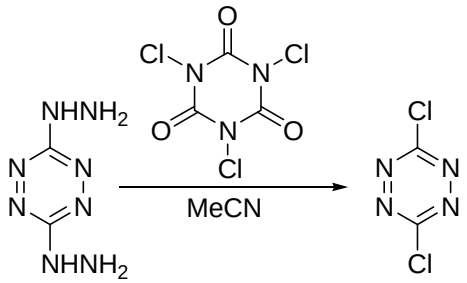
Experimental

General Procedures.

All reactions were conducted in oven or flame-dried glassware under an inert atmosphere of dry nitrogen. Flash chromatography was performed on silica gel (Fluorochem Davisil silica gel 43-60). The solvent system used was a gradient of petroleum ether (40-60), increasing in polarity to ethyl acetate. Thin layer chromatography (TLC) was performed on aluminium backed plates pre-coated with silica (0.2 mm, Merck DC-alufolien Kieselgel 60 F_{254}) which were developed using standard visualizing agents: Ultraviolet light or potassium permanganate.

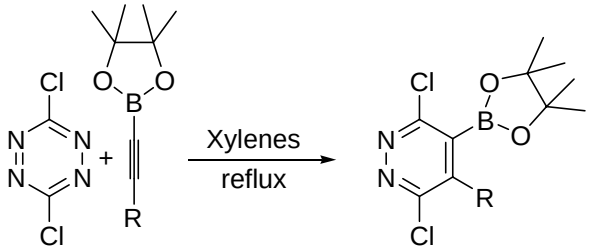
^{1}H NMR spectra were recorded on a Bruker AC-250 (250 MHz) or DRX-500 (500 MHz) supported by an Aspect 3000 data system, unless otherwise stated. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$:δ7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broad, m=multiplet), coupling constants (*J*) in Hz, and assignment. ^{13}C NMR spectra were recorded on a Bruker AC-250 (62.9 MHz) or DRX-500 (125.8 MHz) with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ77.0 ppm). Infrared (FTIR) spectra were recorded on a Perkin Elmer Paragon 100 FTIR spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m) and weak (w). Samples were recorded as thin films using sodium chloride plates. Low resolution mass spectra were recorded on Micromass Autospec, operating in E.I., C.I. or FAB mode; or a Perkin-Elmer Turbomass Benchtop GC-MS operating in either E.I. or C.I mode. High-resolution mass spectra (HRMS) recorded for accurate mass analysis, were performed on either a MicroMass LCT operating in Electrospray mode (TOF ES^+) or a MicroMass Prospec operating in either FAB (FAB^+), EI (EI^+) or CI (CI^+) mode. Melting points were performed on recrystallised solids and recorded on a Gallenkamp melting point apparatus and are uncorrected. All solvents and reagents were purified using standard laboratory techniques.[1]

Formation of 3,6-dichloroterazine (5)

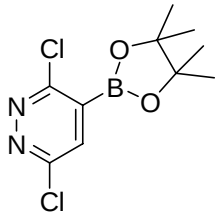


To a slurry of 3,6-di(hydrazino)-1,2,4,5-tetrazine[2] (12.5 g, 0.088 mol) in acetonitrile (350 mL) at 0°C was added dropwise over 30 minutes a solution of trichloroisocyanuric acid (40.8 g, 0.18 mol) in acetonitrile (250 mL). After the addition was finished the reaction vessel was allowed to warm to room temperature and stirred for 20 minutes. The white insoluble precipitate was removed by filtration and the volatiles removed from the resulting orange solution in vacuo to give crude 3,6-dichloro-1,2,4,5-tetrazine as an orange solid. Sublimation under nitrogen at 70 °C using a cold finger at -78 °C gave 3,6-dichloro-1,2,4,5-tetrazine **5** (6.785 g, 51%) as an orange powder. ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 168.1.[3]

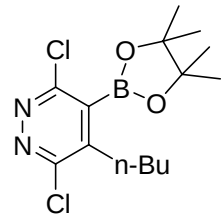
Cycloadditions of 3,6-dichloro-1,2,4,5-tetrazine (5)



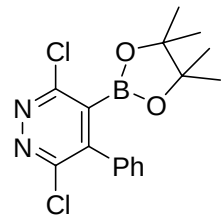
Typical procedure: 3,6-dichloro-1,2,4,5-tetrazine **5** (1 eq) and an alkynylboronate (1.5 eq) were dissolved in xylenes (~0.3 molL^{-1}) and heated at reflux until the colour faded (16-24 h). The xylenes were removed in vacuo and the pyridazine boronic esters purified by chromatography on silica gel.



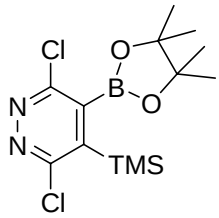
3,6-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridazine (6a) heated for 16 hours, isolated as a light yellow solid (63%) mp 100.3-101.6 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.36 (12H, s, CH_3), 7.74 (1H, s, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 24.7, 85.9, 136.1, 155.9, 158.7. FTIR: 3066 (w), 2980 (m), 2930 (m), 1567 (m), 1496 (w), 1481 (w), 1462 (w), 1415 (s), 1375 (s), 1364 (s), 1311 (s), 1266 (m), 1215 (m), 1174 (m), 1153 (s), 1138 (s), 1080 (s), 967 (m) cm^{-1}. HRMS calcd for $C_{10}H_{13}BN_2O_2Cl_2$: 274.0447. Found: 274.0435.



4-Butyl-3,6-dichloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridazine (6b) heated for 24 hours, isolated as a colourless oil (80%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.93-1.01 (3H, t, *J* =7.0 Hz , CH_3), 1.42 (12H, s, CH_3), 1.44-1.68 (4H, m, CH_2), 2.65-2.75 (2H, t, *J* = 8.0 Hz, CH_2). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 13.7, 23.0, 24.7, 31.5, 33.5, 85.8, 147.7, 156.6, 157.5. FTIR: 2979 (m), 2932 (m), 2873 (m), 1538 (w), 1580 (w), 1467 (w), 1372 (s), 1341 (s), 1288 (m), 1263 (s), 1210 (m), 1183 (m), 1142 (s), 1130 (s), 1098 (m) cm^{-1}. HRMS calcd for $C_{14}H_{21}BN_2O_2NaCl_2$: 353.0971. Found: 353.0966.

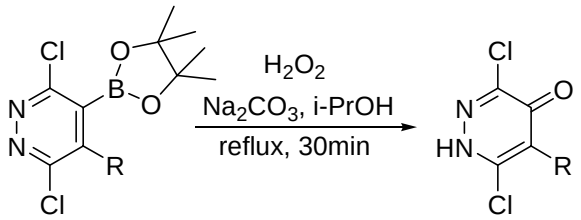


3,6-Dichloro-4-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridazine (6c) heated for 24 hours, isolated as a colourless solid (80%) mp 182.7-183.6 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.10 (12H, s, CH_3), 7.30-7.40 (2H, m, CH), 7.43-7.56 (3H, m, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 24.4, 85.7, 128.5, 129.0, 129.7, 134.2, 146.2, 155.0, 157.3. FTIR: 3058(w), 2984(m), 2913(w), 1970(w), 1896(w), 1531(m), 1486(m), 1443(m), 1391(s), 1373(s), 1346(s), 1252(s), 1216(s), 1133(s) cm^{-1}. HMRS calcd for $C_{16}H_{17}B_1N_2O_2Cl_2$: 350.0760. Found: 350.0756.

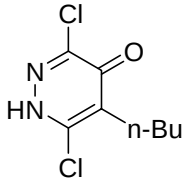


3,6-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)pyridazine (6d) heated for 24 hours, isolated as a colourless solid (86%) mp 131.4-131.9 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.47 (9H, s, CH_3), 1.47 (12H, s, CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 0.0, 26.0, 86.1, 147.4, 158.1, 160.6. FTIR: 2998 (w), 2947 (w), 1501 (w), 1391 (w), 1357 (m), 1342 (m), 1258 (m), 1214 (s), 1162 (w), 1136 (m), 1100 (m), 965 (m) cm^{-1}. HRMS calcd for $C_{13}H_{22}BN_2O_2Cl_2Si$ [M+H]: 347.0921. Found: 347.0911.

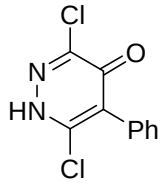
Oxidation of pyridazine boronic esters



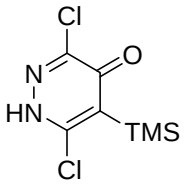
Typical procedure: To a refluxing solution of the pyridazine boronic ester (1 eq) in propan-2-ol (~0.07 molL^{-1}) was added dropwise a solution of sodium carbonate (1 eq) in 30% aqueous hydrogen peroxide (~15 mLg^{-1} pyridazine boronic ester). The reaction was heated at reflux for a further 30 minutes and then after cooling to room temperature, quenched with water. The product was extracted three times with dichloromethane and the combined organic fractions dried over magnesium sulphate. The volatiles were removed in vacuo and the crude materials purified by chromatography on silica gel.



5-Butyl-3,6-dichloropyridazin-4(1H)-one (7a) isolated as a colourless solid (85%) mp 138.0-139.1 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.88-0.99 (3H, t, *J* = 7.5 Hz, CH_3), 1.28-1.64 (4H, m, CH_2), 2.62-2.79 (2H, t, *J* = 7.0 Hz, CH_2). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 13.8, 22.7, 26.3, 29.3, 129.0, 143.8, 149.0, 166.2. FTIR: 3164 (br, w), 3058 (br, w), 2959 (m), 2929 (m), 2871 (m), 2777 (v. br, s), 1577 (s), 1521 (s), 1479 (m), 1435 (m), 1379 (w), 1238 (w), 1196 (m), 1155 (m), 1091 (w). HRMS calcd for $C_8H_{11}N_2OCl_2$: 221.0248. Found: 221.0256.

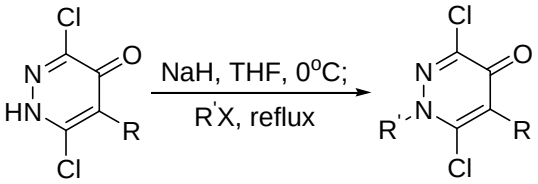


3,6-Dichloro-5-phenylpyridazin-4(1H)-one (7b) isolated as a colourless solid (73%) mp 261.8 ^{o}C (dec). ^{1}H NMR (250 MHz, DMSO): δ 7.28-7.57 (5H, m, CH). ^{13}C NMR (62.9 MHz, DMSO): δ 126.2, 128.1, 128.4, 130.0, 131.2, 142.5, 149.8, 163.7. FTIR: 3134 (m), 3042 (w), 2947 (m), 2877 (br, m), 1659 (w), 1629 (w), 1580 (s), 1560 (m), 1535 (s), 1492 (w), 1466 (w), 1366 (m), 1286 (w), 1206 (m), 1144 (w), 1067 (w) cm^{-1}. HRMS calcd for $C_{10}H_7N_2OCl_2$: 240.9935. Found: 240.9925.

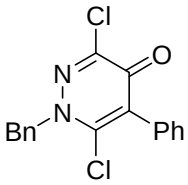


3,6-Dichloro-5-(trimethylsilyl)pyridazin-4(1H)-one (7c) isolated as a colourless solid (78%) mp 148.4 ^{o}C (dec). Yield after purification on silica gel and recrystallisation from ethyl acetate/hexanes. ^{1}H NMR (250 MHz, d^{6}-DMSO): δ 0.29 (9H, s, CH_3). ^{13}C NMR (62.9 MHz, d^{6}-DMSO): δ 0.7, 121.5, 147.4, 149.2, 169.2. FTIR: 3176 (w), 3049 (w), 2956 (m), 2761 (br), 2356 (m), 1547 (s), 1493 (s), 1462 (s), 1406 (w), 1354 (w), 1245 (m), 1197 (s), 1160 (m), 1109 (s) cm^{-1}. HRMS calcd for $C_7H_{11}N_2OSiCl_2$ [M+H]: 237.0018. Found: 237.0016.

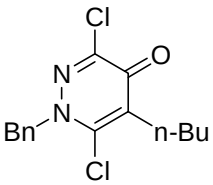
N-alkylation of pyridazinones



Typical procedure: To a solution of the pyridazinone (1 eq) in THF (~0.1 $molL^{-1}$) was added a 60% sodium hydride emulsion in paraffin oil (2 eq) at 0 °C. After stirring for 30 minutes at 0 °C the reaction was warmed to room temperature and the alkyl halide (2 eq) added. The reaction was then heated at reflux until complete consumption of the starting pyridazinone was observed by TLC (approximately 16 hours). The reaction was then quenched with water, extracted three times with dichloromethane, the combined organic fractions dried over magnesium sulphate, the volatiles removed in vacuo and crude materials purified by chromatography on silica gel.

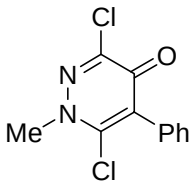


1-Benzyl-3,6-dichloro-5-phenylpyridazin-4(1H)-one (8) R'X = BnBr, isolated as a light yellow solid (45%) mp 127.2-128.3 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.51 (2H, s, CH_2), 7.25-7.47 (10H, m, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 62.2, 127.8, 128.4, 128.9, 129.0, 129.2, 129.9, 131.5, 134.0 (two signals), 143.1, 150.2, 164.2. FTIR: 3058 (w), 3033 (w), 2964 (w), 1714 (w), 1623 (s), 1549 (s), 1510 (w), 1489 (m), 1454 (m), 1442 (m), 1403 (m), 1326 (m), 1306 (m), 1249 (m), 1201 (m), 1168 (s), 1090 (m), 1029 (w) cm^{-1}. HRMS calcd for $C_{17}H_{12}N_2OCl_2$: 330.0327. Found: 330.0317.



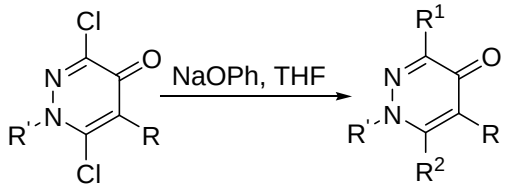
1-Benzyl-5-butyl-3,6-dichloropyridazin-4(1H)-one (9) R'X = BnBr, isolated as a light yellow solid (70%) mp 79.3-80.2 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.80-0.91

(3H, t, J = 7.0 Hz, CH_3), 1.20-1.50 (4H, m, CH_2), 2.54-2.65 (2H, t, J = 7.5 Hz, CH_2), 5.42 (2H, s, CH_2), 7.18-7.38 (5H, m, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 13.8, 22.6, 27.3, 29.2, 61.9, 127.6, 128.8, 129.0, 130.4, 134.1, 142.8, 148.0, 164.8. FTIR: 3031 (w), 2958 (m), 2930 (m), 2871 (m), 1625 (s), 1552 (s), 1497 (m), 1454 (m), 1440 (m), 1415 (m), 1376 (w), 1354 (w), 1332 (w), 1284 (m), 1257 (m), 1219 (m), 1183 (m), 1164 (m), 1093 (w), 1080 (w) cm^{-1}. HRMS calcd for $C_{15}H_{17}N_2OCl_2$ [M+H] : 311.0718. Found: 311.0709.



3,6-Dichloro-1-methyl-5-phenylpyridazin-4(1H)-one (10) R'X = MeI, isolated as a colourless solid (84%) mp 169.2-170.4 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.04 (3H, s, CH_3), 7.21-7.50 (5H, m, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 46.8, 128.4, 128.8, 129.9, 131.5 (2 signals), 143.6, 149.8, 164.1. FTIR: 3058 (w), 2939 (w), 1620 (s), 1550 (m), 1506 (w), 1488 (w), 1459 (w), 1444 (w), 1421 (w), 1389 (w), 1317 (m), 1237 (m), 1213 (s), 1122 (s), 1068 (w), 1022 (w) cm^{-1}. HRMS calcd for $C_{11}H_8N_2OCl_2$: 254.0014. Found: 254.0025.

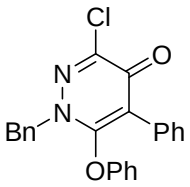
Substitution reactions of dichloropyridazinones with sodium phenoxide



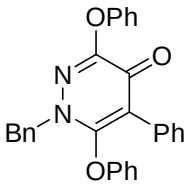
Typical procedure: To a solution of phenol (1.2 eq) in THF (~0.1 $molL^{-1}$) at 0 ^{o}C was added a 60% sodium hydride emulsion in paraffin oil (1.2 eq). The reaction was stirred at 0 ^{o}C for 30 minutes and then allowed to warm to room temperature before a solution of the dichloropyridazinone (1 eq) in THF (~0.1 $molL^{-1}$) was added. Reactions were followed by TLC and upon completion were quenched with water, extracted three times with dichloromethane and the combined organic fractions dried

over magnesium sulphate. The volatiles were removed in vacuo and crude materials purified by chromatography on silica gel.

Reaction of 1-benzyl-3,6-dichloro-5-phenylpyridazin-4(1H)-one (8)

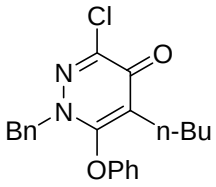


1-Benzyl-3-chloro-6-phenoxy-5-phenylpyridazin-4(1H)-one (11a) heated at 40 ^{o}C for 24h, isolated as a light yellow solid (77%) mp 142.9-143.4 ^{o}C. ^{1}H NMR (250 Hz, $CDCl_3$): δ 5.27 (2H, s, CH_2), 6.51-6.58 (2H, m, CH), 6.86-6.95 (1H, m, CH), 7.00-7.34 (12H, m, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 57.6, 115.6, 119.6, 121.5, 123.8, 125.1, 127.8, 128.7, 129.3, 129.6, 130.2, 134.6, 153.3, 153.4, 154.7, 158.3, 164.9. FTIR: 3061 (w), 3024 (w), 1621 (s), 1563 (s), 1512 (w), 1490 (s), 1455 (m), 1440 (m), 1425 (m), 1331 (w), 1312 (w), 1249 (s), 1193 (m), 1165 (w), 1093 (w), 1073 (w), 1024 (w) cm^{-1}. HRMS calcd for $C_{23}H_{17}N_2O_2Cl$: 388.0979. Found 388.0986.

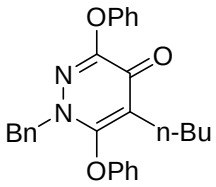


1-benzyl-3,6-diphenoxy-5-phenylpyridazin-4(1H)-one heated at 40 ^{o}C for 24h, isolated as a colourless solid (16%) mp 205.3-206.0 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.93 (2H, s, CH_2), 6.52-6.58 (2H, m, CH), 6.82-6.90 (1H, m, CH), 6.98-7.40 (17H, m, CH). ^{13}C NMR (250 MHz, $CDCl_3$): δ 57.6, 115.7, 119.7, 121.5, 123.8, 125.2, 127.8, 127.9, 128.6, 128.7, 128.8, 129.3, 129.6, 130.2, 134.6, 153.4, 153.5, 154.7, 158.4, 165.0. (One signal missing, unclear where the coalescence is occurring). FTIR: 3050 (w), 2919 (w), 1621 (s), 1589 (m), 1568 (m), 1545 (s), 1490 (s), 1468 (m), 1452 (m), 1439 (m), 1321 (s), 1254 (w), 1192 (s), 1164 (m), 1100 (w) cm^{-1}. HRMS calcd for $C_{29}H_{22}N_2O_3$: 446.1630. Found: 446.1641.

Reaction of 1-benzyl-5-butyl-3,6-dichloropyridazin-4(1H)-one (9)

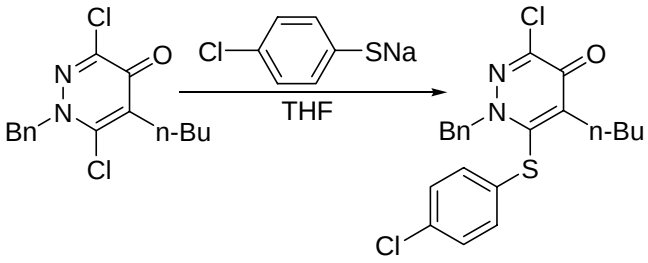


1-Benzyl-5-butyl-3-chloro-6-phenoxypyridazin-4(1H)-one (12a) heated at 40 ^{o}C for 16h, isolated as a colourless oil (70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.71-0.76 (3H, t, *J* = 7.5Hz, CH_3), 1.10-1.20 (2H, m, CH_2), 1.27-1.35 (2H, m, CH_2), 2.26-2.32 (2H, t, *J* = 8.0Hz, CH_2), 5.14 (2H, s, CH_2), 6.75-6.80 (2H, m, CH), 7.10-7.15 (1H, m, CH), 7.16-7.21 (2H, m, CH), 7.24-7.33 (5H, m, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 13.6, 22.5, 23.6, 29.1, 58.6, 115.0, 122.4, 124.4, 128.1, 128.6, 128.8, 130.3, 134.3, 148.2, 153.8, 155.1, 168.0. FTIR: 3065 (w), 3035 (w), 2959 (m), 2930 (m), 2872 (m), 1624 (s), 1594 (m), 1575 (s), 1491 (s), 1455 (s), 1379 (w), 1359 (w), 1333 (w), 1290 (m), 1234 (s), 1193 (s), 1166 (m), 1128 (w), 1105 (w), 1076 (w), 1057 (w), 1024 (w), 1004 (w), 926 (m) cm^{-1}. HRMS calcd for $C_{21}H_{21}N_2O_2Cl$: 368.1292. Found: 368.1281.



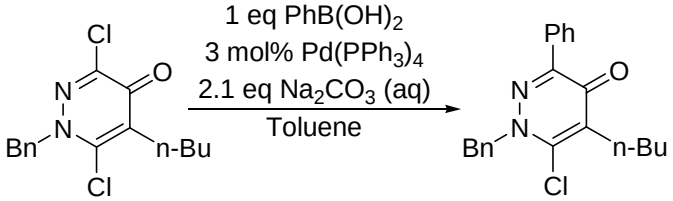
1-Benzyl-5-butyl-3,6-diphenoxypyridazin-4(1H)-one heated at 40 ^{o}C for 16h, isolated as a colourless solid (11%) mp 139.4-140.1 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.65-0.75 (3H, t, *J* = 7.0 Hz, CH_3), 1.05-1.39 (4H, m, CH_2), 2.23-2.33 (2H, t, *J* = 8.0 Hz, CH_2), 4.82 (2H, s, CH_2), 6.73-6.81 (2H, m, CH), 6.92-7.00 (2H, m, CH), 7.03-7.37 (11H, m, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 13.7, 22.6, 23.3, 29.6, 57.4, 115.0, 121.3, 121.6, 124.2, 125.0, 128.4, 128.5, 128.6, 129.3, 130.2, 134.7, 153.1, 153.6, 155.4, 156.9, 166.3. FTIR: 3064 (w), 3031 (w), 2957 (m), 2929 (m), 2860 (w), 1619 (s), 1593 (m), 1572 (s), 1547 (s), 1490 (s), 1471 (m), 1456 (m), 1316 (s), 1253 (m), 1228 (m), 1196 (s), 1164 (m), 1094 (w), 1075 (w) 1024 (m) cm^{-1}. HRMS calcd for $C_{27}H_{26}N_2O_3$: 426.1943. Found: 426.1934.

Substitution of 1-benzyl-5-butyl-3,6-dichloropyridazin-4(1H)-one (9) with a sulphur based nucleophile



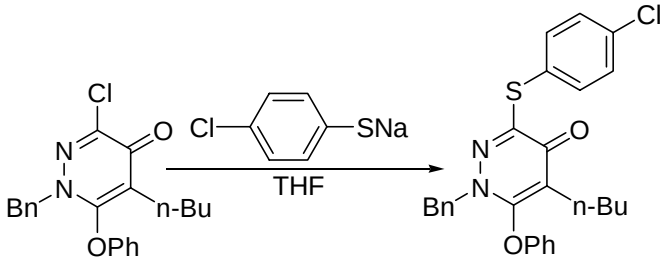
To a solution of 4-chlorobenzenethiol (28 mg, 0.193 mmol) in THF (1 mL) at 0 ^{o}C was added a 60% sodium hydride emulsion in paraffin oil (8 mg, 0.193 mmol). The reaction was stirred at 0 ^{o}C for 30 minutes and then allowed to warm to room temperature before a solution of 1-benzyl-5-butyl-3,6-dichloropyridazin-4(1H)-one **9** (50 mg, 0.161 mmol) in THF (1 mL) was added. The reaction was stirred at room temperature for 30 minutes before being quenched with water, extracted three times with dichloromethane and the combined organic fractions dried over magnesium sulphate. The volatiles were removed in vacuo and crude materials purified by chromatography on silica gel to give pure 1-benzyl-5-butyl-3-chloro-6-(4-chlorophenylthio)pyridazin-4(1H)-one **13a** (65 mg, 96%) as a yellow solid mp 111.0-111.8 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.77-0.87 (3H, t, *J* = 7.0Hz, CH_3), 1.19-1.40 (4H, m, CH_2), 2.64-2.76 (2H, t, *J* = 7.5Hz, CH_2), 5.46 (2H, s, CH_2), 6.83-6.93 (2H, m, CH), 7.09-7.31 (7H, m, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 13.8, 22.9, 28.8, 30.2, 62.3, 127.6, 128.4, 128.5, 128.9, 130.0, 131.1, 133.7, 135.0, 139.5, 144.3, 148.2, 165.3. FTIR: 3067 (w), 3060 (w), 2957 (m), 2927 (m), 2866 (w), 1619 (s), 1531 (m), 1496 (w), 1476 (m), 1455 (w), 1431 (w), 1392 (w), 1353 (w), 1331 (w), 1283 (w), 1244 (m), 1220 (m), 1283 (m), 1152 (m), 1088 (m), 1010 (m) cm^{-1}. HRMS calcd for $C_{21}H_{21}N_2OSCl_2$ [M+H]: 419.0752. Found 419.0764.

Suzuki reaction of 1-benzyl-5-butyl-3,6-dichloropyridazin-4(1H)-one (9)



To 1-benzyl-5-butyl-3,6-dichloropyridazin-4(1H)-one **9** (50 mg, 0.161 mmol) and tetrakis(triphenylphosphine)palladium(0) (6 mg, 4.82 μmol) in toluene (1 mL) was added sodium carbonate (36 mg, 0.337 mmol) in 0.2 mL water. The reaction was heated at reflux for 24 hours before being quenched with water, extracted three times with dichloromethane and the combined organic fractions dried over magnesium sulphate. The volatiles were removed in vacuo and crude materials purified by chromatography on silica gel to give pure 1-benzyl-5-butyl-6-chloro-3-phenylpyridazin-4(1H)-one **14b** as a colourless oil (35 mg, 62%). ^{1}H NMR (250 Hz, $CDCl_3$): δ 0.88-0.97 (3H, t, *J* = 7.0Hz, CH_3), 1.32-1.59 (4H, m, CH_2), 2.64-2.74 (2H, t, *J* = 7.5Hz, CH_2), 5.57 (2H, s, CH_2), 7.29-7.47 (8H, m, CH), 8.11-8.19 (2H, m, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 13.9, 22.9, 27.0, 29.4, 61.8, 127.6, 128.0, 128.5, 128.9, 129.0, 129.5, 131.9, 133.5, 135.0, 141.7, 151.0, 168.9. FTIR: 3057 (w), 3031 (w), 2957 (m), 2925 (m), 2864 (w), 1611 (s), 1597 (s), 1561 (s), 1496 (m), 1446 (m), 1416 (w), 1357 (w), 1331 (m), 1304 (m), 1243 (w) cm^{-1}. HRMS calcd for $C_{21}H_{21}N_2OCl$: 352.1342. Found: 352.1326.

Substitution of 1-benzyl-5-butyl-3-chloro-6-phenoxypyridazin-4(1H)-one (12a) with a sulphur based nucleophile

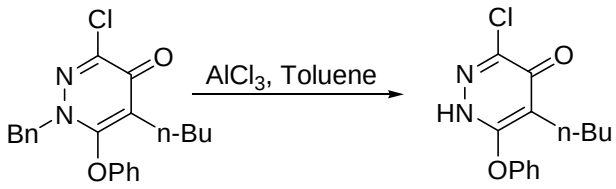


To a solution of 4-chlorobenzenethiol (28 mg, 0.195 mmol) in THF (1 mL) at 0 ^{o}C was added a 60% sodium hydride emulsion in paraffin oil (13 mg, 0.325 mmol). The reaction was stirred at 0 ^{o}C for 30 minutes and then allowed to warm to room temperature before a solution of 1-benzyl-5-butyl-3-chloro-6-phenoxypyridazin-4(1H)-one **12a** (60 mg, 0.163 mmol) in THF (1 mL) was added. The reaction was stirred at room temperature for 7 days before being quenched with water, extracted three times with dichloromethane and the combined organic fractions dried over magnesium sulphate. The volatiles were removed in vacuo and crude materials purified by chromatography on silica gel to give pure 1-benzyl-5-butyl-3-(4-

chlorophenylthio)-6-phenoxypyridazin-4(1H)-one **15** (42 mg, 54 %) and recovered 1-benzyl-5-butyl-3-chloro-6-phenoxypyridazin-4(1H)-one **12a** (20 mg, 33%).

