Unprecedented Regiochemical Control in the Formation of Phenyl[1,2-a]imidazopyridines from Alkynyliodonium Salts: Mechanistic Insights**

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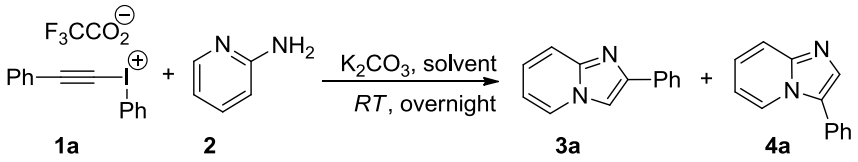
1 Data Tables

Table 1. Solvent optimization for the reaction of **1a** and **2**

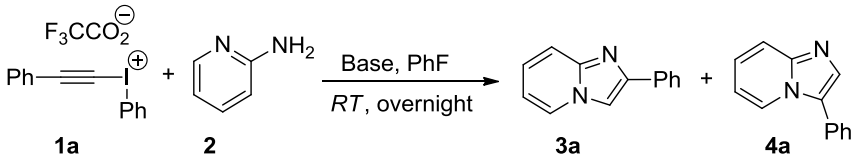


1a **2** **3a** **4a**

Solvent	Yield **3a** (%)	Yield **4a** (%)	Total Yield (%)
Methanol	0	0	0
Tetrahydrofuran	<16[a]	<7[a]	<<23[a]
1,4-Dioxane	15	5	20
Dichloromethane	20	28	48
Dibromomethane	27	24	51
Chloroform	21	36	57
Fluorobenzene	22	33	55

[a] Yields estimated by ^{1}H-NMR due to high impurity levels

Table 2. Base optimization for the reaction **1a** and **2**

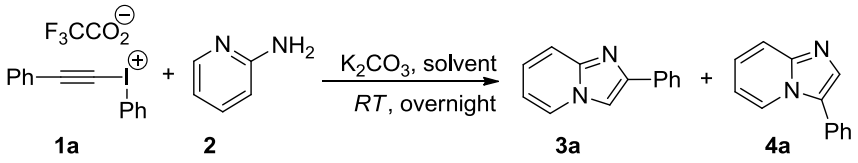


1a **2** **3a** **4a**

[**1a**] (molL^{-1})	Base	Ratio (**3a**) : (**4a**)	Yield
0.11	K_2CO_3	39 : 61	
0.11	Li_2CO_3	36 : 64	
0.11	Cs_2CO_3	43 : 57	
0.11	NEt_3	-	
0.11	*i*Pr_2EtN	-	
0.11	DBU[a]	-	

[a] DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene

Table 3. Effect of solvent on concentration dependence



1a **2** **3a** **4a**

Entry[a]	[**1a**] (molL^{-1})	Solvent	Ratio **3a**:**4a**
1	0.11	PhF	39 : 61[b]
2	0.11	DCM	41 : 59
3	0.11	$CHCl_3$	36 : 64
4	0.02	PhF	73 : 27[b]
5	0.02	DCM	60 : 40
6	0.02	$CHCl_3$	64 : 36

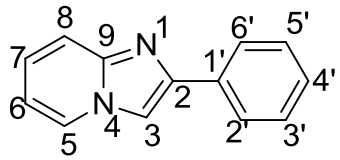
[a] All reactions performed on a 5 mmol scale; [b] Reaction performed in triplicate (n = 3)

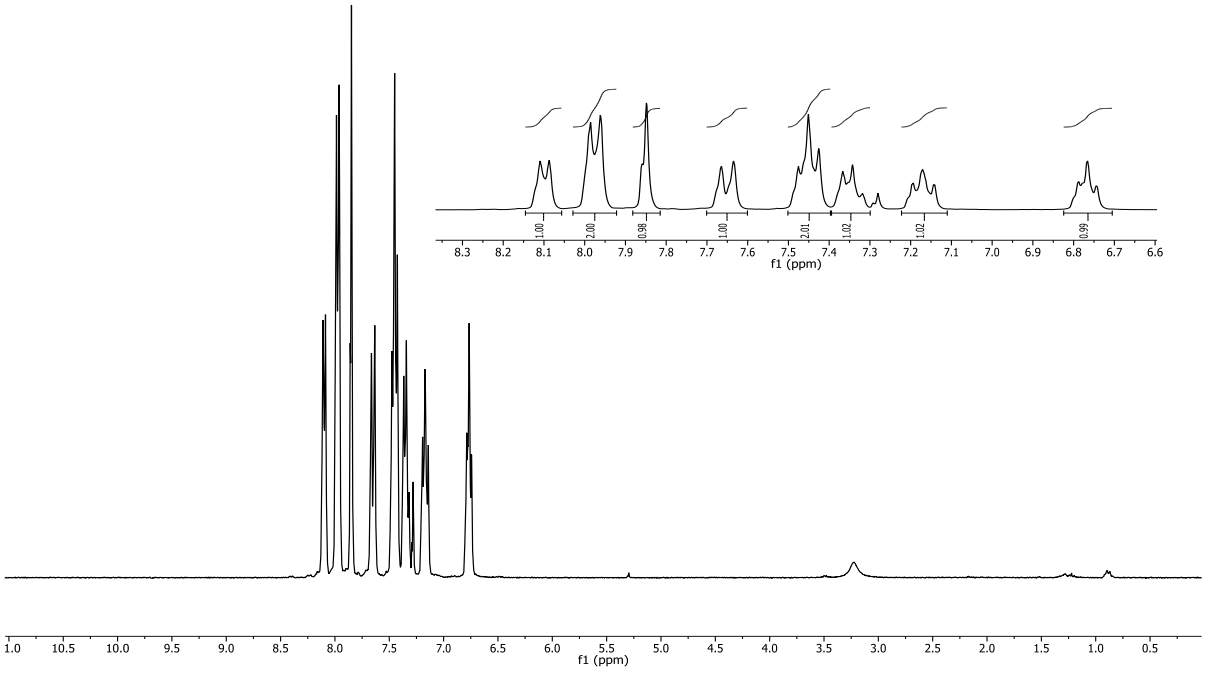
2 Experimental

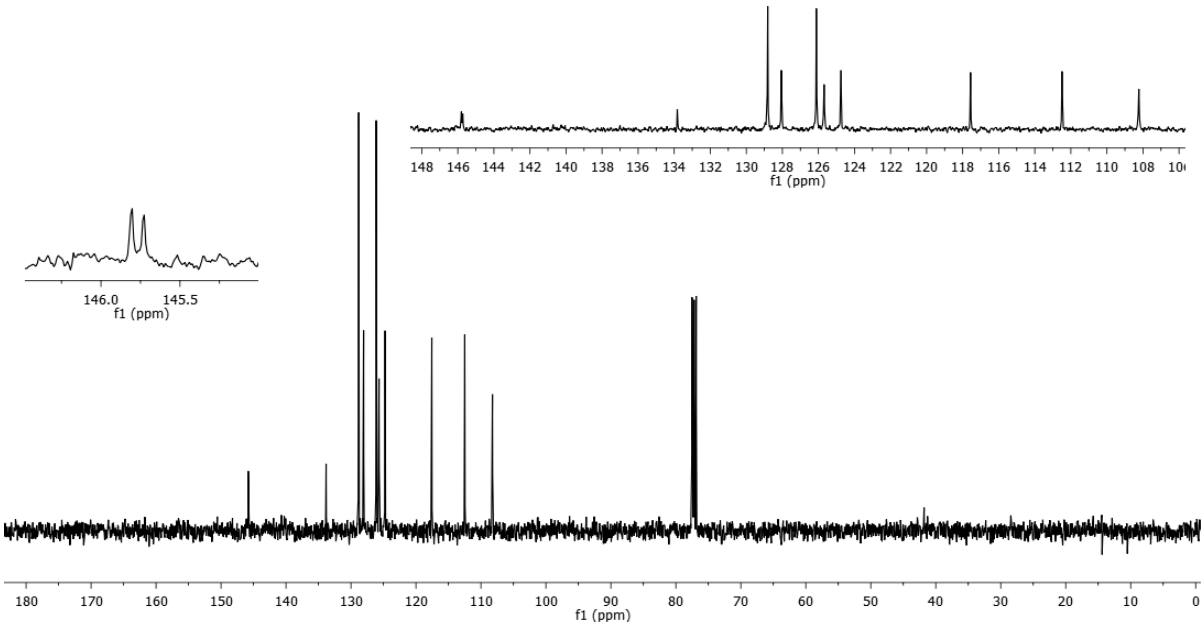
Reactions requiring anhydrous conditions were performed using oven- or flame-dried glassware and conducted under a positive pressure of nitrogen. Anhydrous solvents were prepared thus: DCM and MeCN were refluxed over CaH_2, THF, ether and hexane were refluxed over sodium/benzophenone, toluene was refluxed over sodium and dibromomethane, chloroform, 1,4-dioxane and fluorobenzene were stored over 3Å molecular sieves. Infrared spectra were recorded on a Varian Scimitar Series 800 FT-IR with internal calibration. ^{1}H, ^{13}C and ^{19}F-NMR spectra were recorded on a Bruker Advance 300 MHz spectrometer, a Jeol ECS 400 MHz spectrometer or a Jeol Lamda 500 MHz spectrometer with residual tetramethylsilane solvent as the reference for ^{1}H and ^{13}C. ^{19}F spectra were referenced with $CFCl_3$. Elemental analysis was carried out at London Metropolitan University. Mass spectrometry was recorded at the EPSRC Mass Spectrometry Service, Swansea or on a Waters LCT Premier (TOF-MS) operating in 'W' mode. Melting points were recorded on a Gallenkamp MF-370 melting point apparatus and are uncorrected. Automated flash chromatography was performed using a Varian IntelliFlash 971-FP discovery scale flash purification system. The terms 'ether' and 'petrol' refer to diethyl ether and the fractions boiling between 40 and 60 °C (unless otherwise specified) respectively.

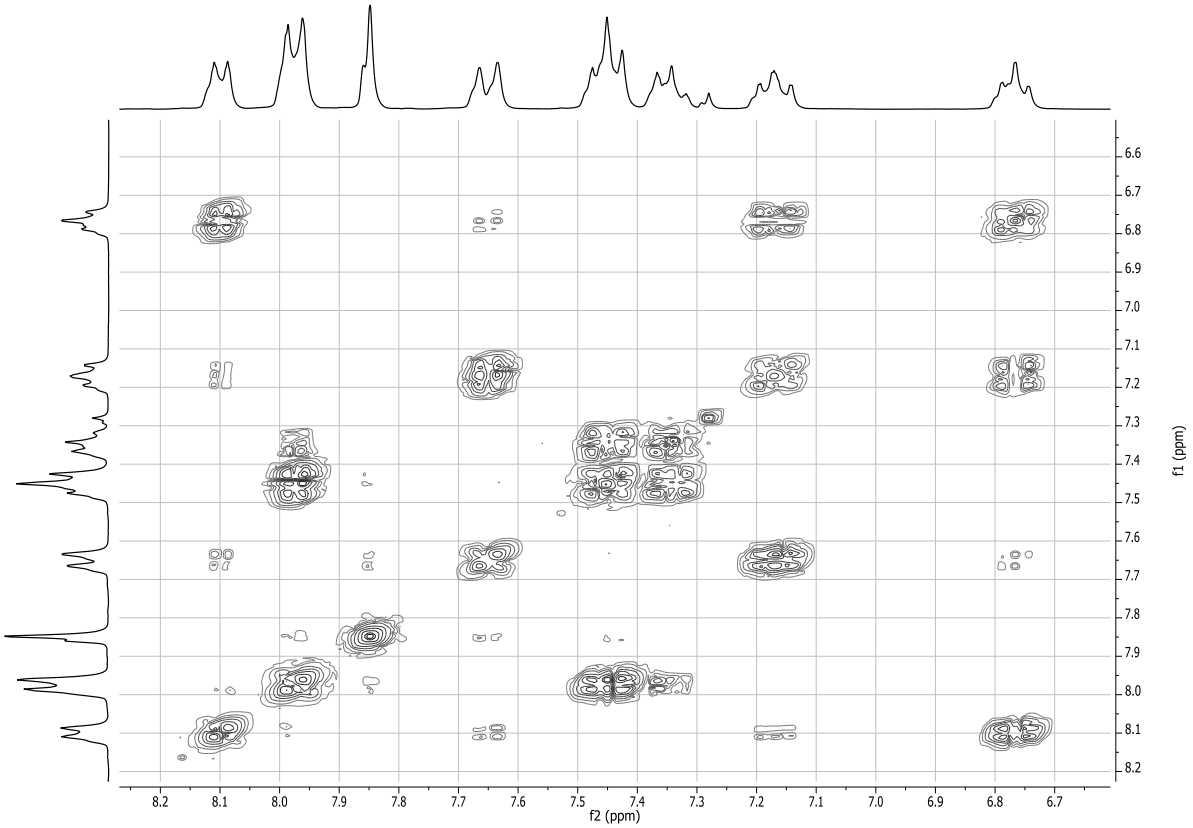
CAUTION: Some hypervalent iodanes are potentially explosive and should be handled taking appropriate precautions.[1-4]

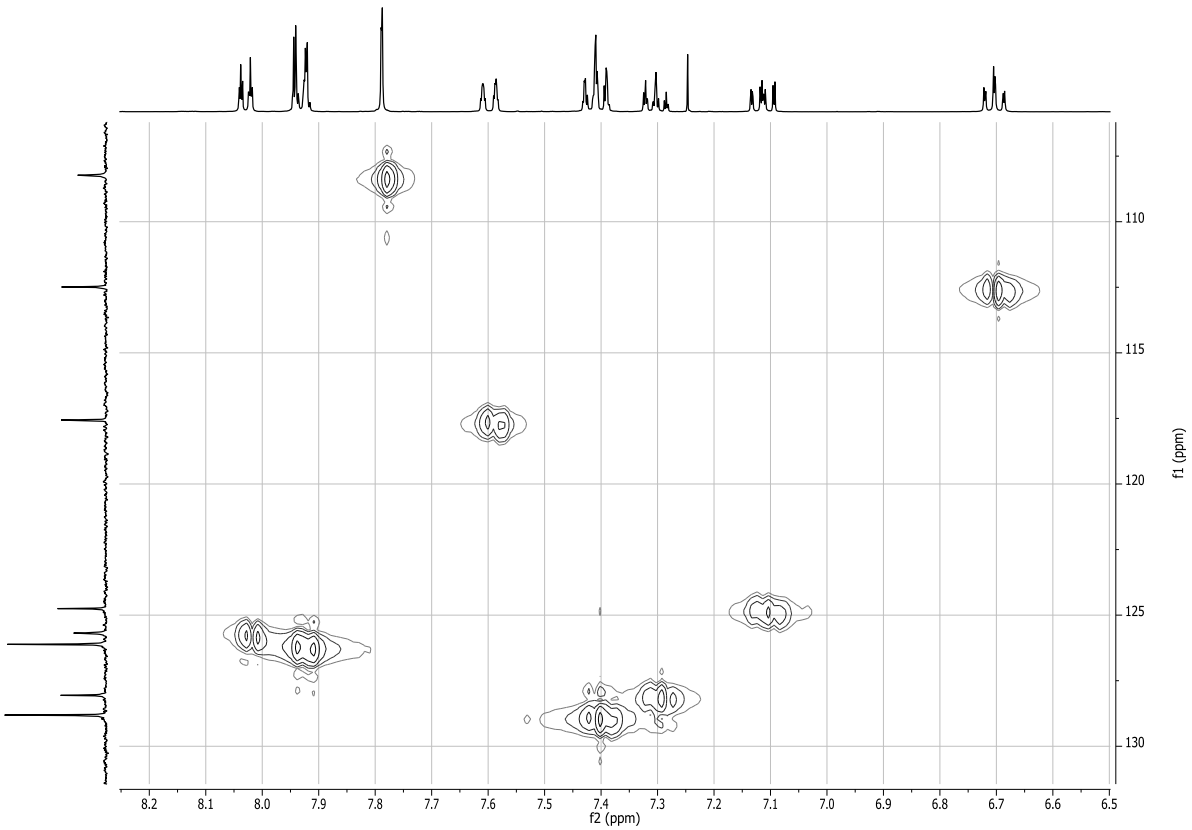
2.1 2-Phenylimidazo[1,2-*a*]pyridine (3a)[5-7]



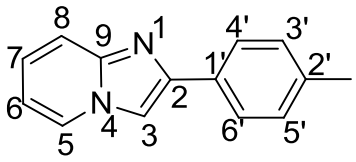




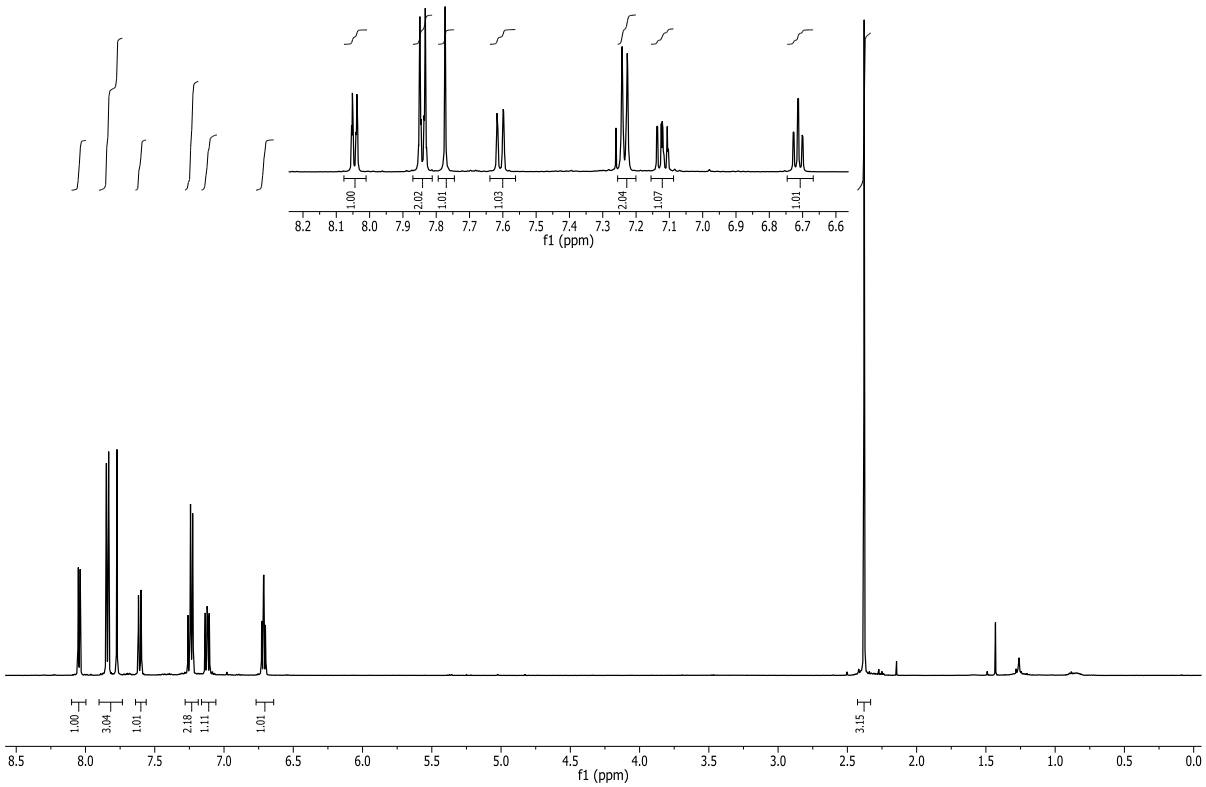


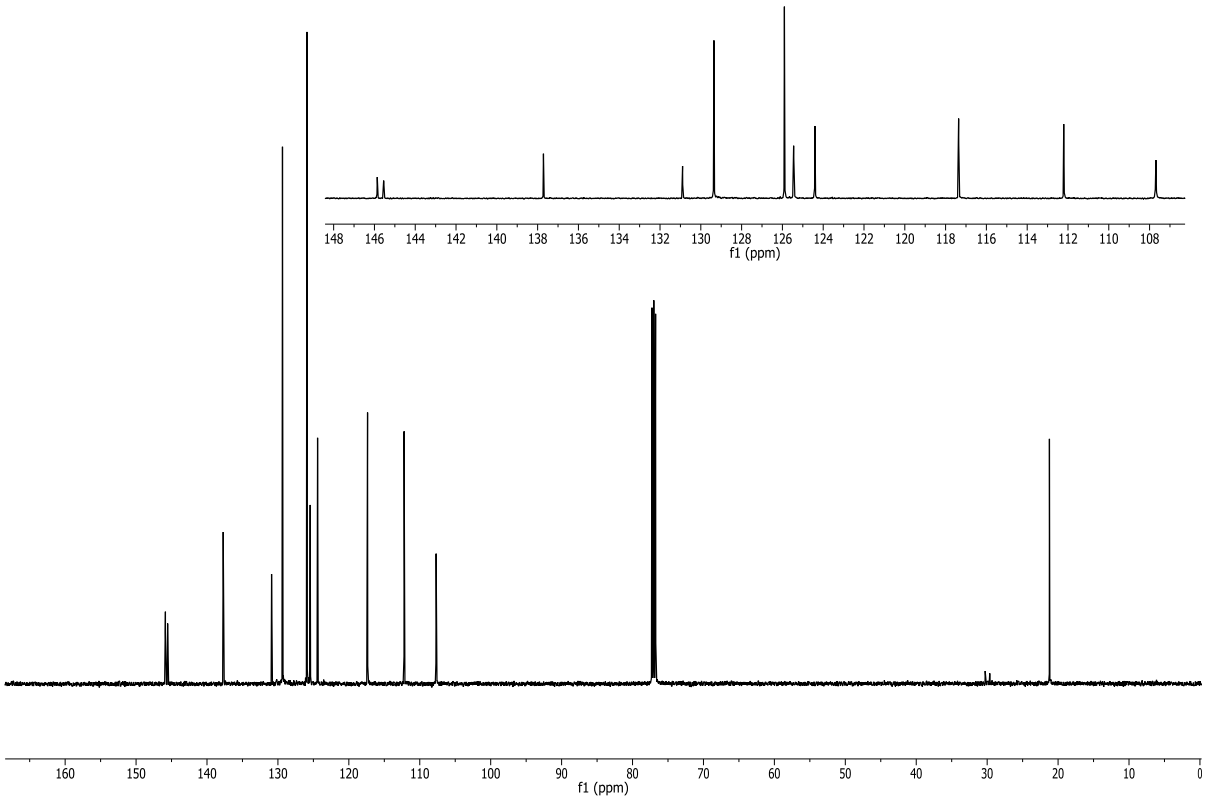


2.2 2-(4′-Methylphenyl)imidazo[1,2-*a*]pyridine (**3b**)[7, 8]

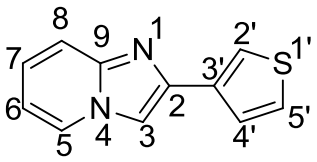


Using K_2CO_3 (1.09 g, 7.89 mmol), **2** (0.32 g, 3.39 mmol), PhF (113 mL) and **1b** (1.11 g, 2.56 mmol). White crystalline solid (0.26 g, 1.25 mmol, 49%). Mp 138-140 °C (from acetone) (lit.[8] mp 145-146 °C); R_f 0.23 (4:1 ether/petrol); IR ν_{max}/cm^{-1} (neat) 3132, 1633, 1506, 1483, 1372, 1349, 1268, 1245, 1202, 1139; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.05 (1H, dt_{app}, H5 J = 6.8 Hz, J = 1.2 Hz), 7.84 (2H, d, H3′/H5′ J = 8.1 Hz), 7.77 (1H, s, H3), 7.60 (1H, dd, H8 J = 9.1 Hz, J = 0.8 Hz), 7.23 (2H, d, H2′/H6′ J = 8.1 Hz), 7.12 (1H, ddd, H7 J = 9.1 Hz, J = 6.8 Hz, J = 1.3 Hz), 6.71 (1H, dt_{app}, H6 J = 6.8 Hz, J = 1.1 Hz), 2.38 (3H, s, Me); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 145.86, 145.55, 137.72, 130.89, 129.36, 125.90, 125.45, 124.41, 117.36, 112.21, 107.69, 21.22; *m/z* (ESI) 209 ($[M+H]^+$, 100%). Found: $[M+H]^+$, 209.1071. $C_{14}H_{13}N_2$ requires 209.1073. Anal. Calcd. for $C_{14}H_{12}N_2$: C, 80.74 ; H, 5.81; N, 13.45. Found: C, 80.85; H, 5.73; N, 13.39.

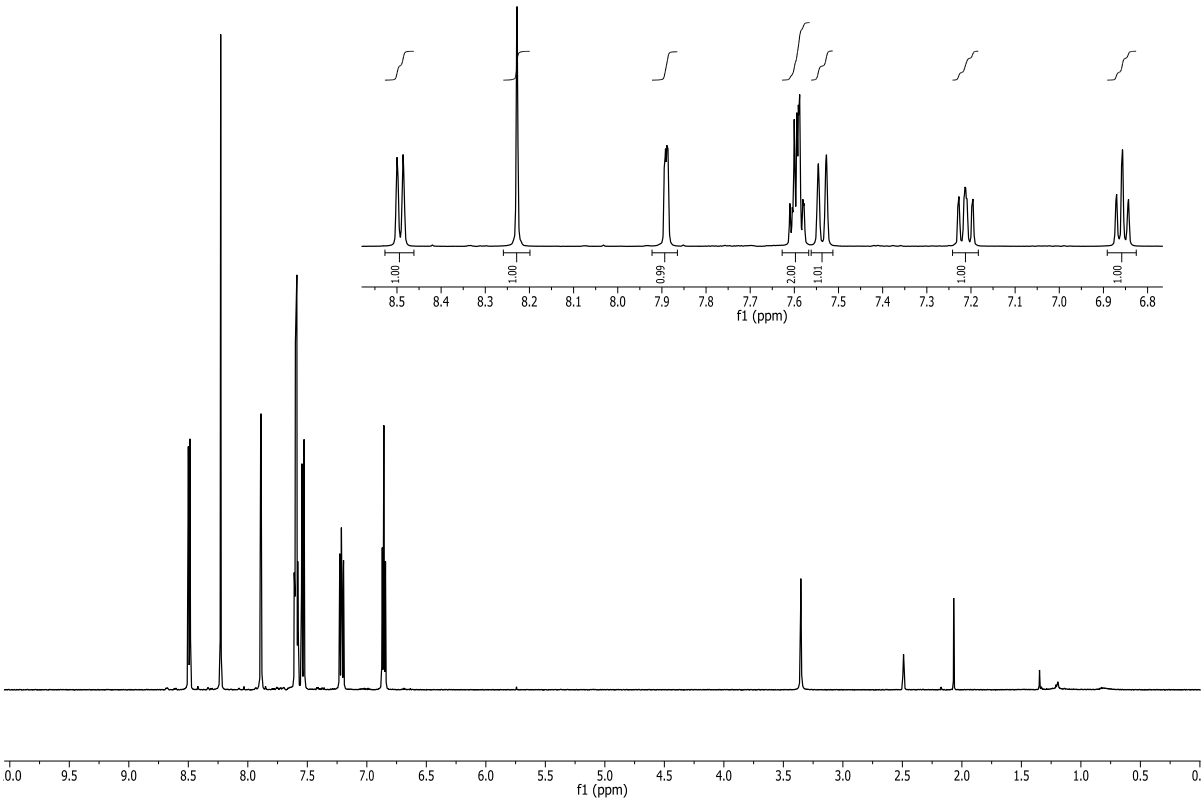


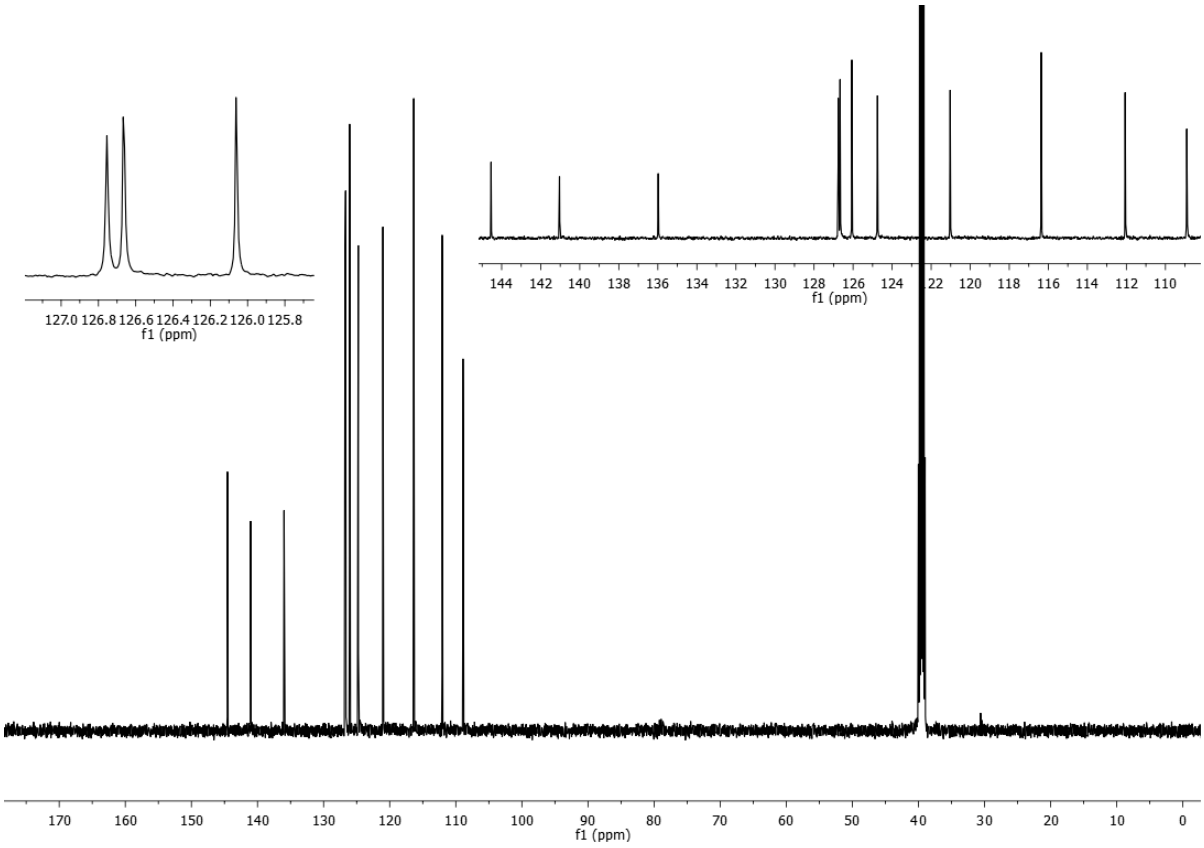


2.3 2-(3′-Thienyl)imidazo[1,2-*a*]pyridine (3c)

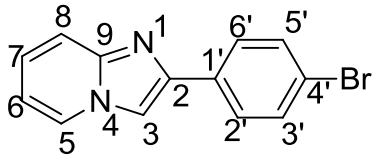


Using K_2CO_3 (1.06 g, 7.64 mmol), **2** (0.32 g, 3.36 mmol), PhF (113 mL) and **1c** (1.03 g, 2.43 mmol). White crystalline solid (0.25 g, 1.21 mmol, 48%). Mp 163-165 °C (from acetone); R_f 0.12 (4:1 ether/petrol); IR ν_{max}/cm^{-1} (neat) 3124, 1632, 1508, 1476, 1338, 1306, 1272, 1242, 1144, 1090; ^{1}H-NMR (500 MHz, d_6-DMSO) δ 8.49 (1H, d, H5 J = 6.7 Hz), 8.23 (1H, s, H3), 7.89 (1H, d, H2′ J = 2.8 Hz), 7.61-7.55 (2H, m, H4′/H5′), 7.54 (1H, d, H8 J = 9.0 Hz), 7.21 (1H, t_{app}, H7 J = 6.6 Hz), 6.86 (1H, t_{app}, H6 J = 6.7 Hz); ^{13}C-NMR (125 MHz, d_6-DMSO) δ 144.94, 141.44, 136.38, 127.16, 127.07, 126.46, 125.15, 121.43, 116.76, 112.46, 109.31; *m/z* (ESI) 201 ([M+H]$^+$, 100%). Found: [M+H]$^+$, 201.0480. $C_{11}H_9N_2S$ requires 201.0481. Anal. Calcd. for $C_{11}H_8N_2S$: C, 60.97 ; H, 4.03; N, 13.99. Found: C, 66.13; H, 3.89; N, 13.82.

