General:

Reactions were conducted under a positive pressure of dry nitrogen within glassware which had been oven dried prior to use unless otherwise noted. Anhydrous solutions of reaction mixtures were transferred via an oven dried syringe or cannula. All solvents were distilled from appropriate drying agents prior to use. Diisopropylamine, benzene, acetonitrile, methylene chloride, pyridine and triethylamine were distilled from calcium hydride. Ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Toluene was distilled from molten sodium. Acetone was distilled from barium oxide. Methanol and ethanol were distilled from magnesium methoxide and ethoxide respectively. Reagents were obtained from Aldrich, Farchan, Fluka, TCI or Lancaster unless otherwise noted.

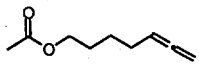
Thin layer chromatography was performed using precoated silica gel plates (Merck, Kieselgel 60, F_{254}). Flash column chromatography was performed with silica gel (Merck, 230-240 mesh). Infrared spectra (IR) were obtained as neat oils on a Perkin Elmer FT-IR spectrometer. ^{1}H and ^{13}C nuclear magnetic resonance spectra (NMR) were obtained on a Varian Gemini 300 (300 and 75 MHz respectively) or a Varian Unity Inova 500 (500 and 125 MHz respectively), and are recorded in δ in ppm downfield of TMS ($\delta = 0$) in deuterochloroform. Signal spitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q.), quintet (quint.), or multiplet (m), with coupling constants (J) in hertz. Elemental analyses (EA) were performed by M-H-W Laboratories, Phoenix, AZ. High resolution mass spectra (HRMS) were performed by the University of California, San Francisco mass spectrometry resource on a Kratos MS9 spectrometer.

Synthesis of Terminal Allenes

The allenes were synthesized from the corresponding terminal acetylene by the method of Crabbé.[i] A standard procedure follows:

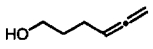
Diisopropylamine (2 eq.) was added to a stirred mixture of the acetylene (1 eq.), paraformaldehyde (2 eq.) and copper (I) bromide (0.33 eq) in dioxane (0.1 M). The reaction was heated to reflux for 4-6 hours, then cooled to room temperature. For nonpolar compounds, the reaction mixture was poured into water and pentane, and the organic layer was washed twice with water, dried over $MgSO_4$ and evaporated under reduced pressure to directly give product. For more polar compounds, the dioxane was removed under reduced pressure, and the resulting crude material chromatographed on silica gel.

In general, this reaction was capricious. Initial optimization found that using approximately 30 mol% copper was best. Higher loadings did not improve the yield. Less than 30% copper gave poor yields as well. One major difficulty in this reaction is removing the dioxane from more volatile products. This could potentially be circumvented by running the reaction on large scale and purifying the products by distillation. Although the allenes were relatively stable, full characterization was not obtained until after the ruthenium reaction was performed.



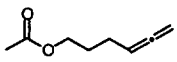
Acetic acid hepta-5,6-dienyl ester

Colorless oil, R_f = 0.45 (8:1 petroleum ether/ether), IR (neat) : 2939, 2861, 2361, 2342, 1957, 1472, 1440, 1388, 1366, 1240, 1041, 969 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 5.09 (quint., J=6.5, 1H), 4.49-4.65 (m, 2H), 4.06 (t, J=6.6, 2H), 2.08-1.99 (m, 2H), 2.05 (s, 3H), 1.72-1.60 (m, 2H), 1.53-1.43 (m, 2H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.5, 171.2, 89.5, 74.9, 64.4, 28.0, 27.8, 25.3, 21.0.



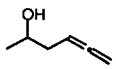
Hexa-4,5-dien-1-ol

Colorless oil, R_f = 0.21 (2:1 petroleum ether/ether), IR (neat) : 3347, 2940, 2871, 1957, 1436, 1337, 1229, 1169, 1122, 1059, 977, 948 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 5.11 (quint., J=6.6, 1H), 4.68-4.64 (m, 2H), 3.65 (t, J=6.5, 2H), 2.11-2.03 (m, 2H), 1.99 (brs, 1H), 1.72-1.62 (m, 2H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.4, 89.4, 75.0, 62.1, 31.8, 24.4. This compound has been previously described, and the data are in agreement.[ii]



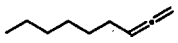
Acetic acid hexa-4,5-dienyl ester

Colorless oil, IR (neat) : 2957, 2855, 1957, 1740, 1438, 1388, 1368, 1243, 1125, 1045, 848, 668 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 5.11 (quint., J=6.6, 1H), 4.71-4.66 (m, 2H), 4.09 (t, J=6.6, 2H), 2.12-2.02 (m, 2H), 2.05 (s, 3H), 1.75 (quint., J=7.2, 2H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.5, 171.2, 88.9, 75.3, 63.8, 27.8, 24.5, 21.0. This compound has been previously described, and the data are in agreement.[iii]



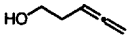
Hexa-4,5-dien-2-ol

Colorless oil, R_f = 0.31 (3:2 petroleum ether/ether), IR (neat) : 3363, 2970, 2930, 2361, 1957, 1430, 1375, 1207, 1127, 1079, 941, 842 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 5.11 (quint., J=7.1, 1H), 4.73-4.69 (m, 2H), 3.91-3.69 (m, 1H), 2.22-2.14 (m, 2H), 1.78 (brs, 1H), 1.22 (d, J=6.4, 3H), ^{13}C NMR (75MHz, $CDCl_3$): δ 209.4, 86.2, 74.8, 67.4, 38.2, 22.6. This compound has been previously described, and the data are in agreement.[iv]



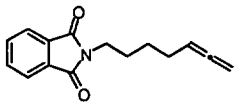
Nona-1,2-diene

Colorless oil, IR (neat) : 2958, 2929, 2857, 2361, 1957, 1458, 1379, 1324, 1169, 1111, 1021, 841 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 5.09 (quint., J=6.7, 1H), 4.67-4.62 (m, 2H), 2.03-1.96 (m, 2H), 1.56-1.29 (m, 8H), 0.89 (t, J=6.8, 3H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.4, 90.1, 74.5, 31.7, 29.1, 28.8, 28.3, 22.6, 14.1. This compound has been previously described, and the data are in agreement.[v]

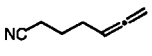


Penta-3,4-dien-1-ol

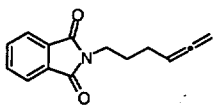
Colorless oil, R_f = 0.30 (1:1 petroleum ether/ether), IR (neat) : 3346, 2626, 2878, 1957, 1657, 1431, 1377, 1233, 1178, 1121, 1049, 844 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 5.19 (quint., J=6.7, 1H), 4.73-4.69 (m, 2H), 3.69 (t, J=6.2, 2H), 2.30-2.21 (m, 2H), 1.90 (brs, 1H), ^{13}C NMR (75MHz, $CDCl_3$): δ 209.0, 86.4, 75.2, 61.9, 31.5. This compound has been previously described, and the data are in agreement.[vi]



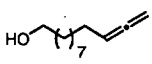
2-Hepta-5,6-dienyl-isoindole-1,3-dione
Colorless oil, R_f = 0.29 (6:1 petroleum ether/ethyl acetate), IR (neat) : 2939, 2861, 1955, 1773, 1712, 1467, 1438, 1397, 1371, 1336, 1040, 720 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 7.84-7.81 (m, 2H), 7.72-7.67 (m, 2H), 5.06 (quint., J=6.6, 1H), 4.66-4.61 (m, 2H), 3.68 (t, J=7.2, 2H), 2.07-2.00 (m, 2H), 1.76-1.66 (m, 2H), 1.51-1.44 (m, 2H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.5, 168.4, 133.8, 132.1, 127.0, 123.1, 89.4, 74.9, 37.8, 28.0, 26.2.



Hepta-5,6-dienenitrile
Colorless oil, IR (neat) : 2940, 2871, 2361, 2341, 2247, 1956, 1436, 1347, 1329, 1006, 850, 668 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 5.08 (quint., J=6.6, 1H), 4.75-4.70 (m, 2H), 2.39 (t, J=7.1, 2H), 2.20-2.10 (m, 2H), 1.79 (quint., J=7.1, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ 208.6, 119.5, 87.9, 75.8, 26.7, 24.5,16.3.



2-Hexa-4,5-dienyl-isoindole-1,3-dione
Colorless oil, R_f = 0.35 (6:1 petroleum ether/ethyl acetate), IR (neat) : 2941, 1956, 1772, 1715, 1468, 1437, 1397, 1372, 1336, 1188, 1112, 1034 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 7.84-7.80 (m, 2H), 7.72-7.66 (m, 2H), 5.11 (quint., J=6.6, 1H), 4.69-4.64 (m, 2H), 3.71 (t, J=7.2, 2H), 2.10-2.00 (m, 2H), 1.85-1.74 (m, 2H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.4, 168.3, 133.8, 132.1, 123.1, 88.9, 75.4, 37.5, 27.7, 25.4.



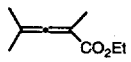
Undeca-10,11-dien-1-ol
Colorless oil. R_f = 0.32 (1:1 petroleum ether/ethyl ether), IR (neat) : 3313, 2926, 2855, 1957, 1653, 1558, 1507, 1458, 1364, 1176, 1124, 1058 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 5.11 (quint., J=6.8, 1H), 4.68-4.65 (m, 2H), 3.65 (t, J=6.7, 2H), 2.03-1.96 (m, 2H), 1.59-1.52 (m, 2H), 1.49-1.31 (m, 12H), 1.12 (brs, 1H). ^{13}C NMR (125MHz, $CDCl_3$): δ 208.4, 90.1, 74.5, 63.0, 32.7, 29.5, 29.4, 29.3, 29.1, 29.0, 28.2, 25.7.

Allenes from Wittig Reactions

To a stirred solution of (Carbethoxyethylidene)triphenyl-phosphorane or Carbethoxymethylenetriphenylphosphorane in dichloromethane is added at 0°C under nitrogen 1.02eq. of acid chloride and 1.02 eq. of triethylamine. The reaction mixture is allowed to warm up to room temperature and stirred overnight. The solvent was evaporated under reduced pressure and the product extracted from the precipitated triphenylphosphine oxide with pentane. The solution is then cooled to -20°C and the rest of the triphenylphosphine oxide is filtered. Removal of the pentane of the filtrate afforded a crude oil, which was purified on silica gel.

Entry	Phosphorane (g/mmol)	Acid chloride (mL/eq)	NEt_3 (mL/eq)	CH_2Cl_2 (mL)	Rxn time (hrs.)	Allene (g)	Yield (%)
1	2/5.52	0.573/1	0.77/1	20	22.5	0.4951	58
2	1.5/4.14	0.964/1.01	0.583/1.01	20	24	0.6863	59
3	9/24.83	1.8/1.02	3.531/1.02	60	20	2.091	67
	2.42/6.68	0.48/1.01	0.94/1.01	30	21	0.2386	28
4	1.5/4.14	0.568/1.01	0.583/1.01	15	20	0.5167	73
	1/2.76	0.38/1.01	0.39/1.01	10	24	0.4732	87
5	1/2.87	0.4/1.05	0.4/1.05	20	21	0.1008	20.5

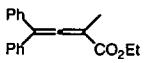
1



Colorless oil

R_f = 0.59 (9:1 petroleum ether/ether), IR (neat): 3083, 3059, 3026, 2982, 2929, 2905, 1942, 1715, 1598, 1494, 1477, 1456, 1444, 1390, 1369, 1264, 1174, 1116, 1075, 1031, 970, 902, 769, 696, 637. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.17 (q, J=6.9, 2H), 1.81 (s, 3H), 1.75 (s, 6H), 1.23 (t,J=6.9, 3H), ^{13}C-NMR (75 MHz, $CDCl_3$): 207.8, 168.4, 98.0, 93.3, 60.5, 19.6, 18.3, 15.5, 14.3. Anal. Calc. for $C_9H_{14}O_2$: C 70.099 H 9.15. Found: C 69.87 H 8.89.

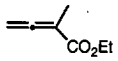
2



Colorless solid (mp = 58°C)

R_f = 0.51 (9:1 ether/ether), IR (neat): 3055, 2980, 1938, 1708, 1598, 1494, 1445, 1264, 1117, 1030, 764 cm-1, ^{1}H-NMR (300 MHz, CDCl3): 7.36 (m, 10H), 4.22 (q, J=7.2, 2H), 2.06 (s, 3H), 1.29 (t, J=7.2, 3H), ^{13}C-NMR (75 MHz, $CDCl_3$): 212.4, 167.3, 135.5, 128.7, 128.5, 127.9, 112.3, 98.2, 61.1, 15.2, 14.3, MS (EI), m/z 278 (M^+), 249 (M^+ - C_2H_5), 205 (M^+ - $CO_2C_2H_5$). HRMS calcd for $C_{19}H_{18}O_2$ (M^+) 278.1307. Found: 278.1303.

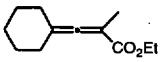
3



Colorless oil

R_f = 0.48 (9:1 petroleum ether/ether), IR (neat): 2985, 2933, 2907, 1970, 1944, 1714, 1448, 1420, 1368, 1279, 1262, 1222, 1173, 1124, 1027, 852 cm^{-1}, ^{1}H-NMR (300 MHz, $CDCl_3$): 5.04 (dd, J=3, 2H), 4.17 (q, J=7.2, 2H), 1.85 (s, 3H), 1.26 (t, J=7.2, 3H), ^{13}C-NMR (75 MHz, $CDCl_3$): 213.5, 167.0, 95.0, 76.2, 60.5, 14.2, 13.7. Anal. Calc. for $C_7H_{10}O_2$: C 66.65 H 7.99. Found: C 66.66 H 8.13.

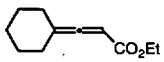
4



Colorless oil

R_f = 0.53 (9:1 petroleum ether/ether), IR (neat): 2981, 2931, 2855, 1962, 1710, 1447, 1367, 1268, 1214, 1120, 1100, 1032, 762 cm-1, ^{1}H-NMR (300 MHz, $CDCl_3$): 4.14 (q, J=7.2, 2H), 2.20-2.12 (m, 4H), 1.82 (s, 3H), 1.66-1.54 (m, 6H), 1.25 (t, J=7.2, 3H), ^{13}C-NMR (75 MHz, CDCl3): 204.8, 168.6, 105.0, 92.9, 60.5, 30.6, 27.2, 25.9, 15.6, 14.2, Anal. Calc. for $C_{12}H_{18}O_2$: C 74.19 H 9.34. Found: C 74.32 H 9.34.

5



Colorless oil

R_f = 0.3 (petroleum ether/ether : 9/1), IR (neat): 2980, 2933, 2856, 1963, 1810, 1720, 1447, 1430, 1366, 1344, 1322, 1253, 1184, 1153, 1040, 831 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 5.44 (m, 1H), 4.17 (q, J=7.2, 2H), 2.27-2.15 (m, 4H), 1.73-1.55 (m, 6H), 1.28 (t, J=7.2,3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 207.6, 166.8, 106.6, 85.8, 60.5, 30.1, 26.8, 25.7, 14.2. Anal. Calc. for $C_{11}H_{16}O_2$: C 73.30 H 8.95. Found: C 73.50 H 9.10.

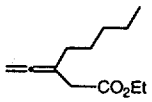
Synthesis of β-allenic esters by a Claisen-rearrangement:

A mixture of the propargyl alcohol, 4-7 equivalents of triethyl orthoacetate and a catalytic amount of propionic acid or montmorillonite KSF were heated to 145°C for several hrs with removal of ethanol by distillation. When the distillation ceased the reaction was mostly done and after 1-2 more hours the reaction mixture was cooled to room temperature and ether was added. The solution was washed twice with 1N H_2SO_4 and then with sat. $NaHCO_3$-solution. Drying over magnesium sulfate and removal of the solvent gave a crude product which was then purified on a silica gel column.