1-Benzyl-5-butyl-3-(4-chlorophenylthio)-6-phenoxypyridazin-4(1H)-one (15) isolated as a yellow solid mp 146.5-148.1 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.70-0.82 (1H, t, *J* = 7.5Hz, CH_3), 1.09 -1.44 (4H, m, CH_2), 2.24-2.35 (2H, t, *J* = 7.0Hz, CH_2), 4.88 (2H, s, CH_2), 6.76-6.95 (4H, m, CH), 7.08-7.54 (10H, m, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 13.7, 22.6, 23.0, 29.4, 57.6, 115.1, 117.8, 124.2, 127.5, 128.4, 128.5, 128.7, 129.2, 130.3, 134.5, 135.3, 137.0, 153.4, 155.4, 157.1, 169.7. FTIR: 3057 (w), 2957 (m), 2930 (m), 2862 (w), 1601 (s), 1565 (s), 1490 (m), 1476 (m), 1455 (m), 1389 (w), 1357 (w), 1336 (w), 1306 (w), 1289 (w), 1236 (s), 1195 (m), 1161 (w), 1093 (m), 1072 (w), 1013 (m), 924 (w) cm^{-1}. HRMS calcd for $C_{27}H_{25}N_2O_2SCl$: 476.1325. Found: 476.1322.

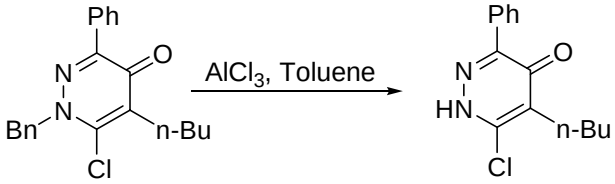
Benzyl deprotection of 1-benzyl-5-butyl-3-chloro-6-phenoxypyridazin-4(1H)-one (12a)



1-Benzyl-5-butyl-3-chloro-6-phenoxypyridazin-4(1H)-one **12a** (117 mg, 0.317 mmol), aluminium trichloride (169 mg, 1.269 mmol) and toluene (10 mL) were heated at 70 ^{o}C for 20 min. The reaction was quenched with water, extracted three times with dichloromethane and the combined organic fractions dried over magnesium sulphate. The volatiles were removed in vacuo and crude materials purified by chromatography on silica gel to give 5-butyl-3-chloro-6-phenoxypyridazin-4(1H)-one (62 mg, 70%) as a colourless solid mp 128.1-128.4 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.79-0.89 (3H, t, *J* = 7.0 Hz, CH_3), 1.18-1.49 (4H, m, CH_2), 2.36-2.54 (2H, t, *J* = 7.5 Hz, CH_2), 6.94-7.02 (2H, m, CH), 7.10-7.19 (1H, m, CH), 7.28-7.38 (2H, m, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 12.4, 21.2, 21.4, 28.2, 116.5, 118.3, 123.7, 128.8, 146.0, 153.2, 156.4, 163.6. FTIR: 3168 (br), 3049 (w), 3007 (w), 2959 (m), 2929 (m), 2861 (m), 2752 (w), 1538 (s), 1489 (s), 1432 (w), 1383

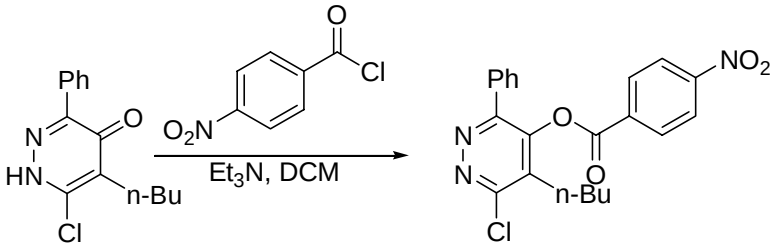
(w), 1357 (w), 1293 (m), 1209 (m), 1197 (m), 1163 (m), 1073 (w), 1023 (w) cm^{-1}. HRMS calcd for $C_{14}H_{15}N_2O_2Cl$: 278.0822. Found: 278.0820.

Benzyl deprotection of 1-benzyl-5-butyl-6-chloro-3-phenylpyridazin-4(1H)-one (14b)



Procedure as previous reaction. 5-butyl-6-chloro-3-phenylpyridazin-4(1H)-one **14b** isolated as a colourless solid (59%) mp 164.3-165.4 ^{o}C. ^{1}H NMR (500 MHz, d^{6}-DMSO): δ 0.89-0.94 (3H, t, *J* = 7.5 Hz, CH_3), 1.30-1.39 (2H, apparent sextet, *J* = 7.5 Hz, CH_2), 1.42-1.50 (2H, m, CH_2), 2.52-2.60 (2H, t, *J* = 7.5 Hz, CH_2), 7.42-7.58 (3H, m, CH), 7.97-8.03 (2H, m, CH), 14.17 (1H, br, NH). ^{13}C NMR (125.8 MHz, d^{6}-DMSO): δ 13.8, 22.1, 25.1, 29.2, 127.8, 128.2, 128.5, 129.2, 133.9, 140.7, 150.5, 168.8. FTIR: 3159 (w), 2964 (w), 2857 (w), 1529 (s), 1443 (m), 1378 (w), 1298 (m), 1272 (w), 1213 (w), 1175 (w), 1090 (m), 1030 (w), 954 (w) cm^{-1}. HRMS calcd for $C_{14}H_{16}N_2OCl$ [M+H]: 263.0951. Found: 263.0951.

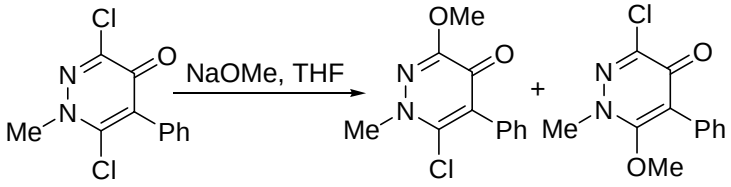
Formation of 5-butyl-6-chloro-3-phenylpyridazin-4-yl 4-nitrobenzoate



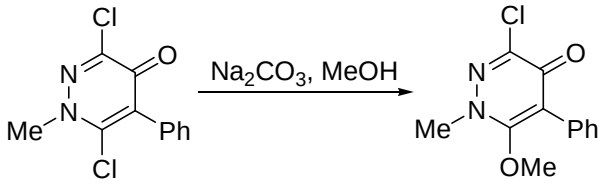
To a suspension of 5-butyl-6-chloro-3-phenylpyridazin-4(1H)-one (55 mg, 0.21 mmol) and 4-nitrobenzoyl chloride (58 mg, 0.31 mmol) in dichloromethane (5 mL) was added triethylamine (58 μL, 0.42 mmol). Upon addition of triethylamine the reaction mixture turned homogeneous and the starting pyridazinone was completely consumed. The reaction was quenched with water, extracted three times with dichloromethane and the combined organic fractions dried over magnesium sulphate.

The volatiles were removed in vacuo and crude materials purified by chromatography on silica gel to give 5-butyl-6-chloro-3-phenylpyridazin-4-yl 4-nitrobenzoate (85 mg, 98%) as colourless solid mp 155.2-156.0 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.82-0.95 (3H, t, *J* = 7.5 Hz, CH_3), 1.29-1.47 (2H, apparent sextet, *J* = 7.5 Hz, CH_2), 1.53-1.70 (2H, apparent quintet, *J* = 8.0 Hz, CH_2), 2.68-2.83 (2H, t, *J* = 8.0 Hz, CH_2), 7.29-7.41 (3H, m, CH), 7.65-7.74 (2H, m, CH), 8.17 (2H, m, CH), 8.29-8.40 (2H, m, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 13.6, 22.7, 27.0, 29.8, 124.1, 128.6, 128.7, 130.0, 131.3, 132.6, 133.1, 135.2, 147.9, 151.4, 155.9, 157.0, 161.4. FTIR: 3111 (w), 3056 (w), 2960 (m), 2932 (m), 2872 (m), 1755 (s), 1608 (m), 1570 (w), 1531 (s), 1466 (w), 1447 (m), 1397 (m), 1347 (s), 1320 (m), 1257 (s), 1233 (s), 1207 (m), 1152 (w), 1096 (m), 1054 (s), 1013 (m) cm^{-1}. HRMS calcd for $C_{21}H_{19}N_3O_4Cl$ [M+H]: 412.1064. Found: 412.1050.

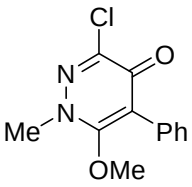
Substitution reactions of 3,6-dichloro-1-methyl-5-phenylpyridazin-4(1H)-one (10)



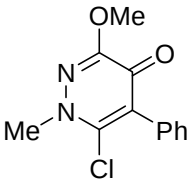
To a solution of methanol (53 μL, 1.3 mmol) in THF (5 mL) at 0 ^{o}C was added a 60% sodium hydride emulsion in paraffin oil (53 mg, 1.3 mmol). The reaction was stirred at 0 ^{o}C for 30 minutes and then allowed to warm to room temperature before a solution of 3,6-dichloro-1-methyl-5-phenylpyridazin-4(1H)-one **10** (280 mg, 1.1 mmol) in THF (10 mL) was added; the reaction was then heated at reflux for 24 hours. The reaction was allowed to cool to room temperature and quenched with water, extracted three times with dichloromethane and the combined organic fractions dried over magnesium sulphate. The volatiles were removed in vacuo and crude materials purified by chromatography on silica gel to give 6-chloro-3-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one **16b** (155 mg, 56%), 3-chloro-6-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one **16a** (74 mg, 27%) and the starting material 3,6-dichloro-1-methyl-5-phenylpyridazin-4(1H)-one **10** (45 mg, 16%).



Methanol (20 mL) was added to a mixture of 3,6-dichloro-1-methyl-5-phenylpyridazin-4(1H)-one **10** (0.314 g, 1.2 mmol) and sodium carbonate (0.196 g, 1.8 mmol) and the reaction was heated at reflux for 2 hours. Upon cooling the reaction was quenched with water, extracted three times with dichloromethane and the combined organic fractions dried over magnesium sulphate. The volatiles were removed in vacuo and crude materials purified by chromatography on silica gel to give 3-chloro-6-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one **16a** (309 mg, 100%).



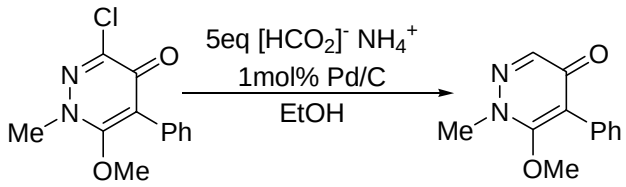
3-Chloro-6-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one (16a) isolated as a colourless solid mp 155.1-155.3 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.51 (3H, s, CH_3), 3.85 (3H, s, CH_3), 7.31-7.51 (5H, m, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 41.9, 61.5, 117.1, 128.4 (2 signals), 130.0, 130.2, 148.8, 159.0, 166.5. FTIR: 3055 (m), 2951 (m), 1613 (s), 1563 (s), 1509 (s), 1495 (s), 1477 (m), 1445 (m), 1422 (m), 1400 (m), 1325 (s), 1264 (s), 1160 (m), 1102 (m), 1073 (w), 1046 (w), 1026 (m), 959 (s) cm^{-1}. HRMS calcd for $C_{12}H_{11}N_2O_2Cl$: 250.0509. Found: 250.0517.



6-Chloro-3-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one (16b) isolated as a colourless solid mp 178.9-179.8 ^{o}C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.91 (3H, s, CH_3), 3.96 (3H, s, CH_3), 7.23-7.46 (5H, m, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 46.1, 54.9, 126.2, 128.2, 128.3, 130.3, 132.5, 142.5, 158.6, 162.8. FTIR: 3057 (w), 3031 (w) 2975 (w), 2942 (w), 2852 (w), 1610 (s), 1579 (m), 1563 (s), 1542 (s), 1496 (m),

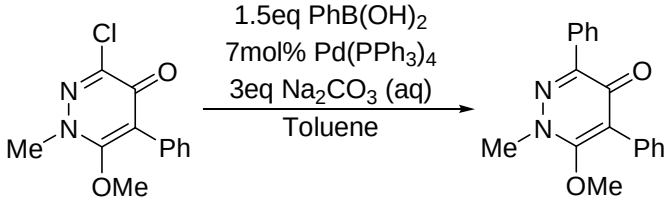
1457 (m), 1401 (m), 1341 (s), 1333 (s), 1280 (m), 1238 (w), 1202 (m), 1157 (m), 1124 (w), 1087 (m), 1074 (w), 1048 (m), 1027 (w), 982 (m) cm^{-1}. HRMS calcd for $C_{12}H_{12}N_2O_2Cl$ [M+H]: 251.0587. Found: 251.0596.

Palladium catalysed dehalogenation reaction of 3-chloro-6-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one (15a)



To 3-chloro-6-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one **16a** (100 mg, 0.399 mmol), ammonium formate (126 mg, 1.99 mmol) and 10% palladium supported on carbon (4 mg, 3.99 μmol) was added ethanol (3 mL). The reaction was heated at reflux for 4 hours until complete conversion was observed by TLC. After cooling to room temperature the 10% palladium supported on carbon was removed by filtration through a pad of celite and the crude products purified on silica gel to give 6-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one (85 mg, 99%) as colourless oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.48 (3H, s, CH_3), 3.82 (3H, s, CH_3), 7.28-7.50 (5H, m, CH), 7.84 (1H, s, CH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 41.6, 61.2, 107.5, 118.0, 128.1, 128.4, 130.1, 147.4, 159.0, 172.2. FTIR: 3042 (w), 2950 (w), 1609 (s), 1593 (s), 1517 (m), 1496 (m), 1474 (m), 1439 (w), 1420 (m), 1328 (m), 1307 (m), 1247 (m), 1159 (m) cm^{-1}. HRMS calcd for $C_{12}H_{12}N_2O_2$: 216.0899. Found: 216.0888.

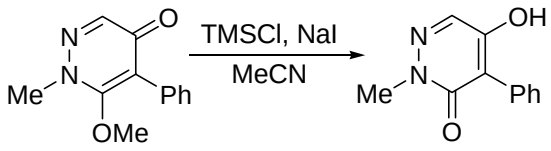
Suzuki cross coupling of 3-chloro-6-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one (15a)



To 3-chloro-6-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one **16a** (50 mg, 0.199 mmol) and tetrakis(triphenylphosphine)palladium(0) (6 mg, 4.99 μmol) in toluene (2 mL) was added sodium carbonate (63 mg, 0.598 mmol) in 0.2 mL water. The reaction

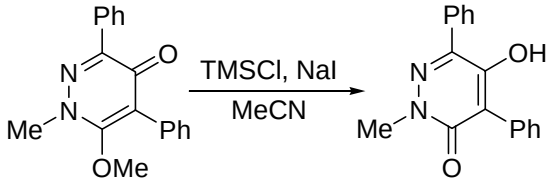
was heated at reflux for 3 days before being quenched with water, extracted three times with dichloromethane and the combined organic fractions dried over magnesium sulphate. The volatiles were removed in vacuo and crude materials purified by chromatography on silica gel to give 6-methoxy-1-methyl-3,5-diphenylpyridazin-4(1H)-one (41 mg, 71%) as a yellow solid mp 126.8 ^{o}C (dec). ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.54 (3H, s, CH_3), 3.93 (3H, s, CH_3), 7.30-7.49 (6H, m, CH), 7.50-7.58 (2H, m, CH), 8.07-8.16 (2H, m, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 42.6, 61.9, 119.0, 128.7, 128.8, 129.1, 129.6, 130.0, 131.2, 131.6, 134.9, 153.6, 158.9, 171.5. FTIR: 3056 (w), 1248 (w), 1637 (w), 1604 (s), 1583 (s), 1569 (s), 1492 (s), 1476 (m), 1444 (m), 1422 (m), 1327 (s), 1308 (s), 1254 (w), 1207 (m), 1158 (m), 1077 (w), 1061 (w), 1026 (w), 957 (m) cm^{-1}. HRMS calcd for $C_{18}H_{16}N_2O_2$: 292.1212. Found 292.1208.

Demethylation of 6-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one



To 6-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one (50 mg, 0.231 mmol) and sodium iodide (42 mg, 0.277 mmol) in acetonitrile (1 mL) was added chlorotrimethylsilane (35 μL, 0.277 mmol). After stirring for 30 minutes the reaction was quenched with brine and extracted three times with dichloromethane and the combined organic fractions dried over magnesium sulphate. The volatiles were removed in vacuo to give analytically pure 5-hydroxy-2-methyl-4-phenylpyridazin-3(2H)-one[4] **17** (42 mg, 90%) as a colourless solid mp 230.1 (dec). ^{1}H NMR (250 MHz, d^{6}-DMSO): δ 3.62 (3H, s, CH_3), 7.26-7.51 (5H, m, CH), 7.79 (1H, s, CH), 11.10 (1H, s, OH). ^{13}C NMR (125 MHz, d^{6}-DMSO): δ 39.5, 116.8, 127.4 (2 signals), 130.3, 131.3, 131.8,154.2, 160.6. FTIR: 3053 (m), 2928 (br), 2664 (w), 1615 (s), 1567 (s), 1404 (m), 1369 (s), 1311 (m), 1150 (m), 1058 (m) cm^{-1}. HRMS calcd for $C_{11}H_{10}N_2O_2$: 202.0742. Found: 202.0752.

Demethylation of 6-methoxy-1-methyl-3,5-diphenylpyridazin-4(1H)-one



To 6-methoxy-1-methyl-3,5-diphenylpyridazin-4(1H)-one (30 mg, 0.103 mmol) and sodium iodide (18 mg, 0.123 mmol) in acetonitrile (0.5 mL) was added chlorotrimethylsilane (16 μL, 0.123 mmol). After stirring for 24 hours the reaction was quenched with water, extracted three times with dichloromethane and the combined organic fractions dried over magnesium sulphate. The volatiles were removed in vacuo and crude materials purified by chromatography on silica gel to give 5-hydroxy-2-methyl-4,6-diphenylpyridazin-3(2H)-one **18** (28mg, 98%) as a colourless solid mp 226.5 (dec). ^{1}H NMR (250 Hz, $CDCl_3$): δ 3.84 (3H, s, CH_3), 6.25 (1H, s, OH), 7.37-7.59 (8H, m, CH), 7.71-7.80 (2H, m, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.5, 119.8, 128.2, 128.5 (2 signals), 129.1, 129.4, 131.1, 131.8, 134.6, 142.1, 153.1, 160.8. FTIR: 3359 (w), 3189 (w), 3053 (w), 2920 (m), 2850 (m), 1729 (m), 1617 (s), 1561 (s), 1520 (w), 1407 (w), 1464 (w), 1440 (w), 1423 (m), 1342 (m), 1300 (m), 1276 (s), 1187 (s), 1156 (w), 1079 (w) cm^{-1}. HRMS calcd for $C_{17}H_{14}N_2O_2$: 278.1055. Found: 278.1065.

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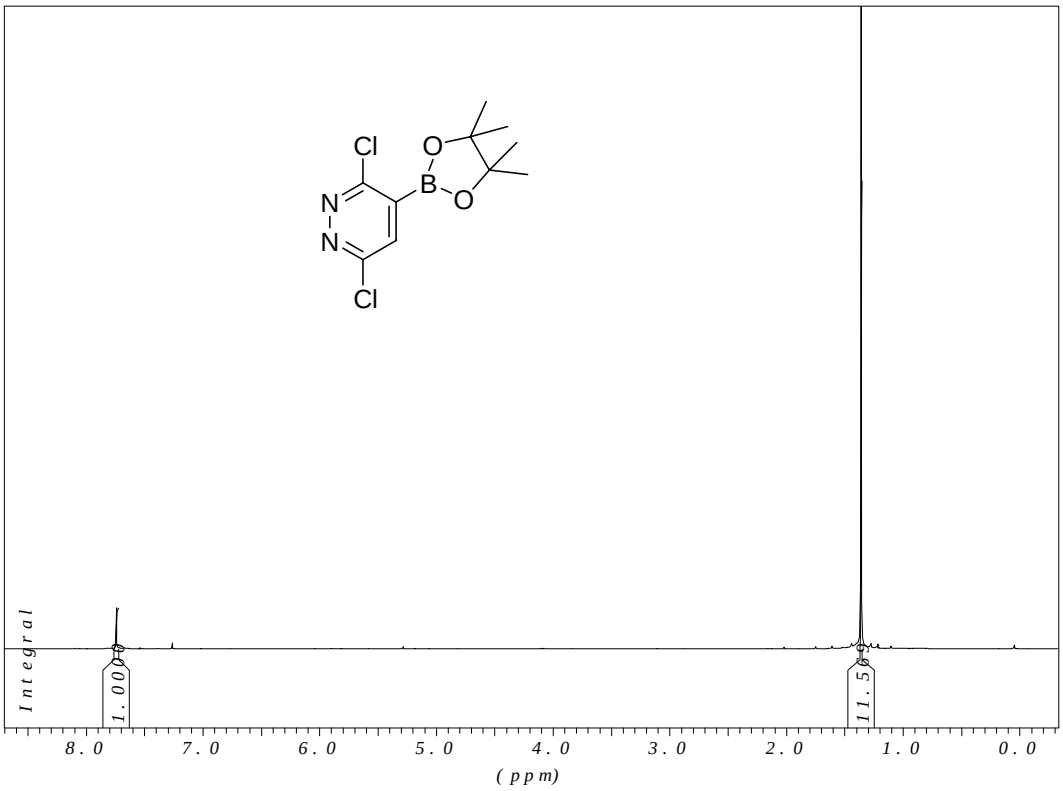
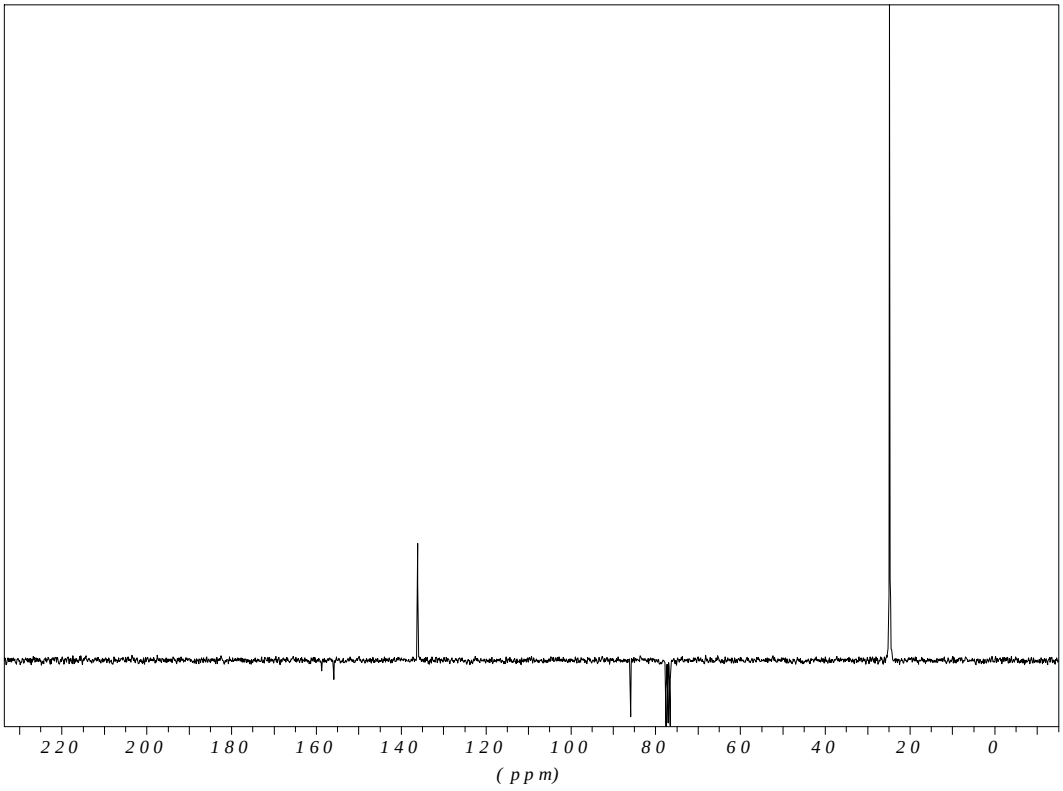
2) M. H. V. Huynth, M. A. Hiskey, J. G. Archuleta, E. L. Roemer, R. Gilardi *Angew. Chem. Int. Ed.* **2004**, *43*, 5658-5661.

3) S. C. Benson, L. Lee, L. Yang, J. K. Snyder *Tetrahedron* **2000**¸ *56*, 1165-1180.

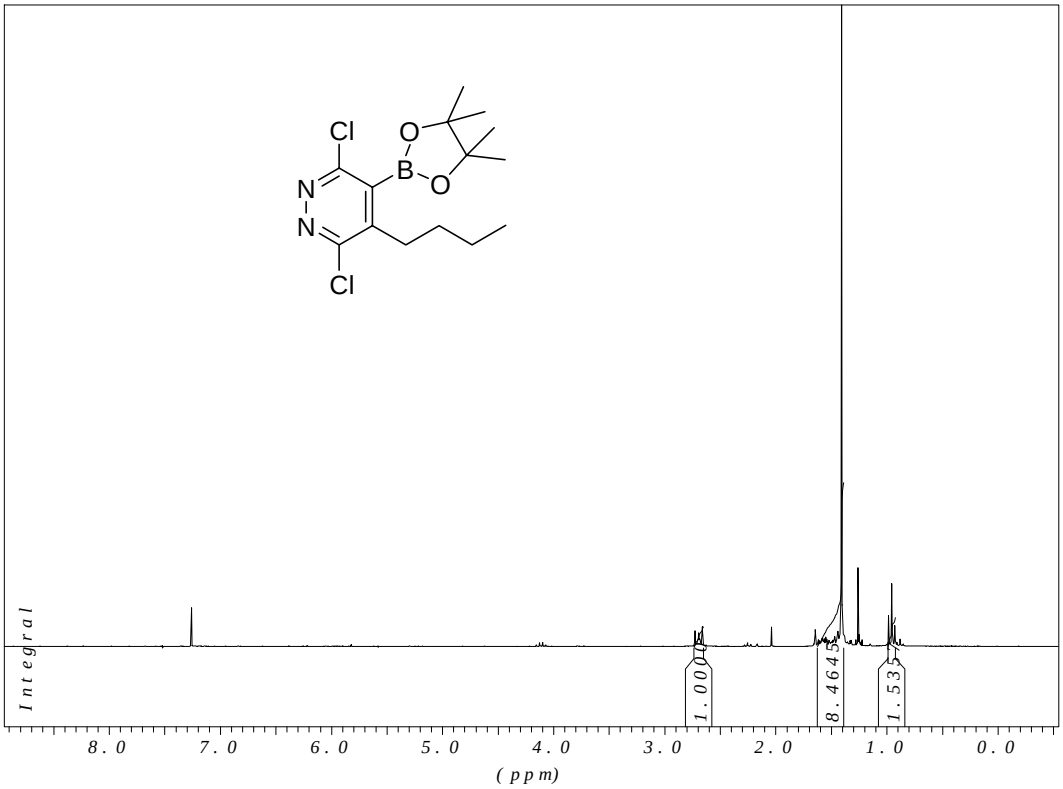
4) B. U. W. Maes, K. Monsieurs, K. T. J. Loones, G. L. F. Lemière, R. Dommisse, P. Mátyus, Z. Riedl, G. Hajós *Tetrahedron* **2002**, *58*, 9713-9721.

