Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2021, **12**, 3070

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 11th November 2020
Accepted 14th January 2021

DOI: 10.1039/d0sc06208a

rsc.li/chemical-science

Iridium-catalyzed enantioselective olefinic C(sp^2)–H allylic alkylation†

Rahul Sarkar and Santanu Mukherjee *

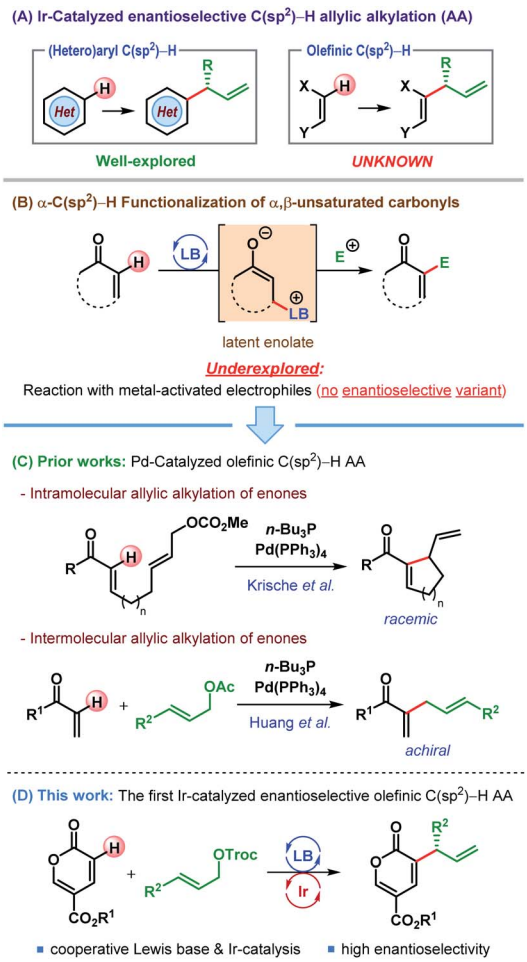
The first iridium-catalyzed enantioselective olefinic C(sp^2)–H allylic alkylation is developed in cooperation with Lewis base catalysis. This reaction, catalyzed by cinchonidine and an *in situ* generated cyclometalated Ir(I)/phosphoramidite complex, makes use of the latent enolate character of an α,β-unsaturated carbonyl compound, namely coumalate ester, to introduce an allyl group at its α-position in a branched-selective manner in moderate to good yield with good to excellent enantioselectivities (up to 98 : 2 er).

Introduction

Within the two decades since the seminal reports by Takeuchi[1] and Helmchen,[2] iridium-catalyzed allylic substitution has been established as an extremely powerful method for enantioselective synthesis.[3] Remarkable advancements in catalyst design[4] and mechanistic understanding[5] have enabled enantioselective construction of a myriad of carbon–carbon and carbon–heteroatom bonds.[3b] Particularly in the realm of Ir-catalyzed allylic alkylation (AA), both stabilized and unstabilized carbon nucleophiles have been deployed, and led to numerous C(sp^3)–H allylic alkylation reactions.[6] In contrast, Ir-catalyzed enantioselective C(sp^2)–H AA has so far been restricted to electron-rich (hetero)aromatic C(sp^2)–H bonds,[7] and allylic alkylation of olefinic C(sp^2)–H bonds remains missing from this repertoire (Scheme 1A).[8] Herein we report the first Ir-catalyzed enantioselective allylic alkylation of an olefinic C(sp^2)–H bond, namely that of an α,β-unsaturated carbonyl compound.

α,β-Unsaturated carbonyl compounds can be visualized as latent enolates and thereby nucleophilic at their α-position, especially under Lewis base (LB) activation (Scheme 1B).[9] The reactions of such latent enolates with a wide range of electrophiles, even in enantioselective fashion, have been well documented and lead to an overall α-C(sp^2)–H functionalization of α,β-unsaturated carbonyls.[9] However, the combinations of these latent enolates with metal-activated electrophiles are rare,[10] and an enantioselective variant is still unknown.

In 2003, Krische and co-workers reported an intramolecular α-C(sp^2)–H allylic alkylation of α,β-unsaturated ketones through the merger of palladium catalysis and Lewis base activation (Scheme 1C).[10c] The same strategy was later on extended to an intermolecular variant of the same reaction by Huang and co-workers (Scheme 1C).[10a] Despite the exciting potential of these reactions, an enantioselective α-C(sp^2)–H allylic alkylation of α,β-unsaturated carbonyl compounds under transition metal catalysis is yet to be accomplished.[11]



Scheme 1 Catalytic C(sp^2)–H allylic alkylation.

