# Preparation of Polyfunctional Indazole Derivatives and Heteroaryl Azo Compounds Using Highly Functionalized Zinc Reagents.

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## Supporting Information

**Table of contents**

**General and Typical Procedures (S2 – S3)**

**Experimental Procedures and Analytical Data (S4 – S33)**

**Crystal Structure (S26)**

**References (S33)**

**NMR Spectra (S34 – S73)**

**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. NMR spectra were recorded on solutions in deuterated chloroform ($CDCl_3$) with residual chloroform (δ 7.24 ppm for $^{1}$H NMR and δ 77.0 ppm for $^{13}$C NMR) and deuterated methanol ($CD_4OD$) with residual methanol (δ 3.34 ppm for $^{1}$H NMR and δ 49.8 ppm for $^{13}$C NMR). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, br, broad. Column chromatography was performed using $SiO_2$ (0.040–0.063 mm, 230–400 mesh ASTM) from Merck if not indicated. TMPH were distilled prior to use. The given Wattnumbers refer to the maximum magnetron power output.

**Preparation of the reagent $ZnBr_2$ (1 M solution in THF).**

A dry and argon-flushed 250 mL Schlenk-flask, equipped with a magnetic stirring bar and a septum, was charged with $ZnBr_2$ (22.54 g, 100 mmol). The salt was heated to 140 °C under high vacuum for 4 h. After cooling to 25 °C, dry THF (100 mL) was added and stirring was continued until the salt was dissolved (4 h).

**Preparation of the reagent $TMP_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$.**

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 25 °C, dry THF (25 mL) and freshly titrated TMPMgCl·LiCl [1] (100 mmol, 1.0 M, 100 mL) was added slowly. The resulting mixture was stirred for 15 h at 25 °C. The freshly prepared $(TMP)_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$ solution was titrated prior to use at 0 °C with benzoic acid using 4-(phenylazo)diphenylamine as indicator. A concentration of 0.4 M in THF was obtained.

**TP1: Typical Procedure for the preparation of 2-aryl-2*H*-indazole derivatives (3a-r).**

To a solution of the 2-iodobenzyl chloride derivative (3.0 mmol) in THF (2 mL) in a dry and argon-flushed Schlenk-flask was added dropwise a solution of *i*PrMgCl·LiCl (3.2 mmol, 1.8 mL, 1.8 M in THF) at -20 °C. The reaction mixture was stirred for 30 min at the same temperature. GC-analysis of a quenched reaction aliquot shows full conversion. $ZnBr_2$ solution (1.6 mL, 1.6 mmol, 1 M in THF) was added to the Grignard reagent at -20 °C and allowed to warm to 25 °C. The solution was stirred for 20 min at the same temperature. To a

solution of diazonium salt (2.0 mmol) in NMP/THF (1:1) (4 mL) the diarylzinc species was added dropwise at -40 °C, allowed slowly to warm up to 25 °C and stirred for 30 min at 25 °C. The reaction mixture was then stirred at 50 °C for 1 h. The reaction mixture was diluted with diethyl ether (5 mL) and quenched with sat. $NH_4Cl$ (aq.) (5 mL). The aqueous layer was extracted with $CH_2Cl_2$ (3x 20 mL). The combined organic phases were dried over $Na_2SO_4$, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography to afford the 2-aryl-*2H*-indazole derivative.

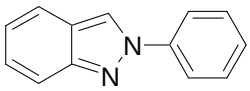
**TP2: Typical Procedure for the preparation of aryldiazonium tetrafluoroborate (2a-k).**

To a solution of the aniline derivative (50 mmol) in tetrafluoroboric acid (0.4 mol, 35 g, 50 w% in $H_2O$) was added dropwise a $NaNO_2$ solution (55 mmol, 3.79 g, 4 M in $H_2O$) under vigorous stirring, while the temperature was kept below -5 °C. The reaction mixture was stirred for additional 30 min at -5 °C. The precipitate was removed by filtration and washed with cold MeOH. The solid was recrystallized from methanol to yield the crystalline aryldiazonium tertrafluoroborate salt.

**TP3: Typical Procedure for the preparation of heterocyclic azo compounds (14a-f).**

To a solution of the haloheteroaryl derivative (3.0 mmol) in THF (2 mL) in a dry and argon-flushed Schlenk-flask was added dropwise a solution of *i*PrMgCl·LiCl (3.2 mmol, 1.8 mL, 1.8 M in THF) at -20 °C. The reaction mixture was stirred for 30 min at the same temperature. GC-analysis of a quenched reaction aliquot shows full conversion. $ZnBr_2$ solution (1.6 mL, 1.6 mmol, 1 M in THF) was added to the Grignard reagent at -20 °C and allowed to warm to 25 °C. The solution was stirred for 20 min at the same temperature. To a solution of diazonium salt (2.0 mmol) in NMP/THF (1:1) (4 mL) the diarylzinc was added dropwise at -40 °C, allowed to slowly warm up to -20 °C and stirred for 2 h at the same temperature. The reaction mixture was diluted with diethyl ether (5 mL) and quenched with sat. $NH_4Cl$ (aq.) (5 mL). The aqueous layer was extracted with $CH_2Cl_2$ (3x 20 mL). The combined organic phases were dried over $Na_2SO_4$, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography to afford the heterocyclic azo compound.

**Synthesis of 2-phenyl-2*H*-indazole (3a):**



According to **TP1** 2-iodobenzyl chloride (757 mg, 3.0 mmol) was converted to the diarylzinc compound and was reacted with phenyldiazonium tetrafluoroborate (**2a**, 383 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded 2-phenyl-2*H*-indazole[2] (**3a**, 380 mg, 98 %) as a pale yellow solid.

**mp** (°C) = 79.2 – 80.6.

**$^{1}$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.38 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 8.4 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H).

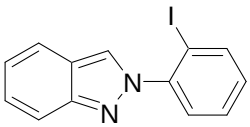
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 149.6, 140.4, 129.5, 127.8, 126.8, 122.7, 122.4, 120.9, 120.4, 120.3, 117.8.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3131, 3054, 1628, 1593, 1519, 1492, 1465, 1456, 1390, 1378, 1312, 1206, 1073, 1046, 950, 905, 780, 747, 683.

**MS** (EI, 70 eV): m/z (%) = 195 (14), 194 ($M^+$, 100), 193 (18), 168 (11), 167 (11), 165 (13), 77 (16), 51 (9).

**HRMS ($C_{13}H_{10}N_2$)**: calc.: 194.0844; found: 194.0857 ($M^+$).

**Synthesis of 2-(2-iodophenyl)-2*H*-indazole (3b) :**



According to **TP1** 2-iodobenzyl chloride (**4a**, 757 mg, 3.2 mmol) was converted to the diarylzinc compound and was reacted with 2-iodophenyldiazonium tetrafluoroborate (**2b**, 636 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded 2-(2-iodophenyl)-2*H*-indazole (**3b**, 531 mg, 83 %) as a pale yellow solid.

**mp** (°C) = 118.4 – 119.8.

**$^{1}$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.19 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.45 - 7.55 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.10 - 7.29 (m, 2 H).

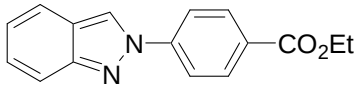
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 149.3, 143.8, 140.0, 130.8, 128.9, 128.3, 126.8, 124.9, 122.4, 121.9, 120.5, 118.0, 94.2.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3393, 2917, 2850, 1697, 1627, 1443, 1239, 1059, 1021, 948, 816, 748, 738, 702.

**MS** (EI, 70 eV): m/z (%) = 321 (14), 320 ($M^+$, 100), 193 (19), 192 (21), 166 (12).

**HRMS ($C_{13}H_9IN_2$)**: calc.: 319.9810; found: 319.9806 ($M^+$).

**Synthesis of ethyl 4-(2*H*-indazol-2-yl)benzoate (3c) :**




According to **TP1** 2-iodobenzyl chloride (**4a**, 757 mg, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**2c**, 528 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded ethyl 4-(2*H*-indazol-2-yl)benzoate [3] (**3c**, 516 mg, 97 %) as a pale yellow solid.

**mp** (°C) = 144.3 – 145.0.

**$^{1}$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.45 (s, 1H), 8.18 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 2 H), 7.77 (d, *J* = 8.7, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.32 (t, *J* = 8.5 Hz, 1H), 7.10 ( t, *J* = 8.0 Hz), 4.42 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H).

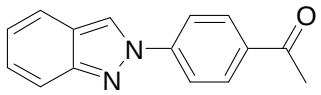
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 165.7, 150.1, 143.5, 131.1, 129.6, 127.4, 123.0, 122.9, 120.4, 120.5, 120.2, 118.0, 61.2, 14.3.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3403, 3138, 3064, 2978, 2902, 1706, 1607, 1522, 1427, 1367, 1270, 1206, 1101, 1037, 856, 749, 684.

**MS** (EI, 70 eV): m/z (%) = 267 (17), 266 ($M^+$, 100), 238 (21), 221 (51), 193 (13), 192 (14), 165 (9).

**HRMS ($C_{16}H_{14}N_2O_2$)**: calc.: 266.1055; found: 266.1049 ($M^+$).

**Synthesis of 1-[4-(2*H*-indazol-2-yl)phenyl]ethanone (3d) :**



According to **TP1** 2-iodobenzyl chloride (**4a**, 757 mg, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-acetylbenzenediazonium tetrafluoroborate (**2d**, 468 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded 1-[4-(2*H*-indazol-2-yl)phenyl]ethanone (**3d**, 396 mg, 84 %) as an off-white solid.

**mp** (°C) = 182.3 – 183.5.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.44 (s, 1 H), 8.08 (d, *J* = 8.7 Hz, 2), 8.00 (d, *J* = 8.7 Hz, 2 H), 7.76 (d, *J* = 8.9, 1H), 7.67 (d, *J* = 8.5 Hz, 1Hz), 7.32 (t, *J* = 7.3 Hz, 1Hz), 7.10 (t, *J* = 7.3 Hz, 1H), 2.62 (s, 3H).

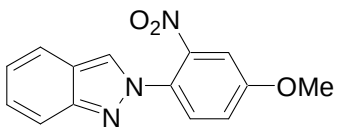
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 196.7, 150.2, 143.5, 136.0, 129.9, 127.5, 123.0, 120.5, 120.4, 120.3, 118.0, 26.6.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3130, 1678, 1602, 1521, 1422, 1381, 1354, 1305, 1259, 1205, 1178, 1116, 1047, 949, 908, 851, 842, 783, 757, 734.

**MS** (EI, 70 eV): m/z (%) = 237 (16), 236 ($M^+$, 94), 222 (13), 221 (100), 193 (20), 192 (22), 166 (11), 110 (12).

**HRMS ($C_{15}H_{12}N_2O$)**: calc.: 236.0950; found: 236.0921 ($M^+$).

**Synthesis of 2-(4-methoxy-2-nitrophenyl)-2*H*-indazole (3e) :**



According to **TP1** 2-iodobenzyl chloride (**4a**, 757 mg, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-methoxy-2-nitrobenzenediazonium tetrafluoroborate (**2e**, 534 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded 2-(4-methoxy-2-nitrophenyl)-2*H*-indazole (**3e**, 516 mg, 96 %) as a pale yellow solid.

**mp** (°C) = 105.3 – 106.1.

**$^1$H-NMR** (600 MHz, $CDCl_3$): δ (ppm) = 8.14 (s, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 2.8, 1H), 7.31 (t, *J* = 8.1 Hz, 1H), 7.21 (dd, *J* = 8.7 Hz, 2.7 Hz, 1H), 7.11 (t, *J* = 8.1 Hz, 1H), 3.91 (s, 3H).

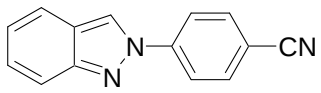
**$^{13}$C-NMR** (150 MHz, $CDCl_3$): δ (ppm) = 159.9, 149.9, 145.7, 129.0, 127.0, 124.1, 122.7, 122.4, 120.3, 118.7, 117.9, 110.1, 56.3.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 1628, 1544, 1525, 1357, 1261, 1246, 1226, 1200, 1044, 1024, 900, 826, 797, 792, 761.

**MS** (EI, 70 eV): m/z (%) = 269 ($M^+$, 7), 252 (23), 251 (100), 225 (15), 210 (12), 77 (18), 63 (12), 57 (10), 51 (11).

**HRMS ($C_{14}H_{11}N_3O_3$)**: calc.: 269.0800; found: 296.0793 ($M^+$).

**Synthesis of 4-(2*H*-indazol-2-yl)benzonitrile (3f) :**




According to **TP1** 2-iodobenzyl chloride (**4a**, 757 mg, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-cyanobenzenediazonium tetrafluoroborate (**2f**, 434 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded 4-(2*H*-indazol-2-yl)benzonitrile[3] (**3f**, 359 mg, 82 %) as a pale yellow solid.

**mp** (°C) = 163.4 – 164.6.

**$^1$H-NMR** (600 MHz, $CDCl_3$): δ (ppm) = 8.38 (s, 1H), 7.97 (d, *J* = 8.6 Hz, 2H), 7.70 – 7.74 (m, 3H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.31 (t, *J* = 8.1, 1H), 7.10 (t, *J* = 7.9 Hz, 1H).

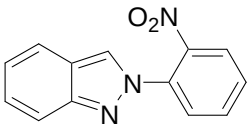
**$^{13}$C-NMR** (150 MHz, $CDCl_3$): δ (ppm) = 150.1, 143.0, 133.4, 127.7, 123.2, 123.0, 120.5, 120.4, 120.2, 118.0, 117.9, 110.9.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 2227, 1629, 1602, 1517, 1423, 1379, 1311, 1208, 1178, 1108, 1041, 951, 838, 820, 783, 758.

**MS** (EI, 70 eV): m/z (%) = 220 (15), 219 ($M^+$, 100), 218 (11), 192 (10), 102 (9).

**HRMS ($C_{14}H_9N_3$)**: calc.: 219.0796; found: 219.0788 ($M^+$).

**Synthesis of 2-(2-nitrophenyl)-2*H*-indazole (3g) :**




According to **TP1** 2-iodobenzyl chloride (**4a**, 757 mg, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 2-nitrobenzenediazonium tetrafluoroborate (**2g**, 474 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded 2-(2-nitrophenyl)-2*H*-indazole[4] (**3g**, 301 mg, 63 %) as a pale yellow solid.

**mp** (°C) = 152.3 – 153.8.

**$^1$H-NMR** (600 MHz, $CDCl_3$): δ (ppm) = 8.21 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.75 – 7.68 (m, 4H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 8.6 Hz, 1H), 7.13 (t, *J* = 7.1 Hz, 1H).

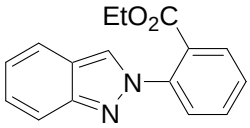
**$^{13}$C-NMR** (150 MHz, $CDCl_3$): δ (ppm) = 150.3, 145.2, 133.1, 129.5, 127.6, 127.3, 125.2, 123.7, 123.0, 122.7, 120.4, 118.1, 114.1.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ (cm$^{-1}$) = 1692, 1606, 1544, 1524, 1499, 1452, 1380, 1369, 1201, 1096, 1047, 952, 850, 782, 759, 749, 701.

**MS** (EI, 70 eV): m/z (%) = 239 ($M^+$, 16), 223 (15), 222 (100), 105 (9), 77 (21).

**HRMS ($C_{13}H_9N_3O_2$)**: calc.: 239.0695; found: 239.0680 ($M^+$).

**Synthesis of ethyl 2-(2*H*-indazol-2-yl)benzoate (3h) :**




According to **TP1** 2-iodobenzyl chloride (**4a**, 757 mg, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 2-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**2h**, 528 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded ethyl 2-(2*H*-indazol-2-yl)benzoate (**3h**, 410 mg, 77 %) as a pale yellow solid.

**mp** (°C) = 140.1 – 141.0.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.17 (s, 1H), 7.91 (d, *J* = 6.8 Hz, 1H), 7.74 (d, *J* = 8.7, 1H), 7.70 (d, *J* = 8.5, 1H), 7.47-7.65 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 1H ), 7.10 (t, *J* = 8.0 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 0.84 (t, *J* = 7.05 Hz, 3H).

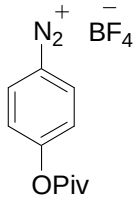
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 166.2, 149.5, 139.7, 131.9, 130.6, 128.8, 126.6, 126.3, 123.9, 122.3, 122.2, 120.3, 120.1, 117.7, 61.4, 13.5.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3131, 2982, 2957, 2898, 1727, 1689, 1681, 1628, 1606, 1584, 1548, 1519, 1499, 1463, 1451, 1379, 1362, 1351, 1300, 1280, 1245, 1234, 1201, 1151, 1131, 1100, 1050, 1018, 950, 856, 797, 762, 757.

**MS** (EI, 70 eV): m/z (%) = 266 ($M^+$, 42), 221 (32), 195 (16), 194 (100), 165 (12), 77 (10).

**HRMS ($C_{16}H_{14}N_2O_2$)**: calc.: 266.1055; found: 266.1049 ($M^+$).

**Synthesis of 4-[(2,2-dimethylpropanoyl)oxy]benzenediazonium tetrafluoroborate (2i):**




According to **TP2** 4-aminophenyl pivalate (9.65 g, 50.0 mmol) was converted to the diazonium salt. Recrystalization from methanol afforded 4-[(2,2-dimethylpropanoyl)oxy]benzenediazonium tetrafluoroborate (**2i**, 11.01 g, 76 %) as white needles.

**mp** (°C) = 125.8 – 133.0 (black when it is melt).

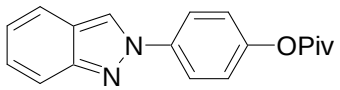
**$^1$H-NMR** (400 MHz, $(D_3C)_2SO$): δ (ppm) = 8.47 (d, *J* = 9.3 Hz, 2H), 7.20 (d, *J* = 9.3 Hz, 2H), 1.14 (s, 9H).

**$^{13}$C-NMR** (100 MHz, $(D_3C)_2SO$): δ (ppm) = 175.2, 169.1, 136.5, 125.0, 100.1, 38.4, 26.7.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3113, 2923, 2854, 2289, 1759, 1576, 1476, 1322, 1237, 1170, 1050, 1027, 890, 854, 796, 752.

**HRMS (**ESI, 70 eV, $C_{11}H_{13}N_2O_2^+$**)**: calc.: 205.0977; found: 205.0971 ($M^+$).

**Synthesis of 4-(2*H*-indazol-2-yl)phenyl pivalate (3i) :**




According to **TP1** 2-iodobenzyl chloride (**4a**, 757 mg, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-[(2,2-dimethylpropanoyl)oxy]benzenediazonium

tetrafluoroborate (**2i**, 584 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded 4-(2*H*-indazol-2-yl)phenyl pivalate (**3i**, 447 mg, 76 %) as a off-white solid.

**mp** (°C) = 146.3 – 147.9.

**$^{1}$H-NMR** (600 MHz, $CDCl_3$): δ (ppm) = 8.36 (s, 1H), 7.90 (d, *J* = 9.0 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.11 (t, *J* = 7.9 Hz, 1H), 1.38 (s, 9H).

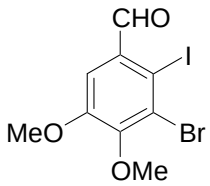
**$^{13}$C-NMR** (150 MHz, $CDCl_3$): δ (ppm) = 176.9, 150.5, 149.8, 137.9, 126.9, 122.8, 122.6, 122.5, 121.9, 120.5, 120.3, 117.9, 39.1, 27.1.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 2977, 2959, 2932, 1745, 1520, 1508, 1478, 1457, 1431, 1395, 1382, 1277, 1200, 1165, 1112, 1049, 1027, 1013, 950, 895, 852, 817, 791, 777, 756.

**MS** (EI, 70 eV): m/z (%) = 294 ($M^+$, 59), 211 (13), 210 (100), 181 (25), 85 (8), 57 (61).

**HRMS ($C_{18}H_{18}N_2O_2$)**: calc.: 294.1368; found: 294.1366 ($M^+$).

**Synthesis of 3-bromo-2-iodo-4,5-dimethoxybenzaldehyde:**




To a solution of 3-bromo-4,5-dimethoxybenzaldehyde (36.75 g, 0.15 mol) in methanol (400 mL) was added silver sulfate (46.77 g, 0.15 mol) and iodine (57.15 g, 0.225 mol) at 25 °C. The reaction mixture was stirred for 24 h at the same temperature, followed by addition of solid $Na_2S_2O_3$ until the solution decolorizes. The solution was filtrated through a pad of silica and concentrated *in vacuo*. Addition of of conc. HCl (30 mL) afforded precipitation of the product which was collected by filtration. Recrystalization from diethyl ether / pentane (1:1) afforded 3-bromo-2-iodo-4,5-dimethoxybenzaldehyde (45.63 g, 82 %) as a white solid.

**mp** (°C) = 104.8 – 105.9.

**$^{1}$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 9.98 (s, 1H), 7.49 (s, 1H), 3.92 (s, 3H), 3.91 (s, 3H).

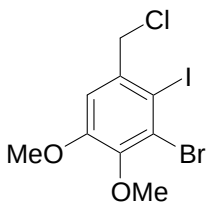
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 196.5, 153.7, 152.1, 133.5, 127.8, 112.4, 99.6, 60.7, 56.3.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ (cm$^{-1}$) = 3068, 3003, 2942, 2846, 1685, 1572, 1538, 1462, 1419, 1390, 1364, 1298, 1264, 1220, 1193, 1163, 1055, 992, 869, 818, 749, 674.

**MS** (EI, 70 eV): m/z (%) = 418 (19), 416 (18), 388 (10), 387 ([$H_2O$+M]$^+$, 100), 386 (12), 385 ([$H_2O$+M]$^+$, 96), 372 (M$^+$, 27), 370 (M$^+$, 29), 244 (10), 127 (10), 75 (22).

**HRMS ($C_9H_8BrIO_3$)**: calc.: 369.8702; found: 369.8703 (M$^+$).

**Synthesis of 3-bromo-1-(chloromethyl)-2-iodo-4,5-dimethoxybenzene :**




To a solution of 3-bromo-2-iodo-4,5-dimethoxybenzaldehyde (11.23 g, 30 mmol) in acetonitrile (150 mL) under argon atmosphere sodium borohydride (1.34 g, 30 mmol) was added in small portions at 0 °C. The reaction mixture was allowed to warm up to 25 °C, was stirred for 1 h and slowly poured on 2 M HCl (120 mL). The reaction mixture was extracted with $CH_2Cl_2$ (3x 100 mL). The combined organic phases were washed with brine (50 mL) and dried over $Na_2SO_4$. The solvent was removed *in vacuo* to afford the crude intermediate. The residue was dissolved in THF (60 mL), followed by addition of $NEt_3$ (6.66 mL, 48 mmol) and LiCl (3.48 g, 82.5 mmol) at 25 °C. At 0 °C $MeSO_2Cl$ (3.23 mL, 42 mmol) was added dropwise to the vigorous stirring solution. The reaction mixture was allowed to warm up to 25 °C and stirred for 12 h at the same temperature, followed by addition of sat. $NH_4Cl$ (aq.) (50 mL). The aqueous layer was extracted with EtOAc (3x 30 mL), the combined organic phases were dried over $Na_2SO_4$ and the solvent was removed *in vacuo*. The crude product was subjected to flash column chromatography (pentane / EtOAc = 9:1) to afford 3-bromo-1-(chloromethyl)-2-iodo-4,5-dimethoxybenzene (9.18 g, 85 %) as white solid.

**mp** (°C) = 119.3 – 120.6.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.08 (s, 1H), 4.73 (s, 2H), 3.88 (s, 3H), 3.82 (s, 3H).

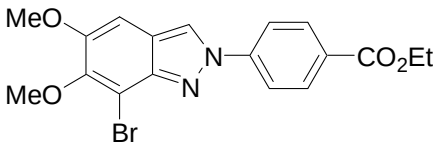
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 153.5, 146.9, 137.7, 127.1, 113.1, 96.2, 60.4, 56.2, 53.3.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ (cm$^{-1}$) = 3008, 2966, 2934, 2842, 1581, 1544, 1452, 1421, 1366, 1308, 1255, 1198, 1166, 1148, 1054, 993, 970, 914, 858, 817, 790, 711.

**MS** (EI, 70 eV): m/z (%) = 394 (11), 392 (51), 390 ($M^+$, 37), 358 (8), 357 (98), 356 (8), 355 (100).

**HRMS ($C_9H_9BrClIO_2$)**: calc.: 389.8519; found: 389.8508 ($M^+$).

**Synthesis of ethyl 4-(7-bromo-5,6-dimethoxy-2*H*-indazol-2-yl)benzoate (3j) :**




According to **TP1** 3-bromo-1-(chloromethyl)-2-iodo-4,5-dimethoxybenzene (**4b**, 1.17 g, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**2c**, 528 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 9:1) afforded 4-(7-bromo-5,6-dimethoxy-2*H*-indazol-2-yl)benzoate (**3j**, 615 mg, 76 %) as a pale yellow solid.

**mp** (°C) = 125.4 – 126.8.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.33 (s, 1H), 8.12 (d, *J* = 8.6 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 6.83 (s, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 3.87 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H).

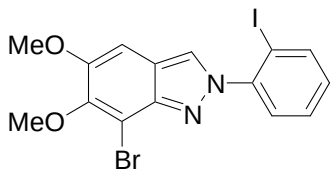
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 165.6, 151.5, 149.6, 145.6, 143.1, 130.9, 129.2, 120.5, 119.8, 119.4, 104.6, 96.9, 61.2, 60.9, 55.9, 14.2.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3127, 2983, 2946, 2849, 1710, 1608, 1546, 1522, 1482, 1426, 1366, 1342, 1282, 1236, 1170, 1104, 1028, 1000, 955, 924, 856, 820, 766.

**MS** (EI, 70 eV): m/z (%) = 407 (25), 406 ($M^+$, 96), 405 (21), 404 (100, $M^+$), 391 (13), 360 (14), 310 (18), 185 (12), 120 (28), 43 (17).

**HRMS ($C_{18}H_{17}BrN_2O_4$)**: calc.: 404.0372; found: 404.0377 ($M^+$).

**Synthesis of 7-bromo-2-(2-iodophenyl)-5,6-dimethoxy-2*H*-indazole (3k) :**



According to **TP1** 3-bromo-1-(chloromethyl)-2-iodo-4,5-dimethoxybenzene (**4b**, 1.17 g, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 2-iodophenyldiazonium tetrafluoroborate (**2b**, 636 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 9:1) afforded 7-bromo-2-(2-iodophenyl)-5,6-dimethoxy-2*H*-indazole (**3k**, 624 mg, 68 %) as a pale yellow solid.

**mp** (°C) = 134.3 – 135.8.

**$^{1}$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.12 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.39 - 7.58 (m, 3H), 7.18 (t, *J* = 7.85, 2H), 6.96 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H).

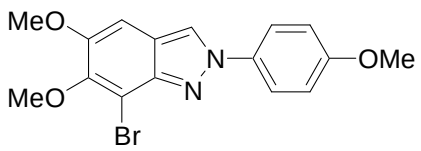
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 151.2, 149.2, 144.9, 143.4, 139.8, 130.8, 129.0, 128.5, 125.2, 118.1, 104.6, 97.3, 94.4, 60.9, 56.0.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3114, 2982, 2954, 2929, 2824, 1631, 1579, 1544, 1507, 1485, 1467, 1440, 1400, 1342, 1228, 1147, 1043, 1028, 1006, 963, 926, 832, 759, 748, 716, 665.

**MS** (EI, 70 eV): m/z (%) = 461 (13), 460 ($M^+$, 90), 459 (12), 458 ($M^+$,100), 364 (10), 288 (6).

**HRMS ($C_{15}H_{12}BrIN_2O_2$)**: calc.: 457.9127; found: 457.9132 ($M^+$).

**Synthesis of 7-bromo-5,6-dimethoxy-2-(4-methoxyphenyl)-2*H*-indazole (3l) :**




According to **TP1** 3-bromo-1-(chloromethyl)-2-iodo-4,5-dimethoxybenzene (**4b**, 1.17 g, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-methoxybenzenediazonium tetrafluoroborate (**2j**, 444 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 9:1) afforded 7-bromo-5,6-dimethoxy-2-(4-methoxyphenyl)-2*H*-indazole (**3l**, 501 mg, 69 %) as a pale white solid.

**mp** (°C) = 116.2 – 117.5.

**$^{1}$H-NMR** (600 MHz, $CDCl_3$): δ (ppm) = 8.17 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.86 (s, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 3.82 (s, 3H).

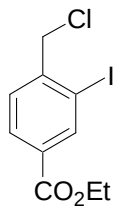
**$^{13}$C-NMR** (150 MHz, $CDCl_3$): δ (ppm) = 159.0, 150.9, 148.7, 144.8, 133.8, 122.2, 120.6, 118.9, 114.4, 104.5, 97.2, 60.9, 55.9, 55.5.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ (cm$^{-1}$) = 3138, 3125, 2923, 2905, 1665, 1593, 1538, 1421, 1363, 1291, 1251, 1189, 1172, 1153, 1139, 1086, 1056, 1011, 880, 844, 808, 776, 751, 698, 669.

**MS** (EI, 70 eV): m/z (%) = 365 (19), 364 ($M^+$, 91), 363 (18), 362 ($M^+$, 100), 348 (29), 347 (27), 268 (16), 253 (11).

**HRMS ($C_{16}H_{15}BrN_2O_3$)**: calc.: 362.0266; found: 362.0252 ($M^+$).

**Synthesis of 4-chloromethyl-3-iodobenzoic acid ethyl ester :**




To a solution of 3-iodo-4-methyl-benzoic acid ethyl ester (1.16 g, 4 mmol) in THF (10 mL) was added N-bromosuccinimide (783 mg, 4.4 mmol) and dibenzoylperoxide (97 mg, 0.4 mmol). The resulting mixture was refluxed for 9 h. Subsequently, the solvent was concentrated *in vacuo*, filtered through a plug of silica and washed with pentane. The solvent was removed *in vacuo*. In a 50 mL round bottom flask the residue was dissolved in THF (15 mL) and LiCl (433 mg, 10 mmol) was added. The resulting mixture was refluxed for 4 h. Subsequently, the solvent was removed *in vacuo*. Purification by flash column chromatography (silica gel, pentane / EtOAc = 100:1) provided 4-chloromethyl-3-iodobenzoic acid ethyl ester (776 mg, 60 %) as a white solid.

**mp** (°C) = 79.2 - 80.4.

**$^1$H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.52 (d, *J* = 1.8 Hz, 1H), 8.04 (dd, *J* = 1.8, 8.1 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 4.70 (s, 2H), 4.41 (q, *J* = 6.9 Hz, 2H), 1.41 (t, *J* = 6.9 Hz, 3H).

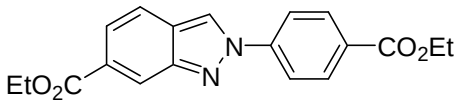
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 164.57, 144.25, 140.73, 131.93, 129.81, 129.77, 98.70, 61.51, 50.32, 14.29.

**IR** (Diamond-ATR, neat): $\tilde{\nu}$ (cm$^{-1}$) = 1708, 1292, 727.

**MS** (EI, 70 eV): m/z (%) = 324 (11), 323 ($M^+$, 19), 288 (100), 123 (13).

**HRMS** ($C_{10}H_{10}ClIO_2$): Calc.: 323.9414; found: 323.9415 ($M^+$).

**Synthesis of 2-(4-ethoxycarbonyl-phenyl)-2*H*-indazole-6-carboxylic acid ethyl ester (3m)**:




According to **TP1** 4-Chloromethyl-3-iodo-benzoic acid ethyl ester (324 mg, 1 mmol) was converted to the diarylzinc compound and reacted with 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (177 mg, 0.67 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 5:1 to 2:1) afforded 2-(4-ethoxycarbonyl-phenyl)-2*H*-indazole-6-carboxylic acid ethyl ester (**3m**, 161 mg, 71 %) as a pale yellow solid.

**mp** (°C) = 140.6 - 142.4.

**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.61 (s, 1H), 8.54 (s, 1H), 8.26 (d, *J* = 8.7 Hz, 2H), 8.06 (d, *J* = 8.7 Hz, 2H), 7.70 – 7. 78 (m, 2H), 4.40 – 4.50 (m, 4H), 1.40 – 1.50 (m, 6H).

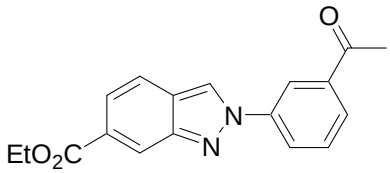
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 166.7, 165.6, 149.4, 143.3, 131.2, 130.2, 129.6, 124.8, 122.5, 121.8, 120.7, 120.4, 61.4, 61.1, 14.3.

**IR** (Diamond-ATR, neat): $\tilde{\nu}$ ($cm^{-1}$) = 3068, 2984, 1697, 1604, 1521, 1363, 1257, 1098, 856, 769, 689.

**MS** (EI, 70 eV): m/z (%): = 339 (20), 338 ($M^+$, 100), 293 (70), 265 (17), 192 (9).

**HRMS** ($C_{19}H_{18}N_2O_4$): Calc.: 338.1267, found: 338.1242 ($M^+$).

**Synthesis of 2-(3-acetylphenyl)-2*H*-indazole-6-carboxylic acid ethyl ester (3n) :**




According to **TP1** 4-chloromethyl-3-iodo-benzoic acid ethyl ester (243 mg, 0.75 mmol) was converted to the diarylzinc compound and reacted with 3-(acetyl)benzenediazonium tetrafluoroborate[5] (**2h**, 117 mg, 0.5 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 5:1 to 3:1) afforded 2-(3-acetylphenyl)-2*H*-indazole-6-carboxylic acid ethyl ester (**3n**, 104 mg, 68 %) as a pale yellow solid.

**mp** (°C) = 128.8 – 130.6.

**$^1$H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.61 (s, 1H), 8.55 (s, 1H), 8.51 (s, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.77 (s, 2H), 6.67 (t, *J* = 8.1 Hz, 1H), 4.46 (dd, *J* = 6.9 Hz, 7.2 Hz, 2H), 2.72 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H).

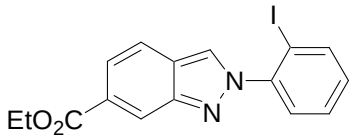
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 196.8, 166.7, 149.2, 140.7, 138.5, 130.1, 129.4, 128.0, 125.3, 124.7, 122.4, 121.7, 120.7, 120.4, 120.3, 61.1, 26.8, 14.3.

**IR** (Diamond-ATR, neat): $\tilde{\nu}$ ($cm^{-1}$) = 3341, 3103, 1707, 1678, 1441, 1368, 1317, 1243, 1060, 795, 741, 592.

**MS** (EI, 70 eV): m/z (%): = 309 (14), 308 ($M^+$, 100), 293 (10), 264 (11), 263 (53), 192 (6).

**HRMS** ($C_{18}H_{16}N_2O_3$): Calc.: 308.1161, found: 308.1148 ($M^+$).

**Synthesis of 2-(2-iodophenyl)-2*H*-indazole-6-carboxylic acid ethyl ester (3o) :**




According to **TP1** 4-chloromethyl-3-iodo-benzoic acid ethyl ester (243 mg, 0.75 mmol) was converted to the diarylzinc compound and reacted with 2-iodobenzenediazonium tetrafluoroborate (**2b**, 160 mg, 0.5 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 5:1) afforded 2-(2-iodo-phenyl)-2*H*-indazole-6-carboxylic acid ethyl ester (**3o**, 177 mg, 90 %) as a yellow oil.

**$^1$H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.60 (s, 1H), 8.22 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.72 - 7.84 (m, 2H), 7.41 – 7.61 (m, 2H), 7.09 - 7.35 (m, 1H), 4.42 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H).

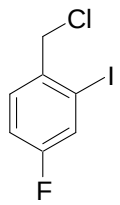
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) =166.9, 148.6, 143.5, 140.1, 131.1, 129.1, 129.0, 128.1, 125.2, 123.8, 122.1, 121.8, 120.5, 94.0, 61.1, 14.3.

**IR** (Diamond-ATR, neat): $\tilde{\nu}$ ($cm^{-1}$) = 2980, 1710, 1504, 1353, 1314, 1224, 1088, 1021, 948, 746.

**MS** (EI, 70 eV): m/z (%): = 393 (21), 392 ($M^+$, 100), 346 (48), 218 (19), 192 (27).

**HRMS** ($C_{16}H_{13}N_2O_2I$): Calc.: 392.0022, found: 392.0034 ($M^+$).

**Synthesis of 1-chloromethyl-4-fluoro-2-iodo-benzene** :




To a solution of 1-fluoro-3-iodo-4-methyl-benzene (2.36 g, 10 mmol) in THF (10 mL) was added N-bromosuccinimide (1.96 g, 11 mmol) and dibenzoylperoxide (242 mg, 1 mmol). The resulting mixture was refluxed for 9 h. Subsequently, the solvent was concentrated *in vacuo*, filtered through a plug of silica and washed with pentane. The solvent was removed *in vacuo*. In a 50 mL round bottom flask the residue was dissolved in THF (15 mL) and LiCl (693 mg, 16 mmol) was added. The resulting mixture was refluxed for 4 h. Subsequently, the solvent was removed *in vacuo*. Purification by flash column chromatography (silica, pentane) provided 4-fluoro-3-chloromethyl-2-iodo-benzene (908 mg, 35 %) as colorless oil.

**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.60 (dd, *J* = 2.7, 7.7 Hz, 1H), 7.47 (dd, *J* = 6.0, 8.6 Hz, 1H), 7.10 (dt, *J* = 2.7, 16.8 Hz, 1H), 4.68 (s, 2H).

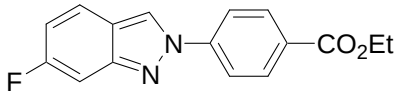
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 163.3 (d, *J* = 251.9 Hz), 136.1 (d, *J* = 3.5 Hz), 131.1 (d, *J* = 8.4 Hz), 126.9 (d, *J* = 23.6 Hz), 116.0 (d, *J* = 20.9 Hz), 99.0 (d, *J* = 8.6 Hz), 50.1 (d, *J* = 0.6 Hz).

**IR** (Diamond-ATR, neat): $\tilde{\nu}$ ($cm^{-1}$) = 1693, 1590, 1225, 863.

**MS** (EI, 70 eV): m/z (%) = 269 ($M^+$, 12), 234 (37), 155 (12).

**HRMS** ($C_7H_5ClFI$): calc.: 269.9109; found: 269.9102 ($M^+$).

**Synthesis of 4-(6-Fluoro-indazol-2-yl)-benzoic acid ethyl ester (3p) :**




According to **TP1** 1-chloromethyl-4-fluoro-2-iodobenzene (**4d**, 406 mg, 1.5 mmol) was converted to the diarylzinc compound and was reacted with 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**2c**, 264 mg, 1 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 5:1) afforded 4-(6-fluoro-indazol-2*H*-yl)-benzoic acid ethyl ester (**3p**, 212 mg, 75 %) as a pale yellow solid.

**mp** (°C) = 159.8-161.2 °C

**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.49 (s, 1H), 8.22 (d, *J* = 9.0 Hz, 2H) , 7.99 (d, *J* = 8.7 Hz, 2H), 7.70 (dd, *J* = 5.4 Hz, 9.2 Hz, 1H), 7.37 (d, *J* = 10.2 Hz, 1H), 6.96 (dt, *J* = 2.1 Hz, 8.7 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.2 Hz, 3H).

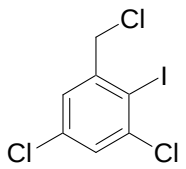
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 165.7, 162.3 (d, *J* = 244.3 Hz), 150.0 (d, *J* = 13.5 Hz), 143.3, 131.1, 129.7, 122.4 (d, *J* = 10.5 Hz), 121.0 (d, *J* = 1.5 Hz), 120.3, 120.1, 115.0 (d, *J* = 28.6 Hz), 101.0 (d, *J* = 24.0 Hz), 61.35, 14.35.

**IR** (Diamond-ATR, neat): $\tilde{\nu}$ ($cm^{-1}$) = 3073, 2986, 1707, 1639, 1607, 1370, 1270, 1101, 808, 763, 728.

**MS** (EI, 70 eV): m/z (%) = 289 (19), 284 ($M^+$, 100), 239 (74), 210 (18), 192 (8).

**HRMS** ($C_{16}H_{13}FN_2O_2$): Calc.: 284.0961, found: 284.0955 ($M^+$)

**Synthesis of 1,5-dichloro-3-chloromethyl-2-iodo-benzene :**




To a solution of 1,5-dichloro-2-iodo-3-methyl-benzene (2.3 g, 8 mmol) in THF (10 mL) was added N-bromosuccinimide (1.6 g, 8.8 mmol) and dibenzoylperoxide (194 mg, 0.8 mmol). The resulting mixture was refluxed for 9 h. Subsequently, the solvent was concentrated *in vacuo*, filtered through a plug of silica and washed with pentane. The solvent was removed *in vacuo*. In a 50 mL round bottom flask the residue was dissolved in THF (15 mL) and LiCl (693 mg, 16 mmol) was added. The resulting mixture was refluxed for 4 h. Subsequently, the solvent was removed *in vacuo*. Purification by flash column chromatography (silica gel, pentane) provided 1,5-dichloro-3-chloromethyl-2-iodo-benzene (716 mg, 54 %) as colorless oil.

