Tetrahedron 67 (2011) 4569–4577

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Alkylation of 1,3-dicarbonyl compounds with benzylic and propargylic alcohols using Ir–Sn bimetallic catalyst: synthesis of fully decorated furans and pyrroles

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ARTICLE INFO

Article history:
Received 9 January 2011
Received in revised form 21 April 2011
Accepted 22 April 2011
Available online 5 May 2011

Keywords:
Bimetallic catalysis
Benzylation
Propargylation
Allenylation
1,3-Dicarbonyl compound
Furan
Pyrrole
Iridium
Tin

ABSTRACT

The heterobimetallic complex $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ catalyzes the direct substitution of hydroxyl groups in benzylic and propargylic alcohols by 1,3-dicarbonyl moiety. In 4-hydroxycoumarin, benzylation and propargylation occurs at the 3-position. Selective propargylation or allenylation takes place depending on the nature of propargylic alcohol. By applying the methodology, multi-substituted furans and pyrroles have been synthesized in good yields.

1. Introduction

Our continuing interest in dual-reagent catalysis involving d^8/d^{10} transition metal partners and tin as a main group metal partner,[1] brought us to parallel investigation on organic activation across discrete M–Sn motif; one of the successful example being the heterobimetallic complex $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ (hereafter Ir^{III}–Sn^{IV}), which can be easily generated from $[Ir(COD)(\mu\text{-}Cl)]_2$ and $SnCl_4$.[2] The Ir^{III}–Sn^{IV} catalyst showed remarkable efficiency in the Friedel–Crafts alkylation of arenes and heteroarenes using π-activated 1°, 2°, and 3° alcohols.[2] In addition, the catalyst mediated the secondary benzylation and propargylation of carbon (arene, heteroarene and allyltrimethylsilane), oxygen (alcohol), nitrogen (amide and sulfonamide) and sulfur (thiol) nucleophiles with respective benzylic and propargylic alcohols.[3] Keeping in view the efficacy of the Ir–Sn motif to activate π-activated alcohols, we aimed to explore the benzylation and propargylation using 1,3-dicarbonyl derivatives as the *C*-nucleophile (Scheme 1).

The functionalization of activated methylene moieties including 1,3-dicarbonyl compounds is one of the important methodologies in C–C bond formation.[4] The standard protocol for these transformations requires the use of an organic halide and an equimolar amount of base or Lewis acid, resulting in large amount of salt by-products. Unquestionably, the alkylation of activated methylene compounds with an alcohol would provide an attractive salt-free, environment friendly and atom-economic[5] procedure with water being the sole by-product. Due to its poor leaving group ability, the hydroxyl group of an alcohol needs in situ pre-activation by a promoter prior to the nucleophilic substitution. In this regard, recent demonstration of Lewis and Brønsted acid catalyzed benzylation and propargylation of 1,3-dicarbonyl derivatives using alcohols is noteworthy.[6,7] However, to the best of our knowledge, there is only one report on the use of a bimetallic catalyst for such transformation. We present here the first example of alkylation of 1,3-dicarbonyl compounds via cooperative heterobimetallic catalysis.

The benzylation of 1,3-dicarbonyl derivatives leads to the generation of structural motifs of many bioactive compounds; Tipranavir (an HIV protease inhibitor), Reglitazar (a potential diabetes drug) and Warfarine (an oral anticoagulant) being representative examples.[6e,8] Similarly propargylation of 1,3-dicarbonyl compounds provides access to useful synthetic intermediates, and heterocycles such as furans and pyrroles (Fig. 1). Substituted furans constitute an important architecture in many natural products, pharmaceuticals, flavours and fragrance compounds.[9] Likewise the

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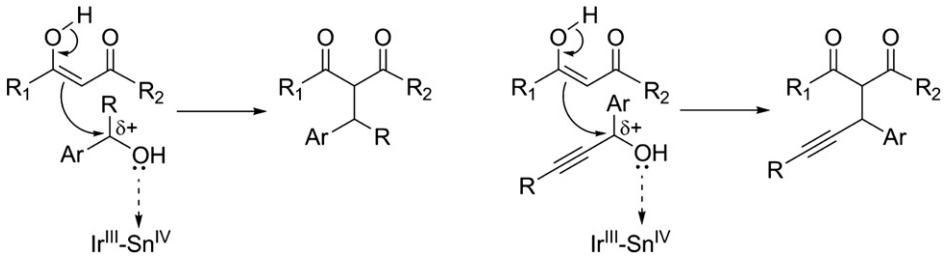
doi:10.1016/j.tet.2011.04.092



Scheme 1. Activation of benzylic and propargylic alcohols by Ir^{III}–Sn^{IV} catalyst towards benzylation and propargylation of 1,3-dicarbonyl derivatives.

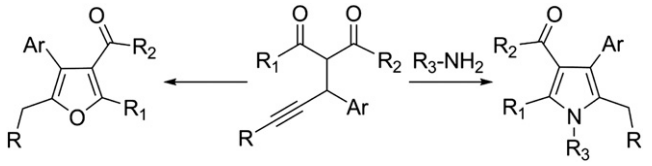


Fig. 1. Synthetic application of propargylated 1,3-dicarbonyl moiety.

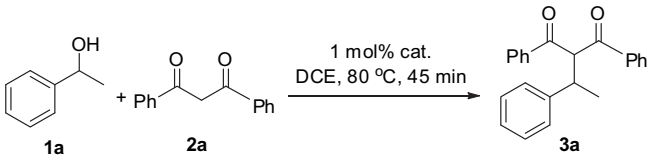
substituted pyrrole ring is an important structural attribute in several bioactive natural products[10] and pharmaceuticals[11] as well as a useful building block in organic synthesis.[12]

In continuation to our exploration on heterobimetallic reactivity, we report here an efficient and highly regioselective substitution of benzylic and secondary/tertiary propargylic alcohols with 1,3-dicarbonyl derivatives and 4-hydroxycoumarin which is catalyzed by $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$. Further, the propargylated 1,3-dicarbonyl products have been steered to ring-closure with the formation of substituted furans and pyrroles.

