Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Efficient One-Pot Synthesis of 2-Carbonyl- 1-indanols by Palladium-Catalyzed Tandem Heck-Aldol Reaction

Song Tu [a] , Long-He Xu [a] & Chun-Rui Yu [a]
[a] State Key Laboratory of Fine Chemicals, Dalian University of Technology , Dalian, China
Published online: 09 Sep 2008.

To cite this article: Song Tu , Long-He Xu & Chun-Rui Yu (2008) Efficient One-Pot Synthesis of 2-Carbonyl- 1-indanols by Palladium-Catalyzed Tandem Heck-Aldol Reaction, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 38:15, 2662-2671, DOI: 10.1080/00397910601038731

To link to this article: http://dx.doi.org/10.1080/00397910601038731

Synthetic Communications®, 38: 2662–2671, 2008

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910601038731

Taylor & Francis
Taylor & Francis Group

Efficient One-Pot Synthesis of 2-Carbonyl-1-indanols by Palladium-Catalyzed Tandem Heck–Aldol Reaction

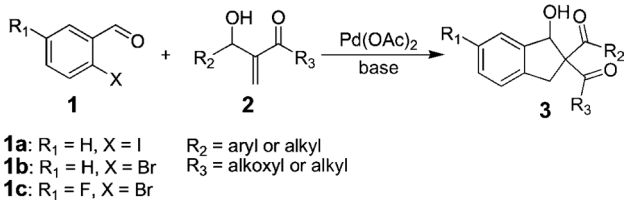
Song Tu, Long-He Xu, and Chun-Rui Yu
State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, China

Abstract: 2-Carbonyl-1-indanols were synthesized in moderate to good yields by the reaction of orthohalogenated aryl aldehyde with Morita–Baylis–Hillman adducts via a one-pot, palladium-catalyzed tandem Heck–aldol reaction. Various Morita–Baylis–Hillman adducts were examined to find the scope and limitations of this process.

Keywords: 2-carbonyl-l-indanol, Morita–Baylis–Hillman adducts, one-pot, palladium-catalyzed

Indanols are important and useful organic intermediates;[1] among these, 2-carbonyl-1-indanols **3** present potential applications in the synthesis of pharmaceutical and bioactive materials.[2] However, very little has been reported about their preparation. This type of compound has been synthesized by the reaction of orthomanganated acetophenone with activated alkenes[3] or by enone-selective reduction using organoiodotin hydride.[4] Nevertheless, with these methodologies, either preparation of starting materials is difficult[3] or yields of desired products are low.[4] In this communication we report an efficient approach for the synthesis of 2-carbonyl-1-indanols **3** using orthohalogenated aryl aldehydes **1** and Morita–Baylis–Hillman adducts **2** via a one-pot, palladium-catalyzed tandem Heck–aldol reaction (Scheme 1). To the best of our knowledge,

Received April 10, 2006
Address correspondence to Long-He Xu, Shenyang Research Institute of Chemical Industry (SYRICI), No. 8 Shenliao Dong Road, Shenyang 110021, China. E-mail: xlhzawt@mail.sy.ln.cn



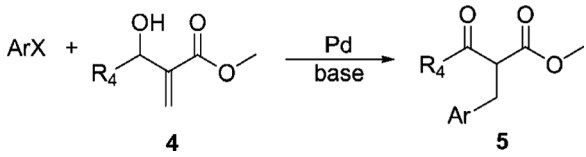
Scheme 1.

it is the first report for the preparation of 2-carbonyl-l-indanols using this process.

In recent years, many reports[5] have focused on the arylation of Morita–Baylis–Hillman adducts **4** via a palladium-catalyzed Heck reaction (Scheme 2), which provides a convenient method to synthesize β-keto esters **5**. Additionally, intramolecular aldol-type reactions have been investigated extensively because of their significance in the construction of carbo-cyclic systems.[6] Furthermore, Gerald Dyker and Grundt reported[7] that 2-carbonyl-substituted indene compounds could be prepared via a palladium-catalyzed process. This previous work led us to develop the new methodology for the synthesis of 2-carbonyl-l-indanols.