**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.46 (d, *J* = 2.4 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 4.71 (s, 2H).

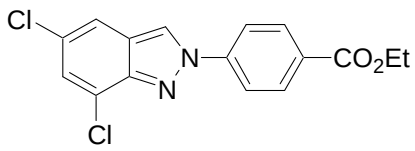
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 143.8, 140.7, 135.1, 128.8, 127.9, 101.4, 51.6.

**IR** (Diamond-ATR, neat): $\tilde{\nu}$ ($cm^{-1}$) = 2362, 1551, 1382, 1266, 1282, 1017, 862, 811.

**MS** (EI, 70 eV): m/z (%) = 321 (26), 319 ($M^+$, 24), 284 (50), 122 (12).

**HRMS** ($C_7H_4Cl_3I$): calc.: 319.8423; found: 319.8408 ($M^+$).

**Synthesis of 4-(5,7-dichloro-indazol-2-yl)-benzoic acid ethyl ester (3q) :**




According to **TP1** 1,5-dichloro-3-chloromethyl-2-iodo-benzene (**4e**, 482 mg, 1.5 mmol) was converted to the diarylzinc compound and was reacted with 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**2c**, 264 mg, 1 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 5:1) afforded 4-(5,7-dichloro-indazol-2*H*-yl)-benzoic acid ethyl ester (**3q**, 219 mg, 66 %) as a pale yellow solid.

**mp** (°C) = 139.6-141.3 °C.

**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.50 (s, 1H), 8.23 (d, *J* = 8.7 Hz, 2H), 8.03 (d, *J* = 9.0 Hz, 2H), 7.63 (d, *J* = 1.8 Hz, 1H), 7.37 (d, *J* = 1.8 Hz, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.2 Hz, 3H).

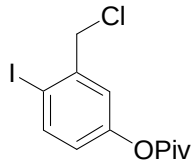
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 165.5, 146.2, 142.9, 131.2, 130.4, 128.0, 127.7, 124.5, 123.8, 121.3, 120.6, 118.0, 61.4, 14.3.

**IR** (Diamond-ATR, neat): $\tilde{\nu}$ ($cm^{-1}$) = 2987, 1701, 1606, 1517, 1365, 1276, 850, 765.

**MS** (EI, 70 eV): m/z (%) = 335 (18), 334 ($M^+$, 100), 288 (41), 226 (14), 191 (5).

**HRMS** ($C_{16}H_{12}Cl_2N_2O_2$): Calc.: 334.0276; found: 334.0280 ($M^+$).

**Synthesis of 3-(chloromethyl)-4-iodophenyl pivalate :**




To a suspension of 3-(hydroxymethyl)-4-iodophenol (30 mmol, 7.50 g) in THF (125 ml) was added sodium hyride (30 mmol, 1.20 g, 60w% in mineral oil) at 0 °C and stirred for 30 min at the same temperature. Trimethylacetic anhydride (30 mmol, 5.58 g) in THF (50 mL) was

added dropwise to the reaction mixture at 0 °C. After stirring the mixture for 3 h at 25 °C, the reaction was quenched with sat. $NH_4Cl$ (aq.) (30 mL). The aqueous layer was extracted with EtOAc (4x 30 mL). The combined organic phases were dried over $Na_2SO_4$ and the solvent was removed *in vacuo*. The residue was dissolved in THF (100 mL) and $NEt_3$ (48 mmol, 6.7 mL), LiCl (82.5 mmol, 3.50 g) were added. At 0 °C, $MeSO_2Cl$ (42 mmol, 3.25 mL) were added dropwise to the stirring solution. The reaction mixture was warmed up to 25 °C and stirred for 12 h at the same temperature, followed by addition of sat. $NH_4Cl$ (aq.) (30 mL). The aqueous layer was extracted with EtOAc(3x 30 mL). The combined organic phases were dried over $Na_2SO_4$, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography (silica gel, pentane / diethyl ether = 199:1) to afford 3-(chloromethyl)-4-iodophenyl pivalate (8.59 g, 88 %) as a colorless oil.

**$^1$H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.85 (d, *J* = 8.6 Hz, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 6.81 (dd, *J* = 8.4 Hz, 1H), 4.65 (s, 2H), 1.38 (s, 9H).

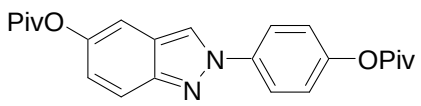
**$^{13}$C NMR** (75 MHz, $CDCl_3$): δ (ppm) = 176.4, 151.5, 140.9, 140.2, 123.4, 123.3, 94.4, 50.4, 39.0, 27.0.

**IR** (Diamond-ATR, neat): $\tilde{\nu}$ ($cm^{-1}$) = 2973, 2935, 2907, 2873, 1751, 1573, 1465, 1396, 1366, 1268, 1223, 1162, 1102, 1015, 942, 899, 827, 794, 732, 680.

**MS** (EI, 70 eV): m/z (%) = 352 ($M^+$, 10), 270 (17), 268 (47), 233 (35), 97 (13), 85 (35), 83 (16), 77 (12), 71 (13), 69 (15), 57 (100), 56 (10), 55 (19), 44 (14), 43 (16).

**HRMS** ($C_{12}H_{14}ClIO_2$): Calc.: 351.9727; found: 351.9729 ($M^+$).

**Syntheisi of 4-{5-[(2,2-dimethylpropanoyl)oxy]-2*H*-indazol-2-yl}phenyl pivalate (3r) :**




According to **TP1** 3-(chloromethyl)-4-iodophenyl pivalate (**2f**, 1.06 g, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-[(2,2-dimethylpropanoyl)oxy]benzenediazonium tetrafluoroborate (**2i**, 584 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded 4-{5-[(2,2-dimethylpropanoyl)oxy]-2*H*-indazol-2-yl}phenyl pivalate (**3r**, 575 mg, 73 %) as a pale pink solid.

**mp** (°C) = 118.3 – 120.6.

**$^1$H-NMR** (600 MHz, $CDCl_3$): δ (ppm) = 8.33 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 9.3 Hz, 1H), 7.36 (d, *J* = 1.65 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.01 (dd, *J* = 9.2 Hz, 2.1 Hz, 1H), 1.38 (s, 9 H), 1.37 (s, 9 H).

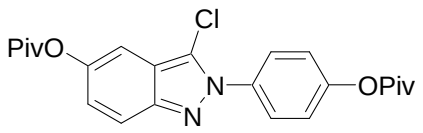
**$^{13}$C-NMR** (150 MHz, $CDCl_3$): δ (ppm) = 177.4, 176.8, 150.6, 148.0, 146.3, 137.8, 123.2, 122.7, 122.3, 121.8, 120.7, 119.1, 110.7, 39.2, 39.1, 27.2, 27.1.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 2964, 2933, 2872, 1740, 1604, 1523, 1477, 1459, 1393, 1366, 1280, 1200, 1150, 1110, 1029, 946, 902, 890, 837, 786, 760, 727.

**MS** (EI, 70 eV): m/z (%) = 394 ($M^+$, 36), 311 (12), 310 (63), 226 (54), 85 (11), 57 (100).

**HRMS ($C_{23}H_{26}N_2O_4$)**: calc.: 394.1893; found: 394.1892 ($M^+$).

**Synthesis of 4-{3-chloro-5-[(2,2-dimethylpropanoyl)oxy]-2*H*-indazol-2-yl}phenyl pivalate**




In an argon-flushed microwave tube was added N-chlorosuccinimide (2 mmol, 267 mg) to a solution of **3r** (2 mmol, 788 mg) in $CCl_4$ (4 mL) at 25 °C. The reaction mixture was heated under microwave irradiation at 80 °C (100 W) for 30 min. After cooling down to 25 °C, sat. aqueous $NH_4Cl$-solution (20 mL) was added to the reaction mixture. The aqueous layer was extracted with EtOAc (3x 10 mL). The combined organic phases were dried over $Na_2SO_4$, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography (silica gel, pentane / EtOAc = 95:5) to afford 4-{3-chloro-5-[(2,2-dimethylpropanoyl)oxy]-2*H*-indazol-2-yl}phenyl pivalate as a pale pink solid (706 mg, 83 %).

**mp** (°C) = 138.4 – 139.2.

**$^1$H-NMR** (600 MHz, $CDCl_3$): δ (ppm) = 7.70 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 9.2 Hz, 1H), 7.29 (d, *J* = 1.6 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.03 (dd, *J* = 9.1 Hz, 2.2 Hz, 1H), 1.39 (s, 9H), 1.38 (s, 9H).

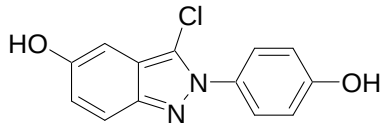
**$^{13}$C-NMR** (150 MHz, $CDCl_3$): δ (ppm) = 177.3, 176.6, 151.5, 146.7, 146.6, 135.6, 126.6, 124.1, 122.3, 119.8, 119.5, 119.5, 109.5, 39.2, 39.1, 27.2, 27.1.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 2969, 2933, 2905, 2873, 1751, 1519, 1478, 1460, 1394, 1368, 1317, 1276, 1204, 1157, 1104, 1030, 1008, 895, 855, 813, 793, 757.

**MS** (EI, 70 eV): m/z (%) = 430 (13), 429 (10), 428 ($M^+$, 33), 345 (22), 344 (14), 343 (68), 262 (15), 260 (49), 225 (16), 85 (13), 57 (100).

**HRMS ($C_{23}H_{25}ClN_2O_4$)**: calc.: 428.1503; found: 428.1494 ($M^+$).

**Synthesis of 3-chloro-2-(4-hydroxyphenyl)-2*H*-indazol-5-ol (7) :**




To a solution of **3r** (5 mmol, 1.97 g) in $CCl_4$ (10 mL) in an argon-flushed microwave tube was added N-chlorosuccinimide (5 mmol, 667 mg) at 25 °C. The reaction mixture was heated under microwave irradiation at 80 °C (100 W) for 30 min. After cooling down to 25 °C, sat. aqueous $NH_4Cl$-solution (20 mL) was added to the reaction mixture. The aqueous layer was extracted with $CH_2Cl_2$ (3x 20 mL). The combined organic phases were dried over $Na_2SO_4$, the solvent was removed *in vacuo*. The residue was dissolved in 20 mL THF/$H_2O$ mixture (2:1) and LiOH·$H_2O$ (50 mmol, 2.10 g) was added and stirred for 12 h at 25 °C. Subsequently, 2M HCl (30 mL) was added to the reaction mixture. The aqueous layer was extracted with $CH_2Cl_2$ (3x 20 mL). The combined organic phases were dried over $Na_2SO_4$, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography (silica gel, pentane / EtOAc = 1:1) to afford 3-chloro-2-(4-hydroxyphenyl)-2*H*-indazol-5-ol[6] as a pink solid (**7**, 1.00 g, 78 %).

**mp** (°C) = 205.8 – 207.0.

**$^1$H-NMR** (400 MHz, $CD_3OD$): δ (ppm) = 7.47 (d, *J* = 9.2 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 2H), 6.99 (dd, *J* = 9.2 Hz, 2.1 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 1.9 Hz, 1H).

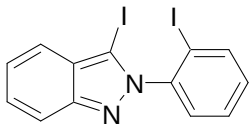
**$^{13}$C-NMR** (100 MHz, $CD_3OD$): δ (ppm) = 157.7, 152.2, 144.3, 129.9, 126.7, 122.1, 119.6, 118.4, 118.0, 115.3, 97.9.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3344, 2926, 1734, 1700, 1640, 1599, 1570, 1527, 1516, 1468, 1428, 1386, 1305, 1281, 1240, 1205, 1116, 1100, 1026, 1010, 942, 839, 821, 805.

**MS** (EI, 70 eV): m/z (%) = 262 (31), 261 (16), 260 ($M^+$, 100), 231 (12), 226 (11), 225 (66), 197 (19), 169 (3).

**HRMS ($C_{13}H_9ClN_2O_2$)**: calc.: 260.0353; found: 260.0343 ($M^+$).

**Synthesis of 3-iodo-2-(2-iodophenyl)-2*H*-indazole (8a) :**



To a solution of **3b** (2 mmol, 640 mg) in $ZnCl_2$ solution (2.0 mmol, 2 mL, 1M in THF) in a dry and argon-flushed microwave tube was added TMPMgCl·LiCl (2.2 mmol, 2.2 mL, 1 M in THF) at 25 °C. The reaction mixture was heated under microwave irradiation at 80 °C (100 W) for 1 h. After cooling to 25 °C, iodine (3 mmol, 762 mg) in THF (3 mL) was added. Subsequently, sat. aqueous $NH_4Cl$-solution (10 mL) was added to the reaction mixture. The aqueous layer was extracted with $CH_2Cl_2$ (3x 10 mL). The combined organic phases were washed with sat. $Na_2S_2O_3$ (aq.) (5 mL) and dried over $Na_2SO_4$, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography (silica gel, pentane / EtOAc = 95:5) to afford 3-iodo-2-(2-iodophenyl)-2*H*-indazole as a pale yellow solid (**8a**, 735 mg, 83 %).

**mp** (°C) = 150.1 – 151.6.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.03 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1 H), 7.49 - 7.62 (m, 2H), 7.38 - 7.47 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 8.1 Hz, 1H).

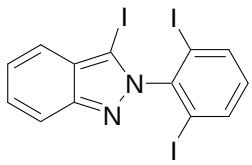
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 150.0, 143.4, 139.6, 132.7, 131.5, 129.2, 128.9, 127.6, 123.2, 120.9, 118.5, 97.2, 78.4.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3055, 1736, 1721, 1622, 1579, 1552, 1541, 1508, 1483, 1427, 1368, 1350, 1266, 1250, 1215, 1148, 1096, 1040, 1020, 996, 980, 918, 816, 763, 736, 714, 693.

**MS** (EI, 70 eV): m/z (%) = 446 (13), 445 ($M^+$, 100), 202 (12), 191 (42), 95 (6), 76 (10).

**HRMS ($C_{13}H_8I_2N_2$)**: calc.: 445.8777; found: 445.8766 ($M^+$).

**Synthesis of 2-(2,6-diiodophenyl)-3-iodo-2*H*-indazole (8b) :**



To $TMP_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$ solution (1.1 mmol, 2.75 mL, 0.4 M in THF) in a dry and argon-flushed microwave tube was added **3b** (1 mmol, 320 mg) and $ZnCl_2$ solution (2.0 mmol, 2 mL, 1M in THF) in THF (1 mL) was added at 25 °C. The reaction mixture was heated under microwave irradiation at 80 °C (100 W) for 1 h. After cooling to 25 °C, iodine (3 mmol, 762 mg) in THF (5 mL) was added. Subsequently, sat. aqueous $NH_4Cl$-solution (10 mL) was added to the reaction mixture. The aqueous layer was extracted with $CH_2Cl_2$ (3x 10 mL). The combined organic phases were washed with sat. $Na_2S_2O_3$ (aq.) (5 mL) and dried over $Na_2SO_4$, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography (silica gel, pentane / EtOAc = 95:5) to afford 2-(2,6-diiodophenyl)-3-iodo-2*H*-indazole as a pale yellow solid (**8b**, 417 mg, 73 %).

**mp** (°C) = 156.4 – 158.1.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.96 (d, *J* = 7.85 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.41 (t, *J* = 6.5 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.91 (t, *J* = 7.9 Hz, 1H).

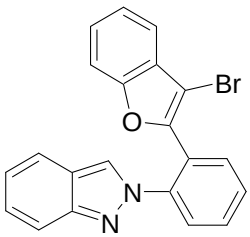
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 150.2, 144.8, 139.3, 132.7, 127.8, 127.6, 123.4, 121.0, 118.8, 97.4, 77.8.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ (cm$^{-1}$) = 3130, 3054, 3041, 1628, 1593, 1518, 1493, 1465, 1456, 1389, 1377, 1312, 1233, 1205, 1128, 1101, 1073, 1045, 950, 905, 802, 780, 746, 683.

**MS** (EI, 70 eV): m/z (%) = 571 ($M^+$, 100), 329 (10), 318 (32), 191 (21), 75 (8).

**HRMS ($C_{13}H_7I_3N_2$)**: calc.: 572.7822; found: 572.7826 ($[M+H]^+$).

**Synthesis of 2-[2-(3-bromo-1-benzofuran-2-yl)phenyl]-2*H*-indazole (9a) :**




A dry and argon flushed microwave tube, equipped with a magnetic stirring bar, was charged with $TMP_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$ (4.95 mmol, 12.34 mL) and 3-bromobenzofuran (9 mmol, 1.77 g) at 25 °C. The reaction mixture was heated under microwave irradiation at 80 °C (100 W) for 20 min. After cooling to 25 °C, the di(3-bromobenzofuran-2-yl)zinc was added dropwise to a solution of **3b** (6 mmol, 1.92 g) and $Pd(PPh_3)_4$ (0.24 mmol, 277 mg) at 25 °C. The mixture

was heated at 50 °C for 6 h. After cooling down the reaction mixture to 25 °C, sat. aqueous $NH_4Cl$-solution (20 mL) was added. The aqueous layer was extracted with $CH_2Cl_2$ (3x 20 mL). The combined organic phases were dried over $Na_2SO_4$, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography (silica gel, pentane / EtOAc = 9:1) to afford 2-[2-(3-bromo-1-benzofuran-2-yl)phenyl]-2*H*-indazole as a pale yellow solid (**9a**, 2.27 g, 97 %).

**mp** (°C) = 67.9 – 68.7.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.81 - 7.90 (m, 3H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.45 (t, *J* = 4.3 Hz, 1H), 7.21 - 7.28 (m, 3H), 7.18 (t, *J* = 4.7 Hz, 1H), 6.99 (t, *J* = 8.1 Hz, 1H).

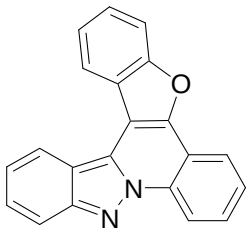
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 153.7, 149.5, 148.9, 139.6, 131.8, 130.8, 128.4, 128.2, 127.1, 126.6, 125.8, 123.9, 123.8, 123.5, 122.5, 122.0, 120.4, 120.0, 117.9, 111.5, 97.5.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3058, 1628, 1590, 1518, 1489, 1447, 1387, 1347, 1259, 1244, 1195, 1145, 1112, 1082, 1068, 1047, 986, 952, 930, 908, 892, 824, 797, 742.

**MS** (EI, 70 eV): m/z (%) = 310 (19), 309 (100), 308 (18), 281 (12), 154 (9).

**HRMS ($C_{21}H_{13}BrN_2O$)**: calc.: 388.0211; found: 388.0202 ($M^+$).

**Synthesis of [1]benzofuro[3,2-*c*]indazolo[2,3-*a*]quinoline (9b) :**




A dry and argon flushed microwave tube, equipped with a magnetic stirring bar, was charged with **9a** (1 mmol, 389 mg), $Pd(OAc)_2$ (0.2 mmol, 44 mg), 1,1'-bis(diphenylphosphino)ferrocene (0.2 mmol, 74 mg), tetrabutylammonium iodide (1 mmol, 369 mg) in DMF:$H_2O$:$NEt_3$ mixture (8:1:1) (5 mL) at 25 °C. The reaction mixture was heated under microwave irradiation at 150 °C (100 W) for 1 h. After cooling down to 25 °C, the reaction mixture was diluted with diethyl ether (5 mL). The precipitate was removed by filtration and washed with methanol. The solid was dissolved in chloroform and filtered through a short plug of silica. Evaporation of the solvent afforded [1]benzofuro[3,2-*c*]indazolo[2,3-*a*]quinoline as a yellow solid (**9b**, 256 mg, 83 %).

**mp** (°C) = 305.8 – 306.7.

**$^{1}$H-NMR** (600 MHz, $CD_2Cl_2$): δ (ppm) = 9.02 (d, *J* = 8.3 Hz, 1H), 8.60 (d, *J* = 8.5 Hz, 1H), 8.54 (d, *J* = 5.8 Hz, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.88 (t, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.0 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.54 - 7.64 (m, 3H), 7.34 (t, *J* = 7.4 Hz, 1H).

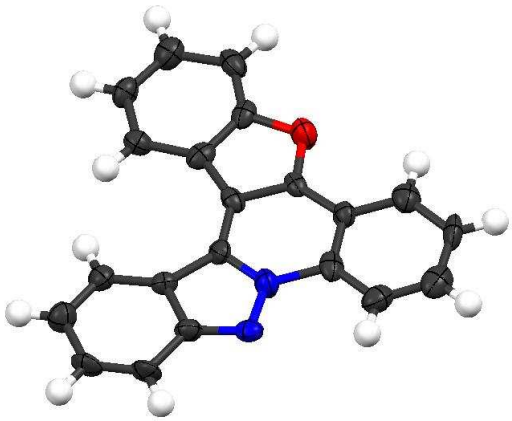
**$^{13}$C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 151.6, 145.0, 143.9, 129.2, 125.4, 124.5, 123.4, 122.3, 122.1, 119.6, 118.9, 118.1, 117.5, 117.1, 116.2, 113.8, 112.4, 111.7, 110.6, 107.7, 106.4.

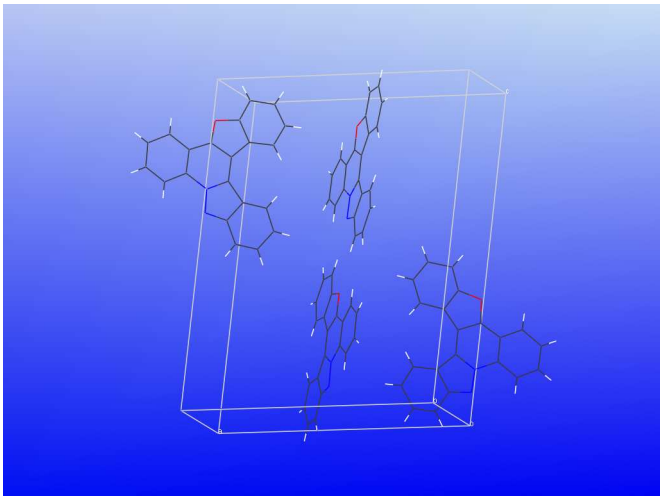
**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3060, 3012, 1631, 1622, 1594, 1556, 1538, 1457, 1396, 1360, 1328, 1309, 1294, 1273, 1218, 1200, 1144, 1121, 1108, 1077, 1069, 1020, 930, 899, 838, 809, 758, 737, 701, 677, 654.

**MS** (EI, 70 eV): m/z (%) = 309 (22), 308 ($M^+$, 100), 307 (8), 278 (8), 154 (17), 126 (6), 117 (7), 91 (7).

**HRMS ($C_{21}H_{12}N_2O$)**: calc.: 308.0950; found: 308.0943($M^+$).

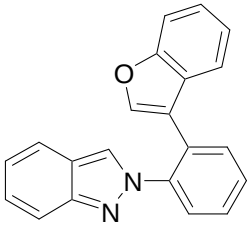
**X-ray Structure of (9b)**:





single-crystal X-ray structural analysis; molecular crystal packing

**Synthesis of 2-[2-(1-benzofuran-3-yl)phenyl]-2*H*-indazole (10a) :**



A dry and argon flushed Schlenk-flask, equipped with a magnetic stirring bar and a septum, was charged with Mg (14.4 mmol, 350 mg) in THF (10 mL) which was activated with 3 drops of 1,2-dibromoethane and 3 drops of $Me_3SiCl$. Then, $ZnCl_2 \cdot LiCl$[1] solution (10.2 mmol, 10.2 mL, 1M in THF) and 3-bromobenzofuran (9 mmol, 1.77 g) were added at 25 °C, followed by stirring for 1 h at the same temperature. To a solution of **3b** (6 mmol, 1.92 g) and $Pd(PPh_3)_4$ (0.24 mmol, 277 mg) in THF (12 mL) was added dropwise the arylzinc reagent at 25 °C. The reaction mixture was stirred for 6 h at 50 °C. After cooling to 25 °C, sat. aqueous $NH_4Cl$-solution (20 mL) was added. The aqueous layer was extracted with $CH_2Cl_2$ (3x 20 mL). The combined organic phases were dried over $Na_2SO_4$, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography (silica gel, pentane / EtOAc = 9:1) to afford 2-[2-(1-benzofuran-3-yl)phenyl]-2*H*-indazole as a yellow solid (**10a**, 1.73 g, 93 %).

**mp** (°C) = 132.5 – 133.5.

**$^1$H-NMR** (600 MHz, $CDCl_3$): δ (ppm) = 7.82 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 5.2 Hz, 1H), 7.23 (s, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.1 Hz, 1H).

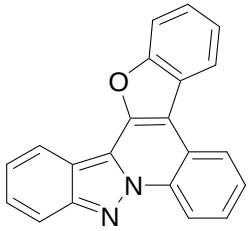
**$^{13}$C-NMR** (150 MHz, $CDCl_3$): δ (ppm) = 155.0, 149.1, 142.4, 139.3, 130.7, 129.3, 128.5, 127.8, 127.6, 126.5, 126.4, 124.9, 124.6, 123.0, 122.1, 122.0, 120.3, 119.6, 117.8, 117.7, 111.5.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 2928, 1627, 1606, 1569, 1518, 1497, 1477, 1450, 1384, 1268, 1213, 1191, 1145, 1103, 1091, 1052, 857, 822, 787, 768, 756, 742, 710, 656.

**MS** (EI, 70 eV): m/z (%) = 310 ($M^+$, 100), 309 (31), 281 (35), 279 (6), 181 (11), 140 (8).

**HRMS ($C_{21}H_{14}N_2O$)**: calc.: 310.1106; found: 310.1097 ($M^+$).

**Synthesis of [1]benzofuro[2,3-*c*]indazolo[2,3-*a*]quinoline (10b) :**



A dry and argon flushed microwave tube, equipped with a magnetic stirring bar, was charged with $TMP_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$ (1.2 mmol, 3.0 mL) and **10a** (1 mmol, 310 mg) at 25 °C. The reaction mixture was heated under microwave irradiation at 80 °C (150 W) for 1 h. After cooling to 25 °C, $CuCN{\cdot}2LiCl$[7] (1 mmol, 1 mL, 1M in THF) was added dropwise to the zinc reagent and further stirred for 10 min at 25 °C. To a solution of chloranil (1.5 mmol, 368 mg) in THF (5 mL) the copper reagent was added dropwise at 25 °C, followed by stirring for 1 h at the same temperature. The reaction mixture was quenched with 2 M aqueous $NH_4OH$ (50 mL) solution. The aqueous layer was extracted with $CH_2Cl_2$ (3x 20 mL). The combined organic phases were washed with 2 M HCl (50 mL) and dried over $Na_2SO_4$, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography (silica gel, pentane / EtOAc = 9:1 with 0.5 % $NEt_3$) to afford [1]benzofuro[2,3-*c*]indazolo[2,3-*a*]quinoline as a yellow solid (**10b**, 232 mg, 75 %).

**mp** (°C) = 259.6 – 260.3.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 9.08 (d, *J* = 8.5 Hz, 1H), 8.58 (d, *J* = 7.6 Hz, 1H), 8.48 (d, *J* = 8.1 Hz, 1H), 8.31 (d, *J* = 7.1 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.79 (t, *J* = 7.1 Hz, 1H), 7.76 (t, *J* = 7.3 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 6.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H).

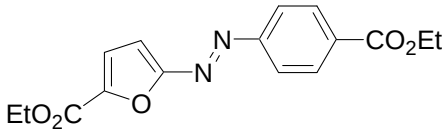
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 156.4, 149.1, 146.1, 132.1, 128.3, 127.6, 126.8, 126.2, 124.4, 124.2, 124.0, 123.7, 121.8, 121.4, 121.2, 120.8, 118.3, 116.7, 115.4, 112.4, 112.4.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3053, 2925, 2852, 1689, 1678, 1650, 1613, 1570, 1539, 1496, 1462, 1448, 1429, 1381, 1356, 1310, 1270, 1230, 1208, 1178, 1107, 1080, 1055, 1023, 992, 946, 937, 883, 806, 771, 739, 712, 698.

**MS** (EI, 70 eV): m/z (%) = 309 (24), 308 ($M^+$, 100), 307 (8), 154 (14), 44 (16).

**HRMS ($C_{21}H_{12}N_2O$)**: calc.: 308.0950; found: 308.0933($M^+$).

**Synthesis of ethyl 5-{(*E*)-[4-(ethoxycarbonyl)phenyl]diazenyl}-2-furoate (14a) :**




According to **TP3** ethyl 5-bromo-2-furoate (657 mg, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**2c**, 528 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded ethyl 5-{(*E*)-[4-(ethoxycarbonyl)phenyl]diazenyl}-2-furoate (**14a**, 562 mg, 89%) as a red solid.

**mp** (°C) = 110.3 – 111.6.

**$^{1}$H-NMR** (600 MHz, $CDCl_3$): δ (ppm) = 8.16 (d, *J* = 8.3 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 3.6 Hz, 1H), 7.11 (d, *J* = 3.5 Hz, 1H), 4.38 - 4.43 (m, 4H), 1.38 - 1.43 (m, 6H).

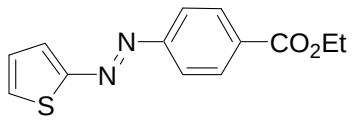
**$^{13}$C-NMR** (150 MHz, $CDCl_3$): δ (ppm) = 165.8, 161.6, 158.5, 155.2, 144.7, 132.9, 130.6, 122.9, 120.0, 110.8, 61.7, 61.3, 14.3.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3136, 3100, 2982, 2938, 2905, 1724, 1702, 1471, 1269, 1245, 1158, 1101, 966, 761, 700.

**MS** (EI, 70 eV): m/z (%) = 316 ($M^+$, 100), 271 (10), 167 (11), 163 (15), 149 (23), 135 (14), 117 (7).

**HRMS ($C_{16}H_{16}N_2O_5$)**: calc.: 316.1059; found: 316.1054 ($M^+$).

**Synthesis of ethyl 4-[(*E*)-2-thienyldiazenyl]benzoate (14b) :**




According to **TP3** 2-iodothiophene (630 mg, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**2c**, 528 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded ethyl 4-[(*E*)-2-thienyldiazenyl]benzoate (**14b**, 431 mg, 83 %) as a red solid.

**mp** (°C) = 115.6 – 117.1.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.15 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 4.6 Hz, 1H), 7.46 (d, *J* = 5.3 Hz, 1H), 7.17 (t, *J* = 4.6 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

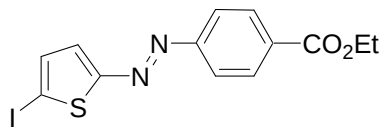
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 166.0, 160.2, 154.6, 133.1, 131.9, 130.5, 129.7, 127.7, 122.5, 61.2, 14.3.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ / $cm^{-1}$ = 3407, 3090, 3075, 2998, 2980, 2962, 2939, 1957, 1820, 1714, 1413, 1376, 1269, 1096, 1008, 774, 704.

**MS** (EI, 70 eV): m/z (%) = 260 ($M^+$, 78), 215 (12), 149 (26), 111 (100), 83 (31), 65 (10).

**HRMS ($C_{13}H_{12}N_2O_2S$)**: calc.: 260.0619; found: 260.0617 ($M^+$).

**Syntheis of ethyl 4-[(*E*)-(5-iodo-2-thienyl)diazenyl]benzoate (14c) :**




According to **TP3** 2,5-diiodothiophene (1.00 g, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**2c**, 528 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded ethyl 4-[(*E*)-(5-iodo-2-thienyl)diazenyl]benzoate (**14c**, 726 mg, 94 %) as a red solid.

**mp** (°C) = 140.1 – 141.0.

**$^1$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.13 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 3.9 Hz, 1H), 7.39 (d, *J* = 3.9 Hz, 1H), 4.39 (q, *J* = 7.0 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).

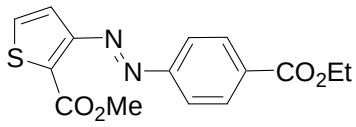
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 165.9, 164.2, 154.3, 137.6, 133.3, 133.1, 132.1, 130.5, 122.6, 122.5, 83.3, 61.2, 14.3.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3396, 3096, 2989, 2972, 2930, 1707, 1599, 1410, 1361, 1266, 1096, 1042, 1008, 804, 772, 695.

**MS** (EI, 70 eV): m/z (%) = 386 ($M^+$, 100), 260 (46), 237 (32), 209 (15), 149 (45), 111 (44), 103 (14), 82 (13).

**HRMS ($C_{13}H_{11}IN_2O_2S$)**: calc.: 385.9586; found: 385.9565 ($M^+$).

**Synthesis of methyl 3-{(*E*)-[4-(ethoxycarbonyl)phenyl]diazenyl}thiophene-2-carboxylate (14d) :**




According to **TP3** methyl 3-bromothiophene-2-carboxylate (663 mg, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**2c**, 528 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded methyl 3-{(*E*)-[4-(ethoxycarbonyl)phenyl]diazenyl}-thiophene-2-carboxylate (**14d**, 528 mg, 83 %) as a red solid.

**mp** (°C) = 103.2 – 104.3.

**$^{1}$H-NMR** (600 MHz, $CDCl_3$): δ (ppm) = 8.17 (d, *J* = 8.3 Hz, 2H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.43 - 7.49 (m, 2H), 4.40 (q, *J* = 7.0 Hz, 2H), 3.97 (s, 3H), 1.41 (t, *J* = 7.0 Hz, 3H).

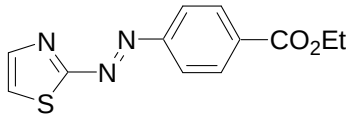
**$^{13}$C-NMR** (150 MHz, $CDCl_3$): δ (ppm) = 165.9, 161.5, 156.3, 155.2, 132.7, 131.5, 130.6, 130.0, 123.0, 118.4, 61.3, 52.5, 14.3.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3427, 3401, 3100, 3000, 2954, 2905, 1721, 1709, 1436, 1278, 1247, 1224, 1097, 1027, 871, 784, 698, 645.

**MS** (EI, 70 eV): m/z (%) = 318 ($M^+$, 100), 273 (11), 169 (80), 149 (73), 125 (39), 103 (16).

**HRMS ($C_{15}H_{14}N_2O_4S$)**: calc.: 318.0674; found: 318.0660 ($M^+$).

**Synthesis of ethyl 4-[(*E*)-1,3-thiazol-2-yldiazenyl]benzoate (14e) :**




According to **TP3** 2-bromothiazole (492 mg, 3.0 mmol) was converted to the diarylzinc compound and was reacted with 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**2c**, 528 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5) afforded ethyl 4-[(*E*)-1,3-thiazol-2-yldiazenyl]benzoate (**14e**, 491 mg, 94 %) as a brown solid.

**mp** (°C) = 121.9 – 123.1.

**$^{1}$H-NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.17 (d, *J* = 7.6 Hz, 2H), 8.06 (d, *J* = 2.7 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 3.1 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

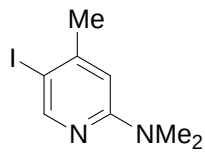
**$^{13}$C-NMR** (75 MHz, $CDCl_3$): δ (ppm) = 176.6, 165.6, 153.8, 144.3, 133.7, 130.6, 123.5, 122.2, 61.4, 14.2.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 3094, 3080, 2978, 2902, 1707, 1601, 1578, 1484, 1450, 1409, 1368, 1322, 1279, 1233, 1192, 1174, 1139, 1122, 1107, 1080, 1022, 1007, 898, 873, 768, 693.

**MS** (EI, 70 eV): m/z (%) = 261 ($M^+$, 34), 233 (31), 215 (32), 187 (83), 150 (29), 121 (88), 104 (32), 76 (56), 65 (100).

**HRMS ($C_{12}H_{11}N_3O_2S$)**: calc.: 261.0572; found: 261.0569 ($M^+$).

**Synthesis of 2-amine-5-iodo-*N*,*N*,4-trimethylpyridine :**




2-Amino-5-iodo-4-methylpyridine (7.4 mmol, 1.70 g) was added to a mixture of formaldehyde solution (30 mL, 0.40 mol, 37 w% in water) and formic acid (0.78 mol, 30 mL). The reaction mixture was refluxed for 18 h. Then, the solution was neutralized with 2 M aqueous NaOH solution. The aqueous layer was extracted with $CH_2Cl_2$ (3x 20 mL). The combined organic phases were dried over $Na_2SO_4$, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography (silica gel, pentane / EtOAc = 95:5) to afford **5-**iodo-2-amino-*N*,*N*,4-trimethylpyridin as a white solid (1.32 g, 68 %).

**mp** (°C) = 35.1 – 36.0.

**$^{1}$H-NMR** (600 MHz, $CDCl_3$): δ (ppm) = 8.31 (s, 1H), 6.42 (s, 1H), 3.03 (s, 6H), 2.29 (s, 3H).

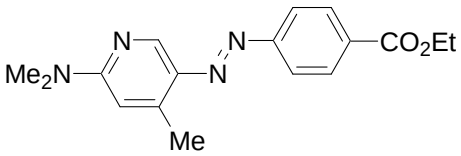
**$^{13}$C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 159.23, 154.34, 149.94, 107.47, 83.22, 38.13, 27.48.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 2920, 2853, 2792, 1584, 1526, 1494, 1432, 1396, 1376, 1338, 1286, 1265, 1228, 1204, 1166, 1065, 1033, 970, 921, 877, 827, 730.

**MS** (EI, 70 eV): m/z (%) = 261 ($M^+$, 88), 246 (44), 232 (73), 149 (100), 107 (27), 92 (35), 79 (19), 65 (23).

**HRMS ($C_8H_{11}IN_2$)**: calc.: 261.9967; found: 261.9953 ($M^+$).

**Synthesis of ethyl 4-{(*E*)-[6-(dimethylamino)-4-methylpyridin-3-yl]diazenyl}benzoate (14f) :**




According to **TP3** 2-amino-5-iodo-*N*,*N*,4-trimethylpyridine (786 mg, 3.0 mmol) was converted to the dipyridylzinc compound and was reacted with 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate (**2c**, 528 mg, 2.0 mmol). Purification by flash column chromatography (silica gel, pentane / EtOAc = 95:5 with 0.5 % $NEt_3$) afforded ethyl 4-{(*E*)-[6-(dimethylamino)-4-methylpyridin-3-yl]diazenyl}benzoate (**14f**, 406 mg, 65 %) as a red solid.

**mp** (°C) = 140.6 – 142.1.

**$^1$H-NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.61 (s, 1H), 8.12 (d, *J* = 8.6 Hz, 2H), 7.82 (d, *J* = 8.6 Hz, 2H), 6.35 (s, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.16 (s, 6H), 2.62 (s, 3H), 1.40 (t, *J* = 7.0 Hz, 3H).

**$^{13}$C-NMR** (100 MHz, $CDCl_3$): δ (ppm) = 166.2, 159.8, 155.9, 147.7, 139.0, 138.5, 130.7, 130.4, 122.1, 105.9, 61.0, 38.2, 18.4, 14.3.

**IR (**Diamond-ATR, neat**)**: $\tilde{\nu}$ ($cm^{-1}$) = 2982, 2931, 2868, 1709, 1657, 1597, 1518, 1477, 1428, 1398, 1350, 1304, 1272, 1229, 1190, 1125, 1098, 1061, 1021, 968, 950, 868, 827, 774, 747, 727, 699.

**MS** (EI, 70 eV): m/z (%) = 313 (18), 312 ($M^+$, 100), 283 (11), 239 (13), 163 (14), 135 (56), 108 (92), 93 (13).

**HRMS ($C_{17}H_{20}N_4O_2$)**: calc.: 312.1586; found: 312.1578 ($M^+$).

References:


(1) (a) Krasovskiy, A.; Knochel, P. *Angew. Chem., Int. Ed*. **2004**, *43*, 3333. (b) Krasovskiy, A.; Straub, B. F.; Knochel, P. *Angew. Chem., Int. Ed*. **2005**, *44*, 159. (c) Krasovskiy, A.; Kopp, F.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 497.

(2) Reissert, A; Lemmer, F *Ber. Chem. Ges., Abt. B* **1926**, *56B*, 351-9.

(3) Armour, M.; Cadogan, J.; Grace, D. *J. Chem Soc., Perk. Trans. 2* **1975**, *11*, 1185-9.

