Efficient and Stereoselective Rearrangement of Baylis–Hillman Acetates Catalyzed by Gold(I) Chloride/Silver(I) Trifluoromethanesulfonate

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Received 24 October 2008; revised 25 November 2008

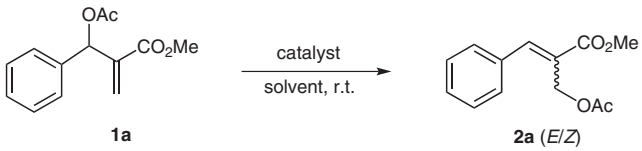
Abstract: Efficient and stereoselective rearrangement catalyzed by only one mole-percent gold(I) chloride/silver(I) trifluoromethanesulfonate of Baylis–Hillman acetates afforded 2-(acetoxymethyl)alk-2-enoates under mild reaction conditions in good to high yields with 100% *E*-selectivity. For cyclohex-2-enone-derived Baylis–Hillman acetates, the reaction gave 2-alkylidenecyclohex-3-enones in good yields.

Key words: gold/silver catalysis, stereoselectivity, rearrangements, Baylis–Hillman acetate, alk-2-enoates

Recently, there has been a growing interest in gold-catalyzed organic transformations, because gold catalysts usually exhibit extraordinary reactivity and show high selectivity in the reactions.[1,2] Indeed, gold catalysts have been able to promote various transformations such as nucleophilic additions to C–C multiple bonds (alkynes, alkenes, allenes), Friedel–Crafts reactions and C–H activations, and hydrogenation and oxidation reactions.[1] Among these transformations, gold-catalyzed skeletal rearrangements of propargylic esters have been extensively studied for their great potential to create diverse product patterns.[3,4] Allylic esters, the alkene counterparts of propargylic esters, have, however, received only little attention.[5,6] To date, only two literature reports have appeared on the isomerization of allylic acetates or allenyl esters catalyzed by gold(I) complexes.[5] Therefore, it is still desirable to extend the scope and reaction patterns involving gold-catalyzed skeletal rearrangements of allylic esters.

The Baylis–Hillman reaction is well known as a powerful C–C bond-forming reaction in organic synthesis.[7] The main attraction of this reaction lies in its atom economy, catalytic process, and the high degree of functionality present in the products for further transformations. For example, Baylis–Hillman acetates, which act as activated Baylis–Hillman adducts bearing allylic acetate parts and Michael acceptor units, are valuable synthons and starting materials for the synthesis of a number of multifunctional molecules.[8]

The isomerization of Baylis–Hillman acetates to (*E*)-2-(acetoxymethyl)alk-2-enoates, which are useful intermediates for the synthesis of (*E*)-cinnamyl alcohols[9,10] and other complicated molecules,[11] has been investigated in the presence of several catalysts, including trimethylsilyl trifluoromethanesulfonate,[12] montmorillonite-K10 clay,[13] 1,4-diazabicyclo[2.2.2]octane,[14] cesium fluoride,[15] palladium(II) acetate,[16] iron(III) chloride, and ytterbium(III) trifluoromethanesulfonate.[6g] However, these procedures usually have one or more limitations, such as high catalyst loading, severe reaction conditions, resulting products mixed with *E*- and *Z*-isomers, and low yields. In view of gold's high reactivity and selectivity in reactions[1,2] and our continued interest in the stereoselective conversion of Baylis–Hillman adducts into trisubstituted alkenes,[17] we have carried out the work reported here, and found an efficient and stereoselective rearrangement of Baylis–Hillman acetates to 2-(acetoxymethyl)alk-2-enoates in good to high yields with 100% *E*-selectivity, catalyzed by only one mole-percent gold(I) chloride/silver(I) trifluoromethanesulfonate under mild reaction conditions (Scheme 1).



