$PdCl_2$-Catalyzed Two-Component Cross-coupling Cyclization of 2,3-Allenoic Acids with 2,3-Allenols. An Efficient Synthesis of 4-(1', 3'-Dien-2'-yl)-2(5H)-furanone Derivatives

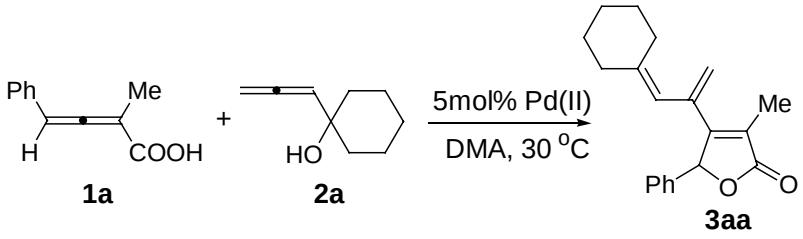
Shengming Ma* and Zhenhua Gu

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, P. R. China

E-mail: masm@mail.sioc.ac.cn Fax: (+86) 21-64167510

Supporting Information

Table S1. Pd(II)-catalyzed cross-coupling cyclization of 2,3-allenoic acid **1a** and 2,3-allenol **2a**[a]

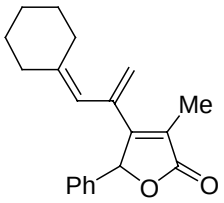


1a **2a** **3aa**

Entry	Catalyst	Solvent	Time (h)	Yield of **3aa** (%)
1	$PdCl_2$	$Cl_2CHCHCl_2$	15	0
2	$PdCl_2$	CH_3CN	13	0
3	$PdCl_2$	NMP	16	45
4	$PdCl_2$	DMSO	7.5	30
5	$PdCl_2$	DMF	16.5	43
6	$PdCl_2$	DMA	16.5	51
7	$Pd(OAc)_2$	DMA	11	0
8	$PdCl_2(PPh_3)_2$	DMA	11	0

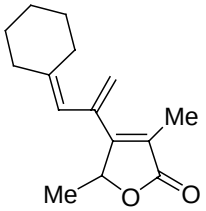
[a] A solution of **1a** (0.25 mmol), **2a** (0.325 mmol), and Pd(II) (5 mol%) in 2 mL of solvent was stirred at 30 °C for the indicated time in the table.

1. 4-(1'-Cyclohexylidenemethyl-vinyl)-3-methyl-5-phenyl-5H-furan-2-one (**3aa**):



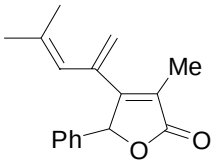
General Procedure for $PdCl_2$-catalyzed cross-coupling cyclization of 2,3-allenoic acids **1** and 2,3-allenols **2**: $PdCl_2$ (2 mg, 4.5 mol%) was added to a mixture of **1a** (44 mg, 0.253 mmol) and **2a** (54 mg, 0.39 mmol) in DMA (3 mL). The mixture was stirred at 30 ^{o}C for 22 h. After complete consumption of starting material as determined by TLC, the mixture was diluted with ether, washed with water, and dried by Na_2SO_4. After evaporation, the residue was purified via flash chromatography on silica gel (petroleum ether/ ethyl acetate =15:1) to afford liquid **3aa** (50 mg, 67%). liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.12 (m, 5 H), 5.86 (s, 1 H), 5.58 (s, 1 H), 5.21 (s, 1 H), 5.17 (s, 1 H), 2.20-1.98 (m, 7 H), 1.64-1.20 (m, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.1, 26.2, 27.3, 28.1, 29.3, 37.0, 83.5, 119.8, 121.5, 123.9, 127.2, 128.5, 128.9, 135.1, 136.7, 145.7, 159.6, 174.5; EIMS: *m/z* 294 (M^+, 8.20), 105 (100); IR (neat): 3032, 2927, 2854, 1756, 1651, 1496, 1447 cm^{-1}; HRMS: cacld. for $C_{20}H_{23}O_2^+$ [M+1], 295.1693; found, 295.1715.

2. 4-(1'-Cyclohexylidenemethylethenyl)-3,5-dimethyl-5H-furan-2-one (**3ba**):



The reaction of **1b** (33 mg, 0.295 mmol), **2a** (62 mg, 0.45 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 3 mL of DMA afforded **3ba** (42 mg, 61%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.71 (s, 1 H), 5.32 (s, 1 H), 5.28 (s, 1 H), 5.10-5.00 (m, 1 H), 2.38-2.08 (m, 4 H), 1.93 (d, *J* = 1.8 Hz, 3 H), 1.78-1.41 (m, 6 H), 1.38 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 9.8, 18.8, 26.3, 27.5, 28.2, 29.5, 37.2, 78.1, 119.8, 120.5, 123.1, 137.0, 145.9, 161.9, 174.4; EIMS *m/z* 232 (M^+, 13.92), 43 (100); IR (neat): 2928, 2854, 1755, 1648 cm^{-1}; HRMS: cacld. for $C_{15}H_{20}O_2$ [M^+], 232.1463; found, 232.1458.

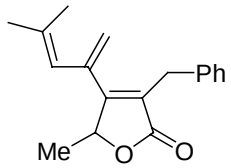
3. 3-Methyl-4-(3'-methyl-1'-methylene-but-2'-enyl)-5-phenyl-5H-furan-2-one (3ab):



The reaction of **1a** (44 mg, 0.253 mmol), **2b** (50 mg, 0.510 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 2 mL of DMA afforded **3ab** (38 mg, 59%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.30 (m, 3 H), 7.23-7.13 (m, 2 H), 5.85 (s, 1 H), 5.63 (s, 1 H), 5.22 (s, 1 H), 5.17 (s, 1 H), 2.03 (s, 3 H), 1.76 (s, 3 H), 1.52 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.1, 19.0, 26.0, 83.6, 121.6, 122.9, 123.9, 127.3, 128.6, 129.0, 135.2, 137.3, 138.3, 159.8, 174.7; EIMS: m/z 254 (M^+, 13.36), 105 (100); IR (neat): 2914, 1755, 1655, 1455 cm^{-1}; HRMS: cacld. for $C_{17}H_{18}O_2$ [M^+], 254.1301; found, 254.1310.

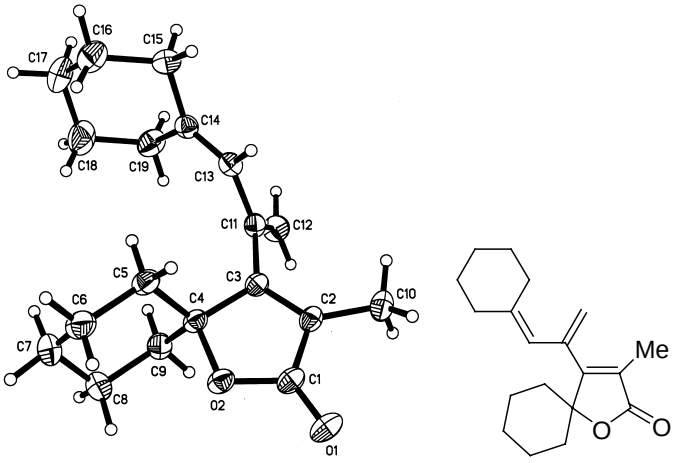
4. 3-Benzyl-5-methyl-4-(3'-methyl-1'-methylenebut-2'-enyl)-5H-furan-2-one

(**3cb**):



The reaction of **1c** (47 mg, 0.25 mmol), **2b** (37 mg, 0.375 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 3 mL of DMA afforded **3cb** (35 mg, 52%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.13 (m, 5 H), 5.72 (s, 1 H), 5.30 (s, 1 H), 5.29 (s, 1 H), 5.08 (q, *J* = 6.6 Hz, 1 H), 3.79 (d, *J* = 14.7 Hz, 1 H), 3.64 (d, *J* = 14.7 Hz, 1 H), 1.80 (s, 3 H), 1.67 (s, 3 H), 1.40 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 19.0, 19.3, 26.3, 29.8, 78.3, 120.9, 122.7, 126.1, 126.2, 128.3, 128.4, 137.2, 138.3, 138.8, 163.3, 173.9; EIMS *m/z* 268 (M^+, 25.07), 91 (100); IR (neat): 2929, 1755, 1651, 1603, 1495, 1453 cm^{-1}; HRMS: cacld. for $C_{18}H_{20}O_2$ [M^+], 268.1463; found, 268.1498.

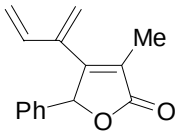
5. 4-(1'-Cyclohexylidenemethylethenyl)-3-methyl-1-oxa-spiro[4.5]dec-3-en-2-one (**3da**):



The reaction of **1d** (41 mg, 0.247 mmol), **2a** (55 mg, 0.399 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 3 mL of DMA afforded **3da** (53 mg, 75%): Solid, m.p. 73-75□

(Chloroform). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.54 (s, 1 H), 5.24 (s, 1 H), 5.09 (d, *J* = 1.8 Hz, 1 H), 2.34 (t, *J* = 5.4 Hz, 2 H), 2.17 (br, 1 H), 1.83 (s, 3 H), 1.80-1.65 (m, 7 H), 1.65-1.40 (m, 7 H), 1.23-1.08 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 9.3, 22.2, 24.6, 26.4, 27.7, 28.3, 29.5, 34.0, 37.5, 87.7, 119.6, 120.2, 123.4, 137.4, 145.2, 167.4, 173.7; EIMS *m/z* 286 (M^+, 23.18), 188 (100); IR (KBr): 2930, 2854, 1755 cm^{-1}; Anal. calcd. for $C_{19}H_{26}O_2$: (%) C 79.68, H 9.15; found, C 79.43, H 9.17; Crystal data for **3da**: $C_{19}H_{26}O_2$, MW = 286.40, Monoclinic, space group C2/c, final R indices [$I > 2\sigma(I)$], R1 = 0.0534, wR2 = 0.1292, a = 28.423(3) Å, *b* = 6.5858(8) Å, c = 17.641(2) Å, $\alpha = 90^{o}$, $\beta = 97.363(2)^{o}$, $\gamma = 90^{o}$, V = 3275.0(7) $Å^3$, Crystal size: 0.432*0.409* 0.327 mm, T = 293(2) K, absorption coefficient: 0.073 mm^{-1}, wavelength: 0.71073 Å, Z = 8, reflections collected/unique: 9178 / 3565 (R_{int} = 0.0589), Data: 3536, restraints: 0, parameters: 252. Supplementary crystallographic dada have been deposited at the Cambridge Crystallographic Data Center. CCDC 256927.

