TMPZnCl·LiCl: A New Active Selective Base for the Directed Zincation of Sensitive Aromatics and Heteroaromatics

Marc Mosrin and Paul Knochel*

Department Chemie & Biochemie, Ludwig-Maximilians-Universität, Butenandtstrasse 5-13, 81377, München (Germany)

Paul.Knochel@cup.uni-muenchen.de

Supporting Information

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1) General considerations

Unless otherwise indicated, all reactions were carried out with magnetic stirring and in flame-dried glassware under argon. Syringes used to transfer reagents and solvents were purged with argon prior to use. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC). TLC was performed with aluminium plates covered with SiO_2 (Merck 60, F-254) and visualized either by UV detection or submerging in $KMnO_4$ solution (1.5 g $KMnO_4$, 10 g K_2CO_3, and 1.25 mL 10% NaOH solution in 200 mL H_2O). Purification via column chromatography was performed using Merck silica gel 60 (40 – 63 μm 230-400 mesh ASTM from Merck). Melting points were measured using a Büchi B-540 apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 and chemical shifts (δ) are reported in parts per million (ppm). Mass spectra and high resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI) except where otherwise noted. GCs were recorded on machines of the types *Hewlett-Packard* 6890 or 5890 Series II

(*Hewlett Packard*, 5% phenylmethylpolysiloxane; length: 10 m, diameter: 0.25 mm; film thickness: 0.25 μm).

*i*PrMgCl·LiCl solution was obtained from Chemetall (Frankfurt, Germany) as 14% solution (in THF), and titrated with iodine prior to use. A CuCN·2LiCl (1 M) solution was prepared by heating 1 equiv CuCN and 2 equiv LiCl under vacuum at 130 °C for 6 h. THF was added slowly and the solution was stirred overnight. Acid chlorides, liquid aldehydes were distilled under argon prior to use.

2) Experimental Procedures and Analytical Data

Typical Procedure 1: Preparation of the reagent TMPZnCl·LiCl (2):

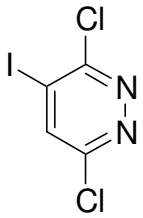
A dry and argon flushed 250 mL Schlenk-flask, equipped with a magnetic stirrer and a septum, was charged with freshly 2,2,6,6-tetramethylpiperidine (10.22 mL, 60 mmol) dissolved in THF (60 mL). This solution was cooled to -40 °C and *n*-BuLi (2.4 M in hexane, 25 mL, 60 mmol) was dropwise added. After the addition was complete, the reaction mixture was allowed to warm up slowly to -10 °C for 1 h. $ZnCl_2$ (1.0 M in THF, 66 mL, 66 mmol) was dropwise added and the resulting solution was stirred for 30 min at -10 °C and then for 30 min at 25 °C. The solvents were then removed under vacuum affording a yellowish solid. Freshly distilled THF was then slowly added under vigorous stirring until the salts were completely dissolved. The freshly prepared TMPZnCl·LiCl (**2**) solution was titrated prior to use at 25 °C with benzoic acid using 4-(phenylazo)diphenylamine[1] as indicator. A concentration of 1.3 M in THF was obtained.

Typical procedure for the zincation of polyfunctionalized aromatics and heterocycles with TMPZnCl·LiCl (TP 2):

A dry and argon flushed 10 mL Schlenk-flask, equipped with a magnetic stirring bar and a septum was charged with the zinc base (**2**; 1.1 equiv). After setting the desired temperature (Table 1), a solution of the corresponding arene (1.0 mmol) in dry THF (2 mL) was dropwise added and stirred at the same

temperature. The completion of the metalation was checked by GC-analysis of reaction aliquots quenched with a solution of I_2 in dry THF.

Synthesis of 3,6-dichloro-4-iodopyridazine (5a):



3,6-Dichloropyridazine (**3**) (149 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 30 min according to **TP 2**. I_2 (381 mg, 1.5 mmol) dissolved in dry THF (2 mL) was then dropwise added and the resulting mixture was stirred for 0.5 h. The reaction mixture was quenched with a sat. aq. $Na_2S_2O_3$ solution (10 mL) and with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:2) furnished compound **5a** (231 mg, 84%) as a colourless solid.

m.p.: 145.1 – 146.6 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.06 (s, 1 H).

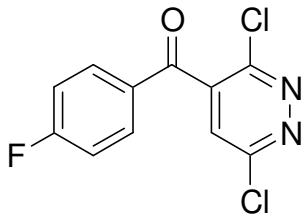
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 159.7, 153.9, 139.7, 105.4.

MS (70 eV, EI) *m/z* (%): 274 (95) [M^+], 127 (23), 123 (10), 121 (10), 119 (100), 86 (15), 84 (43), 49 (8).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3092, 3020, 1796, 1516, 1488, 1464, 1332, 1296, 1276, 1236, 1152, 1136, 1060, 1044, 992, 956, 900, 812, 764, 728, 672, 660, 628, 608, 588, 564.

HRMS (EI) for $\mathbf{C_4HCl_2IN_2}$ (273.8561): 273.8538.

Synthesis of (3,6-dichloropyridazin-4-yl)(4-fluorophenyl)methanone (5b):



3,6-Dichloropyridazine (**3**) (149 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 30 min according to **TP 2**. After cooling to –20 °C, CuCN·2LiCl (1.0 M in THF, 1.1 mmol, 1.1 equiv) was added and the resulting mixture was stirred for 30 min at this temperature. 4-Fluorobenzoyl chloride (317 mg, 2.0 mmol) was then slowly added and the resulting mixture was allowed to warm up slowly to 10 °C. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/ pentane, 1:1) furnished compound **5b** (259 mg, 96%) as a white solid.

m.p.: 71.1 – 72.6 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.79-7.83 (m, 2 H), 7.51 (s, 1 H), 7.19-7.24 (m, 2 H).

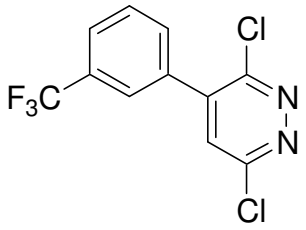
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 187.4, 167.0 (d, *J* (C-F) = 259.9 Hz), 156.3, 151.5, 139.6, 132.8 (d, *J* (C-F) = 9.9 Hz), 130.4 (d, *J* (C-F) = 3.1 Hz), 127.7, 116.8 (d, *J* (C-F) = 22.6 Hz).

MS (70 eV, EI) *m/z* (%): 270 (11) [M^+], 123 (100), 95 (19).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3067, 2927, 2358, 1917, 1673, 1590, 1504, 1414, 1344, 1319, 1256, 1237, 1178, 1157, 1140, 1103, 1041, 1009, 967, 955, 909, 849, 841, 818, 795, 760, 753, 683, 659, 650, 645, 638, 633, 625, 620, 614, 606, 602.

HRMS (EI) for **$C_{11}H_5Cl_2FN_2O$** (269.9763): 269.9762.

Synthesis of 3,6-dichloro-4-(3-(trifluoromethyl)phenyl)pyridazine (5c):



3,6-Dichloropyridazine (**3**) (149 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 30 min according to **TP 2**. $Pd(dba)_2$ (17 mg, 3 mol%) and P(o-furyl)$_3$ (14 mg, 6 mol%) dissolved in THF (2 mL), and mixed with 3-iodobenzomethyltrifluoride (354 mg, 1.3 mmol, 1.3 equiv) were then transferred via cannula to the reaction mixture. The resulting mixture was stirred for 1 h at 25 °C. The reaction mixture was then quenched with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the

solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:2) furnished compound **5c** (243 mg, 83%) as a colourless solid.

m.p.: 93.0 – 94.9 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.66-7.81 (m, 4 H), 7.53 (s, 1 H).

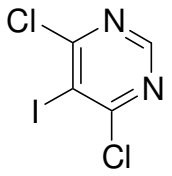
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 156.1, 154.4, 143.3, 141.2, 133.9, 131.5 (q, *J* (C-F) = 33.0 Hz), 129.6 (2), 128.3, 127.0 (q, *J* (C-F) = 3.8 Hz), 125.7 (q, *J* (C-F) = 3.8 Hz), 123.4 (q, *J* (C-F) = 272.5 Hz).

MS (70 eV, EI) *m/z* (%): 294 (60), 292 (100) [M^+], 266 (17), 264 (25), 229 (28), 206 (16), 204 (49), 194 (21), 169 (13), 138 (10), 136 (24), 113 (25), 59 (18).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3048, 2359, 1743, 1614, 1558, 1485, 1435, 1361, 1323, 1309, 1281, 1241, 1226, 1214, 1167, 1144, 1109, 1097, 1078, 1060, 1042, 1001, 933, 917, 903, 884, 803, 782, 755, 709, 697, 660, 645, 639, 632, 625, 620, 614, 606, 601.

HRMS (EI) for **$C_{11}H_5Cl_2F_3N_2$** (291.9782): 291.9785.

Synthesis of 4,6-dichloro-5-iodo-pyrimidine (8a):



4,6-Dichloropyrimidine **6** (149 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 45 min according to **TP 2**. I_2 (381 mg, 1.5 mmol) dissolved in dry THF (2 mL) was then dropwise added and the resulting mixture was stirred for 0.5 h. The reaction mixture was

quenched with a sat. aq. $Na_2S_2O_3$ solution (10 mL) and with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:4) furnished compound **8a** (227 mg, 83%) as a colourless solid.

m.p.: 134.9-136.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.65 (s, 1 H).

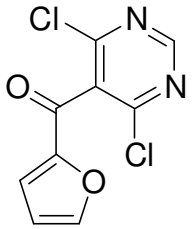
^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.6, 156.8, 98.9.

MS (70 eV, EI) *m/z* (%)**:** 274 (100) [M^+], 239 (27), 97 (12), 83 (12), 57 (21).

IR (ATR) $\tilde{\nu}$ (cm^{-1})**:** 2923, 2855, 1900, 1499, 1386, 11341, 1296, 1214, 1080, 1014, 790, 763, 745.

HRMS (EI) for **$C_4HCl_2IN_2$** (273.8561): 273.8565.

Synthesis of (4,6-dichloropyrimidin-5-yl)(furan-2-yl)methanone (8b):



4,6-Dichloropyrimidine **6** (149 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 45 min according to **TP 2**. CuCN·2LiCl (1.0 M solution in THF, 1.1 mL, 1.1 mmol) was slowly added at -20 °C and the reaction mixture was stirred at the same temperature for 30 min. Then, furan-2-carbonyl chloride (261 mg, 2.0 mmol) was dropwise added at -20 °C and the

resulting mixture was allowed to warm up slowly to 25 °C overnight. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (30 mL), extracted with diethyl ether (5 × 30 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated in vacuo. Purification by flash-chromatography (CH_2Cl_2/pentane 1:1) furnished **8b** as a colourless solid (172 mg, 71%).

m.p.: 143.6 – 145.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ**:** 8.88 (s, 1 H), 7.70 (m, 1 H), 7.28 (m, 1 H), 6.66 (m, 1 H).

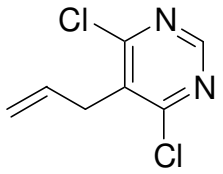
^{13}C NMR (100 MHz, $CDCl_3$) δ**:** 175.6, 158.8, 158.4, 150.8, 149.0, 130.9, 121.5, 113.5.

MS (70 eV, EI) *m/z* (%)**:** 242 (48) [M^+], 167 (49), 95 (100), 58 (21), 43 (33).

IR (ATR) $\tilde{\nu}$ (cm^{-1})**:** 3133, 2969, 2359, 2340, 1738, 1636, 1558, 1540, 1512, 1450, 1403, 1375, 1361, 1297, 1230, 1216, 1168, 1123, 1083, 1032, 956, 904, 888, 878, 815, 789, 781, 746, 738, 668, 626, 615, 609.

HRMS (EI) for **$C_9H_4Cl_2N_2O_2$** (241.9650): 241.9653.

Synthesis of 5-allyl-4,6-dichloropyrimidine (8c):



4,6-Dichloropyrimidine **6** (149 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 45 min according to **TP 2**. CuCN·2LiCl (1 M in THF; 0.05 mL, 5 mol %) was then slowly added at -20 °C. Allyl bromide (242 mg, 2.0 mmol) was then slowly added at -60 °C.

The resulting mixture was then allowed to warm up slowly to 0 °C for 4 h. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (5 × 30 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated in vacuo. Purification by flash-chromatography (CH_2Cl_2/pentane 1:2) furnished **8c** as a colourless solid (215 mg, 89%).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.64 (s, 1 H), 5.80-5.90 (m, 1 H), 5.09–5.18 (m, 2 H), 3.64 (dt, ^3J = 6.4 Hz, ^4J = 1.4 Hz, 2 H).

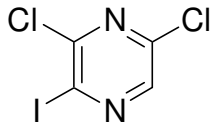
^{13}C NMR (75 MHz, $CDCl_3$) δ: 162.0, 155.8, 130.9, 130.6, 118.2, 34.0.

MS (70 eV, EI) *m/z* (%)**:** 188 (70) [M^+], 125 (22), 117 (44), 90 (59), 64 (35), 49 (43), 41 (100).

IR (ATR) $\tilde{\nu}$ (cm^{-1})**:** 2969, 2360, 1739, 1639, 1539, 1513, 1435, 1406, 1375, 1348, 1313, 1290, 1200, 1162, 1129, 1090, 989, 929, 906, 839, 777, 687, 668, 627, 621, 616.

HRMS (EI) for **$C_7H_6Cl_2N_2$** (187.9908): 187.9913.

Synthesis of 3,5-dichloro-2-iodopyrazine (11a):



2,6-Dichloropyrazine (**9**) (149 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 30 min according to **TP 2**. I_2 (381 mg, 1.5 mmol) dissolved in dry THF (2 mL) was then dropwise added and the resulting mixture was stirred for 0.5 h. The reaction mixture was quenched with a sat. aq. $Na_2S_2O_3$ solution (10 mL) and with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent

was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:2) furnished compound **11a** (251 mg, 90%) as a colourless solid.

m.p.: 101.3 – 103.0 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.30 (s, 1 H).

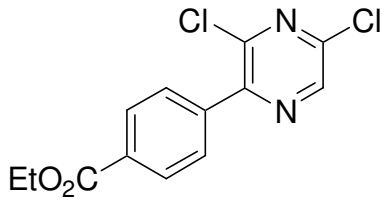
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 153.1, 146.9, 142.4, 115.7.

MS (70 eV, EI) *m/z* (%): 274 (100) [M^+], 147 (75), 127 (18), 86 (32), 57 (21), 44 (94).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2969, 2633, 2281, 1784, 1738, 1510, 1491, 1379, 1353, 1323, 1274, 1230, 1217, 1205, 1175, 1162, 1143, 1018, 893, 843, 655, 634, 618, 611, 604.

HRMS (EI) for **$C_4HCl_2IN_2$** (273.8561): 273.8555.

Synthesis of ethyl 4-(3,5-dichloropyrazin-2-yl)benzoate (11b):



2,6-Dichloropyrazine (**9**) (149 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 30 min according to **TP 2**. $Pd(dba)_2$ (17 mg, 3 mol%) and P(*o*-furyl)$_3$ (14 mg, 6 mol%) dissolved in THF (2 mL), followed by the addition of ethyl 4-iodobenzoate (359 mg, 1.3 mmol), were then transferred *via* cannula to the reaction mixture. The reaction mixture was stirred at 25 °C for 1.5 h. with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried

over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:2) furnished compound **11b** (251 mg, 87%) as a colourless solid.

m.p.: 88.5 – 90.0 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.59 (s, 1 H), 8.14 (d, J = 8.6 Hz, 2 H), 7.84 (d, J = 8.6 Hz, 2 H), 4.40 (q, J = 7.2 Hz, 2 H), 1.40 (t, J = 7.0 Hz, 3 H).

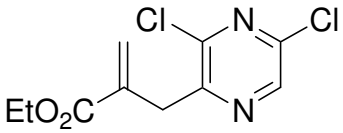
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 165.8, 150.1, 145.9, 142.0, 139.0, 131.6, 129.4 (2), 61.2, 14.3.

MS (70 eV, EI) *m/z* (%): 296 (32) [M^+], 270 (24), 268 (38), 251 (100), 223 (26).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3086, 3005, 2985, 2359, 1966, 1708, 1611, 1569, 1537, 1507, 1482, 1466, 1446, 1423, 1408, 1366, 1310, 1283, 1263, 1190, 1175, 1140, 1131, 1114, 1098, 1028, 1021, 1009, 915, 858, 843, 786, 758, 719, 698, 657, 634, 621, 616, 610, 602.

HRMS (EI) for **$C_{13}H_{10}Cl_2N_2O_2$** (296.0119): 296.0119.

Synthesis of ethyl 2-((3,5-dichloropyrazin-2-yl)methyl)acrylate (11c):



2,6-Dichloropyrazine (**9**) (149 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 30 min according to **TP 2**. After cooling to –50 °C, ethyl (2-bromomethyl)acrylate (230 mg, 1.2 mmol) and CuCN·2LiCl (1.0 M solution in THF, 5 drops) were added and the resulting mixture was allowed to warm up slowly to -20 °C. The reaction mixture was

quenched with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:3) furnished compound **11c** (187 mg, 72%) as a colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.38 (s, 1 H), 6.34 (s, 1 H), 5.56 (s, 1 H), 4.14 (q, J = 7.1 Hz, 2 H), 3.92 (s, 2 H), 1.21 (t, J = 7.1 Hz, 3 H).

