Supporting Information

Synthesis of (*E*)-Oxindolylidene Acetate using Tandem Palladium-Catalyzed Heck and Alkoxycarbonylation Reactions

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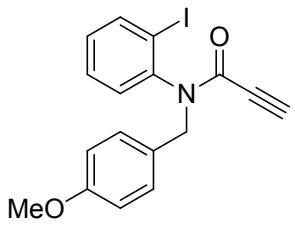
1. General

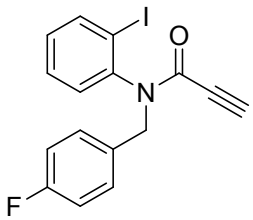
Starting materials were used as received from commercial suppliers unless otherwise stated. Dichloromethane (DCM) and *N*, *N'*-dimethylformamide (DMF) were dried over calcium hydride for 48 h prior to distillation. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl under nitrogen. The proton and carbon NMR

spectra were obtained on Bruker Avance 400 (400 MHz), Varian Unity Inova 500 (500 MHz) and Varian VNMRS600 (600 MHz) spectrometers. Deuterated chloroform of spectrograde was used as solvent. All NMR chemical shifts were reported as δ values in parts per million (ppm), and coupling constants (*J*) were given in hertz (Hz). The splitting pattern abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; br, broad; m, unresolved multiplet due to the field strength of the instrument; dd, doublet of doublet and dt, doublet of triplet. Melting points were measured on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. Mass spectra were carried out on ThermoQuest Finnigan and Microsaic 4000MiD mass spectrometers. Purification was performed by using preparative separations in flash column chromatography (Merck silica gel 60, particle size of 230-400 mesh). Analytical TLC was carried out on precoated plates (Merck silica gel 60, F254). Compounds analyzed on the TLC plates were visualized by using UV light, I_2 vapor, or basic aqueous potassium permanganate ($KMnO_4$) with heating. RPMI 1640 medium, fetal bovine serum (FBS), penicillin, streptomycin, and all other tissue culture regents were obtained from GIBCO/BRL Life Technologies (Grand Island, NY). MTS and PMS were purchased from Promega Corp. (Madison, WI).

2. Characterization data

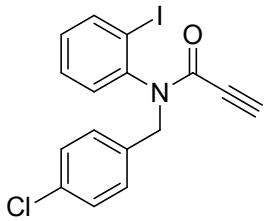


***N*-(2-Iodophenyl)-*N*-(4-methoxybenzyl)propiolamide (1b).** Yield: 78% (two rotamers at a ratio of 7:1). Yellow oil. IR (KBr) νmax: 3278, 2106, 1643, 1512, 1248, 1176 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) major/minor δ: 7.90/7.86 (d, *J* = 7.8 Hz, 1H), 7.19/7.16 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.08/7.10 (d, *J* = 8.4 Hz, 2H), 7.03/6.98 (dt, *J* = 7.8, 1.8 Hz, 1H), 6.77/6.82 (d, *J* = 8.4 Hz, 2H), 6.72/6.60 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.51/5.52 (d, *J* = 14.4 Hz, 1H), 4.00/4.43 (d, *J* = 14.4 Hz, 1H), 3.77/3.76 (s, 3H), 2.71/3.30 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 159.2/159.5, 153.0/152.7, 142.7/141.3, 139.8/139.9, 131.5/130.6, 130.9/130.3, 130.2/130.1, 128.8/128.6, 127.8/127.6, 113.7/113.9, 100.2/98.2, 79.2/80.0, 76.2/71.4, 55.2/54.8, 50.5/55.3. HRMS calcd for $C_{17}H_{15}INO_2$ $(M+1)^+$ 392.0147, found 392.0147.



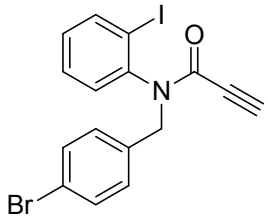
***N*-(4-Fluorobenzyl)-*N*-(2-iodophenyl)propiolamide (1c).** Yield: 83% (two rotamers at a ratio of 9:1). Yellow solid. Mp = 54-55 °C. IR (KBr) νmax: 3202, 2103,

1636, 1508, 1391, 1230 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) major/minor δ: 7.89/7.86 (d, *J* = 7.8 Hz, 1H), 7.20/7.21 (t, *J* = 7.8 Hz, 1H), 7.16-7.13 (m, 2H), 7.04/7.03 (t, *J* = 7.8 Hz, 1H), 6.92/6.96 (t, *J* = 8.4 Hz, 2H), 6.73/6.61 (dd, *J* = 7.8, 0.6 Hz, 1H), 5.47/5.48 (d, *J* = 14.4 Hz, 1H), 4.06/4.51 (d, *J* = 14.4 Hz, 1H), 2.73/3.34 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 162.3/162.5 (d, $^1J_{C\text{-}F}$ = 245.4 Hz), 153.0/152.5, 142.0/141.0, 139.9/140.0, 131.5/131.2 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 131.3/130.1, 131.2/130.6 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 130.3/129.9, 128.8/128.9, 115.3/115.5 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 100.1/98.2, 79.5/80.3, 75.9/76.0, 50.4/54.5. HRMS calcd for $C_{16}H_{12}IFNO$ $(M+1)^+$ 379.9948, found 379.9947.

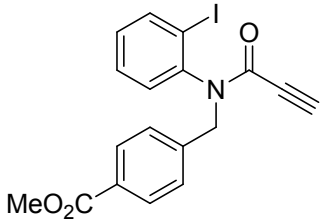


***N*-(4-Chlorobenzyl)-*N*-(2-iodophenyl)propiolamide (1d).** Yield: 85% (two rotamers at a ratio of 9:1). Yellow solid. Mp = 78-80 °C. IR (KBr) νmax: 3213, 2107, 1637, 1389, 1293 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) major/minor δ: 7.90/7.87 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.26-7.21 (m, 3H), 7.12-7.11 (m, 2H), 7.05/6.99 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.75/6.65 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.49/5.50 (d, *J* = 14.4 Hz, 1H), 4.04/4.50 (d, *J* = 14.4 Hz, 1H), 2.74/3.32 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 153.1/152.6, 142.5/141.1, 140.0/140.1, 134.2/134.1, 133.8/134.0, 131.2/130.1, 130.9/130.1, 130.4/129.9, 128.9/129.0, 128.7/128.8, 100.1/98.1, 79.6/80.3, 75.9/76.0,

50.5/54.6. HRMS calcd for $C_{16}H_{12}ClINO$ $(M+1)^+$ 395.9652, found 395.9658.

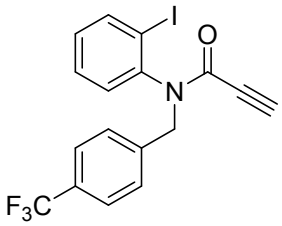


***N*-(4-Bromobenzyl)-*N*-(2-iodophenyl)propiolamide (1e).** Yield: 79% (two rotamers at a ratio of 9:1). Yellow solid. Mp = 94-96 °C. IR (KBr) νmax: 3209, 2105, 1534, 1291 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) major/minor δ: 7.91/7.88 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.38/7.41 (d, *J* = 8.0 Hz, 2H), 7.22/7.19 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.07-7.04 (m, 3H), 6.75/6.65 (dd, *J* = 8.0, 1.5 Hz, 1H), 5.48 (d, *J* = 14.5 Hz, 1H), 4.03/4.47 (d, *J* = 14.5 Hz, 1H), 2.74/3.31 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) major/minor δ: 153.1/152.7, 142.6/141.1, 140.0/140.1, 134.7/134.5, 131.7/131.8, 131.2/130.1, 131.2/130.0, 130.5/130.0, 129.0/129.1, 122.0/122.3, 100.0/98.1, 79.6/80.3, 75.9/76.1, 50.6/54.7. HRMS calcd for $C_{16}H_{11}BrINO$ $(M)^+$ 438.9067, found 438.9070.



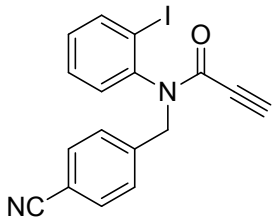
Methyl 4-((*N*-(2-iodophenyl)propiolamido)methyl)benzoate (1f). Yield: 74% (two rotamers at a ratio of 8:1). Light yellow oil. IR (KBr) νmax: 3231, 2106, 1718,

1647, 1468, 1386, 1280, 1106 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) major/minor δ: 7.91/7.94 (d, *J* = 8.4 Hz, 2H), 7.90/7.84 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.25/7.28 (d, *J* = 8.4 Hz, 2H), 7.19/7.18 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.03/6.92 (dt, *J* = 7.8, 1.8 Hz, 1H), 6.74/6.64 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.57/5.58 (d, *J* = 14.4 Hz, 1H), 4.11/4.46 (d, *J* = 14.4 Hz, 1H), 2.76/3.34 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 166.6/166.5, 153.2/152.7, 142.5/141.1, 140.7/140.5, 139.9/140.1, 131.1/130.4, 130.4/129.9, 129.8/129.6, 129.3/129.0, 129.0/128.7, 100.0/98.1, 79.8/80.5, 75.8/75.9, 52.1/55.0, 50.9/52.0. HRMS calcd for $C_{18}H_{15}INO_3$ $(M+1)^+$ 420.0097, found 420.0095.

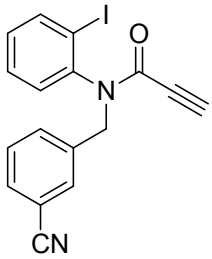


***N*-(2-Iodophenyl)-*N*-(4-(trifluoromethyl)benzyl)propiolamide (1g).** Yield: 78% (two rotamers at a ratio of 8:1). Brown solid. Mp =106-107 °C. IR (KBr) νmax: 3227, 2108, 1637, 1392, 1158, 1114 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) major/minor δ: 7.93/7.90 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.53/7.57 (d, *J* = 8.4 Hz, 2H), 7.33/7.36 (d, *J* = 7.8 Hz, 2H), 7.24/7.21 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.07/7.02 (dt, *J* = 7.8, 1.8 Hz, 1H), 6.78/6.69 (dd, *J* = 7.8, 1.2 Hz, 1H), 5.58/5.59 (d, *J* = 14.4 Hz, 1H), 4.13/4.59 (d, *J* = 14.4 Hz, 1H), 2.76/3.31 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 153.3/153.2, 142.7/142.7, 140.2/140.3, 139.7/139.6, 131.1/130.0, 130.5/130.3, 130.0/129.9 (q, $^2J_{C-F}$ =

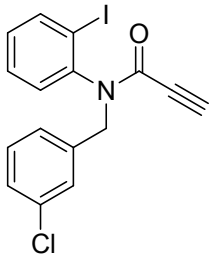
15.4 Hz), 129.8/129.2, 129.1/129.0, 125.5/125.6 (q, $^{3}J_{C\text{-}F}$ = 4.1 Hz), 123.9/123.1 (q, $^{1}J_{C\text{-}F}$ = 270.7 Hz), 100.1/100.0, 79.8/80.4, 75.8/75.9, 50.9/54.9. HRMS calcd for $C_{17}H_{12}F_3INO$ $(M+1)^+$ 429.9916, found 429.9922.



***N*-(4-Cyanobenzyl)-*N*-(2-iodophenyl)propiolamide (1h).** Yield: 83% (two rotamers at a ratio of 8:1). Yellow solid. Mp = 101-102 °C. IR (KBr) νmax: 3260, 2222, 2100, 1647, 1467, 1380, 1304 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) major/minor δ: 7.91/7.87 (d, *J* = 8.0 Hz, 1H), 7.56/7.59 (d, *J* = 8.0 Hz, 2H), 7.32/7.33 (d, *J* = 8.0 Hz, 2H), 7.24/7.20 (t, *J* = 7.0 Hz, 1H), 7.07/6.99 (t, *J* = 7.0 Hz, 1H), 6.78/6.68 (d, *J* = 8.0 Hz, 1H), 5.50/5.52 (d, *J* = 14.5 Hz, 1H), 4.17/4.61 (d, *J* = 14.5 Hz, 1H), 2.77/3.37 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) major/minor δ: 153.3, 142.5, 141.0, 140.2/140.2, 132.3/132.5, 130.9, 130.6, 130.0/129.7, 129.1/129.4, 118.5/118.3, 111.9/112.4, 100.0, 80.1/80.6, 75.6/75.7, 51.0/54.9. HRMS calcd for $C_{17}H_{12}IN_2O$ $(M+1)^+$ 386.9994, found 386.9996.

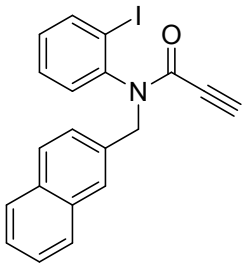


***N*-(3-Cyanobenzyl)-*N*-(2-iodophenyl)propiolamide (1i).** Yield: 74% (two rotamers at a ratio of 8:1). Yellow solid. Mp = 95-96 ^{o}C. IR (KBr) νmax: 3223, 2225, 2102, 1637, 1470, 1392, 1301 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) major/minor δ: 7.91/7.86 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.56-7.53 (m, 1H), 7.50-7.46 (m, 2H), 7.39/7.42 (t, *J* = 8.0 Hz, 1H), 7.25/7.21 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.07/6.98 (dt, *J* = 8.0, 1.5 Hz, 1H), 6.78/6.70 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.45 (d, *J* = 14.5 Hz, 1H), 4.17 (d, *J* = 14.5 Hz, 1H), 2.77/3.37 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) major/minor δ: 153.2/152.5, 142.4/140.8, 140.1/140.2, 137.2/136.3, 133.8/133.6, 132.7/133.2, 131.6/132.2, 130.8/132.1, 130.6/130.1, 129.4/129.7, 129.2/129.6, 118.3/118.2, 112.7/113.0, 99.9/98.1, 80.0/80.7, 75.6/75.8, 50.7/54.6. HRMS calcd for $C_{17}H_{12}IN_2O$ $(M+1)^+$ 386.9994, found 386.9995.



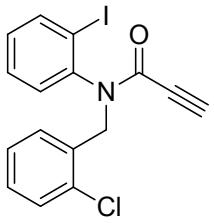
***N*-(3-Chlorobenzyl)-*N*-(2-iodophenyl)propiolamide (1j).** Yield: 80% (two

rotamers at a ratio of 8:1). Yellow solid. Mp = 79-80 ^{o}C. IR (KBr) νmax: 3192, 2103, 1627, 1471, 1387, 1297, 1211 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) major/minor δ: 7.92/7.89 (d, *J* = 8.0 Hz, 1H), 7.29-7.18 (m, 5H), 7.12-7.05 (m, 2H), 6.80/6.69 (d, *J* = 8.0 Hz, 1H), 5.52/5.53 (d, *J* = 14.5 Hz, 1H), 4.05/4.51 (d, *J* = 14.5 Hz, 1H), 2.75/3.33 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) major δ: 153.2, 142.6, 140.1, 137.7, 134.4, 131.2, 130.5, 129.8, 129.5, 129.0, 128.2, 127.6, 100.1, 79.7, 75.9, 50.8. HRMS calcd for $C_{16}H_{12}ClINO$ $(M+1)^+$ 395.9652, found 395.9659.

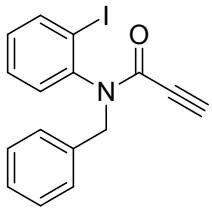


***N*-(2-Iodophenyl)-*N*-(naphthalen-2-ylmethyl)propiolamide (1k).** Yield: 84% (two rotamers at a ratio of 6:1). Orange oil. IR (KBr) νmax: 3447, 2107, 1646, 1467, 1287 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) major/minor δ: 7.92/7.89 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.81-7.76 (m, 2H), 7.73-7.71 (m, 1H), 7.58 (s, 1H), 7.46-7.43 (m, 2H), 7.38 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.11/7.09 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.02/6.95 (dt, *J* = 7.5, 1.5 Hz, 1H), 6.71/6.62 (dd, *J* = 8.0, 1.5 Hz, 1H), 5.78/5.77 (d, *J* = 14.5 Hz, 1H), 4.19/4.62 (d, *J* = 14.5 Hz, 1H), 2.75/3.33 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) major/minor δ: 153.3/152.9, 142.7/141.3, 139.9/140.0, 133.2/133.1, 133.1/133.0, 132.9/132.9, 131.3/130.1,

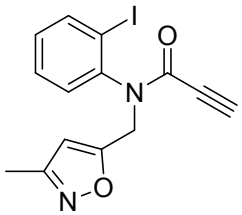
130.3/129.9, 128.9/129.0, 128.5/128.9, 128.4/128.9, 127.8/127.6, 127.6/127.5, 127.2/126.4, 126.1/126.4, 126.0/126.3, 100.1/98.2, 79.5/80.3, 76.1/76.2, 51.3/55.5. HRMS calcd for $C_{20}H_{15}INO$ $(M+1)^+$ 412.0198, found 412.0198.



***N*-(2-Chlorobenzyl)-*N*-(2-iodophenyl)propiolamide (1l).** Yield: 78% (two rotamers at a ratio of 8:1). Brown solid. Mp = 90-93 ^oC. IR (KBr) νmax: 3202, 2103, 1636, 1470, 1387 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) major/minor δ: 7.88/7.86 (d, *J* = 8.0 Hz, 1H), 7.40-7.37 (m, 1H), 7.32-7.25 (m, 1H), 7.19-7.15 (m, 3H), 7.02/6.96 (dt, *J* = 8.0, 1.5 Hz, 1H), 6.82/6.71 (dd, *J* = 8.0, 1.5 Hz, 1H), 5.56/5.57 (d, *J* = 14.5 Hz, 1H), 4.52/4.91 (d, *J* = 14.5 Hz, 1H), 2.75/3.27 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) major/minor δ: 153.2/153.1, 142.4/141.0, 139.9/140.0, 134.5/134.4, 133.2/133.0, 131.8/130.0, 131.4/130.9, 130.3/129.9, 129.5/129.8, 129.4/129.7, 128.9/129.0, 127.1/127.0, 100.2/98.2, 79.6/80.1, 76.0/76.1, 47.8/52.3. HRMS calcd for $C_{16}H_{12}ClINO$ $(M+1)^+$ 395.9652, found 395.9658.

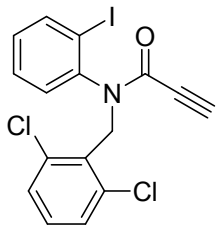


***N*-Benzyl-*N*-(2-iodophenyl)propiolamide (1m).** Yield: 81% (two rotamers at a ratio of 7:1). Dark brown oil. IR (KBr) νmax: 3421, 2958, 2104, 1646, 1469, 1395, 1302 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) major/minor δ: 7.89/7.88 (d, *J* = 7.8 Hz, 1H), 7.28-7.23 (m, 3H), 7.19-7.16 (m, 3H), 7.03/6.96 (t, *J* = 7.8 Hz, 1H), 6.73/6.64 (d, *J* = 7.8 Hz, 1H), 5.57/5.58 (d, *J* = 14.4 Hz, 1H), 4.04/4.48 (d, *J* = 14.4 Hz, 1H), 2.72/3.31 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 153.1/152.8, 142.7/141.3, 139.9/140.0, 135.7/135.5, 131.3/130.2, 130.3/129.8, 129.5/128.9, 128.8/128.7, 128.5/128.6, 127.9/128.2, 100.1/98.2, 79.4/80.1, 51.1/55.3. HRMS calcd for $C_{16}H_{13}INO$ $(M+1)^+$ 362.0042, found 362.0051.

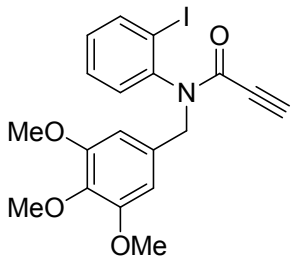


***N*-(2-Iodophenyl)-*N*-((3-methylisoxazol-5-yl)methyl)propiolamide (1n).** Yield: 68% (two rotamers at a ratio of 9:1). Light yellow oil. IR (KBr) νmax: 2454, 3253, 2106, 1650, 1469, 1386, 1298, 1193 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) major/minor δ: 7.92/7.89 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.34/7.31 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.16/6.98 (dd, *J* =

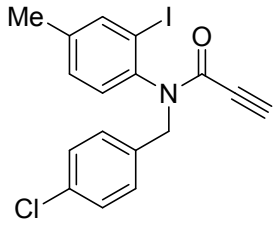
7.8, 1.2 Hz, 1H), 7.10/7.04 (dt, *J* = 7.8, 1.8 Hz, 1H), 6.10 (s, 1H), 5.43 (d, *J* = 15.6 Hz, 1H), 4.27 (d, *J* = 15.6 Hz, 1H), 2.77/3.10 (s, 1H), 2.25/2.10 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 153.2/152.9, 148.2/148.4, 147.6/147.6, 142.2/140.7, 139.8/140.0, 131.2/130.1, 130.4/130.0, 129.0/129.1, 128.0/127.6, 115.6/115.5, 112.4/112.7, 111.1/110.3, 101.9/102.0, 100.3/98.3, 79.7/80.4, 75.9/76.0, 49.9/54.4. HRMS calcd for $C_{14}H_{12}IN_2O_2$ $(M+1)^+$ 366.9943, found 366.9948.



***N*-(2,6-Dichlorobenzyl)-*N*-(2-iodophenyl)propiolamide (1o).** Yield: 77% (two rotamers at a ratio of 8:1). Yellow solid. Mp = 170-171 °C. IR (KBr) νmax: 3238, 2360, 2102, 1647, 1377, 1288 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) major/minor δ: 7.84/7.65 (d, *J* = 8.0 Hz, 1H), 7.21-7.18 (m, 2H), 7.13-7.09 (m, 1H), 7.06/6.91 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.58/6.42 (d, *J* = 7.5 Hz, 1H), 5.76/5.65 (d, *J* = 14.5 Hz, 1H), 4.83/5.26 (d, *J* = 14.5 Hz, 1H), 2.72/3.32 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) major/minor δ: 152.6/153.3, 140.9/140.3, 139.6/139.7, 137.4/137.4, 131.1/130.4, 130.8/131.1, 130.4/131.7, 129.9/130.0, 128.5/128.6, 128.2/128.4, 101.6/99.4, 79.4/80.1, 75.9/76.3, 44.1/49.2. HRMS calcd for $C_{16}H_{11}Cl_2INO$ $(M+1)^+$ 429.9262, found 429.9268.

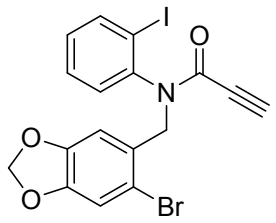


***N*-(2-Iodophenyl)-*N*-(3,4,5-trimethoxybenzyl)propiolamide (1p).** Yield: 81% (two rotamers at a ratio of 8:1). Yellow solid. Mp = 118-120 ^{o}C. IR (KBr) νmax: 3195, 2107, 1633, 1394, 1123 1288 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) major/minor δ: 7.89/7.86 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.22/7.20 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.04/6.98 (dt, *J* = 7.8, 1.8 Hz, 1H), 6.78/6.70 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.36/6.38 (s, 2H), 5.44/5.46 (d, *J* = 13.8 Hz, 1H), 3.97/4.40 (d, *J* = 13.8 Hz, 1H), 3.77/3.79 (s, 3H), 3.71/3.72 (s, 6H), 2.74/3.33 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 153.0/153.2, 153.0/152.6, 142.6/141.3, 139.8/139.9, 137.6/137.8, 131.4/131.0, 131.2/130.1, 130.3/129.9, 128.8/129.0, 106.6/105.7, 100.2/98.2, 79.5/80.1, 76.0/76.2, 60.8/60.8, 56.0/55.6, 51.4/51.4. HRMS calcd for $C_{19}H_{18}NaINO_4$ $(M+Na)^+$ 474.0178, found 474.0178.



***N*-(4-Chlorobenzyl)-*N*-(2-iodo-4-methylphenyl)propiolamide (1q).** Yield: 79% (two rotamers at a ratio of 9:1). Yellow oil. IR (KBr) νmax: 3287, 2108, 1646, 1484,

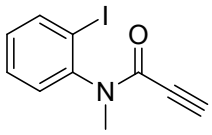
1384, 1291, 1204, 1015 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) major/minor δ: 7.72/7.69 (d, *J* = 1.2 Hz, 1H), 7.21/7.25 (d, *J* = 8.4 Hz, 2H), 7.12/7.14 (d, *J* = 8.4 Hz, 2H), 7.00/6.97 (dd, *J* = 7.8. 1.2 Hz, 1H), 6.61/6.50 (d, *J* = 7.8 Hz, 1H), 5.47/5.48 (d, *J* = 14.4 Hz, 1H), 4.01/4.46 (d, *J* = 14.4 Hz, 1H), 2.74/3.31 (s, 1H), 2.29/2.24 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 153.3/152.7, 140.8/140.6, 140.3/140.4, 139.9/138.4, 134.3/134.1, 133.7/134.0, 130.9/130.1, 130.6/129.8, 129.7/129.5, 128.6/128.8, 99.8/97.8, 79.6/80.2, 76.1/76.0, 50.6/54.7, 20.5/20.6. HRMS calcd for $C_{17}H_{14}ClINO$ $(M+1)^+$ 409.9809, found 409.9814.



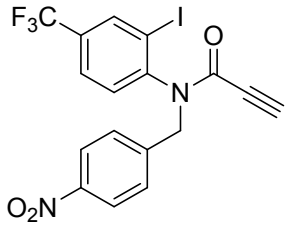
***N*-((6-Bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-*N*-(2-iodophenyl)propiolamide**

(1s). Yield: 72% (two rotamers at a ratio of 8:1). Dark red solid. Mp = 142-143 °C. IR (KBr) νmax: 3220, 2110, 1626, 1481, 1394, 1237, 1033 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) major/minor δ: 7.88/7.86 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.21/7.18 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.04/6.99 (dt, *J* = 7.8, 1.8 Hz, 1H), 6.96/6.89 (s, 1H), 6.86/6.86 (s, 1H), 6.82/6.70 (dd, *J* = 7.8, 1.2 Hz), 5.94/5.97 (dd, *J* = 12.0, 1.2 Hz, 2H), 5.45/5.46 (d, *J* = 14.4 Hz, 2H), 4.46/4.82 (d, *J* = 14.4 Hz, 1H), 2.76/3.30 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 153.2/152.9, 148.2/148.4, 147.6/147.6, 142.2/140.7, 139.8/140.0,

131.2/130.1, 130.4/130.0, 129.0/129.1, 128.1/127.6, 115.6/115.5, 112.4/112.7, 111.2/110.3, 101.9/102.0, 100.3/98.3, 79.7/80.6, 75.9/76.1, 50.0/54.4. HRMS calcd for $C_{17}H_{12}BrINO_3$ $(M+1)^+$ 483.9045, found 483.9050.

