Supporting Information

The $Cu(OTf)_2$- and $Yb(OTf)_3$-catalyzed Claisen Rearrangement of 2-Alkoxycarbonyl-substituted Allyl Vinyl Ethers

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General procedure for the Claisen Rearrangement. The allyl vinyl ether (4 mmol) was dissolved in dry CH_2Cl_2 (4 mL) under Argon. Activated 3 A mol sieves (400 mg) and the catalyst (used as purchased) were added. The reaction mixture was stirred under argon for 24 h at the appropriate temperature. The mol sieves were then removed by filtration. The solvent was then evaporated at reduced pressure. The crude product was then dissolved in heptane/ethyl acetate (1/1) and filtered through a 4 × 0.5 cm silica gel column to remove the catalyst. The solvent was then removed to provide the crude product as a colorless oil. The composition of the product mixture was analyzed by ^1H and ^{13}C NMR spectroscopy. Commercially available 3 A mol sieves were activated by drying for several hours at 250 °C and at 5×10^{-2} mbar. Prior to use, they were stored at 200 °C.

(3*R,4*S**)-3-Benzyl-2-oxo-4-vinyl-heptanoic acid isopropyl ester *syn*-2a**. Following the general procedure, the allyl vinyl ether ***Z,Z*-1a** (0.4 mmol, 121 mg) was stirred with $Cu(OTf)_2$ (0.02 mmol, 7.2 mg) or $Yb(OTf)_3$ (0.03 mmol, 18.6 mg) and crushed 3 A molecular sieves (400 mg) in CH_2Cl_2 (4 mL) to afford the crude product. The catalyst was removed by filtration of the crude product through a 4 × 0.5 cm silica gel column (heptane/ethyl acetate 1/1). The solvent was evaporated and the composition of the product ($Cu(OTf)_2$: 119 mg, 98 %, $Yb(OTf)_3$: 120 mg, 99 %) was analyzed by ^1H and ^{13}C NMR spectroscopy ($Cu(OTf)_2$: ***syn*-2a**:***anti*-2a**= 93:7; $Yb(OTf)_3$: ***syn*-2a**:***anti*-2a**= 96:4). α-keto ester ***syn*-2a**: ^1H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, J = 7 Hz, 3 H), 1.22 (d, J = 6.0 Hz, 3 H), 1.24 (d, J = 6.0 Hz, 3 H), 1.11-1.56 (series of m, 4 H), 2.31-2.43 (m, 1 H), 2.86 (dd, J_1 = 13.8, J_2 = 5.4 Hz, 1 H), 2.95 (dd, J_1 = 13.8, J_2 = 9.7 Hz, 1 H), 3.76 (ddd, J_1 = 9.7, J_2 = 6.5, J_3 = 5.5 Hz, 1 H), 4.93-5.11 (m, 3 H), 5.66 (ddd, J_1 = 17.1, J_2 = 10.0, J_3 = 9.7 Hz, 1 H), 7.11-7.27 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 20.2, 21.4, 33.8, 34.7, 46.1, 52.8, 70.3, 117.3, 126.2, 128.4, 129.0, 138.7, 139.1, 161.0, 197.6. IR 1725 cm^{-1}. Anal. Calcd. for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67. Found: C, 75.55; H, 8.79.

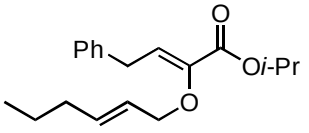
(3*R,4*S**)-3-Benzyl-5-benzyloxy-2-oxo-4-vinyl-pentanoic acid isopropyl ester *syn*-2b**. The allyl vinyl ether ***Z,Z*-1b** (0.4 mmol, 152 mg) was stirred with $Yb(OTf)_3$ (0.04 mmol, 24.8 mg) and crushed 3 A molecular sieves (200 mg) in CH_2ClCH_2Cl (4 mL) at 60 °C (oil bath temperature) for 24 h using a pressured tube with a threaded plug. The mol sieves were then removed by filtration. The solvent was then evaporated at reduced pressure. The catalyst was removed by filtration of the crude product through a 4 × 0.5 cm silica gel column (heptane/ethyl acetate 1/1). The solvent was evaporated and the composition of the product (147 mg, 97%) was analyzed by ^1H and ^{13}C NMR spectroscopy (*syn*:*anti*= 94:6). α-keto ester ***syn*-2b**: ^1H NMR (300 MHz, $CDCl_3$) δ 1.13 (d, J = 6.2 Hz, 3 H), 1.19 (d, J = 6.2 Hz, 3 H), 2.71-2.84 (m, 1 H), 2.79 (dd, J_1 = 13.6, J_2 = 5.8 Hz, 1 H), 2.95 (dd, J_1 = 16.6, J_2 = 9.1 Hz, 1 H), 3.44 (dd, J_1 = 9.1, J_2 = 5.5 Hz, 1 H), 3.56 (dd, J_1 = 9.1, J_2 = 4.6 Hz,

1 H), 3.96 (ddd, J_1 = 9.0, J_2 = J_3 = 5.8 Hz, 1 H), 4.42 (s, 2 H), 4.91 (sept, J = 6.3 Hz, 1 H), 5.09 (d, J = 17.2 Hz, 1 H), 5.17 (dd, J_1 = 10.4, J_2 = 1.6 Hz, 1 H), 5.97 (ddd, J_1 = 17.2, J_2 = 10.2, J_3 = 8.9 Hz, 1 H), 7.14-7.36 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 21.4, 34.8, 46.6, 49.3, 70.2, 71.5, 73.0, 118.0, 126.3, 127.5, 127.6, 128.3, 128.4, 129.1, 136.0, 137.8, 139.0, 160.6, 195.9. IR 1722 cm^{-1}. Anal. Calcd. for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42. Found: C, 75.94; H, 7.52.

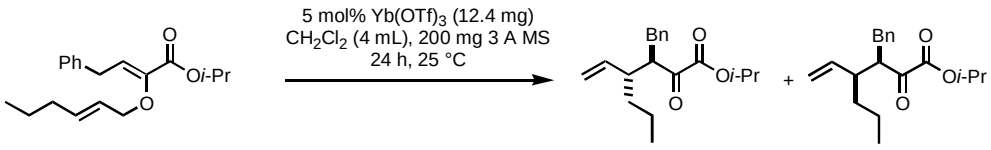
(3*R,4*S**)-3-Isopropyl-2-oxo-4-vinyl-heptanoic acid isopropyl ester *syn*-2c**. Following the general procedure, the allyl vinyl ether ***Z,Z*-1c** (0.4 mmol, 102 mg) was stirred with $Cu(OTf)_2$ (0.02 mmol, 7.2 mg) or $Yb(OTf)_3$ (0.03 mmol, 18.6 mg) and crushed 3 A molecular sieves (400 mg) in CH_2Cl_2 (4 mL) to afford the crude product. The catalyst was removed by filtration of the crude product through a 4 × 0.5 cm silica gel column (heptane/ethyl acetate 1/1). The solvent was evaporated and the composition of the product ($Cu(OTf)_2$: 101 mg, 99 %; $Yb(OTf)_3$: 101 mg, 99%) was analyzed by ^{1}H and ^{13}C NMR spectroscopy ($Cu(OTf)_2$: *syn*:*anti*= 93:7; $Yb(OTf)_3$: *syn*:*anti*= 91:9). α-keto ester ***syn*-2c**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, J = 7.3 Hz, 3 H), 0.88 (d, J = 6.8 Hz, 3 H), 0.96 (d, J = 6.8 Hz, 3 H); 1.08-1.26 (m, 2 H), 1.27-1.47 (m, 2 H), 1.33 (d, J = 6.3 Hz, 3 H), 1.34 (d, J = 6.3 Hz, 3 H), 1.97-2.11 (m, 1 H), 2.37-2.50 (m, 1 H), 3.31 (dd, J_1 = 8.4, J = 6.8 Hz, 1 H), 4.97 (dd, J_1 = 16.9, J_2 = 2.0 Hz, 1 H), 5.03 (dd, J_1 = 10.4, J_2 = 2 Hz, 1 H), 5.10 (sept, J = 6.3 Hz), 5.62 (ddd, J_1 = 16.9, J_2 = J_3 = 9.9 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 19.5, 20.3, 20.5, 21.4, 21.5, 28.5, 34.5, 44.2, 56.0, 70.3, 116.8, 138.4, 161.9, 199.4. IR 1725, 1745 cm^{-1}. Anal. Calcd. for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.96; H, 10.50.

