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Brönsted acid ionic liquid-catalyzed direct benzylation, allylation and propargylation of 1,3-dicarbonyl compounds with alcohols as well as one-pot synthesis of 4*H*-chromenes

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ABSTRACT

Recyclable ionic Brönsted acid was prepared in nearly quantitative yield by reacting 1-butylimidazole with an equimolar amount of 1,3-propanesultone, followed by treatment with an equimolar amount of trifluoromethanesulfonic acid. The ionic Brönsted acid-catalyzed direct benzylation, allylation and propargylation of 1,3-dicarbonyl compounds with various alcohols in ionic liquid [*N*-ethyl-*N*-methyl imidazolium trifluoromethanesulfonate (EMIOTf)], at 100 °C for 3 h proceeded smoothly to give the corresponding products in good to excellent yields without the use of any hazardous or volatile solvents and without any by-product such as salts. Furthermore, tandem benzylation–cyclization–dehydration of 1,3-dicarbonyl compounds to give functionalized 4*H*-chromenes was also achieved in this catalytic reaction.

1. Introduction

The alkylation of 1,3-dicarbonyl compounds usually requires not only the transformation of 1,3-dicarbonyl compounds into more reactive species, such as enolates by reacting the 1,3-dicarbonyl compounds with base, but also the use of alkyl halides, since the hydroxyl group is not a good leaving group and 1,3-dicarbonyl compounds do not have high nucleophilicity. However, these requirements are limitations, as is the production of a salt as a by-product.

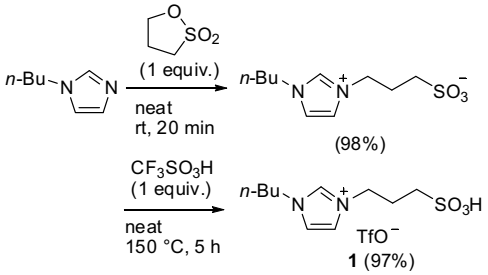
From the standpoint of atom-economical and environmentally friendly chemistry, the catalytic direct carbon–carbon bond formation of 1,3-dicarbonyl compounds using alcohols in place of alkyl halides is one of the most ideal and salt-free reactions in organic synthesis, since steps are not needed for the generation of reactive enolate or for preconversion to the alkyl halides, and only water is generated as a by-product. Although some excellent catalysts, such as indium trichloride,[1] proton-exchanged montmorillonite,[2] trifluoromethanesulfonic acid,[3] *p*-toluenesulfonic acid,[3,4] polymer-supported *p*-toluenesulfonic acid,[4] metal triflate,[5] iron(III) chloride[6] and hetropolyacid[7] have recently been examined for catalytic direct carbon–carbon bond formation in active methylene compounds using alcohols as alkylating reagents, most of the reported reactions require hazardous or volatile solvents, such as nitromethane, dichloromethane, acetonitrile and toluene, and the recovery and reuse of the catalysts far are still limited.[2,4,5b] Therefore, the development of a much more convenient, reusable, environmentally friendly system for the catalytic alkylation of 1,3-dicarbonyl compounds without the use of any hazardous or volatile solvents is needed.

In this report, for the first time, we present our recyclable Brönsted acid-catalyzed direct benzylation, allylation and propargylation of 1,3-dicarbonyl compounds with various alcohols as well as the tandem benzylation–cyclization–dehydration of 1,3-dicarbonyl compounds to give functionalized 4*H*-chromene in an ionic liquid system.

2. Results and discussion

2.1. Preparation of Brönsted acid ionic liquid catalyst 1

Recyclable Brönsted acid ionic liquid catalyst **1**, which was used for esterification, was prepared by modification of the method reported by Forbes et al.[8] as shown in Scheme 1. 1-Butylimidazole



Scheme 1. Preparation of Brönsted acid ionic liquid catalyst **1**.

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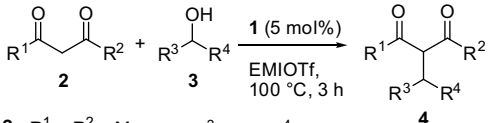
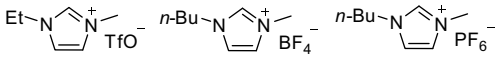
was allowed to react with an equimolar amount of 1,3-propanesultone at room temperature to produce zwitterionic imidazolium salt in quantitative yield. Treatment of this zwitterionic imidazolium salt with an equimolar amount of trifluoromethanesulfonic acid at 150 °C gave the Brönsted acid ionic liquid catalyst **1** in quantitative yield.

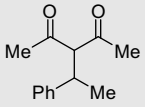
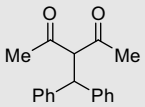
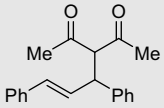
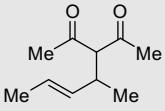
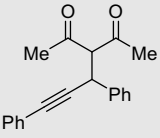
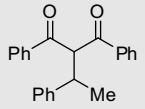
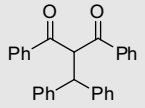
Table 1
Brönsted acid ionic liquid **1**-catalyzed direct benzylation, allylation and propargylation of 1,3-diketones **2a**,**b** with various alcohols **3**



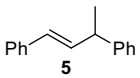
2a $R^1 = R^2 = Me$
2b $R^1 = R^2 = Ph$

3a $R^3 = Ph$, $R^4 = Me$
3b $R^3 = R^4 = Ph$
3c $R^3 = (E)$-PhCH=CH, $R^4 = Ph$
3d $R^3 = (E)$-MeCH=CH, $R^4 = Me$
3e $R^3 = PhC{\equiv}C$, $R^4 = Ph$



Entry	2	3	Product 4		Yield[a] (%)
1	**2a**	**3a**	**4aa**		77 (7)
2[b]	**2a**	**3a**	**4aa**		tr (tr)
3[c]	**2a**	**3a**	**4aa**		94 (tr)
4[d]	**2a**	**3a**	**4aa**		61 (20)
5[e]	**2a**	**3a**	**4aa**		39 (22)
6[f]	**2a**	**3a**	**4aa**		74 (8)
7	**2a**	**3b**	**4ab**		94
8	**2a**	**3c**	**4ac**		90
9	**2a**	**3d**	**4ad**		47
10	**2a**	**3e**	**4ae**		88
11	**2b**	**3a**	**4ba**		81
12	**2b**	**3b**	**4bb**		98

[a] Yields of isolated products. Values in parentheses show the yields of styrene dimer **5**.
[b] $BMIBF_4$ was used in place of EMIOTf. 1,1′-Oxybis (ethane-1,1-diyl) dibenzene was obtained in 33% yield.
[c] $BMIPF_6$ was used in place of EMIOTf.
[d] IL catalyst **1** was not added.
[e] An eqimolar amount of **2a** was used.
[f] Trifluoromethanesulfonic acid was used in place of IL catalyst **1**. 4-Phenylpentan-2-one was also obtained in 20% yield.


