, *J* = 1.1 Hz,3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 169.6, 149.7, 137.9, 133.8, 129.6, 128.3, 127.9, 123.7, 117.7, 87.9, 38.6, 36.4, 18.9; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{11}BrN_2O$ [M-H]$^-$ 288.9971, found 288.9980.

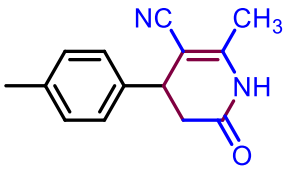


4-(4-Bromophenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (8)[1] Pale yellow solid, yield 189 mg (65%), mp 146 - 148 ^{o}C; **IR** (film): 3258, 2207, 1698, 1644, 1597, 1491 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.84 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J*= 8.5 Hz, 2H), 3.83 (t, *J* = 7.6 Hz, 1H), 2.90 (dd, *J* = 16.3,7.6 Hz, 1H), 2.69 (dd, *J* = 16.8, 5.8 Hz, 1H),

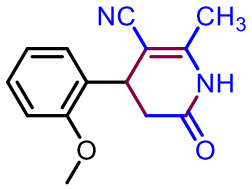
2.21 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$))** δ169.9, 148.7, 138.7, 132.0, 128.1, 122.0, 117.9, 88.8, 38.7, 37.3, 18.6; **LRMS (ESI)** *m/z* calcd for $C_{13}H_{11}BrN_2O$ $[M-H]^-$ 288.9, found 289.0.



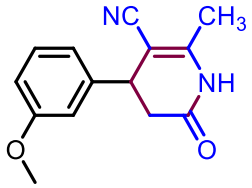
2-Methyl-6-oxo-4-(o-tolyl)-1,4,5,6-tetrahydropyridine-3-carbonitrile carbonitrile (9) Pale yellow solid, yield 140 mg (62%), mp 180 - 184 ^{o}C; **IR** (film): 3247, 2207, 1698, 1651, 1644, 1491 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.91 (s, 1H), 7.19-7.17 (m, 3H), 7.10-7.08 (m, 1H), 4.4 (t, *J* = 7.3 Hz, 1H), 2.88 (dd, *J* = 16.7, 7.8 Hz, 1H), 2.62 (dd, *J* = 16.7, 6.7 Hz, 1H), 2.36 (s, 3H), 2.23 (d, *J* = 1.1 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 170.2, 148.9, 137.5, 135.3, 131.3, 127.8, 126.9, 126.0, 118.1, 89.2, 36.9, 35.3, 19.4, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{14}H_{14}N_2O$ $[M+H]^+$ 227.1179, found 227.1163.



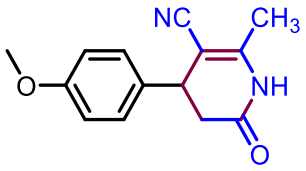
2-Methyl-6-oxo-4-(p-tolyl)-1,4,5,6-tetrahydropyridine-3-carbonitrile (10)[2] Pale yellow solid, yield 143 mg (63%), mp 146 - 148 ^{o}C; **IR** (film): 3262, 2206, 1698, 1650, 1489, 1454 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.79 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.82 (t, *J* = 6.6 Hz, 1H), 2.88 (dd, *J* = 16.7, 7.7 Hz 1H), 2.72 (dd, *J* = 16.7, 6.0 Hz, 1H), 2.32 (s,3H), 2.18 (d, *J* = 1.0 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 170.3, 148.2, 1377, 136.7, 129.8, 126.6, 118.3, 89.6, 38.8, 37.5, 21.0, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{14}H_{14}N_2O$ $[M-H]^-$ 225.1022, found 225.1048.



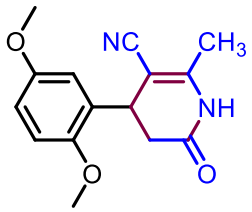
4-(2-Methoxyphenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (11)[2] Pale yellow solid, yield 121 mg (50%); **IR** (film): 3260, 2206, 1698, 1651, 1491, 1464 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.61 (s, 1H), 7.26 (td, *J* = 8.0, 1.6 Hz, 1H), 7.06 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.92-6.87 (m, 2H), 4.17 (t, *J* = 6.4 Hz, 1H), 3.81 (s, 3H), 2.84 (dd, *J* = 16.8, 8.2 Hz 1H), 2.75 (dd, *J* = 16.8, 5.3 Hz, 1H), 2.21 (d, *J* = 1.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.6, 156.9, 148.2, 129.1, 127.6, 127.3, 120.8, 118.3, 110.9, 88.4, 55.1, 35.8, 34.3, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{14}H_{14}N_2O_2$ $[M-H]^-$ 241.0972, found 241.0995.



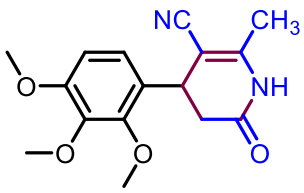
4-(3-Methoxyphenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (12) Pale yellow solid, yield 133 mg (55%), mp 110 - 112 °C; **IR** (film): 3230, 2206, 1704, 1644, 1599, 1491 cm^{-1}; **H NMR (400 MHz, $CDCl_3$)** δ 8.78 (bs, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 6.83-6.77 (m, 2H),6.73 (s, 1H) 3.85-3.82 (m, 1H),3.78 (s, 3H) 2.91 (dd, *J* = 16.7, 7.8 Hz, 1H), 2.75 (dd, *J* = 16.7, 5.7 Hz, 1H), 2.20 (d, *J* = 1.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.1, 160.1, 148.4, 141.3, 130.3, 119.0, 118.1, 113.0, 112.8, 89.2, 55.2, 39.1, 37.3, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{14}H_{14}N_2O_2$ $[M-H]^-$ 241.0972, found 241.0993.



4-(4-Methoxyphenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (13)[1] Pale yellow solid, yield 121 mg (50%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.81 (t, *J* = 6.6 Hz, 1H), 3.77 (s, 3H), 2.88 (dd, *J* = 16.8, 7.7 Hz 1H), 2.70 (dd, *J* = 16.8, 6.1 Hz, 1H), 2.90 (d, *J* = 0.9 Hz,3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 159.2, 148.1, 131.7, 127.9, 118.3, 114.5, 89.8, 55.3, 38.4, 37.6, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{14}H_{14}N_2O_2$ $[M-H]^-$ 241.0972, found 241.0990.

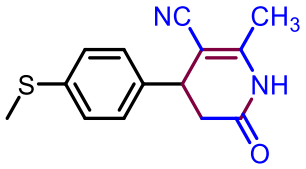


4-(2,5-Dimethoxyphenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (14) Pale yellow solid, yield 131 mg (48%), mp 186 - 188 °C; **IR** (film): 3259, 2206, 1698, 1650, 1503, 1491 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.58 (s, 1H), 6.84 (d, *J* = 8.9 Hz, 1H), 6.79 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.68 (d, *J* = 2.8 Hz 1H), 4.17 (t, *J* = 6.7 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3 H) 2.87 (dd, *J* = 16.8, 8.4 Hz, 1H), 2.77 (dd, *J* = 16.8, 5.4 Hz, 1H), 2.24 (d, *J* = 0.9, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.4, 153.5, 151.0, 148.4, 128.4, 118.3, 114.9, 112.3, 111.7, 88.2, 55.7, 55.6, 35.8, 34.4, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{16}H_{15}N_2O3$ $[M-H]^-$ 271.1077, found 271.1102.

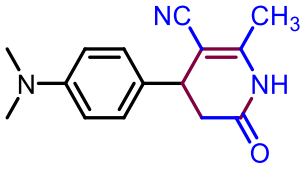


2-Methyl-6-oxo-4-(2,3,4-trimethoxyphenyl)-1,4,5,6-tetrahydropyridine-3-carbonitrile (15) Pale yellow solid, yield 151 mg (50%), mp 104 - 108 °C; **IR** (film): 3260, 2205, 1698, 1651, 1598, 1491 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.87 (s, 1H), 6.76 (d, *J* = 8.3Hz, 1H), 6.59 (d, *J* = 8.3Hz, 1H), 4.07 (t, *J* = 7.3 Hz, 1H), 3.90-3.83 (m, 9H), 2.84 (dd, *J* = 16.6, 8.5 Hz, 1H), 2.67

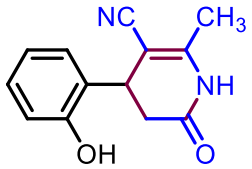
(dd, *J* = 16.6, 5.4 Hz, 1H), 2.20 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ170.5, 153.7, 151.4, 148.0, 142.2, 125.3, 122.1, 118.4, 107.1, 89.0, 60.9, 60.7, 56.0, 36.8, 34.3, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{16}H_{18}N_2O_4$ $[M-H]^-$ 301.1183, found 301.1207.



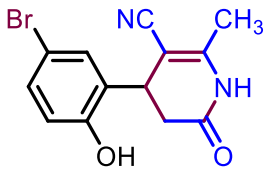
2-Methyl-4-(4-(methylthio)phenyl)-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (16) Pale yellow solid, yield 142 mg (55%), mp 148 - 152 ^{o}C; **IR** (film): 3264, 2205, 1697, 1644, 1598, 1491 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.33 (s, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 3.83 (t, *J* = 6.6 Hz, 1H), 2.90 (dd, *J* = 16.7, 7.6 Hz, 1H), 2.72 (dd, *J* = 16.7, 5.9 Hz, 1H), 2.46 (s, 3H), 2.21 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 169.5, 148.1, 138.4, 136.3, 127.26, 127.21, 118.0, 89.3, 38.7, 37.4, 18.9, 15.7, **HRMS (ESI)** *m/z* calcd for $C_{14}H_{14}N_2OS$ $[M+H]^+$ 259.0900, found 259.0898.



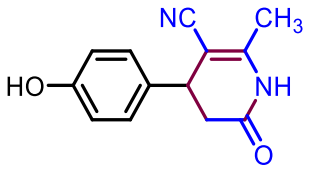
4-(4-(Dimethylamino)phenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (17) Pale yellow solid, yield 179 mg (70%), mp 218 - 220 ^{o}C **IR** (film): 3231, 2207, 1693, 1651, 1598, 1491 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.59 (brs, 1H), 7.06 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J*=8.4 Hz, 2H), 3.77 (t, *J* = 7.3 Hz, 1H), 2.92 (s, 6H), 2.88 (dd, *J* = 16.4, 7.7 Hz, 1H), 2.72 (dd, *J* = 16.4, 5.8 Hz, 1H); 2.13 (d, *J* = 0.8 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ170.2, 150.2, 147.4, 127.5, 127.2, 118.4, 112.9, 90.4, 40.5, 38.3, 37.6, 18.9; **HRMS (ESI)** *m/z* calcd for $C_{15}H_{17}N_3O$ $[M+H]^+$ 256.1444, found 256.1464.



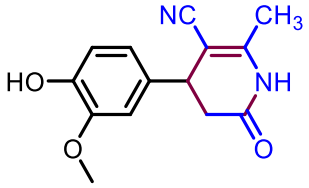
4-(2-Hydroxyphenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (18) Pale yellow solid, yield 148 mg (65%), mp 210 - 212 ^{o}C; **IR** (film): 3431 (brs), 2075, 1634 (brs), 1491 cm^{-1}; **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 10.16 (s, 1H), 9.71 (s, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 6.74 (t, *J* = 7.3 Hz, 1H), 4.05 (t, *J* = 6.3 Hz, 1H), 3.31 (H_2O), 2.81 (dd, *J* = 16.4, 8.0 Hz, 1H), 2.45 (dd, *J* = 16.4, 4.7 Hz, 1H), 2.11 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 169.5, 155.2, 151.0, 128.8, 127.6, 126.5, 119.7, 119.6, 115.7, 85.9, 36.4, 33.5, 18.6; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{12}N_2O_2$ $[M-H]^-$ 227.0815, found 227.0815.



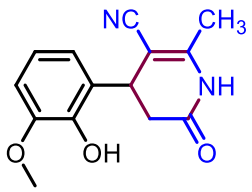
4-(5-Bromo-2-hydroxyphenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (19) Pale yellow solid, yield 184 mg (60%), mp 258 – 260 ^{o}C; **IR** (film): 3241, 3146, 2206, 1678, 1640, 1491 cm^{-1}; **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 10.25 (s, 1H), 10.15 (brs, 1H) 7.28 (dd, *J* = 8.6, 2.5Hz, 1H), 7.09 (d, *J* = 2.5 Hz, 1H),6.82 (d, *J* = 8.6 Hz,1H), 4.07 (t, *J* = 6.5 Hz, 1H), 3.31 (H_2O), 2.83 (dd, *J* = 16.5, 8.0 Hz, 1H), 2.53 (dd, *J* = 16.5, 5.6 Hz, 1H), 2.14 (d, *J* = 1.0 Hz, 3H); **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 170.2, 154.5, 151.4, 131.7, 130.2, 129.1, 119.5, 118.1, 110.8, 85.6, 35.6, 33.5, 18.5; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{11}BrN_2O_2$ $[M+H]^+$ 307.0077, found 307.0060.



4-(4-Hydroxyphenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (20) Pale yellow solid, yield 151 mg (66%), mp 202 - 206 ^{o}C; **IR** (film): 3402, 3230, 2207, 1694, 1644, 1515, 1492 cm^{-1}; **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 10.19 (s, 1H), 9.36 (s, 1H) 6.98 (d, *J* = 8.4, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 3.76 (t, *J* = 6.3 Hz, 1H), 2.80 (dd, *J* = 16.3, 7.6 Hz, 1H), 2.44 (dd, *J* = 16.3, 5.6 Hz, 1H), 2.07 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 169.4, 157.0, 150.4, 131.5, 128.3, 119.7, 116.0, 87.0, 38.4, 38.0, 18.6; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{12}N_2O_2$ [M-H]$^-$ 251.0791, found 251.0808.

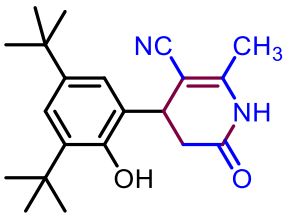


4-(4-Hydroxy-3-methoxyphenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (21) Pale yellow solid, yield 155 mg (60%), mp 202 - 204 ^{o}C; **IR** (film): 3226, 2204, 1693, 1643, 1597, 1491 cm^{-1}; **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 10.19 (s, 1H), 8.91(s, 1H), 6.76 (d, *J* = 1.9,Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 6.55 (dd, *J* = 8.1, 1.9 Hz, 1H) 3.77 (t, *J* = 6.6 Hz, 1H), 3.31 (H_2O), 3.72 (s, 3H), 2.79 (dd, *J* = 16.3, 7.6 Hz 1H), 2.51 (dd, *J* = 16.5, 6.0 Hz, 1H), 2.08 (s, 3H) **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 169.4, 150.5, 148.2, 146.3, 132.1, 119.7, 119.2, 116.0, 111.8, 87.4, 56.0, 38.4, 38.3, 18.6; **HRMS (ESI)** *m/z* calcd for $C_{14}H_{14}N_2O_3$ $[M+H]^+$ 259.1077, found 259.1071.

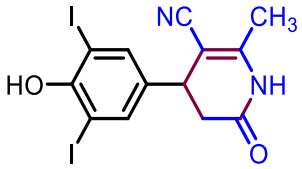


4-(2-Hydroxy-3-methoxyphenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (22) Pale yellow solid, yield 129 mg (50%); Pale yellow solid, yield 0.090 g (86%); **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.48 (brs, 1H), 6.81-6.79 (m, 2H), 6.68-6.66 (m, 1H), 5.91 (brs, 1H), 4.21

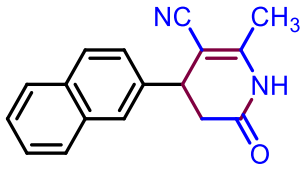
(t, *J* = 6.8 Hz, 1H) 3.86 (s, 3H), 2.85-2.83 (m, 2H), 2.21 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.5, 148.4, 146.7, 143.3, 124.9, 119.9, 119.7, 118.3, 110.2, 88.4, 56.1, 35.7, 34.0, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{14}H_{14}N_2O_3$ $[M-H]^-$ 257.0921, found 257.0900.



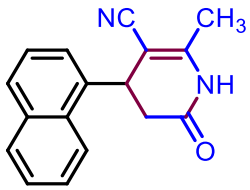
4-(3,5-Di-tert-butyl-2-hydroxyphenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (23) Pale yellow solid, yield 204 mg (60%), mp 236 - 238 ^{o}C; **IR** (film): 3207, 2207, 1674, 1641, 1633, 1598, 1491cm^{-1}; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.25 (s, 1H), 8.04 (s, 1H), 7.10(d, *J* = 2.3 Hz, 1H), 6.83 (d, *J* = 2.3 Hz, 1H), 4.28 (t, *J* = 6.2 Hz, 1H), 3.31 (H_2O), 2.77 (dd, *J* = 16.2, 7.6 Hz, 1H), 2.39 (dd, *J* = 16.2, 5.7 Hz, 1H), 2.13 (s, 3H), 1.34 (s, 9H), 1.18 (s, 9H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ 169.4, 151.5, 150.5, 142.0, 183.3, 128.4, 122.6, 121.5, 119.5, 86.7, 37.6, 35.3, 34.3, 32.8, 31.8 30.3, 18.6; **HRMS (ESI)** *m/z* calcd for $C_{21}H_{28}N_2O_2$ $[M+Na]^+$ 363.2043, found 363.2046.



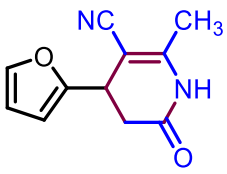
4-(4-Hydroxy-3,5-diiodophenyl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (24) Pale yellow solid, yield 177 mg (37%); **IR** (film): 3511 (brs), 2255, 1681, 1660, 1651, 1595, 1491 cm^{-1}; **^{1}H NMR** (**400 MHz, DMSO-d_6**) δ 10.32 (s, 1H), 9.59 (s, 1H), 7.59 (s, 2H), 3.87 (t, *J* = 6.9 Hz, 1H), 2.80 (dd, *J* = 16.5, 7.5 Hz, 1H), 2.56 (dd, *J* = 16.5, 7.0 Hz, 1H), 2.11 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (100 MHz, DMSO-d_6)** δ169.2, 155.2, 151.2, 138.0, 137.3, 119.4, 88.0, 86.5, 37.8, 36.6, 18.7; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{10}N_2I_2O_2$ $[M-H]^-$ 478.8748, found 478.8743.



