Pd-catalyzed intramolecular C(sp²)–H amination of phenylalanine moieties in the dipeptides: synthesis of indoline-2-carboxylate-containing dipeptides

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**General information**

All the reagents were used without further purification. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker NMR spectrometer with CDCl$_3$ as the solvent and TMS as an internal standard. HRESIMS was measured on an Agilent G6224A TOF spectrometer. HPLC was performed on Chiralcel OD-H column (30% to 50% $i$-PrOH in hexanes, 1 mL/min), $\lambda$ = 254 nm. TLC was performed on pre-coated silica gel GF254 plates (Qingdao Marine Chemical Factory). Column chromatography was performed on silica gel (200–300 mesh, Qingdao Marine Chemical Factory). Visualization was carried out with UV or PMA staining by heating.

**General procedures for preparation of compounds 1a–1l, 3a-3i:**

To a solution of protected-amino acid (1equiv) and phenylalanine methyl ester hydrochloride (1 equiv) in dry DCM (0.2 M) was added DIPEA (2 equiv), HOBr (1.1 equiv), and EDCI-HCl (1.2 equiv) at 0°C. After 1 h, the mixture was warmed to rt and stirred overnight. Water was added and the mixture was extracted with DCM. The combined organic layer was washed with 10% HCl, sat. NaHCO$_3$, and brine, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography (Hexane/EA) to give the desired products. 3j and 3k were prepared by the similar methods.

**General procedure for C–H amiantion:**

A mixture of peptide (0.3 mmol), Phl(OAc)$_2$ (0.6 mmol), Pd(OAc)$_2$ (5 % mol), and toluene (2 mL) in sealed tube was heated at 120 °C for 20 h. The reaction mixture was cooled to room temperature, and concentrated in vacuo. The resulting residue was purified by silica gel flash chromatography (Hexane/EA) to give the products.
Characterization of compounds

According to the general experimental procedure, compound 2a was obtained as yellow oil. Two amide rotamers (1.6:1) exist in NMR spectra.

Major amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, $J = 7.9$ Hz, 1H), 7.28 – 7.15 (m, 2H), 7.07 (t, $J = 7.4$ Hz, 1H), 5.58 (brs, 1H), 4.96 (d, $J = 10.2$ Hz, 1H), 4.20 – 4.07 (m, 1H), 3.90 – 3.79 (m, 1H), 3.78(s, 3H), 3.70 – 3.61 (m, 1H), 3.33 (d, $J = 16.4$ Hz, 1H), 1.47 (s, 9H).

Minor amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.28 – 7.15 (m, 3H), 7.07 (t, $J = 7.4$ Hz, 1H), 5.56 (brs, 1H), 5.23 (d, $J = 8.9$ Hz, 1H), 4.49 – 4.30 (m, 2H), 3.76 (s, 3H), 3.60 – 3.49 (m, 1H), 3.16 (d, $J = 16.9$ Hz, 1H), 1.45 (s, 9H).

Mixture of amide rotamers: $^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.4, 171.3, 167.3, 155.8, 142.2, 139.9, 130.7, 128.4, 128.1, 125.8, 124.6, 124.4, 124.1, 117.4, 114.1, 79.9, 60.2, 59.7, 53.2, 52.6, 45.1, 43.5, 33.7, 31.5, 28.4.

HRMS (ESI) Calcd for C$_{17}$H$_{22}$N$_2$O$_5$Na [M+Na$^+$]: 357.1421, Found: 357.1416.

According to the general experimental procedure, compound 2b was obtained as yellow oil. Two amide rotamers (1.3:1) exist in NMR spectra.

Major amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.25 (d, $J = 8.1$ Hz, 1H), 7.35 – 7.16 (m, 2H), 7.15 – 7.00 (m, 1H), 5.27 (d, $J = 11.1$, 3.5 Hz, 1H), 4.97 (d, $J = 9.2$ Hz, 1H), 4.55 – 4.40 (m, 1H), 3.77 (s, 3H), 3.63 (dd, $J = 16.4$, 10.6 Hz, 1H), 3.36 (d, $J = 16.4$ Hz, 1H), 1.45 (s, 9H), 1.41 (d, $J = 6.8$ Hz, 3H).

Minor amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.16 (m, 3H), 7.15 – 7.00 (m, 1H), 5.52 (d, $J = 7.5$ Hz, 1H), 5.48 (d, $J = 8.3$ Hz, 1H), 5.10 – 5.02 (m, 1H), 3.75 (s, 3H), 3.57 – 3.45 (m, 1H), 3.13 (dd, $J = 16.6$, 3.4 Hz, 1H), 1.55 (d, $J = 6.9$ Hz, 3H), 1.44 (s, 9H).

Mixture of amide rotamers: $^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.8, 171.7, 171.5, 171.4, 155.2, 154.8, 142.3, 139.9, 131.1, 128.7, 128.3, 128.1, 125.9, 124.6, 124.4, 124.1, 117.5, 114.1, 79.8, 79.6, 60.4, 60.2, 53.3, 52.5, 48.6, 48.4, 33.5, 31.3, 28.4, 19.9, 18.8.

HRMS (ESI) Calcd for C$_{18}$H$_{24}$N$_2$O$_5$Na [M+Na$^+$]: 371.1577, Found: 371.1586.
According to the general experimental procedure, compound 2c was obtained as yellow solid. Two amide rotamers (4:1) exist in NMR spectra.