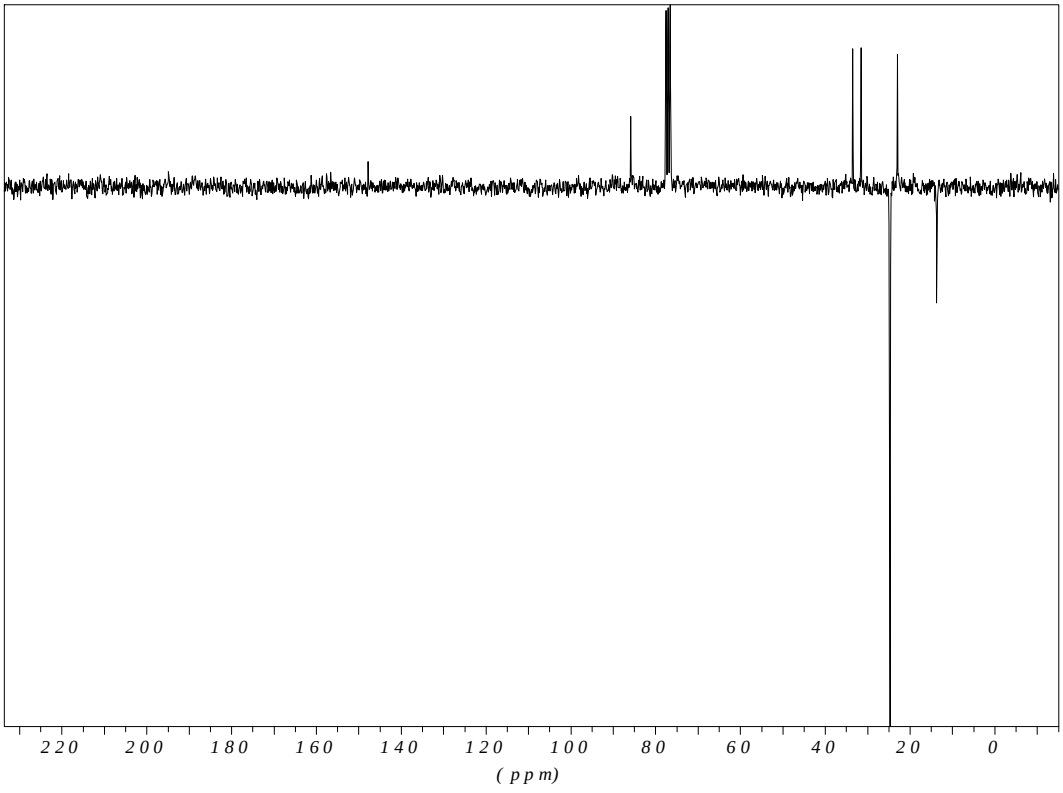
3,6-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridazine (6a)



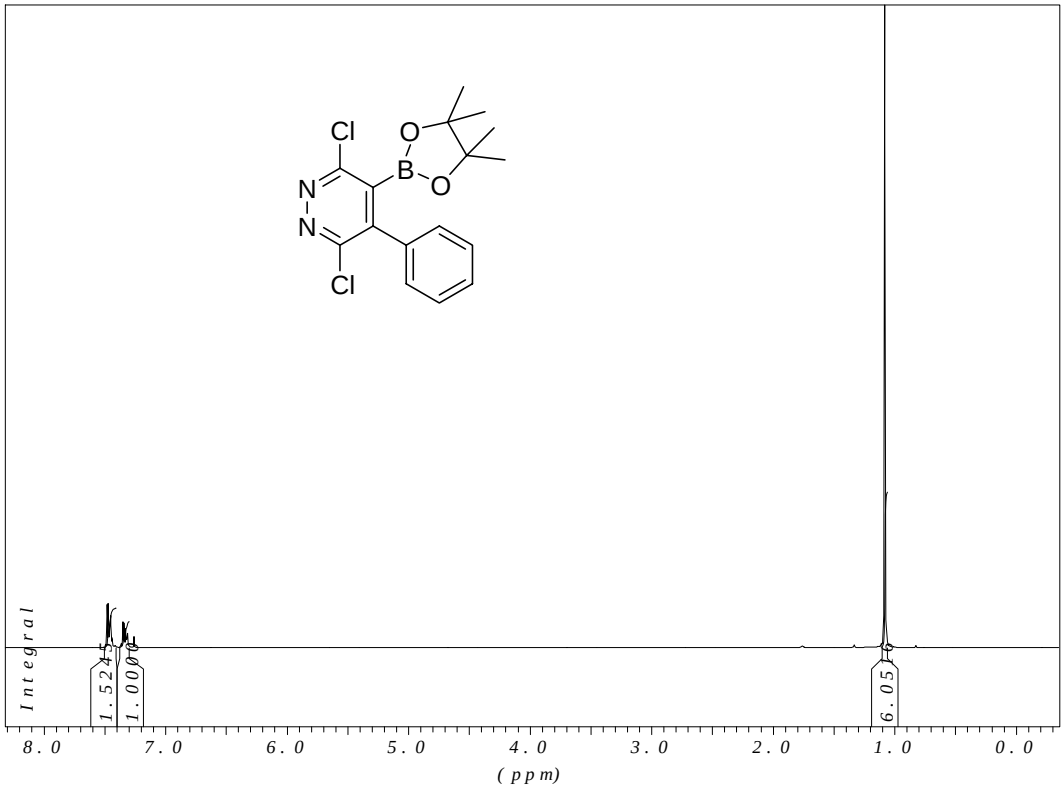


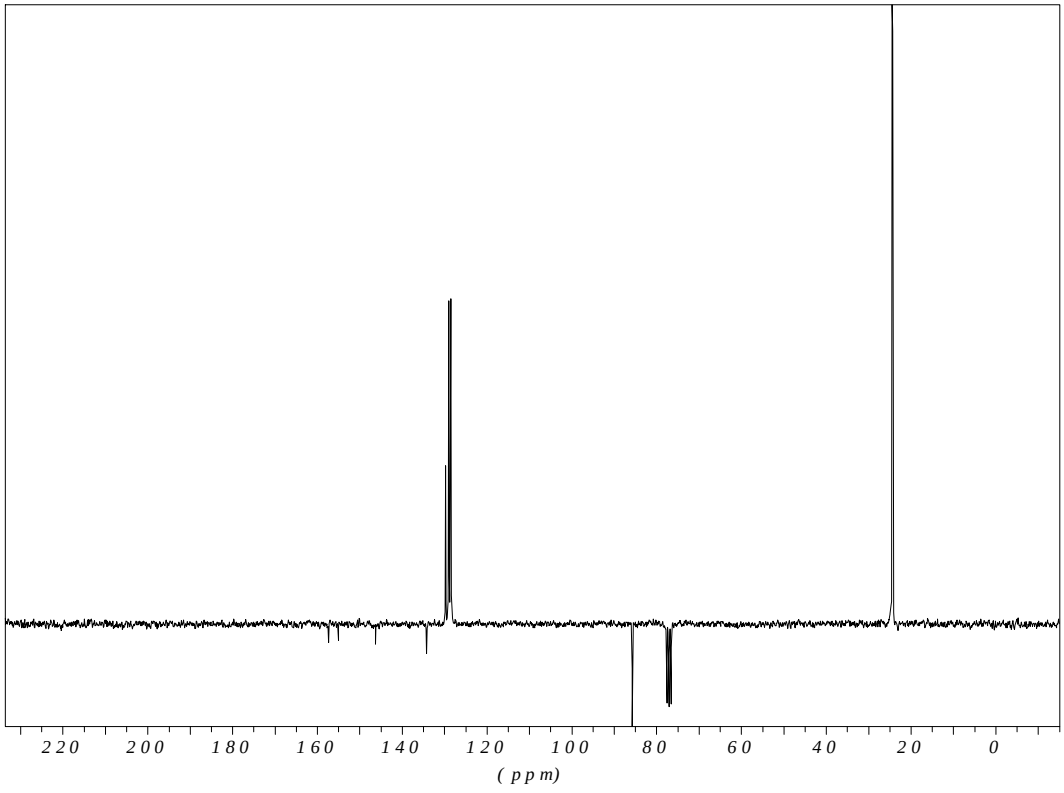
4-Butyl-3,6-dichloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridazine (6b)



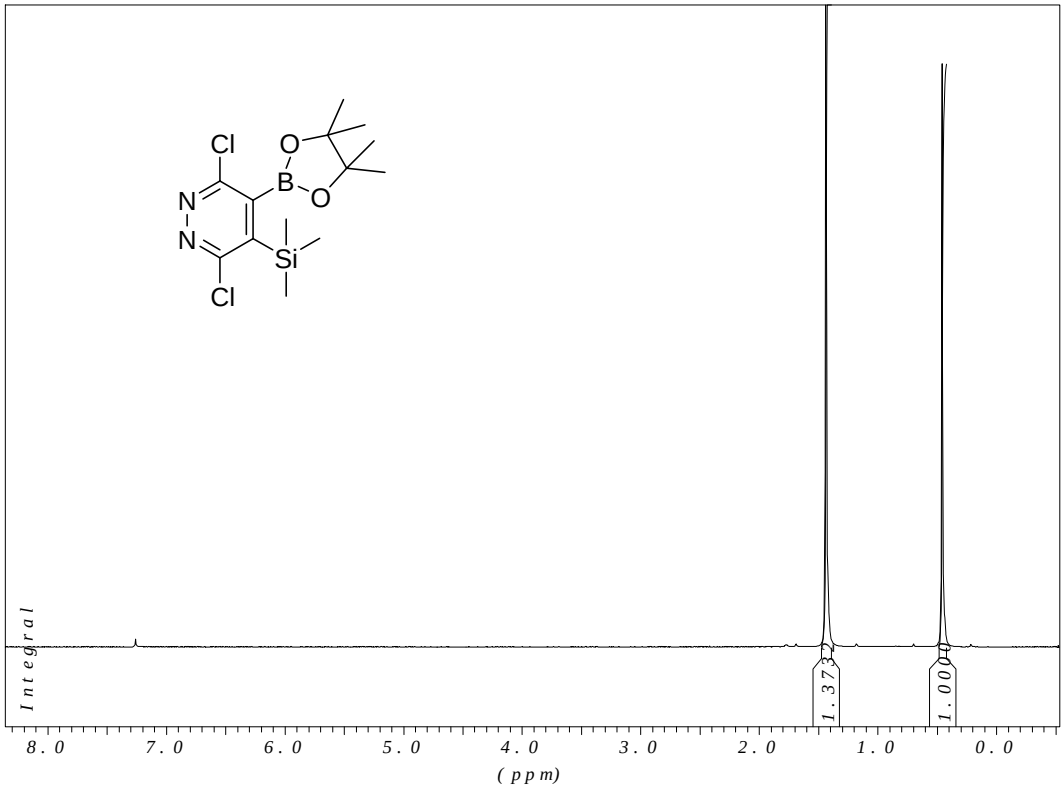


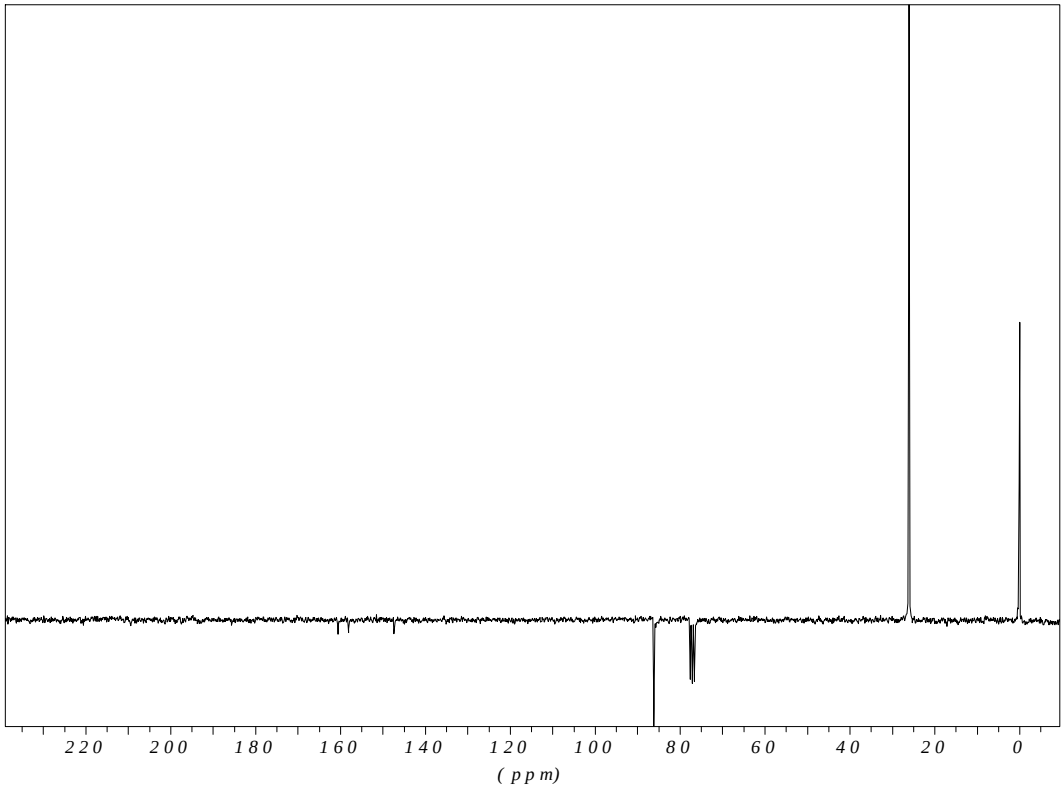
3,6-Dichloro-4-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridazine (6c)



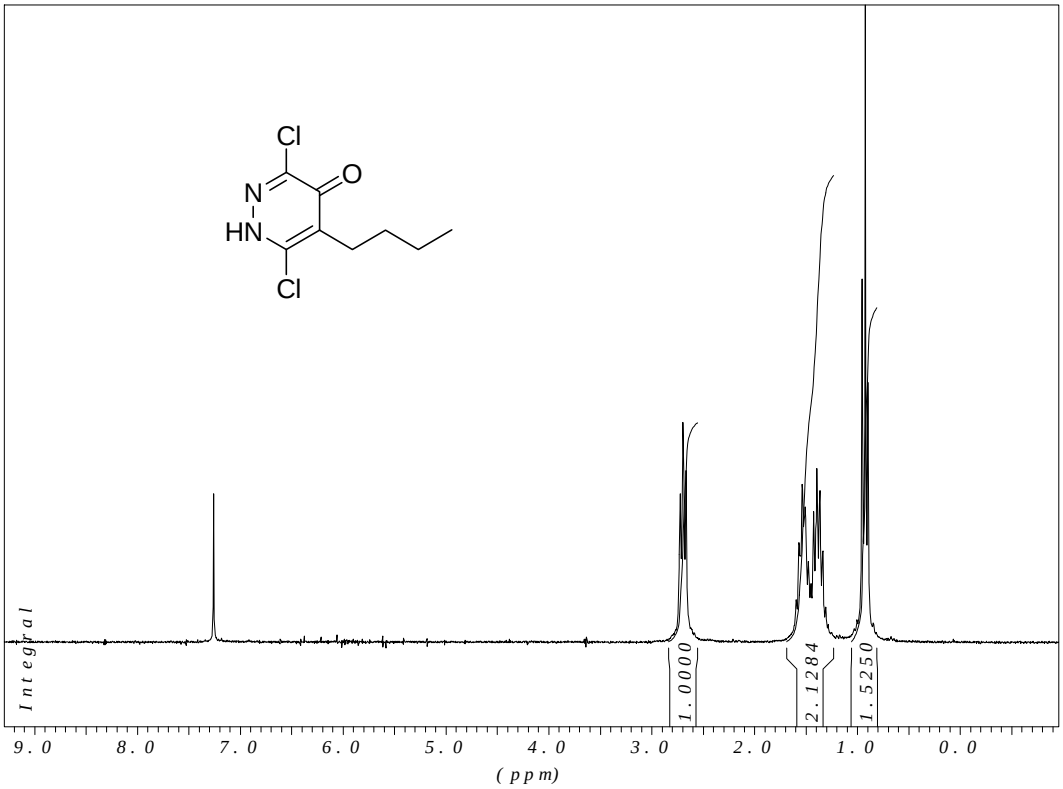


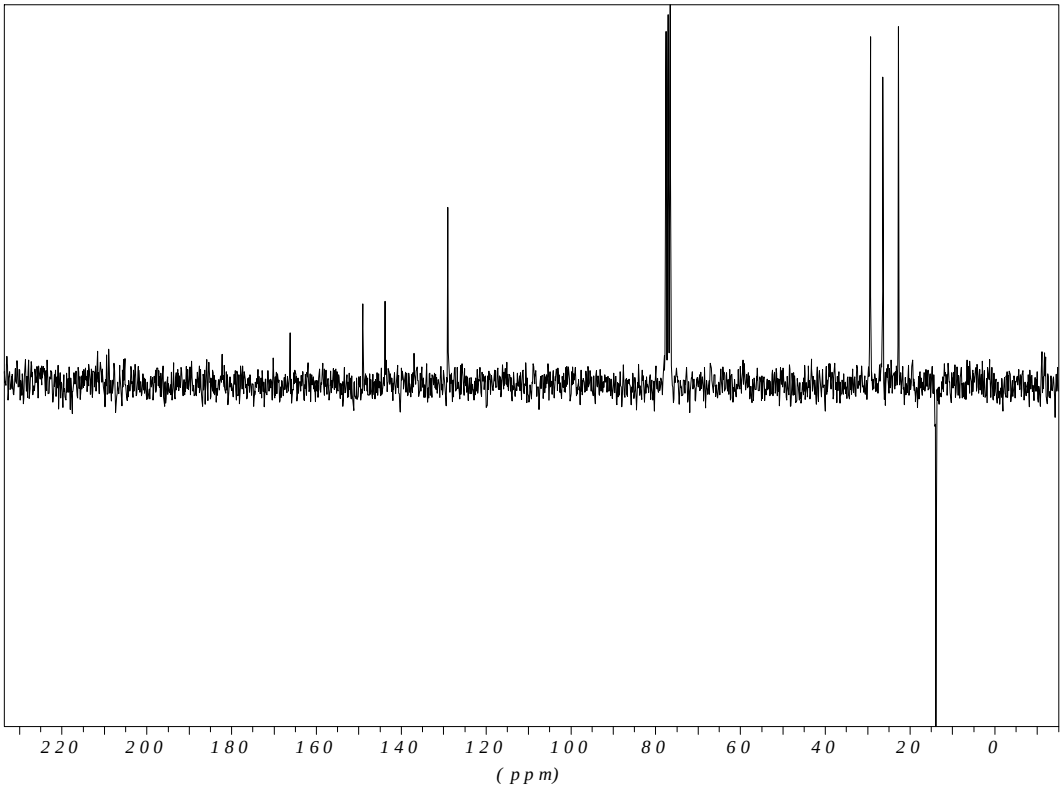
3,6-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)pyridazine (6d)



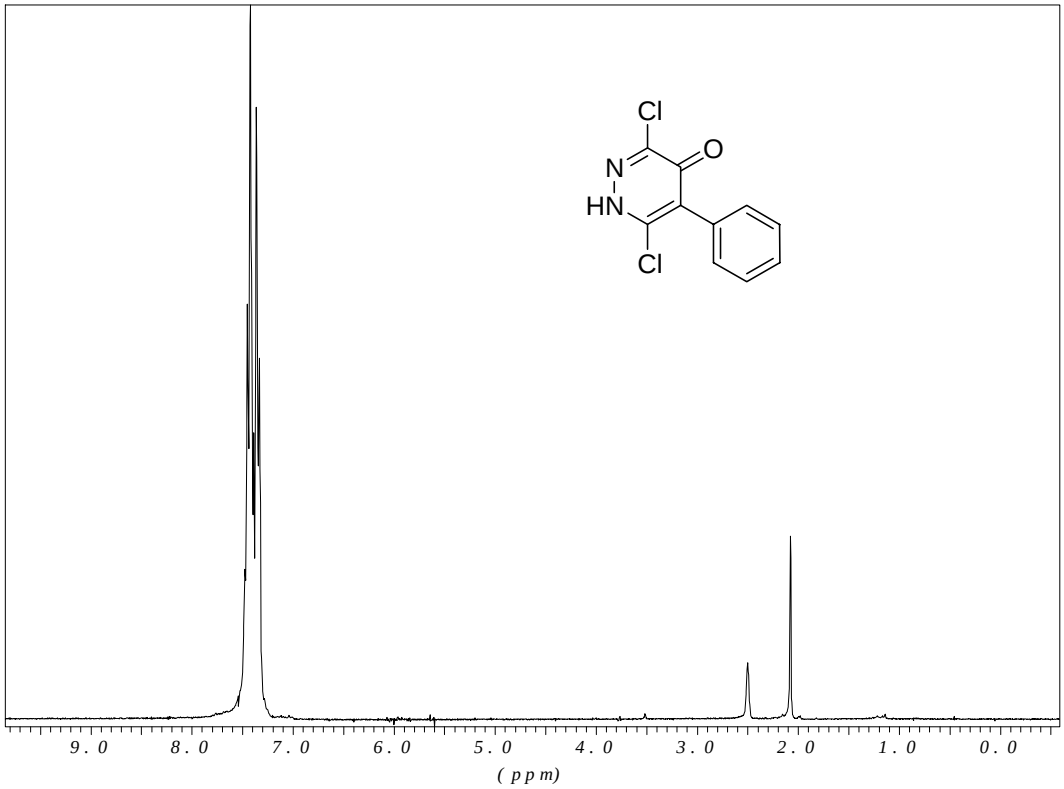


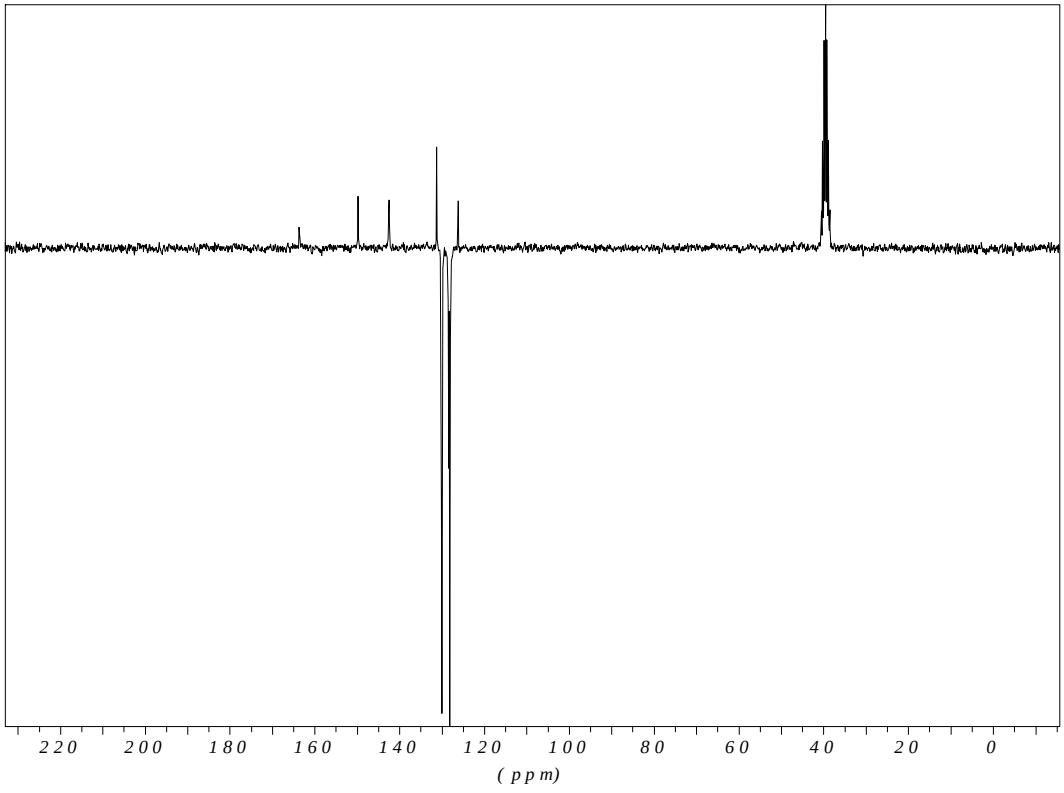
5-Butyl-3,6-dichloropyridazin-4(1H)-one (7a)



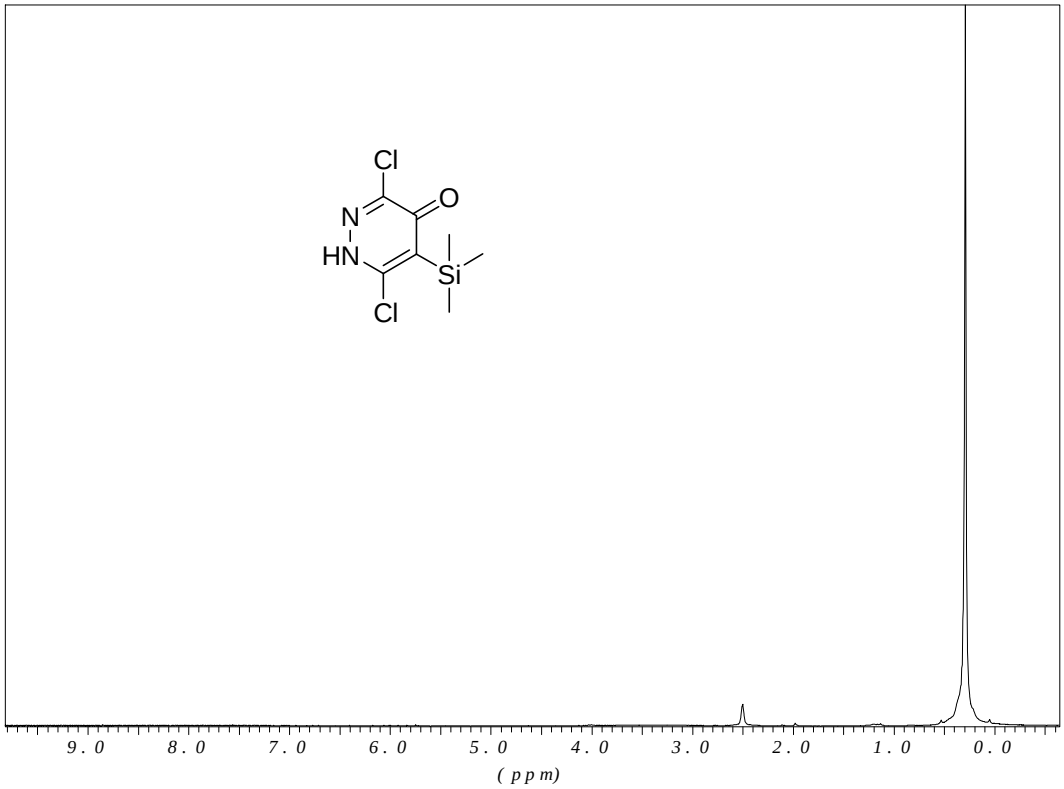


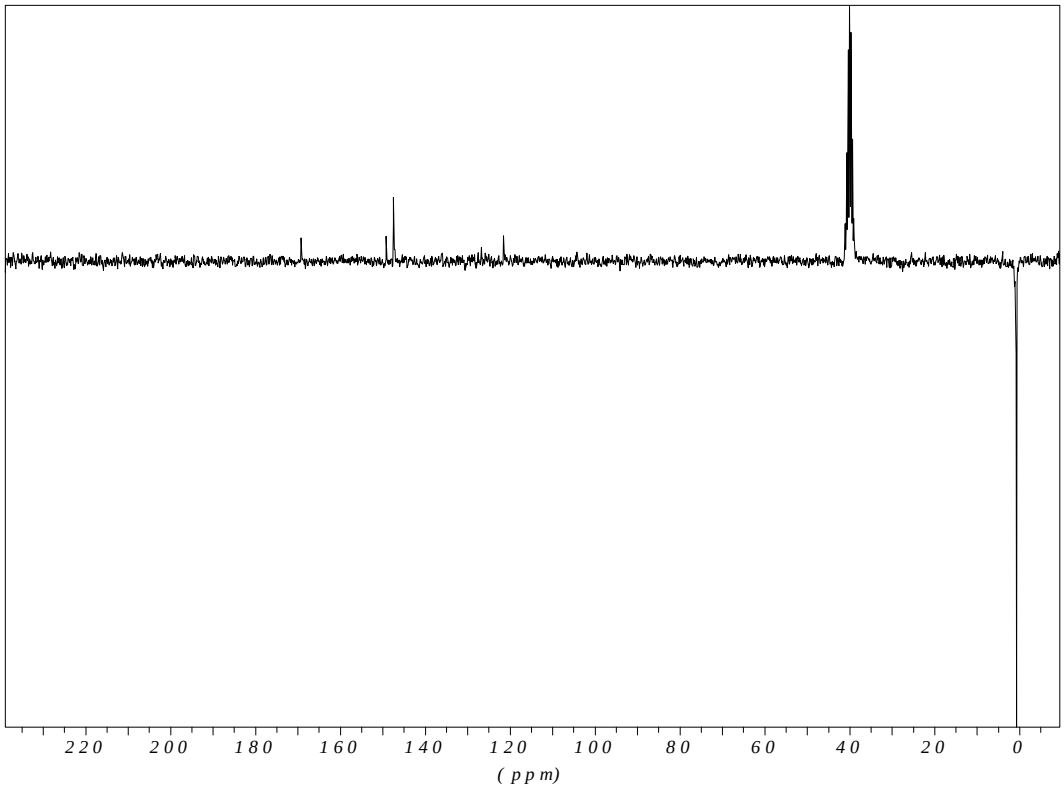
3,6-Dichloro-5-phenylpyridazin-4(1H)-one (7b)