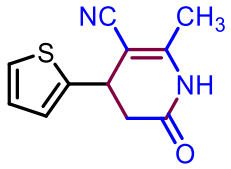
2-Methyl-4-(naphthalen-2-yl)-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (25) Pale yellow solid, yield 97 mg (37%), mp 168 - 170 ^{o}C; **IR** (film): 3219, 2206, 1704, 1694, 1650, 1598, 1491 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.60 (brs, 1H), 7.86-7.78 (m, 3H), 7.62 (s, 1H), 7.47 (t, *J* = 4.3 Hz, 2H), 7.33 (dd, *J* = 8.3,1.3 Hz, 1H) 4.0 (t, *J* = 6.6 Hz, 1H), 2.98 (dd, *J* = 16.8, 7.7 Hz 1H), 2.85 (dd, *J* = 16.8, 5.8 Hz, 1H), 2.22 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 169.9, 148.5, 136.9, 133.4, 132.9, 129.3, 127.9, 127.7, 126.5, 126.3, 125.5, 124.7, 118.2, 89.2, 39.3, 37.3, 18.8; **GC-HRMS** *m/z* calcd for $C_{17}H_{14}N_2O$ $[M]^+$ 262.1101, found 262.1093.



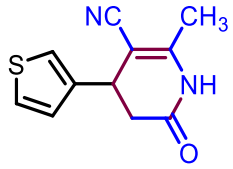
2-Methyl-4-(naphthalen-1-yl)-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (26) Pale yellow solid, yield 89 mg (34%), mp 184 - 186 ^{o}C; **IR** (film): 3238, 2207, 1698, 1651, 1598, 1491 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.87 (s, 1H), 7.96-7.89 (m, 2H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.58-7.40 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 4.73 (t, *J* = 6.7, 1H), 3.06 (dd, *J* = 16.7, 7.9 Hz, 1H); 2.86 (dd, *J* = 16.7, 5.0 Hz, 1H), 2.26 (s, 3H) **^{13}C NMR (100 MHz, CDCl$_3$)** δ 170.0, 149.6, 134.5, 134.2, 130.5, 129.4, 128.8, 126.8, 126.0, 125.5, 124.0, 122.3, 118.2, 88.5, 37.2, 35.1, 18.8, **HRMS (ESI)** *m/z* calcd for $C_{17}H_{14}N_2O$ $[M-H]^-$ 261.1022, found 261.1041.



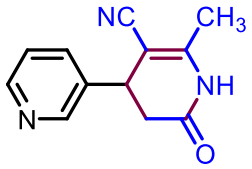
4-(Furan-2-yl)-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (27)[2] Pale yellow solid, yield 91 mg (45%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.97 (brs, 1H), 7.39-7.38 (m, 1H), 6.33-6.32 m, 1H), 6.20 (d, *J* = 3.3 Hz, 1H), 3.96 (t, *J*= 5.9Hz, 1H), 2.93-2.84 (m, 2H), 2.22 (d, *J* = 1.0 Hz, 3H), **^{13}C NMR (100 MHz, $CDCl_3$)** δ170.0, 152.0, 149.1, 142.8, 118.0, 110.4, 106.6, 86.7, 34.5, 33.1, 18.8; **LRMS (ESI)** *m/z* calcd for $C_{11}H_{10}N_2O_2$ $[M-H]^-$ 201.1, found 201.1.



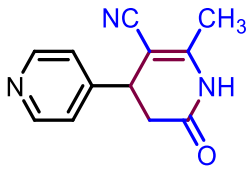
2-methyl-6-oxo-4-(thiophen-2-yl)-1,4,5,6-tetrahydropyridine-3-carbonitrile (28) Pale yellow solid, yield 94 mg (43%), mp 176 - 178 ^{o}C; **IR** (film): 2201, 1697, 1643, 1598, 1491cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.63 (brs, 1H), 7.21 (d, *J* = 5.0, Hz, 1H), 6.95-6.91 (m, 2H), 4.14 (t, *J* = 6.0 Hz, 1H), 2.95 (dd, *J* = 16.7, 7.3 Hz, 1H), 2.83 (dd, *J* = 16.7, 4.6 Hz, 1H), 2.20 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.3, 148.3, 142.7, 127.2, 125.0, 124.8, 117.9, 89.5, 38.0, 34.7, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{11}H_{10}N_2OS$ $[M-H]^-$ 217.0430, found 217.0452.



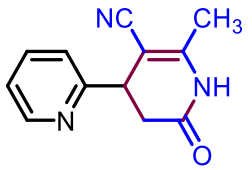
2-Methyl-6-oxo-4-(thiophen-3-yl)-1,4,5,6-tetrahydropyridine-3-carbonitrile (29) Pale yellow solid, yield 83 mg (38%), mp 158 - 160 ^{o}C; **IR** (film): 3235, 2204, 1697, 1644, 1598, 1491 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.44 (s, 1H), 7.32 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.07-7.06 (m, 1H), 7.00 (dd, *J* = 5.0, 1.4 Hz, 1H), 3.94 (t, *J* = 6.0 Hz, 1H), 2.88 (dd, *J* = 16.7, 7.3 Hz, 1H), 2.79 (dd, *J* = 16.7, 4.7 Hz, 1H), 2.17 (d, *J* = 1.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.8, 148.0, 140.0, 127.3, 126.0,121.3 118.3, 89.3, 36.6, 34.6, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{11}H_{10}N_2OS$ $[M-H]^-$ 217.0430, found 217.0460.



2'-Methyl-6'-oxo-1',4',5',6'-tetrahydro-[3,4'-bipyridine]-3'-carbonitrile (30) Pale yellow solid, yield 139 mg (65%), mp 180 - 182 ^{o}C; **IR** (film): 3231, 2204, 1704, 1693, 1643, 1491 cm^{-1}; **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 10.34 (s, 1H), 8.48-8.46 (m, 2H), 7.63 (d, *J* = 7.8,Hz, 1H), 7.38-7.35 (m, 1H), 4.01 (t, *J* = 6.7Hz, 1H) 2.87 (dd, *J* = 16.5, 7.4 Hz 1H), 2.58 (dd, *J* = 16.5, 6.7 Hz, 1H), 2.10 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 169.0, 151.6, 149.2, 149.0, 137.0, 135.1, 124.4, 119.3, 85.9, 37.7, 36.3, 18.7; **HRMS (ESI)** *m/z* calcd for $C_{12}H_{11}N_3O$ $[M-H]^-$ 212.0818, found 212.0827.



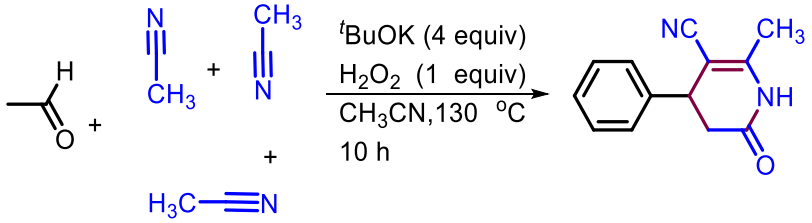
2-Methyl-6-oxo-1,4,5,6-tetrahydro-[4,4'-bipyridine]-3-carbonitrile (31) Pale yellow solid, yield 107 mg (50%); **IR** (film): 3443, 2253, 1667, 1660, 1651, 1591 cm^{-1}; **^{1}H NMR (400 MHz, DMSO-d$_6$)** δ 10.34 (brs, 1H), 8.52 (d, *J* = 4.3,Hz, 2H), 7.24 (d, *J* = 5.3 Hz, 2H), 3.97 (t, *J* = 6.7 Hz, 1H), 2.90 (dd, *J* = 16.5, 7.6 Hz 1H), 2.55 (dd, *J* = 16.5, 5.8 Hz, 1H), 2.10 (s, 3H); **^{13}C NMR (100 MHz, DMSO-d$_6$)** δ 168.9, 151.9, 150.9, 150.1, 122.7, 119.2, 85.0, 37.9, 37.0, 18.7 **HRMS (ESI)** *m/z* calcd for $C_{12}H_{11}N_3O$ $[M+H]^+$ 214.0975, found 214.0964.



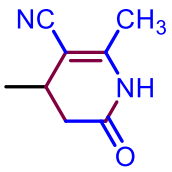
2'-Methyl-6'-oxo-1',4',5',6'-tetrahydro-[2,4'-bipyridine]-3'-carbonitrile (32) Pale yellow solid, yield 117 mg (55%), mp 156 - 160 ^{o}C; **IR** (film): 3269, 2203, 1694, 1682, 1644, 1597, 1491 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.96 (s, 1H), 8.52-8.50 (m, 1H), 7.64 (td, *J* = 7.7, 1.9

Hz, 1H), 7.22 (d, *J* = 7.7 Hz 1H), 7.19 – 7.17 (m, 1H), 3.92 (t, *J* = 6.3 Hz, 1H), 3.01 (dd, *J* = 16.6, 5 Hz, 1H), 2.83 (dd, *J* = 16.6, 7.6 Hz, 1H), 2.16 (d, *J* = 1.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 170.6, 159.0, 150.0, 149.1, 137.1, 122.8, 121.7, 118.4, 87.4, 40.9, 35.0, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{12}H_{11}N_3O$ $[M-H]^-$ 212.0818, found 212.044.

Genral procedure for the dihydropyridinones from aliphatic aldehydes.

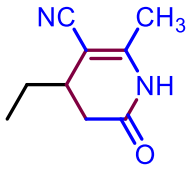


To the stirring solution of acetaldehyde (1 equiv, 2 mmol, 88 mg) in acetonitrile (6 mL) in a sealed tube, KO^{t}Bu (4equiv, 8 mmol, 900 mg) was added followed by the immediate addition of H_2O_2, 30% in H_2O, (1 equiv, 2 mmol, 200 µL), reaction vessel was placed in a pre-heated oil bath at 130 ^{o}C. Progress of the reaction was monitored by TLC. After completion of the reaction, reaction mixture was poured into water (15 mL), extracted with ethyl acetate (3 x 25 mL). Combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. Obtained crude product was purified by column chromatography (silica gel, ethyl acetate/hexane 4:6 mL).

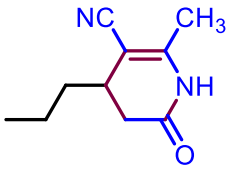


2,4-Dimethyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (33)[1] Pale yellow solid, yield 201 mg (67%), mp 130 - 132 ^{o}C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.98 (brs, 1H), 2.78-2.74 (m, 1H), 2.65 (dd, *J* = 16.6, 6.6 Hz 1H), 2.31 (dd, J = 16.6, 8.2 Hz, 1H), 2.17-2.16 (m, 3H), 1.24-1.22

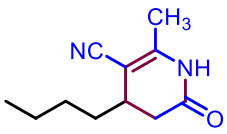
(m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.1, 147.6, 118.0, 91.1, 37.5, 28.0, 19.0, 18.6; **HRMS (ESI)** *m/z* calcd for $C_8H_{10}N_2O$ $[M+H]^+$ 151.0866, found 151.0875.



4-Ethyl-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (34) Pale yellow solid, yield 164 mg (50%), mp 102 - 104 ^oC; **IR** (film): 3180, 2206, 1695, 1647 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.89 (brs, 1H), 2.61 (dd, *J* = 16.3, 7.0 Hz, 1H), 2.54 (t, *J* = 6.7 Hz, 1H), 2.36 (dd, *J* = 16.3, 5.9 Hz, 1H), 2.14 (d, *J* = 1.2 Hz, 3H), 1.72-1.64 (m, 1H), 1.50-1.43 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ171.3, 147.9, 118.5, 89.9, 34.6, 34.4, 26.3, 18.6, 10.6; **HRMS (ESI)** *m/z* calcd for $C_9H_{12}N_2O$ $[M-H]^-$ 163.0866, found 163.0889.

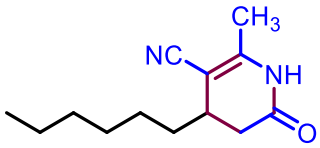


2-Methyl-6-oxo-4-propyl-1,4,5,6-tetrahydropyridine-3-carbonitrile (35)[1] Pale yellow solid, yield 132 mg (37%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.03 (s, 1H), 2.63-2.57 (m, 2H), 2.33 (dd, *J* = 18.6, 8.5 Hz, 1H), 2.12 (s, 3H), 1.61-1.53 (m, 1H), 1.43-1.32 (m, 3H), 0.90 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.4, 147.9, 118.5, 90.0, 35.5, 35.1, 32.8, 19.4, 18.5, 13.8; **HRMS (ESI)** *m/z* calcd for $C_{10}H_{14}N_2O$ $[M-H]^-$ 177.1022, found 177.1050.

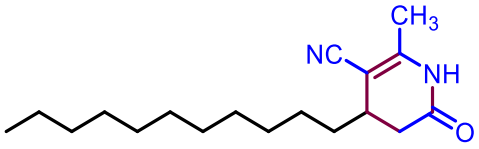


4-Butyl-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (36) Pale yellow solid, yield 115 mg (30%), mp 108 - 112 ^oC; **IR** (film): 3458 (brs), 2202, 1697, 1644, 1598, 1491 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.65 (s, 1H), 2.65-2.57 (m, 2H), 2.39-2.33 (m, 1H), 2.14 (s, 3H),

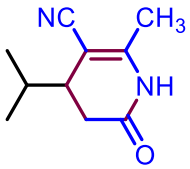
1.56-1.60 (m, 1H), 1.41-1.26 (m, 5H), 0.88 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.0, 147.7, 118.5, 90.2, 35.1, 33.0, 29.6, 28.2, 22.5, 18.6, 13.9; **HRMS (ESI)** *m/z* calcd for $C_{11}H_{16}N_2O$ $[M-H]^-$ 191.1179, found 191.1162.



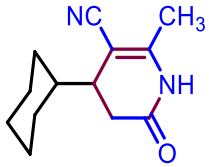
4-Hexyl-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (37) Pale yellow solid, yield 154 mg (35%), mp 78 - 80 °C; **IR** (film): 3275, 2205, 1694, 1650, 1644, 1491 cm^{-1}; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.07 (s, 1H), 2.69-2.59 (m, 2H), 2.36 (m, 1H), 2.17 (s, 3H), 1.67-1.62 (m, 1H), 1.46-1.38 (m, 2H), 1.35-1.27 (m, 7H) 0.88 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 171.4, 147.8, 118.5, 90.1, 35.1, 33.3, 33.0, 31.6, 29.0, 26.1, 22.5, 18.6, 14.0; ; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{20}N_2O$ $[M-H]^-$ 219.1492, found 219.1522.



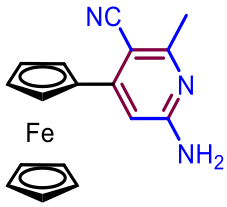
2-Methyl-6-oxo-4-undecyl-1,4,5,6-tetrahydropyridine-3-carbonitrile (38) Pale yellow solid, yield 290 mg (50%), mp 74 - 76 °C; **IR** (film): 3435, 2205, 1653, 1643, 1599, 1491 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (s, 1H), 2.65-2.57 (m, 2H), 2.38-2.31 (m, 1H), 2.14 (s, 3H), 1.63-1.59 (m, 2H), 1.30-1.23 (m, 18H), 0.86 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.2, 147.5, 118.4, 90.3, 35.0, 33.3, 33.1, 31.9, 29.61, 29.60, 29.56, 29.4, 29.3, 26.2, 24.8, 22.6, 18.7, 14.1; **HRMS (ESI)** *m/z* calcd for $C_{18}H_{30}N_2O$ $[M-H]^+$ 289.2274, found 289.2276.



4-Isopropyl-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (39)[1] Pale yellow solid, yield 235 mg (66%), mp 134- 136 ^{o}C; **IR** (film): 3434, 2205, 1653, 1643, 1633, 1491 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.86 (s, 1H), 2.25-2.43 (m, 3H), 2.16 (s, 3H), 1.99-1.91 (m, 1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 171.6, 148.4, 118.9, 88.7, 39.3, 31.6, 31.4, 19.6, 18.6, 18.0; **HRMS (ESI)** *m/z* calcd for $C_{10}H_{14}N_2O$ $[M-H]^-$ 177.1022, found 177.1051

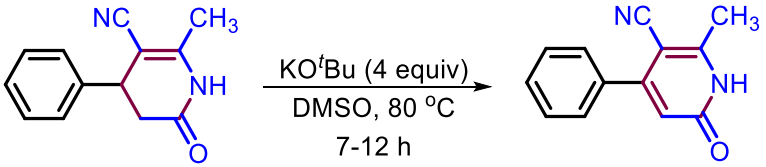


4-Cyclohexyl-2-methyl-6-oxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (40) Pale yellow solid, yield 218 mg (50%), mp 114 - 118 ^{o}C; **IR** (film): 3258, 2204, 1694, 1650, 1644, 1503 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (brs, 1H), 2.58-2.52 (m, 2H), 2.48-2.42 (m, 1H), 2.16 (s, 3H), 1.79-1.69 (m, 2H), 1.67-1.49 (m, 4H), 1.28-1.07 (m,5H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 171.6, 148.3,119.1, 88.6, 41.6, 39.0, 32.2, 30.1, 29.7, 28.6, 26.2, 26.2, 26.1, 18.7; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{18}N_2O$ $[M-H]^-$ 217.1335, found 217.1344.

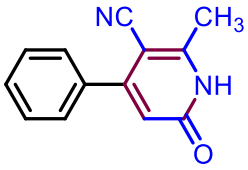


6-Amino-4-ferrocene-2-methylnicotinonitrile (41) Pale yellow solid, yield 143 mg (45%), mp 164 - 170 ^{o}C; **IR** (film): 3442, 2198, 1633, 1586, 1537, 1490, 1449 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 6.40 (s, 1H), 4.91 (t, *J* = 1.8 Hz, 4H), 4.43 (t, *J* = 1.8 Hz, 2H), 4.16 (s, 5H), 2.59 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 163.8, 158.9, 153.4, 119.4, 103.4, 95.7, 79.7, 70.4, 70.3, 68.5, 23.8; **135-DEPT NMR (100 MHz, CDCl$_3$)** δ 103.4, 70.4, 70.3, 68.5, 23.8; **HRMS (ESI)** *m/z* calcd for $C_{17}H_{15}FeN_3$ $[M+H]^+$ 318.0688, found 318.0667.

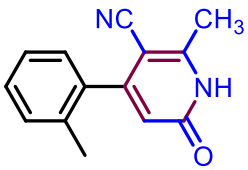
Postmodification of the synthesized dihydropyridinones: Synthesis of pyridinones.



