Electronic Supplementary Material (ESI) for ChemComm.

C1 functionalization of imidazo heterocycles via carbon dioxide fixation

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Supporting Information

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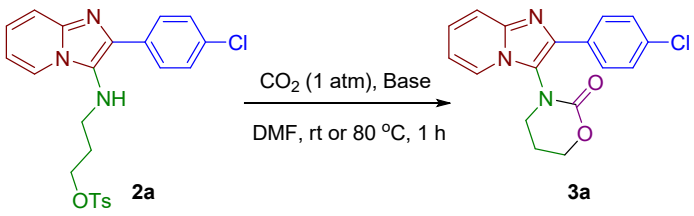
1. Experimental materials and methods

All the reagents and solvents were purchased from Sigma-Aldrich, AK Scientific, Fluorochem, Abcr GmbH, Acros and were used without further purification. Thin layer chromatography was performed on Millipore precoated silica gel plates (0.20 mm thick, particle size 25 μm). Nuclear magnetic resonance spectra were recorded on Bruker Avance 500 spectrometers {^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz)}. Chemical shifts for ^{1}H NMR were reported as δ values and coupling constants were in hertz (Hz). The following abbreviations were used for spin multiplicity: s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = double of doublets, dt = double of triplets, td = triplet of doublets, m = multiplet. Chemical shifts for ^{13}C NMR were reported in ppm relative to the solvent peak. High resolution mass spectra were recorded using a LTQ-Orbitrap-XL (Thermo) at a resolution of 60000@m/z400. Single crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer equipped with a Cu Incoatec microfocus IμS 3.0 source, a Photon II detector operating in shutterless mode and a cryostream 800 system (Oxford Cryosystems) for temperature regulation.

2. Optimization of the CO_2 fixation reaction on a GBB-3CR

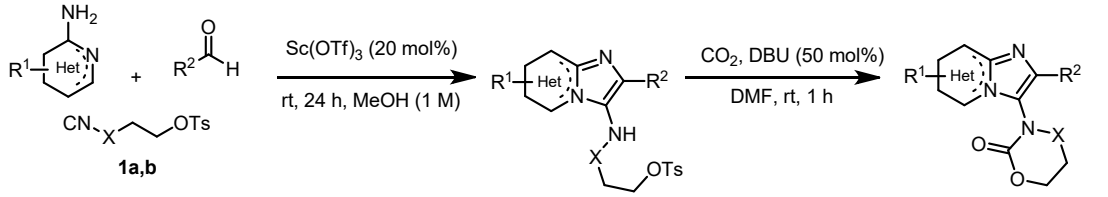
Table S1. Optimization of the reaction



Entry	Base	mol %	CO_2	Temperature (°C)	Yield (%)
1	$NaHCO_3$	200	-	80	-
2	DBU	150	+	80	79
3	DBU	150	+	25	83
4	DBU	50	+	25	54
5	DBU	20	+	25	20
6	DBU	150	-	25	-
7	DABCO	150	+	25	30
8	Et_3N	150	+	25	6

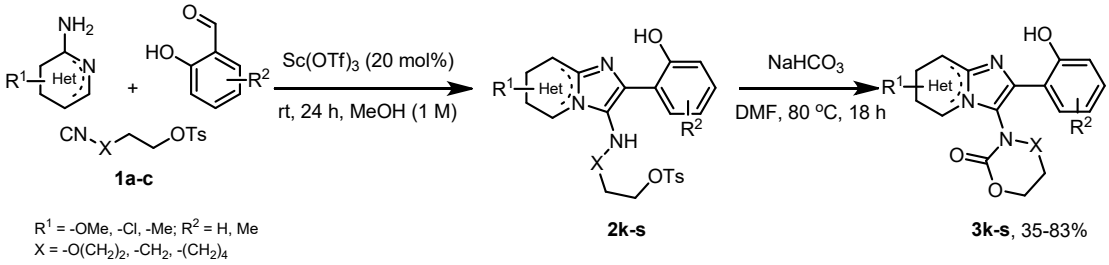
3. Synthetic procedures and analytical data

General procedure for the synthesis of the cyclic carbamates 3a-j



To a stirred solution of aldehyde (3.0 mmol) in MeOH (3.0 mL), the 2-amino pyridine or 2-aminothiazole (3.0 mmol) was added at room temperature. Then, scandium triflate was added (20 mol%) followed by the isocyanide (3.0 mmol) and the reaction mixture was stirred vigorously for 24 h. The solvent was removed under reduced pressure and the reaction mixture was diluted with dichloromethane and extracted with water. The organic layer was collected and dried with sodium sulfate. The mixture was filtrated and the solvent was removed under reduced pressure to afford derivatives **2a-j**. To a stirred solution of this mixture in DMF (0.35 M), DBU (1.5 equiv.) and flow of CO_2 (1 atm) were added at room temperature. The reaction mixture was stirred vigorously for 1 h. The mixture was diluted with dichloromethane and extracted with water. The organic layer was collected and dried with sodium sulfate. The mixture was filtrated and the solvent was removed under reduced pressure. The reaction mixture was purified with column chromatography (PE-EtOAc 2:1-1:10) to yield compounds **3a-j**.

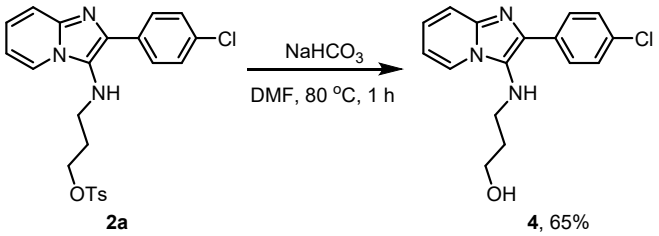
General procedure for the synthesis of the cyclic carbamates 3k-s



To a stirred solution of salicyl aldehyde (1.0 mmol) in MeOH (1.0 mL), the 2-amino pyridine or 2-aminothiazole (1.0 mmol) was added at room temperature. Then, scandium triflate was added (20 mol%) followed by the isocyanide (1.0 mmol) and the reaction mixture was stirred vigorously for 24 h. The solvent was removed under reduced pressure and the reaction mixture was diluted with dichloromethane and extracted with water. The organic layer was collected and dried with sodium sulfate. The mixture was filtrated and the solvent was removed under reduced pressure to afford derivatives **2k-s**. To a stirred solution of this mixture in DMF (0.35 M), $NaHCO_3$ (2 equiv.) was added at 80 °C. The reaction mixture was stirred vigorously for 18 h. The mixture was diluted with dichloromethane and extracted with water. The organic layer was collected and dried with sodium sulfate. The mixture was filtrated and the

solvent was removed under reduced pressure. The reaction mixture was purified with column chromatography (PE-EtOAc 5:1-1:3) to yield compounds **3k-s**.

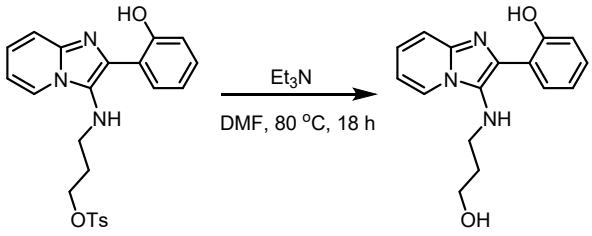
Synthesis of compound 4



2a **4**, 65%

To a stirred solution of **2a** in DMF (0.35 M), $NaHCO_3$ (2 equiv.) was added at 80 °C. The reaction mixture was stirred vigorously for 1 h. The mixture was diluted with dichloromethane and extracted with water. The organic layer was collected and dried with sodium sulfate. The mixture was filtrated and the solvent was removed under reduced pressure. The reaction mixture was purified with column chromatography (PE-EtOAc 5:1-1:3) to yield compound **4**.

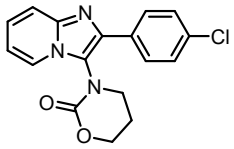
Synthesis of compound 6



2k **6**, 58%

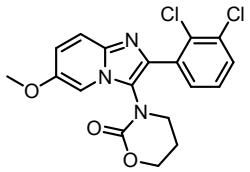
To a stirred solution of **2k** in DMF (0.35 M), triethylamine (2 equiv.) was added at 80 °C. The reaction mixture was stirred vigorously for 18 h. The mixture was diluted with dichloromethane and extracted with water. The organic layer was collected and dried with sodium sulfate. The mixture was filtrated and the solvent was removed under reduced pressure. The reaction mixture was purified with column chromatography (PE-EtOAc 5:1-1:3) to yield compound **6**.

3-(2-(4-chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3a)



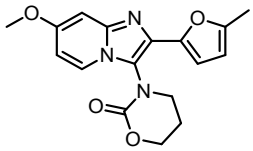
530 mg, 83% yield, light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.81-7.79 (m, 3H), 7.63 (dt, J_1 = 9 Hz, J_2 = 1.5 Hz, 1H), 7.44 (d, J = 8 Hz, 2H), 7.28-7.24 (m, 1H), 6.88 (td, J_1 = 7 Hz, J_2 = 1.5 Hz, 1H), 4.54-4.51 (m, 2H), 3.52-3.49 (m, 2H), 2.24-2.19 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 152.3, 142.9, 137.6, 134.3, 131.5, 129.1, 128.5, 125.6, 122.2, 119.6, 118.0, 112.9, 67.6, 48.1, 22.7. HRMS (ESI) m/z: $[M+H]^+$: $C_{17}H_{15}ClN_3O_2^+$, calculated 328.0853; found 328.0847.

3-(2-(2,3-dichlorophenyl)-6-methoxyimidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3b)



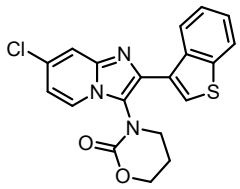
257 mg, 60% yield, dark brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.55-7.50 (m, 3H), 7.30-7.27 (m, 2H), 7.08 (dd, J_1 = 9.5 Hz, J_2 = 2.5 Hz, 1H), 4.49-4.44 (m, 1H), 4.40-4.36 (m, 1H), 3.85 (s, 3H), 3.51-3.46 (m, 1H), 3.38-3.33 (m, 1H), 2.20-2.14 (m, 1H), 2.04-2.00 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 151.7, 149.8, 139.7, 136.5, 134.8, 133.7, 131.8, 130.6, 130.5, 127.4, 122.3, 120.8, 118.4, 104.9, 67.6, 56.4, 48.6, 22.5. HRMS (ESI) m/z: $[M+H]^+$: $C_{18}H_{16}Cl_2N_3O_3^+$, calculated 392.0560; found 392.0559.

3-(7-methoxy-2-(5-methylfuran-2-yl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3c)



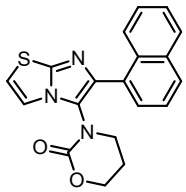
130 mg, 34% yield, dark brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.62 (dd, J_1 = 7 Hz, J_2 = 0.5 Hz, 1H), 6.85 (d, J = 2.5 Hz, 1H), 6.74 (d, J = 3 Hz, 1H), 6.56 (dd, J_1 = 7 Hz, J_2 = 2.5 Hz, 1H), 6.11-6.10 (m, 1H), 4.59-4.53 (m, 2H), 3.90-3.83 (m, 1H), 3.85 (s, 3H), 3.61-3.56 (m, 1H), 2.39 (s, 3H), 2.35-2.28 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 158.6, 152.4, 152.3, 147.0, 144.7, 122.6, 117.5, 108.9, 107.7, 107.6, 95.0, 67.6, 55.6, 48.6, 22.7, 13.8. HRMS (ESI) m/z: $[M+H]^+$: $C_{17}H_{18}N_3O_4^+$, calculated 328.1290; found 328.1289.

3-(2-(benzo[*b*]thiophen-3-yl)-7-chloroimidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3d)



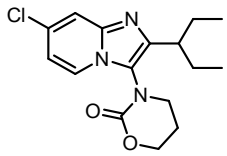
302 mg, 62% yield, brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): 8.23 (dd, J_1 = 8.5 Hz, J_2 = 1 Hz, 1H), 7.92 (dt, J_1 = 8 Hz, J_2 = 1 Hz, 1H), 7.80 (dd, J_1 = 7 Hz, J_2 = 0.5 Hz, 1H), 7.73 (s, 1H), 7.69 (dd, J_1 = 2 Hz, J_2 = 0.5 Hz, 1H), 7.47-7.39 (m, 2H), 6.90 (dd, J_1 = 7 Hz, J_2 = 2 Hz, 1H), 4.45-4.40 (m, 1H), 4.33-4.28 (m, 1H), 3.43-3.38 (m, 1H), 3.31-3.26 (m, 1H), 2.12 (m, 1H), 1.96-1.89 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 152.3, 142.6, 140.2, 137.5, 135.4, 132.0, 128.3, 126.3, 124.9, 124.8, 123.7, 123.2, 122.7, 120.9, 116.8, 114.4, 67.6, 48.3, 22.4. HRMS (ESI) m/z: $[M+H]^+$: $C_{19}H_{15}ClN_3O_2S^+$, calculated 384.0568; found 384.0561.

3-(6-(naphthalen-1-yl)imidazo[2,1-*b*]thiazol-5-yl)-1,3-oxazinan-2-one (3e)



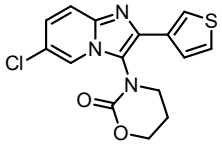
203 mg, 26% yield, brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): 8.19-8.17 (m, 1H), 7.91-7.88 (m, 2H), 7.70 (dd, J_1 = 7 Hz, J_2 = 1 Hz, 1H), 7.55-7.49 (m, 3H), 7.35 (d, J = 4.5 Hz, 1H), 6.89 (d, J = 4.5 Hz, 1H), 4.15 (br s, 2H), 3.09 (br s, 2H), 1.72 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 152.3, 147.2, 138.4, 133.8, 131.2, 130.6, 128.8, 128.3, 127.7, 126.6, 126.0, 125.9, 125.4, 123.2, 117.9, 112.5, 67.3, 48.5, 22.0. HRMS (ESI) m/z: $[M+H]^+$: $C_{19}H_{16}N_3O_2S^+$, calculated 350.0958; found 350.0958.

3-(7-chloro-2-(pentan-3-yl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3f)



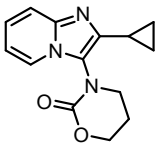
534 mg, 81% yield, brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.64 (d, J = 7 Hz, 1H), 7.55-7.54 (m, 1H), 6.76-6.72 (m, 1H), 4.52 (m, 2H), 3.74-3.68 (m, 1H), 3.60-3.56 (m, 1H), 2.51-2.45 (m, 1H), 2.29-2.25 (m, 2H), 1.89-1.82 (m, 1H), 1.81-1.69 (m, 3H), 0.83-0.77 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 152.0, 145.5, 142.5, 131.1, 122.3, 121.2, 116.5, 113.5, 67.5, 49.2, 41.6, 28.3, 27.3, 22.7, 12.8, 12.2. HRMS (ESI) m/z: $[M+H]^+$: $C_{16}H_{21}ClN_3O_2^+$, calculated 322.1317; found 322.1315.

3-(6-chloro-2-(thiophen-3-yl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3g)



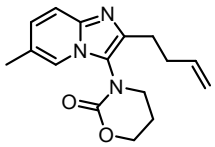
574 mg, 92% yield, gray solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.83 (dd, J_1 = 2 Hz, J_2 = 1 Hz, 1H), 7.75-7.74 (m, 1H), 7.58-7.53 (m, 2H), 7.43 (dd, J_1 = 5 Hz, J_2 = 3 Hz, 1H), 7.21 (dd, J_1 = 9.5 Hz, J_2 = 2 Hz, 1H), 4.58-4.55 (m, 2H), 3.65-3.60 (m, 1H), 3.57-3.52 (m, 1H), 2.29-2.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 152.0, 141.1, 136.3, 133.6, 126.8, 126.6, 126.1, 123.3, 121.3, 120.2, 119.4, 118.2, 67.7, 47.9, 22.6. HRMS (ESI) m/z: $[M+H]^+$: $C_{15}H_{13}ClN_3O_2S^+$, calculated 334.0412; found 334.0412.

3-(2-cyclopropylimidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3h)



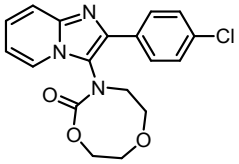
406 mg, 83% yield, brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.70 (d, J = 6.5 Hz, 1H), 7.48 (dt. J_1 = 9 Hz, J_2 = 1 Hz, 1H), 7.16-7.12 (m, 1H), 6.78 (td. J_1 = 7 Hz, J_2 = 1.5 Hz, 1H), 4.53-4.51 (m, 2H), 3.86-3.81 (m, 1H), 3.65-3.60 (m, 1H), 2.30-2.26 (m, 2H), 1.92-1.87 (m, 1H), 1.18-1.15 (m, 1H), 1.00-0.96 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 152.2, 142.4, 142.4, 124.4, 121.7, 120.1, 117.2, 112.0, 67.5, 48.8, 22.7, 7.9, 7.9, 7.3. HRMS (ESI) m/z: $[M+H]^+$: $C_{14}H_{16}N_3O_2^+$, calculated 258.1237; found 258.1237.

3-(2-(but-3-en-1-yl)-6-methylimidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3i)



579 mg, 70% yield, brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): 7.49 (s, 1H), 7.43 (d, J = 9.5 Hz, 1H), 7.02 (d, J = 9.5 Hz, 1H), 5.93-5.85 (m, 1H), 5.07 (dd. J_1 = 17 Hz, J_2 = 2 Hz, 1H), 4.97 (d, J = 11 Hz, 1H), 4.54-4.51 (m, 2H), 3.70-3.65 (m, 1H), 3.62-3.57 (m, 1H), 2.79-2.75 (m, 2H), 2.56-2.51 (m, 2H), 2.30-2.27 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): 152.2, 141.6, 140.4, 137.9, 127.7, 122.0, 119.6, 116.7, 116.6, 115.0, 67.5, 48.7, 32.8, 27.0, 22.6, 18.1. HRMS (ESI) m/z: $[M+H]^+$: $C_{16}H_{20}N_3O_2^+$, calculated 286.1550; found 286.1551.

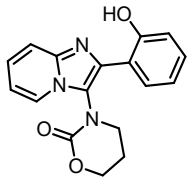
3-(2-(4-chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,6,3-dioxazocan-2-one (3j)



163 mg, 38% yield, brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): 8.17 (dt, J_1 = 7 Hz, J_2 = 1 Hz, 1H), 8.06 (dd, J_1 = 6.5 Hz, J_2 = 2 Hz, 2H), 7.56 (dt, J_1 = 9 Hz, J_2 = 1 Hz, 1H), 7.42

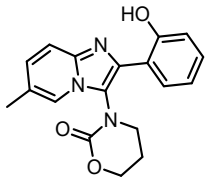
(dd, J_1 = 6.5 Hz, J_2 = 2 Hz, 2H), 7.18-7.15 (m, 1H), 6.83 (td, J_1 = 7 Hz, J_2 = 1.5 Hz, 1H), 3.72-3.66 (m, 4H), 3.61 (dd, J_1 = 5 Hz, J_2 = 4.5 Hz, 2H), 3.25-3.22 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 141.3, 134.1, 133.2, 132.3, 129.8, 129.7, 128.8, 128.2, 125.7, 124.6, 122.5, 117.3, 112.2, 71.0, 70.2, 47.6, 43.1. HRMS (ESI) m/z: $[M+H]^+$: $C_{16}H_{20}N_3O_2^+$, calculated 358.0950; found 358.0953.

3-(2-(2-hydroxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3k)



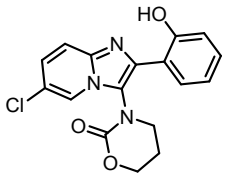
88 mg, 67% yield, gray solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.87 (d, J = 7 Hz, 1H), 7.63 (d, J = 9 Hz, 1H), 7.60 (dt, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 7.35-7.32 (m, 1H), 7.28-7.24 (m, 1H), 7.08 (d, J = 8.5 Hz, 1H), 6.97 (t, J = 6.5 Hz, 1H), 6.92 (t, J = 7 Hz, 1H), 4.60-4.57 (m, 2H), 3.70-3.66 (m, 1H), 3.56-3.52 (m, 1H), 2.31-2.27 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 157.6, 152.1, 140.6, 130.3, 126.5, 126.0, 122.1, 119.3, 118.5, 117.9, 116.9, 115.5, 113.7, 67.7, 47.7, 22.6. HRMS (ESI) m/z: $[M+H]^+$: $C_{17}H_{16}N_3O_3^+$, calculated 310.1189; found 310.1191.

3-(2-(2-hydroxyphenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3l)



81 mg, 69% yield, gray solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.60-7.57 (m, 2H), 7.49 (d, J = 9.5 Hz, 1H), 7.25-7.23 (m, 1H), 7.15 (dd, J_1 = 9 Hz, J_2 = 1.5 Hz, 1H), 7.04 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 6.90 (td, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 4.59 (t, J = 5.5 Hz, 2H), 3.70-3.65 (m, 1H), 3.55-3.51 (m, 1H), 2.36 (s, 3H), 2.31-2.28 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 157.6, 152.1, 139.8, 137.0, 129.9, 129.2, 125.6, 123.4, 119.6, 119.2, 117.7, 116.5, 115.9, 67.6, 47.6, 22.6, 18.3. HRMS (ESI) m/z: $[M+H]^+$: $C_{18}H_{18}N_3O_3^+$, calculated 324.1343; found 324.1347.

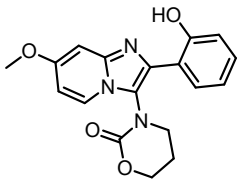
3-(6-chloro-2-(2-hydroxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3m)



73 mg, 53% yield, gray solid. ^{1}H NMR (500 MHz, $CDCl_3$): 7.88 (s, 1H), 7.59-7.57 (m, 2H), 7.32-7.28 (m, 2H), 7.07 (d, J = 8 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 4.62 (t, J = 5.5 Hz, 2H), 3.73-3.69 (m, 1H), 3.58-3.53 (m, 1H), 2.34-2.31 (m, 2H); ^{13}C NMR (125 MHz,

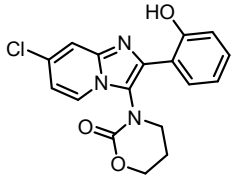
$CDCl_3$): 157.6, 151.9, 139.1, 130.6, 127.7, 125.9, 122.2, 120.1, 119.4, 118.9, 118.0, 117.4, 115.3, 67.8, 47.7, 22.6. HRMS (ESI) m/z: $[M+H]^+$: $C_{17}H_{15}ClN_3O_3^+$, calculated 344.0796; found 344.0798.

3-(2-(2-hydroxyphenyl)-7-methoxyimidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3n)



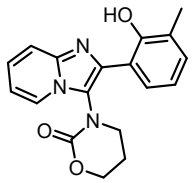
212 mg, 83% yield, brown solid. ^1H NMR (500 MHz, $CDCl_3$): 7.69 (d, J = 7.5 Hz, 1H), 7.54 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.25-7.21 (m, 1H), 7.04 (d, J_1 = 8 Hz, 1H), 6.91-6.87 (m, 2H), 6.64 (dd, J_1 = 7.5 Hz, J_2 = 2.5 Hz, 1H), 4.57-4.55 (m, 2H), 3.88 (s, 3H), 3.69-3.64 (m, 1H), 3.54-3.50 (m, 1H), 2.28-2.25 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 159.3, 157.5, 152.3, 142.2, 129.9, 125.7, 122.7, 119.2, 117.8, 117.6, 115.7, 108.5, 94.4, 67.7, 55.8, 47.8, 22.6. HRMS (ESI) m/z: $[M+H]^+$: $C_{18}H_{18}N_3O_4^+$, calculated 340.1290; found 340.1292.

3-(7-chloro-2-(2-hydroxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3o)



60 mg, 43% yield, gray solid. ^1H NMR (500 MHz, $CDCl_3$): 7.80 (d, J = 7 Hz, 1H), 7.61 (d, J = 2 Hz, 1H), 7.55 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.28-7.25 (m, 1H), 7.05 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 6.93-6.90 (m, 2H), 4.59-4.56 (m, 2H), 3.70-3.65 (m, 1H), 3.55-3.50 (m, 1H), 2.30-2.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 157.5, 152.0, 140.5, 133.1, 130.5, 125.8, 122.6, 119.4, 118.7, 117.9, 115.8, 115.2, 115.2, 67.7, 47.7, 22.5. HRMS (ESI) m/z: $[M+H]^+$: $C_{17}H_{15}ClN_3O_3^+$, calculated 344.0796; found 344.0797.

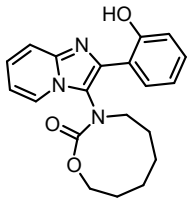
3-(2-(2-hydroxy-3-methylphenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3p)



54 mg, 42% yield, white solid. ^1H NMR (500 MHz, $CDCl_3$): 7.84 (dt, J_1 = 6.5 Hz, J_2 = 1 Hz, 1H), 7.59 (dt, J_1 = 9 Hz, J_2 = 1 Hz, 1H), 7.46 (dd, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 7.33-7.29 (m, 1H), 7.15 (dq, J_1 = 7.5 Hz, J_2 = 1 Hz, 1H), 6.95 (td, J_1 = 7 Hz, J_2 = 1 Hz, 1H), 6.83 (t, J = 7.5 Hz, 1H), 4.60-4.56 (m, 2H), 3.73-3.68 (m, 1H), 3.54-3.49 (m, 1H), 2.34 (s, 3H), 2.33-2.27 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 155.9, 152.1, 140.7, 137.6,

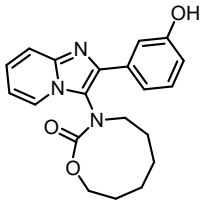
131.2, 126.7, 126.0, 123.4, 122.0, 118.7, 117.1, 114.9, 113.4, 67.6, 47.6, 22.6, 16.3. HRMS (ESI) m/z: $[M+H]^+$: $C_{18}H_{18}N_3O_3^+$, calculated 324,1343; found 324.1346.

