Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Visible light sensitization of benzoyl azides: cascade cyclization toward oxindoles via a non-nitrene pathway

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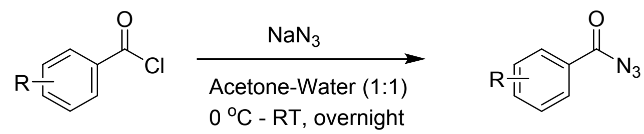
I. General Information

Unless otherwise specified, all chemicals and reagents were purchased from commercial suppliers. All photochemical reactions were degassed at -78 °C by the Freeze-Pump-Thaw method and carried out under Argon atmosphere unless otherwise stated. A 20 W CFL lamp purchased from Philips was used for all reactions. The photocatalyst complexes $Ru(bpy)_3Cl_2$, $Ir(ppy)_3$, and $Ir(ppy)_2(dtbbpy)(PF_6)$ are commercially available and were purchased from Sigma Aldrich. $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)](PF_6)$[S1] and $Cu(dap)_2Cl$[S2] were prepared as previously described.

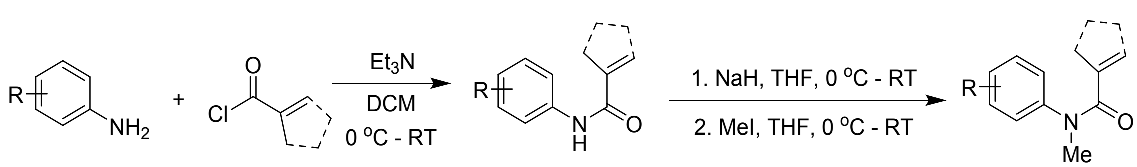
Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm), exposure to treatment with acidic anisaldehyde, phosphomolybdic acid, ninhydrin, or ceric ammonium molybdate stain followed by heating. Silica-gel chromatography was performed using a CombiFlash® $R_f{}^+$ system with RediSep® R_f Silica columns (230-400 mesh) using a proper eluent system. All products were characterized by appropriate techniques such as ^1H NMR, ^{13}C NMR, ^{19}F NMR, and HRMS analysis. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ on Agilent Technologies DD2 (600 MHz) instrument. Chemical shifts were quoted in parts per million (ppm) referenced to the residual solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet and m = multiplet. Coupling constants, J, were reported in hertz (Hz). ^{13}C chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of $CDCl_3$. High resolution mass spectra were obtained by using EI method from Korea Basic Science Institute (Daegu) or ESI method from KAIST Research Analysis Center (Daejeon). Infrared (IR) spectra were acquired on Bruker Alpha ATR FT-IR Spectrometer. Frequencies are given in wave numbers (cm^{-1}) and only selected peaks were reported. Melting point was measured with Buchi Melting Point M-565. Fluorescence emission spectra were collected on Shimadzu (RF-5301pc) Spectrofluorophotometer with excitation and emission slit width of 5.0 nm. Emission spectrum of 20 W CFL bulb was measured on HORIBA (model QM-400) spectrophotometer

II. General Procedure for the Preparation of Benzoyl Azides[S3-S4]



To a solution of benzoyl chloride (10 mmol) in acetone (10 mL), a solution of sodium azide (0.97 g, 15 mmol) in water (10 mL) was added dropwise (over 1 h) at 0 °C. The reaction mixture was warmed up to room temperature and stirred for overnight. After completion, acetone was removed under reduced pressure and the reaction mixture was extracted with EtOAc (10 mL x 3). The combined organic layers were dried over $MgSO_4$ and solvent was removed under reduced pressure. The residue was purified using silica gel column chromatography (*n*-Hexane/EtOAc) to give the corresponding acyl azide.

III. General Procedure for the Synthesis of *N*-Arylacrylamides[S5-S8]



Step 1: Under nitrogen atmosphere, a 50 mL two neck round bottom flask containing dry CH_2Cl_2 was charged with aromatic amine (5 mmol) and triethylamine (10 mmol). The resulting reaction mixture was cooled to 0 °C in ice bath for 15 min and then acryloyl chloride (7.5 mmol) was added via syringe at 0 °C. The reaction mixture was stirred at room temperature for overnight. After completion, the reaction was quenched with water and the product was extracted with

dichloromethane (10 mL x 3). The combined organic layers were dried over $MgSO_4$, concentrated in vacuum, and the residue was subjected to column chromatography (*n*-Hexane/EtOAc) to give the corresponding amide.

Step 2: To the above prepared amide (3.0 mmol) in dry THF (15 mL) was added in portions NaH (94 mg, 3.9 mmol) at 0 °C. After stirring for 15 min at the same temperature, iodomethane (0.59 g, 4.2 mmol) was added and the mixture was stirred until completion at room temperature (monitored by TLC). After addition of water, the mixture was extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent was removed in vacuum. All synthesized *N*-arylacrylamide substrates are known and their ^{1}H NMR and ^{13}C NMR data matched those reported in the literature. [S5-S8]

IV. Reaction Setup

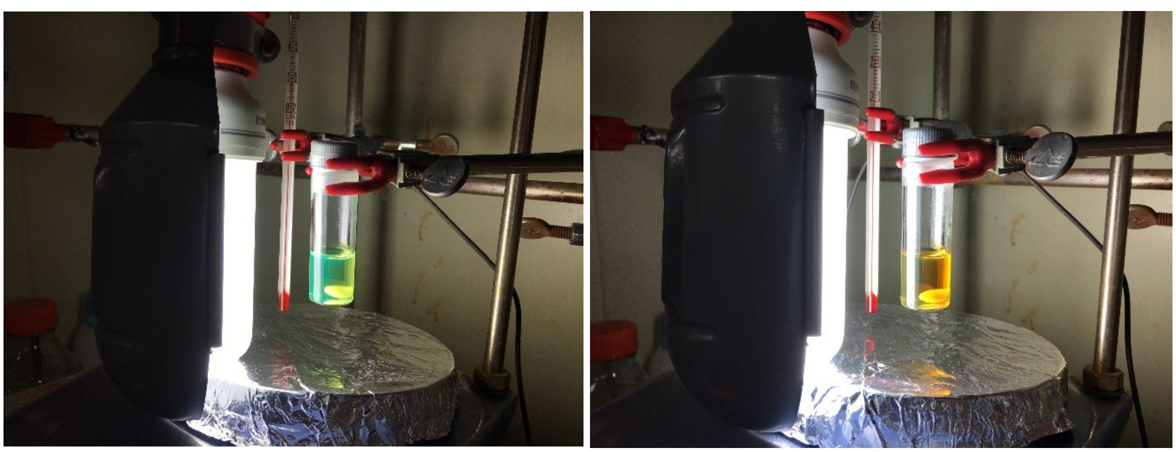
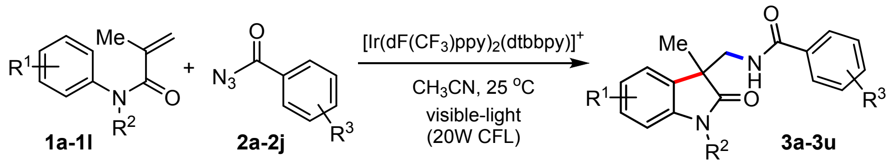


Figure S-1. Reaction setup: (left) before the reaction and (right) after the reaction.

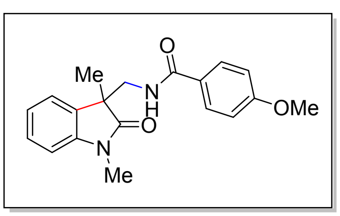
V. General Procedure for Aminoarylation of *N*-Aryl methacrylamides with Benzoyl Azides by Visible Light Photocatalysis



An oven-dried 5 mL borosilicate vial equipped with magnetic stirring bar was charged with substrate (0.20 mmol), benzoyl azide (0.30 mmol, 1.5 equiv), $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (5.6 mg, 2.5 mol %), and MeCN (1.5 mL). The resulting solution was degassed by three freeze-pump-thaw cycles. After the reaction mixture was thoroughly degassed, the vial was positioned approximately 3 cm from a 20 W compact fluorescent lamp. The reaction was stirred at 25 °C for 36 h under argon atmosphere. After completion, the pressure inside the vial was released by a syringe needle and the reaction mixture was diluted with CH_2Cl_2. The combined organic layers were concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (*n*-Hexane/EtOAc) to afford the products.

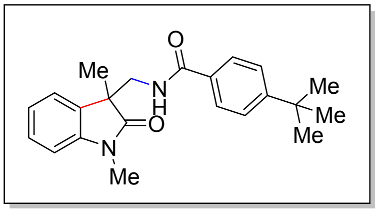
Characterization data of products (Table 2)

***N*-[(1,3-Dimethyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3a)**



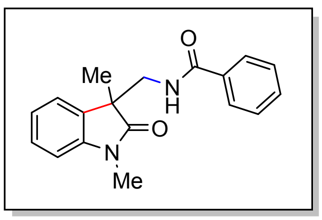
Colorless solid; m.p. 125-126 °C; R_f = 0.26 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 8.7 Hz, 2H), 7.31 (t, J = 6.8 Hz, 2H), 7.23 (d, J = 7.2 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.0 Hz, 1H), 4.23 (dd, J = 13.5, 8.5 Hz, 1H), 3.84 (s, 3H), 3.24 (s, 3H), 3.21 (dd, J = 13.5, 2.7 Hz, 1H), 1.45 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.3, 167.0, 162.2, 142.8, 132.1, 128.7, 128.5, 126.6, 123.1, 123.0, 113.7, 108.3, 55.4, 47.2, 45.1, 26.2, 20.2; **IR** (cm^{-1}) 3313, 3056, 2919, 2833, 1693, 1656, 1606, 1542, 1493, 1454, 1375, 1309, 1245, 1177, 1028, 835, 751, 661; **HRMS** (EI) m/z calculated for $C_{19}H_{20}N_2O_3$ $[M]^+$: 324.1474; found 324.1476.

4-(*tert*-Butyl)-*N*-[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3b)



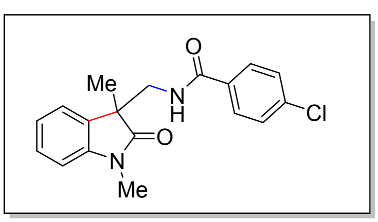
Colorless solid; m.p. 131-132 °C; R_f = 0.50 (1/1, n-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.25 (s, 1H), 7.11 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.9 Hz, 1H), 4.22 (dd, J = 13.5, 8.3 Hz, 1H), 3.26 (d, J = 2.7 Hz, 1H), 3.24 (s, 3H), 1.45 (s, 3H), 1.32 (s, 9H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.2, 167.4, 154.9, 142.8, 132.1, 131.5, 128.5, 126.8, 125.5, 123.1, 123.0, 108.3, 47.3, 45.0, 34.9, 31.1, 26.2, 20.2; **IR** (cm^{-1}) 3336, 2962, 2924, 2864, 1681, 1662, 1611, 1536, 1493, 1423, 1351, 1288, 1125, 1021, 931, 858, 750, 636; **HRMS** (EI) m/z calculated for $C_{22}H_{26}N_2O_2$ $[M]^+$: 350.1994; found: 350.1995.

***N*-[(1,3-Dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3c)**



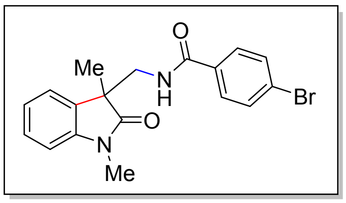
Colorless solid; m.p. 123-124 °C; R_f = 0.35 (1/1, n-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, J = 7.3 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.0 Hz, 3H), 7.12 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 7.7 Hz, 1H), 4.24 (dd, J = 13.5, 8.4 Hz, 1H), 3.25 (s, 3H), 3.24 (dd, J = 13.5, 8.4 Hz, 1H), 1.47 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.3, 167.5, 142.8, 134.3, 132.0, 131.5, 128.6, 128.5, 126.9, 123.8, 123.0, 108.4, 47.2, 45.1, 26.2, 20.2; IR (cm^{-1}) 3397, 3301, 3046, 3017, 2967, 2923, 1708, 1635, 1610, 1527, 1488, 1339, 1287, 1124, 1061, 930, 749, 712, 690; **HRMS** (EI) m/z calculated for $C_{18}H_{18}N_2O_2$ $[M]^+$: 294.1368; found: 294.1370.

4-Chloro-*N*-[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3d)



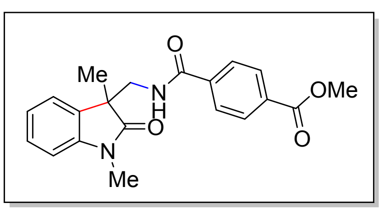
Colorless solid; m.p. 133-134 °C; R_f = 0.42 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 7.1 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.12 (td, J = 7.5, 1.0 Hz, 1H), 6.89 (d, J = 7.7 Hz, 1H), 4.23 (dd, *J* = 13.5, 8.4 Hz, 1H), 3.24 (s, 3H), 3.20 (dd, *J* = 13.5, 2.7 Hz, 1H), 1.45 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.3, 166.4, 142.8, 137.7, 132.7, 131.9, 128.8, 128.6, 128.4, 123.2, 122.9, 108.4, 47.0, 45.2, 26.2, 20.2; **IR** (cm^{-1}) 3319, 2967, 2917, 1681, 1663, 1609, 1539, 1486, 1423, 1385, 1350, 1291, 1090, 1012, 909, 848, 752, 734, 650; **HRMS** (EI) m/z calculated for $C_{18}H_{17}ClN_2O_2$ $[M]^+$: 328.0979; found: 328.0978.

4-Bromo-*N*-[(1,3-dimethyl-2-oxoindolin-3-yl]methyl)benzamide (Table 2, 3e)



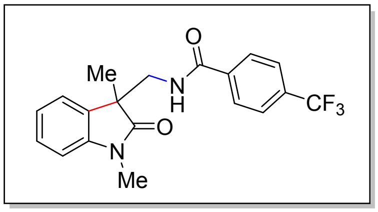
Colorless solid; m.p. 139-140 °C; R_f = 0.46 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 4.24 (dd, *J* = 13.5, 8.4 Hz, 1H), 3.25 (s, 3H), 3.20 (dd, *J* = 13.6, 2.6 Hz, 1H), 1.46 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.3, 166.5, 142.7, 133.1, 131.9, 131.8, 128.6, 126.2, 123.2, 123.0, 108.4, 47.0, 45.2, 26.3, 20.2; **IR** (cm^{-1}) 3324, 3056, 2969, 2916, 1666, 1611, 1589, 1540, 1471, 1425, 1384, 1289, 1102, 1067, 1008, 991, 847, 750, 697; **HRMS** (EI) m/z calculated for $C_{18}H_{17}BrN_2O_2$ $[M]^+$: 372.0473; found: 372.0476.

Methyl-4-{[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]carbamoyl}benzoate (Table 2, 3f)



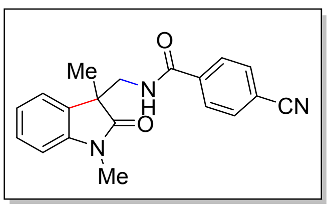
Colorless solid; m.p. 143-145 °C; R_f = 0.29 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 4.24 (dd, *J* = 13.5, 8.4 Hz, 1H), 3.92 (s, 3H), 3.24 (s, 3H), 3.21 (dd, *J* = 2.5 Hz, 1H), 1.46 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.2, 166.6, 166.3, 142.7, 138.1, 132.7, 131.9, 129.8, 128.6, 127.0, 123.2, 123.0, 108.5, 52.3, 47.1, 45.2, 26.3, 20.3; **IR** (cm^{-1}) 3314, 3054, 2969, 2928, 2869, 1697, 1611, 1534, 1492, 1469, 1379, 1349, 1275, 1106, 1017, 729.66; **HRMS** (ESI) m/z calculated for $C_{20}H_{20}N_2NaO_4$ $[M+Na]^+$: 375.1321; found: 375.1322.

***N*-[(1,3-Dimethyl-2-oxoindolin-3-yl)methyl]-4-(trifluoromethyl)benzamide (Table 2, 3g)**



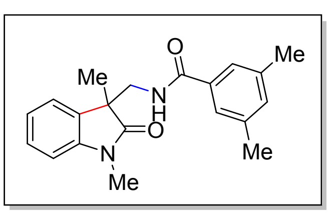
Colorless solid; m.p. 134-135 °C; R_f = 0.46 (1/1, n-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 7.7 Hz, 1H), 7.35-7.28 (m, 2H), 7.13 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 7.7 Hz, 1H), 4.25 (dd, J = 13.5, 8.4 Hz, 1H), 3.25 (s, 3H), 3.23 (dd, J = 13.5, 2.7 Hz, 1H), 1.46 (s, 3H); **^{19}F NMR** (564 MHz, $CDCl_3$) δ -62.9; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.2, 166.1, 142.8, 137.5, 133.2 (q, J = 33.2 Hz), 131.9, 128.6, 127.4, 125.6 (q, J = 3.7 Hz), 123.6 (q, J = 271.8 Hz), 123.2, 122.9, 108.5, 46.9, 45.2, 26.2, 20.3; **IR** (cm^{-1}) 3353, 3062, 2964, 2904, 1696, 1665, 1608, 1544, 1493, 1381, 1327, 1290, 1159, 1109, 1065, 1016, 855, 742, 696; **HRMS** (EI) m/z calculated for $C_{19}H_{17}F_3N_2O_2$ $[M]^+$: 362.1242; found: 362.1245.

4-Cyano-*N*-[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3h)



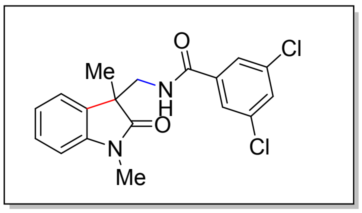
Yellow solid; m.p. 152-153 °C; R_f = 0.28 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.90 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 6.7 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.13 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 4.24 (dd, J = 13.6, 8.4 Hz, 1H), 3.24 (s, 3H), 3.20 (dd, J = 13.6, 2.6 Hz, 1H), 1.45 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.2, 165.7, 142.7, 138.1, 132.4, 131.8, 128.7, 127.7, 123.3, 122.9, 118.0, 115.1, 108.6, 46.9, 45.3, 26.3, 20.3; **IR** (cm^{-1}) 3298, 3061, 2971, 2933, 2873, 2225, 1682, 1656, 1612, 1548, 1493, 1457, 1382, 1339, 1299, 1105, 921, 855, 717, 636; **HRMS** (EI) m/z calculated for $C_{19}H_{17}N_3O_2$ $[M]^+$: 319.1321; found: 319.1322.

***N*-[(1,3-Dimethyl-2-oxoindolin-3-yl)methyl]-3,5-dimethylbenzamide (Table 2, 3i)**



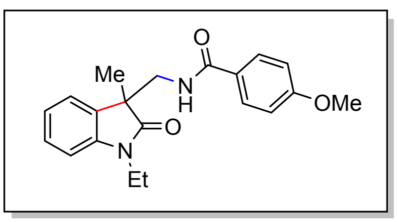
Colorless solid; m.p. 157-159 °C; R_f = 0.44 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 (s, 2H), 7.33-7.26 (m, 2H), 7.21 (d, J = 6.4 Hz, 1H), 7.14 – 7.06 (m, 2H), 6.87 (d, J = 7.7 Hz, 1H), 4.21 (dd, J = 13.5, 8.4 Hz, 1H), 3.24 (dd, J = 12.0 Hz, 8.4 Hz, 1H), 3.23 (s, 3H), 2.34 (s, 6H), 1.45 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.3, 167.9, 142.8, 138.2, 134.3, 133.1, 132.1, 128.5, 124.7, 123.1, 123.1, 108.3, 47.4, 45.1, 26.2, 21.2, 20.2; **IR** (cm^{-1}) 3344, 3053, 2924, 1683, 1661, 1612, 1532, 1493, 1473, 1450, 1426, 1351, 1317, 1243, 1122, 932, 870, 749, 689; **HRMS** (EI) m/z calculated for $C_{20}H_{22}N_2O_2$ $[M]^+$: 322.1681; found: 322.1679.

3,5-Dichloro-*N*-[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3j)



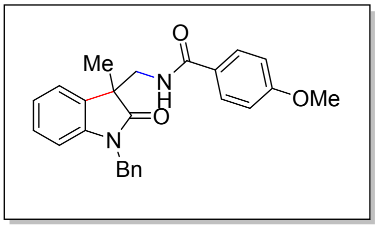
Colorless solid; m.p. 202-203 °C; R_f = 0.61 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.46 (s, 1H), 7.37 – 7.27 (m, 3H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.19 (dd, *J* = 13.5, 8.2 Hz, 1H), 3.25 (s, 3H), 3.22 (s, 1H), 1.45 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.2, 164.9, 142.8, 137.2, 135.4, 131.7, 131.4, 128.7, 125.6, 123.3, 123.0, 108.5, 47.0, 45.3, 26.3, 20.3; **IR** (cm^{-1}) 3322, 3066, 2975, 2921, 1687, 1664, 1612, 1541, 1494, 1469, 1427, 1385, 1346, 1288, 1117, 874, 796, 754, 672; **HRMS** (EI) m/z calculated for $C_{18}H_{16}Cl_2N_2O_2$ $[M]^+$: 362.0589; found: 362.0592.

***N*-[(1-Ethyl-3-methyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3k)**



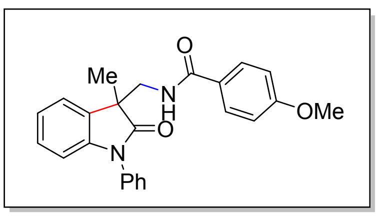
Colorless solid; m.p. 104-105 °C; R_f = 0.30 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.8 Hz, 2H), 7.31-7.26 (m, 2H), 7.23 (d, *J* = 6.9 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 6.92-6.84 (m, 3H), 4.20 (dd, *J* = 13.5, 8.4 Hz, 1H), 3.81 (s, 3H), 3.77 (q, *J* = 7.2 Hz, 2H), 3.21 (dd, *J* = 13.5, 2.8 Hz, 1H), 1.43 (s, 3H), 1.26 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.9, 166.9, 162.2, 141.9, 132.3, 128.7, 128.4, 126.6, 123.2, 122.9, 113.7, 108.5, 55.3, 47.2, 45.1, 34.7, 20.2, 12.7; **IR** (cm^{-1}) 3322, 3047, 2975, 2929, 2833, 1689, 1654, 1604, 1540, 1503, 1466, 1366, 1307, 1245, 1174, 1108, 1024, 992, 836, 748, 606; **HRMS** (EI) m/z calculated for $C_{20}H_{22}N_2O_3$ $[M]^+$: 338.1630; found: 338.1627.

N-[(1-Benzyl-3-methyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3l)



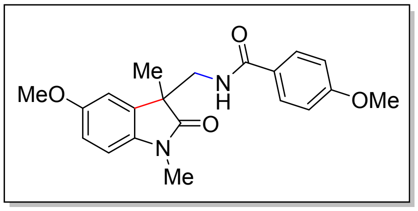
Colorless solid; m.p. 129-130 °C; R_f = 0.40 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 7.4 Hz, 1H), 7.27 (s, 5H), 7.19 (t, J = 7.4 Hz, 1H), 7.07 (t, J = 7.5 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 7.8 Hz, 1H), 4.97 (d, J = 15.7 Hz, 1H), 4.89 (d, J = 15.7 Hz, 1H), 4.24 (dd, J = 13.5, 8.2 Hz, 1H), 3.83 (s, 3H), 3.38 (dd, J = 13.5, 3.1 Hz, 1H), 1.51 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.4, 166.9, 162.2, 141.9, 135.6, 132.0, 128.8, 128.8, 128.4, 127.7, 127.1, 126.5, 123.2, 123.1, 113.7, 109.3, 55.4, 47.6, 45.2, 43.7, 20.5; **IR** (cm^{-1}) 3361, 2993, 2928, 2842, 1709, 1653, 1605, 1544, 1502, 1452, 1383, 1349, 1288, 1247, 1179, 1108, 1028, 845, 742, 610; **HRMS** (EI) m/z calculated for $C_{25}H_{24}N_2O_3$ $[M]^+$: 400.1787; found: 400.1786.

4-Methoxy-*N*-[(3-methyl-2-oxo-1-phenylindolin-3-yl)methyl]benzamide (Table 2, 3m)



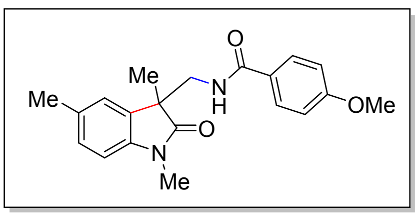
Colorless solid; m.p. 125-126 °C; R_f = 0.40 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, J = 8.7 Hz, 2H), 7.54 (t, J = 7.7 Hz, 2H), 7.42 (t, J = 9.7 Hz, 3H), 7.38 (d, J = 7.3 Hz, 1H), 7.23 (d, J = 7.4 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 7.8 Hz, 1H), 4.34 (dd, J = 13.6, 8.5 Hz, 1H), 3.82 (s, 3H), 3.37 (dd, J = 13.6, 2.7 Hz, 1H), 1.58 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.9, 167.0, 162.2, 142.8, 134.0, 131.9, 129.7, 128.8, 128.4, 128.3, 126.5, 126.4, 123.6, 123.3, 113.7, 109.7, 55.4, 47.5, 45.3, 20.5; **IR** (cm^{-1}) 3354, 3061, 2987, 2927, 2837, 2231, 1692, 1642, 1605, 1545, 1504, 1465, 1371, 1327, 1290, 1251, 1177, 1024, 926, 844, 741, 697; **HRMS** (EI) m/z calculated for $C_{24}H_{22}N_2O_3$ $[M]^+$: 386.1630; found: 386.1632.

4-Methoxy-*N*-[(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3n)



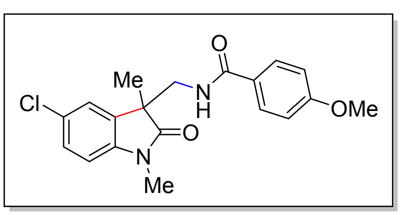
Colorless solid; m.p. 130-131 ºC; R_f = 0.19 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 1H), 6.96 – 6.88 (m, 3H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 4.24 (dd, *J* = 13.5, 8.6 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.22 (s, 3H), 3.16 (dd, *J* = 13.5, 2.4 Hz, 1H), 1.44 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.0, 167.0, 162.2, 156.4, 136.1, 133.4, 128.8, 126.6, 113.7, 113.1, 110.1, 108.8, 55.9, 55.4, 47.5, 45.1, 26.3, 20.2; **IR** (cm^{-1}) 3326, 3063, 2924, 2839, 1679, 1655, 1603, 1545, 1498, 1457, 1433, 1366, 1307, 1250, 1215, 1174, 1125, 1026, 905, 845, 815, 768, 729, 694; **HRMS** (EI) m/z calculated for $C_{20}H_{22}N_2O_4$ $[M]^+$: 354.1580; found: 354.1582.

4-Methoxy-*N*-[(1,3,5-trimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3o)



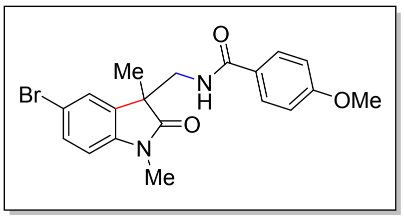
Yellow solid; m.p. 133-134 ºC; R_f = 0.35 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 7.8 Hz, 1H), 4.23 (dd, *J* = 13.5, 8.6 Hz, 1H), 3.83 (s, 3H), 3.21 (s, 3H), 3.14 (dd, *J* = 13.5, 2.4 Hz, 1H), 2.34 (s, 3H), 1.43 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.3, 167.0, 162.2, 140.4, 132.8, 132.2, 128.8, 128.7, 126.7, 123.8, 113.7, 108.1, 55.4, 47.1, 45.1, 26.2, 21.1, 20.2; **IR** (cm^{-1}) 3365, 2963, 2925, 2867, 1692, 1603, 1536, 1496, 1351, 1248, 1176, 1110, 1026, 842, 806, 765, 728; **HRMS** (EI) m/z calculated for $C_{20}H_{22}N_2O_3$ $[M]^+$: 338.1630; found: 338.1628.

***N*-[(5-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3p)**



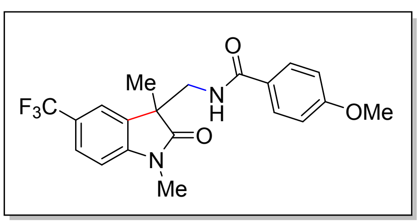
Colorless solid; m.p. 164-165 ºC; R_f = 0.27 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.12 (s, 1H), 6.91 (d, *J* = 7.7 Hz, 2H), 6.79 (t, *J* = 7.0 Hz, 1H), 4.20 (dd, *J* = 13.3, 7.7 Hz, 1H), 3.83 (s, 3H), 3.20 (d, *J* = 14.8 Hz, 4H), 1.45 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.8, 167.0, 162.3, 141.4, 133.8, 128.8, 128.6, 128.4, 126.5, 123.7, 113.8, 109.3, 55.4, 47.6, 44.9, 26.3, 20.1; **IR** (cm^{-1}) 3361, 3311, 3065, 2969, 2927, 1700, 1653, 1606, 1542, 1488, 1339, 1248, 1168, 1029, 834, 770, 660; **HRMS** (EI) m/z calculated for $C_{19}H_{19}ClN_2O_3$ [M]$^+$: 358.1084; found: 358.1085.

***N*-[(5-Bromo-1,3-dimethyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3q)**



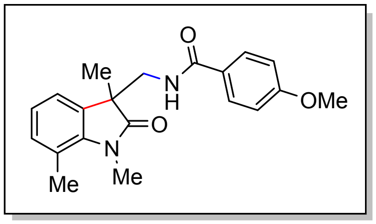
Colorless solid; m.p. 166-167 ^{o}C; R_f = 0.26 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 9.9 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.1 Hz, 1H), 4.22 (dd, *J* = 13.5, 8.5 Hz, 1H), 3.85 (s, 3H), 3.23 (s, 3H), 3.20 (dd, *J* = 13.6, 2.6 Hz, 1H), 1.45 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.7, 167.0, 162.3, 141.9, 134.1, 131.4, 128.8, 126.5, 115.9, 113.8, 109.8, 55.4, 47.5, 44.9, 26.3, 20.1; **IR** (cm^{-1}) 3365, 3315, 3057, 2925, 1699, 1652, 1605, 1540, 1486, 1248, 1169, 1029, 832, 770; **HRMS** (EI) m/z calculated for $C_{19}H_{19}BrN_2O_3$ [M]$^+$: 402.0579; found: 402.0581.

***N*-{[1,3-Dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl]methyl}-4-methoxybenzamide (Table 2, 3r)**



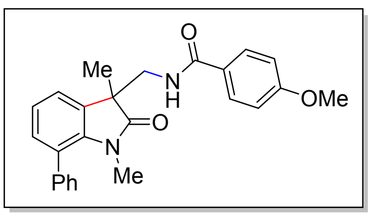
Colorless solid; m.p. 135-136 ^{o}C; R_f = 0.30 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.56 (s, 1H), 7.09 (d, *J* = 6.9 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.24 (dd, *J* = 13.6, 8.5 Hz, 1H), 3.84 (s, 3H), 3.27 (s, 3H), 3.24 (dd, *J* = 13.6, 2.9 Hz, 1H), 1.48 (s, 3H); **^{19}F NMR** (564 MHz, $CDCl_3$) δ -61.5; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.2, 167.0, 162.3, 145.8, 132.7, 128.7, 126.4, 126.3 (q, *J* = 4.0 Hz), 125.3, 123.3, 120.25 (q, *J* = 4.5 Hz), 113.8, 108.1, 55.4, 47.5, 44.8, 26.4, 20.0; **IR** (cm^{-1}) 3358, 2996, 2940, 2925, 2847, 1698, 1653, 1606, 1539, 1502, 1326, 1291, 1252, 1159, 1112, 1065, 1027, 896, 847, 819, 770, 748, 726, 610; **HRMS** (EI) m/z calculated for $C_{20}H_{19}F_3N_2O_3$ [M]$^+$: 392.1348; found: 392.1351.

4-Methoxy-*N*-[(1,3,7-trimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3s)



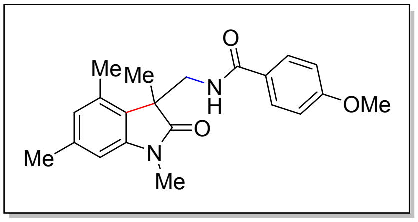
Light brown solid; m.p. 140-141 °C; R_f = 0.27 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 7.6 Hz, 1H), 7.13 (d, J = 7.1 Hz, 1H), 7.02 (d, J = 7.5 Hz, 1H), 6.99 (t, J = 7.4 Hz, 1H), 6.92 (d, J = 8.7 Hz, 2H), 4.21 (dd, J = 13.5, 8.6 Hz, 1H), 3.83 (s, 3H), 3.51 (s, 3H), 3.13 (dd, J = 13.5, 2.4 Hz, 1H), 2.58 (s, 3H), 1.42 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 181.1, 166.9, 162.2, 140.5, 132.8, 132.2, 128.8, 126.7, 123.0, 120.9, 120.0, 113.7, 55.4, 46.4, 45.3, 29.5, 20.5, 18.9; **IR** (cm^{-1}) 3233, 3052, 3009, 2968, 2921, 1698, 1636, 1601, 1555, 1504, 1457, 1354, 1308, 1252, 1171, 1076, 1023, 908, 842, 734, 699; **HRMS** (EI) m/z calculated for $C_{20}H_{22}N_2O_3$ $[M]^+$: 338.1630; found: 338.1632.

***N*-[(1,3-Dimethyl-2-oxo-7-phenylindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3t)**



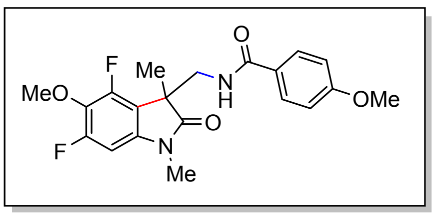
Colorless solid; m.p. 145-146 °C; R_f = 0.38 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, J = 8.8 Hz, 2H), 7.43 – 7.38 (m, 3H), 7.37 – 7.26 (m, 4H), 7.15 – 7.09 (m, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.27 (dd, J = 13.5, 8.5 Hz, 1H), 3.85 (s, 3H), 3.24 (dd, J = 13.5, 2.5 Hz, 1H), 2.76 (s, 3H), 1.50 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 181.3, 167.0, 162.2, 139.6, 138.6, 133.1, 131.5, 129.8, 128.8, 127.8, 127.8, 126.7, 125.8, 122.4, 122.0, 113.8, 55.4, 46.5, 45.4, 30.1, 20.5; **IR** (cm^{-1}) 3269, 2970, 2929, 2839, 1697, 1636, 1608, 1546, 1506, 1441, 1299, 1253, 1176, 1107, 1063, 1025, 838, 765, 752, 700, 630; **HRMS** (EI) m/z calculated for $C_{25}H_{24}N_2O_3$ $[M]^+$: 400.1787; found: 400.1784.

4-Methoxy-*N*-[(1,3,4,6-tetramethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3u)



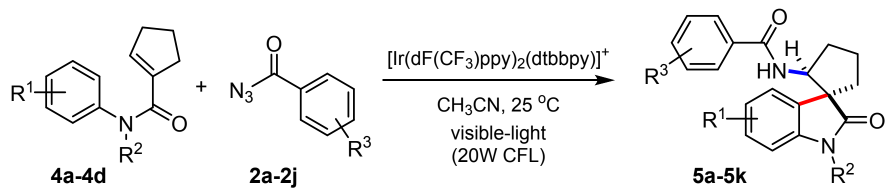
Light yellow solid; m.p. 126-128 °C; R_f = 0.36 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 6.6 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.69 (s, 1H), 6.54 (s, 1H), 4.43 (dd, J = 13.5, 8.2 Hz, 1H), 3.82 (s, 3H), 3.25 (dd, J = 13.5, 2.8 Hz, 1H), 3.20 (s, 3H), 2.43 (s, 3H), 2.33 (s, 3H), 1.50 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.6, 166.9, 162.1, 143.3, 138.4, 134.7, 128.7, 126.7, 126.3, 126.1, 113.7, 107.0, 55.3, 47.9, 43.4, 30.0, 26.2, 21.5, 18.3; **IR** (cm^{-1}) 3338, 3052, 2928, 2835, 1680, 1604, 1543, 1503, 1453,1308, 1245, 1176, 1027, 843, 765, 730, 601; **HRMS** (EI) m/z calculated for $C_{22}H_{19}NO$ $[M]^+$: 352.1787; found: 352.1784.

***N*-[(4,6-Difluoro-5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3v)**



Colorless solid; m.p. 128-129 °C; R_f = 0.26 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.6 Hz, 2H), 7.00 – 6.94 (m, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.46 (d, J = 9.7 Hz, 1H), 4.24 (dd, J = 13.5, 7.8 Hz, 1H), 3.93 (s, 3H), 3.83 (s, 3H), 3.46 (dd, J = 13.5, 3.5 Hz, 1H), 3.17 (s, 3H), 1.53 (s, 3H); **^{19}F NMR** (564 MHz, $CDCl_3$) δ -126.7 (t, J = 9.3 Hz), -133.1 (d, J = 8.9 Hz); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.3, 166.9, 162.2, 156.5 (dd, J = 247.9, 5.6 Hz), 153.3 (dd, J = 251.3, 6.4 Hz), 138.6 (t, J = 12.7 Hz), 132.5(t, J = 14.7 Hz), 128.7, 126.5, 113.8, 113.6 (dd, J = 18.4, 3.4 Hz), 94.0 (dd, J = 25.6, 3.1 Hz), 62.5, 55.4, 48.1, 44.1, 26.6, 18.7; **IR** (cm^{-1}) 3324, 3069, 2937, 2839, 1701, 1634, 1606, 1551, 1507, 1428, 1343, 1287, 1247, 1196, 1057, 1018, 982, 848, 819, 769, 608; **HRMS** (EI) m/z calculated for $C_{20}H_{20}F_2N_2O_4$ $[M]^+$: 390.1391; found: 390.1393.

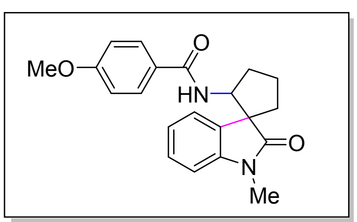
VI. General Procedure for Aminoarylation of *N*-Aryl-cyclopentene-carboxamides with Benzoyl Azides by Visible Light Photocatalysis



An oven-dried 5 mL borosilicate vial equipped with magnetic stirring bar was charged with substrate (0.20 mmol), benzoyl azide (0.30 mmol, 1.5 equiv), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 2.5 mol%), and MeCN (1.5 mL). The resulting solution was degassed by three freeze-pump-thaw cycles and the reaction mixture was irradiated for 36 hours with 20 W CFL light at room temperature from a distance of approximately 3 cm. After completion, the pressure inside the vial was released by a syringe needle and the reaction mixture was diluted with CH_2Cl_2 and directly loaded on silica get. Purification of the crude product was achieved by flash column chromatography using *n*-Hexane/EtOAc as eluent.

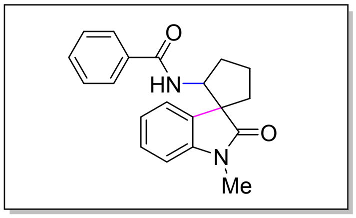
Characterization data of products (Table 3)

4-Methoxy-*N*-[1'-methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5a)



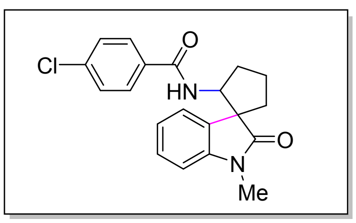
Colorless solid; m.p. 146-147 ^{o}C; R_f = 0.39 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 7.4 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 8.7 Hz, 2H), 6.79 (d, J = 7.7 Hz, 1H), 4.79 (dt, J = 8.0, 6.7 Hz, 1H), 3.82 (s, 3H), 3.20 (s, 3H), 2.38 (m, 2H), 2.13 (m, 2H), 2.04 – 1.97 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.5, 165.9, 162.1, 142.6, 134.5, 128.7, 127.9, 126.6, 123.3, 122.5, 113.6, 108.1, 58.5, 56.7, 55.4, 37.5, 34.3, 26.3, 23.6; **IR** (cm^{-1}) 3299, 2958, 2934, 2834, 1681, 1606, 1556, 1504, 1351, 1304, 1243, 1170, 1088, 1027, 826, 747, 625; **HRMS** (EI) m/z calculated for $C_{21}H_{22}N_2O_3$ $[M]^+$: 350.1630; found: 350.1632.

_N_-(1'-Methyl-2'-oxospiro[cyclopentane-1,3'-indolin]-2-yl)benzamide (Table 3, 5b)



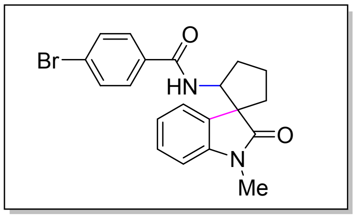
Colorless solid; m.p. 158-160 °C; R_f = 0.52 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 10.9 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 4.80 (q, *J* = 7.1 Hz, 1H), 3.21 (s, 3H), 2.45 – 2.34 (m, 2H), 2.18 – 2.11 (m, 2H), 2.05 – 1.98 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.4, 166.3, 142.6, 134.4, 134.3, 131.4, 128.5, 127.9, 126.9, 123.3, 122.5, 108.1, 58.6, 56.7, 37.5, 34.2, 26.3, 23.6; **IR** (cm^{-1}) 3276, 3079, 2931, 2867, 1697, 1637, 1610, 1545, 1471, 1332, 1157, 1084, 1019, 914, 845, 800, 737, 694; **HRMS** (EI) m/z calculated for $C_{20}H_{20}N_2O_2$ $[M]^+$: 320.1525; found: 320.1523.

4-Chloro-_N_-(1'-methyl-2'-oxospiro[cyclopentane-1,3'-indolin]-2-yl)benzamide (Table 3, 5c)



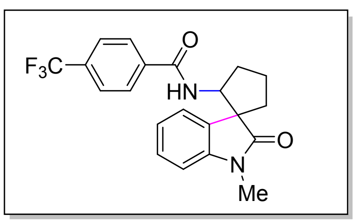
Colorless solid; m.p. 171-172 °C; R_f = 0.59 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 15.4 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 4.73 (q, *J* = 6.8 Hz, 1H), 3.20 (s, 3H), 2.48 - 2.32 (m, 2H), 2.18 – 2.10 (m, 2H), 2.05 – 1.96 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.4, 165.2, 142.5, 137.6, 134.4, 132.6, 128.7, 128.3, 128.0, 123.4, 122.5, 108.2, 58.6, 56.6, 37.6, 34.3, 26.3, 23.6; **IR** (cm^{-1}) 3317, 3046, 2922, 2868, 2853, 1679, 1651, 1613, 1530, 1471, 1379, 1352, 1305, 1272, 1152, 1116, 1086, 1009, 848, 747, 700, 649; **HRMS** (EI) m/z calculated for $C_{20}H_{19}ClN_2O_2$ $[M]^+$: 354.1135; found: 354.1133.

4-Bromo-*N*-[1'-methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5d)



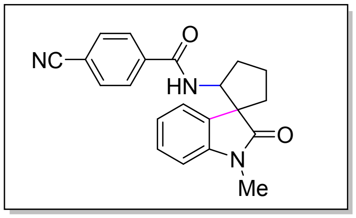
Colorless solid; m.p. 194-195 °C; R_f = 0.59 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.25 (t, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 4.73 (q, *J* = 6.8 Hz, 1H), 3.20 (s, 3H), 2.47 – 2.39 (m, 1H), 2.37 (m, 1H), 2.18 – 2.11 (m, 2H), 2.05 – 1.98 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.4, 165.3, 142.5, 134.4, 133.1, 131.7, 128.5, 128.0, 126.1, 123.4, 122.5, 108.2, 58.6, 56.6, 37.6, 34.3, 26.3, 23.6; **IR** (cm^{-1}) 3320, 3052, 2960, 2945, 2868, 1678, 1650, 1612, 1530, 1471, 1421, 1379, 1352, 1270, 1150, 1115, 1089, 1068, 1006, 846, 746, 697; **HRMS** (EI) m/z calculated for $C_{20}H_{19}BrN_2O_2$ $[M]^+$: 398.0630; found: 398.0633.

***N*-(1'-Methyl-2'-oxospiro[cyclopentane-1,3'-indolin]-2-yl)-4-(trifluoromethyl)-benzamide (Table 3, 5e)**



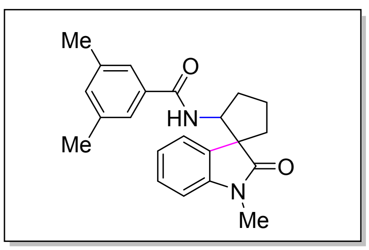
Colorless solid; m.p. 167-168 °C; R_f = 0.65 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 6.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.81 (s, 1H), 4.73 (m, 1H), 3.22 (s, 3H), 2.45 (dq, *J* = 11.6, 5.9, 3.5 Hz, 1H), 2.40 – 2.33 (m, 1H), 2.20 – 2.15 (m, 2H), 2.07 – 1.99 (m, 2H); ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.9; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.3, 165.0, 142.5, 137.5, 134.4, 133.1 (q, *J* = 32.4 Hz), 128.1, 127.4, 125.5 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 273.3), 123.4, 122.5, 108.2, 58.7, 56.5, 37.6, 34.3, 26.3, 23.6; **IR** (cm^{-1}) 3246, 3047, 2950, 2866, 1700, 1638, 1545, 1472, 1320, 1115, 1063, 1015, 865, 773, 737, 669; **HRMS** (EI) m/z calculated for $C_{21}H_{19}F_3N_2O_2$ $[M]^+$: 388.1399; found: 388.1399.

4-Cyano-*N*-[1'-methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5f)



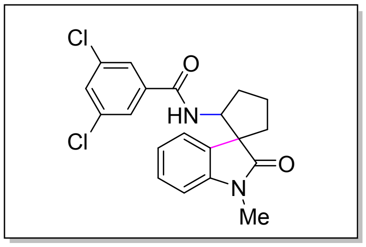
Colorless solid; m.p. 166-167 °C; $R_f = 0.44$ (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 7.3 Hz, 1H), 7.33 – 7.24 (m, 2H), 7.11 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 4.69 (q, J = 6.7 Hz, 1H), 3.21 (s, 3H), 2.45 (q, J = 8.2 Hz, 1H), 2.37 (q, J = 12.3, 8.4 Hz, 1H), 2.19 – 2.12 (m, 2H), 2.06 – 1.97 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.3, 164.5, 142.4, 138.2, 134.3, 132.4, 128.1, 127.6, 123.5, 122.5, 118.1, 114.9, 108.3, 58.7, 56.4, 37.7, 34.4, 26.4, 23.6; **IR** (cm^{-1}) 3310, 3053, 2953, 2869, 2228, 1654, 1610, 1527, 1492, 1468, 1376, 1348, 1269, 1088, 1018, 913, 854, 745; **HRMS** (EI) m/z calculated for $C_{21}H_{19}N_3O_2$ $[M]^+$: 345.1477; found: 345.1475.

