Supporting Information

Synthesis of (E)-Oxindolyldiene Acetate using Tandem Palladium-Catalyzed Heck and Alkoxy carbonylation 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, I₂ vapor, or basic aqueous potassium permanganate (KMnO₄) 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) \( \nu_{\max} \): 3278, 2106, 1643, 1512, 1248, 1176 cm\(^{-1}\). \( ^1 \)H NMR (600 MHz, CDCl\(_3\)) major/minor \( \delta \): 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 \( \delta \): 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) \( \nu_{\max} \): 3202, 2103,
1636, 1508, 1391, 1230 cm\(^{-1}\). \(^1\)H NMR (600 MHz, CDCl\(_3\)) major/minor \(\delta\): 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 \(\delta\): 162.3/162.5 (d, \(^1\)J\(_{C-F}\) = 245.4 Hz), 153.0/152.5, 142.0/141.0, 139.9/140.0, 131.5/131.2 (d, \(^4\)J\(_{C-F}\) = 3.0 Hz), 131.3/130.1, 131.2/130.6 (d, \(^3\)J\(_{C-F}\) = 8.1 Hz), 130.3/129.9, 128.8/128.9, 115.3/115.5 (d, \(^2\)J\(_{C-F}\) = 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.

\[\text{INCl}-(4\text{-Chlorobenzyl})-\text{N-(2-iodophenyl)propiolamide (1d).}\] Yield: 85% (two rotamers at a ratio of 9:1). Yellow solid. Mp = 78-80 °C. IR (KBr) \(\nu\)max: 3213, 2107, 1637, 1389, 1293 cm\(^{-1}\). \(^1\)H NMR (600 MHz, CDCl\(_3\)) major/minor \(\delta\): 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 \(\delta\): 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) vmax: 3209, 2105, 1534, 1291 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) major/minor \(\delta\): 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 \(\delta\): 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) vmax: 3231, 2106, 1718,
1647, 1468, 1386, 1280, 1106 cm\(^{-1}\). \(^1\)H NMR (600 MHz, CDCl\(_3\)) major/minor \(\delta\): 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 \(\delta\) : 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) \(\nu_{\text{max}}\) : 3227, 2108, 1637, 1392, 1158, 1114 cm\(^{-1}\). \(^1\)H NMR (600 MHz, CDCl\(_3\)) major/minor \(\delta\): 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 \(\delta\) : 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, \(^{2}J_{C,F} = \)):
15.4 Hz), 129.8/129.2, 129.1/129.0, 125.5/125.6 (q, \(3J_{C:F} = 4.1 \text{ Hz}\)), 123.9/123.1 (q, \(1J_{C:F} = 270.7 \text{ Hz}\)), 100.1/100.0, 79.8/80.4, 75.8/75.9, 50.9/54.9. HRMS calcd for C\(_{17}\)H\(_{12}\)F\(_3\)INO (M+1)\(^+\) 429.9916, found 429.9922.

![Chemical structure](image)

\(N\)-(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) \(\nu_{\text{max}}\): 3260, 2222, 2100, 1647, 1380, 1304 cm\(^{-1}\). \(^1\)H NMR (500 MHz, CDCl\(_3\)) major/minor \(\delta\): 7.91/7.87 (d, \(J = 8.0 \text{ Hz}, 1H\)), 7.56/7.59 (d, \(J = 8.0 \text{ Hz}, 2H\)), 7.32/7.33 (d, \(J = 8.0 \text{ Hz}, 2H\)), 7.24/7.20 (t, \(J = 7.0 \text{ Hz}, 1H\)), 7.07/6.99 (t, \(J = 7.0 \text{ Hz}, 1H\)), 6.78/6.68 (d, \(J = 8.0 \text{ Hz}, 1H\)), 5.50/5.52 (d, \(J = 14.5 \text{ Hz}, 1H\)), 4.17/4.61 (d, \(J = 14.5 \text{ Hz}, 1H\)), 2.77/3.37 (s, 1H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) major/minor \(\delta\): 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\(_2\)O (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 °C. IR (KBr) v_max: 3223, 2225, 2102, 1637, 1392, 1301 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) 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). ¹³C NMR (125 MHz, CDCl₃) 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}INO (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 °C. IR (KBr) v max: 3192, 2103, 1627, 1471, 1387, 1297, 1211 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) 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). ¹³C NMR (125 MHz, CDCl₃) 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 C₁₆H₁₂IINO (M+1)⁺ 395.9652, found 395.9659.