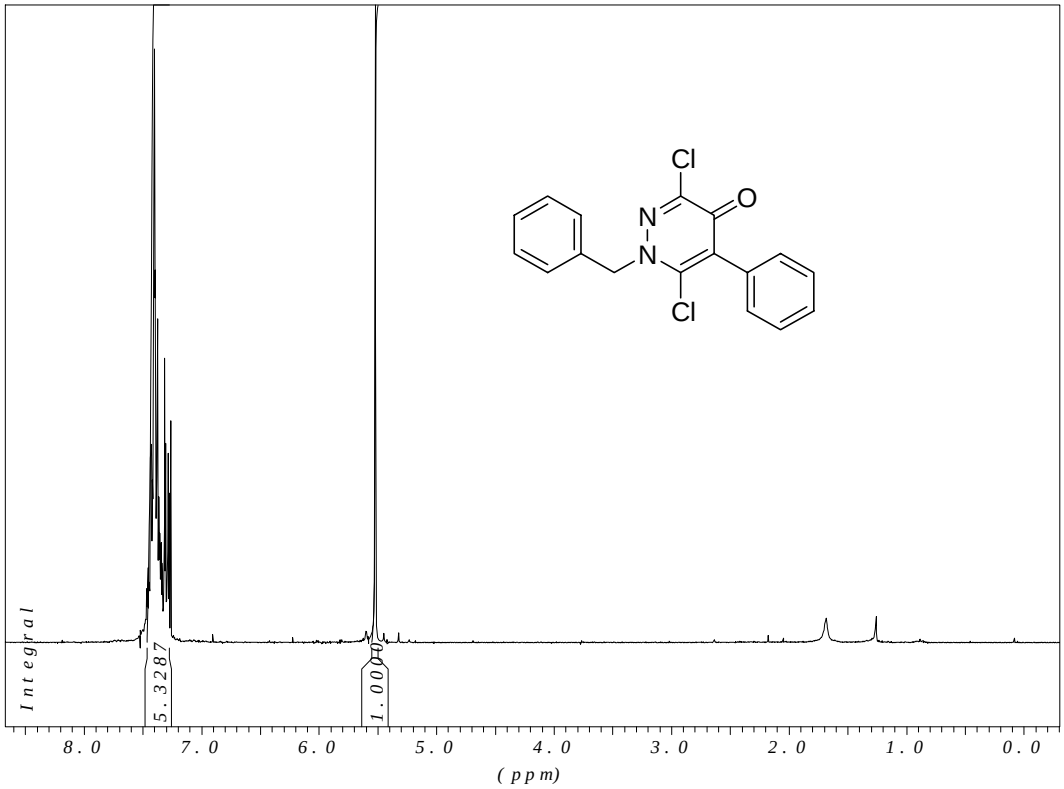


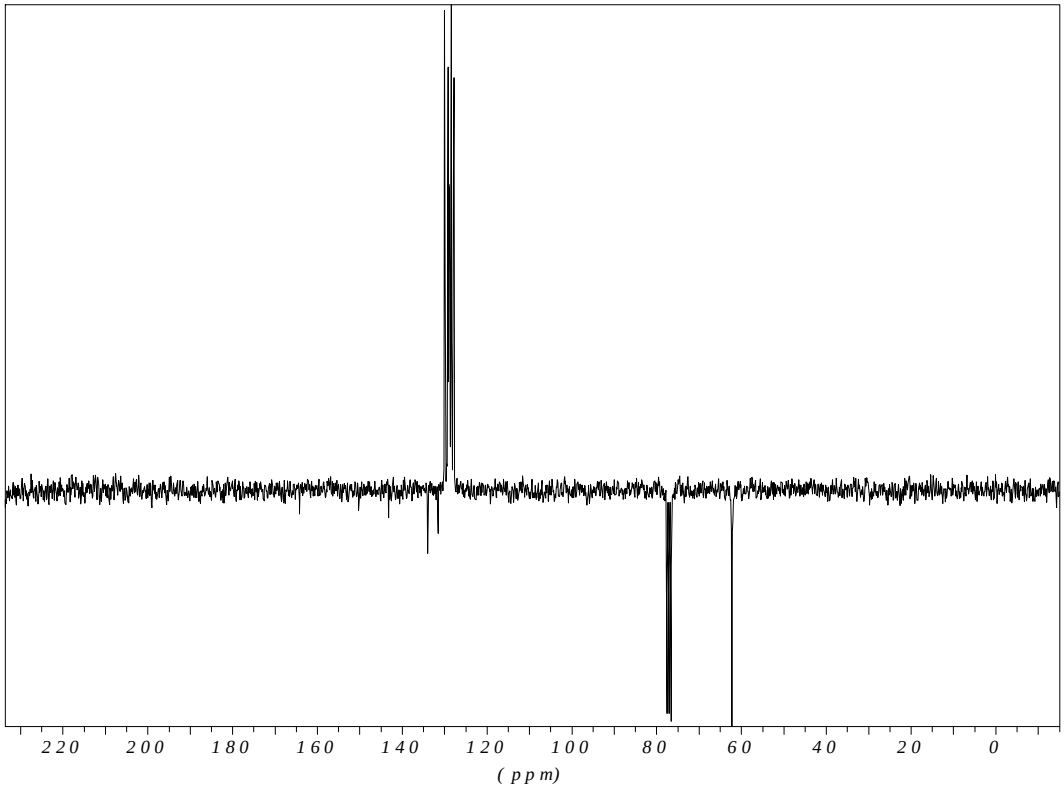
3,6-Dichloro-5-(trimethylsilyl)pyridazin-4(1H)-one (7c)



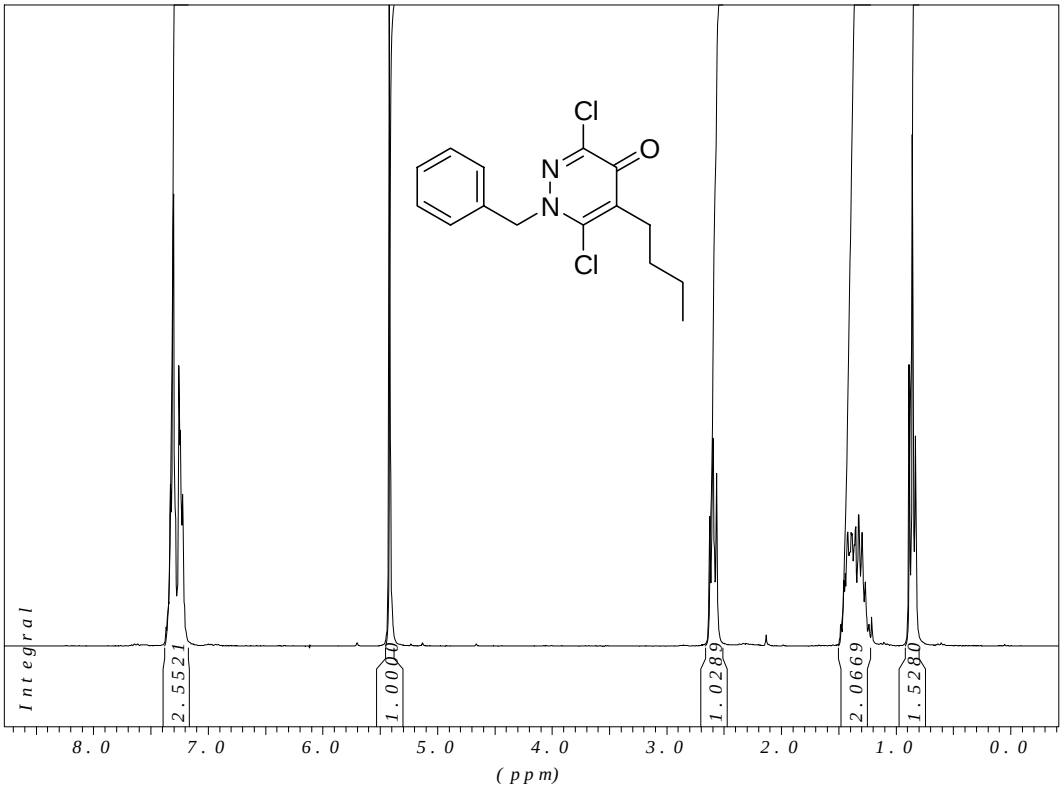


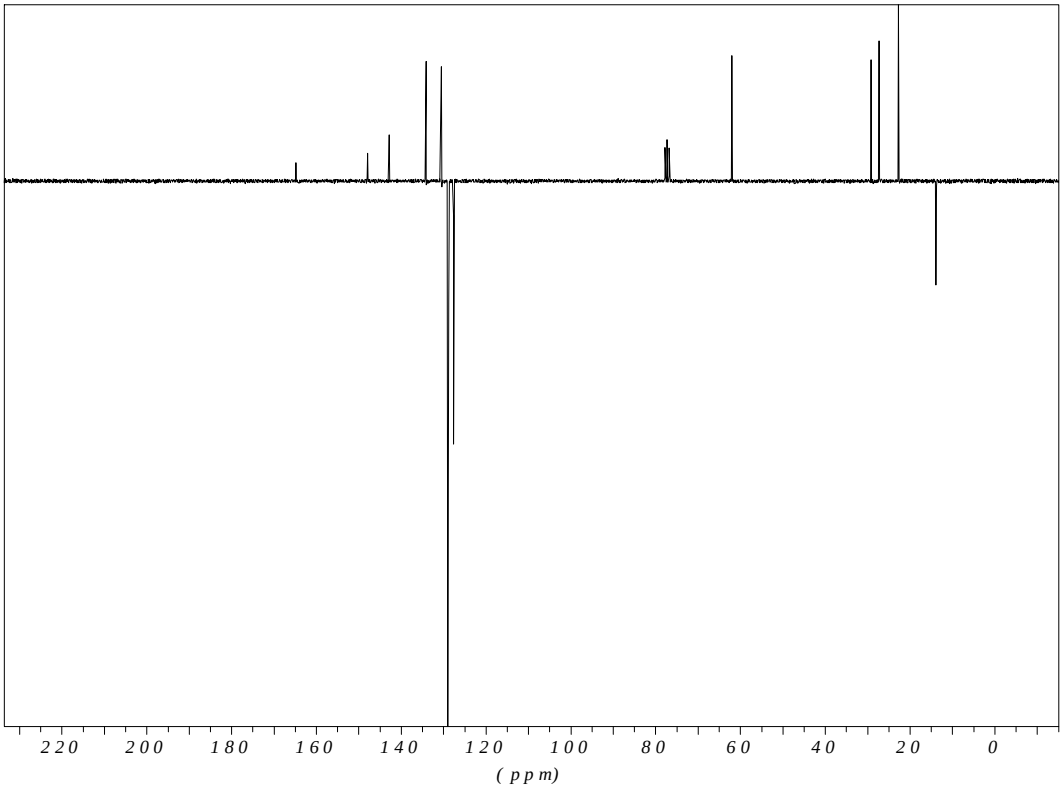
1-Benzyl-3,6-dichloro-5-phenylpyridazin-4(1H)-one (8)



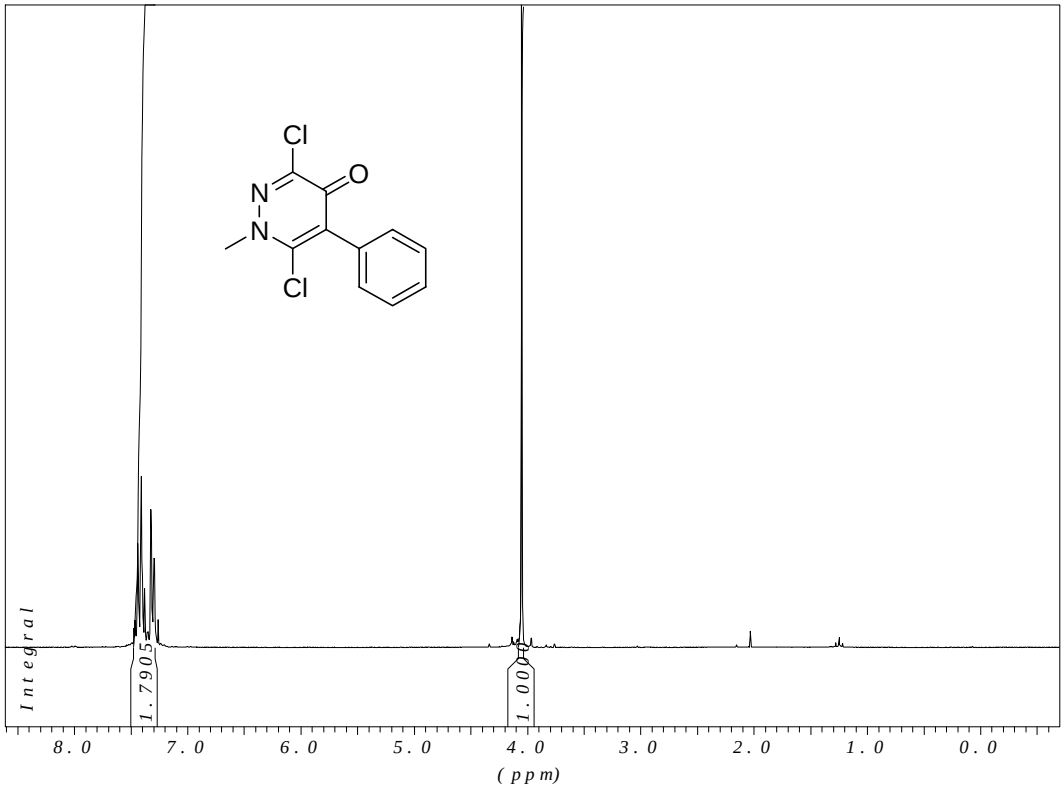


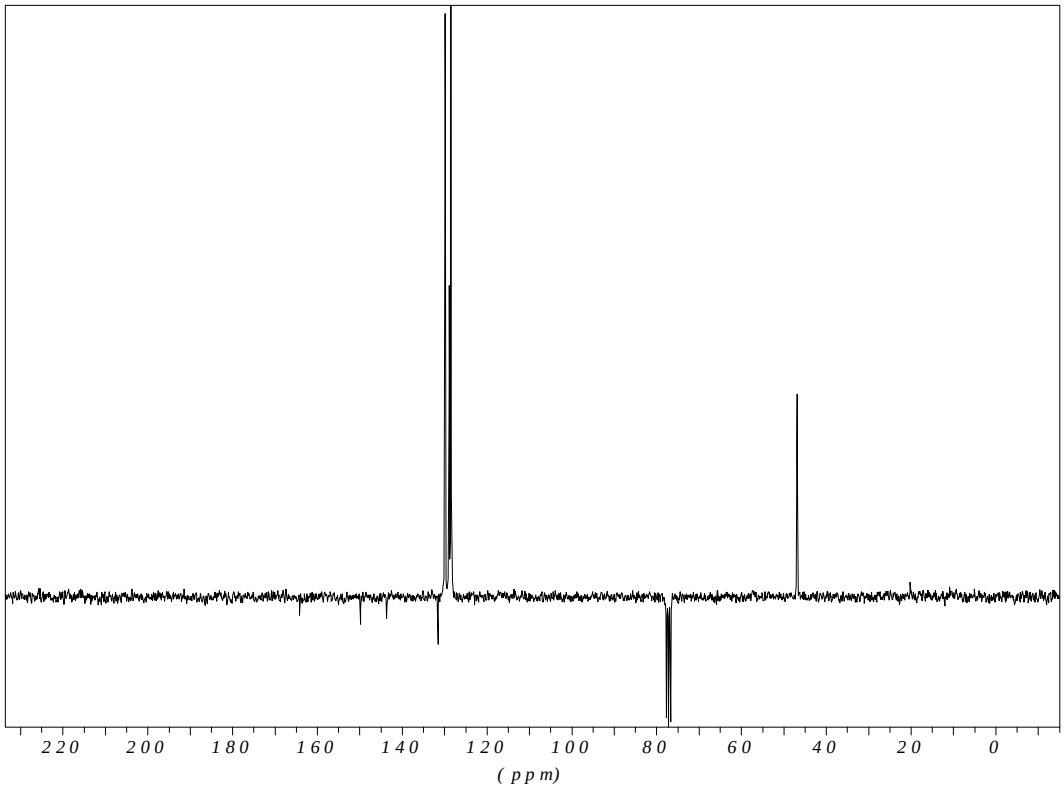
1-Benzyl-5-butyl-3,6-dichloropyridazin-4(1H)-one (9)



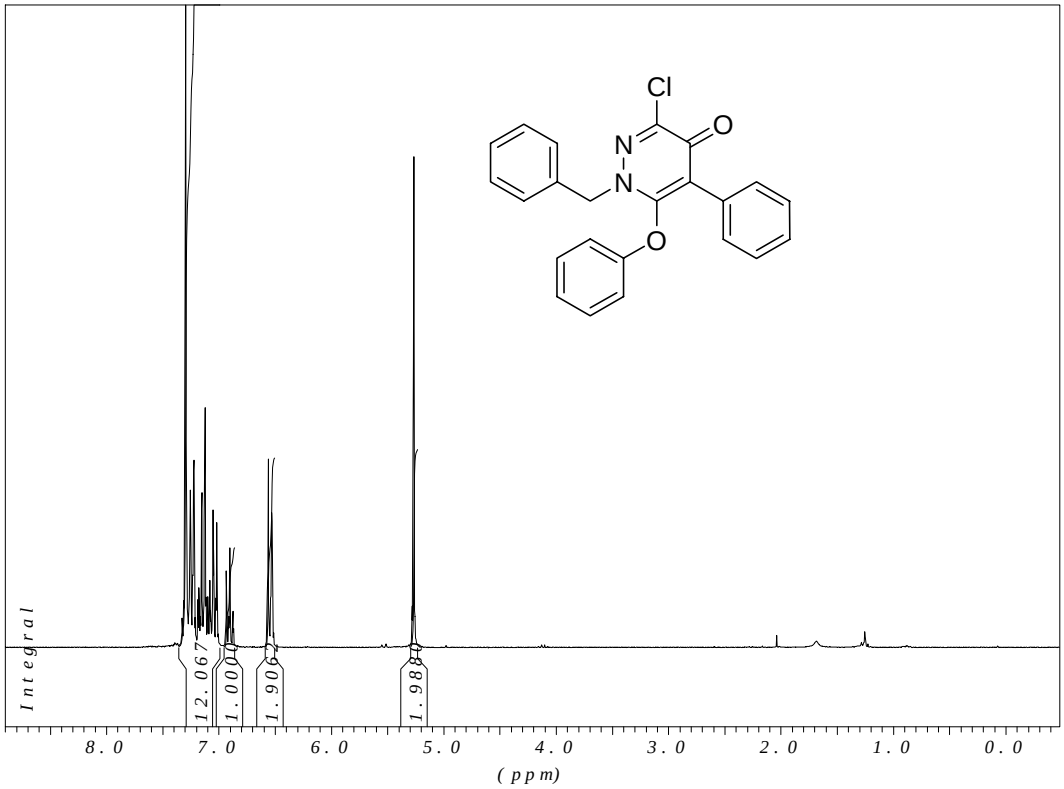


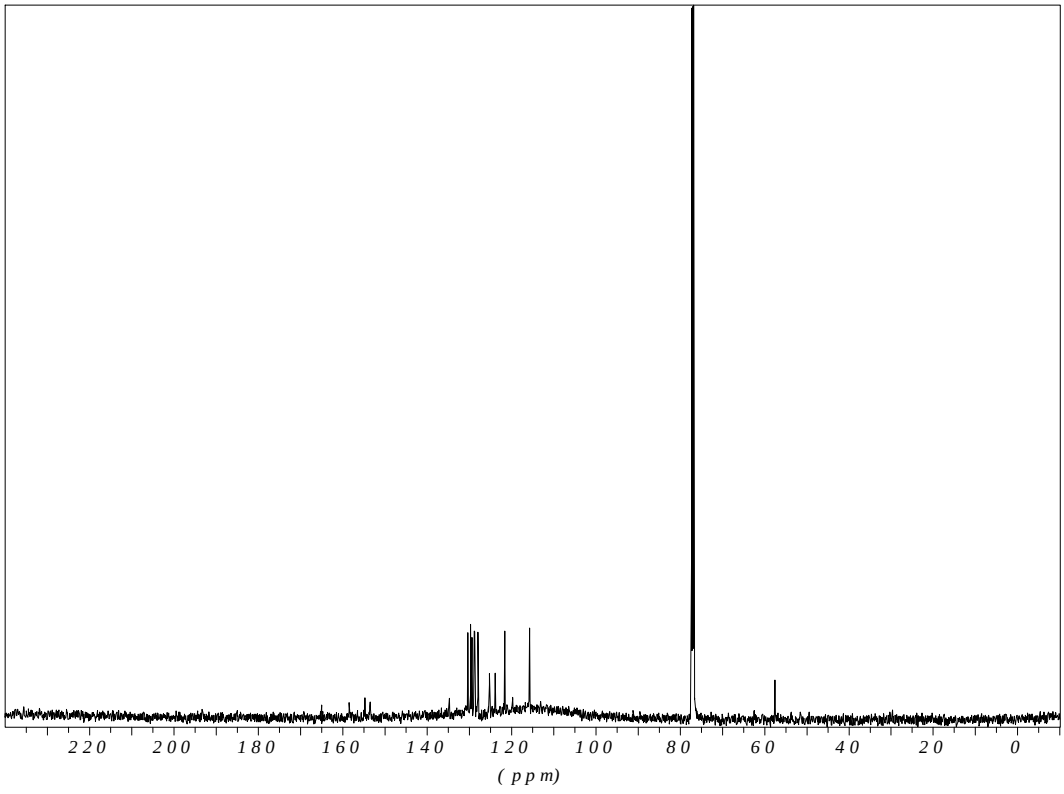
3,6-Dichloro-1-methyl-5-phenylpyridazin-4(1H)-one (10)



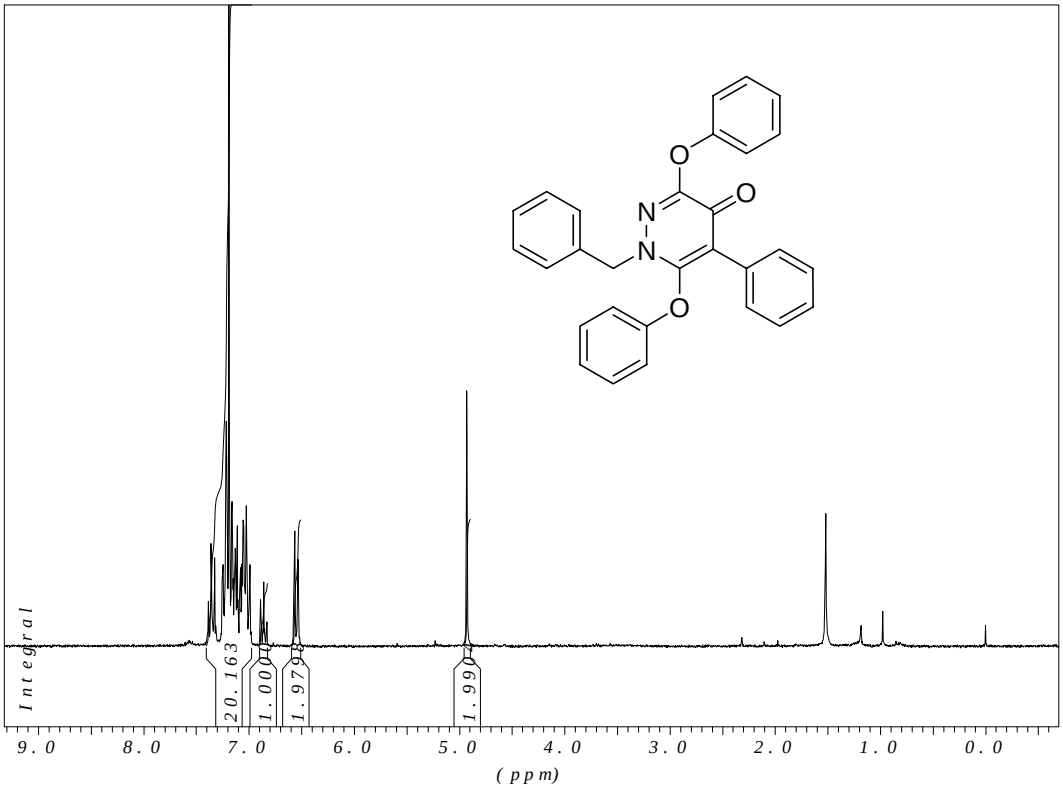


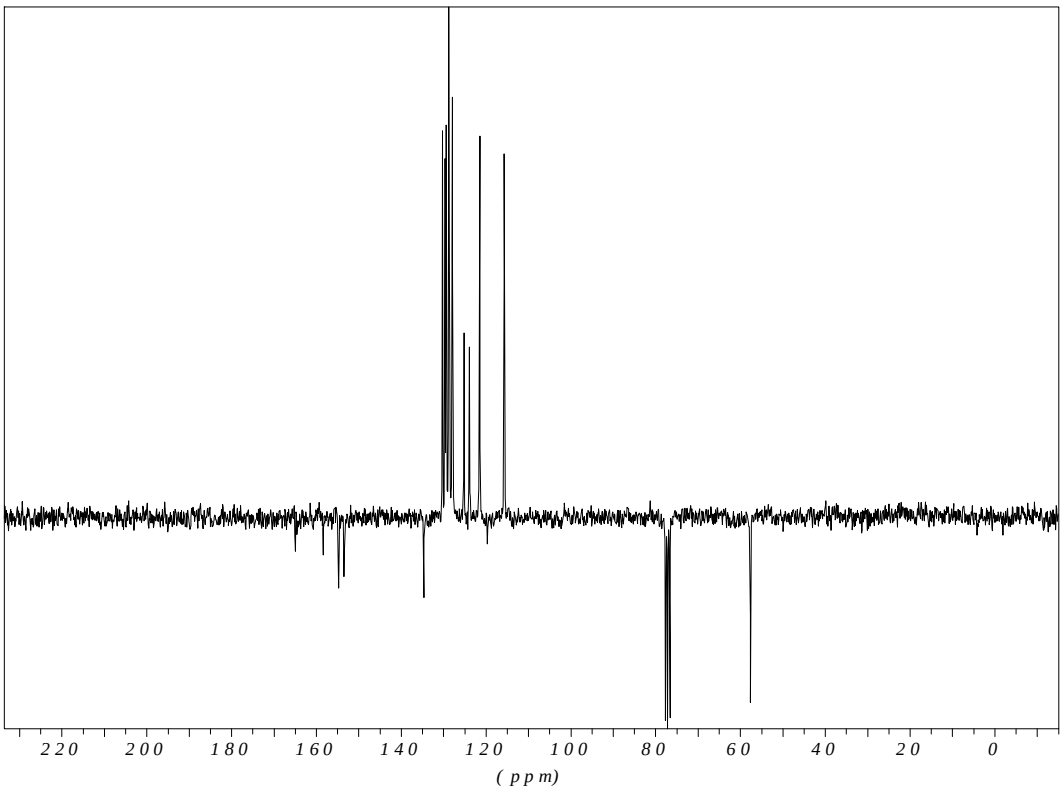
1-Benzyl-3-chloro-6-phenoxy-5-phenylpyridazin-4(1H)-one (11a)