3,5-Dimethyl-*N*-[1'-methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5g)



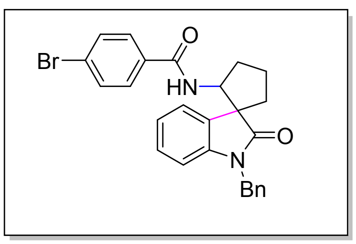
Colorless solid; m.p. 148-149 °C; $R_f = 0.61$ (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.32 (d, J = 7.4 Hz, 1H), 7.27 (s, 2H), 7.24 (d, J = 7.7 Hz, 1H), 7.09 (q, J = 7.9 Hz, 3H), 6.79 (d, J = 7.7 Hz, 1H), 4.83 (q, J = 7.3 Hz, 1H), 3.21 (s, 3H), 2.41 – 2.35 (m, 2H), 2.32 (s, 6H), 2.18 – 2.12 (m, 2H), 2.05 – 1.99 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.4, 166.8, 142.7, 138.1, 134.3, 134.2, 132.9, 127.9, 124.6, 123.3, 122.5, 108.0, 58.6, 56.8, 37.3, 33.9, 26.2, 23.4, 21.2; **IR** (cm^{-1}) 3249, 3051, 2949, 2916, 2868, 1707, 1634, 1609, 1540, 1471, 1334, 1259, 1089, 908, 858, 770, 733, 692, 544, 495, 472; **HRMS** (EI) m/z calculated for $C_{22}H_{24}N_2O_2$ $[M]^+$: 348.1838; found: 348.1840.

3,5-Dichloro-*N*-[1'-methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5h)



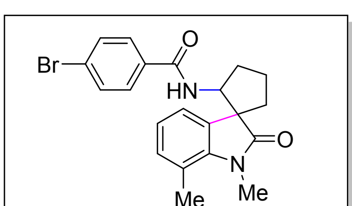
Colorless solid; m.p. 198-199 °C; R_f = 0.77 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 7.55 (d, *J* = 1.8 Hz, 2H), 7.43 (t, *J* = 1.6 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 6.7 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 4.72 (q, *J* = 6.9 Hz, 1H), 3.22 (s, 3H), 2.44 – 2.39 (m, 1H), 2.39 – 2.34 (m, 1H), 2.18 – 2.13 (m, 2H), 2.02 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) *δ* 179.2, 163.9, 142.6, 137.2, 135.3, 134.1, 131.2, 128.1, 125.6, 123.4, 122.5, 108.2, 58.8, 56.6, 37.4, 34.1, 26.3, 23.5; **IR** (cm^{-1}) 3329, 3070, 2969, 2932, 2868, 1678, 1651, 1611, 1561, 1535, 1496, 1461, 1379, 1352, 1306, 1274, 1117, 1089, 904, 875, 794, 748, 699, 670; **HRMS** (EI) m/z calculated for $C_{20}H_{18}Cl_2N_2O_2$ $[M]^+$: 388.0745; found: 388.0748.

***N*-(1'-Benzyl-2'-oxospiro[cyclopentane-1,3'-indolin]-2-yl)-4-bromobenzamide (Table 3, 5i)**



Colorless solid; m.p. 162-163 °C; R_f = 0.70 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 7.49 (q, 4H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.15 (q, *J* = 9.0 Hz, 4H), 7.09 (dt, *J* = 15.8, 7.3 Hz, 4H), 6.69 (d, 1H), 5.02 (d, *J* = 15.8 Hz, 1H), 4.92 (q, *J* = 7.8 Hz, 1H), 4.78 (d, *J* = 15.8 Hz, 1H), 2.47 – 2.39 (m, 2H), 2.22 – 2.11 (m, 2H), 2.10 – 2.00 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) *δ* 179.6, 165.3, 141.9, 135.4, 134.3, 132.8, 131.7, 128.7, 128.5, 127.9, 127.6, 126.9, 126.1, 123.5, 122.6, 109.0, 58.6, 56.8, 43.7, 38.0, 34.3, 23.7; IR (cm^{-1}) 3362, 3053, 3035, 2923, 2853, 1684, 1662, 1609, 1529, 1483, 1462, 1349, 1149, 1070, 1010, 843, 749, 733, 697; **HRMS** (EI) m/z calculated for $C_{26}H_{23}BrN_2O_2$ $[M]^+$: 474.0943; found: 474.0946.

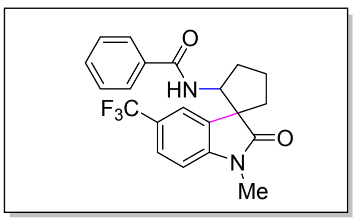
4-Bromo-*N*-[1',7'-dimethyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5j)



Colorless solid; m.p. 130-132 °C; R_f = 0.69 (1/1, *n*-Hexane/EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) *δ* 7.58 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* =

7.9 Hz, 2H), 7.34 (d, J = 7.3 Hz, 1H), 7.14 (t, J = 4.3 Hz, 1H), 6.97 (d, J = 4.4 Hz, 2H), 4.73 (q, J = 7.2 Hz, 1H), 3.48 (s, 3H), 2.53 (s, 3H), 2.43 – 2.31 (m, 2H), 2.15 – 2.06 (m, 2H), 2.02 – 1.94 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 180.1, 165.2, 140.3, 135.2, 133.1, 131.7, 131.7, 128.5, 126.0, 123.3, 120.4, 119.7, 58.8, 56.0, 38.3, 34.5, 29.6, 23.8, 18.9; **IR** (cm^{-1}) 3292, 3049,,2954, 2927, 2870, 1703, 1632, 1591, 1542, 1455, 1332, 1145, 1095, 1068, 1010, 845, 743, 644; **HRMS** (EI) m/z calculated for $C_{21}H_{21}BrN_2O_2$ [M]$^+$: 412.0786; found: 412.0789.

***N*-[1'-Methyl-2'-oxo-5'-(trifluoromethyl)spiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5k)**

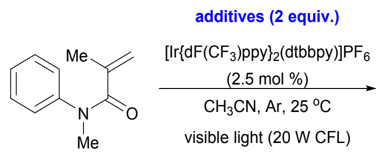


Colorless solid; m.p. 231-232 ^{o}C; R_f = 0.57 (1/1, *n*-Hexane/EtOAc);

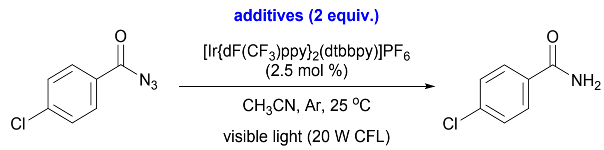
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.39 (t, J = 7.7 Hz, 1H), 7.32 (d, J = 7.2 Hz, 2H), 7.25 (t, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.81 (d, J = 7.7 Hz, 1H), 4.79 (q, J = 6.9 Hz, 1H), 4.59 (s, 2H), 3.21 (s, 3H), 2.45-2.35 (m, 2H), 2.19-2.13 (m, 2H), 2.05-2.00 (m, 2H); **^{19}F NMR** (564 MHz, $CDCl_3$) δ -61.4; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 179.3, 166.5, 145.7, 135.3, 134.1, 131.5, 128.5, 126.8, 125.8 (q, J = 3.9 Hz), 125.5 (q, J = 31.7), 123.4, 119.4 (q, J = 3.7 Hz), 107.9, 58.7, 56.8, 37.7, 34.4, 26.4, 23.9; **IR** (cm^{-1}) 3376, 3063, 2948, 2920, 2851, 1701, 1650, 1619, 1536, 1491, 1324, 1284, 1164, 1139, 1113, 895, 834, 707, 689; **HRMS** (EI) m/z calculated for $C_{21}H_{19}F_3N_2O_2$ [M]$^+$: 388.1399; found: 388.1400.

VII. Procedures for Mechanistic Studies

VII-1. Effect of hydrogen atom sources on benzoyl azide and *N*-arylmethacrylamide under the standard reaction conditions (Scheme 2b (Extended))



additives	yield (%)[a]
none	no reaction
$(Me_3Si)_3SiH$	no reaction



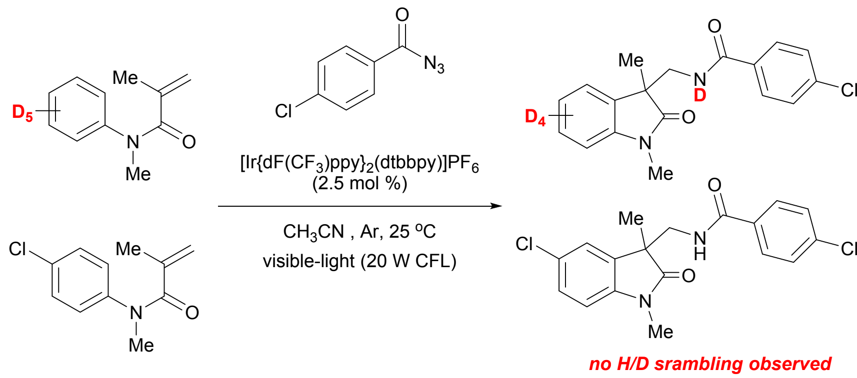
additives	yield (%)[a]	additives	yield (%)[a]
none	no reaction	isopropanol	69
Bu_3SnD	59[b]	butylated hydroxytoluene	78
$(Me_3Si)_3SiH$	>95	CF_3CH_2OH	no reaction
m-cresol	>95	H_3PO_4	no reaction

[a] Yields were determined by ^{1}H-NMR analysis using 1,1,2,2,-tetrachloroethane as an internal standard. In all cases, no side product was detected.
[b] Deuterated benzamide (ArC(O)ND_2) was obtained as the only product.

Procedure A (benzoyl azide) : To an oven-dried borosilicate vial (3 mL) equipped with magnetic stirring bar were added 4-chlorobenzoyl azide (0.20 mmol), additive (0.40 mmol, 2.0 equiv.), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 2.5 mol%) and dry MeCN-*d3* (1.5 mL). The resulting mixture was degassed by three freeze-pump-thaw cycles via a syringe needle and filled with argon. The vial was irradiated using 20 W CFL household light bulb at room temperature. After 36 h of irradiation at room temperature, the reaction mixture was analyzed via ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard to show the results summarized in the above table. For every cases, conversions were same as the yields, thus no side products were detected other than the unreacted starting material (4-chlorobenzoyl azide).

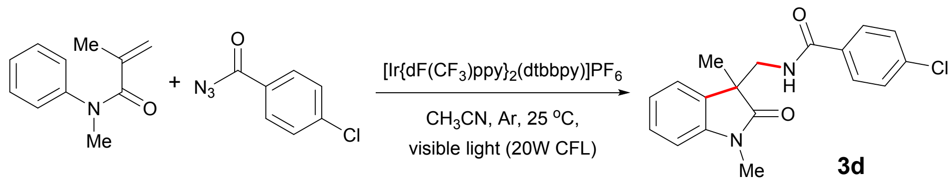
Procedure B (*N*-arylmethacrylamide) : To an oven-dried borosilicate vial (3 mL) equipped with magnetic stirring bar were added *N*-arylmethacrylamide (0.20 mmol), additive (0.40 mmol, 2.0 equiv.), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 2.5 mol%) and dry MeCN-*d3* (1.5 mL). The rest of the experimental details are same as above (Procedure A).

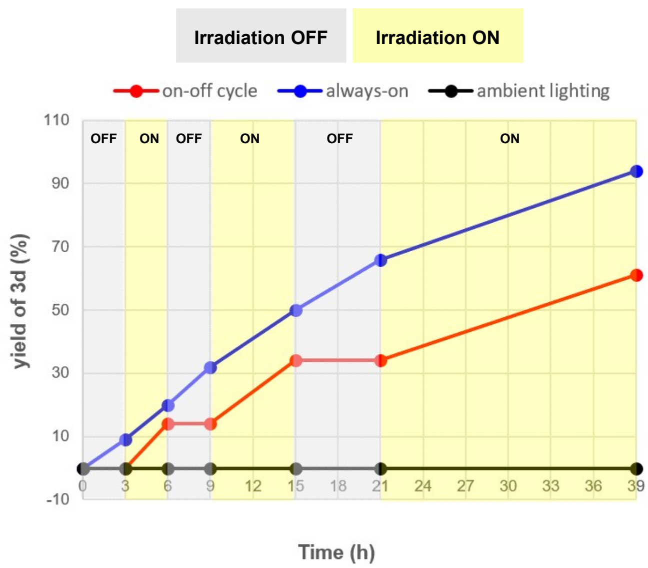
VII-2. H/D scrambling experiment (Scheme 2c)



Procedure: To an oven-dried borosilicate vial (3 mL) equipped with magnetic stirring bar were added 4-chlorobenzoyl azide (0.3 mmol), *N*-(phenyl-d5)methacrylamide (0.1 mmol), *N*-(4-chlorophenyl)methacrylamide (0.1 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (5.6 mg, 2.5 mol%) and dry MeCN-d3 (1.5 mL). The resulting mixture was degassed by three freeze-pump-thaw cycles via a syringe needle and filled with argon. The vial was irradiated using 20 W CFL household light bulb at room temperature. After 36 h of irradiation at room temperature, the reaction mixture was analyzed via ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard to show that no H/D scrambling occurred.

VII-3. Repeated on-off cycling of irradiation experiment



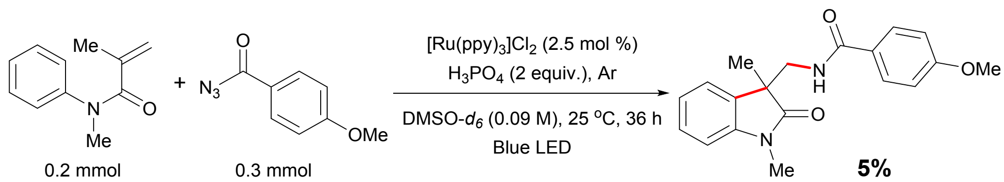


Duration (h)	Yield of 3d (%)		
	always-on	on-off cycle	ambient lighting
0	0	0	0
3	9	0	0
6	20	14	0
9	32	14	0
15	50	34	0
21	66	34	0
39	94	61	0

Procedure: To each of three oven-dried J. Young valve NMR tubes, the solution of 4-chlorobenzoyl azide (0.15 mmol), *N*-phenylmethacrylamide (0.1 mmol), [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (0.0025 mmol (2.5 mol%)) and 1,3,5-trimethoxybenzene (0.1 mmol, NMR internal standard) in dry MeCN-d3 (0.75 mL) was added. The three J Young NMR tubes were degassed by three freeze-pump-thaw cycles and filled with argon. The first sample was irradiated continuously during the course of the experiment (20 W CFL household light bulb at room temperature). The second sample was applied under the on-off cycling of irradiation using aluminum foil wrapping for the 'off' session (20 W CFL household light bulb at room temperature). The last sample was let stand under the ambient laboratory lighting at room temperature through the reaction period. The three samples were analyzed via ^{1}H-NMR using 1,3,5-trimethoxybenzene as an internal standard and the result is summarized as shown above.

VII-4. Evaluation of König's and Yoon's reaction conditions[S4], [S9]

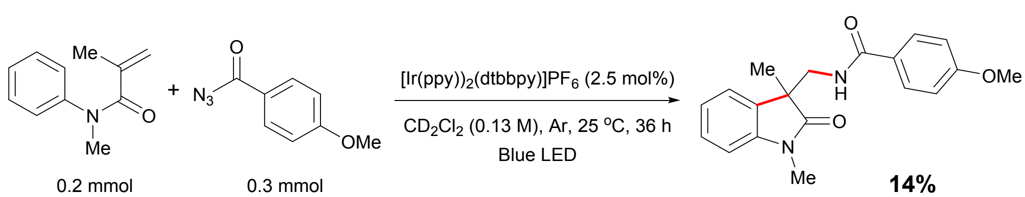
(a) Evaluation of König's reaction conditions to promote photocatalytic cascade cyclization



Conditions developed by König and coworkers for C-H amination of electron-rich heteroarenes[S4] were evaluated for our photocatalytic cascade cyclization reaction.

Procedure: To an oven-dried borosilicate vial (3 mL) equipped with magnetic stirring bar were added 4-methoxybenzoyl azide (0.3 mmol), *N*-phenylmethacrylamide (0.2 mmol), orthophosphoric acid (0.4 mmol), $[Ru(bpy)_3]Cl_2$ (0.005 mmol, 2.5 mol%) and dry DMSO-d_6 (0.09 M). The resulting mixture was degassed by three freeze-pump-thaw cycles via a syringe needle and filled with argon. The vial was irradiated using blue LED strip at room temperature. After 36 h of irradiation at room temperature, the reaction mixture was analyzed via ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. 5% of oxindole product was obtained and no side products were detected.

(b) Evaluation of Yoon's reaction conditions to promote photocatalytic cascade cyclization



Conditions developed by Yoon and coworkers for olefin aziridination[S9] were evaluated for our photocatalytic cascade cyclization reaction.

Procedure: To an oven-dried borosilicate vial (3 mL) equipped with magnetic stirring bar were added 4-methoxybenzoyl azide (0.3 mmol), *N*-phenylmethacrylamide (0.2 mmol), $[Ir(ppy)_2(dtbbpy)]PF_6$ (0.005 mmol, 2.5 mol%) and dry CD_2Cl_2 (0.13 M). The resulting mixture was degassed by three freeze-pump-thaw cycles via a syringe needle and filled with argon. The vial was irradiated using blue LED strip at room temperature. After 36 h of irradiation at room temperature, the reaction mixture was analyzed via ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. 14% of oxindole product was obtained and no side products were detected

VIII. Emission Spectrum of 20 W Compact Fluorescent Lamp (CFL) Utilized in the Photocatalysis

- Emission spectrum was measured on HORIBA (model QM-400) spectrophotometer.

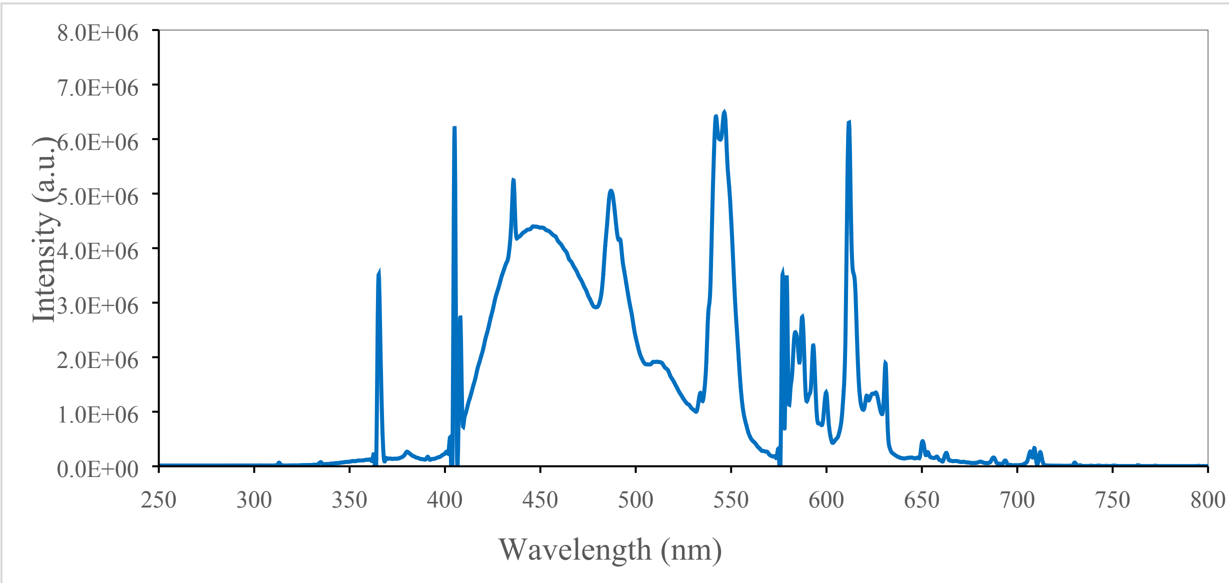


Figure S-2. Emission spectrum of 20 W CFL utilized in the present photoinduced cascade cyclization of *N*-arylacrylamides with benzoyl azides.

IX. Absorption and Emission Spectra of the Visible-Light Photocatalyst [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6

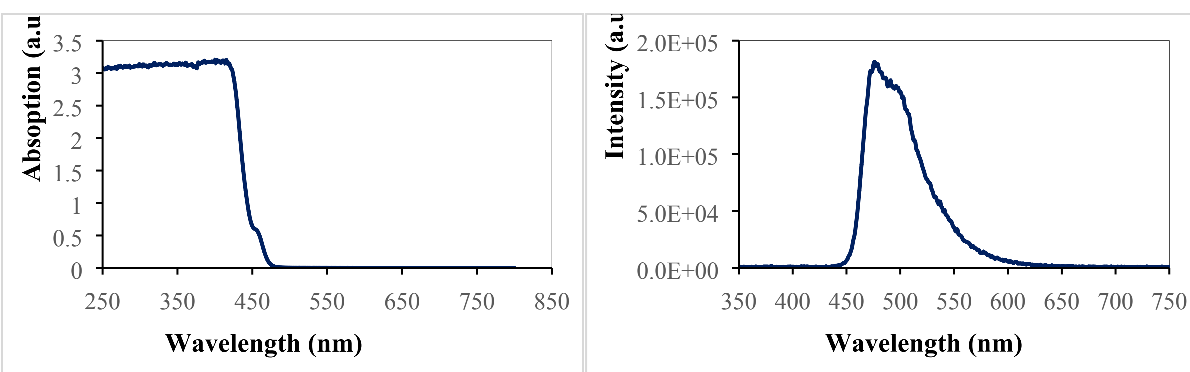


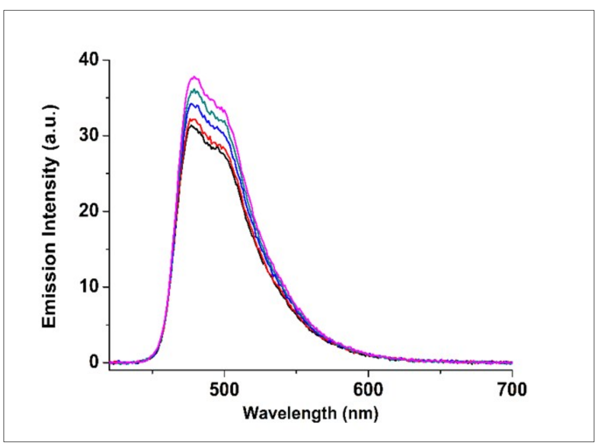
Figure S-1. (left) Absorbance of a 2.5 x 10^{-5} M solution of [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 catalyst in MeCN; (right) Emission spectra of [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 catalyst in MeCN.

X. Emission Quenching Experiment (Stern-Volmer Quenching)

All solutions were prepared volumetrically inside a nitrogen filled glove box. In a typical experiment, [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 catalyst and an appropriate amount of quencher dissolved in MeCN were added to 10 mm quartz cuvette. The quartz cuvette was then sealed with PTFE stopper or rubber septum, placed outside the glovebox, and then spectrum was collected. Fluorescence emission spectra were collected on Shimadzu (RF-5301pc) Spectrofluorophotometer with excitation and emission slit width of 5.0 nm. Samples containing [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 photocatalyst and quenchers were excited at 403 nm and the emission was monitored at 479 nm. All measurements were carried out under the same conditions as in the cyclization reactions.

Stern-Volmer quenching experiment for [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 with benzoyl azide

A solution of [Ir{dF(CF_3)ppy}$_2$(dtbbpy)](PF_6) in MeCN was excited at 403 nm and the intensity of emission spectrum was measured at 479 nm (emission maximum) (10 mm quartz cuvette). For each quenching experiment, the emission intensity of the solution of [Ir{dF(CF_3)ppy}$_2$(dtbbpy)](PF_6) (0.025 mM) with different concentration of quencher (benzoyl azide: 0.0, 0.5 1.0, 1.5, and 2.0 mM) was collected. (I_o : without quencher, I : with quencher)



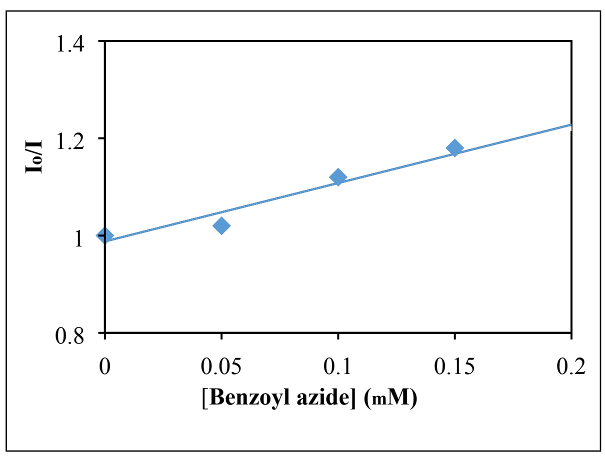


Figure S-2. (left) Changes in the fluorescence spectrum of [Ir{dF(CF_3)ppy}$_2$(dtbbpy)](PF_6) upon successive addition of benzoyl azide and (right) Stern-Volmer plot

XI. DFT Computational Studies and Coordinates of Optimized Structures and Transition States

XI-1. Computational details

DFT calculations was carried out by using UB3LYP method.[S10] To optimize geometry structures and vibrational frequencies, Los Alamos National Laboratory 2 ζ (LANL2DZ) ECP basis set[S11] was used for iridium atom, while using the 6-31G** basis set for other main group atoms. Electronic energies of optimized structures were further corrected by single point calculations of UB3LYP method [S10] with Los Alamos National Laboratory 2 ζ (LANL2DZ) ECP basis set[S11-12] for iridium atom and 6-311++G**[ref] basis set for other main group atoms. Thermodynamic parameters including Gibbs free energies at 298 K were obtained by frequency calculations. Transition states are realized by the presence of single negative frequency. Solvent effects were accounted at the PCM method [S13] in acetonitrile (ε = 37.5) as the experiments were carried out in the same solvent. All calculations performed by Gaussian09 program.[S14-15] Graphical structures were visualized with CYLview.[S16]

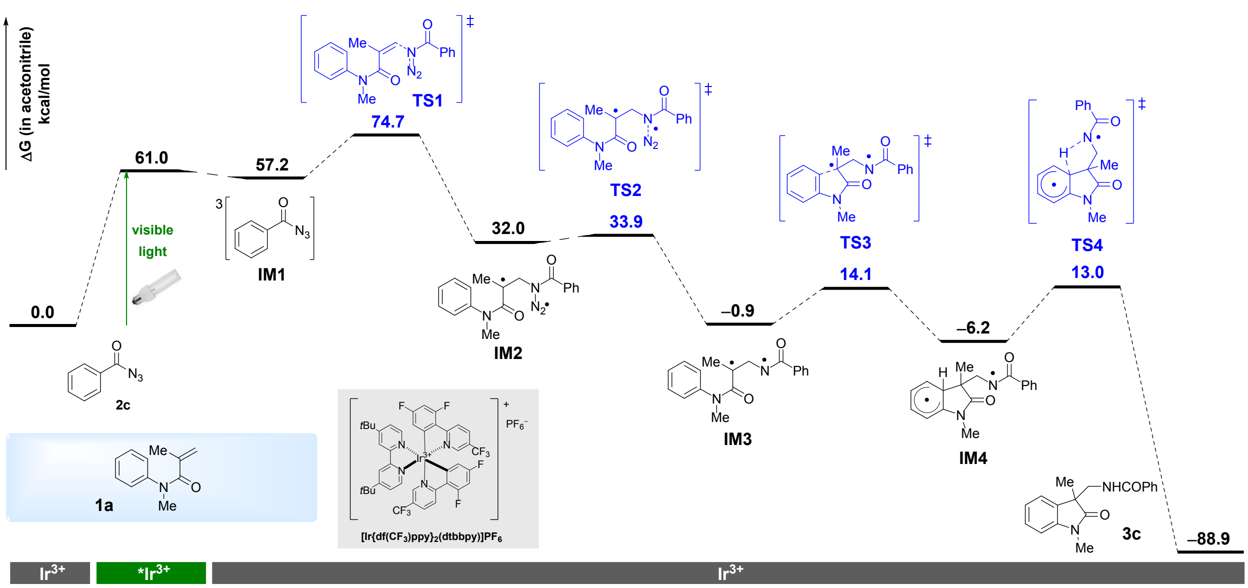
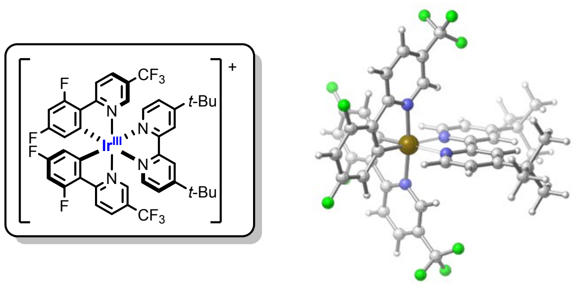


Figure S-3. DFT-calculated reaction energy profile of the photocatalytic cascade cyclization.

XI-2. Cartesian coordinates of optimized structures and geometries of stationary and transition states in 'Figure S-3'

Ir^{3+}



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C	0.86688400	-0.40151200	2.64990000
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H	-0.12656600	-0.48942900	3.07368300
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C	3.31539100	0.17540100	-1.49570300
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C	1.99758900	0.48425000	-3.45390600
H	-0.12677300	0.48959200	-3.07357900
H	1.86093000	0.63598200	-4.51639300
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C	4.29667700	-0.64255900	5.20097800
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H	5.67923500	-1.52563800	2.12992500
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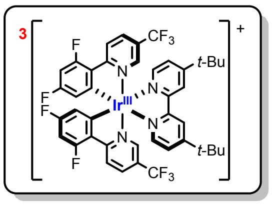
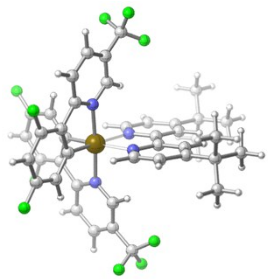
F	1.61256900	-4.83517900	0.87516800

***Ir^{3+}**





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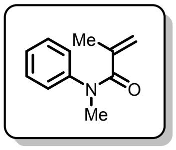
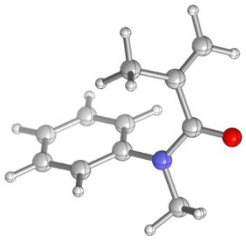
1a





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H	0.26100800	-0.62736000	-1.86238900
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N	-0.57803800	1.08877300	0.02291400
C	-0.64278400	2.54174400	-0.18647500
H	-1.51462000	2.94366800	0.32918100
H	0.26332000	2.99806100	0.21133300
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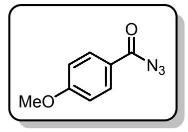
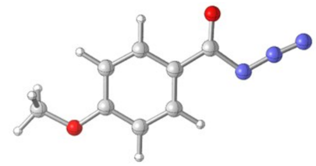
2a





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C	0.50720700	1.21971000	-0.00006600
C	1.87692800	0.98624400	-0.00009100
C	2.35128900	-0.33676300	-0.00011500
H	1.82681400	-2.42132300	0.00005500
H	-0.61966800	-1.99401100	0.00012000
H	0.13029600	2.23665800	-0.00012600
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C	-1.84686300	0.48090800	0.00002800
O	-2.31595800	1.60844600	0.00002700
N	-2.67647000	-0.69391600	0.00001300
N	-3.89869600	-0.46466100	0.00002600
N	-5.02712200	-0.35903200	0.00001500
O	3.65966600	-0.68136000	-0.00012500
C	4.64559600	0.35540400	0.00018400
H	5.60909800	-0.15340600	0.00034800
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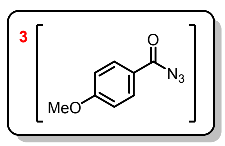
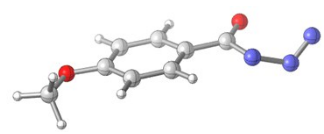
***2a**





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C	1.68207200	1.44198200	0.08293900
C	2.36659600	0.20810500	0.01758400
H	2.15092500	-1.94665900	-0.14248200
H	-0.30080300	-1.88012800	-0.20530600
H	-0.22933400	2.41244900	0.10115100
H	2.26407200	2.35365700	0.16190800
C	-1.89920700	0.35209300	-0.06843300
O	-2.55785200	1.38264000	-0.12852600
N	-2.53277500	-0.94018400	-0.05251100
N	-3.82603400	-0.91085300	0.45351400
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O	3.71069200	0.28918100	0.05778200
C	4.48273400	-0.91708300	0.00808400
H	4.30998200	-1.45561800	-0.92889000
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H	4.25105900	-1.56708500	0.85759700

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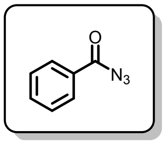

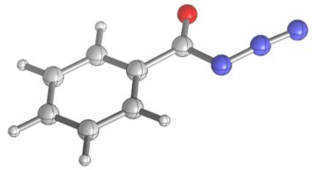

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C	-0.49804800	0.14309300	-0.00000200
C	-1.41035300	1.21053800	0.00000000
C	-2.77864800	0.95808400	0.00000200
C	-3.24540300	-0.36034500	0.00000200
H	-2.70510600	-2.44854500	0.00000000
H	-0.26570400	-2.00260000	-0.00000400
H	-1.02950400	2.22585700	0.00000000
H	-3.48175600	1.78492800	0.00000400
H	-4.31330200	-0.55666300	0.00000400
C	0.94716700	0.46963700	-0.00000500
O	1.40541400	1.59968000	-0.00000100
N	1.77688100	-0.69888600	-0.00000100
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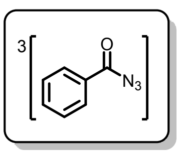

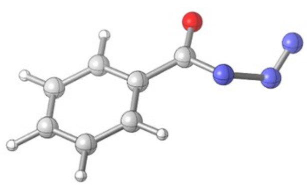

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C	1.34297700	1.22734400	0.05137800
C	2.71427900	1.02877400	0.16485400
C	3.23752600	-0.26922100	0.13415100
H	2.79842200	-2.37427700	-0.03555800
H	0.35291400	-2.03001600	-0.24893700
H	0.91807100	2.22477400	0.07694100
H	3.37738500	1.88021000	0.27847700
H	4.30877400	-0.42146600	0.22266000
C	-0.96577800	0.37321300	-0.19323700
O	-1.49702000	1.47798500	-0.21124000
N	-1.76964300	-0.79229200	-0.37763600
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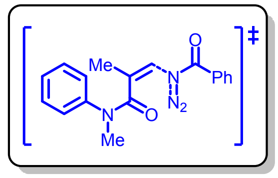
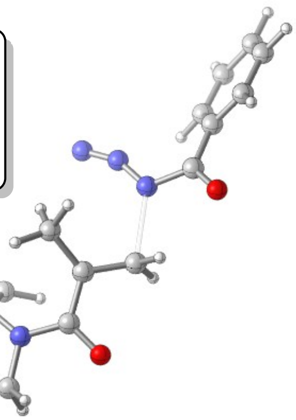
TS1





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C	4.75392300	2.44168100	-0.25111000
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H	4.18188500	4.02469900	1.09989200
H	5.43882300	3.06265000	-0.82055200
C	4.57531500	1.10718600	-0.61168600
H	5.10781100	0.69383600	-1.46265000
O	2.22334000	-2.94364000	-0.07563100
C	2.30198500	-1.71685200	-0.27363800
C	1.08864800	-0.95851400	-0.61086100
C	2.99862100	0.83263800	1.20532400
H	2.33800000	0.19826700	1.78758100
C	3.16642900	2.17535100	1.54837200
H	2.62079700	2.58301200	2.39401000
N	3.53603000	-1.08107900	-0.24734300
C	4.70792300	-1.95406600	-0.10267100
H	4.62228000	-2.79793000	-0.78741800
H	5.60624400	-1.38337400	-0.33669500
H	4.79163000	-2.34482300	0.91871100
C	1.06443100	0.27194000	-1.46311300
H	0.82313700	1.17052700	-0.87519100
H	2.02126800	0.44945200	-1.95626200
H	0.28363300	0.17773200	-2.22657200
C	-0.17029800	-1.62005700	-0.23388700
H	-0.70021700	-2.22800900	-0.96277800
H	-0.33519300	-1.89302100	0.80384200
C	-3.10605900	-0.64186500	-0.42268400
O	-3.12651200	-1.76595100	-0.89787700
C	-4.36368200	0.11280600	-0.12669800
C	-4.50702400	0.96938400	0.97515900
C	-5.46142300	-0.12229500	-0.96922800
C	-5.73053700	1.59339900	1.21751700
H	-3.68485200	1.12964600	1.66380400
C	-6.67467100	0.51942600	-0.73494600
H	-5.34661800	-0.80211600	-1.80633600
C	-6.81095200	1.37837700	0.35926200
H	-5.83944400	2.24403500	2.07929800
H	-7.51406800	0.34706400	-1.40117300
H	-7.75876800	1.87378300	0.54608200
N	-1.84371600	-0.06183100	-0.14423500
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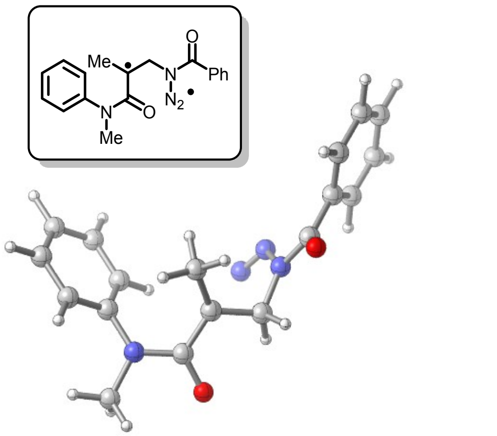

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C	4.39345700	2.54630600	-0.78116500
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H	3.67934900	4.31770100	0.22393500
H	5.04231500	3.09200900	-1.45943000
C	4.32117000	1.15718100	-0.86864500
H	4.90002200	0.62498200	-1.61704200
O	2.27949400	-2.87895100	0.45758600
C	2.26247300	-1.71188900	0.02353100
C	1.00309700	-1.14393900	-0.46833000
C	2.73103500	1.12959900	0.95822000
H	2.10218500	0.57648100	1.64841200
C	2.79305400	2.52258200	1.02646500
H	2.20071800	3.04741900	1.76989200
N	3.43978700	-0.98758900	-0.07919500
C	4.67561200	-1.72059100	0.22521300
H	4.66379400	-2.68446000	-0.28377300
H	5.52840400	-1.13598300	-0.11809300
H	4.77775800	-1.89912500	1.30229400
C	0.87208800	-0.09039900	-1.52120600
H	0.52895400	0.86613800	-1.10270800
H	1.81669900	0.09898900	-2.03180900
H	0.12194400	-0.39856100	-2.25811300
C	-0.23770800	-1.87334500	-0.01972100
H	-0.58067100	-2.56839400	-0.79300700
H	-0.04071500	-2.44412100	0.88937000
C	-2.42192000	-0.81296500	-0.68497400
O	-2.30519000	-1.30505600	-1.80170700
C	-3.64401100	-0.05466000	-0.28088900
C	-4.24475000	-0.16641400	0.98254900
C	-4.25936700	0.72318800	-1.27392800
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H	-3.80045600	-0.79165300	1.74801300
C	-5.43847900	1.41040200	-0.99682200
H	-3.80138100	0.78523000	-2.25513900
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H	-5.90345600	0.40637600	2.22284500
H	-5.89916400	2.02379900	-1.76467300
H	-6.95272300	1.83153900	0.47946700
N	-1.38436100	-0.98225200	0.23828200
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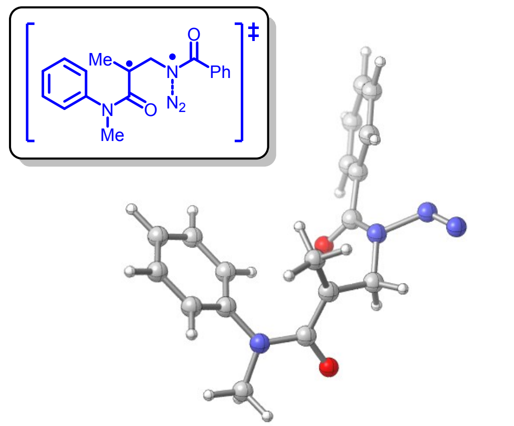
TS2



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H	-2.73173700	4.46553500	0.92657100
H	-4.69237000	3.15922100	1.73066200
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O	-2.28790000	-2.53919200	-1.22557200
C	-2.23153800	-1.56230500	-0.45557000
C	-1.09887600	-1.42464600	0.46425500
C	-2.01513900	1.45505800	-0.50111100
H	-1.27215500	0.98001400	-1.13329800
C	-1.87680700	2.79689600	-0.14071600
H	-1.02066700	3.35946000	-0.50115200
N	-3.28071300	-0.65638000	-0.40387900
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H	-4.73471600	-2.04384400	-1.02334800
H	-5.29187600	-0.35655500	-0.90737900
H	-4.27605500	-0.87222500	-2.27283300
C	-1.13845400	-0.75421200	1.80008000
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H	-0.67705900	-1.40246000	2.55551900
C	0.12745000	-2.22171400	0.10073000
H	0.18971700	-3.10753300	0.74377000
H	0.07355600	-2.55501900	-0.93698700
C	1.72250900	-0.45972500	-0.56096500
O	0.93041300	-0.15405500	-1.45182800
C	3.01459700	0.25807400	-0.36689800
C	3.59058800	0.46512300	0.89582000
C	3.62440200	0.80594600	-1.50565300
C	4.76943100	1.20081700	1.01116900
H	3.10704300	0.07654800	1.78480000
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H	3.16160700	0.65517000	-2.47503900
C	5.38434600	1.72464800	-0.12846900
H	5.20519800	1.36802000	1.99111100
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H	6.30559400	2.29167500	-0.03539800
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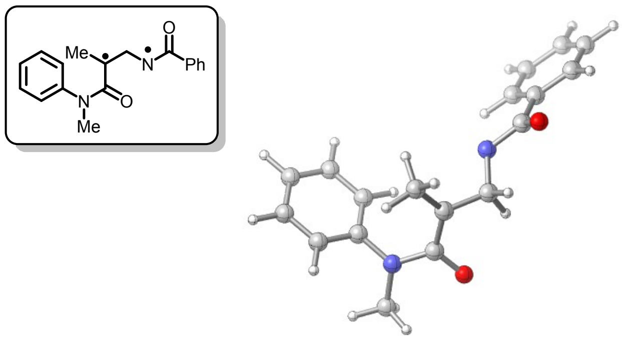

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C	-3.86967100	2.91821300	0.66322800
H	-4.07032800	3.92708200	1.00998900
H	-5.72294500	2.11180000	1.41931200
C	-4.54112800	0.60074500	0.45371900
H	-5.25292900	-0.19455700	0.65167000
O	-1.53878800	-2.49180600	-1.45651300
C	-1.86208100	-1.62486300	-0.62271300
C	-0.96003900	-1.31079200	0.49012800
C	-2.42877200	1.33754500	-0.47339100
H	-1.51841100	1.12259400	-1.02353700
C	-2.68429300	2.63127800	-0.01554800
H	-1.96088100	3.41805700	-0.20691900
N	-3.10740000	-1.01894200	-0.69639700
C	-4.02658800	-1.55582500	-1.70836800
H	-4.03192000	-2.64460700	-1.65622600
H	-5.02918800	-1.17606500	-1.51468900
H	-3.72355200	-1.25915300	-2.71964900
C	-1.36877900	-0.81373700	1.83823300
H	-0.95539900	0.18576600	2.03235200
H	-2.44963600	-0.76378200	1.96549700
H	-0.95562800	-1.47344100	2.61318500
C	0.48348600	-1.67961800	0.30070000
H	0.80490300	-2.46715500	1.00346100
H	0.61742700	-2.09723200	-0.71021800
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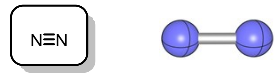
C	2.66488700	-0.78480900	0.84420300
O	2.89948200	-1.58789800	1.75237700
C	3.71914600	0.03868100	0.19508200
C	3.40086400	1.05328400	-0.72138200
C	5.06293900	-0.23002200	0.49851100
C	4.41854900	1.78850600	-1.32701400
H	2.36096400	1.26492900	-0.94452800
C	6.07599800	0.50706000	-0.10753800
H	5.29257400	-1.01868700	1.20695500
C	5.75464000	1.51696000	-1.02105200
H	4.17070200	2.57492000	-2.03296800
H	7.11467100	0.29724000	0.12814500
H	6.54586500	2.09185200	-1.49282900

N_2



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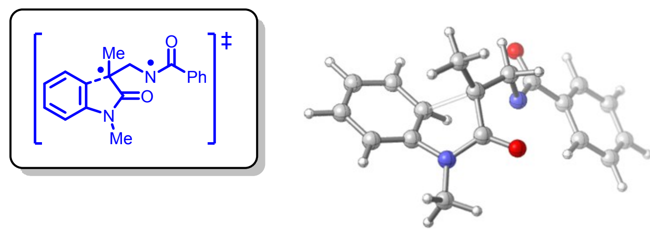
TS3



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O	-0.87813200	-2.35797900	1.23669800
C	-1.44585900	-1.41207600	0.69324300
C	-1.27781300	0.02644000	1.12765600
N	-2.33365000	-1.55281200	-0.35697000
C	-2.85993300	-2.85561100	-0.73905500
H	-2.19643200	-3.61510000	-0.32682100
H	-3.86895700	-3.01242300	-0.34125100
H	-2.88894500	-2.94150500	-1.82758300
C	-2.31323600	0.52332500	2.10854800
H	-2.23653900	1.60821400	2.23412400
H	-3.32784400	0.28767300	1.77565500
H	-2.17040500	0.06256800	3.09661800
C	0.14125000	0.42885500	1.45008300
H	0.19983400	1.48519200	1.74671400
H	0.49473500	-0.15315600	2.32622200
N	1.06360400	0.14924900	0.37738200
C	2.17751700	0.97237100	0.25046400
O	2.05930300	2.19824500	0.34312600
C	3.45408200	0.29767700	-0.10066800
C	3.51774100	-1.08907900	-0.30937900
C	4.62005900	1.07254300	-0.19782200
C	4.73793000	-1.69147400	-0.61113600
H	2.61250700	-1.68284400	-0.24123900
C	5.83590900	0.46735000	-0.50194800
H	4.55385300	2.14226300	-0.03063400
C	5.89580200	-0.91515900	-0.70856200
H	4.78592300	-2.76350300	-0.77432100
H	6.73686900	1.06811000	-0.57755900
H	6.84498300	-1.38616600	-0.94587900
C	-1.86755100	0.72513500	-0.79594800
H	-0.84015800	0.49444400	-1.06692200
C	-2.33409900	2.05188500	-1.01631900
H	-1.62158800	2.87113400	-1.01281900
C	-3.67571800	2.28934700	-1.29741000
H	-4.01646200	3.30542900	-1.47473300
C	-4.58158700	1.22515300	-1.41766500
H	-5.61884700	1.41809100	-1.67168900
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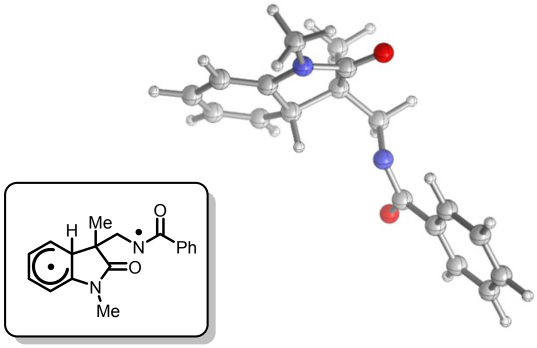
IM4