Scheme 1

Initially, Baylis–Hillman allylic acetate **1a** was chosen as a model substrate for the optimization of the reaction conditions (Scheme 1, Table 1). The desired product **2a** did not form in the presence of trivalent gold catalysts such as gold(III) chloride, sodium tetrachloroaurate(III) dihydrate, and dichloro(pyridine-2-carboxylato)gold(III)[18] (Table 1, entries 1–3). Treatment of **1a** with 1 mol% of gold(I) chloride in dichloromethane gave the isomerized product **2a** in 78% yield (entry 4). The reaction also proceeded smoothly to give **2a** in 75% yield in the presence of 3 mol% of silver(I) trifluoromethanesulfonate (entry 5). Although gold(I) chloride or silver(I) trifluoromethanesulfonate alone was a suitable catalyst for the reaction, the best result was obtained when a combination of gold(I) chloride and silver(I) trifluoromethanesulfonate was used (90% yield, entry 6). According to previous reports,[19,20] the silver salt might play an important role in helping to remove the chloride anion from gold(I) chloride to gener-

SYNTHESIS 2009, No. 7, pp 1170–1174
Advanced online publication: 24.02.2009
DOI: 10.1055/s-0028-1087971; Art ID: F22008SS

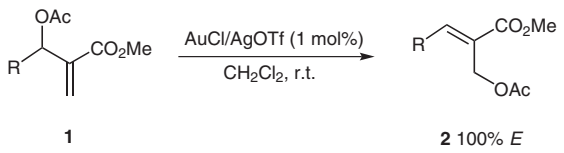
ate a more electrophilic cationic gold(I) species. In the absence of a transition metal salt, the rearrangement did not take place, and the starting material was recovered quantitatively (entry 10). Solvent screening showed that 1,2-dichloroethane was also a good solvent for the reaction (entry 7), while tetrahydrofuran and acetonitrile were less suitable (entries 8 and 9). It is worth noting that the reaction showed excellent stereoselectivity affording the single *E*-isomer exclusively. The stereoconfiguration of the product was assigned by comparing the chemical shifts in ^{1}H NMR and ^{13}C NMR spectra with reported relevant values.[12]

Table 1 Optimization of the Reaction Conditions[a]

Entry	Catalyst (mmol)	Solvent	Time (h)	*E*/*Z* ratio[b]	Yield[c] (%)
1	$AuCl_3$ (0.01)	CH_2Cl_2	8.0	–	0
2	$NaAuCl_4{\cdot}2H_2O$ (0.01)	CH_2Cl_2	8.0	–	0
3	dichloro(pyridine-2-carboxylato)gold(III) (0.01)	CH_2Cl_2	8.0	–	0
4	AuCl (0.01)	CH_2Cl_2	3.0	100:0	78
5	AgOTf (0.03)	CH_2Cl_2	3.0	100:0	75
6	AuCl/AgOTf (0.01)	CH_2Cl_2	3.0	100:0	90
7	AuCl/AgOTf (0.01)	DCE	3.0	100:0	88
8	AuCl/AgOTf (0.01)	THF	3.0	100:0	65
9	AuCl/AgOTf (0.01)	MeCN	3.0	100:0	68
10	none	CH_2Cl_2	8.0	–	0[d]

[a] Reagents and conditions: **1a** (1 mmol), catalyst, solvent (3 mL), r.t.
[b] The *E*/*Z* ratio was determined by ^{1}H NMR analysis.
[c] Isolated yields.
[d] Starting material **1a** was recovered quantitatively.

With the optimized conditions in hand, we next turned our attention to examine the scope of the reaction (Scheme 2, Table 2). The present method was effective for both aryl-substituted (Table 2, entries 1–9) and alkyl-substituted (entry 10) Baylis–Hillman acetates **1**, but a slightly elevated temperature was needed for the latter. The reaction proceeded smoothly with all the aryl-bearing substrates to give isomerized products **2** in good to high yields (78–92%) at room temperature. Various substitution patterns on the phenyl ring were compatible with the reaction conditions and did not alter the stereochemistry of the isomerized products **2**.