(3*R)-3-Benzyl-4,4-dimethyl-2-oxo-hex-5-enoic acid isopropyl ester 2d**. Following the general procedure, the allyl vinyl ether ***Z,Z*-1d** (0.4 mmol, 115 mg) was stirred with $Cu(OTf)_2$ (0.02 mmol, 7.2 mg) or $Yb(OTf)_3$ (0.005 mmol, 3.1 mg) and crushed 3 A molecular sieves (400 mg) in CH_2Cl_2 (4 mL) to afford the crude product. The catalyst was removed by filtration of the crude product through a 4 × 0.5 cm silica gel column (heptane/ethyl acetate 1/1). The solvent was evaporated and the composition of the product ($Cu(OTf)_2$: 114 mg, 99 %; $Yb(OTf)_3$: 114 mg, 99%) was analyzed by ^{1}H and ^{13}C NMR spectroscopy. α-keto ester **2d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (s, 3 H), 1.15 (s, 3 H), 1.18 (d J = 6.3 Hz, 3 H), 1.19 (d, J = 6.3 Hz, 3 H), 2.81 (dd, J_1 = 13.6, J_2 = 3.3 Hz), 2.95 (dd, J_1 = 13.5, J_2 = 11.9 Hz, 1 H), 3.83 (dd, J_1 = 11.9, J_2 = 3.3 Hz, 1 H), 4.92 (sept, J = 6.3 Hz, 1 H), 5.02 (dd, J_1 = 17.2, J_2 = 0.5 Hz, 1 H), 5.04 (dd, J_1 = 10.7, J_2 = 0.5 Hz, 1 H), 5.92 (dd, J_1 = 17.0, J_2 = 10.7 Hz, 1 H), 7.07-7.27 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 21.4, 24.0, 24.2, 33.6, 40.3, 56.1, 70.3, 112.9, 126.1, 128.4, 129.0, 139.4, 145.3, 161.3, 198.1. IR 1745, 1723 cm^{-1}. Anal. Calcd. for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.66; H, 8.88.

NMR spectra (300 MHz or 75 MHz, $CDCl_3$) of starting materials and crude products for different reaction conditions