2. Results and discussion

Initially we examined the efficiency of various catalysts towards the formation of alkylated product **3a** from benzylic alcohol **1a** and dibenzoylmethane **2a** (Table 1). The efficiency of Ir–Sn heterobimetallic catalyst $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ was highest in comparison to others and the desired product **3a** was obtained in 81% yield after 45 min (entry 1). Individually $[Ir(COD)(\mu\text{-}Cl)]_2$ was inactive, while $IrCl_3$ and $SnCl_4$ were poorly active (entries 5–7). Similarly $[Ir(COD)(MeCN)_2]PF_6$ and $[Ir(COD)_2(SnCl_3)]$ showed very negligible efficiencies (entries 8 and 9). A simple 1:1 combination of $IrCl_3/SnCl_4$ and $[Ir(COD)(\mu\text{-}Cl)]_2/SnCl_4$ also led to low conversion (entries 10 and 11). These observations emphasize the importance of high-valent Ir^{III}–Sn^{IV} moiety; although we are yet to fully comprehend the exact nature of synergism in such a motif.

Table 1
Benzylation of dibenzoylmethane **2a** with benzylic alcohol **1a**: catalyst screening[a]



1a 2a 3a

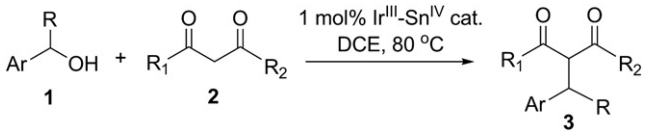
Entry	Catalyst	Yield (%)	TOF (h^{-1})
1	$[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$	81	108
2	$[Ir(COD)(SnBr_3)Br(\mu\text{-}Br)]_2$	65	87
3	$[Ir(COD)(MeSnCl_2)Cl(\mu\text{-}Cl)]_2$	57	76
4	$IrCl(CO)(PPh_3)_2(SnCl_4)$	<5	<7
5	$[Ir(COD)(\mu\text{-}Cl)]_2$	0	0
6	$IrCl_3$	8	11
7	$SnCl_4$	10	14
8	$[Ir(COD)(MeCN)_2]PF_6$	<5	<7
9	$[Ir(COD)_2(SnCl_3)]$	<5	<7
10	$IrCl_3/SnCl_4$ (1:1)	15	20
11	$[Ir(COD)(\mu\text{-}Cl)]_2/SnCl_4$ (1:1)	12	16

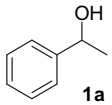
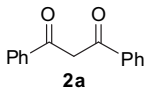
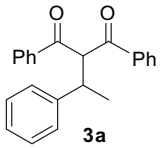
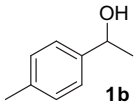
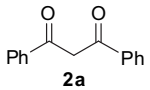
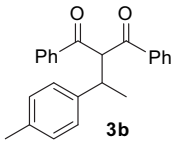
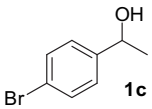
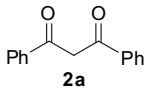
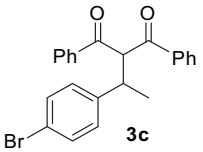
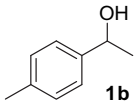
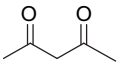
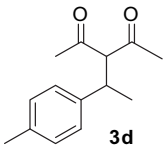
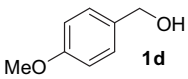
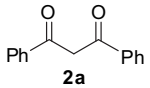
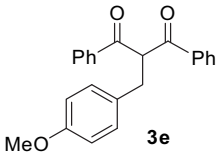
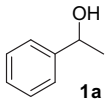
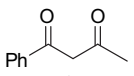
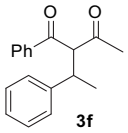
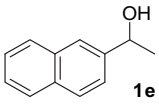
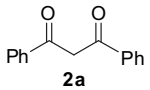
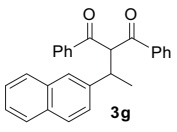
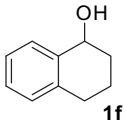
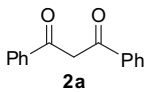
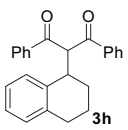
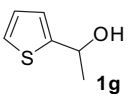
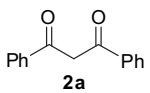
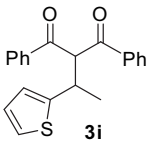
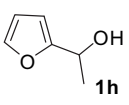
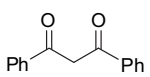
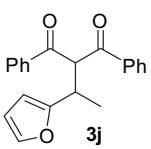
[a] Unless otherwise mentioned, reaction conditions: alcohol (0.5 mmol), nucleophile (0.75 mmol), catalyst (0.005 mmol), solvent DCE (2 mL), 80 °C, 45 min. Yield refers to isolated yield.

Next we explored the benzylation of 1,3-dicarbonyl derivatives **2** taking 1° and 2° benzylic alcohols **1** as electrophiles (alcohol/nucleophile molar ratio is 1:1.5). The reactions were carried out in the presence of 1 mol % of $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ catalyst in 1,2-dichloroethane (DCE) at 80 °C (Table 2). Secondary benzylic alcohols **1a**–**c** and **1e**–**h** (entries 1–3, and 7–10), having a β-hydrogen atom, reacted smoothly with dibenzoylmethane **2a** to provide the desired benzylated products, without forming any alkene side-products. Alcohols **1b** and **1c**, bearing electron-donating and electron-withdrawing substituent at the *para* position of the phenyl ring, afforded the respective benzylated product **3b** and **3c** in good yields (entries 2 and 3). The reaction of 1-(2-naphthyl) ethanol **1e** with **2a** went smoothly affording the **3g** (entry 7). Alcohol **1f** was effective yielding **3h** in 80% yield (entry 8), while no 1,2-dihydronaphthalene was detected as side-product. A mixture of diastereomers was isolated when alcohol **1a** was coupled with unsymmetrical 1,3-dicarbonyl compound **2c** (entry 6). Alcohol **1g** and **1h**, where the π-activation is provided by heteroarenes like thiophene or furan moiety, underwent benzylation of **2a** in good yield (entries 9 and 10). In spite of lower enol ratios,[6d] benzylation of ketoester **2d** and **2e** reacted with activated electrophile, like diphenylmethanol **1i** (entries 11 and 12). The structure of product **3k** was established by X-ray crystallographic analysis (Supplementary data). The benzylation of 1,3-dicarbonyl derivatives was not limited to secondary benzylic substrates. Primary benzylic alcohol **1d** reacted with **2a** leading to **3e** in moderate yield (entry 5).

