Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Nickel-catalyzed coupling of allyl chlorides and enynes

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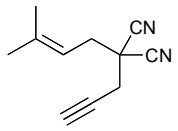
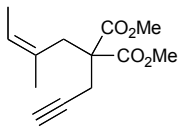
General Comments. All reactions were carried out under dry N_2 atmosphere. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with Me_4Si as an internal standard. MeCN was distilled from P_2O_5. Enynes **2a**, **2c**, **2e**, and **2f** have been already reported (see, S. Ikeda, R.Sanuki, H. Miyachi, H. Miyashita, M. Taniguchi, K. Odashima, *J. Am. Chem. Soc.*, 2004, **126**, 10331). **2b** and **2d** were prepared by allylation followed by propargylation of diethyl or dimethyl malonate or malononitrile. Other materials were obtained from commercial suppliers and used without further purification.



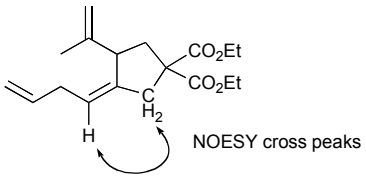
2-(3-methylbut-2-enyl)-2-(prop-2-ynyl)malononitrile (2b): a colorless oil; *Rf* = 0.51 (hexane/AcOEt = 4:1); ^1H NMR (500MHz, $CDCl_3$) δ 1.75 (s, 3 H, CH_3), 1.83 (s, 3 H, CH_3), 2.38 (t, *J* = 2.7 Hz, 1 H, CH), 2.81 (t, *J* = 7.6 Hz, 2 H, CH_2), 2.89 (d, *J* = 2.7 Hz, 2 H, CH_2), 5.26 (t, *J* = 7.6 Hz, 1 H, =CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.43, 26.04, 27.45, 35.07, 36.87 (CH_3, CH_2, and C), 74.81, 75.14 (≡CH and ≡C), 113.89, 114.63 (=CH and =C), 141.76 (CN); IR (neat) 3300, 2930, 1430, 660 cm^{-1}; GCMS (EI, 70 eV) m/z (rel int, %) 172 (M^+, 7), 157 (58), 94 (90), 79 (100). HRMS for $C_{11}H_{12}N_2$ (M^+): calcd 172.1001, found 172.1023.



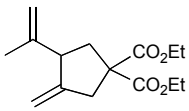
Dimethyl 2-((*Z*)-2-methylbut-2-enyl)-2-(prop-2-ynyl)malonate (2d): a colorless oil; *Rf* = 0.45 (hexane/AcOEt = 7:1); ^1H NMR (500MHz, $CDCl_3$) δ 1.58-1.59 (m, 3 H, CH_3), 1.63 (d, *J* = 7.0 Hz, 3 H, CH_3), 2.02 (t, *J* = 2.7, 1 H, CH), 2.79 (d, *J* = 2.7 Hz, 2 H, CH_2), 2.91 (s, 2 H, CH_2), 3.74 (s, 6 H, OCH_3), 5.45 (q, *J* = 7.0 Hz, 1 H, =CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.98, 22.83 (CH_3), 24.09, 33.74 (CH_2), 52.73 (C), 56.78 (OCH_3), 71.42 (≡CH), 79.75 (≡C), 126.07, 129.76 (=CH and =C), 170.90 (C=O); IR (neat) 3300, 2950,

1740 ($^{\nu}$CO), 1440, 1290, 1200 cm^{-1}; GCMS (EI, 70 eV) *m/z* (rel int, %) 238 (M^+, 8), 163 (92), 147 (100). HRMS for for $C_{13}H_{18}O_4$ (M^+): calcd 238.1190, found 238.1205.

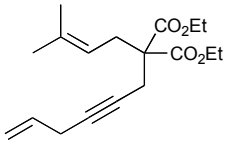
General experimental procedure: In a 20-mL three-necked flask were placed $Ni(cod)_2$ (0.05 mmol), PPh_3 (0.1 mmol), Zn dust (1.0 mmol), and MeCN (3 mL), and the mixture was stirred at room temperature for 10 min. To this suspension was added enyne **2** (0.5 mmol) and allyl chloride **1** (X = Cl, 5 mmol) at room temperature, and the mixture was then stirred at the same temperature for 4 h. After the addition of aqueous HCl (5 %, 30 mL), the aqueous layer was extracted with Et_2O (10 mL x 3). The combined organic layer was washed with brine, dried over $MgSO_4$ for 30 min, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane–AcOEt, 4:1) to yield **3** as a colorless oil. An analytical sample was obtained by bulb-to-bulb distillation.