Entry	Propargyl alc. (g/mmol)	$CH_3C(0Et)_3$ (mL/eq.)	Cat.*	Rxn time	product (g)	s.m. (g)	Yield (%)	Yield (borsm)
1	0.44/3.49	4.4/6	---	3 hrs	0.3157	0.2	40.6	84.5%
	0.44/3.49	4.4/6	A	3 hrs	0.508	**	65.4	?
2	0.864/6.85	7.53/6	A	4 hrs	1.0413	0.1528	78	95%
3	0.5/4.025	4.43/6	A	2.5hrs	0.4725	**	60.4	?
	0.5/4.025	4.43/6	---	2.5hrs	0.0727	**	9.4	?
	0.5/4.025	4.43/6	B	4.5hrs	0.4016	**	51.4	?
4	0.5/3.9	5/7	A	7 hrs	0.1594	**	23	?
5	0.5/4.46	4.9/6	B	4 hrs	0.2075	0.218	25.5	45.3%
	0.25/2.23	2.45/6	A	7 hrs	0.0655	0.1185	16	30.6%
	0.5/3	3.3/6	B	4 hrs	0.0215	0.2574	2.3	4.8%
	0.5/3	6.6/12	A	31 hrs	0.1037	0.1374	11	15.5%
6	0.5/3	3.3/6	B	4 hrs	0.12	0.2574	17	35%
	0.5/3	6.6/12	A	31 hrs	0.2	0.1374	28	39%
7	0.861/10.24	9.4/5	B	4.5hrs	0.5216	**	33	?
	0.861/10.24	9.4/5	A	3 hrs	0.4276	**	27	?
	0.861/10.24	9.4/5	---	4.5hrs	0.1587	**	10	?
8	0.5/3.6	3.84/6	B	28 hrs	0.1034	0.3031	14	35%
	0.7/7.96	8.75/6	A	12 hrs	0.0987	0.3	6	19%
9	0.49/2.33	3/7	A	5 hrs	0.2838	0.2334	43	83%

* A: propionic acid, B: montmorillonite KSF
** An undetermined amount of starting material was recovered
borsm: based on recovered starting material

10

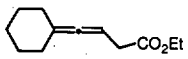


Colorless oil
R_f = 0.21 (15:1 petroleum ether/ether), IR (neat): 2958, 2931, 2860, 1962, 1740, 1466, 1446, 1368, 1329, 1301, 1250, 1157, 1033, 849 cm^{-1}, ^{1}H-NMR (300 MHz, $CDCl_3$): 4.71 (m, 2H), 4.13 (q, J=6.9, 2H), 2.96 (s, 2H), 1.99-1.96 (m, 2H), 1.42-1.22 (m, 9H), 0.87 (t, J=6.9, 3H), 13C-NMR (75 MHz, $CDCl_3$): 206.9, 171.3, 97.4, 76.0, 60.6, 38.7, 31.5, 31.4, 26.9, 22.4, 14.2, 14.0, MS (EI), m/z 196 (M^+), 167 (M^+ - C_2H_5). HRMS calcd for $C_{12}H_{20}O_2$ (M^+) 196.1464. Found: 196.1467.

11

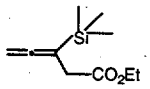
Colorless oil
R_f = 0.39 (petroleum ether/ether : 12/1), IR (neat): 2958, 2929, 2858, 1967, 1740, 1466, 1409, 1368, 1326, 1301, 1245, 1160, 1114, 1097, 1036, 870 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 5.20 (m, 2H), 4.15 (q, J=6.9, 2H), 3.01 (dd, J=3/7.2, 2H), 2.05-1.95 (m, 2H), 1.42-1.15 (m, 9H), 0.89 (t, J=6.9, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 204.9, 171.7, 92.2, 84.0, 60.7, 35.1, 31.3, 28.6, 28.5, 22.5, 14.2, 14.0. Anal. Calc. for $C_{12}H_{20}O_2$: C 72.49 H 9.95 Found C 72.55 H 10.12.

12



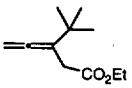
Colorless oil
R_f = 0.34 (petroleum ether/ether : 12/1), IR (neat): 2980, 2930, 2855, 1968, 1739, 1632, 1446, 1367, 1314, 1260, 1235, 1202, 1162, 1096, 1040 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$ = 5.08 (m, 1H), 4.14 (q, J=7.5, 2H), 2.98 (d, J=6.9, 2H), 2.11-2.04 (m, 4H), 1.59-1.49 (m, 6H), 1.26 (t, J=7.5, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 199.6, 172.0, 103.6, 81.7, 60.6, 35.6, 31.3, 28.5, 27.3, 26.0, 14.2. MS (EI), m/z 388 (M^+), 388 (2*M^+), 342, 315 (2*M^+ - $CO_2C_2H_5$). HRMS calcd for $C_{12}H_{18}O_2$ (M^+) 194.1307. Found: 388.2619 (2*M^+)..

13



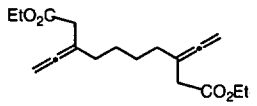
Light yellow oil
R_f = 0.46 (petroleum ether/ether : 10/1), IR (neat): 2959, 2901, 1934, 1739, 1368, 1303, 1250, 1159, 1040, 844 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 4.43 (m, 2H), 4.14 (q, J=7.2, 2H), 2.98 (m, 2H), 1.26 (t, J=7.2, 3H), 0.12 (s, 9H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 210.0, 171.7, 88.7, 69.5, 60.6, 35.6, 14.3, -1.45. Anal. Calc. for $C_{10}H_{18}O_2Si$: C 60.56 H 9.15. Found: C 60.38 H 8.99.

14



Light yellow oil
R_f = 0.29 (petroleum ether/ether : 1/1), IR (neat): 2969, 2907, 2871, 1957, 1744, 1478, 1464, 1393, 1366, 1324, 1257, 1225, 1157, 1034, 847 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 4.75 (t, J=2.7, 2H), 4.13 (q, J=7.2, 2H), 2.98 (t, J=2.7, 2H), 1.25 (t, J=7.2, 3H), 1.05 (s, 9H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 205.5, 171.9, 106.2, 60.6, 52.8, 34.8, 30.7, 28.9, 14.2
EA: Anal. Calc. for $C_{11}H_{18}O_2$: C 72.15 H 9.91. Found: C 72.31 H 9.73.

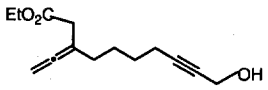
15



Light yellow oil

R_f = 0.28 (petroleum ether/ether : 4/1), IR (neat): 3053, 2982, 2935, 2862, 1961, 1738, 1622, 1446, 1411, 1391, 1368, 1329, 1301, 1246, 1178, 1097, 1032, 852 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 4.73 (m, 4H), 4.14 (q, J=6.9, 4H), 2.97 (s, 4H), 2.02 (m, 4H), 1.54-1.43 (m, 4H), 1.26 (t, J=6.9, 6H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 206.9, 171.2, 97.2, 76.1, 60.7, 38.7, 31.4, 26.8, 14.2. Anal. Calc. for $C_{18}H_{26}O_4$: C 70.56 H 8.55. Found: C 70.65 H 8.65.

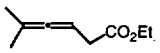
16



Light yellow oil

R_f = 0.45 (petroleum ether/ether : 1/2), IR (neat): 3446, 2982,2937, 2863, 2224, 2285, 1961, 1733, 1436, 1369, 1330, 1259, 1178, 1027, 854 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 4.73 (t, J=3, 2H), 4.21 (bs, 2H), 4.12 (q, J=7.2, 2H), 2.96 (s, 2H), 2.20 (bs, 2H), 2.05-2.01 (m, 3H), 1.54-1.49 (m, 4H), 1.24 (t, J=7.2, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 208.8, 171.3, 96.9, 86.0, 78.5, 76.2, 60.7, 51.2, 38.6, 30.9, 27.8, 26.3, 18.4, 14.2. Anal. Calc. for $C_{14}H_{20}O_3$: C 70.56 H8.55. Found: C 70.68 H 8.56.

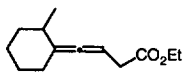
17



Colorless oil

R_f = 0.45 (petroleum ether/ether : 12/1), IR (neat): 2983, 2938, 2910, 1972, 1740, 1447, 1409, 1366, 1320, 1258, 1223, 1169, 1030 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 5.05 (m, 1H), 4.11 (q, J=7.2, 2H), 2.93 (d, J=7.2, 2H), 1.64 (s, 6H), 1.23 (t, J=7.5, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 202.8, 171.9, 96.2, 81.9, 60.5, 35.2, 20.3, 14.1. Anal. Calc. for $C_9H_{14}O_2$: C 70.10 H 9.15. Found: C 69.85 H 9.30.

18

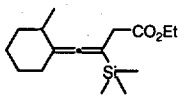


Colorless oil

R_f = 0.41 (petroleum ether/ether : 12/1), IR (neat): 2926, 2852, 1966, 1740, 1446, 1408, 1367, 1319, 1252, 1228, 1157, 1040 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 5.19 (sept, J=3.6, 1H), 4.13 (q, J=7.2, 2H), 2.96 (d, J=7.2, 2H), 2.32-2.28 (m, 1H), 1.99-1.91 (m, 2H), 1.79-1.75 (m, 3H), 1.39-1.17 (m, 5H), 1.11-0.99 (m, 1H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 199.3,

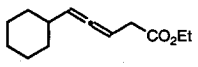
172.0, 109.4, 84.1, 60.5, 35.9, 35.7, 34.4, 31.7, 27.2, 26.0, 19.5, 14.2. MS (EI), m/z 208 (M^+), 179 ($M^+ - C_2H_5$). HRMS calcd for $C_{12}H_{20}O_2$ (M^+) 208.1464. Found: 208.1462.

19

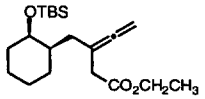


Light yellow oil
R_f = 0.56 (petroleum ether/ether : 10/1), IR (neat): 2957, 2927, 2852, 1944, 1739, 1447, 1367, 1317, 1248, 1156, 1042, 840 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 4.10 (q, J=7.2, 2H), 2.94 (s, 2H), 2.25 (d, J=11.7, 1H), 1.97-1.89 (m, 2H), 1.75-1.73 (m, 3H), 1.34-1.23 (m, 2H), 1.25 (t, J=7.2, 3H), 1.06-1.01 (m, 1H), 0.92 (d, J=6.6, 3H), 0.06 (s, 9H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 202.5, 172.2, 104.4, 90.8, 60.3, 36.9, 36.4, 34.1, 31.0, 27.7, 26.2, 19.5, 14.2, -1.4. Anal. Calc. for $C_{16}H_{28}O_2Si$: C 68.52 H 10.06. Found: C 68.70 H 9.96.

Preparation of the allene **20**:
A solution of 1-Cyclohexyl-prop-2-yn-1-ol (1.0 g, 7.2 mmol) and propionic acid (0.01 mL) in triethylorthoacetate (7.04 g, 8 mL, 43 mmol) was heated to 150 °C for 2.5 hours, with removal of the ethanol that was generated by distillation. It was then cooled to room temperature and chromatographed directly on silica gel (20/1 petroleum ether/ether) to give 946 mg (63%) product.

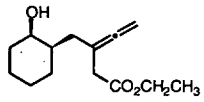


5-Cyclohexyl-penta-3,4-dienoic acid ethyl ester (**20**)
Light yellow oil
R_f = 0.37 (20:1 petroleum ether/ether), IR (neat) : 2981, 2926, 2853, 1966, 1741, 1448, 1368, 1324, 1298, 1246, 1160, 1037cm^{-1}, ^{1}H NMR (300MHz, $CDCl_3$): δ 5.25 (qd, J=7.1, 2.7, 1H), 5.19-5.14 (m, 1H), 4.15 (q, J=7.1, 2H), 3.00 (dd, J=7.1, 2.7, 2H), 2.03-1.93 (m, 1H), 1.76-1.60 (m, 5H), 1.27 (t, J=7.2, 3H), 1.21-1.03 (m, 5H). ^{13}C NMR (75MHz, $CDCl_3$): δ 203.9, 171.7, 98.2, 84.9, 60.6, 37.0, 35.2, 32.9, 26.2, 25.9, 14.2. Anal. Calc'd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.05; H, 9.49.



cis-3-[2-(*tert*-Butyl-dimethyl-silanyloxy)-cyclohexylmethyl]-penta-3,4-dienoic acid ethyl ester (**A**)
A solution of the propargyl alcohol (0.92 g, 3.24 mmol) and propionic acid (0.001 mL) in triethylorthoacetate (3.2 g, 3.6 mL, 19.4 mmol) was heated to 145 °C for 3 h, with removal of the ethanol that was generated by distillation. It was then cooled to room temperature and columned directly on silica gel (6:1 petroleum ether/ethyl ether) to give 551 mg (63%) **A** plus 171 mg (19%) starting material.

Colorless oil. R_f = 0.59 (6:1 petroleum ether/ethyl ether), IR (neat) : 2931, 2857, 1962, 1741, 1464, 1369, 1332, 1253, 1155, 1100, 1064 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 4.76-4.73 (m, 2H), 4.16 (q, J=7.1, 2H), 3.87-3.86 (m, 1H), 2.98-2.93 (m, 2H), 2.11-2.06 (m, 1H), 1.92-1.87 (m, 1H), 1.71-1.60 (m, 4H), 1.57-1.48 (m, 1H), 1.45-1.35 (m, 2H), 1.28 (t, J=7.1, 3H), 1.25-1.22 (m, 2H), 0.92 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$): δ 207.1, 171.2, 96.0, 75.9, 70.0, 60.6, 40.3, 39.1, 34.6, 33.6, 26.4, 25.9, 25.3, 20.5, 18.2, 14.3, -4.3, -5.0. Anal. Calc'd for $C_{20}H_{36}O_3Si$: C, 68.13; H, 10.29. Found: C, 68.20; H, 10.07.



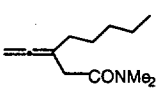
cis-3-(2-Hydroxy-cyclohexylmethyl)-penta-3,4-dienoic acid ethyl ester (**21**)
HF•pyridine (0.0992 g, 4.96 mmol) was added to a solution of allene **A** (500 mg, 1.42 mmol) in THF (3 mL) at rt. The reaction was stirred for 16 h, then worked up by adding TMS-OMe (777 mg, 7.46 mmol) and evaporating all the volatile material by rotary evaporation then on a vacuum pump. The residue was subjected to silica gel chromatography to yield 203 mg **21** (60%) as well as 150 mg (30%) starting material.
Colorless oil. R_f = 0.33 (1:1 petroleum ether/ethyl ether), IR (neat): 3456, 2982, 2931, 2856, 2361, 2342, 1961, 1736, 1250, 1189, 1157, 1031 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 4.77-4.75 (m, 2H), 4.17 (q, J=7.1, 2H), 3.99 (m, 1H), 3.06-2.96 (m, 2H), 2.11-1.97 (m, 3H), 1.85-1.82 (m, 1H), 1.70-1.56 (m, 4H), 1.46-.40 (m, 4H), 1.28 (t, J=7.1, 3H). ^{13}C NMR (125MHz, $CDCl_3$): δ 207.3, 171.7, 95.1, 76.1, 67.8, 60.9, 39.1, 38.8, 34.0, 32.8, 26.9, 25.3, 20.4, 14.2. HRMS: Calc'd for $C_{14}H_{22}O_3$: 238.1569. Found: 238.1568.

