Supporting Information

Double nucleophilic attack on isocyanide carbon: a synthetic strategy for 7-aza-tetrahydroindoles

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I. General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. $^1$H NMR and $^{13}$C NMR spectra were recorded at 25ºC on a Varian 500 MHz and 125 MHz, respectively, and TMS as internal standard. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). Melting points were uncorrected. The substrates, ($E$)-3-oxo-5-substituted-pent-4-enamides 1, were prepared by the similar method as our previously reported papers.$^1$

II. Synthesis and analytical data of 3b–3l

Typical procedure (3b as an example): To the mixture of 1b (414 mg, 1.0 mmol) and ethyl isocyanoacetate (0.136 mL, 1.2 mmol) in CH$_3$CN (5 mL) was added AgOAc (17 mg, 0.1 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.03 mL, 0.2 mmol) in one portion at room temperature. The reaction mixture stirred for 1.5 h until the substrate 1b was consumed as indicated by TLC. Then the resulting mixture was poured into water (40 mL) and extracted with ethyl acetate (40 mL × 3), the organic phase was dried over anhydrous sodium sulphate and concentrated to afford the crude product, which was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 3:1, V/V) to give 3b (524 mg, 99 %). Diastereomers 3b-f, 3h-o and 6a-c were separable to obtain the corresponding pure diastereomers by recrystalization in relevant solvent systems.

3a, white solid, m.p. 286–288 ºC. $^1$H NMR (CDCl$_3$, 500 Hz) δ 0.99 (s, 9H), 1.23 (t, $J$ = 7.5 Hz, 3H), 2.37 (s, 3H), 2.94 (dd, $J$ = 6.0, 2.5 Hz, 1H), 3.06 (dd, $J$ = 6.0, 2.5 Hz, 1H), 3.22–3.41 (m, 4H), 3.53 (d, $J$ = 6.0 Hz, 1H), 4.11–4.16 (m, 2H), 4.82 (d, $J$ = 6.0 Hz, 1H), 7.23–7.27 (m, 4H); $^{13}$C NMR (CDCl$_3$, 125 Hz), δ 14.0, 21.1, 27.9, 32.8, 37.0, 37.4, 49.8, 54.3, 58.5, 61.3, 74.8, 114.8, 127.2, 130.0, 137.3, 139.2, 163.5, 173.2, 185.5, 190.7. HRMS (ESI-TOF) Calcd for C$_{24}$H$_{31}$N$_2$O$_4$S$_2$+ ([M+H$^+$]$^+$) 475.1719. Found 475.1714.

3b-<i>cis</i>, white solid, m.p. 291–293 °C. $^1$H NMR (CDCl₃, 500 Hz) $\delta$ 0.79 (t, $J$ = 7.0 Hz, 3H), 2.39 (s, 3H), 2.96 (t, $J$ = 4.0 Hz, 1H), 3.28–3.30 (m, 2H), 3.35–3.37 (m, 2H), 3.41 (t, $J$ = 6.0 Hz, 1H), 3.58–3.62 (m, 1H), 3.73–3.77 (m, 1H), 4.20–4.26 (m, 2H), 5.56 (t, $J$ = 5.0 Hz, 1H), 7.19 (d, $J$ = 8.0 Hz, 2H), 7.21 (d, $J$ = 7.0 Hz, 2H), 7.26 (d, $J$ = 7.0 Hz, 2H), 7.28 (d, $J$ = 8.0 Hz, 2H); $^{13}$C NMR (CDCl₃, 125 Hz), $\delta$ 13.5, 21.1, 37.1, 37.7, 49.8, 54.6, 61.1, 62.0, 73.4, 113.9, 127.5, 128.6, 129.6, 130.3, 133.3, 137.0, 137.3, 137.6, 163.8, 172.0, 186.3, 188.6.

