Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Light-Mediated, Palladium-Catalyzed Cyclizations of Unactivated 1,6-Dienes

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Electronic Supplementary Information

Experimental Section

General experimental methods

All photoreactions were carried out in quartz reaction tubes irradiated by a Matrix-10 photoreactor with sixteen ultraviolet lamps (10 W per lamp). For spectral distribution of irradiance density for the UV lamps, see Figs S1-4.

Figure S1. The spectral distribution of irradiance density for the UV lamps (185&254 nm) used in Matrix185-10 photoreactor

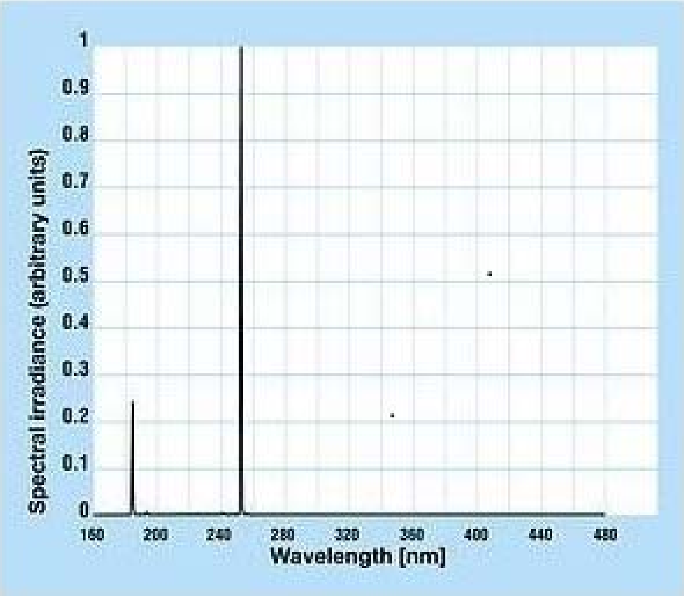


Figure S2. The spectral distribution of irradiance density for the UV lamps (254 nm) used in Matrix254-10 photoreactor

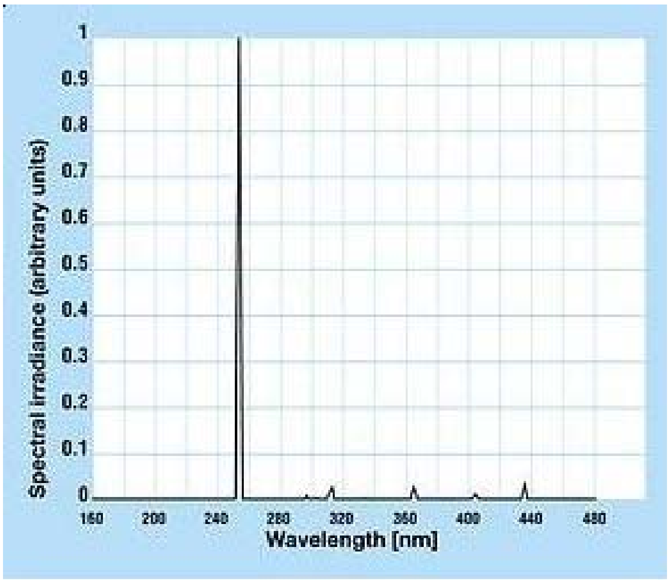


Figure S3. The spectral distribution of irradiance density for the UV lamps (313 nm) used in Matrix313-10 photoreactor

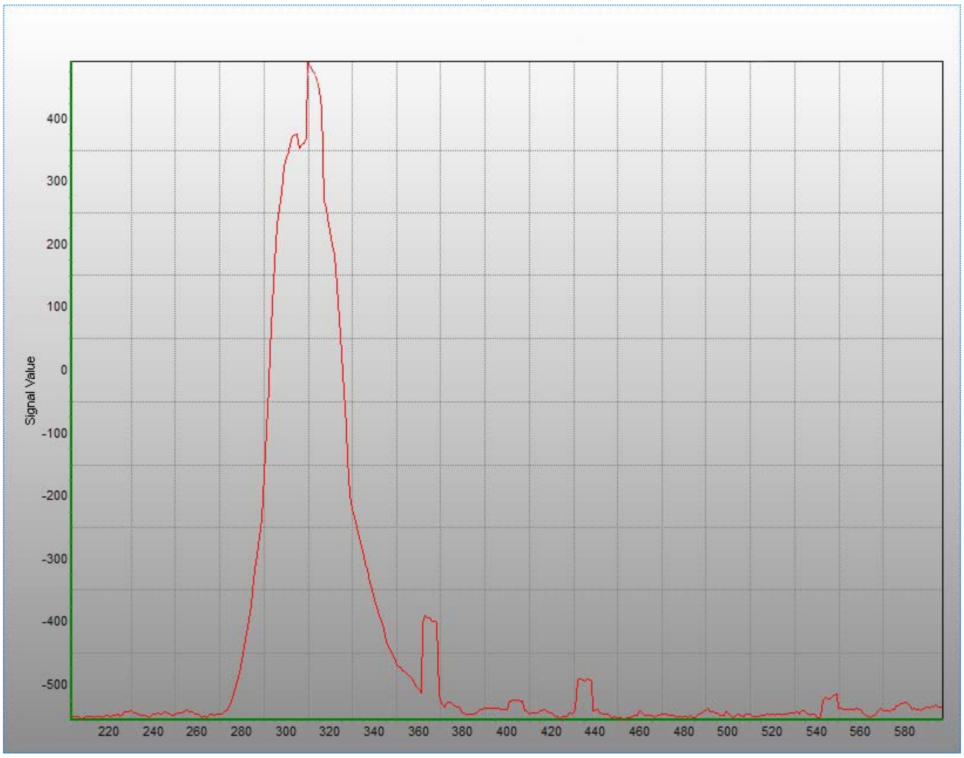
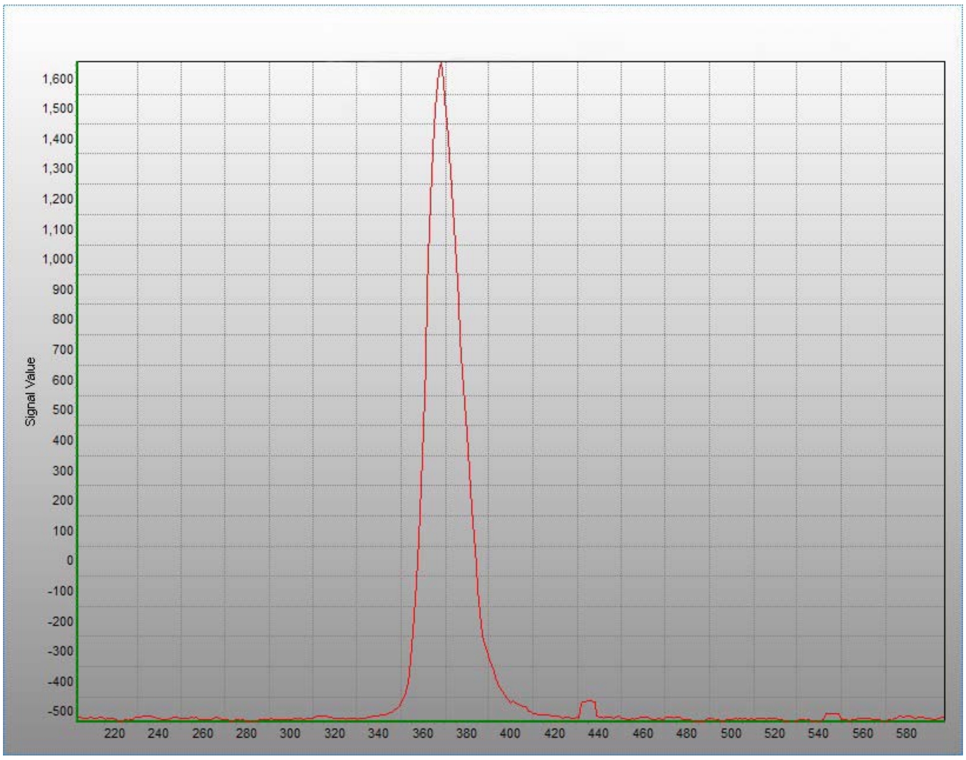
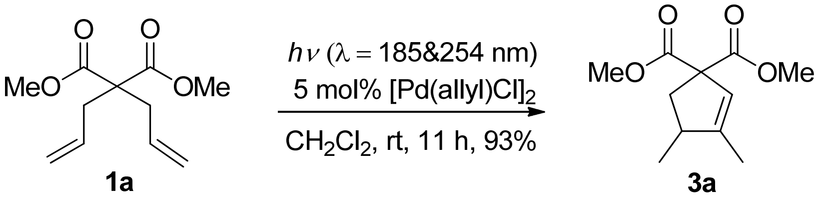


