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One-pot synthesis of indene derivatives by CF_3SO_3H-promoted reactions of benzylic alcohols and 1,3-dicarbonyl compounds

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ABSTRACT

An efficient and convenient one-pot synthesis of indene derivatives was achieved in moderate to high yields by the CF_3SO_3H promoted coupling/cyclization reaction of benzylic alcohols and 1,3-dicarbonyls for the first time. For the reactions of methoxy- or methyl- substituted diarylmethanols with 1,3-dicarbonyls, 2 equiv of CF_3SO_3H was needed to reach the best results; but for the reactions of methoxy-substituted arylethanols with 1,3-dicarbonyls, 0.6 equiv of CF_3SO_3H at lower temperatures was capable of promoting the reaction finished.

Indene frameworks are frequently observed in many molecules with important biological activities such as natural products[1–8] and pharmaceuticals,[9–15] and are also extensively used as ligands in metallocenes in the catalysis of olefin polymerization.[16–18] In addition, indene derivatives are also of important applications in functional materials.[19–21] As a result, various methods to construct indene ring systems have been reported, such as iron-catalyzed annulation of *N*-benzylic sulfonamides with disubstituted alkynes,[22] palladium-catalyzed carboannulation 2-(2-(1-alkynyl)phenyl)malonate with arylhalides,[23] $BF_3{\cdot}Et_2O$-mediated cycloaddition of methylenecyclopropanes with aldehydes,[24] copper-catalyzed [3+2] cycloaddition of α-aryldiazoesters with terminal alkynes,[25] $Cu(OTf)_2$-catalyzed rearrangement of vinylcyclopropenes,[26] $FeCl_3$-catalyzed Friedel–Crafts reaction of arylated allylic alcohols,[27] gold (I)-catalyzed intramolecular carboalkoxylation,[28] ruthenium-mediated ring-closing metathesis,[29] iodonium-promoted 5-*endo*-dig carbocyclization of 2-(2-ethynylphenyl)malonates,[30] and photochemical cyclization of tetrafluoropyridinyl (TFP)-substituted enediynes.[31] Moreover, PPA (polyphosphoric acid)-mediated cyclocondensation reaction of 4-arylbutan-2-ones is also a traditional but efficient method for the synthesis of indene derivatives.[32,33] Although so many methods have been established to construct the indene structure, the synthesis of indene derivatives by Brφnsted acid catalyzed cyclocondensation of the coupling products from benzylic alcohols and 1,3-dicarbonyls is rare. It is well known that the Lewis and Brφnsted acid catalyzed coupling of benzylic alcohols with 1,3-dicarbonyls is a simple and efficient method for the synthesis of 2-benzyl-1,3-dicarbonyls,[34–36] and the cyclocondensation of methyl 3-benzylacetoacetates for the synthesis of methyl indene-2-carboxylates was also reported recently.[37] As continuation of the construction of cyclic compounds by cyclocondensation,[38] we report in this paper a one-pot synthesis of 2-acylindenes by the combination of the coupling of benzylic alcohols and 1,3-dicarbonyls and cyclocondensation (Scheme 1). To the best of our knowledge, the present work provides the first example of Brφnsted acid-catalyzed one-pot synthesis of indene derivatives from benzylic alcohols and 1,3-dicarbonyls.

Initial attempts at the coupling/cyclization reaction were made with benzylic alcohols **1a** and ethyl acetoacetate **2a** as substrates because the efficient coupling or intramolecular cyclization reactions in the previous studies[32,33,37] were limited to arylmethanols in which aromatic rings bear an electron-donating group, such as an alkyl or an alkyloxy group.

Of the catalysts and solvents screened (Table 1), only trifluoromethanesulfonic acid (TfOH) gave the desired cyclization product **3a** as the main product, and the best result (65% yield) was obtained from the combination of 2.0 equiv of TfOH and dichloromethane (entry 5), while reactions under other conditions gave lower yields of **3a** or no **3a** (entries 1–4 and 6–10). Apparently, these conditions were different from conditions reported by Ohwada for the cyclization of ethyl 3-arylmethylacetoacetate in which the large quantity of TfOH (10–50 equiv) was needed.[37] Comparatively, treating substrate **1a** and **2a** with $TiCl_4$ in dichloromethane leads to only the coupling product **5a** (entry 1), and **3a** was not detected even after a prolonged reaction time or elevating the reaction temperature. Similarly, treating substrate **1a** and **2a** with PPA also gave only