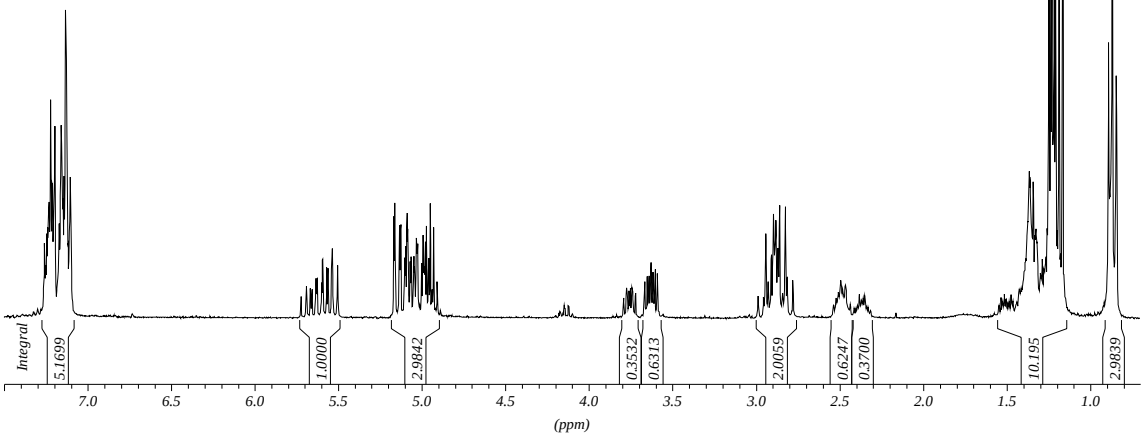


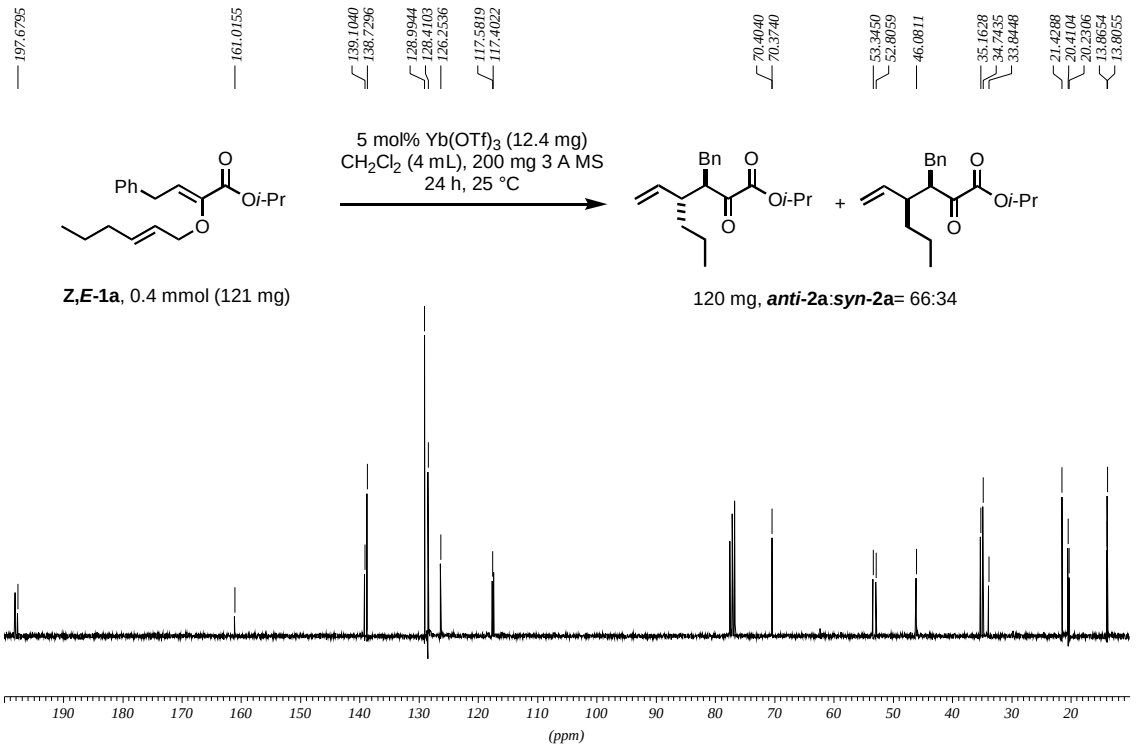
Z,*E*-1a

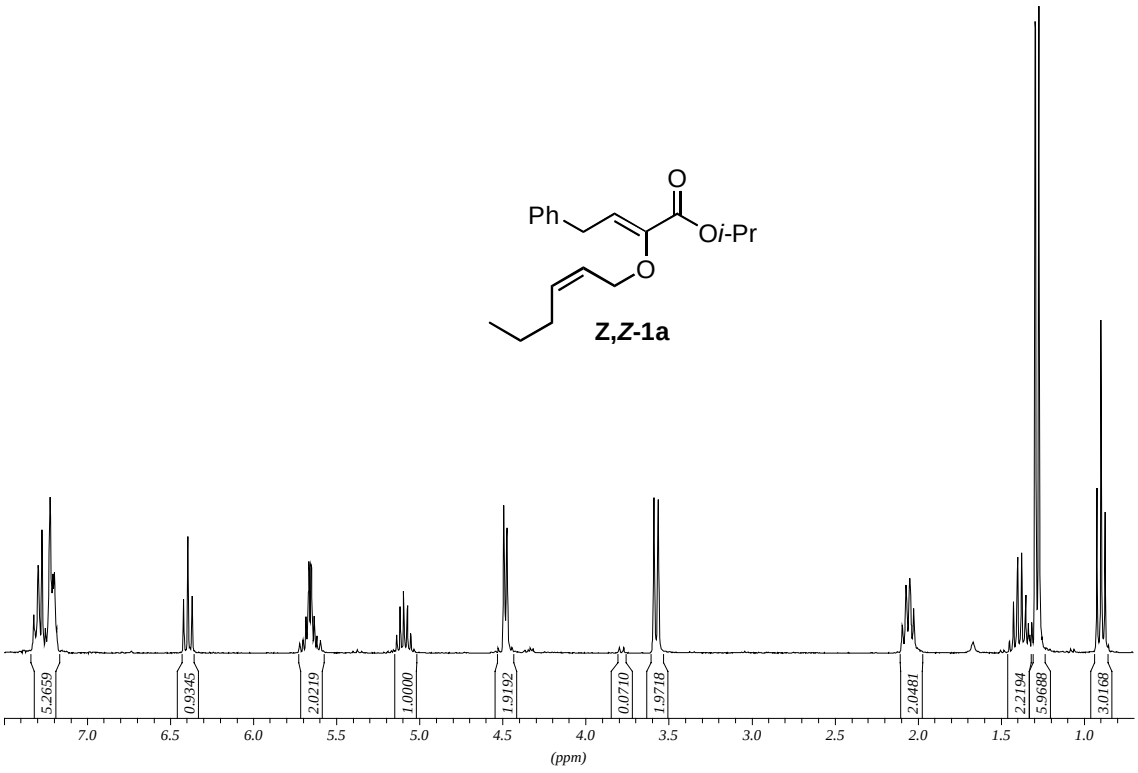


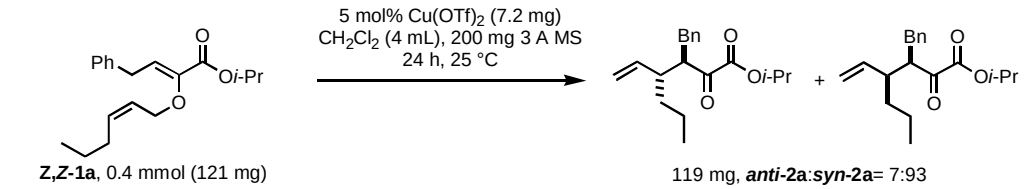
Z,*E*-1a, 0.4 mmol (121 mg)

120 mg, ***anti*-2a**:***syn*-2a**= 66:34



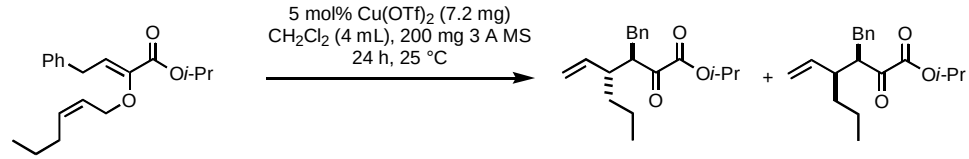

197.6795
161.0155
139.1040
138.7296
128.9944
128.4103
126.2536
117.5819
117.4022
70.4040
70.3740
53.3450
52.8059
46.0811
35.1628
34.7435
33.8448
21.4288
20.4104
20.2306
13.8654
13.8055
5 mol% Yb(OTf)3 (12.4 mg)
CH2Cl2 (4 mL), 200 mg 3 A MS
24 h, 25 °C
Ph
O
Oi-Pr
Bn
+
Z,E-1a, 0.4 mmol (121 mg)
120 mg, anti-2a:syn-2a= 66:34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
(ppm)


Ph
O
Oi-Pr
Z,Z-1a
5.2659
0.9345
2.0219
1.0000
1.9192
0.0710
1.9718
2.0481
2.2194
5.9688
3.0168
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
(ppm)



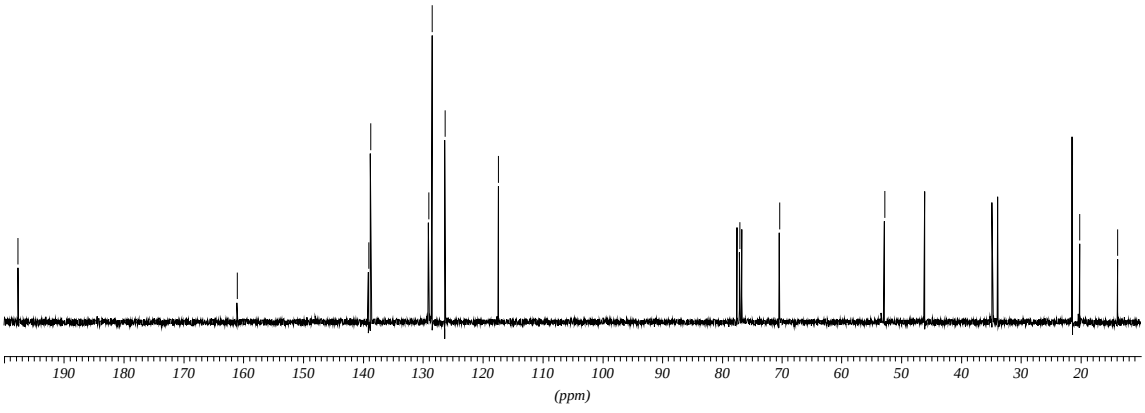
Z,*Z*-1a, 0.4 mmol (121 mg)

