From Allene to Allene: A Palladium-Catalyzed Approach to β-Allenyl Butenolides and Their Application to Synthesis of Polysubstituted Benzene Derivatives†

Shengming Ma,* [a,b] Zhenhua Gu [a] and Youqian Deng [b]

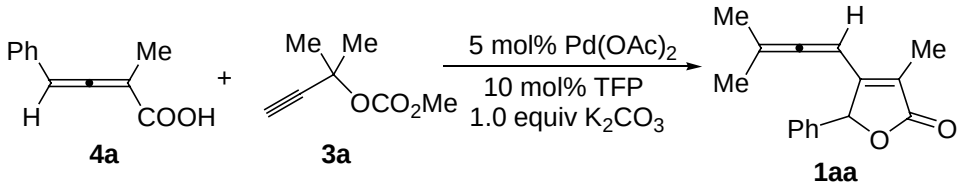
[a]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China*

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

[b]*Laboratory of Molecular Synthesis and Recognition, Department of Chemistry, Zhejiang University, 310027, Hangzhou, Zhejiang (P. R. China)*

Supporting Information

Table S1. The solvent effect of the cross-coupling reaction of **4a** with **3a**[a]

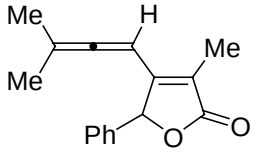


entry	solvent	temp/time (^{o}C/h)	yield of **1aa** (%)[b]
1	DMSO	25/14	59
2	NMP	25/17.5	Trace
3	DMF	30/21	57
4	DMA	30/15.5	33
5	DME	30/22.5	25
6	Dioxane	30/22	15

[a] Under an argon atmosphere, the mixture of 0.25 mmol of **4**, 0.50 mmol of **3**, 5 mol% $Pd(OAc)_2$, and 10 mol% TFP in 3 mL of solvent was stirred for the time indicated in the table. [b] Isolated yield.

General experimental procedure for the synthesis of β-allenyl-2(5*H*)- furanones: Under an argon atmosphere, the mixture of 2,3-allenoic acids **4** (0.25 mmol), propargylic carbonates **3** (0.50 mmol), $Pd(OAc)_2$ (5 mol%), tri-(2'-furyl)phosphine (10 mol%), K_2CO_3 (0.25 mmol), and 1 mL of DMSO was stirred at 35-40 ^oC for 5-17 h. After complete consumption of the starting material **4** as monitored by TLC, the mixture was directly purified via flash chromatography on silica gel (eluent (cold): petroleum ether/ethyl acetate) to afford pure **1**.

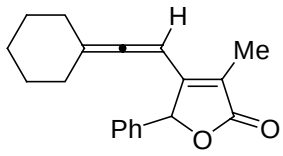
(1) 3-Methyl-4-(3'-methylbuta-1',2'-dienyl)-5-phenylfuran-2(5*H*)-one (1aa)



The reaction of **4a** (42 mg, 0.241 mmol), **3a** (73 mg, 0.514 mmol), $Pd(OAc)_2$ (3 mg, 0.0134 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (36 mg, 0.261 mmol) in 3 mL of DMSO afforded **1aa** (34 mg, 59%). Solid, M.p. 65-67 ^oC (ether); ^1H NMR (300 MHz, $CDCl_3$): δ 7.41-7.23 (m, 3 H), 7.22-7.12 (m, 2 H), 5.98-5.87 (m, 1 H), 5.70 (s, 1 H), 2.00 (s, 3 H), 1.67 (d, *J* = 2.7 Hz, 3 H), 1.05 (d, *J* = 2.7 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 8.7, 18.9, 19.5, 83.3, 83.8, 99.8, 122.3, 127.6, 128.6, 129.0, 135.9, 155.1, 174.4, 208.0; MS(EI): *m/z* (%) 240 (M^+, 62.18), 91 (100); IR (KBr): 1951, 1751, 1651 cm^{-1}; Anal. calcd. for $C_{16}H_{16}O_2$: (%) C 79.97, H 6.71; Found, C 79.73, H 6.77.

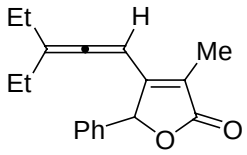
(2) 3-Methyl-4-(3',3'-pentamethenepropa-1',2'-dienyl)-5-phenylfuran-2(5*H*)-one

(1ab)



The reaction of **4a** (44 mg, 0.253 mmol), **3b** (91 mg, 0.50 mmol), $Pd(OAc)_2$ (2 mg, 0.0089 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (34 mg, 0.246 mmol) in 1 mL of DMSO afforded **1ab** (47 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.25 (m, 3 H), 7.22-7.15 (m, 2 H), 5.94 (s, 1 H), 5.73 (s, 1 H), 2.18-2.02 (m, 2 H), 2.00 (d, *J* = 1.8 Hz, 3 H), 1.62-1.48 (m, 3 H), 1.48-1.23 (m, 4 H), 1.22-1.10 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 8.7, 25.4, 25.8, 26.5, 29.6, 30.3, 83.2, 83.6, 105.8, 122.1, 127.8, 128.5, 129.0, 136.0, 155.1, 174.3, 204.7; MS(EI): *m/z* (%) 280 (M^+, 45.47), 77 (100); IR (neat): 1946, 1751, 1650 cm^{-1}; HRMS: cacld. for $C_{19}H_{20}O_2$ [M^+] 280.1463; Found, 280.1484.

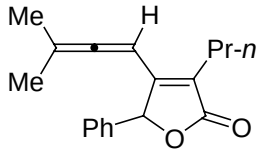
(3) 3-Methyl-4-(3'-ethylpenta-1',2'-dienyl)-5-phenylfuran-2(5*H*)-one (1ac)



The reaction of **4a** (43 mg, 0.247 mmol), **3c** (85 mg, 0.50 mmol), $Pd(OAc)_2$ (3 mg, 0.0134 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (35 mg, 0.254 mmol) in 1 mL of DMSO afforded **1ac** (40 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.25 (m, 3 H), 7.20-7.08 (m, 2 H), 6.15-6.10 (m, 1 H), 5.67 (s, 1 H), 2.01 (d, *J* = 1.2 Hz, 3 H), 2.05-1.80 (m, 2 H), 1.60-1.45 (m, 1 H), 1.45-1.30 (m, 1 H), 1.01 (t, *J* = 7.2 Hz, 3 H), 0.27 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 8.7, 10.8, 12.2, 25.0, 25.3, 83.3, 87.6, 112.2, 121.9, 127.7, 128.5, 129.1, 136.0, 155.2, 174.4, 206.7; MS(EI):

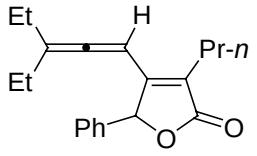
m/z (%) 268 (M^+, 31.57), 239 (100); IR (neat): 1942, 1753, 1649 cm^{-1}; HRMS: cacld. for $C_{18}H_{21}O_2$ [M^++1] 269.1536; Found, 269.1544.

(4) 3-Propyl-4-(3'-methylbuta-1',2'-dienyl)-5-phenylfuran-2(5*H*)-one (1ba)



The reaction of **4b** (50 mg, 0.247 mmol), **3a** (71 mg, 0.50 mmol), $Pd(OAc)_2$ (3 mg, 0.0134 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (35 mg, 0.254 mmol) in 1 mL of DMSO afforded **1ba** (36 mg, 54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.22 (m, 3 H), 7.18-7.04 (m, 2 H), 5.90-5.81 (m, 1 H), 5.63 (s, 1 H), 2.33 (t, *J* = 7.5 Hz, 2 H), 1.70-1.50 (m, 5 H), 0.98 (d, *J* = 2.7 Hz, 3 H), 0.93 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.0, 18.9, 19.5, 21.7, 25.5, 83.1, 83.8, 99.8, 126.7, 127.6, 128.6, 129.0, 136.1, 155.4, 174.1, 208.1; MS(EI): *m/z* (%) 268 (M^+, 24.74), 41 (100); IR (neat): 1951, 1752, 1643 cm^{-1}; HRMS: cacld. for $C_{18}H_{21}O_2$ [M^++1] 269.1536; Found, 269.1523.

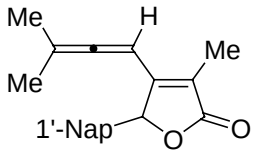
(5) 3-Propyl-4-(3'-ethylpenta-1',2'-dienyl)-5-phenylfuran-2(5*H*)-one (1bc)



The reaction of **4b** (51 mg, 0.252 mmol), **3c** (85 mg, 0.50 mmol), $Pd(OAc)_2$ (3 mg, 0.0134 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (35 mg, 0.254 mmol) in 1 mL of DMSO afforded **1bc** (48 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.20 (m, 3 H), 7.12-7.02 (m, 2 H), 6.12-6.07 (m, 1 H), 5.61 (s, 1 H), 2.34 (t, *J* = 7.5 Hz, 2

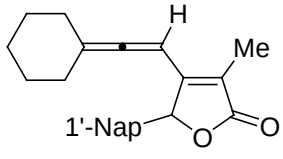
H), 2.00-1.80 (m, 2 H), 1.63-1.55 (m, 2 H), 1.53-1.25 (m, 2 H), 1.00-0.90 (m, 6 H), 0.21 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.8, 12.1, 13.9, 21.7, 25.0, 25.3, 25.5, 83.0, 87.5, 112.2, 126.2, 127.7, 128.5, 129.0, 136.1, 155.5, 174.1, 206.7; MS(EI): *m/z* (%) 296 (M^+, 38.85), 267 (100); IR(neat): 1941, 1753, 1641, 1456, 1003 cm^{-1}. HRMS: calcd. for $C_{20}H_{24}O_2Na$ [M^++Na]: 319.1669; Found: 319.1665.

(6) 3-Methyl-4-(3'-methylbuta-1,2-dienyl)-5-(naphthalen-1'-yl)furan-2(5*H*)-one (1ca)



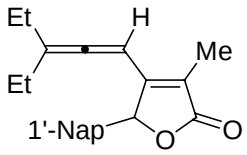
The reaction of **4c** (56 mg, 0.25 mmol), **3a** (71 mg, 0.50 mmol), $Pd(OAc)_2$ (3 mg, 0.0134 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (35 mg, 0.254 mmol) in 1 mL of DMSO afforded **1ca** (46 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.8 Hz, 1 H), 7.92-7.88 (m, 2 H), 7.61-7.50 (m, 2 H), 7.44 (t, *J* = 7.5 Hz, 1 H), 7.25 (d, *J* = 7.8 Hz, 1 H), 6.60 (s, 1 H), 6.00-5.94 (m, 1 H), 2.06 (d, *J* = 1.5 Hz, 3 H), 1.44 (d, *J* = 3.0 Hz, 3 H), 0.50 (d, *J* = 3.0 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 8.8, 18.2, 19.3, 78.5, 84.0, 100.1, 122.5, 122.8, 125.2, 125.4, 125.7, 126.6, 128.8, 129.6, 131.8, 131.9, 133.8, 155.9, 174.6, 208.0; MS(EI): *m/z* (%) 290 (M^+, 100); IR (neat): 1950, 1752, 1650 cm^{-1}; HRMS: cacld. for $C_{20}H_{19}O_2$ [M^++1] 291.1380; Found, 291.1384.

(7) 3-Methyl-4-(3',3'-pentamethenepropa-1',2'-dienyl)-5-(naphthalen-1'-yl)-furan-2(5*H*)-one (1cb)



The reaction of **4c** (56 mg, 0.25 mmol), **3b** (91 mg, 0.50 mmol), $Pd(OAc)_2$ (3 mg, 0.0134 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (35 mg, 0.254 mmol) in 1 mL of DMSO afforded **1cb** (43 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4 Hz, 1 H), 7.78 (t, *J* = 9.3 Hz, 2 H), 7.58-7.39 (m, 2 H), 7.33 (t, *J* = 7.5 Hz, 1 H), 7.20-7.13 (m, 1 H), 6.52 (s, 1 H), 5.96 (s, 1 H), 1.99 (d, *J* = 1.8 Hz, 3 H), 1.95-1.72 (m, 2 H), 1.38-1.15 (m, 2 H), 1.15-0.70 (m, 5 H), 0.20-0.02 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 8.9, 25.2, 25.3, 26.4, 29.1, 30.1, 78.6, 84.0, 106.1, 122.7, 122.9, 125.1, 125.6, 125.8, 126.7, 128.7, 129.7, 131.9, 132.1, 133.8, 155.5, 174.4, 204.8; EIMS: *m/z* (%) 330 (M^+, 2.10), 84 (100); IR (neat): 1946, 1751, 1650 cm^{-1}; HRMS: cacld. for $C_{23}H_{23}O_2$ [M^++1] 331.1693; Found, 331.1706.

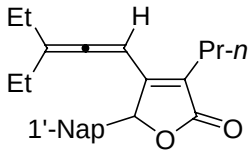
(8) 3-Methyl-4-(3'-ethylpenta-1',2'-dienyl)-5-(naphthalen-1'-yl)furan-2(5H)-one (1cc)



The reaction of **4c** (56 mg, 0.25 mmol), **3c** (85 mg, 0.50 mmol), $Pd(OAc)_2$ (3 mg, 0.0134 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (35 mg, 0.254 mmol) in 1 mL of DMSO afforded **1cc** (54 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.1 Hz, 1 H), 7.90-7.80 (m, 2 H), 7.58-7.38 (m, 3 H), 7.30-7.21 (m, 1 H), 6.59 (s, 1 H), 6.22-6.17 (m, 1 H), 2.07 (d, *J* = 1.2 Hz, 3 H), 1.82-1.60 (m, 2 H), 1.18-1.01 (m, 1 H), 0.90 (t, *J* = 7.5 Hz, 3 H), 0.75-0.58 (m, 1 H), 0.02 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 8.9, 10.7, 12.0, 24.4, 24.9, 78.5, 87.8, 112.4, 122.3, 125.2, 125.5,

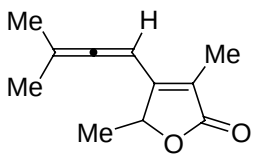
125.6, 126.5, 128.8, 129.6, 131.7, 131.8, 133.8, 156.1, 174.6, 206.6; MS(EI): *m/z* (%) 318 (M^+, 88.78), 289 (100); IR (neat): 1941, 1752, 1648 cm^{-1}; HRMS: cacld. for $C_{22}H_{23}O_2$ [M^++1] 319.1693; Found, 319.1702.

(9) 3-Propyl-4-(3'-ethylpenta-1',2'-dienyl)-5-(naphthalen-1'-yl)furan-2(5*H*)-one (1dc)



The reaction of **4d** (63 mg, 0.25 mmol), **3c** (85 mg, 0.50 mmol), $Pd(OAc)_2$ (3 mg, 0.0134 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (35 mg, 0.254 mmol) in 1 mL of DMSO afforded **1dc** (61 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.1 Hz, 1 H), 7.90-7.79 (m, 2 H), 7.58-7.38 (m, 3 H), 7.30-7.23 (m, 1 H), 6.60 (s, 1 H), 6.25-6.18 (m, 1 H), 2.50 (t, *J* = 7.5 Hz, 2 H), 1.85-1.60 (m, 4 H), 1.18-1.00 (m, 4 H), 0.92 (t, *J* = 7.2 Hz, 3 H), 0.77-0.58 (m, 1 H), 0.03 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.6, 12.0, 14.0, 21.8, 24.4, 24.9, 25.7, 78.2, 87.7, 112.4, 122.4, 125.2, 125.4, 125.6, 126.5, 126.7, 128.7, 129.6, 131.7, 131.9, 133.8, 156.4, 174.2, 206.6; MS(EI): *m/z* (%) 346 (M^+, 68.00), 317 (100); IR (neat): 1940, 1752, 1642 cm^{-1}; HRMS: cacld. for $C_{24}H_{27}O_2$ [M^++1] 347.2006; Found, 347.2014.

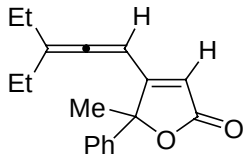
(10) 3,5-Dimethyl-4-(3'-methylbuta-1',2'-dienyl)furan-2(5*H*)-one (1ea)



The reaction of **4e** (28 mg, 0.25 mmol), **3a** (71 mg, 0.50 mmol), $Pd(OAc)_2$ (2 mg,

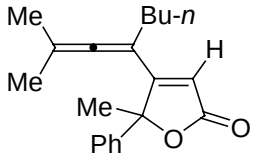
0.0089 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (34 mg, 0.246 mmol) in 1 mL of DMSO afforded **1ea** (24 mg, 54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.02-5.94 (m, 1 H), 4.91 (q, *J* = 6.6 Hz, 1 H), 1.87 (d, *J* = 1.2 Hz, 3 H), 1.81 (d, *J* = 2.4 Hz, 3 H), 1.79 (d, *J* = 2.4 Hz, 3 H), 1.42 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 8.5, 19.6, 19.77, 19.80, 77.7, 83.8, 99.2, 121.5, 157.0, 174.3, 207.0; MS(EI): *m/z* (%) 178 (M^+, 23.83), 91 (100); IR (neat): 1950, 1752, 1649 cm^{-1}; HRMS: cacld. for $C_{11}H_{15}O_2$ [M^++1] 179.1067; Found, 179.1070.