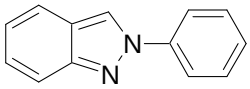
(4) Tsuge, O.; Samura, H. *Org. Prep. Proc. Int.* **1974**, *6*, 161-7.

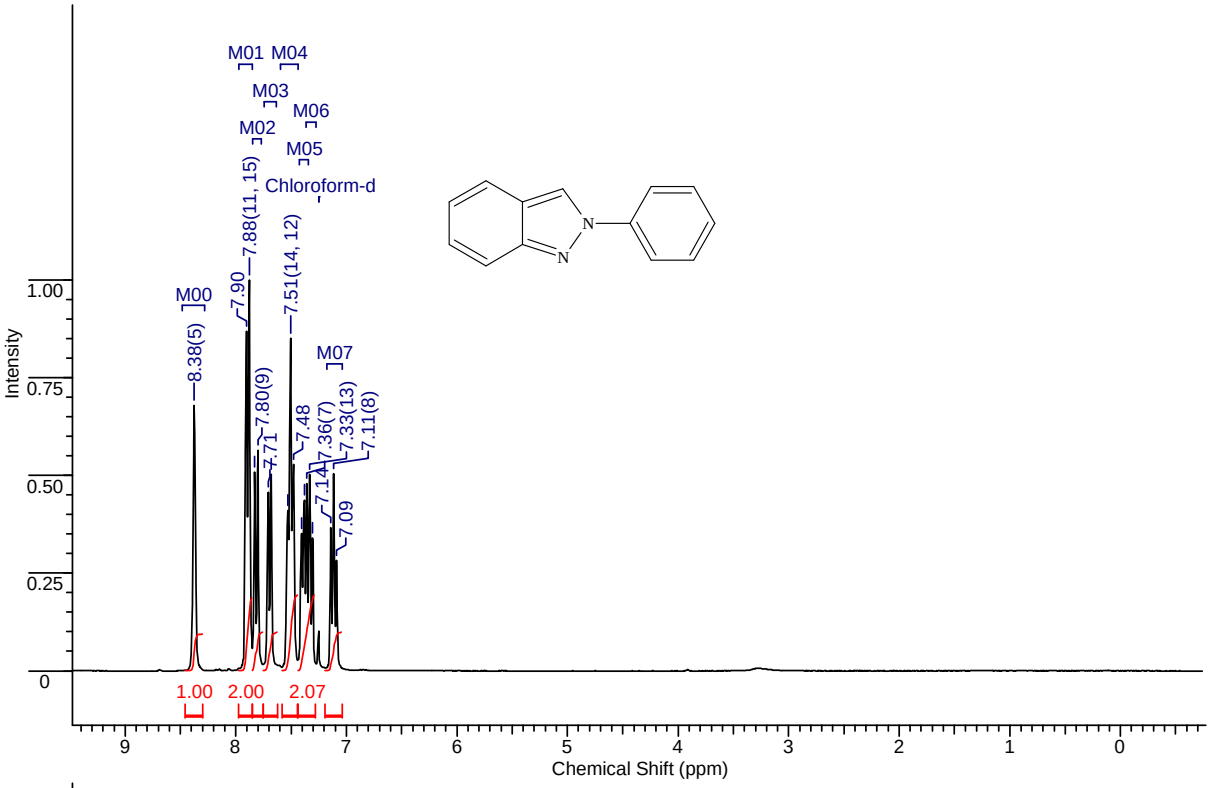
(5) Sengupta, S.; Bhattacharyya, S. *J. Org. Chem*. **1997**, *62*, 3405-3406.

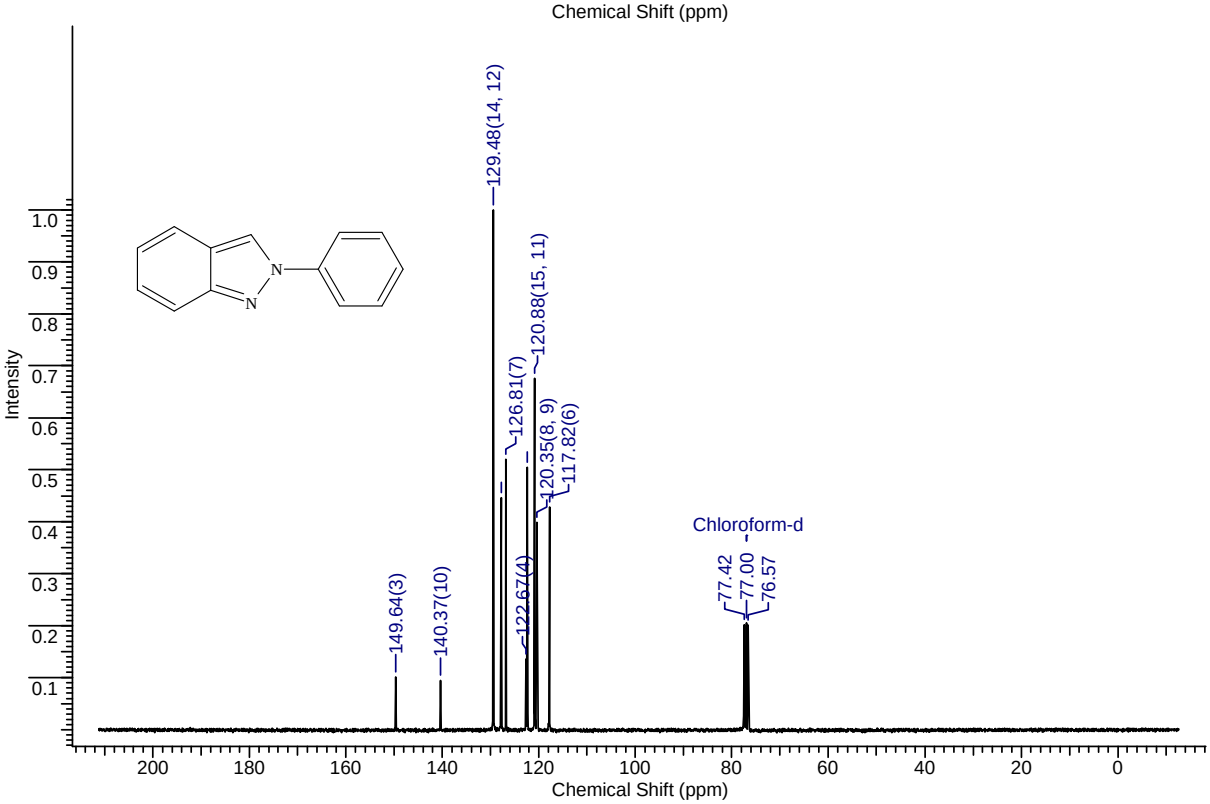
(6) De Angelis, M.; Stossi, F.; Carlson, K.; Katzenellenbogen, B.; Katzenellenbogen, J. *J. Med. Chem.* **2005**, *48*, 1132-1144.

(7) del Amo, V.; Dubbaka, S.; Krasovskiy, A.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 7838-7842.

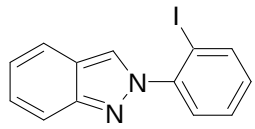
**Synthesis of 2-phenyl-2*H*-indazole (3a):**

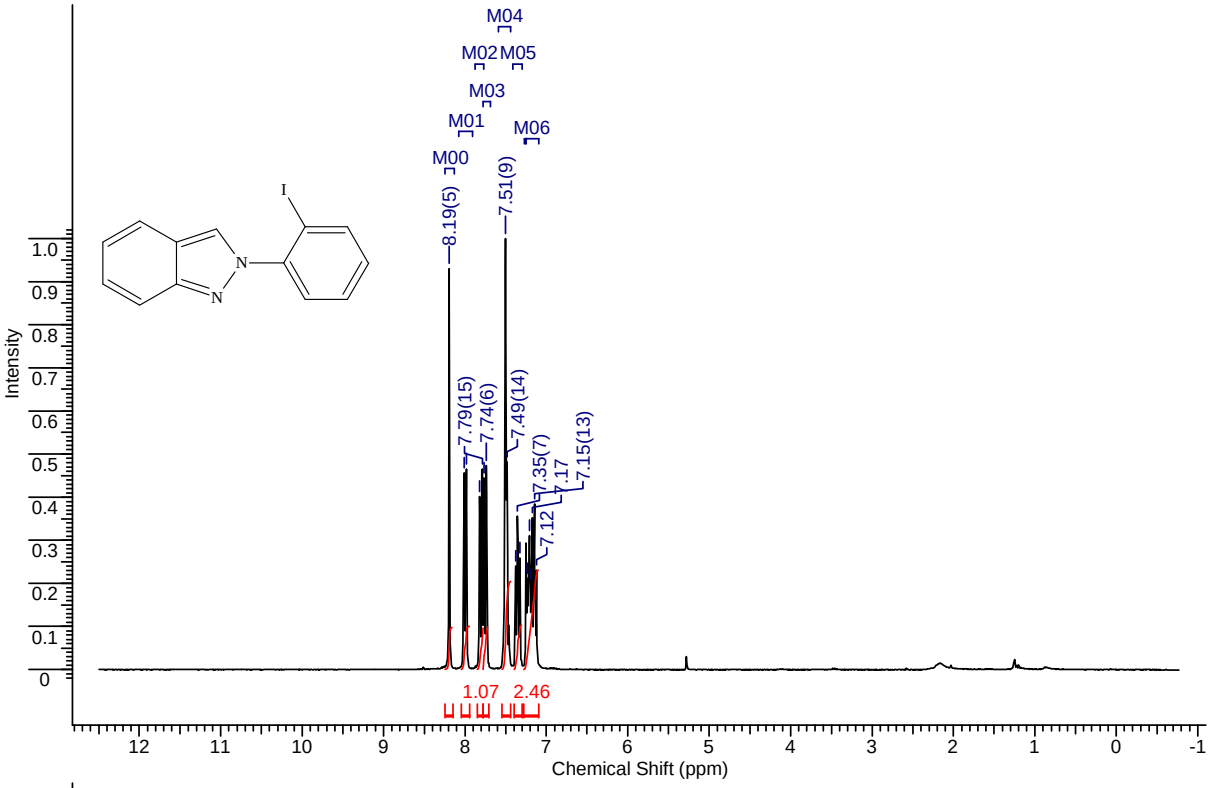


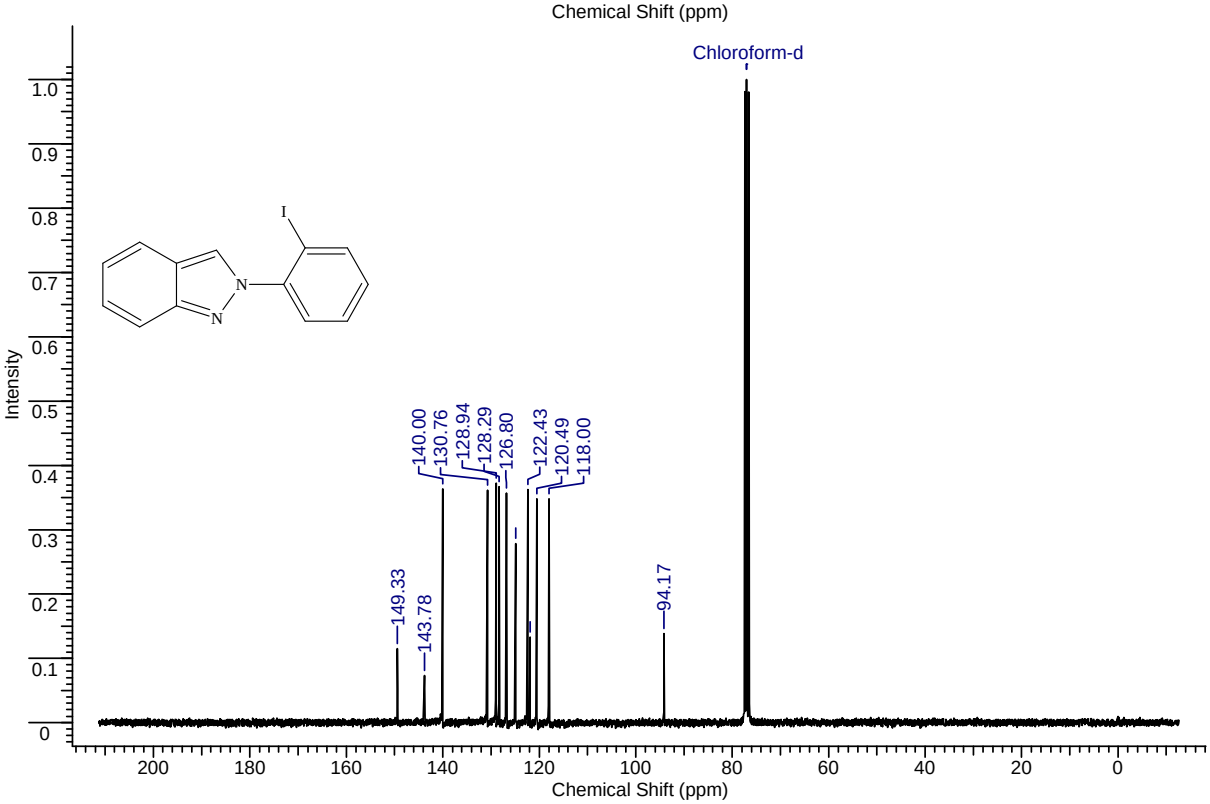


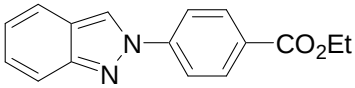
**Synthesis of 2-(2-iodophenyl)-2*H*-indazole (3b) :**

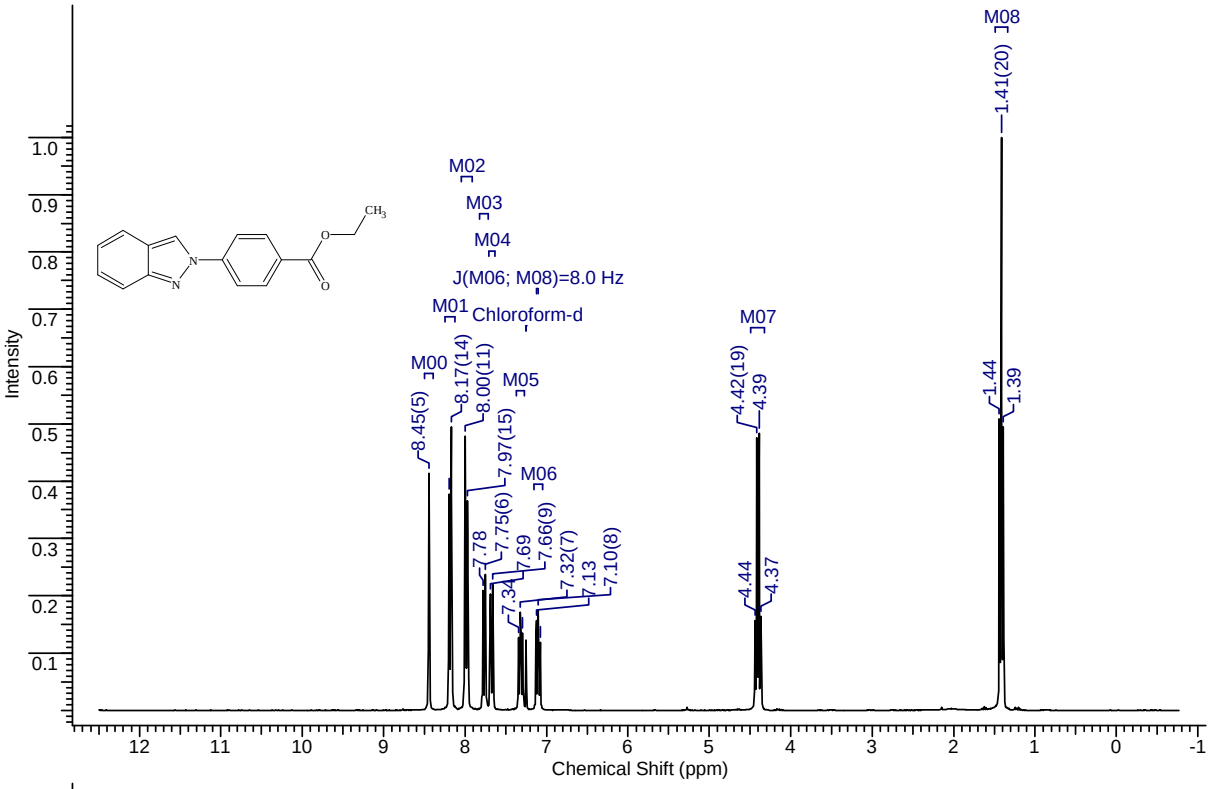


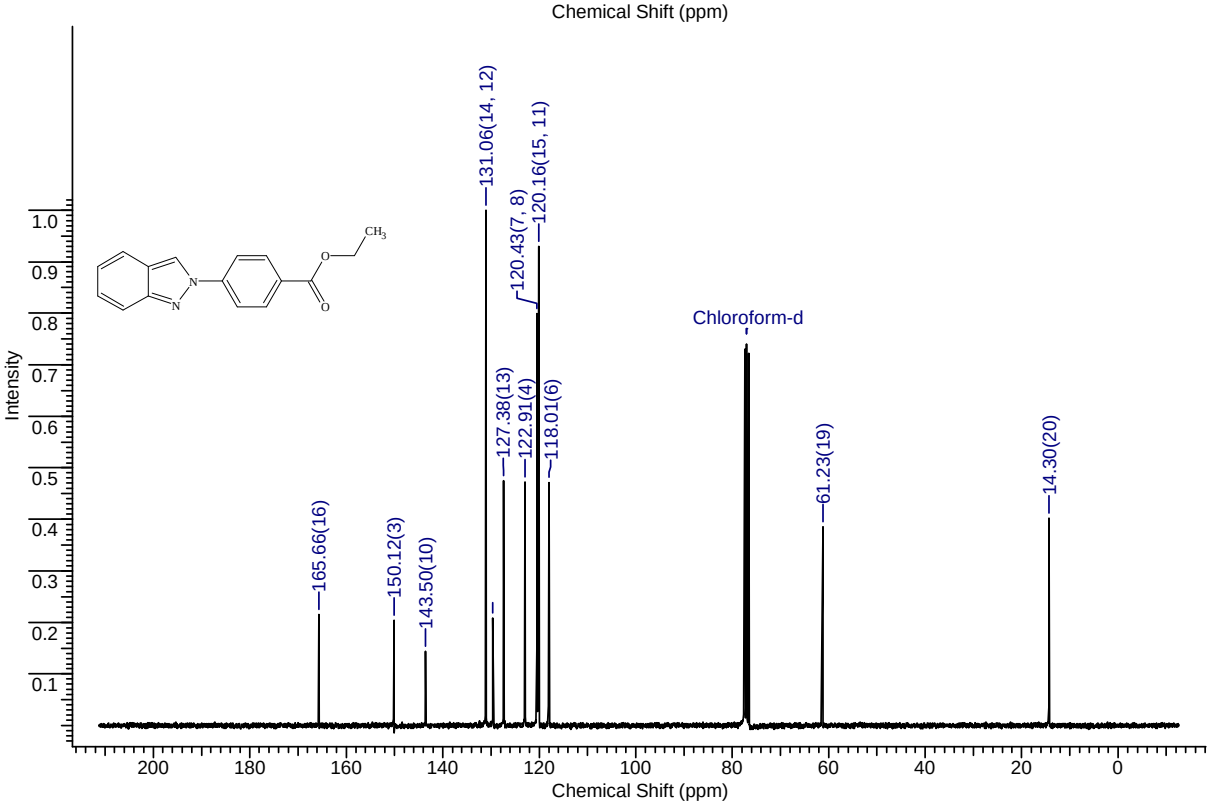


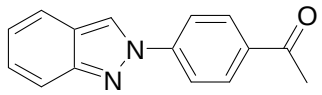
**Synthesis of ethyl 4-(2*H*-indazol-2-yl)benzoate (3c) :**

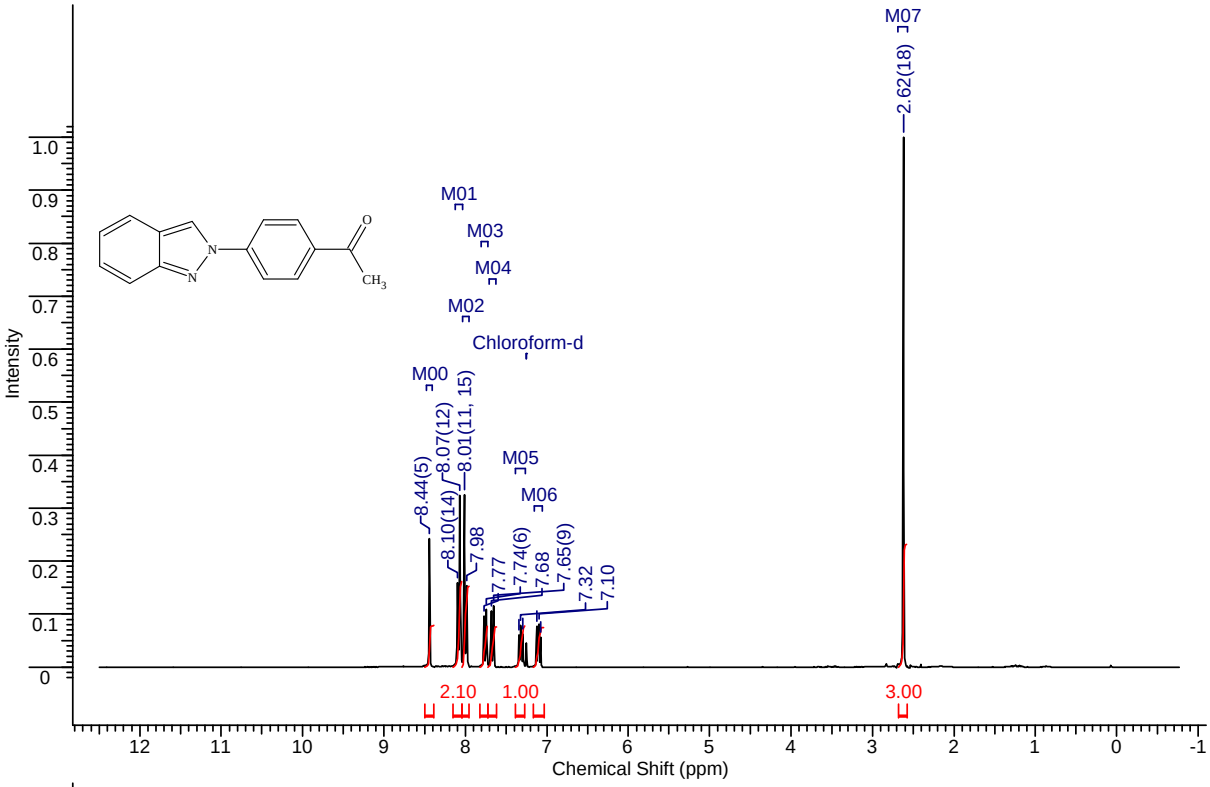


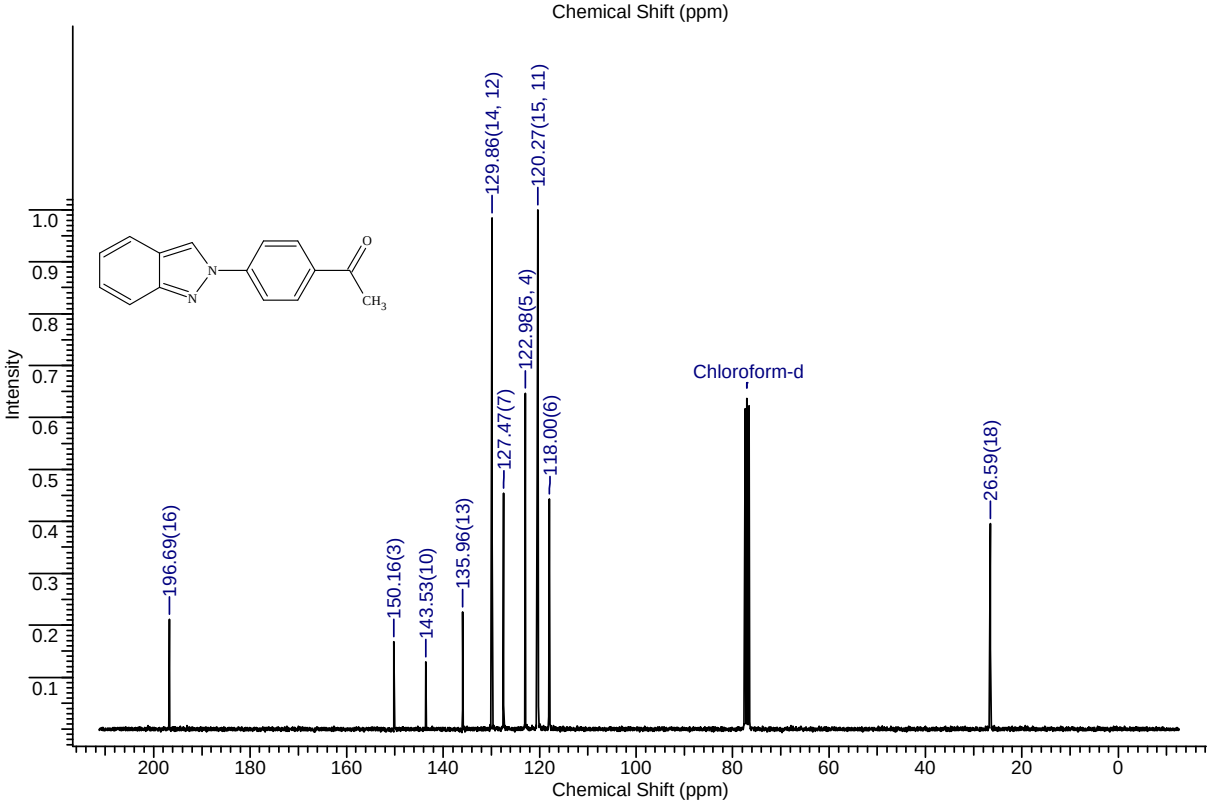



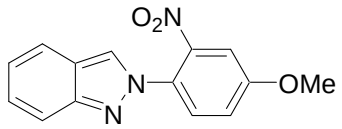
**Synthesis of 1-[4-(2*H*-indazol-2-yl)phenyl]ethanone (3d) :**

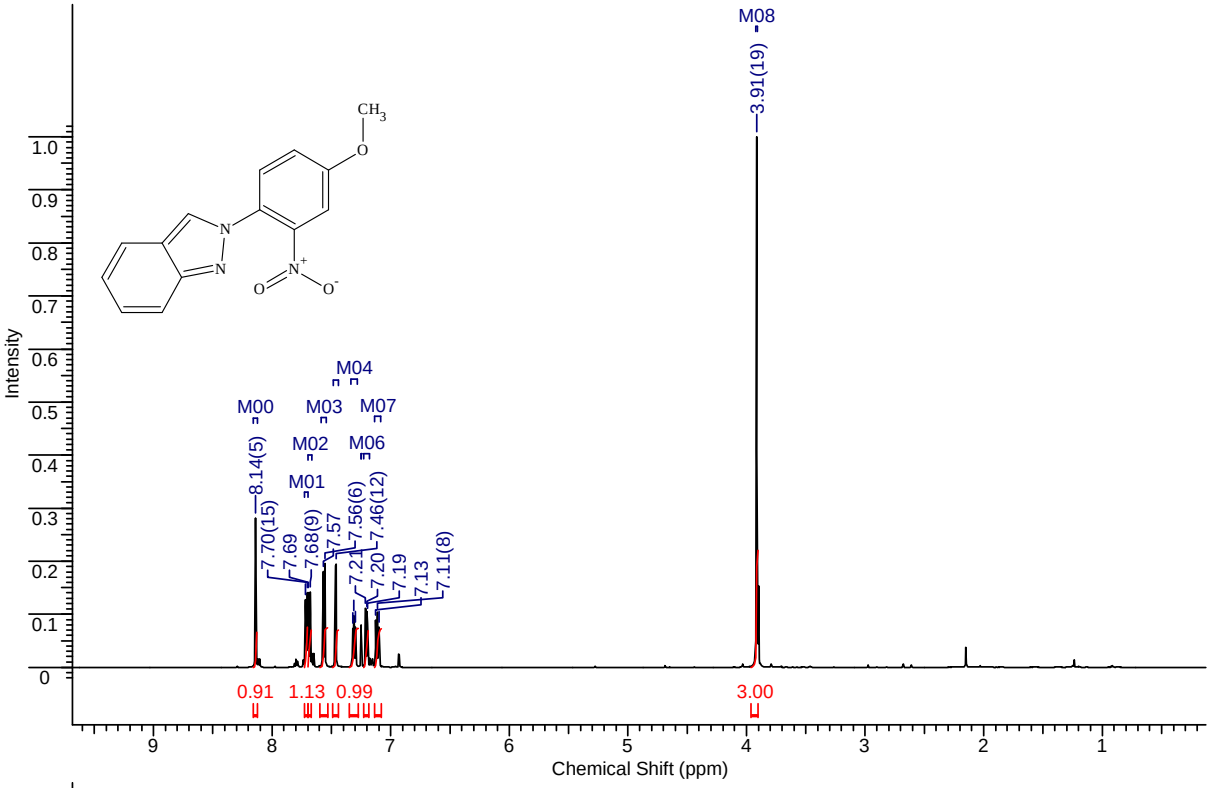


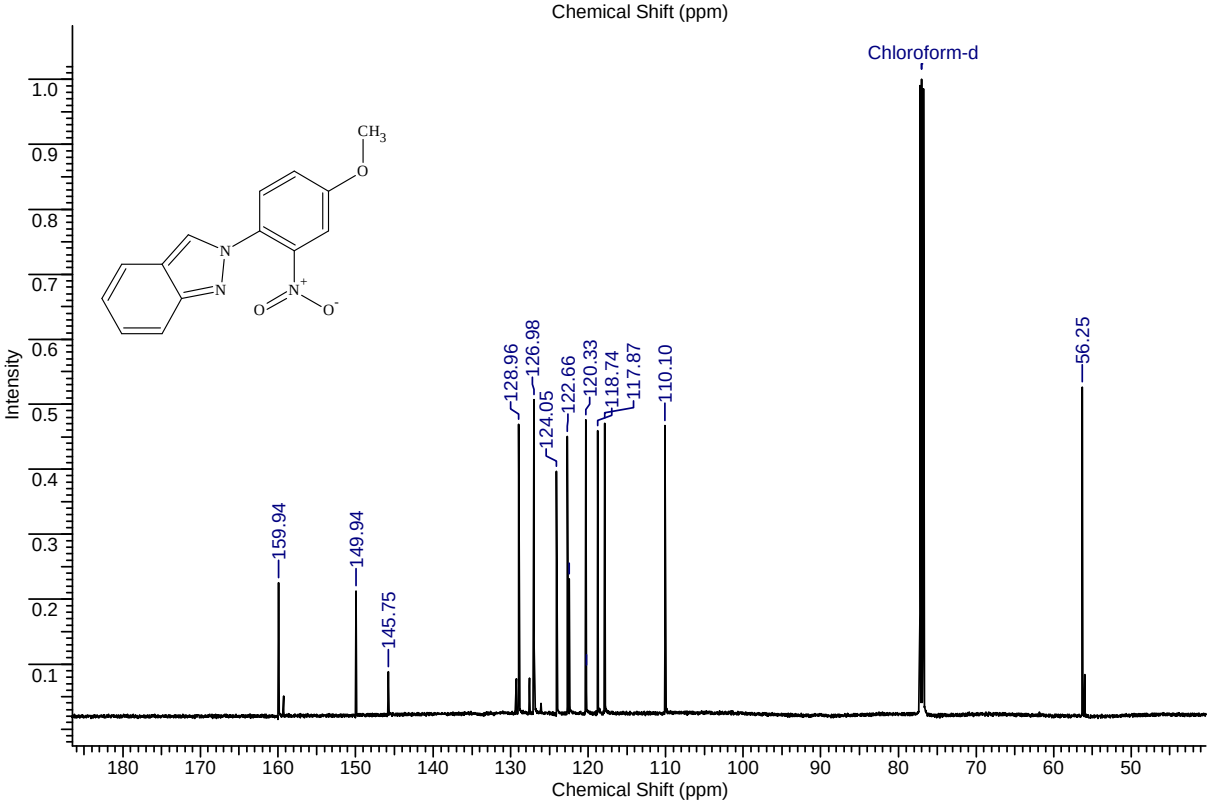


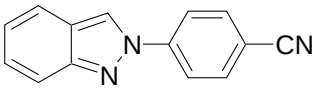
**Synthesis of 2-(4-methoxy-2-nitrophenyl)-2*H*-indazole (3e) :**

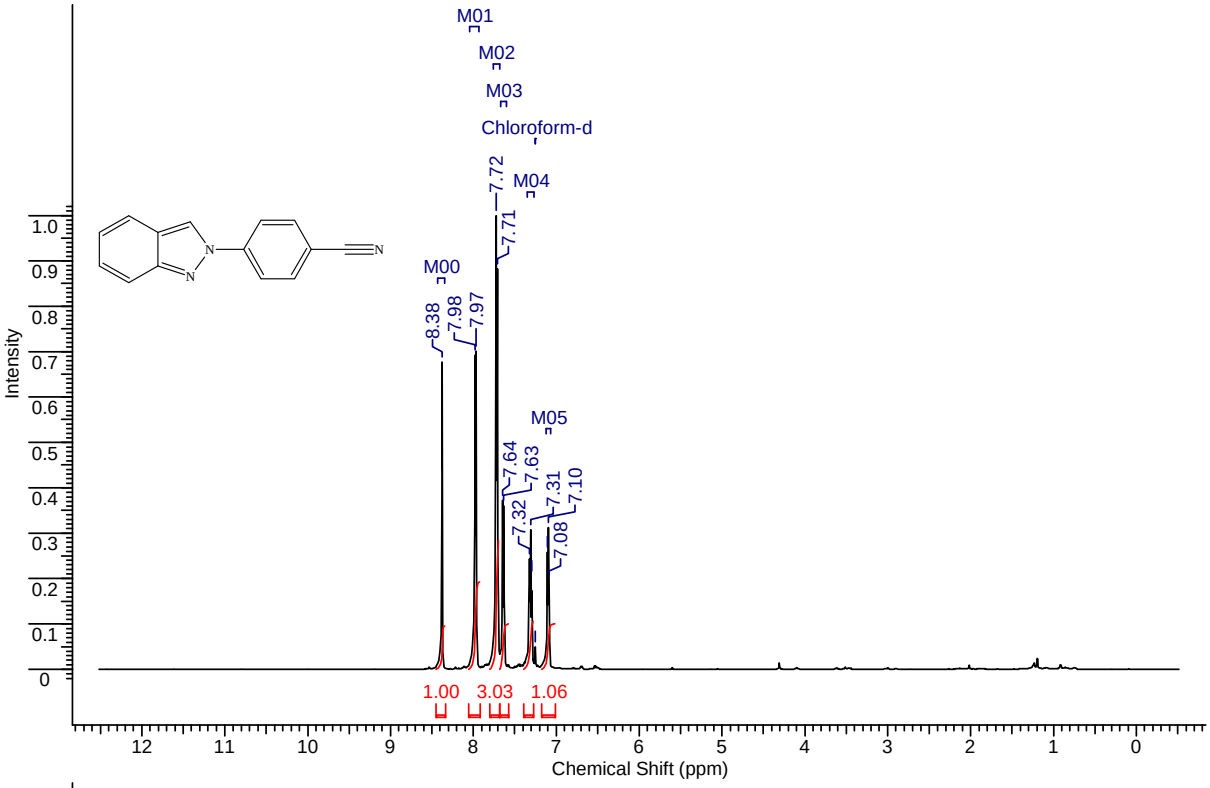


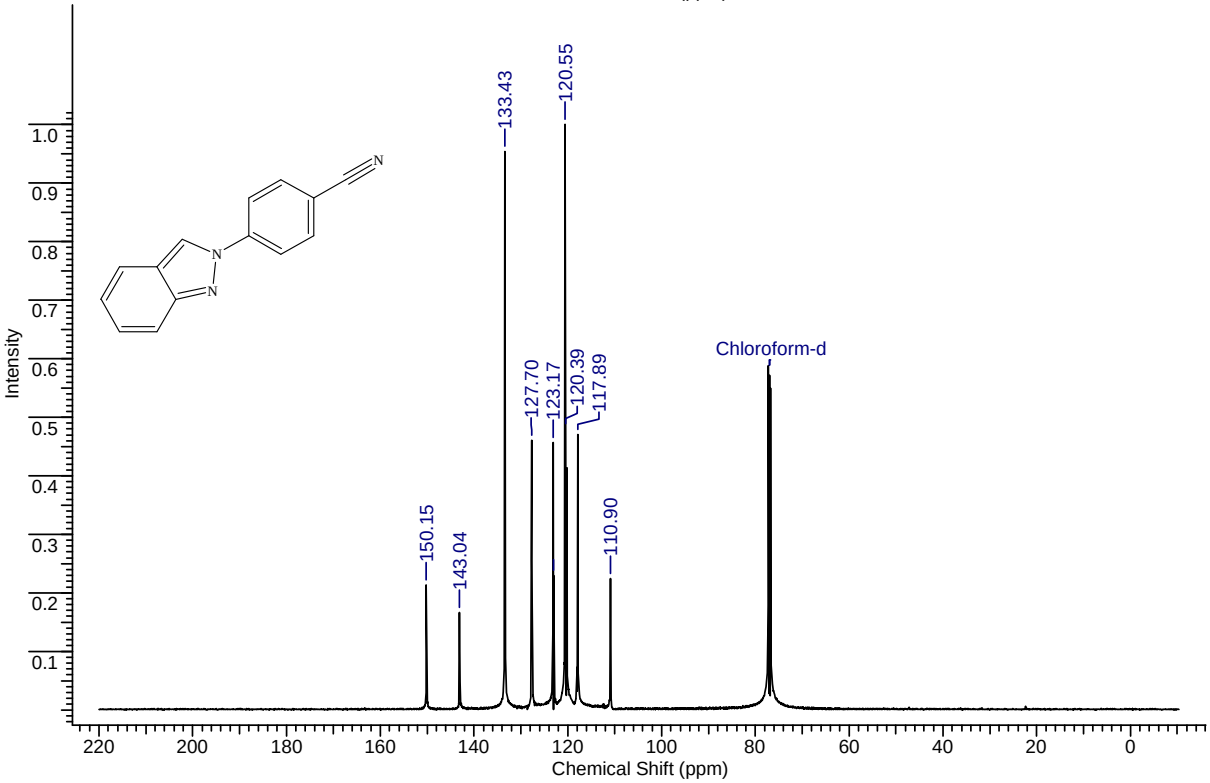



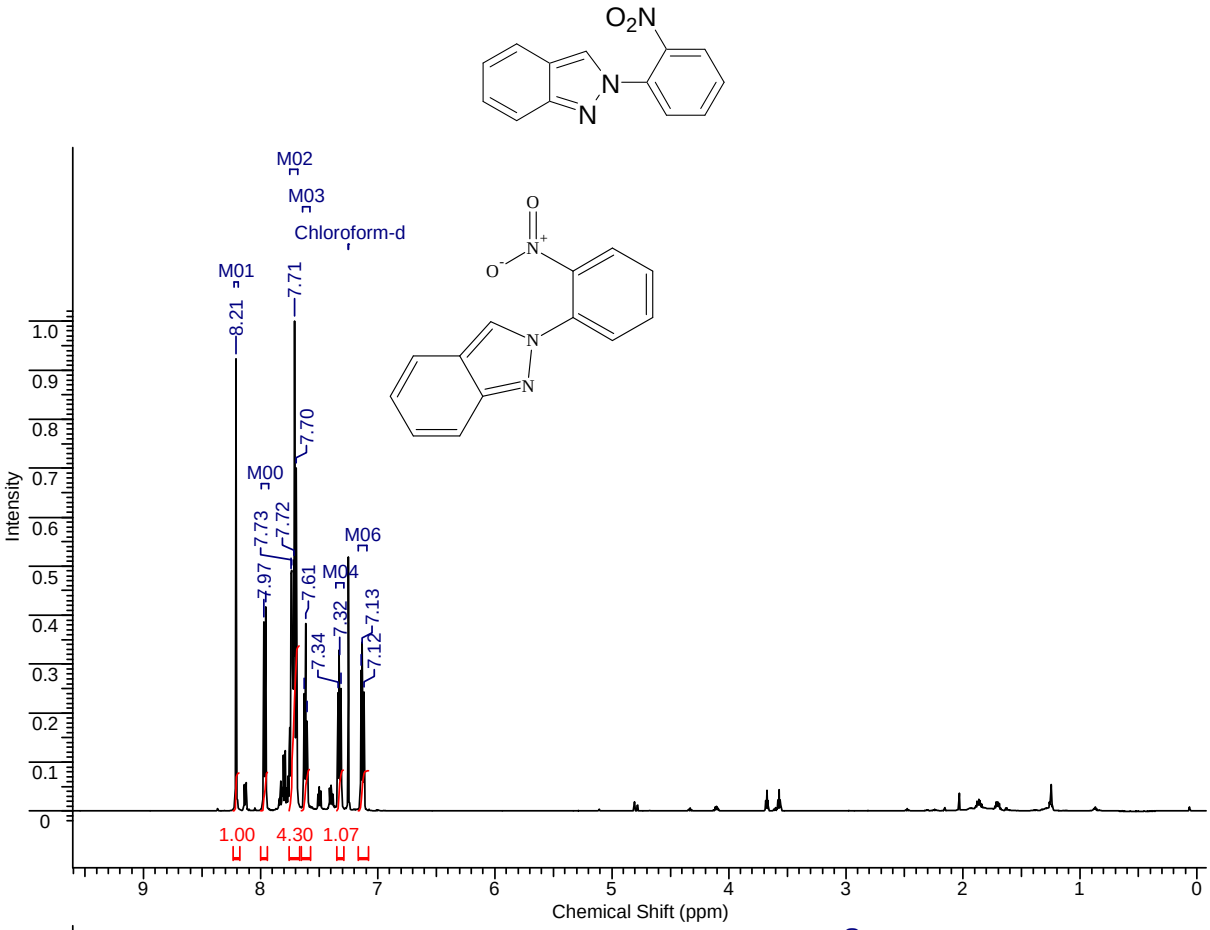
**Synthesis of 4-(2*H*-indazol-2-yl)benzonitrile (3f) :**