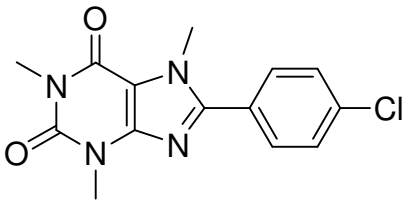
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 166.0, 151.5, 146.8, 145.0, 141.5, 136.0, 127.6, 60.9, 36.7, 14.0.

MS (70 eV, EI) *m/z* (%): 261 (100) [M^+-H], 163 (10).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2969, 2359, 1738, 1503, 1385, 1342, 1294, 1226, 1215, 1084, 1013, 987, 954, 795, 764, 749, 667, 621, 615, 608, 603.

HRMS (ESI) for **$C_{10}H_{10}Cl_2N_2O_2$** (260.0119 (M^+-H)): 261.0196.

Synthesis of 8-(4-chlorophenyl)-1,3,7-trimethyl-1H-purine-2,6(3H,7H)-dione (14a):



TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) was added to a solution of 1,3,7-trimethyl-1H-purine-2,6(3H,7H)-dione (**12**) (194 mg, 1.0 mmol) in THF (2 mL) at 25 °C and the reaction mixture was then stirred at this temperature for max. 5 min. $Pd(dba)_2$ (17 mg, 3 mol%) and P(o-furyl)$_3$ (14 mg, 6 mol%) dissolved in THF (2 mL), and mixed with 1-chloro-4-iodobenzene (310 mg, 1.3 mmol, 1.3 equiv) were then transferred via cannula to the reaction mixture. The resulting mixture was stirred for 1

h at 25 °C. The reaction mixture was then quenched with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/ether, 1:1) furnished compound **14a** (226 mg, 74%) as a colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.62 (d, J = 8.5 Hz, 2 H), 7.48 (d, J = 8.5 Hz, 2 H), 4.03 (s, 3 H), 3.59 (s, 3 H), 3.39 (s, 3 H).

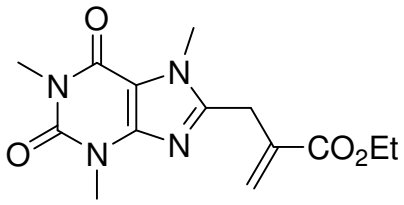
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 155.4, 151.5, 150.7, 148.1, 136.7, 130.4, 129.2, 126.7, 108.6, 33.9, 29.8, 28.0.

MS (70 eV, EI) *m/z* (%): 304 (100) [M^+], 82 (23), 67 (13).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2969, 1738, 1694, 1646, 1605, 1569, 1538, 1473, 1454, 1430, 1408, 1374, 1288, 1229, 1216, 1180, 1108, 1090, 1074, 1030, 1008, 977, 835, 803, 759, 749, 739, 730, 708, 685, 671, 650, 645, 639, 632, 625, 620, 614, 606. 601.

HRMS (ESI) for **$C_{14}H_{13}ClN_4O_2$** (304.0727): 304.0722.

Synthesis of ethyl 2-((1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-8-yl)methyl)acrylate (14b):



TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) was added to a solution of 1,3,7-trimethyl-1H-purine-2,6(3H,7H)-dione (**12**) (194 mg, 1.0 mmol) in THF (2 mL) at 25 °C and the reaction mixture was then stirred at this temperature for max. 5 min. After cooling to –50 °C, ethyl 2-(bromomethyl)acrylate (230 mg, 1.2 mmol) and CuCN·2LiCl (1.0 M solution in THF, 5 drops) were added and the resulting mixture was allowed to warm up slowly overnight. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/ether, 1:1) furnished compound **14b** (211 mg, 69%) as a colourless solid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 6.28 (s, 1 H), 5.49 (s, 1 H), 4.14 (q, J = 7.1 Hz, 2 H), 3.86 (s, 3 H), 3.70 (s, 2 H), 3.45 (s, 3 H), 3.29 (s, 3 H), 1.21 (t, J = 7.1 Hz, 3 H).

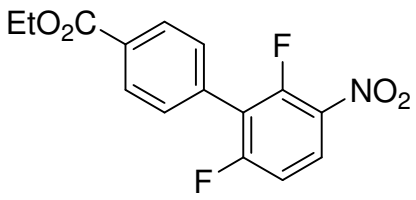
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 165.7, 155.1, 151.4, 150.8, 147.7, 135.0, 127.3, 107.4, 61.1, 31.8, 29.6, 29.3, 27.7, 14.0.

MS (70 eV, EI) *m/z* (%): 306 (78) [M^+], 260 (28), 232 (100), 219 (11), 67 (13).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2998, 2956, 2358, 1719, 1697, 1658, 1548, 1497, 1448, 1426, 1402, 1362, 1340, 1293, 1253, 1215, 1162, 1112, 1033, 978, 960, 939, 894, 858, 831, 812, 759, 743, 718, 693, 663, 641, 630, 602.

HRMS (ESI) for **$C_{14}H_{18}N_4O_4$** (306.1328): 306.1320.

Synthesis of ethyl 2',6'-difluoro-3'-nitrobiphenyl-4-carboxylate (17a):



2,4-Difluoro-1-nitrobenzene **15** (159 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 45 min according to **TP 2**. $Pd(dba)_2$ (17 mg, 3 mol%) and P(*o*-furyl)$_3$ (14 mg, 6 mol%) dissolved in THF (2 mL), followed by the addition of ethyl 4-iodobenzoate (359 g, 1.3 mmol), were then transferred *via* cannula at -20°C. The resulting mixture was allowed to warm up slowly to 25 °C overnight. The reaction mixture was then quenchend with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:2) furnished compound **17a** (281 mg, 92%) as a colourless solid.

m.p.: 85.0 – 86.7 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ**:** 8.09-8.18 (m, 1 H), 8.15 (d, *J* = 8.8 Hz, 2 H), 7.51 (d, *J* = 8.8 Hz, 2 H), 7.11-7.18 (m, 1 H), 4.40 (q, *J* = 7.0 Hz, 3 H), 1.40 (d, *J* = 7.0 Hz, 2 H).

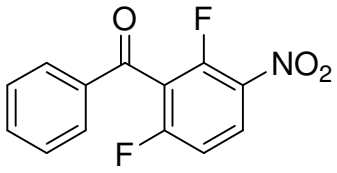
^{13}C NMR (75 MHz, $CDCl_3$) δ**:** 165.8, 162.5 (dd, *J* = 6.0 Hz, *J* = 260.1 Hz), 153.7 (dd, *J* = 6.0 Hz, *J* = 260.1 Hz), 131.2 (dd, *J* = 0.5 Hz, *J* = 3.9 Hz), 130.2 (dd, *J* = 1.8 Hz, *J* = 2.0 Hz), 129.7, 126.6 (dd, *J* = 1.8 Hz, *J* = 21.4 Hz), 120.2 (dd, *J* = 28.1 Hz, *J* = 1.8 Hz), 112.1 (dd, *J* = 4.3 Hz, *J* = 24.7 Hz), 61.3, 14.3.

MS (70 eV, EI) *m/z* (%)**:** 307 (23) [M^+], 279 (48), 262 (100), 216 (43), 188 (34), 44 (12).

IR (ATR) $\tilde{\nu}$ (cm^{-1})**:** 3101, 2969, 2359, 1712, 1621, 1589, 1567, 1535, 1510, 1472, 1404, 1368, 1341, 1304, 1286, 1269, 1215, 1185, 1170, 1148, 1127, 1103, 1070, 1020, 1011, 948, 879, 857, 824, 778, 756, 714, 702, 667, 636, 620, 607, 602.

HRMS (EI) for **$C_{15}H_{11}F_2NO_4$** (307.0656): 307.0651.

Synthesis of (2,6-difluoro-3-nitrophenyl)(phenyl)methanone (17b):



2,4-Difluoro-1-nitrobenzene **15** (159 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 45 min according to **TP 2**. CuCN·2LiCl (1.0 M solution in THF, 1.1 mL, 1.1 mmol) was slowly added at -40 °C and the reaction mixture was stirred at the same temperature for 30 min. Then, benzoyl chloride (281 mg, 2.0 mmol) was added dropwise at -40 °C and the resulting mixture was allowed to warm up slowly to 25 °C overnight. The reaction mixture was then quenchend with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:2) furnished compound **17b** (221 mg, 84%) as a colourless solid.

m.p.: 75.8 – 77.2 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ**:** 7.14-8.31 (m, 7 H).

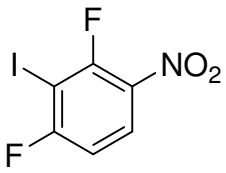
^{13}C NMR (75 MHz, $CDCl_3$) δ**:** 186.2, 162.2 (dd, J = 4.2 Hz, J = 262.4 Hz), 153.7 (dd, J = 9.0 Hz, J = 269.9 Hz), 135.7, 135.1, 133.8, 130.2, 129.6, 129.1, 128.7 (dd, J = 2.1 Hz, J = 10.9 Hz), 128.5, 119.3 (dd, J = 21.9 Hz, J = 2.1 Hz).

MS (70 eV, EI) *m/z* (%)**:** 263 (52) [M^+], 105 (100), 33 (77).

IR (ATR) $\tilde{\nu}$ (cm^{-1})**:** 3100, 1912, 1738, 1675, 1619, 1594, 1530, 1496, 1469, 1450, 1351, 1320, 1311, 1280, 1266, 1217, 1180, 1159, 1128, 1100, 1073, 1034, 1027, 1000, 970, 934, 862, 834, 828, 797, 774, 759, 731, 705, 692, 683, 668, 645, 638, 630, 626, 620, 614, 606, 601.

HRMS (EI) for **$C_{13}H_7F_2NO_3$** (263.0394): 263.0393.

Synthesis of 1,3-difluoro-2-iodo-4-nitrobenzene (17c):



2,4-Difluoro-1-nitrobenzene **15** (159 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 45 min according to **TP 2**. I_2 (381 mg, 1.5 mmol) dissolved in dry THF (2 mL) was then dropwise added and the resulting mixture was stirred for 0.5 h. The reaction mixture was quenched with a sat. aq. $Na_2S_2O_3$ solution (10 mL) and with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:1) furnished compound **17c** (256 mg, 90%) as a colourless solid.

m.p.: 46.1 – 47.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.12-8.17 (m, 1 H), 7.04-7.08 (m, 1 H).

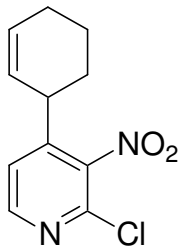
^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.6 (dd, *J* = 5.0 Hz, *J* = 252.6 Hz), 156.4 (dd, *J* = 6.9 Hz, *J* = 264.1 Hz), 127.7 (dd, *J* = 2.3 Hz, *J* = 10.3 Hz), 111.6 (dd, *J* = 4.2 Hz, *J* = 26.1 Hz), 74.3 (dd, *J* = 29.2 Hz, *J* = 1.9 Hz).

MS (70 eV, EI) *m/z* (%)**:** 285 (100) [M^+], 258 (17), 239 (19), 227 (17), 167 (25), 149 (66), 112 (58), 71 (11), 57 (12), 44 (12).

IR (ATR) $\tilde{\nu}$ (cm^{-1})**:** 3098, 2926, 2855, 2359, 1916, 1739, 1602, 1584, 1529, 1463, 1425, 1336, 1301, 1277, 1218, 1147, 1105, 1011, 860, 827, 751, 698, 669, 621, 616.

HRMS (EI) for **$C_6H_2F_2INO_2$** (284.9098): 284.9094.

Synthesis of 2-chloro-4-cyclohex-2-enyl-3-nitro-pyridine (20):



2-Chloro-3-nitropyridine (**18**) (159 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 30 min according to **TP 2**. After cooling to -50 °C, 3-bromo-cyclohexene (192 mg, 1.2 mmol) and CuCN·2LiCl (1.0 M solution in THF, 0.05 mL, 0.05 mmol) were added and the reaction mixture was stirred for 1 h at the same temperature. The reaction mixture was quenched

with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:1) furnished 2-chloro-4-cyclohex-2-enyl-3-nitro-pyridine (**20**) (173 mg, 73%) as a colourless solid.

m.p.: 54.5 – 55.4 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.44 (d, ^3J = 5.1 Hz, 1 H), 7.32 (d, ^3J = 5.1 Hz, 1 H), 6.07 (ddd, ^3J = 10.0 Hz, ^3J = 6.1 Hz, ^4J = 3.7 Hz, 1 H), 5.54 (dd, ^3J = 10.0, ^4J = 1.9 Hz, 1 H), 3.46 (m, 1 H), 2.09 (m, 3 H), 1.76 (m, 1 H), 1.64 (m, 1 H), 1.51 (m, 1 H).

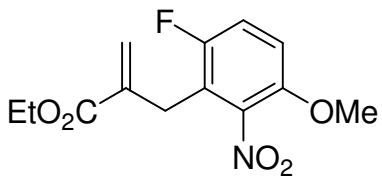
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 150.2, 150.0, 146.5, 141.8, 131.9, 125.9, 123.3, 37.4, 31.3, 24.7, 20.8.

MS (70 eV, EI) *m/z* (%): 237 (3) [M^+-H], 223 (31), 221 (100), 203 (48), 193 (48), 185 (20), 181 (45), 167 (32), 165 (31), 157 (21), 129 (29), 128 (31), 115 (21), 77 (35), 51 (22), 41 (34).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2939, 1589, 1539, 1446, 1361, 1347, 1231, 1137, 1041, 973, 918, 890, 855, 845, 757, 723, 691, 616.

HRMS (EI) for **$C_{11}H_{11}ClN_2O_2$** (237.0431 [M^+-H]): 237.0424 [M^+-H].

Synthesis of ethyl 2-(6-fluoro-3-methoxy-2-nitrobenzyl)acrylate (23):



4-Fluoro-1-methoxy-2-nitrobenzene (**21**) (171 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then

stirred at this temperature for 6 h according to **TP 2**. After cooling to –50 °C, ethyl 2-(bromomethyl)acrylate (230 mg, 1.2 mmol) and CuCN·2LiCl (1.0 M solution in THF, 5 drops) were added at -40 °C and the resulting mixture was stirred at the same temperature for 1 h. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:3) furnished compound **23** (189 mg, 67%) as a colourless oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.15 (m, 1 H), 8.89-8.93 (m, 1 H), 6.24 (s, 1 H), 5.31 (s, 1 H), 4.19 (q, J = 7.1 Hz, 2 H), 3.86 (s, 3 H), 3.63 (bs, 2 H), 1.27 (t, J = 7.1 Hz, 3 H).

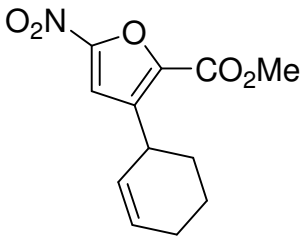
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 165.9, 154.3 (d, J = 243.6 Hz), 147.1 (d, J = 2.8 Hz), 136.2 (d, J = 0.8 Hz), 126.3 (d, J = 0.8 Hz), 120.0 (d, J = 21.9 Hz), 117.6, 117.3, 111.7 (d, J = 8.3 Hz), 61.1, 56.7, 26.9 (d, J = 2.9 Hz), 14.1.

MS (70 eV, EI) *m/z* (%): 283 (1) [M^+], 237 (100), 209 (88), 192 (58), 166 (20), 149 (21), 133 (16), 121 (13), 99 (11).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2969, 2359, 1738, 1503, 1385, 1342, 1294, 1226, 1215, 1084, 1013, 987, 954, 795, 764, 749, 667, 621, 615, 608, 603.

HRMS (ESI) for **$C_{13}H_{14}FNO_5$** (283.0856): 283.0845.

Synthesis of methyl 3-(cyclohex-2-enyl)-5-nitrofuran-2-carboxylate (26):



Methyl 5-nitrofuran-2-carboxylate (**24**) (171 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 30 min according to **TP 2**. After cooling to –50 °C, 3-bromocyclohexene (209 mg, 1.3 mmol) and CuCN·2LiCl (1.0 M solution in THF, 5 drops) were added and the resulting mixture was stirred for 1 h at this temperature. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:2) furnished compound **26** (179 mg, 72%) as a yellowish oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.20 (s, 1 H), 5.94 (m, 1 H), 5.56 (m, 1 H), 4.10 (m, 1 H), 3.92 (s, 3 H), 2.07 (m, 3 H), 1.50-1.69 (m, 3 H).

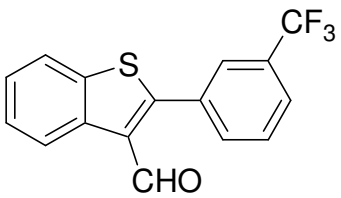
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 157.5, 142.6, 133.9, 130.4, 126.2, 120.1, 52.8, 32.2, 29.0, 24.6, 20.5.

MS (70 eV, EI) *m/z* (%): 252 (2) [M^+], 234 (100), 217 (55), 146 (10).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2936, 2356, 1729.35, 1629, 1594, 1532, 1502, 1435, 1398, 1338, 1288, 1226, 1206, 1110, 1091, 985, 925, 880, 848, 819, 799, 763, 725, 668, 634, 622.

HRMS (EI) for **$C_{12}H_{13}NO_5$** (251.0794): 251.0794.