(11) 4-(3'-Ethylpenta-1',2'-dienyl)-5-methyl-5-phenylfuran-2(5*H*)-one (1fc)



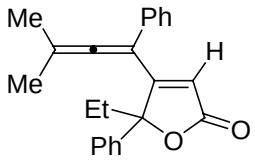
The reaction of **4f** (43 mg, 0.247 mmol), **3c** (84 mg, 0.494 mmol), $Pd(OAc)_2$ (3 mg, 0.0134 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (34 mg, 0.246 mmol) in 1 mL of DMSO afforded **1fc** (54 mg, 82%). Solid, M.p. 79-80 ^{o}C (chloroform); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.18 (m, 5 H), 6.02-5.98 (m, 1 H), 5.88 (s, 1 H), 2.05-1.80 (m, 2 H), 1.87 (s, 3 H), 1.65-1.38 (m, 2 H), 0.96 (t, *J* = 7.5 Hz, 3 H), 0.26 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.8, 11.8, 23.3, 24.8, 25.3, 87.9, 88.1, 111.6, 113.6, 125.8, 128.3, 128.5, 138.0, 168.9, 172.5, 207.6; MS(EI): *m/z* (%) 269 (M^++1, 57.55), 239 (100); IR (KBr): 1942, 1755, 1607, 1229 cm^{-1}; Anal. calcd. for $C_{18}H_{20}O_2$: C 80.56, H 7.51; Found: C 80.24, H 7.43.

(12) 4-(3'-Methy-1'-butylbuta-1',2'-dienyl)-5-methyl-5-phenylfuran-2(5*H*)-one (1fd)



The reaction of **4f** (43 mg, 0.247 mmol), **3d** (99 mg, 0.50 mmol), $Pd(OAc)_2$ (3 mg, 0.0134 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (35 mg, 0.254 mmol) in 1 mL of DMSO afforded **1fd** (68 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.13 (m, 5 H), 5.91 (s, 1 H), 2.11 (t, *J* = 7.2 Hz, 2 H), 1.84 (s, 3 H), 1.58 (s, 3 H), 1.39-1.15 (m, 4 H), 0.88 (s, 3 H), 0.81 (t, *J* = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 13.8, 18.7, 19.6, 22.0, 23.4, 29.4, 30.1, 88.5, 96.8, 99.4, 112.7, 125.7, 128.20, 128.25, 138.5, 170.9, 172.4, 207.1; MS(EI): *m/z* (%) 296 (M^+, 2.52), 183 (100); IR (neat): 1948, 1754, 1600, 1448 cm^{-1}; HRMS: calcd. for $C_{20}H_{25}O_2$ [M^++1]: 297.1849; Found: 297.1863.

(13) 4-(3'-Methyl-1'-phenylbuta-1',2'-dienyl)-5-ethyl-5-phenylfuran-2(5*H*)-one (1ge)

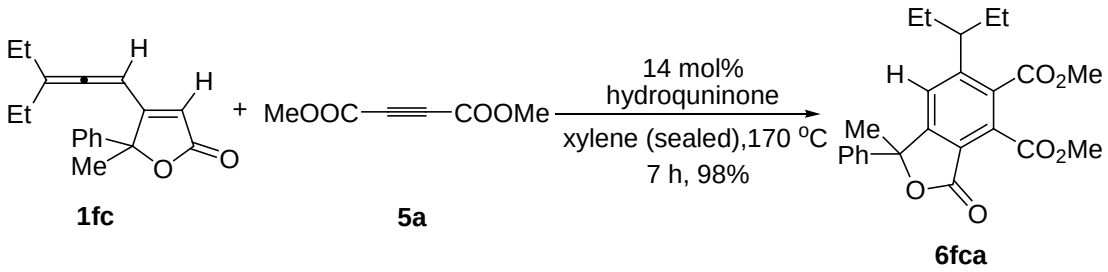


The reaction of **4g** (47 mg, 0.25 mmol), **3e** (110 mg, 0.505 mmol), $Pd(OAc)_2$ (3 mg, 0.0134 mmol), TFP (6 mg, 0.0259 mmol), and K_2CO_3 (34 mg, 0.246 mmol) in 1 mL of DMSO afforded **1ge** (75 mg, 91%). Solid, M.p. 86-88 ^oC (ethyl acetate/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.20 (m, 10 H), 6.02 (s, 1 H), 2.70-2.52 (m, 1 H), 2.50-2.32 (m, 1 H), 1.73 (s, 3 H), 1.16 (s, 3 H), 1.00 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 7.3, 18.9, 19.8, 27.4, 91.3, 99.9, 100.4, 117.1, 125.8, 127.8, 128.3, 128.4, 128.5, 135.8, 138.6, 166.9, 172.4, 207.7; MS(EI):

m/z (%) 330 (M^+, 1.90), 246 (100); IR (KBr): 1944, 1755, 1600, 1447, 1234 cm^{-1}; Anal. calcd. for $C_{23}H_{22}O_2$: C 83.60, H 6.71; Found: C 83.88, H 6.60.

Typical Procedure for the Diels-Alder reaction of **1** with electron-deficient alkynes **6**

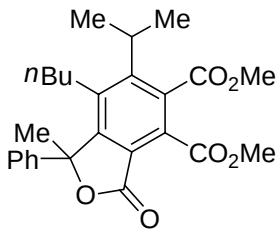
(1) Dimethyl 4-methyl-4-phenyl-7-(pentan-3'-yl)isobenzofuran-2(4*H*)-one-8,9-dicarboxylate (6fca)



1fc **5a** **6fca**

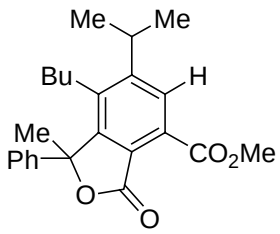
Under the N_2 atmosphere, a mixture of **1fc** (18 mg, 0.067 mmol), **5a** (47 mg, 0.331 mmol), hydroquinone (1 mg, 0.0091 mmol, 14 mol%) and xylene (3 mL) was sealed and stirred at 170 °C for 7 h. Then the mixture was directly submitted to flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford liquid **6fca** (27 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.28 (m, 6 H), 4.00 (s, 3 H), 3.89 (s, 3 H), 2.93-2.80 (m, 1 H), 2.04 (s, 3 H), 1.80-1.42 (m, 4 H), 0.79 (t, *J* = 7.4 Hz, 3 H), 0.69 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 11.7, 11.8, 26.9, 29.0, 45.2, 52.8, 53.2, 86.9, 120.3, 121.7, 125.1, 128.7, 128.8, 131.4, 133.7, 139.8, 152.6, 155.7, 165.9, 166.5, 167.1; MS(EI): *m/z* (%) 410 (M^+, 12.59), 346 (100); IR (neat): 1774, 1736, 1611, 1447, 1254, 993 cm^{-1}; HRMS: calcd. for $C_{24}H_{26}O_6$(M^++Na): 433.1622; Found: 433.1622.

(2) Dimethyl 4-methyl-4-phenyl-6-butyl-7-(isopropyl)isobenzofuran-2(4*H*)-one-8,9-dicarboxylate (6fda)



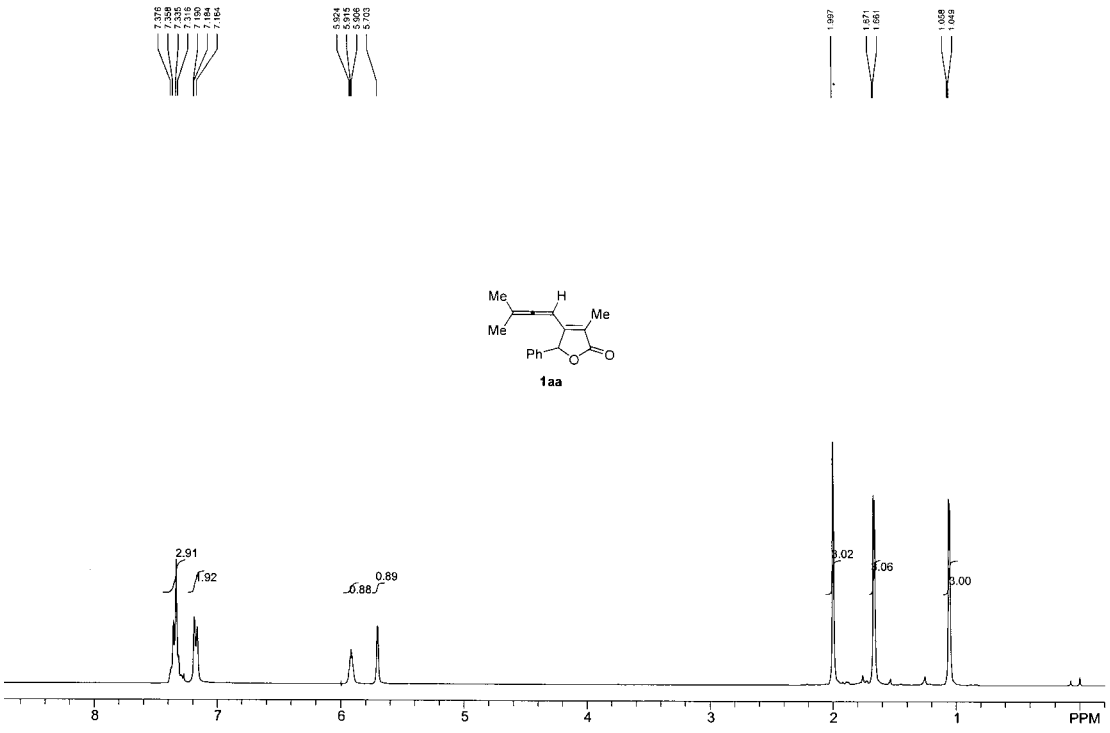
The reaction of **1fd** (30 mg, 0.10 mmol), **5a** (57 mg, 0.40 mmol), hydroquinone (1 mg, 0.0091 mmol, 9 mol%) and xylene (3 mL) was sealed and stirred at 170 ^{o}C for 13 h to afford **6fda** (42 mg, 95%). Solid, M.p. 151-152 ^{o}C (ethyl acetate/petroleum ehter); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.32 (m, 3 H), 7.32-7.23 (m, 2 H), 4.00 (s, 3 H), 3.89 (s, 3 H), 3.40-3.25 (m, 1 H), 2.48-2.32 (m, 2 H), 2.13 (s, 3 H), 1.33 (d, *J* = 7.5 Hz, 3 H), 1.28 (d, *J* = 6.9 Hz, 3 H), 1.20-0.95 (m, 3 H), 0.68 (t, *J* = 6.9 Hz, 3 H), 0.52-0.35 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 13.5, 21.1, 21.6, 23.1, 24.0, 29.2, 29.3, 32.1, 52.8, 53.1, 87.7, 120.8, 126.6, 128.7, 128.9, 129.7, 133.4, 138.3, 138.4, 151.6, 153.7, 166.3, 166.9, 168.4; MS(EI): *m/z* (%) 438 (M^+, 9.68), 406 (100); IR (KBr): 1771, 1745, 1573, 1449, 1228 cm^{-1}; Anal. calcd. for $C_{26}H_{30}O_6$: (%) C 71.21, H 6.90; Found, C 71.37, H 6.88.

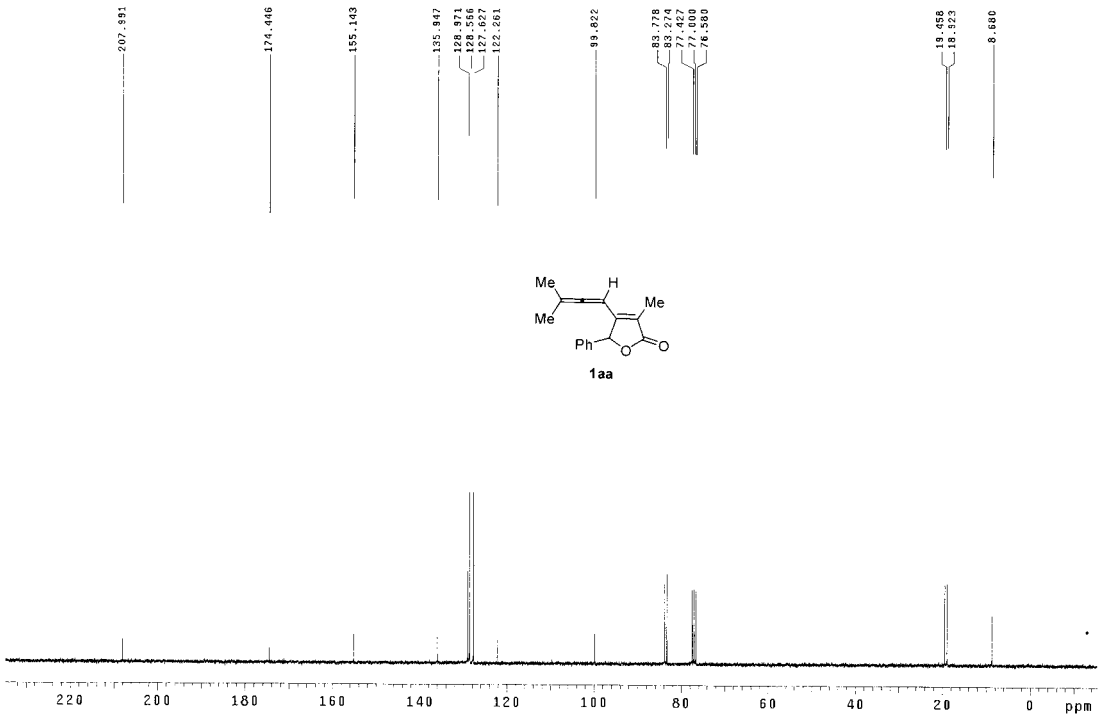
(3) Methyl 4-methyl-4-phenyl-6-butyl-7-(isopropyl)isobenzofuran-2(4*H*)-one-9-carboxylate (6fdb)



The reaction of **1fd** (40 mg, 0.135 mmol), **5b** (46 mg, 0.548 mmol), hydroquinone (1 mg, 0.0091 mmol, 7 mol%) and xylene (3 mL) was sealed and

stirred at 170 ^{o}C for 21 h to afford **6fdb** (32 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (s, 1 H), 7.30-7.18 (m, 5 H), 3.94 (s, 3 H), 3.15-3.00 (m, 1 H), 2.38-2.25 (m, 2 H), 2.06 (s, 3 H), 1.17 (d, *J* = 6.6 Hz, 3 H), 1.16 (d, *J* = 6.6 Hz, 3 H), 1.15-0.90 (m, 3 H), 0.62 (t, *J* = 7.2 Hz, 3 H), 0.50-0.40 (m, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 13.5, 23.2, 23.8, 24.3, 28.6, 28.7, 32.4, 52.8, 86.9, 120.9, 126.6, 127.7, 128.6, 128.7, 129.4, 137.2, 139.1, 153.5, 155.1, 167.2, 167.3; MS(EI): *m/z* (%) 380 (M^+, 20.67), 365 (100); IR (neat): 1767, 1733, 1580, 1452, 1240 cm^{-1}; HRMS: calcd. for $C_{24}H_{29}O_4$ [M^++1]: 381.2060; Found: 381.2052.

