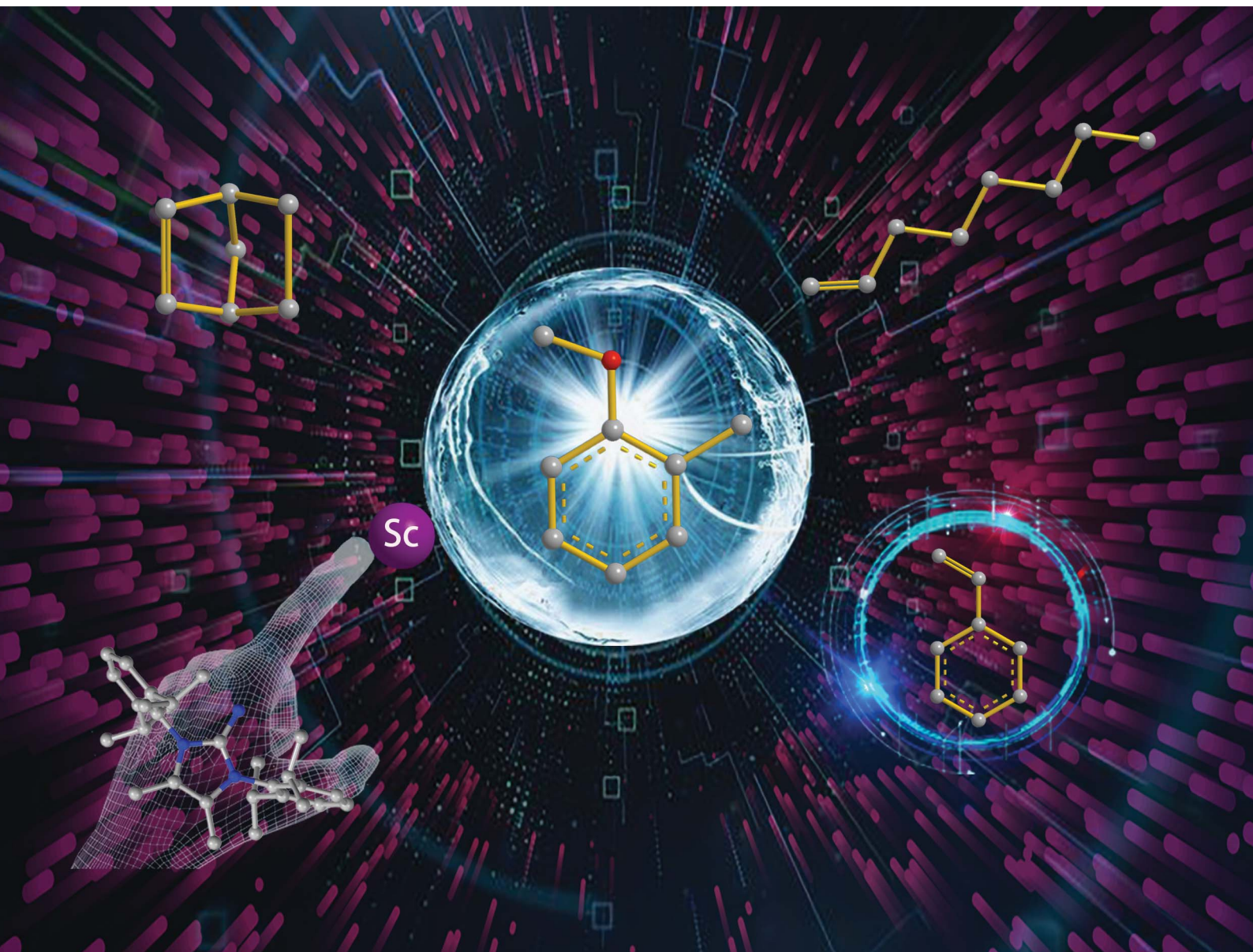


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Regioselective C–H alkylation of anisoles with olefins by cationic imidazolin-2-iminato scandium(III) alkyl complexes†