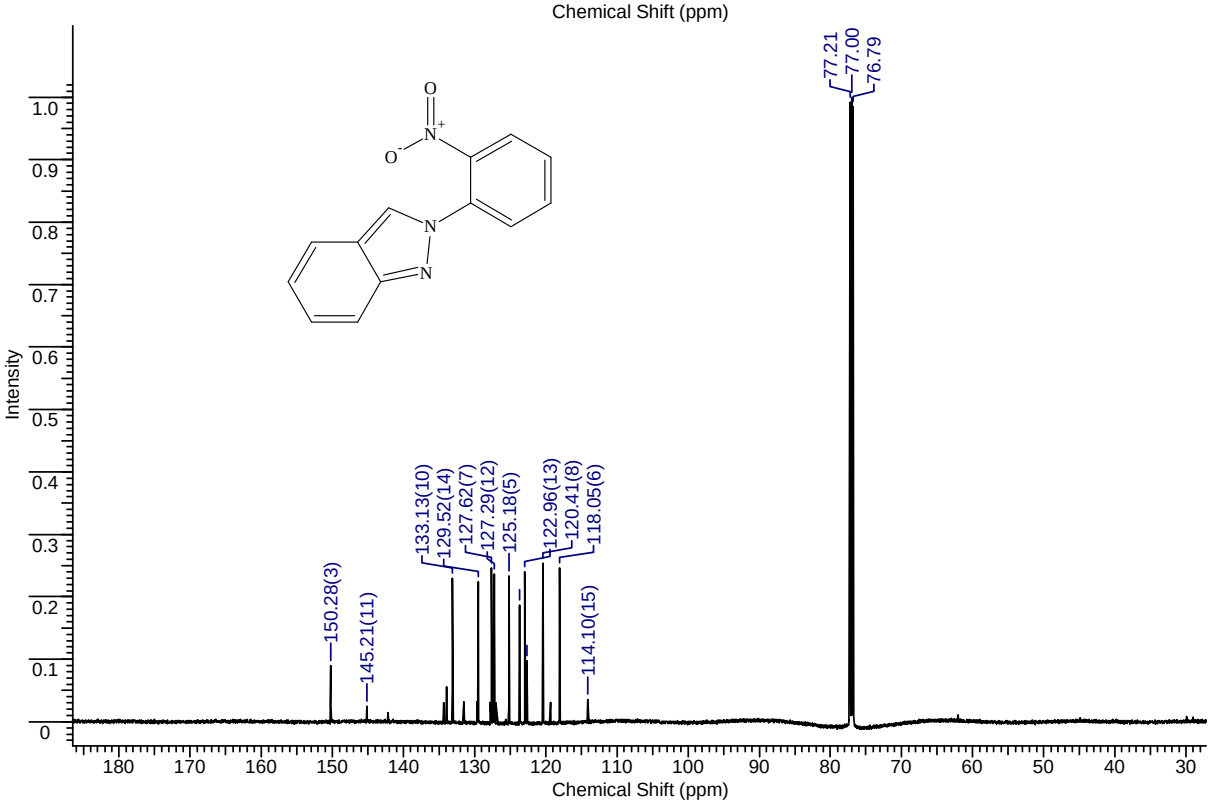


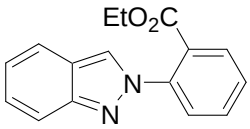



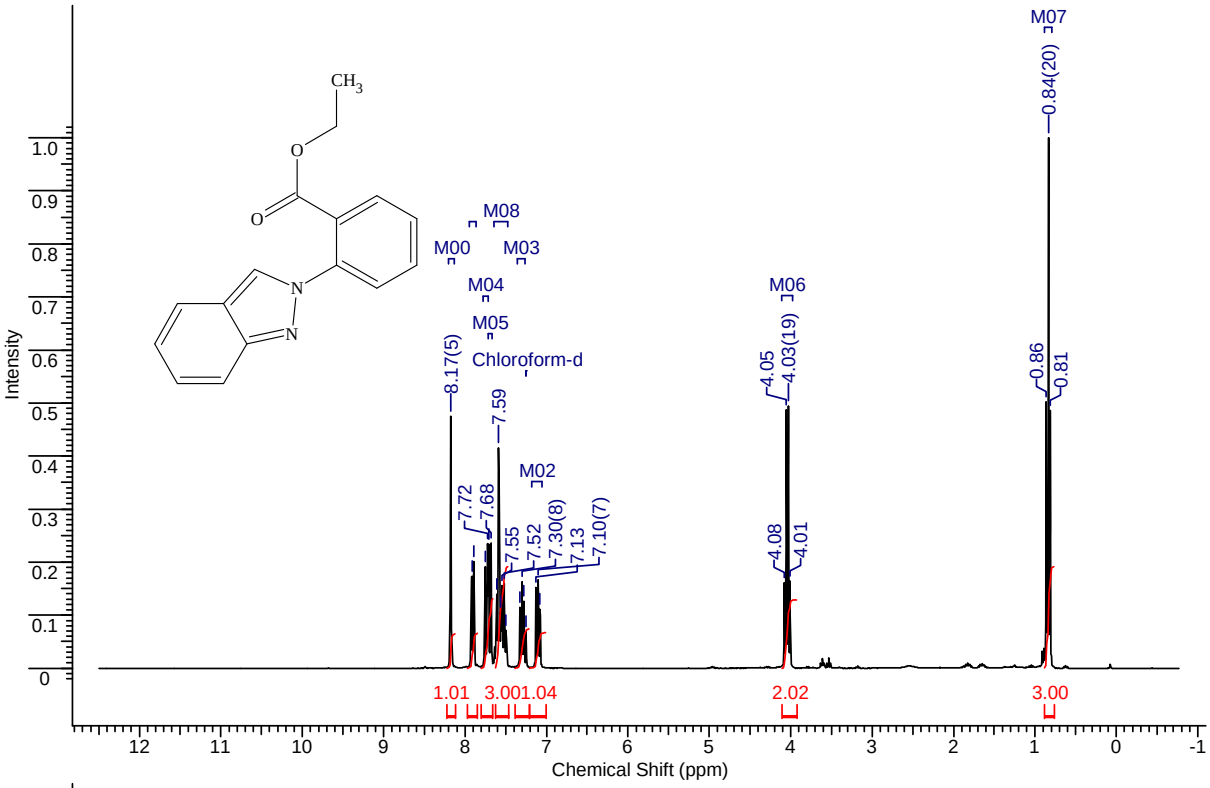
**Synthesis of 2-(2-nitrophenyl)-2*H*-indazole (3g) :**

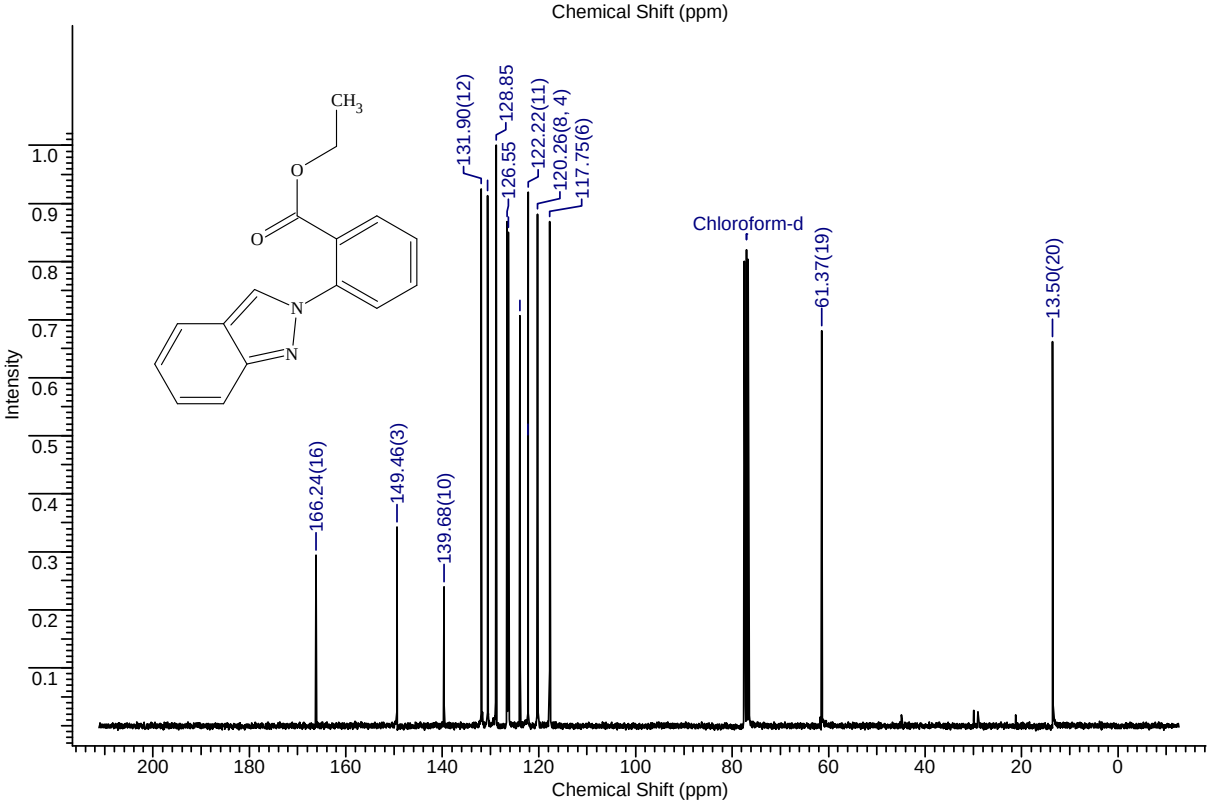


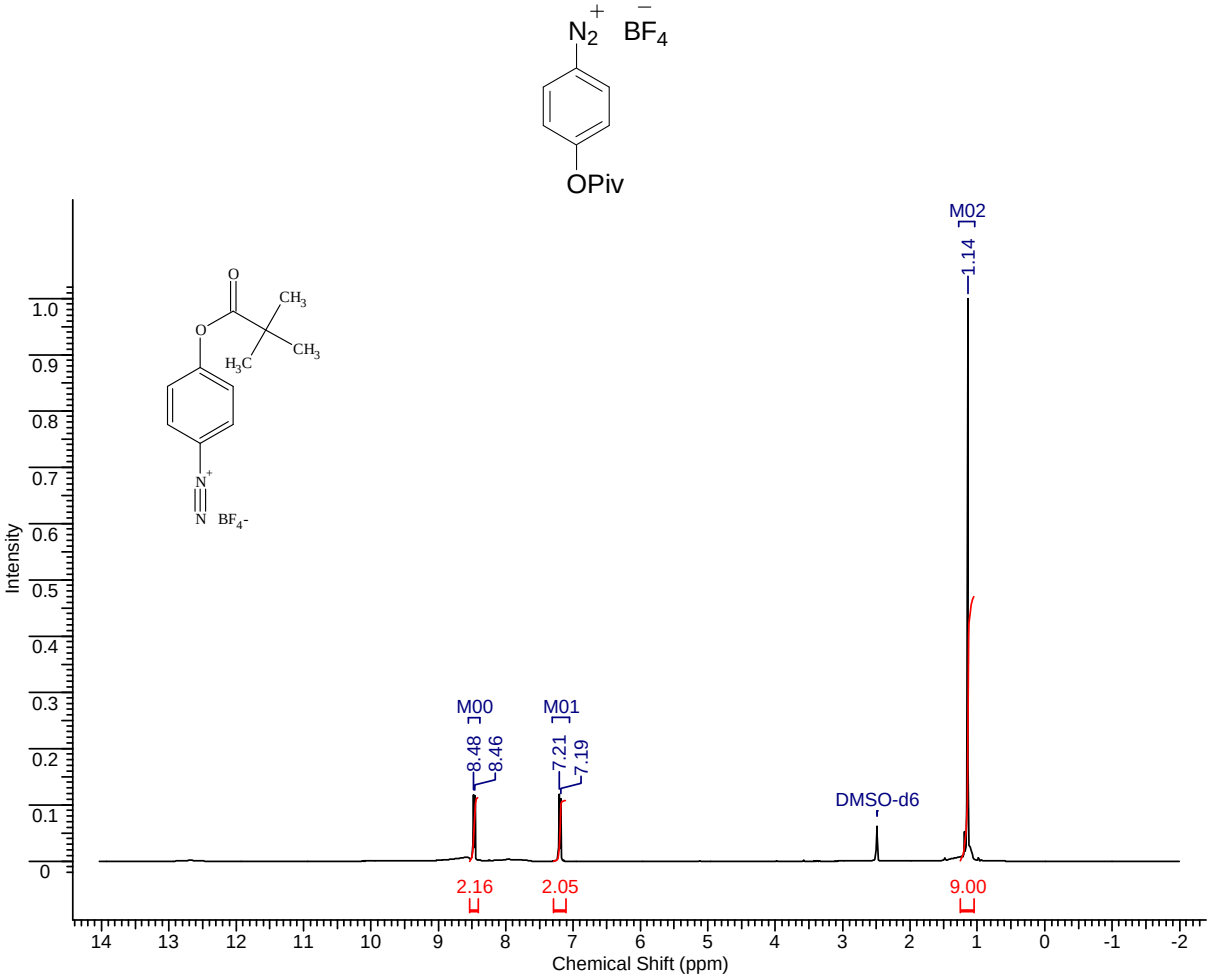
**Synthesis of ethyl 2-(2*H*-indazol-2-yl)benzoate (3h) :**

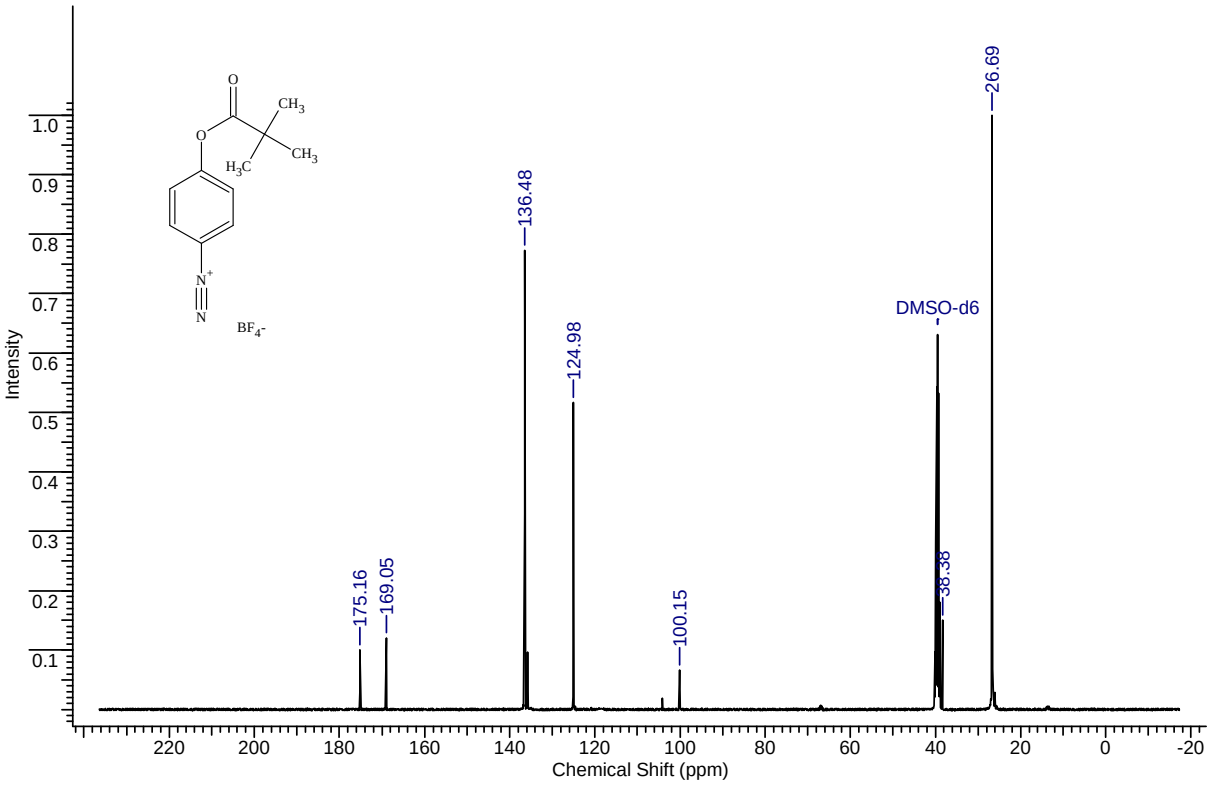


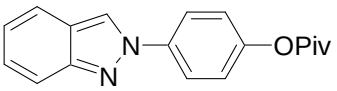



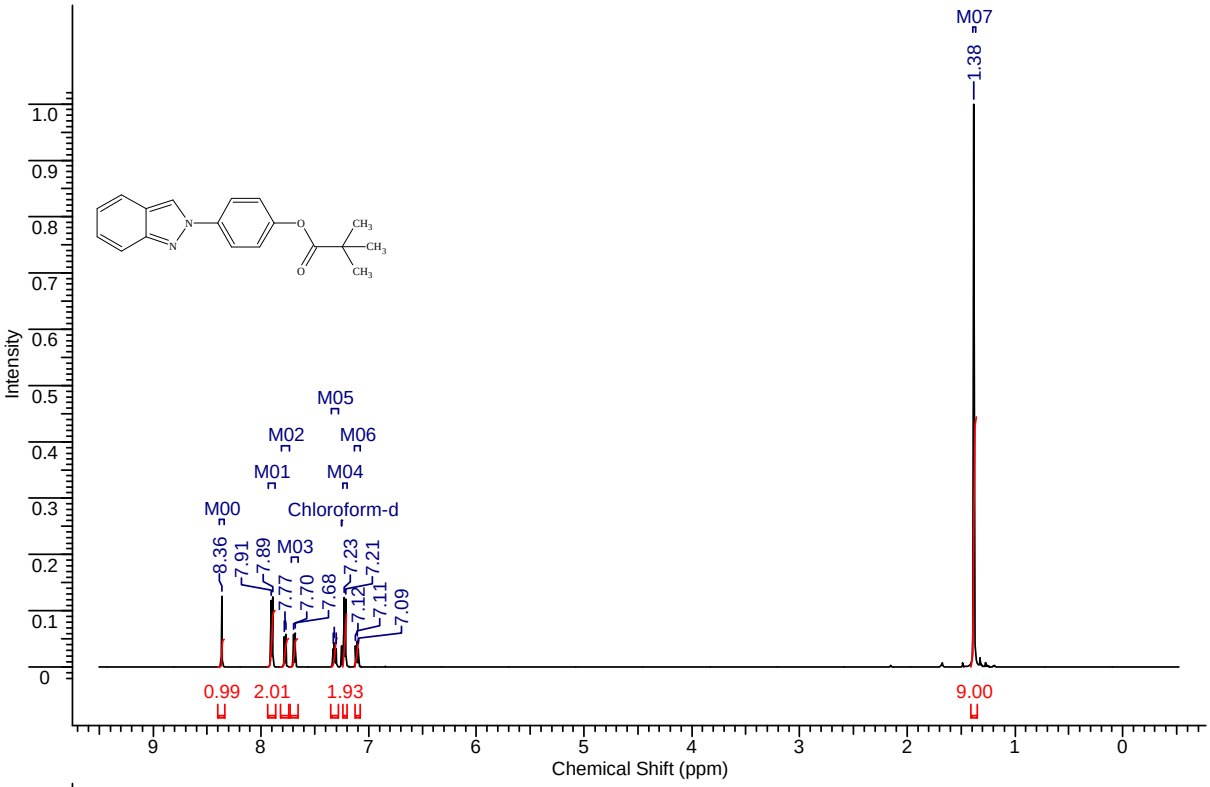
**Synthesis of 4-[(2,2-dimethylpropanoyl)oxy]benzenediazonium tetrafluoroborate (2i):**

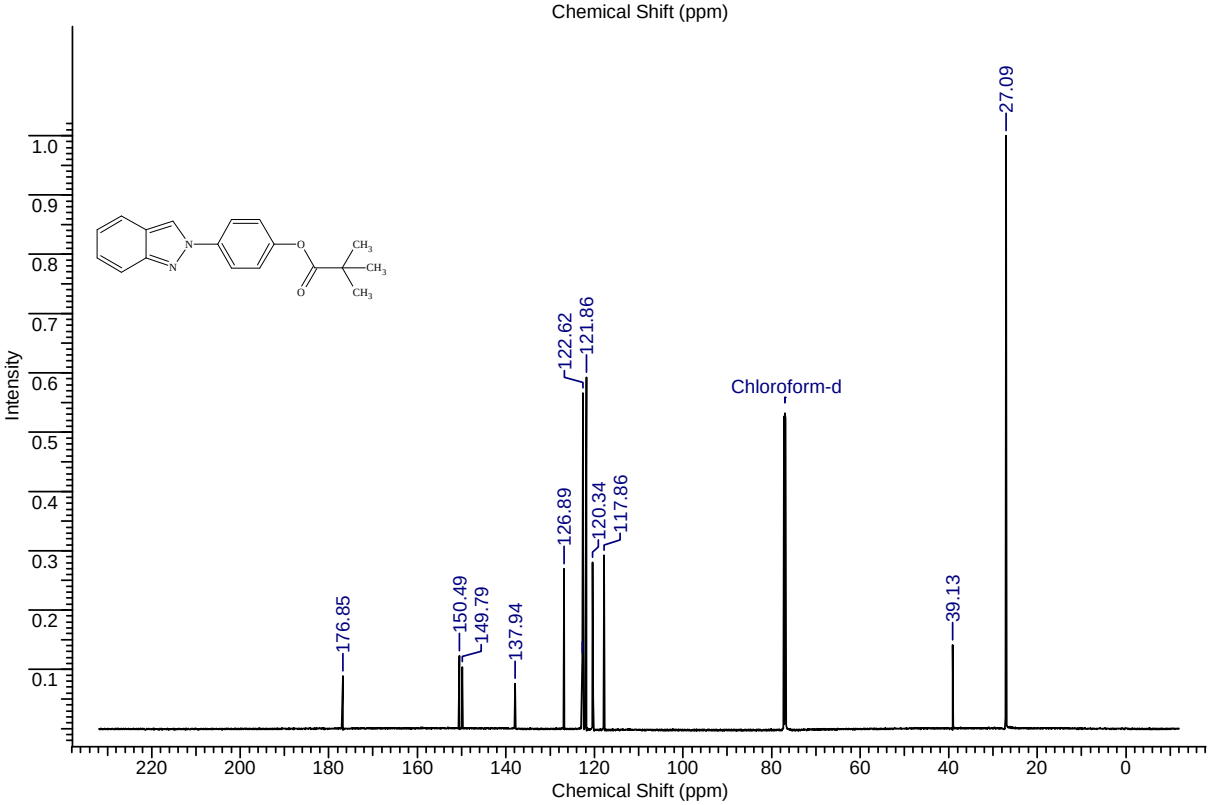


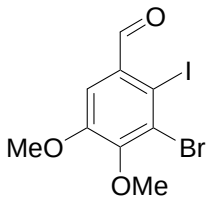
**Synthesis of 4-(2*H*-indazol-2-yl)phenyl pivalate (3i) :**

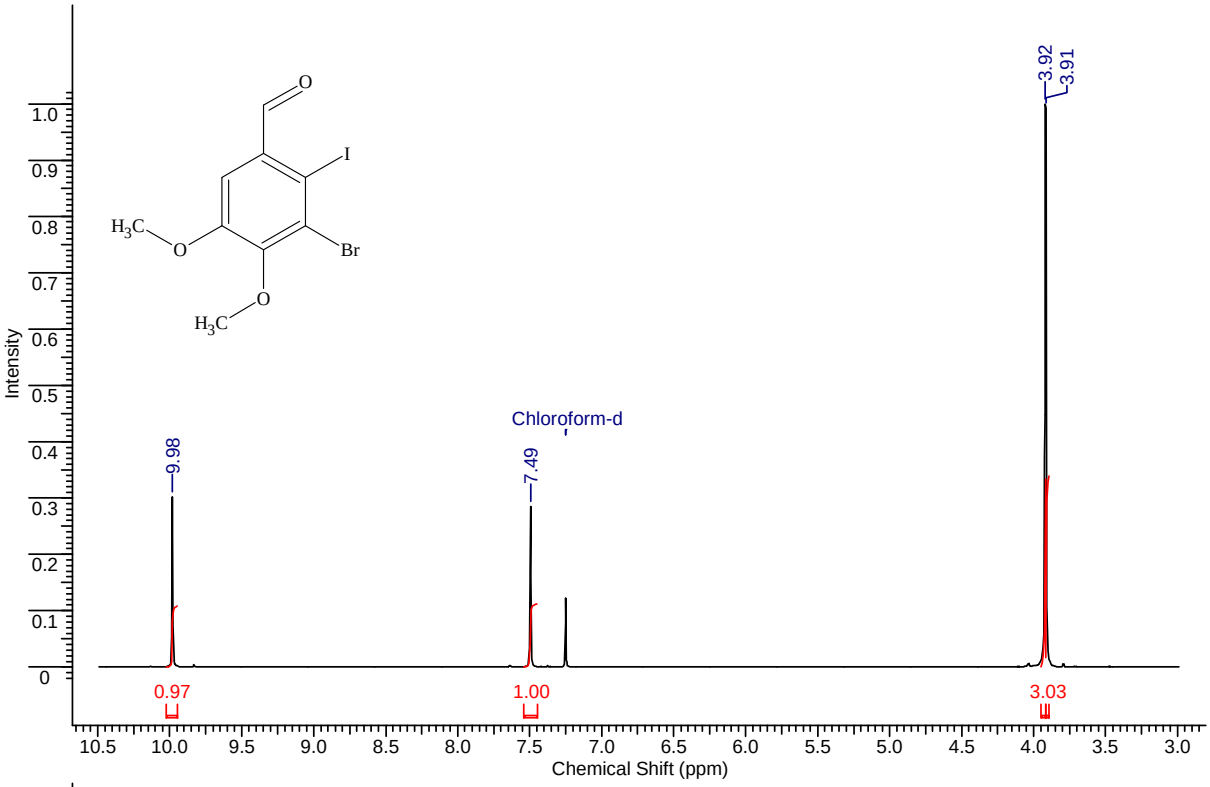


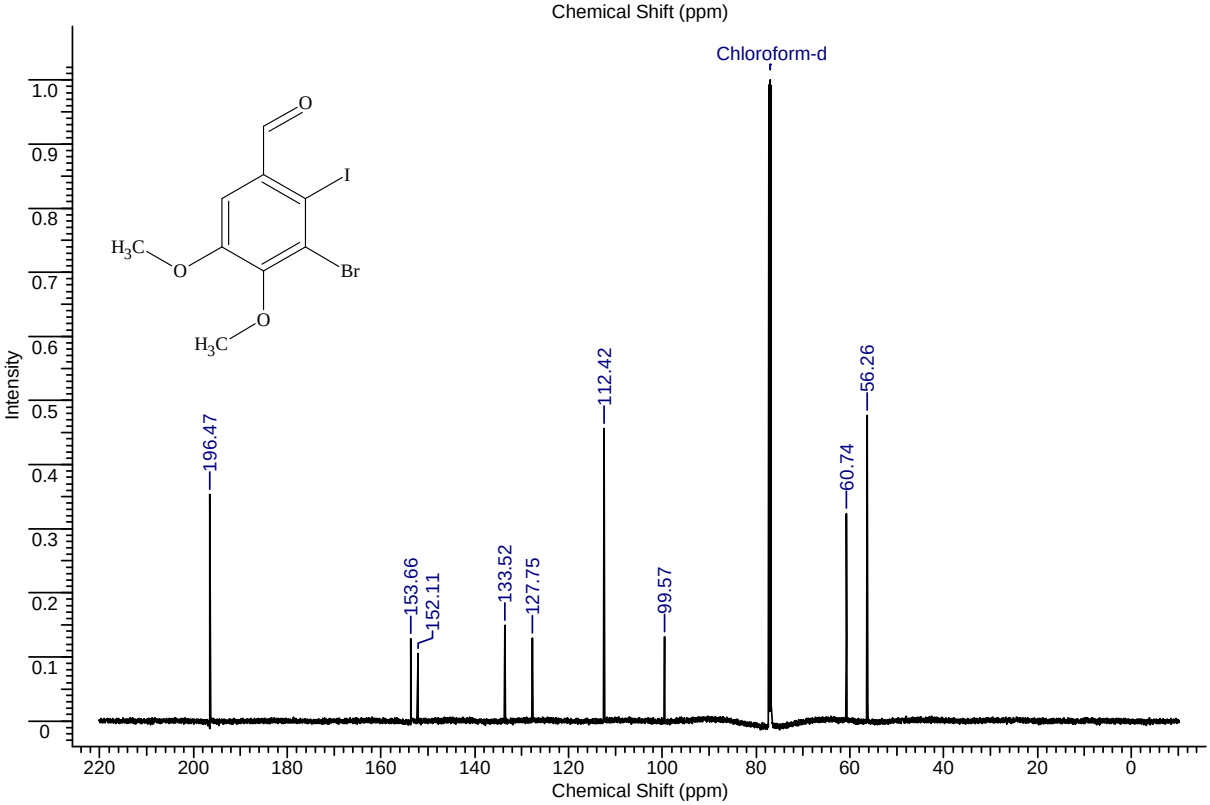



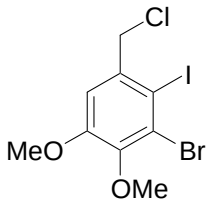
**Synthesis of 3-bromo-2-iodo-4,5-dimethoxybenzaldehyde:**

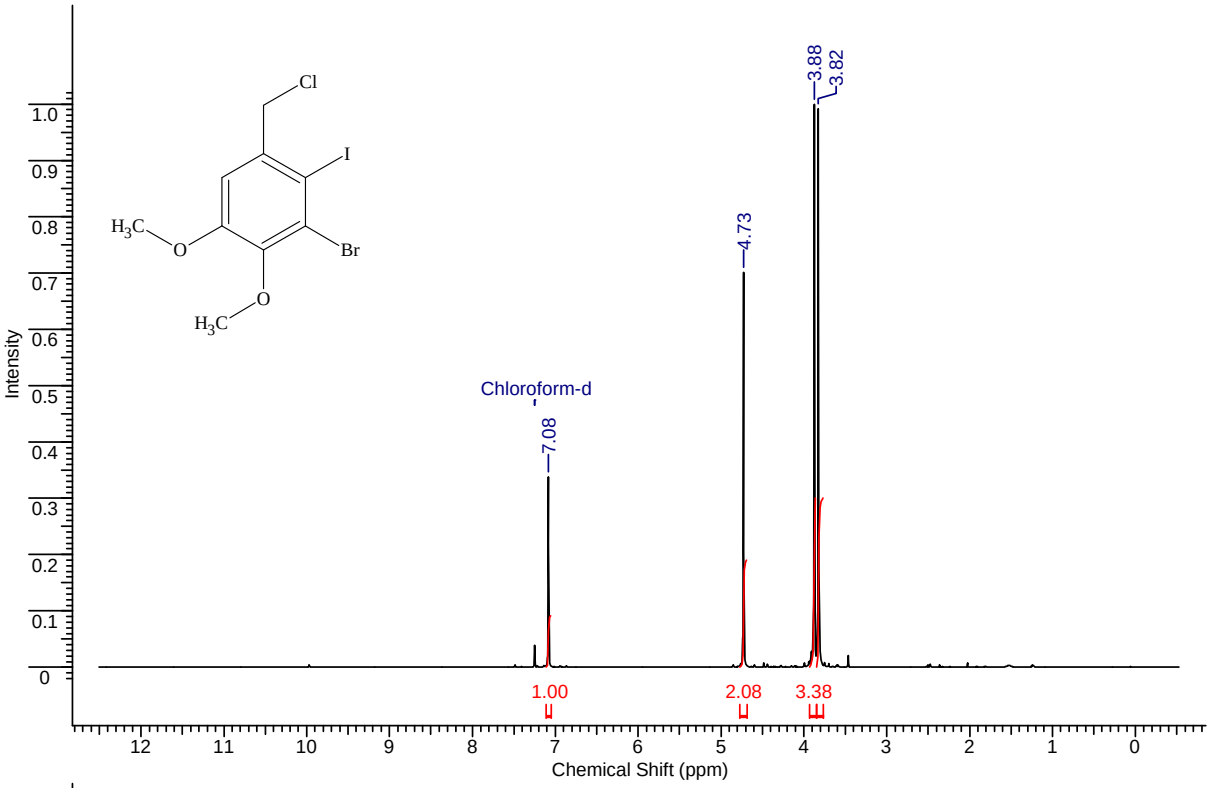


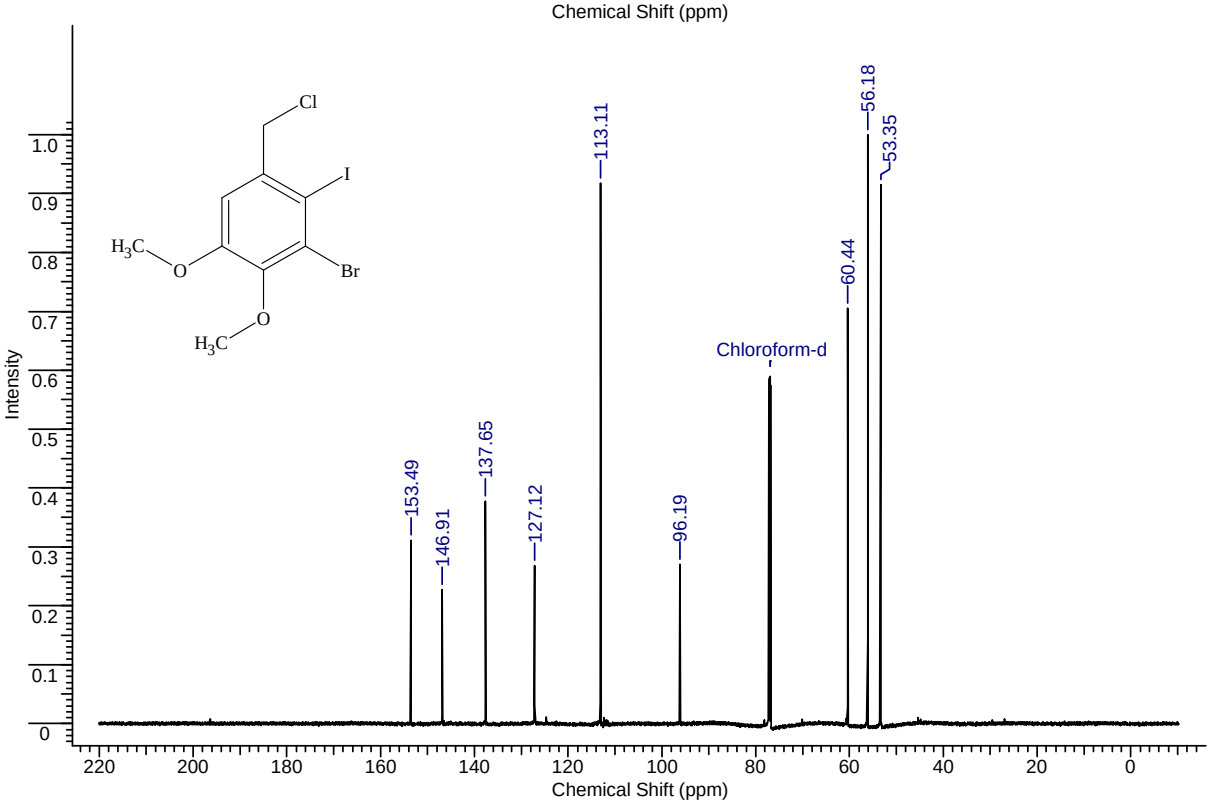



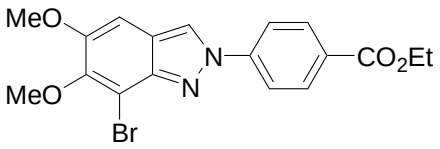
**Synthesis of 3-bromo-1-(chloromethyl)-2-iodo-4,5-dimethoxybenzene :**

