# **Supplementary Information**

# Fenton Chemistry Enables Catalytic Oxidative Rearrangement of Indoles using Hydrogen Peroxide

Guodong Zhao<sup>a,b</sup>, Lixin Liang<sup>b</sup>, Eryu Wang<sup>b</sup>, Shaoyan Lou<sup>a</sup>, Rui Qi<sup>a</sup> and Rongbiao Tong<sup>\*b,c,d</sup>,

<sup>a</sup>School of Chinese Pharmacy, Beijing University of Chinese Medicine, Beijing 102488, China
<sup>b</sup>Department of Chemistry and <sup>c</sup>Hong Kong Branch of the Guangdong Southern Marine Science and Engineering Laboratory (Guangzhou), The Hong Kong University of Science and Technology, Clearwater Bay, Kowloon, Hong Kong, China. E-mail: <a href="https://www.rtong@ust.hk">rtong@ust.hk</a>; Fax: +(852) 23581594; Tel: +(852) 23587357

<sup>d</sup>HKUST Shenzhen Research Institute, Shenzhen 518057, China

# **Table of Contents**

| 1.  | General Information   | S-2  |
|-----|---|------|
| 2.  | Screening of metal catalysts for the oxidation of $1a$ with $H_2O_2$ as the oxidant   | S-3  |
| 3.  | Optimization of the iron and cerium catalysis system  | S-4  |
| 4.  | Preparation of indole substrates  | S-5  |
| 5.  | Oxidation of indoles to 2-oxindoles with H <sub>2</sub> O <sub>2</sub> /FeBr <sub>2</sub> or H <sub>2</sub> O <sub>2</sub> /CeBr <sub>3</sub> | S-12 |
| 6.  | Gram-scale oxidation of indole <b>1ab</b> using $H_2O_2/FeBr_2$ or $H_2O_2/CeBr_3$ at RT  | S-26 |
|     | under open-air condition  |      |
| 7.  | Green chemistry metrics analysis  | S-27 |
| 8.  | Controlled experiments for indole oxidation   | S-28 |
| 9.  | Radical trapping (ABTS) experiments for indole oxidation  | S-28 |
| 10. | EPR spectrum for MBr <sub>x</sub> -H <sub>2</sub> O <sub>2</sub> with the presence of DMPO  | S-29 |
| 11. | RBS trapping and isotopic experiments   | S-29 |
| 12. | References  | S-32 |
| 13. | Copies of <sup>1</sup> H- and <sup>13</sup> C-NMR spectra   | S-33 |

### **1. General Information**

Reactions were carried out in a round-bottom flask with vigorous stirring at room temperature with open-air condition, unless otherwise noted. Tetrahydrofuran (THF), *tert*-Butanol (*t*-BuOH), acetonitrile (MeCN), dichloromethane (DCM) and *N*,*N*-Dimethylformamide (DMF) were used as received without further purification unless otherwise noted. FeBr<sub>2</sub> and CeBr<sub>3</sub> were purchased from Sigma-Aldrich and dried under vacuum before use. 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) and H<sub>2</sub><sup>18</sup>O were purchased from Sigma-Aldrich. Solvents were used as received from commercial suppliers without prior purification for workup, extraction and column chromatography. Reactions were monitored by thin-layer chromatography (TLC, 0.25 mm) on pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040–0.062 mm). <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a 400 MHz spectrometer (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C). Chemical shifts are reported in parts per million (ppm) as values relative to the internal chloroform (7.26 ppm for <sup>1</sup>H and 77.16 ppm for <sup>13</sup>C). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. HRMS spectrometry was detected by CI/ESI-TOF. Infrared spectrometry was recorded on ALPHA FTIR (Bruker). Electron paramagnetic resonance (EPR) spectrum was recorded on Bruker ESP300E.

# 2 Screening of metal catalysts for the oxidation of 1a with H<sub>2</sub>O<sub>2</sub> as the oxidant.



**General Procedure A:** To a stirred solution of the compound  $1a^1$  (27.2 mg, 0.1 mmol) in THF/H<sub>2</sub>O (10/1, 0.6 mL) were added KBr (1.2 mg, 0.01 mmol), metal catalyst (0.01 mmol) and H<sub>2</sub>O<sub>2</sub> (30%, 30 µL, 0.30 mmol). After completion of the addition, the reaction mixture was allowed to stir at RT for 3 h. The reaction was quenched by dilute aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.1 M, 5 mL) and ethyl acetate (10 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2×10 mL). The combined organic fractions were washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Yield was determined by <sup>1</sup>H NMR of the crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal reference.

| entry | Cat. (0.1 eq)                      | Yield (%) | entry | Cat. (0.1 eq)      | Yield (%) |
|-------|------------------------------------|-----------|-------|--------------------|-----------|
| 1     | ScCl <sub>3</sub>                  | 28        | 21    | SnCl <sub>2</sub>  | 12        |
| 2     | TiO <sub>2</sub>                   | trace     | 22    | SbCl <sub>3</sub>  | 27        |
| 3     | NH <sub>4</sub> VO <sub>3</sub>    | 15        | 23    | TaCl <sub>5</sub>  | 62        |
| 4     | CrO <sub>3</sub>                   | trace     | 24    | WCl <sub>6</sub>   | 44        |
| 5     | MnBr <sub>2</sub>                  | trace     | 25    | KReO <sub>4</sub>  | trace     |
| 6     | FeCl <sub>3</sub>                  | 47        | 26    | $K_2OsO_4$         | trace     |
| 7     | CoCl <sub>2</sub>                  | trace     | 27    | $(NH_4)_2[IrCl_6]$ | trace     |
| 8     | NiCl <sub>2</sub>                  | trace     | 28    | PtCl <sub>4</sub>  | 8         |
| 9     | $CuCl_2$                           | 7         | 29    | HgSO <sub>4</sub>  | trace     |
| 10    | $ZnBr_2$                           | trace     | 30    | PbCl <sub>2</sub>  | trace     |
| 11    | GaCl <sub>3</sub>                  | 6         | 31    | BiCl <sub>3</sub>  | trace     |
| 12    | YCl <sub>3</sub>                   | trace     | 32    | LaCl <sub>3</sub>  | trace     |
| 13    | $ZrCl_4$                           | 35        | 33    | CeCl <sub>3</sub>  | 52        |
| 14    | NbCl <sub>5</sub>                  | 64        | 34    | PrCl <sub>3</sub>  | trace     |
| 15    | MoCl <sub>5</sub>                  | 49        | 35    | NdCl <sub>3</sub>  | trace     |
| 16    | RuCl <sub>3</sub>                  | 6         | 36    | SmCl <sub>3</sub>  | trace     |
| 17    | Pd(PPh <sub>3</sub> ) <sub>4</sub> | trace     | 37    | GdCl <sub>3</sub>  | trace     |
| 18    | AgOAc                              | trace     | 38    | TbCl <sub>3</sub>  | trace     |
| 19    | CdCl <sub>2</sub>                  | trace     | 39    | DyCl <sub>3</sub>  | trace     |
| 20    | InCl <sub>3</sub>                  | trace     | 40    | YbCl <sub>3</sub>  | trace     |

### 3. Optimization of the iron and cerium catalysis system.



**General Procedure:** To a stirred solution of compound **1a** (27.2 mg, 0.1 mmol) in Solvent/H<sub>2</sub>O (10/1, 0.6 mL) were added KBr (with or without, 1.2 mg, 0.01 mmol), [Fe] or [Ce] (0.01 mmol) and H<sub>2</sub>O<sub>2</sub> (30 wt%, 30  $\mu$ L, 0.30 mmol). After completion of the addition, the reaction mixture was allowed to stir at RT for 3 h. The reaction was quenched by dilute aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (0.1 M, 5 mL) and ethyl acetate (10 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2×10 mL). The combined organic fractions were washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Yield was determined by <sup>1</sup>H-NMR of the crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal reference.

| entry           | MXn (0.1 eq) + KBr (0.1 eq)             | Solvent                         | <b>Yield</b> <sup><i>c</i></sup> (%) |
|-----------------|---|---------------------------------|--------------------------------------|
| 1               | Fe phthalocyanine + KBr                 | THF/H <sub>2</sub> O            | <5                                   |
| 2               | Hemin Chloride + K <b>Br</b>            | THF/H <sub>2</sub> O            | <5                                   |
| 3               | $Cp_2Fe$ + $KBr$                        | THF/H <sub>2</sub> O            | <5                                   |
| 4               | $Fe(acac)_3 + KBr$                      | THF/H <sub>2</sub> O            | <5                                   |
| $5^a$           | $Fe_2(CO)_9 + KBr$                      | THF/H <sub>2</sub> O            | <5                                   |
| 6               | $Fe(NO_3)_3 + KBr$                      | THF/H <sub>2</sub> O            | 66                                   |
| 7               | FeSO <sub>4</sub> + KBr                 | THF/H <sub>2</sub> O            | 28                                   |
| 8               | <b>Fe</b> Cl <sub>3</sub> + K <b>Br</b> | THF/H <sub>2</sub> O            | 47                                   |
| 9               | $\mathbf{FeCl}_2 + \mathbf{KBr}$        | THF/H <sub>2</sub> O            | 59                                   |
| $10^{b}$        | FeBr <sub>3</sub>                       | THF/H <sub>2</sub> O            | 68                                   |
| 11 <sup>b</sup> | FeBr <sub>2</sub>                       | THF/H <sub>2</sub> O            | 73                                   |
| 12              | $Ce(acac)_3 + KBr$                      | THF/H <sub>2</sub> O            | <5                                   |
| 13              | $Ce(NO_3)_3 + KBr$                      | THF/H <sub>2</sub> O            | 56                                   |
| 14              | Ce(OTf) <sub>3</sub> + KBr              | THF/H <sub>2</sub> O            | 62                                   |
| 15              | $CeCl_3 + KBr$                          | THF/H <sub>2</sub> O            | 52                                   |
| 16 <sup>b</sup> | CeBr <sub>3</sub>                       | THF/H <sub>2</sub> O            | 90                                   |
| 17              | CeBr <sub>3</sub>                       | MeCN/H <sub>2</sub> O           | 93                                   |
| 18              | CeBr <sub>3</sub>                       | <i>t</i> -BuOH/H <sub>2</sub> O | 85                                   |

<sup>*a*</sup>0.005 mmol metal catalyst was added. <sup>*b*</sup>Reaction time was 0.5 h. <sup>*c*</sup>Yield was determined by <sup>1</sup>H NMR of the crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal reference.

### 4. Preparation of indole substrates.

Substrates  $1a^1$ ,  $1b^2$ ,  $1c^2$ ,  $1d^3$ ,  $1e-f^4$ ,  $1h^5$ ,  $1k^4$ ,  $1n^4$ ,  $1o^4$ ,  $1p^4$ ,  $1q^6$ ,  $1ac^7$ ,  $1ad^8$ ,  $1ae^9$ ,  $1ag^{10}$ ,  $1ah^{11}$ ,  $1aj^{12}$  and  $1am-an^{13}$  were prepared according to the published procedures.



**4.1. Preparation of 1i, 1j, 1l and 1m:** To a stirred solution of the compound **S1**<sup>4</sup> (691 mg, 3 mmol), **S2**<sup>4</sup> (559 mg, 3 mmol), **S3**<sup>4</sup> (829 mg, 3 mmol) or **S4**<sup>4</sup> (718 mg, 3 mmol) in DCM (15 mL) was added Et<sub>3</sub>N (836  $\mu$ L, 6 mmol) at 0 °C. Then 2-thiophenecarbonyl chloride (385  $\mu$ L, 3.6 mmol) or Boc<sub>2</sub>O (827  $\mu$ L, 3.6 mmol) was added, and the resulting mixture was stirred for 3 h at RT. The mixture was quenched by H<sub>2</sub>O (100 mL), and extracted with DCM (4 × 50 mL). The combined organic fractions were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give compound **1i, 1j, 1l** and **1m**, respectively.

# (S)-Methyl 2-(Thiophene-2-carbonyl)-1,2,3,4-tetrahydro-9H-pyrido[3,4-b]indole-3-carboxylate (1i)



**1i** (797 mg, 78%) was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a white solid. M.P. 114–116 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.68 (d, *J* = 90.8 Hz, 1H), 7.82–7.23 (m, 4H), 7.23–7.03 (m, 3H), 6.23–4.45 (m, 3H), 3.65 (s, 3H), 3.56 (d, *J* = 15.6 Hz, 1H), 3.31–3.14 (m, 1H). <sup>13</sup>C-NMR (100 MHz, DMSO-d6)  $\delta$ : 170.9, 164.8, 164.1, 136.8, 136.3, 130.5,

130.0, 129.4, 127.4, 126.2, 121.2, 118.7, 117.7, 111.2, 104.6, 57.2, 52.6, 51.9, 44.1, 23.2, 22.5. IR 3389.2, 3290.8, 2952.5, 2911.6, 2853.6, 1735.2, 1606.0, 1520.0, 1429.6, 1318.0, 1270.8, 1229.3, 1196.1, 1109.8, 1019.5, 997.5, 886.0, 851.1, 813.5, 734.1, 648.5 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for  $C_{18}H_{17}N_2O_3S$  [M+H]<sup>+</sup> 341.0954; found 341.0948.

### tert-Butyl 1-Methyl-1,2,3,4-tetrahydro-9H-pyrido[3,4-b]indole-2-carboxylate (1j)



**1j** (644 mg, 75%) was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.22 (d, J = 247.1 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.36–7.29 (m, 1H), 7.21–7.06 (m, 2H), 5.33 (d, J = 84.8 Hz, 1H), 4.41 (d, J = 63.3 Hz, 1H), 3.18 (brs, 1H), 2.92–2.62 (m, 2H), 1.54 (brs, 9H), 1.48 (d, J = 6.7 Hz, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 154.8, 136.2, 135.7, 135.1,

127.0, 121.8, 119.5, 118.2, 111.0, 108.9, 108.0, 80.1, 47.4, 46.9, 38.6, 37.4, 28.7, 21.7, 19.7. IR 3317.6, 2958.5,

2921.2, 2860.7, 1670.0, 1459.6, 1415.3, 1369.0, 1317.9, 1264.7, 1165.9, 1108.3, 1057.5, 1012.8, 922.3, 860.0, 746.1 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> [M]<sup>+</sup> 286.1676; found 286.1685.