Take a oven dried 25 ml RB flask equipped with magnetic bar, dihydropyridinones (1 equiv, 0.5 mmol) and KO^{t}Bu (4 equiv, 2 mmol) were added under nitrogen atmosphere in DMSO and heated at 80 ^{o}C for 7-12 h. Progress of the reaction was monitored by TLC. After completion of the reaction, reaction mixture was poured into water (15 mL), extracted with ethyl acetate (3 x 15 mL). Combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo.* Obtained crude product was purified by column chromatography using ethyl acetate and hexane as eluent.

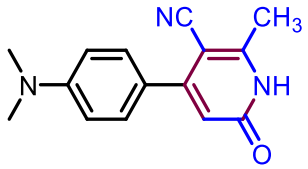


2-Methyl-6-oxo-4-phenyl-1,6-dihydropyridine-3-carbonitrile (42)[2] White solid, yield 84 mg (80%); **^{1}H NMR (500 MHz, DMSO-d$_6$)** δ 12.59 (bs, 1H), 7.55-7.51 (m, 5H) 6.27(s, 1H), 2.49 (s, 3H); **^{13}C NMR (125 MHz, DMSO-d$_6$)** δ 162.0, 156.9, 152.9, 136.5, 130.1, 129.1, 128.3, 117.2, 116.8, 89.7, 19.2; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{11}N_2O$ $[M+H]^+$ 211.0866, found 211.0866.

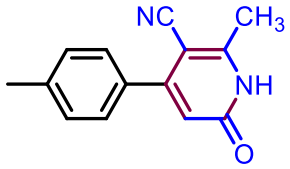


2-Methyl-6-oxo-4-(o-tolyl)-1,6-dihydropyridine-3-carbonitrile (43) Prduct obtained at 110 ^{o}C; White solid, yield 72 mg (64%), mp 210 - 216 ^{o}C; **IR** (film): 2223, 1160, 1654, 1491 cm^{-1}; **^{1}H**

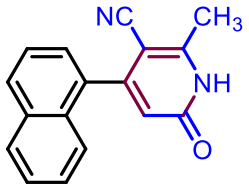
NMR (400 MHz, $CDCl_3$) δ 13.27 (s, 1H), 7.33-7.25 (m, 3H), 7.15-7.13 (m, 1H),7.34 (s, 1H), 2.65 (s, 3H), 2.27 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.3, 156.0, 154.3, 135.8, 134.8, 130.7, 129.5, 128.1,136.1, 117.6, 115.5, 94.3, 19.7, 19.0; **HRMS (ESI)** *m/z* calcd for $C_{14}H_{12}N_2O$ $[M-H]^-$ 223.0866, found 223.0866.



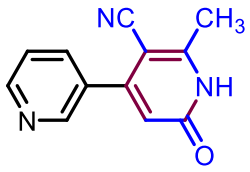
4-(4-(dimethylamino)phenyl)-2-methyl-6-oxo-1,6-dihydropyridine-3-carbonitrile (44). Prduct obtained at 110 °C; Yield 81 mg (64 %); **IR** (film): 2204, 1614, 1598, 1491 cm^{-1}; **^{1}H NMR (500 MHz, DMSO-*d6*)** δ 12.39 (brs, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.17 (s, 1H), 2.98 (s, 6H), 2.47 (s, 3 H); **^{13}C NMR (125 MHz, DMSO-*d6*)** δ 162.1, 156.7, 152.9, 151.6, 129.3, 123.2, 117.8, 114.7, 112.1, 112.2, 32.0, 19.1; **HRMS (ESI)** *m/z* calcd for $C_{15}H_{15}N_3O$ $[M-H]^-$ 252.1131, found 252.1146.



2-Methyl-6-oxo-4-(p-tolyl)-1,6-dihydropyridine-3-carbonitrile (45). Product obtained at 110 °C; White solid, Yield 74 mg (66 %), mp 282 - 284 °C; **IR** (film): 3380, 2222, 1660, 1651, 1633, 1598, 1491 cm^{-1}; **^{1}H NMR (400 MHz, DMSO-*d6*)** δ 12.49 (brs, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.19(s, 1H), 2.44 (s, 3H), 2.33 (s, 3 H); **^{13}C NMR (100 MHz, DMSO-*d6*)** δ 162.0, 156.8, 152.9, 139.9, 133.7, 129.7, 128.2, 117.3, 116.4, 89.7, 21.3, 19.1; **HRMS (ESI)** *m/z* calcd for $C_{14}H_{12}N_2O$ $[M-H]^-$ 223.0866, found 223.0857.

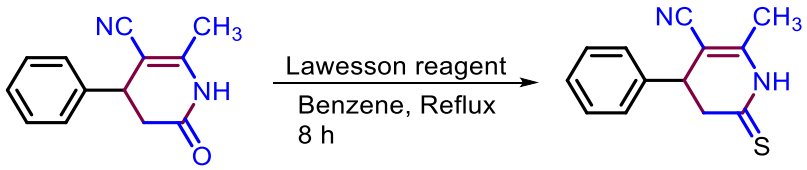


2-Methyl-4-(naphthalen-1-yl)-6-oxo-1,6-dihydropyridine-3-carbonitrile (46) White solid, yield 45 mg (35%), mp 320 - 324 ^{o}C; **IR** (film): 3393, 2225, 1643 (br) 1555, 1491 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 12.63 (s, 1H), 8.01 (t, *J* = 8.1, 2H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.60-7.51 (m, 3H), 7.43 (d, *J* = 6.9, 1H), 6.24 (s, 1H), 3.30 (s, 3H); **^{13}C NMR (176 MHz, CDCl$_3$)** δ 162.0, 156.2, 152.6, 134.6, 133.4, 130.3, 129.8, 128.9, 127.4, 126.9, 126.5, 125.8, 125.3, 118.6, 116.8, 91.8, 19.8; **HRMS (ESI)** *m/z* calcd for $C_{14}H_{10}FNO$ [M-H]$^-$ 259.0866, found 259.0880.



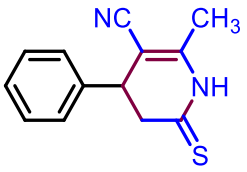
2'-Methyl-6'-oxo-1',6'-dihydro-[3,4'-bipyridine]-3'-carbonitrile (47) White solid, yield 50 mg (47%), mp above 360 ^{o}C; **IR** (film): 3385, 2329, 1651, 1634, 1598, 1491 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 12.53 (brs, 1H), 8.70-8.66 (m, 2H), 7.95 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.52 (dd, *J* = 7.8, 4.9 Hz, 1H), 6.35 (s, 1H), 2.46 (s, 3H); **^{13}C NMR (176 MHz, CDCl$_3$)** δ 161.8, 157.2, 153.8, 151.0, 149.7, 148.6, 136.1, 132.4, 124.0, 117.5, 117.1, 19.2; **HRMS (ESI)** *m/z* calcd for $C_{12}H_9N_3O$ [M-H]$^-$ 210.0662, found 210.0672.

Synthesis of thio-pyridinones

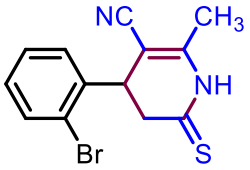


To a stirring solution of pyridinones **1** (53 mg, 1 equiv, 0.25 mmol) in 5 mL benzene, Lawesson reagent (61 mg, 0.6 equiv, 0.15 mmol), was added and reaction mixture was refluxed for 8 h,

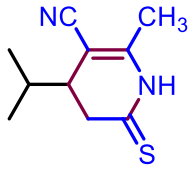
upon completion of reaction, mixture was cooled to room temperature, treated with 50 ml water, and extracted with ethyl acetate (20 mL x 3). Organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Obtained crude product was purified by column chromatography.



2-Methyl-4-phenyl-6-thioxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (48)[3] Pale yellow solid, yield 50 mg (87%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.24 (bs, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.25 (d, 7.6 Hz, 2H), 3.77 (t, *J* = 6.6 Hz, 1H), 3.30 (dd, *J* = 17.3, 5.9 Hz, 1H), 3.22 (dd, *J* = 17.3, 7.5 Hz, 1H), 2.24 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 200.5, 145.3, 139.3, 129.2, 128.0, 126.9, 117.8, 93.3, 45.4, 38.5, 18.5; **HRMS (ESI)** *m/z* calcd for $C_{13}H_{12}N_2S$ $[M-H]^-$ 227.0637, found 227.0659.

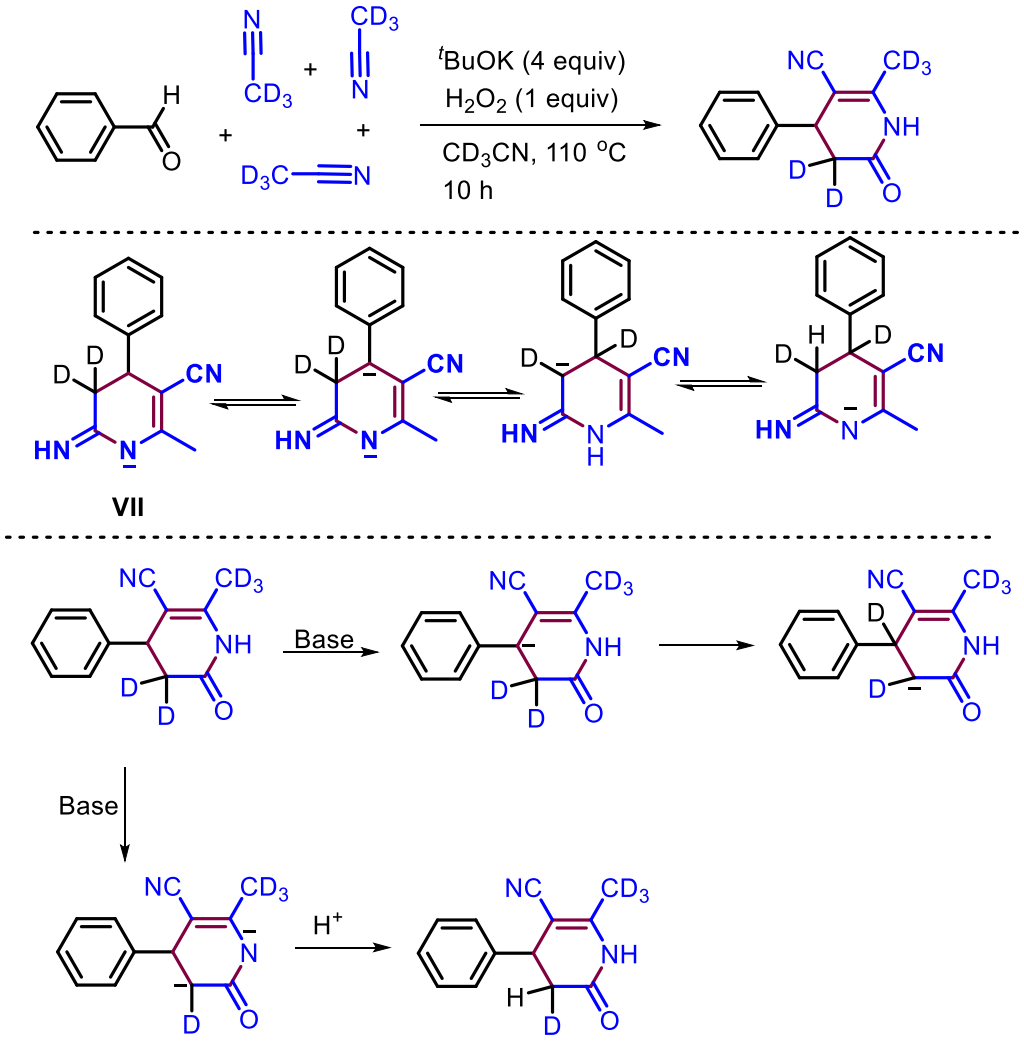


4-(2-Bromophenyl)-2-methyl-6-thioxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (49) Pale yellow solid, yield 67 mg (88%), mp 144 - 146 ^oC; **IR** (film): 3252, 2207, 1650, 1644, 1567, 1491 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.19 (bs, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.15 (t, 7.9 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 4.33 (t, *J* = 6.7 Hz, 1H), 3.25 (dd, *J* = 17.3, 7.5 Hz, 1H), 3.20 (dd, *J* = 17.3, 6.7 Hz, 1H), 2.30 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.9, 146.7, 137.6, 133.8, 129.6, 128.2, 128.0, 123.9, 117.4, 91.8, 44.5, 37.9, 18.6; **HRMS (ESI)** *m/z* calcd for $C_{113}H_{11}BrN_2O$ $[M-H]^-$ 304.9743, found 304.9773.

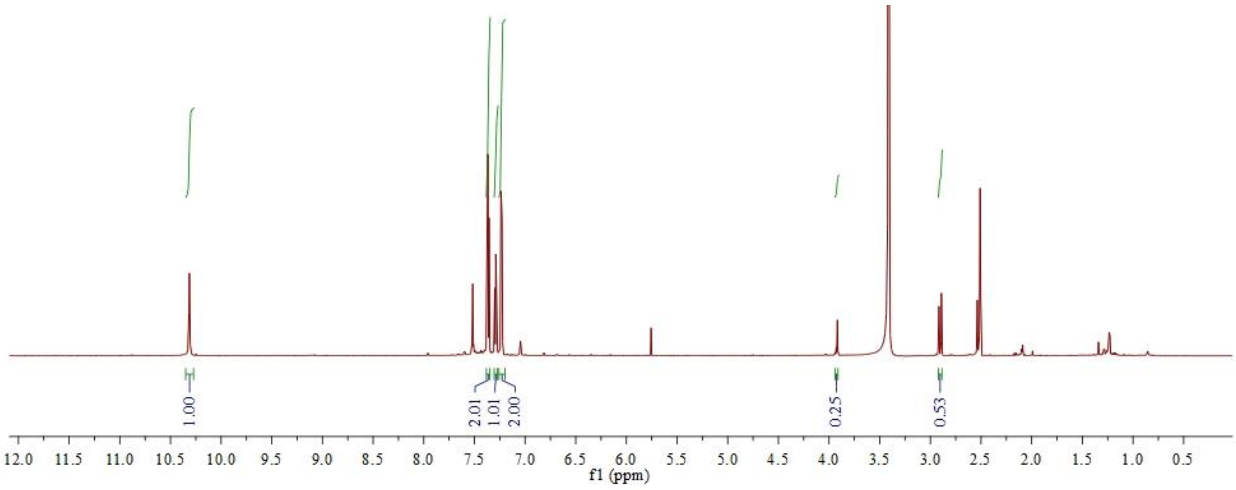


4-Isopropyl-2-methyl-6-thioxo-1,4,5,6-tetrahydropyridine-3-carbonitrile (50) Pale yellow solid, yield 44 mg (90%), mp 116 - 118 ^{o}C; **IR** (film): 3256, 2205, 1651, 1644 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.24 (bs, 1H), 3.09 (dd, *J* = 17.4, 4.9 Hz, 1H), 2.84 (dd, *J* = 17.4, 7.5 Hz, 1H), 2.39-2.34 (m, 1H), 2.21 (s, 3H), 1.95-1.87 (m, 1H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H; **^{13}C NMR (100 MHz, $CDCl_3$)** δ 202.3, 145.6, 118.5, 93.3, 40.5, 38.9, 31.1, 19.8, 18.3; **HRMS (ESI)** *m/z* calcd for $C_{10}H_{14}N_2S$ $[M-H]^-$ 193.0794, found 193.0824.

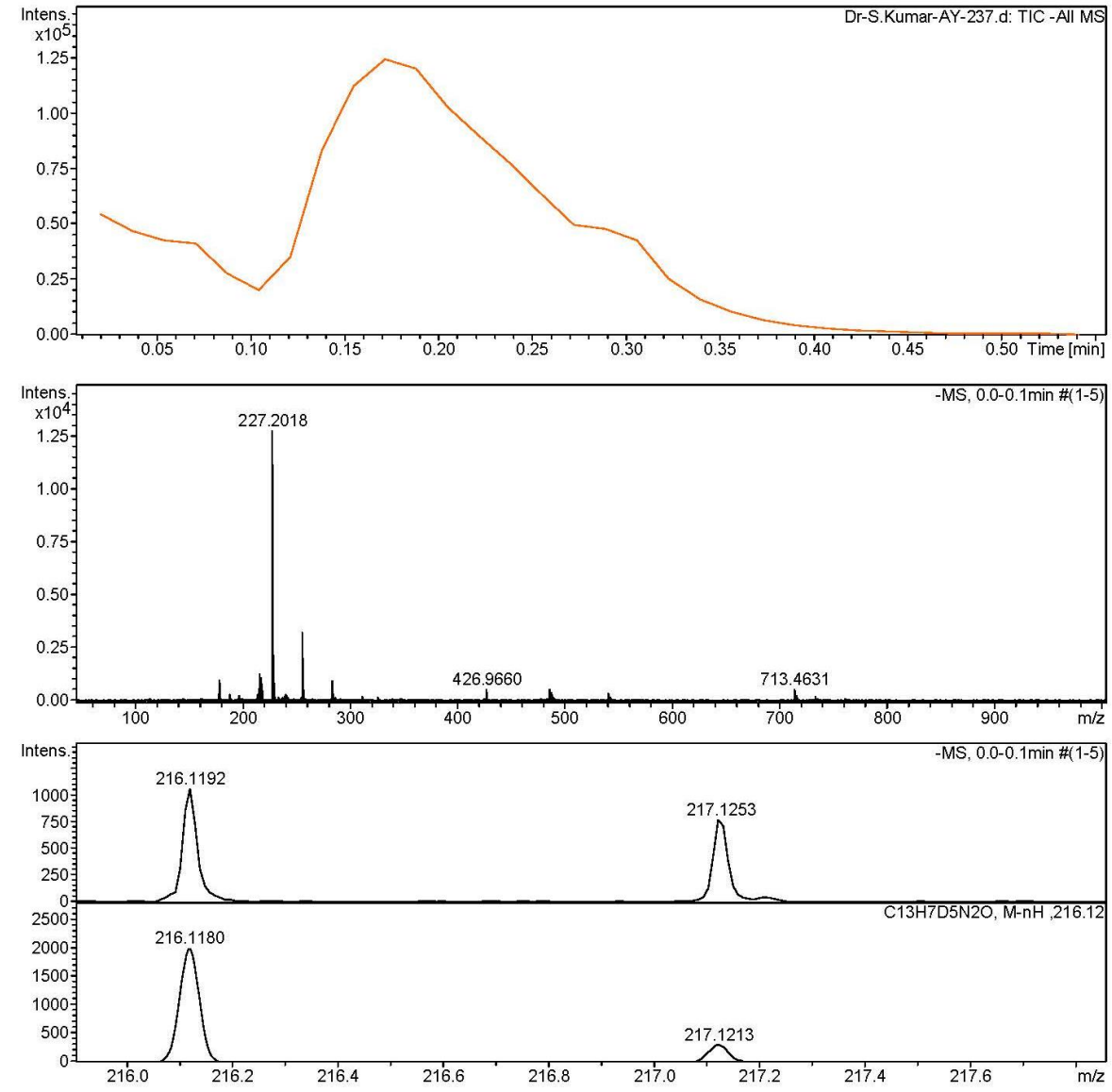
Control experiment



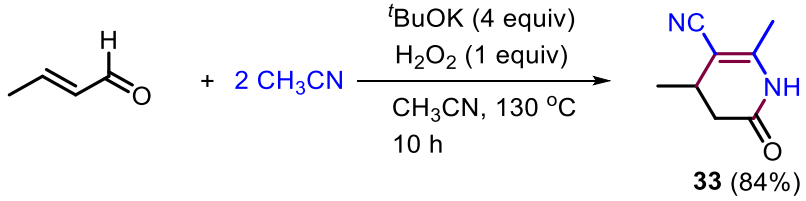
^{1}H NMR data of deutarated compound **51**



