Supporting Information

Easy conjugations between molecules via copper-catalyzed reactions of ortho-aromatic diamines with ketones

Juyou Lu, a,b Haijun Yang, a Yunhe Jin, a Yuyang Jiang, c and Hua Fu a,c*

a Key Laboratory of Bioorganic Phosphorus Chemistry and Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China. *e-mail: fuhua@mail.tsinghua.edu.cn
b Xi’an Modern Chemistry Research Institute, Xi’an 710065, P. R. China
c Key Laboratory of Chemical Biology (Guangdong Province), Graduate School of Shenzhen, Tsinghua University, Shenzhen 518057, P. R. China

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A: General experimental procedures
Proton and carbon magnetic resonance spectra (\(^1\)H NMR and \(^{13}\)C NMR) were recorded using tetramethylsilane (TMS). Chemical shifts (\(\delta\)) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl\(_3\): \(\delta_H = 7.26\) ppm, \(\delta_C = 77.16\) ppm; DMSO-d\(_6\): \(\delta_H = 2.50\) ppm, \(\delta_C = 39.52\) ppm; CD\(_3\)OD: \(\delta_H = 3.31\) ppm, \(\delta_C = 49.00\) ppm).

B: General Procedure for Copper-Catalyzed Conjugations of ortho-Aromatic Diamines with Ketones. A 25 mL flask was charged with a magnetic stirrer and ethanol (2.0 mL) or water/ethanol (v/v = 10:1) (3.3 mL) (for 3g' and 3h'), \(o\)-aromatic diamine (1) (1.0 mmol), ketone (2) (1.2 mmol) and Cu(OAc)\(_2\) (0.05 mmol, 9.1 mg) were added to the flask. The mixture was stirred at room temperature (~25 °C) under air. After the conjugation completed (TLC determination), the resulting solution was concentrated by a rotary evaporator, and the residue was purified by column chromatography on silica gel using an eluent (petroleum ether/ethyl acetate, ethyl acetate/methanol, ethyl acetate/ethanol or diethyl ether) to provide the desired target product (3a-h').

C: Characterization data of compounds 3a-h'

2,2-Dimethyl-2\(^H\)-benzo[\(d\)]imidazole (3a).\(^1\) Eluent: diethyl ether. Yield: 133 mg (91%) as a yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \(\delta 7.19\) (dd, 2H, \(J = 7.3, 2.7\) Hz), 7.00 (dd, 2H, \(J = 7.3, 2.7\) Hz), 1.54 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) \(\delta 159.5, 134.5, 126.0, 104.4, 21.6\). ESI-MS [M+H]\(^+\) m/z 147.3.

2-Ethyl-2-methyl-2\(^H\)-benzo[\(d\)]imidazole (3b).\(^2\) Eluent: diethyl ether. Yield: 152 mg (95%) as a yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \(\delta 7.20\) (dd, 2H, \(J = 7.3, 3.2\) Hz), 7.01 (dd, 2H, \(J = 7.3, 3.2\) Hz), 2.07 (q, 2H, \(J = 7.3\) Hz), 1.51 (s, 3H), 0.74 (t, 3H,
$J = 7.3$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 159.8, 134.4, 125.8, 107.1, 29.3, 19.9, 8.9. ESI-MS [M+H]$^+$ m/z 161.5.

![2-isoPropyl-2-methyl-2H-benzo[d]imidazole (3c).](image)

2-isoPropyl-2-methyl-2H-benzo[d]imidazole (3c). Eluent: diethyl ether. Yield: 136 mg (78%) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.20 (dd, 2H, $J = 7.3$, 2.7 Hz), 7.00 (dd, 2H, $J = 7.3$, 2.7 Hz), 2.30 (m, 1H, $J = 6.8$ Hz), 1.47 (s, 3H), 0.95 (d, 6H, $J = 6.8$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 159.8, 134.4, 125.7, 109.8, 35.0, 18.6, 18.3. HR-MS [M+H]$^+$ m/z calcd for C$_{11}$H$_{15}$N$_2$ 175.1235, found 175.1231.