3b-<i>trans</i>, yellow solid, m.p. 157–159 °C. $^1$H NMR (CDCl₃, 500 Hz) $\delta$ 1.17 (t, $J$ = 7.0 Hz, 3H), 2.38 (s, 3H), 2.84 (d, $J$ = 5.0 Hz, 1H), 3.26–3.35 (m, 3H), 3.36–3.40 (m, 2H), 3.82 (dd, $J$ = 6.5, 5.0 Hz, 1H), 4.02–4.06 (m, 1H), 4.13–4.17 (m, 2H), 5.24 (t, $J$ = 5.0 Hz, 1H), 7.26–7.33 (m, 8H); $^{13}$C NMR (CDCl₃, 125 Hz), $\delta$ 14.0, 21.1, 37.1, 37.6, 49.8, 55.6, 61.5, 64.6, 73.8, 114.1, 127.6, 129.0, 129.1, 130.0, 133.1, 137.5, 137.7, 139.3, 163.5, 172.1, 186.4, 188.5. HRMS (ESI-TOF) Calcd for C$_{26}$H$_{26}$ClN$_2$O$_4$S$_2$ $^{+}$ ([M+H]$^+$) 529.1017. Found 529.1037.

3c, white solid, m.p. 276–278 °C. $^1$H NMR (CDCl₃, 500 Hz) $\delta$ 0.79 (t, $J$ = 7.0 Hz, 3H), 2.38 (s, 3H), 2.96 (t, $J$ = 4.0 Hz, 1H), 3.27–3.30 (m, 2H), 3.34–3.37 (m, 2H), 3.40 (t, $J$ = 6.0 Hz, 1H), 3.59–3.62 (m, 1H), 3.73–3.77 (m, 1H), 4.20–4.26 (m, 2H), 5.56 (dd, $J$ = 6.0, 4.5 Hz, 1H), 7.18–7.21 (m, 4H),
7.25–7.28 (m, 5H); $^{13}$C NMR (CDCl$_3$, 125 Hz), $\delta$ 13.5, 21.1, 37.2, 37.7, 49.8, 54.7, 61.1, 62.1, 73.5, 114.1, 127.6, 128.6, 129.7, 130.3, 133.4, 137.1, 137.5, 137.6, 163.8, 172.0, 186.2, 188.6.

3d, white solid, m.p. 201–203 °C. $^1$H NMR (CDCl$_3$, 500 Hz) $\delta$ 0.75 (t, $J = 7.0$ Hz, 3H), 2.29 (s, 3H), 3.38 (s, 3H), 3.00 (br, 1H), 3.26–3.31 (m, 2H), 3.32–3.36 (m, 2H), 3.40 (t, $J = 6.0$ Hz, 1H), 3.56–3.59 (m 1H), 3.70–3.74 (m, 1H), 4.20 (dd, $J = 9.0$, 3.5 Hz, 1H), 4.27 (dd, $J = 9.0$, 6.5 Hz, 1H), 5.57 (t, $J = 4.5$ Hz, 1H), 7.07 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 Hz), $\delta$ 13.4, 20.9, 21.1, 37.0, 37.6, 49.9, 54.8, 60.8, 62.6, 73.7, 114.2, 127.5, 128.1, 129.0, 130.1, 135.4, 136.9, 137.4, 137.8, 163.8, 172.3, 185.6, 188.9. HRMS (ESI-TOF) Calcd for C$_{27}$H$_{29}$N$_2$O$_4$S$_2$ $^{+}$ ([M+H]$^+$) 509.1563. Found 509.1584.