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India. E-mail: sm@iisc.ac.in; Fax: +91-80-2360-0529; Tel: +91-80-2293-2850

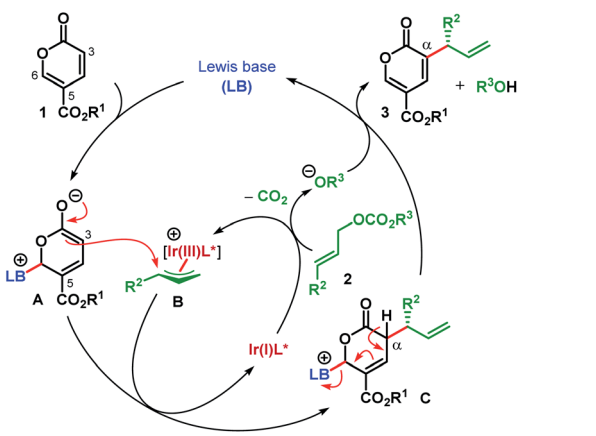
† Electronic supplementary information (ESI) available: Experimental details, characterization and analytical data. See DOI: 10.1039/d0sc06208a

With our interest in catalytic asymmetric AA reactions[6c,12] we sought to address this long-standing problem. Since C(sp^2)–H AA reactions do not generate any stereocenter at the nucleophilic site, an enantioselective version of this reaction must necessarily arise from the prostereogenicity of the electrophilic partner. As iridium-catalyzed AAS reactions with unsymmetrical allylic electrophiles typically lead to the formation of branched products predominantly,[3] we surmised that π-allyl-Ir would be a suitable electrophilic partner for the latent enolate generated from α,β-unsaturated carbonyl compounds.

While contemplating the choice of α,β-unsaturated carbonyl compounds, we were attracted to the report by Liu and Zu on the enantioselective cross-vinylogous Rauhut–Currier (RC) reaction[13] of methyl coumalate with α,β-unsaturated aldehydes under iminium activation.[14] Coumalates are an interesting class of electron-deficient heterocycles, which can act as synthetic precursors for various useful frameworks including electron-deficient arenes and heterocycles.[15] Whereas coumalates are well-known for their use as electron-deficient dienes in various cycloaddition reactions,[16] their applications as latent enolate are scarce. Besides Zu's report, the only other example of the usage of coumalate esters as latent enolate was recently documented in the form of a Morita–Baylis–Hillman (MBH) reaction by Thorimbert, Dechoux and co-worker.[17]

Coumalates (**1**) are known to be electrophilic at their C6 position[18] and could suffer nucleophilic addition by a Lewis base (LB) to generate a dienolate **A** (Scheme 2).[14,17] Although **A** is nucleophilic both at C3 (α-) and C5 (γ-), attack to the *in situ* generated π-allyl-Ir intermediate **B** was expected to take place from the sterically favored C3 of **A**. This enantiodetermining carbon–carbon bond formation would result in the formation of the intermediate **C**. Subsequent removal of the α-proton and elimination of LB from **C** would furnish the desired α-allylic alkylation product **3**.

We envisioned that the enantioinduction in this C(sp^2)–H AA reaction could be achieved either by using a chiral Lewis base (LB) or a chiral ligand (L*) on Ir(I) or both. Combining two different catalytic modes in cooperative fashion has emerged as a very effective strategy for reaction development during the past decade[19] and has also been applied to Ir-catalyzed AA reactions with great effect.[20]

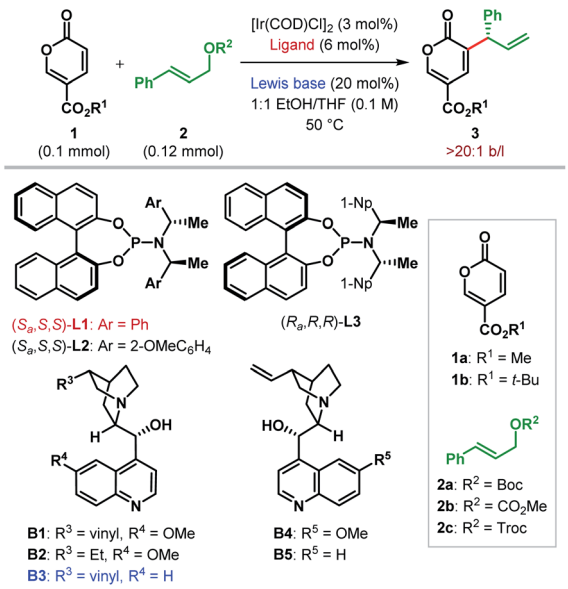


Scheme 2 Cooperative catalytic hypothesis for the α-C(sp^2)–H allylic alkylation of coumalates.

Results and discussion

Accordingly, we began our investigation with the optimization of chiral ligand and Lewis base for the reaction between methyl coumalate **1a** and *tert*-butyl cinnamyl carbonate **2a** at 50 °C (Table 1).[21] In the presence of a catalytic amount of DABCO (20 mol%) as the Lewis base, 3 mol% of $[Ir(COD)Cl]_2$ along with 6 mol% of Feringa's phosphoramidite ligand **L1**[22] was first

Table 1 Optimization of reaction parameters[a]



