NBS-Mediated dinitrogen extrusion of diazoacetamides under catalyst-free conditions: a practical access to the 3-bromooxindole derivatives

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General Information

All reactions were performed in oven-dried (140 °C) glassware under argon atmosphere. DCM (dichloromethane) and toluene were distilled prior to use kept over activated 3 Å molecular sieves. TBME (tert-butyl methyl ether), DMB (2,2-dimethylbutane) acetonitrile and DCCl₃ were purchased from Sigma Aldrich and used without further treatment. Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). Liquid chromatography was performed using flash chromatography of the indicated system on silica gel (300-400 mesh). ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on a Varian Inova-400 NMR spectrometer; chemical shifts were reported in ppm with the solvent signals as reference, and coupling constants (J) were given in Hertz. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI Source).

General Procedure for the Preparation of Diazoacetamides 1.¹,²

![General Procedure for the Preparation of Diazoacetamides 1.¹,²](image)

Synthesis of S-2: To a 50-mL oven-dried flask with a magnetic stirring bar, arylamine S-1 (10.0 mmol) and paraformaldehyde (0.5 g, 15.0 mmol) was dissolved in CH₃OH (20.0 mL), and CH₃ONa (2.7 g, 50 mmol) was added slowly over 5 min. After stirring at room temperature overnight, NaBH₄ (415 mg, 11.0 mmol) was added slowly. The mixture was refluxed for 2-5 h, and then the residue was quenched with saturated ammonium chloride solution (50 mL). The aqueous phase was extracted with ethyl acetate (25.0 mL X 2). The combined organic phase was dried with anhydrous Na₂SO₄, the crude product was purified by column chromatography (silica gel, petroleum ether : ethyl acetate = 20:1) to obtain S-2 in 50-75% yields.
Synthesis of S-4: To a 50-mL oven-dried flask with a magnetic stirring bar, aniline (0.93 g, 10.0 mmol) and aromatic aldehyde S-3 (10.0 mmol) was dissolved in DCM (20.0 mL), anhydrous Na₂SO₄ (2.5 g) was added. The solution was stirred at room temperature overnight. After filter the salt, DCM was evaporated under reduced pressure, then the residue was dissolved in CH₃OH (20.0 mL), and NaBH₄ (415 mg, 11.0 mmol) was added. The mixture was refluxed for 2-5 h, and then the reaction mixture was quenched with saturated ammonium chloride solution (50.0 mL). The aqueous phase was extracted with ethyl acetate (25.0 mL X 2). The combined organic phase was dried with anhydrous Na₂SO₄, the crude product was purified by column chromatography (silica gel, petroleum ether : ethyl acetate = 20:1) to give S-4.

Synthesis of 1: To a 50-mL oven-dried flask with a magnetic stirring bar, amine S-2/S-4 (3.8 mmol) and DIPEA (N,N-Diisopropylethylamine, 0.66 mL, 3.8 mmol) were dissolved in dry DCM (20.0 mL), bromoacetyl bromide (0.34 mL, 3.8 mmol) was added slowly at 0 °C, then the mixture was stirred at room temperature for 2-12 h. After the reaction was completed, DCM was removed under reduced pressure. The obtained crude S-5 was directly used for the next step without further purification. S-5 and N,N'-ditosylhydrazine (3.2 g, 9.5 mmol) were dissolved in THF (20.0 mL), DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene, 2.7 mL, 18.0 mmol) was added slowly over 5 min at 0 °C, and the reaction mixture was stirred for 10-60 minutes until no more gas was generated from the reaction mixture. The reaction was quenched by saturated
NaHCO₃ solution (30 mL), and the aqueous phase was extracted with ethyl acetate (20 mL X 3). The combined organic phase was dried with anhydrous Na₂SO₄, the crude product was purified by column chromatography (silica gel, petroleum ether : ethyl acetate = 10:1 to 2:1) to give the diazoacetamides 1.

Diazoacetamides 1r, 1s and 1t were prepared according to the reported references, and the characteristic data are consistent with the reported reference.

**2-Diazo-N-methyl-N-phenylacetamide (1a)**

Yellow oil. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) (ppm): 7.42-7.37 (m, 2H), 7.34-7.29 (m, 1H), 7.21-7.17 (m, 2H), 4.50 (s, 1H), 3.30 (s, 3H); \(^13\)C NMR (100 MHz, CDCl₃) \(\delta\): 165.9, 143.2, 129.9, 128.0, 127.1, 47.4, 37.2.