#### tert-Butyl 1-Phenethyl-1,2,3,4-tetrahydro-9H-pyrido[3,4-b]indole-2-carboxylate (11)



11 (745 mg, 66%) was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a white solid. M.P. 158–160 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.22 (d, *J* = 268.6 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.38–7.04 (m, 8H), 5.37 (d, *J* = 65.1 Hz, 1H), 4.70–4.21 (m, 1H), 3.30–3.10 (m, 1H), 2.99–2.62 (m, 4H), 2.13 (brs, 2H), 1.58 (brs, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 155.6, 155.1,

141.8, 136.2, 134.8, 134.1, 128.7, 128.4, 127.0, 126.2, 125.9, 121.9, 121.7, 119.6, 119.4, 118.3, 118.1, 111.1, 109.1, 108.1, 80.2, 51.7, 51.0, 38.9, 37.8, 36.9, 36.5, 32.9, 32.6, 28.6, 21.6, 21.3. IR 3318.7, 2957.1, 2921.8, 2857.5, 1667.9, 1461.1, 1414.3, 1367.4, 1318.6, 1263.6, 1164.2, 1107.1, 1036.1, 1005.7, 963.7, 901.7, 865.7, 745.7, 700.0 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>24</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 377.2224; found 377.2219.

#### tert-Butyl 1-(3-cyanopropyl)-1,2,3,4-tetrahydro-9H-pyrido[3,4-b]indole-2-carboxylate (1m)



**1m** (631 mg, 62%) was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.43 (d, J = 215.7 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.32 (d, J = 7.9 Hz, 1H), 7.14 (dt, J = 23.3, 7.2 Hz, 2H), 5.47–5.07 (m, 1H), 4.64–4.19 (m, 1H), 3.15 (brs, 1H), 2.86 (ddd, J = 16.8, 11.7, 5.4 Hz, 1H), 2.71 (dd, J = 15.4, 4.0 Hz, 1H), 2.35 (brs,

2H), 2.14–1.62 (m, 4H), 1.54 (brs, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 155.7, 136.2, 134.0, 126.8, 122.0, 119.7, 119.6, 118.1, 111.1, 108.5, 80.5, 50.0, 38.9, 33.2, 28.6, 22.0, 21.5, 16.8. IR 3322.4, 2956.9, 2922.6, 2861.5, 2245.7, 1672.0, 1461.2, 1414.9, 1368.2, 1264.9, 1164.1, 1108.0, 1010.3, 908.6, 854.3, 751.2 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>20</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub> [M]<sup>+</sup> 339.1941; found 339.1948.



**4.2. Preparation of 1r and 1t:** To a stirred solution of the compound  $S5^{14}$  (1.05 g, 6 mmol) in anhydrous THF (20 mL) was added NaH (60%, 576 mg, 14.4 mmol) at 0 °C under N<sub>2</sub>. After completion of the addition, the reaction mixture was allowed to stir for 0.5 h. Then MeI (1.25 mL, 20 mmol) or allyl bromide (2.34 mL, 27 mmol) was added, and the above residue was stirred at RT for 3 h. The mixture was quenched by saturated NH<sub>4</sub>Cl solution (100 mL) and ethyl acetate (100 mL) at 0 °C. The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (4 × 50 mL). The combined organic fractions were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give compound **1r** or **1t**.

#### **1,3-Dimethyl-2-methoxymethyl-1***H***-indole (1r)**



**1r** (908 mg, 80%) was purified as a light yellow oil by flash column chromatography (ethyl acetate/hexane = 1:5 to 1:1). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.69 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.41–7.32 (m, 2H), 7.23 (ddd, *J* = 7.9, 6.5, 1.5 Hz, 1H), 4.71 (s, 2H), 3.83 (s, 3H), 3.43 (s, 3H), 2.48 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 137.2, 131.5, 127.8, 122.1, 119.1, 118.7, 110.5, 108.9, 63.5, 57.1, 29.7, 8.8. IR 2979.6, 2818.4, 1469.9,

1410.5, 1372.9, 1357.3, 1338.4, 1266.3, 1189.8, 1151.0, 1123.7, 1082.5, 1010.2, 946.9, 900.5, 863.4, 733.6 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for  $C_{12}H_{16}NO$  [M+H]<sup>+</sup> 190.1226; found 190.1223.

### 1,3-Dimethyl-2-(allyloxymethyl)-1*H*-indole (1t)



**1t** (1.06 g, 82%) was purified as a light yellow oil by flash column chromatography (ethyl acetate/hexane = 1:5 to 1:1). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.65 (d, *J* = 7.8 Hz, 1H), 7.38–7.28 (m, 2H), 7.19 (ddd, *J* = 7.9, 6.7, 1.3 Hz, 1H), 6.01 (ddt, *J* = 17.3, 10.4, 5.6 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.29 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.75 (s, 2H), 4.05 (dt, *J* = 5.6, 1.5 Hz, 2H), 3.82 (s, 3H), 2.42 (s, 3H). <sup>13</sup>C-NMR

 $(100 \text{ MHz}, \text{CDCl}_3) \delta$ : 137.3, 134.81, 134.78, 131.68, 127.8, 122.1, 119.1, 118.8, 117.3, 110.4, 108.9, 70.1, 61.2, 29.9, 8.9. IR 3050.7, 2922.9, 2858.1, 1470.5, 1411.7, 1367.8, 1337.2, 1264.4, 1193.2, 1123.2, 1061.7, 1001.4, 925.9, 863.9, 736.6 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>14</sub>H<sub>17</sub>NO [M]<sup>+</sup> 215.1310; found 215.1303.

**4.3. Preparation of 1s:** To a stirred solution of the compound  $S5^{14}$  (1.05 g, 6 mmol) in MeCN (30 mL) were added Et<sub>3</sub>N (1.67 mL, 12 mmol) and TBSCl (995 mg, 6.6 mmol). After completion of the addition, the reaction mixture was allowed to stir for 2 h. Then the mixture was quenched by saturated aqueous NaHCO<sub>3</sub> solution (50 mL) and ethyl acetate (50 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2 × 50 mL). The combined organic fractions were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give compound **1s**.

### 1,3-Dimethyl-2-(((tert-butyldimethylsilyl)oxy)methyl)-1H-indole (1s)



**1s** (1.53 g, 88%) was purified as a light yellow oil by flash column chromatography (ethyl acetate/hexane = 1:20 to 1:5). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.62 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.35 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.29 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.17 (ddd, *J* = 7.9, 6.8, 1.2 Hz, 1H), 4.91 (s, 2H), 3.84 (s, 3H), 2.40 (s, 3H), 0.98 (s, 9H), 0.13 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 137.2, 134.6, 128.0, 121.8, 119.1, 118.7,

108.8, 107.9, 55.3, 30.0, 26.0, 18.4, 8.9, -5.1. IR 2929.3, 2857.5, 1468.4, 1409.3, 1396.5, 1358.4, 1253.0, 1193.4, 1050.8, 947.0, 835.7, 773.6, 735.0, 671.9 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for  $C_{17}H_{28}NOSi [M+H]^+$  290.1935; found 290.1929.



**4.4. Preparation of 1u**. Compound **1u** (1.08 g, 77%) was prepared from **S6**<sup>15</sup> (1.15 g, 6 mmol) and MeI (1.49 mL, 24 mmol) in the presence of NaH (60 wt%, 960 mg, 24 mmol) and DMF (20 mL) and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:2) as a light yellow oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.68 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.38–7.24 (m, 2H), 7.18 (ddd, *J* = 7.9, 6.9, 1.2 Hz, 1H), 4.69 (s, 2H), 3.80 (s, 3H), 3.64 (t, *J* = 7.5 Hz, 2H), 3.42 (d, *J* = 7.6 Hz, 6H), 3.16 (t, *J* = 7.5 Hz, 2H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 137.3, 132.6, 127.1, 122.1, 119.01, 118.96, 111.4, 109.1, 73.5, 63.6, 58.7, 57.4, 29.8, 25.1. IR 3049.5, 2976.7, 2926.0, 2872.8, 2818.1, 1468.6, 1411.9, 1371.2, 1339.5, 1266.4, 1221.5, 1186.6, 1081.9, 1012.2, 949.6, 899.6, 817.8, 736.4 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>14</sub>H<sub>20</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 234.1489; found 234.1474.

**4.5. Preparation of 1v.** Compound **1v** (1.16 g, 70%) was prepared from **S6**<sup>15</sup> (1.15 g, 6 mmol) and Ac<sub>2</sub>O (1.70 mL, 18 mmol) in the presence of Et<sub>3</sub>N (3.35 mL, 24 mmol) and acetonitrile (30 mL) and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.68 (brs, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.23 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.14 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 5.27 (s, 2H), 4.29 (t, *J* = 7.1 Hz, 2H), 3.16 (t, *J* = 7.1 Hz, 2H), 2.09 (d, *J* = 14.3 Hz, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 172.2, 171.2, 135.8, 130.2, 127.4, 123.0, 119.7, 119.1, 111.6, 111.2, 64.7, 57.4, 23.6, 21.1, 21.0. IR 3392.2, 2957.1, 1731.1, 1452.5, 1372.5, 1235.8, 1031.7, 961.1, 753.1, 601.9 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>15</sub>H<sub>18</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 276.1230; found 276.1225.



**4.6. Preparation of 1w, 1x, and 1y:** To a stirred solution of the compound  $\mathbf{S7}^{14}$  (1.04 g, 6 mmol) in MeOH (20 mL) was added allylamine (674 µL, 9 mmol) or MeNH<sub>2</sub> (40% aqueous solution, 775 µL, 9 mmol) at RT. After completion of the addition, the reaction mixture was allowed to stir for 10 h. Then NaBH<sub>4</sub> (454 mg, 12 mmol) was added at 0 °C, and the above reaction mixture was stirred for 0.5 h. The reaction was quenched by saturated aqueous NH<sub>4</sub>Cl solution (100 mL), and the reaction mixture was extracted with ethyl acetate (4 × 50 mL). The combined organic fractions were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. To a stirred solution of the above residue **S8** or **S9** in DCM (30 mL) was added Et<sub>3</sub>N (1.67 mL, 12 mmol) at RT. Then Ac<sub>2</sub>O (681 µL, 7.2 mmol), tosyl chloride (TsCl, 1.37 g, 7.2 mmol) or 2-Furoyl chloride (711 µL, 7.2 mmol) was added at 0 °C, and the above reaction mixture

was quenched by saturated aqueous NaHCO<sub>3</sub> solution (100 mL) and DCM (50 mL). The organic fractions were collected, and the aqueous phase was extracted with DCM ( $4 \times 50$  mL). The combined organic fractions were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give compound **1w**, **1x** or **1y**.

# *N*-Allyl-*N*-((1,3-dimethyl-1*H*-indol-2-yl)methyl)-acetamide (1w)



**1w** (1.14 g, 74% for 2 steps) was purified as a light yellow oil. by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.57 (d, *J* = 7.8 Hz, 1H), 7.32–7.23 (m, 2H), 7.14 (ddd, *J* = 7.9, 6.6, 1.4 Hz, 1H), 5.75–5.60 (m, 1H), 5.30–5.10 (m, 2H), 4.89 (s, 2H), 3.72 (dt, *J* = 4.8, 1.9 Hz, 2H), 3.67 (s, 3H), 2.33 (s, 3H), 2.17 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 170.9, 137.2,

132.3, 130.8, 127.8, 122.1, 118.9, 118.7, 116.5, 111.0, 109.0, 48.0, 36.8, 30.0, 21.6, 8.9. IR 3051.0, 2972.4, 2924.5, 2864.6, 1639.3, 1468.0, 1415.9, 1369.6, 1332.8, 1264.7, 1233.9, 1189.7, 1140.5, 1047.5, 1008.9, 980.7, 928.0, 860.6, 799.7, 734.1, 631.3 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for  $C_{16}H_{21}N_2O$  [M+H]<sup>+</sup> 257.1648; found 257.1647.

# *N*-((1,3-Dimethyl-1*H*-indol-2-yl)methyl)-*N*,4-dimethylbenzenesulfonamide (1x)



**1x** (1.44 g, 70% for 2 steps) was purified as a white solid by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:2). M.P. 150–152 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.84–7.75 (m, 2H), 7.55 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.35 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.32–7.25 (m, 1H), 7.14 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 4.28 (s, 2H), 3.89 (s, 3H), 2.51 (d, *J* = 1.3 Hz, 6H), 2.21 (s, 3H). <sup>13</sup>C-NMR (100

MHz, CDCl<sub>3</sub>) δ: 143.9, 137.4, 132.8, 130.0, 128.0, 127.8, 127.5, 122.3, 118.93, 118.85, 111.0, 109.1, 43.9, 33.6, 30.0, 21.7, 8.8. IR 2953.4, 2919.0, 2860.4, 1463.5, 1340.5, 1267.7, 1195.5, 1161.3, 1090.5, 1027.6, 963.3, 914.2, 810.7, 753.5, 664.2 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>S [M]<sup>+</sup> 342.1397; found 342.1395.

#### N-Methyl-N-((1,3-dimethyl-1H-indol-2-yl)methyl)-furan-2-carboxamide (1y)



**1y** (1.10 g, 65% for 2 steps) was purified as a light yellow oil. by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:2) <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.61 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 1.7 Hz, 1H), 7.35–7.23 (m, 2H), 7.16 (ddd, *J* = 7.9, 6.4, 1.4 Hz, 1H), 7.09 (d, *J* = 3.4 Hz, 1H), 6.53 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.01 (brs, 2H), 3.68 (brs, 3H), 3.06 (brs, 3H), 2.42 (brs, 3H). <sup>13</sup>C-NMR (100

MHz, CDCl<sub>3</sub>)  $\delta$ : 160.1, 147.8, 144.2, 137.2, 130.1, 127.8, 122.1, 118.9, 118.8, 116.7, 111.3, 110.9, 109.0, 40.5, 34.3, 29.9, 8.9. IR 2919.4, 2861.9, 1619.5, 1571.1, 1478.7, 1395.4, 1331.3, 1274.8, 1239.1, 1186.9, 1152.1, 1067.8, 1015.3, 954.0, 925.8, 884.4, 848.8, 738.8, 675.0 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 283.1441; found 283.1436.