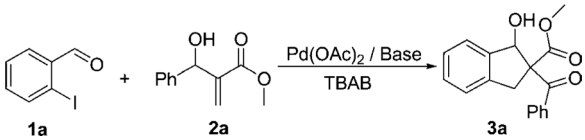
In the first attempt, the starting materials 2-iodobenzaldehyde **1a** (0.5 mmol) and methyl 2-(hydroxy(phenyl)methyl)acrylate **2a**[8] (0.6 mmol) were mixed with NaOAc (1.25 mmol), LiCl (1.0 mmol), and tetra-butyl-ammonium bromide (TBAB) (1.0 mmol) in the presence of $Pd(OAc)_2$ (5 mol %) in dimethyl formamide (DMF) (5 mL). The solution was kept at 80°C under nitrogen for 2 h and 1-indanol **3a** was produced as a mixture of diastereoisomers in 38% yield (Table 1, entry 1).

Other factors were examined to optimize the reaction conditions. When $NaHCO_3$ was used instead of NaOAc as base, 1-indanol **3a** was obtained in 64% yield (Table 1, entry 2). However, using tetrahydrofuran (THF) as solvent decreased the yield of product to 52% (Table 1, entry 3). Prolonging the reaction time also decreased the yield of 1-indanol greatly (Table 1, entry 4). It was noted that a favorable result could not be obtained, and an undetermined compound was produced at higher



Scheme 2.

Table 1. Synthesis of 2-carbonyl-l-indanol under different conditions[a]



Entry	Base	Solvent	Time(h)	Temp. (°C)	Yield (%)[b]
1	NaOAc	DMF	2	80	38[c]
2	$NaHCO_3$	DMF	2	80	64
3	$NaHCO_3$	THF	2	80	52
4	$NaHCO_3$	DMF	8	80	21
5	$NaHCO_3$	DMF	2	100	0
6	$NaHCO_3$	DMF	4	60	trace
7	Et_3N	DMF	3	80	trace[d]

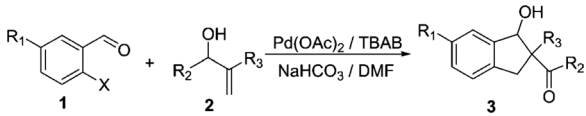
[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), TBAB (1.0 mmol), base (1.25 mmol) except for Et_3N (4.0 mmol), $Pd(OAc)_2$ (5 mol %), and DMF (5 mL).
[b]Isolated yields of diastereoisomer mixtures.
[c]1.0 mmol LiCl was added.
[d]10 mol % PPh_3 was added.

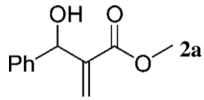
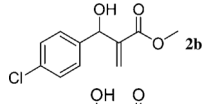
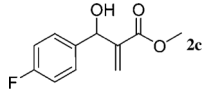
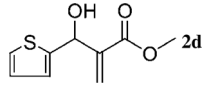
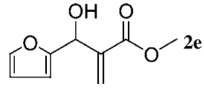
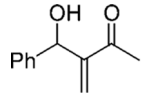
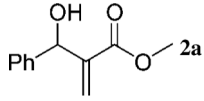
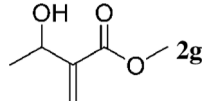
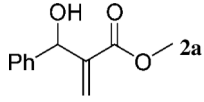
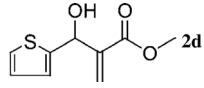
temperature (Table 1, entry 5). Nevertheless, when reducing the temperature to 60°C, only traces of the desired product were obtained (Table 1, entry 6). Using Et_3N in the presence of PPh_3 was inefficient for this process (Table 1, entry 7). Accordingly, the conditions of entry 2 in Table 1 were chosen as optimal for the synthesis of 2-carbonyl-1-indanols.

Under the optimal conditions, a variety of orthohalogenated aryl aldehydes **1** and Morita–Baylis–Hillman adducts **2**[8] were tested, and 1-indanols **3** were produced as a mixture of diastereoisomers in a ratio of approximately 2 : 1 in moderate to good yields. The results are summarized in Table 2.