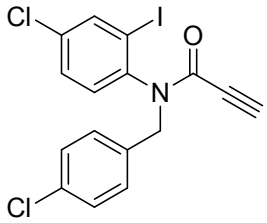


***N*-(2-Iodophenyl)-*N*-methylpropiolamide (1t).** Yield: 79% (two rotamers at a ratio of 8:1). Dark brown solid. Mp = 101-102 °C. IR (KBr) νmax: 3214, 2104, 1635, 1466, 1376, 1298, 1133 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) major/minor δ: 7.90/7.89 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.41/7.39 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.30/7.19 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.09/7.04 (dt, *J* = 7.8, 1.2 Hz, 1H), 3.21/3.47 (s, 3H), 2.71/3.21 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 153.1/152.9, 144.9/143.7, 139.9/140.0, 130.3/129.9, 129.5/129.8, 128.4/128.4, 99.3/97.8, 79.0/79.9, 76.0/76.0, 35.3/39.0. HRMS calcd for $C_{10}H_9INO_4$ $(M+1)^+$ 285.9729, found 285.9732.



***N*-(2-Iodo-4-(trifluoromethyl)phenyl)-*N*-(4-nitrobenzyl)propiolamide (1v).** Yield: 77% (two rotamers at a ratio of 8:1). Colorless oil. IR (KBr) νmax: 3286, 2111,

1651, 1600, 1522, 1347, 1320, 1133 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) major/minor δ: 8.16/8.15 (d, *J* = 1.2 Hz, 1H), 8.15/8.19 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.53/7.47 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.43/7.44 (d, *J* = 8.4 Hz, 2H), 6.93/6.83 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.57/5.61 (dd, *J* = 14.4, 2.4 Hz, 1H), 4.24/4.71 (d, *J* = 14.4 Hz, 1H), 2.83/3.39 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 152.8/152.5, 147.8/148.0, 145.9/144.5, 142.5/142.2, 137.3 (q, $^3J_{C-F}$ = 2.4 Hz), 132.5 (q, $^2J_{C-F}$ = 31.1 Hz), 131.2/130.0, 130.2/129.5, 126.3 (q, $^3J_{C-F}$ = 3.45 Hz), 124.0/124.1, 122.3 (q, $^1J_{C-F}$ = 271.2 Hz), 100.3/98.5, 80.8/81.2, 75.4/75.3, 50.6/54.4. HRMS calcd for $C_{17}H_{11}F_3IN_2O_3$ $(M+1)^+$ 474.9766, found 474.9758.



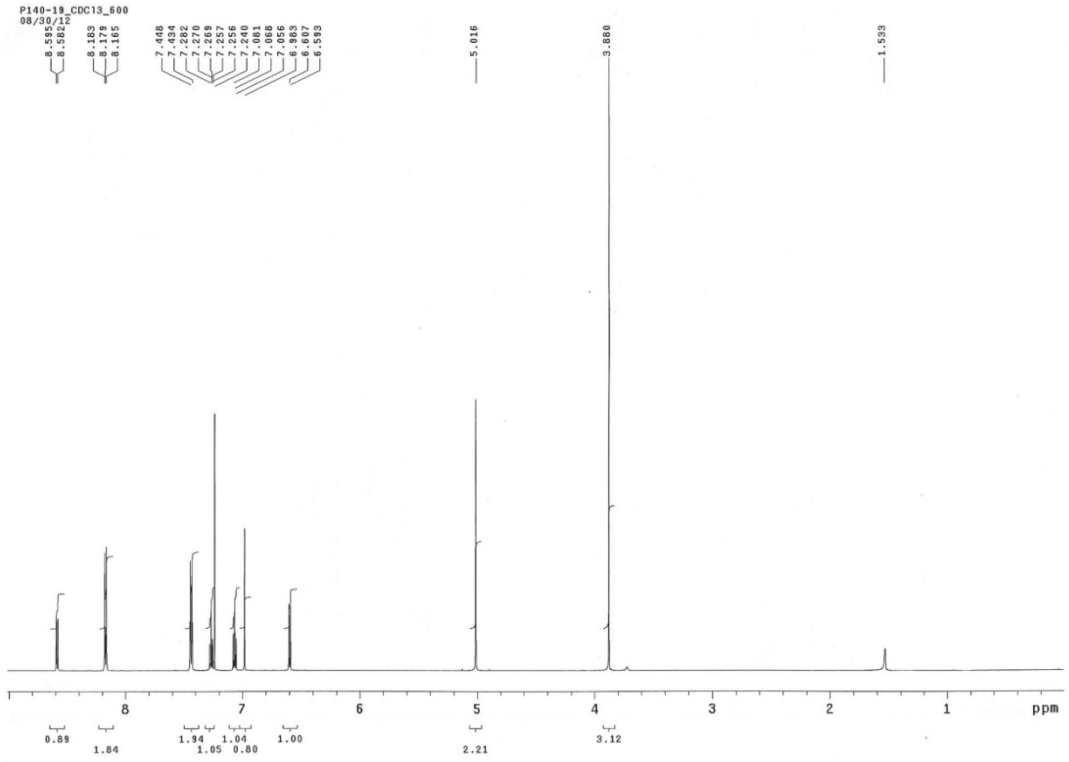
***N*-(4-Chloro-2-iodophenyl)-*N*-(4-chlorobenzyl)propiolamide (1w).** Yield: 75% (two rotamers at a ratio of 8:1). White solid. Mp = 82-85 °C. IR (KBr) νmax: 3253, 2105, 1634, 1465, 1396, 1292, 1090 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) major/minor δ: 7.90/7.86 (d, *J* = 1.8 Hz, 1H), 7.24/7.27 (d, *J* = 8.4 Hz, 2H), 7.20/7.17 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.12/7.13 (d, *J* = 8.4 Hz, 2H), 6.65/6.53 (d, *J* = 8.4, 1H), 5.48/5.50 (d, *J* = 14.4 Hz, 1H), 4.00/4.46 (d, *J* = 14.4 Hz, 1H), 2.79/3.33 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) major/minor δ: 153.0/152.8, 141.3/139.8, 139.4/139.5, 135.5/135.0, 134.1/134.4, 134.0/133.7, 131.6/130.6, 130.9/130.1, 129.2/129.3, 128.8/129.0, 100.5/98.6, 80.0/80.6,

75.8/75.8, 50.5/54.6. HRMS calcd for $C_{16}H_{11}Cl_2INO$ $(M+1)^+$ 429.9262, found 429.9267.

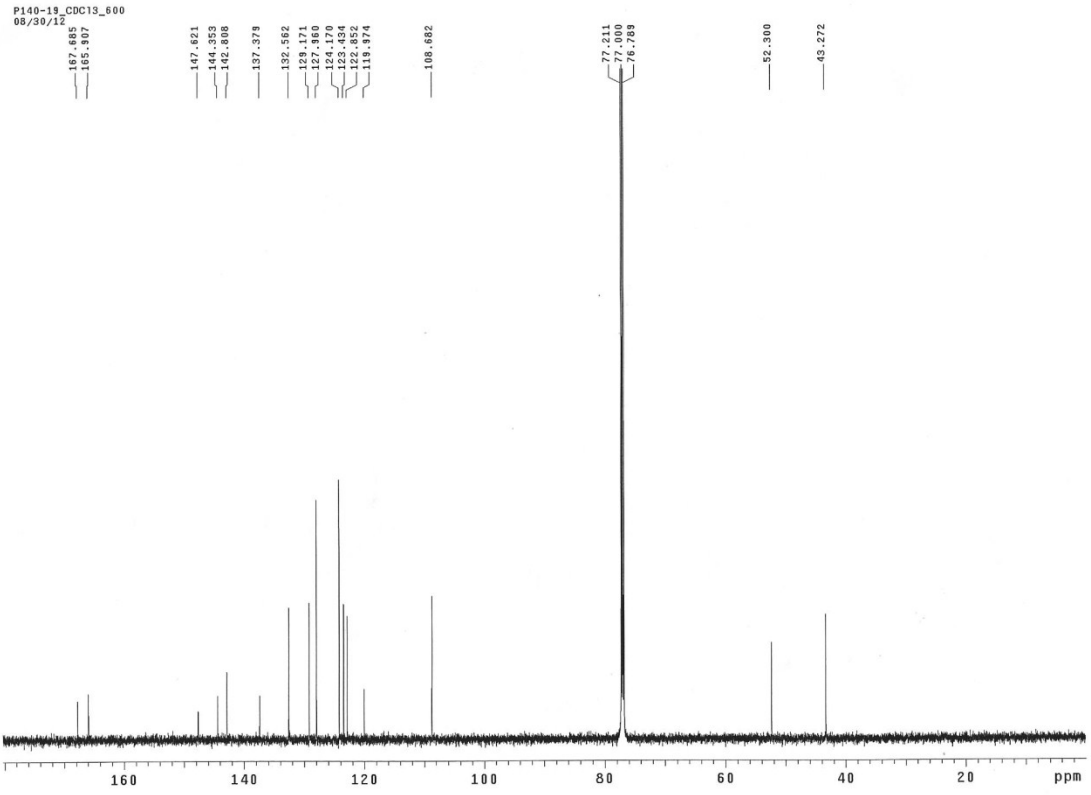
3. NMR Spectra

(E)-Methyl 2-(1-(4-nitrobenzyl)-2-oxoindolin-3-ylidene)acetate (**3a**).

^{1}H NMR

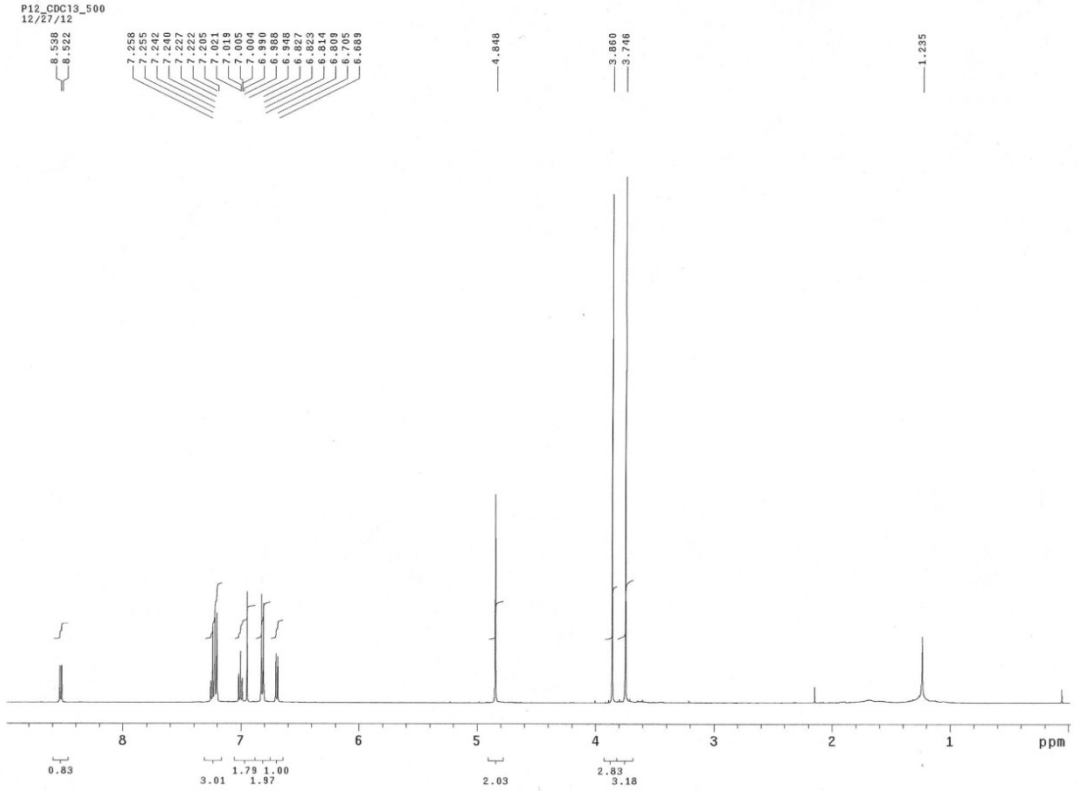


^{13}C NMR

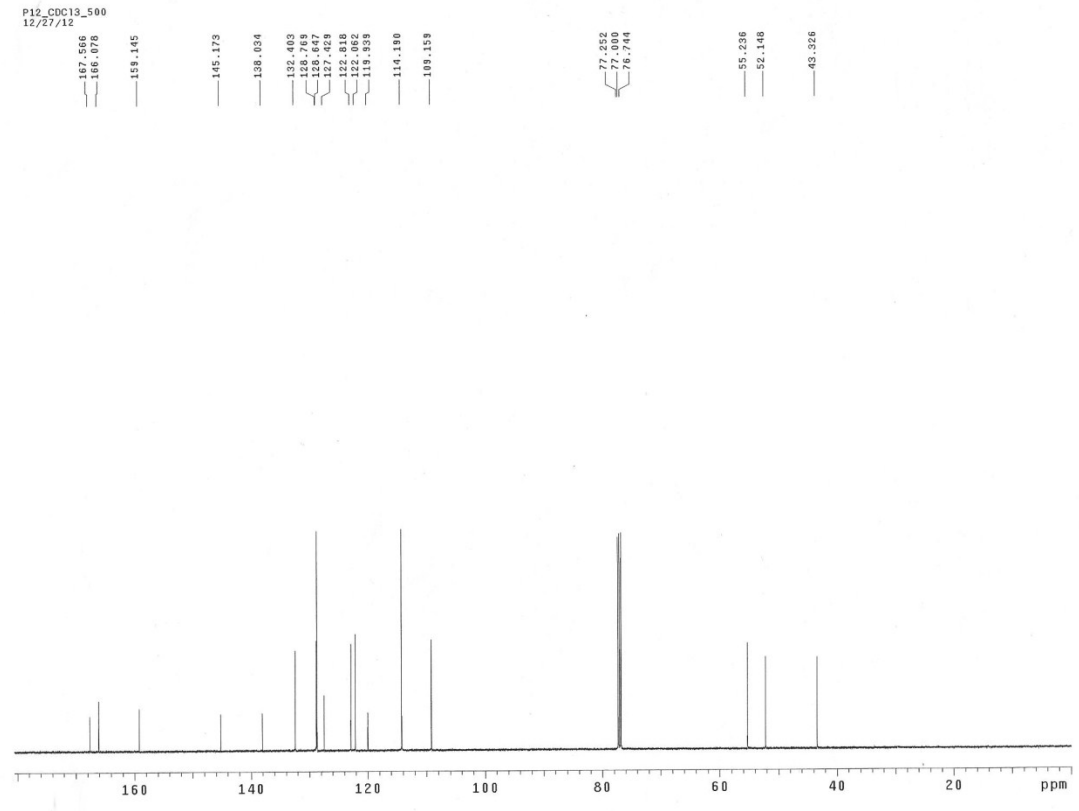


(E)-Methyl 2-(1-(4-methoxybenzyl)-2-oxoindolin-3-ylidene)acetate **(3b)**.

^{1}H NMR

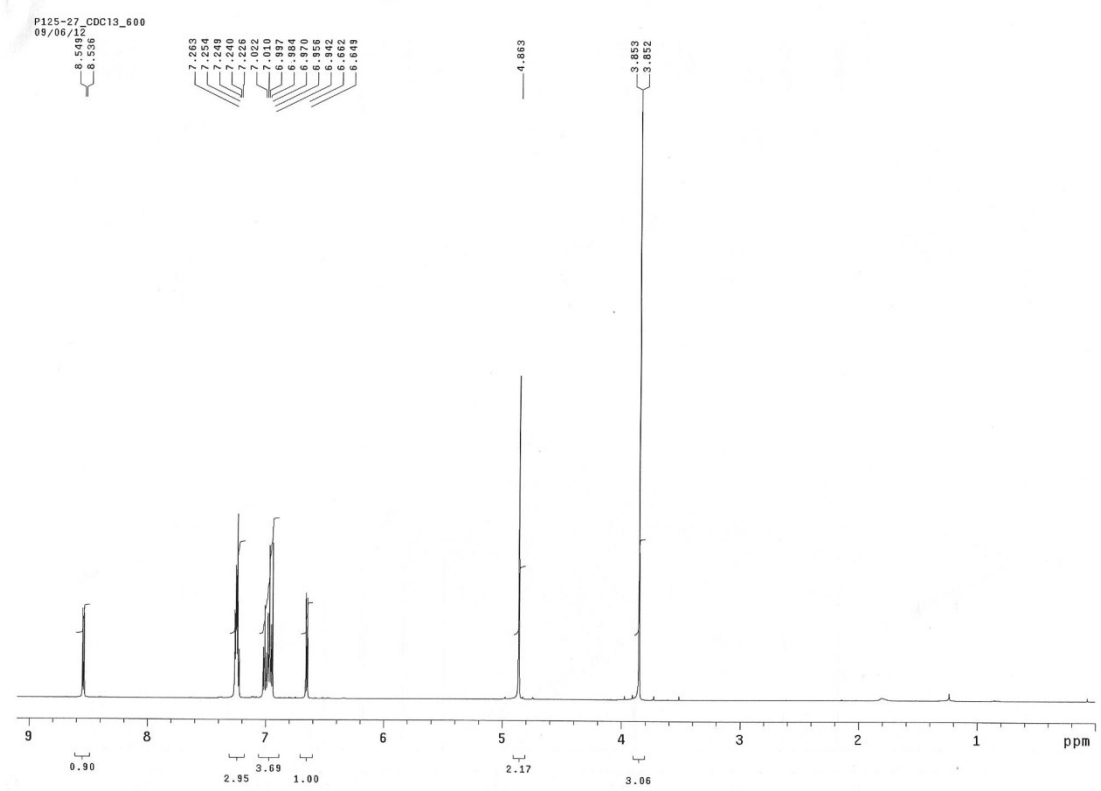


^{13}C NMR

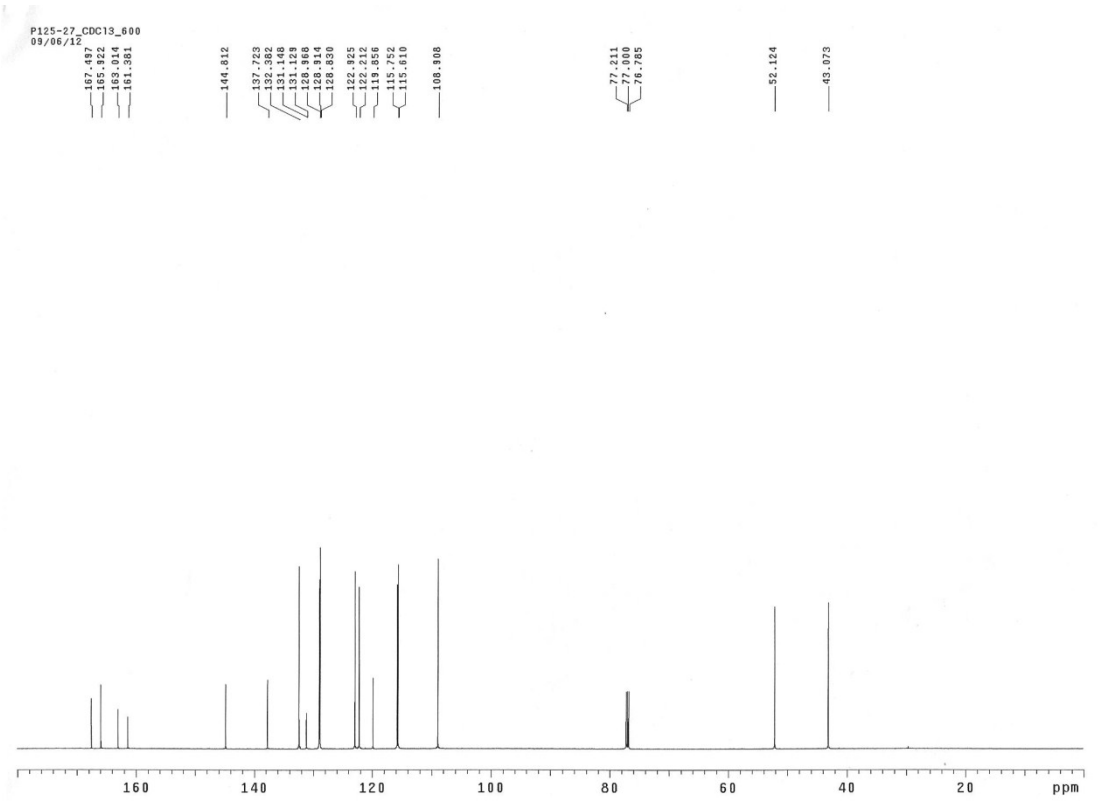


(E)-Methyl 2-(1-(4-fluorobenzyl)-2-oxoindolin-3-ylidene)acetate **(3c)**.

^{1}H NMR

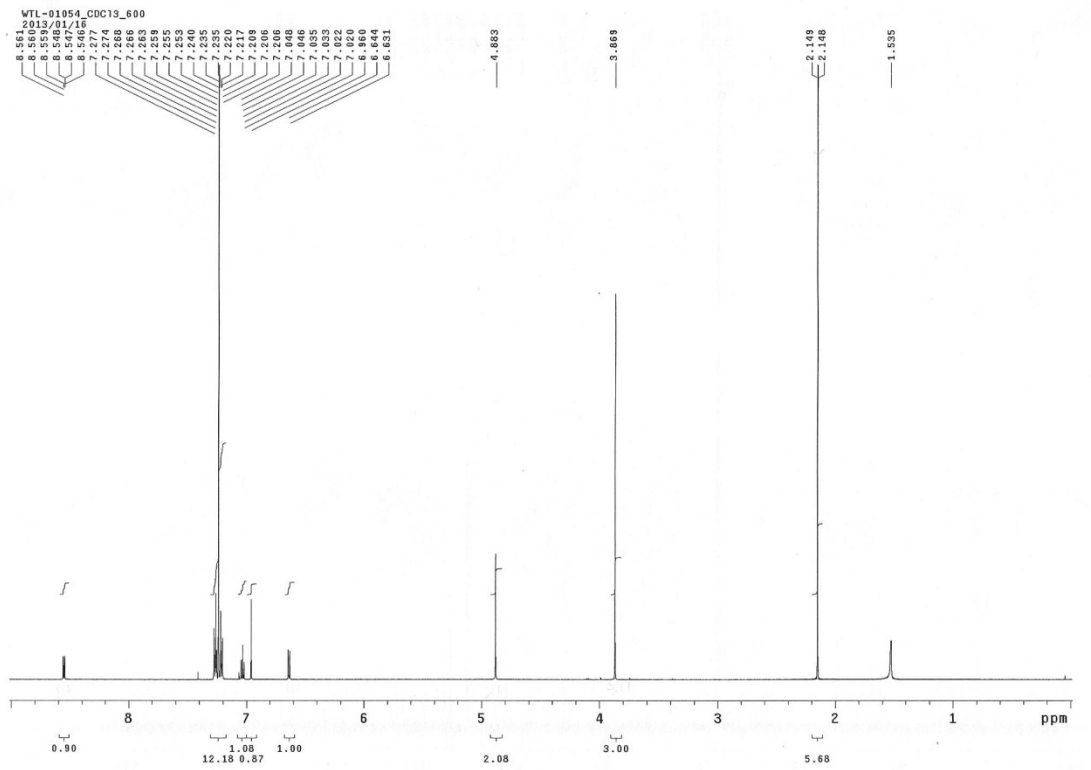


^{13}C NMR

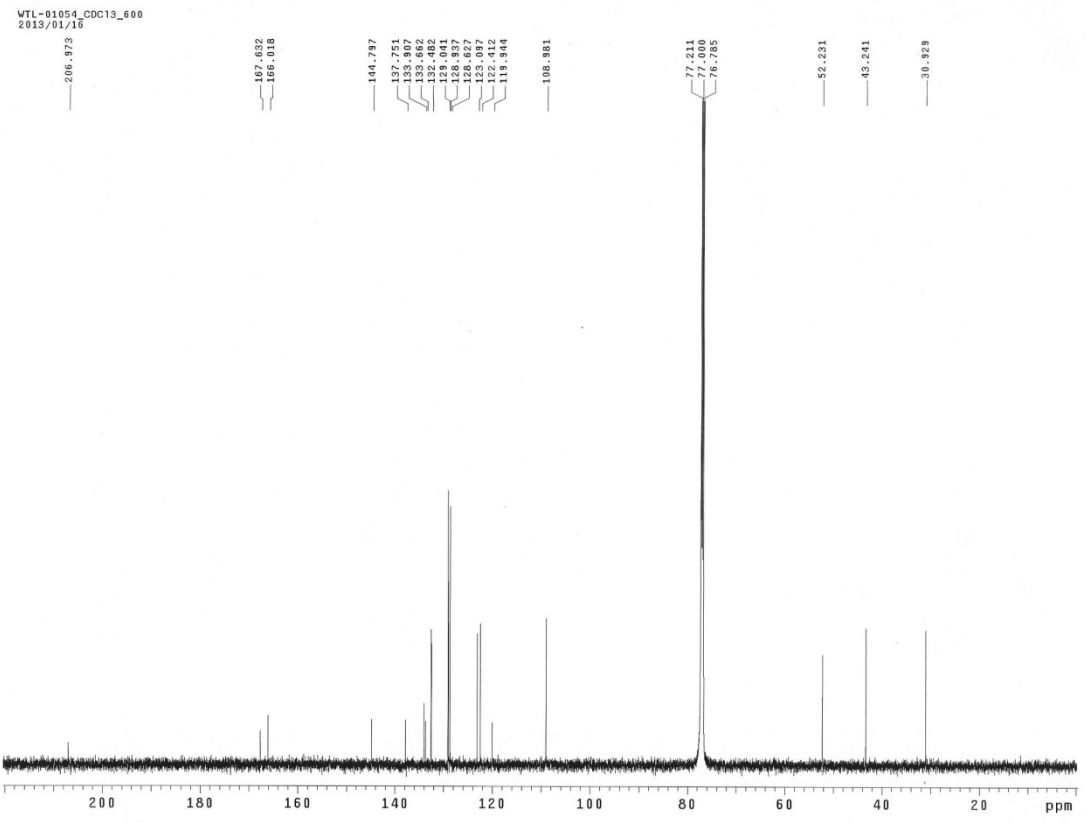


(E)-Methyl 2-(1-(4-chlorobenzyl)-2-oxoindolin-3-ylidene)acetate **(3d)**.

