Supporting Information for

Using weak interactions to control C-H mono-nitration of indolines

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CONTENTS

EXPERIMENTAL SECTION

Instrumentation and Chemicals. Column chromatographic purifications of the compounds were performed using silica gel (mesh 100–200) and hexane – ethyl acetate mixtures as eluent unless otherwise specified. FT-IR spectra were recorded after making pellet of the compounds using anhydrous solid KBr. NMR spectra were recorded on a 400 MHz or 700 MHz instrument at 25 °C. The chemical shift values are reported in parts per million (ppm) with respect to residual trichloromethane (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C) or dimethylsulfoxide (2.50 ppm for ^{1}H and 40.0 ppm for ^{13}C). The peak patterns are designated as follows: s: singlet; d: doublet; t: triplet; q: quartet; m: multiplet; dd: doublet of doublets; td: triplet of doublets; br s broad singlet. The coupling constants (*J*) are reported in hertz (Hz). High-resolution mass spectra (HR-MS) were recorded on an ESI-TOF (time of flight) mass spectrometer. Infrared spectral data are reported in wave number (cm^{-1}). Melting points of the compounds were determined using a digital melting point apparatus and are uncorrected.

Crystallographic Data Collection

Good quality crystals of the compounds **2j** and **2s** were obtained after slow evaporation of ethyl acetate solution. The crystals data were collected with Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an INCOATEC micro source (Mo-Kα radiation, λ = 0.71073 A). SAINT+3 and SADABS4 were used to integrate the intensities and correction of the absorption respectively. The structure was resolved by direct methods and refined on F*2* with SHELXL-97.5.

Crystallographic Data

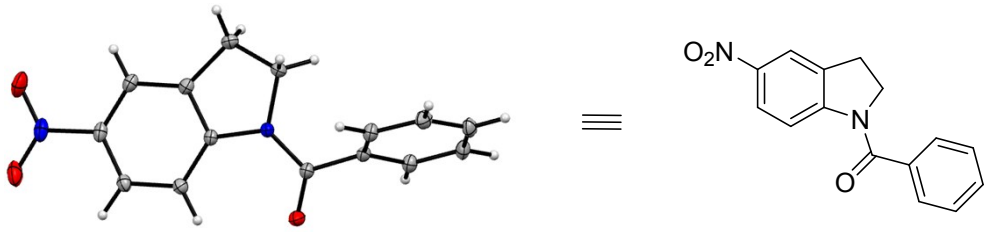

Fig. S1. Crystal structure of **2j**

Table S2. Crystal data and structure refinement for **2j**.

CCDC No.	**1550269**	
Empirical formula	$C_{15}H_{12}N_2O_3$	
Formula weight	268.27	
Temperature/K	296.15	
Crystal system	monoclinic	
Space group	$P2_1$	
Unit cell dimension	a = 8.1122(4) Å	α = 90°
	b = 7.8149(3) Å	β = 102.368(2)°
	c = 10.1296(4) Å	γ = 90°

Volume	627.27(5) $Å^3$
Z	2
Density calculated	1.420 cm^3
Absorption coefficient	0.101 mm^{-1}
F(000)	280.0
Crystal size	0.3 × 0.26 × 0.22 mm^3
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	4.116 to 57.476°
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 9, -13 ≤ l ≤ 13
Reflections collected	11174
Independent reflections	3064 [Rint = 0.0369, Rsigma = 0.0324]
Data/restraints/parameters	3064/1/181
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.0929
Final R indexes [all data]	R_1 = 0.0537, wR_2 = 0.0999
Largest diff. peak/hole	0.12/-0.20 e $Å^{-3}$

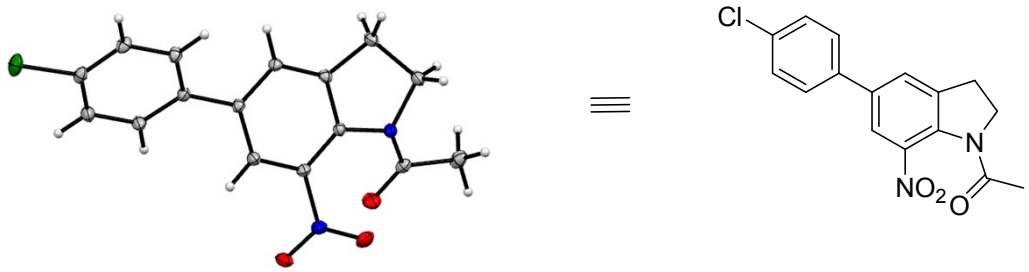

Fig. S2. Crystal structure of **2s**

Table S3. Crystal data and structure refinement for

CCDC No.	**1550265**
Empirical formula	$C_{16}H_{13}ClN_2O_3$
Formula weight	316.73
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
Unit Cell dimensions	a = 10.4606(4) Å α = 90°
	b = 12.8372(4) Å β = 106.445(2)°
	c = 11.2997(4) Å γ = 90°
Volume	1455.30(9) $Å^3$
Z	4
Density calculated	1.446 cm^3
Absorption coefficient	0.277 mm^{-1}
F(000)	656.0
Crystal size	0.3 × 0.27 × 0.22 mm^3
Radiation	MoKα (λ = 0.71073)
Theta range for data collection	4.688 to 60.168 °
Index ranges	$-14 \leq h \leq 10$, $-18 \leq k \leq 14$, $-15 \leq l \leq 15$

Reflections collected	15342
Independent reflections	4271 [Rint = 0.0242, Rsigma = 0.0290]
Data/restraints/parameters	4271/0/200
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0493, wR_2 = 0.1347
Final R indexes [all data]	R_1 = 0.0756, wR_2 = 0.1520
Largest diff. peak/hole	0.36/-0.54 e $Å^{-3}$

SYNTHESIS

Representative procedure for preparation of 1-(5-nitroindolin-1-yl)ethanone (2a)

Method A. To an oven-dried sealed tube charged with a magnetic stirring bar and **1a** (100 mg, 0.62 mmol, 1 equiv), $Cu(NO_3)_2.3H_2O$ (165 mg, 0.68 mmol, 1.1 equiv), and $K_2S_2O_8$ (252 mg, 0.93 mmol, 1.5 equiv) in DCE (2 mL) was added TFA (10 μL, 0.12 mmol, 0.2 equiv). The reaction mixture was allowed to stir at 80 °C for 2 h. After cooling at room temperature, the reaction mixture washed with water and followed by extracted with dichloromethane. Column purification using 25% ethyl acetate-hexane yielded **2a** (105 mg, 82%) as pale yellow solid.

Method B. To an oven-dried sealed tube charged with a magnetic stirring bar and **1a** (100 mg, 0.62 mmol, 1 equiv), $AgNO_3$ (158 mg, 0.93 mmol, 1.5 equiv), and $K_2S_2O_8$ (252 mg, 0.93 mmol, 1.5 equiv) in DCE (2 mL) was added TFA (10 μL, 0.12 mmol, 0.2 equiv). The reaction mixture was allowed to stir at 80 °C for 2 h. After cooling at room temperature, the reaction mixture washed with water and followed by extracted with dichloromethane. Column purification using 25% ethyl acetate-hexane yielded **2a** (102 mg, 80%) as pale yellow solid.

1-(5-Nitroindolin-1-yl)ethanone (2a):[1] R_f = 0.28 (25% ethyl acetate/hexane); pale yellow solid; yield A: 105 mg (82%), B: 102 mg (80%); mp: 175-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.8 Hz, 1H), 8.11 (dd, J = 8.8, 2.4 Hz, 1H), 8.03 (s, 1H), 4.19 (t, J = 8. 4 Hz, 2H), 3.28 (t, J = 8.4 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 148.4, 143.7, 132.4, 124.8, 120.4, 116.3, 49.5, 27.5, 24.4; IR (KBr) $\tilde{\nu}$ 2972, 2812, 2373, 1603, 1515, 1480, 1399, 1258, 1172, 1129, 1074, 1025, 994, 892, 843, 748, 624 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{10}H_{11}N_2O_3$ $[M+H]^+$ 207.0764, found 207.0765.

1-(3-Methyl-5-nitroindolin-1-yl)ethanone (2b): R_f = 0.4 (20% ethyl acetate/hexane); pale yellow solid; yield A: 106 mg (83%), B: 95 mg (75%); mp: 122-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 1H), 8.11 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.00 (s, 1H), 4.33 (t, *J* = 10 Hz, 1H), 3.71 (dd, *J* = 10, 6.8 Hz, 1H), 3.57 (dm, 1H), 2.26 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 147.8, 143.8, 137.7, 124.9, 119.4, 116.3, 57.6, 34.4, 24.4, 20.3; IR (KBr) $\tilde{\nu}$ 2964, 2891, 2191, 1672, 1602, 1510, 1478, 1399, 1329, 1261, 1175, 1116, 1078, 1032, 1012, 916, 836, 787, 732, 620 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{13}N_2O_3$ $[M+H]^+$ 221.0921, found 221.0909.

2-(1-Acetyl-5-nitroindolin-3-yl)acetonitrile (2c): R_f = 0.3 (40% ethyl acetate/hexane); off white solid; yield A: 71 mg (58%), B: 67 mg (55%); mp: 156-168 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.31 (s, 1H), 8.20 (d, *J* = 1.6 Hz, 2H), 4.45 (t, *J* = 9.8 Hz, 1H), 4.00 (dd, *J* = 10.8, 5.6 Hz, 1H), 3.88 (dd, *J* = 9.2, 5.6 Hz, 1H), 3.09 (d, *J* = 6.0, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.4, 148.9, 143.2, 134.6, 126.1, 120.9, 119.3, 115.8, 54.6, 35.8, 24.6, 22.3; IR (KBr) $\tilde{\nu}$ 2995, 2872, 2254, 2128, 1758, 1659, 1551, 1501, 1484, 1338, 1266, 1049, 1025, 1002, 825, 764, 655 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{11}N_3O_3Na$ $[M+Na]^+$ 268.0693, found 268.0693.

1-(Methylsulfonyl)-5-nitroindoline (2d): R_f = 0.42 (25% ethyl acetate/hexane); pale yellow solid; yield A: 90 mg (71%), B: 88 mg (70%); mp: 142-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.07 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 4.13 (t, *J* = 8.8 Hz, 2H), 3.26 (t, *J* = 8.8 Hz, 2H), 2.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 143.9, 132.4, 125.2(2C), 121.4, 112.5, 51.0, 36.3, 27.3; IR (KBr) $\tilde{\nu}$ 2912, 2298, 20978, 1637, 1456, 1339, 1318, 1235, 1108, 1079, 958, 756, 635 cm^{-1}; HRMS (ESI-TOF) calcd for $C_9H_{11}N_2O_4S$ $[M+H]^+$ 243.0434, found 243.0433.

2,2-Dimethyl-1-(2-methyl-5-nitroindolin-1-yl)propan-1-one (2e): R_f = 0.57 (10% ethyl acetate/hexane); off white solid; yield A: 87 mg (72%), B: 79 mg (65%); mp: 157-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 1H), 8.13 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.08 (s, 1H), 4.99 – 4.93 (m, 1H), 3.37 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.71 (d, *J* = 15.2 Hz, 1H), 1.40 (s, 9H), 1.29 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 148.9, 143.7, 131.8, 124.3, 120.5, 118.6, 57.1, 41.0, 36.3, 28.3, 22.0; IR (neat) $\tilde{\nu}$ 2975, 2931, 2874, 1696, 1655, 1599, 1514, 1435, 1298, 1160, 1118, 1066, 992, 754, 671 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{19}N_2O_3$ $[M+H]^+$ 263.1390, found 263.1372.

2,2-Dimethyl-1-(5-nitro-2-(p-tolyl)indolin-1-yl)propan-1-one (2f): R_f = 0.28 (6% ethyl acetate/hexane); yellow solid; yield A: 81 mg (70%), B: 67 mg (58%); mp: 142-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 9.2 Hz, 1H), 8.18 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.94 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 5.91 (d, *J* = 8.8 Hz, 1H), 3.75 (dd, *J* = 15.2, 8.8 Hz, 1H), 3.00 (d, *J* = 15.2 Hz, 1H), 2.28 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 150.5, 144.0, 139.6, 137.4, 130.4, 129.7, 124.7, 124.5, 120.5, 117.7, 63.8, 41.0, 39.2, 28.3, 20.9; IR (KBr) $\tilde{\nu}$ 3407, 2983, 2937, 2365, 1653, 1602, 1520, 1466, 1401, 1301, 1218, 1181, 1068, 970, 890, 754 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{23}N_2O_3$ $[M+H]^+$ 339.1703, found 339.1696.

2,2-Dimethyl-1-(5-nitro-2-phenylindolin-1-yl)propan-1-one (2g): R_f = 0.21 (8% ethyl acetate/hexane); pale yellow solid; yield A: 80 mg (68%), B: 70 mg (60%); mp: 160-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.8 Hz, 1H), 8.17 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.93 (s, 1H), 7.27 – 7.18 (m, 3H), 7.04 (d, *J* = 6.8 Hz, 2H), 5.93 (d, *J* = 8.4 Hz, 1H), 3.76 (dd, *J* = 15.6, 8.4 Hz, 1H), 3.01 (d, *J* = 15.6 Hz, 1H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 150.5,

144.0, 142.6, 130.3, 129.0, 127.7, 124.8, 124.6, 120.5, 117.7, 63.9, 41.0, 39.2, 28.3; IR (KBr) $\tilde{\nu}$ 2971, 2873, 1954, 1748, 1664, 1599, 1492, 1401, 1339, 1254, 1160, 1120, 1029, 936, 839, 754 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{21}N_2O_3$ $[M+H]^+$ 325.1547, found 325.1572.

2,2-Dimethyl-1-(5-nitroindolin-1-yl)propan-1-one (2h): R_f = 0.42 (20% ethyl acetate/hexane); pale yellow solid; yield A: 88 mg (72%), B: 85 mg (70%); mp: 119-122 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 1H), 8.12 (dd, *J* = 8.8, 2.4 Hz, 1H), 8.05 (s, 1H), 4.36 (t, *J* = 8.4 Hz, 2H), 3.24 (t, *J* = 8.4 Hz, 2H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 150.5, 143.7, 132.1, 124.6, 120.0, 117.7, 50.3, 40.7, 28.8, 27.7; IR (KBr) $\tilde{\nu}$ 3056, 2977, 2879, 2307, 2156, 1656, 1515, 1402, 1313, 1160, 921, 835, 739, 703, 614 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{13}H_{17}N_2O_3$ $[M+H]^+$ 249.1234, found 249.1225.

5-Nitro-1-tosylindoline (2i): R_f = 0.28 (18% ethyl acetate/hexane); pale yellow solid; yield A: 82 mg (70%), B: 77 mg (66%); mp: 168-171 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.92 (d, *J* = 1.2 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.28 – 7.23 (m, 2H), 4.00 (t, *J* = 8.8 Hz, 2H), 3.04 (t, *J* = 8.8 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 145.2, 143.8, 133.7, 132.6, 130.2, 127.3, 124.9, 121.1, 113.3, 50.6, 27.2, 21.7; IR (KBr) $\tilde{\nu}$ 2956, 2902, 2307, 2090, 1641, 1599, 1479, 1339, 1306, 1256, 1166, 1091, 1074, 972, 704, 665 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{15}N_2O_4S$ $[M+H]^+$ 319.0747, found 319.0744.

(5-Nitroindolin-1-yl)(phenyl)methanone (2j): R_f = 0.28 (15% ethyl acetate/hexane); yellow solid; yield A: 105 mg (68%), B: 102 mg (62%); mp: 197-200 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.2 Hz, 1H), 7.58 – 7.46 (m, 5H), 7.26 (s, 1H), 4.19 (t, *J* = 8.4 Hz, 2H), 3.22 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 148.4, 143.9, 136.0, 133.7, 131.2, 128.9,

127.3, 124.5, 120.7, 116.5, 51.5, 27.7; IR (KBr) $\tilde{\nu}$ 3005, 2987, 2922, 2315, 2114, 1659, 1551, 1441, 1383, 1317, 1152, 833, 751, 699 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{13}N_2O_3$ $[M+H]^+$ 269.0921, found 269.0931.

2,2-Dimethyl-1-(2-methyl-5,7-dinitroindolin-1-yl)propan-1-one (2k): R_f = 0.42 (20% ethyl acetate/hexane); yellow solid; yield A: 74 mg (63%), B: 65 mg (55%); mp: 158-162 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.86 (s, 1H), 5.06 – 4.99 (m, 1H), 3.43 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.80 (d, *J* = 16.0 Hz, 1H), 1.39 (s, 9H), 1.33 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 148.1, 144.4, 137.0, 134.6, 121.6, 114.2, 57.6, 41.2, 36.4, 28.2, 22.1; IR (KBr) $\tilde{\nu}$ 2973, 2933, 2366, 1655, 1602, 1547, 1528, 1474, 1380, 1319, 1291, 1189, 1110, 1009, 993, 707 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{18}N_3O_5$ $[M+H]^+$ 308.1241, found 308.1243.

1-(5-Bromo-7-nitroindolin-1-yl)ethanone (2l):[1] R_f = 0.42 (20% ethyl acetate/hexane); yellow solid; yield A: 88 mg (74%), B: 86 mg (73%); mp: 196-198 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.52 (s, 1H), 4.23 (t, *J* = 8.0 Hz, 2H), 3.22 (t, *J* = 8.0 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 140.9, 138.5, 133.7, 131.6, 125.4, 116.2, 50.1, 28.8, 23.2; IR (neat) $\tilde{\nu}$ 3055, 2988, 2686, 2411, 2306, 1686, 1596, 1542, 1458, 1421, 1384, 1331, 1265, 896, 737 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{10}H_{10}BrN_2O_4$ $[M+H]^+$ 284.9869, found 284.9876.

1-(7-Nitro-5-(m-tolyl)indolin-1-yl)ethanone (2m): R_f = 0.28 (6% ethyl acetate/hexane); yellow solid; yield A: 68 mg (58%), B: 59 mg (50%); mp: 198-200 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.86 (s, 1H), 7.64 (s, 1H), 7.49 (d, *J* = 6.0 Hz, 2H), 4.29 (t, *J* = 8.0 Hz, 2H), 3.30 (t, *J* = 8.0 Hz, 2H), 2.67 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 148.6, 143.3, 141.1, 137.9, 135.6, 134.8, 131.2, 127.2, 125.8, 125.3, 121.8, 50.4, 29.1, 23.4, 20.9; IR (KBr) $\tilde{\nu}$ 3056, 2975, 2929, 2851, 2377, 2307, 1679, 1609, 1580, 1474, 1307, 1264,

1148, 1031, 982, 966, 739, 704 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{17}N_2O_3$ $[M+H]^+$ 297.1234, found 297.1257.

1-(7-Nitro-5-phenylindolin-1-yl)ethanone (2n): R_f = 0.28 (20% ethyl acetate/hexane); pale yellow solid; yield A: 86 mg (72%), B: 87 mg (73%); mp: 188 -190 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 0.8 Hz, 1H), 7.63 (s, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.39 – 7.36 (m, 1H), 4.27 (t, *J* = 8.0 Hz, 2H), 3.27 (t, *J* = 8.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 141.1, 138.7, 138.4, 137.3, 133.6, 129.2, 128.2, 127.2, 127.0, 121.5, 50.4, 29.2, 23.4; IR (KBr) $\tilde{\nu}$ 2934, 2820, 1618, 1530, 1427, 1387, 1231, 1117, 1069, 1020, 882, 747, 693 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{15}N_2O_3$ $[M+H]^+$ 283.1077, found 283.1080.

1-(5-(4-(tert-Butyl)phenyl)-7-nitroindolin-1-yl)ethanone (2o): R_f = 0.28 (10% ethyl acetate/hexane); yellow solid; yield A: 60 mg (52%), B: 57 mg (50%); mp: 177-180 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.63 (s, 1H), 7.48 (d, *J* = 2.0 Hz, 4H), 4.27 (t, *J* = 8.0 Hz, 2H), 3.27 (t, *J* = 8.0 Hz, 2H), 2.28 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 151.5, 141.2, 138.4, 137.2, 135.8, 133.4, 127.0, 126.7, 126.2, 121.3, 50.4, 34.8, 31.4, 29.3, 23.4; IR (KBr) $\tilde{\nu}$ 3055, 2964, 2927, 2855, 2305, 1678, 1538, 1478, 1409, 1382, 1319, 1265, 1111, 836, 745 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{23}N_2O_3$ $[M+H]^+$ 339.1703, found 339.1679.

1-(5-(4-Ethylphenyl)-7-nitroindolin-1-yl)ethanone (2p): R_f = 0.28 (12% ethyl acetate/hexane); yellow solid; yield A: 88 mg (75%), B: 80 mg (68%); mp: 144-147 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.62 (s, 1H), 7.46 (d, *J* = 8 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 4.27 (t, *J* = 8 Hz, 2H), 3.26 (t, *J* = 8 Hz, 2H), 2.69 (q, *J* = 7.6 Hz, 2H), 2.27 (s, 3H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 144.5, 141.1, 138.4, 137.2, 136.1, 133.3, 128.7, 126.97,

126.95, 121.1, 50.3, 29.2, 28.6, 23.4, 15.6; IR (KBr) $\tilde{\nu}$ 2967, 2931, 2365, 1609, 1567, 1498, 1389, 1288, 1116, 1072, 918, 896, 835, 707, 618 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{19}N_2O_3$ $[M+H]^+$ 311.1390, found 311.1375.

1-(5-(3-Chlorophenyl)-7-nitroindolin-1-yl)ethanone (2q): R_f = 0.42 (15% ethyl acetate/hexane); yellow solid; yield A: 58 mg (50%), B: 58 mg (50%); mp: 145- 148 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.62 (s, 1H), 7.54 (s, 1H), 7.44 – 7.36 (m, 3H), 4.29 (t, *J* = 8.0 Hz, 2H), 3.29 (t, *J* = 8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 141.1, 140.5, 137.6, 136.8, 135.2, 134.2, 130.5, 128.3, 127.16, 127.08, 125.2, 121.6, 50.4, 29.2, 23.5; IR (KBr) $\tilde{\nu}$ 2925, 2853, 2685, 2305, 2125, 1733, 1681, 1641, 1465, 1381, 1264, 1114, 1078, 895, 705 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{13}ClN_2O_3Na$ $[M+Na]^+$ 339.0507, found 339.0508.

1-(5-(4-Fluorophenyl)-7-nitroindolin-1-yl)ethanone (2r): R_f = 0.42 (12% ethyl acetate/hexane); yellow solid; yield A: 53 mg (45%), B: 47 mg (40%); mp: 153-156 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.58 (s, 1H), 7.50 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.14 (t, *J* = 8.8 Hz, 2H), 4.28 (t, *J* = 8.0 Hz, 2H), 3.28 (t, *J* = 8.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 164.2, 161.7, 141.1, 137.4 (d, $^1J_{F\text{-}C}$ = 7.8 Hz), 134.9 (d, $^1J_{F\text{-}C}$ = 3.1 Hz), 133.6, 128.7 (d, $^1J_{F\text{-}C}$ = 8.2 Hz), 127.0, 121.3, 116.2 (d, $^1J_{F\text{-}C}$ = 21.5 Hz), 50.4 , 29.2, 23.4; IR (KBr) $\tilde{\nu}$ 2959, 2927, 2854, 2305, 2114, 1640, 1543, 1512, 1467, 1381, 1265, 1169, 836, 745, 705 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{14}FN_2O_3$ $[M+H]^+$ 301.0983, found 301.0970.

1-(5-(4-Chlorophenyl)-7-nitroindolin-1-yl)ethanone (2s): R_f = 0.28 (18% ethyl acetate/hexane); pale yellow solid; yield A: 72 mg (62%), B: 67 mg (58%); mp: 149-152 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 1.6 Hz, 1H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.47-7.44 (m ,

2H), 7.41 – 7.39 (m, 2H), 4.27 (t, J = 8.0 Hz, 2H), 3.27 (t, J = 8.0 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 140.9, 137.4, 137.0, 136.8, 134.2, 133.7, 129.2, 128.0,126.7, 121.1, 50.2, 29.0, 23.3; IR (KBr) $\tilde{\nu}$ 2937, 2812, 2678, 2165, 1728, 1670, 1634, 1567, , 1256, 1109, 1085, 801, 734 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{13}ClN_2O_3Na$ $[M+Na]^+$ 339.0502, found 339.0502.

Post synthetic application of 1-(5-nitroindolin-1-yl)ethanone (2a)

Synthesis of nitro indole. To an oven-dried sealed tube charged with a magnetic stirring bar, a mixture of **2a** (50 mg, 0.24 mmol, 1 equiv) and DDQ (110 mg, 0.48 mmol, 2 equiv) was added and dissolved in 2 ml of 1,4-dioxane. The reaction mixture was allowed to stir at 120 °C for 16 h. After cooling at room temperature, the reaction mixture was washed with brine solution and followed by extracted with ethyl acetate. Column purification using 8% ethyl acetate-hexane yielded 1-(5-Nitro-1H-indol-1-yl)ethanone (**3a**)[2] as pale yellow solid; R_f = 0.28 (8% ethyl acetate/hexane); yield 35 mg (70%); mp: 173-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57(d, J = 9.2 Hz, 1H), 8.49 (d, J = 2.4 Hz, 1H), 8.24 (dd, J = 9.2, 2.4 Hz, 1H), 7.59 (d, J = 4.0 Hz, 1H), 6.79 (d, J = 2.4 Hz, 1H), 2.69 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 144.4, 138.6, 130.4, 128.2, 120.6, 117.2, 116.9, 109.7, 24.1; IR (KBr) $\tilde{\nu}$ 2928, 2902, 2306, 2114, 1641, 1550, 1421, 1321, 1203, 896, 739, 706 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{10}H_8N_2O_3Na$ $[M+Na]^+$ 227.0427, found 227.0439.

Synthesis of amino indoline. To a mixture of **2a** (50 mg, 0.24 mmol, 1 equiv) and iron powder (134 mg, 2.4 mmol, 10 equiv) in a round bottom flask, 2 mL of EtOH and 0.5 ML of water was added along with 45 µL of conc. HCl. The resulting mixture was allowed to reflux at 80 ºC for 2 h. After cooling at room temperature, the reaction mixture was washed with $NaHCO_3$ solution

and extracted with ethyl acetate. Column chromatographic purification using 40% ethyl acetate-hexane yielded 1-(5-Aminoindolin-1-yl)ethanone (**3b**)[3] as pale yellow solid; R_f = 0.21 (40% ethyl acetate/hexane); yield 34 mg (80%); mp: 180-183 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 (d, *J* = 8.8 Hz, 1H), 6.45 (s, 1H), 6.32 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.85 (s, 2H), 3.97 (t, *J* = 8.4 Hz, 2H), 2.99 (t, *J* = 8.4 Hz, 2H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1, 145.2, 133.7, 133.0, 117.0, 112.3, 111.1, 48.5, 28.0, 24.1; IR (KBr) $\tilde{\nu}$ 3443, 3055, 2376, 2306, 2114, 1642, 1492, 1265, 895, 742, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{10}H_{13}N_2O$ $[M+H]^+$ 177.1022, found 177.1032.

Deprotection of acetyl group. In a round bottom flask **2a** (50 mg, 0.24 mmol, 1 equiv) was taken and 2 ml of 10 M HCl was added to it. The solution was stirred at room temperature for 4 h. Then the reaction mixture was washed with saturated NaOH solution and extracted in dichloromethane. The organic layer was concentrated under reduced pressure and re-crystallised from ethanol to get orange solid of 5-nitroindoline (**3c**);[1] orange solid; yield 33 mg (82%); mp: 91-93 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.83 (s, 1H), 7.25 (s, 1H), 6.44 (d, *J* = 8.8 Hz, 1H), 3.65 (t, *J* = 8.4 Hz, 2H), 3.04 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.2, 136.8, 129.9, 126.9, 121.0, 105.7, 47.0, 27.9; IR (KBr) $\tilde{\nu}$ 3439, 3056, 2926, 1612, 1500, 1321, 1265, 1161, 1072, 897, 741 cm^{-1}; HRMS (ESI-TOF) calcd for $C_8H_9N_2O_2$ $[M+H]^+$ 165.0659, found 165.0648.

Method extended to the synthesis of 1-(6-nitro-3,4-dihydroquinolin-1(2H)-yl)ethanone (5) from 1-(3,4-dihydroquinolin-1(2H)-yl)ethanone 4[4]

1-(6-Nitro-3,4-dihydroquinolin-1(2H)-yl)ethanone (5): R_f = 0.28 (25% ethyl acetate/hexane); yellow solid; yield A: 107 mg (85%), B: 92 mg (73%); mp: 160-163 °C; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.64 (d, *J* = 7.2 Hz, 1H), 3.80 (t, *J* = 6.4, 2H), 2.85 (t, *J* = 6. 4 Hz, 2H), 2.31 (s, 3H), 2.07 – 1.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 144.5, 143.9, 132.5, 124.8, 124.1, 121.8, 45.0, 27.5, 23.8, 23.5; IR (KBr) $\tilde{\nu}$ 2945, 2934, 2371, 1618, 1603, 1511, 1388, 1330, 1280, 1200, 1118, 1073, 1019, 994, 965, 919, 901, 751, 697 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{13}N_2O_3$ $[M+H]^+$ 221.0921, found 221.0917.

Synthesis of starting materials

Synthesis of C2-substituted indole derivative. The corresponding C_2 substituted indole (for **2f, 2g**) derivatives were prepared by literature reported procedures.[5] In a sealed tube under air, a mixture of $Pd(OAc)_2$ (24.0 mg, 0.01 mmol, 5 mol %), dppm (41.0 mg, 0.01 mmol, 5 mol%), AcOK (630 mg, 6.3 mmol, 3.0 equiv), iodobenzene (522 mg, 2.52 mmol, 1.2 equiv) and indole (250 mg, 2.1 mmol, 1.0 equiv) in 5 mL H_2O was vigorously stirred at 110°C. After 24 h the reaction mixture was cooled to room temperature and washed with 1N HCl and ethyl acetate. The organic layer was extracted with ethyl acetate and were dried over $NaSO_4$, and concentrated under reduced pressure. Column purification using 10% ethyl acetate-hexane yielded 2-Phenylindole as white solid.

2-(p-Tolyl)-1H-indole (1f'):[6] R_f = 0.21 (8% ethyl acetate/hexane); white solid; yield 302 mg (68%); mp: 178-180 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.44 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7. 4 Hz, 1H), 6.83 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 138.4, 137.6, 137.5, 130.1, 130.0, 129.3, 125.5, 122.0, 120.5, 119.9, 111.8, 98.7, 21.4; IR (KBr) $\tilde{\nu}$ 3433, 2366, 1627, 1398, 1276, 1122, 1069, 823, 791, 734, 511 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{14}N$ $[M+H]^+$ 208.1121, found 208.1096.

2-Phenyl-1H-indole (1g'):[5] R_f = 0.28 (10% ethyl acetate/hexane); white solid; yield 290 mg (70%); mp: 187-190 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.51 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 138.0, 137.6, 132.6, 129.3, 129.0, 127.8, 125.4, 122.0, 120.5, 119.8, 111.7, 99.1; IR (KBr) $\tilde{\nu}$ 3448, 2366, 1617, 1400, 1299, 1230, 1116, 1073, 907, 764, 743, 689 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{12}N$ $[M+H]^+$ 194.0964, found 194.0944.

Synthesis of C5-substituted indole derivative. The corresponding C_5 substituted indole (for **2m, 2n, 2o, 2p, 2q, 2r, 2s)** derivatives were prepared by literature reported procedure.[7] To an oven-dried sealed tube charged with a magnetic stirring bar and 5-bromoindole (200 mg, 0.84 mmol, 1 equiv), phenylboronic acid (205 mg, 1.68 mmol, 2 equiv), $Pd(PPh_3)_4$ (48.5 mg, 0.04 mmol, 0.05 equiv), K_2CO_3 (175 mg, 1.26 mmol, 1.5 equiv) in 10 ml DMF, Ethanol, H_2O (1.5: 1.5: 1 v/v) mixture were stirred at 120 ^{o}C for 24 h. The reaction mixture was cooled to room temperature and washed with brine solution. The organic layer was extracted with ethyl acetate and were dried over Na_2SO_4, and concentrated under reduced pressure. Column purification using 3% ethyl acetate-hexane yielded 5-phenylindole as white solid.

5-(m-Tolyl)-1H-indole (1m'):[8] R_f = 0.42 (4% ethyl acetate/hexane); off white solid; yield 200 mg (75%); mp: 110-113 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.13 (s, 1H), 7.80 (s, 1H), 7.48-7.43 (m, 3H), 7.39 – 7.36 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.48 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.3, 138.2, 135.9, 131.9, 129.1, 128.7, 127.9, 127.2, 126.4, 124.3, 120.8, 118.5, 112.2, 101.9, 21.6; IR (KBr) $\tilde{\nu}$ 2938, 2874, 1617, 1470, 1380, 1259, 1150, 1079, 1012, 978, 929, 772, 697 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{14}N$ $[M+H]^+$ 208.1121, found 208.1116.

5-Phenyl-1H-indole (1n'): R_f = 0.28 (5% ethyl acetate/hexane); white solid; yield 244 mg (82%); mp: 70-73 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.13 (s, 1H), 7.80 (s, 1H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.36 (m, 5H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.48 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.5, 136.1, 132.0, 129.5, 128.9, 127.3, 126.8, 126.7, 121.0, 118.8, 112.5, 102.3; IR (KBr) $\tilde{\nu}$ 2920, 2882, 1613, 1601, 1468, 1399, 1276, 1174, 1089, 1073, 1035, 994, 916, 880, 780, 756, 738, 701 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{12}N$ $[M+H]^+$ 194.0964, found 194.0960.

5-(4-(tert-Butyl)phenyl)-1H-indole (1o'): R_f = 0.50 (5% ethyl acetate/hexane); white solid; yield 240 mg (75%); mp: 102-104 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.11 (s, 1H), 7.78 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 6.8, 8.0 Hz, 3H), 7.36 (dd, *J* = 5.4, 2.2 Hz, 2H), 6.47 (s, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.9, 139.5, 135.8, 131.7, 128.7, 126.7, 126.4, 125.9, 120.7, 118.3, 112.2, 101.9, 34.6, 31.6; IR (KBr) $\tilde{\nu}$ 2951, 2368, 1602, 1450, 1390, 1364, 1217, 1175, 1111, 1026, 994, 889, 807, 721, 613 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{20}N$ $[M+H]^+$ 250.1590, found 250.1579.

5-(4-Ethylphenyl)-1H-indole (1p'): R_f = 0.28 (6% ethyl acetate/hexane); white solid; yield 221 mg (78%); mp: 100-103 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.10 (s, 1H), 7.77 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.36 (dd, *J* = 5.2, 1.6 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.47 (s, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.1, 139.8, 135.8, 131.8, 128.7, 128.6, 127.0, 126.4, 120.7, 118.3, 112.2, 101.9 , 28.2, 16.1; IR (KBr) $\tilde{\nu}$ 2960, 2930, 2374, 1603, 1399, 1220, 1174, 1113, 1070, 995, 917, 888, 805, 764, 721, 617 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{16}N$ $[M+H]^+$ 222.1277, found 222.1253.

5-(3-Chlorophenyl)-1H-indole (1q'): R_f = 0.42 (8% ethyl acetate/hexane); off white solid; yield 217 mg (62%); mp: 94-97 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.19 (s, 1H), 7.86 (s, 1H), 7.70 – 7.62 (m, 2H), 7.49 –7.32 (m, 5H), 6.49 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.6, 136.2, 134.0, 131.0, 130.2, 128.7, 126.8, 126.7, 126.4, 125.8, 120.7, 118.9, 112.4, 102.1; IR (KBr) $\tilde{\nu}$ 2935, 2369, 2345, 1598, 1458, 1399, 1342, 1251, 1178, 1112, 1074, 1032, 996, 917, 875, 775, 690 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{11}NCl$ $[M+H]^+$ 228.0575, found 228.0571.

5-(4-Fluorophenyl)-1H-indole (1r'):[9] R_f = 0.28 (7% ethyl acetate/hexane); white solid; yield 227 mg (70%); mp: 90-93 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.14 (s, 1H), 7.78 (s, 1H), 7.69 – 7.65 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.25 (t, *J* = 8.8 Hz, 2H), 6.48 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.7 (d, *J* = 241.2 Hz), 138.9 (d, *J* = 3.0 Hz), 135.9, 130.9, 129.0 (d, *J* = 7.9 Hz), 128.8, 126.7, 120.9, 118.7, 116.0 (d, *J* = 21.0 Hz), 112.4, 102.1; IR (KBr) $\tilde{\nu}$ 2933, 2912, 2368, 1612, 1399, 1216, 1115, 1072, 917, 894, 838, 807, 763, 713cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{11}FN$ $[M+H]^+$ 212.0870, found 212.0854.

5-(4-Chlorophenyl)-1H-indole (1s'): R_f = 0.42 (8% ethyl acetate/hexane); off white solid; yield 248 mg (71%); mp: 89-91 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.17 (s, 1H), 7.80 (d, *J* = 1.6 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.47 (t, *J* = 8.4, 2.0 Hz, 3H), 7.39 – 7.36 (m, 2H), 6.48 (d, *J* = 0.8 Hz, 1H); ^{13}C NMR (176 MHz, DMSO-d_6) δ 141.2, 136.1, 131.5, 130.5, 129.2, 128.8, 128.7, 126.7, 120.7, 118.7, 112.4, 102.1; IR (KBr) $\tilde{\nu}$ 3105, 3029, 2924, 2130, 1712, 1599, 1466, 1263, 1091, 1010, 890, 803, 730, 603 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{11}ClN$ $[M+H]^+$ 228.0575, found 228.0561.

Representative procedure for reduction of indole to indoline derivatives.[10] The corresponding indoline derivatives were prepared by literature reported procedure from substituted indoles. In a round bottom flask 2-phenylindole (100 mg, 0.52 mmol, 1 equiv) was dissolved in 6 mL glacial acetic acid and $NaCNBH_3$ (228 mg, 3.6 mmol, 6 equiv) was added in small portions for 30 minutes at 10 ^oC. Temperature was raised to 20 ^oC and reaction was monitored by TLC. After 3 h reaction was quenched with 1 M NaOH solution at 0 ^oC and organic layer was extracted with DCM. The combined organic layer was dried over $NaSO_4$ and concentrated under reduced pressure. The crude residue was directly used in next step without further column purification.

Representative procedure for synthesis of *N*-protected indoline derivatives.[11] In a round bottom flask indoline (250 mg, 2.1 mmol, 1 equiv) was dissolved in 10 ml DCM and Pyridine (216 mg, 2.7 mmol, 1.3 equiv) was added drop wise at 0 ^oC. Maintaining the temperature at 0 ^oC, acetyl chloride (198 mg, 2.25 mmol, 1.1 equiv) was added dropwise. Temperature was raised to RT and reaction was monitored by TLC. After 2 h reaction was quenched with saturated solution of ammonium chloride and organic layer was extracted with DCM. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was re-crystallised from ethanol to get pure *N*-Acylindoline.

1-(Indolin-1-yl)ethanone (1a): White solid; yield: 305 mg (90%); mp: 102-105 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.00 (t, J = 8.0 Hz, 1H), 4.02 (t, J = 8. 4 Hz, 2H), 3.18 (t, J = 8.4 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 142.9, 131.2, 127.6, 124.6, 123.6, 117.0, 48.8, 28.0, 24.3; IR (KBr) $\tilde{\nu}$ 2957, 2909, 2857, 1960, 1924, 1817, 1640, 1594, 1482, 1400, 1321, 1263, 1173, 1093, 1031, 1016, 988, 950, 922, 850,

769, 730, 652, 595 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{10}H_{12}NO$ $[M+H]^+$ 162.0913, found 162.0920.

1-(3-Methylindolin-1-yl)ethanone (1b):[12] White solid; yield: 276 mg (84%); mp: 72-76 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 4.20 (t, *J* = 10 Hz, 1H), 3.57 (dd, *J* = 10, 7.2 Hz, 1H), 3.50 (dd, *J* = 10, 7.2 Hz, 1H), 2.22 (s, 3H), 1.36 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 142.5, 136.4, 127.8, 123.8, 123. 5, 117.0, 57.1, 34.9, 24.3, 20.4; IR (KBr) $\tilde{\nu}$ 3121, 2928, 2832, 2369, 2345, 1602, 1399, 1217, 1114, 994, 918, 851, 762, 706 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{14}NO$ $[M+H]^+$ 176.1070, found 176.1107.

2-(1-Acetylindolin-3-yl)acetonitrile (1c): Pale yellow solid; yield: 263 mg (82%); mp: 82-85 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.29-7.25 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 4.27 (t, *J*= 10 Hz, 1H), 3.85-3.81 (m, 1H), 3.78 – 3.75 (m, 1H), 2.71 – 2.57 (m, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 142.6, 130.9, 129.4, 124.2, 123.8, 117.7, 117.3, 54.1, 37.0, 24.3, 23.4; IR (KBr) $\tilde{\nu}$ 3055, 2986, 2413, 2306, 2249,1664, 1599, 1483, 1353, 1265, 1130, 1023, 738, 703 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{13}N_2O$ $[M+H]^+$ 201.1022, found 201.1043.

1-(Methylsulfonyl)indoline (1d):[13] Light pink solid; yield: 340 mg (88%); mp: 70-72 ^oC; ^1H NMR (700 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.03 (t, *J* = 7.0 Hz, 1H), 3.97 (t, *J* = 8.4 Hz, 1H), 3.15 (t, *J* = 8.4 Hz, 1H), 2.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 131.3, 128.1 (2C), 125.5, 123.8, 113.8, 50.5, 34.4, 28.0; IR (KBr) $\tilde{\nu}$ 3010, 2914, 1600, 1477, 1417, 1325, 1293, 1200, 1102, 1034, 982, 758 cm^{-1}; HRMS (ESI-TOF) calcd for $C_9H_{12}NO_2S$ $[M+H]^+$ 198.0583, found 198.0578.