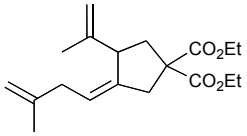
(*Z*)-Diethyl 3-(but-3-enylidene)-4-(prop-1-en-2-yl)cyclopentane-1,1-dicarboxylate (3aa): a colorless oil; bp 135 °C (5 mmHg); *Rf* = 0.57 (hexane/AcOEt = 4:1); ^{1}H NMR (500MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.0 Hz, 6 H, CH_3), 1.75 (s, 3 H, CH_3), 2.03 (dd, *J* = 13.4, 8.4 Hz, 1 H, one of CH_2), 2.68-2.80 (m, 3 H, CH_2 and one of CH_2), 2.91 (d, *J* = 15.4 Hz, 1 H, one of CH_2), 3.04 (dt, *J* = 15.4, 2.5 Hz, 1 H, one of CH_2), 3.44 (t, *J* = 7.5 Hz, 1 H, CH), 4.18-4.27 (m, 4 H, OCH_2), 4.79 (t, *J* = 1.5 Hz, 1 H, one of $=CH_2$), 4.86 (t, *J* = 1.5 Hz, 1 H, one of $=CH_2$), 4.98 (dq, *J* = 10.1, 1.9 Hz, 1 H, =CH), 5.02 (dq, *J* = 17.2, 1.9 Hz, 1 H, =CH), 5.49 (t, *J* = 7.5 Hz, 1 H, =CH), 5.80 (ddt, *J* = 17.2, 10.1, 6.4 Hz, 1 H, =CH); The NOESY cross peaks were observed at δ 5.48 vs. δ 2.91 and 3.04; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.03, 14.06, 19.34 (CH_3), 32.61, 39.80, 42.78 (CH_2), 47.21 (CH), 59.21 (C), 61.40, 61.43 (OCH_2), 111.19, 114.54 ($=CH_2$), 122.59 (=CH), 136.65 (=CH), 140.31, 145.96 (C), 171.40, 171.44 (O=C); IR (neat) 2990, 1730 ($^{\nu}$CO), 1640, 1445, 1365, 1240, 1195, 1160, 1070, 905 cm^{-1}; GCMS (EI, 70 eV) *m/z* (rel int, %) 306 (M^+, 3), 232 (87), 159 (100). Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found C, 70.37; H, 8.61.



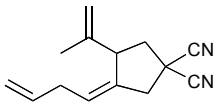
Diethyl 3-methylene-4-(prop-1-en-2-yl)cyclopentane-1,1-dicarboxylate (4a): a colorless oil; bp 120 °C (5 mmHg); *Rf* = 0.50 (hexane/AcOEt = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24-1.27 (m, 6 H, CH_3), 1.66 (s, 3 H, CH_3), 2.12 (dd, *J* = 13.0, 11.3 Hz, 1 H, one of CH_2), 2.51 (ddd, *J* = 13.0, 7.8, 1.5 Hz, 1 H, one of CH_2), 2.91 (dq, *J* = 16.8, 2.4 Hz, 1 H, one of CH_2), 3.06 (dd, *J* = 16.8, 1.5 Hz, 1 H, one of CH_2), 3.27-3.32 (m, 1 H, CH), 4.17-4.23 (m, 4 H, OCH_2), 4.81 (d, *J* = 2.4 Hz, 1 H, one of $=CH_2$), 4.84 (d, *J* = 1.0 Hz, 2 H, $=CH_2$), 5.01-5.02 (br s, 1 H, one of $=CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.03, 18.15 (CH_3), 38.48, 40.77 (CH_2), 51.09 (CH), 58.75 (C), 61.52 (OCH_2), 107.92, 113.36 ($=CH_2$), 144.80, 149.47 (=CH), 171.56, 171.65 (O=C); IR (neat) 2990, 1730 ($^{\nu}$CO), 1270, 1250, 1235, 1190, 1075, 890 cm^{-1}; GCMS (EI, 70 eV) *m/z* (rel int, %) 266 (M^+, 8), 192 (70), 119 (100). Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found C, 67.83; H, 8.54.