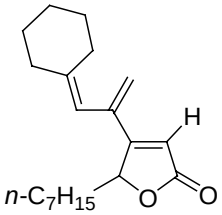
6. 3-Methyl-4-(1-methylene-allyl)-5-phenyl-5H-furan-2-one (**3ac**):



The reaction of **1a** (43 mg, 0.247 mmol), **2c** (44 mg, 0.628 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 3 mL of DMA afforded **3ac** (33 mg, 59%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.22 (m, 3 H), 7.21-7.16 (m, 2 H), 6.30 (dd, *J* = 11.0, 17.4 Hz, 1 H), 5.91 (d, *J* = 1.5 Hz, 1 H), 5.31 (s, 1 H), 5.15 (d, *J* = 11.0 Hz, 1 H), 5.00 (d, *J* = 17.4 Hz, 1 H), 4.88 (s, 1 H), 1.89 (t, *J* = 1.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 9.8, 84.0,

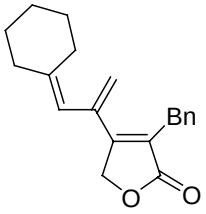
117.4, 120.4, 125.3, 126.5, 128.5, 128.9, 134.4, 135.3, 138.7, 159.0, 174.3; EIMS: m/z 226 (M^+, 1.07), 84 (100); IR (neat): 1760, 1674 cm^{-1}; HRMS: cacld. for $C_{15}H_{14}O_2$ [M^+], 226.0994; found, 226.0980.

7. 4-(1'-Cylohexylidenemethylethenyl)-5-heptyl-5H-furan-2-one (**3ea**):



The reaction of **1e** (45 mg, 0.247 mmol), **2a** (69 mg, 0.50 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 3 mL of DMA afforded **3ea** (39 mg, 52%): liquid; ^1H NMR (300 MHz, $CDCl_3$): δ 5.92 (s, 1 H), 5.72 (s, 1 H), 5.44 (s, 1 H), 5.32 (s, 1 H), 5.22-4.97 (m, 1 H), 2.30-2.08 (m, 4 H), 2.08-1.92 (m, 1 H), 1.72-1.42 (m, 7 H), 1.42-1.15 (m, 10 H), 0.87 (t, *J* = 6.0 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.0, 22.5, 24.3, 26.4, 27.9, 28.5, 29.0, 29.1, 29.8, 31.6, 33.7, 37.1, 82.2, 116.0, 118.3, 120.9, 136.5, 146.7, 167.9, 173.1; EIMS *m/z* 302 (M^+, 7.37), 41 (100.); IR (neat): 2927, 2855, 1758 cm^{-1}; HRMS: cacld. for $C_{20}H_{30}O_2$ [M^+], 302.2246; found, 302.2232.

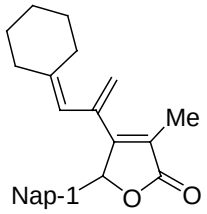
8. 3-Benzyl-4-(1'-cyclohexylidenemethylethenyl)-5H-furan-2-one (**3fa**):



The reaction of **1f** (43 mg, 0.247 mmol), **2a** (51 mg, 0.370 mmol), $PdCl_2$ (2 mg, 0.0113

mmol) in 3 mL of DMA afforded **3fa** (45 mg, 62%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.12 (m, 5 H), 5.76 (s, 1 H), 5.40 (s, 1 H), 5.25 (s, 1 H), 4.85 (s, 2 H), 3.81 (s, 2 H), 2.22-2.08 (m, 4 H), 1.67-1.40 (m, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 26.3, 27.6, 28.2, 29.7, 29.9, 37.1, 70.7, 119.5, 120.6, 126.28, 126.35, 128.38, 128.41, 137.2, 138.3, 146.1, 156.9, 175.1; EIMS *m/z* 294 (M^+, 26.57), 159 (100.); IR (neat): 3086, 3061, 3028, 2928, 2853, 1753 cm^{-1}; HRMS: cacld. for $C_{20}H_{23}O_2$ [M^++1], 295.1692; found, 295.1718.

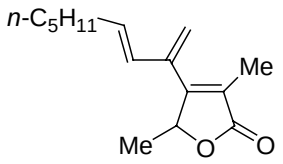
9. 4-(1'-cyclohexylideneprop-2'-en-2'-yl)-3-methyl-5-(naphthalen-1''-yl)furan-2(5H)-one (**3ga**):



The reaction of **1g** (56 mg, 0.250 mmol), **2a** (52 mg, 0.377 mmol), $PdCl_2$ (3 mg, 0.0169 mmol) in 3 mL of DMA afforded **3ga** (48 mg, 56%): Solid, m.p. 138-140 ^{o}C (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ8.16 (d, *J* = 8.5 Hz, 1 H), 7.85 (t, *J* = 8.5 Hz, 2 H), 7.62-7.45 (m, 2 H), 7.40 (t, *J* = 7.3 Hz, 1 H), 7.23 (d, *J* = 7.3 Hz, 1 H), 6.71 (s, 1 H), 5.59 (s, 1 H), 5.26 (s, 1 H), 5.15 (s, 1 H), 2.15 (d, *J* = 1.5 Hz, 3 H), 2.12- 1.90 (m, 4 H), 1.52-1.22 (m, 5 H), 1.18-1.01 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.6, 26.3, 27.3, 28.0, 29.3, 37.1, 79.4, 119.7, 121.9, 122.8, 125.1, 125.3, 125.8, 125.9, 126.7, 128.8, 129.8, 131.1, 131.9, 133.8, 137.2, 146.0, 159.2, 174.6; EIMS: *m/z* 344 (M^+, 37.77), 141 (100); IR (KBr): 2926, 2851, 1756, 1652, 1599, 1511, 1446 cm^{-1}; Anal.

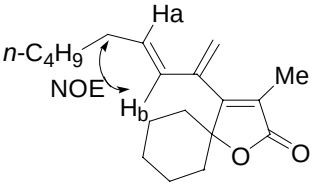
calcd. for $C_{24}H_{24}O_2$: (%) C 83.69, H 7.02; found, C 83.73, H 7.05.

10. 3,5-Dimethyl-4-(1'-methyleneoct-2'(*E*)-enyl)-5H-furan-2-one (*E*-**3bd**):



The reaction of **1b** (33 mg, 0.295 mmol), **2d** (104 mg, 0.743 mmol), $PdCl_2$ (3 mg, 0.0169 mmol) in 3 mL of DMA afforded *E*-**3bd** (36 mg, 52%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.13 (d, *J* = 15.9 Hz, 1 H), 5.53 (td, *J* = 6.9, 15.9 Hz, 1 H), 5.32 (s, 1 H), 5.10-5.00 (m, 1 H), 4.96 (s, 1 H), 2.11 (q, *J* = 6.9 Hz, 2 H), 1.80 (d, *J* = 2.1 Hz, 3 H), 1.44-1.20 (m, 9 H), 0.89 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 9.6, 14.0, 18.3, 22.4, 28.6, 31.3, 32.6, 79.0, 116.6, 124.9, 128.7, 135.3, 139.0, 161.6, 174.1; EIMS *m/z* 234 (M^+, 17.55), 43 (100); IR (neat): 2957, 2928, 2857, 1762 cm^{-1}; HRMS: cacld. for $C_{15}H_{20}O_2$ [M^+], 234.1620; found, 234.1619.

11. 3-Methyl-4-(1'-methyleneoct-2'-enyl)-1-oxa-spiro[4.5]dec-3-en-2-one (*E*-**3dd**):

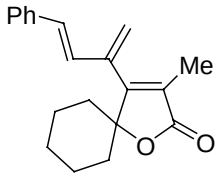


(*E*)-**3dd**

The reaction of **1d** (42 mg, 0.253 mmol), **2d** (52 mg, 0.371 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 3 mL of DMA afforded *E*-**3dd** (40 mg, 55%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.10 (d, *J* = 15.3 Hz, 1 H), 5.42 (td, *J* = 6.9, 15.3 Hz, 1 H), 5.29 (s, 1 H), 4.86 (s, 1 H), 2.09 (q, *J* = 6.9 Hz, 2 H), 1.80-1.60 (m, 10 H), 1.60-1.44 (m, 2 H),

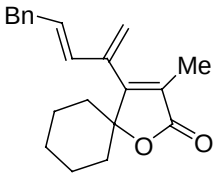
1.42-1.10 (m, 7 H), 0.88 (t, J = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 9.1, 14.0, 22.1, 22.4, 24.4, 28.7, 31.2, 32.5, 33.8, 87.9, 116.1, 124.9, 129.0, 135.0, 139.3, 165.3, 173.5; EIMS *m/z* 288 (M^+, 37.41), 41 (100.); IR (neat): 2931, 2857, 1756 cm^{-1}; HRMS: cacld. for $C_{19}H_{29}O_2$ [M^++1], 289.2162; found, 289.2173.

12. 3-Methyl-4-(1'-methylene-3'-phenyl-2'(*E*)-propenyl)-1-oxa-spiro[4.5]dec-3-en-2-one (*E*-**3de**):



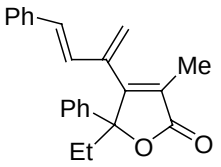
The reaction of **1d** (41 mg, 0.247 mmol), **2e** (92 mg, 0.630 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 3 mL of DMA afforded *E*-**3de** (46 mg, 63%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.23 (m, 5 H), 6.85 (d, J = 16.5 Hz, 1 H), 6.26 (d, J = 16.5 Hz, 1 H), 5.54 (s, 1 H), 5.07 (s, 1 H), 1.85-1.68 (m, 10 H), 1.68-1.50 (m, 2 H), 1.23-1.07 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 9.2, 22.1, 24.4, 33.9, 88.0, 118.8, 125.6, 126.6, 127.6, 128.3, 128.7, 131.9, 136.1, 139.2, 164.6, 173.3; EIMS *m/z* 294 (M^+, 55.81), 84 (100.); IR (neat): 2930, 2856, 1753 cm^{-1}; HRMS: cacld. for $C_{20}H_{23}O_2$ [M^++1], 295.1693; found, 295.1700.

13. 3-Methyl-4-(1'-methylene-4'-phenylbut-2'(*E*)-enyl)-1-oxa-spiro[4.5]dec-3-en-2-one (*E*-**3df**):



The reaction of **1d** (42 mg, 0.253 mmol), **2f** (60 mg, 0.375 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 3 mL of DMA afforded *E*-**3df** (58 mg, 74%): Solid, m.p. 109-111 (ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.10 (m, 5 H), 6.17 (d, *J* = 15.3 Hz, 1 H), 5.58 (td, *J* = 7.5, 15.3 Hz, 1 H), 5.34 (s, 1 H), 4.92 (s, 1 H), 3.43 (d, *J* = 7.5 Hz, 2 H), 1.81-1.61 (m, 10 H), 1.55-1.40 (m, 2 H), 1.24-1.06 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 9.1, 22.1, 24.4, 33.8, 38.7, 87.8, 117.2, 125.1, 126.2, 128.3, 128.4, 130.2, 132.9, 138.9, 139.2, 164.9, 173.3; EIMS *m/z* 308 (M^+, 13.39), 91 (100.); IR (neat): 3061, 83026, 2934, 2861, 1754 cm^{-1}; HRMS: cacld. for $C_{21}H_{24}O_2$ [M^+], 308.1776; found, 308.1801.

