

Supporting Information

for

Morita–Baylis–Hillman reaction of acrylamide with isatin derivatives

Radhey M. Singh¹, Kishor Chandra Bharadwaj^{*1}, Dharmendra Kumar Tiwari²

Address: ¹Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221005, India and ²Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology, Tarnaka, Hyderabad-500007, India

Email: Kishor Chandra Bharadwaj^{*} - kishorbharadwaj@gmail.com

^{*}Corresponding author

This article is dedicated to Dr. Ganesh Pandey, on his 60th birthday.

General remarks, experimental procedures, data and

¹H NMR and ¹³C NMR spectra

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General Remarks

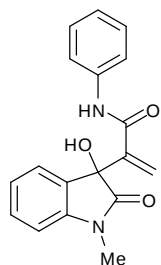
All of the reactions were carried out using dry solvents in inert atmosphere. The designation of room temperature for reaction was 30–35 °C. Column chromatography was performed using a silica gel mesh of 100–200. TLC Aluminium Sheets Silica Gel 60 F254 were used for TLC. The melting Points were recorded on a Perfit (India) capillary melting point apparatus and were uncorrected. The infrared spectra were recorded on a Perkin Elmer FT-IR spectrometer. ^1H NMR and ^{13}C NMR were recorded on a Bruker 400 MHz spectrometer using $\text{DMSO}-d_6$ or CDCl_3 as a solvent. HRMS spectra were recorded on Agilent 6530 Q-TOF HRMS. Single crystal X-ray diffraction measurements were carried out on an Oxford Diffraction Xcalibur system. All the determinations of the unit cell and the intensity data were performed with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Due to the rotamer nature of amide (which is an established phenomenon [1-4]), additional peaks were observed in some of the ^{13}C NMR spectra of acrylamide-derived MBH adducts. Data for major peaks has been given. Additional peaks have also been mentioned at required places. Similarly, in the ^1H NMR data, partial integration has been mentioned at required places.

Procedure for the MBH reaction of *N*-phenylacrylamide (**1a**) with *N*-methylisatin (**2a**)

DABCO (0.112 g, 1.00 mmol) was added to a solution of **2a** (0.08 g, 0.5 mmol), phenol (0.094 g, 1.00 mmol) and **1a** (0.147 g, 1.00 mmol) in acetonitrile (0.5 mL), and the reaction was kept for 2 days. The reaction mixture was then directly subjected to column chromatography (EtOAc/Hexane, 3:10) to obtain the product **3aa** as a yellow solid (0.142 g) at 92% yield.

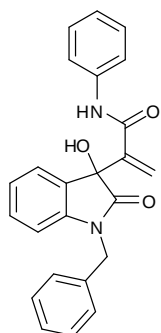
Procedure for the aza-MBH reaction of **3a** with methyl acrylate

DABCO (0.014 g, 0.125 mmol) was added to a solution of **4a** [5,6] (0.130 g, 0.5 mmol) in acetonitrile (0.5 mL) and methyl acrylate (0.14 mL, 1.5 mmol) and the reaction was kept for 6 h. The reaction mixture was then directly subjected to column chromatography (EtOAc/Hexane, 1:5) to obtain the product **5aa** as a white solid at (0.164 g) 95% yield.



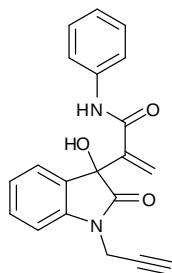
2-(3-Hydroxy-1-methyl-2-oxoindolin-3-yl)-N-phenylacrylamide (3aa)

Yellow solid; Yield: 92%; mp: 168-172 °C; IR (KBr): ν 750, 1564, 1707, 3146, 3202 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 3.11 (s, 3H), 6.22-6.68 (m, 3H), 6.94-7.46 (m, 9H), [9.41 (s, 0.12H), 10.04 (s, 0.87H)]; ^{13}C NMR : δ (100 MHz, $\text{DMSO}-d_6$) 26.38, 75.60, 108.63, 120.20, 121.27, 122.16, 123.20, 123.81, 128.78, 129.60, 131.37, 138.73, 144.46, 144.75, 164.86, 175.80; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3\text{Na}$: 331.1059 ($\text{M}+\text{Na}$) $^+$, found: 331.1046 ($\text{M}+\text{Na}$) $^+$.