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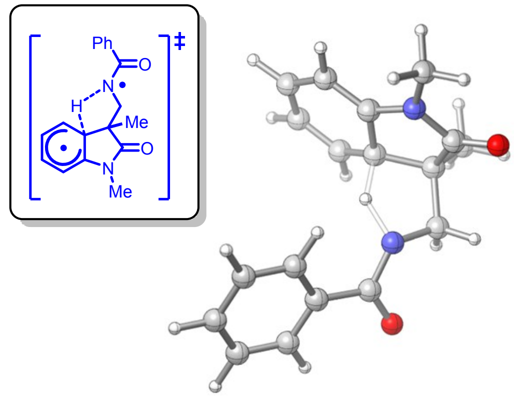
C	-4.42777900	1.15984900	-1.64702900
C	-3.80607800	2.22353800	-0.93687600
H	-4.24657700	3.21557300	-0.99803600
H	-5.30431300	1.35598300	-2.25487900
C	-3.97702600	-0.17655200	-1.47875400
H	-4.54409300	-1.00225500	-1.89727700
O	-0.89304200	-2.32429000	1.39611200
C	-1.46922100	-1.42576100	0.79663400
C	-1.40625700	0.08072200	1.12560000
C	-1.98745100	0.70538200	-0.17905900
H	-1.11929600	0.77867400	-0.86616700
C	-2.68755500	2.03253600	-0.16873200
H	-2.22822500	2.86110600	0.36209600
N	-2.35205400	-1.60553600	-0.25202100
C	-2.80114200	-2.91674400	-0.69018300
H	-2.20811500	-3.66355200	-0.16321600
H	-3.86054900	-3.06000200	-0.45444800
H	-2.65818400	-3.02511600	-1.76850700
C	-2.29911600	0.33394000	2.35715300
H	-2.27820100	1.39181700	2.63394600
H	-3.33776100	0.05995200	2.15175800
H	-1.94910900	-0.25480700	3.20996500
C	0.03515400	0.50235300	1.44316100
H	0.08574200	1.55102300	1.76730600
H	0.39175200	-0.10516600	2.29271600
N	0.93905800	0.26823100	0.34982000
C	2.06479900	1.07843500	0.25048500
O	1.96501700	2.30090000	0.39451000
C	3.32930900	0.40039200	-0.13608900
C	3.37195500	-0.97784000	-0.39916100
C	4.50553100	1.16208400	-0.21113700
C	4.58140200	-1.58503200	-0.73281400
H	2.45894200	-1.56128000	-0.34737000
C	5.71063800	0.55230900	-0.54727800
H	4.45568700	2.22527100	-0.00188500
C	5.74954700	-0.82174400	-0.80808300
H	4.61305200	-2.65046000	-0.93786900
H	6.61953700	1.14293700	-0.60577700
H	6.69035100	-1.29634000	-1.07031100

TS4



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C	-2.48685700	1.10253800	-2.44858200
C	-2.17172600	2.16983200	-1.52299900
H	-2.31694000	3.19331400	-1.85909600
H	-2.80306000	1.34688700	-3.45561800
C	-2.49476800	-0.23418600	-2.00592100
H	-2.85569600	-1.03043300	-2.64853900
O	-1.88429000	-2.36769200	2.19120000
C	-1.86448600	-1.47388500	1.35946700
C	-1.59654600	0.01712000	1.62356200
C	-1.47750900	0.55989900	0.18108500
H	-0.15876000	0.35195800	0.21023500
C	-1.73541000	1.94356300	-0.25026000
H	-1.51558300	2.76658000	0.42160000
N	-2.15028000	-1.65845600	0.00454000
C	-2.60468700	-2.93488200	-0.52649400
H	-2.54372200	-3.66847500	0.27594000
H	-3.63830800	-2.85305300	-0.87510200
H	-1.96754800	-3.24007100	-1.36023700
C	-2.73370100	0.59252500	2.48138400
H	-2.57372800	1.65970100	2.65592000
H	-3.70424000	0.46686700	1.99240000
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C	-0.20396800	0.20516300	2.27642600
H	-0.13516200	1.18121800	2.77059600
H	-0.01280200	-0.56897800	3.02822400
N	0.73202600	0.09329600	1.15901200
C	1.89183400	0.82562400	1.20459100
O	2.30314000	1.33074100	2.26122100
C	2.66362900	0.93150500	-0.07124900
C	2.37711700	0.13532500	-1.19120600
C	3.71159700	1.86204500	-0.13885400
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H	1.58482100	-0.60302800	-1.13769900
C	4.45307600	2.00400400	-1.30913200
H	3.92773600	2.46690200	0.73523400
C	4.15947900	1.21162300	-2.42334500
H	2.89935200	-0.34616600	-3.22168000
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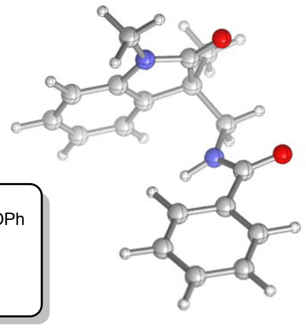
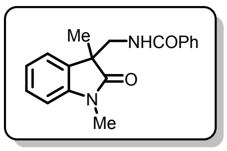
3c





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C	2.83979900	2.34239500	-1.66003400
H	3.09837800	2.93311300	-2.53301700
H	3.05711400	3.99272900	-0.29668700
C	2.48680400	2.20162700	0.74818100
H	2.47142300	2.66991600	1.72636500
O	1.26939500	-2.32998900	1.62472100
C	1.59856300	-1.32407600	1.00870800
C	1.83452800	-1.22430300	-0.51622200
C	2.53172100	0.98021300	-1.80678000
H	2.55388000	0.51832800	-2.78994000
N	1.82956400	-0.08474700	1.56421500
C	1.70996400	0.19895300	2.98232800
H	1.42344600	-0.72745500	3.47974900
H	2.66316300	0.55057600	3.38909600
H	0.94414000	0.95983600	3.16242000
C	2.96857800	-2.18580700	-0.92372100
H	3.13641000	-2.14185800	-2.00376000
H	3.90359600	-1.92220100	-0.42243200
H	2.70634100	-3.21218000	-0.65135400
C	0.53803200	-1.62111900	-1.26345400
H	0.73709300	-1.61468300	-2.34176500
H	0.24988000	-2.63331300	-0.97558500
C	-1.78382300	-1.22511900	-0.49817700
O	-2.00119100	-2.42591800	-0.31143000
C	-2.84177900	-0.18982700	-0.23430800
C	-2.54888700	1.15085600	0.05691200
C	-4.17929900	-0.60918800	-0.25590600
C	-3.57989800	2.05776300	0.30487100
H	-1.51956900	1.48970700	0.12495800
C	-5.20830200	0.29898600	-0.01666800
H	-4.39313400	-1.65178300	-0.46460900
C	-4.91040800	1.63569500	0.26269300
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H	-6.24130800	-0.03413700	-0.04575000
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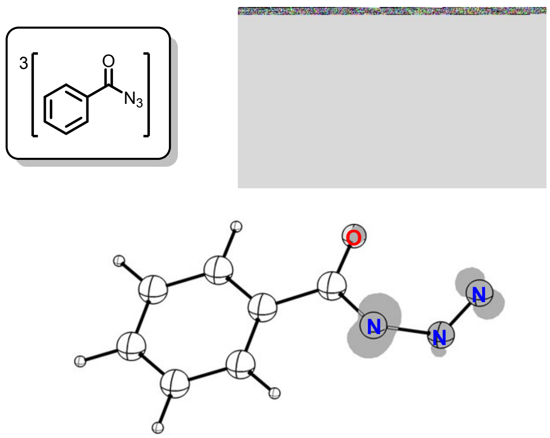
N	-0.58777700	-0.75556300	-0.95699500
H	-0.52271100	0.21144900	-1.23960700

XI-3. Triplet spin density diagrams of the intermediates of the proposed reaction mechanism

IM1 (isosurface value = 0.07 au)



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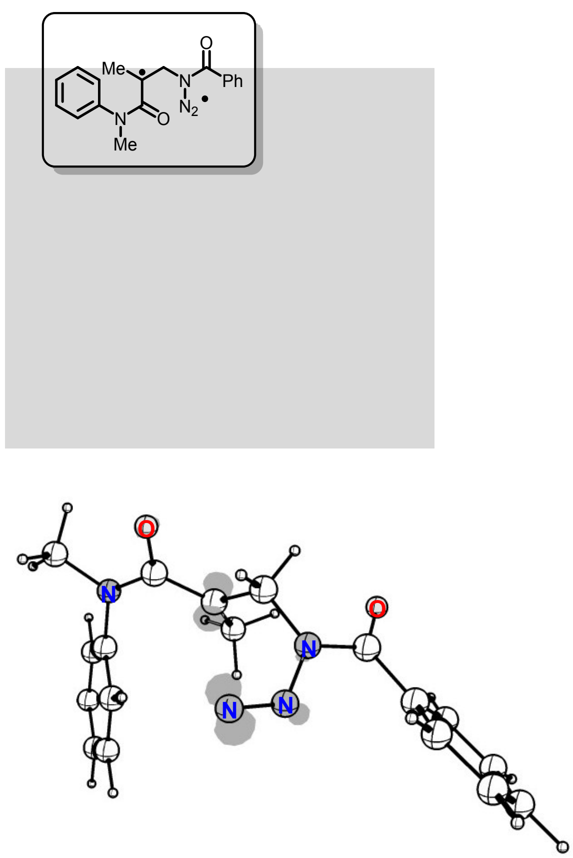

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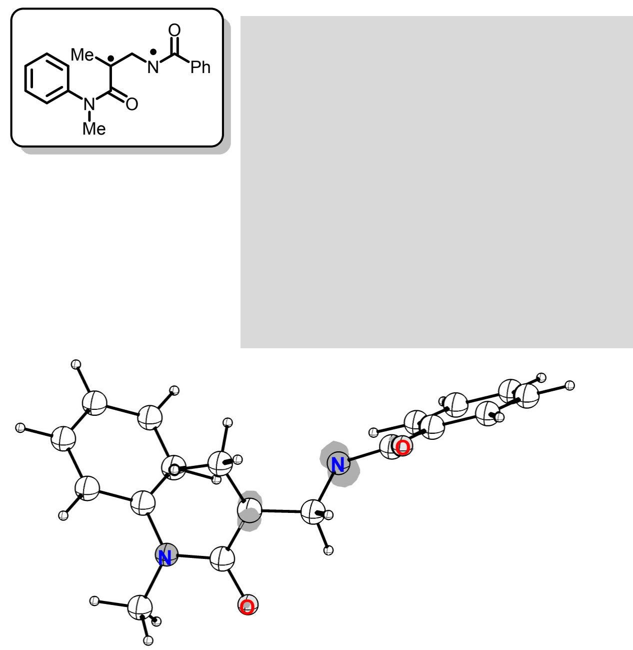

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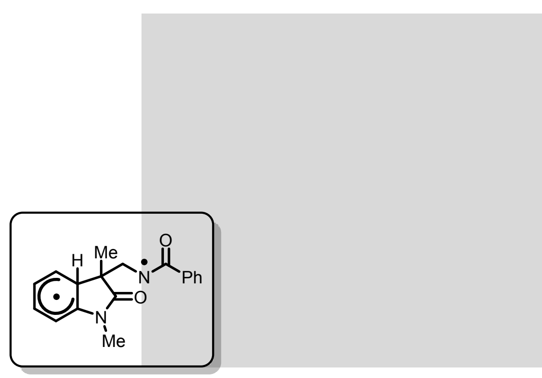

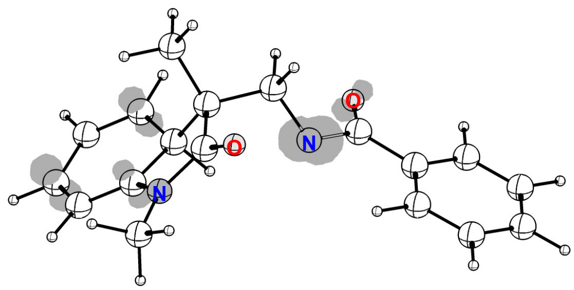
N
O
N
O

XII. References

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[S12] For the single point calculations, we tested total four basis sets for iridium atom (LANL2DZ, LANL2TZ, LANL2TZ(f), and SDD). Upon comparison with the experimental E_{ST} = 60.8 kcal/mol of the photocatalyst, $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]^+$ (E_{ST} : the energy gap between the ground singlet state and the first excited triplet triplet state), LANL2DZ gave the closest theoretical value (61.0 kcal/mol) while other basis sets were less successful in predictability; LANL2TZ (62.7 kcal/mol), LANL2TZ(f) (61.8 kcal/mol), and SDD (64.8 kcal/mol).

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Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Montgomery, J. A. Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D01; Gaussian, Inc., Wallingford, CT, 2009.

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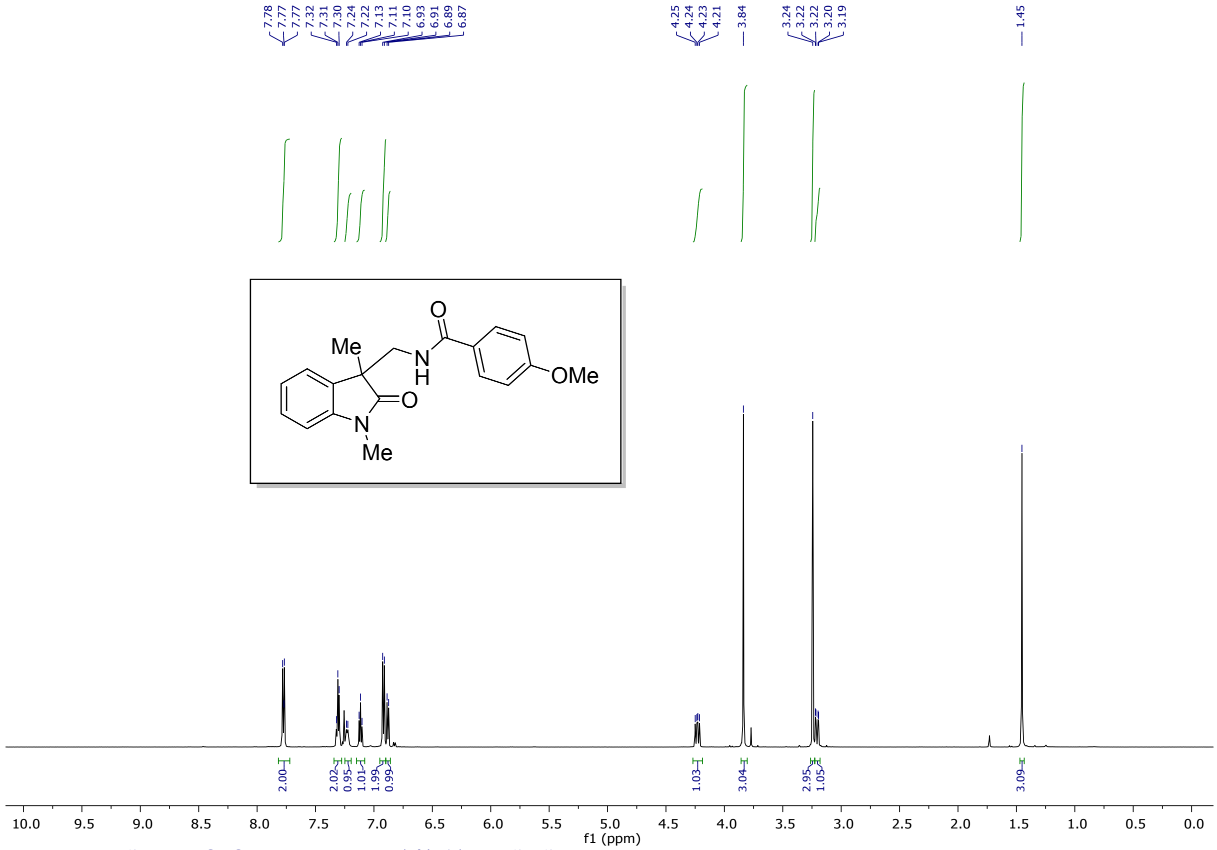
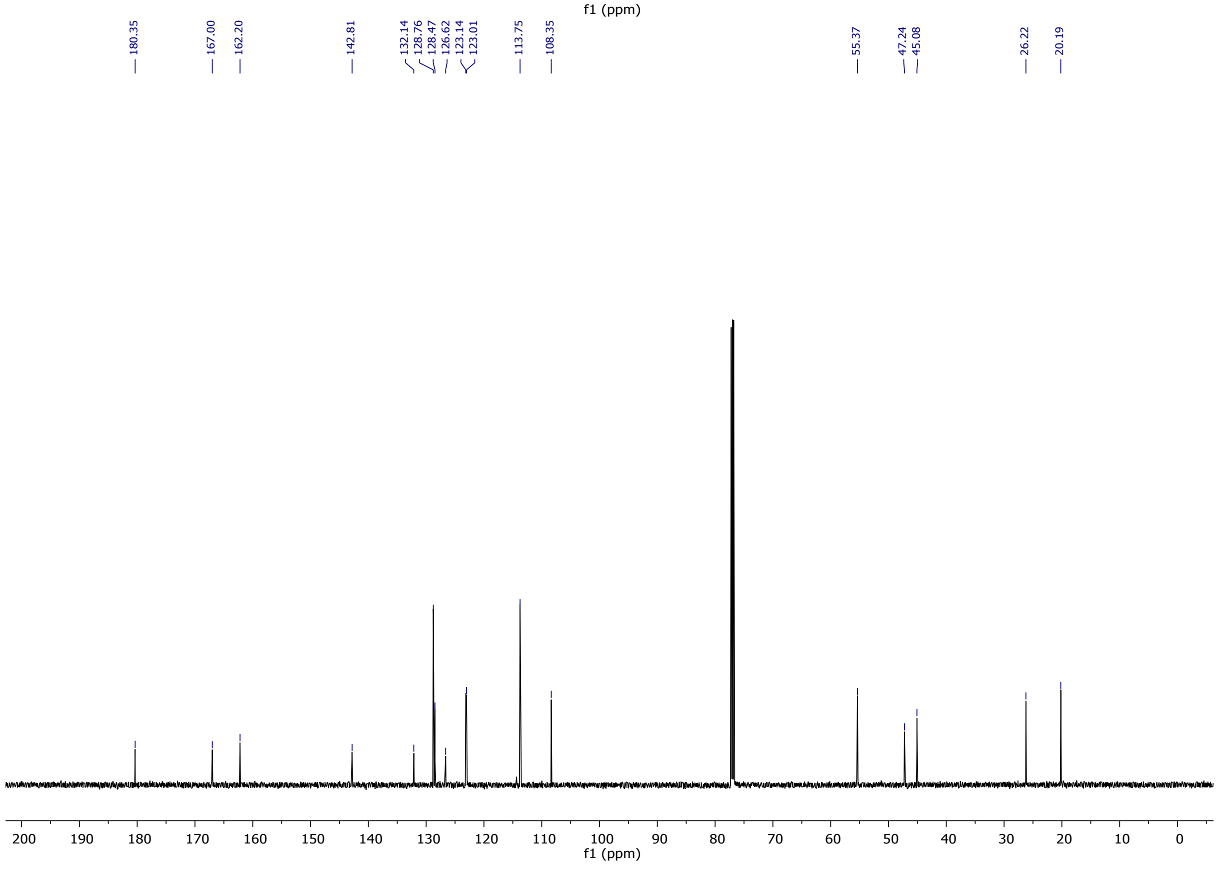
Appendix I

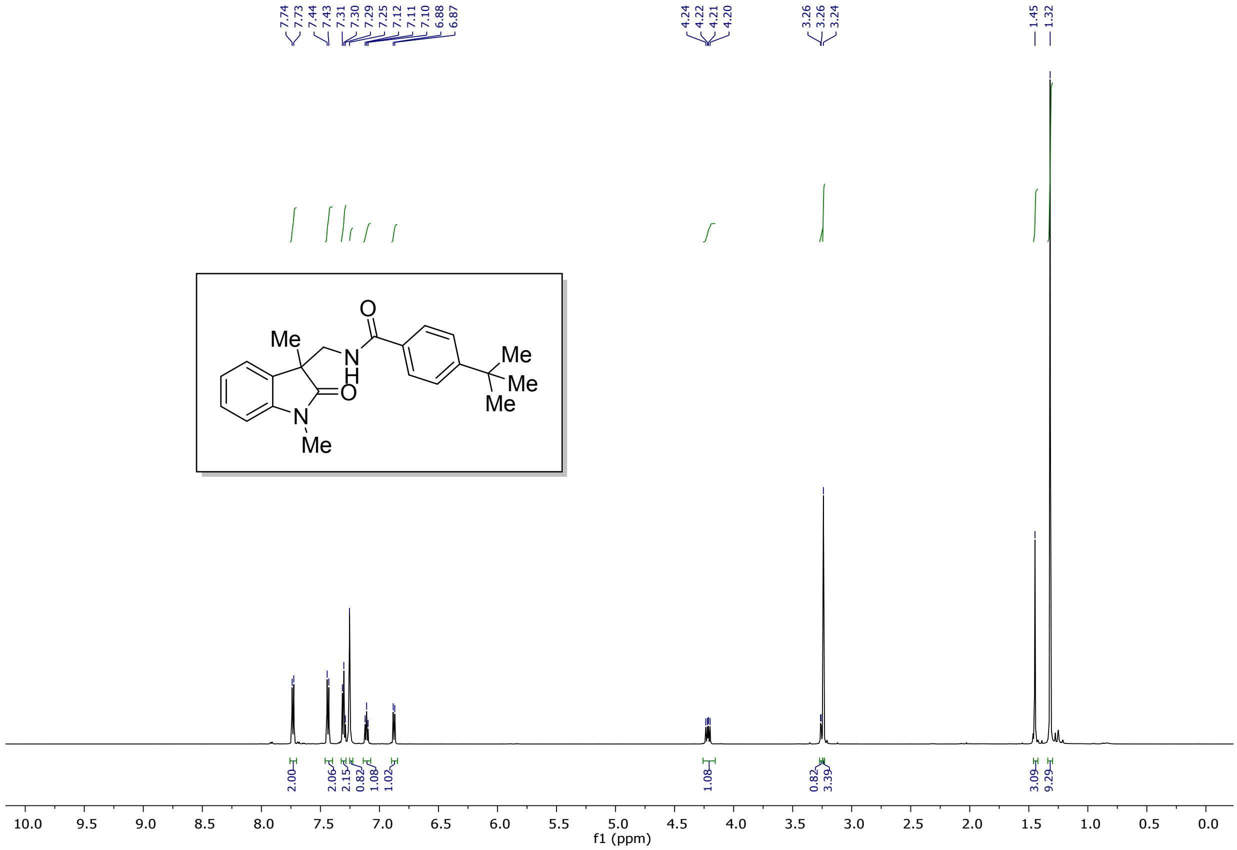
Spectral Copies of ^{1}H, ^{13}C, and ^{19}F NMR of Compounds Obtained in This Study

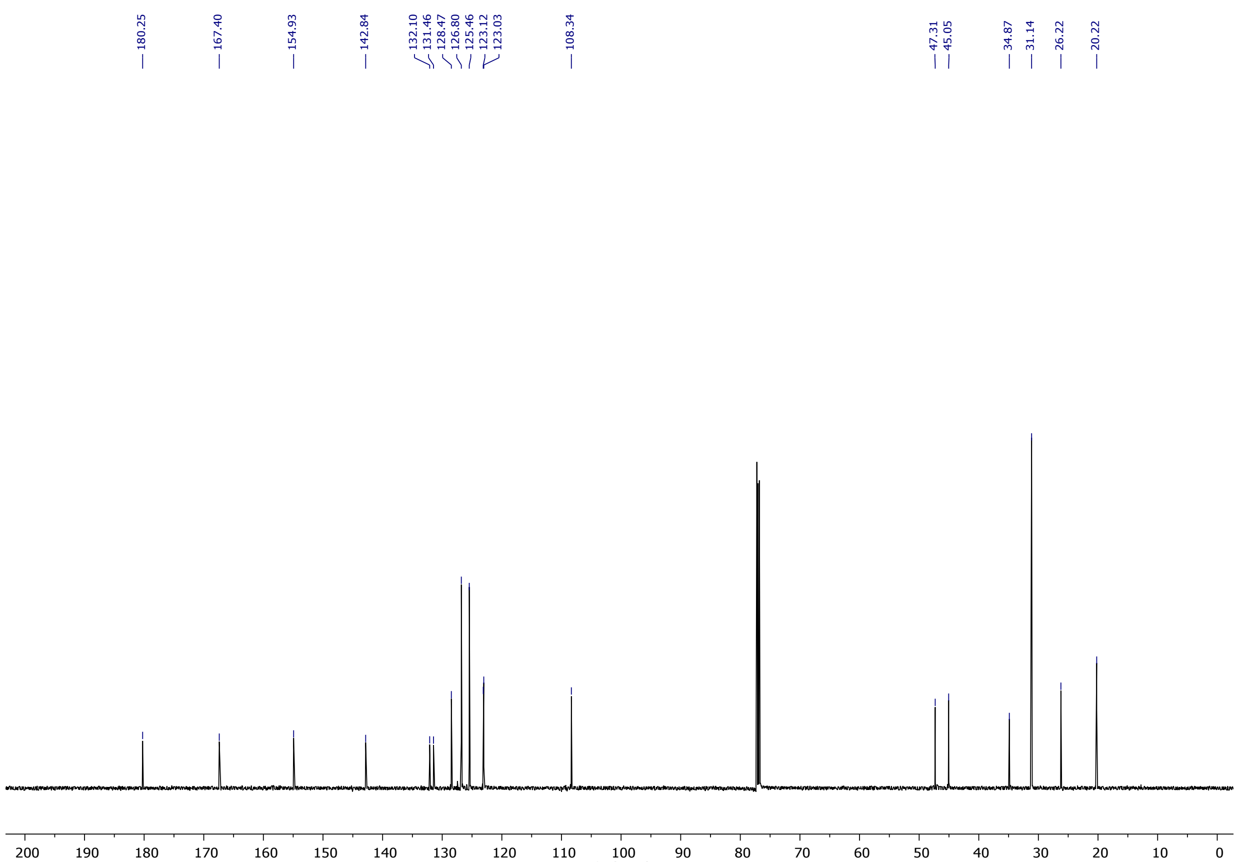
N-[(1,3-Dimethyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3a)



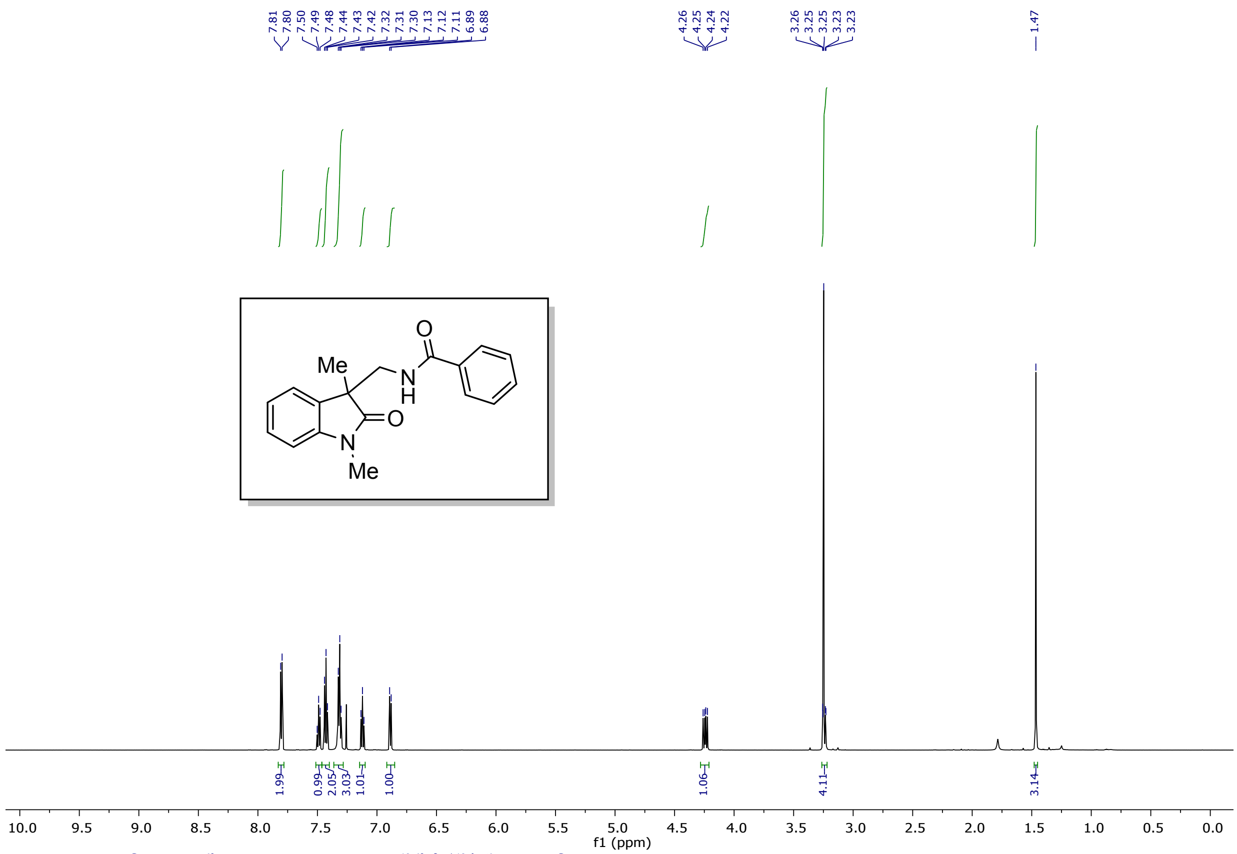


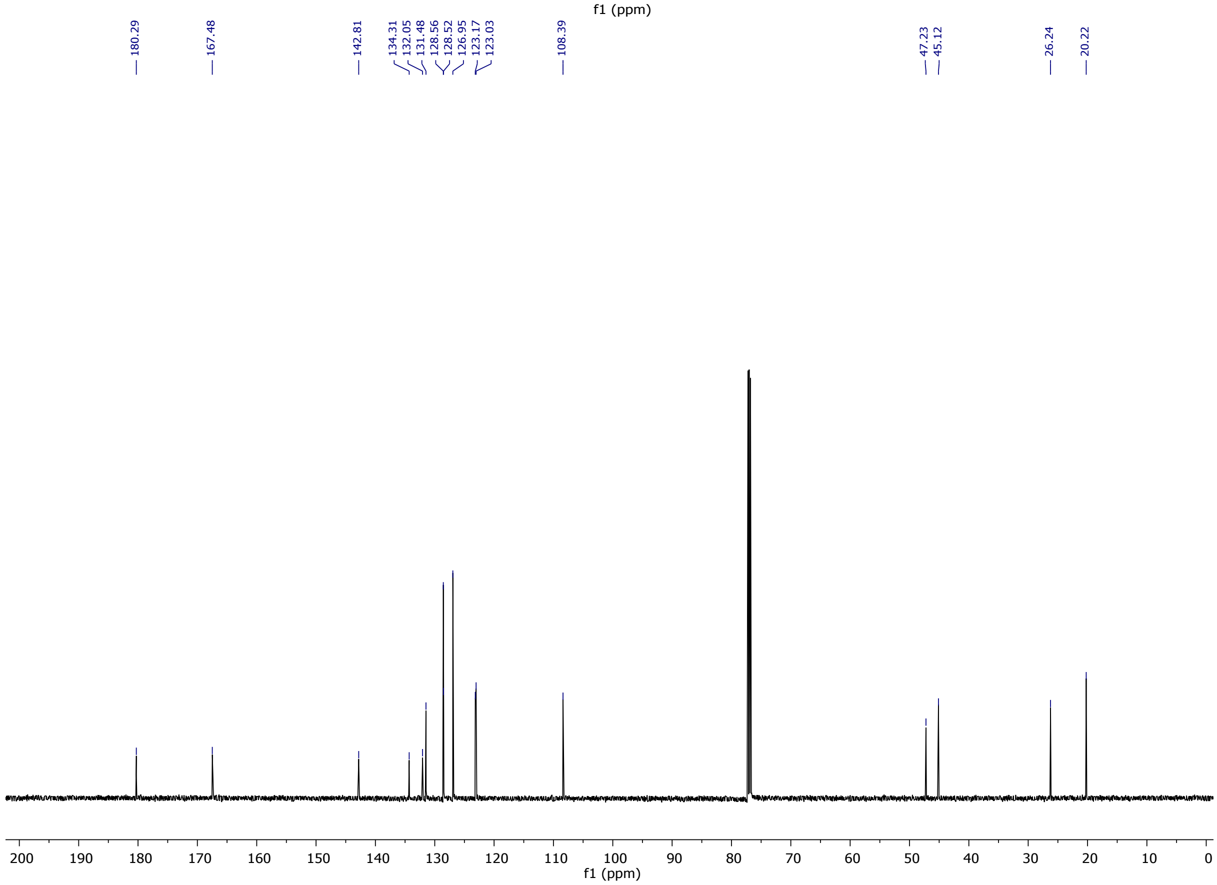
4-(*tert*-Butyl)-*N*-[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3b)



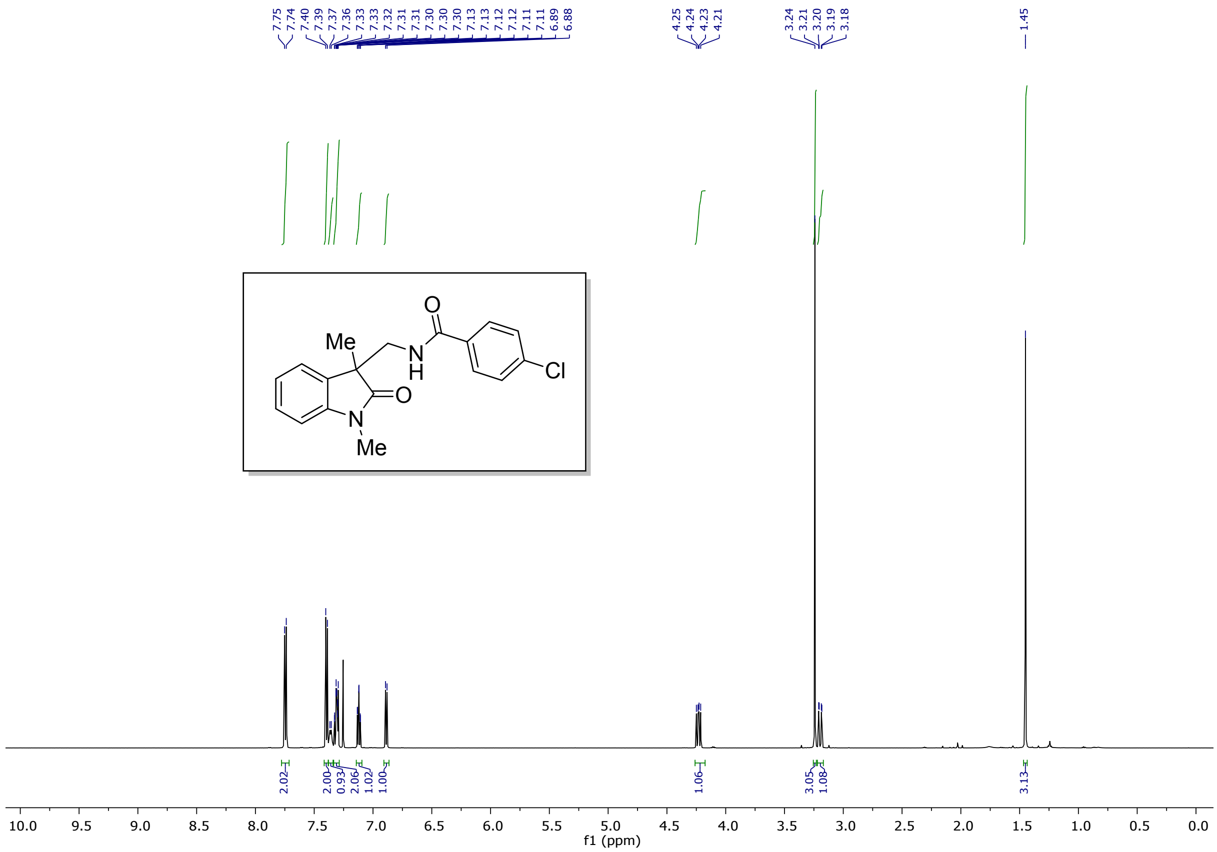


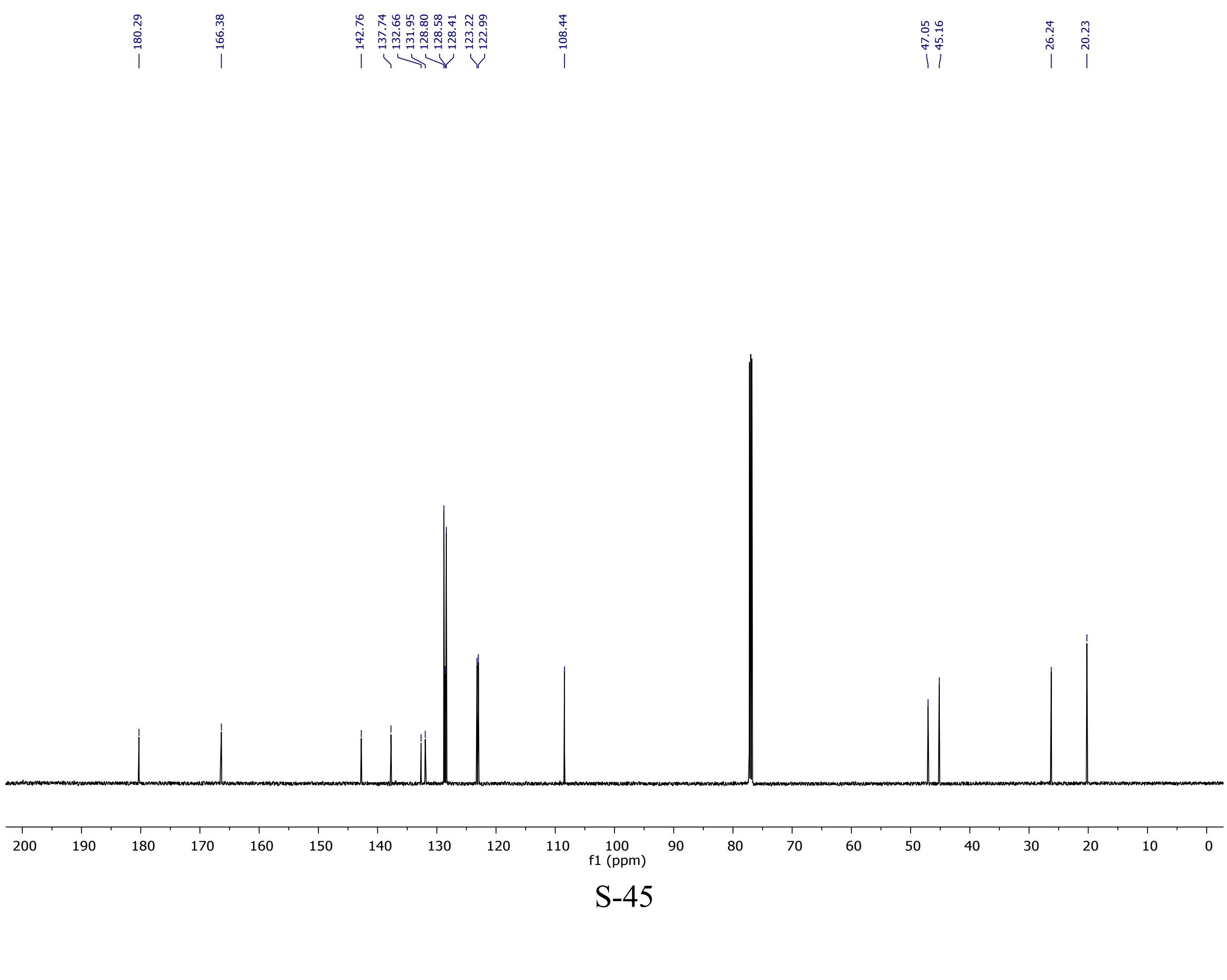
N-[(1,3-Dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3c)



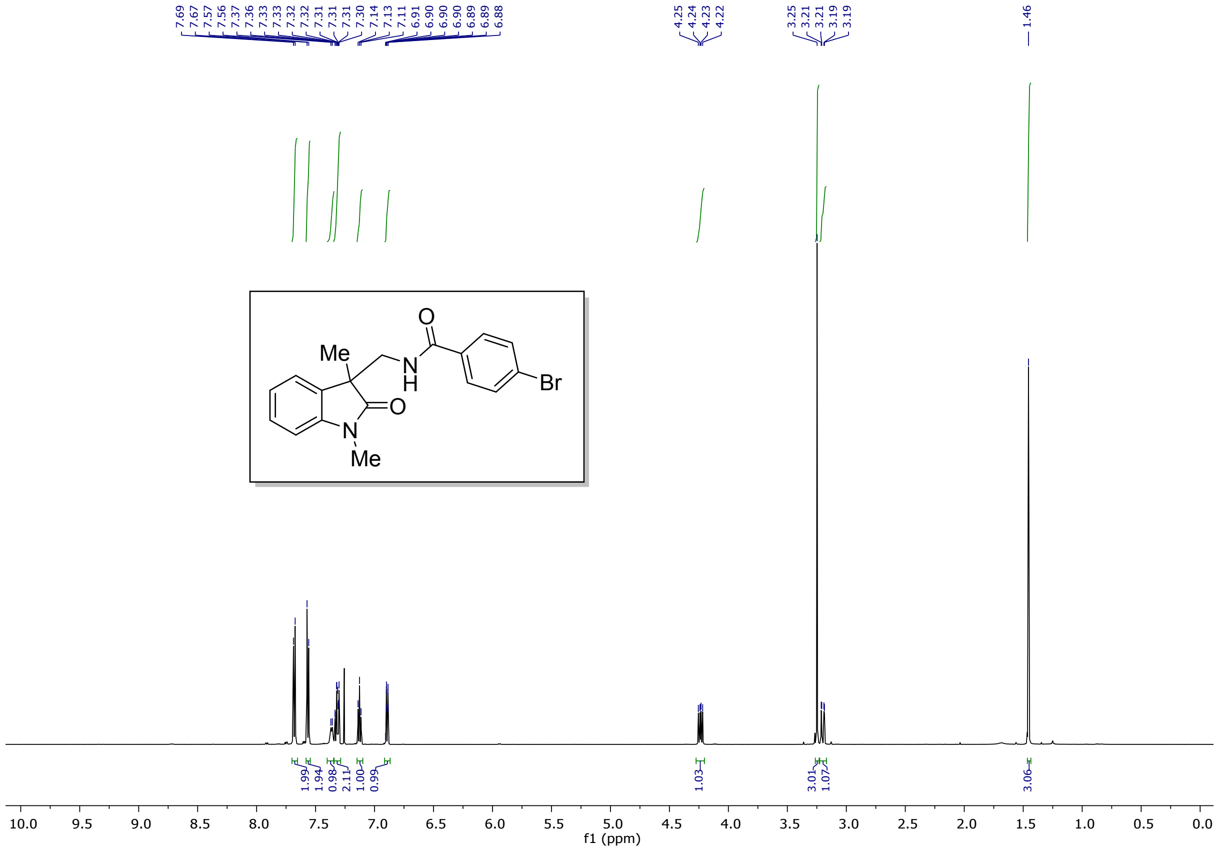


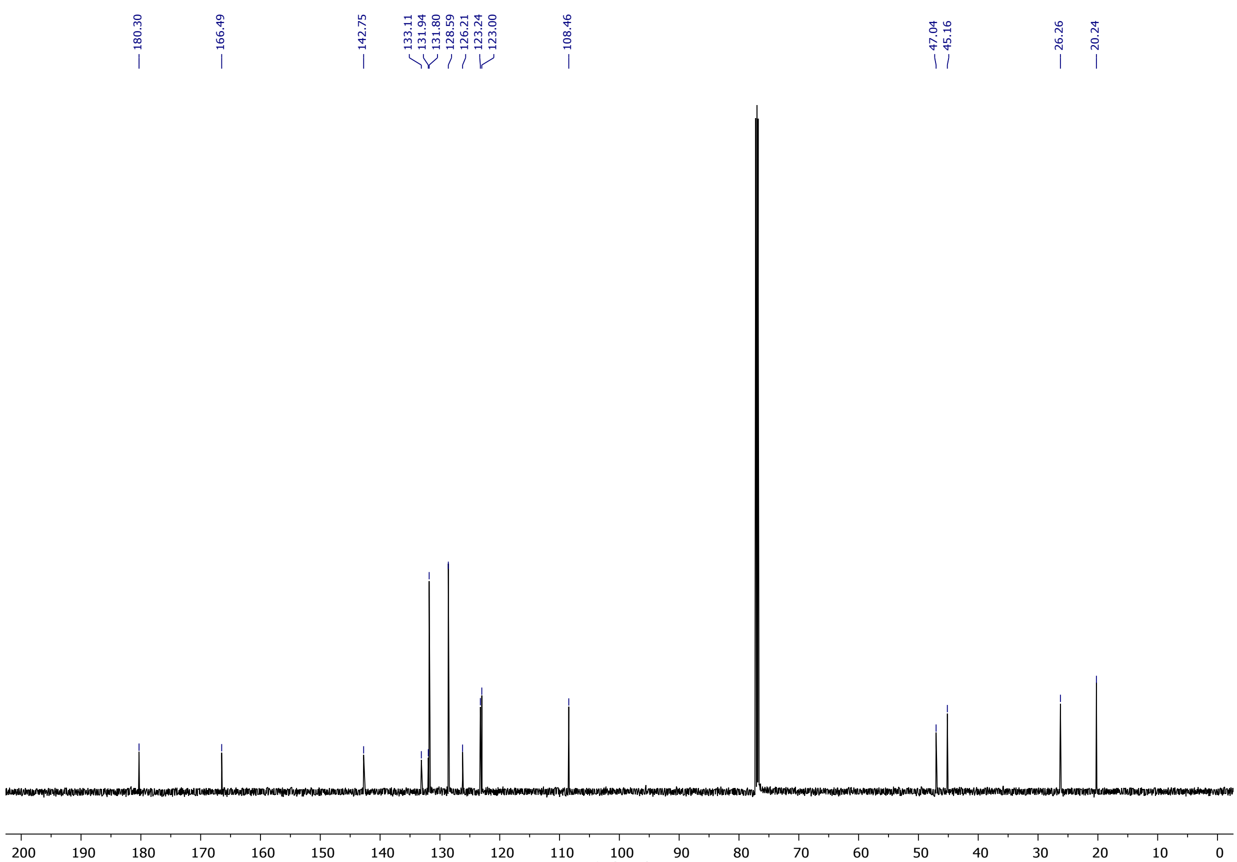
4-Chloro-*N*-[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3d)