Synthesis of β-allenic amides by a Claisen-rearrangement:

A mixture of the propargyl alcohol and 1.5 equivalents of dimethylacetamide dimethyl acetal in toluene (0.25M) was refluxed overnight and then cooled to room temperature and directly chromatographed on silica gel.

Entry	Propargylic alc.	DMA-DMA (mL/eq.)	Toluene (mL)	Rxn time	Product (g)	Yield (%)	Yield (borsm)
1	0.88/6.97	1.53/1.5	30	17 hrs	1.2938	95	95%
2	0.866/6.86	1.505/1.5	30	5 hrs	1.2169	90	90%
3	0.33/2.94	0.65/1.5	12	7.25 hrs	0.3765	70.5	70.5
4	0.5/3.78	0.83/1.5	15	22 hrs	0.215	42.5	42.5

22



Orange-red oil

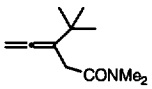
R_f = 0.35 (ether), IR (neat): 3047, 2929, 2859, 1959, 1652, 1497, 1458, 1394, 1265, 1133, 1101, 1060, 847 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 4.69 (m, 2H), 3.01 (m, 2H), 2.98 (s, 3H), 2.91 (s, 3H), 1.97 (q, J=3.9, 2H), 1.42 (m, 2H), 1.28 (m, 4H), 0.85 (t, J=6.6, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 206.1, 170.4, 98.3, 76.0, 38.8, 37.7, 35.3, 31.5, 26.9, 22.4, 14.0. Anal. Calc. for $C_{12}H_{21}ON$: C 73.80 H 10.84 N 7.17. Found: C 73.65 H 10.71 N 7.30

23

Yellow-orange oil

R_f = 0.39 (ether), IR (neat): 2929, 2857, 1964, 1650, 1496, 1466, 1394, 1264, 1133, 1060, 871 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 5.26 (m, 1H), 5.15 (m, 1H), 3.06 (m, 2H), 3.00 (s, 3H), 2.93 (s, 3H), 1.97 (m, 2H), 1.42-1.25 (m, 6H), 0.86 (t, J=6.6, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 204.5, 170.9, 92.0, 84.9, 37.4, 35.4, 34.8, 31.2, 28.8, 28.6, 22.4, 14.0. Anal. Calc. for $C_{12}H_{21}ON$: C 73.80 H 10.84 N 7.17. Found: C 73.66 H 10.61 N 6.97.

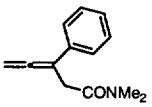
24



Yellow oil

R_f = 0.21 (ether), IR (neat): 3484, 2965, 2870, 1954, 1651, 1499, 1479, 1464, 1395, 1364, 1266, 1134, 844 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 4.68 (t, J=3.6, 2H), 3.01 (t, J=3.6, 2H), 2.91 (s, 3H), 2.86 (s, 3H), 1.03 (s, 9H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 203.9, 171.1, 106.9, 77.4, 37.7, 35.1, 34.7, 32.8, 28.9. Anal. Calc. for $C_{11}H_{19}ON$: C 72.88 H 10.56 N 7.26. Found: C 72.74 H 10.36 N 7.51.

25



Yellow oil

R_f = 0.17 (ether), IR (neat): 3035, 2932, 1943, 1652, 1495, 1453, 1395, 1265, 1135, 857, 766, 696 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 7.40 (d, J=7.5, 2H), 7.32 (t, J=7.5, 2H), 7.21 (t, J=7.5, 1H), 5.15 (t, J=3, 2H), 3.51 (t, J=3, 2H), 3.04 (s, 3H), 2.95 (s, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 208.5, 170.1, 135.8, 128.4, 126.9, 125.7, 100.0, 78.9, 37.7, 36.5, 35.4. MS (EI), m/z 202 (M^++H), 171 (M^+ - 2 CH_3), 129 (M^+ - $CON(CH_3)_2$). HRMS calcd for $C_{13}H_{15}ON$ (M^+) 201.1155. Found: 202.0860.

e) Reduction of β-allenic esters with hydride reagents

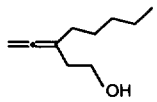
Procedure for the $LiAlH_4$ reduction of β-allenic esters:

To a suspension of LAH in diethyl ether the was added a solution of the β-allenic ester in ether at -78°C under nitrogen. The mixture was let warm up to room temperature in 6 hrs and the 3 mL of water were added at 0°C. The white slurry was filtered and after addition of ether the solution was washed with brine, dried over MgSO4 and the solvent

was removed in vacuo. Purification of the crude oils on silica gel yielded colorless allenic alcohols.

Entry	Ester (mg/mmol)	$LiAlH_4$ (mg/eq.)	solvent Et_2O	Allenic alc. (mg)	Yield (%)
1	200/1.02	42/1.1	10 mL	152.6	97
2	500/2.55	193.3/2	15 ml	360.6	92
3	593/3	227.7/2	15 mL	390	85.4
4	90/0.432	33/2	2 ml	63.7	89

26



Slightly yellow oil

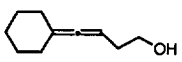
R_f = 0.54 (petroleum ether/ether : 1/1), IR (neat): 3336, 2959, 2928, 2859, 1957, 1700, 1458, 1047, 845 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 4.73 (m, 2H), 3.74 (m, 2H), 2.23-2.17 (m, 2H), 1.98-1.90 (m, 2H), 1.66 (s, 1H), 1.48-1.27 (m, 6H), 0.88 (t, J=6.9Hz, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 205.4, 100.3, 76.3, 60.7, 35.2, 32.2, 31.4, 27.0, 22.5, 14.0, MS (EI), m/z 154 (M^+), 137 (M^+ - OH). HRMS calcd for $C_{12}H_{20}O_2$ (M^+) 154.1358. Found: 154.1352.

27

Colorless oil

R_f = 0.56 (petroleum ether/ether : 1/1), IR (neat): 3336, 2957, 2928, 2858, 1963, 1466, 1378, 1340, 1283, 1179, 1050, 874 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 5.17-5.06 (m, 2H), 3.70 (t, J=6, 2H), 2.28-2.21 (m, 2H), 2.00-1.95 (m, 2H), 1.58 (bs, 1H), 1.45-1.29 (m, 6H), 0.88 (t, J=6.6, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 204.5, 91.7, 87.1, 62.0, 32.3, 31.3, 28.8, 22.5, 17.4, 14.0, MS (EI), m/z 154 (M^+), 137 (M^+ - OH). HRMS calcd for $C_{12}H_{20}O_2$ (M^+) 154.1358. Found: 154.1347.

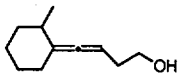
28



Slightly yellow oil

R_f = 0.28 (petroleum ether/ether : 1/1), IR (neat): 3346, 2925, 2854, 1965, 1446, 1345, 1265, 1239, 1174, 1130, 1049 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 4.96 (m, 1H), 3.69 (t, J=6, 2H), 2.22 (q, J=6, 2H), 2.11-2.09 (m, 4H), 1.61-1.51 (m, 7H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 199.0, 103.2, 84.8, 62.0, 32.6, 31.7, 27.4, 26.0. MS (EI), m/z 152 (M^+), 135 (M^+ - OH). HRMS calcd for $C_{10}H_{16}O$ (M^+) 152.1202. Found: 152.1203.

29



Yellow oil

R_f = 0.55 (petroleum ether/ether : 3/2), IR (neat): 3333, 2924, 2851, 1964, 1446, 1375, 1349, 1322, 1243, 1049, cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): 5.08 (sept, J=3, 1H), 3.67 (m, 2H), 2.31-2.20 (3H), 2.03-1.95 (m, 2H), 1.78-1.74 (m, 3H), 1.60-1.57 (m, 1H), 1.43-1.31 (m, 2H), 1.18-1.05 (1H), 0.96 (d, J=6.6, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): 198.8, 108.9, 87.3, 62.2, 36.0, 34.3, 32.8, 32.2, 27.3, 26.1, 19.7. MS (EI), m/z 166 (M^+), 151 (M^+ - CH_3), 135 (M^+ - CH_3O). HRMS calcd for $C_{11}H_{18}O$ (M^+) 166.1358. Found: 166.1355.

General procedure for Optimization Studies

Solvent (1 mL) was added to CpRu(COD)Cl (7.7 mg, 0.025 mmol) and cocatalyst/additive in a pressure tube, followed by the allene (35.0 mg, 0.25 mmol), and methyl vinyl ketone (35.3 mg, 0.5 mmol). The tube was capped, then heated with stirring for 4 h. The reaction was then cooled to room temperature and chromatographed (1/1 petroleum ether/ether) directly.

Optimization Experiments for Eq 5[a]

Entry	Co-catalyst	Additive	Solvent	Temp (°C)	32 (%)
1	15% $SnCl_4 5H_2O$	3.3 eq NH_4Cl	DMF/H_2O 20:1	100	14
2	15% $SnCl_4 5H_2O$	--	DMF/H_2O 20:1	100	35
3	15% $SnCl_4 5H_2O$	--	Acetone	60	21
4	15% $SnCl_4 5H_2O$	--	MeOH	60	--
5	15% $SnCl_4 5H_2O$	--	DMF	100	45
6	15% $SnCl_4 5H_2O$	--	DMF/H_2O 3:1	100	28
7	15% $AlCl_3 6H_2O$	--	DMF	100	28
8	15% $In(OTf)_3$	--	DMF	100	--
9	40% CSA	--	DMF	100	31
10	15% $SnCl_2 2H_2O$	--	DMF	100	34
11	15% $CeCl_3 7H_2O$	--	DMF	100	48
12	--	--	DMF	100	41
13	--	10% PPh_3	DMF	100	26
14	15% $CeCl_3 7H_2O$	--	DMSO	100	25
15	15% $CeCl_3 7H_2O$	--	DMA	100	38
16	15% $CeCl_3 7H_2O$	--	Acetone	100	38
17	--	10% NH_4PF_6	DMF	100	20
18	15% $CeCl_3$	--	DMF	100	44
19	15% $InCl_3$	--	DMF	100	21
20	15% $CeCl_3 7H_2O$	--	NMP	100	38
21[b]	--	10% CSA	DMF	100	10
22	10% AgOTf	--	DMF	100	26

(a) Run as in eq 5 with 10% catalyst **31** (b) 10% $CpRu(C_4H_7)PPh_3$ as catalyst

Effect of Concentration and Amounts of MVK[a]

Entry	Eq. MVK	Allene [M]	32 (%)
1	2.0	0.25	48
2	1.5	0.25	53
3	1.0	0.25	35
4	1.5	0.125	46
5	1.5	0.5	37

(a)Run as in eq 5 with 10% **31** and 15% $CeCl_3 \cdot 7H_20$ in DMF at 100° C

Effect of Amounts of Catalyst, Cocatalyst and Temperature[a]

Entry	Catalyst (mol %)	Cocatalyst (mol %)	Temperature (°C)	32 (%)
1	10	15	100	53
2	5	15	100	36
3	15	15	100	48
4	10	5	100	43
5	10	30	100	50
6	10	15	60	66
7	10	15	40	27 + sm
8	10	15	rt	7 + sm
9[b]	10	15	60	53 + sm
10[c]	10	15	60	70

(a)Run as in eq 5 with **31** and$CeCl_3 \cdot 7H_20$ with 1.5 eq. MVK and 0.25 M allene in DMF (b) reaction time of 2 hours (c) reaction time of 6 hours

Optimization Table

Entry	Co-catalyst (mg, mmol)	Additive (mg, mmol)	Solvent	Temp (°C)	32 (mg, %yield)
1[a]	$SnCl_4 \cdot 5H_20$ 6.3, 0.018	NH_4Cl 21.4, 0.40	DMF/H_20 20:1	100	3.7, 14%
2[b]	$SnCl_4 \cdot 5H_20$ 26.3, 0.075	--	DMF/H_20 20:1	100	36.9, 35%
3	$SnCl_4 \cdot 5H_20$ 13.2, 0.0375	--	Acetone	60	18.9, 21%
4	$SnCl_4 \cdot 5H_20$ 13.2, 0.0375	--	MeOH	60	--
5	$SnCl_4 \cdot 5H_20$ 13.2, 0.0375	--	DMF	100	23.9, 45%
6	$SnCl_4 \cdot 5H_20$ 13.2, 0.0375	--	DMF/H_20 3:1	100	14.7, 28%
7	$AlCl_3 \cdot 6H_20$ 9.1, 0.0375	--	DMF	100	14.8, 28%
8	$In(OTf)_3$ 21.1, 0.0375	--	DMF	100	--
9	CSA 23.2, 0.1	--	DMF	100	16.4, 31%
10	$SnCl_2 \cdot 2H_20$ 8.5, 0.0375	--	DMF	100	18.0, 34%
11	$CeCl_3 \cdot 7H_20$ 14.0, 0.0375	--	DMF	100	25.5, 48%

12	--	--	DMF	100	21.8, 41%
13	--	10% PPh_3 6.6, 0.025	DMF	100	13.6, 26%
14	$CeCl_3 7H_20$ 14.0, 0.0375	--	DMSO	100	13.4, 25%
15	$CeCl_3 7H_20$ 14.0, 0.0375	--	DMA	100	20.1, 38%
16	$CeCl_3 7H_20$ 14.0, 0.0375	--	Acetone	100	20.3, 38%
17	--	10% NH_4PF_6 4.1, 0.025	DMF	100	10.3, 20%
18	$CeCl_3$ 9.2, 0.0375	--	DMF	100	23.3, 44%
19	15% $InCl_3$ 8.3, 0.0375	--	DMF	100	11.0, 21%
20	15% $CeCl_3 7H_20$ 14.0, 0.0375	--	NMP	100	20.2, 38%
21[c]	--	10% CSA 5.8, 0.025	DMF	100	5.5, 10%
22	10% AgOTf 6.4, 0.025	--	DMF	100	13.7, 26%

(a)Run with 18.8 mg(0.12 mmol) allene, 16.9 mg(0.24 mmol) MVK and 3.7 mg(0.012 mmol) CpRu(COD)Cl (b) Run with 18.8 mg(0.12 mmol) allene,16.9 mg(0.24 mmol) MVK and 15.4 mg(0.05 mmol) CpRu(COD)Cl (c) 12.0 mg(0.025 mmol) $CpRu(C_4H_7)PPh_3$ as catalyst

Experimental Details for Concentration and Amounts of MVK Table

Entry	Eq. MVK (mg, mmol)	DMF (mL), Allene [M]	32 (mg, %yield)
1	2.0 (35.3, 0.5)	1.0, 0.25	25.5, 48%
2	1.5 (26.5, 0.375)	1.0, 0.25	28.1, 53%
3	1.0 (17.7, 0.25)	1.0, 0.25	18.7, 35%
4	1.5 (26.5, 0.375)	2.0, 0.125	24.9, 46%
5	1.5 (26.5, 0.375)	0.5, 0.5	19.6, 37%

(a)Run with 7.7 mg (0.025 mmol) CpRu(COD)Cl and 14.0 mg (0.0375 mmol) $CeCl_3 7H_20$ in DMF at 100° C

Experimental Details for Amount of Catalyst, Cocatalyst and Temperature Table

Entry	Catalyst mol% (mg, mmol)	Cocatalyst (mg, mmol)	Temperature (°C)	32 (mg, %yield)
1	10 (7.7, 0.025)	15 (14.0, 0.0375)	100	28.1, 53%
2	5 (3.9, 0.0125)	15 (14.0, 0.0375)	100	19.0, 36%
3	15 (11.6, 0.0375)	15 (14.0, 0.0375)	100	25.5, 48%
4	10 (7.7, 0.025)	5 (4.7, 0.0125)	100	21.7, 43%

