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### THE BAYLIS—HILLMAN REACTION: $TiCl_4$ MEDIATED COUPLING OF ALKYL VINYL KETONES WITH $\alpha$ -KETO ESTERS AND ALDEHYDES

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**THE BAYLIS–HILLMAN REACTION:  
TiCl<sub>4</sub> MEDIATED COUPLING OF  
ALKYL VINYL KETONES WITH  
 $\alpha$ -KETO ESTERS AND ALDEHYDES**

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**ABSTRACT**

TiCl<sub>4</sub> mediated coupling of alkyl vinyl ketones with  $\alpha$ -keto esters and aldehydes provides respectively 2-aryl-2-hydroxy-3-methylene-4-oxoalkanoates and (*Z*)-keto allyl chlorides in 1 h time at room temperature. Similar coupling of trifluoro-methyl phenyl ketone with methyl vinyl ketone produces 1,1,1-trifluoro-2-hydroxy-2-phenyl-3-methylenepentan-4-one.

The Baylis–Hillman reaction is an emerging tertiary amine catalyzed carbon–carbon bond forming reaction between the  $\alpha$ -position of activated alkenes and carbon electrophiles leading to the formation of an important class of multifunctional molecules and is of current interest.<sup>1–7</sup>

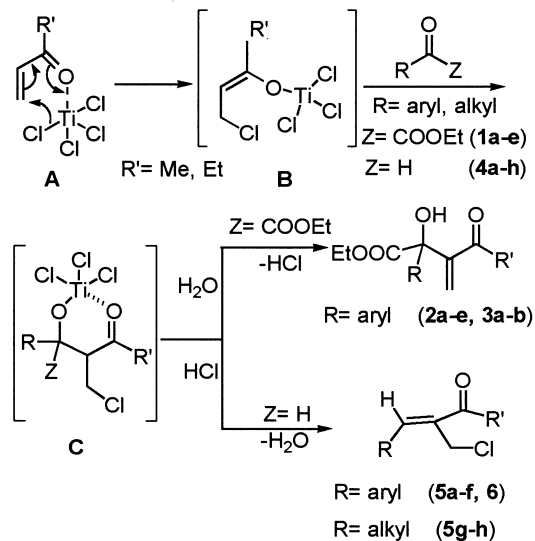
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\*Corresponding author.

In continuation of our interest in the Baylis–Hillman reaction,<sup>8–11</sup> we herein report titanium tetrachloride mediated Baylis–Hillman coupling of  $\alpha$ -keto esters and aldehydes with alkyl vinyl ketones thus providing a simple synthesis of 2-aryl-2-hydroxy-3-methylene-4-oxoalkanoates and (*Z*)-allyl chlorides respectively.

In recent years other catalysts or catalytic systems such as  $R_2S/TiCl_4$  and  $PR_3$  have been successfully employed for the Baylis–Hillman coupling reaction.<sup>12–15</sup>

Li and coworkers have reported the  $TiCl_4$  mediated Baylis–Hillman reaction between cyclic enones and aldehydes.<sup>16</sup> Li and coworkers have also reported that the reaction of aldehydes with acyclic alkyl vinyl ketones under the influence of  $TiX_4$  ( $X = Cl, Br$ ) provides the allyl halides with high (*Z*)-selectivity.<sup>17</sup> Recently we described the application of  $\alpha$ -keto esters<sup>18</sup> as electrophiles in the chalcogeno-Baylis–Hillman reaction with alkyl vinyl ketones in the presence of titanium tetrachloride to produce useful molecules containing four functional groups.<sup>19</sup> It occurred to us that  $TiCl_4$  (in the absence of dimethyl sulphide) can possibly coordinate with the oxygen of alkyl vinyl ketone there by allowing the addition of chlorine to the enone intramolecularly in Michael fashion (**A**) resulting in the generation of enolate (**B**) which in turn might add to  $\alpha$ -keto ester in aldol manner (**C**) thus providing the desired Baylis–Hillman adduct after the elimination of HCl (Scheme 1).

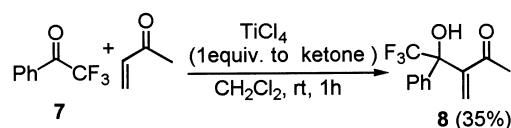


Scheme 1.