Afterwards we examined the propargylation of 1,3-dicarbonyl derivatives **2** with a variety of propargylic alcohols **4** using 1 mol % of Ir^{III}–Sn^{IV} catalyst in DCE at 80 °C (Table 3). As shown in Table 3 (entries 1–5), the reaction was general with respect to substitution in the 1,3-dicarbonyl framework. Variation at the alkyne terminus in propargyl alcohol from an alkyl to an aryl, or trimethylsilane (**4a**–**c**, **4e**) was well tolerated (entries 1–6 and 8). Gratifyingly, alcohol **4d** bearing terminal alkyne group successfully underwent the coupling reaction with **2a** under the same reaction conditions leading to **5g** and no polymerization was detected (entry 7). The structure of **5g** was established by X-ray crystallographic analysis (Supplementary data). The ketoester **2d** reacted equally well with alcohol **4b** affording a mixture of diastereomers (entry 5). Also noteworthy is the fact that attempted reaction of secondary and tertiary propargylic alcohol containing β-hydrogen atom (**4f** and **4g**) with **2a** as nucleophile failed to give the desired propargylated products. The reaction of secondary alcohol **4f** with **2a** ended with unidentified complex mixture, whereas the tertiary alcohol **4g** underwent fast dehydration yielding 1,3-enyne and rearrangement to α,β-unsaturated ketone[3b] simultaneously. We also noted that both the benzylation and propargylation reactions of 1,3-dicarbonyl derivatives can tolerate moisture or air without compromising product yield.

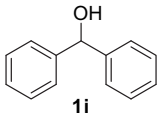
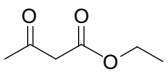
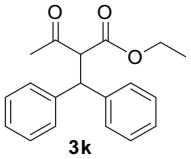
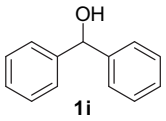
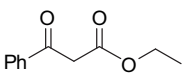
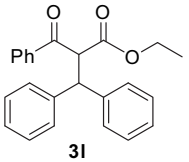
Table 2
Benzylation of 1,3-dicarbonyl derivatives **2** with benzylic alcohols **1**[a]



Entry	Alcohol **1**	Nu–H **2**	Product **3**	Time (min)	Yield (%)
1	 **1a**	 **2a**	 **3a**	45	81
2	 **1b**	 **2a**	 **3b**	30	85
3	 **1c**	 **2a**	 **3c**	55	75
4	 **1b**	 **2b**	 **3d**	80	85
5	 **1d**	 **2a**	 **3e**	85	68
6	 **1a**	 **2c**	 **3f**	35	85[b]
7	 **1e**	 **2a**	 **3g**	30	88
8	 **1f**	 **2a**	 **3h**	45	80
9	 **1g**	 **2a**	 **3i**	60	76
10	 **1h**	 **2a**	 **3j**	70	72

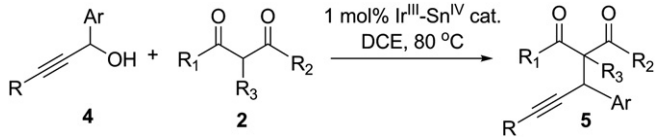
(*continued on next page*)

Table 2 (*continued*)

Entry	Alcohol **1**	Nu–H **2**	Product **3**	Time (min)	Yield (%)
11	 **1i**	 **2d**	 **3k**	30	92
12	 **1i**	 **2e**	 **3l**	30	90

[a] Unless otherwise mentioned, reaction conditions: alcohol (0.25 mmol), nucleophile (0.38 mmol), Ir^{III}–Sn^{IV} cat. (0.0025 mmol), solvent DCE (1 mL), 80 °C.
[b] dr=1:1.3. Yield refers to isolated yield.

Table 3
Propargylation of 1,3-Dicarbonyl Derivatives **2** with Propargylic Alcohols **4**[a]



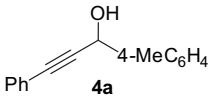
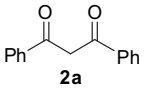
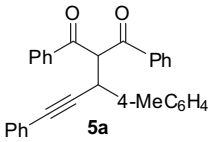
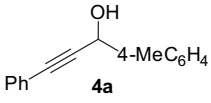
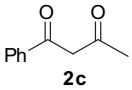
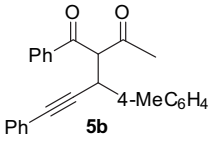
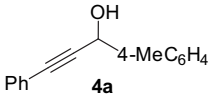
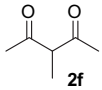
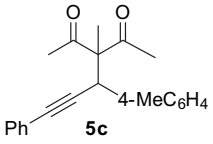
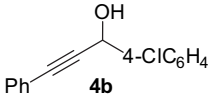
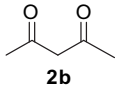
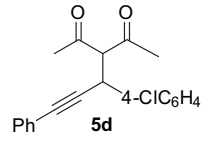
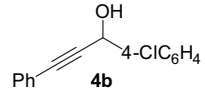
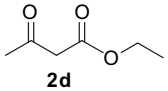
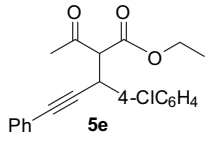
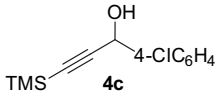
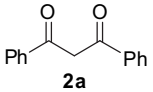
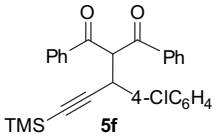
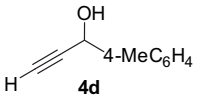
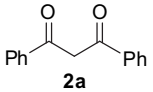
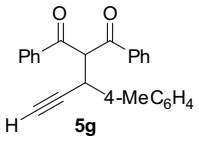
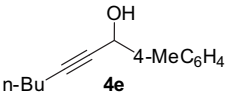
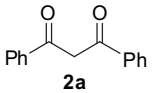
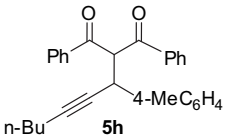
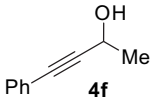
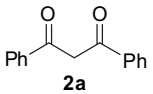
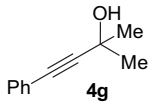
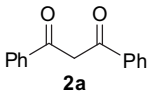
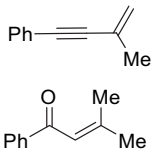
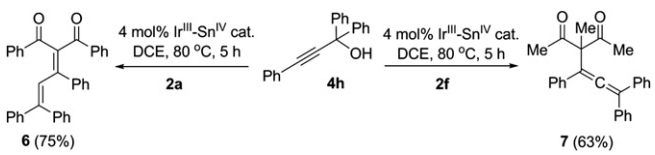
Entry	Alcohol **4**	Nu–H **2**	Product **5**	Time (min)	Yield (%)
1	 **4a**	 **2a**	 **5a**	45	95
2	 **4a**	 **2c**	 **5b**	50	91[b]
3	 **4a**	 **2f**	 **5c**	45	89
4	 **4b**	 **2b**	 **5d**	55	84
5	 **4b**	 **2d**	 **5e**	80	79[c]