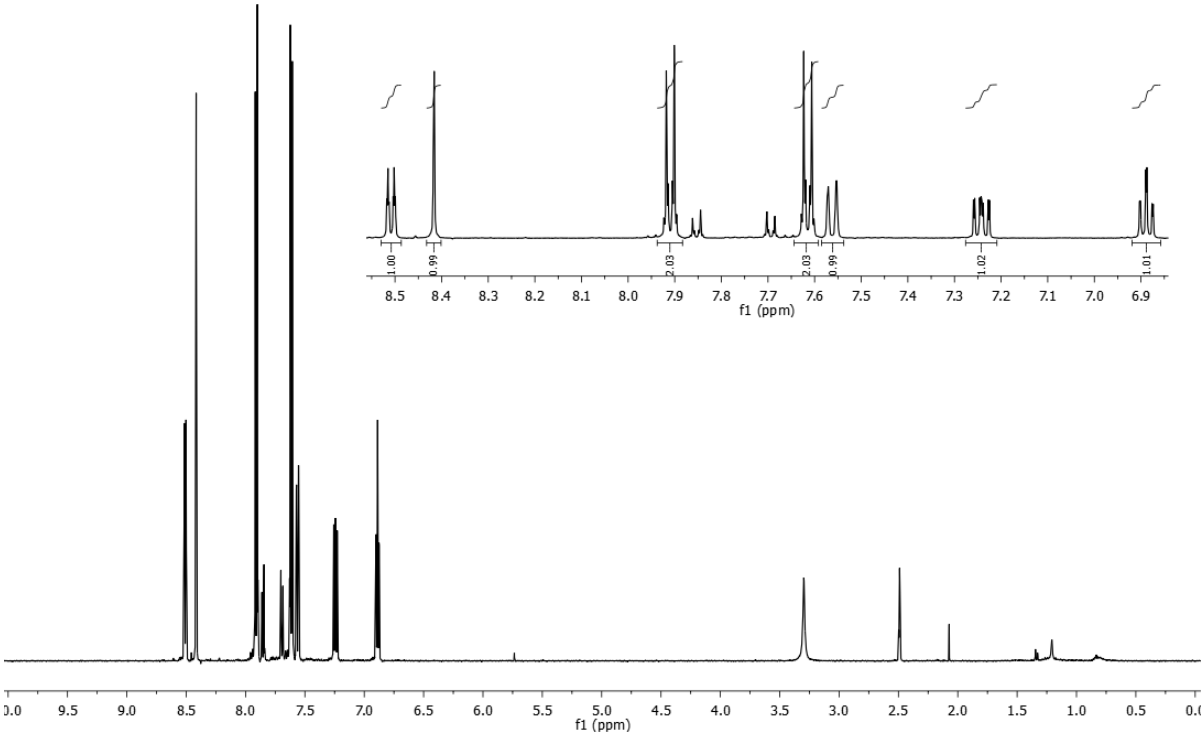


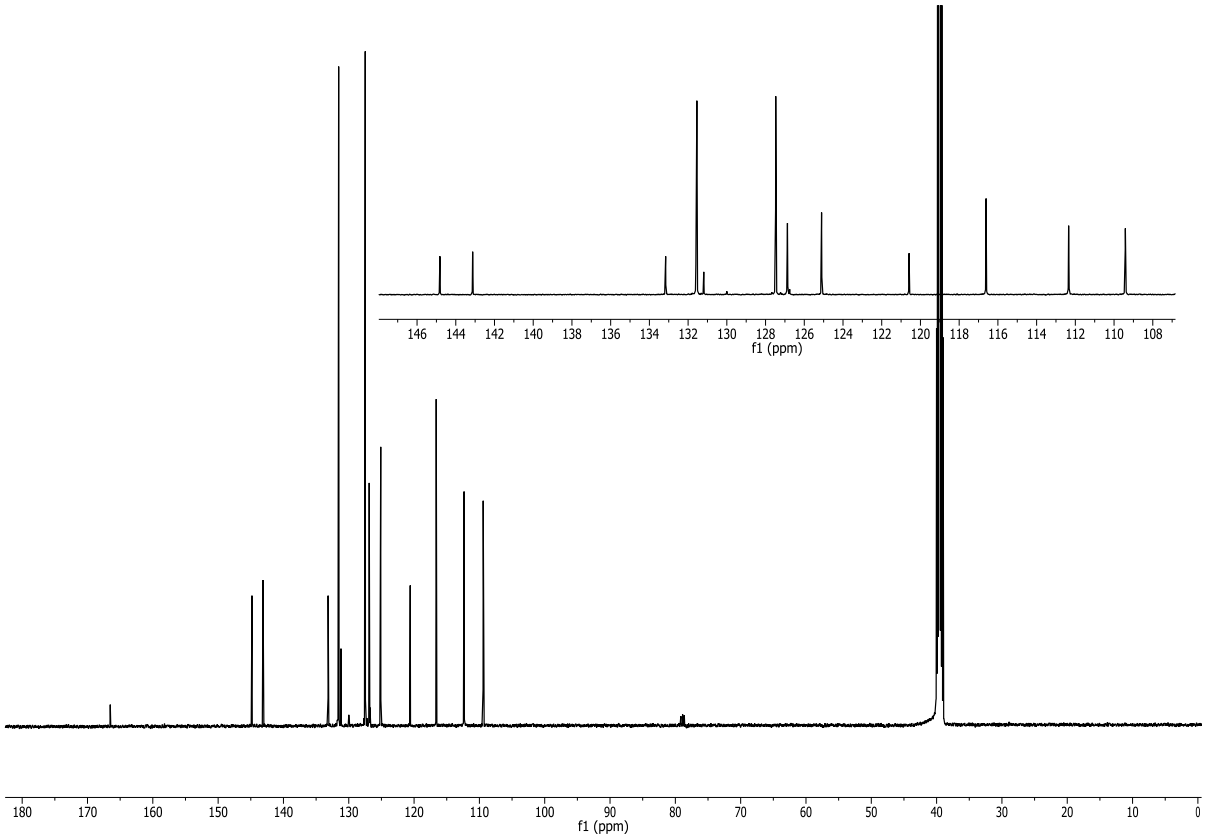


2.4 2-(4′-Bromophenyl)imidazo[1,2-*a*]pyridine (**3d**)[9]

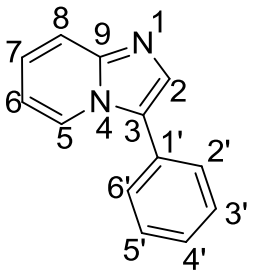


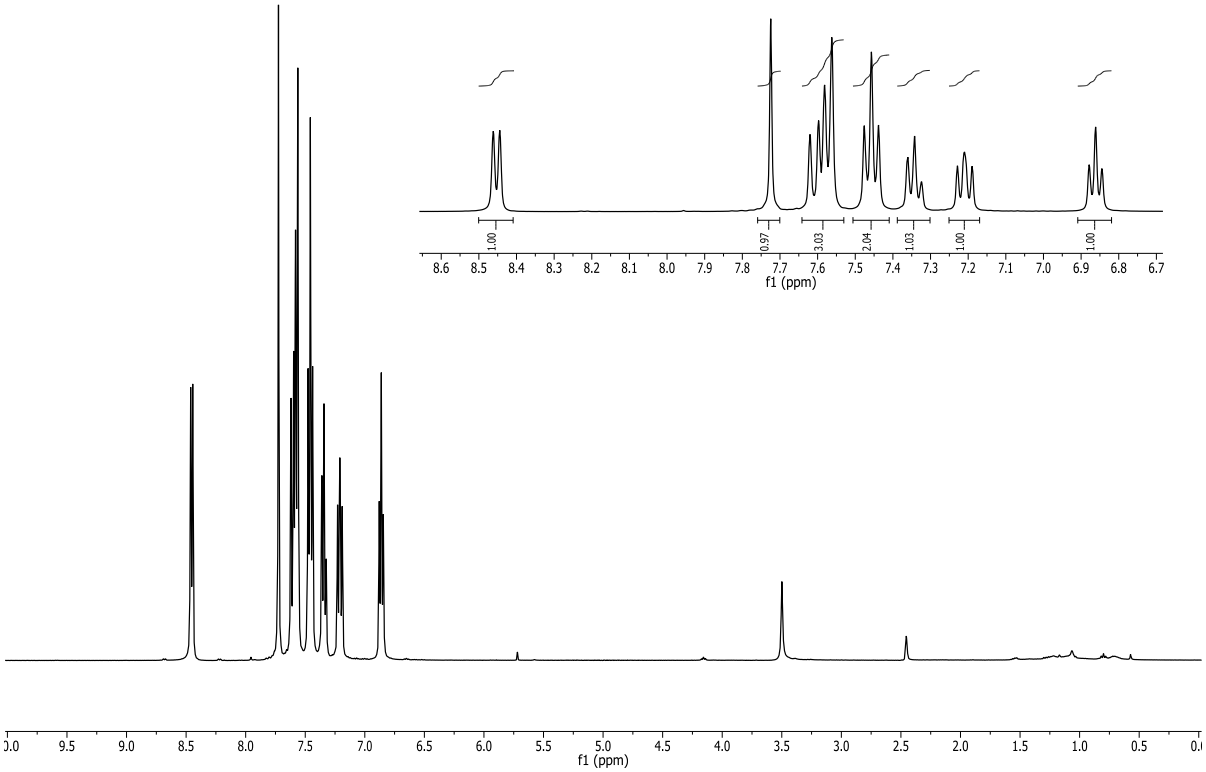
Using K_2CO_3 (0.96 g, 6.91 mmol), **2** (0.28 g, 2.95 mmol), PhF (102 mL) and **1d** (1.13 g, 2.27 mmol). White crystalline solid (0.29 g, 1.47 mmol, 65%). Mp 196-198 °C (from acetone) (lit.[9] mp 215-216 °C from heptane); R_f 0.34 (4:1 ether/petrol); IR ν_{max}/cm^{-1} (neat) 2955, 2924, 1679, 1635, 1428, 1401, 1371, 1321, 1203, 1065, 1006; ^{1}H-NMR (500 MHz, d_6-DMSO) δ 8.51 (1H, dt_{app}, H5 J = 6.8 Hz, J = 1.2 Hz), 8.42 (1H, s, H3), 7.91 (2H, d, H3′/H5′ J = 8.7 Hz), 7.61 (2H, d, H2′/H6′ J = 8.7 Hz), 7.56 (1H, dd, H8 J = 9.1 Hz, J = 1.0 Hz), 7.24 (1H, ddd, H7, J = 9.1 Hz, J = 6.8 Hz, J = 1.3 Hz), 6.89 (1H, td_{app}, H6 J = 6.8, J = 1.0 Hz); ^{13}C-NMR (125 MHz, d_6-DMSO) δ 144.82, 143.13, 133.16, 131.55, 127.47, 126.87, 125.11, 120.59, 116.61, 112.34, 109.42; *m/z* (ESI) 275 ([^{81}Br][M+H]$^+$, 97%), 273 ([^{79}Br][M+H]$^+$, 100%). Found: [M+H]$^+$, 273.0026. $C_{13}H_{10}BrN_2$ requires 273.0022. Anal. Calcd. for $C_{13}H_9BrN_2$: C, 57.17; H, 3.32; N, 10.26. Found: C, 57.29; H, 3.21; N, 10.13.

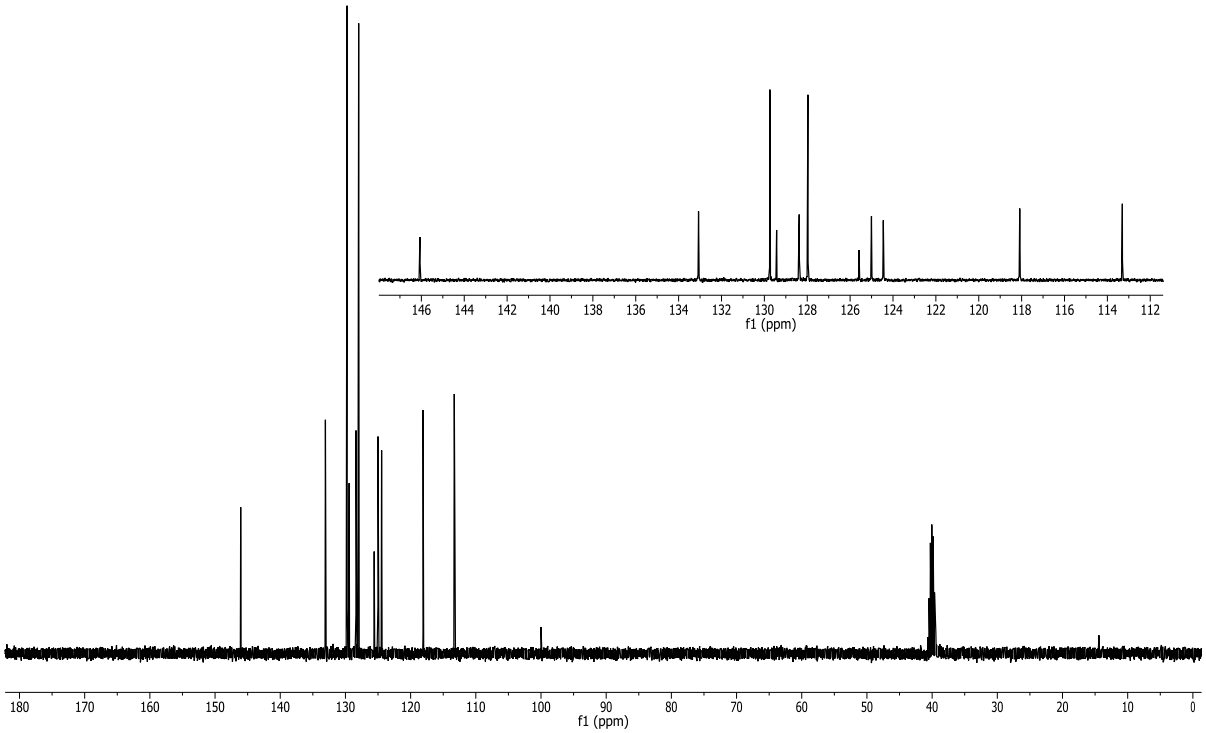


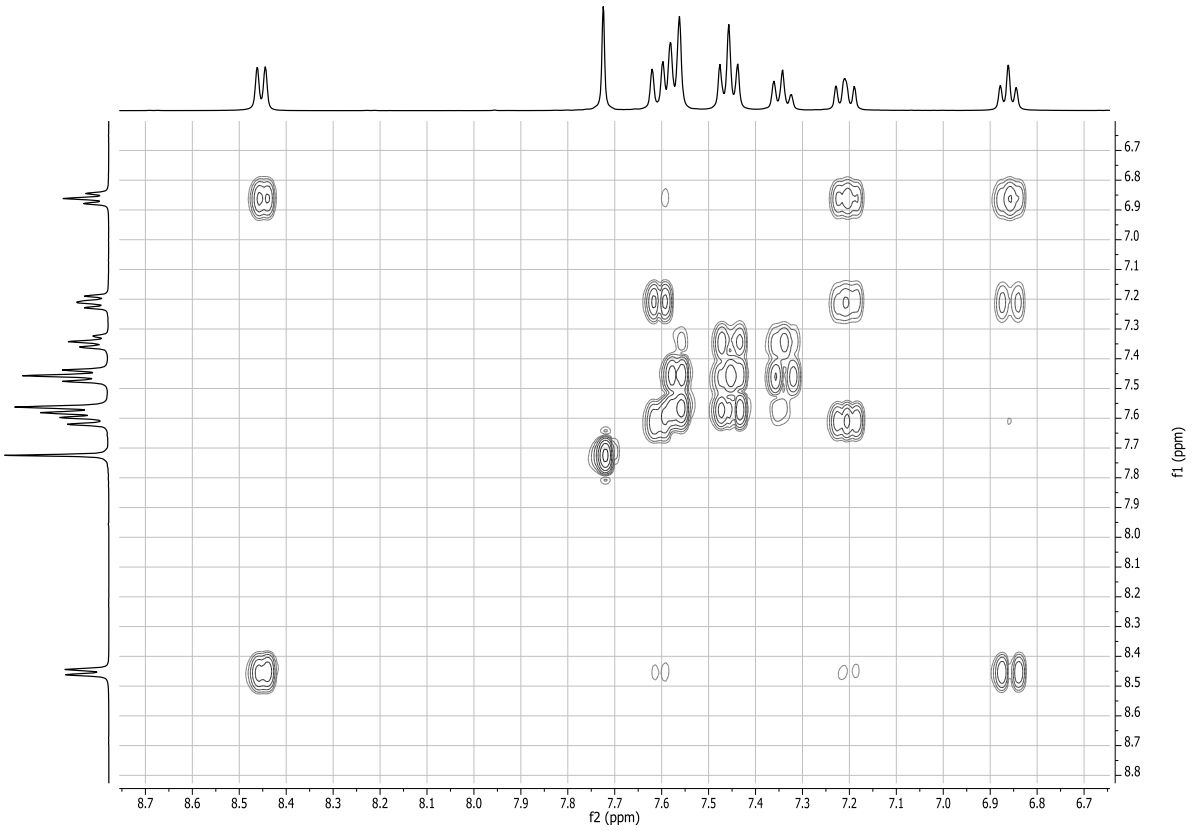


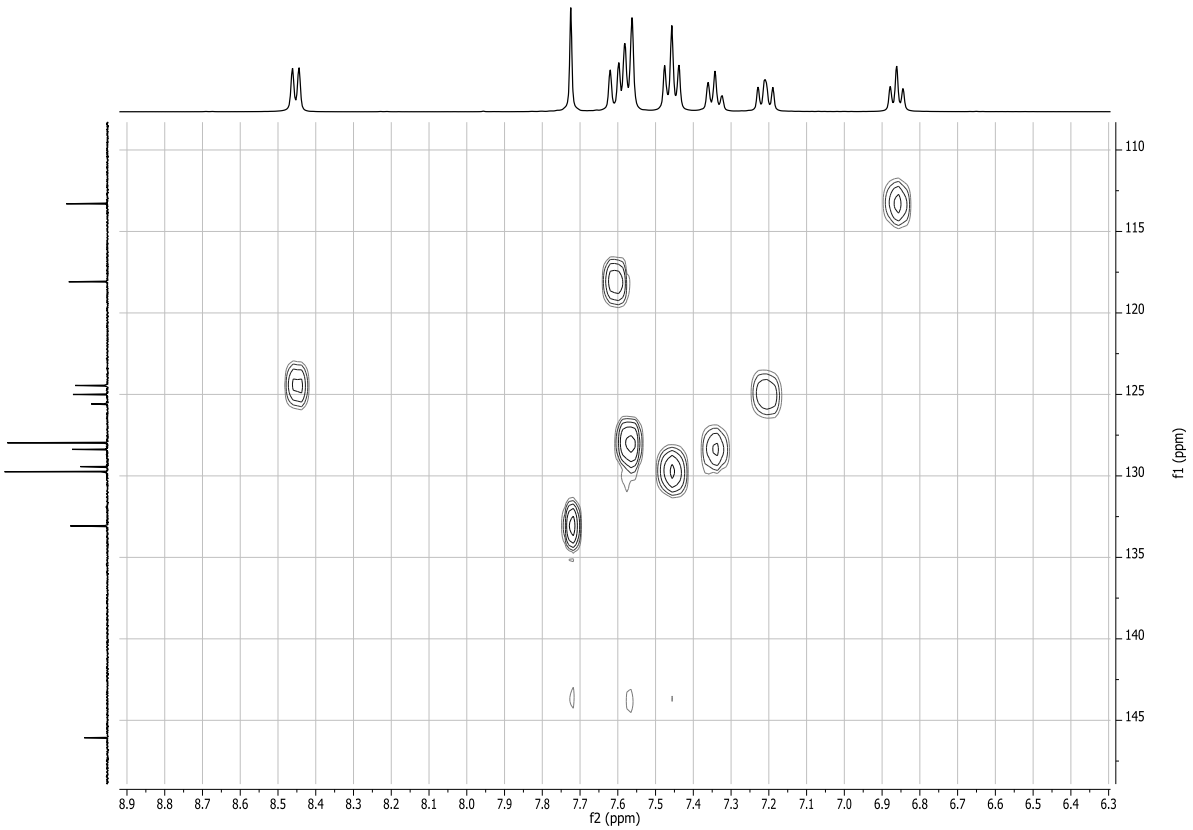
2.5 3-Phenylimidazo[1,2-*a*]pyridine (**4a**)[10]



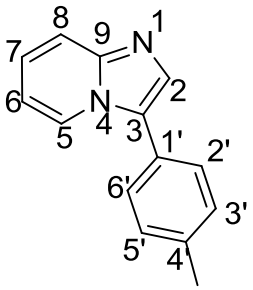




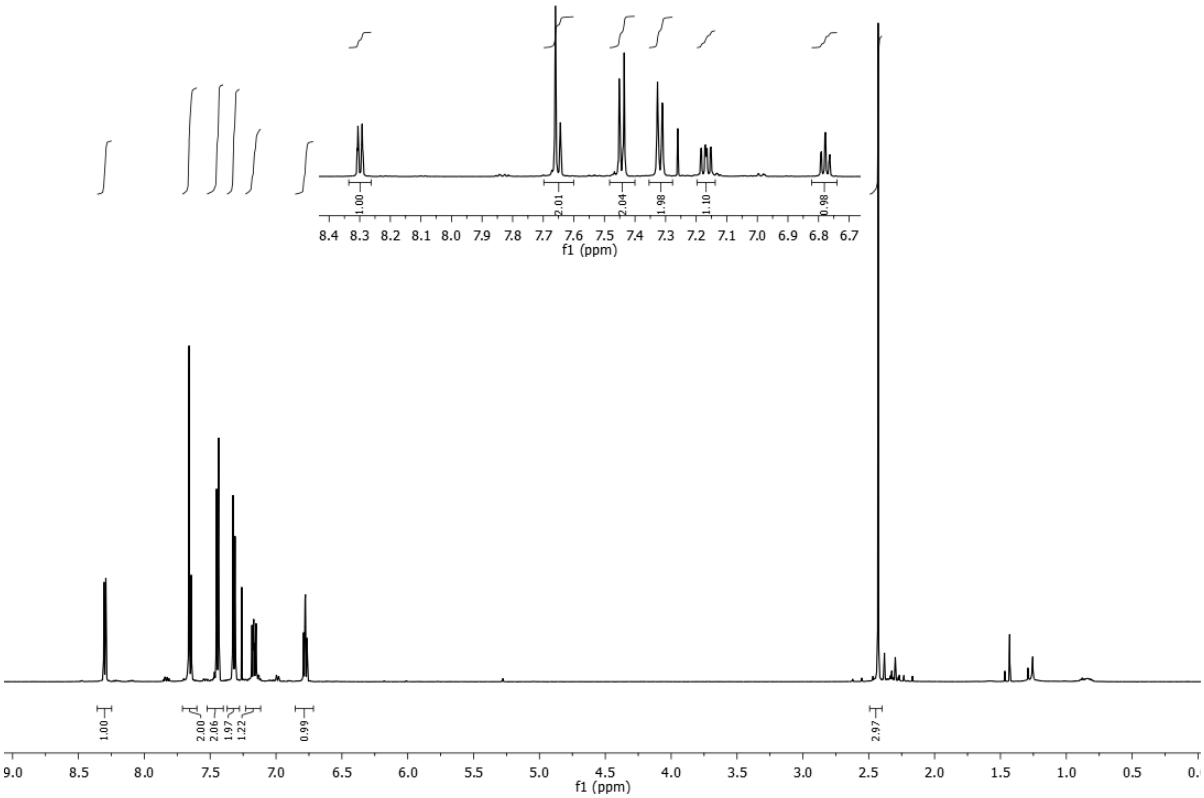


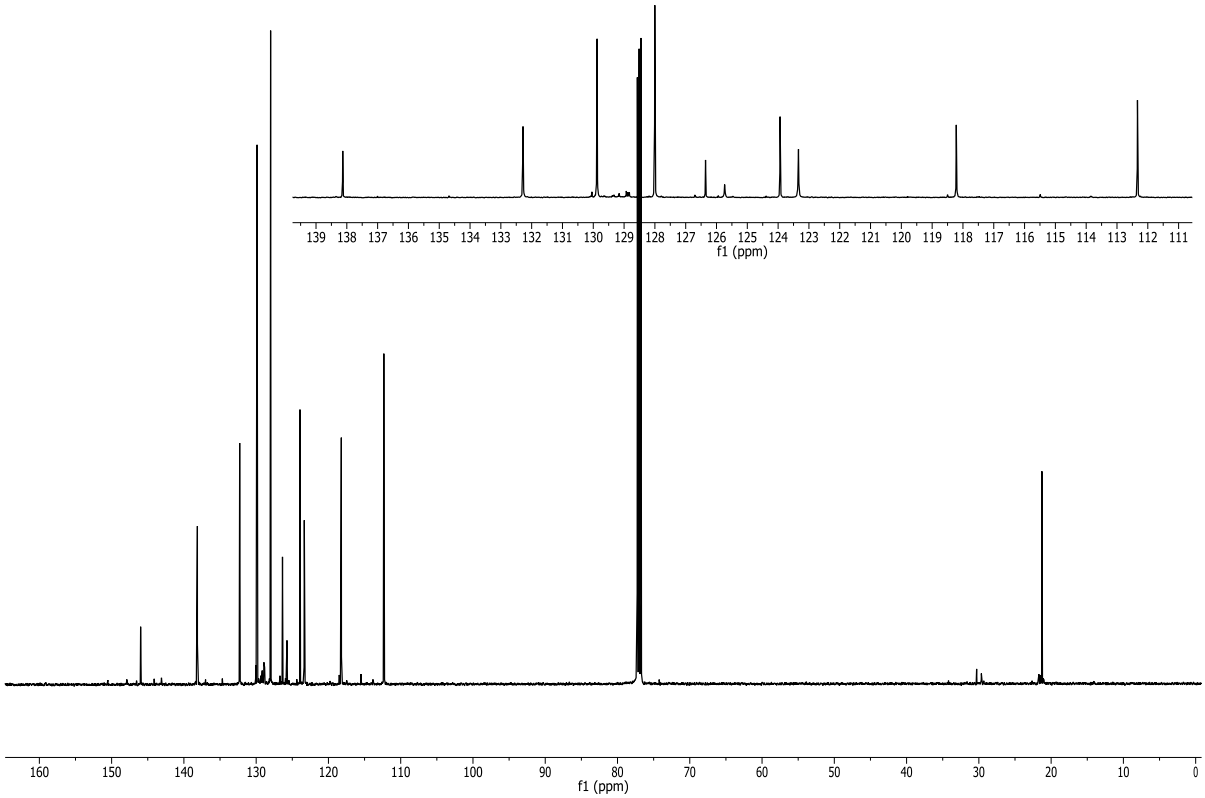


2.6 3-(4′-Methylphenyl)imidazo[1,2-*a*]pyridine (**4b**)

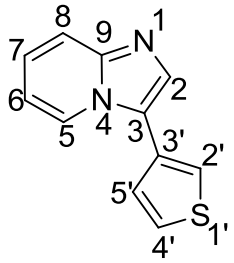


Using K_2CO_3 (1.06 g, 7.65 mmol), **2** (0.31 g, 3.29 mmol), PhF (24 mL) and **1b** (1.07 g, 2.47 mmol). White crystalline solid (0.18 g, 0.88 mmol, 36%). Mp 84-86 °C (from DCM-ether); R_f 0.09 (4:1 ether/petrol); IR ν_{max}/cm^{-1} (neat) 2981, 1634, 1545, 1490, 1353, 1295, 1255, 1166, 1148, 1013; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.30 (1H, dt_{app}, H5 J = 6.9 Hz, J = 1.2 Hz), 7.66 (1H, overlapped s, H2), 7.65 (1H, overlapped d, H8 J = 8.0 Hz), 7.44 (2H, d, H3′/H5′ J = 8.0 Hz), 7.32 (2H, dd, H2′/H6′ J = 8.0 Hz, J = 0.6 Hz), 7.17 (1H, ddd, H6 J = 9.1 Hz, J = 6.9 Hz, J = 1.3 Hz), 6.78 (1H, td_{app} , H7 J = 6.9, J = 1.2), 2.43 (3H, s, Me); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 145.99, 138.13, 132.28, 129.88, 128.00, 126.36, 125.73, 123.94, 123.34, 118.21, 112.34, 21.27. *m/z* (ESI) 209 ($[M+H]^+$, 100%). Found: $[M+H]^+$, 209.1072. $C_{14}H_{13}N_2$ requires 209.1073. Anal. Calcd. for $C_{14}H_{12}N_2$: C, 80.74 ; H, 5.81; N, 13.45. Found: C, 80.85; H, 5.68; N, 13.38.