Figure S4. The spectral distribution of irradiance density for the UV lamps (365 nm) used in Matrix365-10 photoreactor



Melting points were determined on a WRS-2 apparatus. IR spectra were recorded on an Avatar 360 FT-IR spectrometer. ^{1}H (400 MHz), and ^{13}C (100 MHz) NMR spectra of samples were recorded on an AVANCE III HD 400 spectrometer using $CDCl_3$ as solvent and TMS as internal standard. MS (EI, 70 eV) determinations were carried out on a Agilent 5973N or GCT spectrometer. HRMS (EI) determinations were carried out on a Waters Micromass GCT spectrometer. Dienes **1a**,[1] **1b**,[2] **1c**,[3] **1d**,[4] **1e**,[3] **1f**,[5] **1g**,[3] **1h**,[6] **2a**,[7] **9**,[8] **10**,[9] and **11**[10] were prepared according to literature procedures. CH_2Cl_2 was distilled from CaH_2 under argon.

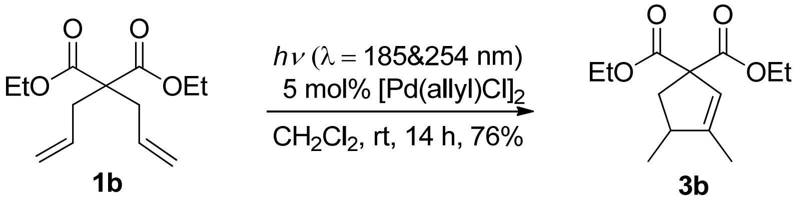
Synthesis of dimethyl 3,4-dimethylcyclopent-2-ene-1,1-dicarboxylate (3a)[11] (General Procedure I)



$[Pd(allyl)Cl]_2$ (4 mg, 0.011 mmol), **1a** (42 mg, 0.20 mmol) and anhydrous CH_2Cl_2 (10 mL) were added into a dried quartz tube under argon atmosphere and degassed with argon for 10 minute. Then the mixture was irradiated at λ = 185&254 nm at rt. The photoreaction was completed after 11 h as monitored by TLC (eluent: petroleum ether /ethyl acetate = 10:1). The solvent was removed and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1→20:1) to afford **3a** as a liquid (39 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 (s, 1 H), 3.73 (s, 3 H), 3.71 (s, 3 H), 2.82-2.62 (m, 2 H), 1.99-1.87 (m, 1 H), 1.73 (s, 3 H), 1.06 (d, J = 6.8 Hz, 3 H).

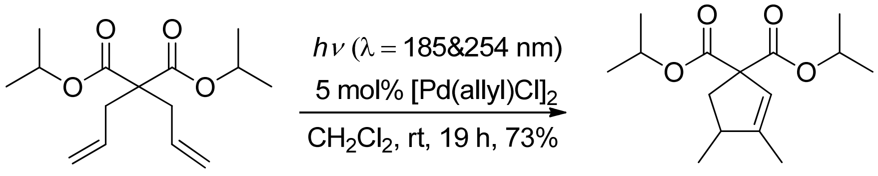
The following compounds were prepared according to General Procedure I.

(1) **Diethyl 3,4-dimethylcyclopent-2-ene-1,1-dicarboxylate (3b)**[5]



The reaction of $[Pd(allyl)Cl]_2$ (4 mg, 0.011 mmol) and **1b** (46 mg, 0.19 mmol) in anhydrous CH_2Cl_2 (10 mL) afforded **3b** as a liquid (35 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 (s, 1 H), 4.24-4.09 (m, 4 H), 2.79-2.64 (m, 2 H), 1.97-1.86 (m, 1 H), 1.73 (s, 3 H), 1.30-1.19 (m, 6 H), 1.06 (d, J = 6.8 Hz, 3 H).

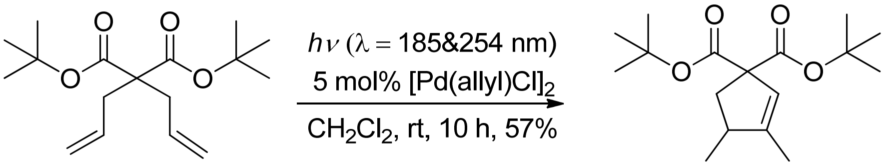
(2) **Diisopropyl 3,4-dimethylcyclopent-2-ene-1,1-dicarboxylate** (**3c**)



1c **3c**

The reaction of $[Pd(allyl)Cl]_2$ (4 mg, 0.011 mmol) and **1c** (49 mg, 0.18 mmol) in anhydrous CH_2Cl_2 (10 mL) afforded **3c** as a liquid (36 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (s, 1 H), 5.08-4.96 (m, 2 H), 2.76-2.67 (m, 2 H), 1.95-1.84 (m, 1 H), 1.72 (s, 3 H), 1.27-1.17 (m, 12 H), 1.05 (d, J = 6.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.6, 171.2, 149.9, 122.2, 68.5, 68.4, 65.1, 41.9, 40.3, 21.5, 19.0, 14.6 ppm; IR (neat) 1720 cm^{-1}; MS (EI, 70 eV) *m/z* 268 (M$^+$, 16.46), 181 (100); HRMS (EI) calcd for $C_{15}H_{24}O_4$ 268.1675, found 268.1676.

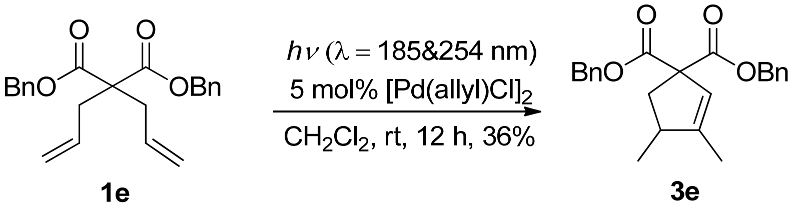
(3) **Di-*tert*-butyl 3,4-dimethylcyclopent-2-ene-1,1-dicarboxylate** (**3d**)



1d **3d**

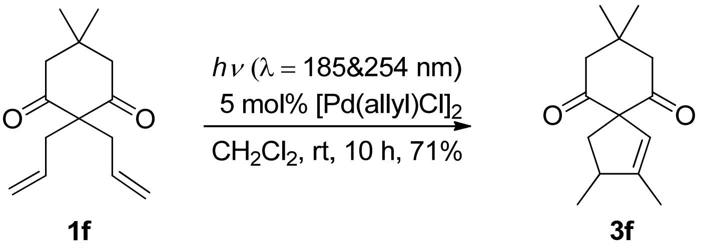
The reaction of $[Pd(allyl)Cl]_2$ (4 mg, 0.011 mmol) and **1d** (56 mg, 0.19 mmol) in anhydrous CH_2Cl_2 (10 mL) afforded **3d** as a liquid (32 mg, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 1 H), 2.75-2.60 (m, 2 H), 1.88-1.81 (m, 1 H), 1.71 (s, 3 H), 1.45 (s, 9 H), 1.44 (s, 9 H), 1.04 (d, J = 6.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.4, 171.0, 149.5, 122.6, 80.9, 80.8, 66.5, 41.9, 40.2, 27.9, 27.8, 19.1, 14.6 ppm; IR (neat) 1717 cm^{-1}; MS (EI, 70 eV) *m/z* 296 (M$^+$, 0.15), 57 (100); HRMS (EI) calcd for $C_{17}H_{28}O_4$ 296.1988, found 296.1993.