5

2.2. Brönsted acid ionic liquid 1-catalyzed direct benzylation, allylation and propargylation of 1,3-dicarbonyl compounds 2 with alcohols 3

The reaction of 2,4-pentanedione (**2a**) with 1-phenylethanol (**3a**) was conducted in the presence of 5 mol % of the prepared Brönsted acid ionic liquid catalyst **1** in a commercially available ionic liquid, *N*-ethyl-*N*-methyl imidazolium trifluoromethanesulfonate (EMIOTf), at 100 °C for 3 h. After the mixture was allowed to cool to room temperature, repeated extraction with a mixed solvent of diethyl ether and hexane (v/v=1:1) from EMIOTf, evaporation under vacuum, and chromatography with silica gel gave 3-(1-phenylethyl)pentane-2,4-dione (**4aa**) in 77% yield, together with a small amount (7%) of (*E*)-but-1-ene-1,3-diyldibenzene (**5**) (styrene dimmer) (Table 1, entry 1).

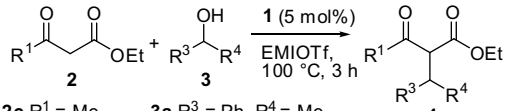
Other ionic liquids carrying other counter anions, such as *N*-butyl-*N*-methylimidazolium tetrafluoroborate ($BMIBF_4$) and *N*-butyl-*N*-methylimidazolium hexafluorophosphite ($BMIPF_6$), were used (entries 2 and 3). As a result, in the case of $BMIBF_4$, only trace amount of the product **4aa** was formed, and 1,1′-oxybis-(ethane-1,1-diyl)dibenzene (bis(1-phenylethyl) ether) was obtained as a main product (33% yield, dr=50: 50) (entry 2). The reaction in $BMIPF_6$ proceeded smoothly to give **4aa** in 94% yield (entry 3). Surprisingly, when the ionic liquid catalyst **1** was not added, the reaction of diketone **2a** with alcohol **3a** also proceeded to give the corresponding product **4aa** in lower yield (61%), together with styrene dimmer **5** (20% yield) (entry 4).[9] The use of an equimolar amount of diketone **2a** resulted in significant decrease of the yield (39%) of **4aa** (entry 5). Employing trifluoromethansulfonic acid in place of the Brönsted acid ionic liquid catalyst **1** gave the similar yield (74%) of **4aa**, together with styrene dimmer **5** (8%) as well as 4-phenylpentan-2-one (20%) (entry 6).

The results of the Brönsted acid ionic liquid **1**-catalyzed reaction of 1,3-diketones **2**, such as 2,4-pentanedione (**2a**) and 1,3-diphenylpropane-1,3-dione (**2b**), with various alcohols, such as 1-phenylethanol (**3a**), diphenylmethanol (**3b**), (*E*)-1,3-diphenylprop-2-en-1-ol (**3c**), (*E*)-pent-3-en-2-ol (**3d**), and 1,3-diphenylprop-2-yn-1-ol (**3e**) in EMIOTf, are summarized in Table 1. In the case of diphenylmethanol (**3b**), the reaction also proceeded smoothly to give 3-benzhydrylpentane-2,4-dione (**4ab**) in 94% yield (entry 7). Allylation and propargylation using (*E*)-1,3-diphenylprop-2-en-1-ol (**3c**), (*E*)-pent-3-en-2-ol (**3d**) and 1,3-diphenylprop-2-yn-1-ol (**3e**) also proceeded to give the corresponding allylated and propargylated diketones **4ac**, **4ad** and **4ae** in 47–90% yields (entries 8–10). 1,3-Diphenylpropane-1,3-dione (**2b**) participated well in the reaction with 1-phenylethanol (**3a**) and diphenylmethanol (**3b**) to produce the corresponding benzylated diketones **4ba** and **4bb** in 81–98% yields, without formation of the styrene dimer **5** (entries 11 and 12).

The results of the Brönsted acid ionic liquid-catalyzed reactions of ethyl 3-oxobutanoate (**2c**), ethyl 3-oxopentanoate (**2d**) and ethyl 3-oxo-3-phenylpropanoate (**2e**) with various alcohols are summarized in Table 2. The use of various alcohols **3a**–**c**,**e** gave the corresponding benzylated, allylated and propargylated products **4cb**, **4cc** and **4ce** in 76–91% yields (entries 2–4). However, the reaction of **2c** with 1-phenylethanol (**3a**) gave the corresponding ketoester **4ca** in 30% yield, together with a moderate amount (40%) of styrene dimer **5**, probably due to lower nucleophilicity of ketoester **2c** than those of diketones **2a**,**b**. Other ketoesters **2d**,**e** also participated well in the catalytic reaction with alcohol **3b** to give the corresponding products **4db** and **4eb** in 89–97% yields (entries 5 and 6). Diastereoselectivities of the products **4ca**, **4cc** and **4ce** are quite low.

To confirm the reaction mechanism for the formation of styrene dimer **5**, the Brönsted acid ionic liquid-catalyzed reaction of 1-phenylethanol (**3a**) in EMIOTf in the absence of 1,3-dicarbonyl compound **2** was carried out, as shown in Scheme 2.

Table 2
Brönsted acid ionic liquid **1**-catalyzed direct benzylation, allylation and propargylation of ester **2** with various alcohols **3**

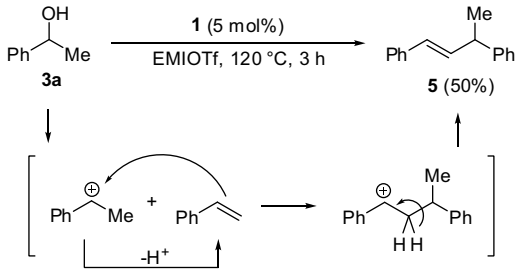


2c R^1 = Me
2d R^1 = Et
2e R^1 = Ph

3a R^3 = Ph, R^4 = Me
3b R^3 = R^4 = Ph
3c R^3 = (*E*)-PhCH=CH, R^4 = Ph
3e R^3 = PhC≡C, R^4 = Ph

Entry	2	3	Product 4	Yield[a] (%) [dr][b]
1	**2c**	**3a**	**4ca**	30 (40) [50:50]
2	**2c**	**3b**	**4cb**	91
3	**2c**	**3c**	**4cc**	76 [51:49]
4	**2c**	**3e**	**4ce**	84 [52:48]
5	**2d**	**3b**	**4db**	89
6	**2e**	**3b**	**4eb**	97

[a] Yields of isolated products. Values in parentheses show the yields of styrene dimer **5**.
[b] Determined by GC.

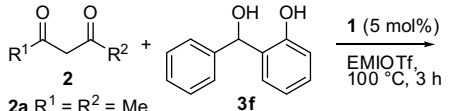


Scheme 2. Proposed reaction mechanism for the formation of **5**.