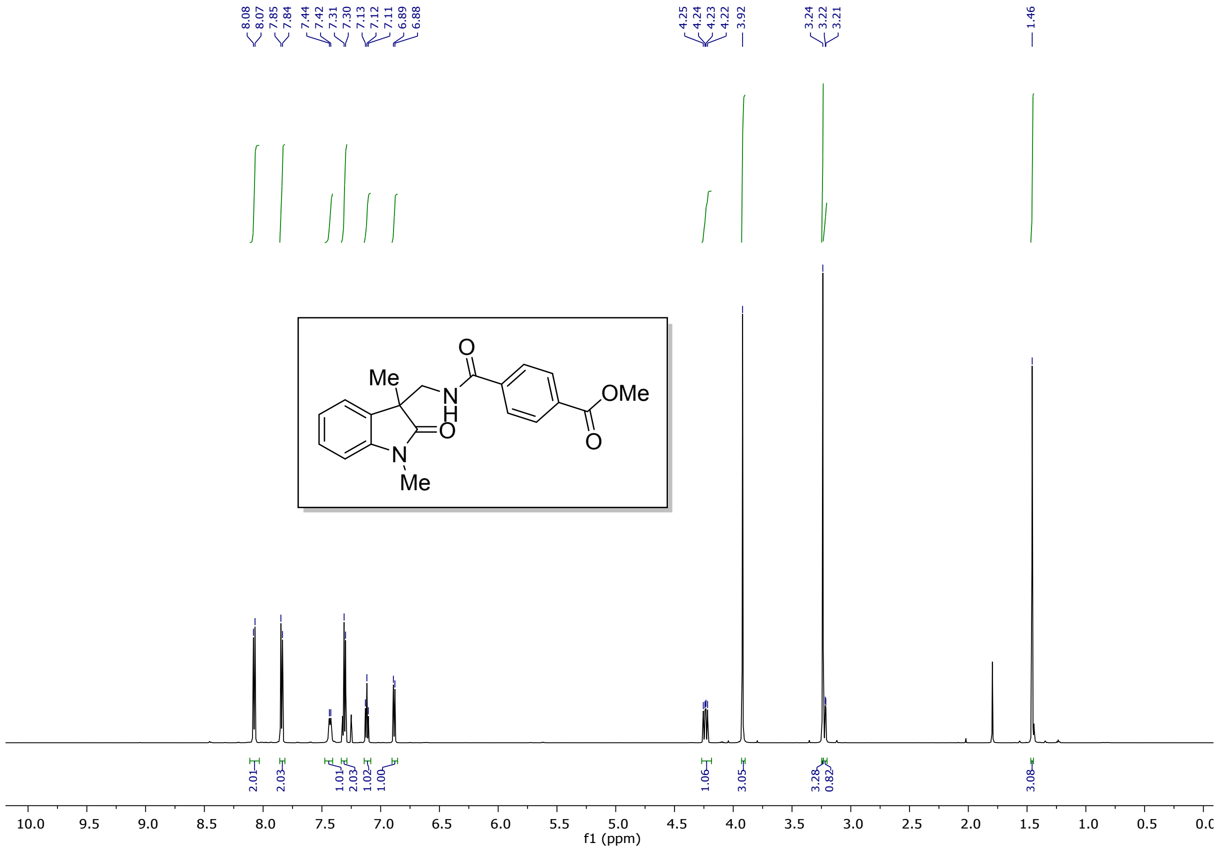


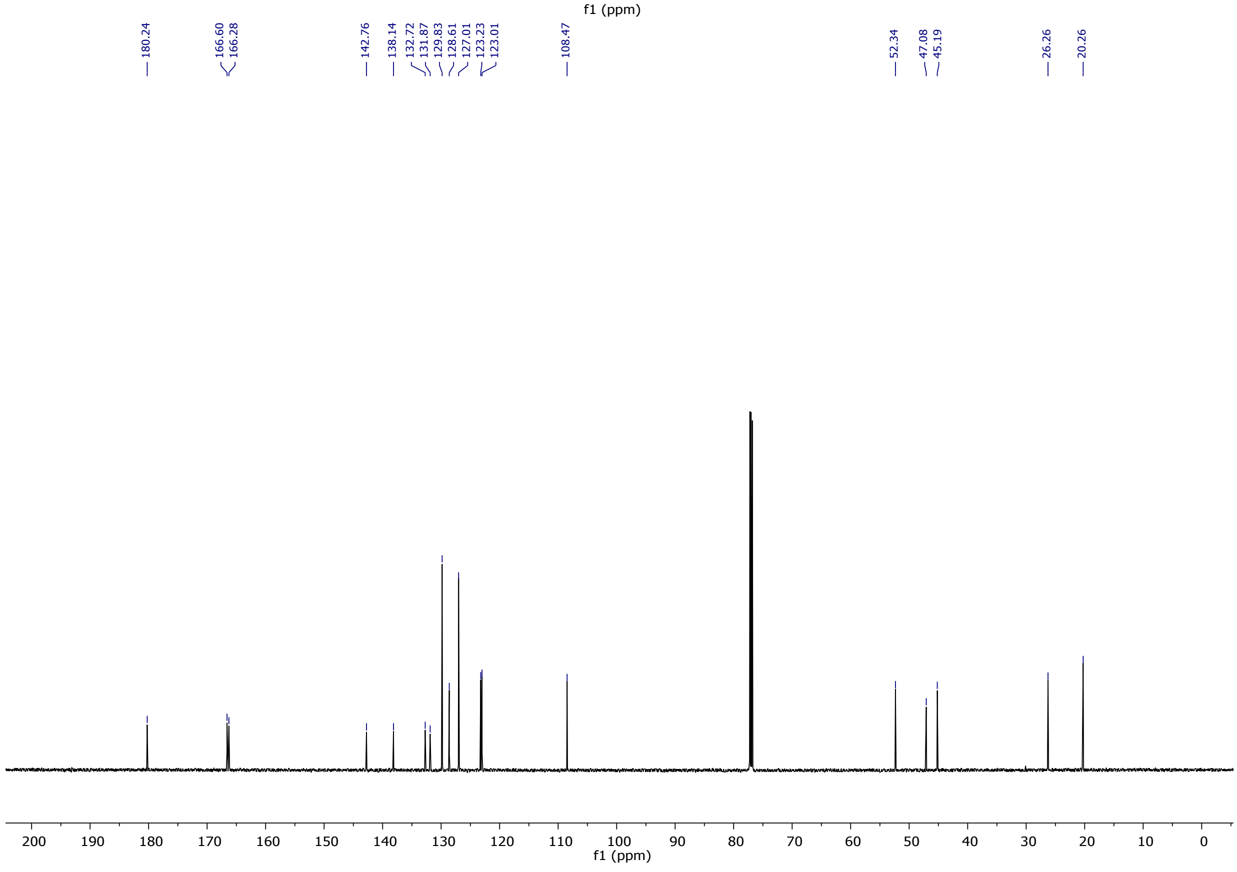
4-Bromo-*N*-[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3e)



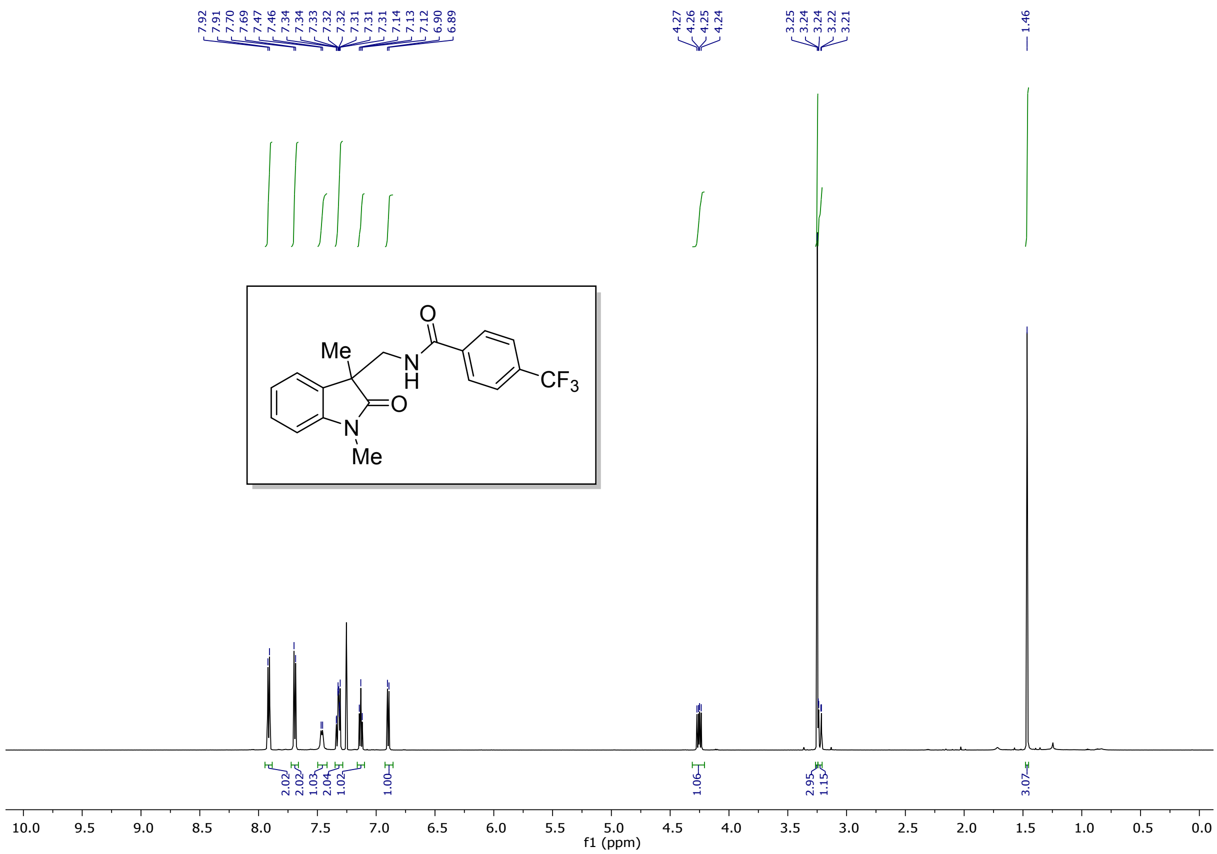


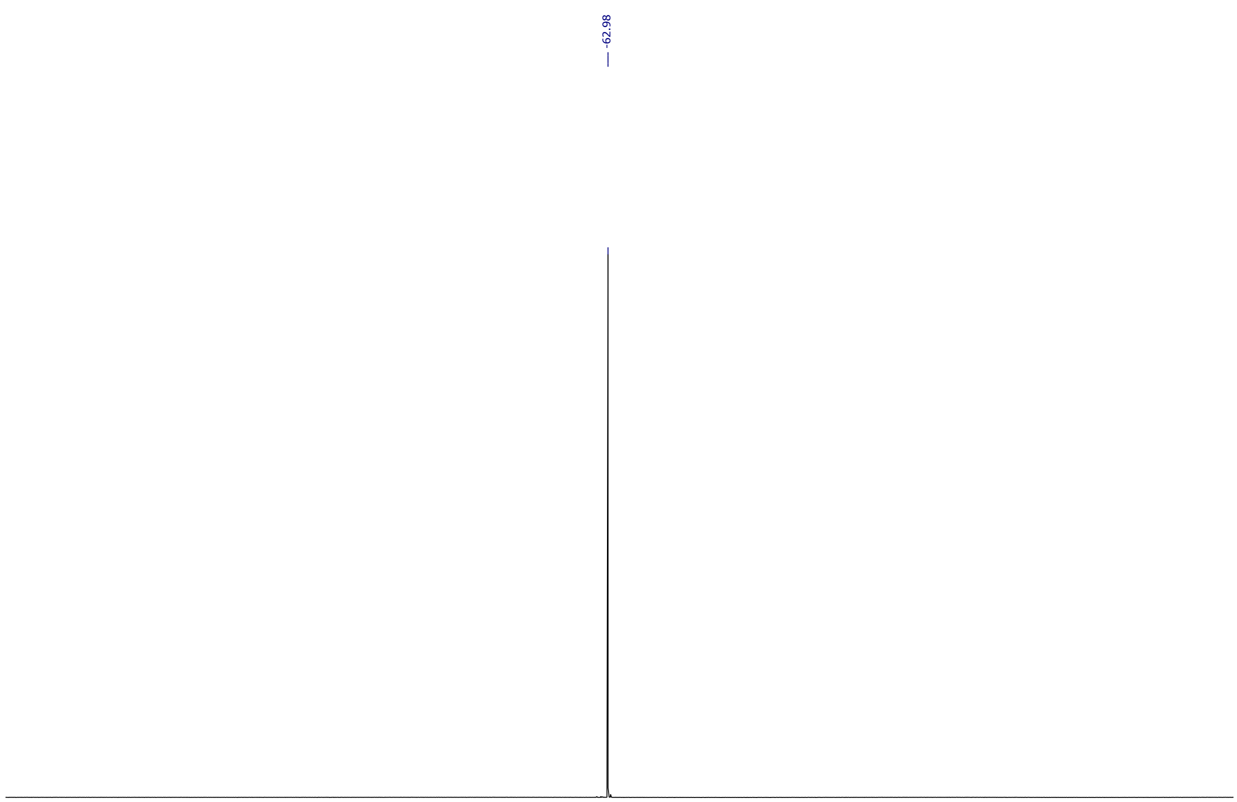
Methyl-4-{[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]carbamoyl}benzoate (Table 2, 3f)

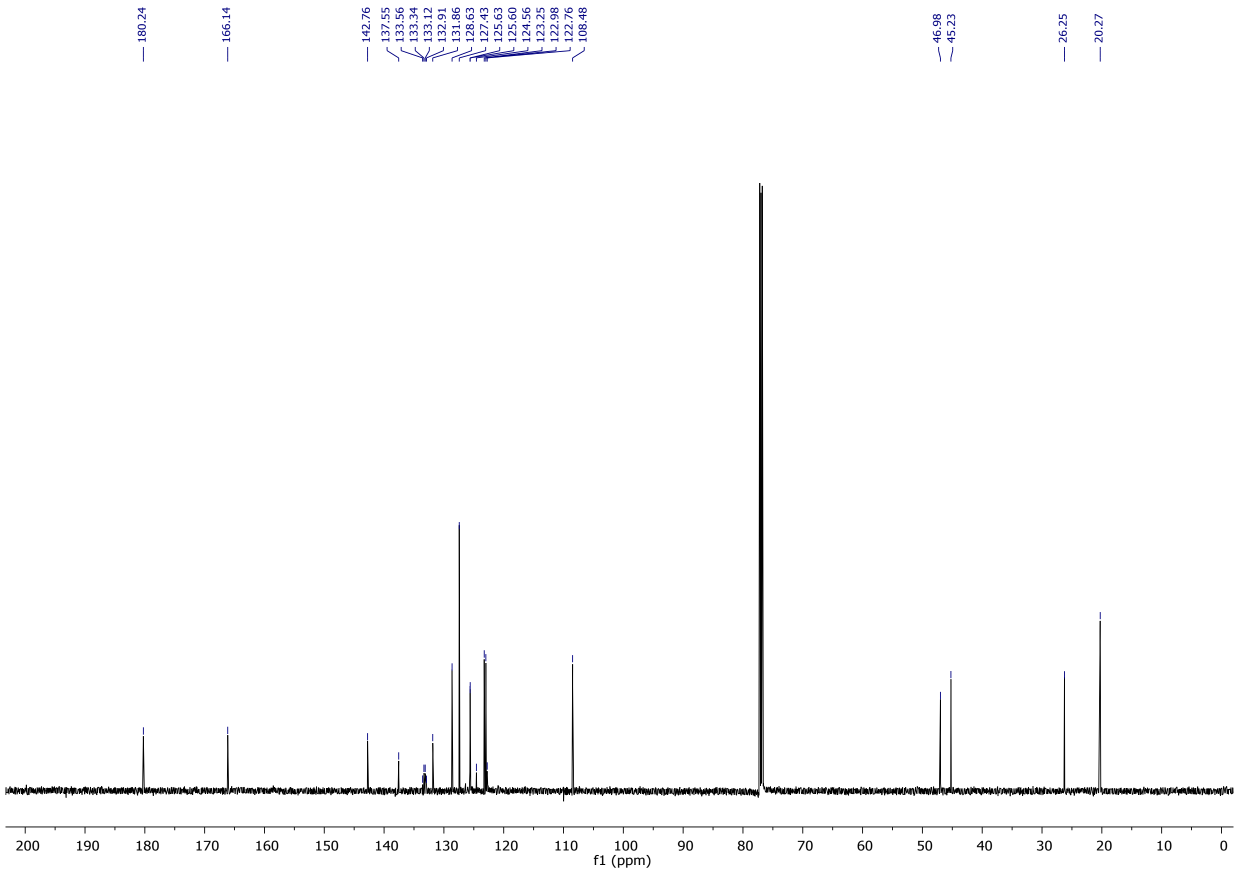




N-[(1,3-Dimethyl-2-oxoindolin-3-yl)methyl)-4-(trifluoromethyl]benzamide (Table 2, 3g)



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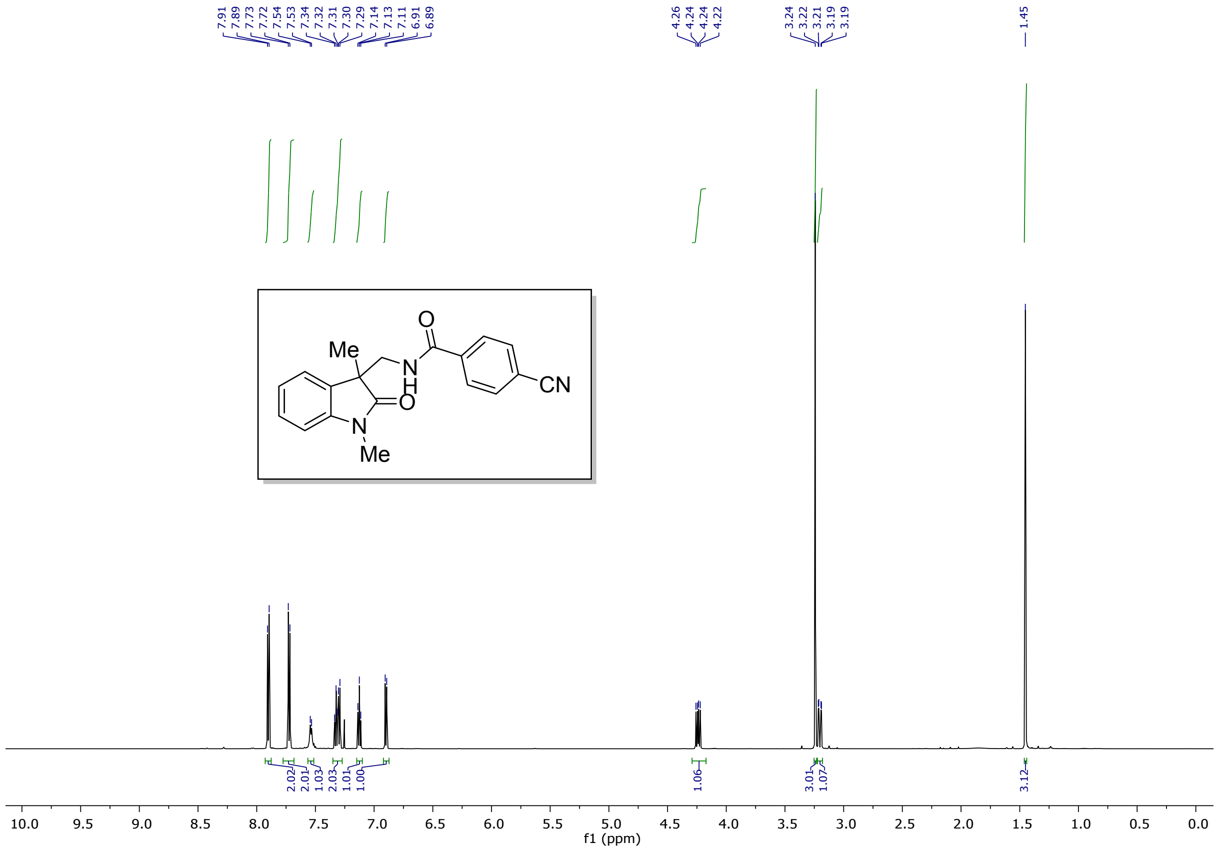
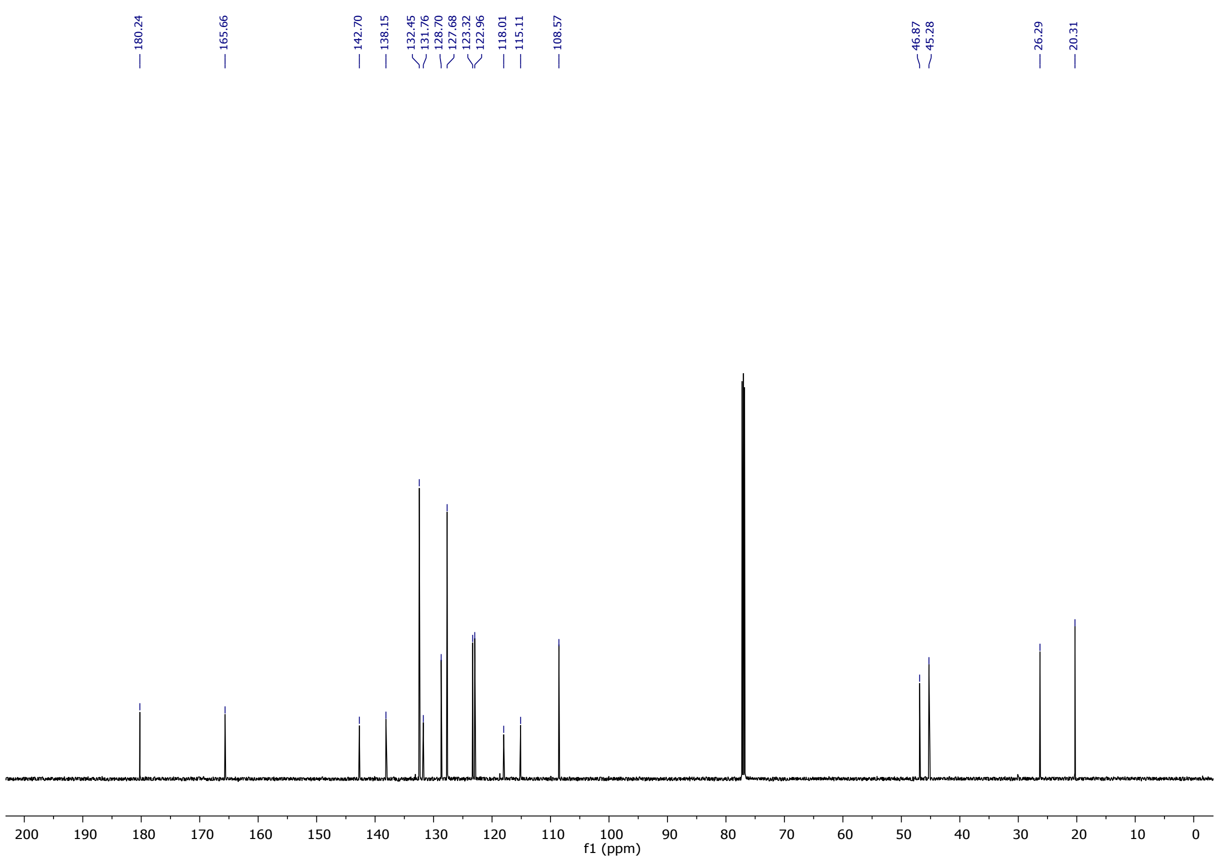
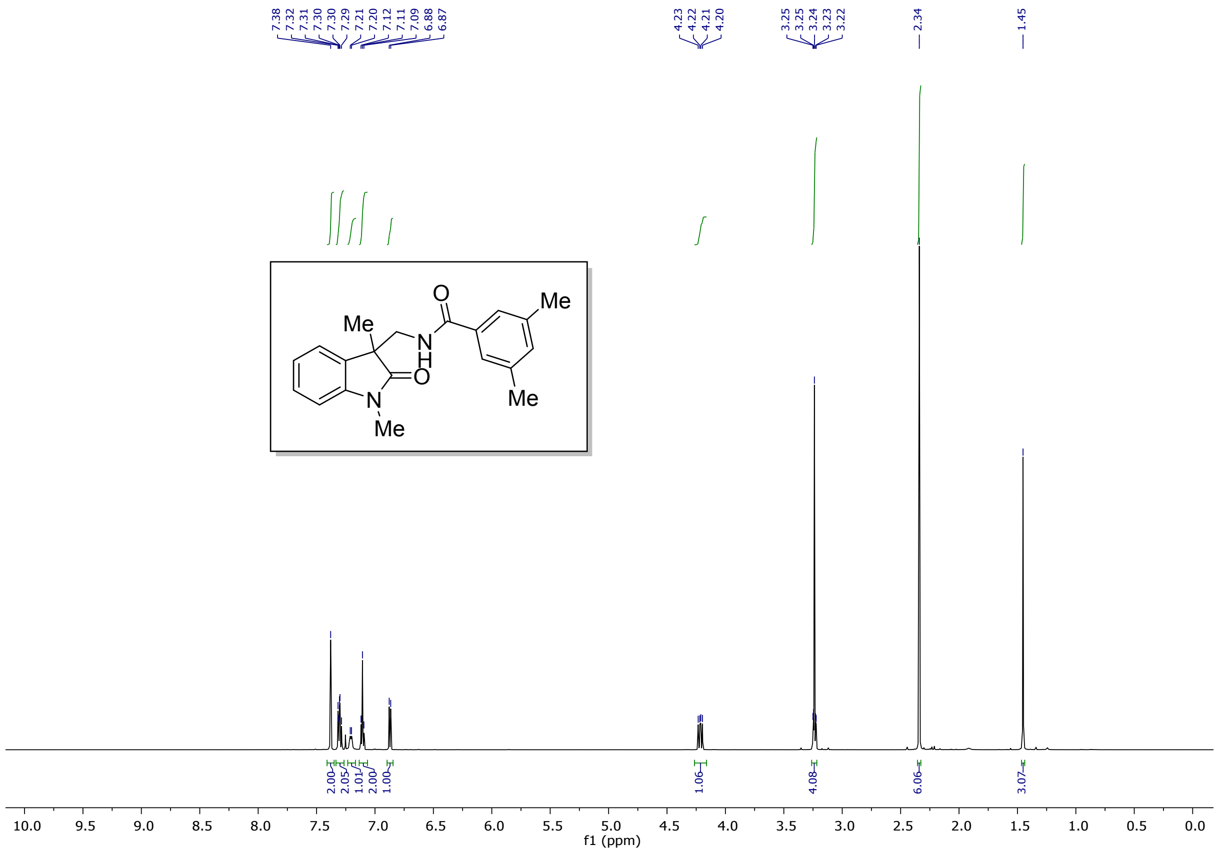
124.56
123.25
122.98
122.76
108.48
46.98
45.23
26.25
20.27
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

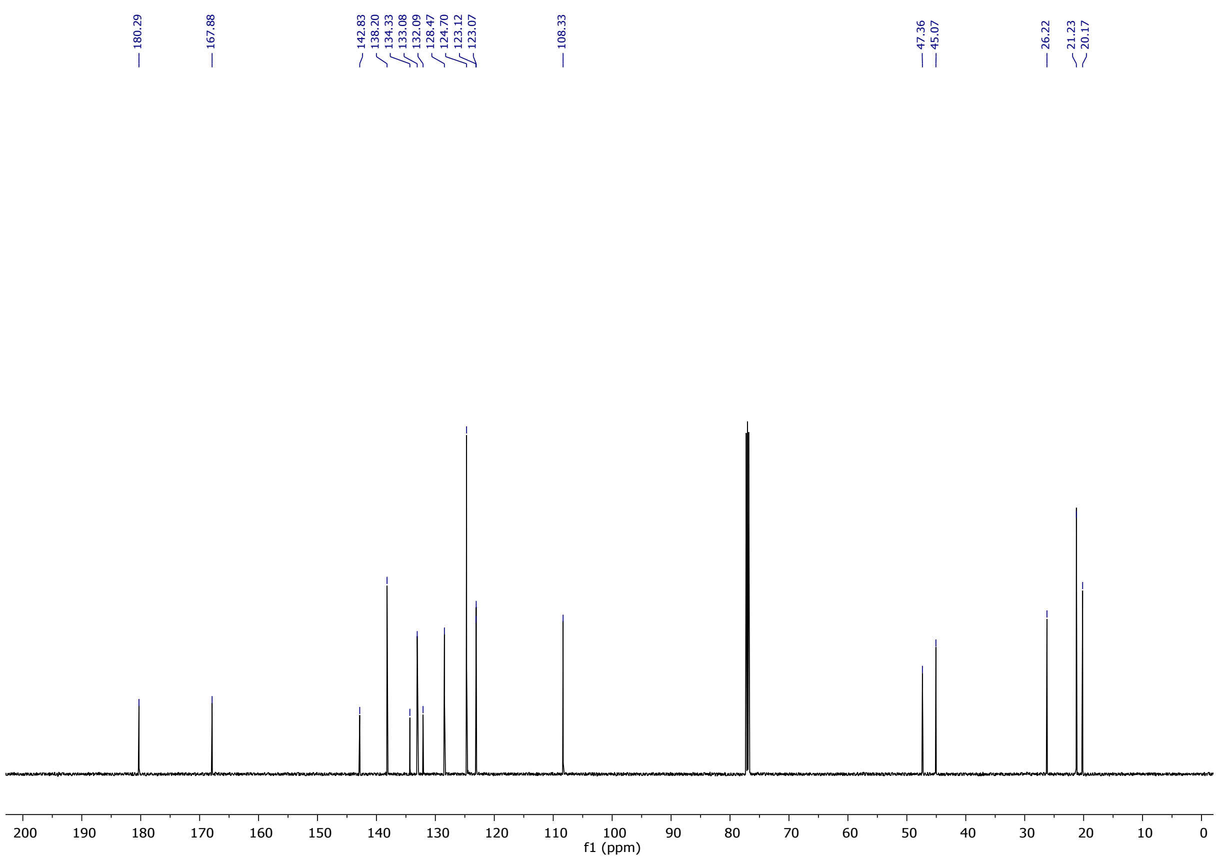
4-Cyano-*N*-[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3h)



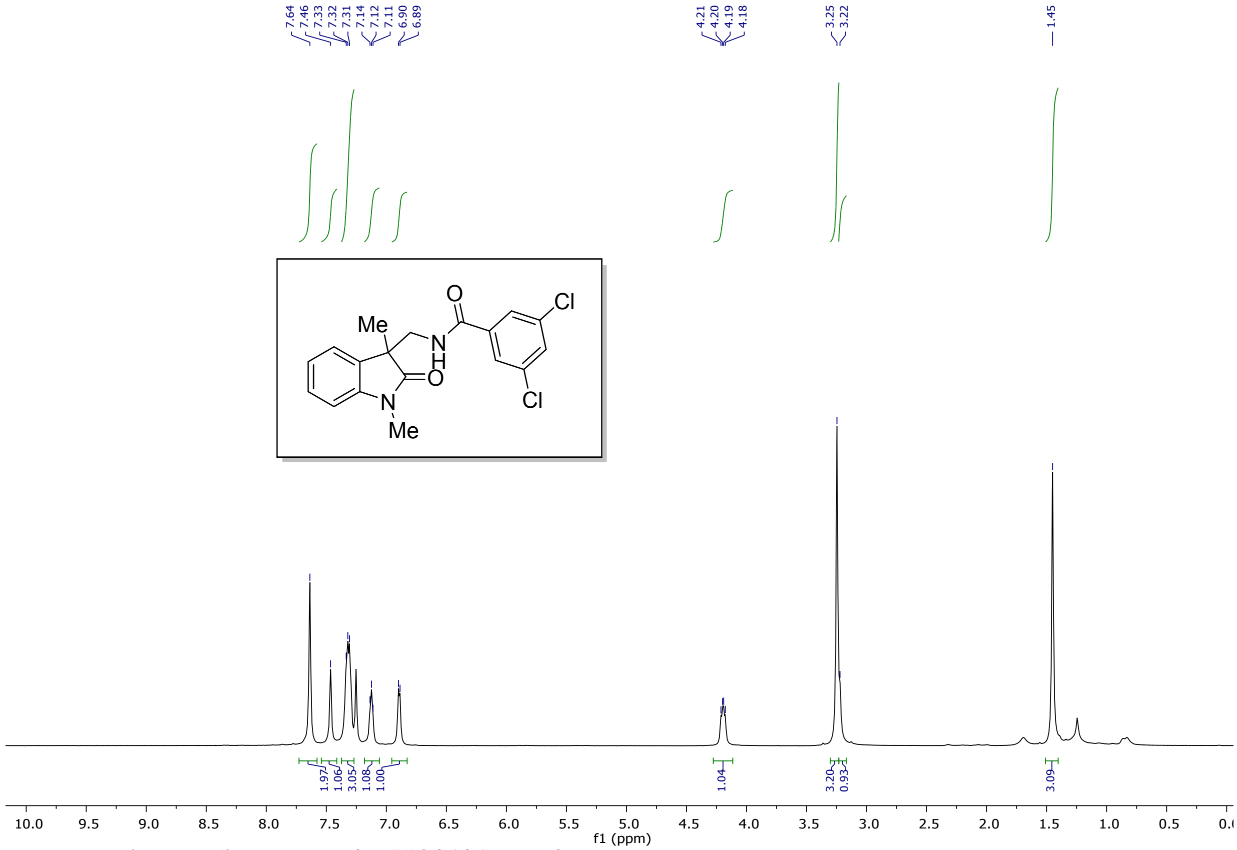


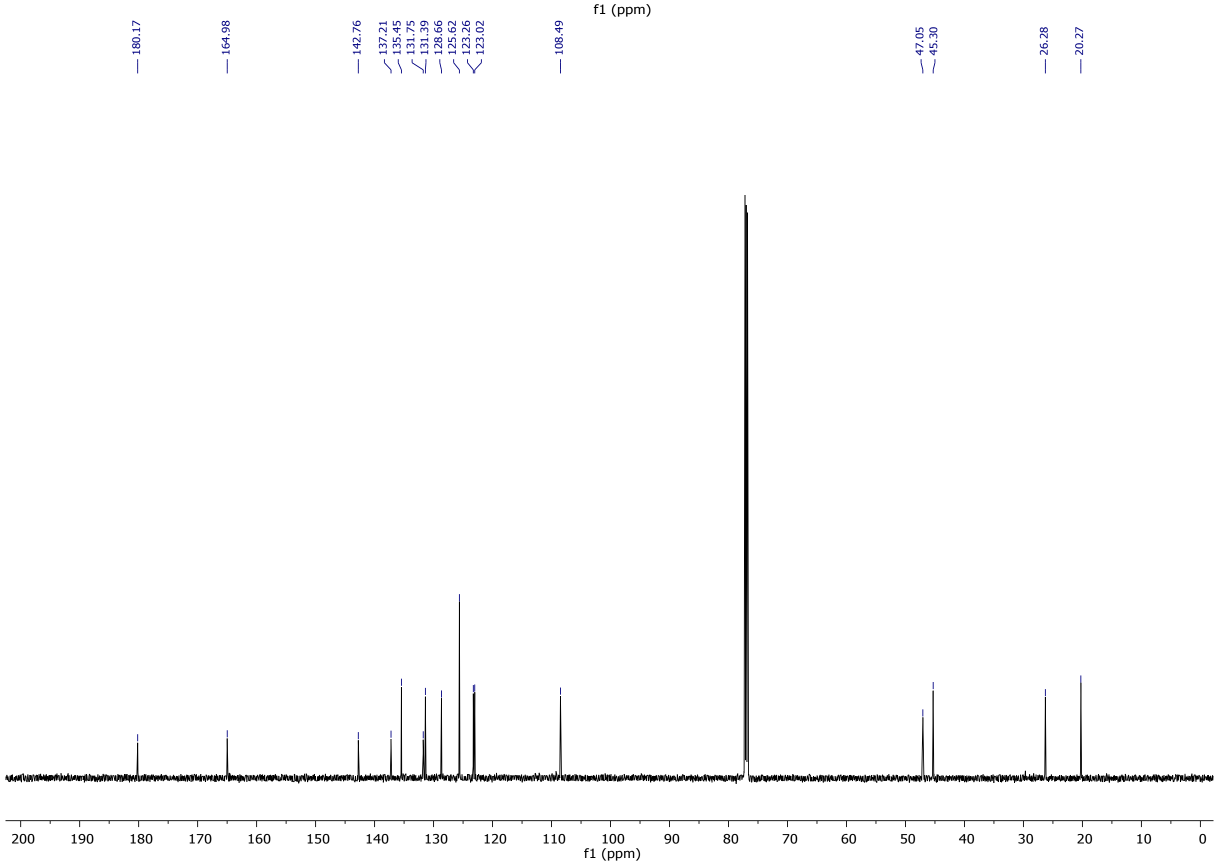
N-[(1,3-Dimethyl-2-oxoindolin-3-yl)methyl]-3,5-dimethylbenzamide (Table 2, 3i)



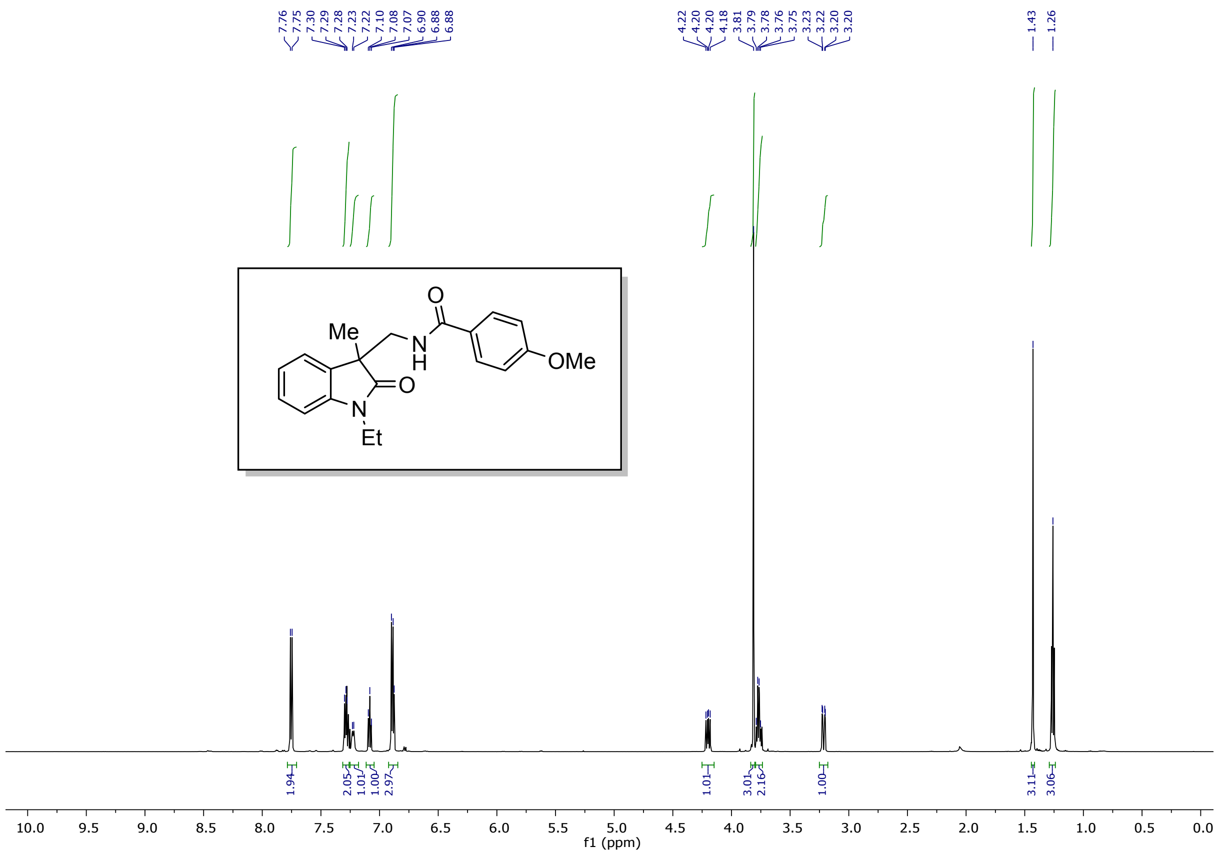


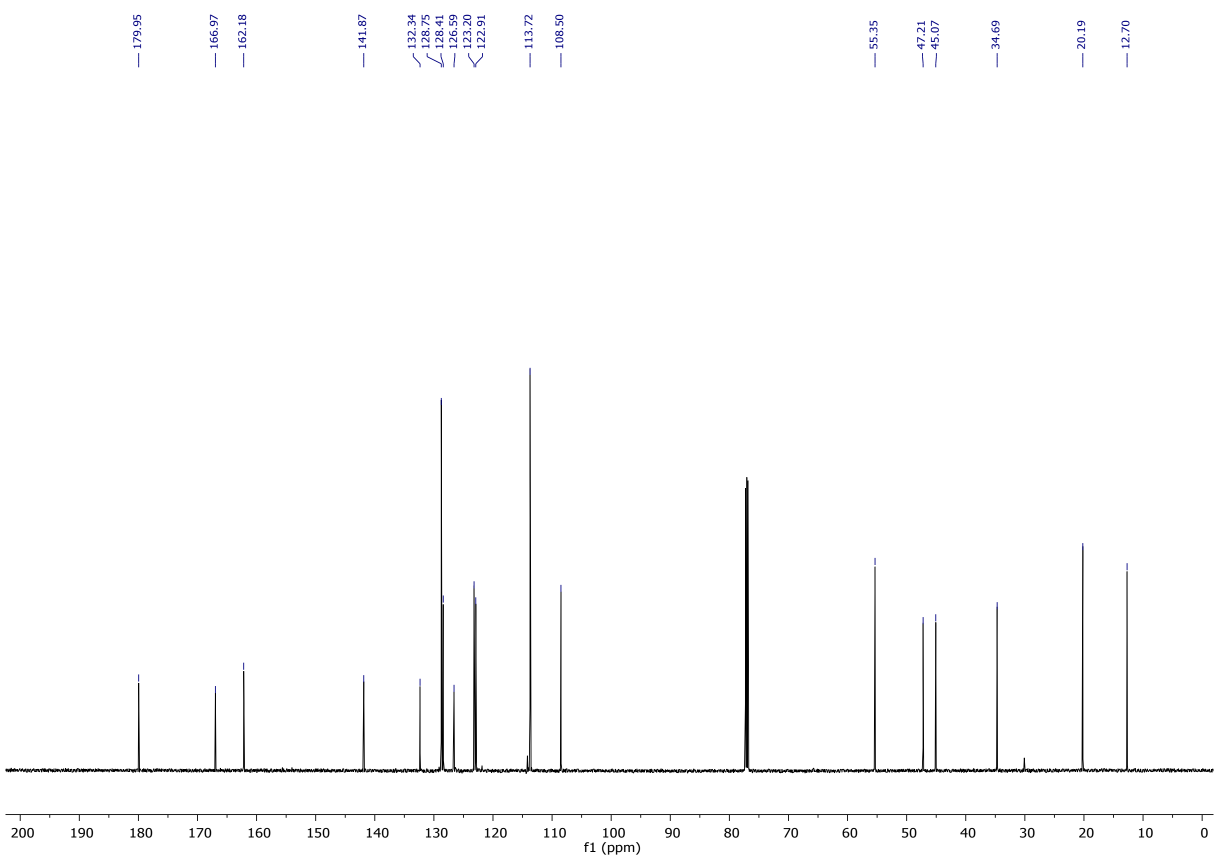
3,5-Dichloro-*N*-[(1,3-dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3j)



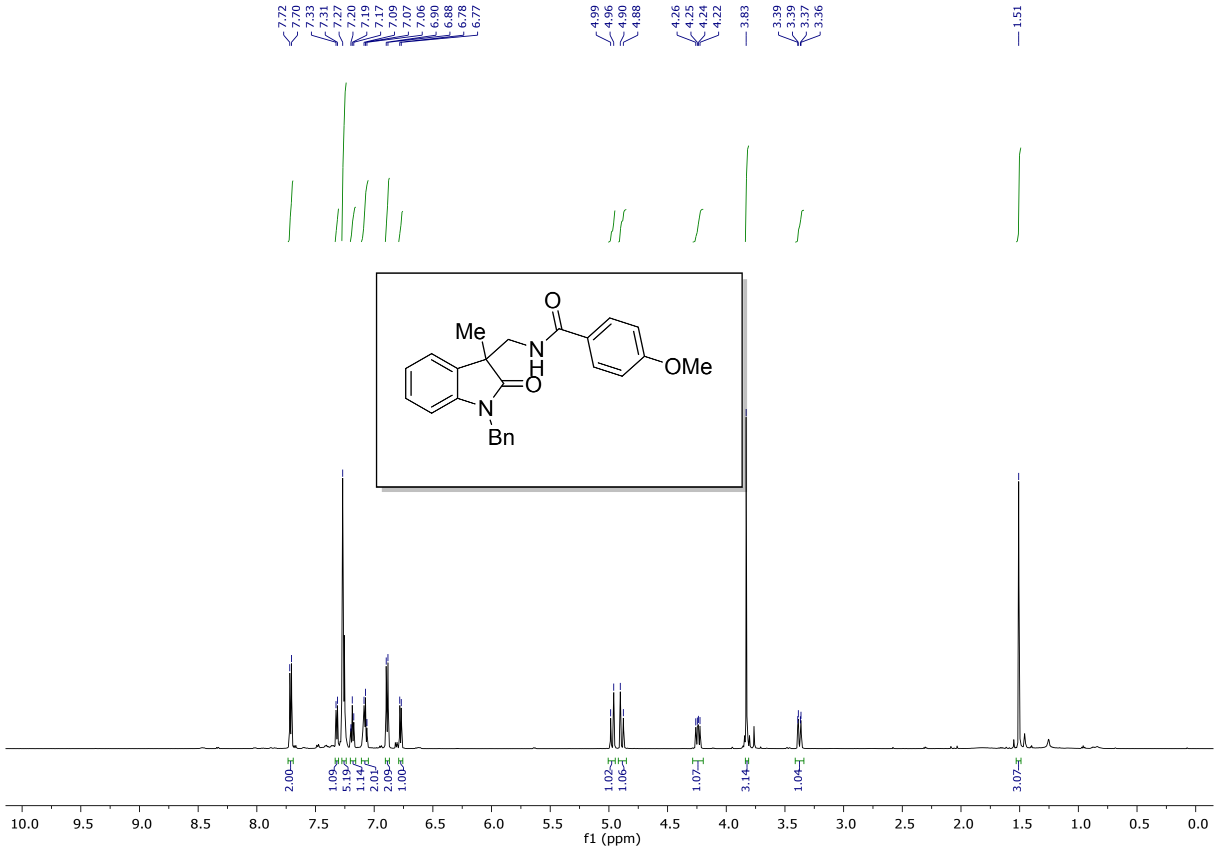


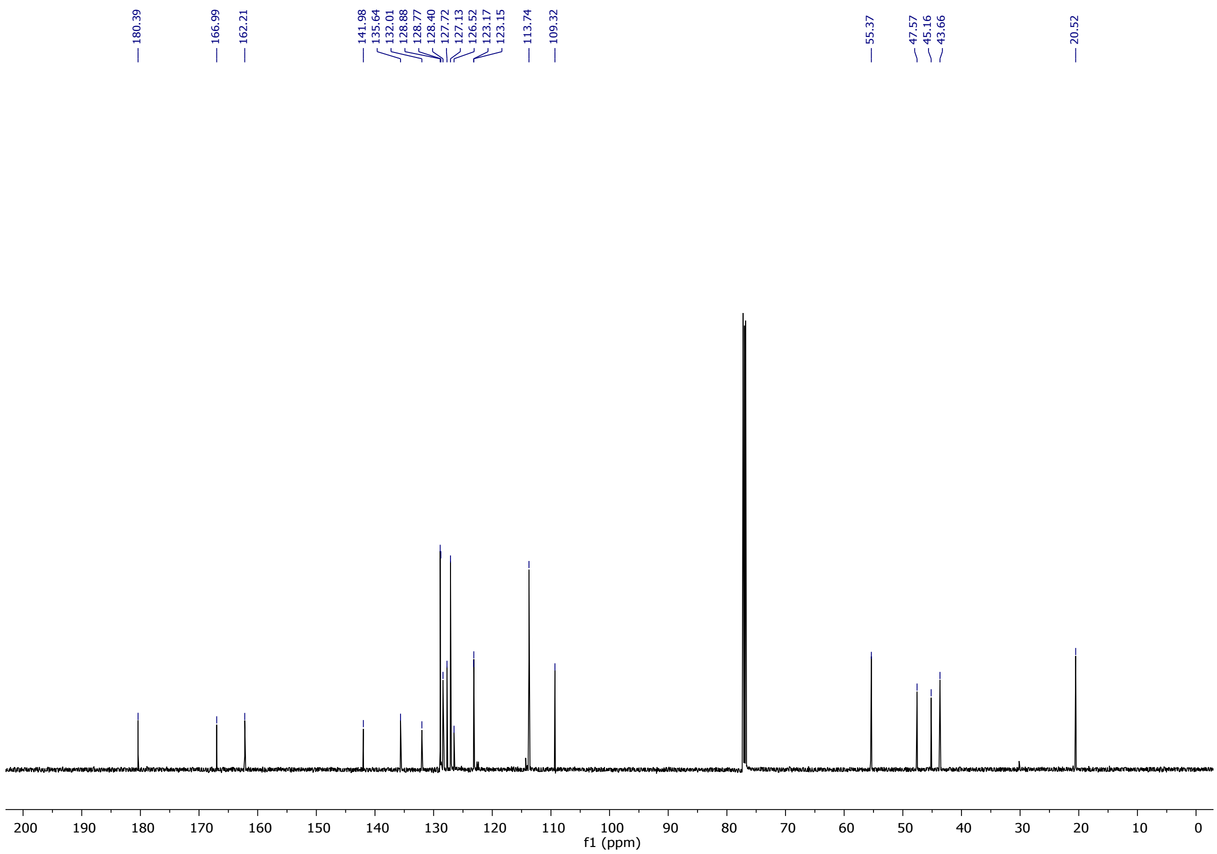
N-[(1-Ethyl-3-methyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3k)