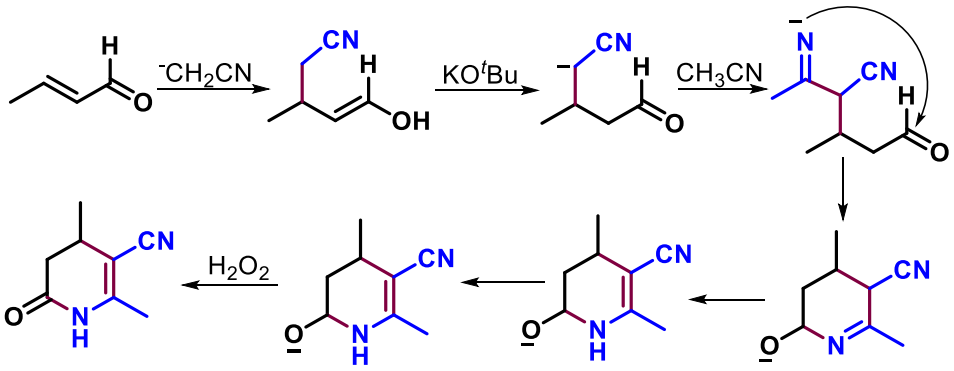
Mass data for deutarated compound **51**



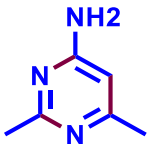
Bruker Compass DataAnalysis 4.0 printed: 12/30/2014 5:04:46 AM Page 1 of 1



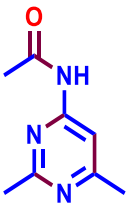
Mechanism



Side products Few side products was also isolated form reaction mixture, it was also observed that installation of reaction without aldehyde provided following product via cascade reaction between three and four acetonitrile molecule respectively and characterized by ^{1}H, ^{13}C, GCMS, and single crystal structure.



2,6-Dimethylpyrimidin-4-amine. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (s, 1H), 5.05 (brs, 2H), 2.43 (s, 3H), 2.27 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.3, 165.7, 163.2, 100.7, 25.6, 23.8; GC-LRMS *m/z* calcd for $C_6H_9N_3$ [M^+] 123.08, found 123.01.

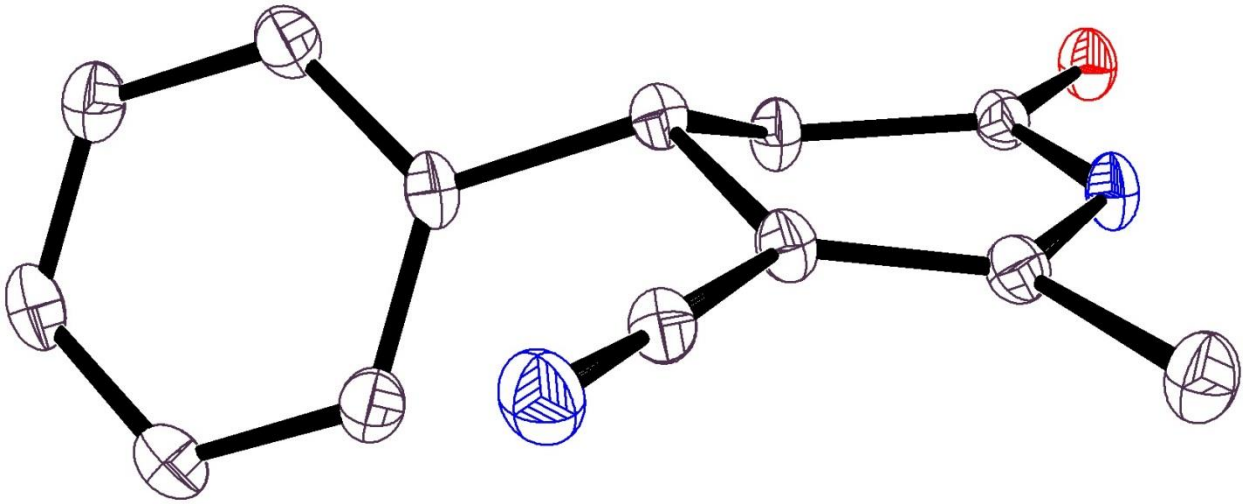


***N*-(2,6-Dimethylpyrimidin-4-yl)acetamide.** **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (brs, 1H), 7.80 (s, 1H), 2.54 (s, 3H), 2.18 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 169.3, 169.0, 167.0, 156.9, 105.9, 25.6, 24.8, 24.4; **LRMS (ESI)** *m/z* calcd for $C_8H_{11}N_3O$ $[M+H]^+$ 165.09, found 165.02.

References

1) B. Wanner, J. Mahatthananchai and J. W. Bode, *Org. Lett.*, **2011**, *13*, 5378.
2) S. K. D. Chowdhury, M. Sarkar, S. R. Chowdhury and K. K. Mahalanabis, *Synth. Commun.*, **1996**, *26*, 4233
3) S. K. D. Chowdhury, M. Sarkar, A. Chatterjee and K. K. Mahalanabis, *Ind. J. Chem. Sec B*, **2003**, *42B*, 2563.

Crystal structure of 1 with 50% ellipsoidal probability



Packing diagram of 1

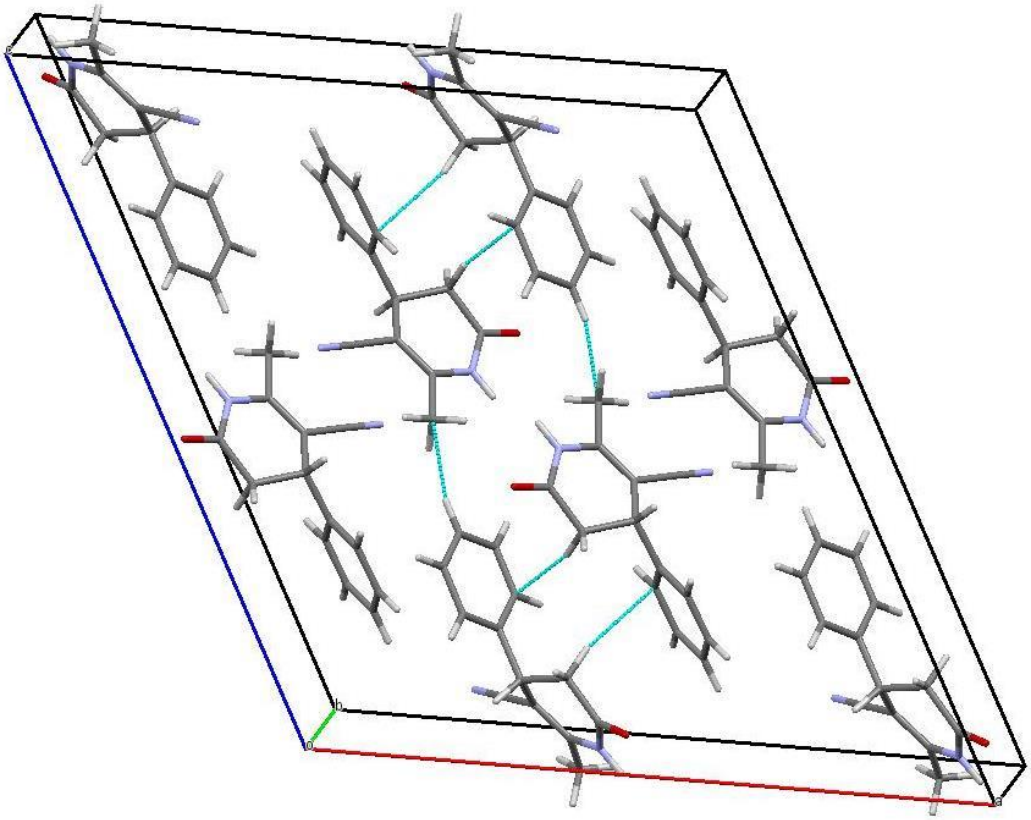


Table 1.Crystal data and structure refinement for 1

Identification code	**AY_237**	
Empirical formula	C_{13} H_{12} N_2 O	
Formula weight	212.25	
Temperature	106(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 18.9282(17) Å	α= 90°.
	b = 6.0959(5) Å	β= 116.768(5)°.
	c = 20.6755(19) Å	γ = 90°.
Volume	2130.0(3) $Å^3$	
Z	8	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	896	
Theta range for data collection	3.553 to 30.564°.	
Index ranges	-26<=h<=26, -8<=k<=8, -13<=l<=29	
Reflections collected	6179	
Independent reflections	3261 [R(int) = 0.0245]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3261 / 0 / 146	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1289	
R indices (all data)	R1 = 0.0592, wR2 = 0.1358	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.688 and -0.270 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	10035(1)	3132(1)	718(1)	20(1)
N(1)	9334(1)	6245(2)	292(1)	17(1)
N(2)	7527(1)	10751(2)	734(1)	22(1)
C(1)	8835(1)	7896(2)	304(1)	15(1)
C(2)	8518(1)	7794(2)	773(1)	16(1)
C(3)	8623(1)	5780(2)	1243(1)	17(1)
C(4)	8591(1)	6260(2)	1951(1)	18(1)
C(5)	8253(1)	4714(2)	2218(1)	21(1)
C(6)	8241(1)	5038(2)	2877(1)	24(1)
C(7)	8571(1)	6912(2)	3281(1)	24(1)
C(8)	8668(1)	9612(2)	-259(1)	20(1)
C(9)	8912(1)	8490(2)	3022(1)	23(1)
C(10)	8921(1)	8156(2)	2356(1)	21(1)
C(11)	9406(1)	4642(2)	1399(1)	18(1)
C(12)	9608(1)	4561(2)	774(1)	16(1)
C(13)	7973(1)	9448(2)	746(1)	16(1)

Table 3. Selected bond lengths [Å] for 1

O1—C12	1.2285 (13)	C5—H9	0.95
N1—C12	1.3601 (15)	C6—C7	1.3863 (19)
N1—C1	1.3886 (14)	C6—H8	0.95
N1—H1	0.88	C7—C9	1.3930 (19)
N2—C13	1.1514 (15)	C7—H2	0.95
C1—C2	1.3510 (15)	C8—H3	0.98

C1—C8	1.4890 (16)	C8—H5	0.98
C2—C13	1.4265 (15)	C8—H4	0.98
C2—C3	1.5225 (16)	C9—C10	1.3992 (17)
C3—C4	1.5196 (15)	C9—H7	0.95
C3—C11	1.5333 (15)	C10—H6	0.95
C3—H10	1	C11—C12	1.5042 (15)
C4—C5	1.3861 (17)	C11—H11	0.99
C4—C10	1.3996 (17)	C11—H12	0.99

Table 4. Selected bond angles [°] for 1

C12—N1—C1	124.92 (9)	C6—C7—H2	120.1
C12—N1—H1	117.5	C9—C7—H2	120.1
C1—N1—H1	117.5	C1—C8—H3	109.5
C2—C1—N1	120.29 (10)	C1—C8—H5	109.5
C2—C1—C8	125.91 (10)	H3—C8—H5	109.5
N1—C1—C8	113.71 (9)	C1—C8—H4	109.5
C1—C2—C13	119.14 (10)	H3—C8—H4	109.5
C1—C2—C3	121.52 (10)	H5—C8—H4	109.5
C13—C2—C3	118.60 (9)	C7—C9—C10	119.43 (12)
C4—C3—C2	114.15 (9)	C7—C9—H7	120.3
C4—C3—C11	109.79 (9)	C10—C9—H7	120.3
C2—C3—C11	109.55 (9)	C9—C10—C4	120.63 (11)
C4—C3—H10	107.7	C9—C10—H6	119.7

C2—C3—H10	107.7	C4—C10—H6	119.7
C11—C3—H10	107.7	C12—C11—C3	115.46 (9)
C5—C4—C10	118.97 (11)	C12—C11—H11	108.4
C5—C4—C3	118.59 (11)	C3—C11—H11	108.4
C10—C4—C3	122.38 (10)	C12—C11—H12	108.4
C4—C5—C6	120.63 (12)	C3—C11—H12	108.4
C4—C5—H9	119.7	H11—C11—H12	107.5
C6—C5—H9	119.7	O1—C12—N1	121.04 (10)
C7—C6—C5	120.46 (12)	O1—C12—C11	122.50 (10)
C7—C6—H8	119.8	N1—C12—C11	116.33 (9)
C5—C6—H8	119.8	N2—C13—C2	178.34 (12)
C6—C7—C9	119.88 (11)		

Table 5. Anisotropic displacement parameters ($Å^2$x 10^3) for 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	22(1)	20(1)	21(1)	1(1)	13(1)	6(1)
N(1)	19(1)	20(1)	16(1)	2(1)	11(1)	5(1)
N(2)	24(1)	20(1)	24(1)	-1(1)	13(1)	4(1)
C(1)	15(1)	16(1)	15(1)	0(1)	7(1)	1(1)
C(2)	17(1)	17(1)	15(1)	0(1)	8(1)	3(1)
C(3)	18(1)	18(1)	17(1)	-1(1)	10(1)	0(1)
C(4)	19(1)	21(1)	16(1)	1(1)	11(1)	5(1)
C(5)	25(1)	22(1)	20(1)	-2(1)	11(1)	1(1)
C(6)	26(1)	27(1)	23(1)	2(1)	15(1)	1(1)
C(7)	27(1)	29(1)	17(1)	0(1)	13(1)	6(1)

C(8)	23(1)	20(1)	22(1)	5(1)	13(1)	5(1)
C(9)	25(1)	23(1)	20(1)	-4(1)	9(1)	2(1)
C(10)	22(1)	22(1)	22(1)	2(1)	12(1)	1(1)
C(11)	22(1)	19(1)	18(1)	3(1)	13(1)	5(1)
C(12)	15(1)	17(1)	15(1)	-2(1)	7(1)	0(1)
C(13)	18(1)	17(1)	16(1)	-1(1)	9(1)	0(1)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1

	x	y	z	U(eq)
H(1)	9485	6291	-53	20
H(10)	8185	4735	959	20
H(9)	8027	3421	1946	26
H(8)	8006	3967	3053	29
H(2)	8564	7119	3733	28
H(3)	8344	10773	-199	30
H(5)	8382	8955	-741	30
H(4)	9167	10237	-208	30
H(7)	9135	9782	3294	28
H(6)	9154	9227	2178	25
H(11)	9839	5409	1807	22
H(12)	9386	3121	1557	22

Table 7. Selected torsion angles [°] for 1

C12—N1—C1—C2	−6.80 (17)	C10—C4—C5—C6	−0.06 (18)
C12—N1—C1—C8	176.32 (11)	C3—C4—C5—C6	177.18 (11)
N1—C1—C2—C13	−176.59 (10)	C4—C5—C6—C7	−0.17 (19)
C8—C1—C2—C13	−0.11 (18)	C5—C6—C7—C9	0.39 (19)
N1—C1—C2—C3	−6.61 (16)	C6—C7—C9—C10	−0.38 (19)

C8—C1—C2—C3	169.87 (11)	C7—C9—C10—C4	0.14 (18)
C1—C2—C3—C4	152.64 (10)	C5—C4—C10—C9	0.07 (18)
C13—C2—C3—C4	−37.33 (14)	C3—C4—C10—C9	−177.06 (11)
C1—C2—C3—C11	29.06 (14)	C4—C3—C11—C12	−165.74 (10)
C13—C2—C3—C11	−160.91 (10)	C2—C3—C11—C12	−39.64 (13)
C2—C3—C4—C5	144.94 (11)	C1—N1—C12—O1	178.30 (10)
C11—C3—C4—C5	−91.62 (12)	C1—N1—C12—C11	−5.75 (16)
C2—C3—C4—C10	−37.92 (15)	C3—C11—C12—O1	−153.96 (11)
C11—C3—C4—C10	85.53 (13)	C3—C11—C12—N1	30.15 (14)