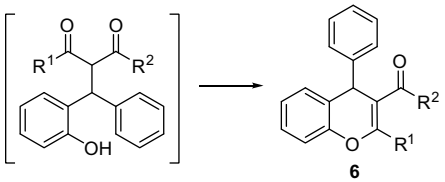
As a result, styrene dimer **5** was formed as a sole product in 50% yield. This result can be explained by the following mechanism: (1) protonation of the hydroxyl group of alcohol **3a** and successive dehydration produces the benzyl cation, and subsequent deprotonation gives styrene. (2) The obtained styrene attacks the other benzyl cation, and deprotonation at the β-carbon gives styrene dimer **5**.

After having successfully developed an efficient benzylation of 1,3-diketones **2a**,**b** and ketoesters **2c**,**d**,**e**, we then sought to apply this methodology to the synthesis of highly functionalized 4*H*-chromene[10] via catalytic tandem benzylation, cyclization and dehydration of the 2-(hydroxy(phenyl)methyl)phenol (**3f**), prepared from salicylaldehyde and phenyllithium, as described in Table 3.

Table 3
Brönsted acid ionic liquid **1**-catalyzed tandem direct benzylation, cyclization and dehydration of **2** with the alcohol **3f**



2a R^1 = R^2 = Me
2b R^1 = R^2 = Ph
2c R^1 = Me, R^2 = OEt
2d R^1 = Et, R^2 = OEt
2e R^1 = Ph, R^2 = OEt



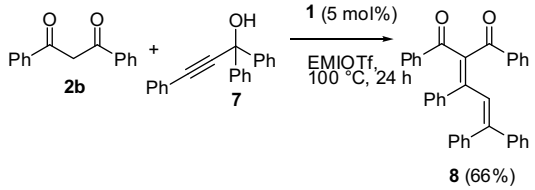
6

Entry	2	Product 6	Yield[a] of 6 (%)
1	**2a**	**6af**	77
2	**2b**	**6bf**	98
3	**2c**	**6cf**	84
4	**2d**	**6df**	80
5	**2e**	**6ef**	83

[a] Yields of isolated products.

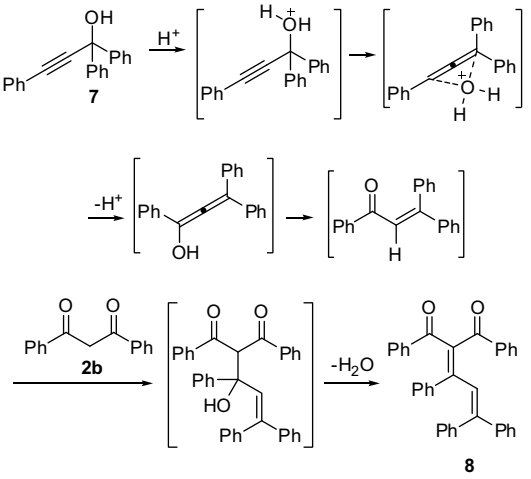
This catalytic tandem reaction of **3f** with diketones **2a**,**b** and ketoesters **2c**,**d**,**e** proceeded smoothly to produce the corresponding 4*H*-chromenes, such as 1-(2-methyl-4-phenyl-4*H*-chromen-3-yl)-ethanone (**6af**), (2,4-diphenyl-4*H*-chromen-3-yl)(phenyl)methanone (**6bf**), ethyl 2-methyl-4-phenyl-4*H*-chromene-3-carboxylate (**6cf**), ethyl 2-ethyl-4-phenyl-4*H*-chromene-3-carboxylate (**6df**) and ethyl 2,4-diphenyl-4*H*-chromene-3-carboxylate (**6ef**), in good to excellent yields (77–98%), respectively.

Furthermore, the Brönsted acid ionic liquid-catalyzed reactions of 1,3-diphenylpropane-1,3-dione (**2b**) with an equimolar amount of a highly activated tertiary alkynol, 1,1,3-triphenylprop-2-yn-1-ol (**7**), also proceeded smoothly to give not a propargylated product, but rather a dienyl product, 1,3-diphenyl-2-(1,3,3-triphenylallylidene)propane-1,3-dione (**8**), in 66% yield, as shown in Scheme 3.



Scheme 3. Brönsted acid ionic liquid **1**-catalyzed reaction of 1,3-diphenylpropane-1,3-dione (**2b**) with tertiary alkynol **7**.

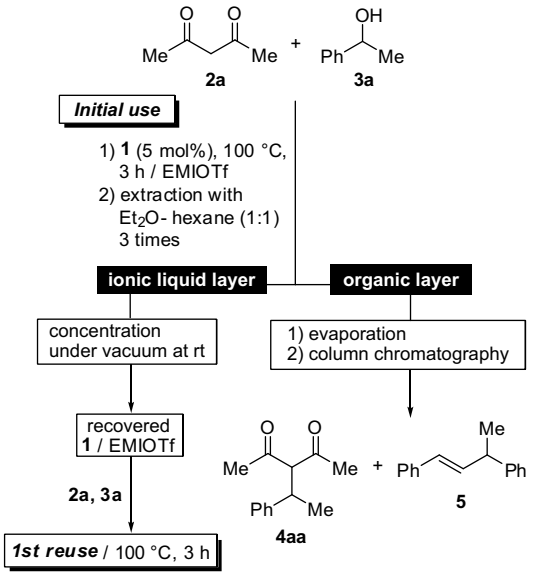
According to the previous report by Sanz et al.,[3b] this product could be produced by the tandem Meyer–Schuster rearrangement of tertiary alkynol **7**, aldol condensation with diketone **2b** and dehydration, as shown in Scheme 4.



Scheme 4. Proposed reaction mechanism for the formation of **8**.

2.3. Reuse of the Brönsted acid ionic liquid catalyst 1

Finally, reuse of the Brönsted acid ionic liquid catalyst **1** was carried out, as shown in Scheme 5.



	Product (%)[a]
initial use	**4aa** (77), **5** (7)
first reuse	**4aa** (77), **5** (7)
second reuse	**4aa** (75), **5** (5)

[a] Yields of isolated products

Scheme 5. Reuse of the Brönsted acid ionic liquid catalyst **1**.

After the initial use of the catalyst **1** in EMIOTf, the product **4aa** and styrene dimer **5** were extracted from EMIOTf three times with a mixed solvent of diethyl ether and hexane (1:1). Concentration of the mixed organic layer and purification by column chromatography gave the product **4aa** with a trace amount of **5**. Reuse of the catalyst in the second and third cycles gave the product **4aa** in almost the same yield along with a trace amount of **5**.

3. Conclusion

In conclusion, we have developed a new recyclable Brönsted acid-catalyzed direct benzylation, allylation and propargylation of 1,3-dicarbonyl compounds with various alcohols in an ionic liquid, *N*-ethyl-*N*-methyl imidazolium trifluoromethanesulfonate (EMIOTf), without the use of any hazardous or volatile solvents and without any by-product such as salts. Furthermore, this method could also be applied to the tandem benzylation–cyclization–dehydration of 1,3-dicarbonyl compounds to give functionalized 4*H*-chromenes in good to excellent yields.