2,2-Dimethyl-1-(2-methylindolin-1-yl)propan-1-one (1e):[2] Colorless oil; yield: 296 mg (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 8.0, 6.8 Hz, 1H), 4.84 (p, *J* = 8.0 Hz, 2H), 3.30 (dd, *J* = 14.8, 6. 4 Hz, 1H), 2.58 (d, *J* = 14.8 Hz, 1H), 1.38 (s, 9H), 1.25 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 143.3, 130.8, 127.2, 124.9, 123.9, 119.7, 56.1, 40.7, 36.9, 28.6, 21.9; IR (neat) $\tilde{\nu}$ 2969, 2931, 2875, 2563, 1793, 1643, 1475, 1462, 1401, 1324, 1278, 1222, 1162, 1062, 991, 759 cm-1; HRMS (ESI-TOF) calcd for $C_{14}H_{20}NO$ $[M+H]^+$ 218.1539, found 218.1569.

2,2-Dimethyl-1-(2-(p-tolyl)indolin-1-yl)propan-1-one (1f): White solid; yield: 283 mg (80%); mp: 122-125 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.6 Hz , 1H), 7.08 – 6.98 (m, 6H), 5.80 (d, *J* = 8.4 Hz, 1H), 3.70 (dd, *J* = 15.0, 8.4 Hz, 1H), 2.89 (d, *J* = 15.0 Hz, 1H), 2.27 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 145.0, 140.8, 136.7, 129.3, 129.1, 127.4, 125.0, 124.8, 124.1, 118.7, 62.9, 40.6, 39.8, 28.6, 20.9; IR (KBr) $\tilde{\nu}$ 3055, 2928, 2307, 2115, 1641, 1550, 1419, 1265, 896, 740, 705 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{24}NO$ $[M+H]^+$ 249.1852, found 294.1844.

2,2-Dimethyl-1-(2-phenylindolin-1-yl)propan-1-one (1g): White solid; yield: 296 mg (82%); mp: 128-130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.22 (m, 3H), 7.19-7.15 (m, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 5.83 (d, *J* = 8. 4 Hz, 1H), 3.73 (dd, *J* = 15.2, 8.8 Hz, 1H), 2.92 (d, *J* = 15.2 Hz, 1H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 145.1, 143.9, 129.1, 128.8, 127.6, 127.2, 125.3, 125.0, 124.3, 118.8, 63.2, 40.7, 39.8, 28.7; IR (KBr) $\tilde{\nu}$ 3015, 2909, 2119, 1635, 1520, 1401, 1237, 870, 735, 698 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{19}H_{22}NO$ $[M+H]^+$ 280.1701, found 280.1692.

1-(Indolin-1-yl)-2,2-dimethylpropan-1-one (1h):[2] Pale yellow solid; yield: 292 mg (92%); mp: 63-66 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 4.22 (t, *J* = 8.4 Hz, 2H), 3.13 (t, *J* = 8.4 Hz, 2H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 144.8, 130.9, 127.4, 124.3, 123.7, 118.5, 49.6, 40.3, 29.4, 27.8; IR (KBr) $\tilde{\nu}$ 2984, 2961, 1644, 1598, 1474, 1401, 1358, 1223, 1198, 1100, 1073, 761, 707 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{13}H_{18}NO$ $[M+H]^+$ 204.1383, found 204.1388.

1-Tosylindoline (1i):[14] Off white solid; yield: 510 mg (89%); mp: 134-136 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.96 (t, *J* = 7.2 Hz, 1H), 3.90 (t, *J* = 8.4 Hz, 2H), 2.87 (t, *J* = 8.4 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 142.1, 134.1, 131.8, 129.7, 127.8, 127.4, 125.2, 123.8, 115.1, 50.0, 28.0, 21.6; IR (KBr) $\tilde{\nu}$ 3393, 3031, 2935, 2874, 2853, 1599, 1508, 1460, 1308, 1239, 1152, 1090, 975, 754, 711, 659 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{16}NO_2S$ $[M+H]^+$ 274.0896, found 274.0902.

Indolin-1-yl(phenyl)methanone (1j):[15] White solid; yield: 480 mg (85%); mp: 114-117 ^{o}C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.0 Hz, 2H), 7.49 – 7.43 (m, 3H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.02 (s, 1H), 4.07 (s, 2H), 3.12 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 142.7, 137.0, 132.4, 130.3, 128.6, 127.1, 124.9, 123.9, 117.4, 50.6, 28.2; IR (KBr) $\tilde{\nu}$ 2945, 2931, 2864, 2370, 1637, 1594, 1482, 1296, 1113, 1073, 996, 862, 763cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{14}NO$ $[M+H]^+$ 224.1070, found 224.1092.

1-(5-Bromoindolin-1-yl)ethanone (1l):[16] White solid; yield: 275 mg (91%); mp: 120-123 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 9.2 Hz, 1H), 7.27-7.24 (m, 2H), 4.04 (t, *J* = 8.4 Hz, 2H), 3.16 (t, *J* = 8.4 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 142.1, 133.5, 130.5,

127.7, 118.3, 116.0, 48.9, 27.8, 24.2; IR (KBr) $\tilde{\nu}$ 2971, 2926, 1654, 1604, 1560, 1475, 1329, 1249, 1169, 1066, 994, 814, 706 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{10}H_{11}BrNO$ $[M+H]^+$ 240.0019, found 240.0044.

1-(5-(m-Tolyl)indolin-1-yl)ethanone (1m): Off white solid; yield: 230 mg (76%); mp: 132-135 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8. 4 Hz, 1H), 7.43 – 7.28 (m, 5H), 7.13 (d, *J* = 7.6 Hz, 1H), 4.10 (t, *J* = 8.8 Hz, 2H), 3.25 (t, *J* = 8.8 Hz, 2H), 2.41 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 142.3, 141.0, 138.4, 137.0, 131.8, 128.8, 127.8 (2 C), 126.7, 124.0, 123.3, 117.1, 49.1, 28.1, 24.3, 21.6; IR (KBr) $\tilde{\nu}$ 2945, 2908, 2136, 1603, 1528, 1398, 1216, 1114, 1072, 994, 918, 699, 618 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{17}NONa$ $[M+Na]^+$ 274.1202, found 274.1210.

1-(5-Phenylindolin-1-yl)ethanone (1n): White solid; yield: 221 mg (72%); mp: 183-185 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.44 – 7.39 (m, 4H), 7.31 (t, *J* = 7.2 Hz, 1H), 4.10 (t, *J* = 8.4 Hz, 2H), 3.26 (t, *J* = 8.4 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 142.5, 141.0, 136.9, 131.9, 128.9, 127.0, 126.9, 126.7, 123.3, 117.2, 49.2, 28.2, 24.3; IR (KBr) $\tilde{\nu}$ 2953, 2907, 2852, 1620, 1600, 1533, 1431, 1110, 1067, 1008, 964, 843, 825, cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1226, found 238.1229.

1-(5-(4-(tert-Butyl)phenyl)indolin-1-yl)ethanone (1o): White solid; yield: 215 mg (73%); mp: 144-147 ^oC; ^1H NMR (400 MHz, CDCl3) δ 8.24 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.45 – 7.40 (m, 4H), 4.09 (t, *J* = 8.8 Hz, 2H), 3.24 (t, *J* = 8.8 Hz, 2H), 2.24 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 150.0, 142.2, 138.1, 136.7, 131.8, 126.6, 126.5, 125.8, 123.1, 117.1, 49.1, 34.6, 31.5, 28.1, 24.3; IR (KBr) $\tilde{\nu}$ 2968, 2922, 2217,1619, 1608, 1508, 1369, 1114,

1035, 994, 897, 707 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{24}NO$ $[M+H]^+$ 294.1852, found 294.1854.

1-(5-(4-Ethylphenyl)indolin-1-yl)ethanone (1p): White solid; yield: 228 mg (76%); mp: 144-147 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8. 4 Hz, 1H), 7.48 (d, *J* = 8 Hz, 2H), 7.41 (t, *J* = 8.4, 5.6 Hz, 2H), 7.25 (d, *J* = 6.8 Hz, 2H), 4.09 (t, *J* = 8.4 Hz, 2H), 3.25 (t, *J* = 8.4 Hz, 2H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.24 (s, 3H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 143.2, 142.2, 138.4, 136.9, 131.8, 128.4, 126.9, 126.4, 123.1, 117.2, 49.1, 28.6, 28.2, 24.3, 15.7; IR (KBr) $\tilde{\nu}$ 2959, 2367, 1663, 1604, 1488, 1395, 1299, 1116, 1068, 993, 822, 700 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{18}H_{20}NO$ $[M+H]^+$ 266.1539, found 266.1540.

1-(5-(3-Chlorophenyl)indolin-1-yl)ethanone (1q): White solid; yield: 202 mg (68%); mp: 136-138 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 2.0 Hz, 1H), 7.44 – 7.31 (m, 5H), 4.11 (t, *J* = 8.4 Hz, 2H), 3.26 (t, *J* = 8.4 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 142.0, 141.9, 134.4, 133.8, 131.1, 129.1, 126.1, 126.0, 125.7, 124.1, 122.3 , 116.3, 48.2, 27.1, 23.3; IR (KBr) $\tilde{\nu}$ 2959, 2927, 2366, 1655, 1606, 1468, 1394, 1355, 1111, 1073, 995, 841, 779, 688 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{15}ClNO$ $[M+H]^+$ 272.0837, found 272.0845.

1-(5-(4-Fluorophenyl)indolin-1-yl)ethanone (1r): White solid; yield: 211 mg (70%); mp: 156-158 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.38 – 7.35 (m, 2H), 7.10 (t, *J* = 8.8 Hz, 2H), 4.10 (t, *J* = 8.8 Hz, 2H), 3.25 (t, *J* = 8.8 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 163.6, 161.2, 142.4, 136.6 (d, $^1J_{F-C}$ = 124.6 Hz), 132.0, 128.5 (d, $^1J_{F-C}$ = 7.9 Hz), 126.6, 123.2, 117.3, 115.7 (d, $^1J_{F-C}$ = 21.4 Hz), 49.2, 28.2, 24.3; IR

(KBr) $\tilde{\nu}$ 2962, 2902, 2363, 1653, 1508, 1488, 1392, 1235, 1159, 1035, 828, 627 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{15}FNO$ $[M+H]^+$ 256.1132, found 256.1138.

1-(5-(4-Chlorophenyl)indolin-1-yl)ethanone (1s): White solid; yield: 193 mg (65%); mp: 169-172 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.49 – 7.46 (m, 2H), 7.38 (dd, *J* = 7.6, 5.8 Hz, 4H), 4.10 (t, *J* = 8.4 Hz, 2H), 3.25 (t, *J* = 8.4 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 142.7, 139.5, 135.6, 133.1, 132.1, 129.0, 128.2, 126.6, 123.1, 117.3, 49.1, 28.1, 24.3; IR (KBr) $\tilde{\nu}$ 2972, 2922, 1635, 1600, 1443, 1352, 1108, 998, 901, 863, 645 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{15}NOCl$ $[M+H]^+$ 272.0837, found 272.0834.

1-(3,4-Dihydroquinolin-1(2H)-yl)ethanone (4): Colorless oily liquid; yield: 303 mg (92%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.08 (m, 4H), 3.78 (t, *J* = 6.4, 2.4 Hz, 2H), 2.71 (t, *J* = 6.4, 2.4 Hz, 2H), 2.22 (s, 3H), 1.95 (p, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 139.4, 128.5 (2 C), 126.1, 125.2, 124.7, 42.9, 26.9, 24.1, 23.2; IR (neat) $\tilde{\nu}$ 3028, 2948, 2081, 1634, 1645, 1580, 1488, 1385, 1294, 1176, 1094, 962, 760 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{14}NO$ $[M+H]^+$ 176.1070, found 176.1088.

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^{1}H and ^{13}C NMR spectra of synthesized compound

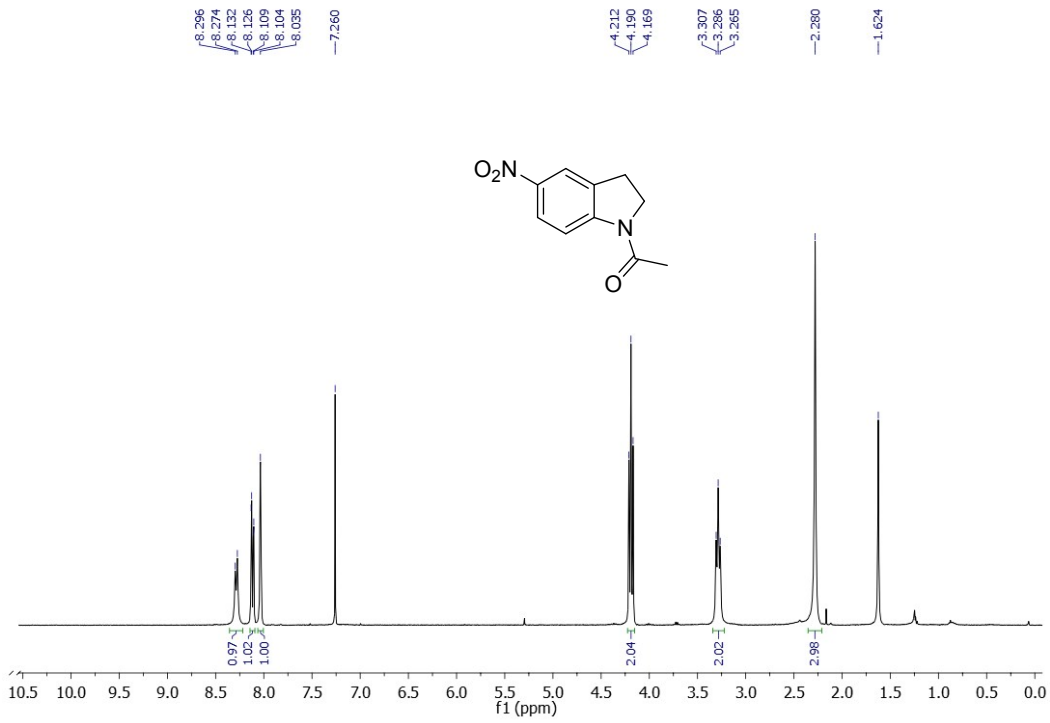

Fig. S3. ^{1}H NMR spectrum of 1-(5-Nitroindolin-1-yl)ethanone **(2a).**

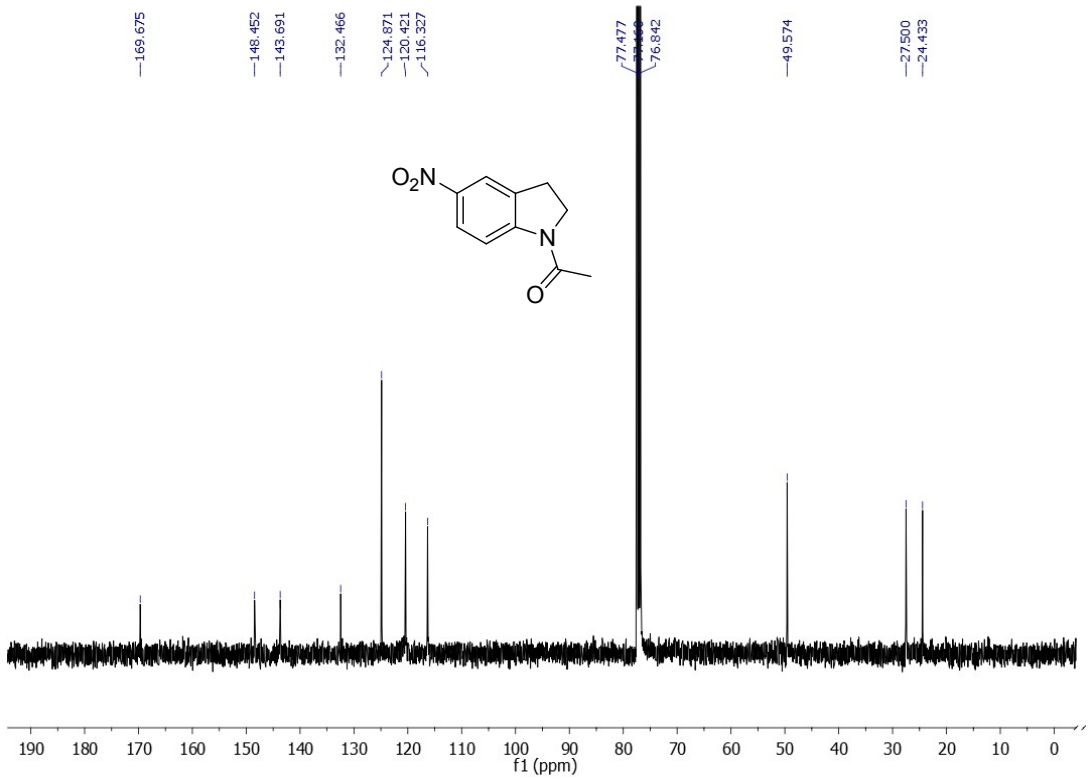

Fig. S4. ^{13}C NMR spectrum of 1-(5-Nitroindolin-1-yl)ethanone **(2a).**

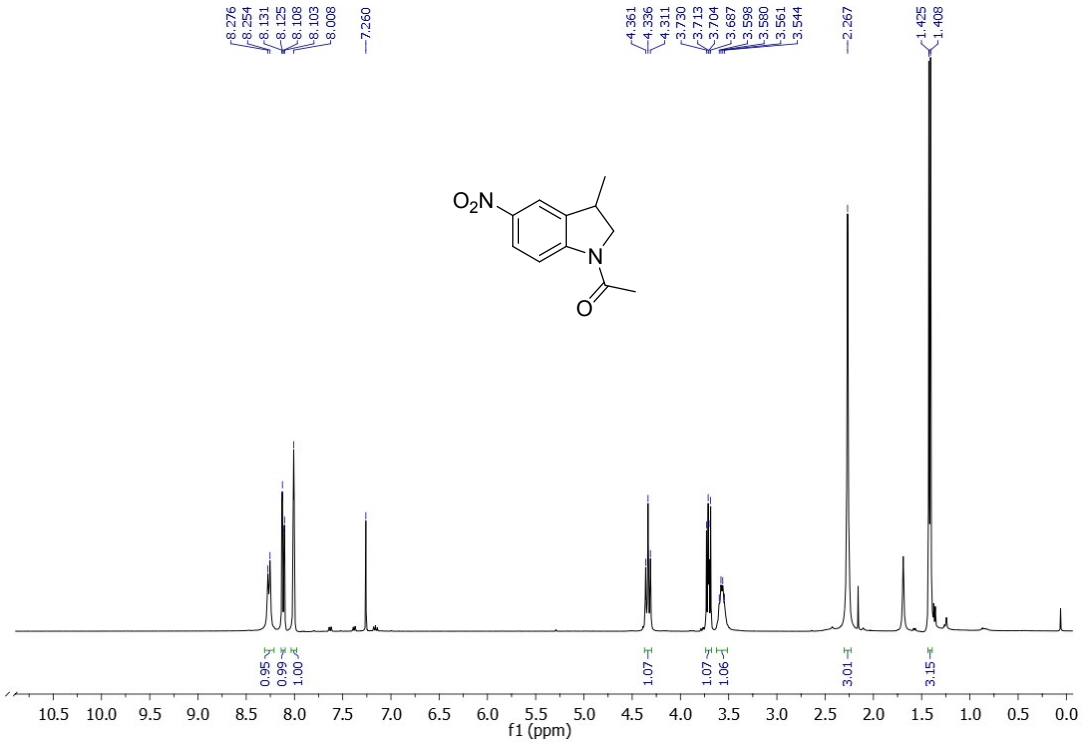

Fig. S5. ^{1}H NMR spectrum of 1-(3-Methyl-5-nitroindolin-1-yl)ethanone **(2b).**

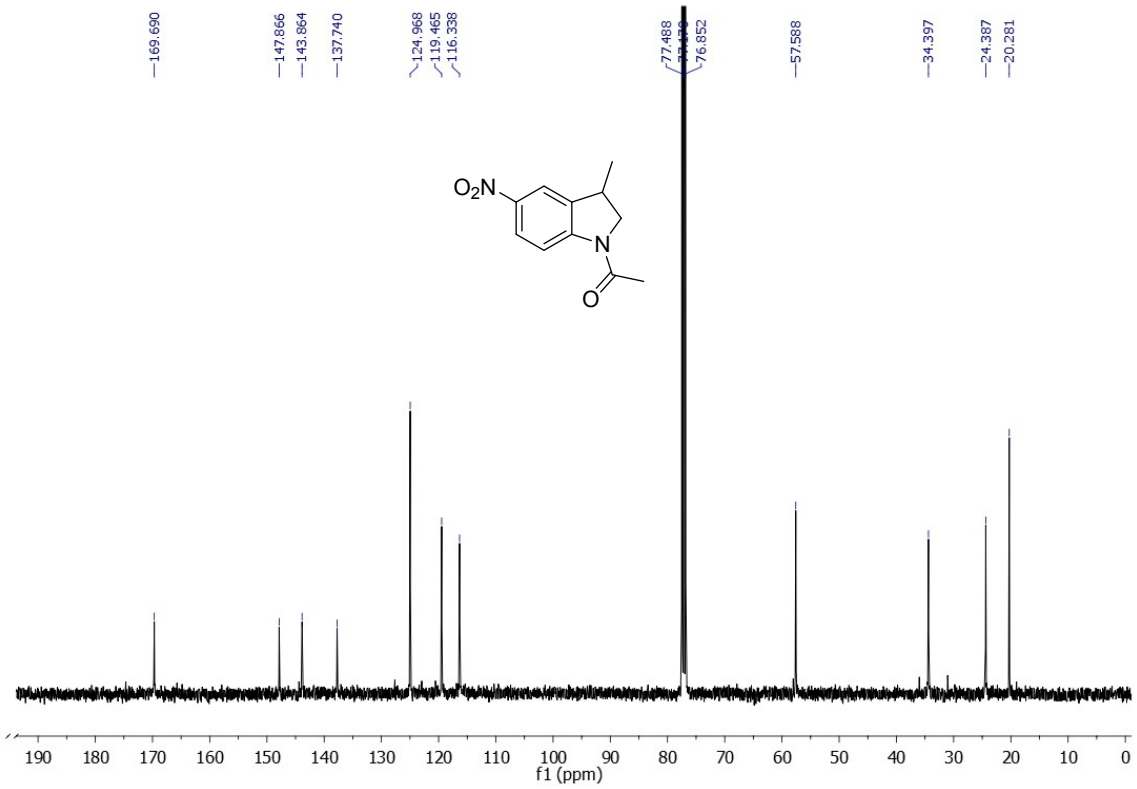

Fig. S6. ^{13}C NMR spectrum of 1-(3-Methyl-5-nitroindolin-1-yl)ethanone **(2b).**

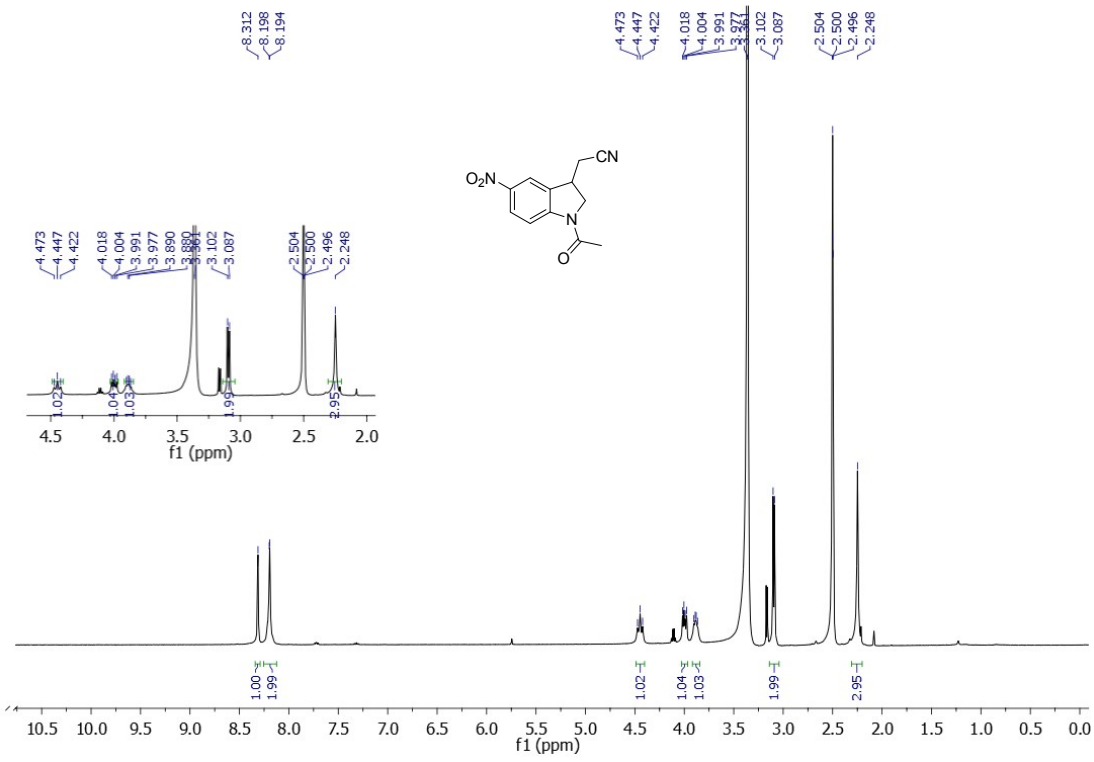

Fig. S7. ^{1}H NMR spectrum of 2-(1-Acetyl-5-nitroindolin-3-yl)acetonitrile **(2c).**

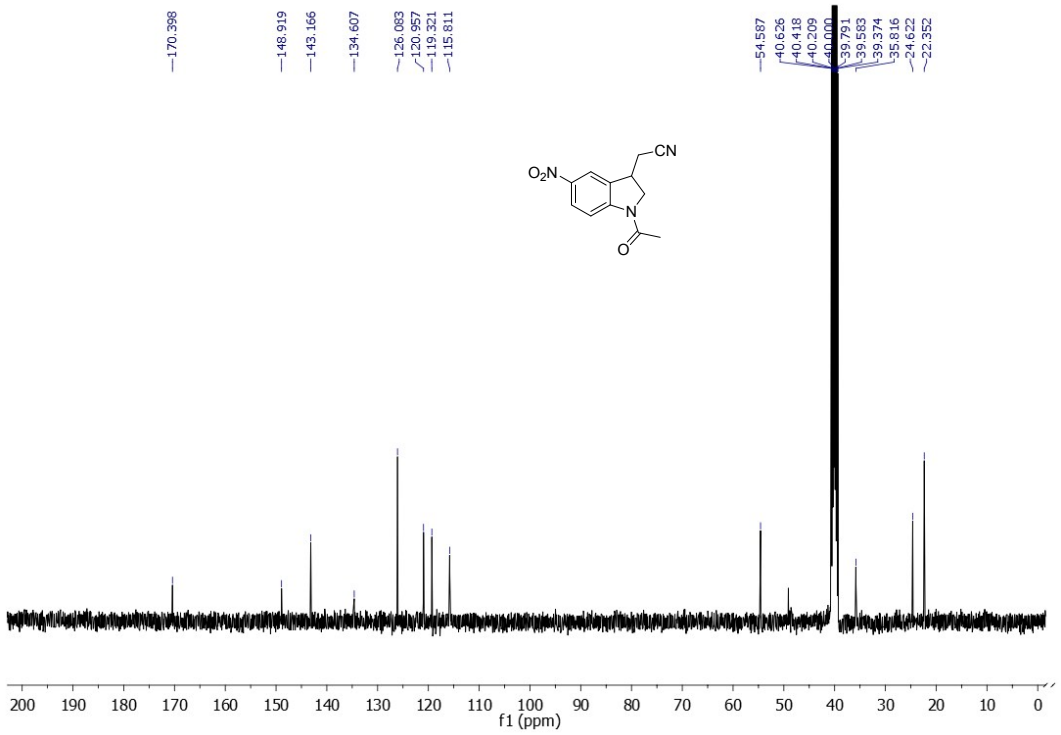

Fig. S8. ^{13}C NMR spectrum of 2-(1-Acetyl-5-nitroindolin-3-yl)acetonitrile **(2c).**

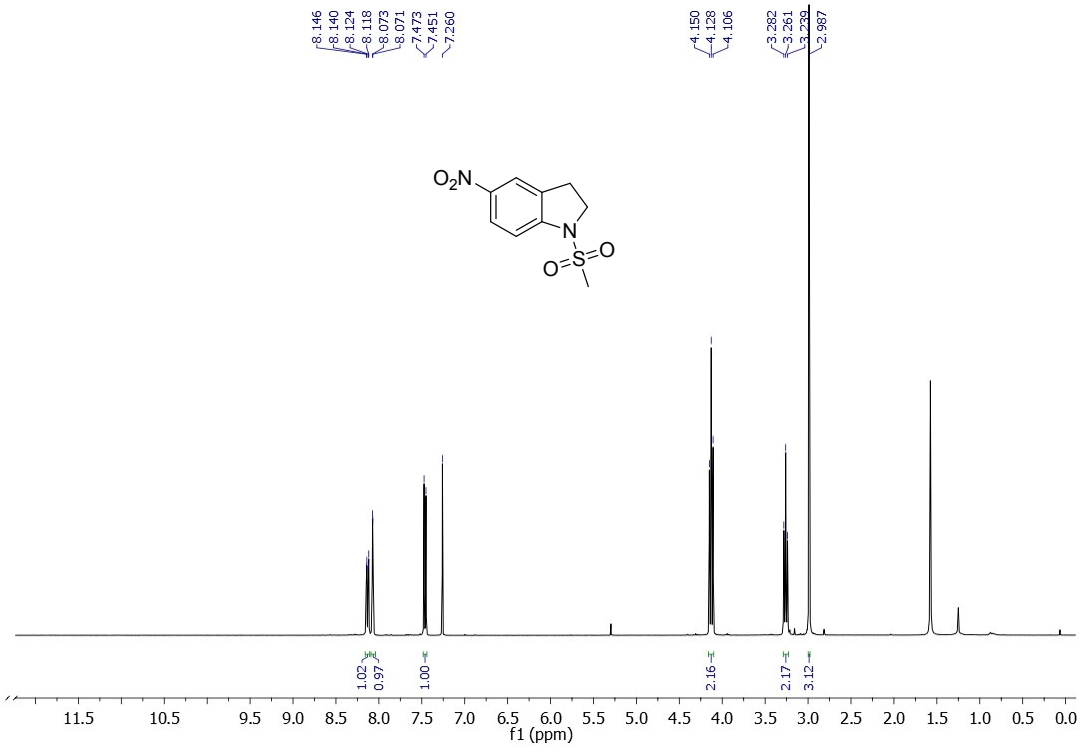

Fig. S9. ^{1}H NMR spectrum of 1-(Methylsulfonyl)-5-nitroindoline **(2d).**

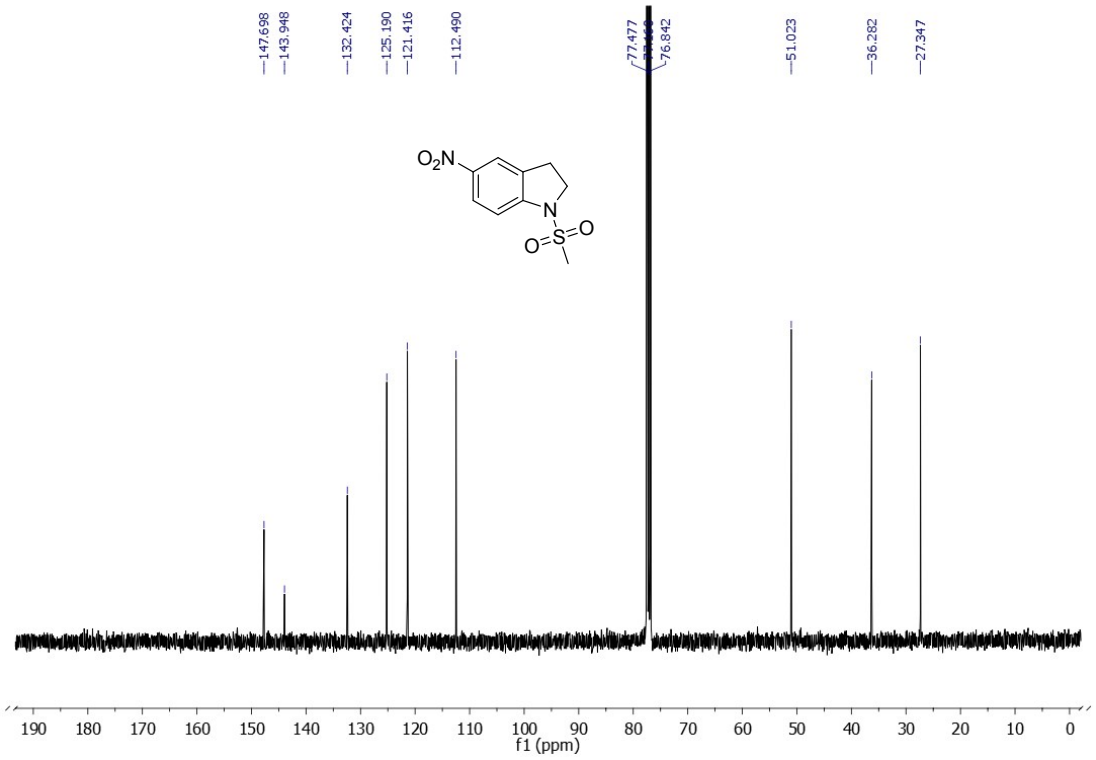

Fig. S10. ^{13}C NMR spectrum of 1-(Methylsulfonyl)-5-nitroindoline **(2d).**

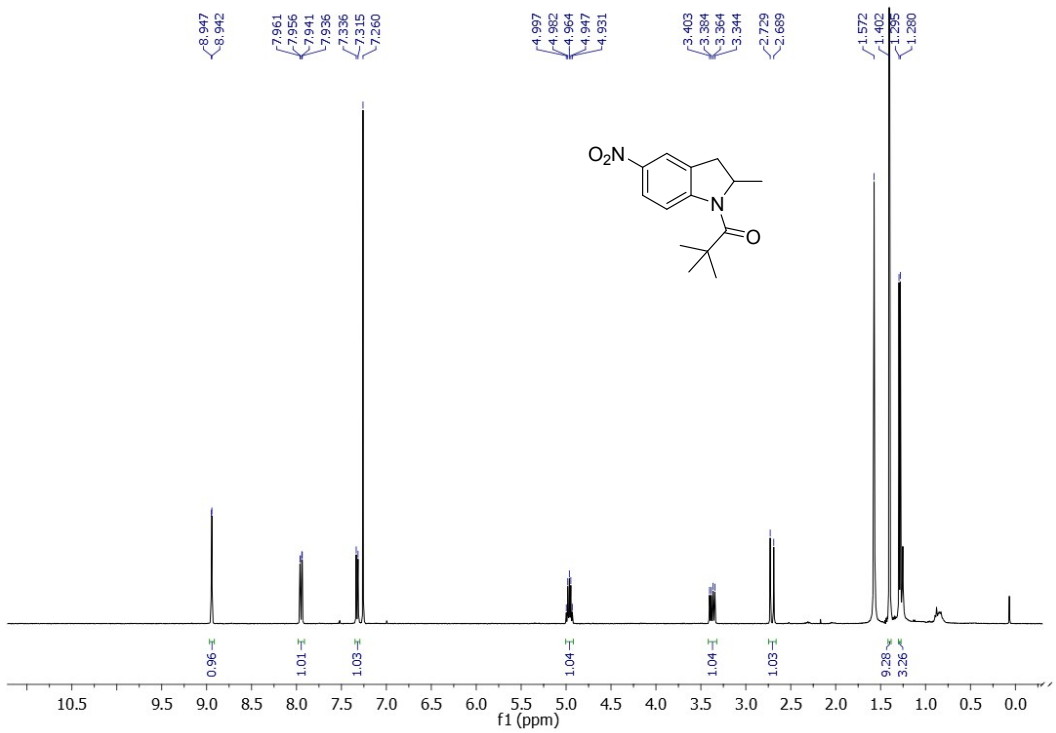

Fig. S11. ^{1}H NMR spectrum of 2,2-Dimethyl-1-(2-methyl-5-nitroindolin-1-yl)propan-1-one **(2e).**

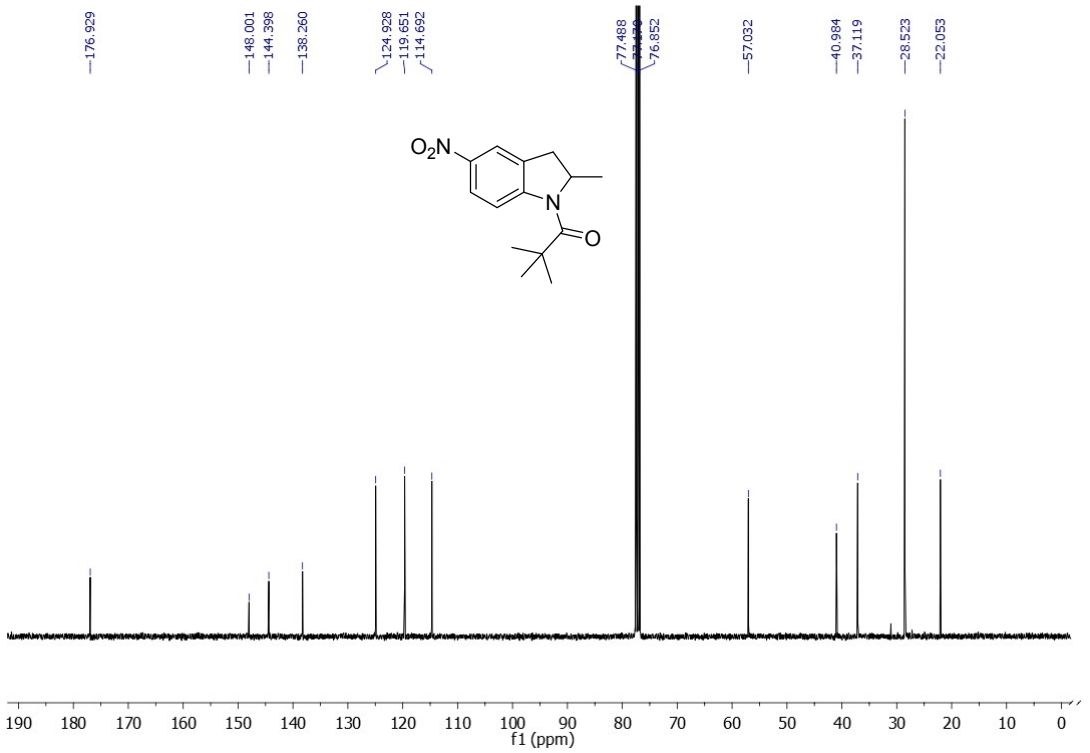

Fig. S12. ^{13}C NMR spectrum of 2,2-Dimethyl-1-(2-methyl-5-nitroindolin-1-yl)propan-1-one **(2e).**

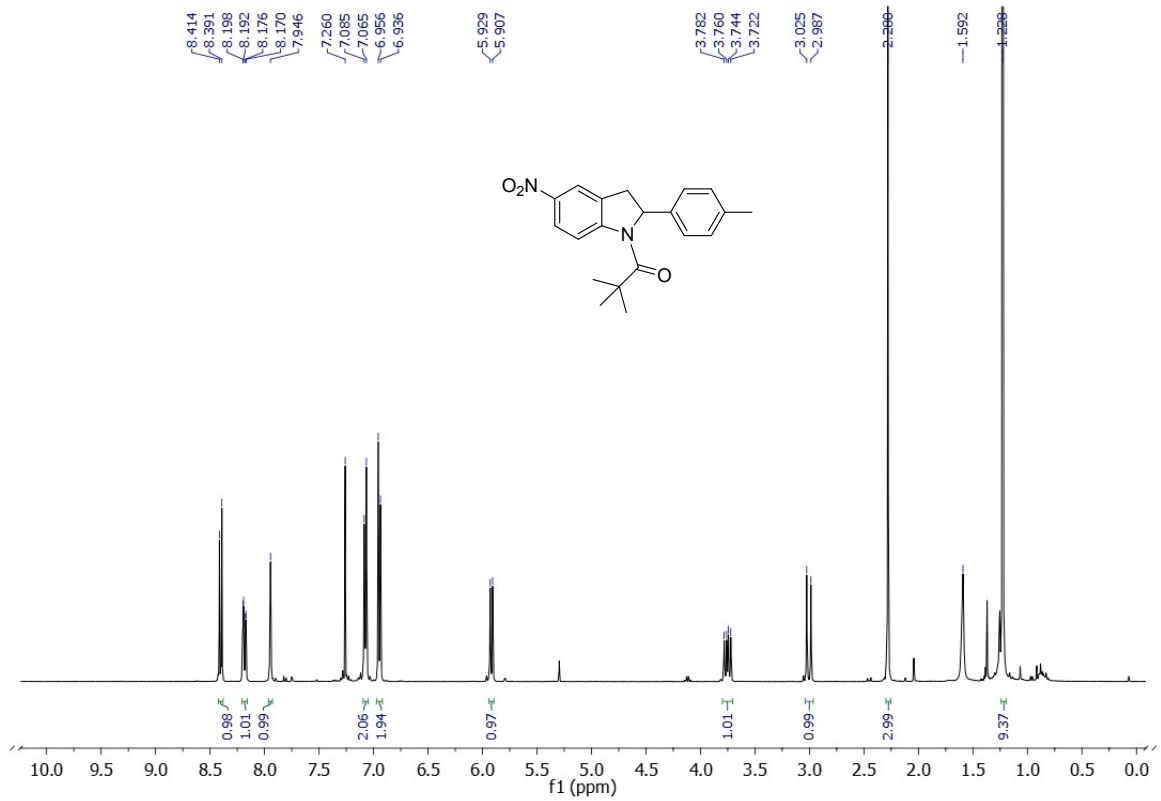

Fig. S13. ^{1}H NMR spectrum of 2,2-Dimethyl-1-(5-nitro-2-(p-tolyl)indolin-1-yl)propan-1-one **(2f).**