5	10 (7.7, 0.025)	30 (28.0, 0.075)	100	26.5, 50%
6	10 (7.7, 0.025)	15 (14.0, 0.0375)	60	35.0, 66%
7	10 (7.7, 0.025)	15 (14.0, 0.0375)	40	14.3, 27% + sm
8	10 (7.7, 0.025)	15 (14.0, 0.0375)	rt	3.8, 7% + sm
9[a]	10 (7.7, 0.025)	15 (14.0, 0.0375)	60	28.1, 53% + sm
10[b]	10 (7.7, 0.025)	15 (14.0, 0.0375)	60	37.2, 70%

(a)Run with 26.5 mg (0.375 mmol) MVK and 0.25 M allene in DMF (1.0 mL) (b) reaction time of 2 hours (c) reaction time of 6 hours

Experimental Details for Table 5[a]

Entry	Additive (mg, mmol)	Catalyst (mg, mmol)	DMF (mL), Allene [M]	32 (mg, %yield)
1	none	7.7, 0.025	1.0, 0.25	37.2, 70%
2	**33** (5.6, 0.025)	7.7, 0.025	1.0, 0.25	42.4, 80%
3	**34** (3.5, 0.025)	7.7, 0.025	1.0, 0.25	36.1, 68%
4	**35** (2.5, 0.025)	7.7, 0.025	1.0, 0.25	42.9, 81%
5	**35** (1.3, 0.0125)	3.9, 0.0125	1.0, 0.25	26.6, 50%
6	**35** (1.3, 0.0125)	3.9, 0.0125	0.5, 0.5	24.3, 46%

(a)Run with 26.5 mg (0.375 mmol) MVK and 14.0 mg (0.0375 mmol) $CeCl_3 7H_20$ in DMF for 6 hours

Experimental Details for Table 6[a]

Entry	Catalyst (mg, mmol)	32 (mg, %yield)
1[b]	CpRu(COD)Cl (7.7, 0.025)	42.9, 81%
2	$CpRu(PPh_3)_2Cl$ (18.2, 0.025)	32.9, 62%
3	(Ind)Ru(COD)Cl (9.0, 0.025)	8.1, 15%
4[b]	$[CpRu(CH_3CN)_3]PF_6$ (10.9, 0.025)	39.4, 74%
5	$[CpRu(CH_3CN)_3]PF_6$ (10.9, 0.025)	40.4, 76%

(a)Run with 10% catalyst and 15% $CeCl_3 7H_20$ with 1.5 eq. MVK and 0.25 M allene in DMF at 60° C for 6 hours. (b)Run with 10% **35**

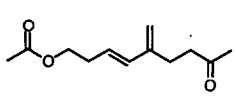
Monosubstituted Allenes

Dimethylformamide (1 mL) was added to CpRu(COD)Cl (7.7 mg, 0.025 mmol) and $CeCl_3 7H_20$ (14.0 mg, 0.0375 mmol) in a pressure tube, followed by the allene (0.25 mmol), the vinyl ketone (0.375 mmol) and hex-3-yn-1-ol (0.003 mL, 0.025 mmol). The tube was capped, then heated to 60° C with stirring for 6 h. The reaction was then cooled to room temperature and chromatographed directly.

A typical example is given below:
Dimethylformamide (1 mL) was added to CpRu(COD)Cl (7.7 mg, 0.025 mmol) and $CeCl_3 7H_20$ (14.0 mg, 0.0375 mmol) in a pressure tube, followed by the acetic acid hexa-4,5-dienyl ester (35 mg, 0.25 mmol), methyl vinyl ketone (26.5 mg, 0.375 mmol) and hex-3-yn-1-ol (0.003 mL, 0.025 mmol). The tube was capped, then heated to 60° C with stirring for 6 h. The reaction was then cooled to room temperature and chromatographed (1/1 petroleum ether/ether) directly to give 42.9 mg (81%) of 1,3-diene **32**.

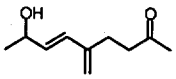
Experimental Details for Table 7

Entry	Allene (mg, mmol)	Enone (mg, mmol)	Product (mg, %yield)
1	(35.0, 0.25)	(26.5, 0.375)	**32** (42.9, 81%)
2	(24.5, 0.25)	(26.5, 0.375)	**39** (31.6, 75%)
3	(31.0, 0.25)	(26.5, 0.375)	**40** (26.4, 55%)
4	(21.0, 0.25)	(26.5, 0.375)	**41** (24.8, 65%)
5	(60.3, 0.25)	(26.5, 0.375)	**42** (52.4, 67%)
6	(26.8, 0.25)	(26.5, 0.375)	**43** (32.7, 74%)
7	(45.5, 0.25)	(26.5, 0.375)	**44** (42.2, 67%)
8	(31.0, 0.25)	(51.8, 0.375)	**45** (35.1, 53%)
9	(24.5, 0.25)	(51.8, 0.375)	**46** (46.7, 79%)
10	(26.8, 0.25)	(51.8, 0.375)	**47** (41.6, 68%)
11	(31.0, 0.25)	(49.5, 0.375)	**48** (27.8, 42%)
12	(38.5, 0.25)	(49.5, 0.375)	**49** (34.6, 48%)
13	(26.8, 0.25)	(49.5, 0.375)	**50** (37.4, 62%)

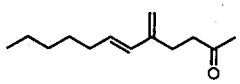


Acetic acid 5-(3-oxo-butyl)-hexa-3,5-dienyl ester (**32**)
Light yellow oil

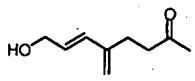
R_f = 0.39 (1:1 petroleum ether/ether), IR (neat) : 2958, 1739, 1716, 1650, 1609, 1434, 1386, 1365, 1240, 1162, 1038, 971 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 6.12 (d, J=15.9, 1H), 5.64 (dt, J_1=15.9, J_2=7.1, 1H), 4.93 (s, 1H), 4.87 (s, 1H), 4.10 (t, J=6.7, 2H), 2.62 (t, J=7.3, 2H), 2.48-2.38 (m, 4H), 2.15 (s, 3H), 2.04 (s, 3H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.2, 171.1, 144.4, 134.1, 125.1, 114.6, 63.6, 42.1, 32.1, 30.0, 25.7, 20.9. Anal. Calc'd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.56; H, 8.55.



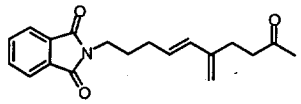
8-Hydroxy-5-methylene-non-6-en-2-one (**39**)
Light yellow oil
R_f = 0.14 (1:1 petroleum ether/ether), IR (neat) : 3407, 2971, 2925, 2361, 1713, 1608, 1415, 1362, 1163, 1145, 1059, 971 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 6.22 (d, J=15.9, 1H), 5.75 (dt, J_1=15.9, J_2=6.4, 1H), 5.02 (s, 1H), 4.94 (s, 1H), 4.41-4.35 (m, 1H), 2.64 (t, J=7.2, 2H), 2.47 (t, J=7.2, 2H), 2.16 (s, 3H), 1.42 (brs, 1H),1.30 (d, J=6.4, 3H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.2, 144.0, 133.1, 131.1, 115.9, 68.7, 42.1, 30.0, 25.7, 23.4. Anal. Calc'd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.18; H, 9.67.



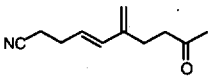
5-Methylene-dodec-6-en-2-one (**40**)
Light yellow oil
R_f = 0.55 (8:1 petroleum ether/ether), IR (neat) : 2957, 2927, 2857, 1718, 1648, 1607, 1457, 1359, 1258, 1160, 968, 890 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 6.04 (d, J=15.9, 1H), 5.70 (dt, J_1=15.9, J_2=6.8, 1H), 4.89 (s, 1H), 4.82 (s, 1H), 2.63 (t, J=7.4, 2H), 2.47 (t, J=7.5, 2H), 2.16 (s, 3H), 2.08 (q, J=7.1, 2H), 1.44-1.25 (m, 6H), 0.88 (t, J=6.7, 3H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.5, 144.9, 131.4, 130.8, 113.3, 42.4, 32.8, 31.4, 30.0, 29.0, 26.0, 22.5, 14.0. HRMS: Calc'd for $C_{13}H_{22}O$: 194.1671. Found: 194.1672.



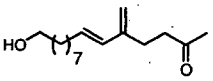
8-Hydroxy-5-methylene-oct-6-en-2-one (**41**)
Light yellow oil
R_f = 0.13 (1:1 petroleum ether/ether), IR (neat) : 3409, 2922, 2853, 1713, 1609, 1431, 1360, 1232, 1162, 1095, 1051, 1019 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 6.27 (d, J=15.9, 1H), 5.86 (dt, J_1=15.9, J_2=5.8, 1H), 5.03 (s, 1H), 4.96 (s, 1H), 4.24-4.20 (m, 2H), 2.65 (t, J=7.2, 2H), 2.49 (t, J=7.3, 2H), 2.16 (s, 3H), 1.61 (brs, 1H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.2, 144.0, 132.8, 128.1, 116.0, 63.5, 42.1, 30.3, 25.8. Anal. Calc'd for $C_9H_{14}O_2$: C, 70.15; H, 9.09. Found: C, 70.32; H, 9.01.



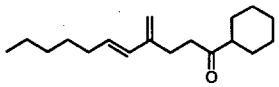
2-[6-(3-Oxo-butyl)-hepta-4,6-dienyl]-isoindole-1,3-dione (**42**)
Colorless oil
R_f = 0.50 (2:3 petroleum ether/ether), IR (neat) : 2938, 2863, 1771, 1714, 1467, 1438, 1397, 1369, 1336, 1157, 1040, 1022 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 7.84-7.81 (m, 2H), 7.71-7.66 (m, 2H), 6.06 (d, J=15.9, 1H), 5.66 (dt, J_1=15.9, J_2=6.8, 1H), 4.88 (s, 1H), 4.81 (s, 1H), 3.71-3.65 (m, 2H), 2.60 (t, J=7.6, 2H), 2.44-2.40 (m, 4H), 2.14 (s, 3H), 1.82-1.68 (m, 2H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.3, 168.4, 144.5, 133.8, 132.4, 129.5, 127.0, 123.1, 114.0, 42.2, 37.5, 30.0, 28.0, 25.9, 21.4 HRMS: Calc'd for $C_{19}H_{21}NO_3$: 311.1521. Found: 311.1521.



6-(3-Oxo-butyl)-hepta-4,6-dienenitrile (**43**)
Colorless oil
R_f = 0.32 (1:1 petroleum ether/ether), IR (neat) : 2922, 2852, 2360, 2341, 1714, 1682, 1651, 1608, 1427, 1360, 1161, 970 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 6.18 (d, J=15.9, 1H), 5.67 (dt, J_1=15.9, J_2=6.6, 1H), 5.00 (s, 1H), 4.94 (s, 1H), 2.64 (t, J=7.4, 2H), 2.49-2.41 (m, 6H), 2.16 (s, 3H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.1, 143.9, 134.8, 125.0, 119.1, 115.7, 42.0, 30.1, 28.5, 25.6, 17.5. HRMS: Calc'd for $C_{11}H_{15}NO$: 177.1154. Found: 177.1156.

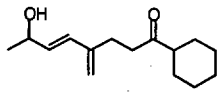


15-Hydroxy-5-methylene-pentadec-6-en-2-one (**44**)
Colorless oil. R_f = 0.10 (2:1 petroleum ether/ethyl ether), IR (neat) : 3410, 2927, 2855, 2361, 2339, 1716, 1458, 1435, 1360, 1162, 1056, 968 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 6.06 (d, J=15.9, 1H), 5.72 (dt, J_1=15.9, J_2=6.9, 1H), 4.92 (s, 1H), 4.84 (s, 1H), 3.66 (t, J=6.6, 2H), 2.65 (t, J=7.7, 2H), 2.49 (t, J=7.6, 2H), 2.18 (s, 3H), 2.10 (q, J=6.8, 2H), 1.61-1.55 (m, 2H), 1.45-1.11 (m, 11H). ^{13}C NMR (125MHz, $CDCl_3$): δ 208.6, 144.8, 131.5, 130.7, 113.3, 63.0, 42.3, 32.8, 32.7, 29.5, 29.4, 29.3, 29.2, 29.1, 25.9, 25.7. HRMS: Calc'd for $C_{16}H_{27}O^+$-H_2O: 235.2064. Found: 235.2062.

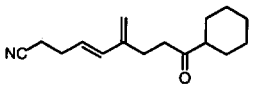


1-Cyclohexyl-4-methylene-undec-5-en-1-one (**45**)
Light yellow oil
R_f = 0.68 (8:1 petroleum ether), IR (neat) : 2929, 2855, 1710, 1607, 1450, 1411, 1377, 1328, 1144, 1086, 995. 968 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 6.03 (d, J=15.9, 1H), 5.70 (dt, J_1=15.8, J_2=7.1, 1H), 4.88 (s, 1H), 4.82 (s, 1H), 2.63 (t, J=7.3, 2H), 2.45 (t,

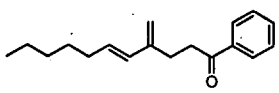
J=7.6, 2H), 2.36-2.29 (m, 1H), 2.08 (q, J=7.1, 2H), 1.85-1.77 (m, 4H), 1.68-1.65 (m, 2H), 1.41-1.25 (m, 10H), 0.89 (t, J=6.7, 3H), ^{13}C NMR (75MHz, $CDCl_3$): δ 213.6,145.3, 131.5, 130.8, 113.2, 50.9, 39.4, 32.8, 31.4, 29.0, 28.5, 25.9, 25.8, 25.7, 22.5, 14.1. Anal. Calc'd for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.50; H, 11.56.



1-Cyclohexyl-7-hydroxy-4-methylene-oct-5-en-1-one (**46**)
Light yellow oil
R_f = 0.30 (1:1 petroleum ether/ether), IR (neat) : 3418, 2932, 2855, 1705, 1451, 1410, 1372, 1312, 1201, 1143, 1058, 970 cm^{-1}, ^{1}H NMR (300MHz, $CDCl_3$): δ 6.22 (d, J=16.1, 1H), 5.75 (dt, J_1=15.9, J_2=6.4, 1H), 5.00 (s, 1H), 4.93 (s, 1H), 4.37 (quint., J=6.4, 1H), 2.63 (t, J=7.2, 2H), 2.45 (t, J=7.4, 2H), 2.36-2.28 (m, 1H), 1.95 (brs, 1H), 1.83-1.63 (m, 6H), 1.35-1.18 (m, 4H), 1.30 (d, J=6.4, 3H), ^{13}C NMR (75MHz, $CDCl_3$): δ 213.4, 144.4, 133.0, 131.2, 115.8, 68.8, 50.9, 42.8, 39.1, 28.9, 28.5, 25.8, 25.7, 25.3, 23.4. HRMS: Calc'd for $C_{15}H_{24}O_2$: 236.1776. Found: 236.1776.