![2-Methyl-2-pentyl-2H-benzo[d]imidazole (3d).](image)

2-Methyl-2-pentyl-2H-benzo[d]imidazole (3d). Eluent: diethyl ether. Yield: 188 mg (93%) as a yellow oil. $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 7.20 (dd, 2H, $J = 7.2$, 2.7 Hz), 7.00 (dd, 2H, $J = 7.2$, 2.7 Hz), 2.00-1.97 (m, 2H), 1.51 (s, 3H), 1.26-1.11 (m, 6H), 0.83 (t, 3H, $J = 6.8$ Hz). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) $\delta$ 159.7, 134.4, 125.8, 107.1, 36.2, 32.0, 24.1, 22.4, 20.4, 14.0. HR-MS [M+H]$^+$ m/z calcd for C$_{13}$H$_{19}$N$_2$ 203.1548, found 203.1543.

![2,2-Diethyl-2H-benzo[d]imidazole (3e).](image)

2,2-Diethyl-2H-benzo[d]imidazole (3e). Eluent: diethyl ether. Yield: 151 mg (87%) as a brown oil. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.20 (dd, 2H, $J = 7.8$, 2.7 Hz), 7.01 (dd, 2H, $J = 7.8$, 2.7 Hz), 2.12 (q, 4H, $J = 7.3$ Hz), 0.67 (t, 6H, $J = 7.3$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 160.3, 134.4, 125.6, 109.9, 27.8, 8.4. ESI-MS [M+H]$^+$ m/z 175.6.

![2,2-Dipropyl-2H-benzo[d]imidazole (3f).](image)

2,2-Dipropyl-2H-benzo[d]imidazole (3f). Eluent: ethyl acetate/petroleum ether = 1:30. Yield: 172 mg (85%) as a brown oil. $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 7.19 (dd, 2H, $J = 7.5$, 3.1 Hz), 7.00 (dd, 2H, $J = 7.5$, 3.1 Hz), 2.06-2.01 (m, 4H), 1.07-0.99 (m, 4H), 0.82 (t, 6H, $J = 7.2$ Hz). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) $\delta$ 160.1, 134.3,
125.6, 109.7, 37.3, 17.2, 14.3. HR-MS \([\text{M+H}]^+\) m/z calcd for \(C_{13}H_{19}N_2\) 203.1548, found 203.1546.

2,2-Dibutyl-2\(H\)-benzo[\(d\)]imidazole (3g). Eluent: ethyl acetate/petroleum ether = 1:20. Yield: 140 mg (61%) as a yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 7.20 (dd, 2H, \(J = 7.3, 2.7\) Hz), 7.00 (dd, 2H, \(J = 7.3, 2.7\) Hz), 2.07-2.02 (m, 4H), 1.26-1.20 (m, 4H), 1.02-0.98 (m, 4H), 0.82 (t, 6H, \(J = 7.3\) Hz). \(^1\)C NMR (100 MHz, CDCl\(_3\), ppm) \(\delta\) 160.0, 134.2, 125.5, 109.4, 37.3, 17.2, 14.3. HR-MS \([\text{M+H}]^+\) m/z calcd for \(C_{13}H_{19}N_2\) 203.1546, found 203.1546.

2-Cyclohexyl-2-methyl-2\(H\)-benzo[\(d\)]imidazole (3h). Eluent: ethyl acetate/petroleum ether = 1:20. Yield: 160 mg (75%) as a yellow oil. \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm) \(\delta\) 7.19 (dd, 2H, \(J = 7.5, 3.1\) Hz), 6.99 (dd, 2H, \(J = 7.5, 3.1\) Hz), 1.99 (tt, 1H, \(J = 11.3, 2.7\) Hz), 1.78-1.60 (m, 5H), 1.45 (s, 3H), 1.25-1.01 (m, 5H). \(^1\)C NMR (75 MHz, CDCl\(_3\), ppm) \(\delta\) 159.7, 134.3, 125.8, 109.6, 44.8, 28.6, 26.7, 26.2, 18.6. HR-MS \([\text{M+H}]^+\) m/z calcd for \(C_{14}H_{19}N_2\) 215.1548, found 215.1542.