Table 3 (*continued*)

Entry	Alcohol **4**	Nu–H **2**	Product **5**	Time (min)	Yield (%)
6	 **4c**	 **2a**	 **5f**	60	85
7	 **4d**	 **2a**	 **5g**	65	62
8	 **4e**	 **2a**	 **5h**	60	85
9	 **4f**	 **2a**	—	90	—
10	 **4g**	 **2a**		35	62 30

[a] Unless otherwise mentioned, reaction conditions: alcohol (0.25 mmol), nucleophile (0.38 mmol), Ir^{III}–Sn^{IV} cat. (0.0025 mmol), solvent DCE (1 mL), 80 °C.
[b] dr=1:1.5.
[c] dr=1:1.1. Yield refers to isolated yield.

We investigated the reactivity of tertiary propargylic alcohol **4h** towards 1,3-dicarbonyl compound **2a** (Scheme 2). However, the conjugated diene-dione **6** was obtained as the only isolable product in this case. We believe that the highly activated tertiary propargylic alcohol **4h** first undergoes isomerization into corresponding α,β-unsaturated ketone,[13] followed by aldol-type condensation with **2a** under catalytic conditions to afford compound **6**. Interestingly, we found that the presence of a substituent at the active methylene carbon of the 1,3-dicarbonyl compound, as, for example, in **2f**, gave rise to substitution reaction with tertiary propargylic alcohol **4h** under Ir^{III}–Sn^{IV} catalysis. In this case a regioselective allenylation took place instead of propargylation and **7** was isolated in 63% yield (Scheme 2). The result suggests that the steric hindrance around hydroxyl group plays a pivotal role in promoting the nucleophile attack at the acetylenic centre of the ambient electrophile. One may note that the carbonyl-functionalized allenes are important building blocks in organic synthesis.



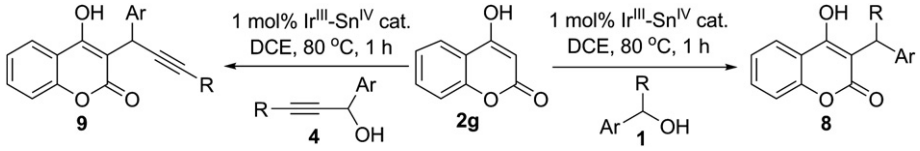
Scheme 2. Differential reactivity of tertiary propargylic alcohol **4h** towards 1,3-dicarbonyl derivatives **2a** and **2f**.

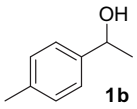
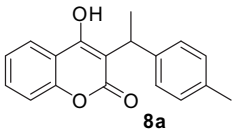
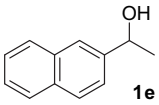
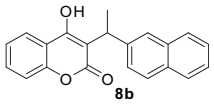
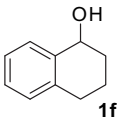
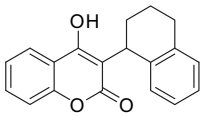
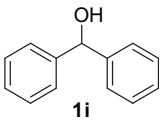
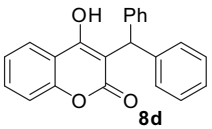
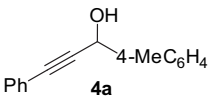
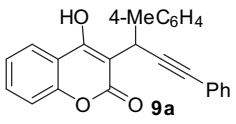
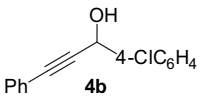
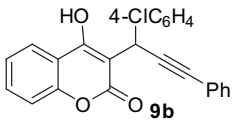
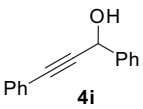
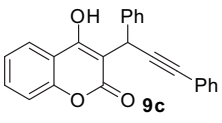
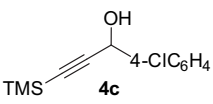
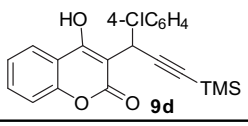
Encouraged by the reactivity of Ir^{III}–Sn^{IV} as above, we sought to synthesize substituted coumarins through the benzylation and propargylation of 4-hydroxycoumarin **2g** with various benzylic and propargylic alcohols (Table 4). Substituted coumarin analogues are of importance as they constitute valuable building blocks for potential new pharmaceuticals, especially anticoagulants.[14] We explored the reaction of 4-hydroxycoumarin **2g** with different benzylic alcohols **1b**, **1e**–**f** and **1i**, and in each case the products **8** were obtained in good yields (entries 1–4). Similar reaction of propargylic alcohols **4a**–**c**, and **4i** with **2g** led to propargylated products **9** in good yields (entries 5–8).