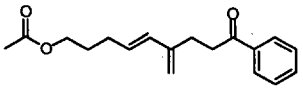


6-(3-Cyclohexyl-3-oxo-propyl)-hepta-4,6-dienenitrile (**47**)
Colorless oil
R_f = 0.26 (3:1 petroleum ether/ether), IR (neat) : 2930, 2854, 1706, 1608, 1450, 1373, 1331, 1292, 1144, 1088, 995, 969 cm^{-1}, ^{1}H NMR (300MHz, $CDCl_3$): δ 6.17 (d, J=15.9, 1H), 5.66 (dt, J_1=15.9, J_2=6.8, 1H), 4.98 (s, 1H), 4.93 (s, 1H), 2.63 (t, J=8.1, 2H), 2.48-2.41 (m, 6H), 2.38-2.33 (m, 1H), 1.85-1.68 (m, 4H), 1.35-1.22 (m, 6H), ^{13}C NMR (75MHz, $CDCl_3$): δ 213.3, 144.3, 134.8, 125.0, 119.1, 115.6, 50.9, 39.0, 28.6, 28.5, 25.8, 25.6, 25.5, 17.5. Anal. Calc'd for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71. Found: C, 78.49; H, 9.39; N, 5.59.

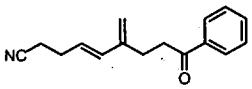


4-Methylene-1-phenyl-undec-5-en-1-one (**48**)
Colorless oil
R_f = 0.30 (30:1 petroleum ether/ether), IR (neat) : 2956, 2927, 2856, 1688, 1449, 1357, 1329, 1260, 1228, 1204, 1180, 1002 cm^{-1}, ^{1}H NMR (300MHz, $CDCl_3$): δ 7.97 (d, J=7.1, 2H), 7.56 (t, J=7.3, 1H), 7.46 (t, J=7.6, 2H), 6.09 (d, J=15.9, 1H), 5.76 (dt, J_1=15.9, J_2=6.8, 1H), 4.94 (s, 1H), 4.90 (s, 1H), 3.17 (t, J=7.8, 2H), 2.65 (t, J=8.1, 2H), 2.10 (q, J=7.1, 2H), 1.41-1.25 (m, 6H), 0.90-0.86 (m, 3H), ^{13}C NMR (75MHz, $CDCl_3$): δ 199.7,

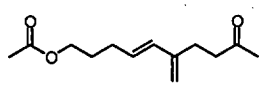
133.0, 131.5, 130.9, 128.6, 128.0, 113.5, 100.2, 37.5, 32.8, 31.4, 28.0, 26.5, 22.5, 14.1. HRMS: Calc'd for $C_{18}H_{24}O$: 256.1827. Found: 256.1834.



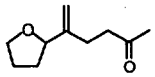
Acetic acid 6-(3-oxo-3-phenyl-propyl)-hepta-4,6-dienyl ester (**49**)
Colorless oil
R_f = 0.37 (3:1 petroleum ether/ether), IR (neat) : 2934, 2859, 1737, 1689, 1598, 1581, 1449, 1388, 1366, 1242, 1181, 1043 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 7.97 (d, J=7.3, 2H), 7.57 (t, J=7.3, 1H), 7.47 (t, J=7.6, 2H), 6.12 (d, J=15.9, 1H), 5.74 (dt, J_1=15.9, J_2=7.1, 1H), 4.95 (s, 1H), 4.93 (s, 1H), 4.08-4.03 (m, 2H), 3.17 (t, J=7.3, 2H), 2.63 (t, J=7.6, 2H), 2.27-2.10 (m, 2H), 2.05 (s, 3H), 1.69-1.59 (m, 2H), ^{13}C NMR (75MHz, $CDCl_3$): δ 199.0, 171.2, 136.8, 133.2, 133.1, 131.5, 128.9, 128.6, 128.0, 114.2, 64.2, 37.2, 29.8, 28.1, 27.4, 25.1. HRMS: Calc'd for $C_{18}H_{22}O_3$- CH_3CO_2H: 226.1349. Found: 226.1357.



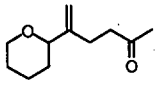
6-(3-Oxo-3-phenyl-propyl)-hepta-4,6-dienenitrile (**50**)
Colorless oil
R_f = 0.22 (2:1 petroleum ether/ether), IR (neat) : 3063, 3028, 2922, 2339, 2246, 1720, 1683, 1599, 1448, 1360, 1333, 1205 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 7.98 (d, J=7.1, 2H), 7.57 (t, J=7.3, 1H), 7.47 (t, J=7.6, 2H), 6.23 (d, J=15.9, 1H), 5.73 (dt, J_1=15.9, J_2=6.6, 1H), 5.04 (s, 1H), 5.02 (s, 1H), 3.18 (t, J=7.3, 2H), 2.66 (t, J=7.4, 2H), 2.51-2.41 (m, 4H), ^{13}C NMR (75MHz, $CDCl_3$): δ 199.5, 144.2, 136.8, 134.8, 133.1, 128.6, 128.0, 125.1, 119.1, 115.9, 37.1, 28.6, 26.1, 17.5. HRMS: Calc'd for $C_{16}H_{17}NO$: 239.1310. Found: 239.1309.



Acetic acid 6-(3-oxo-butyl)-hepta-4,6-dienyl ester (**52**)
Light yellow oil
R_f = 0.46 (1:1 petroleum ether/ether), IR (neat) : 2939, 2361, 1738, 1717, 1433, 1387, 1365, 1243, 1161, 1042, 970, 893 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 6.08 (d, J=16.4, 1H), 5.69 (dt, J_1=16.0, J_2=6.8, 1H), 4.93 (s, 1H), 4.83 (s, 1H), 4.07 (t, J=6.6, 2H), 2.64 (t, J=7.5, 2H), 2.47 (t, J=7.5, 2H), 2.17 (s, 3H), 2.06 (s, 3H), 1.77-1.70 (m, 2H), 1.25-1.22 (m, 2H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.3, 171.2, 144.5, 132.5, 128.8, 114.0, 63.9, 42.2, 30.0, 29.1, 28.2, 25.8, 21.0. HRMS: Calc'd for $C_{13}H_{20}O_3$-CH_3CO_2H= 164.1201. Found: 164.1200.



5-(Tetrahydro-furan-2-yl)-hex-5-en-2-one (**53**)
Colorless oil
R_f = 0.56 (2:3 petroleum ether/ether), IR (neat) : 3085, 2973, 2872, 1716, 1679, 1650, 1433, 1358, 1234, 1162, 1058, 901 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 5.04 (s, 1H), 4.74 (s, 1H), 4.27 (t, J=7.2, 1H), 3.90 (q, J=6.8, 1H), 3.79 (q, J=6.8, 1H), 2.67-2.61 (m, 2H), 2.32-2.23 (m, 2H), 2.15 (s, 3H), 2.07-2.01 (m, 1H), 1.94-1.86 (m, 2H), 1.72-1.62 (m, 1H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.4, 148.8, 108.9, 81.7, 68.3, 42.0, 31.1, 30.0, 25.8, 25.4. Anal. Calc'd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.50; H, 9.39.



5-(Tetrahydro-pyran-2-yl)-hex-5-en-2-one (**54**)
Colorless oil
R_f = 0.50 (1:1 petroleum ether/ether), IR (neat) : 2938, 2850, 1717, 1648, 1440, 1358, 1266, 1204, 1161, 1089, 1051, 1039 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 5.02 (s, 1H), 4.78 (s, 1H), 4.02 (d, J=11.2, 1H), 3.70 (d, J=10.2, 1H), 3.46 (t, J=11.2, 1H), 2.62 (t, J=7.2, 2H), 2.34 (t, J=7.1, 2H), 2.16 (s, 3H), 1.89-1.83 (m, 1H), 1.71-1.44 (m, 5H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.5, 149.2, 109.6, 80.6, 68.7, 42.2, 30.8, 29.9, 26.3, 25.9, 23.7. Anal. Calc'd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.69; H, 9.83.

1,1'-Disubstituted Allenes

General procedure

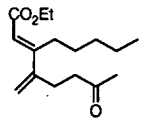
The allene (0.25 mmol) and methyl vinyl ketone (0.375 mmol, 0.032 ml, 1.5eq.) were dissolved in dimethylformamide (1ml) and added to $[CpRu(CH_3CN)_3]PF_6$ (10.9 mg, 0.025 mmol, 0.1eq.) and $CeCl_3 \cdot 7H_2O$ (14.0 mg, 0.0375 mmol, 0.15eq.) in a pressure tube. The tube is capped, then heated to 60°C for 4 h. It is then cooled to room temperature and after adding 50 ml ether the reaction mixture is washed three times with saturated sodium bicarbonate solution and dried over $MgSO_4$. Removal of the solvent by rotary evaporation gave a crude oil which was chromatographed on silica gel.

A typical example is given below:

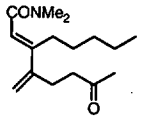
The allene **10** (49 mg, 0.25 mmol) and methyl vinyl ketone (26.5 mg, 0.375 mmol, 0.032 ml, 1.5eq.) were dissolved in dimethylformamide (1ml) and added to $[CpRu(CH_3CN)_3]PF_6$ (10.9 mg, 0.025 mmol, 0.1eq.) and $CeCl_3 \cdot 7H_2O$ (14.0 mg, 0.0375 mmol, 0.15eq.) in a pressure tube. The tube is capped, then heated to 60°C for 4 h. It is then cooled to room temperature and after adding 50 ml ether the reaction mixture is washed three times with saturated sodium bicarbonate solution and dried over $MgSO_4$. Removal of the solvent by rotary evaopration gave a crude oil which was chromatographed (ether) on silica gel to give 53.7 mg (81%) of 1,3-diene **55**.

Experimental Details for Table 8, Entries 1-4

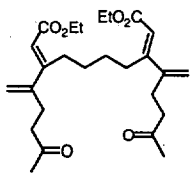
Entry	Allene (mg, mmol)	Product (mg, %yield)
1		**55**
	(49.1, 0.25)	(53.6, 81%)
2		**56**
	(49.0, 0.25)	(53.7, 81%)
3		**57**
	(76.6, 0.25)	(47.0, 42%)
4		**58**
	(59.0, 0.25)	(47.6, 62%)



4-(3-Oxo-butyl)-3-pentyl-penta-2,4-dienoic acid ethyl ester (**55**)
Yellow oil
R_f = 0.38 (petroleum ether/ether : 2/1), IR (neat): 3088, 2968, 2931, 2861, 1716, 1620, 1601, 1463, 1367, 1298, 1275, 1177, 1131, 1096, 1035, 908, 876, 729 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 5.80 (s, 1H), 5.28 (s, 1H), 5.11 (s, 1H), 4.16 (q, J=7.2Hz, 2H), 2.76 (t, J=6.6Hz, 2H), 2.58-2.49 (m, 4H), 2.14 (s, 3H), 1.42-1.28 (m, 9H), 0.87 (t, J=6.6Hz, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 207.7, 166.6, 159.5, 147.2, 116.2, 116.0, 59.8, 42.3, 32.0, 30.0, 29.0, 28.0, 27.8, 22.5, 14.2, 14.0, . Anal.Calc'd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 72.09; H, 9.61.

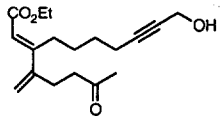


4-(3-Oxo-butyl)-3-pentyl-penta-2,4-dienoic acid dimethylamide (**56**)
Intense yellow oil
R_f = 0.32 (ether), IR (neat): 3090, 2930, 2860, 1717, 1640, 1494, 1461, 1394, 1361, 1265, 1160, 1128, 1059, 899 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 5.94 (s, 1H), 5.15 (s, 1H), 5.00 (s, 1H), 2.98 (s, 3H), 2.96 (s, 3H), 2.55 (t, J=6.9, 2H), 2.48 (t, J=6.9, 2H), 2.40 (t, j=7.2, 2H), 2.12 (s, 3H), 1.40-1.18 (m, 6H), 0.86 (t, J=6.6, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 207.9, 168.5, 149.1, 146.5, 119.4, 114.3, 42.3, 37.8, 34.6, 31.8, 30.0, 29.5, 28.5, 27.7, 22.4, 14.0. Anal. Calc'd for $C_{16}H_{27}O_2N$: C, 72.41; H, 10.25; N, 5.28. Found: C, 72.60; H, 10.37; N, 4.95.

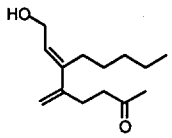


3,8-Bis-[1-(3-oxo-butyl)-vinyl]-deca-2,8-dienedioic acid diethyl ester (**57**)
Yellow oil

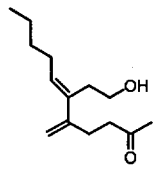
R_f = 0.56 (petroleum ether/ether : 5/1), IR (neat): 3092, 2981, 2865, 1714, 1601, 1446, 1367, 1272, 1160, 1120, 1096, 1035, 911, 877 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 5.78 (s, 2H), 5.26 (s, 2H), 5.09 (s, 2H), 4.13 (q, J=7.2, 4H), 2.78 (bs, 4H), 2.57-2.47 (m, 8H), 2.13 (s, 6H), 1.44 (m, 4H), 1.26 (t, J=7.2, 6H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 207.6, 166.5, 159.2, 147.1, 116.3, 116.1, 59.8, 42.2, 30.0, 29.3, 28.6, 27.8, 14.2. Anal. Calc'd for $C_{26}H_{38}O_6$: C, 69.93; H, 8.58. Found: C, 70.01; H, 8.62.



10-Hydroxy-3-[1-(3-oxo-butyl)-vinyl]-dec-2-en-8-ynoic acid ethyl ester (**58**)
Intense yellow oil
R_f = 0.46 (petroleum ether/ether : 5/1), IR (neat): 3440, 3093, 2936, 2865, 2284, 2223, 1715, 1602, 1434, 1368, 1308, 1160, 1097, 1024, 913, 877 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 5.80 (s, 1H), 5.27 (s, 1H), 5.09 (s, 1H), 4.21 (bs, 2H), 4.13 (q, J=7.5, 2H), 2.77 (t, J=7.5, 2H), 2.59-2.47 (m, 4H), 2.40 (bs, 1H), 2.22 (bs, 2H), 2.14 (s, 3H), 1.54-1.51 (m, 3H), 1.27 (t, J=7.2, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 207.9, 166.6, 159.3, 147.1, 116.3, 116.2, 85.8, 78.8, 59.9, 51.2, 42.1, 30.0, 28.3, 28.2, 27.9, 27.6, 18.2, 14.2. Anal. Calc'd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.41; H, 8.63.

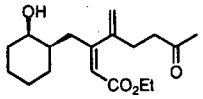


8-Hydroxy-5-methylene-6-pentyl-oct-6-en-2-one (**59a**)
Yellow-orange oil
R_f = 0.58 (petroleum ether/ether : 1/10), IR (neat): 3416, 3091, 2957, 2872, 1715, 1629, 1605, 1459, 1414, 1361, 1162, 1044, 892 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 5.66 (t, J=6.3, 1H), 5.05 (s, 1H), 4.92 (s, 1H), 4.27 (d, J=6.6, 2H), 2.53 (t, J=6, 4H), 2.26-2.14 (m, 2H), 2.14 (s, 3H), 1.53 (bs, 1H), 1.35-1.25 (m, 6H), 0.89 (t, J=6.6, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.4, 146.9, 142.0, 125.9, 112.4, 59.7, 42.7, 31.8, 30.3, 30.0, 28.9, 28.0, 22.5, 14.0.



6-(2-Hydroxy-ethyl)-5-methylene-undec-6-en-2-one (**59b**)
Yellow-orange oil
R_f = 0.48 (petroleum ether/ether : 1/10), IR (neat): 3416, 3091, 2957, 2872, 1715, 1629, 1605, 1459, 1414, 1361, 1162, 1044, 892 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 5.65 (t, J=7.5, 1H), 5.01 (s, 1H), 4.86 (s, 1H), 3.61 (d, J=6.9, 2H), 2.53 (m, 4H), 2.26-2.11 (q, J=6, 2H), 2.14 (s, 3H), 1.70 (bs, 1H), 1.36-1.20 (m, 6H), 0.90 (t, J=6.9, 3H), ^{13}C-NMR

(75 Mhz, $CDCl_3$): δ 208.6, 147.2, 134.4, 131.0, 111.1, 61.5, 42.8, 31.8, 31.2, 28.9, 28.2, 22.5, 14.