**2-Diazo-N-(4-methoxyphenyl)-N-methylacetamide (1b)**

Yellow solid. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) (ppm): 7.10 (d, \(J = 8.9\) Hz, 2H), 6.90 (d, \(J = 8.9\) Hz, 2H), 4.47 (s, 1H), 3.82 (s, 3H), 3.27 (s, 3H); \(^13\)C NMR (100 MHz, CDCl₃) \(\delta\): 166.2, 159.2, 135.9, 128.6, 115.0, 55.6, 47.2, 37.4.

**N-(4-Bromophenyl)-2-diazo-N-methylacetamide (1c)**

Yellow solid. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) (ppm): 7.53 (d, \(J = 8.7\) Hz, 2H), 7.09 (d, \(J = 8.7\) Hz, 2H), 4.52 (s, 1H), 3.28 (s, 3H); \(^13\)C NMR (100 MHz, CDCl₃) \(\delta\): 165.7, 142.3, 133.1, 129.1, 121.7, 47.6, 37.2.

**2-Diazo-N-methyl-N-[4-(trifluoromethyl)phenyl]acetamide (1d)**

Yellow solid. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) (ppm): 7.67 (d, \(J = 8.3\) Hz, 2H), 7.35 (d, \(J = 8.3\) Hz, 2H), 4.57 (s, 1H), 3.33 (s, 3H); \(^13\)C NMR (100 MHz, CDCl₃) \(\delta\): 165.6, 146.5, 129.8 (d, \(J = 32.9\) Hz), 127.5, 127.01 (q, \(J = 3.7\) Hz), 123.8 (d, \(J = 272.2\) Hz), 47.8, 37.1.
N-(3-Bromophenyl)-2-diazo-N-methylacetamide (1e) Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.46-7.43 (m, 1H), 7.37 (t, $J = 1.9$ Hz, 1H), 7.27 (t, $J = 8.0$ Hz, 1H), 7.16-7.12 (m, 1H), 4.54 (s, 1H), 3.28 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 165.6, 144.5, 131.11, 131.12, 130.6, 126.1, 123.0, 47.6, 37.2.

N-(2-Bromophenyl)-2-diazo-N-methylacetamide (1f) Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.66 (dd, $J = 8.0$, 1.4 Hz, 1H), 7.37-7.21 (comp, 3H), 4.27 (s, 1H), 3.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 165.7, 141.6, 134.1, 130.3, 130.2, 129.1, 123.7, 47.3, 35.8.

2-Diazo-N-ethyl-N-phenylacetamide (1g) Red oil. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.43-7.37 (m, 2H), 7.34 (m, 1H), 7.18-7.13 (m, 2H), 4.36 (s, 1H), 3.78 (q, $J = 7.1$ Hz, 2H), 1.10 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 165.4, 141.4, 129.8, 128.6, 128.2, 47.4, 44.1, 13.5.

2-Diazo-N,N-diphenylacetamide (1h) Red oil. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.41-7.37 (comp, 4H), 7.32-7.27 (comp, 6H), 4.67 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 165.9, 142.4, 129.4, 127.5, 127.0, 49.1.

N-Benzyl-2-diazo-N-phenylacetamide (1i) Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.33-7.26 (comp, 4H), 7.26-7.21 (comp, 4H), 7.03-7.00 (comp, 2H), 4.93 (s, 2H), 4.44 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 166.0, 141.6, 137.7, 129.7, 128.8, 128.6, 128.5, 128.3, 127.5, 53.0, 47.5.
\( N-(4\text{-Bromobenzyl})-2\text{-diazo-}N\text{-phenylacetamide} \ (1j) \) Yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.38 (d, \( J = 8.3 \) Hz, 2H), 7.36-7.29 (comp, 3H), 7.10 (d, \( J = 8.3 \) Hz, 2H), 7.00 (d, \( J = 8.3 \), 2H), 4.86 (s, 2H), 4.43 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 166.1, 141.3, 136.7, 131.7, 130.6, 129.9, 128.52, 128.45, 121.5, 52.4, 47.6.

\( N-(4\text{-Chlorobenzyl})-2\text{-diazo-}N\text{-phenylacetamide} \ (1k) \) Yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.37-7.30 (comp, 3H), 7.24-7.21 (comp, 2H), 7.16 (d, \( J = 8.5 \) Hz, 2H), 7.00 (dd, \( J = 7.8, 1.8 \) Hz, 2H), 4.88 (s, 2H), 4.43 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 166.1, 141.3, 136.2, 133.4, 130.2, 129.9, 128.7, 128.6, 128.5, 52.4, 47.6.