Synthesis of 2-(3-(trifluoromethyl)phenyl)benzo[b]thiophene-3-carbaldehyde (29a):



Benzo[b]thiophene-3-carbaldehyde (**27**) (162 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 30 min according to **TP 2**. $Pd(dba)_2$ (17 mg, 3 mol%) and $P(o\text{-furyl})_3$ (14 mg, 6 mol%) dissolved in THF (2 mL), and mixed with 3-iodobenzomethyltrifluoride (354 mg, 1.3 mmol, 1.3 equiv) were then transferred via cannula to the reaction mixture. The resulting mixture was stirred for 1 h at 25 °C. The reaction mixture was then quenched with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:3) furnished compound **29a** (281 mg, 92%) as a colourless solid.

m.p.: 102.8 – 104.2 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 10.02 (s, 1 H), 8.79 (m, 1 H), 7.45-7.87 (m, 7 H).

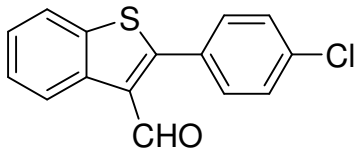
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 185.9, 158.0, 138.0, 136.8, 133.7, 132.4, 131.5 (q, *J* (C-F) = 33.0 Hz), 130.7, 129.5, 127.0 (q, *J* (C-F) = 3.8 Hz), 126.6 (q, *J* (C-F) = 3.8 Hz), 126.5, 126.2, 123.5 (q, *J* (C-F) = 272.5 Hz), 121.7.

MS (70 eV, EI) *m/z* (%): 306 (97) [M^+], 305 (100), 278 (12), 257 (13), 237 (28), 233 (18), 208 (29), 160 (13), 44 (40).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3068, 2866, 2359, 1926, 1745, 1669, 1590, 1520, 1483, 1459, 1438, 1421, 1392, 1351, 1325, 1310, 1288, 1265, 1217, 1178, 1156, 1118, 1097, 1092, 1073, 1051, 1018, 1000, 994, 966, 947, 933, 907, 868, 863, 812, 773, 754, 733, 703, 679, 653, 641, 633, 620, 608, 603.

HRMS (EI) for **$C_{16}H_9F_3OS$** (306.0326): 306.0326.

Synthesis of 2-(4-chlorophenyl)benzo[b]thiophene-3-carbaldehyde (29b):



Benzo[b]thiophene-3-carbaldehyde (**27**) (162 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 30 min according to **TP 2**. $Pd(dba)_2$ (17 mg, 3 mol%) and $P(o\text{-furyl})_3$ (14 mg, 6 mol%) dissolved in THF (2 mL), and mixed with 1-chloro-4-iodobenzene (310 mg, 1.3 mmol, 1.3 equiv) were then transferred via cannula to the reaction mixture. The resulting mixture was stirred for 2 h at 25 °C. The reaction mixture was then quenched with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:3) furnished compound **29b** (236 mg, 87%) as a colourless solid.

m.p.: 99.7 – 101.4 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 10.02 (s, 1 H), 8.76 (d, *J* = 8.0 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.42-7.54 (m, 6 H).

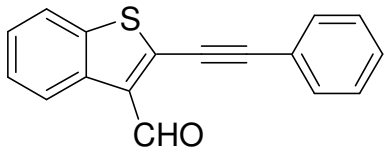
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 186.2, 158.9, 137.8, 136.9, 136.4, 131.6, 130.3, 130.0, 129.2, 126.4, 126.0, 125.2, 121.6.

MS (70 eV, EI) *m/z* (%): 272 (100) [M^+], 237 (54), 208 (34), 165 (12), 118 (20), 104 (23).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3054, 2969, 2867, 2362, 1947, 1739, 1671, 1590, 1562, 1517, 1482, 1457, 1431, 1407, 1397, 1346, 1265, 1218, 1187, 1161, 1135, 1109, 1091, 1050, 1020, 1012, 971, 952, 938, 846, 830, 813, 748, 723, 716, 710, 698, 667, 638, 616, 610, 603.

HRMS (EI) for **$C_{15}H_9ClOS$** (272.0063): 272.0057.

Synthesis of 2-(phenylethynyl)benzo[b]thiophene-3-carbaldehyde (29c):



Benzo[b]thiophene-3-carbaldehyde (**27**) (162 mg, 1.0 mmol) in THF (2 mL) was added to a solution of TMPZnCl·LiCl (**2**) (1.3 M in THF, 0.85 mL, 1.1 mmol) at 25 °C and the reaction mixture was then stirred at this temperature for 30 min according to **TP 2**. I_2 (381 mg, 1.5 mmol) dissolved in dry THF (2 mL) was then dropwise added and the resulting mixture was stirred for 0.5 h. To the solution of freshly generated *in situ* 2-iodobenzo[b]thiophene-3-carbaldehyde, NEt_3 (7 mL), CuI (8 mg, 4 mol%), $Pd(dba)_2$ (17 mg, 3 mol%) and P(o-furyl)$_3$ (14 mg, 6 mol%) in THF (2 mL) and phenylacetylene (254 mg, 1.5 mol, 1.5 equiv) were successively slowly added. The reaction mixture was stirred at rt for 2 h. The reaction mixture was quenched with a sat. aq. $Na_2S_2O_3$ solution (10 mL) and with a sat. aq. NH_4Cl solution (20 mL), extracted with diethyl ether (3 × 50 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2/pentane, 1:2) furnished compound **29c** (165 mg, 63%) as a yellowish solid.

m.p.: 104.9 – 106.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 10.47 (s, 1 H), 8.69 (m, 1 H), 7.77 (m, 1 H), 7.60 (m, 2 H), 7.38-7.51 (m, 5 H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ: 185.6, 138.9, 138.5, 135.9, 135.2, 131.8, 129.8, 128.6, 126.8, 126.5, 124.9, 121.6, 121.3, 102.9, 80.0.

MS (70 eV, EI) *m/z* (%): 262 (100) [M^+], 234 (38), 232 (13), 202 (11), 189 (13).

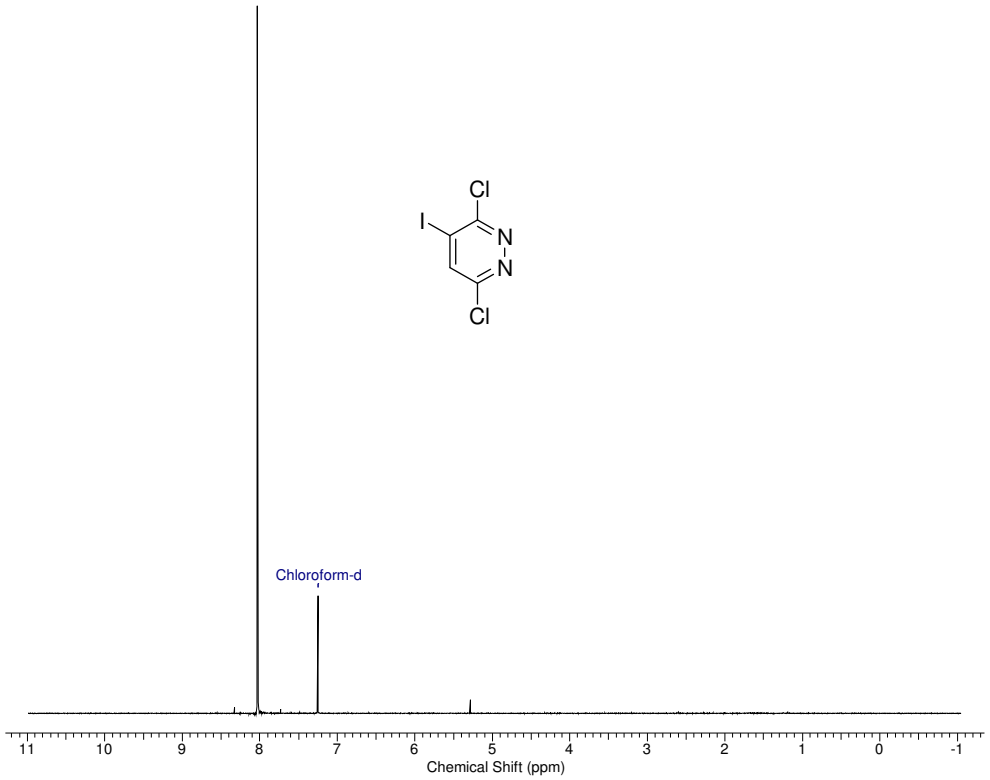
IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2969, 2832, 2359, 2340, 2203, 1739, 1661, 1587, 1569, 1507, 1481, 1458, 1442, 1427, 1361, 1316, 1293, 1250, 1229, 1216, 1177, 1162, 1141, 1119, 1070, 1059, 1043, 1015, 997, 953, 918, 868, 748, 737, 697, 687, 668, 630, 621, 616, 610.

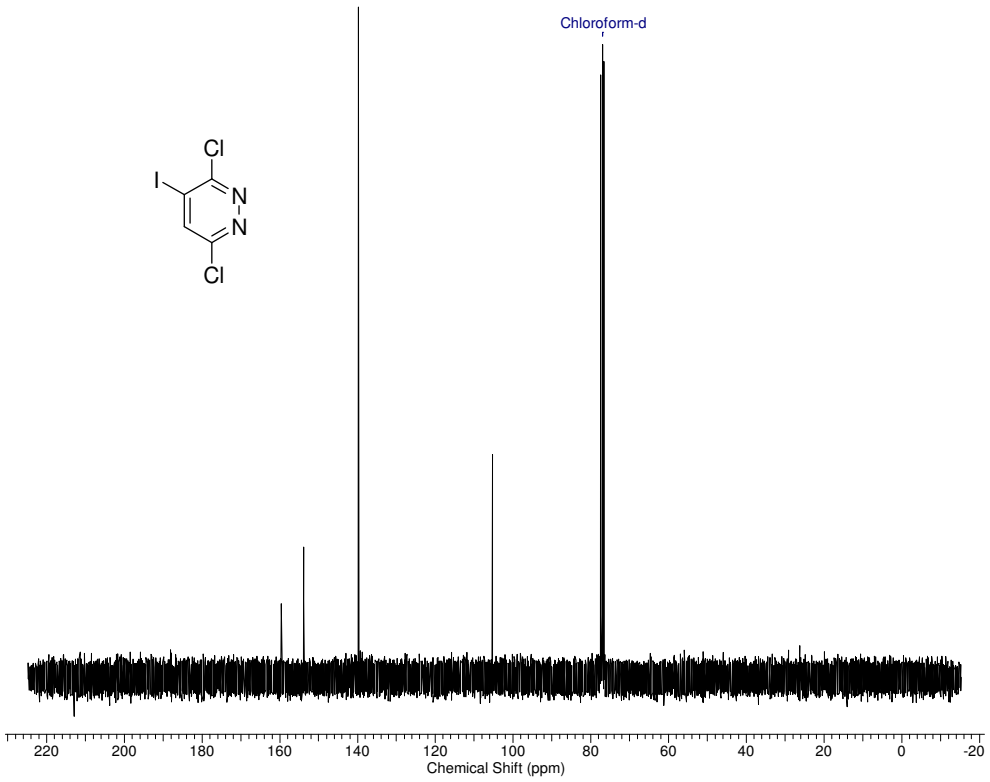
HRMS (EI) for **$C_{17}H_{10}OS$** (262.0452): 262.0459.

[1] Hammett, L. P.; Walden, G. H.; Edmonds, S. M. *J. Am. Chem. Soc*. **1934**, *56*, 1092.

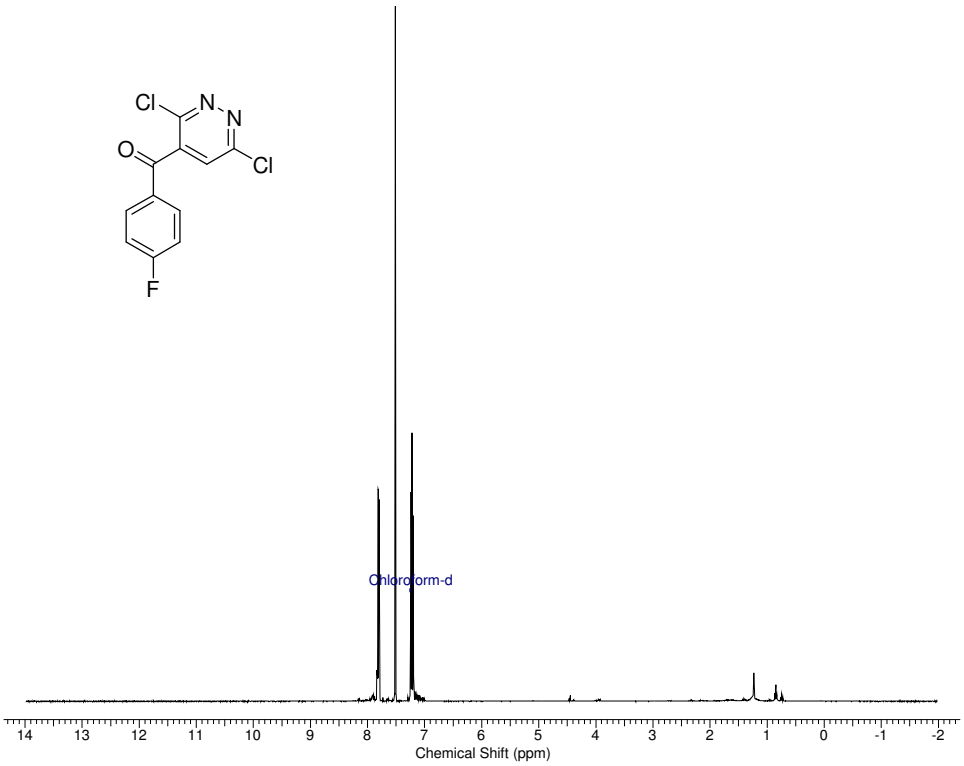
3) NMR-Spectra

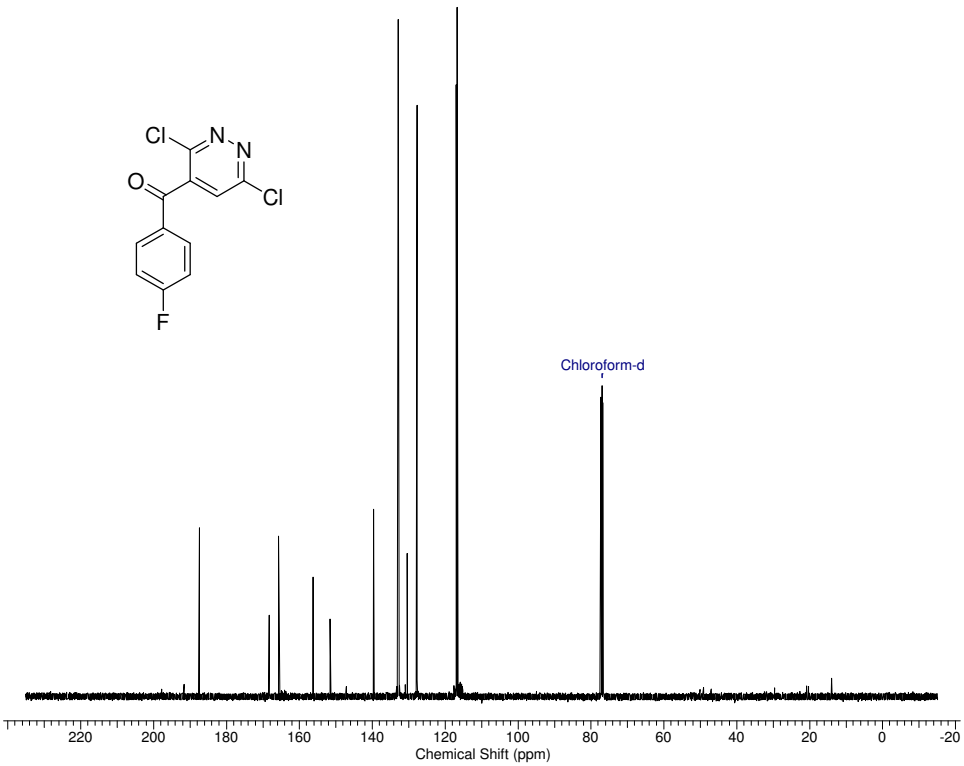
3,6-Dichloro-4-iodopyridazine (5a):