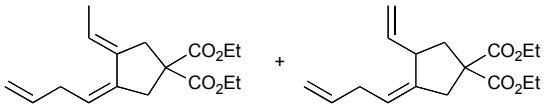
Diethyl 2-(hex-5-en-2-ynyl)-2-(3-methylbut-2-enyl)malonatea (5aa): a colorless oil; bp 120 °C (2 mmHg); *Rf* = 0.56 (hexane/AcOEt = 4:1); ^{1}H NMR (500MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.1 Hz, 6 H, CH_3), 1.65 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 2.75-2.93 (m, 6 H, CH_2), 4.15-4.24 (m, 4 H, OCH_2), 4.93 (t, *J* = 8.0 Hz, 1 H, =CH), 5.07 (d, *J* = 10.0 Hz 1 H, one of $=CH_2$), 5.26 (d, *J* = 17.0 Hz 1 H, one $=CH_2$), 5.75-5.81 (m, 1 H, =CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.06, 17.98 (CH_3), 22.80, 23.00 (CH_2), 26.06 (CH_3), 30.64 (CH_2), 57.28 (C), 61.38 (OCH_2), 79.54, 117.39 (≡C), 128.45, 128.55, 132.75, 136.33 ($=CH_2$, =CH, and =C), 170.35 (C=O); IR (neat) 2980, 1730 ($^{\nu}$CO), 1420, 1290, 1200, 1060 cm^{-1}; DIMS (EI, 70eV) *m/z* (rel int, %) 306 (M^+, 1), 262 (37), 232 (100). Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.90; H, 8.38.



(*Z*)-Diethyl 3-(3-methylbut-3-enylidene)-4-(prop-1-en-2-yl)cyclopentane-1,1-dicarboxylate (3ba): a colorless oil; bp 120 °C (2 mmHg); *Rf* = 0.34 (hexane/AcOEt = 9:1); ^{1}H NMR (500MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.24 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.66 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 1.97 (dd, *J* = 13.1, 8.5 Hz, 1 H, one of CH_2), 2.55-2.74 (m, 3 H, CH_2 and one of CH_2), 2.85 (d, *J* = 15.2 Hz, 1 H, one of CH_2), 3.00 (dt, *J* = 15.2, 2.2 Hz, 1 H, one of CH_2), 3.38 (t, *J* = 8.9 Hz, 1 H, CH), 4.18 (q, *J* = 7.0 Hz, 4 H, OCH_2), 4.62-4.64 (m, 1 H, one of $=CH_2$), 4.65-4.75 (m, 1 H, one of $=CH_2$), 4.70-4.73 (m, 1 H, one of $=CH_2$), 4.77-4.81 (m, 1 H, one of $=CH_2$), 5.47 (t, *J* = 7.6 Hz, 1 H, =CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.03, 14.06, 19.33, 22.57 (CH_3), 36.56, 39.78, 42.91 (CH_2) 47.11 (CH), 59.22 (C), 61.39, 61.42 (OCH_2), 109.99, 111.16 ($=CH_2$), 123.02 (=CH), 140.57, 144.73, 146.06 (=C), 171.42 (C=O); IR (neat) 2990, 1730 ($^{\nu}$CO), 1645, 1445, 1365, 1240, 1190, 1160, 1075, 890 cm^{-1}; GCMS (EI, 70eV) *m/z* (rel int, %) 320 (M^+, 27), 292 (17), 246 (92), 203 (52), 173 (100). Anal. Calcd for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81. Found: C, 71.13; H, 9.05.