Accordingly we have first examined the reaction between methyl vinyl ketone (mvk) and ethyl phenylglyoxylate (**1a**) in the presence of  $\text{TiCl}_4$  under various conditions. The best results were obtained when the reaction was carried out in dichloromethane at room temperature for 1 h thus leading to the formation of the expected product ethyl 2-phenyl-2-hydroxy-3-methylene-4-oxopentanoate (**2a**) in 85% yield. Then we have extended the same methodology for the preparation of the representative class of 2-aryl-2-hydroxy-3-methylene-4-oxoalkanoates (**2b–e**, **3a–b**) via the coupling of various  $\alpha$ -keto esters with methyl vinyl ketone (mvk) and ethyl vinyl ketone (evk) (Scheme 1; Table 1). However our attempts to use ethyl pyruvate in a similar reaction with mvk were unsuccessful.

We also found that trifluoromethyl phenyl ketone (**7**) reacts with methyl vinyl ketone in the presence of  $\text{TiCl}_4$  to provide the desired Baylis–Hillman adduct i.e. 1,1,1-trifluoro-2-hydroxy-2-phenyl-3-methylene-pentan-4-one (**8**) in 35% yield (Eq. (1)).



Equation 1.

Table 1. Syntheses of 2-Aryl-2-hydroxy-3-methylene-4-oxoalkanoates<sup>a,b,c</sup>

Keto Ester	R	Enone	Product	mp/ <sup>o</sup> C	Yield <sup>d</sup> (%)
<b>1a</b>	phenyl	mvk	<b>2a</b>	83	85
<b>1b</b>	<i>p</i> -bromophenyl	mvk	<b>2b</b>	84	67
<b>1c</b>	<i>p</i> -methoxyphenyl	mvk	<b>2c</b>	69–70	50
<b>1d</b>	<i>p</i> -tolyl	mvk	<b>2d</b>	122	59
<b>1e</b>	naphth-1-yl	mvk	<b>2e</b>	64–65	53
<b>1a</b>	phenyl	evk	<b>3a</b>	72–74	57
<b>1b</b>	<i>p</i> -bromophenyl	evk	<b>3b</b>	85–86	58

<sup>a</sup>All reactions were carried out on 1 mmol scale of  $\alpha$ -keto ester with enone (3 mmol) and  $\text{TiCl}_4$  (1 mmol) at room temperature for 1 h. <sup>b</sup>All products (**2a–e**, **3a–b**) were obtained as solids and were characterized by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectral data and elemental analyses. <sup>c</sup>These products were prepared earlier in our laboratory via the chalcogeno-Baylis–Hillman reaction and spectral and physical data were in agreement with earlier data.<sup>19</sup> <sup>d</sup>Yields of products (based on keto esters) after purification by column chromatography (silica gel, 5% EtOAc in hexanes) followed by crystallization.



Encouraged by the fastness of this reaction and also with a view to generalize this reaction we next examined the reaction between methyl vinyl ketone and benzaldehyde (**4a**) in the presence of  $\text{TiCl}_4$  in dichloromethane at room temperature for 1 h which provided after work up (by adding conc. HCl) 3-chloromethyl-4-phenylbut-3-en-2-one (**5a**) in 72% yield with exclusive (*Z*)-stereoselectivity.<sup>20</sup> Then we have prepared variety of (*Z*)-allyl chlorides (**5b–h**, **6**) via the reaction between representative aldehydes and alkyl vinyl ketones mediated by  $\text{TiCl}_4$  (Scheme 1; Table 2).<sup>21</sup> A possible mechanism for the preparation of (*Z*)-keto allyl chlorides has been presented in the Scheme 1.