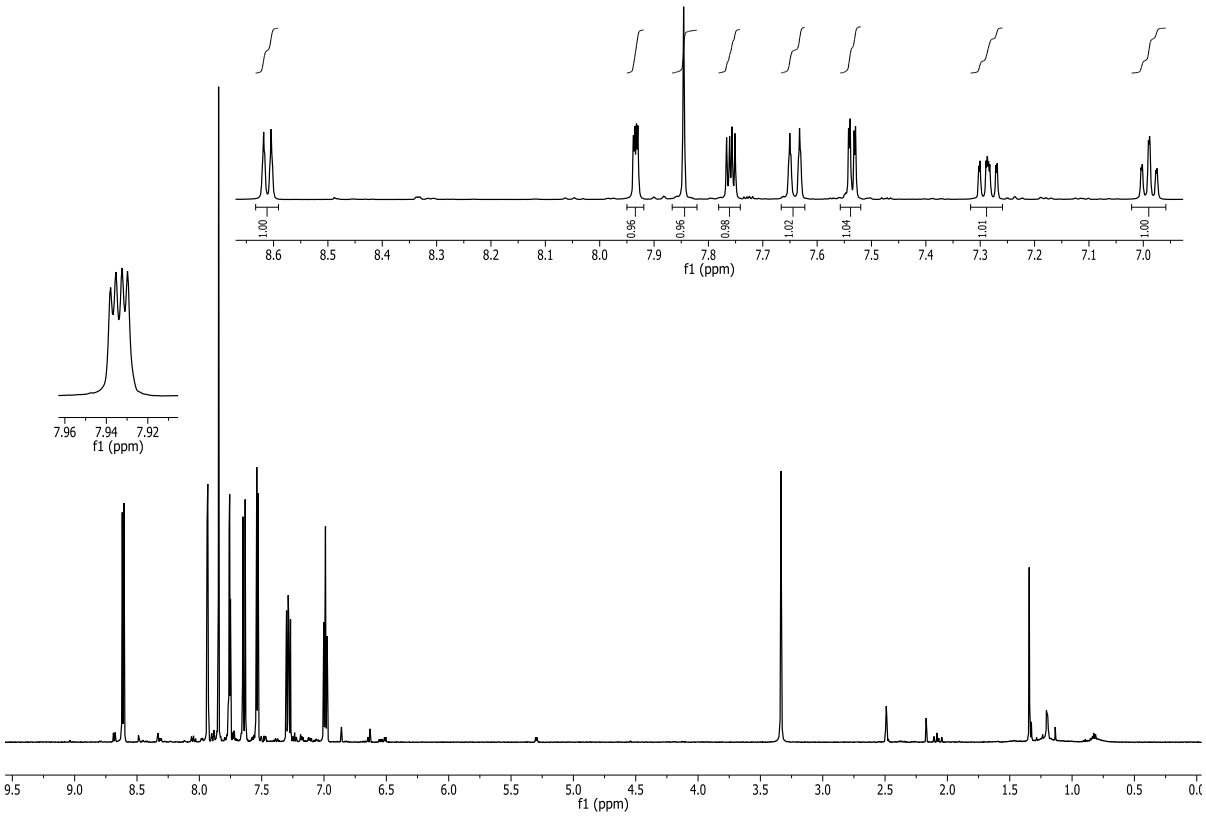


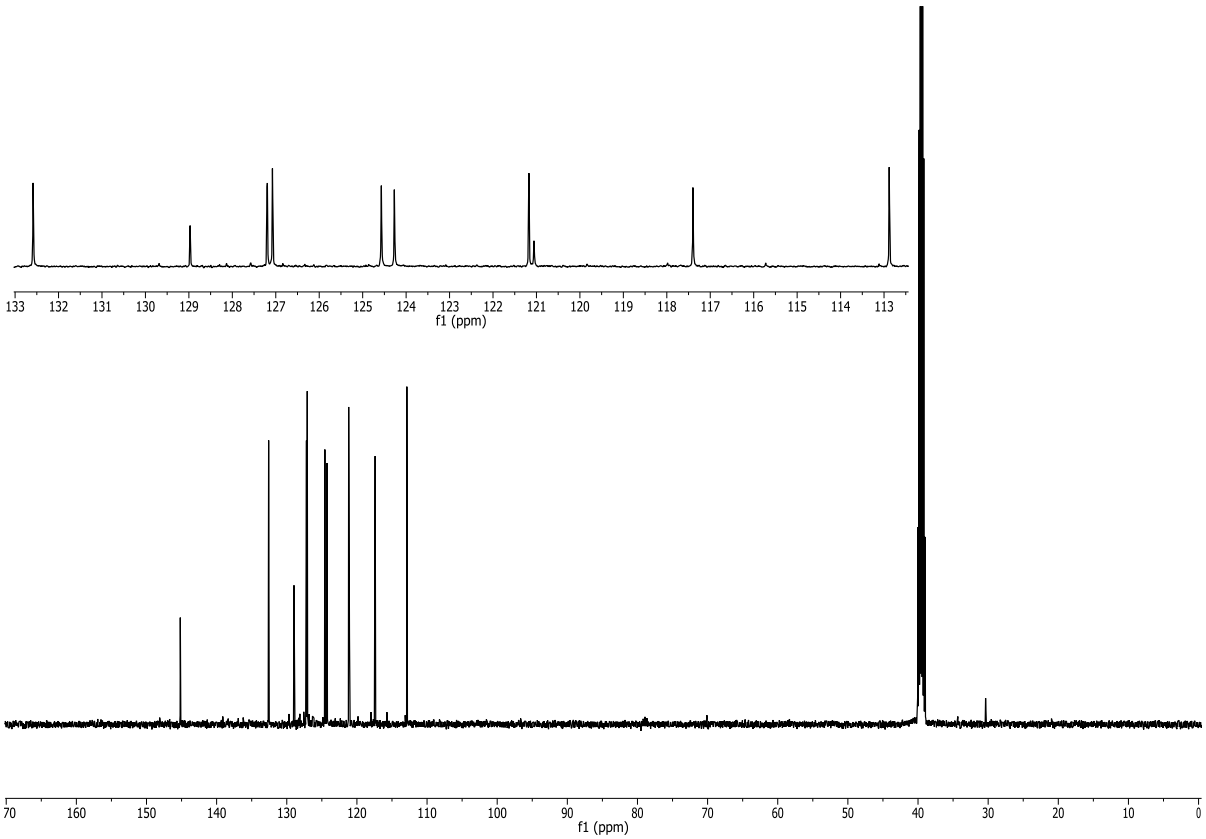


2.7 3-(3′-Thienyl)imidazo[1,2-*a*]pyridine (**4c**)

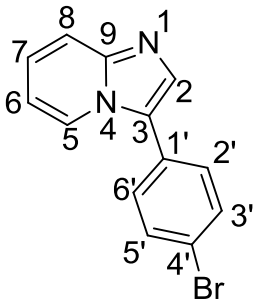


Using K_2CO_3 (1.07 g, 7.76 mmol), **2** (0.32 g, 3.36 mmol), PhF (24 mL) and **1c** (1.05 g, 2.48 mmol). White crystalline solid (0.12 g, 0.62 mmol, 25%). Mp 54-57 °C (from DCM); R_f 0.06 (4:1 ether/petrol); IR ν_{max}/cm^{-1} (neat) 3090, 1690, 1637, 1576, 1501, 1483, 1343, 1330, 1299, 1264, 1225, 1169, 1154, 1128, 1087, 1019; ^{1}H-NMR (500 MHz, d_6-DMSO) δ 8.61 (1H, d, H5 J = 7.0 Hz), 7.93 (1H, dd, H2′ J = 1.7 Hz, J = 1.3 Hz), 7.85 (1H, s, H2), 7.76 (1H, dd, H5′ J = 5.0 Hz, J = 2.1 Hz), 7.64 (1H, d, H8 J = 8.5 Hz), 7.54 (1H, dd, H4′ J = 5.0 Hz, J = 1.3 Hz), 7.29 (1H, ddd, H7 J = 8.5 Hz, J = 6.7 Hz, J = 1.7 Hz), 6.99 (1H, td_{app}, H6 J = 6.8 Hz, J = 1.1 Hz); ^{13}C-NMR (125 MHz, d_6-DMSO) δ 145.18, 132.58, 128.97, 127.20, 127.08, 124.57, 124.27, 121.18, 121.06, 117.40, 112.88; *m/z* (ESI) 201 ([M+H]$^+$, 100%). Found: [M+H]$^+$, 201.0479. $C_{11}H_9N_2S$ requires 201.0481.

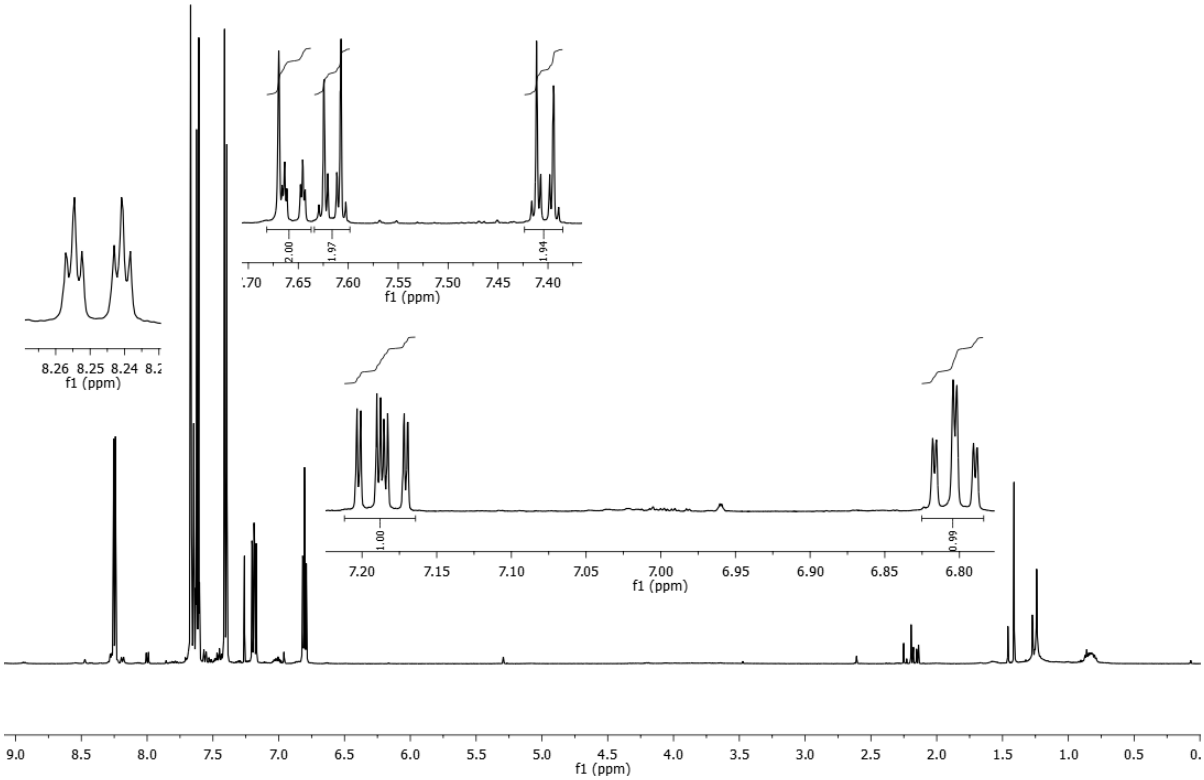


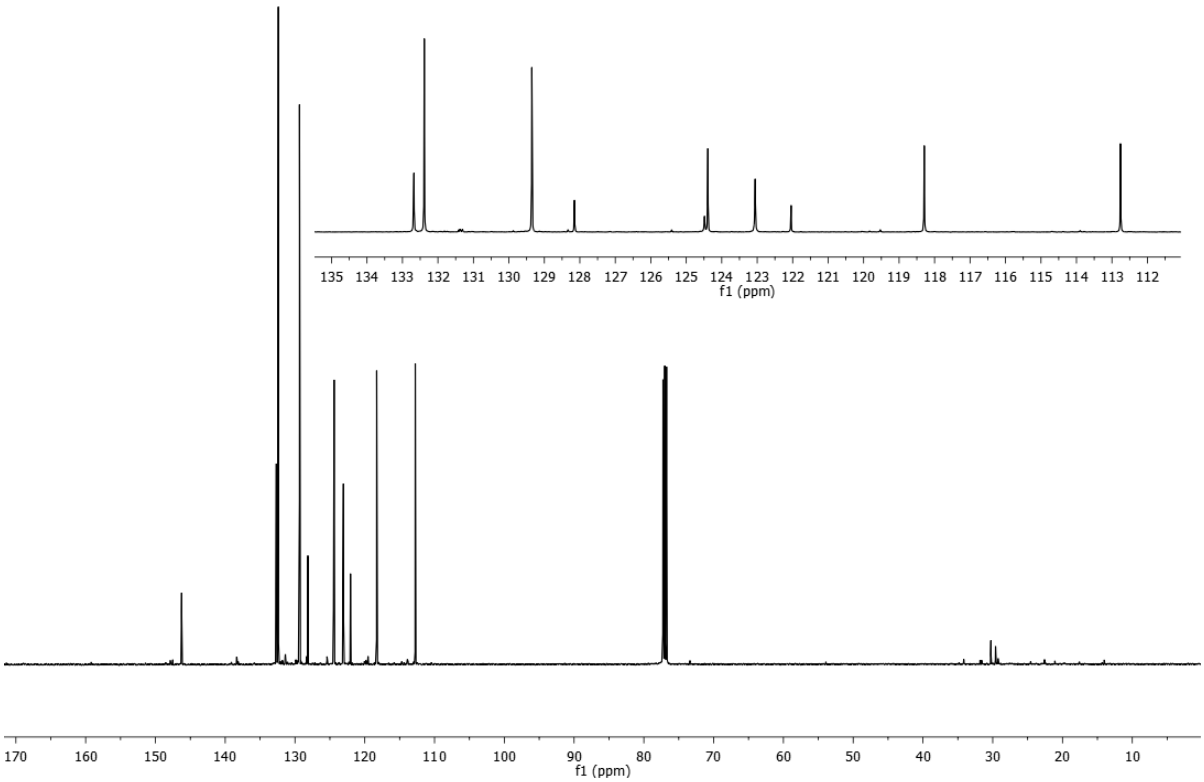


2.8 3-(4′-Bromophenyl)imidazo[1,2-*a*]pyridine (**4d**)[7]

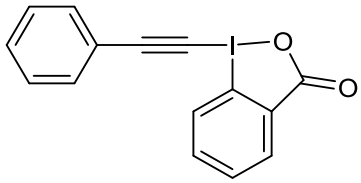


Using K_2CO_3 (1.04 g, 7.55 mmol), **2** (0.31 g, 3.29 mmol), PhF (24 mL) and **1d** (1.23 g, 2.48 mmol). White crystalline solid (0.18 g, 0.65 mmol, 26%). Mp 89-92 °C (from acetone); R_f 0.25 (4:1 ether/petrol); IR ν_{max}/cm^{-1} (neat) 3023, 1537, 1499, 1478, 1398, 1351, 1303, 1291, 1264, 1174, 1151, 1101, 1074, 1007; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.25 (1H, dt_{app}, H5 J = 7.0 Hz, J = 1.2 Hz), 7.67 (1H, s, H2), 7.66 (1H, d, H8 J = 9.1 Hz, J = 1.1 Hz), 7.62 (2H, d, H2′/H6′ J = 8.6 Hz), 7.40 (2H, d, H3′/H5′ J = 8.6 Hz), 7.19 (1H, ddd, H7 J = 9.1 Hz, J = 6.7 Hz, J = 1.3 Hz), 6.80 (1H, td_{app}, H6 J = 6.8 Hz, J = 1.1 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 146.24, 132.68, 132.38, 129.35, 128.15, 124.49, 124.39, 123.06, 122.05, 118.29, 112.76; *m/z* (ESI) 275 ([^{81}Br][M+H]$^+$, 98%), 273 ([^{79}Br][M+H]$^+$, 100%). Found: [M+H]$^+$, 273.0026. $C_{13}H_{10}BrN_2$ requires 273.0022. Anal. Calcd. for $C_{13}H_9BrN_2$: C, 57.17; H, 3.32; N, 10.26. Found: C, 57.13; H, 3.21; N, 10.16.

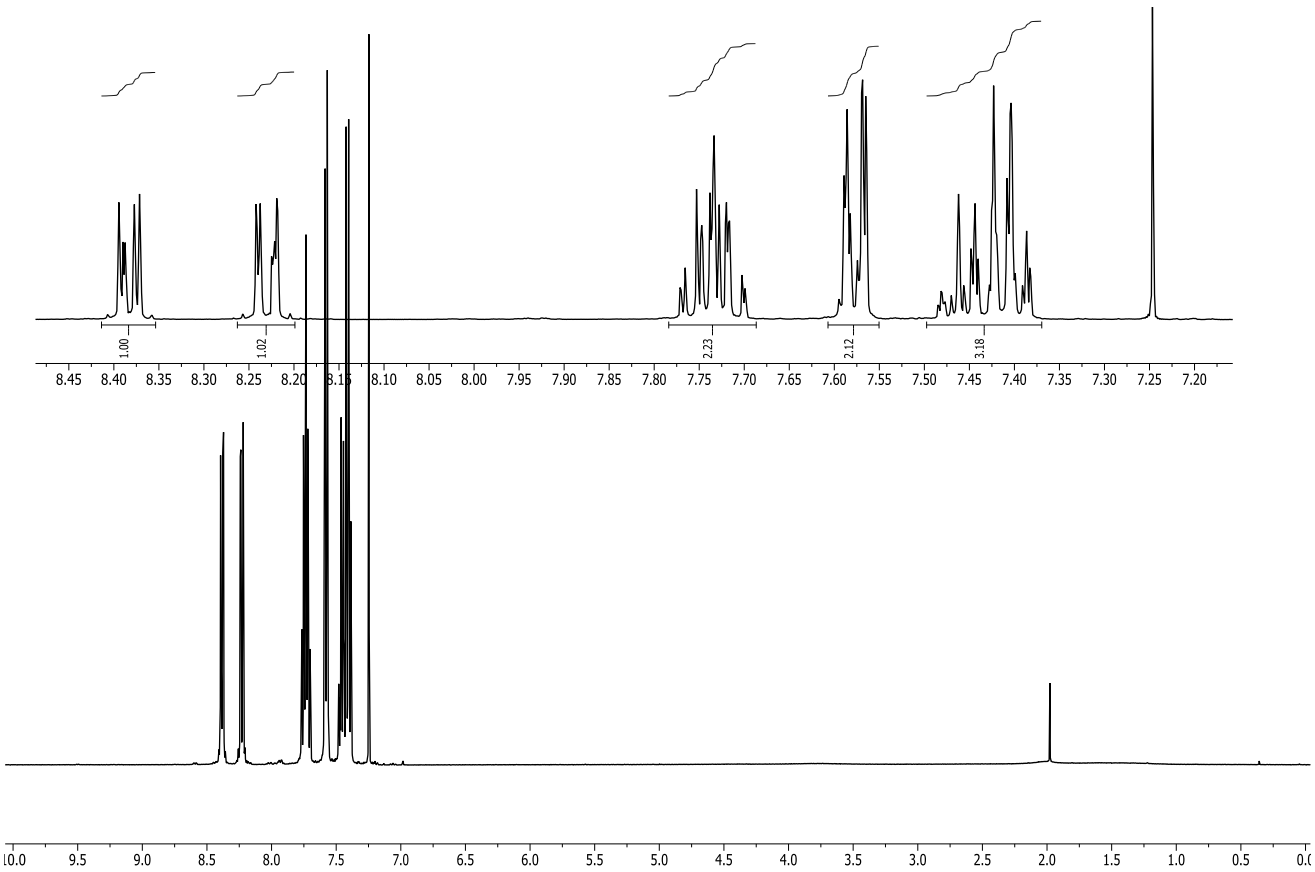


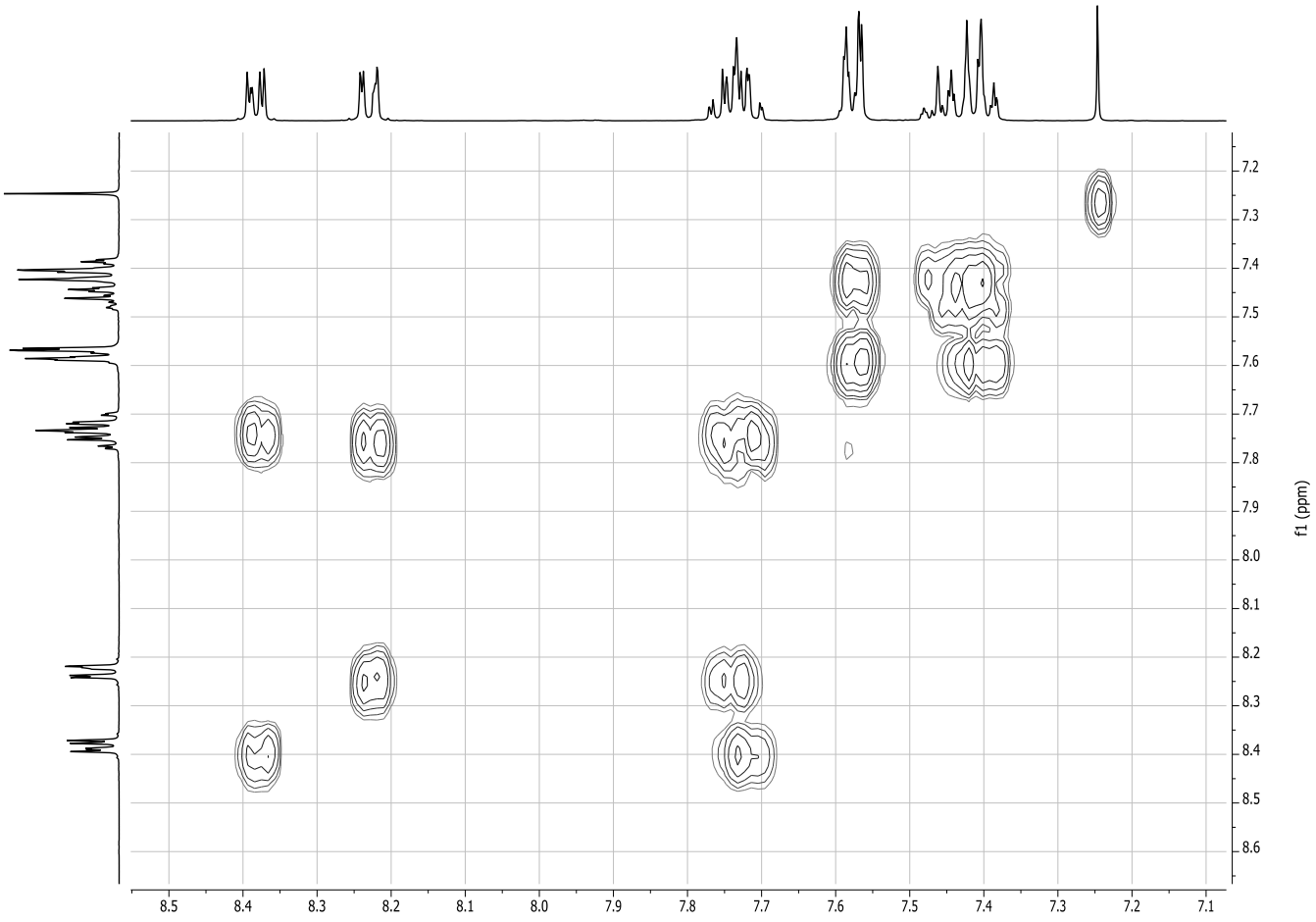


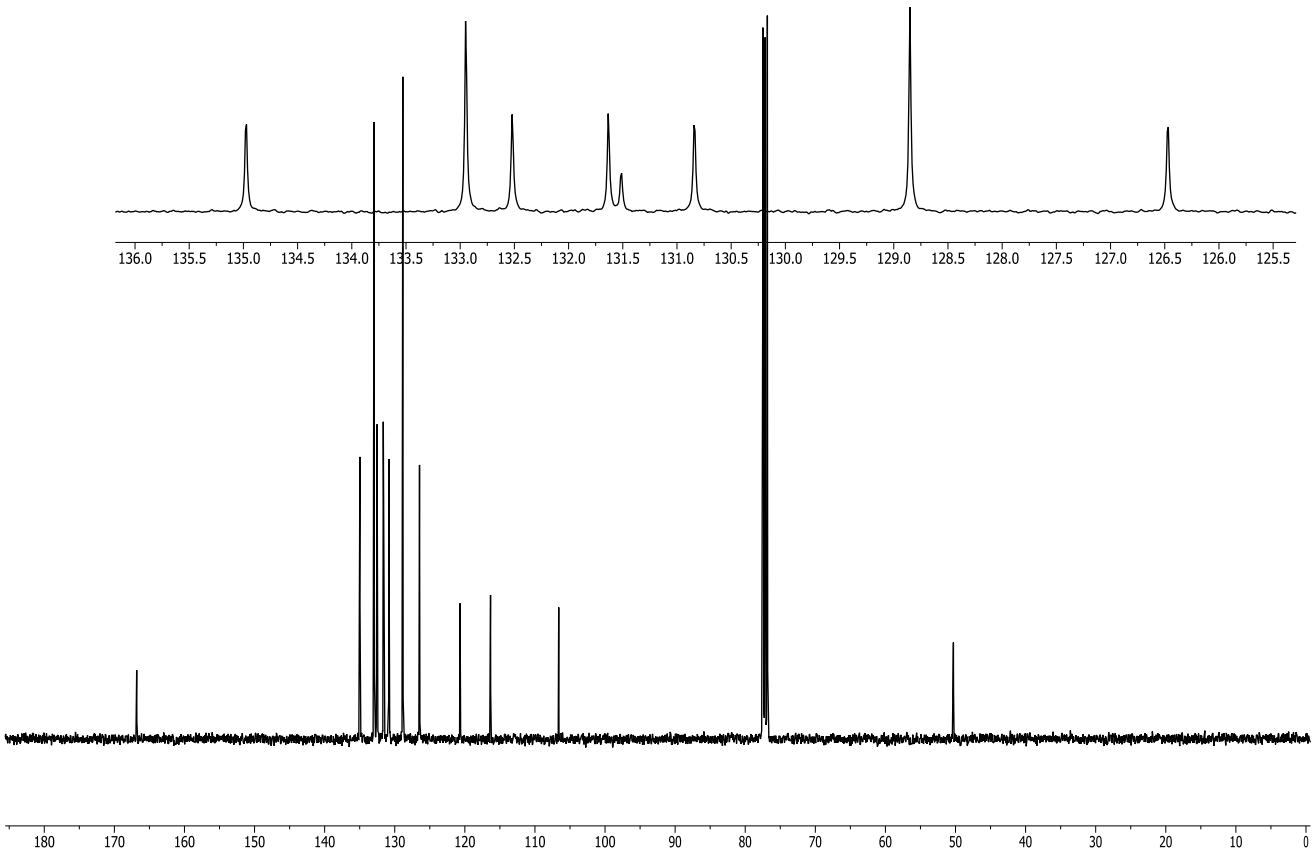
2.9 1-(Phenylethynyl)-1,2-benziodoxol-3(1*H*)-one[11] (7)