3-(2-(2-hydroxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazonan-2-one (3q)



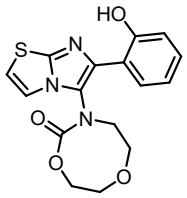
67 mg, 48% yield, brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): 8.11 (dt, J_1 = 6.5 Hz, J_2 = 1 Hz, 1H), 7.97 (dd, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 7.51 (dt, J_1 = 9 Hz, J_2 = 1 Hz, 1H), 7.24-7.19 (m, 2H), 7.04 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 6.93-6.86 (m, 2H), 3.64 (t, J = 6.5 Hz, 2H), 3.11-3.08 (m, 2H), 1.68-1.64 (m, 2H), 1.61-1.55 (m, 2H), 1.49-1.38 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): 157.5, 139.3, 135.1, 129.1, 125.9, 124.8, 124.6, 122.1, 118.8, 117.7, 117.3, 116.7, 112.4, 62.8, 48.1, 32.6, 30.7, 26.9, 25.6. HRMS (ESI) m/z: $[M+H]^+$: $C_{20}H_{22}N_3O_3^+$, calculated 352.1656; found 352.1656.

3-(2-(3-hydroxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazonan-2-one (3r)



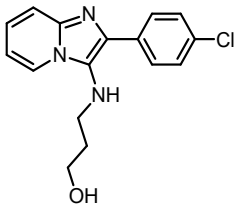
31 mg, 35% yield, light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): 8.08 (dt, J_1 = 6.5 Hz, J_2 = 1 Hz, 1H), 8.05 (s, 1H), 7.68 (t, J = 2 Hz, 1H), 7.61 (dt, J_1 = 9 Hz, J_2 = 1 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.21-7.17 (m, 1H), 6.86 (td, J_1 = 7 Hz, J_2 = 1 Hz, 1H), 6.80 (d, J_1 = 8 Hz, 1H), 4.15 (td, J_1 = 7 Hz, J_2 = 1 Hz, 2H), 3.02 (t, J = 7 Hz, 2H), 1.67-1.61 (m, 2H), 1.59-1.54 (m, 2H), 1.42-1.32 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): 161.2, 157.2, 129.8, 126.5, 122.6, 118.5, 116.7, 115.3, 114.9, 112.5, 63.9, 48.2, 30.4, 28.4, 26.5, 25.6. HRMS (ESI) m/z: $[M+H]^+$: $C_{20}H_{22}N_3O_3^+$, calculated 352.1656; found 352.1656.

3-(6-(2-hydroxyphenyl)imidazo[2,1-*b*]thiazol-5-yl)-1,6,3-dioxazocan-2-one (3s)



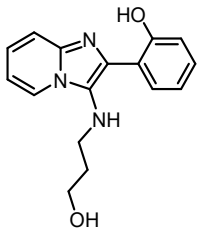
82 mg, 53% yield, brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): 8.21 (d, J = 8 Hz, 1H), 7.55 (d, J = 4.5 Hz, 1H), 7.22-7.18 (m, 1H), 7.01 (d, J = 7.5 Hz, 1H), 6.93-6.88 (m, 2H), 3.92 (dd, J_1 = J_2 = 4.5 Hz, 4H), 3.24-3.22 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): 156.3, 144.8, 129.6, 128.9, 126.8, 118.9, 118.3, 117.5, 117.4, 113.0, 67.3, 50.6. HRMS (ESI) m/z: $[M+H]^+$: $C_{16}H_{16}N_3O_4S^+$, calculated 346.0856; found 346.0856.

3-((2-(4-chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)amino)propan-1-ol (4)



173 mg, 65% yield, light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): 8.08 (dt, J_1 = 7 Hz, J_2 = 1.5 Hz, 1H), 7.96 (dt, J_1 = 9 Hz, J_2 = 2.5 Hz, 2H), 7.54 (dt, J_1 = 9 Hz, J_2 = 1 Hz, 1H), 7.40 (dt, J_1 = 9 Hz, J_2 = 2.5 Hz, 2H), 7.15 (ddd, J_1 = 9 Hz, J_2 = 7 Hz, J_3 = 1.5 Hz, 1H), 6.80 (td, J_1 = 7 Hz, J_2 = 1 Hz, 1H), 3.86 (t, J = 6 Hz, 2H), 3.47 (t, J = 6 Hz, 1H), 3.18 (q, J = 6 Hz, 2H), 1.90 (br s, 1H), 1.86 (quint, J = 6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 141.6, 134.6, 133.1, 132.8, 128.8, 128.2, 126.2, 124.2, 122.4, 117.5, 112.0, 61.5, 46.2, 32.7. HRMS (ESI) m/z: $[M+H]^+$: $C_{16}H_{17}ClN_3O^+$, calculated 302.1054; found 302.1056.

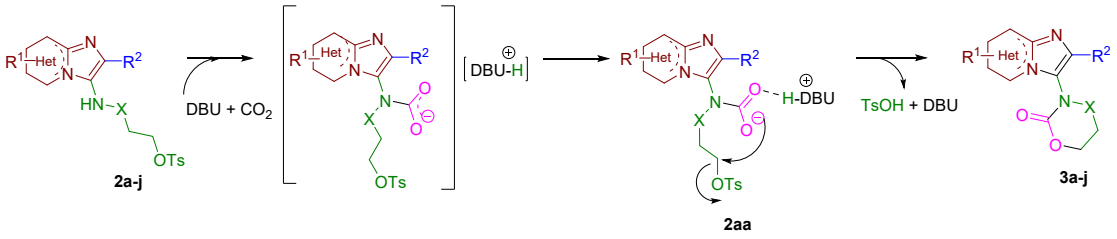
2-(3-((3-hydroxypropyl)amino)imidazo[1,2-*a*]pyridin-2-yl)phenol (6)



109 mg, 58% yield, light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): 8.37 (s, 1H), 8.03 (dt, J_1 = 6.5 Hz, J_2 = 1 Hz, 1H), 7.65 (dt, J_1 = 6 Hz, J_2 = 1 Hz, 1H), 7.55 (dd, J_1 = 8 Hz, J_2 = 1.5 Hz, 1H), 7.41-7.38 (m, 1H), 7.29-7.26 (m, 1H), 7.06 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 1H), 7.02 (td, J_1 = 7 Hz, J_2 = 1 Hz, 1H), 6.89-6.86 (m, 1H), 4.06-4.01 (m, 1H), 3.82-3.77 (m, 1H), 3.75-3.69 (m, 2H), 1.81-1.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 165.3, 158.1, 140.9, 139.7, 130.7, 126.8, 125.4, 121.4, 119.2, 118.2, 117.3, 114.8, 114.3, 59.9, 43.8, 31.2. HRMS (ESI) m/z: $[M+H]^+$: $C_{16}H_{18}N_3O^+$, calculated 284.1394; found 284.1392.

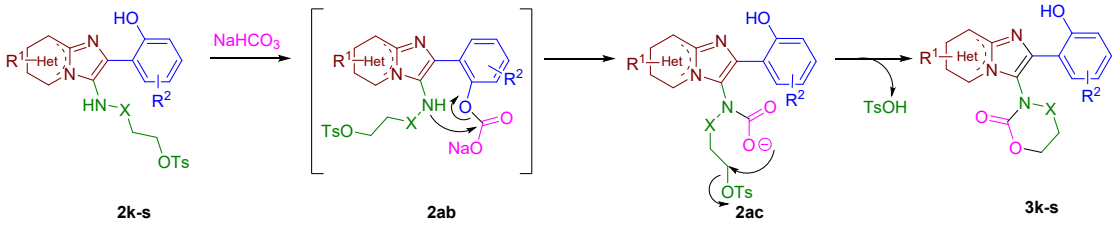
4. Proposed mechanisms for the 3a-j and 3k-s adducts

The proposed mechanism proceeds via the nucleophilic attack of -NH on carbon dioxide to form the carbamate anion **2aa** which can be stabilized by intermolecular hydrogen bond with protonated DBU.[1] A nucleophilic substitution S_N2 of the carbamate anion with the -OTs group affords the cyclic carbamates **3a-j**.



Scheme S1. Plausible mechanism for the CO_2 fixation by GBB adducts **3a-j**.

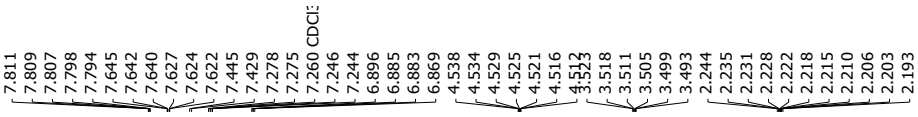
The reaction possibly starts with the nucleophilic addition of the secondary amine to the phenolic intermediate **2ab** and subsequently to the carbamate **2ac**,[2] which through a S_N2 reaction yields carbamates **3k-s** accompanied by the elimination of the leaving group of -OTs.

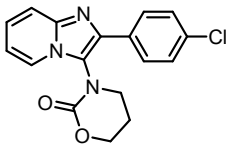


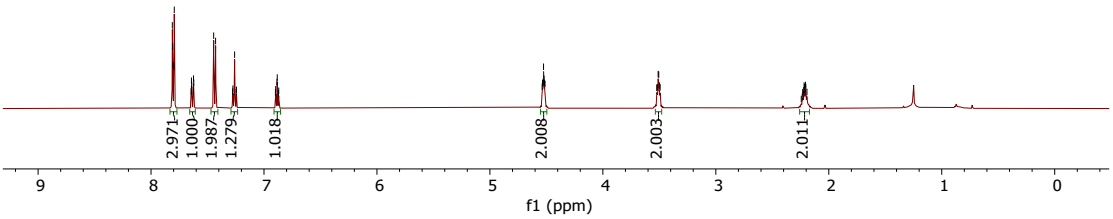
Scheme S2. Proposed mechanism of the synthesis of the cyclic carbamates **3k-s**.

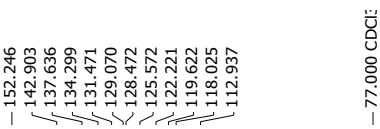
5. Exemplary copies of NMR spectra of novel compounds

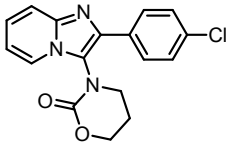
3-(2-(4-chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3a)

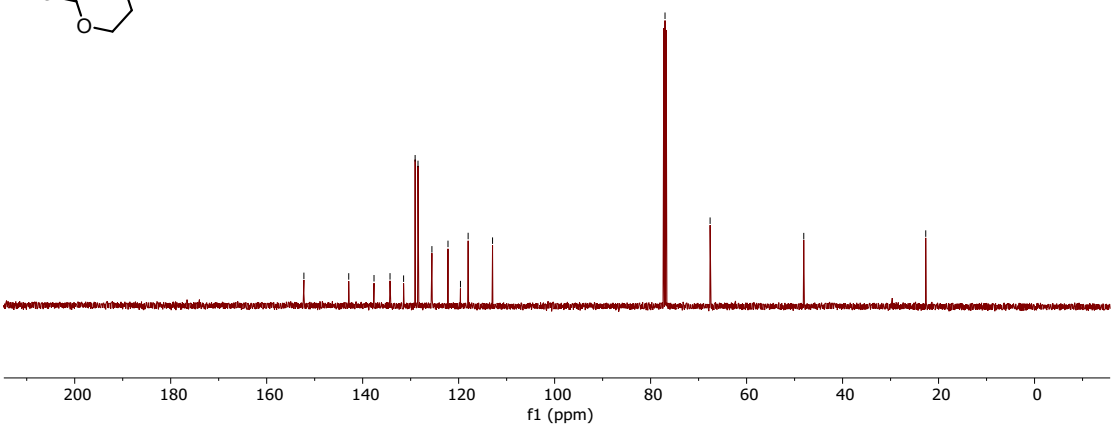




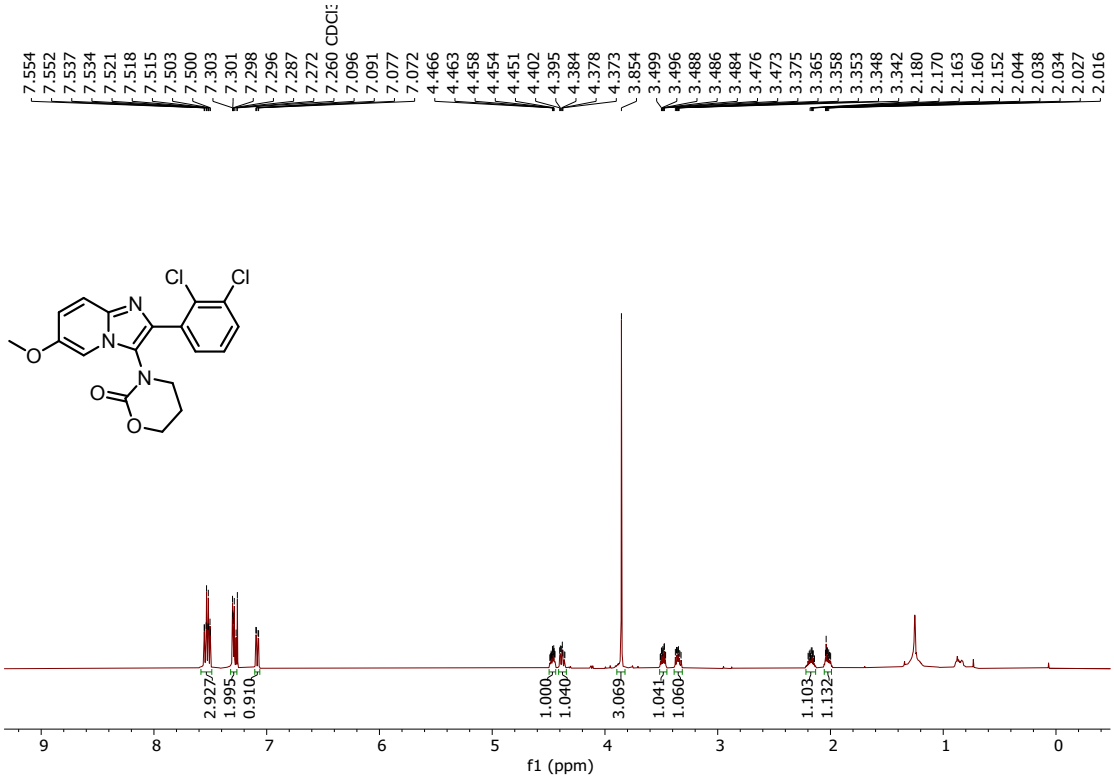


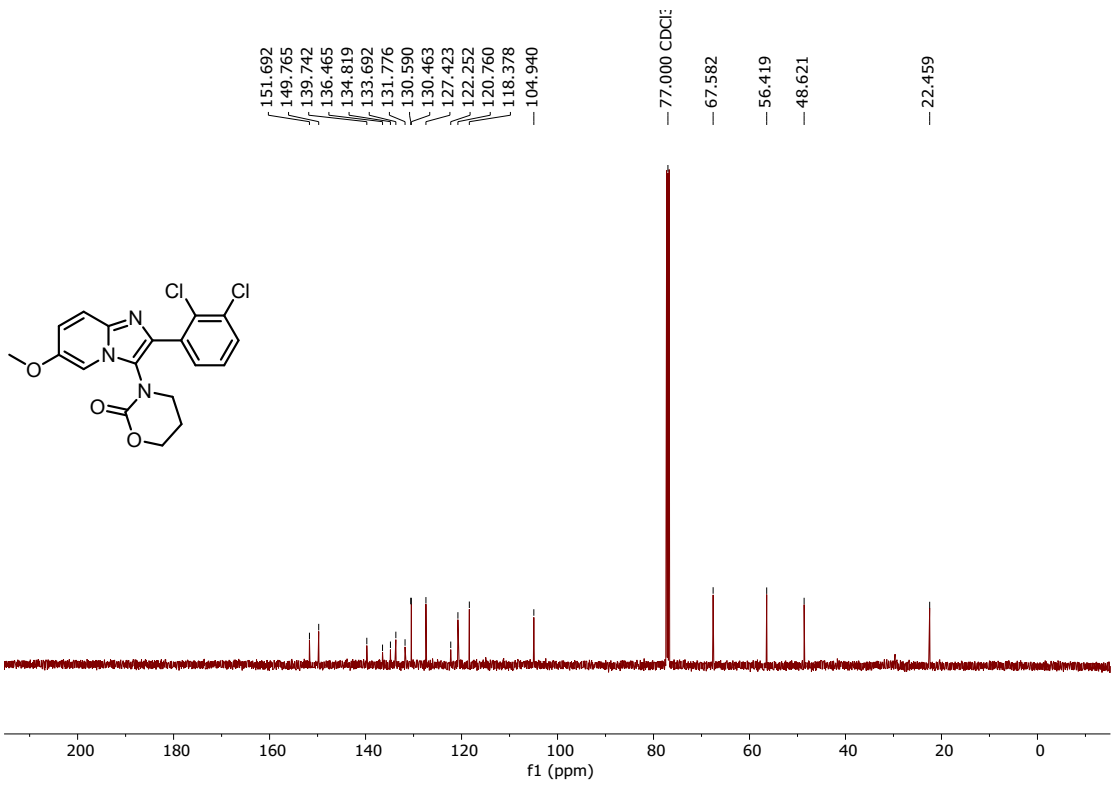




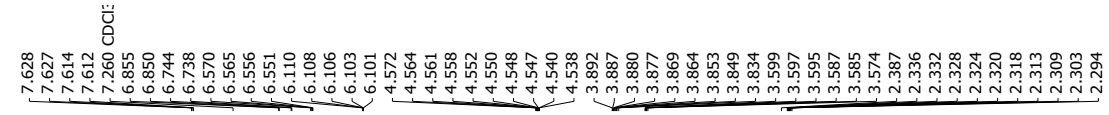


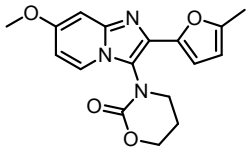
3-(2-(2,3-dichlorophenyl)-6-methoxyimidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3b)

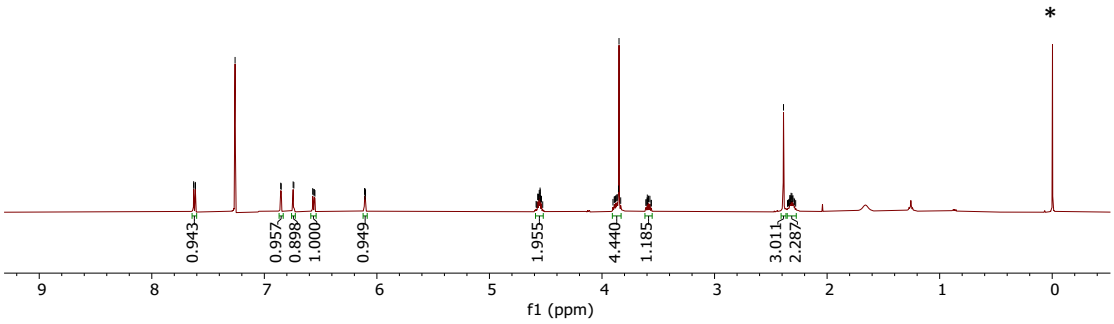




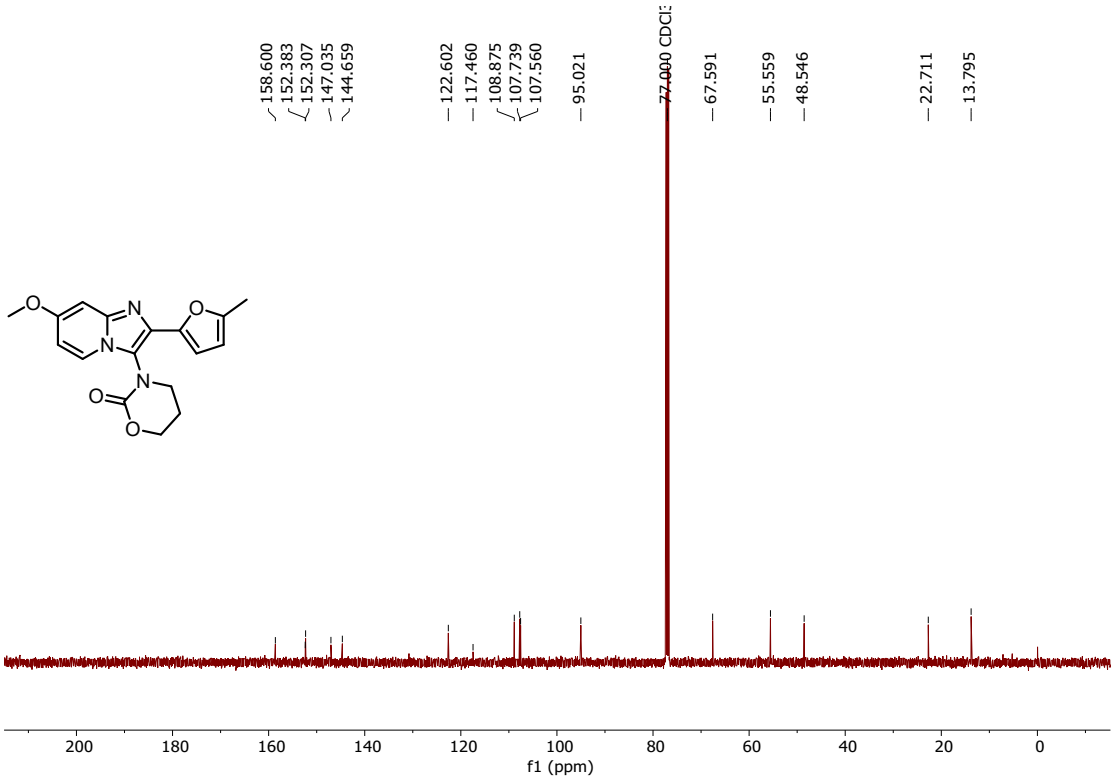
3-(7-methoxy-2-(5-methylfuran-2-yl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3c)