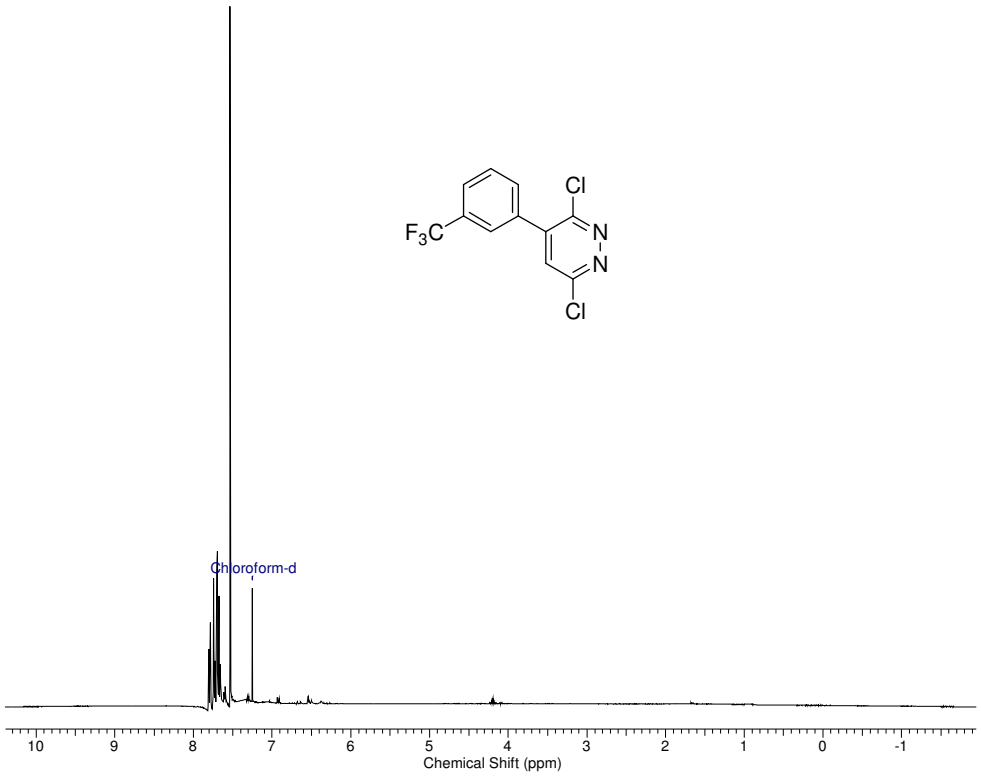


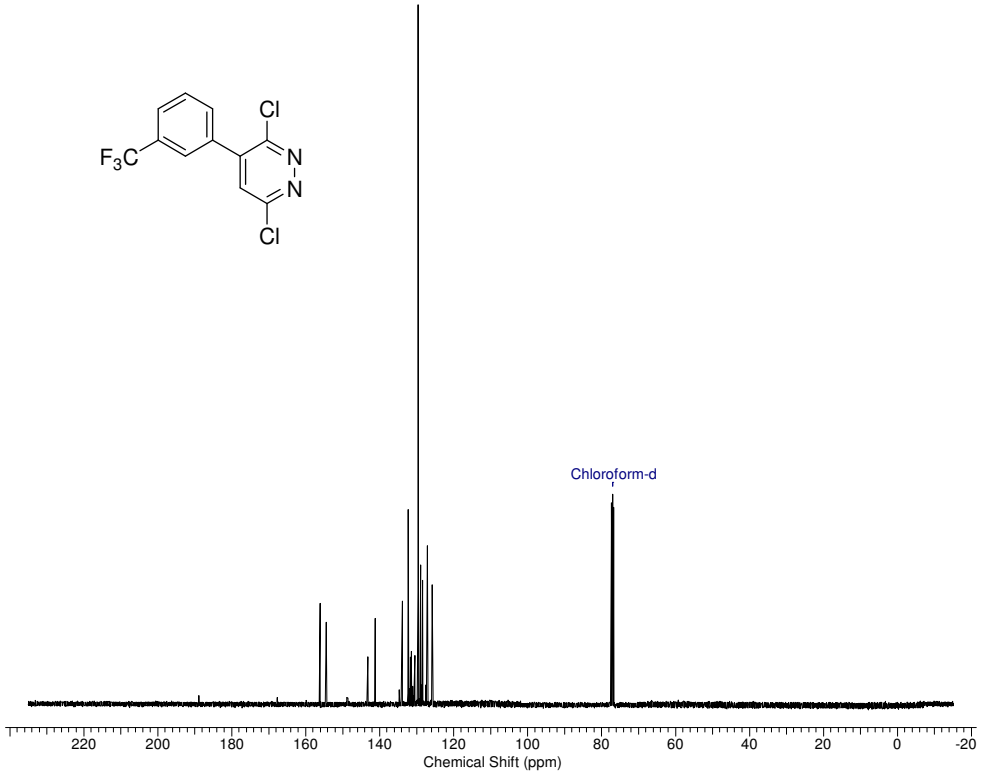
(3,6-Dichloropyridazin-4-yl)(4-fluorophenyl)methanone (5b):



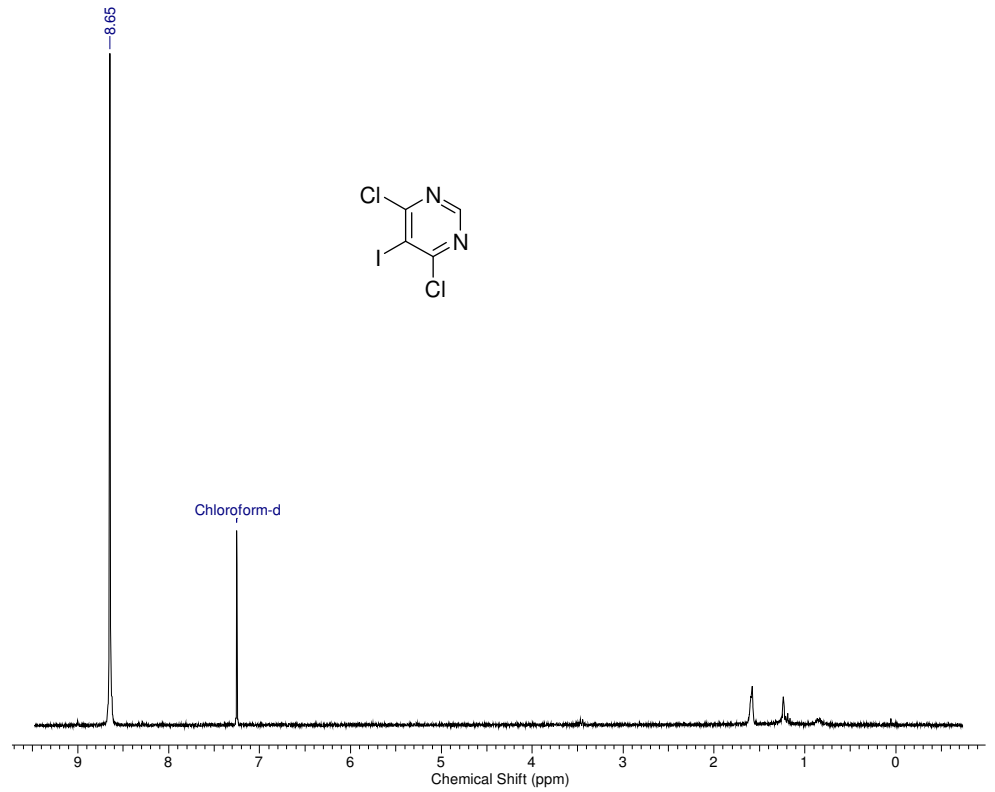


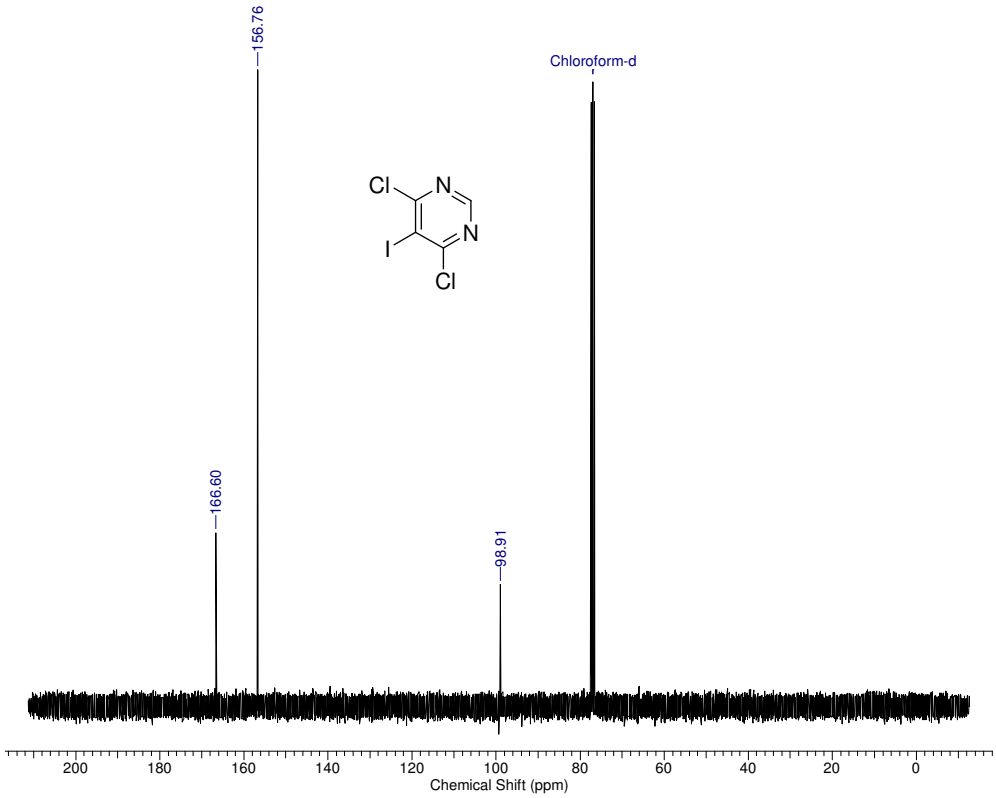
3,6-Dichloro-4-(3-(trifluoromethyl)phenyl)pyridazine (5c):



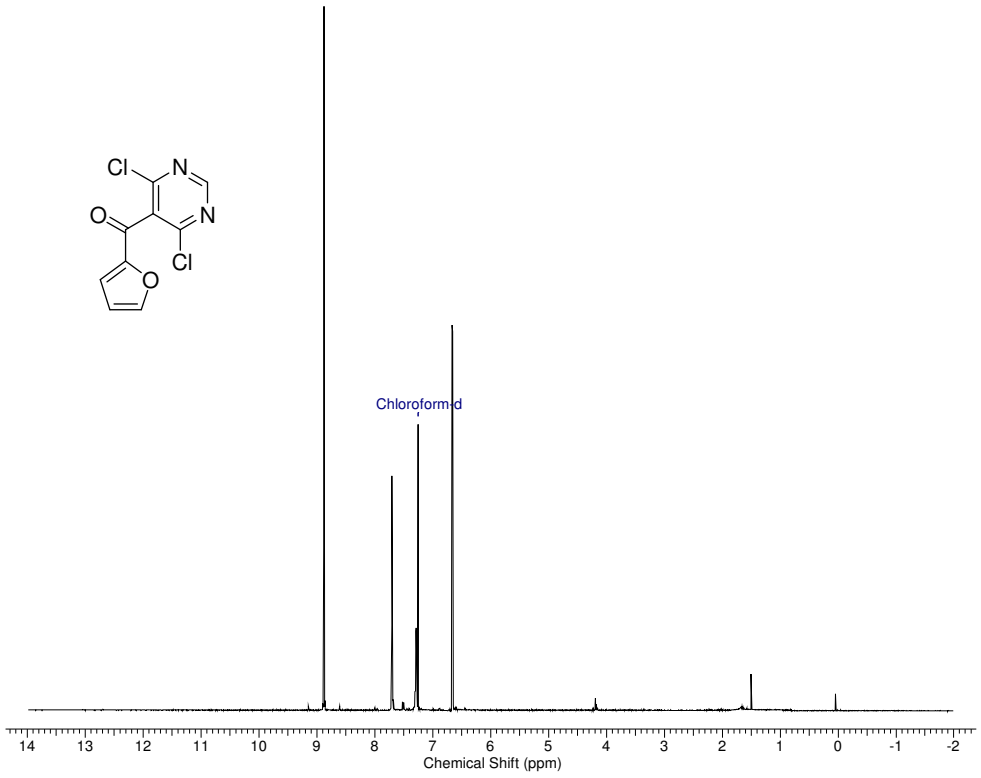


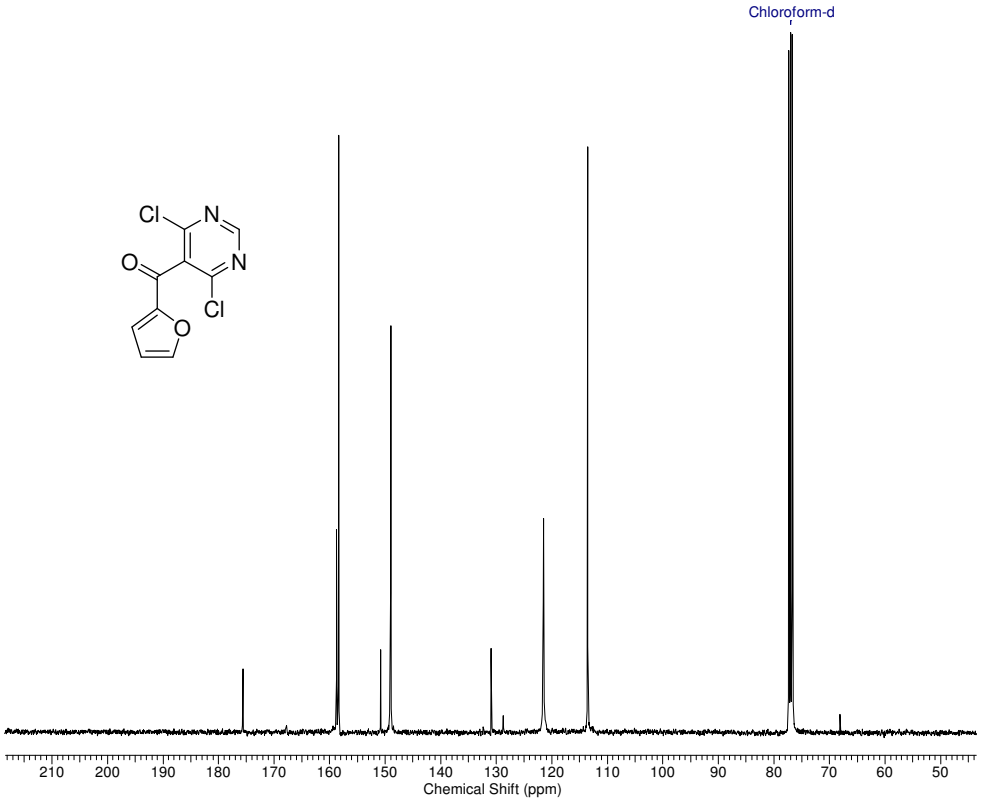
4,6-Dichloro-5-iodo-pyrimidine (8a):



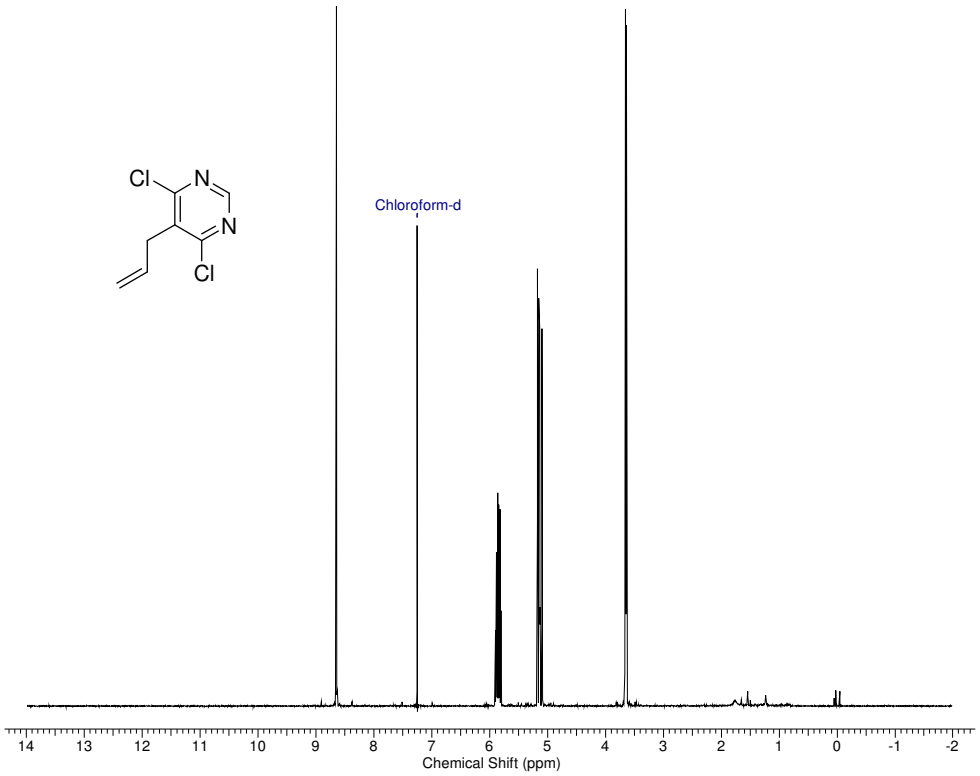


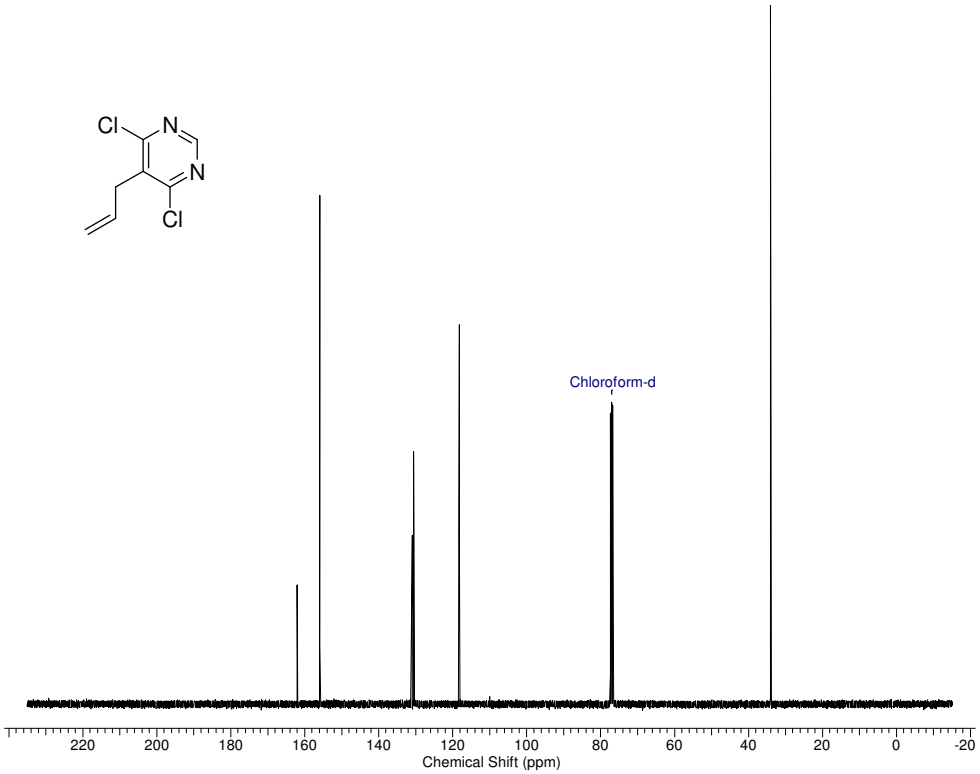
(4,6-Dichloropyrimidin-5-yl)(furan-2-yl)methanone (8b):



