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# **Ceric(IV)-Mediated Reaction of Methylenecyclopropanes in Organic Synthesis: A Facile Access to Dihydrofurans and Cyclobutanones**

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**Abstract:** Alkylidenecyclopropanes undergo CAN-mediated addition reactions with 1,3-dicarbonyl compounds or ring rearrangement reactions leading to dihydrofuran and cyclobutanone derivatives, respectively, in moderate yields.

**Key words:** methylenecyclopropanes, ammonium cerium(IV) nitrate, 1,3-dicarbonyl compounds, dihydrofuran, cyclobutanone

Since the late 1990s, methylenecyclopropanes (MCPs) have become readily available and have been extensively used in organic synthesis.<sup>1</sup> MCPs undergo a variety of ring-opening reactions because the relief of ring-strain provides a potent thermodynamic driving force. Recently, increased attention has been paid to the transition metal-mediated reactions of MCPs, which have been usually employed for the construction of complex and interesting organic molecules.<sup>2</sup>

In the past ten years the oxidative addition of carbon-centered radicals to alkenes mediated by metal salts (Mn<sup>III</sup>, Ce<sup>IV</sup>, Hg<sup>II</sup>, Pd<sup>IV</sup>, Ag<sup>I</sup>, and Cu<sup>II</sup>) has received considerable attention in organic synthesis for the construction of carbon-carbon bonds.<sup>3</sup> Among these, manganese(III) acetate and CAN have been the most efficient. Recently, CAN has found applications in the oxidative cycloaddition of 1,3-dicarbonyl compounds to alkenes, conjugated compounds, silvl enol ethers, and alkynes as well as promoting the dimerization of styrenes, which are all very useful methods for the construction of new C-C bonds and functionalized cyclic compounds.<sup>4</sup> However, there was little information available on the CAN-mediated reaction of MCPs.<sup>5</sup> In continuation of our efforts on the application of MCPs.<sup>6</sup> we wish to report the facile CAN-mediated cvcloaddition reaction of MCPs with 1,3-dicarbonyl compounds and its ring-rearrangement reaction leading to dihydrofuran and cyclobutanone derivatives in moderate yields.

Initially, we tested the reaction of diphenylmethylenecyclopropane (1a) with two equivalents of CAN and 1.2 equivalents of 1, 3-cyclohexanedione in CH<sub>3</sub>CN. After workup and isolation, the product 3a was obtained in 55% yield (Scheme 1). The structure of compound 3a was con-

SYNTHESIS 2006, No. 4, pp 0609–0614 Advanced online publication: 11.01.2006 DOI: 10.1055/s-2006-926298; Art ID: F12005SS © Georg Thieme Verlag Stuttgart · New York firmed by X-ray single crystal diffraction analysis (Figure 1).<sup>7</sup> Further screening demonstrated that  $CH_3CN$ -THF<sup>8</sup> (5:1) and 2.2 equivalents of CAN were more suitable for the reaction and the yield of **3a** could be improved to 81% (Scheme 1).



Scheme 1



Figure 1 X-ray crystal structure of compound 3a

With this result in hand, a series of alkylidenecyclopropanes and 1,3-dicarbonyl compounds were chosen as substrates to afford a range of dihydrofuran derivatives in moderate yields (Table 1).

On the basis of the above results and previous investigation on the CAN-mediated reaction,<sup>4,5</sup> a possible mechanism for the reaction of MCPs with 1,3-dicarbonyl compounds promoted by CAN is shown in Scheme 2. First, the regioselective addition of the carbon-centered conjugated stabilized radical **A** to MCP generates the more stable tertiary carbon radical **B**,<sup>9</sup> which is oxidized by a second equivalent of CAN to the more stable cyclopropylcarbinyl cation **C**,<sup>10</sup> then the cationic species undergoes intramolecular ring closure with the carbonyl oxygen, and the dihydrofuran derivatives **3** were obtained.

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Table 1 Synthesis of Dihydrofuran Derivatives<sup>a</sup> .