4.7. Preparation of 1z and 1aa: To a stirred solution of the compound S10<sup>15</sup> (1.22 g, 6 mmol) in N,Ndimethylformamide (DMF, 20 mL) were added imidazole (817 mg, 12 mmol) and triisopropylsilyl chloride (TIPSCl, 1.93 mL, 9 mmol) at RT. After completion of the addition, the reaction mixture was allowed to stir for 2 h. The mixture was quenched by H<sub>2</sub>O (100 mL), and the mixture was extracted with ethyl acetate ( $4 \times 50$ mL). The combined organic fractions were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. To a stirred solution of the unstable aldehyde S11 in MeOH (30 mL) was added MeNH<sub>2</sub> (40% aqueous solution, 775 µL, 9 mmol) at RT. After completion of the addition, the reaction mixture was allowed to stir for 10 h. Then NaBH<sub>4</sub> (454 mg, 12 mmol) was added at 0 °C, and the above residue was stirred for 0.5 h. The mixture was guenched by saturated NH<sub>4</sub>Cl solution (100 mL), and the mixture was extracted with ethyl acetate ( $4 \times 50$  mL). The combined organic fractions were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. To a stirred solution of the above residue in DCM (30 mL) was added Et<sub>3</sub>N (1.67 mL, 12 mmol) at RT. Then Ac<sub>2</sub>O (681 µL, 7.2 mmol) or 2-thiophenecarbonyl chloride (770 µL, 7.2 mmol) was added at 0 °C, and the resulting reaction mixture was stirred for 1 h before quenched by H<sub>2</sub>O (100 mL). The reaction mixture was extracted with DCM ( $4 \times 50$  mL). The combined organic fractions were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give compound 1z and 1aa.

#### N-Methyl-N-((3-(((triisopropylsilyl)oxy)ethyl)-1H-indol-2-yl)methyl)-thiophene-2-carboxamide (1z)



1z (1.58 g, 56% for 3 steps) was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a white solid. M.P. 130–132 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 9.23 (brs, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 5.0 Hz, 1H), 7.44 (d, J = 3.7 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.24–7.16 (m, 1H), 7.16–7.02 (m, 2H), 4.79 (brs, 2H), 3.94 (t, J = 7.4 Hz, 2H), 3.25 (brs, 3H), 3.11 (t, J = 7.4 Hz, 2H), 1.23–0.96 (m, 21H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 165.8, 137.5, 135.9,

131.5, 130.1, 129.9, 127.7, 127.1, 122.3, 119.2, 118.7, 111.3, 110.9, 64.3, 44.2, 37.6, 28.5, 18.1, 12.1. IR 3265.5, 2951.4, 2920.7, 2860.8, 1645.2, 1598.5, 1527.0, 1454.6, 1389.3, 1274.1, 1091.9, 1057.0, 1005.4, 964.7, 879.7, 853.0, 814.7, 727.6, 679.3, 632.1 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for  $C_{26}H_{38}N_2O_2SSi$  [M]<sup>+</sup> 470.2418; found 470.2419.

# N-Methyl-N-((3-(((triisopropylsilyl)oxy)ethyl)-1H-indol-2-yl)methyl)-acetamide (1aa)



**1aa** (1.40 g, 58% for 3 steps) was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a white solid. M.P. 112–114 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.16 (brs, 1H), 7.58 (dd, J = 7.9, 1.0 Hz, 1H), 7.36–7.30 (m, 1H), 7.18 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.11 (td, J = 7.5, 7.1, 1.1 Hz, 1H), 4.65 (s, 2H), 3.92 (t, J = 7.5 Hz, 2H), 3.09 (t, J = 7.5 Hz, 2H), 3.03 (s, 3H), 2.14 (s, 3H), 1.17–1.03 (m,

21H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 172.2, 135.8, 132.1, 127.6, 122.1, 119.1, 118.6, 111.1, 110.2, 64.3, 42.9, 36.4, 28.4, 21.8, 18.1, 12.0. IR 3261.2, 2926.8, 2862.9, 1634.1, 1459.5, 1407.0, 1340.2, 1269.4, 1204.1, 1097.3, 1012.9, 929.9, 882.8, 818.9, 738.0, 681.7 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>23</sub>H<sub>39</sub>N<sub>2</sub>O<sub>2</sub>Si [M+H]<sup>+</sup> 403.2775; found 403.2792.



**4.8. Preparation of 1ai:** To a stirred solution of the compound **S12**<sup>16</sup> (1.14 g, 6 mmol) in toluene (20 mL) and saturated NaHCO<sub>3</sub> aqueous solution (20 mL) was added methyl chloroformate (510  $\mu$ L, 6.6 mmol). After completion of the addition, the reaction mixture was allowed to stir for 3 h at RT. Then the organic fractions were collected, and the aqueous phase was extracted with ethyl acetate ( $2 \times 30$  mL). The combined organic fractions were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. To a stirred solution of the above residue in THF (30 mL) were added lithium aluminium hydride (LiAlH<sub>4</sub>, 1.02 g, 27 mmol) at 0 °C under N<sub>2</sub>. After completion of the addition, the reaction mixture was allowed to reflux for 4 h. Then the mixture was quenched by saturated NH<sub>4</sub>Cl solution (100 mL) and ethyl acetate (100 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate ( $2 \times 50$  mL). The combined organic fractions were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give crude S14. To a stirred solution of the above residue in DCM (30 mL) were added trimethylamine (Et<sub>3</sub>N, 2.5 mL, 18 mmol) and di-tert-butyl dicarbonate (Boc<sub>2</sub>O, 1.52 mL, 6.6 mmol). After completion of the addition, the reaction mixture was allowed to stir for 3 h at RT. Then the mixture was quenched by H<sub>2</sub>O (100 mL) and DCM (100 mL). The organic fractions were collected, and the aqueous phase was extracted with DCM ( $2 \times 30$  mL). The combined organic fractions were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (ethyl acetate/hexane = 1:20 to 1:5) to give compound **1ai** (1.26 g, 69% for 3 steps) as light yellow oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.42 (brs, 1H), 7.26–7.20 (m, 1H), 7.06 (s, 1H), 6.95 (s, 1H), 6.86 (dd, J = 8.7, 2.4 Hz, 1H), 3.88 (s, 3H), 3.53 (s, 2H), 2.95 (t, J = 7.3 Hz, 2H), 2.88 (s, 3H), 1.60–1.20 (m, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 156.0, 153.9, 131.7, 127.9, 123.0, 112.8, 112.0, 100.7, 79.3, 56.1, 49.6, 34.4, 28.4, 24.0. IR 3316.4, 2955.4, 2921.5, 1669.4, 1584.8, 1480.7, 1452.5, 1395.8, 1365.5, 1302.0, 1261.3, 1212.9, 1165.4, 1061.1, 1032.0, 920.7, 876.4, 828.7, 795.9, 758.4, 636.1 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>17</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub> [M]<sup>+</sup> 304.1781; found 304.1773.

### *N*-Methyl-*N*-[(*S*)-1-acetoxymethyl-2-(1*H*-indol-3-yl)-ethyl]-acetamide (1ak)

 $\begin{array}{c} \text{OAc} \\ \text{N(Ac)Me} \\ \text{$ 

#### 5. Oxidation of Indoles to 2-oxindoles with H<sub>2</sub>O<sub>2</sub>/FeBr<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>/CeBr<sub>3</sub>.

**General Procedure:** To a stirred solution of indole **1** (0.4 mmol) in THF/H<sub>2</sub>O (10/1, 2.2 mL) was added FeBr<sub>2</sub> (8.62 mg, 0.04 mmol) or CeBr<sub>3</sub> (12.2 mg, 0.032 mmol). Then aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%, 88  $\mu$ L, 0.88 mmol) was added to the solution. After completion of the addition, the reaction mixture was stirred at RT for 0.5-3 h before quenched by dilute aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (0.1 M, 10 mL) and ethyl acetate (20 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2×10 mL). The combined organic fractions were washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give compound **2**. Slight modifications including solvents, equivalent of H<sub>2</sub>O<sub>2</sub> and the catalyst may be used for different types of substrates as specified below.

# 1'-(tert-Butoxycarbonyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2a)



**2a**<sup>4</sup> was prepared according to General Procedure and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil (FeBr<sub>2</sub>: 86.5 mg, 75%; CeBr<sub>3</sub>: 107 mg, 93%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.46 (d, *J* = 34.7 Hz, 1H), 7.26–7.10 (m, 2H), 7.08–6.91 (m, 2H), 3.93–3.50 (m, 4H), 2.41 (dt, *J* = 12.6, 8.3 Hz, 1H), 2.15–2.00 (m, 1H), 1.48 (d, *J* = 24.4 Hz, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.7, 180.4, 154.6,

140.5, 140.4, 133.2, 132.8, 128.5, 123.0, 122.8, 110.3, 80.0, 79.9, 54.4, 53.9, 53.5, 52.5, 45.6, 45.3, 36.4, 35.6, 28.6, 28.5. IR 3211.4, 2975.0, 1691.4, 1620.0, 1472.1, 1399.8, 1338.8, 1224.0, 1166.4, 1126.2, 878.2, 735.9, 576.9 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for  $C_{16}H_{20}N_2O_3$  [M]<sup>+</sup> 288.1468; found 288.1473.

# 1'-Tosylspiro[indoline-3,3'-pyrrolidin]-2-one (2b)



 $2b^4$  was prepared according to General Procedure and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil (FeBr<sub>2</sub>: 111 mg, 81%; CeBr<sub>3</sub>: 129 mg, 94%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.00 (s, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 7.20 (td, J = 7.5, 1.6 Hz, 1H), 7.01–6.90 (m, 2H), 6.88 (d, J = 7.7 Hz, 1H), 3.71 (dt, J = 9.4, 7.5 Hz, 1H), 3.60–3.50 (m, 2H), 3.46 (d, J = 9.8 Hz, 1H), 2.45 (s,

3H), 2.29 (dt, J = 12.6, 7.9 Hz, 1H), 2.10–2.00 (m, 1H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 179.5, 144.0, 140.0, 133.3, 132.8, 129.9, 128.6, 127.8, 123.2, 123.1, 110.2, 56.0, 53.0, 47.4, 36.3, 21.7. IR 3283.3, 1710.9, 1617.0, 1471.9, 1337.9, 1224.2, 1157.6, 1015.2, 1015.2, 811.3, 747.1, 662.8, 590.7, 548.8 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 343.1111; found 343.1118.

# 1'-Acetylspiro[indoline-3,3'-pyrrolidin]-2-one (2c)



 $2c^4$  was prepared according to General Procedure (THF/AcOH/H<sub>2</sub>O = 10/10/1, 2.1 mL, when FeBr<sub>2</sub> was used) and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 3:1) as a light yellow oil (FeBr<sub>2</sub>: 62.6 mg, 68%; CeBr<sub>3</sub>: 75.5 mg, 82%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 9.82–9.66 (m, 1H), 7.21 (qd, *J* = 7.8, 1.2 Hz, 1H), 7.12 (dd, *J* = 7.6, 4.2 Hz, 1H), 7.05-6.91 (m, 2H), 4.03-3.91 (m, 1H), 3.90-3.75 (m, 2H), 3.76-3.55 (m, 1H), 2.49-2.33 (m, 1H), 2.27–2.01 (m, 4H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 180.5, 179.5, 169.8, 169.6, 140.9, 140.6, 132.4, 131.7, 128.7, 128.6, 122.9, 122.8, 122.5, 110.5, 110.4, 55.4, 53.6, 53.5, 51.9, 46.7, 45.2, 36.4, 35.0, 22.6, 22.4. IR 3197.1, 1709.1, 1612.9, 1460.1, 1418.9, 1338.9, 1190.0, 728.3 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> [M]<sup>+</sup> 230.1050; found 230.1059.

# 1'-(Methoxycarbonyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2d)



 $2d^4$  was prepared according to General Procedure (THF/AcOH/H<sub>2</sub>O = 10/10/1, 2.1 mL, when FeBr<sub>2</sub> was used) and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil (FeBr<sub>2</sub>: 73.9 mg, 75%; CeBr<sub>3</sub>: 84.7 mg, 86%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.54 (d, J = 21.5 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.14 (dd, *J* = 7.6, 3.4 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.8, 1H), 3.94–3.54

(m, 7H), 2.41 (ddt, J = 16.6, 11.7, 5.3 Hz, 1H), 2.15-2.00 (m, 1H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.5, 180.2, 155.6, 155.5, 140.6, 140.5, 132.6, 132.3, 128.6, 123.0, 122.9, 122.7, 110.4, 54.3, 54.0, 53.4, 52.8, 52.7, 52.5, 45.8, 45.3, 36.4, 35.5. IR 3229.3, 1679.2, 1618.1, 1456.2, 1388.8, 1191.4, 1128.1, 744.7 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub> [M]<sup>+</sup> 246.0999; found 246.1002.

# 1-Methyl-1'-(methoxycarbonyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2e)



 $2e^4$  was prepared according to General Procedure and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 75 mg, 72%; CeBr<sub>3</sub>: 84.3 mg, 81%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.32–7.22 (m, 1H), 7.18– 7.10 (m, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.91–3.47 (m, 7H), 3.20 (brs, 3H), 2.44–2.30 (m, 1H), 2.10–1.90 (m, 1H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 177.5, 177.1, 155.4, 155.3, 142.9, 142.8, 132.3, 131.9, 128.5, 123.04, 122.99, 122.4, 108.3, 54.4, 54.0, 52.8, 52.6, 51.9, 45.7, 45.2, 36.3, 35.4, 26.4. IR 3508.4, 2952.3, 2884.2, 1694.8, 1610.3, 1453.5, 1380.0, 1196.5, 1128.5, 1092.6, 756.8 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub> [M]<sup>+</sup> 260.1155; found 260.1165.

### 1-Benzyl-1'-(methoxycarbonyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2f)



**2f**<sup>4</sup> was prepared according to General Procedure and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 82.1 mg, 61%; CeBr<sub>3</sub>: 94.2 mg, 70%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.38–7.25 (m, 5H), 7.24–7.17 (m, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.78 (dd, *J* = 8.1, 3.3 Hz, 1H), 4.94 (brs, 2H), 4.02–

3.60 (m, 7H), 2.49 (dt, J = 12.7, 8.5 Hz, 1H), 2.25–2.05 (m, 1H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 177.8, 177.4, 155.4, 142.1, 142.0, 135.7, 132.3, 131.8, 128.9, 128.5, 127.8, 127.2, 123.12, 123.07, 122.5, 109.4, 54.6, 54.2, 52.9, 52.7, 52.6, 51.9, 45.8, 45.3, 43.90, 43.85, 36.4, 35.6. IR 2952.3, 2883.0, 1697.7, 1609.2, 1452.0, 1353.7, 1184.5, 1124.9, 963.9, 740.8, 549.5 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub> [M]<sup>+</sup> 336.1468; found 336.1467.