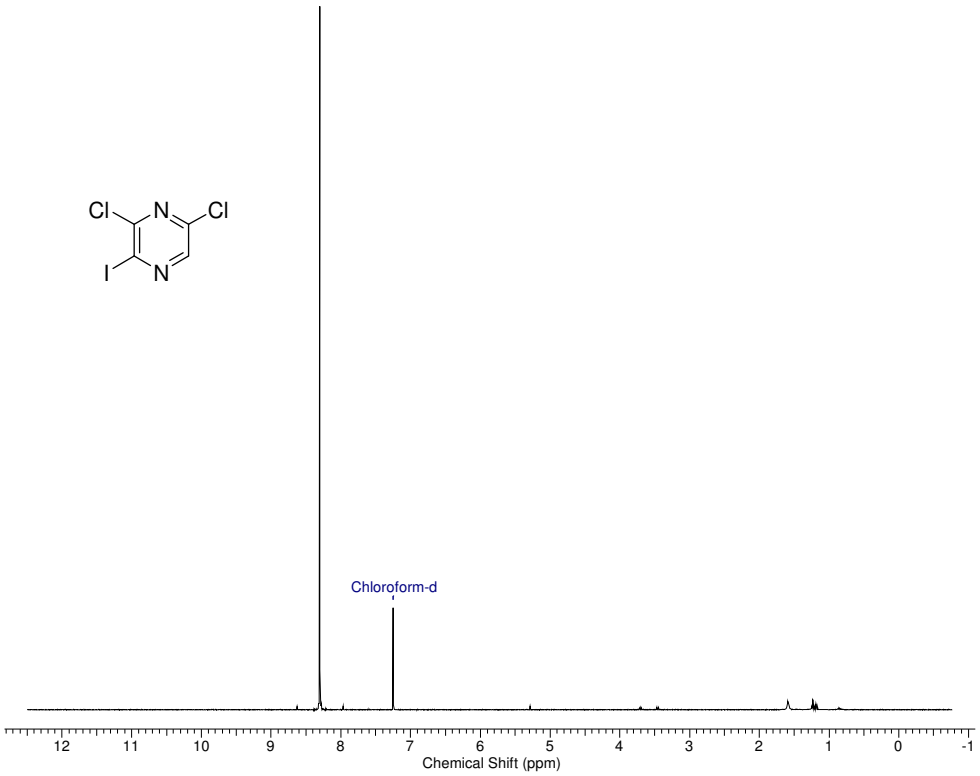


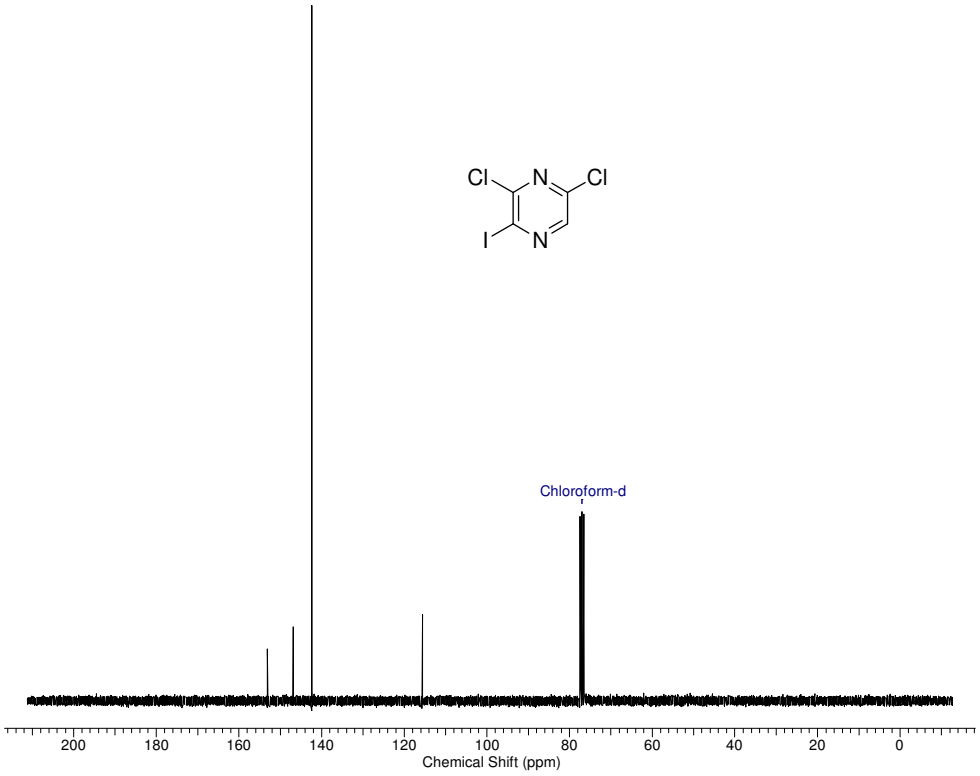
5-Allyl-4,6-dichloropyrimidine (8c):



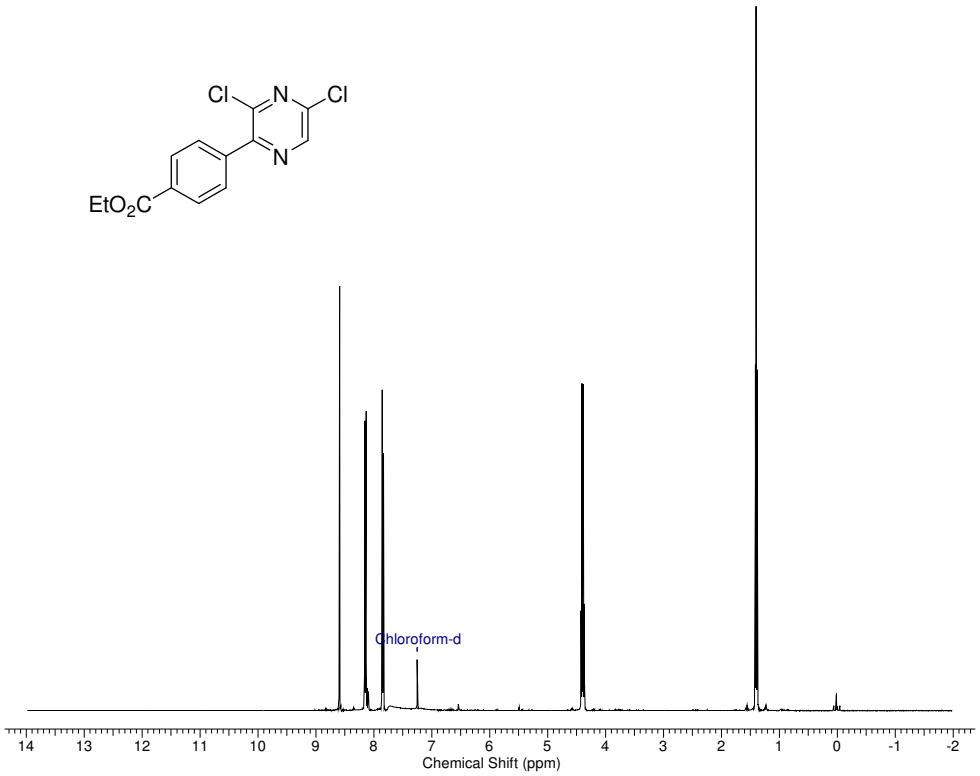


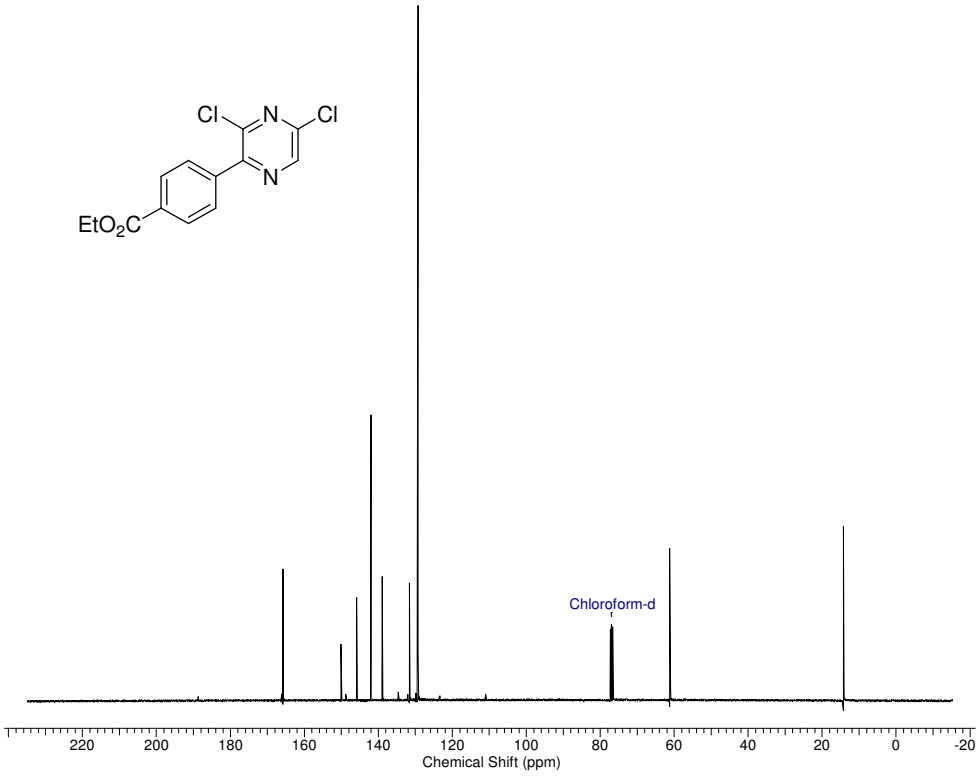
3,5-Dichloro-2-iodopyrazine (11a):



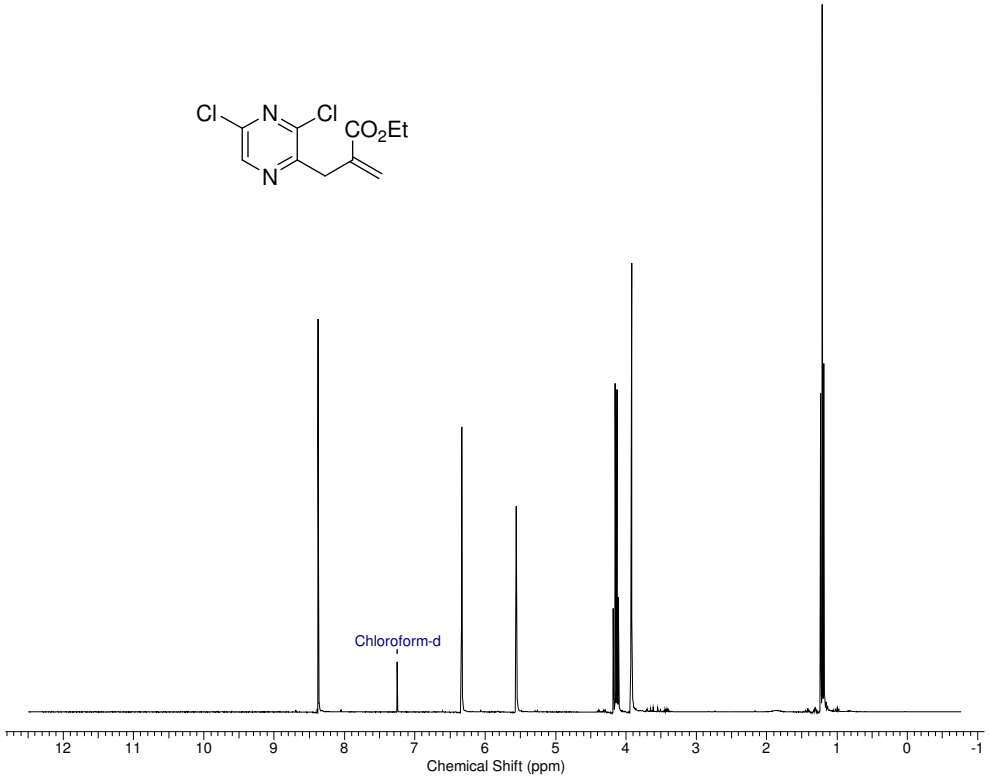


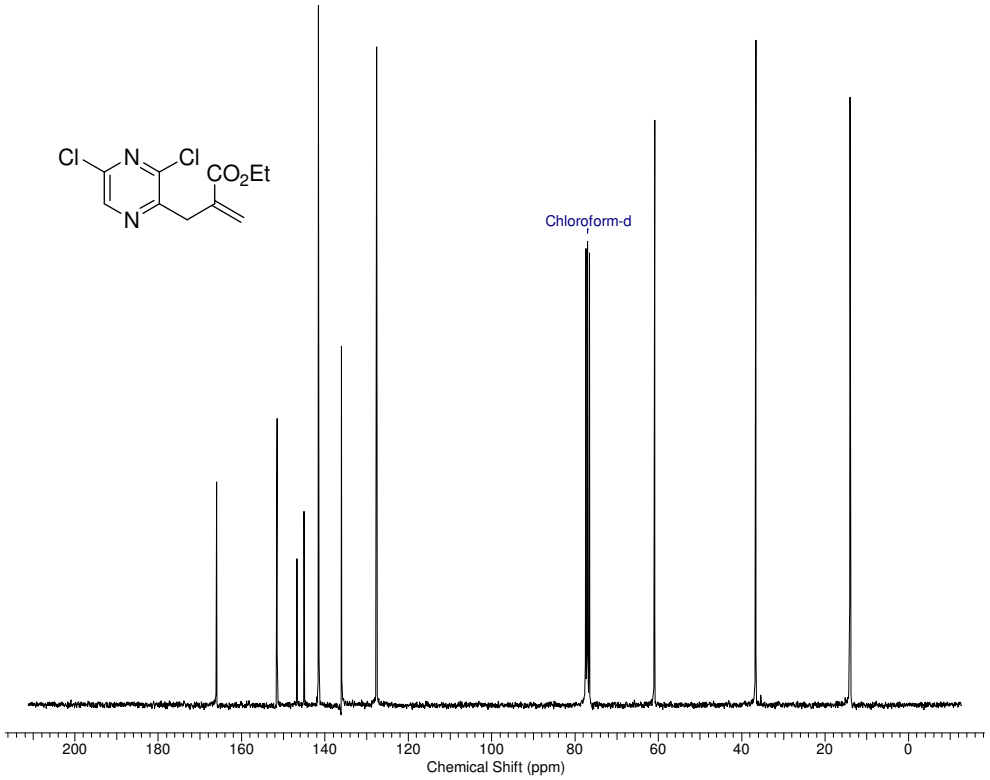
Ethyl 4-(3,5-dichloropyrazin-2-yl)benzoate (11b):