\( 2\text{-Diazo-}N-(4\text{-nitrobenzyl})-N\text{-phenylacetamide} \ (1l) \) Yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 8.13 (d, \( J = 8.7 \) Hz, 2H), 7.41 (d, \( J = 8.7 \) Hz, 2H), 7.39-7.32 (comp, 3H), 7.06-7.01 (comp, 2H), 5.00 (s, 2H), 4.49 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 166.2, 147.3, 145.2, 141.1, 130.0, 129.4, 128.6, 128.2, 123.8, 52.5, 47.6.

\( N-(\text{Beno}[d][1,3]\text{dioxol-5-ylmethyl})-2\text{-diazo-}N\text{-phenylacetamide} \ (1m) \) Yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.41-7.35 (comp, 3H), 7.09-7.05 (comp, 2H), 6.84 (d, \( J = 1.4 \) Hz, 1H), 6.73 (d, \( J = 7.9 \) Hz, 1H), 6.66 (dd, \( J = 7.9, 1.2 \) Hz, 1H), 5.98 (s, 2H), 4.87 (s, 2H), 4.47 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 166.0, 147.8, 147.0, 141.4, 131.6, 129.8, 128.7, 128.3, 122.3, 109.4, 108.1, 101.1, 52.8, 47.6.

\( 2\text{-Diazo-}N-(\text{naphthalen-2-ylmethyl})-N\text{-phenylacetamide} \ (1n) \) Yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.82-7.73 (comp, 3H), 7.61 (s, 1H), 7.47-7.42

S-6
(comp, 3H), 7.30-7.00 (comp, 5H), 5.10 (s, 2H), 4.47 (s, 1H);
\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3 \delta (ppm): 166.1, 141.5, 135.2, \]
133.3, 132.9, 129.7, 128.6, 128.34, 128.30, 127.9, 127.7, 127.5, 126.8, 126.1, 125.9, 53.1, 47.6.

2-Diazo-N-phenyl-N-(prop-2-yn-1-yl)acetamide (1o) Red oil. \[^1\]H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.42-7.35 (comp, 3H), 7.29-7.25 (comp, 2H), 4.47 (d, $J = 2.5$ Hz, 2H), 4.45 (s, 1H), 2.20 (t, $J = 2.5$ Hz, 1H); \[^{13}C\] NMR (100 MHz, CDCl$_3$) δ: 165.6, 140.8, 129.8, 128.7, 128.3, 127.2, 47.6, 38.3.

2-Diazo-N-(2-methoxyethyl)-N-phenylacetamide (1p) Red oil. \[^1\]H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.40-7.34 (m, 2H), 7.33-7.28 (m, 1H), 7.24-7.18 (m, 2H), 4.40 (s, 1H), 3.89 (t, $J = 5.8$ Hz, 2H), 3.49 (t, $J = 5.8$ Hz, 2H), 3.28 (s, 3H); \[^{13}C\] NMR (100 MHz, CDCl$_3$) δ: 165.9, 141.8, 129.7, 128.5, 128.2, 69.8, 58.6, 48.6.

N-Cinnamyl-2-diazo-N-phenylacetamide (1q) Yellow solid. \[^1\]H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.42-7.37 (comp, 2H), 7.36-7.27 (comp, 5H), 7.23-7.18 (comp, 3H), 6.40 (d, $J = 15.9$ Hz, 1H), 6.28 (m, 1H), 4.49 (dd, $J = 6.4, 0.5$ Hz, 2H), 4.46 (s, 1H); \[^{13}C\] NMR (100 MHz, CDCl$_3$) δ: 165.7, 141.6, 136.7, 133.3, 129.8, 128.6, 128.5, 128.3, 127.7, 126.5, 124.7, 51.7, 47.5.

2-Diazo-N-methyl-N-phenyl-2-tosylacetamide (1s) Yellow solid. \[^1\]H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.92 (d, $J = 8.4$ Hz, 2H), 7.47-7.37 (comp, 3H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.24-7.20 (comp, 2H), 3.26 (s, 3H), 2.44 (s, 3H); \[^{13}C\] NMR (100 MHz, CDCl$_3$) δ: 158.3, 144.9, 142.1, 139.5, 130.5, 129.6, 128.8, 128.4, 126.9, 38.3, 21.8.
2-Diazo-N-methyl-N,2-diphenylacetamide (1t) Red oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.36-7.26 (comp, 5H), 7.25-7.09 (comp, 5H), 3.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.2, 144.0, 129.8, 128.7, 127.2, 126.7, 125.6, 125.5, 124.7, 38.6.

General Procedures for the Preparation of 3.