3e, white solid, m.p. 221–223 °C. $^1$H NMR (CDCl$_3$, 500 Hz) $\delta$ 0.78 (t, $J = 7.0$ Hz, 3H), 2.39 (s, 3H), 2.98 (t, $J = 4.0$ Hz, 1H), 3.27–3.30 (m, 2H), 3.34–3.37 (m, 2H), 3.41 (d, $J = 6.0$ Hz, 1H), 3.56–3.60 (m, 1H), 3.72–3.79 (m, 1H), 3.77 (s, 3H), 4.19 (dd, $J = 9.0$, 4.0 Hz, 1H), 4.25 (dd, $J = 9.0$, 6.5 Hz, 1H), 5.57 (t, $J = 5.0$ Hz, 1H), 6.81 (d, $J = 8.5$ Hz, 2H), 7.16 (d, $J = 8.5$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 Hz), $\delta$ 13.5, 21.1, 37.1, 37.6, 49.7, 54.8, 55.2, 60.9, 62.2, 73.6, 113.8, 114.1, 127.5, 129.3, 130.2, 130.3, 137.5, 137.6, 158.8, 163.8, 172.3, 185.7, 189.0. HRMS (ESI-TOF) Calcd for C$_{27}$H$_{29}$N$_2$O$_5$S$_2$$^-$ ([M+H]$^-$) 525.1512. Found 525.1510.
**3f**, white solid, m.p. 218–220°C. $^1$H NMR (CDCl$_3$, 500 Hz) $\delta$ 0.85 (t, $J = 7.0$ Hz, 3H), 2.38 (s, 3H), 2.93 (br, 1H), 3.26–3.28 (m, 2H), 3.32–3.35 (m, 2H), 3.38 (br, 3H), 3.67–3.71 (m, 1H), 3.77–3.80 (m, 1H), 4.17 (s, 2H), 5.55 (br, 1H), 5.91 (s, 1H), 6.71 (s, 1H), 6.73 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 Hz), $\delta$ 13.6, 21.1, 37.1, 37.6, 50.3, 54.9, 60.9, 62.2, 73.5, 100.9, 108.1, 108.7, 114.0, 121.6, 127.5, 127.6, 130.2, 132.2, 137.4, 146.8, 147.6, 163.8, 172.1, 185.7, 188.8. HRMS (ESI-TOF) Calcd for C$_{27}$H$_{27}$N$_2$O$_6$S$_2$ $^{[\text{M+H}^+]^+}$ 539.1305. Found 539.1305.

![Chemical Structure](image)

**3g**, white solid, $^1$H NMR (CDCl$_3$, 500 Hz) $\delta$ 1.01 (t, $J = 7.5$ Hz, 3H), 2.38 (s, 3H), 2.77 (br, 1H), 3.21–3.26 (m, 1H), 3.26–3.34 (m, 4H), 3.39–3.41 (m, 1H), 3.91–3.94 (m, 1H), 4.17–4.21 (m, 1H), 4.57 (dd, $J = 8.0$, 3.0 Hz, 1H), 5.63 (d, $J = 6.0$ Hz, 2H), 6.17 (d, $J = 3.0$ Hz, 1H), 6.27 (d, $J = 3.0$ Hz, 1H), 7.27–7.29 (m, 4H), 7.34 (s, 1H); $^{13}$C NMR (CDCl$_3$, 125 Hz), $\delta$ 13.8, 21.1, 37.0, 37.5, 42.9, 53.2, 60.7, 61.5, 74.0, 107.7, 110.3, 114.7, 127.3, 130.1, 137.3, 139.0, 142.0, 152.3, 163.6, 171.9, 185.9, 188.3. HRMS (ESI-TOF) Calcd for C$_{24}$H$_{25}$N$_2$O$_5$S$_2$ $^{[\text{M+H}^+]^+}$ 485.1199. Found 485.1199.

![Chemical Structure](image)