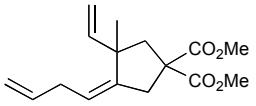


(*Z*)-3-(3-Methylbut-3-enylidene)-4-(prop-1-en-2-yl)cyclopentane-1,1-dicarbonitrile (3ab): a colorless oil; bp 100 °C (2 mmHg); *Rf* = 0.63 (hexane/AcOEt = 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.71 (s, 3 H, CH_3), 2.20-2.25 (m, 1 H, CH_2), 2.74 (t, *J* = 6.0 Hz, 2 H, CH_2), 2.80-2.84 (m, 1 H, CH_2), 2.98-3.12 (m, 2 H, CH_2), 3.56 (t, *J* = 8.5 Hz, 1 H, =CH), 4.88 (s, 1 H, =CH), 4.92 (s, 1 H, =CH), 4.99-5.13 (m, 2 H, =CH) 5.68-5.78 (m, 2 H, =CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.08, 32.48, 32.77, 43.65, 46.16, 46.44 (CH_3, CH_2, CH, and C), 113.46, 115.51, 115.63, 115.73, 127.36, 135.10 ($=CH_2$, =CH, and =C), 143.15 (CN); IR (neat) 2970, 1640, 1420, 910 cm^{-1}; DIMS (EI, 70 eV) m/z (rel int, %) 212 (M^+, 4), 197 (51), 170 (84), 156 (63), 142 (100). HRMS for $C_{14}H_{16}N_2$ (M^+): calcd 212.1314; found 212.1287. Anal. Calcd for $C_{14}H_{16}N_2$ (M^+): calcd C, 79.21; H, 7.60; N, 13.20. found C, 79.20; H, 7.78; N, 13.09.

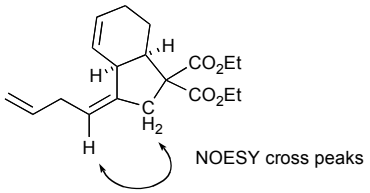


1:1 mixture

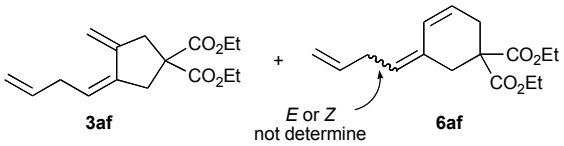
A mixture of (3*Z*,4*E*)-diethyl 3-(but-3-enylidene)-4-ethylidenecyclopentane-1,1-dicarboxylate and (*Z*)-diethyl 3-(but-3-enylidene)-4-vinylcyclopentane-1,1-dicarboxylate (3ac): a colorless oil; bp 100 °C (2 mmHg); *Rf* = 0.34 (hexane/AcOEt = 9:1); ^{1}H NMR of ethylidenecyclopentane (500MHz, $CDCl_3$) δ 1.21-1.27 (m, 6 H, CH_3), 1.73 (d, *J* = 7.0 Hz, 3 H, CH_3), 2.95-3.00 (m, 6 H, CH_2), 4.12-4.23 (m, 4 H, OCH_2), 4.92-5.07 (m, 2 H, $=CH_2$), 5.40 (t, *J* = 7.0 Hz, 1 H, =CH), 5.67-5.88 (m, 2 H, =CH x 2); ^{1}H NMR of vinylcyclopentane (500MHz, $CDCl_3$) δ 1.21-1.27 (m, 6 H, CH_3), 1.98 (dd, *J* = 13.5, 7.4 Hz, 1 H, one of CH_2), 2.70 (ddd, *J* = 13.5, 7.4, 1.8 Hz, 1 H, one of CH_2), 2.73 (t, *J* = 6.8 Hz, 2 H, CH_2), 2.81 (d, *J* = 16.2 Hz, 1 H, one of CH_2), 3.03 (dt, *J* = 16.2, 1.8 Hz, 1 H, one of CH_2), 3.37 (q, *J* = 7.3 Hz, 1 H, CH), 4.12-4.23 (m, 4 H, OCH_2), 4.92-5.07 (m, 4 H, =CH), 5.42 (t, *J* = 7.0 Hz, 1 H, =CH), 5.67-5.88 (m, 2 H, =CH); ^{13}C NMR of the mixture (125 MHz, $CDCl_3$) δ 14.05, 15.35 (CH_3), 32.63, 33.26, 38.28, 40.65, 41.81, 42.92, (CH_2) 43.82 (CH), 57.27, 59.08 (C), 61.42, 61.45, 61.48 (OCH_2), 114.18, 114.62, 114.93 ($=CH_2$), 121.18, 121.76, 122.36, 136.81, 136.85, 136.91 (=CH), 137.10, 140.06, 140.57 (=C), 171.49, 171.59 (C=O); IR (neat) 2990, 1730 ($^{\nu}$CO), 1250, 1190 cm^{-1}; DIMS (EI, 70eV) *m/z* (rel int, %) 292 (M^+, 56), 219 (100). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.62; H 8.42.