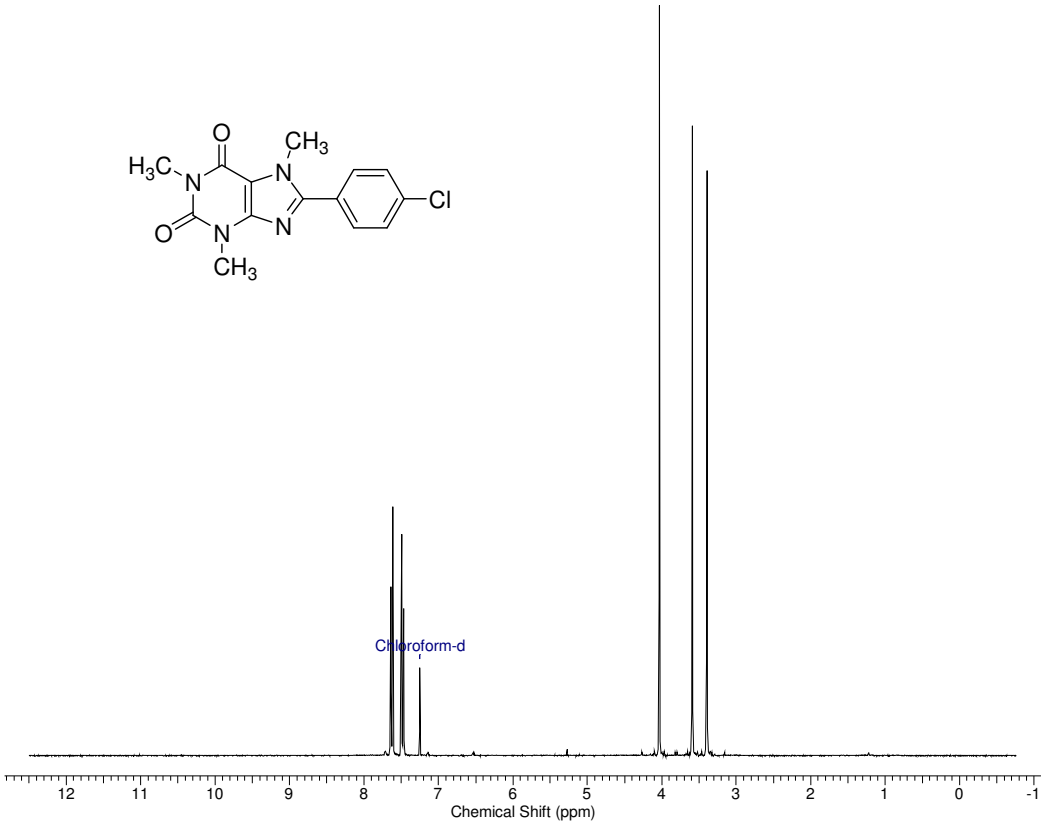


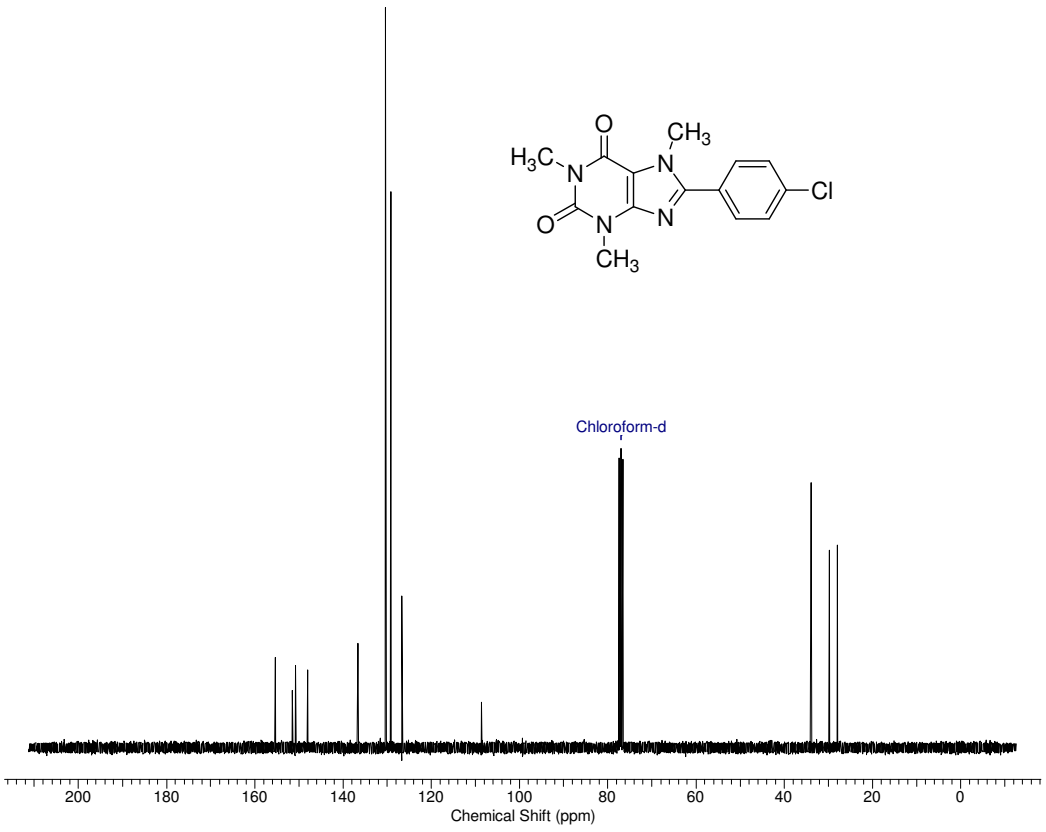
Ethyl 2-((3,5-dichloropyrazin-2-yl)methyl)acrylate (11c):



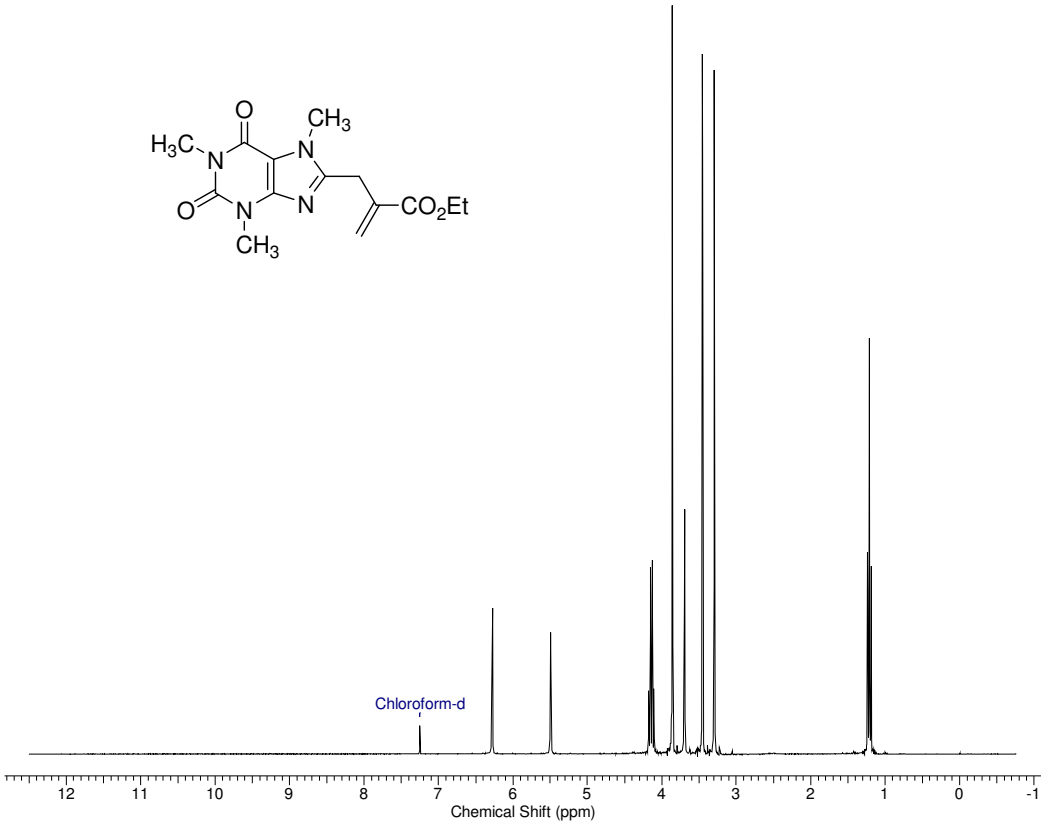


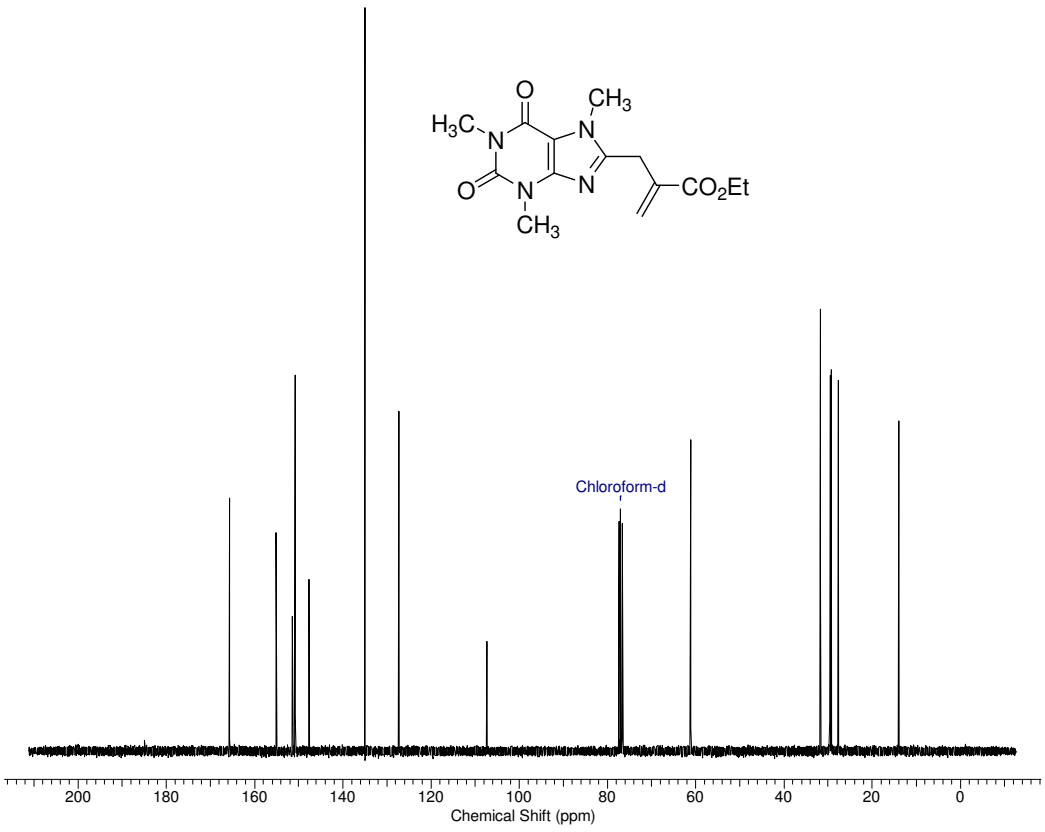
8-(4-Chlorophenyl)-1,3,7-trimethyl-1H-purine-2,6(3H,7H)-dione (14a):



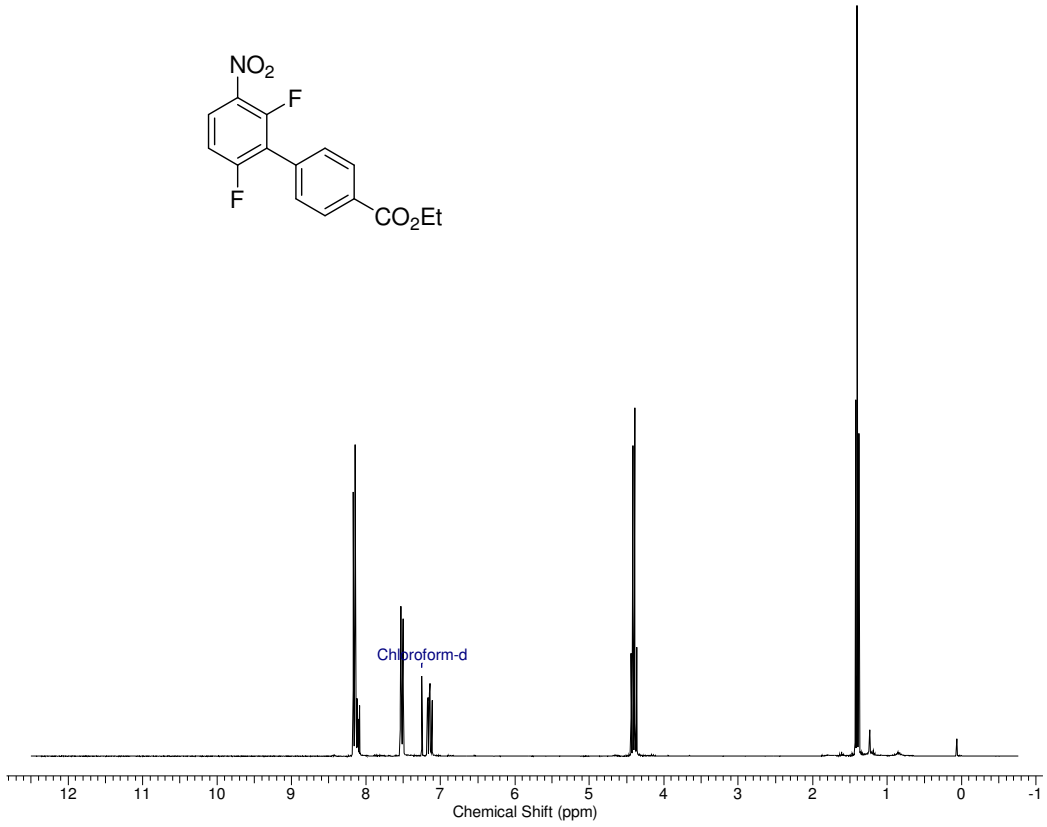


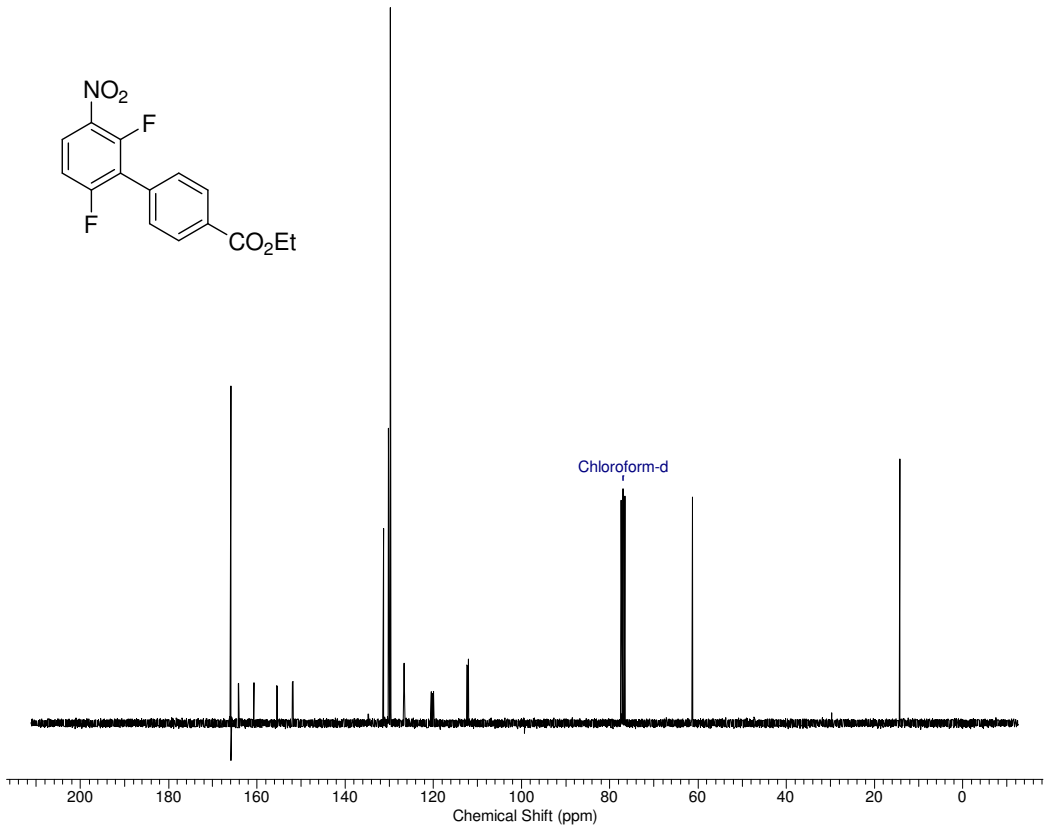
Ethyl 2-((1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-8-yl)methyl)acrylate (14b):