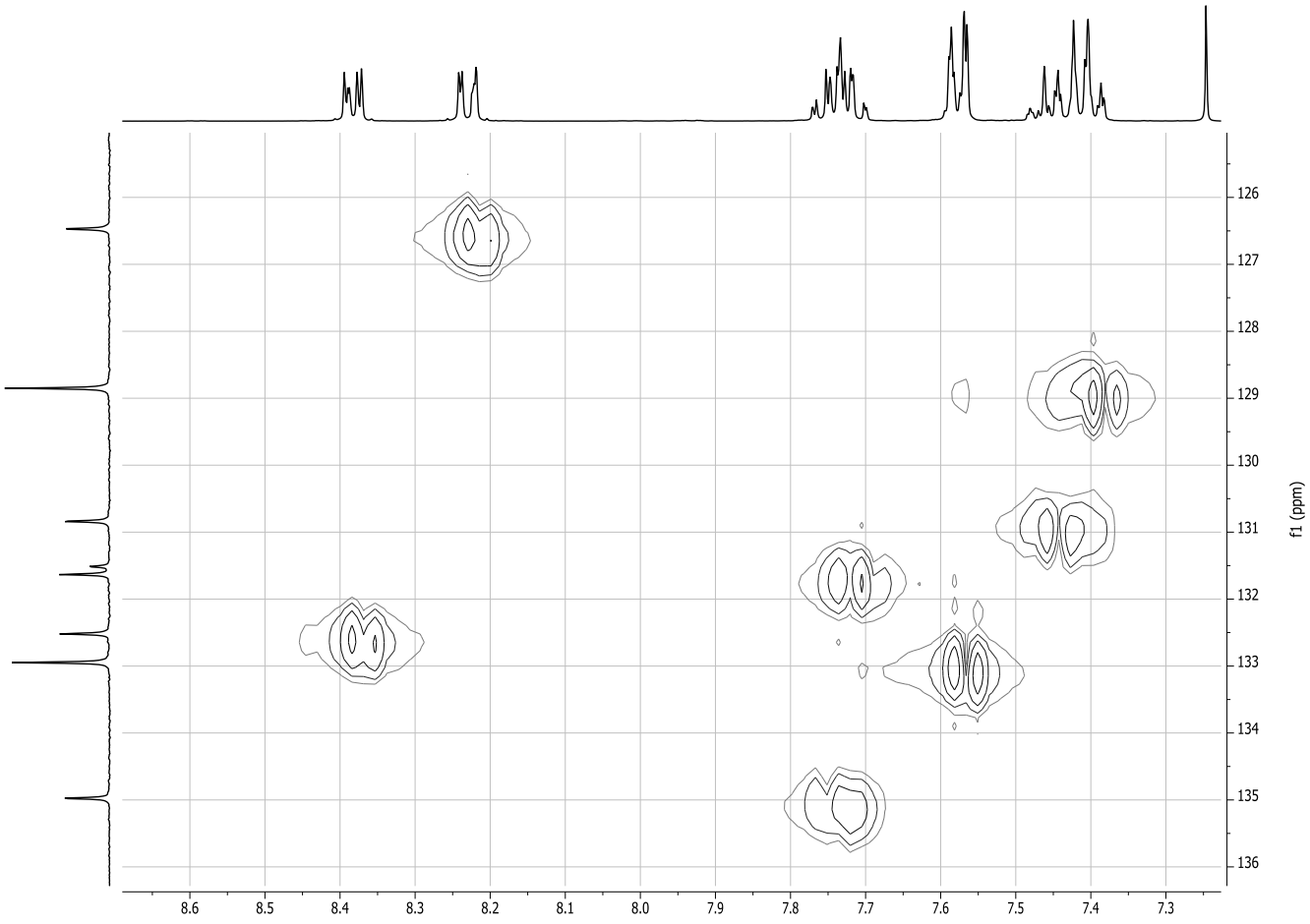


Freshly prepared 2-iodosbenzoic acid[12] (3.00 g, 11.37 mmol) was dispersed in dry acetonitrile (85 mL) in flame dried round bottomed flask under nitrogen before the dropwise addition of freshly distilled trimethylsilyltriflate (2.8 mL, 15.47 mmol) over a period of 10 minutes. After 30 minutes stirring, the solution turned a clear yellow colour, and was stirred for an additional 15 minutes before the slow addition of freshly distilled 1-trimethylsilyl-2-(phenyl)acetylene (2.46 mL, 12.5 mmol). The solution was then stirred for 1 hour before the dropwise addition of dry pyridine (1.2 mL, 15 mmol) then stirred for 45 minutes more. The solvent was then removed under reduced pressure then the reaction mixture was washed with water (130 mL) and extracted into DCM (3 × 65 mL). The organic extracts were combined, dried ($MgSO_4$) and concentrated *in vacuo* to an oily solid. Dissolution in boiling acetonitrile followed by slow cooling afforded the desired product as large, very pale yellow crystals (0.60 g, 1.73 mmol, 15%). Mp 141-143 °C (from MeCN) (lit.[13] mp 153-155 °C – decomp. from MeCN); IR ν_{max}/cm^{-1} (neat) 3060, 2140, 1635, 1616, 1606, 1558, 1487, 1436, 1331, 1304; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.38 (1H, dd, H6 J = 6.84 Hz, J = 2.32 Hz), 8.23 (1H, dd, H3 J = 8.24 Hz, J = 1.84 Hz), 7.77-7.72 (2H, m, H4/H5), 7.58 (2H, d, H2′/H6′ J = 8.24 Hz), 7.46 (1H, tt, H4′ J = 7.32 Hz, J = 1.84 Hz), 7.40 (2H, t, H3′/H5′ J = 7.80 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.66 (CO), 134.82 (C4), 132.80 (C2′/C6′), 132.37 (C6), 131.48 (C5), 131.36, 130.69 (C4′), 128.70 (C3′/C5′), 126.31 (C3), 120.53, 116.18, 106.45 (C7′), 50.14 (C8′); *m/z* (NSI) 349 ($[M+H]^+$, 100%), 318 (5), 279 (21), 217 (25), 199 (10). Found: $[M+H]^+$, 348.9720. $C_{15}H_{10}IO_2$ requires 348.9720. Anal. Calcd. for $C_{15}H_9IO_2$: C, 51.75; H, 2.61. Found: C, 51.83; H, 2.56.

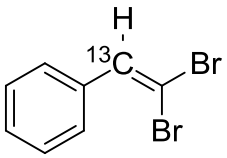




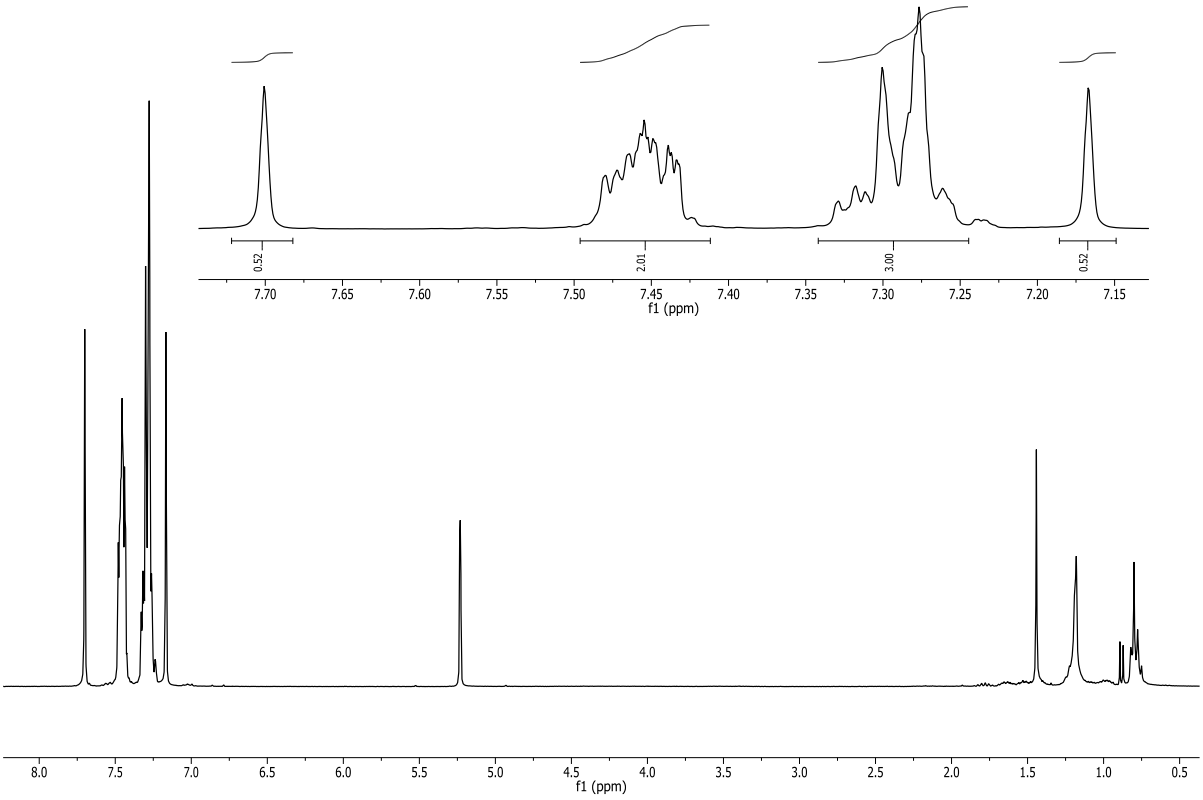


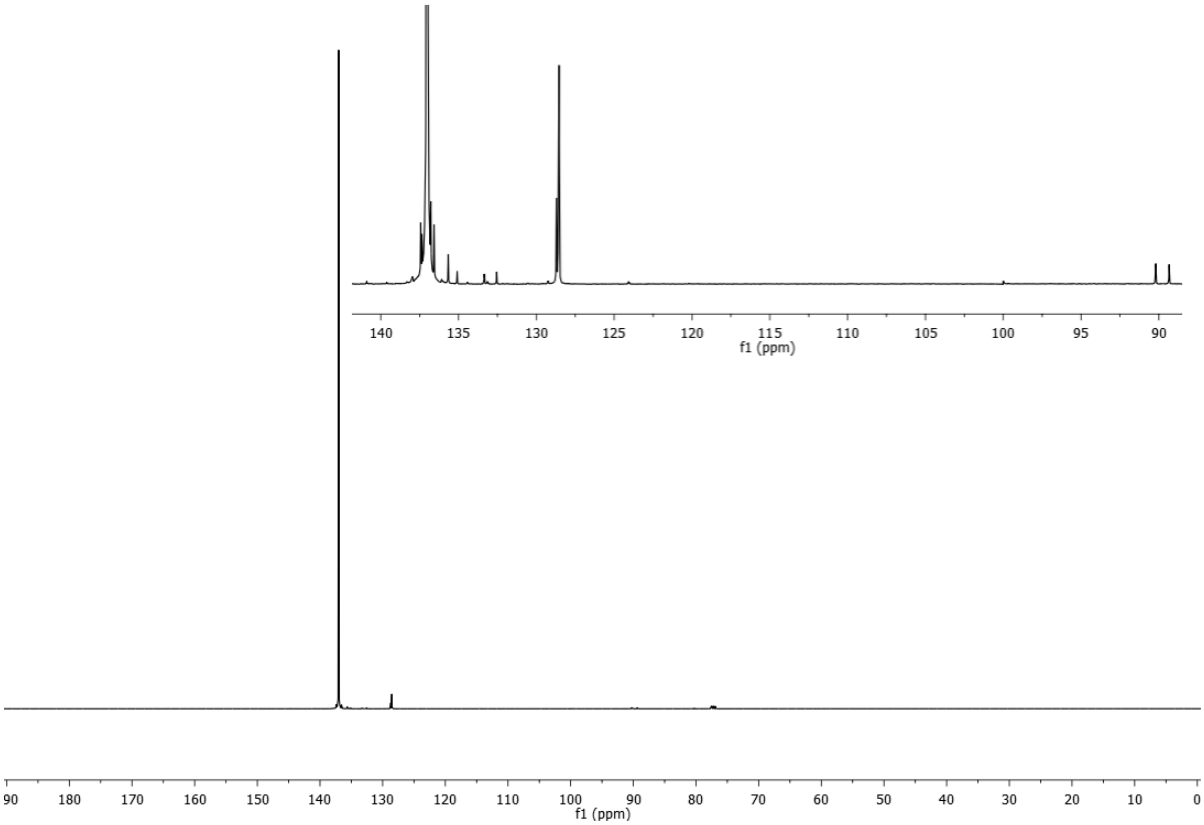


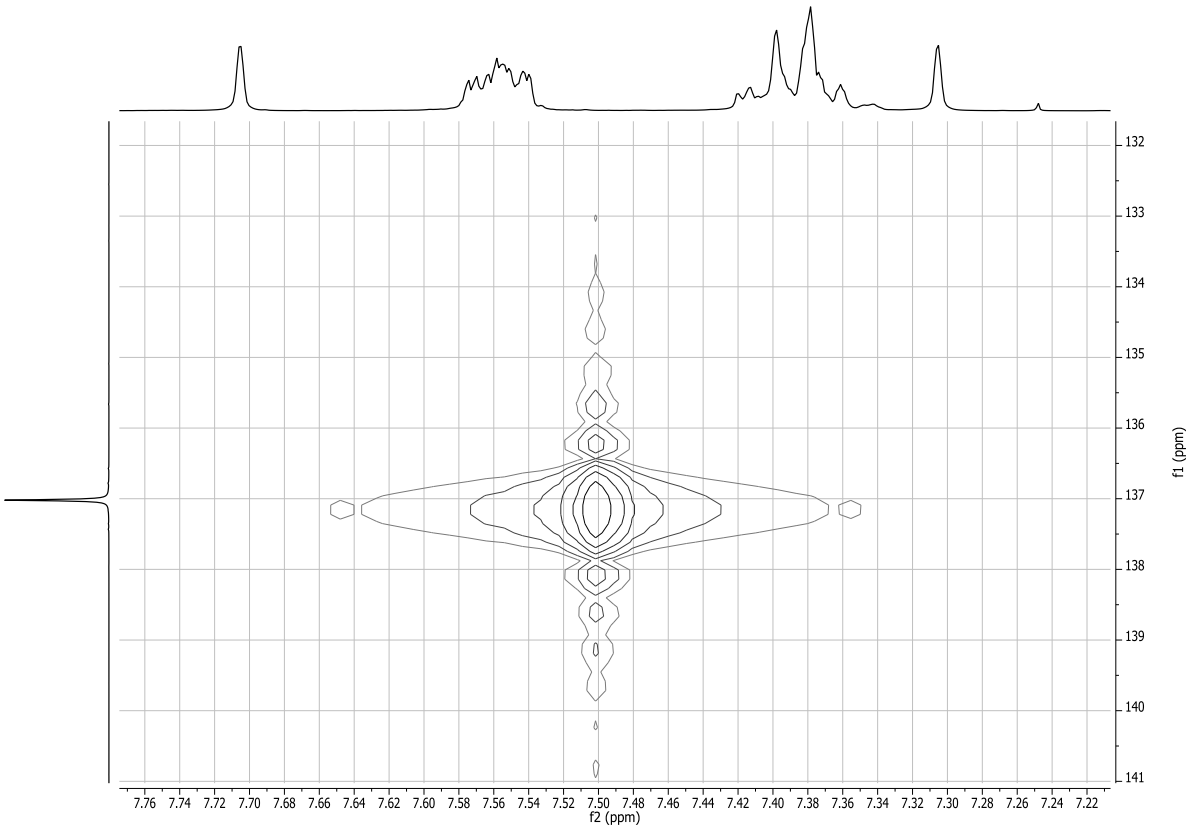
2.10 1′,1′-Dibromo-2′-[^{13}C]-styrene[14] ([^{13}C]-19)



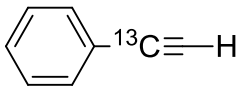
Triphenylphosphine (5.04 g, 19.22 mmol) and dry carbon tetrabromide (3.10 g, 9.34 mmol) were dissolved in dry DCM (30 mL) at 0 °C under an atmosphere of nitrogen. The solution was stirred for 30 minutes before the dropwise addition of benzaldehyde [^{13}C]-carbonyl (0.50 g, 4.67 mmol) over 5 minutes. The solution was stirred at 0 °C for 1 hour before washing with an aqueous 5M solution of $CuSO_4$ (300 mL) followed by extraction into DCM (3 × 50 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated *in vacuo*. The resulting orange oily solid was dry loaded onto silica and purified by column chromatography (silica) to give the product as a pale orange clear oil which crystallized on standing (1.21 g, 4.60 mmol, 98%). Selected data only: R_f 0.74 (petrol 40/60); ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 7.50-7.39 (2H, m), 7.44 (1H, d, J = 159.07 Hz), 7.33-7.23 (3H, m); ^{13}C-NMR (75 MHz, CD_2Cl_2) δ 137.86 (C1′-label). *m/z* (EI) 265 ([^{81}Br,^{81}Br]M^+, 8%), 263 ([^{81}Br,^{79}Br]M^+, 18%), 261 ([^{79}Br,^{79}Br]M^+, 8%), 184 (18), 182 (18), 103 (100). Found: M^+, 260.8868. $C_7{}^{13}C_1H_6{}^{79}Br_2$ requires 260.8864.



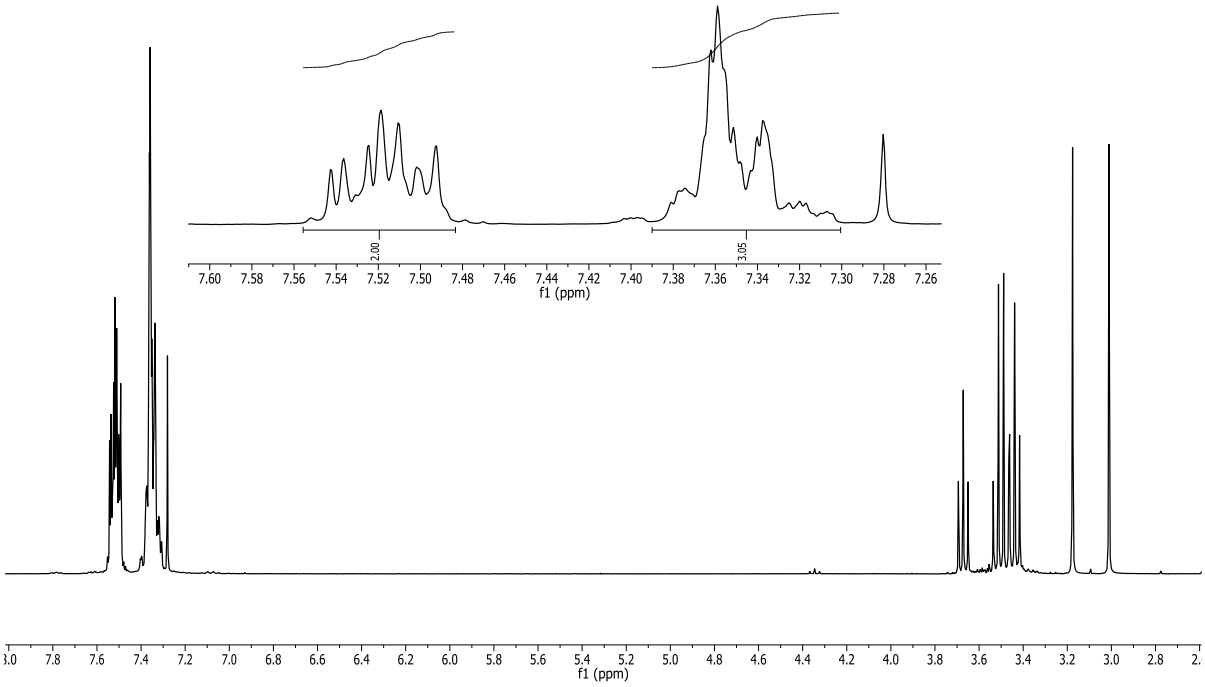




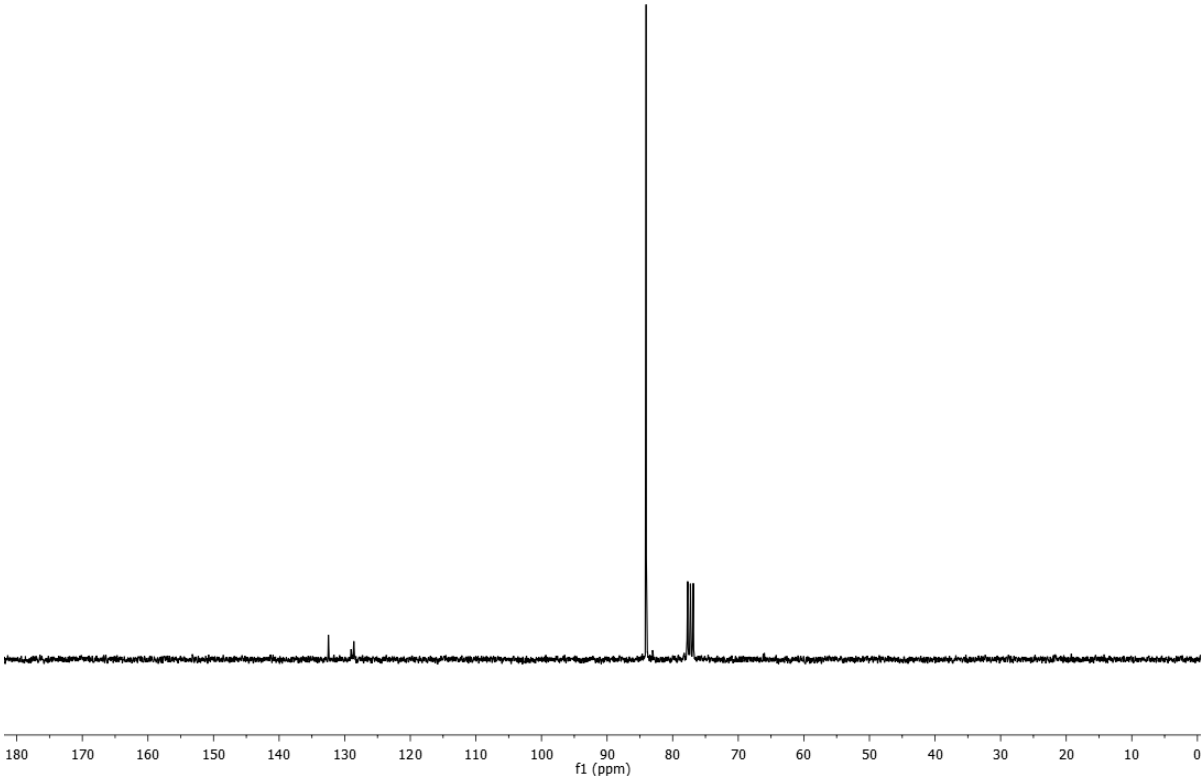
2.11 Phenyl-α-[^{13}C]-acetylene[14] ([^{13}C]-20)



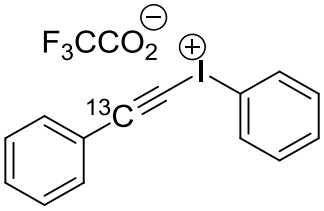
2′,2′-Dibromo[1′-^{13}C]styrene, **[^{13}C]-19**, (1.21 g, 4.60 mmol) was dissolved in dry ether (30 mL) and cooled to -78 °C under an atmosphere of nitrogen. *n*-Butyllithium (2.17M in hexanes, 5.41 mL, 11.75 mmol) was added dropwise over 10 minutes and the solution stirred for a further 30 minutes then for 1 hour at room temperature. The reaction was quenched with water (50 mL), washed with water (50 mL) and extracted into ether (3 × 50 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated *in vacuo* to give the product as a pale yellow oil (0.46 g, 4.43 mmol, 96%)[†] with sufficient purity to be used in subsequent reactions. Selected data only: ^{1}H-NMR (300 MHz, $CDCl_3$) 7.54-7.49 (2H, m), 7.37-7.34 (3H, m), 3.09 (1H, d, J = 49.52 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) 84.05 (C1′-label). *m/z* (EI) 103 ([M]$^+$, 100%). Found: M$^+$, 103.0496. $C_7{}^{13}C_1H_6$ requires 103.0498.



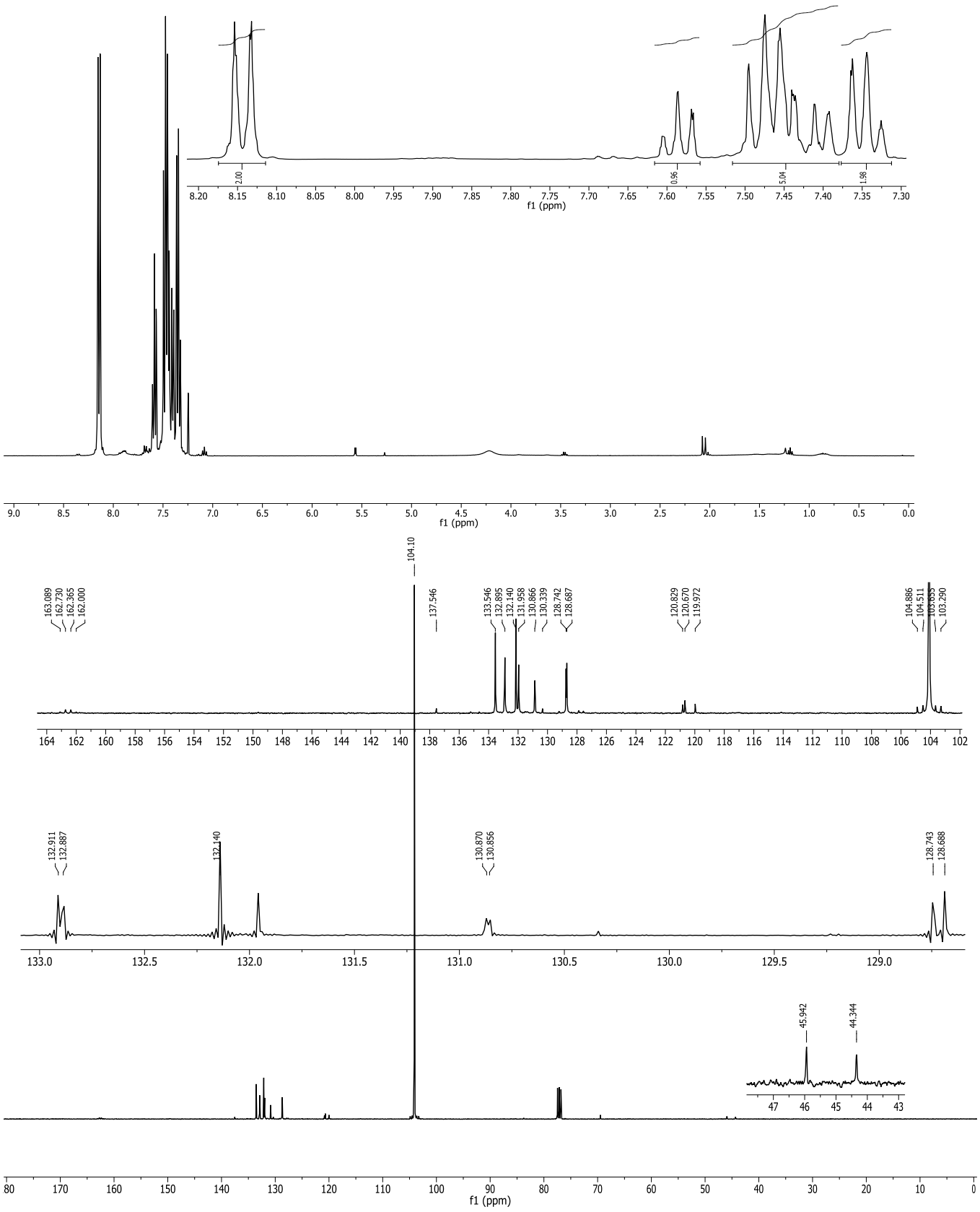
[†] Due to volatility, solvent could not be fully removed; yield calculated from ^{1}H-NMR

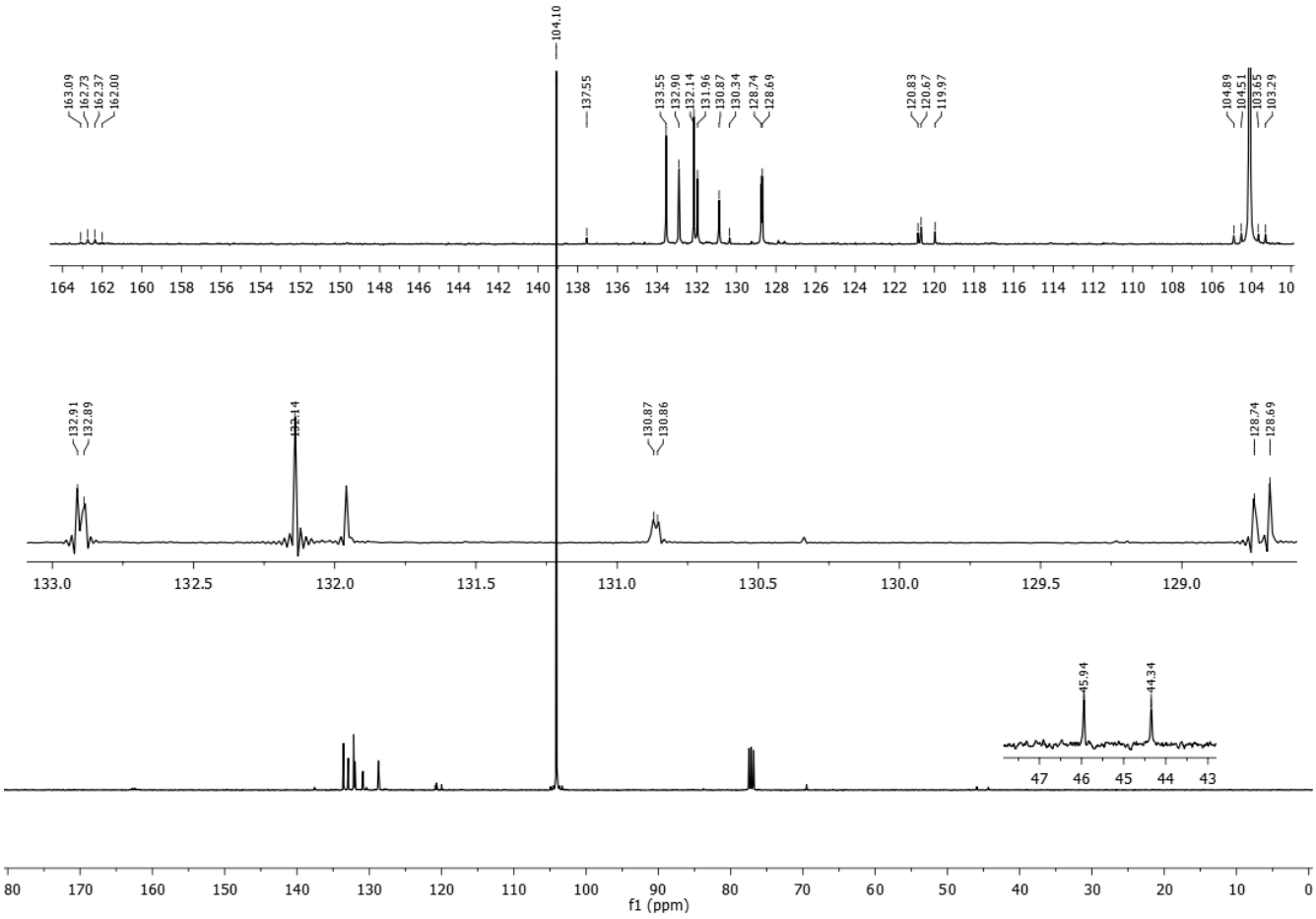


2.12 Phenyl(phenyl-β-[^{13}C]-ethynyl)iodonium trifluoroacetate ([^{13}C]-1a)



Trifluoroacetic acid (1.01 g, 8.82 mmol) was added dropwise at -30 °C to a stirred solution of phenyliodonium bis(acetate) (1.35 g, 4.20 mmol) in dry DCM (25 mL) over a period of 10 minutes. After a further 30 minutes the solution was allowed to warm to room temperature and stirred for 1 hour before being re-cooled to -30 °C for the injection of a solution of phenyl[α-^{13}C]acetylene, **[^{13}C]-24**, (0.46 g, 4.43 mmol) in dry DCM (5 mL) over 5 minutes. The resulting mixture was then allowed to reach room temperature over 3.5 hours in darkness before concentration *in vacuo* (to about 5 mL) followed by crystallization to give the product as a white, crystalline solid (0.63 g, 1.50 mmol, 36%). Selected data only: M.p. 79-81 °C (dec.)(from DCM-ether-petrol) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.14 (2H, d, H2/H6, J = 8.7 Hz), 7.58 (1H, dt, H4, J = 7.8 Hz, J = 0.9 Hz), 7.49-7.39 (5H, m), 7.34 (2H, t, H3/H5 J= 7.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) 162.55 (q, (CO) J = 36.2 Hz), 133.55 (s, C2/C6), 132.90 (d, C3′/C5′, J = 2.4 Hz), 132.14 (s, C3/C5), 131.96 (s, C4), 130.86 (d, C4′, J = 1.4 Hz), 128.72 (d, C2′/C6′, J = 5.5 Hz), 120.67 (s, C1), 120.40 (d, C1′, J = 86.2 Hz), 104.10 (s, C7′-label), 45.14 (d, C8′, J = 160.6 Hz); *m/z* (ESI) 306 ([M-TFA]$^+$, 100%), 294 (14), 179 (19). Found: [M-TFA]$^+$, 305.9861. $C_{13}{}^{13}C_1H_{10}I$ requires 305.9855.