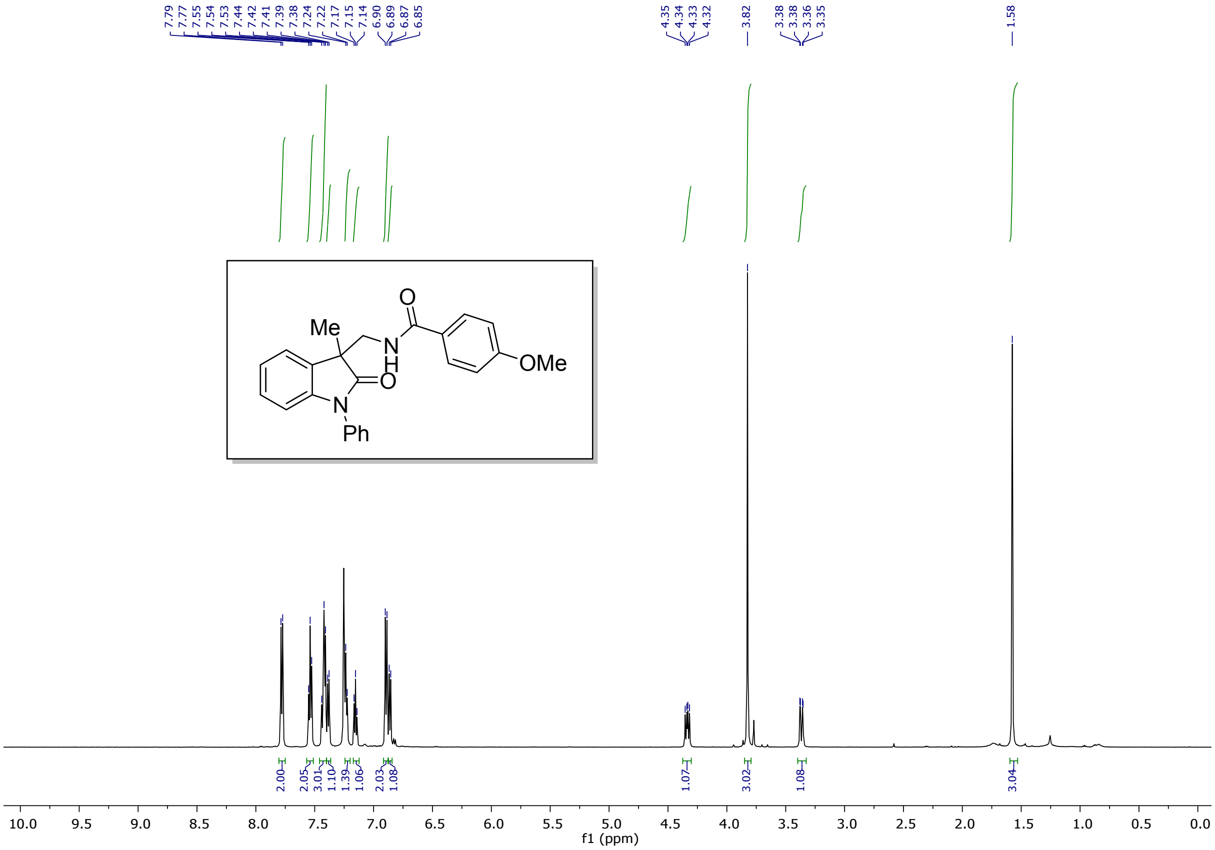


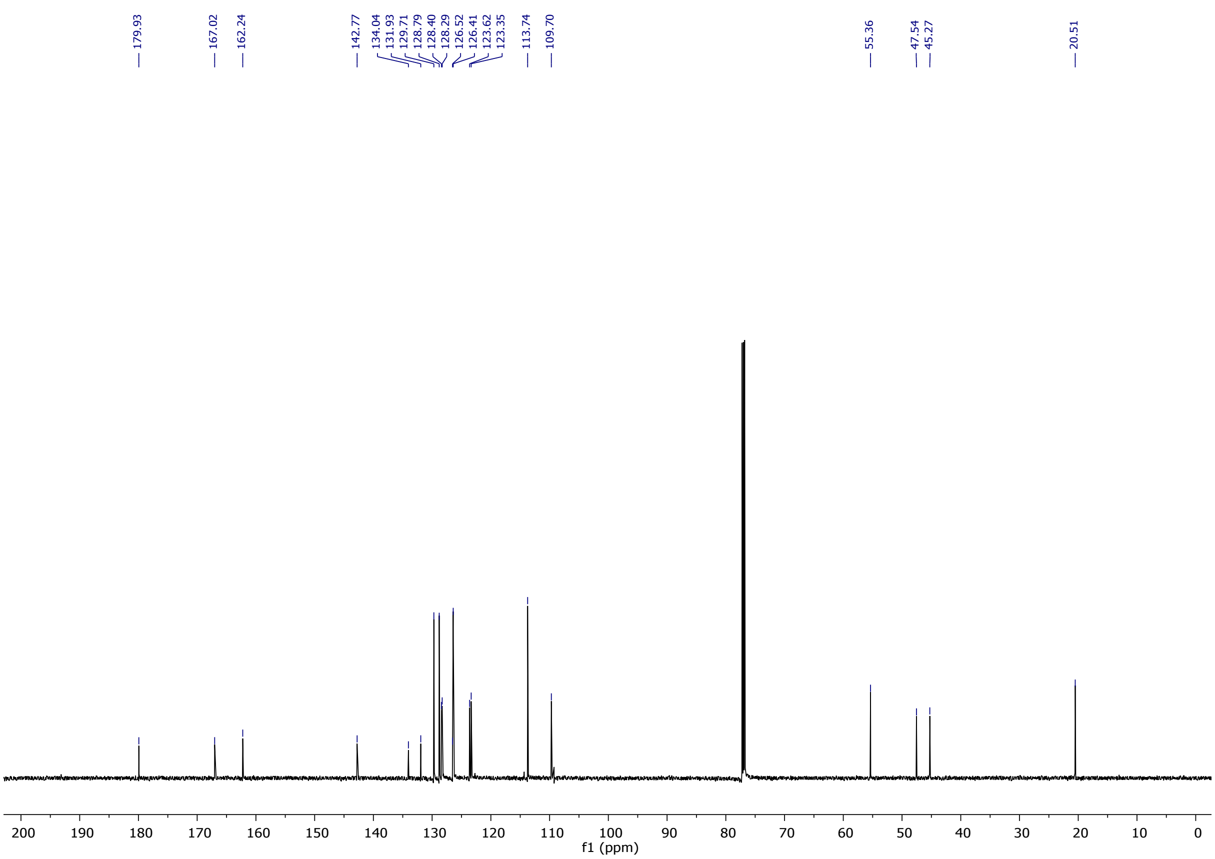
N-[(1-Benzyl-3-methyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3l)



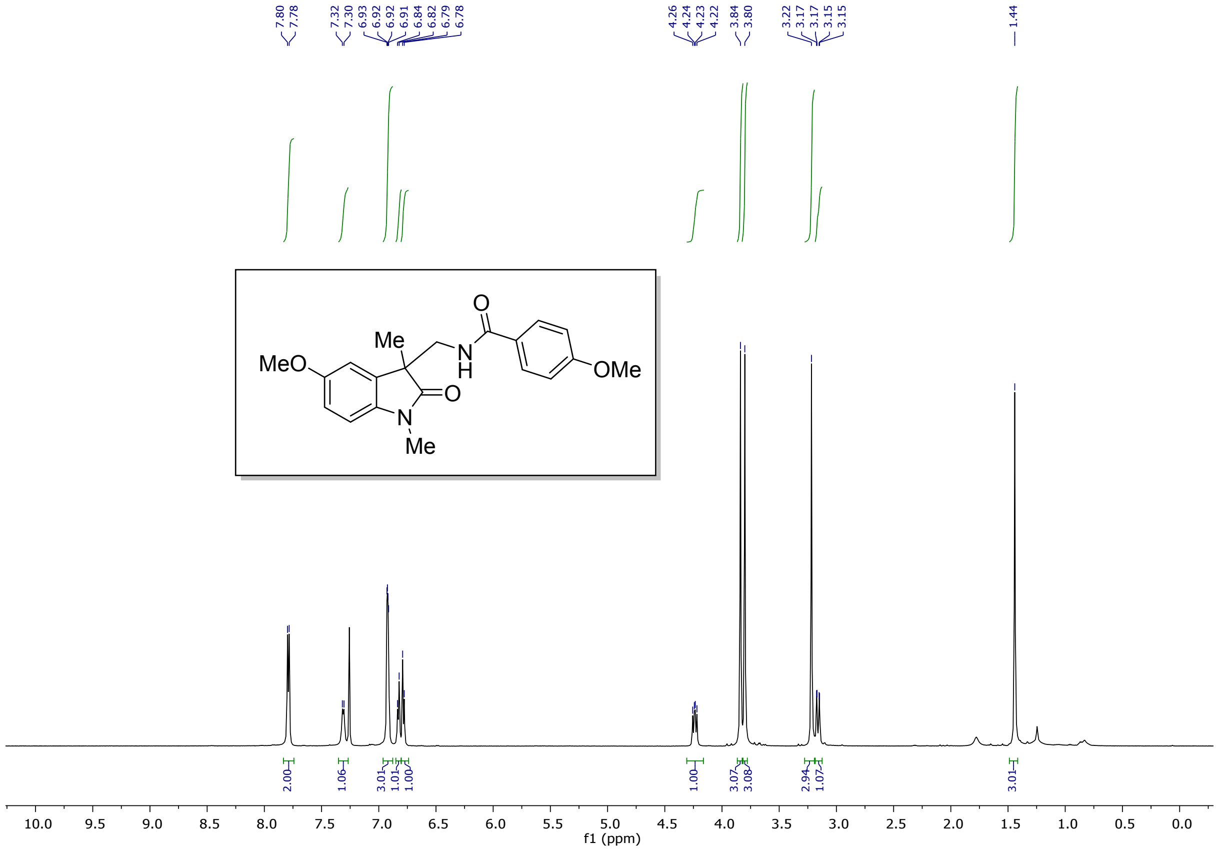


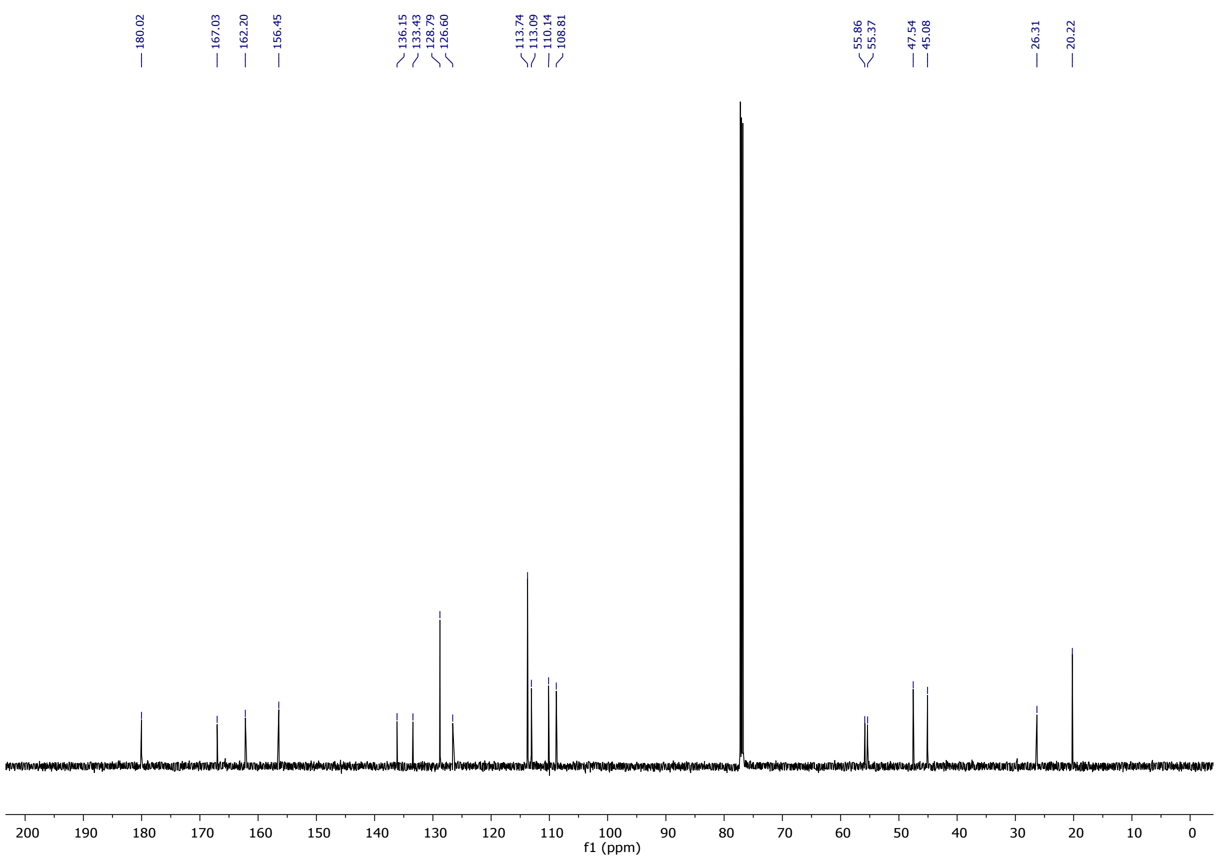
4-Methoxy-*N*-[(3-methyl-2-oxo-1-phenylindolin-3-yl)methyl]benzamide (Table 2, 3m)



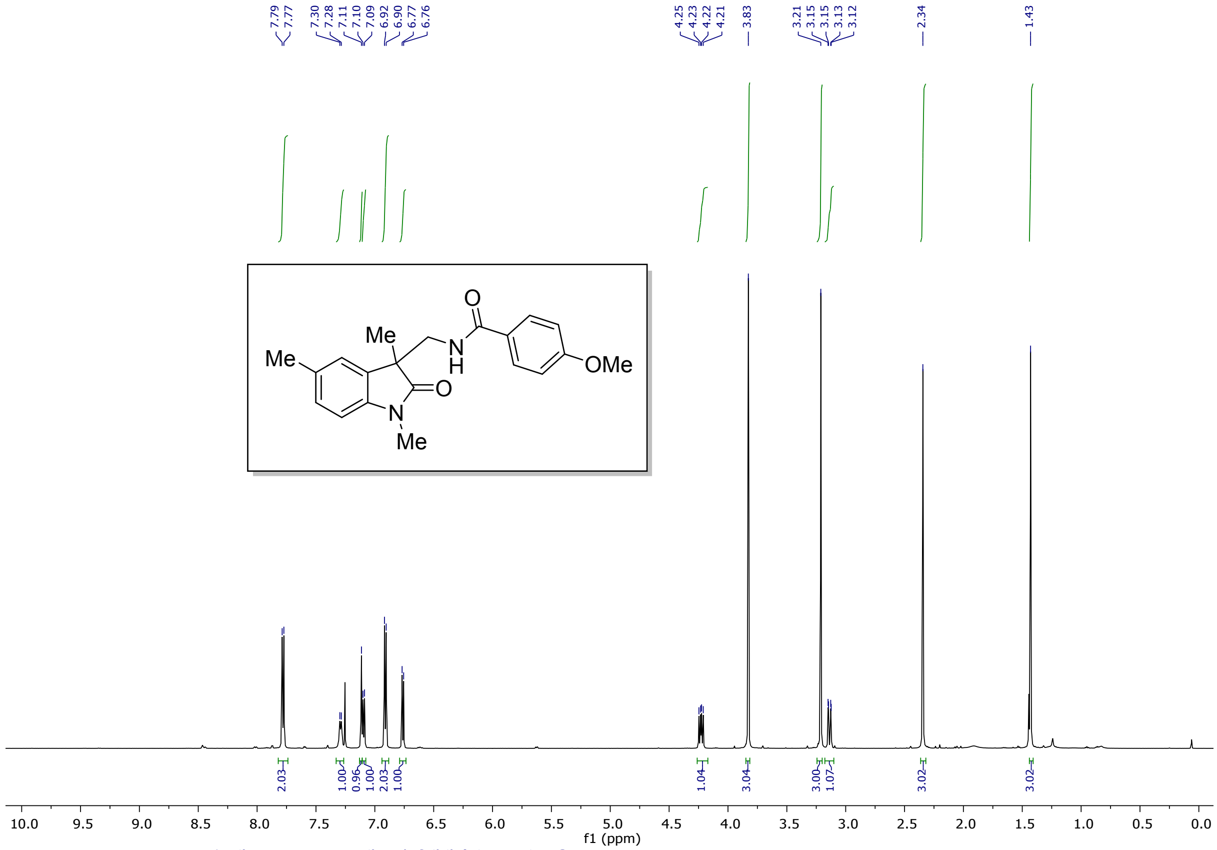


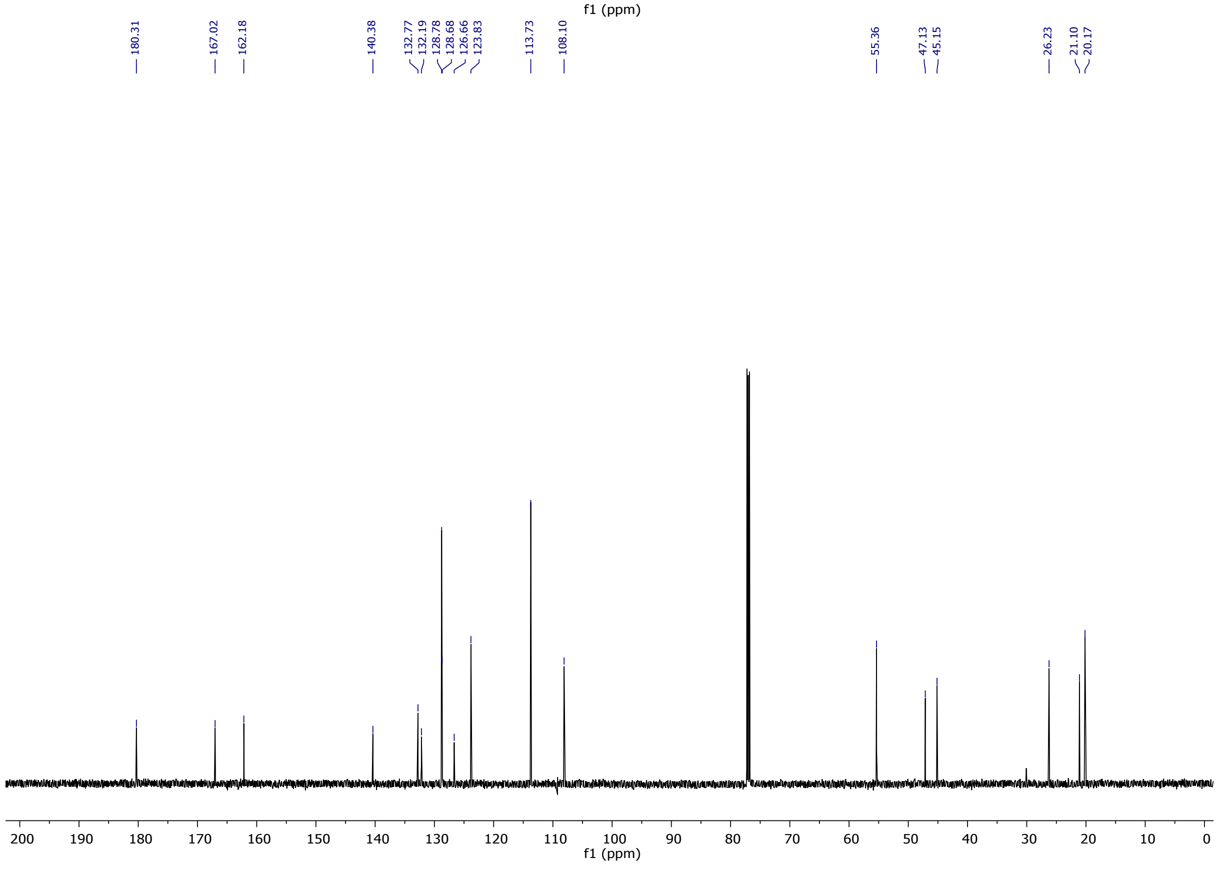
4-Methoxy-*N*-[(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3n)



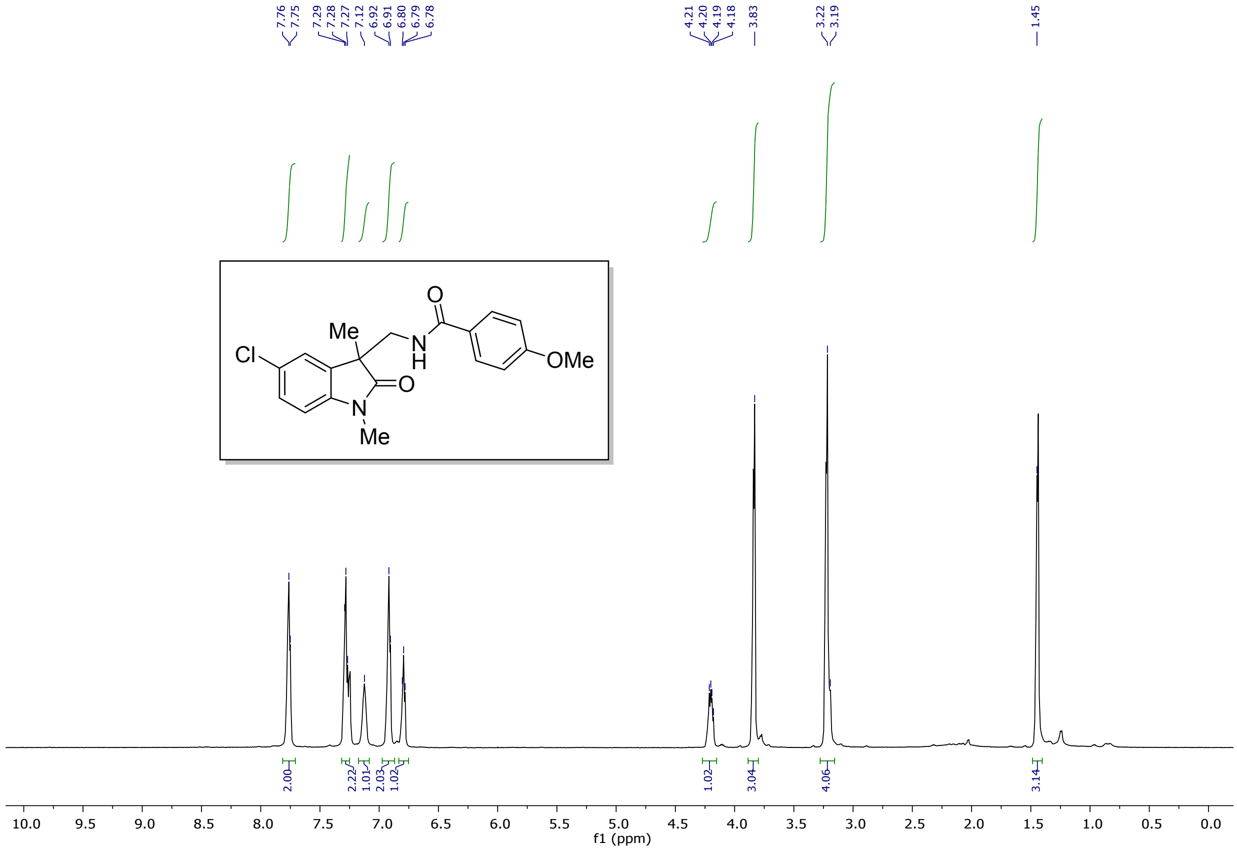


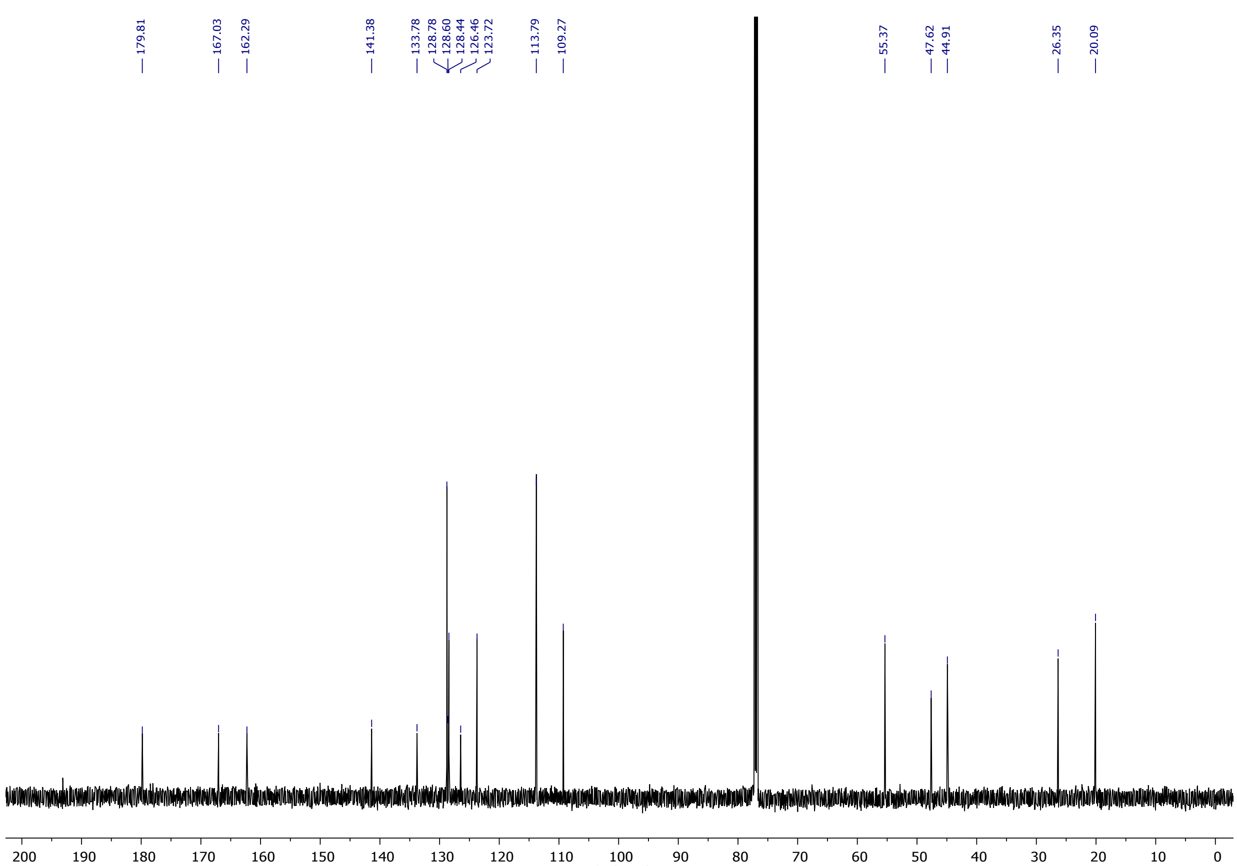
4-Methoxy-*N*-[(1,3,5-trimethyl-2-oxoindolin-3-yl)methyl]benzamide (Table 2, 3o)



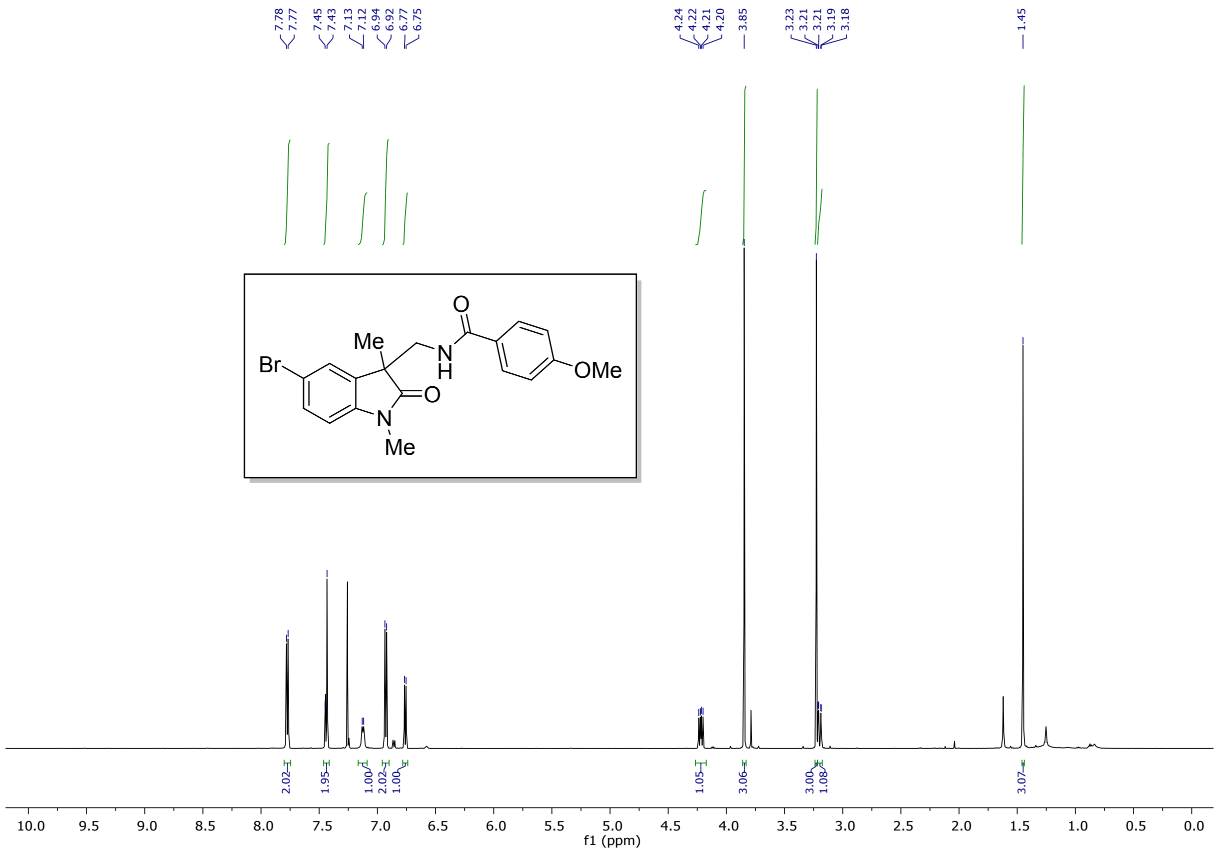


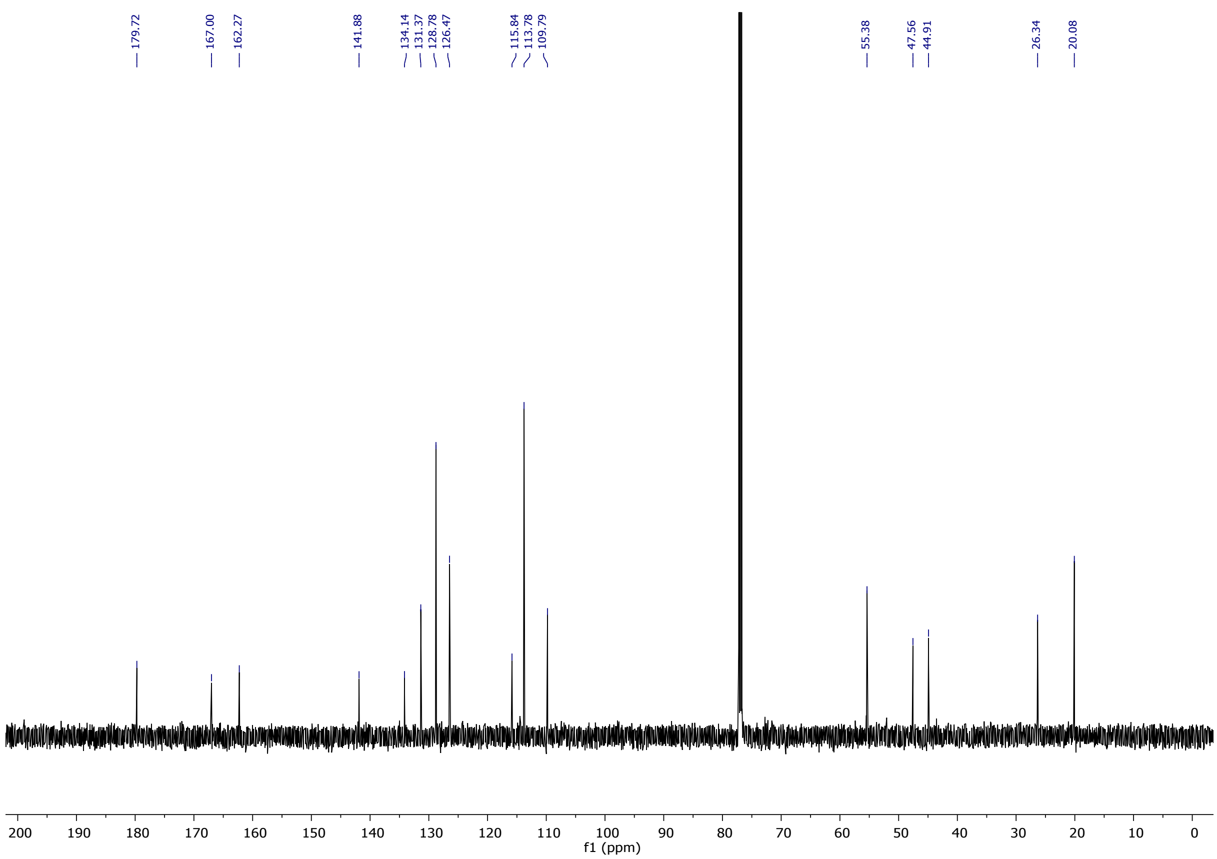
N-[(5-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3p)



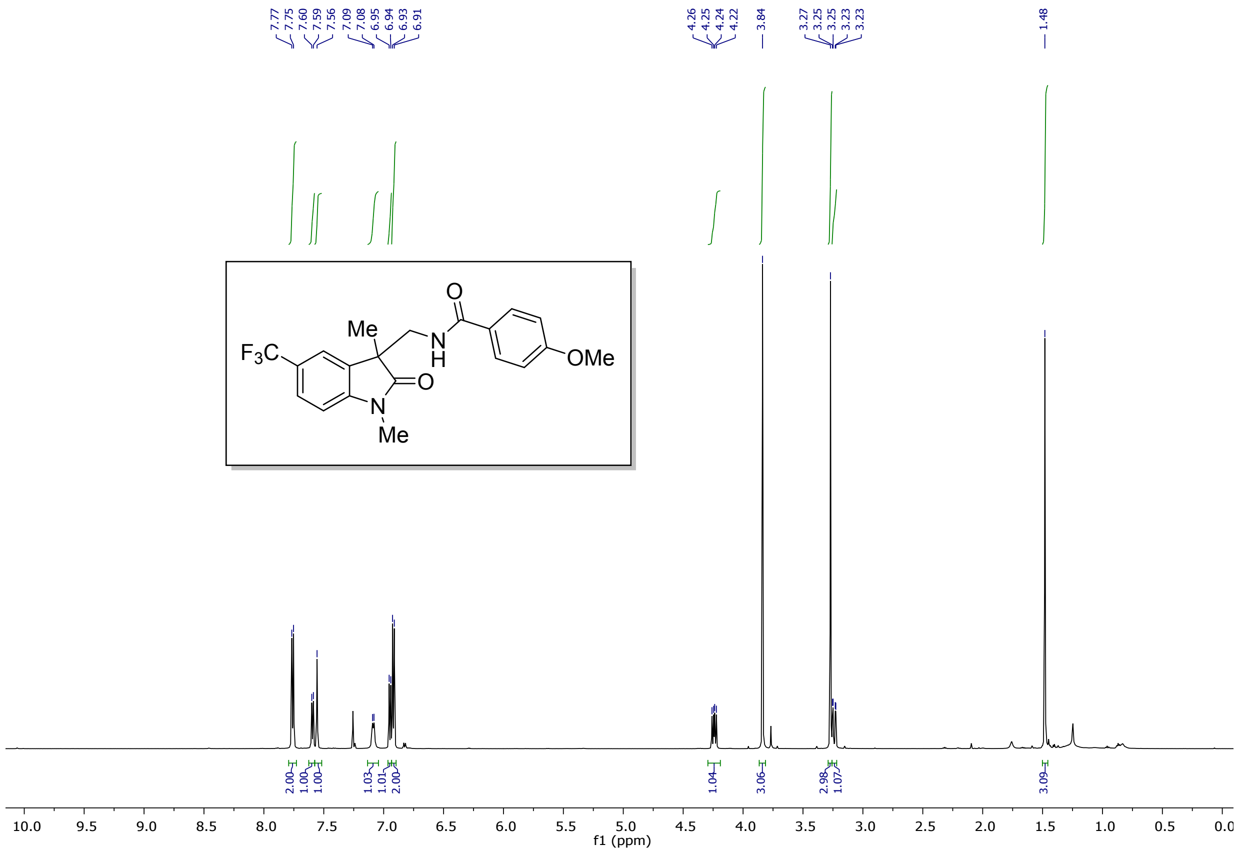


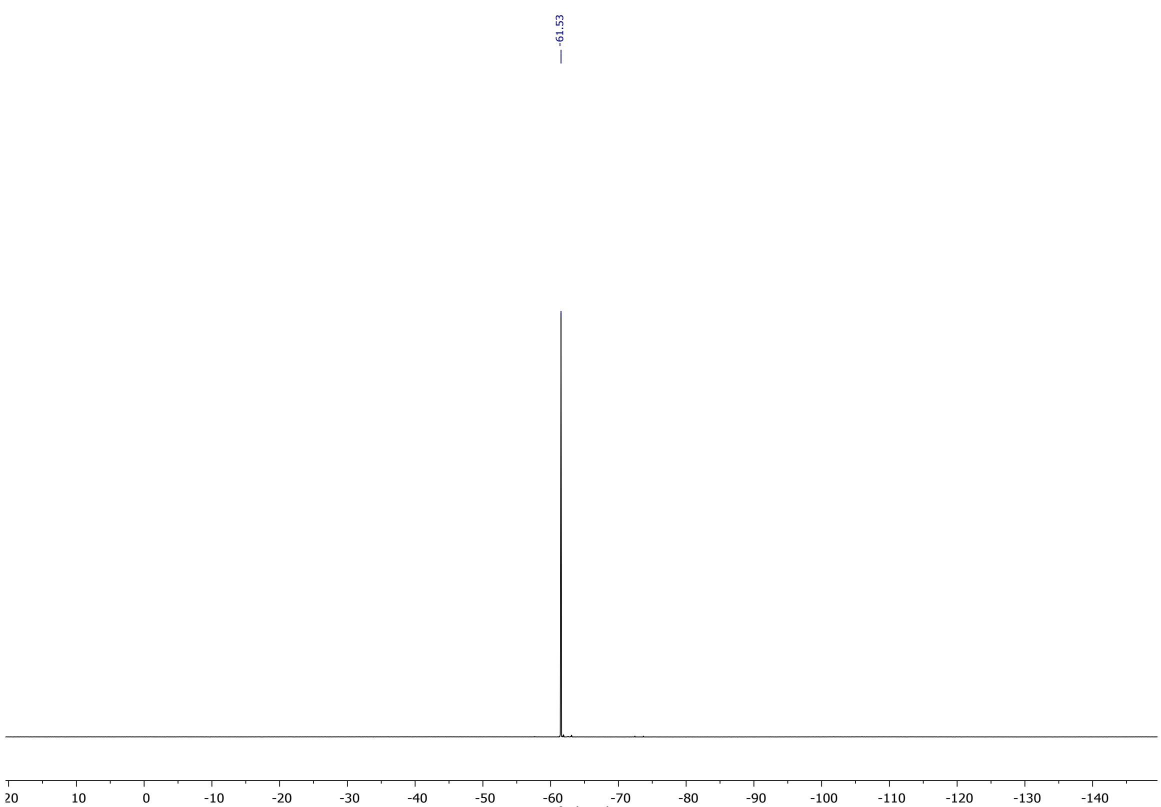
N-[(5-Bromo-1,3-dimethyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3q)

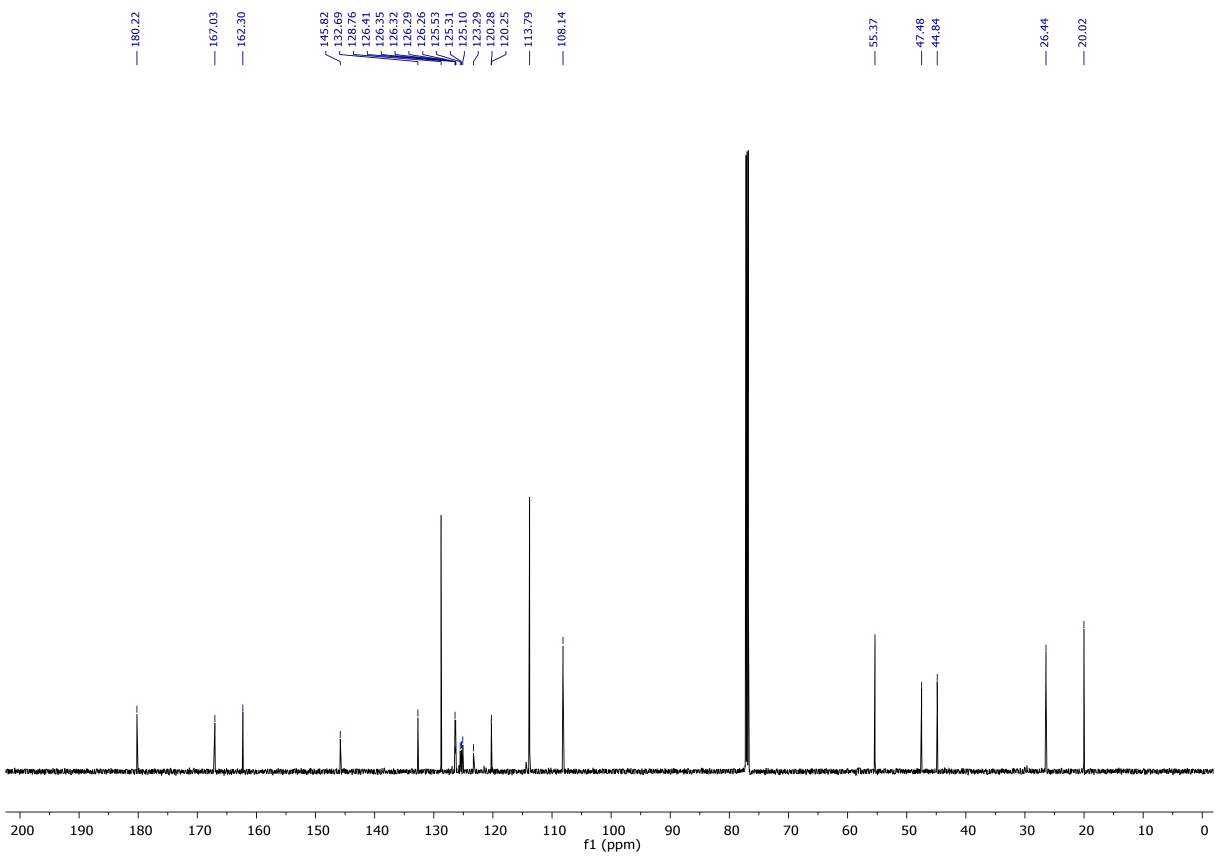




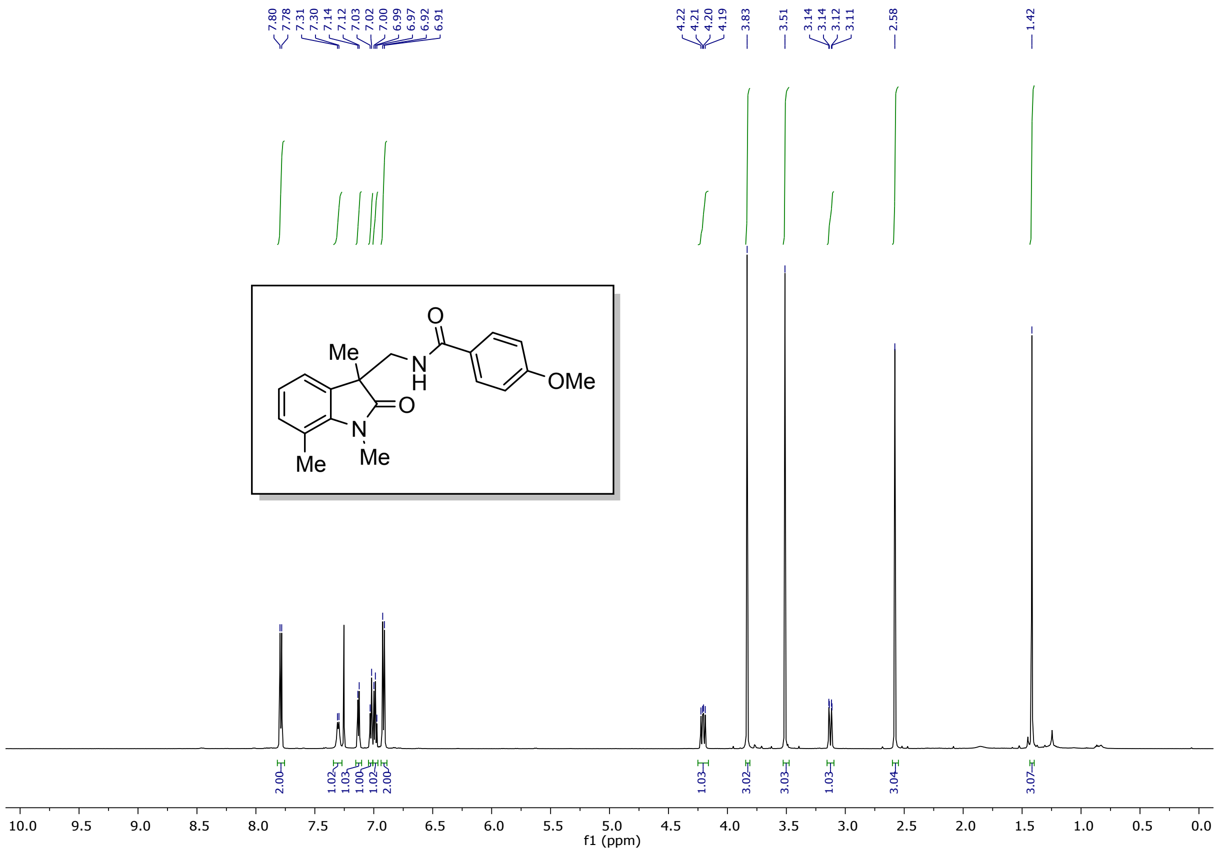
_N_-{[1,3-Dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl]methyl}-4-methoxybenzamide (Table 2, 3r)