$P_{R^{2}} \xrightarrow[compounds]{(2)}{CAN} \xrightarrow[compounds]{(2)}{CAN} \xrightarrow[compounds]{(2)}{R^{1}}$						
Entry	R <sup>1</sup>	R <sup>2</sup>	МСР	1,3-Dicarbonyl compound	Product	Yield (%) <sup>b</sup>
1	Ph	Ph	1a	0,00	<b>3</b> a	81
2	Ph	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	1b	2a 2a	3b	85
3	Ph	Me	1c	2a	3c	78
4	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	Me	1d	2a	3d	75
5	Ph	Н	1e	2a	3e	39
6	p-ClC <sub>6</sub> H <sub>4</sub>	Н	1f	2a	3f	42
7	p-BrC <sub>6</sub> H <sub>4</sub>	Н	1g	2a	3g	41
8	Ph	Ph	1a	0,00	3h	80
9	Ph	Me	1c	2b 2b	3i	77
10 <sup>c</sup>	Ph	Ph	1a		3j	88
11°	Ph	Me	1c	2c 2c	3k	76
12 <sup>c</sup>	p-BrC <sub>6</sub> H <sub>4</sub>	Н	 1g	2c	31	40

<sup>a</sup> Conditions: MCP (0.5 mmol), 1,3-dicarbonyl compound (0.6 mmol), CAN (1.1 mmol), and CH<sub>3</sub>CN-THF (5:1).

<sup>b</sup> Isolated yield.

<sup>c</sup> Solvent: MeOH-THF (5:1).

Interestingly, when **1a** was treated with 2.2 equivalents of CAN in MeOH-THF (5:1) alone, the 2,2-diphenylcyclobutanone 4a was obtained in moderate yield (Scheme 3).

We obtained the carbonyl compound, however, where did the oxygen atom come from? Our reaction was run under nitrogen, so we excluded the possibility of the oxygen atom coming from the atmosphere. This left us with the possibility that the oxygen atom may come from the small



Scheme 2

amount of water in the solvent. Shi and de Meijere had reported the ring expansion of MCPs in the presence of DIAD or DEAD and bicyclopropylidene in the presence of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in wet solvent, respectively.<sup>11</sup> In order to confirm this hypothesis, we repeated the reaction using H<sub>2</sub>O as the solvent,<sup>12</sup> and we isolated compound 4a in 16% yield. After optimization we found that MeOH-THF (5:1), five equivalents of H<sub>2</sub>O, and 2.2 equivalents of CAN gave 4a in an improved 49% yield (Table 2, entry 1). A variety of similar compounds (1b, 1h-j) were also reacted under the same conditions to give the corresponding 2,2-diarylcyclobutanones (4b, 4h-j) in moderate yields (Table 2, entries 2-5). However, under these conditions 1c-e gave complex mixtures.

Scheme 3

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#### Table 2 Synthesis of Cyclobutanone Derivatives<sup>a</sup>

 $^{\rm a}$  Conditions: MCP (0.5 mmol), H\_2O (2.5 mmol), CAN (1.1 mmol), and MeOH–THF (5:1).

<sup>b</sup> Isolated yield.

During the reactions we observed, that CAN reacted faster with 1,3-dicarbonyl compounds than with MCPs because the color of CAN disappeared faster in the former reaction. Previously, CAN had been shown to promote the dimerization of styrenes;<sup>4a</sup> therefore, we believe that the reaction between MCPs and CAN may proceed by another route. On the basis of the above results and previous investigations on the CAN-mediated reaction,4,5,13 a plausible mechanism for the ring-rearrangement reaction of MCPs 1 promoted by CAN is outlined in Scheme 4. An initial oxidative electron transfer from MCP to Ce(IV) affords the radical cation  $\mathbf{D}$ ,<sup>14</sup> then the radical cation  $\mathbf{D}$  rearranges to E, the cationic center of E is quenched by H<sub>2</sub>O to give  $\mathbf{F}$ , whereas the radical center can be oxidized by a second equivalent of CAN to give G. Further rearrangement of the cation **G** affords the product **4**.





In conclusion, we have developed a convenient and efficient method for the synthesis of dihydrofuran derivatives<sup>15</sup> incorporating cyclopropyl groups and cyclobutanones,<sup>11b,16</sup> in moderate yields by the reaction of MCPs in the presence of CAN. The mechanistic details of the reaction and synthetic application of this methodology are underway in our laboratory.

All <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured in CDCl<sub>3</sub> and recorded on a Bruker Avance-400 (400 MHz) spectrometer with TMS as the internal standard. Chemical shifts are given in ppm and coupling constants (J) are given in Hz. IR spectra were run on a Bruker vector 22 spectrometer. Mass spectra (EI) were determined with a HP5989B mass spectrometer. Elemental analyses were performed on an EA-1110 instrument. MPs are uncorrected. All the reactions were performed under  $N_2$ . Solvents were used directly unless otherwise specified. Petroleum ether had a bp range 60–90 °C.