Initially, 2-iodobenzaldehyde **1a** was reacted with Morita–Baylis–Hillman adducts **2a**, **2b**, and **2c** to give the corresponding 1-indanols **3a**, **3b**, and **3c** in 64, 61, and 51% yields respectively (Table 2, entries 1–3). It is interesting that the reaction of heterocyclic substituted adducts **2d** and **2e** with **1a** gave higher yields than those of the aromatic substituted adducts **2a**, **2b**, and **2c**. 1-Indanols **3d** and **3e** were obtained in 70 and 78% yields respectively (Table 2, entries 4 and 5). When 3-(hydroxy(phenyl)methyl)-but-3-en-2-one **2f** was tested, dicarbonyl-substituted 1-indanol **3f** was efficiently prepared in a short time in 74% yield (Table 2, entry 6). On the other hand, the reaction of 2-bromobenzaldehyde **1b** with adduct **2a** gave 1-indanol **3a** in lower yield (Table 2, entry 7

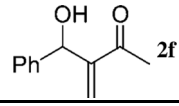
Table 2. Synthesis of 2-carbonyl-l-indanols[a]



Entry	Arylhalide **1**	Morita–Baylis–Hillman adducts **2**	Time (h)	Product **3**	dr[b]	Yield (%)[c]
1	**1a**	 **2a**	2	**3a**	66 : 34	64
2	**1a**	 **2b**	2	**3b**	66 : 34	61
3	**1a**	 **2c**	2	**3c**	68 : 32	51[d]
4	**1a**	 **2d**	2	**3d**	68 : 32	70
5	**1a**	 **2e**	2	**3e**	66 : 34	78
6	**1a**	 **2f**	1	**3f**	69 : 31	74
7	**1b**	 **2a**	2	**3a**	66 : 34	53
8	**1b**	 **2g**	5	**3g**	61 : 39	41
9	**1c**	 **2a**	1.5	**3h**	70 : 30	53
10	**1c**	 **2d**	2.5	**3i**	64 : 36	67

(*Continued*)

Table 2. Continued

Entry	Arylhalide **1**	Morita–Baylis–Hillman adducts **2**	Time (h)	Product **3**	dr[b]	Yield (%)[c]
11	**1c**	 **2f**	1.5	**3j**	71 : 29	62

[a]Reaction conditions: arylhalides **1** (1.0 mmol), Morita-Baylis-Hillman adducts **2** (1.2 mmol), TBAB (2.0 mmol), $NaHCO_3$ (2.5 mmol), and $Pd(OAc)_2$ (5 mol %), DMF (10 mL) at 80°C.

[b]Ratio of the diastereoisomers was determined by ^1H NMR.

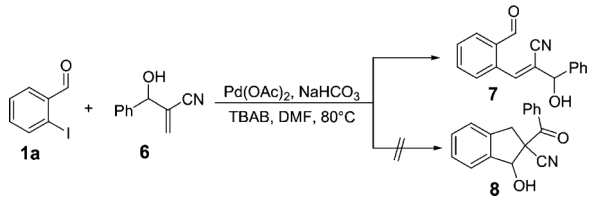
[c]Isolated yields of diastereoisomer mixtures.

[d]Lower isolated yield due to hard purification of the product from the mixture of starting material **2c** and indanol **3c**.

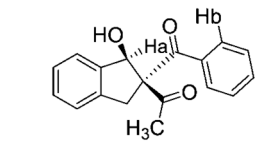
compared with entry 1). At the same time, the reaction of 2-bromobenzaldehyde **lb** with alkyl substituted adduct **2g** gave a lower yield than that of the aromatic substituted adduct **2a** (Table 2, entry 8 compared with entry 7). 2-Bromo-5-fluoro-benzaldehyde **lc** also smoothly reacted with the representative Morita–Baylis–Hillman adducts **2a**, **2d**, and **2f** to produce the corresponding 1-indanols **3h**, **3i**, and **3j** in moderate yields (Table 2, entries 9–11). It is important to note that the structure of Morita–Baylis–Hillman adducts had little effect on the ratio of diastereoisomers.

Next, 2-(hydroxy(phenyl)methyl)acrylonitrile **6** was also tested to broaden the scope of this process. Surprisingly, under identical conditions 1-indanol **8** could not be obtained when Morita–Baylis–Hillman adduct **6** was used (Scheme 3). Only the Heck cross-coupling product **7** was produced in 49% yield.

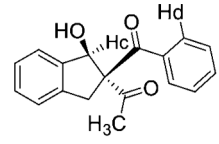
The relative configuration of diastereoisomers was determined by ^1H-^1H nuclear overhause effect spectroscopy (NOESY). In Fig. 1, nuclear overhause effect (NOE) was observed between Ha ($\delta = 5.60$) and Hb ($\delta = 7.90$) in the minor diastereoisomer. On the other hand, Ha ($\delta = 5.60$) and acetyl protons ($\delta = 2.22$) had little NOE in them. However, NOE



Scheme 3.