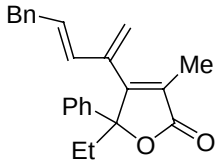
14. 5-Ethyl-3-methyl-4-(1'-methylene-3'-phenyl-2'(*E*)-propenyl)-5-phenyl-5H-furan-2-one (*E*-**3he**):



The reaction of **1h** (51 mg, 0.252 mmol), **2e** (91 mg, 0.623 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 3 mL of DMA afforded *E*-**3he** (55 mg, 66%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.08 (m, 10 H), 6.62 (d, *J* = 15.9 Hz, 1 H), 5.69 (d, *J* = 15.9 Hz, 1 H), 5.47 (s, 1 H), 4.79 (s, 1 H), 2.50-2.34 (m, 1 H), 2.18-1.98 (m, 1 H), 1.78 (s, 3 H), 0.97 (t, *J* = 7.2 Hz, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 8.1, 9.4, 29.7, 91.2, 119.0,

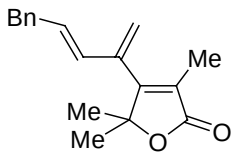
124.8, 125.3, 126.4, 127.3, 127.92, 127.94, 128.3, 128.4, 132.0, 136.1, 137.4, 138.8, 163.5, 173.9; EIMS *m/z* 330 (M^+, 6.42), 84 (100.); IR (neat): 3059, 3027, 2976, 2925, 1758 cm^{-1}; HRMS: cacld. for $C_{23}H_{22}O_2$ [M^+], 330.1620; found, 330.1606.

15. 5-Ethyl-3-methyl-4-(1'-methylene-4'-phenylbut-2'(*E*)-enyl)-5-phenyl-5H-furan-2-one (*E*-**3hf**):



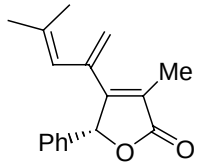
The reaction of **1h** (51 mg, 0.252 mmol), **2f** (61 mg, 0.375 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 3 mL of DMA afforded *E*-**3hf** (71 mg, 82%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.10 (m, 8 H), 6.86 (d, *J* = 6.6 Hz, 2 H), 5.95 (d, *J* = 15.6 Hz, 1 H), 5.29 (s, 1 H), 5.04 (td, *J* = 6.3, 15.6 Hz, 1 H), 4.72 (s, 1 H), 3.25-3.05 (m, 2 H), 2.42-2.28 (m, 1 H), 2.10-1.90 (m, 1 H), 1.71 (s, 3 H), 0.91 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 8.0, 9.4, 29.8, 38.5, 91.1, 117.2, 124.5, 125.2, 126.0, 127.7, 128.1, 128.26, 128.28, 129.8, 132.9, 137.6, 138.7, 139.0, 163.4, 173.8; EIMS *m/z* 344 (M^+, 2.87), 91 (100.); IR (neat): 3061, 3027, 2977, 2939, 1759 cm^{-1}; HRMS: cacld. for $C_{24}H_{24}O_2$ [M^+], 344.1776; found, 344.1786.

16. 3,5,5-trimethyl-4-(5'-phenylpenta-1',3'-dien-2'(*E*)-yl)furan-2(5H)-one (*E*-**3if**):

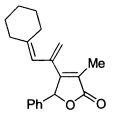


The reaction of **1i** (32 mg, 0.254 mmol), **2f** (61 mg, 0.381 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 2 mL of DMA afforded **3if** (48 mg, 71%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ7.31-7.10 (m, 5 H), 6.18 (d, *J* = 15.1 Hz, 1 H), 5.61 (dt, *J* = 7.2, 15.1 Hz, 1 H), 5.35 (s, 1 H), 4.98 (s, 1 H), 3.44 (d, *J* = 7.2 Hz, 2 H), 1.70 (s, 3 H), 1.41 (s, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ9.2, 25.2, 38.6, 86.1, 117.2, 124.9, 126.2, 128.3, 128.4, 130.0, 132.8, 138.7, 139.1, 164.1, 172.8; EIMS *m/z* 268 (M^+, 59.68), 91 (100.); IR (neat): 2982, 2928, 1758, 1677, 1597, 1494,1454, 1287 cm^{-1}; HRMS: cacld. for $C_{18}H_{21}O_2$ [M^++1], 269.1536; found, 269.1549.

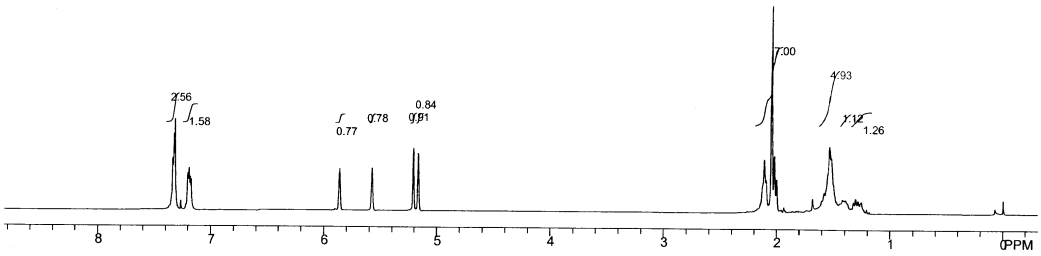
17. R-(-)-3-Methyl-4-(3'-methyl-1'-methylene-but-2'-enyl)-5-phenyl-5H-furan-2-one (**R-(-)-3ab**):

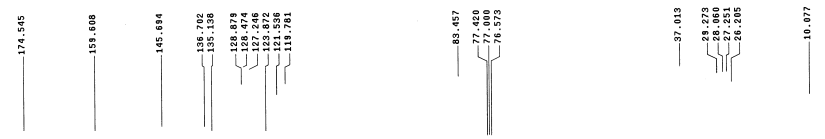


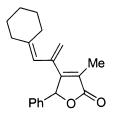
The mixture of **R-(-)-1a** (44 mg, 0.253 mmol, 98% ee), **2b** (49 mg, 0.50 mmol), TFA (23 mg, 0.20 mmol), $PdCl_2$ (2 mg, 0.0113 mmol) in 2 mL of DMA stirred at 35 ^{o}C for 10 hours to afford **R-(-)-3ab** (40 mg, 62%, 98% ee): HPLC conditions: AD column; rate, 0.8 mL/min; eluent, hexane/*i*-PrOH 95/5. λ = 589 nm. $[\alpha]_D^{20}$ = - 437 ^{o} (c = 1.600, $CHCl_3$).