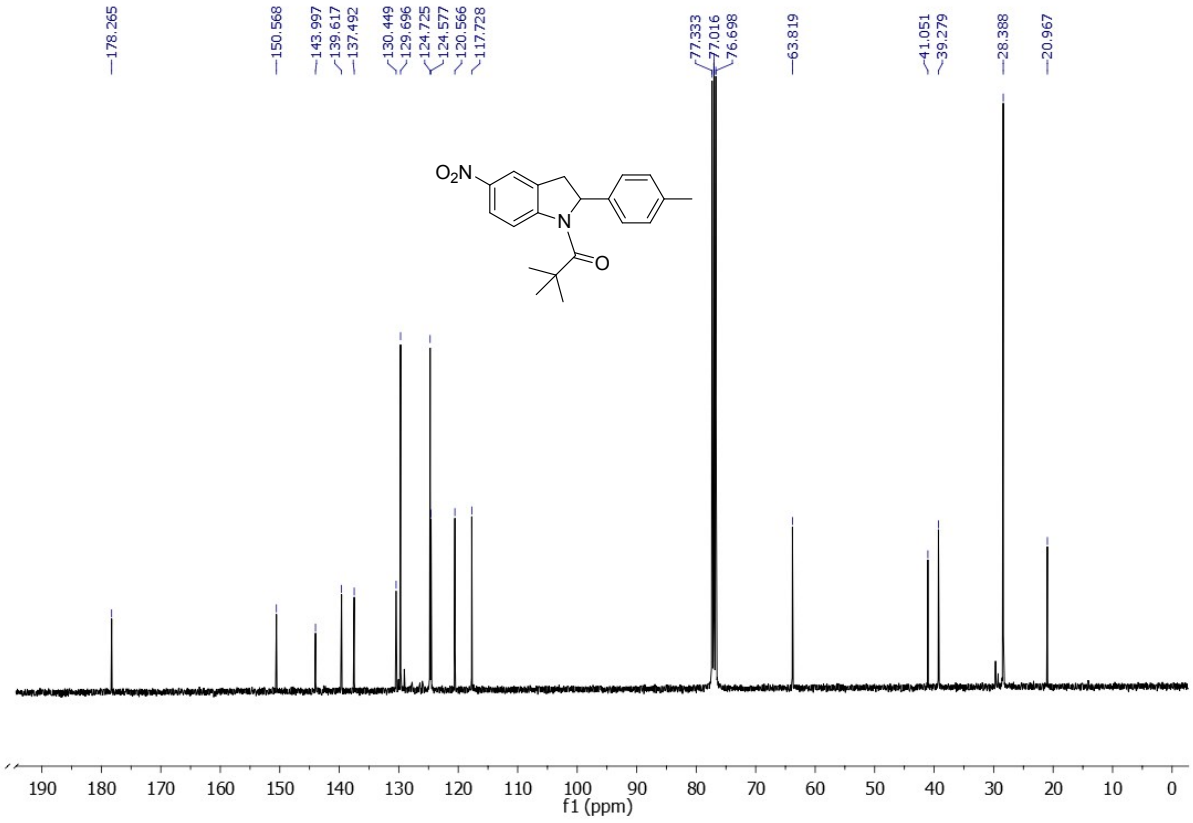

Fig. S14. ^{13}C NMR spectrum of 2,2-Dimethyl-1-(5-nitro-2-(p-tolyl)indolin-1-yl)propan-1-one **(2f).**

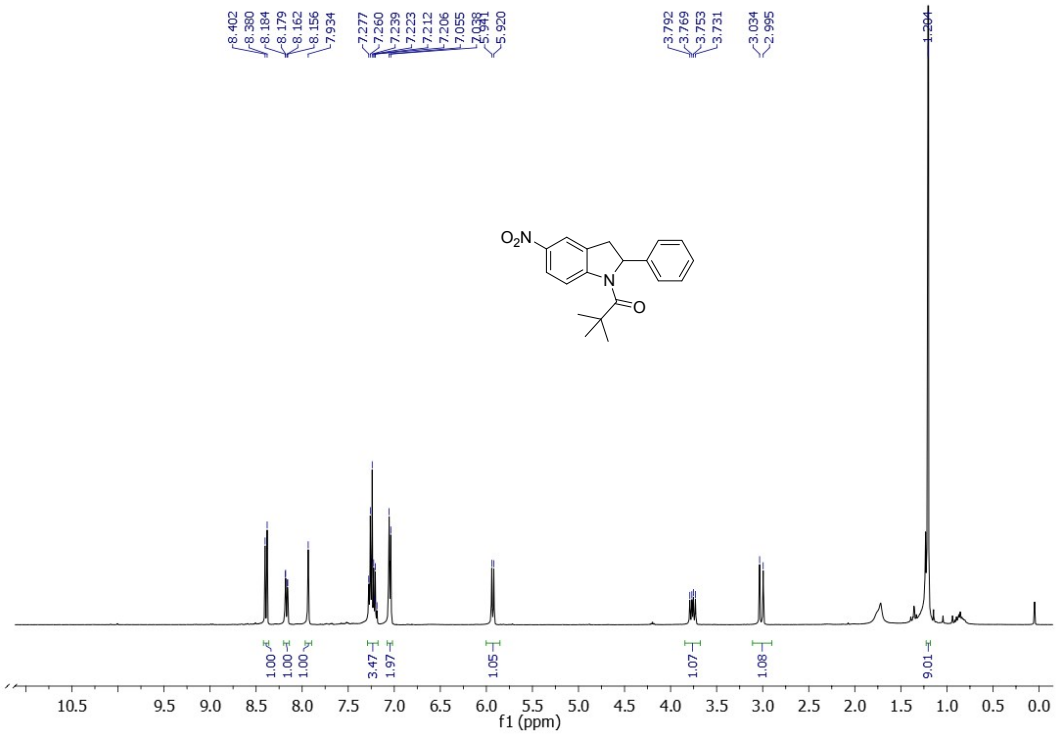

Fig. S15. [1]H NMR spectrum of 2,2-Dimethyl-1-(5-nitro-2-phenylindolin-1-yl)propan-1-one **(2g).**

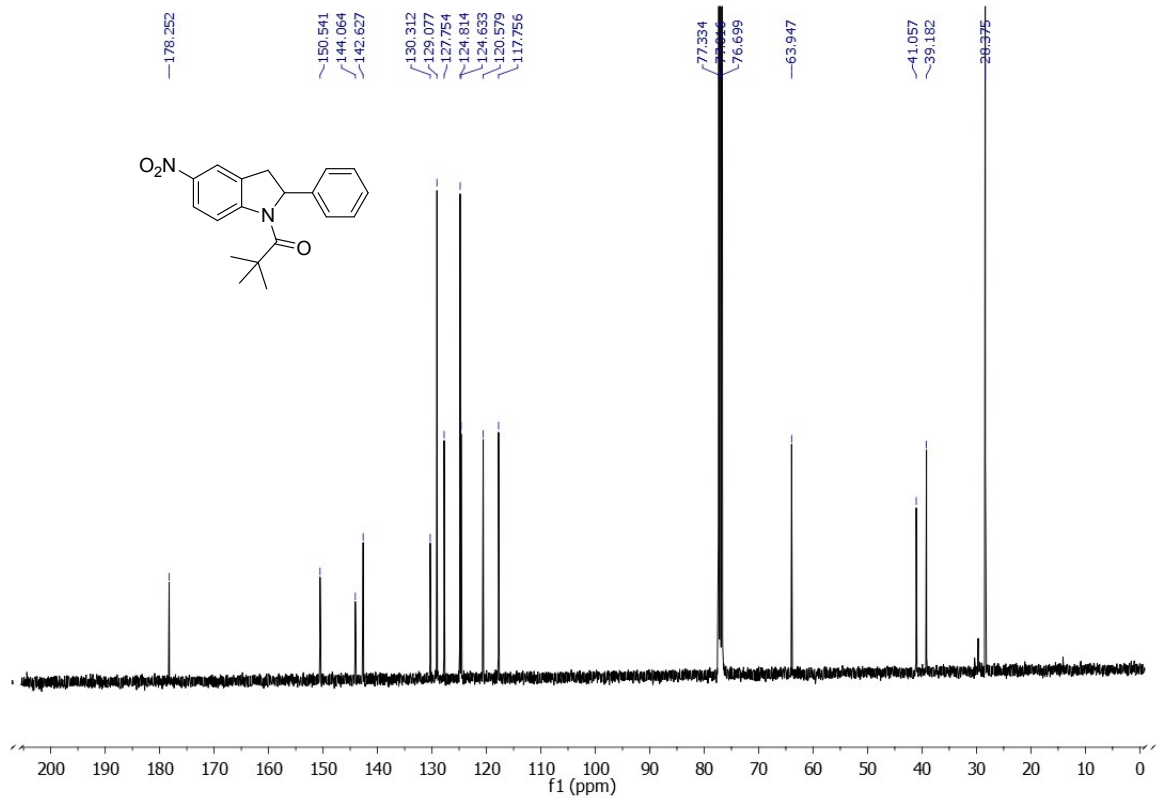

Fig. S16. ^{13}C NMR spectrum of 2,2-Dimethyl-1-(5-nitro-2-phenylindolin-1-yl)propan-1-one **(2g).**

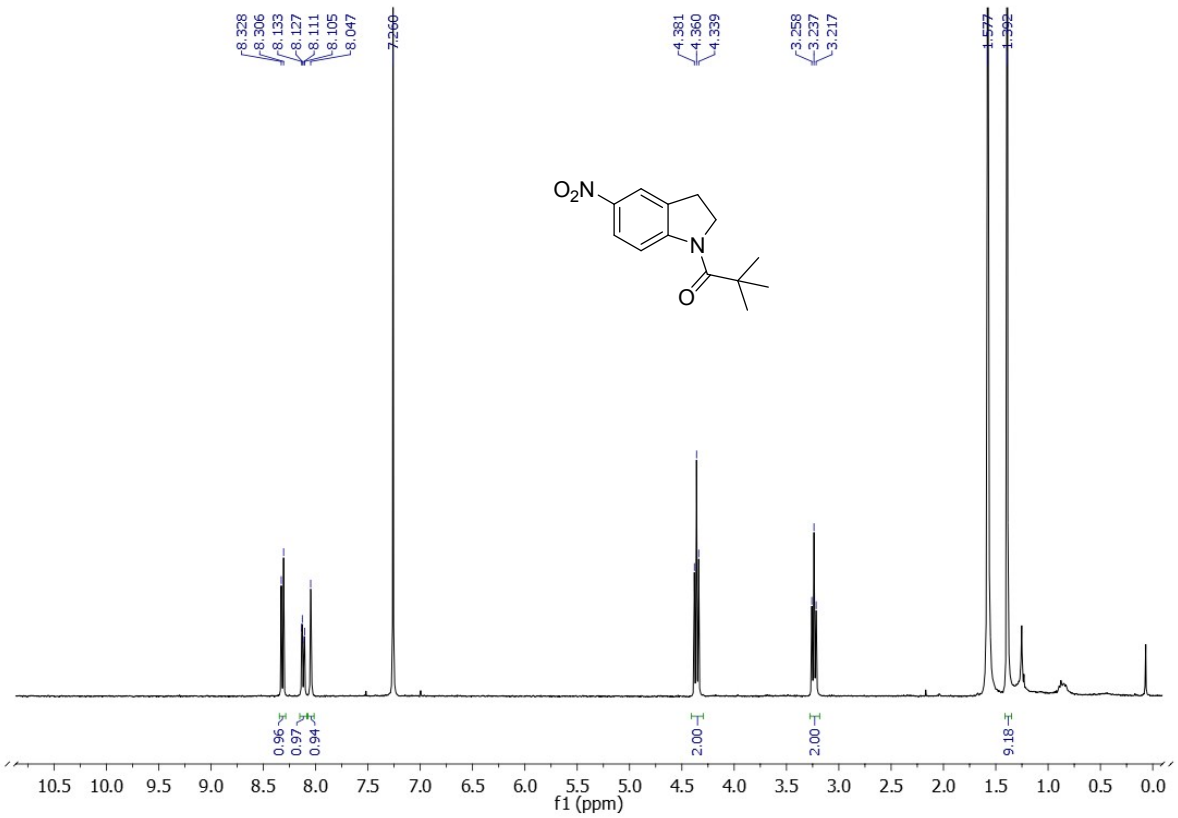

Fig. S17. ^{1}H NMR spectrum of 2,2-Dimethyl-1-(5-nitroindolin-1-yl)propan-1-one **(2h).**

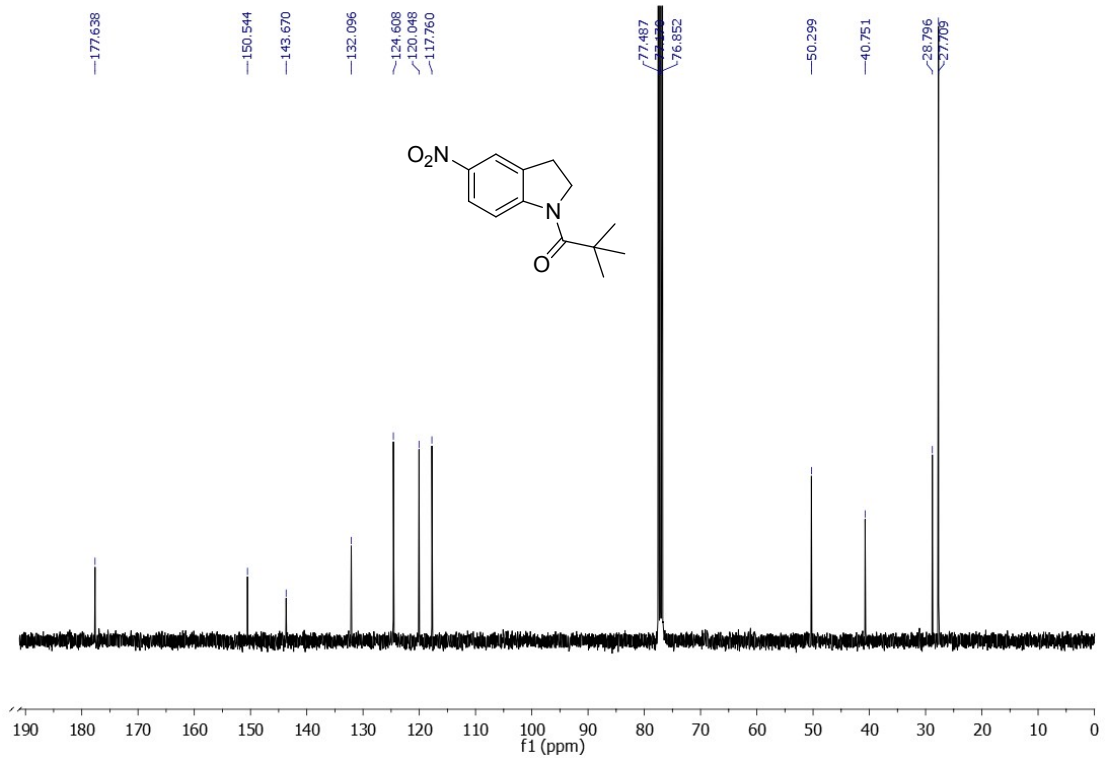

Fig. S18. ^{13}C NMR spectrum of 2,2-Dimethyl-1-(5-nitroindolin-1-yl)propan-1-one **(2h).**

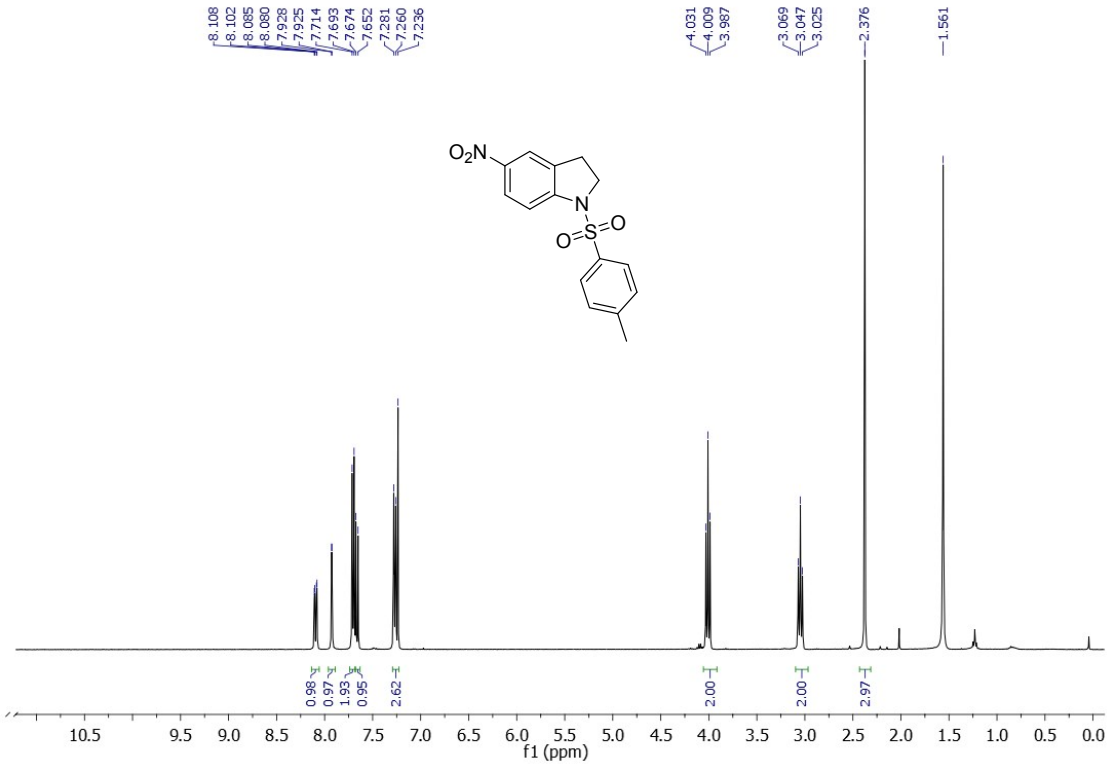

Fig. S19. ^{1}H NMR spectrum of 5-Nitro-1-tosylindoline **(2i).**

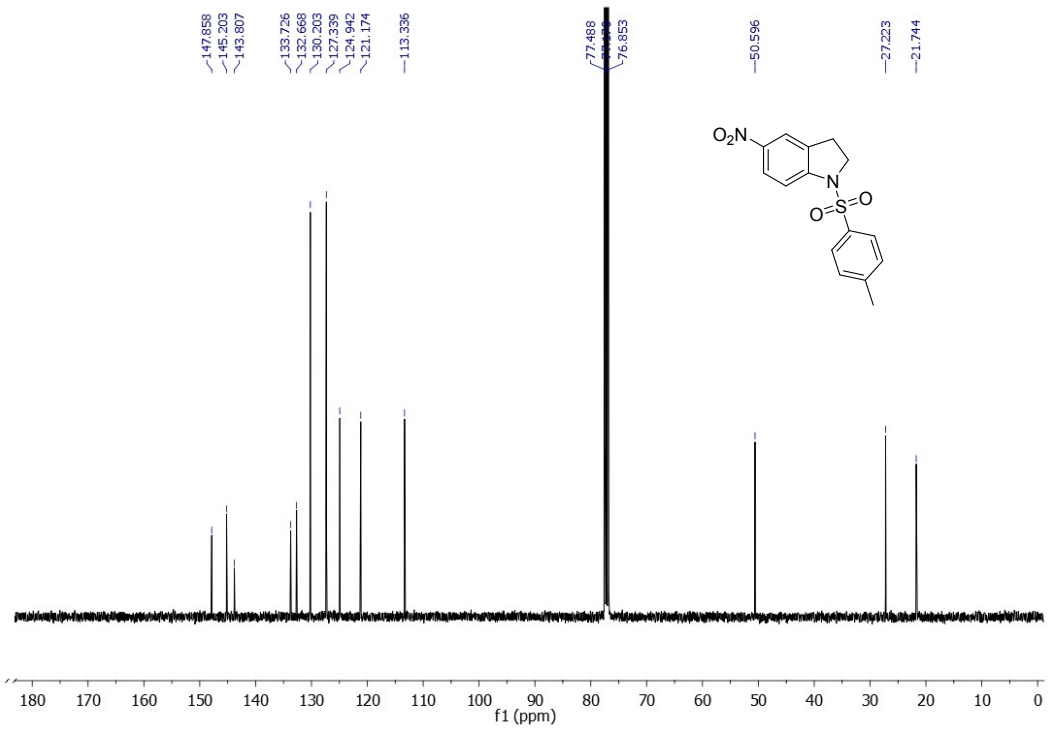

Fig. S20. ^{13}C NMR spectrum of 5-Nitro-1-tosylindoline **(2i).**

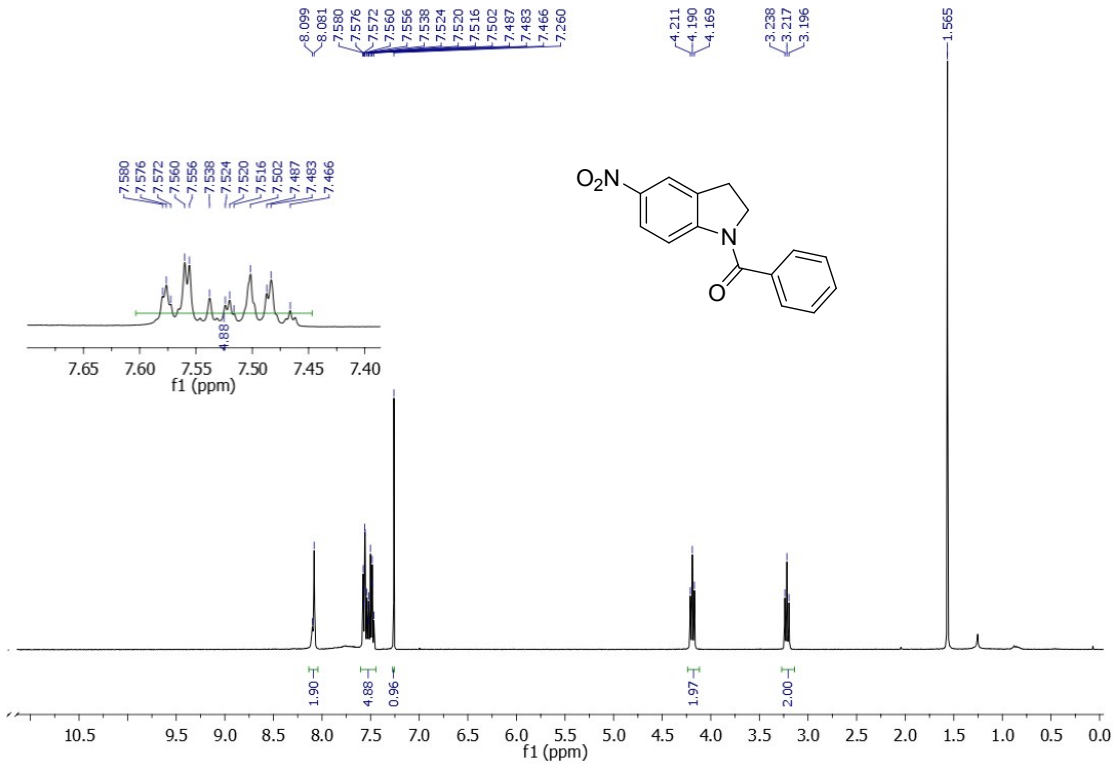

Fig. S21. ^{1}H NMR spectrum of (5-Nitroindolin-1-yl)(phenyl)methanone **(2j).**

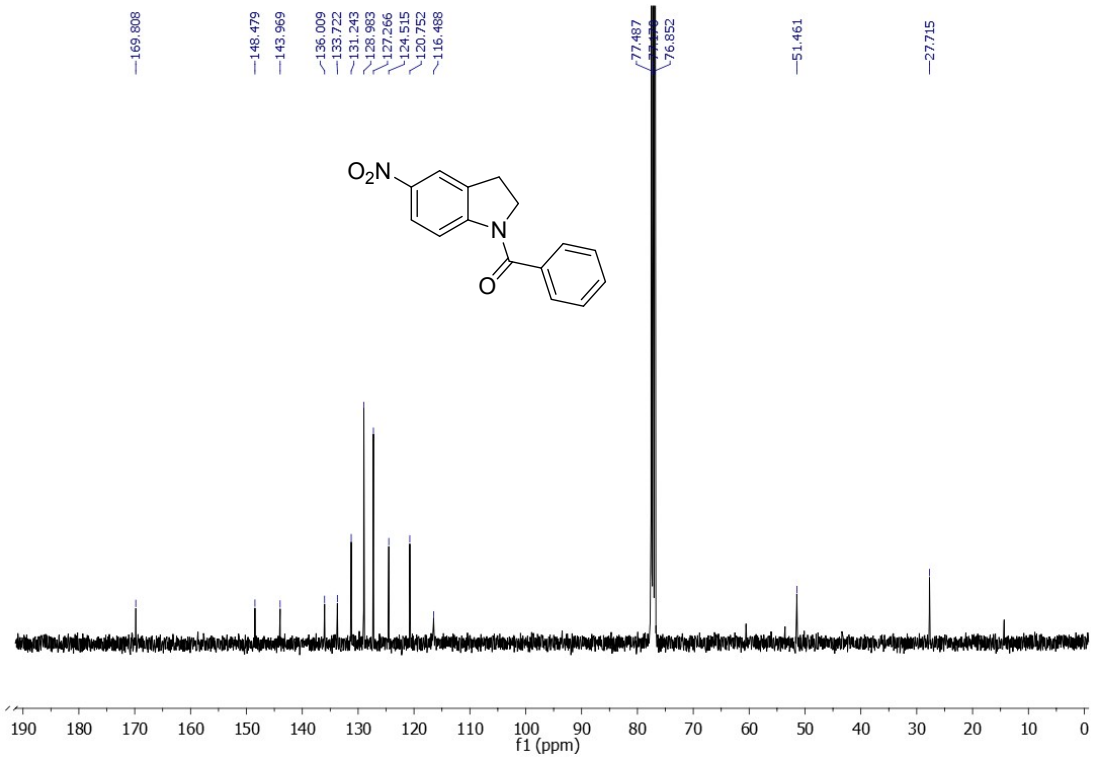

Fig. S22. ^{13}C NMR spectrum of (5-Nitroindolin-1-yl)(phenyl)methanone **(2j).**

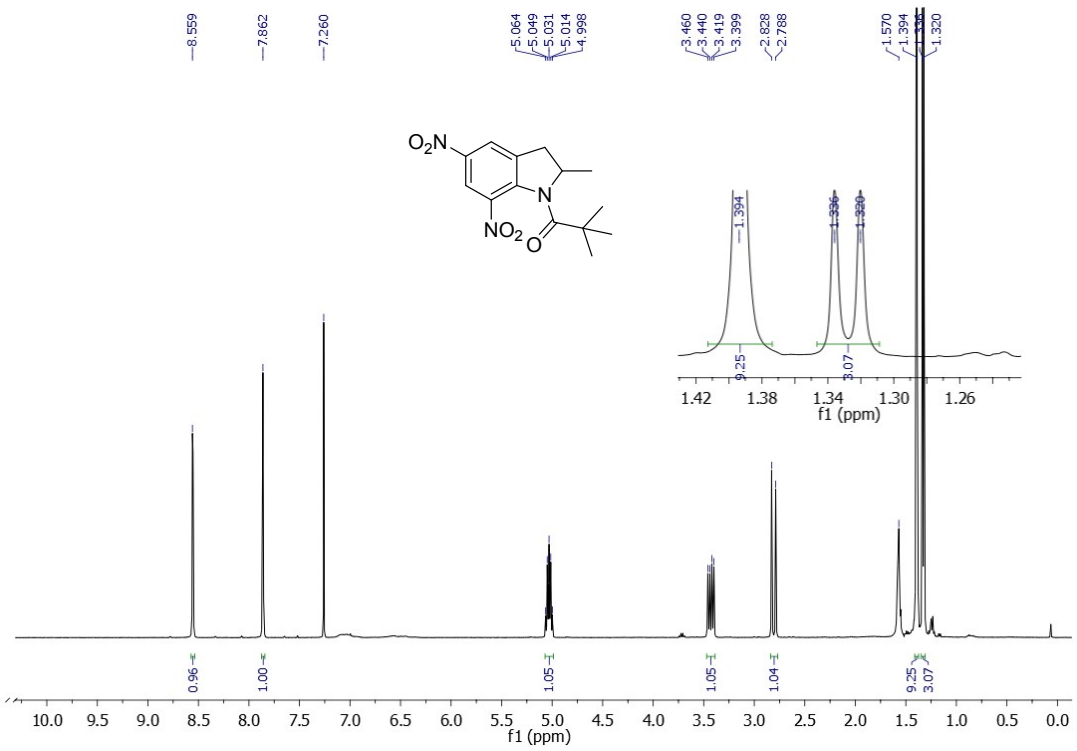

Fig. S23. ^{1}H NMR spectrum of 2,2-Dimethyl-1-(2-methyl-5,7-dinitroindolin-1-yl)propan-1-one (**2k**).

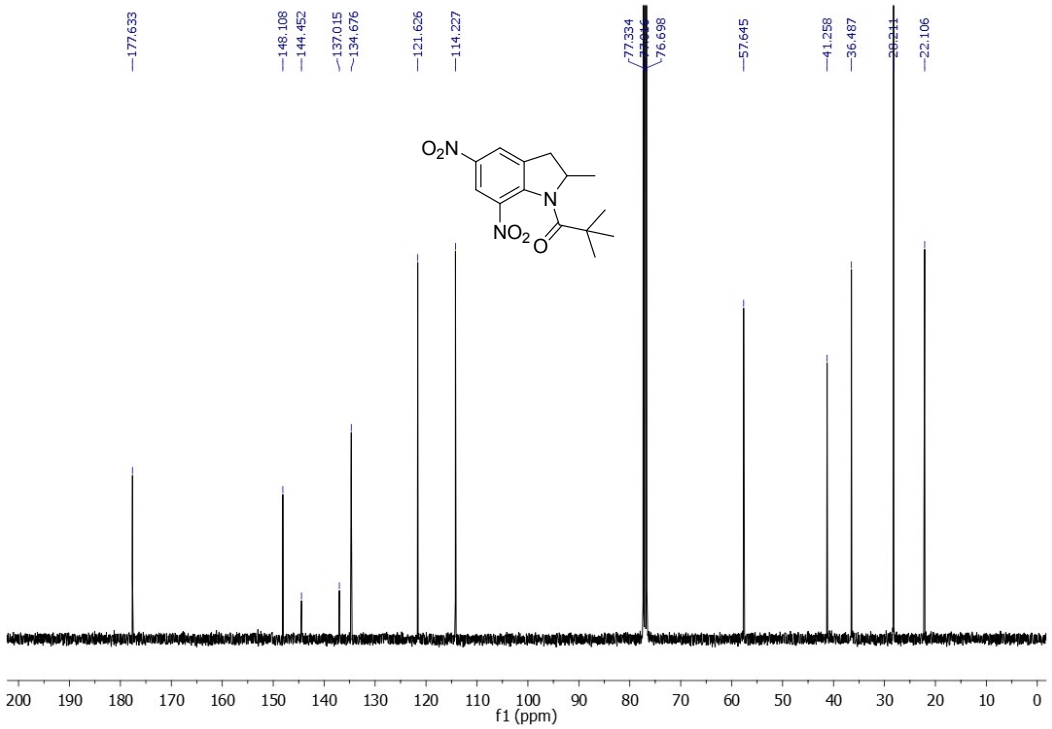

Fig. S24. ^{13}C NMR spectrum of 2,2-Dimethyl-1-(2-methyl-5,7-dinitroindolin-1-yl)propan-1-one **(2k).**

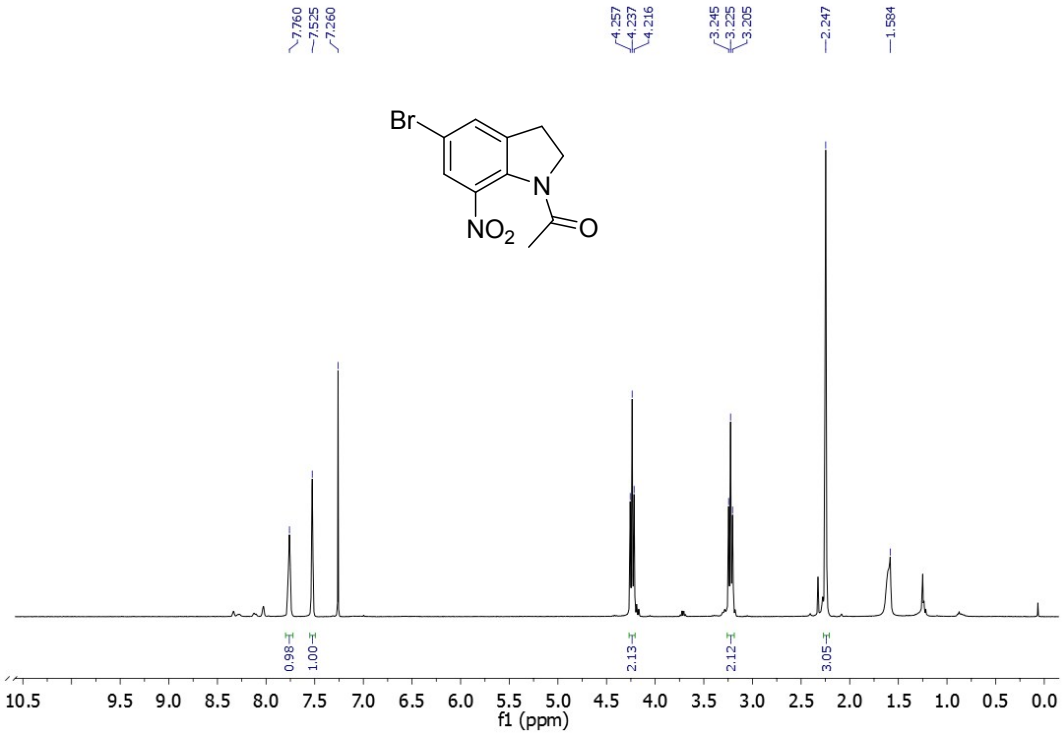

Fig. S25. ^{1}H NMR spectrum of 1-(5-Bromo-7-nitroindolin-1-yl)ethanone **(2l).**

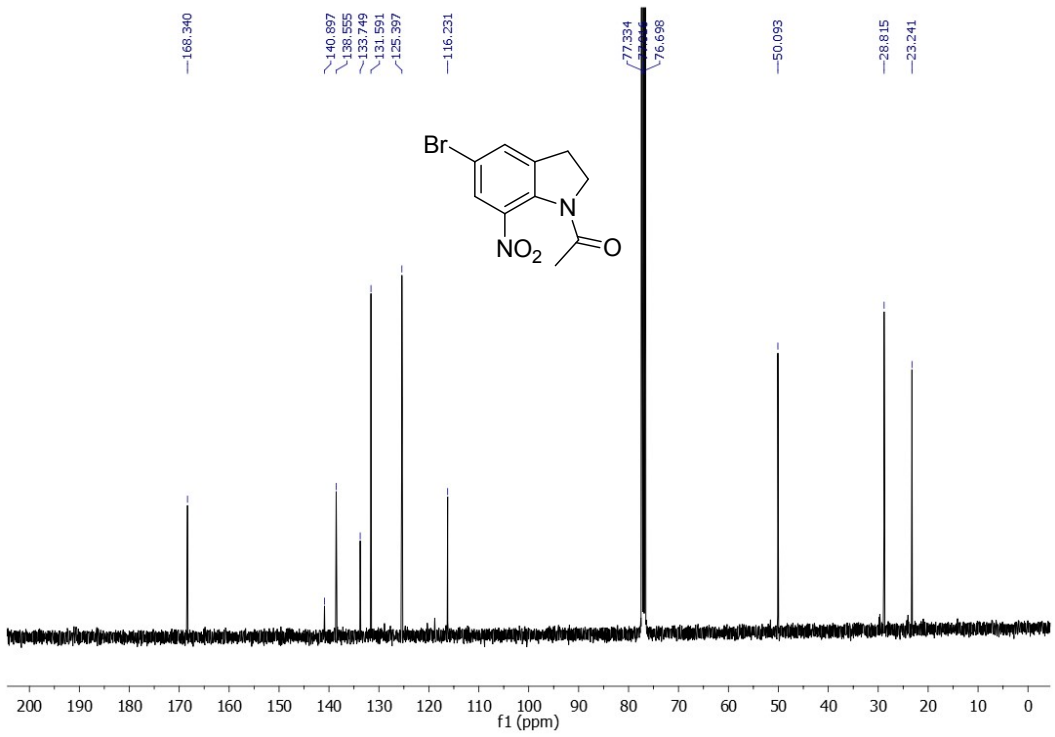

Fig. S26. ^{13}C NMR spectrum of 1-(5-Bromo-7-nitroindolin-1-yl)ethanone **(2l).**

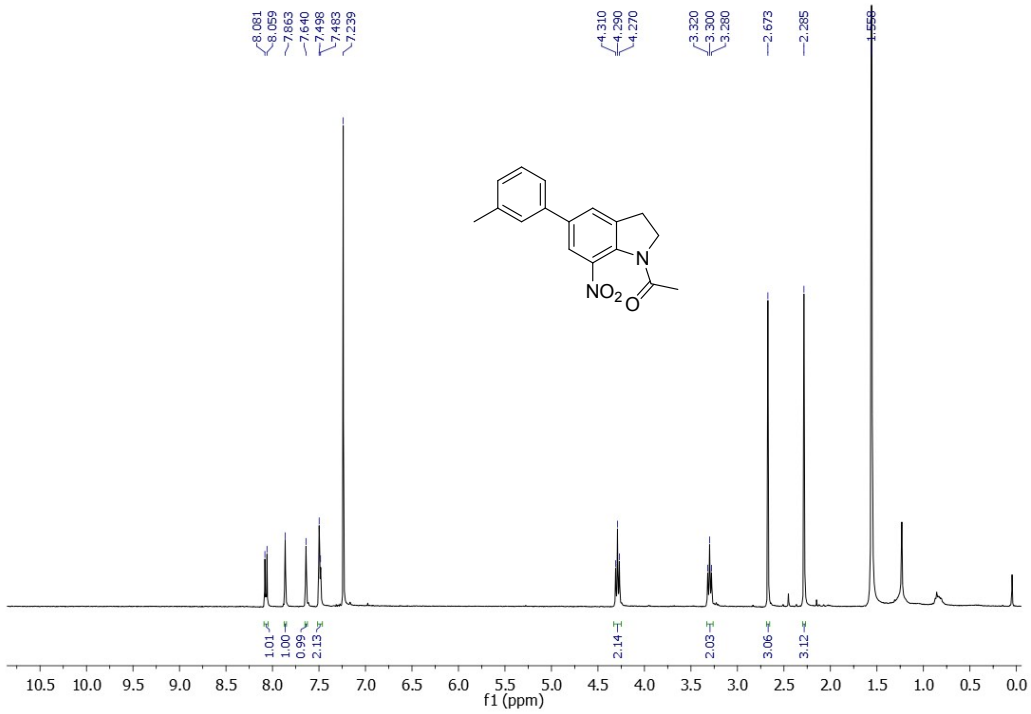

Fig. S27. ^{1}H NMR spectrum of 1-(7-Nitro-5-(m-tolyl)indolin-1-yl)ethanone **(2m).**

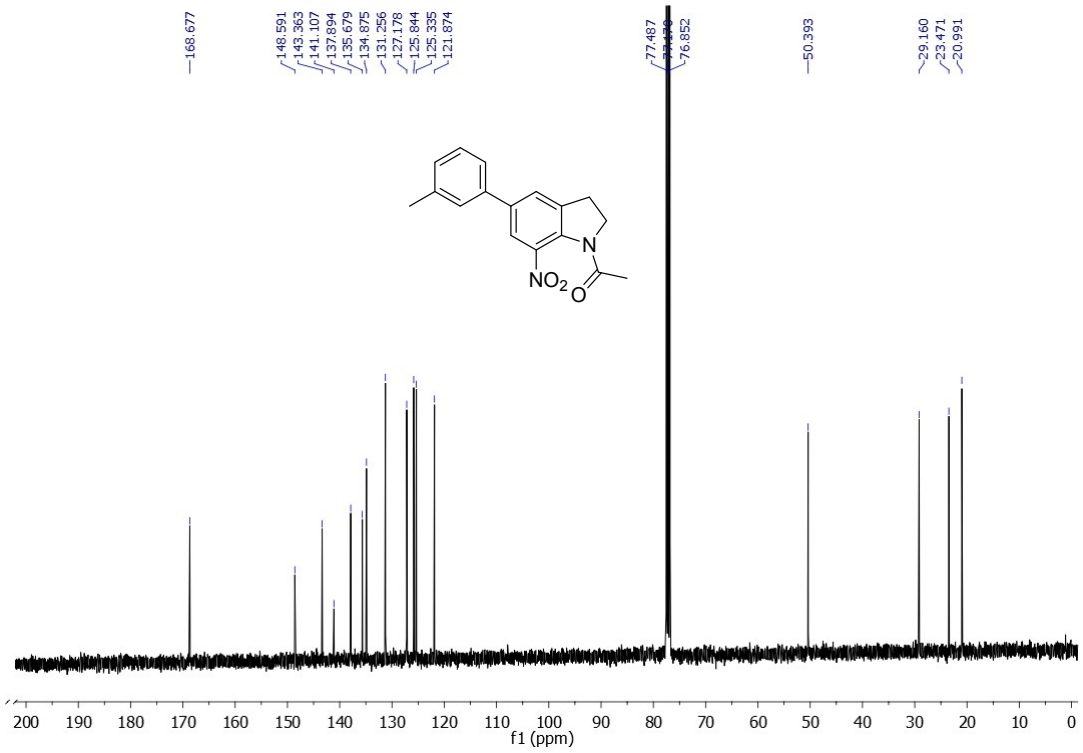

Fig. S28. ^{13}C NMR spectrum of 1-(7-Nitro-5-(m-tolyl)indolin-1-yl)ethanone **(2m).**