Entry	1	2	L	Lewis base	*t* [h]	3	Yield[b] [%]	er[c]
1[d]	**1a**	**2a**	**L1**	DABCO	40	**3aa**	11	88 : 12
2	**1a**	**2a**	**L1**	DABCO	72	**3aa**	10	92.5 : 7.5
3	**1a**	**2b**	**L1**	DABCO	48	**3aa**	16	95 : 5
4	**1a**	**2b**	**L1**	**B1**	48	**3aa**	14	97 : 3
5	**1a**	**2c**	**L1**	**B1**	60	**3aa**	32	97 : 3
6	**1a**	**2c**	**L1**	**B2**	72	**3aa**	21	97 : 3
7	**1a**	**2c**	**L1**	**B3**	72	**3aa**	42	98 : 2
8	**1a**	**2c**	**L1**	**B4**	72	**3aa**	38	97 : 3
9	**1a**	**2c**	**L1**	**B5**	72	**3aa**	25	97 : 3
10	**1a**	**2c**	**L1**	—	48	**3aa**	<5	—
11	**1b**	**2c**	**L1**	**B3**	72	**3bc**	44	98 : 2
12	**1b**	**2c**	**L2**	**B3**	72	**3bc**	42	98 : 2
13	**1b**	**2c**	**L3**	**B3**	72	**3bc**	40	3 : 97
14[e]	**1b**	**2c**	**L1**	**B3**	72	**3bc**	51	97.5 : 2.5
15[f]	**1b**	**2c**	**L1**	**B3**	72	**3bc**	54	97 : 3
16[g]	**1b**	**2c**	**L1**	**B3**	72	**3bc**	53(51)	97 : 3

[a] The catalyst was prepared *via* *n*-$PrNH_2$ activation. [b] Yields were determined by ^1H NMR spectroscopy with mesitylene as internal standard. Isolated yields are given in the parentheses. [c] Enantiomeric ratios (er) were determined by HPLC analysis on a chiral stationary phase. [d] EtOH was used as the solvent. [e] With 1.5 : 1 ratio of **1b** and **2c**. [f] With 2 : 1 ratio of **1b** and **2c**. [g] With 2 : 1 ratio of **1b** and **2c**, and $MeOCH_2CH_2OH$/THF (1 : 1) as the solvent.

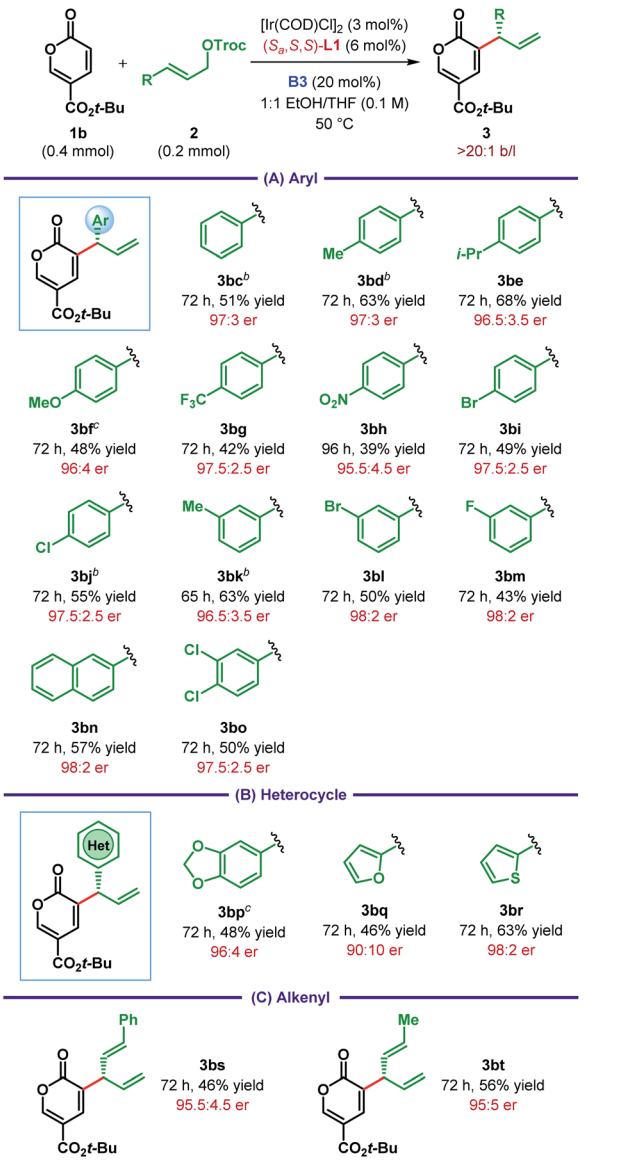
employed as the pre-catalyst for a reaction in EtOH. To our delight, the desired α-C(sp^2)–H allylic alkylation was indeed found to take place to furnish **3aa** with promising enantioselectivity (88 : 12 er), albeit in only 11% yield (entry 1). It is important to note that the use of EtOH as the solvent is crucial, as polar aprotic solvents such as THF and 1,2-dichloroethane failed to produce any **3aa**.[21] However, a significant increase in enantioselectivity was observed in a 1 : 1 mixture of EtOH and THF, although the yield remained low (entry 2). Changing the allylic electrophile to methyl cinnamyl carbonate **2b** further improved the enantioselectivity (entry 3).

Cinchona alkaloids and their derivatives as Lewis base are known to promote MBH and RC reactions.[9,23] This fact inspired us to use quinine **B1** as a Lewis base catalyst. As anticipated, **B1** facilitated the reaction to generate **3aa** with improved er (entry 4). We realized that the low yield of the reaction, among other reasons, is due to the decomposition of **2b** to cinnamyl alcohol under the reaction conditions. With 2,2,2-trichloroethyl cinnamyl carbonate **2c** as an allylic electrophile, this decomposition was suppressed, and the product was obtained in 32% yield with the same level of enantioselectivity (entry 5).