^{1}H NMR

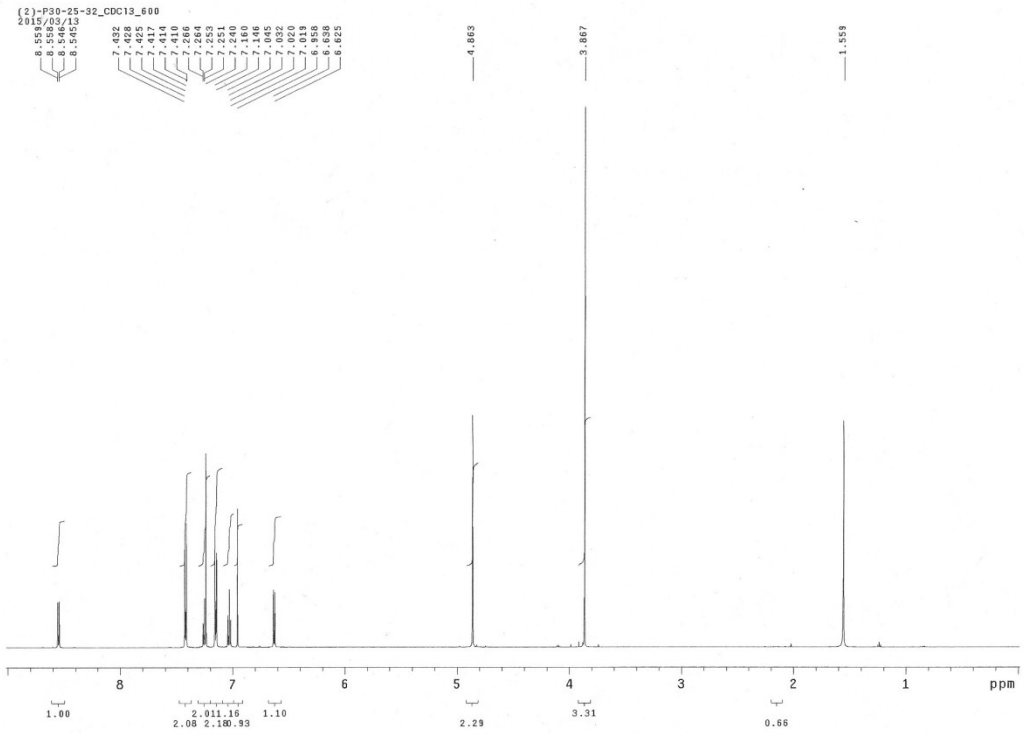


^{13}C NMR

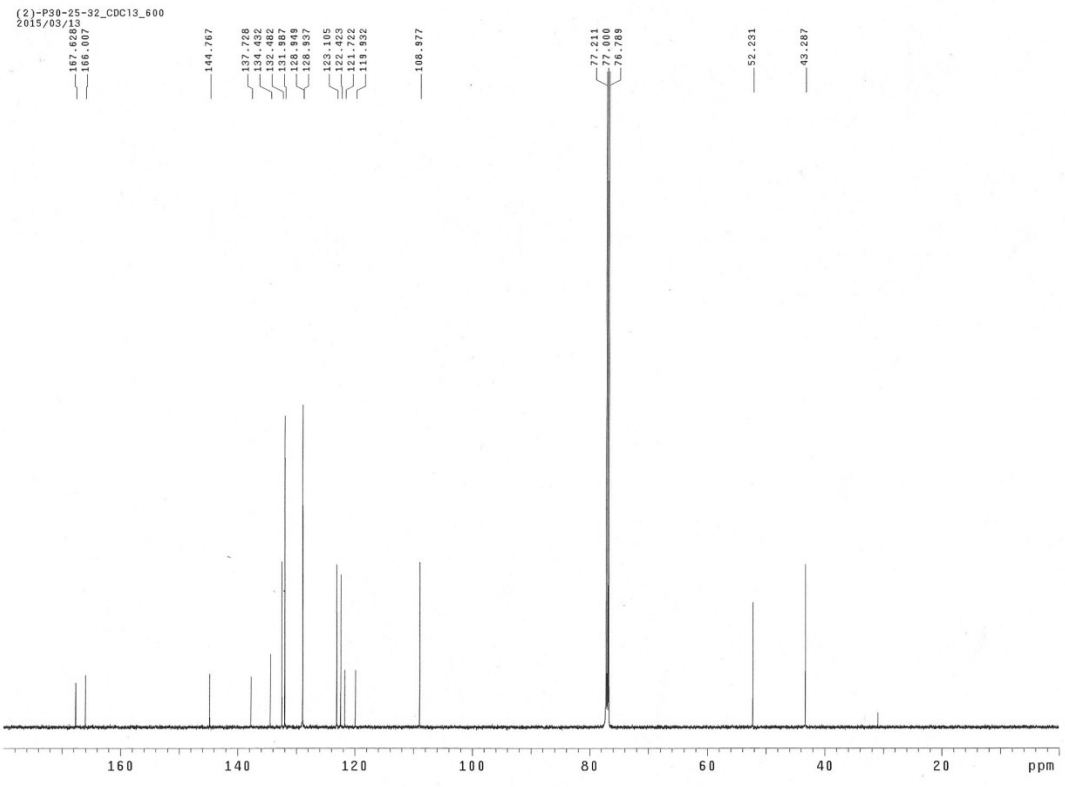


(E)-Methyl 2-(1-(4-bromobenzyl)-2-oxoindolin-3-ylidene)acetate **(3e)**.

^{1}H NMR

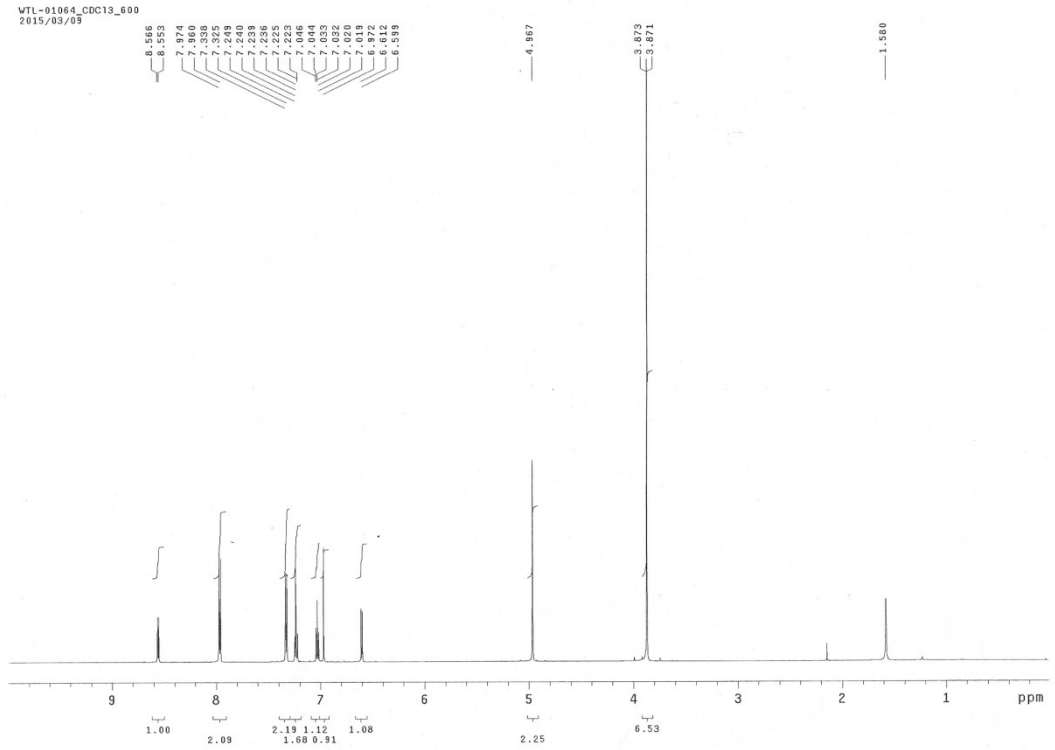


^{13}C NMR

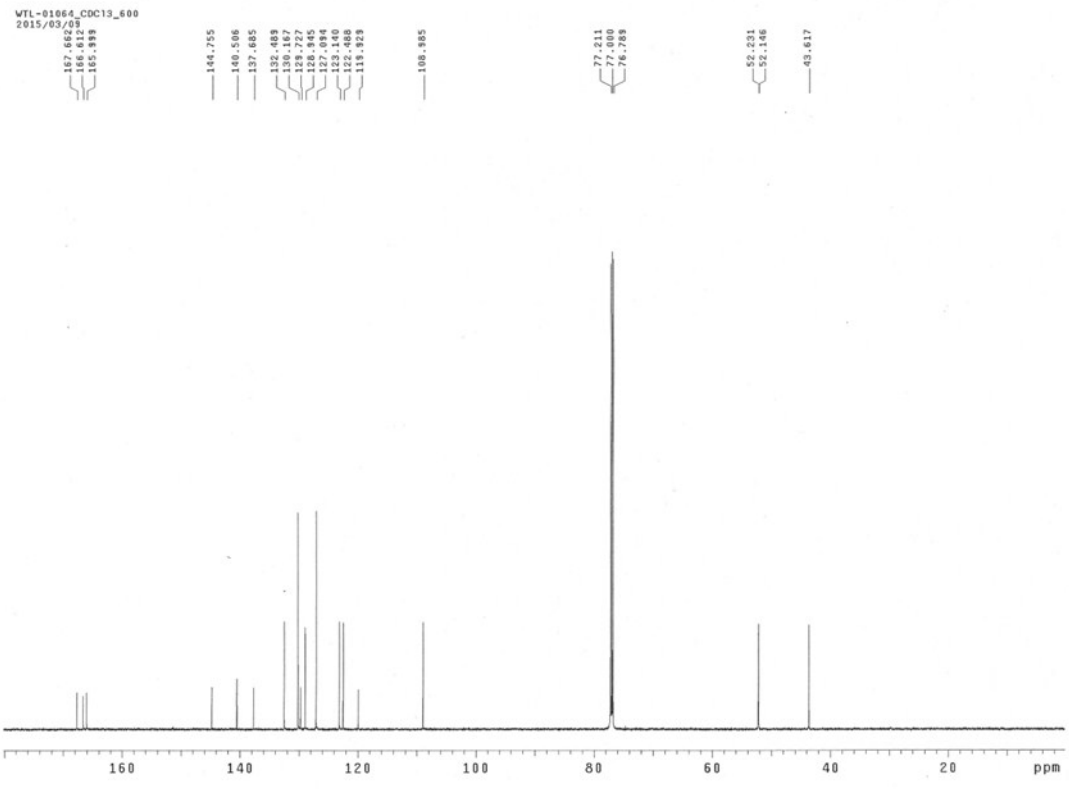


(E)-Methyl 4-((3-(2-methoxy-2-oxoethylidene)-2-oxoindolin-1-yl)methyl)benzoate **(3f)**.

^{1}H NMR

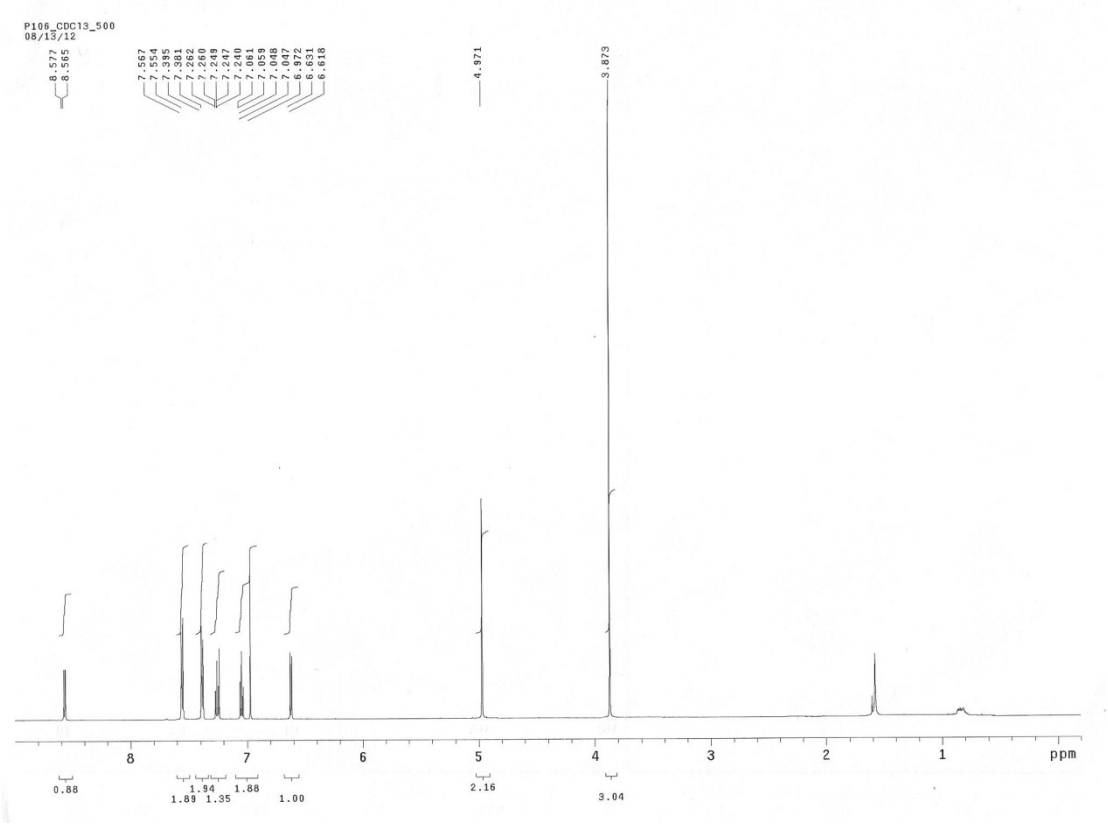


^{13}C NMR

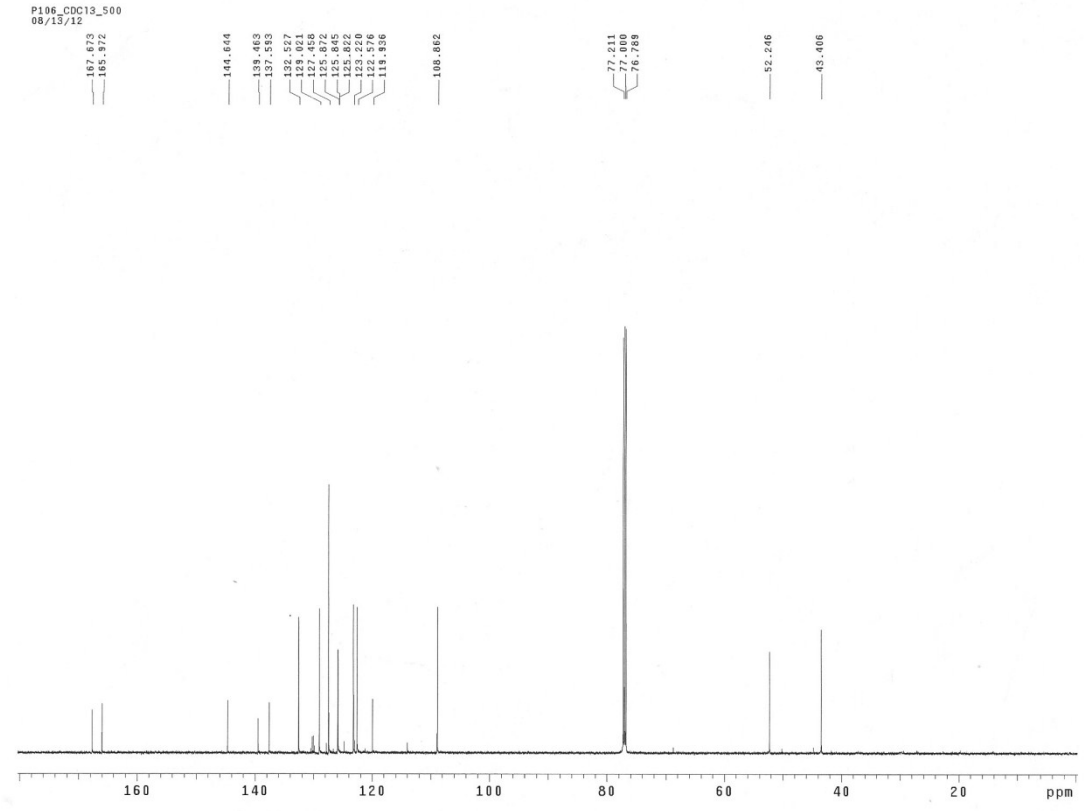


(E)-Methyl 2-(2-oxo-1-(4-(trifluoromethyl)benzyl)indolin-3-ylidene)acetate (**3g**).

^{1}H NMR

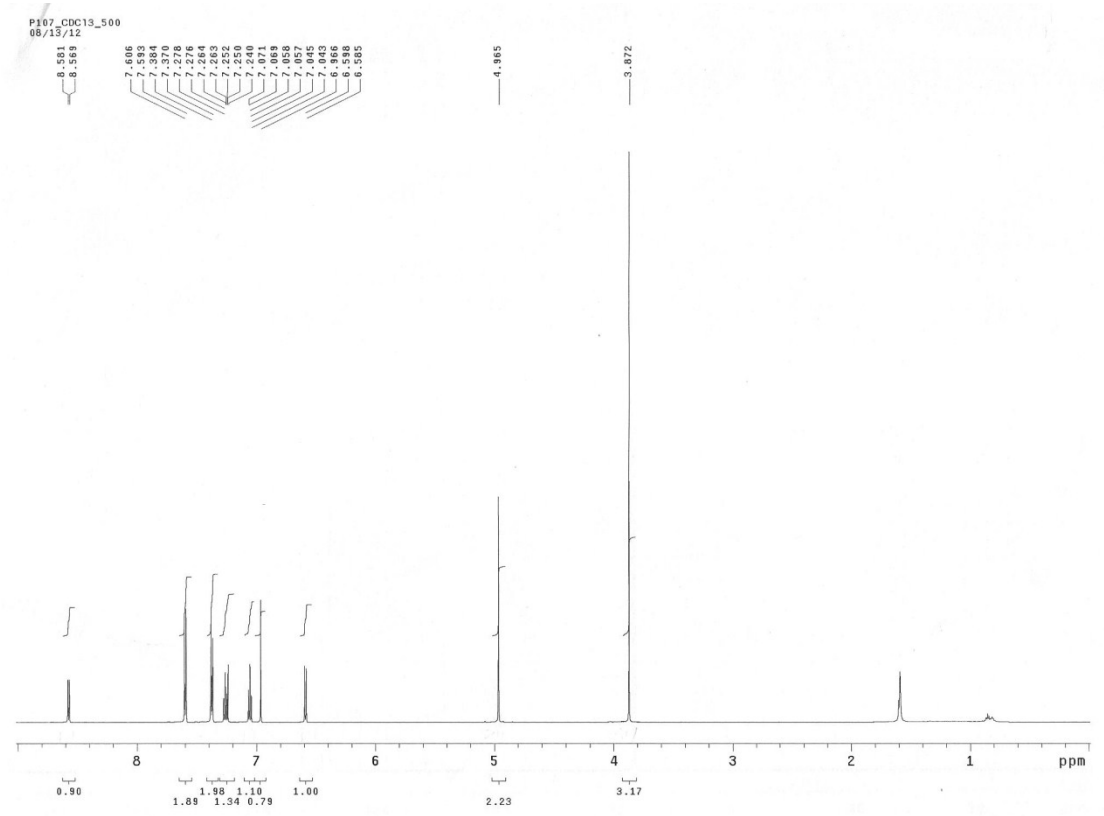


^{13}C NMR



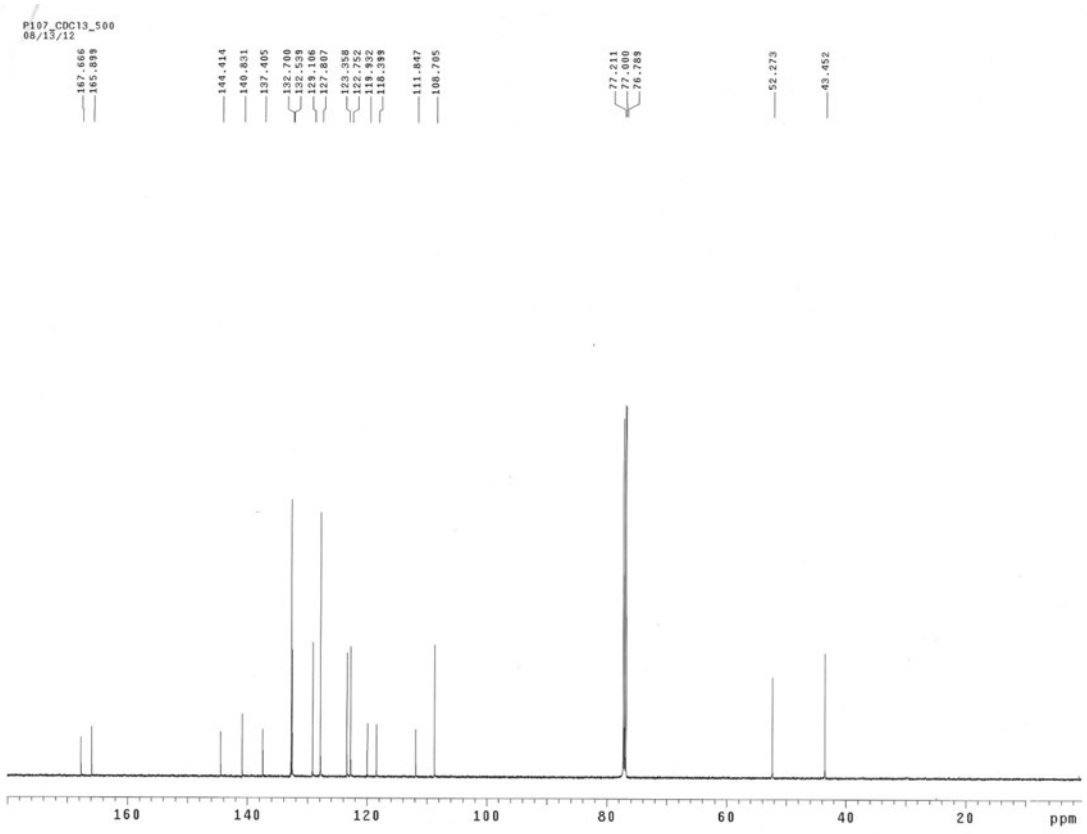
(E)-Methyl 2-(1-(4-cyanobenzyl)-2-oxoindolin-3-ylidene)acetate **(3h)**.

^{1}H NMR



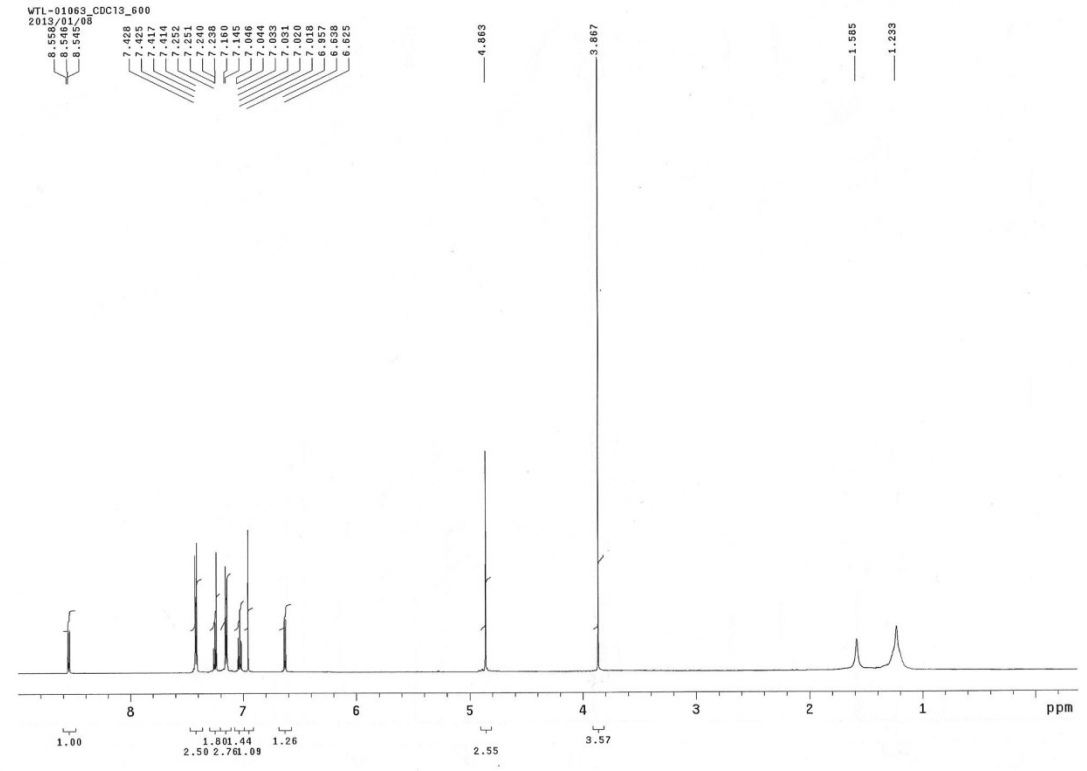
13

C NMR

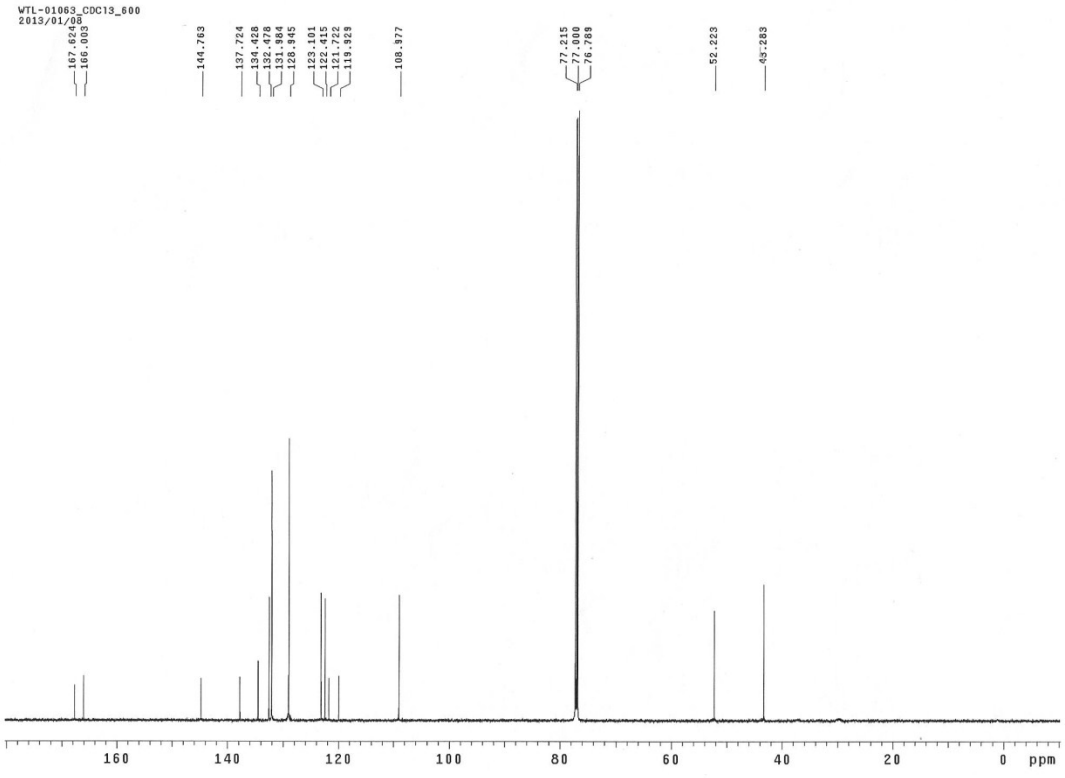


(E)-Methyl 2-(1-(3-cyanobenzyl)-2-oxoindolin-3-ylidene)acetate **(3i)**.