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A new type of rare-earth alkyl complexes supported by monoanionic imidazolin-2-iminato ligands were synthesised and structurally characterised by X-ray diffraction and NMR analyses. The utility of these imidazolin-2-iminato rare-earth alkyl complexes in organic synthesis was demonstrated by their performance in highly regioselective C–H alkylation of anisoles with olefins. With as low as 0.5 mol% catalyst loading, various anisole derivatives without *ortho*-substitution or 2-methyl substituted anisoles reacted with several alkenes under mild conditions, producing the corresponding *ortho*-Csp²-H and benzylic Csp³-H alkylation products in high yield (56 examples, 16–99% yields). Control experiments revealed that rare-earth ions, ancillary imidazolin-2-iminato ligands, and basic ligands were crucial for the above transformations. Based on deuterium-labelling experiments, reaction kinetic studies, and theoretical calculations, a possible catalytic cycle was provided to elucidate the reaction mechanism.

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Introduction

Anisole and its derivatives are frequently occurring structural units in many pharmaceuticals, natural products, and functional materials.¹ The development of succinct and efficient approaches for the production of anisoles and their derivatives has therefore attracted significant interest in the past few decades.^{2–5} In particular, the C–H alkylation of anisoles with alkenes represents one of the most atom-efficient and environmentally benign synthetic routes.^{2–4} Although the well-known Friedel–Crafts type reactions of anisoles with alkenes *via* carbocation intermediates have been extensively investigated with Lewis and Brønsted acids as the catalysts, the control of regioselectivity has been problematic; a mixture of *ortho*- and *para*-regioisomers are always concomitantly generated in the reaction process (Scheme 1a).² The metal–organic complex-mediated C–H alkylation of anisoles with alkenes *via* C–H activation is an alternative pathway to obtain alkylated anisoles.^{3,4} However, owing to the weak interaction between late-transition metals and the ether moiety, the use of transition metal-based catalysts in such transformations is fruitless.⁶ In contrast, rare-earth organic complexes benefit from their unique chemical properties and have been successfully

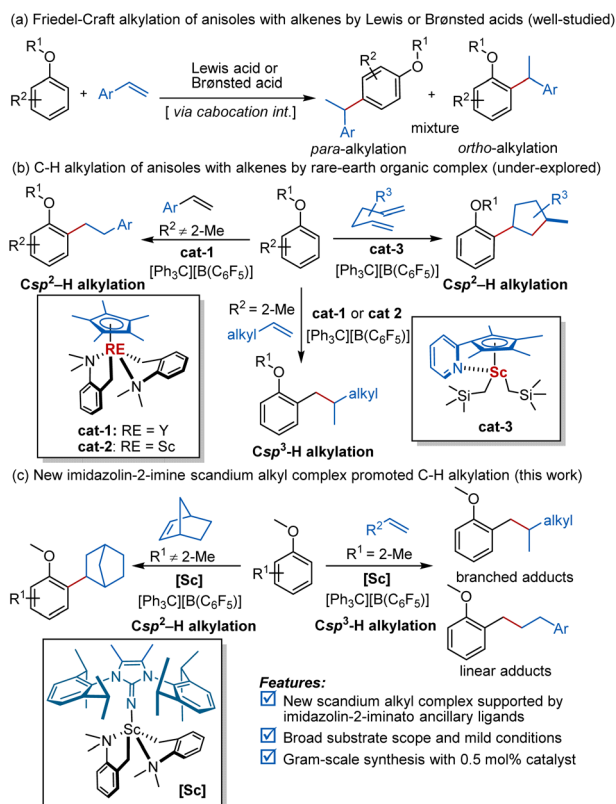
disclosed to be efficient promoters by Hou and others.³ Taking advantage of the strong oxophilicity of rare-earth metal ions and their high activity towards olefin migration insertion, Hou and co-workers first accomplished intermolecular and intramolecular C–H bond addition of anisoles to various alkenes with cationic half-sandwich yttrium(III) or scandium(III) alkyl complexes as the catalysts (**cat-1** and **cat-2**; Scheme 1b, left).^{3a,c} In 2019, the group of Chen extended alkene substrates to 1,5-dienes and 1,6-dienes under the influence of cationic 2-picoline-tether-half-sandwich scandium(III) alkyl catalyst (**cat-3**). The cyclisation/hydroarylation reaction of aromatic ethers took place successfully, delivering several anisole derivatives in good yield with high regio- and diastereoselectivity (Scheme 1b, right).^{3b} Overall, despite such impressive advances in this field, there is still ample room for improvement in terms of new catalysts and product distribution.