(4) **Dibenzyl 3,4-dimethylcyclopent-2-ene-1,1-dicarboxylate** (**3e**)[5]



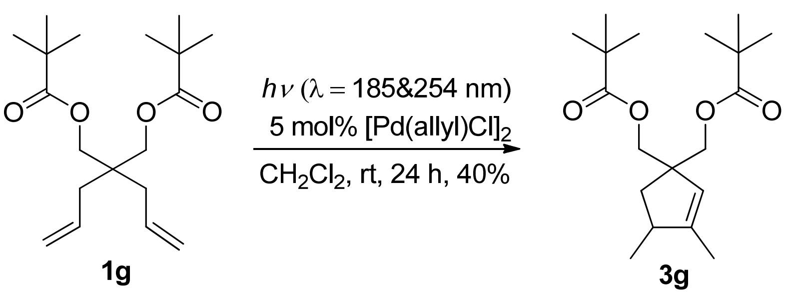
The reaction of $[Pd(allyl)Cl]_2$ (4 mg, 0.011 mmol) and **1e** (73 mg, 0.20 mmol) in anhydrous CH_2Cl_2 (10 mL) afforded **3e** as a liquid (26 mg, 36%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.19 (m, 10 H), 5.46 (s, 1 H), 5.17-5.04 (m, 4 H), 2.84-2.67 (m, 2 H), 2.00-1.93 (m, 1 H), 1.72 (s, 3 H), 1.04 (d, $J = 6.4$ Hz, 3 H).

(5) **2,3,8,8-tetramethylspiro[4.5]dec-1-ene-6,10-dione** (**3f**)



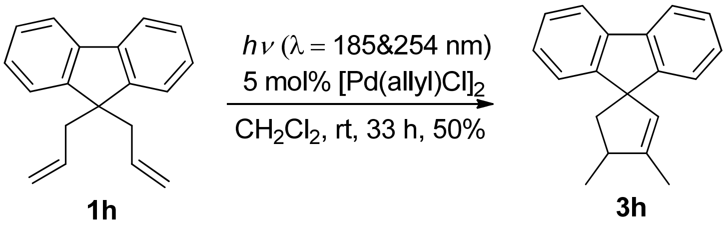
The reaction of $[Pd(allyl)Cl]_2$ (4 mg, 0.011 mmol) and **1f** (42 mg, 0.19 mmol) in anhydrous CH_2Cl_2 (10 mL) afforded **3f** as a solid (30 mg, 71%); mp: 106.9-107.2 °C (ethyl acetate / petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 5.31 (s, 1 H), 2.80-2.55 (m, 4 H), 2.54-2.41 (m, 2 H), 2.09-1.99 (m, 1 H), 1.67 (s, 3 H), 1.13 (s, 3 H), 1.06 (d, $J = 7.2$ Hz, 3 H), 0.87 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 206.32, 206.30, 150.1, 122.3, 78.7, 52.3, 52.0, 41.8, 33.7, 30.6, 29.9, 27.0, 19.1, 14.6 ppm; IR (neat) 1721, 1692 cm^{-1}; MS (EI, 70 eV) m/z 220 (M^+, 53.00), 83 (100); HRMS (EI) calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1465.

(6) **3,3-bis(trimethylacetoxymethyl)-1,5-dimethylcyclopentene** (**3g**)[11]



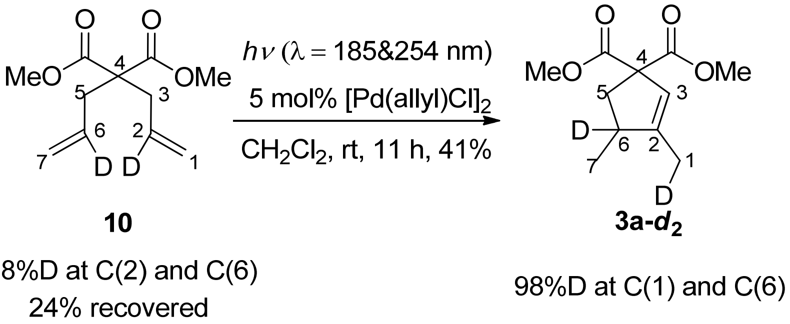
The reaction of $[Pd(allyl)Cl]_2$ (4 mg, 0.011 mmol) and **1g** (63 mg, 0.19 mmol) in anhydrous CH_2Cl_2 (10 mL) afforded **3g** as a liquid (25 mg, 40%); ^1H NMR (400 MHz, CDCl$_3$) δ 5.14 (s, 1 H), 4.11-4.04 (m, 1 H), 4.02-3.96 (m, 1 H) 3.94-3.85 (m, 2 H), 2.72-2.59 (m, 1 H), 2.13-2.02 (m, 1 H), 1.67 (s, 3 H), 1.20 (s, 9 H), 1.19 (s, 9 H), 1.05 (d, J = 6.8 Hz, 3 H).

(7) **3,4-dimethylspiro[cyclopent-2-ene-1,9´-fluorene]** (**3h**)[5]



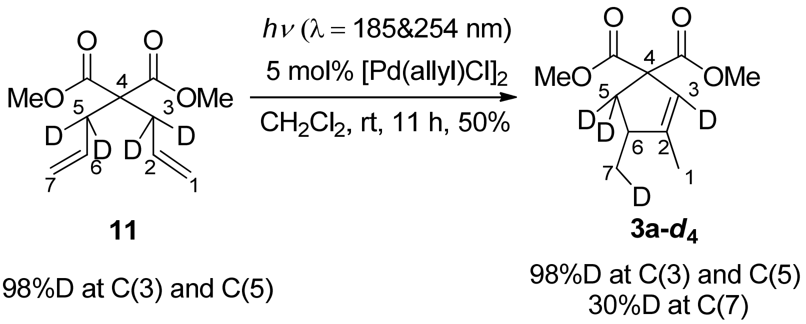
The reaction of [Pd(allyl)Cl]$_2$ (4 mg, 0.011 mmol) and **1h** (50 mg, 0.20 mmol) in anhydrous CH$_2$Cl$_2$ (10 mL) afforded **3h** as a solid (25 mg, 50%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.71-7.64 (m, 2 H), 7.41-7.21 (m, 6 H), 5.05 (s, 1 H), 3.19-3.07 (m, 1 H), 2.58-2.48 (m, 1 H), 2.08-1.98 (m, 1 H), 1.85 (s, 3 H), 1.26 (d, J = 6.8 Hz, 3 H).