2-(1-Benzyl-3-hydroxy-2-oxoindolin-3-yl)-N-phenylacrylamide (3ba)

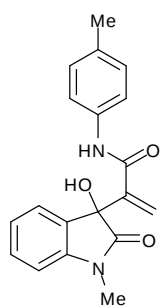
White solid; Yield: 91%; mp: 196-200 °C; IR (KBr): ν 748, 1368, 1606, 1697, 3205 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 4.88 (s, 2H), 6.29 (s, 2H), 6.65 (s, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.91-6.95 (m, 1H), 7.00-7.03 (m, 1H), 7.10-7.17 (m, 2H), 7.23-7.28 (m, 3H), 7.31-7.34 (m, 2H), 7.47-7.48 (m, 2H), 7.51-7.53 (m, 2H), 10.10 (s, 1H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 42.89, 75.52, 109.08, 119.85, 121.24, 122.00, 123.17, 123.55, 127.23, 127.34, 128.41, 128.58, 129.19, 131.41, 136.44, 138.73, 143.68, 144.28, 164.70, 175.83; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_3\text{Na}$: 407.1372 ($\text{M}+\text{Na}$) $^+$, found: 407.1364 ($\text{M}+\text{Na}$) $^+$.



2-(3-Hydroxy-2-oxo-1-(prop-2-ynyl)indolin-3-yl)-N-phenylacrylamide (3ca)

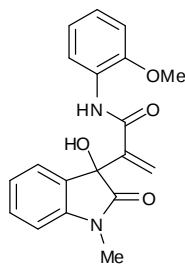
White solid; Yield: 79%; mp: 158-162 °C; IR (KBr): ν 753, 1169, 1361, 1557, 1709, 3291 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 3.29 (s, 1H) * , 4.39 (d, J = 18.0 Hz, 1H), 4.60 (d, J = 18.0 Hz, 1H) § , 6.25 (s, 1H), 6.27 (s, 1H), 6.64 (s, 1H), 6.98-7.13 (m, 4H), 7.20-7.31 (m, 3H), 7.45-7.47 (m, 2H), 10.04 (s, 1H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 29.01, 74.52, 75.39, 78.16, 109.14, 119.97, 121.28, 122.28, 123.25, 123.57, 128.56, 129.30, 131.09, 138.59, 142.82, 144.17, 164.52, 174.70; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_3\text{Na}$: 355.1059 ($\text{M}+\text{Na}$) $^+$, found: 355.1053 ($\text{M}+\text{Na}$) $^+$. * This proton partially got merged with

moisture. ^{\$}This proton came less in integration. We re-recorded the ¹H NMR using CDCl₃ as a solvent and the integration was found to be normal. Data of ¹H NMR (400 MHz, CDCl₃): δ 2.25 (s, 1H), 4.44-4.54 (m, 2H), 4.72 (s, 1H), 5.56 (s, 1H), 6.07 (s, 1H), 7.08-7.14 (m, 3H), 7.30-7.34 (m, 2H), 7.37-7.42 (m, 2H), 7.55-7.57 (m, 2H), 9.09 (s, 1H).



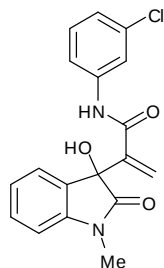
2-(3-Hydroxy-1-methyl-2-oxoindolin-3-yl)-N-p-tolylacrylamide (3ab)

White solid; Yield: 89 %; mp: 180-184 °C; IR (KBr): ν 1610, 1703, 3257 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.20 (s, 3H), 3.11 (s, 3H), 6.20 (s, 1H), 6.22 (s, 1H), 6.49 (s, 1H), 6.94-6.96 (m, 2H), 7.01-7.03 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.24-7.28 (m, 1H), 7.33-7.35 (m, 2H), 9.95 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 20.45, 26.15, 75.43, 108.32, 108.46, 119.94, 120.23, 120.81, 121.96, 123.06, 128.87, 128.99, 129.30, 131.33, 132.45, 136.14, 144.42, 144.60, 164.40, 175.60; HRMS (ESI) calcd for C₁₉H₁₈N₂O₃Na: 345.1215 (M+Na)⁺, found: 345.1223 (M+Na)⁺.