# 5-Methoxy-1'-(methoxycarbonyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2g)



**2g**<sup>4</sup> was prepared according to General Procedure (THF/AcOH/H<sub>2</sub>O = 10/10/1, 2.1 mL, when FeBr<sub>2</sub> was used) and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil (FeBr<sub>2</sub>: 95.0 mg, 86%; CeBr<sub>3</sub>: 91.7 mg, 83%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.60–9.42 (m, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.74 (brs, 2H), 3.96–3.51 (m, 10H), 2.45–2.30 (m, 1H), 2.15–

2.00 (m, 1H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.4, 180.1, 156.13, 156.07, 155.5, 133.9, 133.8, 133.7, 112.7, 112.5, 110.7, 110.6, 110.3, 110.1, 55.8, 54.3, 53.9, 53.8, 52.9, 52.7, 45.7, 45.2, 36.3, 35.5. IR 3225.7, 2953.1, 1684.2, 1450.5, 1388.8, 1307.9, 1193.0, 1033.2, 812.6, 729.5 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> [M]<sup>+</sup> 276.1105; found 276.1108.

# (5'S,3R)-1'-(tert-Butoxycarbonyl)-5'-(methoxycarbonyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2h)



**2h**<sup>4</sup> was prepared according to General Procedure and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 3:1) as a light yellow oil (FeBr<sub>2</sub>: 109 mg, 79%; CeBr<sub>3</sub>: 118 mg, 85%). [ $\alpha$ ]<sub>D</sub><sup>22</sup> = -11.3 (*c* 1, MeOH). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.44 (d, *J* = 10.9 Hz, 1H), 7.26–7.20 (m, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.06–7.00 (m, 1H), 6.97 (dd, *J* = 7.8, 4.4 Hz, 1H), 4.79–4.57 (m, 1H), 3.87–3.66 (m, 5H), 2.55 (ddd, *J* = 14.6, 12.7, 9.0 Hz, 1H), 2.44–2.31 (m, 1H), 1.45 (d, *J* = 12.6 Hz, 9H). <sup>13</sup>C-NMR (100

MHz, CDCl<sub>3</sub>)  $\delta$ : 178.4, 178.3, 172.6, 172.3, 154.4, 153.5, 140.10, 140.07, 133.3, 133.1, 128.8, 123.2, 123.1, 122.4, 110.6, 81.0, 59.1, 58.7, 55.4, 54.8, 53.2, 52.6, 52.4, 52.3, 40.5, 39.6, 28.4. IR 3254.5, 2977.0, 1697.3, 1619.3, 1470.4, 1207.1, 1161.5, 900.4, 739.3 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>5</sub> [M]<sup>+</sup> 346.1523; found 346.1530.

# (5'S,3R)-1'-(Thiophene-2-carbonyl)-5'-(methoxycarbonyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2i)



**2i** was prepared according to General Procedure and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 3:1) as a white solid (FeBr<sub>2</sub>: 98.4 mg, 69%; CeBr<sub>3</sub>: 128 mg, 90%). M.P. 88–90 °C;  $[\alpha]_D^{22}$  = +51.2 (*c* 1, MeOH). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.75 (brs, 1H), 7.52–7.36 (m, 2H), 7.18 (td, *J* = 7.7, 1.2 Hz, 1H), 7.08–6.90 (m, 4H), 5.16 (dd, *J* = 10.2, 7.8 Hz, 1H), 4.32 (d, *J* = 10.1 Hz, 1H), 3.72 (s, 3H), 2.60 (dd, *J* = 12.6, 10.4 Hz, 1H),

2.40 (dd, *J* = 12.7, 8.1 Hz, 1H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 176.9, 171.3, 162.5, 140.1, 137.2, 132.3, 130.90, 130.87, 128.8, 127.4, 123.0, 122.2, 110.7, 59.6, 57.6, 53.7, 52.6, 38.4. IR 3209.6, 2953.6, 2921.1, 2876.8, 1715.7, 1608.5, 1520.2, 1470.9, 1430.1, 1396.3, 1341.4, 1267.6, 1204.2, 1100.8, 1032.2, 910.7, 854.6, 731.7, 672.0 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 357.0904; found 357.0915.

### 1'-(tert-Butoxycarbonyl)-2'-methylspiro[indoline-3,3'-pyrrolidin]-2-one (2j)



**2j** was prepared according to General Procedure using THF/AcOH/H<sub>2</sub>O (10/10/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil (FeBr<sub>2</sub>: 64.2 mg, 53.1%; CeBr<sub>3</sub>: 59.0 mg, 48.8%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.55 (brs, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 4.17–3.59 (m, 3H), 2.63–2.25 (m, 1H), 2.10–2.00

(m, 1H), 1.48 (brs, 9H), 1.29 (d, J = 6.5 Hz, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 179.7, 179.2, 154.5, 140.5, 133.2, 132.3, 128.4, 122.8, 122.6, 110.0, 79.9, 60.9, 56.8, 45.4, 44.7, 34.1, 33.3, 28.6, 16.6, 15.5. IR 3238.7, 2968.5, 2924.0, 1693.7, 1620.4, 1468.1, 1395.8, 1337.6, 1255.4, 1169.1, 1131.7, 1109.3, 1019.3, 980.3, 860.8, 744.8, 674.5, 638.0 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub> [M]<sup>+</sup> 302.1625; found 302.1635.

# 1'-(tert-Butoxycarbonyl)-2'-methylspiro[indoline-3,3'-pyrrolidin]-2-one (2j')



**2j**' was prepared according to General Procedure using THF/AcOH/H<sub>2</sub>O (10/10/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil (FeBr<sub>2</sub>: 22.9 mg, 18.9%; CeBr<sub>3</sub>: 26.9 mg, 22.2%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.41 (brs, 1H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 4.20–3.57 (m, 3H), 2.31 (dt, *J* = 12.6, 8.1 Hz, 1H), 2.08 (brs, 1H), 1.48 (brs,

9H), 1.10 (brs, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.8, 155.1, 141.1, 129.9, 128.5, 125.1, 122.4, 110.4, 79.9, 59.0, 58.1, 45.9, 33.9, 28.6, 17.8. IR 3237.1, 2966.3, 2923.3, 1696.6, 1621.3, 1467.1, 1393.4, 1336.7, 1251.5, 1223.7, 1171.2, 1134.7, 1103.7, 1025.1, 860.8, 750.1, 704.3, 673.7, 638.9, 600.8 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub> [M]<sup>+</sup> 302.1625; found 302.1629.

# 1'-(tert-Butoxycarbonyl)-2'-(isobutyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2k)



**2**k<sup>4</sup> was prepared according to General Procedure using THF/AcOH/H<sub>2</sub>O (10/10/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil (FeBr<sub>2</sub>: 58.2 mg, 42.2%; CeBr<sub>3</sub>: 59.2 mg, 43.0%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.75 (brs, 1H), 7.25–7.17 (m, 1H), 7.12–6.96 (m, 2H), 6.92 (d, *J* = 7.7 Hz, 1H), 4.08–3.56 (m, 3H), 2.52 (brs, 1H), 2.10–1.98 (m, 1H), 1.85 (brs, 1H),

1.60–1.30 (m, 11H), 0.82 (brs, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.5, 154.8, 139.5, 134.9, 128.2, 123.1, 122.7, 109.9, 80.3, 63.7, 55.9, 44.0, 40.3, 34.0, 28.7, 25.2, 23.1, 22.8. IR 3229.8, 2961.3, 1693.6, 1619.5, 1469.7, 1395.6, 1167.3, 1116.9, 743.7 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub> [M]<sup>+</sup> 344.2094; found 344.2089.

# 1'-(tert-Butoxycarbonyl)-2'-(isobutyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2k')



**2**k<sup>\*4</sup> was prepared according to General Procedure using THF/AcOH/H<sub>2</sub>O (10/10/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil (FeBr<sub>2</sub>: 34.2 mg, 24.8%; CeBr<sub>3</sub>: 53.7 mg, 39.0%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.32 (s, 1H), 7.26 (ddd, *J* = 8.0, 3.9, 1.2 Hz, 2H), 7.05 (td, *J* 

= 7.6, 1.1 Hz, 1H), 6.97 (dd, J = 8.1, 1.0 Hz, 1H), 4.14 (d, J = 78.5 Hz, 2H), 3.60 (ddd, J = 11.2, 8.6, 7.1 Hz, 1H), 2.33 (dt, J = 12.4, 8.5 Hz, 1H), 2.05–1.98 (m, 1H), 1.76 (s, 1H), 1.52 (s, 9H), 1.38 (s, 1H), 1.02 (s, 1H), 0.85 (d, J = 6.4 Hz, 3H), 0.60 (d, J = 6.5 Hz, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 181.4, 155.4, 140.9, 130.1, 128.4, 125.2, 122.2, 110.4, 80.0, 61.2, 57.4, 45.8, 41.0, 35.8, 28.7, 24.7, 23.4, 22.0. IR 3238.2, 2961.0, 1699.8, 1620.0, 1468.7, 1393.0, 1168.1, 1108.8, 745.9 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub> [M]<sup>+</sup> 344.2094; found 344.2101.

# 1'-(tert-Butoxycarbonyl)-2'-(phenylethyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2l)



**21** was prepared according to General Procedure using THF/AcOH/H<sub>2</sub>O (10/10/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil (FeBr<sub>2</sub>: 61.5 mg, 39.2%; CeBr<sub>3</sub>: 47.6 mg, 30.3%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.14 (brs, 1H), 7.25–7.00 (m, 8H), 6.93 (d, J = 7.7 Hz, 1H), 4.23–3.69 (m, 3H), 2.51 (brs, 3H), 2.30–1.90 (m, 3H),

1.48 (brs, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 179.2, 178.7, 154.8, 142.0, 139.6, 134.7, 133.9, 128.5, 128.4, 125.8, 123.2, 122.7, 110.1, 80.3, 79.9, 65.2, 64.9, 55.9, 45.1, 44.2, 35.7, 34.3, 33.8, 33.3, 32.9, 28.6. IR 3233.3, 2963.9, 2925.8, 1950.3, 1691.3, 1617.9, 1469.0, 1393.9, 1249.4, 1166.3, 1119.8, 1029.3, 989.0, 868.0, 740.6, 696.9, 636.1 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub> [M]<sup>+</sup> 392.2094; found 392.2108.

# 1'-(tert-Butoxycarbonyl)-2'-(phenylethyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2l')



**21'** was prepared according to General Procedure using THF/AcOH/H<sub>2</sub>O (10/10/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a white solid (FeBr<sub>2</sub>: 27.9 mg, 17.8%; CeBr<sub>3</sub>: 34.1 mg, 21.7%). M.P. 98–100 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.27 (s, 1H), 7.35–7.26 (m, 2H), 7.15 (t, *J* = 7.0 Hz, 2H), 7.12–7.05 (m, 2H), 7.02 (d, *J* = 7.7 Hz, 1H),

6.85–6.79 (m, 2H), 4.13 (d, J = 65.3 Hz, 2H), 3.63 (ddd, J = 11.2, 8.5, 7.1 Hz, 1H), 2.50–2.11 (m, 3H), 2.11– 1.60 (m, 3H), 1.50 (s, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 181.2, 155.4, 141.8, 141.0, 129.8, 128.7, 128.4, 128.3, 125.8, 125.3, 122.5, 110.5, 80.0, 63.1, 57.3, 46.0, 35.7, 34.6, 32.4, 28.6. IR 3236.2, 2957.0, 2920.9, 2866.8, 1701.7, 1620.1, 1464.2, 1391.3, 1337.6, 1263.2, 1224.1, 1165.9, 1115.2, 1020.9, 974.8, 857.1, 750.6, 700.4 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub> [M]<sup>+</sup> 392.2094; found 392.2101.

### 1'-(tert-Butoxycarbonyl)-2'-(cyanopropyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2m)



**2m** was prepared according to General Procedure using THF/AcOH/H<sub>2</sub>O (10/10/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:2 to 3:1) as a light yellow oil (FeBr<sub>2</sub>: 61.6 mg, 43.3%; CeBr<sub>3</sub>: 53.3 mg, 37.5%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.43 (s, 1H), 7.25–7.15 (m, 1H), 7.05–6.90 (m, 3H), 4.05–3.61 (m, 3H), 2.58–2.37 (m, 1H), 2.29 (brs, 2H), 2.11–1.74

(m, 3H), 1.70–1.40 (m, 11H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.7, 178.2, 154.7, 139.7, 139.6, 134.2, 133.6, 128.4, 123.1, 122.3, 119.6, 110.2, 80.6, 80.1, 64.3, 63.9, 55.7, 55.4, 44.8, 44.0, 35.0, 33.8, 30.6, 30.4, 28.5, 22.8, 22.6, 17.1, 17.0. IR 3246.2, 2965.1, 2929.1, 2247.2, 1692.6, 1619.7, 1470.9, 1395.8, 1338.7, 1264.3, 1169.5, 1124.8, 1028.4, 985.9, 879.3, 746.3, 635.1 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>20</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub> [M]<sup>+</sup> 355.1890; found 355.1884.

#### 1'-(tert-Butoxycarbonyl)-2'-(cyanopropyl)spiro[indoline-3,3'-pyrrolidin]-2-one (2m')



**2m'** was prepared according to General Procedure using THF/AcOH/H<sub>2</sub>O (10/10/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:2 to 3:1) as a white solid (FeBr<sub>2</sub>: 30.8 mg, 21.7%; CeBr<sub>3</sub>(53.3 mg, 37.5%). M.P. 176–178 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.49 (brs, 1H), 7.28–6.83 (m, 4H), 4.15–3.50 (m, 3H), 2.55–1.87 (m, 6H), 1.60–1.20 (m, 11H). <sup>13</sup>C-NMR

 $(100 \text{ MHz}, \text{CDCl}_3)$   $\delta$ : 181.0, 155.5, 154.7, 141.1, 128.8, 128.4, 125.0, 123.0, 122.4, 122.3, 119.4, 110.5, 110.2, 80.1, 61.9, 56.3, 45.5, 34.8, 31.3, 28.5, 21.9, 16.9. IR 3248.4, 2973.0, 2940.2, 2248.8, 1688.0, 1620.0, 1470.5, 1393.6, 1336.9, 1262.6, 1231.3, 1166.2, 1122.6, 1027.4, 884.2, 868.8, 735.8, 638.2 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>20</sub>H<sub>25</sub>N<sub>3</sub>O<sub>3</sub> [M]<sup>+</sup> 355.1890; found 355.1895.

