Supporting information for:

Nickel-Catalyzed Cyclization of α,ω-Dienes: Formation vs. Cleavage of C-C Bonds

David Nečas,*a Matyáš Turský,a Iva Tišlerováa and Martin Kotora*a,b

†Department of Organic and Nuclear Chemistry, Faculty of Science, Charles University, Albertov 2030, 128 43 Prague 2, Czech Republic and ‡Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic

1. General Methods.
Solvents were dried by standard methods (THF, toluene-Na, benzophenone; dichloromethane-CaH₂) and distilled under argon before use. All other reagents were obtained from commercial sources and used without further purification. GC analyses were obtained on a Shimadzu GC-17A chromatograph equipped with a Zebron ZB-5 column (5% phenyl-95% dimethyl polysiloxane). Infrared spectra were recorded on a Bruker IFS 88 spectrometer as CHCl₃ solutions and are reported in wave numbers (cm⁻¹). ¹H and ¹³C NMR spectra were recorded as CDCl₃ solutions on a Varian UNITY 400 INOVA instrument (¹H at 400 MHz, ¹³C at 100 MHz) with Me₄Si as an internal standard. Mass spectra were obtained on a FINNIGAN MAT INCOS 50 instrument. Ni-catalyzed reactions were carried out under argon atmosphere in oven-dried Schlenk tubes. Yields were determined by the means of ¹H NMR with mesitylene as an internal standard. HPLC separations were performed on a 25×250 mm preparative silica gel column (Labio, Czech Republic), filled with BIOSPHER PSI 100 (7µm mesh).

2. Preparation of Starting Materials
Diethyl di(prop-2´-en-1´-yl)propandioate (1a).
Allylation of allylmalonate was carried out according to the previously reported procedure. Sodium metal (0.58 g, 25 mmol) was dissolved in absolute ethanol (25 mL), then was slowly added diethyl allylmalonate (4 g, 25 mmol) followed by dropwise addition of allyl bromide (3.2 g, 26.4 mmol), and the reaction mixture was refluxed for 60 min. The mixture was then acidified with glacial acetic acid, filtered, and concentrated under reduced pressure. The residue was dissolved in water, extracted with diethylether, collected organic fractions were dried (MgSO₄), and concentrated on rotary evaporator. Distillation of the residue under reduced pressure afforded 4.69g (78%) of the title compound as a colourless liquid: ¹H NMR (CDCl₃, Me₄Si) δ 1.25 (t, J = 7.0 Hz, 6H), 2.64 (dt, J = 7.1, 1.0 Hz, 4H), 4.18 (q, J = 7.0 Hz, 4H), 5.07-5.15 (m, 4H), 5.60-5.72 (m, 2H). The spectral characteristics of 1a were in agreement with the previously published data.

Dibenzyl di(prop-2´-en-1´-yl)propandioate (1b).

Dibenzylmalonate (1.07 g, 3.8 mmol), K₂CO₃ (2.2 g, 16 mmol) and tetrabutylammonium hydrogensulfate (200 mg, 0.6 mmol) were dissolved in CH₃CN (10 mL). Then allylbromide (0.95 g, 7.8 mmol) was added and the reaction mixture was refluxed for 72 h, at which time it was added a 10-mL portion of water and the reaction mixture was extracted with Et₂O (3×10 mL). Organic fraction were dried (MgSO₄), concentrated on a rotary evaporator, and column chromatography on silica gel (5/1 hexane/EtOAc) afforded 888 mg (68%) of the title compound as a colourless liquid: ¹H NMR (CDCl₃, Me₄Si) δ 2.67 (d, J = 6.4 Hz, 4H), 5.00-5.08 (m, 4H), 5.10 (s, 4H), 5.54-5.66 (m, 2H), 7.24-7.33 (m, 10H); ¹³C NMR (CDCl₃) δ 36.71 (2C), 57.53, 66.99 (2C), 119.39 (2C), 128.20 (4C), 128.26 (2C), 128.46 (4C), 131.94 (2C), 135.34 (2C), 170.39 (2C). The spectral characteristics of 1b were in agreement with the previously published data.