(8) 3,3-bis(carbomethoxy)-5-deuterio-1-(deuteriomethyl)-5-methylcyclopentene (3a-d_2)[12]



The reaction of [Pd(allyl)Cl]$_2$ (5 mg, 0.014 mmol) and **10** (37 mg, 0.17 mmol) in anhydrous CH$_2$Cl$_2$ (10 mL) after 11 h afforded **3a-d_2** (15 mg, 41%) and recovered **10** (9 mg, 24%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.42 (s, 1 H), 3.73 (s, 3 H), 3.71 (s, 3 H), 2.76 (d, J = 13.6 Hz, 1 H), 1.93 (d, J = 13.6 Hz, 1 H), 1.71 (q, J_{HD} = J_{HH} = 2 Hz, 2 H), 1.05 (s, 3 H).

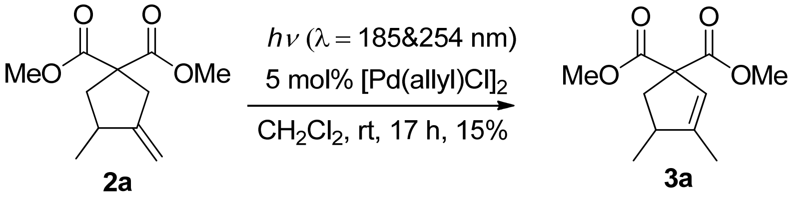
(9) 3,3-bis(carbomethoxy)-2,4,4-trideuterio-5-(deuteriomethyl)-1-methylcyclo pente ne (3a-d_4)[12]



The reaction of [Pd(allyl)Cl]$_2$ (4 mg, 0.011 mmol) and **11** (40 mg, 0.19 mmol) in anhydrous CH$_2$Cl$_2$ (10 mL) after 11 h afforded **3a-*d*$_4$** as a liquid (20 mg, 50%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.73 (s, 3 H), 3.71 (s, 3 H), 2.76-2.65 (m, 1 H), 1.72 (s, 3 H), 1.08-1.01 (m, 3 H).

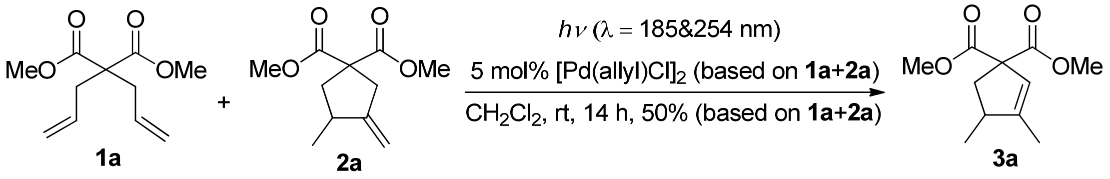
The following photoreactions were also carried out according to General Procedure I.

(1) **The photoreaction of 2a under Condition A in the absence of 1a**



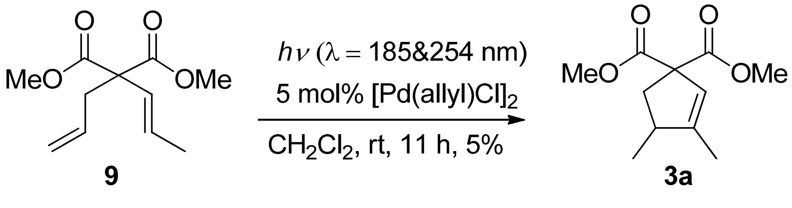
The reaction of [Pd(allyl)Cl]$_2$ (4 mg, 0.011 mmol) and **2a** (39 mg, 0.19 mmol) in anhydrous CH$_2$Cl$_2$ (10 mL) after 17 h afforded **3a** (6 mg, 15%) and **2a** (8 mg, 21%).

(2) **The photoreaction of 2a under Conditions A in the presence of 1a**



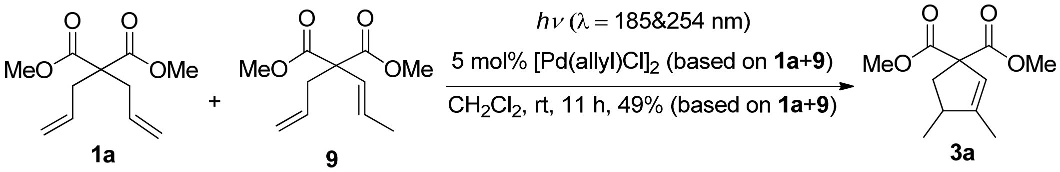
The reaction of [Pd(allyl)Cl]$_2$ (4 mg, 0.011 mmol), **1a** (19 mg, 0.09 mmol) and **2a** (21 mg, 0.10 mmol) in anhydrous CH$_2$Cl$_2$ (10 mL) afforded **3a** [20 mg, 50% (based on **1a** + **2a**)].

(3) **The photoreaction of 9 under Conditions A in the absence of 1a**

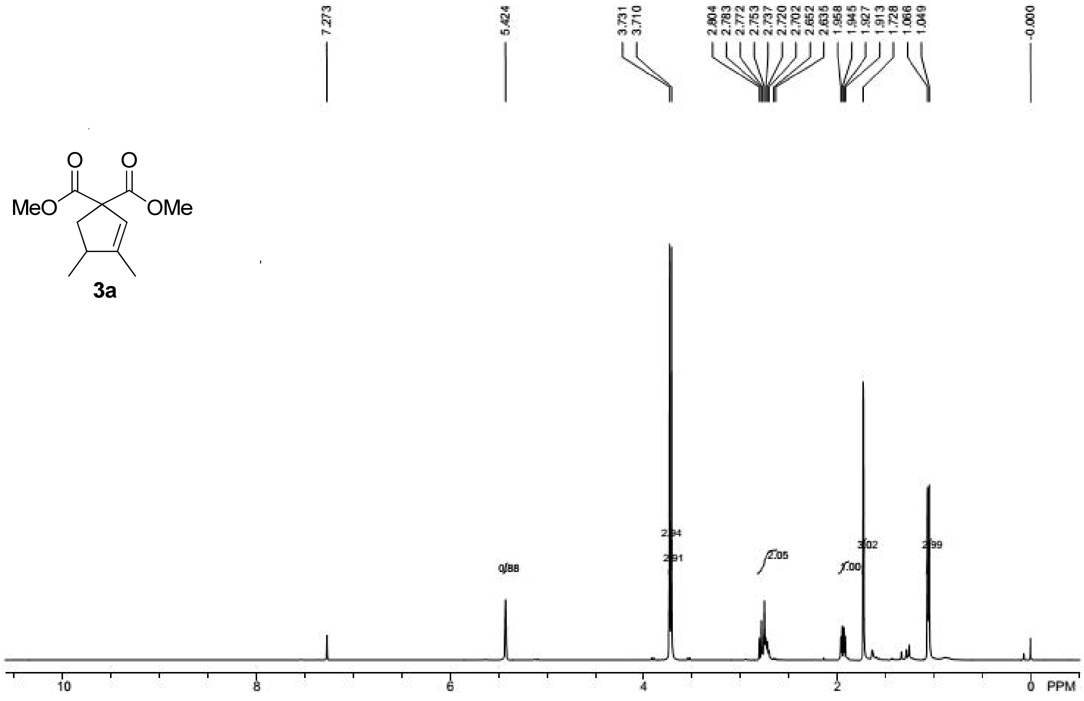


The reaction of $[Pd(allyl)Cl]_2$ (4 mg, 0.011 mmol) and **9** (38 mg, 0.18 mmol) in anhydrous CH_2Cl_2 (10 mL) afforded **3a** (2 mg, 5%) and recovered **9** (16 mg, 42%).