Mixture of amide rotamers: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 (d, $J = 8.1$ Hz, 1H), 7.39 – 7.17 (m, 9H), 7.15 – 7.01 (m, 2.6H), 5.59 (d, $J = 8.7$ Hz, 1H), 5.42 – 5.24 (m, 0.7H), 4.62 (td, $J = 9.4$, 5.2 Hz, 1H), 4.14 (d, $J = 9.0$ Hz, 1H), 3.78 (s, 0.7 H), 3.69 (s, 3H), 3.21 – 2.98 (m, 3.7H), 2.83 (dd, $J = 16.2$, 10.5 Hz, 1H), 1.46 (s, 9H), 1.37 (s, 2.1H).

Mixture of amide rotamers: $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.2, 170.8, 154.7, 141.5, 136.2, 129.7, 129.4, 129.1, 128.7, 128.4, 127.8, 127.1, 124.6, 124.3, 117.6, 79.7, 77.4, 60.5, 60.4, 54.6, 53.1, 52.6, 41.6, 38.2, 32.8, 31.4, 28.4.

HRMS (ESI) Calcd for C$_{24}$H$_{28}$N$_2$O$_5$Na [M+Na$^+$]: 447.1890, Found: 447.1884.

According to the general experimental procedure, compound 2d was obtained as yellow solid. Two amide rotamers (1.7:1) exist in NMR spectra.

Major amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.26 (d, $J = 8.1$ Hz, 1H), 7.40 – 7.21 (m, 2H), 5.36 – 5.33 (m, 1H), 4.98 (dd, $J = 10.6$, 1.9 Hz, 1H), 4.47 (td, $J = 9.8$, 3.6 Hz, 1H), 3.77 (s, 3H), 3.71 – 3.57 (m, 1H), 3.35 (d, $J = 15.5$ Hz, 1H), 1.73-1.68 (m, 2H), 1.62 – 1.56 (m, 1H), 1.43 (s, 9H), 1.03 (d, $J = 6.5$ Hz, 3H), 0.96 (d, $J = 6.7$ Hz, 3H).

Minor amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 – 7.21 (m, 3H), 7.06 (m, 1H), 5.36 – 5.33 (m, 1H), 5.22 (dd, $J = 11.1$, 4.2 Hz, 1H), 5.17 – 5.14 (m, 1H), 3.74 (s, 3H), 3.56 – 3.42 (m, 1H), 3.12 (dd, $J = 16.6$, 4.0 Hz, 1H), 1.73-1.68 (m, 2H), 1.62 – 1.56 (m, 1H), 1.42 (s, 9H), 1.16 (d, $J = 6.5$ Hz, 3H), 1.00 (d, $J = 6.7$ Hz, 3H).

Mixture of amide rotamers: $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.2, 172.1, 171.5, 171.4, 155.7, 155.2, 142.4, 140.1, 131.0, 128.7, 128.5, 128.1, 128.0, 125.9, 124.5, 124.4, 124.0, 117.4, 114.0, 79.7, 79.4, 60.5, 60.4, 53.3, 52.4, 51.3, 51.2, 43.7, 41.2, 33.6, 31.2, 28.3, 24.9, 24.6, 23.6, 23.4, 21.9, 21.7.

HRMS (ESI) Calcd for C$_{21}$H$_{30}$N$_2$O$_5$Na [M+Na$^+$]: 413.2047, Found: 413.2046.
According to the general experimental procedure, compound 2e was obtained as yellow solid. Two amide rotamers (1.3:1) exist in NMR spectra.

**Major amide rotamer:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.31 (d, $J = 8.1$ Hz, 1H), 7.27 – 7.18 (m, 2H), 7.12 – 7.05 (m, 1H), 5.34 (d, $J = 9.4$ Hz, 1H), 5.09 (d, $J = 9.1$ Hz, 1H), 4.32 – 4.21 (m, 1H), 3.76 (s, 3H), 3.62 (dt, $J = 19.0$, 9.5 Hz, 1H), 3.36 (d, $J = 16.4$ Hz, 1H), 1.76 (td, $J = 9.9$, 4.8 Hz, 1H), 1.72 – 1.57 (m, 2H), 1.45 (s, 9H), 0.99 (d, $J = 6.8$ Hz, 3H), 0.93 (t, $J = 7.9$ Hz, 3H).

**Minor amide rotamer:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27 – 7.18 (m, 3H), 7.12 – 7.05 (m, 1H), 5.40 (d, $J = 9.0$ Hz, 1H), 5.26 (dd, $J = 11.2$, 4.6 Hz, 1H), 5.03 (dd, $J = 9.2$, 3.3 Hz, 1H), 3.74 (s, 3H), 3.50 (dd, $J = 16.6$, 11.3 Hz, 1H), 3.15 (dd, $J = 16.6$, 4.5 Hz, 1H), 1.76 (td, $J = 9.9$, 4.8 Hz, 1H), 1.72 – 1.57 (m, 2H), 1.18 (d, $J = 6.8$ Hz, 3H), 0.92 (t, $J = 7.9$ Hz, 3H).

**Mixture of amide rotamers:** $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.6, 171.3, 171.0, 155.4, 142.3, 131.1, 128.9, 128.3, 128.0, 125.9, 124.6, 124.5, 124.0, 117.5, 114.0, 79.7, 79.4, 60.7, 60.5, 57.1, 56.8, 53.3, 52.4, 39.4, 37.3, 33.4, 31.2, 29.7, 28.3, 24.2, 22.6, 15.8, 15.5, 11.7, 11.4.

