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Supporting Information

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$(TMP)_2Zn•2MgCl_2•2LiCl$: A New Highly Chemoselective Base for the Directed Zincation of Sensitive Aromatics and Heteroaromatics**

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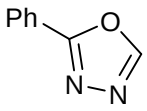
General All reactions were carried out under an argon atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by ^{1}H-NMR (25 °C) and capillary GC. Column chromatography was performed using SiO_2 (0.040 – 0.063 mm, 230 – 400 mesh ASTM) from Merck if not indicated.

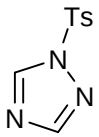
Preparation of the starting materials:

Synthesis of 2-phenyl-[1,3,4]-oxadiazole (3):



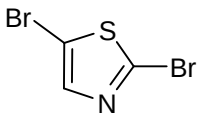
This compound was prepared from commercially available benzoic acid hydrazide according to the procedure of the literature.[1]

Synthesis of 1-tosyl-1*H*-[1,2,4]-triazole (8):



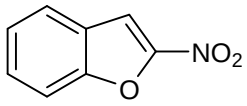
This compound was prepared from commercially available 1*H*-[1,2,4]-triazole according to the procedure of the literature.[2]

Synthesis of 2,4-dibromothiazole (9a):



This compound was prepared from commercially available 2,4-thiazolidinedione according to the procedure of the literature.[3]

Synthesis of 2-nitrobenzofuran (17a):



This compound was prepared from commercially available 2-hydroxybenzaldehyde according to the procedure of the literature.[4]

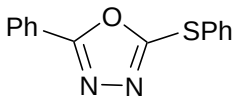
Typical Procedure 1: Preparation of the reagent $(TMP)_2Zn•2MgCl_2•2LiCl$ (2):

In an argon-flushed Schlenk-flask, $ZnCl_2$ (53.0 mmol, 7.22 g) was dried *in vacuo* at 140 °C for 4 h. After cooling to room temperature, freshly titrated TMPMgCl•LiCl[5] (100 mmol, 1.00 M, 100 mL) was added dropwise. The resulting mixture was stirred for 15 h at 25 °C. The freshly prepared $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) solution was titrated prior to use at 0°C with benzoic acid using 4-(phenylazo)diphenylamine as indicator. A concentration of 0.5 M in THF was obtained.

Typical procedure for the zincation of polyfunctionalized aromatics and heterocycles with $(TMP)_2Zn•2MgCl_2•2LiCl$ (TP 2):

A dry and argon flushed 10 mL Schlenk-flask, equipped with a magnetic stirring bar and a septum was charged with a solution of the corresponding arene (1.0 mmol) in dry THF (1 mL). After setting the desired temperature (Table 1), the zinc base (0.55 mmol) was added dropwise 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 2-phenyl-5-phenylsulfanyl-[1,3,4]oxadiazole (7a):



2-Phenyl-[1,3,4]oxadiazole (**3**) (0.146 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 20 min according to **TP 2**. $PhSSO_2Ph$ (0.300 g, 1.2 mmol) dissolved in dry THF (2 mL) was then added dropwise at 25 °C, the resulting mixture was stirred for 9 h. The reaction mixture was

quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2) furnished 2-phenyl-5-phenylsulfanyl-[1,3,4]oxadiazole (**7a**) as a colorless solid (0.191 g, 75%).

m.p.: 62.4 – 63.1°C.

^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.96 (d, ^3J = 7.5 Hz, 2 H), 7.68 (m, 2 H), 7.51 (t, ^3J = 7.3 Hz, 1 H), 7.45 (m, 5 H).

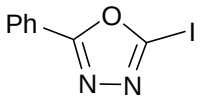
^{13}C-NMR (150 MHz, $CDCl_3$) δ: 166.6, 166.0, 133.9, 132.0, 130.1, 130.0, 129.3, 127.3, 127.0, 123.8.

MS (70 eV, EI) *m/z* (%): 255 (7), 254 (68) [M^+], 198 (8), 145 (100), 121 (17), 109 (21), 105 (21), 103 (22), 77 (81), 65 (12).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1465, 1439, 1171, 1062, 1000, 770, 745, 703, 682.

HRMS (EI) for **$C_{14}H_{10}N_2OS$** (254.0514): 254.0493.

Synthesis of 5-iodo-2-phenyl-[1,3,4]oxadiazole (7b)



2-Phenyl-[1,3,4]oxadiazole (**3**) (0.146 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M

in THF, 1.10 mL, 0.55 mmol) at 25 °C for 20 min according to **TP 2**. I_2 (0.381 g, 1.5 mmol) dissolved in dry THF (2 mL) was then added dropwise at 0 °C, the resulting mixture was warmed to 25 °C and stirred for 0.5 h. The reaction mixture was quenched with a sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/CH_2Cl_2 1:1) furnished 5-iodo-2-phenyl-[1,3,4]oxadiazole (**7b**) (0.220 g, 80%) as a colorless solid.

m.p.: 166.4 – 167.9 °C.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 8.04 (m, 2 H), 7.55 (m, 3 H).

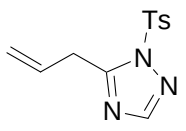
^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 169.6, 132.5, 129.4, 127.2, 123.1, 107.2.

MS (EI, 70 eV) *m/z* (%): 272 (48) [M^+], 146 (18), 145 (100), 105 (22), 103 (26), 89 (14), 77 (73).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1604, 1552, 1446, 1139, 1065, 1028, 979, 958, 775, 703.

HRMS (EI) for **$C_8H_5N_2OI$** (271.9447): 271.9459.

Synthesis of 5-allyl-1-tosyl 1*H*-[1,2,4]triazole (8a):



1-Tosyl 1*H*-[1,2,4]triazole (**4**) (0.223 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at -25 °C for 40 min according to **TP 2**. Allyl bromide (0.145 g, 1.2 mmol) and CuCN•2LiCl (1.0 M solution in THF, 0.05 mL, 0.05 mmol) was added and the reaction mixture was stirred for 30 min. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2) furnished 5-allyl-1-tosyl 1*H*-[1,2,4]triazole (**8a**) (0.224 g, 85%) as a colorless solid.

m.p.: 54.0 – 54.7 °C.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.93 (dd, ^3J = 8.0 Hz, ^4J = 0.7 Hz, 2 H), 7.83 (s, 1 H), 7.35 (dd, ^3J = 8.0 Hz, ^4J = 0.7 Hz, 2 H), 6.03 (m, 1 H), 5.21 (m, 2 H), 3.93 (dt, ^3J = 6.5 Hz, ^4J = 1.5 Hz, 2 H), 2.44 (s, 3 H).

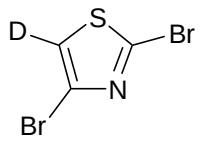
^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 157.6, 152.0, 147.1, 133.8, 131.5, 130.6, 130.4, 128.9, 128.8, 119.0, 32.3, 22.1.

MS (EI, 70 eV) *m/z* (%): 264 (15), 263 (54) [M^+], 262 (24), 108 (67), 92 (13), 91 (100), 65 (23), 53 (11).

IR (ATR) $\tilde{\nu}$ **(**cm^{-1}**)**: 1718, 1706, 1601, 1350, 1274, 1119, 947, 913, 762, 724, 615.

HRMS (EI) for **$C_{12}H_{13}N_3O_2S$** (263.0728): 263.0741.

Synthesis of 2,4-dibromo-5-deuterothiazole (8b):



2,4-Dibromothiazole (**9a**) (0.243 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 15 min according to **TP 2**. D_2O (0.2 mL, 10 mmol) was added dropwise at 5 °C, the resulting mixture was warmed to 25 °C and stirred for 20 min. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/CH_2Cl_2 5:1) furnished 2,4-dibromo-5-deuterothiazole (**8b**) (0.223 g, 91%) as a colorless solid.

m.p.: 81.8 – 82.8 °C.

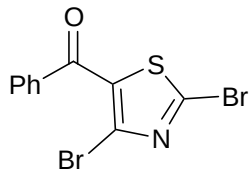
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 136.5, 124.4, 121.0.

MS (70 eV, EI) *m/z*: 246 (52), 245 (28), 244 (100), 243 (49), 242 (53) [^{79}Br-M^+], 241 (27), 139 (33), 138 (17), 137 (28), 136 (14), 125 (13), 123 (13), 84 (10), 58 (25), 57 (11).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1726, 1528, 1434, 1352, 1336, 1276, 1236, 1196, 1168, 1142, 1120, 1028, 978, 968, 956, 924, 888, 826, 812, 800, 766, 740, 692.

HRMS (EI) for **$C_3{}^{79}Br_2DNS$** (241.8259): 241.8262.

Synthesis of 5-benzoyl-2,4-dibromothiazole (8c):



2,4-Dibromothiazole (**9a**) (0.243 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 15 min according to **TP 2**. The reaction mixture was cooled to -20 °C, CuCN•2LiCl (1.0 M solution in THF, 1.1 mL, 1.1 mmol) was added and the reaction mixture was stirred for 15 min. Then, benzoyl chloride (0.353 g, 2.5 mmol) was added at -20 °C. The reaction mixture was slowly warmed to 25 °C and stirred at this temperature for 8 h. Then the reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2)

furnished 5-benzoyl-2,4-dibromothiazole (**8c**) (0.289 g, 84%) as a colorless oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.82 (d, ^{3}J = 8.2 Hz, 2 H), 7.65 (t, ^{3}J = 7.4 Hz, 1 H). 7.51 (t, ^{3}J = 7.5 Hz, 2 H).

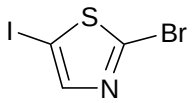
^{13}C-NMR (150 MHz, $CDCl_3$) δ: 186.0, 141.1, 136.9, 135.7, 134.1, 129.8, 128.1.

MS (70 eV, EI) *m/z* (%): 349 (20), 347 (38), 345 (18) [^{79}Br-M^+], 270 (7), 251 (19), 106 (7), 105 (100), 77 (35), 51 (12).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1654, 1594, 1460, 1375, 1279, 1248, 1207, 1026, 920, 874, 851, 827, 716, 696.

HRMS (EI) for **$C_{10}H_5{}^{79}Br_2NOS$** (344.8459): 344.8444.

Synthesis of 2-bromo-5-iodo-thiazole (8d)



2-Bromothiazole (**9a**) (0.163 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn{\bullet}2MgCl_2{\bullet}2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 ^{o}C for 20 min according to **TP 2**. I_2 (0.381 g, 1.5 mmol) dissolved in dry THF (2 mL) was then added dropwise at 0 °C, the resulting mixture was warmed to 25 ^{o}C and stirred for 0.5 h. The reaction mixture was quenched with a sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted

with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/CH_2Cl_2 1:1) furnished 2-bromo-5-iodo-thiazole (**8d**) (0.245 g, 84%) as a colorless solid.

m.p.: 112.5 – 113.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.65 (s, 1 H).

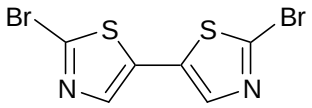
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 150.8, 139.6, 72.6.

MS (70 eV, EI) *m/z* (%): 291 (96), 289 [^{79}Br-M^+] (100), 164 (91), 162 (99), 127 (21), 83 (38), 57 (76).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1692, 1478, 1378, 1250, 1136, 1004, 978, 958, 848, 734, 698, 676, 666.

HRMS (EI) for **$C_3H^{79}BrINS$** (288.8058): 288.8044.

Synthesis of 2,2'-dibromo-[5,5']bithiazolyl (8e):



2-Bromothiazole (**9a**) (0.163 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn{\bullet}2MgCl_2{\bullet}2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 20 min according to **TP 2**. Chloranil (0.292 g, 1.2 mmol) dissolved in dry THF (7 mL) was then added dropwise at -40 °C, the resulting mixture was slowly warmed to 0 °C and stirred for 5 h. The reaction

mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2) furnished 2,2'-dibromo-[5,5']bithiazolyl (**8e**) (0.148 g, 91%) as a red solid.

m.p.: 122.2 – 124.7 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.63 (s, 2 H).

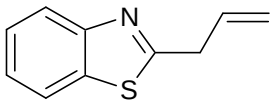
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 140.8, 136.5, 131.0.

MS (70 eV, EI) *m/z* (%): 328 (53), 327 (7), 326 (100), 324 (47) [^{79}Br-M^+], 247 (17), 245 (15), 221 (11), 219 (8), 166 (8), 140 (24), 96 (12), 69 (9).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1682, 1477, 1375, 1153, 1000, 893, 850, 829, 735.

HRMS (EI) for **$C_6H_2{}^{79}Br_2N_2S_2$** (323.8026): 323.8023.

Synthesis of 2-allyl-benzothiazole (8f):



Benzothiazole (**10a**) (0.135 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 30 min according to **TP 2**. The mixture was then cooled to 0°C and allyl bromide

(0.145 g, 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 30 min. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/diethyl ether, 9:1) furnished 2-allyl-benzothiazole (**8f**) (0.135 g, 77%) as a pale yellow liquid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.83 – 8.02 (m, 2 H), 7.29 – 7.49 (m, 2 H), 6.12 (m, 1 H), 5.31 (m, 2 H), 3.89 (dt, ^3J = 6.8 Hz, ^4J = 1.4 Hz, 2 H).

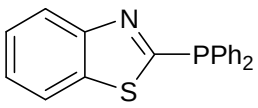
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 170.3, 153.6, 135.6, 133.4, 126.2, 125.0, 123.0, 121.7, 119.2, 38.9.

MS (70 eV, EI) *m/z* (%): 176 (25), 175 (100) [M^+], 174 (63), 173 (11), 149 (47), 75 (10) 44 (10).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1490, 1456, 1434, 1314, 1284, 1218, 1202, 1126, 954, 938, 926, 756, 726, 708, 696, 650, 610.

HRMS (EI) for **$C_{10}H_9NS$** (175.0456): 175.0471.

Synthesis of 2-diphenylphosphanyl-benzothiazole (8f):



Benzothiazole (**10a**) (0.135 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 30 min according to **TP 2**. The mixture was then cooled to 0 °C and PPh_2Cl (0.265 g, 1.2 mmol) was then added dropwise at 0 °C. The resulting mixture was warmed to 25 °C and stirred for 5 h. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/diethyl ether, 4:1) furnished 2-diphenyl-phosphanyl-benzothiazole (**8g**) (0.252 g, 79%) as a pale yellow solid.

m.p.: 79.9 – 80.8 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.25 (d, ^3J = 7.9 Hz, 1 H), 7.84 (d, ^3J = 7.9 Hz, 1 H), 7.56 (m, 5 H), 7.43 (m, 7 H).

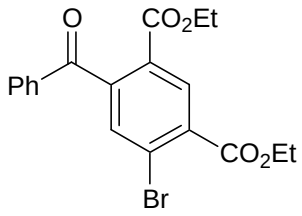
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 174.3 (d, $^1J_{CP}$ = 22 Hz), 156.1 (d, $^1J_{CP}$ = 12 Hz), 137.7, 135.2 (d, $^1J_{CP}$ = 10 Hz), 134.4, 134.1, 132.9, 132.3, 132.2, 130.2, 129.1, 129.0, 128.8, 126.4, 125.5, 125.0, 123.7, 121.6, 105.0.

MS (70 eV, EI) *m/z* (%): 320 (25), 319 (100) [M^+], 318 (63), 242 (15), 241 (13), 183 (45), 152 (6), 107 (9).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1452, 1435, 1414, 1312, 1236, 1089, 1000, 988, 767, 742, 734, 690.

HRMS (EI) for **$C_{19}H_{14}NPS$** (319.0585): 319.0569.

Synthesis of 4-benzoyl-6-bromo-isophthalic acid diethyl ester (13a):



6-Bromo-isophthalic acid diethyl ester (**11a**) (0.301 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 10 h according to **TP 2**. The reaction mixture was cooled to -20 °C, CuCN•2LiCl (1.0 M solution in THF, 1.1 mL, 1.1 mmol) was added and the reaction mixture was stirred for 15 min. Then, benzoyl chloride (0.353 g, 2.5 mmol) was added at -20 °C. The reaction mixture was slowly warmed to 25 °C and stirred at this temperature for 1 h. Then the reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/diethyl ether, 3:1) furnished 4-benzoyl-6-bromo-isophthalic acid diethyl ester (**13a**) (0.336 g, 83%) as a colorless solid.

m.p.: 66.9 – 68.1 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ : 8.43 (s, 1 H), 7.72 (m, 2 H), 7.66 (s, 1 H), 7.58 (m, 1 H), 7.44 (m , 2 H), 4.46 (q, ^{3}J = 7.1 Hz, 2 H), 4.09 (q, ^{3}J = 7.1 Hz, 2 H), 1.44 (t, ^{3}J = 7.5 Hz, 3 H), 1.04 (t, ^{3}J = 7.1 Hz, 3 H).

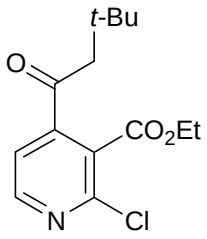
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 165.0, 164.4, 144.7, 136.3, 133.7, 133.6, 133.3, 132.9, 129.4, 128.7, 128.3, 126.4, 62.3, 62.1, 14.2, 13.6.

MS (70 eV, ESI) *m/z* (%): 406 (10), 404 (11) [^{79}Br-M^+], 361 (17), 359 (16), 329 (21), 327 (21), 301 (30), 299 (30), 151 (12), 105 (100), 77 (32).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1734, 1710, 1670, 1578, 1470, 1448, 1322, 1278, 1238, 1226, 1100, 1020, 970, 886, 862, 778, 734, 704, 692, 682.

HRMS (ESI) for **$C_{19}H_{17}{}^{79}BrO_5$** (405.0338 (M^+ + H)): 405.0326 (M^+ + H).

Synthesis of 2-chloro-4-(3,3-dimethyl-butyryl)-nicotinic acid ethyl ester (13b):



2-Chloro-nicotinic acid ethyl ester (**11b**) (0.186 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 5 h according to **TP 2**. The reaction mixture was cooled to -20 °C, CuCN•2LiCl (1.0 M solution in THF, 1.1 mL, 1.1 mmol) was added and the reaction mixture was stirred for 15 min. Thereafter, *t*-$BuCH_2COCl$ (0.336 g, 2.5 mmol) was added at -20 °C. The reaction mixture was slowly warmed to 25 °C and stirred at this temperature for 2 h. Then, the reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (CH_2Cl_2) furnished 2-chloro-4-(3,3-dimethyl-butyryl)-nicotinic acid ethyl ester (**13b**) (0.212 g, 75%) as a colorless oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.66 (d, ^3J = 5.1 Hz, 1 H), 7.51 (d, ^3J = 5.1 Hz, 1 H), 4.45 (q, ^3J = 7.3 Hz, 2 H), 2.78 (s, 2 H), 1.40 (t, ^3J = 7.2 Hz, 3 H), 1.04 (s, 9 H).

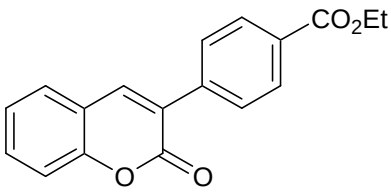
^{13}C-NMR (150 MHz, $CDCl_3$) δ: 199.0, 165.7, 150.9, 149.8, 149.7, 146.6, 120.4, 62.7, 51.2, 32.0, 30.0, 14.1.

MS (70 eV, EI) *m/z* (%): 283 [M^+] (2), 237 (13), 222 (23), 214 (14), 212 (19), 212 (46), 210 (56), 186 (40), 185 (11), 184 (100), 183 (32), 182 (34), 181 (93), 57 (29), 41 (12).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2951, 1731, 1690, 1571, 1540, 1362, 1261, 1186, 1119, 1055, 876, 732, 677.

HRMS (EI) for **$C_{14}H_{18}ClNO_3$** (283.0975): 283.0969.

Synthesis of 4-(2-oxo-2*H*-chromen-3-yl)-benzoic acid ethyl ester (13c):



Coumarine (**11c**) (0.146 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 4 h according to **TP 2**. $Pd(dba)_2$ (28 mg, 5 mol%) and P(*o*-furyl)$_3$ (23 mg, 10 mol%) dissolved in THF (2 mL) were then transferred *via* cannula to the reaction mixture, followed by the addition of ethyl 4-iodobenzoate (0.414 g, 1.5 mmol) dissolved in THF (1 mL). The reaction mixture was stirred at 25 °C for 2 h. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/diethyl ether, 3:1) furnished the compound **13c** (0.244 g, 83%) as a colorless solid.

m.p.: 193.3 – 194.4 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, ^{3}J = 8.5 Hz, 2 H), 7.89 (s, 1 H), 7.79 (d, ^{3}J = 8.7 Hz, 2 H), 7.56 (m, 2 H), 7.35 (m, 2 H), 4.40 (d, ^{3}J = 7.2 Hz, 2 H), 1.41 (t, ^{3}J = 7.0 Hz, 3 H).

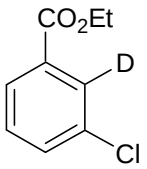
^{13}C-NMR (100 MHz, $CDCl_3$) δ: 166.4, 160.4, 154.0, 141.0, 139.2, 132.2, 130.9, 123.0, 128.7, 128.4, 127.6, 124.9, 119.6, 116.8, 61.4, 14.6.

MS (70 eV, EI) *m/z* (%): 295 (17), 294 (81) [M^+], 266 (23), 250 (22), 249 (100), 238 (16), 222 (11), 221 (39), 165 (45), 163 (10), 44 (26).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1710, 1606, 1560, 1478, 1366, 1292, 1272, 1234, 1104, 954, 864, 856, 784, 766, 752, 738, 730, 698, 640, 622.

HRMS (EI) for **$C_{18}H_{14}O_4$** (294.0892): 294.0915.