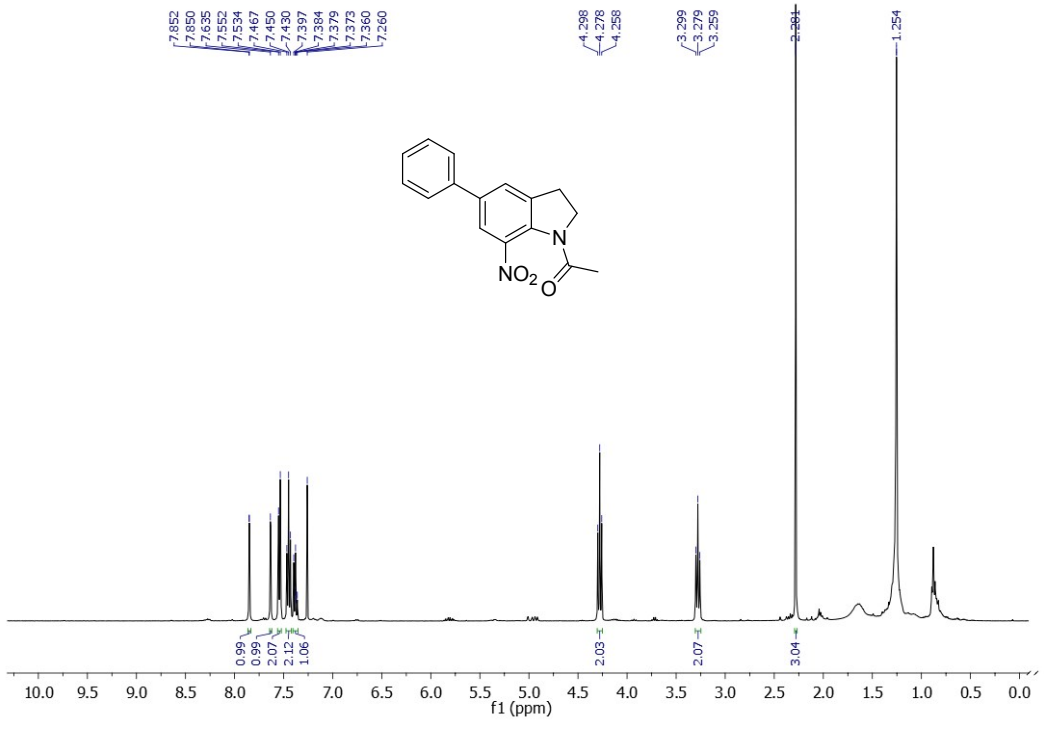

Fig. S29. ^{1}H NMR spectrum of 1-(7-Nitro-5-phenylindolin-1-yl)ethanone **(2n).**

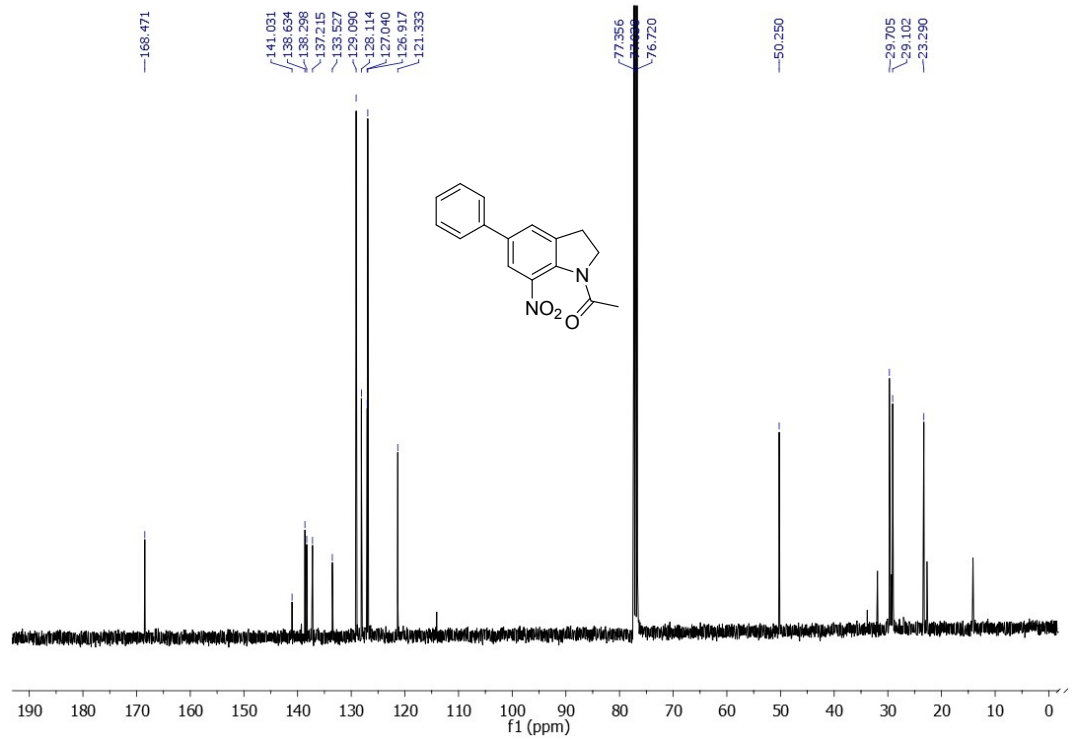

Fig. S30. ^{13}C NMR spectrum of 1-(7-Nitro-5-phenylindolin-1-yl)ethanone **(2n).**

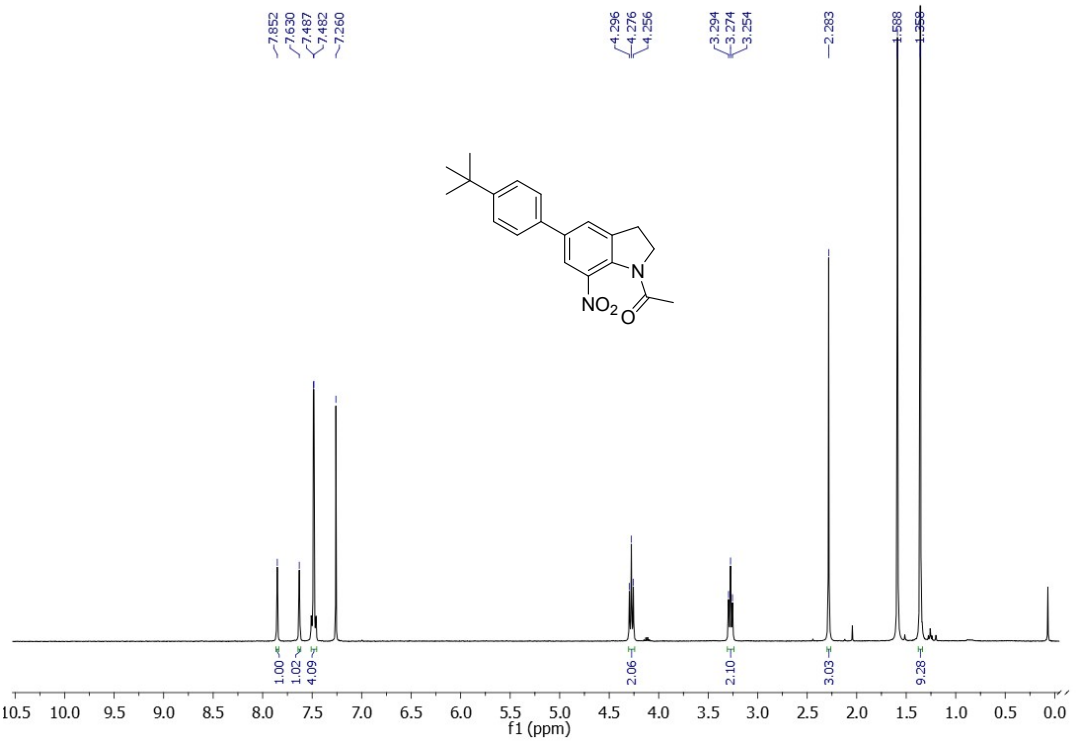

Fig. S31. ^{1}H NMR spectrum of 1-(5-(4-(tert-Butyl)phenyl)-7-nitroindolin-1-yl)ethanone **(2o).**

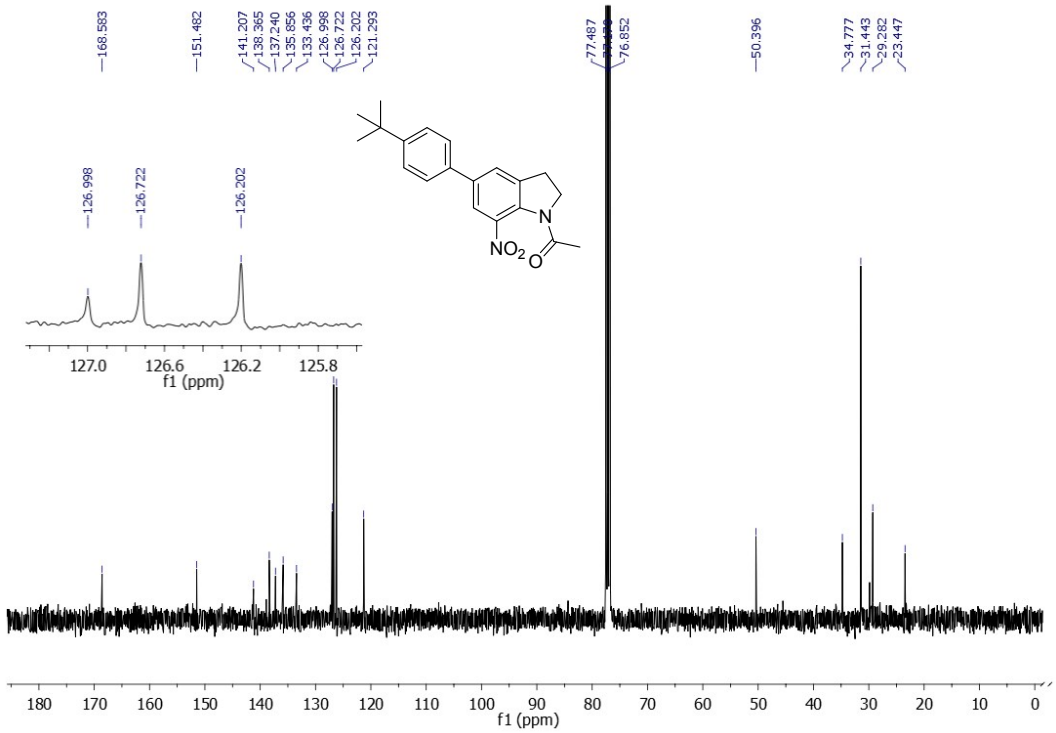

Fig. S32. ^{13}C NMR spectrum of 1-(5-(4-(tert-Butyl)phenyl)-7-nitroindolin-1-yl)ethanone **(2o).**

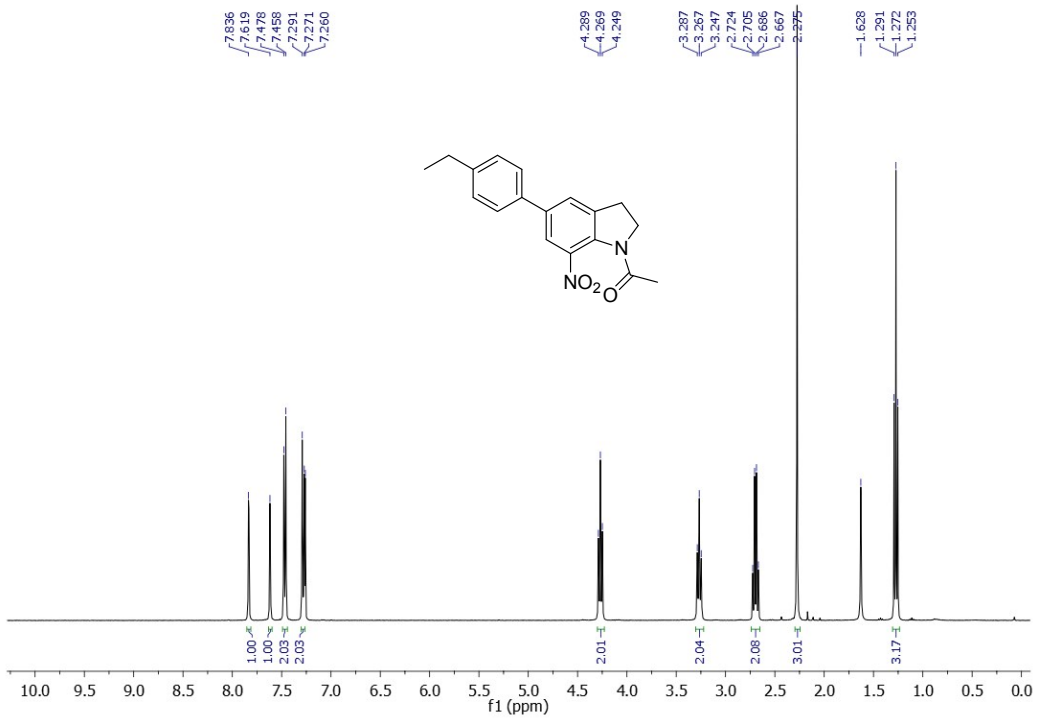

Fig. S33. ^{1}H NMR spectrum of 1-(5-(4-Ethylphenyl)-7-nitroindolin-1-yl)ethanone **(2p).**

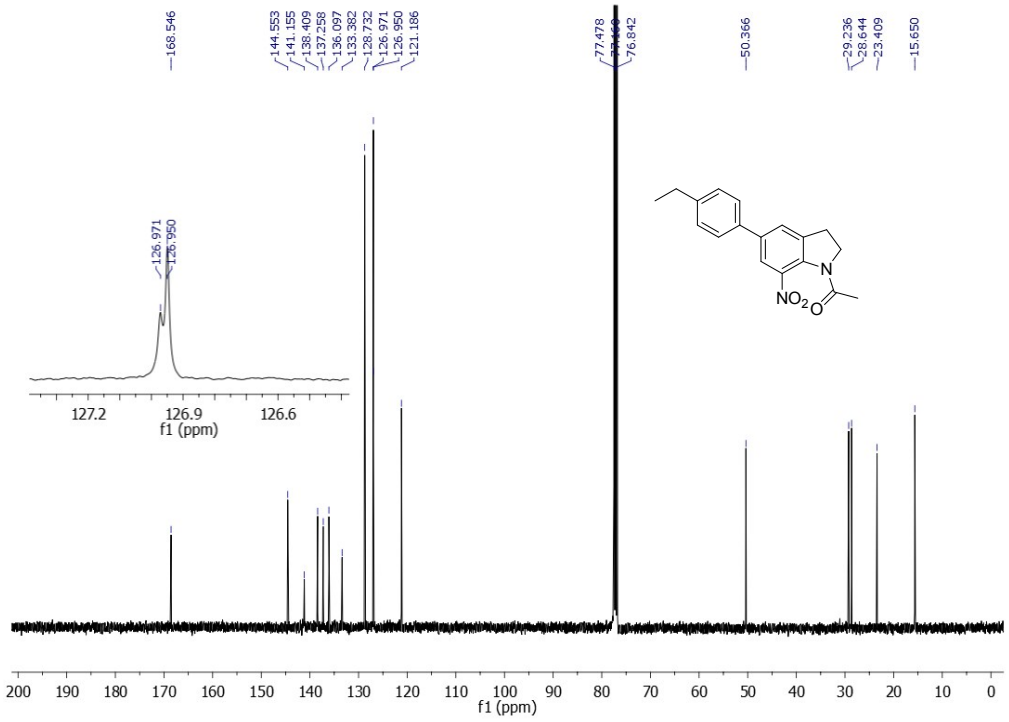

Fig. S34. ^{13}C NMR spectrum of 1-(5-(4-Ethylphenyl)-7-nitroindolin-1-yl)ethanone **(2p).**

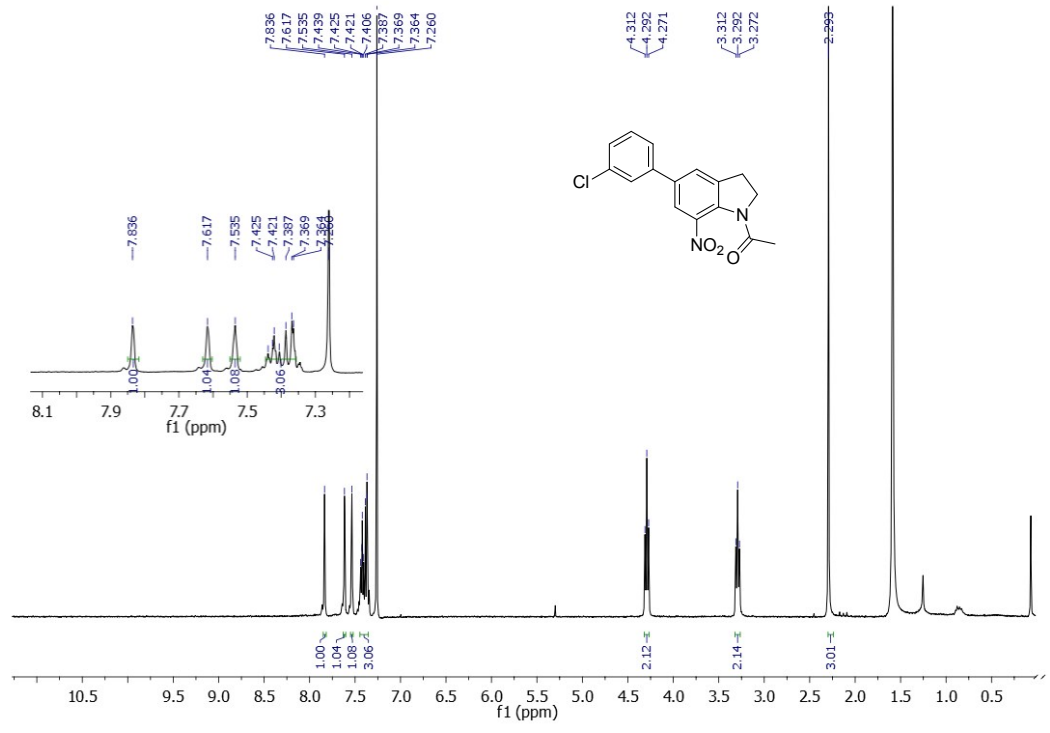

Fig. S35. ^{1}H NMR spectrum of 1-(5-(3-Chlorophenyl)-7-nitroindolin-1-yl)ethanone **(2q).**

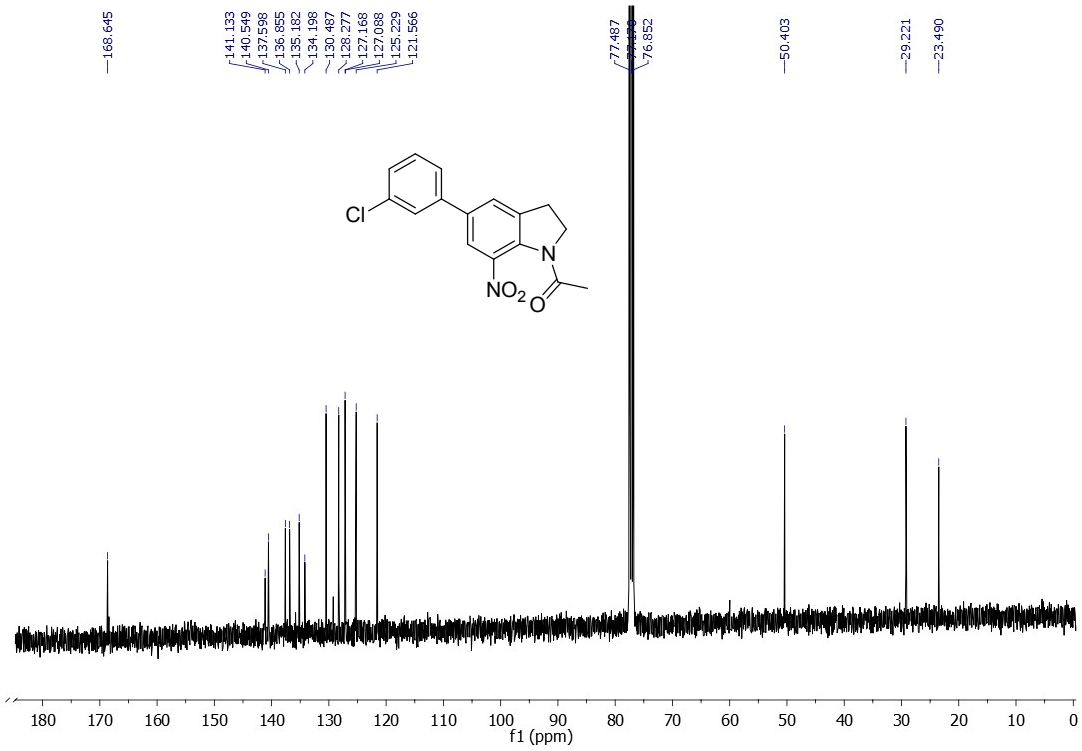

Fig. S36. ^{13}C NMR spectrum of 1-(5-(3-Chlorophenyl)-7-nitroindolin-1-yl)ethanone **(2q).**

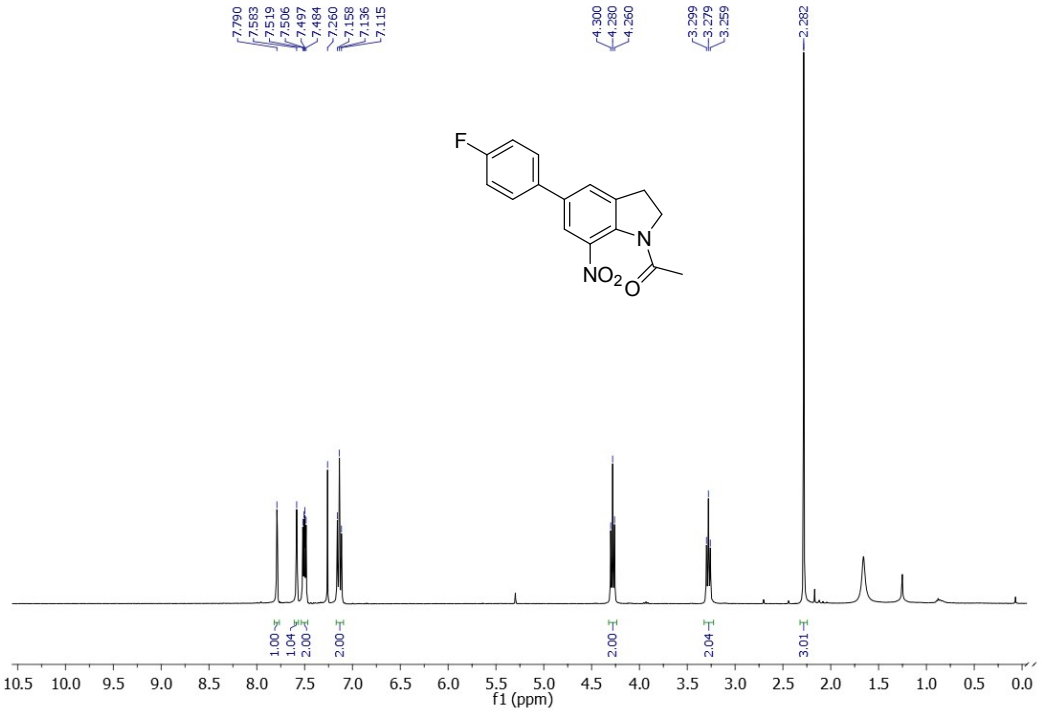

Fig. S37. ^{1}H NMR spectrum of 1-(5-(4-Fluorophenyl)-7-nitroindolin-1-yl)ethanone **(2r).**

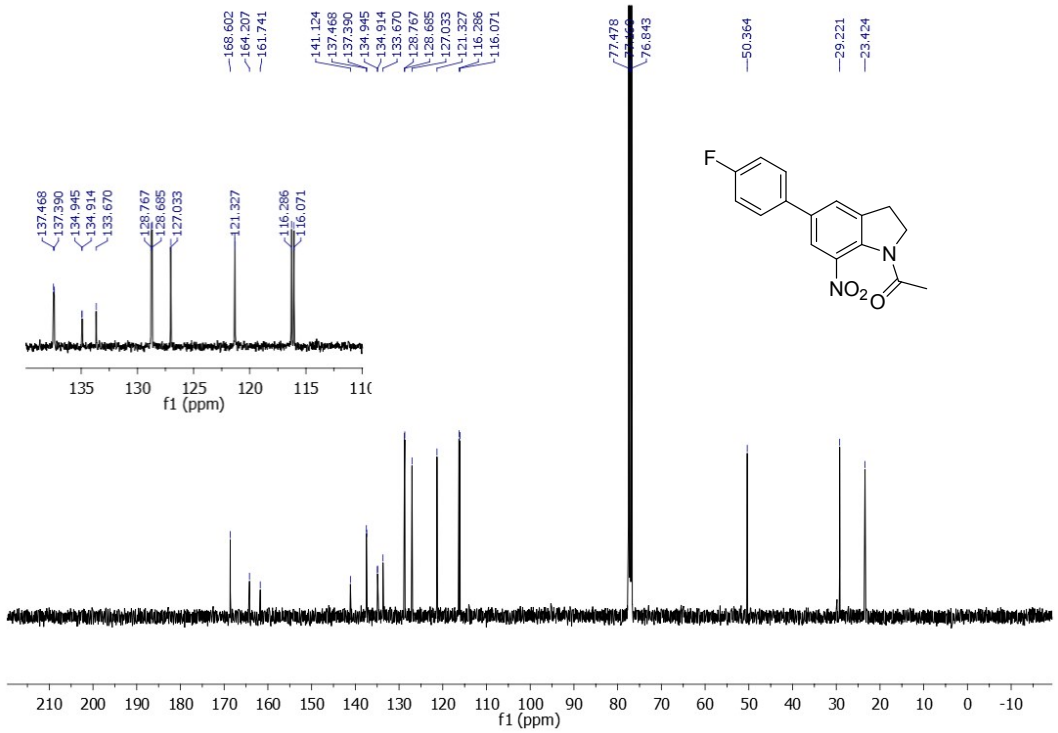

Fig. S38. ^{13}C NMR spectrum of 1-(5-(4-Fluorophenyl)-7-nitroindolin-1-yl)ethanone **(2r).**

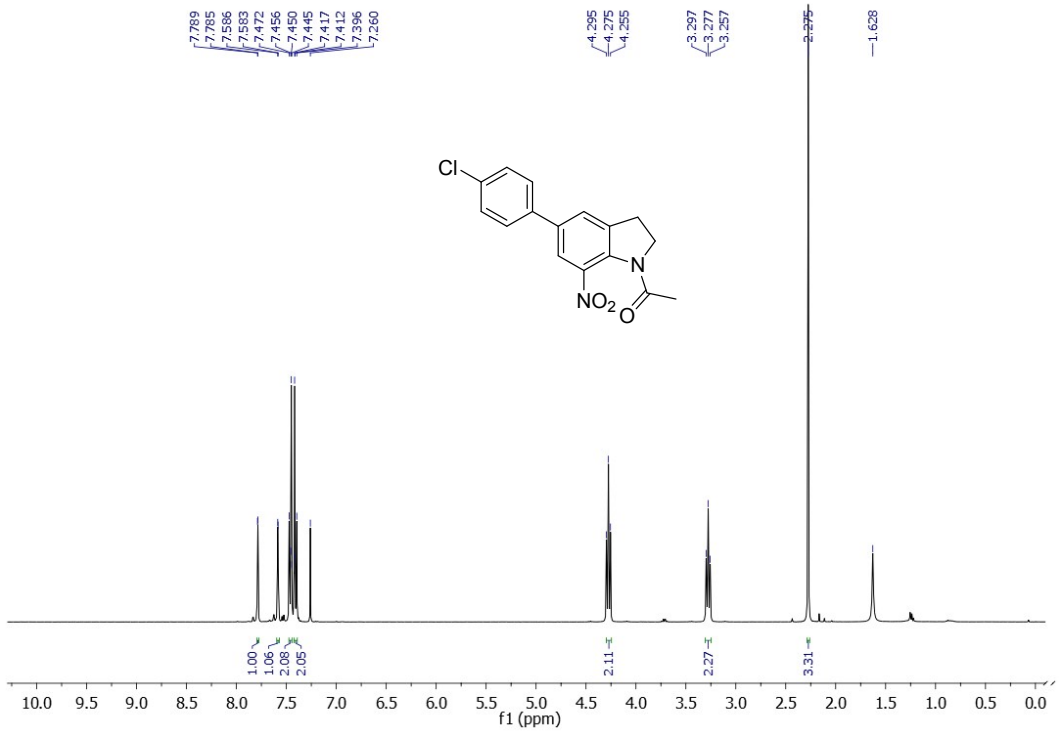

Fig. S39. ^{1}H NMR spectrum of 1-(5-(4-Chlorophenyl)-7-nitroindolin-1-yl)ethanone **(2s).**

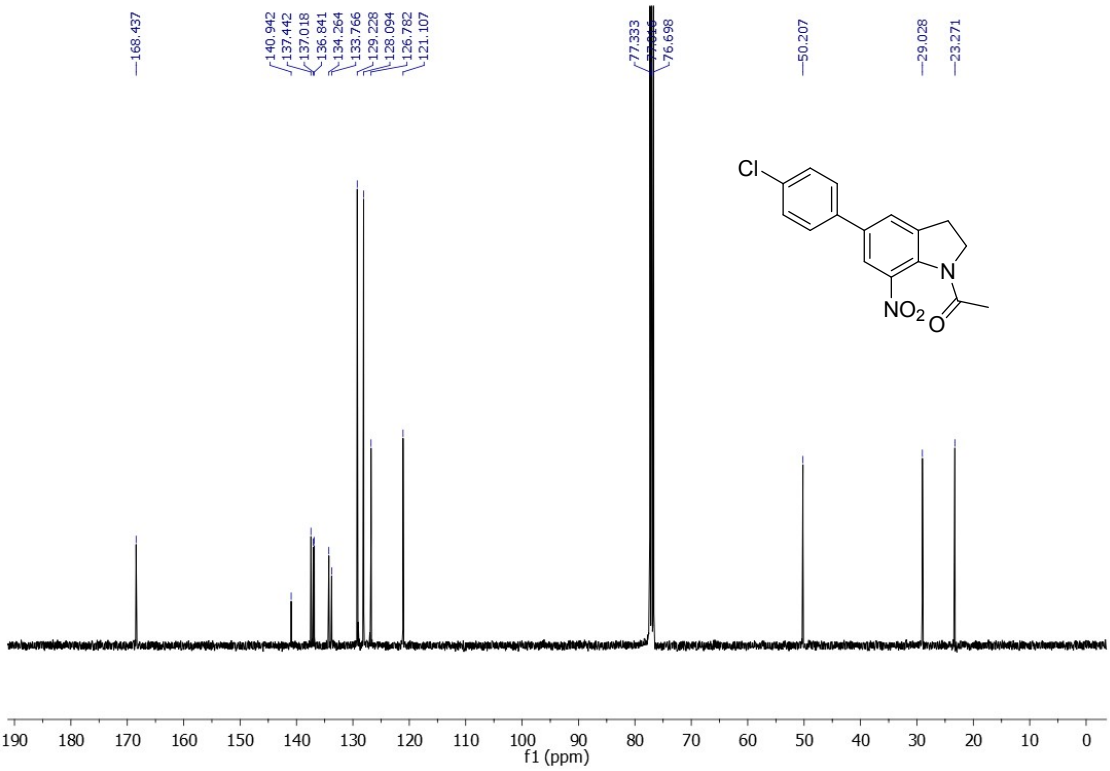

Fig. S40. ^{13}C NMR spectrum of 1-(5-(4-Chlorophenyl)-7-nitroindolin-1-yl)ethanone **(2s).**