# **Dihydrofurans 3; General Procedure**

A solution of CAN (603 mg, 1.1 mmol) in MeCN–THF (5:1, 10 mL) was added dropwise to an ice-cooled, stirred mixture of dicarbonyl compound **2** (0.6 mmol) and MCP<sup>17</sup> **1** (0.5 mmol) in MeCN–THF (5:1, 2 mL). The reaction mixture was slowly warmed to r.t. and stirring continued for 3 h. The solvent was evaporated and H<sub>2</sub>O (15 mL) was added. The aqueous layer was extracted with Et<sub>2</sub>O (3 × 15 mL), the organic layer was dried over anhyd MgSO<sub>4</sub>, and the solvent evaporated. The residue was subjected to preparative TLC (petroleum ether–EtOAc, 10:1–4:1) to afford dihydrofuran derivative **3**.

### 3a

(%)<sup>b</sup>

Solid; mp 149-150 °C.

IR: 1649, 1629, 1409, 1234, 703 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta$  = 0.35–0.38 (m, 2 H), 1.53–1.56 (m, 2 H), 1.98–2.01 (m, 2 H), 2.31 (t, 2 H, *J* = 6.3 Hz), 2.42 (t, 2 H, *J* = 6.3 Hz), 7.31 (s, 10 H).

<sup>13</sup>C NMR (100 MHz): δ = 194.46, 174.29, 141.32, 128.01, 127.58, 115.79, 97.67, 37.37, 31.29, 24.44, 21.70, 9.51.

MS (70 eV, EI): m/z (%) = 316 (M<sup>+</sup>, 100).

Anal. Calcd for  $C_{22}H_{20}O_2$ : C, 83.51; H, 6.37. Found: C, 83.31; H, 6.40.

#### 3b Oil.

IR: 1625, 1408, 756 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta$  = 0.31–0.40 (m, 2 H), 1.48–1.60 (m, 2 H), 1.97–2.00 (m, 2 H), 2.30 (t, 2 H, *J* = 6.3 Hz), 2.33 (s, 3 H), 2.40 (t, 2 H, *J* = 6.3 Hz), 7.10–7.32 (m, 9 H).

<sup>13</sup>C NMR (100 MHz): δ = 194.41, 174.33, 141.28, 138.38, 137.70, 128.62, 127.89, 127.86, 127.57, 127.37, 115.69, 97.66, 37.26, 31.21, 24.38, 21.62, 21.03, 9.52, 9.34.

MS (70 eV, EI): m/z (%) = 330 (M<sup>+</sup>, 45.88).

Anal. Calcd for  $C_{23}H_{22}O_2$ : C, 83.60; H, 6.71. Found: C, 83.40; H, 6.75.

### 3c

Solid; mp 115–116 °C.

IR: 1640, 1624, 1254, 1046, 766, 707 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta$  = 0.10–0.11 (m, 1 H), 0.79–0.80 (m, 1 H), 1.16–1.18 (m, 1 H), 1.63–1.65 (m, 1 H), 1.78 (s, 3 H), 2.19 (t, 2 H, *J* = 6.2 Hz), 2.41–2.45 (m, 2 H), 2.65 (dd, 2 H, *J* = 6.2, 5.7 Hz), 7.33–7.46 (m, 5 H).

<sup>13</sup>C NMR (100 MHz): δ = 194.85, 175.04, 142.07, 128.33, 127.81, 125.17, 114.65, 93.26, 37.52, 34.53, 24.53, 23.86, 21.90, 10.27, 6.97.

MS (70 eV, EI): m/z (%) = 254 (M<sup>+</sup>, 100).

Anal. Calcd for  $C_{17}H_{18}O_2$ : C, 80.28; H, 7.13. Found: C, 80.08; H, 7.18.

### 3d

Oil.