1 **2** 100% *E*

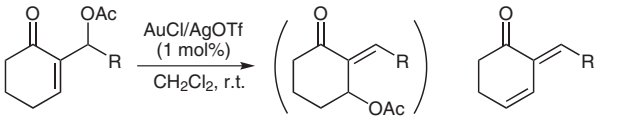
Scheme 2

Table 2 Isomerization of Baylis–Hillman Acetates **1** into **2** Catalyzed by Gold(I) Chloride/Silver(I) Trifluoromethanesulfonate[a]

Entry	R	**1**	Time (h)	Product[b]	Yield[c] (%)
1	Ph	**1a**	3.0	**2a**	90
2	Tol	**1b**	3.0	**2b**	92
3	4-$MeOC_6H_4$	**1c**	3.0	**2c**	78
4	2-$MeOC_6H_4$	**1d**	3.0	**2d**	82
5	1,3-benzodioxol-5-yl	**1e**	3.0	**2e**	85
6	4-ClC_6H_4	**1f**	3.0	**2f**	88
7	2-ClC_6H_4	**1g**	3.0	**2g**	87
8	4-BrC_6H_4	**1h**	3.0	**2h**	92
9	2,4-$Cl_2C_6H_3$	**1i**	3.5	**2i**	78
10	*n*-C_7H_{15}	**1j**	6.0	**2j**	76[d]

[a] Reagents and conditions: **1** (1 mmol), AuCl (0.01 mmol), AgOTf (0.01 mmol), CH_2Cl_2 (3 mL), r.t.
[b] In all cases, ^{1}H and ^{13}C NMR spectroscopy indicate the formation of only *E*-isomers.
[c] Isolated yields.
[d] The reaction was carried out at 45 °C.

Interestingly, for cyclohex-2-enone-derived Baylis–Hillman acetates **3**, the reaction gave 2-alkylidenecyclohex-3-enones **5** instead of isomerized product **4** by elimination of one molecule of acetic acid from **3** (Scheme 3).[21]

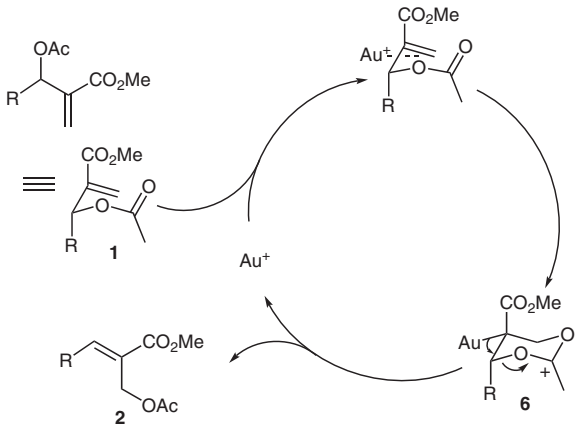


3 **4** (not detected) **5a** R = 4-ClC_6H_4 82%
5b R = 4-BrC_6H_4 84%

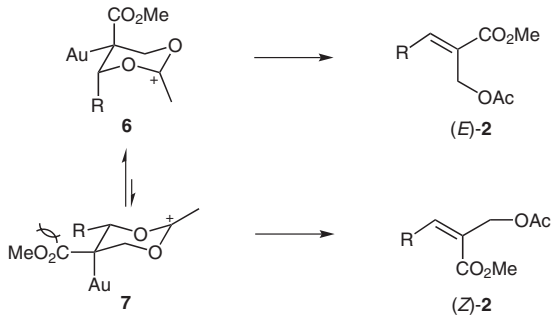
Scheme 3

A possible mechanism for the reaction, postulated on the basis of previous reports,[5,12] involving gold(I)-catalyzed isomerization of Baylis–Hillman acetates **1** is depicted in Scheme 4. Firstly, the C=C bond in **1** is activated by π-coordination of the alkene moiety to the cationic gold center, which then induces nucleophilic attack of the carbonyl at the double bond, resulting in the formation of the six-membered-ring stabilized cationic species **6**. Finally, the internal olefin is established to form **2** by concerted fragmentation of the corresponding C–O and Au–C bond in **6**, leading to 1,3-shift of the acetate group and regeneration of the gold catalyst.