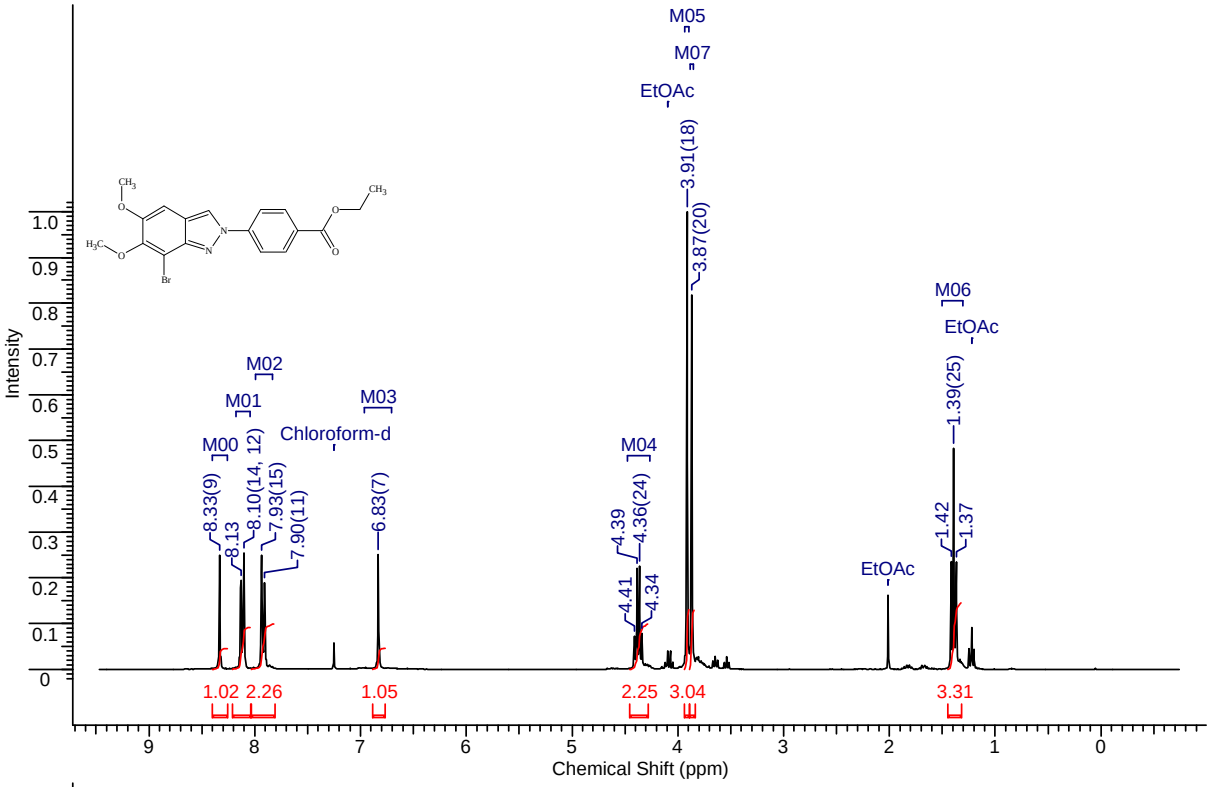


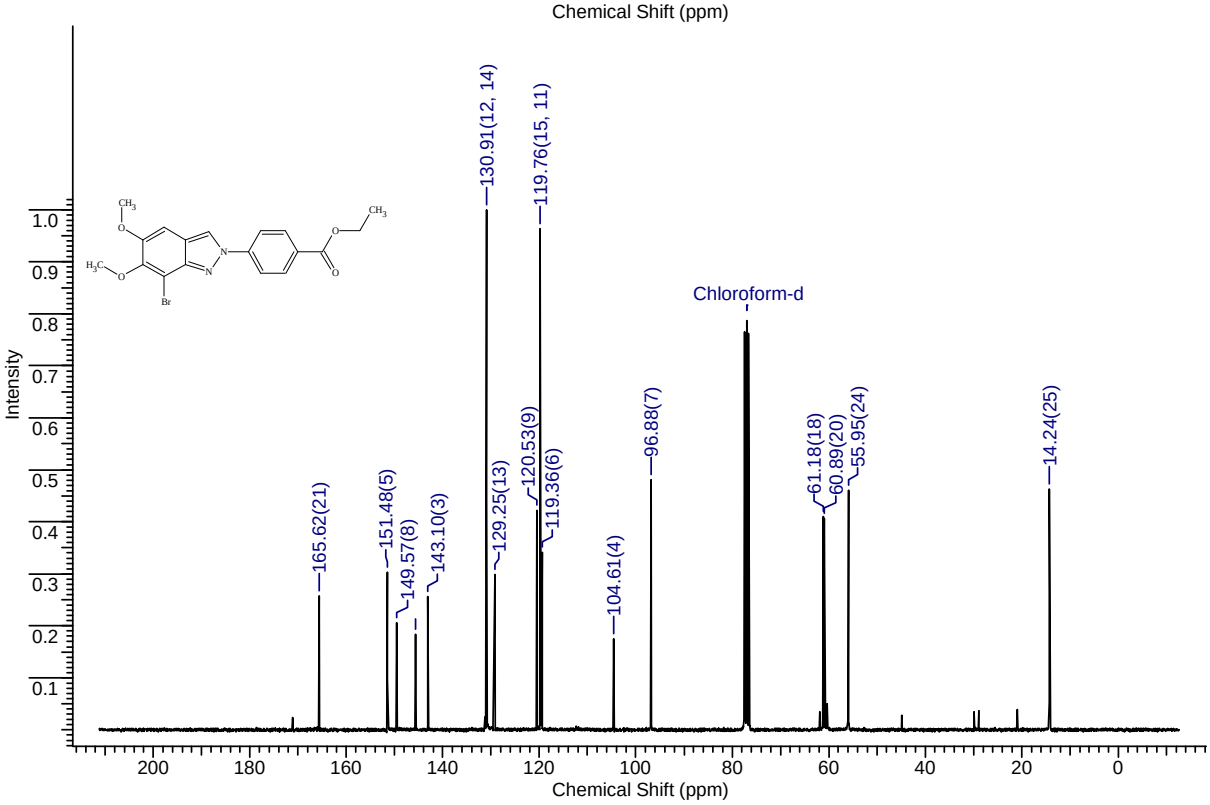



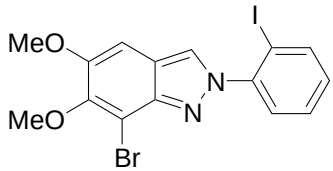
**Synthesis of ethyl 4-(7-bromo-5,6-dimethoxy-2*H*-indazol-2-yl)benzoate (3j) :**

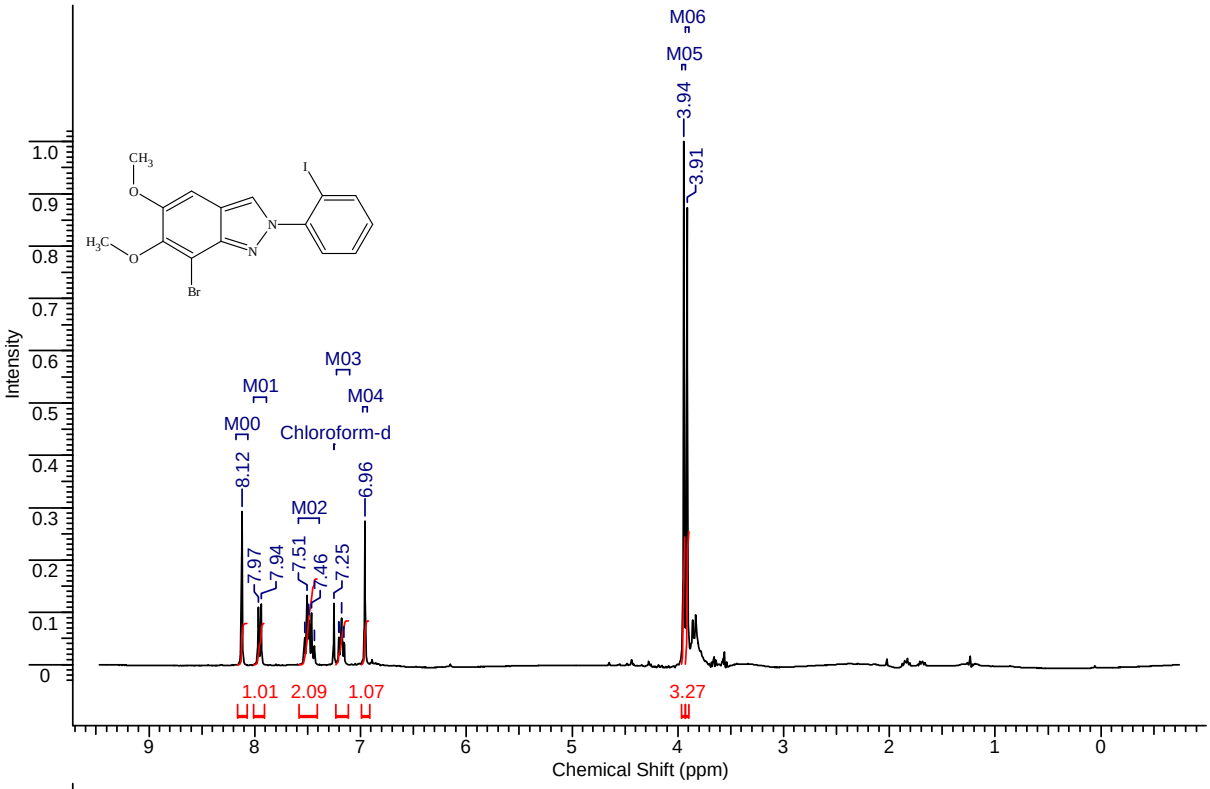


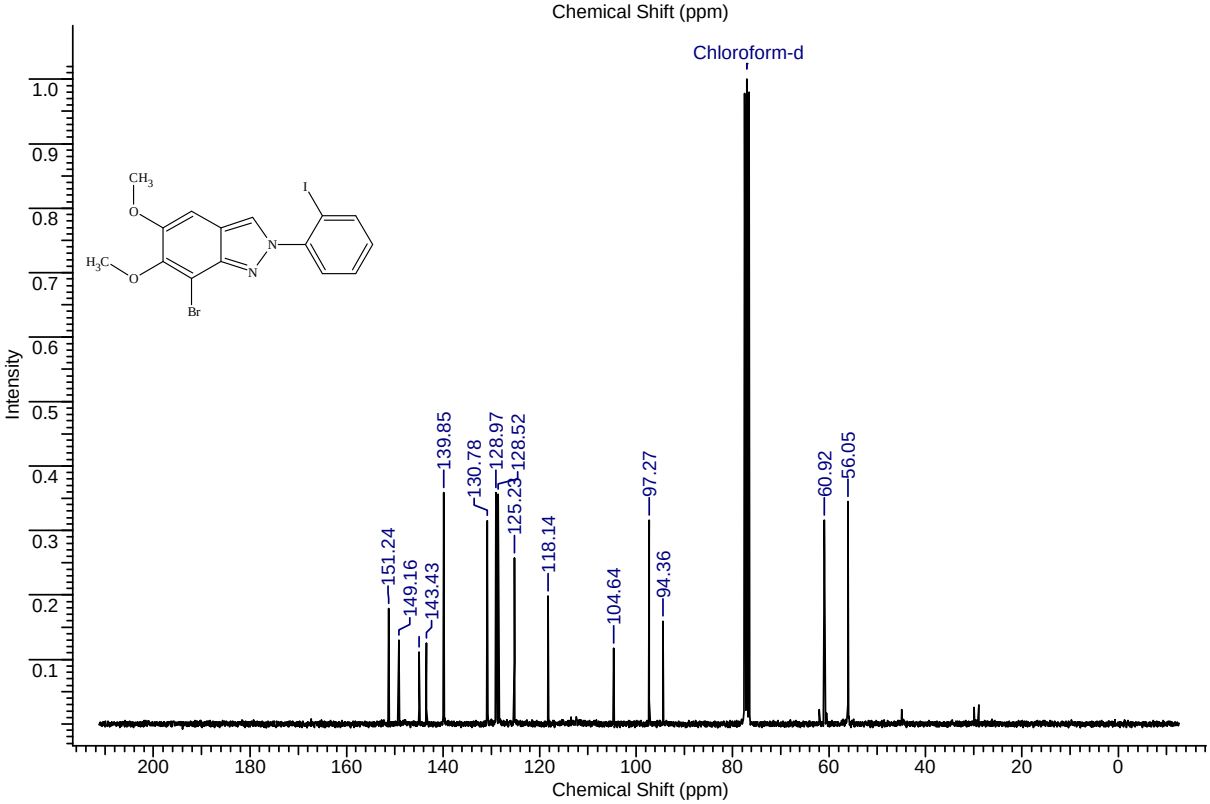



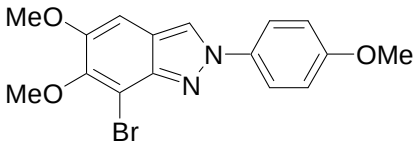
**Synthesis of 7-bromo-2-(2-iodophenyl)-5,6-dimethoxy-2*H*-indazole (3k) :**

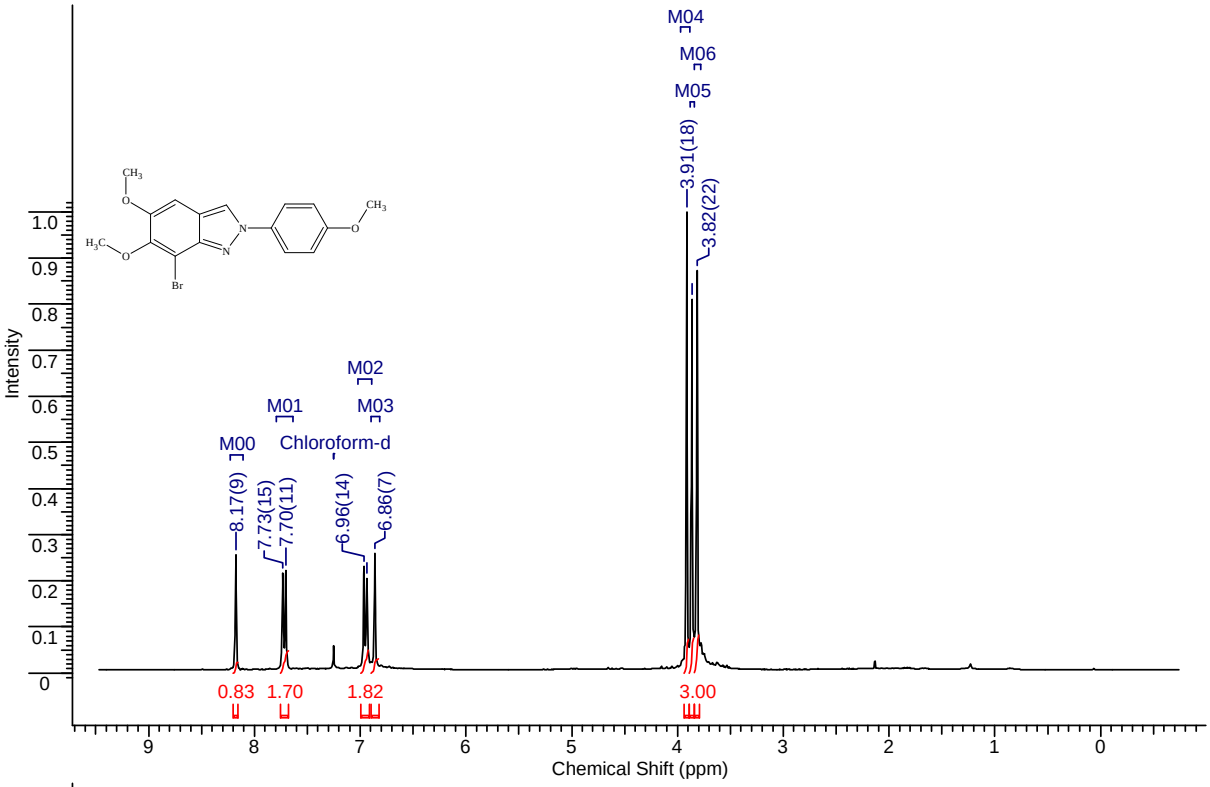


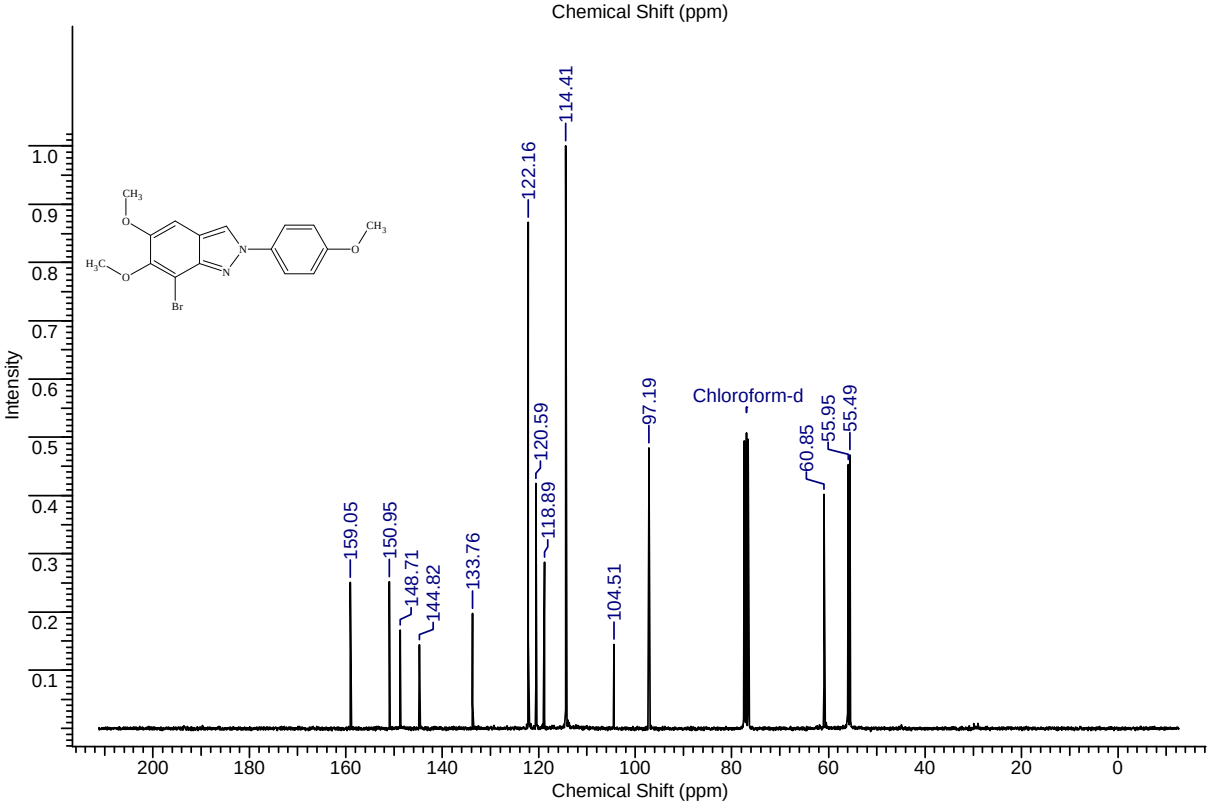



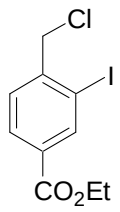
**Synthesis of 7-bromo-5,6-dimethoxy-2-(4-methoxyphenyl)-2*H*-indazole (3l) :**

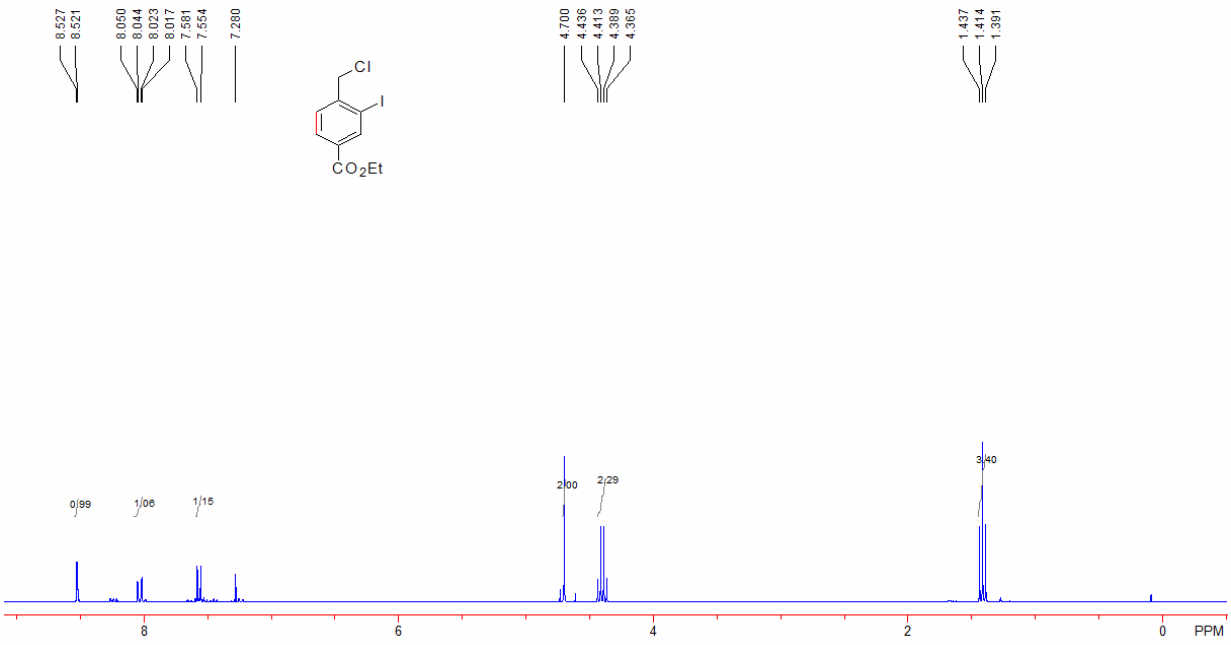


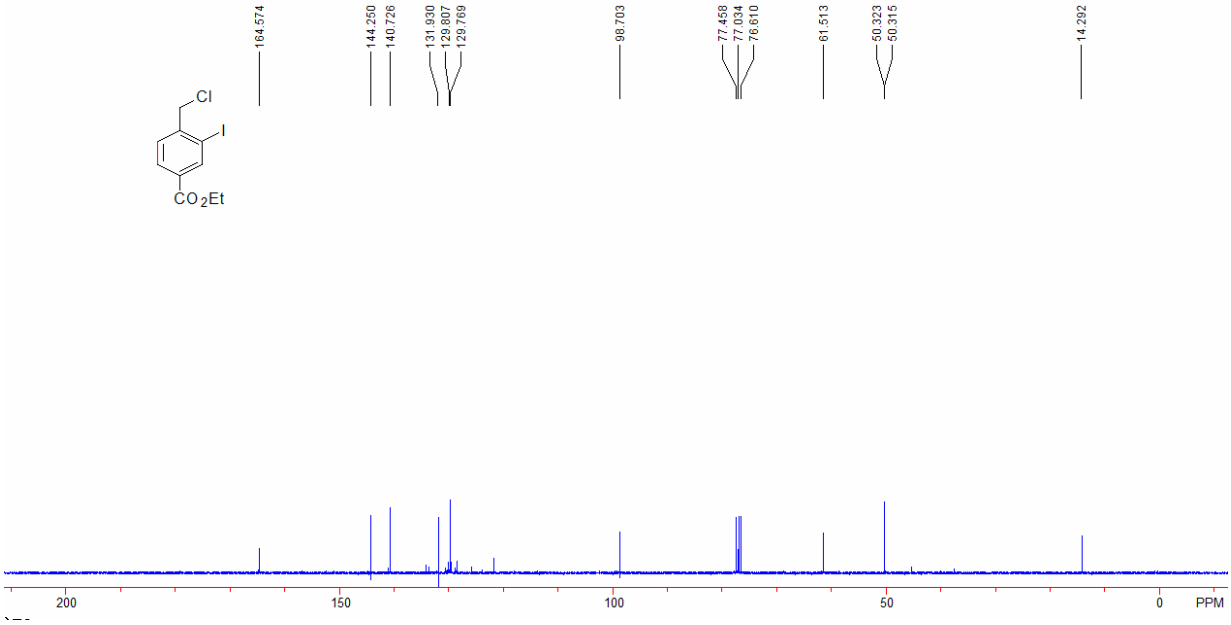



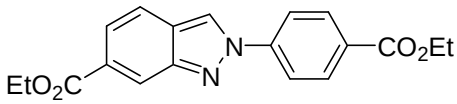
**Synthesis of 4-chloromethyl-3-iodo-benzoic acid ethyl ester :**

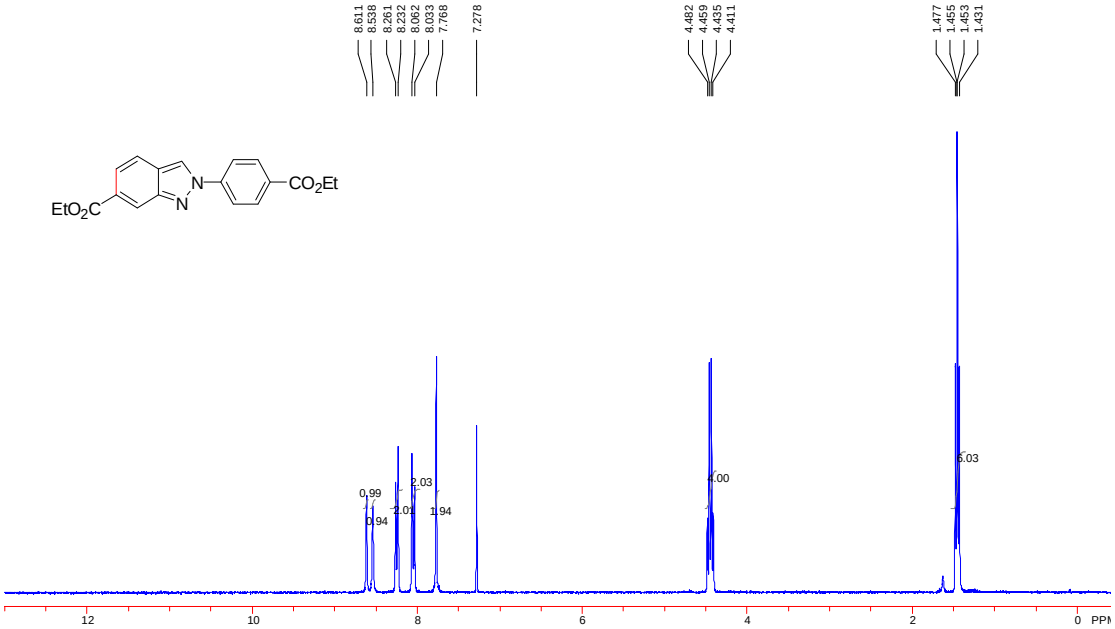


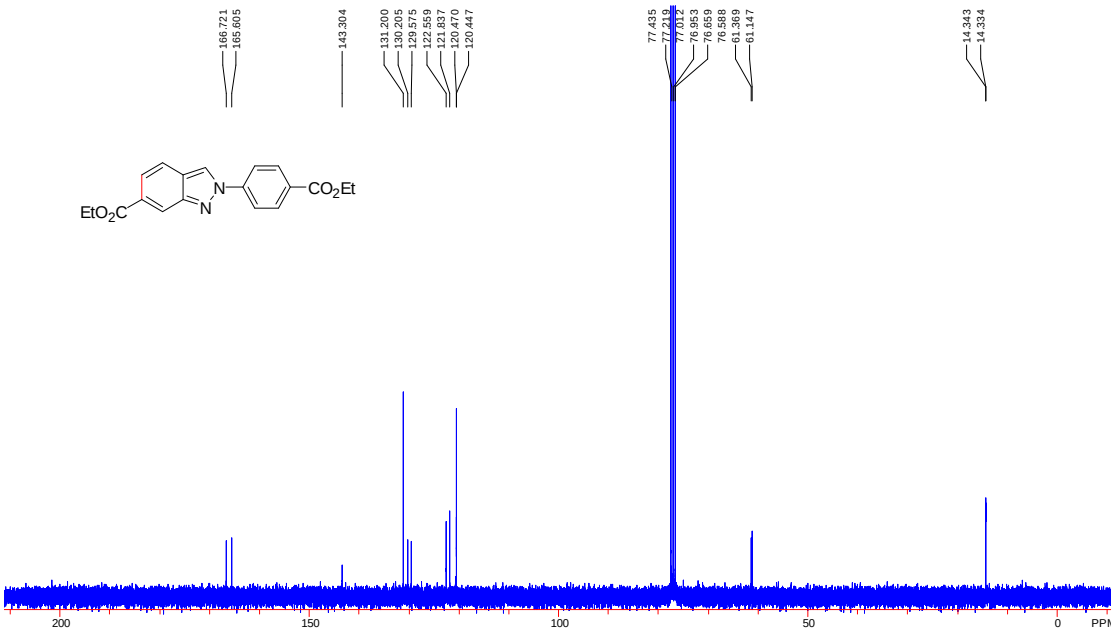



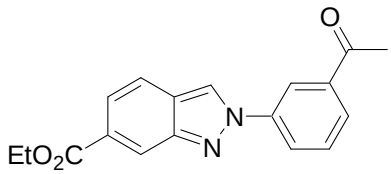
**Synthesis of 2-(4-ethoxycarbonyl-phenyl)-2*H*-indazole-6-carboxylic acid ethyl ester (3m)**:

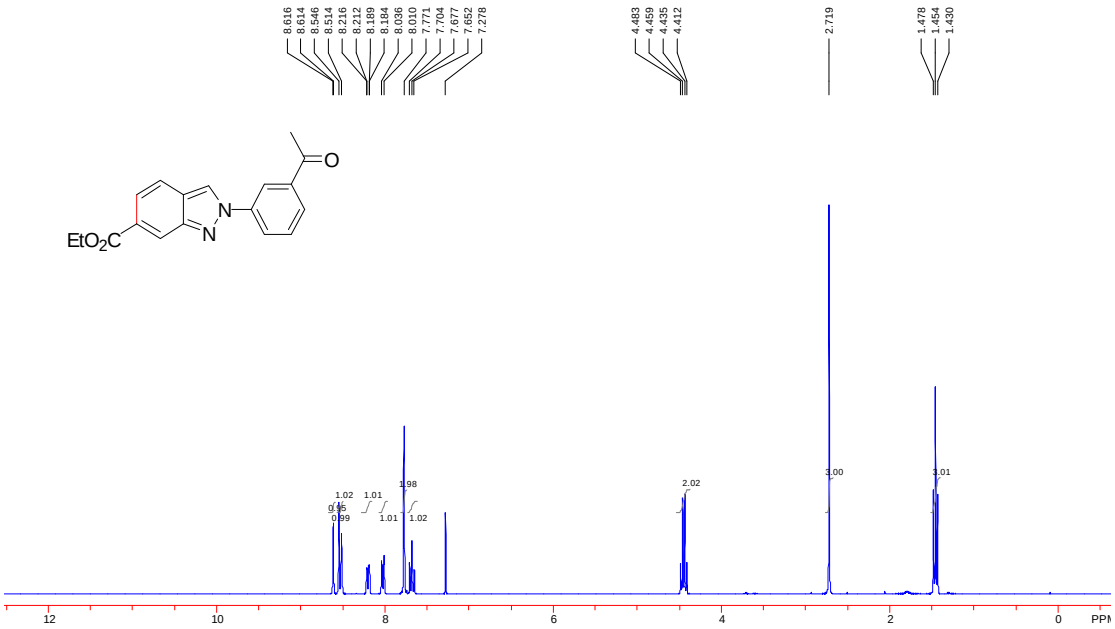


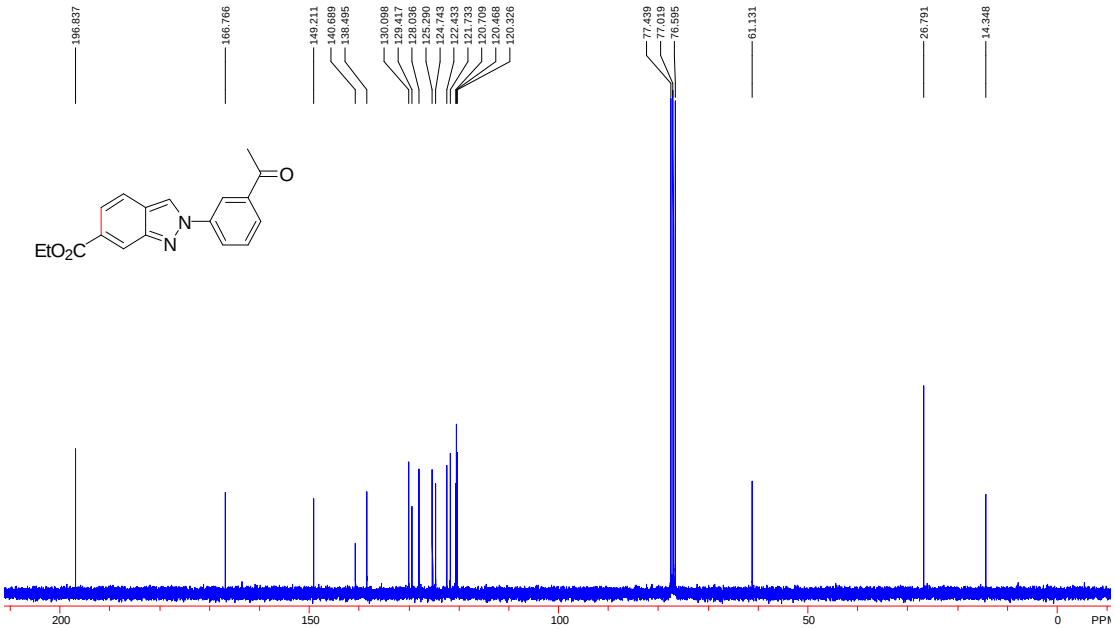



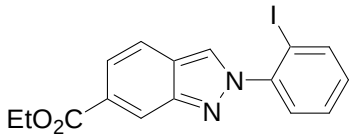
**Synthesis of 2-(3-acetylphenyl)-2*H*-indazole-6-carboxylic acid ethyl ester (3n) :**

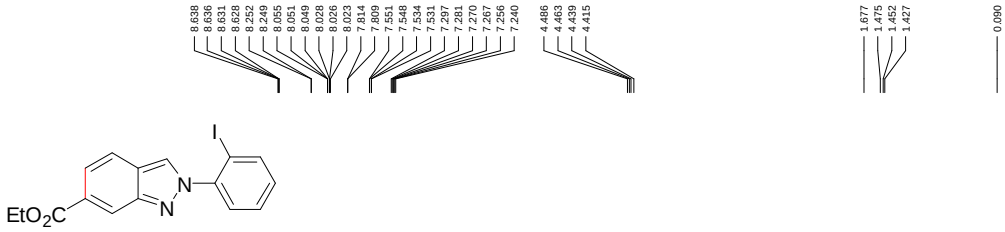


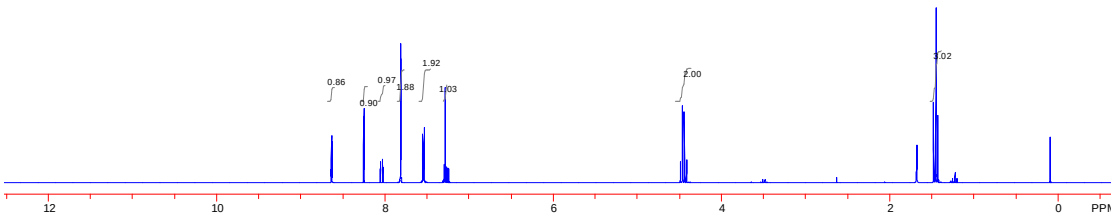



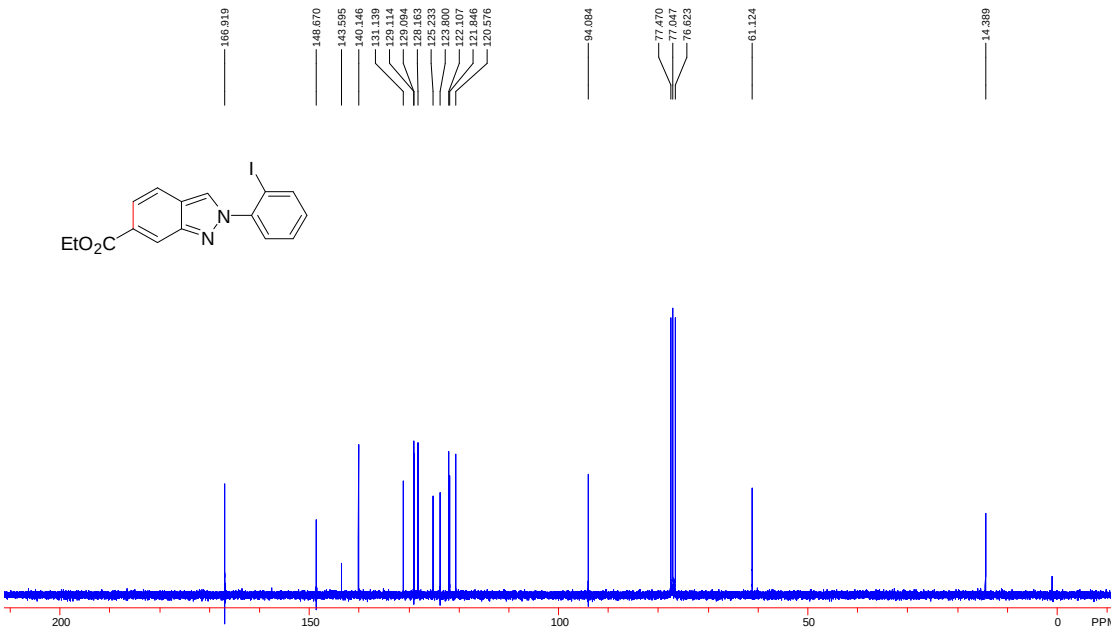



**Synthesis of 2-(2-iodophenyl)-2*H*-indazole-6-carboxylic acid ethyl ester (3o) :**

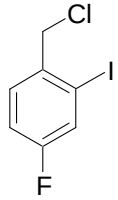


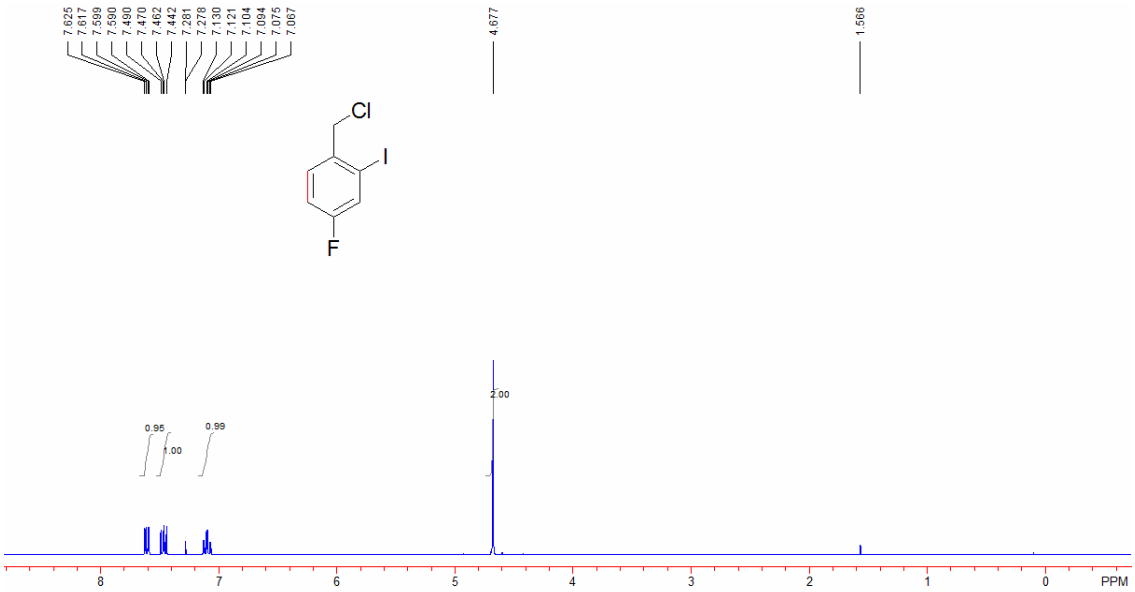



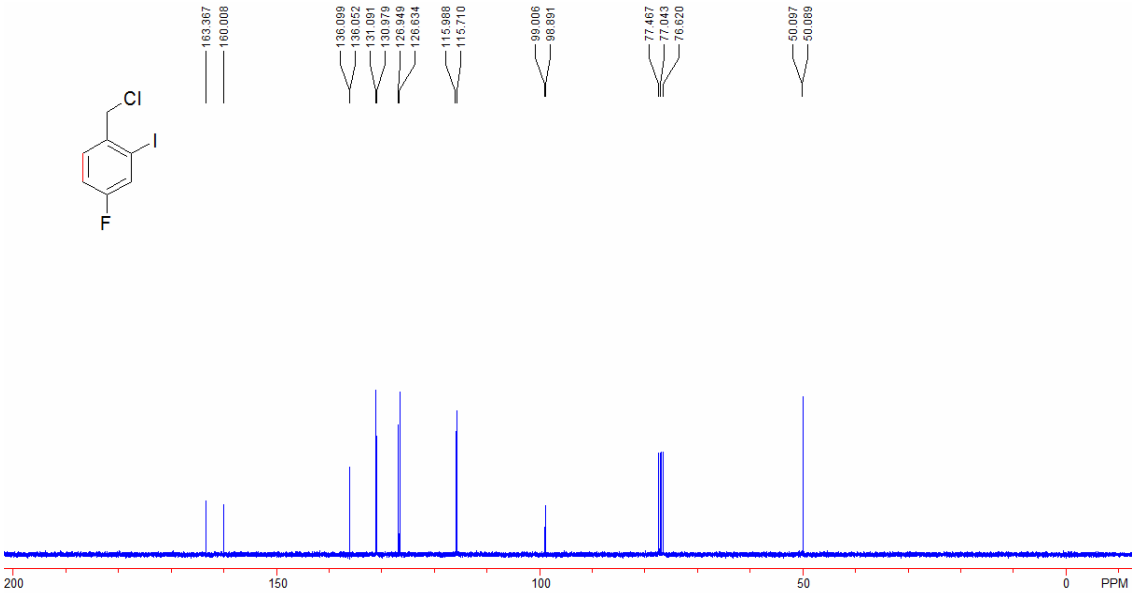



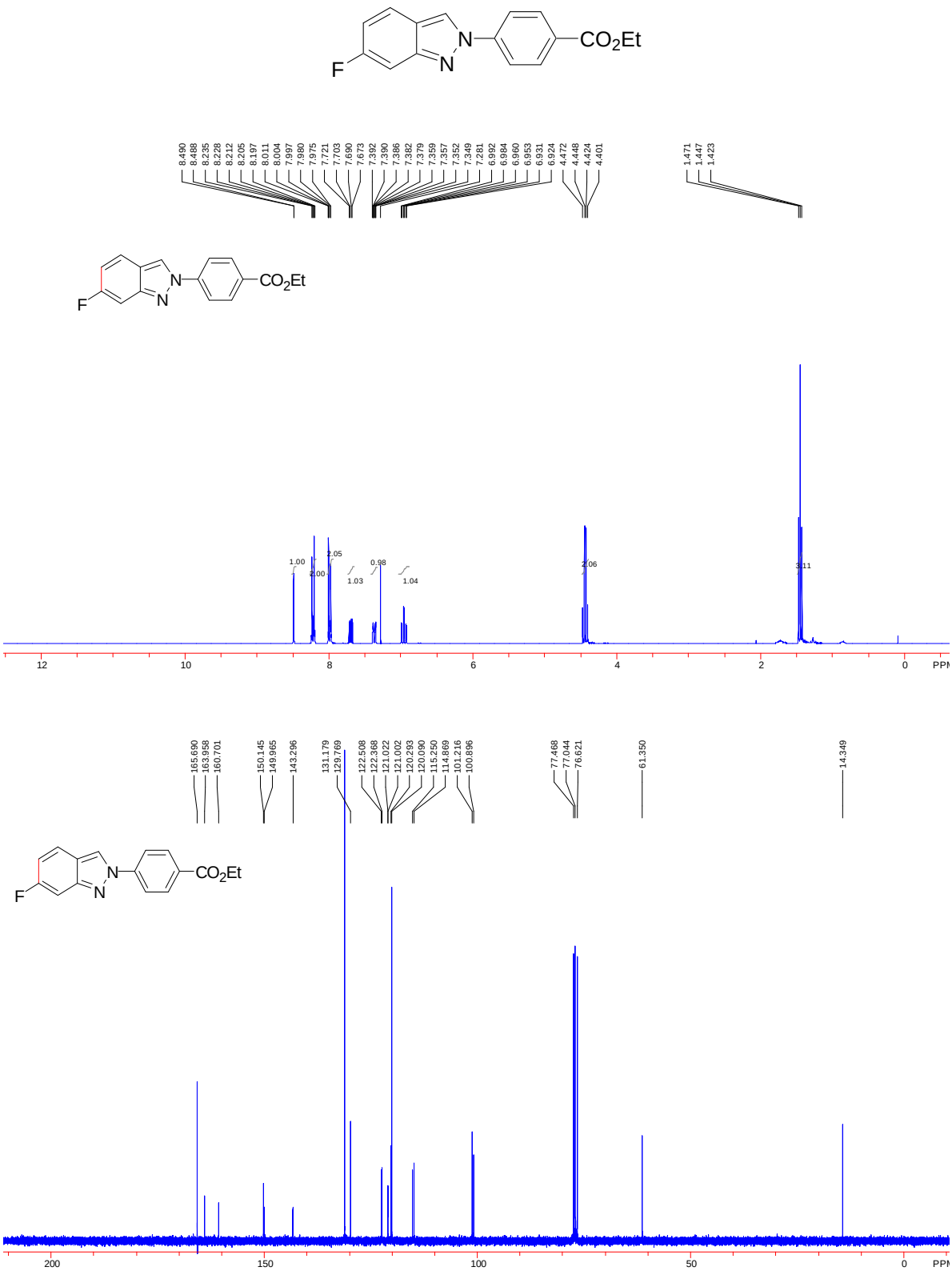
**Synthesis of 1-chloromethyl-4-fluoro-2-iodo-benzene** :