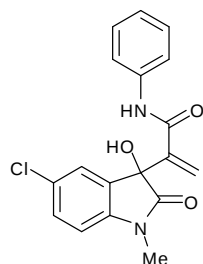


2-(3-Hydroxy-1-methyl-2-oxoindolin-3-yl)-N-(2-methoxyphenyl)acrylamide (3ac)

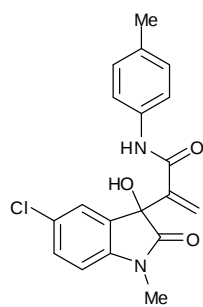
Light Yellow solid; Yield: 90 %; mp: 176-180 °C; IR (KBr): ν 756, 1463, 1544, 1610, 1719, 3246 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆): δ 3.11 (s, 3H), 3.79 (s, 3H), 5.85 (s, 1H), 6.21 (s, 1H), 6.66-6.88 (m, 2H), 6.98-7.09 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.29-7.33 (m, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 9.63 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 26.17, 55.98, 75.90, 108.75, 111.35, 120.23, 120.42, 121.93, 122.21, 123.51, 124.87, 126.91, 129.55, 130.95, 143.85, 144.09, 150.00, 163.86, 175.48; HRMS (ESI) calcd for C₁₉H₁₈N₂O₄Na: 361.1165 (M+Na)⁺, found: 361.1158 (M+Na)⁺.



***N*-(3-Chlorophenyl)-2-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)acrylamide (3ad)** Yellow solid; Yield: 94%; mp: 116-120 °C; IR (KBr): ν 1591, 1613, 1707, 2925, 3311 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 3.13 (s, 3H), 6.26-6.69 (m, 3H), 6.96-7.63 (m, 8H), 10.23 (s, 1H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 26.13, 75.30, 108.44, 118.20, 119.15, 121.65, 121.92, 122.97, 123.21, 129.39, 130.30, 131.13, 132.86, 140.10, 144.08, 144.57, 164.90, 175.43; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{ClN}_2\text{O}_3\text{Na}$: 365.0669 ($\text{M}+\text{Na}$) $^+$, found: 365.0654 ($\text{M}+\text{Na}$) $^+$.

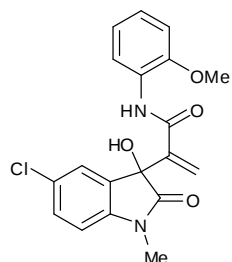


2-(5-Chloro-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-*N*-phenylacrylamide (3da) Dirty White solid; Yield: 93%; mp: 102-108 °C; IR (KBr): ν 747, 1100, 1488, 1613, 1720, 3310, 3416 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 3.11 (s, 3H), 6.27-6.71 (m, 3H), 6.99-7.47 (m, 8H), [9.46, (s, 0.14H), 10.06 (s, 0.8H)]; ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 26.28, 75.25, 109.92, 110.04, 119.97, 120.11, 121.67, 122.98, 123.09, 123.61, 123.71, 125.78, 128.58, 129.02, 133.44, 138.52, 143.54, 143.70, 164.46, 175.21; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{ClN}_2\text{O}_3\text{Na}$: 365.0669 ($\text{M}+\text{Na}$) $^+$, found: 365.0661 ($\text{M}+\text{Na}$) $^+$.

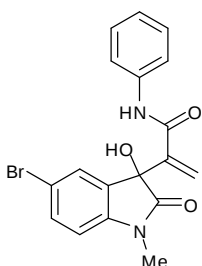


2-(5-Chloro-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-*N*-p-tolylacrylamide (3db) White solid; Yield: 83%; mp: 90-94 °C; IR (KBr): ν 1610, 1710, 3318 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 2.21 (s, 2H) * , [3.11 (s, 1.88H), 3.13 (s, 1.13H)], 6.25-6.71 (m, 3H), 6.98-7.42 (m, 7H), [9.47 (s, 0.3H), 9.98 (s, 0.66H)]; ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 20.53, 26.36, 75.36, 76.81, 110.05, 110.53, 115.06, 120.14, 121.54, 123.13, 124.43, 125.88, 126.78, 126.96, 129.10, 130.87, 132.76, 133.53, 135.26, 136.04, 142.27, 143.60, 143.78, 157.21, 164.35, 175.34, 176.76; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{17}\text{ClN}_2\text{O}_3\text{Na}$: 379.0826 ($\text{M}+\text{Na}$) $^+$, found: 379.0819 ($\text{M}+\text{Na}$) $^+$. * Due to rotamer nature of compound (as reflected by ^1H and ^{13}C NMR spectra), part of the peak

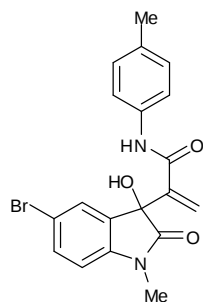
has probably merged with DMSO peak. Similar observation has been found for similar compound **3eb**.