3-(2-Hydroxy-cyclohexylmethyl)-4-(3-oxo-butyl)-penta-2,4-dienoic acid ethyl ester (**60a**) Colorless oil. R_f = 0.23 (1:1 petroleum ether/ethyl ether), IR (neat) : 3487, 2981, 2931, 2855, 1716, 1695, 1601, 1446, 1370, 1283, 1193, 1031 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 5.94 (s, 1H), 5.26 (s, 1H), 5.13 (s, 1H), 4.23-4.16 (m, 2H), 3.87 (m, 1H), 3.66 (m, 1H), 3.31 (dd, J_1=13.6, J_2=10.8, 1H), 2.59-2.51 (m, 4H), 2.19-2.15 (m, 1H), 2.17 (s, 3H), 1.86-1.84 (m, 1H), 1.73-1.59 (m, 3H), 1.54-1.51 (m, 1H), 1.49-1.33 (m, 4H), 1.31-1.28 (m, 3H). ^{13}C NMR (125MHz, $CDCl_3$): δ 207.4, 168.2, 158.5, 147.2, 117.5, 116.7, 66.1, 60.6, 41.9, 41.3, 32.5, 31.4, 30.0, 27.7, 27.5, 26.1, 19.9, 14.1. Anal. Calc'd for $C_{18}H_{24}O_4$: C, 70.10; H, 9.15. Found: C, 70.26; H, 9.29.

1,3-Disubstituted Allenes

General procedure

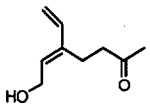
The allene (0.25 mmol) and methyl vinyl ketone (0.375 mmol, 0.032 ml, 1.5eq.) were dissolved in dimethylformamide (1ml) and added to $[CpRu(CH_3CN)_3]PF_6$ (10.9 mg, 0.025 mmol, 0.1eq.) and $CeCl_3 \cdot 7H_2O$ (14.0 mg, 0.0375 mmol, 0.15eq.) in a pressure tube. The tube is capped, then heated to 60°C for 4 h. It is then cooled to room temperature and, after adding 50 ml ether, the reaction mixture is washed three times with saturated sodium bicarbonate solution and dried over $MgSO_4$. Removal of the solvent by rotary evaporation gave a crude oil which was chromatographed on silica gel.

A typical example is given below:
The allene **20** (52.1 mg, 0.25 mmol) and methyl vinyl ketone (26.5 mg, 0.375 mmol, 0.032 ml, 1.5eq.) were dissolved in dimethylformamide (1ml) and added to $[CpRu(CH_3CN)_3]PF_6$ (10.9 mg, 0.025 mmol, 0.1eq.) and $CeCl_3 \cdot 7H_2O$ (14.0 mg, 0.0375 mmol, 0.15eq.) in a pressure tube. The tube is capped, then heated to 60°C for 4 h. It is then cooled to room temperature and, after adding 50 ml ether, the reaction mixture is washed three times with saturated sodium bicarbonate solution and dried over $MgSO_4$. Removal of the solvent by rotary evaporation gave a crude oil which was chromatographed (2/1 petroleum ether/ether) on silica gel to give 51 mg (73%) 1,3-diene **65**.

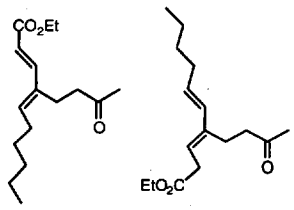
Experimental Details for Table 8, Entries 5-9

Entry	Allene (mg, mmol)	Product (mg, %yield)	Ratio
5		**69**	---
	(39.0, 0.25)	(10.0, 26%)	
6		**66a + 66b**	1.2/1
	(49.1, 0.25)	(49.2, 74%)	
7		**67a + 67b**	1/1

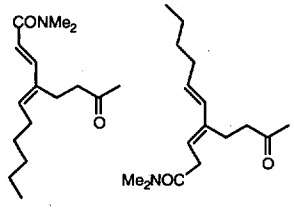
	(49.0, 0.25)	(49.8, 75%)	
8		**68a + 68b**	1/1
	(39.0, 0.25)	(32.5, 58%)	
9		**69**	---
	(52.1, 0.25)	(51.0, 73%)	



7-Hydroxy-5-vinyl-hept-5-en-2-one (**61**)
Yellow oil
R_f = 0.23 (petroleum ether/ether : 1/5), IR (neat): 3424, 3089, 2925, 1713, 1605, 1413, 1361, 1164, 996, 908 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 6.56 (dd, J=6.3/15, 1H), 6.25 (dd, J=6.9/18, 1H), 5.71 (t, J=7.2, 1H), 5.57 (t, J=6.6, 1H), 5.31-5.05 (m, 2H), 4.28 (t, J=6.6, 2H), 2.65-2.47 (m, 4H), 2.15 (s, 3H), 2.13 (s, 3H), 1.63 (bs, 1H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.8, 208.2, 139.3, 139.0, 138.1, 131.7, 131.4, 128.4, 115.7, 113.2, 58.9, 58.5, 42.5, 42.2, 30.2, 30.0, 29.7, 26.9, 19.8. MS (EI), m/z 153 (M^+), 153 (M^+ - H), 137 (M^+ - OH). HRMS: Calc'd for $C_9H_{14}O_2$ (M^+) 154.0994. Found: 153.0913.

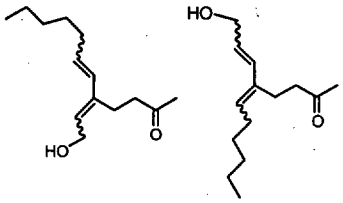


4-(3-Oxo-butyl)-deca-2,4-dienoic acid ethyl ester (**62a**)
4-(3-Oxo-butyl)-deca-3,5-dienoic acid ethyl ester (**62b**)
Yellow oil
R_f = 0.38 (petroleum ether/ether : 2/1) , IR (neat): 2958, 2929, 2859, 1715, 1626, 1465, 1412, 1366, 1305, 1276, 1177, 1039, 983 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 7.65 (d, J=15.9 Hz, 1H), 7.21 (d, J=16.2Hz, 1H), 5.89 (t, J=8.7Hz, 2H), 5.76 (t, J=8.0Hz, 2H), 4.18 (q, J=6.9Hz, 2H), 4.10 (q, J=6.9Hz, 2H), 3.15 (t, J=7.2Hz, 2H), 2.60-2.44 (m), 2.28-2.06 (m), 1.42-1.23 (m), 0.87 (t, J=6.9Hz, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 207.7, 171.8, 167.5, 148.1, 143.6, 140.2, 139.9, 135.7, 133.4, 132.6, 132.0, 129.4, 125.0, 121.3, 118.6, 117.6, 115.2, 60.7, 60.4, 60.2, 42.9, 42.6, 42.5, 42.2, 33.7, 33.0, 32.5, 31.6, 31.5, 31.3, 30.1, 29.2, 28.8, 28.6, 27.9, 27.3, 22.4, 22.2, 20.9, 20.3, 14.3, 14.0, Anal. Calc'd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.08. Found: C, 72.21; H, 9.23.

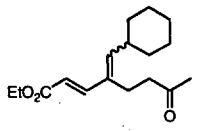


4-(3-Oxo-butyl)-deca-2,4-dienoic acid dimethylamide (**63a**)

4-(3-Oxo-butyl)-deca-3,5-dienoic acid dimethylamide (**63b**)
Yellow oil
R_f = 0.42 (petroleum ether/acetone : 1/1), IR (neat): 3090, 2927, 2858, 1715, 1650, 1601, 1493, 1466, 1393, 1361, 1265, 1142, 1060, 980 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 7.60 (d, 15.6, 1H), 7.57 (d, J=18, 1H), 7.15 (d, J=15.6, 1H), 6.30 (d, J=15.3, 1H), 6.16 (d, J=15.9, 1H), 6.08 (d, J=15.3, 1H), 5.95 (d, J=15.9, 1H), 5.82 (t, J=7.5, 1H), 5.76-5.74 (m), 5.64 (t, J=9.8, 1H), 5.54 (t, J=6.3, 1H), 5.48-5.40 (m), 3.17 (t, J=6.6, 1H), 3.05 (s, 3H), 3.00 (s, 3H), 2.91 (s, 3H), 2.60-2.45 (m), 2.36-2.04 (m), 2.11 (s, 3H), 1.39-1.17 (m), 0.85 (m), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.6, 208.3, 208.2, 171.1, 167.2, 154.5, 143.0, 142.8, 141.6, 140.0, 139.0, 138.2, 137.6, 137.4, 137.0, 136.7, 135.9, 133.6, 132.4, 132.2, 128.8, 128.6, 126.8, 125.2, 122.7, 120.2, 119.8, 118.2, 116.7, 114.3, 42.8, 42.7, 42.3, 37.3, 35.7, 35.5, 33.0, 32.8, 32.7, 32.4, 31.6, 31.5, 31.4, 31.35, 31.3, 30.2, 30.15, 30.1, 29.3, 29.1, 28.8, 28.5, 28.4, 28.1, 27.8, 22.4, 22.2, 22.15, 20.1. Anal. Calc'd for $C_{16}H_{27}O_2N$: C, 72.41; H, 10.25; N, 5.28. Found: C, 72.28; H, 10.49; N, 5.25.



5-(2-Hydroxy-ethylidene)-dodec-6-en-2-one (**64a**)
5-But-1-enyl-undec-5-en-2-one (**64b**)
Red-brown oil
R_f = 0.66 (ether), IR (neat): 3418, 2924, 2858, 1715, 1648, 1456, 1412, 1360, 1271, 1228, 1162, 1097, 1048, 1015, 987 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 6.53 (d, J=15.9, 1H), 6.29 (d, J=15.9, 1H), 6.14 (d, J=15.6, 1H), 5.93 (d, J=15.6, 1H), 5.83 (t, J=6), 5.78 (t, J=6), 5.73-5.57 (m), 5.48 (t, J=7.5), 5.36 (q, J=6.9), 5.24 (t, J=7.5), 4.20 (dq, J=5.4/15.6), 3.64 (d, J=6), 2.61-2.35 (m), 2.31-2.21 (m), 2.16-2.05 (m), 1.76 (s), 1.64 (bs), 1.40-1.19 (m), 1.17-0.85 (m), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.7, 208.5, 139.3, 137.8, 135.8, 134.8, 134.7, 133.8, 132.4, 131.8, 128.6, 127.6, 127.1, 126.4, 125.2, 124.8, 123.7, 64.0, 62.4, 62.3. Anal. Calc'd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.82; H, 10.60.



5-Cyclohexyl-4-(3-oxo-butyl)-penta-2,4-dienoic acid ethyl ester (**65**)
Light yellow oil
Rf = 0.45 (2:1 petroleum ether/ether), IR (neat) : 2980, 2927, 2852, 1713, 1624, 1449, 1365, 1272, 1178, 1124, 1039, 984 cm^{-1}, ^{1}H NMR (500MHz, $CDCl_3$): δ 7.69 (d, J=15.6, 0.5H), 7.22 (d, J=15.9, 0.5H), 5.89 (d, J=15.9, 0.5H), 5.76 (d, J=16.0, 0.5H), 5.74 (d, J=8.6, 0.5H), 5.58 (d, J=9.8, 0.5H), 4.24 (q, J=7.1, 1H), 4.21 (q, J=7.3, 1H), 2.59 (t, J=7.5, 1H), 2.54-2.52 (m, 2H), 2.47 (t, J=7.5, 1H), 2.36-2.28 (m, 1H), 2.17 (s, 1.5H), 2.15

(s, 1.5H), 1.77-1.66 (m, 2H), 1.62-1.57 (m, 2H), 1.37-1.24 (m, 5H), 1.23-1.05 (m, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ 207.9, 207.7, 167.6, 167.3, 148.8, 148.4, 145.8, 140.2, 133.8, 131.6, 117.6, 115.4, 60.4, 60.2, 42.8, 42.7, 37.6, 36.7, 33.1, 32.6, 30.1, 30.0, 27.4, 25.7, 25.5, 20.5, 14.3. Anal. Calc'd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41. Found: C, 73.31; H, 9.63.

Trisubstituted Allenes
General procedure

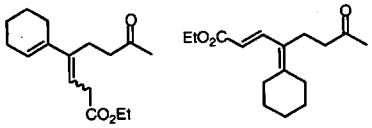
The allene (0.25 mmol) and methyl vinyl ketone (0.375 mmol, 0.032 ml, 1.5eq.) were dissolved in dimethylformamide (1ml) and added to $[CpRu(CH_3CN)_3]PF_6$ (10.9 mg, 0.025 mmol, 0.1eq.) and $CeCl_3 \cdot 7H_2O$ (14.0 mg, 0.0375 mmol, 0.15eq.) in a pressure tube. The tube is capped, then heated to 60°C for 4 h. It is then cooled to room temperature and after adding of 50 ml ether the reaction mixture is washed three times with saturated sodium bicarbonate solution and dried over $MgSO_4$. Removal of the solvent by rotary evaporation gave a crude oil which was chromatographed on silica gel.

A typical example is given below:
The allene **17** (39 mg, 0.25 mmol) and methyl vinyl ketone (26.5 mg, 0.375 mmol, 0.032 ml, 1.5eq.) were dissolved in dimethylformamide (1ml) and added to $[CpRu(CH_3CN)_3]PF_6$ (10.9 mg, 0.025 mmol, 0.1eq.) and $CeCl_3 \cdot 7H_2O$ (14.0 mg, 0.0375 mmol, 0.15eq.) in a pressure tube. The tube is capped, then heated to 60°C for 4 h. It is then cooled to room temperature and after adding of 50 ml ether the reaction mixture is washed three times with saturated sodium bicarbonate solution and dried over $MgSO_4$. Removal of the solvent by rotary evaporation gave a crude oil which was chromatographed on silica gel to give 38 mg (68%) of 1,3-diene **68**.

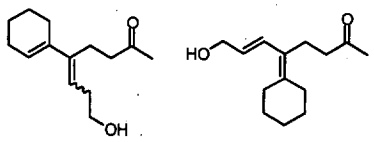
Experimental Details for Table 9, Entries 1-6

Entry	Allene (mg, mmol)	Product (mg, %yield)	Ratio
1[a]	(388.5, 2.0)	**66a + 66b** (371, 70%)	8.3/1
2	(38.0, 0.25)	**67a + 67b** (38.1, 69%)	5/1
3	(39.0, 0.25)	**68** (38.0, 68%)	---
4	(25.0, 0.25)	**69** (19.0, 45%)	---
5	(35.0, 0.25)	**70a + 70b** (25.0, 50%)	1.8/1
6	(45.0, 0.25)	**71** (35.0, 56%)	---

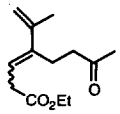
(a)Run with 87.2 mg **38** and 112.0 mg cerium in 8 mL DMF.