4. Experimental

4.1. General

^{1}H (400 MHz) or ^{13}C (100 MHz) NMR spectra were measured with a JEOL α-400 FT-NMR spectrometer in deuteriochloroform ($CDCl_3$) solution with tetramethylsilane (Me_4Si) as an internal standard. Melting points were obtained on a Yanagimoto MP-S2 micro melting point apparatus and are uncorrected. IR spectra were measured on a SHIMADZU FT-IR 8100A spectrometer. HRMS were measured on a JEOL JMS-700 mass spectrometer. LRMS were measured on a JEOL JMS-K9 mass spectrometer. The pure products were isolated by column chromatography using silica gel (Wakogel C-200, 100–200 mesh, Wako Pure Chemical Ind., Ltd.). *N*-Ethyl-*N*-methyl imidazolium trifluoromethanesulfonate (EMIOTf) was a gift from the Central Glass Co., Ltd. All chemicals were of reagent grade and, if necessary, purified in the usual manner prior to use.

4.2. Preparation of 1-butyl-3-(3-sulfopropyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate (1)

To propanesultone (3.908 g, 31.97 mmol) in a two-necked flask under argon was slowly added 1-butylimidazole (4.005 g, 32.25 mmol), and the mixture was stirred for 30 min at room temperature. Repeated washing of the obtained solid with toluene (20 ml×5) and Et_2O (20 ml×5), and evaporation under vacuum at room temperature gave 3-(1-butyl-1*H*-imidazol-3-ium-3-yl)propane-1-sulfonate in 98% yield (7.797 g).

4.2.1. 3-(1-Butyl-1H-imidazol-3-ium-3-yl)propane-1-sulfonate

Yield 98%; Mp 176.7–177.1 °C; IR (KBr) 1566 (C=C), 1179 (SO), 1038 (SO) cm^{-1}; ^{1}H NMR (D_2O, 400 MHz) δ 0.99 (t, J=7.37 Hz, 3H, $CH_3CH_2CH_2CH_2$), 1.38 (sext, J=7.37 Hz, 2H, $CH_3CH_2CH_2CH_2$), 1.88 (quint, J=7.37 Hz, 2H, $CH_3CH_2CH_2CH_2$), 2.32 (quint, J=7.37 Hz, 2H, $-CH_2CH_2SO_3^-$), 2.80 (t, J=7.37 Hz, 2H, $-CH_2SO_3^-$), 4.23 (t, J=7.37 Hz, 2H, $-CH_2N=$), 4.43 (t, J=7.37 Hz, 2H, $-CH_2N^+\equiv$), 7.68 (d, J=15.46 Hz, 1H, imidazolium-H), 7.68 (d, J=15.46 Hz, 1H, imidazolium-H), 9.02 (s, 1H, imidazolium-H); ^{13}C NMR (D_2O, 100 MHz) δ 24.2 (s), 30.4 (s), 36.7 (s), 42.8 (s), 58.8 (s), 59.3 (s), 61.0 (s), 133.9 (s), 134.2 (s), 147.0 (s); HRMS found m/z 247.1112, calcd for $C_{10}H_{19}N_2O_3S$: M+H, 247.1118.

A mixture of 3-(1-butyl-1*H*-imidazol-3-ium-3-yl)propane-1-sulfonate (2.473 g, 10.0 mmol) and trifluoromethanesulfonic acid (1.628 g, 10.85 mmol) was heated to 150 °C and stirred at the same temperature for 5 h. After being allowed to cool to room temperature, the obtained ionic liquid was washed repeatedly with toluene (20 ml×5) and Et_2O (20 ml×5) to remove non-ionic residues, and dried under vacuum at room temperature to give 1-butyl-3-(3-sulfopropyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1**) (3.924 g, 99%).

*4.2.2. 1-Butyl-3-(3-sulfopropyl)-1H-imidazol-3-ium trifluoromethanesulfonate (**1**)*

Yield 99%; IR (neat) 3415 (SO_3H), 1566 (C=C), 1227 (SO), 1170 (SO), 1030 (SO) cm^{-1}; ^{1}H NMR (D_2O, 400 MHz) δ 0.92 (t, 3H, J=7.34 Hz,

$CH_3CH_2CH_2CH_2$), 1.33 (sext, 2H, J=7.34 Hz, $CH_3CH_2CH_2CH_2$), 1.87 (quint, J=7.34 Hz, $CH_3CH_2CH_2CH_2$), 2.34 (quint, J=7.34 Hz, 2H, $-CH_2CH_2SO_3^-$), 2.93 (t, 2H, J=7.34 Hz, $-CH_2SO_3^-$), 4.22 (t, 2H, J=7.34 Hz, $-CH_2N$=), 4.38 (t, 2H, J=7.34 Hz, $-CH_2N^+$≡), 7.54 (d, 1H, J=9.42 Hz, imidazolium-H), 7.54 (d, 1H, J=9.42 Hz, imidazolium-H), 8.82 (s, 1H, imidazolium-H); ^{13}C NMR (D_2O, 100 MHz) δ 23.2 (s), 29.4 (s), 35.8 (s), 41.8 (s), 57.9 (s), 58.4 (s), 60.1 (s), 50.2 (s), 130.3 (q, J=317.9 Hz), 133.0 (s), 133.3 (s), 146.0 (s); HRMS found m/z 247.1123, calcd for $C_{10}H_{19}N_2O_3S$: M−CF_3SO_3, 247.1116.

4.3. Typical procedure for the recyclable Brönsted acid 1-catalyzed direct carbon–carbon bond formation of 1,3-dicarbonyl compounds with alcohols

A mixture of 1-butyl-3-(3-sulfopropyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1**) (0.060 g, 0.151 mmol), 1-phenylethanol (**3a**) (0.370 g, 3.029 mmol) and pentane-2,4-dione (**2a**) (1.503 g, 15.01 mmol) in 1-ethyl-3-methyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (1 ml) under argon was stirred at 100 °C for 3 h. The mixture was then cooled to room temperature and extracted from the ionic liquid with a mixed solvent of Et_2O/hexane (1:1) (30 ml×3). After the solvent was removed under reduced pressure, the product was purified by column chromatography on silica gel with hexane/EtOAc (20:1) to give 3-(1-phenylethyl)pentane-2,4-dione (**4aa**) (0.478 g, 77%) and (*E*)-but-1-ene-1,3-diyldibenzene (**5**) (0.022 g, 7%).