Compound 3i.\(^3\) Eluent: ethyl acetate/petroleum ether = 1:30. Yield: 165 mg (89%) as a brown oil. \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm) \(\delta\) 7.22 (dd, 2H, \(J = 7.2, 3.1\) Hz), 7.00 (dd, 2H, \(J = 7.2, 3.1\) Hz), 2.20-1.92 (m, 4H), 1.79-1.72 (m, 2H), 1.65-1.64 (m, 4H). \(^1\)C NMR (75 MHz, CDCl\(_3\), ppm) \(\delta\) 159.4, 134.2, 126.0, 107.2, 32.6, 25.6, 24.7. ESI-MS \([\text{M+H}]^+\) m/z 187.3.

Compound 3j.\(^4\) Eluent: ethyl acetate/petroleum ether = 1:30. Yield: 180 mg (90%) as a brown oil. \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm) \(\delta\) 7.26-7.18 (m, 2H), 7.01-6.98 (m,
2H), 2.40 (t, 2H, J = 12.3 Hz), 1.92-1.89 (m, 2H), 1.74-1.66 (m, 3H), 1.09 (d, 3H, J = 5.5 Hz), 0.96 (d, 2H, J = 12.3 Hz). 13C NMR (75 MHz, CDCl3, ppm) δ 159.8, 159.1, 134.2, 134.1, 126.0, 125.9, 117.0, 33.1, 32.3, 31.9, 21.9. ESI-MS [M+H]+ m/z 201.2.

![Compound 3k](image)

Compound 3k. Eluent: ethyl acetate/petroleum ether = 1:30. Yield: 193 mg (90%) as a brown oil. 1H NMR (300 MHz, CDCl3, ppm) δ 7.26-7.18 (m, 2H), 7.01-6.98 (m, 2H), 2.38 (td, 2H, J = 13.0, 3.4 Hz), 2.00-1.95 (m, 2H), 1.74-1.60 (m, 2H), 1.52-1.40 (m, 3H), 1.00-0.95 (m, 5H). 13C NMR (75 MHz, CDCl3, ppm) δ 159.8, 159.0, 134.2, 134.1, 126.0, 125.9, 107.4, 38.7, 32.3, 30.8, 30.5, 29.2, 11.7. HR-MS [M+H]+ m/z calcd for C14H19N2 215.1548, found 215.1542.

![Compound 3l](image)

Compound 3l. Eluent: ethyl acetate/petroleum ether = 1:30. Yield: 225 mg (93%) as a white solid. mp 141-143 °C. 1H NMR (300 MHz, CDCl3, ppm) δ 7.27-7.18 (m, 2H), 6.99 (dd, 2H, J = 7.5, 3.1 Hz), 2.47 (td, 2H, J = 13.4, 3.1 Hz), 1.99-1.95 (m, 2H), 1.76 (qd, 2H, J = 12.7, 2.7 Hz), 1.39-1.26 (m, 2H), 0.97 (s, 9H), 0.92-0.87 (m, 1H). 13C NMR (75 MHz, CDCl3, ppm) δ 159.8, 159.0, 134.1, 126.1, 125.9, 107.1, 47.9, 33.1, 32.5, 27.8, 25.8. HR-MS [M+H]+ m/z calcd for C14H23N2 243.1861, found 243.1863.