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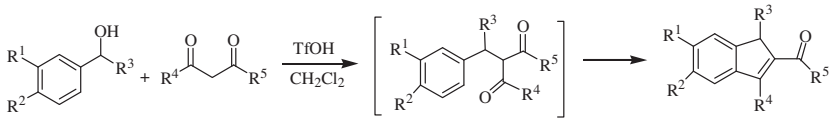
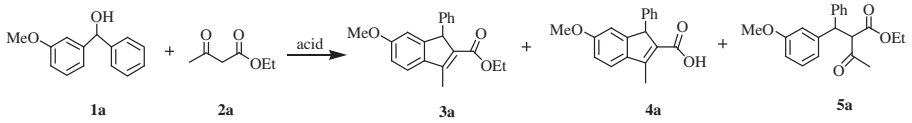


Scheme 1. Synthesis of 2-acylindene derivatives by the one-pot reaction of benzylic alcohols and 1,3-dicarbonyls.

Table 1
Screening catalysts and optimization of reaction conditions

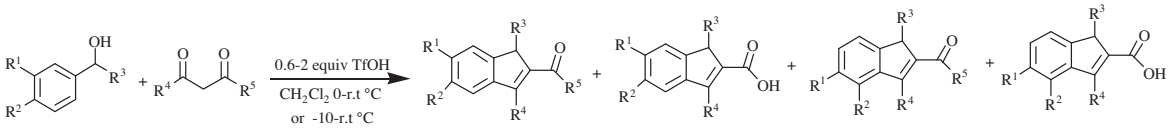


1a **2a** **3a** **4a** **5a**

Entry	Solvent	Acid	*t* (h)	*T* (°C)	Product	Yield (%)
1	CH_2Cl_2[a]	2 Equiv $TiCl_4$	12	0–rt	**5a**	32
2	CH_2Cl_2[a]	2 Equiv $SnCl_4$	12	0–rt	**3a** + **5a**	40 + 10
3	CH_2Cl_2[a]	0.5 Equiv TfOH	12	0–rt	**5a**	55
4	CH_2Cl_2[a]	1.0 Equiv TfOH	12	0–rt	**3a** + **5a**	50 + 20
5	CH_2Cl_2[a]	2.0 Equiv TfOH	2	0–rt	**3a**	65
6	CH_2Cl_2[a]	10 Equiv TfOH	2	0–rt	**3a** + **4a**	13 + 20
7	CH_3CN[a]	2.0 Equiv TfOH	12	0–rt	**5a**	40
8	DCE[a]	2.0 Equiv TfOH	12	0–rt	Complex	—
9	None[b]	5 Equiv PPA	24	rt	**5a**	84
10	None[c]	5 Equiv PPA	12	60	**5a**	85

[a] The reaction was carried out with **1a** (1.0 mmol), **2a** (1.2 mmol), and 0.5–10 equiv of catalyst which was slowly added in solvent (20 mL) at 0 °C, and the reactions mixture was allowed to reach to room temperature.
[b] The reaction was carried out with **1a** (1.0 mmol), **2a** (1.2 mmol), and 5 equiv of PPA (polyphosphoric acid) with no solvent at room temperature.
[c] The reaction was carried out with **1a** (1.0 mmol), **2a** (1.2 mmol), and 5 equiv of PPA with no solvent at room temperature and the reactions mixture was allowed to reach to 60 °C.

Table 2
One-pot coupling/cyclization reaction of benzylic alcohols and 1,3-dicarbonyls promoted by trifluoromethanesulfonic acid[a]



