

Supporting information for:

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

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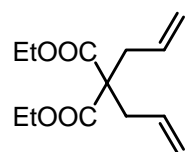
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1. General Methods.

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 (Labiop, Czech Republic), filled with BIOSPHER PSI 100 (7µm mesh).

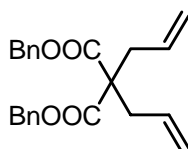
2. Preparation of Starting Materials

Diethyl di(prop-2'-en-1'-yl)propandioate (1a).



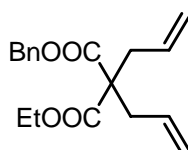
Allylation of allylmalonate was carried out according to the previously reported procedure.¹ Sodium metal (0.58 g, 25 mmol) was dissolved in absolute ethanol (25 mL), then was slowly added diethyl allylmalonate (4 g, 25 mmol) followed by dropwise addition of allyl bromide (3.2 g, 26.4 mmol), and the 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).



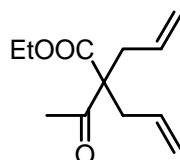
Dibenzylmalonate (1.07 g, 3.8 mmol), K₂CO₃ (2.2 g, 16 mmol) and tetrabutylammonium hydrogensulfate (200 mg, 0.6 mmol) were dissolved in CH₃CN (10 mL). Then allylbromide (0.95 g, 7.8 mmol) was added and the reaction mixture was refluxed for 72 h, at which time it was added a 10-mL portion of water and 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.²

Ethyl benzyl di(prop-2'-en-1'-yl)propandioate (1c).



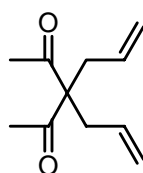
The preparation was analogous to **1b**. Benzylethylmalonate (0.6 g, 2.7 mmol), K₂CO₃ (1.8 g, 13 mmol) and tetrabutylammonium hydrogensulfate (168 mg, 0.5 mmol) and CH₃CN (8 mL). Column chromatography on silica gel (3/1 hexane/EtOAc) afforded 720 mg (88%) as a colourless liquid: ¹H NMR (CDCl₃, Me₄Si) 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); ¹³C NMR (CDCl₃) 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 (CHCl₃) 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 calcd for C₁₈H₂₂O₄ 302.1518, found 302.1507.

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



The preparation was analogous to **1b**. Ethyl 3-oxobutanoate (13 g, 100 mmol), K₂CO₃ (10 g, 40 mmol), tetrabutylammonium hydrogensulfate (5 g, 15 mmol), allyl bromide (25 g, 206.6 mmol) and CH₃CN (100 mL). column chromatography on silica gel (3/1 hexane/EtOAc) afforded 18.3 g (87%) of the title compound as a colourless liquid: ¹H NMR (CDCl₃, Me₄Si) 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

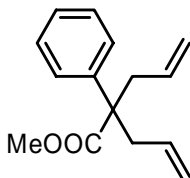
3,3-Diallylpentane-2,4-dione (**1e**).



The preparation was analogous to **1b**. 2,4-Pentanedione (10 mL, 97.4 mmol), K₂CO₃ (10 g, 40 mmol), tetrabutylammonium hydrogensulfate (5 g, 15 mmol), allyl bromide (25 g, 206.6 mmol) and CH₃CN (100 mL). Column chromatography on silica gel (3/1 hexane/EtOAc) afforded 14.9 g (85%) of the title compound as a colourless liquid: ¹H NMR (CDCl₃, Me₄Si)

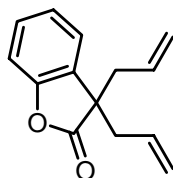
δ 2.11 (s, 6H), 2.66 (dm, $J = 7.3$ Hz, 4H), 5.08-5.15 (m, 4H), 5.54 (ddt, $J = 16.4, 8.0, 7.3$ Hz, 2H). The spectral characteristics of **1e** were in agreement with the previously published data.³

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



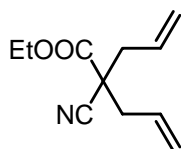
The preparation was analogous to **1b**. Methyl 2-phenylacetate (1.13 g, 7.5 mmol), K_2CO_3 (5.6 g, 40 mmol), Bu_4NHSO_4 (0.5 g, 1.5 mmol), allyl bromide (1.86 g, 15.5 mmol) and CH_3CN (15 mL). Column chromatography on silica gel (3/1 hexane/EtOAc) afforded 1.19 g (69%) of the title compound as a colourless liquid: 1H NMR ($CDCl_3$, Me_4Si) δ 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 ($CDCl_3$) δ 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).