1-benzyl-3,6-diphenoxy-5-phenylpyridazin-4(1H)-one





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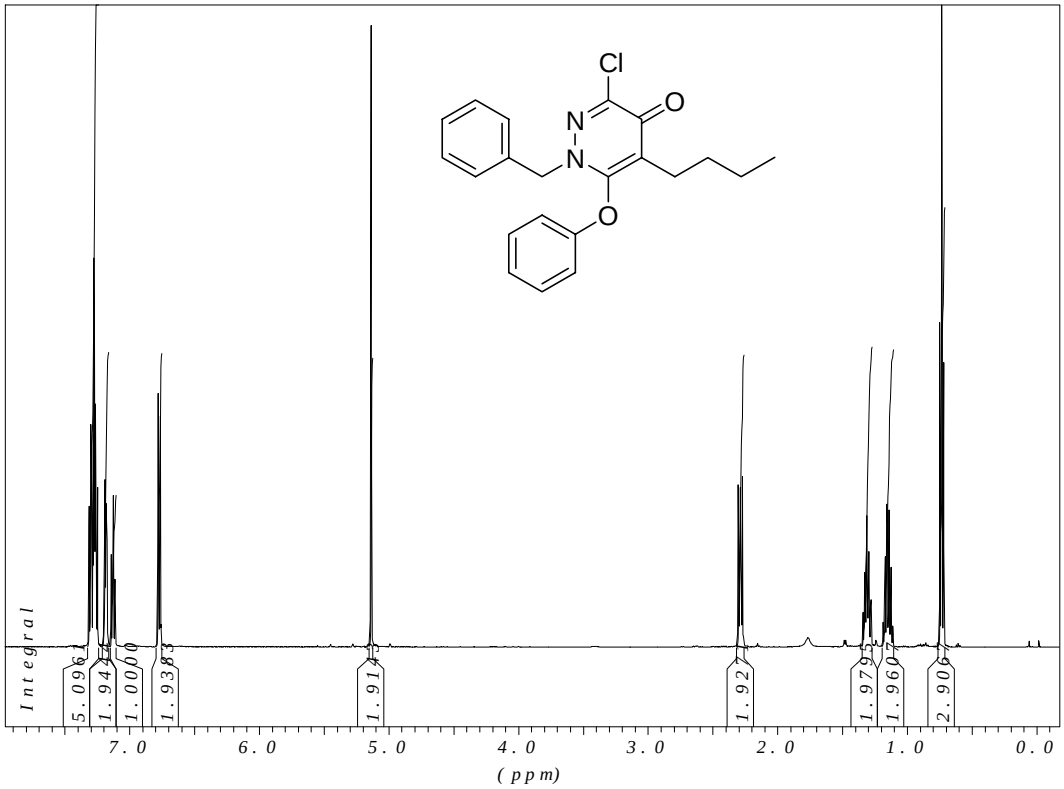
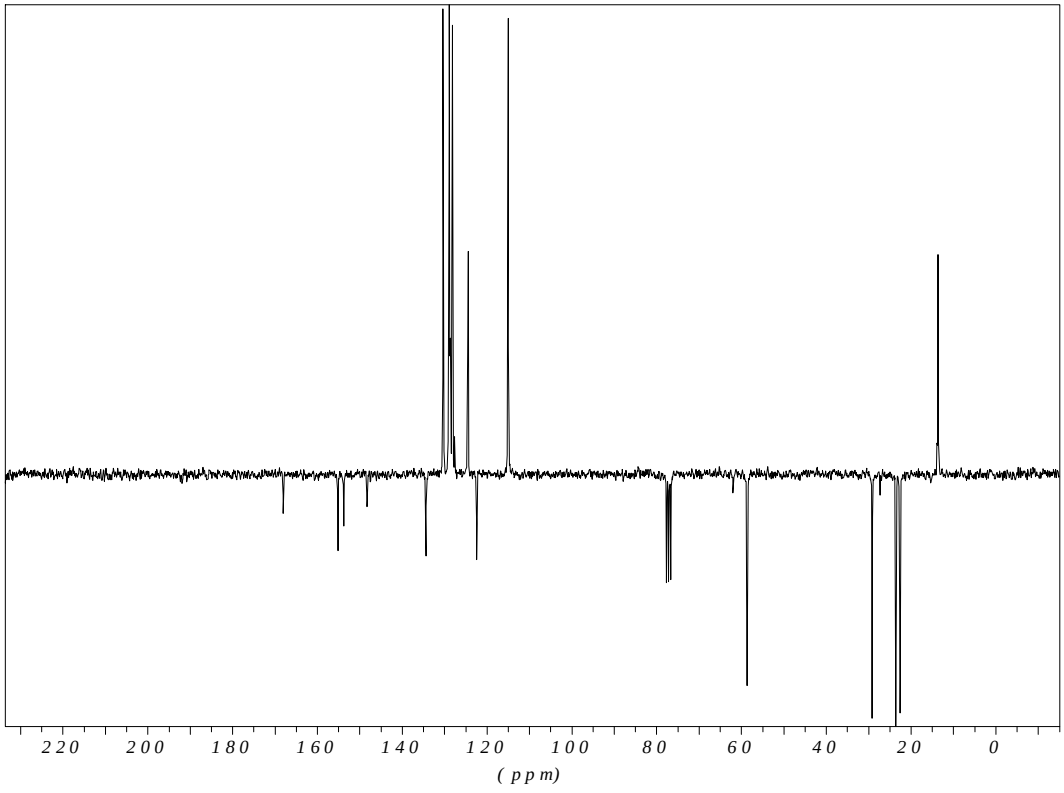
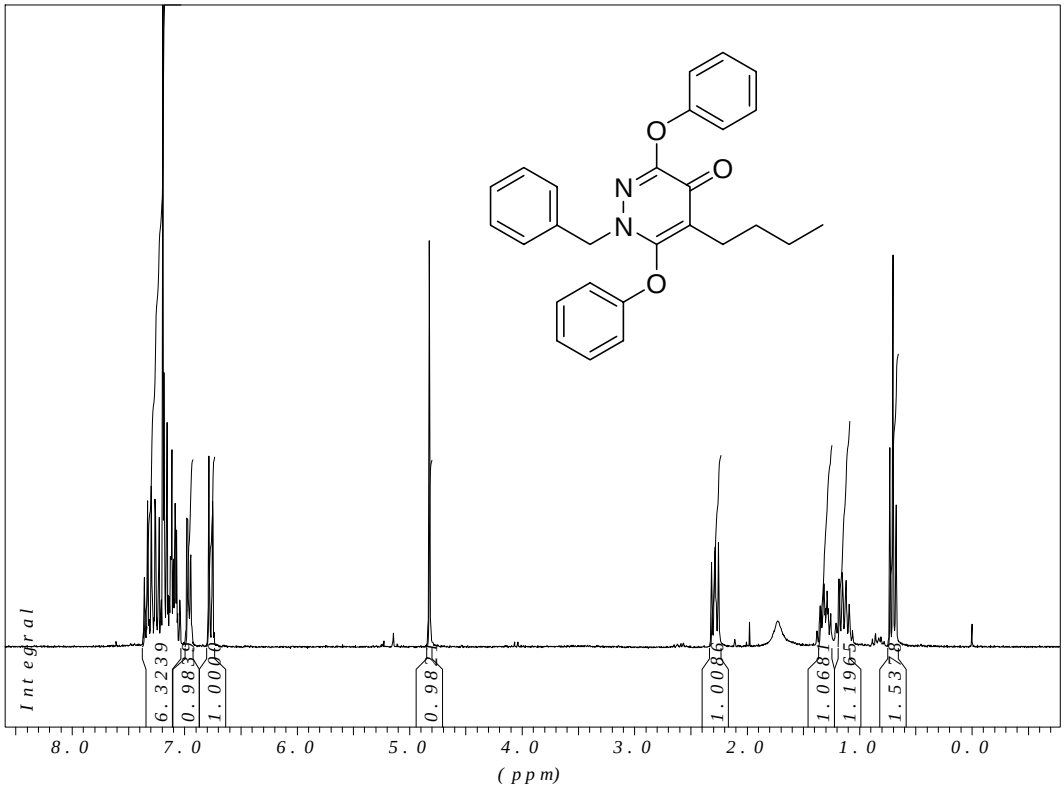
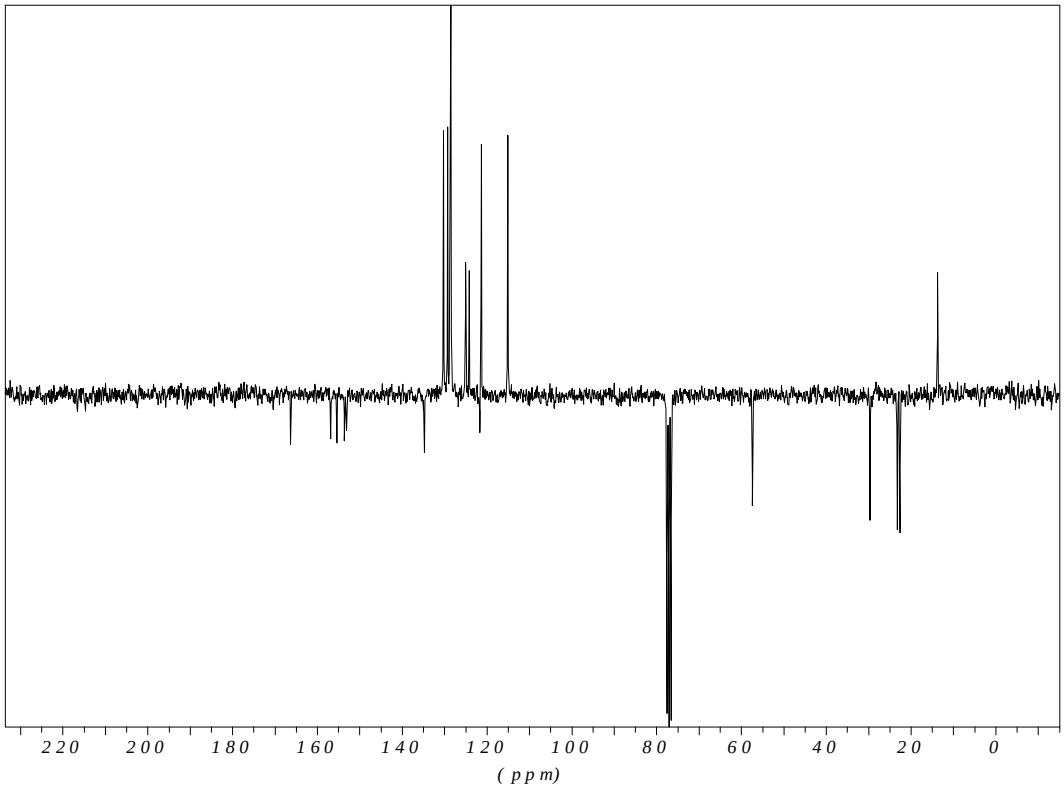




1-Benzyl-5-butyl-3,6-diphenoxypyridazin-4(1H)-one





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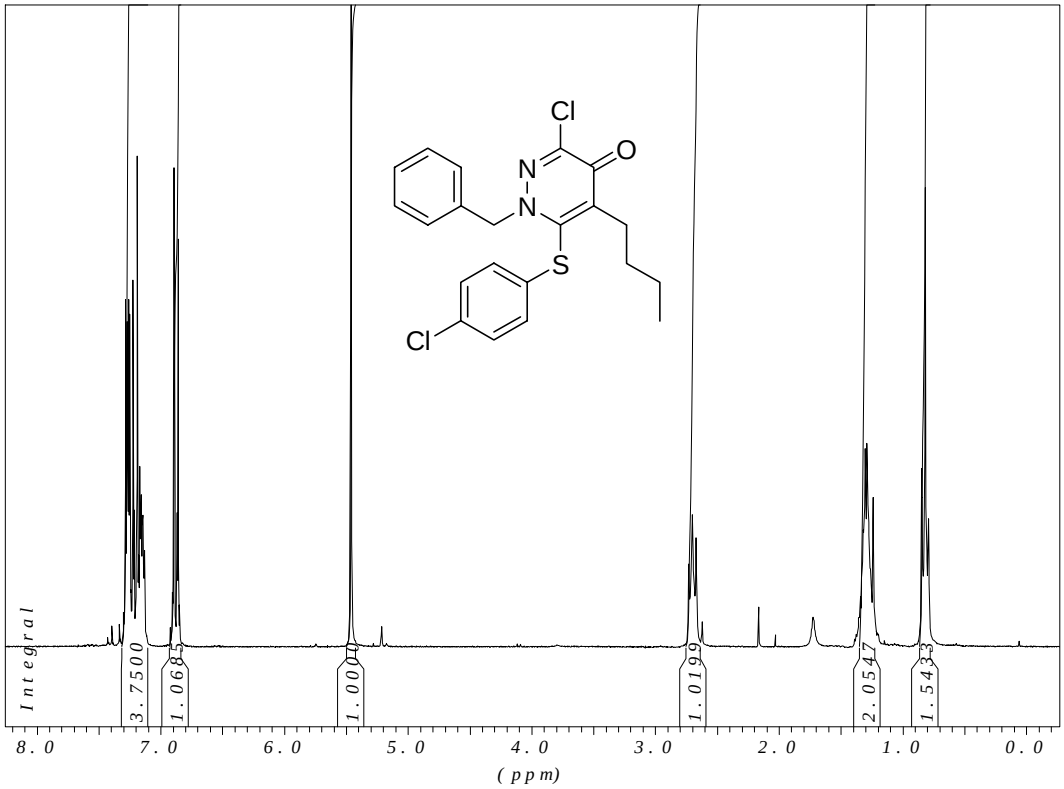
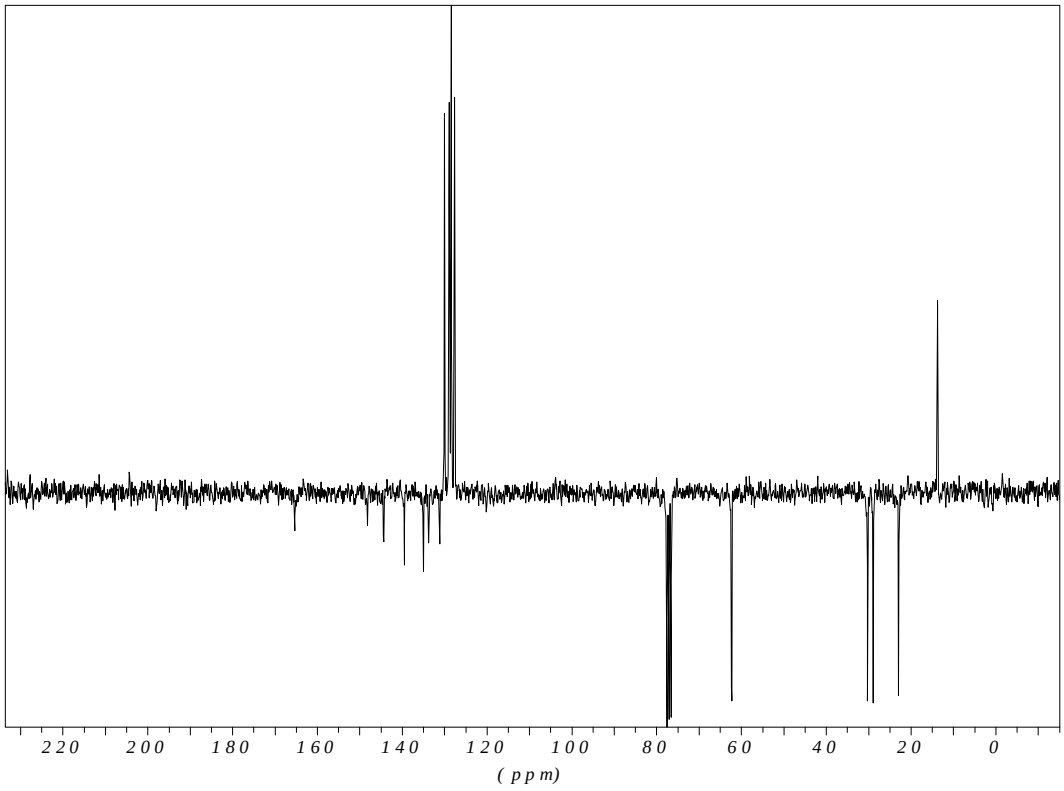
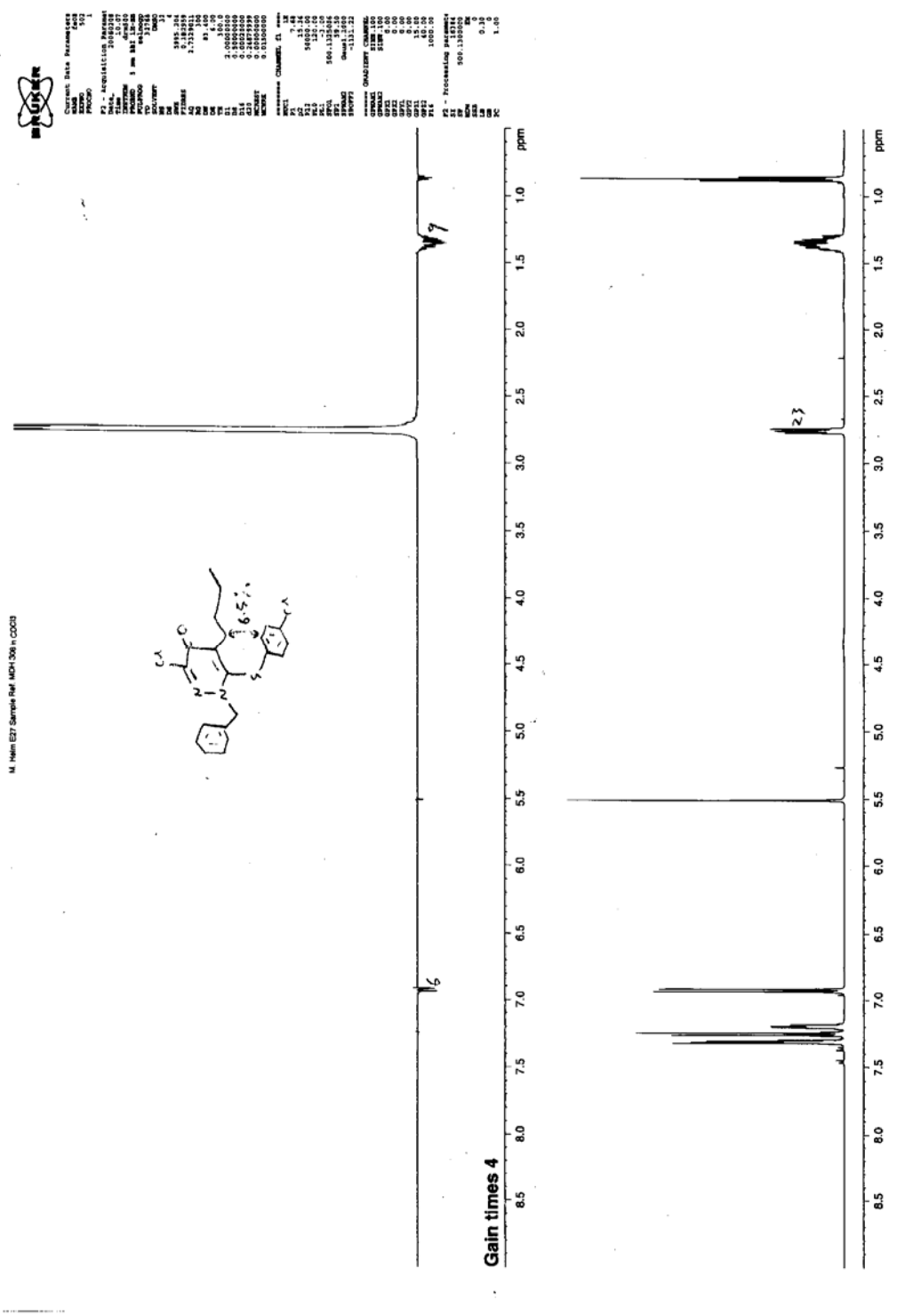
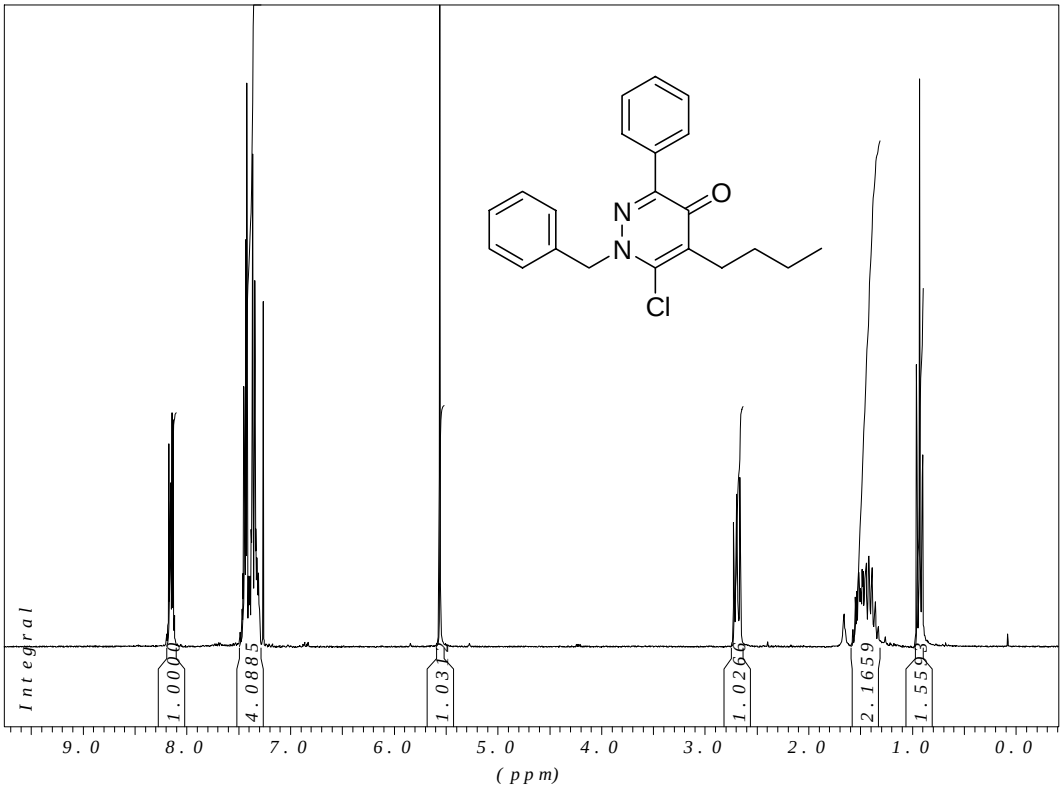


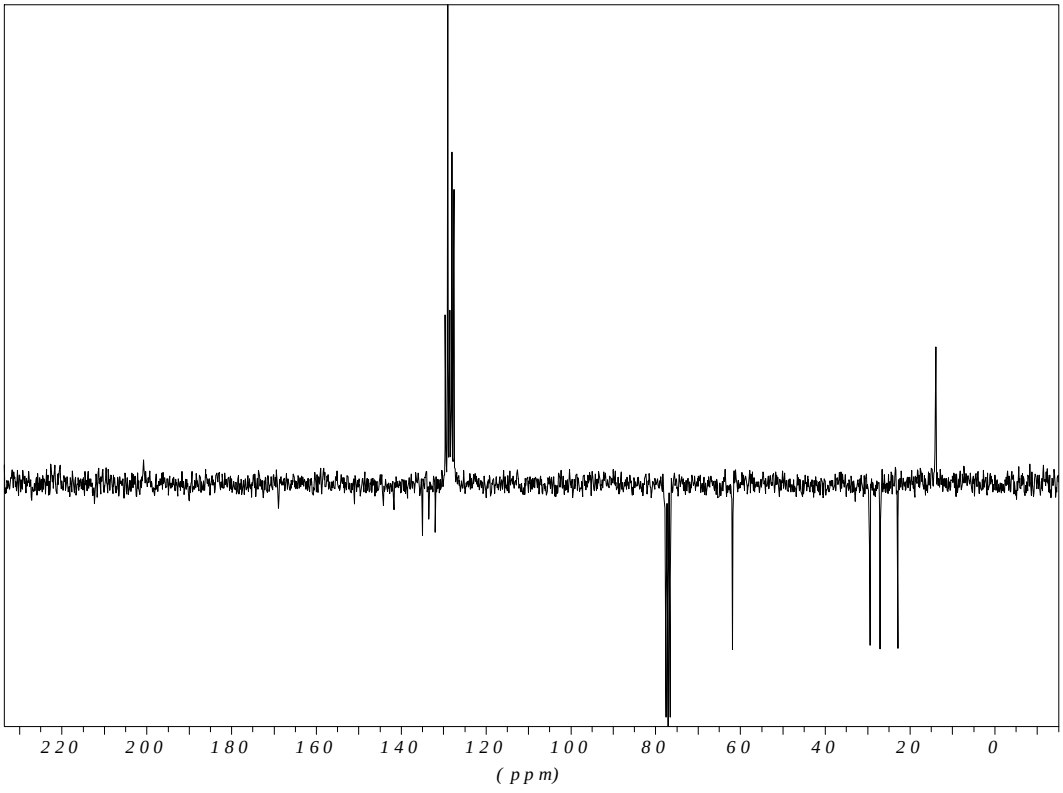


13a nOe

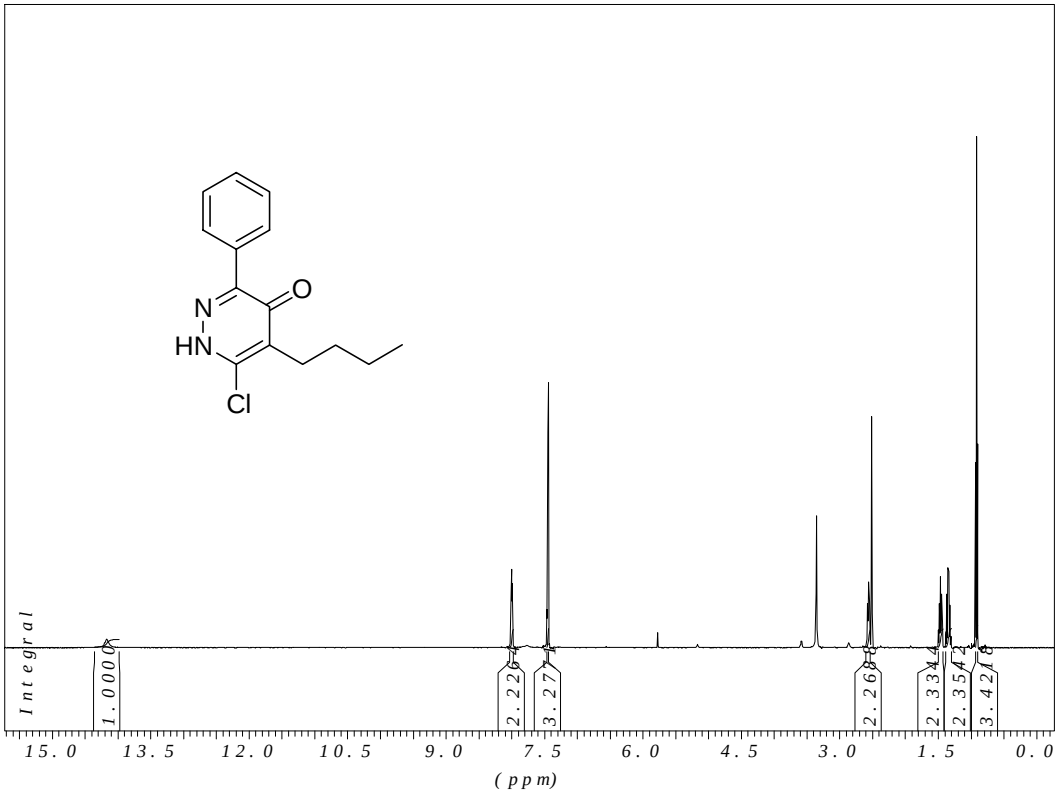


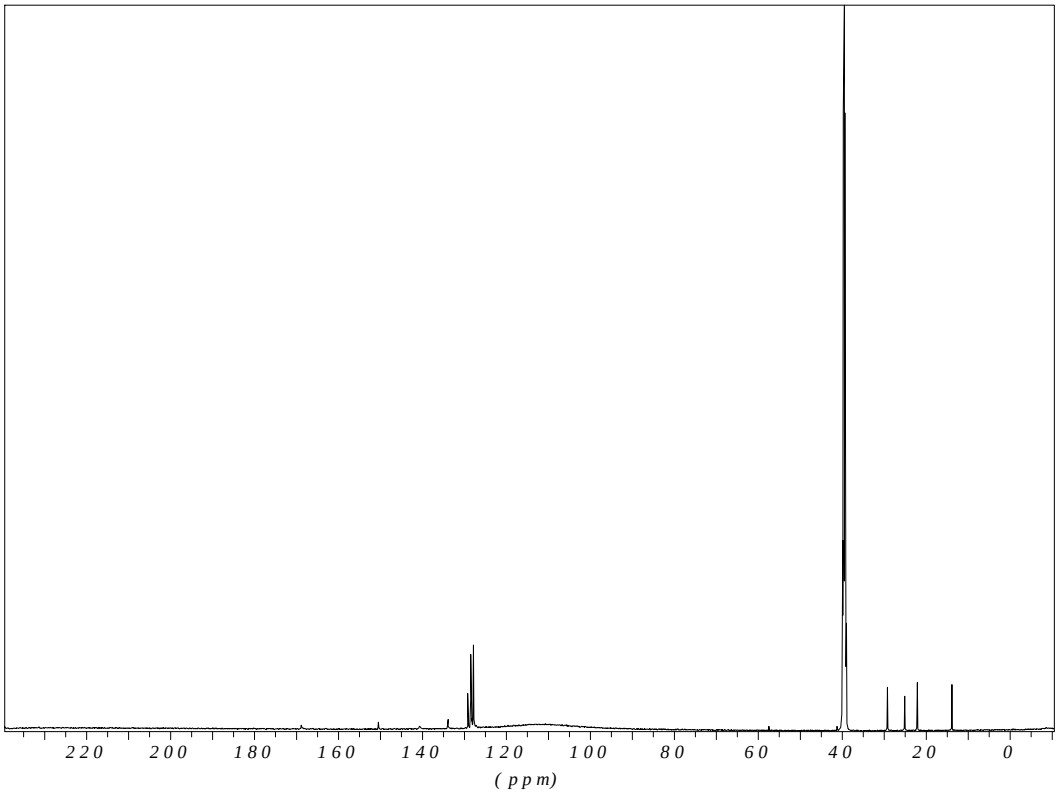
1-benzyl-5-butyl-6-chloro-3-phenylpyridazin-4(1H)-one (14b)