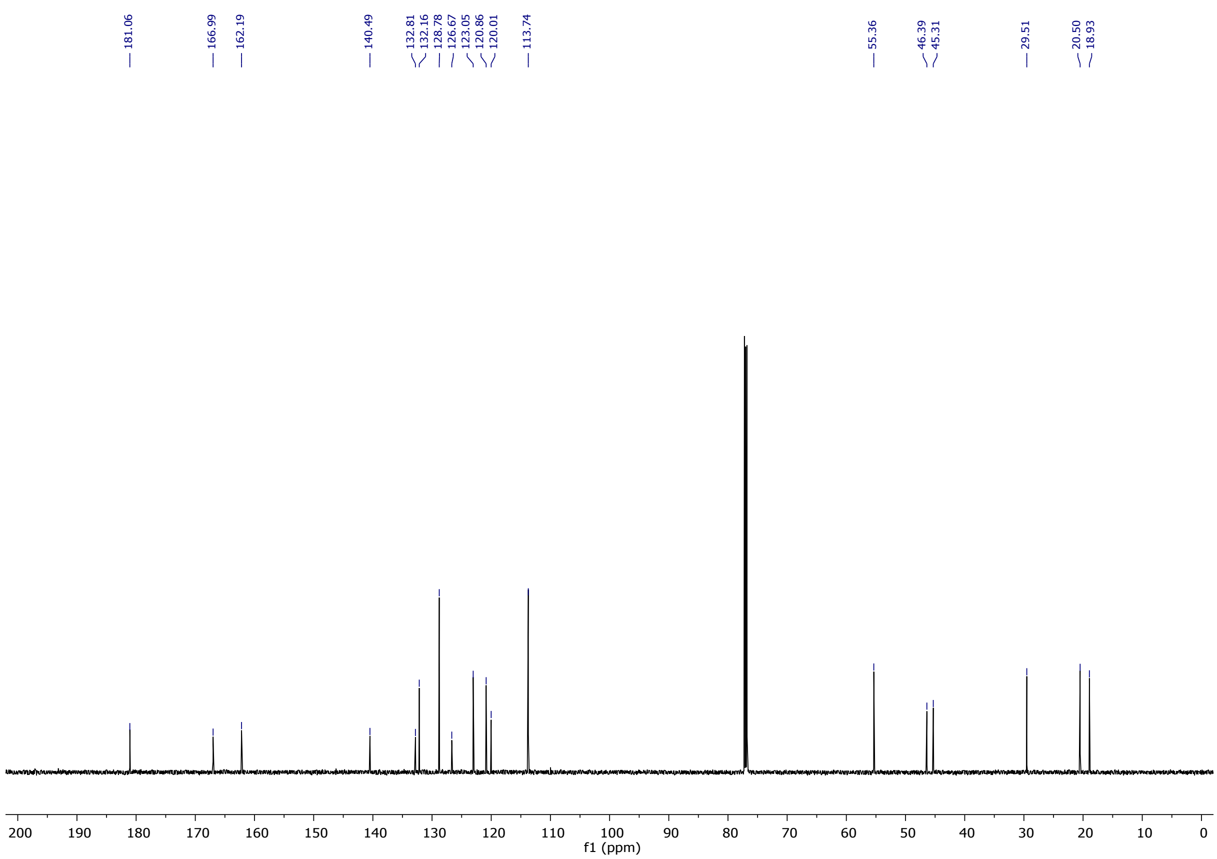




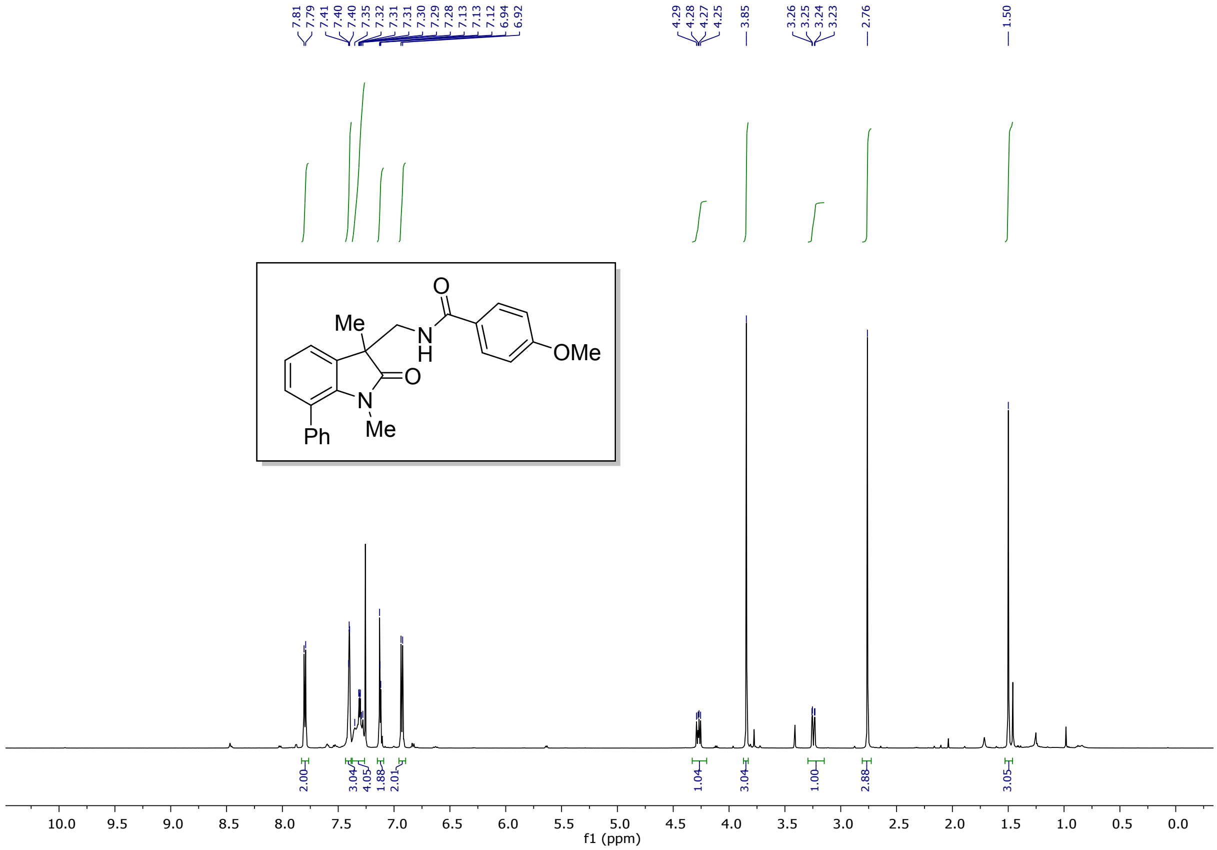

180.22
167.03
162.30
145.82
132.69
128.76
126.41
126.35
126.32
126.29
126.26
125.53
125.31
125.10
123.29
120.28
120.25
113.79
108.14
55.37
47.48
44.84
26.44
20.02
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

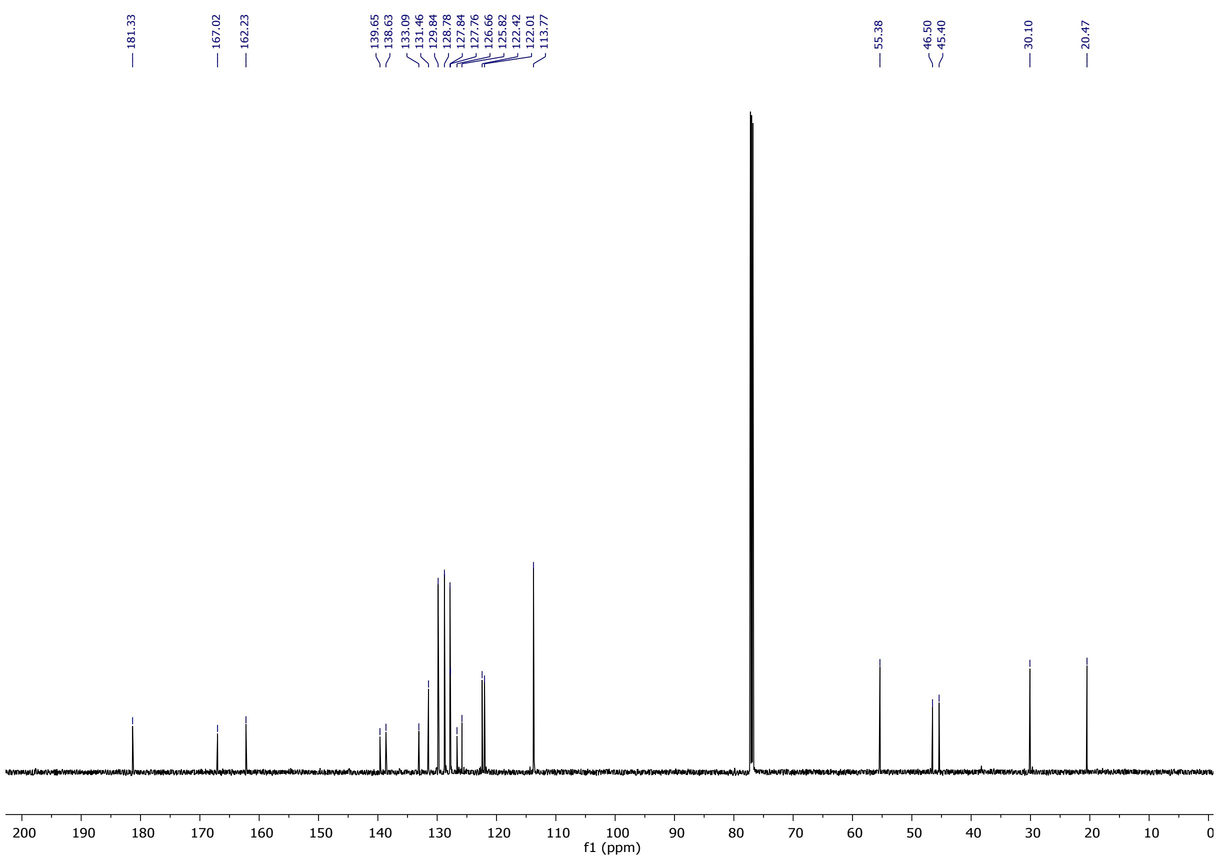
4-Methoxy-*N*-[(1,3,7-trimethyl-2-oxoindolin-3-yl]methyl)benzamide (Table 2, 3s)



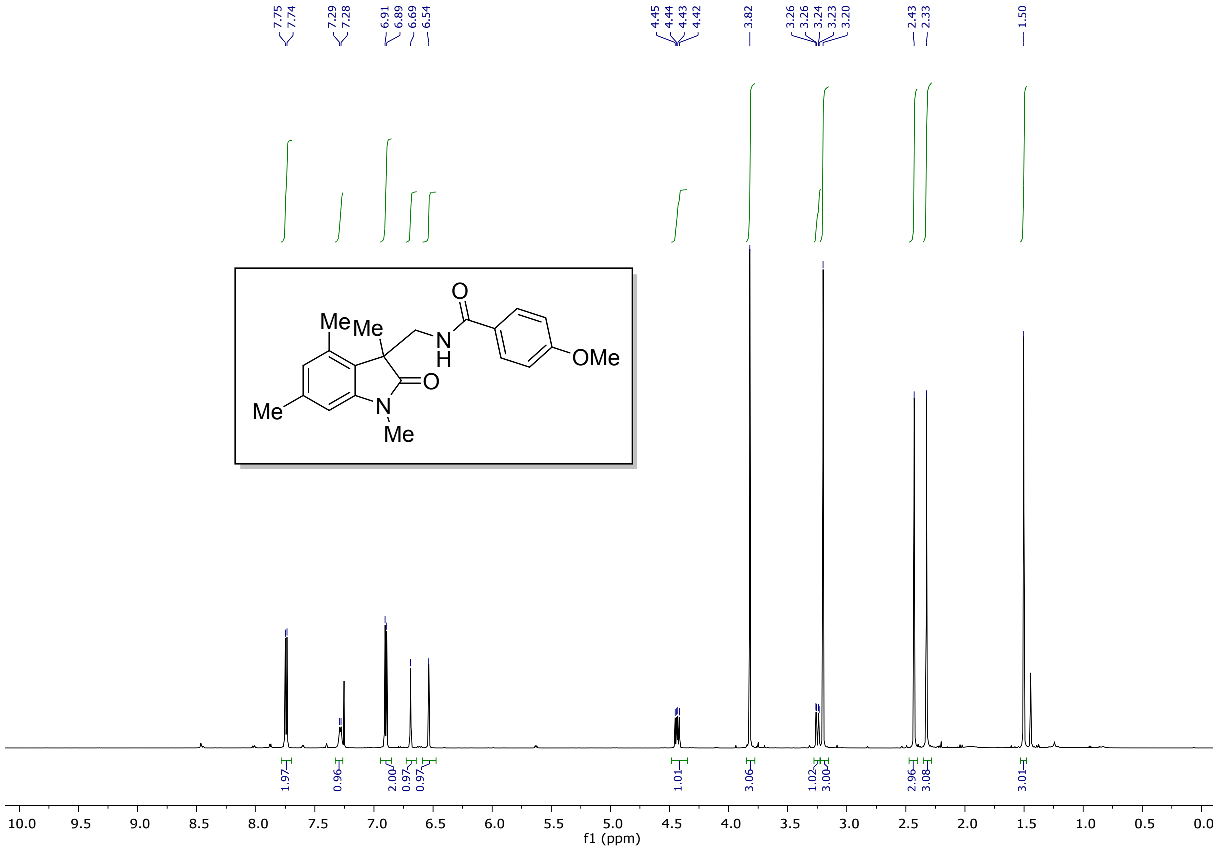


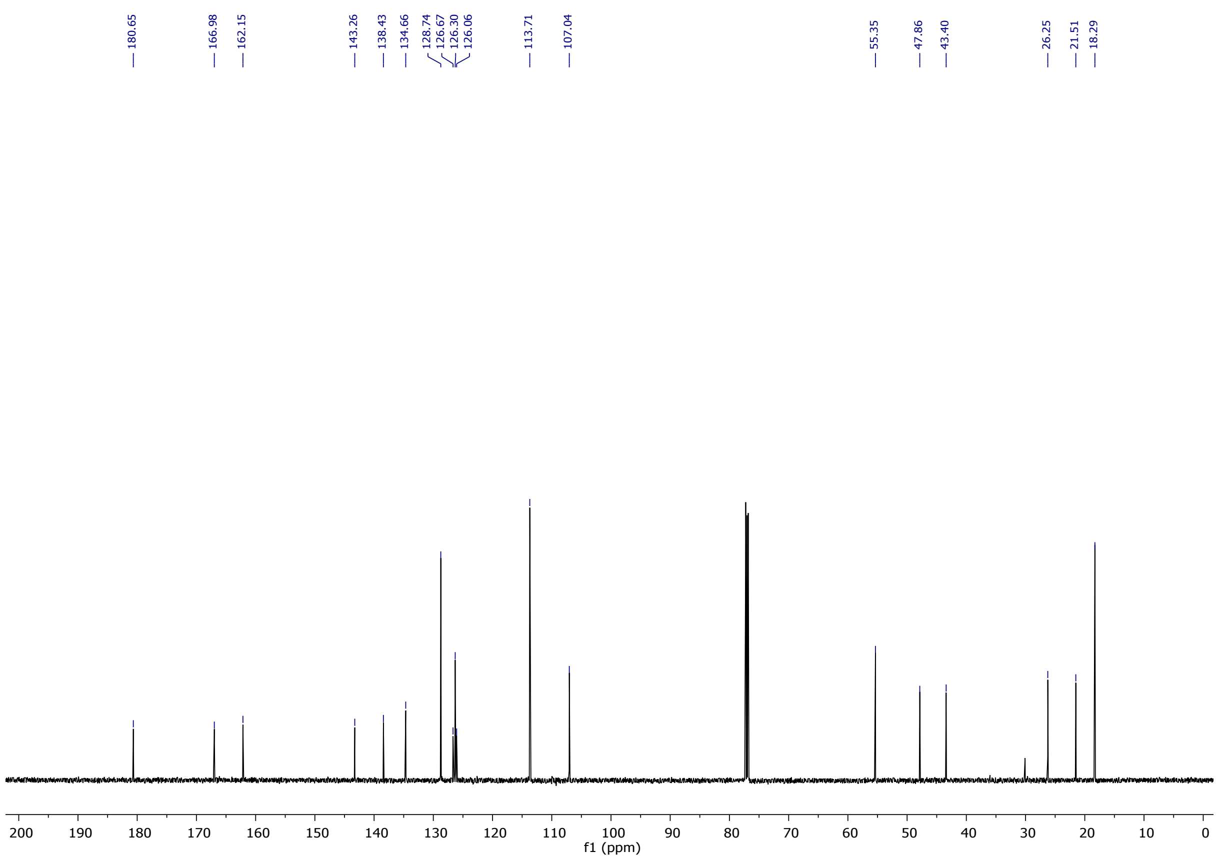
_N_-[(1,3-Dimethyl-2-oxo-7-phenylindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3t)



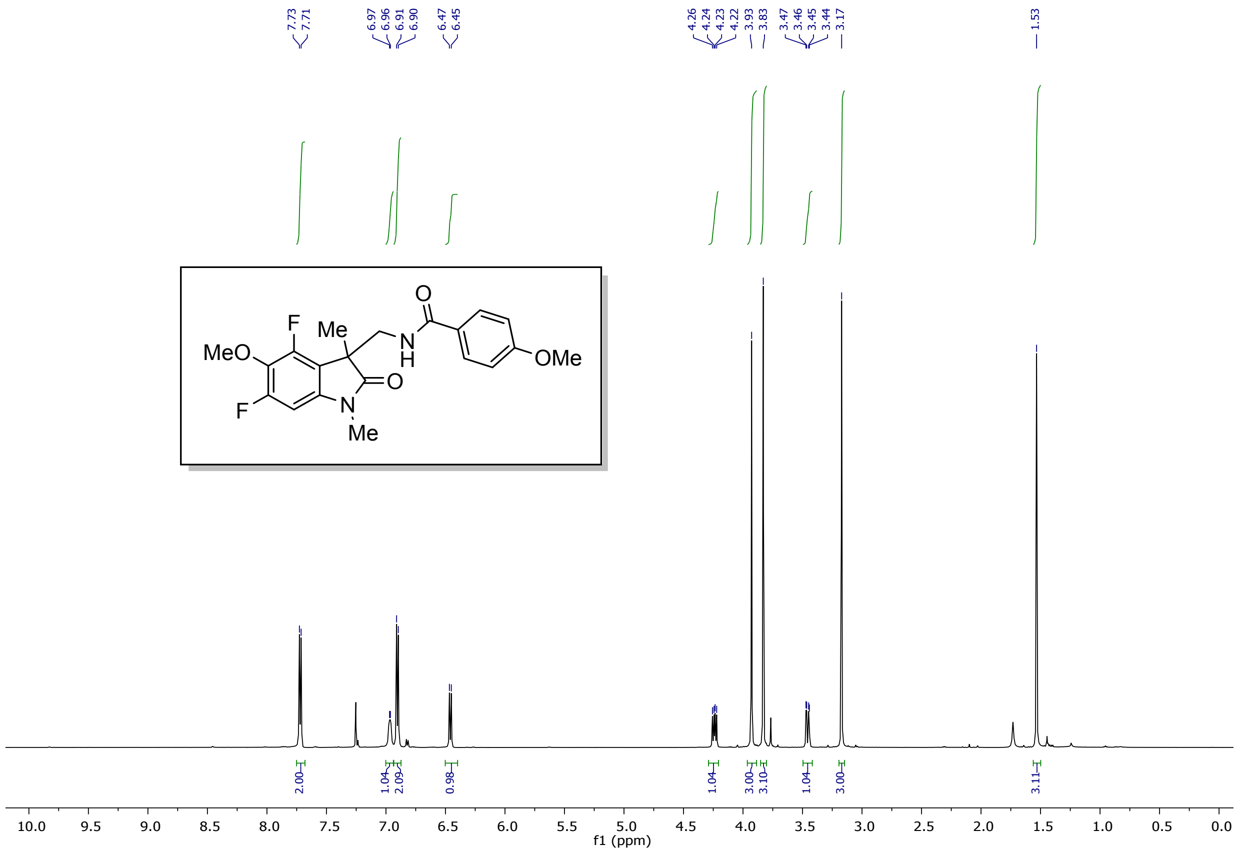


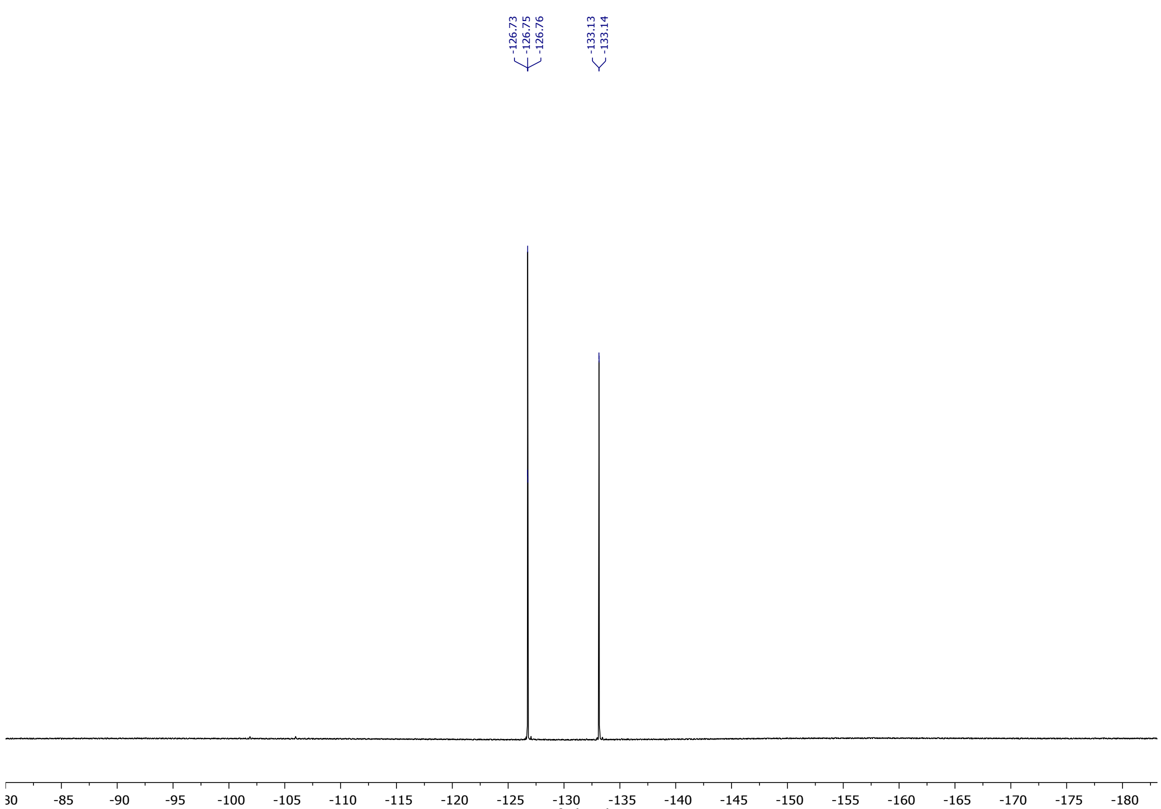
4-Methoxy-*N*-[(1,3,4,6-tetramethyl-2-oxoindolin-3-yl]methyl)benzamide (Table 2, 3u)

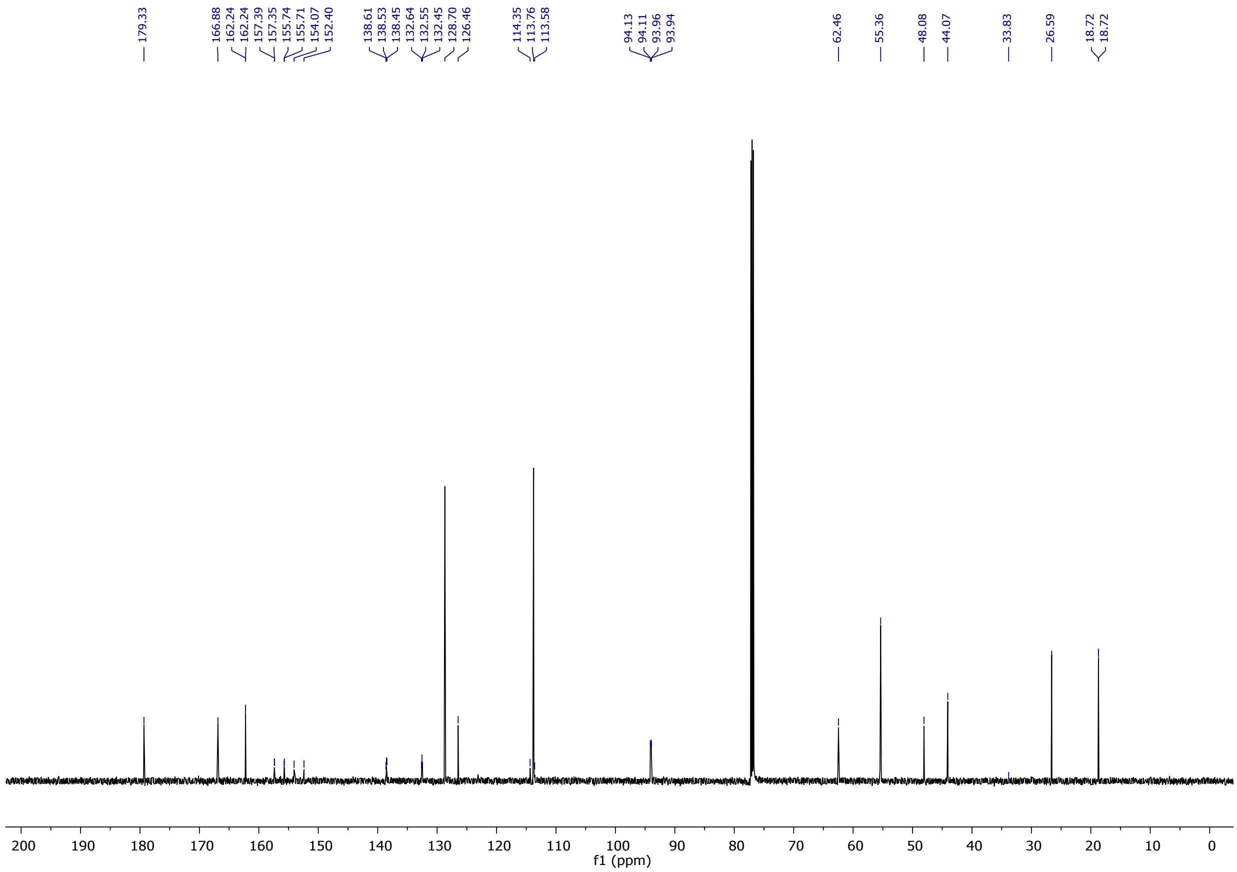




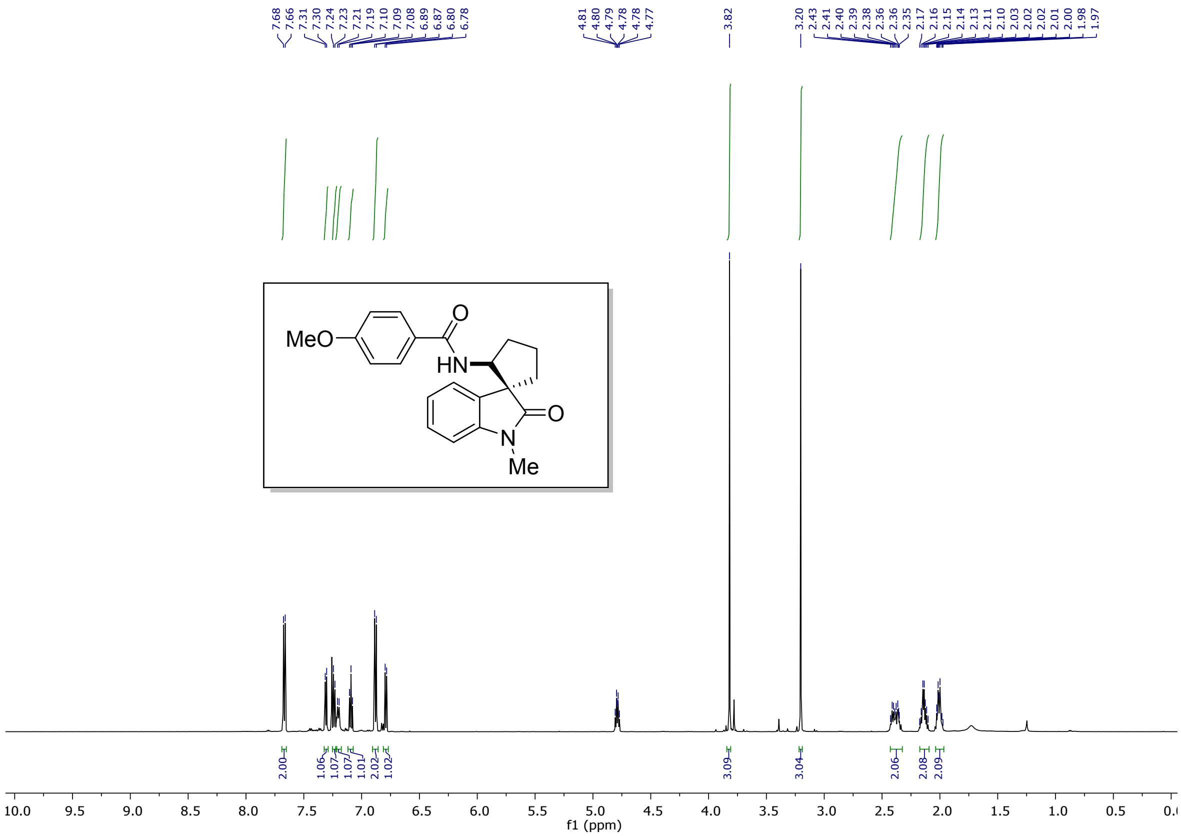
***N*-[(4,6-Difluoro-5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3v)**

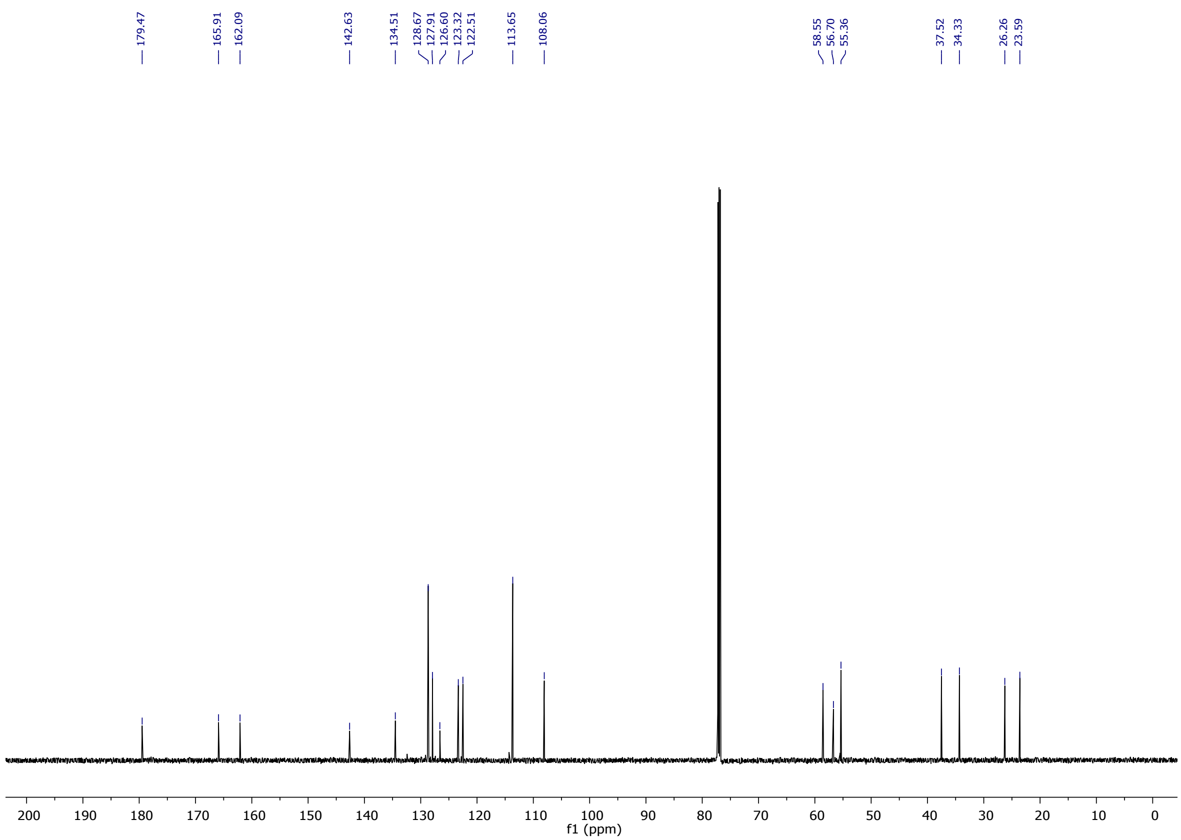




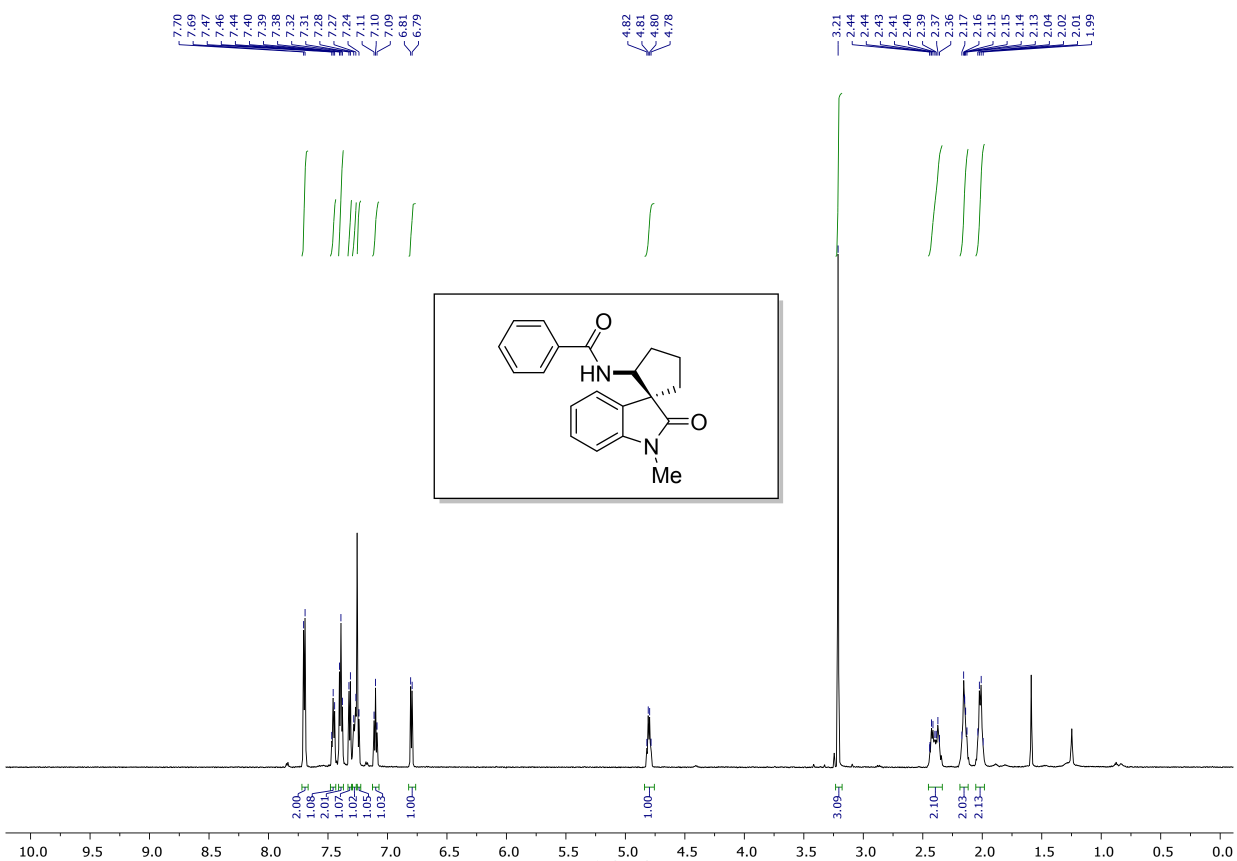

179.33
166.88
162.24
162.24
157.39
157.35
155.74
155.71
154.07
152.40
138.61
138.53
138.45
132.64
132.55
132.45
128.70
126.46
114.35
113.76
113.58
94.13
94.11
93.96
93.94
62.46
55.36
48.08
44.07
33.83
26.59
18.72
18.72
f1 (ppm)

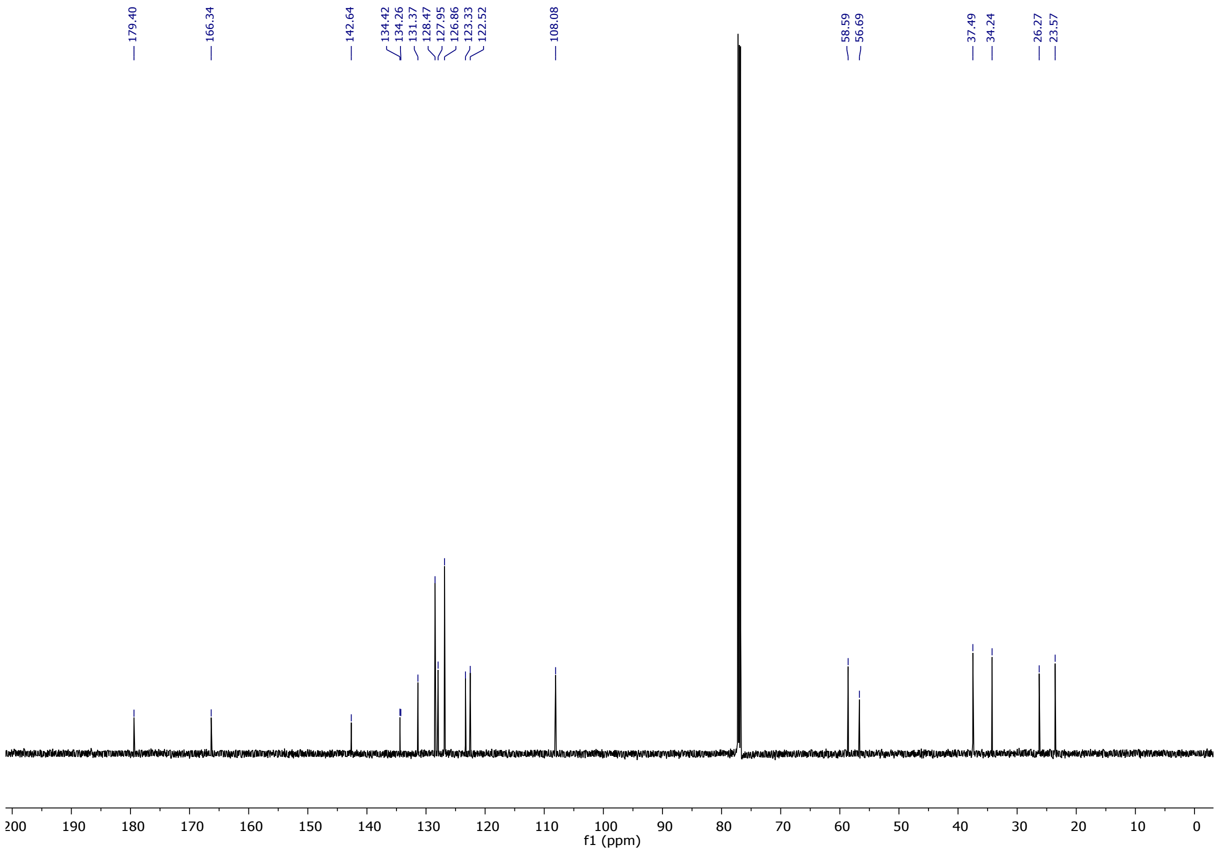
4-Methoxy-*N*-[1'-methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5a)



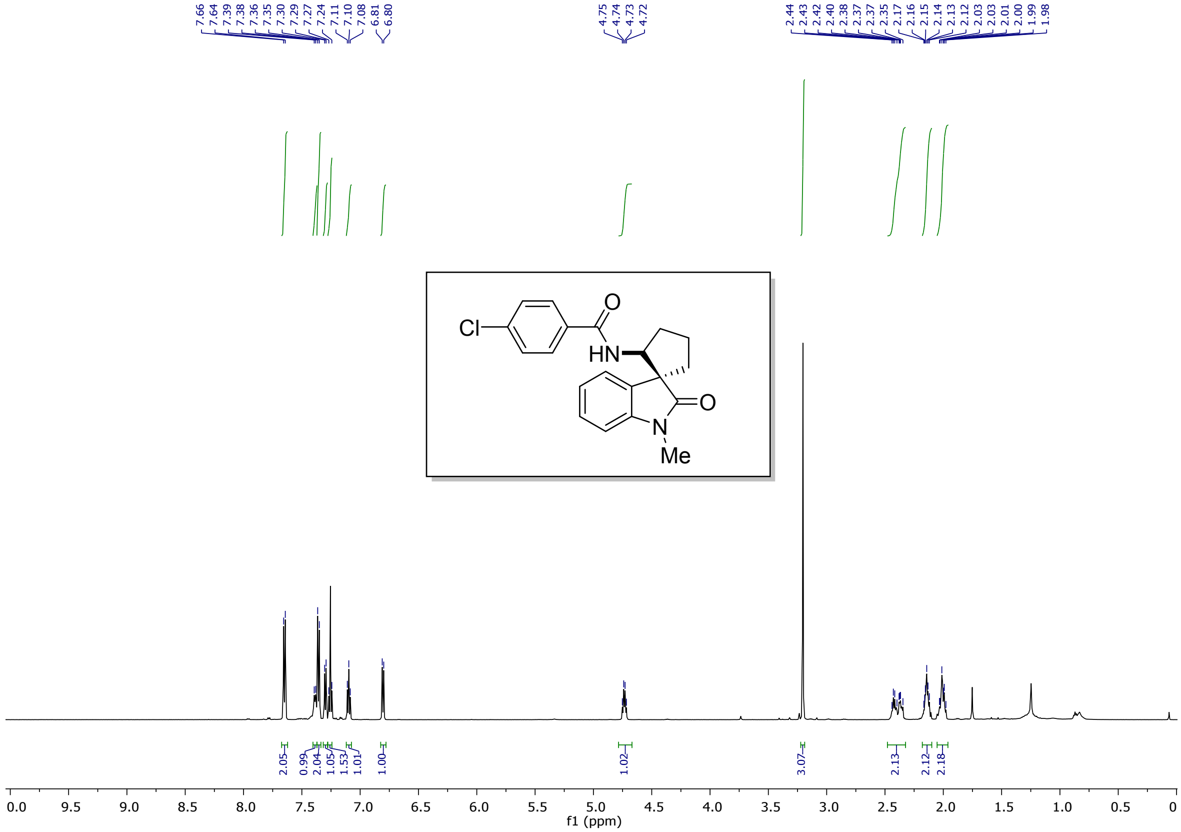


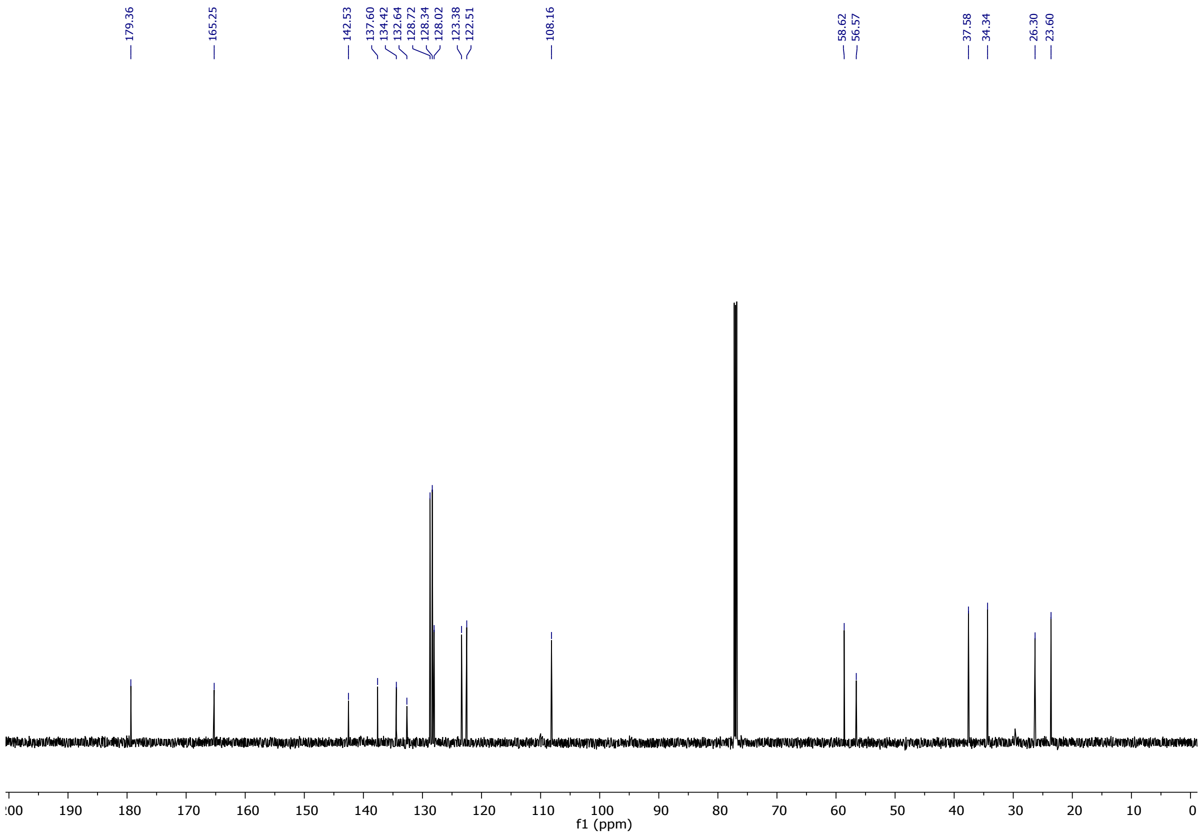
N-(1'-Methyl-2'-oxospiro[cyclopentane-1,3'-indolin]-2-yl)benzamide (Table 3, 5b)