![Compound 3m](image)

Compound 3m. Eluent: ethyl acetate/petroleum ether = 1:30. Yield: 235 mg (91%) as a brown oil. 1H NMR (300 MHz, CDCl3, ppm) δ 7.26-7.18 (m, 2H), 7.03 (dd, 2H, J = 7.5, 2.7 Hz), 4.19 (q, 2H, J = 7.2 Hz), 2.70-2.63 (m, 1H), 2.27-2.18 (m, 6H), 1.29 (t, 3H, J = 7.2 Hz), 1.26-1.22 (m, 2H). 13C NMR (75 MHz, CDCl3, ppm) δ 175.0, 159.9, 159.4, 134.5, 134.4, 125.9, 125.8, 106.1, 60.3, 42.0, 31.3, 26.9, 14.2. HR-MS [M+H]+ m/z calcd for C15H19N2O2 259.1447, found 259.1441.

![Compound 3n](image)

Compound 3n. Eluent: ethyl acetate/petroleum ether = 1:20. Yield: 176 mg (88%) as a
yellow solid. mp 92-93 °C. $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 7.18 (dd, 2H, $J = 7.5, 3.1$ Hz), 6.97 (dd, 2H, $J = 7.5, 3.1$ Hz), 1.98-1.96 (m, 4H), 1.84-1.80 (m, 4H), 1.72-1.69 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) δ 158.9, 134.2, 126.0, 110.9, 34.0, 29.9, 25.1. HR-MS [M+H]$^+$ m/z calcd for C$_{13}$H$_{17}$N$_2$ 201.1392, found 201.1389.

 Compound 3o. Eluent: ethyl acetate/petroleum ether = 1:20. Yield: 156 mg (73%) as a yellow solid. mp 103-105 °C. $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 7.20 (dd, 2H, $J = 7.5, 3.1$ Hz), 6.98 (dd, 2H, $J = 7.5, 3.1$ Hz), 1.99-1.98 (m, 4H), 1.84-1.73 (m, 6H), 1.68-1.64 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) δ 159.2 134.3, 126.2, 110.8, 30.0, 28.6, 25.1, 25.0. HR-MS [M+H]$^+$ m/z calcd for C$_{14}$H$_{19}$N$_2$ 215.1548, found 215.1543.

 Compound 3p. Eluent: ethyl acetate/petroleum ether = 1:20. Yield: 189 mg (70%) as a white solid. mp 111-112 °C. $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 7.73-7.70 (m, 1H), 7.29-7.24 (m, 1H), 7.20 (dd, 2H, $J = 6.1, 3.1$ Hz), 4.09 (t, 2H, $J = 7.5$ Hz), 2.89 (t, 2H, $J = 7.5$ Hz), 2.00-1.85 (m, 4H), 1.50-1.31 (m, 12H), 1.23-1.20 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) δ 155.1, 142.8, 135.4, 121.8, 121.6, 119.2, 109.2, 42.5, 26.9, 25.9, 25.6, 25.5, 25.2, 25.1, 24.6, 24.5, 23.8. HR-MS [M+H]$^+$ m/z calcd for C$_{18}$H$_{27}$N$_2$ 271.2174, found 271.2171.

 Compound 3q. Eluent: ethyl acetate/petroleum ether = 1:30. Yield: 178 mg (57%) as a yellow solid. mp 56-58 °C. $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 7.20 (dd, 2H, $J = 7.3, 2.7$ Hz), 6.99 (dd, 2H, $J = 7.3, 2.7$ Hz), 1.76-1.73 (m, 4H), 1.59-1.55 (m, 4H), 1.41-1.40 (m, 20H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 159.4, 134.3, 126.1, 110.3, 32.6, 27.8, 27.1, 26.7, 26.6, 26.4, 24.7. HR-MS [M+H]$^+$ m/z calcd for C$_{21}$H$_{33}$N$_2$
313.2644, found 313.2643.

