Supporting Information

Manganese-mediated/-catalyzed oxidative carboazidation of acrylamides

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**General methods**

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AV-500 spectrometer (500 MHz and 126 MHz MHz, respectively). $^1$H, $^{13}$C NMR chemical shifts are reported vs tetramethylsilane signal or residual protio solvent signals. High resolution mass spectra (HRMS) was recorded on Agilent G6500 iFunnel Q-TOF LC/MS.

Toluene, dioxane and THF were distilled over sodium benzophenone ketyl under nitrogen. Acetonitrile (ACN) and 1,2-Dichloroethane (DCE) were distilled over CaH$_2$ under nitrogen. Dimethyl sulfoxide, N,N-dimethylformamide and N,N-dimethylacetamide were used before vacuum distillation over CaH$_2$ under nitrogen.

Acrylamides substrates were synthesized following the literature procedures$^1$. All other chemicals and solvents were purchased from commercial company and used as received.

**Experimental Details and Characterization Data**

**Experimental Procedures for Table 2 & 3.**

**Procedure for Mn-catalytic reactions:**

An oven-dried 10 mL seal tube was charged with Mn(OAc)$_3$•2H$_2$O 8.0 mg (0.03 mmol, 10 mol%) and acrylamide 1(0.30 mmol, 1.0 equiv.), 2 mL DCE, TBPB 84 μL (0.45 mmol, 1.5 equiv.) and TMSN$_3$ 78 μL (0.60 mmol, 2.0 equiv.) under nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 12 h monitored by TLC and then was concentrated under vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether and ethyl acetate (typically, petroleum ether/ethyl acetate = 10/1) to obtain the desired product.

Sometimes benzoic acid, the decomposition product of TBPB, is easy to come out along with the desired product through the silica gel. There are two methods listed below to deal with this problem.

1) Neutralized with NaHCO$_3$: After the reactions cool to room temperature, 2 mL water, 2 mL ethyl acetate and 150 mg NaHCO$_3$ is added to the tube. The mixture is stirred vigorously for 30 min, then it is extracted with 30 mL ethyl acetate. The organic phase was dried over MgSO$_4$, filtered and concentrated under vacuum. Then the residue was purified by flash chromatography.

2) Flash chromatography under alkaline condition: An easier way is to add 1~2% Et$_3$N to the eluent.

**Procedure for Mn-mediated reactions:**

An oven-dried 10 mL seal tube was charged with Mn(OAc)$_3$•2H$_2$O 241 mg (0.90
mmol, 3.0 equiv.) and acrylamide 1 (0.30 mmol, 1.0 equiv.) 2 mL DCE and TMSN₃ 78 μL (0.60 mmol, 2.0 equiv.) under nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 12 h monitored by TLC and then was concentrated under vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether and ethyl acetate (typically, petroleum ether/ethyl acetate = 10/1) to obtain the desired product.

**Diazidation of styrene**

\[
\text{C}_6\text{H}_{5}\text{CH} = \text{CH} + \text{TBPB} + \text{TMSN}_3 \rightarrow \text{C}_6\text{H}_{5}\text{CH} = \text{CH}_2\text{N}_3\text{N}_3
\]

1.0 equiv. 1.5 equiv. 3.0 equiv.

An oven-dried 10 mL Schlenk tube was charged with 2 mL DCE, styrene 34 μL (0.30 mmol, 1.0 equiv.), TBPB 84 μL (0.45 mmol, 1.5 equiv.) and TMSN₃ 118 μL (0.9 mmol, 3.0 equiv.) under nitrogen atmosphere. The reaction mixture was stirred at 25 °C for 12 h and then was concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether and ether (petroleum ether/ether = 40/1) to afford the diazidation product 51 mg (90%).