(*Z*)-Dimethyl 4-(but-3-enylidene)-3-methyl-3-vinylcyclopentane-1,1-dicarboxylate (3ad): colorless oil; bp 120 °C (2 mmHg); *Rf* = 0.45 (hexane/AcOEt = 4:1); ^{1}H NMR (500MHz, $CDCl_3$) δ 1.26 (s, 3 H, CH_3), 2.30 (d, *J* = 13.7 Hz, 1 H, one of CH_2), 2.50 (d, *J* = 13.7 Hz, 1 H, one of CH_2), 2.73-2.79 (m, 2 H, CH_2), 3.02-3.04 (m, 2 H, CH_2) 3.68 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 4.95-5.00 (m, 4 H, $=CH_2$), 5.38 (tt, *J* = 7.5, 1.9 Hz, 1 H, =CH), 5.75 (ddt, *J* = 17.1, 10.1, 6.1 Hz, 1 H, =CH), 5.83 (dd, *J* = 17.4, 10.3 Hz, 1 H, =CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.31 (CH_3), 32.41, 42.92 (CH_2), 46.89 (C), 49.82 (CH_2), 52.59, 52.74 (OCH_3), 58.09 (C), 111.21, 114.71 ($=CH_2$), 122.13, 137.06 (=CH), 143.99 (C), 144.84 (=CH), 171.81, 172.28 (C=O); IR (neat) 2960, 1740 ($^{\nu}$CO), 1430, 1260, 910 cm^{-1}; DIMS (EI, 70eV) *m/z* (rel int, %) 278 (M^+, 6), 218 (73), 177 (55), 164 (50), 159 (100). HRMS for $C_{16}H_{22}O_4$ (M^+): calcd 278.1518, found 278.1528. Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.86; H, 8.03.

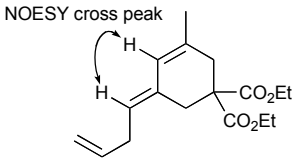


(3*Z*,3a*S*,7a*R*)-Diethyl 3-(but-3-enylidene)-3,3a,7,7a-tetrahydro-2*H*-indene-1,1(6*H*)-dicarboxylate (3ae): a colorless oil; bp 120 °C (2 mmHg); *Rf* = 0.66 (hexane/AcOEt = 4:1); ^{1}H NMR (500MHz, $CDCl_3$) δ 1.22-1,26 (m, 6 H, CH_3), 1.39-1.46 (m, 1 H, one of CH_2), 1.94-2.04 (m, 2 H, CH_2), 2.65 (d, *J* = 15.8 Hz, 1 H, one of CH_2), 2.75-2.84 (m, 2 H, CH_2), 2.88-2.98 (m, 1 H, CH), 3.23 (d, *J* = 15.8 Hz, 1 H, one of CH_2), 3.34-3.40 (m, 1 H, CH), 4.11-4.28 (m, 4 H, OCH_2), 4.95-5.24 (m, 2 H, $=CH_2$), 5.30 (t, *J* = 7.3 Hz, 1 H, =CH), 5.75-5.85 (m, 3 H, =CH); The NOESY cross peaks were observed at δ vs. δ 2.65 and 3.23; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.06, 14.16 (CH_3), 22.41, 23.51, 32.99, 39.21 (CH_2), 40.20, 42.30 (CH), 61.24, 61.35 (OCH_2), 63.09 (C), 114.81 (=CH2), 120,71, 126.96, 127.14, 136.86 (=CH), 140.79 (=C), 169.76, 171.43 (C=O); IR (neat) 2980, 1730 ($^{\nu}$CO), 1250 cm^{-1}; GCMS (EI, 70eV) *m/z* (rel int, %) 273 (M^+ – OEt, 7), 203 (100). Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 71.33; H 8.33.