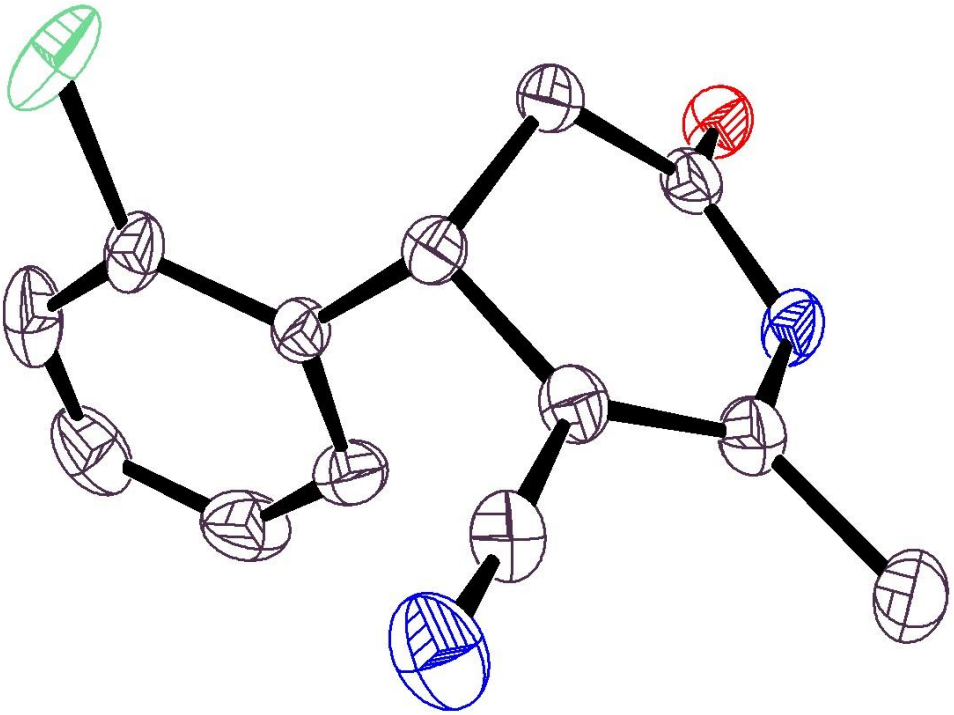
Table 8. Hydrogen bonds for 1 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(8)-H(4)...O(1)#1	0.98	2.58	3.2670(16)	127.5
C(8)-H(3)...N(2)#2	0.98	2.61	3.4738(16)	147.8
N(1)-H(1)...O(1)#3	0.88	1.99	2.8588(12)	168.7
C(8)-H(4)...O(1)#1	0.98	2.58	3.2670(16)	127.5
C(8)-H(3)...N(2)#2	0.98	2.61	3.4738(16)	147.8
N(1)-H(1)...O(1)#3	0.88	1.99	2.8588(12)	168.7
N(1)-H(1)...O(1)#3	0.88	1.99	2.8588(12)	168.7
C(8)-H(3)...N(2)#2	0.98	2.61	3.4738(16)	147.8
C(8)-H(4)...O(1)#1	0.98	2.58	3.2670(16)	127.5
N(1)-H(1)...O(1)#3	0.88	1.99	2.8588(12)	168.7
C(8)-H(3)...N(2)#2	0.98	2.61	3.4738(16)	147.8
C(8)-H(4)...O(1)#1	0.98	2.58	3.2670(16)	127.5
N(1)-H(1)...O(1)#3	0.88	1.99	2.8588(12)	168.7
C(8)-H(3)...N(2)#2	0.98	2.61	3.4738(16)	147.8
C(8)-H(4)...O(1)#1	0.98	2.58	3.2670(16)	127.5

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 -x+3/2,-y+5/2,-z #3 -x+2,-y+1,-z

Crystal structure of 5 with 50% ellipsoidal probability



Packing diagram of 5

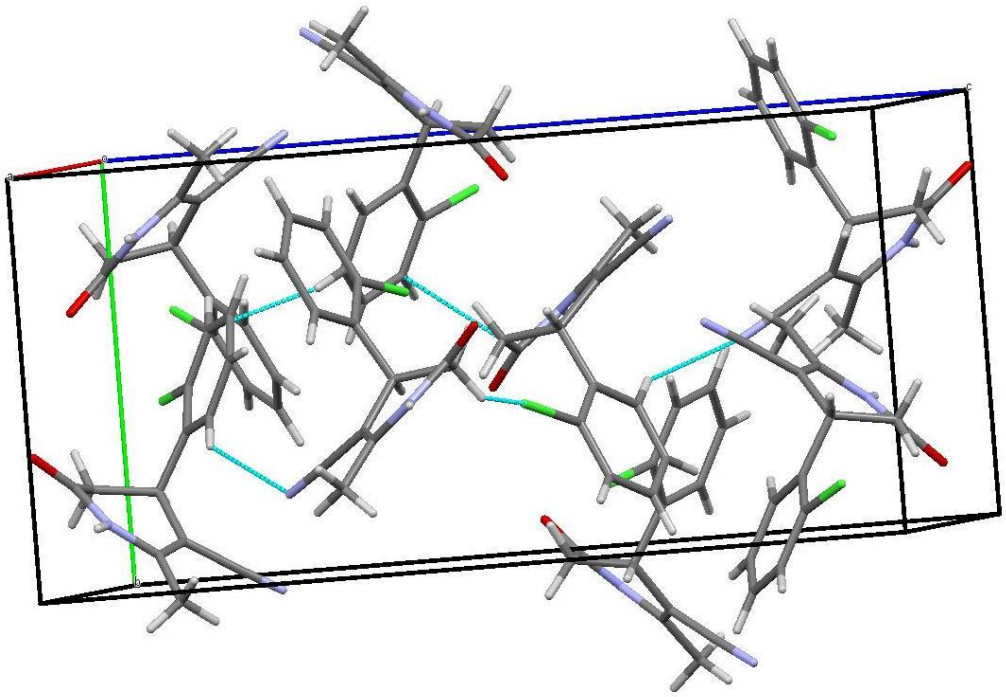


Table 9. Crystal data and structure refinement for 5

Identification code	AY_183_1_B	
Empirical formula	$4(C_{13}\ H_{11}\ Cl\ N_2\ O)$	
Formula weight	4(246.68)	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P\ 2_1$	
Unit cell dimensions	a = 13.4732(5) Å	α= 90°.
	b = 9.5123(4) Å	β= 109.801(2)°.
	c = 19.7950(8) Å	γ = 90°.
Volume	2386.95(17) $Å^3$	
Z	2	
Density (calculated)	1.373 Mg/m^3	
Absorption coefficient	0.304 mm^{-1}	
F(000)	1024	
Theta range for data collection	1.093 to 30.600°.	
Index ranges	-19<=h<=18, -13<=k<=13, -28<=l<=28	
Reflections collected	51691	
Independent reflections	14351 [R(int) = 0.0725]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14351 / 1 / 617	
Goodness-of-fit on F^2	0.793	
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.0813	
R indices (all data)	R1 = 0.0734, wR2 = 0.0935	
Absolute structure parameter	0.05(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.247 and -0.357 $e.Å^{-3}$	

Table 10. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for 5. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(4)	12269(1)	8689(1)	9555(1)	40(1)
Cl(3)	7719(1)	6307(1)	5485(1)	49(1)
Cl(2)	7247(1)	3478(1)	4160(1)	53(1)
O(2)	11558(2)	4292(2)	5404(1)	30(1)
O(3)	3409(2)	5970(2)	4670(1)	30(1)
N(5)	3752(2)	4304(3)	5533(1)	26(1)
Cl(1)	3122(1)	5665(1)	829(1)	48(1)
N(3)	11245(2)	5985(2)	4557(1)	24(1)
O(1)	6168(2)	6679(2)	-371(1)	30(1)
O(4)	8715(1)	8468(2)	10354(1)	29(1)
N(1)	6673(2)	8359(3)	485(1)	24(1)
C(37)	6724(3)	8716(4)	6767(2)	44(1)
C(26)	8162(2)	3095(3)	3738(2)	36(1)
C(21)	8928(2)	4080(3)	3739(2)	27(1)
C(20)	9066(2)	5451(3)	4152(1)	24(1)
C(16)	9519(2)	6602(3)	3817(1)	23(1)
C(17)	10567(2)	6819(3)	4020(1)	23(1)
C(18)	11102(2)	7857(3)	3697(2)	31(1)
C(14)	10934(2)	5102(3)	4986(1)	23(1)
C(15)	9799(2)	5239(3)	4933(2)	25(1)
C(27)	4023(2)	5120(3)	5056(1)	24(1)
C(31)	4462(2)	3469(3)	6058(2)	26(1)
C(30)	5506(2)	3618(3)	6186(1)	25(1)
C(33)	6244(2)	2854(3)	6757(2)	28(1)
N(6)	6871(2)	2289(3)	7218(2)	41(1)
C(29)	5934(2)	4637(3)	5764(1)	23(1)
C(34)	6242(2)	6042(3)	6136(1)	23(1)

C(28)	5101(2)	4832(3)	5016(2)	27(1)
C(32)	3974(2)	2518(3)	6456(2)	34(1)
C(10)	6544(3)	4744(4)	2017(2)	40(1)
C(9)	6256(2)	6045(3)	1693(2)	30(1)
C(8)	5205(2)	6370(3)	1305(1)	25(1)
C(3)	4907(2)	7743(3)	897(1)	24(1)
C(4)	5671(2)	8922(3)	1228(1)	23(1)
N(4)	8216(2)	7965(3)	2766(2)	38(1)
C(6)	7333(2)	10268(3)	1330(2)	28(1)
C(11)	5786(3)	3745(4)	1969(2)	45(1)
C(13)	4459(2)	5338(3)	1281(2)	31(1)
N(7)	8213(2)	6810(3)	9484(1)	26(1)
C(44)	8413(2)	5965(3)	8968(1)	25(1)
C(43)	9337(2)	6082(3)	8855(1)	23(1)
C(42)	10182(2)	7104(3)	9271(1)	21(1)
C(47)	10146(2)	8485(3)	8877(1)	22(1)
C(48)	9209(2)	9057(3)	8426(2)	30(1)
C(49)	9171(3)	10355(3)	8101(2)	38(1)
C(50)	10089(3)	11103(4)	8206(2)	38(1)
C(51)	11039(2)	10567(3)	8643(2)	34(1)
C(45)	7521(2)	5032(3)	8555(2)	36(1)
C(40)	8955(2)	7630(3)	9967(1)	24(1)
C(41)	10076(2)	7349(3)	10010(2)	25(1)
C(46)	9529(2)	5291(3)	8297(2)	27(1)
N(8)	9726(2)	4704(3)	7852(2)	40(1)
N(2)	5414(2)	10260(3)	2286(2)	43(1)
C(5)	6504(2)	9185(3)	1019(1)	23(1)
C(1)	5950(2)	7458(3)	55(1)	24(1)
C(2)	4870(2)	7551(3)	114(2)	27(1)
C(7)	5537(2)	9684(3)	1811(2)	28(1)
C(12)	4742(3)	4036(4)	1601(2)	43(1)
C(35)	5702(2)	6605(3)	6561(2)	32(1)

C(38)	7286(2)	8189(4)	6354(2)	41(1)
C(39)	7030(2)	6882(3)	6035(2)	30(1)
C(36)	5932(3)	7918(4)	6864(2)	42(1)
C(52)	11057(2)	9286(3)	8978(2)	25(1)
C(22)	9612(2)	3712(3)	3374(2)	34(1)
C(24)	8825(3)	1451(4)	3074(2)	54(1)
C(23)	9572(3)	2406(4)	3053(2)	48(1)
C(25)	8101(3)	1792(4)	3402(2)	51(1)
C(19)	8812(2)	7384(3)	3236(2)	26(1)

Table 11. Selected bond lengths [Å] for 5

Cl4—C52	1.740 (3)	C8—C3	1.517 (4)
Cl3—C39	1.741 (3)	C3—C4	1.514 (4)
Cl2—C26	1.746 (4)	C3—C2	1.543 (4)
O2—C14	1.230 (3)	C3—H3A	0.98
O3—C27	1.222 (3)	C4—C5	1.345 (4)
N5—C27	1.363 (4)	C4—C7	1.426 (4)
N5—C31	1.398 (3)	N4—C19	1.145 (4)
N5—H5	0.86	C6—C5	1.491 (4)
Cl1—C13	1.747 (3)	C6—H6A	0.96
N3—C14	1.359 (3)	C6—H6B	0.96
N3—C17	1.392 (3)	C6—H6C	0.96
N3—H3	0.86	C11—C12	1.376 (5)
O1—C1	1.230 (3)	C11—H11	0.93
O4—C40	1.223 (3)	C13—C12	1.384 (5)
N1—C1	1.359 (3)	N7—C40	1.369 (4)

N1—C5	1.396 (3)	N7—C44	1.396 (3)
N1—H1	0.86	N7—H7	0.86
C37—C36	1.375 (5)	C44—C43	1.342 (4)
C37—C38	1.383 (5)	C44—C45	1.494 (4)
C37—H37	0.93	C43—C46	1.431 (4)
C26—C21	1.394 (4)	C43—C42	1.512 (4)
C26—C25	1.396 (5)	C42—C47	1.521 (4)
C21—C22	1.394 (4)	C42—C41	1.535 (4)
C21—C20	1.516 (4)	C42—H42	0.98
C20—C16	1.513 (4)	C47—C48	1.387 (4)
C20—C15	1.540 (4)	C47—C52	1.400 (4)
C20—H20	0.98	C48—C49	1.386 (4)
C16—C17	1.346 (4)	C48—H48	0.93
C16—C19	1.428 (4)	C49—C50	1.379 (5)
C17—C18	1.489 (4)	C49—H49	0.93
C18—H18A	0.96	C50—C51	1.378 (5)
C18—H18B	0.96	C50—H50	0.93
C18—H18C	0.96	C51—C52	1.384 (4)
C14—C15	1.502 (4)	C51—H51	0.93
C15—H15A	0.97	C45—H45A	0.96
C15—H15B	0.97	C45—H45B	0.96
C27—C28	1.507 (4)	C45—H45C	0.96

C31—C30	1.349 (4)	C40—C41	1.507 (4)
C31—C32	1.490 (4)	C41—H41A	0.97
C30—C33	1.426 (4)	C41—H41B	0.97
C30—C29	1.515 (4)	C46—N8	1.147 (4)
C33—N6	1.147 (4)	N2—C7	1.148 (4)
C29—C34	1.515 (4)	C1—C2	1.502 (4)
C29—C28	1.536 (4)	C2—H2A	0.97
C29—H29	0.98	C2—H2B	0.97
C34—C35	1.392 (4)	C12—H12	0.93
C34—C39	1.395 (4)	C35—C36	1.375 (5)
C28—H28A	0.97	C35—H35	0.93
C28—H28B	0.97	C38—C39	1.384 (4)
C32—H32A	0.96	C38—H38	0.93
C32—H32B	0.96	C36—H36	0.93
C32—H32C	0.96	C22—C23	1.388 (4)
C10—C11	1.374 (5)	C22—H22	0.93
C10—C9	1.387 (4)	C24—C23	1.367 (6)
C10—H10	0.93	C24—C25	1.381 (6)
C9—C8	1.397 (4)	C24—H24	0.93
C9—H9	0.93	C23—H23	0.93
C8—C13	1.394 (4)	C25—H25	0.93

Table 12. Selected bond angles [°] for 5

C27—N5—C31	124.2 (2)	H6A—C6—H6C	109.5

C27—N5—H5	117.9	H6B—C6—H6C	109.5
C31—N5—H5	117.9	C10—C11—C12	120.0 (3)
C14—N3—C17	124.6 (2)	C10—C11—H11	120
C14—N3—H3	117.7	C12—C11—H11	120
C17—N3—H3	117.7	C12—C13—C8	122.1 (3)
C1—N1—C5	124.3 (2)	C12—C13—Cl1	118.0 (2)
C1—N1—H1	117.8	C8—C13—Cl1	119.9 (3)
C5—N1—H1	117.8	C40—N7—C44	124.2 (2)
C36—C37—C38	119.3 (3)	C40—N7—H7	117.9
C36—C37—H37	120.4	C44—N7—H7	117.9
C38—C37—H37	120.4	C43—C44—N7	119.6 (2)
C21—C26—C25	121.5 (3)	C43—C44—C45	125.3 (3)
C21—C26—Cl2	120.1 (3)	N7—C44—C45	115.0 (2)
C25—C26—Cl2	118.4 (3)	C44—C43—C46	120.3 (3)
C26—C21—C22	116.7 (3)	C44—C43—C42	122.2 (2)
C26—C21—C20	122.3 (3)	C46—C43—C42	117.3 (2)
C22—C21—C20	120.9 (3)	C43—C42—C47	112.9 (2)
C16—C20—C21	112.3 (2)	C43—C42—C41	108.7 (2)
C16—C20—C15	108.5 (2)	C47—C42—C41	111.2 (2)
C21—C20—C15	110.4 (2)	C43—C42—H42	108
C16—C20—H20	108.5	C47—C42—H42	108
C21—C20—H20	108.5	C41—C42—H42	108

C15—C20—H20	108.5	C48—C47—C52	116.2 (3)
C17—C16—C19	120.4 (3)	C48—C47—C42	122.2 (2)
C17—C16—C20	121.3 (2)	C52—C47—C42	121.5 (2)
C19—C16—C20	118.1 (2)	C49—C48—C47	122.0 (3)
C16—C17—N3	119.4 (2)	C49—C48—H48	119
C16—C17—C18	125.8 (3)	C47—C48—H48	119
N3—C17—C18	114.7 (2)	C50—C49—C48	120.0 (3)
C17—C18—H18A	109.5	C50—C49—H49	120
C17—C18—H18B	109.5	C48—C49—H49	120
H18A—C18—H18B	109.5	C51—C50—C49	119.9 (3)
C17—C18—H18C	109.5	C51—C50—H50	120
H18A—C18—H18C	109.5	C49—C50—H50	120
H18B—C18—H18C	109.5	C50—C51—C52	119.2 (3)
O2—C14—N3	121.4 (2)	C50—C51—H51	120.4
O2—C14—C15	123.3 (3)	C52—C51—H51	120.4
N3—C14—C15	115.2 (2)	C44—C45—H45A	109.5
C14—C15—C20	111.9 (2)	C44—C45—H45B	109.5
C14—C15—H15A	109.2	H45A—C45—H45B	109.5
C20—C15—H15A	109.2	C44—C45—H45C	109.5
C14—C15—H15B	109.2	H45A—C45—H45C	109.5
C20—C15—H15B	109.2	H45B—C45—H45C	109.5
H15A—C15—H15B	107.9	O4—C40—N7	121.6 (2)

O3—C27—N5	121.8 (2)	O4—C40—C41	123.5 (3)
O3—C27—C28	123.2 (3)	N7—C40—C41	114.8 (2)
N5—C27—C28	114.9 (2)	C40—C41—C42	112.8 (2)
C30—C31—N5	119.1 (2)	C40—C41—H41A	109
C30—C31—C32	125.7 (3)	C42—C41—H41A	109
N5—C31—C32	115.1 (2)	C40—C41—H41B	109
C31—C30—C33	119.9 (3)	C42—C41—H41B	109
C31—C30—C29	122.1 (2)	H41A—C41—H41B	107.8
C33—C30—C29	118.0 (2)	N8—C46—C43	176.4 (3)
N6—C33—C30	176.8 (3)	C4—C5—N1	119.7 (2)
C30—C29—C34	112.9 (2)	C4—C5—C6	126.1 (3)
C30—C29—C28	108.6 (2)	N1—C5—C6	114.2 (2)
C34—C29—C28	110.6 (2)	O1—C1—N1	121.6 (2)
C30—C29—H29	108.2	O1—C1—C2	123.4 (3)
C34—C29—H29	108.2	N1—C1—C2	114.9 (2)
C28—C29—H29	108.2	C1—C2—C3	112.5 (2)
C35—C34—C39	116.5 (3)	C1—C2—H2A	109.1
C35—C34—C29	121.3 (2)	C3—C2—H2A	109.1
C39—C34—C29	122.1 (2)	C1—C2—H2B	109.1
C27—C28—C29	112.0 (2)	C3—C2—H2B	109.1
C27—C28—H28A	109.2	H2A—C2—H2B	107.8
C29—C28—H28A	109.2	N2—C7—C4	177.8 (3)