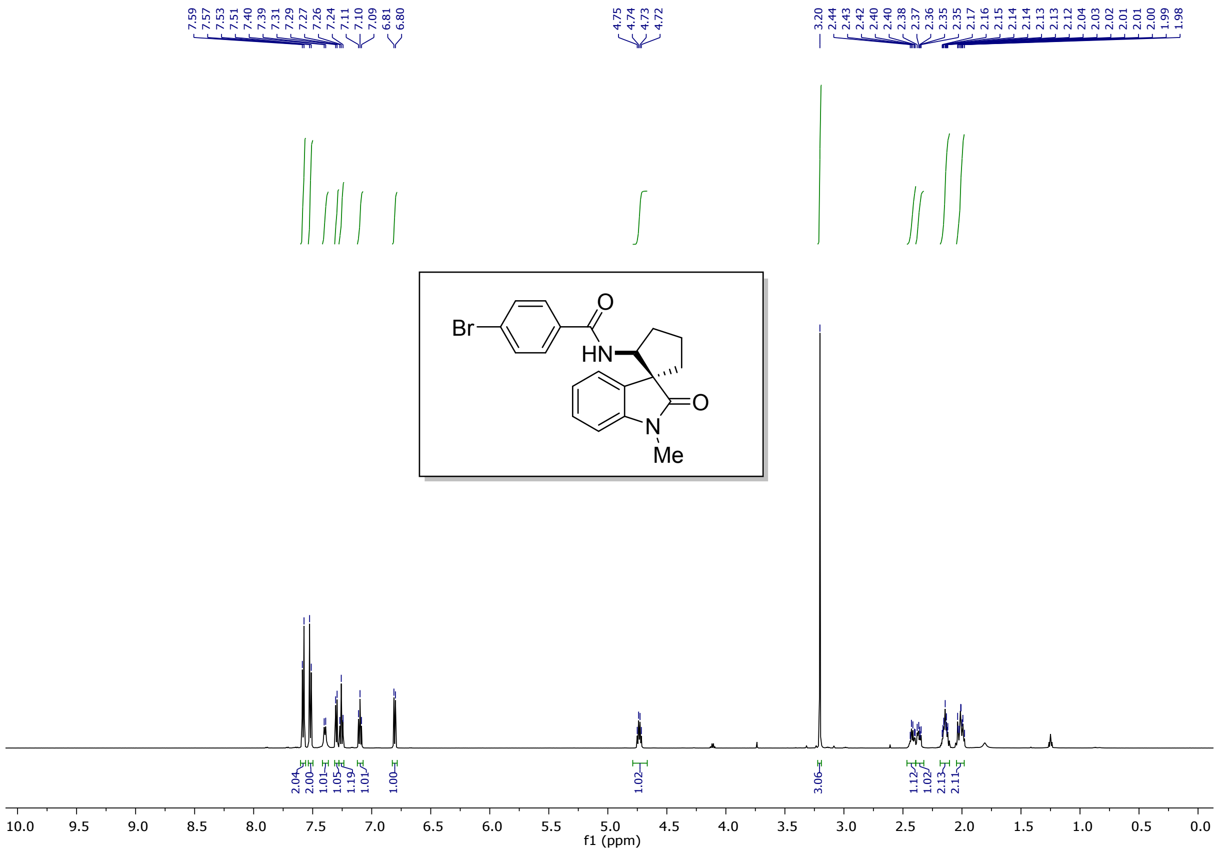


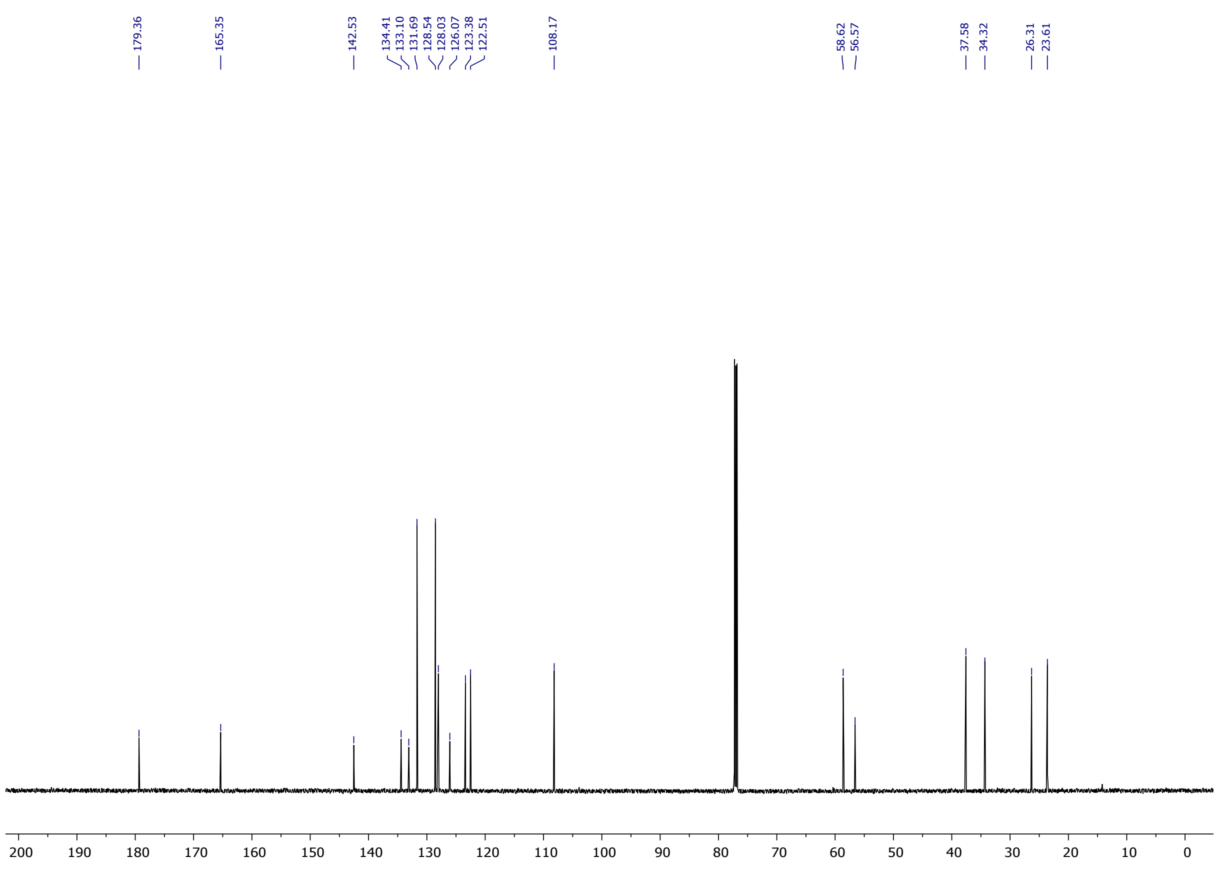
4-Chloro-*N*-[1'-methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5c)



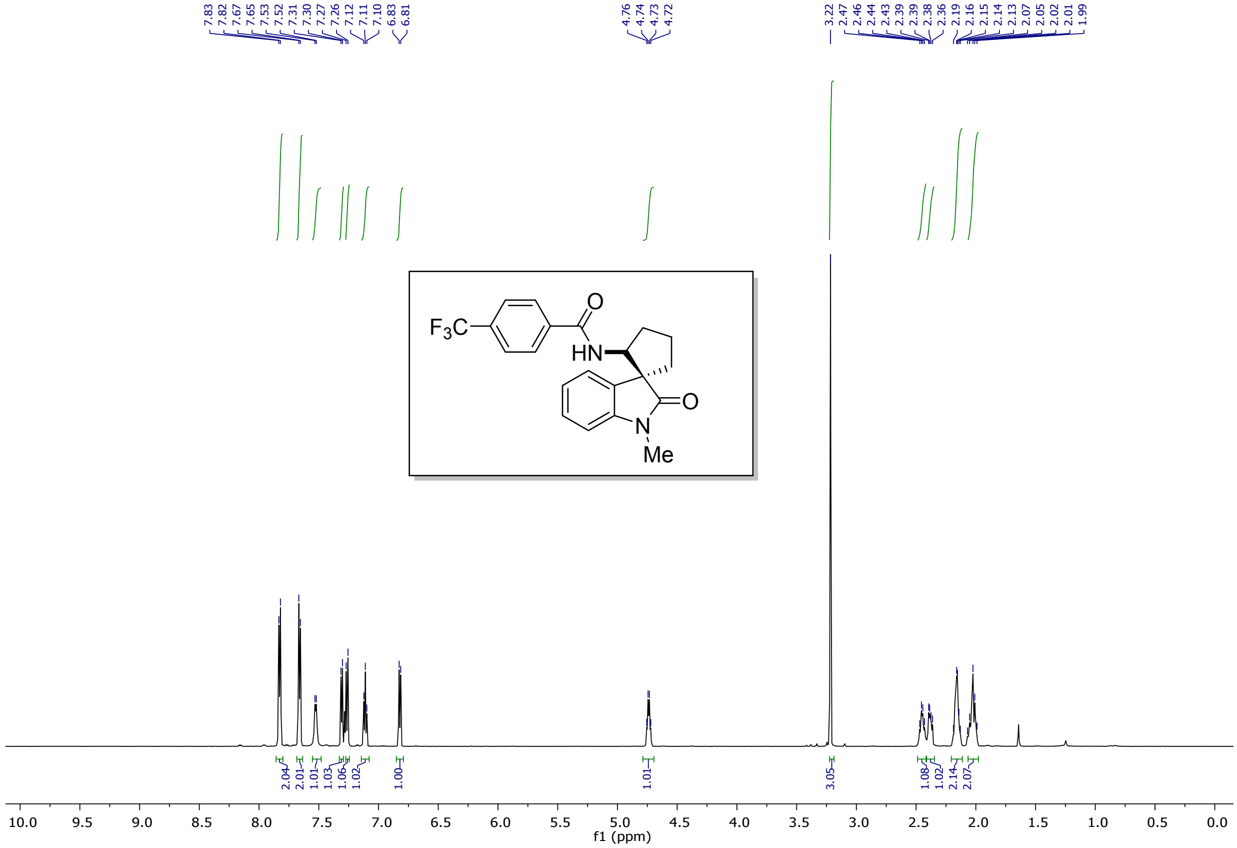


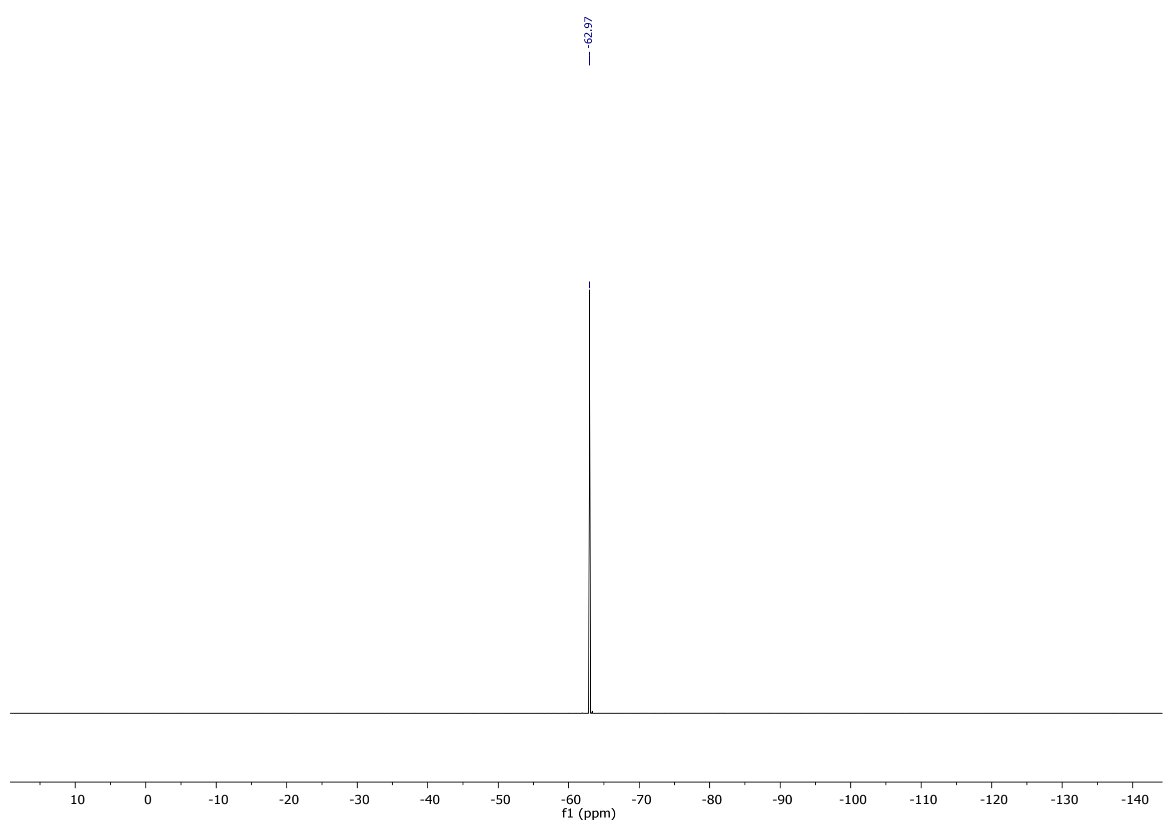
4-Bromo-*N*[1'-methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5d)

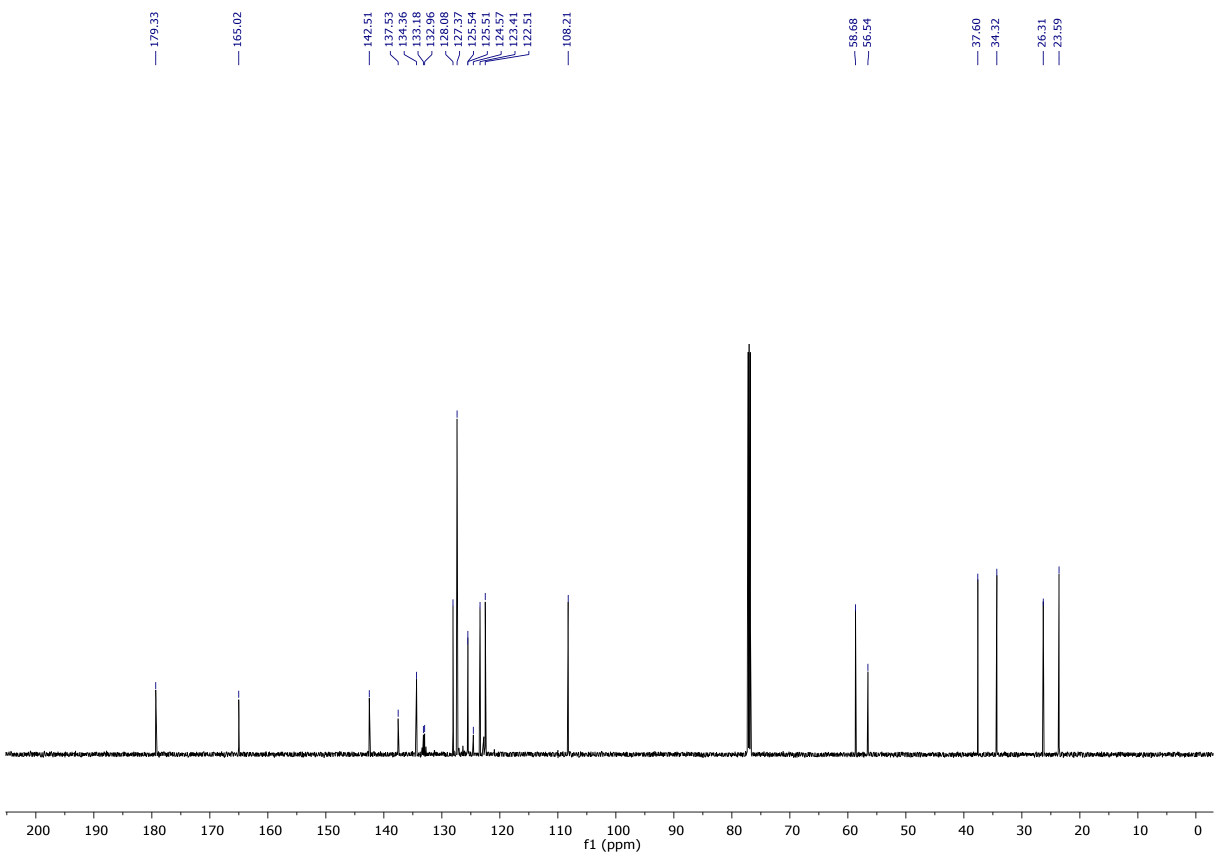

7.59 7.57 7.53 7.51 7.40 7.39 7.31 7.29 7.27 7.26 7.24 7.11 7.10 7.09 6.81 6.80
4.75 4.74 4.73 4.72
3.20 2.44 2.43 2.42 2.40 2.40 2.38 2.37 2.36 2.35 2.35 2.17 2.16 2.15 2.14 2.14 2.13 2.13 2.12 2.04 2.03 2.02 2.01 2.00 1.99 1.98
Br
O
HN
O
N
Me
2.04 2.00 1.01 1.05 1.19 1.01 1.00
1.02
3.06
1.12 1.02 2.13 2.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


179.36
165.35
142.53
134.41 133.10 131.69 128.54 128.03 126.07 123.38 122.51
108.17
58.62 56.57
37.58 34.32
26.31 23.61
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

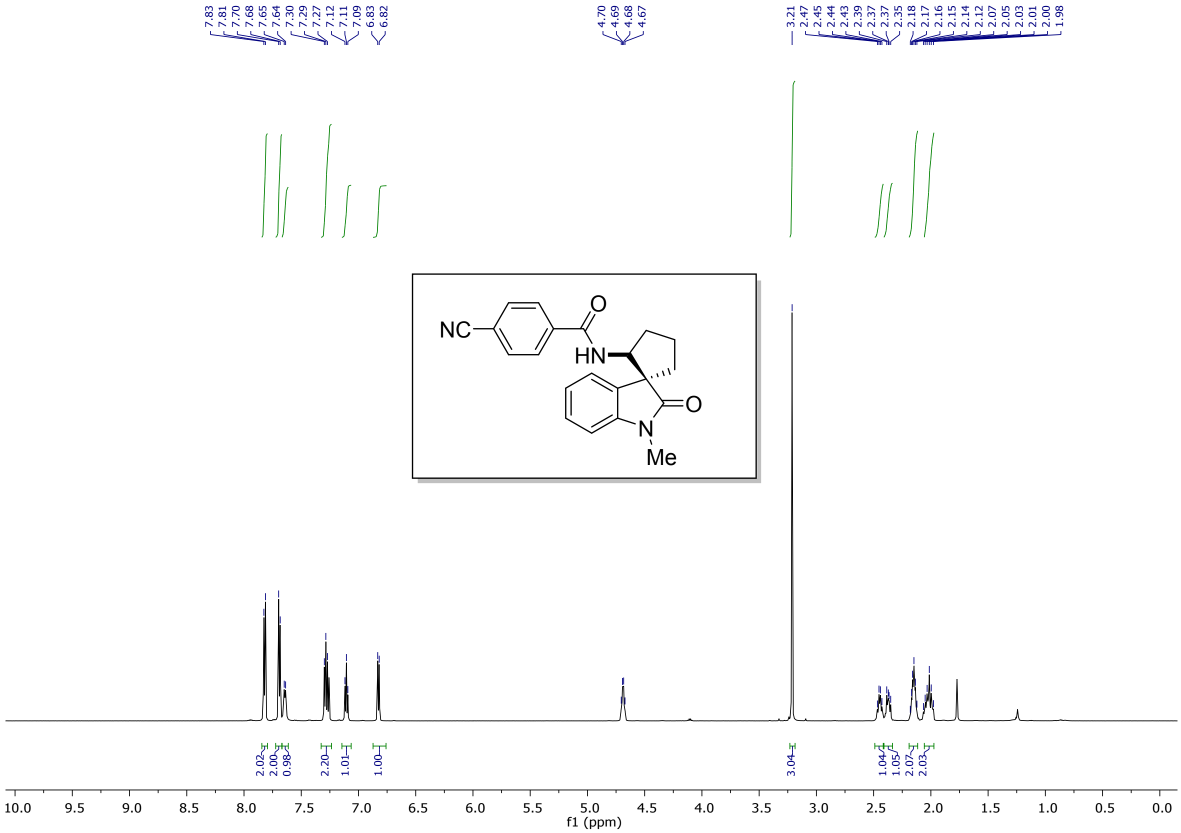
_N_-[1'-Methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]-4-(trifluoromethyl)-benzamide (Table 3, 5e)

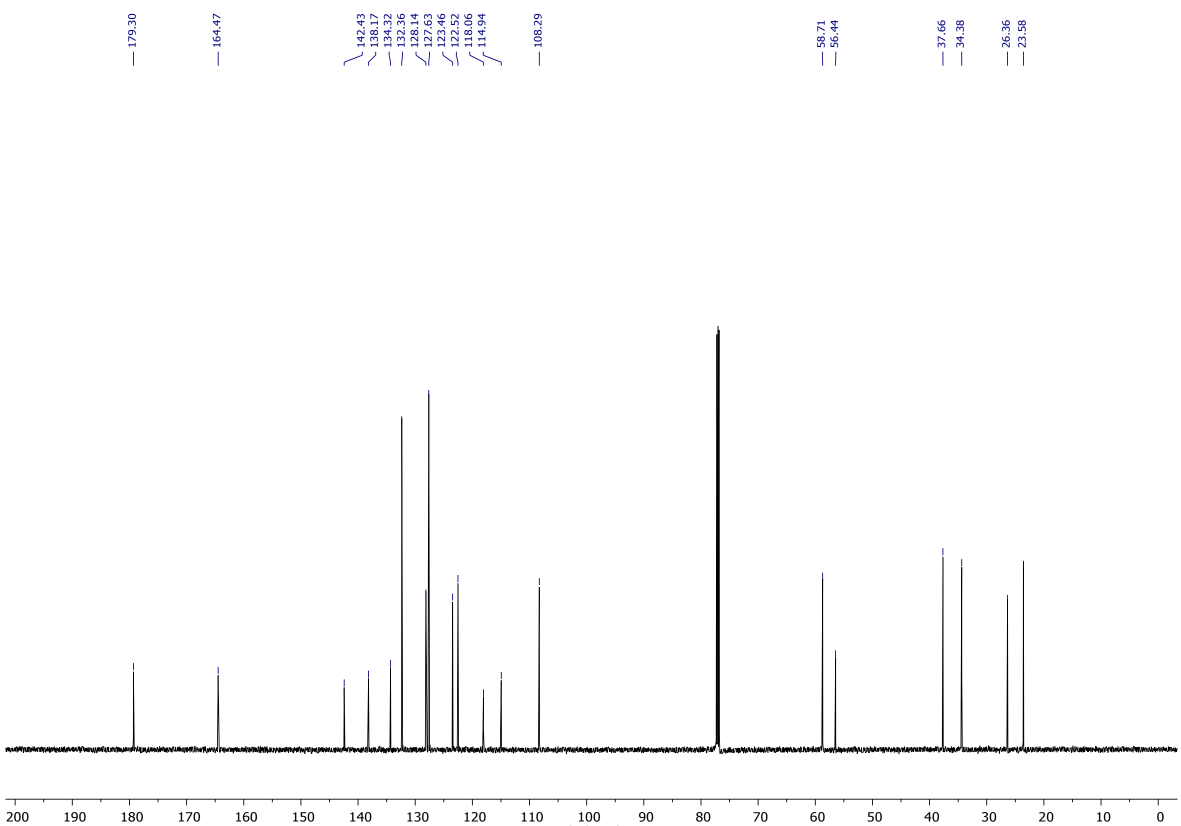




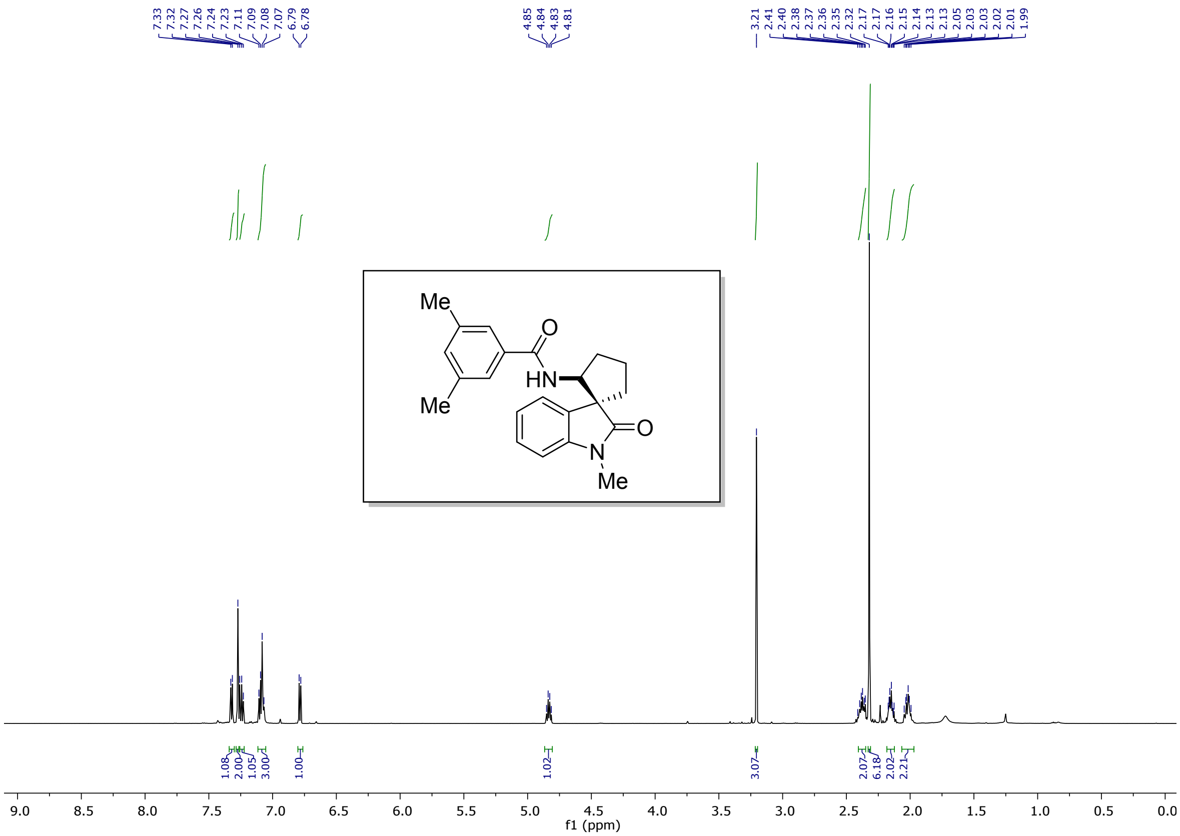

179.33
165.02
142.51
137.53
134.36
133.18
132.96
128.08
127.37
125.54
125.51
124.57
123.41
122.51
108.21
58.68
56.54
37.60
34.32
26.31
23.59
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

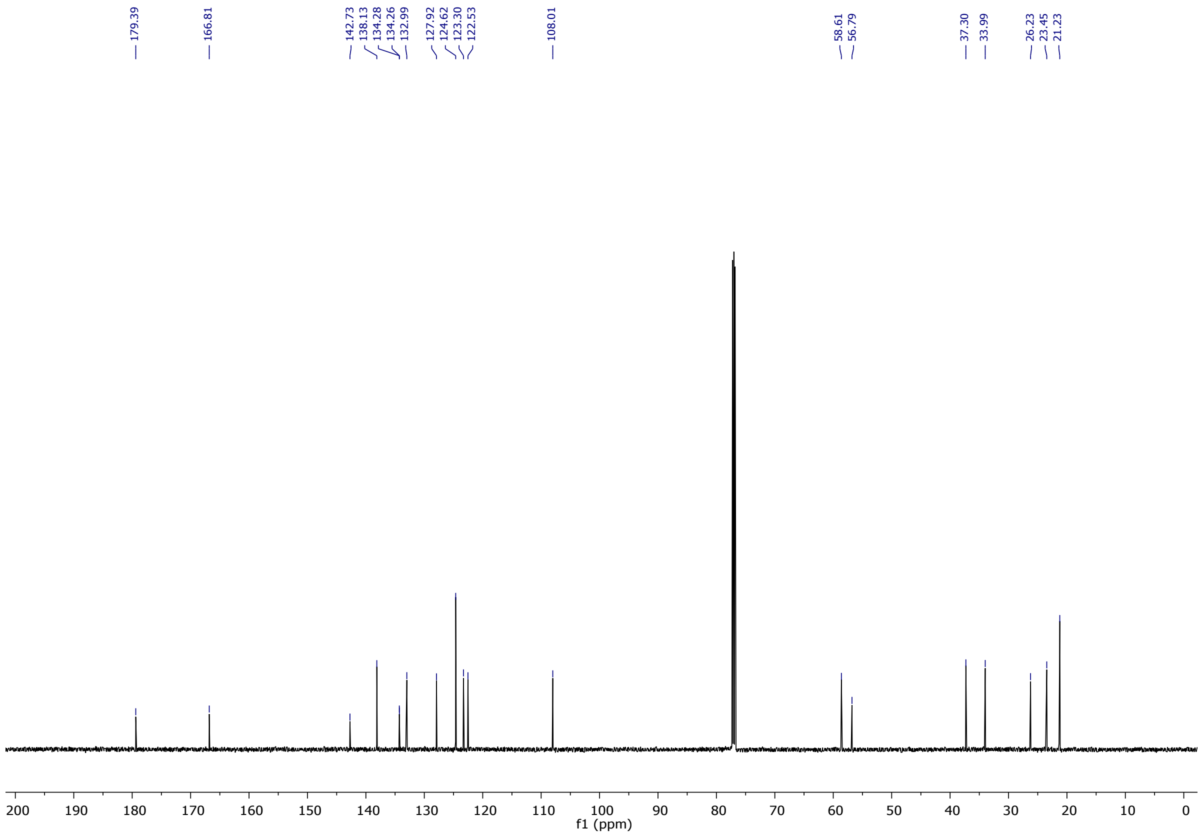
4-Cyano-*N*-[1'-methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5f)



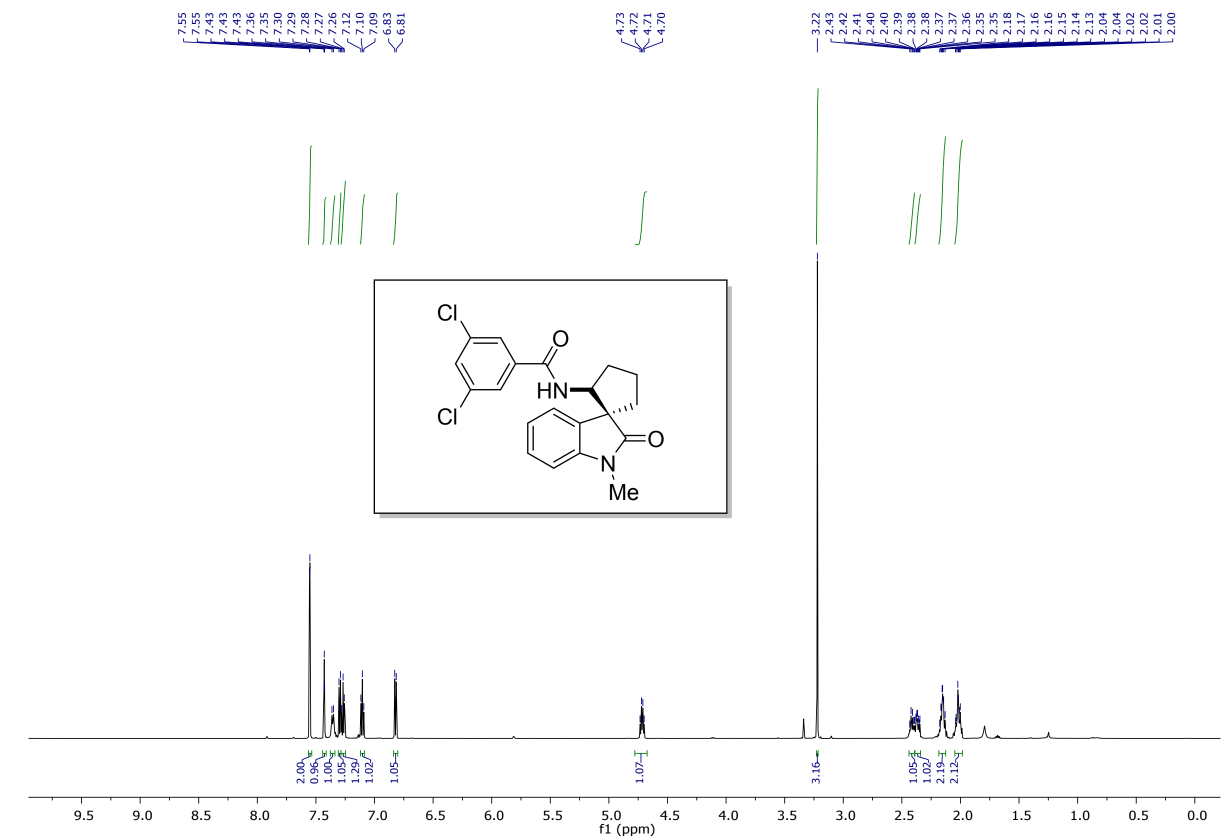


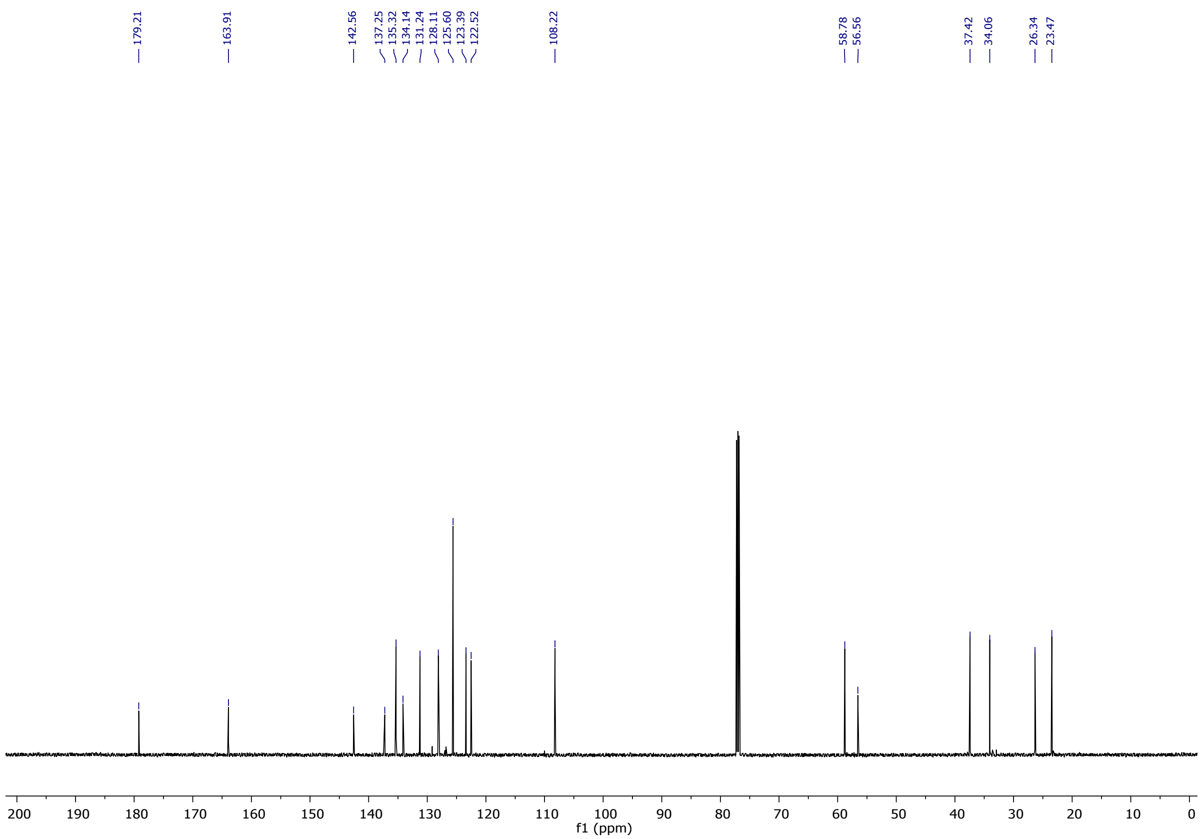
3,5-Dimethyl-*N*-[1'-methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5g)



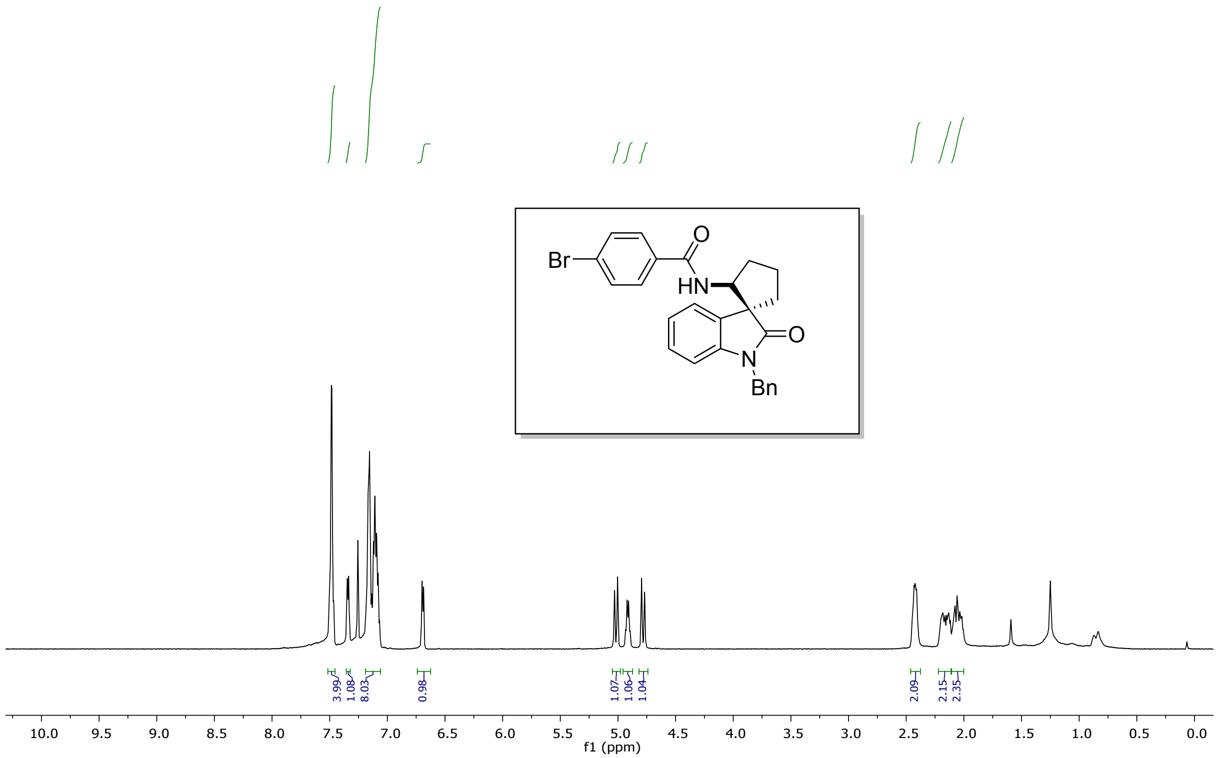


3,5-Dichloro-*N*-[1'-methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5h)

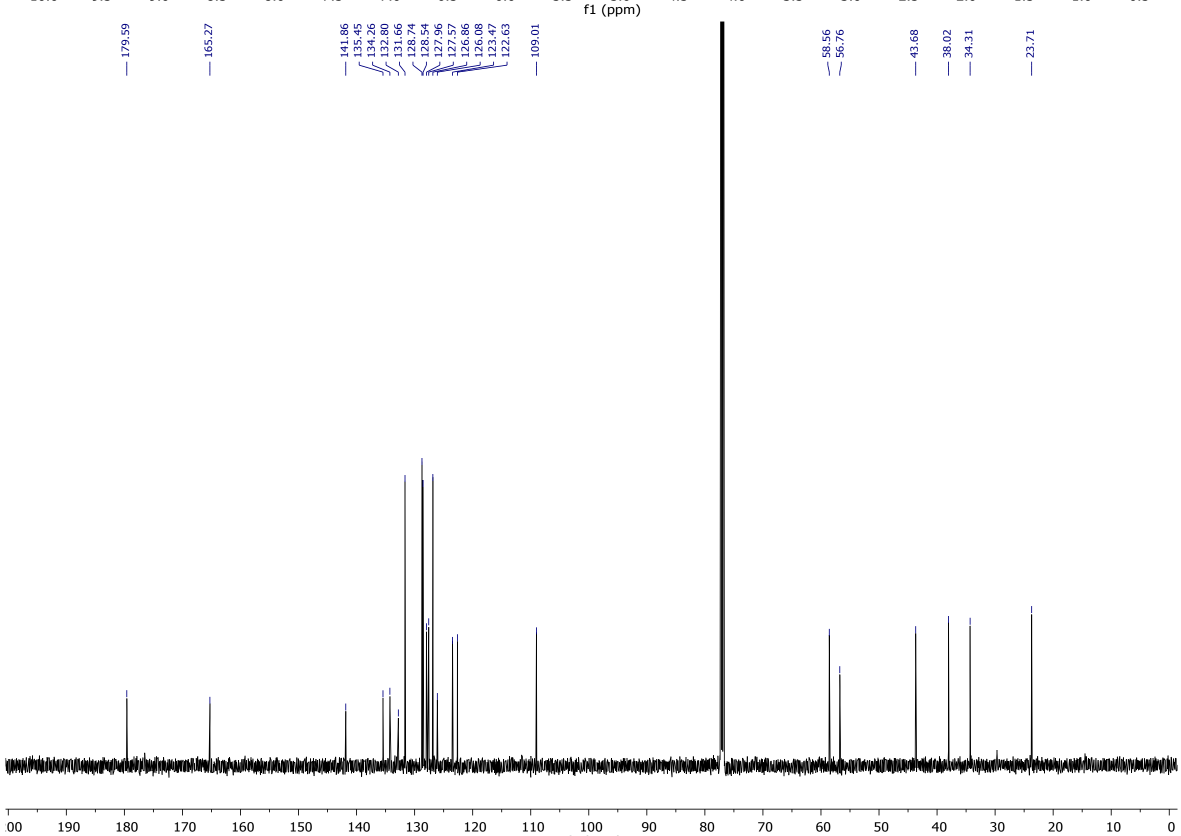




_N_-[1'-Benzyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]-4-bromobenzamide (Table 3, 5i)

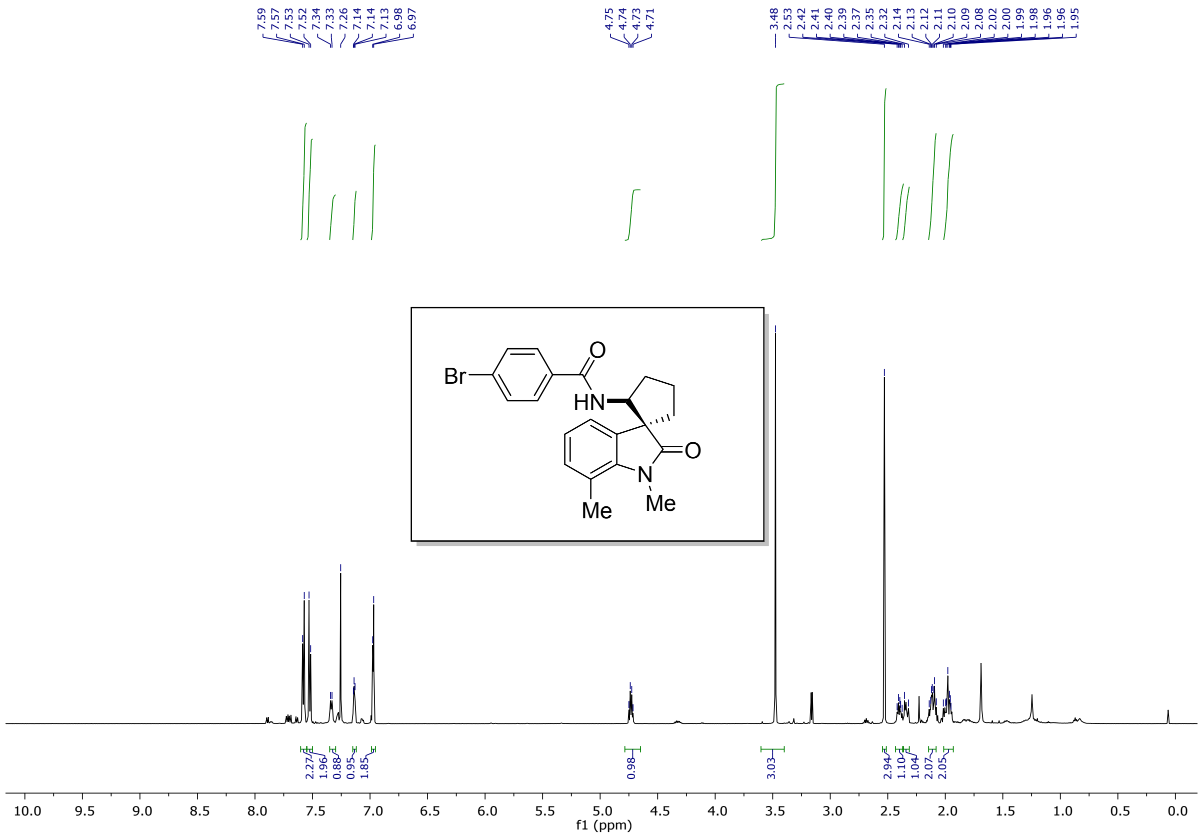


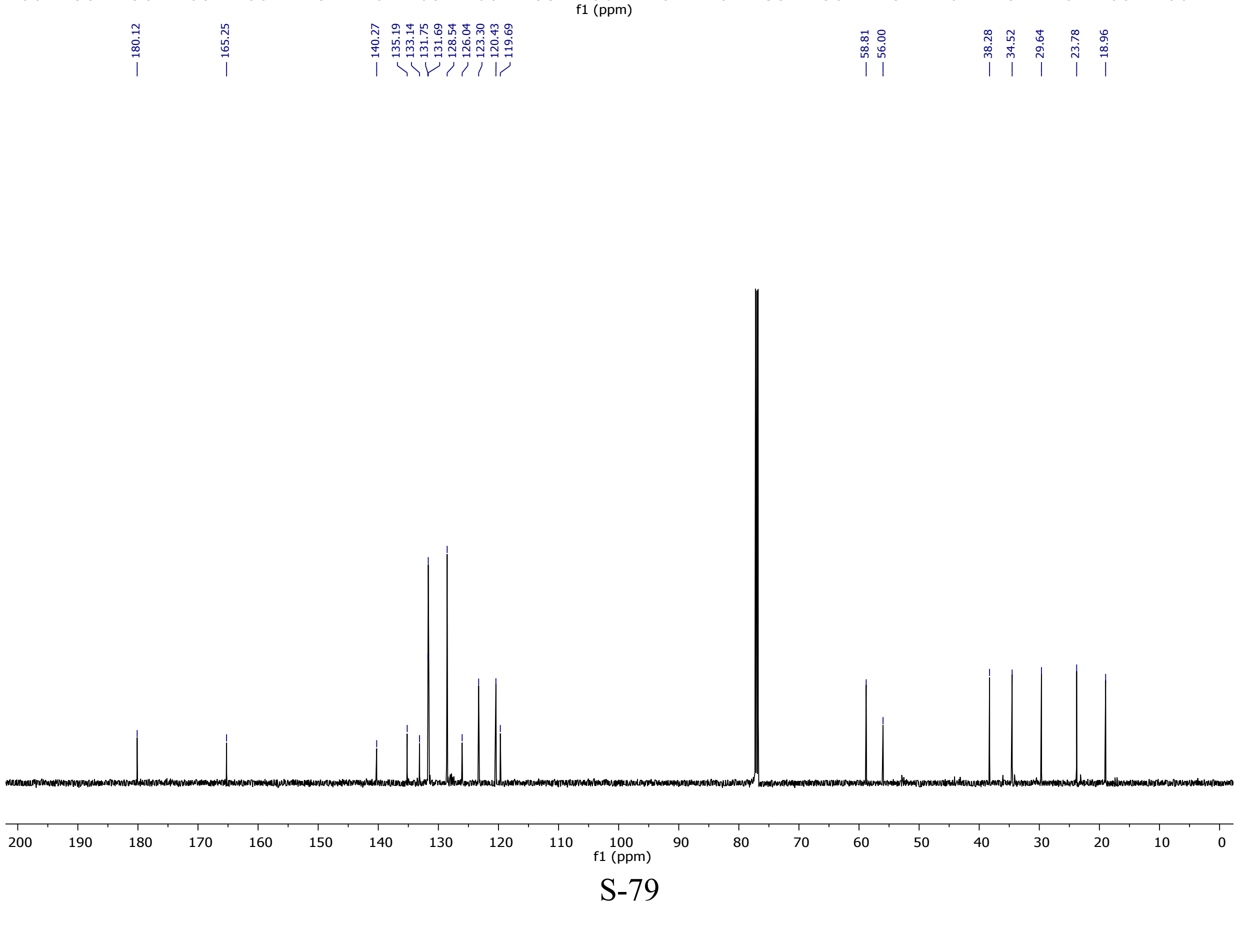
Br
O
HN
O
N
Bn
3.99
1.08
8.03
0.98
1.07
1.06
1.04
2.09
2.15
2.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