IR: 1624, 1512, 1247, 757 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta$  = 0.71–0.79 (m, 2 H), 1.13–1.14 (m, 1 H), 1.19 (s, 3 H), 1.62–1.65 (m, 1 H), 1.70–1.90 (m, 2 H), 2.08–2.13 (m, 2 H), 2.28–2.33 (m, 2 H), 2.53 (d, 1 H, *J* = 14.1 Hz), 2.88 (d, 1 H,

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J = 14.1 Hz), 3.77 (s, 3 H), 6.80 (d, 2 H, J = 8.5 Hz), 7.13 (d, 2 H, J = 8.5 Hz).

<sup>13</sup>C NMR (100 MHz): δ = 194.54, 175.33, 158.43, 131.67, 128.52, 115.49, 113.35, 92.00, 55.31, 44.22, 37.25, 31.76, 24.39, 23.10, 21.59, 7.90, 7.13.

MS (70 eV, EI): m/z (%) = 298 (M<sup>+</sup>, 5.42).

Anal. Calcd for  $C_{19}H_{22}O_3$ : C, 76.48; H, 7.43. Found: C, 76.28; H, 7.48.

3e

Oil.

IR: 1628, 1411, 1176, 1066, 755 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta$  = 0.22–0.25 (m, 1 H), 0.51–0.53 (m, 1 H), 1.26–1.30 (m, 1 H), 1.60–1.63 (m, 1 H), 2.10–2.15 (m, 2 H), 2.37 (t, 2 H, *J* = 6.4 Hz), 2.58 (t, 2 H, *J* = 6.4 Hz), 5.50 (s, 1 H), 7.24–7.48 (m, 5 H).

<sup>13</sup>C NMR (100 MHz): δ = 194.77, 176.88, 137.74, 128.79, 128.64, 127.10, 114.98, 91.42, 37.44, 29.30, 24.44, 21.94, 10.38, 9.43.

MS (70 eV, EI): m/z (%) = 240 (M<sup>+</sup>, 100).

Anal. Calcd for  $C_{16}H_{16}O_2$ : C, 79.97; H, 6.71. Found: C, 79.76; H, 6.75.

### 3f

Oil.

IR: 1629, 1409, 1175, 824 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz): δ = 0.15–0.17 (m, 1 H), 0.44–0.46 (m, 1 H), 1.21–1.24 (m, 1 H), 1.55–1.58 (m, 1 H), 2.04–2.08 (m, 2 H), 2.31 (t, 2 H, J = 6.2 Hz), 2.51 (t, 2 H, J = 6.2 Hz), 5.41 (s, 1 H), 7.14 (d, 2 H, J = 8.4 Hz), 7.31 (d, 2 H, J = 8.4 Hz).

<sup>13</sup>C NMR (100 MHz): δ = 194.66, 176.59, 136.32, 134.65, 128.88, 128.49, 114.85, 90.49, 37.41, 29.29, 24.38, 21.90, 10.44, 9.44.

MS (70 eV, EI): m/z (%) = 274 (M<sup>+</sup>, 100).

Anal. Calcd for  $C_{16}H_{15}ClO_2$ : C, 69.95; H, 5.50. Found: C, 69.85; H, 5.55.

# 3g

Oil.

IR: 1629, 1428, 1409, 1176, 1067, 756 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta$  = 0.18–0.19 (m, 1 H), 0.46–0.48 (m, 1 H), 1.23–1.26 (m, 1 H), 1.57–1.59 (m, 1 H), 2.06–2.09 (m, 2 H), 2.32 (t, 2 H, *J* = 6.3 Hz), 2.53 (t, 2 H, *J* = 6.3 Hz), 5.42 (s, 1 H), 7.09 (d, 2 H, *J* = 8.4 Hz), 7.48 (d, 2 H, *J* = 8.4 Hz).

<sup>13</sup>C NMR (100 MHz): δ = 194.53, 176.53, 136.72, 131.71, 128.68, 122.69, 114.70, 90.36, 37.29, 29.15, 24.26, 21.79, 10.33, 9.32.

MS (70 eV, EI): m/z (%) = 318 (M<sup>+</sup>, 100).

Anal. Calcd for  $C_{16}H_{15}BrO_2$ : C, 60.21; H, 4.74. Found: C, 60.10; H, 4.80.

### 3h

Solid; mp 141-142 °C.

IR: 1648, 1627, 1447, 1224, 873, 762, 704 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta$  = 0.35–0.38 (m, 2 H), 1.06 (s, 6 H), 1.51–1.54 (m, 2 H), 2.20 (s, 2 H), 2.28 (s, 2 H), 7.32 (s, 10 H).