^{1}H NMR

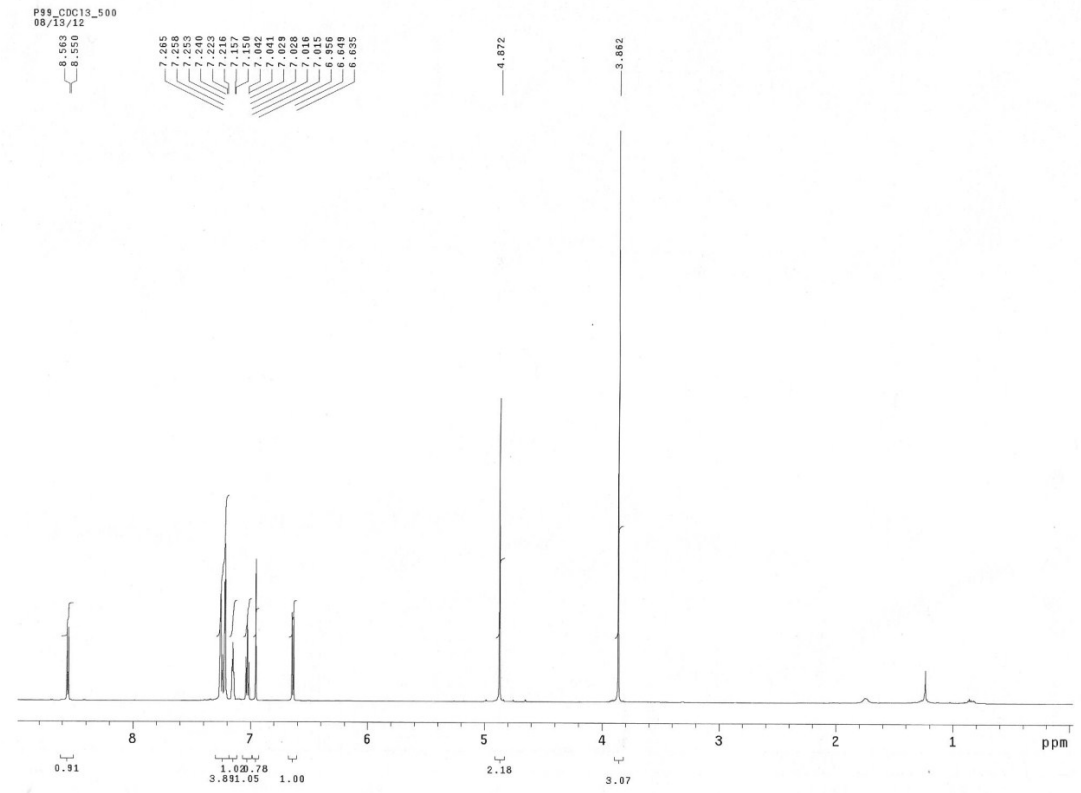


^{13}C NMR

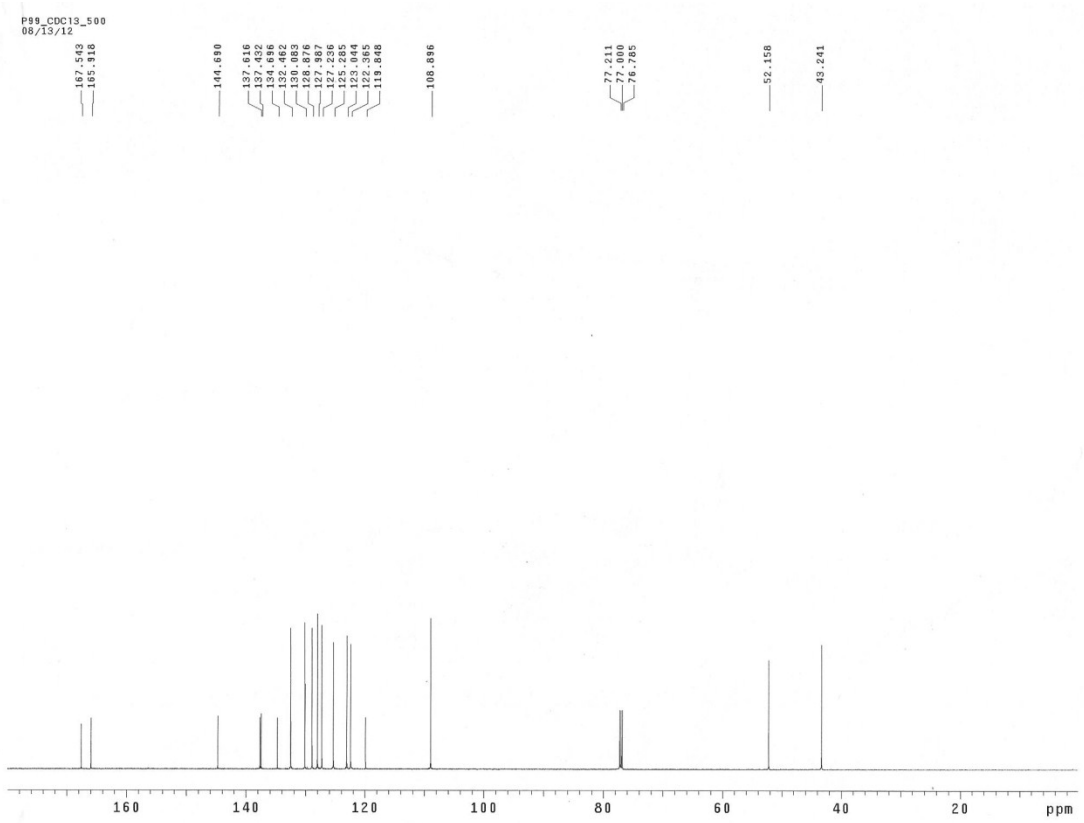


(E)-Methyl 2-(1-(3-chlorobenzyl)-2-oxoindolin-3-ylidene)acetate **(3j)**.

^{1}H NMR

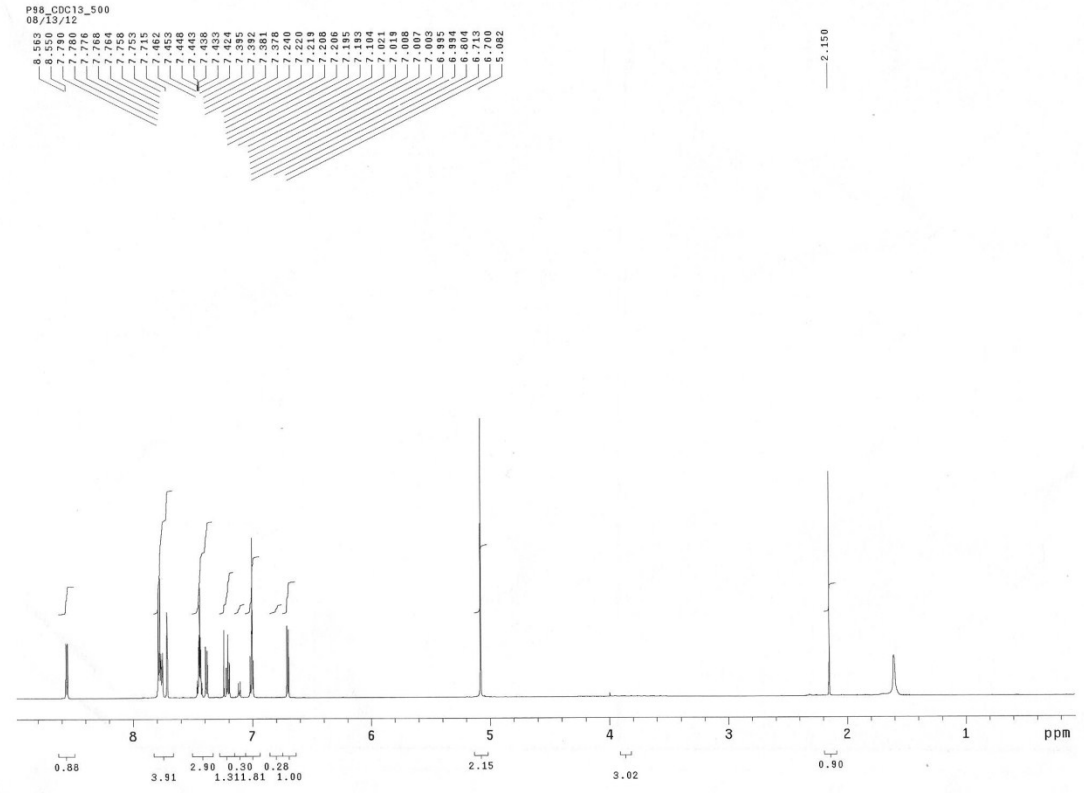


^{13}C NMR

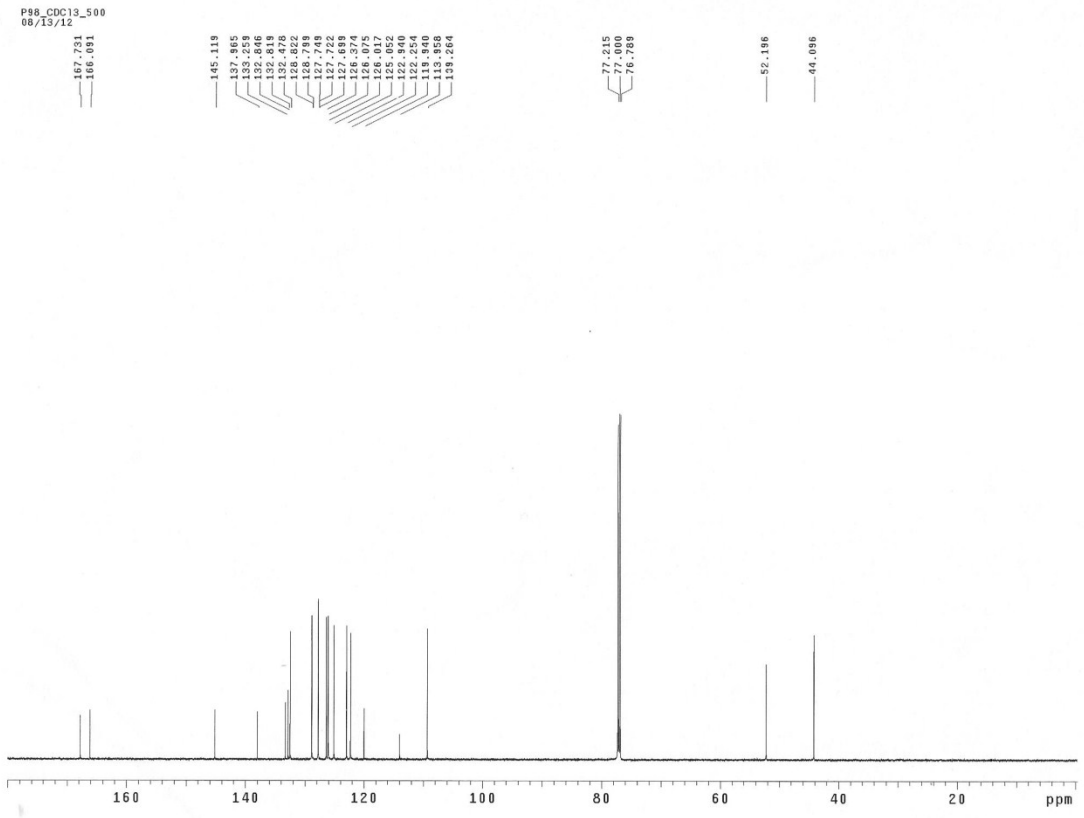


(E)-Methyl 2-(1-(naphthalen-2-ylmethyl)-2-oxoindolin-3-ylidene)acetate **(3k)**.

^{1}H NMR

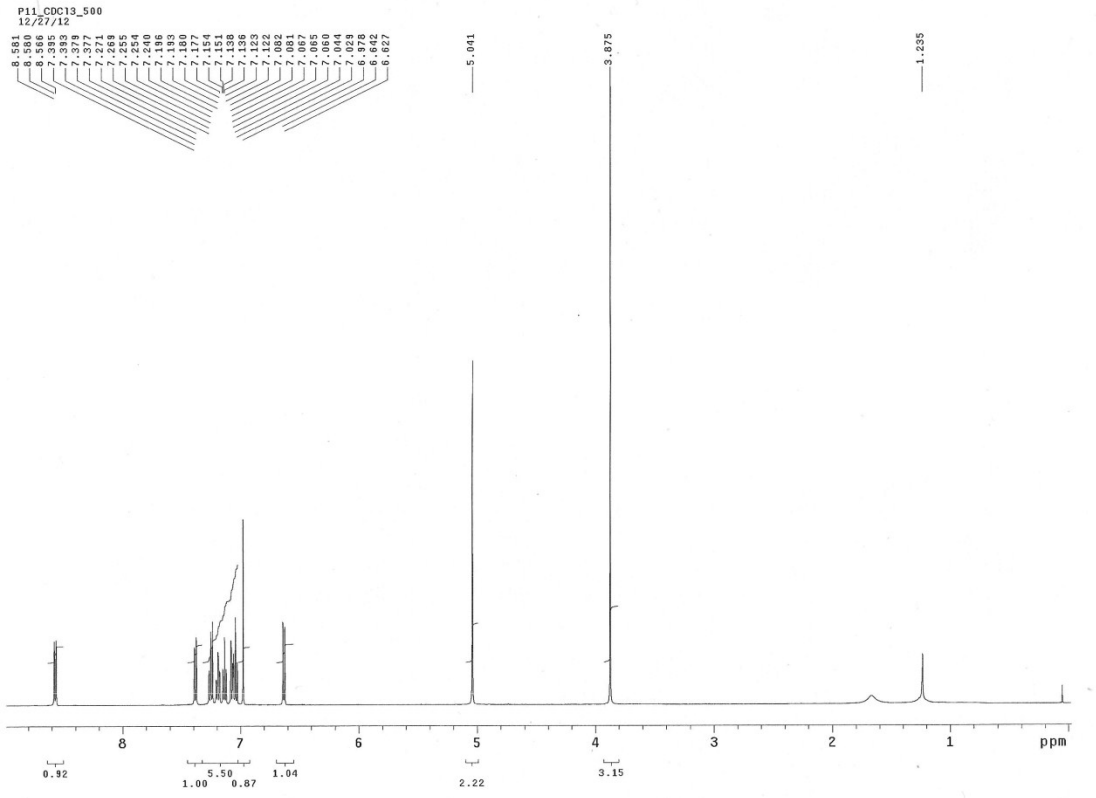


^{13}C NMR

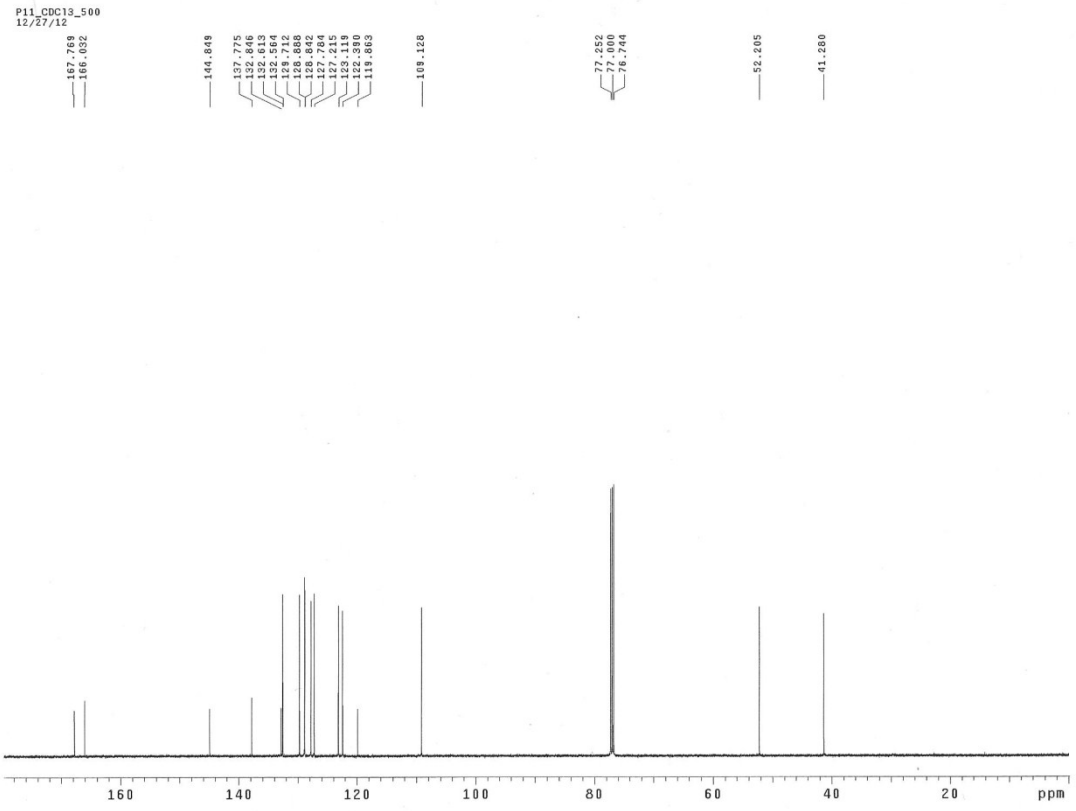


(E)-Methyl 2-(1-(2-chlorobenzyl)-2-oxoindolin-3-ylidene)acetate **(3l)**.

^{1}H NMR

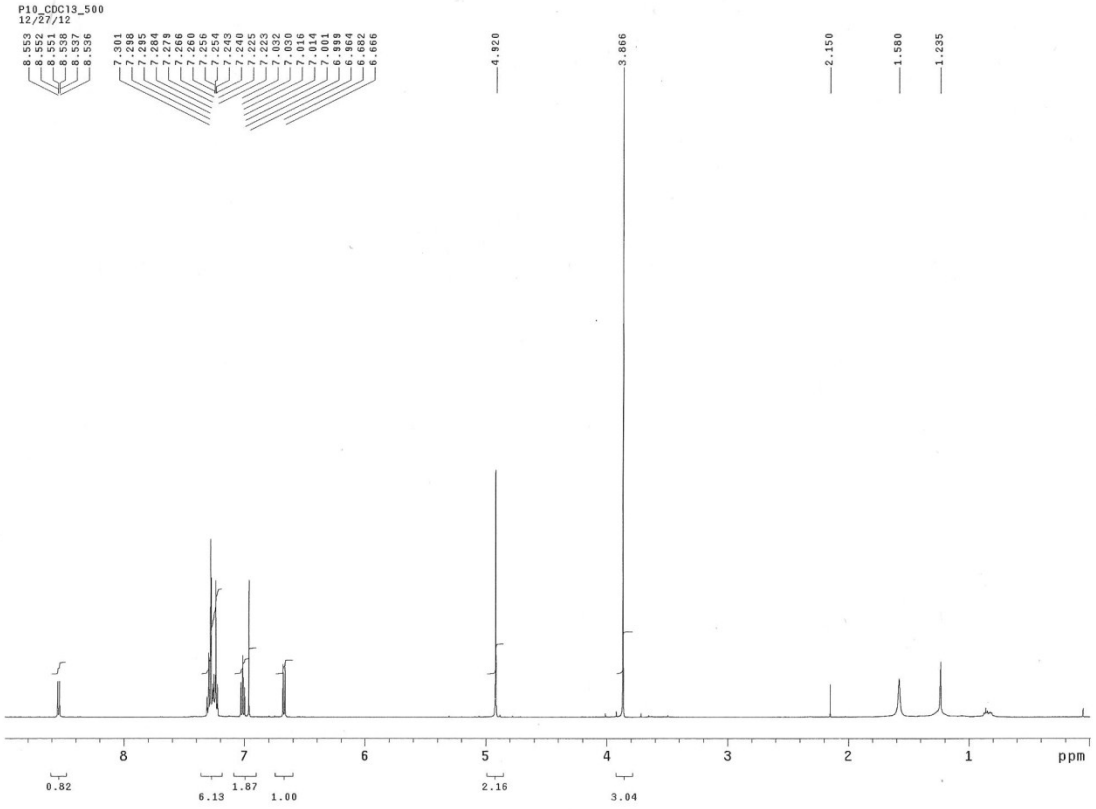


^{13}C NMR

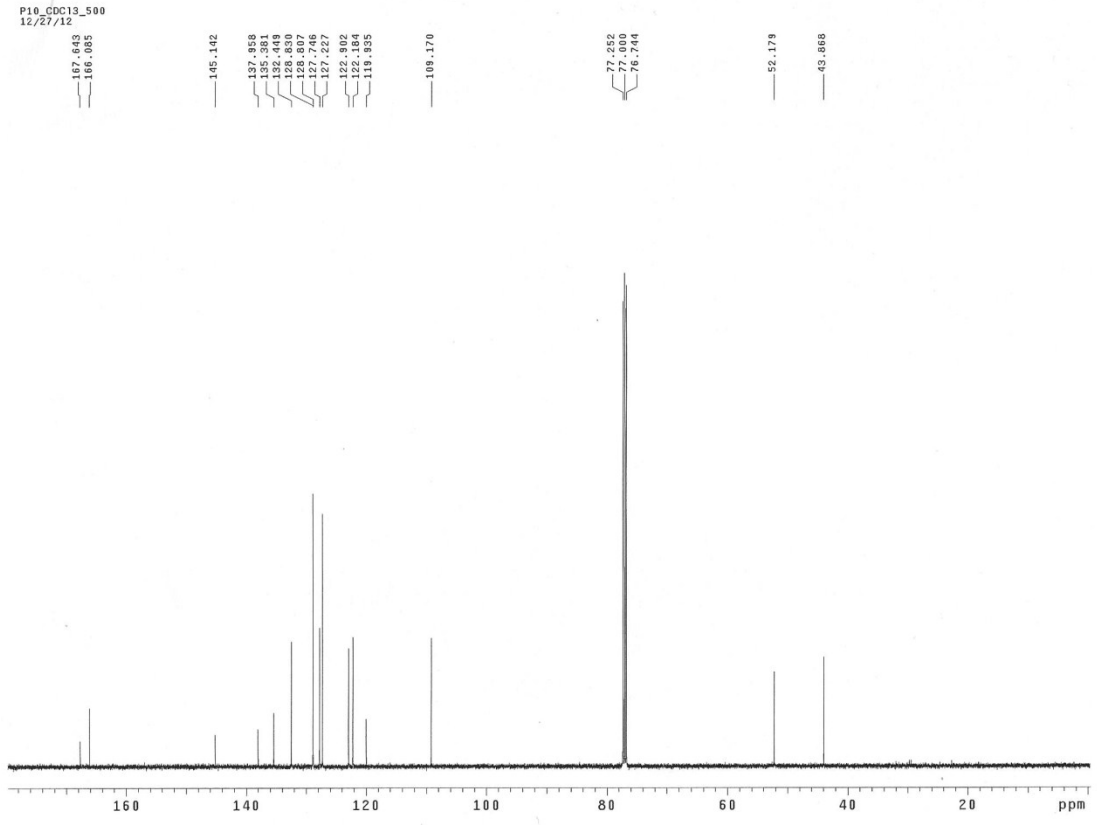


(E)-Methyl 2-(1-benzyl-2-oxoindolin-3-ylidene)acetate (**3m**).

^{1}H NMR

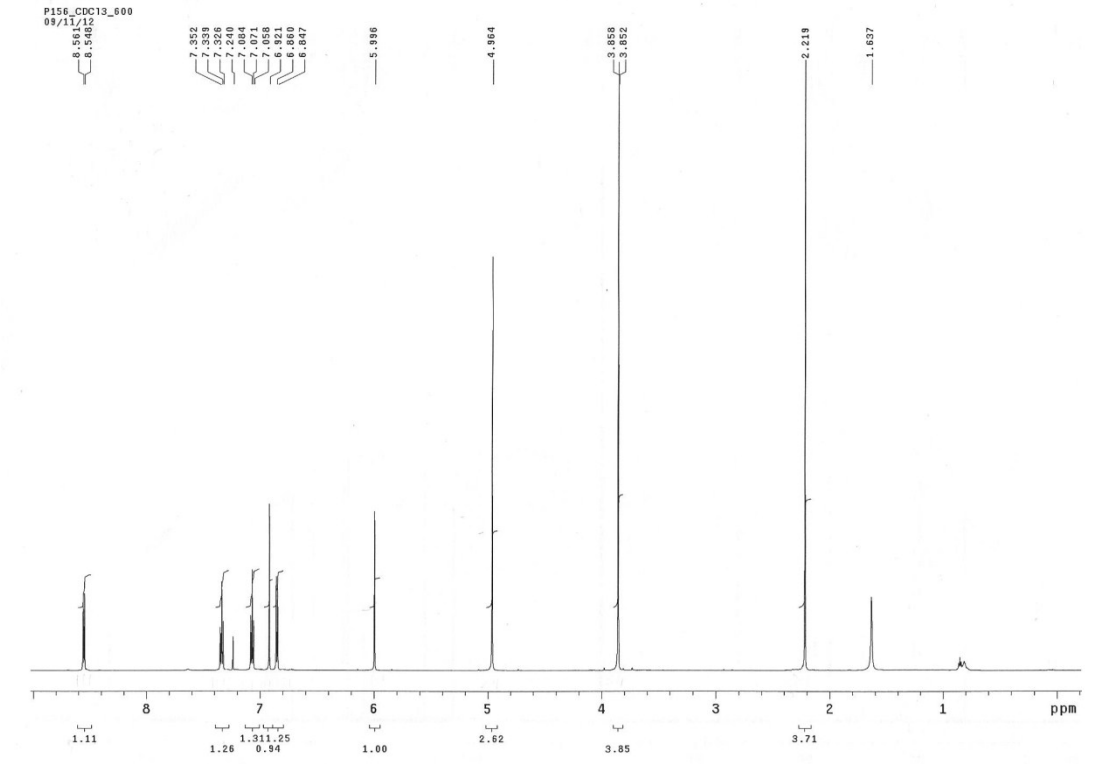


^{13}C NMR

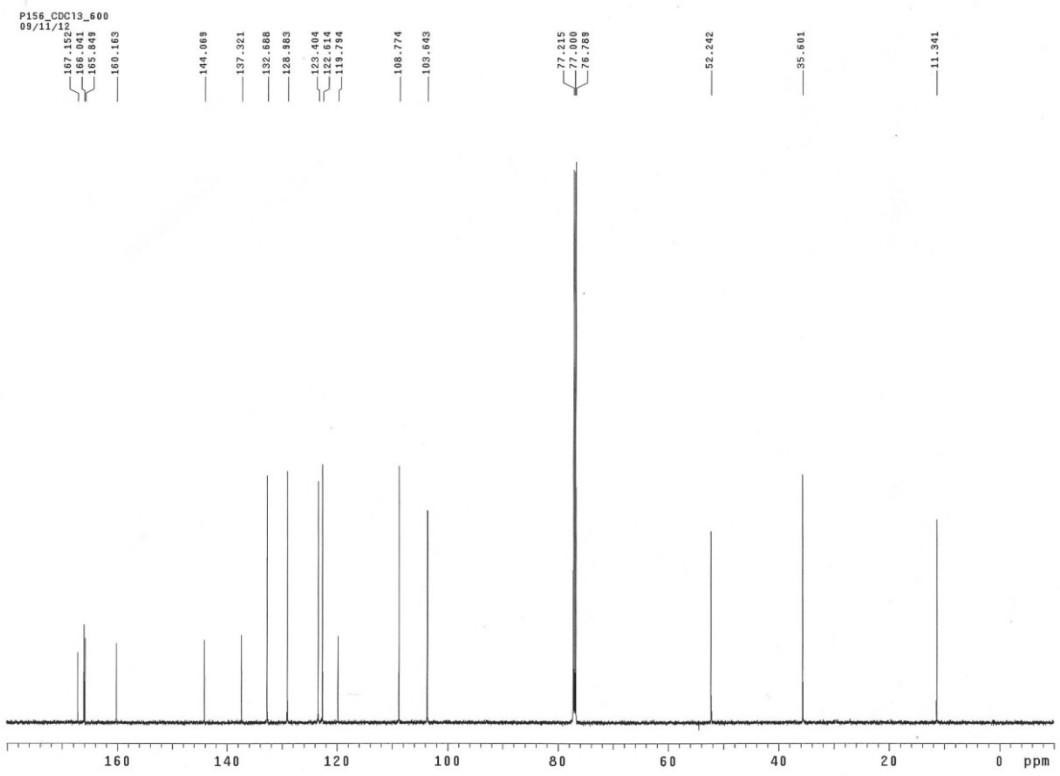


(E)-Methyl 2-(1-((3-methylisoxazol-5-yl)methyl)-2-oxoindolin-3-ylidene)acetate **(3n)**.