A Lewis base screening at this point revealed cinchonidine **B3** as the optimal both in terms of the reaction efficiency and enantioselectivity (entries 6–9). Please note that the same sense of stereochemical outcome as **B1** and **B3** was observed with pseudoenantiomeric quinidine (**B4**) and cinchonine (**B5**), which shows that the phosphoramidite ligand on Ir(I) is primarily responsible for enantioinduction. However, the presence of Lewis base is essential as no product formation was observed in the absence of any Lewis base (entry 10), thereby indicating the cooperative interplay between iridium and Lewis base. The use of *tert*-butyl coumalate **1b** instead of methyl coumalate **1a**, along with **B3**, resulted in a much cleaner reaction, delivering the product **3bc** in 44% yield (entry 11). Efforts to ameliorate the reaction outcome using other phosphoramidite ligands (**L2** and **L3**) met with failure (entries 12–13). Increasing the amount of **1b** turned out to be beneficial as excess of allylic electrophile (**2**) led to considerable side reactions. A 2 : 1 ratio of **1b** and **2c** provided the best results, generating **3bc** in 54% yield and with 97 : 3 er (entry 15). A 1 : 1 mixture of 2-methoxyethanol and THF as the solvent was proven to be equally effective as 1 : 1 EtOH/THF mixture and afforded the product **3bc** with 51% isolated yield and 97 : 3 er (entry 16).

After optimizing the ligand, Lewis base and other parameters for the reaction between **1b** and **2c** (Table 1, entry 15), we chose to test the generality of our protocol for other substrate combinations. The Ir(I)/**L1** catalyst system in cooperation with the Lewis base **B3** was found to be rather general and catalyzes the enantioselective α-C(sp^2)–H allylic alkylation of coumalates **1** with a large variety of allylic carbonates **2**. As illustrated in Table 2A, *tert*-butyl coumalate **1b** smoothly underwent allylic alkylation with cinnamyl carbonates (**2c–o**) bearing either electron-donating or electron-withdrawing substituent at various positions of the aryl ring. While the enantioselectivity of the reaction was found to be independent of the electronic nature of the substituents, highly electron-deficient aryl groups (*e.g.* **2g–h**) adversely affected the yield of the reaction. In the case

Table 2 Scope of allylic carbonates in enantioselective α-C(sp^2)–H allylic alkylation of *tert*-butyl coumalate[a]



[a] Yields correspond to the isolated product after chromatographic purification. Er was determined by HPLC analysis on a chiral stationary phase. [b] Reaction in $MeOCH_2CH_2OH$/THF (1 : 1). [c] Reaction performed using 1 : 1.2 ratio of **1b** : **2**.

of *p*-methoxyphenyl substituted allylic carbonate **2f**, the product **3bf** was obtained as an inseparable mixture with unreacted **1b**.

However, switching the stoichiometry of **1b** and **2f** from 2 : 1 to 1 : 1.2 facilitated the isolation of **3bf**. For a particular substituent, very similar level of yield and enantioselectivity was observed, irrespective of its position (*meta vs. para*). Along the same line of observation, 3,4-dichlorocinnamyl carbonate **2o** afforded the product **3bo** with 97.5 : 2.5 er.

Apart from simple aryls, pharmaceutically relevant heterocycles can also be incorporated into the products. For example, dioxolane, furan and thiophene containing allylic carbonates (**2p–r**) reacted to give the corresponding products (**3bp–br**) with

good to high enantioselectivity (Table 2B). In addition, alkenyl substituted allylic carbonates (**2s–t**) were well tolerated under the optimum reaction conditions to provide the products (**3bs–bt**) as a single regioisomer with high er (Table 2C).

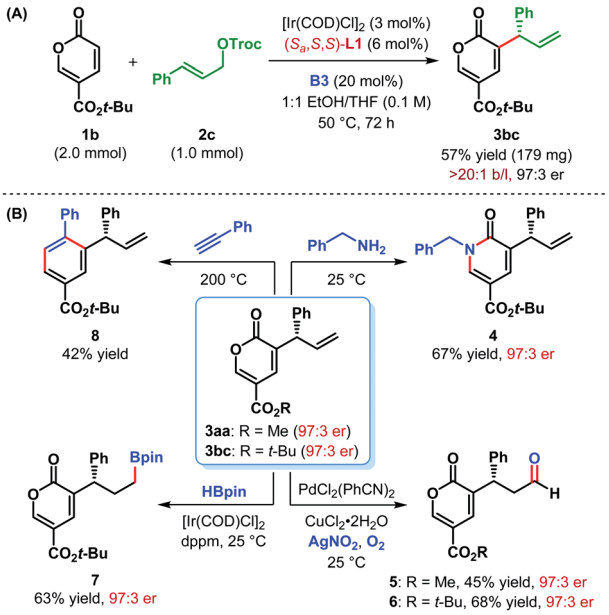
The effect of the ester substituent of coumalate was next examined (Table 3). The bulky *tert*-butyl group can be replaced with simple methyl (**1a**), isopropyl (**1c**) and benzyl (**1d**) without affecting the enantioselectivity, even though the yield of these reactions remained relatively low compared to the *tert*-butyl coumalate **1b**.