**3h**, white solid, m.p. 217–219°C. $^1$H NMR (CDCl$_3$, 500 Hz) $\delta$ 0.79 (t, $J = 7.0$ Hz, 3H), 2.37 (s, 3H), 2.96 (br, 1H), 3.28–3.30 (m, 2H), 3.35–3.37 (m, 2H), 3.40 (t, $J = 5.5$ Hz, 1H), 3.59–3.62 (m, 1H), 3.73–3.77 (m, 1H), 4.21 (s, 2H), 5.55 (t, $J = 5.0$ Hz, 1H), 7.13 (d, $J = 8.5$ Hz, 2H), 7.20 (d, $J = 8.5$ Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 Hz), $\delta$ 13.5, 21.1, 37.2, 37.7, 49.9, 54.6, 61.1, 62.1, 73.5, 114.0, 121.4, 127.5, 130.0, 130.3, 131.6, 137.4, 137.6, 163.8, 172.0, 186.3, 188.6. HRMS (ESI-TOF) Calcd for C$_{26}$H$_{26}$BrN$_2$O$_5$S$_2$ $^{[\text{M+H}^+]^+}$ 573.0512. Found 573.0519.
3i, white solid, m.p. 190–192 °C. 1H NMR (CDCl3, 500 Hz) δ 1.06–1.25 (m, 5H), 1.28 (t, J = 7.0 Hz, 3H), 1.61–1.75 (m, 6H), 2.37 (s, 3H), 2.83 (br, 1H), 3.03–3.06 (m, 1H), 3.17 (t, J = 5.5 Hz, 1H), 3.24–3.33 (m, 2H), 3.34–3.37 (m, 2H), 3.94 (d, J = 8.5 Hz, 1H), 4.16 (q, J = 7.0 Hz, 2H), 5.28 (d, J = 6.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H); 13C NMR (CDCl3, 125 Hz), δ 14.1, 21.1, 26.1, 26.4, 26.6, 29.5, 32.7, 37.1, 37.2, 37.4, 49.5, 50.0, 60.3, 61.2, 73.8, 115.0, 127.5, 130.0, 137.2, 138.5, 163.5, 173.7, 184.9, 191.0. HRMS (ESI-TOF) Calcd for C26H33N2O4S2 + ([M+H]+) 501.1876. Found 501.1873.

3j, white solid, m.p. 255–257 °C. 1H NMR (CDCl3, 500 Hz) δ 1.10 (t, J = 7.0 Hz, 3H), 2.38 (s, 3H), 3.08 (t, J = 5.0 Hz, 1H), 3.17 (t, J = 5.0 Hz, 1H), 3.26–3.41 (m, 4H), 3.97–4.00 (m, 1H), 4.03–4.08 (m, 3H), 5.44 (t, J = 6.0 Hz, 1H), 5.99 (dd, J = 15.0, 10.0 Hz, 1H), 6.60 (d, J = 15.0 Hz, 1H), 7.21 (d, J = 8.0 Hz, 4H), 7.27–7.30 (m, 5H); 13C NMR (CDCl3, 125 Hz), δ 14.2, 21.1, 37.1, 37.6, 47.5, 54.2, 61.3 (2C), 73.6, 114.7, 125.1, 126.3, 127.5, 127.8, 128.5, 130.1, 134.0, 136.4, 137.5, 138.6, 163.7, 172.5, 185.7, 188.5. HRMS (ESI-TOF) Calcd for C28H29N2O4S2 + ([M+H]+) 521.1563. Found 521.1562.

3k, white solid, m.p. 233–235 °C. 1H NMR (CDCl3, 500 Hz) δ 0.79 (t, J = 7.0 Hz, 3H), 2.97 (br, 1H), 3.29–3.32 (m, 2H), 3.36–3.39 (m, 1H), 3.41 (t, J = 5.5 Hz, 1H), 3.59–3.63 (m, 1H), 3.74–3.77 (m, 1H), 4.20–4.29 (m, 2H), 5.60 (t, J = 5.0 Hz, 1H), 7.19 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 7.33 (d,
$J = 7.5$ Hz, 2H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 Hz), δ 13.5, 37.2, 37.7, 49.7, 54.6, 61.1, 62.1, 73.5, 114.0, 127.7, 127.8, 128.6, 129.6, 129.7, 133.4, 137.3, 140.3, 163.7, 172.1, 186.4, 188.6. HRMS (ESI-TOF) Calcd for C$_{25}$H$_{24}$ClN$_2$O$_4$S$_2$ $^+$ ([M+H]$^+$) 515.0861. Found 515.0854.