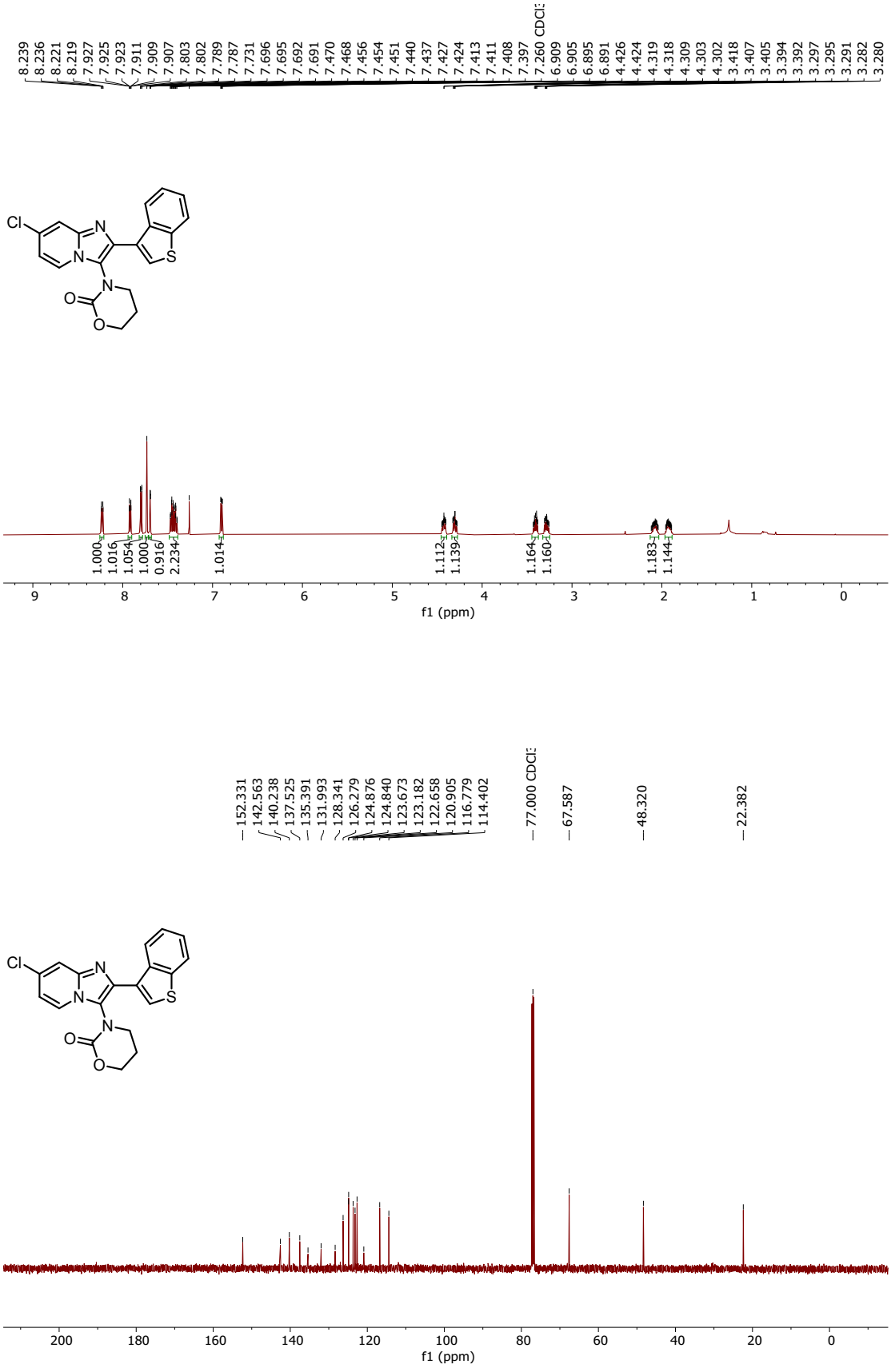




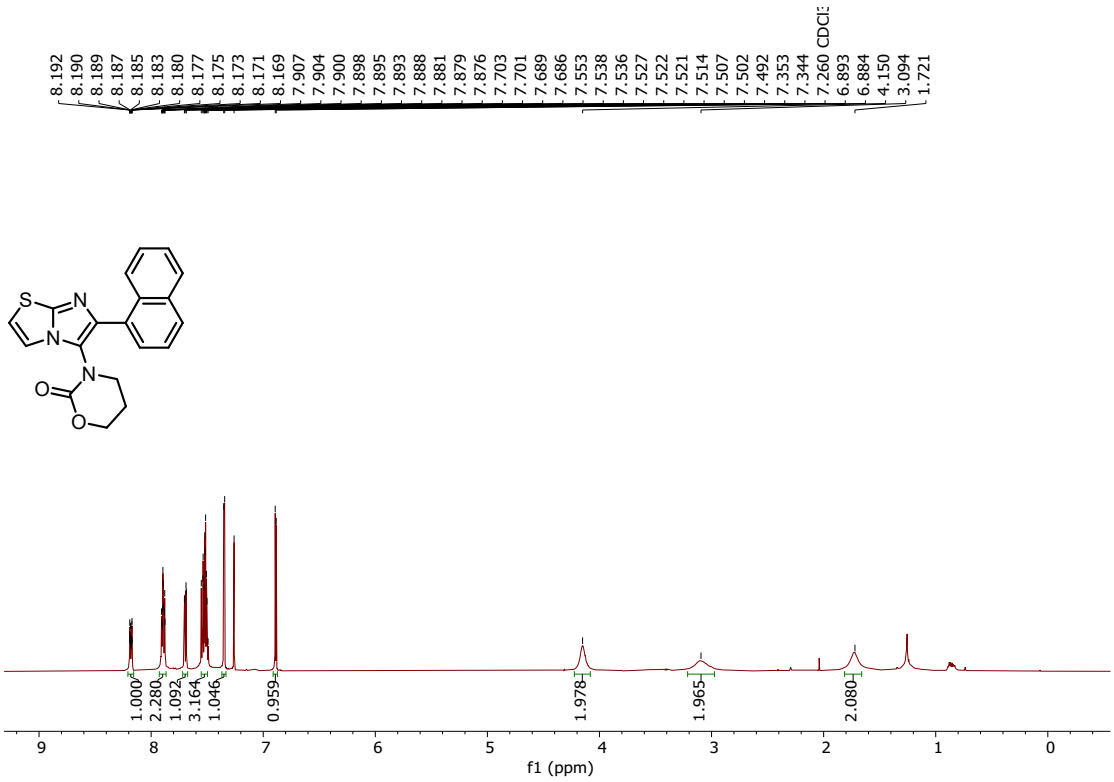
***:** TMS

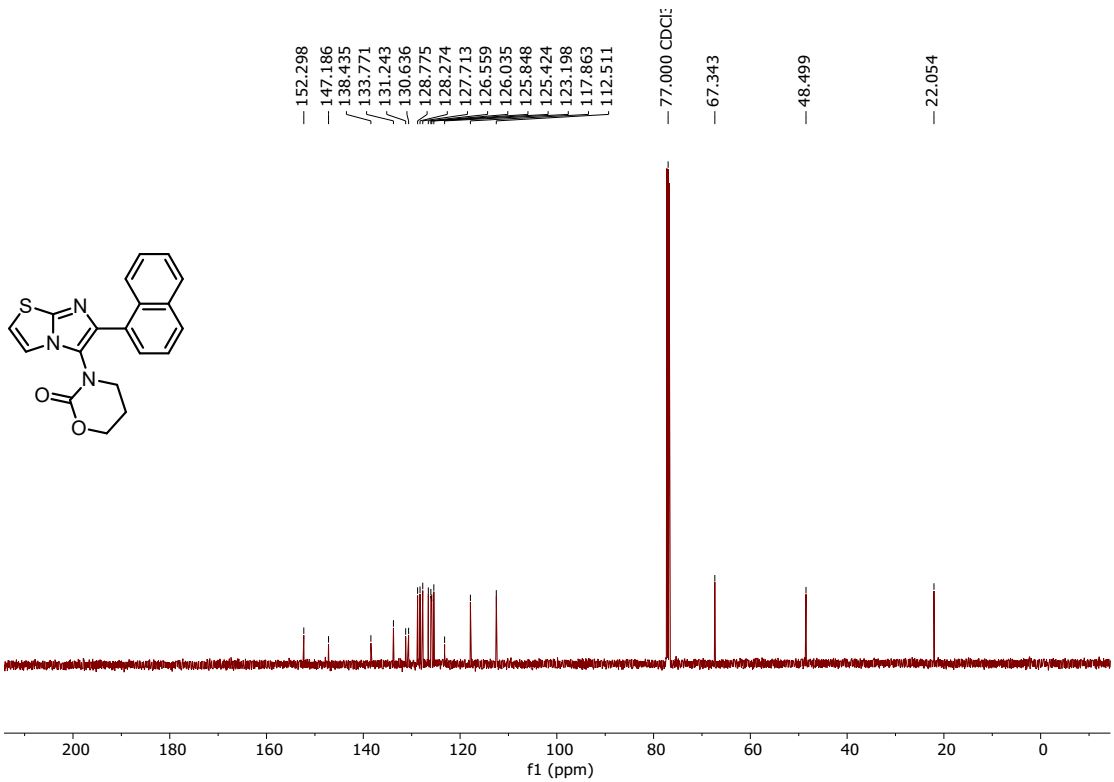


3-(2-(benzo[*b*]thiophen-3-yl)-7-chloroimidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3d)

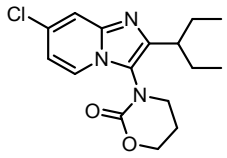


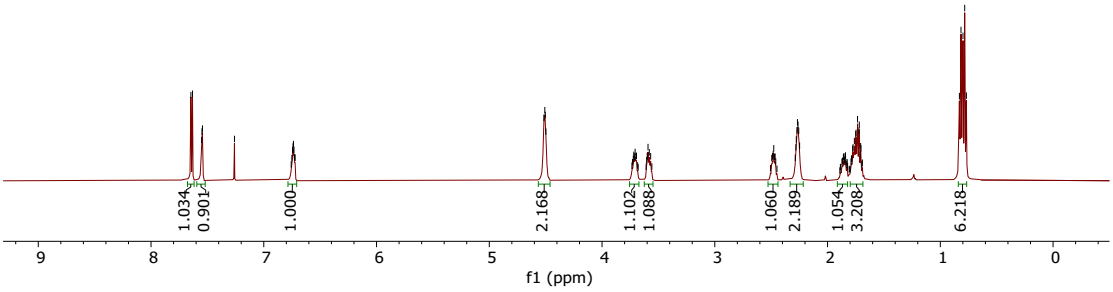
3-(6-(naphthalen-1-yl)imidazo[2,1-*b*]thiazol-5-yl)-1,3-oxazinan-2-one (3e)

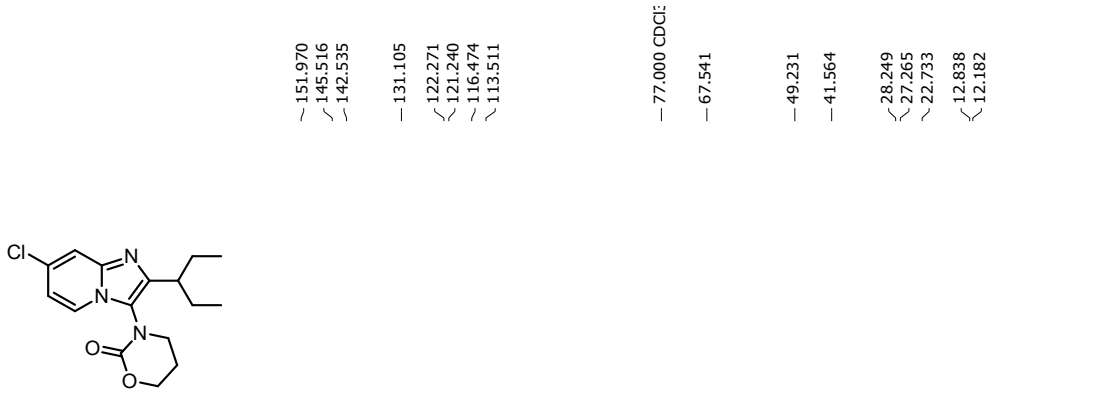


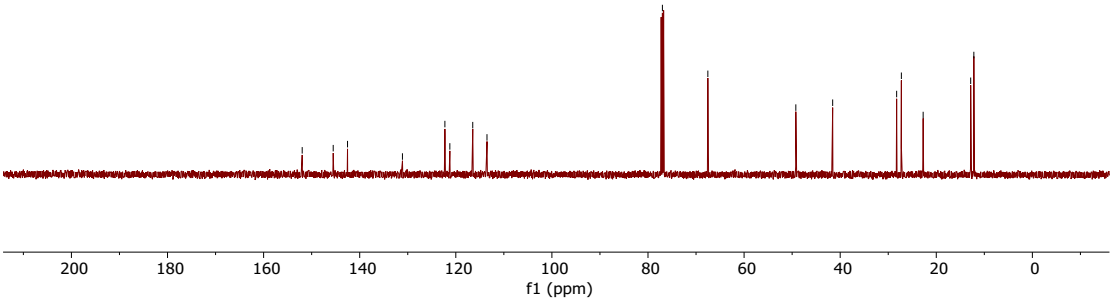


3-(7-chloro-2-(pentan-3-yl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3f)

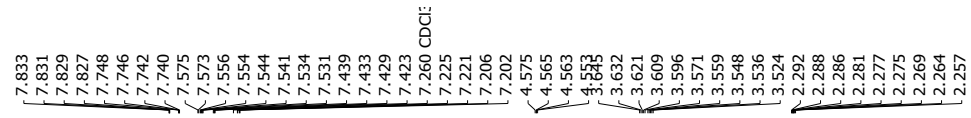


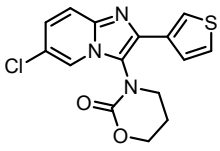


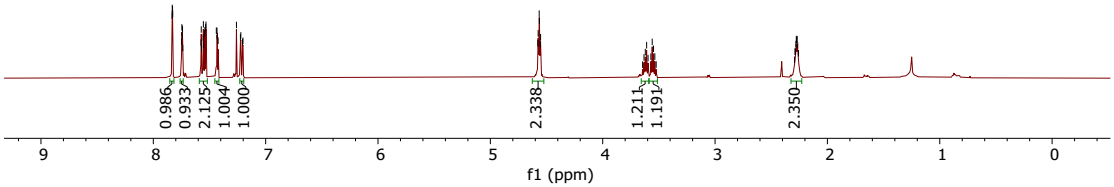


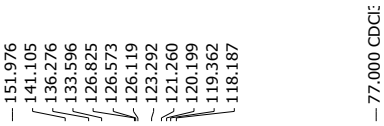


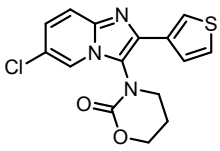
3-(6-chloro-2-(thiophen-3-yl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3g)

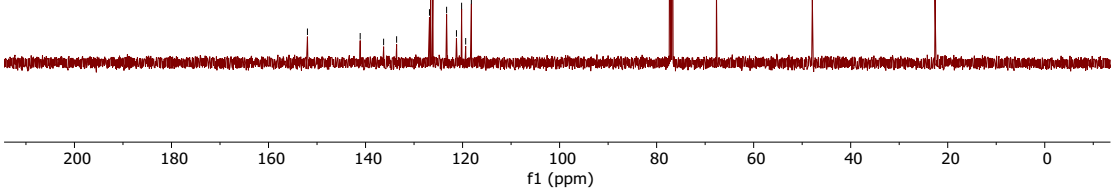




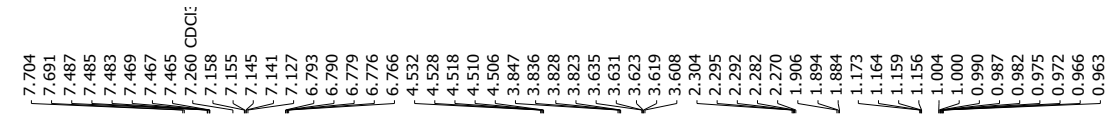


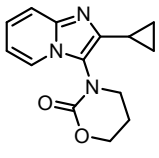


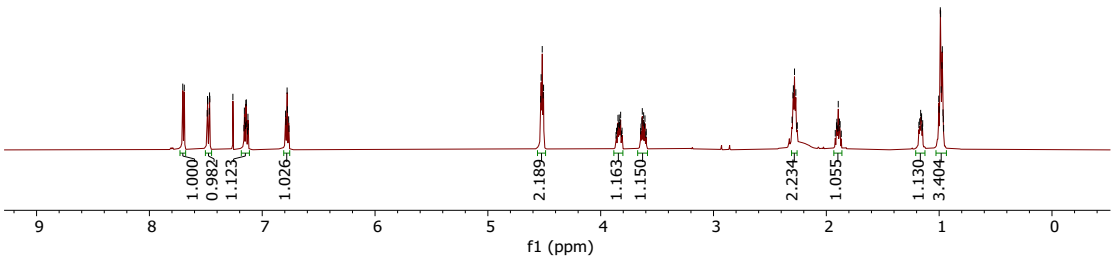


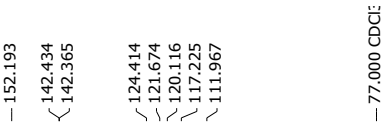


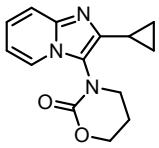
3-(2-cyclopropylimidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3h)

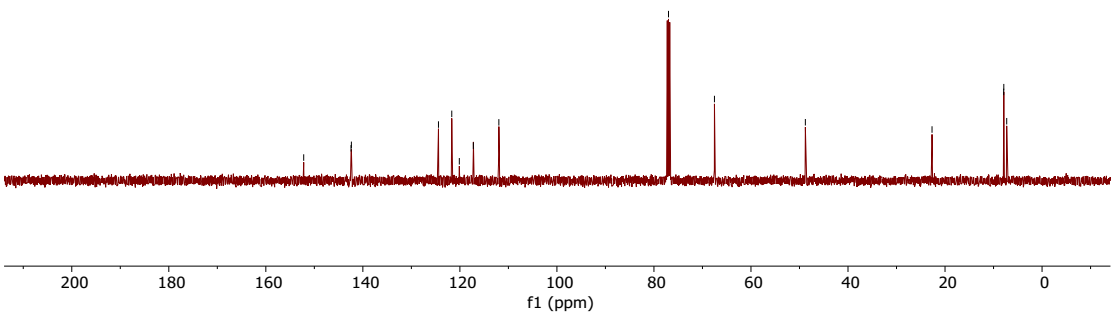




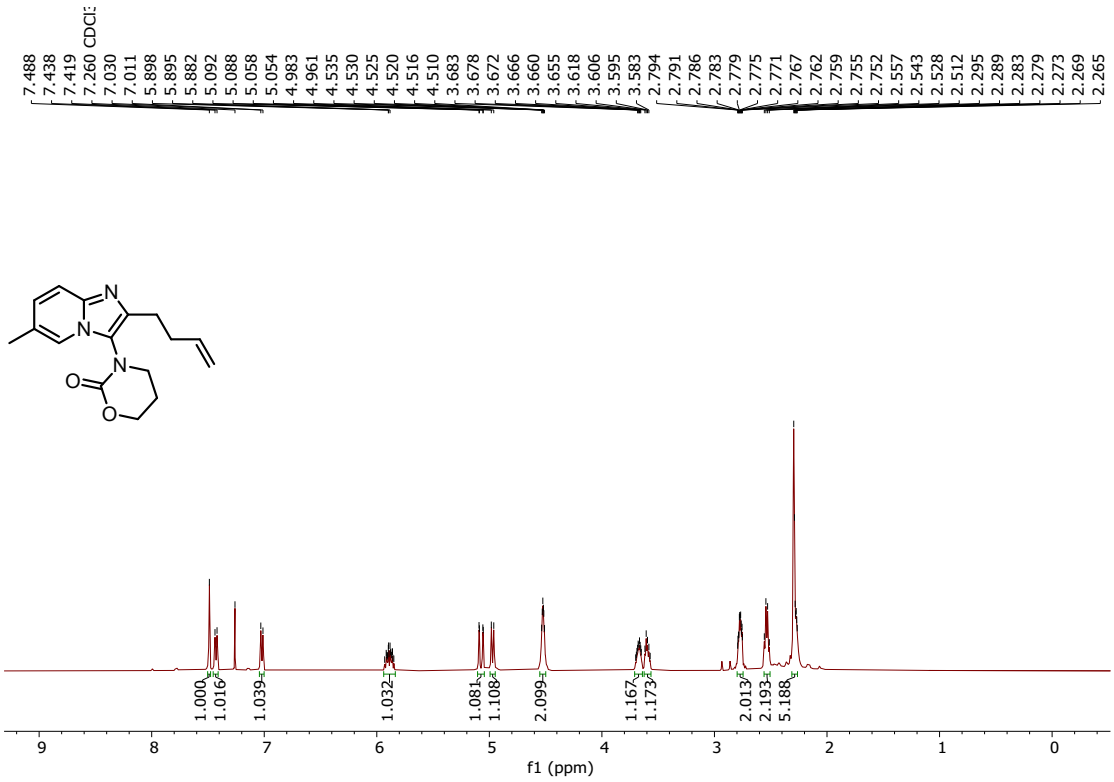


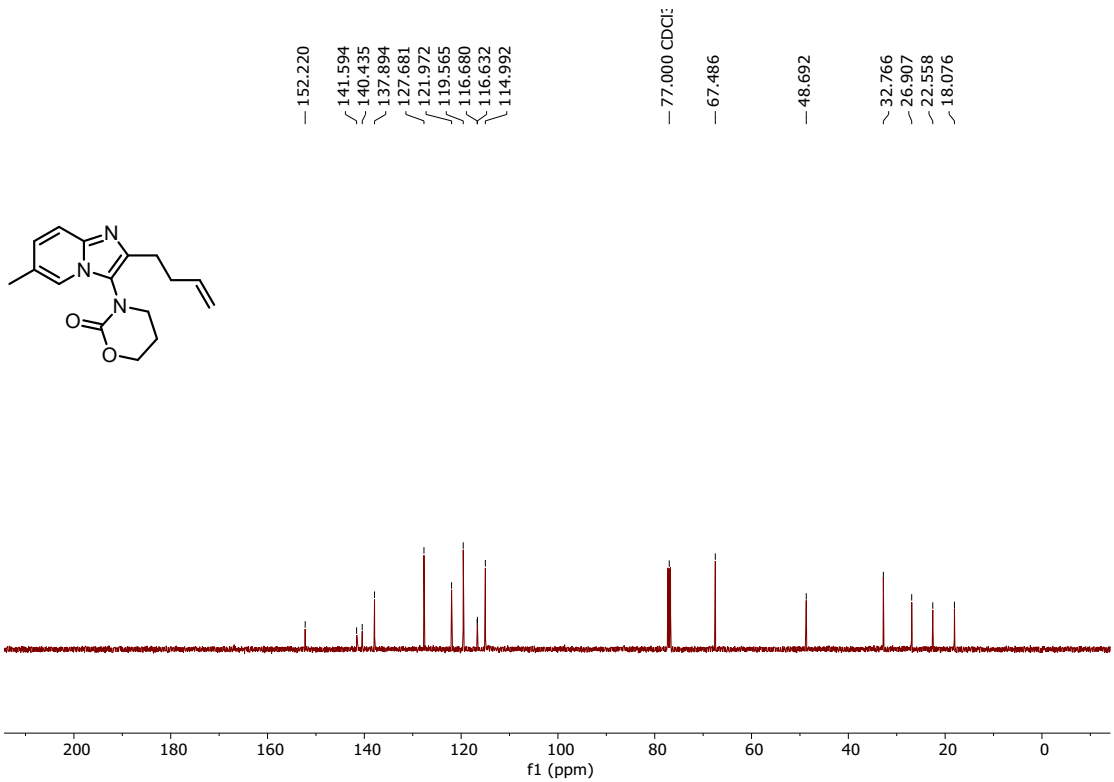




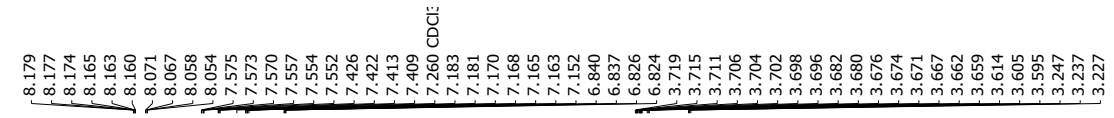


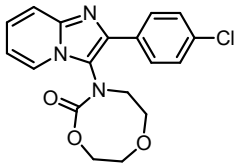
3-(2-(but-3-en-1-yl)-6-methylimidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3i)

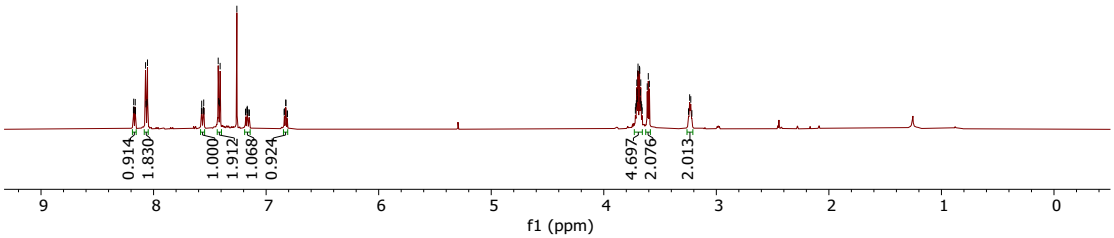


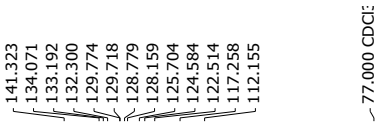


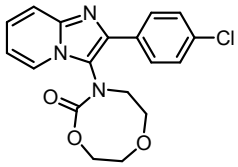
3-(2-(4-chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,6,3-dioxazocan-2-one (3j)



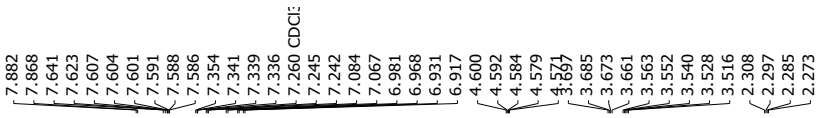


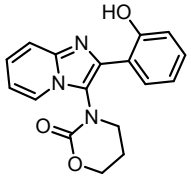


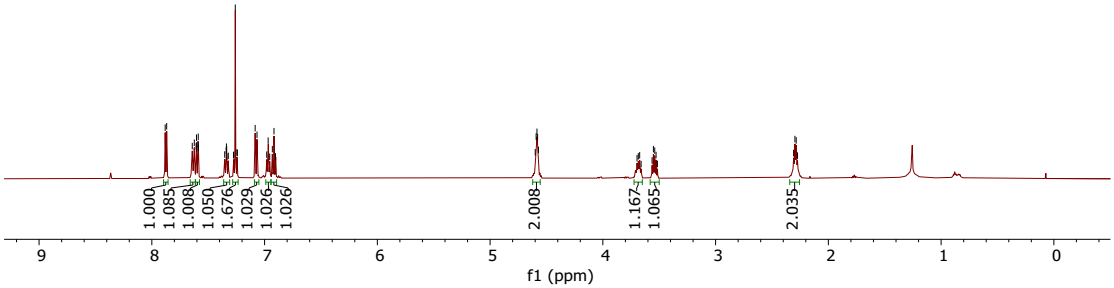


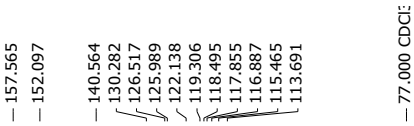


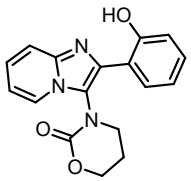
3-(2-(2-hydroxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3k)

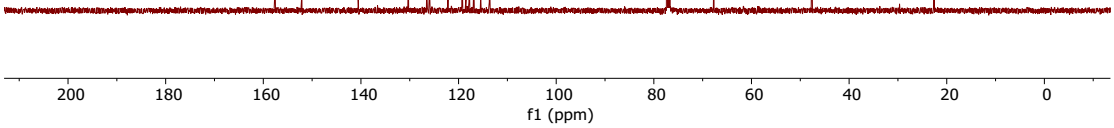




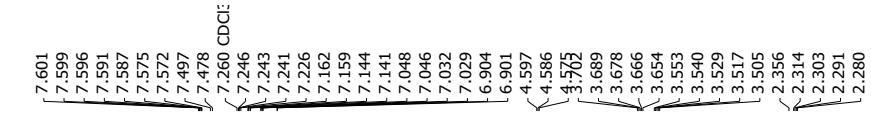


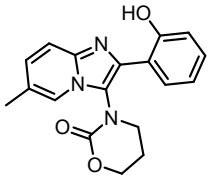


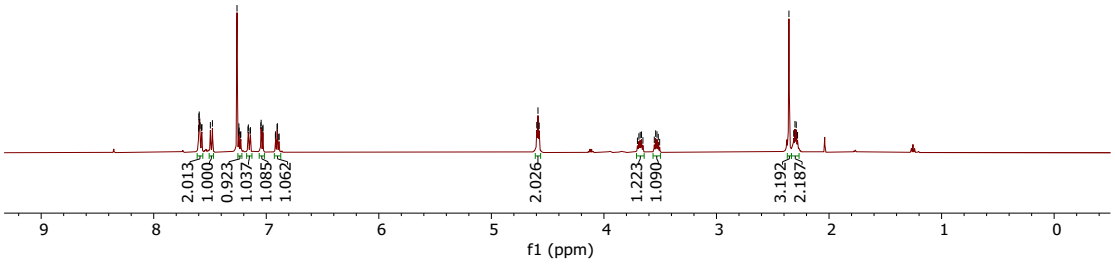


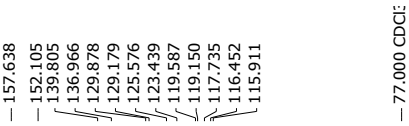


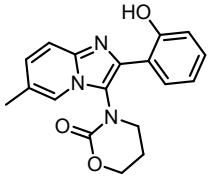
3-(2-(2-hydroxyphenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3l)