4.3.1. 3-(1-Phenylethyl)pentane-2,4-dione (**4aa**)[3a]

Yield 77%; Mp 46.9–47.9 °C (lit. 43–45 °C); R_f 0.38 (hexane/EtOAc=5:1); IR ($CHCl_3$) 1697 (C=O), 1722 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (d, J=7.00 Hz, 3H, $CHCH_3$), 1.78 (s, 3H, $COCH_3$), 2.22 (s, 3H, $COCH_3$), 3.51–3.59 (m, 1H, $CHCH_3$), 3.99 (d, J=7.00 Hz, 1H, $CHCOCH_3$), 7.13–7.26 (m, 5H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6 (s), 30.4 (s), 30.5 (s), 41.1 (s), 77.4 (s), 127.7 (s), 128.0 (s), 130.0 (s), 143.8 (s), 204.1 (s), 204.2 (s); HRMS found m/z 204.1151, calcd for $C_{13}H_{16}O_2$: M, 204.1154.

4.3.2. (E)-But-1-ene-1,3-diyldibenzene (**5**)[3a]

Yield 7%; R_f 0.38 (hexane); IR (neat) 1600 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.38 (d, J=7.00 Hz, 3H, $CHCH_3$), 3.55 (quint, J=7.00 Hz, 1H, $CHCH_3$), 6.30–6.32 (m, 2H, 2×vinyl H), 7.08–7.28 (m, 10H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4 (s), 42.7 (s), 126.3 (s), 126.4 (s), 127.2 (s), 127.4 (s), 128.6 (s), 135.3 (s), 137.7 (s), 145.7 (s); HRMS found m/z 208.1259, calcd for $C_{16}H_{16}$: M, 208.1253.

4.3.3. 1,1′-Oxybis(ethane-1,1-diyl)dibenzene

Yield 33%; dr=50:50; R_f 0.60 (hexane/CH_2Cl_2=1:1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (d, 6H, J=6.52 Hz, 2×$CHCH_3$), 1.39 (d, 6H, J=6.52 Hz, 2×$CHCH_3$), 4.18 (q, 2H, J=6.52 Hz, 2×$CHCH_3$), 4.46 (q, 2H, J=6.52 Hz, 2×$CHCH_3$), 7.13–7.31 (m, 20H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.9 (s), 25.6 (s), 75.3 (s), 75.5 (s), 127.1 (s), 127.2 (s), 128.0 (s), 128.3 (s), 129.1 (s), 129.4 (s), 145.0 (s), 145.1 (s); MS (EI) m/z 226 (M, 7.5%).

4.3.4. 4-Phenylpentan-2-one[11]

Yield 20%; R_f 0.29 (hexane/CH_2Cl_2=1:1); IR (neat) 1716 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (d, 3H, J=7.00 Hz, CH_3CHPh), 2.09 (s, 3H, $COCH_3$), 2.68 (dd, 1H, J=7.00, 16.18 Hz, CH_2CO), 2.78 (dd, 1H, J=7.00, 16.18 Hz, CH_2CO), 2.78 (sext, J=7.00 Hz, 1H, CH_3CHPh), 7.20–7.35 (m, 5H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.9 (s), 30.5 (s), 35.3 (s), 51.9 (s), 126.2 (s), 126.6 (s), 128.4 (s), 146.1 (s), 207.8 (s); MS (EI) m/z 162 (M, 34.3%).

4.3.5. 3-benzhydrylpentane-2,4-dione (**4ab**)[3a]

Yield 94%; Mp 114.9–116.1 °C (lit. 112–114 °C); R_f 0.43 (hexane/CH_2Cl_2=1:3); IR ($CHCl_3$) 1697 (C=O), 1719 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.00 (s, 6H, 2×$COCH_3$), 4.81 (d, J=12.32 Hz, 1H, $CHPh$), 4.73 (d, J=12.32 Hz, 1H, $CHCOCH_3$), 7.15–7.20 (m, 2H, aryl H), 7.24–7.29 (m, 8H, arlyl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.5 (s), 52.1 (s), 75.4 (s), 127.9 (s), 128.6 (s), 129.8 (s), 142.1 (s), 203.8 (s); HRMS found m/z 266.1308, calcd for $C_{18}H_{18}O_2$: M, 266.1307.

4.3.6. (Z)-3-(1,3-Diphenylallyl)pentane-2,4-dione (**4ac**)[1]

Yield 90%; Mp 83.0–83.8 °C (lit. 85 °C); R_f 0.20 (hexane/Et_2O=5:1); IR ($CHCl_3$) 1682 (C=O), 1732 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.92 (s, 3H, $COCH_3$), 2.25 (s, 3H, $COCH_3$), 4.30–4.37 (m, 2H, $CHCOCH_3$ and CHPh), 6.16–6.22 (m, 1H, PhCH=C*H*), 6.43 (d, J=15.70 Hz, 1H, Ph*CH*=CH), 7.20–7.33 (m, 10H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.4 (s), 30.7 (s), 49.8 (s), 127.0 (s), 127.9 (s), 128.4 (s), 128.6 (s), 129.2 (s), 129.7 (s), 129.9 (s), 132.3 (s), 137.2 (s), 140.7 (s), 141.9 (s), 203.4 (s), 203.5 (s); HRMS found m/z 292.1475, calcd for $C_{20}H_{20}O_2$: M, 292.1464.

4.3.7. (E)-3-(Pent-3-en-2-yl)pentane-2,4-dione (**4ad**)

Yield 47%; R_f 0.18 (hexane/Et_2O=5:1); IR (neat) 1698 (C=O), 1722 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.96 (d, J=7.19 Hz, 3H, $CHCH_3$), 1.62 (d, J=7.19 Hz, 3H, CH_3CH:CH), 2.11 (s, 3H, $COCH_3$), 2.19 (s, 3H, $COCH_3$), 2.97 (sext, J=7.19 Hz, 1H, $CHCH_3$), 3.56 (d, J=7.19 Hz, 1H, $CHCOCH_3$), 5.19–5.25 (m, 1H, CH_3CH=C*H*), 5.46–5.55 (m, 1H, CH_3CH=CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.8 (s), 19.0 (s), 29.5 (s), 30.0 (s), 37.7 (s), 75.8 (s), 126.4 (s), 132.3 (s), 204.0 (s), 204.0 (s); HRMS found m/z 168.1158, calcd for $C_{10}H_{16}O_2$: M, 168.1151.

4.3.8. 3-(1,3-Diphenylprop-2-ynyl)pentane-2,4-dione (**4ae**)[3b]

Yield 88%; Mp 95.4–96.0 °C (lit. 90–92 °C); R_f 0.50 (hexane/CH_2Cl_2=1:3); IR ($CHCl_3$) 1701 (C=O), 1733 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.93 (s, 3H, $COCH_3$), 2.39 (s, 3H, $COCH_3$), 4.22 (d, J=10.87 Hz, 1H, $CHPh$), 4.67 (d, J=10.87 Hz, 1H, $CHCOCH_3$), 7.25–7.42 (m, 10H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.7 (s), 31.1 (s), 38.0 (s), 75.6 (s), 84.9 (s), 88.0 (s), 122.7 (s), 127.7 (s), 128.1 (s), 128.2 (s), 128.3 (s), 128.9 (s), 131.6 (s), 138.2 (s), 201.6 (s), 201.6 (s); HRMS found m/z 290.1310, calcd for $C_{20}H_{18}O_2$: M, 290.1307.