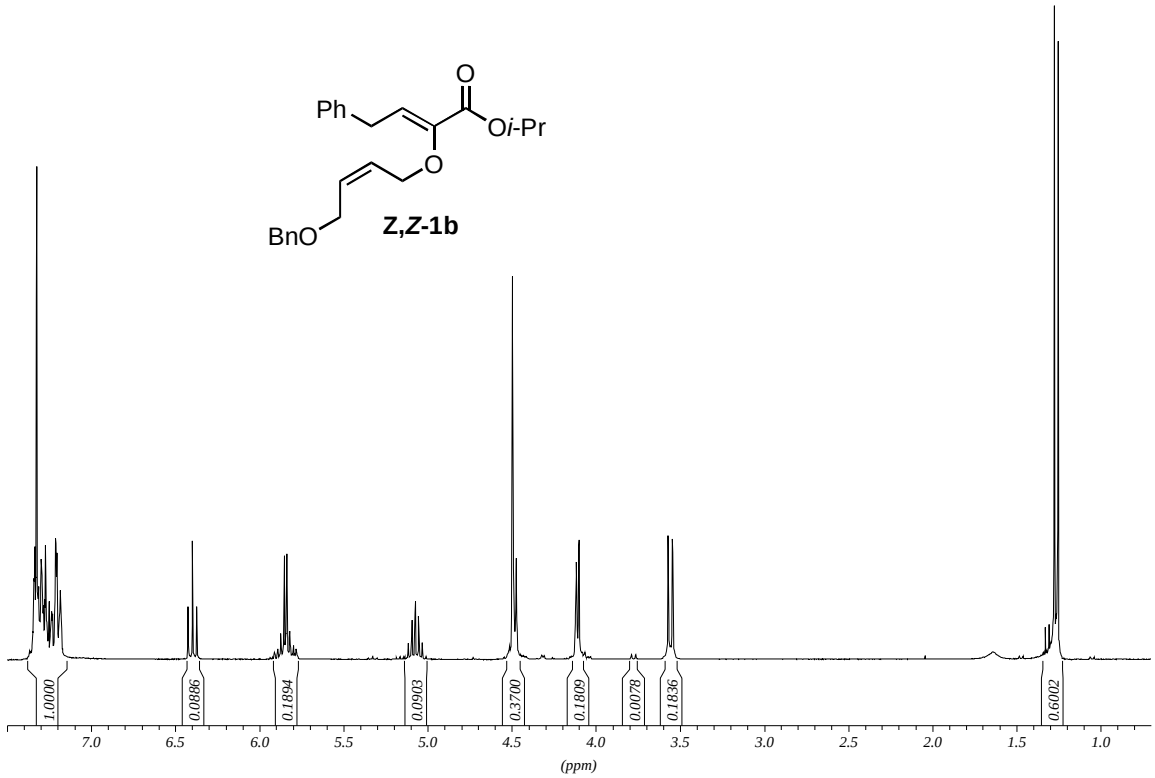
119 mg, ***anti*-2a**:***syn*-2a**= 7:93

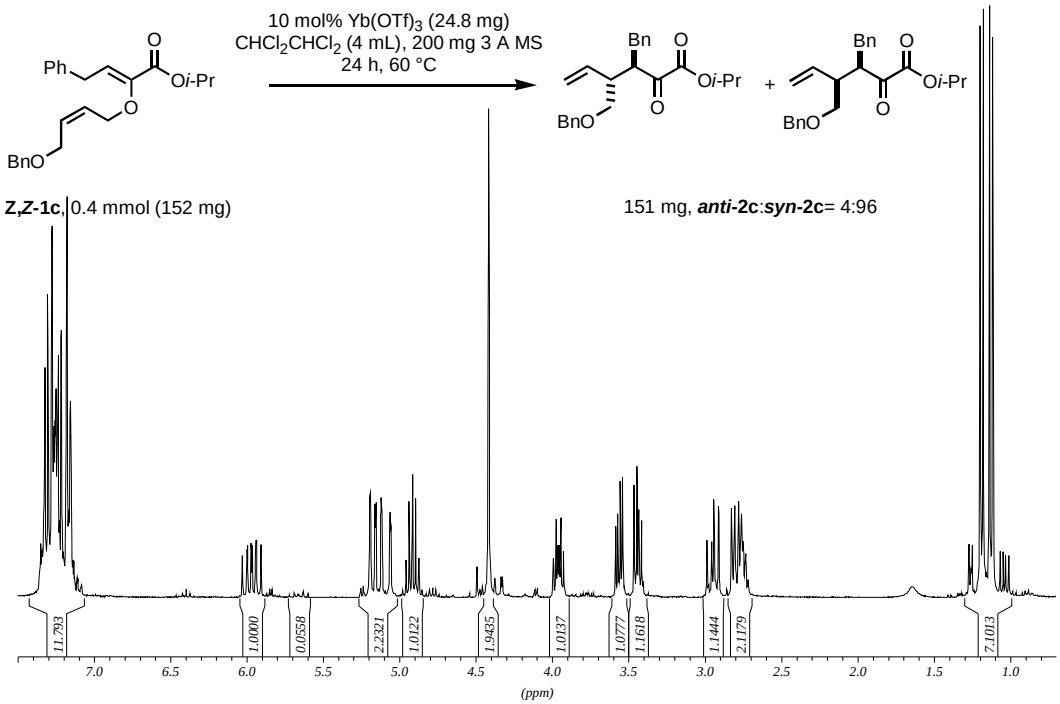


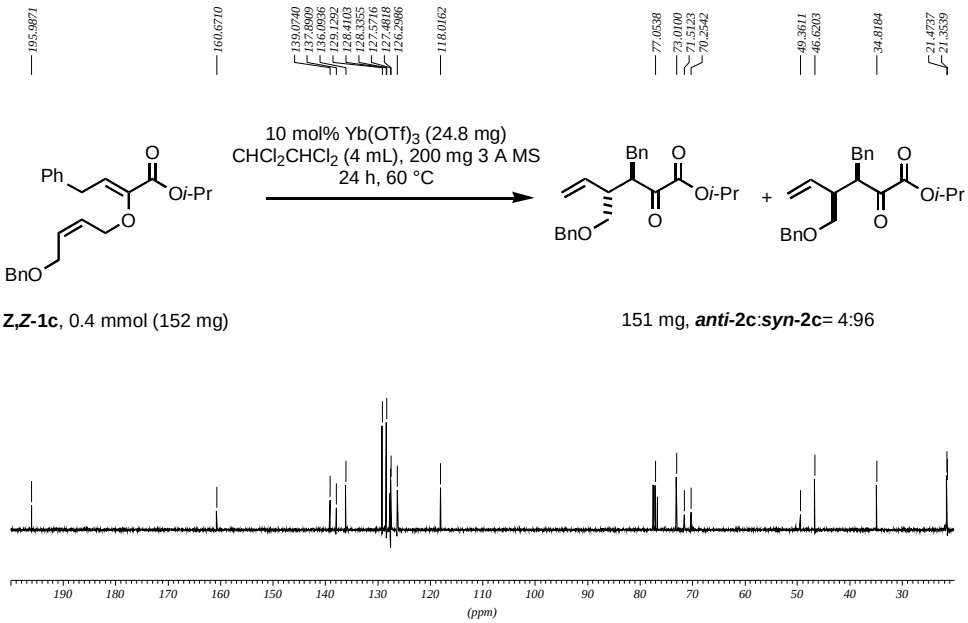
Z,*Z*-1a, 0.4 mmol (121 mg)