(4) **The photoreaction of 9 under Conditions A in the presence of 1a**



The reaction of $[Pd(allyl)Cl]_2$ (4 mg, 0.011 mmol), **1a** (21 mg, 0.10 mmol), and **9** (18 mg, 0.09 mmol) in anhydrous CH_2Cl_2 (10 mL) afforded **3a** [19 mg, 49% (based on **1a** + **9**)].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2.652
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1.927
1.913
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1.066
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3.02
2.99
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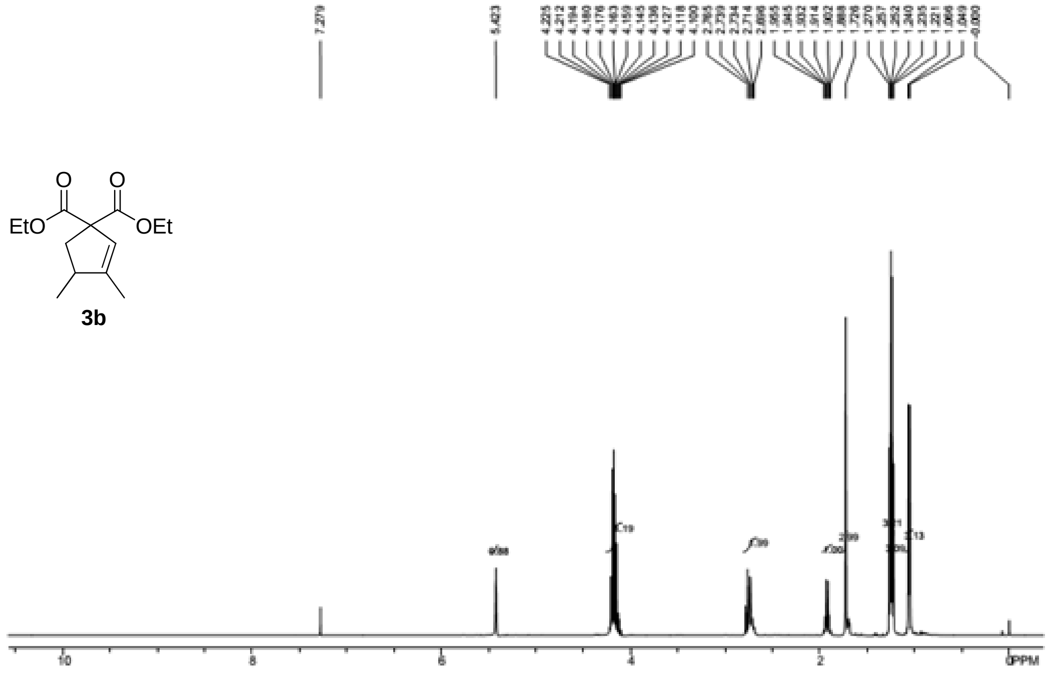
8
6
4
2
0
PPM

3a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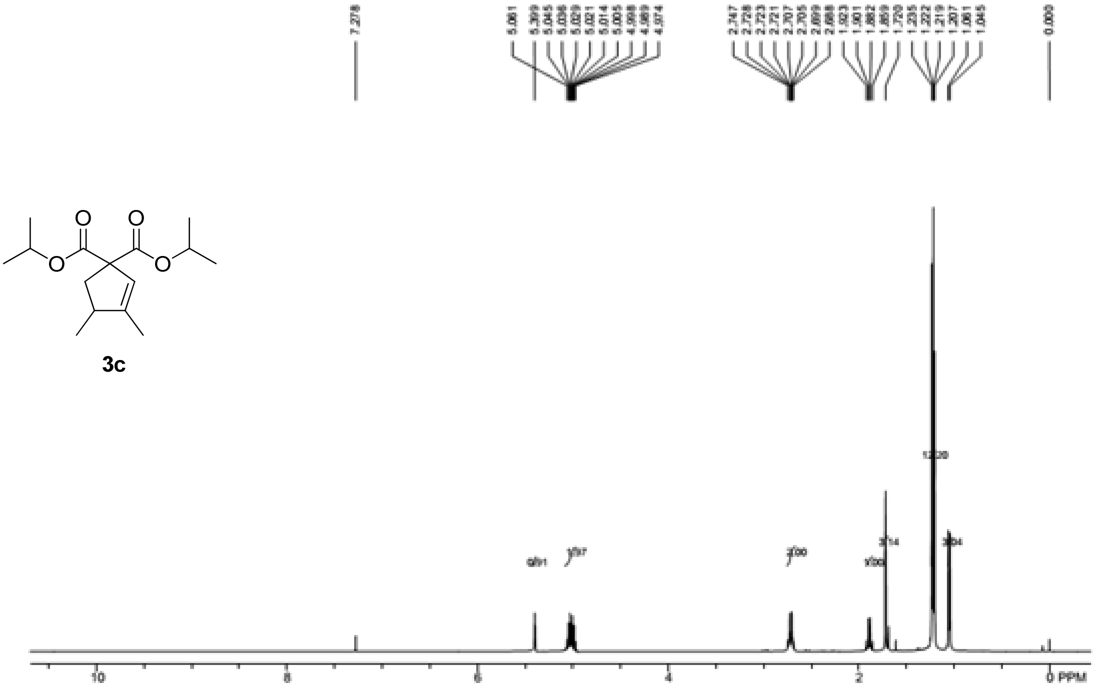
PPM

3b



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2.747
2.728
2.723
2.721
2.707
2.705
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1.901
1.882
1.859
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4
2
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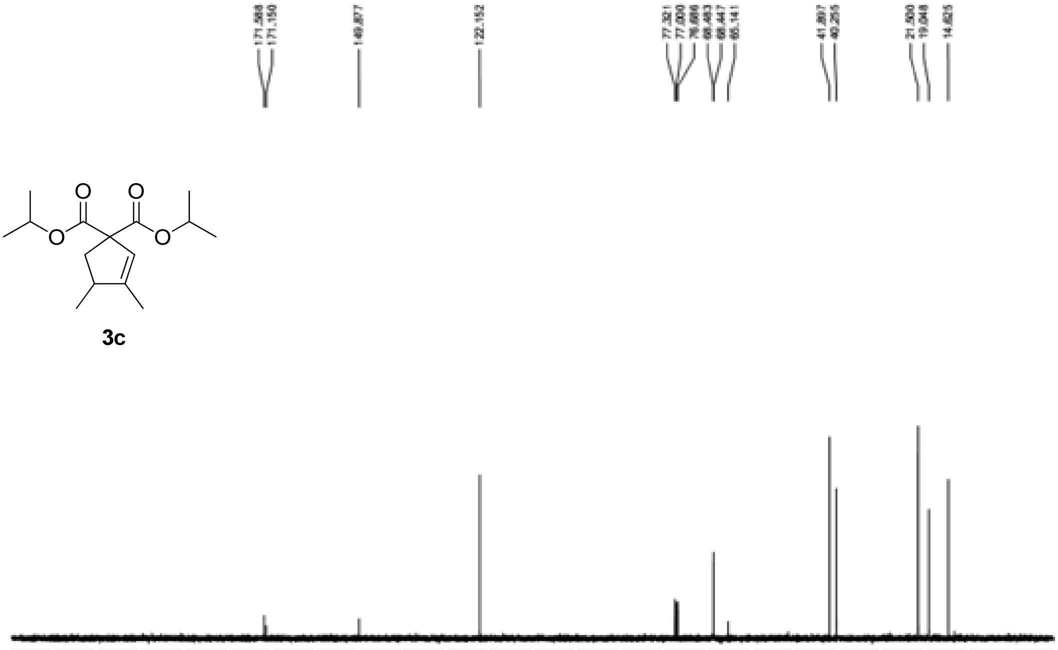