4.3.9. 1,3-Diphenyl-2-(1-phenylethyl)propane-1,3-dione (**4ba**)[3a]

Yield 81%; Mp 126.1–126.8 °C (lit. 126–127 °C); R_f 0.15 (hexane/EtOAc=20:1); IR (KBr) 1683 (C=O), 1733 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (d, J=7.00 Hz, 3H, $CHCH_3$), 4.03–4.11 (m, 1H, $CHPh$), 5.63 (d, J=7.00 Hz, 1H, $CHCOPh$), 7.04 (t, J=7.35 Hz, 1H, aryl H), 7.14 (t, J=7.35 Hz, 2H, aryl H), 7.22–7.26 (m, 4H, aryl H), 7.35–7.42 (m, 3H, aryl H), 7.52 (t, J=7.35 Hz, 1H, aryl H), 7.73 (d, J=7.35 Hz, 2H, aryl H), 8.02 (d, J=7.35 Hz, 2H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5 (s), 41.5 (s), 65.0 (s), 126.9 (s), 128.0 (s), 128.7 (s), 128.8 (s), 129.1 (s), 129.1 (s), 133.3 (s), 133.9 (s), 137.1 (s), 137.4 (s), 144.1 (s), 194.9 (s), 195.3 (s); HRMS found m/z 328.1467, calcd for $C_{23}H_{20}O_2$: M, 328.1464.

4.3.10. 2-Benzhydryl-1,3-diphenylpropane-1,3-dione (**4bb**)[12]

Yield 98%; Mp 221.6–222.3 °C (lit. 228.6–230.2 °C); R_f 0.28 (hexane/CH_2Cl_2=1:1); IR (KBr) 1661 (C=O), 1683 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.32 (d, J=11.71 Hz, 1H, $CHCOPh$), 6.35 (d, J=11.71 Hz, 1H, CHPh), 7.05 (t, J=7.46 Hz, 2H, aryl H), 7.15 (t, J=7.46 Hz, 4H, aryl H), 7.24 (s, 4H, aryl H), 7.33 (t, J=7.46 Hz, 4H, aryl H), 7.47 (t, J=7.46 Hz, 2H, aryl H), 7.83 (d, J=7.46 Hz, 4H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 52.4 (s), 62.3 (s), 126.6 (s), 128.3 (s), 128.5 (s), 128.6 (s), 128.6 (s), 133.2 (s), 136.9 (s), 141.7 (s), 194.1 (s); HRMS found m/z 390.1618, calcd for $C_{28}H_{22}O_2$: M, 390.1621.

4.3.11. Ethyl 2-acetyl-3-phenylbutanoate (**4ca**)[2b]

Yield 30%; R_f 0.63 (hexane/EtOAc=5:1); IR (neat) 1717 (C=O), 1747 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.85 (t, J=7.10 Hz, 3H, $COOCH_2CH_3$), 1.16 (d, J=8.88 Hz, 3H, $CHCH_3$), 1.21 (t, J=7.10 Hz, 3H, $COOCH_2CH_3$), 1.22 (d, J=8.88 Hz, 3H, $CHCH_3$), 1.85 (s, 3H,

$COCH_3$), 2.22 (s, 3H, $COCH_3$), 3.44–3.48 (m, 2H, PhCH), 3.67 (d, J=8.88 Hz, 1H, $CHCOCH_3$), 3.72 (d, J=8.88 Hz, 1H, $CHCOCH_3$), 3.80 (q, J=7.10 Hz, 2H, $COOCH_2CH_3$), 4.14 (q, J=7.10 Hz, 2H, $COOCH_2CH_3$), 7.11–7.21 (m, 10H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7 (s), 14.2 (s), 20.4 (s), 20.6 (s), 29.6 (s), 29.9 (s), 39.8 (s), 40.1 (s), 61.2 (s), 61.5 (s), 67.0 (s), 67.6 (s), 76.8 (s), 77.1 (s), 77.4 (s), 126.8 (s), 126.9 (s), 127.4 (s), 127.5 (s), 128.5 (s), 128.7 (s), 143.1 (s), 143.3 (s), 168.2 (s), 168.6 (s), 202.4 (s); HRMS found m/z 234.1263, calcd for $C_{14}H_{18}O_3$: M, 234.1256.

4.3.12. Ethyl 2-benzhydryl-3-oxobutanoate (**4cb**)[3a]

Yield 91%; Mp 87.8–89.0 °C (lit. 84–86 °C); R_f 0.38 (hexane/CH_2Cl_2=1:1); IR ($CHCl_3$) 1716 (C=O), 1738 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.00 (t, J=7.10 Hz, 3H, $COOCH_2CH_3$), 2.09 (s, 3H, $COCH_3$), 3.98 (q, J=7.10 Hz, 2H, $COOCH_2CH_3$), 4.52 (d, J=12.20 Hz, 1H, CHPh), 4.76 (d, J=12.20 Hz, 1H, $CHCOCH_3$), 7.14–7.18 (m, 2H, aryl H), 7.23–7.30 (m, 8H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.4 (s), 29.7 (s), 50.5 (s), 61.2 (s), 64.9 (s), 126.5 (s), 126.6 (s), 127.4 (s), 127.5 (s), 128.3 (s), 128.5 (s), 140.9 (s), 141.2 (s), 167.3 (s), 201.4 (s); HRMS found m/z 296.1419, calcd for $C_{19}H_{20}O_3$: M, 296.1413. Found: C, 76.91; H, 6.87. $C_{19}H_{20}O_3$ requires C, 77.00; H, 6.80.

4.3.13. (Z)-Ethyl 2-acetyl-3,5-diphenylpent-4-enoate (**4cc**)[7]

Yield 76%; R_f 0.20 (hexane/EtOAc=20:1); IR (neat) 1714 (C=O), 1741 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.93 (t, J=7.10 Hz, 3H, $COOCH_2CH_3$), 1.16 (t, J=7.10 Hz, 3H, $COOCH_2CH_3$), 1.99 (s, 3H, $COCH_3$), 2.26 (s, 3H, $COCH_3$), 3.89 (q, J=7.10 Hz, 2H, $COOCH_2CH_3$), 4.05 (d, J=10.99 Hz, 2H, $CHCOCH_3$), 4.08 (d, J=10.99 Hz, 2H, $CHCOCH_3$), 4.12 (q, J=7.10 Hz, 2H, $COOCH_2CH_3$), 4.26 (t, J=10.99 Hz, 2H, CHPh), 6.18–6.30 (m, 2H, PhCH=CH), 6.39 (d, J=10.99 Hz, 1H, PhCH=CH), 6.43 (d, J=10.99 Hz, 1H, PhCH=CH), 7.12–7.29 (m, 20H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.3 (s), 13.7 (s), 29.4 (s), 29.5 (s), 48.3 (s), 48.5 (s), 60.9 (s), 61.1 (s), 64.8 (s), 65.1 (s), 125.9 (s), 125.9 (s), 126.6 (s), 126.7 (s), 127.1 (s), 127.1 (s), 127.5 (s), 127.5 (s), 128.0 (s), 128.2 (s), 128.4 (s), 128.8 (s), 129.0 (s), 131.0 (s), 131.3 (s), 136.2 (s), 136.3 (s), 139.7 (s), 139.9 (s), 167.1 (s), 167.4 (s), 200.9 (s), 201.2 (s); HRMS found m/z 322.1574, calcd for $C_{21}H_{22}O_3$: M, 322.1570.