HRMS (ESI) Calcd for C$_{21}$H$_{30}$N$_2$O$_5$Na [M+Na$^+$]: 413.2047, Found: 413.2044.

According to the general experimental procedure, compound 2f was obtained as yellow solid. Two amide rotamers (1.3:1) exist in NMR spectra.

**Major amide rotamer:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.30 (d, $J = 8.1$ Hz, 1H), 7.35 – 7.16 (m, 2H), 7.09 – 7.05 (m, 1H), 5.37 (d, $J = 9.4$ Hz, 1H), 5.08 (dd, $J = 10.6$, 1.8 Hz, 1H), 4.25 (dd, $J = 9.3$, 6.6 Hz, 1H), 3.77 (s, 3H), 3.61 (dt, $J = 15.9$, 7.9 Hz, 1H), 3.38 – 3.34 (m, 1H), 2.10 – 1.96 (m, 1H), 1.46 (s, 9H), 1.02 (d, $J = 6.8$ Hz, 3H), 0.98 (d, $J = 6.7$ Hz, 3H).

**Minor amide rotamer:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 – 7.16 (m, 3H), 7.09 – 7.05 (m, 1H), 5.45 (d, $J = 9.0$ Hz, 1H), 5.25 (dd, $J = 11.2$, 4.7 Hz, 1H), 5.03 (dd, $J = 9.1$, 2.9 Hz, 1H), 3.74 (s, 3H), 3.49 (dd, $J = 16.6$, 11.3 Hz, 1H), 3.14 (dd, $J = 16.6$, 4.6 Hz, 1H), 2.48 – 2.37 (m, 1H), 1.46 (s, 9H), 1.18 (d, $J = 6.8$ Hz, 3H), 0.95 (d, $J = 6.7$ Hz, 3H).

**Mixture of amide rotamers:** $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 171.59, 171.44, 171.31, 170.86, 156.06, 155.44, 142.27, 140.08, 131.04, 128.81, 128.28, 128.02, 125.90,

HRMS (ESI) Calcd for C_{20}H_{28}N_{2}O_{5}Na [M+Na^+]: 399.1890, Found: 399.1891.

According to the general experimental procedure, compound 2g was obtained as white powder. Two amide rotamers (3:1) exist in NMR spectra.

Major amide rotamer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.22 (d, J = 8.1 \text{ Hz}, 1H), 7.33 - 7.18 (m, 2H), 7.12 - 7.08 (m, 1H), 5.46 (d, J = 8.8 \text{ Hz}, 1H), 5.29 (dd, J = 10.4, 1.6 \text{ Hz}, 1H), 4.81 (dd, J = 14.6, 7.3 \text{ Hz}, 1H), 4.35 (dd, J = 11.1, 5.7 Hz, 1H), 4.12 - 4.03 (m, 1H), 3.75 (s, 3H), 3.61 (dd, J = 16.3, 10.5 Hz, 1H), 3.40 (d, J = 16.6 \text{ Hz}, 1H), 2.05 (s, 3H), 1.45 (s, 9H).

Minor amide rotamer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.52 (d, J = 8.1 \text{ Hz}, 1H), 7.30 - 7.23 (m, 2H), 7.10 - 7.07 (m, 1H), 5.54 (d, J = 8.4 \text{ Hz}, 1H), 5.42 (d, J = 4.7 \text{ Hz}, 1H), 5.27 - 5.22 (m, 1H), 4.53 (dd, J = 11.3, 4.6 Hz, 1H), 4.25 (dd, J = 11.2, 7.9 Hz, 1H), 3.72 (s, 3H), 3.50 (dd, J = 16.4, 11.3 Hz, 1H), 3.14 (dd, J = 16.7, 3.2 Hz, 1H), 2.08 (s, 3H), 1.43 (s, 9H).

Mixture of amide rotamers: \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 171.27, 171.13, 170.83, 170.78, 168.17, 167.77, 155.26, 154.96, 141.89, 129.10, 128.53, 128.06, 125.89, 124.98, 124.58, 117.61, 114.47, 80.20, 80.09, 65.14, 63.85, 60.63, 60.53, 53.33, 52.66, 51.73, 51.58, 33.32, 31.34, 28.27, 20.77.

HRMS (ESI) Calcd for C_{20}H_{26}N_{2}O_{7}Na [M+Na^+]: 429.1632, Found: 429.1623.

According to the general experimental procedure, compound 2h was obtained as yellow solid. Two amide rotamers (3:1) exist in NMR spectra.

Major amide rotamer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.23 (d, J = 8.1 \text{ Hz}, 1H), 7.93 (d, J = 8.3 \text{ Hz}, 1H), 7.70 (d, J = 8.3 \text{ Hz}, 2H), 7.49 (s, 1H), 7.24 (t, J = 7.7 \text{ Hz}, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.1 Hz, 3H), 7.02 (m, 4H), 5.59 (d, J = 8.6 \text{ Hz}, 1H), 4.71 (dd, J = 14.8, 8.1 Hz, 1H), 4.14 (d, J = 9.5 Hz, 1H), 3.70 (s, 3H), 3.25 - 3.15 (m, 2H), 2.81 (d, J = 14.3 Hz, 1H), 2.33 (s, 3H), 2.27 - 2.20 (m, 1H), 1.47 (s, 9H).