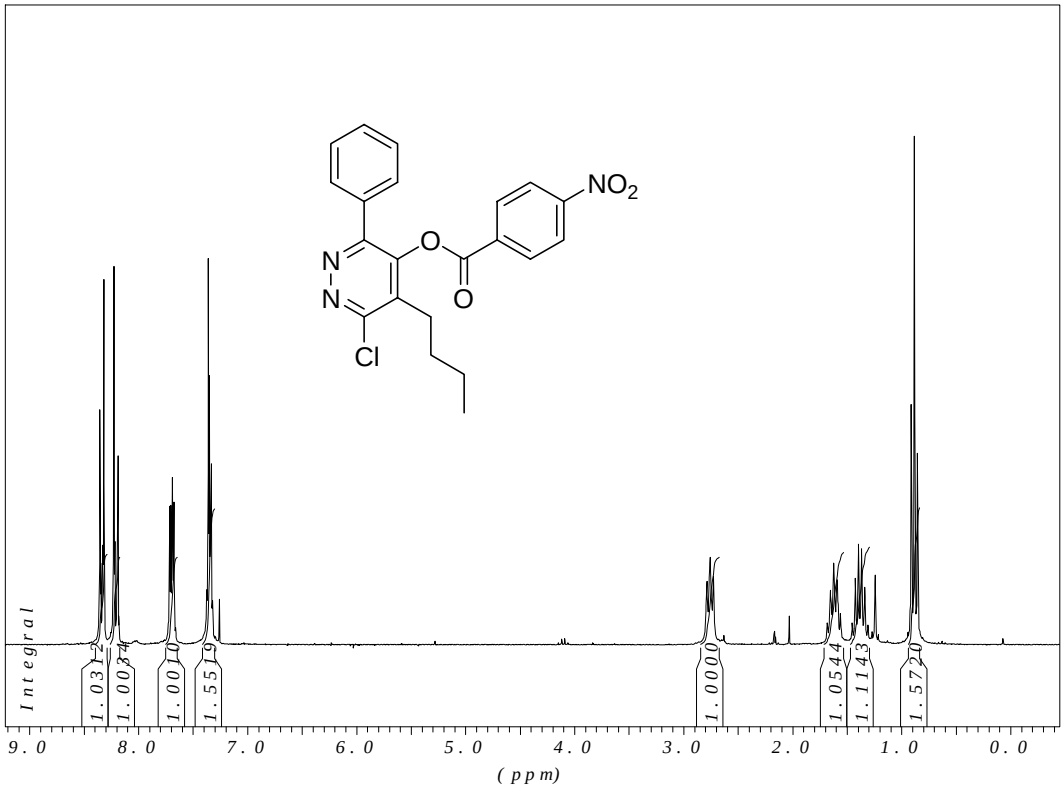


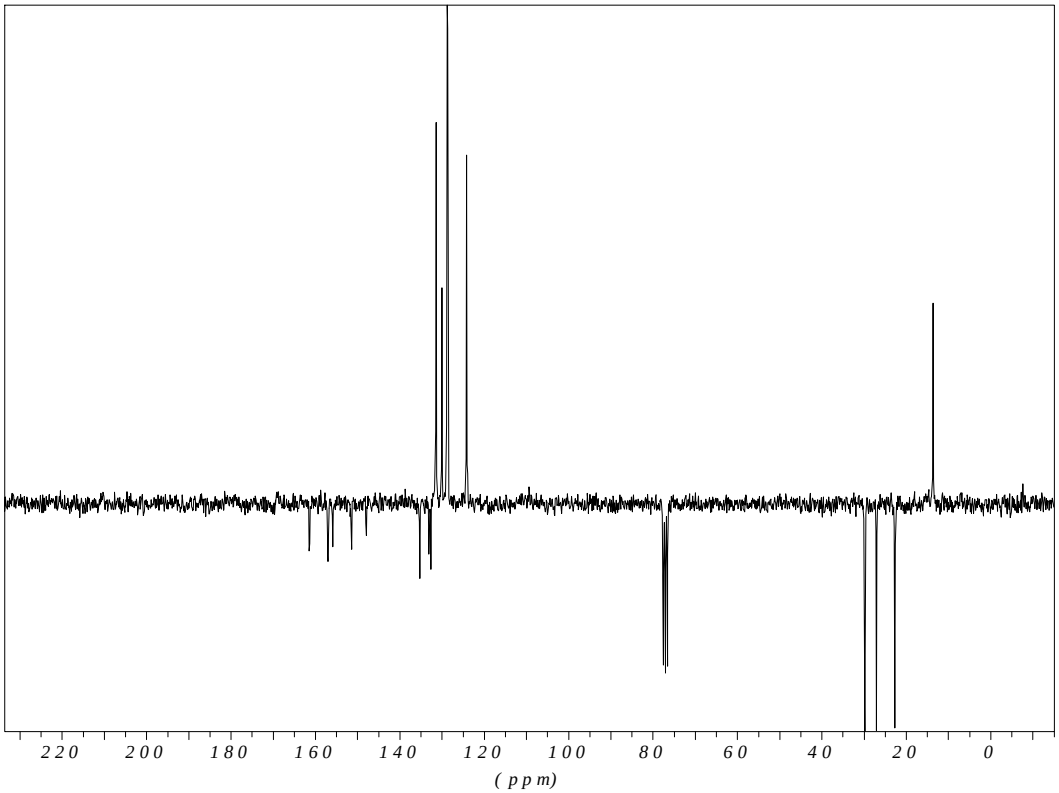
5-butyl-6-chloro-3-phenylpyridazin-4(1H)-one





5-butyl-6-chloro-3-phenylpyridazin-4-yl 4-nitrobenzoate





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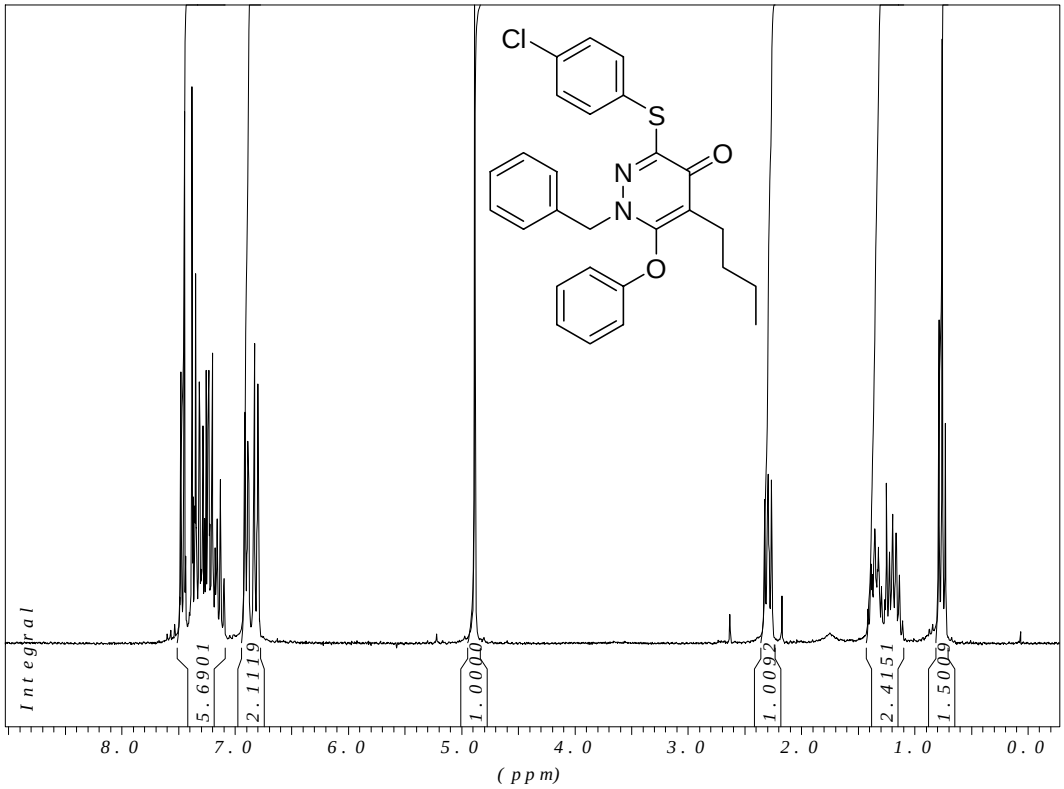
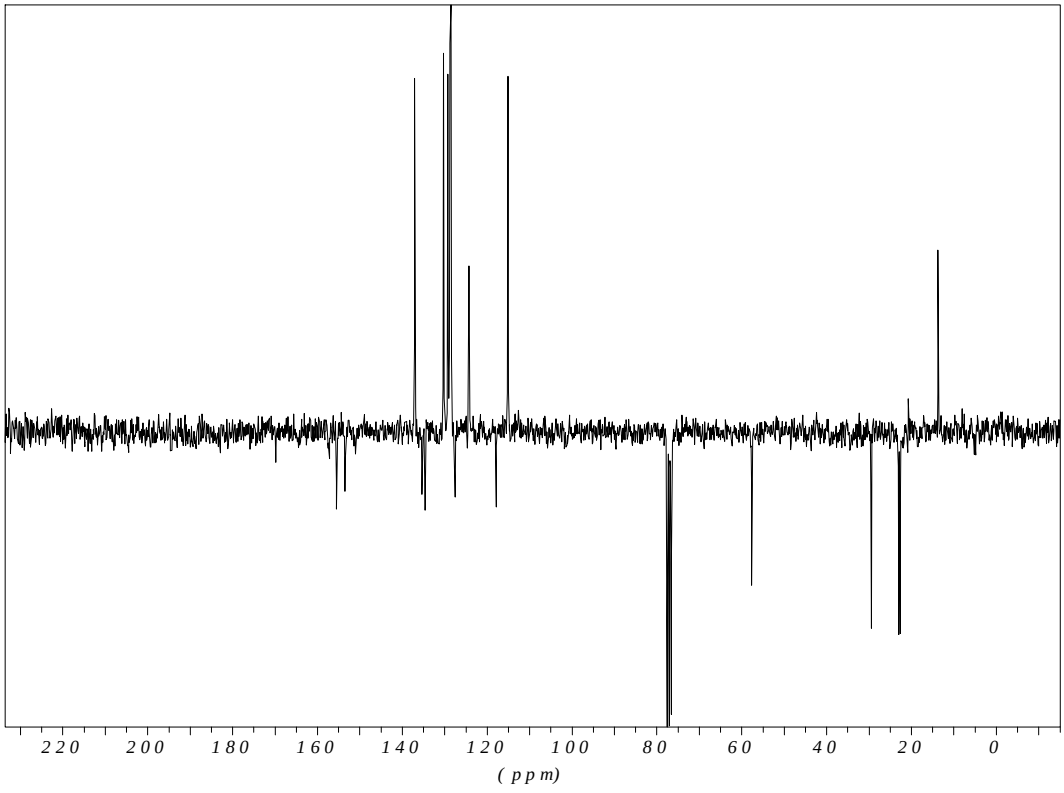
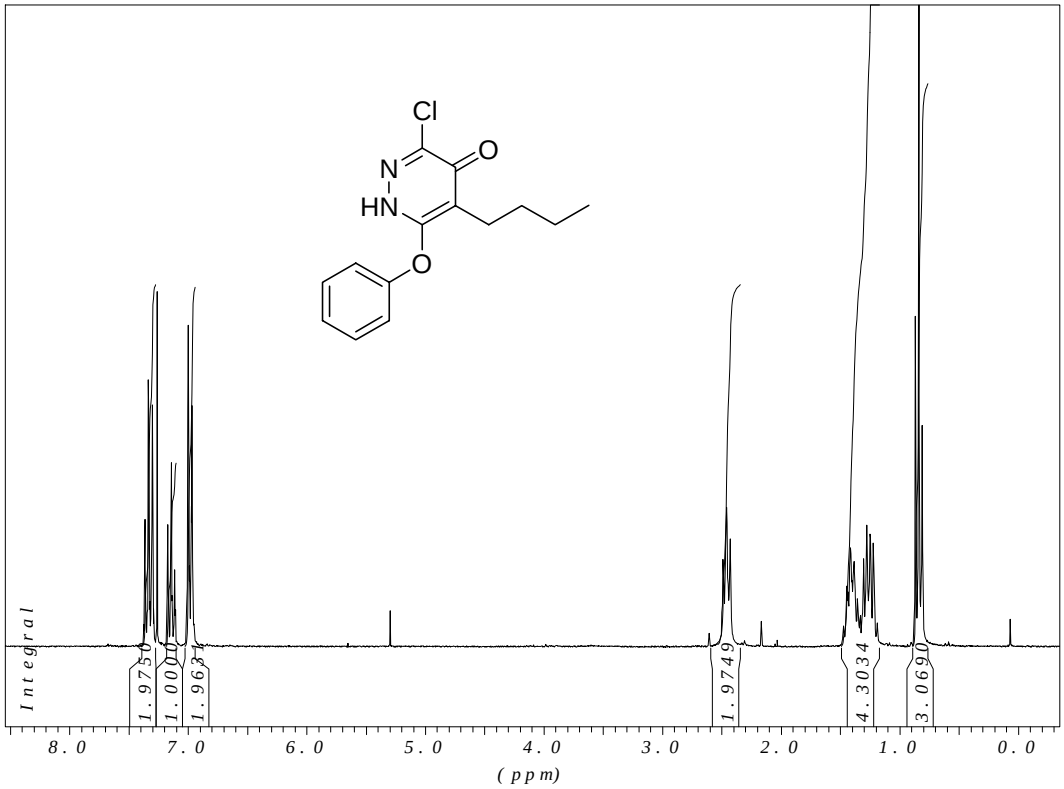
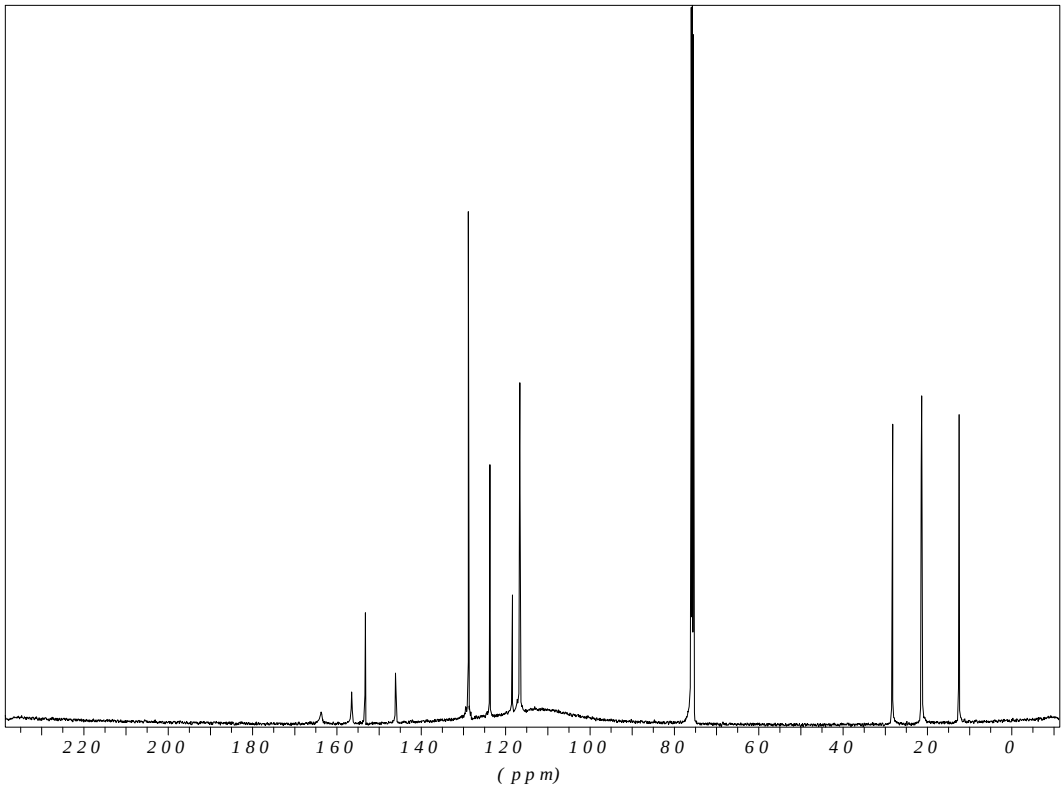


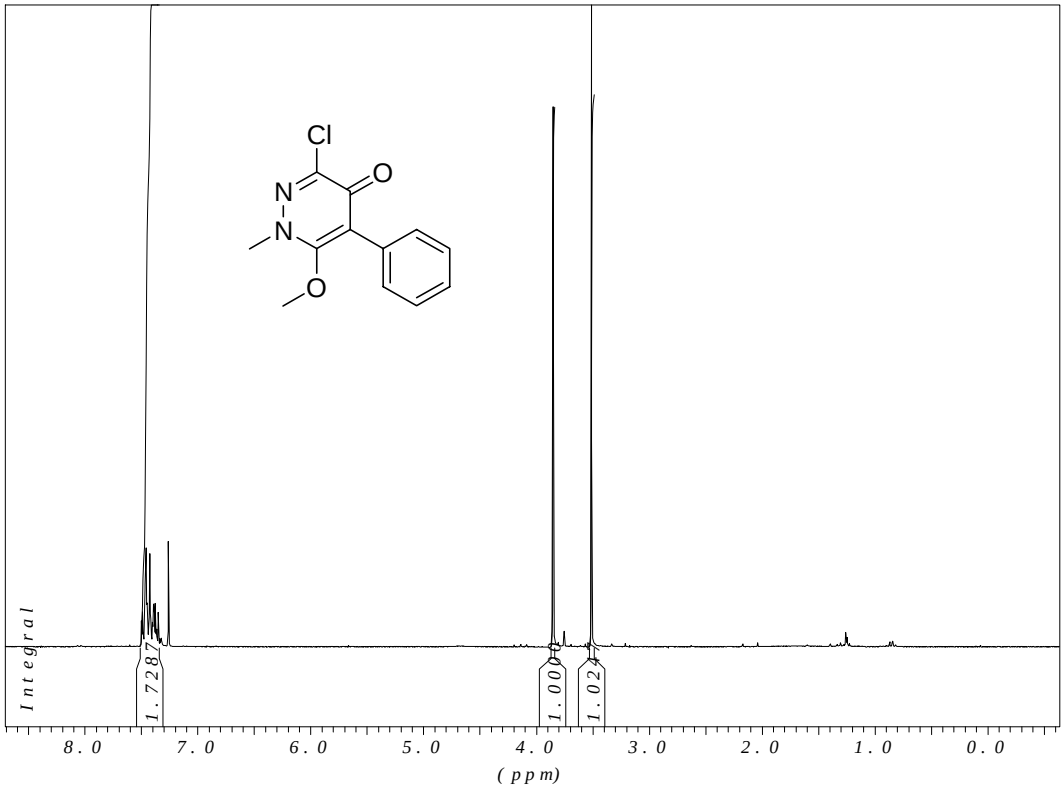


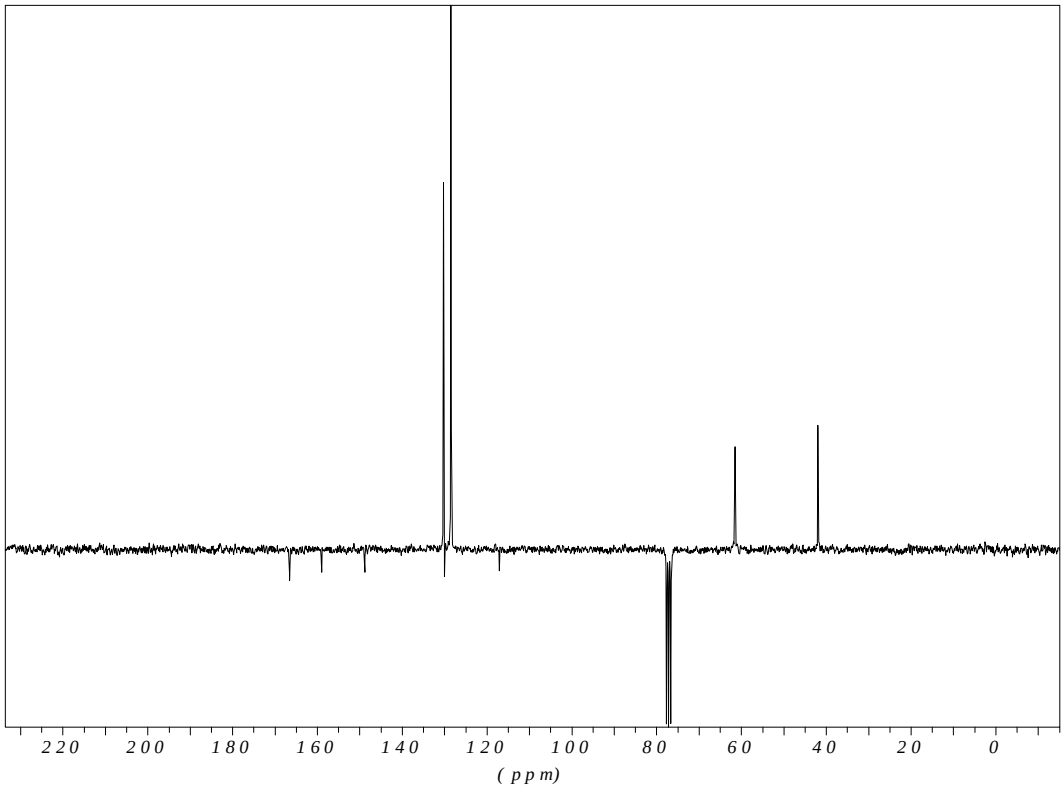
5-butyl-3-chloro-6-phenoxypyridazin-4(1H)-one



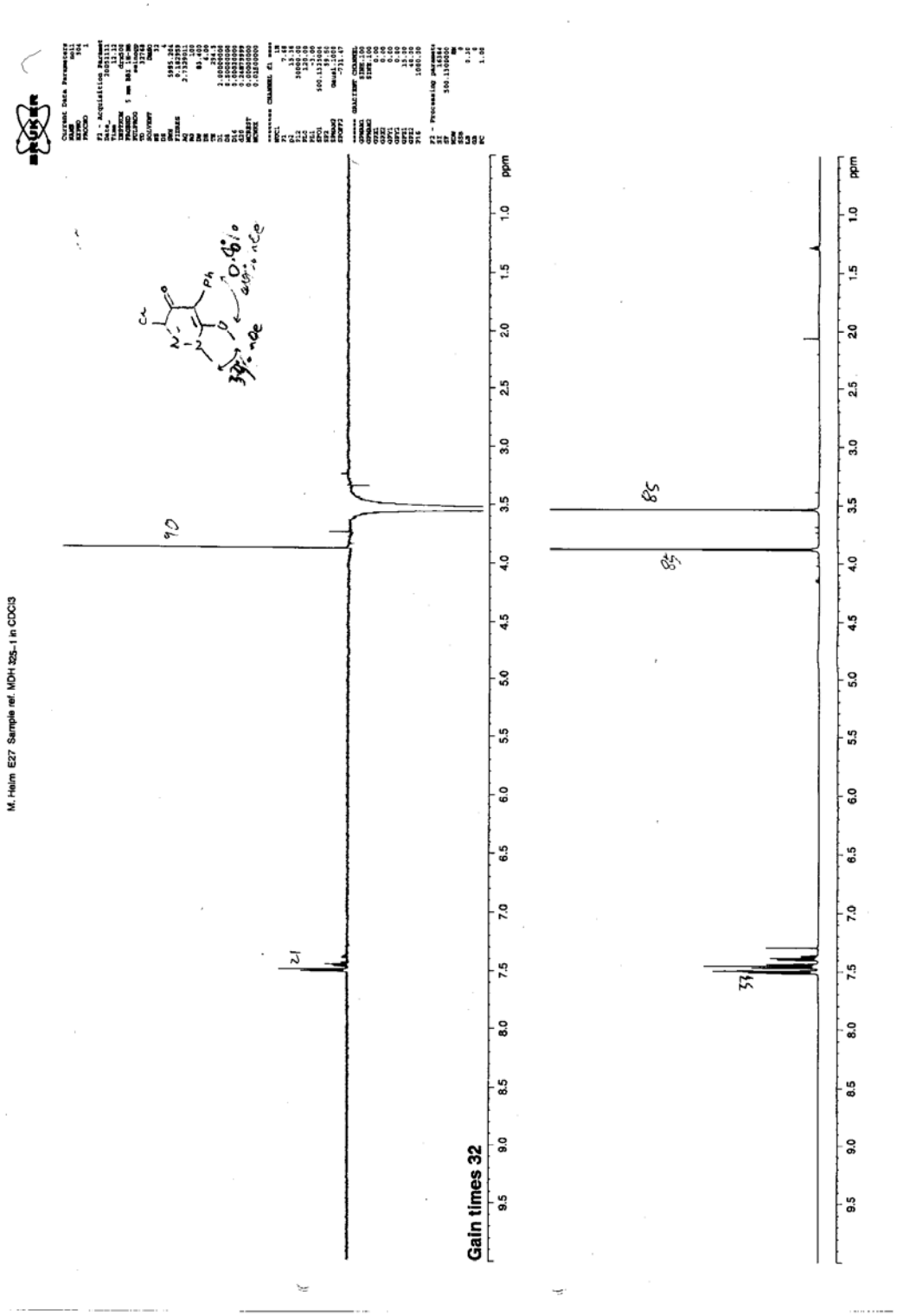


3-Chloro-6-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one (16a)