Ethyl benzyl di(prop-2´-en-1´-yl)propandioate (1c).
The preparation was analogous to 1b. Benzylethylmalonate (0.6 g, 2.7 mmol), K$_2$CO$_3$ (1.8 g, 13 mmol) and tetrabutylammonium hydrogensulfate (168 mg, 0.5 mmol) and CH$_3$CN (8 mL). Column chromatography on silica gel (3/1 hexane/EtOAc) afforded 720 mg (88%) as a colourless liquid: $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 1.16 (t, J = 7.2 Hz, 3H), 2.66 (d, J = 7.2 Hz, 4H), 4.00 (q, J = 7.2 Hz, 2H), 5.04-5.11 (m, 4H), 5.15 (s, 2H), 5.56-5.68 (m, 2H), 7.29-7.38 (m, 5H); $^{13}$C NMR (CDCl$_3$) δ 13.99, 36.68 (2C), 57.36, 61.30, 66.87, 119.26 (2C), 128.24 (2C), 128.27, 128.45 (2C), 132.11 (2C), 135.48, 170.51, 170.57; IR (CHCl$_3$) 925, 993, 1028, 1143, 1194, 1226, 1287, 1455, 1641, 1728 cm$^{-1}$; EI-MS m/z (%) 302 (M$^+$, 16), 284 (15), 261 (29), 256 (52), 238 (16), 211 (13), 167 (8), 130 (9), 91 (100); HRMS calecd for C$_{18}$H$_{22}$O$_4$ 302.1518, found 302.1507.

**Ethyl 2-acetyl-2-allylpent-4-enoate (1d).**

![Ethyl 2-acetyl-2-allylpent-4-enoate](image)

The preparation was analogous to 1b. Ethyl 3-oxobutanoate (13 g, 100 mmol), K$_2$CO$_3$ (10 g, 40 mmol), tetrabutylammonium hydrogensulfate (5 g, 15 mmol), allyl bromide (25 g, 206.6 mmol) and CH$_3$CN (100 mL). Column chromatography on silica gel (3/1 hexane/EtOAc) afforded 18.3 g (87%) of the title compound as a colourless liquid: $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 1.27 (t, J = 7.2 Hz, 3H), 2.14 (s, 3H), 2.55-2.69 (m, 4H), 4.20 (q, J = 7.2 Hz, 2H), 5.07-5.14 (m, 4H), 5.54-5.66 (m, 2H). The spectral characteristics of 1d were in agreement with the previously published data.$^3$

**3,3-Diallylpentane-2,4-dione (1e).**

![3,3-Diallylpentane-2,4-dione](image)

The preparation was analogous to 1b. 2,4-Pentanediene (10 mL, 97.4 mmol), K$_2$CO$_3$ (10 g, 40 mmol), tetrabutylammonium hydrogensulfate (5 g, 15 mmol), allyl bromide (25 g, 206.6 mmol) and CH$_3$CN (100 mL). Column chromatography on silica gel (3/1 hexane/EtOAc) afforded 14.9 g (85%) of the title compound as a colourless liquid: $^1$H NMR (CDCl$_3$, Me$_4$Si)
$\delta$ 2.11 (s, 6H), 2.66 (dm, $J = 7.3$ Hz, 4H), 5.08-5.15 (m, 4H), 5.54 (ddt, $J = 16.4$, 8.0, 7.3 Hz, 2H). The spectral characteristics of 1e were in agreement with the previously published data.\(^3\)

**Methyl 2-allyl-2-phenylpent-4-enoate (1f).**

![Methyl 2-allyl-2-phenylpent-4-enoate](image)

The preparation was analogous to 1b. Methyl 2-phenylacetate (1.13 g, 7.5 mmol), K$_2$CO$_3$ (5.6 g, 40 mmol), Bu$_4$NHSO$_4$ (0.5 g, 1.5 mmol), allyl bromide (1.86 g, 15.5 mmol) and CH$_3$CN (15 mL). Column chromatography on silica gel (3/1 hexane/EtOAc) afforded 1.19 g (69%) of the title compound as a colourless liquid: $^1$H NMR (CDCl$_3$, Me$_4$Si) $\delta$ 2.73-2.84 (m, 4H), 3.65 (s, 3H), 5.03-5.09 (m, 4H), 5.47-5.57 (m, 2H), 7.23-7.27 (m, 3H), 7.31-7.36 (m, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 38.86 (2C), 51.99, 53.54, 118.61 (2C), 126.31 (2C), 126.84, 128.34 (2C), 133.31(2C), 141.68, 175.44; IR (CHCl$_3$) 922, 996, 1141, 1229, 1275, 1445, 1640, 1727, 2952, 3011, 3028 cm$^{-1}$; EI-MS m/z (%) 230 ($M^+$, 8), 189 (34), 171 (26), 157 (19), 129 (100), 121 (46), 115 (26), 91 (39); HRMS calcd for C$_{15}$H$_{18}$O$_2$ 230.1307, found 230.1313.