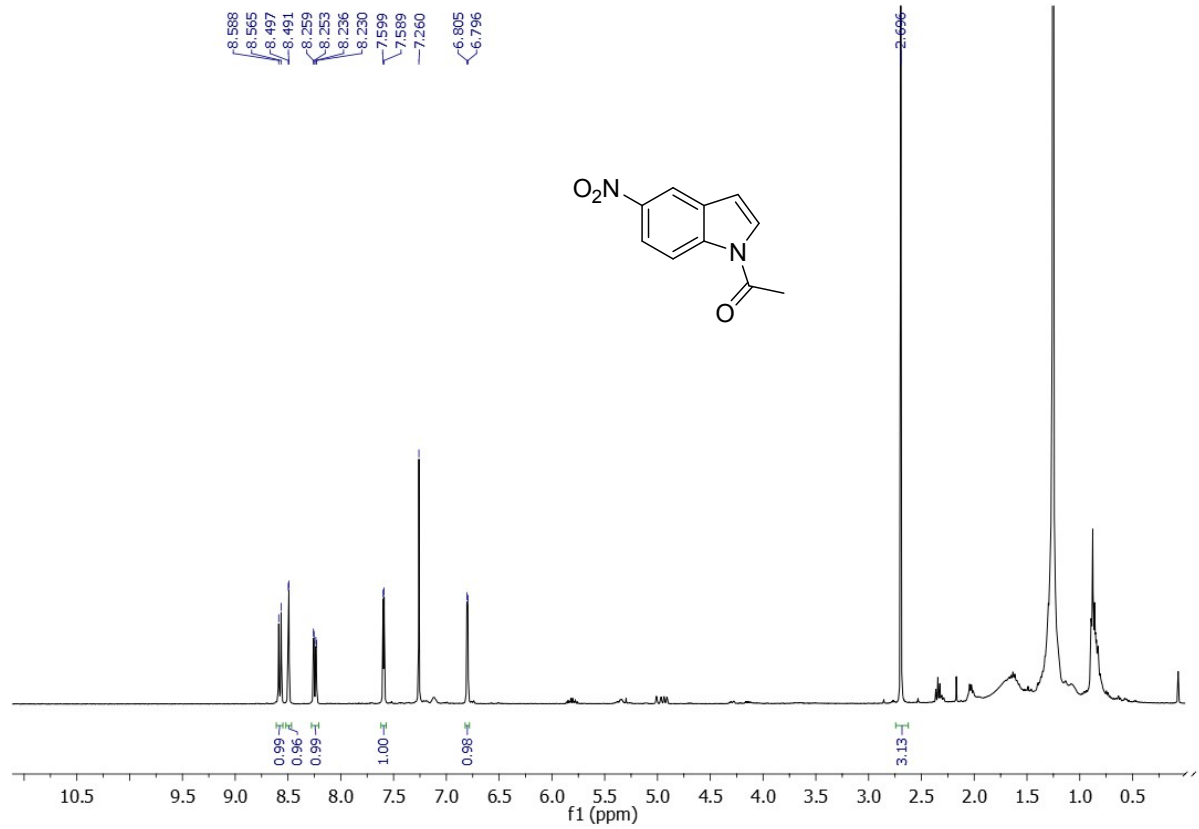

Fig. S41. ^{1}H NMR spectrum of 1-(5-Nitro-1H-indol-1-yl)ethanone (**3a).**

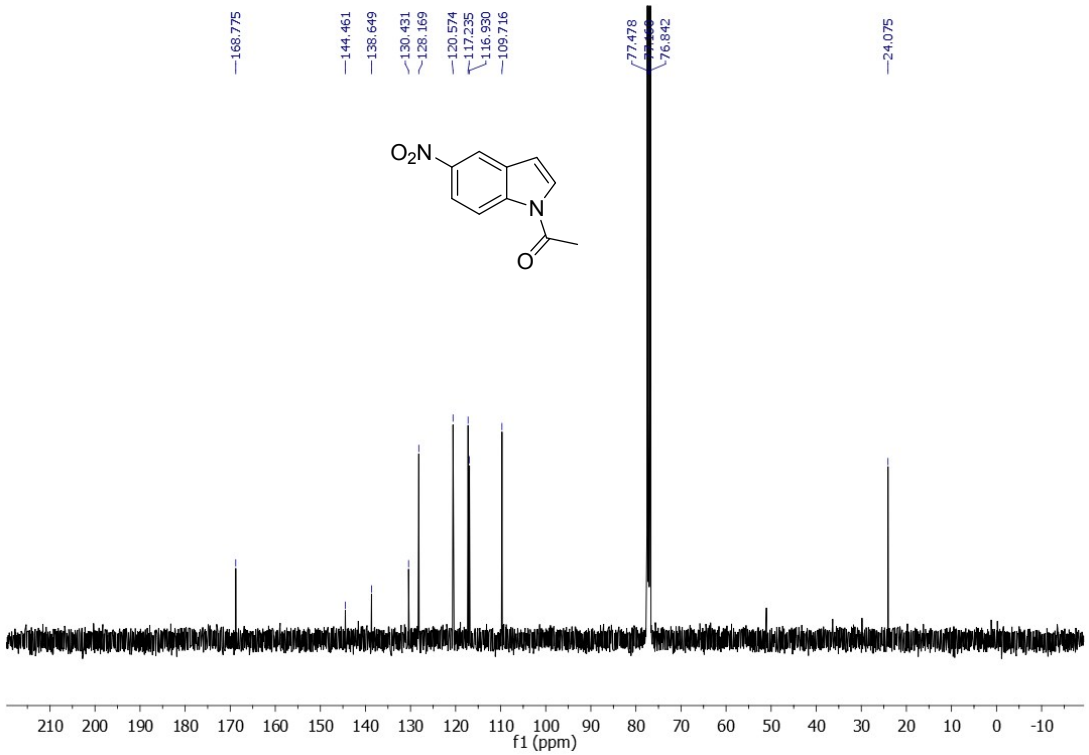

Fig. S42. ^{13}C NMR spectrum of 1-(5-Nitro-1H-indol-1-yl)ethanone (**3a).**

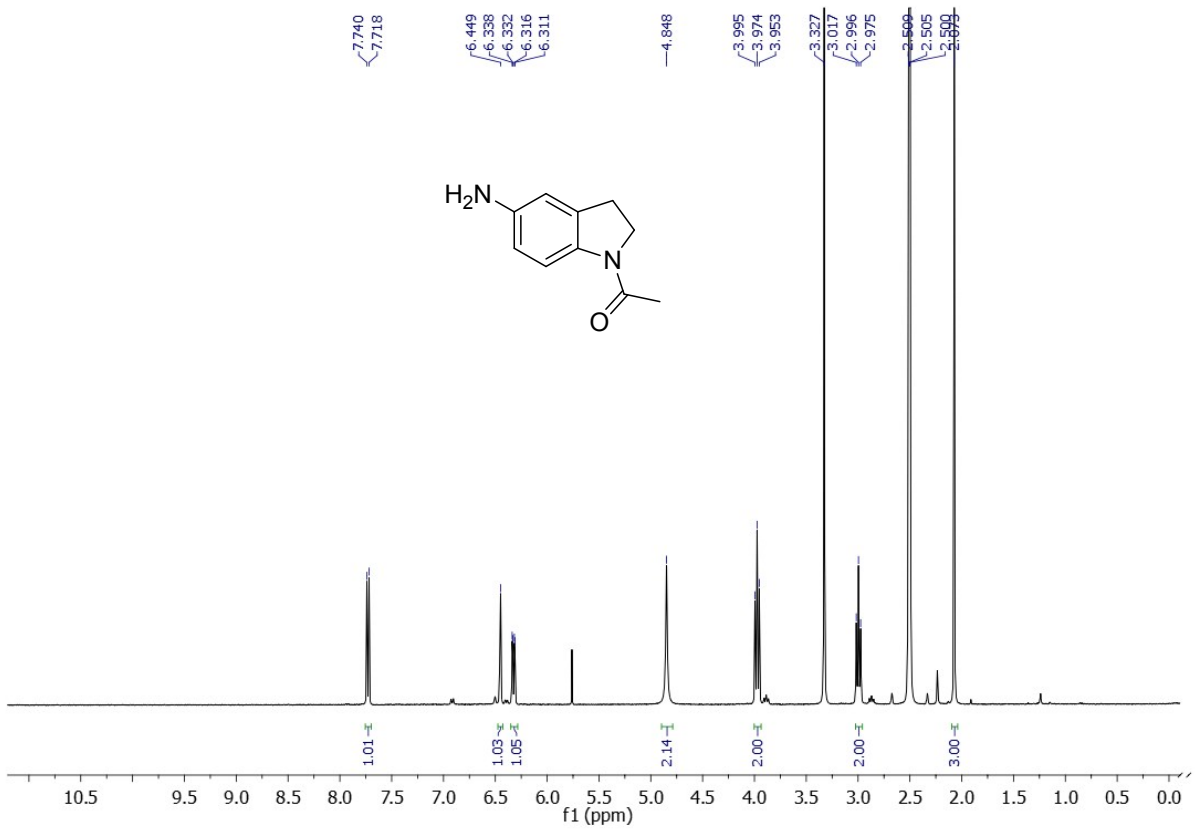

Fig. S43. ^{1}H NMR spectrum of 1-(5-Aminoindolin-1-yl)ethanone **(3b).**

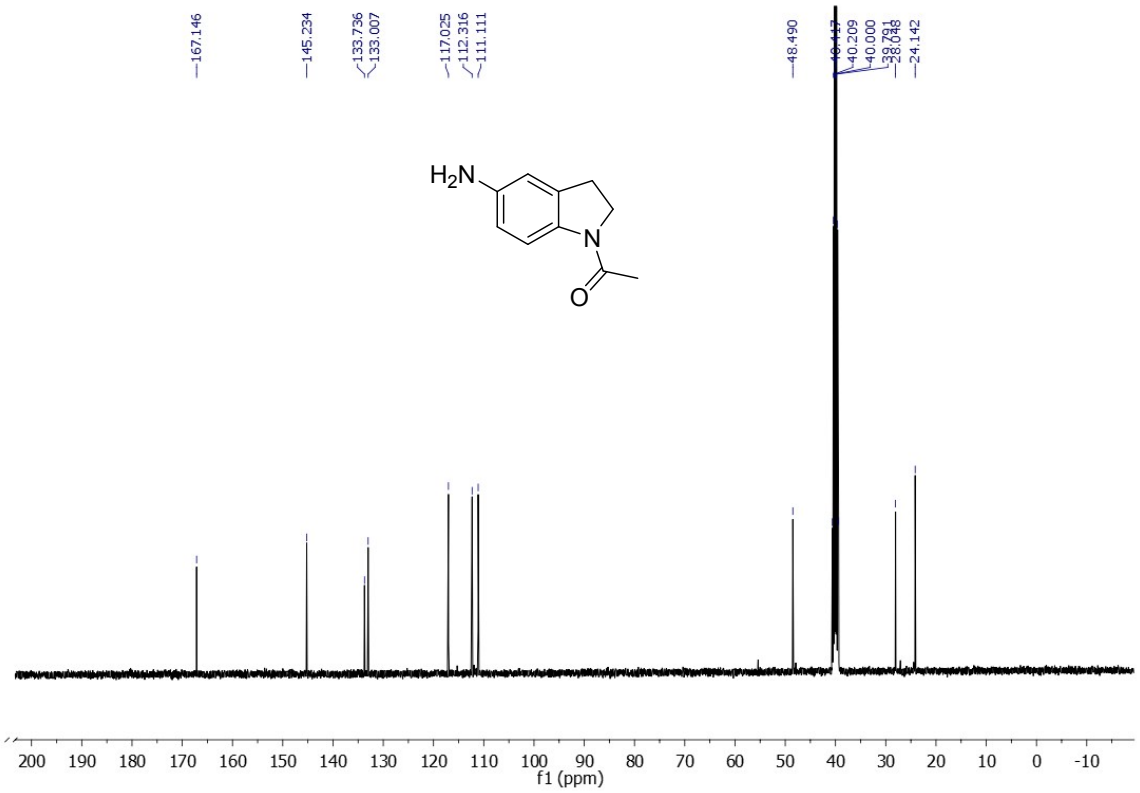

Fig. S44. ^{13}C NMR spectrum of 1-(5-Aminoindolin-1-yl)ethanone **(3b).**

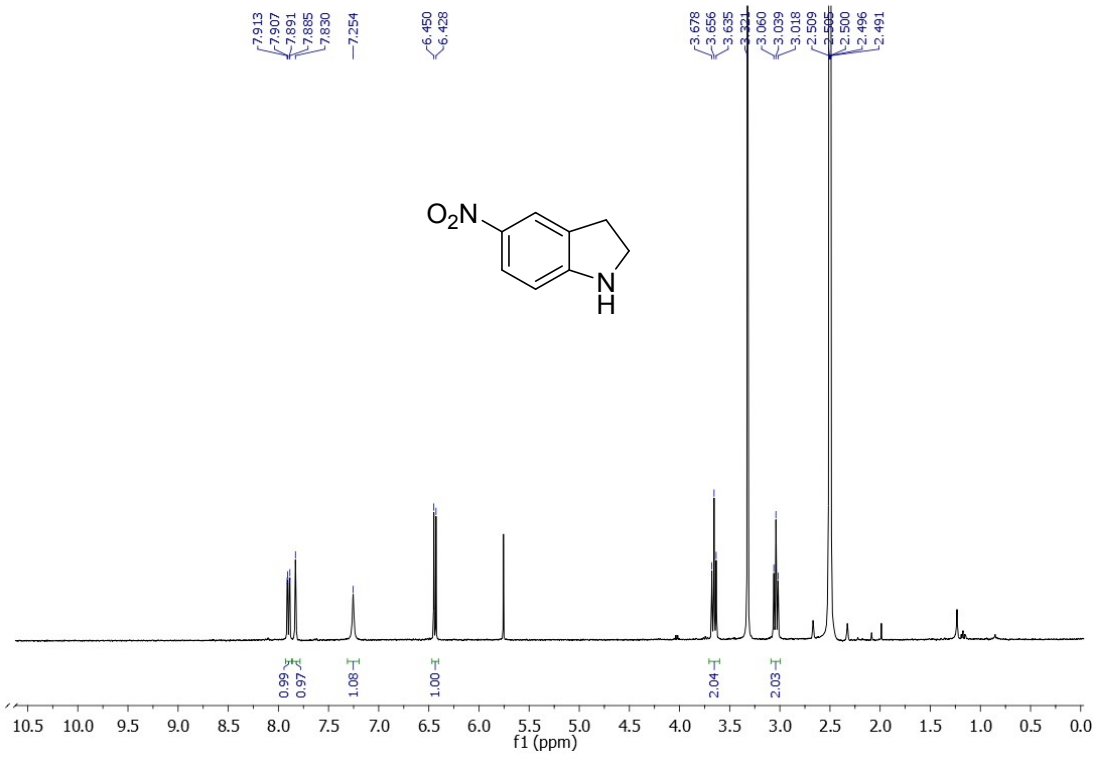

Fig. S45. ^{1}H NMR spectrum of 5-Nitroindoline **(3c).**

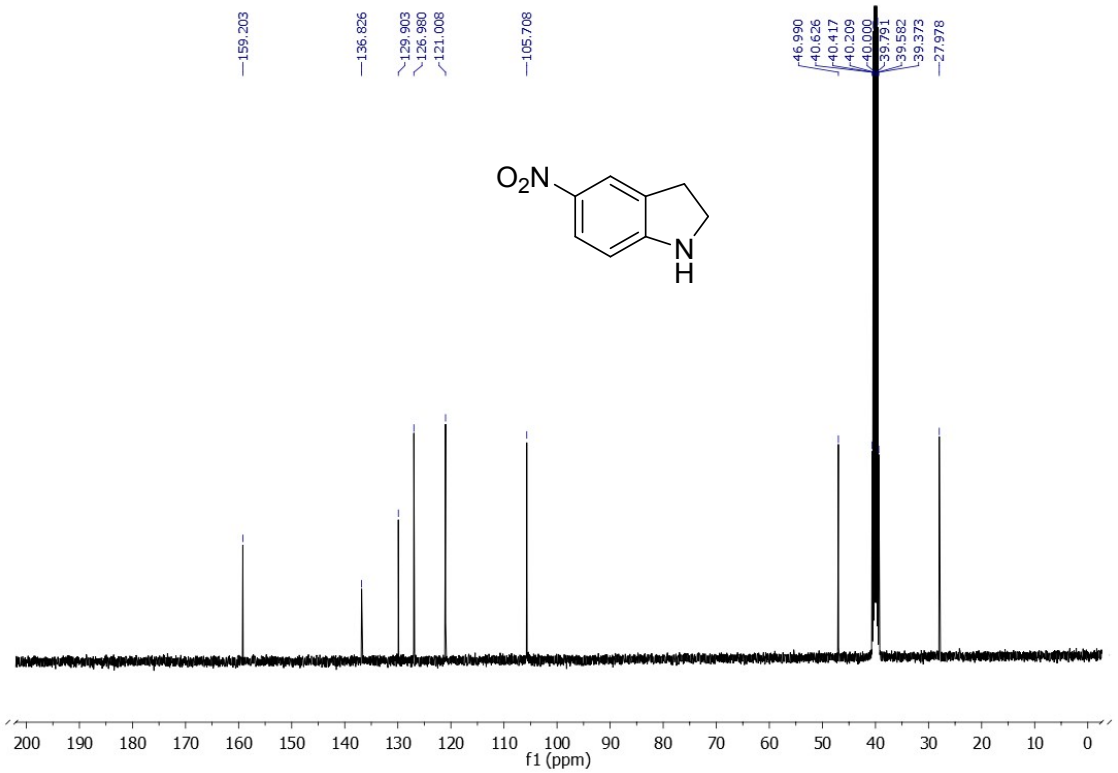

Fig. S46. ^{13}C NMR spectrum of 5-Nitroindoline **(3c).**

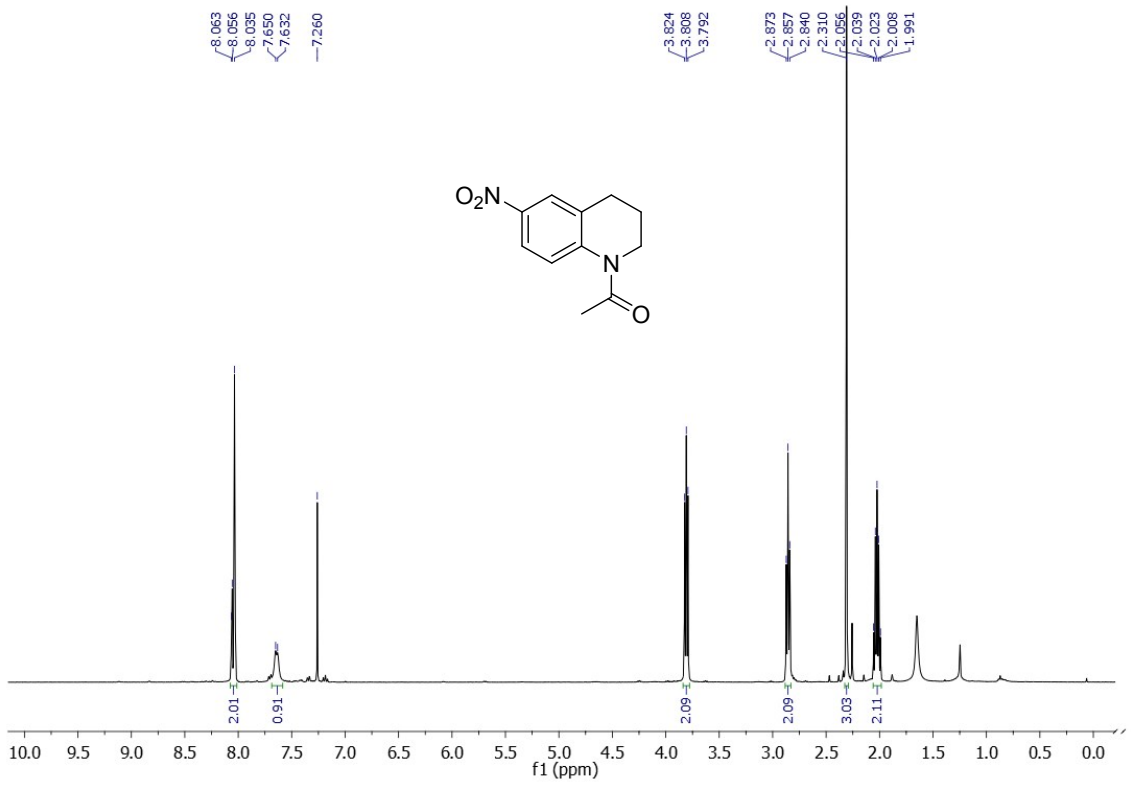

Fig. S47. ^{1}H NMR spectrum of 1-(6-Nitro-3,4-dihydroquinolin-1(2H)-yl)ethanone **(5).**

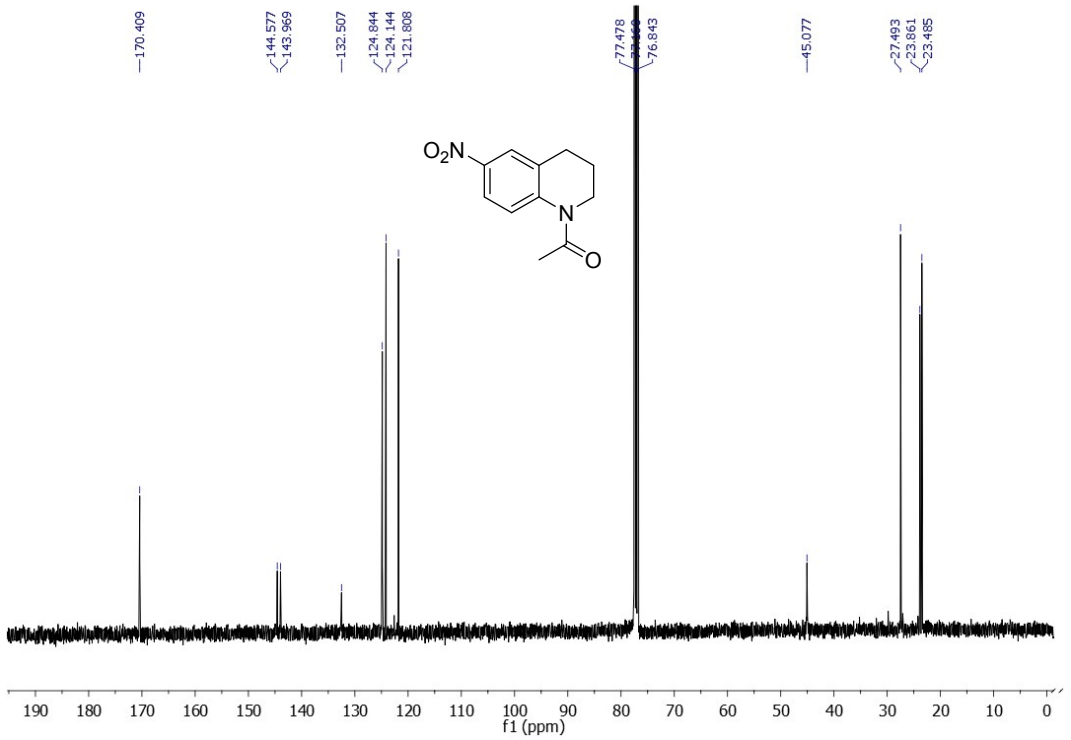

Fig. S48. ^{13}C NMR spectrum of 1-(6-Nitro-3,4-dihydroquinolin-1(2H)-yl)ethanone **(5).**

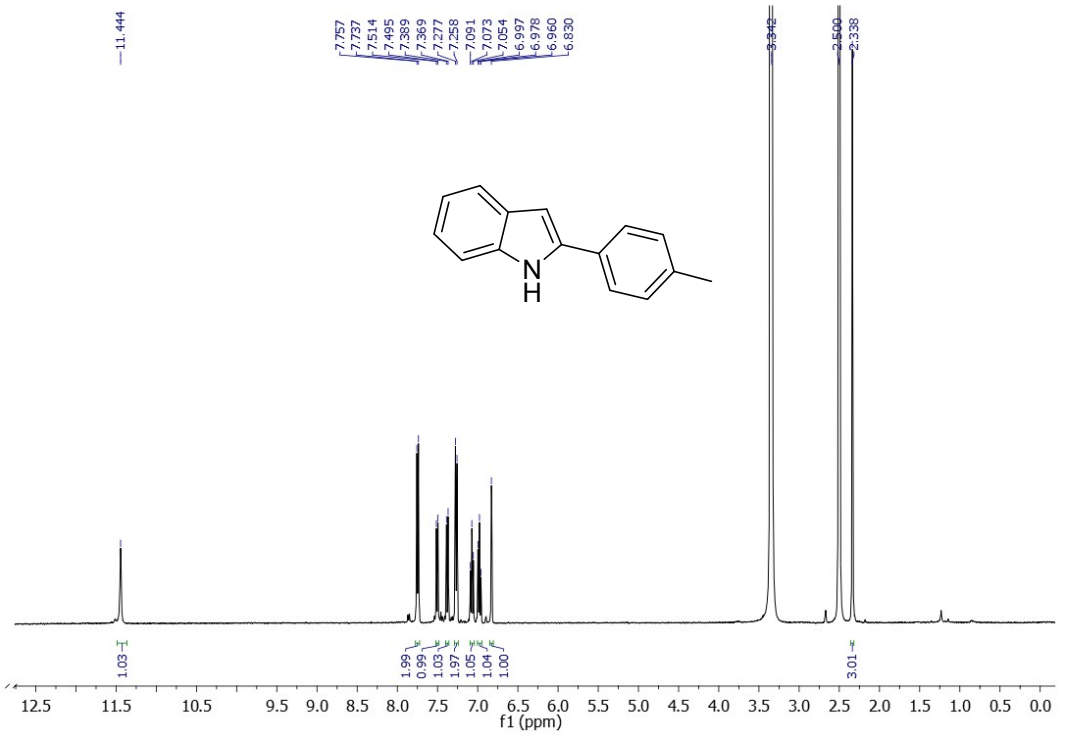

Fig. S49. ^{1}H NMR spectrum of 2-(p-Tolyl)-1H-indole **(1f').**

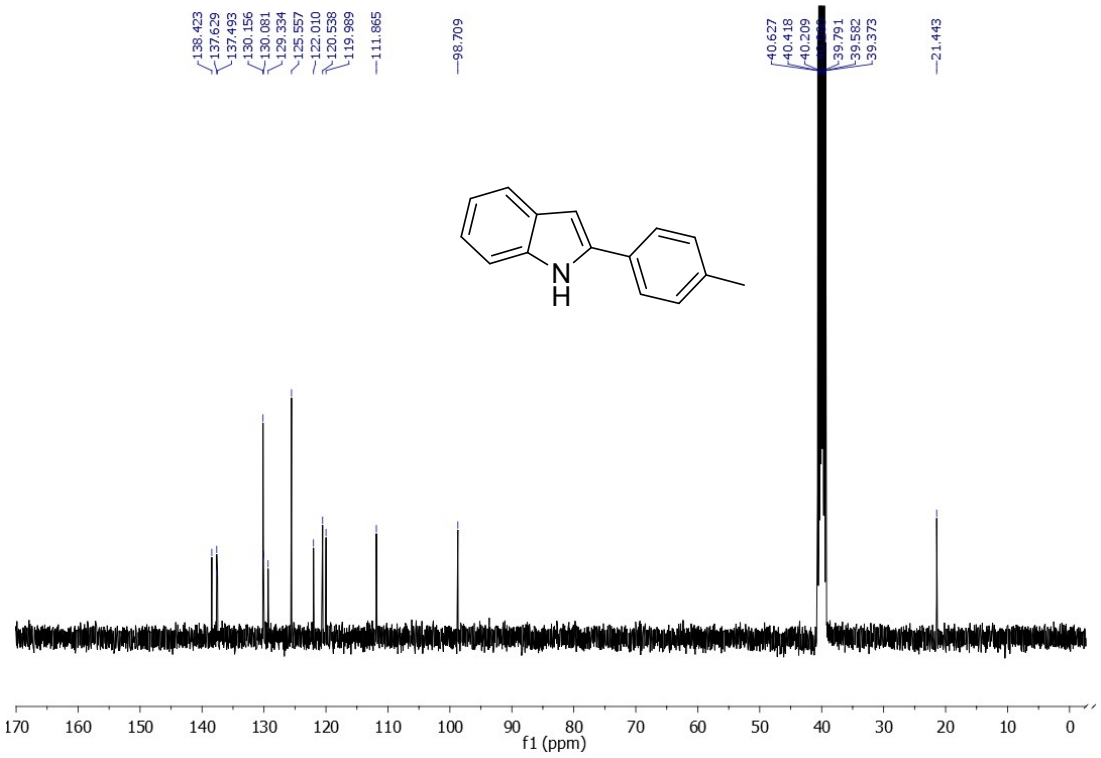

Fig. S50. ^{13}C NMR spectrum of 2-(p-Tolyl)-1H-indole **(1f').**

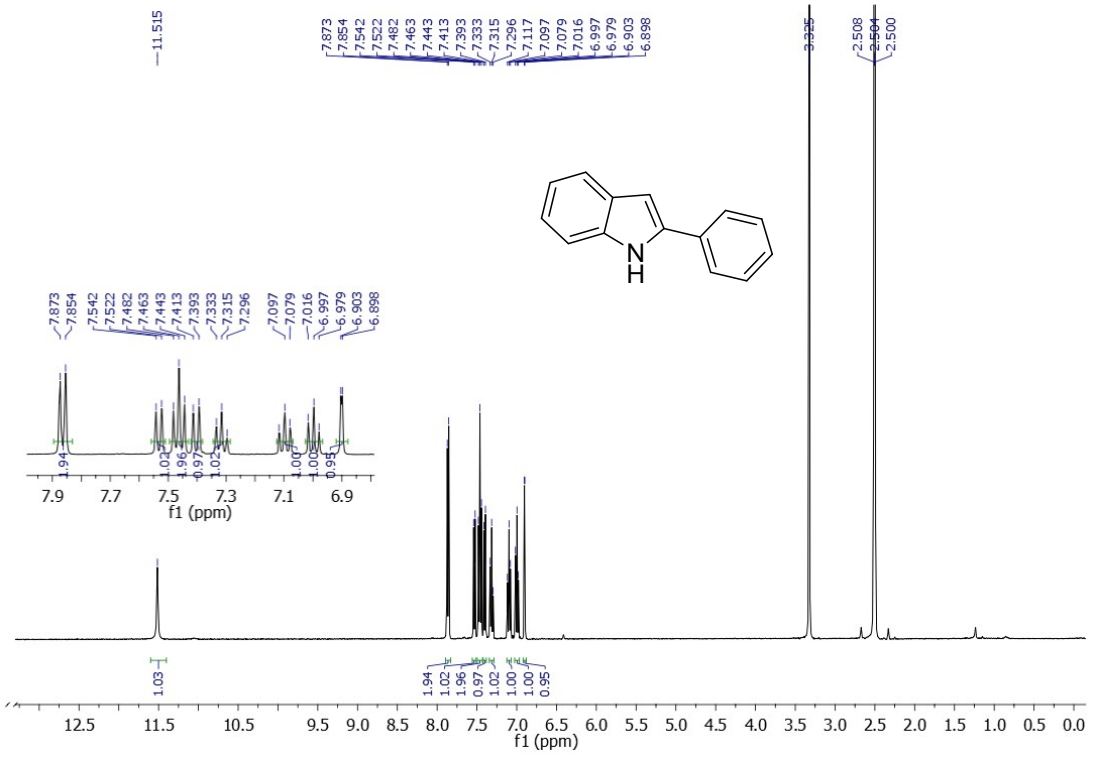

Fig. S51. ^{1}H NMR spectrum of 2-Phenyl-1H-indole **(1g').**

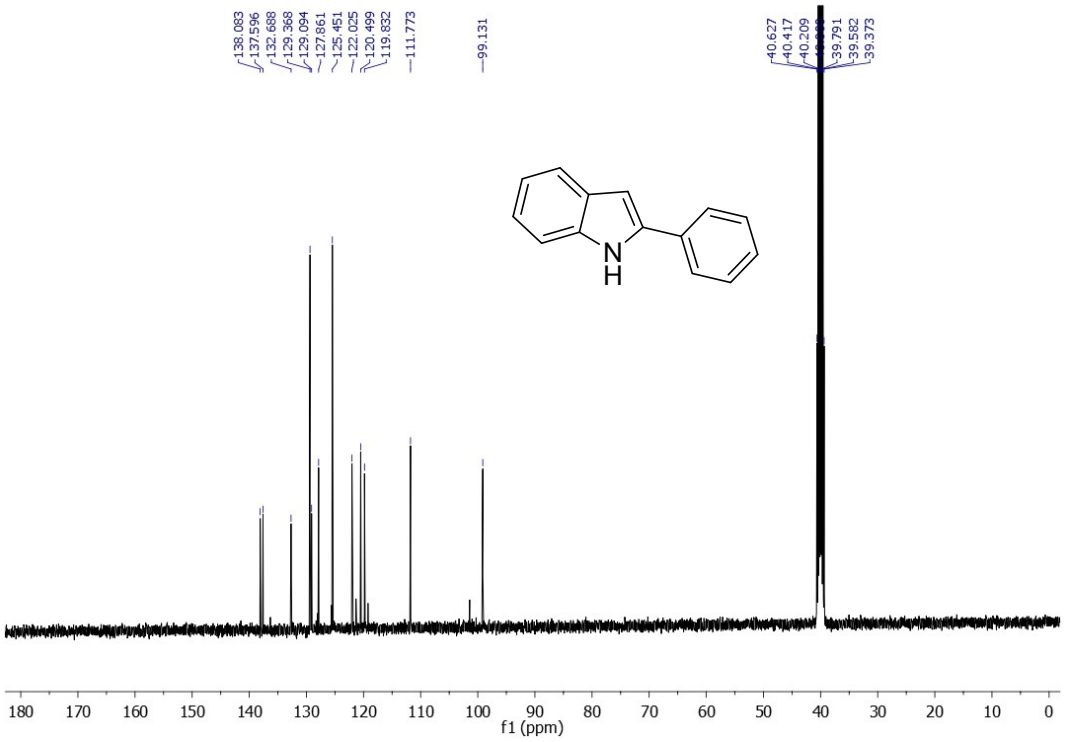

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Fig. S52. ^{13}C NMR spectrum of 2-Phenyl-1H-indole **(1g').**