Regarding stereoselectivity observed in the reaction, it could be explained by the two possible transition state **6** and **7**, which are key precursors to form *E*- and *Z*-isomers, respectively (Scheme 5). The transition state **6** is energetically more favored because both the ester and R group



Scheme 4 Possible mechanism for the isomerization



Scheme 5 Explanation for the stereoselectivity

adopt axial positions with an opposite orientation, thus avoiding the steric 1,2-interaction between these two groups which exists in transition state **7**.[22]

In conclusion, we have described an efficient and stereoselective isomerization of Baylis–Hillman acetates into 2-(acetoxymethyl)alk-2-enoates catalyzed by only one mole-percent gold(I) chloride/silver(I) trifluoromethanesulfonate with 100% *E*-selectivity. The attractiveness of the present method lies in its low catalyst loading, excellent stereoselectivity, good yields, and mild reaction conditions.

IR spectra were recorded on a Bruker EQUINOX 55 spectrometer. ^{1}H and ^{13}C NMR spectra of samples in $CDCl_3$ were obtained on a Bruker AVANCE III 500 (500 MHz) instrument; TMS was used as internal standard. Mass spectra were obtained on an HP 5989B mass spectrometer. Elemental analyses were performed on an EA-1110 instrument. GC-MS experiments were performed with an Agilent 6890N GC system equipped with a 5973N mass-selective detector. The Baylis–Hillman acetate starting materials **1** and **3** were prepared according to literature procedures.[23]

Isomerization of Baylis–Hillman Acetates 1 into 2, and Conversion of 3 into 5; General Procedure

AuCl (2.3 mg, 0.01 mmol), AgOTf (2.6 mg, 0.01 mmol), and CH_2Cl_2 (2 mL) were added to a 10-mL flask. The mixture was stirred at r.t. for 5 min before a CH_2Cl_2 soln (1 mL) of Baylis–Hillman acetate **1** or **3** (1 mmol) was added. The mixture was stirred at r.t. for the time given in Table 1 or 2. Upon completion of the reaction, the resulting mixture was dissolved in pentane and filtered through Celite. After evaporation of the solvent, the residue was purified by chromatography (cyclohexane–EtOAc, 8:1); this gave pure **2** or **5**.

Methyl (2*E*)-2-(Acetoxymethyl)-3-phenylprop-2-enoate (2a)[12]

Colorless liquid; R_f = 0.56 (cyclohexane–EtOAc, 8:1).

IR (neat): 1721 (C=O), 1635 (C=C) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.10 (s, 3 H, COCH_3), 3.84 (s, 3 H, OCH_2), 4.96 (s, 2 H, CH_2), 7.37–7.42 (m, 5 H, Ar*H*), 7.99 (s, 1 H, ArC*H*=).

MS (EI, 70 eV): *m*/*z* = 234 [M$^+$].

Methyl (2*E*)-2-(Acetoxymethyl)-3-(4-tolyl)prop-2-enoate (2b)[12]

Colorless liquid; R_f = 0.53 (cyclohexane–EtOAc, 8:1).

IR (neat): 1717 (C=O), 1633 (C=C) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.11 (s, 3 H, $COCH_3$), 2.37 (s, 3 H, ArCH_3), 3.84 (s, 3 H, OCH_3), 4.96 (s, 2 H, CH_2), 7.21 (d, *J* = 8.0 Hz, 2 H, Ar*H*), 7.28 (d, *J* = 8.0 Hz, 2 H, Ar*H*), 7.96 (s, 1 H, ArC*H*=).

MS (EI, 70 eV): *m*/*z* = 248 [M$^+$].

Methyl (2*E*)-2-(Acetoxymethyl)-3-(4-methoxyphenyl)prop-2-enoate (2c)

Colorless liquid; R_f = 0.50 (cyclohexane–EtOAc, 8:1).

IR (neat): 1712 (C=O), 1604 (C=C) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, COCH_3), 3.82 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 4.98 (s, 2 H, CH_2), 6.93 (d, *J* = 8.0 Hz, 2 H, Ar*H*), 7.36 (d, *J* = 8.0 Hz, 2 H, Ar*H*), 7.93 (s, 1 H, ArC*H*=).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.89, 52.10, 55.25, 59.51, 114.21, 124.04, 126.61, 131.52, 145.30, 160.88, 167.55, 170.75.