**3-Bis-(prop-2′-en-1′-yl)coumaran-2-one (1g).**

![3-Bis-(prop-2′-en-1′-yl)coumaran-2-one](image)

The preparation was analogous to 1b. 2-Coumaranone (1 g, 7.46 mmol), K$_2$CO$_3$ (5.6 g, 40 mmol), tetrabutylammonium hydrogensulfate (0.5 g, 1.5 mmol), allyl bromide (1.82 g, 15 mmol) and CH$_3$CN (15 mL). Column chromatography on silica gel (3/1 hexane/EtOAc) afforded 1.14 g (71%) of the title compound as an yellowish oil: $^1$H NMR (CDCl$_3$, Me$_4$Si) $\delta$ 2.57-2.67 (m, 4H), 4.98-5.09 (m, 4H), 5.40-5.51 (m, 2H), 7.06-7.32 (m, 4H). The spectral characteristics of 1g were in agreement with the previously published data.\(^4\)

**Ethyl bis-(prop-2′-en-1′-yl)cyanoacetate (1h).**

![Ethyl bis-(prop-2′-en-1′-yl)cyanoacetate](image)
The preparation was analogous to 1b. Ethyl cyanoacetate (4.52 g, 40 mmol), K$_2$CO$_3$ (33 g, 240 mmol), Bu$_4$NHSO$_4$ (2 g, 8 mmol), allyl bromide (9.68 g, 80 mmol) and CH$_3$CN (80 mL). Column chromatography on silica gel (3/1 hexane/EtOAc) afforded 5.2 g (67%) of the title compound as a colourless liquid: $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 1.31 (t, $J = 7.0$ Hz, 3H), 2.55 (dd, $J = 13.8$, 7.2 Hz, 2H), 2.65 (dd, $J = 13.9$, 7.4 Hz, 2H), 4.25 (q, $J = 7.2$ Hz, 2H), 5.21-5.24 (m, 2H), 5.22-5.28 (m, 2H), 5.76-5.87 (m, 2H). The spectral characteristics of 1h were in agreement with the previously published data.

4,4-Bis(benzyloxymethyl)-1,6-heptadiene (1i).

2,2-Diallylpropane-1,3-diol (1.52 g, 9.7 mmol) was dissolved in THF (10 mL) and NaH (2.2 g of 50% disp. in oil, 45.8 mmol) was added. Then benzyl bromide (5.1 g, 30 mmol) dissolved in THF (15 mL) was added and the reaction mixture was stirred for 12 h, at which time it was added ice and a 10 mL portion of water, and the reaction mixture was extracted with Et$_2$O (3×15 mL). Collected organic fractions were dried (MgSO$_4$), concentrated on a rotary evaporator, and column chromatography on silica gel (40/1 hexane/EtOAc) afforded 1.55 g (47%) of the title compound as a colourless liquid: $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 2.12 (d, $J = 7.6$ Hz, 4H), 3.31 (s, 4H), 4.47 (s, 4H), 5.02 (bs, 2H), 5.05 (dm, $J = 5.6$ Hz, 2H), 5.74-5.85 (m, 2H), 7.26-7.38 (m, 10H). The spectral characteristics of 1i were in agreement with the previously published data.

t-Butyl(hepta-1,6-dien-4-yloxy)dimethylsilane (1j).

Hepta-1,6-dien-4-ol (2.02 g, 18 mmol) and Et$_3$N (2.8 mL, 20 mmol) were dissolved in dichloromethane (40 mL), then TBSCI (3.72 g, 24.7 mmol) and DMAP (0.4 g, 3.2 mmol) were added and the reaction mixture was refluxed for 3 h. The reaction mixture was quenched by water (10 mL), extracted with Et$_2$O (3×15 mL). Collected organic fractions were dried (MgSO$_4$), concentrated on a rotary evaporator. Distillation of the residue under reduced pressure afforded 1.94 g (47%) of the title compound as a colorless liquid: $^1$H NMR
(CDCl$_3$, Me$_4$Si) $\delta$ 0.03 (s, 6H), 0.87 (s, 9H), 2.13-2.26 (m, 4H), 3.69-3.76 (m, 1H), 5.00 (bs, 2H), 5.04 (dm, $J$ = 5.6 Hz, 2H), 5.75-5.85 (m, 2H). The spectral characteristics of 1j were in agreement with the previously published data.$^7$

**9,9-Diallylfluorene (1k).**

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Allylation of fluorene was carried out according to the previously reported procedure.$^8$ Yield 86% (5.2 g, 21 mmol) of an yellowish liquid: $^1$H NMR (CDCl$_3$, Me$_4$Si) $\delta$ 2.71 (d, $J$ = 7.2 Hz, 4H), 4.74 (ddt, $J$ = 10.1, 2.1, 2.1 Hz, 2H), 4.83 (ddt, $J$ = 17.1, 2.1, 2.1 Hz, 2H), 5.19-5.30 (m, 2H), 7.27-7.48 (m, 6H), 7.64-7.72 (m, 2H). The spectral characteristics of 1k were in agreement with the previously published data.$^9$