1a-j **2a-d** **3a-u** **4d, 4h-i, 4k, 4q, 4t** **3'q-u** **4'q,t**

Entry		Substrate						Time (h)	Product		Yield (%)
		R^1	R^2	R^3		R^4	R^5		**3**:**4**		
1	**1a**	OMe	H	Ph	**2a**	Me	OEt	2	**3a**		65
2	**1a**	OMe	H	Ph	**2b**	Me	Me	12	**3b**		70
3	**1a**	OMe	H	Ph	**2c**	Me	Ph	12	**3c**		55
4	**1a**	OMe	H	Ph	**2d**	Ph	OEt	12	**3d** + **4d**	4:1	53
5	**1b**	OMe	OMe	Ph	**2a**	Me	OEt	1	**3e**		84
6	**1b**	OMe	OMe	Ph	**2b**	Me	Me	1	**3f**		90
7	**1b**	OMe	OMe	Ph	**2c**	Me	Ph	8	**3g**		50
8	**1b**	OMe	OMe	Ph	**2d**	Ph	OEt	12	**3h** + **4h**	7:1	55
9	**1c**	Cl	H	Ph	**2a**	Me	OEt	24	**3i** + **4i**	1:1	38
10	**1c**	Cl	H	Ph	**2b**	Me	Me	24	**3j**		40
11	**1d**	H	H	Ph	**2a**	Me	OEt	24	**3k** + **4k**	4:1	60
12	**1e**	OMe	H	Me	**2a**	Me	OEt	12	**3l**		40[b]
13	**1f**	OMe	OMe	Me	**2a**	Me	OEt	2	**3m**		60[b]
14	**1f**	OMe	OMe	Me	**2b**	Me	Me	12	**3n**		80[b]
15	**1f**	OMe	OMe	Me	**2c**	Me	Ph	12	**3o**		84[b]
16	**1f**	OMe	OMe	Me	**2d**	Ph	OEt	12	**3p**		60[b]
17	**1g**	Me	H	Ph	**2a**	Me	OEt	12	**3q** + **4q** **3q′** + **4q'**	**3q**:**3q′** = 2:1 **4q**:**4q′** = 2:1	51
18	**1g**	Me	H	Ph	**2b**	Me	Me	12	**3r** + **3r′**	**3r**:**3r′** = 2:1	72
19	**1g**	Me	H	Ph	**2c**	Me	Ph	12	**3s** + **3s′**	**3s**:**3s′** = 2:1	64
20	**1h**	Me	Me	Ph	**2a**	Me	OEt	24	**3t** + **4t** **3t′**	**3t**:**3t′** = 2:1	72
21	**1h**	Me	Me	Ph	**2b**	Me	Me	24	**3u** + **3u′**	**3u**:**3u′** = 2:1	87
22	**1i**	H	OMe	Ph	**2a**	Me	OEt	24	**5i**	—	[c]
23	**1j**	H	Me	Ph	**2b**	Me	Me	24	**5j**	—	[c]

[a] The reaction was carried out with **1** (1.0 mmol), **2** (1.2 mmol), and 2 equiv of TfOH which was slowly added in CH_2Cl_2 (20 mL) at 0 °C, and the reactions mixture was allowed to reach to room temperature.
[b] The reaction was carried out with **1** (1.0 mmol), **2** (1.2 mmol), and 0.6 equiv of TfOH which was slowly added in CH_2Cl_2 (20 mL) at −10 °C, then the reactions mixture was allowed to reach to room temperature.
[c] Yield of the coupling product **5** and no cyclization products **3** and **4** were formed.

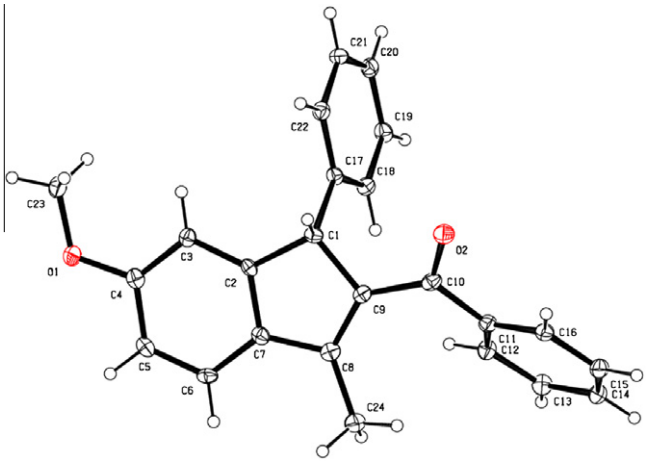


Figure 1. X-ray crystal structure of product **3c**.

the coupling product **5a** (entries 9 and 10), even at an elevated temperature. Thus, using 2.0 equiv of TfOH as the promoter in dichloromethane at 0 °C was selected as the optimized condition for the synthesis of **3a**.