Me
Ph
O
O

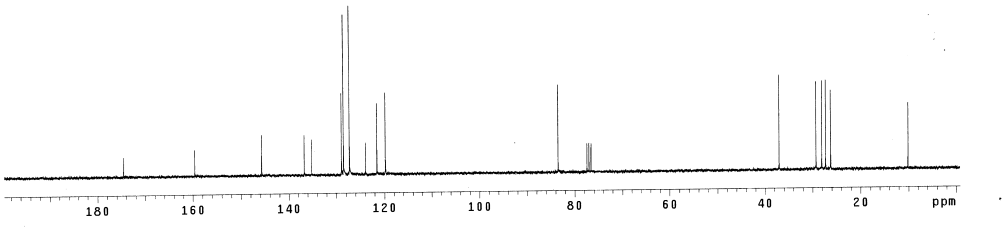
3aa

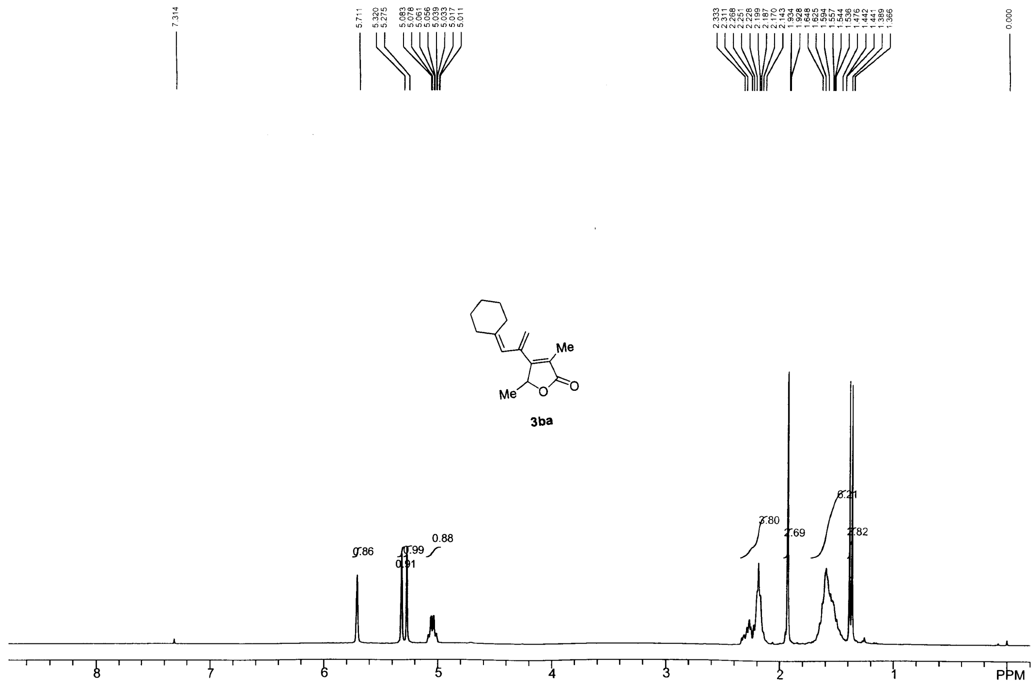

2.56
1.58
0.77
0.78
0.84
0.81
7.00
4.93
1.12
1.26
8
7
6
5
4
3
2
1
PPM

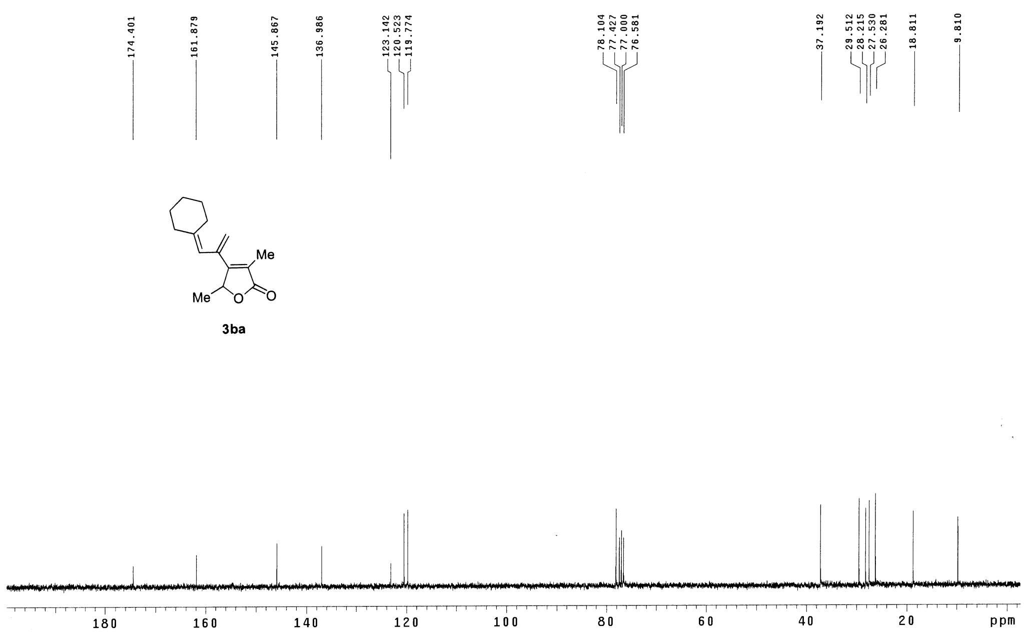


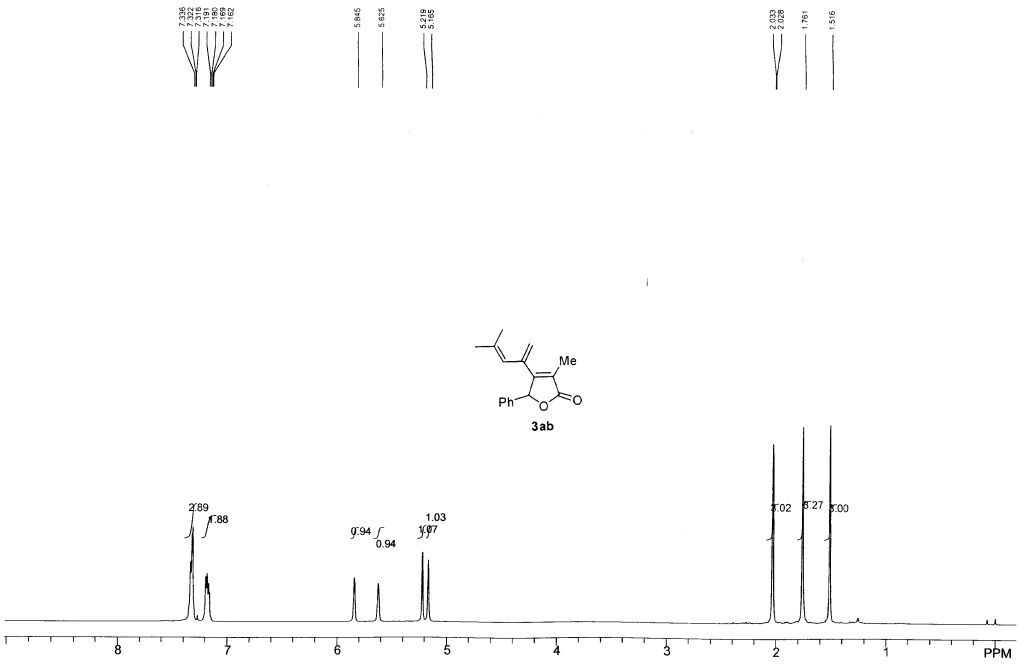

Me
Ph
O
O

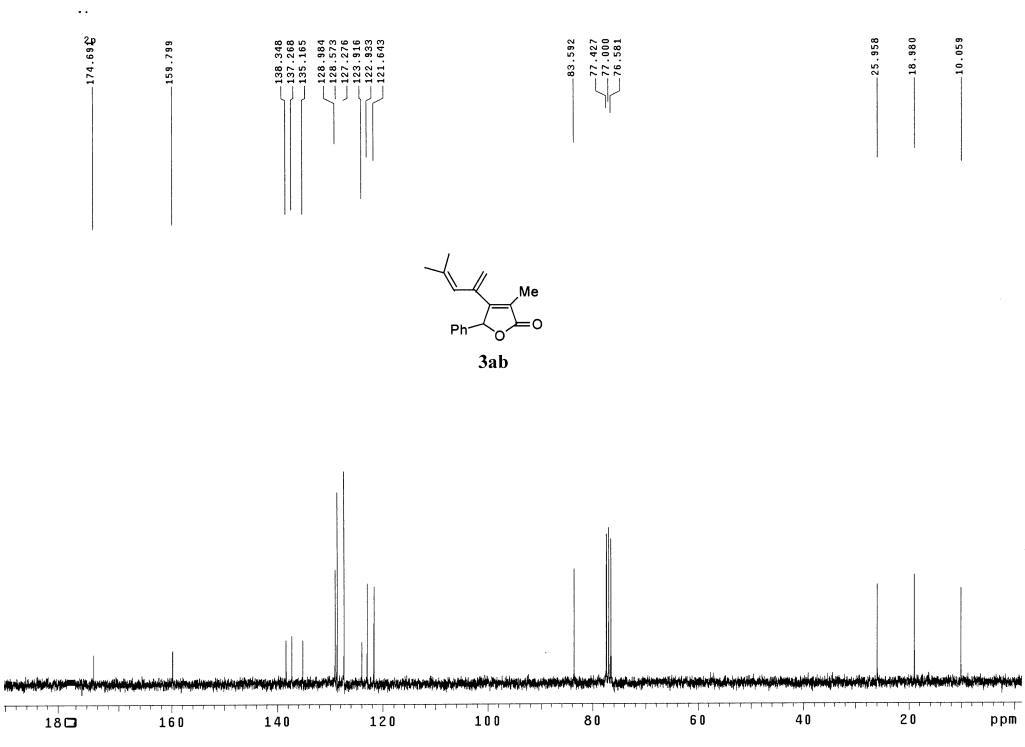
3aa

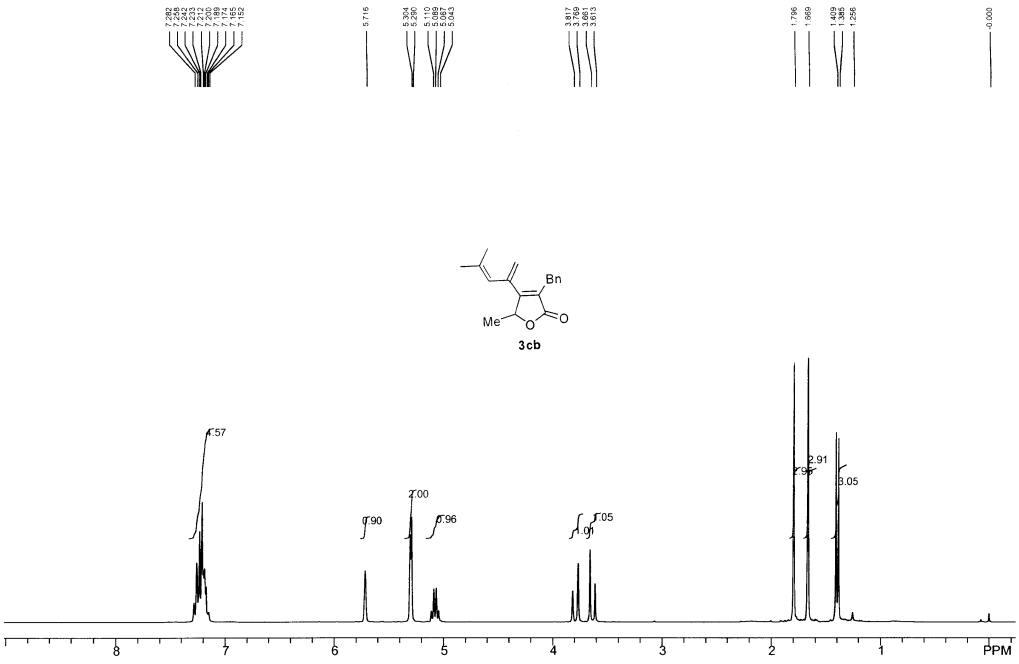

180
160
140
120
100
80
60
40
20
ppm

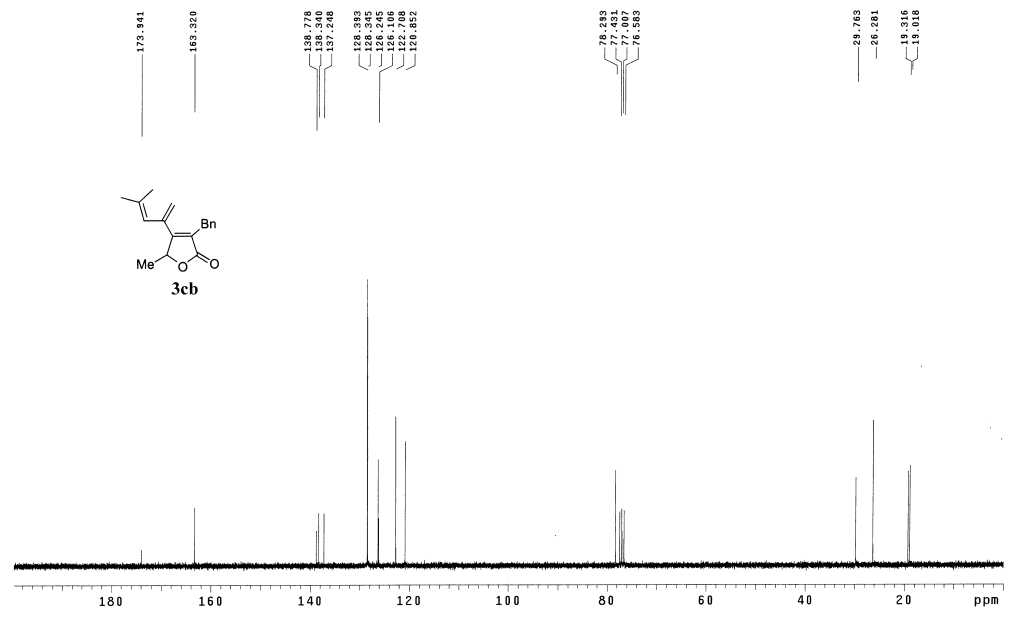

Me
Me
O
O
3ba
PPM

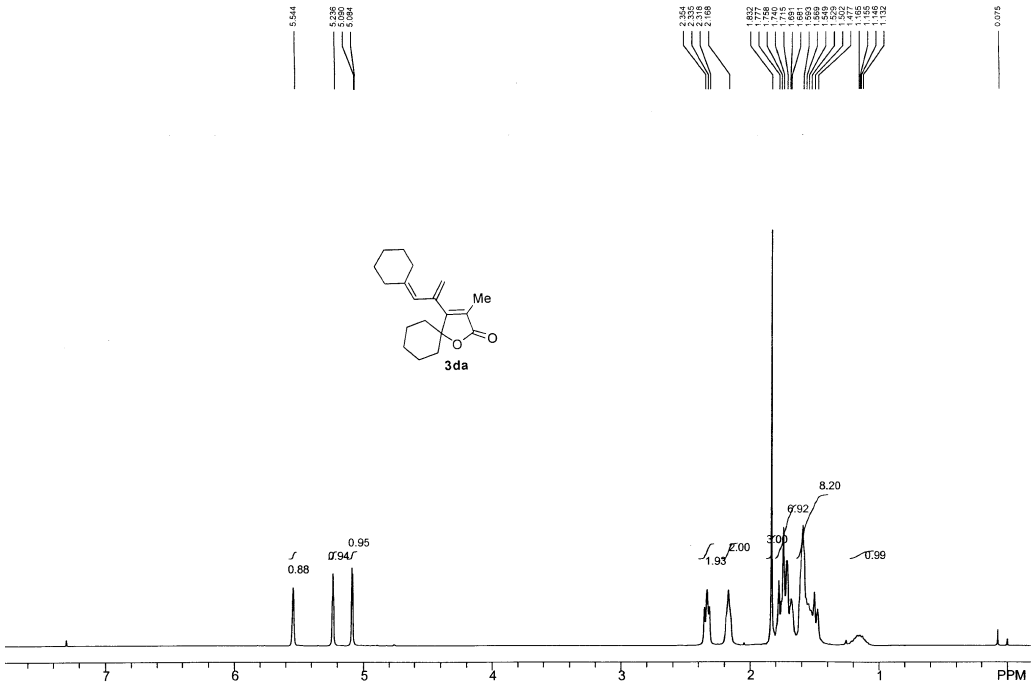

174.401
161.879
145.867
136.986
123.142
120.523
119.774
78.104
77.427
77.000
76.581
37.192
29.512
28.215
27.530
26.281
18.811
9.810
Me
Me
O
O
3ba
ppm