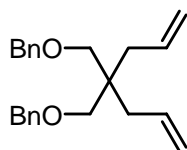
The preparation was analogous to **1b**. 2-Coumaranone (1 g, 7.46 mmol), K_2CO_3 (5.6 g, 40 mmol), tetrabutylammonium hydrogensulfate (0.5 g, 1.5 mmol), allyl bromide (1.82 g, 15 mmol) and CH_3CN (15 mL). Column chromatography on silica gel (3/1 hexane/EtOAc) afforded 1.14 g (71%) of the title compound as an yellowish oil: 1H NMR ($CDCl_3$, Me_4Si) δ 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)cynoacetate (1h).



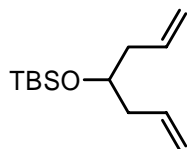
The preparation was analogous to **1b**. Ethyl cyanoacetate (4.52 g, 40 mmol), K_2CO_3 (33 g, 240 mmol), Bu_4NHSO_4 (2 g, 8 mmol), allyl bromide (9.68 g, 80 mmol) and CH_3CN (80 mL). Column chromatography on silica gel (3/1 hexane/EtOAc) afforded 5.2 g (67%) of the title compound as a colourless liquid: 1H NMR ($CDCl_3$, Me_4Si) 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.⁵

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_2O (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: 1H NMR ($CDCl_3$, Me_4Si) 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.⁶

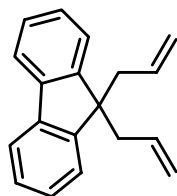
t-Butyl(hepta-1,6-dien-4-yloxy)dimethylsilane (**1j**).



Hepta-1,6-dien-4-ol (2.02 g, 18 mmol) and Et_3N (2.8 mL, 20 mmol) were dissolved in dichloromethane (40 mL), then TBSCl (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_2O (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: 1H NMR

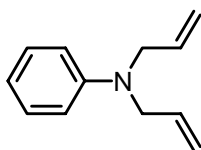
(CDCl₃, Me₄Si) δ 0.03 (s, 6H), 0.87 (s, 9H), 2.13-2.26 (m, 4H), 3.69-3.76 (m, 1H), 5.00 (bs, 2H), 5.04 (dm, $J = 5.6$ Hz, 2H), 5.75-5.85 (m, 2H). The spectral characteristics of **1j** were in agreement with the previously published data.⁷

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



Allylation of fluorene was carried out according to the previously reported procedure.⁸ Yield 86% (5.2 g, 21 mmol) of a yellowish liquid: ¹H NMR (CDCl₃, Me₄Si) δ 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**).



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: ¹H NMR (CDCl₃, Me₄Si) δ 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

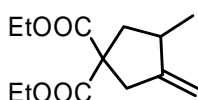
3. General Procedure for Ni-catalyzed Cyclization of Dienes

To a solution of a diene (**1a–1l**) (0.5 mmol) was added NiBr₂(PBU₃)₂ (15.6 mg, 0.025 mmol) in dry toluene (3 mL) and 1.8M solution of Et₂AlCl in toluene (55 μ L, 0.1 mmol) (cond. **B**) or NiBr₂(PPh₃)₂ (18.6 mg, 0.025 mmol) and 1.9M solution of Et₃Al in toluene (53 μ 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 (MgSO₄). The products isolated HPLC (silica gel, hexane/EtOAc).

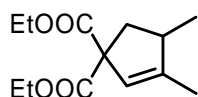
4. Products of Ni-complex Catalyzed Cyclization

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



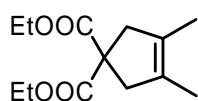
Yield 92% (cond. **B**): ¹H NMR (CDCl₃, Me₄Si) δ 1.11 (d, *J* = 6.4 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.71-1.79 (m, 1H), 2.51-2.60 (m, 2H), 2.94 (d, *J* = 16.9 Hz, 1H), 3.05 (dm, *J* = 17.1 Hz, 1H), 4.14-4.23 (m, 4H), 4.78-4.82 (m, 1H), 4.89-4.92 (m, 1H). The spectral characteristics of **2a** were in agreement with the previously published data.¹²