To a 10-mL oven-dried vial with a magnetic stirring bar, NBS (35.6 mg, 0.2 mol) was dissolved in CH$_3$CN (1.0 mL), diazo compound 1 (0.2 mmol) in CH$_3$CN (1.0 mL) was added under argon over 60 min. After stirring at room temperature for 1-5 h, the crude reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 10:1 to 3:1) to give the desired products 3 with high yields.

Characteristic data of products 3r and 3t are consistent with the reported references.$^7$

3-Bromo-1-methylindolin-2-one (3a) White solid, 43.8 mg, 97% yield, mp: 107~109 $^\circ$C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.40 (d, $J = 7.5$ Hz, 1H), 7.34 (t, $J = 7.8$ Hz, 1H), 7.13-7.08 (m, 1H), 6.82 (d, $J = 7.8$ Hz, 1H), 5.26 (s, 1H), 3.23 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 172.6, 143.9, 130.5, 126.2, 126.1, 123.5, 108.9, 38.8, 26.9; HRMS (ESI) calculated for C$_9$H$_9$BrNO [M+H]$^+$: 227.9847, found 227.9866.

3-Bromo-5-methoxy-1-methylindolin-2-one (3b) White solid, 49.7 mg, 97% yield, mp: 122~124 $^\circ$C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.01 (d, $J = 2.3$ Hz, 1H), 6.86 (dd, $J = 8.5, 2.5$ Hz, 1H), 6.72 (d, $J = 8.5$ Hz, 1H), 5.22 (s, 1H), 3.80 (s, 3H), 3.20 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 172.6, 143.9, 130.5, 126.2, 126.1, 123.5, 108.9, 38.8, 26.9; HRMS (ESI) calculated for C$_{10}$H$_{10}$BrNNaO$_2$ [M+Na]$^+$: 277.9793, found 277.9796.
3,5-Dibromo-1-methylindolin-2-one (3c) White solid, 51.8 mg, 85% yield, mp: 150–151 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.29-7.26 (comp, 2H), 7.00 (s, 1H), 5.21 (s, 1H), 3.22 (s, 3H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \): 171.9, 142.9, 133.4, 129.3, 128.1, 116.0, 110.3, 37.7, 27.0; HRMS (ESI) calculated for C\(_9\)H\(_7\)Br\(_2\)NNaO [M+Na]\(^+\): 327.8772, found 327.8767.

3-Bromo-1-methyl-5-(trifluoromethyl)indolin-2-one (3d) White solid, 38.2 mg, 65% yield, mp: 150–152 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.67-7.61 (comp, 2H), 6.92 (d, \( J = 8.1 \) Hz, 1H), 5.28 (s, 1H), 3.27 (s, 3H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \): 165.6, 146.5, 130.0, 129.6, 127.5, 127.0 (q, \( J = 3.7 \) Hz), 125.1, 122.4, 47.8, 37.1; HRMS (ESI) calculated for C\(_{10}\)H\(_7\)Br\(_3\)NNaO [M+Na]\(^+\): 315.9561, found 315.9556.

3,6-Dibromo-1-methylindolin-2-one (3e) Yellow solid, 51.8 mg, 85% yield, mp: 186–188 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.25-7.20 (comp, 2H), 6.98 (s, 1H), 5.19 (s, 1H), 3.20 (s, 3H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \): 172.3, 145.1, 127.3, 126.3, 125.0, 124.3, 112.5, 37.8, 27.0; HRMS (ESI) calculated for C\(_9\)H\(_7\)Br\(_2\)NNaO [M+Na]\(^+\): 327.8772, found 327.8763.

3,7-Dibromo-1-methylindolin-2-one (3f) White solid, 30.5 mg, 50% yield, mp: 157–160 °C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.44 (d, \( J = 8.2 \) Hz, 1H), 7.34 (d, \( J = 7.4 \) Hz, 1H), 6.95 (t, \( J = 8.1 \) Hz, 1H), 5.24 (s, 1H), 3.61 (s, 3H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \): 172.9, 141.2, 136.1, 129.1, 125.5, 124.6, 103.0, 37.9, 30.6; HRMS (ESI) calculated for C\(_9\)H\(_7\)Br\(_2\)NNaO [M+Na]\(^+\): 327.8772, found 327.8769.

3,3,7-Tribromo-1-methylindolin-2-one (3f') White solid, 17.6 mg, 23% yield, mp:
104-107 °C; **1**H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.59 (dd, $J = 7.5, 1.2$ Hz, 1H), 7.44 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.02 (dd, $J = 8.1, 7.6$ Hz, 1H), 3.64 (s, 3H); **1**3C NMR (100 MHz, CDCl$_3$) δ: 170.4, 137.4, 137.1, 133.8, 125.6, 125.3, 103.1, 44.0, 31.1; HRMS (ESI) calculated for C$_9$H$_7$Br$_3$NO [M+H]$^+$: 383.8057, found 383.8069.