\[
\begin{array}{c}
\text{I} \\
\text{N} \\
\text{N-}\text{(2-Iodophenyl)-N-(naphthalen-2-ylmethyl)propiolamide (1k). Yield: 84% (two rotamers at a ratio of 6:1). Orange oil. IR (KBr) v max: 3447, 2107, 1646, 1467, 1287 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) major/minor δ: 7.92/7.89 (dd, J = 7.8, 1.2 Hz, 1H), 7.81-7.76 (m, 2H), 7.73-7.71 (m, 1H), 7.58 (s, 1H), 7.46-7.43 (m, 2H), 7.38 (dd, J = 8.5, 1.5 Hz, 1H), 7.11/7.09 (dt, J = 8.0, 1.5 Hz, 1H), 7.02/6.95 (dt, J = 7.5, 1.5 Hz, 1H), 6.71/6.62 (dd, J = 8.0, 1.5 Hz, 1H), 5.78/5.77 (d, J = 14.5 Hz, 1H), 4.19/4.62 (d, J = 14.5 Hz, 1H), 2.75/3.33 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) major/minor δ: 153.3/152.9, 142.7/141.3, 139.9/140.0, 133.2/133.1, 133.1/133.0, 132.9/132.9, 131.3/130.1,
\end{array}
\]
HRMS calcd for C_{20}H_{15}INO (M+1)^+ 412.0198, found 412.0198.

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.

\[ \text{HRMS calcd for C}_{16}\text{H}_{12}\text{ClINO (M+1)}^+ 395.9652, \text{found 395.9658.} \]

\[ \text{N-(2-Chlorobenzyl)-N-(2-iodophenyl)propiolamide (II). Yield: 78\% (two rota} \text{mers at a ratio of 8:1). Brown solid. Mp = 90-93 } \text{°C. IR (KBr) } \text{vmax: 3202, 2103, 1636, 1470, 1387 cm}^{-1}. \text{ } ^1\text{H NMR (500 MHz, CDCl}_3{\text{ major/minor } \delta: 7.88/7.86 (d, } \text{J = 8.0 Hz, 1H), 7.40-7.37 } \text{m, 1H), 7.32-7.25 (m, 1H), 7.19-7.15 } \text{(m, 3H), 7.02/6.96 (dt, } \text{J = 8.0, 1.5 Hz, 1H), 6.82/6.71 (dd, } \text{J = 8.0, 1.5 Hz, 1H), 5.56/5.57 (d, } \text{J = 14.5 Hz, 1H), 4.52/4.91 (d, } \text{J = 14.5 Hz, 1H), 2.75/3.27 (s, 1H). } ^{13}\text{C NMR (125 MHz, CDCl}_3{\text{ major/minor } \delta: 153.2/153.1, 142.4/141.0, 139.9/140.0, 134.5/134.4, 133.2/133.0, 131.8/130.0, 131.4/130.9, 130.3/129.9, 129.5/129.8, 129.4/129.7, 128.9/129.0, 127.1/127.0, 100.2/98.2, 79.6/80.1, 76.0/76.1, 47.8/52.3. HRMS calcd for C}_{16}\text{H}_{12}\text{ClINO (M+1)}^+ 395.9652, \text{found 395.9658.} \]
_**N-Benzyl-N-(2-iodophenyl)propiolamide (1m).** Yield: 81% (two rotamers at a ratio of 7:1). Dark brown oil. IR (KBr) \( \text{vmax} \): 3421, 2958, 2104, 1646, 1395, 1302 cm\(^{-1}\). \(^1\)H NMR (600 MHz, CDCl\(_3\)) major/minor \( \delta \): 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 \( \delta \): 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.

\[ \text{N-Benzyl-N-(2-iodophenyl)propiolamide (1m).} \]

_**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) \( \text{vmax} \): 2454, 3252, 2106, 1650, 1469, 1386, 1298, 1193 cm\(^{-1}\). \(^1\)H NMR (600 MHz, CDCl\(_3\)) major/minor \( \delta \): 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, \( J = 11\)]
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$_2$O$_2$ (M+1)$^+$ 366.9943, found 366.9948.

![Chemical structure](image)

**N-(2,6-Dichlorobenzyl)-N-(2-iodophenyl)propiolamide (1o).** Yield: 77% (two rotamers at a ratio of 8:1). Yellow solid. Mp = 170-171 ºC. IR (KBr) v max: 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$_2$INO (M+1)$^+$ 429.9262, found 429.9268.
INOMeO-(2-Iodophenyl)-N-(3,4,5-trimethoxybenzyl)propiolamide (1p). Yield: 81%
(two rotamers at a ratio of 8:1). Yellow solid. Mp = 118-120 oC. IR (KBr) vmax: 3195, 2107, 1633, 1394, 1123 1288 cm⁻¹. \(^1\)H NMR (600 MHz, CDCl₃) 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). \(^1\)C NMR (150 MHz, CDCl₃) 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 C₁₉H₁₈I₅N₄O (M+Na)⁺ 474.0178, found 474.0178.

INOClMeO-(4-Chlorobenzyl)-N-(2-iodo-4-methylphenyl)propiolamide (1q). Yield: 79%
(two rotamers at a ratio of 9:1). Yellow oil. IR (KBr) vmax: 3287, 2108, 1646, 1484,
1384, 1291, 1204, 1015 cm\(^{-1}\). \(^1\)H NMR (600 MHz, CDCl\(_3\)) major/minor \(\delta\): 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 \(\delta\): 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.