Minor amide rotamer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.10 (d, J = 8.4 \text{ Hz}, 1H), 7.90 (d, J = 8.4 \text{ Hz}, 1H), 7.75 (d, J = 8.2 \text{ Hz}, 2H), 7.69 - 7.66 (m, 1H), 7.60 (dd, J = 13.7, 5.5
Hz, 2H), 7.48 (s, 1H), 7.24 (t, \(J = 7.7\) Hz, 3H), 7.18 (d, \(J = 8.1\) Hz, 2H), 5.46 – 5.37 (m, 2H), 5.29 (dd, \(J = 11.1, 4.0\) Hz, 1H), 3.82 (s, 3H), 3.16 – 3.10 (m, 3H), 2.24 – 2.20 (m, 1H), 2.19 (s, 3H), 1.40 (s, 9H).

Mixture of amide rotamers: \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 171.76, 170.91, 170.61, 155.16, 154.79, 144.89, 144.64, 143.53, 141.53, 135.02, 134.94, 134.70, 130.36, 129.90, 129.76, 129.04, 129.00, 128.27, 127.84, 127.14, 126.88, 126.73, 125.96, 125.41, 125.31, 124.95, 124.78, 124.70, 124.62, 124.23, 123.35, 123.16, 120.35, 119.68, 119.55, 117.65, 117.26, 116.47, 114.05, 113.61, 113.50, 109.36, 104.93, 80.03, 76.81, 60.52, 60.30, 53.30, 53.15, 52.82, 51.96, 32.28, 31.35, 30.56, 29.73, 28.36, 28.31, 21.61.


According to the general experimental procedure, compound 2i was obtained as yellow oil. Two amide rotamers (3:1) exist in NMR spectra.

Major amide rotamer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.20 (d, \(J = 8.0\) Hz, 1H), 7.28 – 7.12 (m, 2 H), 7.10 – 6.99 (t, \(J = 7.4\) Hz, 1H), 5.68 (d, \(J = 10.2\) Hz, 1 H), 5.30 (d, \(J = 8.3\) Hz, 1 H), 4.47 – 4.34 (m, 1H), 3.75 (s, 3H), 3.61 (dd, \(J = 16.2, 10.9\) Hz, 1 H), 3.32 (d, \(J = 16.3\) Hz, 1 H), 1.41 (m, 3 H), 1.40 (s, 9H).

Minor amide rotamer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.35 (m, 1H), 7.28 – 7.12 (m, 2 H), 7.10 – 6.99 (t, \(J = 7.4\) Hz, 1H), 5.68 – 5.67 (m, 1 H), 5.20 – 5.17 (m, 2 H), 3.73 (s, 3H), 3.50 (d, \(J = 8.3\) Hz, 1 H), 3.13 (d, \(J = 15.6\) Hz, 1H), 1.44 (m, 3H), 1.38 (s, 9H).

Mixture of amide rotamers: \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 172.3, 172.1, 171.5, 155.4, 142.3, 131.0, 129.5, 128.3, 127.8, 125.8, 124.5, 124.4, 124.1, 117.9, 114.5, 79.9, 77.5, 77.2, 76.8, 61.1, 60.5, 52.9, 52.5, 49.0, 48.1, 33.3, 31.4, 29.7, 28.3, 18.7, 18.2.


According to the general experimental procedure, compound 2j was obtained as yellow solid. Two amide rotamers (1.5:1) exist in NMR spectra.

Major amide rotamer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.21 (d, \(J = 7.7\) Hz, 1H), 7.43 – 7.15 (m, 7H), 7.08 (t, \(J = 7.4\) Hz, 2H), 5.90 (br s, 1H), 5.17 (s, 2H), 4.96 (d, \(J = 9.9\) Hz, 2H), 2.24 – 2.20 (m, 1H), 2.19 (s, 3H), 1.40 (s, 9H).

Mixture of amide rotamers: \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 171.76, 170.91, 170.61, 155.16, 154.79, 144.89, 144.64, 143.53, 141.53, 135.02, 134.94, 134.70, 130.36, 129.90, 129.76, 129.04, 129.00, 128.27, 127.84, 127.14, 126.88, 126.73, 125.96, 125.41, 125.31, 124.95, 124.78, 124.70, 124.62, 124.23, 123.35, 123.16, 120.35, 119.68, 119.55, 117.65, 117.26, 116.47, 114.05, 113.61, 113.50, 109.36, 104.93, 80.03, 76.81, 60.52, 60.30, 53.30, 53.15, 52.82, 51.96, 32.28, 31.35, 30.56, 29.73, 28.36, 28.31, 21.61.

Hz, 1H), 4.15 (d, J = 13.1 Hz, 1H), 3.95 (d, J = 16.3 Hz, 1H), 3.79 (s, 3H), 3.70 – 3.61 (m, 1H), 3.34 (d, J = 16.5 Hz, 1H),

Minor amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 – 7.15 (m, 10H), 5.79 (br s, 1H), 5.28 – 5.20 (m, 1H), 5.15 (s, 2H), 4.55 – 4.37 (m, 2H), 3.76 (s, 3H), 3.59 – 3.52 (m, 1H), 3.16 (d, J = 16.4 Hz, 1H).

Mixture of amide rotamers: $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.3, 167.0, 156.4, 142.1, 139.8, 136.4, 130.8, 129.4, 128.5, 128.4, 128.1, 125.9, 124.7, 124.4, 124.2, 117.4, 114.1, 67.0, 60.3, 59.8, 53.2, 52.7, 45.4, 43.9, 33.6, 31.5.