<sup>13</sup>C NMR (100 MHz): δ = 193.83, 173.52, 141.42, 128.11, 128.10, 127.66, 114.58, 98.15, 51.86, 38.38, 34.39, 31.30, 28.68, 9.47.

MS (70 eV, EI): m/z (%) = 344 (M<sup>+</sup>, 51.98).

Anal. Calcd for  $C_{24}H_{24}O_2$ : C, 83.69; H, 7.02. Found: C, 83.50; H, 7.12.

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**3i** Solid; mp 77–78 °C.

IR: 1632, 1240, 843, 783, 761 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta$  = 0.10–0.12 (m, 1 H), 0.78–0.81 (m, 1 H), 1.14–1.19 (m, 1 H), 1.25 (s, 6 H), 1.60–1.63 (m, 1 H), 1.79 (s, 3 H), 2.31 (dd, 2 H, *J* = 16.1, 6.8 Hz), 2.51 (s, 2 H), 7.33–7.46 (m, 5 H).

<sup>13</sup>C NMR (100 MHz): δ = 194.08, 174.05, 142.07, 128.34, 127.82, 125.19, 113.28, 93.63, 51.90, 38.41, 34.44, 34.19, 28.92, 28.60, 23.92, 10.21, 6.94.

MS (70 eV, EI): m/z (%) = 282 (M<sup>+</sup>, 100).

Anal. Calcd for  $C_{19}H_{22}O_2$ : C, 80.82; H, 7.85. Found: C, 80.62; H, 7.93.

## 3j

Solid; mp 109-110 °C.

IR: 1633, 1610, 1387, 1233, 702 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz): δ = 0.24–0.27 (m, 2 H), 1.58–1.61 (m, 2 H), 2.25 (s, 3 H), 2.28 (s, 3 H), 7.30–7.35 (m, 10 H).

<sup>13</sup>C NMR (100 MHz): δ = 193.37, 165.34, 141.86, 127.94, 127.92, 127.87, 117.20, 94.94, 33.06, 30.74, 17.07, 9.16.

MS (70 eV, EI): m/z (%) = 304 (M<sup>+</sup>, 6.09).

Anal. Calcd for  $C_{21}H_{20}O_2$ : C, 82.86; H, 6.62. Found: C, 82.69; H, 6.69.

#### 3k Oil

л.

IR: 1601, 1239, 763 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz): δ = -0.10 to -0.08 (m, 1 H), 0.59–0.61 (m, 1 H), 1.09–1.11 (m, 1 H), 1.60–1.64 (m, 1 H), 1.66 (s, 3 H), 2.30 (s, 3 H), 2.39 (s, 3 H), 7.28–7.39 (m, 5 H).

<sup>13</sup>C NMR (100 MHz): δ = 193.52, 166.12, 142.24, 128.24, 127.64, 125.31, 115.70, 90.39, 36.42, 30.72, 23.70, 16.97, 10.53, 6.65.

MS (70 eV, EI): m/z (%) = 242 (M<sup>+</sup>, 8.42).

Anal. Calcd for  $C_{16}H_{18}O_2$ : C, 79.31; H, 7.49. Found: C, 79.15; H, 7.55.

# 31

Oil.

IR: 1612, 1393, 1199, 757 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta = 0.08-0.12$  (m, 1 H), 0.32-0.36 (m, 1 H), 1.25-1.29 (m, 1 H), 1.59-1.63 (m, 1 H), 2.28 (s, 3 H), 2.34 (s, 3 H), 5.26 (s, 1 H), 7.10 (d, 2 H, J = 8.2 Hz), 7.48 (d, 2 H, J = 8.2 Hz).

<sup>13</sup>C NMR (100 MHz): δ = 193.27, 167.38, 137.12, 131.73, 128.81, 122.61, 115.88, 88.66, 31.50, 30.62, 16.69, 10.43, 9.68.

MS (70 eV, EI): m/z (%) = 306 (M<sup>+</sup>, 2.87).

Anal. Calcd for C<sub>15</sub>H<sub>15</sub>BrO<sub>2</sub>: C, 58.65; H, 4.92. Found: C, 58.75; H, 4.96.