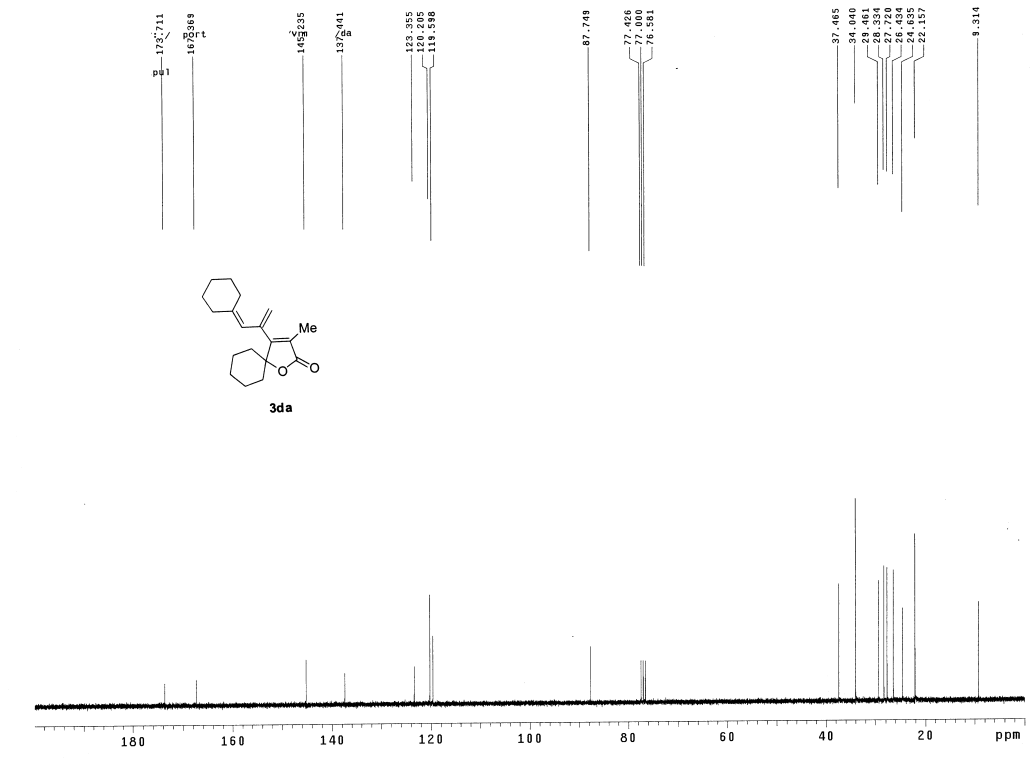

7.338
7.322
7.316
7.303
7.180
7.168
7.162
5.845
5.625
5.219
5.165
2.033
2.028
1.761
1.516
Me
Ph
O
O
3ab
2.89
1.88
0.94
0.94
1.03
1.00
3.02
3.27
3.00
8
7
6
5
4
3
2
1
PPM


174.694
159.799
138.348
137.268
135.165
128.884
128.573
127.276
123.916
122.933
121.643
83.592
77.427
77.000
76.581
25.958
18.980
10.059
Me
Ph
O
O
3ab
180
160
140
120
100
80
60
40
20
ppm

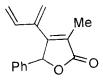

7.282
7.265
7.242
7.233
7.212
7.200
7.189
7.174
7.155
7.152
5.716
5.304
5.295
5.110
5.089
5.067
5.043
3.817
3.789
3.641
3.613
1.706
1.699
1.409
1.385
1.256
0.000
Bn
Me
O
O
3cb
7.57
0.90
2.00
0.96
1.01
1.05
2.96
2.91
3.05
8
7
6
5
4
3
2
1
PPM


173.941
163.320
138.778
138.340
137.298
128.393
128.345
126.245
126.106
122.708
120.852
78.293
77.481
77.057
76.583
29.763
26.281
19.316
19.018
Bn
Me
O
O
3cb
180
160
140
120
100
80
60
40
20
ppm

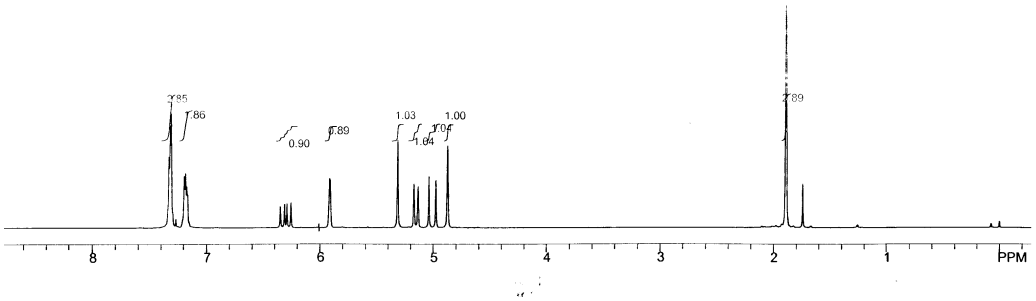

5.544
5.536
5.090
5.084
2.354
2.335
2.318
2.168
1.832
1.777
1.758
1.746
1.715
1.691
1.681
1.569
1.548
1.529
1.477
1.472
1.165
1.155
1.145
1.132
0.075
Me
O
O
3da
8.20
6.92
3.00
2.00
1.99
0.95
0.94
0.88
1.93
7
6
5
4
3
2
1
PPM

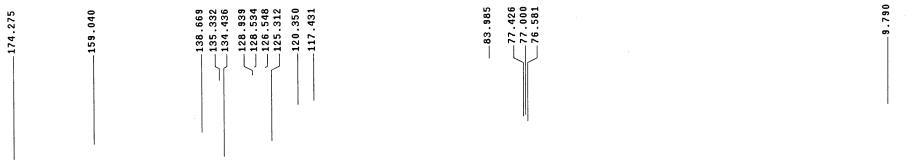

173.711
167.369
145.235
137.041
123.355
120.265
114.598
87.749
77.426
77.000
76.581
37.465
34.040
29.461
28.334
27.720
26.434
24.435
22.157
9.314
pul
rrt
Me
O
O
3da
180
160
140
120
100
80
60
40
20
ppm

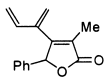

7.331
7.330
7.318
7.310
7.297
7.289
7.192
7.181
7.169
7.163
6.350
6.315
6.292
6.256
5.916
5.914
5.314
5.168
5.132
5.032
4.978
4.875
1.891
1.889
1.880
1.744


Me
Ph
O
O

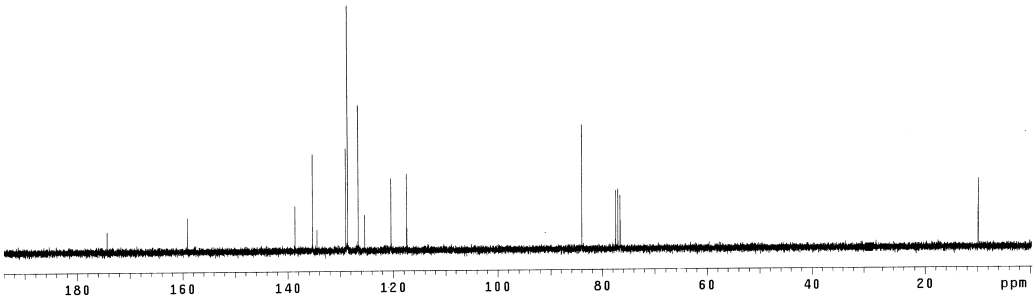
3ac

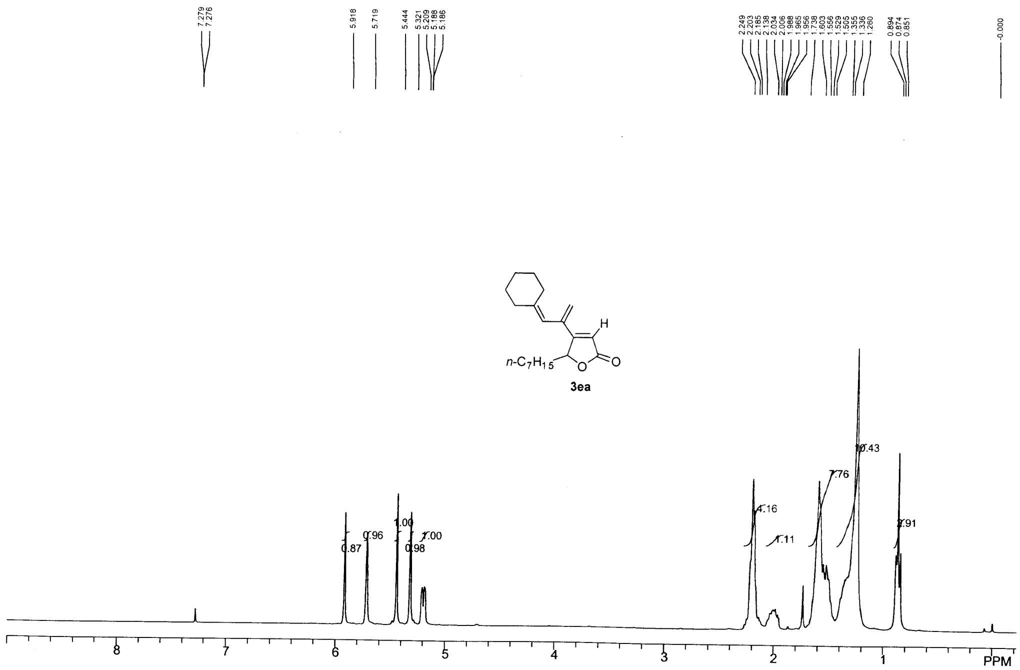

2.85
1.86
0.90
0.89
1.03
1.04
1.04
1.00
2.89
8
7
6
5
4
3
2
1
PPM


174.275
159.040
138.669
135.332
134.436
128.939
128.534
126.548
125.312
120.350
117.431
83.985
77.406
77.000
76.581
9.790