**N,N-Diallylaniline (1l).**

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Allylation of aniline was carried out according to the previously reported procedure.$^{10}$ Yield 72% (3.2 g, 18.5 mmol) of a colourless liquid: $^1$H NMR (CDCl$_3$, Me$_4$Si) $\delta$ 3.89-3.94 (m, 4H), 5.14 (ddt, $J$ = 10.4, 1.7, 1.7 Hz, 2H), 5.18 (ddt, $J$ = 17.2, 1.7, 1.7 Hz, 2H), 5.81-5.90 (m, 2H), 6.66-6.73 (m, 3H), 7.17-7.24 (m, 2H). The spectral characteristics of 1l were in agreement with the previously published data.$^{11}$

**3. General Procedure for Ni-catalyzed Cyclization of Dienes**

To a solution of a diene (1a–1l) (0.5 mmol) was added NiBr$_2$(PBu$_3$)$_2$ (15.6 mg, 0.025 mmol) in dry toluene (3 mL) and 1.8M solution of Et$_2$AlCl in toluene (55 $\mu$L, 0.1 mmol) (cond. B) or NiBr$_2$(PPh$_3$)$_2$ (18.6 mg, 0.025 mmol) and 1.9M solution of Et$_3$Al in toluene (53 $\mu$L, 0.1 mmol) (cond. A) under argon. The reaction mixture was stirred at 20°C for 1 or 3 h, respectively. After that it was quenched with a portion of water (1 mL) followed addition of
3M solution of HCl (3 mL). Organic layer was separated and dried (MgSO$_4$). The products isolated HPLC (silica gel, hexane/EtOAc).

4. Products of Ni-complex Catalyzed Cyclization

**Diethyl 3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (2a).**

![Chemical Structure Diagram]

Yield 92% (cond. **B**): $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 1.11 (d, J = 6.4 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.71-1.79 (m, 1H), 2.51-2.60 (m, 2H), 2.94 (d, J = 16.9 Hz, 1H), 3.05 (dm, J = 17.1 Hz, 1H), 4.14-4.23 (m, 4H), 4.78-4.82 (m, 1H), 4.89-4.92 (m, 1H). The spectral characteristics of 2a were in agreement with the previously published data.

**Diethyl 3,4-dimethylcyclopent-2-ene-1,1-dicarboxylate (3a).**

![Chemical Structure Diagram]

Yield 18% (cond. **A**): $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 1.05 (d, J = 6.8 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.73 (s, 3H), 1.88-1.96 (m, 1H), 2.69-2.79 (m, 2H), 4.16 (q, J = 7.2 Hz, 2H), 4.18 (q, J = 7.2 Hz, 2H), 5.42 (bs, 1H). The spectral characteristics of 3a were in agreement with the previously published data.

**Diethyl 3,4-dimethylcyclopent-3-ene-1,1-dicarboxylate (4a).**

![Chemical Structure Diagram]

Yield 6% (cond. **A**): $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 1.24 (t, J = 7.0 Hz, 6H), 1.59 (s, 6H), 2.92 (bs, 6H), 4.18 (q, J = 7.2 Hz, 4H). The spectral characteristics of 4a were in agreement with the previously published data.

**Dibenzyl 3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (2b).**

![Chemical Structure Diagram]

Yield 75% (cond. **B**): $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 1.08 (d, J = 6.4 Hz, 3H), 1.73-1.85 (m, 1H), 2.51-2.63 (m, 2H), 2.97 (dd, J = 17.2, 1.6 Hz, 1H), 3.08 (d, J = 16.8 Hz, 1H), 4.80 (d, J = 1.6
Hz, 1H), 4.90 (bs, 1H), 5.10 (d, J = 3.6 Hz, 4H), 7.21-7.26 (m, 4H), 7.29-7.34 (m, 6H); $^{13}$C NMR (CDCl$_3$) δ 17.97, 37.21, 40.53, 42.08, 58.32, 67.07, 67.14, 105.64 (2C), 127.91 (4C), 128.20 (2C), 128.47 (4C), 135.45, 153.07, 171.45, 171.61; IR (CHCl$_3$) 890, 1167, 1227, 1254, 1275, 1729 cm$^{-1}$; EI-MS m/z (%) 364 (M$^+$, 1), 273 (15), 229 (38), 211 (19), 91 (100); HRMS calcd for C$_{23}$H$_{24}$O$_4$ 364.1675, found 364.1671.

Dibenzyl 3,4-dimethylcyclopent-2-ene-1,1-dicarboxylate (3b).