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18.458
18.323
8.680
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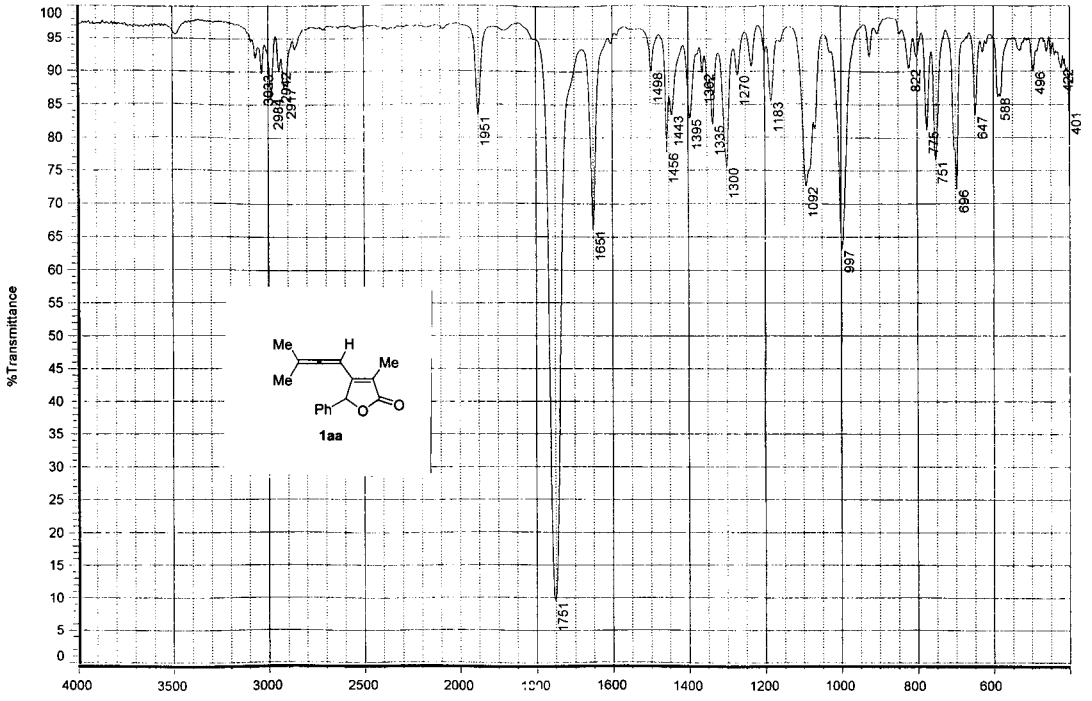
0
ppm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1395
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1270
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775
751
696
647
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422
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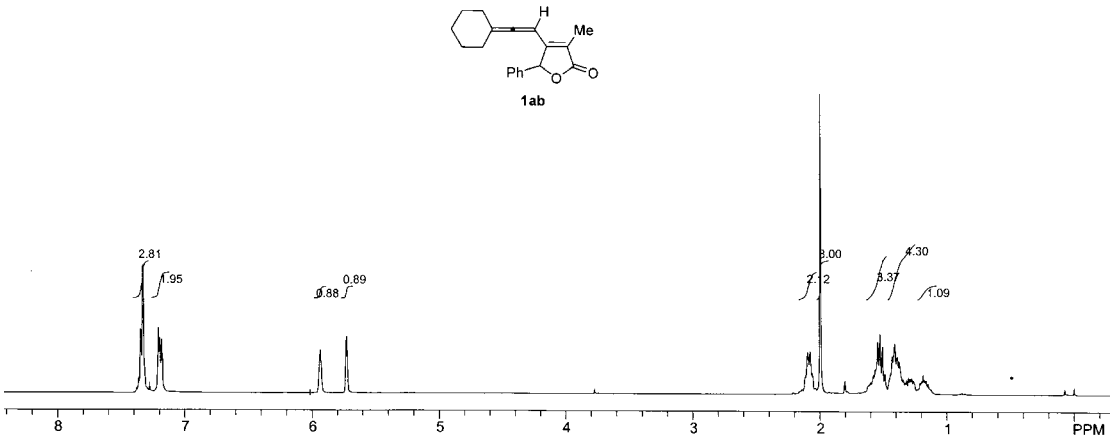
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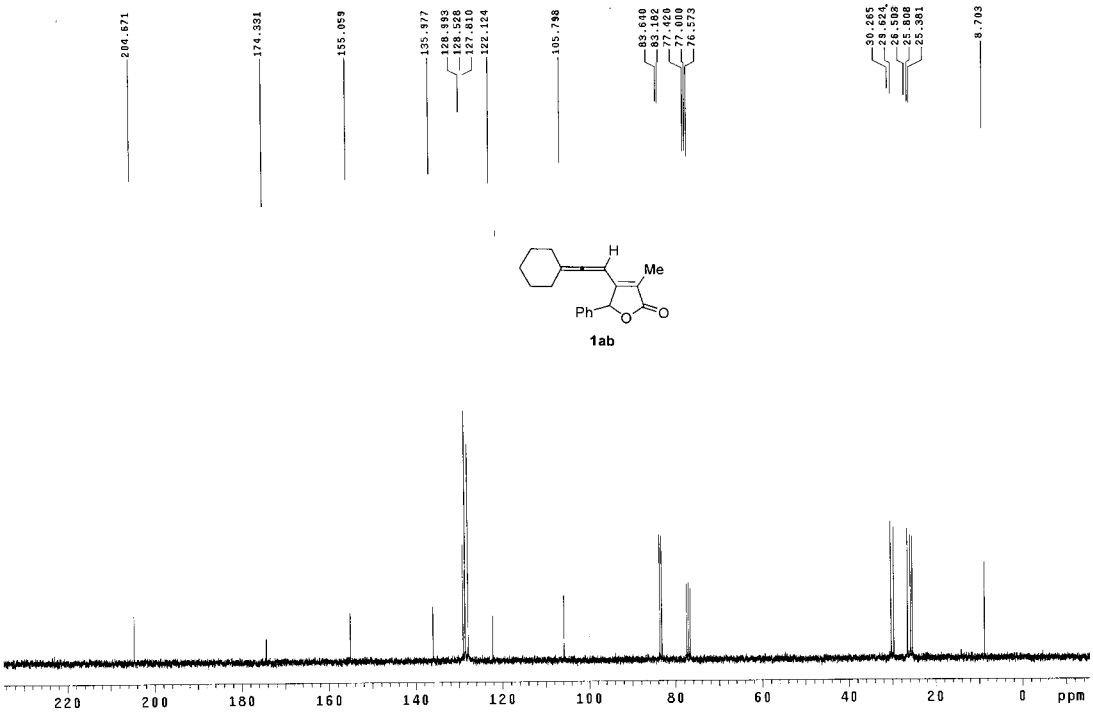
7
6
5
4
3
2
1
PPM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26.508
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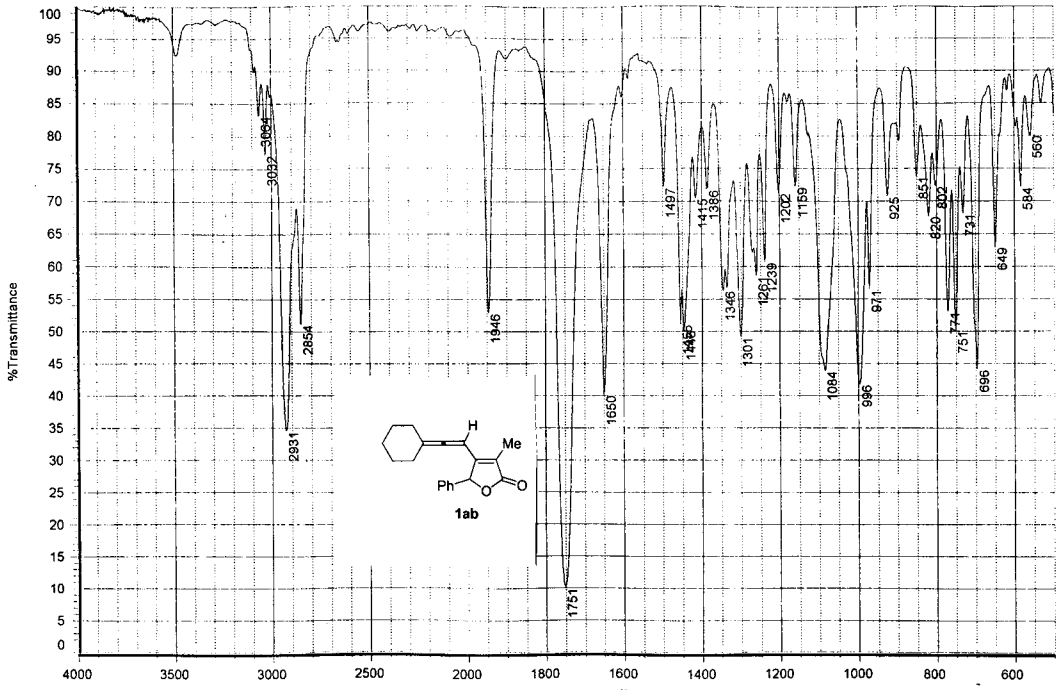
ppm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1159
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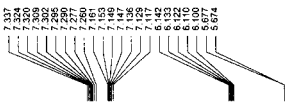
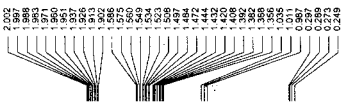
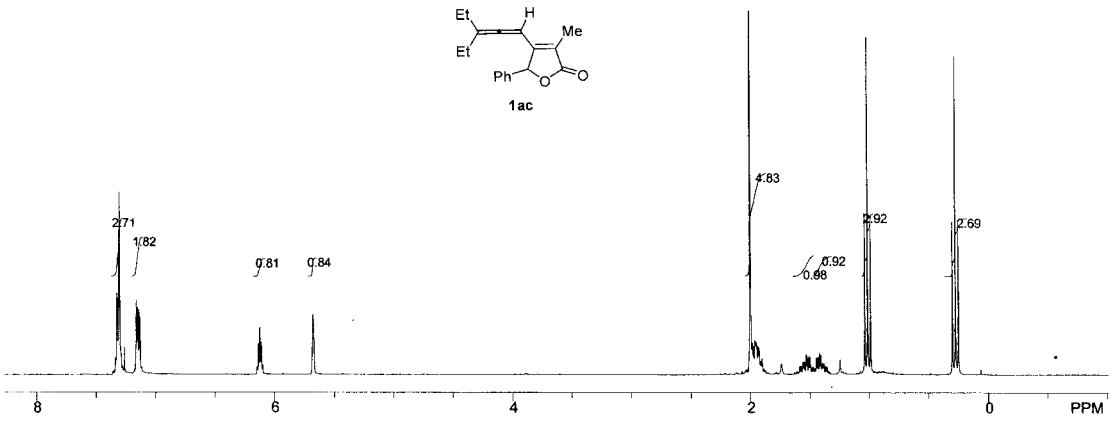
Ph
O
1ab



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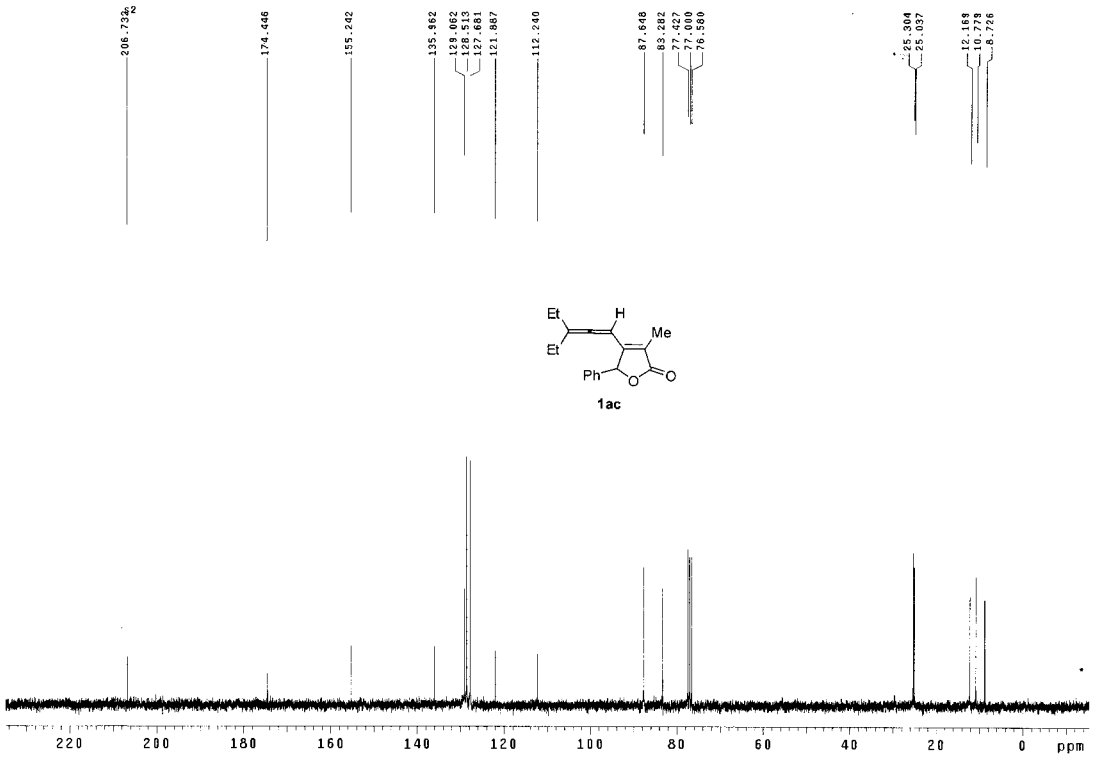
2
0
PPM



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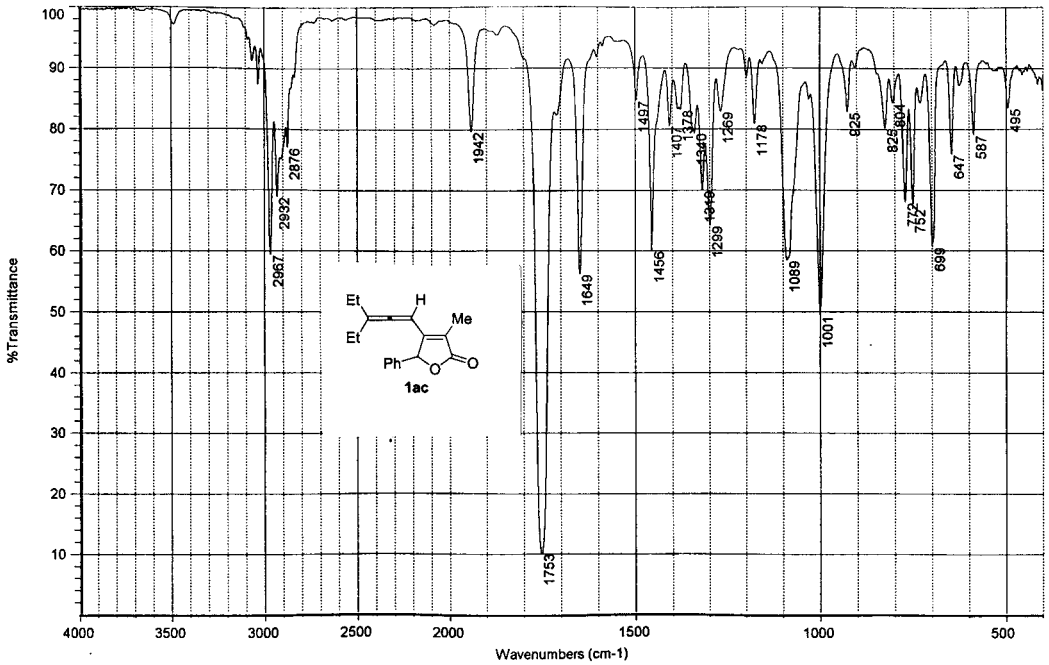
Wed Dec 01 08:25:02 2004

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7.090
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5.857
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1.600
1.591
1.566
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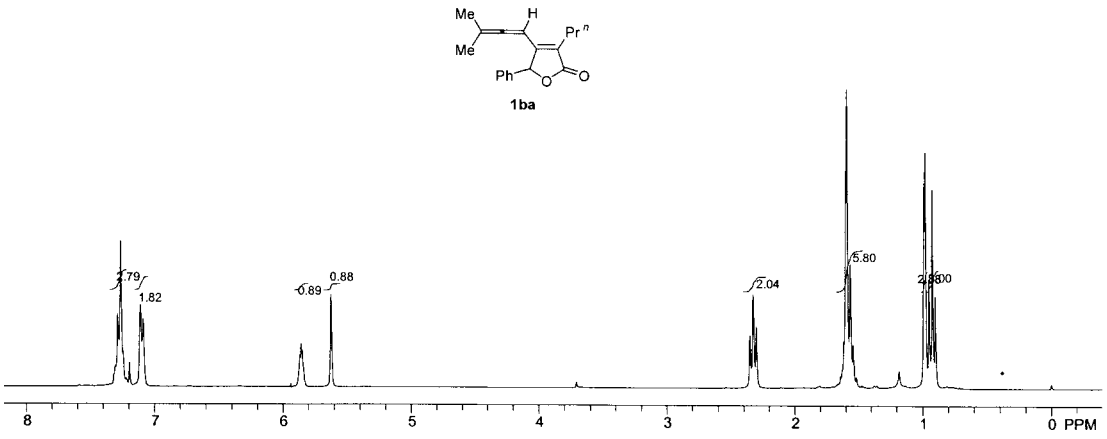
0.951
0.926
0.902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Pr n
Ph
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6
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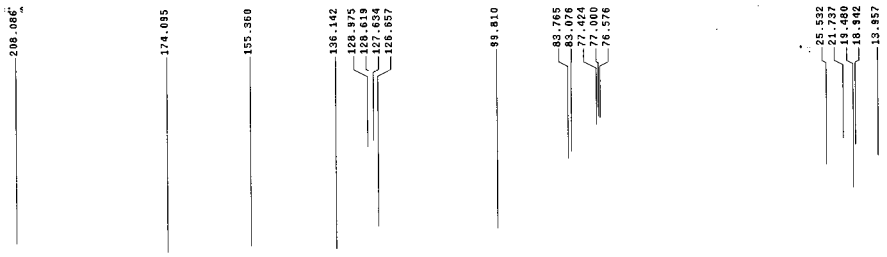
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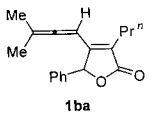
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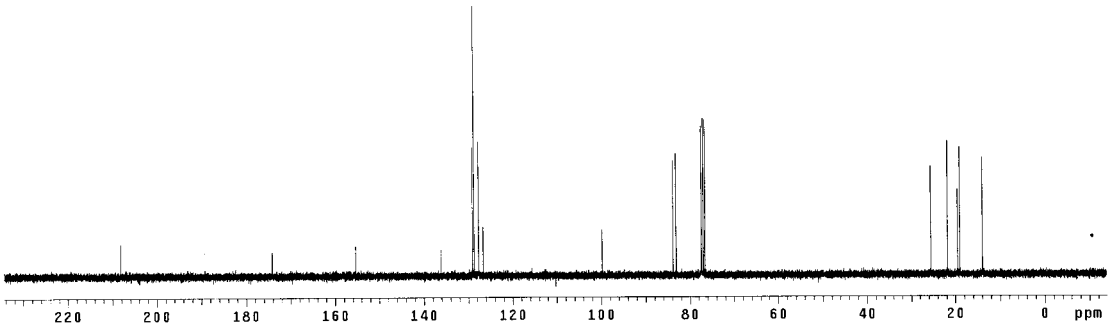
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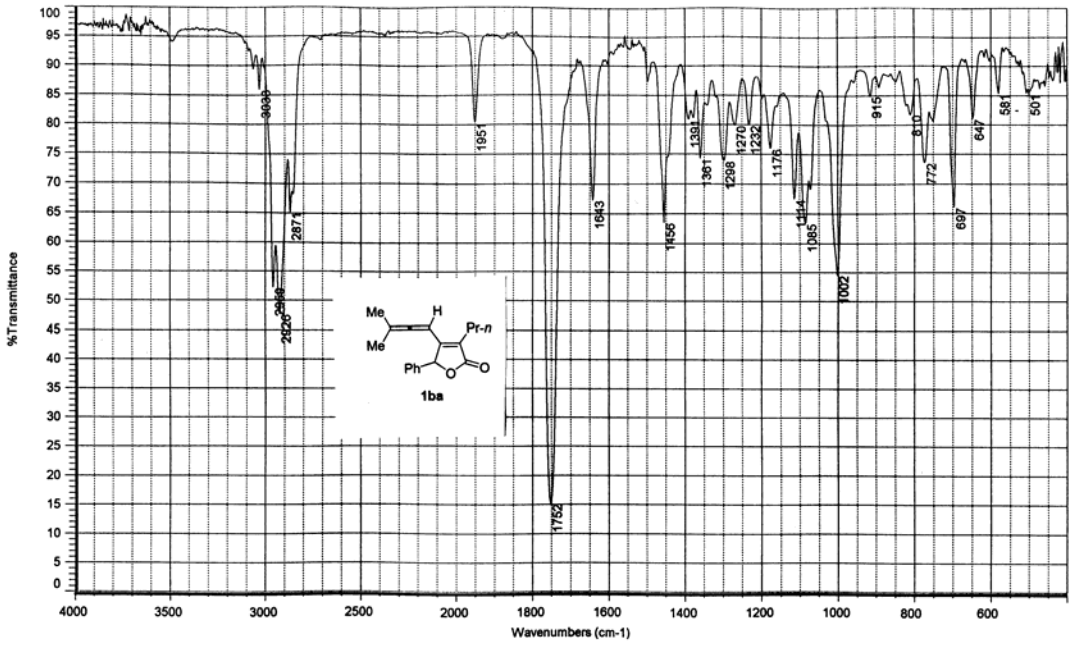
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810
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697
647
581
501
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H
Pr-n
Me
Ph
O
O
1ba