Having successfully developed an efficient propargylation of 1,3-dicarbonyl derivatives, we finally turned our attention to the application of this methodology to a one-pot synthesis of substituted furans.[7a–g,i,l–m] The reaction of propargylic alcohol **4i** with 1,3-dicarbonyl derivatives **2** and a catalytic amount of $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ in DCE followed by the addition of cesium carbonate (Cs_2CO_3) allowed the synthesis of functionalized furans **10** in good yields (Scheme 3). Remarkably, for 1,3-dicarbonyl compound **2d** the cyclization went regioselectively since only the keto group participated in the cyclization process while the ester function remained as a spectator. On the other hand, for unsymmetric 1,3-dicarbonyl compound **2c**, a mixture of substituted furans (**10c**-**1** and **10c**-**2**) was isolated. In the presence of inorganic base the propargylated 1,3-dicarbonyl **5** tautomerises to **A**, which subsequently isomerizes to **10** in a 5-*exo*-*dig* fashion.

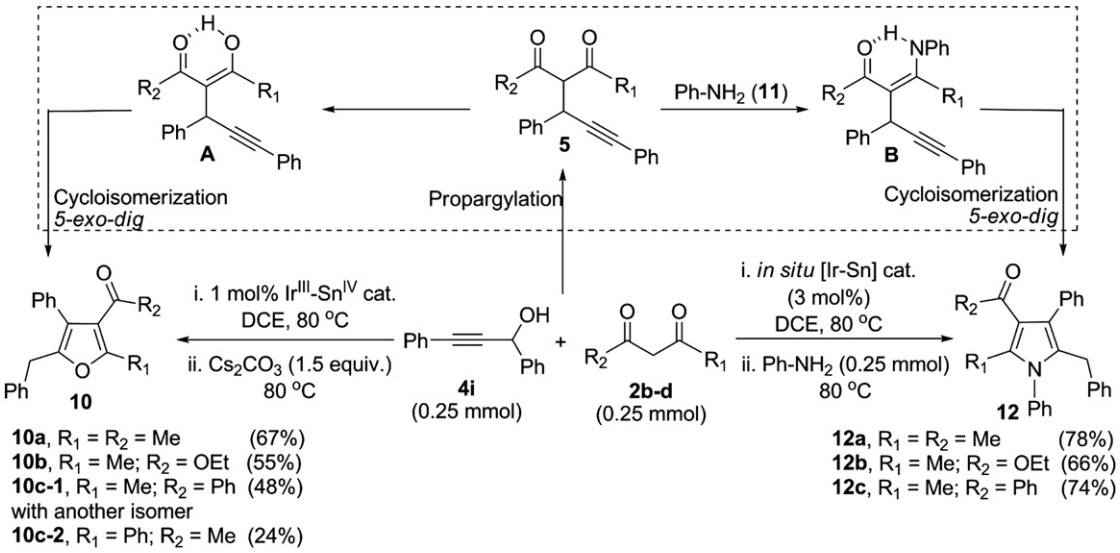
We also found that when a primary aromatic amine was introduced in the reaction medium, substituted pyrroles could be selectively formed.[7a,15] Thus reaction of propargylic alcohol **4i** with 1,3-dicarbonyl derivatives **2** and in situ generated [Ir–Sn] catalyst[2a] in DCE was followed by the addition of primary aromatic amines **11** giving rise to tetrasubstituted pyrroles **12** in good yields (Scheme 3). However, aliphatic amines remained unreactive under the condition. Interestingly, unsymmetric 1,3-dicarbonyl compound **2c** led to

Table 4
Syntheses of coumarin analogue by Ir^{III}–Sn^{IV} catalyzed benzylation and propargylation of 4-hydroxycoumarin **2g**[a]



Entry	Alcohol	Product	Yield (%)
1	 **1b**	 **8a**	82
2	 **1e**	 **8b**	85
3	 **1f**	 **8c**	78
4	 **1i**	 **8d**	95
5	 **4a**	 **9a**	93
6	 **4b**	 **9b**	90
7	 **4i**	 **9c**	89
8	 **4c**	 **9d**	84

[a] Unless otherwise mentioned, reaction conditions: alcohol (0.25 mmol), nucleophile **2g** (0.38 mmol), Ir^{III}–Sn^{IV} cat. (0.0025 mmol), solvent DCE (1 mL), 80 °C. Yield refers to isolated yield.



Scheme 3. Synthesis of substituted furans **10** and pyrroles **12** from 1,3-dicarbonyl derivatives.

the regioselective formation of substituted pyrrole **12c**. The formation of pyrroles may be explained by the following steps: (i) generation of intermediate **B** via the condensation of amine **11** with **5**, followed by tautomerization; (ii) the cycloisomerization of **B** in a 5-*exo*-*dig* manner.[15d,e]

3. Conclusions

In summary, we presented here a facile benzylation and propargylation of 1,3-dicarbonyl derivatives with benzylic and propargylic alcohols catalyzed by $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ heterobimetallic complex. Selective propargylation or allenylation products can be obtained depending on the structure of the propargylic alcohol. In addition, the Ir^{III}–Sn^{IV} catalyst can promote the benzylation and propargylation of 4-hydroxycoumarin at the 3-position. Furthermore, we have introduced one more strategy for the synthesis of substituted furans and pyrroles by employing Ir–Sn catalyzed nucleophilic substitution of propargylic alcohols with 1,3-dicarbonyl compounds as the key step. By virtue of their generality, selectivity and efficiency, the strategies presented here could be a meaningful addition to the existing methods of benzylation, propargylation of 1,3-dicarbonyl compounds.

4. Experimental

4.1. General remarks

^1H NMR spectra were recorded at 400 MHz and 200 MHz on Bruker Spectrometers. Chemical shifts are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 7.26 ppm). ^{13}C NMR spectra were recorded at 100 MHz and 54.6 MHz with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 77.0 ppm). ESI-MS was recorded using a Waters LCT mass spectrometer. Elemental analyses were carried out using a CHNS/O Analyzer Perkin–Elmer 2400 Series II instrument. Melting points were determined on an Electrothermal 9100 melting point apparatus and are uncorrected.