Yield 30% (cond. A): $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 1.04 (d, J = 6.8 Hz, 3H), 1.72 (s, 3H), 1.96 (ddd, J = 7.2, 4.8, 1.2 Hz, 1H), 2.64-2.79 (m, 1H), 2.75-2.84 (m, 1H), 5.04-5.17 (m, 4H), 5.47 (bs, 1H), 7.21-7.34 (m, 10H). The spectral characteristics of 3b were in agreement with the previously published data.$^{14}$

1-Benzyl 1-ethyl 3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (2c).

Yield 91% (cond. B) (3:2 mixture of diastereoisomers). Major diastereomer: $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 1.10 (d, J = 6.3 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H), 1.73-1.82 (m, 1H), 2.54-2.63 (m, 2H), 2.95 (dm, J = 16.9 Hz, 1H), 3.06 (d, J = 16.8 Hz, 1H), 4.08-4.17 (m, 2H), 4.80 (s, 1H), 4.91 (s, 1H), 5.17 (d, J = 1.8 Hz, 2H), 7.39-7.48 (m, 5H); $^{13}$C NMR (CDCl$_3$) δ 13.87, 17.92, 37.22, 40.45, 42.04, 58.17, 61.49, 66.95, 105.48, 127.98, 128.20, 128.45, 135.57, 153.22, 171.62, 171.77. Minor diastereomer: $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 1.10 (d, J = 6.3 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H), 1.73-1.82 (m, 1H), 2.54-2.63 (m, 2H), 2.95 (dm, J = 16.9 Hz, 1H), 3.06 (d, J = 16.8 Hz, 1H), 4.08-4.17 (m, 2H), 4.80 (s, 1H), 4.91 (s, 1H), 5.17 (d, J = 1.8 Hz, 2H), 7.39-7.48 (m, 5H); $^{13}$C NMR (CDCl$_3$) δ 13.87, 17.97, 37.22, 40.50, 42.08, 58.26, 61.49, 67.01, 105.51, 127.98, 128.20, 128.45, 135.61, 153.22, 171.62, 171.77. IR (CHCl$_3$) 888, 1029, 1067, 1173, 1216, 1255, 1278, 1727 cm$^{-1}$; EI-MS m/z (%) 302 (M$^+$, 4), 258 (33), 211 (22), 165 (34), 137 (20), 91 (100); HRMS calcd for C$_{18}$H$_{22}$O$_4$ 302.1518, found 302.1516.

Ethyl 1-acetyl-3-methyl-4-methylenecyclopentanecarboxylate (2d).
Yield 60% (cond. B) (3:2 mixture of diastereoisomers). Major diastereomer: $^1$H NMR (CDCl$_3$, Me$_4$Si) $\delta$ 1.09 (d, $J = 6.4$ Hz, 3H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.74 (dd, $J = 12.1$, 10.1 Hz, 1H), 2.18 (s, 3H), 2.39-2.48 (m, 1H), 2.44-2.54 (m, 1H), 2.88-2.92 (m, 1H), 2.93-3.02 (m, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 4.76-4.79 (m, 1H), 4.89-4.91 (m, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 13.99, 17.86, 25.94, 38.97, 40.65, 61.52, 64.29, 105.38, 153.29, 172.52, 203.67. Minor diastereomer: $^1$H NMR (CDCl$_3$, Me$_4$Si) $\delta$ 1.10 (d, $J = 6.6$ Hz, 3H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.62 (dd, $J = 12.5$, 11.0 Hz, 1H), 2.16 (s, 3H), 2.44-2.54 (m, 1H), 2.55-2.64 (m, 1H), 2.84-2.87 (m, 1H), 4.02 (q, $J = 7.2$ Hz, 2H), 4.77-4.80 (m, 1H), 4.88-4.90 (m, 1H); $^{13}$C NMR (CDCl$_3$) $\delta$ 13.99, 17.73, 26.49, 37.38, 38.78, 41.03, 61.58, 64.92, 105.43, 153.25, 172.73, 203.37. IR (CHCl$_3$) 889, 1183, 1232, 1360, 1454, 1710, 2967 cm$^{-1}$; EI-MS m/z (%) 210 (M$^+$, 8), 192 (9), 167 (82), 139 (49), 121 (38), 93 (53), 43 (100); HRMS calcd for C$_{12}$H$_{18}$O$_3$ 210.1256, found 210.1255.

1,1´-Diacetyl-3-methyl-4-methylenecyclopentane (2e).

Yield 28% (cond. B): $^1$H NMR (CDCl$_3$, Me$_4$Si) $\delta$ 1.08 (d, $J = 6.7$ Hz, 3H), 1.59 (dd, $J = 12.8$, 10.8 Hz, 1H), 2.10 (s, 3H), 2.13 (s, 3H), 2.37-2.48 (m, 1H), 2.58 (dd, $J = 12.8$, 7.3 Hz, 1H), 2.88 (dm, $J = 16.9$ Hz, 1H), 2.96 (dm, $J = 16.9$ Hz, 1H), 4.76-4.79 (m, 1H), 4.89-4.92 (m, 1H). The spectral characteristics of 2e were in agreement with the previously published data.