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



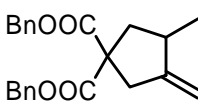
Yield 18% (cond. **A**): ¹H NMR (CDCl₃, Me₄Si) δ 1.05 (d, *J* = 6.8 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.73 (s, 3H), 1.88-1.96 (m, 1H), 2.69-2.79 (m, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 5.42 (bs, 1H). The spectral characteristics of **3a** were in agreement with the previously published data.¹²

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



Yield 6% (cond. **A**): ¹H NMR (CDCl₃, Me₄Si) 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.¹³

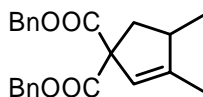
Dibenzyl 3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (**2b**).



Yield 75% (cond. **B**): ¹H NMR (CDCl₃, Me₄Si) 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

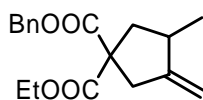
Hz, 1H), 4.90 (bs, 1H), 5.10 (d, $J = 3.6$ Hz, 4H), 7.21-7.26 (m, 4H), 7.29-7.34 (m, 6H); ^{13}C NMR (CDCl_3) δ 17.97, 37.21, 40.53, 42.08, 58.32, 67.07, 67.14, 105.64 (2C), 127.91 (4C), 128.20 (2C), 128.47 (4C), 135.45, 153.07, 171.45, 171.61; IR (CHCl_3) 890, 1167, 1227, 1254, 1275, 1729 cm^{-1} ; EI-MS m/z (%) 364 (M^+ , 1), 273 (15), 229 (38), 211 (19), 91 (100); HRMS calcd for $\text{C}_{23}\text{H}_{24}\text{O}_4$ 364.1675, found 364.1671.

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



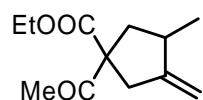
Yield 30% (cond. **A**): ^1H NMR (CDCl_3 , Me_4Si) δ 1.04 (d, $J = 6.8$ Hz, 3H), 1.72 (s, 3H), 1.96 (ddd, $J = 7.2, 4.8, 1.2$ Hz, 1H), 2.64-2.79 (m, 1H), 2.75-2.84 (m, 1H), 5.04-5.17 (m, 4H), 5.47 (bs, 1H), 7.21-7.34 (m, 10H). The spectral characteristics of **3b** were in agreement with the previously published data.¹⁴

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



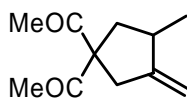
Yield 91% (cond. **B**) (3:2 mixture of diastereoisomers). Major diastereomer: ^1H NMR (CDCl_3 , Me_4Si) δ 1.10 (d, $J = 6.3$ Hz, 3H), 1.14 (t, $J = 7.1$ Hz, 3H), 1.73-1.82 (m, 1H), 2.54-2.63 (m, 2H), 2.95 (dm, $J = 16.9$ Hz, 1H), 3.06 (d, $J = 16.8$ Hz, 1H), 4.08-4.17 (m, 2H), 4.80 (s, 1H), 4.91 (s, 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: ^1H NMR (CDCl_3 , Me_4Si) 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 $\text{C}_{18}\text{H}_{22}\text{O}_4$ 302.1518, found 302.1516.

Ethyl 1-acetyl-3-methyl-4-methylenecyclopentanecarboxylate (**2d**).



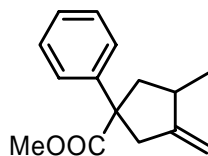
Yield 60% (cond. **B**) (3:2 mixture of diastereoisomers). Major diastereomer: ^1H NMR (CDCl_3 , Me_4Si) δ 1.09 (d, $J = 6.4$ Hz, 3H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.74 (dd, $J = 12.1, 10.1$ Hz, 1H), 2.18 (s, 3H), 2.39-2.48 (m, 1H), 2.44-2.54 (m, 1H), 2.88-2.92 (m, 1H), 2.93-3.02 (m, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 4.76-4.79 (m, 1H), 4.89-4.91 (m, 1H); ^{13}C NMR (CDCl_3) δ 13.99, 17.86, 25.94, 37.05, 38.97, 40.65, 61.52, 64.29, 105.38, 153.29, 172.52, 203.67. Minor diastereomer: ^1H NMR (CDCl_3 , Me_4Si) δ 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), 2.93-3.02 (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) δ 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, 2967cm^{-1} ; EI-MS m/z (%) 210 (M^+ , 8), 192 (9), 167 (82), 139 (49), 121 (38), 93 (53), 43 (100); HRMS calcd for $\text{C}_{12}\text{H}_{18}\text{O}_3$ 210.1256, found 210.1255.