HRMS (ESI) Calcd for C$_{20}$H$_{20}$N$_2$O$_5$Na $[M+Na^+]$: 391.1264, Found: 391.1265.

According to the general experimental procedure, compound 2k was obtained as white solid. Two amide rotamers (1.1:1) exist in NMR spectra.

Major amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 7.5 Hz, 2H), 7.65 (d, J = 7.4 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.32 – 7.18 (m, 2H), 7.11 (t, J = 7.4 Hz, 1H), 5.91 (brs, 1H), 4.98 (d, J = 10.3 Hz, 1H), 4.58 – 4.48 (m, 1H), 4.42 (d, J = 6.5 Hz, 2H), 4.27 (t, J = 7.2 Hz, 1H), 4.18 – 4.24 (m, 1H), 3.78 (s, 3H), 3.71 – 3.60 (m, 1H), 3.37 (d, J = 16.3 Hz, 1H).

Minor amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, J = 7.5 Hz, 2H), 7.65 (d, J = 7.4 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.32 – 7.18 (m, 3H), 7.11 (t, J = 7.4 Hz, 1H), 5.89 (brs, 1H), 5.26 (d, J = 9.2 Hz, 1H), 4.60 – 4.56 (m, 1H), 4.42 (d, J = 6.5 Hz, 2H), 4.27 (t, J = 7.2 Hz, 1H), 3.97 (d, J = 15.0 Hz, 1H), 3.78 (s, 3H), 3.59 – 3.47 (m, 1H), 3.28 – 3.12 (m, 1H).

Mixture of amide rotamers: $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.2, 166.9, 156.3, 143.9, 142.1, 141.3, 139.8, 129.4, 128.2, 127.7, 127.1, 126.0, 125.2, 124.8, 124.5, 120.0, 117.4, 114.0, 67.3, 60.3, 59.8, 53.2, 52.7, 47.1, 45.4, 43.9, 33.7, 31.5, 29.7.

HRMS (ESI) Calcd for C$_{27}$H$_{24}$N$_2$O$_5$Na $[M+Na^+]$: 479.1577, Found: 479.1579.

According to the general experimental procedure, compound 2l was obtained as white solid. Two amide rotamers (1.4:1) exist in NMR spectra.

Major amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (d, J = 8.0 Hz, 1H), 7.39 – 7.26 (m, 2H), 7.10 (t, J = 7.5 Hz, 1H), 6.62 (s, 1H), 4.98 (d, J = 10.5 Hz, 1H), 4.28
(dd, J = 17.2, 4.4 Hz, 1H), 3.94 (d, J = 17.2 Hz, 1H), 3.79 (s, 3H), 3.71 – 3.60 (m, 1H), 3.37 (d, J = 16.6 Hz, 1H), 2.09 (s, 3H).

Minor amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.26 (m, 3H), 7.10 (s, J = 7.5 Hz, 1H), 6.62 (s, 1H), 5.23 (d, J = 8.1 Hz, 1H), 4.52 – 4.48 (m, 2H), 3.77 (s, 3H), 3.59 – 3.48 (m, 1H), 3.19 (d, J = 16.4 Hz, 1H), 2.09 (s, 3H).

Mixture of amide rotamers: $^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.1, 170.2, 166.9, 142.0, 128.4, 128.1, 125.9, 124.8, 124.45, 124.4, 117.3, 114.1, 60.3, 59.8, 53.3, 52.7, 44.1, 42.6, 33.6, 31.5, 23.0.

HRMS (ESI) Calcd for C$_{14}$H$_{16}$N$_2$O$_4$Na [M+Na$^+$/]: 299.1002, Found: 299.1002.

According to the general experimental procedure, compound 4a was obtained as yellow oil. Two amide rotamers (2:1) exist in NMR spectra.

Major amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 (s, 1H), 6.77 (d, J = 7.9 Hz, 1H), 5.51 (br s, 1H), 4.99 (d, J = 9.9 Hz, 1H), 4.07 (d, J = 13.2 Hz, 1H), 3.81 (d, J = 17.4 Hz, 1H), 3.72 (s, 3H), 3.59 – 3.39 (m, 1H), 3.28 (d, J = 16.5 Hz, 1H), 2.27 (s, 3H), 1.46 (s, 9H).

Minor amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.21 – 7.06 (m, 2H), 6.85 (s, 1H), 5.58 (br s, 1H), 5.20 (d, J = 8.4 Hz, 1H), 4.40 – 4.18 (m, 2H), 3.71 (s, 3H), 3.59 – 3.39 (m, 1H), 3.19 – 3.03 (m, 1H), 2.27 (s, 3H), 1.46 (s, 9H).

Mixture of amide rotamers: $^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.1, 169.5, 167.6, 167.2, 155.8, 150.4, 143.1, 128.1, 126.0, 125.9, 124.5, 121.6, 117.7, 117.4, 111.4, 108.2, 79.9, 61.0, 60.4, 53.2, 52.7, 45.0, 43.5, 33.2, 31.0, 29.7, 28.3, 21.0.

HRMS (ESI) Calcd for C$_{19}$H$_{24}$N$_2$O$_7$Na [M+Na$^+$/]: 415.1476, Found: 415.1470.

According to the general experimental procedure, compound 4b was obtained as yellow solid. Two amide rotamers (2:1) exist in NMR spectra.