All reactions were carried out under an argon atmosphere in flame-dried glassware using Schlenk techniques. Chromatographic purifications were done using either 60–120 or 100–200 mesh silica gel. For reaction monitoring, pre-coated silica gel 60 F_{254} TLC sheets were used. Petroleum ether refers to the fraction boiling in the range 60–80 °C. 1,2-Dichloroethane (DCE) was dried and distilled prior to use. $IrCl_3 \cdot xH_2O$, 1,5-cyclooctadiene and tin tetrachloride were commercially available. $[Ir(COD)(\mu\text{-}Cl)]_2$ was prepared according to the literature procedure[16] and the heterobimetallic catalysts $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$,[2] $[Ir(COD)(SnBr_3)Br(\mu\text{-}Br)]_2$,[2b] $[Ir(COD)(MeSnCl_2)Cl(\mu\text{-}Cl)]_2$,[2b] $[IrCl(CO)(PPh_3)_2(SnCl_4)]$,[17] $[Ir(COD)_2(SnCl_3)]$[18] were prepared according to literature procedure. Benzylic alcohols (**1d**, **1a**–**c** and **1e**–**i**)[19] and propargylic alcohols (**4a**–**i**)[20] were also prepared according to literature.

4.2. Representative procedure for the benzylation of dibenzoylmethane 2a with 1-phenylethanol 1a catalyzed by $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$

A 10 mL Schlenk flask equipped with a magnetic bar was charged with $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ (0.0025 mmol), dibenzoylmethane **2a** (0.38 mmol), 1-phenylethanol **1a** (0.25 mmol) and 1,2-dichloroethane (1 mL). The flask was degassed, flushed with argon and placed in a constant temperature bath at 80 °C. The reaction was allowed to continue at 80 °C, and monitored by TLC. After completion, solvent was removed under reduced pressure and the mixture was subjected to column chromatography over silica gel (eluent: gradient mixture of EtOAc/pet ether) to afford the benzylated product **3a** in 81% isolated yield.

4.3. Representative procedure for the propargylation of dibenzoylmethane 2a with 3-phenyl-1-(*p*-tolylprop)-2-yn-1-ol 4a catalyzed by $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$

A 10 mL Schlenk flask equipped with a magnetic bar was charged with $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ (0.0025 mmol), dibenzoylmethane **2a** (0.38 mmol), 3-phenyl-1-(*p*-tolylprop)-2-yn-1-ol **4a** (0.25 mmol) and 1,2-dichloroethane (1 mL). The flask was degassed, flushed with argon and placed in a constant temperature bath at 80 °C. The reaction was allowed to continue at 80 °C, and monitored by TLC. After completion, solvent was removed under reduced pressure and the mixture was subjected to column chromatography over silica gel (eluent: gradient mixture of EtOAc/pet ether) to afford the propargylated product **5a** in 95% isolated yield.

4.4. General procedure for the synthesis of substituted furans 10

A 10 mL Schlenk flask equipped with a magnetic bar was charged with $[Ir(COD)(SnCl_3)Cl(\mu\text{-}Cl)]_2$ (0.0025 mmol), 1,3-dicarbonyl compound **2** (0.25 mmol), propargylic alcohol **4** (0.25 mmol) and 1,2-dichloroethane (1 mL). The flask was degassed with argon, placed in a constant temperature bath at 80 °C, and monitored for propargylic alcohol (vide TLC). Upon completion, Cs_2CO_3 (1.5 equiv) was added, and the reaction was continued at 80 °C until intermediate **5** was consumed (vide TLC). The mixture was cooled to room temperature, solvent removed under reduced pressure and the mixture was subjected to column chromatography over silica gel (eluent: gradient mixture of ethyl acetate/petroleum ether) to afford the corresponding furan **10**.

4.5. General procedure for the synthesis of substituted pyrroles 12

In a 10 mL Schlenk flask equipped with a magnetic bar were added $[Ir(COD)(\mu\text{-}Cl)]_2$ (0.0075 mmol), $SnCl_4$ (0.03 mmol) and 1,2-dichloroethane (0.5 mL) under an argon atmosphere. After stirring for 10 min at room temperature, a solution of propargylic alcohol **4** (0.25 mmol) and 1,3-dicarbonyl compound **2** (0.25 mmol) in 1,2-dichloroethane (0.5 mL) was added to the mixture, and the reaction was monitored for propargylic alcohol (vide TLC). Upon completion, $PhNH_2$ (0.25 mmol) was added, and the mixture was stirred at 80 °C until intermediate **5** is consumed (vide TLC). The mixture was cooled to room temperature, solvent removed under reduced pressure and the mixture was subjected to column chromatography over silica gel (eluent: gradient mixture of ethyl acetate/petroleum ether) to afford the corresponding pyrrole **12**.

4.6. Spectral and analytical data of products

The spectral data of compound **3a**,[6d] **3b**,[6d] **3d**,[21] **3e**,[6d] **3f**,[6f] **3g**,[22] **3h**,[23] **3k**,[6g] **3l**,[23] **5a**,[7e] **5d**,[7e] **6**,[7d] **7**,[7d] **8a**,[6k] **8b**,[6k] **8c**,[24] **8d**,[6k] **9b**,[6j] **9c**,[7e] **10a**,[7d] **10b**,[7d] **12a**,[15e] **12b**,[15e] **12c**,[15e] were in excellent agreement with those in the literature. The spectral data for the products **3c**, **3i**, **3j**, **5b**, **5c**, **5e**, **5f**, **5g**, **5h**, **9a**, **9d**, **10c-1** and **10c-2** are shown below.

*4.6.1. 2-(1-(4-Bromophenyl)ethyl)-1, 3-diphenylpropane-1,3-dione (**3c**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 1.29 (t, 3H, J=6.8 Hz), 4.05 (dq, 1H, J=6.8 and 10.2 Hz), 5.55 (d, 1H, J=10.2 Hz), 7.14 (d, 2H, J=8.4 Hz), 7.25–7.33 (m, 4H), 7.41–7.61 (m, 4H), 7.75 (d, 2H, J=8.6 Hz), 8.04 (d, 2H, J=8.6 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ (ppm) 20.3, 40.7, 64.3, 120.4, 128.5, 128.6, 128.8, 129.0, 129.6, 131.5, 133.4, 133.8, 136.7, 136.9, 142.9, 194.4, 194.8. Anal. ($C_{23}H_{19}BrO_2$) calcd, C: 67.82, H: 4.70; found, C: 68.41, H: 4.51.