119 mg, ***anti*-2a**:***syn*-2a**= 7:93



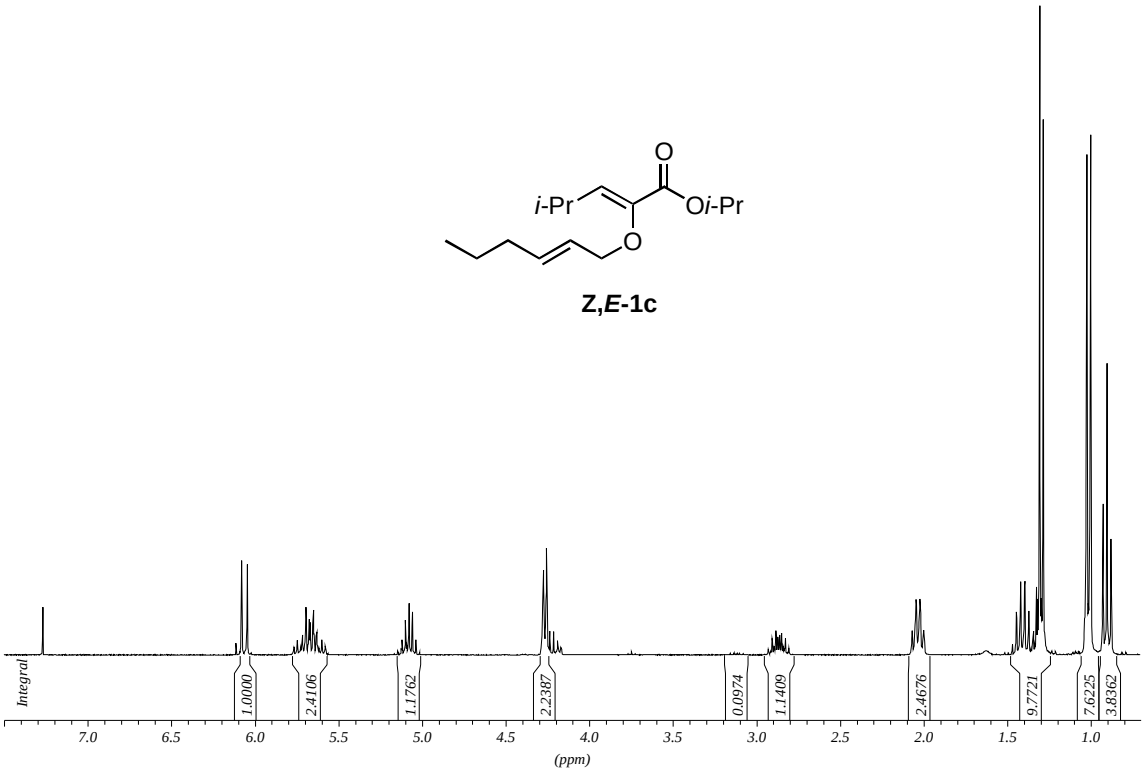

Ph
O
Oi-Pr
O
BnO
Z,Z-1b
1.0000
0.0886
0.1894
0.0903
0.3700
0.1809
0.0078
0.1836
0.6002
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)


10 mol% Yb(OTf)3 (24.8 mg)
CHCl2CHCl2 (4 mL), 200 mg 3 A MS
24 h, 60 °C
Ph
O
Oi-Pr
O
BnO
Bn
O
Oi-Pr
O
BnO
+
Bn
O
Oi-Pr
O
BnO
Z,Z-1c, 0.4 mmol (152 mg)
151 mg, anti-2c:syn-2c= 4:96
11.793
1.0000
0.0558
2.2321
1.0122
1.9435
1.0137
1.0777
1.1618
1.1444
2.1179
7.1013
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)

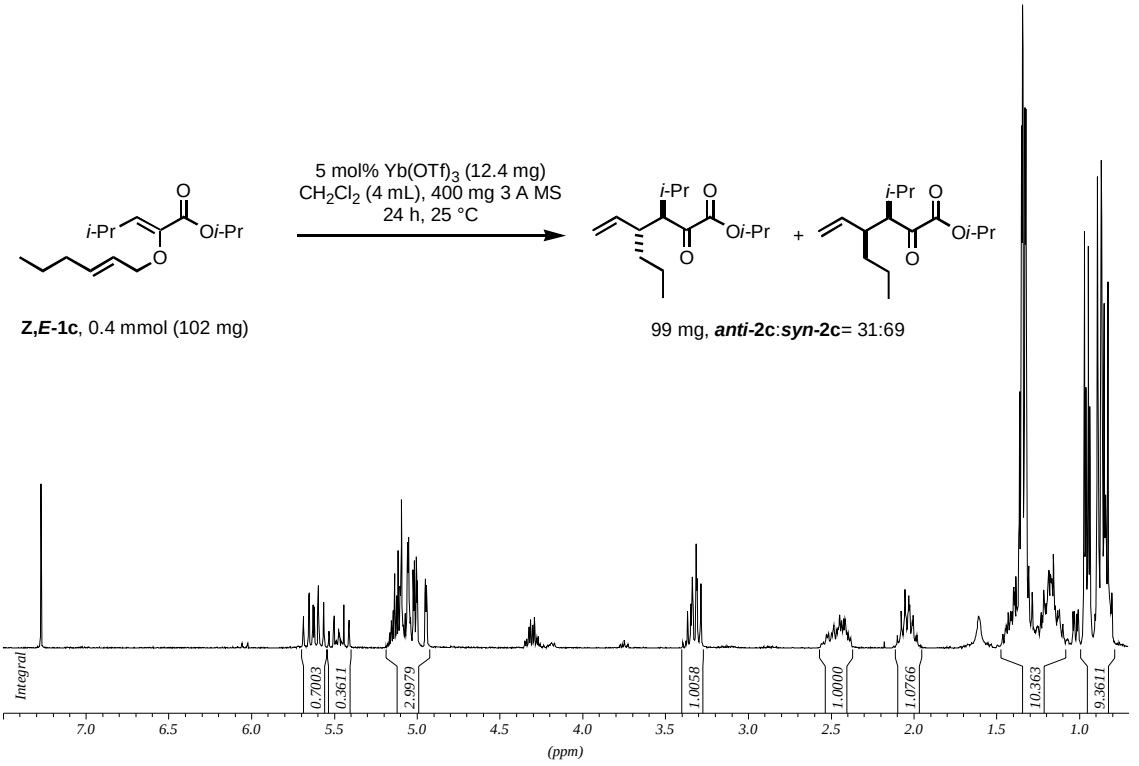


Z,*Z*-1c, 0.4 mmol (152 mg)

151 mg, ***anti*-2c**:***syn*-2c**= 4:96

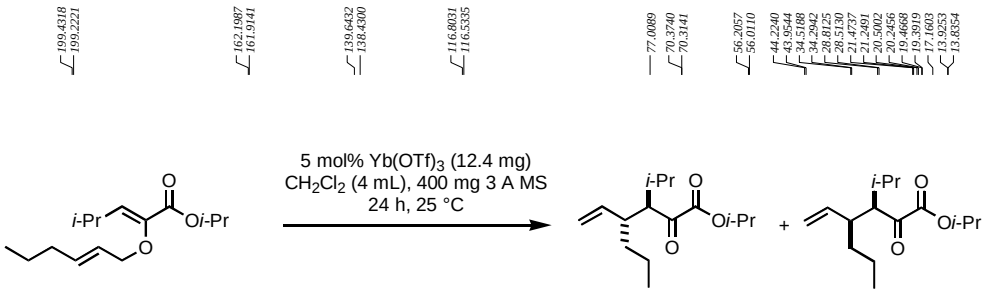


Z,*E*-1c



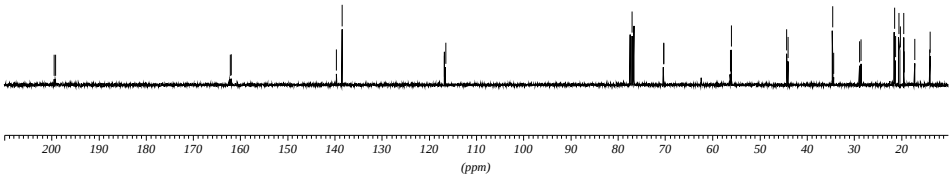
Z,*E*-1c, 0.4 mmol (102 mg)