The minor diastereoisomer of **3f**



The major diastereoisomer of **3f**

Figure 1. The relative configuration of diastereoisomer **3f**.

was observed obviously between He ($\delta = 6.10$) and acetyl protons ($\delta = 2.18$) in the major diastereoisomer. As expected, He ($\delta = 6.10$) and Hd ($\delta = 7.88$) had no NOE in this diastereoisomer. Accordingly, it was concluded that the minor diastereoisomer had a *trans* configuration and the major had a *cis*configuration. Other diastereoisomers **3** also were examined similarly to determine their relative configuration.

A possible mechanism for this one-pot, palladium-catalyzed reaction can be explained as follows. First, β-keto esters or 1,3-diketones are formed by arylation of Morita–Baylis–Hillman adducts **2** with elimination of palladium hydride toward the hydroxy side and tautomerization to the keto forms.[5b,9] Then an intramolecular aldol-type condensation occurs and produces 1-indanols **3**.

In conclusion, we have developed an efficient and convenient process to synthesize 2-carbonyl-1-indanols *via* a one-pot, palladium-catalyzed reaction. The application of this new methodology for the synthesis of bioactive products is currently under way in our laboratories. Furthermore, the investigation of the stereochemistry for this process is also in progress now.

EXPERIMENTAL

The spectra of ^{1}H NMR and ^{13}C NMR were recorded on a Varian Mercury V $\times$ 300 NMR spectrophotometer with TMS as the internal standard. A Perkin Elmer 983 was used to determine the IR spectra. The mass spectra were obtained on an Apex II-FTMS. Silica gel (100–140 mesh) was used for column chromatography. DMF, THF, and Et_3N were distilled and dried over 4-Å sieves.

General Procedure

2-Iodobenzaldehyde **1a** (232 mg, 1.0 mmol), Morita–Baylis–Hillman adduct **2a** (230 mg, 1.2 mmol), TBAB (644 mg, 2.0 mmol), $NaHCO_3$ (210 mg, 2.5 mmol), and $Pd(OAc)_2$ (12 mg, 5 mol %) were added to a sealed flask. After the flask was evacuated and purged with nitrogen,

10 mL of DMF was added into the flask via syringe. Then the flask was placed into an 80°C oil bath, and stirring was continued for 2 h. The reaction mixture was extracted with EtOAc. The combined organic layers were dried over anhydrous Mg_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (hexane/EtOAc = 5/1) to afford the product (2-benzoyl-l-hydroxy-indan)-2-yl-carboxylic acid methyl ester **3a** as a viscous liquid; yield: 64%. The product was a mixture of diastereoisomers. The following data is based on the major diastereoisomer: IR (film): v = 3480, 2950, 1730, 1680, 1255, 1075, 1030, 755, 690 cm^{-1}. ^1H NMR ($CDC1_3$, 300 MHz): $\delta = 3.39$ (1H, d, $j = 17.1$ Hz, CH*H*), 3.70 (3H, s, OCH_3), 4.12 (1H, d, $J = 17.1$ Hz, CH*H*), 6.05 (1H, s, C*H*OH), 7.20 (1H, m, ArH), 7.29 (2H, dd, $J = 6.0$ Hz, Hz, 3.0 Hz, ArH), 7.44–7.49 (3H, m, ArH), 7.58 (1H, m, ArH); 7.91(2H, m, ArH). ^{13}C NMR ($CDC1_3$, 75 MHz): $\delta = 38.92$ (CH_3), 52.70 (CH_2), 69.22 [*C*COPh($COOCH_3$)], 79.44 (CHOH), 124.45, 124.76, 127.53, 128.62, 129.09, 133.12, 134.77, 138.58, 139.98, 141.50, 142.20, 171.55 ($COOCH_3$), 194.58 (COPh). MS: m/z 278 ($M^+ - H_2O$), 174, 146, 143, 115.

Other Data

3b: Viscous liquid. IR (film): $\nu = 3480, 2955, 1710, 1670, 1260, 1080, 755\ cm^{-1}$. ^1H NMR ($CDC1_3$, 300 MHz):$\delta = 3.36$ (1H, d, $J = 16.8$ Hz, C*H*H), 3.66 (3H, s, OCH_3), 4.08 (1H, d, $J = 16.8$ Hz, C*H*H), 5.99 (1H, s, C*H*OH), 7.23–7.26 (3H, m, ArH), 7.42–7.45 (3H, m, ArH), 7.84–7.87 (2H, m, ArH).