Synthesis of 2-deutero-3-chloro-benzoic acid ethyl ester (13d):



3-Chloro-benzoic acid ethyl ester (**11d**) (0.185 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn{\bullet}2MgCl_2{\bullet}2LiCl$ (**2**)

(0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 25 h according to **TP 2**. D_2O (0.2 mL, 10 mmol) was added dropwise at 5 °C, the resulting mixture was warmed to 25 °C and stirred for 30 min. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/CH_2Cl_2 4:1) furnished 2-deutero-3-chloro-benzoic acid ethyl ester (**13d**) (0.155 g, 84%) as a colorless liquid.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.93 (m, 1 H), 7.35 – 7.54 (m, 2 H), 4.38 (q, ^3J = 7.5 Hz, 2 H), 1.40 (t, ^3J = 7.1 Hz, 3 H).

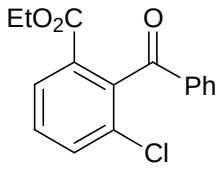
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 165.6, 134.7, 134.6, 133.0, 132.4, 130.0, 127.9, 61.6, 14.9.

MS (70 eV, EI) *m/z* (%): 185 (19) [M^+], 159 (10), 157 (33), 156 (10), 142 (28), 141 (16), 140 (100), 139 (29), 112 (24).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1718, 1572, 1418, 1366, 1274, 1256, 1210, 1196, 1122, 1080, 768, 748, 728, 626.

HRMS (EI) for **$C_9H_8DClO_2$** (185.0354): 185.0374.

Synthesis of 2-benzoyl-3-chloro benzoic acid ethyl ester (13e):



3-Chloro-benzoic acid ethyl ester (**11d**) (0.185 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 25 h according to **TP 2**. The reaction mixture was cooled to -20 °C, CuCN•2LiCl (1.0 M solution in THF, 1.1 mL, 1.1 mmol) was added and the reaction mixture was stirred for 15 min. Then, benzoyl chloride (0.353 g, 2.5 mmol) was added at -20 °C. The reaction mixture was slowly warmed to 25 °C and stirred at this temperature for 2 h. Then, the reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/diethyl ether, 3:1) furnished 2-benzoyl-3-chloro-benzoic acid ethyl ester (**13e**) (0.228 g, 79%) as a colorless solid.

m.p.: 108.6 – 109.6 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.08 (m, 1 H), 7.81 (m, 2 H), 7.44 – 7.68 (m, 5 H), 4.17 (q, ^{3}J = 7.1 Hz, 2 H), 1.10 (t, ^{3}J = 7.1 Hz, 3 H).

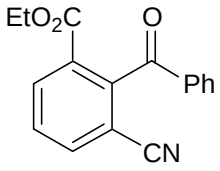
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 164.7, 140.4, 136.7, 133.9, 133.4, 131.7, 130.6, 129.9, 129.0, 128.7, 61.8, 13.6.

MS (70 eV, EI) *m/z* (%): 290 (19), 288 (43) [M^+], 242 (32), 211 (73), 211 (26), 185 (32), 183 (100), 152 (10), 151 (13), 105 (87), 77 (31).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1706, 1672, 1584, 1564, 1430, 1366, 1284, 1202, 1152, 1074, 1028, 928, 866, 764, 744, 734, 702, 652, 618.

HRMS (EI) for **$C_{16}H_{13}ClO_3$** (288.0553): 288.0569.

Synthesis of 2-benzoyl-3-cyano benzoic acid ethyl ester (13e):



3-Cyano-benzoic acid ethyl ester (**11d**) (0.175 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 ^{o}C for 30 h according to **TP 2**. The reaction mixture was cooled to -20 ^{o}C, CuCN•2LiCl (1.0 M solution in THF, 1.1 mL, 1.1 mmol) was added and the reaction mixture was stirred

for 15 min. Then, benzoyl chloride (0.353 g, 2.5 mmol) was added at -20 °C. The reaction mixture was slowly warmed to 25 °C and stirred at this temperature for 5 h. Then, the reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/diethyl ether, 3:2) furnished 2-benzoyl-3-cyano-benzoic acid ethyl ester (**13f**) (0.203 g, 73%) as a colorless solid.

m.p.: 138.4 – 140.6 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.34 (d, ^3J = 7.9 Hz, 1 H), 7.93 (d, ^3J = 7.9 Hz, 1 H), 7.75 (d, ^3J = 7.5 Hz, 2 H), 7.69 (t, ^3J = 7.9 Hz, 1 H), 7.60 (d, ^3J = 7.3 Hz, 1 H), 7.47 (t, ^3J = 7.8 Hz, 2 H), 4.14 (q, ^3J = 7.2 Hz, 2 H), 1.06 (t, ^3J = 7.2 Hz, 3 H).

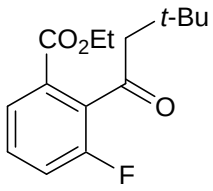
^{13}C-NMR (150 MHz, $CDCl_3$) δ: 193.8, 164.2, 145.7, 136.8, 138.3, 134.6, 134.2, 130.4, 130.0, 129.5, 129.1, 116.1, 111.9, 62.5, 13.8.

MS (70 eV, EI) *m/z* (%): 280 (9), 279 (46) [M^+], 235 (88), 234 (18), 206 (8), 174 (28), 105 (100), 77 (24).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1716, 1670, 1474, 1444, 1366, 1272, 1160, 1018, 936, 923, 768, 707, 659.

HRMS (EI) for **$C_{17}H_{13}NO_3$** (279.0895): 279.0873.

Synthesis of 2-(3,3-dimethyl-butyryl)-3-fluoro-benzoic acid ethyl ester (13g):



3-Fluoro-benzoic acid (**11f**) (0.168 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 12 h according to **TP 2**. The reaction mixture was cooled to -20 °C, CuCN•2LiCl (1.0 M solution in THF, 1.1 mL, 1.1 mmol) was added and the reaction mixture was stirred for 15 min. Then, *t*-$BuCH_2COCl$ (0.335 g, 2.2 mmol) was added at -20 °C. The reaction mixture was slowly warmed to 0 °C and stirred at this temperature for 3 h. Then, the reaction was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/ CH_2Cl_2, 2:1) furnished 2-(3,3-dimethyl-butyryl)-3-fluoro-benzoic acid ethyl ester (**13g**) (0.202 g, 76%) as a colorless oil.

^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.74 (d, ^3J = 7.9 Hz, 1 H), 7.38 (m, 1 H), 7.24 (t, ^3J = 8.6 Hz, 1 H), 4.34 (q, ^3J = 7.1 Hz,

2 H), 2.77 (s, 2 H), 1.35 (t, ^{3}J = 7.2 Hz, 3 H), 1.13 (s, 9 H).

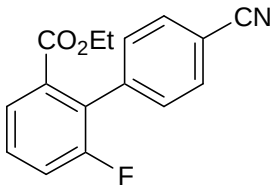
^{13}C-NMR (150 MHz, $CDCl_3$) δ: 201.0, 165.3, 158.8 (d, $^{1}J_{CF}$ = 247 Hz), 132.6 (d, $^{2}J_{CF}$ = 20 Hz), 130.3 (d, $^{3}J_{CF}$ = 8 Hz), 130.1 (d, $^{3}J_{CF}$ = 4 Hz), 126.2, 120.2 (d, $^{2}J_{CF}$ = 22 Hz), 62.0, 56.5, 31.0, 29.6, 14.4.

MS (70 eV, EI) *m/z* (%): 266 (2) [M^+], 210 (19), 195 (29), 167 (100), 165 (11), 164 (30), 94 (7), 41 (7).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1713, 1604, 1450, 1365, 1277, 1135, 1021, 1008, 956, 907, 760, 747, 675.

HRMS (EI) for **$C_{15}H_{19}FO_3$** (266.1318): 266.1318.

Synthesis of 4'-cyano-6-fluoro-biphenyl-2-carboxylic acid ethyl ester (13h):



3-Fluoro-benzoic acid (**11f**) (0.168 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn{\bullet}2MgCl_2{\bullet}2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 ^{o}C for 12 h according to **TP 2**. $Pd(dba)_2$ (28 mg, 5 mol%) and P(*o*-furyl)$_3$ (23 mg, 10 mol%) dissolved in THF (2 mL) were then transferred *via* cannula to the reaction mixture, followed by the addition of

4-iodobenzonitrile (0.343 g, 1.5 mmol) dissolved in THF (2 mL). The reaction mixture was stirred at 25 °C for 2 h. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/diethyl ether, 3:1) furnished 4'-cyano-6-fluoro-biphenyl-2-carboxylic acid ethyl ester (**13h**) (0.185 g, 69%) as a colorless solid.

m.p.: 94.5 – 95.3 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.76 (d, ^3J = 7.7 Hz, 1 H), 7.70 (d, ^3J = 8.2 Hz, 2 H), 7.47 (m, 1 H), 7.40 (d, ^3J = 8.2 Hz, 2 H), 7.32 (t, ^3J = 8.7 Hz, 1 H), 4.08 (q, ^3J = 7.1 Hz, 2 H), 1.02 (t, ^3J = 7.2 Hz, 3 H).

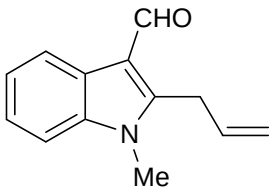
^{13}C-NMR (150 MHz, $CDCl_3$) δ: 166.5, 159.6 (d, $^1J_{CF}$ = 247 Hz,) 139.7, 133.0, 131.9, 130.4, 130.0 (d, $^3J_{CF}$ = 8 Hz), 128.6, (d, $^2J_{CF}$ = 17 Hz), 126.3 (d, $^3J_{CF}$ = 4 Hz), 119.5 (d, ^2J = 23 Hz,), 119.0, 111.9, 61.6, 13.9.

MS (70 eV, EI) *m/z* (%): 270 (9), 269 (51) [M^+], 241 (23), 225 (17), 224 (100), 196 (17), 195 (16), 169 (13).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2228, 1709, 1612, 1450, 1362, 1279, 1262, 1183, 1147, 1028, 1007, 953, 840, 825, 815, 760.

HRMS (EI) for **$C_{16}H_{12}FNO_2$** (269.0852): 269.0851.

Synthesis of 2-allyl-1-methyl-1*H*-indole-3-carbaldehyde (16a):



1-Methyl-1*H*-indole-3-carbaldehyde (**14a**) (0.159 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 30 min according to **TP 2**. The mixture was then cooled to 0 °C and allyl bromide (0.145 g, 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 10 min. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/CH_2Cl_2, 2:1) furnished 2-allyl-1-methyl-1*H*-indole-3-carbaldehyde (**16a**) (0.141 g, 71%) as a red solid.

m.p.: 65.9 – 68.6 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 10.10 (s, 1 H), 8.30 (m, 1 H), 7.30 (m, 3 H), 5.98 (m, 1 H), 5.21 (m, 1 H), 5.02 (m, 1 H), 3.87 (dt, ^3J = 5.8 Hz, ^4J = 1.4 Hz, 2 H), 3.71 (s, 3 H).

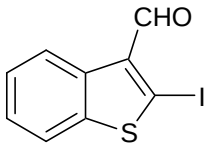
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 184.4, 148.4, 137.4, 133.3, 125.9, 123.6, 121.3, 118.1, 114.6, 109.6, 30.1, 28.8.

MS (70 eV, EI) *m/z* (%): 199 (48) [M^+], 185 (36), 184 (100), 167 (11), 154 (13).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1640, 1580, 1470, 1434, 1392, 1376, 1324, 1260, 1186, 1128, 1044, 1010, 992, 922, 884, 756, 742, 728.

HRMS (EI) for **$C_{13}H_{13}NO$** (199.0997): 199.1005.

Synthesis of 2-iodo-benzo[b]thiophene-3-carbaldehyde (16b):



Benzo[b]thiophene-3-carbaldehyde (**14b**) (0.162 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn{\bullet}2MgCl_2{\bullet}2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 15 min according to **TP 2**. I_2 (0.381 g, 1.5 mmol) dissolved in dry THF (2 mL) was then added dropwise at 0 °C, the resulting mixture was warmed to 25 °C and stirred for 0.5 h. The reaction mixture was quenched with a sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-

chromatography (*n*-pentane/CH_2Cl_2 2:1) furnished 2-iodo-benzo[b]thiophene-3-carbaldehyde (**16b**) (0.236 g, 82%) as a yellow solid.

m.p.: 97.6 – 99.3 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 10.02 (s, 1 H), 8.75 (m, 1 H), 7.76 (m, 1 H), 7.44 (m, 2 H).

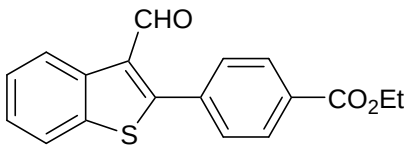
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 188.9, 143.3, 138.3, 134.4, 126.4, 126.3, 123.3, 121.3, 100.0.

MS (70 eV, EI) *m/z* (%): 289, (12), 288 (100) [M^+], 287 (55), 259 (9), 160 (14), 132 (24), 89 (16).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1655, 1482, 1455, 1416, 1374, 1342, 1256, 1102, 1048, 929, 745, 727, 694.

HRMS (EI) for **C_9H_5IOS** (287.9106): 287.9108.

Synthesis of 4-(3-formyl-benzo[b]thiophen-2-yl)-benzoic acid ethyl ester (16c):



Benzo[b]thiophene-3-carbaldehyde (**14b**) (0.162 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn{\bullet}2MgCl_2{\bullet}2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at 25 °C for 20 min according to **TP 2**. $Pd(dba)_2$ (28 mg, 5 mol%) and P(*o*-furyl)$_3$

(23 mg, 10 mol%) dissolved in THF (2 mL) were then transferred *via* cannula to the reaction mixture, followed by the addition of ethyl 4-iodobenzoate (0.331 g, 1.2 mmol) dissolved in THF (1 mL). The reaction mixture was stirred at 25 °C for 6 h. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/diethyl ether, 3:1) furnished 4-(3-formyl-benzo[b]thiophen-2-yl)-benzoic acid ethyl ester (**16c**) (0.208 g, 67%) as a yellow solid.

m.p.: 104.9 – 107.2 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 10.10 (s, 1 H), 8.82 (d, ^3J = 7.9 Hz, 1 H), 8.22 (d, ^3J = 8.4 Hz, 2 H), 7.89 (d, ^3J = 7.9 Hz, 1 H), 7.69 (d, ^3J = 8.4 Hz, 2 H), 7.52 (m, 2 H), 4.47 (q, ^3J = 7.1 Hz, 2 H), 1.46 (t, ^3J = 7.1 Hz, 3 H).

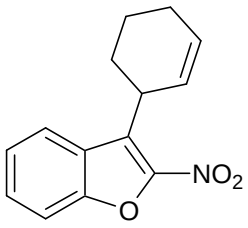
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 186.5, 166.0, 159.0, 143.6, 138.4, 137.3, 136.1, 132.0, 130.8, 130.7, 130.2, 129.2, 128.6, 126.8, 125.7, 121.9, 61.7, 14.6.

MS (70 eV, EI) *m/z* (%): 311 (20), 310 (100) [M^+], 309 (26), 282 (12), 281 (57), 265 (18), 238 (14), 237 (76), 236 (11), 209 (8), 208 (25), 165 (16), 104 (11).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1714, 1675, 1606, 1459, 1431, 1409, 1348, 1284, 1224, 1181, 1104, 1091, 1050, 1022, 757, 748, 724, 699.

HRMS (EI) for **$C_{18}H_{14}O_3S$** (310.0664): 310.0664.

Synthesis of 3-cyclohex-2-enyl-2-nitro-benzofuran (19a):



2-Nitro-benzofuran (**17a**) (0.163 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at -25 °C for 1.5 h according to **TP 2**. 3-Bromo-cyclohexene (0.192 g, 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 30 min. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/CH_2Cl_2, 2:1) furnished 3-cyclohex-2-enyl-2-nitro-benzofuran (**19a**) (0.195 g, 80%) as a pale yellow solid.

m.p.: 104.4 – 107.6 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.96 (d, ^{3}J = 8.2 Hz, 1 H), 7.56 (m, 2 H), 7.32 (m, 1 H), 6.04 (m, 1 H), 5.80 (d, ^{3}J = 10.1 Hz, 1 H), 4.60 (d, ^{3}J = 2.2 Hz, 1 H), 2.23 (d, ^{3}J = 1.8 Hz, 2 H), 2.17 (m, 1 H), 1.93 (s, 1 H), 1.80 (t, ^{3}J = 8.0 Hz, 2 H).

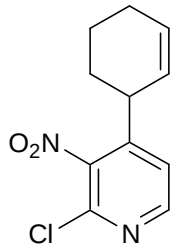
^{13}C-NMR (150 MHz, $CDCl_3$) δ: 152.0, 130.1, 129.7, 127.8, 126.9, 124.8, 124.5, 112.8, 33.7, 29.4, 25.0, 22.2.

MS (70 eV, EI) *m/z* (%): 243 (13) [M^+], 227 (17), 226 (100), 225 (42), 209 (37), 208 (32), 196 (22), 183 (13), 182 (16), 181 (17), 170 (49), 169 (23), 165 (22), 156 (14), 153 (16), 152 (18), 141 (13), 139 (14), 133 (24), 128 (15), 121 (52), 120 (29), 115 (25), 105 (14), 101 (22), 92 (19), 89 (23), 81 (17), 77 (22), 76 (13), 65 (16), 63 (26), 59 (36), 58 (23), 51 (13), 43 (94), 41 (20).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1564, 1507, 1478, 1444, 1366, 1322, 1280, 1244, 1187, 978, 921, 874, 860, 832, 779, 766, 754, 744, 728, 644.

HRMS (EI) for **$C_{14}H_{13}NO_3$** (243.0895): 243.0890.

Synthesis of 2-chloro-4-cyclohex-2-enyl-3-nitro-pyridine (19b):



2-Chloro-3-nitropyridine (**17b**) (0.159 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at -40 °C for 1.5 h according to **TP 2**. 3-Bromo-cyclohexene (0.192 g, 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 30 min. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/CH_2Cl_2, 1:1) furnished 2-chloro-4-cyclohex-2-enyl-3-nitro-pyridine (**19b**) (0.196 g, 82%) as a yellow 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).

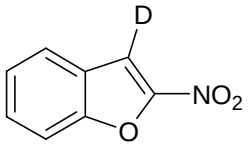
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 150.2, 150.0, 146.5, 141.8, 131.9, 125.9, 123.3, 37.4, 31.3, 24.7, 20.8.

MS (70 eV, EI) *m/z* (%): 237 (3) [M^+-H], 223 (31), 221 (100), 105 (19), 204 (14), 203 (48), 195 (18), 193 (48), 191 (14), 185 (20), 184 (14), 183 (18), 182 (15), 181 (45), 167 (32), 165 (31), 157 (21), 155 (18), 154 (14), 142 (15), 140 (18), 130 (17), 129 (29), 128 (31), 127 (19), 117 (15), 116 (17), 115 (21), 102 (17), 89 (14), 77 (35), 63 (16), 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 3-deutero-2-nitro-benzofuran (19c):



2-Nitro-benzofuran (**17a**) (0.163 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn{\bullet}2MgCl_2{\bullet}2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at -25 °C for 1.5 h according to **TP 2**. D_2O (0.2 mL, 10 mmol) was added dropwise at -25 °C, the

resulting mixture was warmed to -10 ^{o}C and stirred for 20 min. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/CH_2Cl_2 3:1) furnished 3-deutero-2-nitro-benzofuran (**19c**) (0.134 g, 82%) as a pale yellow solid.

m.p.: 134.8 – 135.7.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.89 (d, ^{3}J = 7.9 Hz, 1 H), 7.63 (m, 2 H), 7.45 (m, 1 H).

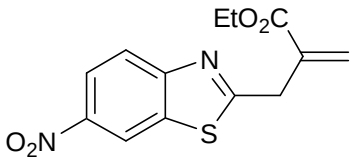
^{13}C-NMR (75 MHz, $CDCl_3$) δ: 153.6, 130.2, 126.0, 125.6, 124.3, 124.2, 113.0, 107.5.

MS (70 eV, EI) *m/z* (%): 165 (10), 164 (100) [M^+], 163 (39), 134 (56), 133 (23), 106 (24), 105 (11), 90 (48), 78 (22), 77 (9), 64 (22), 63 (28), 62 (11).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 1611, 1559, 1544, 1508, 1476, 1441, 1366, 1308, 1241, 1177, 1111, 1091, 1007, 920, 885, 866, 790, 765, 753, 661.

HRMS (ESI) for **$C_8H_4DNO_3$** (164.0331): 164.0345.

Synthesis of 2-(6-nitro-benzothiazol-2-ylmethyl)-acrylic acid ethyl ester (19d):



6-Nitro-benzothiazole (**17c**) (0.266 g, 1.0 mmol) was reacted with a solution of $(TMP)_2Zn•2MgCl_2•2LiCl$ (**2**) (0.5 M in THF, 1.10 mL, 0.55 mmol) at -50 °C for 0.5 h according to **TP 2**. 2-Bromomethyl-acrylic acid ethyl ester (0.230 g, 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 30 min. The reaction mixture was quenched with a sat. aq. NH_4Cl solution (5 mL), extracted with diethyl ether (3 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. Purification by flash-chromatography (*n*-pentane/CH_2Cl_2, 2:1) furnished 2-(6-nitro-benzothiazol-2-ylmethyl)-acrylic acid ethyl ester (**19d**) (0.221 g, 76%) as a pale yellow solid.

m.p.: 74.7 – 75.3 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.79 (d, ^3J = 2.2 Hz, 1 H), 8.34 (dd, ^3J = 8.9 Hz, ^4J = 2.3 Hz, 1 H), 8.08 (d, ^3J = 9.0 Hz, 1 H), 6.49 (s, 1 H), 5.93 (s, 1 H), 4.25 (q, ^3J = 7.2 Hz, 2 H), 4.20 (d, ^4J = 0.9 Hz, 2 H), 1.29 (t, ^3J = 7.2 Hz, 3 H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ: 175.5, 166.0, 157.2, 145.1, 136.2, 129.5, 124.3, 121.8, 118.3, 61.6, 37.6, 14.4.