Comparison of our methodology for the synthesis of (*Z*)-keto allyl chlorides with that of Li, clearly indicates that our procedure needs 1 h time with one equivalent of  $\text{TiCl}_4$  to produce the desired (*Z*)-allyl chlorides in 41–77% yields while the Li method requires 24 h time with 0.5 equivalents of  $\text{TiX}_4$  (or 0.26 equivalents of  $\text{TiX}_4$  along with 0.26 equivalents of *n*-tetra-butyl ammonium iodide) to provide the required (*Z*)-allyl halides in 62–92% yields.<sup>17</sup>

In conclusion, this methodology describes the  $\text{TiCl}_4$  mediated coupling of alkyl vinyl ketones with  $\alpha$ -keto esters and aldehydes leading to the formation of 2-aryl-2-hydroxy-3-methylene-4-oxoalkanoates and (*Z*)-keto allyl

**Table 2.** Syntheses of (*Z*)-Keto Allyl Chlorides<sup>a,b,c</sup>

Aldehydes	R	Enone	Product <sup>d</sup>	Yield <sup>e</sup> (%)
<b>4a</b>	phenyl	mvk	<b>5a</b> <sup>21</sup>	72
<b>4b</b>	<i>o</i> -tolyl	mvk	<b>5b</b> <sup>f</sup>	60
<b>4c</b>	<i>p</i> -tolyl	mvk	<b>5c</b> <sup>21</sup>	65
<b>4d</b>	<i>p</i> -chlorophenyl	mvk	<b>5d</b> <sup>21</sup>	62
<b>4e</b>	<i>p</i> -ethylphenyl	mvk	<b>5e</b> <sup>f</sup>	55
<b>4f</b>	naphth-1-yl	mvk	<b>5f</b> <sup>f</sup>	41
<b>4g</b>	<i>n</i> -propyl	mvk	<b>5g</b> <sup>21</sup>	75
<b>4h</b>	<i>n</i> -heptyl	mvk	<b>5h</b> <sup>21</sup>	63
<b>4a</b>	phenyl	evk	<b>6</b> <sup>f</sup>	77

<sup>a</sup>All reactions were carried out on 5 mmol scale (aldehydes **4a–h**) with alkyl vinyl ketone (15 mmol) in the presence of  $\text{TiCl}_4$  (5 mmol) for 1 h at room temperature. <sup>b</sup>Satisfactory spectral [IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR] and elemental analyses were obtained for all molecules (**5a–h**, **6**). <sup>c</sup><sup>1</sup>H NMR and <sup>13</sup>C NMR indicate the absence of any (*E*)-isomer. <sup>d</sup>These molecules (except **5d**, **5f** which were obtained as solids) were obtained as colorless liquids. <sup>e</sup>Isolated yields of the products after column chromatography (2% EtOAc in hexanes). <sup>f</sup>The (*Z*)-stereochemistry was assigned on the basis of chemical shift value of vinylic proton in <sup>1</sup>H NMR spectral analysis in analogy with **5a**, **5c–d**.



chlorides respectively in 1 h time at room temperature thus further expanding the scope of the Baylis–Hillman reaction.

## EXPERIMENTAL

All melting points were recorded on a Superfit (India) capillary melting point apparatus and are uncorrected. IR spectra were recorded on JASCO-FT-IR model 5300 spectrometer using samples as neat liquids and solid samples were recorded as KBr wafers.  $^1\text{H}$  NMR (200 MHz) and  $^{13}\text{C}$  NMR (50 MHz) spectra were recorded in deuterio chloroform ( $\text{CDCl}_3$ ) on Bruker-AC-200 spectrometer using tetramethylsilane (TMS,  $\delta=0$ ) as internal standard. Elemental analyses were recorded on Perkin-Elmer 240C-CHN analyzer. Mass spectra were recorded on a micromass VG 7070 H instrument.

### General Procedure for the Preparation of 2-Aryl-2-hydroxy-3-methylene-4-oxoalkanoates

To a stirred solution of ethyl aryl glyoxylate (**1a–e**, 1 mmol) and alkyl vinyl ketone (3 mmol) in dichloromethane (2 mL) was added titanium tetrachloride (1 mmol, 0.2 mL of 5 M solution in  $\text{CH}_2\text{Cl}_2$ ) at room temperature. After 1 h the reaction mixture was diluted with water (5 mL) and extracted with ether. Organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated. Purification of the crude product by column chromatography (silica gel, 5% EtOAc in hexanes) followed by crystallization (from hexanes) furnished the product (**2a–e** and **3a–b**) as a colorless solid.