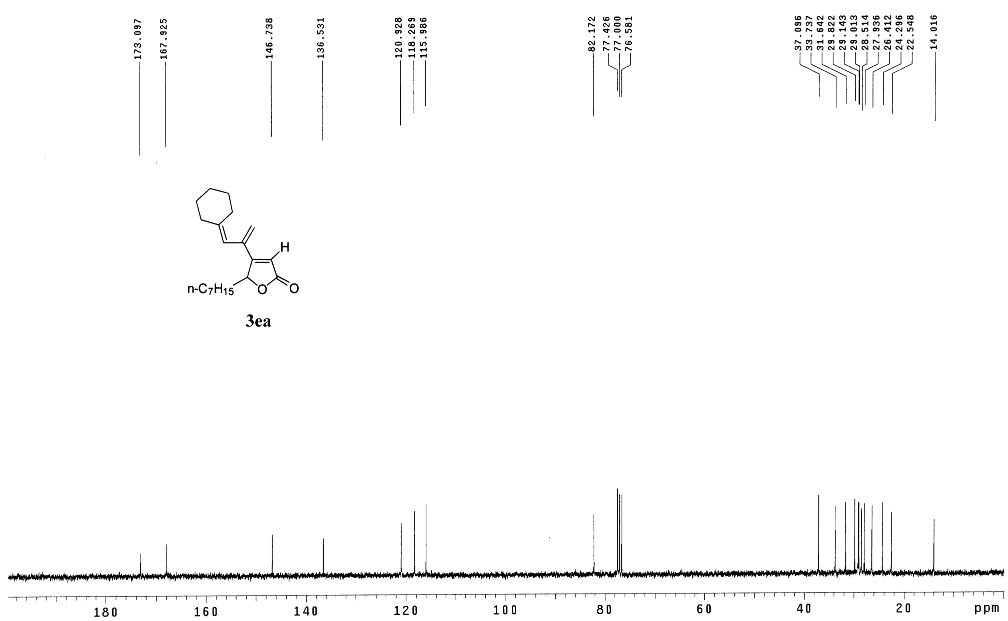

Me
Ph
O
O

3ac

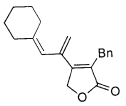

180
160
140
120
100
80
60
40
20
ppm



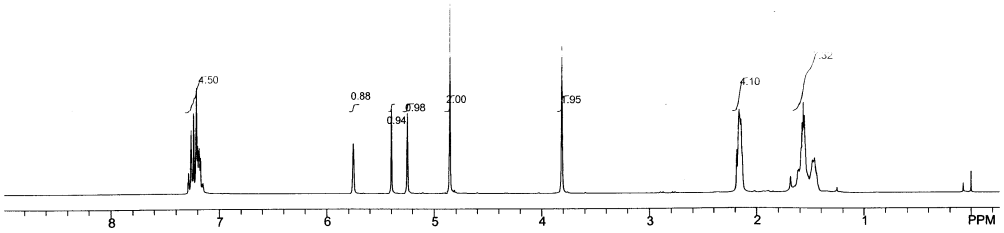
7.279
7.276
5.918
5.719
5.444
5.321
5.209
5.189
5.186
2.249
2.203
2.185
2.138
2.034
2.006
1.988
1.965
1.956
1.738
1.603
1.556
1.529
1.505
1.355
1.336
1.260
0.894
0.874
0.851
-0.000
H
n-C_7H_{15}
O
O
3ea
0.87
0.96
1.00
0.98
1.00
4.16
1.11
7.76
10.43
2.91
8
7
6
5
4
3
2
1
PPM

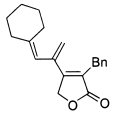


173.097
167.925
146.738
136.531
120.928
118.269
115.986
82.172
77.426
77.000
76.581
37.096
33.737
31.642
29.822
29.143
29.013
28.514
27.936
26.412
24.296
22.548
14.016
H
n-C_7H_{15}
O
O
3ea
180
160
140
120
100
80
60
40
20
ppm

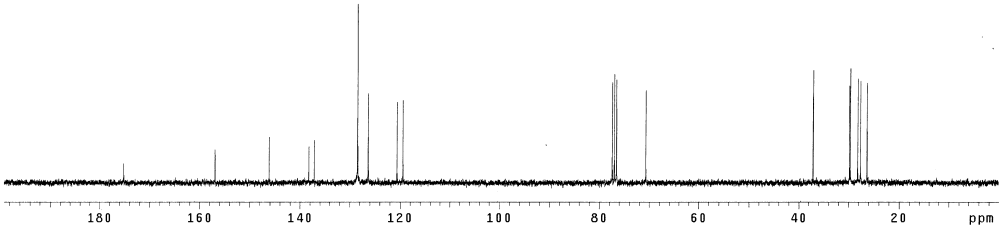

Bn
O
O

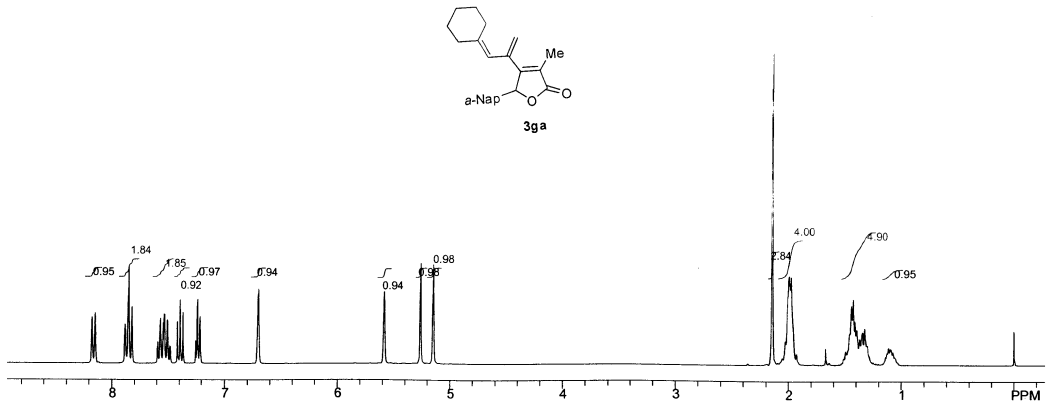
3fa

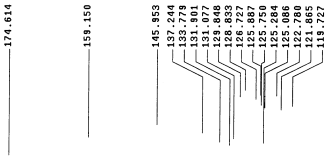

4.50
0.88
0.94
0.98
2.00
1.95
4.10
8
7
6
5
4
3
2
1
PPM

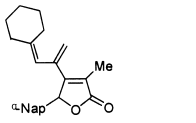

Bn
O
O

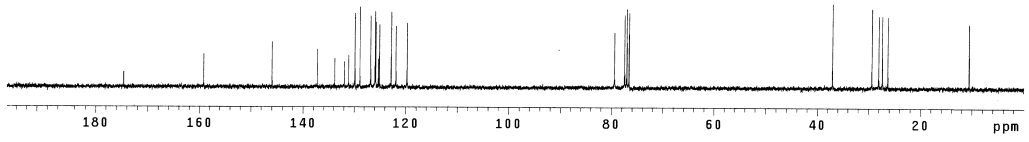
3fa

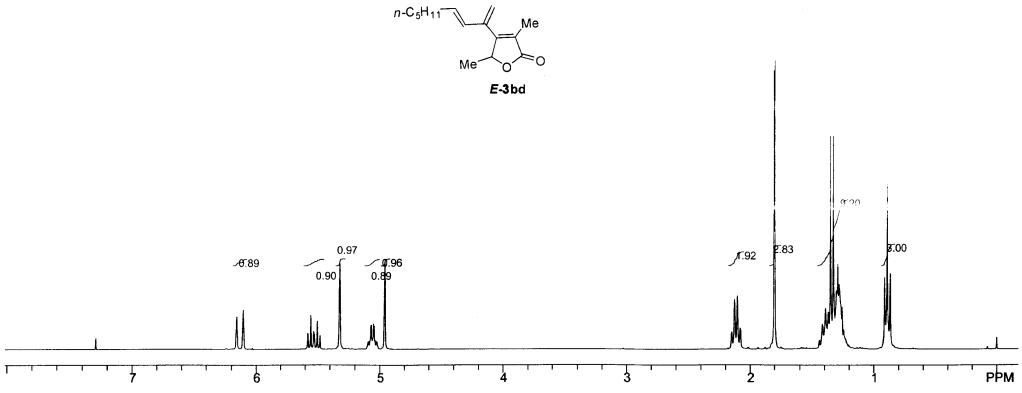

180
160
140
120
100
80
60
40
20
ppm

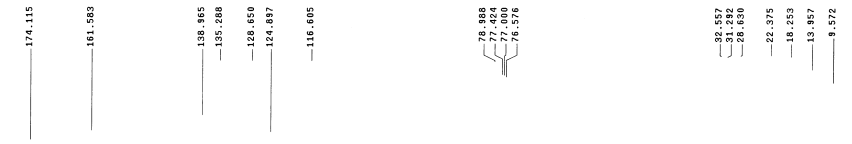

Me
a-Nap
O
O
3ga
1.84
1.85
0.92
0.97
0.94
0.95
0.94
0.98
4.00
2.84
4.90
0.95
PPM

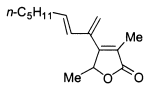



Me
α-Nap
O
O
3ga

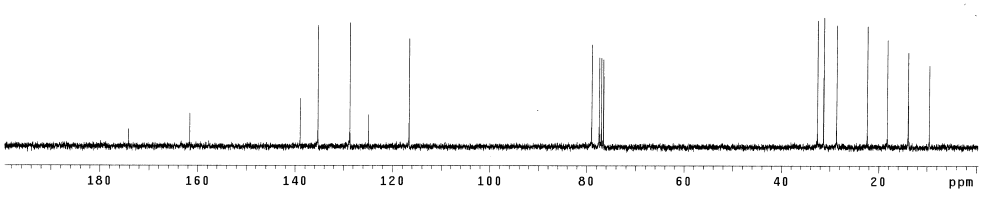

180
160
140
120
100
80
60
40
20
ppm

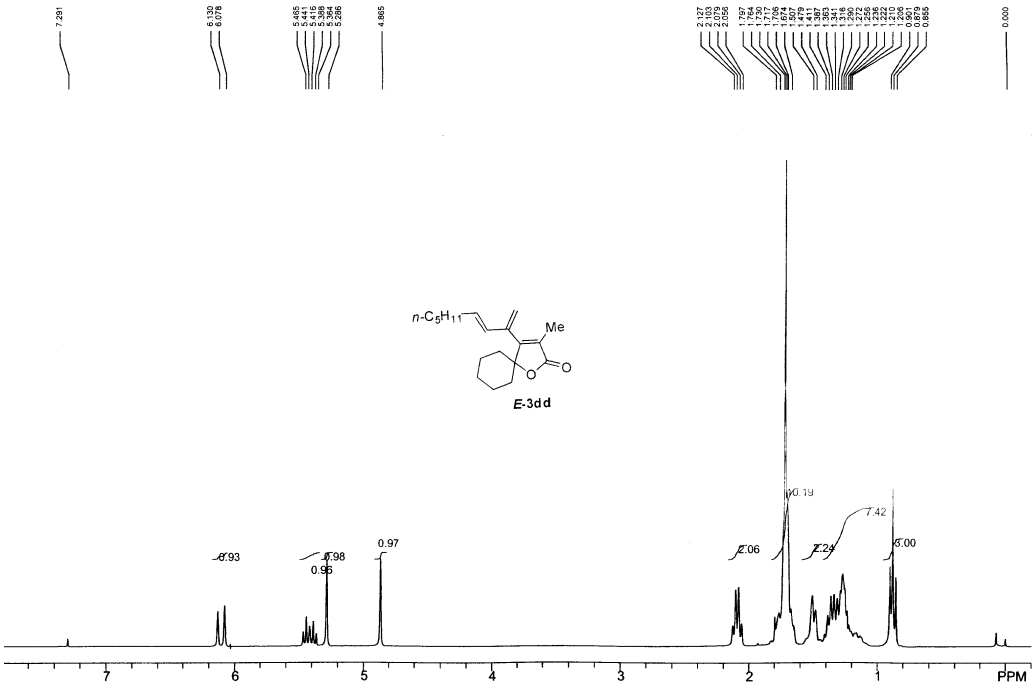

n-C5H11
Me
Me
O
O
E-3bd
0.89
0.97
0.90
0.89
0.96
1.92
2.83
3.00
7
6
5
4
3
2
1
PPM