MS (70 eV, EI) *m/z* (%): 293 (14), 292 (91) [M^+], 263 (22), 247 (28), 246 (61), 220 (28), 219 (49), 218 (100), 201 (12), 174 (12), 173 (48), 172 (39), 63 (22).

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3111, 1698, 1269, 1601, 1570, 1517, 1478, 1439, 1425, 1409, 1371, 1321, 1298, 1273, 1219, 1173, 1123, 1092, 1040, 1022, 969, 902, 830, 754, 721.

HRMS (EI) for **$C_{13}H_{12}N_2O_4S$** (292.0518): 292.0511.

References

[1] C. Ainsworth, *J. Am. Chem. Soc.* **1955**, *77*, 1148.

[2] H. Law, I. Baussanne, J. M. García Fernandéz, Jaques Defaye, *Carbohydr. Res.* **2003**, 451.

[3] P. Reynaud, M. Robba, R. C. Moreau, *Bull. Chim. Fr.* **1962**, 1735.

[4] A. Tromelin, P. Demerseman, R. Royer, *Synthesis* **1985**, *11*, 1074.

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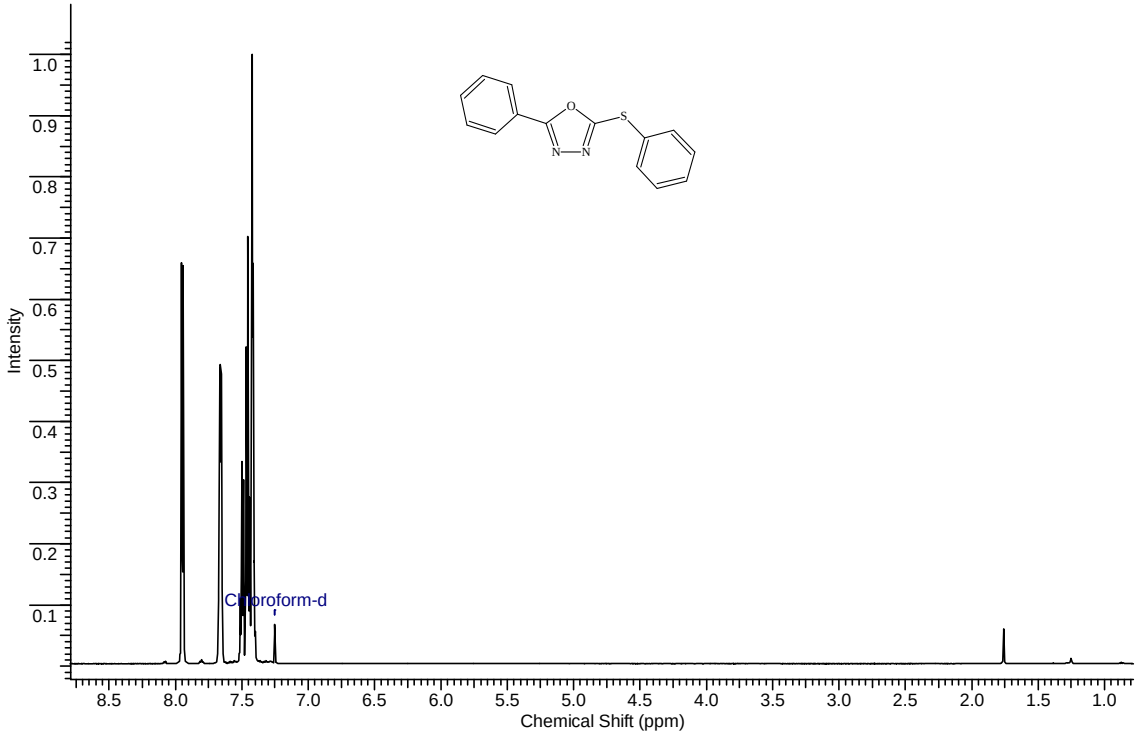
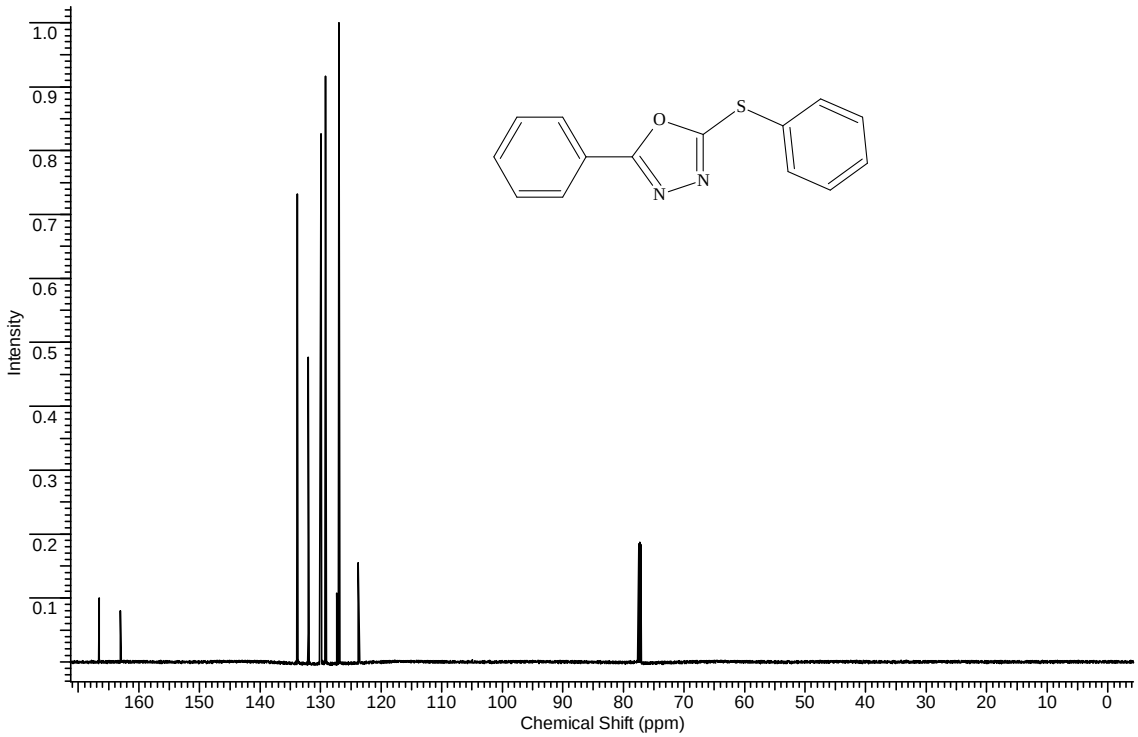
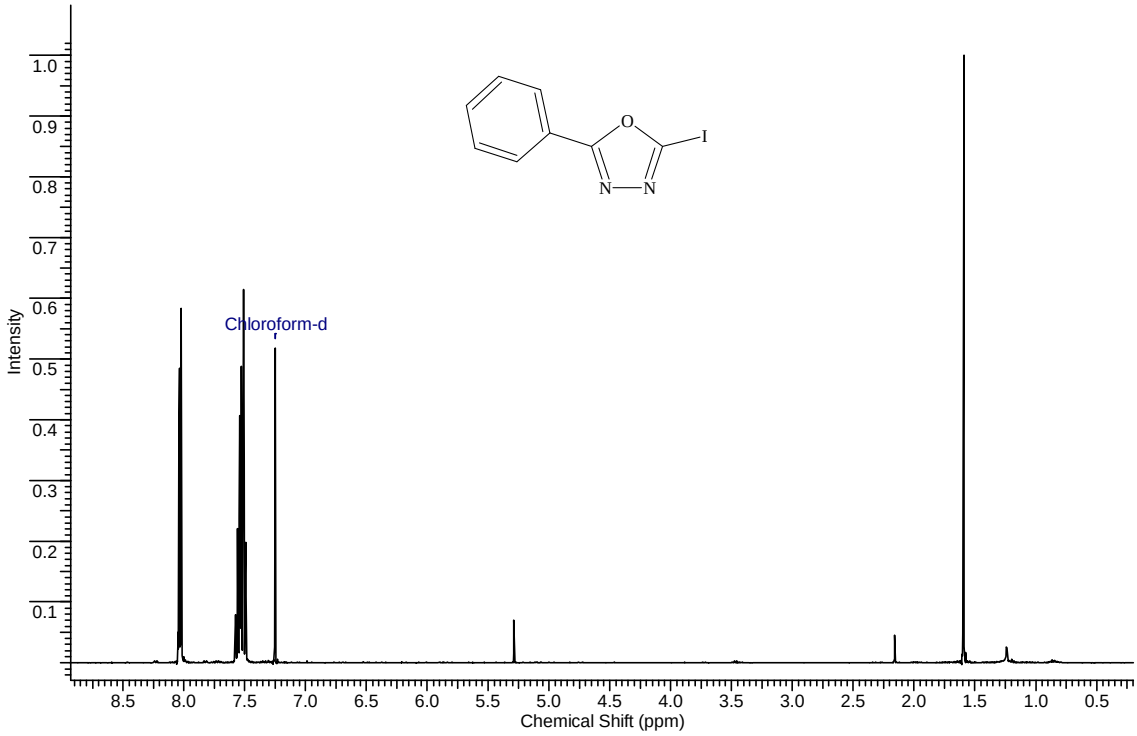
NMR-Spectras

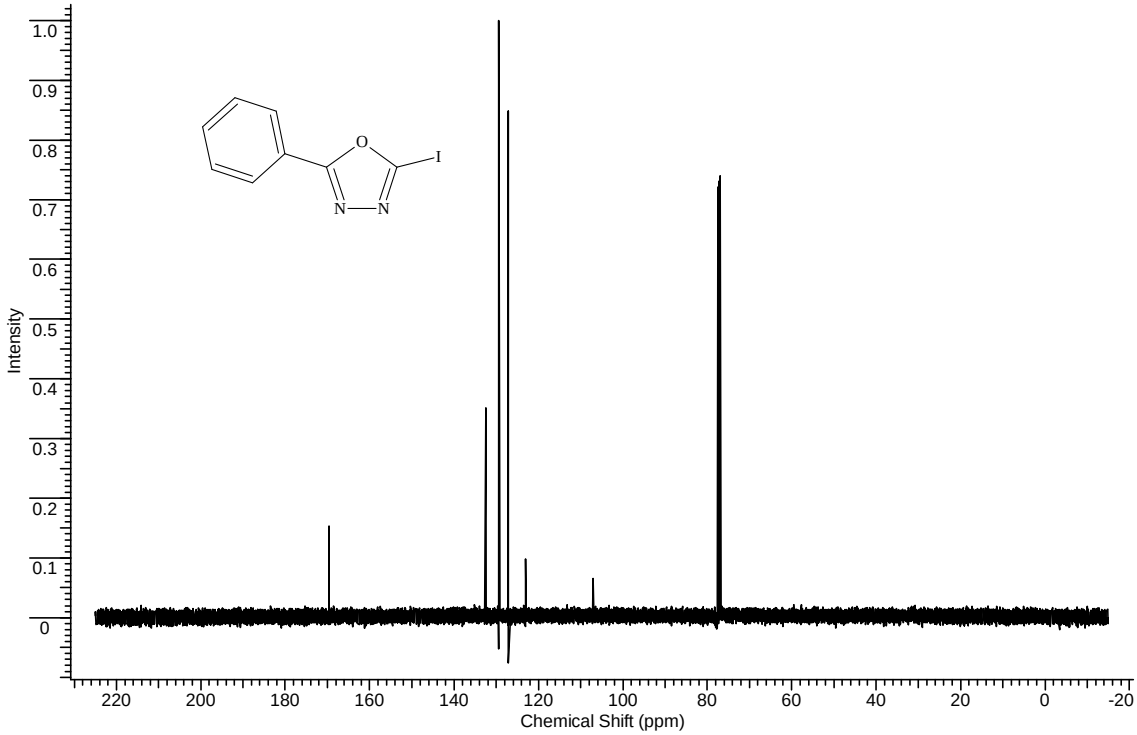
2-Phenyl-5-phenylsulfanyl-[1,3,4]oxadiazole (7a)



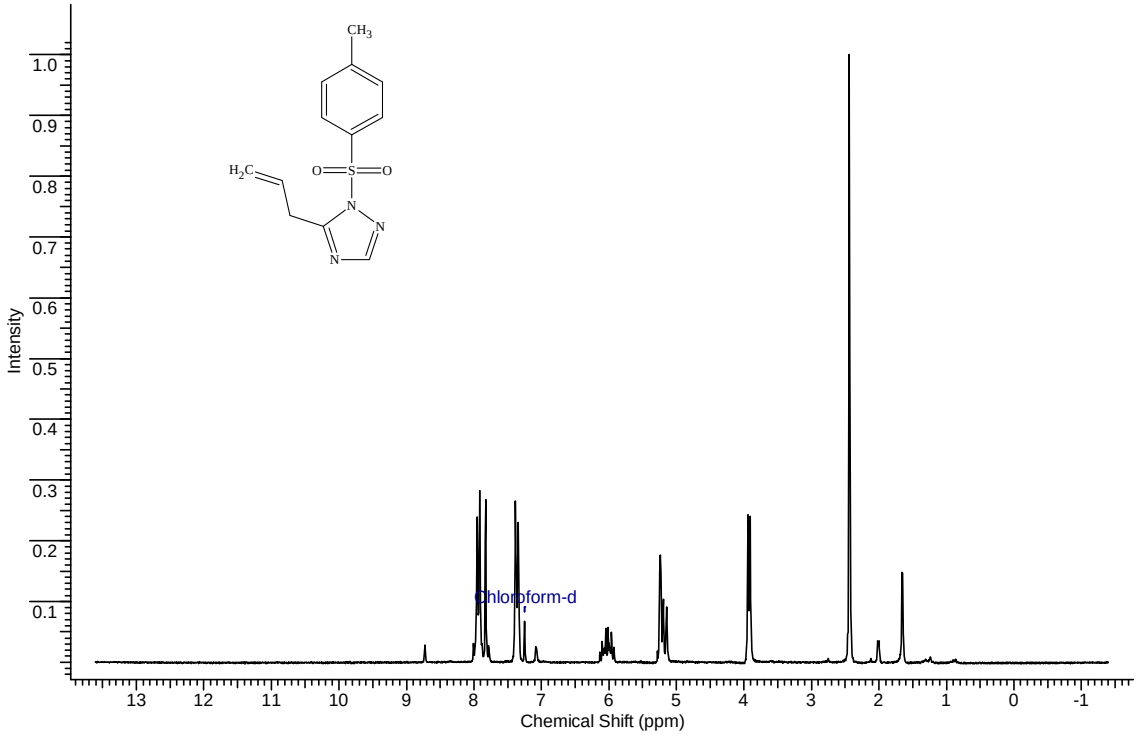


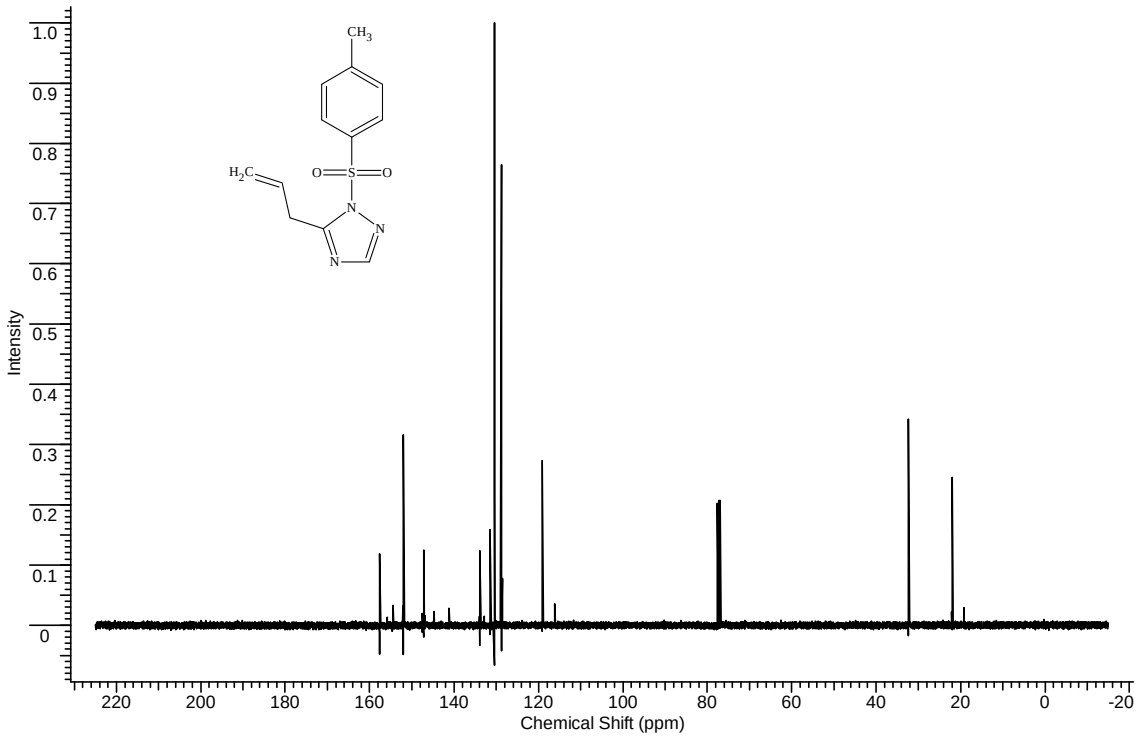
5-Iodo-2-phenyl-[1,3,4]oxadiazole (7b)



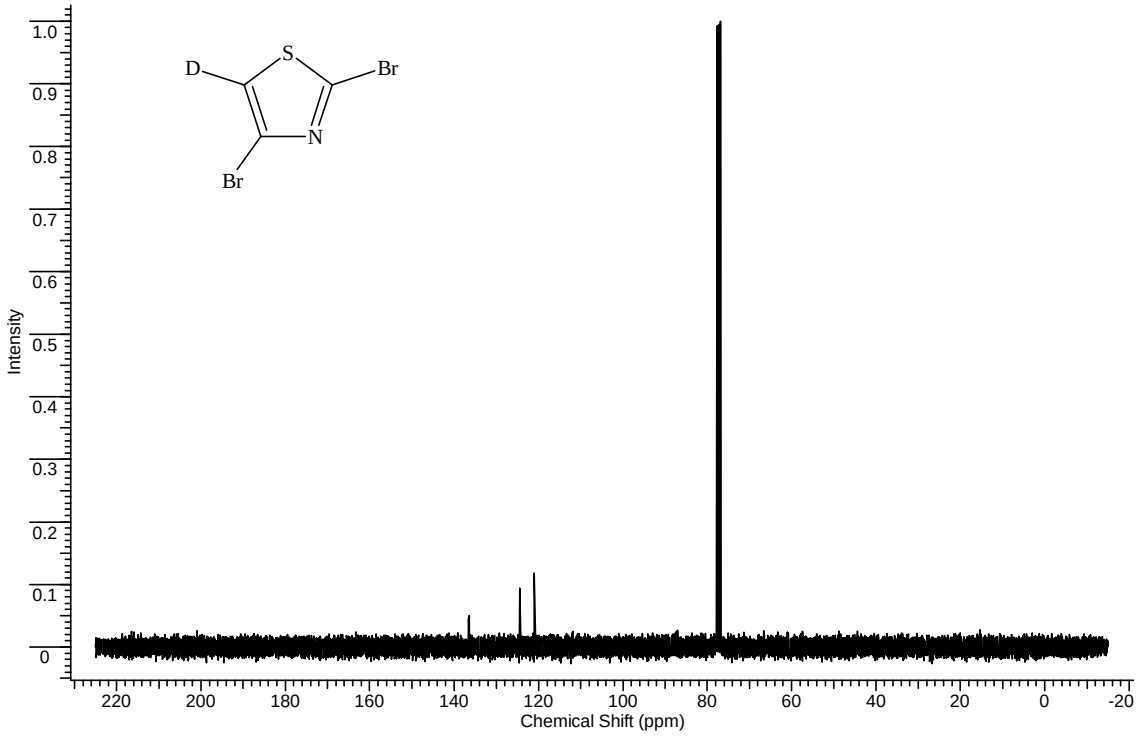


5-Allyl-1-tosyl 1*H*-[1,2,4]triazole (8a)