# 2-Methyl-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2'-one (2n)



**2n**<sup>4</sup> was prepared according to General Procedure and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 60.1 mg, 74%; CeBr<sub>3</sub>: 72.3 mg, 89%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.04 (brs, 1H), 7.30–7.18 (m, 2H), 7.14–7.02 (m, 1H), 7.02–6.91 (m, 1H), 4.37–4.09 (m, 3H), 2.73 (ddd, *J* = 12.7, 9.5, 6.6 Hz, 1H), 2.24 (ddd, *J* = 12.6, 8.2, 5.6 Hz, 1H), 0.94 (d, *J* = 6.2 Hz, 3H). <sup>13</sup>C-NMR (100

MHz, CDCl<sub>3</sub>) δ: 180.2, 140.3, 131.8, 128.1, 124.7, 122.8, 110.1, 82.4, 67.3, 58.4, 38.2, 15.2. IR 3230.3, 2978.0,

2877.6, 1707.5, 1619.7, 1471.8, 1344.7, 1224.7, 1106.2, 1046.2, 751.3 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for  $C_{12}H_{13}NO_2$  [M]<sup>+</sup> 203.0941; found 203.0943.

#### 2-Phenyl-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2'-one (20)



**20<sup>4</sup>** was prepared according to General Procedure and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 81.7 mg, 77%; CeBr<sub>3</sub>: 96.6 mg, 91%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 9.63 (brs, 1H), 7.20–7.14 (m, 3H), 7.13–6.99 (m, 4H), 6.92 (td, *J* = 7.6, 1.1 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 5.29 (s, 1H), 4.52 (td, *J* = 8.3, 6.9 Hz, 1H), 4.43 (td, *J* = 9.2, 5.4 Hz, 1H), 2.90 (ddd, *J* = 12.5,

9.4, 6.9 Hz, 1H), 2.38 (ddd, *J* = 12.5, 8.0, 5.4 Hz, 1H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 180.3, 139.9, 136.6, 131.2, 127.8, 127.6, 127.5, 125.4, 124.7, 122.2, 109.7, 87.5, 67.3, 59.8, 38.1. IR 3223.7, 2882.3, 1702.2, 1618.0, 1471.7, 1219.5, 1061.4, 479.9, 704.8 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>17</sub>H<sub>15</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 266.1176; found 266.1178.

### 2-Cyclohexyl-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2'-one (2p)



**2p**<sup>4</sup> was prepared according to General Procedure using THF/AcOH/H<sub>2</sub>O (10/10/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 76.0 mg, 70%; CeBr<sub>3</sub>: 95.5 mg, 88%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.64 (brs, 1H), 7.30–7.20 (m, 2H), 7.06 (td, J = 7.6, 1.0 Hz, 1H), 6.95 (d, J = 7.7 Hz, 1H), 4.26–4.07 (m, 2H), 3.81 (d, J = 7.6)

9.8 Hz, 1H), 2.64 (ddd, J = 12.5, 9.3, 7.4 Hz, 1H), 2.09 (ddd, J = 12.6, 7.8, 5.1 Hz, 1H), 2.00 (d, J = 12.1 Hz, 1H), 1.65 (dd, J = 12.0, 4.3 Hz, 1H), 1.48 (d, J = 12.0 Hz, 1H), 1.43–1.27 (m, 2H), 1.15–0.94 (m, 3H), 0.91–0.64 (m, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.6, 140.0, 132.1, 128.0, 124.7, 122.8, 110.1, 90.1, 66.4, 56.6, 40.6, 39.4, 31.1, 27.4, 26.2, 25.5. IR 3224.6, 2925.3, 1705.0, 1618.6, 1471.3, 1344.1, 1222.4, 1073.1, 750.4 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>17</sub>H<sub>21</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 272.1645; found 272.1649.

# 2,2-Dimethyl-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2'-one (2q)



**2q** [FeBr<sub>2</sub>(55.6 mg, 64%), CeBr<sub>3</sub>(66.1 mg, 76%)] was prepared according to General Procedure using THF/AcOH/H<sub>2</sub>O (10/10/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as white solid. mp 128–130 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.50 (brs, 1H), 7.28–7.23 (m, 1H), 7.20 (td, *J* = 7.7,

1.3 Hz, 1H), 7.01 (td, J = 7.6, 1.1 Hz, 1H), 6.95 (d, J = 7.7 Hz, 1H), 4.28 (td, J = 9.0, 5.6 Hz, 1H), 4.18 (td, J = 8.9, 5.9 Hz, 1H), 2.65 (ddd, J = 12.7, 9.3, 5.9 Hz, 1H), 2.32 (ddd, J = 12.7, 9.1, 5.6 Hz, 1H), 1.34 (s, 3H), 1.11 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.8, 141.0, 131.6, 128.1, 124.9, 122.3, 110.0, 84.8, 64.4, 60.1, 35.9, 24.4, 23.3. IR 3247.4, 2961.0, 2924.2, 2883.2, 1703.3, 1619.9, 1376.2, 1333.4, 1224.2, 1182.8, 1152.0, 1109.9, 1047.5, 972.0, 885.0, 834.8, 743.3, 691.0, 635.1 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>13</sub>H<sub>16</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 218.1176; found 218.1186.

#### 1,3-Dimethyl-3-(methoxymethyl)indolin-2-one (2r)



**2r<sup>18</sup>** was prepared according to General Procedure using MeCN/H<sub>2</sub>O (10/1, 2.2 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 64.9 mg, 79%; CeBr<sub>3</sub>: 73.9 mg, 90%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.29–7.22 (m, 2H), 7.05 (td, J = 7.5, 1.0 Hz, 1H), 6.85–6.80 (m, 1H), 3.62 (s, 2H), 3.20 (d, J = 3.1 Hz, 6H), 1.32 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ :

179.1, 143.5, 132.8, 128.0, 122.9, 122.5, 108.0, 77.1, 59.5, 49.4, 26.3, 19.8. IR 3501.4, 2928.3, 2880.0, 2826.1, 1703.2, 1609.5, 1462.4, 1346.6, 1309.3, 1249.9, 1104.6, 970.8, 748.6 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for  $C_{12}H_{15}NO_2$  [M]<sup>+</sup> 205.1097; found 205.1107.

#### 1,3-Dimethyl-3-(((*tert*-butyldimethylsilyl)oxy)methyl)indolin-2-one (2s)



**2s<sup>19</sup>** was prepared according to General Procedure using MeCN/H<sub>2</sub>O (10/1, 2.2 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:2) as a light yellow oil (FeBr<sub>2</sub>: 97.8 mg, 80%; CeBr<sub>3</sub>: 86.8 mg, 71%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.30–7.20 (m, 2H), 7.03 (td, *J* = 7.5, 1.0 Hz, 1H), 6.83–6.78 (m, 1H), 3.78 (d, *J* = 1.2 Hz, 2H), 3.18 (s, 3H), 1.32 (s, 3H), 0.71 (s, 9H), -0.08

(s, 3H), -0.15 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 179.3, 143.8, 133.2, 127.8, 123.2, 122.2, 107.7, 68.2, 50.7, 26.1, 25.6, 18.4, 18.0, -5.5, -5.7. IR 2933.4, 2857.9, 1714.4, 1612.4, 1465.8, 1377.5, 1347.7, 1253.2, 1106.6, 842.1, 777.0, 746.4 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>17</sub>H<sub>27</sub>NO<sub>2</sub>Si [M+H]<sup>+</sup> 306.1884; found 306.1893.

# 1,3-Dimethyl-3-(allyloxymethyl)indolin-2-one (2t)



**2t** was prepared according to General Procedure using MeCN/H<sub>2</sub>O (10/1, 2.2 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 72.2 mg, 78%; CeBr<sub>3</sub>: 84.2 mg, 91%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.30–7.22 (m, 2H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 5.72 (ddt, *J* = 17.2, 10.5, 5.4 Hz, 1H), 5.16–5.03 (m, 2H),

3.93–3.79 (m, 2H), 3.72–3.58 (m, 2H), 3.19 (s, 3H), 1.33 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 178.9, 143.4, 134.5, 132.9, 127.9, 123.0, 122.3, 116.6, 107.9, 74.3, 72.2, 49.3, 26.2, 19.6. IR 3055.5, 2971.2, 2927.9, 2857.9, 1707.8, 1611.5, 1468.3, 1429.5, 1350.2, 1258.5, 1094.9, 1026.8, 999.5, 927.2, 741.5, 700.0, 641.6 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>14</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 232.1332; found 232.1341.

1-Methyl-3-methoxymethyl-3-(methoxyethyl)indolin-2-one (2u)



**2u** was prepared according to General Procedure using MeCN/H<sub>2</sub>O (10/1, 2.2 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 84.8 mg, 85%; CeBr<sub>3</sub>: 90.7 mg, 91%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.30–7.20 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 1H), 3.67 (d, *J* = 8.8 Hz, 1H), 3.58 (d, *J* = 8.8 Hz, 1H), 3.20 (d, *J* = 6.0 Hz, 6H), 3.15–2.99 (m, 5H), 2.23 (dt, *J* = 13.7, 7.8 Hz, 1H), 2.04 (ddd, *J* = 13.7, 6.9, 4.6 Hz, 1H). <sup>13</sup>C-NMR

 $(100 \text{ MHz}, \text{CDCl}_3) \ \delta: \ 178.2, \ 144.2, \ 130.3, \ 128.1, \ 123.4, \ 122.2, \ 107.9, \ 76.8, \ 68.3, \ 59.5, \ 58.4, \ 51.9, \ 33.0, \ 26.2. \\ \text{IR } 2980.0, \ 2925.6, \ 2880.5, \ 2823.6, \ 1707.7, \ 1609.9, \ 1465.2, \ 1376.9, \ 1346.9, \ 1261.3, \ 1194.5, \ 1107.5, \ 1023.3, \ 961.2, \ 927.5, \ 840.7, \ 747.2, \ 696.9, \ 641.2 \ \text{cm}^{-1}; \ \text{HRMS} \ (\text{CI}^+) \ (\text{m/z}) \ \text{calcd. for } \ C_{14}\text{H}_{20}\text{NO}_3 \ [\text{M}+\text{H}]^+ \ 250.1438; \ \text{found} \ 250.1451. \\$ 

### 3-Acetoxymethyl-3-(acetoxyethyl)indolin-2-one (2v)



**2v** was prepared according to General Procedure using MeCN/H<sub>2</sub>O (10/1, 2.2 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:2 to 5:1) as a white solid (FeBr<sub>2</sub>: 53.6 mg, 46%; CeBr<sub>3</sub>: 59.4 mg, 51%). M.P. 124–126 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.48 (brs, 1H), 7.25–7.18 (m, 2H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 4.51 (d, *J* = 10.7 Hz, 1H), 4.17 (d, *J* = 10.8 Hz, 1H),

3.99 (dt, J = 11.9, 6.2 Hz, 1H), 3.83 (ddd, J = 11.3, 7.5, 6.5 Hz, 1H), 2.33 (dt, J = 14.1, 7.0 Hz, 1H), 2.22 (dt, J = 14.1, 6.2 Hz, 1H), 1.90 (s, 3H), 1.84 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 179.2, 170.7, 170.5, 141.2, 129.0, 128.9, 124.1, 122.9, 110.1, 67.5, 60.3, 51.2, 31.9, 20.70, 20.67. IR 3276.7, 2955.4, 2919.7, 2856.4, 1733.4, 1623.3, 1466.0, 1373.0, 1231.8, 1047.5, 755.5 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>15</sub>H<sub>17</sub>NO<sub>5</sub> [M]<sup>+</sup> 291.1101; found 291.1101.

### N-Allyl-N-((3-methyl-2-oxoindolin-3-yl)methyl)-acetamide (2w)



**2w** was prepared according to General Procedure using MeCN/H<sub>2</sub>O (10/1, 2.2 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil (FeBr<sub>2</sub>: 68.6 mg, 63%; CeBr<sub>3</sub>: 83.9 mg, 77%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.30 (dd, J = 7.4, 1.2 Hz, 1H), 7.23–7.10 (m, 1H), 7.05–6.98 (m, 1H), 6.75 (dd, J = 17.5, 7.8 Hz, 1H), 5.58–5.33 (m, 1H), 5.05–4.90 (m, 1H),

4.85–4.70 (m, 1H), 4.20 (d, J = 14.0 Hz, 1H), 3.92–3.52 (m, 2H), 3.43 (d, J = 14.0 Hz, 1H), 3.20–3.05 (m, 3H), 2.00–1.75 (m, 3H), 1.35–1.20 (m, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.0, 178.5, 171.55, 171.50, 143.4, 142.9, 132.7, 132.4, 131.6, 131.5, 128.7, 128.0, 124.4, 123.1, 122.5, 122.4, 116.6, 115.9, 108.5, 107.6, 53.5, 51.1, 50.0, 49.5, 49.3, 48.1, 26.3, 26.2, 22.4, 22.0, 21.6, 21.1. IR 2971.1, 2928.6, 1701.7, 1642.9, 1614.7, 1467.2, 1416.1, 1349.0, 1296.2, 1246.6, 1163.5, 1119.0, 1027.4, 985.7, 924.0, 872.0, 750.0, 696.9, 644.5, 600.2 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>16</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 273.1598; found 273.1613.

# *N*-((1,3-Dimethyl-2-oxoindolin-3-yl)methyl)-*N*,4-dimethylbenzenesulfonamide (2x)



**2x** was prepared according to General Procedure using MeCN/H<sub>2</sub>O (10/1, 2.2 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 71.7 mg, 50%; CeBr<sub>3</sub>: 84.6 mg, 59%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.50–7.41 (m, 2H), 7.38 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.29 (td, *J* = 7.8, 1.3 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 6.84 (d, *J* =

7.8 Hz, 1H), 3.77 (d, J = 13.9 Hz, 1H), 3.22 (d, J = 13.9 Hz, 1H), 3.18 (s, 3H), 2.45 (s, 3H), 2.37 (s, 3H), 1.37 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 179.3, 143.4, 143.2, 134.5, 131.3, 129.6, 128.3, 127.5, 124.5, 122.8, 108.1, 55.7, 48.9, 36.8, 26.4, 22.2, 21.5. IR 3055.6, 2967.9, 2925.9, 1706.0, 1609.4, 1480.6, 1462.7, 1378.5, 1339.1, 1265.4, 1219.3, 1159.0, 1125.8, 1093.7, 994.1, 922.8, 876.7, 811.3, 731.8, 651.1 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 359.1424; found 359.1417.