Methyl 3-methyl-4-methylene-1-phenylcyclopentanecarboxylate (2f).

Yield 94% (cond. B) (3:2 mixture of diastereoisomers). Major diastereomer: $^1$H NMR (CDCl$_3$, Me$_4$Si) $\delta$ 1.14 (d, $J = 6.6$ Hz, 3H), 1.60 (dd, $J = 11.9$ Hz, 1H), 2.53-2.61 (m, 1H), 2.69 (dq, $J = 16.3$, 2.6 Hz, 1H), 2.99 (ddd, $J = 11.9$, 7.2, 2.1 Hz, 1H), 3.54 (dm, $J = 16.3$ Hz, 1H), 3.61 (s, 3H), 4.81-4.86 (m, 1H), 4.97-5.02 (m, 1H), 7.22-7.38 (m, 5H). Minor diastereomer: $^1$H NMR (CDCl$_3$, Me$_4$Si) $\delta$ 1.10 (d, $J = 6.6$ Hz, 3H), 2.16-2.22 (m, 1H), 2.35-2.41 (m, 1H), 2.42-2.46 (m, 1H), 3.00-3.05 (m, 1H), 3.14 (dm, $J = 16.5$ Hz, 1H), 3.62 (s, 3H), 4.81-4.86 (m, 1H), 4.97-5.02 (m, 1H), 7.22-7.38 (m, 5H). The spectral characteristics of 2f were in agreement with the previously published data.
3-Methylene-4-methylspiro[cyclopentane-1,3′-coumaran-2-one] (2g).

Yield 93% (cond. B) (5:1 mixture of diastereoisomers): \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) \(\delta\) 1.25 (d, \(J = 6.8\) Hz, 3H), 1.70 (dd, \(J = 13.1, 10.8\) Hz, 1H), 2.46 (dd, \(J = 13.1, 8.1\) Hz, 1H), 2.70 (dm, \(J = 16.5\) Hz, 1H), 3.02 (dm, \(J = 16.5\) Hz, 1H), 3.08-3.16 (m, 1H), 4.95-4.97 (m, 1H), 4.99-5.01 (m, 1H), 7.09 (d, \(J = 7.8\) Hz, 1H), 7.15 (dd, \(J = 7.5, 1.1\) Hz, 1H), 7.15-7.30 (m, 1H), 7.20 (dd, \(J = 7.5\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 17.47, 37.18, 44.77, 46.80, 51.20, 105.82, 110.42, 122.66, 124.38, 128.50, 132.70, 132.89, 153.59, 180.85; IR (CHCl\(_3\)) 888, 1052, 1224, 1466, 1796 cm\(^{-1}\); EI-MS m/z (%) 214 (M\(^+\), 100), 199 (25), 186 (45), 171 (53), 128 (25), 115 (33); HRMS calcd for C\(_{14}\)H\(_{14}\)O\(_2\) 214.1000, found 214.0994.

Ethyl 1-cyano-3-methyl-4-methylenecyclopentanecarboxylate (2h).

Yield 30% (cond. B) (3:2 mixture of diastereoisomers). Major diastereomer: \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) \(\delta\) 1.18 (d, \(J = 6.6\) Hz, 3H), 1.29 (t, \(J = 7.0\) Hz, 3H), 1.86 (dd, \(J = 12.4\) Hz, 1H), 2.49 (dd, \(J = 12.4, 7.2\) Hz, 1H), 2.81-2.87 (m, 1H), 2.98-3.06 (m, 2H), 4.20-4.29 (m, 2H), 4.92-4.98 (m, 1H), 4.98-5.05 (m, 1H). Minor diastereomer: \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) \(\delta\) 1.18 (d, \(J = 6.6\) Hz, 3H), 1.29 (t, \(J = 7.0\) Hz, 3H), 1.92 (dd, \(J = 12.1, 8.7\) Hz, 1H), 2.58-2.64 (m, 1H), 2.81-2.87 (m, 1H), 2.95 (dq, \(J = 16.8, 2.1\) Hz, 1H), 3.11-3.17 (m, 1H), 4.20-4.29 (m, 2H), 4.88-4.94 (m, 1H), 4.98-5.05 (m, 1H). The spectral characteristic of 2h was in agreement with the previously published methylester derivative of the title compound.\(^{15}\)

Ethyl 2-allyl-2-cyanopent-3-enoate (5h).