C27—C28—H28B	109.2	C11—C12—C13	119.7 (3)
C29—C28—H28B	109.2	C11—C12—H12	120.1
H28A—C28—H28B	107.9	C13—C12—H12	120.1
C31—C32—H32A	109.5	C36—C35—C34	121.7 (3)
C31—C32—H32B	109.5	C36—C35—H35	119.2
H32A—C32—H32B	109.5	C34—C35—H35	119.2
C31—C32—H32C	109.5	C37—C38—C39	119.5 (3)
H32A—C32—H32C	109.5	C37—C38—H38	120.2
H32B—C32—H32C	109.5	C39—C38—H38	120.2
C11—C10—C9	120.0 (3)	C38—C39—C34	122.2 (3)
C11—C10—H10	120	C38—C39—Cl3	117.6 (2)
C9—C10—H10	120	C34—C39—Cl3	120.2 (2)
C10—C9—C8	121.6 (3)	C37—C36—C35	120.8 (3)
C10—C9—H9	119.2	C37—C36—H36	119.6
C8—C9—H9	119.2	C35—C36—H36	119.6
C13—C8—C9	116.6 (3)	C51—C52—C47	122.6 (3)
C13—C8—C3	122.0 (3)	C51—C52—Cl4	117.5 (2)
C9—C8—C3	121.3 (3)	C47—C52—Cl4	119.9 (2)
C4—C3—C8	112.9 (2)	C23—C22—C21	122.2 (3)
C4—C3—C2	108.0 (2)	C23—C22—H22	118.9
C8—C3—C2	110.2 (2)	C21—C22—H22	118.9
C4—C3—H3A	108.6	C23—C24—C25	120.2 (3)

C8—C3—H3A	108.6	C23—C24—H24	119.9
C2—C3—H3A	108.6	C25—C24—H24	119.9
C5—C4—C7	120.2 (3)	C24—C23—C22	119.7 (4)
C5—C4—C3	121.4 (2)	C24—C23—H23	120.1
C7—C4—C3	118.3 (2)	C22—C23—H23	120.1
C5—C6—H6A	109.5	C24—C25—C26	119.7 (3)
C5—C6—H6B	109.5	C24—C25—H25	120.2
H6A—C6—H6B	109.5	C26—C25—H25	120.2
C5—C6—H6C	109.5	N4—C19—C16	177.2 (3)

Table 13. Anisotropic displacement parameters ($Å^2$x 103) for 5. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h2a*2U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cl(4)	17(1)	39(1)	58(1)	-7(1)	4(1)	0(1)
Cl(3)	38(1)	49(1)	76(1)	19(1)	40(1)	10(1)
Cl(2)	36(1)	64(1)	58(1)	16(1)	13(1)	-20(1)
O(2)	23(1)	35(1)	29(1)	6(1)	7(1)	5(1)
O(3)	21(1)	36(1)	31(1)	6(1)	7(1)	4(1)
N(5)	15(1)	33(1)	32(1)	4(1)	7(1)	-1(1)
Cl(1)	30(1)	67(1)	47(1)	-9(1)	14(1)	-23(1)
N(3)	14(1)	30(1)	27(1)	4(1)	5(1)	1(1)
O(1)	26(1)	38(1)	27(1)	-6(1)	11(1)	-1(1)
O(4)	26(1)	33(1)	29(1)	-7(1)	12(1)	-1(1)
N(1)	18(1)	31(1)	27(1)	-2(1)	11(1)	-2(1)
C(37)	50(2)	30(2)	40(2)	-4(2)	-2(2)	-5(2)
C(26)	33(2)	33(2)	30(2)	9(1)	-4(1)	-9(1)
C(21)	24(1)	23(1)	27(1)	3(1)	0(1)	-1(1)

C(20)	16(1)	27(1)	28(1)	0(1)	6(1)	0(1)
C(16)	20(1)	22(1)	25(1)	-3(1)	6(1)	1(1)
C(17)	21(1)	23(1)	24(1)	-2(1)	7(1)	0(1)
C(18)	27(2)	34(2)	30(2)	3(1)	7(1)	-4(1)
C(14)	22(1)	26(2)	21(1)	-3(1)	7(1)	0(1)
C(15)	21(1)	30(2)	26(1)	-1(1)	10(1)	0(1)
C(27)	19(1)	29(2)	23(1)	-3(1)	4(1)	-1(1)
C(31)	22(1)	25(1)	28(1)	1(1)	6(1)	-1(1)
C(30)	22(1)	24(1)	27(1)	-2(1)	6(1)	1(1)
C(33)	24(1)	26(2)	34(2)	-1(1)	8(1)	-1(1)
N(6)	35(2)	36(2)	44(2)	2(1)	2(1)	5(1)
C(29)	16(1)	28(1)	25(1)	-2(1)	8(1)	4(1)
C(34)	18(1)	28(2)	21(1)	5(1)	4(1)	0(1)
C(28)	21(1)	34(2)	25(1)	-2(1)	8(1)	0(1)
C(32)	27(2)	35(2)	38(2)	7(1)	8(1)	-7(1)
C(10)	46(2)	35(2)	37(2)	8(2)	9(2)	4(2)
C(9)	29(2)	30(2)	32(2)	2(1)	9(1)	-2(1)
C(8)	27(1)	28(2)	24(1)	-6(1)	13(1)	-6(1)
C(3)	16(1)	31(2)	26(1)	-3(1)	8(1)	0(1)
C(4)	21(1)	25(1)	25(1)	2(1)	9(1)	2(1)
N(4)	30(1)	33(2)	42(2)	7(1)	0(1)	-2(1)
C(6)	27(1)	29(2)	30(2)	-1(1)	11(1)	-4(1)
C(11)	69(3)	28(2)	37(2)	5(2)	19(2)	-6(2)
C(13)	34(2)	38(2)	24(1)	-6(1)	12(1)	-13(1)
N(7)	20(1)	32(1)	30(1)	-7(1)	11(1)	-4(1)
C(44)	25(1)	26(2)	25(1)	-1(1)	10(1)	-1(1)
C(43)	23(1)	22(1)	24(1)	0(1)	9(1)	0(1)
C(42)	16(1)	23(1)	25(1)	0(1)	7(1)	2(1)
C(47)	21(1)	23(1)	23(1)	-3(1)	9(1)	-1(1)
C(48)	22(1)	30(2)	31(2)	3(1)	2(1)	-1(1)
C(49)	38(2)	29(2)	37(2)	7(1)	2(1)	4(1)
C(50)	54(2)	26(2)	34(2)	4(1)	16(2)	-3(2)

C(51)	38(2)	27(2)	41(2)	-5(1)	20(2)	-8(1)
C(45)	34(2)	40(2)	37(2)	-11(1)	14(1)	-13(1)
C(40)	22(1)	28(2)	23(1)	1(1)	9(1)	-1(1)
C(41)	20(1)	32(2)	22(1)	1(1)	5(1)	1(1)
C(46)	30(2)	24(2)	29(1)	0(1)	12(1)	-5(1)
N(8)	49(2)	37(2)	40(2)	-8(1)	24(1)	-5(1)
N(2)	53(2)	40(2)	47(2)	-10(1)	31(2)	-8(1)
C(5)	20(1)	24(1)	23(1)	1(1)	6(1)	2(1)
C(1)	20(1)	29(2)	21(1)	3(1)	5(1)	2(1)
C(2)	17(1)	35(2)	25(1)	1(1)	4(1)	0(1)
C(7)	27(2)	24(1)	36(2)	0(1)	15(1)	-2(1)
C(12)	63(2)	37(2)	32(2)	-9(1)	22(2)	-25(2)
C(35)	37(2)	35(2)	28(2)	-2(1)	16(1)	-4(1)
C(38)	27(2)	32(2)	55(2)	11(2)	1(2)	-8(1)
C(39)	17(1)	34(2)	36(2)	10(1)	7(1)	2(1)
C(36)	58(2)	37(2)	31(2)	-7(2)	17(2)	-2(2)
C(52)	20(1)	27(1)	30(1)	-5(1)	10(1)	-1(1)
C(22)	37(2)	26(2)	34(2)	-5(1)	7(1)	0(1)
C(24)	80(3)	27(2)	35(2)	-4(2)	-6(2)	2(2)
C(23)	61(2)	35(2)	40(2)	-10(2)	7(2)	5(2)
C(25)	61(2)	33(2)	37(2)	10(2)	-14(2)	-22(2)
C(19)	22(1)	24(1)	33(2)	-2(1)	8(1)	-3(1)

Table 14. Hydrogen coordinates (x 104) and isotropic displacement parameters ($Å^2$x 103) for 5

	x	y	z	U(eq)
H(5)	3103	4304	5509	32
H(3)	11909	6031	4621	29
H(1)	7274	8425	424	29
H(37)	6881	9600	6977	53

H(20)	8373	5756	4157	28
H(18A)	10582	8385	3332	47
H(18B)	11551	7371	3487	47
H(18C)	11519	8485	4063	47
H(15A)	9725	6032	5221	30
H(15B)	9587	4398	5126	30
H(29)	6563	4217	5704	27
H(28A)	5307	5609	4775	32
H(28B)	5072	3990	4733	32
H(32A)	4518	2076	6843	51
H(32B)	3565	1811	6136	51
H(32C)	3524	3055	6645	51
H(10)	7249	4549	2267	48
H(9)	6774	6716	1734	36
H(3A)	4203	8021	891	29
H(6A)	7149	10820	1676	42
H(6B)	7387	10868	954	42
H(6C)	7999	9813	1560	42
H(11)	5980	2872	2185	54
H(7)	7582	6816	9499	32
H(42)	10870	6666	9346	25
H(48)	8586	8554	8339	36
H(49)	8528	10722	7812	45
H(50)	10066	11968	7982	45
H(51)	11662	11061	8712	40
H(45A)	7724	4495	8213	55
H(45B)	6916	5597	8308	55
H(45C)	7350	4407	8880	55
H(41A)	10336	6528	10308	30
H(41B)	10512	8143	10239	30
H(2A)	4481	6700	-81	32
H(2B)	4495	8336	-172	32

H(12)	4228	3360	1567	51
H(35)	5171	6079	6642	38
H(38)	7832	8709	6290	50
H(36)	5548	8271	7138	50
H(22)	10111	4363	3345	41
H(24)	8805	568	2868	64
H(23)	10050	2183	2824	57
H(25)	7575	1156	3399	62

Table 15. Torsion angles [°] for 5

C25—C26—C21—C22	1.5 (4)	N7—C44—C43—C46	−175.9 (3)
Cl2—C26—C21—C22	−178.3 (2)	C45—C44—C43—C46	0.9 (4)
C25—C26—C21—C20	−174.9 (3)	N7—C44—C43—C42	0.1 (4)
Cl2—C26—C21—C20	5.3 (4)	C45—C44—C43—C42	176.9 (3)
C26—C21—C20—C16	−152.3 (3)	C44—C43—C42—C47	−95.9 (3)
C22—C21—C20—C16	31.5 (3)	C46—C43—C42—C47	80.2 (3)
C26—C21—C20—C15	86.5 (3)	C44—C43—C42—C41	27.9 (4)
C22—C21—C20—C15	−89.8 (3)	C46—C43—C42—C41	−155.9 (2)
C21—C20—C16—C17	−91.5 (3)	C43—C42—C47—C48	32.4 (4)
C15—C20—C16—C17	30.9 (3)	C41—C42—C47—C48	−90.1 (3)
C21—C20—C16—C19	83.6 (3)	C43—C42—C47—C52	−151.0 (2)
C15—C20—C16—C19	−154.1 (2)	C41—C42—C47—C52	86.5 (3)
C19—C16—C17—N3	−176.0 (2)	C52—C47—C48—C49	−0.8 (4)
C20—C16—C17—N3	−1.1 (4)	C42—C47—C48—C49	176.1 (3)
C19—C16—C17—C18	1.1 (4)	C47—C48—C49—C50	1.7 (5)
C20—C16—C17—C18	176.0 (3)	C48—C49—C50—C51	−1.0 (5)

C14—N3—C17—C16	−11.6 (4)	C49—C50—C51—C52	−0.7 (5)
C14—N3—C17—C18	171.0 (3)	C44—N7—C40—O4	171.7 (3)
C17—N3—C14—O2	172.8 (3)	C44—N7—C40—C41	−11.8 (4)
C17—N3—C14—C15	−9.6 (4)	O4—C40—C41—C42	−142.8 (3)
O2—C14—C15—C20	−142.0 (3)	N7—C40—C41—C42	40.8 (3)
N3—C14—C15—C20	40.4 (3)	C43—C42—C41—C40	−46.9 (3)
C16—C20—C15—C14	−48.9 (3)	C47—C42—C41—C40	78.0 (3)
C21—C20—C15—C14	74.6 (3)	C7—C4—C5—N1	175.0 (2)
C31—N5—C27—O3	−170.2 (3)	C3—C4—C5—N1	0.0 (4)
C31—N5—C27—C28	13.0 (4)	C7—C4—C5—C6	−1.9 (4)
C27—N5—C31—C30	10.6 (4)	C3—C4—C5—C6	−176.9 (3)
C27—N5—C31—C32	−172.1 (3)	C1—N1—C5—C4	13.0 (4)
N5—C31—C30—C33	175.2 (3)	C1—N1—C5—C6	−169.7 (3)
C32—C31—C30—C33	−1.8 (5)	C5—N1—C1—O1	−174.5 (3)
N5—C31—C30—C29	−1.6 (4)	C5—N1—C1—C2	8.6 (4)
C32—C31—C30—C29	−178.6 (3)	O1—C1—C2—C3	142.8 (3)
C31—C30—C29—C34	95.4 (3)	N1—C1—C2—C3	−40.4 (3)
C33—C30—C29—C34	−81.5 (3)	C4—C3—C2—C1	49.1 (3)
C31—C30—C29—C28	−27.6 (4)	C8—C3—C2—C1	−74.6 (3)
C33—C30—C29—C28	155.5 (3)	C10—C11—C12—C13	−0.1 (5)
C30—C29—C34—C35	−32.5 (3)	C8—C13—C12—C11	1.4 (5)
C28—C29—C34—C35	89.4 (3)	Cl1—C13—C12—C11	−179.3 (3)

C30—C29—C34—C39	151.9 (2)	C39—C34—C35—C36	0.0 (4)
C28—C29—C34—C39	−86.3 (3)	C29—C34—C35—C36	−175.8 (3)
O3—C27—C28—C29	140.2 (3)	C36—C37—C38—C39	1.1 (5)
N5—C27—C28—C29	−43.1 (3)	C37—C38—C39—C34	−2.3 (5)
C30—C29—C28—C27	48.2 (3)	C37—C38—C39—Cl3	176.9 (2)
C34—C29—C28—C27	−76.2 (3)	C35—C34—C39—C38	1.7 (4)
C11—C10—C9—C8	−0.7 (5)	C29—C34—C39—C38	177.5 (3)
C10—C9—C8—C13	2.0 (4)	C35—C34—C39—Cl3	−177.5 (2)
C10—C9—C8—C3	−174.4 (3)	C29—C34—C39—Cl3	−1.7 (4)
C13—C8—C3—C4	154.9 (3)	C38—C37—C36—C35	0.6 (5)
C9—C8—C3—C4	−28.9 (4)	C34—C35—C36—C37	−1.2 (5)
C13—C8—C3—C2	−84.3 (3)	C50—C51—C52—C47	1.7 (4)
C9—C8—C3—C2	91.9 (3)	C50—C51—C52—Cl4	−177.3 (2)
C8—C3—C4—C5	91.8 (3)	C48—C47—C52—C51	−1.0 (4)
C2—C3—C4—C5	−30.3 (3)	C42—C47—C52—C51	−177.8 (3)
C8—C3—C4—C7	−83.3 (3)	C48—C47—C52—Cl4	178.0 (2)
C2—C3—C4—C7	154.6 (2)	C42—C47—C52—Cl4	1.2 (4)
C9—C10—C11—C12	−0.2 (5)	C26—C21—C22—C23	−3.1 (4)
C9—C8—C13—C12	−2.3 (4)	C20—C21—C22—C23	173.4 (3)
C3—C8—C13—C12	174.1 (3)	C25—C24—C23—C22	1.3 (5)
C9—C8—C13—Cl1	178.4 (2)	C21—C22—C23—C24	1.7 (5)
C3—C8—C13—Cl1	−5.2 (4)	C23—C24—C25—C26	−2.7 (5)

C40—N7—C44—C43	−9.8 (4)	C21—C26—C25—C24	1.3 (5)
C40—N7—C44—C45	173.1 (3)	Cl2—C26—C25—C24	−178.9 (3)

Table 16. Hydrogen bonds for 5 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2B)...Cl(4)#1	0.97	2.88	3.472(3)	120.2
N(7)-H(7)...O(1)#2	0.86	2.01	2.868(3)	173.5
C(6)-H(6B)...Cl(4)#3	0.96	2.96	3.818(3)	149.9
C(15)-H(15A)...Cl(3)	0.97	2.93	3.486(3)	117.2
C(18)-H(18C)...Cl(3)#3	0.96	2.90	3.764(3)	149.6
C(18)-H(18A)...N(8)#3	0.96	2.57	3.379(4)	142.6
N(1)-H(1)...O(4)#4	0.86	1.99	2.852(3)	175.2
N(3)-H(3)...O(3)#5	0.86	1.99	2.847(3)	172.9
N(5)-H(5)...O(2)#6	0.86	2.02	2.880(3)	177.4
C(2)-H(2B)...Cl(4)#1	0.97	2.88	3.472(3)	120.2
N(7)-H(7)...O(1)#2	0.86	2.01	2.868(3)	173.5
C(6)-H(6B)...Cl(4)#3	0.96	2.96	3.818(3)	149.9
C(15)-H(15A)...Cl(3)	0.97	2.93	3.486(3)	117.2
C(18)-H(18C)...Cl(3)#3	0.96	2.90	3.764(3)	149.6
C(18)-H(18A)...N(8)#3	0.96	2.57	3.379(4)	142.6
N(1)-H(1)...O(4)#4	0.86	1.99	2.852(3)	175.2
N(3)-H(3)...O(3)#5	0.86	1.99	2.847(3)	172.9
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C(15)-H(15A)...Cl(3)	0.97	2.93	3.486(3)	117.2
N(5)-H(5)...O(2)#6	0.86	2.02	2.880(3)	177.4
N(3)-H(3)...O(3)#5	0.86	1.99	2.847(3)	172.9
N(1)-H(1)...O(4)#4	0.86	1.99	2.852(3)	175.2
C(18)-H(18A)...N(8)#3	0.96	2.57	3.379(4)	142.6