# *N*-Methyl-*N*-((1,3-dimethyl-2-oxoindolin-3-yl)methyl)-furan-2-carboxamide (2y)



**2y** was prepared according to General Procedure using MeCN/H<sub>2</sub>O (10/1, 2.2 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 87.1 mg, 73%; CeBr<sub>3</sub>: 96.6 mg, 81%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.37–7.10 (m, 3H), 6.93–6.72 (m, 3H), 6.35 (brs, 1H), 4.58 (d, *J* = 14.0 Hz, 1H), 3.90–3.36 (m, 1H), 3.19 (s, 3H), 2.92 (brs, 3H),

1.36 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.0, 160.4, 147.6, 143.8, 143.1, 131.1, 128.3, 124.2, 122.7, 116.3, 111.2, 107.9, 53.4, 49.5, 37.6, 26.4, 22.2. IR 2968.0, 2928.2, 1704.2, 1615.4, 1573.7, 1485.1, 1384.8, 1348.2, 1282.0, 1159.9, 1116.6, 1074.0, 1021.2, 938.2, 886.1, 835.9, 740.8, 699.7, 632.7 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 299.1390; found 299.1407.

### N-Methyl-N-((3-(((triisopropylsilyl)oxy)ethyl)-2-oxoindolin-3-yl)methyl)-thiophene-2-carboxamide (2z)



**2z** was prepared according to General Procedure using MeCN/H<sub>2</sub>O (10/1, 2.2 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a white solid (FeBr<sub>2</sub>: 115 mg, 59%; CeBr<sub>3</sub>: 111 mg, 57%). M.P. 134–136 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.43 (brs, 1H), 7.35–7.20 (m, 2H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.98–6.78 (m, 4H), 4.66 (d, *J* = 13.8 Hz, 1H), 3.67 (s, 1H), 3.58–3.38 (m, 2H), 2.93 (s, 3H), 2.35–2.20 (m, 1H), 2.11 (brs, 1H), 0.93–

0.88 (m, 21H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 182.1, 165.2, 141.4, 137.3, 129.3, 129.0, 128.7, 128.4, 126.6, 125.0, 122.4, 109.9, 59.3, 54.2, 52.8, 39.2, 38.5, 17.9, 11.9. IR 3221.3, 2934.8, 2863.8, 1712.1, 1613.7, 1523.7, 1464.1, 1391.0, 1336.8, 1289.1, 1265.3, 1191.4, 1104.5, 1058.9, 1003.1, 921.0, 882.1, 849.8, 807.7, 743.5, 680.6, 649.4 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>26</sub>H<sub>39</sub>N<sub>2</sub>O<sub>3</sub>SSi [M+H]<sup>+</sup> 487.2445; found 487.2438.

# N-Methyl-N-((3-(((triisopropylsilyl)oxy)ethyl)-2-oxoindolin-3-yl)methyl)-acetamide (2aa)



**2aa** was prepared according to General Procedure using MeCN/H<sub>2</sub>O (10/1, 2.2 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil (FeBr<sub>2</sub>: 100 mg, 60%; CeBr<sub>3</sub>: 109 mg, 65%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.26 (d, J = 27.8 Hz, 1H), 7.31–7.07 (m, 2H), 7.05–6.92 (m, 1H), 6.87 (dd, J = 15.8, 7.7 Hz, 1H), 4.20 (dd, J = 207.9, 14.2 Hz, 1H), 3.75–3.31 (m, 3H), 2.78–2.57 (m, 3H), 2.32–2.16 (m, 1H), 2.12–2.02 (m, 1H), 2.00–1.75 (m, 3H), 0.96–0.84

(m, 21H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 182.2, 180.5, 171.9, 171.3, 141.8, 141.3, 129.6, 129.5, 128.8, 128.2, 125.3, 124.2, 122.3, 122.2, 110.6, 109.6, 59.3, 59.2, 57.6, 53.1, 52.8, 52.6, 38.4, 37.8, 37.2, 35.8, 21.6, 21.5, 17.9, 11.9. IR 3199.1, 2934.5, 2864.6, 1713.2, 1625.5, 1467.4, 1398.8, 1336.0, 1259.2, 1192.1, 1104.4, 1000.6, 915.2, 882.4, 808.0, 741.4, 679.8, 650.4 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>23</sub>H<sub>39</sub>N<sub>2</sub>O<sub>3</sub>Si [M+H]<sup>+</sup> 419.2724; found 419.2737.

# 3-Methylindolin-2-one (2ab)



**2ab**<sup>4</sup> was prepared according to General Procedure with FeBr<sub>2</sub> (4.3 mg, 0.02 mmol) or CeBr<sub>3</sub> (3.1 mg, 0.008 mmol) as the catalyst and using *tert*-butanol/H<sub>2</sub>O (20/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 3:1) as a light yellow oil (FeBr<sub>2</sub>: 52.4 mg, 89%; CeBr<sub>3</sub>: 51.2 mg, 87%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.69 (s, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.07–7.00 (m, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 3.49 (q, *J* = 7.7

Hz, 1H), 1.52 (d, J = 7.7 Hz, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 182.2, 141.5, 131.3, 127.9, 123.8, 122.4, 110.0, 41.3, 15.3. IR 3150.6, 1680.2, 1613.9, 1461.6, 1332.4, 1215.4, 1169.6, 791.3, 741.7, 657.3, 543.9 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>9</sub>H<sub>9</sub>NO [M]<sup>+</sup> 147.0679; found 147.0687.

# 1,3-Dimethylindolin-2-one (2ac)



**2ac**<sup>4</sup> was prepared according to General Procedure with FeBr<sub>2</sub> (4.3 mg, 0.02 mmol) or CeBr<sub>3</sub> (3.1 mg, 0.008 mmol) as the catalyst and using *tert*-butanol/H<sub>2</sub>O (20/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 56.7 mg, 88%; CeBr<sub>3</sub>(63.2 mg, 98%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.29–7.19 (m, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 3.41 (q, *J* = 7.7 Hz, 1H), 3.19

(s, 3H), 1.46 (d, J = 7.7 Hz, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.6, 143.9, 130.6, 127.8, 123.4, 122.3, 107.9, 40.5, 26.1, 15.3. IR 3502.9, 2971.9, 2932.9, 1702.7, 1610.2, 1463.8, 1345.9, 1255.6, 1093.2, 754.0 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>10</sub>H<sub>11</sub>NO [M]<sup>+</sup> 161.0835; found 161.0845.

### 1-Benzyl-3-methylindolin-2-one (2ad)



**2ad**<sup>4</sup> was prepared according to General Procedure with FeBr<sub>2</sub> (4.3 mg, 0.02 mmol) or CeBr<sub>3</sub> (3.1 mg, 0.008 mmol) as the catalyst and using *tert*-butanol/H<sub>2</sub>O (20/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 90.2 mg, 95%; CeBr<sub>3</sub>: 82.6 mg, 87%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.36–7.31 (m, 4H), 7.29 (ddt, *J* = 8.9, 5.5, 1.7 Hz, 2H), 7.19 (tt, *J* = 7.7, 1.1 Hz, 1H), 7.06 (td, *J* =

7.5, 1.0 Hz, 1H), 6.76 (d, J = 7.8 Hz, 1H), 4.95 (s, 2H), 3.57 (q, J = 7.6 Hz, 1H), 1.58 (d, J = 7.7 Hz, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.8, 143.1, 136.1, 130.7, 128.8, 127.8, 127.6, 127.3, 123.6, 122.5, 109.0, 43.7, 40.6, 15.7. IR 2053.9, 2972.5, 2927.4, 1706.7, 1608.9, 1480.9, 1458.4, 1350.9, 1166.5, 973.7, 743.8, 699.8 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>16</sub>H<sub>25</sub>NO [M]<sup>+</sup> 237.1148; found 237.1150.

### 3-(((*tert*-butyldimethylsilyl)oxy)ethyl)indolin-2-one (2ae)



**2ae<sup>10</sup>** was prepared according to General Procedure with FeBr<sub>2</sub> (4.3 mg, 0.02 mmol) or CeBr<sub>3</sub> (3.1 mg, 0.008 mmol) as the catalyst and using *tert*-butanol/H<sub>2</sub>O (20/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 99.1 mg, 85%; CeBr<sub>3</sub>: 97.9 mg, 84%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.68 (s, 1H), 7.26–7.16 (m, 2H), 7.01 (td, *J* = 7.5, 1.0 Hz, 1H), 6.94 (d,

J = 7.7 Hz, 1H), 3.88–3.76 (m, 2H), 3.62 (t, J = 6.4 Hz, 1H), 2.23 (dq, J = 13.8, 6.2 Hz, 1H), 2.11 (dq, J = 13.5, 6.6 Hz, 1H), 0.87 (s, 9H), 0.01 (d, J = 4.7 Hz, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 181.6, 142.0, 129.6, 127.9, 124.4, 122.1, 110.0, 59.8, 43.1, 33.3, 26.0, 18.3, -5.36, -5.41. IR 3205.7, 2934.0, 2858.4, 1703.7, 1619.6, 1469.9, 1248.4, 1101.1, 946.0, 833.4, 776.1, 742.8, 661.9 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>16</sub>H<sub>25</sub>NO<sub>2</sub>Si [M]<sup>+</sup> 291.1649; found 291.1645.

### 7-Ethyl-3-(((tert-butyldimethylsilyl)oxy)ethyl)indolin-2-one (2af)



**2af** was prepared according to General Procedure with FeBr<sub>2</sub> (4.3 mg, 0.02 mmol) or CeBr<sub>3</sub> (3.1 mg, 0.008 mmol) as the catalyst and using *tert*-butanol/H<sub>2</sub>O (20/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a white solid (FeBr<sub>2</sub>: 105 mg, 82%; CeBr<sub>3</sub>: 93.3 mg, 73%).M.P. 66–68 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 10.2 (s, 1H), 7.10 (t, *J* = 8.5 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.91 (t, *J* = 8.5 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.91 (t, *J* = 8.5 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.91 (t, *J* = 8.5 Hz, 2H), 6.91 (t, J = 8.5 Hz, 2H), 6.91 (t

1H), 3.96-3.79 (m, 2H), 3.65 (t, J = 6.6 Hz, 1H), 2.70 (q, J = 7.6 Hz, 2H), 2.25-2.10 (m, 2H), 1.30 (t, J = 7.6 Hz, 3H), 0.89 (brs, 9H), 0.04 (d, J = 4.2 Hz, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 182.1, 140.3, 129.5, 127.4, 125.8, 122.2, 121.7, 59.9, 43.3, 33.6, 26.0, 24.0, 18.4, 14.2, -5.3, -5.4. IR 3184.4, 2954.1, 2928.8, 2860.7, 1703.7, 1623.1, 1455.0, 1389.1, 1333.2, 1258.4, 1203.0, 1104.3, 1078.7, 1006.2, 946.0, 837.2, 750.9, 671.5 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>18</sub>H<sub>30</sub>NO<sub>2</sub>Si [M+H]<sup>+</sup> 320.2040; found 320.2038.

### Benzyl N-methyl-N-(2-(2-oxoindolin-3-yl)ethyl)carbamate (2ag)



 $2ag^{10}$  was prepared according to General Procedure with FeBr<sub>2</sub> (4.3 mg, 0.02 mmol) or CeBr<sub>3</sub> (3.1 mg, 0.008 mmol) as the catalyst and using *tert*-butanol/H<sub>2</sub>O (20/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 112 mg, 86%; CeBr<sub>3</sub>: 126

mg, 97%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 9.34 (d, *J* = 32.3 Hz, 1H), 7.40–7.30 (m, 6H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.12–6.98 (m, 1H), 6.90–6.85 (m, 1H), 5.18–5.00 (m, 2H), 3.76–3.27 (m, 3H), 2.92 (s, 3H), 2.30–2.05 (m, 2H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 180.4, 180.1, 156.2, 141.8, 136.9, 136.7, 129.2, 128.9, 128.5, 128.0, 127.8, 124.3, 123.9, 122.5, 122.4, 110.0, 67.2, 67.1, 46.3, 45.7, 43.8, 34.8, 34.2, 28.4, 28.2. IR 3218.6, 2930.1, 1698.6,

1618.3, 1471.8, 1403.2, 1188.0, 1135.8, 739.1, 695.2 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for  $C_{19}H_{20}N_2O_3$  [M]<sup>+</sup> 324.1468; found 124.1465.

#### tert-Butyl N-methyl-N-(2-(2-oxoindolin-3-yl)ethyl)carbamate (2ah)



**2ah** was prepared according to General Procedure with FeBr<sub>2</sub> (4.3 mg, 0.02 mmol) or CeBr<sub>3</sub> (3.1 mg, 0.008 mmol) as the catalyst and using *tert*-butanol/H<sub>2</sub>O (20/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 96.4 mg, 83%; CeBr<sub>3</sub>: 112 mg, 96%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.42–9.07 (m, 1H), 7.50–7.10 (m, 2H),

7.01 (t, J = 7.5 Hz, 1H), 6.91 (brs, 1H), 3.68–3.21 (m, 3H), 2.84 (brs, 3H), 2.30–1.98 (m, 2H), 1.42 (s, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.5, 180.2, 155.8, 141.8, 141.7, 129.4, 129.2, 128.1, 124.5, 124.0, 122.5, 110.0, 109.9, 79.7, 79.6, 46.0, 45.8, 43.9, 34.4, 28.5. IR 3233.7, 3056.1, 2978.2, 2932.4, 1692.9, 1620.7, 1472.5, 1396.9, 1326.2, 1264.6, 1230.0, 1163.3, 1050.4, 877.1, 733.3 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>16</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 291.1703; found 291.1705.

#### tert-Butyl N-methyl-N-(2-(5-methoxy-2-oxoindolin-3-yl)ethyl)carbamate (2ai)



**2ai** was prepared according to General Procedure with FeBr<sub>2</sub> (4.3 mg, 0.02 mmol) or CeBr<sub>3</sub> (3.1 mg, 0.008 mmol) as the catalyst and using *tert*-butanol/H<sub>2</sub>O (20/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 100 mg, 78%; CeBr<sub>3</sub>:

118 mg, 92%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.58 (d, J = 35.9 Hz, 1H), 7.06–6.59 (m, 3H), 3.73 (s, 3H), 3.63–3.15 (m, 3H), 2.80 (s, 3H), 2.13 (brs, 2H), 1.39 (brs, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.5, 180.1, 155.7, 135.3, 130.5, 112.6, 112.2, 111.5, 110.2, 79.5, 55.8, 45.9, 45.6, 44.3, 34.3, 28.4. IR 3233.6, 2956.4, 2923.1, 2870.8, 1689.4, 1605.0, 1483.3, 1451.7, 1395.1, 1367.0, 1302.6, 1269.0, 1205.0, 1146.4, 1033.0, 874.8, 809.8, 759.4, 646.3, 606.4 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>17</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 321.1809; found 321.1817.