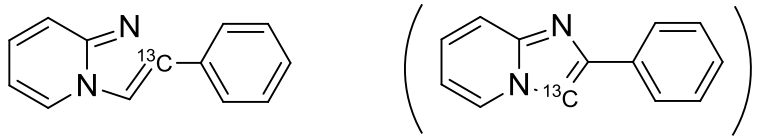




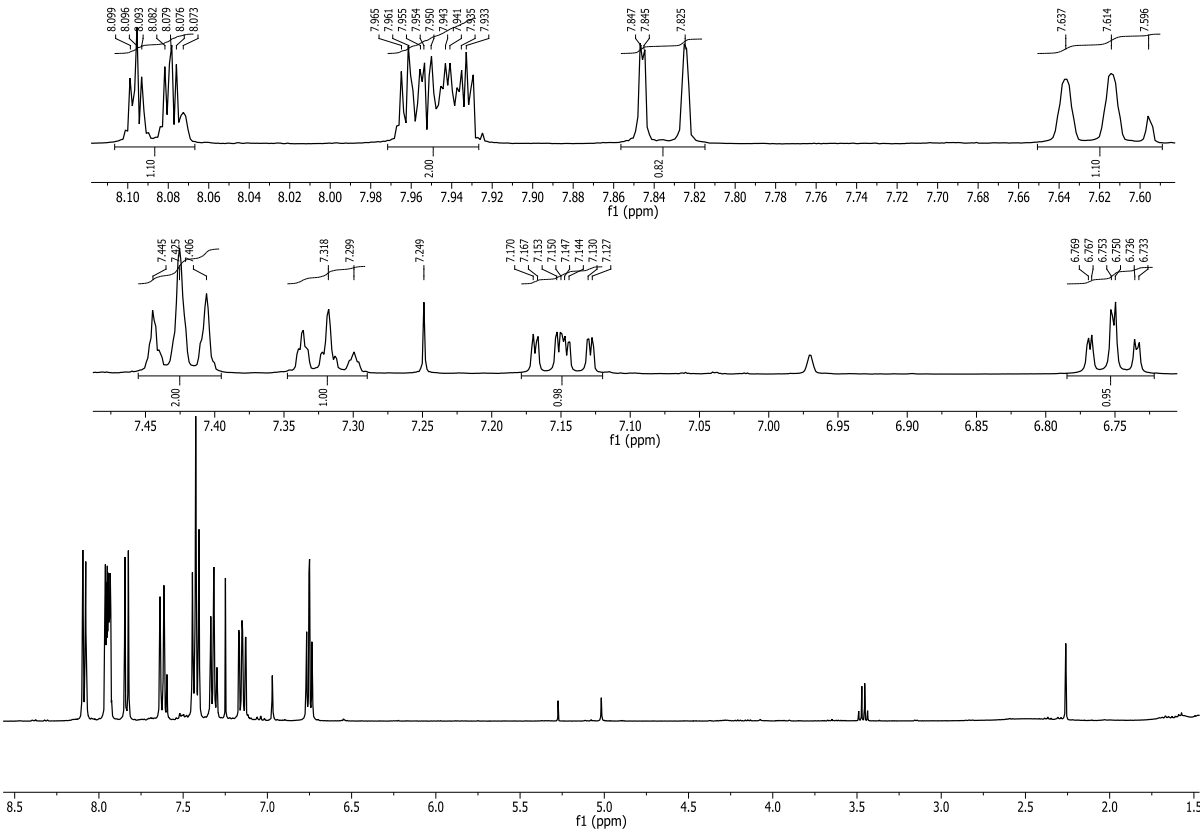
2.13 2-Phenyl-2/3-[^{13}C]-imidazo[1,2-*a*]pyridine ([^{13}C]-**3a**) and 3-Phenyl-3-[^{13}C]-imidazo[1,2-*a*]pyridine ([^{13}C]-**4a**)

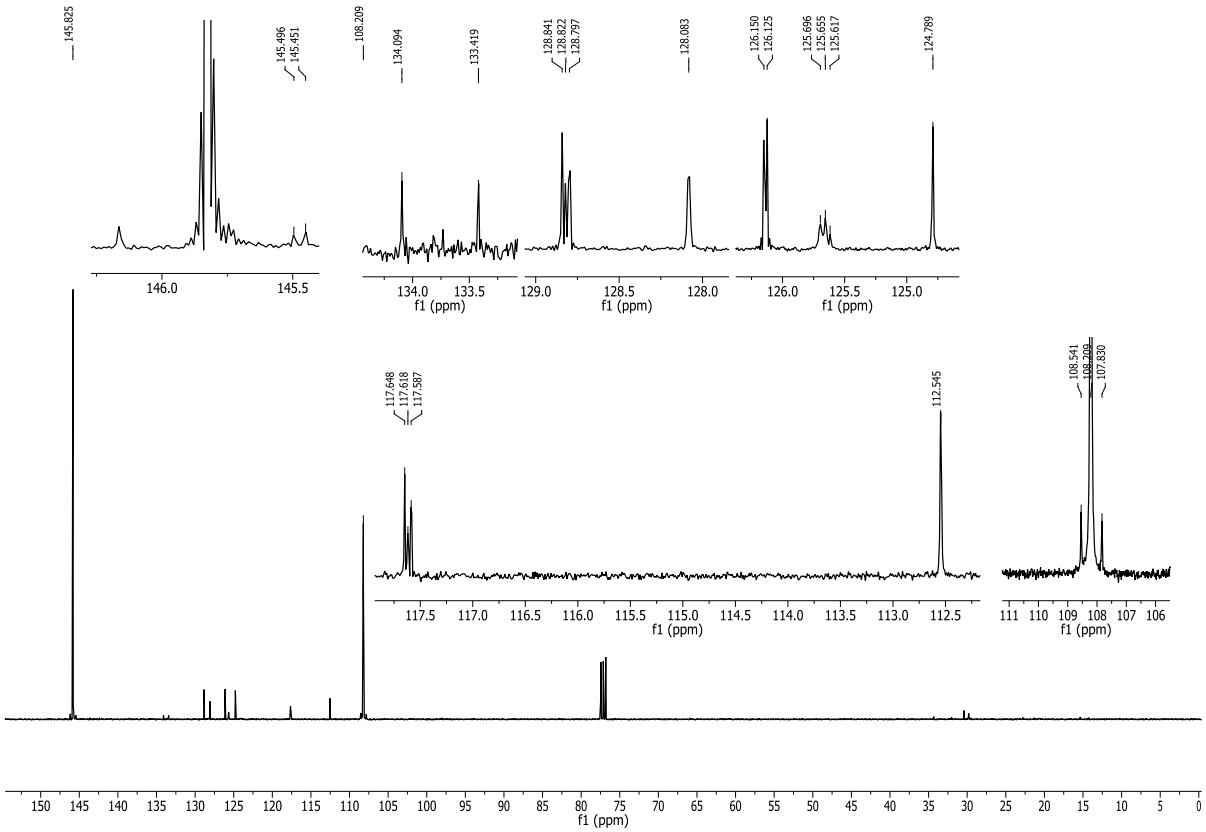
Potassium carbonate (0.30 g, 2.18 mmol) and 2-aminopyridine (0.09 g, 0.97 mmol) were stirred together in dry fluorobenzene (6.3 mL) for 45 minutes under an atmosphere of nitrogen before the addition of phenyl(phenyl[β-^{13}C]ethynyl)iodonium trifluoroacetate (0.30 g, 0.70 mmol) by powder funnel. The solution was then stirred in darkness, at room temperature, overnight before being washed with water (150 mL) and extracted into DCM (4 × 30 mL). The organic fractions were combined, dried ($NaSO_4$), filtered and concentrated *in vacuo* to a brown oil. The crude product was purified by column chromatography (Grace Resolve 70g, 150 mL silica cartridge; 1:0 hexane/ether for 5 min then to 3:7 over 120 min and holding at this solvent mixture until elution was complete), loading the sample in DCM, to give the products as a white, crystalline solids; 2-Phenyl-2/3-[^{13}C]-imidazo[1,2-*a*]pyridine ([^{13}C]-**3a**) (0.03 g, 0.14 mmol, 20%) and 3-Phenyl-3-[^{13}C]-imidazo[1,2-*a*]pyridine ([^{13}C]-**4a**) (0.04 g, 0.21 mmol, 30%).

Selected data for 2-Phenyl-2/3-[^{13}C]-imidazo[1,2-*a*]pyridine ([^{13}C]-**3a**):

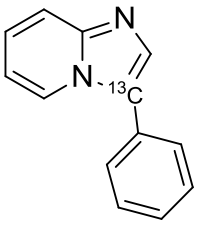


R_f 0.55 (4:1 ether/petrol); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09 (1H, dt, H5 J = 6.8 Hz, J = 1.2 Hz), 7.97-7.93 (2H, m, H2′/H6′), 7.84 (0.82H, dd, H3 J = 8.4 Hz, J = 0.8 Hz), 7.84 (0.18H, d, H3 J = 190.7 Hz) 7.63 (1H, d, H8 J = 9.2 Hz), 7.43 (2H, $t_{app.}$, H3′/H5′ J = 8.0 Hz), 7.32 (1H, t, H4′ J = 7.6 Hz), 7.15 (1H, ddd, H7 J = 9.2 Hz, J = 6.6 Hz, J = 1.2 Hz), 6.75 (1H, $dt_{app.}$, H6 J = 6.6 Hz, J = 0.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) 145.82 (C2-label), 145.47 (d, C9 J = 4.5 Hz), 133.76 (d, C1′ J = 67.9 Hz), 133.76 (s, C1'), 128.82 (d, C3′/C5′ J = 4.4 Hz), 128.82 (s, C3′/C5′), 128.08 (s, C4′), 126.14 (d, C2′/C6′ J = 2.5 Hz), 125.66 (d, C5 J = 7.9 Hz), 125.66 (s, C5), 124.79 (C7), 117.62 (d, C8 J = 6.1 Hz), 117.62 (s, C8) 112.55 (C6), 108.21 (C3-label); *m/z* (CI) 196 ($[M+H]^+$, 100%), 184 (12). Found: $[M+H]^+$, 196.0947. $C_{12}{}^{13}C_1H_{11}N_2$ requires 196.0950.

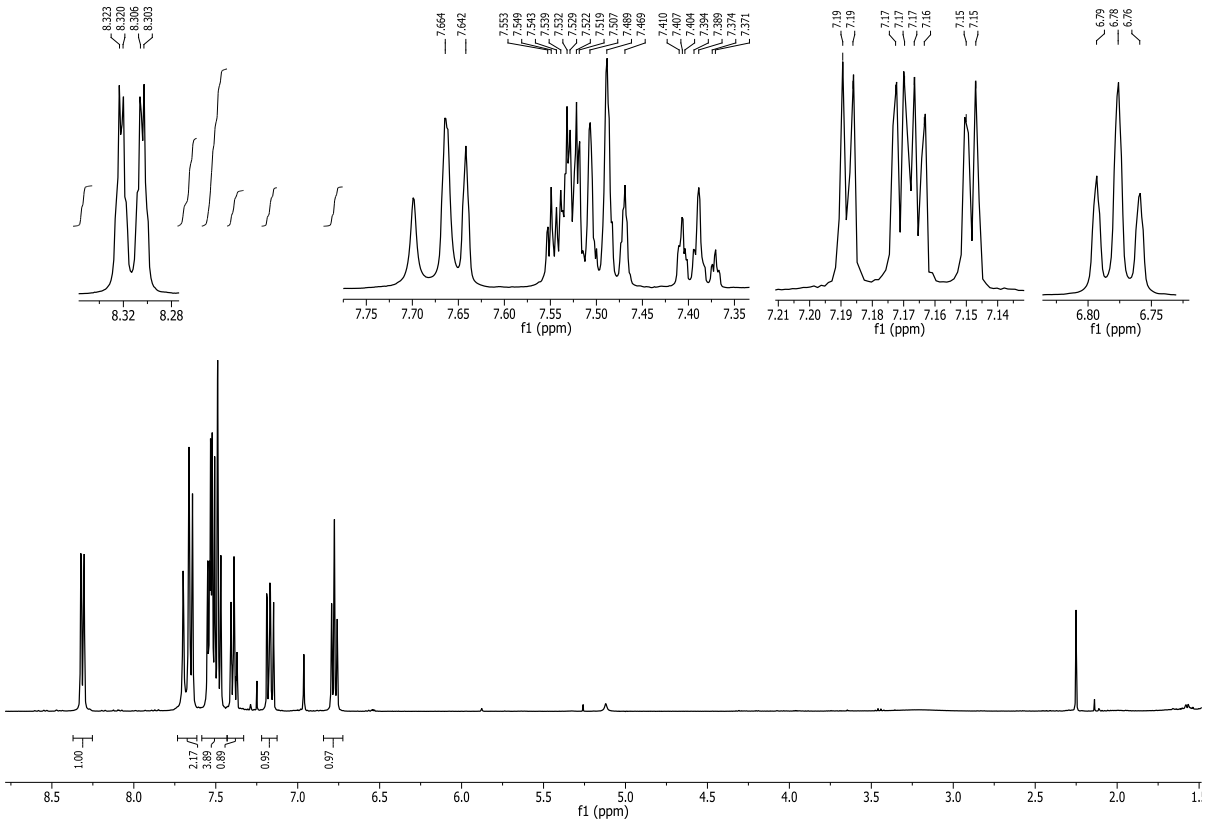


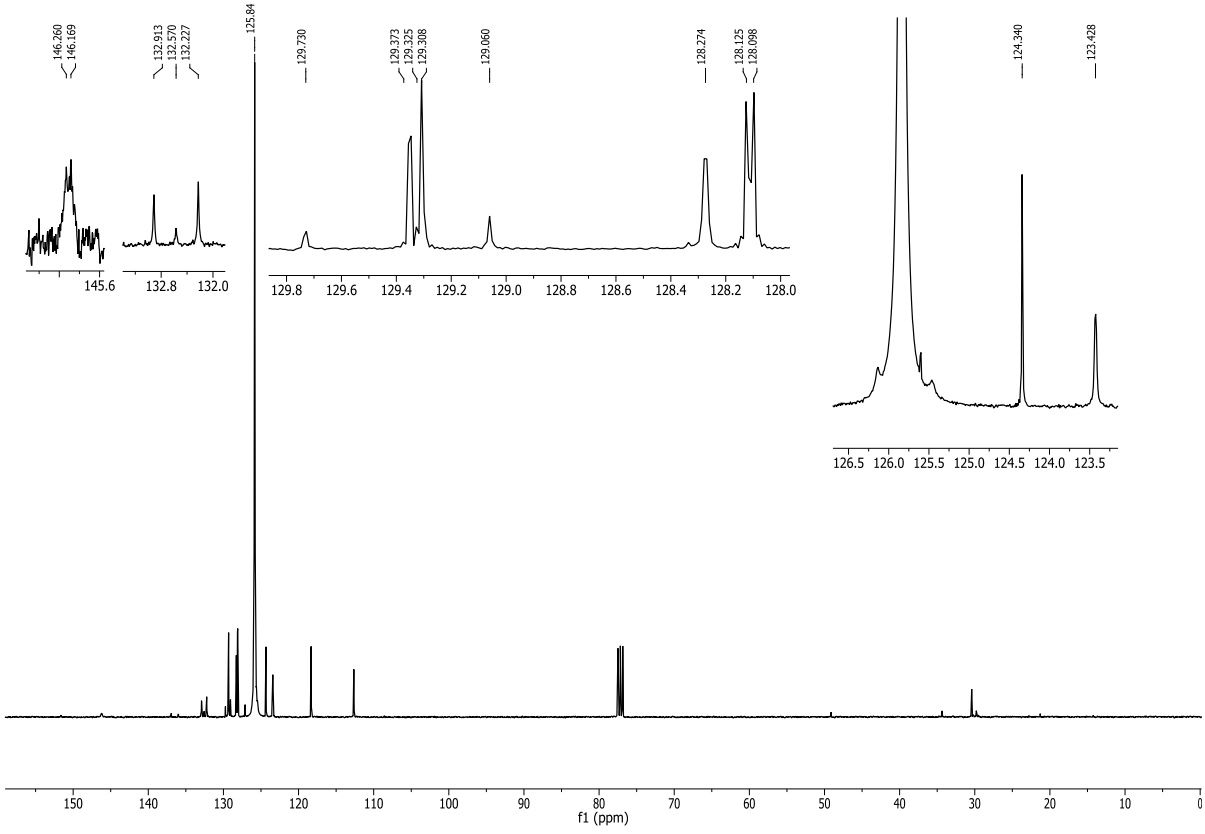


Selected data for 3-Phenyl-3-[^{13}C]-imidazo[1,2-*a*]pyridine ([^{13}C]-**4a**):



R_f 0.13 (4:1 ether/petrol); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.31 (1H, dd, H5 J = 6.8 Hz, J = 1.2 Hz), 7.68 (1H, od, H2 J = 12.4 Hz), 7.65 (1H, od, H8 J = 8.8 Hz), 7.55-7.52 (2H, m, H2′/H6′), 7.49 (2H, $t_{app.}$, H3′/H5′ J = 8.0 Hz), 7.39 (1H, tt, H4′ J = 7.2 Hz, J = 1.2 Hz), 7.17 (1H, ddd., H7 J = 9.2 Hz, J = 6.4 Hz, J = 1.2 Hz), 6.86 (1H, $t_{app.}$, H6 J = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 146.21 (d, C9 J = 9.1 Hz), 132.57 (d, C2 J = 69.0 Hz), 132.52 (s, C9), 129.40 (d, C1' J = 67.4 Hz), 129.33 (d, C3′/C5' J = 4.2 Hz), 129.33 (s, C3'/C5'), 128.27 (s, C4′), 128.11 (d, C2′/C6′ J = 2.7 Hz), 125.84 (C3-label), 124.34 (s, C7), 123.43 (s, C5), 118.09 (C8), 113.30 (C6); *m/z* (CI) 196 ([M+H]$^+$, 100%). Found: [M+H]$^+$, 196.0945. $C_{12}{}^{13}C_1H_{11}N_2$ requires 196.0950.





3 X-ray Crystallography

Data for compounds **3a**, **3a**.HCl.H_2O, **4a**.HCl.2H_2O and **7** were measured at 150 K on an Oxford Diffraction (now Agilent Technologies) Gemini A Ultra diffractometers with Cu (**3a**) or Mo (others) Kα radiation (λ = 1.54184 and 0.71073 Å respectively). The structures were determined by direct methods and refined on all unique F^2 values. Details are given in the tables below, together with Figures illustrating the structures including intermolecular interactions.

3a: the asymmetric unit contains 4 independent molecules with essentially identical structure.

3a.HCl.H_2O: H atoms bonded to N and O were refined freely.

4a.HCl.2H_2O: H atoms bonded to N and O were refined with distance restraints, and with U(H) = 1.2U_{eq}(N) or 1.5U_{eq}(O).

7: The structure of this compound was recently reported by Waser et al.,[7] and has the refcode CARJAI in the Cambridge Structural Database. Our structure is essentially the same, but has higher precision.

Computer programs were standard Oxford Diffraction CrysAlisPRO for data collection and processing, SHELXTL for structure solution and refinement, and SHELXTL and Mercury for graphics.[8]

Table X1. Crystal data and structure refinement for **3a**.

Identification code	mac87	
Chemical formula (moiety)	$C_{13}H_{10}N_2$	
Chemical formula (total)	$C_{13}H_{10}N_2$	
Formula weight	194.23	
Temperature	150(2) K	
Radiation, wavelength	CuKα, 1.54184 Å	
Crystal system, space group	monoclinic, $P2_1/c$	
Unit cell parameters	a = 28.7348(14) Å	α = 90°
	b = 5.8963(2) Å	β = 90.806(3)°
	c = 23.3995(8) Å	γ = 90°
Cell volume	3964.2(3) $Å^3$	
Z	16	
Calculated density	1.302 g/cm^3	
Absorption coefficient μ	0.614 mm^{-1}	
F(000)	1632	
Crystal colour and size	colourless, 0.15 × 0.10 × 0.01 mm^3	
Reflections for cell refinement	4237 (θ range 1.9 to 62.2°)	
Data collection method	Oxford Diffraction Gemini A Ultra diffractometer	
	ω scans	
θ range for data collection	3.1 to 62.3°	
Index ranges	h −29 to 32, k −6 to 5, l −26 to 17	
Completeness to θ = 62.3°	97.7 %	
Reflections collected	11230	
Independent reflections	6140 (R_{int} = 0.0265)	
Reflections with $F^2>2\sigma$	4212	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.913 and 0.994	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.1460, 0.6250	
Data / restraints / parameters	6140 / 0 / 541	
Final R indices [$F^2>2\sigma$]	R1 = 0.0784, wR2 = 0.2092	
R indices (all data)	R1 = 0.1073, wR2 = 0.2275	
Goodness-of-fit on F^2	1.048	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.79 and −0.29 e $Å^{-3}$	

Table X2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **3a**. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
N(1)	0.23645(10)	0.6139(6)	0.59419(12)	0.0443(8)
C(2)	0.26328(13)	0.7828(7)	0.62274(16)	0.0470(10)
C(3)	0.28055(13)	0.7281(7)	0.67485(16)	0.0472(10)
C(4)	0.27143(14)	0.5202(8)	0.70001(17)	0.0534(11)
C(5)	0.24634(14)	0.3616(8)	0.67322(16)	0.0531(10)
C(6)	0.22857(13)	0.4036(6)	0.61993(16)	0.0423(9)
N(7)	0.20342(11)	0.2734(6)	0.58246(13)	0.0471(8)
C(8)	0.19522(12)	0.4073(6)	0.53583(14)	0.0343(8)
C(9)	0.21551(13)	0.6162(7)	0.54106(16)	0.0464(9)
C(10)	0.16773(13)	0.3196(7)	0.48528(16)	0.0434(9)
C(11)	0.14645(13)	0.1109(7)	0.48964(15)	0.0481(10)
C(12)	0.11912(14)	0.0237(7)	0.44311(18)	0.0522(10)
C(13)	0.11326(13)	0.1570(7)	0.39476(15)	0.0461(10)
C(14)	0.13565(13)	0.3619(7)	0.39278(17)	0.0491(10)
C(15)	0.16274(14)	0.4384(8)	0.43681(17)	0.0510(10)
N(21)	0.51934(10)	0.4290(5)	0.61767(12)	0.0383(7)
C(22)	0.55650(13)	0.3623(7)	0.58438(17)	0.0476(10)
C(23)	0.57130(13)	0.5033(8)	0.54293(16)	0.0489(10)
C(24)	0.54901(14)	0.7140(8)	0.53353(16)	0.0502(10)
C(25)	0.51307(13)	0.7777(7)	0.56590(15)	0.0463(9)
C(26)	0.49775(12)	0.6395(6)	0.60996(14)	0.0361(8)
N(27)	0.46466(10)	0.6714(5)	0.64857(12)	0.0384(7)
C(28)	0.46545(12)	0.4785(6)	0.68132(14)	0.0344(8)
C(29)	0.49833(12)	0.3288(6)	0.66316(15)	0.0406(9)
C(30)	0.43302(12)	0.4538(6)	0.72962(14)	0.0370(8)
C(31)	0.43144(14)	0.2576(7)	0.76192(16)	0.0492(10)
C(32)	0.40131(15)	0.2394(8)	0.80746(17)	0.0556(11)
C(33)	0.37318(14)	0.4163(8)	0.82205(16)	0.0523(11)
C(34)	0.37364(14)	0.6141(8)	0.78929(16)	0.0525(11)
C(35)	0.40378(14)	0.6316(7)	0.74397(16)	0.0473(10)
N(41)	0.32427(9)	1.1515(5)	0.52118(11)	0.0326(7)
C(42)	0.33347(12)	1.3254(6)	0.55951(14)	0.0377(8)
C(43)	0.36467(12)	1.2914(6)	0.60186(15)	0.0382(8)
C(44)	0.38840(12)	1.0818(6)	0.60690(14)	0.0380(8)
C(45)	0.37987(12)	0.9124(6)	0.56888(14)	0.0390(8)
C(46)	0.34718(12)	0.9422(6)	0.52467(14)	0.0336(8)
N(47)	0.33194(10)	0.8035(5)	0.48336(11)	0.0365(7)
C(48)	0.29887(11)	0.9233(6)	0.45287(13)	0.0337(8)
C(49)	0.29329(12)	1.1365(6)	0.47545(14)	0.0363(8)
C(50)	0.27419(12)	0.8221(6)	0.40350(13)	0.0358(8)
C(51)	0.23594(12)	0.9286(7)	0.37854(14)	0.0413(9)
C(52)	0.21320(13)	0.8310(7)	0.33196(15)	0.0474(10)
C(53)	0.22770(13)	0.6254(7)	0.30982(14)	0.0466(10)
C(54)	0.26546(14)	0.5183(7)	0.33462(15)	0.0462(9)
C(55)	0.28885(13)	0.6167(6)	0.38126(14)	0.0410(9)
N(61)	−0.00866(11)	1.0453(6)	0.86370(13)	0.0476(8)
C(62)	−0.04203(15)	1.1474(8)	0.89421(18)	0.0562(11)
C(63)	−0.05802(15)	1.0451(11)	0.9419(2)	0.0715(15)
C(64)	−0.03960(15)	0.8244(10)	0.95826(17)	0.0647(14)
C(65)	−0.00665(15)	0.7273(8)	0.92583(17)	0.0557(11)
C(66)	0.00917(13)	0.8371(7)	0.87745(16)	0.0451(9)

N(67)	0.04101(11)	0.7719(5)	0.83880(14)	0.0486(8)
C(68)	0.04291(12)	0.9461(6)	0.80126(15)	0.0412(9)
C(69)	0.01338(14)	1.1166(7)	0.81452(16)	0.0481(10)
C(70)	0.07652(12)	0.9415(8)	0.75335(14)	0.0447(10)
C(71)	0.08132(14)	1.1242(7)	0.71570(17)	0.0521(10)
C(72)	0.11440(15)	1.1127(8)	0.67242(17)	0.0554(11)
C(73)	0.14078(14)	0.9298(8)	0.66546(17)	0.0552(11)
C(74)	0.13631(14)	0.7489(8)	0.70088(18)	0.0540(11)
C(75)	0.10489(14)	0.7506(7)	0.74372(16)	0.0466(10)

Table X3. Bond lengths [Å] and angles [°] for **3a**.