^{1}H NMR

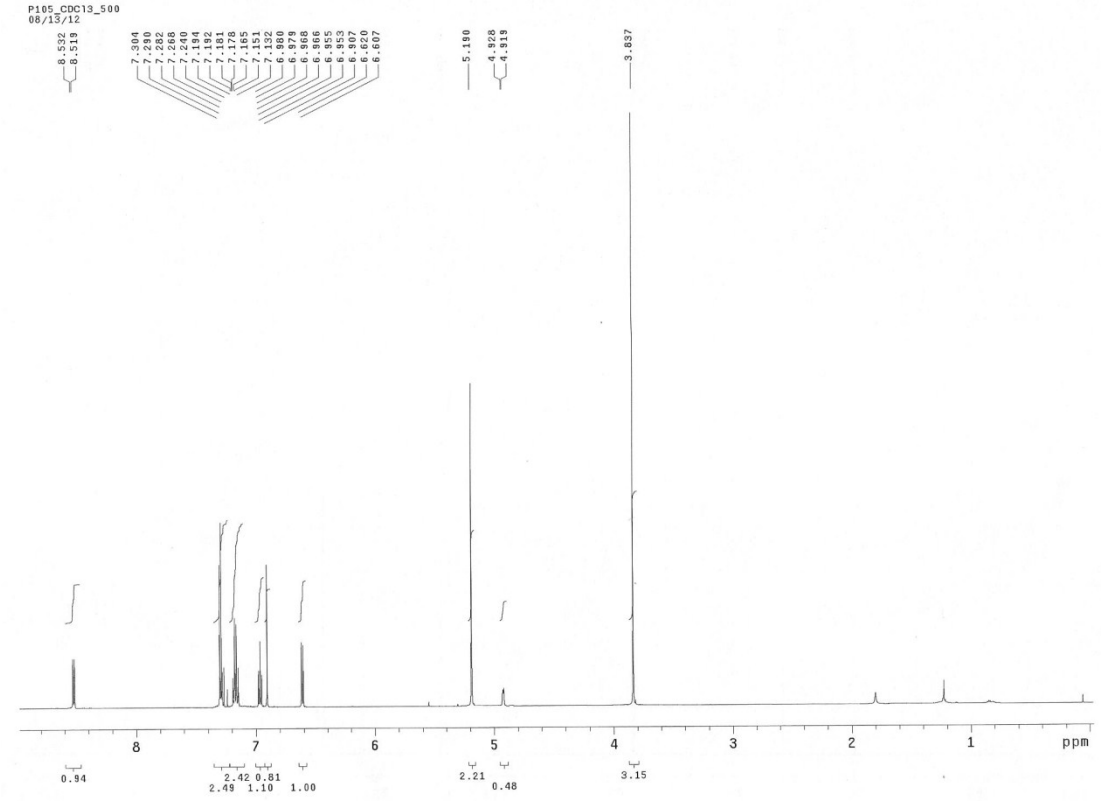


^{13}C NMR

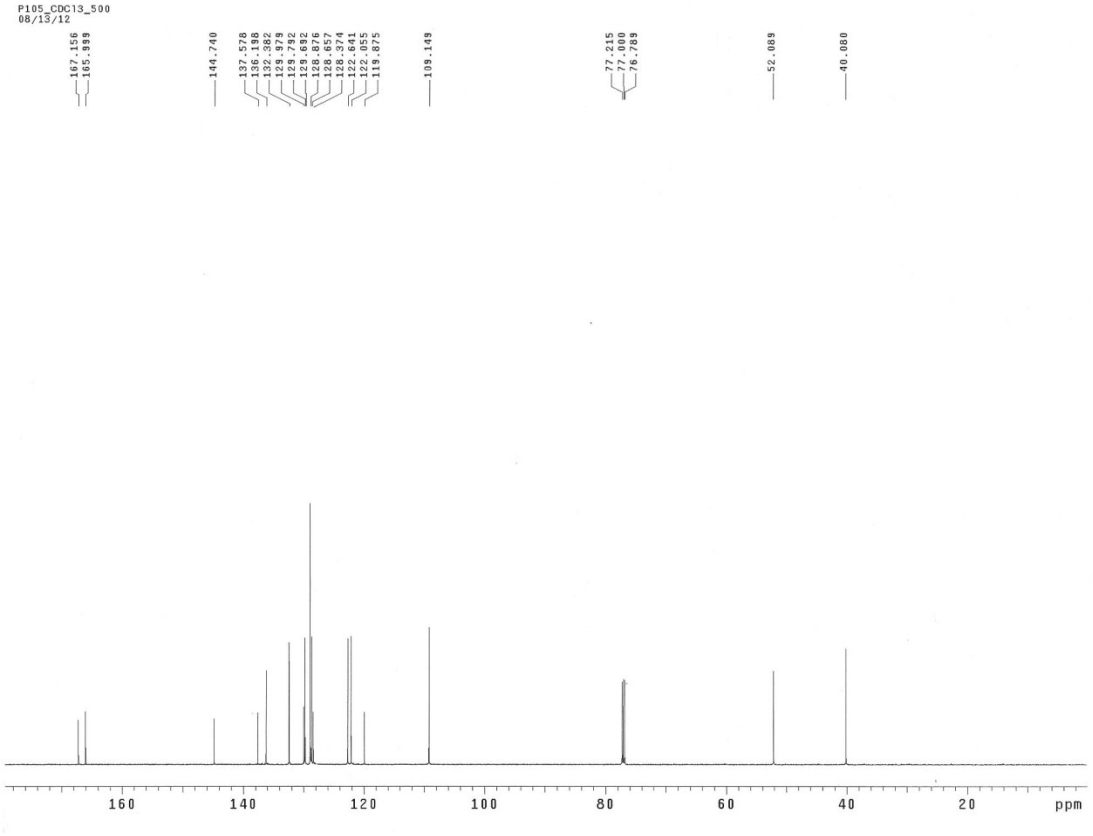


(E)-Methyl 2-(1-(2,6-dichlorobenzyl)-2-oxoindolin-3-ylidene)acetate **(3o)**.

^{1}H NMR

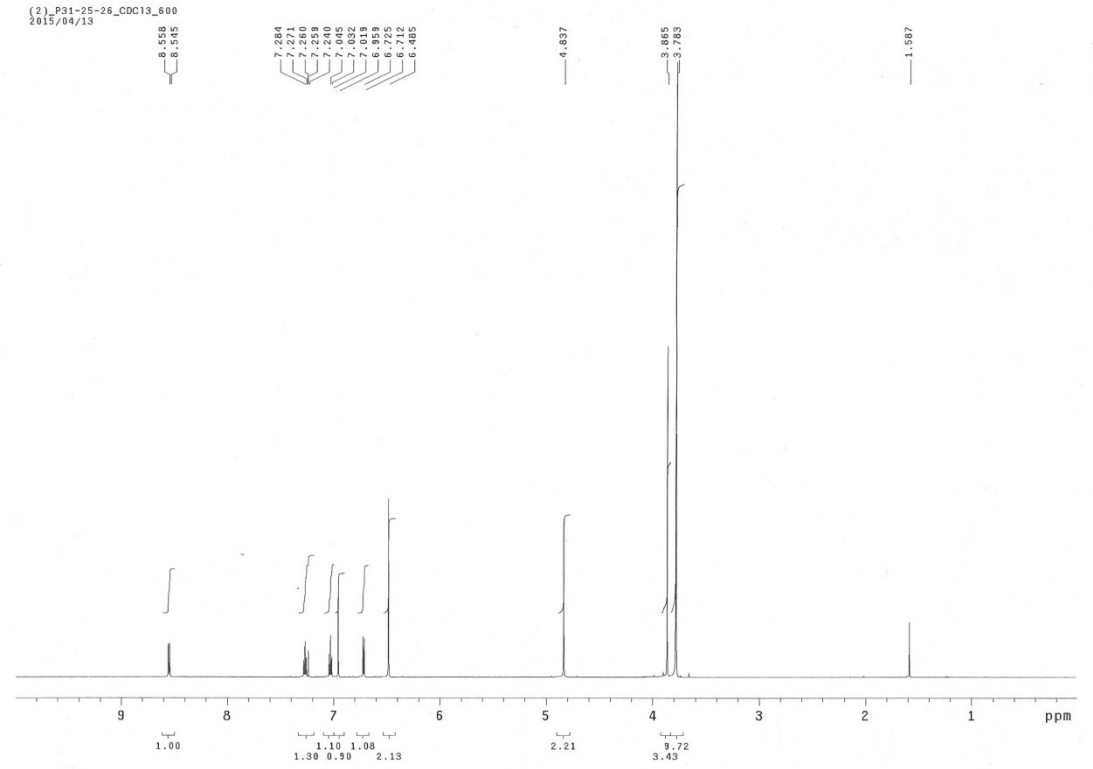


^{13}C NMR

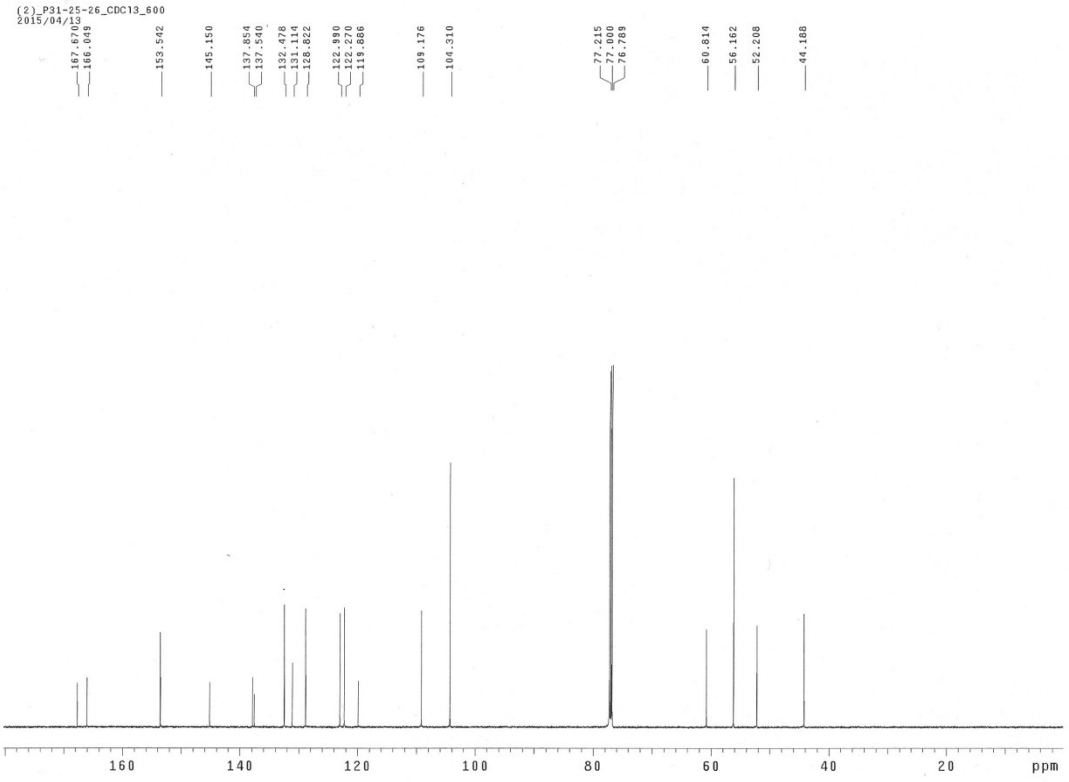


(E)-Methyl 2-(2-oxo-1-(3,4,5-trimethoxybenzyl)indolin-3-ylidene)acetate (**3p**)

^{1}H NMR

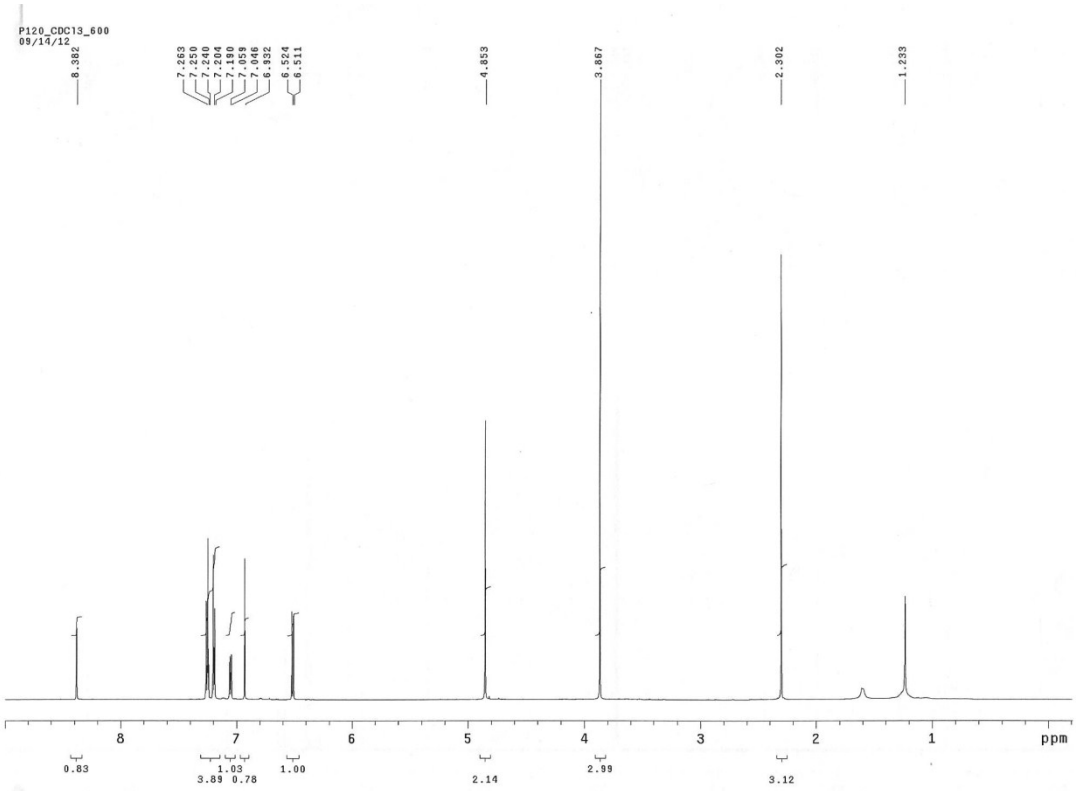


^{13}C NMR

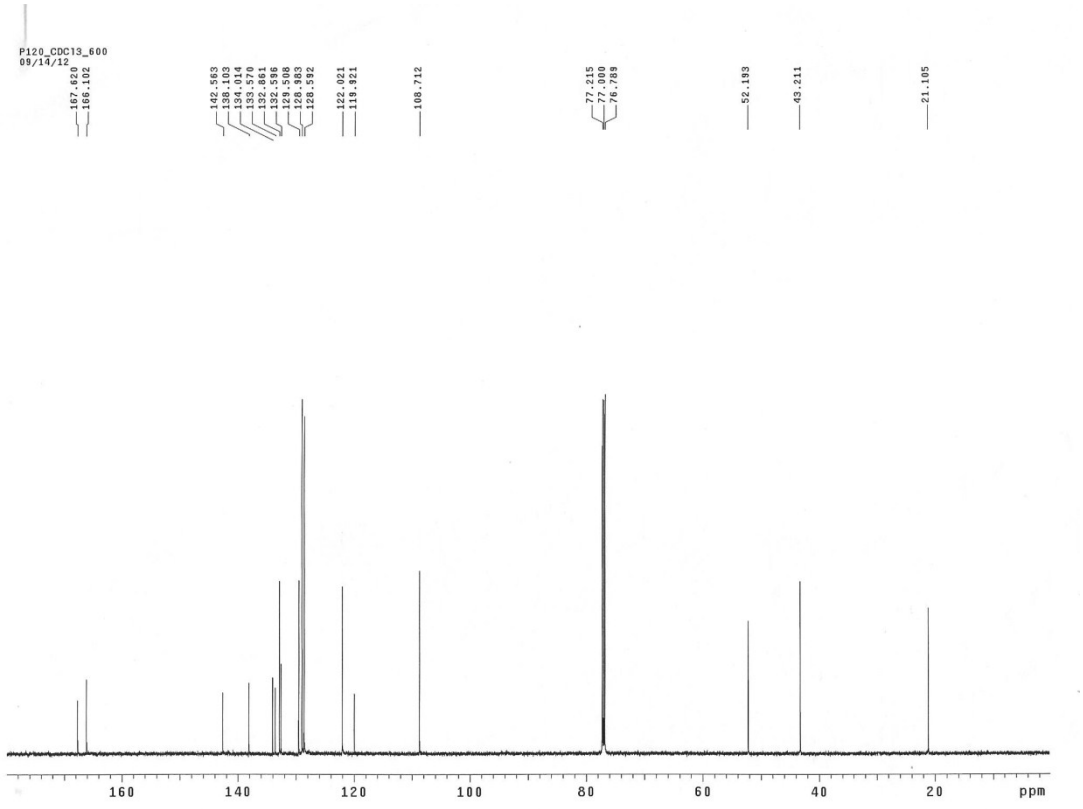


(E)-Methyl 2-(1-(4-chlorobenzyl)-5-methyl-2-oxoindolin-3-ylidene)acetate (**3q**).

^{1}H NMR

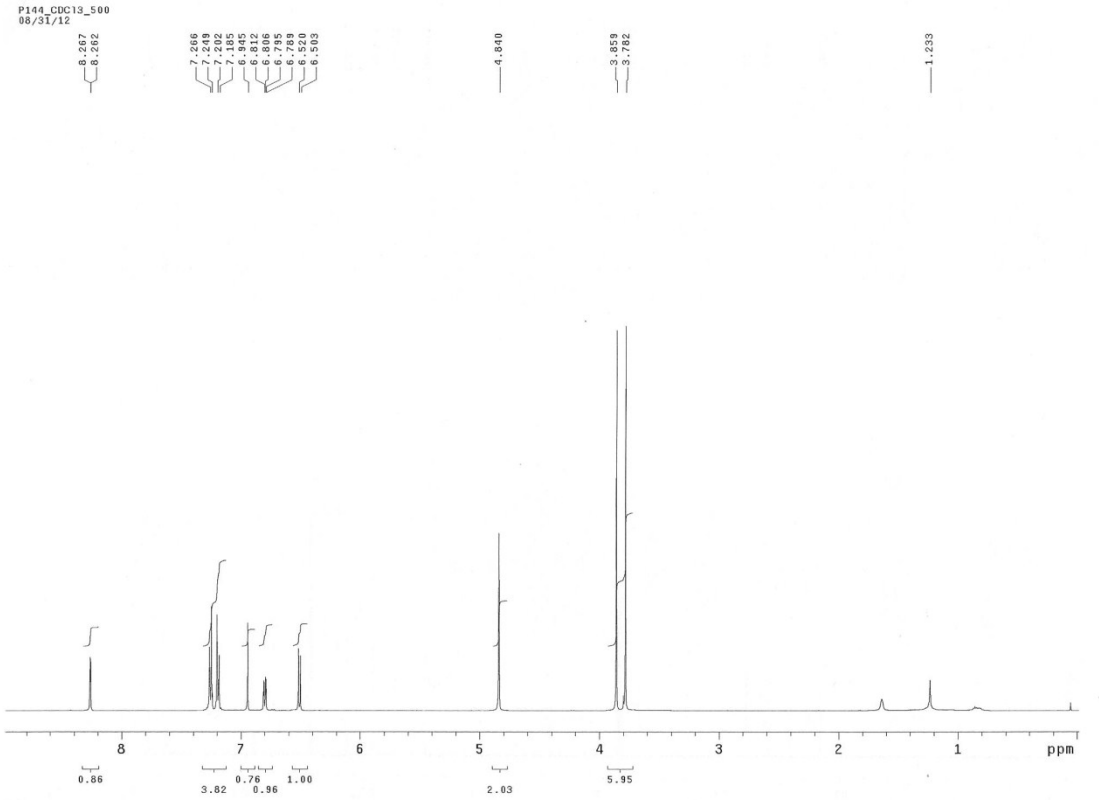


^{13}C NMR



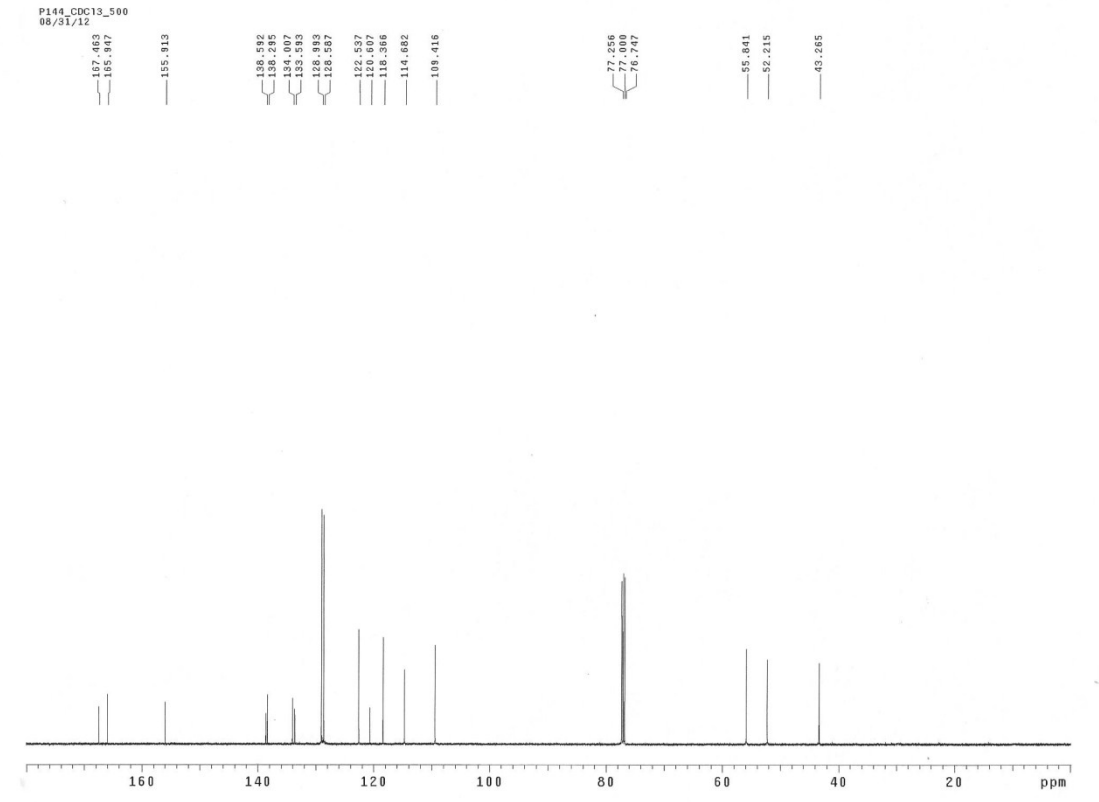
(E)-Methyl 2-(1-(4-chlorobenzyl)-5-methoxy-2-oxoindolin-3-ylidene)acetate **(3r)**.

^{1}H NMR



13

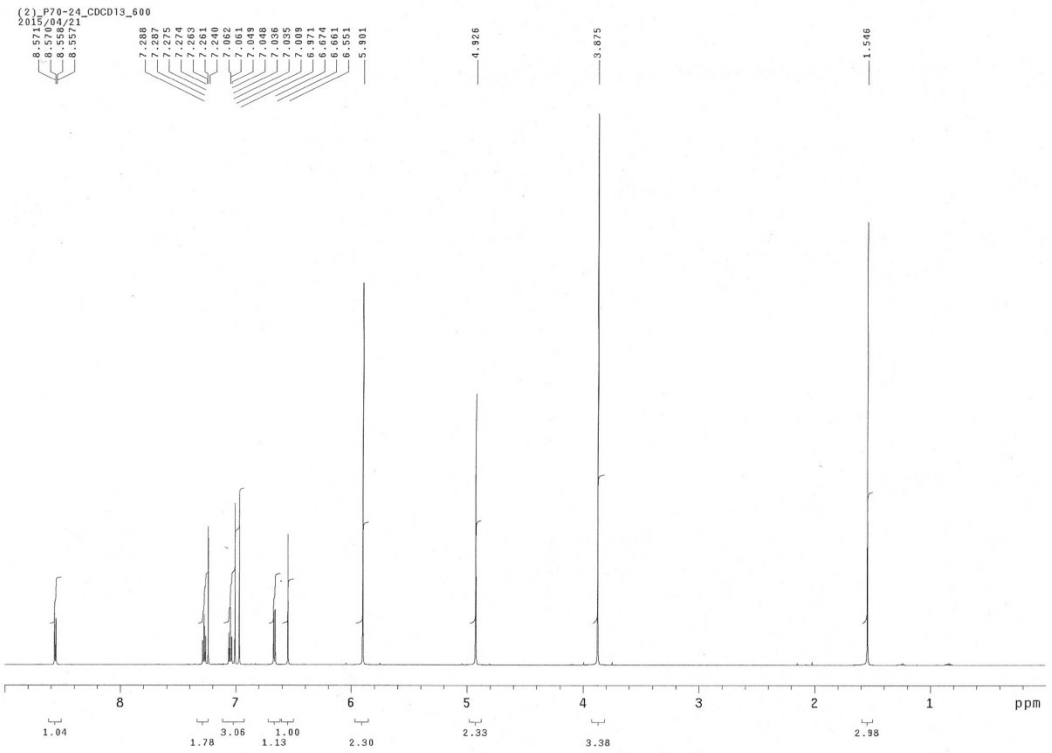
C NMR



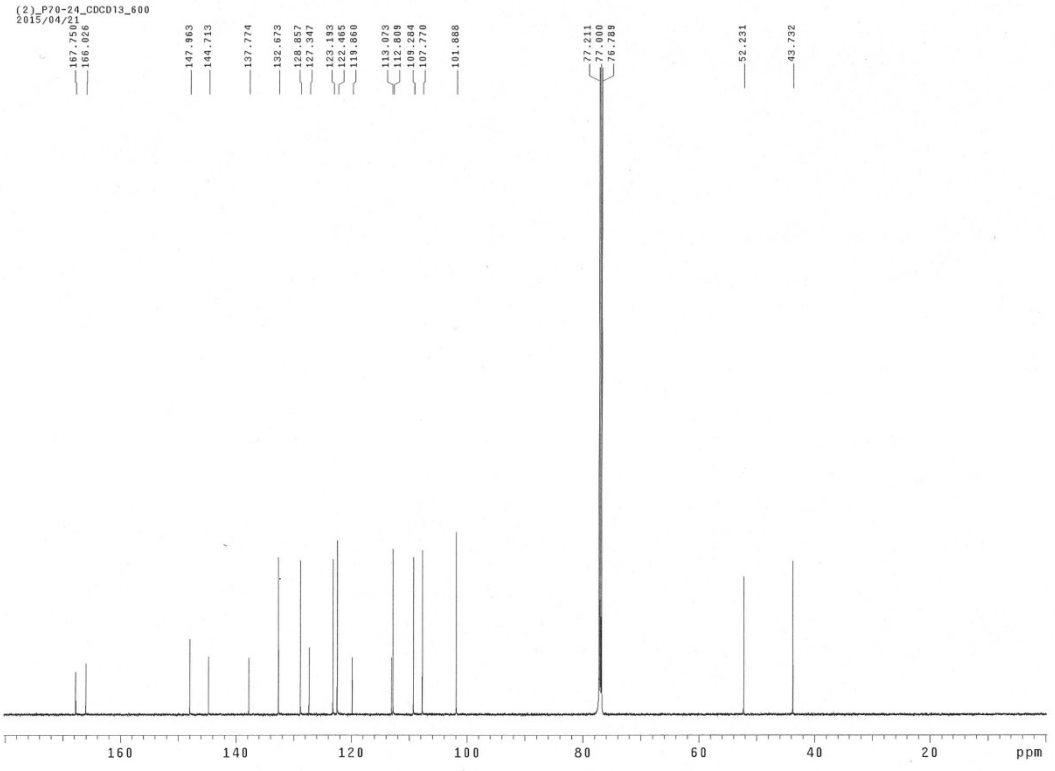
(E)-Methyl 2-(1-((6-bromobenzo[d][1,3]dioxol-5-yl)methyl)-2-oxoindolin-3-ylidene)

acetate (**3s**).