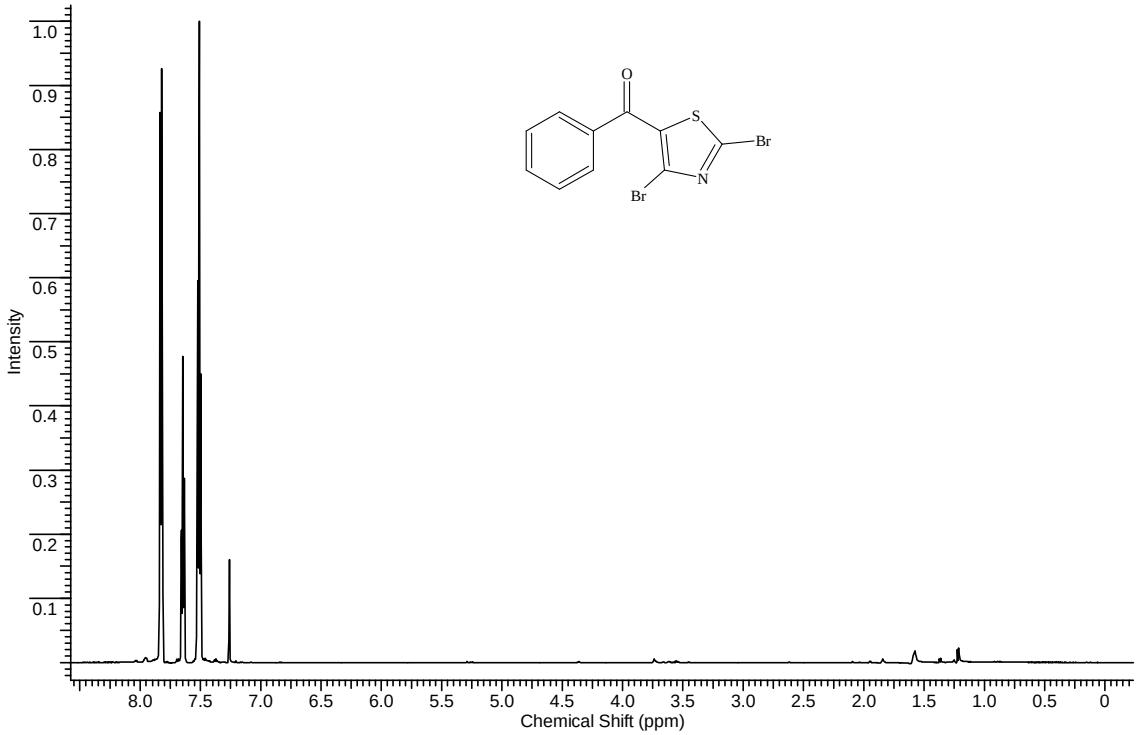


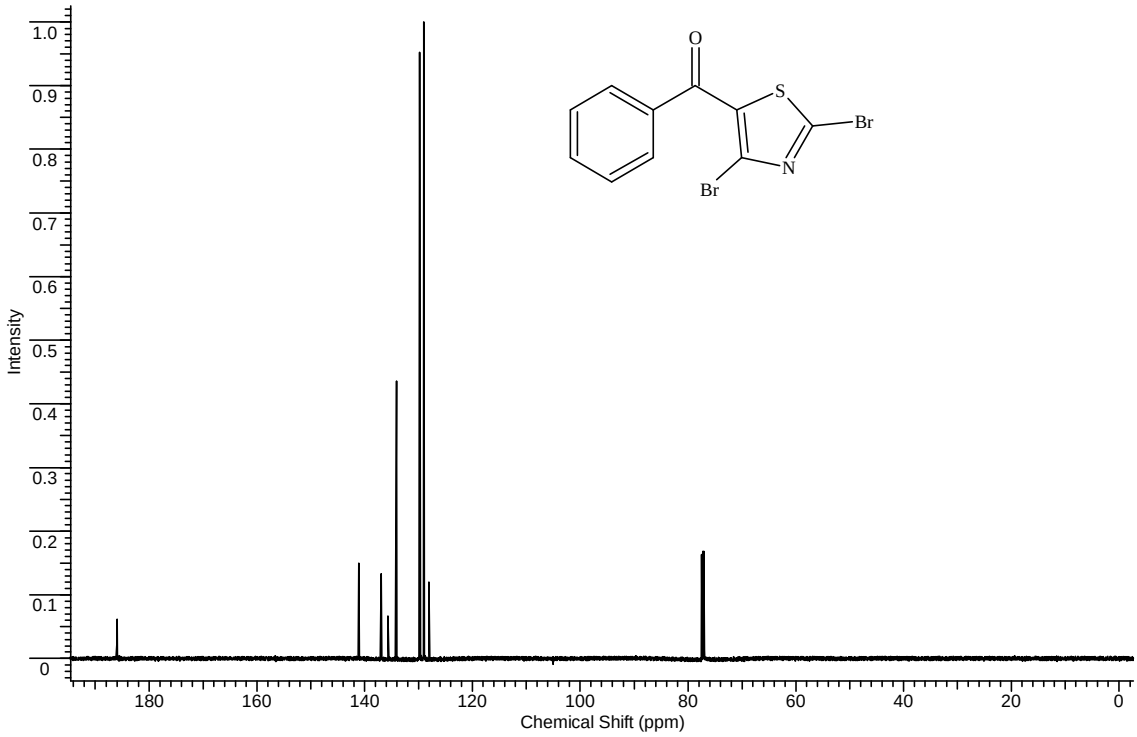


2,4-Dibromo-5-deuterothiazole (8c)

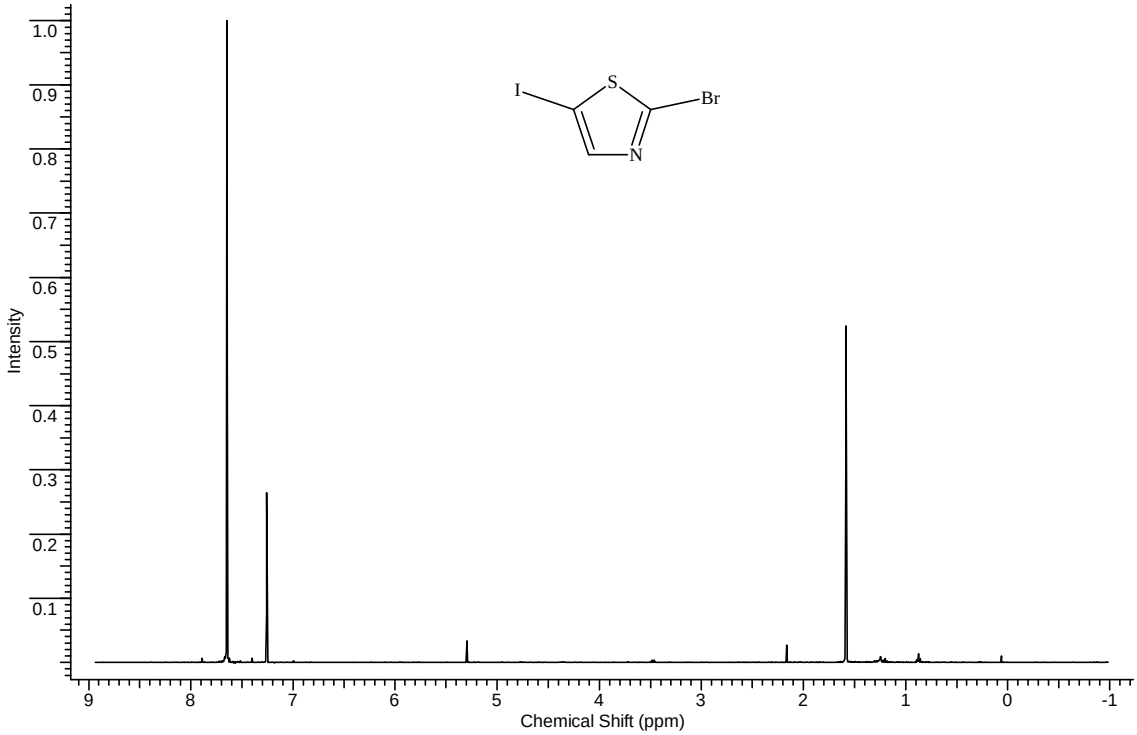


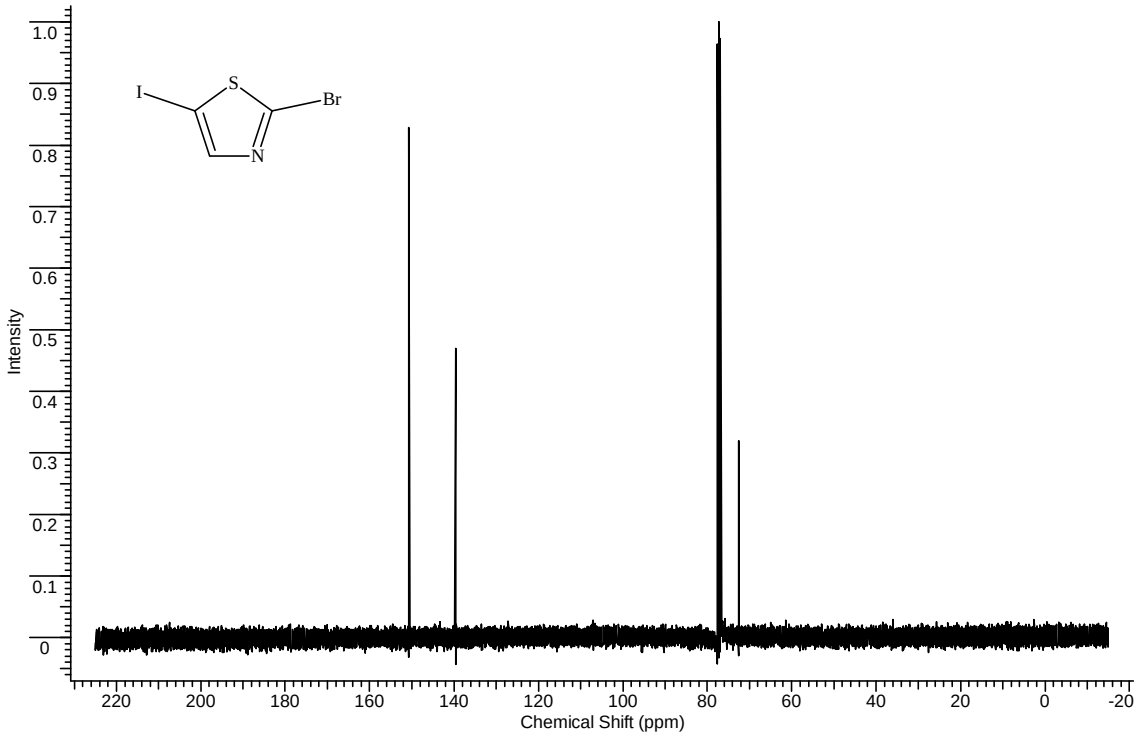
5-Benzoyl-2,4-dibromothiazole (8b)



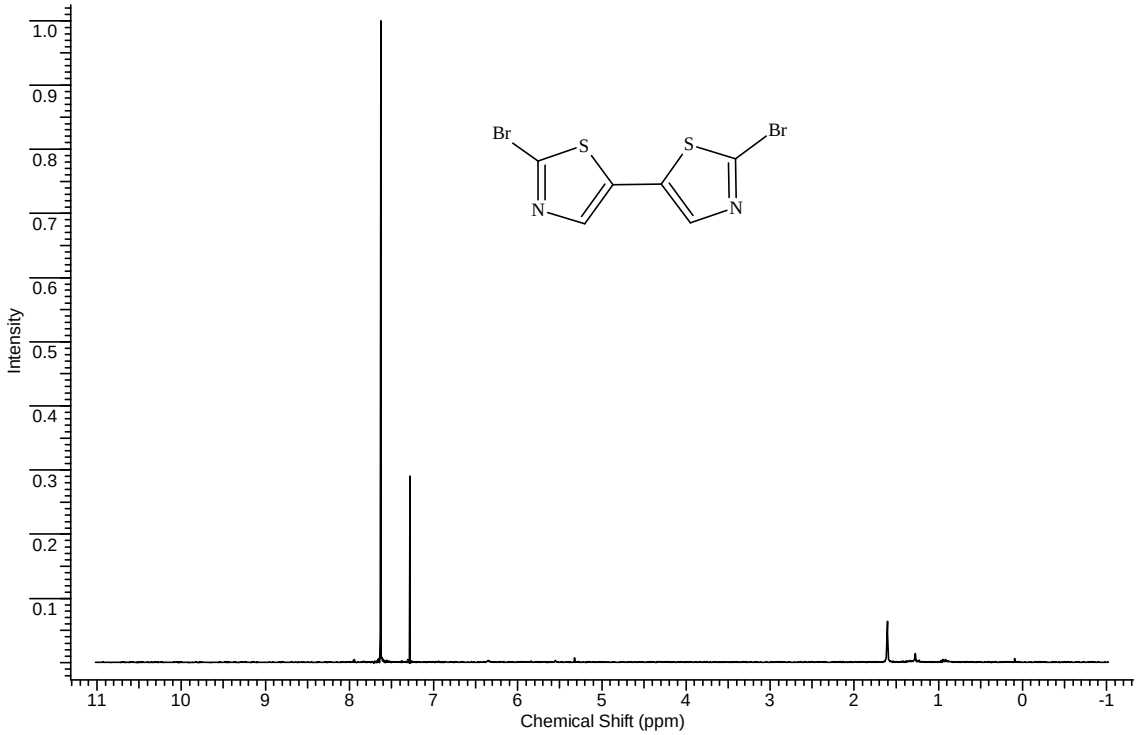


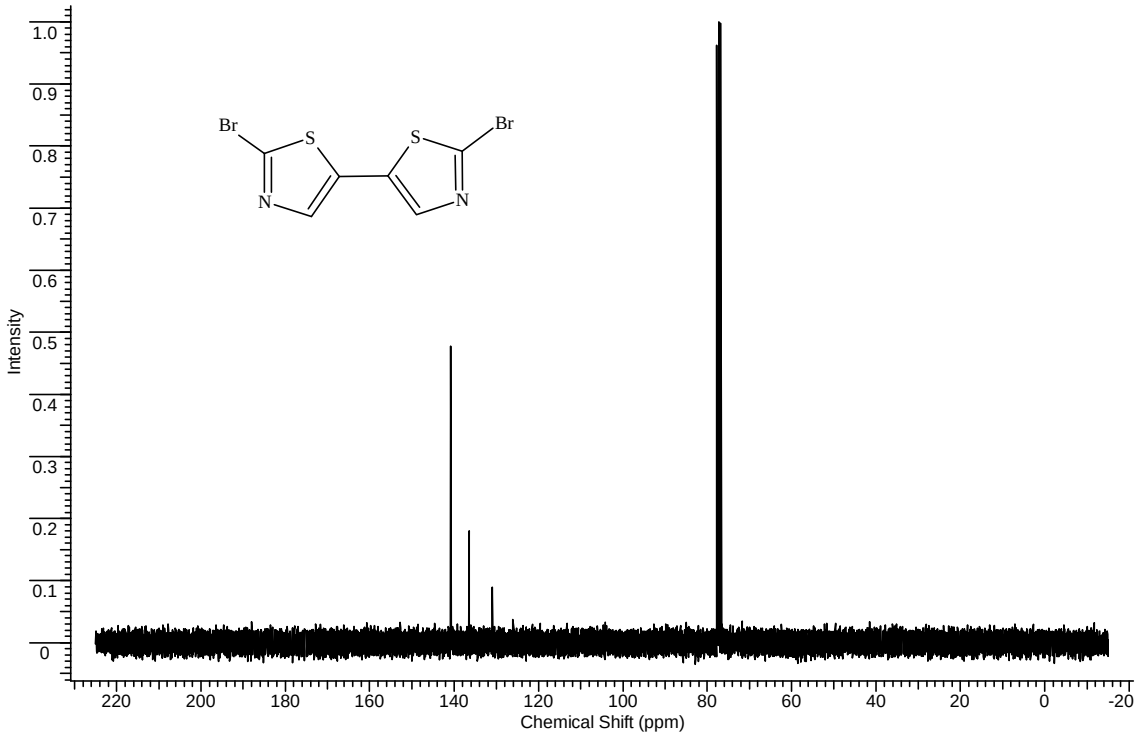
2-Bromo-5-iodo-thiazole (8d)



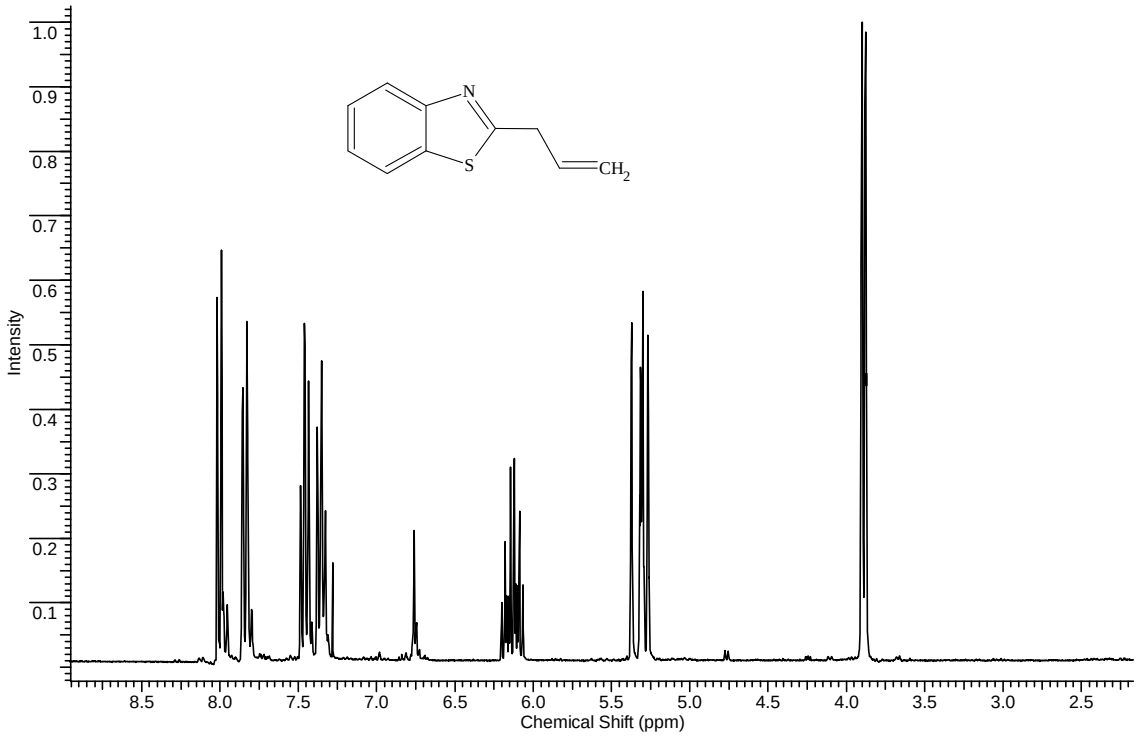


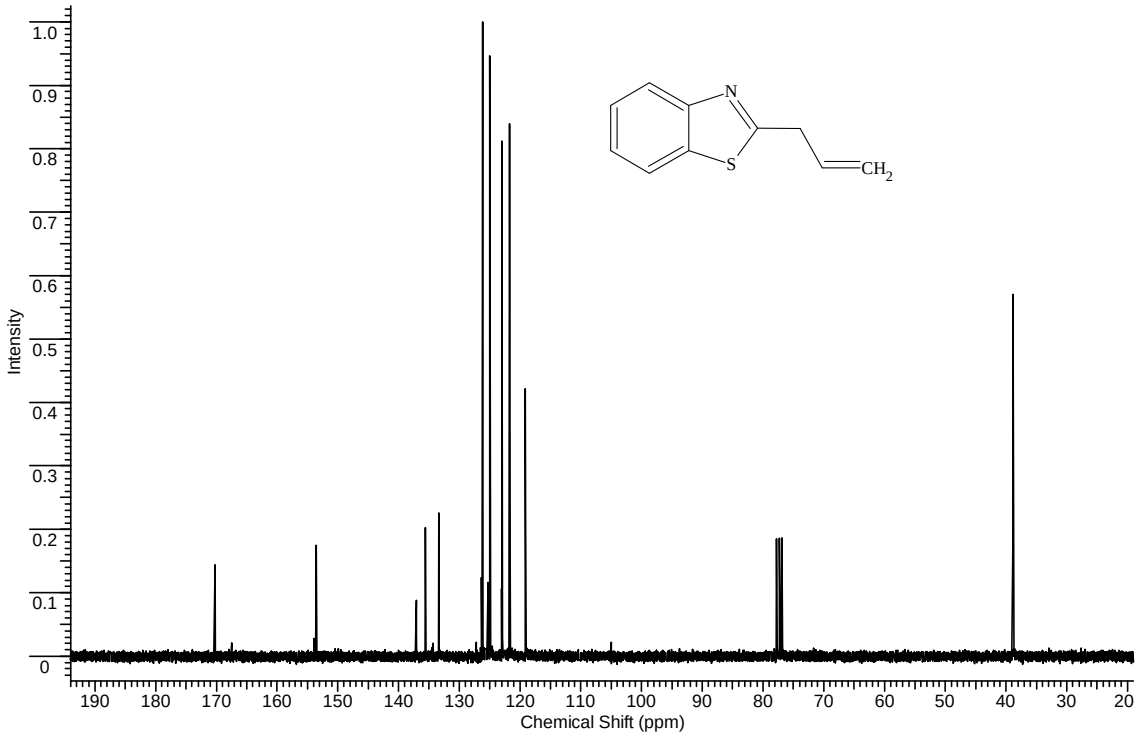
2,2'-Dibromo-[5,5']bithiazolyl (8e)