N(1)–C(2)	1.421(5)	N(1)–C(6)	1.398(5)
N(1)–C(9)	1.374(5)	C(2)–H(2)	0.950
C(2)–C(3)	1.349(5)	C(3)–H(3)	0.950
C(3)–C(4)	1.387(6)	C(4)–H(4)	0.950
C(4)–C(5)	1.332(6)	C(5)–H(5)	0.950
C(5)–C(6)	1.363(5)	C(6)–N(7)	1.365(5)
N(7)–C(8)	1.365(4)	C(8)–C(9)	1.367(5)
C(8)–C(10)	1.505(5)	C(9)–H(9)	0.950
C(10)–C(11)	1.378(6)	C(10)–C(15)	1.339(5)
C(11)–H(11)	0.950	C(11)–C(12)	1.429(6)
C(12)–H(12)	0.950	C(12)–C(13)	1.386(5)
C(13)–H(13)	0.950	C(13)–C(14)	1.370(6)
C(14)–H(14)	0.950	C(14)–C(15)	1.360(6)
C(15)–H(15)	0.950	N(21)–C(22)	1.388(5)
N(21)–C(26)	1.399(4)	N(21)–C(29)	1.365(5)
C(22)–H(22)	0.950	C(22)–C(23)	1.351(6)
C(23)–H(23)	0.950	C(23)–C(24)	1.413(6)
C(24)–H(24)	0.950	C(24)–C(25)	1.343(5)
C(25)–H(25)	0.950	C(25)–C(26)	1.391(5)
C(26)–N(27)	1.334(4)	N(27)–C(28)	1.371(4)
C(28)–C(29)	1.365(5)	C(28)–C(30)	1.482(5)
C(29)–H(29)	0.950	C(30)–C(31)	1.383(5)
C(30)–C(35)	1.388(5)	C(31)–H(31)	0.950
C(31)–C(32)	1.387(6)	C(32)–H(32)	0.950
C(32)–C(33)	1.366(6)	C(33)–H(33)	0.950
C(33)–C(34)	1.396(6)	C(34)–H(34)	0.950
C(34)–C(35)	1.382(5)	C(35)–H(35)	0.950
N(41)–C(42)	1.385(4)	N(41)–C(46)	1.401(4)
N(41)–C(49)	1.385(4)	C(42)–H(42)	0.950
C(42)–C(43)	1.342(5)	C(43)–H(43)	0.950
C(43)–C(44)	1.416(5)	C(44)–H(44)	0.950
C(44)–C(45)	1.358(5)	C(45)–H(45)	0.950
C(45)–C(46)	1.399(5)	C(46)–N(47)	1.335(4)
N(47)–C(48)	1.375(4)	C(48)–C(49)	1.374(5)
C(48)–C(50)	1.473(5)	C(49)–H(49)	0.950
C(50)–C(51)	1.388(5)	C(50)–C(55)	1.386(5)
C(51)–H(51)	0.950	C(51)–C(52)	1.388(5)
C(52)–H(52)	0.950	C(52)–C(53)	1.385(6)
C(53)–H(53)	0.950	C(53)–C(54)	1.376(5)
C(54)–H(54)	0.950	C(54)–C(55)	1.399(5)
C(55)–H(55)	0.950	N(61)–C(62)	1.346(5)
N(61)–C(66)	1.367(5)	N(61)–C(69)	1.387(5)
C(62)–H(62)	0.950	C(62)–C(63)	1.354(7)
C(63)–H(63)	0.950	C(63)–C(64)	1.454(8)
C(64)–H(64)	0.950	C(64)–C(65)	1.349(6)
C(65)–H(65)	0.950	C(65)–C(66)	1.386(6)
C(66)–N(67)	1.351(5)	N(67)–C(68)	1.353(5)
C(68)–C(69)	1.354(5)	C(68)–C(70)	1.490(5)
C(69)–H(69)	0.950	C(70)–C(71)	1.400(6)
C(70)–C(75)	1.410(6)	C(71)–H(71)	0.950
C(71)–C(72)	1.400(6)	C(72)–H(72)	0.950
C(72)–C(73)	1.329(6)	C(73)–H(73)	0.950
C(73)–C(74)	1.358(6)	C(74)–H(74)	0.950
C(74)–C(75)	1.359(6)	C(75)–H(75)	0.950

C(2)–N(1)–C(6)	120.6(3)	C(2)–N(1)–C(9)	130.3(3)
C(6)–N(1)–C(9)	109.1(3)	N(1)–C(2)–H(2)	121.7
N(1)–C(2)–C(3)	116.6(4)	H(2)–C(2)–C(3)	121.7
C(2)–C(3)–H(3)	119.1	C(2)–C(3)–C(4)	121.7(4)
H(3)–C(3)–C(4)	119.1	C(3)–C(4)–H(4)	119.2
C(3)–C(4)–C(5)	121.7(4)	H(4)–C(4)–C(5)	119.2
C(4)–C(5)–H(5)	120.1	C(4)–C(5)–C(6)	119.7(4)
H(5)–C(5)–C(6)	120.1	N(1)–C(6)–C(5)	119.6(4)
N(1)–C(6)–N(7)	108.0(3)	C(5)–C(6)–N(7)	132.4(4)
C(6)–N(7)–C(8)	105.8(3)	N(7)–C(8)–C(9)	112.4(3)
N(7)–C(8)–C(10)	120.8(3)	C(9)–C(8)–C(10)	126.8(3)
N(1)–C(9)–C(8)	104.7(3)	N(1)–C(9)–H(9)	127.7
C(8)–C(9)–H(9)	127.7	C(8)–C(10)–C(11)	118.5(3)
C(8)–C(10)–C(15)	122.3(4)	C(11)–C(10)–C(15)	119.2(4)
C(10)–C(11)–H(11)	119.9	C(10)–C(11)–C(12)	120.3(4)
H(11)–C(11)–C(12)	119.9	C(11)–C(12)–H(12)	120.7
C(11)–C(12)–C(13)	118.5(4)	H(12)–C(12)–C(13)	120.7
C(12)–C(13)–H(13)	120.8	C(12)–C(13)–C(14)	118.4(4)
H(13)–C(13)–C(14)	120.8	C(13)–C(14)–H(14)	119.0
C(13)–C(14)–C(15)	122.1(4)	H(14)–C(14)–C(15)	119.0
C(10)–C(15)–C(14)	121.4(4)	C(10)–C(15)–H(15)	119.3
C(14)–C(15)–H(15)	119.3	C(22)–N(21)–C(26)	121.5(3)
C(22)–N(21)–C(29)	131.9(3)	C(26)–N(21)–C(29)	106.5(3)
N(21)–C(22)–H(22)	120.6	N(21)–C(22)–C(23)	118.8(4)
H(22)–C(22)–C(23)	120.6	C(22)–C(23)–H(23)	119.8
C(22)–C(23)–C(24)	120.4(3)	H(23)–C(23)–C(24)	119.8
C(23)–C(24)–H(24)	119.7	C(23)–C(24)–C(25)	120.6(4)
H(24)–C(24)–C(25)	119.7	C(24)–C(25)–H(25)	119.7
C(24)–C(25)–C(26)	120.6(4)	H(25)–C(25)–C(26)	119.7
N(21)–C(26)–C(25)	118.1(3)	N(21)–C(26)–N(27)	110.9(3)
C(25)–C(26)–N(27)	131.0(3)	C(26)–N(27)–C(28)	104.8(3)
N(27)–C(28)–C(29)	111.6(3)	N(27)–C(28)–C(30)	120.1(3)
C(29)–C(28)–C(30)	128.3(3)	N(21)–C(29)–C(28)	106.2(3)
N(21)–C(29)–H(29)	126.9	C(28)–C(29)–H(29)	126.9
C(28)–C(30)–C(31)	121.6(3)	C(28)–C(30)–C(35)	120.0(3)
C(31)–C(30)–C(35)	118.4(3)	C(30)–C(31)–H(31)	119.7
C(30)–C(31)–C(32)	120.7(4)	H(31)–C(31)–C(32)	119.7
C(31)–C(32)–H(32)	119.6	C(31)–C(32)–C(33)	120.7(4)
H(32)–C(32)–C(33)	119.6	C(32)–C(33)–H(33)	120.3
C(32)–C(33)–C(34)	119.4(4)	H(33)–C(33)–C(34)	120.3
C(33)–C(34)–H(34)	120.2	C(33)–C(34)–C(35)	119.6(4)
H(34)–C(34)–C(35)	120.2	C(30)–C(35)–C(34)	121.1(4)
C(30)–C(35)–H(35)	119.4	C(34)–C(35)–H(35)	119.4
C(42)–N(41)–C(46)	122.0(3)	C(42)–N(41)–C(49)	131.5(3)
C(46)–N(41)–C(49)	106.5(3)	N(41)–C(42)–H(42)	120.4
N(41)–C(42)–C(43)	119.1(3)	H(42)–C(42)–C(43)	120.4
C(42)–C(43)–H(43)	119.7	C(42)–C(43)–C(44)	120.5(3)
H(43)–C(43)–C(44)	119.7	C(43)–C(44)–H(44)	119.8
C(43)–C(44)–C(45)	120.3(3)	H(44)–C(44)–C(45)	119.8
C(44)–C(45)–H(45)	119.8	C(44)–C(45)–C(46)	120.4(3)
H(45)–C(45)–C(46)	119.8	N(41)–C(46)–C(45)	117.6(3)
N(41)–C(46)–N(47)	110.4(3)	C(45)–C(46)–N(47)	132.0(3)
C(46)–N(47)–C(48)	106.2(3)	N(47)–C(48)–C(49)	110.7(3)
N(47)–C(48)–C(50)	121.4(3)	C(49)–C(48)–C(50)	127.9(3)
N(41)–C(49)–C(48)	106.2(3)	N(41)–C(49)–H(49)	126.9
C(48)–C(49)–H(49)	126.9	C(48)–C(50)–C(51)	121.1(3)
C(48)–C(50)–C(55)	120.2(3)	C(51)–C(50)–C(55)	118.7(3)

C(50)–C(51)–H(51)	119.9	C(50)–C(51)–C(52)	120.3(4)
H(51)–C(51)–C(52)	119.9	C(51)–C(52)–H(52)	119.5
C(51)–C(52)–C(53)	121.1(4)	H(52)–C(52)–C(53)	119.5
C(52)–C(53)–H(53)	120.6	C(52)–C(53)–C(54)	118.9(4)
H(53)–C(53)–C(54)	120.6	C(53)–C(54)–H(54)	119.8
C(53)–C(54)–C(55)	120.4(4)	H(54)–C(54)–C(55)	119.8
C(50)–C(55)–C(54)	120.6(4)	C(50)–C(55)–H(55)	119.7
C(54)–C(55)–H(55)	119.7	C(62)–N(61)–C(66)	123.0(4)
C(62)–N(61)–C(69)	129.9(4)	C(66)–N(61)–C(69)	107.1(3)
N(61)–C(62)–H(62)	120.3	N(61)–C(62)–C(63)	119.3(5)
H(62)–C(62)–C(63)	120.3	C(62)–C(63)–H(63)	120.3
C(62)–C(63)–C(64)	119.3(4)	H(63)–C(63)–C(64)	120.3
C(63)–C(64)–H(64)	120.4	C(63)–C(64)–C(65)	119.1(4)
H(64)–C(64)–C(65)	120.4	C(64)–C(65)–H(65)	119.9
C(64)–C(65)–C(66)	120.1(4)	H(65)–C(65)–C(66)	119.9
N(61)–C(66)–C(65)	119.0(4)	N(61)–C(66)–N(67)	110.7(3)
C(65)–C(66)–N(67)	130.3(4)	C(66)–N(67)–C(68)	104.6(3)
N(67)–C(68)–C(69)	112.6(3)	N(67)–C(68)–C(70)	120.5(3)
C(69)–C(68)–C(70)	126.9(4)	N(61)–C(69)–C(68)	105.1(3)
N(61)–C(69)–H(69)	127.5	C(68)–C(69)–H(69)	127.5
C(68)–C(70)–C(71)	122.0(4)	C(68)–C(70)–C(75)	121.1(4)
C(71)–C(70)–C(75)	116.8(3)	C(70)–C(71)–H(71)	120.3
C(70)–C(71)–C(72)	119.5(4)	H(71)–C(71)–C(72)	120.3
C(71)–C(72)–H(72)	119.3	C(71)–C(72)–C(73)	121.5(4)
H(72)–C(72)–C(73)	119.3	C(72)–C(73)–H(73)	119.9
C(72)–C(73)–C(74)	120.2(4)	H(73)–C(73)–C(74)	119.9
C(73)–C(74)–H(74)	119.5	C(73)–C(74)–C(75)	120.9(4)
H(74)–C(74)–C(75)	119.5	C(70)–C(75)–C(74)	121.0(4)
C(70)–C(75)–H(75)	119.5	C(74)–C(75)–H(75)	119.5

Table X4. Anisotropic displacement parameters ($Å^2$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	0.0431(18)	0.053(2)	0.0367(16)	–0.0036(15)	0.0000(13)	0.0142(16)
C(2)	0.050(2)	0.036(2)	0.056(2)	0.0002(19)	0.0162(18)	0.0042(18)
C(3)	0.045(2)	0.051(3)	0.045(2)	–0.016(2)	–0.0026(16)	0.0008(19)
C(4)	0.059(3)	0.057(3)	0.044(2)	–0.002(2)	0.0055(18)	0.010(2)
C(5)	0.060(3)	0.051(3)	0.048(2)	–0.001(2)	0.0061(19)	0.002(2)
C(6)	0.044(2)	0.028(2)	0.055(2)	–0.0049(18)	0.0075(17)	0.0020(17)
N(7)	0.059(2)	0.0358(18)	0.0471(17)	0.0076(15)	0.0065(15)	0.0015(16)
C(8)	0.0393(19)	0.0263(18)	0.0376(17)	0.0049(15)	0.0034(14)	0.0040(15)
C(9)	0.055(2)	0.036(2)	0.048(2)	0.0049(18)	0.0053(17)	0.0068(19)
C(10)	0.040(2)	0.037(2)	0.054(2)	–0.0063(18)	0.0109(16)	0.0022(18)
C(11)	0.053(2)	0.053(3)	0.039(2)	0.0132(19)	0.0057(17)	0.020(2)
C(12)	0.050(2)	0.035(2)	0.073(3)	0.004(2)	0.012(2)	0.0022(19)
C(13)	0.044(2)	0.053(3)	0.041(2)	–0.0110(19)	–0.0054(16)	0.0112(19)
C(14)	0.048(2)	0.049(3)	0.051(2)	0.009(2)	–0.0050(17)	0.003(2)
C(15)	0.048(2)	0.045(2)	0.060(2)	0.000(2)	0.0028(19)	0.0020(19)
N(21)	0.0420(17)	0.0318(16)	0.0411(16)	–0.0012(14)	–0.0060(13)	–0.0035(14)
C(22)	0.043(2)	0.037(2)	0.062(2)	–0.016(2)	–0.0104(18)	0.0127(18)
C(23)	0.045(2)	0.055(3)	0.047(2)	–0.014(2)	0.0054(17)	0.001(2)
C(24)	0.052(2)	0.052(3)	0.047(2)	0.0052(19)	0.0012(18)	0.002(2)
C(25)	0.050(2)	0.040(2)	0.049(2)	0.0039(18)	–0.0041(17)	0.0037(19)
C(26)	0.0355(19)	0.0280(19)	0.0449(19)	–0.0022(16)	–0.0036(15)	0.0038(15)
N(27)	0.0403(17)	0.0276(16)	0.0471(16)	0.0050(14)	–0.0041(13)	0.0020(13)
C(28)	0.0377(18)	0.0247(18)	0.0406(18)	0.0002(15)	–0.0121(14)	0.0000(15)
C(29)	0.044(2)	0.0251(18)	0.053(2)	0.0006(17)	–0.0102(16)	0.0045(17)
C(30)	0.0338(18)	0.037(2)	0.0405(18)	–0.0022(16)	–0.0097(14)	–0.0044(16)
C(31)	0.049(2)	0.042(2)	0.056(2)	0.006(2)	–0.0076(18)	0.0051(19)
C(32)	0.060(3)	0.054(3)	0.053(2)	0.018(2)	–0.0098(19)	–0.005(2)
C(33)	0.053(2)	0.068(3)	0.0359(19)	0.000(2)	–0.0022(16)	–0.014(2)
C(34)	0.047(2)	0.056(3)	0.054(2)	–0.016(2)	–0.0031(18)	0.003(2)
C(35)	0.057(2)	0.039(2)	0.046(2)	0.0083(18)	–0.0039(18)	–0.010(2)
N(41)	0.0345(15)	0.0293(16)	0.0342(14)	0.0025(13)	0.0030(11)	0.0030(12)
C(42)	0.039(2)	0.0290(19)	0.0453(19)	0.0008(16)	0.0076(16)	0.0060(16)
C(43)	0.040(2)	0.032(2)	0.0422(19)	–0.0017(16)	0.0017(15)	–0.0004(16)
C(44)	0.0381(19)	0.038(2)	0.0379(18)	0.0045(16)	–0.0041(14)	–0.0010(17)
C(45)	0.040(2)	0.031(2)	0.0453(19)	0.0020(17)	–0.0026(15)	0.0036(16)
C(46)	0.0390(19)	0.0242(18)	0.0378(17)	0.0021(15)	0.0051(14)	0.0037(15)
N(47)	0.0452(17)	0.0242(15)	0.0399(15)	0.0035(13)	–0.0015(13)	0.0048(13)
C(48)	0.0345(18)	0.0314(19)	0.0354(17)	0.0066(15)	0.0040(14)	0.0036(15)
C(49)	0.0379(19)	0.0316(19)	0.0394(18)	0.0088(16)	0.0023(15)	0.0069(16)
C(50)	0.042(2)	0.0319(19)	0.0336(17)	0.0054(15)	0.0040(14)	–0.0010(16)
C(51)	0.045(2)	0.044(2)	0.0356(18)	0.0018(17)	0.0021(15)	0.0049(18)
C(52)	0.046(2)	0.056(3)	0.040(2)	0.0091(19)	–0.0041(16)	0.001(2)
C(53)	0.051(2)	0.056(3)	0.0326(18)	0.0054(18)	–0.0010(16)	–0.009(2)
C(54)	0.057(2)	0.038(2)	0.043(2)	–0.0026(17)	0.0086(17)	0.0006(19)
C(55)	0.046(2)	0.035(2)	0.0420(19)	0.0062(17)	0.0006(15)	0.0014(17)
N(61)	0.0437(18)	0.051(2)	0.0483(18)	–0.0039(16)	–0.0072(14)	–0.0117(16)
C(62)	0.061(3)	0.050(3)	0.057(2)	–0.013(2)	–0.012(2)	0.000(2)
C(63)	0.045(2)	0.106(4)	0.064(3)	–0.042(3)	–0.002(2)	0.002(3)
C(64)	0.056(3)	0.096(4)	0.042(2)	0.009(2)	–0.0039(19)	–0.034(3)

C(65)	0.058(3)	0.048(3)	0.061(3)	0.002(2)	–0.014(2)	–0.009(2)
C(66)	0.041(2)	0.047(2)	0.047(2)	–0.0048(19)	–0.0063(16)	–0.0099(19)
N(67)	0.0495(19)	0.0360(18)	0.060(2)	0.0089(16)	–0.0116(15)	–0.0052(15)
C(68)	0.043(2)	0.0273(19)	0.053(2)	0.0036(17)	–0.0215(17)	–0.0027(17)
C(69)	0.054(2)	0.037(2)	0.053(2)	0.0060(18)	–0.0125(18)	–0.0091(19)
C(70)	0.035(2)	0.063(3)	0.0356(18)	–0.0031(19)	–0.0070(15)	–0.0186(19)
C(71)	0.053(2)	0.036(2)	0.067(3)	–0.006(2)	–0.019(2)	0.0052(19)
C(72)	0.061(3)	0.055(3)	0.050(2)	0.017(2)	–0.0069(19)	–0.022(2)
C(73)	0.047(2)	0.067(3)	0.051(2)	–0.001(2)	–0.0032(18)	–0.004(2)
C(74)	0.048(2)	0.051(3)	0.063(2)	–0.006(2)	–0.0063(19)	0.009(2)
C(75)	0.053(2)	0.036(2)	0.049(2)	0.0156(18)	–0.0143(18)	–0.0079(19)

Table X5. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **3a**.

	x	y	z	U
H(2)	0.2688	0.9269	0.6060	0.056
H(3)	0.2994	0.8349	0.6948	0.057
H(4)	0.2834	0.4900	0.7373	0.064
H(5)	0.2408	0.2198	0.6912	0.064
H(9)	0.2152	0.7362	0.5140	0.056
H(11)	0.1500	0.0247	0.5237	0.058
H(12)	0.1053	–0.1222	0.4453	0.063
H(13)	0.0942	0.1073	0.3637	0.055
H(14)	0.1321	0.4535	0.3596	0.059
H(15)	0.1785	0.5793	0.4331	0.061
H(22)	0.5713	0.2202	0.5906	0.057
H(23)	0.5968	0.4606	0.5200	0.059
H(24)	0.5595	0.8114	0.5041	0.060
H(25)	0.4980	0.9184	0.5586	0.056
H(29)	0.5052	0.1840	0.6790	0.049
H(31)	0.4512	0.1339	0.7528	0.059
H(32)	0.4002	0.1023	0.8288	0.067
H(33)	0.3535	0.4048	0.8542	0.063
H(34)	0.3534	0.7360	0.7981	0.063
H(35)	0.4045	0.7677	0.7223	0.057
H(42)	0.3179	1.4669	0.5559	0.045
H(43)	0.3709	1.4089	0.6287	0.046
H(44)	0.4104	1.0596	0.6371	0.046
H(45)	0.3962	0.7729	0.5723	0.047
H(49)	0.2724	1.2506	0.4623	0.044
H(51)	0.2253	1.0690	0.3934	0.050
H(52)	0.1873	0.9065	0.3150	0.057
H(53)	0.2118	0.5593	0.2780	0.056
H(54)	0.2757	0.3769	0.3200	0.055
H(55)	0.3150	0.5420	0.3978	0.049
H(62)	–0.0542	1.2899	0.8824	0.067
H(63)	–0.0810	1.1166	0.9644	0.086
H(64)	–0.0506	0.7496	0.9914	0.078
H(65)	0.0057	0.5834	0.9362	0.067
H(69)	0.0088	1.2551	0.7945	0.058
H(71)	0.0623	1.2550	0.7195	0.063
H(72)	0.1181	1.2383	0.6475	0.066
H(73)	0.1628	0.9257	0.6356	0.066
H(74)	0.1554	0.6193	0.6956	0.065
H(75)	0.1020	0.6211	0.7676	0.056

Table X6. Torsion angles [°] for **3a**.

C(6)–N(1)–C(2)–C(3)	0.5(5)	C(9)–N(1)–C(2)–C(3)	−178.3(3)
N(1)–C(2)–C(3)–C(4)	−1.9(5)	C(2)–C(3)–C(4)–C(5)	2.1(6)
C(3)–C(4)–C(5)–C(6)	−0.7(6)	C(4)–C(5)–C(6)–N(1)	−0.7(6)
C(4)–C(5)–C(6)–N(7)	177.7(4)	C(2)–N(1)–C(6)–C(5)	0.8(5)
C(2)–N(1)–C(6)–N(7)	−177.9(3)	C(9)–N(1)–C(6)–C(5)	179.8(3)
C(9)–N(1)–C(6)–N(7)	1.1(4)	N(1)–C(6)–N(7)–C(8)	−1.9(4)
C(5)–C(6)–N(7)–C(8)	179.6(4)	C(6)–N(7)–C(8)–C(9)	2.1(4)
C(6)–N(7)–C(8)–C(10)	−179.5(3)	N(7)–C(8)–C(9)–N(1)	−1.4(4)
C(10)–C(8)–C(9)–N(1)	−179.7(3)	C(2)–N(1)–C(9)–C(8)	179.0(3)
C(6)–N(1)–C(9)–C(8)	0.2(4)	N(7)–C(8)–C(10)–C(11)	7.4(5)
N(7)–C(8)–C(10)–C(15)	−173.6(3)	C(9)–C(8)–C(10)–C(11)	−174.5(3)
C(9)–C(8)–C(10)–C(15)	4.5(6)	C(8)–C(10)–C(11)–C(12)	178.5(3)
C(15)–C(10)–C(11)–C(12)	−0.5(5)	C(10)–C(11)–C(12)–C(13)	−2.3(5)
C(11)–C(12)–C(13)–C(14)	2.8(5)	C(12)–C(13)–C(14)–C(15)	−0.7(6)
C(8)–C(10)–C(15)–C(14)	−176.3(3)	C(11)–C(10)–C(15)–C(14)	2.7(6)
C(13)–C(14)–C(15)–C(10)	−2.1(6)	C(26)–N(21)–C(22)–C(23)	−1.4(5)
C(29)–N(21)–C(22)–C(23)	−177.1(4)	N(21)–C(22)–C(23)–C(24)	−0.4(6)
C(22)–C(23)–C(24)–C(25)	0.5(6)	C(23)–C(24)–C(25)–C(26)	1.3(6)
C(24)–C(25)–C(26)–N(21)	−3.0(5)	C(24)–C(25)–C(26)–N(27)	176.8(4)
C(22)–N(21)–C(26)–C(25)	3.1(5)	C(22)–N(21)–C(26)–N(27)	−176.7(3)
C(29)–N(21)–C(26)–C(25)	179.7(3)	C(29)–N(21)–C(26)–N(27)	−0.1(4)
N(21)–C(26)–N(27)–C(28)	0.2(4)	C(25)–C(26)–N(27)–C(28)	−179.5(4)
C(26)–N(27)–C(28)–C(29)	−0.3(4)	C(26)–N(27)–C(28)–C(30)	179.6(3)
N(27)–C(28)–C(29)–N(21)	0.3(4)	C(30)–C(28)–C(29)–N(21)	−179.6(3)
C(22)–N(21)–C(29)–C(28)	176.0(3)	C(26)–N(21)–C(29)–C(28)	−0.1(4)
N(27)–C(28)–C(30)–C(31)	177.1(3)	N(27)–C(28)–C(30)–C(35)	−4.0(5)
C(29)–C(28)–C(30)–C(31)	−3.0(6)	C(29)–C(28)–C(30)–C(35)	175.9(4)
C(28)–C(30)–C(31)–C(32)	179.0(4)	C(35)–C(30)–C(31)–C(32)	0.0(6)
C(30)–C(31)–C(32)–C(33)	−1.2(6)	C(31)–C(32)–C(33)–C(34)	2.4(6)
C(32)–C(33)–C(34)–C(35)	−2.5(6)	C(33)–C(34)–C(35)–C(30)	1.3(6)
C(28)–C(30)–C(35)–C(34)	−179.1(3)	C(31)–C(30)–C(35)–C(34)	−0.1(6)
C(46)–N(41)–C(42)–C(43)	−1.2(5)	C(49)–N(41)–C(42)–C(43)	177.5(3)
N(41)–C(42)–C(43)–C(44)	0.9(5)	C(42)–C(43)–C(44)–C(45)	0.0(5)
C(43)–C(44)–C(45)–C(46)	−0.7(5)	C(44)–C(45)–C(46)–N(41)	0.4(5)
C(44)–C(45)–C(46)–N(47)	−178.3(3)	C(42)–N(41)–C(46)–C(45)	0.5(4)
C(42)–N(41)–C(46)–N(47)	179.5(3)	C(49)–N(41)–C(46)–C(45)	−178.5(3)
C(49)–N(41)–C(46)–N(47)	0.5(3)	N(41)–C(46)–N(47)–C(48)	−0.1(4)
C(45)–C(46)–N(47)–C(48)	178.7(4)	C(46)–N(47)–C(48)–C(49)	−0.4(4)
C(46)–N(47)–C(48)–C(50)	−179.9(3)	N(47)–C(48)–C(49)–N(41)	0.7(4)
C(50)–C(48)–C(49)–N(41)	−179.9(3)	C(42)–N(41)–C(49)–C(48)	−179.6(3)
C(46)–N(41)–C(49)–C(48)	−0.7(3)	N(47)–C(48)–C(50)–C(51)	169.7(3)
N(47)–C(48)–C(50)–C(55)	−10.1(5)	C(49)–C(48)–C(50)–C(51)	−9.7(5)
C(49)–C(48)–C(50)–C(55)	170.5(3)	C(48)–C(50)–C(51)–C(52)	179.8(3)
C(55)–C(50)–C(51)–C(52)	−0.5(5)	C(50)–C(51)–C(52)–C(53)	0.7(5)
C(51)–C(52)–C(53)–C(54)	−0.3(5)	C(52)–C(53)–C(54)–C(55)	−0.3(5)
C(48)–C(50)–C(55)–C(54)	179.6(3)	C(51)–C(50)–C(55)–C(54)	−0.2(5)
C(53)–C(54)–C(55)–C(50)	0.5(5)	C(66)–N(61)–C(62)–C(63)	2.2(6)
C(69)–N(61)–C(62)–C(63)	−179.1(4)	N(61)–C(62)–C(63)–C(64)	−1.5(6)
C(62)–C(63)–C(64)–C(65)	0.5(6)	C(63)–C(64)–C(65)–C(66)	−0.2(6)
C(62)–N(61)–C(66)–C(65)	−1.9(5)	C(62)–N(61)–C(66)–N(67)	178.1(3)
C(69)–N(61)–C(66)–C(65)	179.2(3)	C(69)–N(61)–C(66)–N(67)	−0.9(4)
C(64)–C(65)–C(66)–N(61)	0.8(6)	C(64)–C(65)–C(66)–N(67)	−179.1(4)

N(61)–C(66)–N(67)–C(68)	0.8(4)	C(65)–C(66)–N(67)–C(68)	−179.3(4)
C(66)–N(67)–C(68)–C(69)	−0.5(4)	C(66)–N(67)–C(68)–C(70)	176.8(3)
N(67)–C(68)–C(69)–N(61)	0.0(4)	C(70)–C(68)–C(69)–N(61)	−177.1(3)
C(62)–N(61)–C(69)–C(68)	−178.3(4)	C(66)–N(61)–C(69)–C(68)	0.5(4)
N(67)–C(68)–C(70)–C(71)	−176.3(3)	N(67)–C(68)–C(70)–C(75)	4.1(5)
C(69)–C(68)–C(70)–C(71)	0.6(6)	C(69)–C(68)–C(70)–C(75)	−179.0(4)
C(68)–C(70)–C(71)–C(72)	178.2(3)	C(75)–C(70)–C(71)–C(72)	−2.1(5)
C(70)–C(71)–C(72)–C(73)	1.4(6)	C(71)–C(72)–C(73)–C(74)	−0.4(6)
C(72)–C(73)–C(74)–C(75)	0.3(6)	C(73)–C(74)–C(75)–C(70)	−1.1(6)
C(68)–C(70)–C(75)–C(74)	−178.4(3)	C(71)–C(70)–C(75)–C(74)	2.0(5)

Table X7. Crystal data and structure refinement for **3a**.HCl.H_2O.