Yield 16% (cond. B): \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) \(\delta\) 1.32 (t, \(J = 7.2\) Hz, 3H), 1.77 (dd, \(J = 6.4, 1.6\) Hz, 3H), 2.57 (dd, \(J = 13.6, 6.8\) Hz, 1H), 2.75 (dd, \(J = 13.6, 8.0\) Hz, 1H), 4.33 (q, \(J = 7.2\) Hz, 2H), 5.21 (bs, 1H), 5.23 (dm, \(J = 4.7\) Hz, 1H), 5.44 (dq, \(J = 15.4, 1.7\) Hz, 1H), 5.72-5.83
(m, 1H), 6.07 (dq, J = 15.6, 6.7 Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 13.99, 17.60, 41.99, 51.83, 62.90, 117.48, 120.90, 124.82, 130.48 (2C), 167.47; IR (CHCl\(_3\)) 1220, 1603, 1729, 2919, 3695 cm\(^{-1}\); EI-MS m/z (%) 193 (M\(^+\), 10), 166 (11), 152 (11), 124 (16), 120 (18), 106 (20), 93 (31), 41 (32), 32 (100); HRMS calcd for C\(_{11}\)H\(_{15}\)NO \(193.1103\), found 193.1099.

1,1-Bisbenzyloxymethyl-3-methylene-4-methylcyclopentane (2i).

Yield 37% (cond. A): \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) \(\delta\) 1.05 (d, \(J = 6.7\) Hz, 3H), 1.11 (dd, \(J = 13.0, 10.7\) Hz, 1H), 1.96 (dd, \(J = 12.9, 7.2\) Hz, 1H), 2.27-2.33 (m, 2H), 2.45-2.56 (m, 1H), 3.33-3.43 (m, 4H), 4.50 (d, \(J = 2\) Hz, 4H), 4.71-4.73 (m, 1H), 4.79-4.83 (m, 1H), 7.24-7.34 (m, 10H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 18.63, 36.58, 39.80, 40.58, 45.56, 73.00, 73.15 (2C), 74.77, 104.39, 127.30 (4C), 127.34 (2C), 128.24 (4C), 138.90 (2C), 156.61. The spectral characteristics of 2i were in agreement with the previously published data.\(^{16}\)

1,1-Bisbenzyloxymethyl-3,4-dimethylcyclopent-2-ene (3i).

Yield 65% (cond. B): \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) \(\delta\) 1.01 (d, \(J = 5.2\) Hz, 3H), 1.27 (dd, \(J = 6.8, 6.4\) Hz, 1H), 1.66 (s, 3H), 2.05 (dd, \(J = 13.2, 8.4\) Hz, 1H), 2.58 (qdd, \(J = 7.2, 2.0, 1.2\) Hz, 1H), 3.35-3.47 (m, 4H), 4.48-4.51 (m, 4H), 5.26-5.28 (m, 1H), 7.23-7.34 (m, 10H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 14.80, 20.07, 39.57, 41.48, 53.22, 73.19, 73.21, 73.96, 75.19, 127.19, 127.23 (2C), 127.32 (2C), 127.38 (2C), 128.19 (4C), 138.96, 139.00, 146.28; IR (CHCl\(_3\)) 920, 1141, 1191, 1280, 1450, 1730 cm\(^{-1}\); EI-MS m/z (%) 276 (10), 243 (15), 229 (20), 154 (25), 139 (50), 123 (48), 107 (41), 105 (95), 91 (100), 77 (23). It does not have molecular peak.

(3-Methyl-4-methylene cyclopentyloxy)(tert-butyl)dimethylsilane (2j).

Yield 71% (cond. A) (3:2 mixture of diastereoisomers). Major diastereomer: \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) \(\delta\) 0.04 (s, 6H), 0.87 (s, 9H), 1.07 (d, \(J = 6.9\) Hz, 3H), 1.37 (ddd, \(J = 12.4, 9.6, 4.9\) Hz, 1H), 1.83-1.91 (m, 1H), 2.33 (dm, \(J = 16.8\) Hz, 1H), 2.56 (dm, \(J = 16.6\) Hz, 1H), 2.68-2.77 (m, 1H), 4.22-4.30 (m, 1H), 4.78-4.81 (m, 1H), 4.84-4.87 (m, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\)
-4.75 (2C), 18.12, 18.80, 25.86 (3C), 35.61, 43.31, 44.61, 71.51, 104.67, 156.03. Minor
diastereomer: $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 0.05 (s, 6H), 0.88 (s, 9H), 1.12 (d, $J = 6.9$ Hz, 3H),
1.31 (ddd, $J = 12.0$, 10.7, 8.1 Hz, 1H), 2.05-2.13 (m, 1H), 2.28 (ddq, $J = 16.3$, 7.3, 2.4 Hz,
1H), 2.34-2.44 (m, 1H), 2.62 (ddm, $J = 16.3$, 7.0 Hz, 1H), 4.14-4.22 (m, 1H), 4.76-4.79 (m,
1H), 4.83-4.86 (m, 1H); $^{13}$C NMR (CDCl$_3$) δ -4.75 (2C), 18.13, 19.45, 25.87 (3C), 36.34,
42.82, 44.32, 71.90, 105.05, 155.11. IR (CHCl$_3$) 838, 1097, 1120, 1219, 1257, 1463, 1732,
2933, 2960, 3024 cm$^{-1}$; EI-MS m/z (%) 169 (49), 101 (2), 93 (3), 75 (100), 59 (3), 41 (3). It
does not have molecular peak.