### **Cyclobutanone Derivatives 4; General Procedure**

A solution of CAN (603 mg, 1.1 mmol) in distilled MeOH–THF (5:1, 10 mL) was added dropwise to an ice-cooled, stirred mixture of MCP 1 (0.5 mmol) and  $H_2O$  (2.5 mmol) in distilled MeOH–THF (5:1, 2 mL). Then the reaction mixture was slowly warmed to r.t. and stirring continued. When the reaction was complete (TLC), the solvent was evaporated, and  $H_2O$  (15 mL) was added. The aqueous layer was extracted with  $Et_2O$  (3 × 15 mL), the organic layer was dried over anhyd MgSO<sub>4</sub>, and the solvent was evaporated. The residue was subjected to preparative TLC (petroleum ether–EtOAc, 10:1) to afford the cyclobutanone derivatives **4**.

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# 4a<sup>11a</sup>

Oil.

IR: 1781, 1492, 1078, 702 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta$  = 2.83 (t, 2 H, *J* = 8.4 Hz), 3.15 (t, 2 H, *J* = 8.4 Hz), 7.20–7.38 (m, 10 H).

 $^{13}\text{C}$  NMR (100 MHz):  $\delta$  = 209.22, 142.51, 129.14, 127.33, 126.83, 76.62, 43.80, 26.02.

MS (70 eV, EI): m/z (%) = 222 (M<sup>+</sup>, 20.14).

# 4b

Oil.

IR: 1780, 1509, 1492, 1077 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz): δ = 2.29 (s, 3 H), 2.80 (t, 2 H, J = 8.6 Hz), 3.14 (t, 2 H, J = 8.6 Hz), 7.10–7.37 (m, 9 H).

<sup>13</sup>C NMR (100 MHz): δ = 209.11, 142.33, 139.23, 136.66, 129.46, 128.74, 126.88, 126.44, 126.36, 75.98, 43.40, 25.66, 21.02.

MS (70 eV, EI): m/z (%) = 236 (M<sup>+</sup>, 2.82).

Anal. Calcd for  $C_{17}H_{16}O$ : C, 86.40; H, 6.82. Found: C, 86.30; H, 6.85.

# 4h

Oil.

IR: 1782, 1490, 1077 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta$  = 2.75–2.83 (m, 2 H), 3.11–3.17 (m, 2 H), 7.20–7.34 (m, 9 H).

<sup>13</sup>C NMR (100 MHz): δ = 208.27, 141.65, 140.60, 132.84, 128.88, 128.85, 127.82, 127.17, 126.32, 75.54, 43.48, 25.59.

MS (70 eV, EI): m/z (%) = 256 (M<sup>+</sup>, 16.21).

Anal. Calcd for  $C_{16}H_{13}$ ClO: C, 74.85; H, 5.10. Found: C, 74.68; H, 5.15.

# 4i

Oil.

IR: 1781, 1507 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta$  = 2.76–2.84 (m, 2 H), 3.11–3.18 (m, 2 H), 6.96–7.35 (m, 9 H).

<sup>13</sup>C NMR (100 MHz): δ = 208.55, 161.69 (d,  $J_{C,F}$  = 244.0 Hz), 141.89, 137.88 (d,  $J_{C,F}$  = 3.3 Hz), 128.82, 128.05 (d,  $J_{C,F}$  = 8.2 Hz), 127.06, 126.33, 115.52 (d,  $J_{C,F}$  = 21.1 Hz), 75.47, 43.42, 25.72.

MS (70 eV, EI) m/z (%) = 240 (M<sup>+</sup>, 5.15).

Anal. Calcd for  $C_{16}H_{13}FO$ : C, 79.98; H, 5.45. Found: C, 79.88; H, 5.51.

# 4j<sup>11</sup>

Oil.

IR: 1782, 1601, 1507, 1230, 832 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz):  $\delta$  = 2.79 (t, 2 H, *J* = 8.4 Hz), 3.18 (t, 2 H, *J* = 8.4 Hz), 6.97–7.02 (m, 4 H), 7.29–7.31 (m, 4 H).

<sup>13</sup>C NMR (100 MHz): δ = 208.28, 161.74 (d,  $J_{C,F} = 244.9$  Hz), 137.66 (d,  $J_{C,F} = 3.2$  Hz), 127.98 (d,  $J_{C,F} = 8.1$  Hz), 115.64 (d,  $J_{C,F} = 21.8$  Hz), 74.76, 43.44, 25.86.

MS (70 eV, EI): m/z (%) = 258 (M<sup>+</sup>, 15.11).

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