A mixture of (*Z*)-diethyl 3-(but-3-enylidene)-4-methylenecyclopentane-1,1-dicarboxylate (3af) and diethyl 5-(but-3-enylidene)cyclohex-3-ene-1,1-dicarboxylate (6af): a colorless oil; bp 100 °C (2 mmHg), *Rf* = 0.34 (hexane/AcOEt = 9:1); ^{1}H NMR of **3af** (500MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.3 Hz, 6 H, CH_3), 2.94-3.06 (m, 6 H, CH_2), 4.18 (q, *J* = 7.3 Hz, 4 H, OCH_2), 5.02 (dq, *J* = 10.1, 1.7 Hz, 1 H, one of $=CH_2$), 5.07 (dq, *J* = 17.1, 1.7 Hz, 1 H, one of $=CH_2$), 5.14 (s, 1 H, one of $=CH_2$), 5.20 (s, 1 H, one of $=CH_2$), 5.54 (t, *J* = 6.5 Hz, 1 H, =CH), 5.78-5.88 (m. 1 H, =CH); ^{1}H NMR of **6af** (500MHz, $CDCl_3$) δ 1.19-1.27 (m, 6 H, CH_3), 2.80-2.94 (m, 6 H, CH_2), 4.16-4.21 (m, 4 H, OCH_2), 4.90-5..20 (m, 2 H, $=CH_2$), 5.41 (t, *J* = 7.4 Hz, 1 H, =CH), 5.63-5.67 (m, 1 H, =CH), 5.78-5.88 (m, 1 H, =CH), 6.01-6.11 (m. 1 H, =CH); ^{13}C NMR of **3af** (125 MHz, $CDCl_3$) δ 14.03 (CH_3), 35.27, 42.50, 42.77 (CH_2), 57.49 (C), 61.39 (OCH_2), 110.77, 115.50 ($=CH_2$), 124.35 (=CH), 136.17 (=C), 136.32 (=CH), 171.12, 171.33 (O=C); ^{13}C NMR of **6af** (125 MHz, $CDCl_3$) δ 14.09 (CH_3), 30.51, 31.20, 31.70 (CH_2), 53.78 (C), 61.38, 61.42 (OCH_2), 115.23, 123.76, 124.36, 126.77, 130.35,

132.08 (=CH_2, =CH, and =C), 172.39, 172.64 (O=C); IR (neat) 2990, 1730 ($^{\nu}$CO), 1445, 1365, 1250, 1190, 1160, 1075 cm^{-1}; DIMS (EI, 70eV) *m/z* (rel int, %) 278 (M^+, 28), 218 (100). Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.75; H 7.83.



(5*E*)-Diethyl 5-(but-3-enylidene)-3-methylcyclohex-3-ene-1,1-dicarboxylate (6ag): a colorless oil; bp 145 °C (5 mmHg); *Rf* = 0.57 (hexane/AcOEt = 6:1); ^{1}H NMR (500MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.0 Hz, 6 H, CH_3), 1.79 (s, 3 H, CH_3), 2.57 (s, 2 H, CH_2), 2.79 (s, 2 H, CH_2) 2.88 (t, *J* = 6.7 Hz, 2 H, CH_2), 4.16 (q, *J* = 7.0 Hz, 4 H, CH_2), 4.97 (dq, *J* = 10.0, 1.7 Hz, 1 H, one of =CH_2), 5.03 (dq, *J* = 17.1, 1.7 Hz, 1 H, one of =CH_2), 5.30 (t, *J* = 7.4 Hz, 1 H, =CH), 5.80 (ddt, *J* = 17.1, 10.0, 7.4 Hz, 1 H, =CH), 5.83 (s, 1 H, =CH); The NOESY cross peak was observed at δ 5.30 vs. δ 5.83; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.02, 23.37 (CH_3), 30.18, 31.77, 35.90 (CH_2) 54.30 (C), 61.42 (OCH_2), 114.76 (=CH_2), 124.18, 125.66, 132.50 (=CH), 132.73, 136.60 (=C), 171.14 (C=O); IR (neat) 2995, 1735 ($^{\nu}$CO), 1445, 1365, 1300, 1250, 1185, 1100, 1080, 1055, 910, 860 cm^{-1}; DIMS (EI, 70eV) *m/z* (rel int, %) 292 (M^+, 44), 218 (95), 145 (100). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.89; H, 8.41.