Major amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.02 (s, J = 1.6 Hz, 1H), 7.20 – 7.14 (m, 1H), 6.86 – 6.80 (m, 1H), 5.42 (d, J = 8.3 Hz, 1H), 5.00 (dd, J = 10.6, 1.7 Hz, 1H), 4.52 – 4.40 (m, 1H), 3.78 (s, 3H), 3.60 (dd, J = 16.4, 10.8 Hz, 1H), 3.36 (d, J = 16.3 Hz, 1H), 2.30 (s, 3H), 1.46 (s, 9H), 1.40 (d, J = 6.8 Hz, 3H).

Minor amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.24 – 7.19 (m, 1H), 6.93 (s, 1H), 6.86 – 6.80 (m, 1H), 5.52 (d, J = 7.4 Hz, 1H), 5.28 (dd, J = 11.1, 3.8 Hz, 1H),
4.97−4.91 (m, 1H), 3.76 (s, 3H), 3.48 (dd, \(J = 16.5, 11.3\) Hz, 1H), 3.12 (dd, \(J = 16.6, 3.5\) Hz, 1H), 2.34 (s, 3H), 1.54 (d, \(J = 6.9\) Hz, 3H), 1.46 (s, 9H).

Mixture of amide rotamers: \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta 171.98, 171.56, 171.15, 169.56, 169.29, 155.14, 154.75, 150.70, 150.43, 143.26, 140.75, 128.31, 126.14, 125.97, 124.56, 117.79, 117.22, 111.66, 108.27, 79.86, 79.70, 61.06, 60.39, 53.33, 52.57, 48.61, 33.10, 31.58, 30.73, 29.70, 28.35, 22.65, 21.19, 21.03, 19.82, 18.64, 14.20, 14.11.


According to the general experimental procedure, compound 4c was obtained as yellow solid. Two amide rotamers (>10:1) exist in NMR spectra.

Major amide rotamer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.02 (d, J = 1.9\) Hz, 1H), 7.28−7.17 (m, 5H), 7.05 (d, \(J = 8.0\) Hz, 1H), 6.84−6.75 (m, 1H), 5.53 (d, \(J = 8.7\) Hz, 1H), 4.59 (td, \(J = 9.4, 5.2\) Hz, 1H), 4.16 (d, \(J = 9.2\) Hz, 1H), 3.70 (s, 3H), 3.20−2.94 (m, 3H), 2.81 (dd, \(J = 16.2, 10.5\) Hz, 1H), 2.29 (s, 3H), 1.43 (s, 9H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 171.03, 170.95, 169.53, 154.69, 150.21, 142.43, 136.07, 129.40, 128.74, 127.15, 126.50, 124.40, 117.84, 111.67, 79.79, 61.01, 54.57, 53.21, 41.54, 32.38, 28.34, 21.06.


According to the general experimental procedure, compound 4d was obtained as yellow solid. Two amide rotamers (3:1) exist in NMR spectra.

Major amide rotamer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.00 (d, J = 1.6\) Hz, 1H), 7.14 (t, \(J = 10.6\) Hz, 1H), 6.79 (dd, \(J = 8.0, 2.1\) Hz, 1H), 5.22 (dd, \(J = 13.8, 6.9\) Hz, 1H), 5.03−4.94 (m, 1H), 4.43 (td, \(J = 9.8, 3.6\) Hz, 1H), 3.77 (s, 3H), 3.66−3.55 (m, 1H), 3.32 (d, \(J = 16.4\) Hz, 1H), 2.28 (s, 3H), 1.79−1.70 (m, 1H), 1.60−1.52 (m, 2H), 1.43 (s, 9H), 1.01 (d, \(J = 6.5\) Hz, 3H), 0.95 (d, \(J = 6.7\) Hz, 3H).

Minor amide rotamer: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.17 (d, J = 9.2\) Hz, 1H), 7.03 (d, \(J = 20.4\) Hz, 1H), 6.79 (dd, \(J = 8.0, 2.1\) Hz, 1H), 5.29 (d, \(J = 8.7\) Hz, 1H), 5.03−4.94 (m, 1H), 4.43 (td, \(J = 9.8, 3.6\) Hz, 1H), 3.73 (s, 3H), 3.45 (dd, \(J = 16.5, 11.3\) Hz, 1H), 3.17−3.05 (m, 1H), 2.28 (s, 3H), 1.90 (m, 1H), 1.59 (m, 1H), 1.43 (s, 9H), 1.39 (m, 1H), 1.12 (d, \(J = 6.5\) Hz, 3H), 0.98 (d, \(J = 6.7\) Hz, 3H).
Mixture of amide rotamers: $^{13}$C NMR (126 MHz, CDCl$_3$) δ 172.33, 171.90, 171.26, 171.14, 169.54, 169.21, 155.65, 150.68, 150.42, 143.34, 140.91, 128.28, 126.14, 125.94, 124.53, 117.69, 117.04, 111.56, 108.40, 79.76, 79.52, 61.26, 61.05, 53.35, 52.51, 51.45, 51.18, 43.62, 40.93, 33.16, 31.58, 30.74, 29.69, 28.31, 24.80, 24.64, 23.57, 23.40, 22.64, 21.90, 21.35, 21.01, 14.11. 

HRMS (ESI) Calcd for C$_{23}$H$_{32}$N$_2$O$_7$Na [M+Na$^+$]: 471.2102, Found: 471.2120.

According to the general experimental procedure, compound 4e was obtained as yellow oil. Two amide rotamers (2:1) exist in NMR spectra.