**3-Bromo-1-ethylindolin-2-one (3g)** White solid, 44.2 mg, 92% yield, mp: 112~114 °C; **1**H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.41 (d, $J = 7.4$ Hz, 1H), 7.33 (t, $J = 7.8$ Hz, 1H), 7.09 (td, $J = 7.6, 0.7$ Hz, 1H), 6.84 (d, $J = 7.9$ Hz, 1H), 5.24 (s, 1H), 3.80-3.74 (m, 2H), 1.29 (t, $J = 7.2$ Hz, 3H); **1**3C NMR (100 MHz, CDCl$_3$) δ: 172.1, 143.0, 130.4, 126.4, 126.3, 123.3, 109.0, 39.0, 35.4, 12.5; HRMS (ESI) calculated for C$_{10}$H$_{10}$BrNNaO [M+Na]$^+$: 261.9843, found 261.9855.

**3-Bromo-1-phenylindolin-2-one (3h)** White solid, 50.1 mg, 87% yield, mp: 123~125 °C; **1**H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.57-7.51 (m, 2H), 7.48 (d, $J = 7.5$ Hz, 1H), 7.46-7.41 (comp, 3H), 7.26 (t, $J = 3.8$ Hz, 1H), 7.14 (td, $J = 7.6, 0.7$ Hz, 1H), 6.80 (d, $J = 7.9$ Hz, 1H), 5.44 (s, 1H); **1**3C NMR (100 MHz, CDCl$_3$) δ: 171.8, 144.0, 133.9, 130.4, 129.9, 128.7, 126.54, 126.47, 126.1, 123.9, 110.2, 39.1; HRMS (ESI) calculated for C$_{14}$H$_{10}$BrNNaO [M+Na]$^+$: 309.9843, found 309.9828.

**1-Benzyl-3-bromoindolin-2-one (3i)** White solid, 54.2 mg, 90% yield, mp: 142~144 °C; **1**H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.41 (d, $J = 7.5$ Hz, 1H), 7.37-7.26 (comp, 5H), 7.25-7.18 (m, 1H), 7.09-7.04(m, 1H), 6.71 (d, $J = 7.9$ Hz, 1H), 5.35 (s, 1H), 4.92 (q, $J = 15.7$ Hz, 2H); **1**3C NMR (100 MHz, CDCl$_3$) δ: 172.7, 143.0, 135.2, 130.4, 129.0, 128.0, 127.4, 126.24, 126.22, 123.5, 109.9, 44.3, 38.8; HRMS (ESI) calculated for C$_{15}$H$_{12}$BrNNaO [M+Na]$^+$: 324.0000, found 324.0010.
3-Bromo-1-(4-bromobenzyl)indolin-2-one (3j) White solid, 73.0 mg, 96% yield, mp: 140–142 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.47-7.44 (m, 2H), 7.42 (d, \(J = 7.4\) Hz, 1H), 7.26-7.15 (comp, 3H), 7.01-7.05 (m, 1H), 6.67 (d, \(J = 7.9\) Hz, 1H), 5.35 (s, 1H), 4.86 (q, \(J = 15.8\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 172.7, 142.7, 134.2, 132.2, 130.5, 129.1, 126.3, 126.2, 123.7, 122.0, 109.7, 43.7, 38.6; HRMS (ESI) calculated for C\(_{15}\)H\(_{11}\)Br\(_2\)NNaO \([M+Na]^+\): 403.9085, found 403.9103.

3-Bromo-1-(4-chlorobenzyl)indolin-2-one (3k) White solid, 63.9 mg, 95% yield, mp: 126–128 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.42 (d, \(J = 7.5\) Hz, 1H), 7.32-7.29 (m, 2H), 7.26-7.20 (comp, 3H), 7.10-7.06 (m, 1H), 6.67 (d, \(J = 7.9\) Hz, 1H), 5.35 (s, 1H), 4.88 (q, \(J = 15.8\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 172.8, 142.7, 133.9, 133.7, 130.5, 129.3, 128.8, 126.4, 126.2, 123.7, 109.7, 43.6, 38.6; HRMS (ESI) calculated for C\(_{15}\)H\(_{12}\)BrClNO \([M+H]^+\): 335.9791, found 335.9796.