**Procedure for Reactions for detecting oxy-radical**

An oven-dried 10 mL seal tube was charged with acrylamide 1a 35 mg (0.20 mmol, 1.0 equiv.), 2 mL DCM, TBPB 38 μL (0.20 mmol, 1.0 equiv.) (for Eq. a, or TBPB 75 μL (0.4 mmol, 2.0 equiv.) and Mn(OAc)₂ 69 mg (0.4 mmol, 2.0 equiv) for Eq. b) under nitrogen atmosphere. The reaction mixture was stirred at 105 °C for 15 h and then was filtered through short silica gel column, concentrated under vacuum and NMR yields were obtained using 40 μL CBr₂H₂ as internal standard.
Eq. a: conv.: 76%, yield: 70%
TBPB conv.: 94%

Eq. b: conv.: 31%, yield: 30%
TBPB conv.: 93%

3. conv.: 11%, yield: 3%
TBPB conv.: 90%
An oven-dried 10 mL seal tube was charged with acrylamide 1a 53 mg (0.30 mmol, 1.0 equiv.), 3 mL DCM, TBPB 57 μL (0.30 mmol, 1.0 equiv.) and Mn(OAc)₃ 241 mg (0.9 mmol, 3.0 equiv.) under nitrogen atmosphere. The reaction mixture was stirred at 105 °C then was filtered through short silica gel column, concentrated under vacuum and NMR yields were obtained using 40 μL CBr₂H₂ as internal standard.

**Eq. c1:** conv.: 11%, yield: 3%
TBPB conv.: 90%
4 h at 105 °C.

Reference:

Characterization of products

![Characterization of products](image)

3-(azidomethyl)-1,3-dimethylindolin-2-one

Table 2, 2a. (CAS: 1449116-88-4). Colorless oil. 86% yield for manganese-catalyzed reaction; 97% yield for manganese-mediated reaction. **¹H NMR** (500 MHz, CDCl₃) δ 7.33 (td, J = 7.7, 1.3 Hz, 1H), 7.28 (dd, J = 7.4, 1.3 Hz, 1H), 7.10 (td, J = 7.5, 1.0 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 3.66 – 3.59 (m, 2H), 3.23 (s, 3H), 1.37 (s, 3H). **¹³C NMR**
(126 MHz, CDCl₃) δ 177.5, 142.4, 133.4, 131.4, 126.3, 115.4, 109.7, 56.9, 48.8, 26.4, 20.3.

3-(azidomethyl)-1,3,5-trimethylindolin-2-one

Table 2, 2b. (CAS: 1449116-92-0). Colorless oil. 66% yield for manganese-catalyzed reaction; 70% yield for manganese-mediated reaction. ¹H NMR (500 MHz, CDCl₃) δ 7.17 – 7.10 (m, 2H), 6.79 (d, J = 7.8 Hz, 1H), 3.65 (s, 2H), 3.24 (s, 2H), 2.38 (s, 3H), 1.39 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 178.1, 141.0, 132.3, 131.3, 128.8, 123.8, 108.0, 57.2, 48.7, 26.3, 21.1, 20.5.

3-(azidomethyl)-5-methoxy-1,3-dimethylindolin-2-one

Table 2, 2c. (CAS: 1449116-93-1). White solid. 77% yield for manganese-catalyzed reaction; 83% yield for manganese-mediated reaction. ¹H NMR (500 MHz, CDCl₃) δ 6.89 (d, J = 2.5 Hz, 1H), 6.83 (dd, J = 8.5, 2.5 Hz, 1H), 6.77 (d, J = 8.5 Hz, 1H), 3.79 (s, 3H), 3.61 (s, 2H), 3.19 (s, 3H), 1.35 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 177.7, 156.1, 136.8, 132.7, 112.6, 110.7, 108.6, 57.1, 55.7, 49.0, 26.3, 20.4.