Major amide rotamer: $^1$H NMR (500 MHz, CDCl$_3$) δ 8.12 (d, $J = 8.4$ Hz, 1H), 7.25 – 7.13 (m, 2H), 5.46 (s, 1H), 4.97 (d, $J = 10.0$ Hz, 1H), 4.19 – 4.06 (m, 1H), 3.81 (d, $J = 18.8$ Hz, 1H), 3.78 (s, 3H), 3.68 – 3.55 (m, 1H), 3.30 (d, $J = 16.5$ Hz, 1H), 1.46 (s, 9H).

Minor amide rotamer: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.07 (s, 1H), 7.25 – 7.13 (m, 2H), 5.53 (s, 1H), 5.21 (s, 1H), 4.43 – 4.25 (m, 2H), 3.75 (s, 3H), 3.50 (d, $J = 14.1$ Hz, 1H), 3.13 (d, $J = 15.5$ Hz, 1H), 1.46 (s, 9H).

Mixture of amide rotamers: $^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.0, 167.4, 155.8, 140.9, 130.4, 129.4, 128.0, 126.0, 124.6, 118.1, 114.8, 79.9, 77.1, 60.7, 59.9, 53.3, 52.7, 45.0, 43.4, 33.4, 31.3, 29.7, 28.3.

HRMS (ESI) Calcd for C$_{17}$H$_{21}$ClN$_2$O$_5$Na [M+Na$^+$]: 391.1031, Found: 391.1027.

According to the general experimental procedure, compound 4f was obtained as yellow solid. Two amide rotamers (1.4:1) exist in NMR spectra.

Major amide rotamer: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.98 (d, $J = 6.6$ Hz, 1H), 7.22 (d, $J = 8.1$ Hz, 1H), 6.78 (d, $J = 8.4$ Hz, 1H), 5.46 (br s, 1H), 5.01 (d, $J = 8.5$ Hz, 1H), 4.11 (d, $J = 14.1$ Hz, 1H), 3.85 – 3.80 (m, 1H), 3.79 (s, 3H), 3.70 – 3.54 (m, 1H), 3.41 (d, $J = 16.4$ Hz, 1H), 1.46 (s, 9H).

Minor amide rotamer: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.22 (d, $J = 8.1$ Hz, 1H), 6.98 (d, $J = 27.8$ Hz, 1H), 6.78 (d, $J = 8.4$ Hz, 1H), 5.50 (d, $J = 16.0$ Hz, 1H), 5.24 (s, 1H), 4.37 (d, $J = 24.2$ Hz, 2H), 3.76 (s, 3H), 3.46 (d, $J = 12.3$ Hz, 1H), 3.28 – 3.11 (m, 1H), 1.46 (s, 9H).
Mixture of amide rotamers: $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.9, 167.4, 159.8, 157.4, 155.8, 144.5, 142.3, 130.1, 128.9, 117.4, 114.8, 113.2, 111.5, 111.3, 109.8, 80.0, 60.7, 60.1, 53.3, 52.7, 45.1, 43.6, 30.1, 29.7, 28.3, 28.1, 27.8.

HRMS (ESI) Calcd for C$_{17}$H$_{21}$FN$_2$O$_5$Na [M+Na$^+$]: 375.1327, Found: 375.1325.

According to the general experimental procedure, compound 4g was obtained as yellow solid. Two amide rotamers (3:1) exist in NMR spectra.

Major amide rotamer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.39 (s, 1H), 7.19 – 7.16 (m, 1H), 7.03 (d, $J$ = 7.4 Hz, 1H), 5.45 (br s, 1H), 4.97 (d, $J$ = 9.9 Hz, 1H), 4.19 – 4.06 (m, 1H), 3.81 (d, $J$ = 12.5 Hz, 1H), 3.78 (s, 3H), 3.57 (dd, $J$ = 33.9, 17.9 Hz, 1H), 3.27 (d, $J$ = 16.3 Hz, 1H), 1.46 (s, 9H).

Minor amide rotamer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.28 – 7.20 (m, 2H), 7.06 (s, 1H), 5.48 (br s, 1H), 5.21 (s, 1H), 4.34 – 4.26 (m, 2H), 3.74 (s, 3H), 3.46 – 3.43 (m, 1H), 3.08 (d, $J$ = 14.0 Hz, 1H), 1.47 (s, 9H).

Mixture of amide rotamers: $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 171.0, 167.6, 155.8, 143.4, 127.5, 127.4, 127.1, 126.9, 125.5, 121.4, 120.4, 80.0, 77.5, 60.7, 60.1, 53.3, 52.7, 45.0, 43.5, 33.3, 31.1, 29.7, 28.3.

HRMS (ESI) Calcd for C$_{17}$H$_{21}$BrN$_2$O$_5$Na [M+Na$^+$]: 435.0526, Found: 435.0529.

According to the general experimental procedure, compound 4h was obtained as yellow solid. Two amide rotamers (>20:1) exist in NMR spectra.

Major amide rotamer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.95 (s, 1H), 7.93 (dd, $J$ = 8.2, 1.7 Hz, 1H), 7.41 – 7.26 (m, 2H), 5.51 (s, 1H), 5.14 (d, $J$ = 9.7 Hz, 1H), 4.25 – 4.10 (m, 1H), 3.80 (s, 3H), 3.72 (m, 2H), 3.41 (d, $J$ = 17.6 Hz, 1H), 1.46 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.7, 168.1, 155.9, 148.1, 143.1, 135.8, 124.6, 120.0, 112.3, 80.2, 60.26, 53.4, 43.5, 33.6, 28.3.