### tert-Butyl N-benzyl-N-((S)-1-methoxycarbonyl-2-(2-oxoindolin-3-yl)ethyl)carbamate (2aj)



**2aj** was prepared according to General Procedure with FeBr<sub>2</sub> (4.3 mg, 0.02 mmol) or CeBr<sub>3</sub> (3.1 mg, 0.008 mmol) as the catalyst and using *tert*-butanol/H<sub>2</sub>O (20/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:1) as a light yellow oil (FeBr<sub>2</sub>: 153 mg, 90%; CeBr<sub>3</sub>: 156 mg, 92%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.83 (d, *J* = 44.5 Hz, 1H), 7.48–

7.11 (m, 6H), 7.05–6.80 (m, 3H), 5.15–4.03 (m, 3H), 3.66–3.27 (m, 4H), 2.80–2.50 (m, 1H), 2.49–1.95 (m, 1H), 1.63–1.33 (m, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.5, 180.2, 171.9, 171.8, 155.8, 141.6, 141.3, 138.0, 129.6, 129.3, 129.0, 128.4, 128.3, 128.1, 127.5, 123.9, 122.5, 110.0, 109.8, 81.1, 56.8, 56.5, 52.1, 52.0, 51.7, 42.8, 42.0, 31.5, 28.5. IR 3271.1, 2923.2, 2867.1, 1696.5, 1619.9, 1464.1, 1363.6, 1326.6, 1247.7, 1220.7, 1160.6, 1007.7, 863.3, 745.0, 699.0, 667.0 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub> [M]<sup>+</sup> 424.1993; found 424.1993.

### *N*-Methyl-*N*-[(*S*)-1-acetoxymethyl-2-(2-oxoindolin-3-yl)-ethyl]-acetamide (2ak)



2ak was prepared according to General Procedure with FeBr<sub>2</sub> (4.3 mg, 0.02 mmol) or CeBr<sub>3</sub> (3.1 mg, 0.008 mmol) as the catalyst and using *tert*-butanol/H<sub>2</sub>O (20/1, 2.1 mL) as the solvent and purified by flash column chromatography (ethyl acetate/hexane = 1:1 to 5:1) as a light yellow oil (FeBr<sub>2</sub>: 92.5 mg, 76%; CeBr<sub>3</sub>: 106 mg, 87%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 9.84–9.45 (m, 1H), 7.44–7.04 (m,

2H), 7.03–6.73 (m, 2H), 5.22–3.87 (m, 3H), 3.46–3.13 (m, 1H), 2.89–2.69 (m, 3H), 2.40–2.20 (m, 1H), 2.00– 1.92 (m, 4H), 1.91 (s, 1.5 H), 1.66 (s, 1.5 H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 179.8, 179.5, 179.0, 172.6, 172.1, 171.8, 170.6, 170.4, 142.5, 142.2, 141.9, 129.1, 128.5, 128.1, 128.0, 127.9, 124.5, 123.7, 123.6, 122.3, 122.19, 122.16, 110.4, 110.0, 109.9, 64.0, 63.9, 63.4, 53.0, 43.3, 43.0, 42.1, 28.9, 28.74, 28.67, 26.8, 22.2, 22.1, 20.73, 20.70, 20.60. IR 3223.1, 2955.9, 2924.5, 1707.9, 1621.5, 1472.4, 1403.3, 1372.4, 1334.8, 1231.2, 1102.8, 1039.0, 980.8, 752.7, 664.7, 600.7 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>16</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 305.1496; found 305.1510.

#### Indolin-2-one (2al)



2al<sup>20</sup> was prepared according to General Procedure with FeBr<sub>2</sub> (17.2 mg, 0.08 mmol) or CeBr<sub>3</sub> (24.4 mg, 0.064 mmol) and H<sub>2</sub>O<sub>2</sub> (30%, 176 µL, 1.76 mmol) and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 3:1) as a light yellow oil (FeBr<sub>2</sub>: 35.2 mg, 66%; CeBr<sub>3</sub>: 26.1 mg, 49%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 9.22 (brs, 1H), 7.25–7.16 (m, 2H), 7.01 (td, J = 7.5, 1.0 Hz, 1H), 6.92-6.85 (m, 1H), 3.54 (s, 2H).<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.3, 142.7, 128.0, 125.4, 124.7, 122.4, 110.0, 36.4. IR 3139.5, 3074.8, 1680.7, 1616.1, 1470.1, 1386.8, 1329.0, 1231.9, 1202.6, 863.3, 734.7, 672.1, 541.8 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>8</sub>H<sub>7</sub>NO [M]<sup>+</sup> 133.0522; found 133.0526.

# 1-(Methyl)indolin-2-one (2am)



**2am<sup>21</sup>** was prepared according to General Procedure with FeBr<sub>2</sub> (17.2 mg, 0.08 mmol) or CeBr<sub>3</sub> (24.4 mg, 0.064 mmol) and H<sub>2</sub>O<sub>2</sub> (30%, 176 µL, 1.76 mmol) and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as light yellow oil (FeBr<sub>2</sub>: 31.2 mg, 53%; CeBr<sub>3</sub>: 34.2 mg, 58%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.30–7.18 (m, 2H), 7.02 (td, J =

7.5, 1.0 Hz, 1H), 6.79 (d, J = 7.8 Hz, 1H), 3.48 (s, 2H), 3.18 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 175.1, 145.2, 127.9, 124.5, 124.3, 122.4, 108.1, 35.8, 26.2. IR 3388.3, 3057.4, 1695.9, 1611.2, 1464.8, 1346.0, 1263.0, 1125.9, 1089.0, 753.7, 655.4 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>9</sub>H<sub>9</sub>NO [M]<sup>+</sup> 147.0679; found 147.0687.

### 1-(Benzyl)indolin-2-one (2an)



2an<sup>22</sup> was prepared according to General Procedure with FeBr<sub>2</sub> (17.2 mg, 0.08 mmol) or CeBr<sub>3</sub> (24.4 mg, 0.064 mmol) and  $H_2O_2$  (30%, 176 µL, 1.76 mmol) and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light yellow oil (FeBr<sub>2</sub>: 49.1 mg, 55%; CeBr<sub>3</sub>: 50.0 mg, 56%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.37–7.23 (m, 6H), 7.17 (td, J = 7.8, 1.2

Hz, 1H), 7.01 (td, J = 7.5, 1.0 Hz, 1H), 6.74 (d, J = 7.8 Hz, 1H), 4.93 (s, 2H), 3.62 (s, 2H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 175.1, 144.3, 135.9, 128.8, 127.8, 127.6, 127.4, 124.5, 124.4, 122.4, 109.1, 43.7, 35.7. IR 3442.7, 3032.4, 2920.0, 1701.4, 1608.3, 1460.6, 1347.8, 1224.2, 1195.5, 1162.1, 877.0, 737.6, 600.9, 615.1, 544.7 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>15</sub>H<sub>13</sub>NO [M]<sup>+</sup> 223.0992; found 223.0996.

# 4-Methylindolin-2-one (2ap)



**2ap**<sup>23</sup> was prepared according to General Procedure with FeBr<sub>2</sub> (17.2 mg, 0.08 mmol) or CeBr<sub>3</sub> (24.4 mg, 0.064 mmol) and H<sub>2</sub>O<sub>2</sub> (30%, 176  $\mu$ L, 1.76 mmol) and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 3:1) as a light yellow oil (FeBr<sub>2</sub>: 49.5 mg, 84%; CeBr<sub>3</sub>: 45.9 mg, 78%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.90 (brs, 1H), 7.12 (t, *J* =

7.8 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 6.74 (d, J = 7.7 Hz, 1H), 3.42 (s, 2H), 2.25 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.0, 142.3, 134.4, 128.0, 124.3, 123.6, 107.4, 35.4, 18.7. IR 3082.4, 2911.8, 2836.9, 1722.4, 1663.3, 1463.3, 1463.0, 1317.4, 1258.7, 761.9 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>9</sub>H<sub>9</sub>NO [M+H]<sup>+</sup> 148.0757; found 148.0759.

#### 6-Fluoroindolin-2-one (2aq)



**2aq** was prepared according to General Procedure with FeBr<sub>2</sub> (17.2 mg, 0.08 mmol) or CeBr<sub>3</sub> (24.4 mg, 0.064 mmol) and H<sub>2</sub>O<sub>2</sub> (30%, 176  $\mu$ L, 1.76 mmol) and purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a white solid (FeBr<sub>2</sub>: 46.9 mg, 71%; CeBr<sub>3</sub>: 48.9 mg, 74%). M.P. 98–100 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.13 (dd,

J = 7.7, 5.3 Hz, 1H), 6.68 (ddd, J = 10.1, 8.1, 2.4 Hz, 1H), 6.52 (dd, J = 8.9, 2.4 Hz, 1H), 3.44 (s, 2H), 3.15 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 175.4, 161.8 (d,  $J_{C,F} = 243$  Hz), 146.6 (d,  $J_{C,F} = 11.5$  Hz), 125.1 (d,  $J_{C,F} = 9.5$  Hz), 119.6 (d,  $J_{C,F} = 3$  Hz), 108.2 (d,  $J_{C,F} = 22$  Hz), 96.8 (d,  $J_{C,F} = 27.5$  Hz), 35.2, 26.3. IR 3063.5, 2952.7, 2921.4, 1712.2, 1659.5, 1616.1, 1501.2, 1459.5, 1374.3, 1334.7, 1294.6, 1259.7, 1209.9, 1121.7, 1065.7, 961.3, 869.2, 799.2, 651.8, 608.7 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>9</sub>H<sub>9</sub>FNO [M+NH<sub>4</sub>]<sup>+</sup> 183.0928; found 183.0929.

#### 6. Gram-scale oxidation of indole 1ab using H<sub>2</sub>O<sub>2</sub>/FeBr<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>/CeBr<sub>3</sub> at RT under open-air condition



To a stirred solution of compound **1ab** (1.00 g, 7.62 mmol) in *t*-BuOH/H<sub>2</sub>O (20/1, 21 mL) was added FeBr<sub>2</sub> (49.6 mg, 0.23 mmol) or CeBr<sub>3</sub> (34.6 mg, 0.091 mmol). A solution of H<sub>2</sub>O<sub>2</sub> (30%, 1.68 mL, 16.8 mmol) in *t*-BuOH/H<sub>2</sub>O (20/1, 4.2 mL) was added dropwise to the reaction mixture. After completion of the addition, the

resulting mixture was allowed to stir for additional 1-5 h. The reaction was quenched by dilute aqueous  $Na_2S_2O_3$  solution (0.3 M, 100 mL) and ethyl acetate (100 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2×40 mL). The combined organic fractions were washed with H<sub>2</sub>O, dried over  $Na_2SO_4$ , filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (ethyl acetate/hexane = 1:2 to 3:1) to give compound **2ab** (FeBr<sub>2</sub>: 931 mg, 83%; CeBr<sub>3</sub>: 909 mg, 81%).

# 7. Green chemistry metrics analysis:

# E-Factor for 2ab using H<sub>2</sub>O<sub>2</sub>/FeBr<sub>2</sub> (This Work):



Total amount of reactants: 52.5 mg + 4.3 mg + 29.3 mg = 86.1 mgAmount of final product: 52.4 mgAmount of waste: 86.1 mg - 52.4 mg = 33.7 mgE-Factor = Amount of waste/Amount of product = 33.7/52.4 = 0.64

#### AE for 2ab using H<sub>2</sub>O<sub>2</sub>/FeBr<sub>2</sub> (This Work):



Molecular weight of product: 147.2

Sum of molecular weight of reagent: 131.2 + 34 = 165.2

Atom economy = Molecular weight of product/Sum of molecular weight of reagent = 147.2/165.2 = 89.1%

### RME for 2ab using H<sub>2</sub>O<sub>2</sub>/FeBr<sub>2</sub> (This Work):



Mass of product: 52.4 mg

Total mass of reagent: 52.5 mg + 29.3 mg = 81.8 mgRME = Mass of product/Total mass of reagent = 52.4/81.8 = 64.1%

# PMI for 2ab using H<sub>2</sub>O<sub>2</sub>/FeBr<sub>2</sub> (This Work):



Total mass in process: 52.5 mg + 4.3 mg + 29.3 mg = 86.1 mg Mass of product: 52.4 mg

PMI = Total mass in process/Mass of product = 86.1/52.4 = 1.64

Green chemistry metrics for other compounds and protocols were calculated following the above procedures, which were similar to compound **1ab**.

#### 8. Controlled experiments for indole oxidation.



To a stirred solution of compound **1a** (27.2 mg, 0.1 mmol) in THF/H<sub>2</sub>O (10/1, 0.6 mL) were added KBr (with or without, 1.2 mg, 0.01 mmol), metal catalyst (0.01 mmol) and H<sub>2</sub>O<sub>2</sub> (30 wt%, 30  $\mu$ L, 0.3 mmol). After completion of the addition, the reaction mixture was allowed to stir 3 h at RT. The reaction was quenched by dilute aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (0.1 M, 5 mL) and ethyl acetate (10 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2×10 mL). The combined organic fractions were washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Yield was determined by <sup>1</sup>H-NMR of the crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal reference.

#### 9. Radical trapping (ABTS) experiments for indole oxidation.



**Procedure using H<sub>2</sub>O<sub>2</sub>/FeBr<sub>2</sub> or CeBr<sub>3</sub> protocol**: To a stirred solution of compound **1a** (54.5 mg, 0.2 mmol) in THF/H<sub>2</sub>O (10/1, 1.2 mL) were added ABTS (with or without, 110 mg, 0.2 mmol), and the mixture was stirred for 5 min. Then H<sub>2</sub>O<sub>2</sub> (30%, 60  $\mu$ L, 0.6 mmol) and FeBr<sub>2</sub> (0.02 mmol) or CeBr<sub>3</sub> (0.02 mmol) were added, and the resulting solution was stirred at rt for 3 h. The reaction was quenched by dilute aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (0.1 M, 4 mL) and ethyl acetate (10 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2×4 mL). The combined organic fractions were washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Yield was determined by <sup>1</sup>H-NMR of the crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal reference.