3-(azidomethyl)-1,3-dimethyl-2-oxoindoline-5-carbonitrile

Table 2, 2d. (CAS: 1449116-98-6). Yellow oil. 88% yield for manganese-catalyzed reaction; 92% yield for manganese-mediated reaction. ¹H NMR (500 MHz, CDCl₃) δ 7.64 (dd, J = 8.1, 1.7 Hz, 1H), 7.53 (d, J = 1.6 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 3.71 – 3.59 (m, 2H), 3.25 (s, 3H), 1.38 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 177.8, 147.3, 133.9, 132.4, 126.4, 118.9, 108.7, 105.9, 56.8, 48.5, 26.6, 20.2.

3-(azidomethyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one
Table 2, 2e. (CAS: 1449116-91-9). Yellow oil. 75% yield for manganese-catalyzed reaction; 80% yield for manganese-mediated reaction.\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 7.60 (dd, \( J = 8.0, 1.9 \) Hz, 1H), 7.51 (d, \( J = 1.8 \) Hz, 1H), 6.95 (d, \( J = 8.2 \) Hz, 1H), 3.71 – 3.62 (m, 2H), 3.26 (s, 3H), 1.39 (s, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \( \delta \) 178.1, 146.4 (q, \( J_{F-C} = 1.1 \) Hz), 132.0, 126.4 (q, \( J_{F-C} = 4.0 \) Hz), 125.0 (q, \( J_{F-C} = 32.5 \) Hz), 124.3 (q, \( J_{F-C} = 269.9 \) Hz), 120.1 (q, \( J_{F-C} = 3.6 \) Hz), 108.1, 56.9, 48.6, 26.5, 20.2.

![ethyl 3-(azidomethyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate](image)

Table 2, 2f. Yellow oil. 86% yield for manganese-catalyzed reaction; 88% yield for manganese-mediated reaction.\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 8.06 (dd, \( J = 8.2, 1.7 \) Hz, 1H), 7.92 (d, \( J = 1.7 \) Hz, 1H), 6.90 (d, \( J = 8.2 \) Hz, 1H), 4.35 (q, \( J = 7.1 \) Hz, 2H), 3.67 (s, 2H), 3.25 (s, 3H), 1.38 (t, \( J = 7.1 \) Hz, 3H), 1.37 (s, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \( \delta \) 178.5, 166.2, 147.5, 131.32, 131.28, 125.0, 124.2, 107.9, 61.0, 57.0, 48.6, 26.6, 20.4, 14.4. HRMS m/z (ESI) calcd. for C\textsubscript{14}H\textsubscript{17}N\textsubscript{4}O\textsubscript{3} (M+H): 289.1295, found 289.1298.

![3-(azidomethyl)-1,3-dimethyl-5-nitroindolin-2-one](image)

Table 2, 2g. (CAS: 1543011-86-4). Yellow oil. 75% yield for manganese-catalyzed reaction; 82% yield for manganese-mediated reaction.\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 8.31 (dd, \( J = 8.6, 2.3 \) Hz, 1H), 8.17 (d, \( J = 2.3 \) Hz, 1H), 6.97 (d, \( J = 8.6 \) Hz, 1H), 3.73 (s, 2H), 3.31 (s, 3H), 1.43 (s, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \( \delta \) 178.3, 166.2, 147.5, 131.32, 131.28, 125.0, 124.2, 107.9, 61.0, 57.0, 48.6, 26.8, 20.2.

![3-(azidomethyl)-5-fluoro-1,3-dimethylindolin-2-one](image)

Table 2, 2h. (CAS: 1449116-94-2). Colorless oil. 68% yield for manganese-catalyzed reaction; 92% yield for manganese-mediated reaction.\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 7.06 – 6.99 (m, 2H), 6.80 (dd, \( J = 8.3, 4.1 \) Hz, 1H), 3.63 (s, 2H), 3.22 (s, 3H), 1.37 (s, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \( \delta \) 177.7 (d, \( J_{F-C} = 1.3 \) Hz), 159.4 (d, \( J_{F-C} = 239.4 \) Hz), 139.3 (d, \( J_{F-C} = 2.0 \) Hz), 133.0 (d, \( J_{F-C} = 7.8 \) Hz), 114.8 (d, \( J_{F-C} = 23.4 \) Hz), 111.3

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(d, $J_{F-C} = 24.8$ Hz), 108.8 (d, $J_{F-C} = 8.1$ Hz), 57.0, 49.1 (d, $J_{F-C} = 1.9$ Hz), 26.46, 20.33.