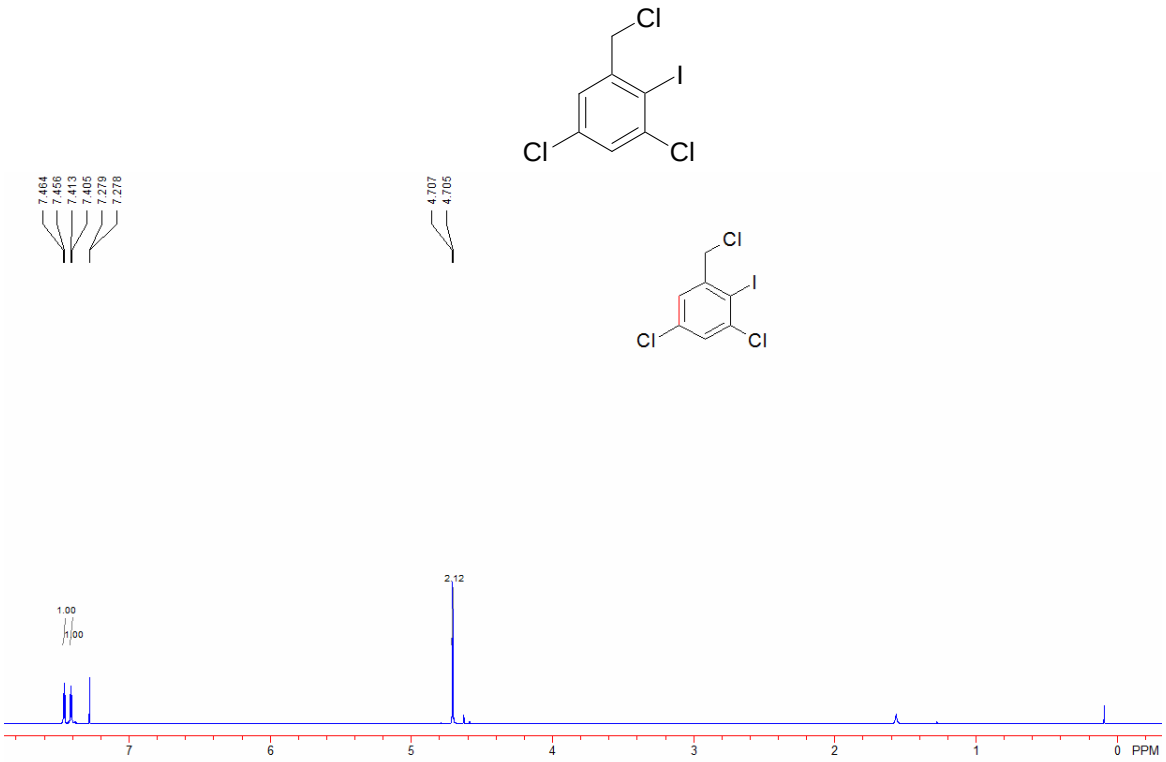



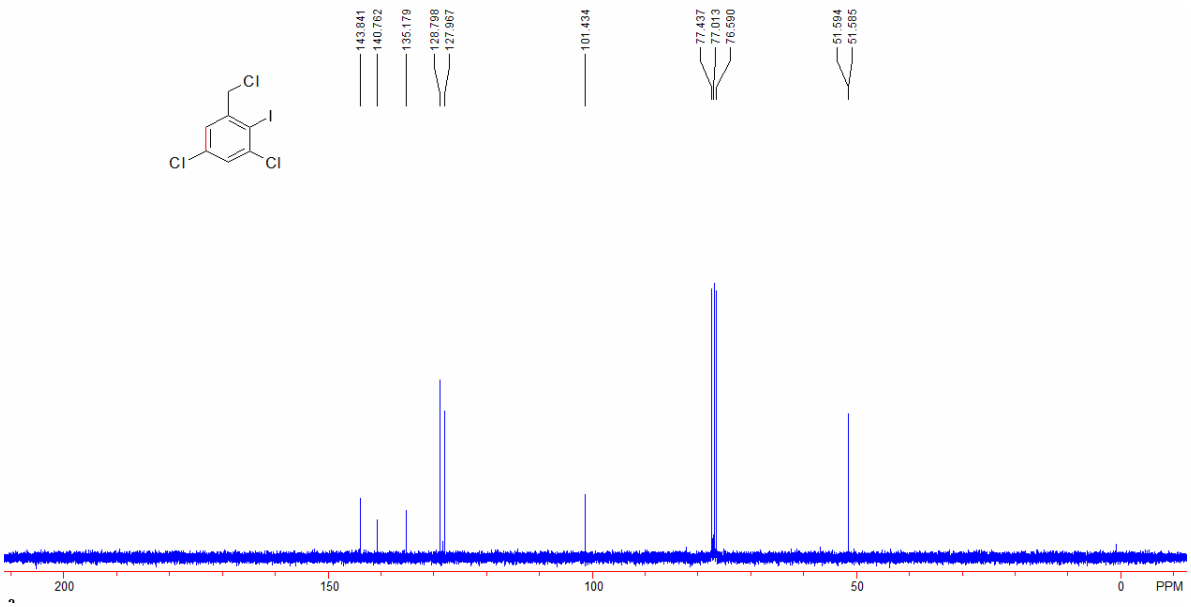



**Synthesis of 4-(6-Fluoro-indazol-2-yl)-benzoic acid ethyl ester (3p) :**

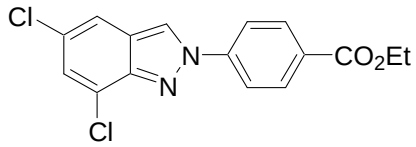


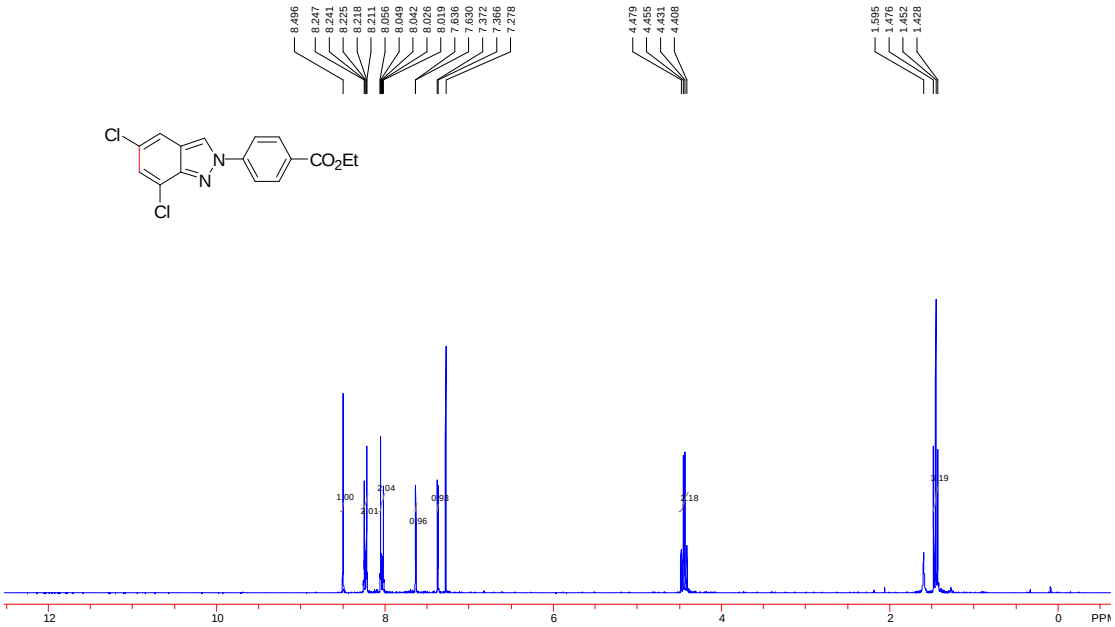
**Synthesis of 1,5-dichloro-3-chloromethyl-2-iodo-benzene :**

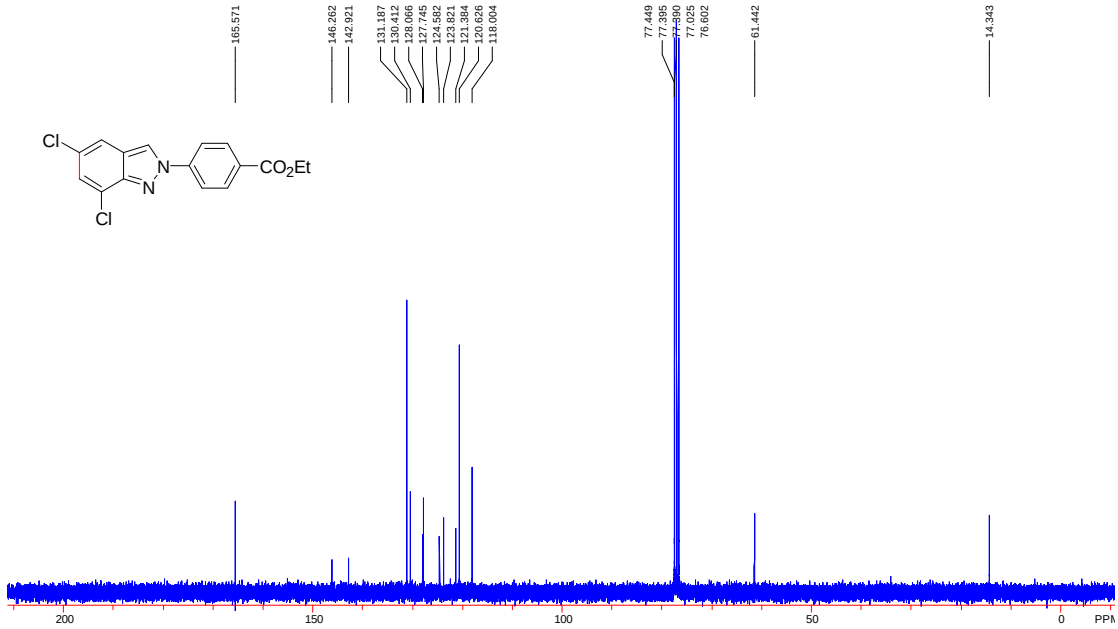


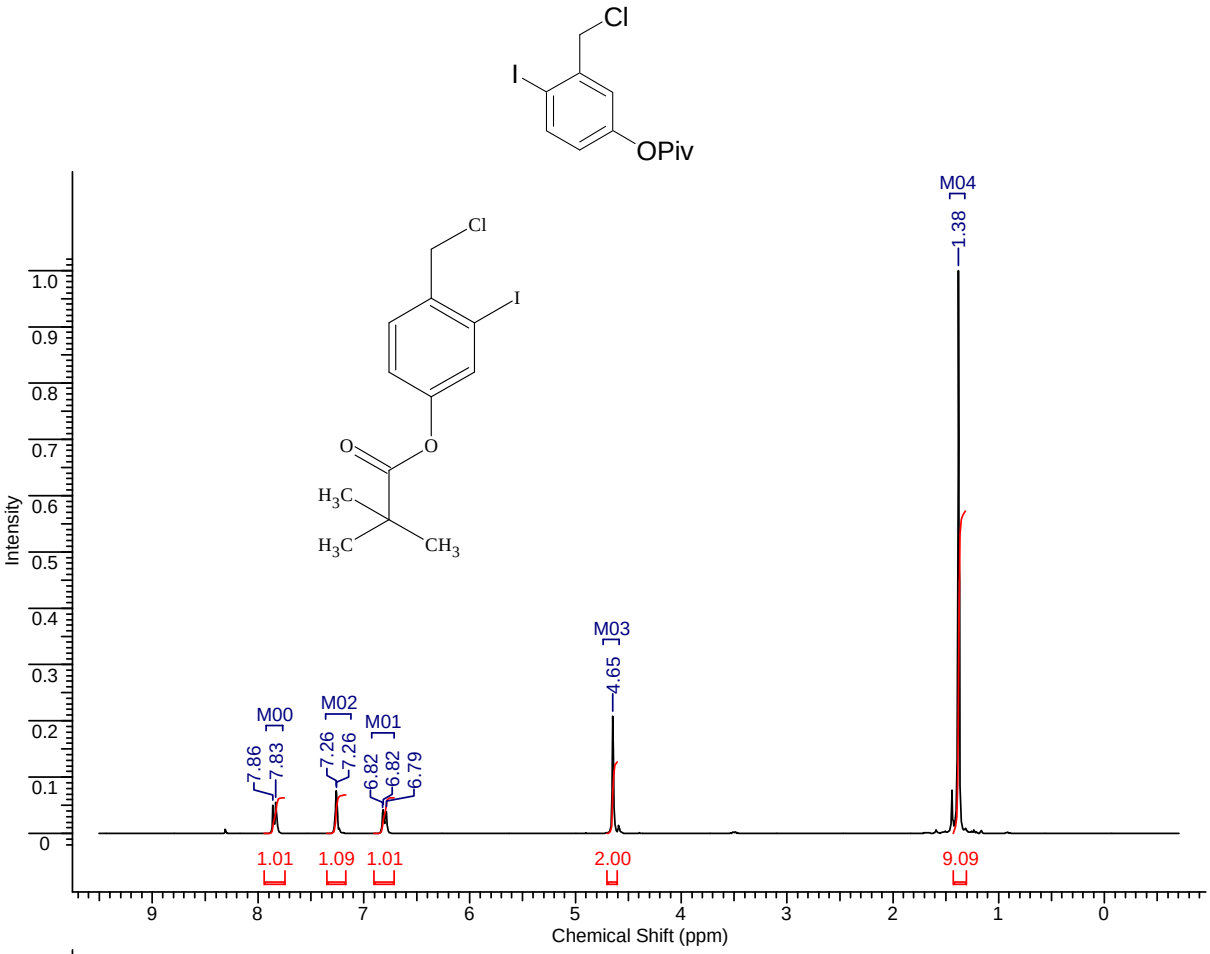
**Synthesis of 4-(5,7-dichloro-indazol-2-yl)-benzoic acid ethyl ester (3q) :**

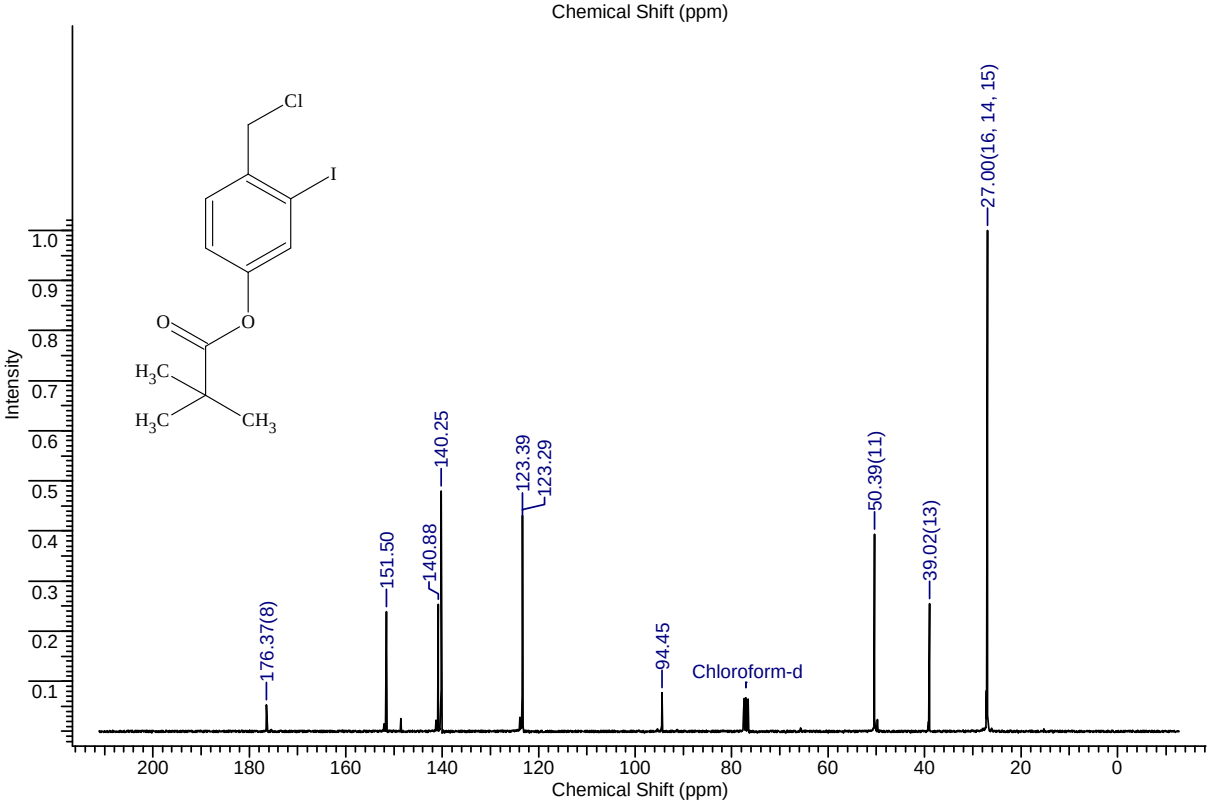


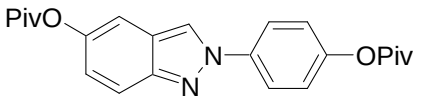



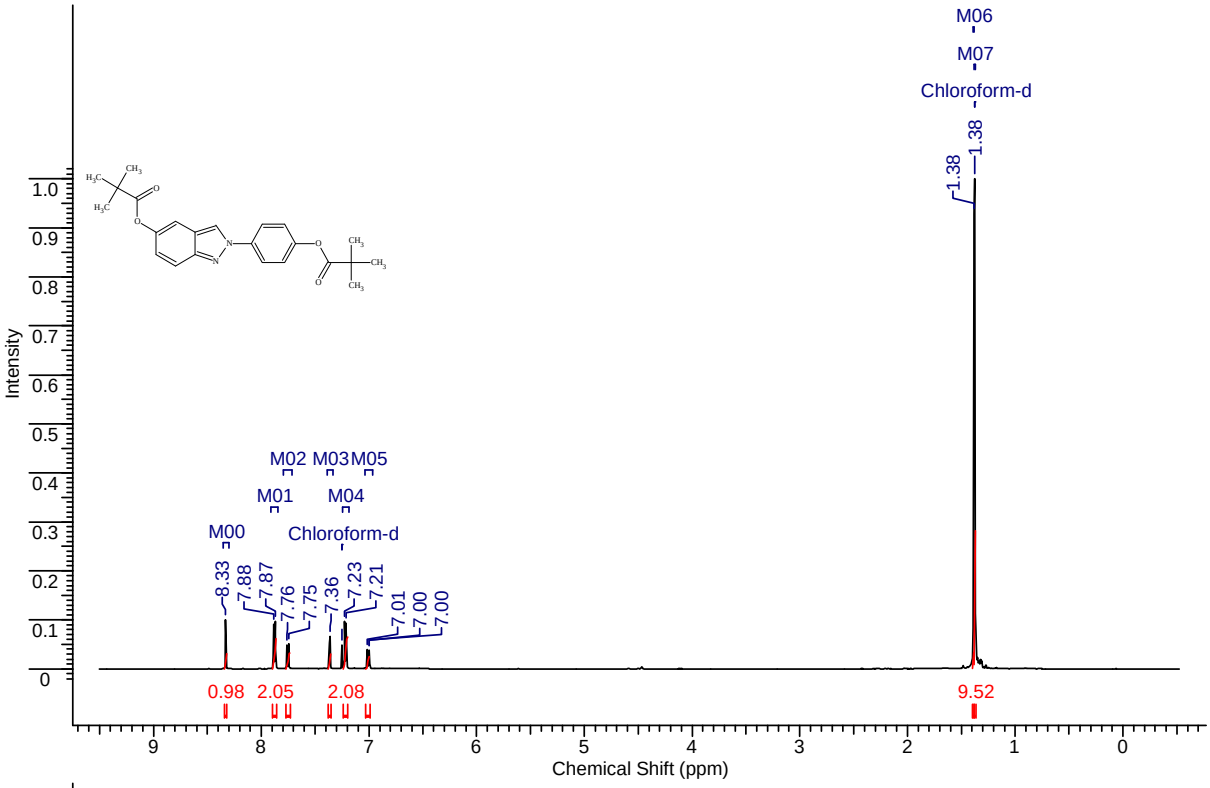
**Synthesis of 3-(chloromethyl)-4-iodophenyl pivalate :**

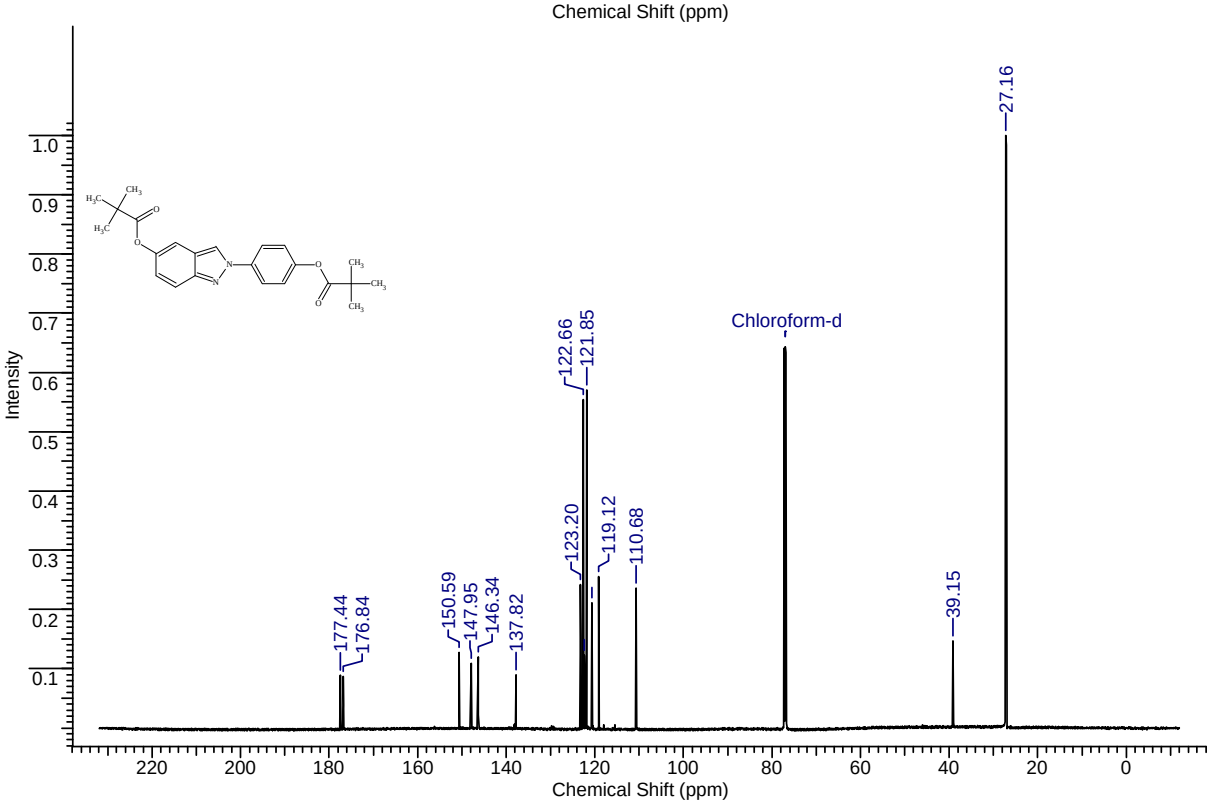


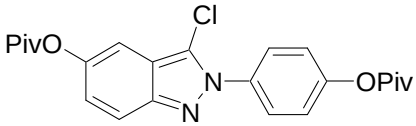
**Syntheisi of 4-{5-[(2,2-dimethylpropanoyl)oxy]-2*H*-indazol-2-yl}phenyl pivalate (3r) :**

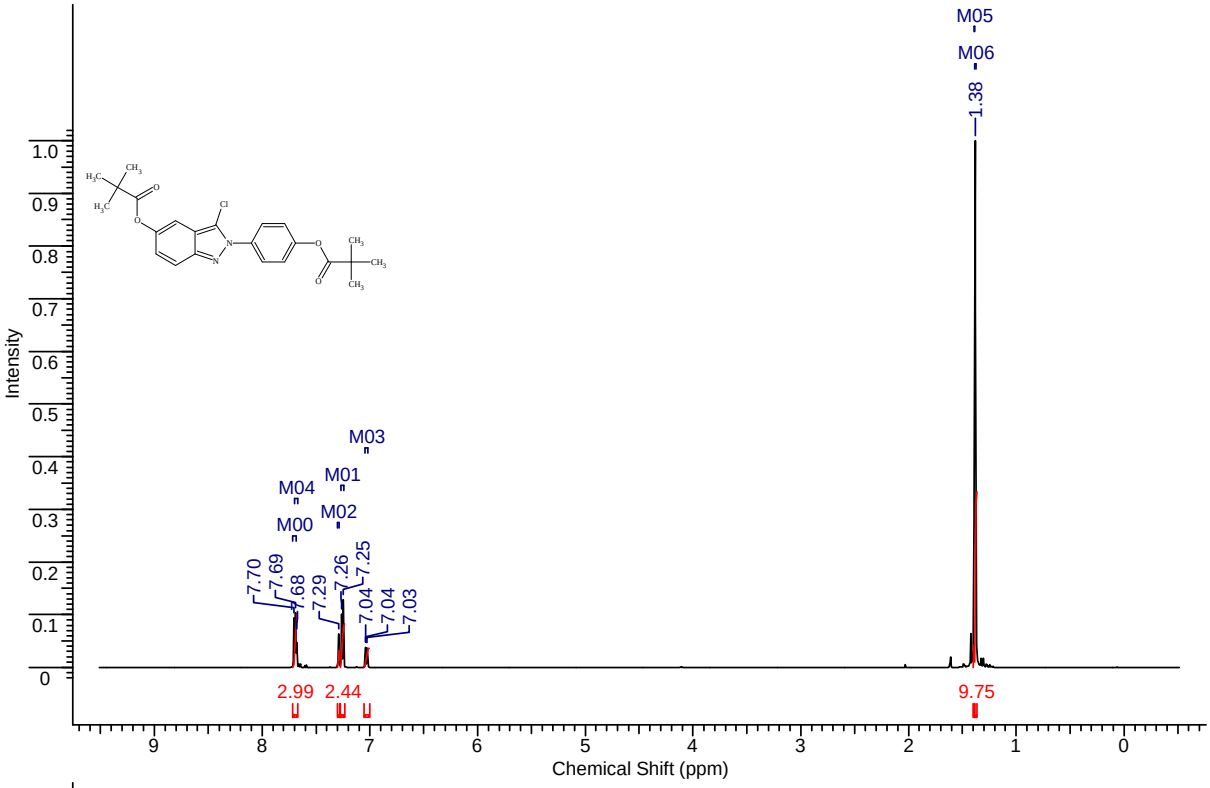


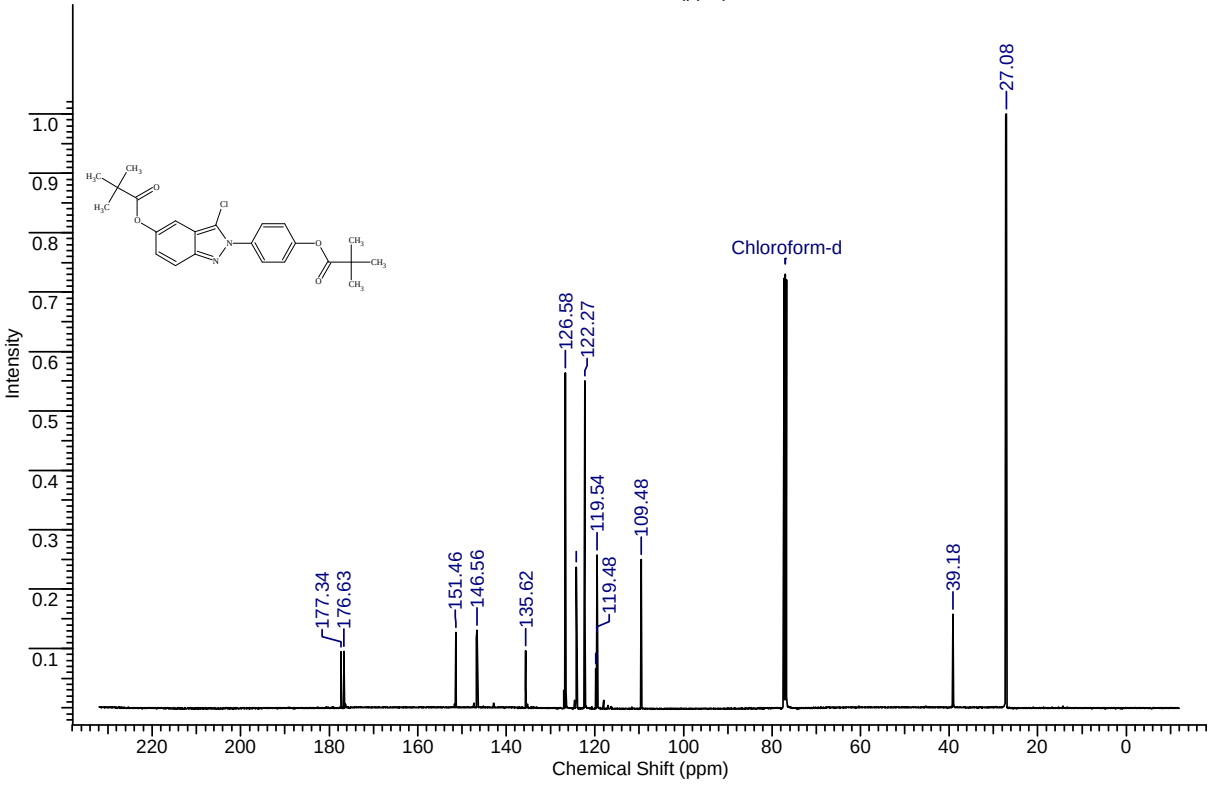



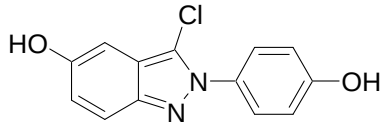
**Synthesis of 4-{3-chloro-5-[(2,2-dimethylpropanoyl)oxy]-2*H*-indazol-2-yl}phenyl pivalate**

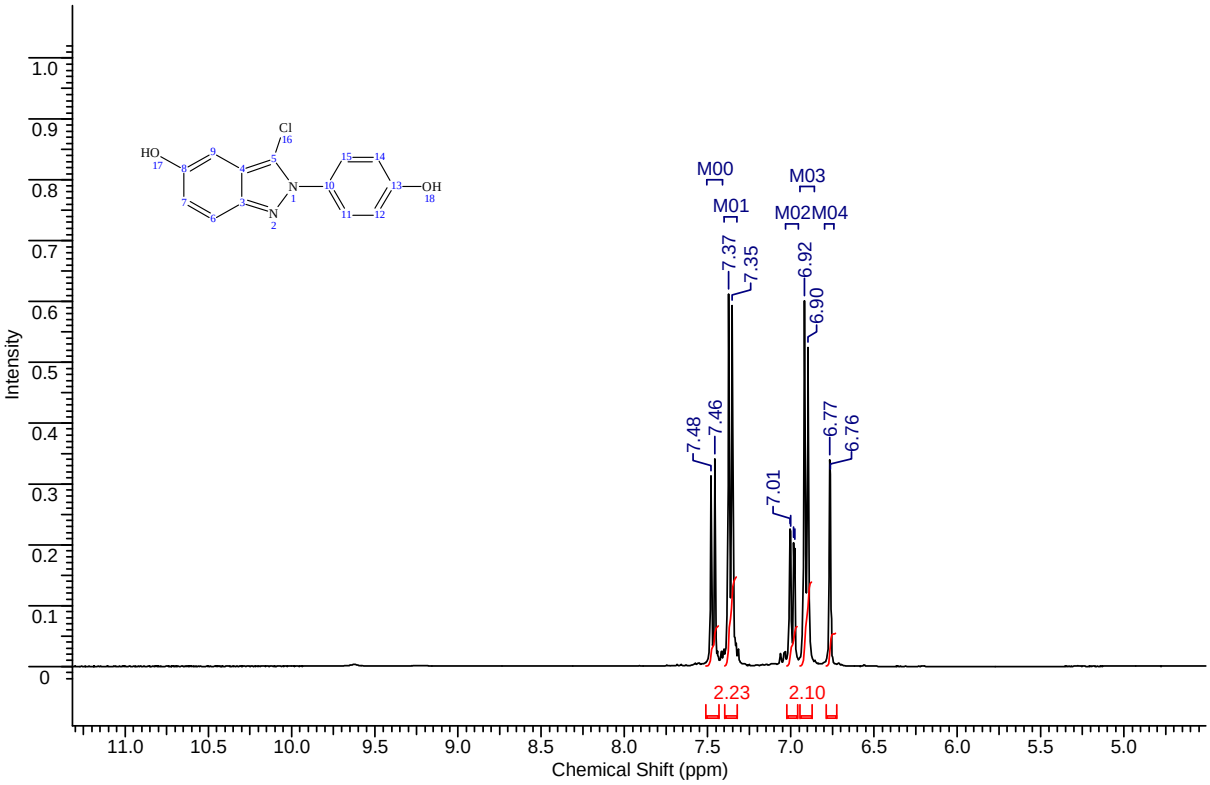


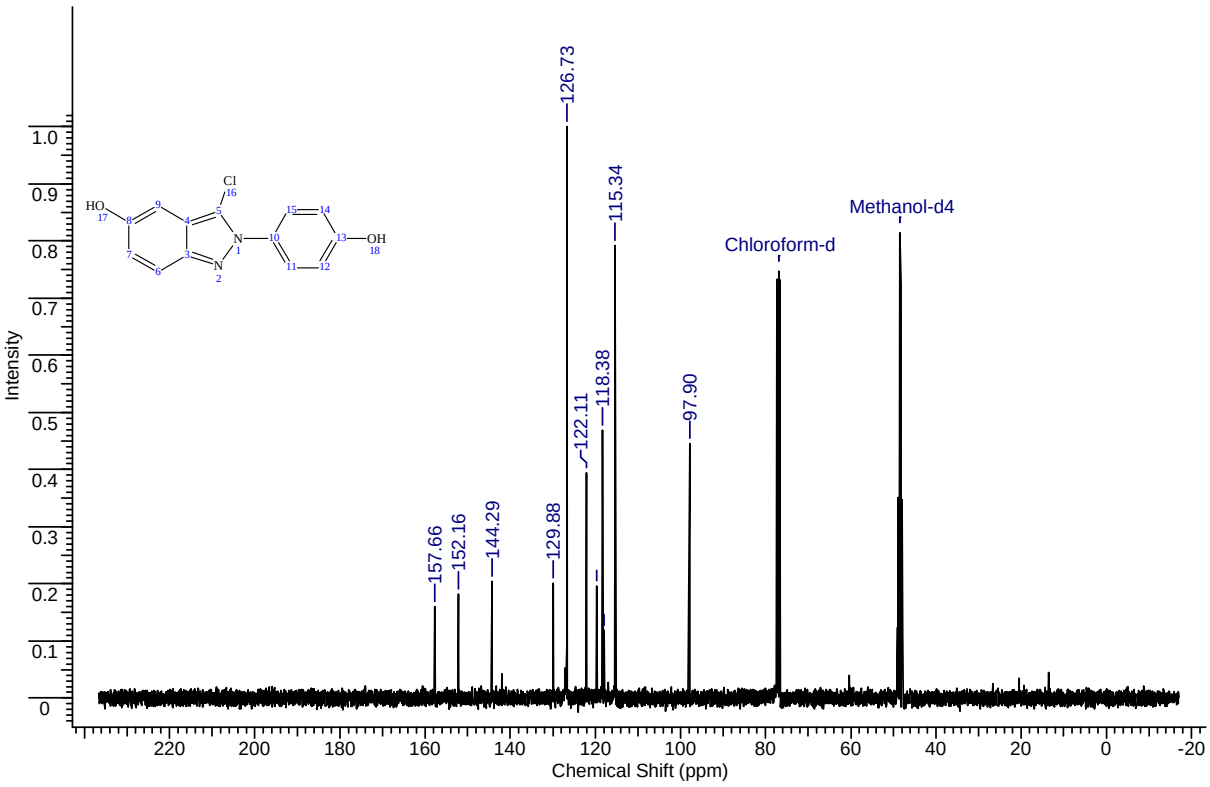



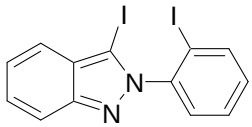
**Synthesis of 3-chloro-2-(4-hydroxyphenyl)-2*H*-indazol-5-ol (7) :**