![Structural formula of 3r](image)

**2-Methyl-2-(4-nitrophenyl)-2H-benzo[d]imidazole (3r).** Eluent: ethyl acetate/petroleum ether = 1:20. Yield: 147 mg (58%) as a yellow solid. mp 168-169 °C. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 8.18 (d, 2H, $J = 8.7$ Hz), 7.96 (d, 2H, $J = 9.1$ Hz), 7.25 (dd, 2H, $J = 7.3$, 3.2 Hz), 7.06 (dd, 2H, $J = 7.3$, 3.2 Hz), 1.80 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 160.4, 147.4, 146.0, 135.5, 128.7, 125.8, 123.5, 107.4, 25.6. HR-MS [M+H]$^+$ m/z calcd for C$_{14}$H$_{12}$N$_3$O$_2$ 254.0930, found 254.0925.

![Structural formula of 3s](image)

**2,2,5-Trimethyl-2H-benzo[d]imidazole (3s).** Eluent: diethyl ether. Yield: 149 mg (93%) as a brown oil. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.12 (d, 1H, $J = 9.6$ Hz), 6.92 (s, 1H), 6.85 (d, 1H, $J = 9.1$ Hz), 2.23 (s, 3H), 1.52 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 159.6, 158.7, 144.9, 138.7, 124.9, 122.2, 104.4, 22.7, 21.9. HR-MS [M+H]$^+$ m/z calcd for C$_{10}$H$_{13}$N$_2$ 161.1079, found 161.1072.

![Structural formula of 3t](image)

**2-Ethyl-2,5-dimethyl-2H-benzo[d]imidazole (3t).** Eluent: diethyl ether. Yield: 165 mg (95%) as a brown oil. $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 7.12 (d, 1H, $J = 9.6$ Hz), 6.94 - 6.92 (m, 1H), 6.85 (dd, 1H, $J = 9.6$, 1.3 Hz), 2.24 (d, 3H, $J = 1.3$ Hz), 2.05 (q, 2H, $J = 7.5$ Hz), 1.50 (s, 3H), 0.71 (t, 3H, $J = 7.5$ Hz). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) $\delta$ 160.1, 159.2, 144.9, 138.7, 124.8, 122.1, 107.1, 29.6, 22.7, 20.4, 8.8. HR-MS [M+H]$^+$ m/z calcd for C$_{11}$H$_{15}$N$_2$ 175.1235, found 175.1228.

**Compound 3u.** Eluent: diethyl ether. Yield: 233 mg (91%) as a brown solid. mp 77-78 °C. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.15 (dd, 1H, $J = 25.1$, 9.6 Hz), 6.96 (dd, 2H, $J = 28.8$, 1.3 Hz), 6.84 (dt, 1H, $J = 9.6$, 1.8 Hz), 2.43 (td, 2H, $J = 13.2$, 3.2 Hz), 2.22...
(s, 3H), 1.82 (dd, 2H, $J = 12.8, 1.8$ Hz), 1.61 (qd, 2H, $J = 13.2, 1.3$ Hz), 1.20 (tt, 1H, $J = 12.3, 2.7$ Hz), 0.83 (s, 9H), 0.81-0.78 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) $\delta$ 160.0, 159.2, 159.1, 158.3, 144.5, 138.3, 125.1, 124.9, 122.5, 122.2, 107.1, 47.9, 41.3, 33.4, 32.5, 27.8, 27.6, 25.8, 22.7, 22.6. HR-MS [M+H]$^+$ m/z calcd for C$_{17}$H$_{25}$N$_2$ 257.2018, found 257.2016.

Compound 3v. Eluent: diethyl ether. Yield: 245 mg (90%) as a brown oil. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.18-7.12 (m, 1H), 6.95 (d, 1H, $J = 14.2$ Hz), 6.88 (d, 1H, $J = 9.6$ Hz), 4.19 (q, 2H, $J = 6.8$ Hz), 2.68-2.65 (m, 1H), 2.25 (s, 3H), 2.22-2.17 (m, 6H), 1.29 (t, 3H, $J = 7.3$ Hz), 1.26-1.22 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) $\delta$ 175.0, 160.0, 159.6, 159.2, 158.7, 145.0, 144.9, 138.6, 125.0, 124.8, 122.3, 122.1, 106.0, 60.2, 42.0, 41.9, 31.6, 31.5, 27.0, 26.9, 25.2, 23.1, 22.7, 22.6, 14.2. HR-MS [M+H]$^+$ m/z calcd for C$_{16}$H$_{21}$N$_2$O$_2$ 273.1603, found 273.1596.