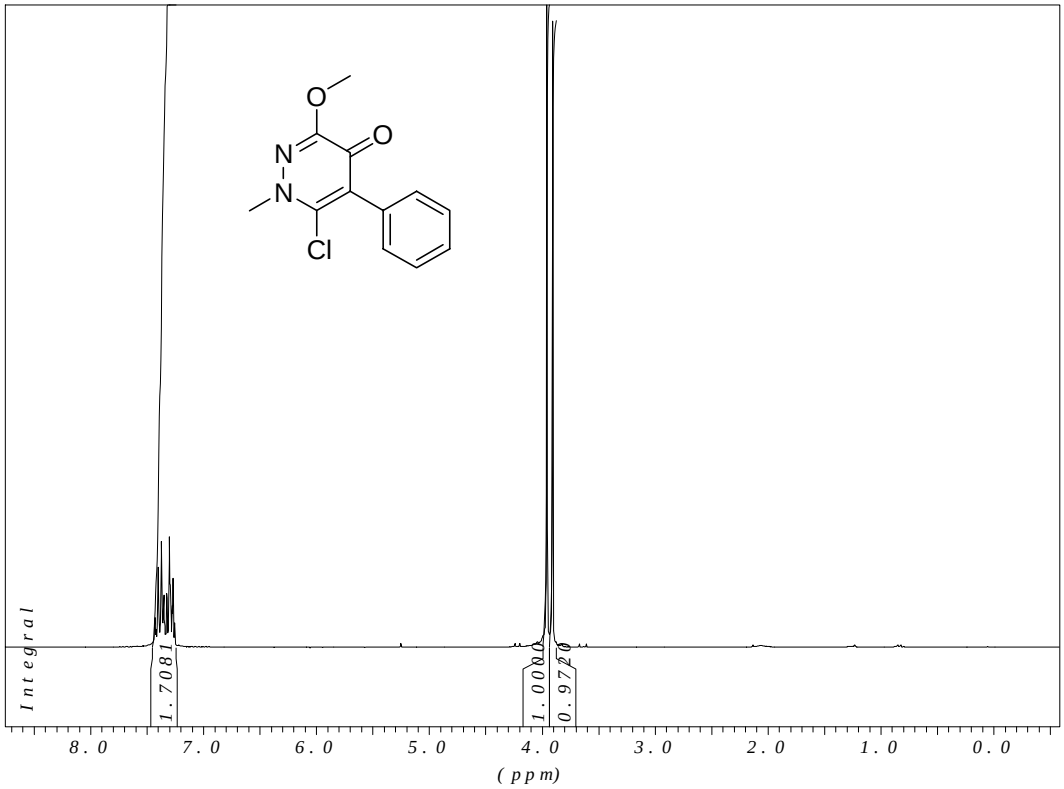


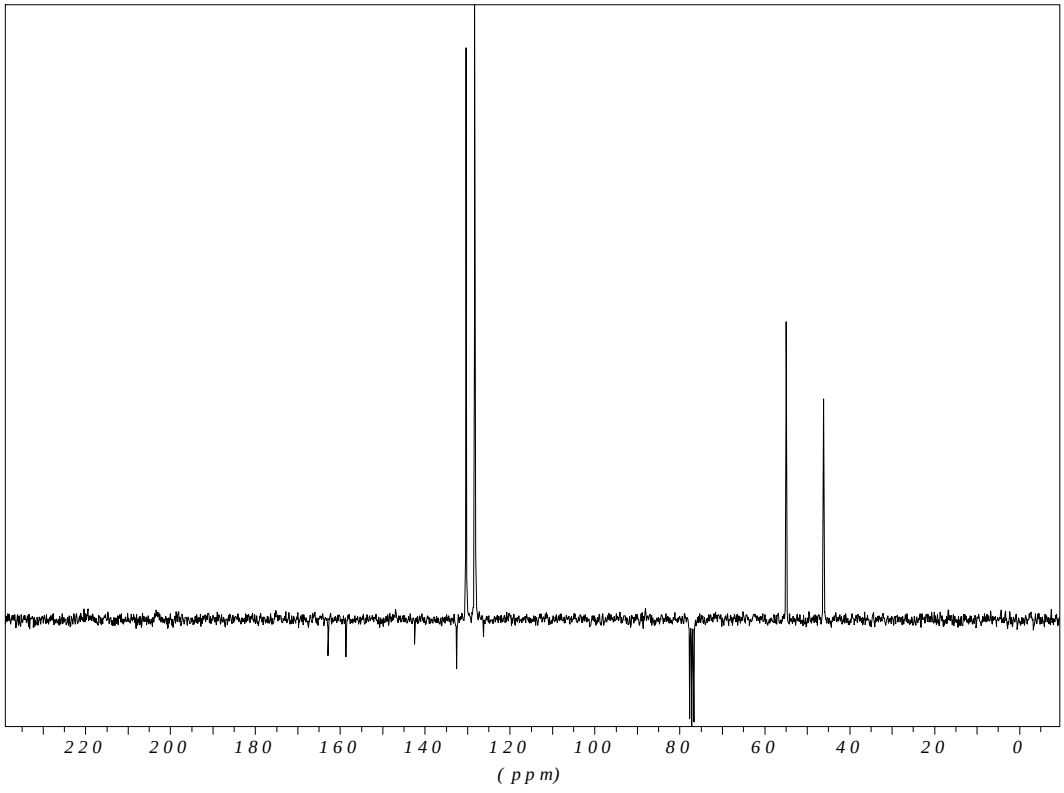


16a nOe

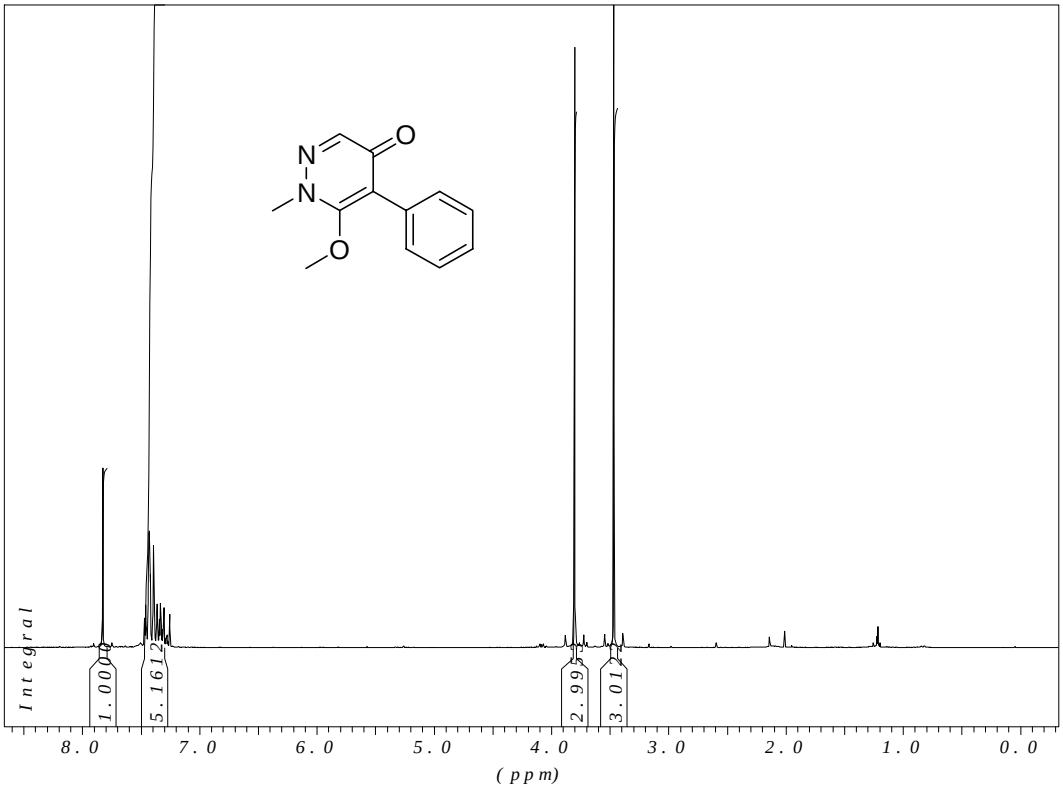


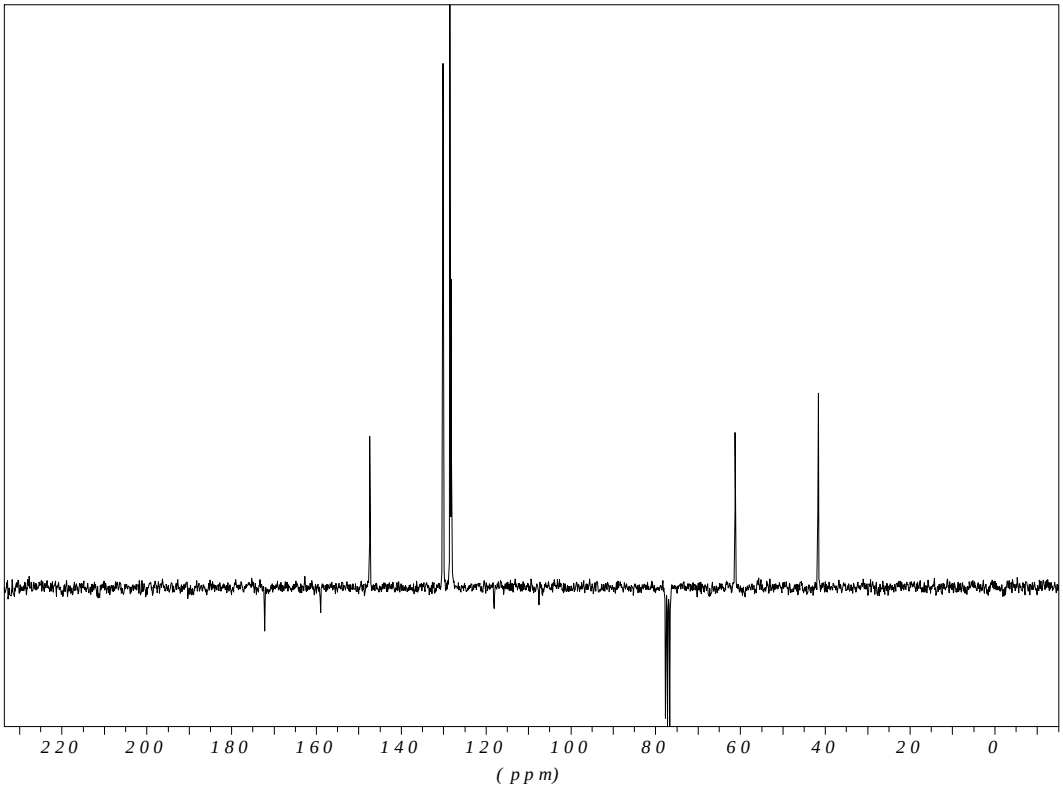
6-Chloro-3-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one (16b)



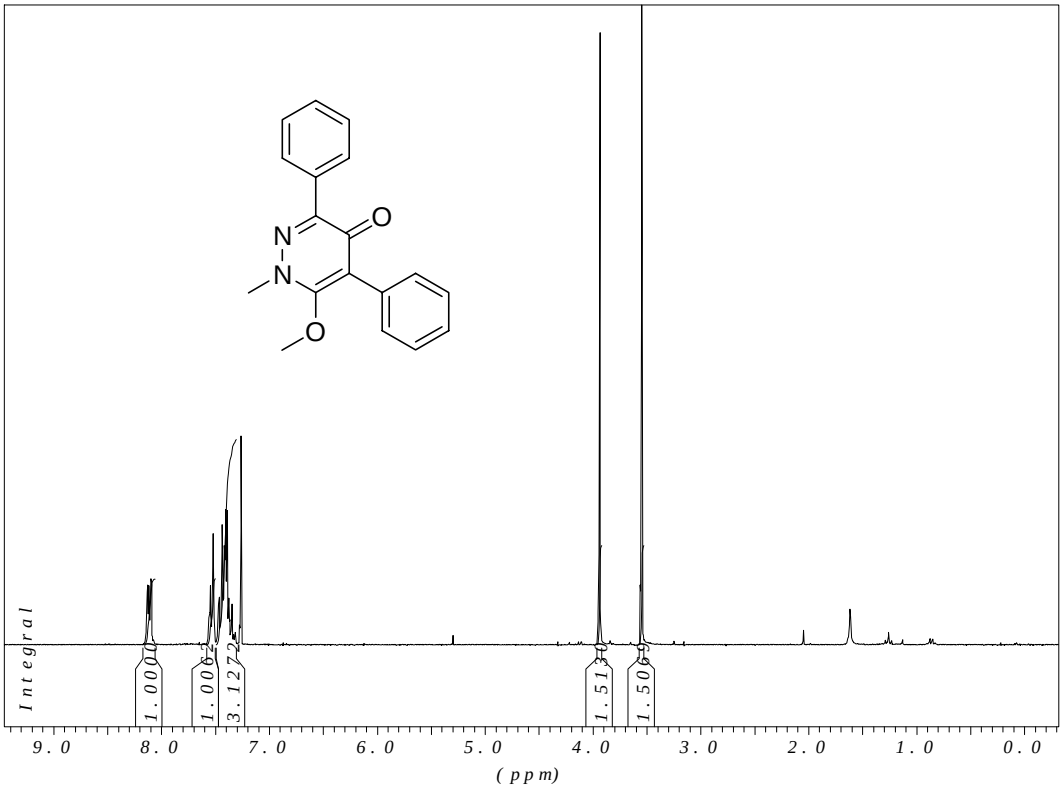


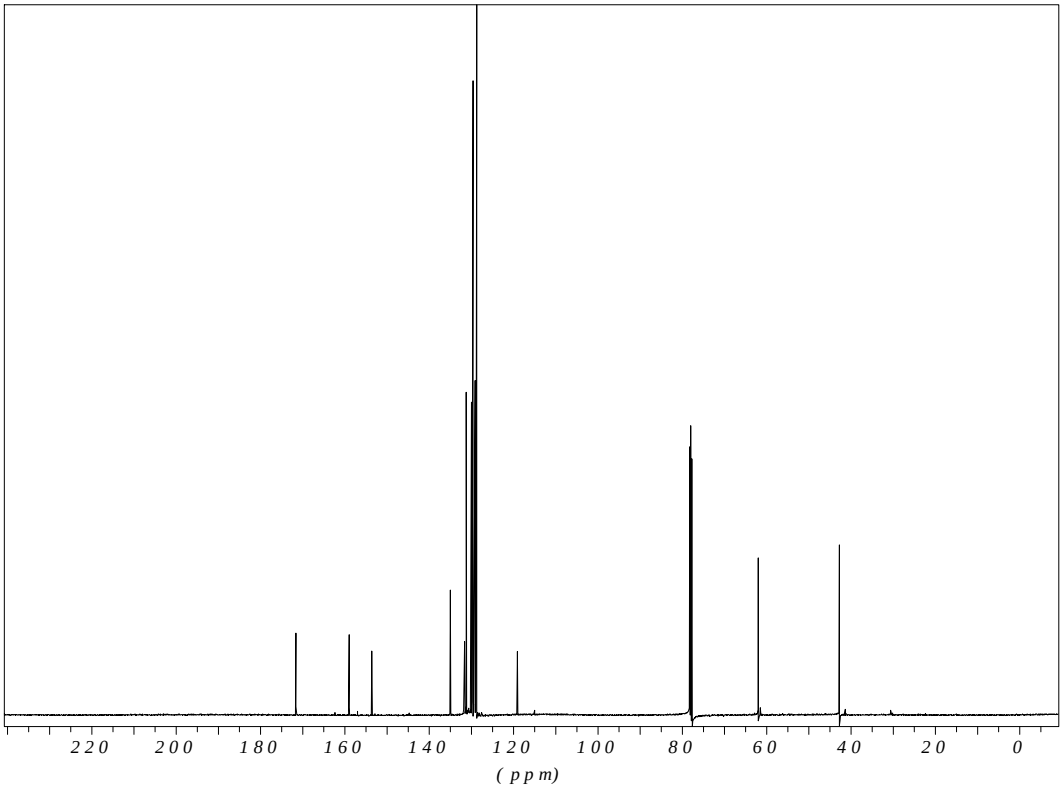
6-methoxy-1-methyl-5-phenylpyridazin-4(1H)-one



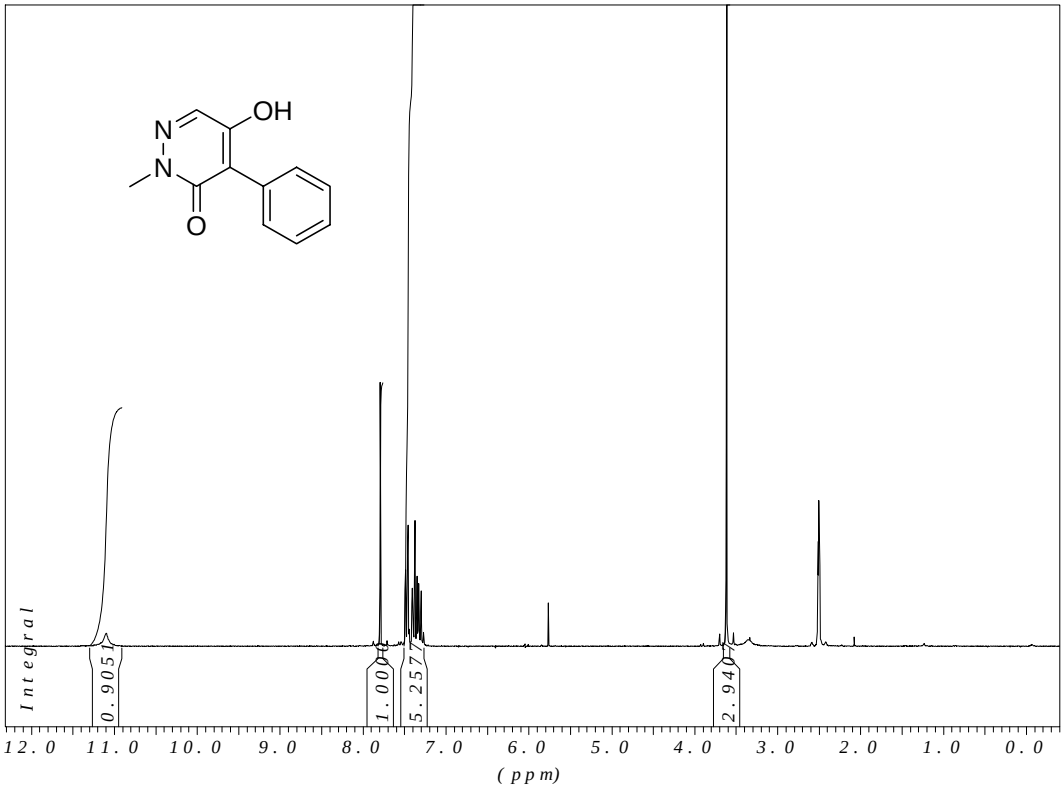


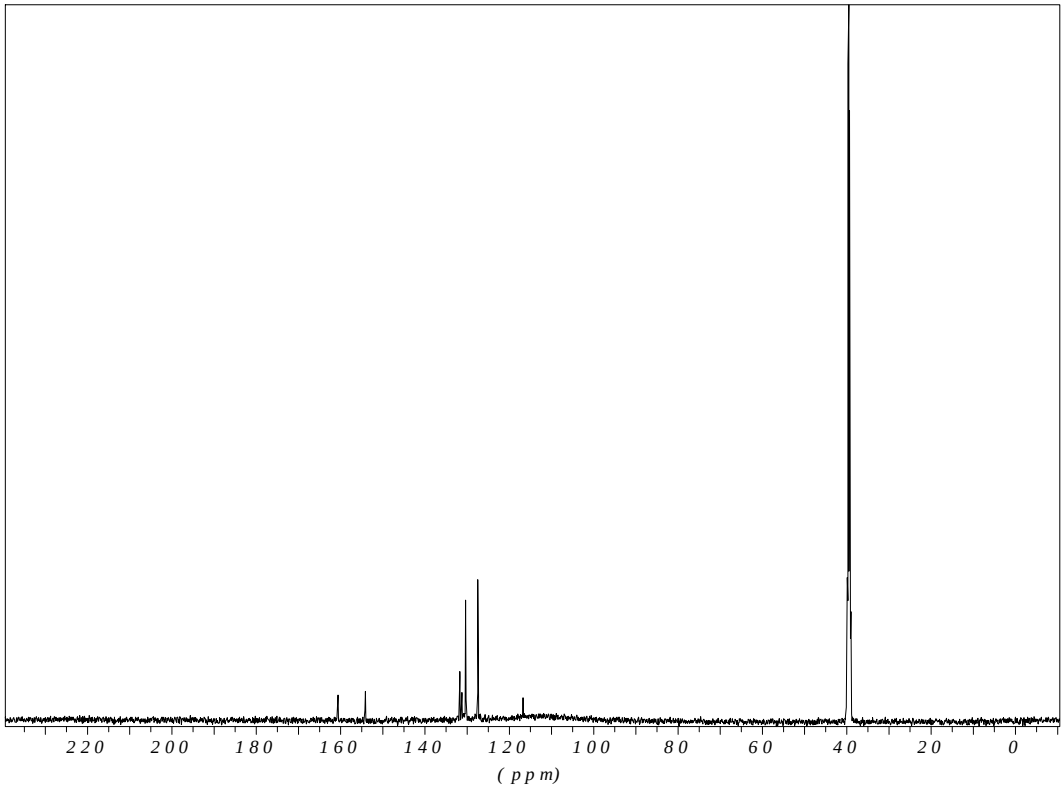
6-methoxy-1-methyl-3,5-diphenylpyridazin-4(1H)-one



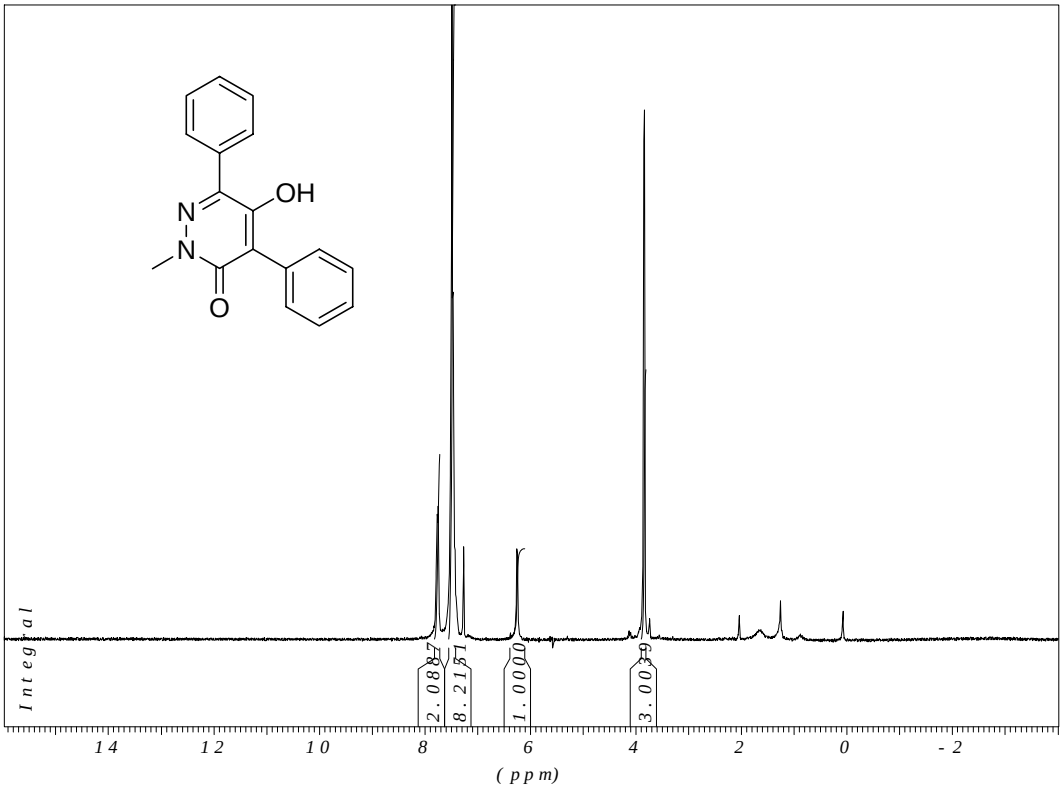


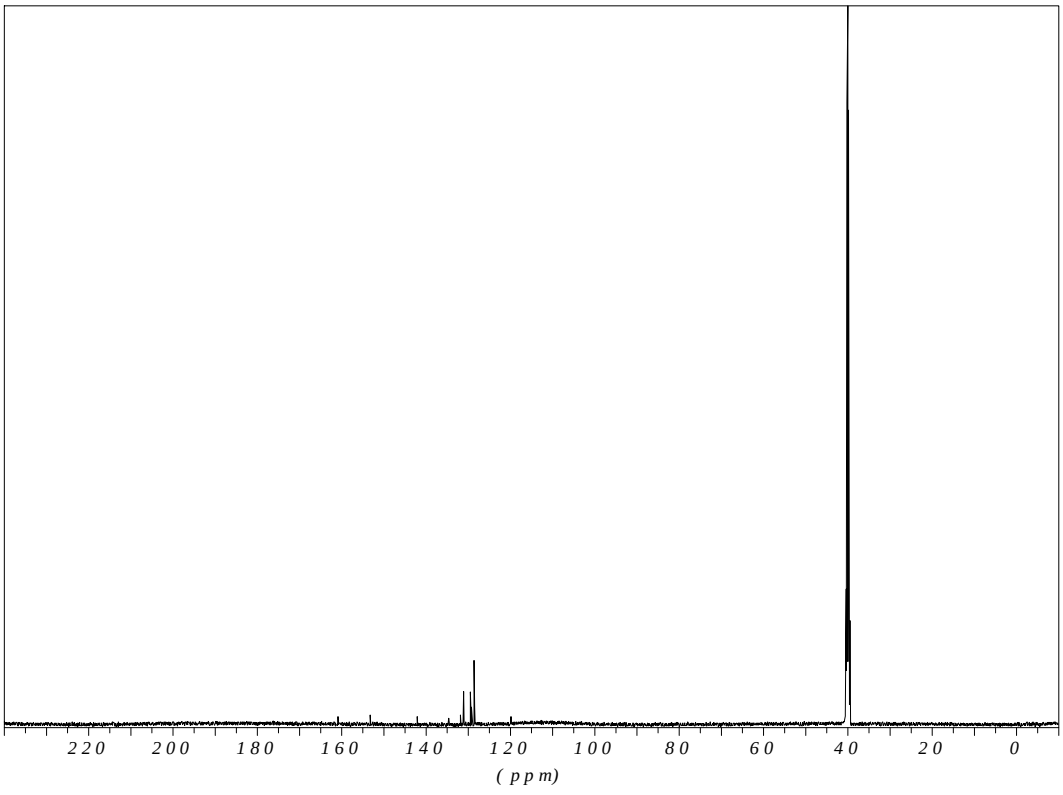
5-hydroxy-2-methyl-4-phenylpyridazin-3(2H)-one (17)



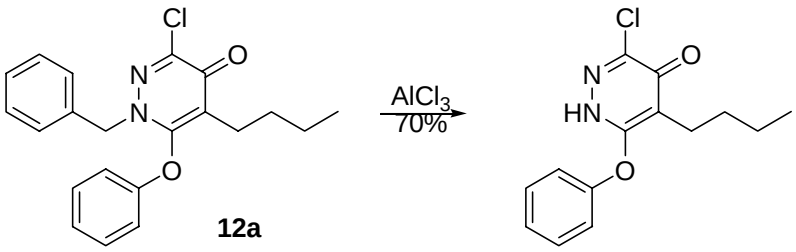


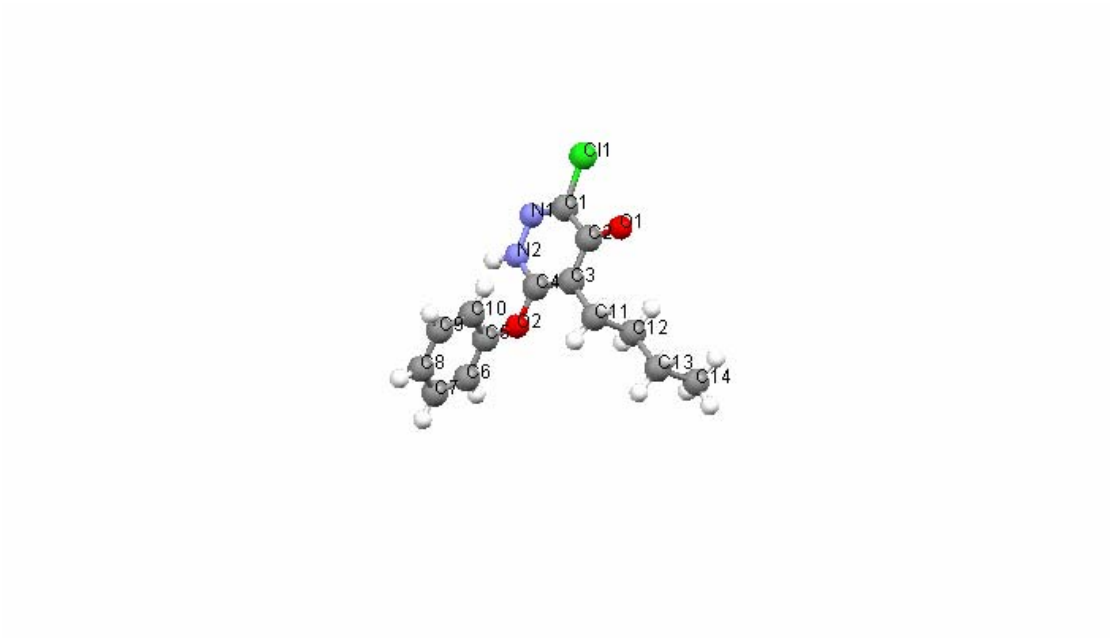
5-hydroxy-2-methyl-4,6-diphenylpyridazin-3(2H)-one (18)





X-ray crystal structure assignments of compounds **12a**:





Crystal structure obtained by H. Adams at the university of Sheffield

Table 1. Crystal data and structure refinement for ohj78_0m.

Identification code	ohj78_0m	
Empirical formula	C14 H15 Cl N2 O2	
Formula weight	278.73	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.227(2) Å	α= 90°.
	b = 12.144(3) Å	β= 91.550(15)°.
	c = 12.904(3) Å	γ = 90°.
Volume	1445.5(6) $Å^3$	

Z	4
Density (calculated)	1.281 Mg/m^3
Absorption coefficient	0.264 mm^{-1}
F(000)	584
Crystal size	0.16 x 0.08 x 0.04 mm^3
Theta range for data collection	2.30 to 27.62°.
Index ranges	-11<=h<=11, -12<=k<=15, -16<=l<=16
Reflections collected	11319
Independent reflections	3280 [R(int) = 0.0401]
Completeness to theta = 27.62°	98.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9895 and 0.9590
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3280 / 0 / 174
Goodness-of-fit on F^2	0.990
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1055
R indices (all data)	R1 = 0.0916, wR2 = 0.1266
Largest diff. peak and hole	0.218 and -0.144 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ohj78_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	4290(1)	4458(1)	1513(1)	82(1)
N(1)	5563(2)	3223(1)	2855(1)	53(1)
N(2)	6516(2)	2436(1)	3146(1)	50(1)
O(1)	6149(2)	3186(1)	132(1)	65(1)
O(2)	8179(1)	1085(1)	2918(1)	58(1)
C(1)	5498(2)	3443(2)	1873(2)	48(1)
C(2)	6312(2)	2909(2)	1060(1)	46(1)

C(3)	7284(2)	2071(2)	1427(1)	45(1)
C(4)	7337(2)	1890(2)	2469(2)	45(1)
C(5)	9600(2)	1349(2)	3236(1)	51(1)
C(6)	10351(3)	497(2)	3711(2)	74(1)
C(7)	11763(3)	685(3)	4060(2)	97(1)
C(8)	12382(3)	1697(3)	3941(2)	101(1)
C(9)	11637(3)	2532(3)	3465(2)	86(1)
C(10)	10202(2)	2363(2)	3104(2)	64(1)
C(11)	8103(2)	1381(2)	670(2)	58(1)
C(12)	7130(2)	485(2)	181(2)	58(1)
C(13)	7882(3)	-221(2)	-608(2)	79(1)
C(14)	6893(3)	-1075(2)	-1102(2)	93(1)

Table 3. Bond lengths [Å] and angles [°] for ohj78_0m.