Identification code	mac68	
Chemical formula (moiety)	$C_{13}H_{11}N_2^+ \cdot Cl^- \cdot H_2O$	
Chemical formula (total)	$C_{13}H_{13}ClN_2O$	
Formula weight	248.70	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	triclinic, $P\bar{1}$	
Unit cell parameters	a = 6.8922(4) Å	α = 74.573(5)°
	b = 9.1653(6) Å	β = 74.634(5)°
	c = 10.6422(6) Å	γ = 71.501(5)°
Cell volume	602.44(6) $Å^3$	
Z	2	
Calculated density	1.371 g/cm^3	
Absorption coefficient μ	0.301 mm^{-1}	
F(000)	260	
Crystal colour and size	colourless, 0.30 × 0.20 × 0.20 mm^3	
Reflections for cell refinement	6311 (θ range 3.2 to 28.0°)	
Data collection method	Oxford Diffraction Gemini A Ultra diffractometer	
	ω scans	
θ range for data collection	3.2 to 28.0°	
Index ranges	h −8 to 8, k −11 to 11, l −13 to 13	
Completeness to θ = 26.0°	98.4 %	
Reflections collected	9325	
Independent reflections	2571 (R_{int} = 0.0237)	
Reflections with $F^2>2\sigma$	2116	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.915 and 0.942	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0462, 0.2544	
Data / restraints / parameters	2571 / 0 / 171	
Final R indices [$F^2>2\sigma$]	R1 = 0.0350, wR2 = 0.0948	
R indices (all data)	R1 = 0.0446, wR2 = 0.0981	
Goodness-of-fit on F^2	1.092	
Largest and mean shift/su	0.001 and 0.000	
Largest diff. peak and hole	0.58 and −0.45 e $Å^{-3}$	

Table X8. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **3a**.HCl.H_2O. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
N(1)	0.2984(2)	0.24512(15)	0.70697(13)	0.0217(3)
C(2)	0.3149(3)	0.10594(19)	0.79873(17)	0.0272(4)
C(3)	0.2756(3)	0.1121(2)	0.92928(17)	0.0296(4)
C(4)	0.2215(3)	0.2569(2)	0.97008(16)	0.0278(4)
C(5)	0.2064(2)	0.39422(19)	0.87877(16)	0.0235(3)
C(6)	0.2438(2)	0.38613(17)	0.74511(15)	0.0180(3)
N(7)	0.2319(2)	0.49929(15)	0.63510(13)	0.0197(3)
C(8)	0.2782(2)	0.43095(17)	0.52594(15)	0.0180(3)
C(9)	0.3205(2)	0.27295(18)	0.57065(15)	0.0194(3)
C(10)	0.2726(2)	0.51903(17)	0.38991(15)	0.0183(3)
C(11)	0.3283(2)	0.43732(19)	0.28631(16)	0.0232(3)
C(12)	0.3198(3)	0.5189(2)	0.15775(16)	0.0270(4)
C(13)	0.2558(3)	0.6818(2)	0.12973(17)	0.0278(4)
C(14)	0.2015(3)	0.7632(2)	0.23183(17)	0.0272(4)
C(15)	0.2095(2)	0.68264(18)	0.36145(16)	0.0233(3)
Cl(16)	0.12712(7)	0.82702(5)	0.70427(5)	0.03662(15)
O(17)	–0.2874(2)	0.96891(18)	0.58208(18)	0.0419(4)

Table X9. Bond lengths [Å] and angles [°] for **3a**.HCl.H_2O.

N(1)–C(2)	1.378(2)	N(1)–C(6)	1.3661(19)
N(1)–C(9)	1.380(2)	C(2)–H(2)	0.950
C(2)–C(3)	1.356(2)	C(3)–H(3)	0.950
C(3)–C(4)	1.412(2)	C(4)–H(4)	0.950
C(4)–C(5)	1.364(2)	C(5)–H(5)	0.950
C(5)–C(6)	1.395(2)	C(6)–N(7)	1.343(2)
N(7)–H(7)	0.92(2)	N(7)–C(8)	1.3811(19)
C(8)–C(9)	1.359(2)	C(8)–C(10)	1.462(2)
C(9)–H(9)	0.85(2)	C(10)–C(11)	1.399(2)
C(10)–C(15)	1.394(2)	C(11)–H(11)	0.950
C(11)–C(12)	1.380(2)	C(12)–H(12)	0.950
C(12)–C(13)	1.388(2)	C(13)–H(13)	0.950
C(13)–C(14)	1.384(2)	C(14)–H(14)	0.950
C(14)–C(15)	1.387(2)	C(15)–H(15)	0.950
O(17)–H(17A)	0.82(3)	O(17)–H(17B)	0.84(3)

C(2)–N(1)–C(6)	121.49(13)	C(2)–N(1)–C(9)	130.05(14)
C(6)–N(1)–C(9)	108.40(13)	N(1)–C(2)–H(2)	120.9
N(1)–C(2)–C(3)	118.12(15)	H(2)–C(2)–C(3)	120.9
C(2)–C(3)–H(3)	119.5	C(2)–C(3)–C(4)	121.02(16)
H(3)–C(3)–C(4)	119.5	C(3)–C(4)–H(4)	119.7
C(3)–C(4)–C(5)	120.61(15)	H(4)–C(4)–C(5)	119.7
C(4)–C(5)–H(5)	121.2	C(4)–C(5)–C(6)	117.68(15)
H(5)–C(5)–C(6)	121.2	N(1)–C(6)–C(5)	121.07(14)
N(1)–C(6)–N(7)	107.63(13)	C(5)–C(6)–N(7)	131.28(14)
C(6)–N(7)–H(7)	122.5(13)	C(6)–N(7)–C(8)	109.08(13)
H(7)–N(7)–C(8)	128.4(13)	N(7)–C(8)–C(9)	107.40(13)
N(7)–C(8)–C(10)	124.18(13)	C(9)–C(8)–C(10)	128.38(14)
N(1)–C(9)–C(8)	107.48(13)	N(1)–C(9)–H(9)	123.2(13)
C(8)–C(9)–H(9)	129.1(13)	C(8)–C(10)–C(11)	119.27(14)
C(8)–C(10)–C(15)	121.46(14)	C(11)–C(10)–C(15)	119.26(14)
C(10)–C(11)–H(11)	120.1	C(10)–C(11)–C(12)	119.89(15)
H(11)–C(11)–C(12)	120.1	C(11)–C(12)–H(12)	119.6
C(11)–C(12)–C(13)	120.75(15)	H(12)–C(12)–C(13)	119.6
C(12)–C(13)–H(13)	120.2	C(12)–C(13)–C(14)	119.57(15)
H(13)–C(13)–C(14)	120.2	C(13)–C(14)–H(14)	119.9
C(13)–C(14)–C(15)	120.25(15)	H(14)–C(14)–C(15)	119.9
C(10)–C(15)–C(14)	120.27(15)	C(10)–C(15)–H(15)	119.9
C(14)–C(15)–H(15)	119.9	H(17A)–O(17)–H(17B)	107(3)

Table X10. Anisotropic displacement parameters ($Å^2$) for **3a**.HCl.H_2O. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	0.0223(7)	0.0215(7)	0.0215(7)	–0.0044(5)	–0.0027(5)	–0.0074(5)
C(2)	0.0308(9)	0.0198(8)	0.0292(9)	–0.0005(6)	–0.0061(7)	–0.0078(7)
C(3)	0.0333(9)	0.0292(9)	0.0247(9)	0.0037(7)	–0.0064(7)	–0.0130(7)
C(4)	0.0271(8)	0.0377(9)	0.0193(8)	–0.0035(7)	–0.0036(7)	–0.0119(7)
C(5)	0.0214(8)	0.0300(9)	0.0209(8)	–0.0087(6)	–0.0020(6)	–0.0080(6)
C(6)	0.0143(7)	0.0201(7)	0.0199(7)	–0.0042(6)	–0.0022(6)	–0.0059(6)
N(7)	0.0202(6)	0.0190(7)	0.0206(7)	–0.0062(5)	–0.0027(5)	–0.0052(5)
C(8)	0.0152(7)	0.0214(7)	0.0192(7)	–0.0074(6)	–0.0017(6)	–0.0057(6)
C(9)	0.0225(8)	0.0193(7)	0.0176(7)	–0.0070(6)	–0.0018(6)	–0.0062(6)
C(10)	0.0139(7)	0.0223(8)	0.0191(7)	–0.0047(6)	–0.0018(6)	–0.0061(6)
C(11)	0.0238(8)	0.0244(8)	0.0232(8)	–0.0065(6)	–0.0041(6)	–0.0077(6)
C(12)	0.0284(9)	0.0357(9)	0.0210(8)	–0.0087(7)	–0.0034(7)	–0.0130(7)
C(13)	0.0260(8)	0.0353(9)	0.0219(8)	0.0017(7)	–0.0058(7)	–0.0129(7)
C(14)	0.0261(8)	0.0240(8)	0.0276(9)	–0.0004(7)	–0.0044(7)	–0.0061(7)
C(15)	0.0234(8)	0.0225(8)	0.0229(8)	–0.0065(6)	–0.0010(6)	–0.0059(6)
Cl(16)	0.0417(3)	0.0261(2)	0.0392(3)	–0.00644(18)	–0.0048(2)	–0.00772(18)
O(17)	0.0361(8)	0.0372(8)	0.0493(10)	–0.0047(7)	–0.0043(7)	–0.0122(7)

Table X11. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **3a**.HCl.H_2O.

	x	y	z	U
H(2)	0.3528	0.0084	0.7713	0.033
H(3)	0.2847	0.0176	0.9943	0.036
H(4)	0.1953	0.2586	1.0620	0.033
H(5)	0.1715	0.4920	0.9053	0.030(5)
H(7)	0.201(3)	0.604(3)	0.637(2)	0.034(5)
H(9)	0.346(3)	0.201(2)	0.5278(19)	0.028(5)
H(11)	0.3718	0.3258	0.3044	0.028
H(12)	0.3583	0.4630	0.0876	0.032
H(13)	0.2494	0.7370	0.0411	0.033
H(14)	0.1585	0.8747	0.2130	0.033
H(15)	0.1718	0.7392	0.4311	0.028
H(17A)	–0.251(4)	1.021(3)	0.509(3)	0.053(8)
H(17B)	–0.180(5)	0.925(4)	0.615(3)	0.076(10)

Table X12. Torsion angles [°] for **3a**.HCl.H_2O.

C(6)–N(1)–C(2)–C(3)	–0.1(2)	C(9)–N(1)–C(2)–C(3)	–176.89(16)
N(1)–C(2)–C(3)–C(4)	–0.7(3)	C(2)–C(3)–C(4)–C(5)	0.3(3)
C(3)–C(4)–C(5)–C(6)	0.7(2)	C(2)–N(1)–C(6)–C(5)	1.2(2)
C(2)–N(1)–C(6)–N(7)	–177.34(13)	C(9)–N(1)–C(6)–C(5)	178.60(14)
C(9)–N(1)–C(6)–N(7)	0.08(16)	C(4)–C(5)–C(6)–N(1)	–1.5(2)
C(4)–C(5)–C(6)–N(7)	176.66(15)	N(1)–C(6)–N(7)–C(8)	0.21(16)
C(5)–C(6)–N(7)–C(8)	–178.10(15)	C(6)–N(7)–C(8)–C(9)	–0.43(16)
C(6)–N(7)–C(8)–C(10)	177.57(13)	N(7)–C(8)–C(9)–N(1)	0.47(17)
C(10)–C(8)–C(9)–N(1)	–177.41(14)	C(2)–N(1)–C(9)–C(8)	176.78(15)
C(6)–N(1)–C(9)–C(8)	–0.35(17)	N(7)–C(8)–C(10)–C(11)	178.21(14)
N(7)–C(8)–C(10)–C(15)	–2.9(2)	C(9)–C(8)–C(10)–C(11)	–4.2(2)
C(9)–C(8)–C(10)–C(15)	174.62(15)	C(8)–C(10)–C(11)–C(12)	178.75(14)
C(15)–C(10)–C(11)–C(12)	–0.1(2)	C(10)–C(11)–C(12)–C(13)	–0.2(2)
C(11)–C(12)–C(13)–C(14)	0.5(3)	C(12)–C(13)–C(14)–C(15)	–0.4(3)
C(13)–C(14)–C(15)–C(10)	0.1(2)	C(8)–C(10)–C(15)–C(14)	–178.66(14)
C(11)–C(10)–C(15)–C(14)	0.2(2)		

Table X13. Hydrogen bonds for **3a**.HCl.H_2O [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N(7)–H(7)...Cl(16)	0.92(2)	2.21(2)	3.0991(14)	163(2)
O(17)–H(17A)...Cl(16A)	0.82(3)	2.42(3)	3.2404(18)	177(2)
O(17)–H(17B)...Cl(16)	0.84(3)	2.36(3)	3.2024(18)	174(3)

Symmetry operations for equivalent atoms
A –x,–y+2,–z+1

Table X14. Crystal data and structure refinement for **4a**.HCl.2H_2O.

Identification code	mac67	
Chemical formula (moiety)	$C_{13}H_{11}N_2^+ \cdot Cl^- \cdot 2H_2O$	
Chemical formula (total)	$C_{13}H_{15}ClN_2O_2$	
Formula weight	266.72	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	monoclinic, $P2_1/n$	
Unit cell parameters	a = 11.2615(9) Å	α = 90°
	b = 7.2071(6) Å	β = 101.751(8)°
	c = 16.8121(15) Å	γ = 90°
Cell volume	1335.92(19) $Å^3$	
Z	4	
Calculated density	1.326 g/cm^3	
Absorption coefficient μ	0.282 mm^{-1}	
F(000)	560	
Crystal colour and size	colourless, 0.30 × 0.20 × 0.20 mm^3	
Reflections for cell refinement	3286 (θ range 2.8 to 29.5°)	
Data collection method	Oxford Diffraction Gemini A Ultra diffractometer	
	ω scans	
θ range for data collection	3.1 to 29.5°	
Index ranges	h –13 to 14, k –8 to 9, l –22 to 19	
Completeness to θ = 26.0°	99.8 %	
Reflections collected	7628	
Independent reflections	3170 (R_{int} = 0.0281)	
Reflections with $F^2>2\sigma$	2167	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.920 and 0.946	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0507, 0.0000	
Data / restraints / parameters	3170 / 7 / 178	
Final R indices [$F^2>2\sigma$]	R1 = 0.0393, wR2 = 0.0958	
R indices (all data)	R1 = 0.0643, wR2 = 0.1002	
Goodness-of-fit on F^2	1.033	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.34 and –0.30 e $Å^{-3}$	

Table X15. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **4a**.HCl.2H_2O. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
N(1)	0.56504(11)	0.2690(2)	0.26833(9)	0.0189(3)
C(2)	0.56838(16)	0.1967(3)	0.34455(11)	0.0234(4)
C(3)	0.46332(16)	0.1500(3)	0.36619(12)	0.0268(4)
C(4)	0.35171(16)	0.1711(3)	0.31128(12)	0.0288(4)
C(5)	0.34761(15)	0.2377(3)	0.23473(12)	0.0271(4)
C(6)	0.45704(15)	0.2874(2)	0.21400(11)	0.0214(4)
N(7)	0.48285(13)	0.3516(2)	0.14452(9)	0.0239(4)
C(8)	0.60505(15)	0.3763(3)	0.15402(11)	0.0233(4)
C(9)	0.65952(14)	0.3256(2)	0.23035(10)	0.0198(4)
C(10)	0.78802(15)	0.3256(2)	0.27038(11)	0.0201(4)
C(11)	0.87323(15)	0.2733(2)	0.22442(11)	0.0234(4)
C(12)	0.99571(15)	0.2760(3)	0.25896(12)	0.0294(5)
C(13)	1.03461(16)	0.3280(3)	0.33887(13)	0.0325(5)
C(14)	0.95106(16)	0.3786(3)	0.38473(12)	0.0306(5)
C(15)	0.82810(16)	0.3809(3)	0.35050(11)	0.0253(4)
Cl(16)	0.26329(4)	0.48186(7)	0.01601(3)	0.02627(14)
O(17)	0.14042(15)	0.8769(2)	–0.02956(10)	0.0459(4)
O(18)	0.11147(14)	0.1579(2)	0.07810(10)	0.0479(4)

Table X16. Bond lengths [Å] and angles [°] for **4a**.HCl.2H_2O.

N(1)–C(2)	1.377(2)	N(1)–C(6)	1.371(2)
N(1)–C(9)	1.408(2)	C(2)–H(2)	0.950
C(2)–C(3)	1.349(2)	C(3)–H(3)	0.950
C(3)–C(4)	1.408(3)	C(4)–H(4)	0.950
C(4)–C(5)	1.366(3)	C(5)–H(5)	0.950
C(5)–C(6)	1.394(2)	C(6)–N(7)	1.342(2)
N(7)–H(7)	0.869(9)	N(7)–C(8)	1.364(2)
C(8)–H(8)	0.950	C(8)–C(9)	1.355(2)
C(9)–C(10)	1.466(2)	C(10)–C(11)	1.401(2)
C(10)–C(15)	1.389(3)	C(11)–H(11)	0.950
C(11)–C(12)	1.383(2)	C(12)–H(12)	0.950
C(12)–C(13)	1.378(3)	C(13)–H(13)	0.950
C(13)–C(14)	1.381(3)	C(14)–H(14)	0.950
C(14)–C(15)	1.387(3)	C(15)–H(15)	0.950
O(17)–H(17A)	0.854(10)	O(17)–H(17B)	0.866(10)
O(18)–H(18A)	0.841(10)	O(18)–H(18B)	0.865(9)

C(2)–N(1)–C(6)	120.62(14)	C(2)–N(1)–C(9)	130.68(14)
C(6)–N(1)–C(9)	108.64(14)	N(1)–C(2)–H(2)	120.5
N(1)–C(2)–C(3)	119.08(16)	H(2)–C(2)–C(3)	120.5
C(2)–C(3)–H(3)	119.6	C(2)–C(3)–C(4)	120.74(18)
H(3)–C(3)–C(4)	119.6	C(3)–C(4)–H(4)	119.7
C(3)–C(4)–C(5)	120.67(17)	H(4)–C(4)–C(5)	119.7
C(4)–C(5)–H(5)	121.2	C(4)–C(5)–C(6)	117.64(16)
H(5)–C(5)–C(6)	121.2	N(1)–C(6)–C(5)	121.21(16)
N(1)–C(6)–N(7)	107.06(14)	C(5)–C(6)–N(7)	131.71(16)
C(6)–N(7)–H(7)	123.2(13)	C(6)–N(7)–C(8)	109.58(15)
H(7)–N(7)–C(8)	126.3(13)	N(7)–C(8)–H(8)	125.5
N(7)–C(8)–C(9)	109.09(16)	H(8)–C(8)–C(9)	125.5
N(1)–C(9)–C(8)	105.63(14)	N(1)–C(9)–C(10)	123.92(15)
C(8)–C(9)–C(10)	130.45(16)	C(9)–C(10)–C(11)	118.02(16)
C(9)–C(10)–C(15)	122.71(15)	C(11)–C(10)–C(15)	119.23(15)
C(10)–C(11)–H(11)	120.0	C(10)–C(11)–C(12)	120.08(17)
H(11)–C(11)–C(12)	120.0	C(11)–C(12)–H(12)	119.8
C(11)–C(12)–C(13)	120.34(17)	H(12)–C(12)–C(13)	119.8
C(12)–C(13)–H(13)	120.0	C(12)–C(13)–C(14)	119.91(17)
H(13)–C(13)–C(14)	120.0	C(13)–C(14)–H(14)	119.8
C(13)–C(14)–C(15)	120.49(18)	H(14)–C(14)–C(15)	119.8
C(10)–C(15)–C(14)	119.91(17)	C(10)–C(15)–H(15)	120.0
C(14)–C(15)–H(15)	120.0	H(17A)–O(17)–H(17B)	104.4(19)
H(18A)–O(18)–H(18B)	109.6(19)		

Table X17. Anisotropic displacement parameters ($Å^2$) for **4a**.HCl.2H_2O. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	0.0192(7)	0.0204(8)	0.0174(7)	0.0026(6)	0.0047(5)	0.0029(6)
C(2)	0.0260(9)	0.0253(10)	0.0186(9)	0.0021(8)	0.0035(7)	0.0029(8)
C(3)	0.0311(10)	0.0292(11)	0.0224(10)	0.0026(8)	0.0109(8)	0.0020(8)
C(4)	0.0255(9)	0.0310(11)	0.0337(11)	–0.0020(9)	0.0151(8)	0.0015(8)
C(5)	0.0202(9)	0.0294(11)	0.0309(11)	0.0001(9)	0.0034(7)	0.0040(8)
C(6)	0.0217(8)	0.0212(9)	0.0205(10)	0.0005(7)	0.0028(7)	0.0042(7)
N(7)	0.0227(8)	0.0261(9)	0.0212(8)	0.0047(7)	0.0007(6)	0.0036(6)
C(8)	0.0272(9)	0.0219(10)	0.0219(9)	0.0013(8)	0.0078(7)	–0.0005(7)
C(9)	0.0210(8)	0.0200(9)	0.0199(9)	0.0011(7)	0.0078(7)	0.0017(7)
C(10)	0.0214(8)	0.0160(9)	0.0234(9)	0.0016(7)	0.0057(7)	–0.0004(7)
C(11)	0.0271(9)	0.0214(10)	0.0232(10)	0.0026(8)	0.0087(7)	0.0002(8)
C(12)	0.0247(9)	0.0276(11)	0.0396(12)	0.0030(9)	0.0150(8)	0.0010(8)
C(13)	0.0206(9)	0.0284(11)	0.0463(13)	0.0012(10)	0.0013(8)	–0.0008(8)
C(14)	0.0284(10)	0.0327(11)	0.0273(11)	–0.0046(9)	–0.0023(8)	–0.0015(8)
C(15)	0.0253(9)	0.0248(10)	0.0261(10)	–0.0018(8)	0.0058(7)	0.0031(8)
Cl(16)	0.0237(2)	0.0340(3)	0.0197(2)	0.0003(2)	0.00116(15)	0.00173(19)
O(17)	0.0548(10)	0.0425(10)	0.0433(10)	0.0010(8)	0.0168(8)	0.0042(8)
O(18)	0.0469(9)	0.0529(11)	0.0424(10)	–0.0002(8)	0.0054(8)	–0.0064(8)

Table X18. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **4a**.HCl.2H_2O.

	x	y	z	U
H(2)	0.6436	0.1799	0.3814	0.028
H(3)	0.4647	0.1025	0.4191	0.032
H(4)	0.2785	0.1386	0.3276	0.035
H(5)	0.2728	0.2498	0.1969	0.033
H(7)	0.4278(14)	0.390(3)	0.1039(9)	0.029
H(8)	0.6455	0.4217	0.1136	0.028
H(11)	0.8469	0.2359	0.1695	0.028
H(12)	1.0533	0.2418	0.2274	0.035
H(13)	1.1188	0.3290	0.3624	0.039
H(14)	0.9780	0.4121	0.4401	0.037
H(15)	0.7714	0.4203	0.3818	0.030
H(17A)	0.185(2)	0.790(3)	–0.0053(14)	0.069
H(17B)	0.133(2)	0.953(3)	0.0089(12)	0.069
H(18A)	0.131(2)	0.248(3)	0.0517(15)	0.072
H(18B)	0.0337(10)	0.143(4)	0.0658(16)	0.072

Table X19. Torsion angles [°] for **4a**.HCl.2H_2O.

C(6)–N(1)–C(2)–C(3)	–2.3(3)	C(9)–N(1)–C(2)–C(3)	–178.90(17)
N(1)–C(2)–C(3)–C(4)	1.3(3)	C(2)–C(3)–C(4)–C(5)	0.6(3)
C(3)–C(4)–C(5)–C(6)	–1.4(3)	C(2)–N(1)–C(6)–C(5)	1.4(3)
C(2)–N(1)–C(6)–N(7)	–176.85(16)	C(9)–N(1)–C(6)–C(5)	178.74(16)
C(9)–N(1)–C(6)–N(7)	0.46(19)	C(4)–C(5)–C(6)–N(1)	0.4(3)
C(4)–C(5)–C(6)–N(7)	178.2(2)	N(1)–C(6)–N(7)–C(8)	–0.7(2)
C(5)–C(6)–N(7)–C(8)	–178.70(19)	C(6)–N(7)–C(8)–C(9)	0.6(2)
N(7)–C(8)–C(9)–N(1)	–0.3(2)	N(7)–C(8)–C(9)–C(10)	179.93(17)
C(2)–N(1)–C(9)–C(8)	176.86(18)	C(2)–N(1)–C(9)–C(10)	–3.4(3)
C(6)–N(1)–C(9)–C(8)	–0.08(19)	C(6)–N(1)–C(9)–C(10)	179.69(16)
N(1)–C(9)–C(10)–C(11)	141.80(18)	N(1)–C(9)–C(10)–C(15)	–40.4(3)
C(8)–C(9)–C(10)–C(11)	–38.5(3)	C(8)–C(9)–C(10)–C(15)	139.3(2)
C(9)–C(10)–C(11)–C(12)	178.26(16)	C(15)–C(10)–C(11)–C(12)	0.4(3)
C(10)–C(11)–C(12)–C(13)	0.7(3)	C(11)–C(12)–C(13)–C(14)	–0.3(3)
C(12)–C(13)–C(14)–C(15)	–1.2(3)	C(13)–C(14)–C(15)–C(10)	2.4(3)
C(9)–C(10)–C(15)–C(14)	–179.68(17)	C(11)–C(10)–C(15)–C(14)	–1.9(3)

Table X20. Hydrogen bonds for **4a**.HCl.2H_2O [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N(7)–H(7)...Cl(16)	0.869(9)	2.223(10)	3.0800(15)	169(2)
O(17)–H(17A)...Cl(16)	0.854(10)	2.388(13)	3.1902(18)	157(2)
O(17)–H(17B)...O(18A)	0.866(10)	1.924(10)	2.779(2)	169(2)
O(18)–H(18A)...Cl(16)	0.841(10)	2.403(12)	3.1924(17)	157(2)
O(18)–H(18B)...O(17B)	0.865(9)	1.936(10)	2.799(2)	175(2)

Symmetry operations for equivalent atoms
A x,y+1,z B –x,–y+1,–z

Table X21. Crystal data and structure refinement for **7**.