3c

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149.877
122.152
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77.050
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68.483
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50
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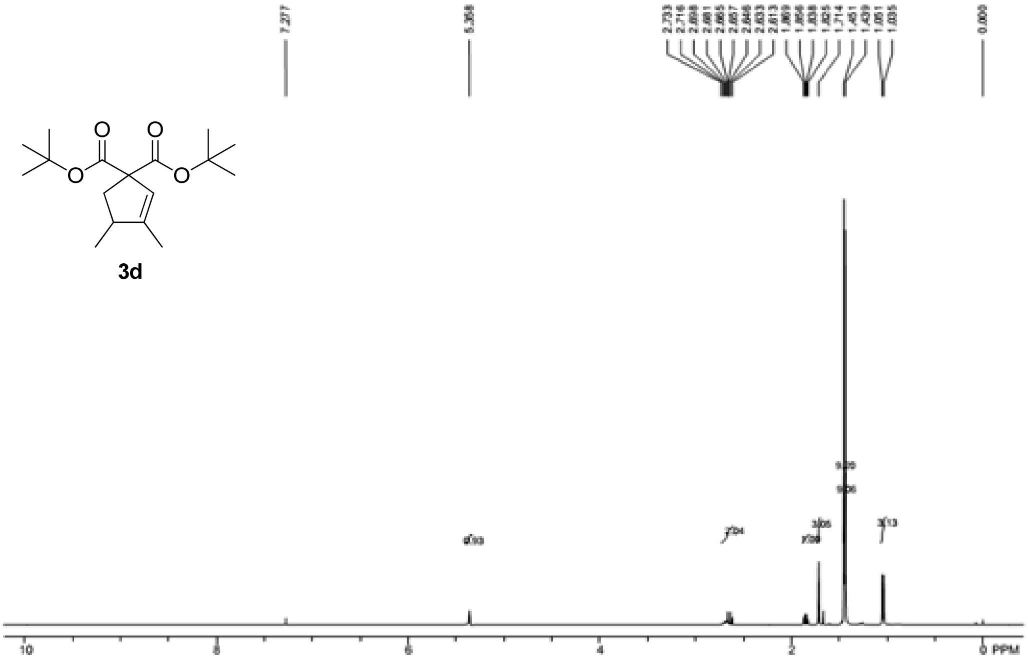
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1.838
1.825
1.714
1.451
1.439
1.051
1.035
0.000
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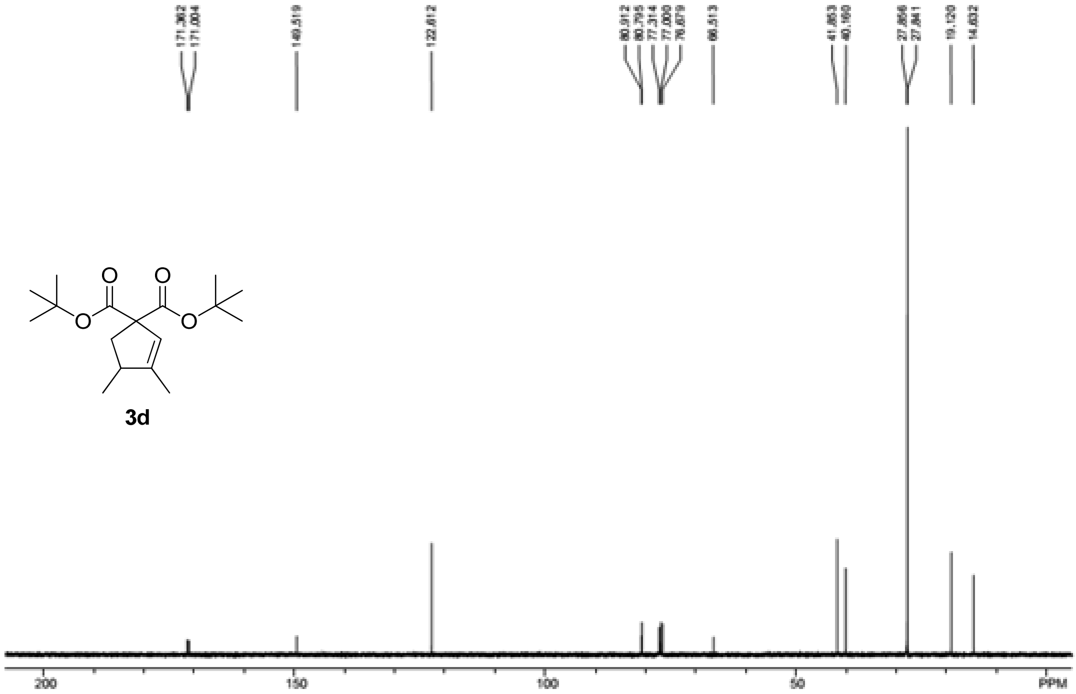
6
4
2
0 PPM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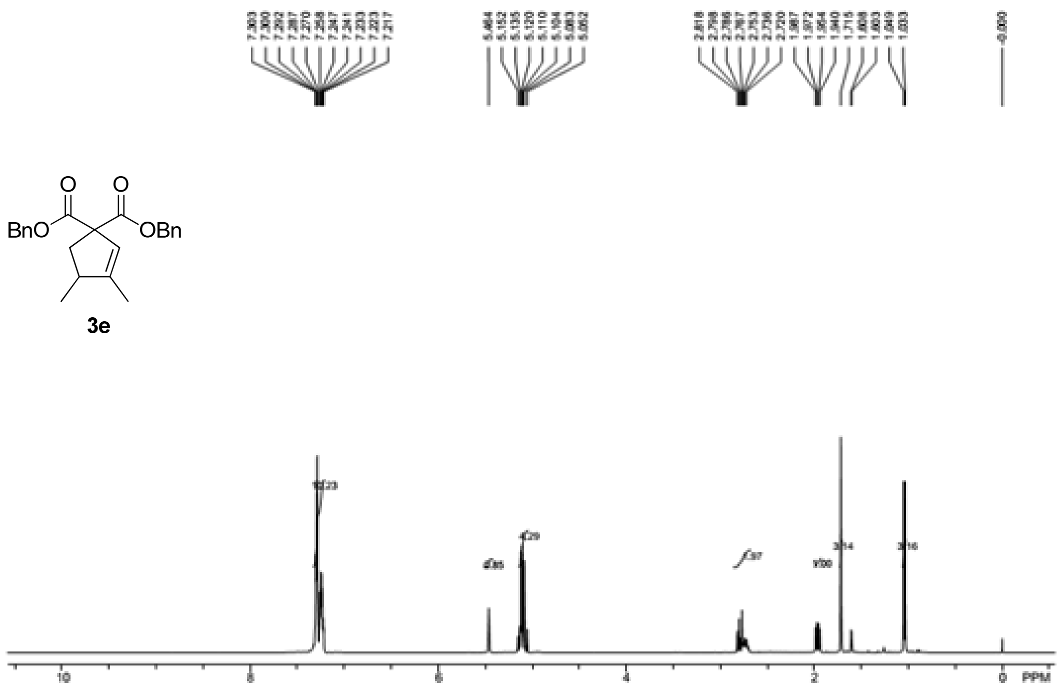
PPM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5.135
5.120
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5.104
5.083
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2.736
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1.954
1.940
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1.608
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OBn
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8
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4
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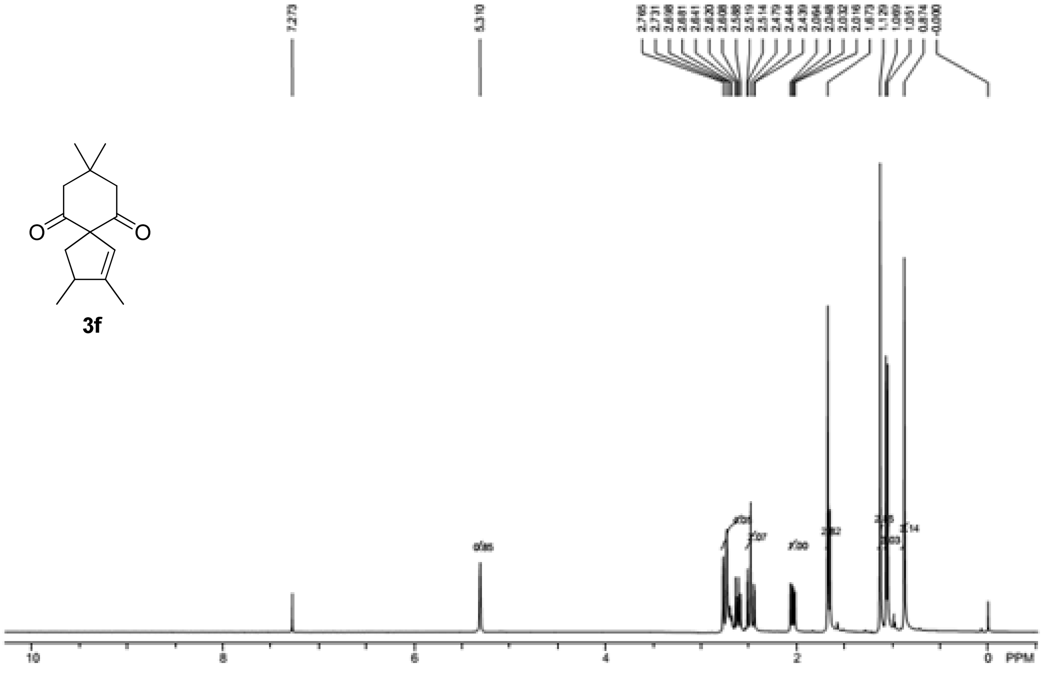
PPM