The scalability of our α-C(sp^2)–H allylic alkylation protocol was showcased by performing the reaction between **1b** and **2c** on a 1.0 mmol scale (Scheme 3A). Under the optimum reaction conditions, product **3bc** was isolated in a slightly improved yield with the same level of enantiopurity as the smaller scale reaction.

Although further investigation is required, the generally low yield of these C(sp^2)–H allylic alkylation reactions may be attributed to the possible oligomerization of coumalates under Lewis basic conditions. In addition, 2*H*-pyran-2-ones are known to undergo ring-opening and decarboxylation.[24]

The densely functionalized enantioenriched α-allylic coumalates can serve as synthetically important building blocks for electron-deficient arenes and heterocycles. In addition, the newly installed allyl unit can be transformed into other useful functionalities. For example, treatment of **3bc** with benzylamine in MeOH furnished 3-allyl-substituted 2-pyridone derivative **4** in 67% yield (Scheme 3B). The regioselective Wacker oxidation[25] of **3aa** and **3bc** provided the corresponding aldehydes **5** and **6**, respectively. The absolute configuration of **5** was previously established by Zu *et al.*[14] The stereochemistry of **6** and the other allylated products **3**, shown in Tables 2 and 3 were inferred in analogy with **5**.[21]

Ir-catalyzed hydroboration[26] of the terminal double bond of **3bc** resulted in the formation of alkyl boronate **7** in 63% yield. The 2*H*-pyran-2-one core of the coumalate esters is known to participate in [4+2]-cycloaddition reactions.[27] The 2*H*-pyran-2-one moiety present in compound **3bc** was found to undergo [4+2]-cycloaddition/decarboxylative retro-cycloaddition cascade reaction when treated with phenylacetylene to give 3-allyl *tert*-butyl benzoate **8** as a single regioisomer in 42% yield (Scheme 3B). Direct synthesis of **8** would require an enantioselective allylic alkylation of an electron-deficient arene and would be electronically disfavoured. This strategy, therefore, compliments the usual Friedel–Crafts type C(sp^2)–H allylic alkylation, which are generally favoured with electron-rich arenes.[7] Enantiopurity of **3** was preserved during all these synthetic elaborations.

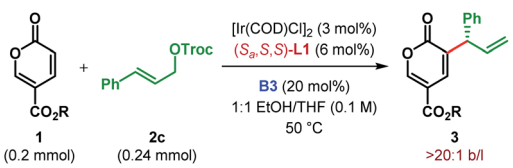


Scheme 3 (A) Scale-up of α-C(sp^2)–H allylic alkylation and (B) synthetic elaborations of α-allyl-coumalates.

Conclusions

In conclusion, we have developed the first Ir-catalyzed enantioselective allylic alkylation of an olefinic C(sp^2)–H bond – that of an α,β-unsaturated carbonyl compound, namely coumalate ester. Using linear allylic carbonates as the allylic electrophile, this reaction, cooperatively catalyzed by cinchonidine and an *in situ* generated cyclometalated Ir(I)/phosphoramidite complex, makes use of the latent enolate character of coumalate ester to introduce an allyl group at its α-position in a branched-selective manner with good to excellent enantioselectivities. This is also the first example of the enantioselective coupling of an α,β-unsaturated carbonyl-derived latent enolate with a metal-activated electrophile. The densely functionalized products allowed for the synthetic elaboration through functionalization of not only the newly installed allyl unit but also the 2*H*-pyran-2-one core of the coumalate ester. These maneuvers led to the formal C(sp^2)–H allylic alkylation of electron-deficient arene – inaccessible by direct Friedel–Crafts type allylic alkylation.

Table 3 Effect of coumalate ester substituent on enantioselective α-C(sp^2)–H allylic alkylation



Entry	R (**1**)	*t* [h]	**3**	Yield[a] [%]	er[b]
1[c]	Me (**1a**)	96	**3aa**	37	97 : 3
2[c,d]	*t*-Bu (**1b**)	72	**3bc**	51	97 : 3
3	*i*-Pr (**1c**)	72	**3cc**	44	97 : 3
4	Bn (**1d**)	88	**3dc**	40	97 : 3

[a] Isolated yield after chromatographic purification. [b] Er was determined by HPLC analysis on a chiral stationary phase. [c] Reaction in $MeOCH_2CH_2OH$/THF (1 : 1). [d] Reaction performed using 2 : 1 ratio of **1b** : **2c**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial supports from the Science and Engineering Research Board (SERB) [Grant No. EMR/2016/005045] and the Council of Scientific and Industrial Research (CSIR) [Grant No. 02(0385)/19/EMR-II] are gratefully acknowledged. R. S. thanks CSIR for a doctoral fellowship. High resolution mass spectra (HR-MS) were recorded on an equipment procured under the Department of Science and Technology (DST)-FIST grant [Grant No. SR/FST/CS II-040/2015].