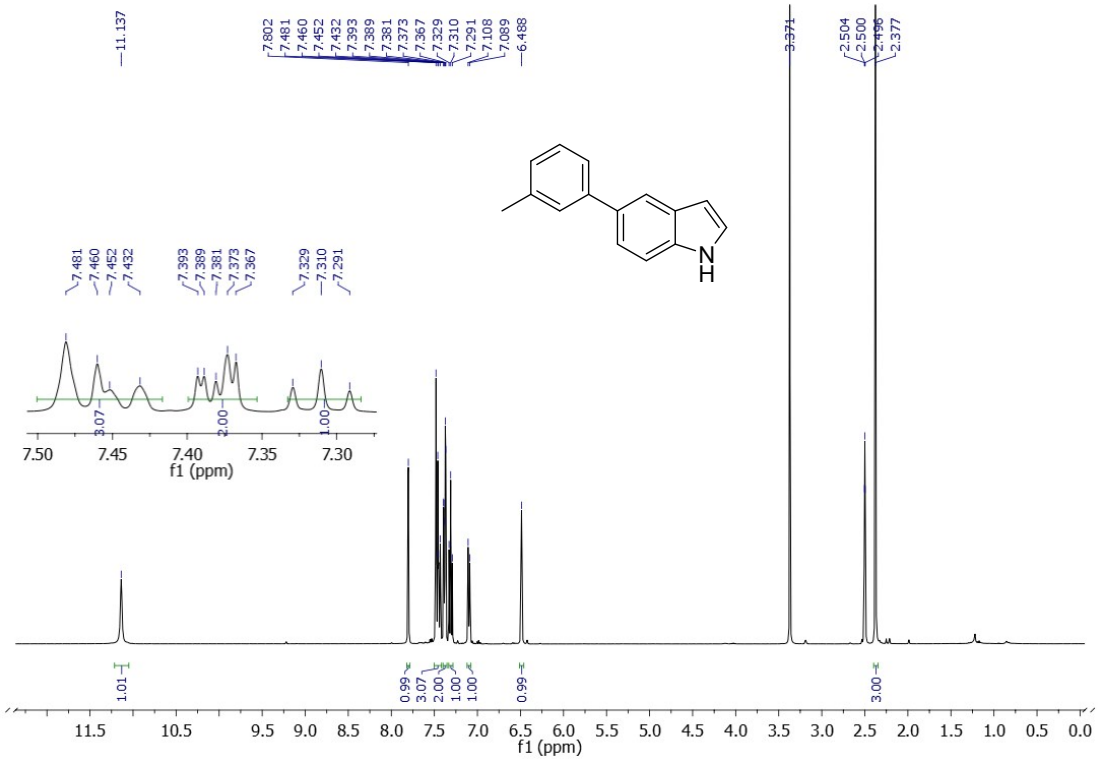

Fig. S53. ^{1}H NMR spectrum of 5-(m-Tolyl)-1H-indole **(1m').**

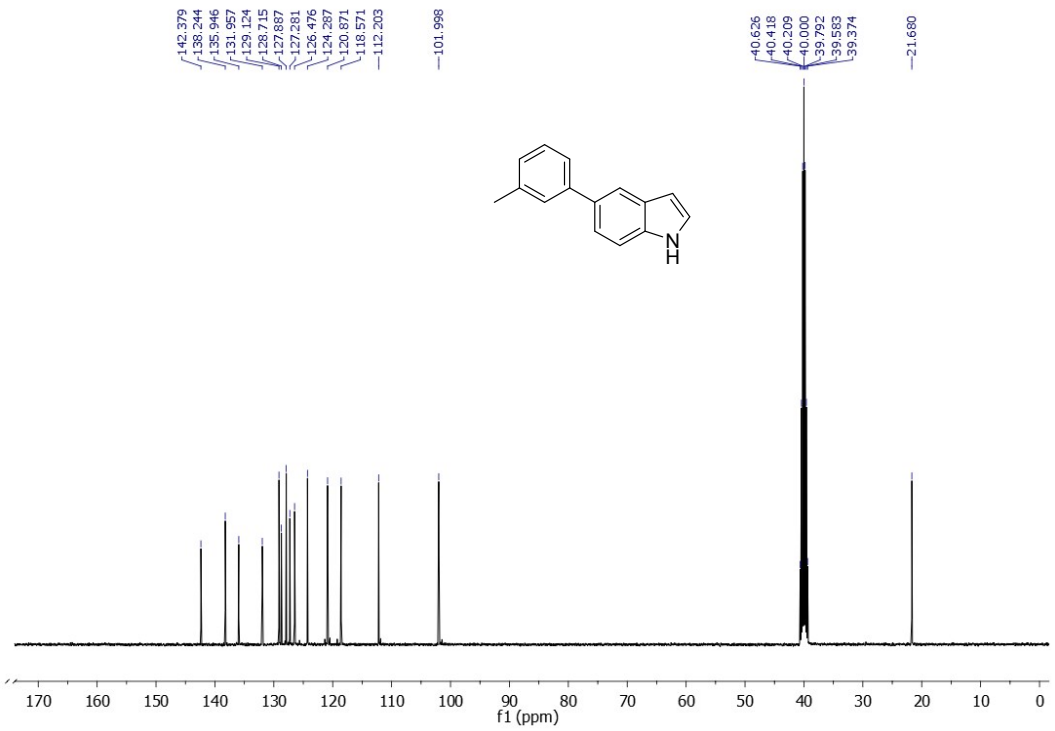

Fig. S54. ^{13}C NMR spectrum of 5-(m-Tolyl)-1H-indole **(1m').**

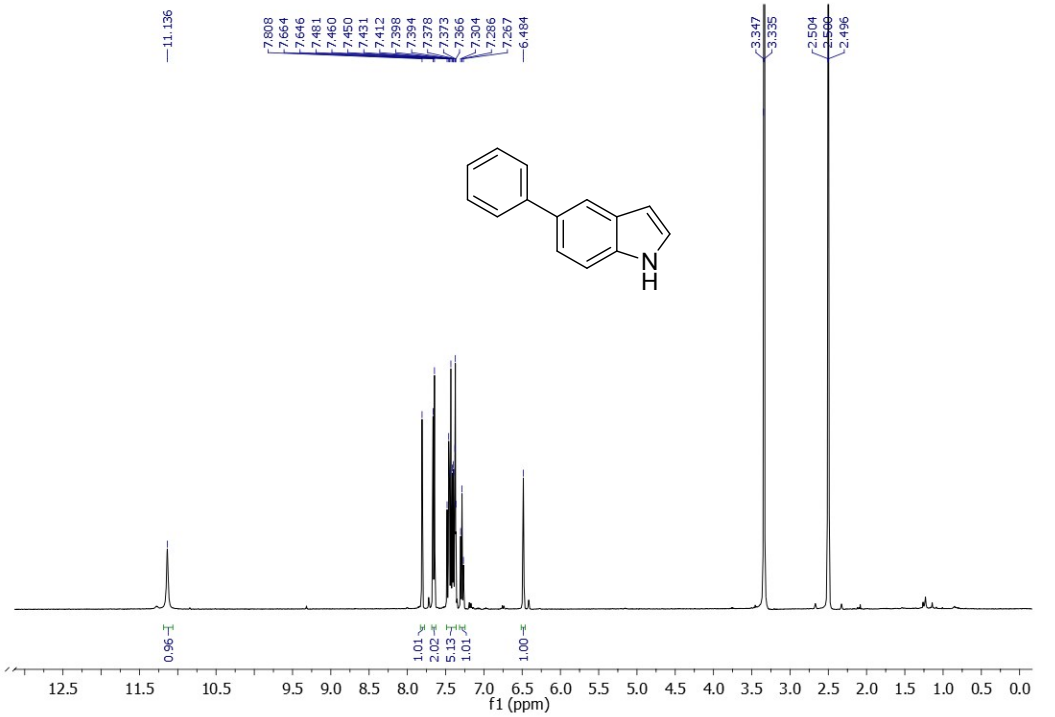

Fig. S55. ^{1}H NMR spectrum of 5-Phenyl-1H-indole**(1n').**

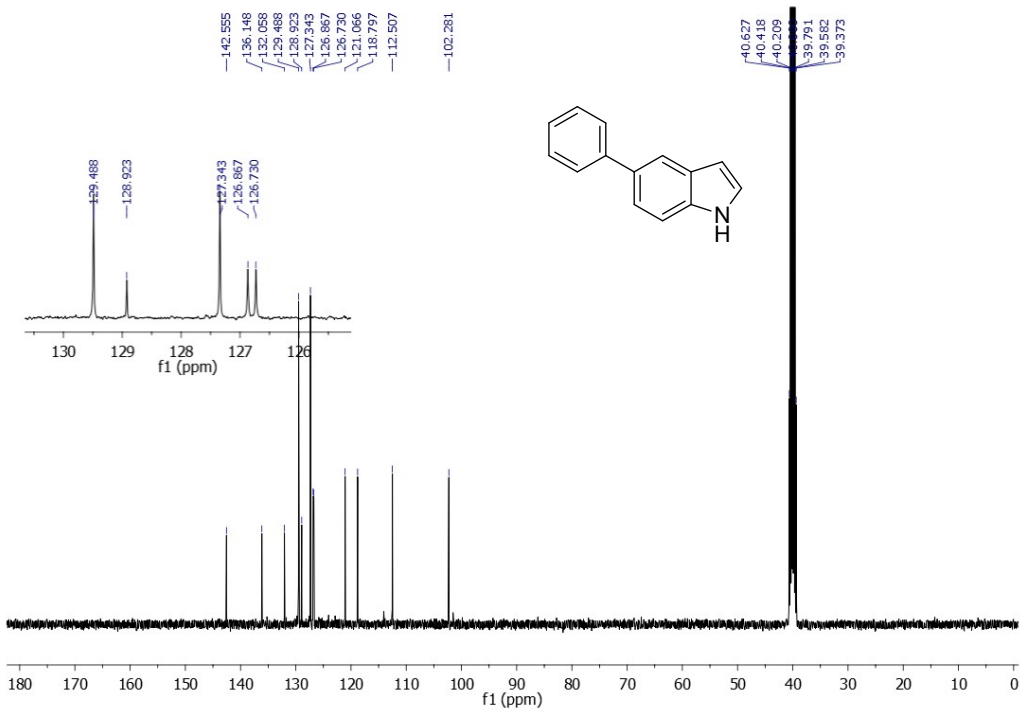

Fig. S56. ^{13}C NMR spectrum of 5-Phenyl-1H-indole**(1n').**

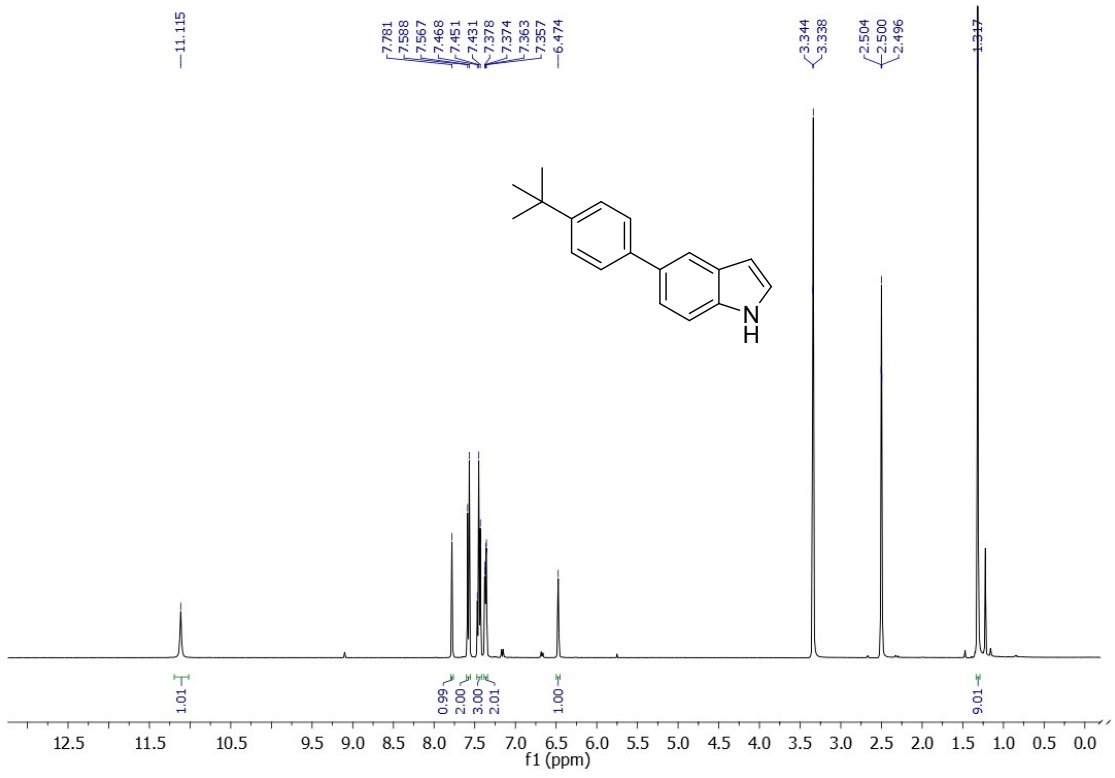

Fig. S57. ^{1}H NMR spectrum of 5-(4-(tert-Butyl)phenyl)-1H-indole **(1o').**

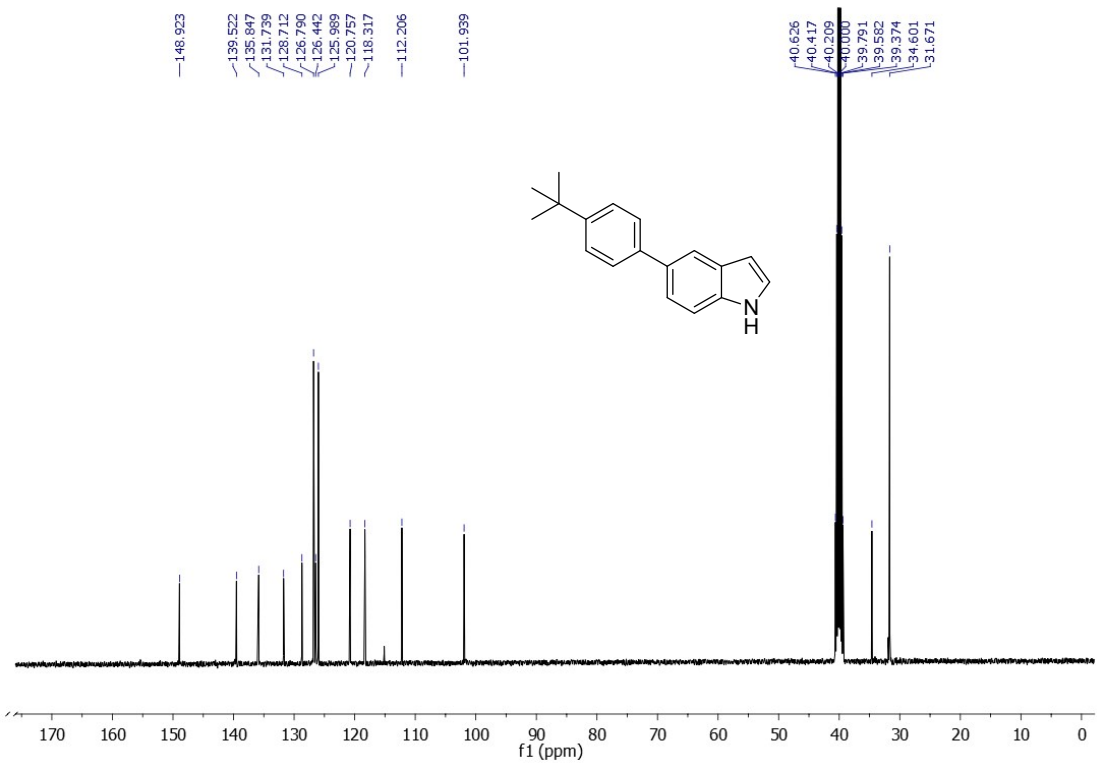

Fig. S58. ^{13}C NMR spectrum of 5-(4-(tert-Butyl)phenyl)-1H-indole **(1o').**

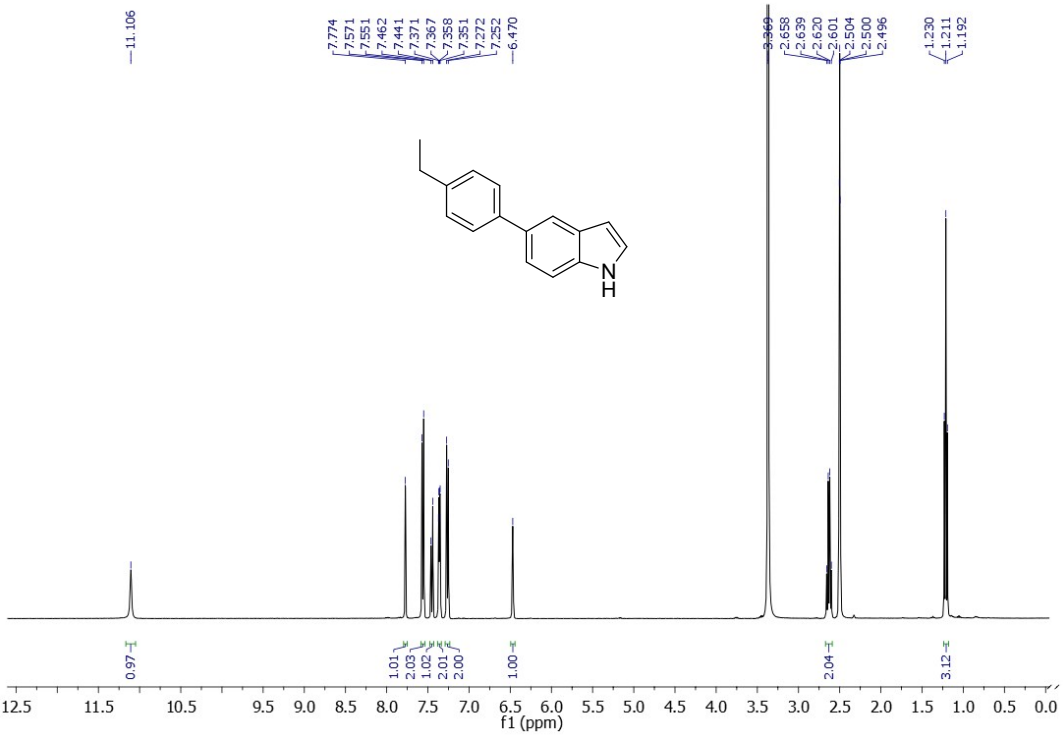

Fig. S59. ^{1}H NMR spectrum of 5-(4-Ethylphenyl)-1H-indole **(1p').**

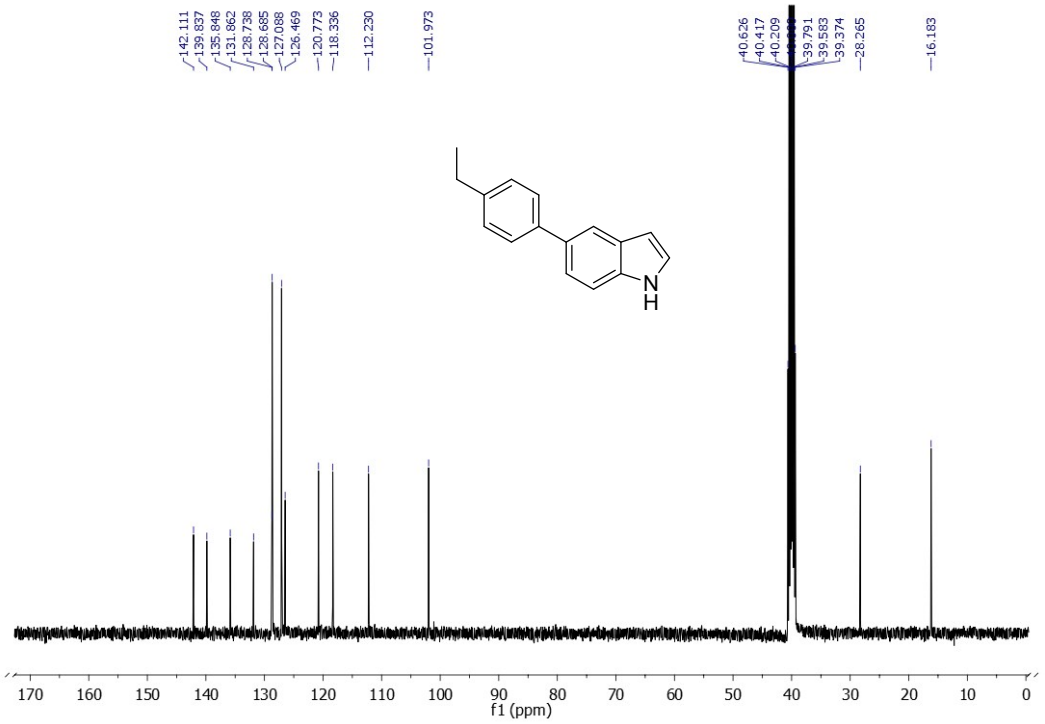

Fig. S60. ^{13}C NMR spectrum of 5-(4-Ethylphenyl)-1H-indole **(1p').**

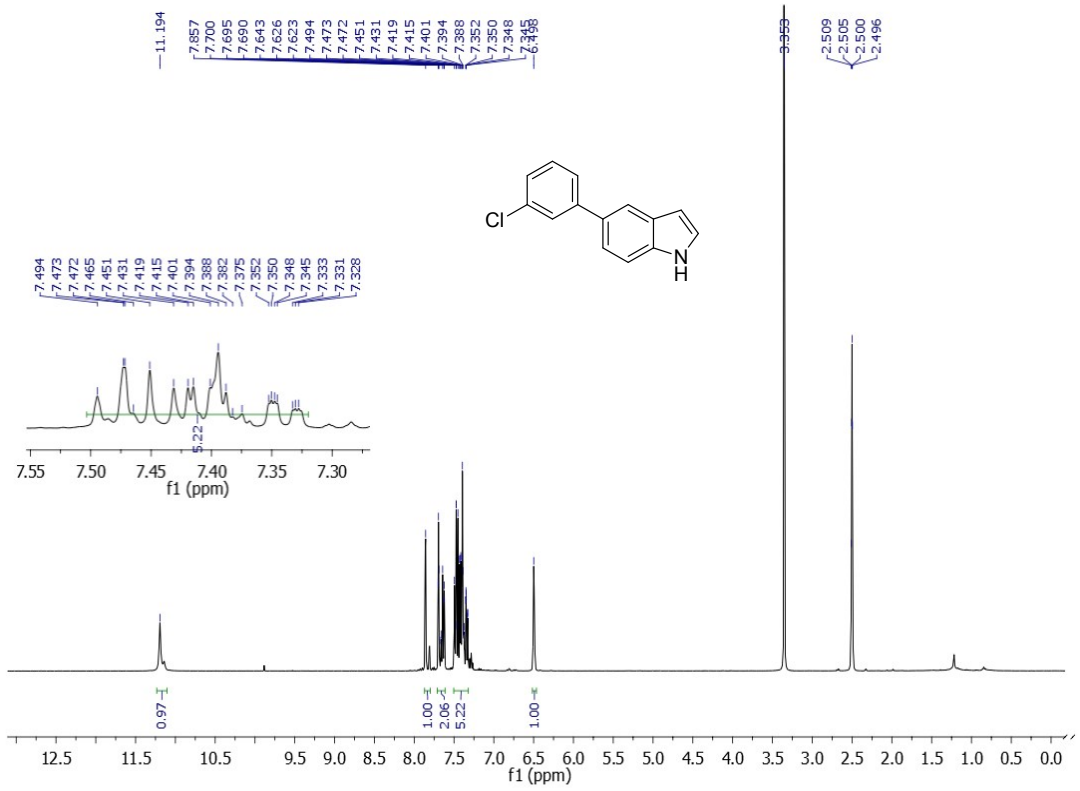

Fig. S61. ^{1}H NMR spectrum of 5-(3-Chlorophenyl)-1H-indole **(1q').**

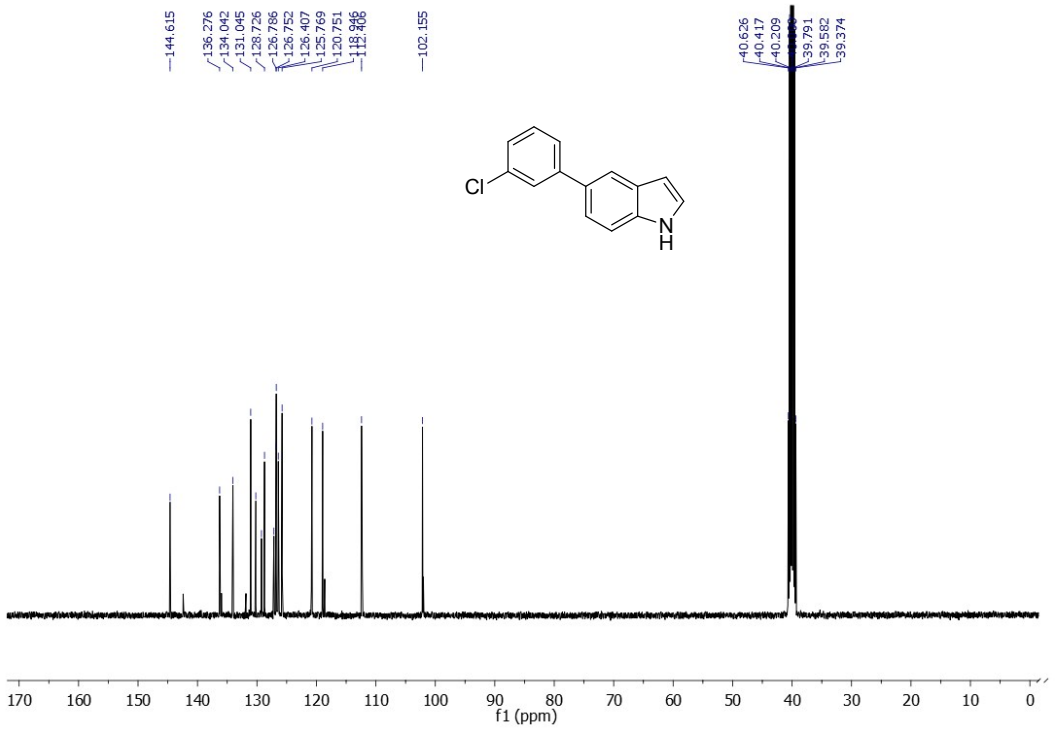

Fig. S62. ^{13}C NMR spectrum of 5-(3-Chlorophenyl)-1H-indole **(1q').**

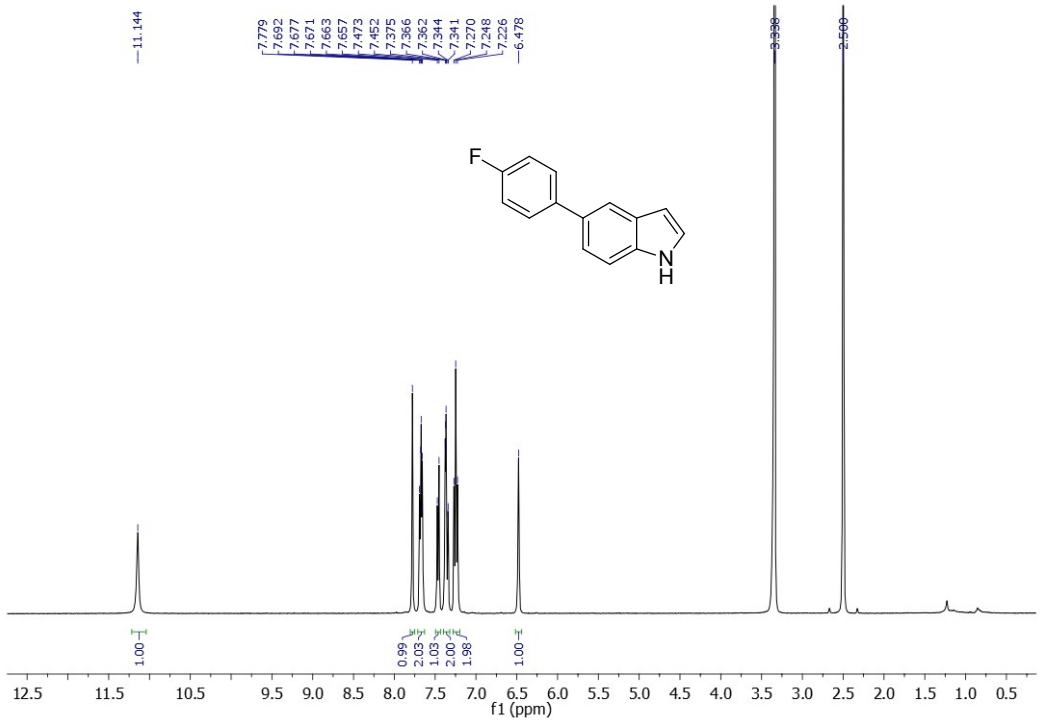

Fig. S63. ^{1}H NMR spectrum of 5-(4-Fluorophenyl)-1H-indole **(1r').**

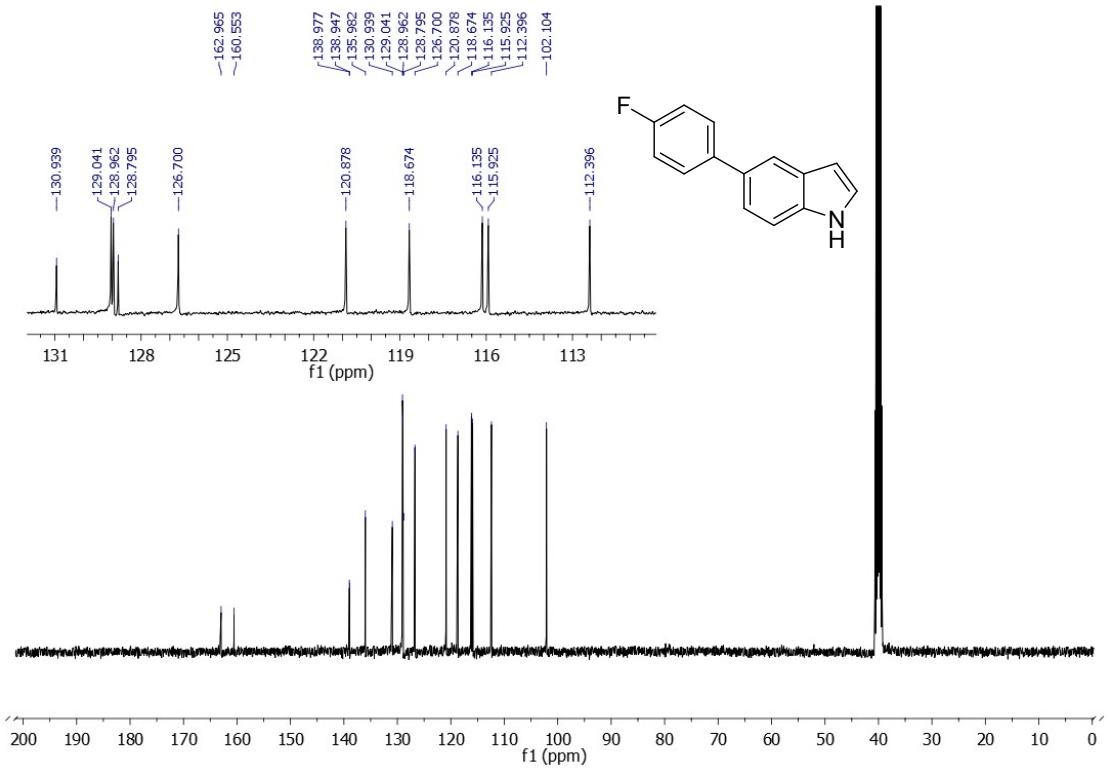

Fig. S64. ^{13}C NMR spectrum of 5-(4-Fluorophenyl)-1H-indole **(1r').**

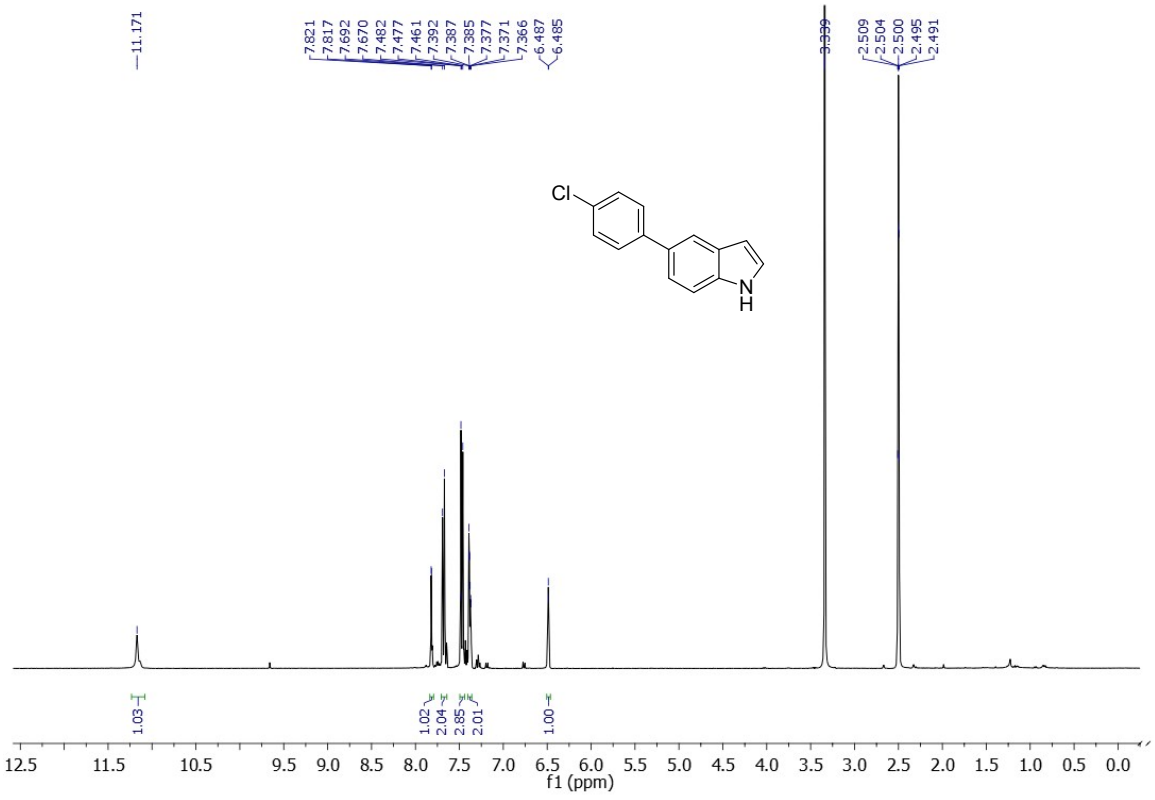

Fig. S65. ^{1}H NMR spectrum of 5-(4-Chlorophenyl)-1H-indole **(1s').**

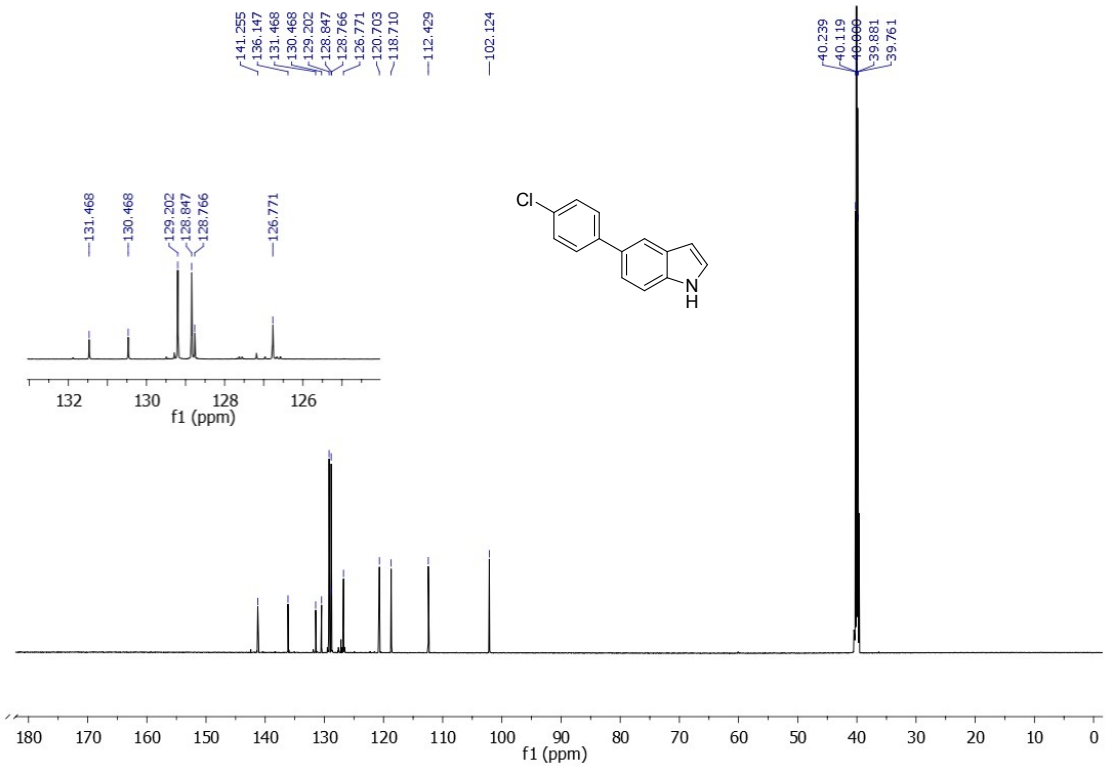

Fig. S66. 13C NMR spectrum of 5-(4-Chlorophenyl)-1H-indole **(1s').**

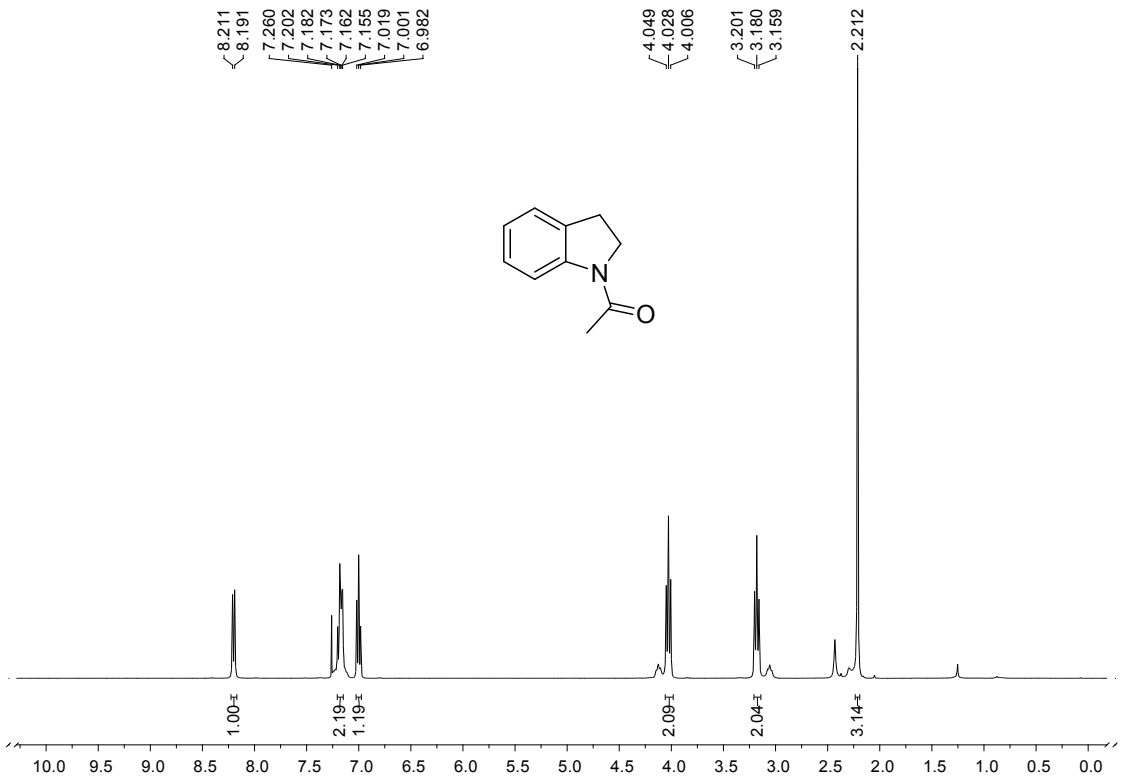

Fig. S67. [1]H NMR spectrum of 1-(Indolin-1-yl)ethanone **(1a).**

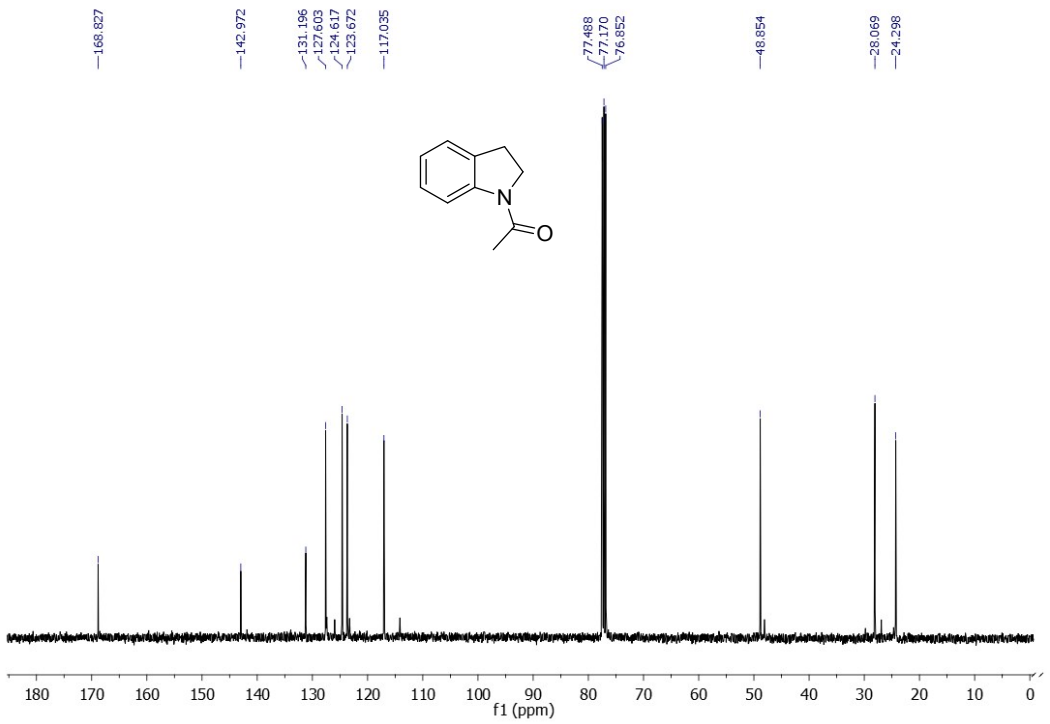

Fig. S68. ^{13}C NMR spectrum of 1-(Indolin-1-yl)ethanone **(1a).**

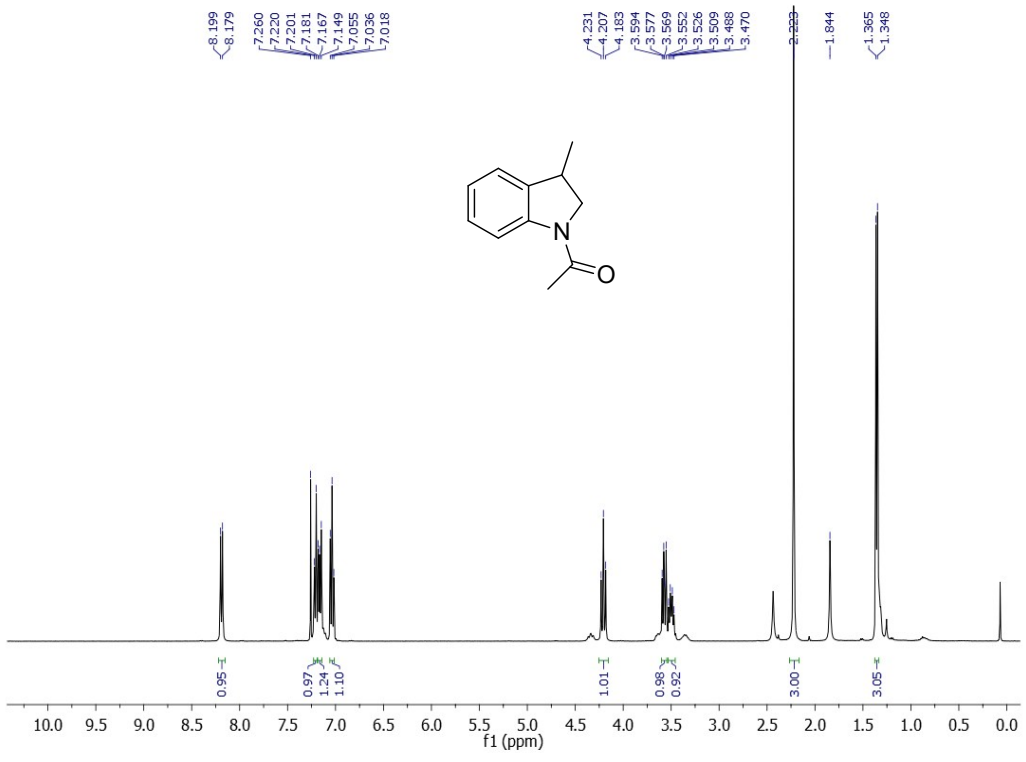

Fig. S69. ^{1}H NMR spectrum of 1-(3-Methylindolin-1-yl)ethanone **(1b).**

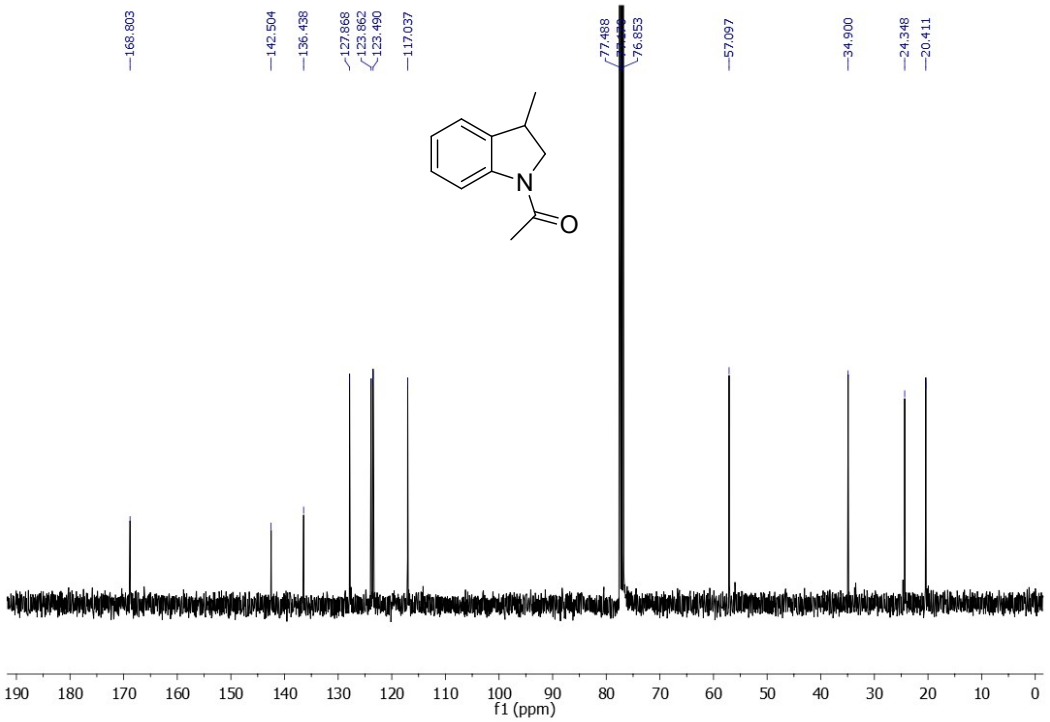

Fig. S70: ^{13}C NMR spectrum of 1-(3-Methylindolin-1-yl)ethanone **(1b).**

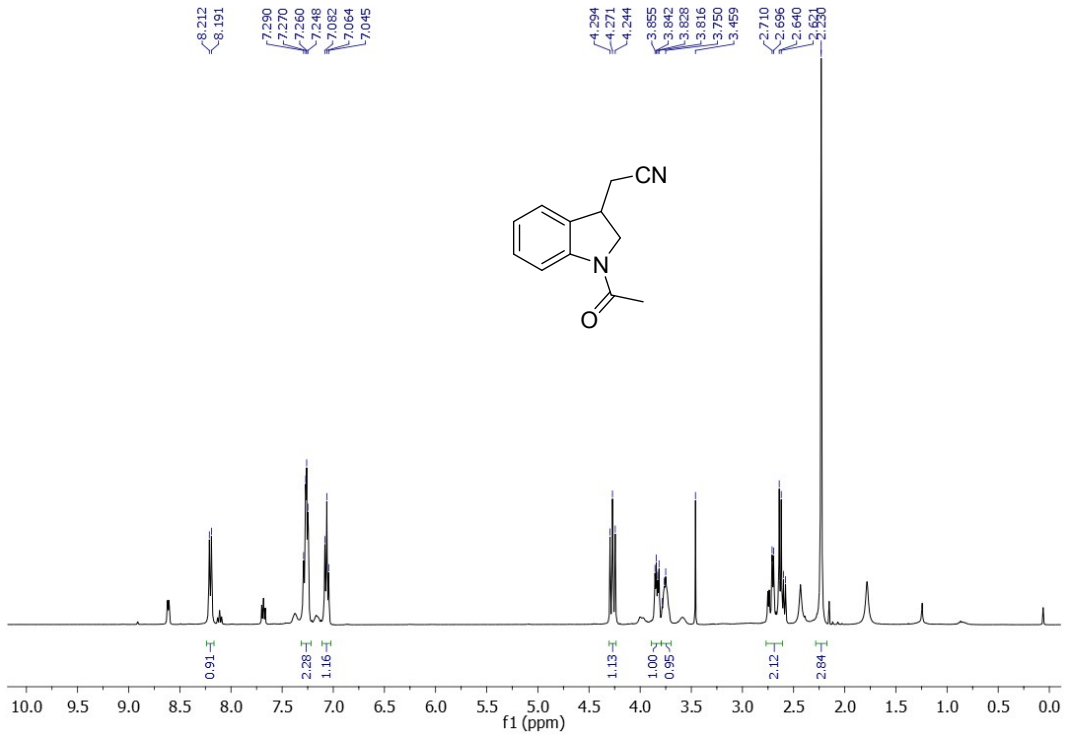

Fig. S71. ^{1}H NMR spectrum of 2-(1-Acetylindolin-3-yl)acetonitrile **(1c).**

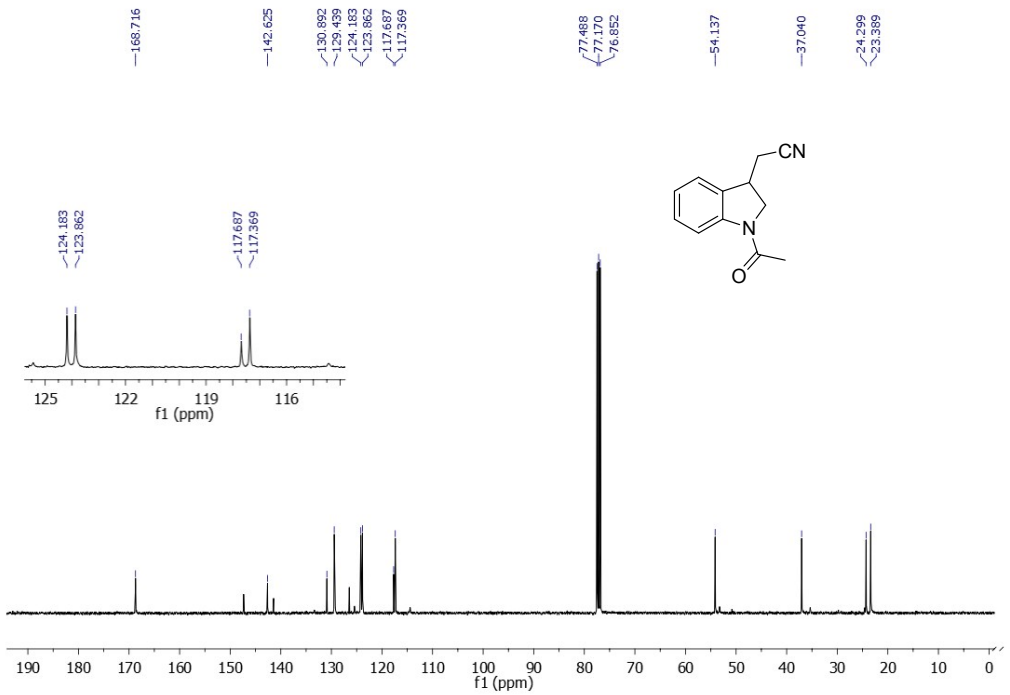

Fig. S72. ^{13}C NMR spectrum of 2-(1-Acetylindolin-3-yl)acetonitrile **(1c).**

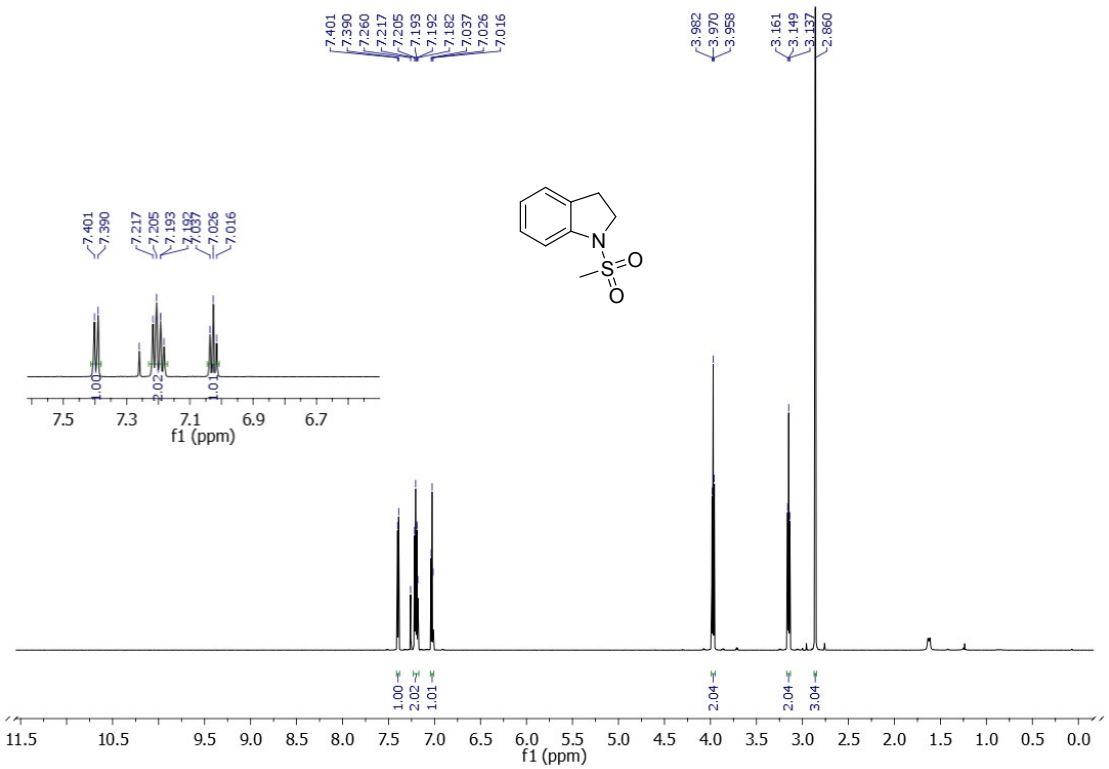

Fig. S73. ^{1}H NMR spectrum of 1-(Methylsulfonyl)indoline **(1d).**

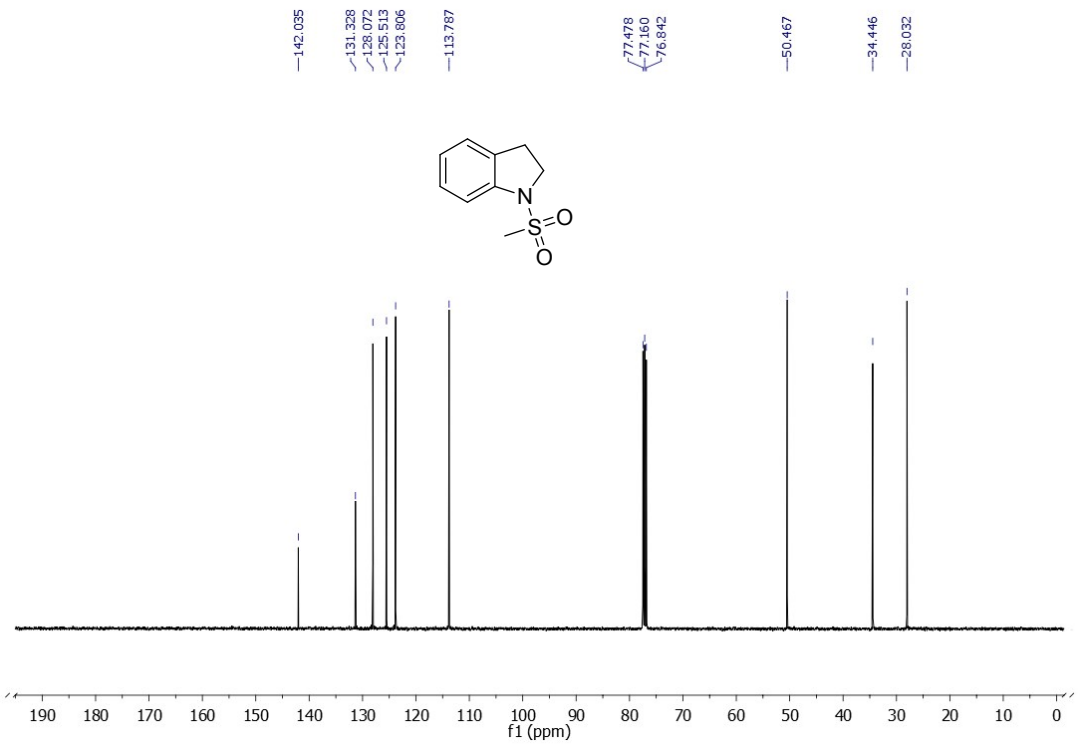

Fig. S74. ^{13}C NMR spectrum of 1-(Methylsulfonyl)indoline **(1d).**

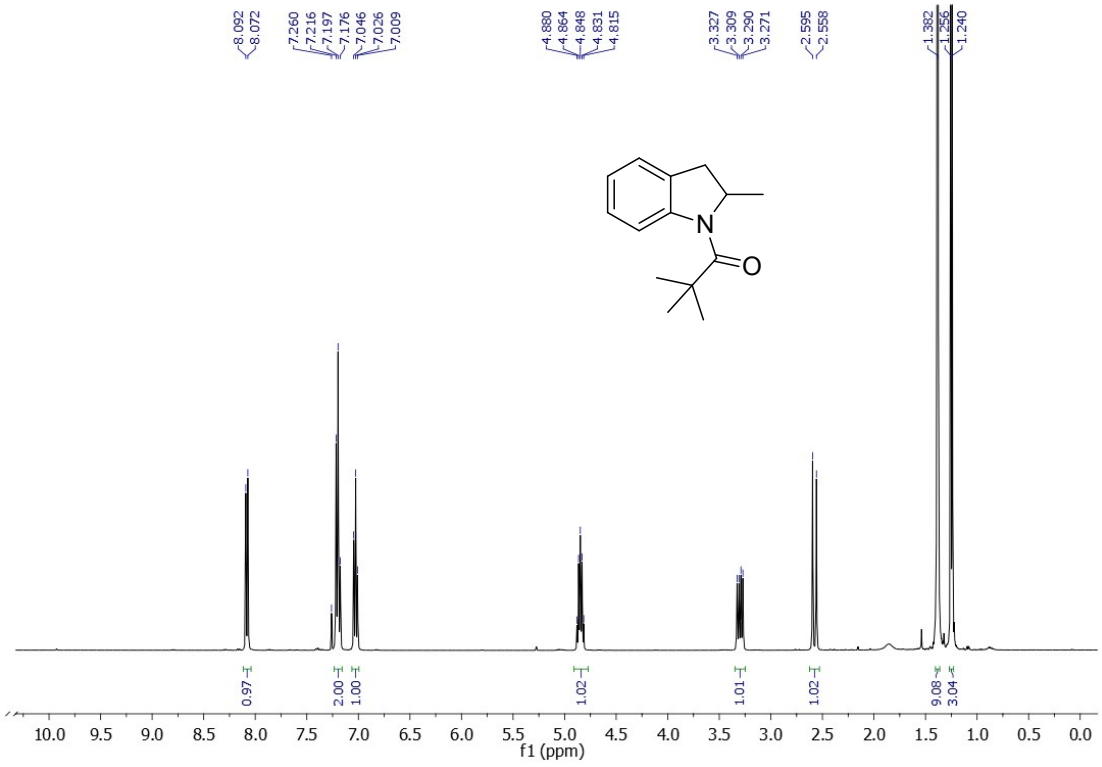

Fig. S75. ^{1}H NMR spectrum of 2,2-Dimethyl-1-(2-methylindolin-1-yl)propan-1-one **(1e).**