3c: Viscous liquid. IR (film): $\nu = 3470$, 2950, 1720, 1680, 1600, 1510, 1430, 1240, 1040 cm^{-1}. ^1H NMR ($CDC1_3$, 300 MHz): $\delta = 3.36$ (1H, d, y = 17. 1 Hz, CH*H*), 3.66 (3H, s, OCH_3), 4.09 (1H, d, $J = 17.1$ Hz, CH*H*), 5.99 (1H, s, C*H*OH), 7.10–7.15 (3H, m, ArH), 7.42–7.45 (2H, m, ArH), 7.56–7.62 (1H, m, ArH), 7.92–7.97 (2H, m, ArH).

3d: Viscous liquid. IR (film): $\nu = 3480$, 2950, 1730, 1660, 1405, 1260, 1070, 1020, 760, 730 cm^{-1}. ^1H NMR ($CDC1_3$, 300 MHz): $\delta = 3.49$ (1H, d, $J = 16.8$ Hz, CH*H*), 3.68 (3H, s, OCH_3), 4.06 (1H, d, $J = 16.8$, C*H*H), 5.95 (1H, s, C*H*OH), 7.12–7..14 (1H, m, ArH), 7.16–7.28 (3H, m, ArH), 7.42–7.44 (1H, m, ArH), 7.63–7.66 (1H, m, ArH), 7.71–7.75 (1H, m, ArH). ^{13} C NMR (CDCI3, 75 MHz): $\delta = 38.98$ (*C*H_3), 52.78 (*C*H_2), 69.63 [*C*COPh (*C*$OOCH_3$)], 78.94 (*C*HOH), 124.28, 124.68, 129.05, 132.19, 134.13, 138.92, 141.38, 142.14, 171.29 (*C*$OOCH_3$), 187.76 (*C*OPh). MS: m/z 284 ($M^+ - H_2O$), 226, 115, 111, 83.

3e: Viscous liquid. IR (film): $\nu = 3460$, 2950, 1730, 1670, 1460, 1280, 1020, 755 cm^{-1}. ^{1} H NMR ($CDC1_3$, 300 MHz): $\delta = 3.28$ (1H, d, $J = 17.1$,

CH*H*), 3.65 (3H, s, OCH_3), 4.04 (1H, d, $J = 17.1$, CH*H*), 5.96 (1H, s, C*H*OH), 6.52–6.54 (1H, m, ArH), 7.15–7.25 (4H, m, ArH), 7.40–7.43 (1H, m, ArH), 7.57–7.58 (1H, m, ArH). ^{13}C NMR ($CDC1_3$, 75 MHz): $\delta = 38.14$ (CH_3), 52.58 (CH_2), 67.35 [*C*COAr(COOCH_3)], 78.11 (*C*HOH), 112.36, 118.39, 124.33, 124.63, 127.35, 128.91, 138.87, 141.44, 146.51, 151.08, 170.59 (*C*OOCH_3), 183.87 (*C*OAr). MS: m/z 268 ($M^+ - H_2O$), 210, 115, 95.

3f: Viscous liquid. IR (film): $\nu = 3460$, 2920, 1710, 1670, 1595, 1445, 1355, 1240, 750, 700 cm^{-1}. ^{1} H NMR ($CDC1_3$, 300 MHz): $\delta = 2.18$ (3H, s, COCH_3), 3.30 (1H, d, $J = 17.1$ Hz, CH*H*), 4.18 (1H, d, $J = 17.1$ Hz, C*H*H), 6.10 (1H, s, C*H*OH), 7.16–7.19 (1H, m, ArH), 7.23–7.25 (2H, m, ArH), 7.42–7.48 (3H, m, ArH), 7.55–7.62 (1H, m, ArH), 7.86–7.91 (2H, m, ArH). ^{13}C NMR (CDCI3, 75 MHz): $\delta = 29.17$ (CH_3), 37.21 (CH_2), 76.48 [*C*COPh(COCH_3)], 79.43 (*C*HOH), 123.92, 124.73, 127.66, 128.77, 128.95, 129.23, 133.46, 134.92, 135.50, 137.94, 139.35, 141.77, 196.77 (*C*OCH_3), 204.92 (*C*OPh). MS: m/z 262 ($M^+ - H_2O$), 158, 143, 115, 43.