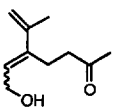
4-Cyclohex-1-enyl-7-oxo-oct-3-enoic acid ethyl ester (**66a**)
4-Cyclohexylidene-7-oxo-oct-2-enoic acid ethyl ester (**66b**)
Yellow oil
Rf = 0.33 (petroleum ether/ether : 2/1), IR (neat): 2980, 2930, 2859, 1736, 1612, 1448, 1411, 1366, 1303, 1261, 1162, 1032 cm-1, 1H-NMR (300 Mhz, CDCl3): _ 7.84 (d, J=15.9, 1H) minor isomer, 5.81 (s, 1H) minor isomer, 5.77 (s, 1H), 5.60 (t, J=6.6, 1H), 4.19 (q, J=6.6, 2H) minor isomer, 4.12 (q, J=7.2, 2H), 3.14 (d, J=7.2, 2H), 2.48 (s, 2H), 2.12 (s, 3H), 1.66-1.53 (m, 4H), 1.28 (t, J=6.9, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.4, 172.1, 142.1, 135.6, 124.1, 116.3, 115.7, 60.6, 42.9, 33.9, 32.1, 30.0, 28.5, 26.6, 26.1, 25.8, 22.8, 22.1, 21.5. Anal. Calc'd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.61; H, 8.98.



5-Cyclohex-1-enyl-8-hydroxy-oct-5-en-2-one (**67a**)
5-Cyclohexylidene-8-hydroxy-oct-6-en-2-one (**67b**)
Brown oil
R_f = 0.47 (ether), IR (neat): 3412, 3038, 2924, 1715, 1436, 1361, 1274, 1162, 1137, 1048, 964, 920 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 6.63 (d, J=15, 1H) minor isomer, 5.74 (m, 1H), 5.43 (t, J=7.5, 1H), 4.28 (J=7.5, 2H) minor isomer, 3.67 (t, J=6.3, 2H), 2.55-2.47 (m, 4H), 2.38(q, J=6.6, 2H), 2.30 (m), 2.26 (m), 2.17 (m), 2.13-2.11 (m), 1.74 (bs), 1.67-1.55 (m), 1.42 (s), 1.24 (m), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.9, 141.8, 135.9, 128.8, 126.0, 123.5, 120.7, 64.3, 62.5, 43.3, 43.1, 31.7, 31.5, 30.3, 30.0, 28.5, 28.3, 26.8, 26.3, 25.8, 22.9, 22.2, 22.1, 21.4. Anal. Calc'd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.88; H, 9.99.

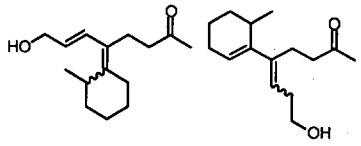


5-Methyl-4-(3-oxo-butyl)-hexa-3,5-dienoic acid ethyl ester (**68**)
Yellow oil
R_f = 0.26 (petroleum ether/ether : 2/1), IR (neat): 3093, 2980, 1736, 1718, 1608, 1447, 1411, 1367, 1257, 1163, 1034, 892 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 5.74 (t, J=6.9, 1H), 4.96 (d, J=6.9, 2H), 4.13 (q, J=7.2, 2H), 3.17 (d, J=7.2, 2H), 2.52 (s, 4H), 2.11 (s, 3H), 1.88 (s, 3H), 1.25 (t, J=7.2, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.2, 171.8, 142.4, 141.2, 119.8, 112.4, 60.7, 42.6, 34.0, 30.0, 21.6, 21.2, 14.1 MS (EI), m/z 224 (M^+), 224 (M^+ - H), 209. HRMS: Calc'd for $C_{13}H_{20}O_3$ (M^+): 224.1413. Found: 224.1413.

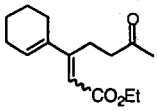


7-Hydroxy-5-isopropenyl-hept-5-en-2-one (**69**)

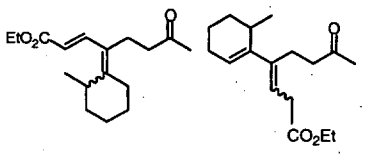
Orange oil
R_f = 0.34 (petroleum ether/ether : 1/5), IR (neat): 3414, 3093, 2925, 1713, 1608, 1412, 1361, 1164, 1079, 1009, 893 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 5.79 (t, J=6.9, 1H), 4.99 (s, 2H), 4.28 (d, J=6.9, 2H), 2.58 (s, 4H), 2.12 (s, 3H), 1.88 (s, 3H), 1.42 (s, 1H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.8, 142.5, 140.9, 126.9, 113.0, 59.4, 42.7, 30.2, 21.21, 21.18.. Anal. Calc'd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.50; H, 9.41.



8-Hydroxy-5-(2-methyl-cyclohexylidene)-oct-6-en-2-one (**70a**)
8-Hydroxy-5-(6-methyl-cyclohex-1-enyl)-oct-5-en-2-one (**70b**)
Slightly yellow oil
R_f = 0.58 (ether), IR (neat): 3408, 2926, 2857, 1714, 1444, 1360, 1163, 1096, 1047, 964 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 6.63 (d, J=15.6, 1H), 5.74 (dt, J=6/15.6, 1H), 5.56 (t, J=3.6, 1H), 5.34 (t, J=7.2, 1H), 4.21 (bs, 2H), 3.66 (bs, 2H), 2.92 (bs, 1H), 2.74-2.70 (m, 1H), 2.62-2.26 (m), 2.14 (s, 3H), 2.11 (s, 3H), 2.04-1.90 (m), 1.82-1.42 (m), 1.24-1.08 (m), 1.07 (d, J=6.9, 3H), 0.92 (d, J=6.9, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.9, 145.0, 143.2, 142.3, 129.1, 126.2, 125.7, 123.6, 121.9, 64.4, 62.5, 43.5, 42.4, 33.6, 32.2, 31.6, 30.8, 30.3, 30.1, 28.9, 28.0, 25.8, 24.8, 22.2, 22.0, 20.7, 20.1, 18.8, 18.3. Anal. Calc'd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.23; H, 10.04.

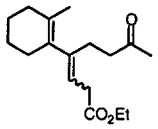


3-Cyclohex-1-enyl-6-oxo-hept-2-enoic acid ethyl ester (**71**)
Yellow oil
R_f = 0.4 (petroleum ether/ether : 2/1), IR (neat): 2980, 2932, 2861, 1713, 1605, 1449, 1410, 1392, 1364, 1332, 1275, 1243, 1219, 1160, 1097, 1044, 1012, 924, 879, 840 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 6.21 (s, 1H), 5.78 (s, 1H), 4.14 (q, J=7.2, 2H), 3.03 (t, J=6.9, 2H), 2.57 (t, J=7.8, 2H), 2.16 (m, 7H), 1.67-1.57 (m, 4H), 1.27 (t, J=7.2, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.3, 167.1, 158.4, 135.7, 130.9, 113.5, 59.7, 43.6, 29.7, 26.3, 26.0, 22.6, 22.5, 21.7, 14.3. Anal. Calc'd for $C_{15}H_{22}O_3$: C, 71.97; H, 9.26. Found: C, 72.05; H, 9.02.



4-(2-Methyl-cyclohexylidene)-7-oxo-oct-2-enoic acid ethyl ester
4-(6-Methyl-cyclohex-1-enyl)-7-oxo-oct-3-enoic acid ethyl ester
Yellow oil

R_f = 0.37 (petroleum ether/ether : 2/1) ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 7.82 (d, J=15.6, 1H), 5.79 (d, J=15.6, 1H), 5.61 (t, J=3.6, 1H), 5.52 (t, J=7.5, 1H), 4.19, (q, J=6.9, 2H), 4.11 (q, J=6.9, 2H), 3.12 (d, J=7.5, 1H), 2.98-2.86 (m, 1H), 2.54-2.40 (m, 6H), 2.30-2.27 (m, 1H), 2.14-2.11 (m, 2H), 2.12 (s, 3H), 2.03 (m, 2H), 1.89-1.85 (m, 1H), 1.67-1.41 (m)1.31-1.19 (m), 1.08 (d, J=7.2, 3H), 0.92 (d, J=6.9, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.4, 208.1, 172.1, 168.0, 154.7, 142.7, 141.7, 141.1, 126.0, 124.1, 117.3, 116.0, 60.5, 60.2, 43.0, 42.2, 33.8, 33.6, 33.3, 32.8, 30.7, 30.2, 29.6, 28.2, 28.0, 25.8, 25.4, 22.3, 21.5, 20.5, 20.0, 18.6, 18.3, 14.3, 14.2. Anal. Calc'd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41. Found: C, 73.18; H, 9.22.



4-(2-Methyl-cyclohex-1-enyl)-7-oxo-oct-3-enoic acid ethyl ester
R_f = 0.37 (petroleum ether/ether : 2/1) ^{1}H-NMR (300 Mhz, $CDCl_3$) : δ 5.68 (t, J=7.8, 1H), 4.13 (q, J=7.2, 2H), 3.05, (d, J=7.5, 2H), 2.58 (t, J=8.1, 2H), 2.39-2.26 (m, 2H), 2.14 (s, 3H), 1.74-1.49 (m, 7H), 1.36-1.23 (m, 4H), 0.72 (d, J=6.6, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.6, 172.1, 147.6, 116.5, 77.2, 60.7, 43.6, 38.5, 37.5, 33.9, 30.2, 29.9, 25.9, 21.6, 21.3, 15.8, 14.2, MS (EI), m/z 278 (M^+), 209, 253, 221, 207, 193. HRMS: Calc'd for $C_{17}H_{23}O_3$ (M^+): 278.1883. Found: 278.1880.

Tetrasubstituted Allenes
General procedure

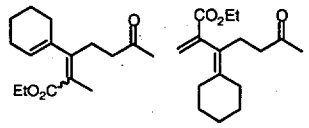
The allene (0.25 mmol) and methyl vinyl ketone (0.375 mmol, 0.032 ml, 1.5eq.) were dissolved in dimethylformamide (1ml) and added to $[CpRu(CH_3CN)_3]PF_6$ (10.9 mg, 0.025 mmol, 0.1eq.) and $CeCl_3 \cdot 7H_2O$ (14.0 mg, 0.0375 mmol, 0.15eq.) in a pressure tube. The tube is capped, then heated to 60°C for 4 h. It is then cooled to room temperature and after adding 50 ml ether the reaction mixture is washed three times with saturated sodium bicarbonate solution and dried over $MgSO_4$. Removal of the solvent by rotary evaporation gave a crude oil which was chromatographed on silica gel.

A typical example is given below:
The allene **4** (49 mg, 0.25 mmol) and methyl vinyl ketone (26.5 mg, 0.375 mmol, 0.032 ml, 1.5eq.) were dissolved in dimethylformamide (1ml) and added to $[CpRu(CH_3CN)_3]PF_6$ (10.9 mg, 0.025 mmol, 0.1eq.) and $CeCl_3 \cdot 7H_2O$ (14.0 mg, 0.0375 mmol, 0.15eq.) in a pressure tube. The tube is capped, then heated to 60°C for 4 h. It is then cooled to room temperature and after adding 50 ml ether the reaction mixture is washed three times with saturated sodium bicarbonate solution and dried over $MgSO_4$. Removal of the solvent by rotary evaporation gave a crude oil which was chromatographed (5/1 petroleum ether/ether) on silica gel to give 28.7 mg (44%) of 1,3-dienes **73a** and **73b**.

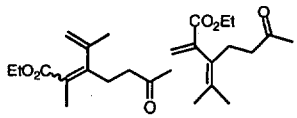
Experimental Details for Table 9, Entries 7-8

Entry	Allene (mg, mmol)	Product (mg, %yield)	Ratio	Yield (%)

1	(49.0, 0.25)	**73a + 73b** (28.7, 44%)	20/1	44
2	(39.0, 0.25)	**74a + 74b** (8.0, 14%)	10/1	14



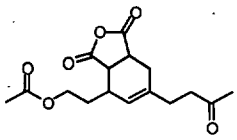
3-Cyclohex-1-enyl-2-methyl-6-oxo-hept-2-enoic acid ethyl ester (**73a**)
2-(1-Cyclohexylidene-4-oxo-pentyl)-acrylic acid ethyl ester (**73b**)
Yellow oil
R_f = 0.29 (petroleum ether/ether : 5/1), IR (neat): 2936, 2861, 1760, 1449, 1366, 1312, 1283, 1229, 1177, 1125, 1101, 1047, 999, 975 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 5.31 9s, 1H), 4.89 (s, 1H) minor isomer, 4.81 (s, 1H) minor isomer, 4.08 (q, J=7.2, 2H), 2.48-2.39 (m, 4H), 2.14 (s, 3H), 2.08-1.97 (m, 4H), 1.86 (s, 3H), 1.70-1.59 (m, 4H), 1.24 t, J=7.2, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 208.0, 171.2, 147.1, 139.1, 124.3, 65.1, 60.2, 41.1, 30.0, 27.3, 25.2, 24.5, 22.6, 21.9, 15.3, 14.3. Anal. Calc'd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.54; H, 9.12.



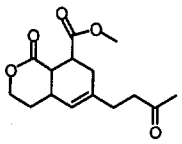
2,4-Dimethyl-3-(3-oxo-butyl)-penta-2,4-dienoic acid ethyl ester (**74a**)
4-Methyl-2-methylene-3-(3-oxo-butyl)-pent-3-enoic acid ethyl ester (**74b**)
Yellow oil
R_f = 0.23 (petroleum ether/ether : 2.5/1), IR (neat): 3079, 2979, 2924, 1714, 1673, 1462, 1446, 1413, 1366, 1313, 1269, 1160, 1097, 1027, 899 cm^{-1}, ^{1}H-NMR (300 Mhz, $CDCl_3$): δ 4.80 (s, 1H), 4.60 (s, 1H), 4.10 (q, J=6.9, 2H), 2.47 (t, J=6, 2H), 2.45 (t, J=6, 2H), 2.14 (s, 3H), 1.88 (s, 3H), 1.85 (s, 3H), 1.24 (t, J=6.9, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 207.7, 170.6, 146.8, 146.2, 125.2, 113.2, 60.3, 40.9, 30.0, 24.4, 21.6, 15.0, 13.8
Anal. Calc'd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.42; H, 8.80.

Intermolecular Diels-Alder Reactions
Synthesis of bicyclic lactone 76

The diene **32** (50 mg, 0.24 mmol) and maleic anhydride (25.6 mg, 0.26 mmol) were heated in benzene (4 mL) at 80 °C for 2 h. The benzene was evaporated under reduced pressure, and the crude material (**82**) redissolved in methanol (10 mL). This solution was cooled to 0° C and acetyl chloride (0.051 mL, 0.71 mmol) was added to generate anhydrous HCl. The reaction was allowed to warm to room temperature and stirred for 18 hours. The solvent was then evaporated by rotary evaporation and the crude material chromatographed 1/1 petroleum ether/ethyl acetate) on silica gel to yield 50 mg **76** (72% over 2 steps) of a colorless oil.

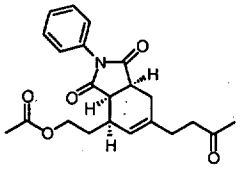


Acetic acid 2-[1,3-dioxo-6-(3-oxo-butyl)-1,3,3a,4,7,7a-hexahydro-isobenzofuran-4-yl]-ethyl ester (**75**)
Due to the instability of this compound, only partial characterization was obtained.
Colorless oil
R_f = 0.15 (1:1 petroleum ether/ethyl acetate), IR (neat) : 3411, 2956, 2852, 2361, 1846, 1776, 1736, 1441, 1366, 1244, 1164, 1074 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 5.46 (brs, 1H), 4.36-4.29 (m, 1H), 4.21-4.14 (m, 1H), 3.50-3.38 (m, 2H), 2.61 (d, J=15.9, 1H), 2.54-2.51 (m, 2H), 2.48-2.17 (m, 8H), 2.15 (s, 3H), 2.06 (s, 3H).