3e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2.444
2.439
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2.032
2.016
1.673
1.129
1.069
1.051
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10
8
6
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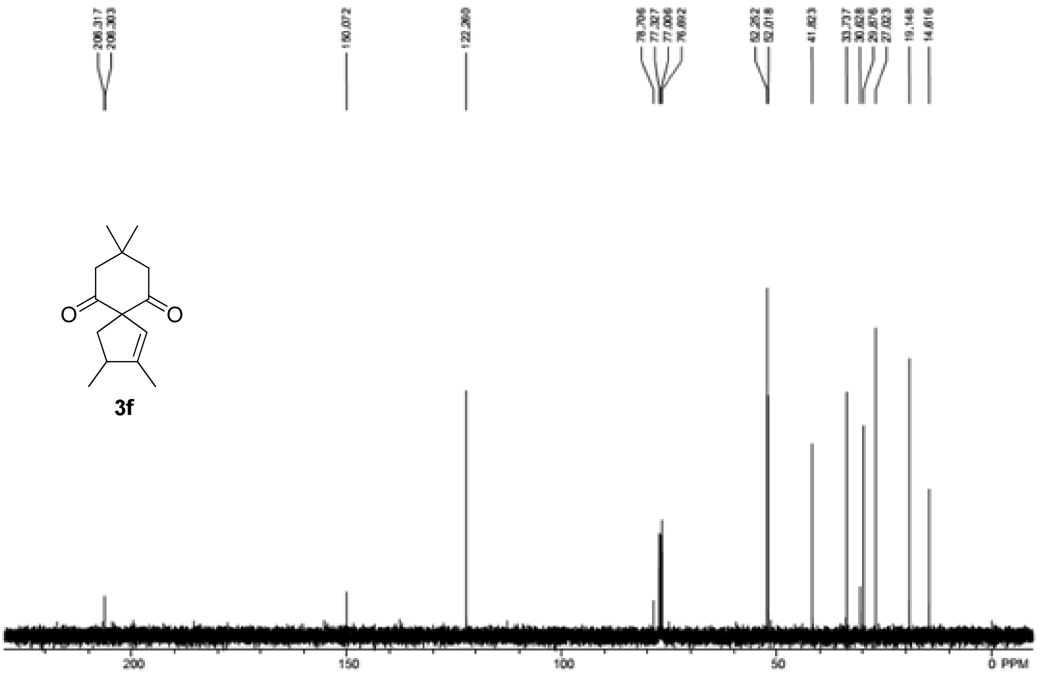
2
0
PPM

3f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150
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50
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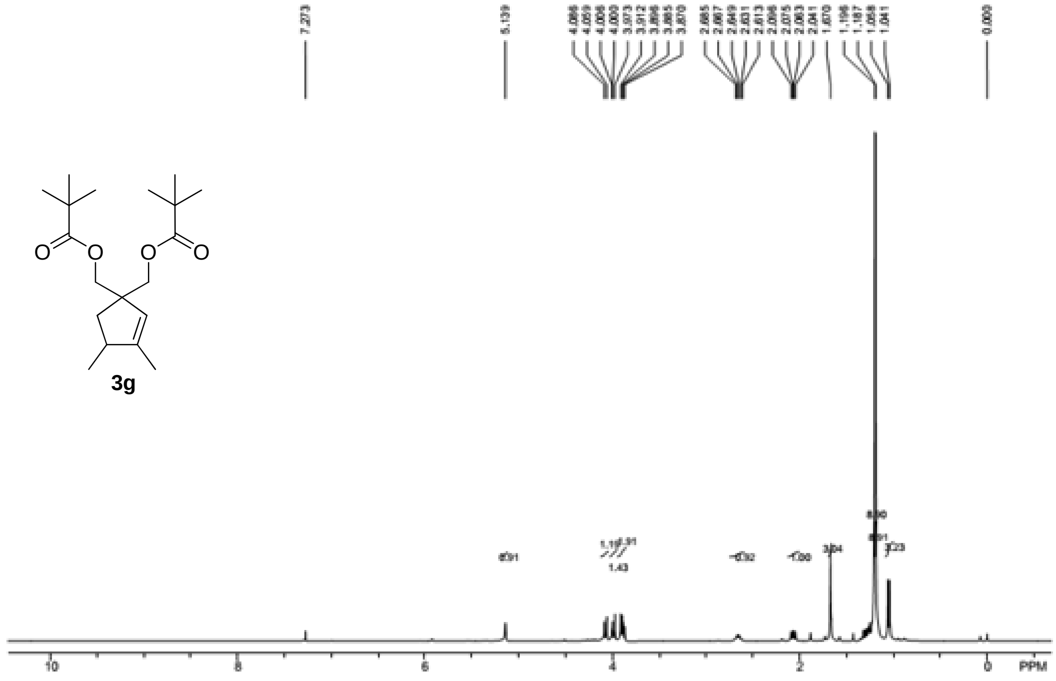
3f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4.059
4.006
4.000
3.973
3.912
3.896
3.885
3.870
2.685
2.667
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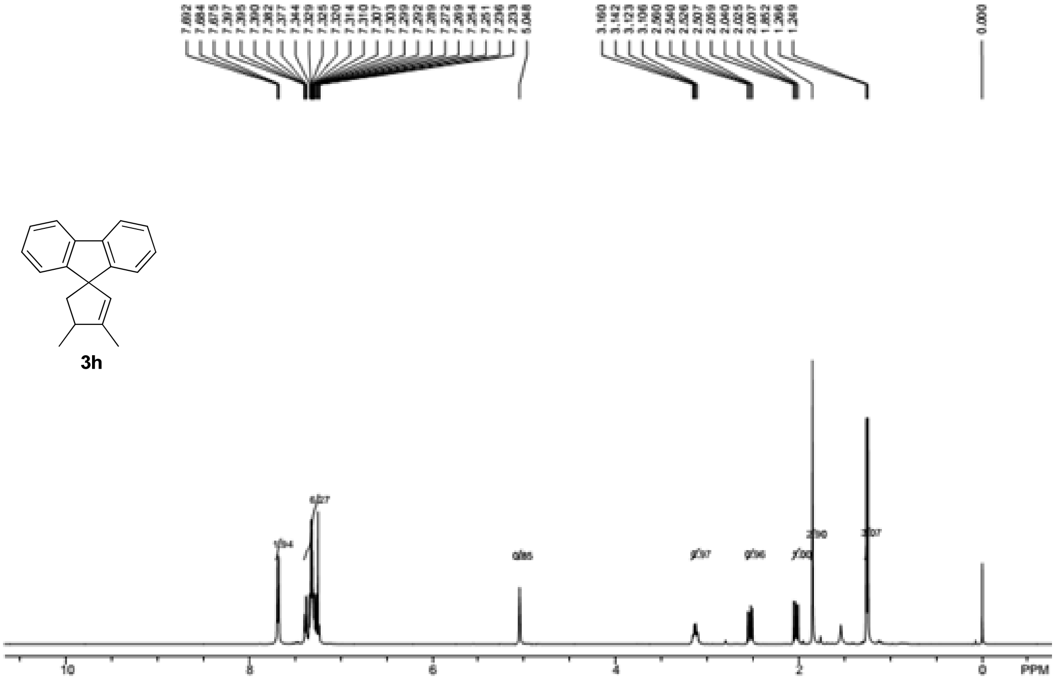
2.631
2.613
2.096
2.075
2.063
2.041
1.670
1.198
1.187
1.058
1.041
0.000
O
O
O
O
0.91
1.19
0.91
1.43
0.92
1.00
3.04
8.90
8.91
3.23
10
8
6
4
2
0
PPM