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

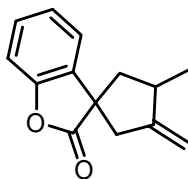


Yield 28% (cond. **B**): ^1H NMR (CDCl_3 , Me_4Si) δ 1.08 (d, $J = 6.7$ Hz, 3H), 1.59 (dd, $J = 12.8, 10.8$ Hz, 1H), 2.10 (s, 3H), 2.13 (s, 3H), 2.37-2.48 (m, 1H), 2.58 (dd, $J = 12.8, 7.3$ Hz, 1H), 2.88 (dm, $J = 16.9$ Hz, 1H), 2.96 (dm, $J = 16.9$ Hz, 1H), 4.76-4.79 (m, 1H), 4.89-4.92 (m, 1H). The spectral characteristics of **2e** were in agreement with the previously published data.

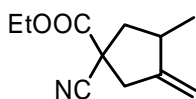
Methyl 3-methyl-4-methylene-1-phenylcyclopentanecarboxylate (**2f**).



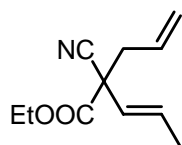
Yield 94% (cond. **B**) (3:2 mixture of diastereoisomers). Major diastereomer: ^1H NMR (CDCl_3 , Me_4Si) δ 1.14 (d, $J = 6.6$ Hz, 3H), 1.60 (dd, $J = 11.9$ Hz, 1H), 2.53-2.61 (m, 1H), 2.69 (dq, $J = 16.3, 2.6$ Hz, 1H), 2.99 (ddd, $J = 11.9, 7.2, 2.1$ Hz, 1H), 3.54 (dm, $J = 16.3$ Hz, 1H), 3.61 (s, 3H), 4.81-4.86 (m, 1H), 4.97-5.02 (m, 1H), 7.22-7.38 (m, 5H). Minor diastereomer: ^1H NMR (CDCl_3 , Me_4Si) δ 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.¹⁵

3-Methylene-4-methylspiro[cyclopentane-1,3'-coumaran-2-one] (2g).

Yield 93% (cond. **B**) (5:1 mixture of diastereoisomers): ^1H NMR (CDCl_3 , Me_4Si) δ 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) δ 17.47, 37.18, 44.77, 46.80, 51.20, 105.82, 110.42, 122.66, 124.38, 128.50, 132.70, 152.89, 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 $\text{C}_{14}\text{H}_{14}\text{O}_2$ 214.1000, found 214.0994.

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

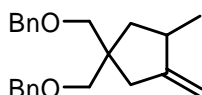
Yield 30% (cond. **B**) (3:2 mixture of diastereoisomers). Major diastereomer: ^1H NMR (CDCl_3 , Me_4Si) δ 1.18 (d, $J = 6.6$ Hz, 3H), 1.29 (t, $J = 7.0$ Hz, 3H), 1.86 (dd, $J = 12.4$ Hz, 1H), 2.49 (dd, $J = 12.4, 7.2$ Hz, 1H), 2.81-2.87 (m, 1H), 2.98-3.06 (m, 2H), 4.20-4.29 (m, 2H), 4.92-4.98 (m, 1H), 4.98-5.05 (m, 1H). Minor diastereomer: ^1H NMR (CDCl_3 , Me_4Si) δ 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**): ^1H NMR (CDCl_3 , Me_4Si) δ 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

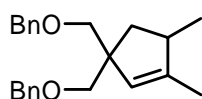
(m, 1H), 6.07 (dq, $J = 15.6, 6.7$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.99, 17.60, 41.99, 51.83, 62.90, 117.48, 120.90, 124.82, 130.48 (2C), 167.47; IR (CHCl_3) 1220, 1603, 1729, 2919, 3695 cm^{-1} ; EI-MS m/z (%) 193 (M^+ , 10), 166 (11), 152 (11), 124 (16), 120 (18), 106 (20), 93 (31), 41 (32), 32 (100); HRMS calcd for $\text{C}_{11}\text{H}_{15}\text{NO}_2$ 193.1103, found 193.1099.