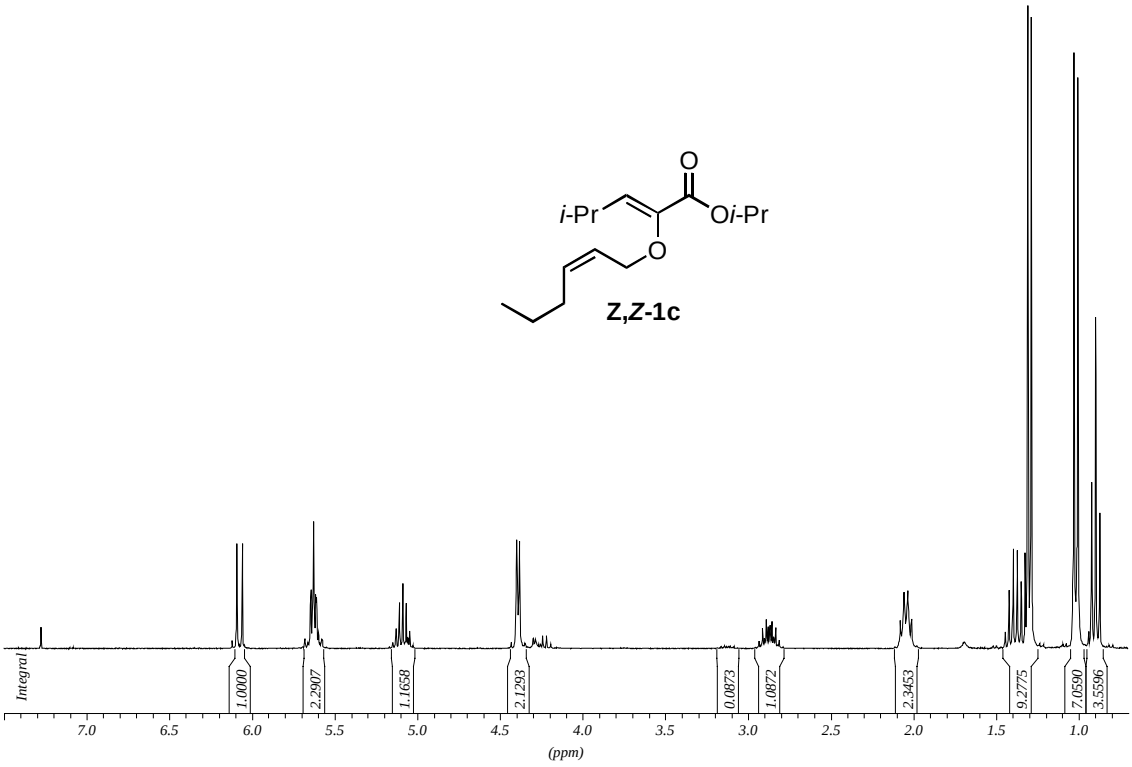
99 mg, ***anti*-2c**:***syn*-2c**= 31:69