Notes and references

1 R. Takeuchi and M. Kashio, *Angew. Chem., Int. Ed.*, 1997, **36**, 263–265.

2 J. P. Janssen and G. Helmchen, *Tetrahedron Lett.*, 1997, **38**, 8025–8026.

3 For selected reviews, see: (*a*) S. L. Rössler, D. A. Petrone and E. M. Carreira, *Acc. Chem. Res.*, 2019, **52**, 2657–2672; (*b*) Q. Cheng, H.-F. Tu, C. Zheng, J.-P. Qu, G. Helmchen and S.-L. You, *Chem. Rev.*, 2019, **119**, 1855–1969; (*c*) J. Qu and G. Helmchen, *Acc. Chem. Res.*, 2017, **50**, 2539–2555; (*d*) J. C. Hethcox, S. E. Shockley and B. M. Stoltz, *ACS Catal.*, 2016, **6**, 6207–6213; (*e*) P. Tosatti, A. Nelson and S. P. Marsden, *Org. Biomol. Chem.*, 2012, **10**, 3147–3163; (*f*) J. F. Hartwig and L. M. Stanley, *Acc. Chem. Res.*, 2010, **43**, 1461–1475.

4 (*a*) W.-B. Liu, C. Zheng, C.-X. Zhuo, L.-X. Dai and S.-L. You, *J. Am. Chem. Soc.*, 2012, **134**, 4812–4821; (*b*) C. Defieber, M. A. Ariger, P. Moriel and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2007, **46**, 3139–3143; (*c*) T. Ohmura and J. F. Hartwig, *J. Am. Chem. Soc.*, 2002, **124**, 15164–15165.

5 (*a*) S. L. Rössler, S. Krautwald and E. M. Carreira, *J. Am. Chem. Soc.*, 2017, **139**, 3603–3606; (*b*) J. A. Raskatov, S. Spiess, C. Gnamm, K. Brödner, F. Rominger and G. Helmchen, *Chem.–Eur. J.*, 2010, **16**, 6601–6615; (*c*) S. T. Madrahimov, D. Markovic and J. F. Hartwig, *J. Am. Chem. Soc.*, 2009, **131**, 7228–7229; (*d*) D. Markovic and J. F. Hartwig, *J. Am. Chem. Soc.*, 2007, **129**, 11680–11681. Also see 4a.

6 For selected examples of C(sp^3)–H allylic alkylation, see: (*a*) X.-J. Liu, S. Jin, W.-Y. Zhang, Q.-Q. Liu, C. Zheng and S.-L. You, *Angew. Chem., Int. Ed.*, 2020, **59**, 2039–2043; (*b*) Y. Sempere, J. L. Alfke, S. L. Rössler and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2019, **58**, 9537–9541; (*c*) R. Sarkar and S. Mukherjee, *Org. Lett.*, 2019, **21**, 5315–5320; (*d*) C.-Y. Shi, J.-Z. Xiao and L. Yin, *Chem. Commun.*, 2018, **54**, 11957–11960; (*e*) B.-B. Yue, Y. Deng, Y. Zheng, K. Wei and Y.-R. Yang, *Org. Lett.*, 2019, **21**, 2449–2452; (*f*) S. E. Shockley, J. C. Hethcox and B. M. Stoltz, *Angew. Chem., Int. Ed.*, 2017, **56**, 11545–11548; (*g*) X. Jiang and J. F. Hartwig, *Angew. Chem., Int. Ed.*, 2017, **56**, 8887–8891; (*h*) M. Bos and E. Riguet, *Chem. Commun.*, 2017, **53**, 4997–5000; (*i*) X. J. Liu and S. L. You, *Angew. Chem., Int. Ed.*, 2017, **56**, 4002–4005; (*j*) M. Zhan, R.-Z. Li, Z.-D. Mou, C.-G. Cao, J. Liu, Y.-W. Chen and D. Niu, *ACS Catal.*, 2016, **6**, 3381–3386; (*k*) J. Y. Hamilton, D. Sarlah and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2015, **54**, 7644–7647; (*l*) W. Chen, M. Chen and J. F. Hartwig, *J. Am. Chem. Soc.*, 2014, **136**, 15825–15828; (*m*) W. Chen and J. F. Hartwig, *J. Am. Chem. Soc.*, 2013, **135**, 2068–2071.

7 (*a*) H. Tian, P. Zhang, F. Peng, H. Yang and H. Fu, *Org. Lett.*, 2017, **19**, 3775–3778; (*b*) M. A. Schafroth, S. M. Rummelt, D. Sarlah and E. M. Carreira, *Org. Lett.*, 2017, **19**, 3235–3238; (*c*) Z.-L. Zhao, Q. Gu, X.-Y. Wu and S.-L. You, *Chem.–Asian J.*, 2017, **12**, 2680–2683; (*d*) Q.-L. Xu, C.-X. Zhuo, L.-X. Dai and S.-L. You, *Org. Lett.*, 2013, **15**, 5909–5911; (*e*) Q.-L. Xu, L.-X. Dai and S.-L. You, *Org. Lett.*, 2012, **14**, 2579–2581; (*f*) W.-B. Liu, H. He, L.-X. Dai and S.-L. You, *Org. Lett.*, 2008, **10**, 1815–1818.

8 For Ir-AAA of alkenyl trifluoroborate, see: J. Y. Hamilton, D. Sarlah and E. M. Carreira, *J. Am. Chem. Soc.*, 2013, **135**, 994–997.