3l, white solid, m.p. 212–214°C. $^1$H NMR (CDCl$_3$, 500 Hz) δ 0.72 (t, $J = 7.0$ Hz, 3H), 3.03 (br, 1H), 3.28–3.33 (m, 2H), 3.34–3.39 (m, 2H), 3.44 (t, $J = 5.5$ Hz, 1H), 3.53–3.57 (m, 1H), 3.69–3.73 (m, 1H), 4.24 (d, $J = 9.0$ Hz, 1H), 4.34 (dd, $J = 9.0$, 6.0 Hz, 1H), 5.63 (d, $J = 6.0$ Hz, 1H), 7.24 (d, $J = 7.0$ Hz, 2H), 7.28 (t, $J = 8.0$ Hz, 3H), 7.36 (t, $J = 8.0$ Hz, 3H), 7.48 (t, $J = 8.0$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 Hz), δ 13.4, 37.1, 37.6, 50.1, 54.7, 60.9, 62.1, 73.7, 114.2, 127.4, 127.6, 127.8, 128.2, 128.5, 129.5, 138.7, 140.6, 163.7, 186.0, 188.9.

### III. Synthesis and analytical data of 3m-o

Typical procedure (3m as an example): To the mixture of 1m (339 mg, 1.0 mmol) and ethyl isocyanocacetate (0.136 mL, 1.2 mmol) in CH$_3$CN (5 mL) was added AgOAc (17 mg, 0.1 mmol) and 1,8-diazabicyclo [5.4.0.]undec-7-ene (DBU) (0.076 mL, 0.5 mmol) in one portion at room temperature. After stirred for 2.0 h, the substrate 1b was consumed as indicated by TLC. Then another portion of DBU (0.152 mL, 1.0 mmol) was added, the reaction mixture was stirred for another 5.0 h. The resulting mixture was poured into water (40 mL) and extracted with ethyl acetate (40 mL×3), the organic phase was dried over anhydrous sodium sulphate and concentrated to afford the crude product, which was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 3: 1, V/V) to give 3m (362 mg, 80%).
3m, white solid, m.p. 201–203 °C. ^1^H NMR (CDCl$_3$, 500 Hz) δ 1.21 (t, $J = 7.0$ Hz, 3H), 3.17–3.19 (m, 1H), 3.18 (s, 3H), 3.30–3.32 (m, 2H), 3.34–3.36 (m, 2H), 3.88 (d, $J = 6.5$ Hz, 1H), 3.91 (t, $J = 6.5$ Hz, 1H), 4.10–4.18 (m, 2H), 4.87 (d, $J = 6.5$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 Hz), δ 14.1, 32.1, 37.0, 37.5, 50.6, 56.3, 61.6, 65.1, 73.5, 114.0, 129.0 (2C), 133.2, 139.1, 163.5, 172.4, 184.6, 188.5.

3n, white solid, m.p. 182–184 °C. ^1^H NMR (CDCl$_3$, 500 Hz) δ 1.21 (t, $J = 7.0$ Hz, 3H), 3.18–3.21 (m, 1H), 3.19 (s, 3H), 3.29–3.34 (m, 4H), 3.93 (d, $J = 6.5$ Hz, 1H), 4.02 (t, $J = 6.5$ Hz, 1H), 4.10–4.17 (m, 2H), 4.89 (d, $J = 6.0$ Hz, 1H), 7.32–7.35 (m, 5H); $^{13}$C NMR (CDCl$_3$, 125 Hz), δ 14.0, 32.5, 36.9, 37.5, 51.1, 56.2, 61.5, 65.0, 73.7, 114.1, 127.3, 127.6, 128.8, 140.9, 163.5, 172.7, 184.2, 188.8. HRMS (ESI-TOF) Calcd for C$_{20}$H$_{23}$N$_{2}$O$_{4}$S$_{2}$ $^{([M+H])}$ 419.1094. Found 419.1085.