^{1}H NMR

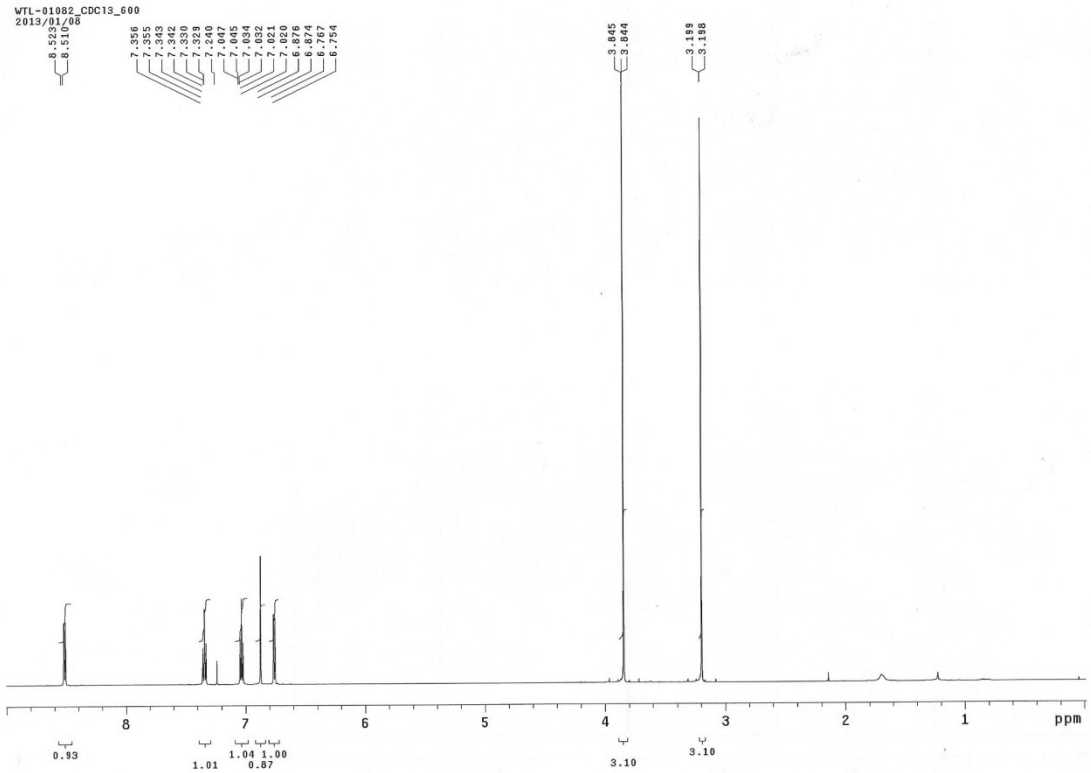


^{13}C NMR

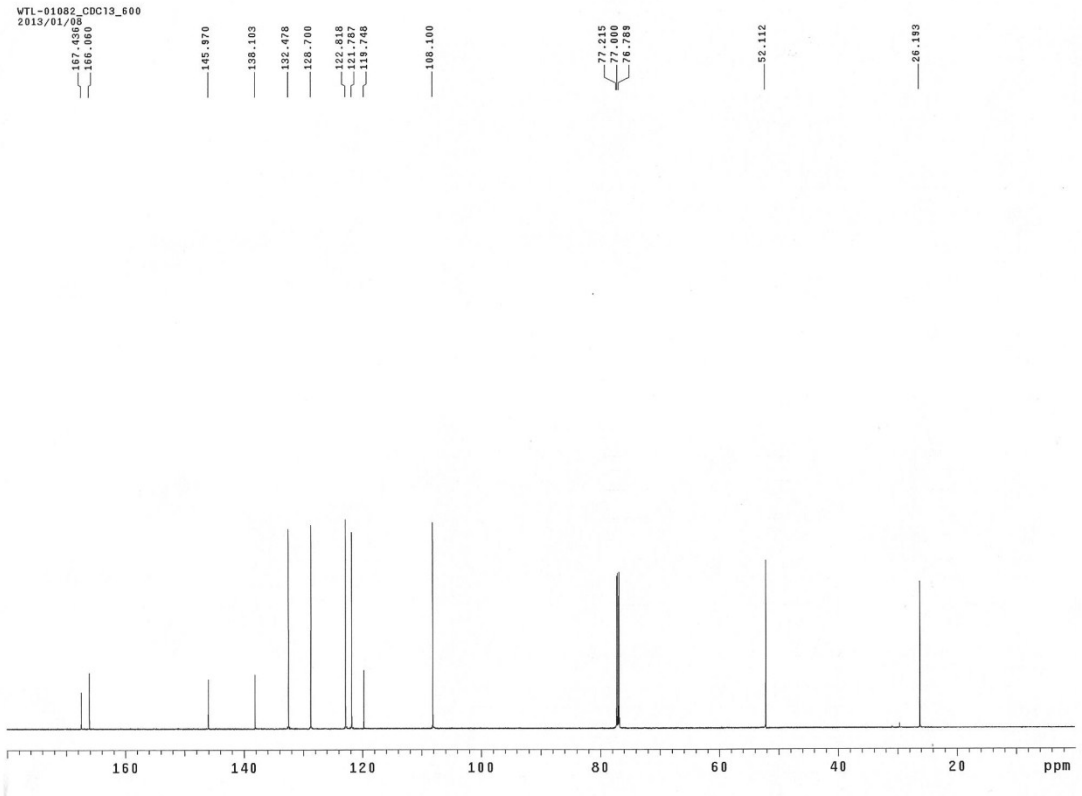


(E)-Methyl 2-(1-methyl-2-oxoindolin-3-ylidene)acetate (**3t**).

^{1}H NMR

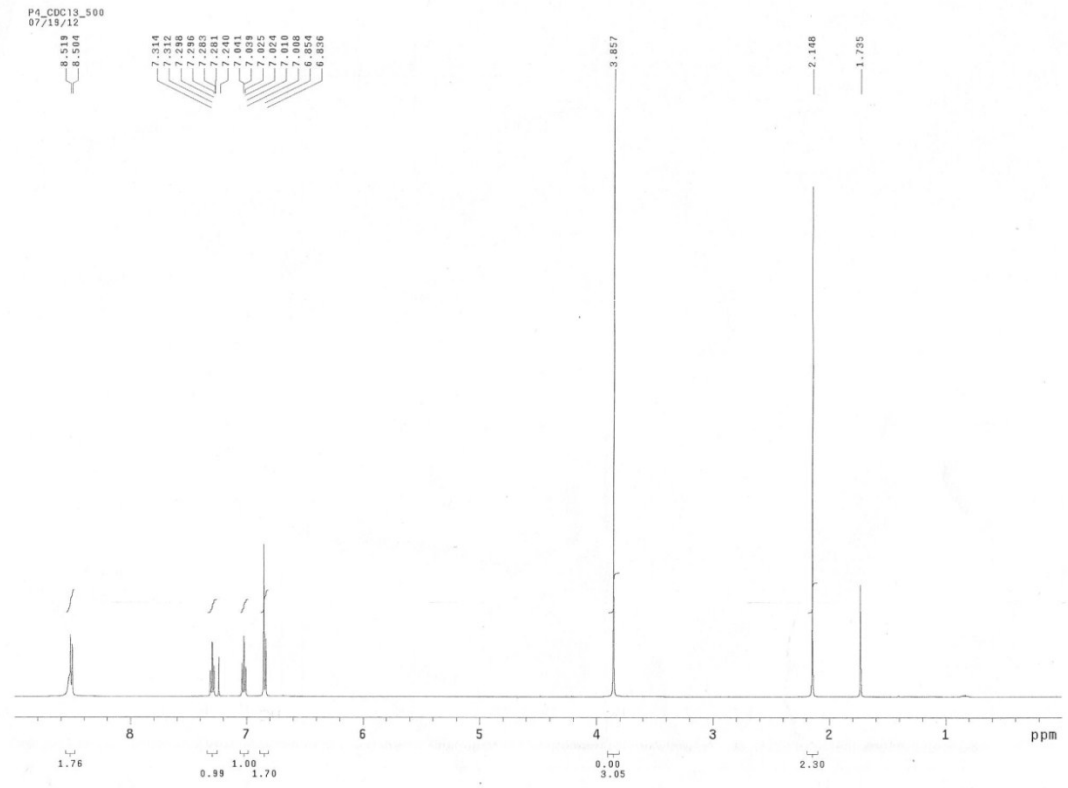


^{13}C NMR

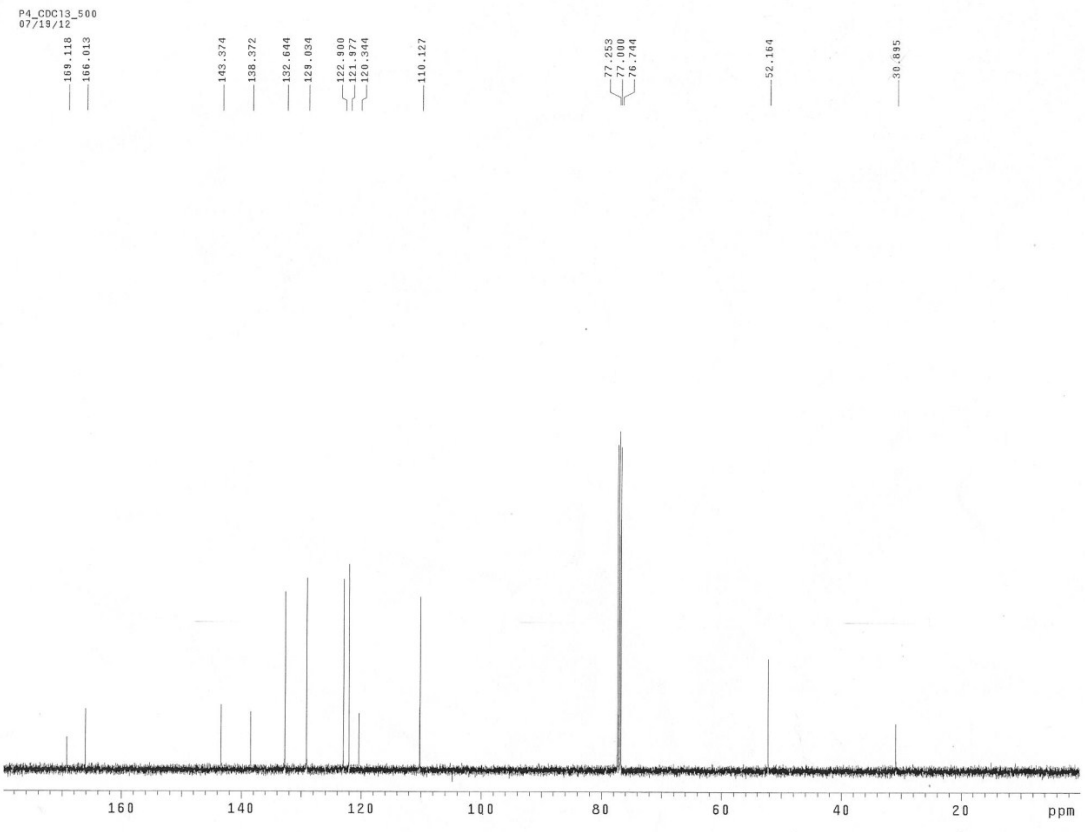


(E)-Methyl 2-(2-oxoindolin-3-ylidene)acetate **(3u)**.

^{1}H NMR

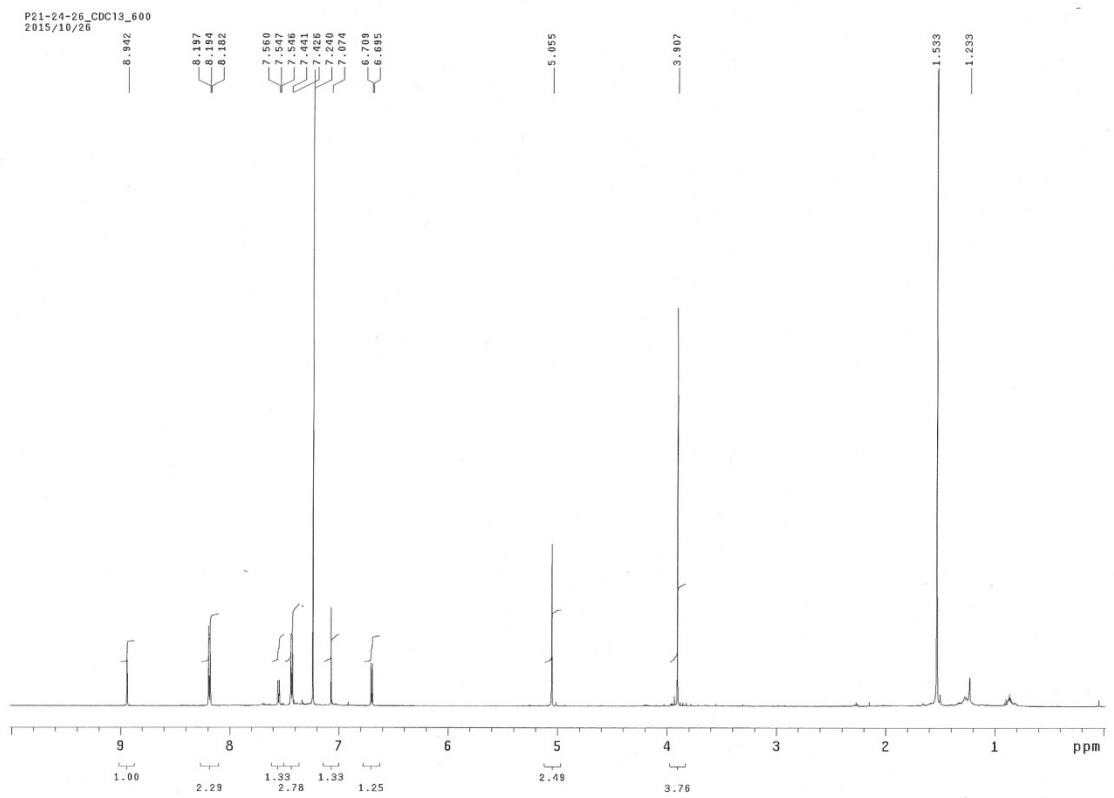


^{13}C NMR

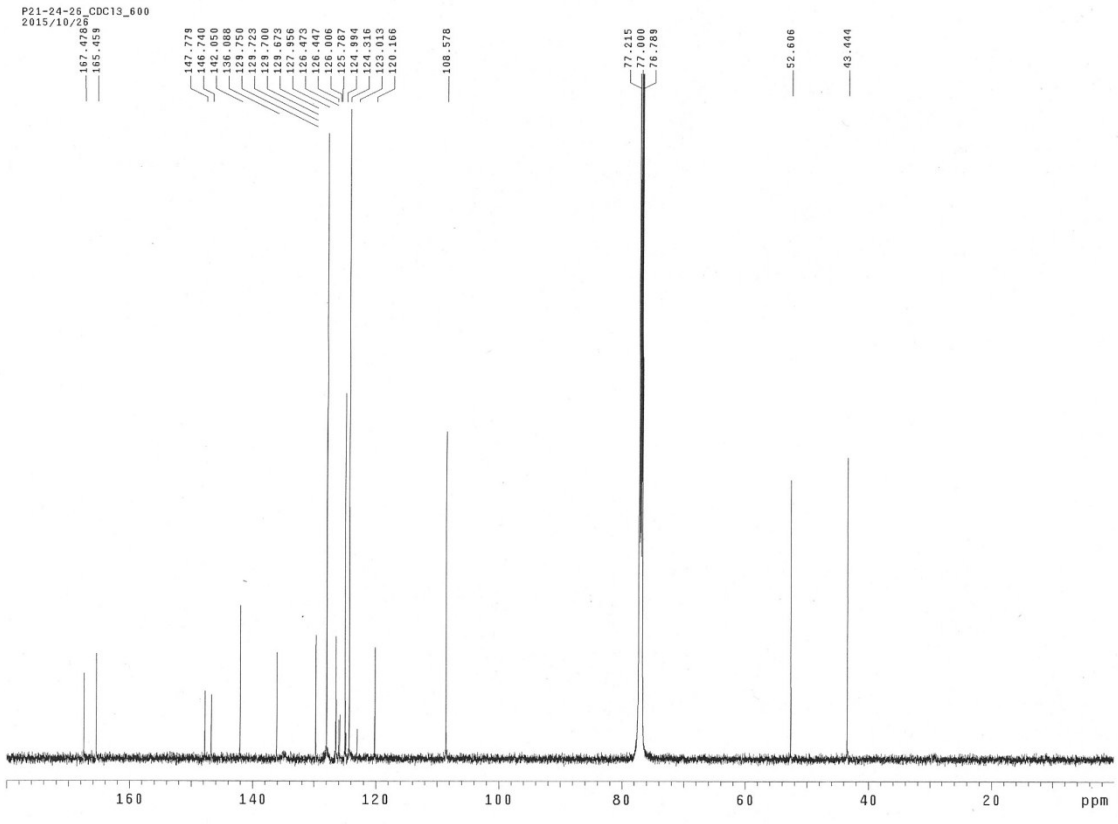


(E)-Methyl 2-(1-(4-nitrobenzyl)-2-oxo-5-(trifluoromethyl)indolin-3-ylidene) acetate **(3v).**

^{1}H NMR

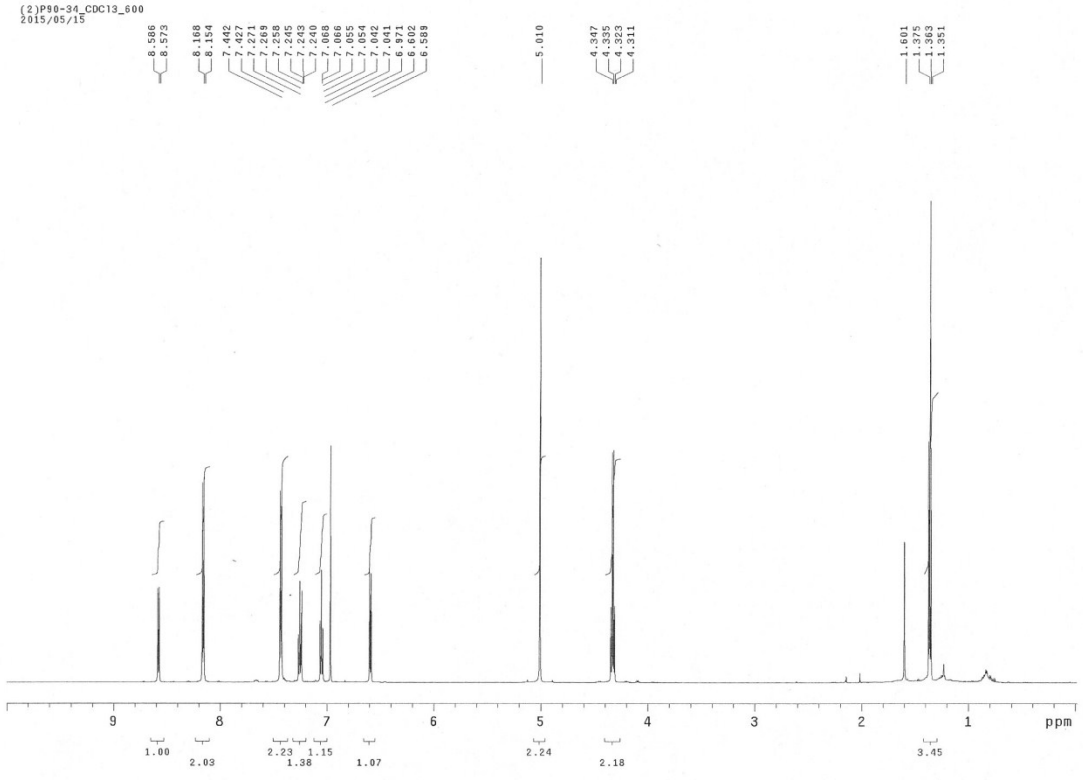


^{13}C NMR

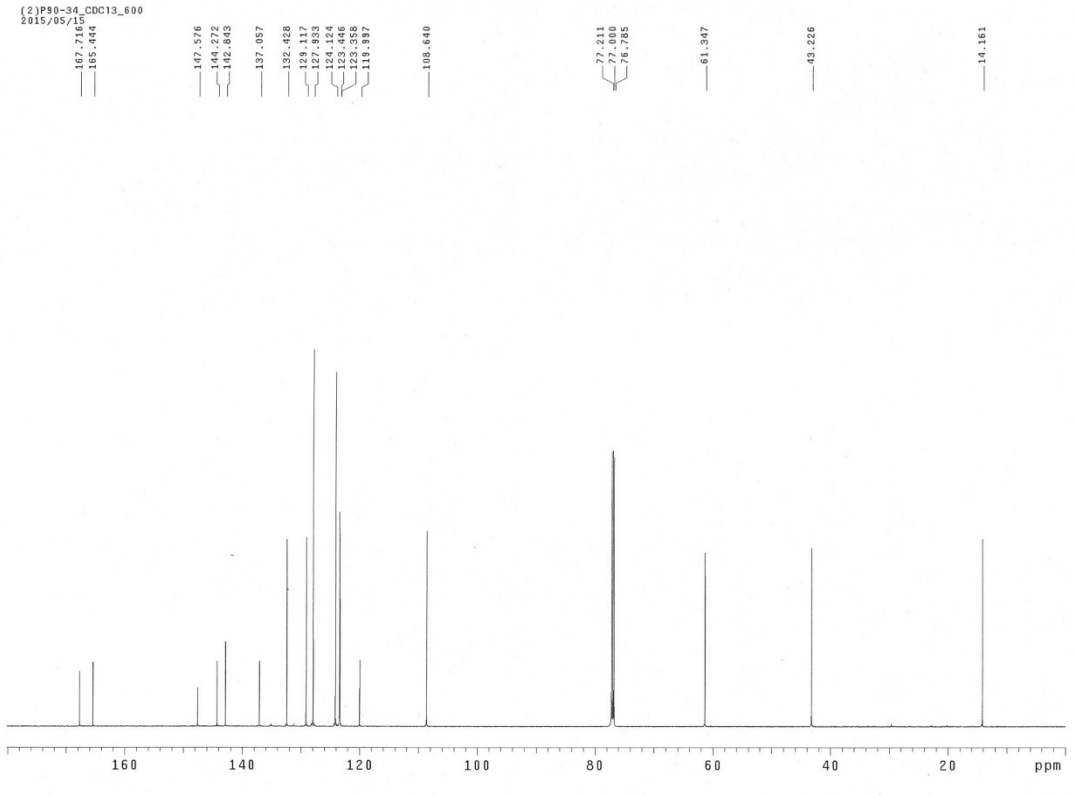


(E)-Ethyl 2-(1-(4-nitrobenzyl)-2-oxoindolin-3-ylidene)acetate (**4a**).