9 (*a*) Y. Wei and M. Shi, *Chem. Rev.*, 2013, **113**, 6659–6690; (*b*) D. Basavaiah, B. S. Reddy and S. S. Badsara, *Chem. Rev.*, 2010, **110**, 5447–5674; (*c*) R. R. Huddleston and M. J. Krische, *Synlett*, 2003, 12–21.

10 (*a*) Y.-Q. Li, H.-J. Wang and Z.-Z. Huang, *J. Org. Chem.*, 2016, **81**, 4429–4433; (*b*) P. K. Koech and M. J. Krische, *J. Am. Chem. Soc.*, 2004, **126**, 5350–5351; (*c*) B. G. Jellerichs, J.-R. Kong and M. J. Krische, *J. Am. Chem. Soc.*, 2003, **125**, 7758–7759.

11 For a recent report on organocatalytic enantioselective α-C(sp^2)–H allylic alkylation of allenyl ketones, see: (*a*) Y. Hu, W. Shi, B. Zheng, J. Liao, W. Wang, Y. Wu and H. Guo, *Angew. Chem., Int. Ed.*, 2020, **59**, 19820–19824; for an indirect approach using dienolsilane, see: (*b*) W. Chen and J. F. Hartwig, *J. Am. Chem. Soc.*, 2012, **134**, 15249–15252.

12 (*a*) A. Chakrabarty and S. Mukherjee, *Org. Lett.*, 2020, **22**, 7752–7756; (*b*) R. Sarkar, S. Mitra and S. Mukherjee, *Chem. Sci.*, 2018, **9**, 5767–5772; (*c*) S. Kayal and S. Mukherjee, *Org. Lett.*, 2017, **19**, 4944–4947; (*d*) S. J. Singha Roy and S. Mukherjee, *Chem. Commun.*, 2014, **50**, 121–123.

13 (*a*) L.-C. Wang, A. L. Luis, K. Agapiou, H.-Y. Jang and M. J. Krische, *J. Am. Chem. Soc.*, 2002, **124**, 2402–2403; (*b*) S. A. Frank, D. J. Mergott and W. R. Roush, *J. Am. Chem. Soc.*, 2002, **124**, 2404–2405. For a review, see: (*c*) C. E. Aroyan, A. Dermenci and S. J. Miller, *Tetrahedron*, 2009, **65**, 4069–4084.

14 Q. Liu and L. Zu, *Angew. Chem., Int. Ed.*, 2018, **57**, 9505–9509.

15 For selected examples, see: (*a*) G. A. Kraus and S. Wang, *RSC Adv.*, 2017, **7**, 56760–56763; (*b*) T. Pfennig, J. M. Carraher, A. Chemburkar, R. L. Johnson, A. T. Anderson, J.-P. Tessonnier, M. Neurock and B. H. Shanks, *Green Chem.*, 2017, **19**, 4879–4888; (*c*) K. Liu, H.-L. Teng and C.-J. Wang, *Org. Lett.*, 2014, **16**, 4508–4511; (*d*) J. J. Lee and G. A. Kraus, *Green Chem.*, 2014, **16**, 2111–2116; (*e*) T. Guney, J. J. Lee and G. A. Kraus, *Org. Lett.*, 2014, **16**, 1124–1127; (*f*) G. A. Kraus, S. Riley and T. Cordes, *Green Chem.*, 2011, **13**, 2734–2736; (*g*) P. M. Delaney, J. E. Moore and J. P. A. Harrity, *Chem. Commun.*, 2006, 3323–3325.

16 For selected examples, see: (*a*) C. J. F. Cole, L. Fuentes and S. A. Snyder, *Chem. Sci.*, 2020, **11**, 2175–2180; (*b*) M. Saktura, P. Grzelak, J. Dybowska and Ł. Albrecht, *Org. Lett.*, 2020, **22**, 1813–1817; (*c*) X. Liang, W. Ye, W. Thor, L. Sun, B. Wang, S. He, Y.-K. Cheng and C.-S. Lee, *Org.*

Chem. Front., 2020, **7**, 840–845; (*d*) X. Gao, M. Xia, C. Yuan, L. Zhou, W. Sun, C. Li, B. Wu, D. Zhu, C. Zhang, B. Zheng, D. Wang and H. Guo, *ACS Catal.*, 2019, **9**, 1645–1654; (*e*) S. Zheng and X. Lu, *Org. Lett.*, 2009, **11**, 3978–3981; (*f*) R. A. Jones and M. J. Krische, *Org. Lett.*, 2009, **11**, 1849–1851; (*g*) C.-H. Chen and C.-C. Liao, *Org. Lett.*, 2000, **2**, 2049–2052; (*h*) B. M. Trost and S. Schneider, *Angew. Chem., Int. Ed.*, 1989, **28**, 213–215; (*i*) M. E. Jung, L. J. Street and Y. Usui, *J. Am. Chem. Soc.*, 1986, **108**, 6810–6811.