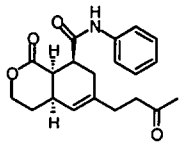
1-Oxo-6-(3-oxo-butyl)-3,4,4a,7,8,8a-hexahydro-1*H*-isochromene-8-carboxylic acid methyl ester (**76**)
Colorless oil
R_f = 0.22 (1:1 petroleum ether/ethyl acetate), IR (neat) : 2952, 2919, 1732, 1438, 1407, 1359, 1312, 1251, 1213, 1165, 1134, 1076 cm^{-1}, ^1H NMR (300MHz, $CDCl_3$): δ 5.27 (brs, 1H), 4.32-4.25 (m, 1H), 4.17 (td, J_1=9.3, J_2=3.9, 1H), 3.74 (s, 3H), 3.42-3.39 (m, 1H), 2.92 (brs, 1H), 2.66-2.48 (m, 3H), 2.42-2.32 (m, 1H), 2.30-2.15 (m, 3H), 2.12 (s, 3H), 1.76-1.66 (m, 2H), ^{13}C NMR (75MHz, $CDCl_3$): δ 208.0, 173.2, 171.4, 138.3, 122.9, 66.2, 52.0, 41.4, 40.9, 40.4, 32.6, 31.1, 30.0, 28.7, 26.2. HRMS: Calc'd for $C_{15}H_{20}O_5$: 280.1311. Found 280.1319.

Synthesis of bicyclic lactone 78
The diene **32** (50 mg, 0.24 mmol) and N-phenylmaleimide (54.0 mg, 0.33 mmol) were heated in toluene (1 mL) at 80 °C for 2 h. The toluene was evaporated under reduced pressure, and the crude material purified by chromatograpy on silica gel to yield 68 mg of **77** (77%) as a colorless oil. The Diels-Alder adduct **77** (30.0 mg, 0.081 mmol) was redissolved in methanol (4 mL). This solution was cooled to 0 °C and acetyl chloride (15.8 mg, 0.014 mL, 0.202 mmol) was added to generate anhydrous HCl. The reaction was allowed to warm to room temperature and stirred for 16 h. The solvent was then evaporated by rotary evaporation and the crude material chromatographed (1/3 petroleum ether/ether) on silica gel to yield 18.0 mg (68%) of **78** as a colorless oil.



Acetic acid 2-[1,3-dioxo-6-(3-oxo-butyl)-2-phenyl-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-4-yl]-ethyl ester (**77**)

Colorless oil. R_f = 0.11 (1:3 petroleum ether/ethyl ether), IR (neat) : 2954, 2852, 1733, 1707, 1598, 1500, 1439, 1386, 1244, 1184, 1039, 952 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 7.47 (t, J=7.7, 2H), 7.39 (t, J=7.4, 1H), 7.20 (d, J=7.3, 2H), 5.49 (, 1H), 4.40-4.35 (m, 1H), 4.26-4.21 (m, 1H), 3.49-3.28 (m, 2H), 2.70 (d, J=14.9, 1H), 2.54-2.50 (m, 2H), 2.47-2.46 (m, 1H), 2.41-2.38 (m, 1H), 2.35-2.26 (m, 3H), 2.16-2.10 (m, 1H), 2.09 (s, 3H), 2.0 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$): δ 207.4, 178.6, 176.7, 171.1, 139.8, 131.7, 129.0, 128.6, 126.4, 125.7, 62.6, 42.5, 40.9, 40.6, 33.3, 30.3, 30.2, 29.8, 28.2, 21.0. Anal. Calc'd for $C_{22}H_{25}NO_5$: C, 68.92; H, 6.52; N, 3.65. Found: C, 68.75; H, 6.28; N, 3.51.

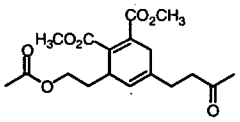


1-Oxo-6-(3-oxo-butyl)-3,4,4a,7,8,8a-hexahydro-1*H*-isochromene-8-carboxylic acid phenylamide (**78**)

Colorless oil. R_f = 0.13 (1:2 petroleum ether/ethyl acetate), IR (neat) : 3342, 2922, 2854, 1711, 1599, 1536, 1497, 1441, 1409, 1359, 1320, 1161 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 8.75 (brs, 1H), 7.57 (d, J=7.6, 2H), 7.35 (t, J=8.1, 1H), 7.13 (t, J=7.4, 2H), 5.36 (s, 1H), 4.37-4.32 (m, 1H), 4.30-4.25 (m, 1H), 3.73 (d, J=7.6, 1H), 3.40 (dd, J=6.6, 2.9, 1H), 3.03 (m, 1H), 2.87-2.83 (m, 1H), 2.61 (t, J=7.2, 2H), 2.39-2.31 (m, 2H), 2.28-2.33 (m, 1H), 2.18 (s, 3H), 1.80-1.74 (m, 2H). ^{13}C NMR (125MHz, $CDCl_3$): δ 210.6, 184.7, 137.9, 137.5, 128.9, 124.3, 123.9, 120.3, 119.9, 66.5, 45.2, 41.5, 40.7, 33.6, 30.9, 30.1, 28.7, 28.0. HRMS: Calc'd for $C_{20}H_{34}NO_4$: 341.1627. Found: 341.1620.

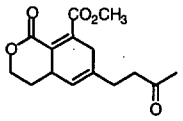
Synthesis of bicyclic lactone 80

The diene **32** (50 mg, 0.24 mmol) and dimethylacetylene dicarboxylate (48.0 mg, 0.33 mmol) were heated in toluene (1 mL) at 80 °C for 18 hours. The toluene was evaporated under reduced pressure, and the crude material purified by chromatograpy on silica gel to yield 69 mg of **79** (81%) as a colorless oil. The Diels-Alder adduct **79** (39.0 mg, 0.111 mmol) was redissolved in methanol (5 mL). This solution was cooled to 0 °C and acetyl chloride (22.0 mg, 0.020 mL, 0.277 mmol) was added to generate anhydrous HCl. The reaction was allowed to warm to room temperature and stirred for 17 hours. The solvent was then evaporated and the crude material chromatographed (1/3 petroleum ether/ether) on silica gel to yield 18.0 mg (58%) of **80** as a colorless oil as well as 14.0 mg (40%) of the unlactonized product, which could be converted into the lactone by stiring with base in MeOH.



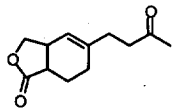
3-(2-Acetoxy-ethyl)-5-(3-oxo-butyl)-cyclohexa-1,4-diene-1,2-dicarboxylic acid dimethyl ester (**79**)

Colorless oil. R_f = 0.20 (1:3 petroleum ether/ethyl ether), IR (neat) : 2954, 1724, 1649, 1630, 1435, 1368, 1263, 1163, 1052, 939, 852, 804 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 5.41-5.40 (m, 1H), 4.06 (td, J=6.8, 1.0, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 3.39-3.35 (m, 1H), 3.02-2.95 (m, 1H), 2.81 (dd, J=22.2, 6.5, 1H), 2.60 (t, J=7.5, 2H), 2.32 (t, J=7.6, 2H), 2.18 (s, 3H), 2.03 (s, 3H), 1.93-1.82 (m, 2H). ^{13}C NMR (125MHz, $CDCl_3$): δ 207.6, 171.0, 168.4, 167.6, 137.3, 133.6, 131.6, 120.8, 61.2, 52.2 (x2), 41.3, 35.7, 32.5, 30.5, 30.0 (x2), 20.9. Anal. Calc'd for $C_{18}H_{24}O_7$: C, 61.38; H, 6.81. Found: C, 61.52; H, 6.88.



1-Oxo-6-(3-oxo-butyl)-3,4,4a,7-tetrahydro-1*H*-isochromene-8-carboxylic acid methyl ester (**80**)
Colorless oil. R_f = 0.25 (1:2 petroleum ether/ethyl acetate), IR (neat) : 2952, 1716, 1645, 1434, 1407, 1360, 1268, 1248, 1153, 1095, 1074, 1006 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 5.38 (m, 1H), 4.48-4.38 (m, 2H), 3.86 (s, 3H), 3.23-3.17 (m, 1H), 3.13-2.95 (m, 1H), 2.89-2.82 (m, 1H), 2.62 (t, J=6.2, 2H), 2.33 (t, J=6.3, 2H), 2.19 (s, 3H), 2.13-2.09 (m, 1H), 1.93-1.84 (m, 1H). ^{13}C NMR (125MHz, $CDCl_3$): δ 207.4, 169.9, 163.5, 140.9, 133.1, 127.1, 125.1, 121.3, 68.6, 52.7, 41.1, 34.6, 32.8, 30.3, 29.7. HRMS: Calc'd for $C_{15}H_{18}O_5$: 278.1154. Found: 278.1158.

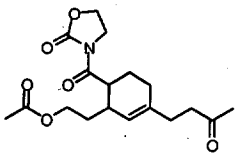
Reaction of the 1,3-diene 41 with ethyl acrylate
The diene **41** (30 mg, 0.195 mmol) and ethyl acrylate (19.5 mg, 0.21 mL, 1.95 mmol) were heated in toluene (3 mL) at 110 °C for 21 hours. The toluene was evaporated under reduced pressure, and the crude material purified by chromatograpy (3/1 petroleum ether/ether) on silica gel to yield 29 mg of **81** (72%) as a colorless oil.



5-(3-Oxo-butyl)-3a,6,7,7a-tetrahydro-3*H*-isobenzofuran-1-one (**81**)
Colorless oil. R_f = 0.22 (3:1 petroleum ether/ethyl ether), IR (neat) : 2855, 2822, 1767, 1713, 1434, 1368, 1212, 1154, 1116, 1039, 1020, 995 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 5.34 (brs, 1H), 4.36 (dd, J_1=8.8, J_2=6.4, 1H), 4.03 (dd, J_1=8.8, J_2=2.2, 1H), 3.07 (m, 1H), 2.83-2.80 (m, 1H), 2.55 (t, J=7.8, 2H), 2.27 (t, J=7.5, 2H), 2.16 (s, 3H), 2.15-2.12 (m, 1H), 2.10-1.99 (m, 1H), 1.91-1.88 (m, 1H), 1.82-1.75 (m, 1H). ^{13}C NMR (125MHz, $CDCl_3$): δ 208.1, 178.6, 140.5, 119.7, 72.4, 41.5, 37.6, 35.6, 31.6, 30.0, 24.4, 20.1. Anal. Calc'd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.36; H, 7.86.

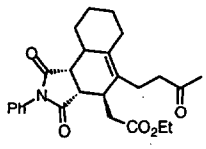
Reaction of 32 with acroyl oxazolidinone
The diene **32** (22 mg, 0.105 mmol) and acroyloxazolidinone (16.2 mg, 1.95 mmol) were heated in toluene (2 mL) at 100 °C for 25 hours. The toluene was evaporated under reduced pressure, and the crude material purified by chromatograpy (1/1 petroleum ether/ethyl acetate) on silica gel to yield 20.4 mg of **82** (55%, 75% brsm) as a colorless

oil in an approximately a 3.4:1 mixture of diastereomers as determined by NMR and 4.4 mg starting material.



Acetic acid 2-[3-(3-oxo-butyl)-6-(2-oxo-oxazolidine-3-carbonyl)-cyclohex-2-enyl]-ethyl ester (**82**)
Colorless oil. R_f = 0.11 (1:1 petroleum ether/ethyl acetate), IR (neat) : 2923, 1777, 1735, 1698, 1477, 1434, 1387, 1365, 1320, 1243, 1112, 1041 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$): δ 5.42 (d, J=3.7, 1H), 4.47-4.44 (m, 2H), 4.17-4.02 (m, 4H), 3.84-3.81 (m, 1H), 2.78-2.74 (m, 1H), 2.57 (t, J=7.7, 2H), 2.25 (t, J=7.2, 2H), 2.18 (s, 3H), 2.06 (s, 3H), 2.05-2.02 (m, 1H), 1.96-1.88 (m, 1H), 1.82-1.80 (m, 1H), 1.67-1.55 (m, 3H). ^{13}C NMR (125MHz, $CDCl_3$): δ 208.5, 175.0, 171.2, 153.1, 136.9, 122.8, 62.5, 62.0, 42.8, 41.9, 41.8, 31.8, 31.1, 30.7, 30.0, 27.7, 21.0, 20.7. HRMS: Calc'd for $C_{18}H_{425}NO_6$: 351.1682. Found: 351.1680.

Reaction details for eq 14
A mixture of the 1,3-diene **66a** (60 mg, 0.225 mmol) and N-phenylmaleimide (0.43 mg, 0.248 mmol, 1.1 eq.) in 2 ml of xylenes was heated to 155 °C and stirred for 22 hours. It was then allowed to cool to room temperature and the crude solution was directly chromatographed on silica gel (petroleum ether/ether : 2/1 then petroleum ether/ether : 1/3), which gave 7.8 mg (12.5%) starting material and 84 mg of the desired product **83**, an orange solid (85%, 97.5% based on recovered starting material).



[1,3-Dioxo-5-(3-oxo-butyl)-2-phenyl-2,3,3a,4,6,7,8,9,9a,9b-decahydro-1*H*-benzo[*e*]isoindol-4-yl]-acetic acid ethyl ester (**83**)
Yellow solid, mp = 28-30 °C
R_f = 0.5 (petroleum ether/ether : 1/3), IR (neat): 3459, 3067, 2936, 2868, 2254, 1770, 1731, 1715, 1598, 1499, 1456, 1385, 1298, 1179, 1096, 1026, 916 cm^{-1}, ^1H-NMR (300 Mhz, $CDCl_3$): δ 7.48-7.30 (m, 3H), 7.12 (d, J=7.2, 2H), 4.17 (q, J=6.9, 2H), 3.37 (dd, J=5.1/9, 1H), 3.21-3.13 (m, 2H), 2.99-2.96 (m, 1H), 2.86 (dd, J=6/16.5, 1H), 2.45-2.05 (m, 7H), 1.99 (s, 3H), 1.93-1.78 (m, 2H), 1.74-1.64 (m, 1H), 1.57-1.51 (m, 1H), 1.27 (t, J=6.9, 3H), ^{13}C-NMR (75 Mhz, $CDCl_3$): δ 207.4, 177.6, 176.8, 172.8, 136.7, 131.7, 130.1, 129.5, 129.2, 129.0, 128.5, 126.3, 60.7, 44.09, 43.8, 43.2, 37.9, 35.6, 33.1, 29.6, 24.2, 23.8, 21.8, 21.4, 21.2, 14.1. MS (EI), m/z 430, 429, 427, 402, 358, 357, 331, 330, 316, 243, 201. HRMS: Calc'd for $C_{26}H_{31}NO_5$ (M^+) 437.2203. Found: 437.220.

[i] Crabbé, P.; Fillion, H.; André, D.; Luche, J.-L. *J. Chem. Soc.-Chem. Commun.* **1979**, 859.
[ii] Lautens, M.; Meyer, C.; Van Oereren, A. *Tetrahedron Lett.* **1997**, *38*, 3833.
[iii] Pornet, J.; Damour, D.; Miginiac, L. *J. Organomet. Chem.* **1987**, *319*, 333.
[iv] Bertrand, M.; Dulcere, J. P.; Gil, G.; Grimaldi, J.; Sylvestre-Panthet, P. *Tetrahedron Lett.* **1976**, *37*, 3305.
[v] Crabbé, P.; Fillion, H.; André, D.; Luche, J.-L. *J. Chem. Soc.-Chem. Commun.* **1979**, 859.
[vi] Yoneda, E.; Kaneko, T.; Zhang, S.-W.; Onitsuka, K.; Takahashi, S. *Org. Lett.* **2000**, 2, 441.