**Ethyl 2-hydroxy-2-phenyl-3-methylene-4-oxopentanoate (2a):** Colorless solid. Yield: 85%; m.p.:  $83^\circ\text{C}$ ; IR (KBr): 3477, 1722,  $1668\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR:  $\delta$  1.26 (t, 3H,  $J=6.8\text{ Hz}$ ), 2.41 (s, 3H), 4.25 (q, 2H,  $J=6.8\text{ Hz}$ ), 4.33 (s, 1H), 5.53 (s, 1H), 6.20 (s, 1H), 7.32–7.47 (m, 3H), 7.54–7.66 (m, 2H);  $^{13}\text{C}$  NMR:  $\delta$  13.95, 26.35, 62.23, 78.84, 126.78, 128.19, 128.93, 138.16, 151.36, 173.39, 200.11; Analysis calculated for  $\text{C}_{14}\text{H}_{16}\text{O}_4$ : C, 67.7, H, 6.5 found C, 67.7, H, 6.5.

**Ethyl 2-(4-bromophenyl)-2-hydroxy-3-methylene-4-oxopentanoate (2b):** Colorless solid. Yield: 67%; m.p.:  $84^\circ\text{C}$ ; IR (KBr): 3454, 1730,  $1670\text{ cm}^{-1}$ ,  $^1\text{H}$  NMR:  $\delta$  1.25 (t, 3H,  $J=6.9\text{ Hz}$ ), 2.40 (s, 3H), 4.25 (q, 2H,  $J=6.9\text{ Hz}$ ), 4.32 (s, 1H), 5.53 (s, 1H), 6.21 (s, 1H), 7.49 (s, 4H);  $^{13}\text{C}$  NMR:  $\delta$  13.90, 26.27, 62.41, 78.36, 122.51, 128.61, 129.03, 131.28, 137.16, 150.81, 172.94, 199.84; Analysis calculated for  $\text{C}_{14}\text{H}_{15}\text{O}_4\text{Br}$ : C, 51.4, H, 4.6 found C, 51.6, H, 4.6.



**Ethyl 2-hydroxy-2-(4-methoxyphenyl)-3-methylene-4-oxopentanoate (2c):**

Colorless solid. Yield: 50%; m.p.: 69–70°C; IR (KBr): 3483, 1743, 1674 cm<sup>-1</sup>; <sup>1</sup>H NMR: δ 1.26 (t, 3H, J = 7.6 Hz), 2.41 (s, 3H), 3.82 (s, 3H), 4.26 (q, 2H, J = 7.6 Hz), 4.30 (s, 1H), 5.58 (s, 1H), 6.20 (s, 1H), 6.90 (d, 2H, J = 8.8 Hz), 7.51 (d, 2H, J = 8.8 Hz); <sup>13</sup>C NMR: δ 13.94, 26.35, 55.23, 62.13, 78.42, 113.55, 127.97, 129.01, 129.97, 151.41, 159.52, 173.53, 200.22; Analysis calculated for C<sub>15</sub>H<sub>18</sub>O<sub>5</sub>: C, 64.7, H, 6.5 found C, 64.6, H, 6.6.

**Ethyl 2-hydroxy-2-(4-methylphenyl)-3-methylene-4-oxopentanoate (2d):**

Colorless solid. Yield: 59%; m.p.: 122°C; IR (KBr): 3476, 1718, 1670 cm<sup>-1</sup>; <sup>1</sup>H NMR: δ 1.26 (t, 3H, J = 7.4 Hz), 2.35 (s, 3H), 2.41 (s, 3H), 4.22 (q, 2H, J = 7.4 Hz), 4.30 (s, 1H), 5.56 (s, 1H), 6.19 (s, 1H), 7.17 (d, 2H, J = 8.0 Hz), 7.48 (d, 2H, J = 8.0 Hz); <sup>13</sup>C NMR: δ 13.42, 20.49, 25.84, 61.65, 78.14, 126.09, 128.35, 128.58, 134.47, 137.42, 150.76, 173.01, 199.69; Analysis calculated for C<sub>15</sub>H<sub>18</sub>O<sub>4</sub>: C, 68.7, H, 6.9 found C, 68.9, H, 6.9.