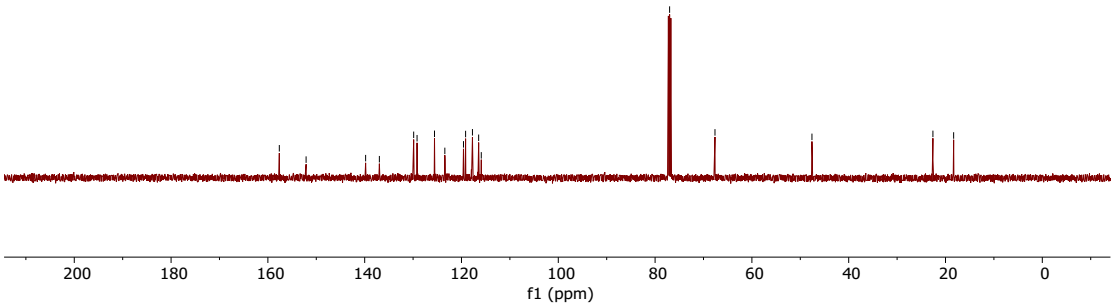




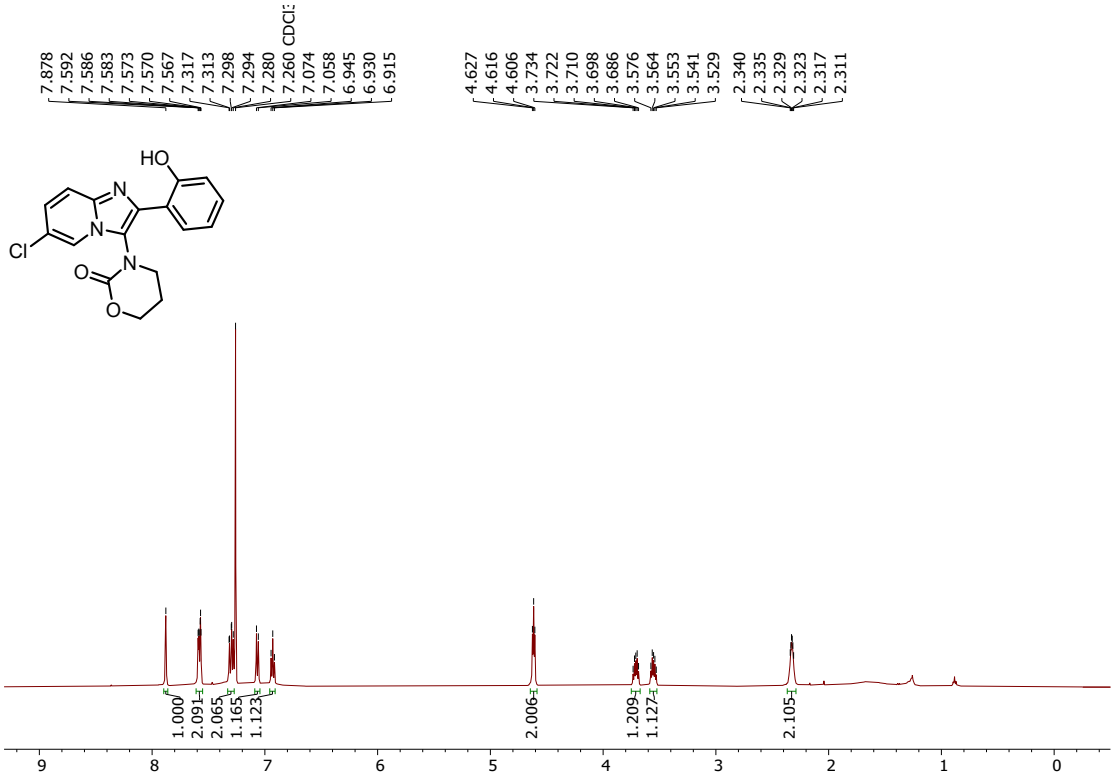


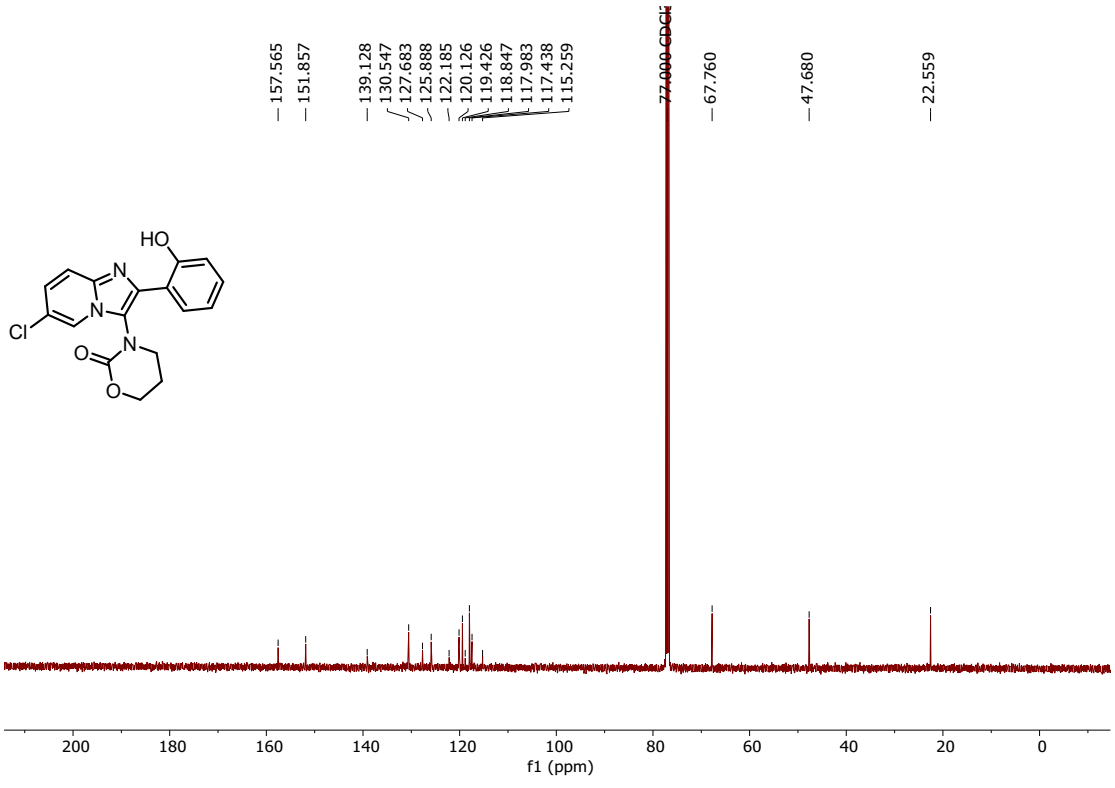




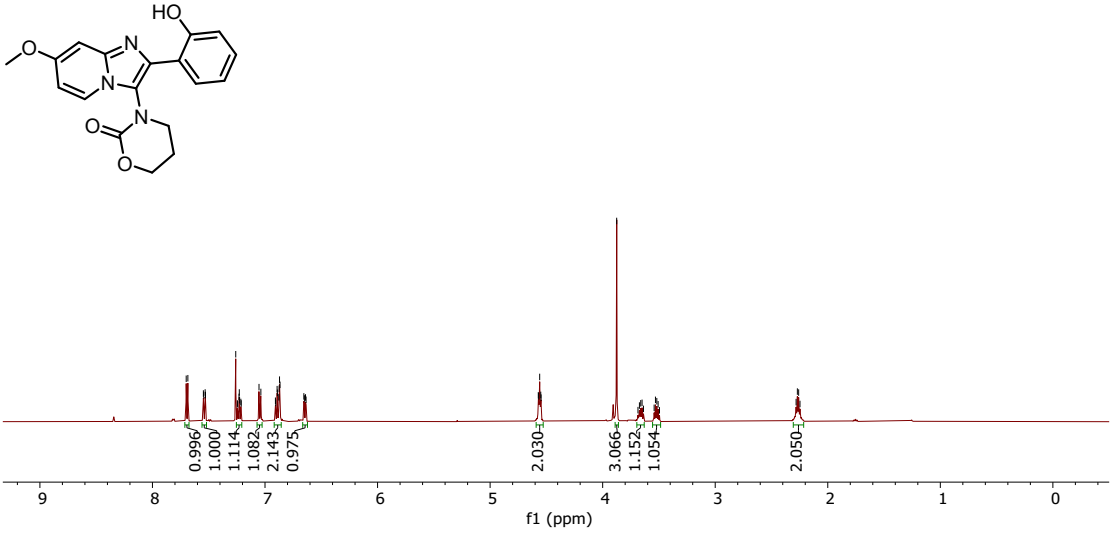


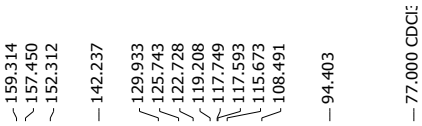
3-(6-chloro-2-(2-hydroxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3m)

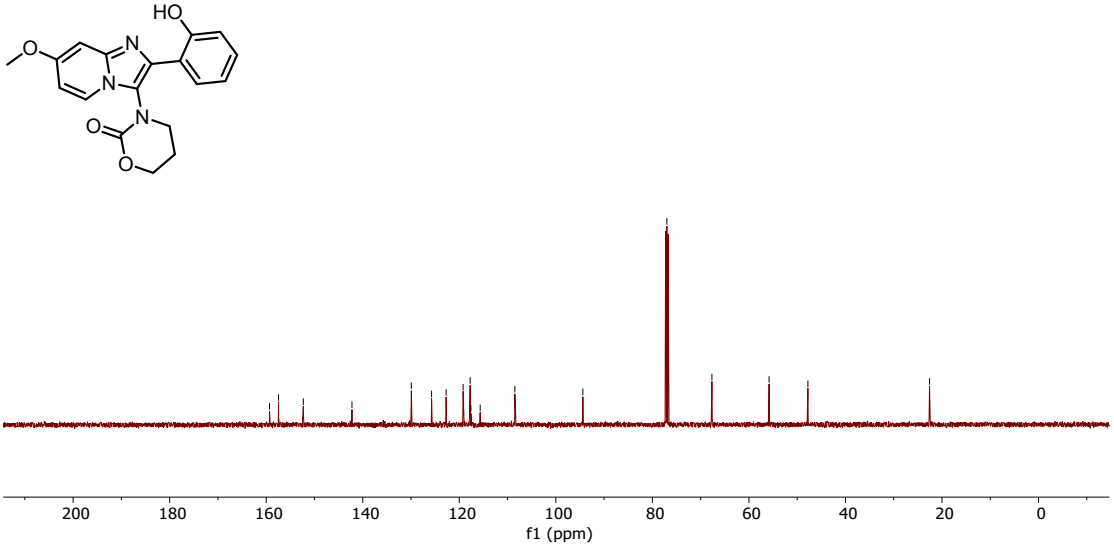




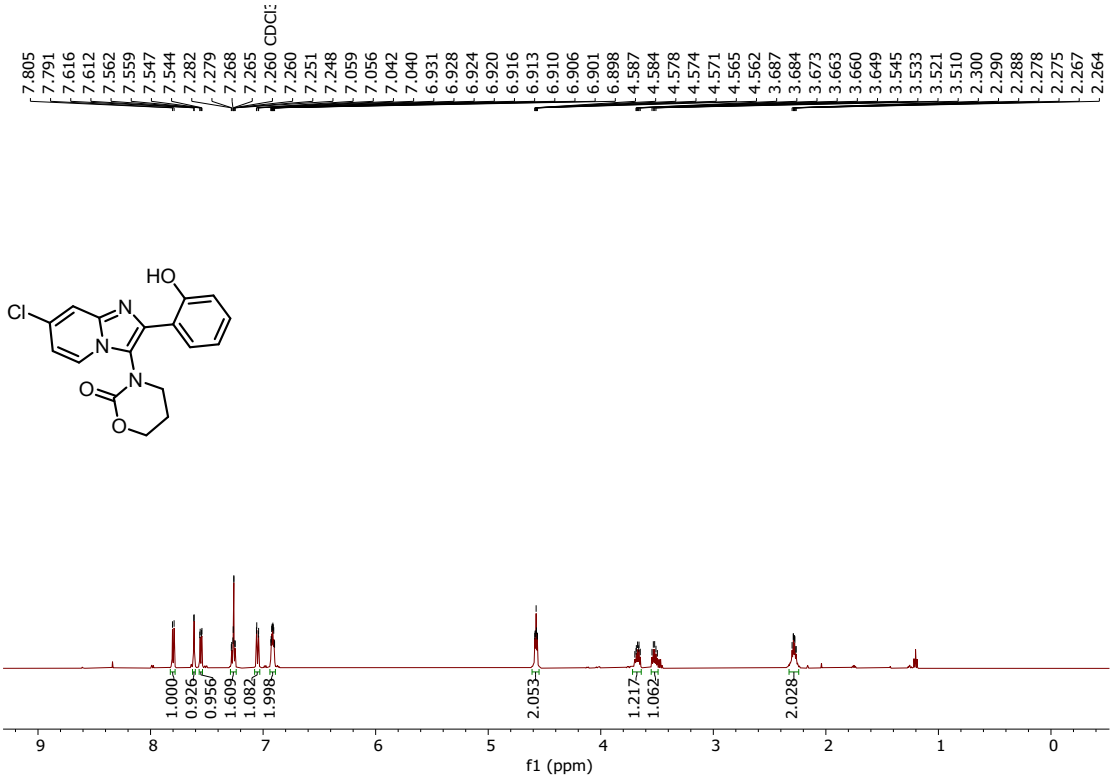
3-(2-(2-hydroxyphenyl)-7-methoxyimidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3n)

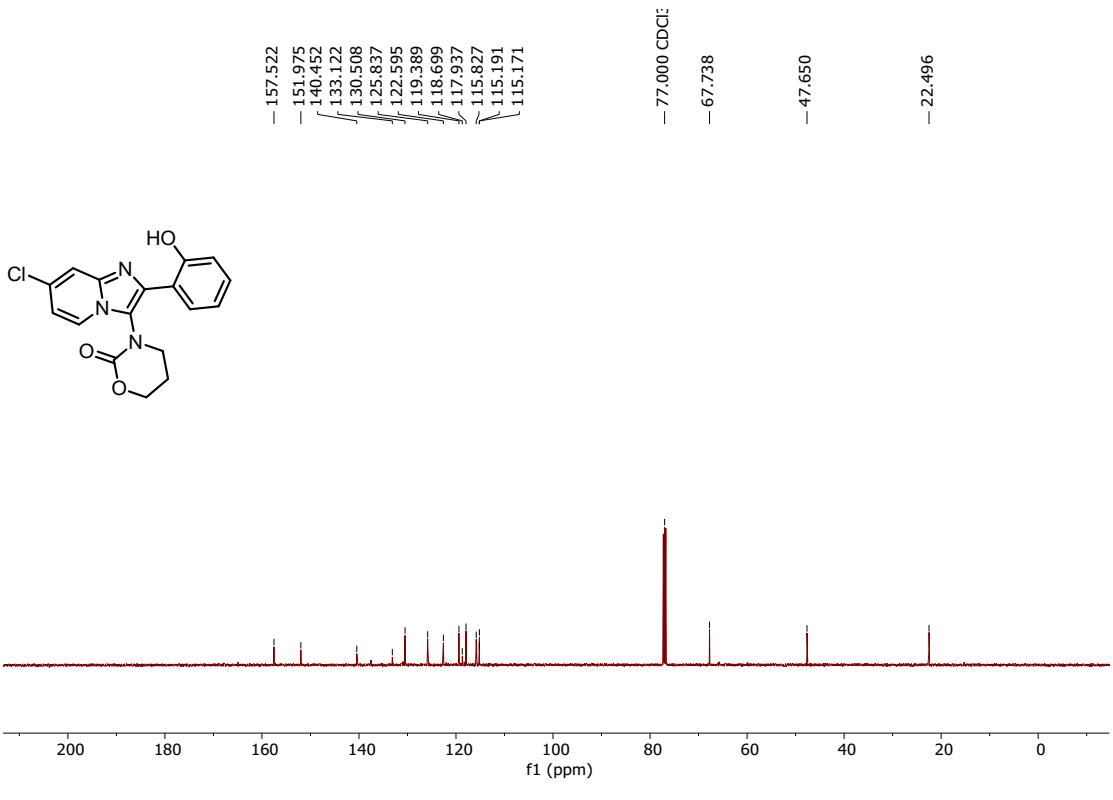




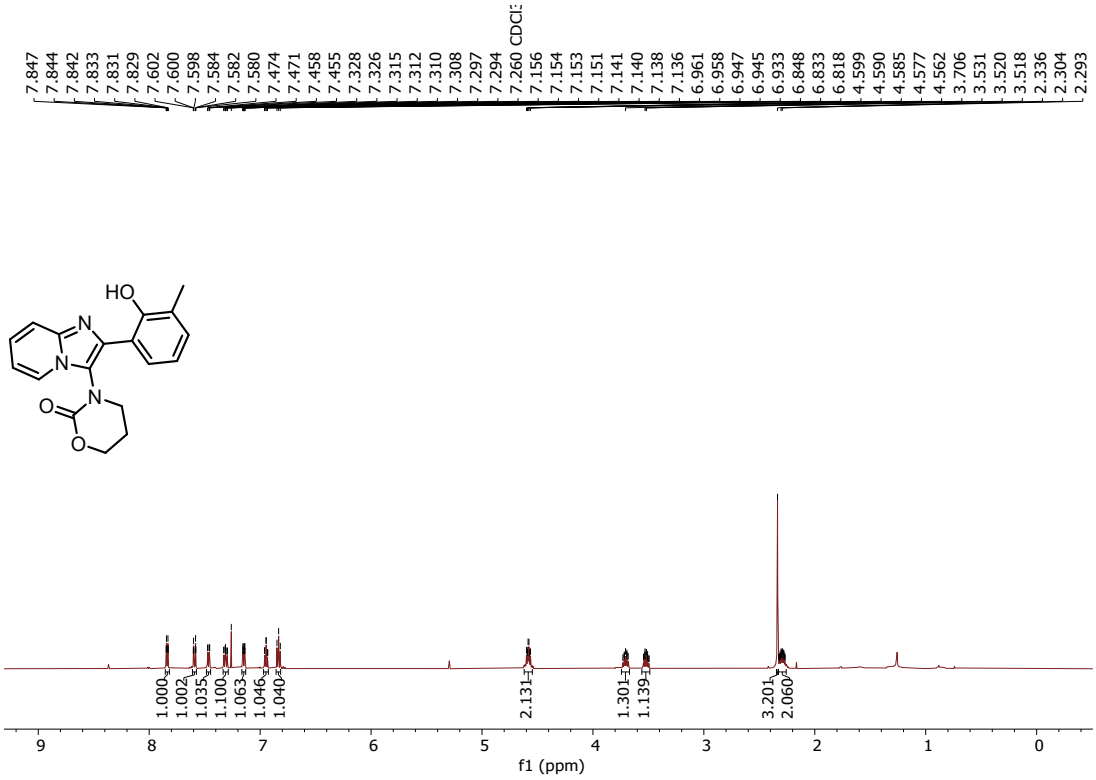


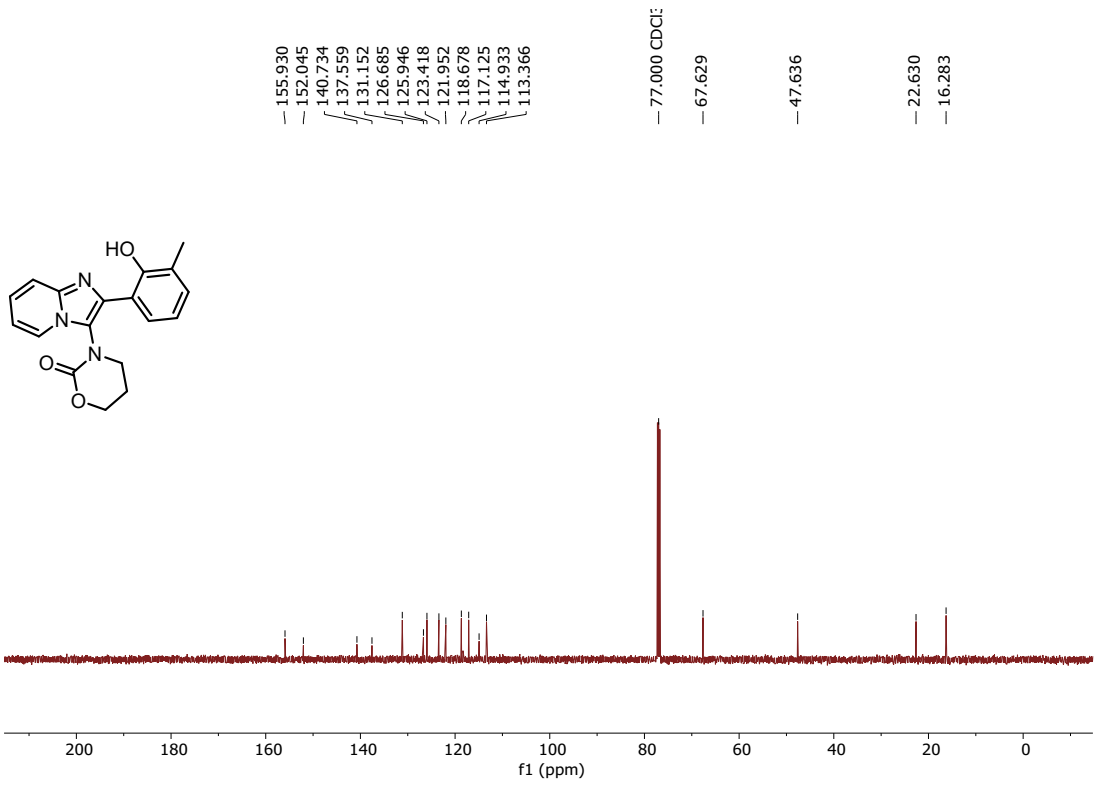
3-(7-chloro-2-(2-hydroxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3o)



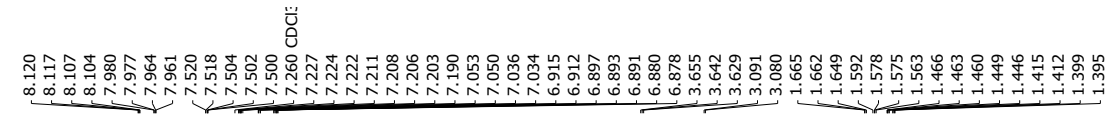


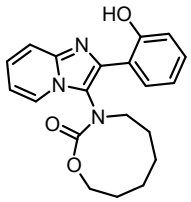
3-(2-(2-hydroxy-3-methylphenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazinan-2-one (3p)

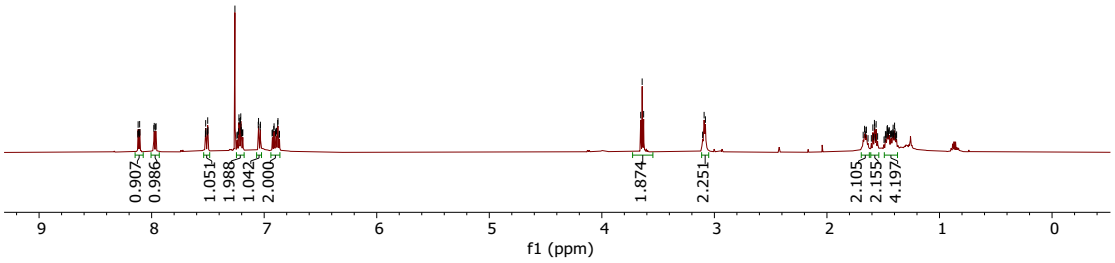


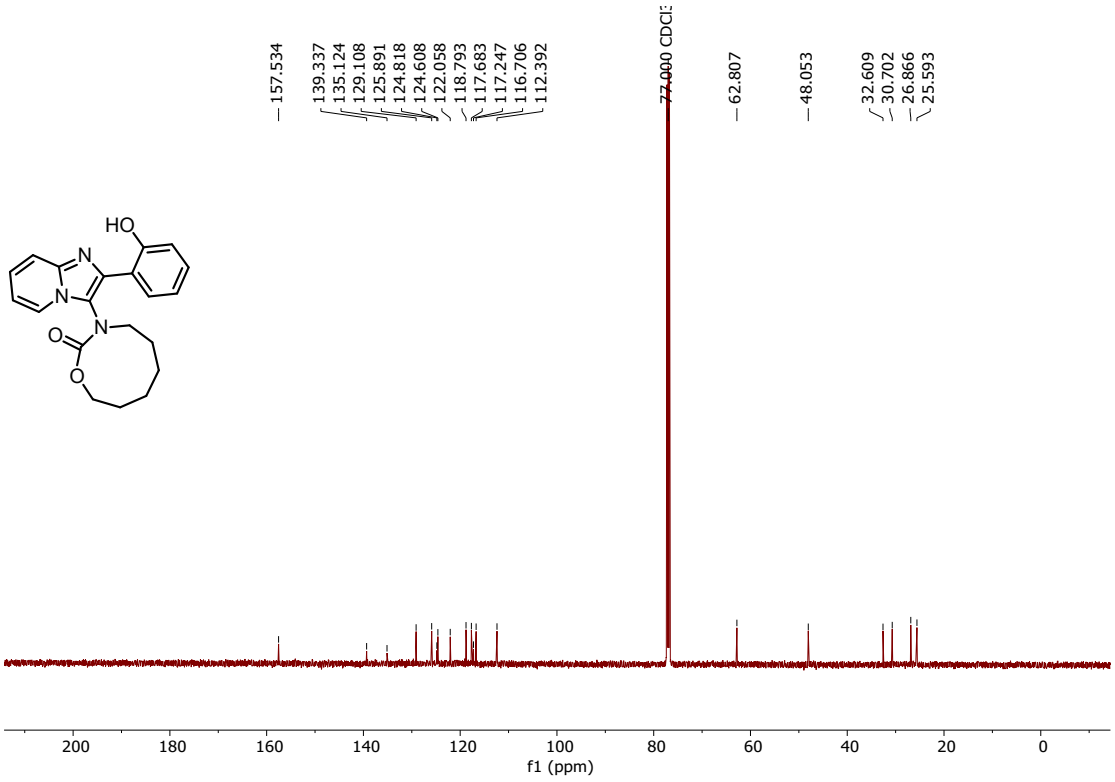


3-(2-(2-hydroxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazonan-2-one (3q)