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1.907
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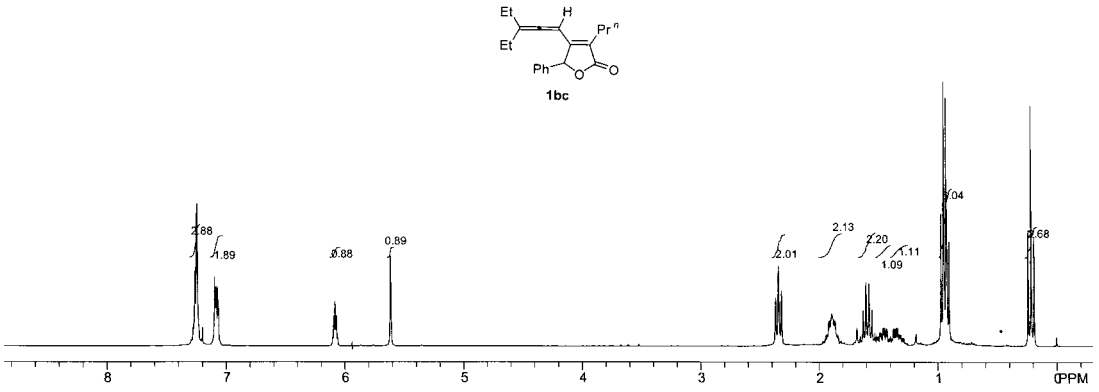
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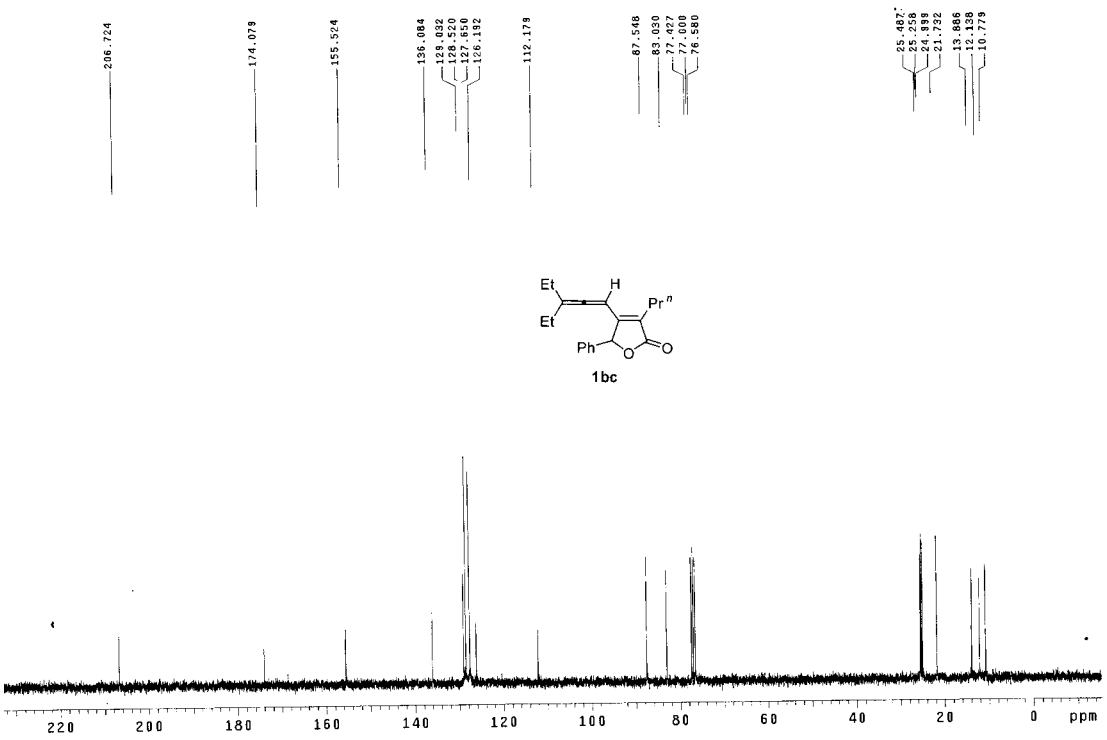
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12.138
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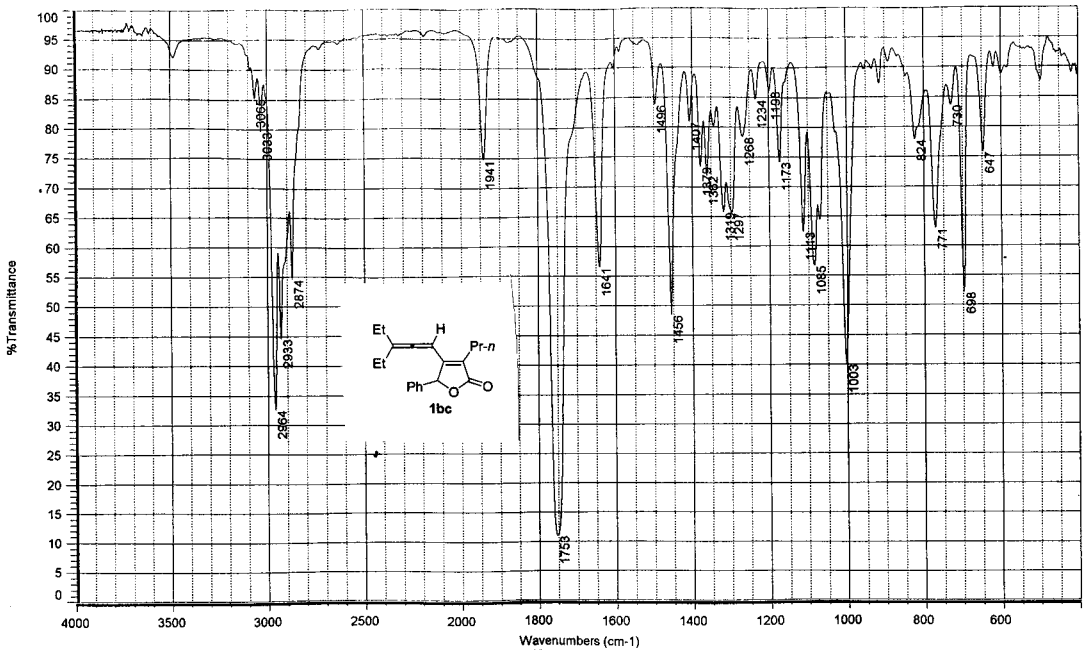
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1753
1641
1496
1456
1401
1379
1362
1339
1297
1268
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1119
1085
1003
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730
698
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Wavenumbers (cm-1)


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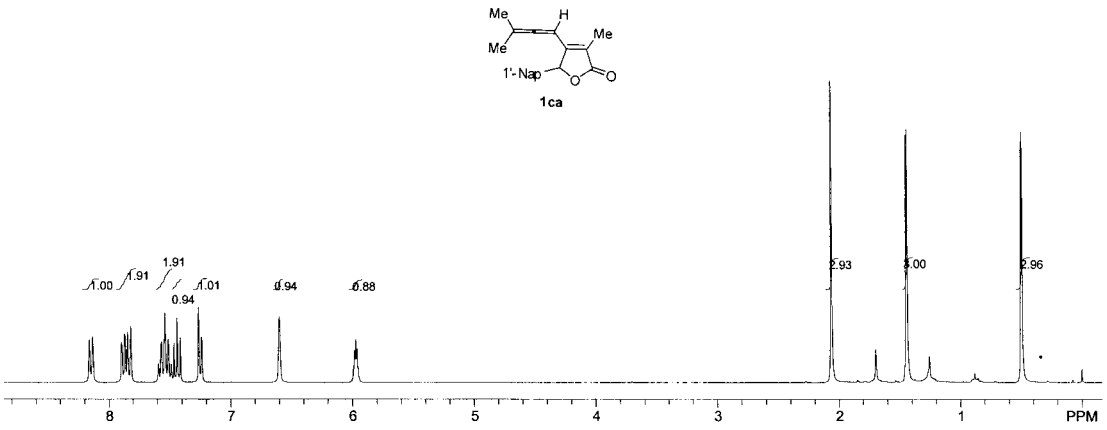
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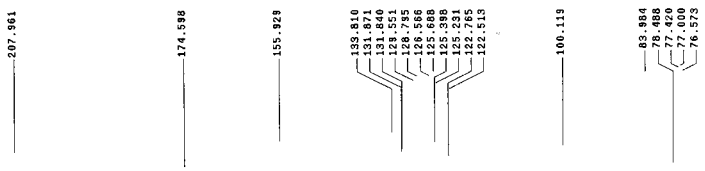
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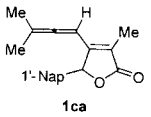
8.648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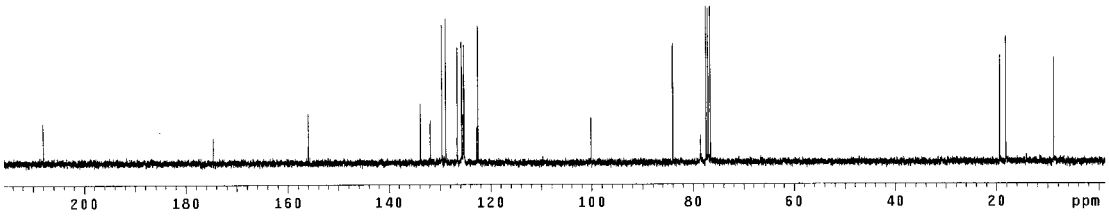
Me
Me
1'-Nap
O
O
1ca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180
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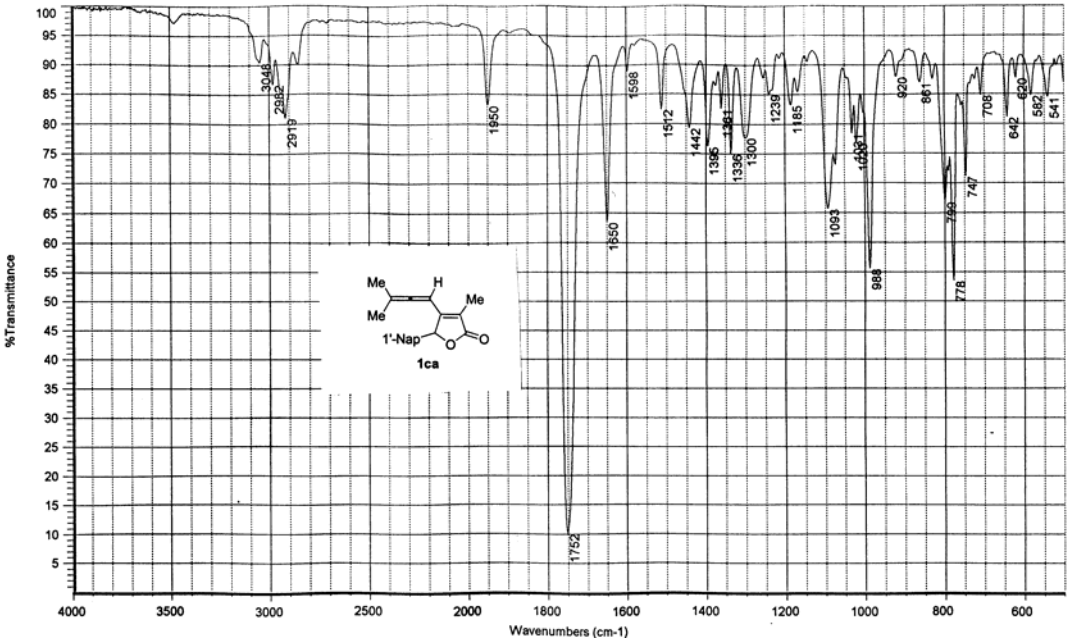
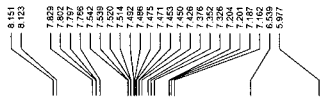
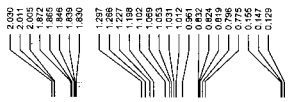
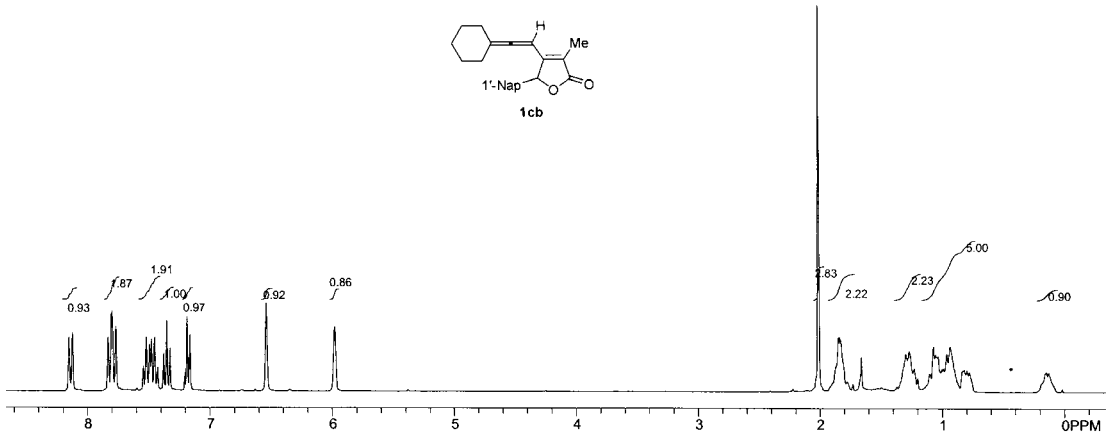
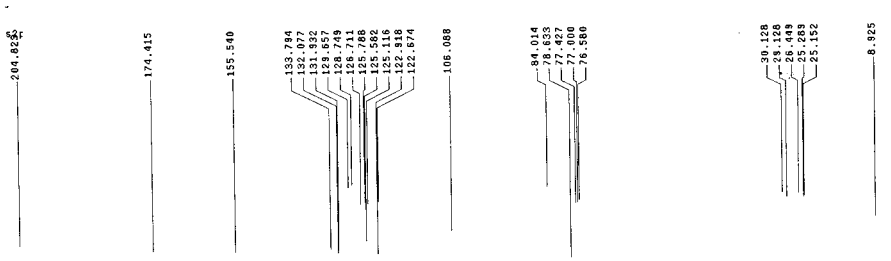
80
60
40
20
ppm

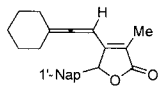

%Transmittance
Wavenumbers (cm-1)
Me
H
Me
Me
1'-Nap
O
O
1ca
3048
2982
2919
1950
1752
1598
1550
1512
1442
1395
1361
1336
1300
1239
1185
1093
1037
988
920
861
793
778
747
708
642
620
582
541