Compound 3w. Eluent: diethyl ether. Yield: 190 mg (89%) as a yellow solid. mp 96-98 °C. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.11 (d, 1H, $J = 9.1$ Hz), 6.91 (s, 1H), 6.82 (d, 1H, $J = 9.1$ Hz), 2.22 (s, 3H), 1.96-1.95 (m, 4H), 1.82-1.81 (m, 4H), 1.71-1.70 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 159.2, 158.3, 144.7, 138.5, 125.1, 122.3, 110.9, 34.3, 30.0, 25.1, 22.7. HR-MS [M+H]$^+$ m/z calcd for C$_{14}$H$_{19}$N$_2$ 215.1548, found 215.1546.

5-Methoxy-2,2-dimethyl-2H-benzo[d]imidazole (3x). Eluent: diethyl ether. Yield: 167 mg (95%) as a yellow solid. mp 83-85 °C. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.14 (d, 1H, $J = 10.0$ Hz), 6.78 (dd, 1H, $J = 10.0, 2.2$ Hz), 6.26 (d, 1H, $J = 1.8$ Hz), 3.83 (s, 3H), 1.52 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 163.5, 159.6, 158.1, 134.3, 126.1, 104.7, 96.3, 55.8, 22.3. HR-MS [M+H]$^+$ m/z calcd for C$_{10}$H$_{13}$N$_2$O 177.1028, found 177.1021.

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2-Ethyl-5-methoxy-2-methyl-2H-benzo[d]imidazole (3y). Eluent: diethyl ether. Yield: 182 mg (96%) as a yellow solid. mp 93-94 °C. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.02 (d, 1H, $J = 9.6$ Hz), 6.66 (dd, 1H, $J = 9.6$, 1.3 Hz), 6.15 (s, 1H), 3.71 (s, 3H), 1.91 (q, 2H, $J = 7.3$ Hz), 1.37 (s, 3H), 0.61 (t, 3H, $J = 7.3$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 163.5, 160.0, 158.5, 134.2, 125.9, 107.4, 96.3, 55.7, 29.8, 20.7, 8.8. HR-MS [M+H]$^+$ m/z calcd for C$_{11}$H$_{13}$N$_2$O 191.1184, found 191.1179.

Compound 3z. Eluent: diethyl ether. Yield: 145 mg (72%) as a yellow solid. mp 83-85 °C. $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 7.16 (d, 1H, $J = 9.6$ Hz), 6.78 (dd, 1H, $J = 10.0$, 2.2 Hz), 6.30 (d, 1H, $J = 2.2$ Hz), 3.82 (s, 3H), 2.23-2.20 (m, 4H), 2.03-2.00 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) $\delta$ 163.4, 159.6, 158.1, 133.9, 125.8, 114.7, 96.2, 55.7, 33.7, 26.1. HR-MS [M+H]$^+$ m/z calcd for C$_{12}$H$_{15}$N$_2$O 203.1184, found 203.1178.

Compound 3a'. Eluent: ethyl acetate/petroleum ether = 1:20. Yield: 212 mg (92%) as a yellow solid. mp 101-103 °C. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.13 (d, 1H, $J = 9.9$ Hz), 6.75 (dd, 1H, $J = 9.6$, 2.0 Hz), 6.27 (d, 1H, $J = 2.0$ Hz), 3.81 (s, 3H), 1.95-1.91 (m, 4H), 1.82-1.77 (m, 4H), 1.74-1.68 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 163.4, 159.2, 157.6, 134.1, 126.2, 111.2, 96.5, 55.7, 34.8, 29.9, 25.0. HR-MS [M+H]$^+$ m/z calcd for C$_{14}$H$_{19}$N$_2$O 231.1497, found 231.1492.