^{1}H NMR

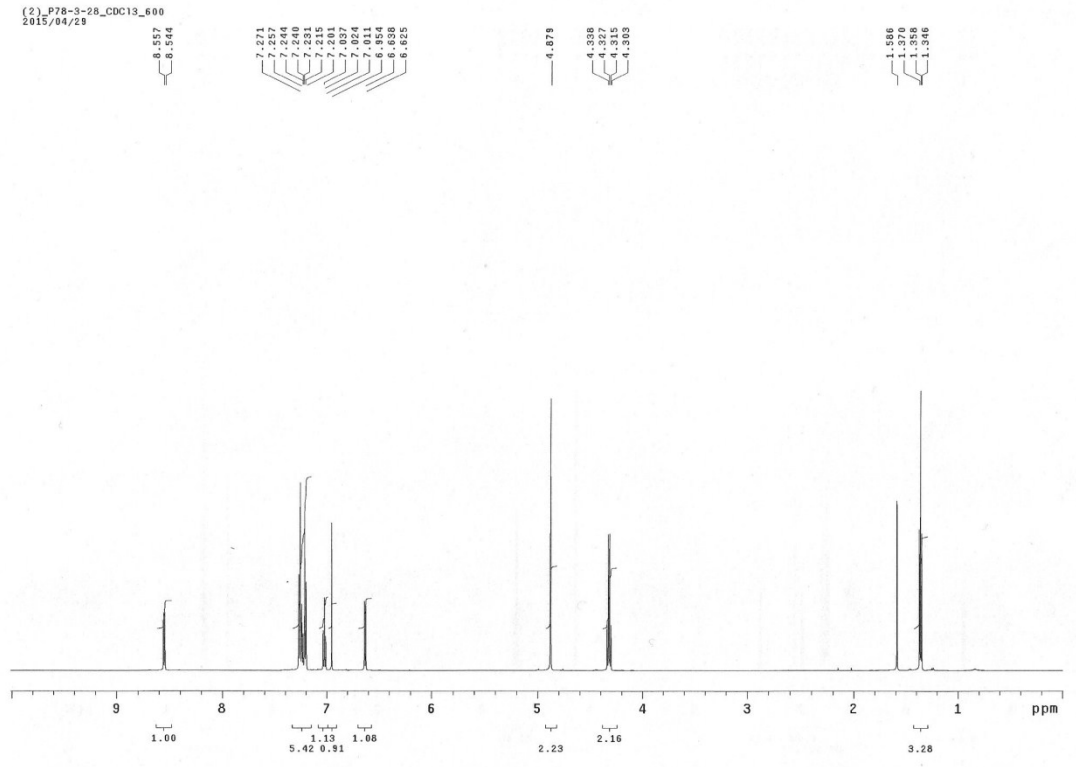


^{13}C NMR

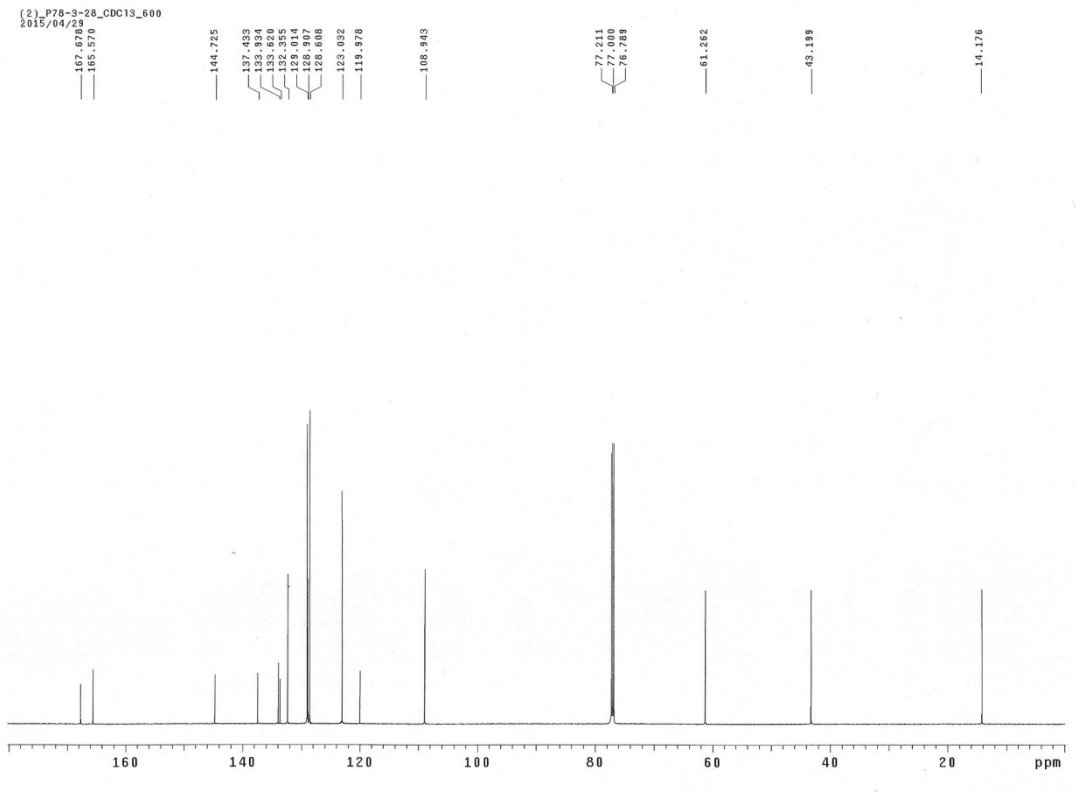


(E)-Ethyl 2-(1-(4-chlorobenzyl)-2-oxoindolin-3-ylidene)acetate **(4b)**.

^{1}H NMR

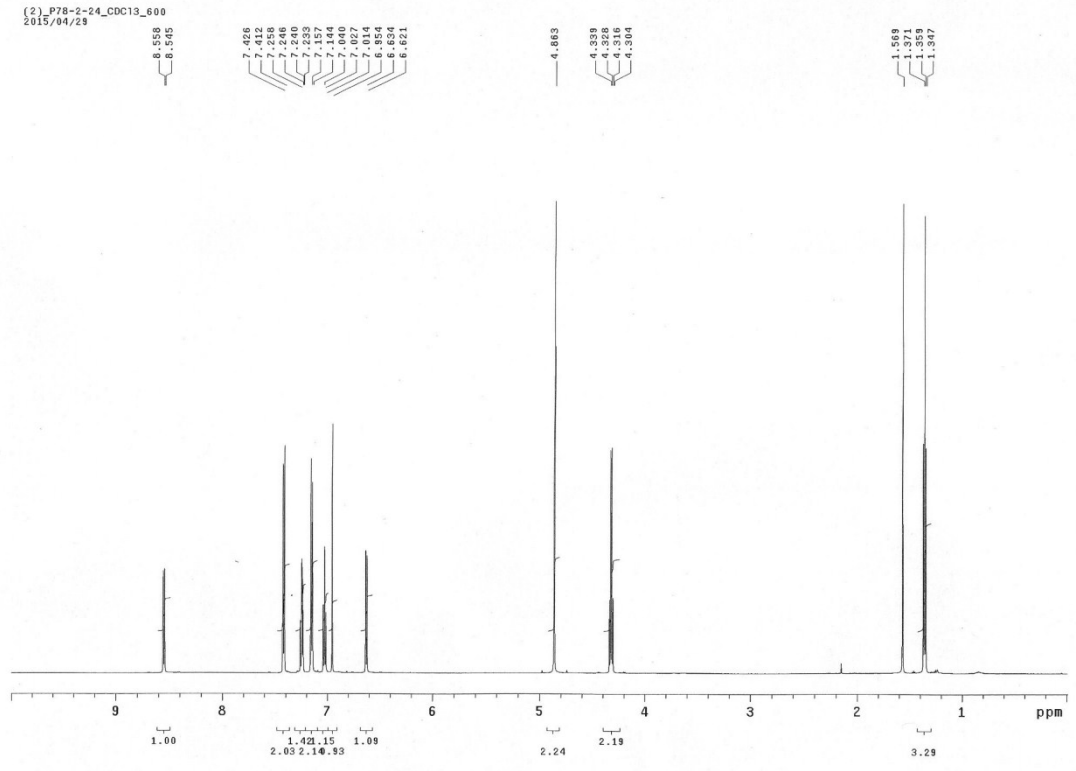


^{13}C NMR

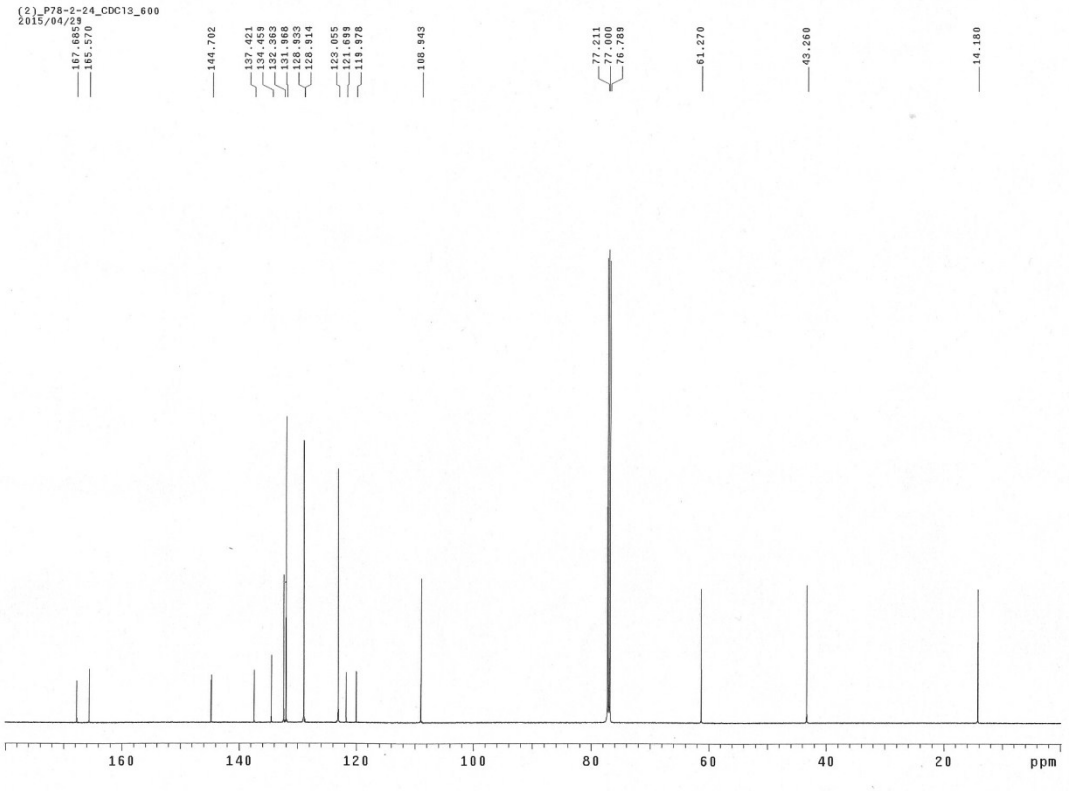


(E)-Ethyl 2-(1-(4-bromobenzyl)-2-oxoindolin-3-ylidene)acetate (**4c**).

^{1}H NMR

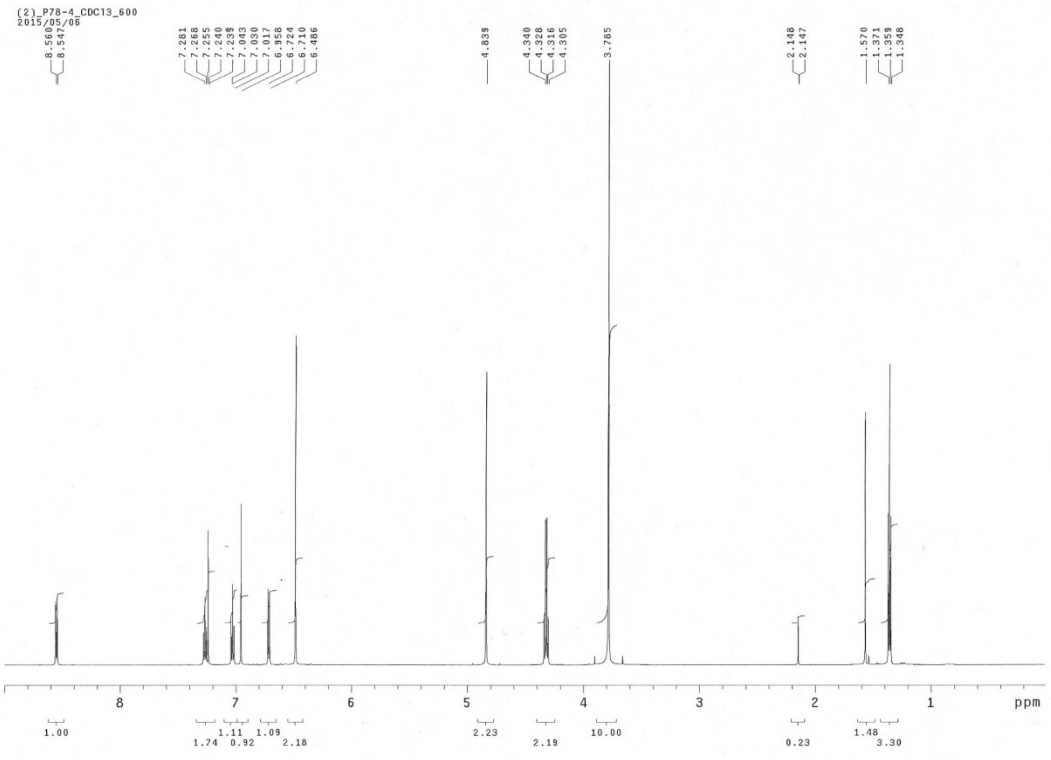


^{13}C NMR

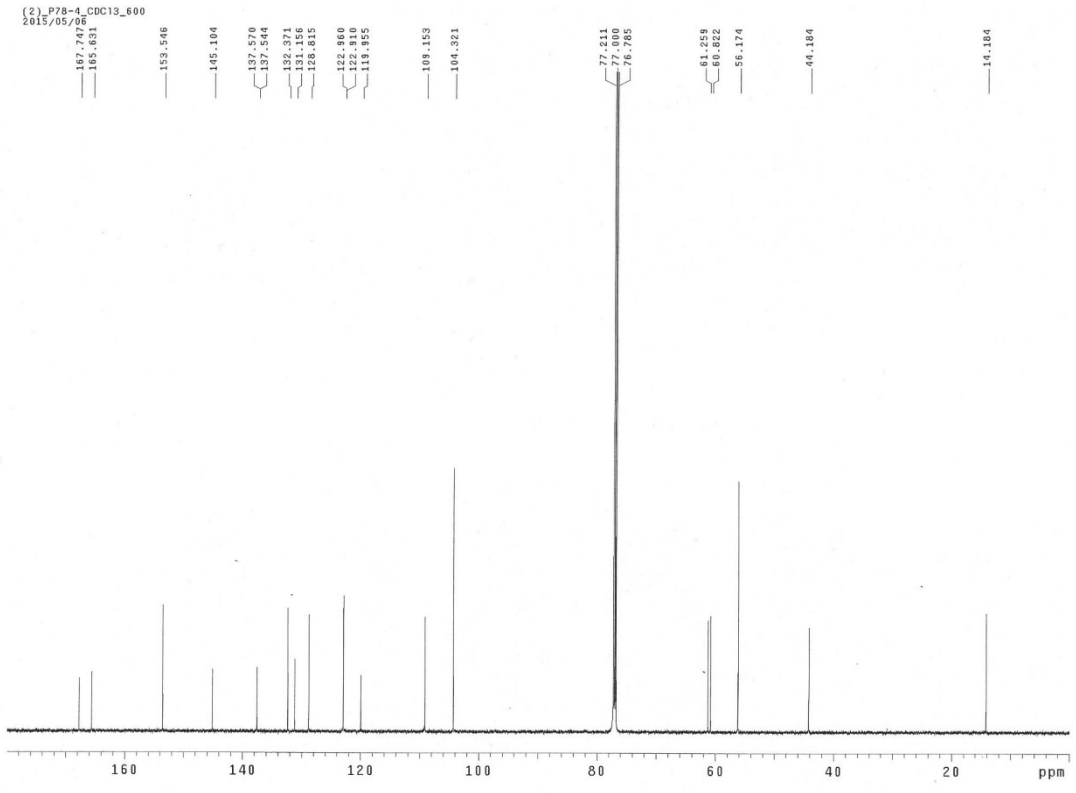


(E)-Ethyl 2-(2-oxo-1-(3,4,5-trimethoxybenzyl)indolin-3-ylidene)acetate **(4d)**.

^{1}H NMR

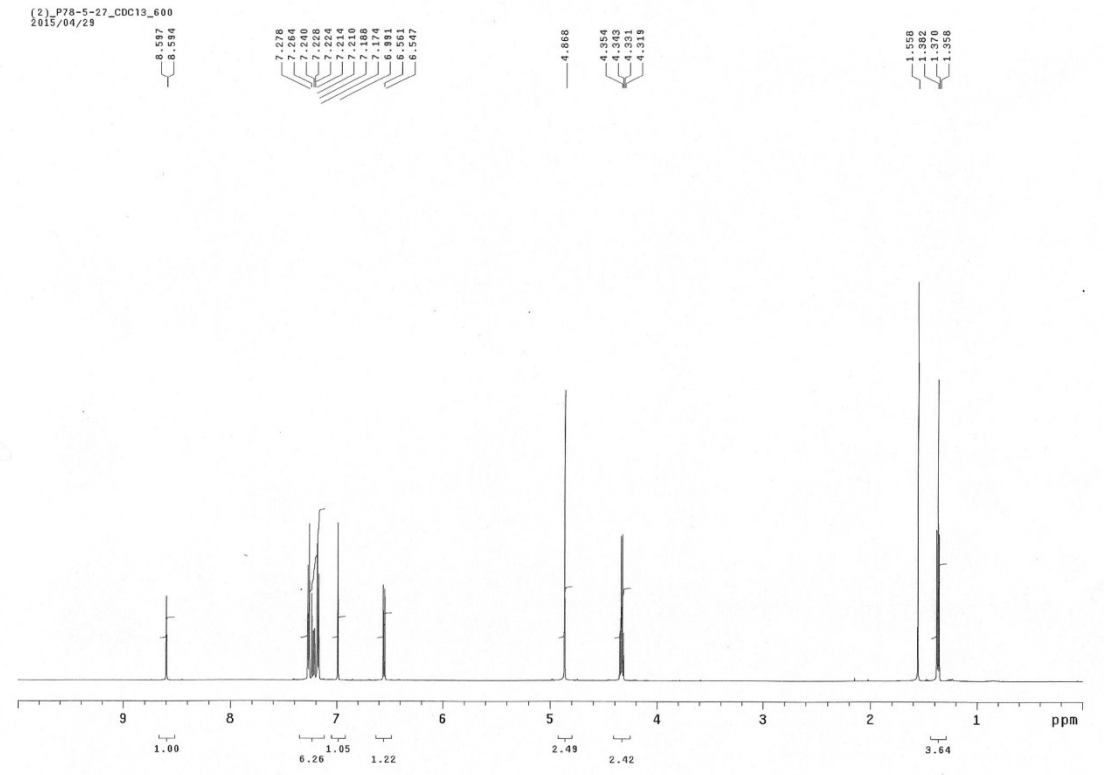


^{13}C NMR

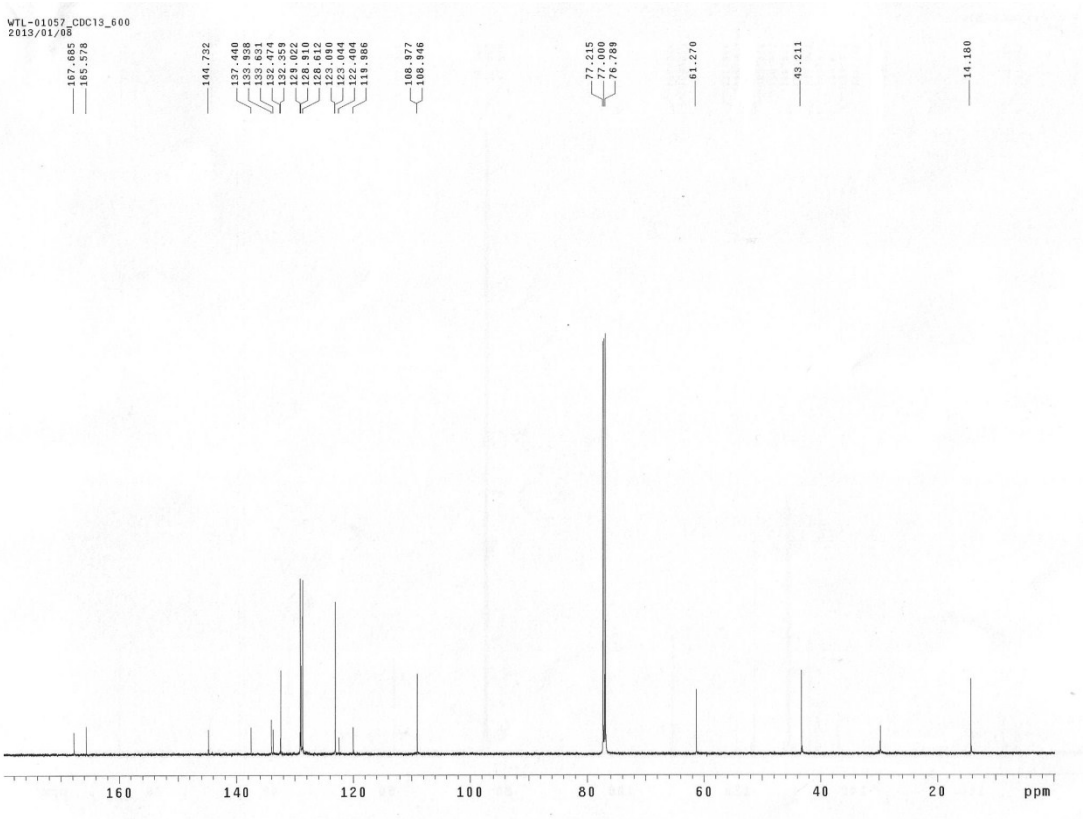


(E)-Ethyl 2-(5-chloro-1-(4-chlorobenzyl)-2-oxoindolin-3-ylidene)acetate **(4e)**.

^{1}H NMR

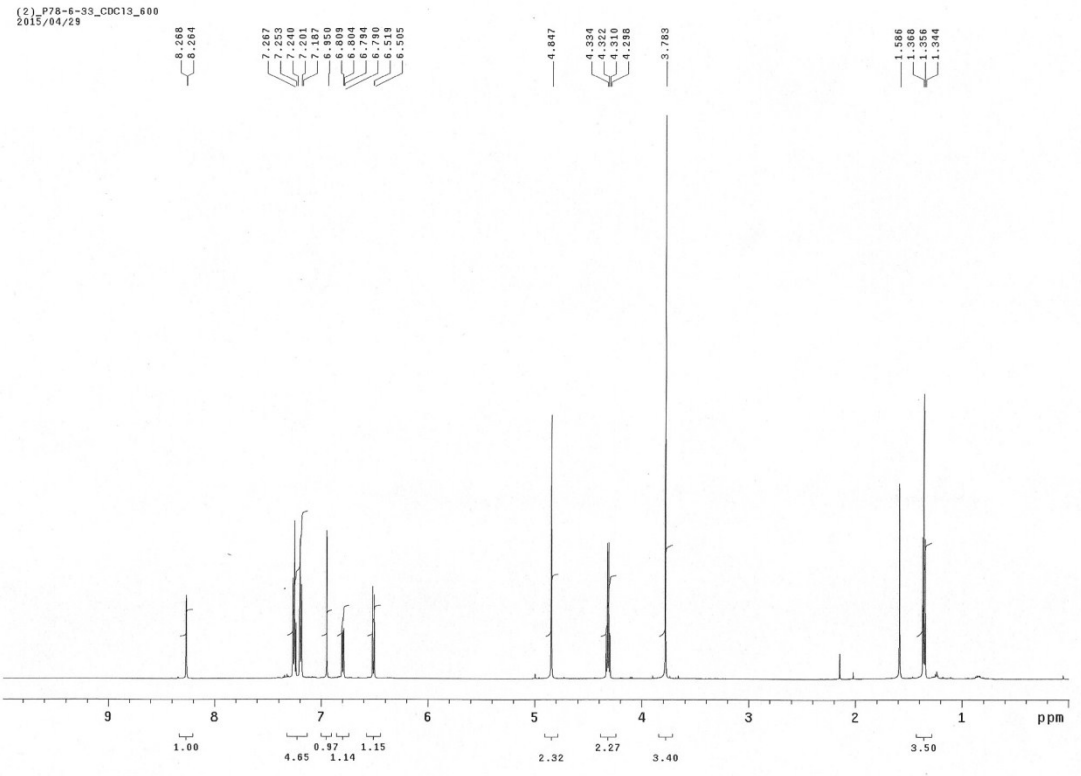


^{13}C NMR

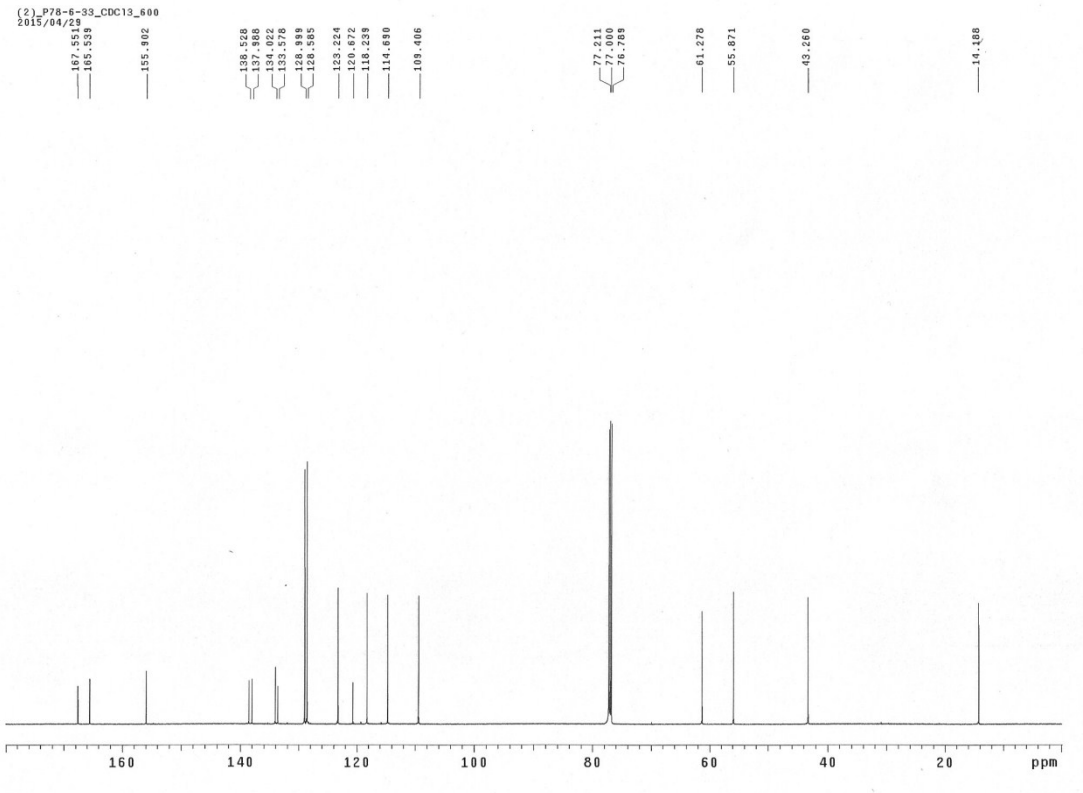


(E)-Ethyl 2-(1-(4-chlorobenzyl)-5-methoxy-2-oxoindolin-3-ylidene)acetate **(4f)**.