3o, white solid, m.p. 220–222 °C. ^1^H NMR (CDCl$_3$, 500 Hz) δ 1.21 (t, $J = 7.0$ Hz, 3H), 2.33(s, 3H), 3.16–3.20 (m, 1H), 3.19 (s, 3H), 3.29–3.35 (m, 4H), 3.91 (d, $J = 6.5$ Hz, 1H), 3.95 (d, $J = 6.5$ Hz, 1H), 4.09–4.17 (m, 2H), 4.87 (d, $J = 5.5$ Hz, 1H), 7.15 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 125 Hz), δ 14.1, 21.0, 32.3, 36.9, 37.5, 50.8, 56.4, 61.5, 65.1, 73.6, 114.1, 127.4, 129.5, 136.9, 137.7, 163.5, 172.8, 184.1, 188.8. HRMS (ESI-TOF) Calcd for C$_{21}$H$_{25}$N$_{2}$O$_{4}$S$_{2}$ $^{([M+H])}$ 433.1250. Found 433.1260.

IV. Synthesis and analytical data of 6a-6c

Typical procedure (6a as an example): To the mixture of 5a (338 mg, 1.0 mmol) and ethyl isocyanoacetate (0.136 mL, 1.2 mmol) in CH$_3$CN (5 mL) was added AgOAc (17 mg, 0.1 mmol) and 1,8-diazabicyclo [5.4.0.]undec-7-ene (DBU) (0.152 mL, 1.0 mmol) in one portion at room temperature.
The reaction mixture stirred for 22.0 h until the substrate 5a was consumed as indicated by TLC. Then the resulting mixture was poured into water (40 mL) and extracted with ethyl acetate (40 mL× 3), the organic phase was dried over anhydrous sodium sulphate and concentrated to afford the crude product, which was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 3: 1, V/V) to give 6a (366 mg, 81 %).

6a, white solid, m.p. 226–227°C. 1H NMR (CDCl3, 500 Hz) δ 0.79 (t, J = 7.0 Hz, 3H), 1.71 (d, J = 5.5 Hz, 2H), 1.87 (t, J = 5.5 Hz, 2H), 2.39 (s, 3H), 3.04 (br, 1H), 3.37 (t, J = 6.0 Hz, 1H), 3.60–3.63 (m, 1H), 3.75–3.78 (m, 1H), 4.24–4.30 (m, 2H), 5.69 (t, J = 5.5 Hz, 1H), 7.16 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 4H); 13C NMR (CDCl3, 125 Hz), δ 13.5, 21.1, 24.1, 25.2, 32.4, 48.7, 56.1, 61.2, 61.9, 74.0, 127.3, 128.7, 129.5, 130.3, 133.6, 136.4, 137.6, 137.8, 168.3, 172.1, 203.1. HRMS (ESI-TOF) Calcd for C25H26ClN2O4+ ([M+H]+) 453.1576. Found 453.1550.

6b, white solid, m.p. 184–186°C. 1H NMR (CDCl3, 500 Hz) δ 0.72 (t, J = 7.0 Hz, 3H), 1.69–1.72 (m, 2H), 1.83–1.87 (m, 2H), 2.39 (s, 3H), 3.07 (t, J = 3.5 Hz, 1H), 3.41 (t, J = 6.0 Hz, 1H), 3.53–3.57 (m, 1H), 3.70–3.74 (m, 1H), 4.26 (dd, J = 9.0, 3.5 Hz, 1H), 4.33 (dd, J = 9.0, 6.0 Hz, 1H), 5.73 (t, J = 5.0 Hz, 1H), 7.19–7.21 (m, 4H), 7.24–7.30 (m, 4H); 13C NMR (CDCl3, 125 Hz), δ 13.4, 21.1, 23.9, 25.0, 32.4, 49.2, 56.2, 61.0, 62.0, 74.2, 127.3, 127.7, 128.1, 128.6, 130.2, 133.7, 137.9, 168.7, 172.4, 203.3.
6c, white solid, m.p. 216–218 °C. 1H NMR (CDCl3, 500 Hz) δ 0.75 (t, J = 7.0 Hz, 3H), 1.70 (d, J = 5.5 Hz, 2H), 1.85 (d, J = 5.0 Hz, 2H), 2.30 (s, 3H), 2.39 (s, 3H), 3.05 (t, J = 3.5 Hz, 1H), 3.39 (t, J = 6.0 Hz, 1H), 3.57–3.60 (m, 1H), 3.72–3.76 (m, 1H), 4.22–4.31 (m, 2H), 5.70 (t, J = 5.0 Hz, 1H), 7.08 (s, 4H), 7.18 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H); 13C NMR (CDCl3, 125 Hz), δ 13.4, 21.0, 21.1, 23.7, 25.0, 32.4, 49.0, 56.3, 61.0, 62.1, 74.2, 127.4, 128.0, 129.2, 130.2, 134.6, 137.3, 137.7, 137.8, 168.8, 172.4, 203.3. HRMS (ESI-TOF) Calcd for C26H29N2O4+ ([M+H]+) 433.2122. Found 433.2123.