Cl(1)-C(1)	1.7176(19)
N(1)-C(1)	1.294(2)
N(1)-N(2)	1.346(2)
N(2)-C(4)	1.346(2)
N(2)-H(2)	0.9859
O(1)-C(2)	1.250(2)
O(2)-C(4)	1.369(2)
O(2)-C(5)	1.401(2)
C(1)-C(2)	1.458(3)
C(2)-C(3)	1.429(2)
C(3)-C(4)	1.361(3)
C(3)-C(11)	1.506(3)
C(5)-C(10)	1.364(3)
C(5)-C(6)	1.380(3)
C(6)-C(7)	1.386(3)
C(6)-H(6)	0.9300
C(7)-C(8)	1.367(4)
C(7)-H(7)	0.9300

C(8)-C(9)	1.362(4)
C(8)-H(8)	0.9300
C(9)-C(10)	1.406(3)
C(9)-H(9)	0.9300
C(10)-H(10)	0.9300
C(11)-C(12)	1.536(3)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.513(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(14)	1.511(3)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600

C(1)-N(1)-N(2)	115.59(16)
N(1)-N(2)-C(4)	122.93(16)
N(1)-N(2)-H(2)	112.4
C(4)-N(2)-H(2)	124.3
C(4)-O(2)-C(5)	118.45(15)
N(1)-C(1)-C(2)	126.97(17)
N(1)-C(1)-Cl(1)	115.18(15)
C(2)-C(1)-Cl(1)	117.84(14)
O(1)-C(2)-C(3)	124.60(18)
O(1)-C(2)-C(1)	121.27(17)
C(3)-C(2)-C(1)	114.13(16)
C(4)-C(3)-C(2)	116.59(17)
C(4)-C(3)-C(11)	123.07(17)
C(2)-C(3)-C(11)	120.18(17)
N(2)-C(4)-C(3)	123.75(17)
N(2)-C(4)-O(2)	113.56(16)

C(3)-C(4)-O(2)	122.59(18)
C(10)-C(5)-C(6)	122.1(2)
C(10)-C(5)-O(2)	123.51(18)
C(6)-C(5)-O(2)	114.39(19)
C(5)-C(6)-C(7)	118.5(3)
C(5)-C(6)-H(6)	120.7
C(7)-C(6)-H(6)	120.7
C(8)-C(7)-C(6)	120.2(3)
C(8)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9
C(9)-C(8)-C(7)	120.9(3)
C(9)-C(8)-H(8)	119.6
C(7)-C(8)-H(8)	119.6
C(8)-C(9)-C(10)	120.0(3)
C(8)-C(9)-H(9)	120.0
C(10)-C(9)-H(9)	120.0
C(5)-C(10)-C(9)	118.3(2)
C(5)-C(10)-H(10)	120.9
C(9)-C(10)-H(10)	120.9
C(3)-C(11)-C(12)	111.30(17)
C(3)-C(11)-H(11A)	109.4
C(12)-C(11)-H(11A)	109.4
C(3)-C(11)-H(11B)	109.4
C(12)-C(11)-H(11B)	109.4
H(11A)-C(11)-H(11B)	108.0
C(13)-C(12)-C(11)	113.87(18)
C(13)-C(12)-H(12A)	108.8
C(11)-C(12)-H(12A)	108.8
C(13)-C(12)-H(12B)	108.8
C(11)-C(12)-H(12B)	108.8
H(12A)-C(12)-H(12B)	107.7
C(14)-C(13)-C(12)	113.0(2)
C(14)-C(13)-H(13A)	109.0
C(12)-C(13)-H(13A)	109.0

C(14)-C(13)-H(13B)	109.0
C(12)-C(13)-H(13B)	109.0
H(13A)-C(13)-H(13B)	107.8
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for ohj78_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

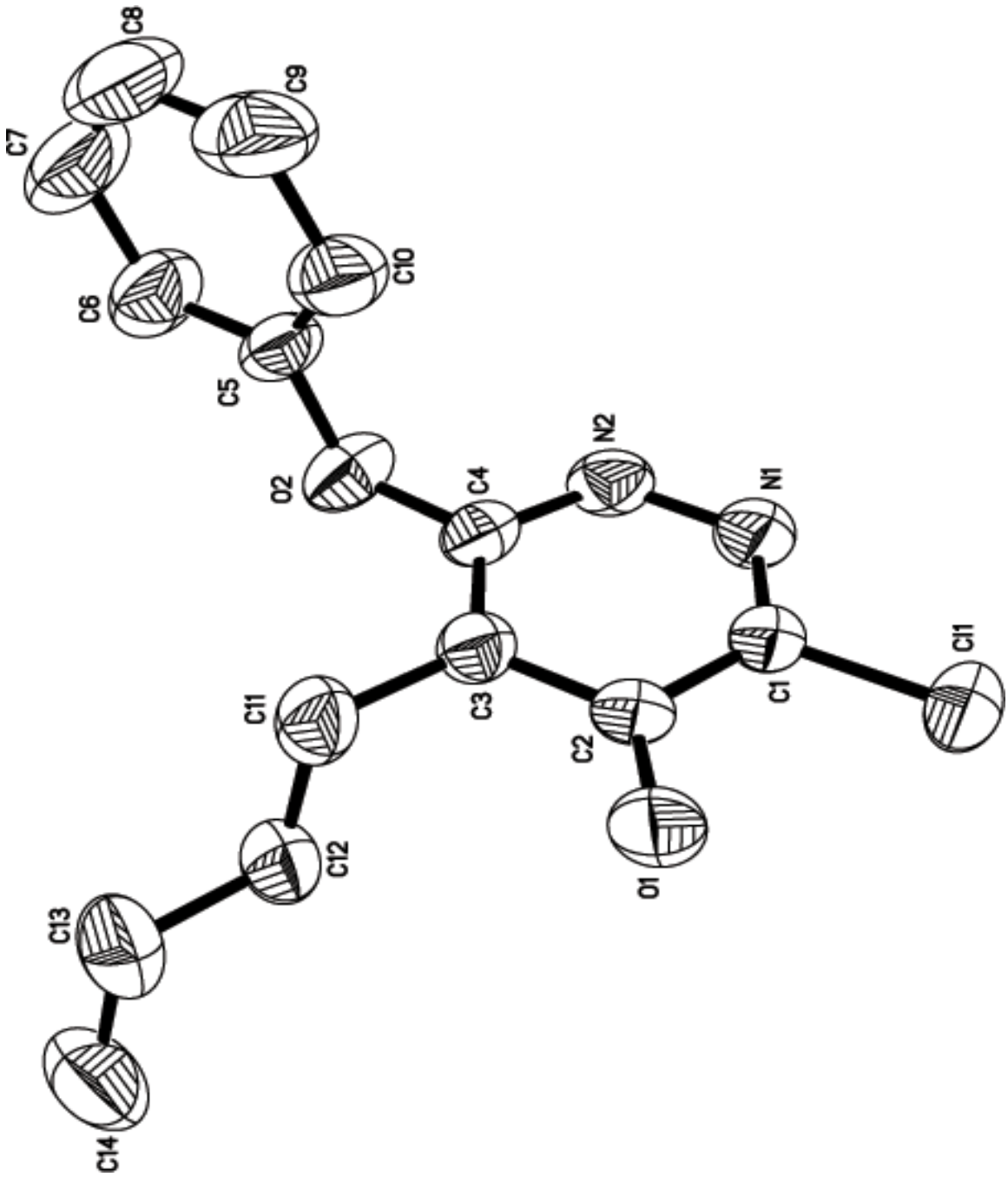
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	90(1)	83(1)	71(1)	-13(1)	-19(1)	45(1)
N(1)	56(1)	65(1)	39(1)	-7(1)	-2(1)	9(1)
N(2)	55(1)	64(1)	32(1)	1(1)	-2(1)	0(1)
O(1)	92(1)	73(1)	30(1)	0(1)	-4(1)	19(1)
O(2)	48(1)	58(1)	68(1)	17(1)	-13(1)	-2(1)
C(1)	49(1)	54(1)	41(1)	-8(1)	-6(1)	9(1)
C(2)	51(1)	53(1)	33(1)	-5(1)	-4(1)	2(1)
C(3)	43(1)	53(1)	41(1)	-1(1)	0(1)	4(1)
C(4)	39(1)	48(1)	46(1)	3(1)	-8(1)	-1(1)
C(5)	41(1)	73(1)	39(1)	1(1)	-7(1)	8(1)
C(6)	69(2)	92(2)	61(2)	9(1)	-12(1)	20(1)
C(7)	68(2)	144(3)	79(2)	7(2)	-21(2)	34(2)
C(8)	54(2)	167(3)	81(2)	-22(2)	-21(2)	13(2)
C(9)	60(2)	116(2)	80(2)	-20(2)	-2(1)	-20(2)
C(10)	52(1)	78(2)	62(1)	-8(1)	-4(1)	-3(1)

C(11)	53(1)	70(1)	51(1)	0(1)	8(1)	14(1)
C(12)	59(1)	62(1)	54(1)	-6(1)	6(1)	11(1)
C(13)	74(2)	83(2)	80(2)	-18(1)	16(1)	16(1)
C(14)	106(2)	84(2)	89(2)	-33(2)	11(2)	3(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for ohj78_0m.

	x	y	z	U(eq)
H(2)	6462	2253	3888	87(8)
H(6)	9919	-187	3796	89
H(7)	12290	119	4377	117
H(8)	13325	1818	4189	121
H(9)	12077	3214	3378	103
H(10)	9678	2929	2784	77
H(11A)	8926	1039	1025	70
H(11B)	8469	1851	128	70
H(12A)	6780	13	727	70
H(12B)	6294	833	-153	70
H(13A)	8256	250	-1146	94
H(13B)	8700	-590	-271	94
H(14A)	6497	-1532	-572	139
H(14B)	7435	-1523	-1566	139
H(14C)	6120	-714	-1480	139

Ortep diagram:



Crystal data for $C_{14}H_{15}ClN_2O_2$; M = 278.73, crystallises from *unknown solvent* as colorless blocks; crystal dimensions 0.16 x 0.08 x 0.04 mm^3. Monoclinic, *a* = 9.227(2), *b* = 12.144(3), *c* = 12.904(3) Å, β = 91.550(15)° *U* = 1445.5(6) $Å^3$, *Z* = 4, D_c = 1.281 Mg/m^3, space group $P2_1/c$ ($P2_1/c$ C_{2h}^5, No.14), Mo-K_α radiation ($\bar{\lambda}$ = 0.71073 Å), μ(Mo-K_α) = 0.264 mm^{-1}, F(000) = 584.

Data collected were measured on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Cell parameters were refined from the setting angles of 1835 reflections (θ range 2.77 < 22.80°).

Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega. Of the 11319 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections (minimum and maximum transmission coefficients 0.9590 and 0.9895), 1865 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final R = 0.0418 (wR_2 = 0.1266, for all 3280 data, 174 parameters, mean and maximum δ/σ 0.000, 0.000) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.144 and 0.218 e.Å^{-3}. A weighting scheme $w = 1/[\sigma^2(Fo^2) + (0.0605*P)^2 + 0.00*P]$ where $P = (Fo^2 + 2 * Fc^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL[Y] as implemented on the Pentium computer.

Reference Y SHELXTL version, An integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Bruker AXS LTD

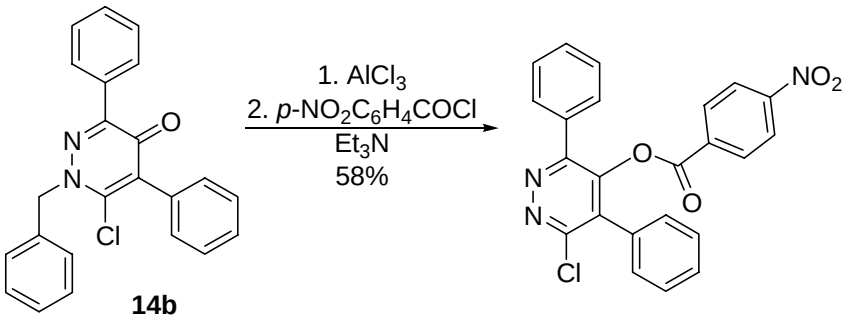
Supplementary material

anisotropic thermal vibrational parameters with e.s.d.s

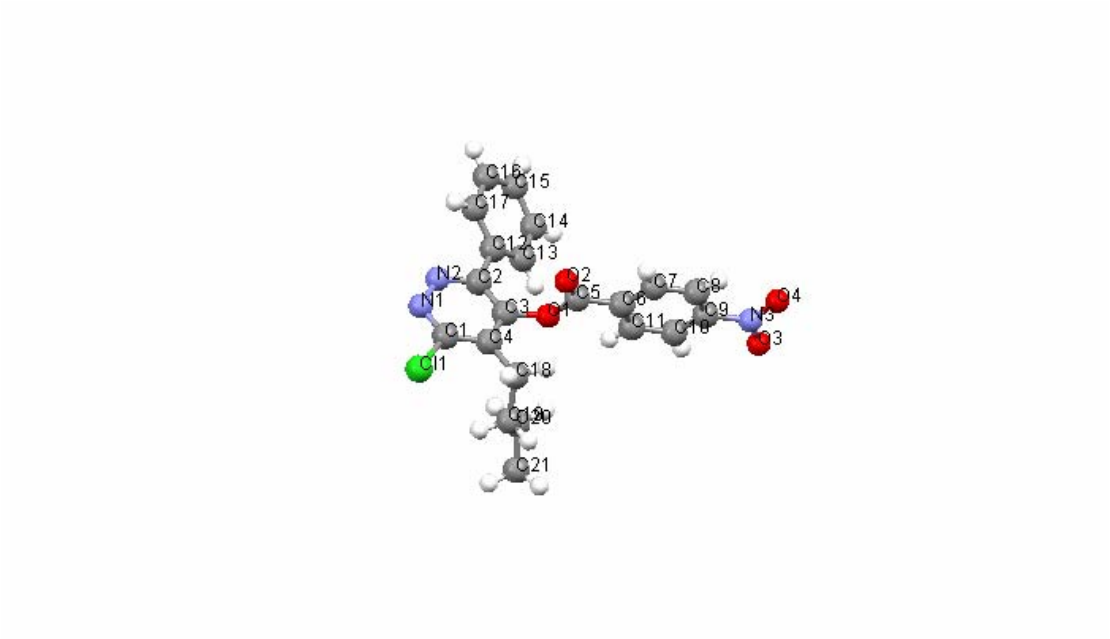
hydrogen atom position parameters

observed structure amplitudes and calculated structure factors.

X-ray crystal structure assignments of compounds **14b**:



14b



Crystal structure obtained by H. Adams at the university of Sheffield

Table 1. Crystal data and structure refinement for ohj84.

Identification code	ohj84	
Empirical formula	C21 H18 Cl N3 O4	
Formula weight	411.83	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4/n	
Unit cell dimensions	a = 25.7394(10) Å	α= 90°.
	b = 25.7394(10) Å	β= 90°.
	c = 5.9168(6) Å	γ = 90°.
Volume	3920.0(5) Å^3	
Z	8	

Density (calculated)	1.396 Mg/m^3
Absorption coefficient	0.228 mm^{-1}
F(000)	1712
Crystal size	0.18 x 0.08 x 0.06 mm^3
Theta range for data collection	1.58 to 25.00°.
Index ranges	-30<=h<=30, -30<=k<=30, -7<=l<=7
Reflections collected	53474
Independent reflections	3445 [R(int) = 0.1151]
Completeness to theta = 25.00°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9864 and 0.9600
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3445 / 0 / 263
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.0966
R indices (all data)	R1 = 0.0801, wR2 = 0.1143
Largest diff. peak and hole	0.340 and -0.396 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ohj84. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	10769(1)	2986(1)	2906(1)	38(1)
N(1)	10019(1)	3278(1)	5440(4)	26(1)
N(2)	9646(1)	3234(1)	7017(4)	24(1)
N(3)	9271(1)	-413(1)	12129(4)	27(1)
O(1)	9780(1)	1875(1)	8654(3)	21(1)
O(2)	9326(1)	1590(1)	5636(3)	28(1)
O(3)	9522(1)	-492(1)	13854(3)	32(1)
O(4)	8969(1)	-729(1)	11317(4)	43(1)

C(1)	10304(1)	2867(1)	4954(5)	24(1)
C(2)	9566(1)	2782(1)	8069(4)	20(1)
C(3)	9866(1)	2345(1)	7518(4)	20(1)
C(4)	10251(1)	2372(1)	5898(5)	23(1)
C(5)	9494(1)	1509(1)	7491(5)	21(1)
C(6)	9442(1)	1018(1)	8783(4)	20(1)
C(7)	9148(1)	625(1)	7784(4)	21(1)
C(8)	9093(1)	151(1)	8884(4)	22(1)
C(9)	9332(1)	88(1)	10955(4)	21(1)
C(10)	9625(1)	473(1)	11983(5)	22(1)
C(11)	9677(1)	943(1)	10872(4)	21(1)
C(12)	9137(1)	2789(1)	9749(4)	20(1)
C(13)	9158(1)	2513(1)	11786(4)	22(1)
C(14)	8759(1)	2554(1)	13338(5)	24(1)
C(15)	8330(1)	2865(1)	12878(5)	26(1)
C(16)	8305(1)	3135(1)	10869(5)	27(1)
C(17)	8704(1)	3102(1)	9310(5)	24(1)
C(18)	10584(1)	1916(1)	5194(5)	30(1)
C(19)	11131(1)	1921(1)	6195(5)	38(1)
C(20)	11139(1)	1949(1)	8712(6)	40(1)
C(21)	11686(1)	1876(1)	9686(7)	54(1)

Table 3. Bond lengths [Å] and angles [°] for ohj84.

Cl(1)-C(1)	1.731(3)
N(1)-C(1)	1.321(3)
N(1)-N(2)	1.342(3)
N(2)-C(2)	1.336(3)
N(3)-O(4)	1.223(3)
N(3)-O(3)	1.225(3)
N(3)-C(9)	1.475(3)
O(1)-C(5)	1.380(3)
O(1)-C(3)	1.402(3)

O(2)-C(5)	1.198(3)
C(1)-C(4)	1.398(4)
C(2)-C(3)	1.402(3)
C(2)-C(12)	1.487(4)
C(3)-C(4)	1.379(4)
C(4)-C(18)	1.513(4)
C(5)-C(6)	1.482(3)
C(6)-C(11)	1.390(4)
C(6)-C(7)	1.394(4)
C(7)-C(8)	1.389(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.381(4)
C(8)-H(8)	0.9500
C(9)-C(10)	1.384(3)
C(10)-C(11)	1.385(3)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(12)-C(17)	1.399(4)
C(12)-C(13)	1.400(3)
C(13)-C(14)	1.382(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.390(4)
C(14)-H(14)	0.9500
C(15)-C(16)	1.379(4)
C(15)-H(15)	0.9500
C(16)-C(17)	1.382(4)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-C(19)	1.527(4)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.491(4)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900

C(20)-C(21)	1.533(4)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800

C(1)-N(1)-N(2)	118.7(2)
C(2)-N(2)-N(1)	120.5(2)
O(4)-N(3)-O(3)	123.6(2)
O(4)-N(3)-C(9)	117.7(2)
O(3)-N(3)-C(9)	118.8(2)
C(5)-O(1)-C(3)	115.72(19)
N(1)-C(1)-C(4)	126.1(2)
N(1)-C(1)-Cl(1)	113.3(2)
C(4)-C(1)-Cl(1)	120.6(2)
N(2)-C(2)-C(3)	120.4(2)
N(2)-C(2)-C(12)	114.5(2)
C(3)-C(2)-C(12)	125.1(2)
C(4)-C(3)-O(1)	119.3(2)
C(4)-C(3)-C(2)	121.0(2)
O(1)-C(3)-C(2)	119.6(2)
C(3)-C(4)-C(1)	113.2(2)
C(3)-C(4)-C(18)	124.0(2)
C(1)-C(4)-C(18)	122.8(2)
O(2)-C(5)-O(1)	122.1(2)
O(2)-C(5)-C(6)	126.1(2)
O(1)-C(5)-C(6)	111.9(2)
C(11)-C(6)-C(7)	120.8(2)
C(11)-C(6)-C(5)	122.5(2)
C(7)-C(6)-C(5)	116.7(2)
C(8)-C(7)-C(6)	119.6(2)
C(8)-C(7)-H(7)	120.2
C(6)-C(7)-H(7)	120.2

C(9)-C(8)-C(7)	118.2(2)
C(9)-C(8)-H(8)	120.9
C(7)-C(8)-H(8)	120.9
C(8)-C(9)-C(10)	123.3(2)
C(8)-C(9)-N(3)	118.2(2)
C(10)-C(9)-N(3)	118.5(2)
C(11)-C(10)-C(9)	118.0(2)
C(11)-C(10)-H(10)	121.0
C(9)-C(10)-H(10)	121.0
C(10)-C(11)-C(6)	120.1(2)
C(10)-C(11)-H(11)	119.9
C(6)-C(11)-H(11)	119.9
C(17)-C(12)-C(13)	118.8(2)
C(17)-C(12)-C(2)	118.4(2)
C(13)-C(12)-C(2)	122.7(2)
C(14)-C(13)-C(12)	120.3(2)
C(14)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8
C(13)-C(14)-C(15)	120.3(3)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9
C(16)-C(15)-C(14)	119.7(3)
C(16)-C(15)-H(15)	120.1
C(14)-C(15)-H(15)	120.1
C(15)-C(16)-C(17)	120.6(3)
C(15)-C(16)-H(16)	119.7
C(17)-C(16)-H(16)	119.7
C(16)-C(17)-C(12)	120.3(3)
C(16)-C(17)-H(17)	119.9
C(12)-C(17)-H(17)	119.9
C(4)-C(18)-C(19)	114.1(2)
C(4)-C(18)-H(18A)	108.7
C(19)-C(18)-H(18A)	108.7
C(4)-C(18)-H(18B)	108.7

C(19)-C(18)-H(18B)	108.7
H(18A)-C(18)-H(18B)	107.6
C(20)-C(19)-C(18)	113.7(3)
C(20)-C(19)-H(19A)	108.8
C(18)-C(19)-H(19A)	108.8
C(20)-C(19)-H(19B)	108.8
C(18)-C(19)-H(19B)	108.8
H(19A)-C(19)-H(19B)	107.7
C(19)-C(20)-C(21)	112.5(3)
C(19)-C(20)-H(20A)	109.1
C(21)-C(20)-H(20A)	109.1
C(19)-C(20)-H(20B)	109.1
C(21)-C(20)-H(20B)	109.1
H(20A)-C(20)-H(20B)	107.8
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for ohj84. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	40(1)	35(1)	39(1)	12(1)	15(1)	3(1)
N(1)	29(1)	23(1)	26(1)	2(1)	0(1)	-3(1)
N(2)	26(1)	20(1)	26(1)	1(1)	-1(1)	-1(1)

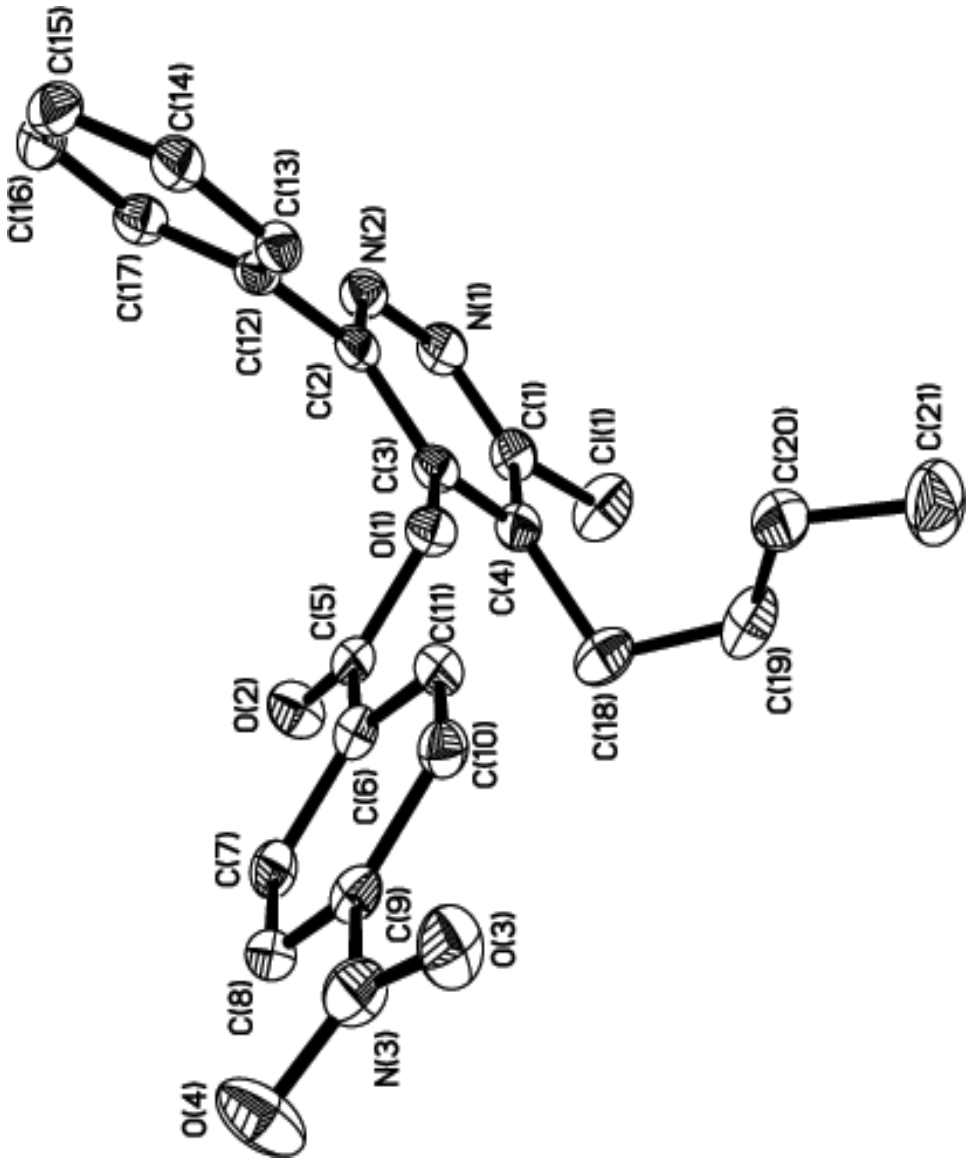
N(3)	30(1)	24(1)	28(1)	4(1)	1(1)	3(1)
O(1)	26(1)	16(1)	22(1)	3(1)	-1(1)	-1(1)
O(2)	35(1)	25(1)	24(1)	4(1)	-7(1)	-2(1)
O(3)	33(1)	31(1)	32(1)	11(1)	-9(1)	2(1)
O(4)	59(2)	28(1)	43(1)	6(1)	-16(1)	-18(1)
C(1)	24(2)	24(2)	25(2)	3(1)	1(1)	-3(1)
C(2)	22(1)	18(1)	20(1)	0(1)	-6(1)	-1(1)
C(3)	24(1)	16(1)	20(1)	2(1)	-4(1)	-2(1)
C(4)	23(1)	21(1)	25(2)	-1(1)	-1(1)	-1(1)
C(5)	19(1)	19(1)	25(2)	-2(1)	0(1)	3(1)
C(6)	17(1)	21(1)	21(1)	2(1)	2(1)	3(1)
C(7)	20(1)	24(1)	20(1)	3(1)	-2(1)	4(1)
C(8)	21(1)	20(1)	25(2)	-3(1)	-1(1)	-1(1)
C(9)	21(1)	19(1)	23(2)	2(1)	4(1)	3(1)
C(10)	21(1)	23(1)	22(1)	0(1)	-2(1)	3(1)
C(11)	20(1)	21(1)	23(1)	-2(1)	-1(1)	-2(1)
C(12)	23(1)	16(1)	22(1)	-3(1)	-3(1)	-1(1)
C(13)	21(1)	22(1)	22(1)	-1(1)	-4(1)	1(1)
C(14)	26(2)	23(1)	24(2)	0(1)	-3(1)	-1(1)
C(15)	28(2)	27(2)	25(2)	-2(1)	4(1)	1(1)
C(16)	24(2)	26(2)	31(2)	0(1)	-2(1)	5(1)
C(17)	31(2)	17(1)	24(2)	2(1)	-3(1)	1(1)
C(18)	36(2)	27(2)	28(2)	4(1)	11(1)	5(1)
C(19)	30(2)	31(2)	51(2)	11(2)	12(2)	6(1)
C(20)	36(2)	29(2)	56(2)	-6(2)	-6(2)	4(1)
C(21)	43(2)	40(2)	80(3)	8(2)	-17(2)	7(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for ohj84.

	x	y	z	U(eq)

H(7)	8986	681	6362	26
H(8)	8896	-122	8228	27
H(10)	9785	415	13409	26
H(11)	9874	1215	11538	26
H(13)	9449	2298	12104	26
H(14)	8777	2368	14723	29
H(15)	8055	2891	13944	32
H(16)	8011	3347	10552	33
H(17)	8684	3291	7936	29
H(18A)	10612	1913	3525	36
H(18B)	10409	1590	5658	36
H(19A)	11316	1603	5710	45
H(19B)	11322	2223	5578	45
H(20A)	10908	1677	9333	48
H(20B)	11002	2291	9196	48
H(21A)	11815	1530	9293	81
H(21B)	11674	1913	11334	81
H(21C)	11919	2140	9054	81

ORTEP diagram:



Crystal data for $C_{21}H_{18}ClN_3O_4$; M = 411.83. Crystallises from ethyl acetate as colourless needles; crystal dimensions 0.18 x 0.08 x 0.06 mm^3. Tetragonal, *a* = 25.7394(10), *b* = 25.7394(10), *c* = 5.9168(6) Å, *U* = 3920.0(5) $Å^3$, *Z* = 8, D_C = 1.396 Mg/m^3, space group P4/n (No.96), Mo-K_α radiation ($\bar{\lambda}$ = 0.71069 Å), μ(Mo-K_α) = 1.396 mm^{-1}, F(000) = 1712.

Data collected were measured on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Cell parameters were refined from the setting angles of 3469 reflections (θ range 1.58 < 25.00°).

Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega. Of the 53474 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi empirical methods based on symmetry-equivalent and repeated reflections (minimum and maximum transmission coefficients 0.9600 and 0.9864), 2407 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Refinement converged at a final R = 0.0450 (wR_2 = 0.1143, for all 3445 data, 263 parameters, mean and maximum δ/σ 0.000, 0.000) with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.396 and 0.340 e.Å^{-3}. A weighting scheme $w = 1/[\sigma^2(Fo^2) + (0.0469*P)^2 + 2.7885*P]$ where $P=(Fo^2 + 2 * Fc^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL[Y] as implemented on the Viglen pentium computer.

Reference Y SHELXTL version, an integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Bruker AXS LTD

Supplementary material

anisotropic thermal vibrational parameters with e.s.d.s

hydrogen atom position parameters

observed structure amplitudes and calculated structure factors.