3-(azidomethyl)-5-chloro-1,3-dimethylindolin-2-one

Table 2, 2i. (CAS: 1449116-95-3). Yellow oil. 77% yield for manganese-catalyzed reaction; 99% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.28 (dd, $J = 8.3$, 2.1 Hz, 1H), 7.25 (d, $J = 2.1$ Hz, 1H), 6.79 (d, $J = 8.3$ Hz, 1H), 3.66 – 3.59 (m, 2H), 3.21 (s, 3H), 1.36 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 177.6, 141.9, 133.0, 128.5, 128.1, 123.6, 109.2, 56.9, 48.8, 26.4, 20.3.

3-(azidomethyl)-5-bromo-1,3-dimethylindolin-2-one

Table 2, 2j. (CAS: 1449116-96-4). Yellow oil. 84% yield for manganese-catalyzed reaction; 87% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.43 (dt, $J = 8.3$, 1.5 Hz, 1H), 7.38 (s, 1H), 6.75 (d, $J = 8.2$ Hz, 1H), 3.62 (s, 2H), 3.20 (s, 3H), 1.35 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 177.5, 142.4, 133.4, 131.4, 126.3, 115.3, 109.7, 56.9, 48.8, 26.4, 20.3.

3-(azidomethyl)-5-iodo-1,3-dimethylindolin-2-one

Table 2, 2k. (CAS: 1449116-97-5). Yellow oil. 68% yield for manganese-catalyzed reaction; 86% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.63 (dd, $J = 8.2$, 1.7 Hz, 1H), 7.55 (d, $J = 1.7$ Hz, 1H), 6.66 (d, $J = 8.2$ Hz, 1H), 3.66 – 3.58 (m, 2H), 3.20 (s, 3H), 1.35 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 177.3, 143.1, 137.4, 133.8, 131.9, 110.3, 85.2, 56.9, 48.7, 26.4, 20.3.

3-(azidomethyl)-1,3,7-trimethylindolin-2-one
Table 2, 2l. (CAS: 1449117-01-4). Yellow oil. 68% yield for manganese-catalyzed reaction; 88% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.11 (dd, $J = 7.2$, 1.4, 0.6 Hz, 1H), 7.05 (ddd, $J = 7.7$, 1.4, 0.7 Hz, 1H), 6.98 (t, $J = 7.5$ Hz, 1H), 3.65 – 3.58 (m, 2H), 3.52 (s, 3H), 2.60 (s, 3H), 1.34 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.9, 141.2, 132.4, 132.0, 122.7, 120.8, 120.0, 57.5, 48.0, 29.7, 20.9, 19.0.

3-(azidomethyl)-7-chloro-1,3-dimethylindolin-2-one

Table 2, 2m. (CAS: 1449117-04-7). Yellow oil. 70% yield for manganese-catalyzed reaction; 87% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.24 (dd, $J = 8.2$, 1.2 Hz, 1H), 7.16 (dd, $J = 7.4$, 1.2 Hz, 1H), 7.00 (dd, $J = 8.2$, 7.3 Hz, 1H), 3.65 – 3.58 (m, 2H), 3.60 (s, 3H), 1.36 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.4, 139.4, 134.2, 131.0, 123.5, 121.5, 115.8, 57.3, 48.5, 29.7, 20.7.

3-(azidomethyl)-7-bromo-1,3-dimethylindolin-2-one

Table 2, 2n. (CAS: 1449117-05-8). Yellow oil. 56% yield for manganese-catalyzed reaction; 77% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.42 (dd, $J = 8.2$, 1.2 Hz, 1H), 7.19 (dd, $J = 7.3$, 1.2 Hz, 1H), 6.94 (dd, $J = 8.2$, 7.3 Hz, 1H), 3.68 – 3.57 (m, 2H), 3.61 (s, 3H), 1.36 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.6, 140.8, 134.5, 134.3, 123.9, 122.0, 102.7, 57.3, 48.4, 30.0, 20.7.