V. Analytical data of 4b

4b-trans, yellow solid, m.p. 167–169 °C. 1H NMR (CDCl3, 500 Hz) δ 1.32 (t, J = 7.0 Hz, 3H), 2.28 (s, 3H), 3.25–3.37 (m, 4H), 4.21–4.29 (m, 2H), 4.33 (d, J = 5.0 Hz, 1H), 4.61 (d, J = 5.0, 1H), 5.82 (s, 1H), 7.07 (d, J = 8.0 Hz, 2H), 7.25–7.37 (m, 6H), 7.51 (d, J = 3.0 Hz, 1H), 8.76 (s, 1H); 13C NMR (CDCl3, 125 Hz), δ 14.0, 20.7, 36.8, 38.0, 48.8, 62.0, 69.0, 116.4, 119.8, 121.2, 128.6, 128.7, 129.1, 132.7, 133.3, 135.3, 141.0, 154.2, 161.8, 162.3, 170.9, 186.4.

4b-cis, yellow solid, m.p. 217–219 °C. 1H NMR (CDCl3, 500 Hz) δ 0.86 (t, J = 7.0 Hz, 3H), 2.29 (s, 3H), 3.24–3.28 (m, 1H), 3.28–3.40 (m, 3H), 3.62–3.66 (m, 1H), 3.76–3.80 (m, 1H), 4.69 (d, J = 12.0, 1H), 4.94 (d, J = 12.0, 1H), 5.70 (br, 1H), 7.07 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 4H), 7.35 (d, J = 8.5 Hz, 2H), 7.56 (d, J = 3.5 Hz, 1H), 8.67 (s, 1H); 13C NMR (CDCl3, 125 Hz), δ 13.5, 20.8, 37.0, 38.2, 48.0, 61.4, 66.8, 117.0, 119.9, 121.4, 128.2, 129.3, 129.9, 133.0, 133.4, 135.5, 137.2, 154.8, 161.4, 162.5, 169.2, 186.2.
VI. Copies of NMR spectra for compounds 3a-3l, 3m-3o, 4b, 4m, 6a-6c
Electronic Supplementary Material (ESI) for Chemical Communications
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STANDARD PROTON PARAMETERS

Archive directory: /export/home/ouy/vnmrsvsys/data
Sample directory:

Pulse Sequence: s2puls
Solvent: CDCl3
Ambient Temperature
file: s359
NMR-500 "MERLIN"

Relax. delay 1,000 sec
Pulse 45.0 degrees
Acq. time 1,892 sec
Width 0.067 mHz
3 repetitions

OBSERVED: 489.30259 MHz
DATA PROCESSING
FF size 8535
Total time 8 min, 23 sec

3d-cis
STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: ZG313
Solvent: DMSO-d6
Ambient temperature
User: 1-14-08
File: m423
INova-500 "MREV590"

Relax delay 0.500 sec
Pulse 45.0 degree
Acq. time 1.380 sec
Width 31421.6 Hz
5120 repetitions

OBSERVE C11, 125.257 MHz
DECUPLE M1, 489.0650805 MHz
Power 40 dB
continuously on
VALTZ-15 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

22
STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouuy/vnmrsys/data
Sample directory:

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: l-15-07
File: 051
INOV-500 "8cENUS500"

