

Supporting Information For

Highly Stereoselective Synthesis of *cis*- β -Enaminones Mediated by Diethyl Azodicarboxylate

Xiaoliang Xu,^{*,a} Ping Du,^a Dongping Cheng,^b Hong Wang,^a and Xiaonian Li^{*,a}

^a Institute of Industrial Catalysis, College of Chemical Engineering and Materials Science,
Zhejiang University of Technology, Hangzhou 310014, People's Republic of China

^b College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou 310014,
People's Republic of China

E-mail: xuxiaoliang@zjut.edu.cn; xnli@zjut.edu.cn

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Experimental Section

All reactions were carried out without exclusion of air or moisture. DMF, ClCH₂CH₂Cl, CH₂Cl₂, THF, toluene, and CH₃CN were analytical reagents and used directly as received. Propargyamines were prepared according to literature (L. W. Bieber, M. F. da Silva, *Tetrahedron Lett.*, **2004**, *45*, 8281-8283). ¹H and ¹³C NMR spectra were recorded at room temperature in CDCl₃ or DMSO-*d*₆ on Bruker AMX-500 MHz instrument with TMS as internal standard. Low-resolution MS was obtained using ESI ionization. HRMS was obtained using ESI ionization.

In a typical procedure: To a 10 mL two-necked round-bottom flask on an ice-water bath with a mixture of 1-(3-phenylprop-2-ynyl)piperidine (0.199 g, 1 mmol) and H₂O (0.027 mL, 1.5 mmol), was dropwise added diethyl azodicarboxylate (0.235 mL, 1.5 mmol) in 8-10 min. The resulting mixture was stirred for 6h. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether and ethyl acetate (1:3 - 1:6) as the eluent to give the pure product.

2a: ¹H NMR (500 MHz, CDCl₃) δ= 1.56-1.70 (m, 6H), 3.38 (brs, 4H), 5.55-5.57 (d, *J*= 8.5Hz, 1H), 7.28-7.31 (m, 2H), 7.42-7.47 (m, 3H), 8.63-8.65 (d, *J*= 8.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ= 24.3, 25.9, 49.3, 103.8, 128.5, 129.3, 129.5, 134.4, 167.9, 191.6; MS (ESI): ([M+H]⁺) 216.1; HRMS (ESI) calcd for C₁₄H₁₇NO ([M+H]⁺) 216.1388, found 216.1392.

2b: ¹H NMR (500 MHz, DMSO-*d*₆) δ= 1.51-1.61 (m, 6H), 3.21 (brs, 4H), 3.81 (s, 3H), 5.34-5.36 (d, *J*= 8.5Hz, 1H), 7.03-7.05 (m, 2H), 7.25-7.26 (m, 2H), 8.55-8.57 (d, *J*= 8.5 Hz, 1H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ= 23.8, 25.2, 48.5, 55.2, 102.8, 113.9, 126.1, 130.5, 160.0, 166.9, 189.0; MS (ESI): ([M+H]⁺) 246.2; HRMS (ESI) calcd for C₁₅H₁₉NO₂ ([M+H]⁺) 246.1494, found 246.1499.

2c: ¹H NMR (500 MHz, CDCl₃) δ= 1.58-1.70 (m, 6H), 3.24 (brs, 4H), 5.48-5.50 (d, *J*= 8.5Hz, 1H), 7.11-7.15 (t, *J*= 8.6 Hz, 2H), 7.29-7.30 (m, 2H), 8.68-8.70 (d, *J*= 8.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ= 24.3, 25.7, 49.3, 104.3, 115.6 and 115.8 (d, *J*= 22 Hz), 130.4 and 130.39 (d, *J*= 3.4 Hz), 131.2 and 131.3 (d, *J*= 8 Hz), 162.4 and 164.3 (d, *J*= 248 Hz), 166.7, 191.3; MS (ESI): ([M+H]⁺) 234.1 ; HRMS (ESI) calcd for C₁₄H₁₆FNO ([M+H]⁺) 234.1294, found 234.1296.

2d: ^1H NMR (500 MHz, CDCl_3) δ = 1.57-1.68 (m, 6H), 3.20 (brs, 4H), 5.47-5.48 (d, J = 8.5Hz, 1H), 7.23-7.24 (m, 2H), 7.40-7.42 (m, 2H), 8.68-8.70 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ = 24.2, 25.7, 49.2, 104.2, 128.9, 130.7, 132.9, 135.7, 166.4, 191.1; MS (ESI): ($[\text{M}+\text{H}]^+$) 250.1; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{ClNO}$ ($[\text{M}+\text{H}]^+$) 250.0999, found 250.0994.