2-(5-Chloro-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-N-(2-methoxyphenyl)acrylamide (3dc) White solid; Yield: 87%; mp: 178-184 °C; IR (KBr): ν 752, 1463, 1609, 1651, 1726, 3253 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 3.10 (s, 3H), 3.78 (s, 3H), 6.04-6.71 (m, 2H), 6.83-7.16 (m, 6H), 7.35-7.58 (m, 2H), 9.46 (s, 1H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 26.32, 55.84, 75.62, 110.13, 111.35, 120.27, 123.00, 123.17, 123.36, 123.53, 125.39, 126.07, 126.53, 129.05, 129.29, 133.19, 143.27, 143.36, 150.60, 163.94, 175.20; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{17}\text{ClN}_2\text{O}_4\text{Na}$: 395.0775 ($\text{M}+\text{Na}$) $^+$, found: 395.0768 ($\text{M}+\text{Na}$) $^+$.



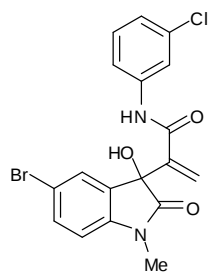
2-(5-Bromo-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-N-phenylacrylamide (3ea) Light Yellow solid; Yield: 88 %; mp: 90-96 °C; IR (KBr): ν 1486, 1608, 1720, 3313, 3413 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 3.11 (s, 3H), 6.28-6.71 (m, 3H), 6.95-7.55 (m, 8H), [9.47 (s, 0.22H), 10.06 (s, 0.8H)]; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 26.27, 75.19, 76.68, 110.60, 110.91, 113.44, 119.92, 120.13, 120.32, 121.68, 123.66, 125.71, 126.89, 128.58, 131.94, 133.79, 138.51, 143.68, 143.95, 157.14, 164.43, 175.09; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{BrN}_2\text{O}_3\text{Na}$: 409.0164 ($\text{M}+\text{Na}$) $^+$, found: 409.0149 ($\text{M}+\text{Na}$) $^+$. **Crystal data:** empirical formula: $\text{C}_{18}\text{H}_{15}\text{BrN}_2\text{O}_3$; formula weight: 405.24; crystal color, habit: white, rectangular; crystal system: Monoclinic; lattice type: primitive; lattice parameters: $a = 13.5133(16)$ Å, $b = 13.5483(8)$ Å, $c = 9.6825(5)$ Å, $\alpha = 90$, $\beta = 92.293(7)$, $\gamma = 90$; $V = 1771.3(3)$ Å 3 ; space group: P21/c; $Z = 4$; D calcd = 1.520 g/cm^3 ; $F(000) = 728$; $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å; $R(I > 2\sigma I) = 0.0639$; $wR_2 = 0.1060$. (CCDC 1023410).



2-(5-Bromo-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-N-p-tolylacrylamide (3eb) Light Yellow solid; Yield: 76 %; mp: 90-94 °C; IR

(KBr): ν 1608, 1712, 2922, 3356 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 2.21 (s, 2H)*, 3.11 (s, 3H), 6.24-6.70 (m, 3H), 6.95-7.55 (m, 7H), [9.47 (s, 0.29H), 9.98 (s, 0.69H)]; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 20.52, 26.30, 75.28, 76.76, 110.57, 111.01, 113.51, 114.45, 115.06, 120.10,