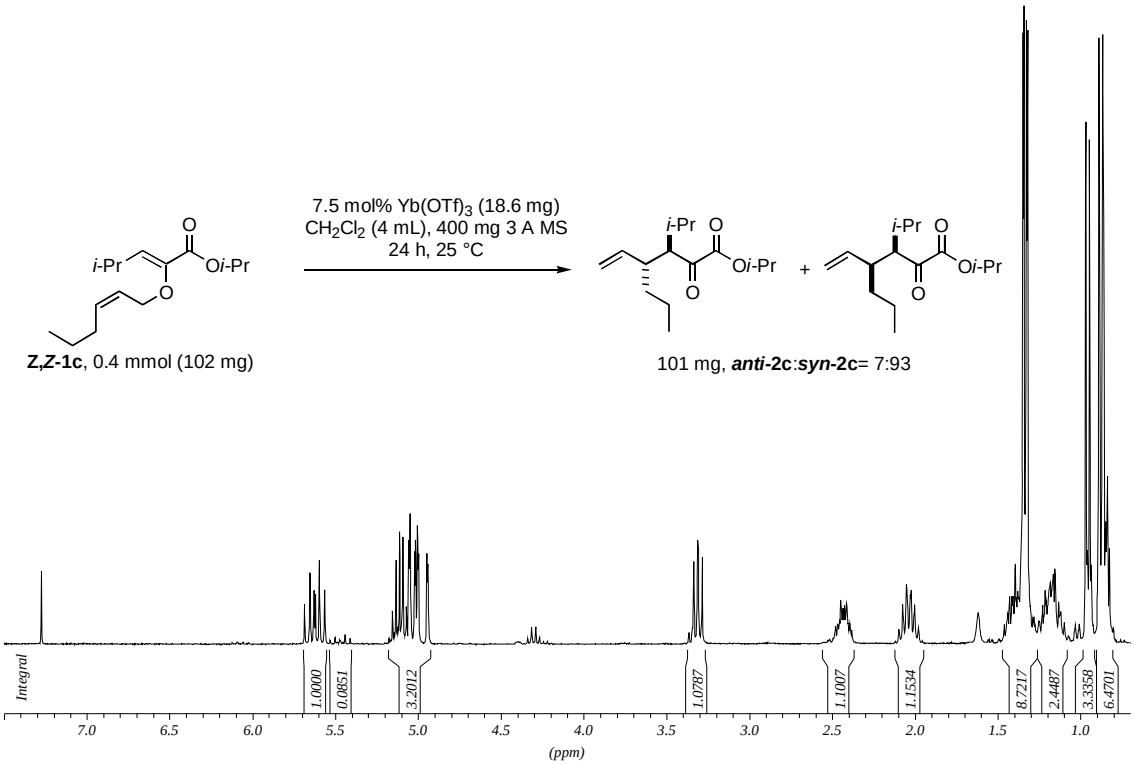


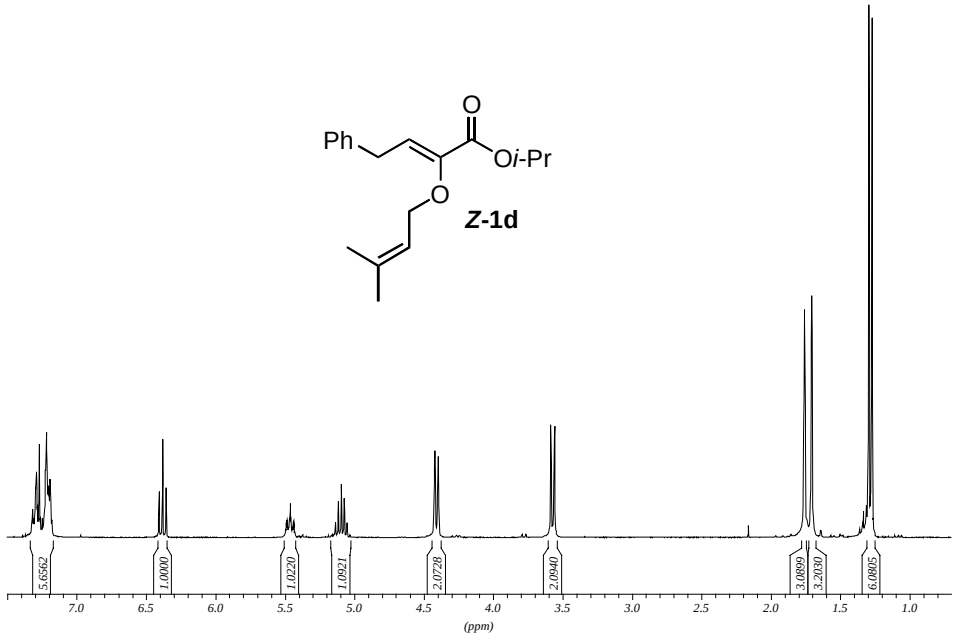
***Z*,*E*-1c**, 0.4 mmol (102 mg)

99 mg, ***anti*-2c**:***syn*-2c**= 31:69






7.5 mol% Yb(OTf)3 (18.6 mg)
CH2Cl2 (4 mL), 400 mg 3 A MS
24 h, 25 °C
i-Pr
Oi-Pr
O
+
Z,Z-1c, 0.4 mmol (102 mg)
101 mg, anti-2c:syn-2c= 7:93
Integral
1.0000
0.0851
3.2012
1.0787
1.1007
1.1534
8.7217
2.4487
3.3358
6.4701
(ppm)


Ph
Oi-Pr
O
Z-1d
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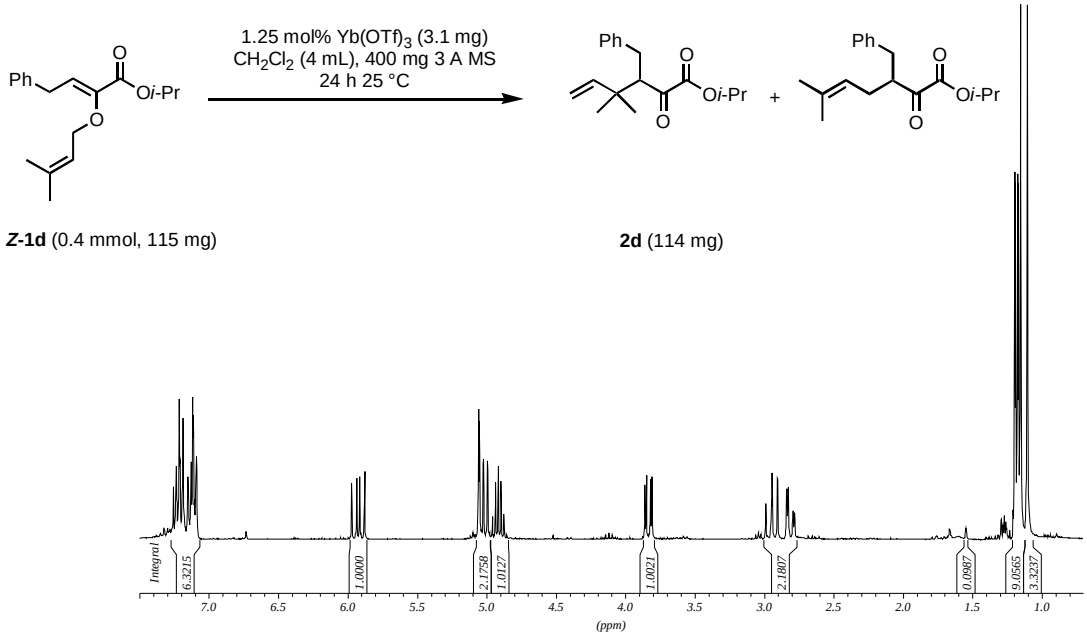
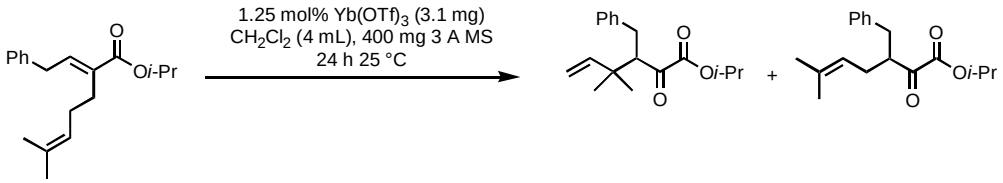
2.0940
3.0899
3.2030
6.0805
(ppm)



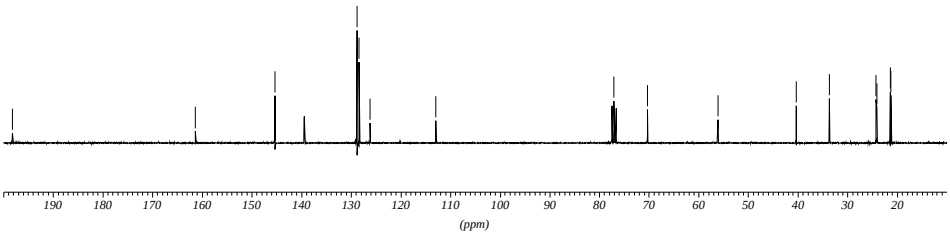
***Z*-1d** (0.4 mmol, 115 mg)

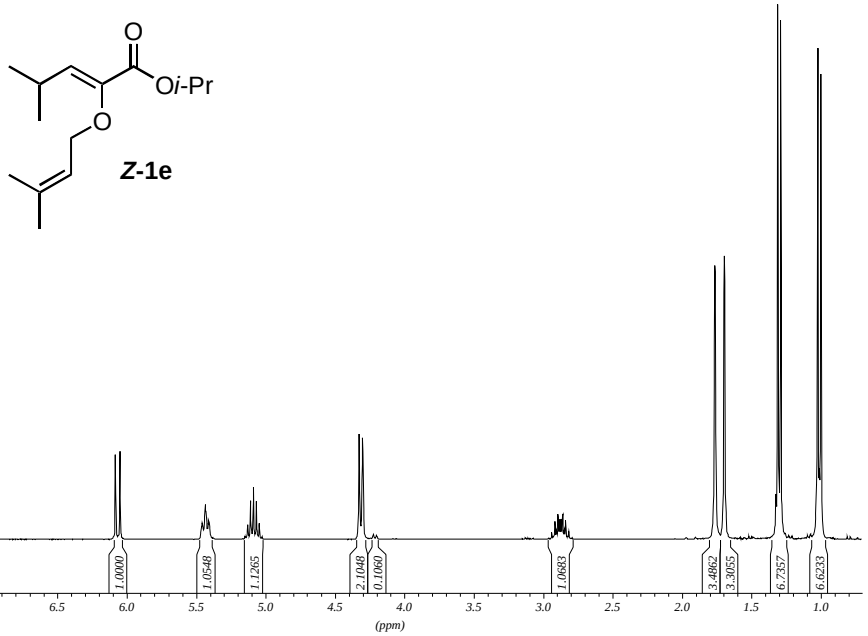
2d (114 mg)