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



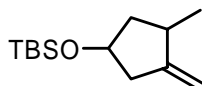
Yield 37% (cond. **A**): ^1H NMR (CDCl_3 , Me_4Si) δ 1.05 (d, $J = 6.7$ Hz, 3H), 1.11 (dd, $J = 13.0, 10.7$ Hz, 1H), 1.96 (dd, $J = 12.9, 7.2$ Hz, 1H), 2.27-2.33 (m, 2H), 2.45-2.56 (m, 1H), 3.33-3.43 (m, 4H), 4.50 (d, $J = 2$ Hz, 4H), 4.71-4.73 (m, 1H), 4.79-4.83 (m, 1H), 7.24-7.34 (m, 10H); ^{13}C NMR (CDCl_3) δ 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**): ^1H NMR (CDCl_3 , Me_4Si) δ 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) δ 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.

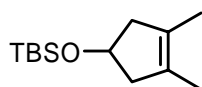
(3-Methyl-4-methylenecyclopentyloxy)(tert-butyl)dimethylsilane (2j).



Yield 71% (cond. **A**) (3:2 mixture of diastereoisomers). Major diastereomer: ^1H NMR (CDCl_3 , Me_4Si) δ 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) δ

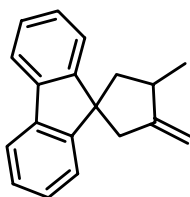
-4.75 (2C), 18.12, 18.80, 25.86 (3C), 35.61, 43.31, 44.61, 71.51, 104.67, 156.03. Minor diastereomer: ^1H NMR (CDCl_3 , Me_4Si) δ 0.05 (s, 6H), 0.88 (s, 9H), 1.12 (d, $J = 6.9$ Hz, 3H), 1.31 (ddd, $J = 12.0, 10.7, 8.1$ Hz, 1H), 2.05-2.13 (m, 1H), 2.28 (ddq, $J = 16.3, 7.3, 2.4$ Hz, 1H), 2.34-2.44 (m, 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).



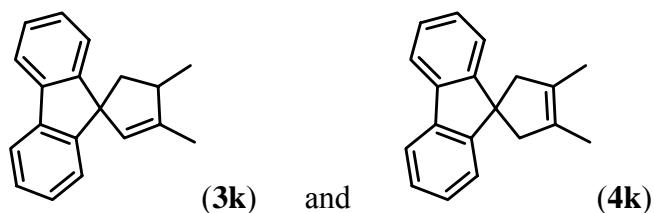
Yield 44% (cond. **B**): ^1H NMR (CDCl_3 , Me_4Si) δ 0.06 (s, 6H), 0.89 (s, 9H), 1.59 (bs, 6H), 2.24 (dm, $J = 16.0$ Hz, 2H), 2.53 (ddm, $J = 14.8, 7.2$ Hz, 2H), 4.41-4.46 (m, 1H); ^{13}C NMR (CDCl_3) δ -4.70 (2C), 13.68 (2C), 18.34, 25.99 (3C), 48.34 (2C), 70.92, 128.43 (2C); IR (CHCl_3) 836, 900, 1086, 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).



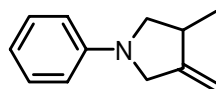
Yield 85% (cond. **A**): ^1H NMR (CDCl_3 , Me_4Si) δ 1.29 (d, $J = 6.8$ Hz, 3H), 1.97 (dd, $J = 12.8, 10.8$ Hz, 1H), 2.12 (ddd, $J = 12.8, 8.0, 1.2$ Hz, 1H), 2.68 (dd, $J = 16.4$ Hz, 1H), 3.02 (dq, $J = 16.4$ Hz, 1H), 3.08-3.22 (m, 1H), 5.05 (dd, $J = 4.8, 2.4$ Hz, 2H), 7.21-7.34 (m, 4H), 7.41-7.49 (m, 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**: ^1H NMR (CDCl_3 , Me_4Si) δ 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) δ 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**): ^1H NMR (CDCl_3 , Me_4Si) δ 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) δ 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**): ^1H NMR (CDCl_3 , Me_4Si) δ 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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