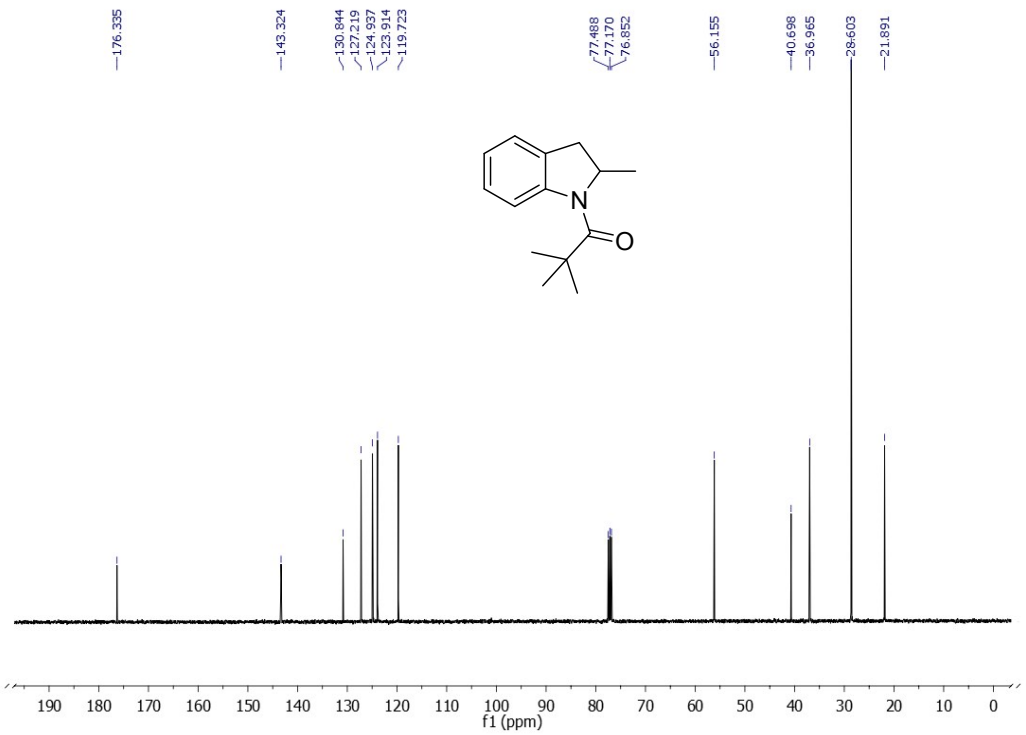

Fig. S76. ^{13}C NMR spectrum of 2,2-Dimethyl-1-(2-methylindolin-1-yl)propan-1-one **(1e).**

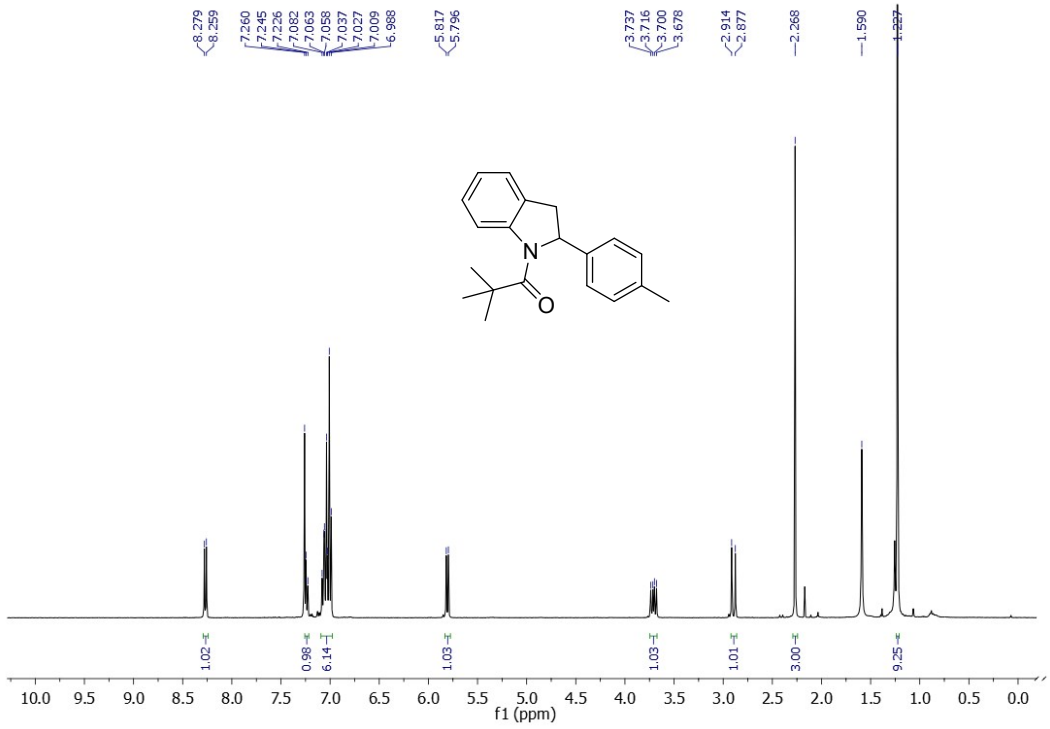

Fig. S77. ^{1}H NMR spectrum of 2,2-Dimethyl-1-(2-(p-tolyl)indolin-1-yl)propan-1-one **(1f).**

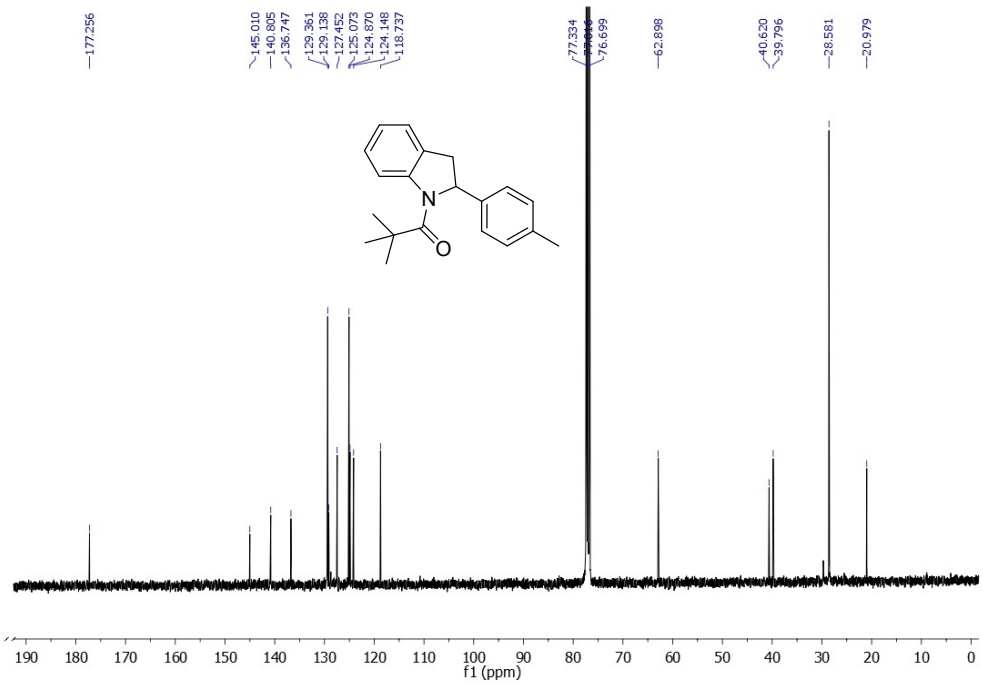

Fig. S78. ^{13}C NMR spectrum of 2,2-Dimethyl-1-(2-(p-tolyl)indolin-1-yl)propan-1-one **(1f).**

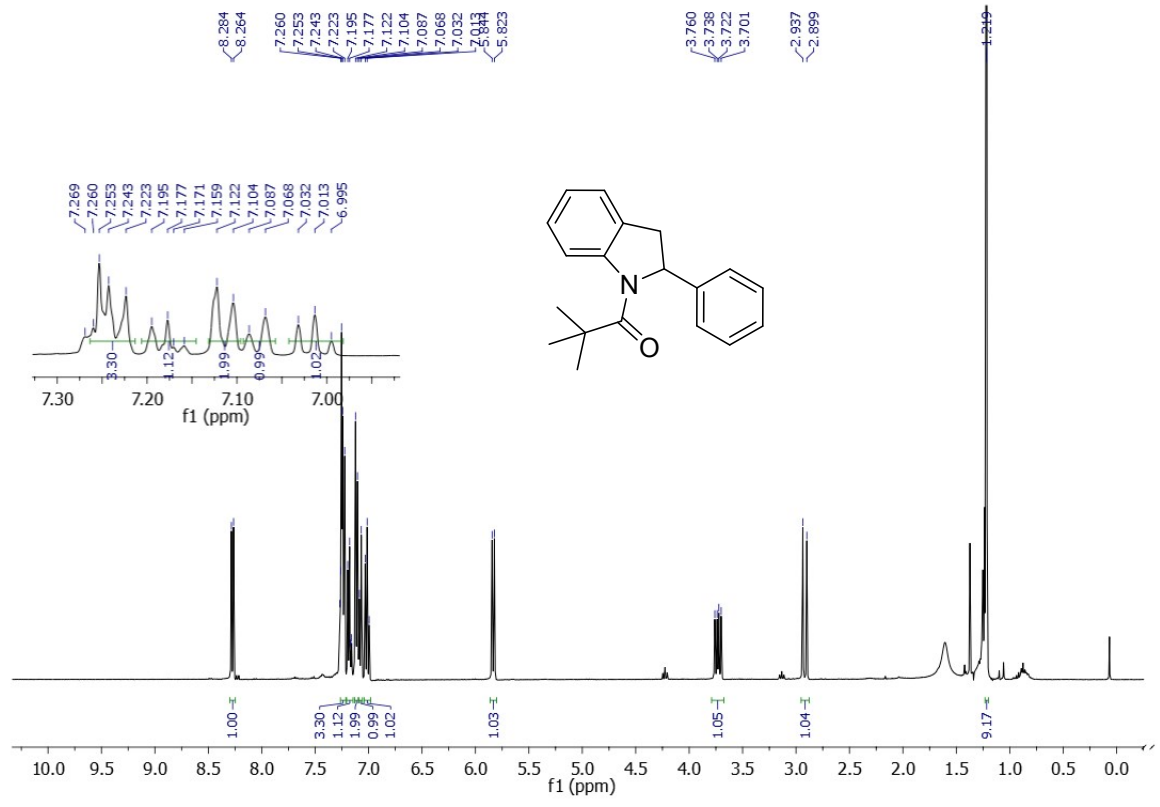

Fig. S79. ^{1}H NMR spectrum of 2,2-Dimethyl-1-(2-phenylindolin-1-yl)propan-1-one **(1g).**

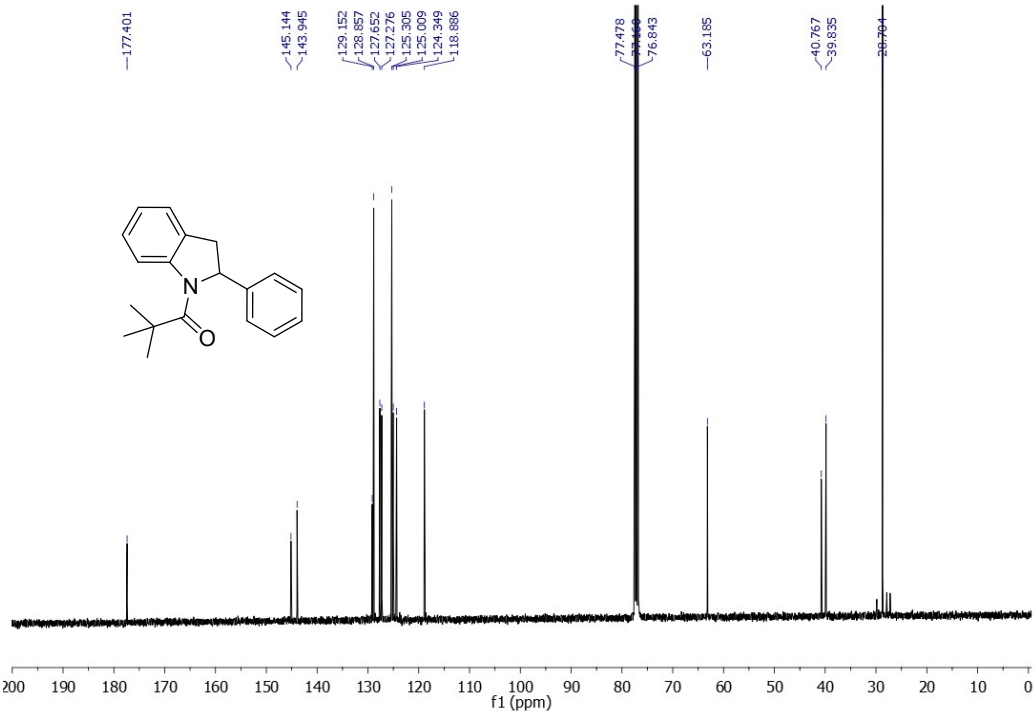

Fig. S80. ^{13}C NMR spectrum of 2,2-Dimethyl-1-(2-phenylindolin-1-yl)propan-1-one **(1g).**

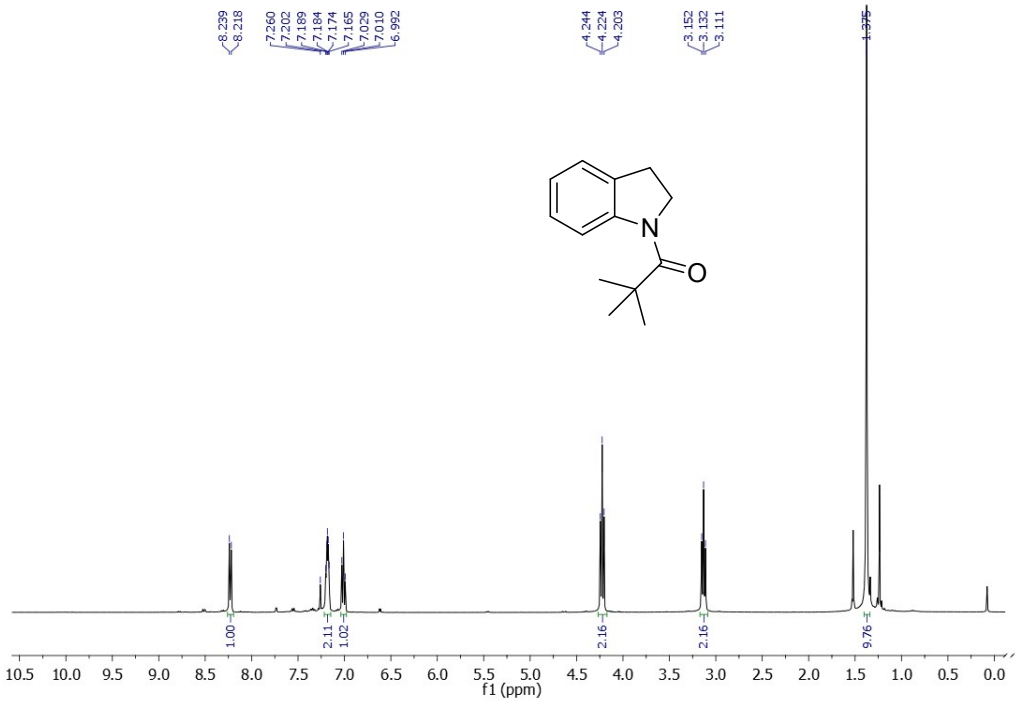

Fig. S81. ^{1}H NMR spectrum of 1-(Indolin-1-yl)-2,2-dimethylpropan-1-one **(1h).**

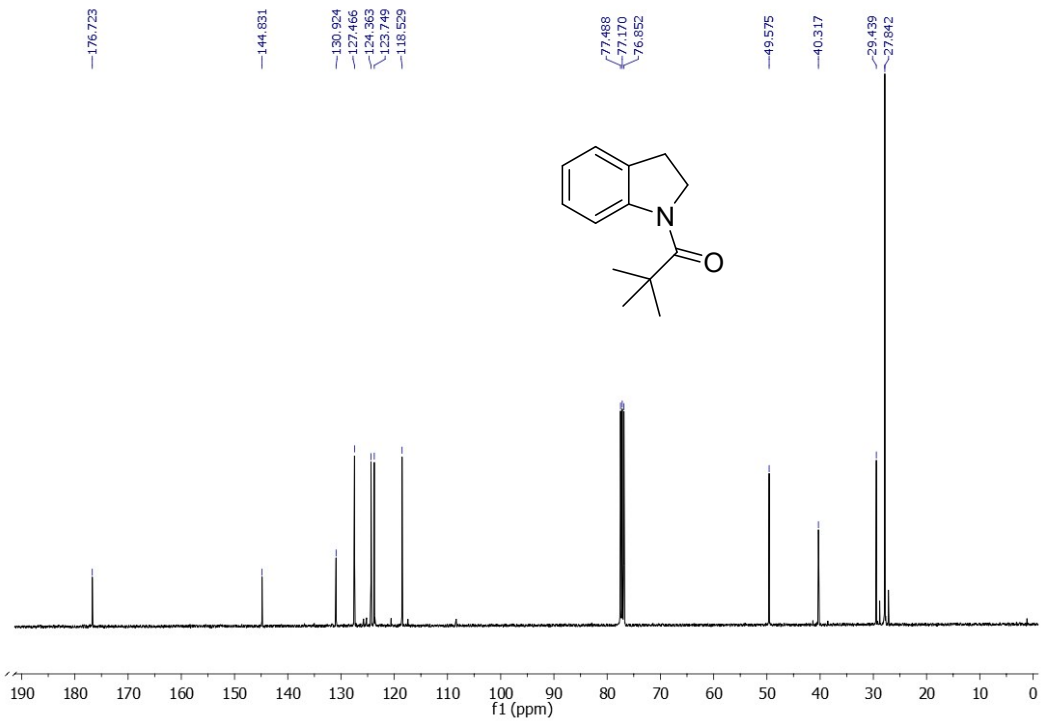

Fig. S82. ^{13}C NMR spectrum of 1-(Indolin-1-yl)-2,2-dimethylpropan-1-one **(1h).**