5-Bromo-2,2-dimethyl-2H-benzo[d]imidazole (3b'). Eluent: diethyl ether. Yield: 162 mg (72%) as a brown oil. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.51 (s, 1H), 7.14-7.05 (m, 2H), 1.54 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 158.9, 157.4, 138.9, 130.3, 127.5, 126.6, 105.6, 21.5. HR-MS [M+H]$^+$ m/z calcd for C$_{6}$H$_{10}$BrN$_2$...
225.0027, found 225.0023.

Methyl 4-(2,2-dimethyl-2H-benzo[d]imidazol-5-yloxy)benzoate (3c'). Eluent: diethyl ether. Yield: 266 mg (90%) as a brown oil. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 8.08 (d, 2H, $J = 8.7$ Hz), 7.25-7.23 (m, 1H), 7.15 (d, 2H, $J = 8.7$ Hz), 6.94 (dd, 1H, $J = 9.6$, 2.2 Hz), 6.25 (d, 1H, $J = 2.2$ Hz), 3.90 (s, 3H), 1.48 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 166.1, 161.6, 159.1, 158.0, 157.5, 133.1, 131.9, 127.4, 127.3, 120.4, 105.5, 103.8, 52.3, 22.1. HR-MS [M+H]$^+$ m/z calcd for C$_{17}$H$_{17}$N$_2$O$_3$ 297.1239, found 297.1238.

Ethyl 2-(2,2-dimethyl-2H-benzo[d]imidazol-5-yloxy)acetate (3d'). Eluent: diethyl ether. Yield: 223 mg (90%) as a brown oil. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.05 (d, 1H, $J = 9.6$ Hz), 6.77 (dd, 1H, $J = 10.0$, 2.2 Hz), 6.05 (d, 1H, $J = 1.8$ Hz), 4.49 (s, 2H), 4.16 (q, 2H, $J = 7.3$ Hz), 1.38 (s, 6H), 1.19 (t, 3H, $J = 7.3$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 167.1, 161.6, 159.1, 157.9, 133.8, 126.5, 105.0, 97.7, 65.1, 61.7, 22.1, 14.1. HR-MS [M+H]$^+$ m/z calcd for C$_{13}$H$_{17}$N$_2$O$_3$ 249.1239, found 249.1233.

Ethyl 2-(2-ethyl-2-methyl-2H-benzo[d]imidazol-5-yloxy)acetate (3e'). Eluent: diethyl ether. Yield: 231 mg (88%) as a brown oil. $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.19 (d, 1H, $J = 9.6$ Hz), 6.90 (dd, 1H, $J = 9.6$, 2.2 Hz), 6.19 (d, 1H, $J = 1.8$ Hz), 4.62 (s, 2H), 4.29 (q, 2H, $J = 7.3$ Hz), 2.01 (q, 2H, $J = 7.3$ Hz), 1.48 (s, 3H), 1.32 (t, 3H, $J = 7.3$ Hz), 0.74 (t, 3H, $J = 7.3$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 167.1, 161.7, 159.6, 158.3, 133.7, 126.4, 107.8, 97.7, 65.1, 61.7, 29.7, 20.5, 14.1, 8.9. HR-MS [M+H]$^+$ m/z calcd for C$_{14}$H$_{19}$N$_2$O$_3$ 263.1396, found 263.1392.
Compound 3f'. Eluent: ethyl acetate/ methanol = 15:1. Yield: 335 mg (74%) as a brown solid. mp 88-90 °C. ¹H NMR (400 MHz, CD₃OD, ppm) δ 7.88 (s, 1H), 7.20-7.12 (m, 4H), 6.23 (t, 1H, J = 5.9 Hz), 4.51-4.49 (m, 1H), 3.88-3.70 (m, 3H), 2.53-2.50 (m, 1H), 2.36-2.25 (m, 4H), 2.20-2.11 (m, 2H), 2.03-2.00 (m, 2H), 1.84 (s, 3H), 1.02 (d, 2H, J = 12.3 Hz). ¹³C NMR (100 MHz, CD₃OD, ppm) δ 177.0, 165.0, 160.3, 159.4, 151.0, 136.8, 135.9, 135.4, 125.0, 124.5, 110.1, 105.4, 85.4, 84.5, 61.2, 48.9, 43.5, 37.4, 31.5, 27.5, 27.3, 11.2. HR-MS [M+H]⁺ m/z calcd for C₂₃H₂₈N₅O₅ 454.2090, found 454.2080.