4.3.14. Ethyl 2-acetyl-3,5-diphenylpent-4-ynoate (**4ce**)[3b]

Yield 84%; R_f 0.50 (hexane/EtOAc=15:1); IR (neat) 1719 (C=O), 1746 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.00 (t, J=7.06 Hz, 3H, $COOCH_2CH_3$), 1.24 (t, J=7.06 Hz, 3H, $COOCH_2CH_3$), 1.97 (s, 3H, $COCH_3$), 2.39 (s, 3H, $COCH_3$), 3.95 (q, J=7.06 Hz, 2H, $COOCH_2CH_3$), 3.98 (d, J=10.69 Hz, 1H, $CHCOCH_3$), 4.04 (d, J=10.69 Hz, 1H, $CHCOCH_3$), 4.22 (q, J=7.06 Hz, 2H, $COOCH_2CH_3$), 4.60 (d, J=10.69 Hz, 1H, CHPh), 4.63 (d, J=10.69 Hz, 1H, CHPh), 7.20–7.42 (m, 20H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.8 (s), 14.1 (s), 29.8 (s), 30.6 (s), 37.8 (s), 37.8 (s), 61.6 (s), 61.8 (s), 66.5 (s), 66.8 (s), 84.1 (s), 84.7 (s), 88.2 (s), 88.5 (s), 122.8 (s), 123.1 (s), 127.6 (s), 127.7 (s), 128.1 (s), 128.2 (s), 128.2 (s), 128.2 (s), 128.3 (s), 128.6 (s), 128.7 (s), 131.6 (s), 138.2 (s), 138.3 (s), 166.8 (s), 167.1 (s), 200.3 (s), 200.7 (s); HRMS found m/z 320.1413, calcd for $C_{21}H_{20}O_3$: M, 320.1415.

4.3.15. Ethyl 2-benzhydryl-3-oxopentanoate (**4db**)

Yield 89%; Mp 87.8–88.1 °C; R_f 0.38 (hexane/CH_2Cl_2=1:1); IR (KBr) 1714 (C=O), 1747 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84 (t, J=7.25 Hz, 3H, $COCH_2CH_3$), 0.97 (t, J=7.25 Hz, 3H, $COOCH_2CH_3$), 2.18–2.28 (m, 1H, $COCH_2CH_3$), 2.46–2.56 (m, 1H, $COCH_2CH_3$), 3.90–4.01 (m, 2H, $COOCH_2CH_3$), 4.56 (d, J=12.20 Hz, 1H, CHPh), 4.82 (d, J=12.20 Hz, 1H, $CHCOCH_2CH_3$), 7.11–7.32 (m, 10H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.1 (s), 13.6 (s), 36.6 (s), 50.7 (s), 61.2 (s), 64.0 (s), 126.6 (s), 126.7 (s), 127.5 (s), 127.7 (s), 128.4 (s), 128.6 (s), 141.3 (s), 141.5 (s), 167.5 (s), 204.1 (s); MS (EI) m/z 292 (M−H_2O, 19.3%).

4.3.16. Ethyl 2-benzhydryl-3-oxo-3-phenylpropanoate (**4eb**)[11]

Yield 97%; Mp 137.0–137.5 °C (lit. 141.9–143.1 °C); R_f 0.54 (hexane/CH_2Cl_2=1:1); IR (KBr) 1682 (C=O), 1730 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.93 (t, J=7.12 Hz, 3H, $COOCH_2CH_3$), 3.85–3.99 (m, 2H, $COOCH_2CH_3$), 5.08 (d, J=11.83 Hz, 1H, CHCOPh), 5.41 (d, J=11.83 Hz, 1H, CHPh), 7.03–7.07 (m, 1H, arlyl H), 7.12–7.30 (m, 7H, arlyl H), 7.34–7.45 (m, 4H, arlyl H), 7.53–7.57 (m, 1H, arlyl H), 8.00–8.02 (m, 2H, arlyl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7 (s), 50.9 (s), 59.4 (s), 61.5 (s), 126.5 (s), 126.8 (s), 127.7 (s), 128.2 (s), 128.5 (s), 128.6 (s), 128.6 (s), 128.7 (s), 133.5 (s), 136.6 (s), 141.7 (s), 167.7 (s), 192.8 (s); MS (EI) m/z 340 (M−H_2O, 46.4%).

4.4. Typical procedure for the recyclable Brönsted acid 1-catalyzed tandem direct benzylation, cyclization and dehydration of the alcohol 3f

A mixture of 1-butyl-3-(3-sulfopropyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1**) (0.020 g, 0.050 mmol), 2-(hydroxy(phenyl)methyl)phenol (**3f**) (0.199 g, 0.994 mmol) and pentane-2,4-dione (**2a**) (0.503 g, 5.024 mmol) in 1-ethyl-3-methyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (1 ml) under argon was stirred at 100 °C for 3 h. The mixture was then cooled to room temperature and extracted from the ionic liquid with a mixed solvent of Et_2O/hexane (1:1) (30 ml×3). After the solvent was removed under reduced pressure, the product was purified by column chromatography on silica gel with hexane/CH_2Cl_2 (1:4) to give 1-(2-methyl-4-phenyl-4*H*-chromen-3-yl)ethanone (**6af**) (0.204 g, 77%).

4.4.1. 1-(2-Methyl-4-phenyl-4H-chromen-3-yl)ethanone (**6af**)

Yield 77%; R_f 0.58 (hexane/CH_2Cl_2=1:4); IR (neat) 1682 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.13 (s, 3H, $COCH_3$), 2.43 (s, 3H, CCH_3), 4.99 (s, 1H, CHPh), 6.92–6.99 (m, 2H, aryl H), 7.06–7.14 (m, 3H, aryl H), 7.19–7.30 (m, 4H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5 (s), 30.5 (s), 42.6 (s), 114.5 (s), 116.7 (s), 124.9 (s), 125.2 (s), 127.2 (s), 127.9 (s), 128.0 (s), 129.3 (s), 129.3 (s), 146.2 (s), 149.4 (s), 159.5 (s), 199.2 (s); HRMS found m/z 264.1147, calcd for $C_{18}H_{16}O_2$: M, 264.1151.