MS (EI, 70 eV): *m*/*z* = 264 [M$^+$].

Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.82; H, 6.06.

Methyl (2*E*)-2-(Acetoxymethyl)-3-(2-methoxyphenyl)prop-2-enoate (2d)[13b]

Colorless liquid; R_f = 0.51 (cyclohexane–EtOAc, 8:1).

IR (neat): 1739 (C=O), 1635 (C=C) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.08 (s, 3 H, COCH_3), 3.83 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3), 4.91 (s, 2 H, CH_2), 6.90 (d, *J* = 8.0 Hz, 1 H, Ar*H*), 6.96 (t, *J* = 8.0 Hz, 1 H, Ar*H*), 7.26 (d, *J* = 8.0 Hz, 1 H, Ar*H*), 7.36 (t, *J* = 8.0 Hz, 1 H, Ar*H*), 8.15 (s, 1 H, ArC*H*=).

MS (EI, 70 eV): *m*/*z* = 264 [M$^+$].

Methyl (2*E*)-2-(Acetoxymethyl)-3-(1,3-benzodioxol-5-yl)prop-2-enoate (2e)

Colorless liquid; R_f = 0.48 (cyclohexane–EtOAc, 8:1).

IR (KBr): 1719 (C=O), 1618 (C=C) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, COCH_3), 3.83 (s, 3 H, OCH_3), 4.96 (s, 2 H, CH_2), 6.0 (s, 2 H, OCH_2O), 6.84 (d, *J* = 7.5 Hz, 1 H, Ar*H*), 6.90–6.93 (m, 2 H, Ar*H*), 7.87 (s, 1 H, ArC*H*=).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.91, 52.19, 59.35, 101.55, 108.57, 109.28, 124.71, 125.0, 128.11, 145.33, 148.07, 149.01, 167.43, 170.70.

MS (EI, 70 eV): *m*/*z* = 278 [M$^+$].

Anal. Calcd for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.71; H, 5.10.

Methyl (2*E*)-2-(Acetoxymethyl)-3-(4-chlorophenyl)prop-2-enoate (2f)[12]

Colorless liquid; R_f = 0.55 (cyclohexane–EtOAc, 8:1).

IR (neat): 1744 (C=O), 1636 (C=C) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.10 (s, 3 H, COCH_3), 3.85 (s, 3 H, OCH_3), 4.93 (s, 2 H, CH_2), 7.32 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.38 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.91 (s, 1 H, ArC*H*=).

MS (EI, 70 eV): *m*/*z* = 268 [M$^+$], 270 [M$^+$ + 2].

Methyl (2*E*)-2-(Acetoxymethyl)-3-(2-chlorophenyl)prop-2-enoate (2g)[13b]

Colorless liquid; R_f = 0.54 (cyclohexane–EtOAc, 8:1).

IR (neat): 1735 (C=O), 1638 (C=C) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.07 (s, 3 H, COCH_3), 3.87 (s, 3 H, OCH_3), 4.85 (s, 2 H, CH_2), 7.29–7.35 (m, 3 H, Ar*H*), 7.44 (d, *J* = 8.5 Hz, 1 H, Ar*H*), 8.05 (s, 1 H, ArC*H*=).

MS (EI, 70 eV): *m*/*z* = 268 [M$^+$], 270 [M$^+$ + 2].

Methyl (2*E*)-2-(Acetoxymethyl)-3-(4-bromophenyl)prop-2-enoate (2h)

Colorless liquid; R_f = 0.54 (cyclohexane–EtOAc, 8:1).

IR (neat): 1742 (C=O), 1637 (C=C) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.10 (s, 3 H, COCH_3), 3.84 (s, 3 H, OCH_3), 4.92 (s, 2 H, CH_2), 7.25 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.54 (d, *J* = 8.5 Hz, 2 H, Ar*H*), 7.88 (s, 1 H, ArC*H*=).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.83, 52.33, 59.01, 124.0, 127.30, 130.93, 131.93, 133.0, 143.95, 166.93, 170.46.

