Supporting Information

The First Tandem Free-Radical Cyclization Reaction of Alkylenecyclopropanes: A Novel and Efficient Method for the Preparation of 2-(3,4-Dihydronaphthalen-2-yl)malonic Acid Diethyl Esters

Hongwei Zhou, [a] Xian Huang*, [a, b] and Wanli Chen [a]

[a]*Department of Chemistry, Zhejiang University(Campus Xixi), Hangzhou 310028, P.R. China*

[b]*State Key Laboratory of Oganometallic Chemistry, Shanghai Institue of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P.R. China*

huangx@mail. hz.zj.cn Fax: +86-571-88807077

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Experimental Section

Typical experimental procedure

General. All ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on 400 MHz spectrometer with TMS as the internal standard. Chemical shifts are expressed in ppm and *J* values are given in Hz. Thin layer chromatography (TLC) was performed on SiO_2 plates eluting with a 6:1 mixture of hexane/EtOAc as the eluent unless noted otherwise.

Typical Procedure. A solution of **1a** (130 mg, 1.0 mmol) with $Mn(OAc)_3 \cdot 2H_2O$ (530 mg, 2.0 mmol) and malonic acid diethyl ester (160 mg, 1.0 mmol) in $HOAc/Ac_2O$ (9:1, 5 mL) was stirred at 65°C under N_2 atmosphere for 10 h. The mixture was then diluted with 40 mL of saturated NaCl and extracted three times with EtOAc. The organic phases were combined and dried over $MgSO_4$. After evaporation, the residues were purified via chromatography on silica gel with *n*-hexane/ EtOAc (10:1) as the eluent to afford 196 mg (68%) of **2a**.

2-(3,4-dihydro-naphthalen-2-yl)-malonic acid diethyl ester (2a): oil, 196mg, TLC: Rf = 0.58. ^{1}H NMR (400M Hz, $CDCl_3$): δ 7.13-7.17(m, 3H), 7.04-7.05 (m, 1H), 6.46 (s, 1H), 4.22-4.28 (q, 4H, *J* = 6.8 Hz), 2.87-2.90 (t, 2H, *J* = 7.6 Hz), 2.45-2.49 (t, 2H, *J* = 7.6 Hz), 1.29-1.33 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR (100M Hz, $CDCl_3$): δ 168.5 (C=O), 138.7, 137.7, 134.2, 127.5, 127.1, 126.5, 126.3, 122.3, 61.5 (CH_2), 56.5(CH), 27.6 (CH_2), 27.2 (CH_2), 13.9 (CH_3). EIMS m/z (relative intensity, %): 289 [M^++1,

58.47], 288[M^+, 65.04]. IR (neat): 1725.2 cm^{-1}Anal. Calcd. For $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.57; H, 6.59.

2-(6-Methyl-3,4-dihydro-naphthalen-2-yl)-malonic acid diethyl ester (2b): oil, 211mg, TLC: Rf = 0.59. ^{1}H NMR (400M Hz, $CDCl_3$): δ 7.10 (m, 1H), 6.83-6.85(m, 2H), 6.41 (s, 1H), 4.21-4.27 (q, 4H, *J* = 6.8 Hz), 2.85-2.88 (t, 2H, *J* = 7.6 Hz), 2.42-2.45 (t, 2H, *J* = 7.6 Hz), 2.30(s, 3H), 1.28-1.32 (t, 6H, *J* = 6.8 Hz). ^{13}C NMR (100M Hz, $CDCl_3$): δ 168.2 (C=O), 138.1, 136.8, 136.2, 133.9, 126.5, 125.7, 125.2, 122.0, 61.2 (CH_2), 56.2 (CH), 26.9 (CH_2), 26.7 (CH_2), 21.7 (CH_3), 13.8 (CH_3). EIMS m/z (relative intensity, %): 303 [M^++1, 31.28], 302 [M^+, 58.24]. IR (neat): 1726.5 $cm^{-1.}$ Anal. Calcd. For $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.28; H, 7.17.

2-(1-Phenyl-3,4-dihydro-naphthalen-2-yl)-malonic acid diethyl ester (2c): solid, mp: 55-58^{o}C, 262mg, TLC: Rf = 0.58. ^{1}H NMR (400M Hz, $CDCl_3$): δ 7.12-7.30 (m, 8H), 7.03-7.04(m, 1H), 4.24-4.29 (q, 4H, *J* = 6.8 Hz), 2.88-2.91 (t, 2H, *J* = 7.6 Hz), 2.46-2.50 (t, 2H, *J* = 7.6 Hz), 1.29-1.33 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR (100M Hz, $CDCl_3$): δ 168.8 (C=O), 137.5, 135.2, 134.7, 133.8, 128.7, 128.2, 127.5, 127.3, 127.0, 126.8, 125.8, 124.3, 61.2 (CH_2), 51.8 (CH), 27.8 (CH_2), 27.5 (CH_2), 13.7 (CH_3). EIMS m/z (relative intensity, %): 365 [M^++1, 25.16], 364 [M^+, 44.40]. IR (neat): 1728.0 cm^{-1}Anal. Calcd. For $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.56; H, 6.45.

2-(1-Methyl-3,4-dihydro-naphthalen-2-yl)-malonic acid diethyl ester (2d): oil, 178mg, TLC: Rf = 0.59. ^{1}H NMR (400M Hz, $CDCl_3$): δ 7.10-7.14(m, 3H), 7.01-7.04 (m, 1H), 4.21-4.27 (q, 4H, *J* = 7.2 Hz), 2.86-2.89 (t, 2H, *J* = 7.2 Hz), 2.43-2.46 (t, 2H,

J = 7.6 Hz), 1.95 (s, 3H), 1.28-1.32 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR (100M Hz, $CDCl_3$): δ 168.5 (C=O), 135.7, 133.8, 129.5, 128.8, 127.8, 127.5, 127.0, 125.2, 61.1 (CH_2), 53.2 (CH), 27.0 (CH_2), 26.6 (CH_2), 19.5 (CH_3), 13.8 (CH_3). EIMS m/z (relative intensity, %): 303 [M^++1, 35.48], 302 [M^+, 48.77]. IR (neat): 1727.0 cm^{-1}. Anal. Calcd. For $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.33; H, 7.15.