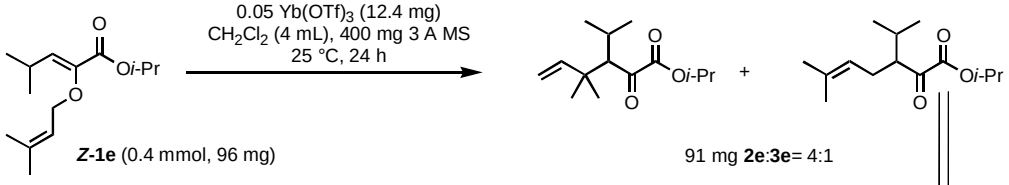


***Z*-1d** (0.4 mmol, 115 mg)

2d (114 mg)

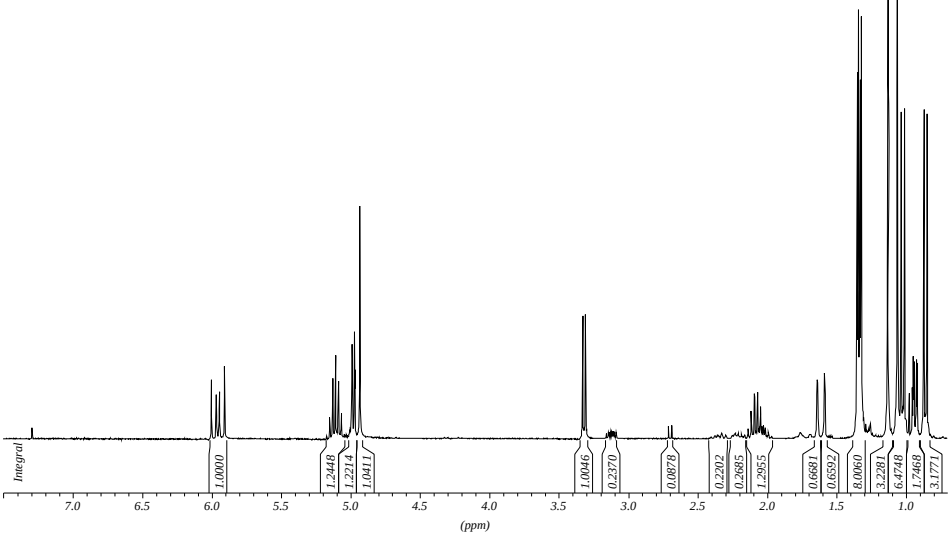


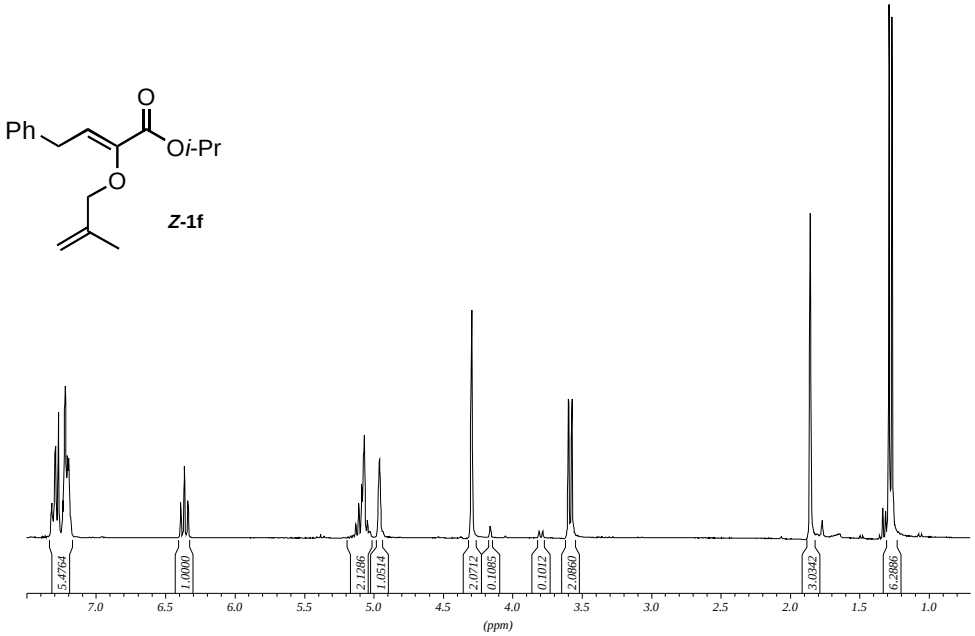


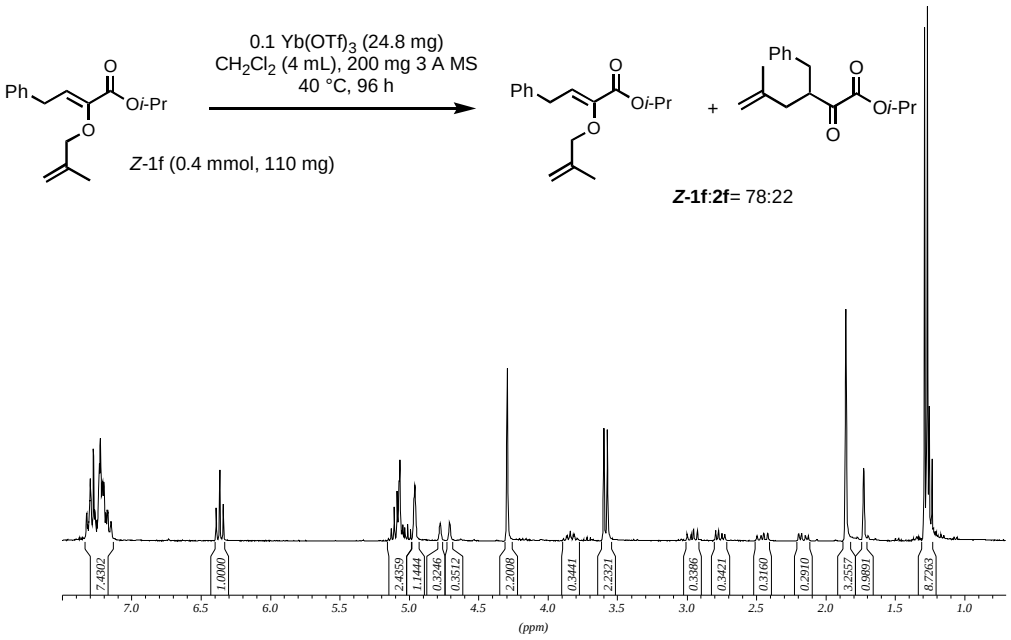


***Z*-1e** (0.4 mmol, 96 mg)

91 mg **2e**:**3e**= 4:1




Ph
O
Oi-Pr
O
Z-1f
5.4764
1.0000
2.1286
1.0514
2.0712
0.1085
0.1012
2.0860
3.0342
6.2886
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)


0.1 Yb(OTf)3 (24.8 mg)
CH2Cl2 (4 mL), 200 mg 3 A MS
40 °C, 96 h
Ph
O
Oi-Pr
O
Z-1f (0.4 mmol, 110 mg)
Ph
O
Oi-Pr
O
+
Ph
O
Oi-Pr
O
Z-1f:2f= 78:22
7.4302
1.0000
2.4359
1.1444
0.3246
0.3512
2.2008
0.3441
2.2321
0.3386
0.3421
0.3160
0.2910
3.2557
0.9891
8.7263
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
(ppm)