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.280 sec
Width 31421.5 Hz
832 repetitions
Observ. qL, 125.6754567 MHz
DECOUPLE H1, 498.805965 MHz
Power 42 dB
Continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec

220 200 180 160 140 120 100 80 60 40 20 0 ppm
STANDARD CARBON PARAMETERS

Archive directory: /export/home/ovyy/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1
Solvent: CDCl3
Ambient temperature
User: L-14-87
File: 1982
INOMA-500 "MKM0500"

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.360 sec
Width 31421.8 Hz
329 repetitions
OBSERVE CI3, 125.6754661 MHz
REDUCE HI, 498.8050469 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec
STANDARD PROTON PARAMETERS

Archive directory: /export/home/nguy/vnmrsys/data
Sample directory:

Pulse Sequence: z2pul
Solvent: CDCl3
Ambient temperature
File: z8866
INOVAS-500 "MERUS-500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.812 sec
Width 2237.4 Hz
8 repetitions

DESSPINE H1, 400.0025500 MHz
DATA PROCESSING
FT size 65536
Total time 8 min, 23 sec

3k-cis
STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: t2pul
Solvent: CCl4
Ambient temperature
User: I.16-87
File: t108
INNOVA-500 "NENUS6A"

Relax. delay 0.50 sec
Pulse 45.0 degrees
Acq. time 1.360 sec
Width 31431.8 Hz
512 repetitions

OBSERVE G1, 125.675646 MHz
DECSUPLE H1, 408.8050405 MHz

Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 58 sec
STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: 62pul
Solvent: CDCl3
Ambient temperature
User: 1-10-87
File: w65
INOVAM-SEQ "HENUS90"

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 3423.0 Hz
192 repetitions

OBSERVE C13, 125.6754870 MHz
DECouple H1, 499.8856805 MHz
Power 42 dB continuously on
WALTZ-10 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 331272
Total time 3 hr, 56 sec
STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouy/vnmrsys/data
Sample directory:

Pulse Sequence: s1p1
Solvent: CDC13
Ambient temperature
User: 3-16-87
f116: m417
INOVO-100 "NERUS80"

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.380 sec
Field Width 31421.0 Hz
320 repetitions

OBSERVE C13, 125.6754461 MHz
DECOUPLE H1, 498.8000000 MHz
Power 46 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING:
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec
STANDARD CARBON PARAMETERS

Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s1p1
Solvent: CDCl3
Ambient temperature
User: L-14-87
File: L746
INVA-500 "NMR500"

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.580 sec
Width 31421.0 Hz
256 repetitions

OBSERVE C13, 125.6754632 MHz
DECUPLE H1, 498.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec
STANDARD CARBON PARAMTERS

 любимый родной

 Archive directory: /export/home/ouy/wnmrkys/data
 Sample directory:
 Pulse Sequence: s2pal
 Solvent: CDC13
 Ambient temperature
 User: 1-14-67
 File: a647
 INOVA-500 "WEN508"
 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 1.360 sec
 Width 31521.0 Hz
 192 repetitions
 OBSERVE CL2, 125.6754642 MHz
 DECOUPLE H1, 499.8059085 MHz
 Power 42 dB
 continuously on
 WAIT 15 seculated
 DATA PROCESSING
 Line broadening 1.5 Hz
 FT size 131072
 Total time 2 hr, 3 min, 31 sec

 6b: cis

 220 200 180 160 140 120 100 80 60 40 20 0 ppm
STANDARD CARBON PARAMETERS

Archive directory: /export/home/nguy/vnmrsys/data
Sample directory:

Pulse Sequence: t2pul
Solvent: CDCl3
Ambient temperature
User: 2-14-07
File: 1566
INova-500 "HEMU500"

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.380 sec
Width 31421.8 Hz
794 repetitions

OBSERVE C13, 125.6754627 MHz
DECOUPLE H1, 498.6050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 128162
Total time 15 hr, 4 min, 41 sec