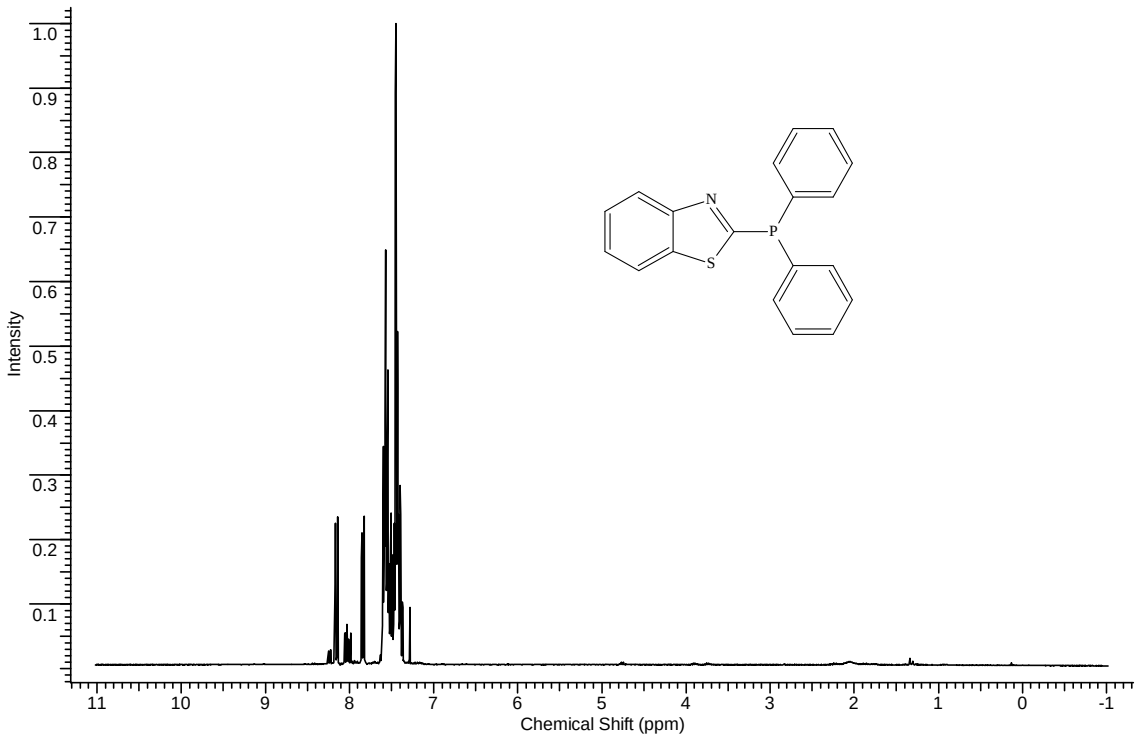


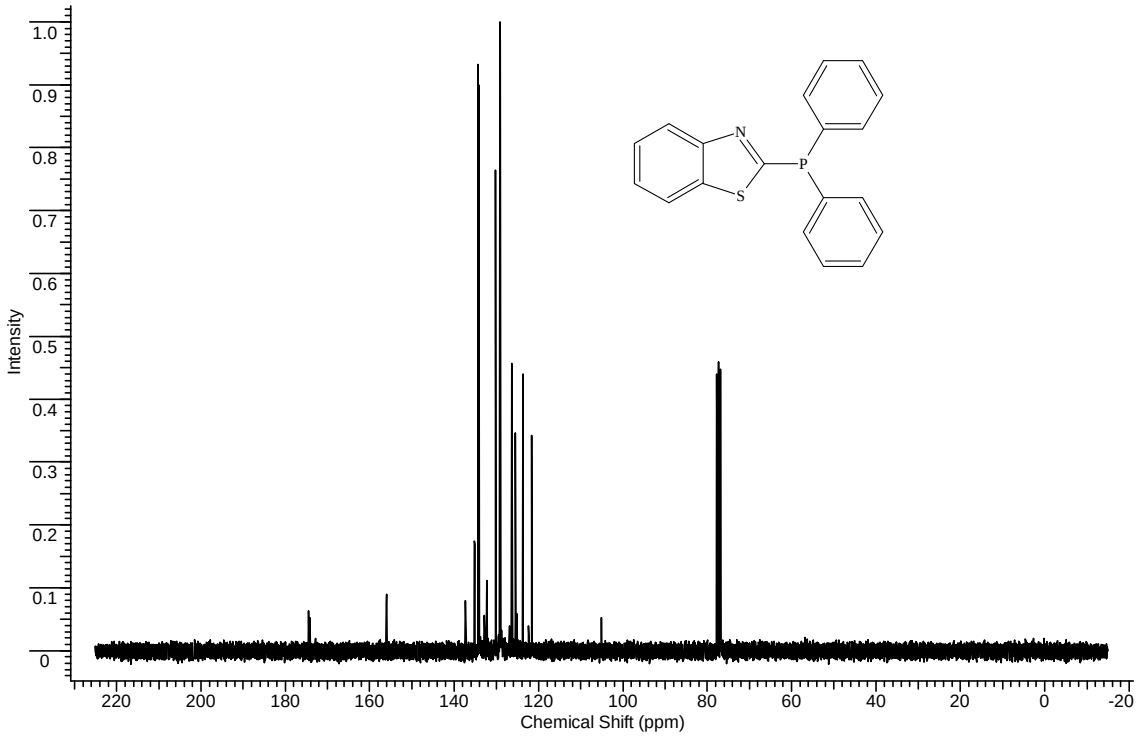
2-Allyl-benzothiazole (8f)



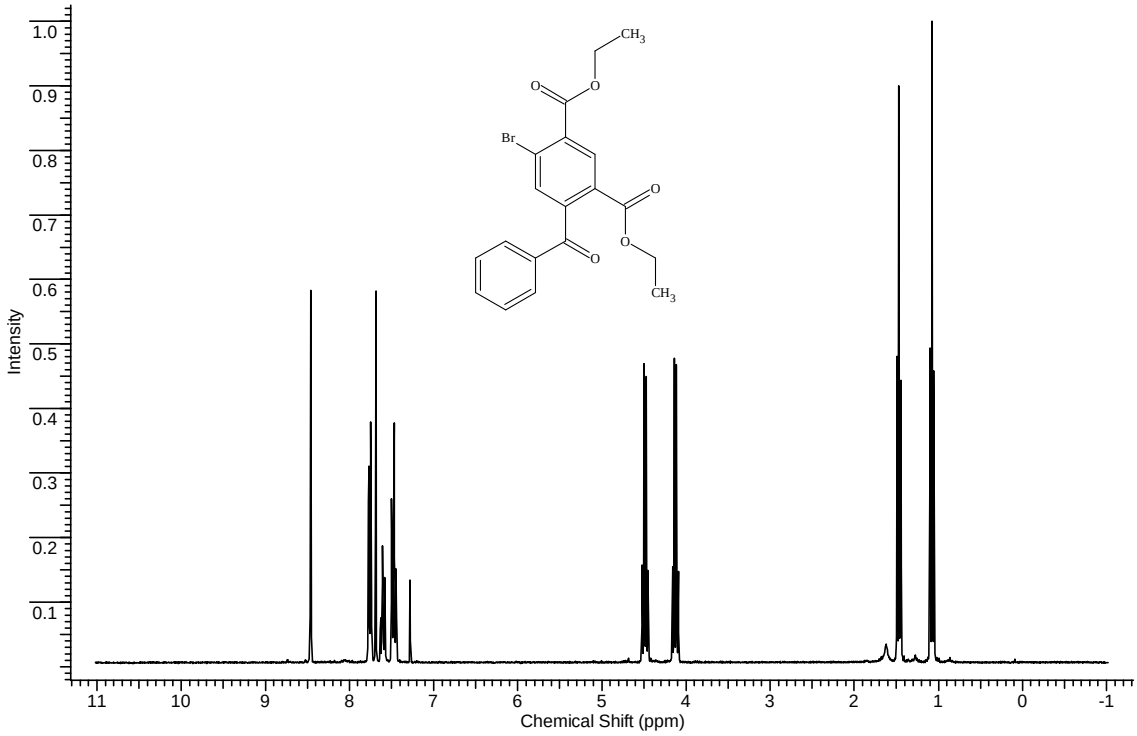


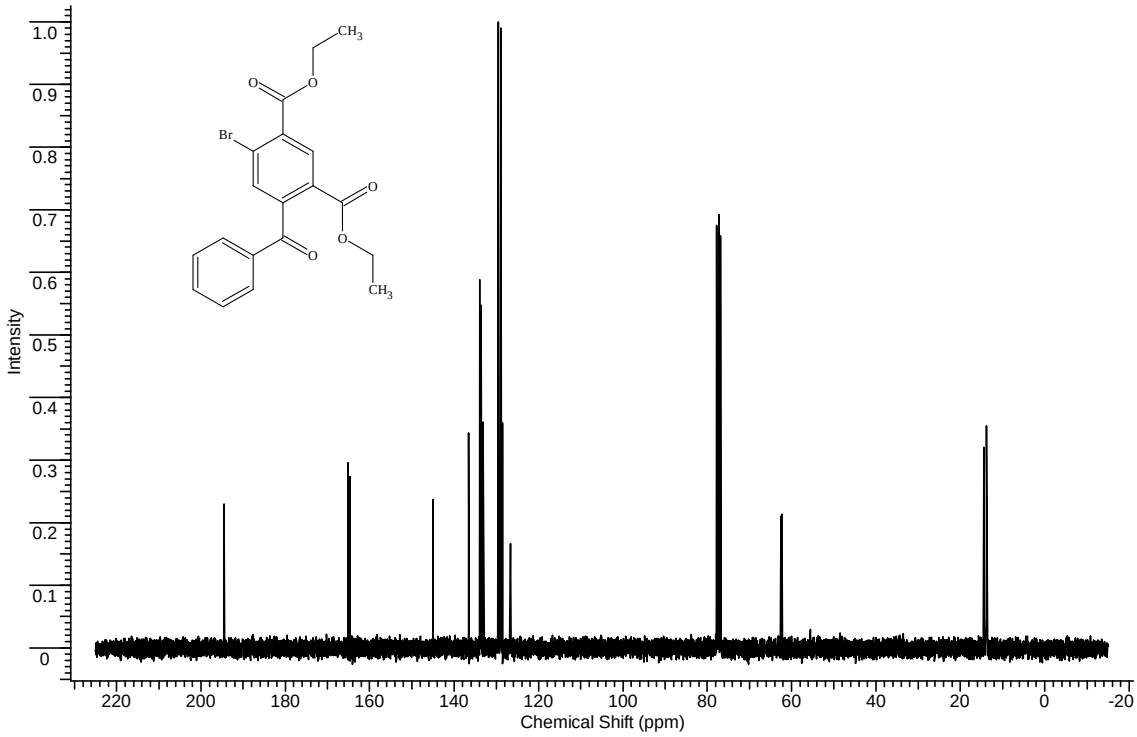
2-Diphenylphosphanyl-benzothiazole (8f)



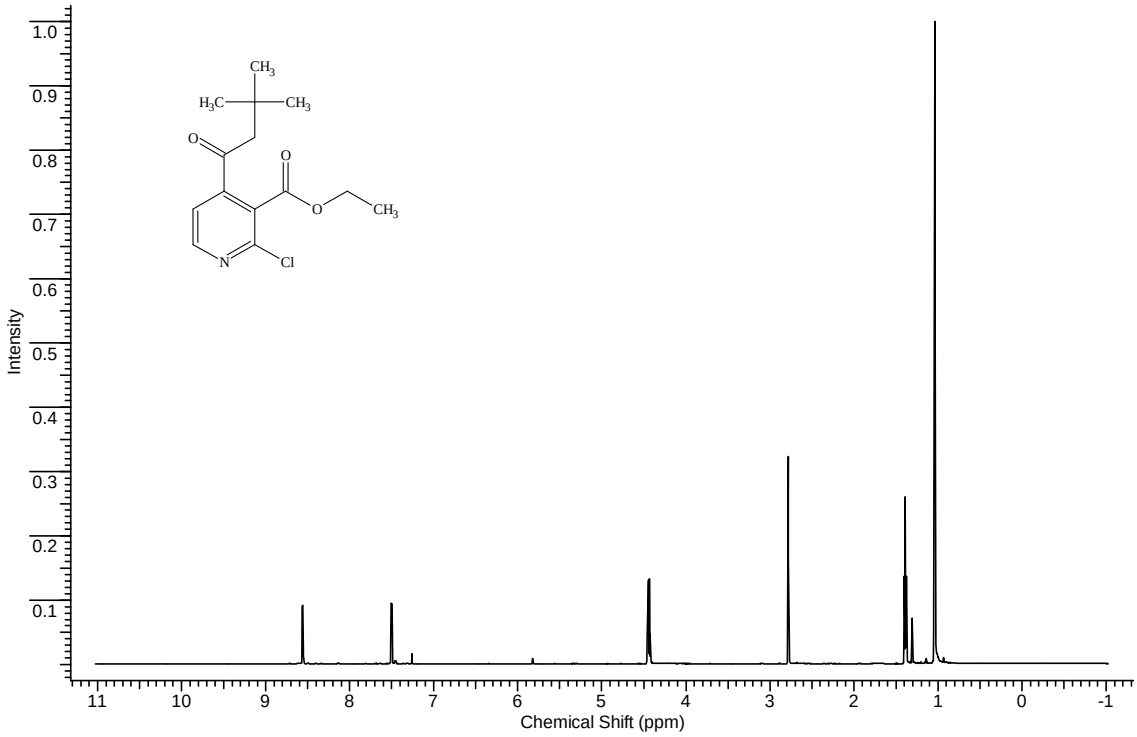


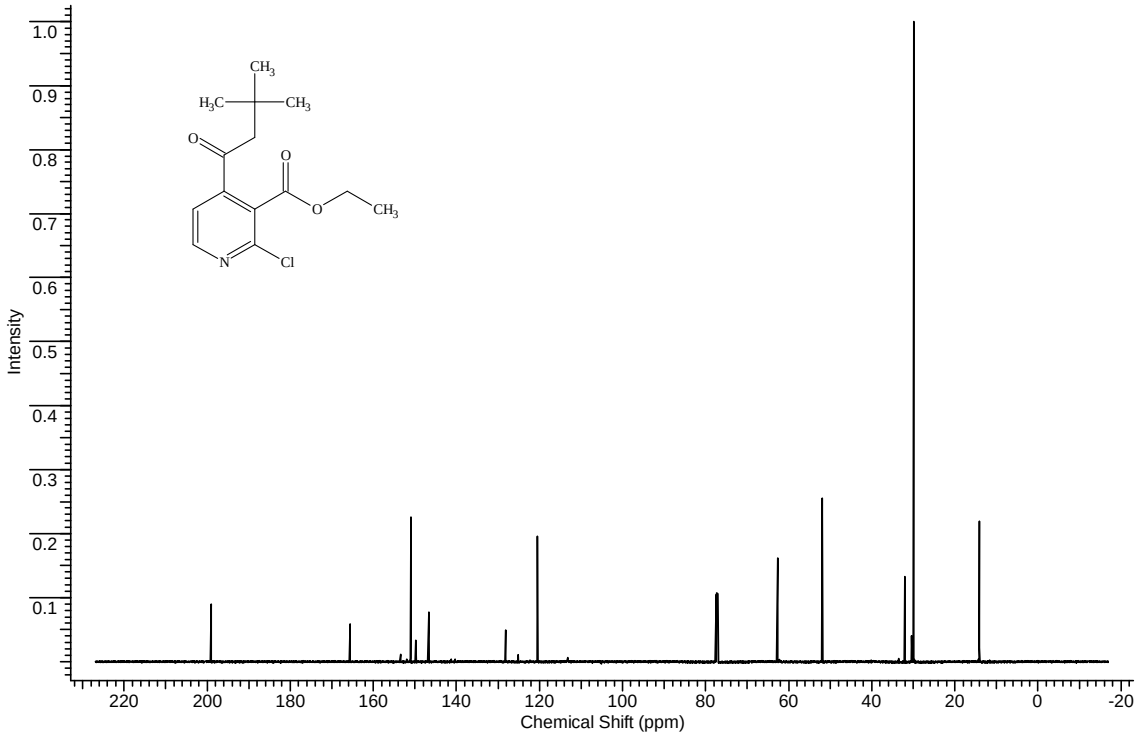
4-Benzoyl-6-bromo-isophthalic acid diethyl ester (13a)



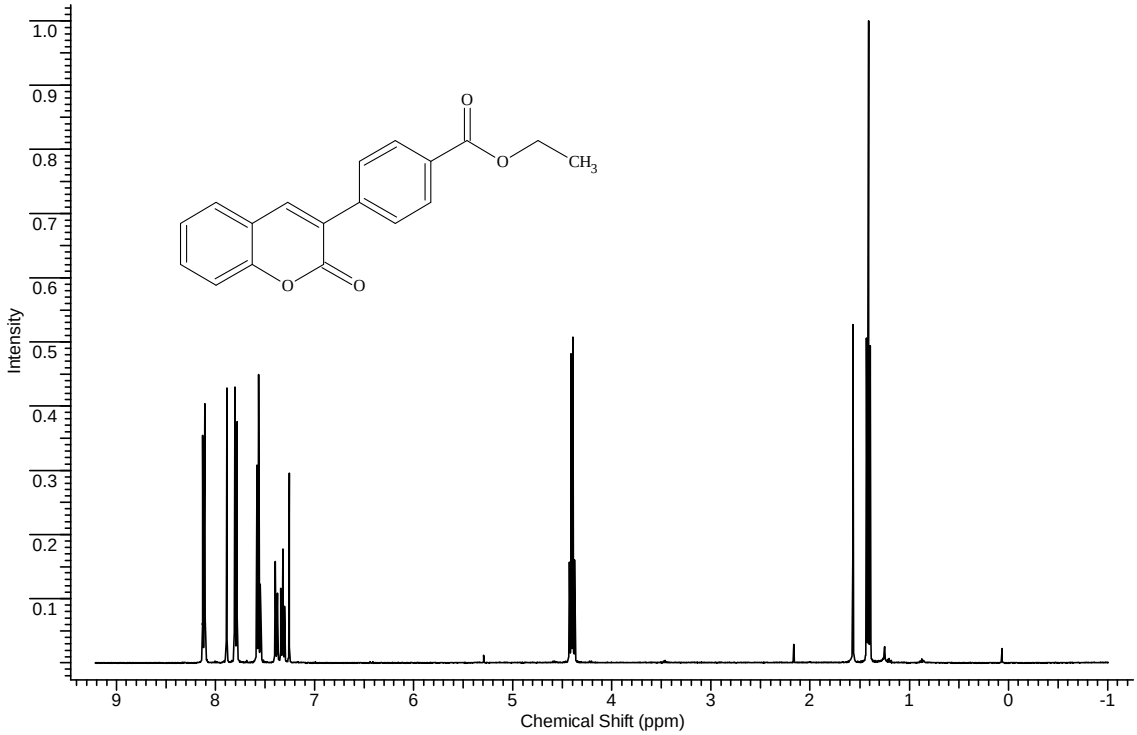


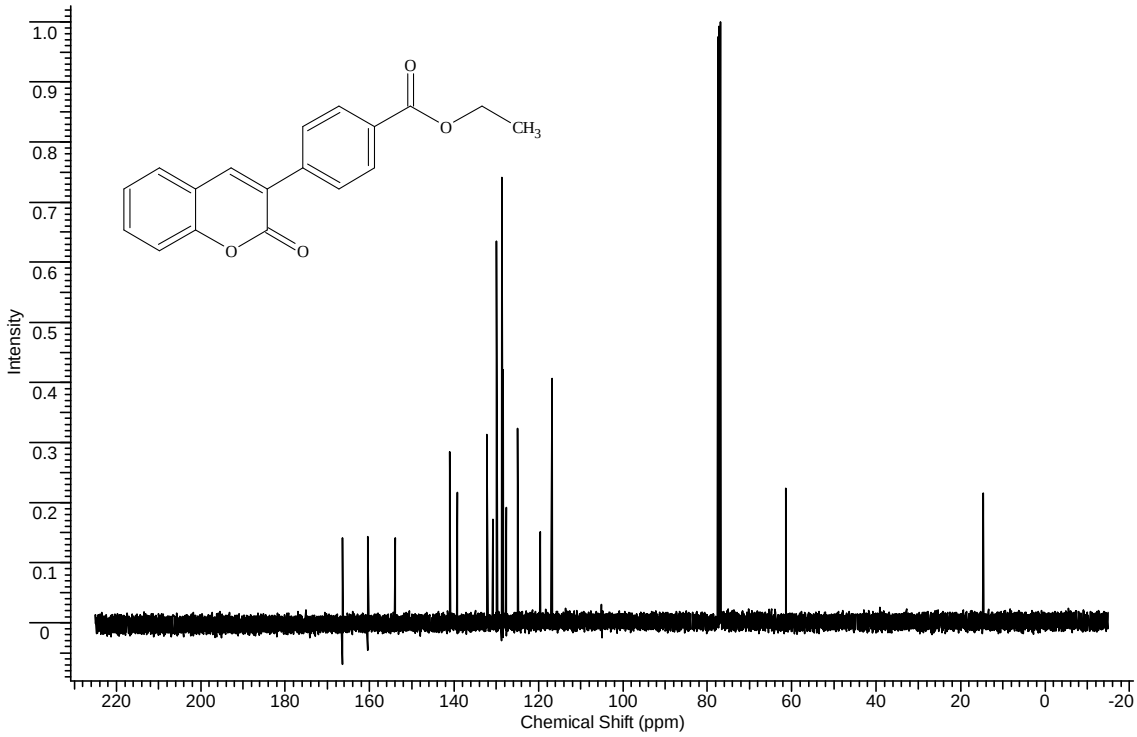
2-Chloro-4-(3,3-dimethyl-butyryl)-nicotinic acid ethyl ester (13b)