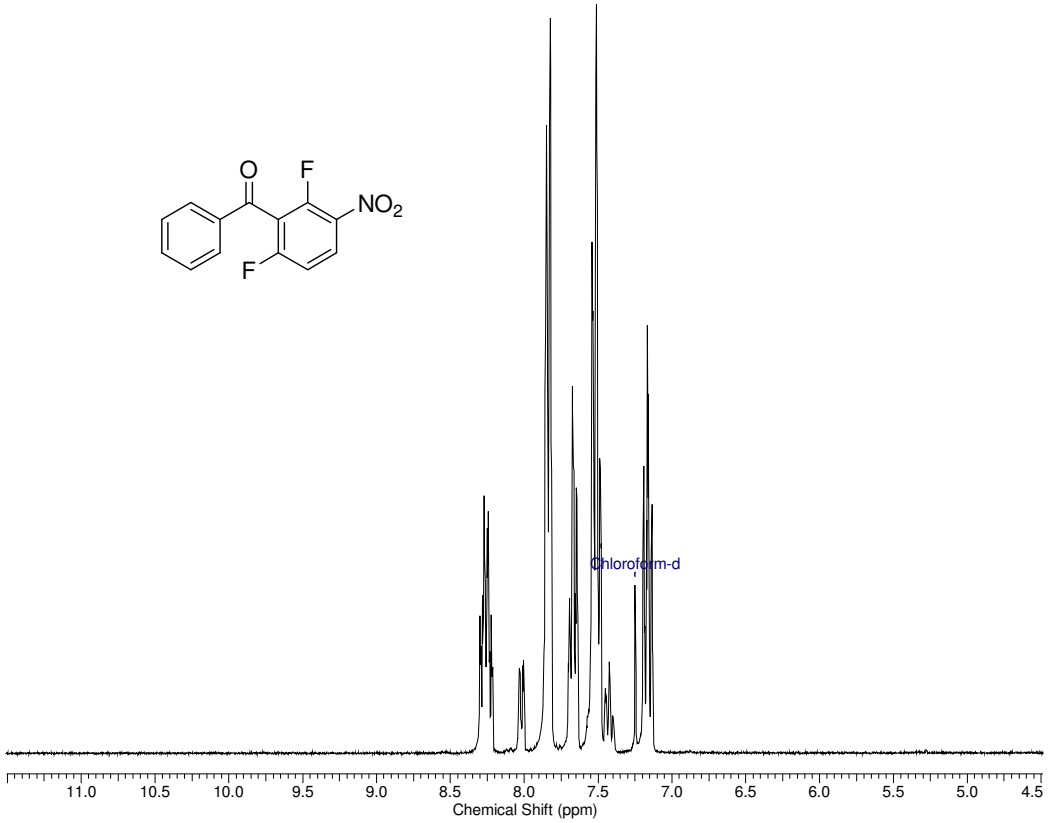


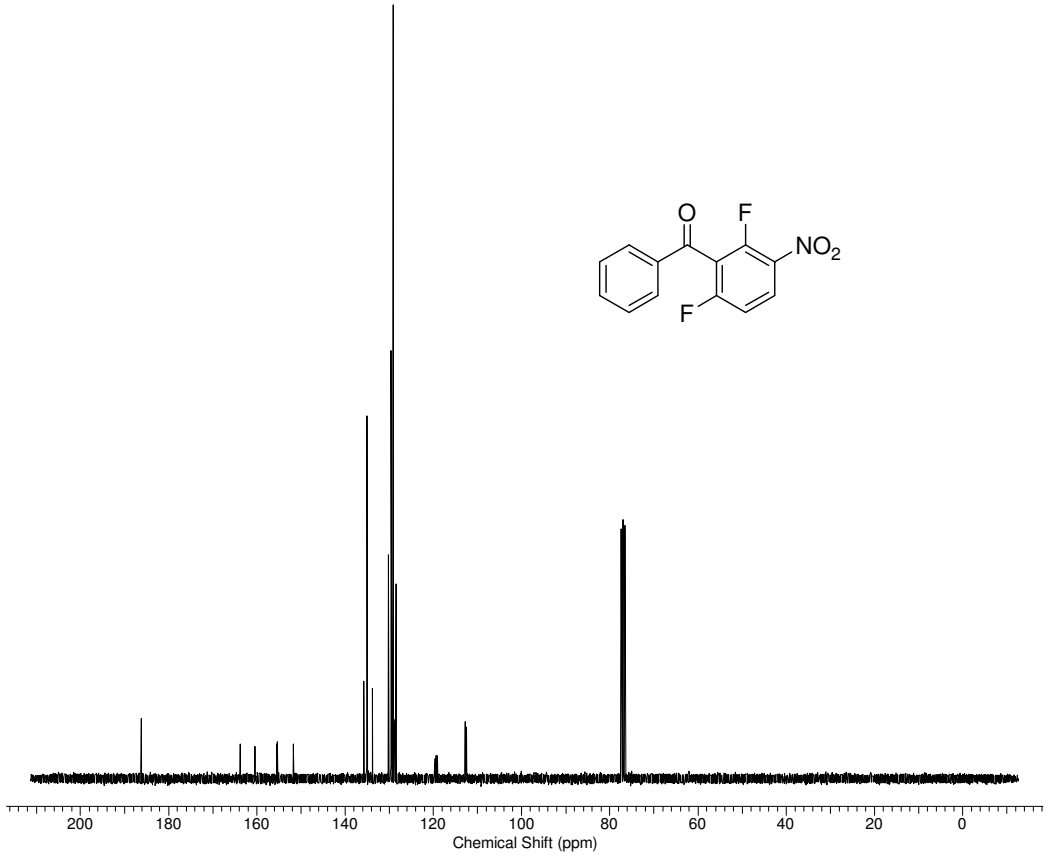
Ethyl 2',6'-difluoro-3'-nitrobiphenyl-4-carboxylate (17a):



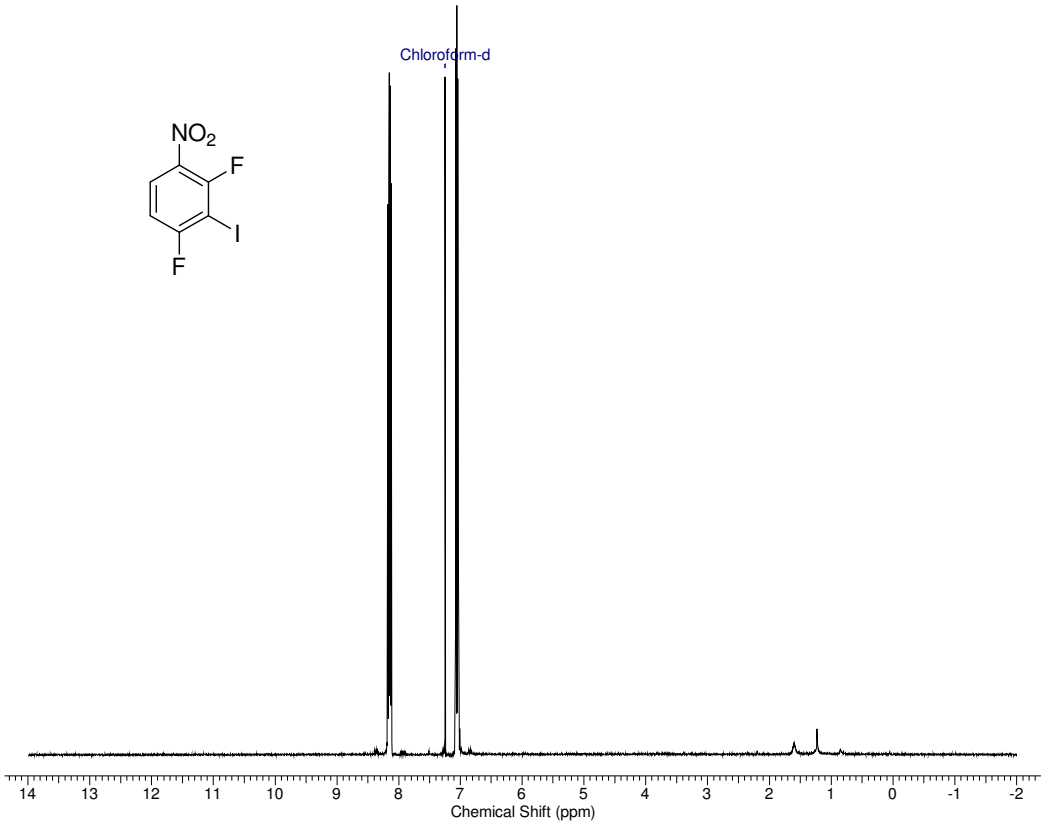


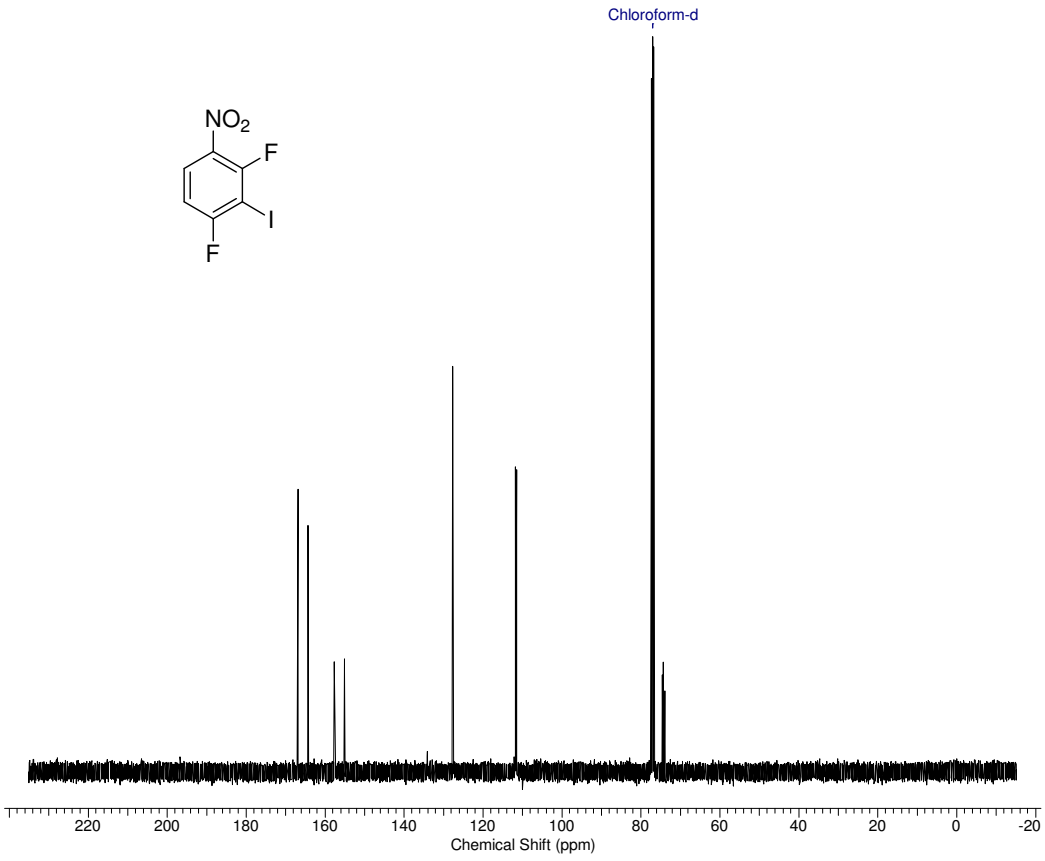
(2,6-Difluoro-3-nitrophenyl)(phenyl)methanone (17b):



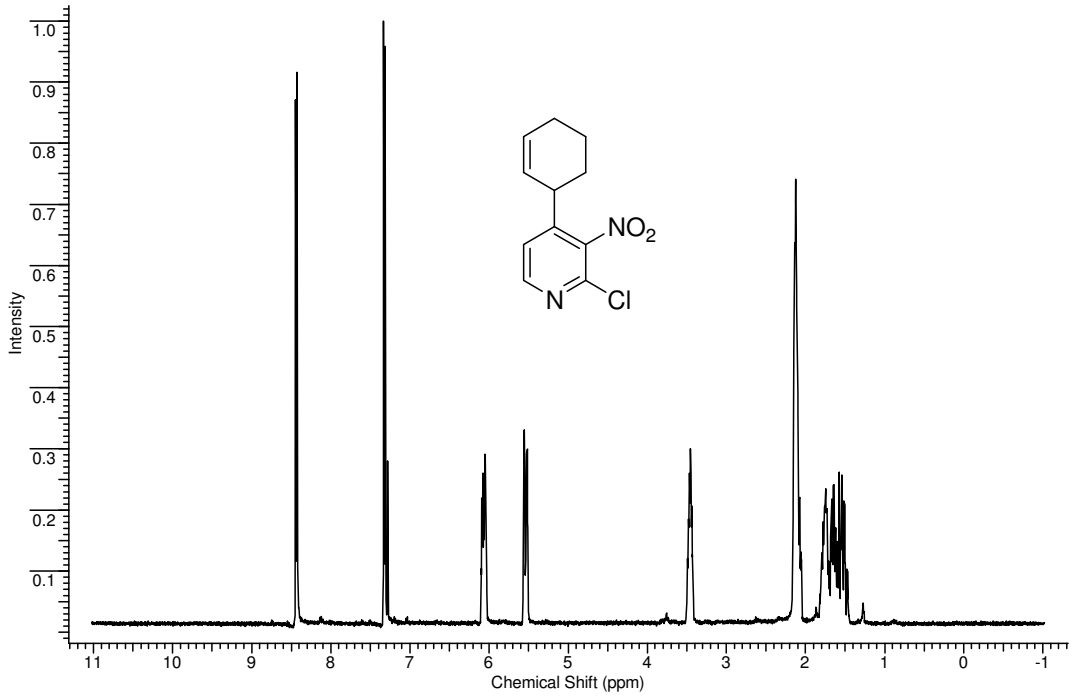


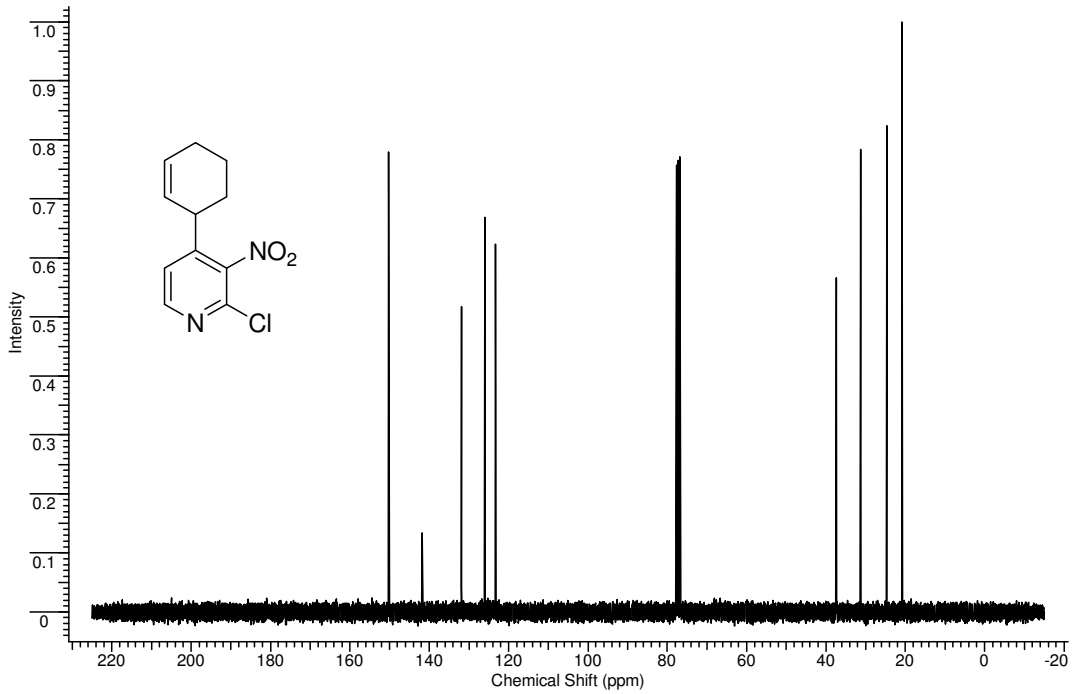
1,3-Difluoro-2-iodo-4-nitrobenzene (17c):



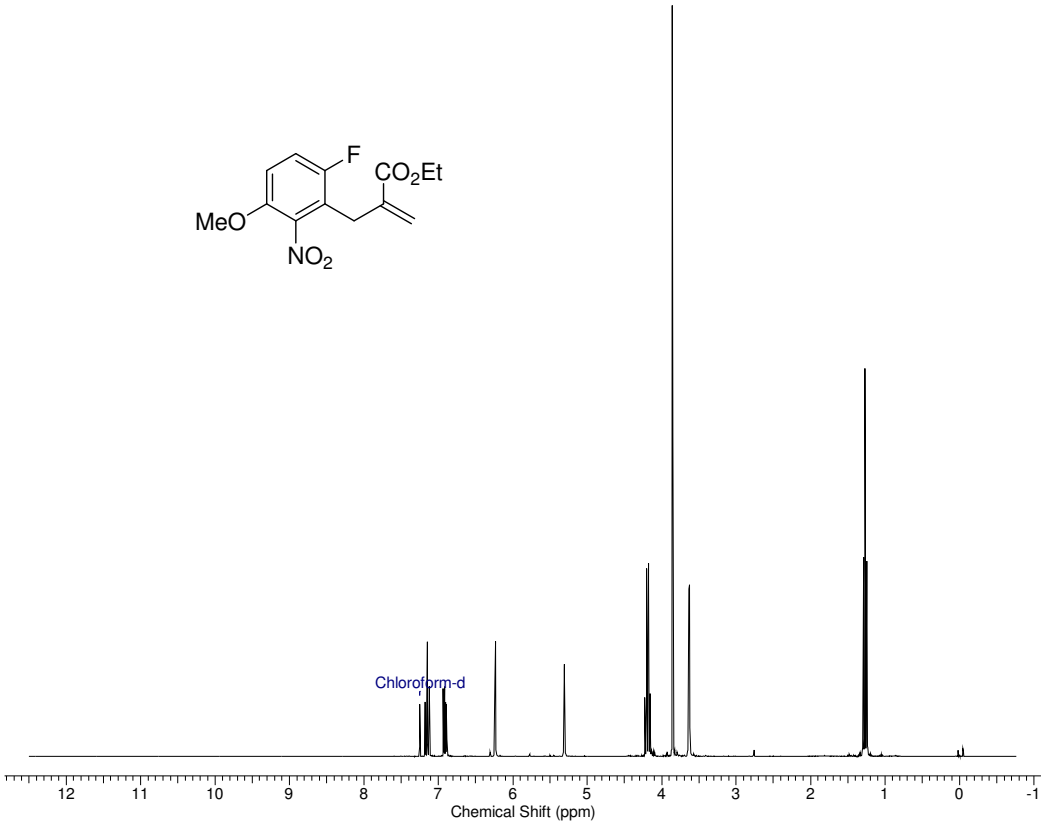


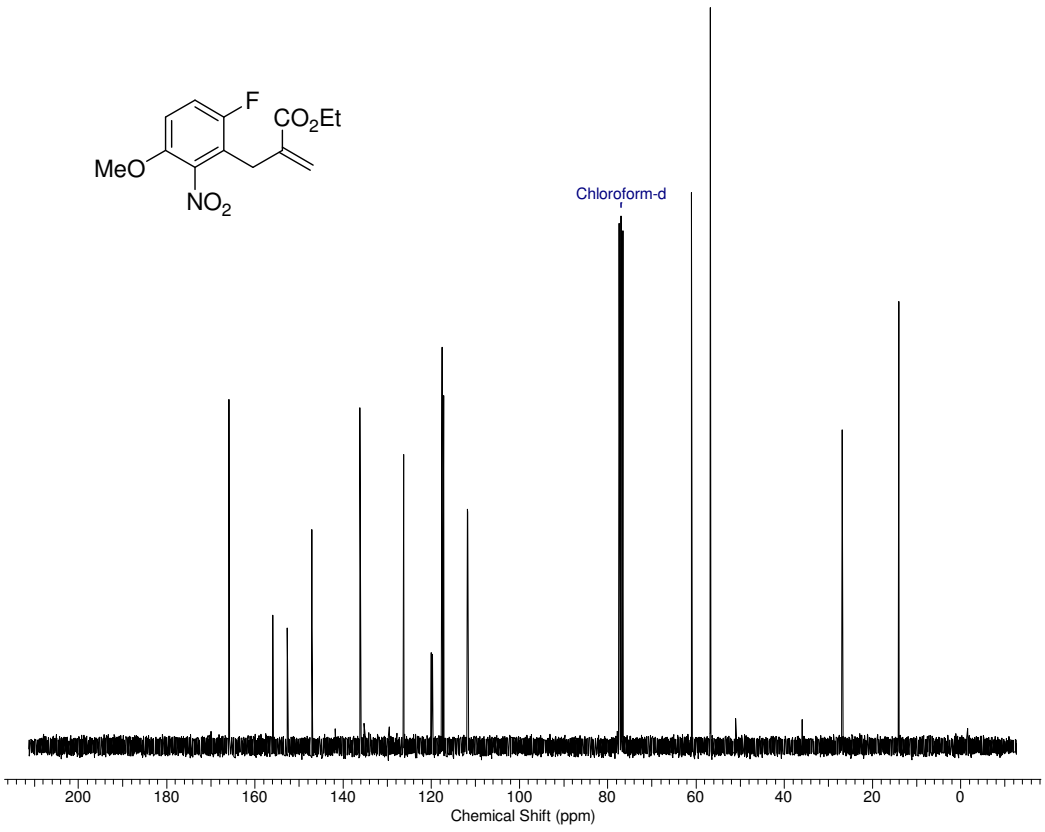
2-Chloro-4-cyclohex-2-enyl-3-nitro-pyridine (20):