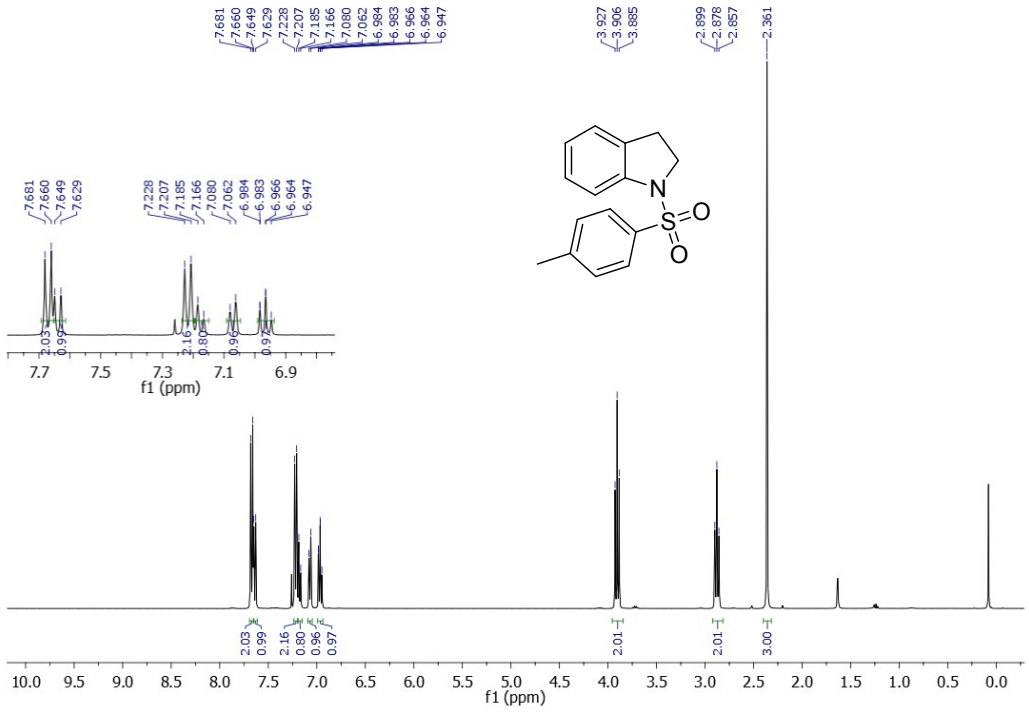

Fig. S83. ^{1}H NMR spectrum of 1-Tosylindoline **(1i).**

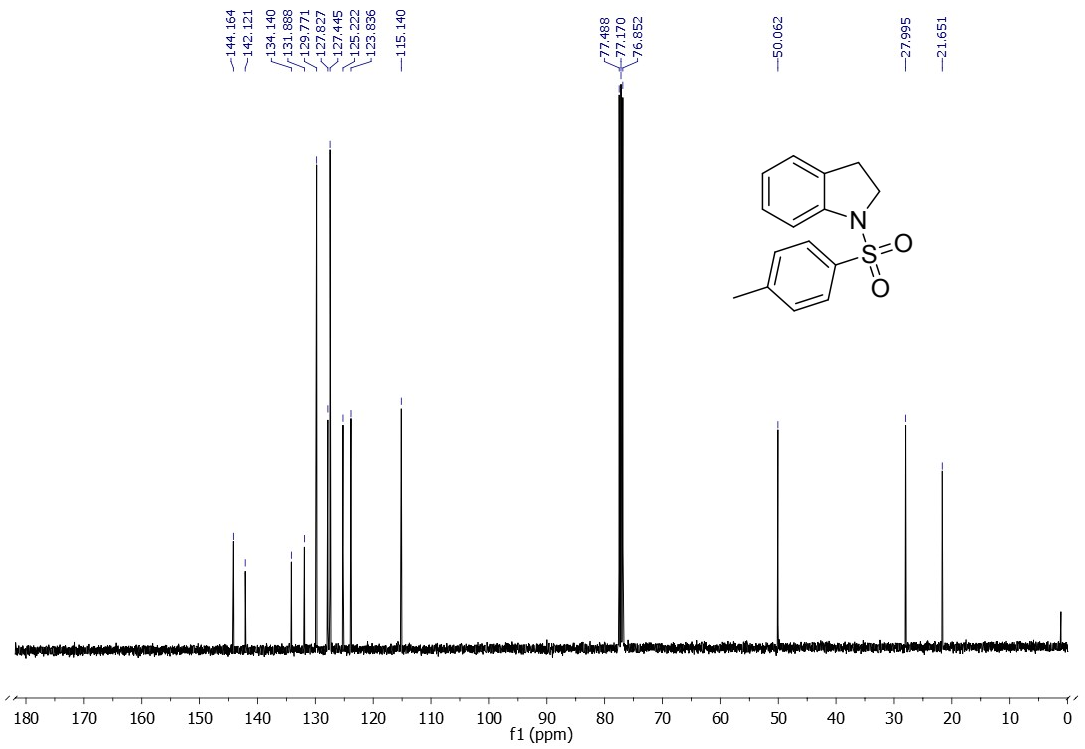

Fig. S84. ^{13}C NMR spectrum of 1-Tosylindoline **(1i).**

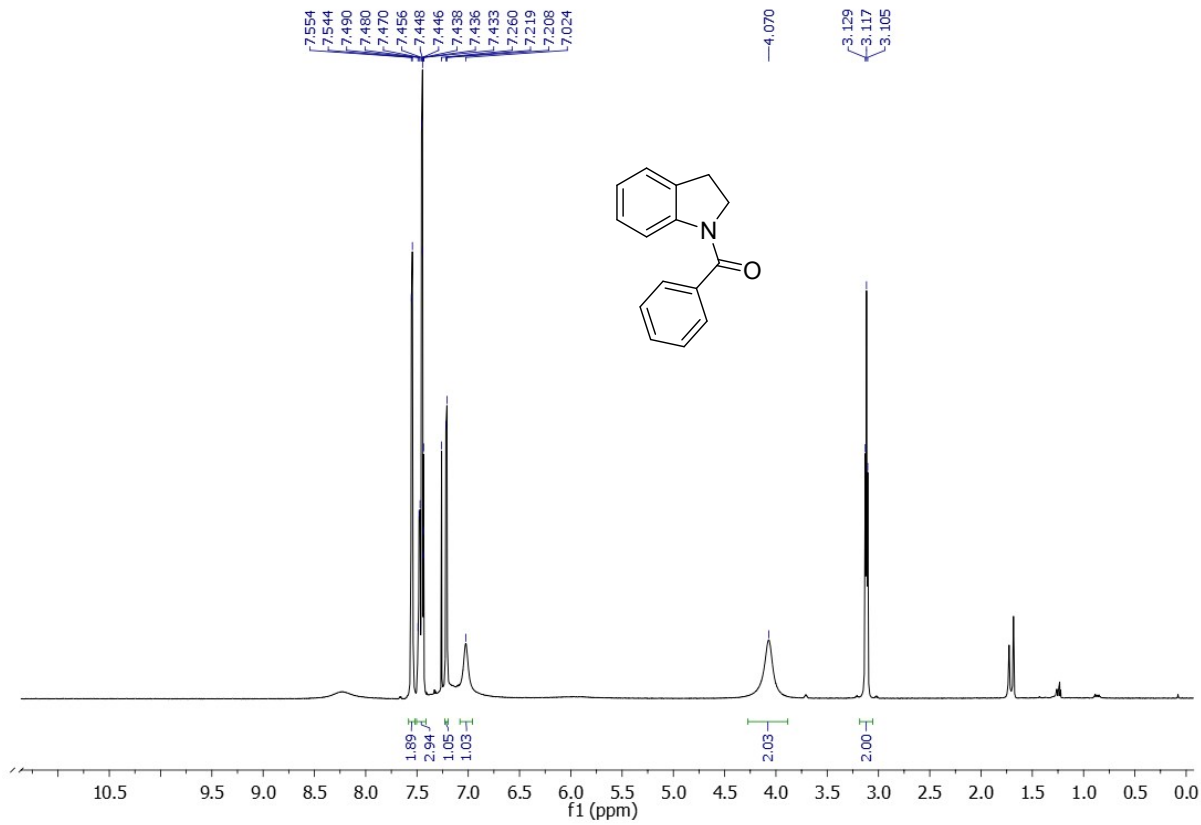

Fig. S85. ^{1}H NMR spectrum of Indolin-1-yl(phenyl)methanone **(1j).**

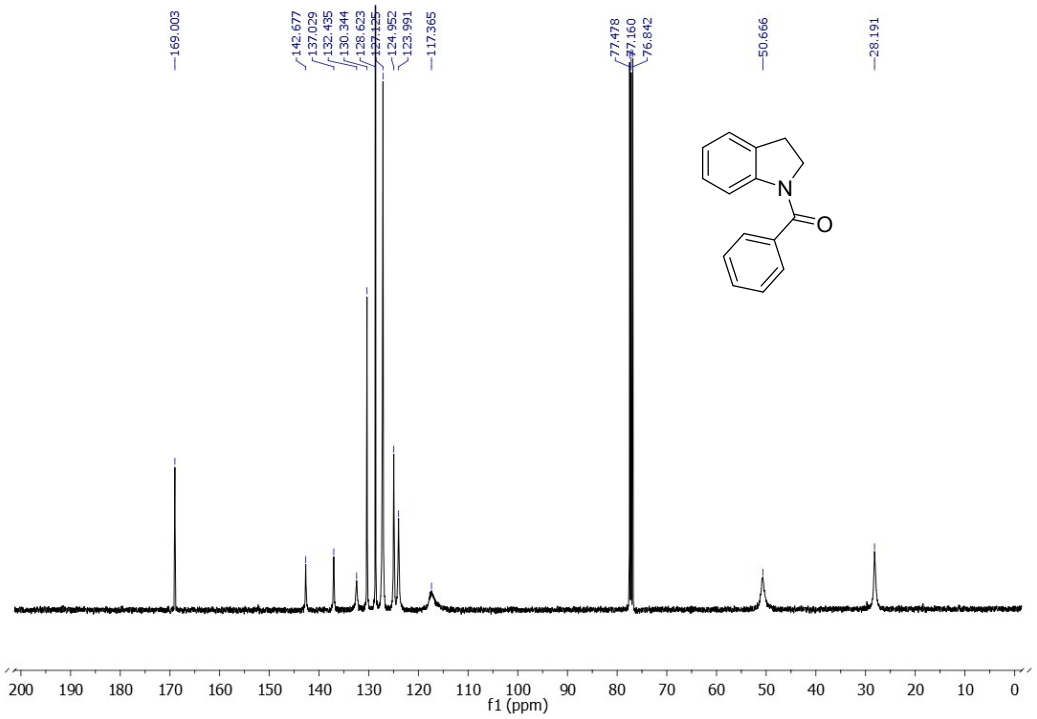

Fig. S86. ^{13}C NMR spectrum of Indolin-1-yl(phenyl)methanone **(1j).**

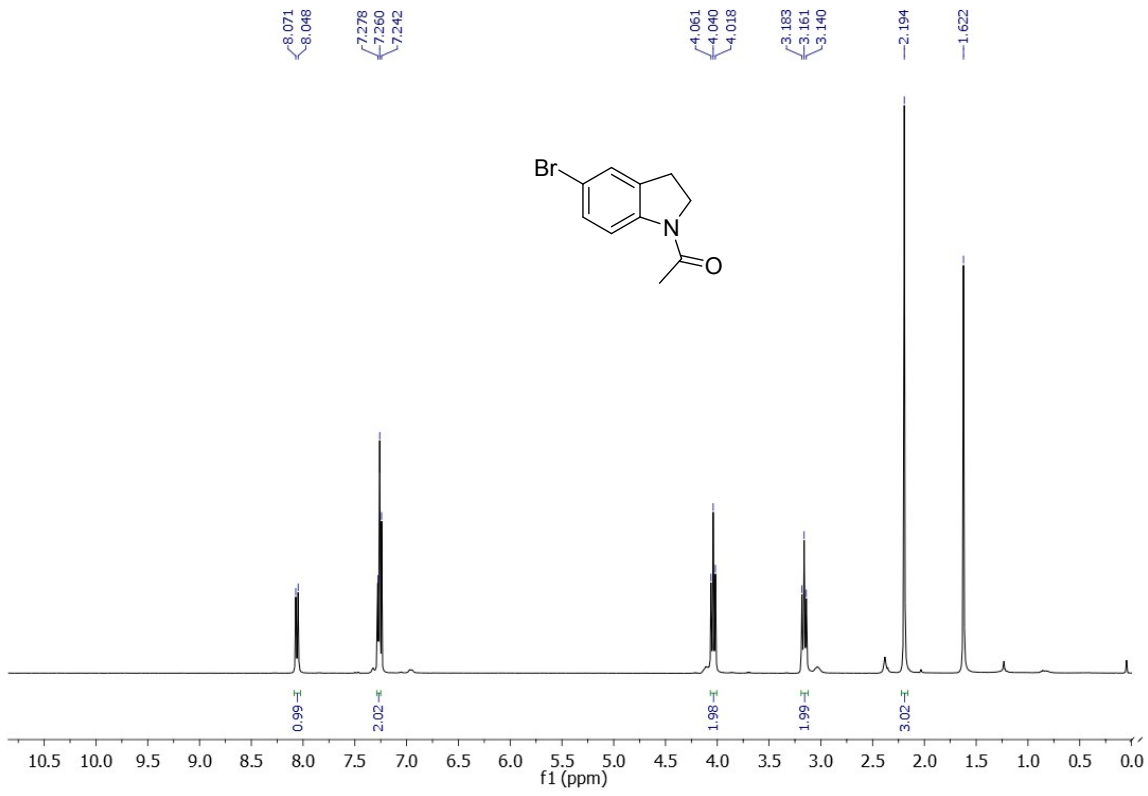

Fig. S87. ^{1}H NMR spectrum of 1-(5-Bromoindolin-1-yl)ethanone **(1l).**

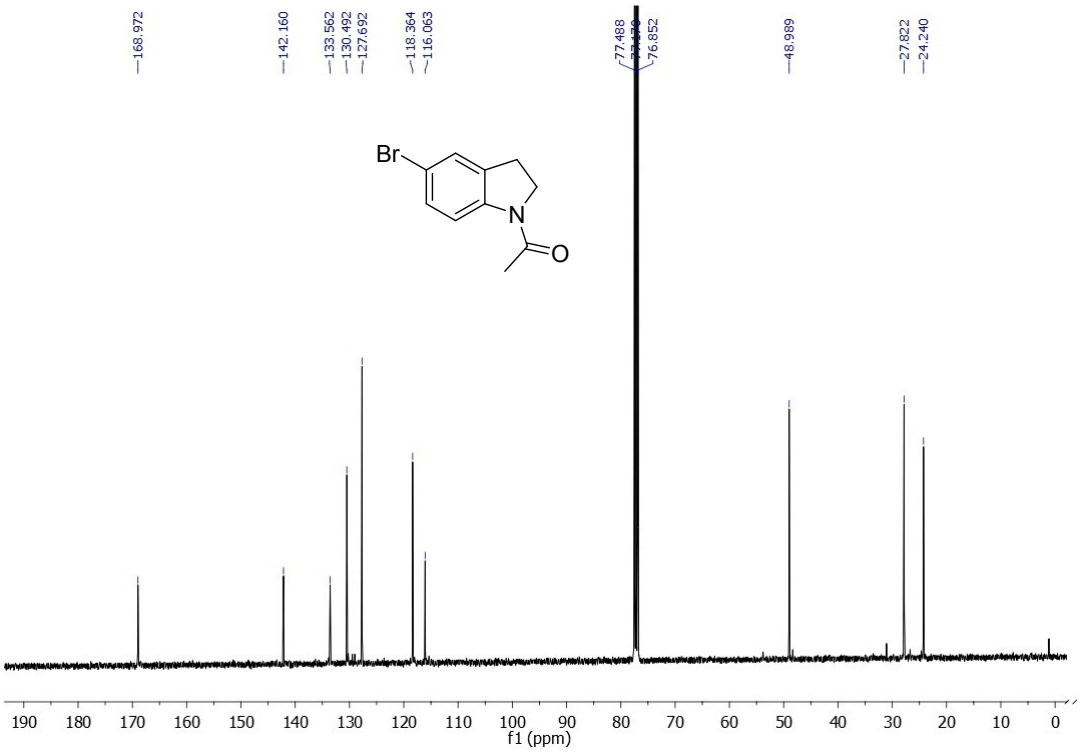

Fig. S88. ^{13}C NMR spectrum of 1-(5-Bromoindolin-1-yl)ethanone **(1l).**

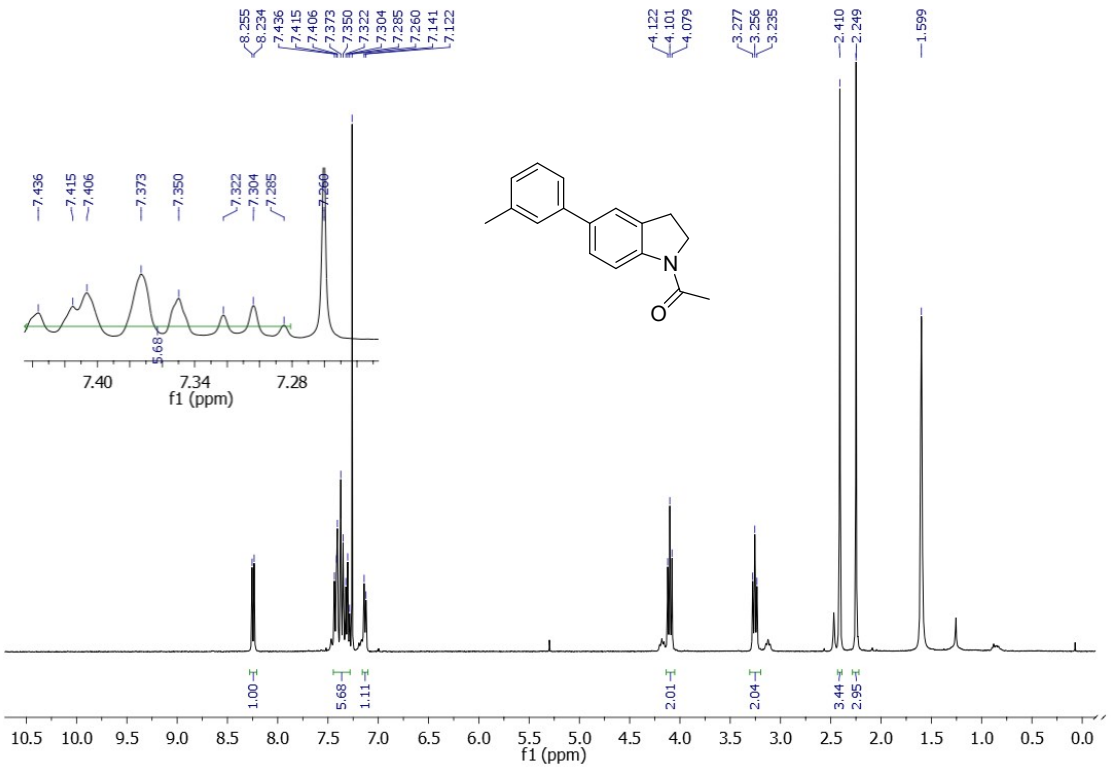

Fig. S89. ^{1}H NMR spectrum of 1-(5-(m-Tolyl)indolin-1-yl)ethanone **(1m).**

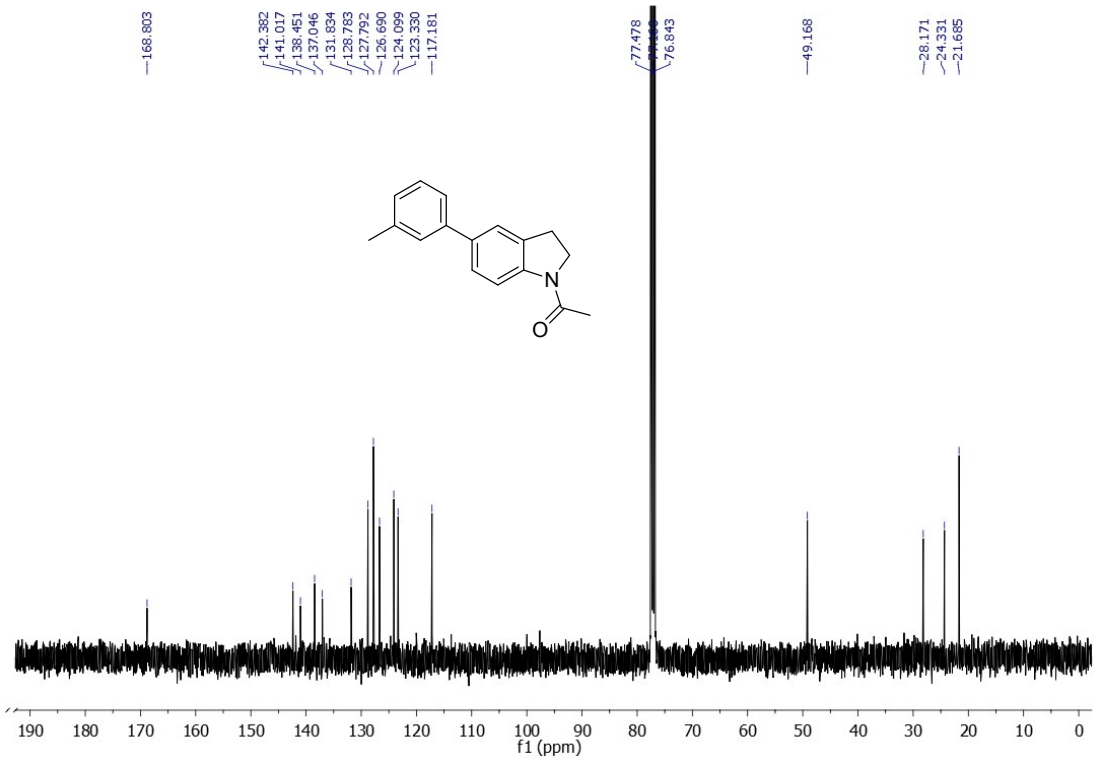

Fig. S90. ^{13}C NMR spectrum of 1-(5-(m-Tolyl)indolin-1-yl)ethanone **(1m).**

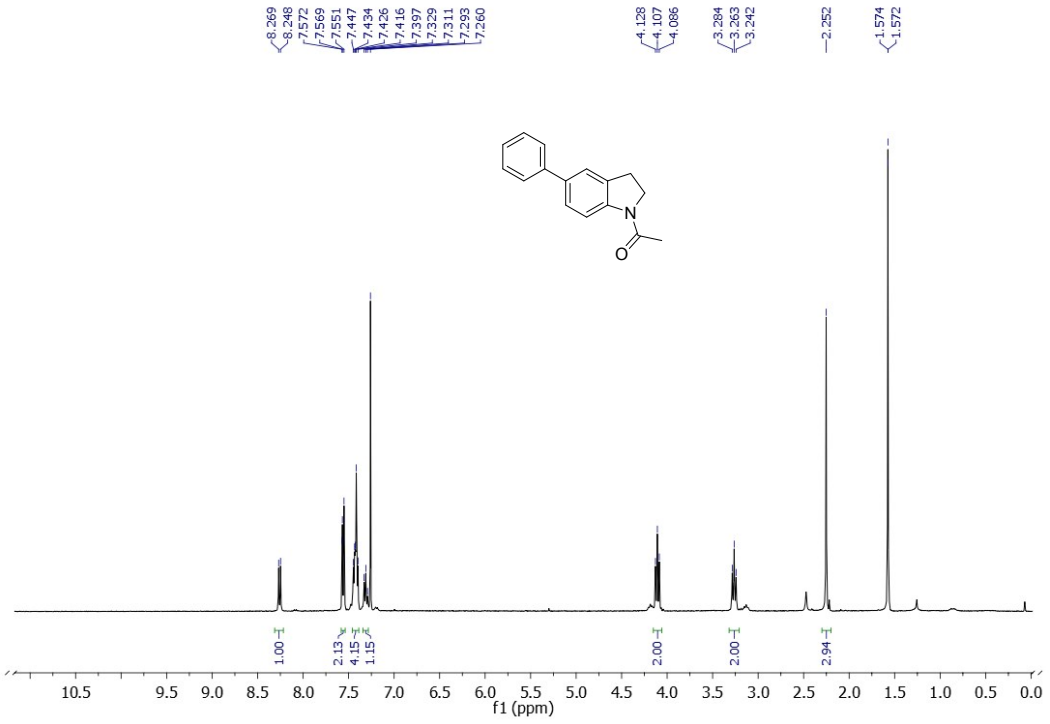

Fig. S91. ^{1}H NMR spectrum of 1-(5-Phenylindolin-1-yl)ethanone **(1n).**

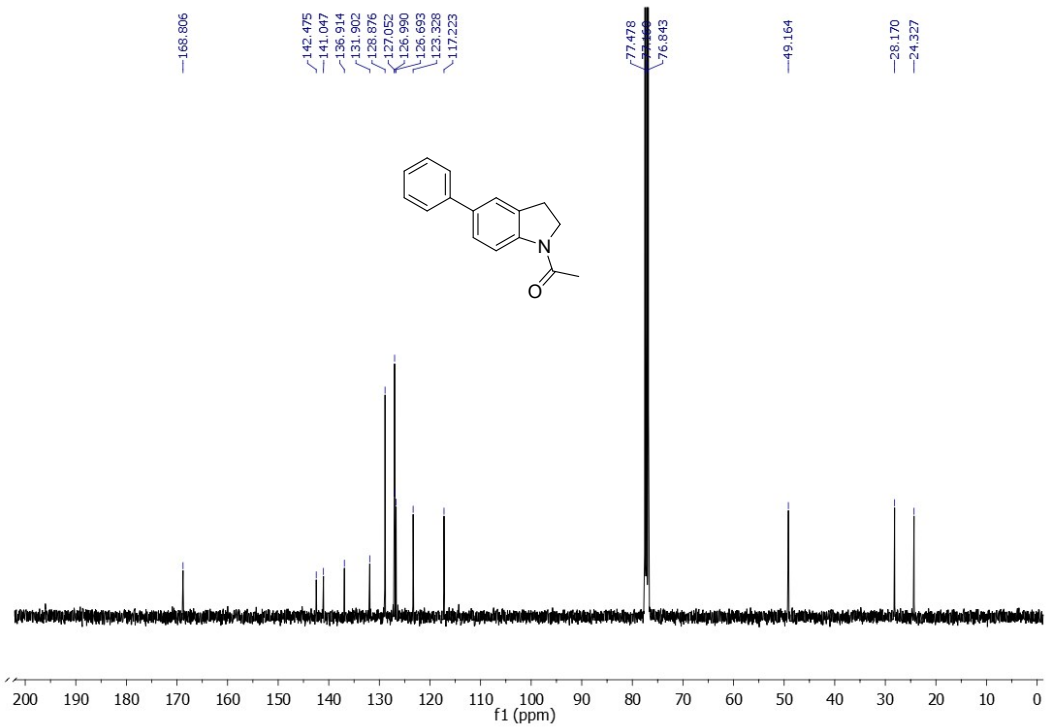

Fig. S92. ^{13}C NMR spectrum of 1-(5-Phenylindolin-1-yl)ethanone **(1n).**

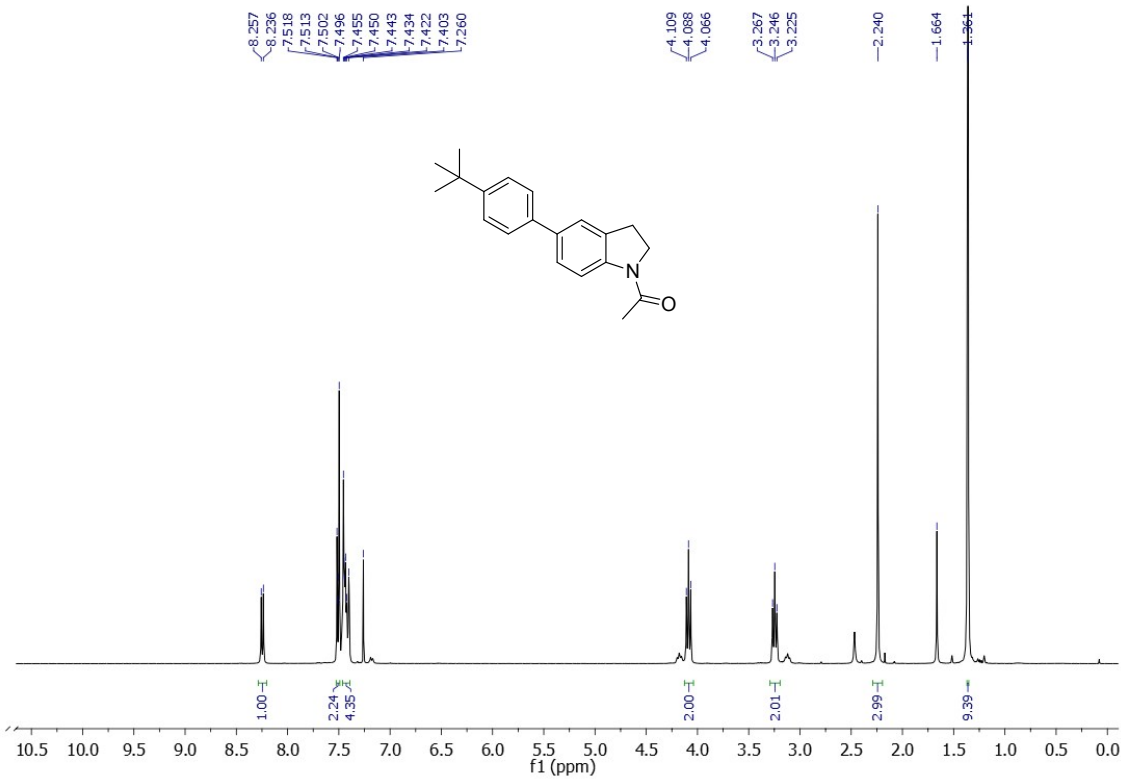

Fig. S93. ^{1}H NMR spectrum of 1-(5-(4-(tert-Butyl)phenyl)indolin-1-yl)ethanone **(1o).**

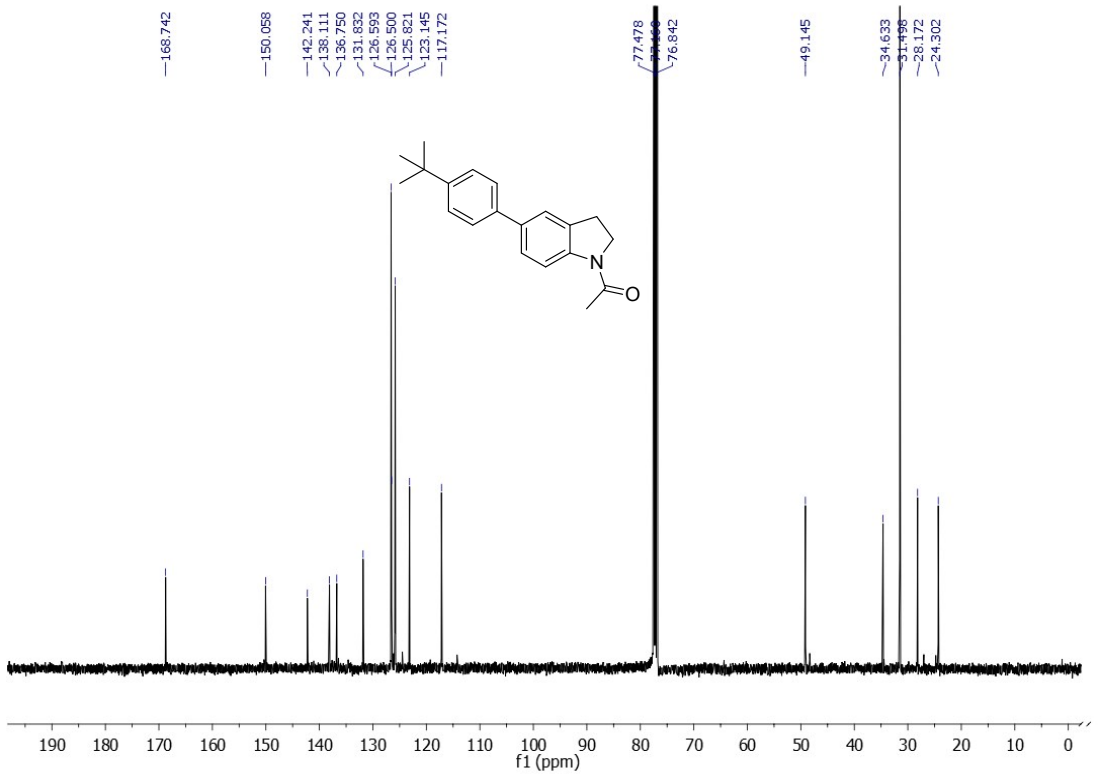

Fig. S94. ^{13}C NMR spectrum of 1-(5-(4-(tert-Butyl)phenyl)indolin-1-yl)ethanone **(1o).**

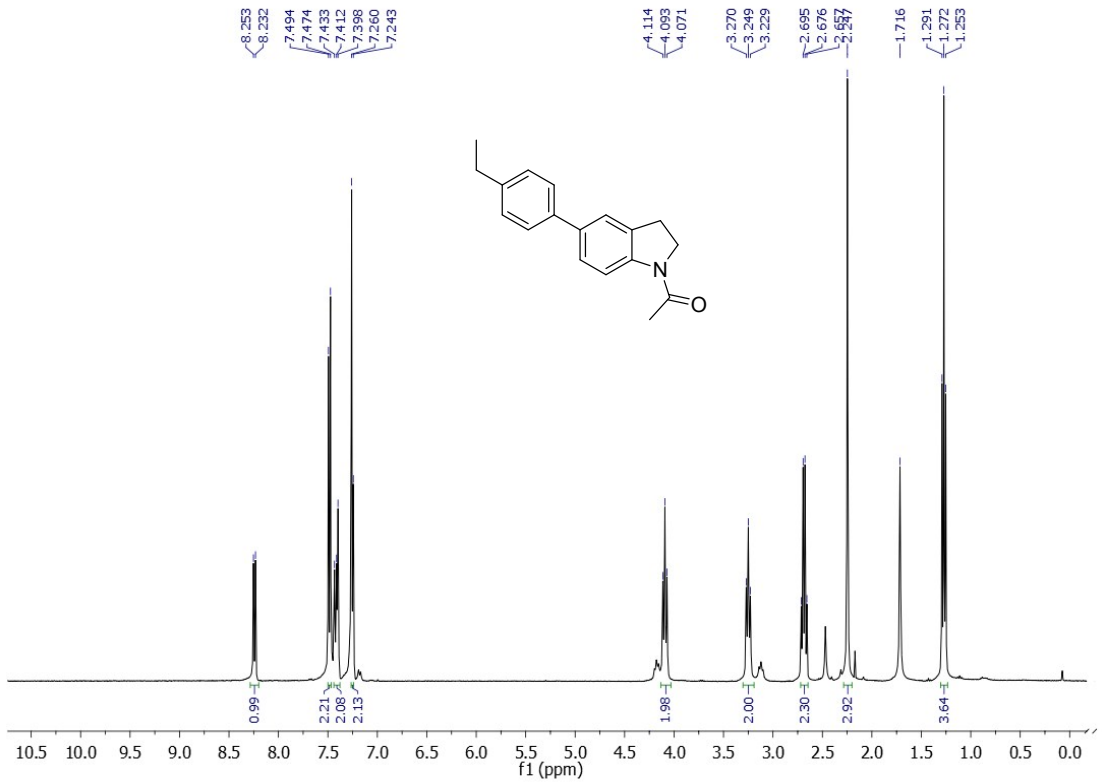

Fig. S95. ^{1}H NMR spectrum of 1-(5-(4-Ethylphenyl)indolin-1-yl)ethanone **(1p).**

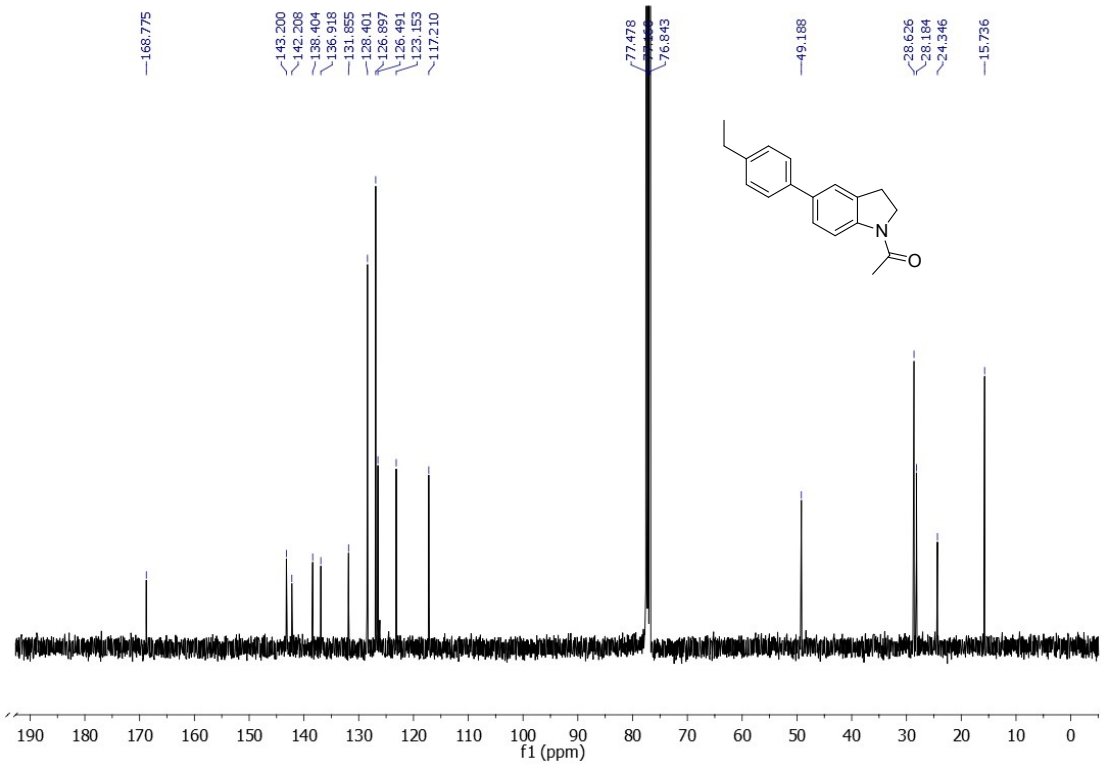

Fig. S96. ^{13}C NMR spectrum of 1-(5-(4-Ethylphenyl)indolin-1-yl)ethanone **(1p).**

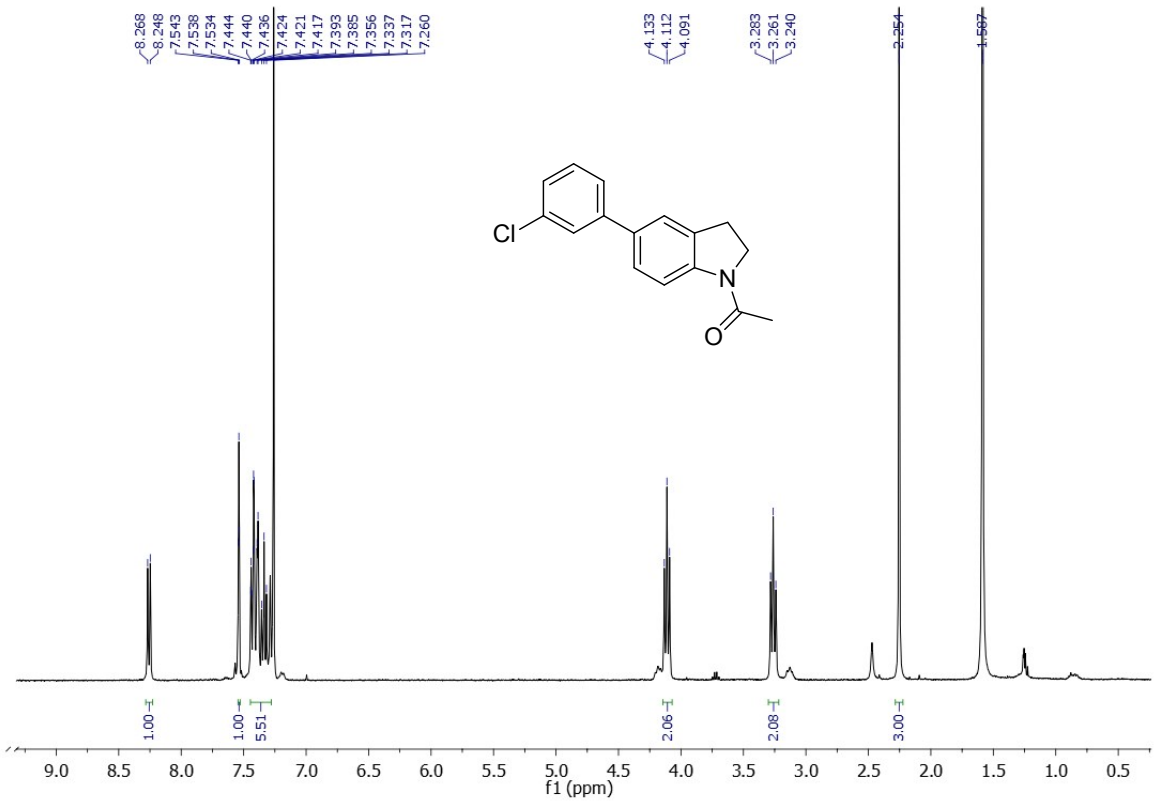

Fig. S97. ^{1}H NMR spectrum of 1-(5-(3-Chlorophenyl)indolin-1-yl)ethanone **(1q).**

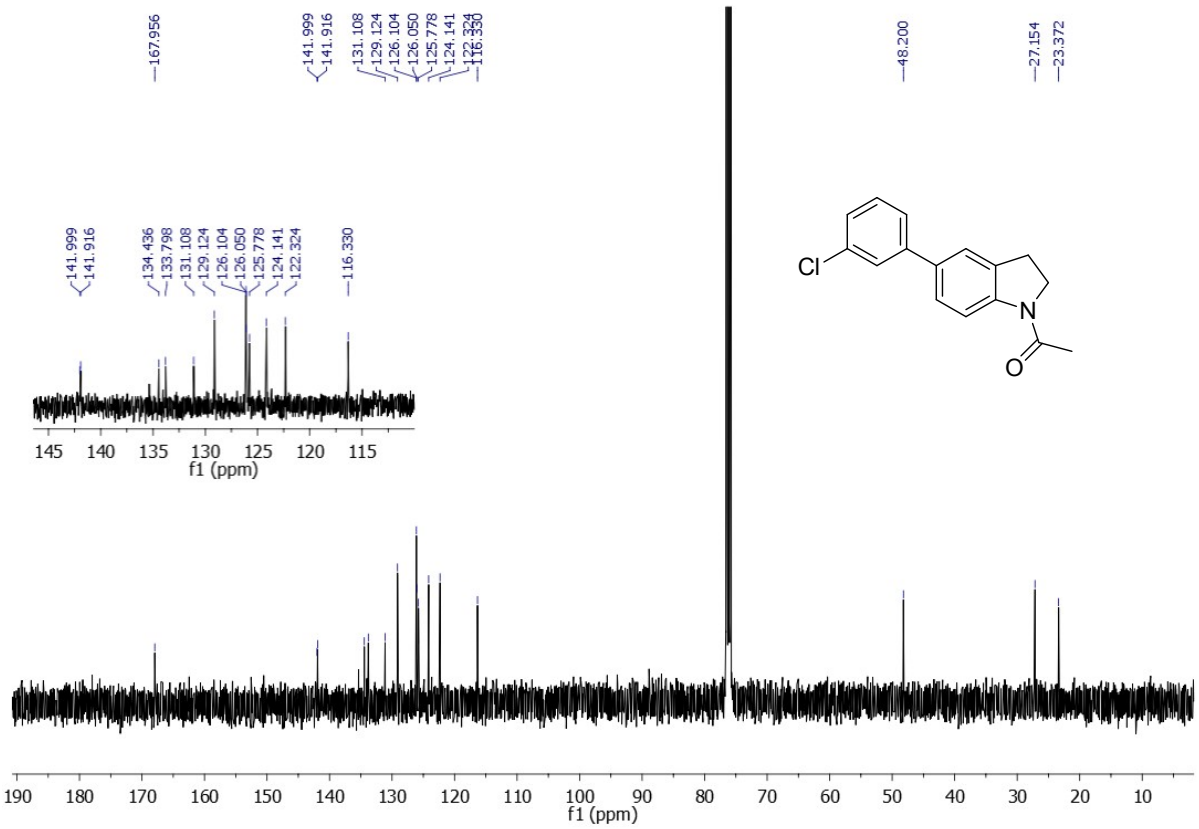

Fig. S98. ^{13}C NMR spectrum of 1-(5-(3-Chlorophenyl)indolin-1-yl)ethanone **(1q).**

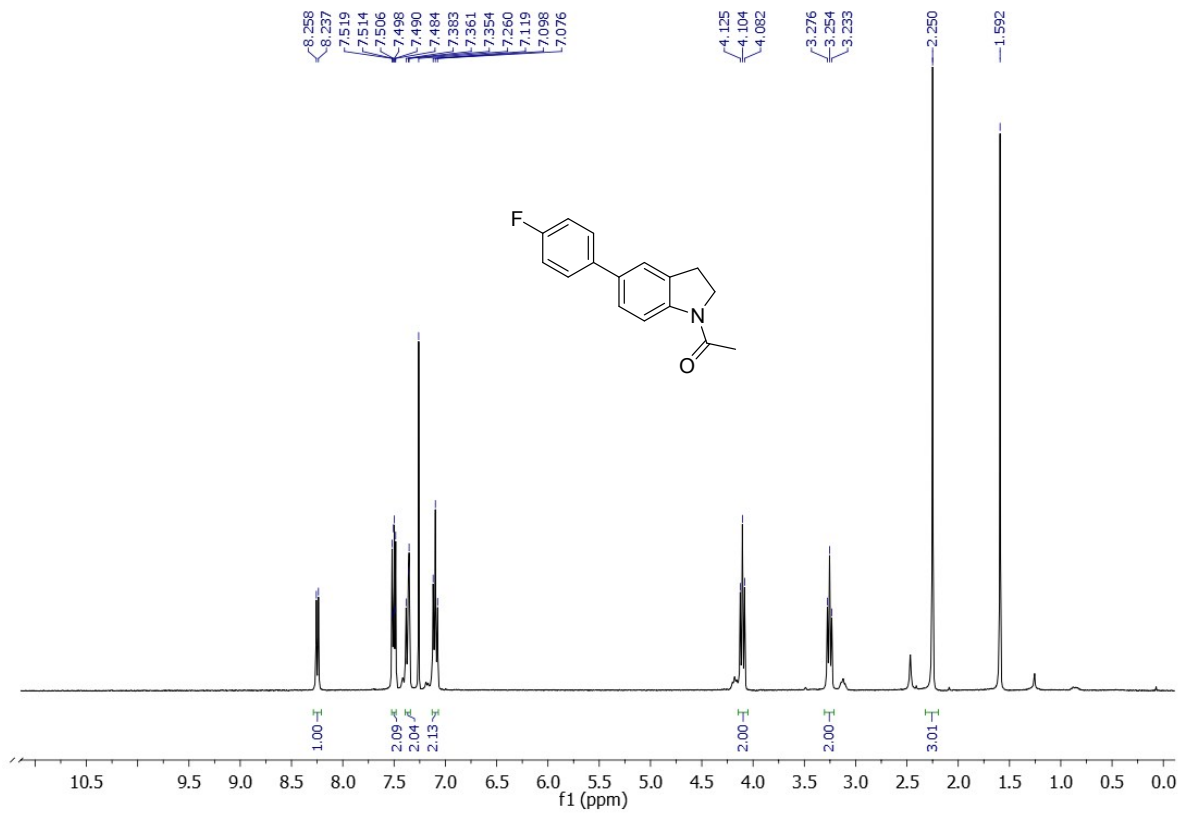

Fig. S99. ^{1}H NMR spectrum of 1-(5-(4-Fluorophenyl)indolin-1-yl)ethanone **(1r).**

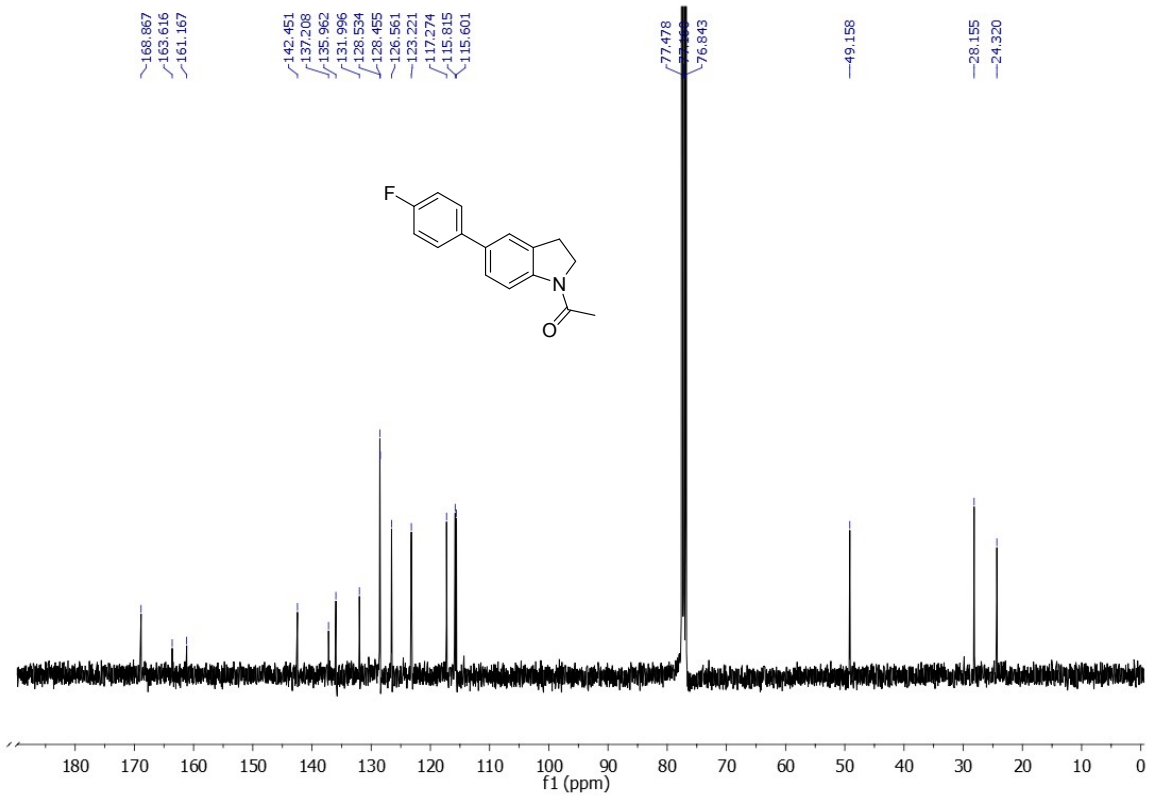

Fig. S100. ^{13}C NMR spectrum of 1-(5-(4-Fluorophenyl)indolin-1-yl)ethanone **(1r).**

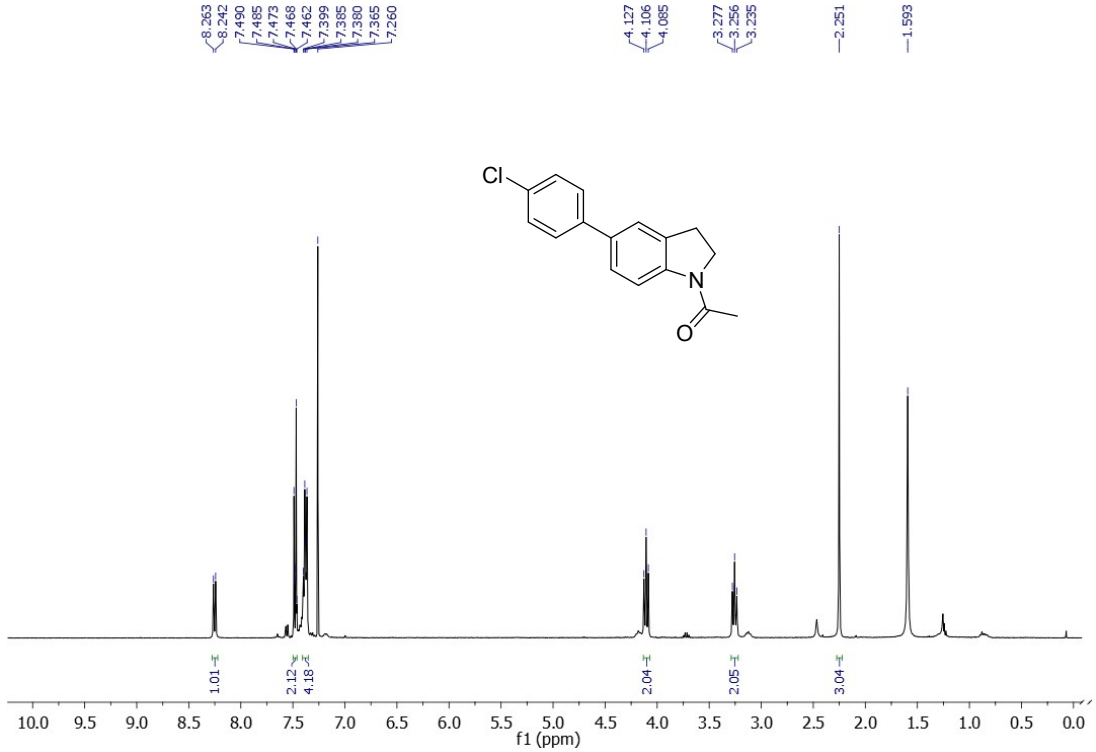

Fig. S101. ^{1}H NMR spectrum of 1-(5-(4-Chlorophenyl)indolin-1-yl)ethanone **(1s).**

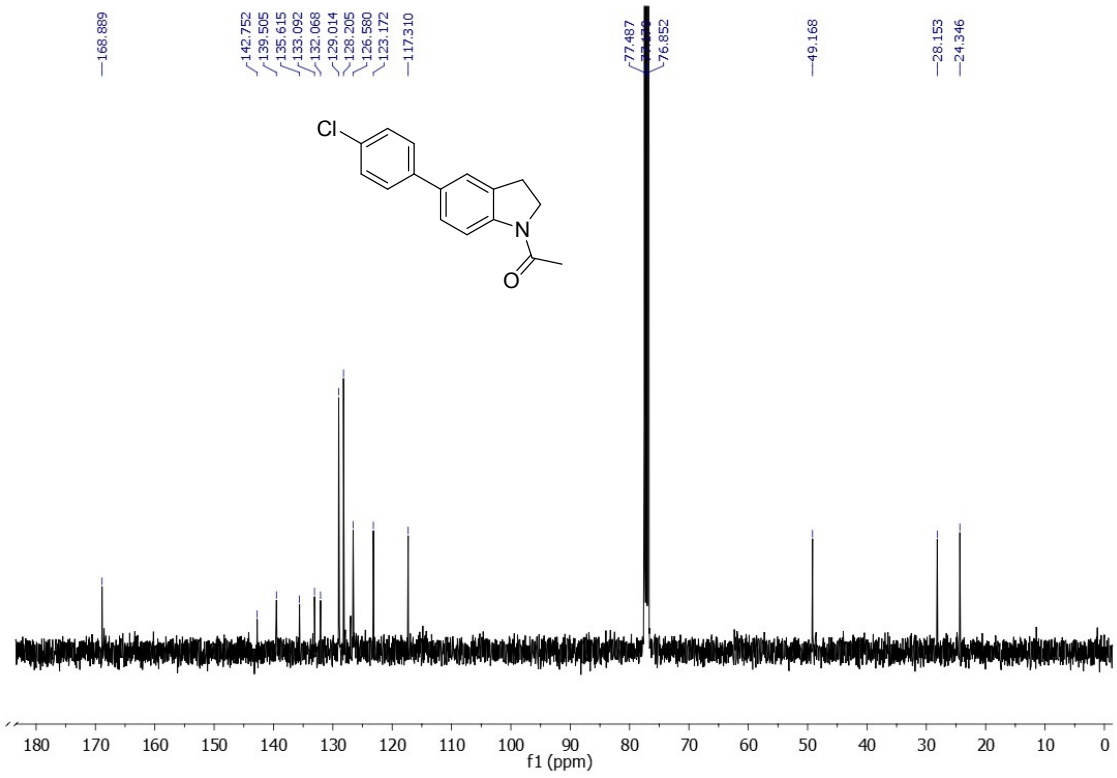

Fig. S102. ^{13}C NMR spectrum of 1-(5-(4-Chlorophenyl)indolin-1-yl)ethanone **(1s).**

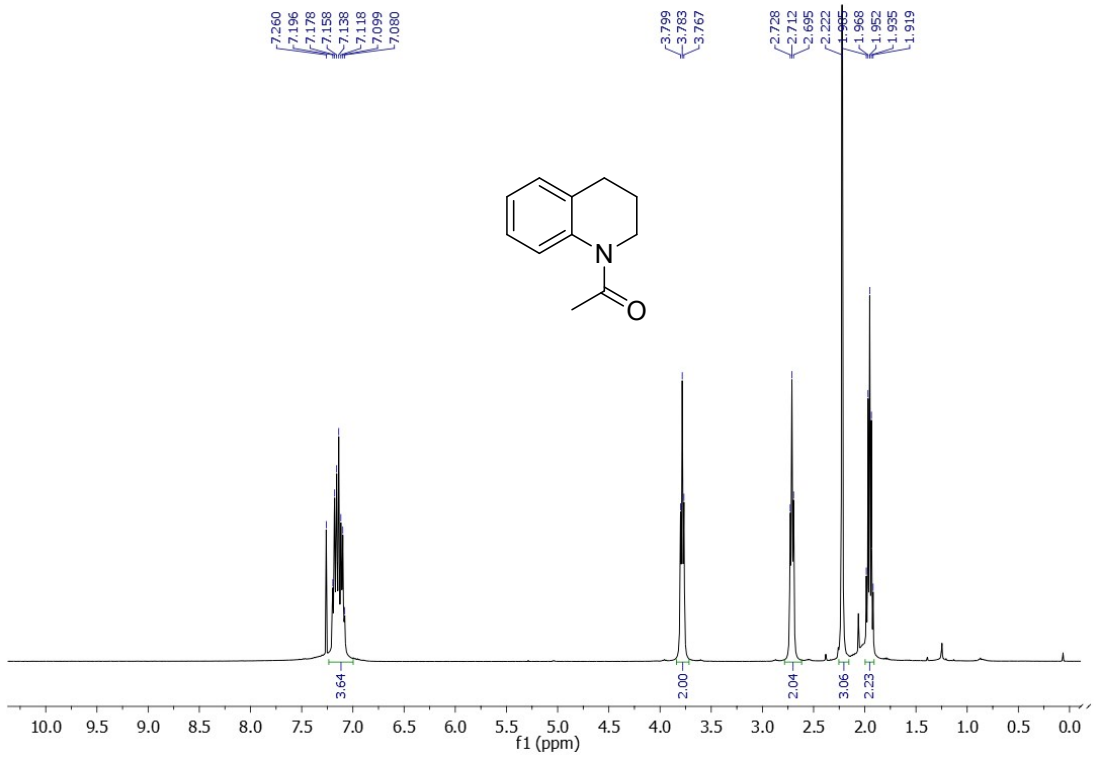

Fig. S103. ^{1}H NMR spectrum of 1-(3,4-Dihydroquinolin-1(2H)-yl)ethanone **(4).**

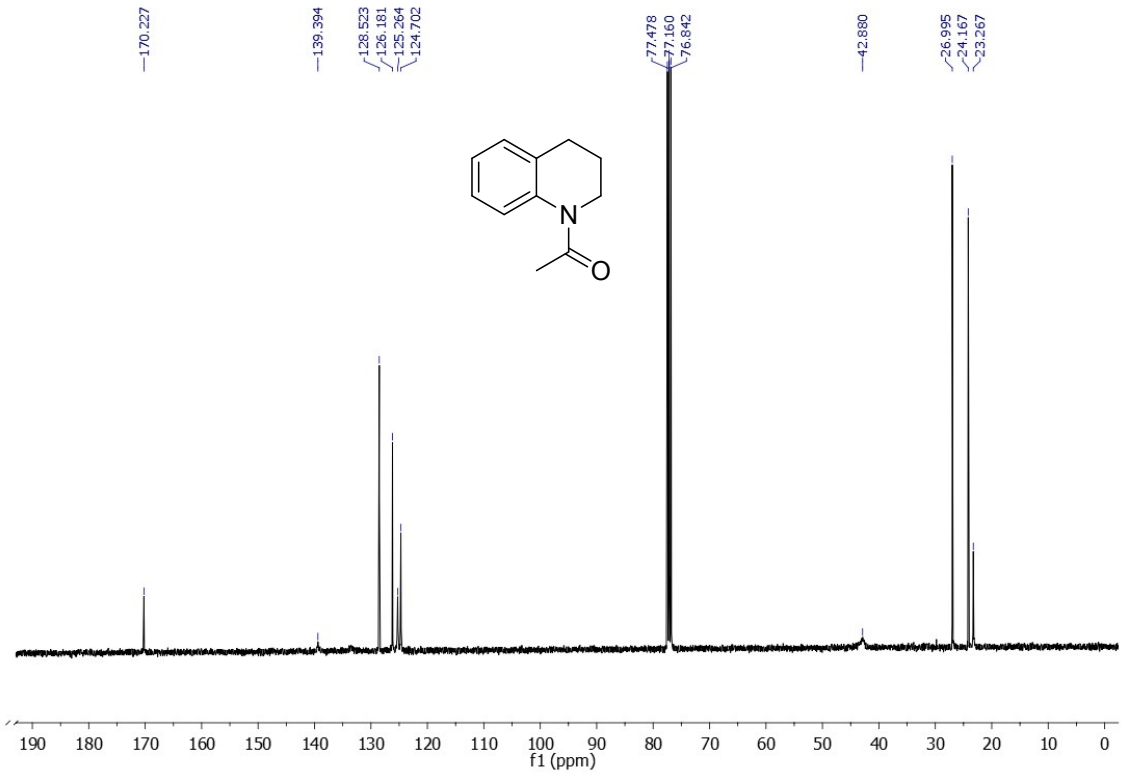

Fig. S104. ^{13}C NMR spectrum of 1-(3,4-Dihydroquinolin-1(2H)-yl)ethanone **(4).**