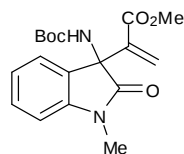
121.55, 125.75, 126.92, 127.09, 129.02, 130.84, 131.92, 132.69, 133.89, 135.62, 136.04, 142.66, 143.77, 144.00, 157.21, 164.29, 175.20, 176.62; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{17}\text{BrN}_2\text{O}_3\text{Na}$: 423.0321 ($\text{M}+\text{Na}$)⁺, found: 423.0304 ($\text{M}+\text{Na}$)⁺. *Part of peak probably merges with DMSO. We re-recorded ^1H NMR spectrum in CDCl_3 where normal integration was observed, although molecule still existed in rotameric forms. Data of ^1H NMR (400 MHz, CDCl_3): δ [2.31 (s, 2.38H), 3.22-3.23 (m, 3.22H), 3.38 (s, 0.36H)], [4.41 (bs, 0.7H), 5.36 (bs, 0.26H)], [5.74 (s, 0.81H), 6.04 (s, 0.81H), 6.74-6.79 (m, 1.74H), 7.11-7.13 (m, 1.60H), 7.22-7.26 (m, 0.89H), 7.38-7.49 (m, 3.61H), 8.49 (bs, 0.68H)]. Thus total integration of two methyl groups gave six protons, hydroxyl moiety gave one proton and rest of the proton together gave ten protons in ^1H NMR in CDCl_3 .



2-(5-Bromo-3-hydroxy-1-methyl-2-oxoindolin-3-yl)-N-(3-chlorophenyl)acrylamide (3ed) Dirty White solid; Yield: 90 %; mp:

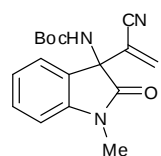
166-170 °C; IR (KBr): ν 1592, 1710, 2924, 3317 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 3.12 (s, 3H), 6.32-6.72 (m, 3H), 6.96-7.63 (m, 7H), [9.47 (s, 0.09H), 10.24 (s, 0.9H)]; ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ

26.26, 75.11, 110.62, 113.50, 118.31, 119.26, 122.40, 123.36, 125.70, 130.35, 131.95, 132.91, 133.65, 140.00, 143.38, 143.91, 164.73, 175.00; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{14}\text{BrClN}_2\text{O}_3\text{Na}$: 442.9774 ($\text{M}+\text{Na}$)⁺, found: 442.9756 ($\text{M}+\text{Na}$)⁺.



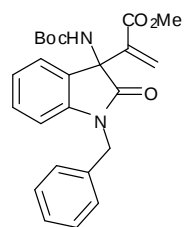
Methyl 2-(3-(*tert*-butoxycarbonylamino)-1-methyl-2-oxoindolin-3-yl)acrylate (5aa) White solid; Yield: 95%; mp: 130-134 °C; IR (KBr): ν

761, 1174, 1609, 1704, 1738, 2974, 3276 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.23 (s, 9H), 3.22 (s, 3H), 3.66 (s, 3H), 5.82 (s, 1H), 6.10 (bs, 1H), 6.25 (s, 1H), 6.78-6.79 (m, 1H), 6.96-6.99 (m, 1H), 7.20-7.26 (m, 1H)^{*}, 7.38-7.39 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 26.69, 28.11, 52.35, 64.04, 80.32, 108.31, 122.75, 124.58, 127.67, 129.29, 136.86, 143.82, 153.96, 166.02, 174.55; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_5\text{Na}$: 369.1427 ($\text{M}+\text{Na}$)⁺, found: 369.1417 ($\text{M}+\text{Na}$)⁺. ^{*} This peak merges with CHCl_3 .



***tert*-Butyl 3-(1-cyanovinyl)-1-methyl-2-oxoindolin-3-ylcarbamate (5ab)**

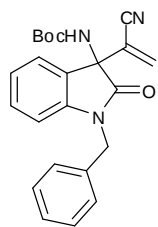
White solid; Yield: 93%; mp: 194-198 °C; IR (KBr): ν 763, 1171, 1611, 1704, 2228, 2974, 3248 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.33 (s, 9H), 3.25 (s, 3H), 5.50 (bs, 1H), 5.92 (s, 1H), 6.11 (s, 1H), 6.89 (d, J = 8.0 Hz, 1H), 7.14-7.17 (m, 1H), 7.37-7.41 (m, 1H), 7.65 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 26.96, 28.13, 62.95, 81.41, 108.90, 115.71, 122.00, 123.71, 125.54, 127.15, 130.39, 133.40, 143.34, 153.91, 172.58; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3\text{Na}$: 336.1324 ($\text{M}+\text{Na}$)⁺, found: 336.1314 ($\text{M}+\text{Na}$)⁺.