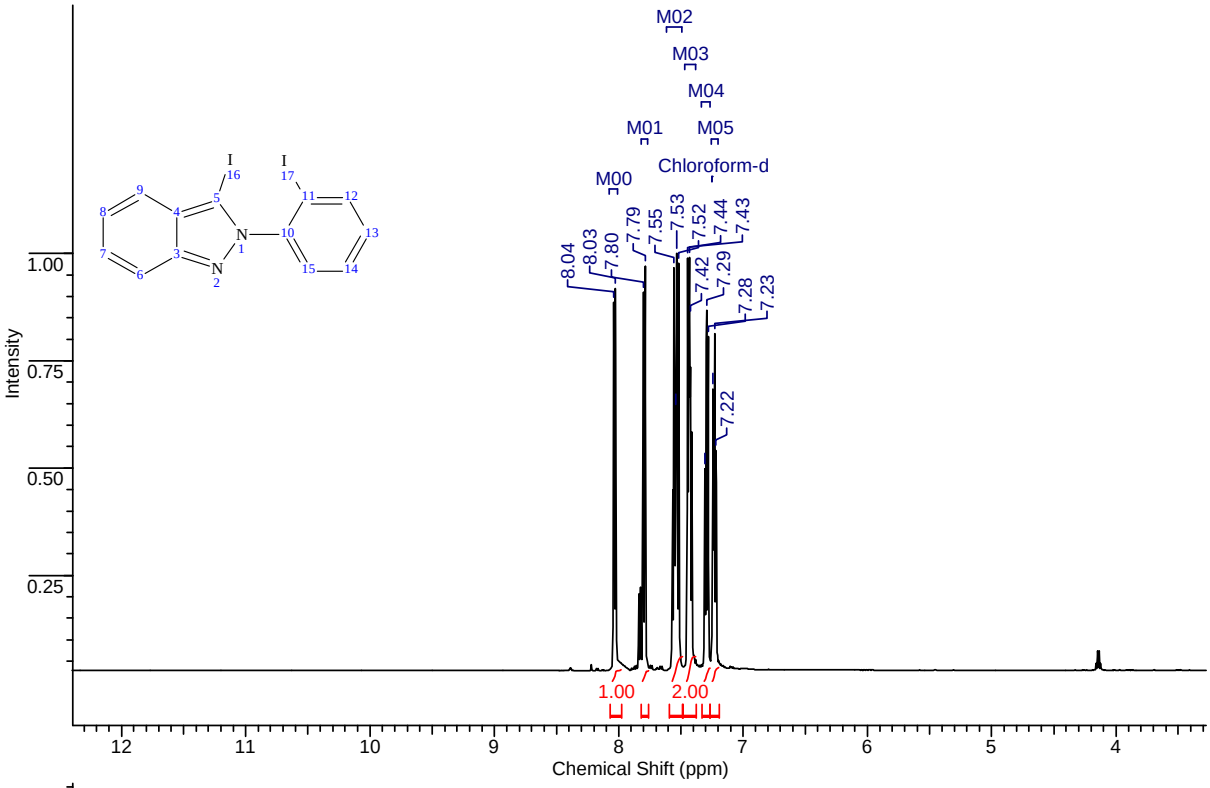


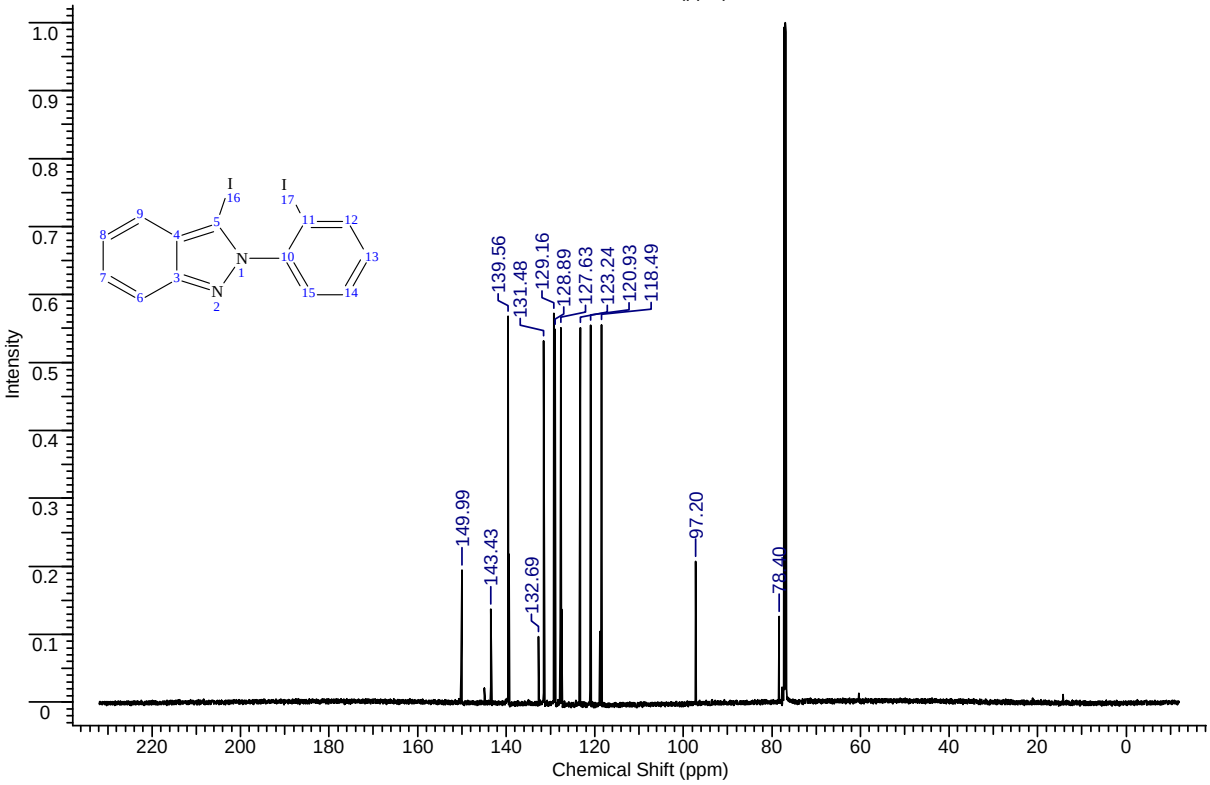



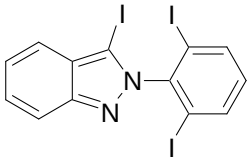
**Synthesis of 3-iodo-2-(2-iodophenyl)-2*H*-indazole (8a) :**

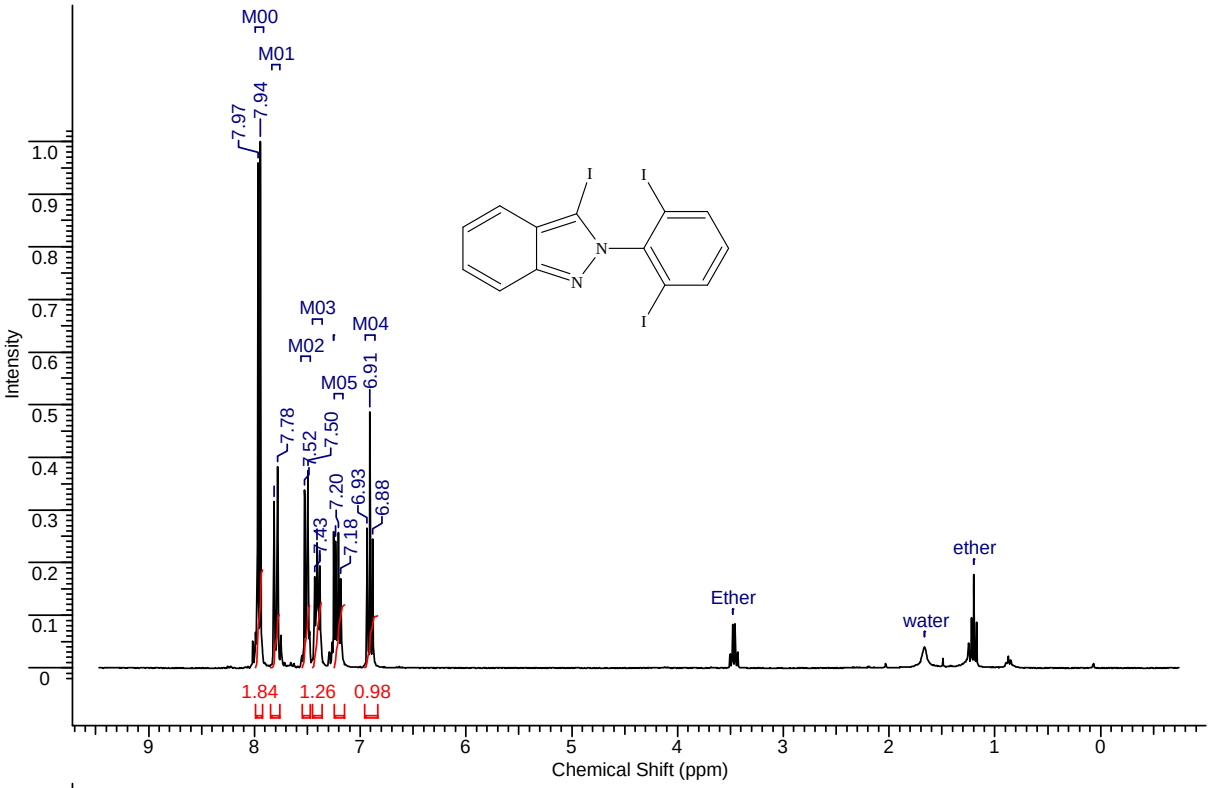


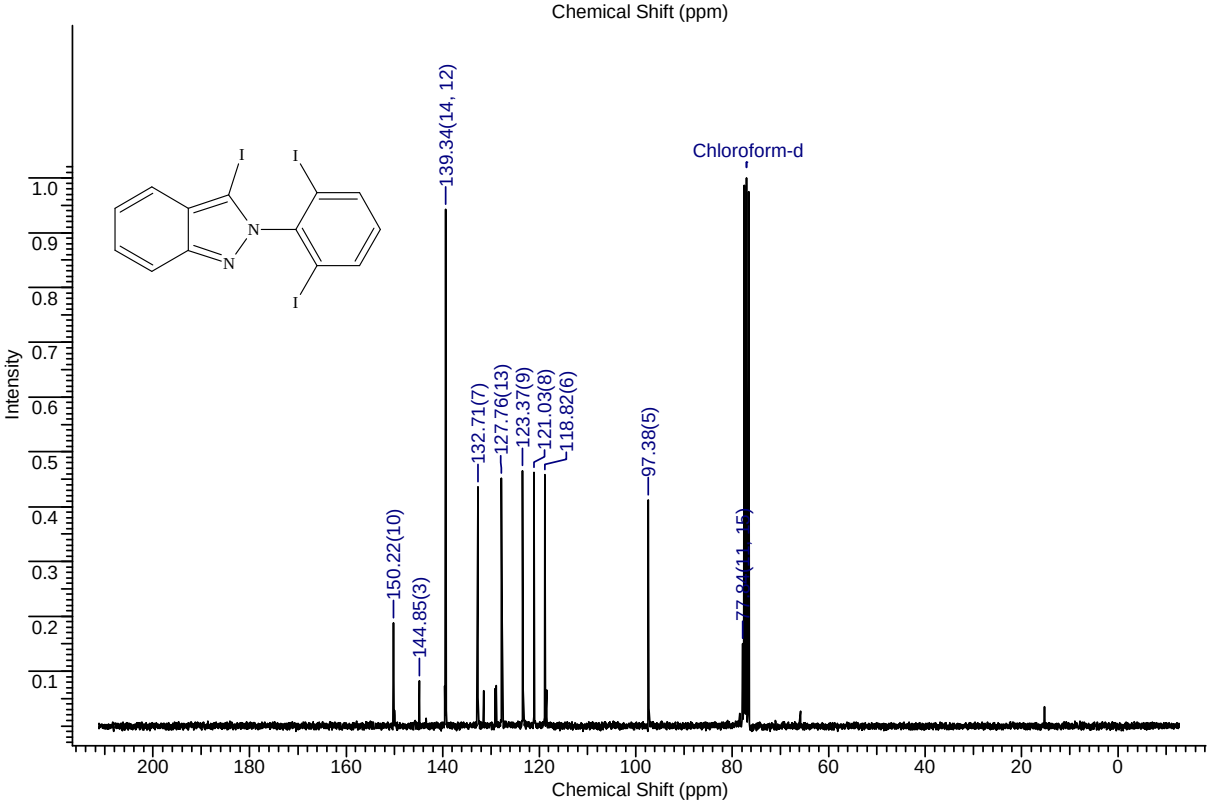


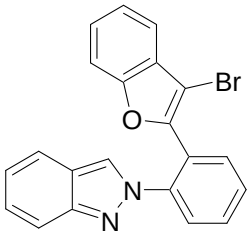
**Synthesis of 2-(2,6-diiodophenyl)-3-iodo-2*H*-indazole (8b) :**

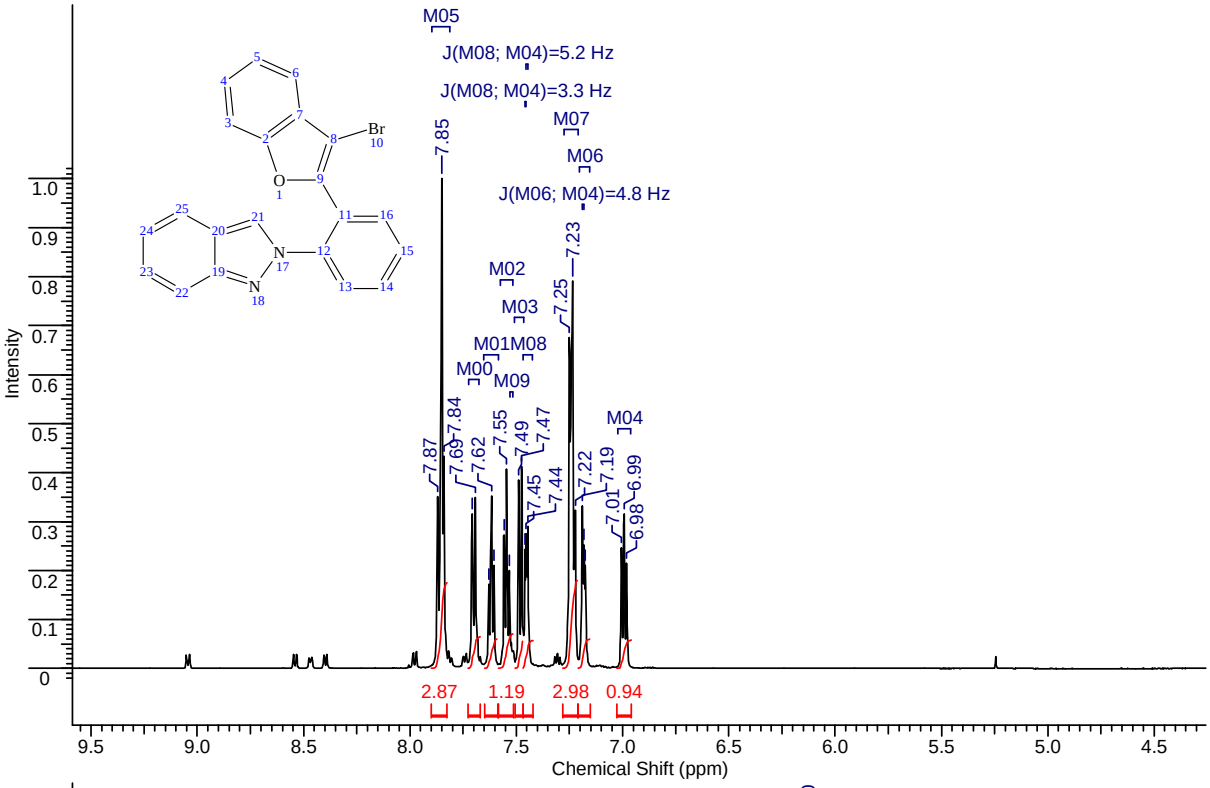


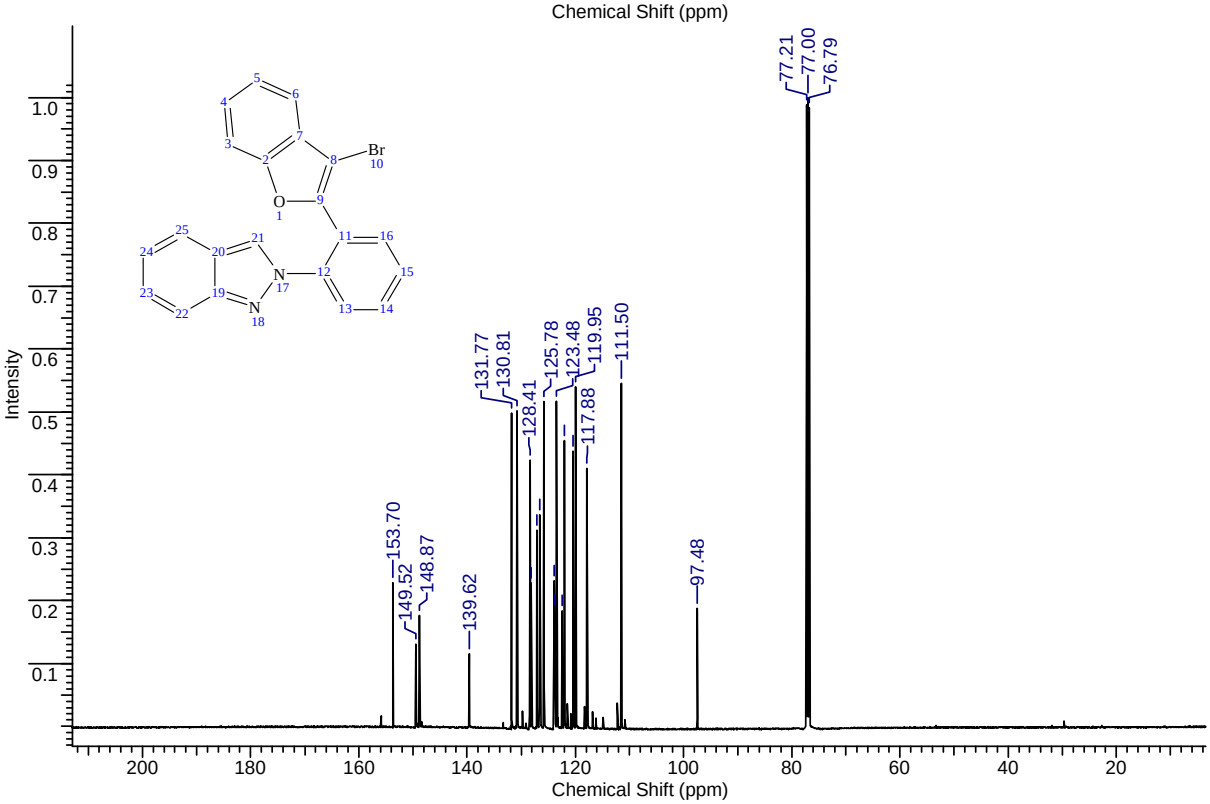


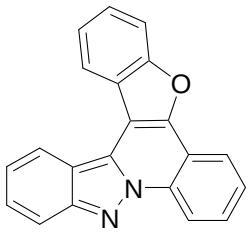
**Synthesis of 2-[2-(3-bromo-1-benzofuran-2-yl)phenyl]-2*H*-indazole (9a) :**

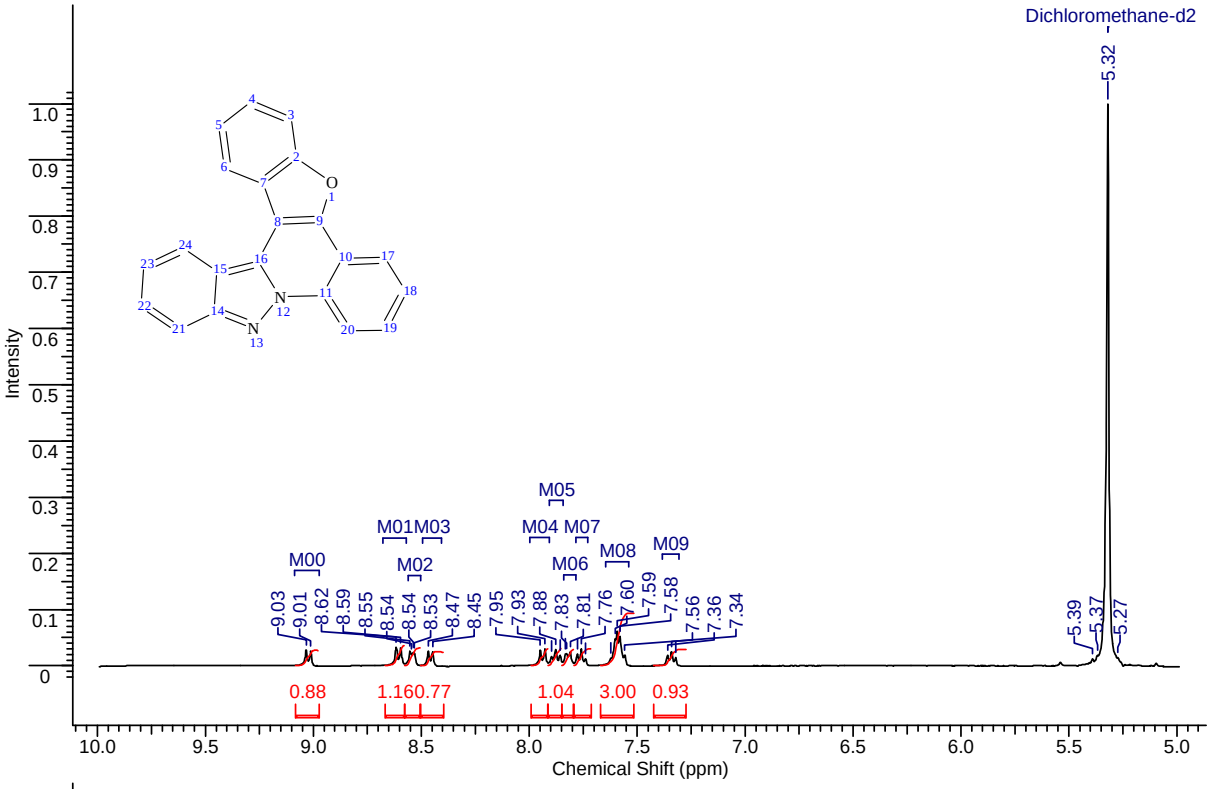


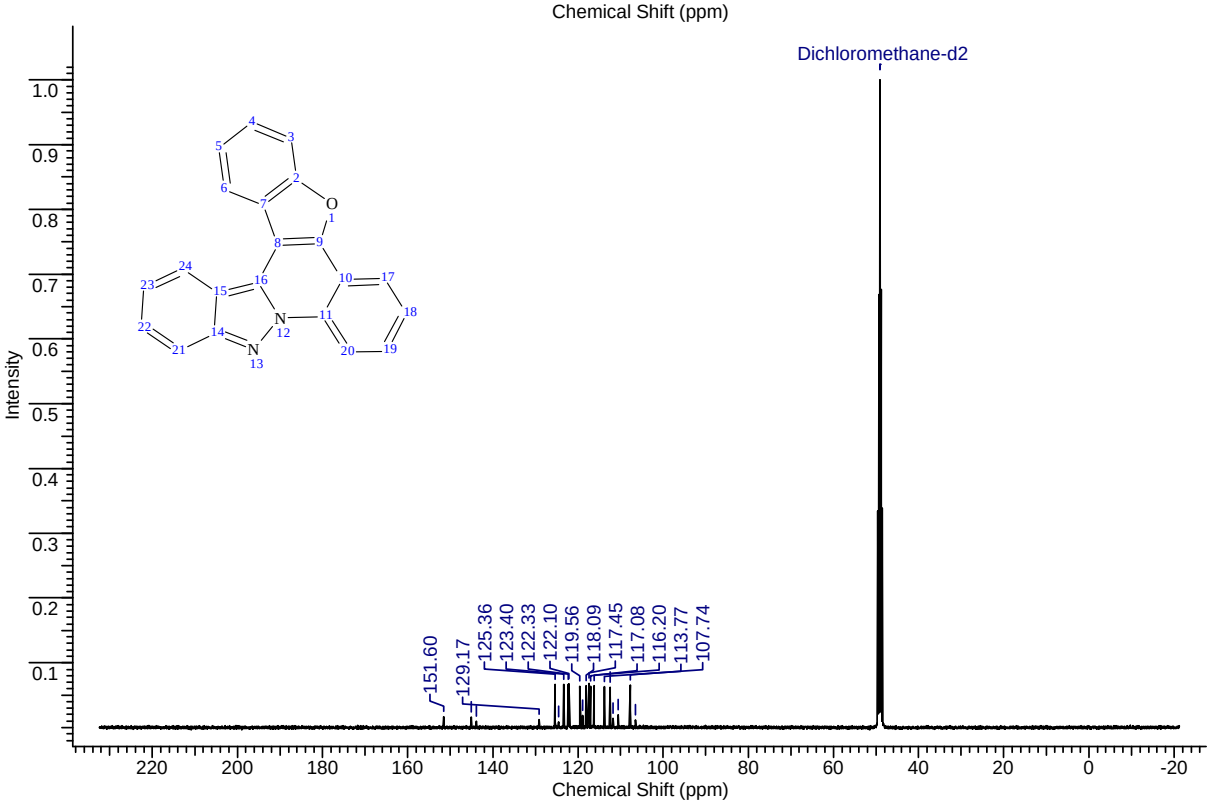



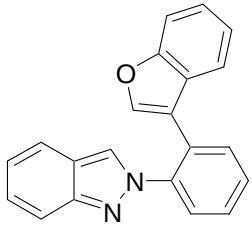
**Synthesis of [1]benzofuro[3,2-*c*]indazolo[2,3-*a*]quinoline (9b) :**

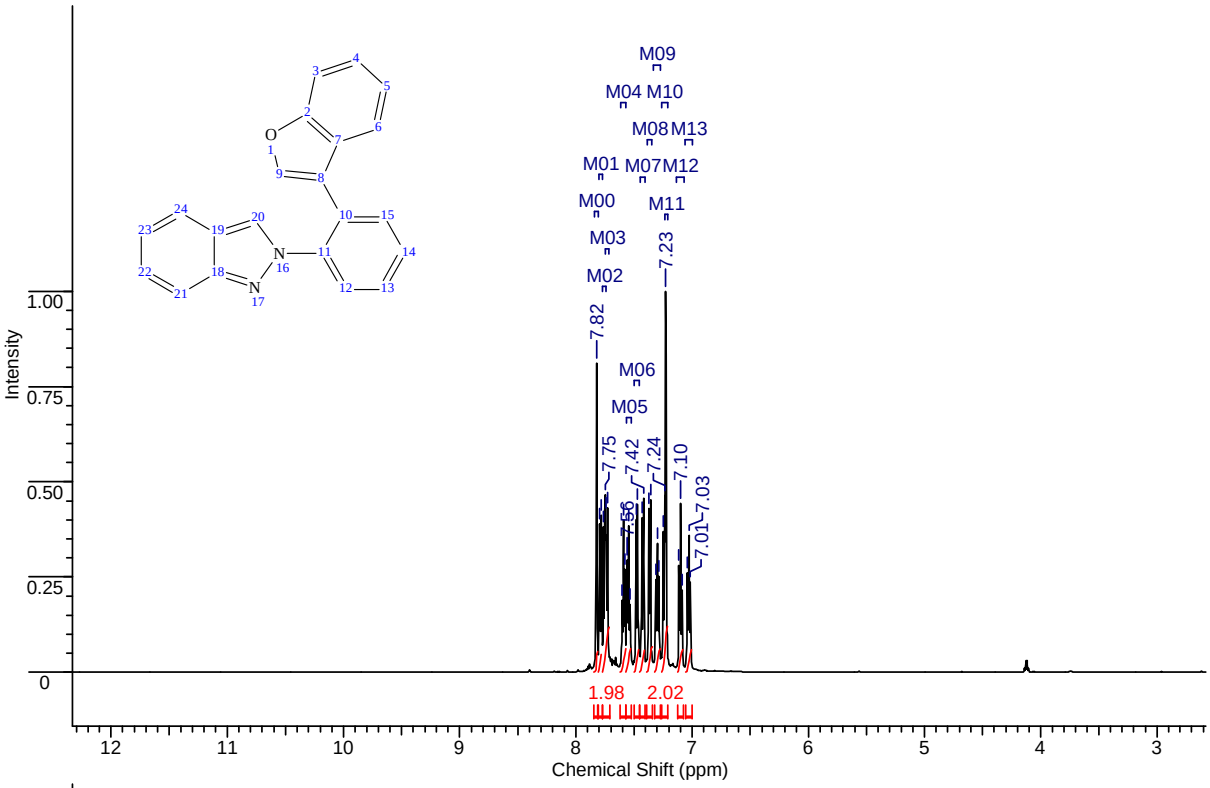


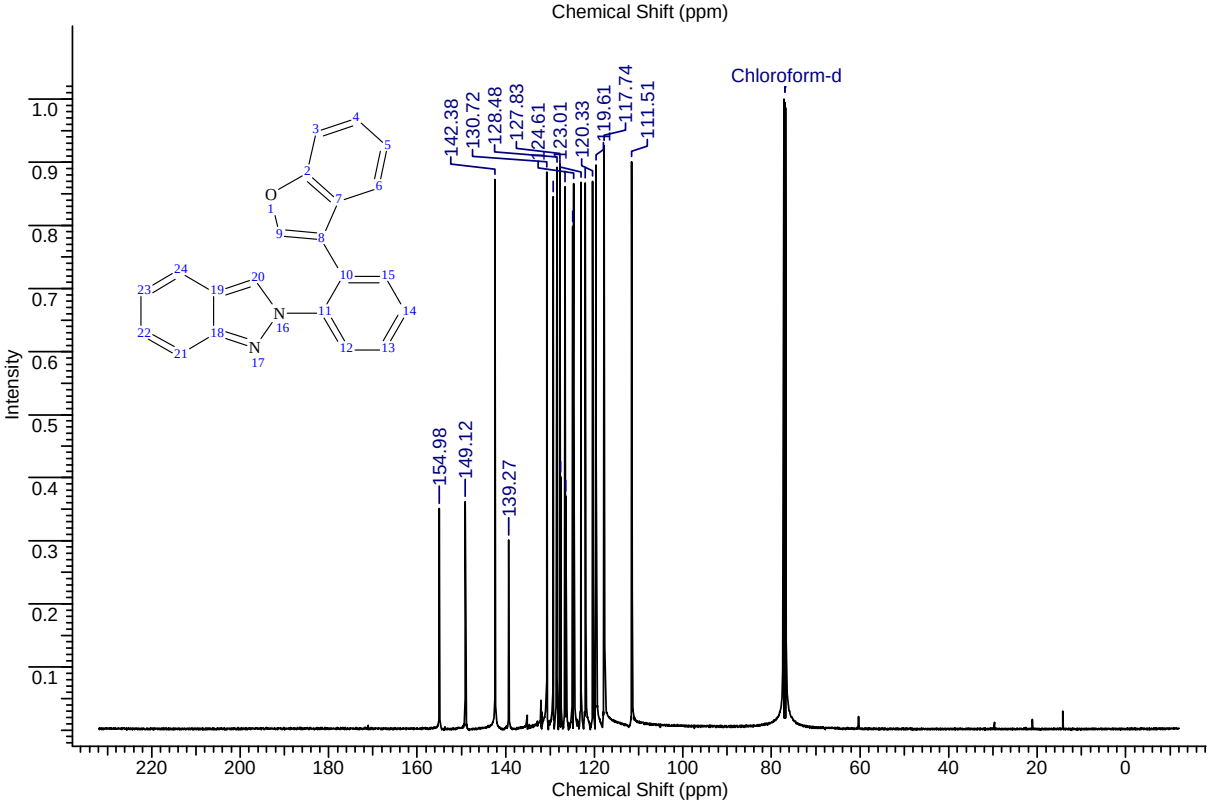


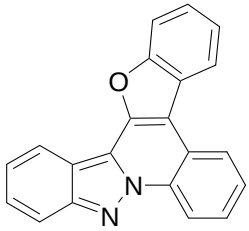
**Synthesis of 2-[2-(1-benzofuran-3-yl)phenyl]-2*H*-indazole (10a) :**

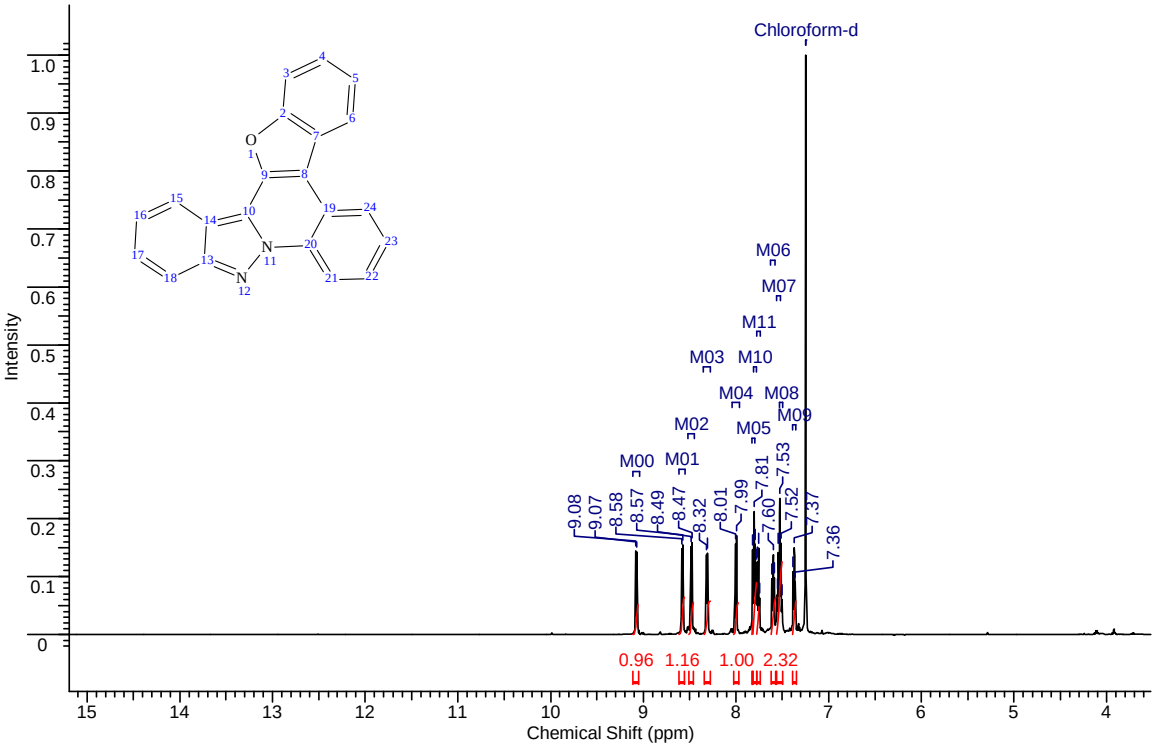


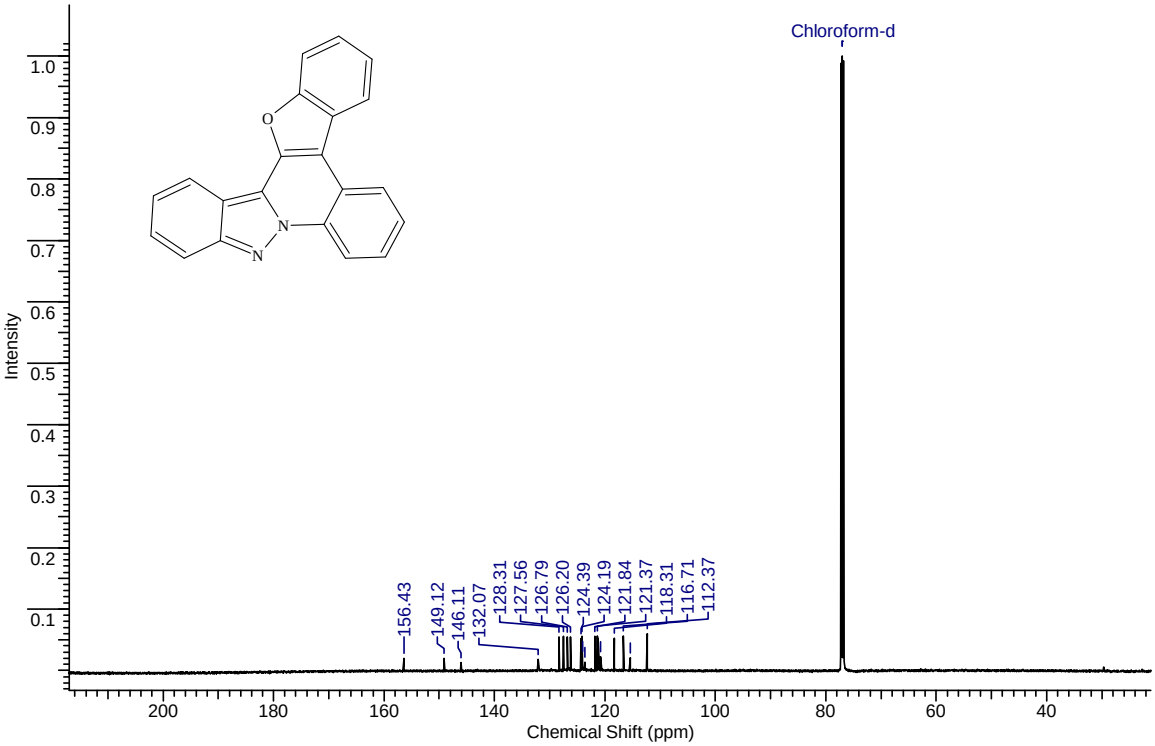


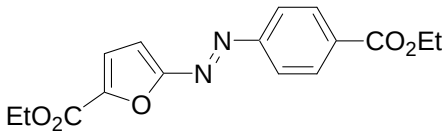
**Synthesis of [1]benzofuro[2,3-*c*]indazolo[2,3-*a*]quinoline (10b) :**

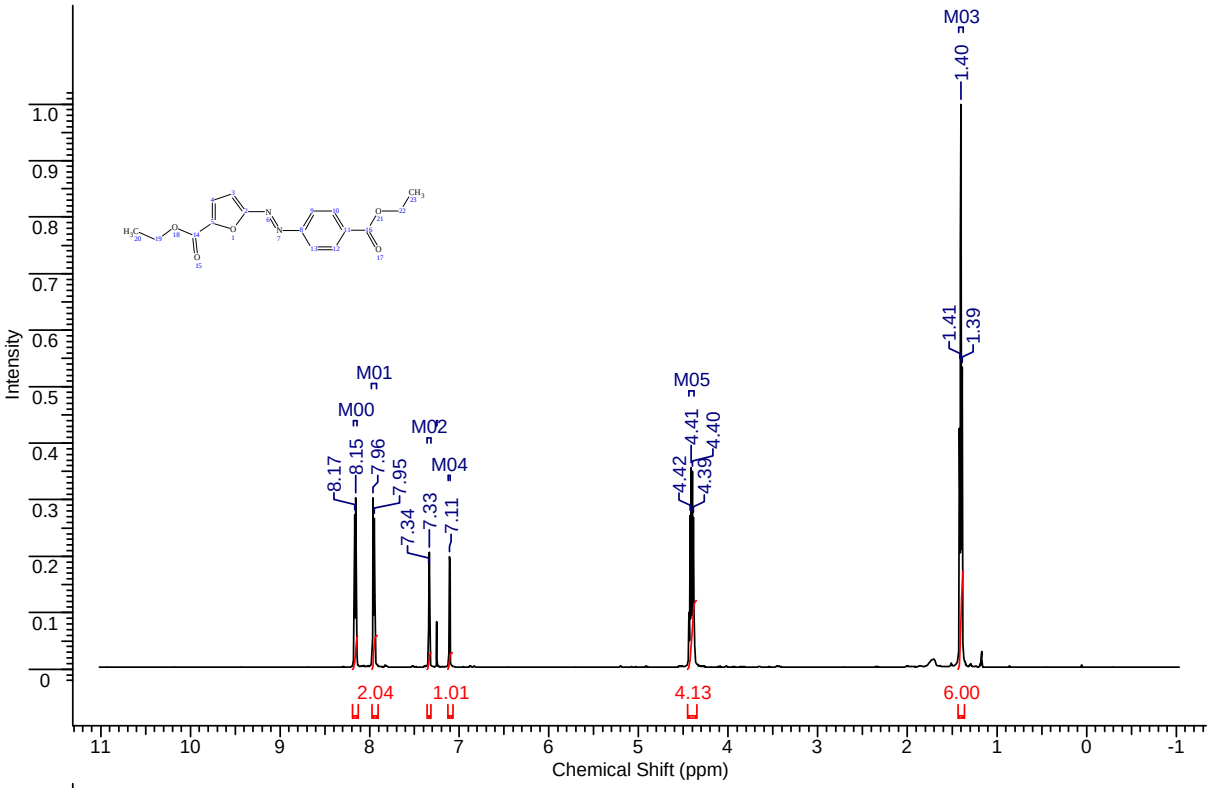


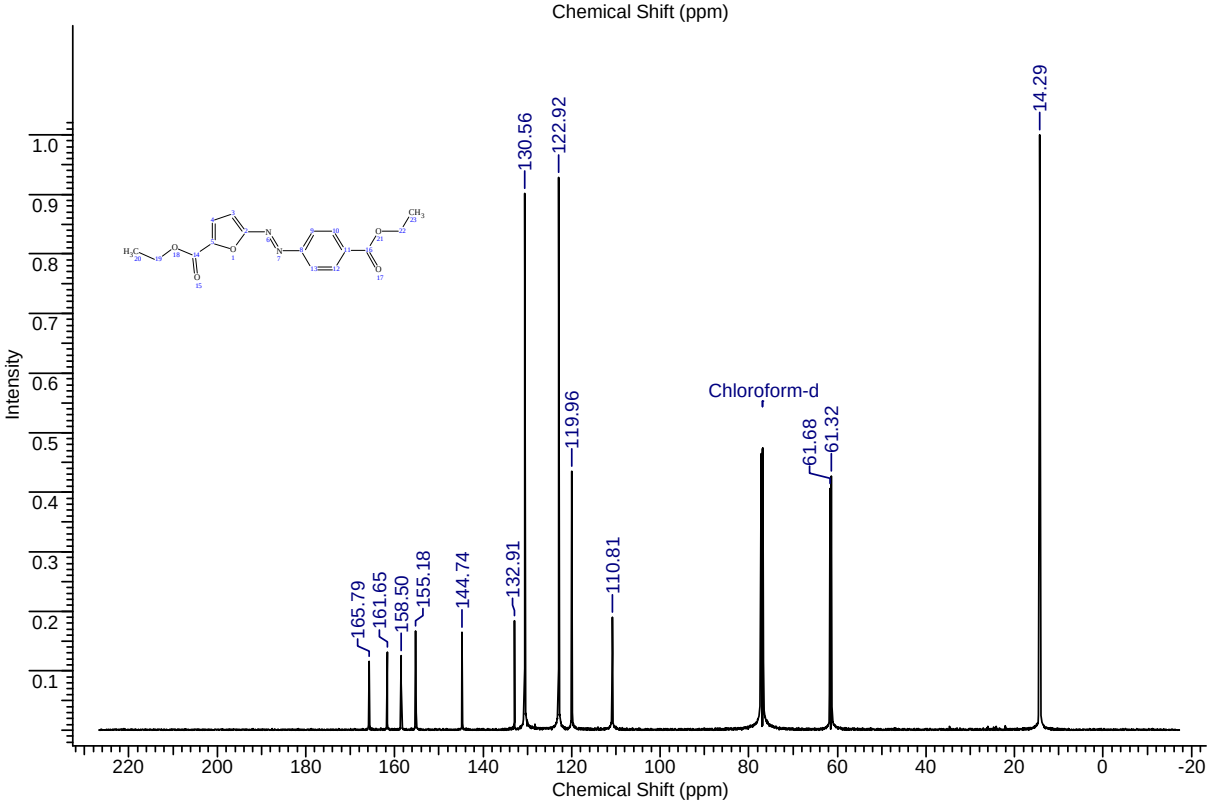


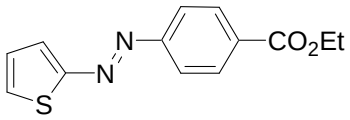
**Synthesis of ethyl 5-{(*E*)-[4-(ethoxycarbonyl)phenyl]diazenyl}-2-furoate (14a) :**