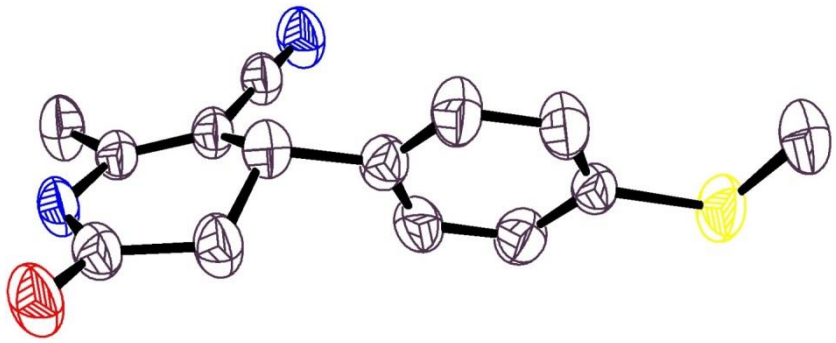
C(18)-H(18C)...Cl(3)#3	0.96	2.90	3.764(3)	149.6
C(15)-H(15A)...Cl(3)	0.97	2.93	3.486(3)	117.2
C(6)-H(6B)...Cl(4)#3	0.96	2.96	3.818(3)	149.9
N(7)-H(7)...O(1)#2	0.86	2.01	2.868(3)	173.5
C(2)-H(2B)...Cl(4)#1	0.97	2.88	3.472(3)	120.2

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z-1 #2 x,y,z+1 #3 -x+2,y+1/2,-z+1

#4 x,y,z-1 #5 x+1,y,z #6 x-1,y,z

Crystal structure of 16 with 50% ellipsoidal probability



Packing diagram of 16

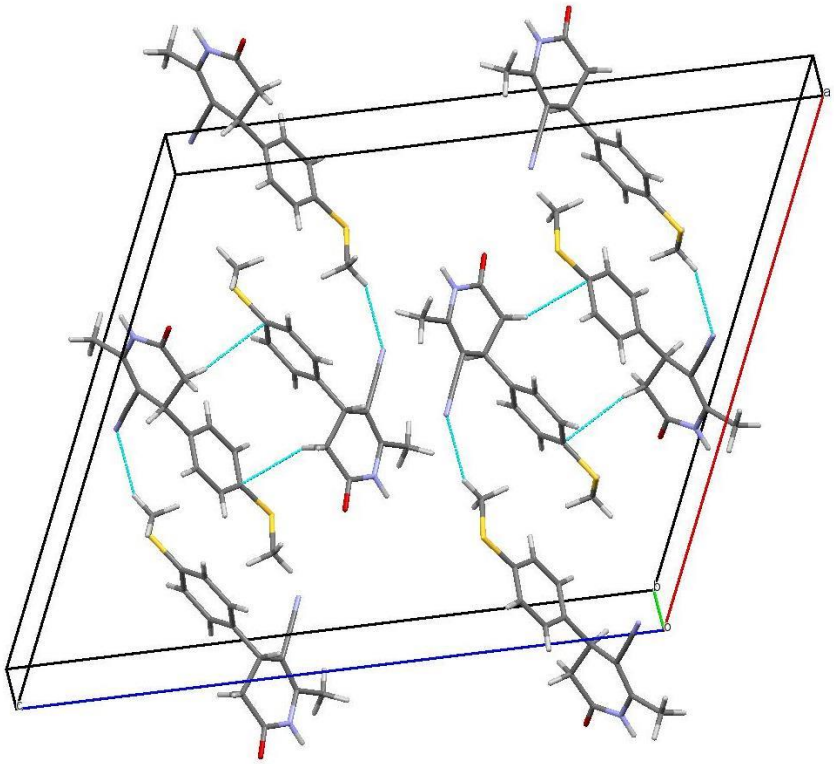


Table 17. Crystal data and structure refinement for 16

Identification code	AY_4_SMe	
Empirical formula	C_{14} H_{14} N_2 O S	
Formula weight	258.33	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 20.924(5) Å	α= 90°.
	b = 5.7267(11) Å	β= 112.393(7)°.
	c = 23.879(6) Å	γ = 90°.
Volume	2645.6(10) $Å^3$	
Z	8	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.234 mm^{-1}	
F(000)	1088	
Crystal size	0.10 x 0.08 x 0.05 mm^3	
Theta range for data collection	2.208 to 25.680°.	
Index ranges	-24<=h<=24, -6<=k<=6, -28<=l<=28	
Reflections collected	33413	
Independent reflections	2397 [R(int) = 0.0584]	
Completeness to theta = 25.242°	99.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2397 / 0 / 165	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1270	
R indices (all data)	R1 = 0.0753, wR2 = 0.1414	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.633 and -0.203 $e.Å^{-3}$	

Table 18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 16. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2745(1)	4653(2)	1649(1)	67(1)
O(002)	6967(1)	9133(4)	4344(1)	65(1)
N(1)	6635(1)	6079(4)	4758(1)	50(1)
N(2)	4552(1)	1916(4)	4448(1)	64(1)
C(5)	6146(1)	4461(4)	4775(1)	43(1)
C(7)	4980(1)	3092(4)	4425(1)	46(1)
C(4)	5490(1)	4625(4)	4380(1)	44(1)
C(11)	3452(1)	5323(5)	2320(1)	46(1)
C(8)	4608(1)	6180(5)	3385(1)	48(1)
C(1)	6522(1)	7715(5)	4322(1)	50(1)
C(10)	3506(1)	7303(5)	2660(1)	60(1)
C(13)	4571(1)	4203(5)	3048(1)	59(1)
C(2)	5834(1)	7589(5)	3802(1)	55(1)
C(12)	3990(1)	3737(5)	2516(1)	57(1)
C(3)	5242(1)	6708(5)	3959(1)	51(1)
C(9)	4073(1)	7708(5)	3185(1)	60(1)
C(6)	6410(1)	2733(5)	5269(1)	62(1)
C(14)	2197(2)	7137(7)	1533(2)	83(1)

Table 19. Selected bond lengths [Å] for 16

S1—C11	1.759 (2)	C10—C9	1.379 (4)
S1—C14	1.782 (4)	C10—H10	0.95
O002—C1	1.221 (3)	C13—C12	1.411 (4)
N1—C1	1.353 (3)	C13—H13	0.95
N1—C5	1.394 (3)	C2—C3	1.512 (3)

N1—H1	0.88	C2—H2A	0.99
N2—C7	1.139 (3)	C2—H2B	0.99
C5—C4	1.339 (3)	C12—H12	0.95
C5—C6	1.476 (4)	C3—H3	1
C7—C4	1.417 (3)	C9—H9	0.95
C4—C3	1.518 (4)	C6—H6A	0.98
C11—C10	1.374 (4)	C6—H6B	0.98
C11—C12	1.382 (4)	C6—H6C	0.98
C8—C9	1.357 (4)	C14—H14A	0.98
C8—C13	1.373 (4)	C14—H14B	0.98
C8—C3	1.531 (3)	C14—H14C	0.98
C1—C2	1.502 (3)		

Table 20. Selected bond angles [°] for 16

C11—S1—C14	103.69 (14)	C3—C2—H2A	108.4
C1—N1—C5	124.54 (19)	C1—C2—H2B	108.4
C1—N1—H1	117.7	C3—C2—H2B	108.4
C5—N1—H1	117.7	H2A—C2—H2B	107.5
C4—C5—N1	120.0 (2)	C11—C12—C13	119.5 (3)
C4—C5—C6	125.6 (2)	C11—C12—H12	120.3
N1—C5—C6	114.4 (2)	C13—C12—H12	120.3
N2—C7—C4	177.5 (3)	C2—C3—C4	108.7 (2)
C5—C4—C7	120.1 (2)	C2—C3—C8	110.8 (2)

C5—C4—C3	121.5 (2)	C4—C3—C8	113.5 (2)
C7—C4—C3	117.3 (2)	C2—C3—H3	107.9
C10—C11—C12	118.0 (2)	C4—C3—H3	107.9
C10—C11—S1	124.7 (2)	C8—C3—H3	107.9
C12—C11—S1	117.3 (2)	C8—C9—C10	121.3 (3)
C9—C8—C13	118.1 (2)	C8—C9—H9	119.3
C9—C8—C3	120.3 (2)	C10—C9—H9	119.3
C13—C8—C3	121.6 (2)	C5—C6—H6A	109.5
O002—C1—N1	121.3 (2)	C5—C6—H6B	109.5
O002—C1—C2	122.8 (2)	H6A—C6—H6B	109.5
N1—C1—C2	115.8 (2)	C5—C6—H6C	109.5
C11—C10—C9	121.7 (3)	H6A—C6—H6C	109.5
C11—C10—H10	119.2	H6B—C6—H6C	109.5
C9—C10—H10	119.2	S1—C14—H14A	109.5
C8—C13—C12	121.4 (2)	S1—C14—H14B	109.5
C8—C13—H13	119.3	H14A—C14—H14B	109.5
C12—C13—H13	119.3	S1—C14—H14C	109.5
C1—C2—C3	115.4 (2)	H14A—C14—H14C	109.5
C1—C2—H2A	108.4	H14B—C14—H14C	109.5

Table 21. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 16. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}

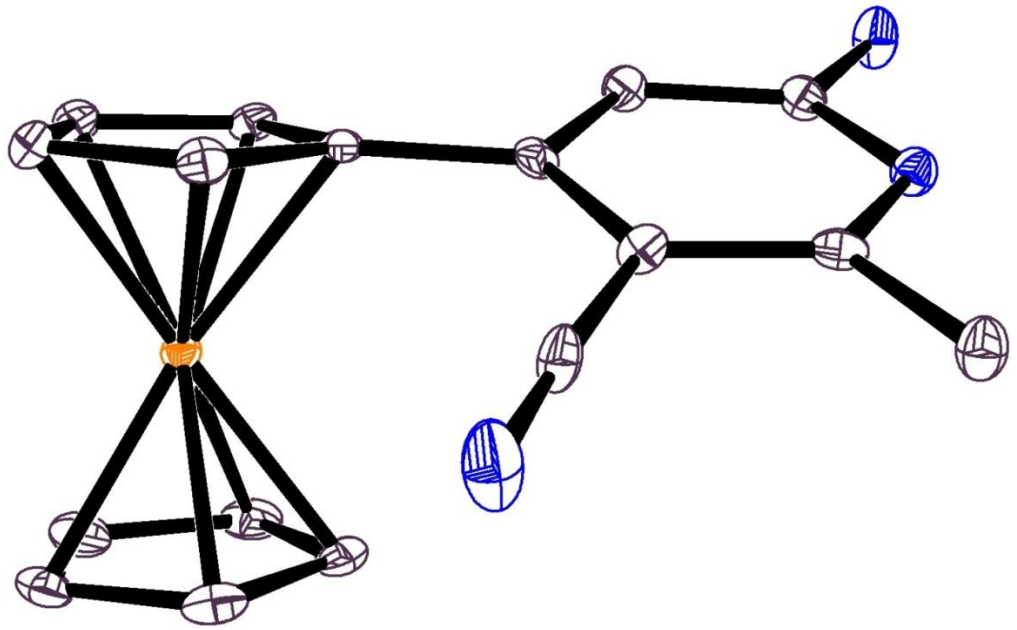
S(1)	51(1)	84(1)	51(1)	-9(1)	0(1)	-13(1)
O(002)	45(1)	73(1)	70(1)	8(1)	13(1)	-23(1)
N(1)	32(1)	62(1)	47(1)	4(1)	4(1)	-11(1)
N(2)	48(1)	72(2)	65(2)	6(1)	13(1)	-15(1)
C(5)	36(1)	49(1)	39(1)	-3(1)	10(1)	-6(1)
C(7)	37(1)	52(1)	42(1)	1(1)	8(1)	-6(1)
C(4)	36(1)	53(1)	37(1)	1(1)	8(1)	-8(1)
C(11)	35(1)	61(2)	40(1)	3(1)	11(1)	-7(1)
C(8)	43(1)	53(2)	45(1)	0(1)	13(1)	-10(1)
C(1)	40(1)	58(2)	49(1)	-1(1)	14(1)	-10(1)
C(10)	47(2)	62(2)	57(2)	-5(1)	4(1)	5(1)
C(13)	44(1)	71(2)	56(2)	14(1)	14(1)	16(1)
C(2)	42(1)	63(2)	51(2)	11(1)	9(1)	-12(1)
C(12)	59(2)	58(2)	51(2)	-3(1)	16(1)	2(1)
C(3)	44(1)	55(2)	49(1)	-2(1)	11(1)	-3(1)
C(9)	54(2)	57(2)	55(2)	-6(1)	3(1)	1(1)
C(6)	47(2)	67(2)	57(2)	14(1)	2(1)	-9(1)
C(14)	45(2)	117(3)	67(2)	6(2)	1(1)	8(2)

Table 22. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 16

	x	y	z	U(eq)
H(1)	7047	6034	5052	60
H(10)	3143	8421	2530	72
H(13)	4945	3126	3177	70
H(2A)	5880	6556	3487	66
H(2B)	5715	9168	3624	66
H(12)	3969	2344	2293	69
H(3)	5112	7974	4185	62
H(9)	4089	9084	3412	72

H(6A)	6530	3524	5660	93
H(6B)	6822	1973	5252	93
H(6C)	6053	1556	5223	93
H(14A)	2054	7311	1877	124
H(14B)	1787	6928	1160	124
H(14C)	2447	8538	1497	124

Crystal structure of 41 with 50% ellipsoidal probability



Packing diagram of 41

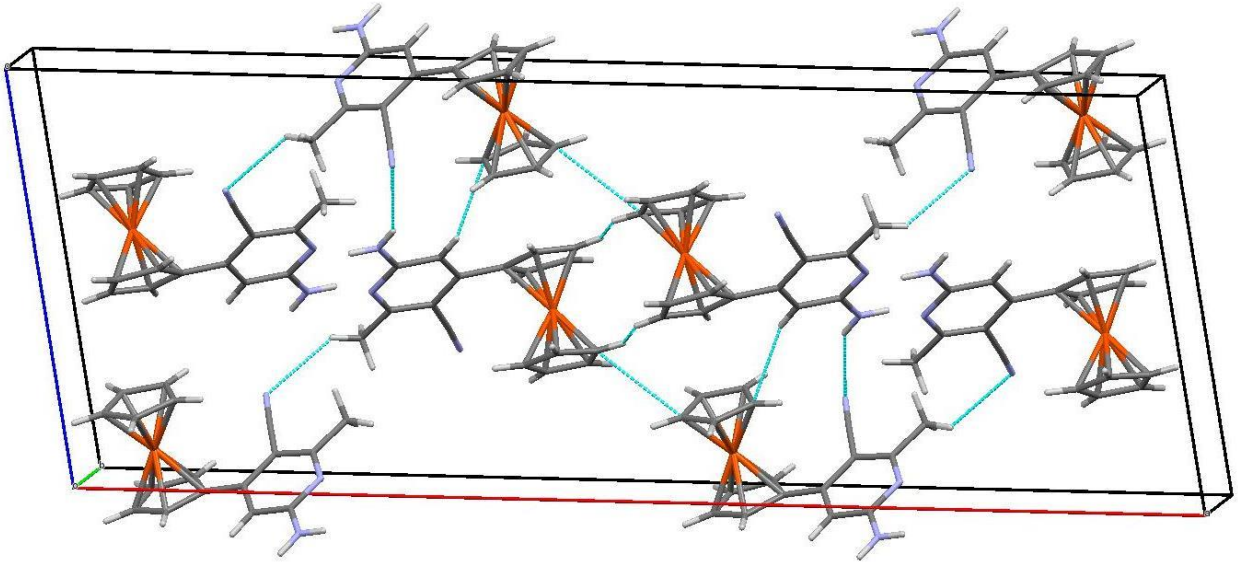


Table 23. Crystal data and structure refinement for 41

Identification code	AY_Ferrocene	
Empirical formula	C_{17} H_{15} Fe N_3	
Formula weight	317.17	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 35.793(4) Å	α= 90°.
	b = 5.7087(6) Å	β= 99.709(4)°.
	c = 13.3460(11) Å	γ = 90°.
Volume	2688.0(4) $Å^3$	
Z	8	
Density (calculated)	1.568 Mg/m^3	
Absorption coefficient	1.117 mm^{-1}	
F(000)	1312	
Theta range for data collection	3.097 to 26.019°.	
Index ranges	-44<=h<=44, -7<=k<=7, -16<=l<=16	
Reflections collected	17590	
Independent reflections	2597 [R(int) = 0.1157]	
Completeness to theta = 25.242°	97.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2597 / 0 / 191	
Goodness-of-fit on F^2	1.168	
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.1079	
R indices (all data)	R1 = 0.0971, wR2 = 0.1660	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.151 and -1.388 $e.Å^{-3}$	

Table 24. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 41. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	4302(1)	7724(1)	4156(1)	10(1)
N(1)	2794(1)	4986(5)	4625(3)	13(1)
N(2)	2990(1)	2144(5)	5814(3)	18(1)
N(3)	3326(1)	11255(7)	2981(3)	25(1)
C(9)	4257(1)	6574(7)	5587(3)	12(1)
C(8)	3925(1)	7882(6)	5147(3)	11(1)
C(16)	4527(1)	8550(7)	2871(3)	15(1)
C(3)	3538(1)	6920(6)	4947(3)	11(1)
C(10)	4577(1)	8046(7)	5642(3)	14(1)
C(2)	3240(1)	7874(6)	4210(3)	12(1)
C(5)	3080(1)	4034(7)	5304(3)	13(1)
C(11)	4453(1)	10276(7)	5238(3)	14(1)
C(13)	4015(1)	6105(7)	2898(3)	19(1)
C(12)	4054(1)	10188(6)	4936(3)	12(1)
C(4)	3450(1)	5002(6)	5481(3)	13(1)
C(7)	3295(1)	9773(7)	3553(3)	16(1)
C(15)	4667(1)	6333(7)	3269(3)	18(1)
C(17)	4125(1)	8401(8)	2640(3)	18(1)
C(6)	2557(1)	7913(7)	3360(3)	15(1)
C(1)	2876(1)	6864(7)	4095(3)	12(1)
C(14)	4352(1)	4835(7)	3277(3)	19(1)

Table 25. Selected bond lengths [Å] for 41

Fe1—C13	2.036 (4)	C3—C4	1.371 (6)
Fe1—C12	2.041 (4)	C3—C2	1.431 (5)