Methyl 2-(1-benzyl-3-(*tert*-butoxycarbonylamino)-2-oxoindolin-3-yl)acrylate (5ba) Light Yellow solid; Yield: 89%; mp: 130-134 °C; IR

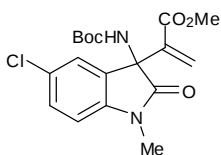
(KBr): ν 1169, 1700, 1731, 2978, 3290 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.32 (s, 9H), 3.70 (s, 3H), 4.85 (d, J = 16.0 Hz, 1H)[§], 5.13 (d, J = 16.0 Hz, 1H), 5.90 (s, 1H), 6.23 (bs, 1H), 6.33 (s, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.98-7.02 (m, 1H), 7.15-7.20 (m, 1H), 7.24-7.38 (m, 5H)^{*}, 7.46 (d, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 28.19, 44.36, 52.44, 64.14, 80.47, 109.39, 122.87, 124.70, 127.32, 127.59, 127.95, 128.78, 129.23, 135.70, 136.93, 143.00, 154.04, 166.11, 174.75; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}_5\text{Na}$: 445.1740 ($\text{M}+\text{Na}$)⁺, found: 445.1757

(M+Na)⁺. ^{\$}This proton came less in integration similar to that of **3ca**. ^{*}It contains CHCl₃ peak also.



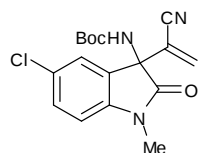
tert-Butyl 1-benzyl-3-(1-cyanovinyl)-2-oxoindolin-3-ylcarbamate (5bb)

Light Yellow solid; Yield: 77 %; mp: 134-138 °C; IR (KBr): ν 764, 1161, 1281, 1704, 2227, 2969, 3320 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.37 (s, 9H), 4.84 (d, *J* = 16.0 Hz, 1H), 5.06 (d, *J* = 16.0 Hz, 1H), 5.54 (s, 1H), 5.92 (s, 1H), 6.14 (s, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 7.10-7.14 (m, 1H) 7.24-7.34 (m, 6H)^{*}, 7.66 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 28.10, 44.37, 63.02, 81.42, 109.88, 115.71, 122.08, 123.67, 125.42, 127.13, 127.20, 127.86, 128.90, 130.20, 133.34, 135.03, 142.40, 153.96, 172.79; HRMS (ESI) calcd for C₂₃H₂₃N₃O₃Na: 412.1637 (M+Na)⁺, found: 412.1633 (M+Na)⁺. ^{*}It merges with CHCl₃.



Methyl 2-(3-(tert-butoxycarbonylamino)-5-chloro-1-methyl-2-oxoindolin-3-yl)acrylate (5ca)

Yellow solid; Yield: 91%; mp: 114-118 °C; IR (KBr): ν 1160, 1704, 2926, 3248 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.32 (s, 9H), 3.27 (s, 3H), 3.74 (s, 3H), 5.90 (s, 1H), 6.10 (s, 1H), 6.36 (s, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 7.28 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.45 (d, *J* = 4.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 26.83, 28.11, 52.51, 63.94, 80.75, 109.28, 125.03, 128.07, 128.36, 129.20, 130.89, 136.36, 142.49, 153.98, 165.65, 174.26; HRMS (ESI) calcd for C₁₈H₂₁ClN₂O₅Na: 403.1037 (M+Na)⁺, found: 403.1057 (M+Na)⁺.



tert-Butyl 5-chloro-3-(1-cyanovinyl)-1-methyl-2-oxoindolin-3-ylcarbamate (5cb)

Light Pink solid; Yield: 78%; mp: 174-178 °C; IR (KBr): ν 1708, 2230, 2980, 3290 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.37 (s, 9H), 3.25 (s, 3H), 5.44 (s, 1H), 5.93 (s, 1H), 6.14 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.64 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 27.07, 28.11, 62.93, 81.71, 109.88, 115.39, 121.35, 125.80, 128.71, 129.06, 130.33, 133.64, 141.93,

153.83, 172.18; HRMS (ESI) calcd for C₁₇H₁₈ClN₃O₃Na: 370.0935 (M+Na)⁺, found: 370.0930 (M+Na)⁺.

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