*4.6.2. 1,3-Diphenyl-2-(1-(thiophen-2-yl)ethyl)propane-1,3-dione (**3i**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 1.40 (d, 3H, J=6.8 Hz), 4.21–4.47 (dq, 1H, J=6.8 and 9.6 Hz), 5.56 (d, 1H, J=9.6 Hz), 6.70–6.77 (m, 2H), 6.99 (dd, 1H, J=1.2 and 3.6 Hz), 7.23–7.56 (m, 6H), 7.75 (dd, 2H, J=1.6 and 7.0 Hz), 7.95 (dd, 2H, J=1.6 and 7.0 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ (ppm) 21.2, 36.6, 65.1, 123.3, 125.0, 126.5, 128.5, 128.7, 128.8, 133.2, 133.6, 136.8, 136.9, 147.4, 194.3, 194.4. ESI-MS: for $C_{21}H_{18}O_2S$, $[M+Na]^+$=357.00. Anal. ($C_{21}H_{18}O_2S$) calcd, C: 75.42, H: 5.43; found, C: 75.66, H: 5.26.

*4.6.3. 2-(1-(Furan-2-yl)ethyl)-1,3-diphenylpropane-1,3-dione (**3j**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 1.36 (d, 3H, J=7.0 Hz), 4.05–4.20 (dq, 1H, J=7.0 and 9.0 Hz), 5.71 (d, 1H, J=9.0 Hz), 5.95 (d, 1H, J=3.2 Hz), 6.08 (dd, 1H, J=1.8 and 3.2 Hz), 7.17 (d, 1H, J=1.8 Hz), 7.32–7.57 (m, 6H), 7.82–7.93 (m, 4H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ (ppm) 17.2, 34.4, 61.1, 106.2, 110.2, 128.5, 128.6, 128.8, 133.2, 133.5, 136.4, 136.9, 141.1, 156.2, 194.4, 194.8. ESI-MS: for $C_{21}H_{18}O_3$, $[M+Na]^+$=341.01. Anal. ($C_{21}H_{18}O_3$) calcd, C: 79.22, H: 5.70; found, C: 79.63, H: 5.36.

*4.6.4. 1-Phenyl-2-(3-phenyl-1-p-tolylprop-2-ynyl)butane-1,3-dione (**5b**).* Diastereomers ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 1.99 (s, 3H), 2.24 (s, 3H), 2.34 (s, 3H), 2.38 (s, 3H), 4.85 (d, 1H, J=10.6 Hz), 4.95 (d, 1H, J=11.0 Hz), 5.03 (d, 1H, J=11.0 Hz), 5.14 (d, 1H, J=10.6 Hz), 7.04 (d, 2H, J=8.0 Hz), 7.04 (d, 2H, J=8.0 Hz), 7.13 (d, 2H, J=8.0 Hz), 7.13 (d, 2H, J=8.0 Hz), 7.27–7.42 (m, 6H), 7.27–7.42 (m, 6H), 7.48–7.63 (m, 2H), 7.48–7.63 (m, 2H), 7.86 (d, 1H, J=7.2 Hz), 7.86 (d, 1H, J=7.2 Hz), 8.10 (d, 1H, J=7.2 Hz), 8.10 (d, 1H, J=7.2 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ (ppm) 21.2, 21.3, 27.8, 29.8, 38.0, 38.4, 69.2, 71.2, 83.5, 85.3, 88.8, 89.3, 123.1, 128.2, 128.3, 128.4, 128.9, 129.0, 129.1, 129.5, 129.8, 131.6, 131.9, 133.9, 135.7, 136.7, 137.3, 137.6, 193.4, 194.1, 200.9, 201.8. ESI-MS: for $C_{26}H_{22}O_2$, $[M+Na]^+$=389.07. Anal. ($C_{26}H_{22}O_2$) calcd, C: 85.22, H: 6.05; found, C: 85.40, H: 6.13.

*4.6.5. 3-Methyl-3-(3-phenyl-1-p-tolylprop-2-ynyl)pentane-2,4-dione (**5c**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 1.47 (s, 3H), 1.94 (s, 3H), 2.32 (s, 3H), 2.39 (s, 3H), 5.17 (s, 1H), 7.08–7.13 (m, 2H), 7.28–7.32 (m, 5H), 7.36–7.39 (m, 2H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ (ppm) 14.9, 21.0, 26.5, 28.0, 41.7, 72.2, 85.3, 88.4, 122.9, 128.3, 128.9, 129.6, 131.6, 133.55, 137.3, 203.9, 206.1. ESI-MS: for $C_{22}H_{22}O_2$, $[M+Na]^+$=341.05. Anal. ($C_{22}H_{22}O_2$) calcd, C: 82.99, H: 6.96; found, C: 83.21, H: 7.09.

*4.6.6. Ethyl-2-acetyl-3-(4-chlorophenyl)-5-phenylpent-4-ynoate (**5e**).* Diastereomers ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.08 (t, 3H, J=7.0 Hz), 1.26 (t, 3H, J=7.2 Hz), 2.06 (s, 3H), 2.41 (s, 3H), 3.94–4.04 (m, 2H), 3.94–4.04 (m, 2H), 4.22–4.29 (m, 1H), 4.22–4.29 (m, 1H), 4.59 (d, 1H, J=10.8 Hz), 4.64 (d, 1H, J=10.0 Hz), 7.28–7.39 (m, 9H), 7.28–7.39 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 13.8, 14.1, 29.8, 30.5, 36.9, 37.1, 61.7, 61.9, 66.4, 66.5, 84.3, 84.9, 87.5, 87.8, 122.5, 122.7, 128.1, 128.2, 128.3, 128.7, 128.8, 129.6, 129.7, 131.5, 133.4, 136.7, 136.9, 166.5, 166.8, 199.9, 200.3. Anal. ($C_{21}H_{19}ClO_3$) calcd, C: 71.08, H: 5.40; found, C: 71.33, H: 5.14.