Fe1—C8	2.045 (5)	C10—C11	1.424 (5)
Fe1—C14	2.048 (4)	C10—H10	0.95
Fe1—C9	2.052 (4)	C2—C1	1.408 (6)
Fe1—C11	2.058 (4)	C2—C7	1.428 (6)
Fe1—C15	2.063 (5)	C5—C4	1.418 (5)
Fe1—C16	2.067 (4)	C11—C12	1.419 (5)
Fe1—C10	2.068 (4)	C11—H11	0.95
N1—C1	1.344 (5)	C13—C14	1.425 (6)
N1—C5	1.361 (5)	C13—C17	1.428 (6)
N2—C5	1.344 (5)	C13—H13	0.95
N2—H2A	0.88	C12—H12	0.95
N2—H2B	0.88	C4—H4	0.95
N3—C7	1.158 (6)	C15—C14	1.418 (6)
C9—C10	1.412 (6)	C15—H15	0.95
C9—C8	1.441 (5)	C17—H17	0.95
C9—H9	0.95	C6—C1	1.499 (5)
C8—C12	1.438 (5)	C6—H6A	0.98
C8—C3	1.474 (5)	C6—H6B	0.98
C16—C17	1.423 (6)	C6—H6C	0.98
C16—C15	1.430 (6)	C14—H14	0.95
C16—H16	0.95		

Table 26. Selected bond angles [°] for 41

C13—Fe1—C12	121.99 (17)	C2—C3—C8	123.5 (4)
C13—Fe1—C8	104.82 (17)	C9—C10—C11	108.4 (3)
C12—Fe1—C8	41.21 (15)	C9—C10—Fe1	69.3 (2)
C13—Fe1—C14	40.84 (17)	C11—C10—Fe1	69.4 (2)
C12—Fe1—C14	159.06 (17)	C9—C10—H10	125.8
C8—Fe1—C14	122.41 (17)	C11—C10—H10	125.8
C13—Fe1—C9	120.89 (17)	Fe1—C10—H10	127
C12—Fe1—C9	68.65 (16)	C1—C2—C7	117.6 (3)
C8—Fe1—C9	41.19 (15)	C1—C2—C3	119.2 (4)
C14—Fe1—C9	107.65 (16)	C7—C2—C3	123.2 (4)
C13—Fe1—C11	159.34 (16)	N2—C5—N1	116.0 (3)
C12—Fe1—C11	40.50 (15)	N2—C5—C4	121.8 (3)
C8—Fe1—C11	68.81 (16)	N1—C5—C4	122.2 (4)
C14—Fe1—C11	159.03 (16)	C12—C11—C10	108.0 (3)
C9—Fe1—C11	68.03 (16)	C12—C11—Fe1	69.1 (2)
C13—Fe1—C15	68.52 (18)	C10—C11—Fe1	70.2 (2)
C12—Fe1—C15	158.46 (17)	C12—C11—H11	126
C8—Fe1—C15	159.81 (16)	C10—C11—H11	126
C14—Fe1—C15	40.33 (17)	Fe1—C11—H11	126.3
C9—Fe1—C15	124.60 (16)	C14—C13—C17	107.5 (4)
C11—Fe1—C15	123.94 (17)	C14—C13—Fe1	70.0 (2)
C13—Fe1—C16	68.53 (18)	C17—C13—Fe1	70.2 (2)

C12—Fe1—C16	121.99 (16)	C14—C13—H13	126.3
C8—Fe1—C16	156.64 (16)	C17—C13—H13	126.3
C14—Fe1—C16	68.03 (17)	Fe1—C13—H13	125.2
C9—Fe1—C16	161.40 (16)	C11—C12—C8	108.5 (3)
C11—Fe1—C16	109.11 (17)	C11—C12—Fe1	70.4 (2)
C15—Fe1—C16	40.51 (16)	C8—C12—Fe1	69.5 (2)
C13—Fe1—C10	157.38 (16)	C11—C12—H12	125.8
C12—Fe1—C10	68.08 (16)	C8—C12—H12	125.8
C8—Fe1—C10	68.54 (16)	Fe1—C12—H12	125.9
C14—Fe1—C10	123.21 (16)	C3—C4—C5	120.9 (3)
C9—Fe1—C10	40.08 (16)	C3—C4—H4	119.6
C11—Fe1—C10	40.37 (15)	C5—C4—H4	119.6
C15—Fe1—C10	109.89 (17)	N3—C7—C2	176.5 (4)
C16—Fe1—C10	125.92 (17)	C14—C15—C16	107.9 (4)
C1—N1—C5	117.5 (3)	C14—C15—Fe1	69.3 (3)
C5—N2—H2A	120	C16—C15—Fe1	69.9 (2)
C5—N2—H2B	120	C14—C15—H15	126
H2A—N2—H2B	120	C16—C15—H15	126
C10—C9—C8	108.5 (3)	Fe1—C15—H15	126.4
C10—C9—Fe1	70.6 (2)	C16—C17—C13	108.2 (4)
C8—C9—Fe1	69.2 (2)	C16—C17—H17	125.9
C10—C9—H9	125.7	C13—C17—H17	125.9

C8—C9—H9	125.7	C1—C6—H6A	109.5
Fe1—C9—H9	126.1	C1—C6—H6B	109.5
C12—C8—C9	106.6 (3)	H6A—C6—H6B	109.5
C12—C8—C3	128.9 (3)	C1—C6—H6C	109.5
C9—C8—C3	124.5 (3)	H6A—C6—H6C	109.5
C12—C8—Fe1	69.2 (2)	H6B—C6—H6C	109.5
C9—C8—Fe1	69.7 (2)	N1—C1—C2	123.3 (3)
C3—C8—Fe1	124.8 (3)	N1—C1—C6	116.9 (3)
C17—C16—C15	107.8 (4)	C2—C1—C6	119.8 (4)
C17—C16—Fe1	69.2 (2)	C15—C14—C13	108.5 (4)
C15—C16—Fe1	69.6 (2)	C15—C14—Fe1	70.4 (2)
C17—C16—H16	126.1	C13—C14—Fe1	69.1 (2)
C15—C16—H16	126.1	C15—C14—H14	125.7
Fe1—C16—H16	126.6	C13—C14—H14	125.7
C4—C3—C2	116.9 (4)	Fe1—C14—H14	126.3
C4—C3—C8	119.6 (3)		

Table 27. Anisotropic displacement parameters ($Å^2$x 10^3) for 41. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	11(1)	9(1)	9(1)	0(1)	1(1)	-1(1)
N(1)	13(2)	12(2)	14(2)	0(1)	2(1)	-1(1)
N(2)	14(2)	16(2)	23(2)	7(2)	0(2)	-2(1)

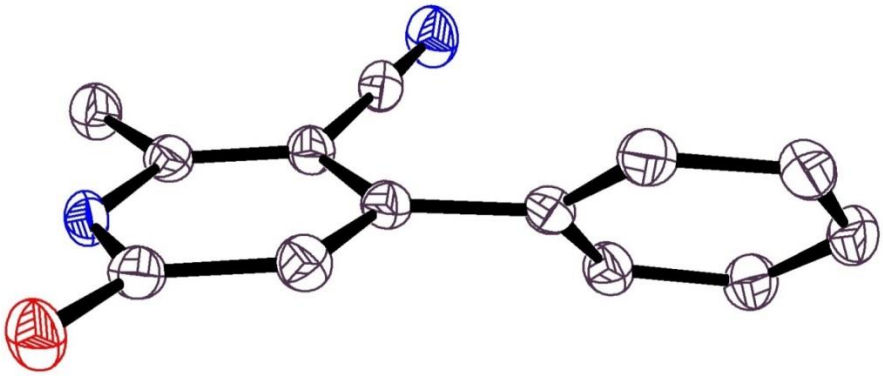
N(3)	15(2)	28(2)	31(2)	17(2)	-2(2)	-2(2)
C(9)	15(2)	12(2)	8(2)	1(2)	-1(2)	1(2)
C(8)	10(2)	15(2)	7(2)	-2(2)	2(2)	1(1)
C(16)	22(2)	14(2)	11(2)	0(2)	8(2)	0(2)
C(3)	11(2)	12(2)	12(2)	-2(2)	5(2)	2(1)
C(10)	13(2)	19(2)	10(2)	0(2)	0(2)	-1(2)
C(2)	14(2)	10(2)	12(2)	1(2)	0(2)	0(1)
C(5)	14(2)	11(2)	13(2)	1(2)	4(2)	0(1)
C(11)	13(2)	15(2)	13(2)	-3(2)	1(2)	-3(2)
C(13)	24(2)	23(2)	10(2)	-6(2)	2(2)	-8(2)
C(12)	14(2)	11(2)	13(2)	-2(2)	3(2)	3(1)
C(4)	12(2)	14(2)	13(2)	1(2)	2(2)	1(2)
C(7)	8(2)	19(2)	20(2)	1(2)	-2(2)	0(2)
C(15)	23(2)	17(2)	15(2)	0(2)	7(2)	6(2)
C(17)	24(2)	20(2)	9(2)	0(2)	0(2)	3(2)
C(6)	12(2)	14(2)	18(2)	3(2)	1(2)	0(2)
C(1)	17(2)	11(2)	10(2)	-1(2)	4(2)	2(2)
C(14)	34(3)	11(2)	13(2)	-3(2)	7(2)	-1(2)

Table 28. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 41

	x	y	z	U(eq)
H(2A)	2757	1596	5700	22
H(2B)	3164	1456	6263	22
H(9)	4260	4988	5803	14
H(16)	4676	9885	2779	18
H(10)	4831	7621	5904	17
H(11)	4611	11592	5180	17
H(13)	3763	5529	2830	23
H(12)	3898	11441	4644	15

H(4)	3640	4313	5976	15
H(15)	4926	5934	3489	21
H(17)	3959	9620	2361	21
H(6A)	2323	7057	3396	22
H(6B)	2615	7805	2669	22
H(6C)	2526	9561	3533	22
H(14)	4363	3250	3498	23

Crystal structure of 42with 50% ellipsoidal probability



Packing diagram of 42

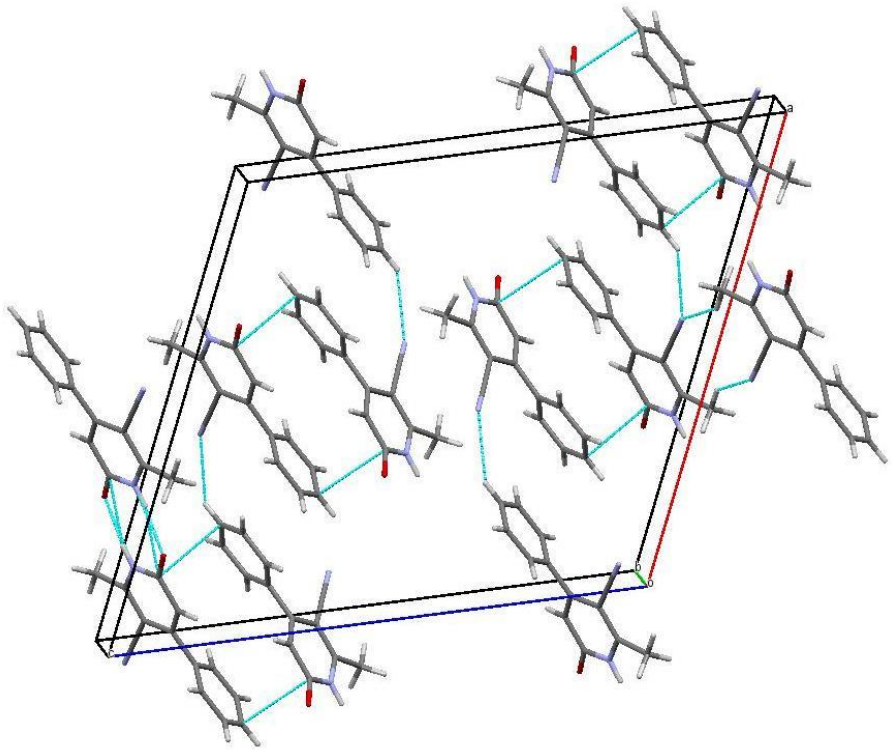


Table 29. Crystal data and structure refinement for 42

Identification code	**AY_256**	
Empirical formula	C_{13} H_{10} N_2 O	
Formula weight	210.23	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 17.9438(17) Å	α= 90°.
	b = 6.3301(6) Å	β= 113.492(3)°.
	c = 19.758(2) Å	γ = 90°.
Volume	2058.2(3) $Å^3$	
Z	8	
Density (calculated)	1.357 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	880	
Theta range for data collection	2.248 to 25.171°.	
Index ranges	-21<=h<=18, -7<=k<=7, -23<=l<=23	
Reflections collected	6639	
Independent reflections	1854 [R(int) = 0.0268]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1854 / 0 / 146	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.0980	
R indices (all data)	R1 = 0.0498, wR2 = 0.1069	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.162 and -0.252 $e.Å^{-3}$	

Table 30. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 42. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(001)	6834(1)	9318(2)	4323(1)	29(1)
N(002)	6546(1)	6191(2)	4726(1)	24(1)
N(003)	4303(1)	1594(2)	4214(1)	36(1)
C(1)	6331(1)	7885(2)	4246(1)	24(1)
C(4)	5286(1)	4506(2)	4171(1)	23(1)
C(5)	6055(1)	4573(2)	4721(1)	23(1)
C(3)	5023(1)	6128(2)	3617(1)	23(1)
C(2)	5533(1)	7779(2)	3677(1)	24(1)
C(9)	4032(1)	4088(2)	2561(1)	26(1)
C(7)	4745(1)	2871(2)	4190(1)	25(1)
C(8)	4227(1)	5944(2)	2976(1)	24(1)
C(13)	3687(1)	7631(2)	2761(1)	27(1)
C(10)	3318(1)	3938(3)	1938(1)	30(1)
C(12)	2964(1)	7455(3)	2146(1)	31(1)
C(6)	6396(1)	2984(3)	5323(1)	31(1)
C(11)	2781(1)	5620(3)	1732(1)	32(1)

Table 31. Selected bond lengths [Å] for 42.

O001—C1	1.2458 (17)	C9—C8	1.395 (2)
N002—C5	1.3487 (18)	C9—H9	0.93
N002—C1	1.3808 (19)	C8—C13	1.391 (2)
N002—H002	0.86	C13—C12	1.384 (2)
N003—C7	1.1472 (19)	C13—H13	0.93
C1—C2	1.427 (2)	C10—C11	1.384 (2)

C4—C5	1.375 (2)	C10—H10	0.93
C4—C7	1.430 (2)	C12—C11	1.383 (2)
C4—C3	1.437 (2)	C12—H12	0.93
C5—C6	1.490 (2)	C6—H6A	0.96
C3—C2	1.362 (2)	C6—H6B	0.96
C3—C8	1.488 (2)	C6—H6C	0.96
C2—H2	0.93	C11—H11	0.93
C9—C10	1.381 (2)		

Table 32. Selected bond angles [°] for 42.

C5—N002—C1	125.54 (13)	C13—C8—C9	119.06 (14)
C5—N002—H002	117.2	C13—C8—C3	121.07 (13)
C1—N002—H002	117.2	C9—C8—C3	119.81 (13)
O001—C1—N002	119.38 (13)	C12—C13—C8	120.13 (15)
O001—C1—C2	125.53 (14)	C12—C13—H13	119.9
N002—C1—C2	115.05 (13)	C8—C13—H13	119.9
C5—C4—C7	118.68 (13)	C9—C10—C11	119.93 (15)
C5—C4—C3	120.06 (13)	C9—C10—H10	120
C7—C4—C3	121.17 (13)	C11—C10—H10	120
N002—C5—C4	118.44 (13)	C13—C12—C11	120.38 (15)
N002—C5—C6	116.58 (13)	C13—C12—H12	119.8
C4—C5—C6	124.98 (13)	C11—C12—H12	119.8
C2—C3—C4	118.51 (14)	C5—C6—H6A	109.5

C2—C3—C8	121.18 (13)	C5—C6—H6B	109.5
C4—C3—C8	120.26 (13)	H6A—C6—H6B	109.5
C3—C2—C1	122.18 (14)	C5—C6—H6C	109.5
C3—C2—H2	118.9	H6A—C6—H6C	109.5
C1—C2—H2	118.9	H6B—C6—H6C	109.5
C10—C9—C8	120.55 (15)	C12—C11—C10	119.92 (15)
C10—C9—H9	119.7	C12—C11—H11	120
C8—C9—H9	119.7	C10—C11—H11	120
N003—C7—C4	178.26 (16)		

Table 33. Anisotropic displacement parameters ($Å^2$x 10^3) for 42. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(001)	26(1)	26(1)	33(1)	0(1)	9(1)	-8(1)
N(002)	18(1)	27(1)	23(1)	-1(1)	5(1)	-4(1)
N(003)	32(1)	36(1)	38(1)	1(1)	11(1)	-10(1)
C(1)	25(1)	24(1)	25(1)	-2(1)	12(1)	-2(1)
C(4)	22(1)	24(1)	24(1)	-3(1)	9(1)	-3(1)
C(5)	24(1)	24(1)	24(1)	-4(1)	11(1)	-3(1)
C(3)	21(1)	25(1)	23(1)	-4(1)	10(1)	-1(1)
C(2)	24(1)	24(1)	25(1)	1(1)	10(1)	0(1)
C(9)	23(1)	28(1)	28(1)	0(1)	9(1)	-2(1)
C(7)	23(1)	26(1)	23(1)	-1(1)	6(1)	-1(1)

C(8)	20(1)	30(1)	23(1)	0(1)	10(1)	-4(1)
C(13)	27(1)	30(1)	27(1)	-2(1)	12(1)	-1(1)
C(10)	27(1)	34(1)	27(1)	-5(1)	9(1)	-8(1)
C(12)	24(1)	39(1)	30(1)	7(1)	11(1)	5(1)
C(6)	29(1)	32(1)	30(1)	3(1)	10(1)	-3(1)
C(11)	22(1)	45(1)	25(1)	1(1)	5(1)	-6(1)

Table 34. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 42.

	x	y	z	U(eq)
H(002)	7035	6166	5056	28
H(2)	5354	8873	3335	29
H(9)	4385	2942	2706	32
H(13)	3811	8880	3032	33
H(10)	3199	2709	1657	36
H(12)	2600	8577	2010	37
H(6A)	6832	2232	5264	46
H(6B)	5978	2006	5301	46
H(6C)	6599	3690	5792	46
H(11)	2298	5516	1315	38