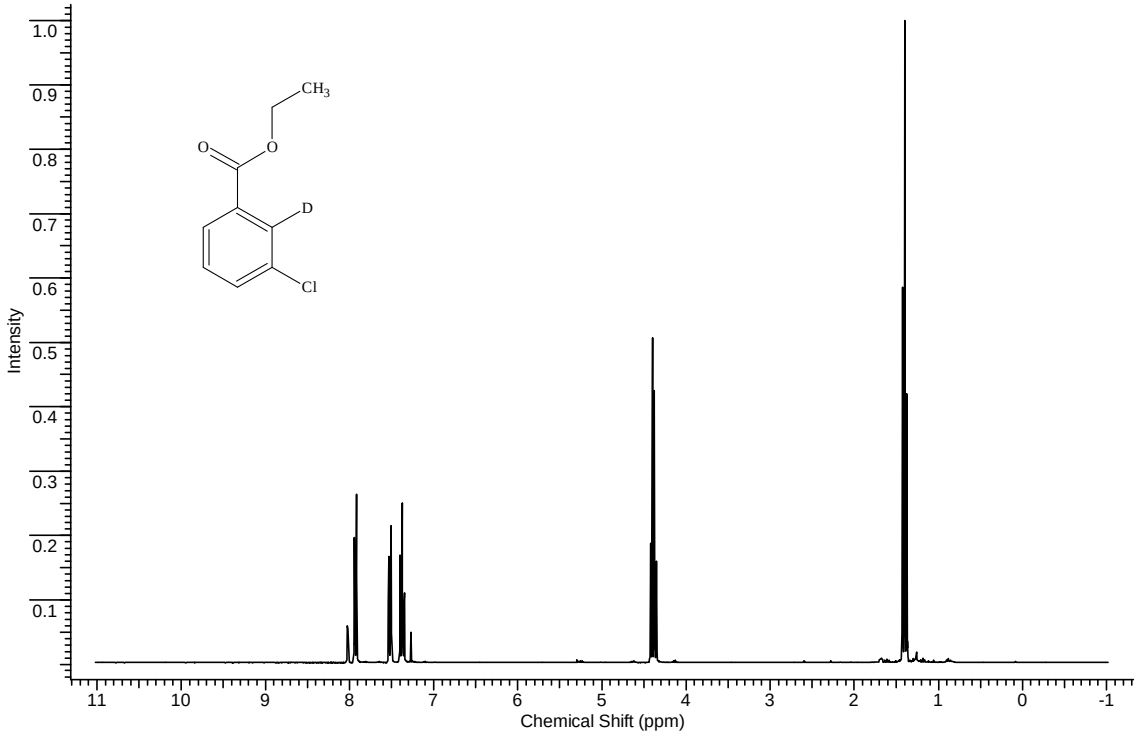


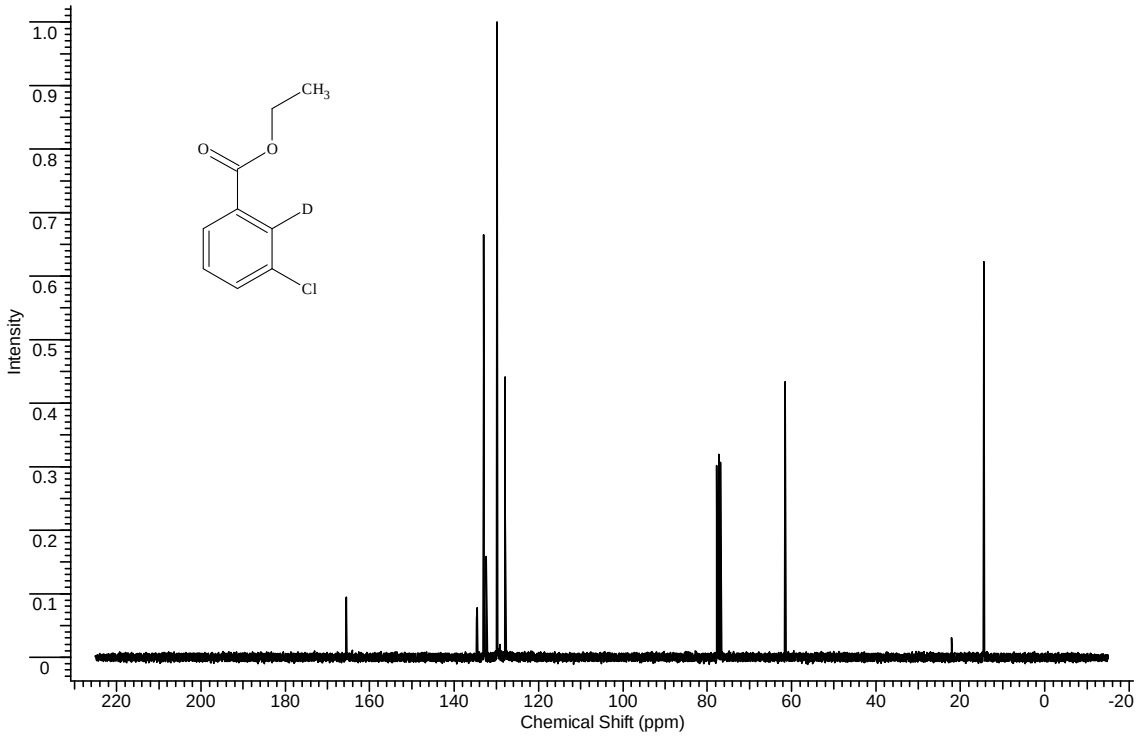
4-(2-Oxo-2*H*-chromen-3-yl)-benzoic acid ethyl ester (13c)



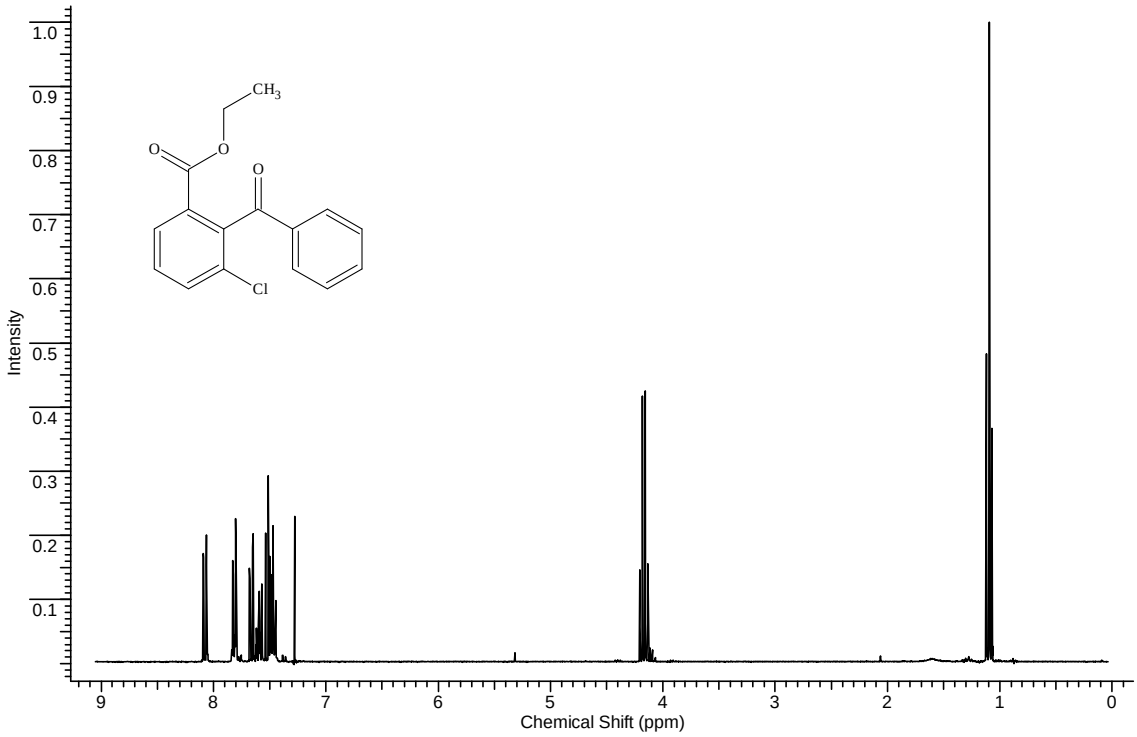


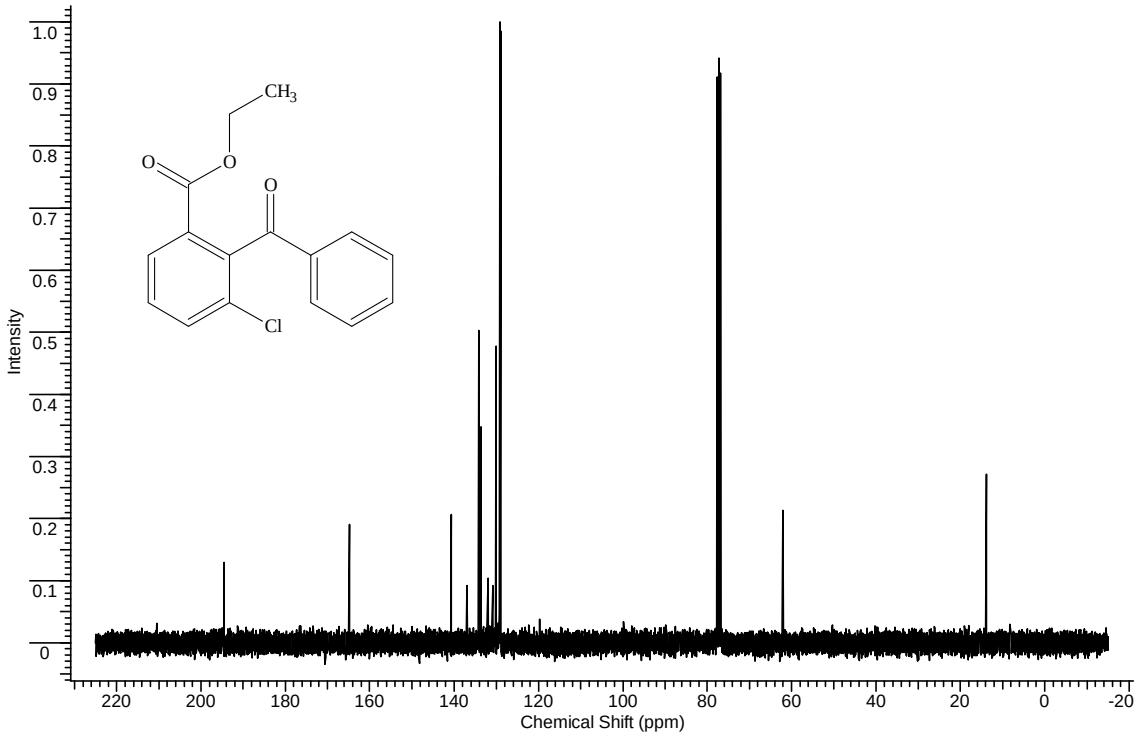
2-Deutero-3-chloro-benzoic acid ethyl ester (13d)



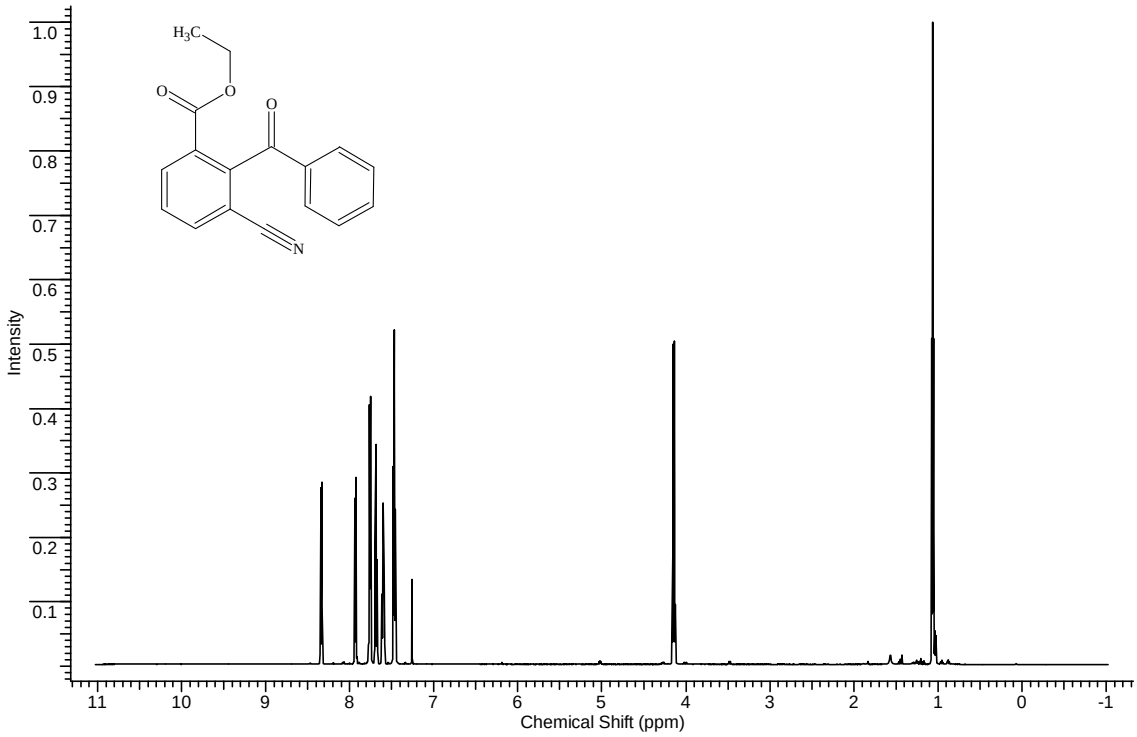


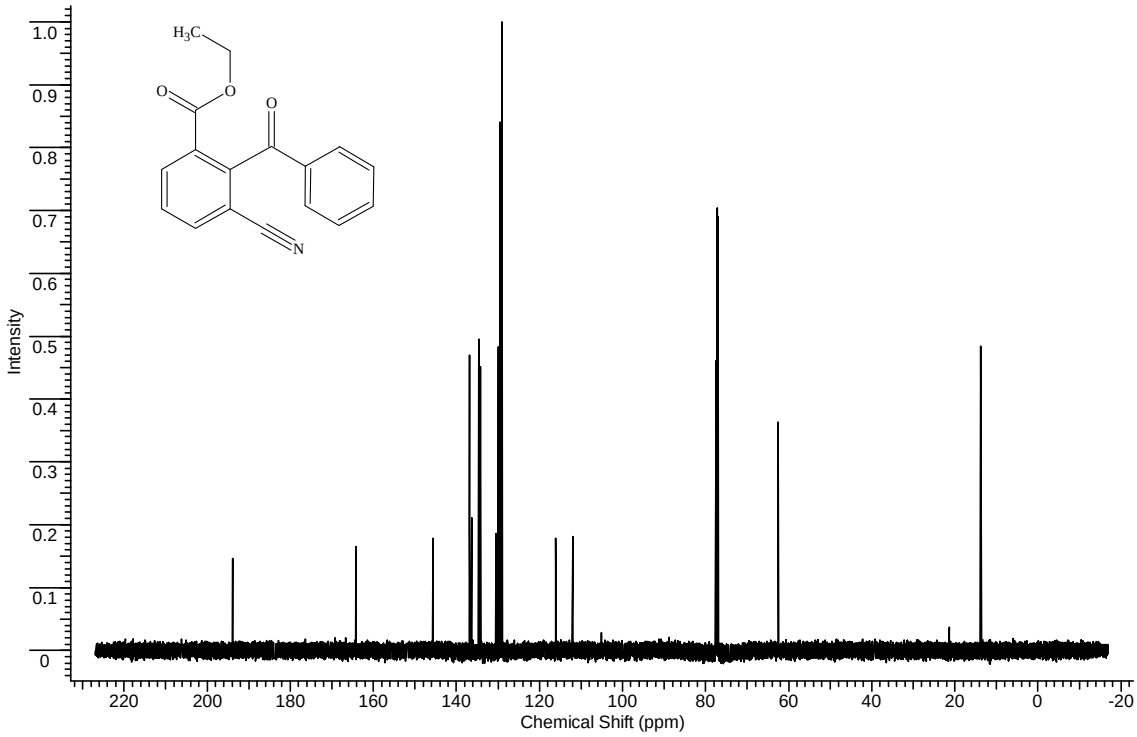
2-Benzoyl-3-chloro benzoic acid ethyl ester (13e)



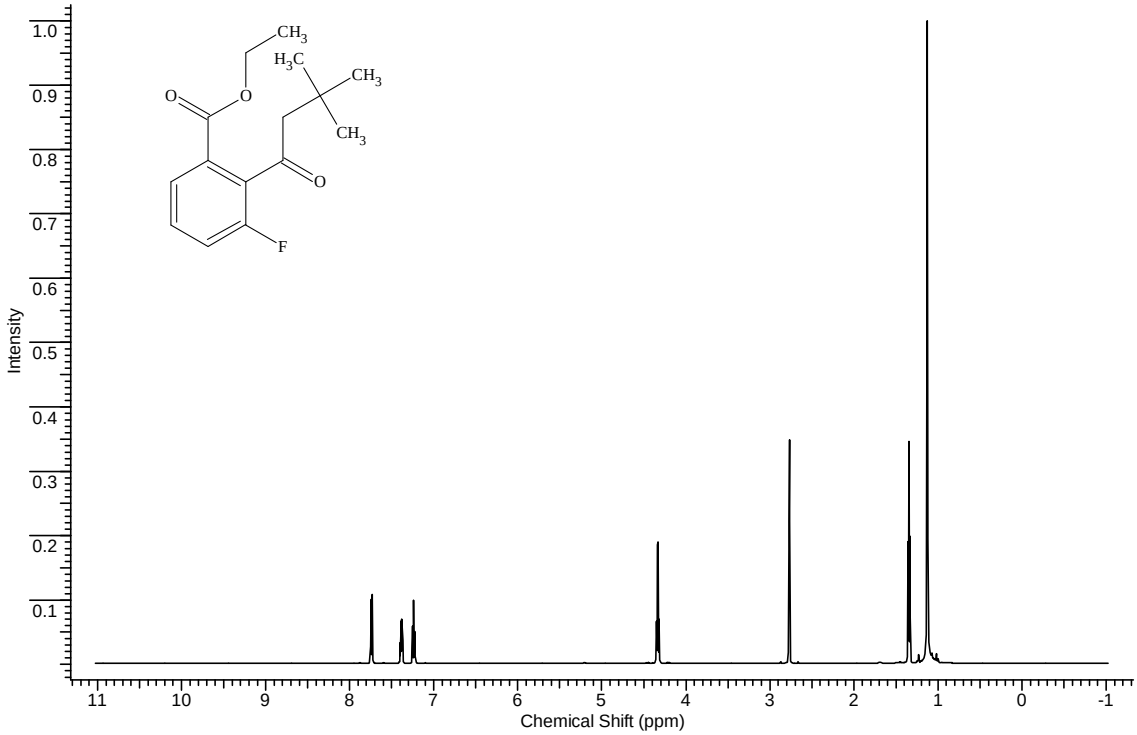


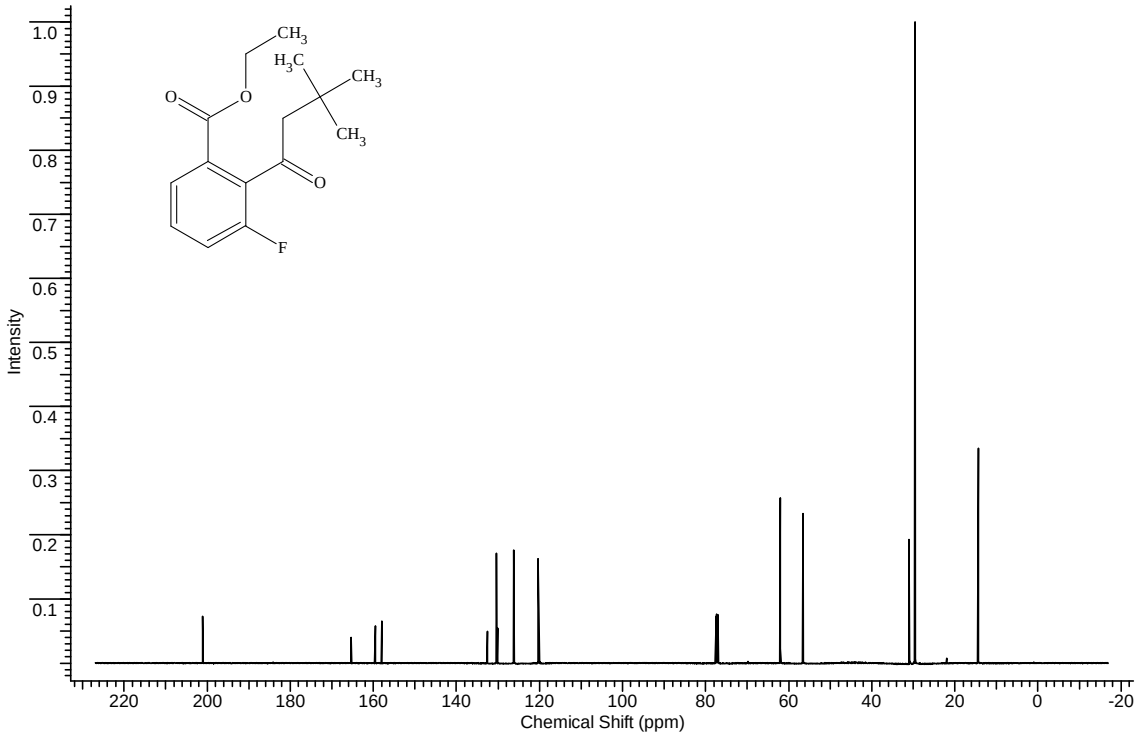
2-Benzoyl-3-cyano benzoic acid ethyl ester (13e)