**Ethyl 2-hydroxy-2-(naphth-1-yl)-3-methylene-4-oxopentanoate (2e):**

Colorless solid. Yield: 53%; m.p.: 64–65°C; IR (KBr): 3493, 1747, 1672 cm<sup>-1</sup>; <sup>1</sup>H NMR: δ 1.25 (t, 3H, J = 7.2 Hz), 2.52 (s, 3H), 4.30 (q, 2H, J = 7.2 Hz), 5.07 (s, 1H), 5.41 (s, 1H), 6.19 (s, 1H), 7.35–7.66 (m, 4H), 7.84 (m, 2H), 8.24 (m, 1H); <sup>13</sup>C NMR: δ 13.93, 27.04, 62.40, 81.89, 124.85, 125.47, 127.59, 128.80, 129.74, 129.84, 131.13, 134.29, 134.65, 148.58, 173.36, 201.74; Analysis calculated for C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>: C, 72.5, H, 6.1 found C, 72.7, H, 6.1.

**Ethyl 2-hydroxy-2-phenyl-3-methylene-4-oxohexanoate (3a):** Colorless solid. Yield: 57%, m.p.: 72–74°C; IR (KBr): 3477, 1720, 1670 cm<sup>-1</sup>; <sup>1</sup>H NMR: δ 1.15 (t, 3H, J = 7.4 Hz), 1.26 (t, 3H, J = 7.4 Hz), 2.77 (q, 2H, J = 7.4 Hz), 4.24 (q, 2H, J = 7.4 Hz), 4.38 (s, 1H), 5.49 (s, 1H), 6.19 (s, 1H), 7.30–7.49 (m, 3H), 7.54–7.66 (m, 2H); <sup>13</sup>C NMR: δ 8.22, 14.02, 31.68, 62.27, 79.21, 126.89, 127.59, 128.23, 138.28, 151.06, 173.51, 203.16; Analysis calculated for C<sub>15</sub>H<sub>18</sub>O<sub>4</sub>: C, 68.7, H, 6.9 found C, 68.5, H, 6.9.

**Ethyl 2-(4-bromophenyl)-2-hydroxy-3-methylene-4-oxohexanoate (3b):**

Colorless solid. Yield: 58%; m.p.: 85–86°C; IR (KBr): 3487, 1722, 1674 cm<sup>-1</sup>; <sup>1</sup>H NMR: δ 1.13 (t, 3H, J = 7.4 Hz), 1.25 (t, 3H, J = 7.6 Hz), 2.78 (q, 2H, J = 7.4 Hz), 4.24 (q, 2H, J = 7.6 Hz), 4.37 (s, 1H), 5.49 (s, 1H), 6.20 (s, 1H), 7.50 (s, 4H); <sup>13</sup>C NMR: δ 8.17, 14.01, 31.61, 62.50, 78.80, 122.62, 127.65, 128.74, 131.38, 137.32, 150.58, 173.12, 202.92; Analysis calculated for C<sub>15</sub>H<sub>17</sub>O<sub>4</sub>Br: C, 52.8, H, 5.0 found C, 52.7, H, 5.0.

### General Procedure for the Preparation of (*Z*)-Allyl Chlorides

To a stirred solution of aldehyde (**4a–h**, 5 mmol), and alkyl vinyl ketone (15 mmol), in dichloromethane (7.5 mL), was added titanium tetrachloride



(5 mmol, 1 mL of 5 M solution in  $\text{CH}_2\text{Cl}_2$ ) at room temperature. After 1 h, the reaction mixture was treated with aq. HCl (36%) (2 mL) for a minute at room temperature, diluted with water (5 mL) and extracted with ether. Organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated. The crude product on purification by column chromatography (silica gel, 2% EtOAc in hexanes) afforded the pure allyl chloride (**5a-h**, **6**). Compounds **5a**, **5c**, **5d**, **5g** and **5h** were earlier prepared in our laboratory by a different methodology and were well characterized.<sup>22</sup> The present spectral data are in agreement with earlier data.