MS (EI, 70 eV): *m*/*z* = 312 [M$^+$], 314 [M$^+$ + 2].

Anal. Calcd for $C_{13}H_{13}BrO_4$: C, 49.86; H, 4.18. Found: C, 49.61; H, 4.21.

Methyl (2*E*)-2-(Acetoxymethyl)-3-(2,4-dichlorophenyl)prop-2-enoate (2i)

Colorless liquid; R_f = 0.55 (cyclohexane–EtOAc, 8:1).

IR (neat): 1740 (C=O), 1644 (C=C) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.07 (s, 3 H, COCH_3), 3.87 (s, 3 H, OCH_3), 4.82 (s, 2 H, CH_2), 7.28–7.30 (m, 2 H, Ar*H*), 7.46 (s, 1 H), 7.97 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.81, 52.45, 59.11, 127.28, 129.23, 129.67, 130.92, 131.44, 135.02, 135.93, 140.82, 166.43, 170.36.

MS (EI, 70 eV): *m*/*z* = 302 [M$^+$], 304 [M$^+$ + 2].

Anal. Calcd for $C_{13}H_{12}Cl_2O_4$: C, 51.51; H, 3.99. Found: C, 51.72; H, 3.96.

Methyl (2*E*)-2-(Acetoxymethyl)dec-2-enoate (2j)

Colorless liquid; R_f = 0.65 (cyclohexane–EtOAc, 8:1).

IR (neat): 1733 (C=O), 1651 (C=C) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.5 Hz, 3 H), 1.27–1.47 (m, 10 H), 2.05 (s, 3 H, COCH_3), 2.30 (q, *J* = 7.5 Hz, 2 H), 3.78 (s, 3 H, OCH_3), 4.84 (s, 2 H), 7.06 (t, *J* = 7.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.02, 20.87, 22.57, 28.58, 28.75, 29.02, 29.21, 31.69, 51.91, 58.02, 126.84, 149.88, 166.94, 170.79.

MS (EI, 70 eV): *m*/*z* = 256 [M$^+$].

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.89; H, 9.38.

(*E*)-2-(4-Chlorobenzylidene)cyclohex-3-enone (5a)

Colorless liquid; R_f = 0.60 (cyclohexane–EtOAc, 8:1).

IR (neat): 1687 (C=O), 1614 (C=C) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.59–2.69 (m, 4 H), 6.16–6.20 (m, 1 H), 6.84–6.87 (m, 1 H), 7.34–7.36 (m, 5 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.59, 38.19, 124.82, 128.75, 130.53, 131.22, 131.51, 131.73, 133.89, 134.49, 199.95.

MS (EI, 70 eV): *m*/*z* = 218 [M$^+$], 220 [M$^+$ + 2].

Anal. Calcd for $C_{13}H_{11}ClO$: C, 71.40; H, 5.07. Found: C, 71.21; H, 5.02.

(*E*)-2-(4-Bromobenzylidene)cyclohex-3-enone (5b)

Colorless liquid; R_f = 0.61 (cyclohexane–EtOAc, 8:1).

IR (neat): 1692 (C=O), 1614 (C=C) cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.57–2.69 (m, 4 H), 6.16–6.21 (m, 1 H), 6.84–6.86 (m, 1 H), 7.27–7.52 (m, 5 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.61, 38.19, 122.77, 124.81, 130.57, 131.46, 131.56, 131.71, 131.81, 134.33, 199.97.

MS (EI, 70 eV): *m*/*z* = 262 [M$^+$], 264 [M$^+$ + 2].

Anal. Calcd for $C_{13}H_{11}BrO$: C, 59.34; H, 4.21. Found: C, 59.02; H, 4.26.

Acknowledgment

Financial support was provided by the Natural Science Foundation of Zhejiang Province (No. Y407168) and the Opening Foundation of Zhejiang Provincial Top Key Discipline.

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