3g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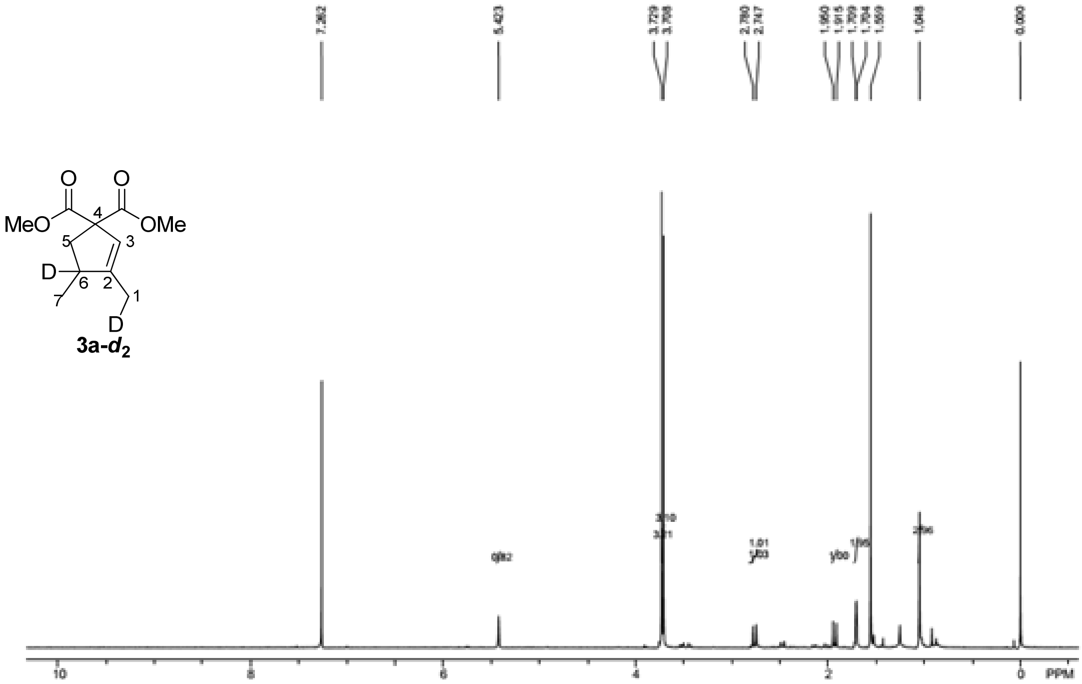
7.314
7.310
7.307
7.303
7.299
7.292
7.289
7.272
7.269
7.254
7.251
7.236
7.233
5.048
3.160
3.142
3.123
3.106
2.560
2.540
2.526
2.507
2.059
2.040
2.025
2.007
1.852
1.266
1.249
0.000
1.94
6.27
0.85
0.97
0.96
1.00
2.90
3.07
10
8
6
4
2
0
PPM

3h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2.747
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1.915
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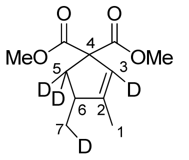
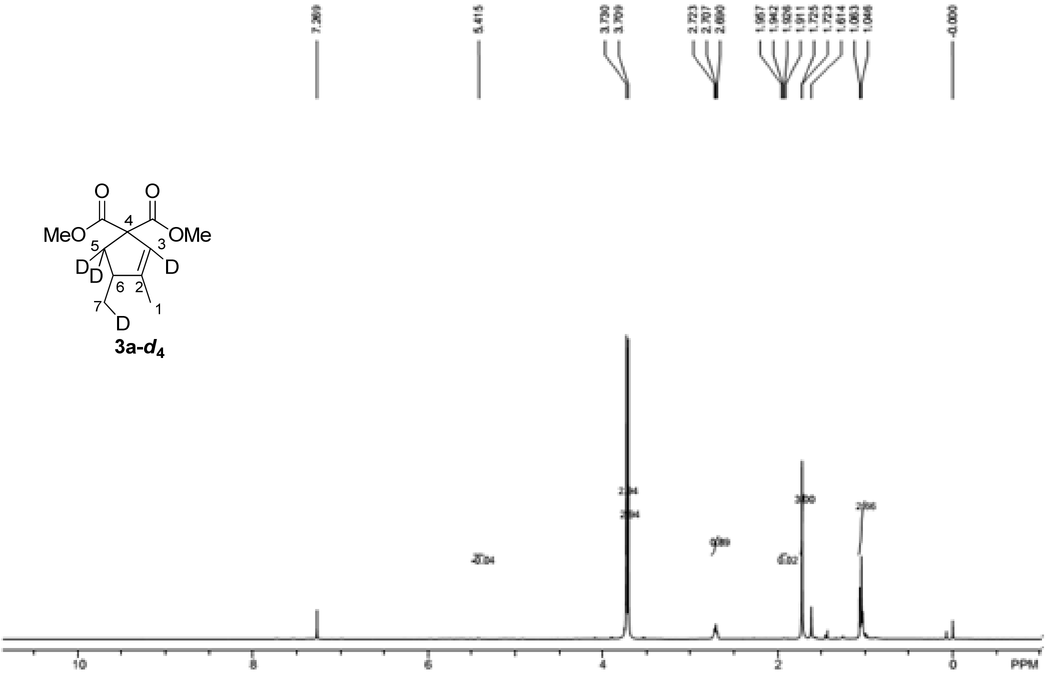
1.559
1.048
0.000
O
O
MeO
OMe
4
5
3
D
6
2
7
1
D
0.82
3.10
3.21
1.01
1.03
1.00
1.95
2.96
10
8
6
4
2
0
PPM

3a-d_2


O
O
MeO
OMe
4
5
3
D
D
D
6
2
7
1
D

3a-*d*₄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1.725
1.723
1.614
1.063
1.046
-0.000
0.04
2.94
2.94
0.99
0.02
3.00
2.96
10
8
6
4
2
0
PPM

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