^{1}H NMR

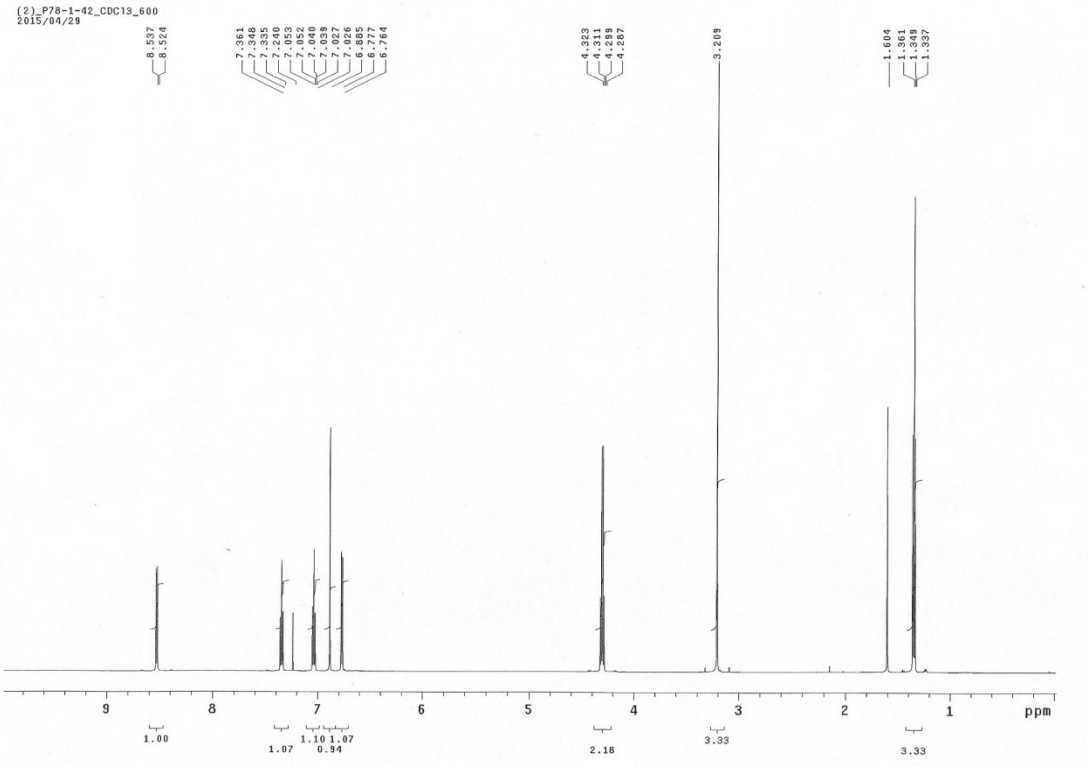


^{13}C NMR

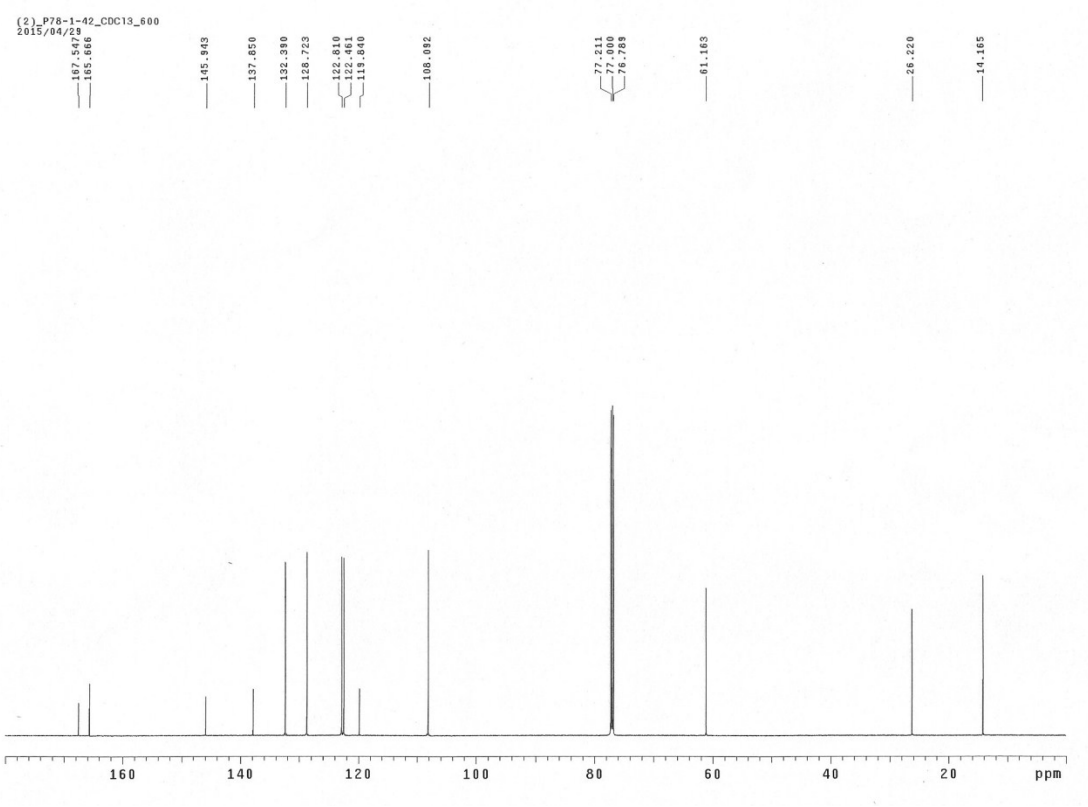


(E)-Ethyl 2-(1-methyl-2-oxoindolin-3-ylidene)acetate (**4g**).

^{1}H NMR

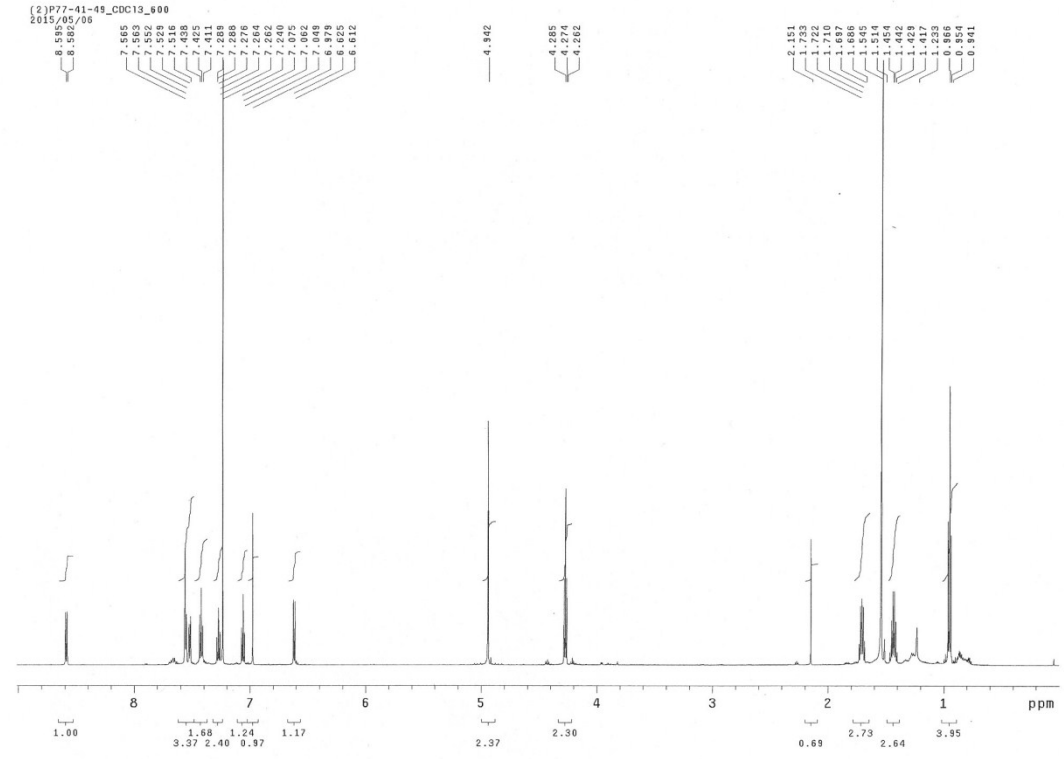


^{13}C NMR

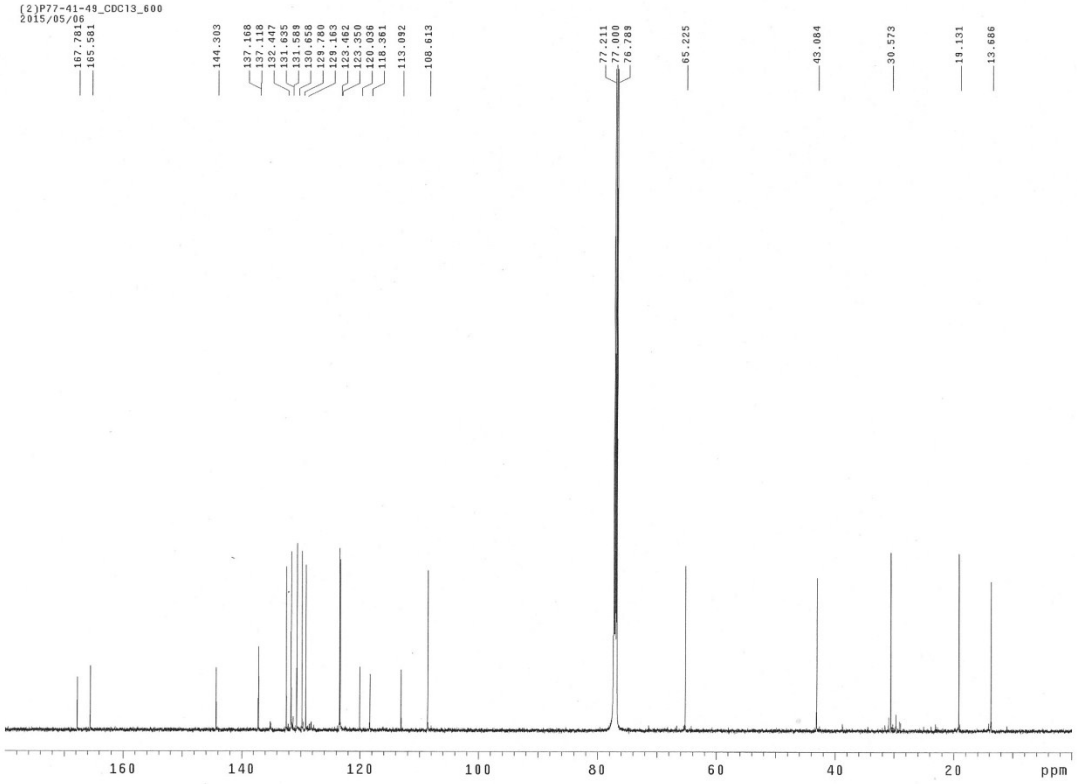


(E)-Butyl 2-(1-(3-cyanobenzyl)-2-oxoindolin-3-ylidene)acetate (**5a**).

^{1}H NMR

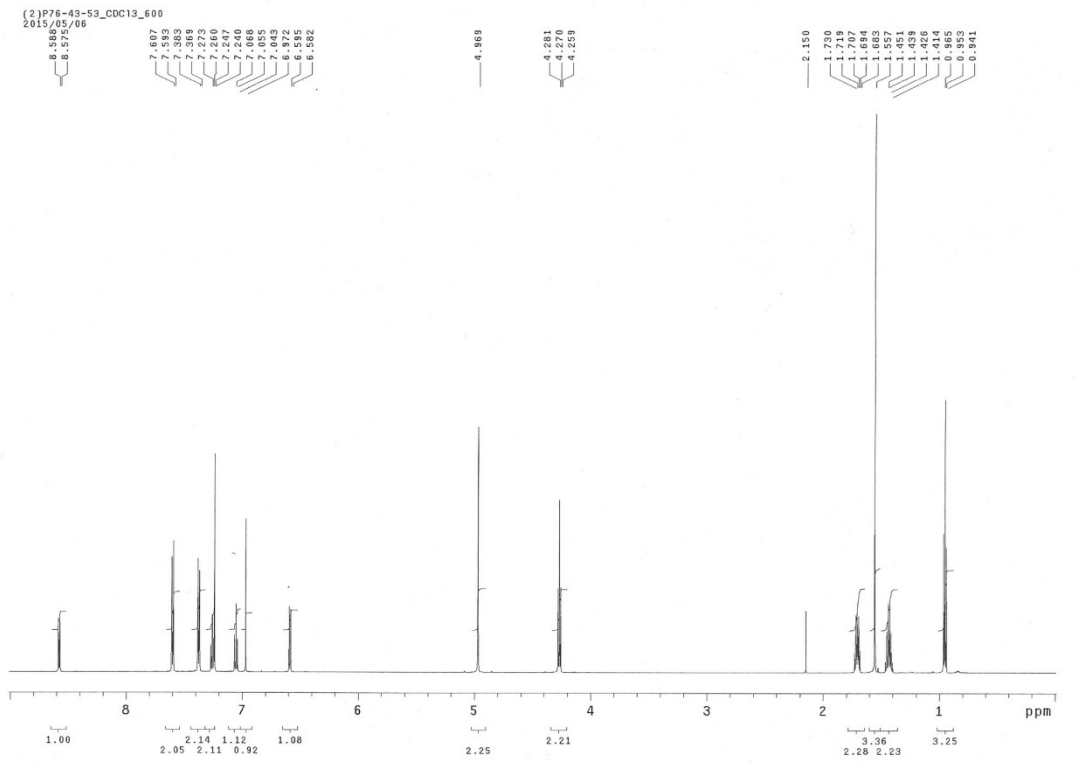


^{13}C NMR

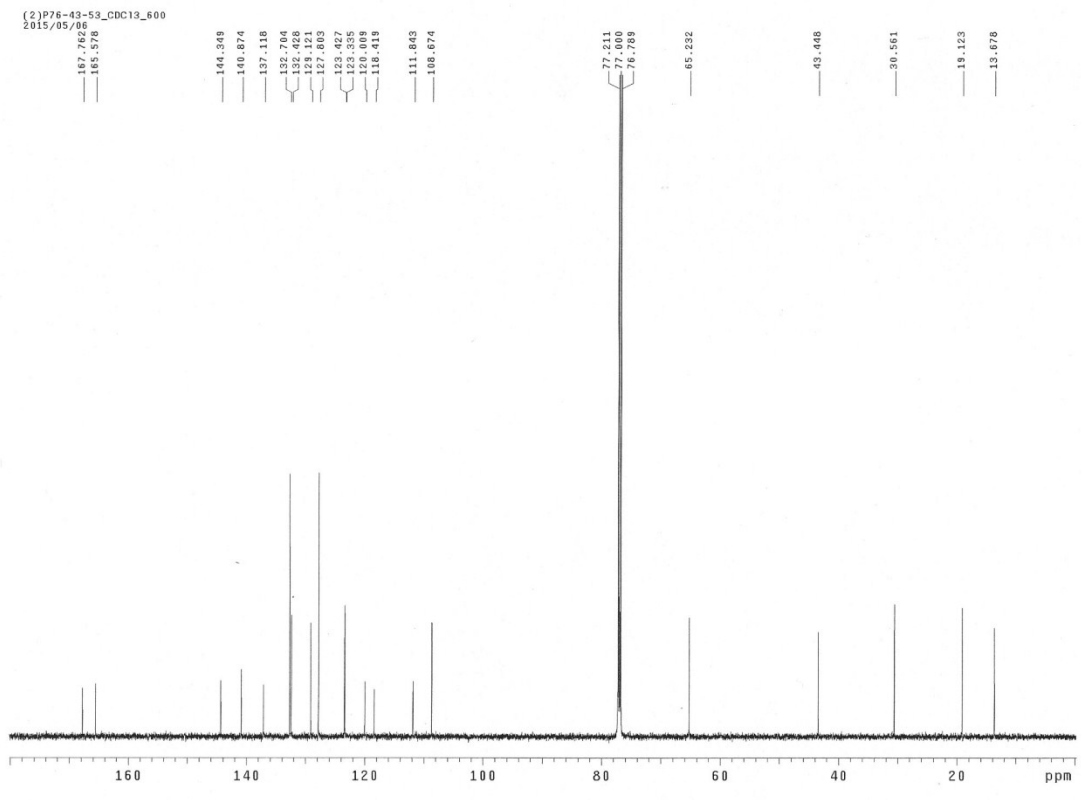


(E)-Butyl 2-(1-(4-cyanobenzyl)-2-oxoindolin-3-ylidene)acetate (**5b**).

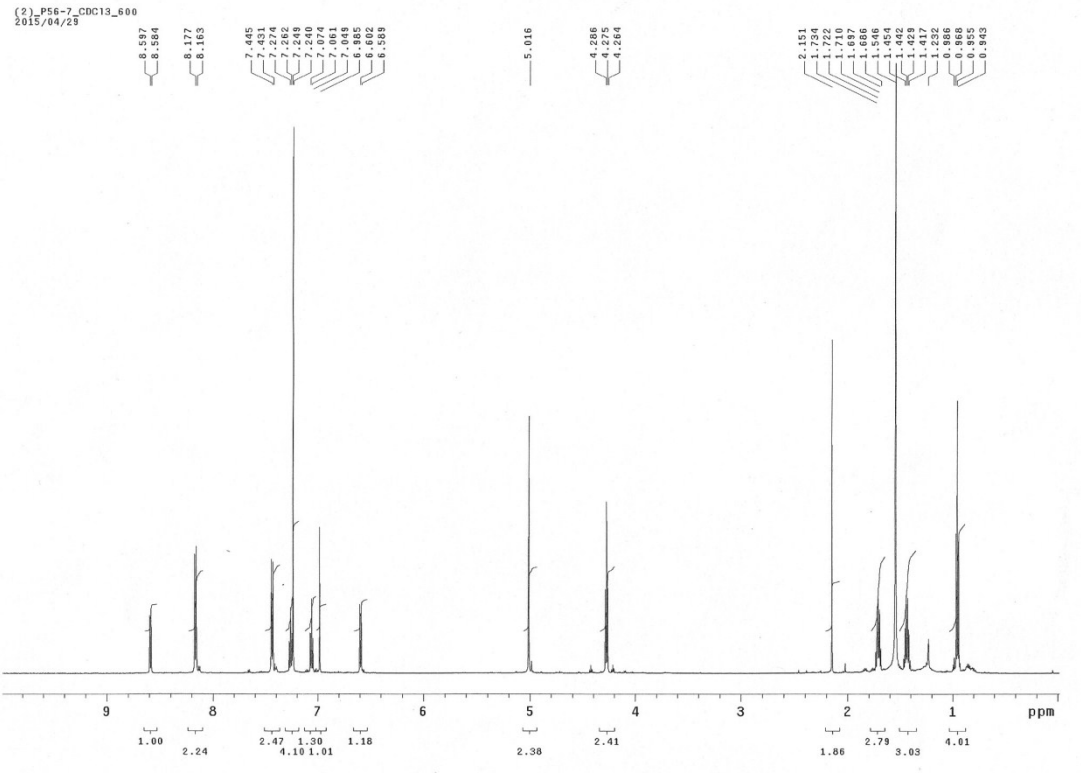
^{1}H NMR



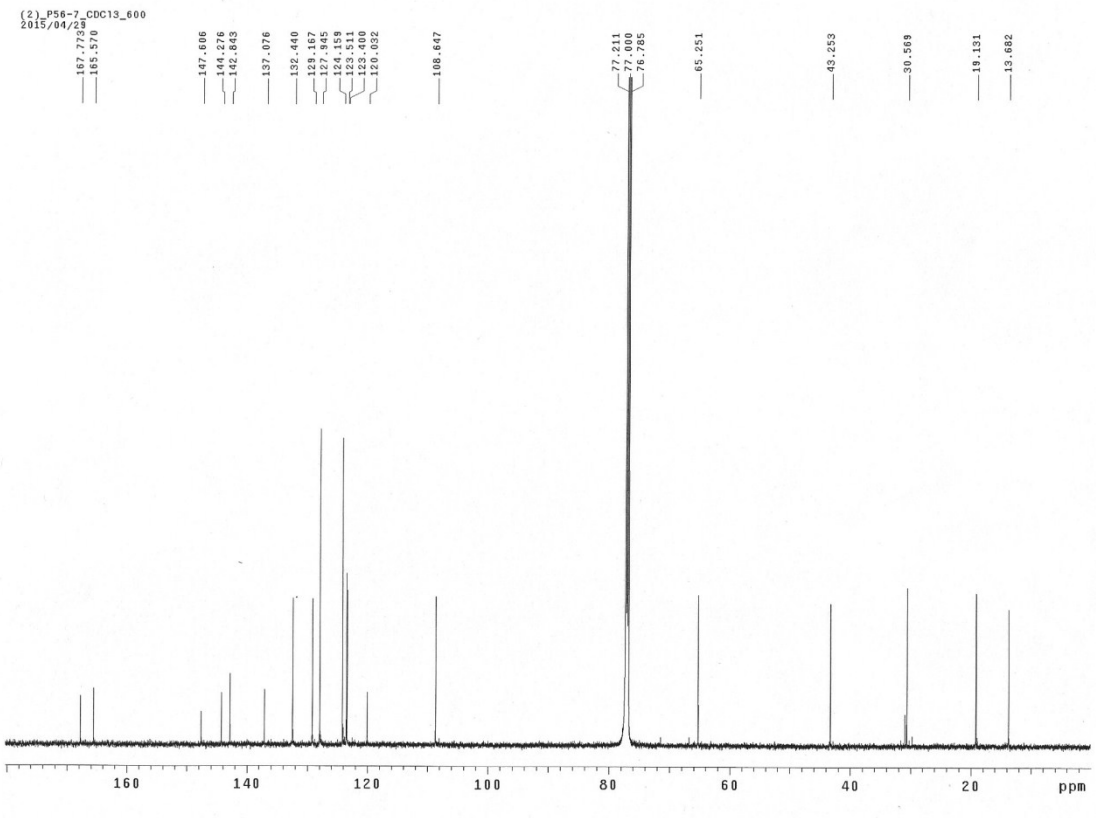
^{13}C NMR



(E)-Butyl 2-(1-(4-nitrobenzyl)-2-oxoindolin-3-ylidene)acetate **(5c)**.
^{1}H NMR

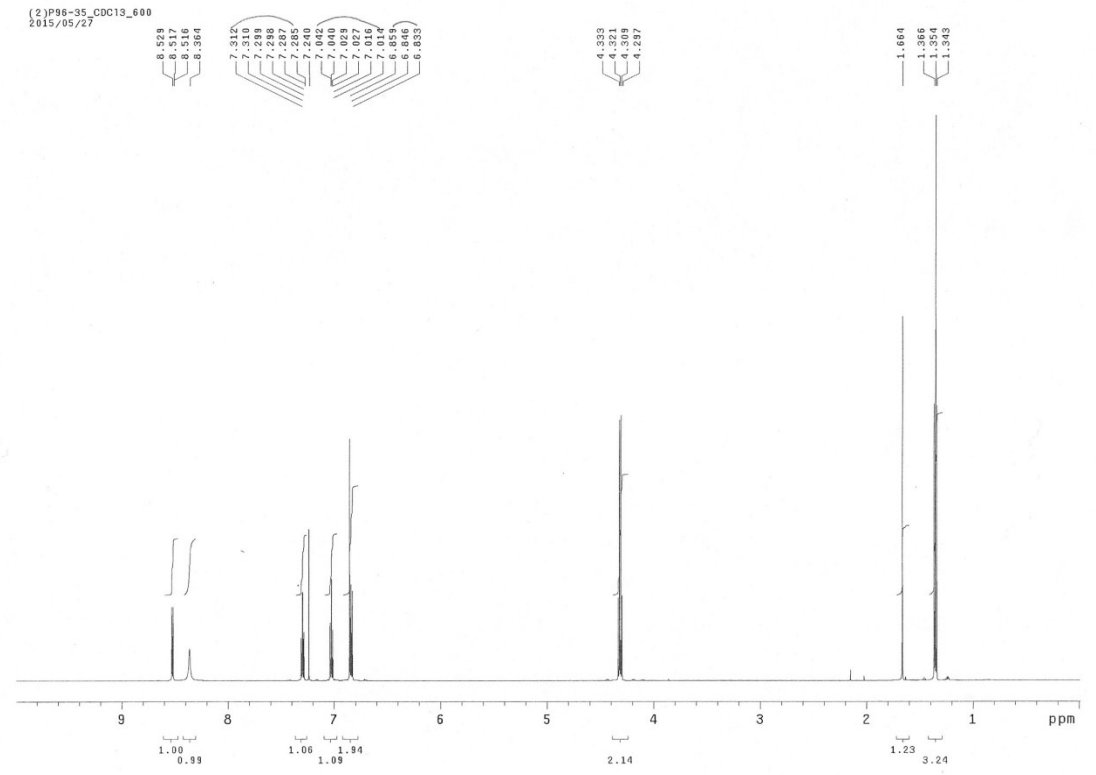


^{13}C NMR

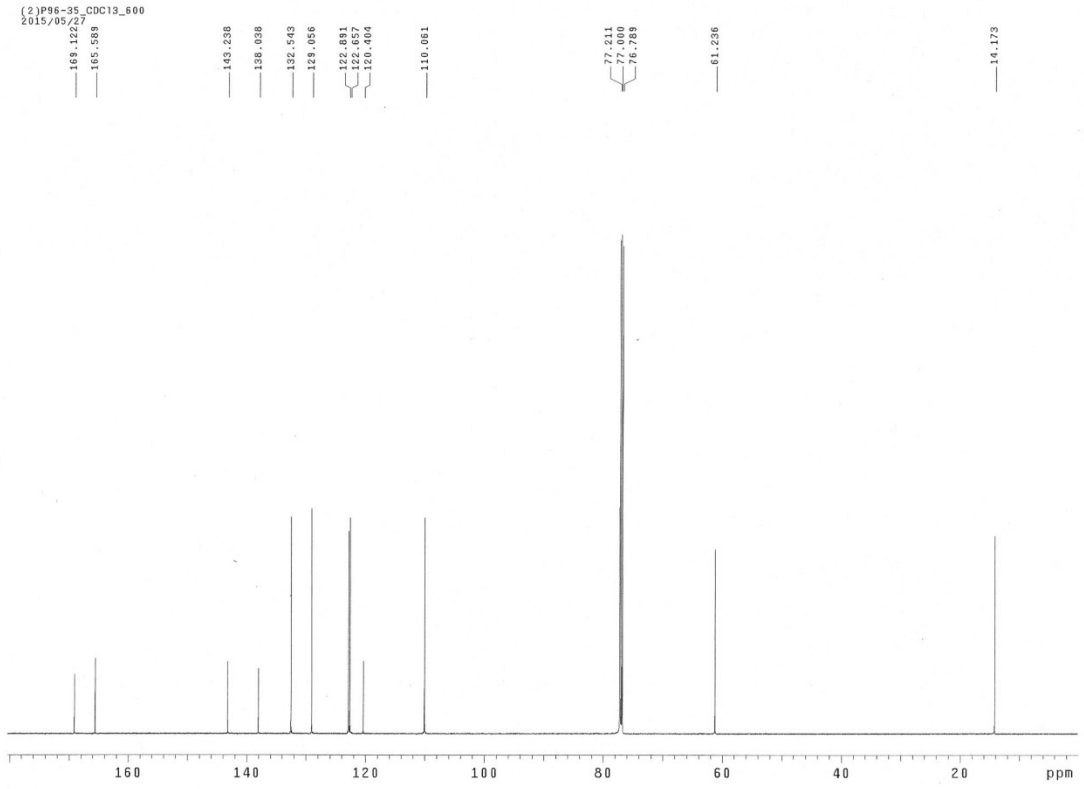


(E)-Ethyl 2-(2-oxoindolin-3-ylidene)acetate (**4h**).

^{1}H NMR



^{13}C NMR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