**(3Z)-3-(Chloromethyl)-4-(2-methylphenyl)but-3-en-2-one (5b):** Colorless oil. Yield: 60%; IR (neat): 1676, 1622  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$  2.32 (s, 3H), 2.52 (s, 3H), 4.34 (s, 2H), 7.22–7.37 (m, 3H), 7.58 (m, 1H), 7.78 (s, 1H);  $^{13}\text{C NMR}$ :  $\delta$  19.69, 25.83, 37.62, 126.05, 128.23, 129.40, 130.22, 133.38, 136.74, 137.79, 142.13, 196.97; Analysis calculated for  $\text{C}_{12}\text{H}_{13}\text{OCl}$ : C, 69.1, H, 6.3 found C, 69.1, H, 6.3.

**(3Z)-3-(Chloromethyl)-4-(4-ethylphenyl)but-3-en-2-one (5e):** Colorless oil. Yield: 55%; IR (neat): 1670, 1622  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$  1.23 (t, 3H,  $J=7.4$  Hz), 2.44 (s, 3H), 2.66 (q, 2H,  $J=7.4$  Hz), 4.43 (s, 2H), 7.26 (d, 2H,  $J=8.0$  Hz), 7.50 (d, 2H,  $J=8.0$  Hz), 7.64 (s, 1H);  $^{13}\text{C NMR}$ :  $\delta$  15.10, 25.67, 28.63, 37.69, 128.38, 129.87, 131.44, 136.12, 143.75, 146.52, 197.12; Analysis calculated for  $\text{C}_{13}\text{H}_{15}\text{OCl}$ : C, 70.1, H, 6.8 found C, 70.4, H, 6.8.

**(3Z)-3-(Chloromethyl)-4-(naphth-1-yl)but-3-en-2-one (5f):** Colorless solid. Yield: 41%; m.p.: 87–89°C; IR (KBr): 1666, 1626  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$  2.62 (s, 3H), 4.38 (s, 2H), 7.49–8.02 (m, 7H), 8.26 (s, 1H);  $^{13}\text{C NMR}$ :  $\delta$  26.12, 38.06, 123.95, 125.34, 126.44, 126.68, 126.86, 128.76, 129.96, 131.25, 133.43, 139.08, 141.25, 196.99; Analysis calculated for  $\text{C}_{15}\text{H}_{13}\text{OCl}$ : C, 73.6, H, 5.4 found C, 73.4, H, 5.4.

**(4Z)-4-(Chloromethyl)-5-phenylpent-4-en-3-one (6):** Colorless oil. Yield: 77%; IR (neat): 1676, 1624  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$  1.20 (t, 3H,  $J=7.6$  Hz), 2.88 (q, 2H,  $J=7.6$  Hz), 4.47 (s, 2H), 7.38–7.64 (m, 5H), 7.69 (s, 1H);  $^{13}\text{C NMR}$ :  $\delta$  8.50, 31.10, 38.04, 128.99, 129.65, 129.76, 134.40, 136.87, 142.21, 200.14; Analysis calculated for  $\text{C}_{12}\text{H}_{13}\text{OCl}$ : C, 69.1, H, 6.3 found C, 68.8, H, 6.3.

**1,1,1-Trifluoro-2-hydroxy-2-phenyl-3-methylenepentan-4-one (8):** This compound was prepared from trifluoromethyl phenyl ketone (**7**) and mvk under the influence of  $\text{TiCl}_4$  following a similar procedure described for the preparation of 2-aryl-2-hydroxy-3-methylene-4-oxoalkanoates, as a colorless oil. Yield: 35%; IR (neat): 3416, 1672, 1620  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$  2.37 (s, 3H), 5.85 (s, 1H), 6.29 (s, 1H), 6.46 (s, 1H), 7.31–7.44 (m, 3H), 7.48–7.59 (m, 2H);  $^{13}\text{C NMR}$ :  $\delta$  27.44, 80.00 (q,  $J=28.0$  Hz), 124.29 (q,  $J=283$  Hz), 126.81, 128.37, 128.92, 129.44, 137.40, 143.89, 202.94; MS ( $m/z$ ): 244 ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{12}\text{H}_{11}\text{O}_2\text{F}_3$ : C, 59.0, H, 4.5 found C, 59.1, H, 4.5.





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  21. We have prepared these molecules (except **5b**, **5e**, **5f**, **6**) in our laboratory earlier by different procedure and assignment of (*Z*)-stereochemistry and spectral data of these molecules were in agreement with earlier data.<sup>22</sup>
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