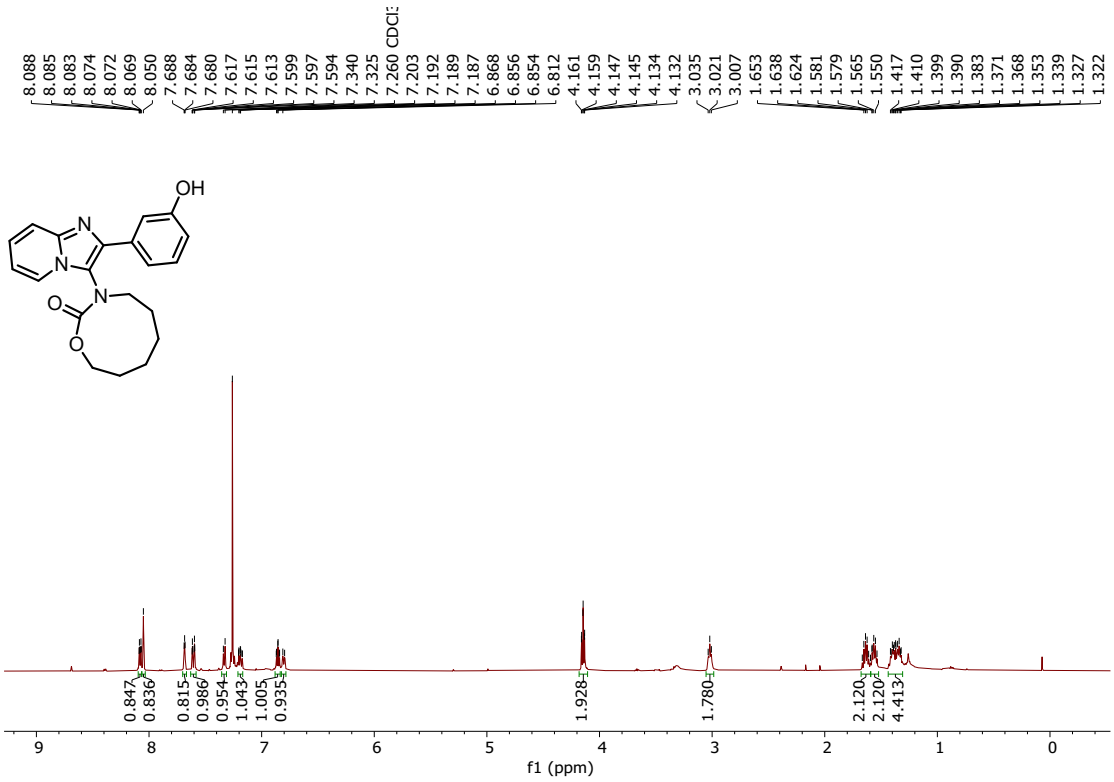


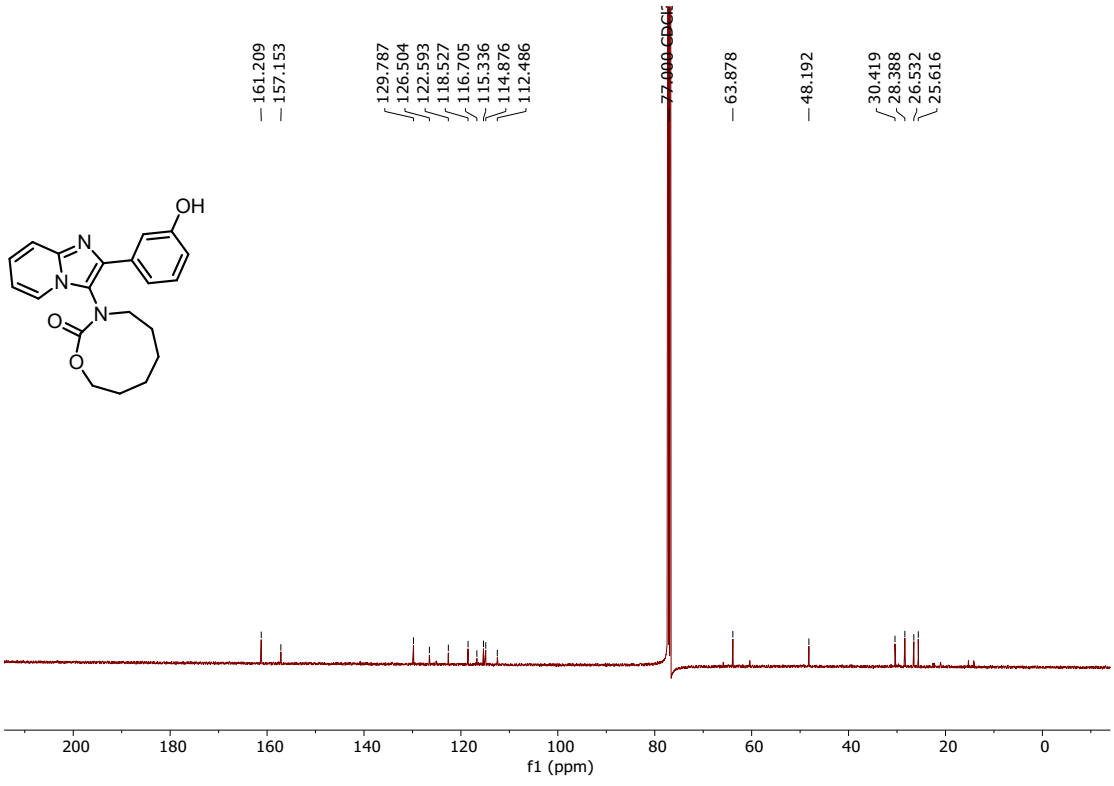




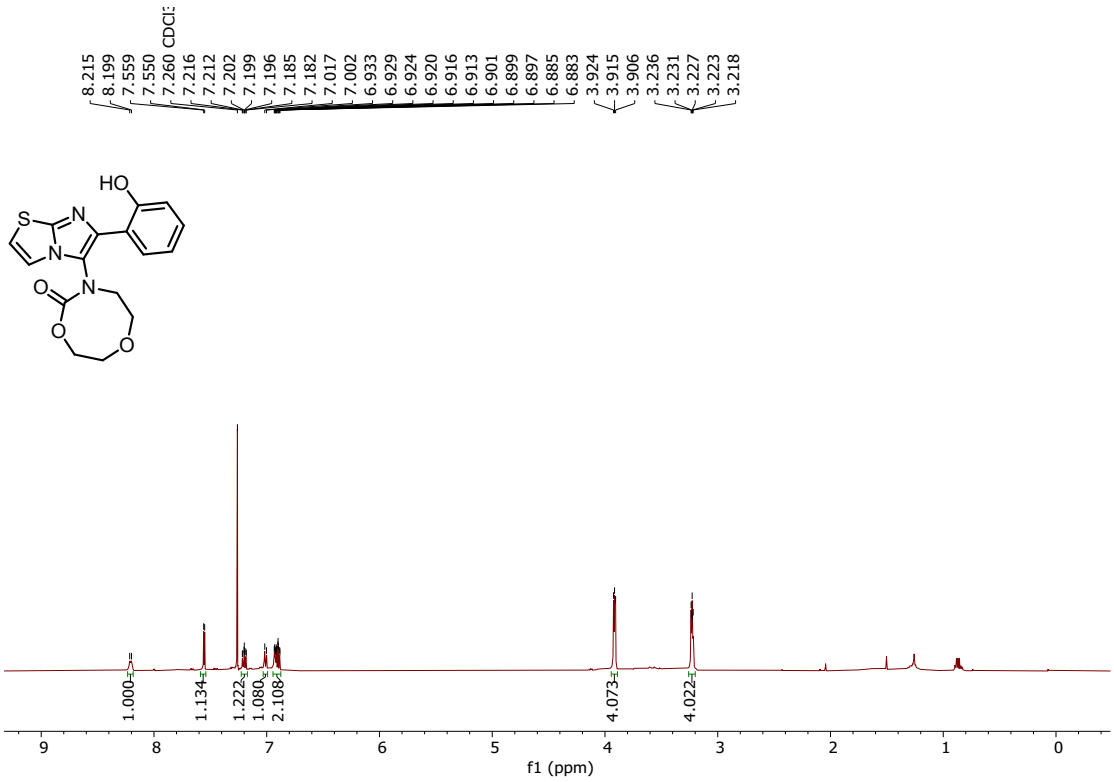


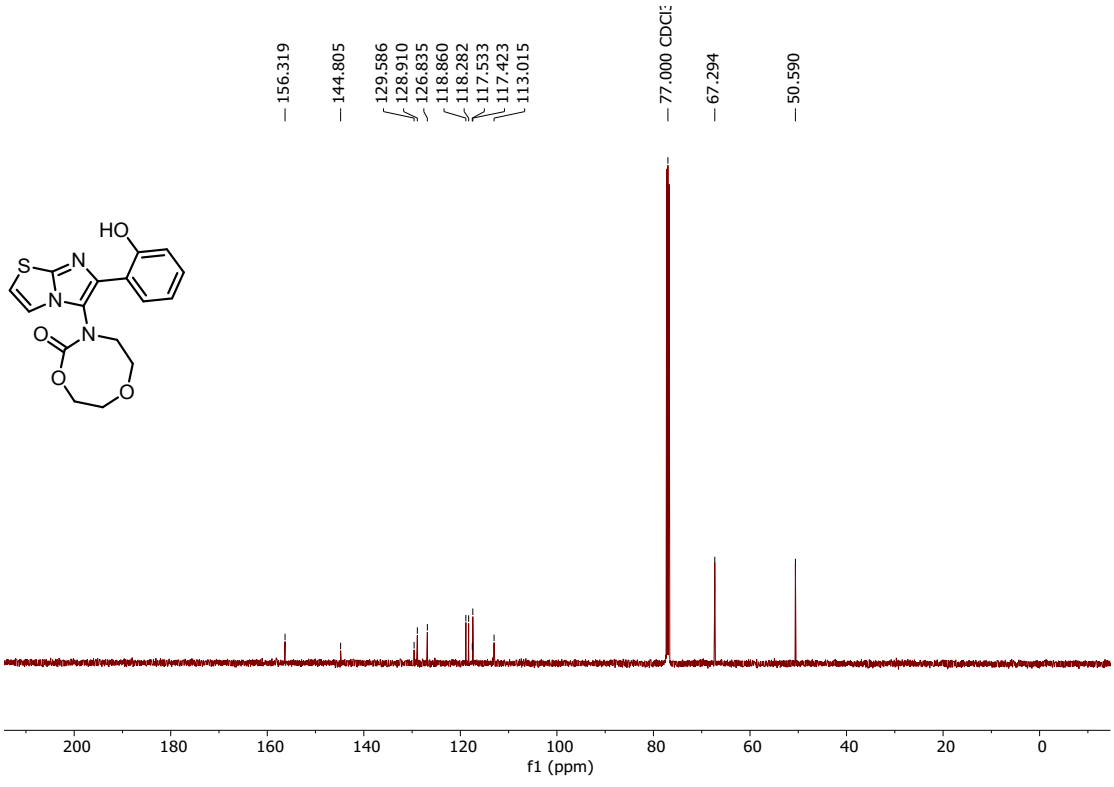
3-(2-(3-hydroxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)-1,3-oxazonan-2-one (3r)



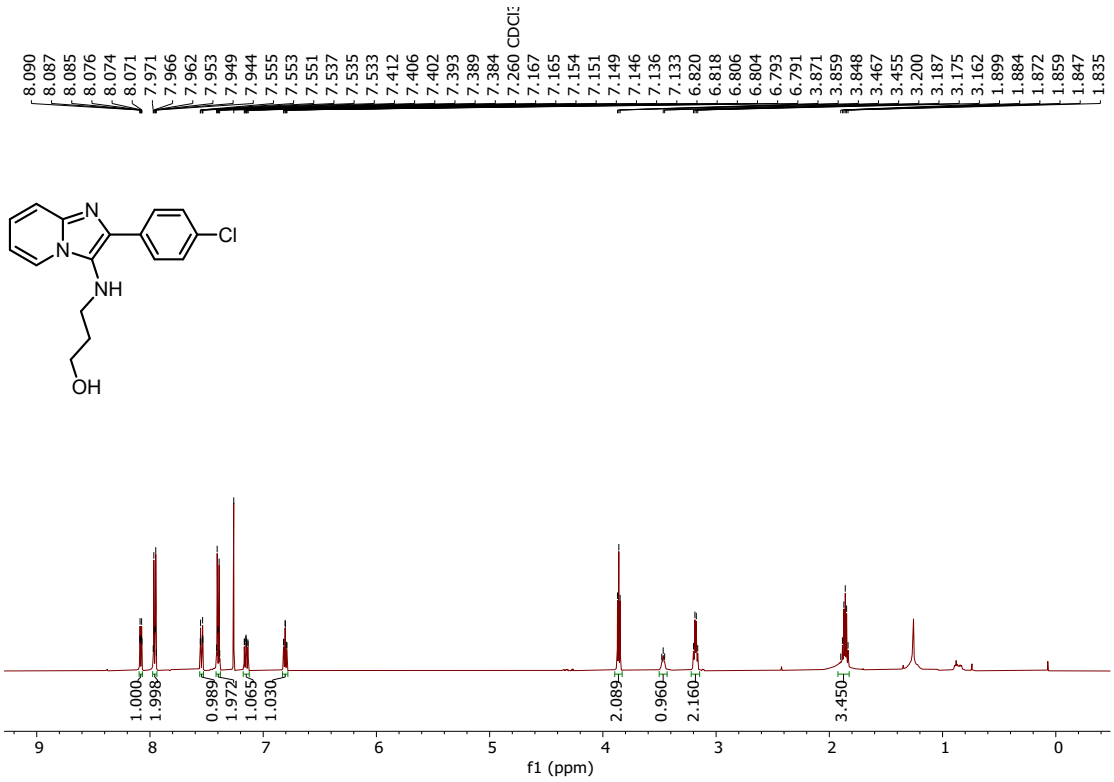


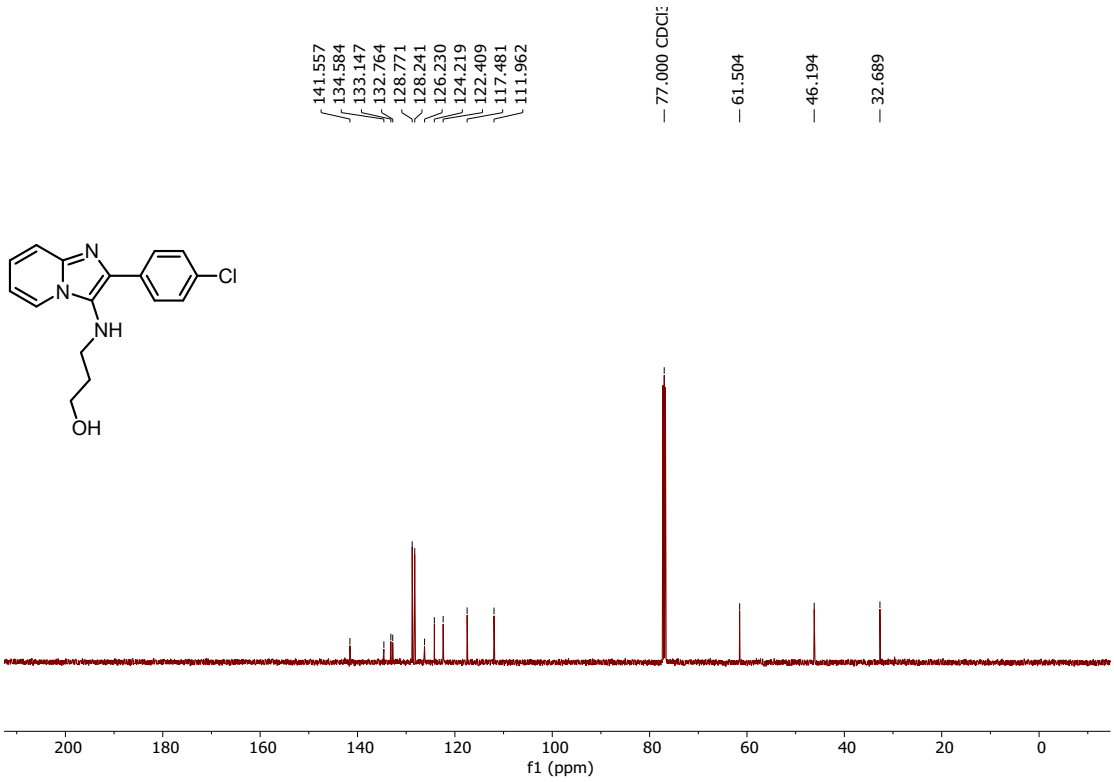
3-(6-(2-hydroxyphenyl)imidazo[2,1-*b*]thiazol-5-yl)-1,6,3-dioxazocan-2-one (3s)



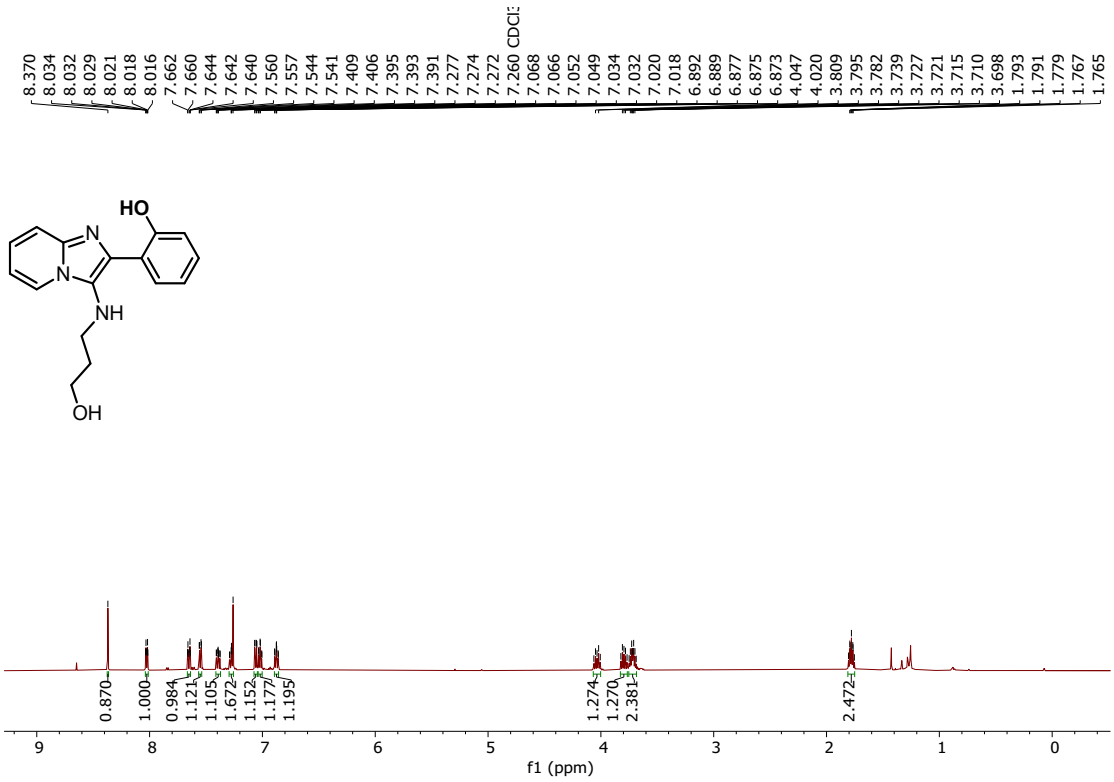


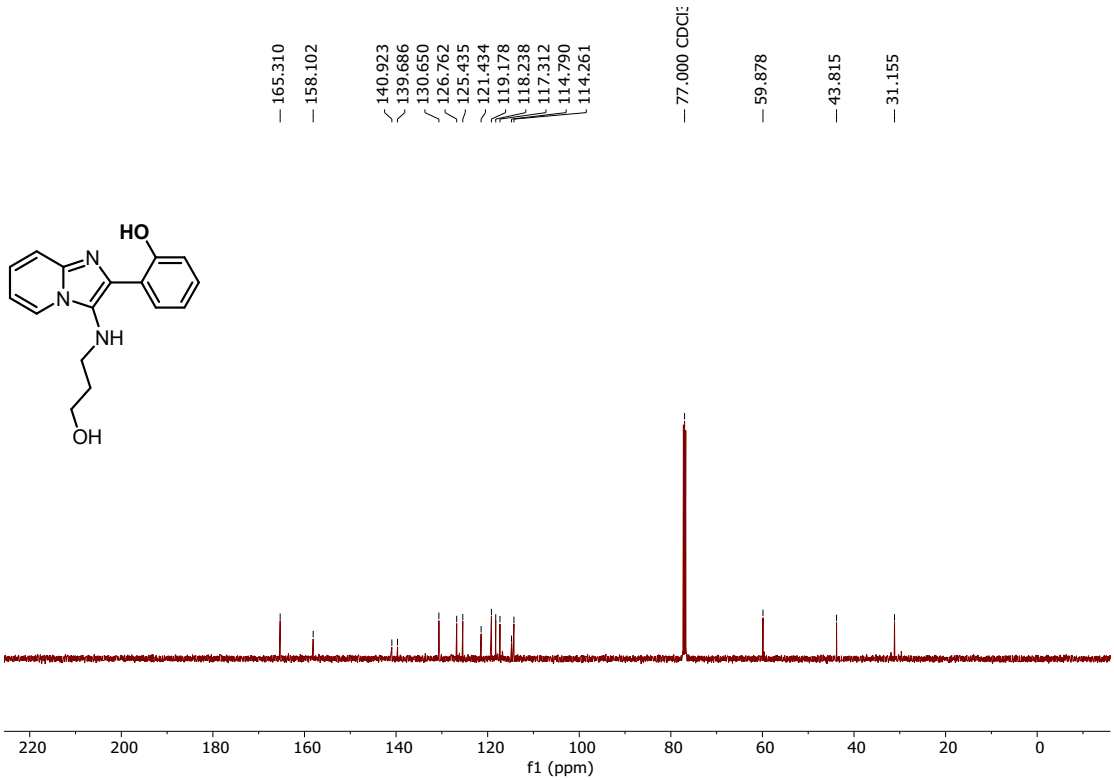
3-((2-(4-chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)amino)propan-1-ol (4)





2-(3-((3-hydroxypropyl)amino)imidazo[1,2-*a*]pyridin-2-yl)phenol (6)





6. Single crystal x-ray structure determination

Single crystal structure of compound 3a

A translucent pale yellow-colourless rectangular plate-like specimen of $C_{17}H_{14}ClN_3O_2$, approximate dimensions 0.077 mm x 0.087 mm x0.089 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

The total exposure time was 13.64 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 71443 reflections to a maximum θ angle of 26.00° (0.81 Å resolution), of which 2856 were independent (average redundancy 25.015, completeness = 100.0%, R_{int} = 12.10%, R_{sig} = 3.18%) and 2043(71.53%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.1476(9) Å, b = 7.1242(6) Å, c = 18.6955(15) Å, β = 101.839(3)°, volume = 1453.2(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 719 reflections above 20 σ(I) with 4.416° < 2θ < 42.47°.Data were corrected for absorption effects using the Numerical Mu Calculated method (SADABS). The ratio of minimum to maximum apparent transmission was 0.858.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, $C_{17}H_{14}ClN_3O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 265 variables converged at R1 = 4.17%, for the observed data and wR2 = 10.98% for all data. The goodness-of-fit was 1.041. The largest peak in the final difference electron density synthesis was 0.192 $e^-/Å^3$ and the largest hole was -0.186 $e^-/Å^3$ with an RMS deviation of 0.048 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.498 g/cm^3 and F(000), 680 e^-. The CCDC number is 2294778.

Table S2. Crystal data and structure refinement for $C_{17}H_{14}ClN_3O_2$ at 293(2) K.