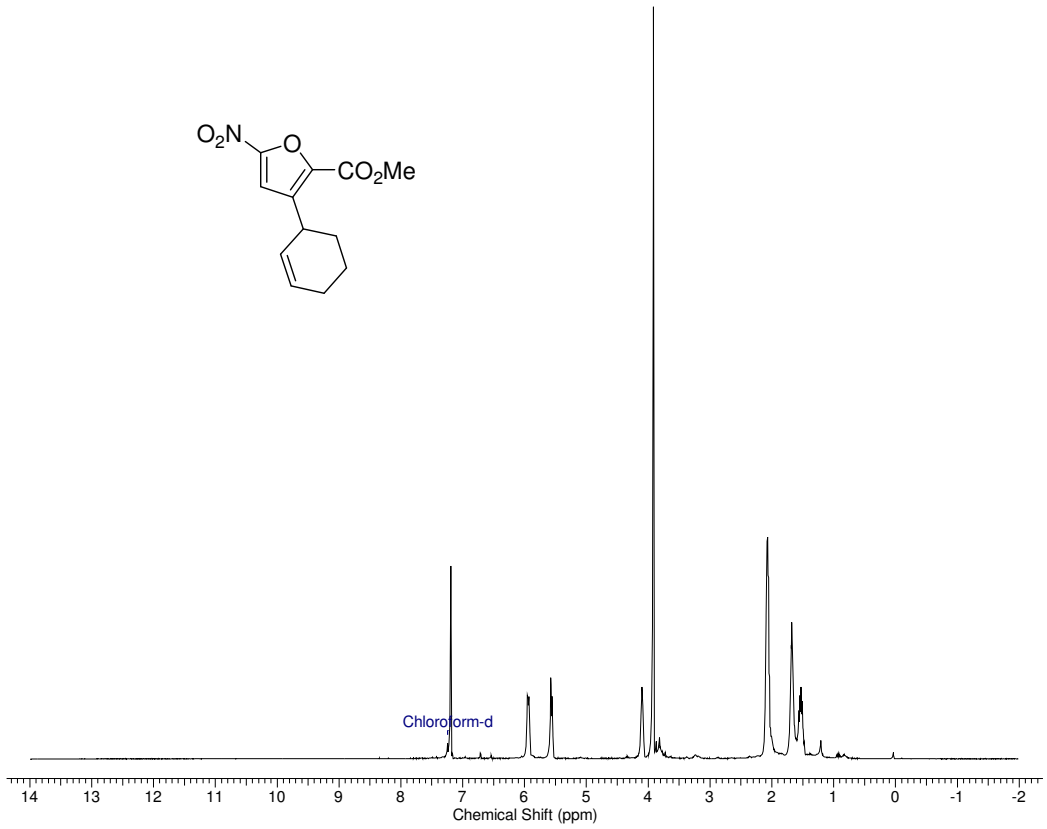


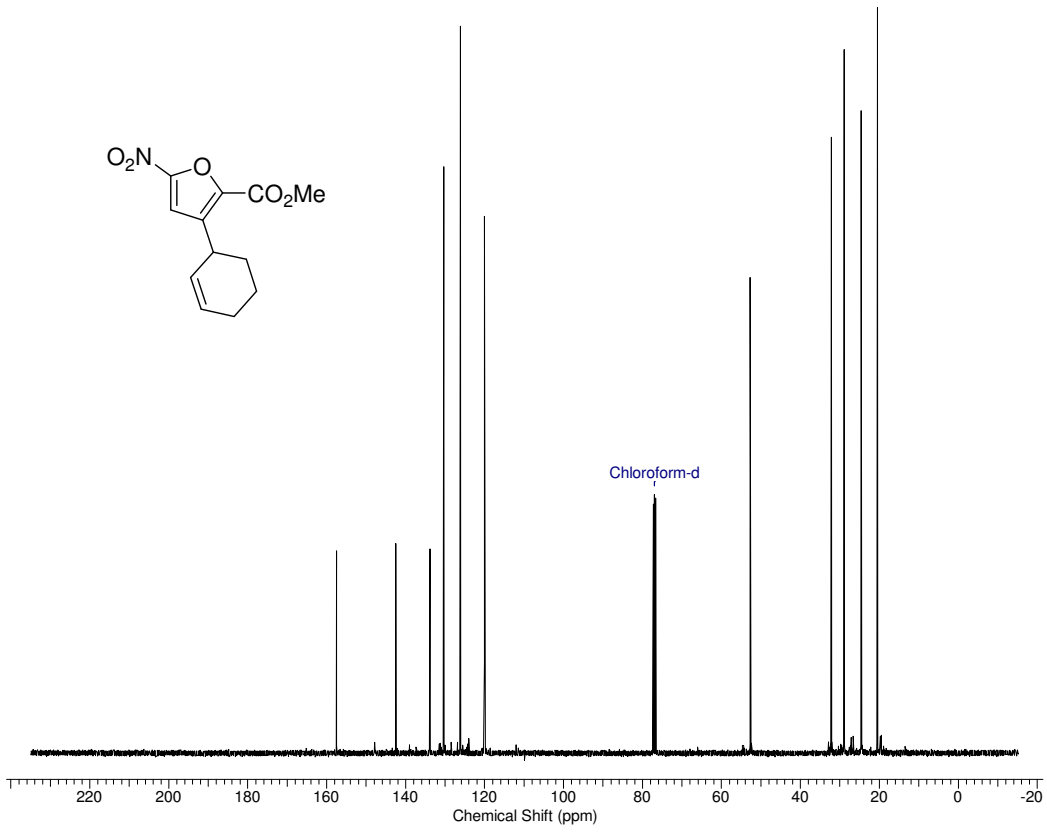
Ethyl 2-(6-fluoro-3-methoxy-2-nitrobenzyl)acrylate (23):



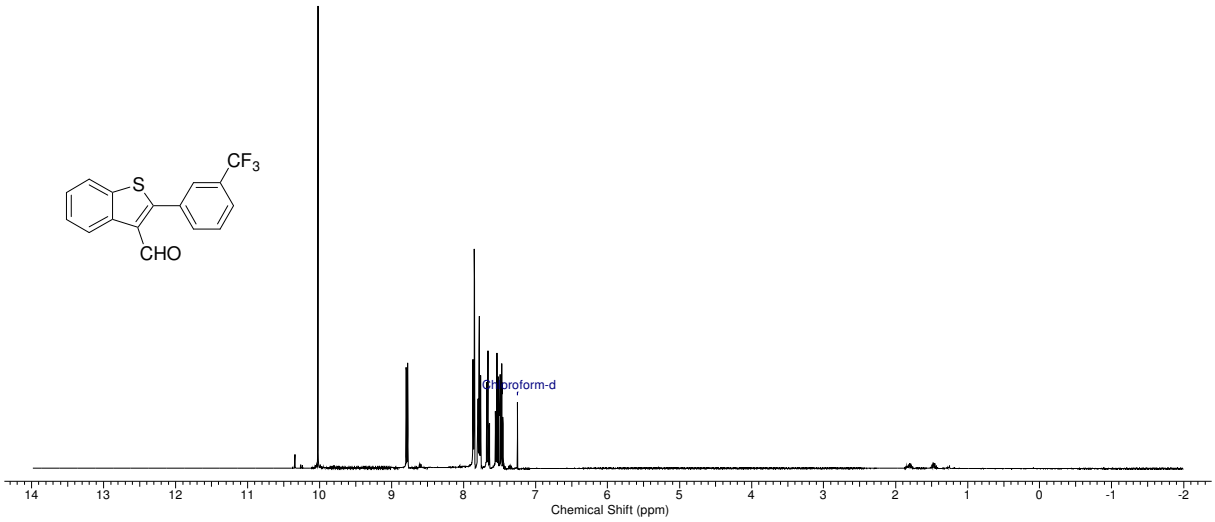


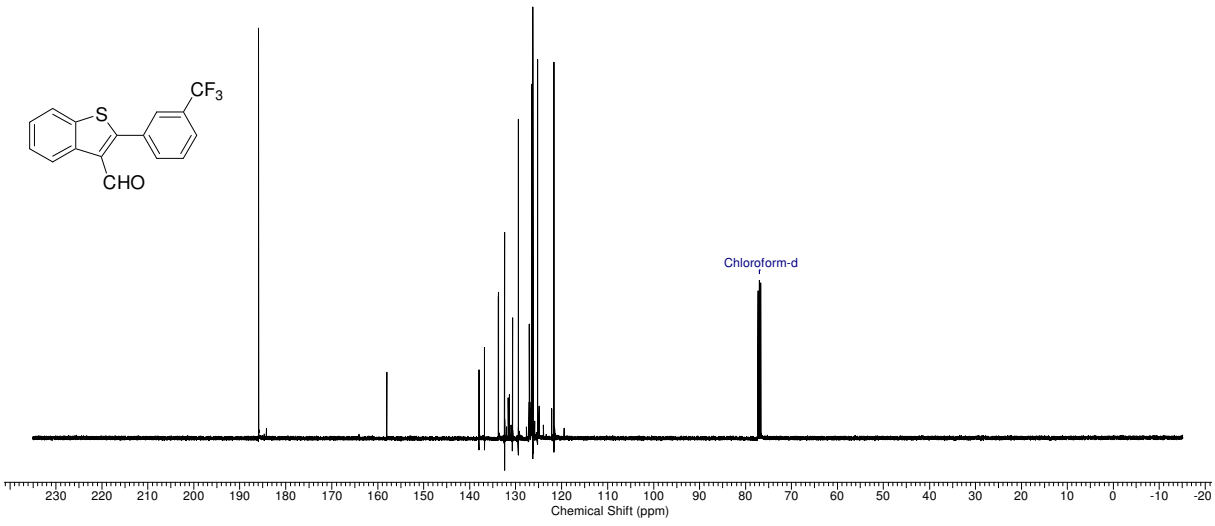
Methyl 3-(cyclohex-2-enyl)-5-nitrofuran-2-carboxylate (26):



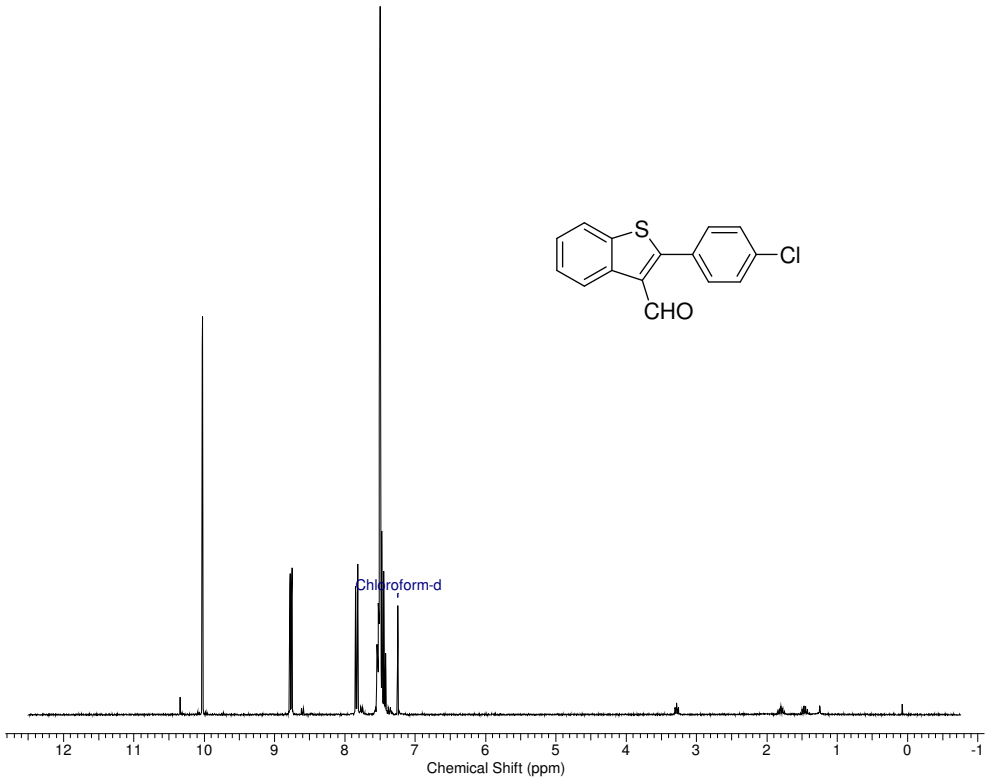


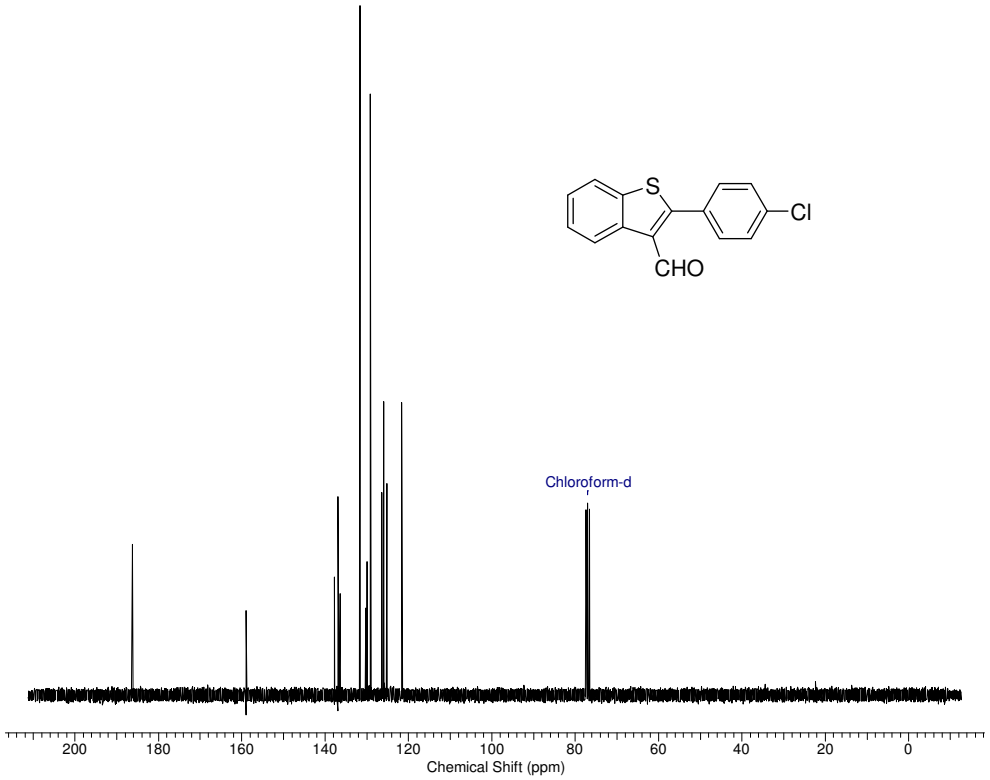
2-(3-(Trifluoromethyl)phenyl)benzo[b]thiophene-3-carbaldehyde (29a):





2-(4-Chlorophenyl)benzo[b]thiophene-3-carbaldehyde (29b):





2-(Phenylethynyl)benzo[b]thiophene-3-carbaldehyde (29c):