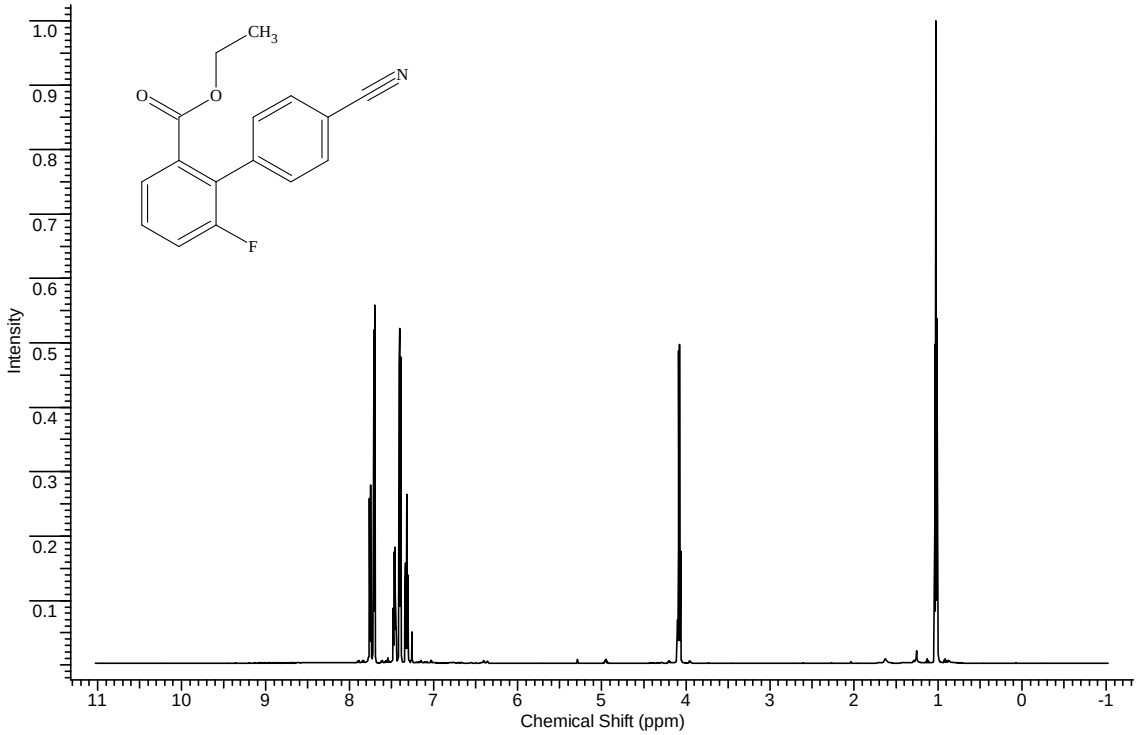


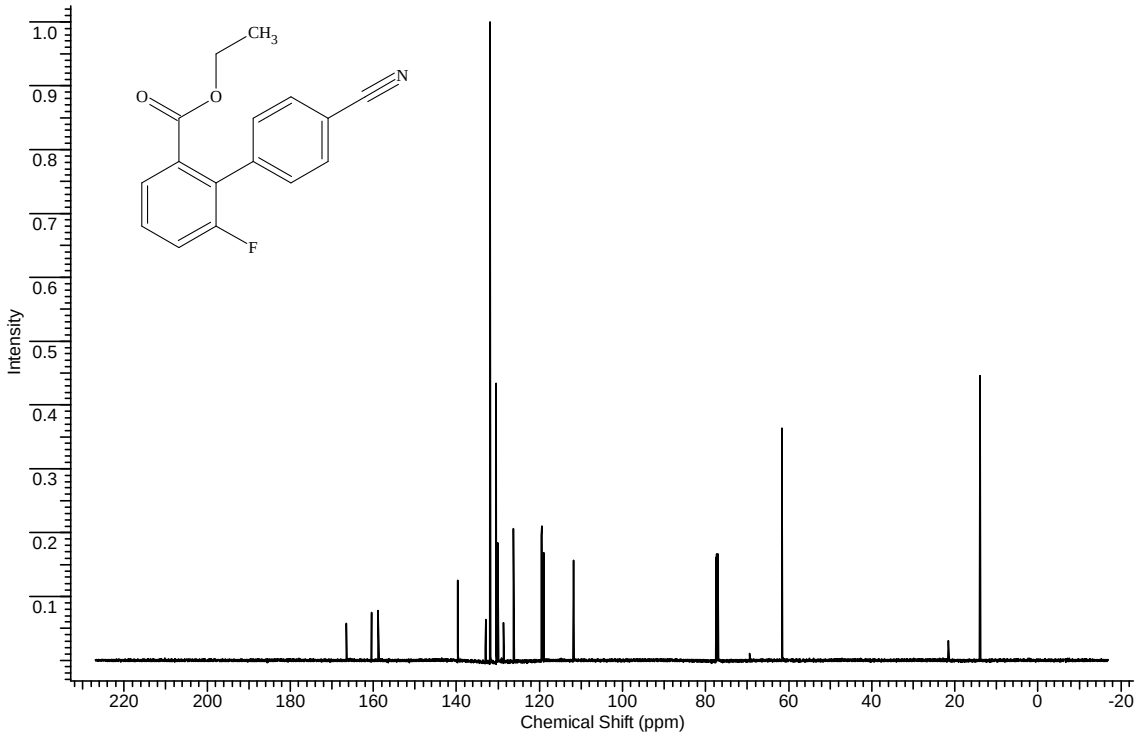
2-(3,3-Dimethyl-butyryl)-3-fluoro-benzoic acid ethyl ester (13g)



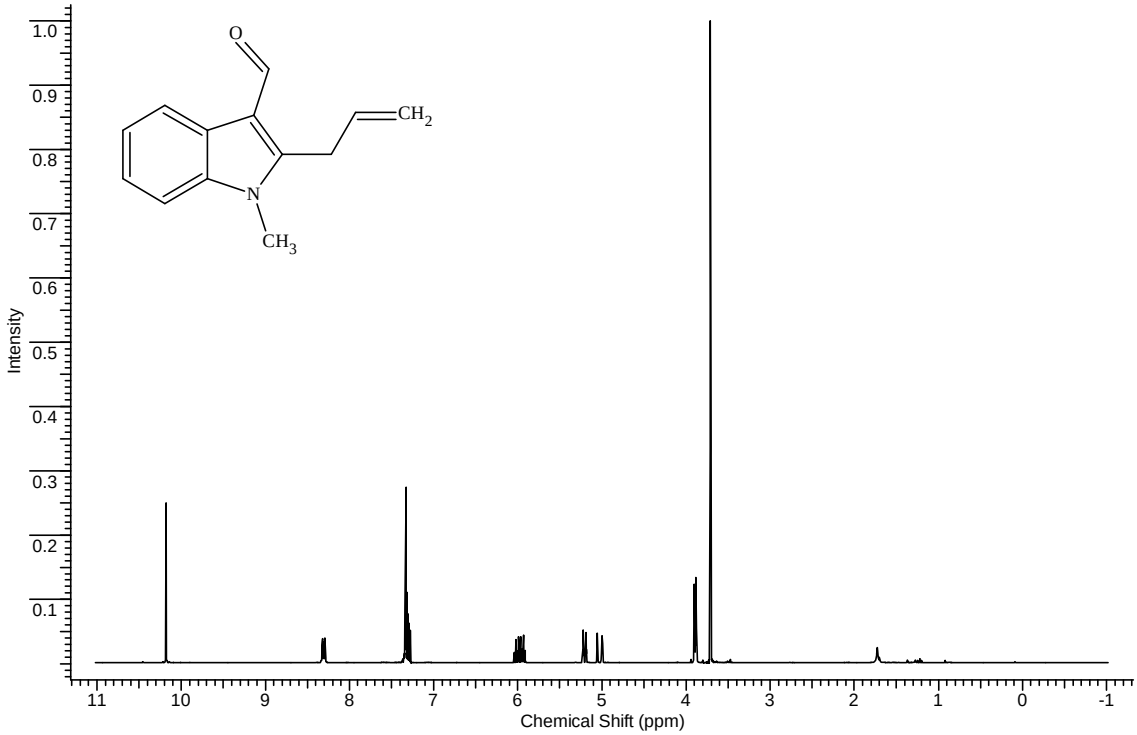


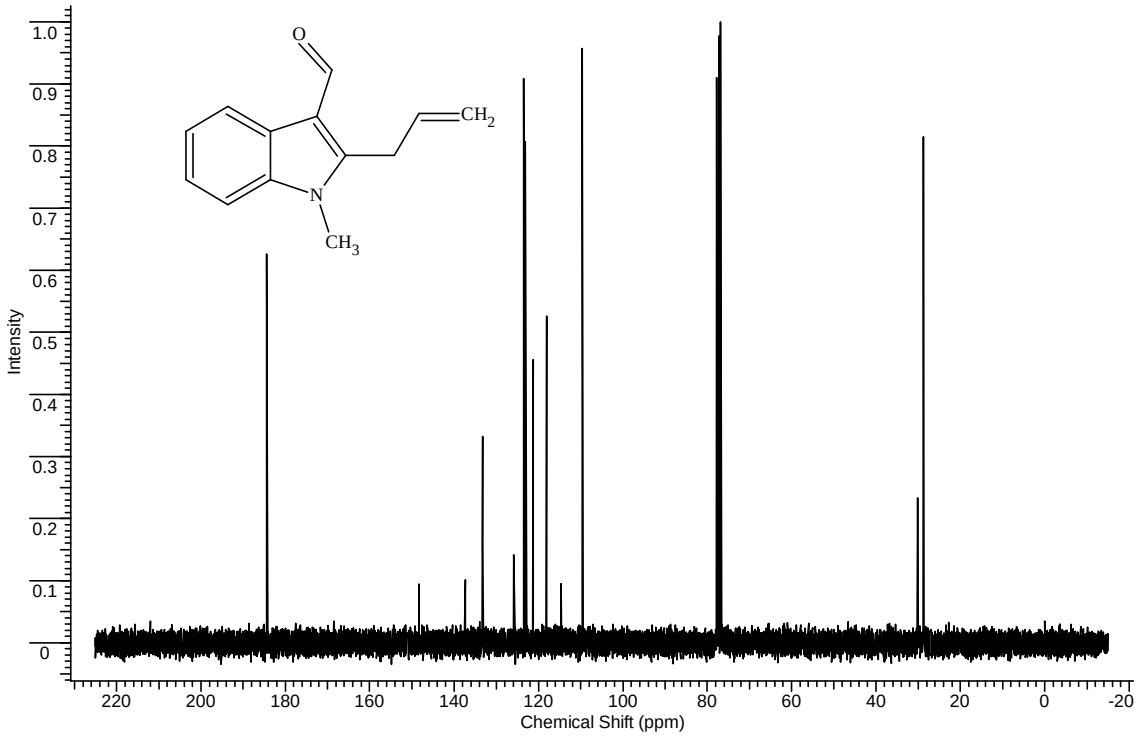
4'-Cyano-6-fluoro-biphenyl-2-carboxylic acid ethyl ester (13h)



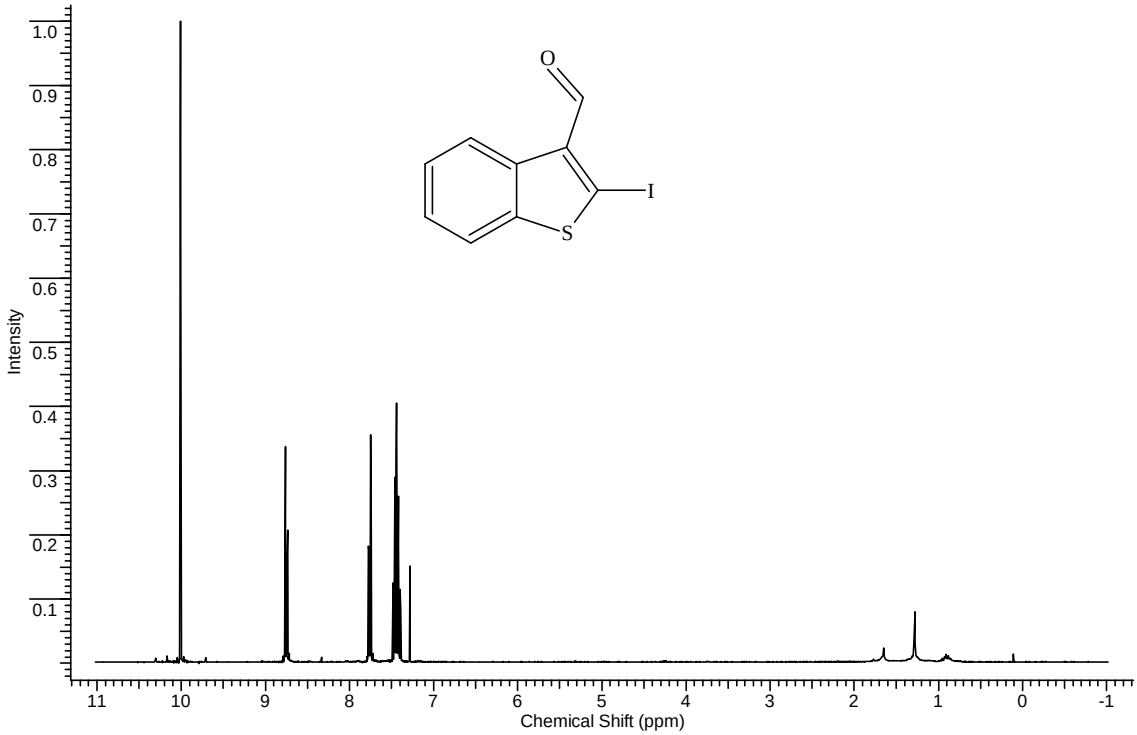


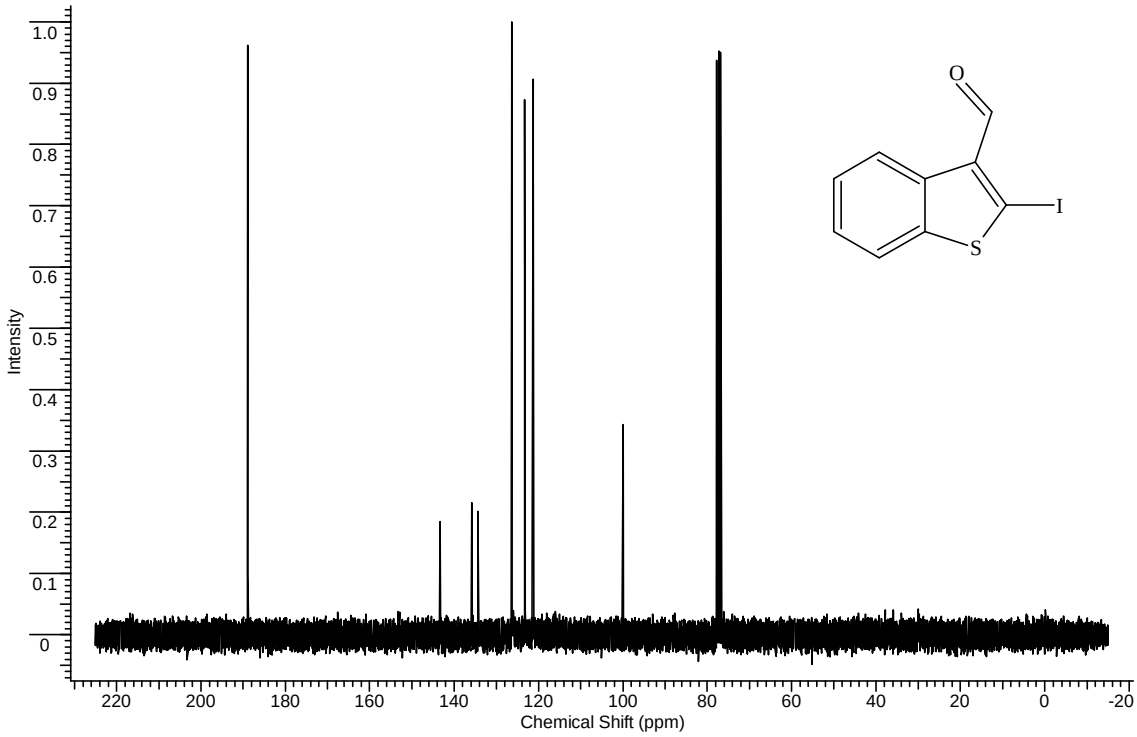
2-Allyl-1-methyl-1*H*-indole-3-carbaldehyde (16a)



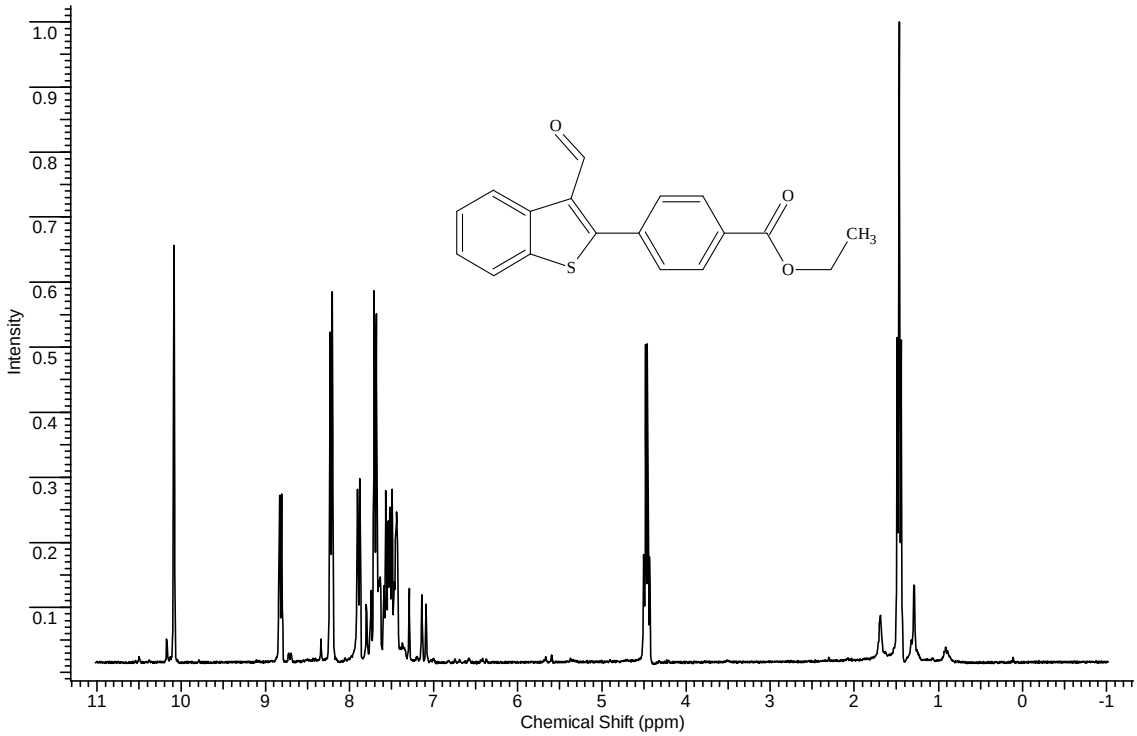


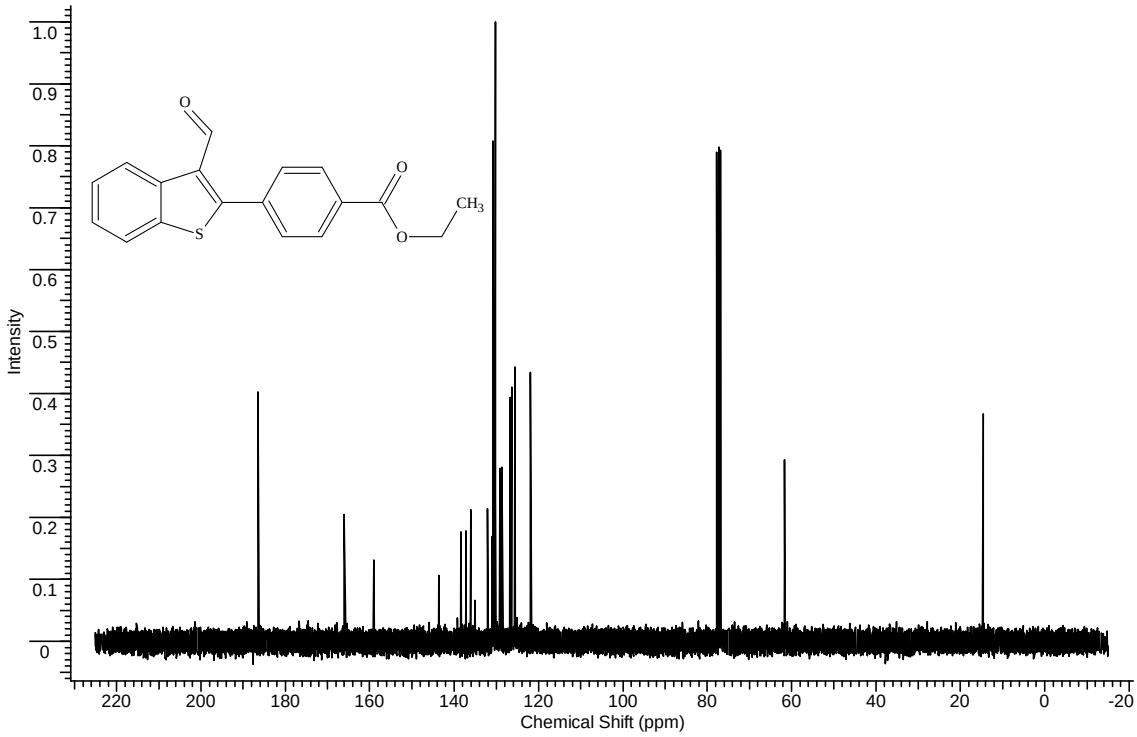
2-iodo-benzo[b]thiophene-3-carbaldehyde (16b)