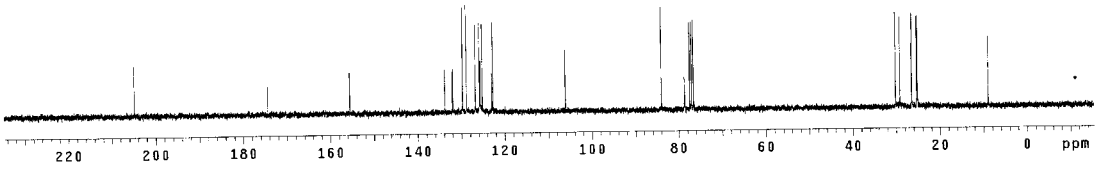


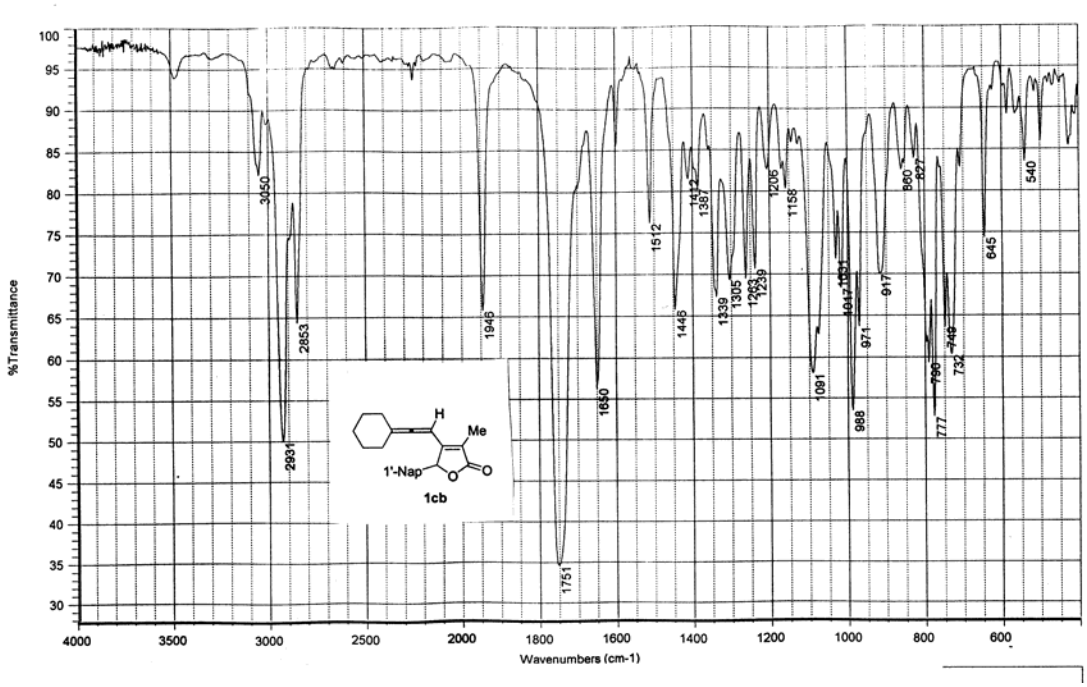

H
Me
1'-Nap
O
O
1cb
0.93
1.87
1.91
1.00
0.97
0.92
0.86
2.83
2.22
2.23
5.00
0.90
8
7
6
5
4
3
2
1
0PPM

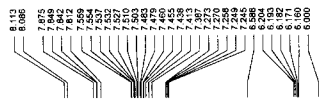

204.825
174.415
155.540
133.794
132.977
131.892
128.657
128.749
126.711
125.788
125.582
125.116
122.838
122.674
106.088
84.014
78.633
77.427
77.000
76.580
39.128
29.428
28.408
25.283
25.152
8.925

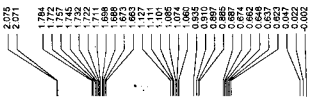

H
Me
1'-Nap
O
O

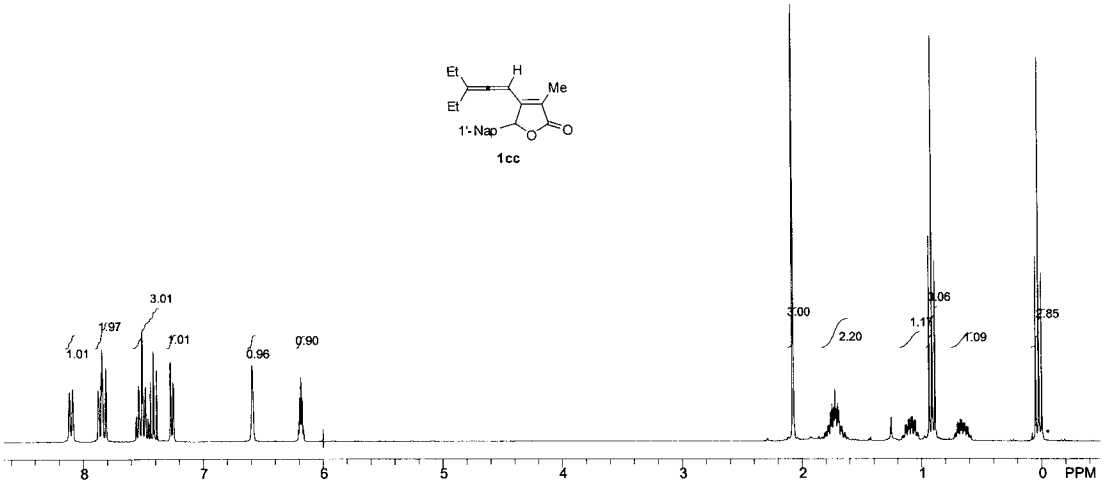
1cb

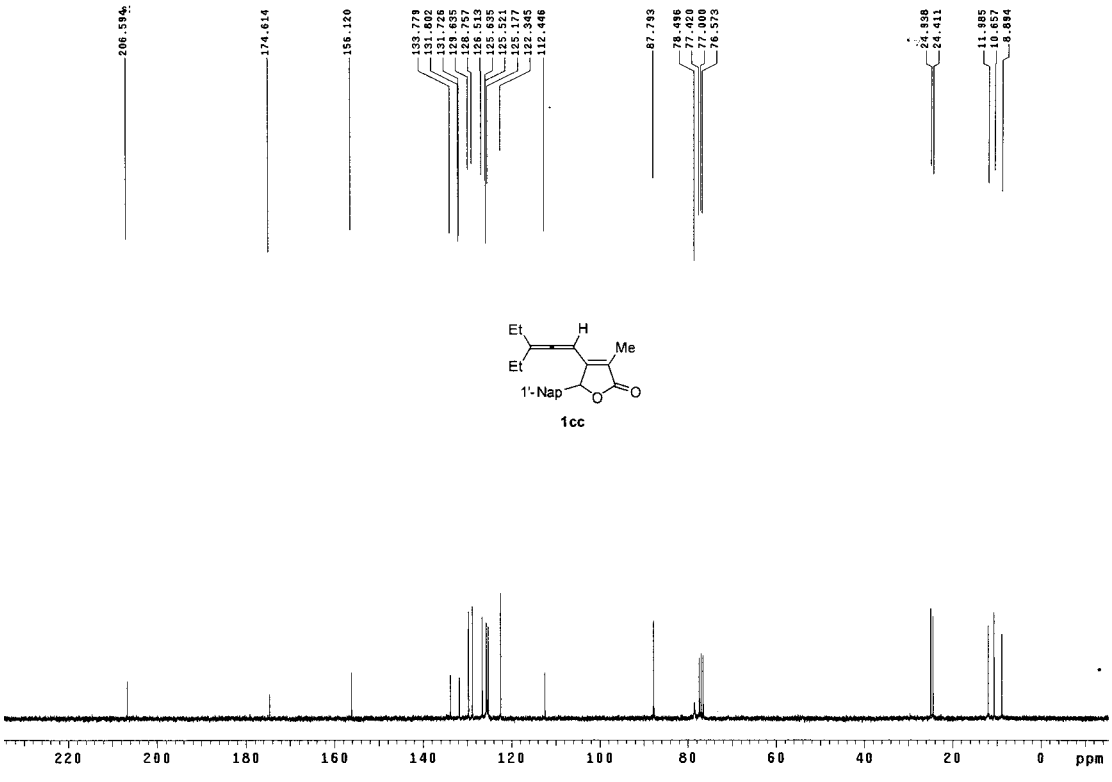

220
200
180
160
140
120
100
80
60
40
20
0
ppm

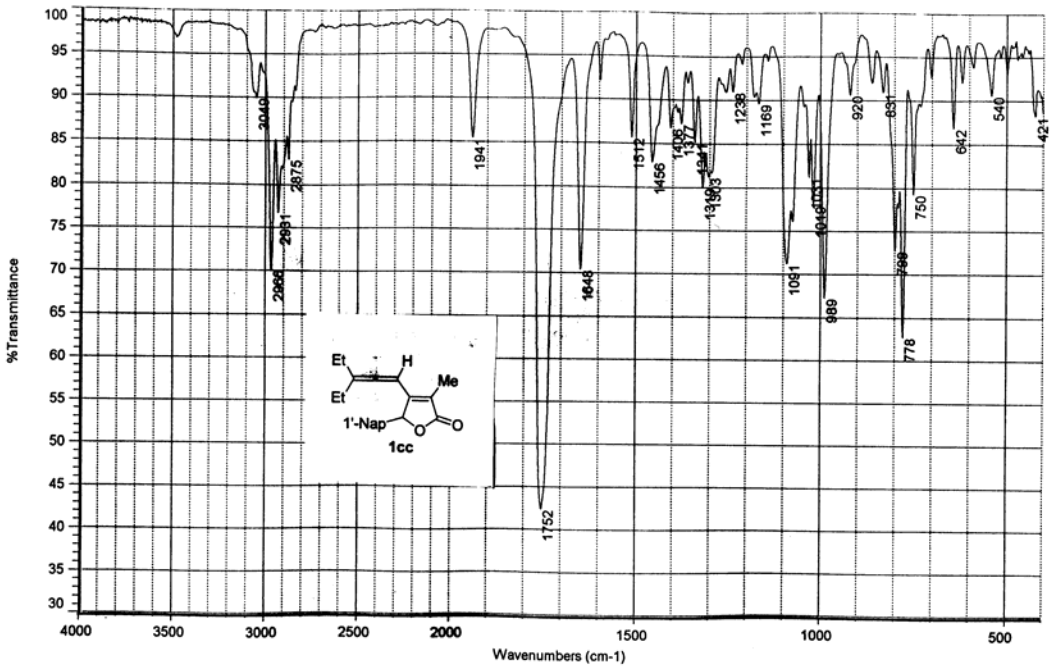

%Transmittance
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
3050
2931
2853
1946
1751
1650
1512
1446
1387
1339
1305
1253
1239
1206
1158
1091
1031
988
971
917
860
827
777
748
732
645
540
H
Me
1'-Nap
O
O
1cb

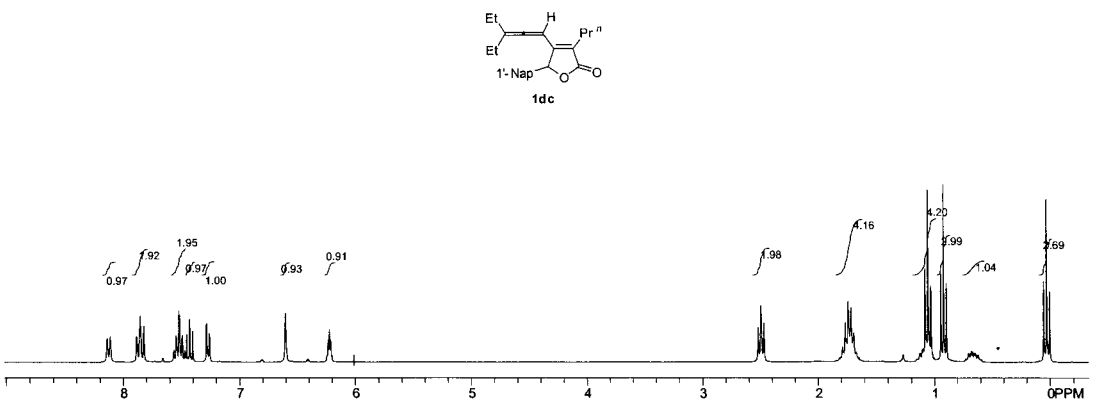


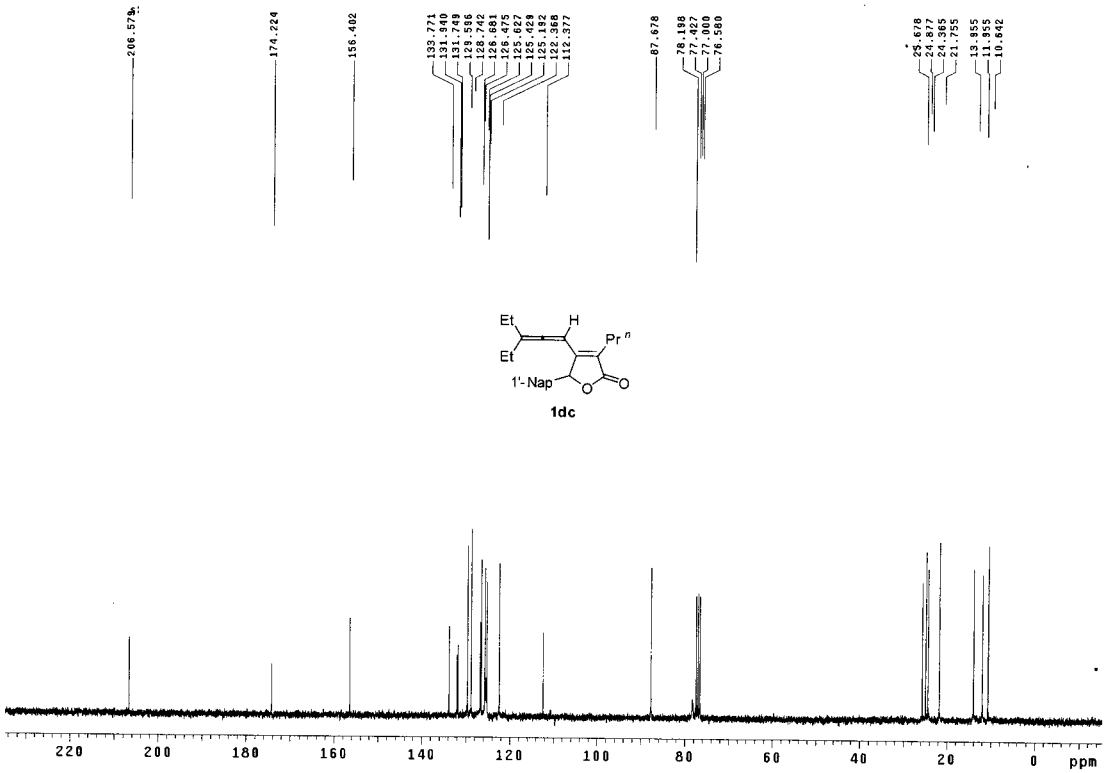


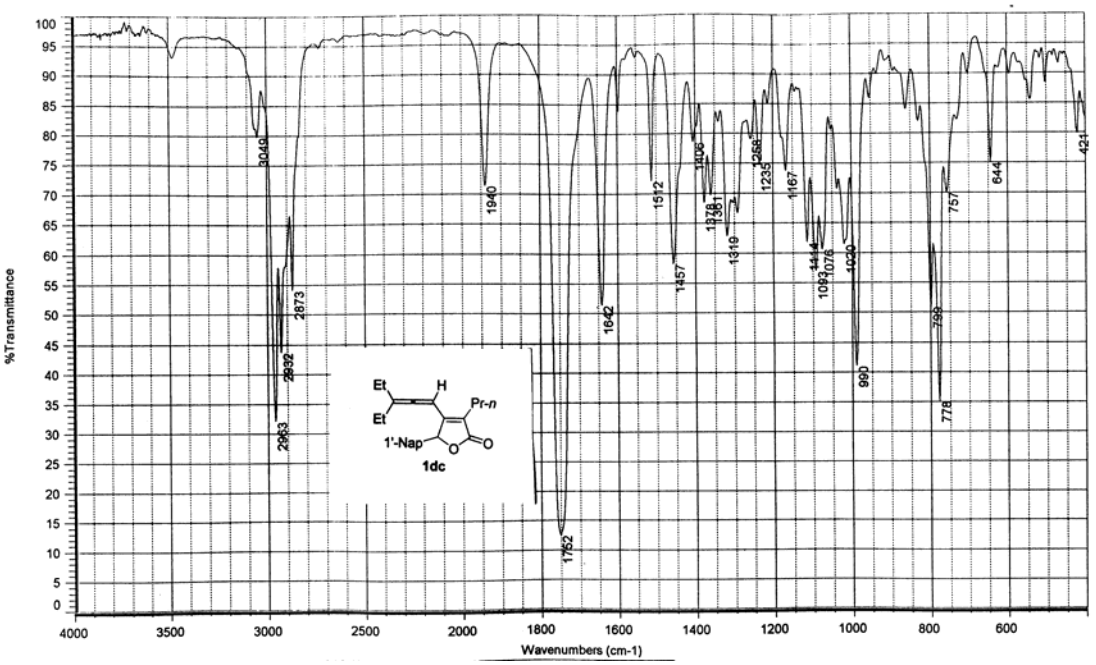

Et
H
Me
Et
1'-Nap
O
O
1cc
1.01
1.97
3.01
1.01
0.96
0.90
3.00
2.20
1.11
3.06
1.09
2.85
8
7
6
5
4
3
2
1
0
PPM