(3,4-Dimethylcyclopent-3-enyloxy)(tert-butyl)dimethylsilane (4j).

Yield 44% (cond. B): $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 0.06 (s, 6H), 0.89 (s, 9H), 1.59 (bs, 6H),
2.24 (dm, $J = 16.0$ Hz, 2H), 2.53 (ddm, $J = 14.8$, 7.2 Hz, 2H), 4.41-4.46 (m, 1H); $^{13}$C NMR
(CDCl$_3$) δ -4.70 (2C), 13.68 (2C), 18.34, 25.99 (3C), 48.34 (2C), 70.92, 128.43 (2C); IR
(CHCl$_3$) 836, 900, 1086, 1254, 1367, 1466, 1682, 2856, 2929, 2956, 3529 cm$^{-1}$; EI-MS m/z
(%) 169 (53), 95 (9), 75 (100), 67 (5), 59 (8), 47 (7), 41 (12). It does not have molecular peak.

3-Methylene-4-methylspiro[cyclopentane-1,9'-fluorene] (2k).

Yield 85% (cond. A): $^1$H NMR (CDCl$_3$, Me$_4$Si) δ 1.29 (d, $J = 6.8$ Hz, 3H), 1.97 (dd, $J = 12.8$,
10.8 Hz, 1H), 2.12 (ddd, $J = 12.8$, 8.0, 1.2 Hz, 1H), 2.68 (dd, $J = 16.4$ Hz, 1H), 3.02 (dq, $J =$
16.4 Hz, 1H), 3.08-3.22 (m, 1H), 5.05 (dd, $J = 4.8$, 2.4 Hz, 2H), 7.21-7.34 (m, 4H), 7.41-7.49
(m, 2H), 7.67-7.72 (m, 2H). The spectral characteristics of 2k were in agreement with the
previously published data.$^{17}$

3,4-Dimethylspiro[cyclopent-2-ene-1,9'-fluorene] (3k) and 3,4-dimethylspiro[cyclopent-3-ene-1,9'-fluorene] (4k).
Obtained as an inseparable mixture in yield 98% (3k: 72%, 4k: 26%) (cond. B). 3k: \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) \(\delta\) 1.24 (d, \(J = 6.0\) Hz, 3H), 1.84 (s, 3H), 2.02 (dd, \(J = 13.3, 7.5\) Hz, 1H), 2.51 (dd, \(J = 13.3, 7.9\) Hz, 1H), 3.05-3.15 (m, 1H), 5.04 (s, 1H), 7.20-7.40 (m, 6H), 7.65-7.70 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 14.75, 20.35, 43.07, 46.93, 62.38, 119.45, 119.59, 123.59, 123.99, 126.95, 126.98, 127.32, 127.36, 129.28, 139.28, 139.37, 146.97, 152.54, 152.80.

4k: Yield 26% (cond. B): \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) \(\delta\) 1.75 (s, 6H), 2.79 (s, 4H), 7.20-7.40 (m, 6H), 7.65-7.70 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 13.85 (2C), 51.19 (2C), 54.20, 119.52 (2C), 122.31 (2C), 126.77 (2C), 127.55 (2C), 130.27 (2C), 139.31 (2C), 154.53 (2C).

3-Methyl-4-methylene-1-phenylpyrrolidine (2l).

Yield 71% (cond. B): \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si) \(\delta\) 1.22 (d, \(J = 6.4\) Hz, 3H), 2.68-2.95 (m, 2H), 3.63-3.69 (m, 1H), 3.87 (dd, \(J = 13.7, 1.6\) Hz, 1H), 4.08 (d, \(J = 13.9\) Hz, 1H), 4.96 (d, \(J = 2.3\) Hz, 1H), 5.03 (d, \(J = 1.9\) Hz, 1H), 6.57-6.74 (m, 3H), 7.21-7.28 (m, 2H). The spectral characteristics of 2l were in agreement with the previously published data.\(^{17}\)

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