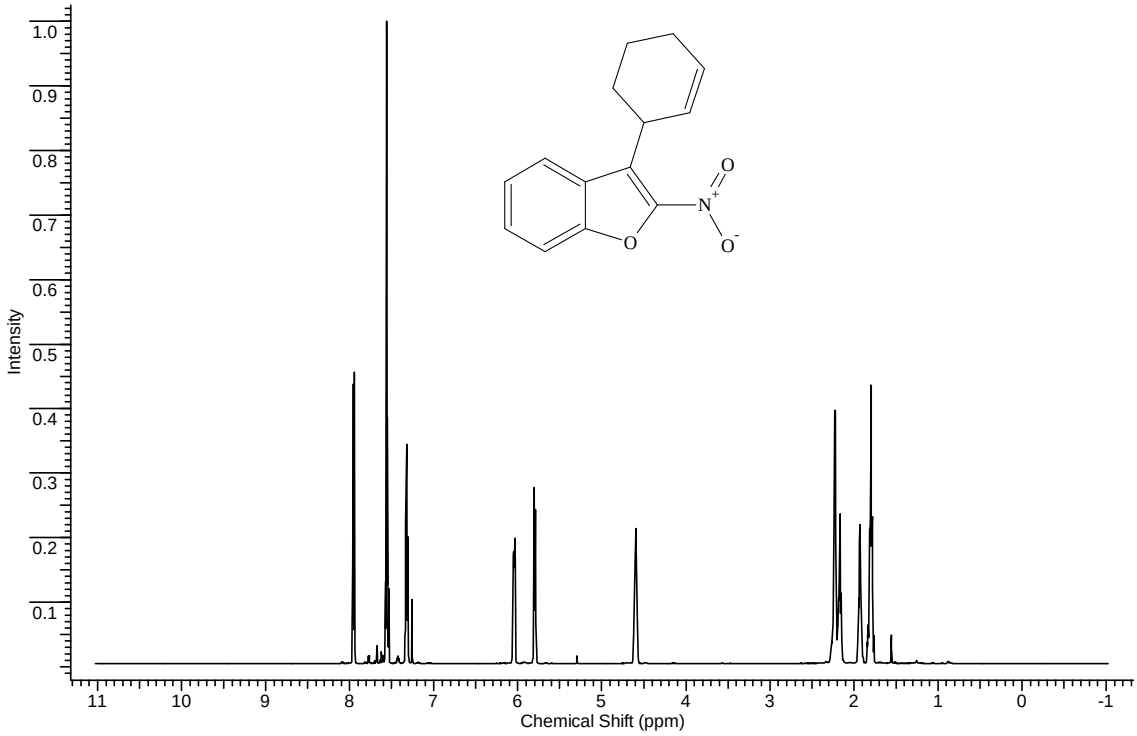


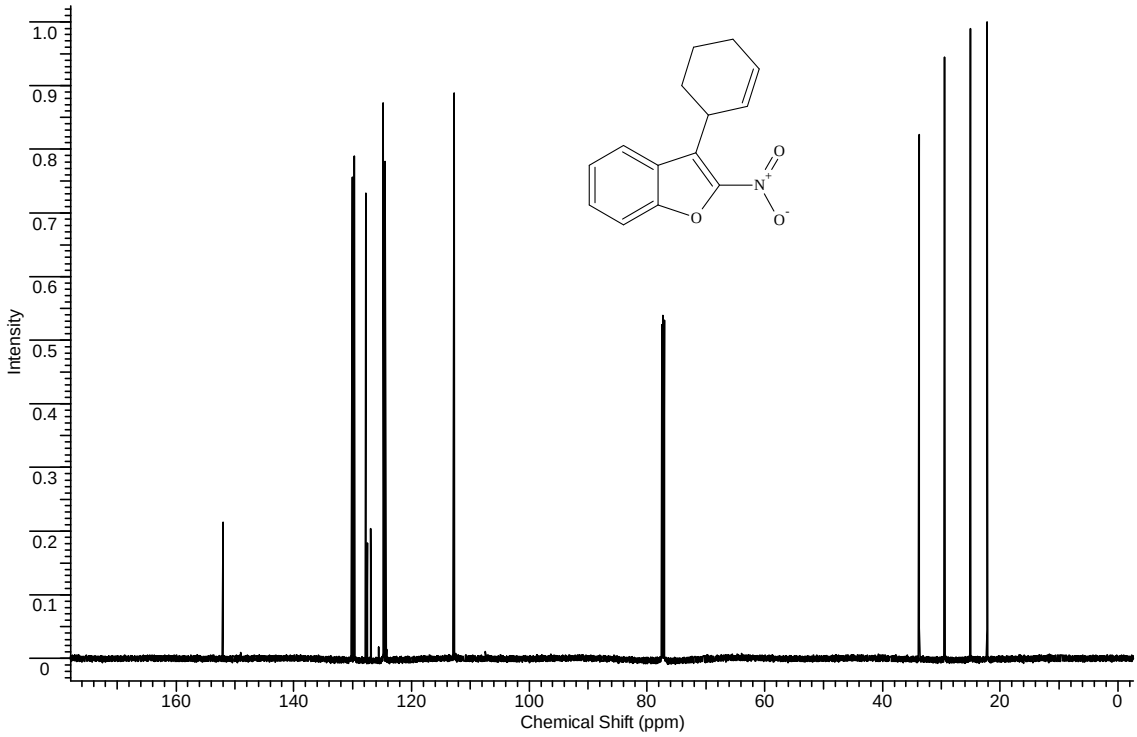
4-(3-Formyl-benzo[b]thiophen-2-yl)-benzoic acid ethyl ester (16c)



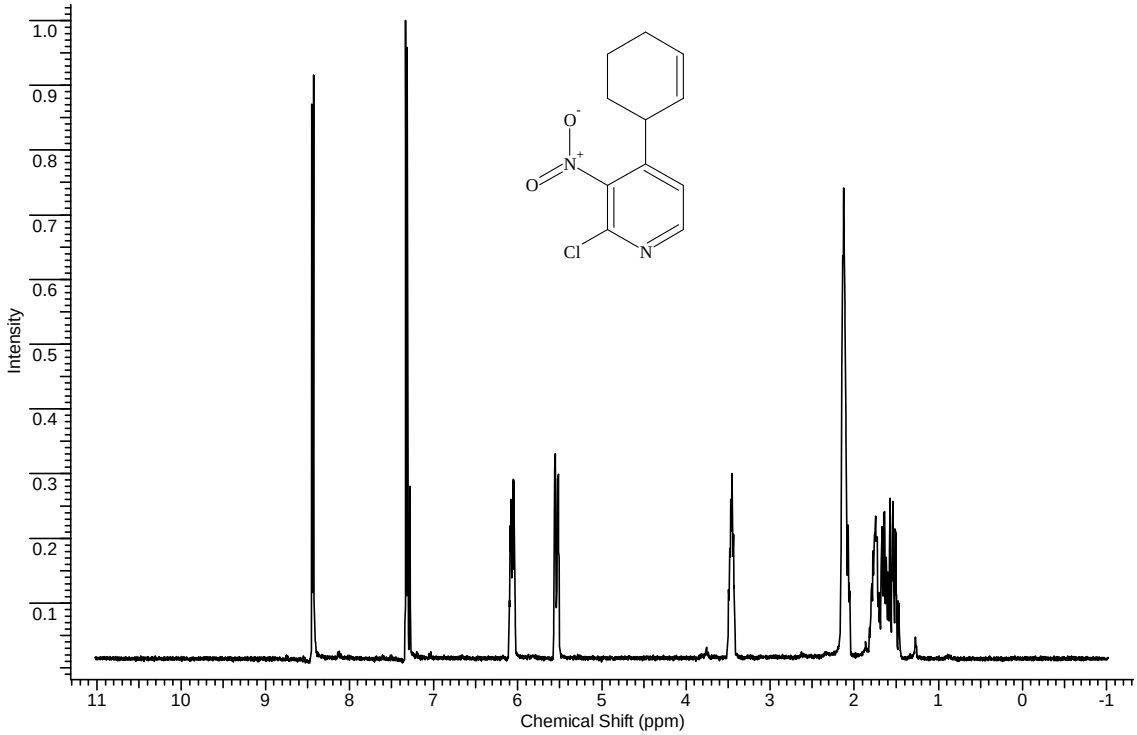


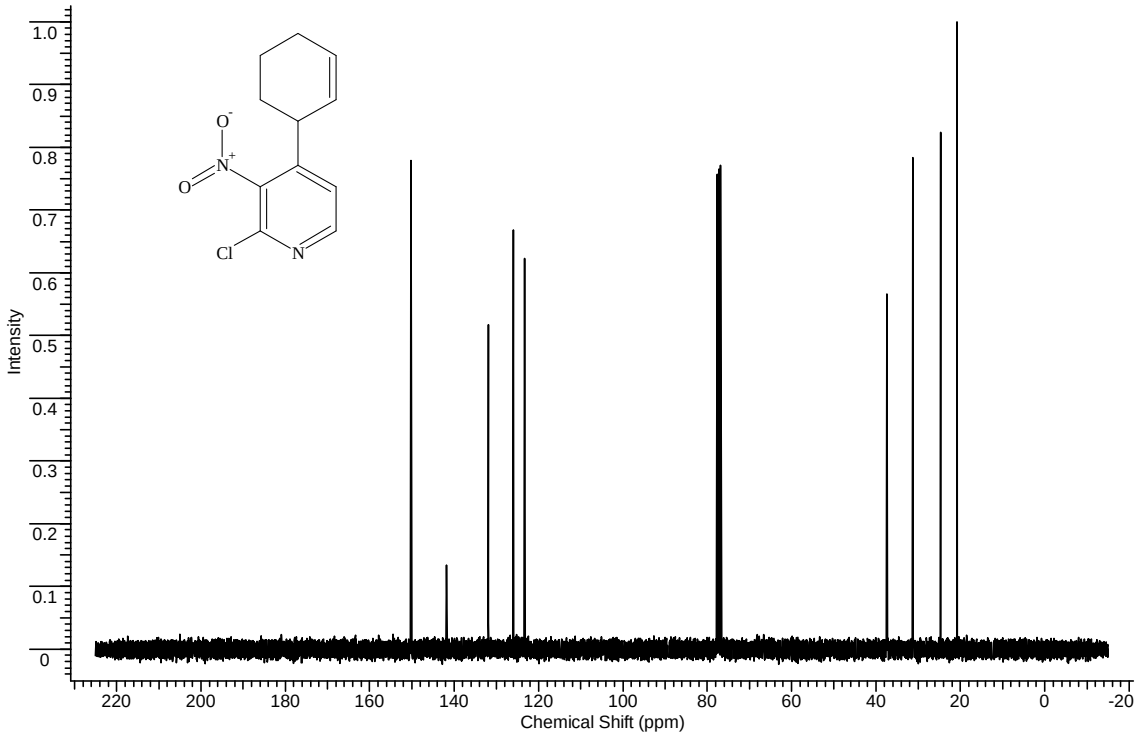
3-Cyclohex-2-enyl-2-nitro-benzofuran (19a)



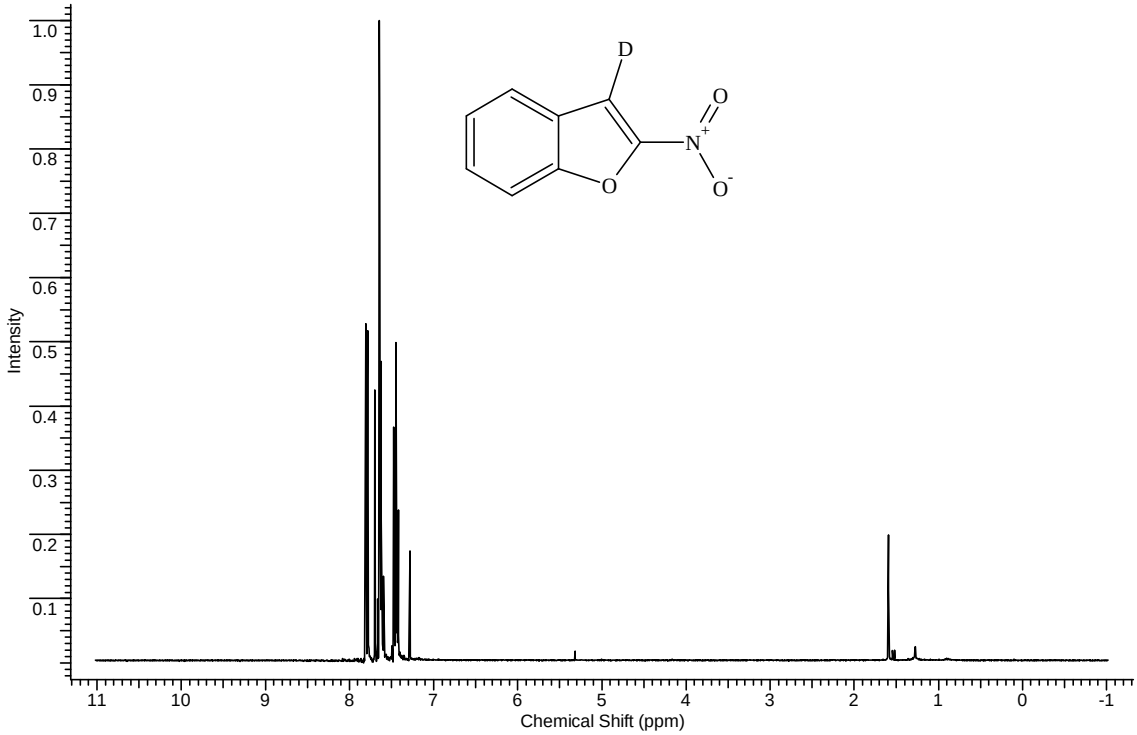


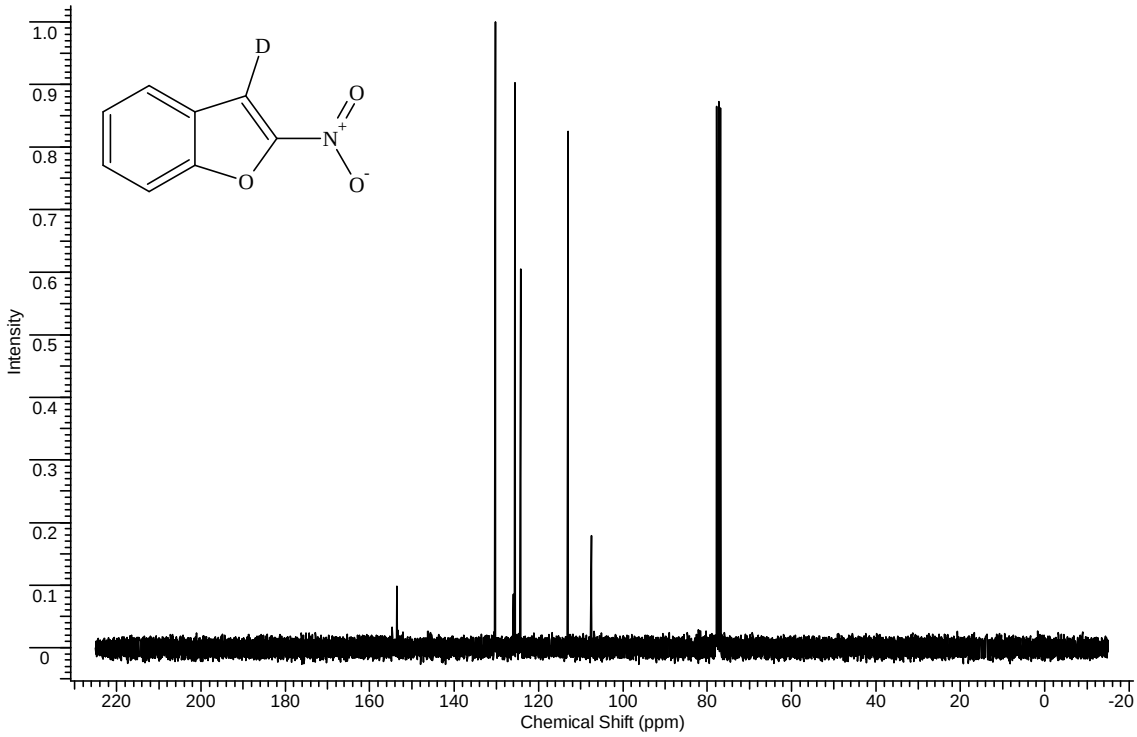
2-Chloro-4-cyclohex-2-enyl-3-nitro-pyridine (19b)



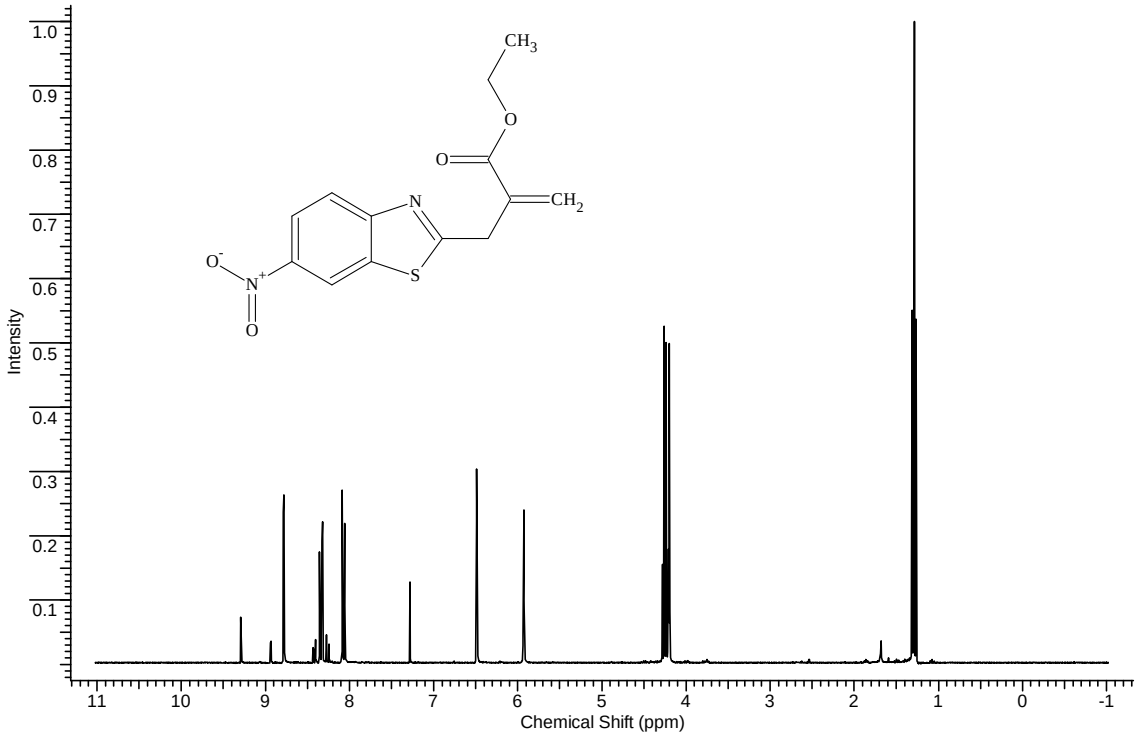


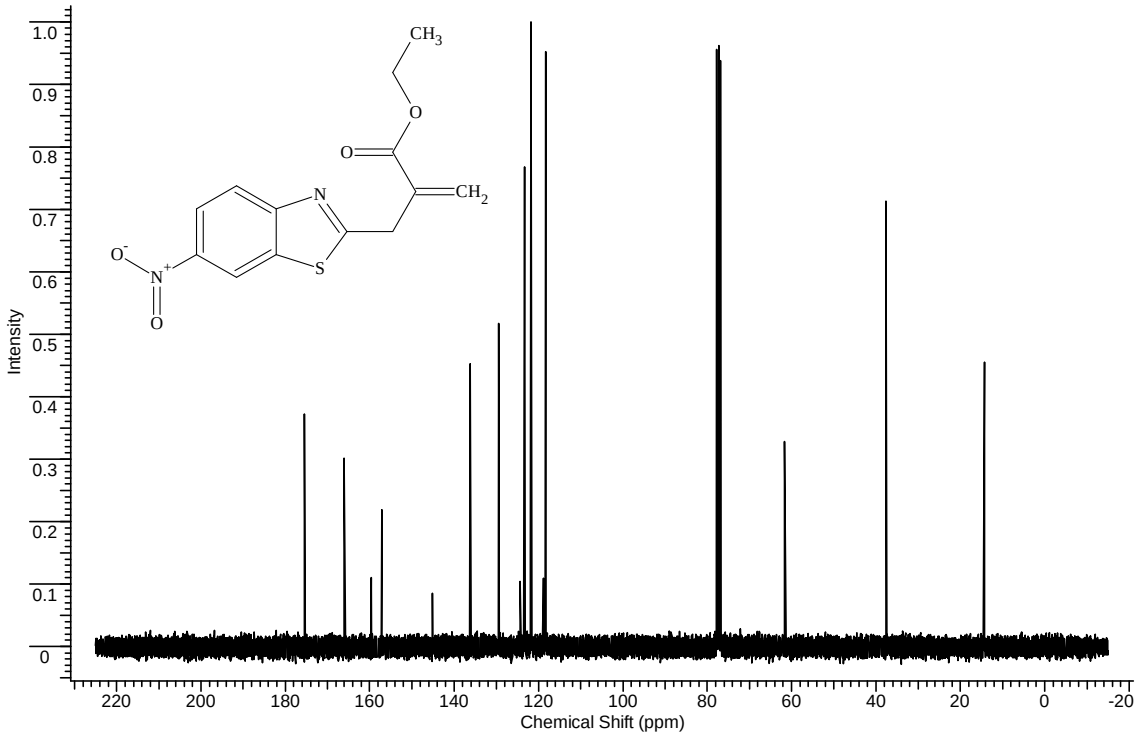
3-Deutero-2-nitro-benzofuran (19c)





2-(6-Nitro-benzothiazol-2-ylmethyl)-acrylic acid ethyl ester (19d)





NMR- Comparison of selected Bases:

	^{1}H (400 MHz, THF-d_8, -30 °C)	^{13}C (100 MHz, THF-d_8, -30 °C)
LiTMP	1.60 (m, 2H), 1.19 (m, 4 H), 1.11 (s, 12 H).	52.2, 42.2, 35.4, 20.0.
TMPMgCl·LiCl	1.53 (m, 2H), 1.24 (m, 4 H), 1.13 (s, 12 H).	51.3, 42.0, 35.0, 19.9.
$Zn(TMP)_2$·2LiCl	1.64 (m, 2H), 1.27 (m, 4 H), 1.18 (s, 12 H).	52.5, 39.0, 36.4, 19.0.
$Zn(TMP)_2$·2$MgCl_2$·2LiCl	1.61 (m, 2H), 1.7 (m, 4 H), 1.16 (s, 12 H).	52.5, 38.9, 36.4, 19.0.