3-Bromo-1-(4-nitrobenzyl)indolin-2-one (3l) White solid, 65.0 mg, 94% yield, mp: 160–162 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 8.19 (d, \(J = 8.6\) Hz, 2H), 7.49-7.42 (comp, 3H), 7.23 (d, \(J = 7.6\) Hz, 1H), 7.11 (t, \(J = 7.6\) Hz, 1H), 6.64 (d, \(J = 7.9\) Hz, 1H), 5.38 (s, 1H), 5.01 (q, \(J = 16.3\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 172.8, 147.8, 142.6, 142.3, 130.6, 128.1, 126.6, 126.2, 124.1, 109.4, 43.6, 38.3; HRMS (ESI) calculated for C\(_{15}\)H\(_{11}\)BrN\(_2\)NaO\(_3\) \([M+Na]^+\): 368.9851, found 368.9865.

1-(Benzo[d][1,3]dioxol-5-ylmethyl)-3-bromoindolin-2-one (3m) White solid, 64.1 mg, 93% yield, mp: 139–141 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.40 (d, \(J = 7.4\) Hz, 1H), 7.23 (t, \(J = 7.8\) Hz, 2H), 7.01-6.95 (m, 1H), 6.69 (d, \(J = 7.9\) Hz, 1H), 5.38 (s, 1H), 4.88 (q, \(J = 15.8\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 172.8, 147.8, 142.6, 142.3, 130.6, 128.1, 126.6, 124.1, 109.4, 43.6, 38.3; HRMS (ESI) calculated for C\(_{15}\)H\(_{11}\)BrN\(_2\)NaO\(_3\) \([M+Na]^+\): 368.9851, found 368.9865.
Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 6.83-6.71 (comp, 4H), 5.93 (s, 2H), 5.33 (s, 1H), 4.82 (q, J = 15.5 Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 172.7, 148.3, 147.4, 142.9, 130.4, 129.0, 126.23, 126.23, 123.5, 121.0, 109.9, 108.6, 108.0, 101.3, 44.1, 38.8; HRMS (ESI) calculated for C\(_{16}\)H\(_{13}\)BrNO\(_3\) [M+H]^+: 346.0079, found 346.0062.

3-Bromo-1-(naphthalen-2-ylmethyl)indolin-2-one (3n) White solid, 65.2 mg, 93% yield, mp: 140~142 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.89-7.74 (comp, 4H), 7.72 (s, 1H), 7.53 (d, J = 1.3 Hz, 1H), 7.50-7.46 (m, 2H), 7.38 (dd, J = 8.4, 1.6 Hz, 1H), 7.29 (dd, J = 8.4, 1.9 Hz, 1H), 6.61 (d, J = 8.4 Hz, 1H), 5.36 (s, 1H), 5.06 (q, J = 15.7 Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 172.3, 142.0, 133.4, 133.3, 133.1, 132.1, 129.4, 129.2, 128.2, 127.91, 127.88, 126.7, 126.5, 126.3, 125.0, 116.1, 111.5, 44.7, 37.7; HRMS (ESI) calculated for C\(_{19}\)H\(_{14}\)BrNNaO [M+Na]^+: 374.0156, found 374.0147.

3-Bromo-1-(prop-2-yn-1-yl)indolin-2-one (3o) White solid, 44.8 mg, 90% yield, mp: 126~129 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.43 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.14 (td, J = 7.7, 0.7 Hz, 1H), 7.05 (d, J = 7.9 Hz, 1H), 5.30 (s, 1H), 4.60 (dd, J = 17.7, 2.5 Hz, 1H), 4.44 (dd, J = 17.7, 2.5 Hz, 1H), 2.27 (t, J = 2.5 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 171.6, 142.0, 130.5, 126.3, 126.1, 123.9, 110.0, 76.3, 73.1, 38.5, 30.0; HRMS (ESI) calculated for C\(_{11}\)H\(_{8}\)BrNNaO [M+Na]^+: 271.9687, found 271.9691.

3-Bromo-1-(2-methoxyethyl)indolin-2-one (3p) White solid, 46.8 mg, 87% yield, mp: 104~106 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm):7.38 (d, J = 7.5 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.08 (td, J = 7.6, 0.8 Hz, 1H), 6.96 (d, J = 7.9 Hz, 1H), 5.26 (s, 1H), 3.96-3.82 (m, 2H), 3.63 (t, J = 5.6 Hz, 2H), 3.33 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 172.8, 143.7, 130.4, 126.10, 126.07, 123.3, 109.8, 69.9, 59.1, 40.8, 38.8; HRMS
(ESI) calculated for C\(_{11}H_{12}BrNNaO_2\) [M+Na]\(^+\): 291.9949, found 291.9939.