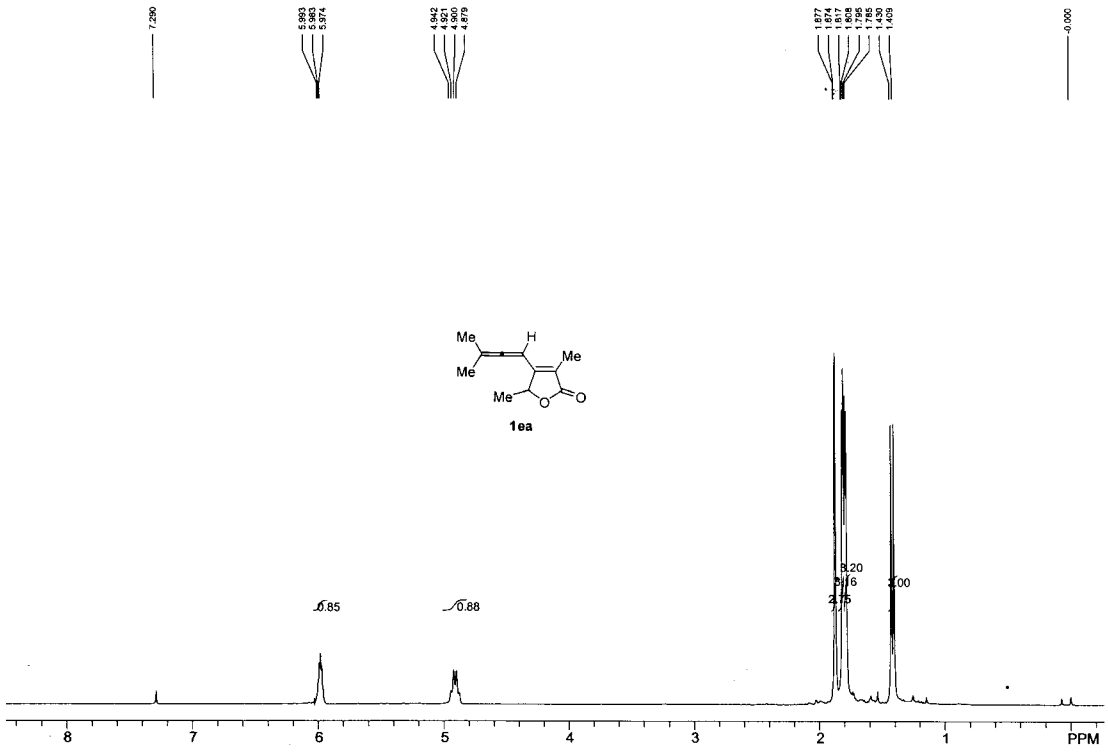

206.594
174.614
156.120
133.779
131.802
131.726
129.695
128.757
126.513
125.635
125.521
125.177
122.345
112.446
87.793
78.496
77.420
77.000
76.573
24.838
24.411
11.985
10.657
8.894
Et
H
Me
Et
1'-Nap
O
O
1cc
220
200
180
160
140
120
100
80
60
40
20
0
ppm

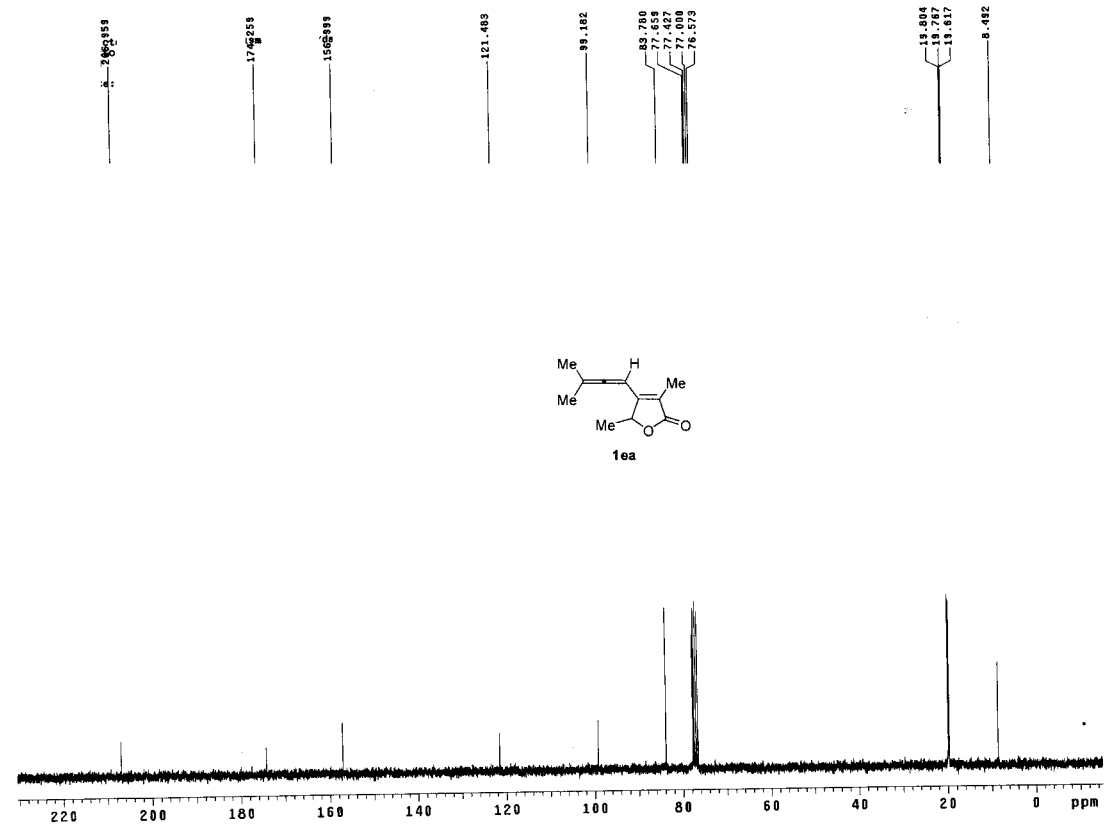

%Transmittance
Wavenumbers (cm-1)
Et
H
Me
Et
1'-Nap
O
O
1cc

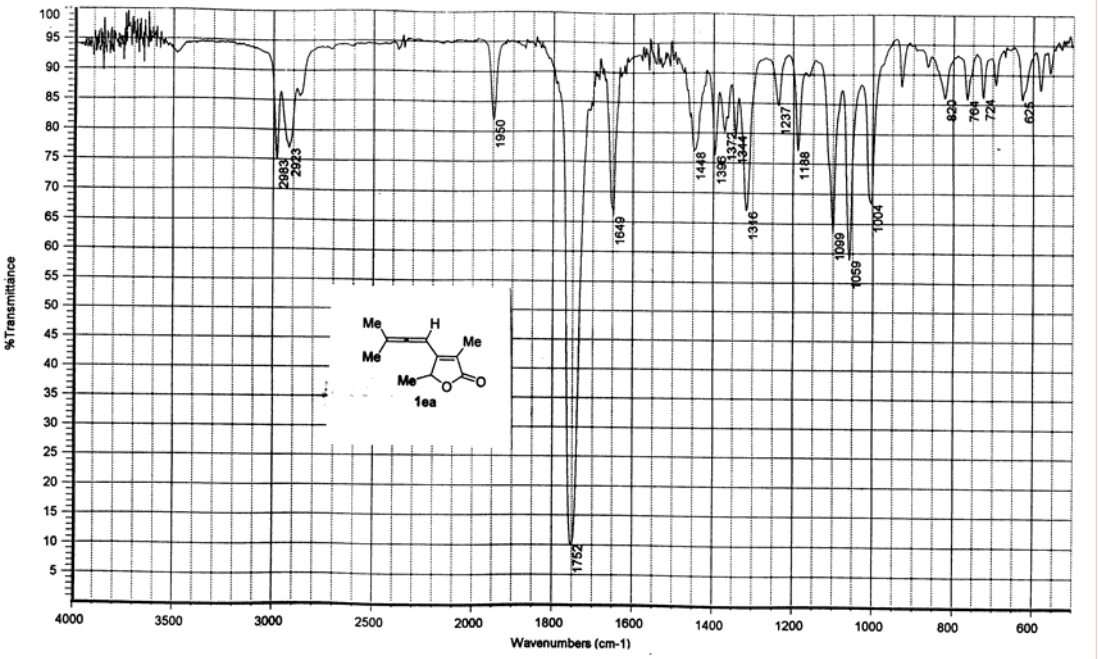

Et
H
Pr n
Et
1'-Nap
O
O
1dc
0.97
1.92
1.95
0.97
1.00
0.93
0.91
1.98
4.16
4.20
3.99
1.04
2.69
0PPM

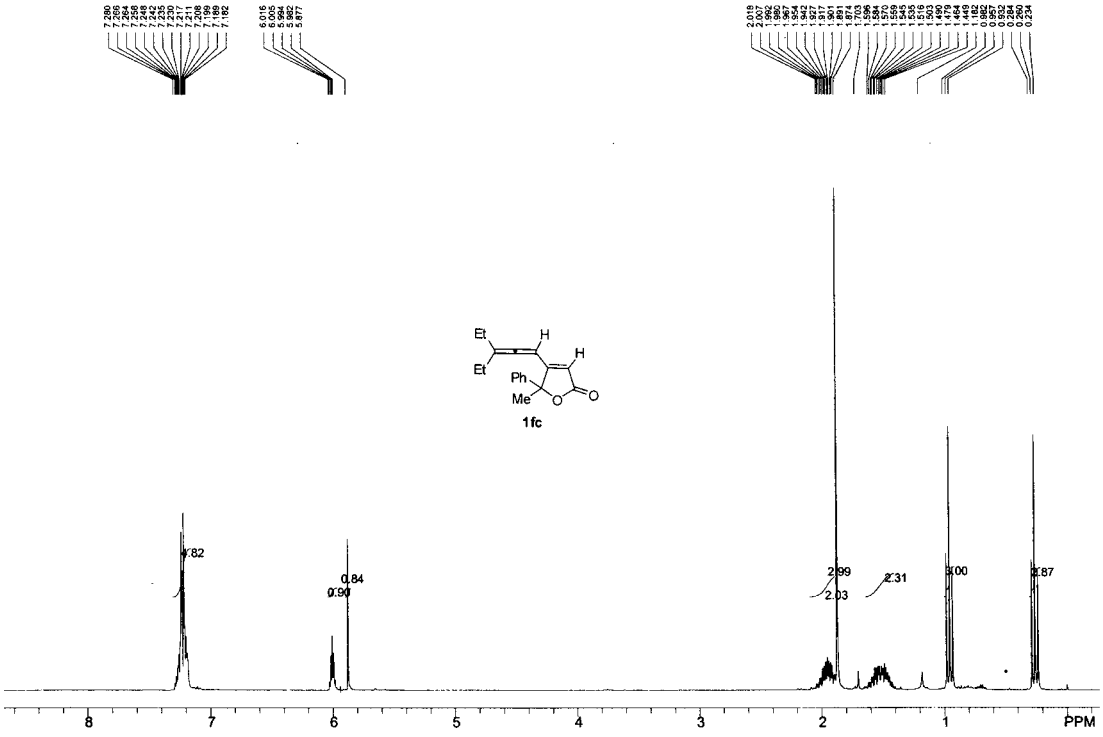

206.575
174.224
156.402
133.771
131.840
131.749
129.596
128.742
126.681
126.475
125.627
125.429
125.152
122.386
112.377
87.678
78.198
77.427
77.000
76.580
25.678
24.877
24.365
21.755
13.955
11.355
10.642
Et
H
Et
Pr n
1'-Nap
O
O
1dc
220
200
180
160
140
120
100
80
60
40
20
0
ppm

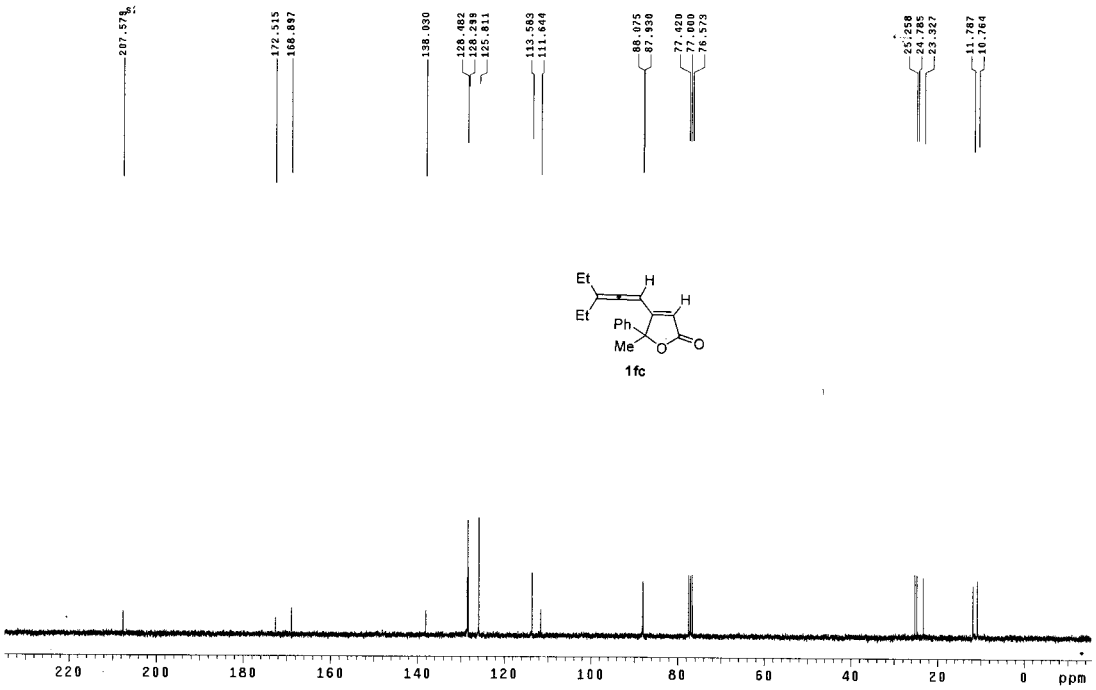

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
3049
2963
2932
2873
1940
1752
1642
1512
1457
1406
1378
1361
1319
1268
1235
1167
1093
1076
1020
990
778
757
644
Et
H
Et
Pr-n
1'-Nap
O
O
1dc
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
Wavenumbers (cm-1)

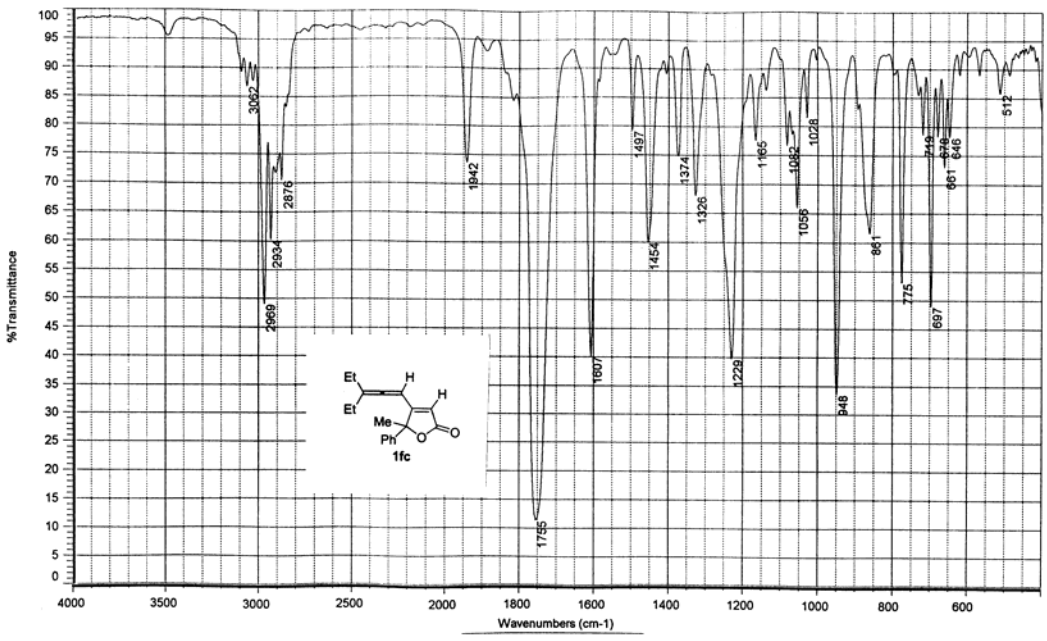

7.290
5.993
5.983
5.974
4.942
4.921
4.900
4.879
1.877
1.854
1.817
1.808
1.795
1.785
1.430
1.409
0.000
Me
H
Me
Me
Me
O
1ea
0.85
0.88
3.20
3.16
2.75
2.00
8
7
6
5
4
3
2
1
PPM

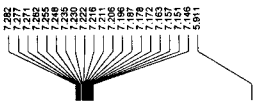

174.253
156.399
121.483
99.182
83.760
77.659
77.427
77.008
76.573
19.804
19.767
19.617
8.492
Me
H
Me
Me
Me
O
1ea
220
200
180
160
140
120
100
80
60
40
20
0
ppm

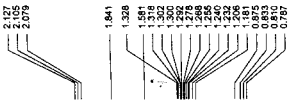

%Transmittance
Wavenumbers (cm-1)
2983
2923
1950
1752
1649
1448
1396
1372
1344
1316
1237
1188
1099
1059
1004
820
764
724
625
Me
H
Me
Me
Me
O
O
1ea