2-(6-Methoxyl-3,4-dihydro-naphthalen-2-yl)-malonic acid diethyl ester (2e): oil, 203mg, TLC: Rf = 0.57. ^{1}H NMR (400M Hz, $CDCl_3$): δ 7.12 (m, 1H), 6.61-6.63(m, 2H), 6.42 (s, 1H), 4.19-4.25 (q, 4H, *J* = 7.2 Hz), 3.72(s, 3H), 2.79-2.82 (t, 2H, *J* = 7.2 Hz), 2.37-2.40 (t, 2H, *J* = 7.6 Hz), 1.27-1.31 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR (100M Hz, $CDCl_3$): δ 168.1 (C=O), 159.9, 138.2, 135.5, 130.0, 126.8, 121.7, 115.9, 115.6, 61.2 (CH_2), 57.8 (CH), 56.0 (CH_3), 26.8 (CH_2), 26.5 (CH_2), 13.7 (CH_3). EIMS m/z (relative intensity, %): 319 [M^++1, 22.27], 318 [M^+, 45.78]. IR (neat): 1726.5 cm^{-1}. Anal. Calcd. For $C_{18}H_{22}O_5$: C, 67.91; H, 6.97; Found: C, 67.73; H, 6.77.

2-(6-Chloro-3,4-dihydro-naphthalen-2-yl)-malonic acid diethyl ester (2f): solid, mp: 45-47^{o}C, 193mg, TLC: Rf = 0.55. ^{1}H NMR (400M Hz, $CDCl_3$): δ 7.15 (m, 1H), 7.05-7.08 (m, 2H), 6.46 (s, 1H), 4.22-4.28 (q, 4H, *J* = 7.2 Hz), 2.84-2.87 (t, 2H, *J* = 7.6 Hz), 2.41-2.45 (t, 2H, *J* = 7.6 Hz), 1.29-1.33 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR: (100M Hz, $CDCl_3$): δ 166.7 (C=O), 140.0, 134.7, 132.8, 132.2, 128.6, 127.2, 126.0, 122.5, 61.6 (CH_2), 56.8 (CH), 28.6 (CH_2), 28.4 (CH_2), 13.9 (CH_3).. EIMS m/z (relative intensity, %) 324 [M^++2, 10.47], 323 [M^++1, 15.70], 322 [M^+, 44.97]. IR (neat): 1727.9 cm^{-1}. Anal. Calcd. For $C_{17}H_{19}ClO_4$: C, 63.26; H, 5.93; Found: C, 63.47; H,

6.07.

2-(6-Bromo-3,4-dihydro-naphthalen-2-yl)-malonic acid diethyl ester (2g): solid, mp: 48-50°C, 245mg, TLC: Rf = 0.55. ^{1}H NMR (400M Hz, $CDCl_3$) δ 7.14 (m, 1H), 7.04-7.08 (m, 2H), 6.44 (s, 1H), 4.21-4.27 (q, 4H, *J* = 6.8 Hz), 2.83-2.86 (t, 2H, *J* = 7.2 Hz), 2.41-2.45 (t, 2H, *J* = 7.6 Hz), 1.28-1.32 (t, 6H, *J* = 7.2 Hz) ^{13}C NMR (100M Hz, $CDCl_3$): δ 166.6 (C=O), 140.8, 135.6, 133.7, 130.9, 128.3, 127.8, 123.3, 122.0, 61.5 (CH_2), 56.5 (CH), 28.5 (CH_2), 28.3 (CH_2), 13.8 (CH_3). EIMS m/z (relative intensity, %): 368 [M^++2, 33.95], 367 [M^++1, 24.37], 366 [M^+, 39.17]. IR (neat) 1727.0 cm^{-1}. Anal. Calcd. For $C_{17}H_{19}BrO_4$: C, 55.60; H, 5.21; Found: C, 55.73; H, 5.35.

2-[3-(4-methoxy-phenyl)-2-methyl-1-vinyl- propenyl] malonic acid diethyl ester (2j): oil, 142mg, TLC: Rf = 0.61. ^{1}H NMR (400M Hz, $CDCl_3$): δ 7.02-7.04 (m, 2H), 6.73-6.75 (m, 2H), 6.33-6.36 (m, 1H), 5.43-5.46 (d, 1H, *J* = 15.2 Hz), 5.32-5.35 (d, 1H, *J* = 9.2 Hz), 4.22-4.28 (q, 4H, *J* = 7.2 Hz), 3.76 (s, 3H), 3.19(s, 2H), 1.98 (s, 3H), 1.27-1.31 (t, 6H, *J* = 7.2 Hz). ^{13}C NMR (100M Hz, $CDCl_3$): δ 166.2 (C=O), 158.8, 136.7, 134.5, 132.2, 130.1, 129.8, 118.2, 116.5, 61.3 (CH_2), 56.2 (CH), 55.8 (CH_3), 40.9 (CH_2), 18.9 (CH_3), 13.8 (CH_3). EIMS m/z (relative intensity, %): 347 [M^++1, 1.97], 346 [M^+, 10.33]. IR (neat): 1725.2 cm^{-1}. Anal. Calcd. For $C_{20}H_{26}O_5$: C, 69.34; H, 7.56; Found: C, 69.12; H, 7.45.