**Procedure using Oxone protocol**: To a stirred solution of compound **1a** (54.5 mg, 0.2 mmol) in MeCN/H<sub>2</sub>O (10/1, 2 mL) were added ABTS (with or without, 110 mg, 0.2 mmol), and the mixture was stirred for 5 min. Then Oxone (MW = 307, 73.7 mg, 0.24 mmol) and KBr (1.2 mg, 0.01 mmol) were added at 0 °C, and the resulting solution was stirred at RT for 3 h. The reaction was quenched by dilute aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (0.1 M, 4 mL) and ethyl acetate (10 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2×4 mL). The combined organic fractions were washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Yield was determined by <sup>1</sup>H-NMR of the crude reaction mixture using CH<sub>2</sub>Br<sub>2</sub> as the internal reference.

# 10. EPR spectrum for MBr<sub>x</sub>-H<sub>2</sub>O<sub>2</sub> with the presence of DMPO:



**Experimental procedure:** The above spectra were obtained with a solution containing DMPO (33 mM),  $H_2O_2$  (10 mM), FeBr<sub>2</sub> (1 mM) or CeBr<sub>3</sub> (1 mM) in distilled water. To a solution of FeBr<sub>2</sub> or CeBr<sub>3</sub> and DMPO in distilled water was added  $H_2O_2$ , and the incubation time was 1 min (FeBr<sub>2</sub>) or 10 min (CeBr<sub>3</sub>) before EPR spectrum were recorded.

# 11. RBS trapping and isotopic experiments.



**11.1. Preparation of compound 4:** To a stirred solution of arene  $3^{24}$  (58.0 mg, 0.3 mmol) in MeCN (1.5 mL) was added FeBr<sub>2</sub> (97.1 mg, 0.45 mmol) or CeBr<sub>3</sub> (79.8 mg, 0.21 mmol). To the reaction mixture was added aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%, 99 µL, 0.99 mmol when FeBr<sub>2</sub> was used; or 30 wt%, 66 µL, 0.66 mmol when CeBr<sub>3</sub> was used) portionwise in 4 time over 1 h. After completion of the addition, the reaction mixture was stirred at RT for 0.5-1 h. The reaction was quenched by dilute aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (0.1 M, 10 mL) and ethyl acetate (20 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2×10 mL). The combined organic fractions were washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give compound **4**.

# N-(tert-Butoxycarbonyl)-4-bromoaniline (4)

NHBoc  $4^{25}$  was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:4) as a light yellow oil (FeBr<sub>2</sub>: 58.0 mg, 71%; CeBr<sub>3</sub>: 69.4 mg, 85%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.39 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 6.65 (s, 1H), 1.53 (s, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 152.7, 137.6, 131.9, 120.2, 115.5, 81.0, 28.4. IR 3365.3, 2980.1, 1693.6, 1589.4, 1515.4, 1392.7, 1238.4, 1159.0, 1061.8, 816.5, 765.7, 615.2, 528.7 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (m/z) calcd. for C<sub>11</sub>H<sub>14</sub>BrNO<sub>2</sub>





**11.2. Isotopic experiment using H**<sub>2</sub><sup>18</sup>**O**: To a stirred solution of indole **1a** (27.2 mg, 0.1 mmol) in THF/H<sub>2</sub><sup>18</sup>**O** (1/1, 0.6 mL) was added FeBr<sub>2</sub> (2.16 mg, 0.01 mmol) or CeBr<sub>3</sub> (3.80 mg, 0.01 mmol). Then aqueous H<sub>2</sub>O<sub>2</sub> (30 wt%, 22  $\mu$ L, 0.22 mmol) was added to the solution. After completion of the addition, the reaction mixture was stirred at RT for 3 h before quenched by dilute aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (0.1 M, 3 mL) and ethyl acetate (20 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2×10 mL). The combined organic fractions were washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give compound **2a** (FeBr<sub>2</sub>: 17.6 mg; CeBr<sub>3</sub>: 23.1 mg). HRMS (ESI<sup>+</sup>) (m/z) calcd. for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>Na<sup>18</sup>O [M+Na]<sup>+</sup> 313.1409; found FeBr<sub>2</sub>: 313.1405; CeBr<sub>3</sub>: 313.1404.



# 12. References:

- M. Géraldy, M. Morgen, P. Sehr, R. R. Steimbach, D. Moi, J. Ridinger, I. Oehme, O. Witt, M. Malz, M. S. Nogueira, O. Koch, N. Gunkel and A. K. Miller, *J. Med. Chem.*, 2019, **62**, 4426-4443.
- 2. J. Ye, J. Wu, T. Lv, G. Wu, Y. Gao and H. Chen, *Angew. Chem., Int. Ed.*, 2017, **56**, 14968-14972.
- 3. J. Ye, Y. Lin, Q. Liu, D. Xu, F. Wu, B. Liu, Y. Gao and H. Chen, *Org. Lett.*, 2018, **20**, 5457-5460.
- 4. J. Xu, L. Liang, H. Zheng, Y. R. Chi and R. Tong, *Nat. Commun.*, 2019, **10**, 4754-4764.
- 5. L. Chen, J. Xie, H. Song, Y. Liu, Y. Gu, L. Wang and Q. Wang, J. Agr. Food Chem., 2016, 64, 6508-6516.
- 6. X. Zhang, X. Li, J. C. Lanter and Z. Sui, *Org. Lett.*, 2005, **7**, 2043-2046.
- Z. Zhang, V. Smal, P. Retailleau, A. Voituriez, G. Frison, A. Marinetti and X. Guinchard, J. Am. Chem. Soc., 2020, 142, 3797-3805.
- 8. C. Shao, G. Shi, Y. Zhang, S. Pan and X. Guan, *Org. Lett.*, 2015, **17**, 2652-2655.
- 9. J. Zhang and F.-S. Han, J. Org. Chem., 2019, 84, 13890-13896.
- 10. S. De, M. K. Das, S. Bhunia and A. Bisai, Org. Lett., 2015, **17**, 5922-5925.
- 11. R. H. Snell, M. J. Durbin, R. L. Woodward and M. C. Willis, *Chem.–Eur. J.*, 2012, **18**, 16754-16764.
- 12. F. Zamani, S. G. Pyne and C. J. T. Hyland, *J. Org. Chem.*, 2017, **82**, 6819-6830.
- 13. S. K. Banjare, T. Nanda and P. C. Ravikumar, *Org. Lett.*, 2019, **21**, 8138-8143.
- 14. X. Jiang, J. Yang, F. Zhang, P. Yu, P. Yi, Y. Sun and Y. Wang, *Org. Lett.*, 2016, **18**, 3154-3157.
- 15. Z. Hou, L.-F. Zhu, X.-c. Yu, M.-Q. Sun, F. Miao and L. Zhou, J. Agr. Food Chem., 2016, 64, 2847-2854.
- 16. S. Gore, S. Baskaran and B. König, *Org. Lett.*, 2012, **14**, 4568-4571.
- 17. M.-M. Liang, Y.-Y. Ma, L. Zhu, Y.-J. Jia, H.-J. Zhu, W. Li and B.-D. Zhou, *Tetrahedron*, 2018, **74**, 4197-4204.
- 18. W. Kong, Q. Wang and J. Zhu, Angew. Chem., Int. Ed., 2017, 56, 3987-3991.
- 19. X.-L. Liu, Y.-H. Liao, Z.-J. Wu, L.-F. Cun, X.-M. Zhang and W.-C. Yuan, J. Org. Chem., 2010, **75**, 4872-4875.
- 20. T. V. Nykaza, G. Li, J. Yang, M. R. Luzung and A. T. Radosevich, *Angew. Chem., Int. Ed.*, 2020, **59**, 4505-4510.
- 21. Z.-Z. Zhou, J.-H. Zhao, X.-Y. Gou, X.-M. Chen and Y.-M. Liang, Org. Chem. Front., 2019, 6, 1649-1654.
- 22. S.-L. Ding, Y. Ji, Y. Su, R. Li and P. Gu, J. Org. Chem., 2019, 84, 2012-2021.
- 23. M. Kawase, T. Kitamura and Y. Kikugawa, J. Org. Chem., 1989, 54, 3394-3403.
- 24. M. Chen, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, J. Org. Chem., 2015, 80, 1258-1263.
- 25. S. M. Maddox, C. J. Nalbandian, D. E. Smith and J. L. Gustafson, *Org. Lett.*, 2015, **17**, 1042-1045.







S-35




































S-53









·····

11





| Li 2.000000 sec<br>Di 2.000000 sec<br>Di 0.0300000 sec<br>Di 0.0300000 sec<br>Di 0.0300000 sec<br>Di 0.0300000 sec<br>Di 0.0300000 sec<br>NUCL 13C<br>PLI 8.60 usec<br>PLI -3.00 dB<br>PLW 60.64365387 W<br>SFOO<br>CRANNEL F2<br> |       |       | OTIPS      | <br>42.882<br>36.351<br>28.368 | 21.777<br> | NAME<br>EXPNO<br>PROCNO<br>Date<br>Time<br>INSTRUM<br>PROBHD<br>PULPROG<br>TD<br>SOLVENT<br>NS<br>DS<br>SWH<br>FIDRES<br>AQ<br>RG<br>DW<br>DE<br>TF | zgx154<br>4<br>1<br>20200502<br>15.30<br>spect<br>5 mm PABBO BB-<br>zgpg30<br>65536<br>CDC13<br>79<br>0<br>24038.461 Hz<br>0.366798 Hz<br>1.3631988 sec<br>161<br>20.800 usec<br>6.00 usec<br>205 2 K           |
|--|-------|-------|------------|--------------------------------|------------|---|---|
|  | Í     | N H N | √_Ac<br>1e |                                |            | D1<br>D11<br>TD0<br>========<br>NUC1<br>P1<br>PL1<br>PL1W<br>SF01   | 2.00000000 sec<br>0.03000000 sec<br>1<br>CHANNEL f1<br>8.60 usec<br>-3.00 dB<br>60.64365387 W<br>100.6228298 MHz  |
|  | 11111 |       |            |                                |            | CPDPRG2<br>NUC2<br>PCPD2<br>PL12<br>PL13<br>PL13W<br>PL12W<br>PL13W<br>SF02<br>SF<br>WDW<br>SSB<br>LB<br>GB<br>PC                                   | CHANNEL f2<br>waltz16<br>1H<br>80.00 usec<br>-1.00 dB<br>14.39 dB<br>18.00 dB<br>12.17476940 W<br>0.3519357 W<br>0.15327126 W<br>400.1316005 MHz<br>32768<br>100.6127676 MHz<br>EM<br>0<br>1.00 Hz<br>0<br>1.40 |













·\*\*\*\*













3111



















































































































77


































S-147

|  | 142.73  | 128.03  | 109.99  |         |   | SCH NAME<br>EXPND<br>Date<br>Time<br>PROB<br>PULP<br>TD<br>SOLV<br>NS<br>DS<br>SWH<br>FIDR<br>AQ<br>RG<br>DW<br>DE<br>TE<br>D1<br>D11<br>TD0 | zgx155<br>C 5<br>NO 1<br>- 20200502<br>- 22.15<br>RUM spect<br>HD 5 mm PABBO BB-<br>ROG 2gpg30<br>65536<br>ENT CDC13<br>43<br>0<br>24038.461 Hz<br>ES 0.366798 Hz<br>1.3631988 sec<br>144<br>20.800 usec<br>6.00 usec<br>296.7 K<br>2.00000000 sec<br>0.03000000 sec<br>1 |
|--|---|---------|---------|---------|---|--|---|
| ⊣<br>2al   |   |         |         |         |   | ====<br>NUC1<br>P1<br>PL1<br>PL1W<br>SF01  | ==== CHANNEL f1 =======<br>13C<br>8.60 usec<br>-3.00 dB<br>60.64365387 W<br>100.6228298 MHz   |
| ב להאל קינטראי או היינט לעני או היינט או איז | i sa ana ji ci wa a ji ci kati ula<br>V pacingan ja pangana ang |         |         |         | novika til å støtte og to gette kal kal kal som | CPDP<br>NUC2<br>PCPD<br>PL12<br>PL13<br>PL12<br>PL13<br>SF02<br>SI<br>SF<br>WDW<br>SSB<br>LB<br>GB<br>PC                                     | === CHANNEL f2 =====<br>RG2 waltz16<br>1H<br>2 80.00 usec<br>-1.00 dB<br>14.39 dB<br>12.17476940 W<br>W 0.35193357 W<br>W 0.15327126 W<br>400.1316005 MHz<br>32768<br>100.6127590 MHz<br>EM<br>0<br>1.00 Hz<br>0<br>1.40  |
| 210 200 190 180 170 160  | 150 140   | 130 120 | 110 100 | 90 80 7 | 0 60 50   | 40 30 2  | 20 10 0 –10 ppn   |



S-149













|                     |                |             | 96.8186              | 9895<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>100<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1000<br>1 | zgx185<br>5<br>1<br>20200508<br>14.50<br>4 spect<br>5 mm PABBO BB-<br>3 zgpg30<br>65536<br>F CDC13<br>41<br>0<br>24038.461 Hz<br>0 366798 Hz  |
|---------------------|----------------|-------------|----------------------|--|---|
| F<br>2ac            | N O<br>Me<br>a |             | 1                    | AQ<br>AQ<br>RG<br>DW<br>DE<br>TE<br>D1<br>D11<br>TD0<br>NUC1<br>P1<br>PL1<br>PL1W  | 1.3631988 sec<br>128<br>20.800 usec<br>301.2 K<br>2.0000000 sec<br>0.03000000 sec<br>1<br>== CHANNEL f1<br>8.60 usec<br>-3.00 dB<br>60.64365387 W   |
|                     |                |             |                      | SFO1<br>   | 100.6228298 MHz<br>== CHANNEL f2 ========<br>2 waltz16<br>1H<br>80.00 usec<br>-1.00 dB<br>14.39 dB<br>12.17476940 W<br>0.35193357 W<br>0.15327126 W<br>400.1316005 MHz<br>32768<br>100.6127620 MHz<br>EM<br>0<br>1.00 Hz<br>0<br>1.40 |
| 210 200 190 180 170 | 160 150 140    | 130 120 110 | 100 90 80 70 60 50 4 | lo 30 20   | 10 0 –10 ppm  |