17 L. Chang, S. Thorimbert and L. Dechoux, *Org. Biomol. Chem.*, 2019, **17**, 2784–2791.

18 (*a*) D. S. Ziegler, L. Klier, N. Müller, K. Karaghiosoff and P. Knochel, *Synthesis*, 2018, **50**, 4383–4394; (*b*) L. Chang, N. Klipfel, L. Dechoux and S. Thorimbert, *Green Chem.*, 2018, **20**, 1491–1498; (*c*) L. Chang, K. Plevová, S. Thorimbert and L. Dechoux, *J. Org. Chem.*, 2017, **82**, 5499–5505; (*d*) K. Plevová, L. Chang, E. Martin, Q. Llopis, L. Dechoux and S. Thorimbert, *Adv. Synth. Catal.*, 2016, **358**, 3293–3297; (*e*) J. Agarwal, O. Bayounes, S. Thorimbert and L. Dechoux, *RSC Adv.*, 2014, **4**, 2772–2775.

19 For selected reviews, see: (*a*) J. Fu, X. Huo, B. Li and W. Zhang, *Org. Biomol. Chem.*, 2017, **15**, 9747–9759; (*b*) G. Jindal, H. K. Kisan and R. B. Sunoj, *ACS Catal.*, 2015, **5**, 480–503; (*c*) S. M. Inamdar, V. S. Shinde and N. T. Patil, *Org. Biomol. Chem.*, 2015, **13**, 8116–8162; (*d*) D.-F. Chen, Z.-Y. Han, X.-L. Zhou and L.-Z. Gong, *Acc. Chem. Res.*, 2014, **47**, 2365–2377; (*e*) Z. Du and Z. Shao, *Chem. Soc. Rev.*, 2013, **42**, 1337–1378; (*f*) A. E. Allen and D. W. C. MacMillan, *Chem. Sci.*, 2012, **3**, 633–658; (*g*) Z. Shao and H. Zhang, *Chem. Soc. Rev.*, 2009, **38**, 2745–2755.

20 For selected examples, see: (*a*) S. Singha, E. Serrano, S. Mondal, C. G. Daniliuc and F. Glorius, *Nat. Catal.*, 2020, **3**, 48–54; (*b*) Z.-C. Chen, Z. Chen, Z.-H. Yang, L. Guo, W. Du and Y.-C. Chen, *Angew. Chem., Int. Ed.*, 2019, **58**, 15021–15025; (*c*) Z.-T. He, X. Jiang and J. F. Hartwig, *J. Am. Chem. Soc.*, 2019, **141**, 13066–13073; (*d*) C. M. Pearson, J. W. B. Fyfe and T. N. Snaddon, *Angew. Chem., Int. Ed.*, 2019, **58**, 10521–10527; (*e*) X. Huo, J. Zhang, J. Fu, R. He and W. Zhang, *J. Am. Chem. Soc.*, 2018, **140**, 2080–2084; (*f*) X. Jiang, P. Boehm and J. F. Hartwig, *J. Am. Chem. Soc.*, 2018, **140**, 1239–1242; (*g*) R. He, P. Liu, X. Huo and W. Zhang, *Org. Lett.*, 2017, **19**, 5513–5516; (*h*) Y.-L. Su, Y.-H. Li, Y.-G. Chen and Z.-Y. Han, *Chem. Commun.*, 2017, **53**, 1985–1988; (*i*) X. Jiang, J. J. Beiger and J. F. Hartwig, *J. Am. Chem. Soc.*, 2017, **139**, 87–90; (*j*) L. Næsborg, K. S. Halskov, F. Tur, S. M. N. Mønsted and K. A. Jørgensen, *Angew. Chem., Int. Ed.*, 2015, **54**, 10193–10197; (*k*) S. Krautwald, D. Sarlah, M. A. Schafroth and E. M. Carreira, *Science*, 2013, **340**, 1065–1068.

21 See the ESI† for details.

22 J. F. Teichert and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2010, **49**, 2486–2528.

23 (*a*) L. A. Bryant, R. Fanelli and A. J. A. Cobb, *Beilstein J. Org. Chem.*, 2016, **12**, 429–443; (*b*) G. Masson, C. Housseman and J. Zhu, *Angew. Chem., Int. Ed.*, 2007, **46**, 4614–4628; (*c*) T. Marcelli, J. H. van Maarseveen and H. Hiemstra, *Angew. Chem., Int. Ed.*, 2006, **45**, 7496–7504.

24 M. Chia, M. A. Haider, G. Pollock, G. A. Kraus, M. Neurock and J. A. Dumesic, *J. Am. Chem. Soc.*, 2013, **135**, 5699–5708.

25 (*a*) K. E. Kim, J. Li, R. H. Grubbs and B. M. Stoltz, *J. Am. Chem. Soc.*, 2016, **138**, 13179–13182; (*b*) Z. K. Wickens, B. Morandi and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2013, **52**, 11257–11260.

26 Y. Yamamoto, R. Fujikawa, T. Umemoto and N. Miyaura, *Tetrahedron*, 2004, **60**, 10695–10700.

27 (*a*) G. A. Kraus, G. R. Pollock Iii, C. L. Beck, K. Palmer and A. H. Winter, *RSC Adv.*, 2013, **3**, 12721–12725; (*b*) J. J. Lee and G. A. Kraus, *Tetrahedron Lett.*, 2013, **54**, 2366–2368.