3g: Viscous liquid. IR (film): $\nu = 3460$, 2955, 1730, 1710, 1360, 1250, 920, 755 cm^{-1}. ^{1}H NMR ($CDC1_3$, 300 MHz): $\delta = 2.18$ (3H, s, COCH_3), 3.28 (1H, d, $J = 17.1$ Hz, CH*H*), 3.68 (1H, d, $J = 17.1$ Hz, C*H*H), 3.75 (3H, s, OCH_3), 5.73 (1H, s, C*H*OH), 1.22–125 (3H, m, ArH), 7.28–7.38 (2H, m, ArH).

3h: Viscous liquid. IR (film): $\nu = 3450$, 2955, 1730, 1680, 1600, 1580, 1490, 1240, 1025, 700 cm^{-1}. ^{1}H NMR ($CDC1_3$, 300 MHz): $\delta = 3.31$ (1H, d, $J = 16.5$ Hz, CH*H*), 3.66 (3H, s, OCH_3), 4.03 (1H, d, $J = 16.5$ Hz, C*H*H), 6.01 (1H, s, C*H*OH), 7.11–7.14 (2H, m, ArH), 7.34–7.37 (1H, m, ArH), 7.47–7.49 (2H, m, ArH), 7.58–7.60 (1H, m, ArH), 7.88–7.91 (2H, m, ArH).

3i: Viscous liquid. IR (film): $\nu = 3460$, 2955, 1730, 1660, 1485, 1405, 1260, 1025, 730 cm^{-1}. ^{1} H NMR ($CDC1_3$, 300 MHz): $\delta = 3.43$ (1H, d, $J = 16.8$ Hz, CH*H*), 3.67 (3H, s, OCH_3), 3.98 (1H, d, $J = 16.8$ Hz, C*H*H), 5.92 (1H, s, C*H*OH), 6.93–6.98 (1H, m, ArH), 7.09–7.15 (3H, m, ArH), 7.66–7.72 (2H, m, ArH).

3j: Viscous liquid. IR (film): $\nu = 3440$, 2920, 1710, 1670, 1485, 1440, 1360, 1240 cm^{-1}. ^{1}H NMR ($CDC1_3$, 300 MHz): $\delta = 2.17$ (3H, s, COCH_3), 3.25 (1H, d, $J = 16.8$ Hz, C*H*H), 4.07 (1H, d, $J = 16.8$ Hz, C*H*H), 6.05 (1H, s, C*H*OH), 6.90–6.99 (1H, m, ArH), 7.07–7.14 (2H, m, ArH), 7.43–7.50 (2H, m, ArH), 7.56–7.62 (1H, m, ArH), 7.84–7.89

(2H, m, ArH). ^{13}C NMR ($CDC1_3$, 75 MHz): $\delta = 29.21$ (CH_3), 36.65 (CH_2), 76.62 [*C*COPh($COCH_3$)], 79.12 (*C*HOH), 111.13, 111.78, 115.84, 116.64, 125.92, 128.89, 129.24, 133.04, 133.64, 134.51, 134.86, 143.75, 196.78 (*C*OPh), 204.81 ($COCH_3$). MS: m/z 280 ($M^+ - H_2O$), 238, 133, 115, 95, 77. All these data are based on the major diastereoisomer.

7: Viscous liquid. IR (film): $\nu = 3430$, 2920, 1840, 2220,1690, 1565, 1450, 1290, 1190, 1045, 760, 725, 700 cm^{-1}. ^1H NMR ($CDC1_3$, 300 MHz): $\delta = 2.82$ (1H, bs, CUO*H*), 5.54 (1H, s, C*H*OH), 7.37–7.45 (3H, m, ArH), 7.52–7.55 (2H, m, ArH), 7.61–7.66 (2H, m, ArH), 7.79 (1H, dd, $J = 6.6$Hz, 0.9 Hz, ArH), 7.87 (1H, dd, $J = 6.6$ Hz, 2.1 Hz, ArH), 8.13 (1H, s, ArC*H* = C), 10.09 (1H, s, ArC*H*O).

ACKNOWLEDGMENT

The authors thank Shenyang BMD Chemical Co., Ltd., for financial support of this investigation.