2e: ^1H NMR (500 MHz, CDCl_3) δ = 1.60-1.70 (m, 6H), 3.23 (brs, 4H), 5.50-5.51 (d, J = 8.5Hz, 1H), 7.19-7.20 (m, 2H), 7.58-7.60 (m, 2H), 8.70-8.72 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ = 24.2, 25.8, 49.2, 104.2, 124.0, 131.0, 131.9, 133.4, 166.4, 191.2; MS (ESI): ($[\text{M}+\text{H}]^+$) 294.0; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{BrNO}$ ($[\text{M}+\text{H}]^+$) 294.0494, found 294.0489.

2f: ^1H NMR (500 MHz, CDCl_3) δ = 1.59-1.69 (m, 6H), 3.22 (brs, 4H), 5.48-5.49 (d, J = 8.5Hz, 1H), 7.19-7.20 (d, J = 7.5 Hz, 1H), 7.28-7.31 (d, J = 15.2Hz, 1H), 7.37-7.39 (m, 1H), 7.43-7.45 (m, 1H), 8.69-8.71 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ = 24.2, 25.8, 49.2, 104.1, 127.6, 129.3, 129.7, 129.9, 134.7, 136.2, 165.9, 191.2; MS (ESI): ($[\text{M}+\text{H}]^+$) 250.1; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{16}\text{ClNO}$ ($[\text{M}+\text{H}]^+$) 250.0999, found 250.0995.

2g: ^1H NMR (500 MHz, CDCl_3) δ = 3.23 (brs, 4H), 3.73 (brs, 4H), 5.48-5.50 (d, J = 8.5Hz, 1H), 7.31-7.34 (m, 2H), 7.44-7.50 (m, 3H), 8.81-8.83 (d, J = 8.5Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ = 48.1, 66.4, 104.9, 128.7, 129.6, 129.9, 133.5, 167.9, 191.8; MS (ESI): ($[\text{M}+\text{H}]^+$) 218.3; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$ ($[\text{M}+\text{H}]^+$) 218.1181, found 218.1182.

2h: ^1H NMR (500 MHz, CDCl_3) δ = 0.99-1.02 (m, 3H), 1.26-1.30 (m, 3H), 3.02 (brs, 2H), 3.43 (brs, 2H), 5.43-5.45 (d, J = 8.5Hz, 1H), 7.28-7.29 (m, 2H), 7.43-7.45 (m, 3H), 8.55-8.57 (d, J = 8.5Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ = 11.8, 14.2, 43.7, 45.0, 103.1, 128.3, 129.1, 129.1, 134.2, 166.8, 191.0; MS (ESI): ($[\text{M}+\text{Na}]^+$) 226.1; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{17}\text{NO}$ ($[\text{M}+\text{Na}]^+$) 226.1208, found 226.1207.

2i: ^1H NMR (500 MHz, CDCl_3) δ =; ^{13}C NMR (125 MHz, CDCl_3) δ = 0.68-0.70 (m, 3H), 0.95-1.01 (m, 5H), 1.36 (s, 4H), 1.67 (s, 2H), 2.89 (s, 2H), 3.29 (s, 2H), 5.36-5.38 (d, J = 8.5Hz, 1H), 7.20-7.22 (m, 2H), 7.38-7.39 (m, 3H), 8.52-8.53 (d, J = 8.4Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ = 13.4, 13.7, 19.6, 20.2, 28.0, 31.0, 49.3, 51.0, 103.1, 128.1, 128.3, 129.0, 134.0, 167.2, 190.9; MS (ESI): ($[\text{M}+\text{H}]^+$) 260.2; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{15}\text{NOS}$ ($[\text{M}+\text{H}]^+$) 260.2014, found 260.2006.

2j: ^1H NMR (500 MHz, CDCl_3) δ = 0.84-0.87 (m, 3H), 1.29-1.34 (m, 4H), 1.47-1.51 (m, 2H), 1.54-1.59 (m, 4H), 1.63-1.66 (m, 2H), 2.60-2.63 (m, 2H), 3.31-3.33 (m, 4H), 5.20-5.21 (d, J = 8.3Hz, 1H), 9.51-9.53 (d, J = 8.3Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ = 13.9, 22.3, 24.3, 25.8, 28.0, 29.1, 31.5, 48.0, 100.9, 167.0, 187.6; MS (ESI): ($[\text{M}+\text{H}]^+$) 210.2; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{23}\text{NO}$ ($[\text{M}+\text{H}]^+$) 210.1858, found 210.1858.

2k: ^1H NMR (500 MHz, CDCl_3) δ = 1.57-1.66 (m, 6H), 3.22 (brs, 4H), 5.47-5.49 (d, J = 8.3 Hz, 1H), 7.02-7.03 (m, 1H), 7.33-7.35 (m, 1H), 7.39-7.41 (m, 1H), 8.81-8.83 (d, J = 8.3 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ = 24.3, 25.7, 49.2, 104.5, 126.5, 127.2, 128.2, 134.7, 162.7, 191.4; MS (ESI): ($[\text{M}+\text{H}]^+$) 222.1; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{15}\text{NOS}$ ($[\text{M}+\text{H}]^+$) 222.0953, found 222.0943.











