Empirical formula	$C_{17}H_{14}ClN_3O_2$
Formula weight	327.76
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 11.1476(9) Å, α = 90° b = 7.1242(6) Å, β = 101.839(3)° c = 18.6955(15) Å, γ = 90°
Volume	1453.2(2) $Å^3$
Z	4
Density (calculated)	1.498 g/cm^3
Absorption coefficient	0.277 mm^{-1}
F(000)	680

Crystal size	0.089 x 0.087 x 0.077 mm^3
θ range for data collection	2.226 to 25.999°
Index ranges	-13<=h<=13, -8<=k<=8, -23<=l<=23
Reflections collected	71443
Independent reflections	2856 [R_{int} = 0.1210]
Completeness to θ = 25.242°	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2856 / 0 / 265
Goodness-of-fit	1.041
Final R indices [I > 2σ(I)]	R_{obs} = 0.0417, wR_{obs} = 0.0953
R indices [all data]	R_{all} = 0.0672, wR_{all} = 0.1098
Extinction coefficient	0.0104(14)
Largest diff. peak and hole	0.192 and -0.186 e·$Å^{-3}$

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0438P)^2+0.7417P]$ where $P=(Fo^2+2Fc^2)/3$

Table S3. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for $C_{17}H_{14}ClN_3O_2$ at 293(2) K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}^*
Cl(01)	-958(1)	3461(1)	4104(1)	1	57(1)
O(002)	6321(2)	4248(2)	4719(1)	1	48(1)
O(003)	5751(2)	6097(3)	3768(1)	1	52(1)
N(004)	5238(2)	3015(3)	3627(1)	1	37(1)
N(005)	5134(2)	3318(3)	2328(1)	1	39(1)
N(006)	3112(2)	3509(3)	1875(1)	1	41(1)
C(007)	5761(2)	4537(3)	4015(2)	1	39(1)
C(008)	3323(2)	3409(3)	2625(2)	1	37(1)
C(009)	4556(2)	3305(3)	2914(2)	1	38(1)
C(00A)	2291(2)	3408(3)	3003(2)	1	36(1)
C(00B)	4210(2)	3464(3)	1706(2)	1	40(1)
C(00C)	6341(2)	905(4)	4564(2)	1	48(1)
H(11)	6280(20)	-310(40)	4782(14)	1	57(8)
H(10)	7170(30)	990(40)	4468(14)	1	64(8)
C(00D)	2443(2)	3756(4)	3751(2)	1	46(1)
H(0)	3260(30)	4040(40)	4060(14)	1	63(8)
C(00E)	1114(2)	3060(3)	2610(2)	1	41(1)
H(3)	1000(20)	2760(30)	2108(14)	1	45(6)
C(00F)	295(2)	3430(3)	3681(2)	1	42(1)
C(00G)	1450(2)	3764(4)	4090(2)	1	47(1)

H(1)	1530(20)	4030(40)	4609(15)	1	64(8)
C00H()	122(2)	3070(4)	2942(2)	1	45(1)
H(2)	-670(20)	2850(30)	2675(13)	1	48(7)
C(00I)	4564(2)	3516(4)	1022(2)	1	47(1)
H(4)	3930(20)	3620(40)	581(15)	1	61(8)
C(00J)	5376(3)	1047(4)	3876(2)	1	48(1)
H(9)	5590(20)	270(40)	3496(15)	1	59(8)
H(8)	4570(20)	630(40)	3975(13)	1	55(7)
C(00K)	6353(2)	3203(4)	2298(2)	1	50(1)
H(7)	6860(30)	3120(40)	2725(15)	1	62(8)
C(00L)	6170(3)	2463(4)	5064(2)	1	50(1)
H(13)	6770(30)	2500(40)	5533(16)	1	65(8)
H(12)	5320(20)	2480(30)	5174(13)	1	55(7)
C(00M)	5760(3)	3389(4)	995(2)	1	54(1)
H(5)	6020(30)	3430(40)	530(15)	1	66(8)
C00N()	6669(3)	3227(4)	1638(2)	1	57(1)
H(6)	7490(30)	3130(40)	1609(15)	1	67(8)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Anisotropic displacement parameters ($Å^2x10^3$) for $C_{17}H_{14}ClN_3O_2$ at 293(2) K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(01)	44(1)	73(1)	58(1)	-4(1)	21(1)	2(1)
O(002)	47(1)	59(2)	32(1)	-7(1)	-4(1)	-2(1)
O(003)	55(2)	50(2)	48(1)	-7(1)	0(1)	3(1)
N(004)	36(1)	44(2)	29(1)	-2(1)	0(1)	0(1)
N(005)	35(1)	50(2)	32(1)	-2(1)	5(1)	-3(1)
N(006)	38(1)	52(2)	30(1)	-3(1)	4(1)	-3(1)
C(007)	30(2)	53(2)	32(2)	-3(1)	3(1)	-3(1)
C(008)	39(2)	41(2)	30(2)	-4(1)	2(1)	-3(1)
C(009)	36(2)	48(2)	28(1)	-2(1)	4(1)	-2(1)
C(00A)	36(2)	38(2)	34(2)	-2(1)	4(1)	-2(1)
C(00B)	42(2)	46(2)	31(2)	-5(1)	3(1)	-4(1)
C(00C)	43(2)	54(2)	46(2)	0(2)	7(2)	9(2)
C(00D)	36(2)	63(2)	37(2)	-6(2)	3(1)	-10(2)
C(00E)	38(2)	47(2)	35(2)	-2(1)	1(1)	-1(1)
C(00F)	39(2)	45(2)	41(2)	-3(1)	10(1)	2(1)
C(00G)	43(2)	61(2)	36(2)	-6(2)	9(1)	-6(2)

C00H()	32(2)	55(2)	45(2)	-4(2)	0(1)	2(2)
C(00I)	50(2)	60(2)	32(2)	-8(2)	9(2)	-6(2)
C(00J)	52(2)	49(2)	41(2)	-3(2)	5(2)	1(2)
C(00K)	36(2)	71(2)	42(2)	-1(2)	5(2)	-4(2)
C(00L)	47(2)	64(2)	37(2)	-3(2)	4(2)	5(2)
C(00M)	60(2)	65(2)	41(2)	-7(2)	19(2)	-4(2)
C00N()	43(2)	79(2)	52(2)	-4(2)	18(2)	-5(2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S5. Bond lengths [Å] for $C_{17}H_{14}ClN_3O_2$ at 293(2) K with estimated standard deviations in parentheses.

Label	Distances
Cl(01)-C(00F)	1.741(2)
O(002)-C(007)	1.352(3)
O(002)-C(00L)	1.452(3)
O(003)-C(007)	1.203(3)
N(004)-C(007)	1.366(3)
N(004)-C(009)	1.407(3)
N(004)-C(00J)	1.475(3)
N(005)-C(00K)	1.374(3)
N(005)-C(009)	1.380(3)
N(005)-C(00B)	1.389(3)
N(006)-C(00B)	1.326(3)
N(006)-C(008)	1.375(3)
C(008)-C(009)	1.372(3)
C(008)-C(00A)	1.469(3)
C(00A)-C(00E)	1.389(3)
C(00A)-C(00D)	1.395(3)
C(00B)-C(00I)	1.415(3)
C(00C)-C(00L)	1.488(4)
C(00C)-C(00J)	1.502(3)
C(00C)-H(11)	0.97(3)
C(00C)-H(10)	0.98(3)
C(00D)-C(00G)	1.384(3)
C(00D)-H(0)	0.99(3)
C(00E)-C00H()	1.374(3)
C(00E)-H(3)	0.94(2)
C(00F)-C(00G)	1.376(3)

C(00F)-C00H()	1.379(3)
C(00G)-H(1)	0.98(3)
C00H()-H(2)	0.93(3)
C(00I)-C(00M)	1.348(4)
C(00I)-H(4)	0.97(3)
C(00J)-H(9)	0.97(3)
C(00J)-H(8)	0.99(3)
C(00K)-C00N()	1.350(4)
C(00K)-H(7)	0.88(3)
C(00L)-H(13)	0.99(3)
C(00L)-H(12)	1.01(3)
C(00M)-C00N()	1.409(4)
C(00M)-H(5)	0.97(3)
C00N()-H(6)	0.94(3)

Symmetry transformations used to generate equivalent atoms.

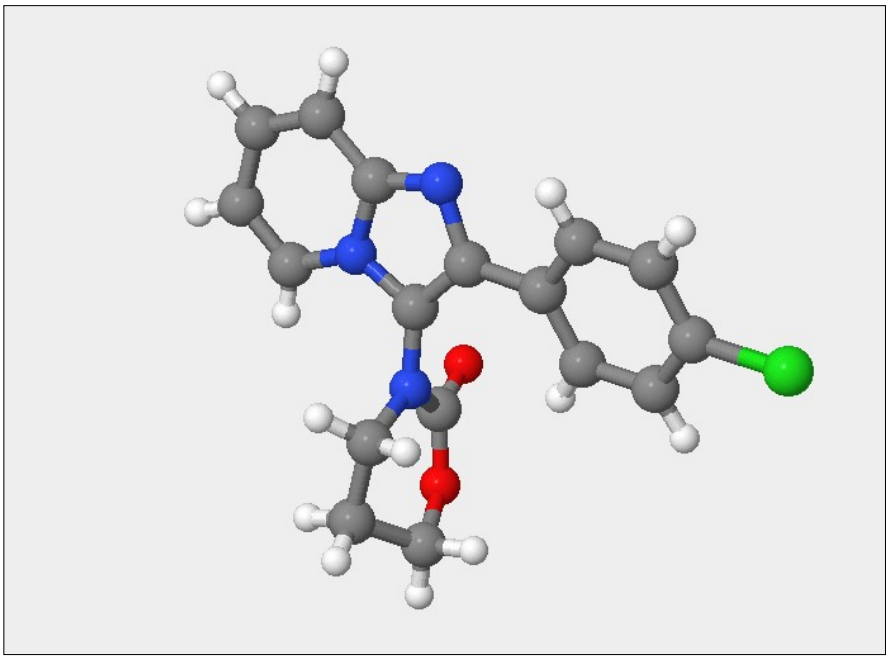
Table S6. Bond angles [°] for $C_{17}H_{14}ClN_3O_2$ at 293(2) K with estimated standard deviations in parentheses.

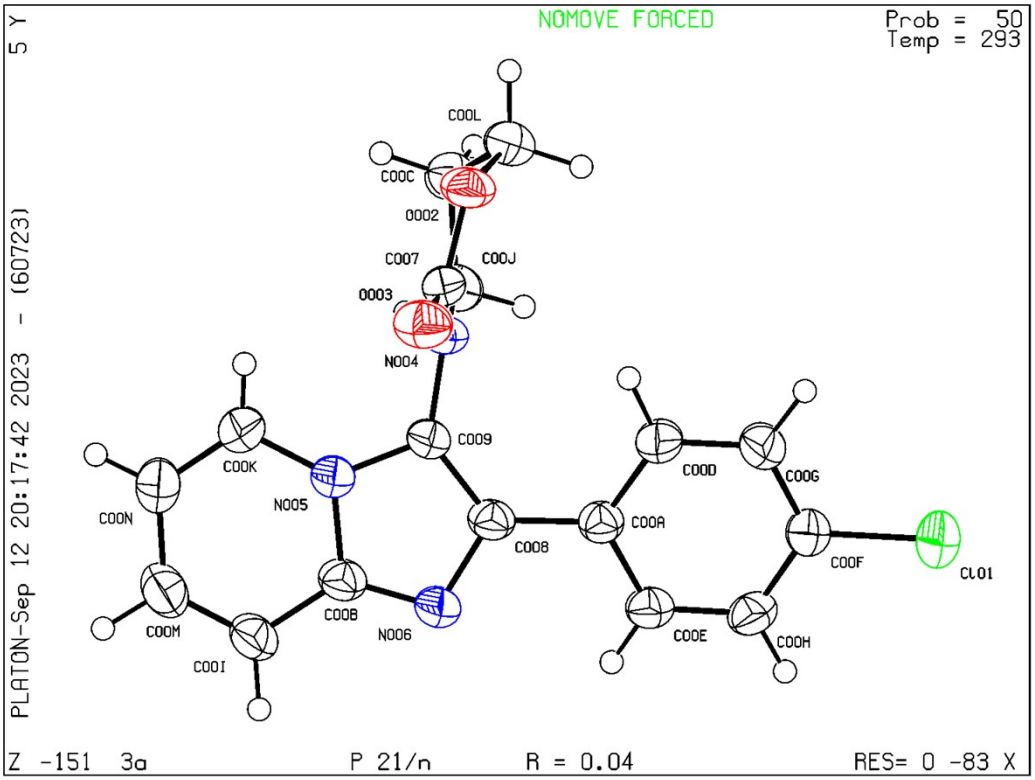
Label	Angles
C(007)-O(002)-C(00L)	119.59(19)
C(007)-N(004)-C(009)	118.36(19)
C(007)-N(004)-C(00J)	125.52(18)
C(009)-N(004)-C(00J)	116.04(18)
C(00K)-N(005)-C(009)	131.2(2)
C(00K)-N(005)-C(00B)	122.65(19)
C(009)-N(005)-C(00B)	106.15(17)
C(00B)-N(006)-C(008)	105.53(18)
O(003)-C(007)-O(002)	118.7(2)
O(003)-C(007)-N(004)	124.1(2)
O(002)-C(007)-N(004)	117.2(2)
C(009)-C(008)-N(006)	110.69(19)
C(009)-C(008)-C(00A)	129.08(19)
N(006)-C(008)-C(00A)	120.23(18)
C(008)-C(009)-N(005)	106.21(18)
C(008)-C(009)-N(004)	133.2(2)
N(005)-C(009)-N(004)	120.23(19)
C(00E)-C(00A)-C(00D)	118.0(2)

C(00E)-C(00A)-C(008)	119.57(19)
C(00D)-C(00A)-C(008)	122.43(19)
N(006)-C(00B)-N(005)	111.41(18)
N(006)-C(00B)-C(00I)	131.1(2)
N(005)-C(00B)-C(00I)	117.5(2)
C(00L)-C(00C)-C(00J)	109.1(2)
C(00L)-C(00C)-H(11)	112.0(15)
C(00J)-C(00C)-H(11)	108.7(15)
C(00L)-C(00C)-H(10)	108.5(16)
C(00J)-C(00C)-H(10)	112.1(16)
H(11)-C(00C)-H(10)	106(2)
C(00G)-C(00D)-C(00A)	121.0(2)
C(00G)-C(00D)-H(0)	117.0(15)
C(00A)-C(00D)-H(0)	122.0(15)
C00H()-C(00E)-C(00A)	121.3(2)
C00H()-C(00E)-H(3)	119.7(14)
C(00A)-C(00E)-H(3)	119.0(14)
C(00G)-C(00F)-C00H()	120.7(2)
C(00G)-C(00F)-Cl(01)	119.48(18)
C00H()-C(00F)-Cl(01)	119.82(18)
C(00F)-C(00G)-C(00D)	119.4(2)
C(00F)-C(00G)-H(1)	118.4(16)
C(00D)-C(00G)-H(1)	122.3(16)
C(00E)-C00H()-C(00F)	119.6(2)
C(00E)-C00H()-H(2)	121.1(15)
C(00F)-C00H()-H(2)	119.3(15)
C(00M)-C(00I)-C(00B)	119.6(2)
C(00M)-C(00I)-H(4)	121.6(15)
C(00B)-C(00I)-H(4)	118.7(16)
N(004)-C(00J)-C(00C)	110.1(2)
N(004)-C(00J)-H(9)	109.8(16)
C(00C)-C(00J)-H(9)	110.3(16)
N(004)-C(00J)-H(8)	107.6(15)
C(00C)-C(00J)-H(8)	109.5(14)
H(9)-C(00J)-H(8)	109(2)
C00N()-C(00K)-N(005)	118.9(2)

C00N()-C(00K)-H(7)	126.0(18)
N(005)-C(00K)-H(7)	115.1(18)
O(002)-C(00L)-C(00C)	109.4(2)
O(002)-C(00L)-H(13)	104.7(16)
C(00C)-C(00L)-H(13)	115.4(16)
O(002)-C(00L)-H(12)	106.2(14)
C(00C)-C(00L)-H(12)	112.5(14)
H(13)-C(00L)-H(12)	108(2)
C(00I)-C(00M)-C00N()	121.1(2)
C(00I)-C(00M)-H(5)	120.8(17)
C00N()-C(00M)-H(5)	118.1(17)
C(00K)-C00N()-C(00M)	120.3(3)
C(00K)-C00N()-H(6)	119.8(17)
C(00M)-C00N()-H(6)	120.0(17)

Symmetry transformations used to generate equivalent atoms

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C00A
C00D
C00G
C00F
CL01
C00E
C00H
Z -151 3a
P 21/n
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RES= 0 -83 X

Single crystal structure of compound 3g

A translucent light yellow-colourless rectangular plate-like specimen of $C_{15}H_6ClN_3O_2S$, approximate dimensions 0.074 mm x 0.119 mm x0.138 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

The total exposure time was 11.43 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 59753 reflections to a maximum θ angle of 26.00° (0.81 Å resolution), of which 2886 were independent (average redundancy 20.704, completeness = 100.0%, R_{int} = 10.53%, R_{sig} = 3.29%) and 1963(68.02%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.2004(5) Å, b = 11.4906(8) Å, c = 18.0070(13) Å, β = 99.310(3)°, volume = 1470.22(18) $Å^3$, are based upon the refinement of the XYZ-centroids of 126 reflections above 20 σ(I) with 5.844° < 2θ < 42.97°.Data were corrected for absorption effects using the Numerical Mu Calculated method (SADABS). The ratio of minimum to maximum apparent transmission was 0.787. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.3845 and0.4885.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, $C_{15}H_6ClN_3O_2S$. The final anisotropic full-matrix least-squares refinement on F^2 with 199 variables converged at R1 = 5.78%, for the observed data and wR2 = 17.29% for all data. The goodness-of-fit was 1.028. The largest peak in the final difference electron density synthesis was 0.317 $e^-/Å^3$ and the largest hole was -0.420 $e^-/Å^3$ with an RMS deviation of 0.061 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.481 g/cm^3 and F(000), 664 e^-. The CCDC number is: 2294775

Table S7. Crystal data and structure refinement for $C_{15}H_{12}ClN_3O_2S$ at 293(2) K.

Empirical formula	$C_{15}H_{12}ClN_3O_2S$
Formula weight	333.79
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 7.2004(5) Å, α = 90° b = 11.4906(8) Å, β = 99.310(3)° c = 18.0070(13) Å, γ = 90°
Volume	1470.22(18) $Å^3$
Z	4
Density (calculated)	1.481 g/cm^3
Absorption coefficient	0.412 mm^{-1}
F(000)	664
Crystal size	0.138 x 0.119 x 0.074 mm^3
θ range for data collection	2.111 to 25.998°

Index ranges	-8<=h<=8, -14<=k<=14, -22<=l<=22
Reflections collected	59753
Independent reflections	2886 [R_{int} = 0.1053]
Completeness to θ = 25.242°	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2886 / 0 / 199
Goodness-of-fit	1.028
Final R indices [I > 2σ(I)]	R_{obs} = 0.0578, wR_{obs} = 0.1489
R indices [all data]	R_{all} = 0.0892, wR_{all} = 0.1729
Extinction coefficient	.
Largest diff. peak and hole	0.317 and -0.420 e·Å^{-3}

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0804P)^2+1.3591P]$ where $P=(Fo^2+2Fc^2)/3$

Table S8. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for $C_{15}H_{12}ClN_3O_2S$ at 293(2) K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}^*
Cl(01)	4024(2)	8188(1)	7506(1)	1	74(1)
S(002)	3950(2)	5845(2)	2192(1)	1	80(1)
N(003)	3769(3)	6942(2)	5467(2)	1	42(1)
N(004)	5620(4)	7831(2)	4608(2)	1	47(1)
O(005)	3274(5)	9135(3)	4278(2)	1	77(1)
N(006)	2339(4)	5481(3)	4766(2)	1	51(1)
O(7)	6096(5)	9611(2)	4081(2)	1	79(1)
C(008)	4320(4)	7006(3)	4769(2)	1	43(1)
C(009)	3421(4)	6110(3)	4348(2)	1	46(1)
C(00A)	4212(4)	7625(3)	6092(2)	1	46(1)
H(00G)	5018.41	8257.36	6093.15	1	56
C(00B)	2543(4)	5996(3)	5436(2)	1	48(1)
C(00C)	4915(6)	8873(3)	4327(2)	1	55(1)
C(00D)	3507(4)	5799(3)	3571(2)	1	49(1)
C(00E)	3445(5)	7356(3)	6708(2)	1	50(1)
C(00F)	2972(5)	4615(3)	2483(2)	1	56(1)
H(00H)	2599.16	3970.31	2183.78	1	67
C(00G)	1752(5)	5744(3)	6080(2)	1	54(1)
H(00I)	924.09	5122.09	6077.47	1	65
C00H()	2818(5)	4728(3)	3242(2)	1	58(1)
H(00J)	2307.66	4150.28	3509.73	1	70
C(00I)	2195(5)	6406(3)	6708(2)	1	58(1)

H(00K)	1677.78	6236.16	7136.78	1	69
C(00J)	4170(5)	6481(4)	3049(2)	1	61(1)
H(00L)	4686.11	7216.51	3154.5	1	74
C(00K)	7618(5)	7501(4)	4709(3)	1	77(2)
H(00A)	7981.15	7156.19	5202.35	1	92
H(00B)	7801.34	6922.24	4335.02	1	92
C(00L)	8058(9)	9339(5)	4135(3)	1	109(2)
H(00C)	8286.55	9112.76	3639.24	1	130
H(00D)	8767.55	10046.21	4271.29	1	130
C(00M)	8780(8)	8478(5)	4637(5)	1	128(3)
H(00E)	9107.97	8831.21	5129.92	1	153
H(00F)	9938.04	8197.69	4489.77	1	153

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S9. Anisotropic displacement parameters ($Å^2x10^3$) for $C_{15}H_{12}ClN_3O_2S$ at 293(2) K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(01)	77(1)	91(1)	56(1)	-18(1)	18(1)	-22(1)
S(002)	82(1)	106(1)	56(1)	0(1)	20(1)	-10(1)
N(003)	38(2)	45(2)	43(2)	-6(2)	5(2)	1(2)
N(004)	48(2)	44(2)	50(2)	-7(2)	10(2)	6(2)
O(005)	83(2)	78(2)	72(2)	22(2)	15(2)	21(2)
N(006)	46(2)	59(2)	51(2)	-15(2)	10(2)	-4(2)
O(7)	106(3)	60(2)	71(2)	-24(2)	15(2)	16(2)
C(008)	37(2)	46(2)	48(2)	-5(2)	9(2)	3(2)
C(009)	37(2)	52(2)	47(2)	-2(2)	6(2)	1(2)
C(00A)	41(2)	48(2)	50(2)	-5(2)	7(2)	-2(2)
C(00B)	41(2)	51(2)	52(2)	-9(2)	7(2)	2(2)
C(00C)	78(3)	56(2)	34(2)	-6(2)	12(2)	3(2)
C(00D)	38(2)	62(2)	47(2)	3(2)	5(2)	-2(2)
C(00E)	45(2)	58(2)	44(2)	-2(2)	5(2)	-5(2)
C(00F)	51(2)	59(2)	54(2)	6(2)	2(2)	-10(2)
C(00G)	51(2)	62(2)	52(2)	-17(2)	14(2)	0(2)
C00H()	55(2)	59(2)	58(2)	-1(2)	3(2)	-7(2)
C(00I)	52(2)	71(2)	53(2)	-11(2)	16(2)	0(2)
C(00J)	63(2)	73(2)	51(2)	-8(2)	17(2)	-6(2)
C(00K)	45(2)	72(3)	115(4)	-8(2)	18(2)	19(2)
C(00L)	108(5)	116(4)	104(4)	-58(4)	22(3)	30(3)

C(00M)	66(3)	116(5)	205(7)	-24(3)	34(4)	49(5)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S10. Bond lengths [Å] for $C_{15}H_{12}ClN_3O_2S$ at 293(2) K with estimated standard deviations in parentheses.

Label	Distances
Cl(01)-C(00E)	1.721(3)
S(002)-C(00J)	1.692(4)
S(002)-C(00F)	1.699(4)
N(003)-C(00A)	1.366(4)
N(003)-C(008)	1.381(4)
N(003)-C(00B)	1.396(4)
N(004)-C(00C)	1.366(5)
N(004)-C(008)	1.395(4)
N(004)-C(00K)	1.470(5)
O(005)-C(00C)	1.209(5)
N(006)-C(00B)	1.330(4)
N(006)-C(009)	1.373(4)
O(7)-C(00C)	1.327(4)
O(7)-C(00L)	1.434(7)
C(008)-C(009)	1.376(4)
C(009)-C(00D)	1.455(5)
C(00A)-C(00E)	1.353(5)
C(00A)-H(00G)	0.9300
C(00B)-C(00G)	1.404(5)
C(00D)-C(00J)	1.367(5)
C(00D)-C00H()	1.421(5)
C(00E)-C(00I)	1.415(5)
C(00F)-C00H()	1.395(5)
C(00F)-H(00H)	0.9300
C(00G)-C(00I)	1.357(5)
C(00G)-H(00I)	0.9300
C00H()-H(00J)	0.9300
C(00I)-H(00K)	0.9300
C(00J)-H(00L)	0.9300
C(00K)-C(00M)	1.418(6)
C(00K)-H(00A)	0.9700
C(00K)-H(00B)	0.9700

C(00L)-C(00M)	1.383(8)
C(00L)-H(00C)	0.9700
C(00L)-H(00D)	0.9700
C(00M)-H(00E)	0.9700
C(00M)-H(00F)	0.9700

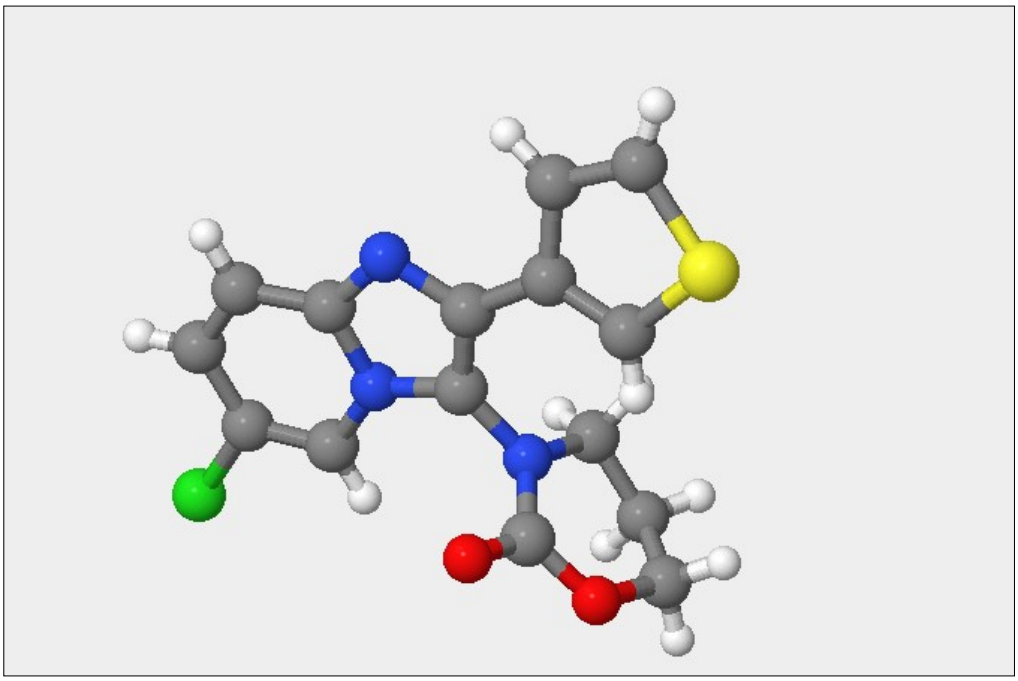
Symmetry transformations used to generate equivalent atoms:

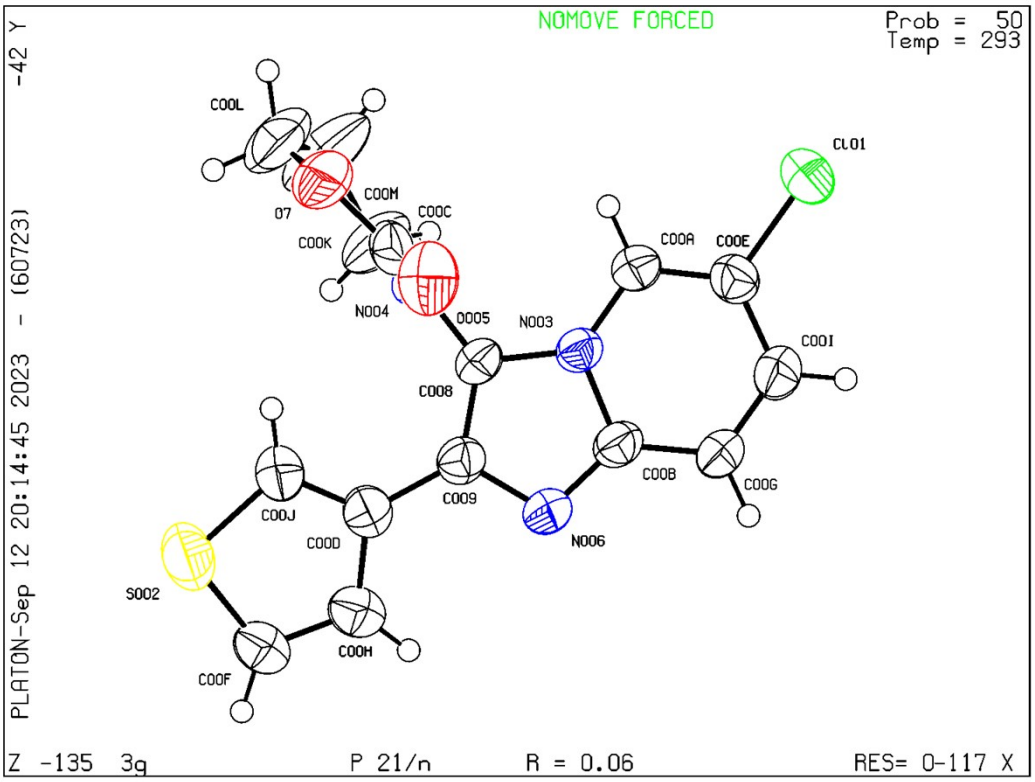
Table S11. Bond angles [°] for $C_{15}H_{12}ClN_3O_2S$ at 293(2) K with estimated standard deviations in parentheses.