Identification code	mac93	
Chemical formula (moiety)	$C_{15}H_9IO_2$	
Chemical formula (total)	$C_{15}H_9IO_2$	
Formula weight	348.12	
Temperature	150(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system, space group	monoclinic, $P2_1/c$	
Unit cell parameters	a = 9.2369(3) Å	α = 90°
	b = 9.8428(2) Å	β = 103.321(3)°
	c = 14.2265(4) Å	γ = 90°
Cell volume	1258.63(6) $Å^3$	
Z	4	
Calculated density	1.837 g/cm^3	
Absorption coefficient μ	2.534 mm^{-1}	
F(000)	672	
Crystal colour and size	colourless, 0.40 × 0.40 × 0.25 mm^3	
Reflections for cell refinement	5062 (θ range 3.1 to 28.4°)	
Data collection method	Oxford Diffraction Gemini A Ultra diffractometer	
	ω scans	
θ range for data collection	3.1 to 28.5°	
Index ranges	h –11 to 8, k –13 to 13, l –18 to 18	
Completeness to θ = 26.0°	97.0 %	
Reflections collected	6097	
Independent reflections	2619 (R_{int} = 0.0148)	
Reflections with $F^2>2\sigma$	2392	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.431 and 0.570	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0192, 0.8029	
Data / restraints / parameters	2619 / 0 / 164	
Final R indices [$F^2>2\sigma$]	R1 = 0.0166, wR2 = 0.0396	
R indices (all data)	R1 = 0.0194, wR2 = 0.0403	
Goodness-of-fit on F^2	1.048	
Extinction coefficient	0.0013(2)	
Largest and mean shift/su	0.004 and 0.000	
Largest diff. peak and hole	0.40 and –0.41 e $Å^{-3}$	

TableX2 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **7**. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
I	0.829481(14)	0.548094(12)	0.617274(9)	0.02051(6)
O(1)	0.99273(16)	0.39632(15)	0.70951(10)	0.0256(3)
O(2)	1.10426(16)	0.19734(15)	0.69929(10)	0.0280(3)
C(1)	1.0214(2)	0.2910(2)	0.66383(14)	0.0204(4)
C(2)	0.9444(2)	0.28878(19)	0.55869(14)	0.0182(4)
C(3)	0.9656(2)	0.1830(2)	0.49862(15)	0.0233(4)
C(4)	0.8896(3)	0.1806(2)	0.40300(16)	0.0280(5)
C(5)	0.7930(3)	0.2855(2)	0.36609(15)	0.0294(5)
C(6)	0.7710(2)	0.3932(2)	0.42371(15)	0.0245(4)
C(7)	0.8479(2)	0.39165(19)	0.51913(13)	0.0180(4)
C(8)	0.6843(2)	0.6564(2)	0.51300(16)	0.0287(5)
C(9)	0.6106(2)	0.7421(2)	0.46513(15)	0.0259(5)
C(10)	0.5237(2)	0.8471(2)	0.40782(15)	0.0230(4)
C(11)	0.5814(2)	0.9177(2)	0.33999(16)	0.0295(5)
C(12)	0.5006(3)	1.0230(2)	0.28881(17)	0.0314(5)
C(13)	0.3629(3)	1.0579(2)	0.30422(17)	0.0302(5)
C(14)	0.3044(2)	0.9861(2)	0.37046(17)	0.0298(5)
C(15)	0.3843(2)	0.8819(2)	0.42287(16)	0.0267(5)

Table X23. Bond lengths [Å] and angles [°] for **7**.

I–O(1)	2.3056(14)	I–O(2A)	2.9337(14)
I–C(7)	2.1117(18)	I–C(8)	2.054(2)
O(1)–C(1)	1.283(2)	O(2)–IB	2.9337(14)
O(2)–C(1)	1.230(2)	C(1)–C(2)	1.501(3)
C(2)–C(3)	1.390(3)	C(2)–C(7)	1.380(3)
C(3)–H(3)	0.950	C(3)–C(4)	1.380(3)
C(4)–H(4)	0.950	C(4)–C(5)	1.386(3)
C(5)–H(5)	0.950	C(5)–C(6)	1.383(3)
C(6)–H(6)	0.950	C(6)–C(7)	1.380(3)
C(8)–C(9)	1.194(3)	C(9)–C(10)	1.441(3)
C(10)–C(11)	1.391(3)	C(10)–C(15)	1.396(3)
C(11)–H(11)	0.950	C(11)–C(12)	1.383(3)
C(12)–H(12)	0.950	C(12)–C(13)	1.383(3)
C(13)–H(13)	0.950	C(13)–C(14)	1.383(3)
C(14)–H(14)	0.950	C(14)–C(15)	1.378(3)
C(15)–H(15)	0.950		

O(1)–I–O(2A)	80.98(5)	O(1)–I–C(7)	76.23(6)
O(1)–I–C(8)	168.50(7)	O(2A)–I–C(7)	157.10(6)
O(2A)–I–C(8)	110.51(7)	C(7)–I–C(8)	92.27(8)
I–O(1)–C(1)	114.80(12)	IB–O(2)–C(1)	136.29(13)
O(1)–C(1)–O(2)	125.41(18)	O(1)–C(1)–C(2)	114.26(17)
O(2)–C(1)–C(2)	120.33(18)	C(1)–C(2)–C(3)	121.48(18)
C(1)–C(2)–C(7)	120.58(17)	C(3)–C(2)–C(7)	117.93(18)
C(2)–C(3)–H(3)	119.8	C(2)–C(3)–C(4)	120.45(19)
H(3)–C(3)–C(4)	119.8	C(3)–C(4)–H(4)	120.1
C(3)–C(4)–C(5)	119.9(2)	H(4)–C(4)–C(5)	120.1
C(4)–C(5)–H(5)	119.5	C(4)–C(5)–C(6)	121.0(2)
H(5)–C(5)–C(6)	119.5	C(5)–C(6)–H(6)	121.2
C(5)–C(6)–C(7)	117.5(2)	H(6)–C(6)–C(7)	121.2
I–C(7)–C(2)	114.09(13)	I–C(7)–C(6)	122.74(15)
C(2)–C(7)–C(6)	123.16(18)	I–C(8)–C(9)	165.99(19)
C(8)–C(9)–C(10)	179.1(2)	C(9)–C(10)–C(11)	119.87(19)
C(9)–C(10)–C(15)	120.2(2)	C(11)–C(10)–C(15)	119.90(19)
C(10)–C(11)–H(11)	120.2	C(10)–C(11)–C(12)	119.6(2)
H(11)–C(11)–C(12)	120.2	C(11)–C(12)–H(12)	119.8
C(11)–C(12)–C(13)	120.5(2)	H(12)–C(12)–C(13)	119.8
C(12)–C(13)–H(13)	120.0	C(12)–C(13)–C(14)	119.9(2)
H(13)–C(13)–C(14)	120.0	C(13)–C(14)–H(14)	119.8
C(13)–C(14)–C(15)	120.3(2)	H(14)–C(14)–C(15)	119.8
C(10)–C(15)–C(14)	119.8(2)	C(10)–C(15)–H(15)	120.1
C(14)–C(15)–H(15)	120.1		

Symmetry operations for equivalent atoms
A –x+2,y+1/2,–z+3/2 B –x+2,y–1/2,–z+3/2

Table X24. Anisotropic displacement parameters (Å^2) for **7**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ...+ 2hka^*b^*U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I	0.02469(9)	0.01689(8)	0.01958(8)	–0.00211(5)	0.00433(5)	0.00173(5)
O(1)	0.0298(8)	0.0283(8)	0.0165(7)	–0.0012(6)	0.0010(6)	0.0025(6)
O(2)	0.0264(8)	0.0296(8)	0.0266(8)	0.0106(7)	0.0033(6)	0.0056(7)
C(1)	0.0179(10)	0.0235(10)	0.0198(9)	0.0057(9)	0.0042(7)	–0.0034(8)
C(2)	0.0183(10)	0.0160(9)	0.0202(9)	0.0026(8)	0.0046(7)	–0.0022(7)
C(3)	0.0260(11)	0.0169(9)	0.0288(11)	0.0003(9)	0.0101(9)	0.0013(8)
C(4)	0.0376(13)	0.0208(10)	0.0276(11)	–0.0062(9)	0.0118(9)	–0.0040(9)
C(5)	0.0394(13)	0.0284(11)	0.0181(10)	–0.0027(9)	0.0020(9)	–0.0041(10)
C(6)	0.0287(11)	0.0217(10)	0.0209(10)	0.0028(9)	0.0009(8)	0.0008(9)
C(7)	0.0235(10)	0.0126(9)	0.0181(9)	–0.0020(8)	0.0049(8)	–0.0016(7)
C(8)	0.0312(12)	0.0213(10)	0.0326(11)	0.0002(10)	0.0056(9)	0.0052(9)
C(9)	0.0277(11)	0.0198(10)	0.0295(11)	–0.0046(10)	0.0052(9)	0.0004(9)
C(10)	0.0226(10)	0.0168(9)	0.0261(10)	–0.0030(9)	–0.0014(8)	0.0013(8)
C(11)	0.0227(11)	0.0334(12)	0.0315(11)	–0.0007(10)	0.0046(9)	0.0034(9)
C(12)	0.0317(12)	0.0309(12)	0.0300(11)	0.0050(10)	0.0039(9)	–0.0019(10)
C(13)	0.0293(12)	0.0231(11)	0.0315(11)	–0.0010(10)	–0.0066(9)	0.0051(9)
C(14)	0.0202(11)	0.0309(11)	0.0354(12)	–0.0050(10)	0.0007(9)	0.0043(9)
C(15)	0.0239(11)	0.0241(11)	0.0308(11)	–0.0007(10)	0.0037(9)	–0.0008(8)

Table X25. Hydrogen coordinates and isotropic displacement parameters (Å^2) for **7**.

	x	y	z	U
H(3)	1.0329	0.1117	0.5235	0.028
H(4)	0.9034	0.1073	0.3625	0.034
H(5)	0.7411	0.2834	0.3002	0.035
H(6)	0.7054	0.4655	0.3985	0.029
H(11)	0.6757	0.8936	0.3289	0.035
H(12)	0.5400	1.0718	0.2427	0.038
H(13)	0.3085	1.1311	0.2694	0.036
H(14)	0.2088	1.0088	0.3799	0.036
H(15)	0.3445	0.8339	0.4691	0.032

Table X26. Torsion angles [°] for **7**.

O(2A)–I–O(1)–C(1)	−177.64(14)	C(7)–I–O(1)–C(1)	0.17(14)
C(8)–I–O(1)–C(1)	−1.0(4)	IB–O(2)–C(1)–O(1)	38.7(3)
IB–O(2)–C(1)–C(2)	−141.67(15)	I–O(1)–C(1)–O(2)	−179.40(16)
I–O(1)–C(1)–C(2)	0.9(2)	O(1)–C(1)–C(2)–C(3)	178.88(18)
O(1)–C(1)–C(2)–C(7)	−2.2(3)	O(2)–C(1)–C(2)–C(3)	−0.8(3)
O(2)–C(1)–C(2)–C(7)	178.10(18)	C(1)–C(2)–C(3)–C(4)	177.67(19)
C(7)–C(2)–C(3)–C(4)	−1.3(3)	C(2)–C(3)–C(4)–C(5)	1.0(3)
C(3)–C(4)–C(5)–C(6)	−0.1(3)	C(4)–C(5)–C(6)–C(7)	−0.4(3)
C(5)–C(6)–C(7)–I	179.51(16)	C(5)–C(6)–C(7)–C(2)	0.1(3)
C(1)–C(2)–C(7)–I	2.3(2)	C(1)–C(2)–C(7)–C(6)	−178.20(19)
C(3)–C(2)–C(7)–I	−178.70(14)	C(3)–C(2)–C(7)–C(6)	0.8(3)
O(1)–I–C(7)–C(2)	−1.29(13)	O(1)–I–C(7)–C(6)	179.24(18)
O(2A)–I–C(7)–C(2)	4.3(3)	O(2A)–I–C(7)–C(6)	−175.19(13)
C(8)–I–C(7)–C(2)	178.47(15)	C(8)–I–C(7)–C(6)	−0.99(18)
O(1)–I–C(8)–C(9)	−155.5(7)	O(2A)–I–C(8)–C(9)	21.0(9)
C(7)–I–C(8)–C(9)	−156.6(8)	C(9)–C(10)–C(11)–C(12)	−176.7(2)
C(10)–C(11)–C(12)–C(13)	−0.4(3)	C(11)–C(12)–C(13)–C(14)	−0.7(3)
C(12)–C(13)–C(14)–C(15)	1.5(3)	C(13)–C(14)–C(15)–C(10)	−1.1(3)
C(9)–C(10)–C(15)–C(14)	177.4(2)	C(11)–C(10)–C(15)–C(14)	0.0(3)

Symmetry operations for equivalent atoms
A –x+2,y+1/2,–z+3/2 B –x+2,y–1/2,–z+3/2

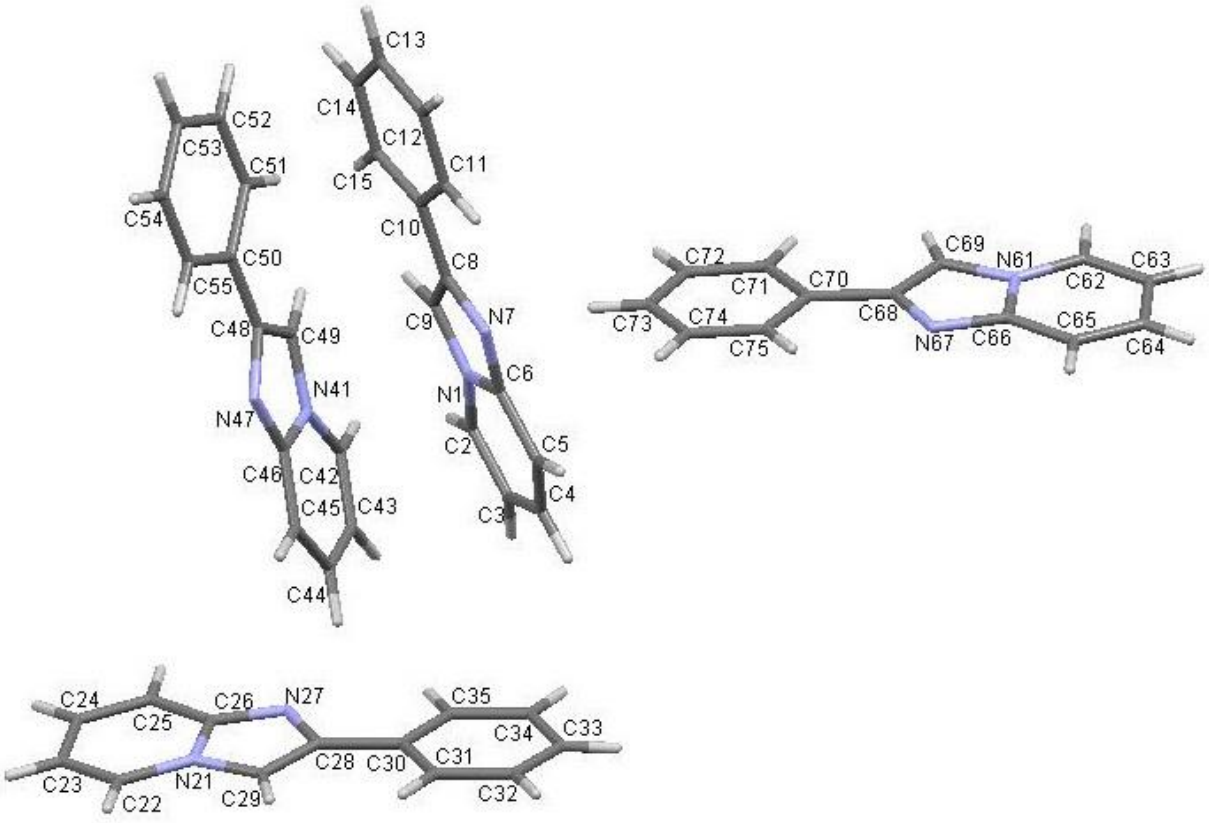


Figure X1. The asymmetric unit of **3a**, containing four molecules.

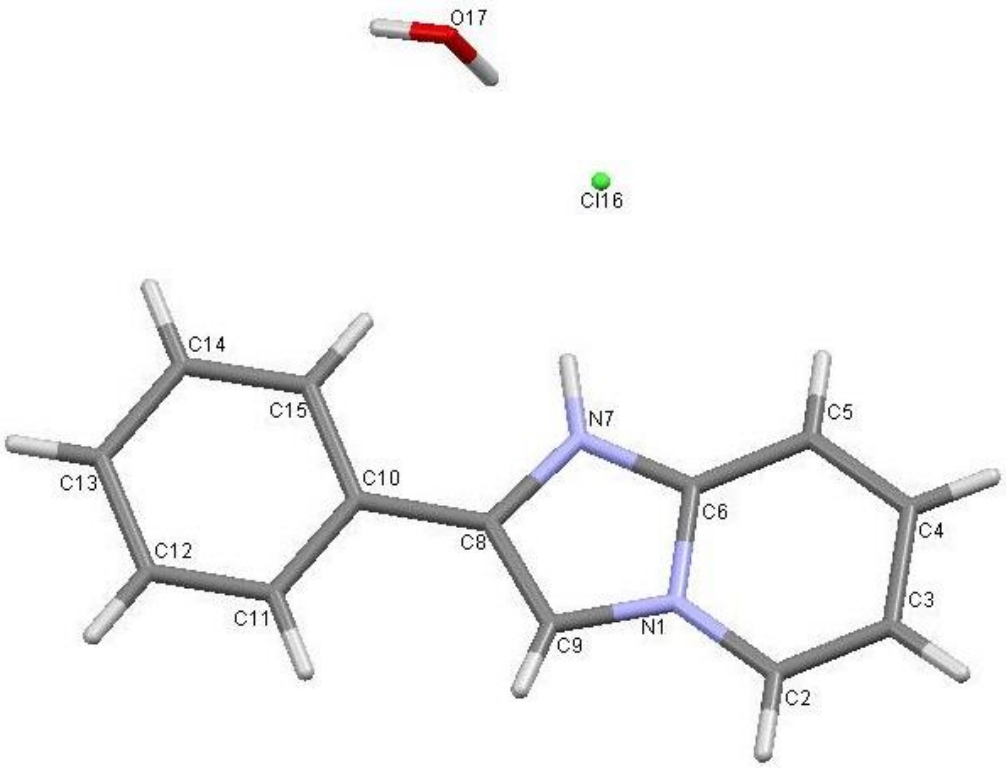


Figure X2. The asymmetric unit of **3a**.HCl.H_2O.

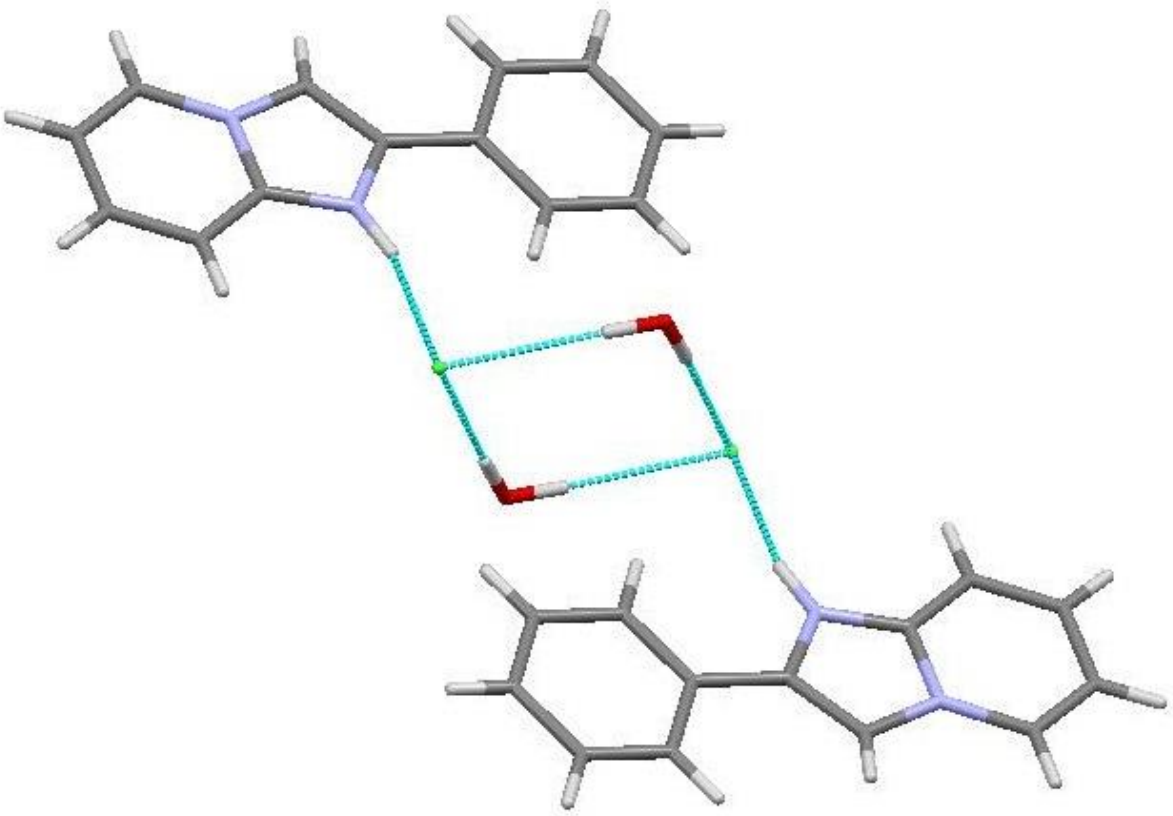


Figure X3. The formation of discrete dimeric units of **3a**.HCl.H_2O through hydrogen bonding.

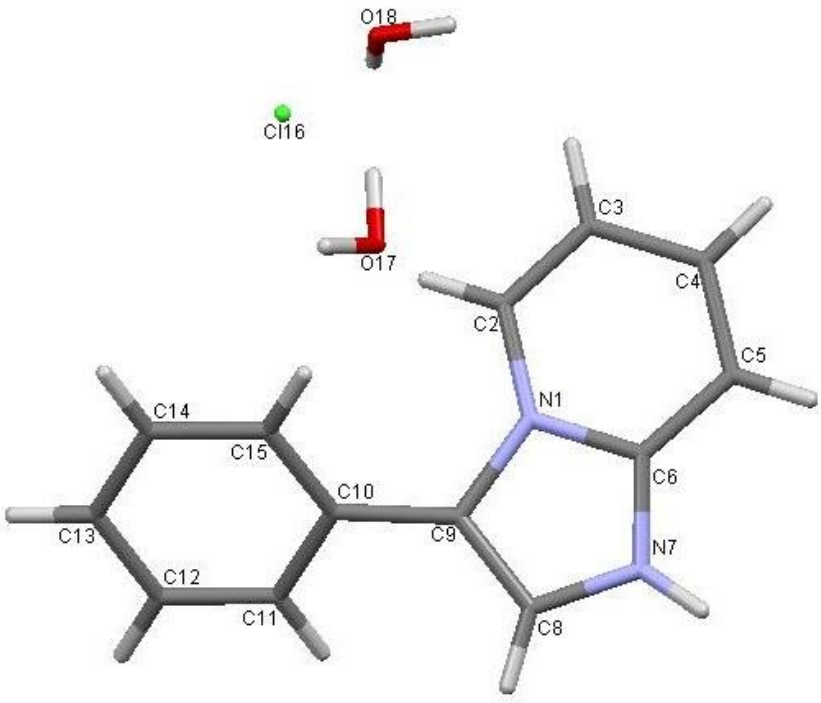


Figure X4. The asymmetric unit of **4a**.HCl.2H_2O

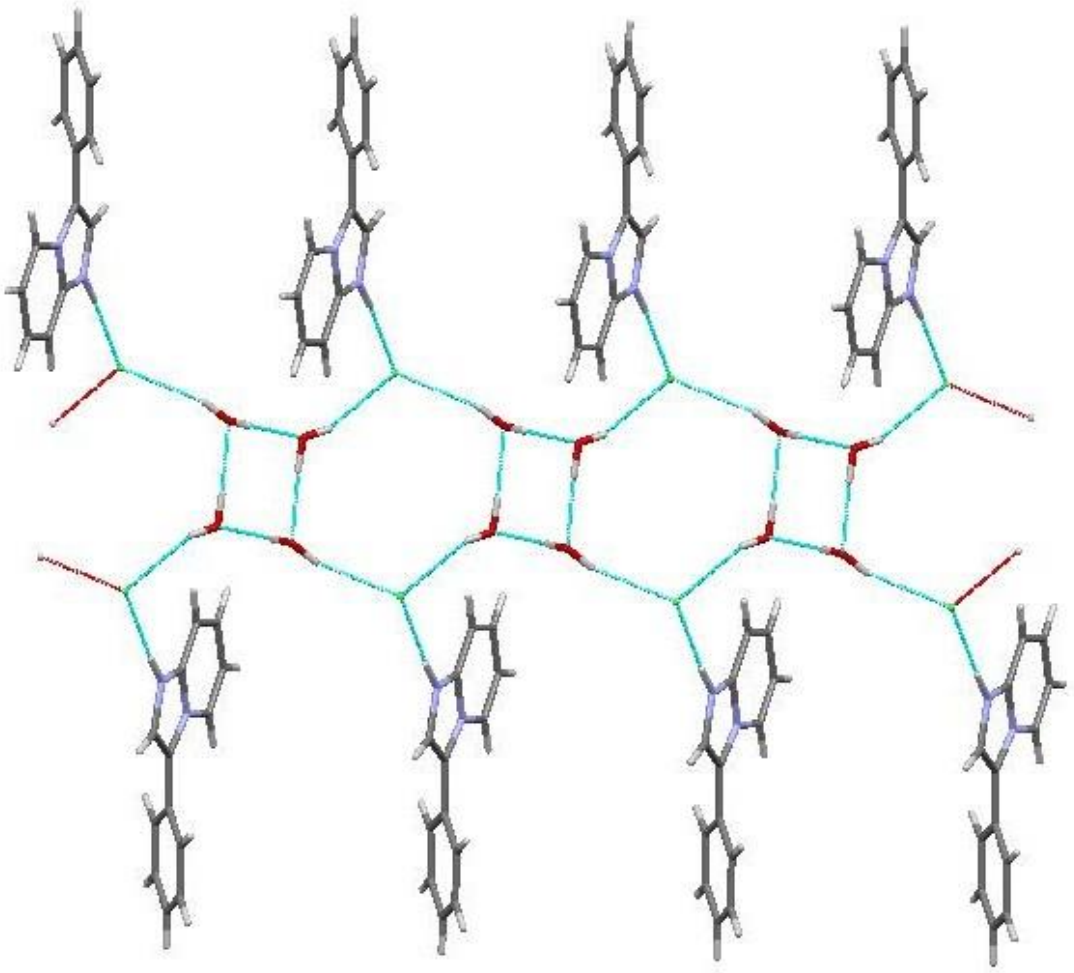


Figure X5. The formation of chains of **4a**.HCl.2H_2O through hydrogen bonding

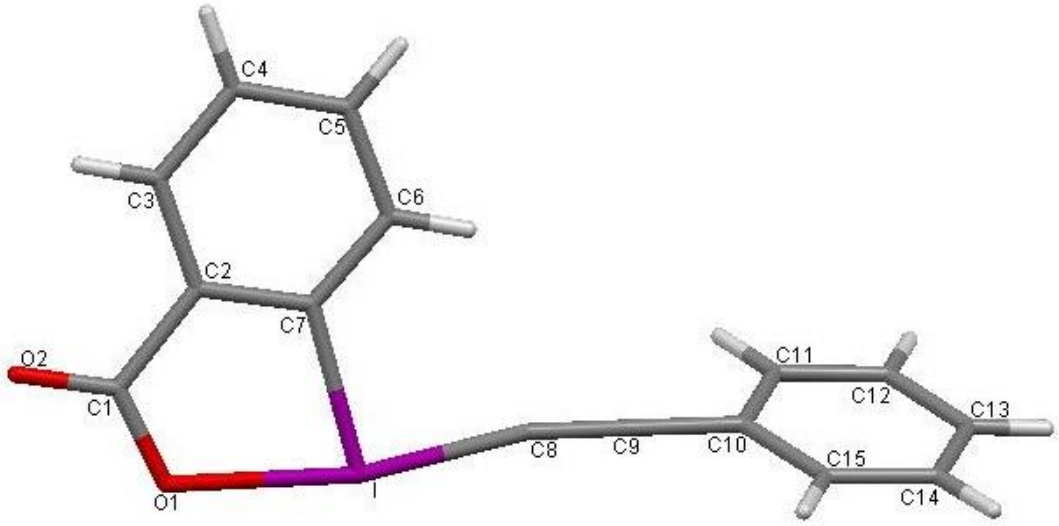


Figure X6. The asymmetric unit of **7**.

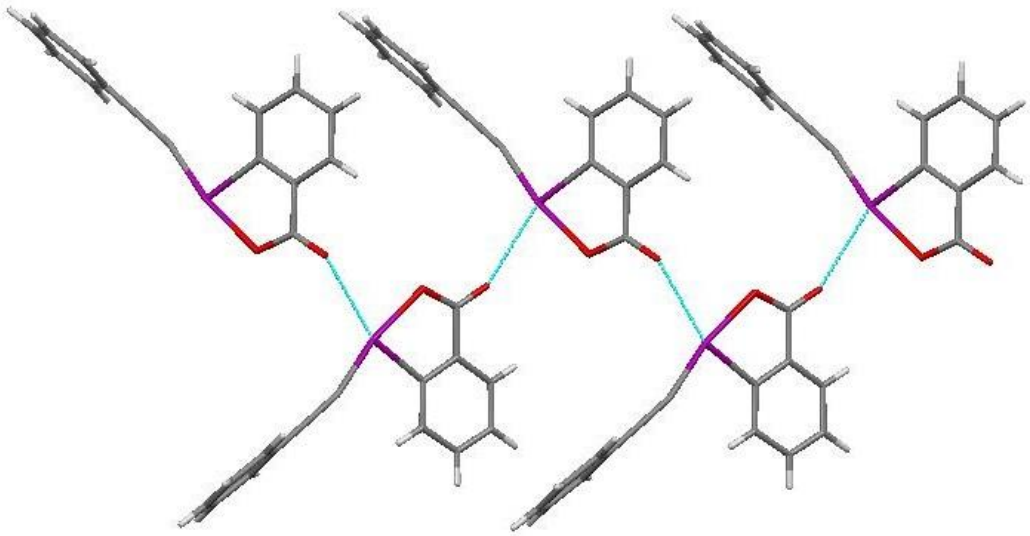


Figure X7. The formation of chains of **7** by intermolecular I…O interactions.

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