4.4.2. (2,4-Diphenyl-4H-chromen-3-yl)(phenyl)methanone (**6bf**)

Yield 98%; Mp 152.5–153.0 °C; R_f 0.30 (hexane/CH_2Cl_2=2:1); IR (KBr) 1643 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.35 (s, 1H, CHPh), 7.02–7.19 (m, 9H, aryl H), 7.22–7.28 (m, 4H, aryl H), 7.36–7.39 (m, 2H, aryl H), 7.43–7.51 (m, 4H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 43.9 (s), 114.4 (s), 116.5 (s), 124.6 (s), 126.7 (s), 127.6 (s), 127.8 (s), 127.9 (s), 128.1 (s), 128.6 (s), 129.1 (s), 129.3 (s), 129.5 (s), 129.7 (s), 131.7 (s), 133.3 (s), 138.4 (s), 145.2 (s), 150.3 (s), 155.3 (s), 197.2 (s); HRMS found m/z 388.1471, calcd for $C_{28}H_{20}O_2$: M, 388.1464.

4.4.3. Ethyl 2-methyl-4-phenyl-4H-chromene-3-carboxylate (**6cf**)[9]

Yield 84%; R_f 0.75 (hexane/CH_2Cl_2=1:4); IR (neat) 1710 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (t, J=7.12 Hz, 3H, $COOCH_2CH_3$), 2.51 (s, 3H, CCH_3), 4.02–4.15 (m, 2H, $COOCH_2CH_3$), 5.04 (s, 1H, CHPh), 6.94–6.98 (m, 1H, aryl H), 7.00–7.06 (m, 2H, aryl H), 7.09–7.15 (m, 2H, aryl H), 7.20–7.24 (m, 4H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.6 (s), 19.0 (s), 41.0 (s), 59.6 (s), 105.6 (s), 115.7 (s), 124.0 (s), 124.3 (s), 125.9 (s), 127.0 (s), 127.3 (s), 127.9 (s), 128.7 (s), 146.2 (s), 148.8 (s), 159.5 (s), 166.6 (s), HRMS found m/z 294.1265, calcd for $C_{19}H_{18}O_3$: M, 294.1256.

4.4.4. Ethyl 2-ethyl-4-phenyl-4H-chromene-3-carboxylate (**6df**)

Yield 80%; R_f 0.50 (hexane/CH_2Cl_2=1:1); IR (neat) 1703 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.17 (t, J=7.30 Hz, 3H, CCH_2CH_3), 1.29 (t, J=7.30 Hz, 3H, $COOCH_2CH_3$), 2.84–3.00 (m, 2H, CCH_2CH_3), 4.02–4.15 (m, 2H, $COOCH_2CH_3$), 5.03 (s, 1H, CHPh), 6.94–6.98 (m, 1H, aryl H), 7.02–7.07 (m, 2H, aryl H), 7.10–7.16 (m, 2H, aryl H), 7.21–7.23 (m, 4H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.9 (s),

14.0 (s), 25.9 (s), 41.5 (s), 60.0 (s), 105.3 (s), 116.1 (s), 124.3 (s), 124.8 (s), 126.3 (s), 127.4 (s), 127.7 (s), 128.3 (s), 129.1 (s), 146.6 (s), 149.4 (s), 164.7 (s), 166.8 (s); MS *m*/*z* 306 (M, 9.4%).

*4.4.5. Ethyl 2,4-diphenyl-4H-chromene-3-carboxylate (**6ef**)*[9]

Yield 83%; R_f 0.43 (hexane/CH_2Cl_2=1:1); IR (neat) 1700 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, J=7.10 Hz, 3H, $COOCH_2CH_3$), 3.94 (q, J=7.10 Hz, 2H, $COOCH_2CH_3$), 5.23 (s, 1H, CHPh), 7.07–7.11 (m, 1H, aryl H), 7.15–7.26 (m, 4H, aryl H), 7.29–7.36 (m, 2H, aryl H), 7.42–7.52 (m, 5H, aryl H), 7.58–7.67 (m, 2H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2 (s), 43.0 (s), 60.8 (s), 108.2 (s), 117.2 (s), 125.3 (s), 125.4 (s), 127.4 (s), 128.4 (s), 128.5 (s), 129.3 (s), 129.4 (s), 129.9 (s), 130.2 (s), 135.9 (s), 146.7 (s), 150.6 (s), 159.1 (s), 167.7 (s); MS *m*/*z* 356 (M, 20.6%).

4.5. Procedure for the recyclable Brönsted acid 1-catalyzed reaction of 1,3-diphenylpropan-1,3-dione (2b) with tertiary alkynol 7

A mixture of 1-butyl-3-(3-sulfopropyl)-1*H*-imidazol-3-ium trifluoromethanesulfonate (**1**) (0.020 g, 0.050 mmol), 1,1,3-triphenylprop-2-yn-1-ol (**7**) (0.285 g, 1.002 mmol) and 1,3-diphenylpropane-1,3-dione (**2b**) (0.224 g, 0.999 mmol) in 1-ethyl-3-methyl-1*H*-imidazol-3-ium trifluoromethanesulfonate (1 ml) under argon was stirred at 100 °C for 24 h. The mixture was then cooled to room temperature and extracted from the ionic liquid with a mixed solvent of Et_2O/hexane (1:1) (30 ml×3). After the solvent was removed under reduced pressure, the product was purified by column chromatography on silica gel with hexane/CH_2Cl_2 (5:2) to give 1,3-diphenyl-2-(1,3,3-triphenylallylidene)propane-1,3-dione (**8**) (0.324 g, 66%).

*4.5.1. 1,3-Diphenyl-2-(1,3,3-triphenylallylidene)propane-1,3-dione (**8**)*[3b]

Yield 66%; Mp 152.1–153.4 °C (lit. 152–153 °C); R_f 0.08 (hexane/CH_2Cl_2=5:2); IR (KBr) 1648 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.58 (s, 1H, CH), 6.88–6.91 (m, 2H, aryl H), 6.98–7.03 (m, 3H, aryl H), 7.07–7.10 (m, 2H, aryl H), 7.16–7.25 (m, 11H, aryl H), 7.34–7.37 (m, 1H, aryl H), 7.43–7.47 (m, 2H, aryl H), 7.53–7.57 (m, 1H, aryl H), 7.69–7.71 (m, 2H, aryl H), 7.95–7.98 (m, 2H, aryl H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 126.9 (s), 127.6 (s), 127.6 (s), 127.7 (s), 127.8 (s), 127.9 (s), 128.0 (s), 128.4 (s), 128.4 (s), 129.3 (s), 129.3 (s), 129.4 (s), 129.9 (s), 132.5 (s), 132.7 (s), 137.0 (s), 137.6 (s), 137.7 (s), 138.7 (s), 139.4 (s), 141.9 (s), 147.8 (s), 148.9 (s), 194.3 (s), 195.7 (s); HRMS found *m*/*z* 490.1938, calcd for $C_{36}H_{26}O_2$: M, 490.1934.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.07.012.

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