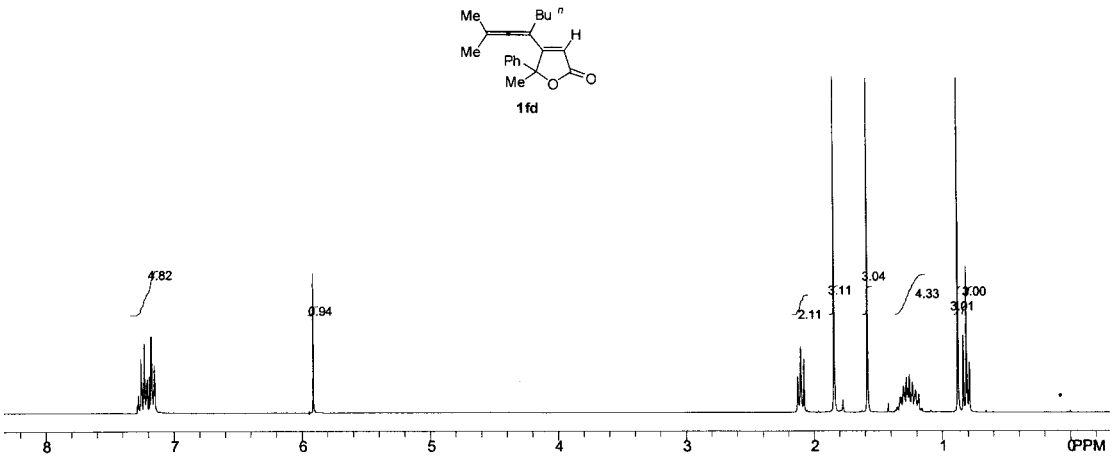

Et
H
Et
H
Ph
Me
O
O
1fc
0.82
0.84
0.90
2.99
2.03
2.31
3.00
2.87
PPM

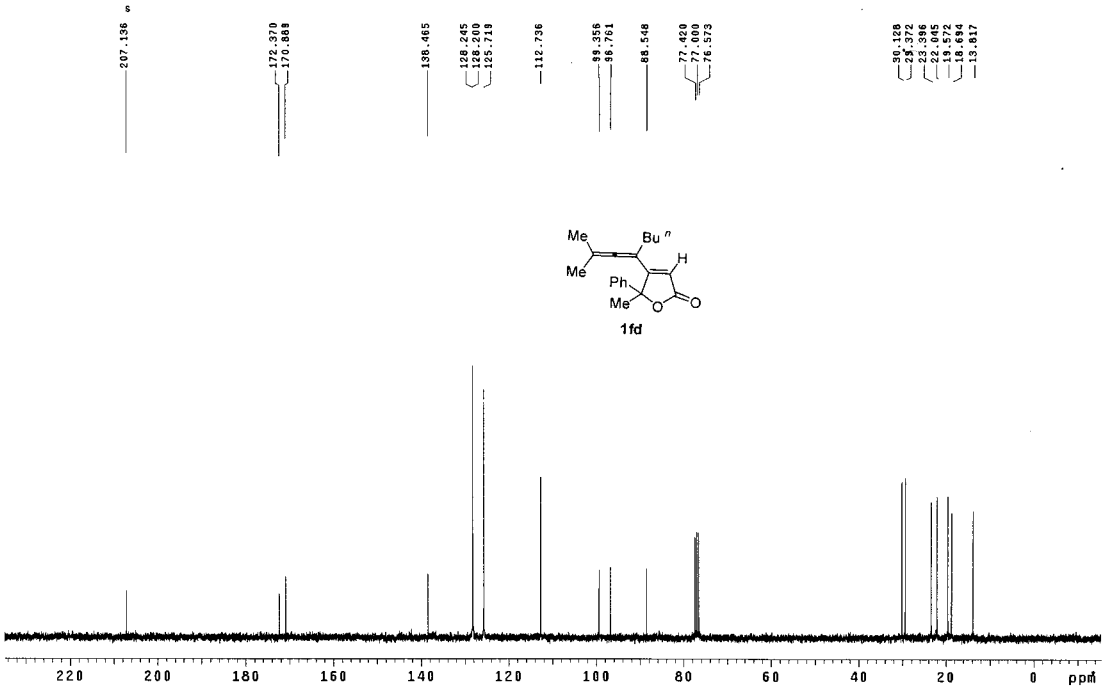

207.579
172.515
166.897
138.030
128.482
128.299
125.811
113.583
111.644
88.075
87.930
77.420
77.000
76.579
25.258
24.785
23.327
11.787
10.764
Et
H
Et
H
Ph
Me
O
O
1fc
220
200
180
160
140
120
100
80
60
40
20
0
ppm

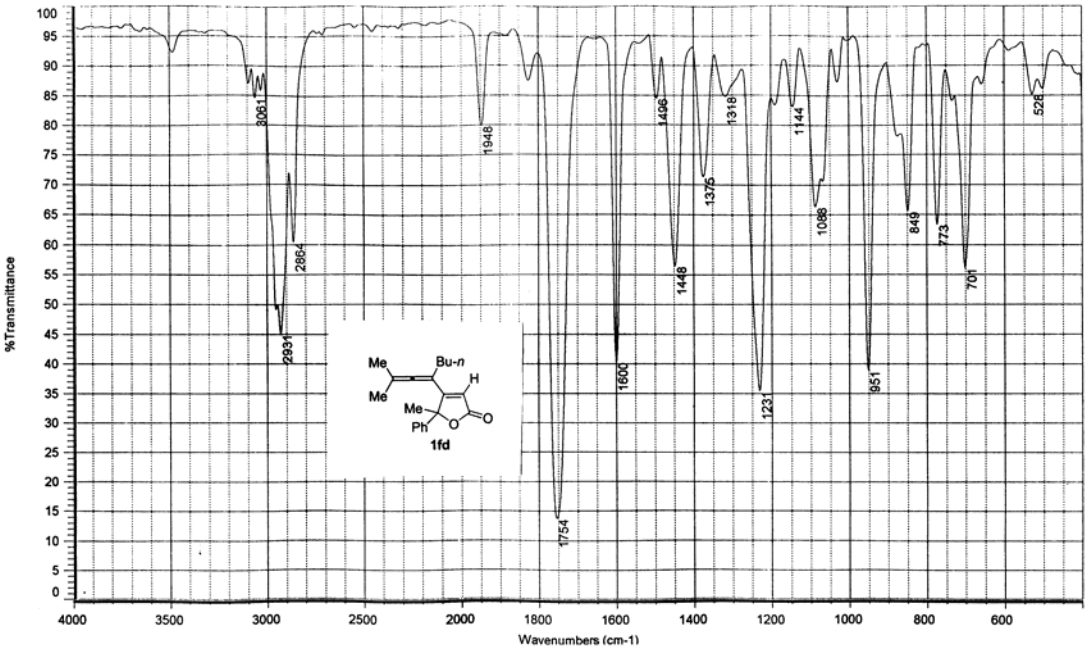

%Transmittance
Wavenumbers (cm-1)
3062
2969
2934
2876
1942
1765
1607
1497
1454
1374
1326
1229
1165
1082
1056
1028
948
841
775
697
661
646
512
Et
H
Et
H
Me
Ph
O
O
1fc

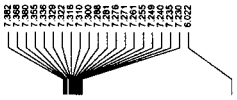


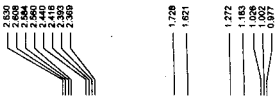


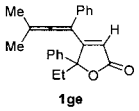

Me
Bu n
H
Me
Ph
Me
O
O
1fd
4.82
0.94
2.11
3.11
3.04
4.33
3.01
3.00
8
7
6
5
4
3
2
1
0PPM

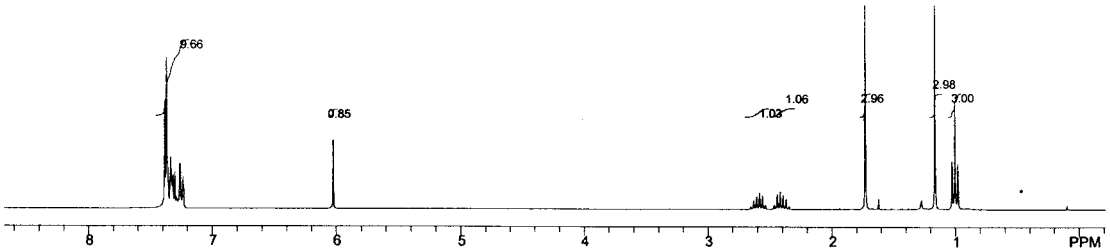

Me
Bu n
H
Me
Ph
Me
O
O
1fd
220
200
180
160
140
120
100
80
60
40
20
0
ppm

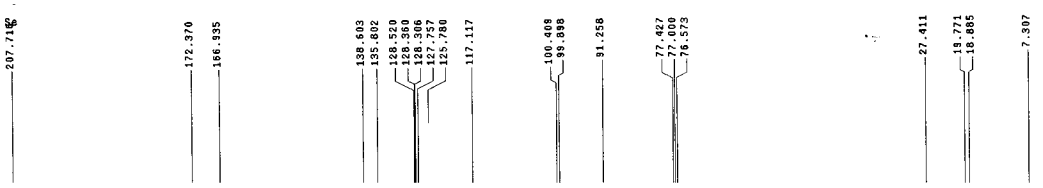

%Transmittance
Wavenumbers (cm-1)
3061
2931
2864
1948
1754
1600
1496
1448
1376
1318
1231
1144
1088
951
849
773
701
526
Me
Me
Bu-n
H
Me
Ph
O
O
1fd

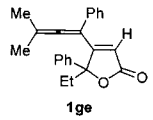

7.362
7.348
7.339
7.335
7.326
7.322
7.316
7.310
7.300
7.289
7.276
7.271
7.261
7.255
7.249
7.240
7.235
7.230
6.022


2.630
2.608
2.594
2.560
2.510
2.415
2.393
2.369
1.728
1.621
1.272
1.183
1.026
1.002
0.977

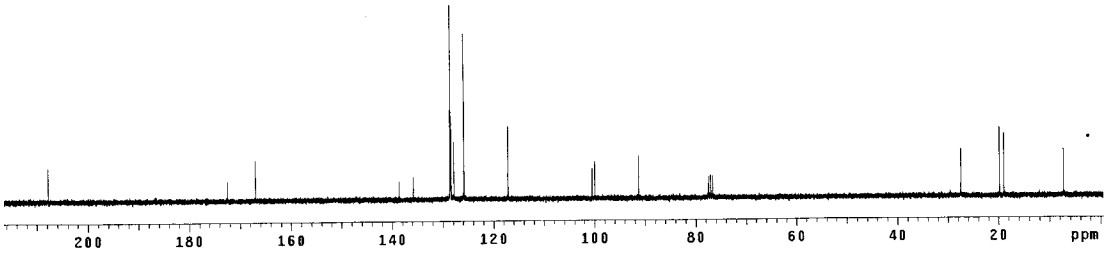

Me
Me
Ph
Ph
Et
O
O
1ge

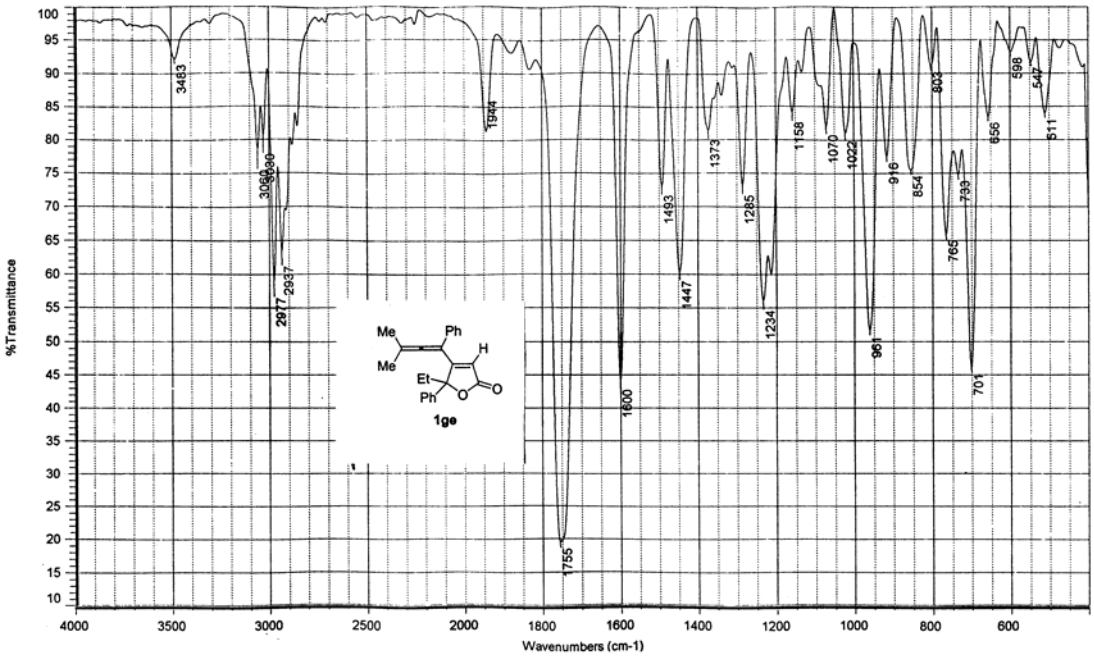

6.66
0.85
1.03
1.06
2.96
2.98
3.00
8
7
6
5
4
3
2
1
PPM

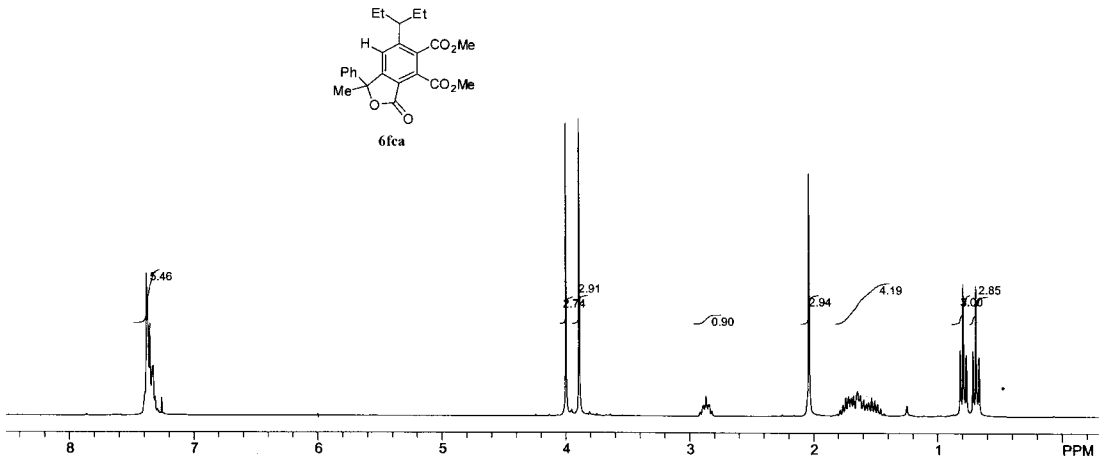

207.718
172.370
166.935
138.603
135.802
128.520
128.360
128.306
127.757
125.780
117.117
100.408
99.898
91.258
77.427
77.000
76.573
27.411
19.771
18.885
7.397

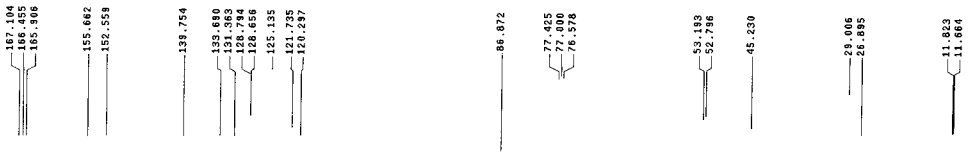

Me
Ph
H
Me
Ph
Et
O
O

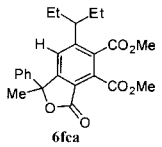
1ge

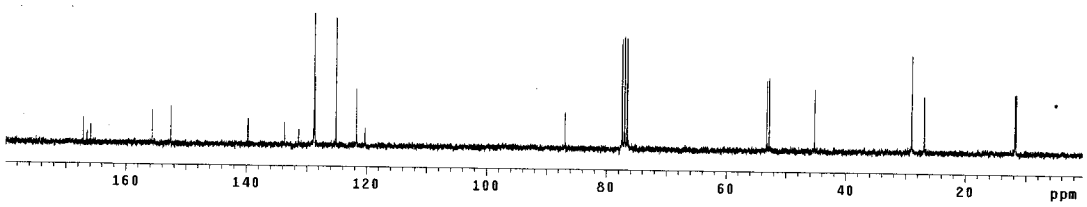

200
180
160
140
120
100
80
60
40
20
ppm

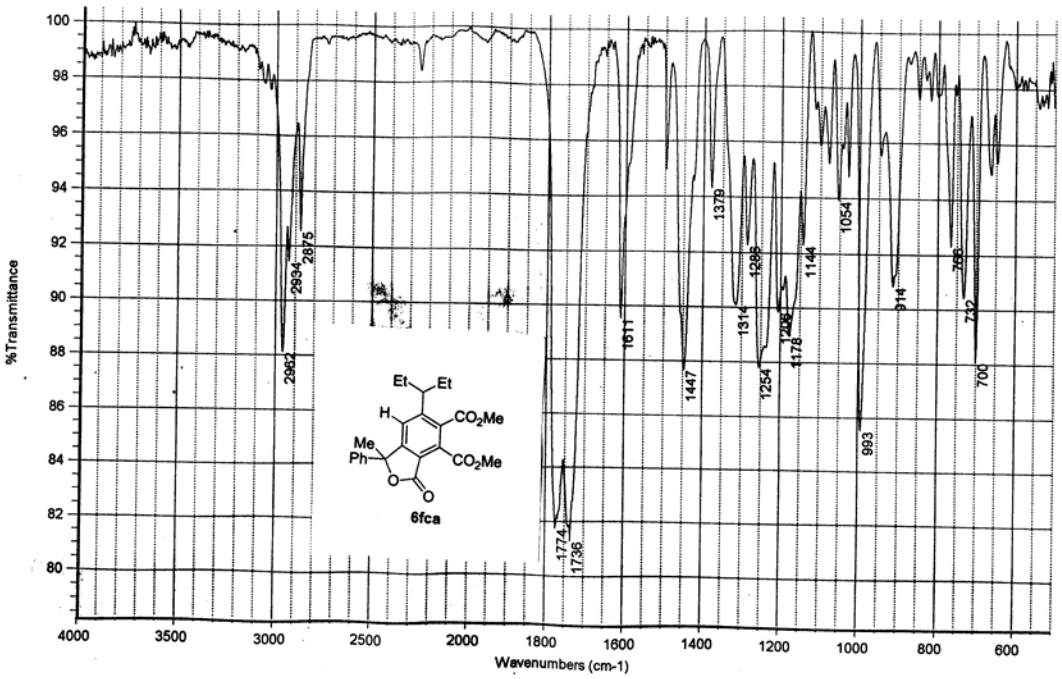

%Transmittance
Wavenumbers (cm-1)
3483
3060
3030
2977
2937
1944
1755
1600
1493
1447
1373
1285
1234
1158
1070
1022
961
916
854
803
793
765
701
656
598
542
511
Me
Ph
H
Me
Et
Ph
O
O
1ge