Under the optimized condition described above, the reactions of a group of benzylic alcohols **1a–h** and 1,3-diarbonyls **2a–d** were examined.[39] In most cases, the substrates underwent the one-pot reaction smoothly to afford the corresponding products **3** in moderate to good yields (Table 2, entries 1–11). Moreover, the better results could be obtained for the reactions of 1-arylethanol **1e–f** with **2a–d** under the catalysis of only 0.6 equiv of trifluoromethanesulfonic acid (TfOH) at −10 °C in CH_2Cl_2 (Table 2, entries 12–16).

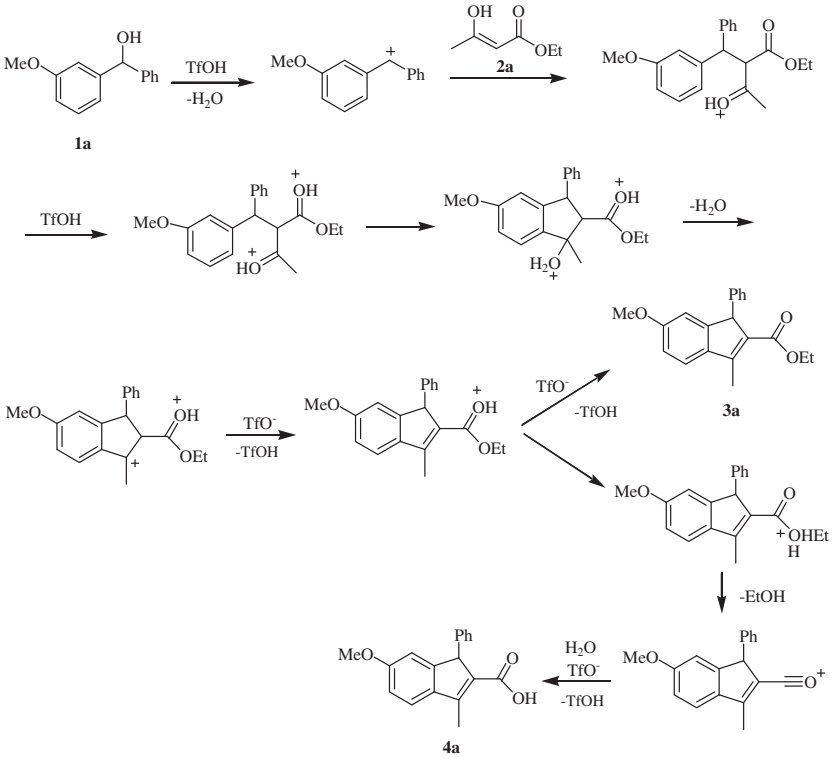
Among these results, the reaction of substrate **1b** with **2b** gave the best result (Table 2, entry 6). Obviously, the electron-donating group ($R^1 = R^2 = OMe$) favored both the coupling reaction and the cyclization reaction. In contrast, the substrate bearing the electron-attracting substituent on the aromatic ring ($R^1 = Cl$) gave a poor result (Table 2, entries 9 and 10). Comparatively, the reaction of ethyl acetoacetate (**2a**) generally gave the cyclization products **3** in lower yields than the reaction of acetoacetone (**2b**); and the reaction of diarylmethanols (**1a–d**) generally gave the cyclization products **3** in higher yields than the reaction of arylethanols (**1e–1f**). Unexpectedly, for the *para*-methyl-, *para*-methoxy-substituted diarylmethanol, the cyclization reactions were totally blocked (Table 2, entries 22 and 23), and only the coupling reactions could proceed normally. All these observations are in accordance with the previously reported results for the cyclization of 2-benzyl-1,3-dicarbonyls.[32,33,37]

In addition, it was also observed from Table 2 that the TfOH-promoted coupling/cyclization reaction of ethyl 2-acylacetate (**2a** and **2d**) affords the products as a mixture of ester (**3d**, **3h**, **3i**, **3k**) and carboxylic acid (**4d**, **4h**, **4i**, **4k**) (entries 4, 8, 9, and 11). While the less reaction time (entries 1 and 5) or the smaller quantity of TfOH could stop the formation of acid (entries 12, 13, and 16).

Reactions of the unsymmetric methyl-substituted substrate **1g–h** with **2a–c** also afforded the products as mixtures (Table 2). The products were not only derived from the hydrolysis of ester, but also from a different regioselectivity which was different from that in the reactions of methoxy-substituted substrates **1a–f** with **2a–d**. All products were fully identified by ^1H NMR, ^{13}C NMR, IR, and HRMS and the structure of **3c** was further confirmed by X-ray crystallography (Fig. 1).[39]

A plausible mechanism was proposed for the formation of indene derivatives from the TfOH-promoted coupling/cyclization reactions of benzylic alcohols and 1,3-dicarbonyl compounds according to the results and Ohwada's study[38] (Scheme 2).