3-Bromo-1-cinnamylindolin-2-one (3q) White solid, 52.3 mg, 80% yield, mp: 146~146 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.42 (d, \(J = 7.5\) Hz, 1H), 7.36-7.29 (comp, 4H), 7.28-7.22 (m, 2H), 7.09 (td, \(J = 7.6\), 0.8 Hz, 1H), 6.88 (d, \(J = 7.9\) Hz, 1H), 6.63 (d, \(J = 15.9\) Hz, 1H), 6.18 (dt, \(J = 15.9\), 6.0 Hz, 1H), 5.31 (s, 1H), 4.51 (dd, \(J = 6.0\), 1.4 Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 172.3, 143.1, 136.1, 133.6, 130.5, 128.7, 128.2, 126.6, 126.3, 123.5, 122.2, 109.8, 42.6, 38.8; HRMS (ESI) calculated for C\(_{17}H_{14}BrNNaO\) [M+Na]\(^+\): 350.0156, found 350.0153.

3-Bromo-1-methyl-3-tosylindolin-2-one (3s) Yellow solid, 60.8 mg, 80% yield, mp: 184~186 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.74 (dd, \(J = 7.6\), 0.8 Hz, 1H), 7.66 (d, \(J = 8.4\) Hz, 2H), 7.40 (td, \(J = 7.8\), 1.2 Hz, 1H), 7.27 (s, 1H), 7.25 (s, 1H), 7.18 (td, \(J = 7.7\), 0.9 Hz, 1H), 6.72 (d, \(J = 7.9\) Hz, 1H), 3.07 (s, 3H), 2.42 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 167.5, 146.4, 143.9, 132.4, 131.7, 130.3, 129.2, 128.2, 124.0, 122.2, 109.0, 66.9, 27.2, 21.9; HRMS (ESI) calculated for C\(_{16}H_{15}BrNO_3S\) [M+H]\(^+\): 379.9956, found 379.9955.

3-Bromo-1-methyl-3-phenylindolin-2-one (3t) Yellow solid, 42.7 mg, 71% yield, mp: 124 ~126 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.67 (dd, \(J = 7.9\), 1.8 Hz, 2H), 7.50 (dd, \(J = 7.5\), 0.8 Hz, 1H), 7.41-7.32 (comp, 4H), 7.18 (td, \(J = 7.6\), 0.9 Hz, 1H), 6.90 (d, \(J = 7.9\) Hz, 1H), 3.25 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 173.7, 142.3, 136.5, 130.5, 130.4, 129.0, 128.62, 128.61, 126.7, 123.6, 109.2, 57.0, 27.1; HRMS (ESI) calculated for C\(_{15}H_{13}BrNO\) [M+H]\(^+\): 302.0181, found 302.0167.
General Procedures for the Preparation of 5a and 5b.

To a 10-mL oven-dried vial with a magnetic stirring bar, NCS (26.7 mg, 0.2 mol) was dissolved in CH₃CN (1.0 mL), diazo compound 1 (0.2 mmol) in CH₃CN (1.0 mL) was added under argon over 60 min. After stirring at room temperature for 5 h, The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 10:1 to 3:1) to give the desired products.

3-Chloro-1-methylindolin-2-one (5a) White solid, 19.0 mg, 53% yield, mp: 97~100 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.42 (d, J = 7.4 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.12 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 5.13 (s, 1H), 3.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 172.2, 144.0, 130.6, 125.83, 125.75, 123.5, 108.8, 51.6, 26.8; HRMS (ESI) calculated for C₉H₉ClNO [M+H]⁺: 182.0373, found 182.0385.

1-Benzyl-3-chloroindolin-2-one (5b) White solid, 30.0 mg, 59% yield, mp: 146~148 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.43 (d, J = 7.4 Hz, 1H), 7.34-7.27 (comp, 5H), 7.23 (d, J = 7.8 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 5.23 (s, 1H), 4.92 (q, J = 15.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 172.4, 143.1, 135.1, 130.5, 129.0, 128.0, 127.4, 125.83, 123.5, 109.9, 51.6, 44.3; HRMS (ESI) calculated for C₁₅H₁₃ClNO [M+H]⁺: 258.0686, found 258.0595.