HRMS (ESI) Calcd for C$_{17}$H$_{21}$N$_3$O$_7$Na [M+Na$^+$]: 402.1272, Found: 402.1277.
According to the general experimental procedure, compound 4i was obtained as yellow solid. 4i contains two amide rotamers (>20:1).

Major amide rotamer: 1H NMR (400 MHz, CDCl3) δ 9.09 (d, J = 2.0 Hz, 1H), 7.96 (dd, J = 8.2, 1.9 Hz, 1H), 7.27 – 7.16 (m, 6H), 5.54 (d, J = 8.8 Hz, 1H), 4.65 (td, J = 9.7, 5.2 Hz, 1H), 4.20 (d, J = 9.3 Hz, 1H), 3.71 (s, 3H), 3.19 – 2.97 (m, 3H), 2.83 (dd, J = 17.1, 10.7 Hz, 1H), 1.47 (s, 9H).

13C NMR (101 MHz, CDCl3) δ 171.48, 170.39, 154.70, 148.15, 142.40, 136.27, 135.96, 129.42, 128.78, 127.29, 124.43, 120.18, 112.66, 80.02, 60.79, 54.53, 53.37, 41.55, 32.72, 28.33.


According to the general experimental procedure, compound 4j was obtained as yellow solid.

1H NMR (400 MHz, CDCl3) δ 7.94 (d, J = 2.2 Hz, 1H), 7.28 – 7.20 (m, 5H), 7.02 (d, J = 8.2 Hz, 1H), 6.61 (dd, J = 8.2, 2.4 Hz, 1H), 5.45 (d, J = 8.8 Hz, 1H), 4.76 (dd, J = 14.8, 8.4 Hz, 1H), 4.21 – 4.09 (m, 1H), 3.86 (s, 3H), 3.42 (td, J = 10.2, 6.3 Hz, 1H), 3.19 – 2.94 (m, 3H), 2.86 – 2.72 (m, 1H), 1.44 (s, 9H).

13C NMR (101 MHz, CDCl3) δ 170.2, 159.3, 155.2, 143.4, 136.2, 129.4, 128.5, 127.0, 124.7, 123.6, 110.7, 103.4, 79.9, 55.6, 54.2, 48.7, 40.0, 28.3, 27.2.


According to the general experimental procedure, compound 4k was obtained as yellow oil.
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.18 (d, $J = 8.0$ Hz, 1H), 7.26 – 7.17 (m, 2H), 7.08 (t, $J = 7.4$ Hz, 1H), 5.59 (s, 1H), 4.24 – 4.10 (m, 1H), 4.04 (d, $J = 4.3$ Hz, 2H), 3.62 – 3.47 (m, 2H), 1.48 (s, 9H), 1.36 (d, $J = 6.4$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.5, 155.9, 142.0, 136.2, 127.8, 124.3, 123.5, 116.8, 79.8, 54.6, 43.9, 35.0, 28.4, 20.3.

HRMS (ESI) Calcd for C$_{16}$H$_{22}$N$_2$O$_3$Na [M+Na$^+$]: 313.1523, Found: 313.1518.
$^1$H and $^{13}$C NMR spectra of 2a (two amide rotamers, 1.6:1)
$^1$H and $^{13}$C NMR spectra of 2b (two amide rotamers, 1.3:1)
$^1$H and $^{13}$C NMR spectra of \textbf{2c} (two amide rotamers, 4.5:1)
$^1$H and $^{13}$C NMR spectra of 2d (two amide rotamers, 1.7:1)
$^1$H and $^{13}$C NMR spectra of 2e (two amide rotamers, 1.3:1)
$^1$H and $^{13}$C NMR spectra of 2f (two amide rotamers, 1.3:1)
$^1$H and $^{13}$C NMR spectra of 2g (two amide rotamers, 3:1)
$^1$H and $^{13}$C NMR spectra of 2h (two amide rotamers, 3:1)
$^1$H and $^{13}$C NMR spectra of 2i (two amide rotamers, 3:1)
$^1$H and $^{13}$C NMR spectra of 2j (two amide rotamers, 1.5:1)
$^1$H and $^{13}$C NMR spectra of 2k (two amide rotamers, 1.1:1)
$^1$H and $^{13}$C NMR spectra of 2I (two amide rotamers, 1.4:1)
$^1$H and $^{13}$C NMR spectra of 4a (two amide rotamers, 2:1)
$^1$H and $^{13}$C NMR spectra of 4b (two amide rotamers, 1.9:1)
$^{1}H$ and $^{13}C$ NMR spectra of 4e (two amide rotamers, 10:1)
$^1$H and $^{13}$C NMR spectra of 4d (two amide rotamers, 3:1)
$^1$H and $^{13}$C NMR spectra of 4e (two amide rotamers, 2:1)
\(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of 4f (two amide rotamers, 1.4:1)
$^1$H and $^{13}$C NMR spectra of 4g (two amide rotamers, 3:1)
$^1$H and $^{13}$C NMR spectra of 4h (two amide rotamers, >20:1)
$^1$H and $^{13}$C NMR spectra of 4i (two amide rotamers, >20:1)
$^1$H and $^{13}$C NMR spectra of 4j
$^1$H and $^{13}$C NMR spectra of 4k
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