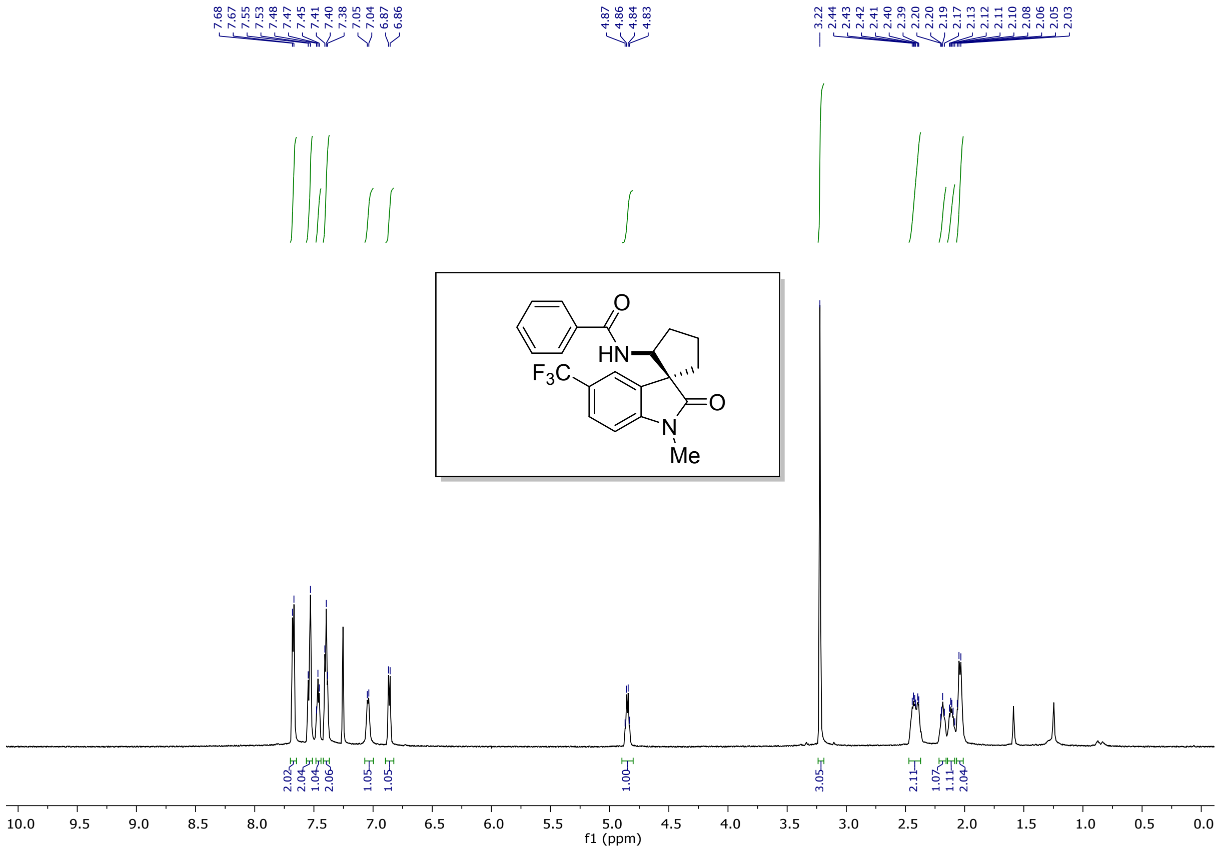
179.59
165.27
141.86
135.45
134.26
132.80
131.66
128.74
128.54
127.96
127.57
126.86
126.08
123.47
122.63
109.01
58.56
56.76
43.68
38.02
34.31
23.71
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

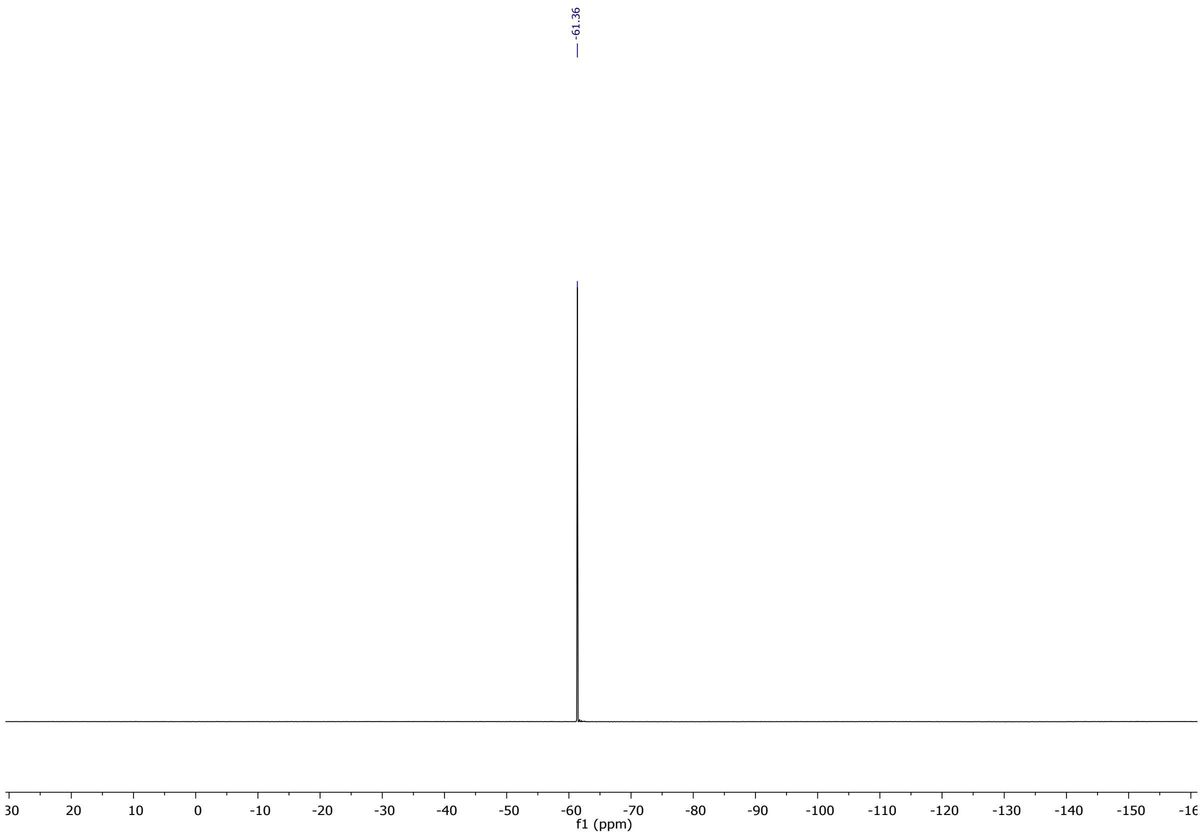
4-Bromo-*N*-[1',7'-dimethyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5j)

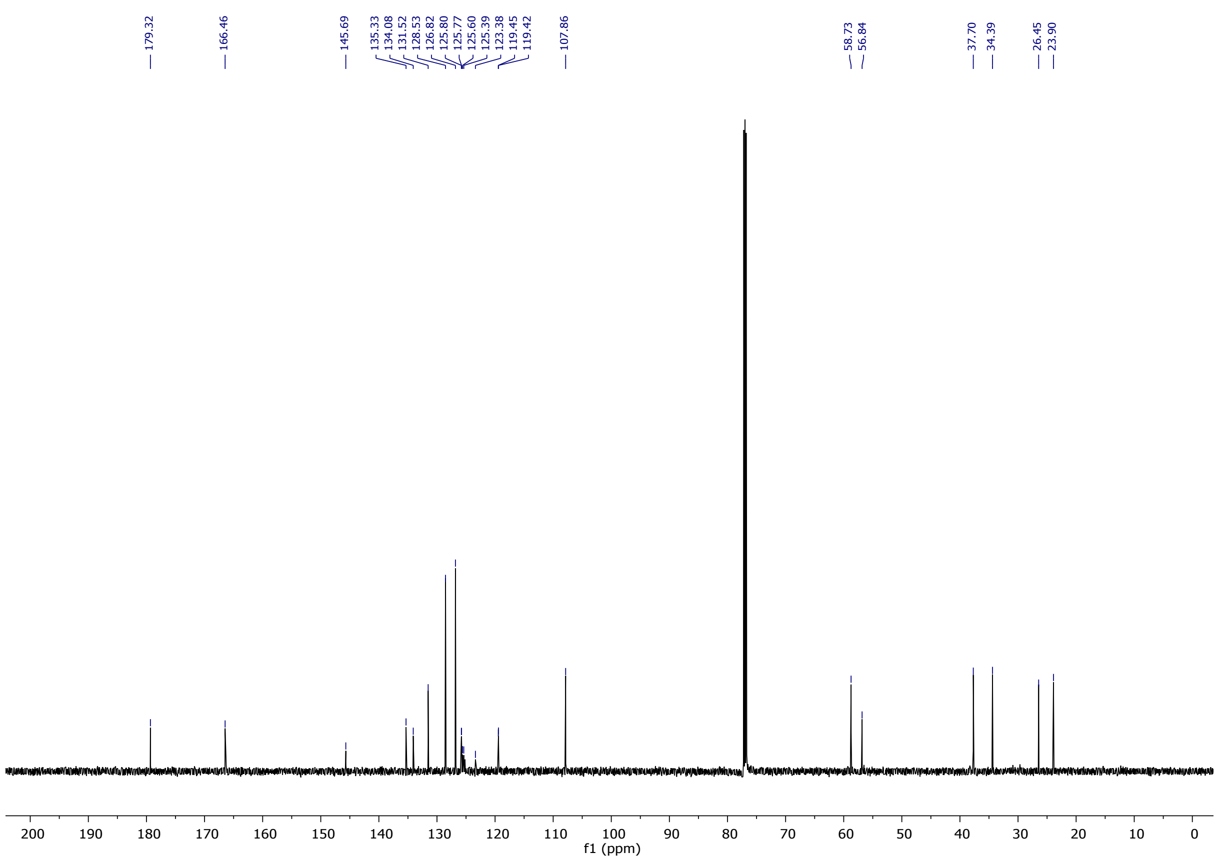




N-[1'-Methyl-2'-oxo-5'-(trifluoromethyl)spiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5k)




-61.36
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


179.32
166.46
145.69
135.33
134.08
131.52
128.53
126.82
125.80
125.77
125.60
125.39
123.38
119.45
119.42
107.86
58.73
56.84
37.70
34.39
26.45
23.90
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Appendix II

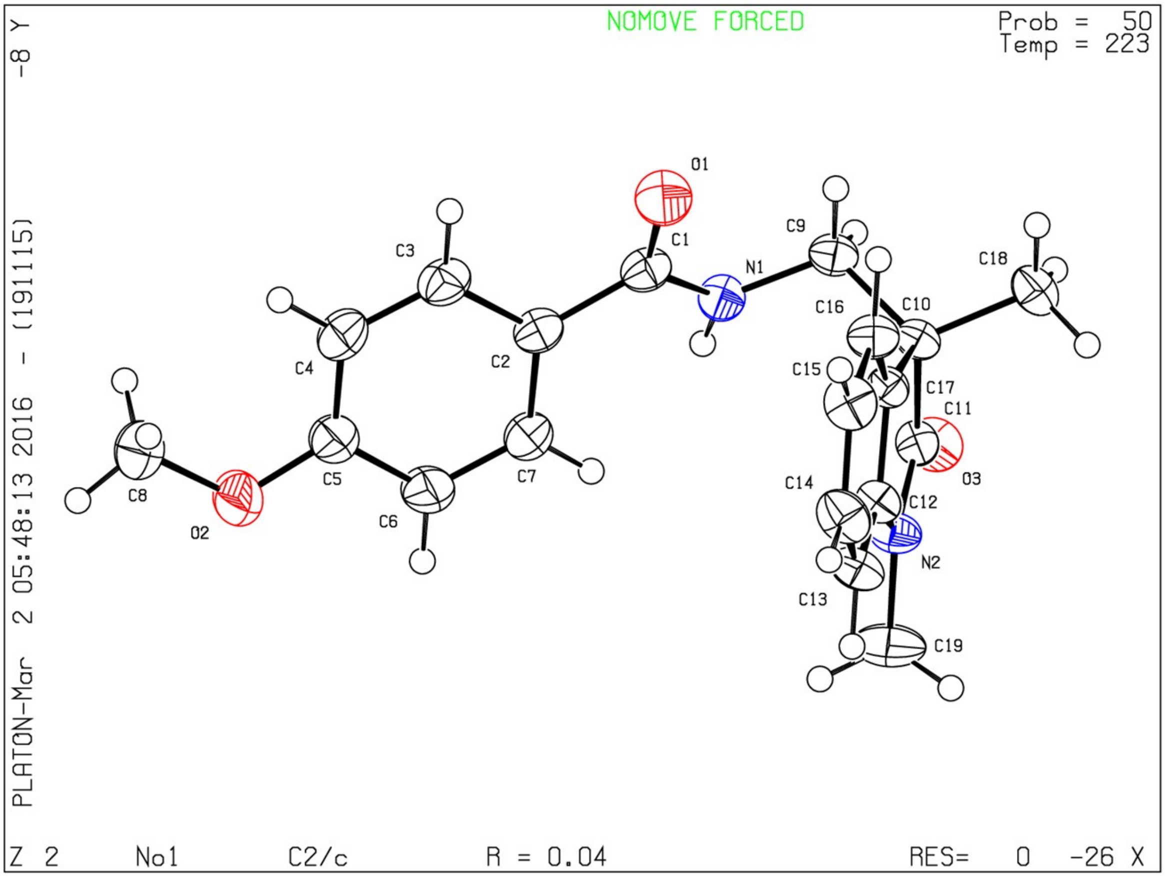
Crystallographic Data for

3a (CCDC 1505485)

and

5d (CCDC 1505486)

***N*-[(1,3-Dimethyl-2-oxoindolin-3-yl)methyl]-4-methoxybenzamide (Table 2, 3a)**



- CCDC 1505485

Table S1. Crystal data and structure refinement for **3a**.

Identification code	**3a**	
Empirical formula	$C_{19} H_{20} N_2 O_3$	
Formula weight	324.37	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 17.4957(4) Å	α = 90°.
	b = 13.0591(4) Å	β = 113.4471(11)°.
	c = 16.2596(5) Å	γ = 90°.
Volume	3408.21(17) $Å^3$	
Z	8	
Density (calculated)	1.264 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	1376	
Crystal size	0.23 x 0.15 x 0.10 mm^3	
Theta range for data collection	2.13 to 28.33°.	
Index ranges	-23<=h<=23, -17<=k<=17, -21<=l<=21	
Reflections collected	80577	
Independent reflections	4246 [R(int) = 0.0572]	
Completeness to theta = 28.33°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9914 and 0.9804	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4246 / 0 / 220	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.1073	
R indices (all data)	R1 = 0.0621, wR2 = 0.1180	
Largest diff. peak and hole	0.245 and -0.164 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1468(1)	9720(1)	970(1)	32(1)
O(1)	1598(1)	10610(1)	1238(1)	45(1)
C(2)	784(1)	9099(1)	1050(1)	32(1)
C(3)	107(1)	9597(1)	1108(1)	38(1)
C(4)	-542(1)	9059(1)	1185(1)	42(1)
C(5)	-519(1)	8002(1)	1211(1)	41(1)
C(6)	161(1)	7492(1)	1166(1)	51(1)
C(7)	801(1)	8033(1)	1084(1)	43(1)
O(2)	-1129(1)	7393(1)	1271(1)	61(1)
C(8)	-1839(1)	7874(2)	1318(2)	60(1)
N(1)	1926(1)	9246(1)	584(1)	31(1)
C(9)	2664(1)	9709(1)	548(1)	30(1)
C(10)	3472(1)	9254(1)	1241(1)	26(1)
C(11)	3507(1)	8102(1)	1080(1)	28(1)
O(3)	3467(1)	7710(1)	381(1)	40(1)
N(2)	3597(1)	7595(1)	1843(1)	32(1)
C(12)	3613(1)	8280(1)	2519(1)	28(1)
C(13)	3714(1)	8063(1)	3388(1)	37(1)
C(14)	3703(1)	8890(1)	3923(1)	40(1)
C(15)	3593(1)	9880(1)	3602(1)	38(1)
C(16)	3500(1)	10083(1)	2725(1)	33(1)
C(17)	3517(1)	9276(1)	2187(1)	26(1)
C(18)	4232(1)	9762(1)	1169(1)	35(1)
C(19)	3659(1)	6490(1)	1935(1)	52(1)

Table S3. Bond lengths [Å] and angles [°] for **3a**.

C(1)-O(1)	1.2296(17)
C(1)-N(1)	1.3508(17)
C(1)-C(2)	1.493(2)
C(2)-C(3)	1.3873(19)
C(2)-C(7)	1.394(2)
C(3)-C(4)	1.382(2)
C(3)-H(3)	0.9400
C(4)-C(5)	1.382(2)
C(4)-H(4)	0.9400
C(5)-O(2)	1.3653(19)
C(5)-C(6)	1.390(2)
C(6)-C(7)	1.376(2)
C(6)-H(6)	0.9400
C(7)-H(7)	0.9400
O(2)-C(8)	1.420(2)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(8)-H(8C)	0.9700
N(1)-C(9)	1.4468(17)
N(1)-H(1A)	0.8700
C(9)-C(10)	1.5347(18)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(10)-C(17)	1.5091(17)
C(10)-C(18)	1.5313(18)
C(10)-C(11)	1.5317(18)
C(11)-O(3)	1.2233(16)
C(11)-N(2)	1.3592(18)
N(2)-C(12)	1.4094(17)
N(2)-C(19)	1.4499(18)
C(12)-C(13)	1.3816(19)
C(12)-C(17)	1.3919(18)
C(13)-C(14)	1.392(2)
C(13)-H(13)	0.9400
C(14)-C(15)	1.379(2)

C(14)-H(14)	0.9400
C(15)-C(16)	1.394(2)
C(15)-H(15)	0.9400
C(16)-C(17)	1.3775(19)
C(16)-H(16)	0.9400
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(18)-H(18C)	0.9700
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(19)-H(19C)	0.9700

O(1)-C(1)-N(1)	122.52(14)
O(1)-C(1)-C(2)	121.63(13)
N(1)-C(1)-C(2)	115.84(12)
C(3)-C(2)-C(7)	118.07(14)
C(3)-C(2)-C(1)	119.15(13)
C(7)-C(2)-C(1)	122.77(13)
C(4)-C(3)-C(2)	121.54(14)
C(4)-C(3)-H(3)	119.2
C(2)-C(3)-H(3)	119.2
C(5)-C(4)-C(3)	119.68(14)
C(5)-C(4)-H(4)	120.2
C(3)-C(4)-H(4)	120.2
O(2)-C(5)-C(4)	124.77(14)
O(2)-C(5)-C(6)	115.69(14)
C(4)-C(5)-C(6)	119.54(15)
C(7)-C(6)-C(5)	120.38(15)
C(7)-C(6)-H(6)	119.8
C(5)-C(6)-H(6)	119.8
C(6)-C(7)-C(2)	120.79(14)
C(6)-C(7)-H(7)	119.6
C(2)-C(7)-H(7)	119.6
C(5)-O(2)-C(8)	118.08(14)
O(2)-C(8)-H(8A)	109.5
O(2)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5

O(2)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(1)-N(1)-C(9)	122.09(11)
C(1)-N(1)-H(1A)	119.0
C(9)-N(1)-H(1A)	119.0
N(1)-C(9)-C(10)	112.59(11)
N(1)-C(9)-H(9A)	109.1
C(10)-C(9)-H(9A)	109.1
N(1)-C(9)-H(9B)	109.1
C(10)-C(9)-H(9B)	109.1
H(9A)-C(9)-H(9B)	107.8
C(17)-C(10)-C(18)	112.04(11)
C(17)-C(10)-C(11)	101.74(10)
C(18)-C(10)-C(11)	108.52(11)
C(17)-C(10)-C(9)	113.62(11)
C(18)-C(10)-C(9)	110.50(11)
C(11)-C(10)-C(9)	109.98(11)
O(3)-C(11)-N(2)	125.91(13)
O(3)-C(11)-C(10)	125.37(12)
N(2)-C(11)-C(10)	108.72(11)
C(11)-N(2)-C(12)	111.17(11)
C(11)-N(2)-C(19)	123.80(12)
C(12)-N(2)-C(19)	125.04(12)
C(13)-C(12)-C(17)	122.35(13)
C(13)-C(12)-N(2)	128.43(13)
C(17)-C(12)-N(2)	109.22(11)
C(12)-C(13)-C(14)	116.83(14)
C(12)-C(13)-H(13)	121.6
C(14)-C(13)-H(13)	121.6
C(15)-C(14)-C(13)	121.74(13)
C(15)-C(14)-H(14)	119.1
C(13)-C(14)-H(14)	119.1
C(14)-C(15)-C(16)	120.45(14)
C(14)-C(15)-H(15)	119.8
C(16)-C(15)-H(15)	119.8
C(17)-C(16)-C(15)	118.71(13)

C(17)-C(16)-H(16)	120.6
C(15)-C(16)-H(16)	120.6
C(16)-C(17)-C(12)	119.90(12)
C(16)-C(17)-C(10)	131.01(12)
C(12)-C(17)-C(10)	109.07(11)
C(10)-C(18)-H(18A)	109.5
C(10)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(10)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
N(2)-C(19)-H(19A)	109.5
N(2)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
N(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	36(1)	26(1)	30(1)	-4(1)	10(1)	3(1)
O(1)	51(1)	30(1)	56(1)	-15(1)	24(1)	-2(1)
C(2)	36(1)	29(1)	29(1)	-3(1)	12(1)	4(1)
C(3)	42(1)	29(1)	44(1)	-5(1)	18(1)	6(1)
C(4)	41(1)	38(1)	52(1)	-2(1)	23(1)	10(1)
C(5)	42(1)	35(1)	53(1)	3(1)	25(1)	4(1)
C(6)	53(1)	28(1)	83(1)	6(1)	40(1)	8(1)
C(7)	41(1)	32(1)	62(1)	2(1)	29(1)	8(1)
O(2)	52(1)	42(1)	106(1)	8(1)	50(1)	7(1)
C(8)	47(1)	56(1)	88(2)	11(1)	40(1)	10(1)
N(1)	33(1)	25(1)	33(1)	-8(1)	12(1)	-2(1)
C(9)	37(1)	28(1)	26(1)	1(1)	12(1)	-1(1)
C(10)	31(1)	24(1)	24(1)	-2(1)	11(1)	-3(1)
C(11)	30(1)	27(1)	30(1)	-4(1)	14(1)	-2(1)
O(3)	52(1)	36(1)	36(1)	-11(1)	22(1)	-3(1)
N(2)	43(1)	22(1)	33(1)	-1(1)	17(1)	0(1)
C(12)	32(1)	26(1)	28(1)	-1(1)	13(1)	-4(1)
C(13)	47(1)	33(1)	33(1)	6(1)	18(1)	-5(1)
C(14)	48(1)	49(1)	27(1)	1(1)	19(1)	-6(1)
C(15)	44(1)	41(1)	30(1)	-9(1)	18(1)	-2(1)
C(16)	40(1)	27(1)	30(1)	-3(1)	13(1)	0(1)
C(17)	28(1)	27(1)	24(1)	0(1)	11(1)	-2(1)
C(18)	37(1)	38(1)	32(1)	0(1)	16(1)	-8(1)
C(19)	82(1)	24(1)	51(1)	1(1)	27(1)	3(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for **3a**.

	x	y	z	U(eq)
H(3)	89	10316	1096	46
H(4)	-997	9412	1219	50
H(6)	182	6772	1192	61
H(7)	1256	7679	1051	51
H(8A)	-1665	8310	1844	89
H(8B)	-2220	7356	1357	89
H(8C)	-2115	8285	784	89
H(1A)	1774	8642	349	37
H(9A)	2654	10447	653	36
H(9B)	2655	9612	-54	36
H(13)	3786	7388	3607	44
H(14)	3772	8770	4518	48
H(15)	3581	10422	3977	45
H(16)	3428	10758	2506	39
H(18A)	4223	10491	1278	53
H(18B)	4217	9651	573	53
H(18C)	4737	9465	1610	53
H(19A)	3547	6183	1355	78
H(19B)	3255	6244	2160	78
H(19C)	4215	6305	2352	78

Table S6. Torsion angles [°] for **3a**.

O(1)-C(1)-C(2)-C(3)	24.0(2)
N(1)-C(1)-C(2)-C(3)	-155.67(13)
O(1)-C(1)-C(2)-C(7)	-154.87(16)
N(1)-C(1)-C(2)-C(7)	25.5(2)
C(7)-C(2)-C(3)-C(4)	-1.0(2)
C(1)-C(2)-C(3)-C(4)	-179.90(14)
C(2)-C(3)-C(4)-C(5)	0.5(3)
C(3)-C(4)-C(5)-O(2)	-178.99(16)
C(3)-C(4)-C(5)-C(6)	0.4(3)
O(2)-C(5)-C(6)-C(7)	178.60(18)
C(4)-C(5)-C(6)-C(7)	-0.9(3)
C(5)-C(6)-C(7)-C(2)	0.4(3)
C(3)-C(2)-C(7)-C(6)	0.5(3)
C(1)-C(2)-C(7)-C(6)	179.41(16)
C(4)-C(5)-O(2)-C(8)	-0.5(3)
C(6)-C(5)-O(2)-C(8)	-179.91(18)
O(1)-C(1)-N(1)-C(9)	7.2(2)
C(2)-C(1)-N(1)-C(9)	-173.17(12)
C(1)-N(1)-C(9)-C(10)	102.99(15)
N(1)-C(9)-C(10)-C(17)	-53.63(15)
N(1)-C(9)-C(10)-C(18)	179.44(11)
N(1)-C(9)-C(10)-C(11)	59.65(14)
C(17)-C(10)-C(11)-O(3)	178.09(13)
C(18)-C(10)-C(11)-O(3)	-63.62(17)
C(9)-C(10)-C(11)-O(3)	57.36(17)
C(17)-C(10)-C(11)-N(2)	-2.54(14)
C(18)-C(10)-C(11)-N(2)	115.74(12)
C(9)-C(10)-C(11)-N(2)	-123.27(12)
O(3)-C(11)-N(2)-C(12)	-179.50(13)
C(10)-C(11)-N(2)-C(12)	1.14(15)
O(3)-C(11)-N(2)-C(19)	-0.1(2)
C(10)-C(11)-N(2)-C(19)	-179.49(14)
C(11)-N(2)-C(12)-C(13)	-178.40(14)
C(19)-N(2)-C(12)-C(13)	2.2(2)
C(11)-N(2)-C(12)-C(17)	0.94(16)

C(19)-N(2)-C(12)-C(17)	-178.42(15)
C(17)-C(12)-C(13)-C(14)	1.0(2)
N(2)-C(12)-C(13)-C(14)	-179.79(14)
C(12)-C(13)-C(14)-C(15)	0.3(2)
C(13)-C(14)-C(15)-C(16)	-0.9(2)
C(14)-C(15)-C(16)-C(17)	0.3(2)
C(15)-C(16)-C(17)-C(12)	0.9(2)
C(15)-C(16)-C(17)-C(10)	-176.98(13)
C(13)-C(12)-C(17)-C(16)	-1.5(2)
N(2)-C(12)-C(17)-C(16)	179.07(12)
C(13)-C(12)-C(17)-C(10)	176.75(13)
N(2)-C(12)-C(17)-C(10)	-2.64(15)
C(18)-C(10)-C(17)-C(16)	65.41(19)
C(11)-C(10)-C(17)-C(16)	-178.86(14)
C(9)-C(10)-C(17)-C(16)	-60.71(19)
C(18)-C(10)-C(17)-C(12)	-112.63(13)
C(11)-C(10)-C(17)-C(12)	3.10(14)
C(9)-C(10)-C(17)-C(12)	121.25(12)

Symmetry transformations used to generate equivalent atoms:

4-Bromo-*N*-[1'-methyl-2'-oxospiro(cyclopentane-1,3'-indolin)-2-yl]benzamide (Table 3, 5d)

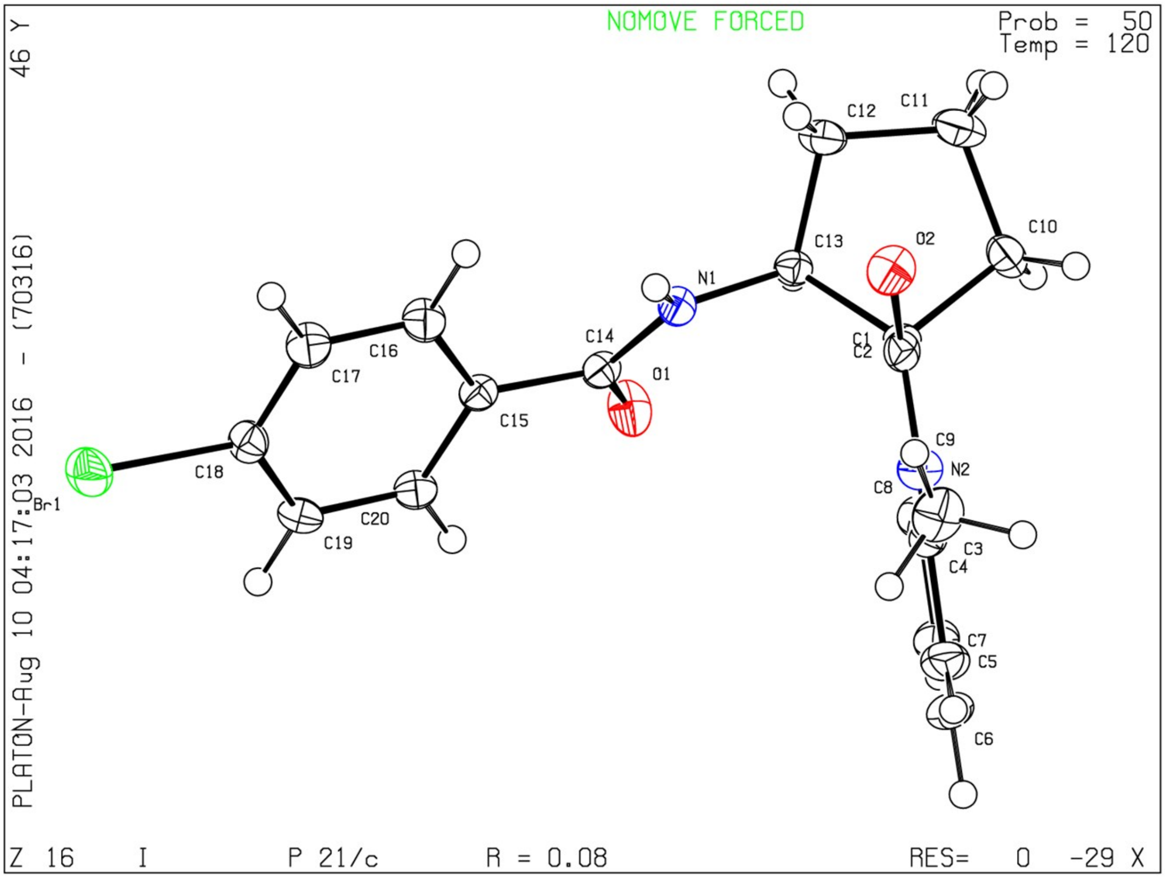


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Table S7. Crystal data and structure refinement for **5d**.

Identification code	**5d**	
Empirical formula	$C_{20} H_{19} Br N_2 O_2$	
Formula weight	399.28	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.5310(5) Å	α = 90°.
	b = 9.5367(4) Å	β = 93.809(2)°.
	c = 19.5389(9) Å	γ = 90°.
Volume	1772.05(14) $Å^3$	
Z	4	
Density (calculated)	1.497 Mg/m^3	
Absorption coefficient	2.335 mm^{-1}	
F(000)	816	
Crystal size	0.310 x 0.240 x 0.210 mm^3	
Theta range for data collection	2.891 to 39.502°.	
Index ranges	-15<=h<=16, -17<=k<=15, -34<=l<=34	
Reflections collected	42182	
Independent reflections	9950 [R(int) = 0.0551]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6249	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9950 / 0 / 227	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0818, wR2 = 0.1503	
R indices (all data)	R1 = 0.1562, wR2 = 0.1710	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.691 and -0.730 e.$Å^{-3}$	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-372(1)	7728(1)	7746(1)	32(1)
C(1)	4295(2)	7934(2)	3728(1)	16(1)
C(2)	5541(2)	8343(2)	4227(1)	19(1)
C(3)	7527(2)	7103(3)	4861(1)	32(1)
C(4)	5526(2)	5956(2)	4163(1)	20(1)
C(5)	5885(2)	4560(3)	4264(1)	30(1)
C(6)	5034(3)	3558(3)	3929(1)	31(1)
C(7)	3858(3)	3943(2)	3516(1)	28(1)
C(8)	3510(2)	5358(2)	3422(1)	23(1)
C(9)	4354(2)	6365(2)	3743(1)	18(1)
C(10)	4504(3)	8578(2)	3013(1)	26(1)
C(11)	3886(4)	10054(3)	3022(2)	44(1)
C(12)	3027(2)	10144(2)	3657(1)	27(1)
C(13)	2897(2)	8631(2)	3902(1)	18(1)
C(14)	1532(2)	7613(2)	4794(1)	18(1)
C(15)	1123(2)	7682(2)	5520(1)	17(1)
C(16)	1307(2)	8876(2)	5931(1)	25(1)
C(17)	874(2)	8877(2)	6595(1)	26(1)
C(18)	258(2)	7690(2)	6845(1)	22(1)
C(19)	63(2)	6489(2)	6449(1)	22(1)
C(20)	499(2)	6498(2)	5788(1)	21(1)
N(1)	2537(2)	8507(2)	4610(1)	18(1)
N(2)	6212(2)	7142(2)	4443(1)	22(1)
O(1)	948(2)	6765(2)	4392(1)	29(1)
O(2)	5911(2)	9534(2)	4394(1)	28(1)

Table S9.   Bond lengths [Å] and angles [°] for **5d**.

Br(1)-C(18)	1.898(2)
C(1)-C(9)	1.498(3)
C(1)-C(2)	1.537(3)
C(1)-C(13)	1.546(3)
C(1)-C(10)	1.550(3)
C(2)-O(2)	1.227(3)
C(2)-N(2)	1.364(3)
C(3)-N(2)	1.450(3)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-C(5)	1.385(3)
C(4)-C(9)	1.396(3)
C(4)-N(2)	1.400(3)
C(5)-C(6)	1.390(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.386(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.399(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.378(3)
C(8)-H(8)	0.9500
C(10)-C(11)	1.526(4)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.534(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.528(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-N(1)	1.451(2)
C(13)-H(13)	1.0000
C(14)-O(1)	1.234(2)
C(14)-N(1)	1.349(3)

C(14)-C(15)	1.497(3)
C(15)-C(20)	1.394(3)
C(15)-C(16)	1.398(3)
C(16)-C(17)	1.388(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.379(3)
C(17)-H(17)	0.9500
C(18)-C(19)	1.387(3)
C(19)-C(20)	1.383(3)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
N(1)-H(1)	0.8800

C(9)-C(1)-C(2)	102.32(15)
C(9)-C(1)-C(13)	117.18(16)
C(2)-C(1)-C(13)	113.07(16)
C(9)-C(1)-C(10)	114.01(17)
C(2)-C(1)-C(10)	109.35(16)
C(13)-C(1)-C(10)	101.13(16)
O(2)-C(2)-N(2)	125.10(19)
O(2)-C(2)-C(1)	126.80(19)
N(2)-C(2)-C(1)	108.07(17)
N(2)-C(3)-H(3A)	109.5
N(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
N(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(5)-C(4)-C(9)	122.2(2)
C(5)-C(4)-N(2)	128.0(2)
C(9)-C(4)-N(2)	109.80(18)
C(4)-C(5)-C(6)	117.6(2)
C(4)-C(5)-H(5)	121.2
C(6)-C(5)-H(5)	121.2
C(7)-C(6)-C(5)	121.1(2)
C(7)-C(6)-H(6)	119.5
C(5)-C(6)-H(6)	119.5

C(6)-C(7)-C(8)	120.5(2)
C(6)-C(7)-H(7)	119.7
C(8)-C(7)-H(7)	119.7
C(9)-C(8)-C(7)	119.1(2)
C(9)-C(8)-H(8)	120.5
C(7)-C(8)-H(8)	120.5
C(8)-C(9)-C(4)	119.60(19)
C(8)-C(9)-C(1)	131.81(18)
C(4)-C(9)-C(1)	108.58(17)
C(11)-C(10)-C(1)	106.40(18)
C(11)-C(10)-H(10A)	110.4
C(1)-C(10)-H(10A)	110.4
C(11)-C(10)-H(10B)	110.4
C(1)-C(10)-H(10B)	110.4
H(10A)-C(10)-H(10B)	108.6
C(10)-C(11)-C(12)	106.72(19)
C(10)-C(11)-H(11A)	110.4
C(12)-C(11)-H(11A)	110.4
C(10)-C(11)-H(11B)	110.4
C(12)-C(11)-H(11B)	110.4
H(11A)-C(11)-H(11B)	108.6
C(13)-C(12)-C(11)	105.05(19)
C(13)-C(12)-H(12A)	110.7
C(11)-C(12)-H(12A)	110.7
C(13)-C(12)-H(12B)	110.7
C(11)-C(12)-H(12B)	110.7
H(12A)-C(12)-H(12B)	108.8
N(1)-C(13)-C(12)	113.89(17)
N(1)-C(13)-C(1)	115.91(15)
C(12)-C(13)-C(1)	104.34(16)
N(1)-C(13)-H(13)	107.4
C(12)-C(13)-H(13)	107.4
C(1)-C(13)-H(13)	107.4
O(1)-C(14)-N(1)	122.79(19)
O(1)-C(14)-C(15)	119.83(18)
N(1)-C(14)-C(15)	117.38(17)
C(20)-C(15)-C(16)	118.98(19)

C(20)-C(15)-C(14)	117.71(17)
C(16)-C(15)-C(14)	123.29(18)
C(17)-C(16)-C(15)	120.2(2)
C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(18)-C(17)-C(16)	119.3(2)
C(18)-C(17)-H(17)	120.3
C(16)-C(17)-H(17)	120.3
C(17)-C(18)-C(19)	121.7(2)
C(17)-C(18)-Br(1)	118.72(16)
C(19)-C(18)-Br(1)	119.55(17)
C(20)-C(19)-C(18)	118.52(19)
C(20)-C(19)-H(19)	120.7
C(18)-C(19)-H(19)	120.7
C(19)-C(20)-C(15)	121.20(19)
C(19)-C(20)-H(20)	119.4
C(15)-C(20)-H(20)	119.4
C(14)-N(1)-C(13)	121.55(17)
C(14)-N(1)-H(1)	119.2
C(13)-N(1)-H(1)	119.2
C(2)-N(2)-C(4)	111.12(17)
C(2)-N(2)-C(3)	124.44(19)
C(4)-N(2)-C(3)	124.26(19)

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2 x 10^3$) for **5d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	43(1)	32(1)	19(1)	0(1)	3(1)	0(1)
C(1)	17(1)	10(1)	20(1)	1(1)	1(1)	-2(1)
C(2)	15(1)	20(1)	23(1)	-1(1)	4(1)	-2(1)
C(3)	20(1)	42(1)	32(1)	-1(1)	-6(1)	3(1)
C(4)	18(1)	19(1)	24(1)	2(1)	4(1)	2(1)
C(5)	25(1)	25(1)	39(1)	8(1)	4(1)	6(1)
C(6)	32(1)	17(1)	46(1)	3(1)	13(1)	4(1)
C(7)	33(1)	16(1)	35(1)	-4(1)	9(1)	-4(1)
C(8)	23(1)	21(1)	25(1)	-2(1)	1(1)	-2(1)
C(9)	20(1)	15(1)	19(1)	0(1)	3(1)	1(1)
C(10)	32(1)	25(1)	21(1)	4(1)	7(1)	-2(1)
C(11)	74(2)	24(1)	35(1)	12(1)	17(1)	10(1)
C(12)	30(1)	19(1)	33(1)	8(1)	4(1)	3(1)
C(13)	17(1)	17(1)	19(1)	1(1)	0(1)	0(1)
C(14)	16(1)	16(1)	23(1)	-2(1)	1(1)	-1(1)
C(15)	15(1)	14(1)	22(1)	-2(1)	1(1)	-3(1)
C(16)	30(1)	17(1)	29(1)	-5(1)	7(1)	-9(1)
C(17)	32(1)	18(1)	29(1)	-8(1)	6(1)	-9(1)
C(18)	23(1)	25(1)	16(1)	0(1)	-1(1)	1(1)
C(19)	25(1)	16(1)	24(1)	3(1)	0(1)	-3(1)
C(20)	21(1)	17(1)	23(1)	-2(1)	-1(1)	-3(1)
N(1)	16(1)	17(1)	22(1)	-2(1)	2(1)	-4(1)
N(2)	17(1)	23(1)	27(1)	1(1)	-2(1)	-1(1)
O(1)	29(1)	31(1)	27(1)	-9(1)	5(1)	-15(1)
O(2)	23(1)	25(1)	35(1)	-7(1)	1(1)	-7(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **5d**.

	x	y	z	U(eq)
H(3A)	7719	8030	5061	47
H(3B)	8292	6838	4576	47
H(3C)	7458	6412	5229	47
H(5)	6683	4298	4553	35
H(6)	5262	2593	3983	38
H(7)	3283	3241	3296	33
H(8)	2702	5621	3139	28
H(10A)	5517	8616	2929	31
H(10B)	4013	8009	2648	31
H(11A)	3276	10224	2600	52
H(11B)	4647	10763	3048	52
H(12A)	3516	10730	4017	33
H(12B)	2087	10551	3537	33
H(13)	2126	8178	3609	21
H(16)	1730	9691	5755	30
H(17)	1001	9687	6876	32
H(19)	-360	5678	6629	26
H(20)	371	5683	5511	25
H(1)	2985	9027	4926	22

Table S12. Torsion angles [°] for **5d**.

C(9)-C(1)-C(2)-O(2)	-178.8(2)
C(13)-C(1)-C(2)-O(2)	-51.9(3)
C(10)-C(1)-C(2)-O(2)	59.9(3)
C(9)-C(1)-C(2)-N(2)	3.2(2)
C(13)-C(1)-C(2)-N(2)	130.13(17)
C(10)-C(1)-C(2)-N(2)	-118.04(19)
C(9)-C(4)-C(5)-C(6)	0.3(3)
N(2)-C(4)-C(5)-C(6)	179.9(2)
C(4)-C(5)-C(6)-C(7)	-1.0(4)
C(5)-C(6)-C(7)-C(8)	0.8(4)
C(6)-C(7)-C(8)-C(9)	0.1(3)
C(7)-C(8)-C(9)-C(4)	-0.8(3)
C(7)-C(8)-C(9)-C(1)	177.8(2)
C(5)-C(4)-C(9)-C(8)	0.6(3)
N(2)-C(4)-C(9)-C(8)	-179.06(19)
C(5)-C(4)-C(9)-C(1)	-178.3(2)
N(2)-C(4)-C(9)-C(1)	2.1(2)
C(2)-C(1)-C(9)-C(8)	178.2(2)
C(13)-C(1)-C(9)-C(8)	53.9(3)
C(10)-C(1)-C(9)-C(8)	-63.9(3)
C(2)-C(1)-C(9)-C(4)	-3.1(2)
C(13)-C(1)-C(9)-C(4)	-127.39(18)
C(10)-C(1)-C(9)-C(4)	114.82(19)
C(9)-C(1)-C(10)-C(11)	159.4(2)
C(2)-C(1)-C(10)-C(11)	-86.8(2)
C(13)-C(1)-C(10)-C(11)	32.7(2)
C(1)-C(10)-C(11)-C(12)	-13.0(3)
C(10)-C(11)-C(12)-C(13)	-12.6(3)
C(11)-C(12)-C(13)-N(1)	160.8(2)
C(11)-C(12)-C(13)-C(1)	33.4(2)
C(9)-C(1)-C(13)-N(1)	68.8(2)
C(2)-C(1)-C(13)-N(1)	-49.8(2)
C(10)-C(1)-C(13)-N(1)	-166.63(17)
C(9)-C(1)-C(13)-C(12)	-165.10(17)
C(2)-C(1)-C(13)-C(12)	76.3(2)

C(10)-C(1)-C(13)-C(12)	-40.54(19)
O(1)-C(14)-C(15)-C(20)	22.8(3)
N(1)-C(14)-C(15)-C(20)	-157.49(19)
O(1)-C(14)-C(15)-C(16)	-155.7(2)
N(1)-C(14)-C(15)-C(16)	24.1(3)
C(20)-C(15)-C(16)-C(17)	0.1(3)
C(14)-C(15)-C(16)-C(17)	178.5(2)
C(15)-C(16)-C(17)-C(18)	-0.2(4)
C(16)-C(17)-C(18)-C(19)	0.3(3)
C(16)-C(17)-C(18)-Br(1)	-178.36(18)
C(17)-C(18)-C(19)-C(20)	-0.3(3)
Br(1)-C(18)-C(19)-C(20)	178.41(15)
C(18)-C(19)-C(20)-C(15)	0.1(3)
C(16)-C(15)-C(20)-C(19)	0.0(3)
C(14)-C(15)-C(20)-C(19)	-178.54(18)
O(1)-C(14)-N(1)-C(13)	6.6(3)
C(15)-C(14)-N(1)-C(13)	-173.14(17)
C(12)-C(13)-N(1)-C(14)	134.1(2)
C(1)-C(13)-N(1)-C(14)	-104.8(2)
O(2)-C(2)-N(2)-C(4)	179.8(2)
C(1)-C(2)-N(2)-C(4)	-2.1(2)
O(2)-C(2)-N(2)-C(3)	-4.9(3)
C(1)-C(2)-N(2)-C(3)	173.1(2)
C(5)-C(4)-N(2)-C(2)	-179.5(2)
C(9)-C(4)-N(2)-C(2)	0.1(2)
C(5)-C(4)-N(2)-C(3)	5.2(4)
C(9)-C(4)-N(2)-C(3)	-175.2(2)

Symmetry transformations used to generate equivalent atoms:

Table S13. Hydrogen bonds for **5d** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(3)-H(3B)...O(1)#1	0.98	2.58	3.461(3)	149.3
C(13)-H(13)...Br(1)#2	1.00	2.95	3.9449(19)	171.0
C(17)-H(17)...Br(1)#3	0.95	3.06	3.931(2)	152.9
N(1)-H(1)...O(2)#4	0.88	2.14	3.014(2)	173.5

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z   #2 x,-y+3/2,z-1/2   #3 -x,y+1/2,-z+3/2
#4 -x+1,-y+2,-z+1