3-Iodo-1-methylindolin-2-one (5c) Yellow solid, 36.6 mg, 67% yield, mp: 97~99 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.35 (d, J = 7.5 Hz, 1H), 7.32-7.26 (m, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 5.66 (s, 1H), 3.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ(ppm):174.3, 143.2, 129.9, 127.9, 126.2, 123.4, 109.0, 27.1, 12.8; HRMS (ESI) calculated for C₉H₉INO [M+H]⁺: 273.9729, found: 273.9740.
3-Fluoro-1-methylindolin-2-one (5d) White solid, mp: 64–66 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.46 (d, $J = 7.3$ Hz, 1H), 7.40 (t, $J = 7.8$ Hz, 1H), 7.11 (t, $J = 7.6$ Hz, 1H), 6.83 (d, $J = 7.9$ Hz, 1H), 5.66 (d, $J = 51.0$ Hz, 1H), 3.19 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 171.2 (d, $J = 18.2$ Hz), 144.8 (d, $J = 5.3$ Hz), 131.6 (d, $J = 3.3$ Hz), 126.1 (d, $J = 1.2$ Hz), 123.4 (d, $J = 2.9$ Hz), 122.9 (d, $J = 16.2$ Hz), 108.9 (d, $J = 1.3$ Hz), 85.6, 26.3; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -193.33; HRMS (ESI) calculated for C$_9$H$_9$FNO [M+H]$^+$: 166.0668, found 166.0667.

**General Procedures for the Preparation of 6.**

To a 10-mL oven-dried vial with a magnetic stirring bar, NBS (35.6 mg, 0.2 mol) was dissolved in CH$_3$CN (1.0 mL), 1-methylindolin-2-one 4 (30.0 mg, 0.2 mmol) in CH$_3$CN (1.0 mL) was added under argon over 60 min. After stirring at room temperature for 5 h, the crude reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 10:1 to 3:1) to give the desired products 6 with high yield (>95%). And the characteristic data are consistent with the reported reference.8

**General Procedures for the Preparation of 7.**

To a 10-mL oven-dried vial with a magnetic stirring bar, NBS (35.6 mg, 0.2 mol) was dissolved in CH$_3$CN (1.0 mL), 3,5-Dibromo-1-methylindolin-2-one 3c (61.0 mg, 0.2 mmol) in CH$_3$CN (1.0 mL) was added under argon over 60 min. After stirring at room
temperature for 5 h. The crude reaction mixture was purified by flash column chromatography on silica gel (elu-ent: petroleum ether:EtOAc = 8:1) to give the compound 7 as white solid (59.2 mg, 78%). White solid, 60.5 mg, 78% yield, mp: 111~113 °C; \( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) (ppm): 7.74 (d, \( J = 1.9 \) Hz, 1H), 7.47 (dd, \( J = 8.4, 2.0 \) Hz, 1H), 6.71 (d, \( J = 8.4 \) Hz, 1H), 3.25 (s, 3H). \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 169.4, 138.9, 134.5, 132.7, 129.1, 116.6, 110.7, 43.7, 27.5; HRMS (ESI) calculated for C\(_9\)H\(_7\)Br\(_3\)NO [M+H\(^+\)]: 383.8057, found 383.8066.

**General Procedures for the Preparation of 8.**

![Diagram of the reaction](image)

To a 10-mL oven-dried vial with a magnetic stirring bar, K\(_3\)PO\(_4\) (42.4 mg, 0.2 mol) was dissolved in CH\(_3\)CN (1.0 mL), 3-Bromo-1-methylindolin-2-one 3\( a \) (44.5 mg, 0.2 mmol) in CH\(_3\)CN (1.0 mL) was added under argon over 30 min. After stirring at room temperature overnight, the crude product was purified by flash column chromatography on silica gel (elu-ent: petroleum ether:EtOAc = 10:1) to give the compound 8 as dark violet solid (49.0 mg, 85%). And the characteristic data are consistent with the reported reference.\(^9\)

**Control Reactions with TEMPO**

![Diagram of the reaction](image)

To a 10-mL oven-dried vial with a magnetic stirring bar, NBS (35.6 mg, 0.2 mmol) and TEMPO (28.3 mg, 0.2 mmol) were dissolved in CH\(_3\)CN (1.0 mL), diazo compound 1\( a \) (35.4 mg, 0.2 mmol) in CH\(_3\)CN (1.0 mL) was added under argon over 60 min. After stirring at room temperature for 7 h, the crude reaction mixture was
purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 10:1 to 5:1) to give the desired products 26.2mg (yield: 58%).

To a 10-mL oven-dried vial with a magnetic stirring bar, TEMPO (28.3 mg, 0.2 mmol) were dissolved in CH$_3$CN (1.0 mL), diazo compound 1a (35.4mg, 0.2 mmol) in CH$_3$CN (1.0 mL) was added under argon over 60 min. After stirring at room temperature for 5 h, the TLC analysis showed that no reaction was occurred at all. And all the diazo compound 1a was recovered.

References
Single-crystal X-ray diffraction of 3a

![Chemical structure of 3a](image)

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