3-(azidomethyl)-7-methoxy-1,3-dimethylindolin-2-one

Table 2, 2o. (CAS: 1449117-02-5). White solid. 72% yield for manganese-catalyzed reaction; 91% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.04 (td, $J = 7.9$, 1.1 Hz, 1H), 6.93 – 6.85 (m, 2H), 3.86 (s, 3H), 3.64 – 3.57 (m, 2H), 3.50 (s, 3H), 1.34 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.3, 145.4, 132.9, 131.2, 123.3, 115.5, 112.4, 57.3, 55.8, 48.7, 29.6, 20.6.
ethyl 3-(azidomethyl)-1,3-dimethyl-2-oxoindoline-7-carboxylate

Table 2, 2p. Colorless oil. 32% yield for manganese-catalyzed reaction; 59% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.58 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.37 (dd, $J = 7.3, 1.4$ Hz, 1H), 7.11 (t, $J = 7.7$ Hz, 1H), 4.40 (q, $J = 7.1$ Hz, 2H), 3.64 (s, 2H), 3.30 (s, 3H), 1.41 (t, $J = 7.1$ Hz, 3H), 1.38 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 179.2, 166.8, 142.2, 133.3, 129.8, 125.6, 122.0, 116.4, 61.7, 57.3, 47.6, 30.2, 20.6, 14.3. HRMS m/z (ESI) calcd. for C$_{14}$H$_{17}$N$_4$O$_3$ (M+H)$^+$: 289.1295, found 289.1298.

3-(azidomethyl)-4,6-dimethoxy-1,3-dimethylindolin-2-one

Table 2, 2q. White solid. 59% yield for manganese-catalyzed reaction; 72% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 6.46 (q, $J = 2.3$ Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 3.63 – 3.53 (m, 2H), 3.44 (s, 3H), 1.32 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.0, 156.8, 146.1, 133.6, 124.7, 100.7, 99.7, 57.3, 55.9, 49.3, 29.6, 20.7. HRMS m/z (ESI) calcd. for C$_{13}$H$_{17}$N$_4$O$_3$ (M+H)$^+$: 277.1295, found 277.1299.

3-(azidomethyl)-4,6-dichloro-1,3-dimethylindolin-2-one

Table 2, 2r. (CAS: 1613294-66-8). White solid. 80% yield for manganese-catalyzed reaction; 87% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 6.46 (q, $J = 2.3$ Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 3.63 – 3.53 (m, 2H), 3.44 (s, 3H), 1.32 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 177.9, 138.1, 135.4, 130.3, 128.2, 122.2, 116.1, 57.0, 48.7, 29.7, 20.6.
Table 2. 2s. 82% yield (1.8/1) for manganese-catalyzed reaction; 93% yield (1.7/1) for manganese-mediated reaction.

3-(azidomethyl)-6-methoxy-1,3-dimethylindolin-2-one

CAS: 1502874-49-8. White solid. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.27 (m, 1H), 6.67 – 6.62 (m, 1H), 6.55 (dd, $J = 7.8, 0.7$ Hz, 1H), 3.97 (d, $J = 11.8$ Hz, 1H), 3.87 (d, $J = 1.1$ Hz, 3H), 3.63 (d, $J = 11.7$ Hz, 1H), 3.21 (s, 3H), 1.39 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.8, 156.1, 144.9, 123.0, 116.2, 105.8, 101.7, 54.9, 49.3, 26.5, 18.8.