Label	Angles
C(00J)-S(002)-C(00F)	93.49(19)
C(00A)-N(003)-C(008)	131.0(3)
C(00A)-N(003)-C(00B)	122.9(3)
C(008)-N(003)-C(00B)	106.1(3)
C(00C)-N(004)-C(008)	116.8(3)
C(00C)-N(004)-C(00K)	124.7(3)
C(008)-N(004)-C(00K)	118.4(3)
C(00B)-N(006)-C(009)	105.9(3)
C(00C)-O(7)-C(00L)	121.0(3)
C(009)-C(008)-N(003)	106.4(3)
C(009)-C(008)-N(004)	131.7(3)
N(003)-C(008)-N(004)	121.8(3)
N(006)-C(009)-C(008)	110.5(3)
N(006)-C(009)-C(00D)	120.9(3)
C(008)-C(009)-C(00D)	128.6(3)
C(00E)-C(00A)-N(003)	118.2(3)
C(00E)-C(00A)-H(00G)	120.9
N(003)-C(00A)-H(00G)	120.9
N(006)-C(00B)-N(003)	111.1(3)
N(006)-C(00B)-C(00G)	131.2(3)
N(003)-C(00B)-C(00G)	117.7(3)
O(005)-C(00C)-O(7)	119.2(4)
O(005)-C(00C)-N(004)	123.1(3)
O(7)-C(00C)-N(004)	117.7(4)
C(00J)-C(00D)-C00H()	110.3(3)
C(00J)-C(00D)-C(009)	126.4(3)
C00H()-C(00D)-C(009)	123.2(3)
C(00A)-C(00E)-C(00I)	121.4(3)

C(00A)-C(00E)-Cl(01)	118.8(3)
C(00I)-C(00E)-Cl(01)	119.8(3)
C00H()-C(00F)-S(002)	109.1(3)
C00H()-C(00F)-H(00H)	125.4
S(002)-C(00F)-H(00H)	125.4
C(00I)-C(00G)-C(00B)	120.1(3)
C(00I)-C(00G)-H(00I)	119.9
C(00B)-C(00G)-H(00I)	119.9
C(00F)-C00H()-C(00D)	114.3(4)
C(00F)-C00H()-H(00J)	122.9
C(00D)-C00H()-H(00J)	122.9
C(00G)-C(00I)-C(00E)	119.7(3)
C(00G)-C(00I)-H(00K)	120.1
C(00E)-C(00I)-H(00K)	120.1
C(00D)-C(00J)-S(002)	112.8(3)
C(00D)-C(00J)-H(00L)	123.6
S(002)-C(00J)-H(00L)	123.6
C(00M)-C(00K)-N(004)	111.4(4)
C(00M)-C(00K)-H(00A)	109.3
N(004)-C(00K)-H(00A)	109.3
C(00M)-C(00K)-H(00B)	109.3
N(004)-C(00K)-H(00B)	109.3
H(00A)-C(00K)-H(00B)	108.0
C(00M)-C(00L)-O(7)	117.6(4)
C(00M)-C(00L)-H(00C)	107.9
O(7)-C(00L)-H(00C)	107.9
C(00M)-C(00L)-H(00D)	107.9
O(7)-C(00L)-H(00D)	107.9
H(00C)-C(00L)-H(00D)	107.2
C(00L)-C(00M)-C(00K)	117.4(5)
C(00L)-C(00M)-H(00E)	107.9
C(00K)-C(00M)-H(00E)	107.9
C(00L)-C(00M)-H(00F)	107.9
C(00K)-C(00M)-H(00F)	107.9
H(00E)-C(00M)-H(00F)	107.2

Symmetry transformations used to generate equivalent atoms

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C00G
C009
N006
C00J
C00D
S002
C00H
C00F
Z -135 3g
P 21/n
R = 0.06
RES= 0-117 X

Single crystal structure of compound 4

A translucent light colourless-yellow elongated needle-like specimen of $C_{16}H_{16}ClN_3O$, approximate dimensions 0.028 mm x 0.084 mm x 0.206 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

The total exposure time was 11.38 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 63756 reflections to a maximum θ angle of 26.00° (0.81 Å resolution), of which 5791 were independent (average redundancy 11.009, completeness = 100.0%, R_{int} = 32.86%, R_{sig} = 18.14%) and 2157 (37.25%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.835(17) Å, b = 10.00(2) Å, c = 19.25(5) Å, α = 96.49(6)°, β = 96.89(5)°, γ = 90.46(4)°, volume = 1487.(10) Å^3, are based upon the refinement of the XYZ-centroids of 123 reflections above 20 σ(I) with 4.304° < 2θ < 24.58°. Data were corrected for absorption effects using the Numerical Mu Calculated method (SADABS). The ratio of minimum to maximum apparent transmission was 0.663. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9480 and 0.9920.

The structure was solved and refined using the Bruker SHELXTL Software Package, with Z = 4 for the formula unit, $C_{16}H_{16}ClN_3O$. The final anisotropic full-matrix least-squares refinement on F^2 with 381 variables converged at R1 = 14.87%, for the observed data and wR2 = 45.28% for all data. The goodness-of-fit was 1.172. The largest peak in the final difference electron density synthesis was 0.518 e^-/Å^3 and the largest hole was -0.452 e^-/Å^3 with an RMS deviation of 0.105 e^-/Å^3. On the basis of the final model, the calculated density was 1.366 g/cm^3 and F(000), 632 e^-. The CCDC number is: 2294777.

Table S12. Crystal data and structure refinement for $C_{16}H_{16}ClN_3O$ at 293(2) K.

Empirical formula	$C_{16}H_{16}ClN_3O$
Formula weight	301.77
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 7.804(3) Å, α = 96.538(13)° b = 9.955(4) Å, β = 96.978(11)° c = 19.163(7) Å, γ = 90.269(13)°
Volume	1467.8(9) Å^3
Z	4
Density (calculated)	1.366 g/cm^3
Absorption coefficient	0.263 mm^{-1}
F(000)	632
Crystal size	0.205 x 0.081 x 0.029 mm^3

θ range for data collection	2.060 to 26.000°
Index ranges	-9<=h<=9, -12<=k<=12, -23<=l<=23
Reflections collected	63756
Independent reflections	5791 [R_{int} = 0.3286]
Completeness to θ = 25.242°	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5791 / 0 / 381
Goodness-of-fit	1.172
Final R indices [I > 2σ(I)]	R_{obs} = 0.1487, wR_{obs} = 0.3815
R indices [all data]	R_{all} = 0.2790, wR_{all} = 0.4528
Extinction coefficient	.
Largest diff. peak and hole	0.518 and -0.452 e·Å^{-3}

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.2000P)^2]$ where $P=(Fo^2+2Fc^2)/3$

Table S13. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for $C_{16}H_{16}ClN_3O$ at 293(2) K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}^*
Cl(01)	6089(4)	5176(3)	3236(2)	1	108(2)
Cl(02)	2954(5)	-372(4)	7915(2)	1	119(2)
O(003)	1818(8)	-1397(6)	621(4)	1	72(2)
H(003)	2247.32	-1986.08	364.72	1	108
N(004)	2115(10)	658(8)	3726(4)	1	70(2)
N(005)	1389(10)	4352(8)	-836(4)	1	71(2)
N(006)	1690(9)	2506(7)	-86(4)	1	68(2)
H(006)	820.11	2241.9	101.84	1	82
N(007)	2771(10)	-1075(7)	4348(4)	1	72(2)
N(008)	2665(10)	6100(7)	-100(4)	1	70(2)
N(009)	1543(10)	2486(7)	4588(4)	1	68(2)
H(009)	494.42	2740.66	4599.5	1	81
C(00A)	2397(11)	49(9)	4797(5)	1	63(2)
C(00B)	2697(11)	4936(9)	241(5)	1	64(2)
C(00C)	2513(12)	-37(9)	5568(5)	1	66(2)
O(0)	769(11)	6537(7)	4208(5)	1	109(3)
H(0)	1183.89	6950.87	4585.93	1	164
C(00D)	3539(12)	4964(9)	984(5)	1	64(2)
C(00F)	1895(12)	5725(10)	-750(5)	1	73(3)
C(00G)	1931(11)	3854(9)	-210(5)	1	63(2)
C00H()	5106(13)	5118(11)	2352(5)	1	77(3)

C(00I)	1980(12)	1153(9)	4425(5)	1	66(2)
C(00J)	4407(12)	6132(10)	1320(6)	1	75(3)
H(00J)	4459.13	6882.06	1074.51	1	89
C(00K)	2560(14)	-703(10)	3696(5)	1	76(3)
C(00L)	5173(12)	6197(10)	1992(5)	1	75(3)
H(00L)	5747.3	6986.08	2206.88	1	90
C(00M)	1989(13)	998(10)	6032(5)	1	76(3)
H(00M)	1548.84	1777.43	5857.08	1	91
C00N()	2549(12)	132(9)	-218(5)	1	69(2)
H(00A)	1417.31	-82.12	-478.06	1	83
H(00B)	3366.2	-475.35	-425.85	1	83
C00O()	2770(14)	-241(12)	7010(5)	1	80(3)
C(00P)	3044(12)	1578(9)	-304(5)	1	73(3)
H(00C)	4132.68	1829.27	-16.05	1	88
H(00D)	3190.3	1645.96	-794.29	1	88
C(00Q)	252(13)	4465(12)	-2013(6)	1	86(3)
H(00Q)	-315.19	4063.6	-2441.17	1	103
C(00R)	604(12)	3702(11)	-1472(5)	1	76(3)
H(00R)	329.87	2782.9	-1526.55	1	92
C(00S)	2105(13)	902(11)	6759(5)	1	82(3)
H(00S)	1736.32	1603.45	7065.57	1	98
C(00T)	2513(12)	-115(10)	536(5)	1	74(3)
H(00E)	3681.4	-32.25	777.42	1	88
H(00F)	1836.02	582.08	762.94	1	88
C(00U)	4264(14)	3955(11)	2048(5)	1	83(3)
H(00U)	4220.21	3220.2	2304.68	1	100
C(00V)	2767(14)	-1388(10)	3057(6)	1	83(3)
H(00V)	3129.56	-2279.24	3032.14	1	99
C(00W)	3056(12)	3443(9)	4744(6)	1	79(3)
H(00G)	3784.85	3306.3	4367.59	1	94
H(00H)	3734.27	3276.13	5183.21	1	94
C(00X)	1790(14)	1299(11)	3139(5)	1	84(3)
H(00X)	1476.91	2202.66	3170.64	1	101
C(00Y)	3174(15)	-1162(10)	5846(5)	1	88(3)
H(00Y)	3579.43	-1859.62	5548.22	1	106
C(00Z)	694(15)	5778(12)	-1950(6)	1	88(3)
H(00Z)	452.82	6248.99	-2341.88	1	106

C(010)	3479(13)	3866(10)	1360(6)	1	78(3)
H(010)	2912.8	3070.15	1150.68	1	93
C(011)	1478(13)	6447(10)	-1340(6)	1	79(3)
H(011)	1737.03	7366.48	-1308.45	1	95
C(012)	1935(14)	581(12)	2497(5)	1	87(3)
H(012)	1690.53	999.27	2087.23	1	105
C(013)	1504(15)	5252(10)	4128(6)	1	90(3)
H(01A)	2311.69	5238.75	3780.68	1	108
H(01B)	601.34	4583.96	3950.67	1	108
C(014)	2424(12)	4877(10)	4805(6)	1	84(3)
H(01C)	1650.59	4987.58	5166.44	1	100
H(01D)	3402.58	5489.92	4955.66	1	100
C(015)	2442(17)	-771(12)	2442(6)	1	98(4)
H(015)	2559.26	-1243.99	2003.59	1	118
C(016)	3250(16)	-1282(12)	6565(6)	1	101(4)
H(016)	3630.03	-2077.64	6739.01	1	122

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S14. Anisotropic displacement parameters ($Å^2x10^3$) for $C_{16}H_{16}ClN_3O$ at 293(2) K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(01)	126(3)	116(2)	76(2)	6(2)	-15(2)	18(2)
Cl(02)	158(3)	133(3)	66(2)	-11(2)	-3(2)	30(2)
O(003)	74(4)	53(4)	90(5)	6(3)	9(3)	12(3)
N(004)	74(5)	64(5)	70(5)	-4(4)	3(4)	10(4)
N(005)	65(5)	66(5)	83(6)	8(4)	8(4)	19(4)
N(006)	65(5)	52(4)	90(5)	3(4)	18(4)	15(4)
N(007)	84(6)	48(4)	85(6)	4(4)	13(4)	3(4)
N(008)	83(6)	56(5)	74(5)	4(4)	8(4)	15(4)
N(009)	75(5)	57(5)	70(5)	8(4)	-5(4)	19(4)
C(00A)	56(5)	68(6)	66(5)	8(4)	8(4)	15(5)
C(00B)	55(5)	59(6)	81(6)	10(4)	16(5)	10(5)
C(00C)	74(6)	54(5)	67(6)	4(5)	-1(5)	8(4)
O(0)	109(6)	67(5)	161(8)	24(5)	45(6)	20(5)
C(00D)	62(6)	59(6)	74(6)	16(5)	16(5)	9(5)
C(00F)	73(7)	76(7)	71(6)	16(5)	5(5)	22(5)
C(00G)	63(6)	64(6)	63(5)	4(5)	6(4)	10(5)
C00H()	74(7)	74(7)	79(7)	5(5)	-11(5)	7(6)

C(00I)	79(7)	50(5)	66(6)	1(5)	-3(5)	4(4)
C(00J)	70(6)	67(6)	90(7)	6(5)	6(5)	30(6)
C(00K)	103(8)	65(6)	61(6)	-3(5)	13(5)	10(5)
C(00L)	72(7)	66(6)	83(7)	-17(5)	6(5)	1(5)
C(00M)	94(7)	70(6)	65(6)	13(5)	2(5)	17(5)
C00N()	69(6)	70(6)	71(6)	8(5)	11(5)	19(5)
C00O()	86(7)	88(8)	69(6)	3(6)	13(5)	18(6)
C(00P)	66(6)	60(6)	96(7)	6(5)	17(5)	12(5)
C(00Q)	78(7)	82(8)	91(8)	5(6)	-10(6)	4(6)
C(00R)	73(6)	81(7)	69(6)	2(5)	-9(5)	1(5)
C(00S)	75(7)	103(8)	63(6)	15(6)	1(5)	1(6)
C(00T)	70(6)	71(6)	81(7)	1(5)	13(5)	10(5)
C(00U)	110(9)	68(7)	76(7)	9(6)	9(6)	27(5)
C(00V)	91(8)	67(6)	90(8)	-3(5)	17(6)	3(6)
C(00W)	64(6)	65(6)	106(8)	4(5)	4(5)	11(5)
C(00X)	107(8)	81(7)	68(7)	1(6)	8(6)	24(6)
C(00Y)	127(9)	69(7)	66(6)	31(6)	-3(6)	11(5)
C(00Z)	104(9)	96(9)	65(7)	14(7)	-2(6)	24(6)
C(010)	82(7)	63(6)	87(7)	-9(5)	6(6)	14(5)
C(011)	82(7)	68(6)	90(8)	3(5)	10(6)	22(6)
C(012)	103(9)	105(9)	56(6)	-11(7)	11(5)	19(6)
C(013)	94(8)	66(7)	119(9)	12(6)	25(7)	32(6)
C(014)	64(6)	69(7)	118(9)	2(5)	6(6)	13(6)
C(015)	138(11)	84(8)	75(7)	-13(7)	29(7)	1(6)
C(016)	131(10)	76(8)	102(9)	28(7)	2(7)	41(7)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S15. Bond lengths [Å] for $C_{16}H_{16}ClN_3O$ at 293(2) K with estimated standard deviations in parentheses.

Label	Distances
Cl(01)-C00H()	1.766(10)
Cl(02)-C00O()	1.742(10)
O(003)-C(00T)	1.418(10)
O(003)-H(003)	0.8200
N(004)-C(00X)	1.355(11)
N(004)-C(00I)	1.390(11)
N(004)-C(00K)	1.397(12)
N(005)-C(00G)	1.372(11)
N(005)-C(00R)	1.384(12)
N(005)-C(00F)	1.407(12)
N(006)-C(00G)	1.404(11)
N(006)-C(00P)	1.474(11)
N(006)-H(006)	0.8600
N(007)-C(00K)	1.334(11)
N(007)-C(00A)	1.387(11)
N(008)-C(00F)	1.328(12)
N(008)-C(00B)	1.392(11)
N(009)-C(00I)	1.382(11)
N(009)-C(00W)	1.493(12)
N(009)-H(009)	0.8600
C(00A)-C(00I)	1.396(12)
C(00A)-C(00C)	1.482(12)
C(00B)-C(00G)	1.386(12)
C(00B)-C(00D)	1.492(13)
C(00C)-C(00Y)	1.370(12)
C(00C)-C(00M)	1.379(13)
O(0)-C(013)	1.404(11)
O(0)-H(0)	0.8200
C(00D)-C(010)	1.380(13)
C(00D)-C(00J)	1.393(13)
C(00F)-C(011)	1.413(13)
C00H()-C(00L)	1.346(13)
C00H()-C(00U)	1.363(14)
C(00J)-C(00L)	1.348(13)

C(00J)-H(00J)	0.9300
C(00K)-C(00V)	1.360(14)
C(00L)-H(00L)	0.9300
C(00M)-C(00S)	1.400(13)
C(00M)-H(00M)	0.9300
C00N()-C(00T)	1.496(12)
C00N()-C(00P)	1.521(12)
C00N()-H(00A)	0.9700
C00N()-H(00B)	0.9700
C00O()-C(016)	1.349(15)
C00O()-C(00S)	1.365(14)
C(00P)-H(00C)	0.9700
C(00P)-H(00D)	0.9700
C(00Q)-C(00Z)	1.338(15)
C(00Q)-C(00R)	1.356(14)
C(00Q)-H(00Q)	0.9300
C(00R)-H(00R)	0.9300
C(00S)-H(00S)	0.9300
C(00T)-H(00E)	0.9700
C(00T)-H(00F)	0.9700
C(00U)-C(010)	1.377(14)
C(00U)-H(00U)	0.9300
C(00V)-C(015)	1.387(14)
C(00V)-H(00V)	0.9300
C(00W)-C(014)	1.509(12)
C(00W)-H(00G)	0.9700
C(00W)-H(00H)	0.9700
C(00X)-C(012)	1.368(14)
C(00X)-H(00X)	0.9300
C(00Y)-C(016)	1.390(14)
C(00Y)-H(00Y)	0.9300
C(00Z)-C(011)	1.354(14)
C(00Z)-H(00Z)	0.9300
C(010)-H(010)	0.9300
C(011)-H(011)	0.9300
C(012)-C(015)	1.401(15)
C(012)-H(012)	0.9300

C(013)-C(014)	1.491(14)
C(013)-H(01A)	0.9700
C(013)-H(01B)	0.9700
C(014)-H(01C)	0.9700
C(014)-H(01D)	0.9700
C(015)-H(015)	0.9300
C(016)-H(016)	0.9300

Symmetry transformations used to generate equivalent atoms:

Table S16. Bond angles [°] for $C_{16}H_{16}ClN_3O$ at 293(2) K with estimated standard deviations in parentheses.

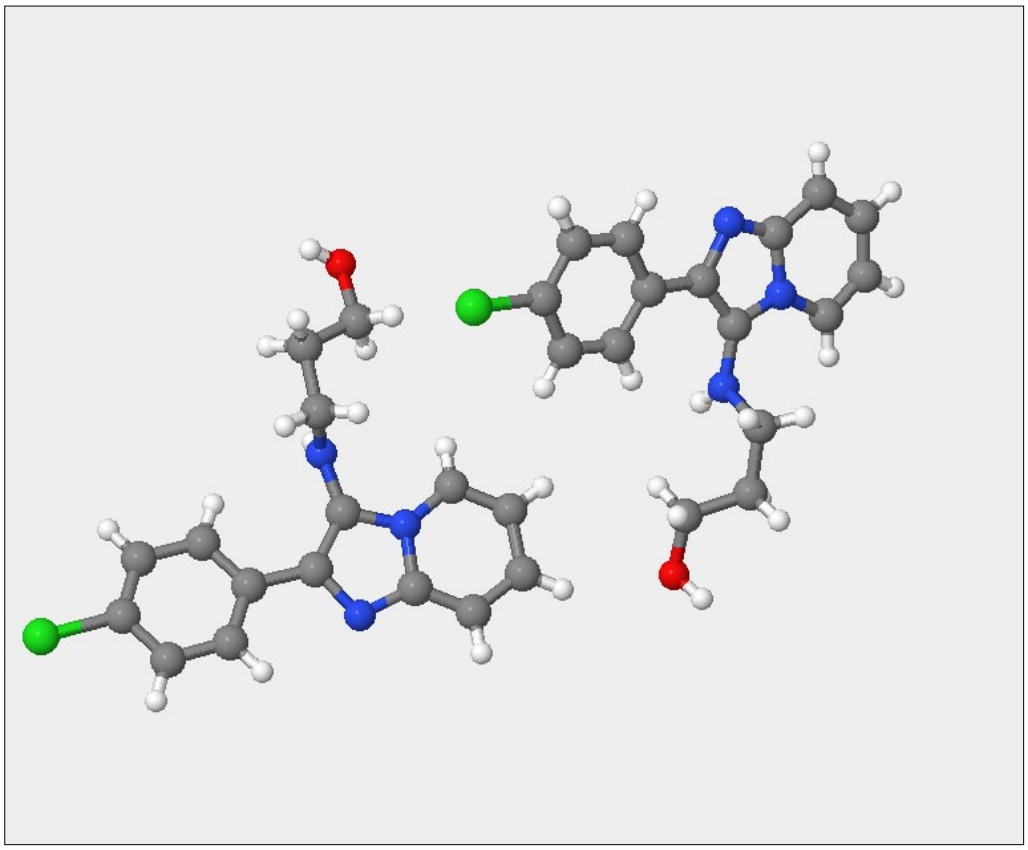
Label	Angles
C(00T)-O(003)-H(003)	109.5
C(00X)-N(004)-C(00I)	128.5(8)
C(00X)-N(004)-C(00K)	122.4(9)
C(00I)-N(004)-C(00K)	109.0(7)
C(00G)-N(005)-C(00R)	130.4(9)
C(00G)-N(005)-C(00F)	106.8(8)
C(00R)-N(005)-C(00F)	122.6(8)
C(00G)-N(006)-C(00P)	114.8(7)
C(00G)-N(006)-H(006)	122.6
C(00P)-N(006)-H(006)	122.6
C(00K)-N(007)-C(00A)	106.2(7)
C(00F)-N(008)-C(00B)	105.2(8)
C(00I)-N(009)-C(00W)	114.0(7)
C(00I)-N(009)-H(009)	123.0
C(00W)-N(009)-H(009)	123.0
N(007)-C(00A)-C(00I)	111.4(8)
N(007)-C(00A)-C(00C)	119.5(8)
C(00I)-C(00A)-C(00C)	129.1(8)
C(00G)-C(00B)-N(008)	110.8(8)
C(00G)-C(00B)-C(00D)	128.9(8)
N(008)-C(00B)-C(00D)	120.3(8)
C(00Y)-C(00C)-C(00M)	117.6(9)
C(00Y)-C(00C)-C(00A)	120.4(8)
C(00M)-C(00C)-C(00A)	122.0(8)
C(013)-O(0)-H(0)	109.5
C(010)-C(00D)-C(00J)	118.1(9)