REFERENCES

1. (a) Hisaindee, S.; Clive, D. L. J. A synthesis of puraquinonic acid. *Tetrahedron Lett.* **2001**, *42*, 2253–2256.; (b) Barboni, L.; Lambertucci, C; Appendino, G.; Velde, D. G. V.; Himes, R. H.; Bombardelli, E.; Wang, M.; Snyder, J. P. Synthesis and NMR-driven conformational analysis of Taxol analogues confor-mationally constrained on the C13 side chain. *J. Med. Chem.* **2001**, *44*, 1576–1587.; (c) Clive, D. L. J.; Yu, M.; Sannigrihi, M. Synthesis of optically pure (+)-puraquinonic acid and assignment of absolute configuration to natural (−)-puraquinonic acid: Use of radical cyclization for asymmetric generation of a quaternary center, *J. Org. Chem.* **2004**, *69*, 4116–4125.
2. Emelen, K. V.; Wit, T. D.; Hoornaert, G. J.; Compernolle, F. Diastereoselective intramolecular Ritter reaction: Generation of a cis-fused hexahydro-4a*H*-indeno[l,2-b]pyridine ring system with 4a,9b-diangular substituents. *Org. Lett.* **2000**, *2*, 3083–3086.
3. Grigsby, W. J.; Main, M.; Nicholson, B. K. Nickel-promoted coupling of ortho-manganated aryl ketones with alkenes as a route to indanols. *J. Organomet. Chem.* **1997**, *540*, 185–187.
4. Suwa, T.; Nishino, K.; Miyatake, M.; Shibata, I.; Baba, A. Synthesis of carbocycles by enone-selective reduction using organoiodotin hydride. *Tetrahedron Lett.* **2000**, *41*, 3403–3406.
5. (a) Basavaiah, D.; Muthukumaran, K. Arylation of the Baylis-Hillman adducts. *Tetrahedron.* **1998**, *54*, 4943–4948.; (b) Sundar, N.; Bhat, S. V. Facile synthesis of 1,3-diaryl-propanones through Heck reaction. *Synth. Commun.* **1998**, *28*, 2311–2316.

6. (a) Alcaide, B.; Polanco, C; Saez, E.; Sierra, M. A. The intramolecular aldol con-densation route to fused bi- and tricyclic β-Lactams. *J. Org. Chem.* **1996**, *61*, 3967125–7132; (b) Wood, A. J.; Holt, D. J.; Dominguez, M.-C; Jenkins, P. R. The stereoselective preparation of an enantiomerically pure cyclopentane using intra-molecular aldol cyclopentaannulation of a glucose derivative, *j. Org. Chem. 63*, 8522–8529; (c) Chapdelaine, D.; Belzile, J.; Deslongchamps, P. A con-vergent synthesis of the cardenolide skeleton: Intra-molecular aldol condensation via reduction of α-bromoketones. *J. Org. Chem.* **2002**, *67*, 5669–5672.
7. Dyker, G.; Grundt, P. Annulated ring-systems by domino–Heck–aldol–conden-sation and domino–Heck–Michael–addition processes. *Tetrahedron Lett.* **1996**, *37*, 619–622.
8. Morita–Baylis–Hillman adducts were prepared according to the literature; (a) Yu, C; Liu, B.; Hu, L. Efficient Baylis–Hillman reaction using stoichiometric base catalyst and an aqueous medium. *J. Org. Chem.* **2001**, *66*, 5413–5418.; (b) Cai, J.; Zhou, Z.; Zhao, G.; Tang, C. Dramatic rate acceleration of the Baylis-Hillman reaction in homogeneous medium in the presence of water. *Org. Lett.* **2002**, *4*, 4723–4725.
9. (a) Melpolder, J. B.; Heck, R. F. A palladium-catalyzed arylation of allylic alcohol with aryl halides. *J. Org. Chem.* **1976**, *42*, 265–272.; (b) Larock, R. C; Leung, W.-Y.; Stolz-Dumm, S. Synthesis of aryl-substituted aldehydes and ketones via palladium-catalyzed coupling of aryl halides and non-allylic unsatu-rated alcohols. *Tetrahedron Lett.* **1989**, *30*, 6629–6632.; (c) Jeffery, T. Palladium-catalysed arylation of allylic alcohols: Highly selective synthesis of β-aromatic carbonyl compounds or β-aromatic a,β-unsaturated alcohols. *Tetrahedron Lett.* **1991**, *32*, 2121–2124.; (d) Larock, R. C; Yum, E. K.; Yang, H. Palladium-catalyzed intermolecular arylation of functionally-substituted cycloalkenes by aryl iodides. *Tetrahedron.* **1994**, *50*, 305–321.