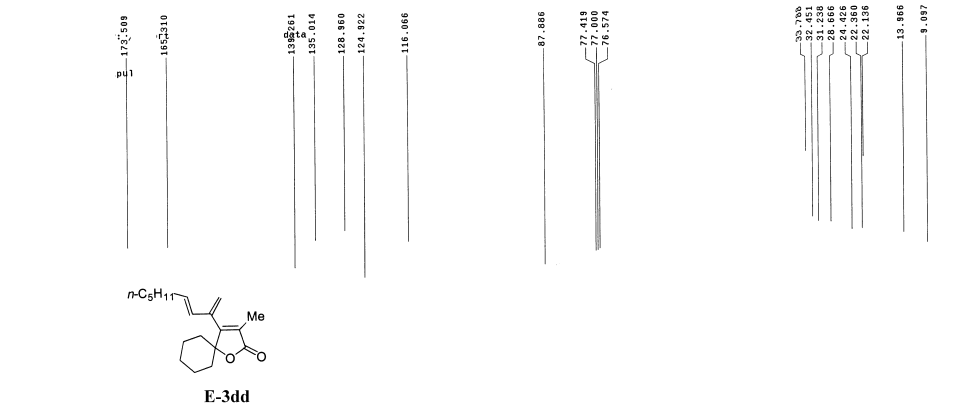


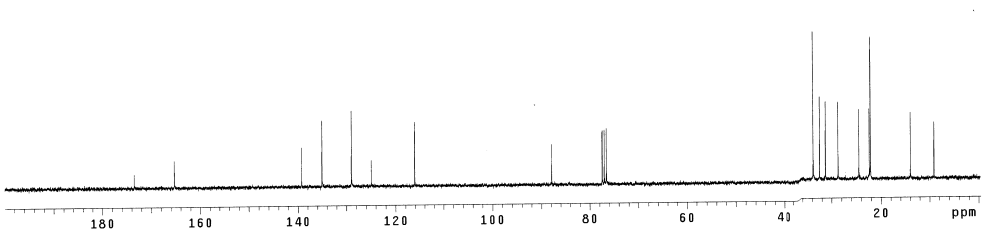

n-C5H11
Me
Me
O
O

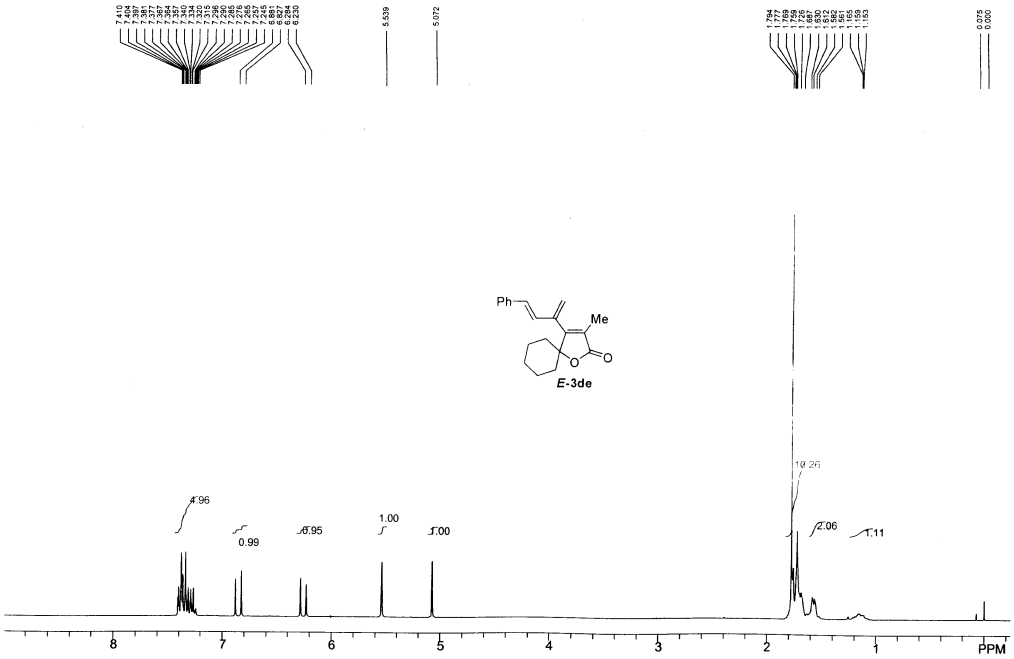
E-3bd

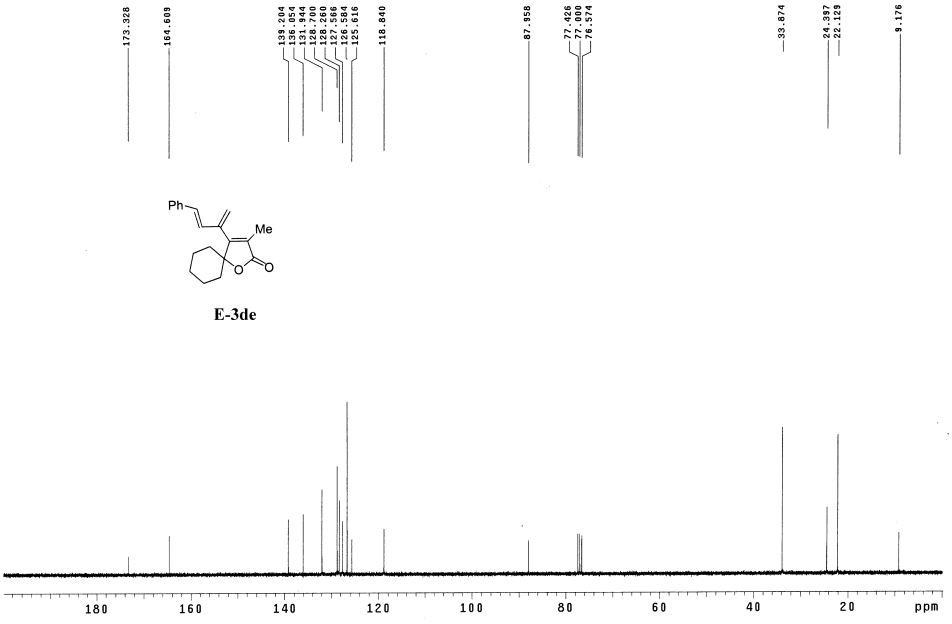

180
160
140
120
100
80
60
40
20
ppm

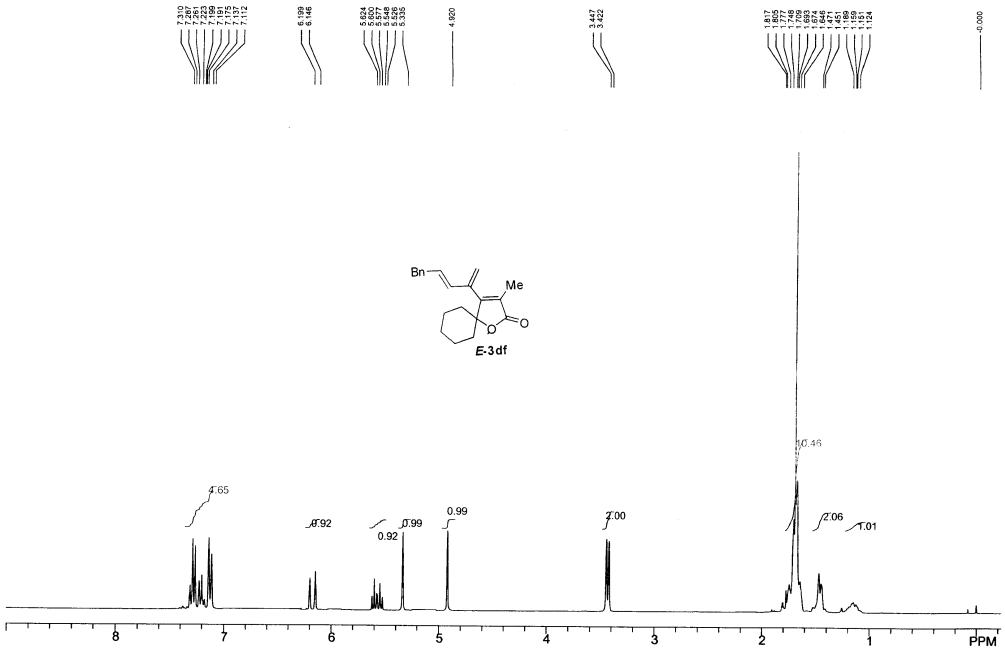

n-C5H11
Me
O
O
E-3dd
0.93
0.98
0.95
0.97
2.06
10.19
2.24
7.42
6.00
7
6
5
4
3
2
1
PPM