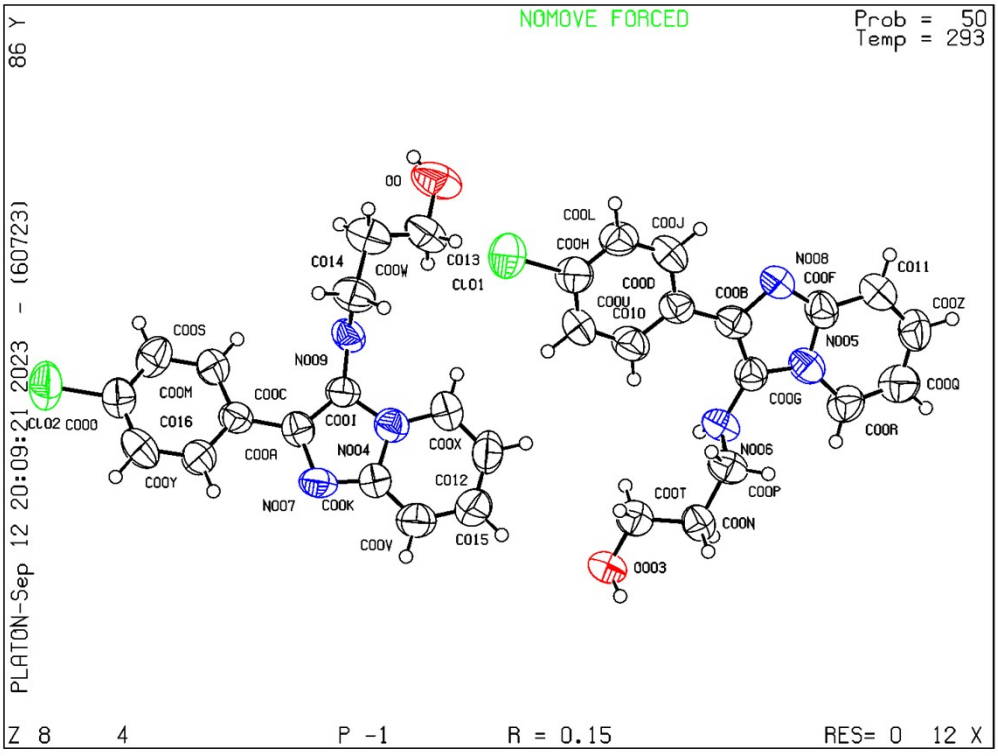
C(010)-C(00D)-C(00B)	122.1(9)
C(00J)-C(00D)-C(00B)	119.7(8)
N(008)-C(00F)-N(005)	111.2(8)
N(008)-C(00F)-C(011)	132.1(10)
N(005)-C(00F)-C(011)	116.7(9)
N(005)-C(00G)-C(00B)	106.0(8)
N(005)-C(00G)-N(006)	124.3(8)
C(00B)-C(00G)-N(006)	129.7(8)
C(00L)-C00H()-C(00U)	120.9(9)
C(00L)-C00H()-Cl(01)	120.9(9)
C(00U)-C00H()-Cl(01)	118.2(8)
N(009)-C(00I)-N(004)	119.7(8)
N(009)-C(00I)-C(00A)	136.6(8)
N(004)-C(00I)-C(00A)	103.7(7)
C(00L)-C(00J)-C(00D)	121.4(9)
C(00L)-C(00J)-H(00J)	119.3
C(00D)-C(00J)-H(00J)	119.3
N(007)-C(00K)-C(00V)	131.6(10)
N(007)-C(00K)-N(004)	109.7(8)
C(00V)-C(00K)-N(004)	118.7(9)
C00H()-C(00L)-C(00J)	119.8(10)
C00H()-C(00L)-H(00L)	120.1
C(00J)-C(00L)-H(00L)	120.1
C(00C)-C(00M)-C(00S)	121.4(9)
C(00C)-C(00M)-H(00M)	119.3
C(00S)-C(00M)-H(00M)	119.3
C(00T)-C00N()-C(00P)	113.6(8)
C(00T)-C00N()-H(00A)	108.8
C(00P)-C00N()-H(00A)	108.8
C(00T)-C00N()-H(00B)	108.8
C(00P)-C00N()-H(00B)	108.8
H(00A)-C00N()-H(00B)	107.7
C(016)-C00O()-C(00S)	120.9(10)
C(016)-C00O()-Cl(02)	119.6(8)
C(00S)-C00O()-Cl(02)	119.5(8)
N(006)-C(00P)-C00N()	110.0(7)
N(006)-C(00P)-H(00C)	109.7

C00N()-C(00P)-H(00C)	109.7
N(006)-C(00P)-H(00D)	109.7
C00N()-C(00P)-H(00D)	109.7
H(00C)-C(00P)-H(00D)	108.2
C(00Z)-C(00Q)-C(00R)	122.2(11)
C(00Z)-C(00Q)-H(00Q)	118.9
C(00R)-C(00Q)-H(00Q)	118.9
C(00Q)-C(00R)-N(005)	117.0(10)
C(00Q)-C(00R)-H(00R)	121.5
N(005)-C(00R)-H(00R)	121.5
C00O()-C(00S)-C(00M)	118.7(10)
C00O()-C(00S)-H(00S)	120.6
C(00M)-C(00S)-H(00S)	120.6
O(003)-C(00T)-C00N()	114.3(8)
O(003)-C(00T)-H(00E)	108.7
C00N()-C(00T)-H(00E)	108.7
O(003)-C(00T)-H(00F)	108.7
C00N()-C(00T)-H(00F)	108.7
H(00E)-C(00T)-H(00F)	107.6
C00H()-C(00U)-C(010)	120.2(9)
C00H()-C(00U)-H(00U)	119.9
C(010)-C(00U)-H(00U)	119.9
C(00K)-C(00V)-C(015)	120.6(10)
C(00K)-C(00V)-H(00V)	119.7
C(015)-C(00V)-H(00V)	119.7
N(009)-C(00W)-C(014)	109.4(7)
N(009)-C(00W)-H(00G)	109.8
C(014)-C(00W)-H(00G)	109.8
N(009)-C(00W)-H(00H)	109.8
C(014)-C(00W)-H(00H)	109.8
H(00G)-C(00W)-H(00H)	108.2
N(004)-C(00X)-C(012)	118.1(10)
N(004)-C(00X)-H(00X)	121.0
C(012)-C(00X)-H(00X)	121.0
C(00C)-C(00Y)-C(016)	121.4(9)
C(00C)-C(00Y)-H(00Y)	119.3
C(016)-C(00Y)-H(00Y)	119.3

C(00Q)-C(00Z)-C(011)	122.6(10)
C(00Q)-C(00Z)-H(00Z)	118.7
C(011)-C(00Z)-H(00Z)	118.7
C(00D)-C(010)-C(00U)	119.6(10)
C(00D)-C(010)-H(010)	120.2
C(00U)-C(010)-H(010)	120.2
C(00Z)-C(011)-C(00F)	118.9(10)
C(00Z)-C(011)-H(011)	120.6
C(00F)-C(011)-H(011)	120.6
C(00X)-C(012)-C(015)	121.5(10)
C(00X)-C(012)-H(012)	119.2
C(015)-C(012)-H(012)	119.2
O(0)-C(013)-C(014)	112.5(10)
O(0)-C(013)-H(01A)	109.1
C(014)-C(013)-H(01A)	109.1
O(0)-C(013)-H(01B)	109.1
C(014)-C(013)-H(01B)	109.1
H(01A)-C(013)-H(01B)	107.8
C(013)-C(014)-C(00W)	113.0(9)
C(013)-C(014)-H(01C)	109.0
C(00W)-C(014)-H(01C)	109.0
C(013)-C(014)-H(01D)	109.0
C(00W)-C(014)-H(01D)	109.0
H(01C)-C(014)-H(01D)	107.8
C(00V)-C(015)-C(012)	118.5(10)
C(00V)-C(015)-H(015)	120.8
C(012)-C(015)-H(015)	120.8
C00O()-C(016)-C(00Y)	119.8(9)
C00O()-C(016)-H(016)	120.1
C(00Y)-C(016)-H(016)	120.1

Symmetry transformations used to generate equivalent atoms

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R = 0.15
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Single crystal structure of compound 3n

A translucent light colourless rectangular needle-like specimen of $C_{18}H_{17}N_3O_4$, approximate dimensions 0.040 mm x 0.049 mm x 0.206 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

The total exposure time was 11.18 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 79029 reflections to a maximum θ angle of 26.00° (0.81 Å resolution), of which 3141 were independent (average redundancy 25.160, completeness = 100.0%, R_{int} = 21.20%, R_{sig} = 5.52%) and 1700(54.12%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.7816(13) Å, b = 7.4720(7) Å, c = 18.3634(18) Å, β = 99.553(4)°, volume = 1594.2(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 400 reflections above 20 σ(I) with 4.499° < 2θ < 68.77°.Data were corrected for absorption effects using the Numerical Mu Calculated method (SADABS). The ratio of minimum to maximum apparent transmission was 0.512.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{18}H_{17}N_3O_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 295 variables converged at R1 = 5.87%, for the observed data and wR2 = 16.84% for all data. The goodness-of-fit was 1.018. The largest peak in the final difference electron density synthesis was 0.235 $e^-/Å^3$ and the largest hole was -0.258 $e^-/Å^3$ with an RMS deviation of 0.059 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.414 g/cm^3 and F(000), 712 e^-. The CCDC number is: 2294776

Table S17. Crystal data and structure refinement for $C_{18}H_{17}N_3O_4$ at 293(2) K.

Empirical formula	$C_{18}H_{17}N_3O_4$
Formula weight	337.361
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.7816(13) Å, α = 90° b = 7.4720(7) Å, β = 99.553(4)° c = 18.3634(18) Å, γ = 90°
Volume	1594.2(3) $Å^3$
Z	4
Density (calculated)	1.414 g/cm^3
Absorption coefficient	0.102 mm^{-1}
F(000)	712
Crystal size	0.206 x 0.049 x 0.040 mm^3
θ range for data collection	2.249 to 25.999°

Index ranges	-14<=h<=14, -9<=k<=9, -22<=l<=22
Reflections collected	79029
Independent reflections	3141 [R_{int} = 0.2120]
Completeness to θ = 25.242°	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3141 / 0 / 295
Goodness-of-fit	1.018
Final R indices [I > 2σ(I)]	R_{obs} = 0.0587, wR_{obs} = 0.1322
R indices [all data]	R_{all} = 0.1188, wR_{all} = 0.1684
Extinction coefficient	0.039(4)
Largest diff. peak and hole	0.235 and -0.258 e·Å^{-3}

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0856P)^2+0.0679P]$ where $P=(Fo^2+2Fc^2)/3$

Table S18. Atomic coordinates (x10^4) and equivalent isotropic displacement parameters (Å^{2}x10^3) for $C_{18}H_{17}N_3O_4$ at 293(2) K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}^*
O(001)	9017(2)	2567(3)	7047(2)	1	62(1)
O(002)	5405(2)	3739(3)	3380(2)	1	66(1)
H(2)	5030(40)	3090(60)	3800(30)	1	118(15)
O(3)	2269(2)	409(3)	6103(2)	1	69(1)
N(004)	5447(2)	2269(3)	5876(2)	1	47(1)
N(005)	7388(2)	3404(3)	6226(2)	1	49(1)
O(006)	8136(2)	605(3)	6260(2)	1	76(1)
N(007)	5108(2)	2626(3)	4661(2)	1	48(1)
C(008)	4653(3)	2093(4)	5238(2)	1	45(1)
C(009)	6453(3)	2929(4)	5679(2)	1	47(1)
C(00A)	8165(3)	2109(5)	6498(2)	1	52(1)
C(00B)	6226(3)	3145(4)	4927(2)	1	47(1)
C(00C)	3545(3)	1434(4)	5284(2)	1	49(1)
H(0)	2950(30)	1290(40)	4820(17)	1	57(8)
C(00D)	6961(3)	3829(4)	4417(2)	1	48(1)
C(00E)	6512(3)	4123(4)	3671(2)	1	50(1)
C(00F)	3298(3)	1020(4)	5961(2)	1	53(1)
C(00G)	5192(3)	1830(4)	6560(2)	1	56(1)
H(6)	5760(30)	2070(40)	6981(16)	1	50(8)
C(00H)	7208(3)	4833(5)	3204(2)	1	60(1)
H(14)	6860(30)	5090(50)	2690(20)	1	86(12)
C(00I)	4139(3)	1215(5)	6604(2)	1	60(1)

H(5)	3990(30)	880(50)	7060(20)	1	87(12)
C(00J)	8345(3)	5217(5)	3452(2)	1	66(1)
H(15)	8840(30)	5780(40)	3120(19)	1	74(10)
C(00K)	8122(3)	4221(5)	4655(2)	1	65(1)
H(13)	8470(30)	4050(40)	5170(20)	1	79(11)
C(00L)	7418(3)	5277(5)	6487(2)	1	63(1)
H(12)	6730(40)	5430(60)	6790(20)	1	107(14)
H(11)	7230(40)	5970(50)	6030(20)	1	106(15)
C(00M)	8912(4)	4184(5)	7463(2)	1	69(1)
H(10)	8370(40)	3950(50)	7820(20)	1	91(13)
H(9)	9800(40)	4270(50)	7770(20)	1	98(13)
C(00N)	8560(4)	5700(5)	6949(2)	1	73(2)
H(8)	8460(40)	6890(60)	7210(20)	1	105(13)
H(7)	9170(40)	5900(50)	6620(20)	1	96(14)
C(00O)	8805(3)	4881(6)	4182(2)	1	73(2)
H(16)	9590(30)	5180(50)	4350(20)	1	85(11)
C(00P)	1333(4)	350(7)	5495(2)	1	76(2)
H(4)	730(40)	-110(60)	5690(20)	1	95(14)
H(3)	1200(30)	1590(50)	5290(20)	1	80(12)
H(1)	1570(40)	-590(50)	5070(20)	1	104(14)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S19. Anisotropic displacement parameters ($Å^2x10^3$) for $C_{18}H_{17}N_3O_4$ at 293(2) K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(001)	49(2)	83(2)	48(2)	8(2)	-8(1)	-7(2)
O(002)	52(2)	99(2)	42(2)	-11(2)	-4(2)	8(2)
O(3)	57(2)	94(2)	57(2)	-19(2)	10(2)	3(2)
N(004)	42(2)	60(2)	37(2)	1(2)	1(2)	1(1)
N(005)	43(2)	61(2)	40(2)	3(2)	-3(2)	-4(2)
O(006)	81(2)	67(2)	71(2)	13(2)	-17(2)	-11(2)
N(007)	41(2)	60(2)	39(2)	0(2)	0(2)	1(2)
C(008)	42(2)	51(2)	38(2)	4(2)	-2(2)	0(2)
C(009)	42(2)	60(2)	37(2)	-1(2)	-2(2)	-3(2)
C(00A)	46(2)	72(2)	37(2)	5(2)	0(2)	2(2)
C(00B)	41(2)	57(2)	41(2)	5(2)	0(2)	-3(2)
C(00C)	45(2)	56(2)	45(2)	0(2)	0(2)	-2(2)
C(00D)	43(2)	60(2)	41(2)	2(2)	5(2)	-2(2)

C(00E)	47(2)	56(2)	45(2)	1(2)	3(2)	-3(2)
C(00F)	49(2)	59(2)	51(2)	-7(2)	8(2)	0(2)
C(00G)	56(2)	72(2)	38(2)	0(2)	-1(2)	2(2)
C(00H)	61(2)	73(2)	46(2)	-1(2)	7(2)	1(2)
C(00I)	56(2)	77(2)	44(2)	-6(2)	4(2)	2(2)
C(00J)	56(2)	86(2)	56(2)	-2(2)	15(2)	7(2)
C(00K)	46(2)	99(3)	48(2)	-5(2)	3(2)	2(2)
C(00L)	52(2)	72(2)	62(2)	8(2)	-2(2)	-16(2)
C(00M)	57(2)	97(3)	51(2)	2(2)	-2(2)	-18(2)
C(00N)	58(2)	78(2)	79(3)	0(2)	-3(2)	-24(2)
C(00O)	47(2)	106(3)	64(2)	-13(2)	5(2)	9(2)
C(00P)	55(3)	100(3)	71(3)	-18(2)	3(2)	5(2)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Table S20. Bond lengths [Å] for $C_{18}H_{17}N_3O_4$ at 293(2) K with estimated standard deviations in parentheses.

Label	Distances
O(001)-C(00A)	1.344(3)
O(001)-C(00M)	1.445(4)
O(002)-C(00E)	1.356(4)
O(002)-H(2)	1.06(5)
O(3)-C(00F)	1.361(4)
O(3)-C(00P)	1.433(4)
N(004)-C(00G)	1.379(4)
N(004)-C(008)	1.379(3)
N(004)-C(009)	1.386(4)
N(005)-C(00A)	1.368(4)
N(005)-C(009)	1.407(3)
N(005)-C(00L)	1.478(4)
O(006)-C(00A)	1.204(4)
N(007)-C(008)	1.325(4)
N(007)-C(00B)	1.382(4)
C(008)-C(00C)	1.412(4)
C(009)-C(00B)	1.373(4)
C(00B)-C(00D)	1.469(4)
C(00C)-C(00F)	1.357(4)
C(00C)-H(0)	1.02(3)
C(00D)-C(00K)	1.396(5)

C(00D)-C(00E)	1.401(4)
C(00E)-C(00H)	1.387(5)
C(00F)-C(00I)	1.417(4)
C(00G)-C(00I)	1.338(5)
C(00G)-H(6)	0.95(3)
C(00H)-C(00J)	1.371(5)
C(00H)-H(14)	0.98(4)
C(00I)-H(5)	0.92(4)
C(00J)-C(00O)	1.382(5)
C(00J)-H(15)	1.00(4)
C(00K)-C(00O)	1.371(5)
C(00K)-H(13)	0.97(3)
C(00L)-C(00N)	1.501(5)
C(00L)-H(12)	1.06(5)
C(00L)-H(11)	0.98(4)
C(00M)-C(00N)	1.488(6)
C(00M)-H(10)	1.01(4)
C(00M)-H(9)	1.11(4)
C(00N)-H(8)	1.03(4)
C(00N)-H(7)	1.03(4)
C(00O)-H(16)	0.95(4)
C(00P)-H(4)	0.92(4)
C(00P)-H(3)	1.00(4)
C(00P)-H(1)	1.11(4)

Symmetry transformations used to generate equivalent atoms:

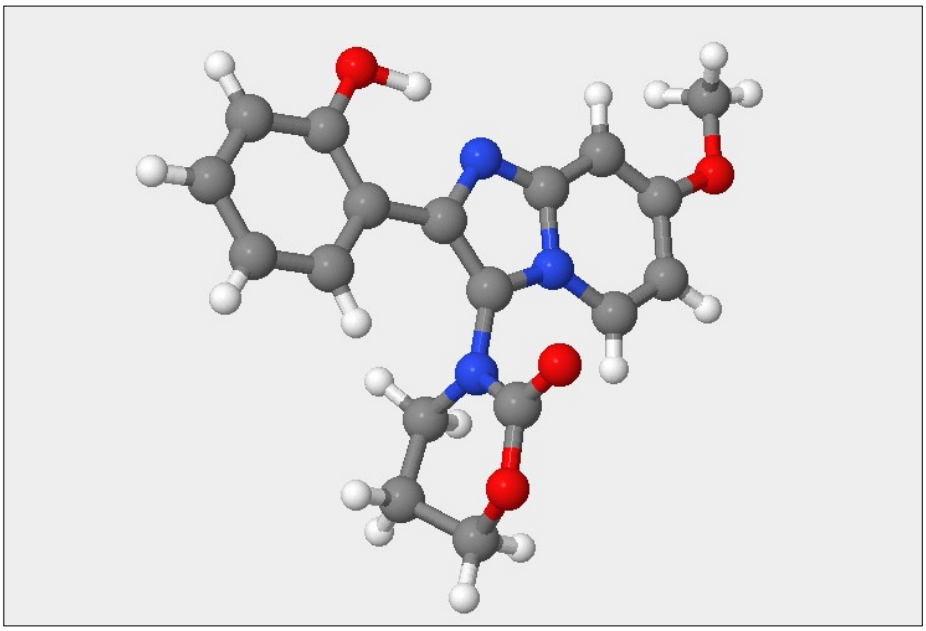
Table S21. Bond angles [°] for $C_{18}H_{17}N_3O_4$ at 293(2) K with estimated standard deviations in parentheses.

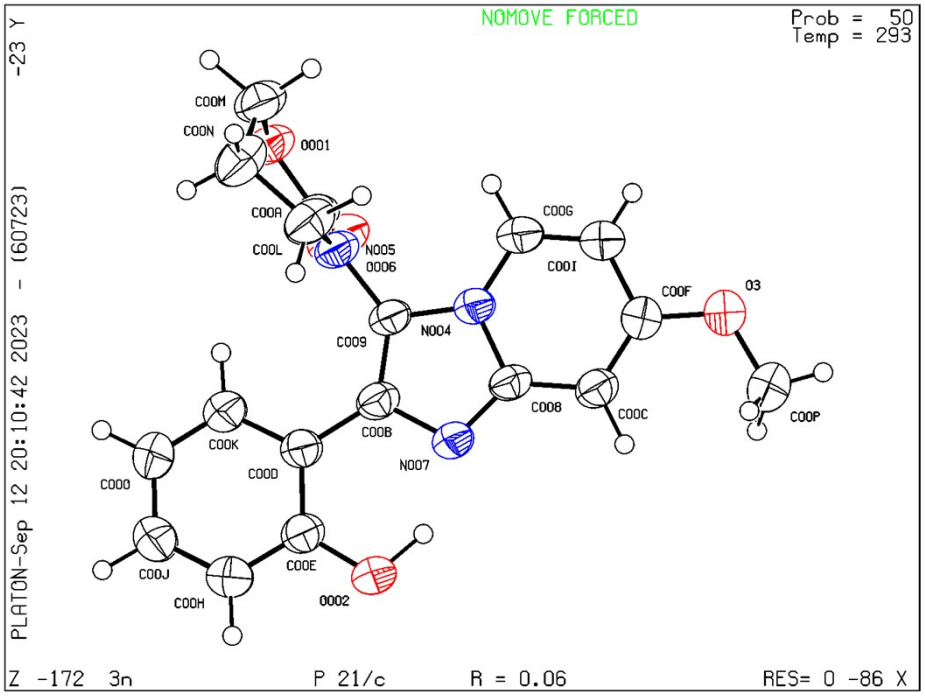
Label	Angles
C(00A)-O(001)-C(00M)	119.4(3)
C(00E)-O(002)-H(2)	108(2)
C(00F)-O(3)-C(00P)	117.1(3)
C(00G)-N(004)-C(008)	122.1(3)
C(00G)-N(004)-C(009)	130.3(2)
C(008)-N(004)-C(009)	107.5(2)
C(00A)-N(005)-C(009)	118.7(2)
C(00A)-N(005)-C(00L)	124.9(3)
C(009)-N(005)-C(00L)	116.4(2)
C(008)-N(007)-C(00B)	106.8(2)

N(007)-C(008)-N(004)	110.1(3)
N(007)-C(008)-C(00C)	130.8(3)
N(004)-C(008)-C(00C)	119.0(3)
C(00B)-C(009)-N(004)	105.8(2)
C(00B)-C(009)-N(005)	133.5(3)
N(004)-C(009)-N(005)	120.4(2)
O(006)-C(00A)-O(001)	118.9(3)
O(006)-C(00A)-N(005)	123.4(3)
O(001)-C(00A)-N(005)	117.7(3)
C(009)-C(00B)-N(007)	109.8(3)
C(009)-C(00B)-C(00D)	130.2(3)
N(007)-C(00B)-C(00D)	120.0(2)
C(00F)-C(00C)-C(008)	118.4(3)
C(00F)-C(00C)-H(0)	121.5(18)
C(008)-C(00C)-H(0)	120.1(17)
C(00K)-C(00D)-C(00E)	117.7(3)
C(00K)-C(00D)-C(00B)	121.6(3)
C(00E)-C(00D)-C(00B)	120.7(3)
O(002)-C(00E)-C(00H)	117.8(3)
O(002)-C(00E)-C(00D)	122.3(3)
C(00H)-C(00E)-C(00D)	119.9(3)
C(00C)-C(00F)-O(3)	125.8(3)
C(00C)-C(00F)-C(00I)	120.9(3)
O(3)-C(00F)-C(00I)	113.4(3)
C(00I)-C(00G)-N(004)	118.8(3)
C(00I)-C(00G)-H(6)	123.5(17)
N(004)-C(00G)-H(6)	117.6(18)
C(00J)-C(00H)-C(00E)	121.3(3)
C(00J)-C(00H)-H(14)	120(2)
C(00E)-C(00H)-H(14)	118(2)
C(00G)-C(00I)-C(00F)	120.8(3)
C(00G)-C(00I)-H(5)	118(2)
C(00F)-C(00I)-H(5)	121(3)
C(00H)-C(00J)-C(00O)	119.3(3)
C(00H)-C(00J)-H(15)	121.1(19)
C(00O)-C(00J)-H(15)	120(2)
C(00O)-C(00K)-C(00D)	121.6(3)

C(00O)-C(00K)-H(13)	118(2)
C(00D)-C(00K)-H(13)	120(2)
N(005)-C(00L)-C(00N)	110.7(3)
N(005)-C(00L)-H(12)	107(2)
C(00N)-C(00L)-H(12)	112(2)
N(005)-C(00L)-H(11)	103(2)
C(00N)-C(00L)-H(11)	115(3)
H(12)-C(00L)-H(11)	108(3)
O(001)-C(00M)-C(00N)	109.9(3)
O(001)-C(00M)-H(10)	108(2)
C(00N)-C(00M)-H(10)	114(2)
O(001)-C(00M)-H(9)	99(2)
C(00N)-C(00M)-H(9)	115(2)
H(10)-C(00M)-H(9)	110(3)
C(00M)-C(00N)-C(00L)	109.1(4)
C(00M)-C(00N)-H(8)	114(2)
C(00L)-C(00N)-H(8)	107(2)
C(00M)-C(00N)-H(7)	110(2)
C(00L)-C(00N)-H(7)	110(2)
H(8)-C(00N)-H(7)	107(3)
C(00K)-C(00O)-C(00J)	120.2(4)
C(00K)-C(00O)-H(16)	121(2)
C(00J)-C(00O)-H(16)	118(2)
O(3)-C(00P)-H(4)	105(2)
O(3)-C(00P)-H(3)	108(2)
H(4)-C(00P)-H(3)	115(3)
O(3)-C(00P)-H(1)	108(2)
H(4)-C(00P)-H(1)	110(3)
H(3)-C(00P)-H(1)	111(3)

Symmetry transformations used to generate equivalent atoms

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