*4.6.7. 2-(1-(4-Chlorophenyl)-3-(trimethylsilyl)prop-2-ynyl)-1,3-diphenylpropane-1,3-dione (**5f**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 0.10 (s, 9H), 4.96 (d, 1H, J=10.0 Hz), 5.75 (d, 1H, J=10.0 Hz), 7.19–7.33 (m, 5H), 7.41–7.61 (m, 5H), 7.71 (dd, 2H, J=1.4 and 7.2 Hz), 8.07 (dd, 2H, J=1.4 and 7.2 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ (ppm) 0.43, 38.5, 62.9, 90.3, 105.1, 128.5, 128.7, 128.8, 129.2, 130.0, 133.3, 133.6, 136.3, 136.9, 137.7, 192.1, 193.1. Anal. ($C_{27}H_{25}ClO_2Si$) calcd, C: 72.87, H: 5.66; found, C: 72.65, H: 5.51.

*4.6.8. 1,3-Diphenyl-2-(1-p-tolylprop-2-ynyl)propane-1,3-dione (**5g**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 2.13 (d, 1H, J=1.8 Hz), 2.19 (s, 3H), 4.89 (dd, 1H, J=1.8 and 8.2 Hz), 5.78 (d, 1H. J=8.2 Hz), 6.99 (d, 2H, J=8.0 Hz), 7.12–7.59 (m, 8H), 7.68 (d, 2H. J=8.0 Hz), 7.99 (d, 2H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ (ppm) 20.9, 37.7, 63.3, 72.6, 84.1, 128.3, 128.6, 128.8, 129.0, 129.3, 133.4, 133.6, 135.3, 136.4, 136.8, 137.2, 192.7, 193.2. ESI-MS: for $C_{25}H_{20}O_2$, $[M+Na]^+$=375.04. Anal. ($C_{25}H_{20}O_2$) calcd, C: 85.20, H: 5.72; found, C: 85.53, H: 5.56.

*4.6.9. 1,3-Diphenyl-2-(1-p-tolylhept-2-ynyl)propane-1,3-dione (**5h**).* ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 0.74 (t, 3H, J=7.6 Hz), 1.14–1.15 (m, 4H), 1.90–1.92 (m, 2H), 2.24 (s, 3H), 4.89 (dt, 1H, J=2.4 and 10.0 Hz), 5.76 (d, 1H, J=10.0 Hz), 7.03 (d, 2H, J=8.0 Hz), 7.29 (d, 2H, J=8.0 Hz), 7.35 (d, 2H, J=8.0 Hz), 7.41–7.50 (m, 3H), 7.58 (t, 1H, J=7.6 Hz), 7.73 (d, 2H, J=8.4 Hz), 8.08 (d, 2H, J=8.4 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ (ppm) 13.6, 18.3, 21.0, 21.7, 30.5, 37.9, 63.6, 79.9, 85.4, 128.3, 128.5, 128.6, 128.7, 129.1, 133.3, 133.4, 136.6, 136.8,

136.9, 137.1, 192.8, 193.7. ESI-MS: for $C_{29}H_{28}O_2$, $[M+Na]^+$=431.09. Anal. ($C_{29}H_{28}O_2$) calcd, C: 85.26, H: 6.91; found, C: 85.14, H: 7.02.

*4.6.10. 4-Hydroxy-3-(3-phenyl-1-p-tolylprop-2-ynyl)-2H-chromen-2-one (**9a**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 2.34 (s, 3H), 5.77 (s, 1H), 7.18 (d, 2H, J=8.0 Hz), 7.25–7.39 (m, 5H), 7.50–7.54 (m, 5H), 7.87 (dd, 1H, J=1.2 and 6.8 Hz), 8.38 (s, 1H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ (ppm) 21.1, 33.1, 86.7, 87.7, 105.2, 116.0, 116.5, 121.5, 123.4, 124.1, 127.0, 128.6, 129.2, 129.7, 131.9, 132.8, 135.5, 137.6, 152.7, 161.1, 162.6. ESI-MS: for $C_{25}H_{18}O_3$, $[M+H]^+$=367.02. Anal. ($C_{25}H_{18}O_3$) calcd, C: 81.95, H: 4.95; found, C: 82.24, H: 4.81.

*4.6.11. 3-(1-(4-Chlorophenyl)-3-(trimethylsilyl)prop-2-ynyl)-4-hydroxy-2H-chromen-2-one (**9d**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 0.31 (s, 9H), 5.49 (s, 1H), 7.30–7.36 (m, 4H), 7.48–7.62 (m, 3H), 7.92 (dd, 1H, J=1.2 and 6.8 Hz), 8.97 (s, 1H). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ (ppm) 0.28, 33.6, 94.1, 103.6, 104.0, 116.0, 116.5, 123.6, 124.2, 128.6, 129.0, 132.5, 133.5, 137.1, 152.6, 161.4, 162.4. Anal. ($C_{21}H_{19}ClO_3Si$) calcd, C: 65.87, H: 5.00; found, C: 66.13, H: 4.85.

*4.6.12. (5-Benzyl-2-methyl-4-phenylfuran-3-yl)(phenyl)methanone (**10c-1**)+1-(5-benzyl-2,4-di-phenylfuran-3-yl)ethanone (**10c-2**).* ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 2.08 (s, 3H), 2.36 (s, 3H), 4.00 (s, 2H), 4.02 (s, 2H), 7.06–7.47 (m, 13H), 7.06–7.47 (m, 13H), 7.69 (d, 2H, J=7.2 Hz), 7.77 (d, 2H, J=7.0 Hz). ^{13}C NMR ($CDCl_3$, 54.6 MHz): δ (ppm) 13.8, 31.6, 32.3, 121.9, 123.1, 123.4, 124.4, 126.6, 126.8, 127.6, 127.7, 128.0, 128.2, 128.5, 128.6, 129.1, 129.4, 129.5, 129.6, 130.1, 132.4, 137.9, 138.3, 138.4, 148.6, 150.1, 152.7, 155.8, 192.5, 198.1. Anal. ($C_{25}H_{20}O_2$) calcd, C: 85.20, H: 5.72; found, C: 84.98, H: 6.01.

Acknowledgements

We thank DST (financial support to S.R.), and IIT Kharagpur (fellowship to PNC). S.R. thanks Prof. Manish Bhattacharjee for encouragement and many help.

Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.04.092.

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