Methyl 2-(2-(2-(2,2-dimethyl-2H-benzo[d]imidazol-6-yl)oxy)acetamido)-3-methylbutanamido)acetate (3g'). Eluent: ethyl acetate/ ethanol = 30:1. Yield: 312 mg (80%) as a brown oil. ¹H NMR (400 MHz, DMSO-d₆, ppm) δ 8.49 (t, 1H, J = 5.5 Hz), 8.09 (d, 1H, J = 8.7 Hz), 7.19 (d, 1H, J = 9.6 Hz), 6.93 (d, 1H, J = 9.6 Hz), 6.26 (s, 1H), 4.67-4.53 (m, 2H), 4.24 (t, 1H, J = 7.3 Hz), 3.81 (qd, 2H, J = 17.4, 5.5 Hz), 3.58 (s, 3H), 2.00-1.97 (m, 1H), 1.31 (s, 6H), 0.86-0.81 (m, 6H). ¹³C NMR (100 MHz, DMSO-d₆, ppm) δ 171.7, 170.6, 166.8, 161.9, 159.3, 157.9, 134.6, 126.7, 105.1, 98.2, 67.3, 57.8, 52.1, 41.0, 31.1, 22.6, 19.5, 18.4. HR-MS [M+H]⁺ m/z calcd for C₁₉H₂₇N₄O₅ 391.1981, found 391.1977.

Compound 3h'. Eluent: ethyl acetate/ ethanol = 10:1. Yield: 474 mg (68%) as a brown solid. mp 96-98 °C. ¹H NMR (400 MHz, DMSO-d₆, ppm) δ 11.20 (s, 1H), 8.45 (t, 1H, J = 4.5 Hz), 8.21 (d, 1H, J = 6.8 Hz), 8.06 (d, 1H, J = 8.7 Hz), 7.71 (s, 1H), 7.16 (d,
1H, J = 9.6 Hz), 6.91 (d, 1H, J = 9.6 Hz), 6.28 (s, 1H), 6.13 (t, 1H, J = 5.9 Hz), 5.00 (s, 1H), 4.63-4.49 (m, 2H), 4.28 (s, 1H), 4.19 (t, 1H, J = 7.7 Hz), 3.84-3.70 (m, 3H), 3.58-3.48 (m, 5H), 3.28 (s, 1H), 2.45-2.35 (m, 3H), 2.16-1.79 (m, 8H), 1.70 (s, 3H), 0.85-0.77 (m, 6H). 13C NMR (100 MHz, DMSO-\textit{d}_6, ppm) δ 175.4, 171.7, 170.6, 166.8, 164.2, 161.9, 159.9, 157.8, 150.9, 136.7, 134.6, 126.6, 109.9, 106.8, 98.5, 85.8, 84.0, 67.3, 61.9, 57.8, 49.4, 43.3, 41.0, 37.5, 32.3, 31.1, 27.9, 27.8, 25.6, 19.5, 18.5, 12.7. HR-MS [M+H]^+ m/z calcd for C_{33}H_{44}N_{7}O_{10} 698.3150, found 698.3143.

D: References

E: The $^1$H NMR and $^{13}$C NMR spectra of compounds 3a-h'
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