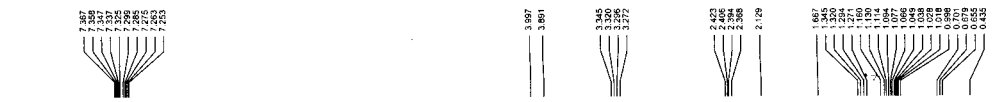

Et
Et
H
CO2Me
Ph
Me
CO2Me
O
O
6fca
5.46
2.91
2.74
0.90
2.94
4.19
2.85
3.00
8
7
6
5
4
3
2
1
PPM

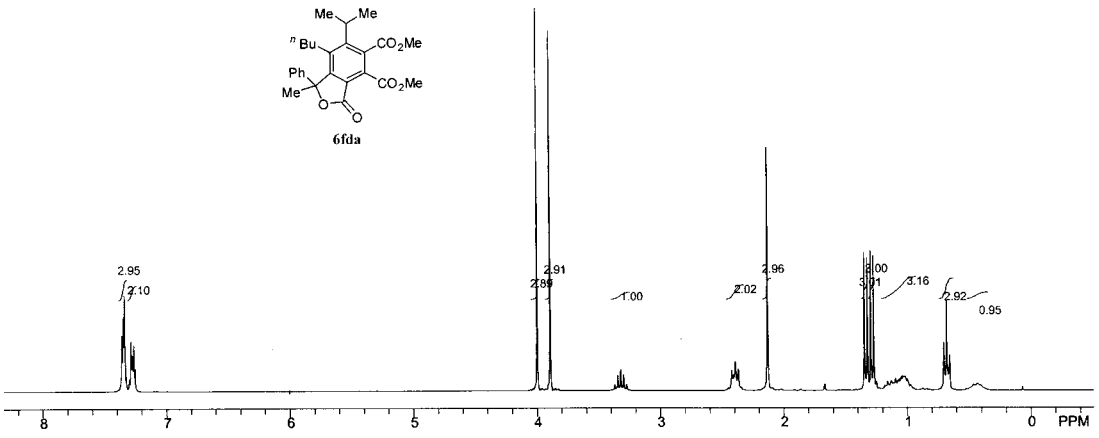


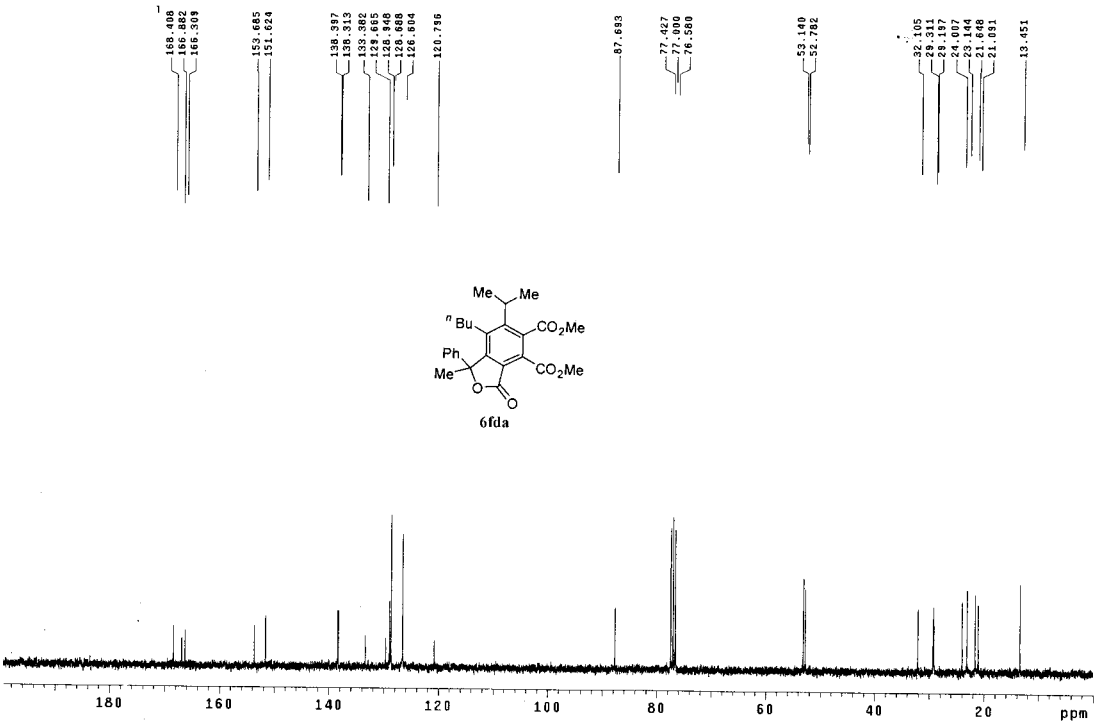

Et
Et
H
CO2Me
Ph
Me
CO2Me
O
O
6fca

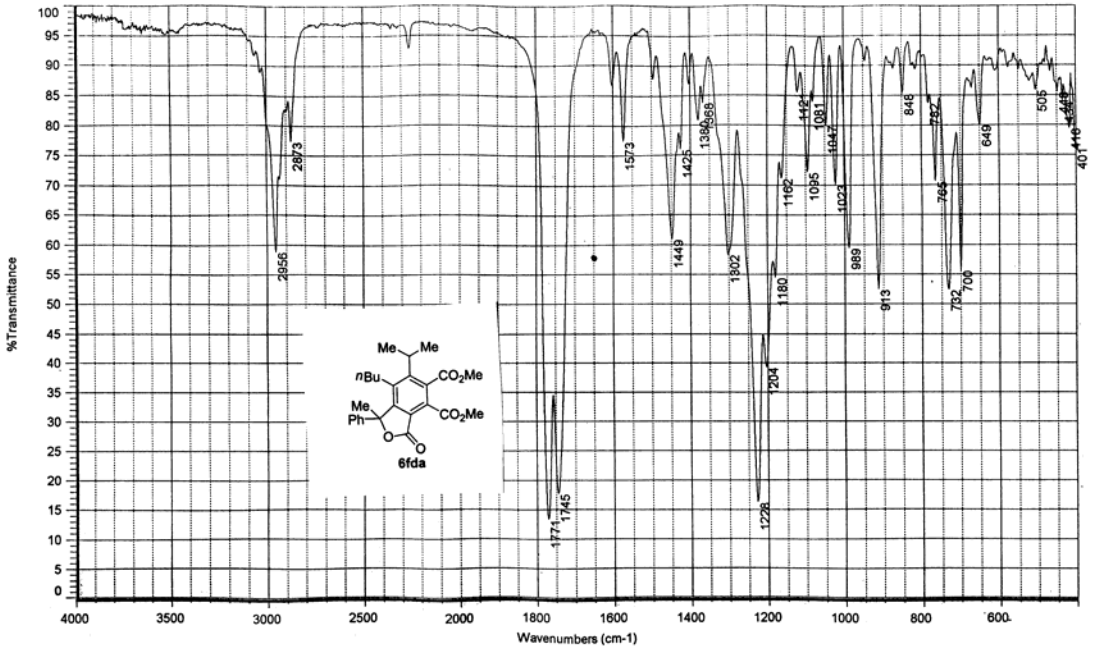

160
140
120
100
80
60
40
20
ppm

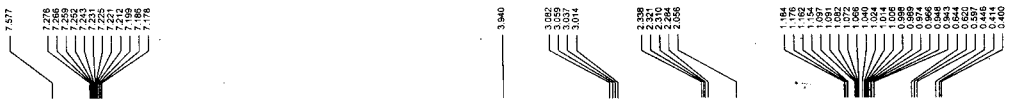

%Transmittance
Wavenumbers (cm-1)
2962
2934
2875
1774
1736
1611
1447
1379
1314
1254
1178
1144
1054
993
914
766
732
700
6fca

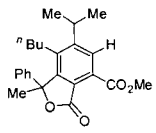



6fda
2.95
2.10
2.91
2.86
1.00
2.02
2.96
3.00
3.01
3.16
2.92
0.95
PPM

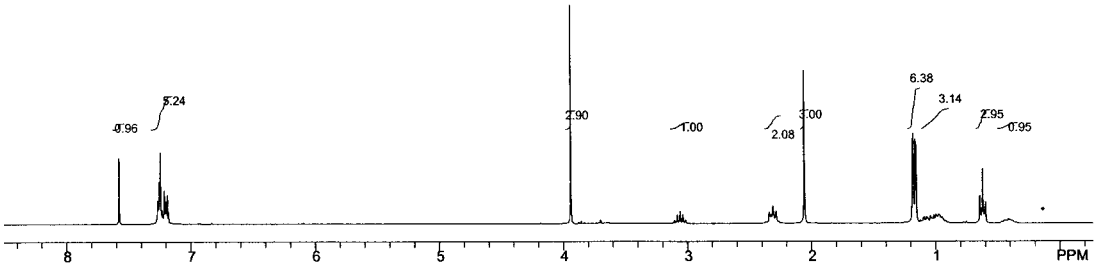

168.408
165.892
166.309
153.685
151.624
138.397
138.313
133.382
129.665
128.948
128.688
126.604
120.796
87.693
77.427
77.000
76.580
53.140
52.782
32.105
29.311
29.197
24.007
23.144
21.646
21.091
13.451
Me
Me
nBu
CO2Me
Ph
Me
CO2Me
O
O
6fda
180
160
140
120
100
80
60
40
20
ppm

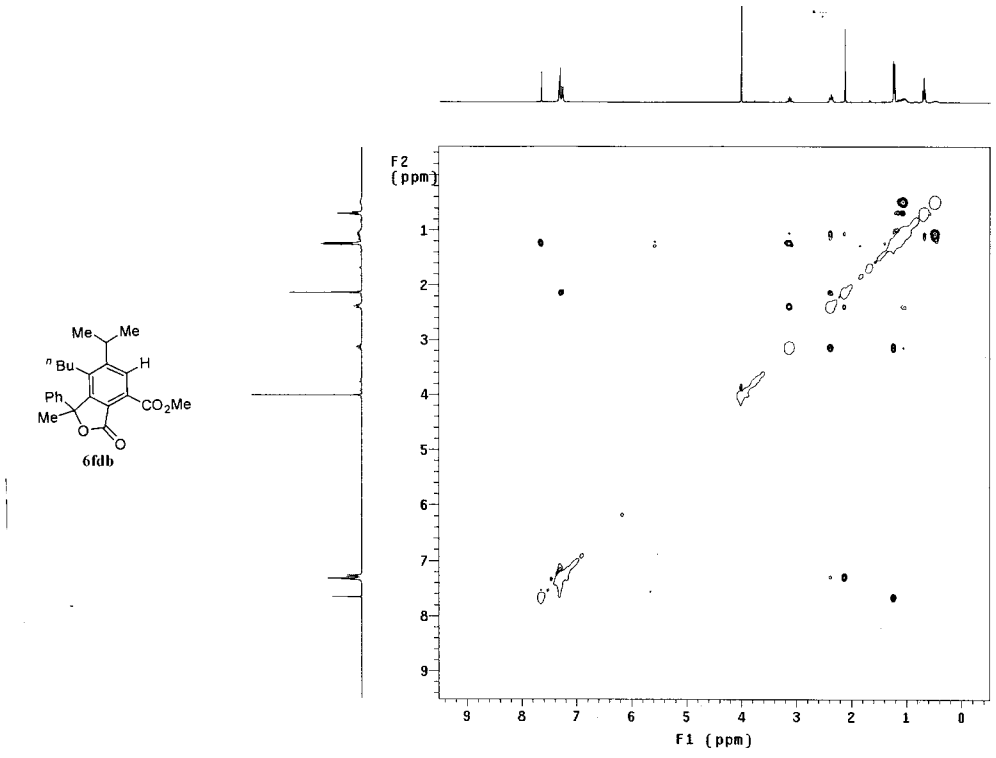

%Transmittance
Wavenumbers (cm-1)
2956
2873
1771
1745
1573
1449
1425
1380
1302
1228
1204
1180
1162
1095
1081
1022
989
913
848
784
732
700
649
505
Me
Me
nBu
CO2Me
Me
Ph
CO2Me
6fda



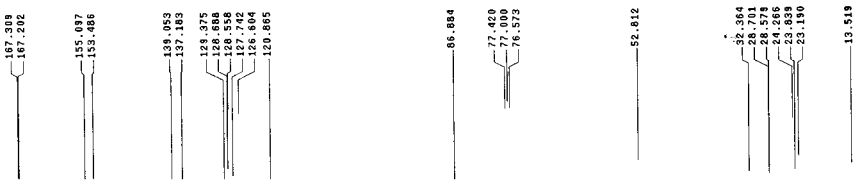


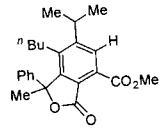
6fdb


0.96
5.24
2.90
1.00
2.08
3.00
6.38
3.14
2.95
0.95
8
7
6
5
4
3
2
1
PPM

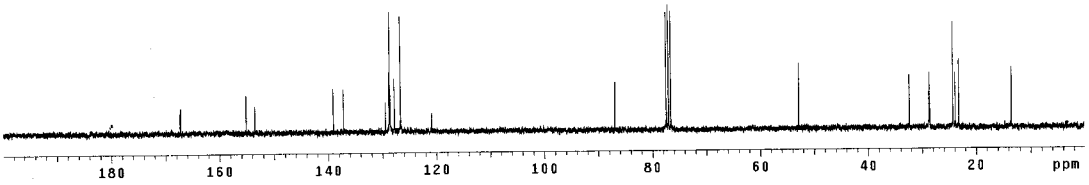

F2 (ppm)
F1 (ppm)

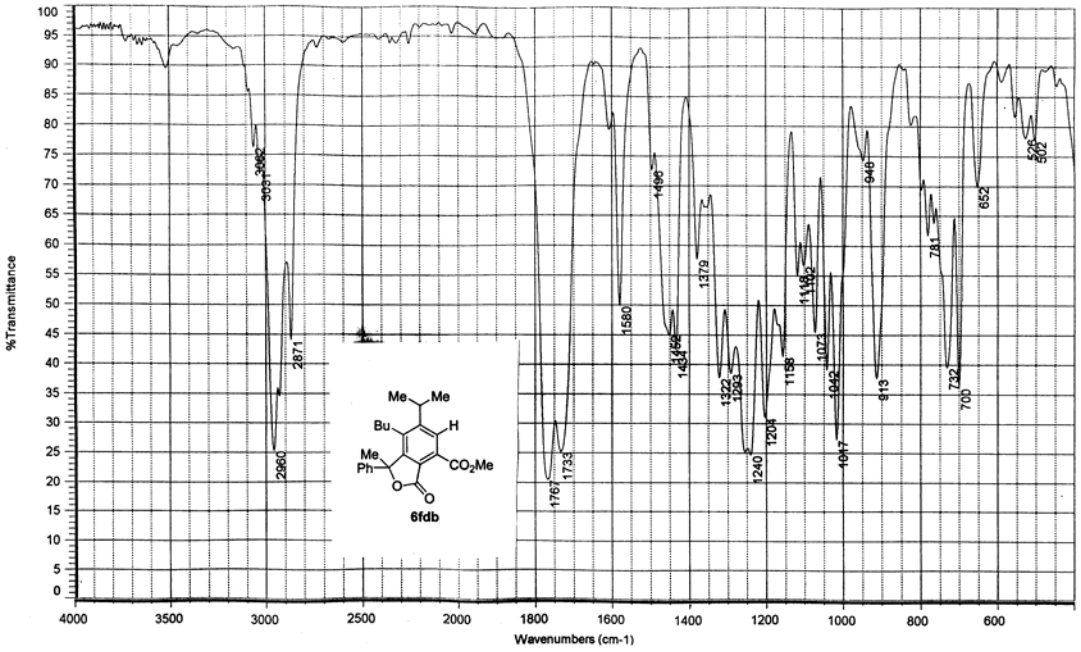
6fdb


167.309
167.202
155.697
153.486
139.053
137.183
129.375
128.688
128.358
127.702
126.804
120.865
86.884
77.420
77.000
76.573
52.812
32.364
28.701
28.578
24.266
23.839
23.190
13.519


Me
Me
n Bu
H
Ph
Me
CO2Me
O
O

6fdb


180
160
140
120
100
80
60
40
20
ppm


%Transmittance
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
2960
2871
1767
1733
1580
1379
1322
1293
1240
1204
1158
1017
946
852
781
732
700
613
526
502
Me
Me
Bu
H
Me
Ph
CO2Me
O
O
6fdb