![Image](image.png)

\(N\)-((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) \(\nu\) max: 3220, 2110, 1626, 1481, 1394, 1237, 1033 cm\(^{-1}\). \(^1\)H NMR (600 MHz, CDCl\(_3\)) major/minor \(\delta\): 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 \(\delta\): 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.

\[
\begin{align*}
&\text{IN} \quad \text{O} \\
&\text{N} - (2\text{-Iodophenyl}) - \text{N} - \text{methylpropiolamide (1t). Yield: 79\% (two rotamers at a ratio of 8:1). Dark brown solid. Mp = 101-102 \degree C. IR (KBr) v\text{max: 3214, 2104, 1635, 1466, 1376, 1298, 1133 cm}^{-1}. \text{H NMR (600 MHz, CDCl}_3) \text{major/minor } \delta: 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). \text{C NMR} (150 MHz, CDCl}_3) \text{major/minor } \delta: 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_{9}INO_4 (M+1)\(^+\) 285.9729, found 285.9732. \\
\end{align*}
\]

\[
\begin{align*}
&\text{F}_3\text{C} - \text{I} - \text{O} \\
&\text{N} - (2\text{-Iodo-4-(trifluoromethyl)phenyl}) - \text{N} - (4\text{-nitrobenzyl})\text{propiolamide (1v). Yield: 77\% (two rotamers at a ratio of 8:1). Colorless oil. IR (KBr) v\text{max: 3286, 2111,}
\end{align*}
\]
1651, 1600, 1522, 1347, 1320, 1133 cm$^{-1}$. $^1$H 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, $^3$J$_{C,F} = 2.4$ Hz), 132.5 (q, $^2$J$_{C,F} = 31.1$ Hz), 131.2/130.0, 130.2/129.5, 126.3 (q, $^2$J$_{C,F} = 3.45$ Hz), 124.0/124.1, 122.3 (q, $^1$J$_{C,F} = 271.2$ 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$_3$IN$_2$O$_3$ (M+1)$^+$ 474.9766, found 474.9758.

\[
\begin{align*}
\text{N-(4-Chloro-2-iodophenyl)-N-(4-chlorobenzyl)propiolamide (1w). Yield: 75\%} \\
\text{(two rotamers at a ratio of 8:1). White solid. Mp = 82-85 °C. IR (KBr) v\text{max: 3253, 2105, 1634, 1465, 1396, 1292, 1090 cm}^{-1}.} \\
\text{$^1$H NMR (600 MHz, CDCl$_3$) major/minor δ:} \\
7.90/7.86 (d, $J = 1.8$ Hz, 1H), 7.24/7.27 (d, $J = 8.4$ Hz, 2H), 7.20/7.17 (dd, $J = 8.4$, 1.8 Hz, 1H), 7.12/7.13 (d, $J = 8.4$ Hz, 2H), 6.65/6.53 (d, $J = 8.4$, 1H), 5.48/5.50 (d, $J = 14.4$ Hz, 1H), 4.00/4.46 (d, $J = 14.4$ Hz, 1H), 2.79/3.33 (s, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) major/minor δ: 153.0/152.8, 141.3/139.8, 139.4/139.5, 135.5/135.0, 134.1/134.4, 134.0/133.7, 131.6/130.6, 130.9/130.1, 129.2/129.3, 128.8/129.0, 100.5/98.6, 80.0/80.6, 80.0/80.6, 
\end{align*}
\]
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).
(E)-Methyl 2-(1-(4-fluorobenzyl)-2-oxoindolin-3-ylidene)acetate (3c).
(E)-Methyl 2-(1-(4-chlorobenzyl)-2-oxoindolin-3-ylidene)acetate (3d).
(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

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-((3-methylisoxazol-5-yl)methyl)-2-oxoindolin-3-ylideneacetate (3n).

$^1$H NMR

$^{13}$C NMR
(E)-Methyl 2-((1-(2,6-dichlorobenzyl)-2-oxoindolin-3-ylidene)acetate (3o).

$^1$H NMR

\[ 
\text{Signal 1} \quad \text{Signal 2} \quad \text{Signal 3} 
\]
$^{13}$C NMR

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

$^1$H NMR
\[ ^{13}C \text{ NMR} \]

\( (E)-\text{Methyl 2-}(1-(4\text{-chlorobenzyl})\text{-}5\text{-methyl-2-oxoindolin-3-ylidene})\text{acetate (3q).} \)

\[ ^1H \text{ NMR} \]
$^{13}$C NMR

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

$^1$H NMR
(E)-Methyl 2-((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).

37
$^1$H NMR

$^{13}$C NMR

(E)-Methyl 2-(2-oxoindolin-3-ylidene)acetate (3u).
$^1$H NMR

$^{13}$C NMR
\textbf{1H NMR}

\textbf{13C 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-oxindolin-3-ylidene)acetate (4h).

$^1$H NMR

$^{13}$C NMR