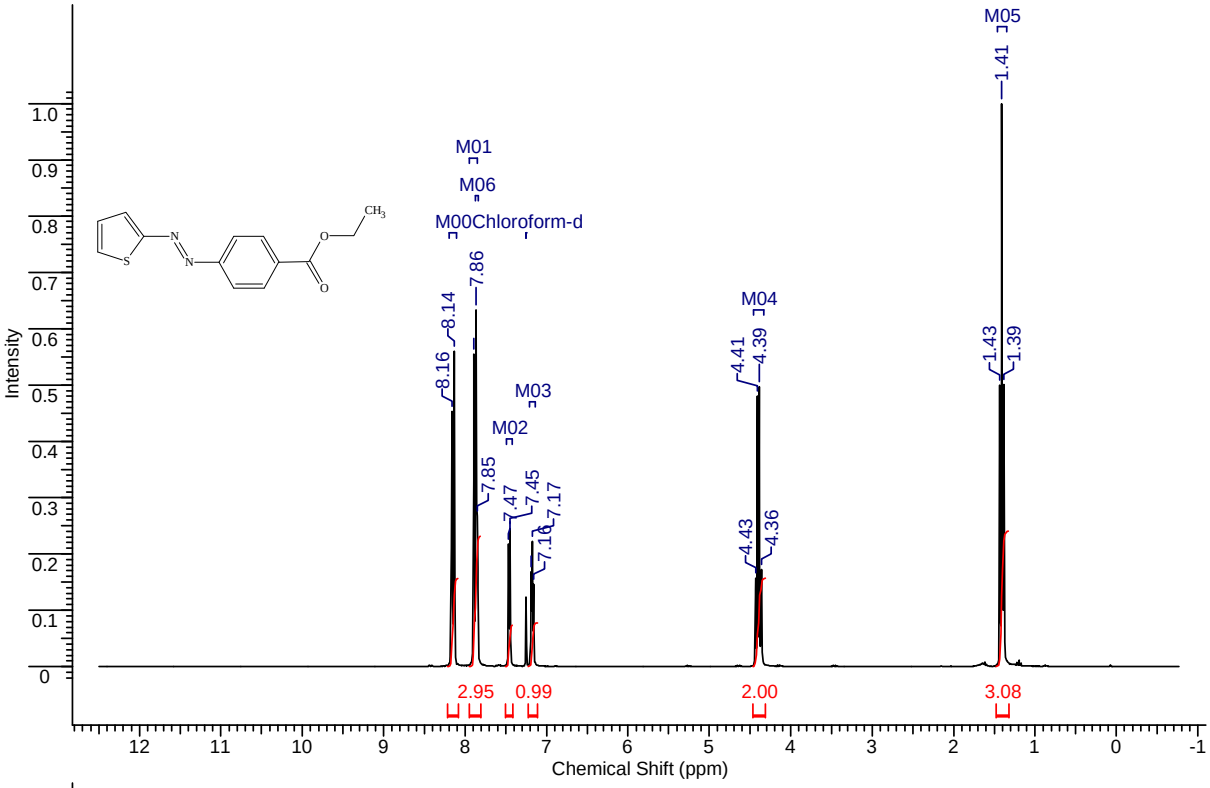


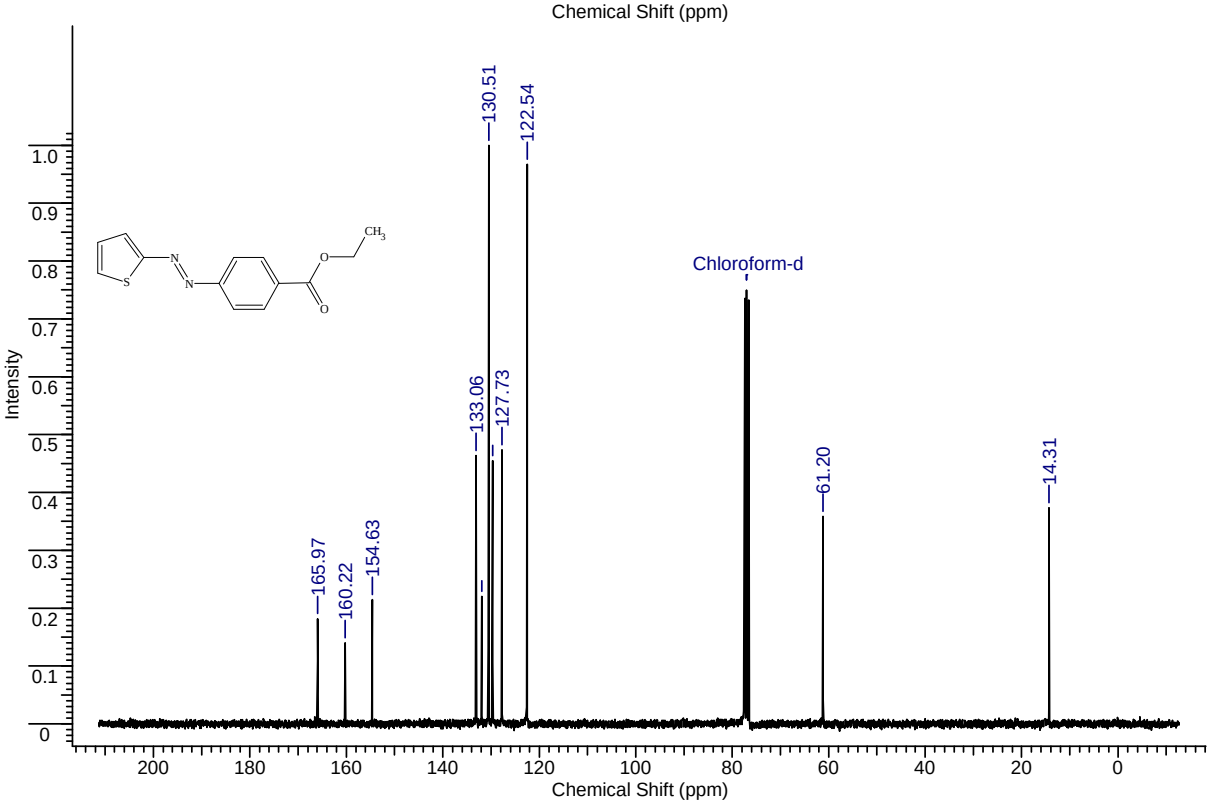



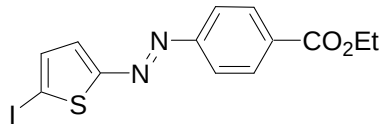
**Synthesis of ethyl 4-[(*E*)-2-thienyldiazenyl]benzoate (14b) :**

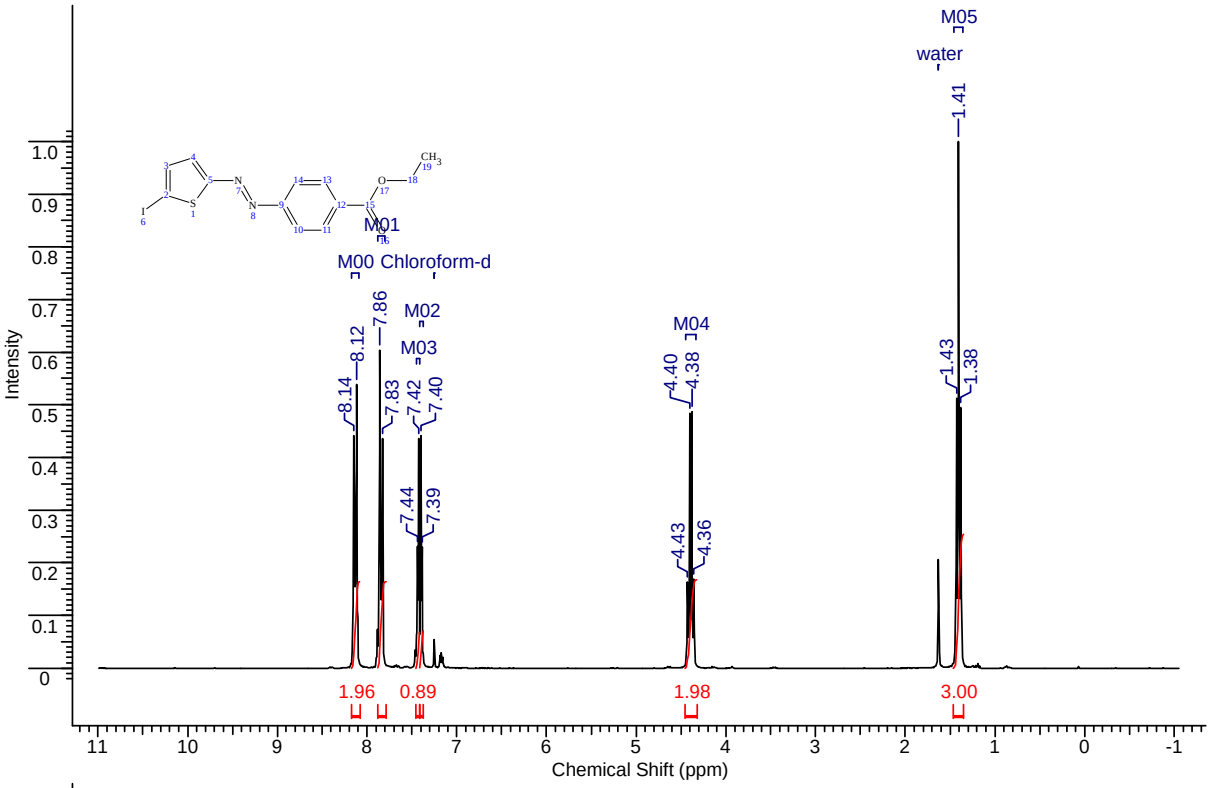


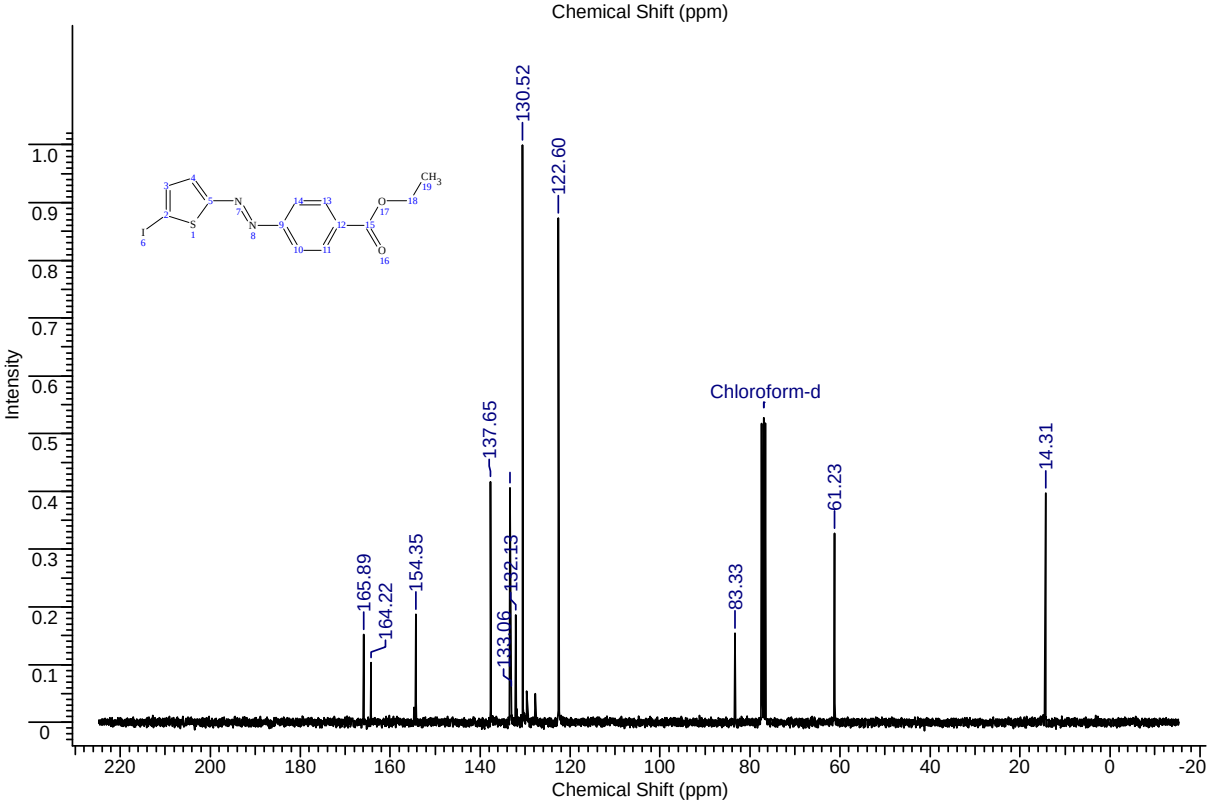



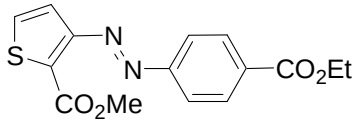
**Syntheis of ethyl 4-[(*E*)-(5-iodo-2-thienyl)diazenyl]benzoate (14c) :**

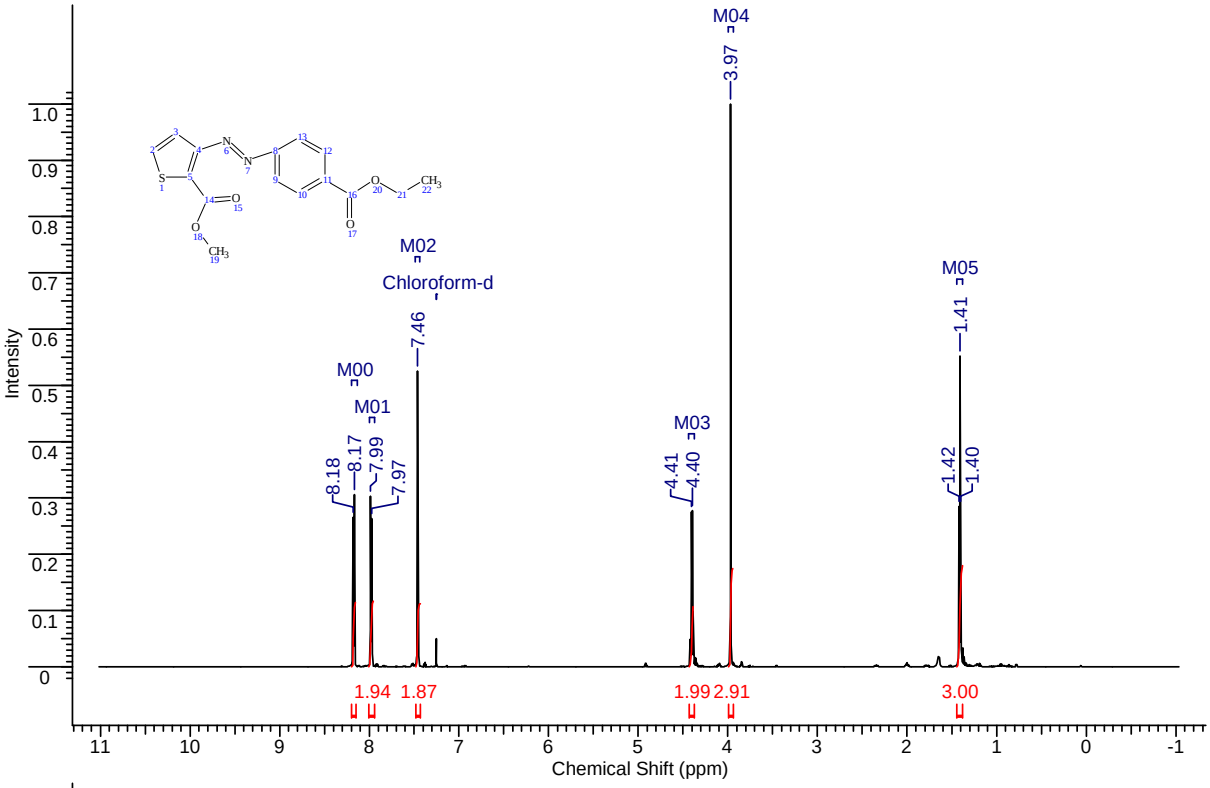


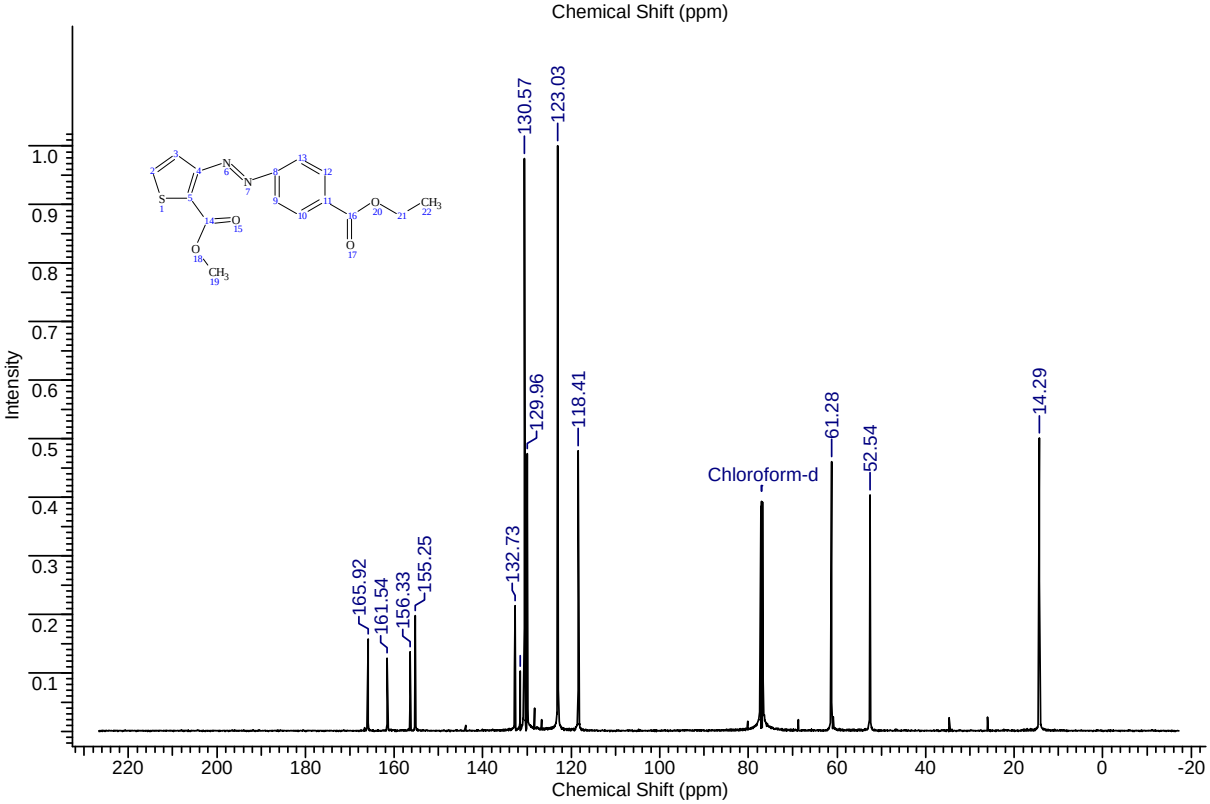



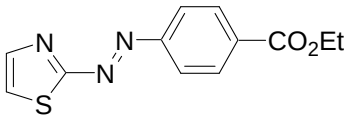
**Synthesis of methyl 3-{(*E*)-[4-(ethoxycarbonyl)phenyl]diazenyl}thiophene-2-carboxylate (14d) :**

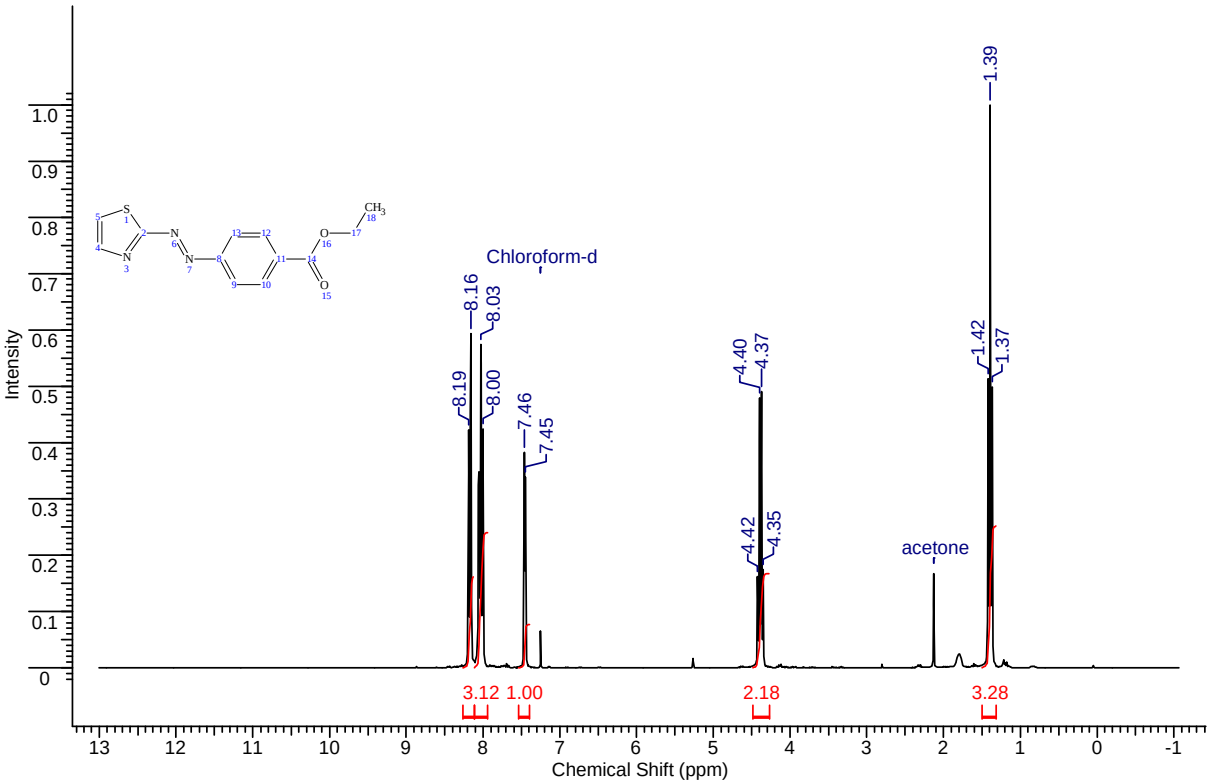


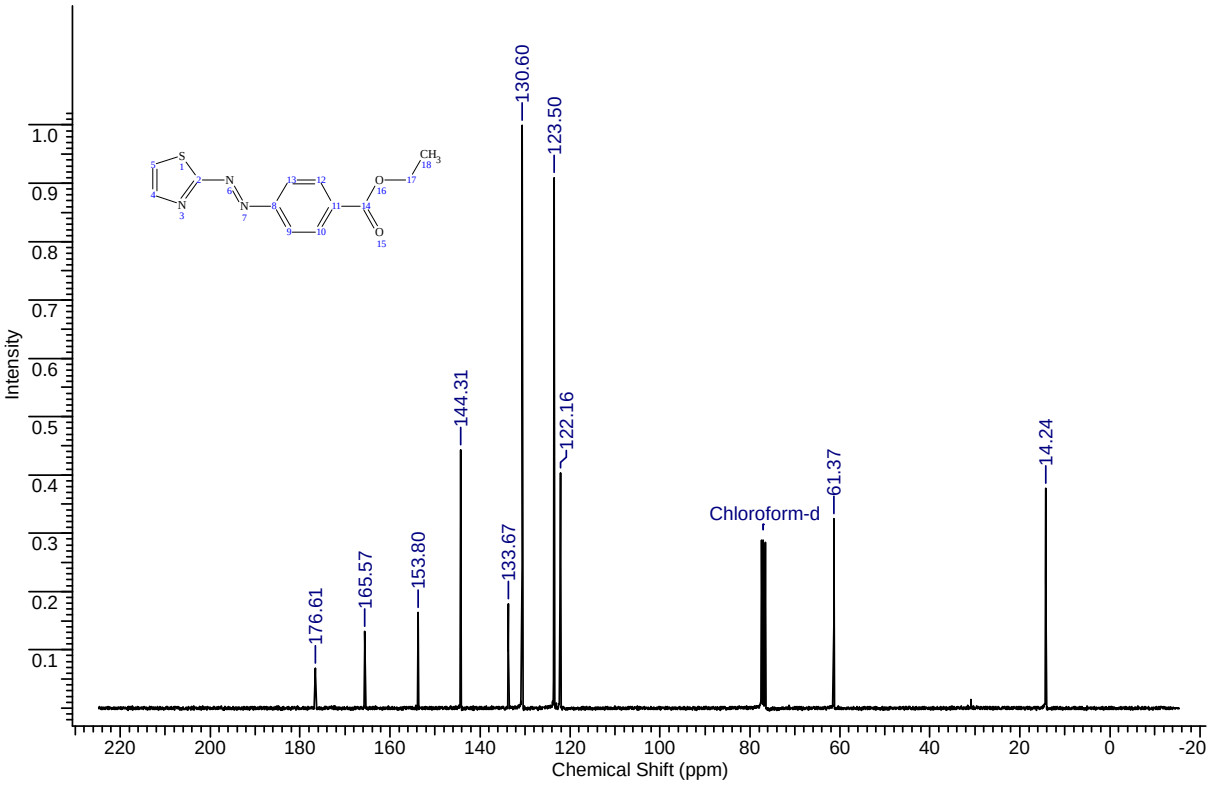



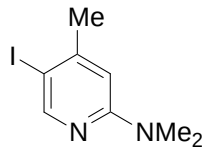
**Synthesis of ethyl 4-[(*E*)-1,3-thiazol-2-yldiazenyl]benzoate (14e) :**

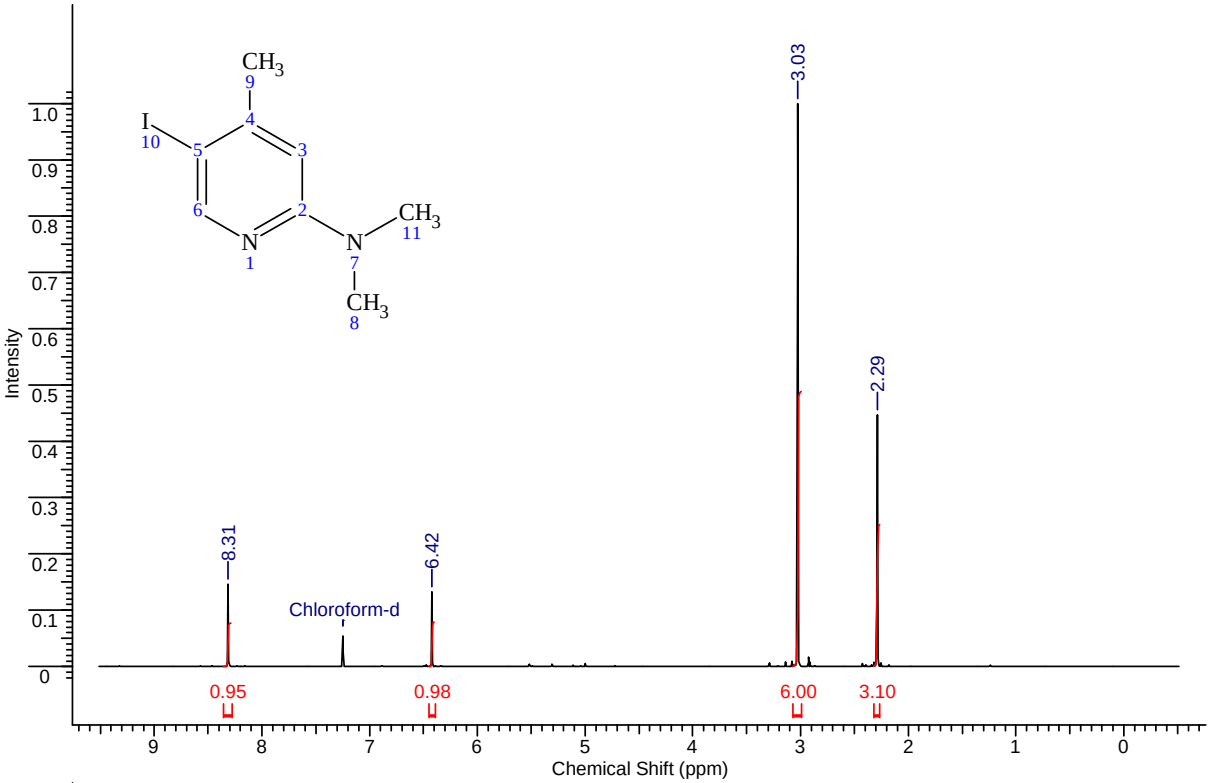


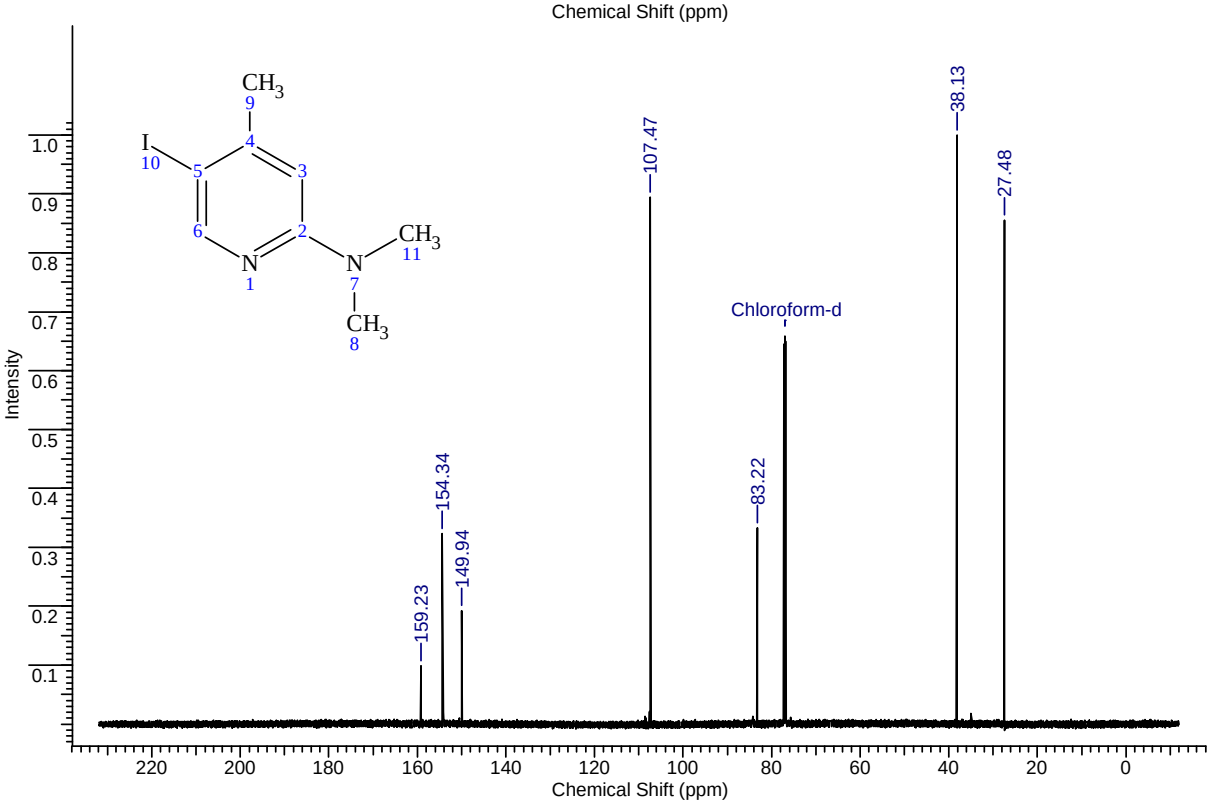
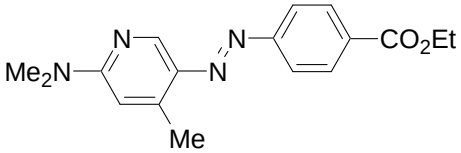
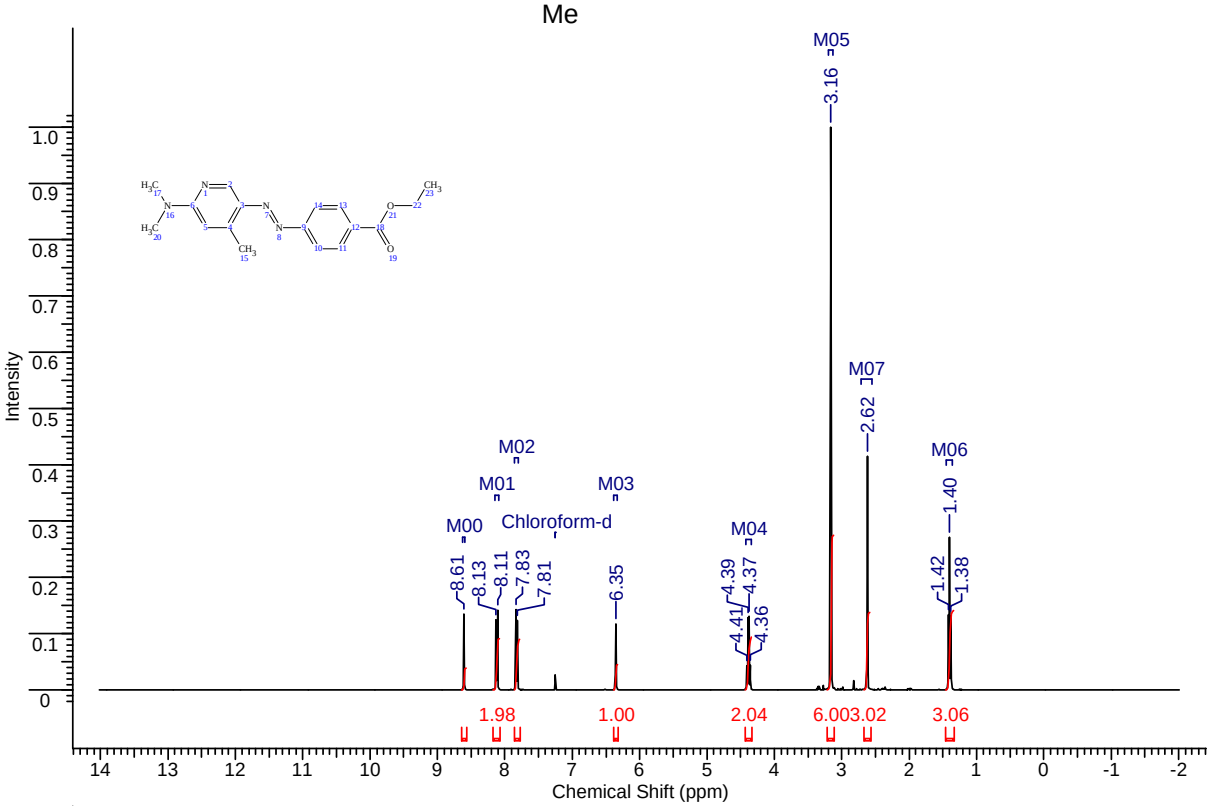
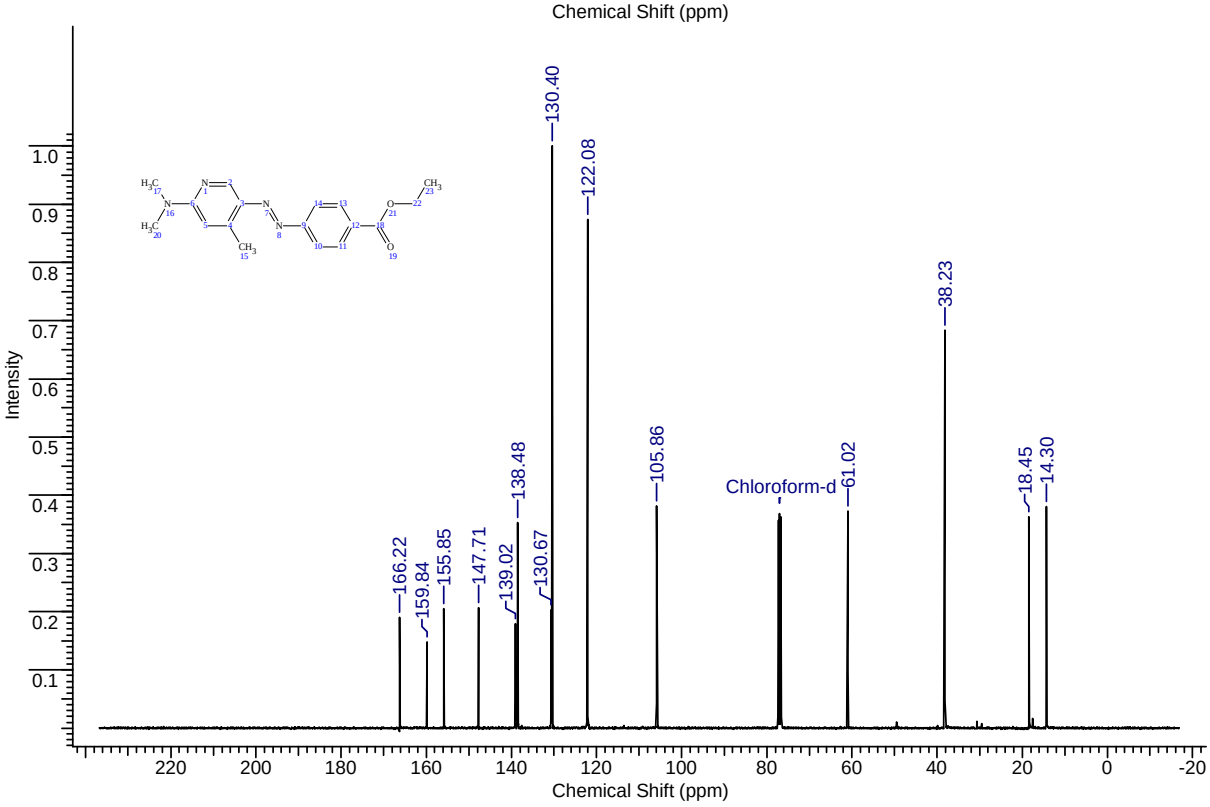



**Synthesis of 5-iodo-*N*,*N*,4-trimethylpyridin-2-amine :**






**Synthesis of ethyl 4-{(*E*)-[6-(dimethylamino)-4-methylpyridin-3-yl]diazenyl}benzoate (14f) :**