Table 2. 2t. Yellow oil. 74% yield (2.2/1) for manganese-catalyzed reaction; 87% yield (2.1/1) for manganese-mediated reaction.
3-(azidomethyl)-6-chloro-1,3-dimethylindolin-2-one
CAS: 1613294-63-5. \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.30 – 7.26 (m, 1H), 7.06 – 7.01 (m, 1H), 6.79 (d, \(J = 7.8\) Hz, 1H), 4.17 (d, \(J = 12.0\) Hz, 1H), 3.73 (d, \(J = 11.9\) Hz, 1H), 3.24 (s, 3H), 1.47 (s, 3H). \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 177.8, 145.5, 130.7, 130.0, 127.1, 123.7, 106.9, 54.2, 50.5, 26.6, 18.2.

3-(azidomethyl)-4-chloro-1,3-dimethylindolin-2-one
CAS: 1613294-60-2. \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.19 (d, \(J = 7.8\) Hz, 1H), 7.08 (dd, \(J = 7.8, 1.8\) Hz, 1H), 6.88 (d, \(J = 1.9\) Hz, 1H), 3.62 (s, 2H), 3.22 (s, 3H), 1.36 (s, 3H). \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 178.1, 144.6, 134.5, 129.7, 123.9, 122.6, 109.1, 57.1, 48.5, 26.4, 20.4.

3-(azidomethyl)-1,3-dimethyl-1,3-dihydro-2H-benzo[g]indol-2-one
Table 2, 2u. (CAS: 1449117-10-5). White solid. 48% yield for manganese-catalyzed reaction; 71% yield for manganese-mediated reaction. \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.79 (dd, 1H), 7.61 – 7.53 (m, 2H), 7.50 – 7.42 (m, 2H), 7.00 (dd, 1H), 4.20 (d, \(J = 11.9\) Hz, 1H), 3.69 (d, \(J = 11.8\) Hz, 1H), 3.57 (s, 3H), 1.66 (s, 3H). \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 171.3, 136.4, 135.2, 133.4, 126.9, 126.9, 126.5, 122.9, 122.8, 119.7, 108.9, 62.0, 48.2, 29.9, 27.6.

3-(azidomethyl)-3-methyl-1-phenylindolin-2-one
Table 2, 2v. (CAS: 1502874-62-5). White solid. 96% yield for manganese-catalyzed reaction; 98% yield for manganese-mediated reaction. \(^1H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.58 – 7.52 (m, 2H), 7.47 – 7.41 (m, 3H), 7.36 (dd, \(J = 7.5, 1.3\) Hz, 1H), 7.27 (td, \(J = 7.8, 1.3\) Hz, 1H), 7.15 (td, \(J = 7.5, 1.0\) Hz, 1H), 6.88 (dt, \(J = 7.9, 0.7\) Hz, 1H), 3.82 – 3.69 (m, 2H), 1.51 (s, 3H). \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 177.6, 143.4, 134.2, 131.1, 129.5, 128.5, 128.1, 126.5, 123.18, 123.13, 109.6, 57.6, 48.9, 20.6.

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3-(azidomethyl)-1-benzyl-3-methylindolin-2-one

Table 2, 2w. (CAS: 1449116-90-8). Yellow oil. 85% yield for manganese-catalyzed reaction; 85% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.25 – 7.15 (m, 6H), 7.11 (td, $J = 7.5$, 1.1 Hz, 1H), 6.98 (t, $J = 7.5$ Hz, 1H), 6.66 (d, $J = 7.8$ Hz, 1H), 4.94 (d, $J = 15.7$ Hz, 1H), 4.78 (d, $J = 15.7$ Hz, 1H), 3.68 – 3.58 (m, 2H), 1.35 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.3, 142.5, 135.5, 131.2, 128.7, 128.5, 127.5, 127.0, 122.9, 122.7, 109.3, 57.3, 48.7, 43.7, 20.6.

3-(azidomethyl)-1-methyl-3-phenylindolin-2-one

Table 2, 2x. (CAS: 1449117-13-8). White solid. 68% yield for manganese-catalyzed reaction; 93% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.48 – 7.39 (m, 4H), 7.37 – 7.28 (m, 3H), 7.20 (td, $J = 7.6$, 1.1 Hz, 1H), 7.00 – 6.93 (m, 1H), 4.10 (s, 2H), 3.25 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 178.3, 142.5, 135.5, 131.2, 128.7, 128.5, 127.5, 127.0, 122.9, 122.7, 109.3, 57.3, 48.7, 43.7, 20.6.