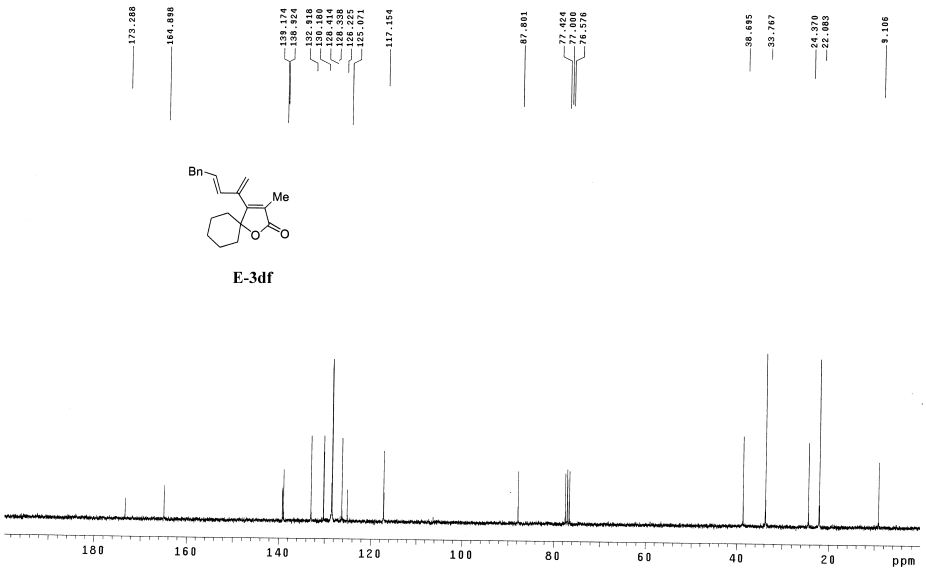

n-C5H11
Me
O
O
E-3dd

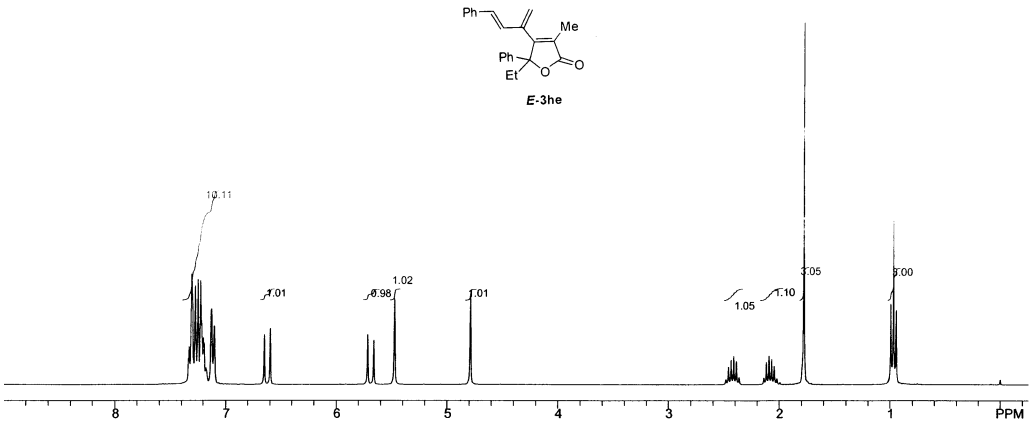

180
160
140
120
100
80
60
40
20
ppm


Ph
Me
O
O
E-3de
4.96
0.99
0.95
1.00
1.00
10.26
2.06
1.11
8
7
6
5
4
3
2
1
PPM

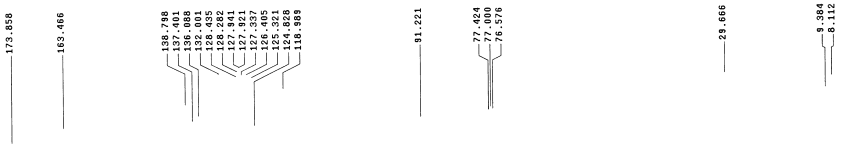

Ph
Me
O
O
E-3de
180
160
140
120
100
80
60
40
20
ppm

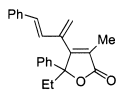

Bn
Me
O
O
E-3df
4.65
0.92
0.92
0.99
0.99
7.00
10.46
2.06
1.01
8
7
6
5
4
3
2
1
PPM


Bn
Me
O
O
E-3df
180
160
140
120
100
80
60
40
20
ppm

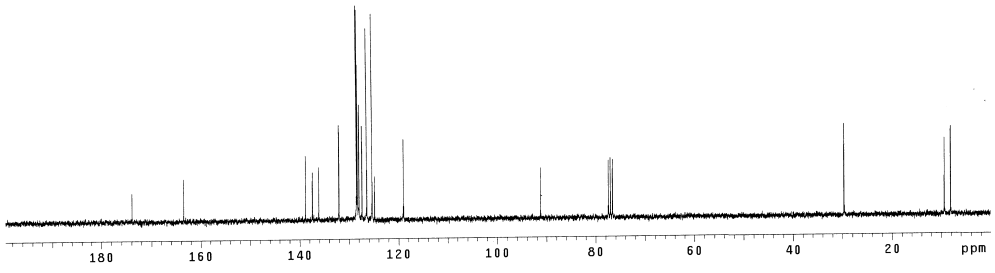

Ph
Me
Ph
Et
O
O
10.11
1.01
0.98
1.02
1.01
1.05
1.10
3.05
3.00
8
7
6
5
4
3
2
1
PPM

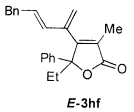
E-3he



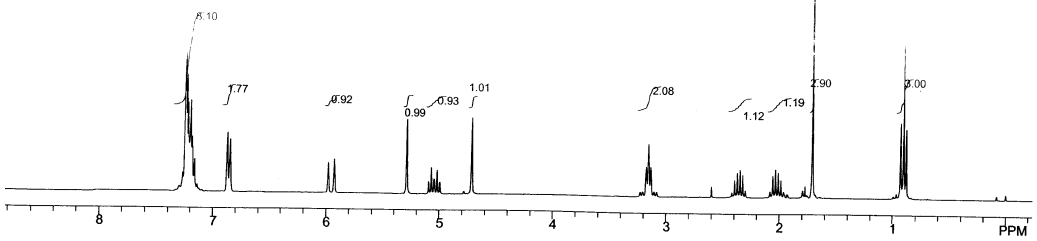

Ph
Me
Ph
Et
O
O

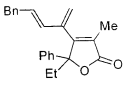
E-3he


180
160
140
120
100
80
60
40
20
ppm

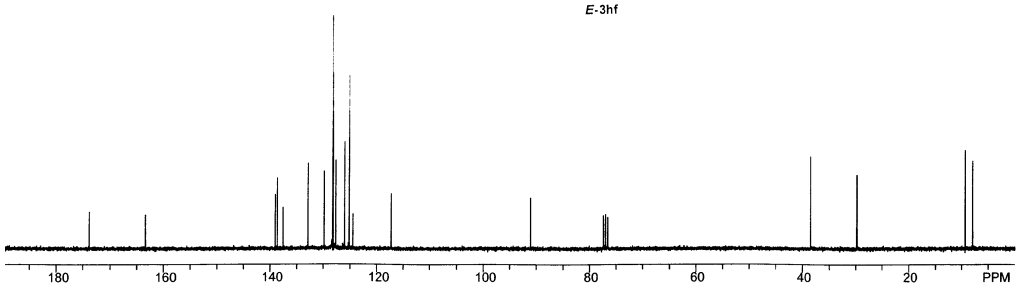

Bn
Me
Ph
Et
O
O

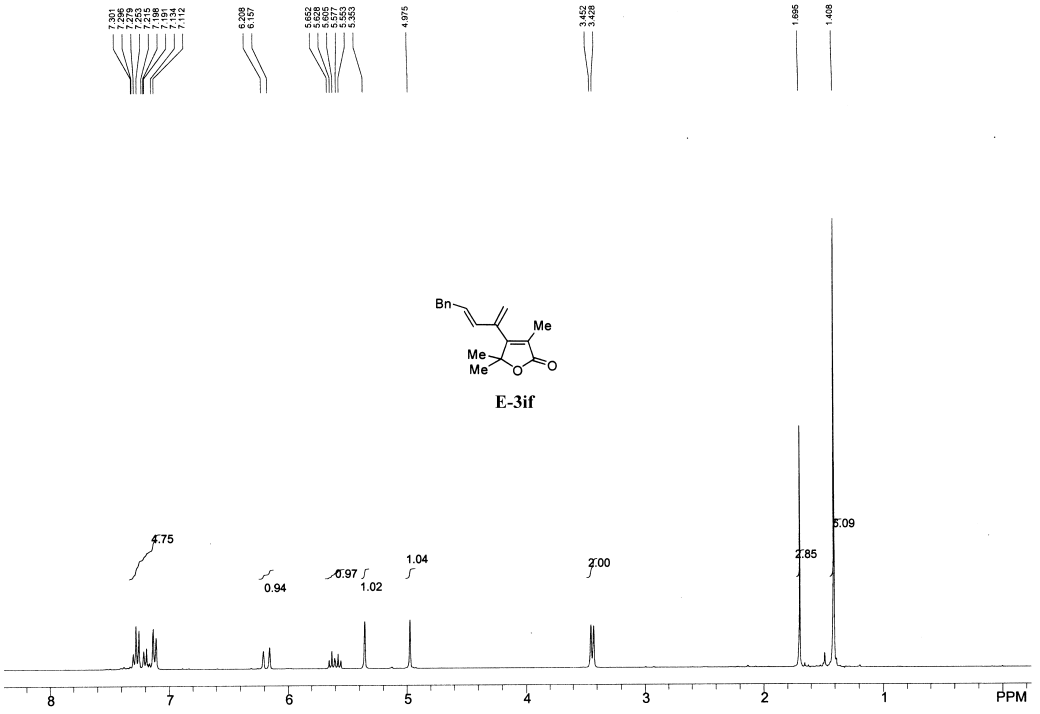
***E*-3hf**

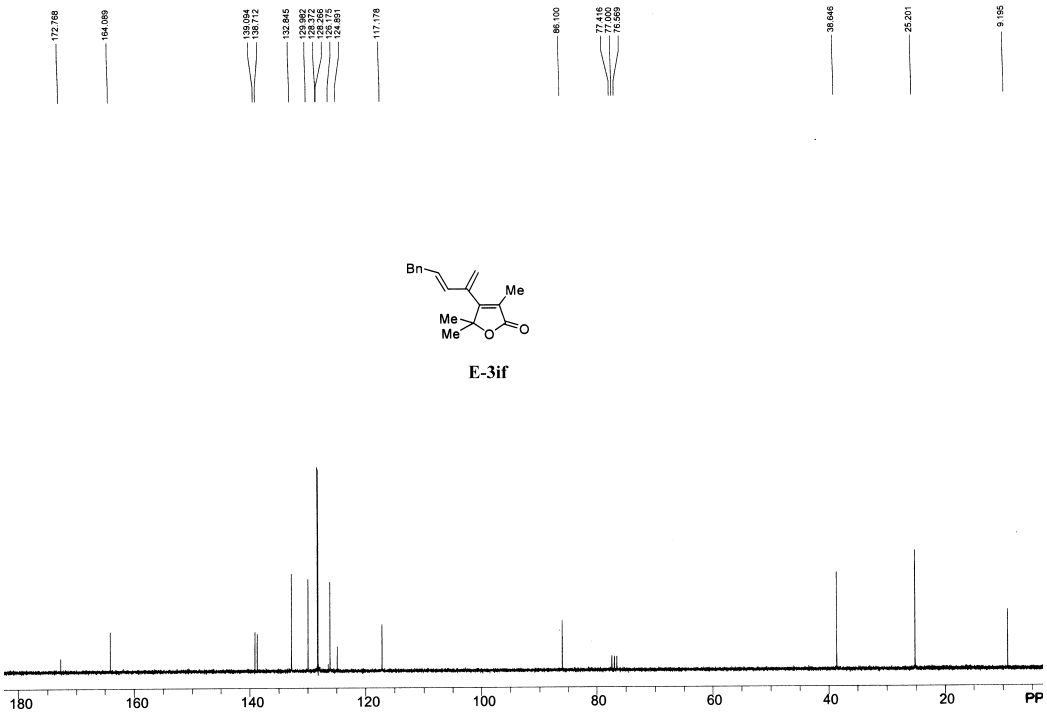

5.10
1.77
0.92
0.99
0.93
1.01
2.08
1.12
1.19
2.90
3.00
8
7
6
5
4
3
2
1
PPM


Bn
Me
Ph
Et
O
O

***E*-3hf**


180
160
140
120
100
80
60
40
20
PPM


7.301
7.296
7.279
7.263
7.215
7.198
7.181
7.134
7.112
6.209
6.107
5.652
5.626
5.605
5.577
5.553
5.353
4.975
3.452
3.428
1.695
1.408
Bn
Me
Me
Me
O
O
E-3if
4.75
0.94
0.97
1.02
1.04
2.00
2.85
5.09
8
7
6
5
4
3
2
1
PPM


172.768
164.089
139.094
136.712
132.845
129.982
128.372
128.266
126.175
124.891
117.178
86.100
77.416
77.000
76.569
38.646
25.201
9.195
Bn
Me
Me
Me
O
O
E-3if
180
160
140
120
100
80
60
40
20
PP