In summary, we have developed a mild and efficient method for the one-pot synthesis of indene derivates in moderate to high yields by trifluoromethanesulfonic acid (TfOH)-promoted



Scheme 2. A plausible reaction mechanism for the formation of 2-acylindenes in the presence of trifluoromethanesulfonic acid.

coupling/cyclization reaction of benzylic alcohols and 1,3-dicarbonyls. For the reactions of methoxy- or methyl-substituted diarylmethanols with 1,3-dicarbonyls, 2 equiv of TfOH was needed to give better results; but for the reactions of methoxy-substituted arylethanols with 1,3-dicarbonyls, 0.6 equiv of TfOH at lower temperatures was capable of promoting the reaction finished.

Acknowledgment

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.01.088.

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39. Synthesis of **3a**: A 50 mL round-bottom flask was charged with **1a** (1 mmol), **2a** (1.2 mmol), anhydrous CH_2Cl_2 (20 mL) and a stirring bar. After the solution was cooled to 0 °C and stirred for 10 min, CF_3SO_3H (2 mmol) was added portion wise, and the reactions mixture was allowed to reach rt. The mixture was stirred for 2 h at room temperature till **1a** disappeared completely, 2 mL water poured into the flask, and the mixture extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried with anhydrous Na_2SO_4, and concentrated in vacuo. The residue was isolated by flash column chromatography on silica gel to give the products **3a** (65%).
Compound **3a**: Yellow grease; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, J = 8.4 Hz, 1H), 7.24–7.16 (m, 3H), 7.06–7.04 (m, 2H), 6.87 (dd, J = 2.4, 8.4 Hz, 1H), 6.72 (d, J = 2.4 Hz, 1H), 4.76 (d, J = 2.0 Hz, 1H), 4.13 (dt, J = 3.6, 7.2 Hz, 1H), 4.02 (dt, J = 3.6, 7.2 Hz, 1H),3.74 (s, 3H), 2.58 (d, J = 2.0 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.3, 160.7, 151.9, 151.2, 139.9, 136.9, 132.7, 128.3, 127.9, 126.5, 121.9, 113.1, 109.9, 59.5, 55.7, 55.4, 14.1, 12.5 ppm. IR (KBr): 3023, 2925, 2854, 1671, 1427, 908, 737 cm^{-1}. ESI-HRMS: m/z Calcd for $C_{20}H_{20}O_3$+H$^+$: 309.1485. Found 309.1487.
Compound **3c**: Yellow grease; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.41–7.35 (m, 3H), 7.24–7.11 (m, 2H), 7.09–7.05 (m, 2H), 6.93 (dd, J = 2.4, 8.4 Hz, 1H), 6.78 (d, J = 1.6 Hz, 1H), 5.14 (d, J = 1.6 Hz, 1H), 3.76 (s, 3H),3.10 (d, J = 2.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.4, 160.6, 151.0, 147.2, 142.8, 140.3, 138.9, 137.4, 131.9, 128.7, 128.5, 128.2, 128.0, 126.7, 122.0, 113.6, 109.8, 56.8, 55.5, 13.6 ppm. IR (KBr): 3061, 3003, 2916, 1654, 1223, 910, 133 cm^{-1}. ESI-HRMS: m/z Calcd for $C_{24}H_{20}O_2$+H$^+$: 341.1536. Found 341.1539.
Crystal data for compound **3c** (recrystallized from ethanol): $C_{24}H_{20}O_2$, M_r = 380.25, trigonal, a = 28.7569(13) Å, b = 28.7569(13) Å, c = 11.5446(10) Å, β = 90.00°, V = 8267.8(9) Å^3, clear light yellow plate, Dc = 1.375 g cm^{-3}, T = 296 (2) K, space group P2(1)/c, Z = 4, μ(MoKa) = 0.71073 mm^{-1}, $2\theta_{max}$ = 52.64, 4107 reflection collected, 2382 unique (R_{init} = 0.0838) which was used in all calculations. Final wR(F^2) = 0.1381 (all data). CCDC file No. 899272.