(3-(azidomethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate

Table 2, 2y. (CAS: 1449117-17-2). White solid. 66% yield for manganese-catalyzed reaction; 93% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.38 – 7.31 (m, 2H), 7.09 (td, $J = 7.6$, 1.0 Hz, 1H), 6.89 (dt, $J = 7.8$, 0.8 Hz, 1H), 4.51 (d, $J = 11.1$ Hz, 1H), 4.17 (d, $J = 11.0$ Hz, 1H), 3.81 (d, $J = 12.1$ Hz, 1H), 3.68 (d, $J = 12.1$ Hz, 1H), 3.23 (s, 3H), 1.94 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 174.9, 170.1, 144.0, 129.3, 127.1, 124.9, 122.8, 108.4, 64.6, 53.6, 52.3, 26.4, 20.5.

1-(azidomethyl)-1-methyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one

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Table 2, 2z. (CAS: 1449116-89-5). Colorless oil. 69% yield for manganese-catalyzed reaction; 90% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.13 – 7.09 (m, 1H), 7.09 – 7.05 (m, 1H), 6.99 (t, $J = 7.5$ Hz, 1H), 3.78 – 3.69 (m, 2H), 3.63 (s, 2H), 2.85 – 2.75 (m, 2H), 2.07 – 1.97 (m, 2H), 1.38 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 176.9, 139.1, 129.9, 127.4, 122.2, 120.8, 120.4, 57.1, 50.0, 38.9, 24.5, 21.1, 20.2.

![Structure of 2,3-diazido-2-methyl-N-phenylpropanamide](image)

2,3-diazido-2-methyl-N-phenylpropanamide

3. White solid. 67% yield for manganese-catalyzed reaction; 61% yield for manganese-mediated reaction. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.36 (s, 1H), 7.55 (d, $J = 8.4$ Hz, 2H), 7.41 – 7.29 (m, 2H), 7.22 – 7.11 (m, 1H), 3.81 (d, $J = 12.7$ Hz, 1H), 3.64 (d, $J = 12.8$ Hz, 1H), 1.66 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 167.5, 136.7, 129.0, 125.0, 120.0, 67.1, 57.6, 20.1. HRMS m/z (ESI) calcd. for C$_{14}$H$_7$N$_4$O$_3$ (M+H)$^+$: 246.1103, found 246.1099.

![Structure of (1,2-diazidoethyl)benzene](image)

(1,2-diazidoethyl)benzene

4. CAS: 22710-73-2. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38 (ddd, 5H), 4.68 (dd, $J = 8.4$, 4.8 Hz, 1H), 3.48 (dd, $J = 21.6$, 12.8 Hz, 1H), 3.51 (dd, $J = 12.8$, 8.4 Hz, 1H), 3.44 (dd, $J = 12.8$, 4.9 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 136.2, 129.0, 128.9, 126.9, 65.4, 55.8.

![Structure of 3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one](image)

3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one

5. CAS: 1627605-52-0. Colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.35 (td, $J = 7.7$, 1.3 Hz, 1H), 7.22 (dd, $J = 7.4$, 1.4 Hz, 1H), 7.13 (td, $J = 7.6$, 1.0 Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 5.41 (dd, $J = 9.2$, 4.1 Hz, 1H), 3.23 (s, 3H), 3.06 (dd, $J = 14.8$, 9.3 Hz, 1H), 2.73 (dd, $J = 14.8$, 4.1 Hz, 1H), 1.42 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 178.9, 143.3, 131.0, 128.6, 122.6, 122.6, 108.6, 69.6, 50.1, 47.1, 26.4, 25.4.
$2t, \text{ d.r.} = 2.2/1$
$2y$