Rare-earth organic complexes have been emerging as competent catalysts for several important organic transformations,⁷ including C–H functionalisation⁸ and polymerisation reactions.⁹ The development of this area, in particular C–H functionalisation, heavily relies on the use of cyclopentadienyl (Cp) and its analogues as ancillary ligands. The quest for alternatives of Cp and related aromatic ligands is of great interest and significance, but has met with limited success to date.¹⁰ Among them, *N*-heterocyclic iminato (NHI) ligands, for example, monoanionic imidazolin-2-iminato groups, have been successfully investigated as Cp-analogous ligands by the groups of Tamm, Inoue, Eisen, and others.¹¹ Structurally, imidazolin-2-iminato groups are isolobally related to the Cp moiety. As shown in Scheme 2a, the two mesomeric structures

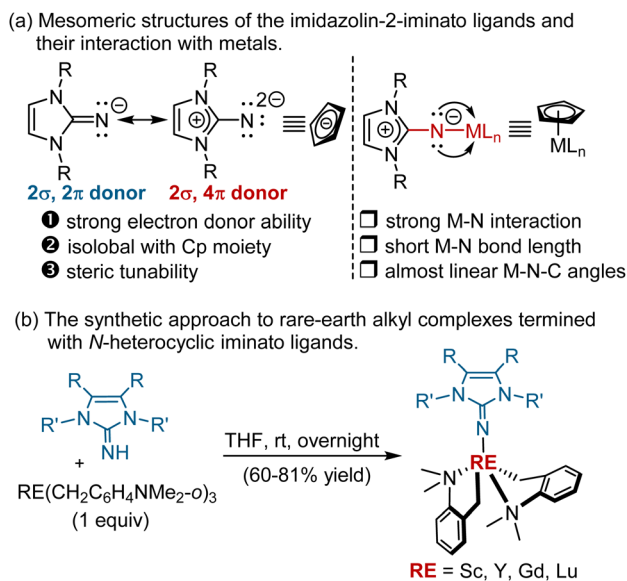
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† Electronic supplementary information (ESI) available: ¹H, ¹³C{¹H} and ¹⁹F{¹H} NMR. X-ray crystallographic data. CCDC [2219241–2219245]. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2sc06725k>





Scheme 1 Catalytic synthesis of anisoles derivatives through C–H alkylation of anisoles with alkenes.



Scheme 2 (a) The structural features of *N*-heterocyclic iminato ligands; and (b) synthetic method for their rare-earth alkyl complexes.

of the imidazolin-2-iminato groups indicated that they can serve as strong 2σ,4π-electron N-donor ligands (Scheme 2a).¹² Thanks to their strong electron donation and steric tunability, the related imidazolin-2-iminato rare-earth alkyl complexes exhibit

high activity toward several reactions, including hydroamination,¹³ hydrosilylation,¹³ nucleophilic addition,¹⁴ and polymerisation.¹⁵ Nevertheless, it remains unclear whether imidazolin-2-iminato rare-earth alkyl complexes could be used in C–H activation. Motivated by the distinct selectivity and functional group tolerance frequently shown in rare-earth mediated C–H functionalisation⁸ and elegant work¹¹ from Tamm's group, we envisaged that the judicious choice of rare-earth ions and basic ligands, as well as modification of imidazolin-2-iminato supporting ligands, may have the potential to achieve C–H alkylation with olefins. Herein, we wish to disclose our preliminary results along this line. An array of imidazolin-2-iminato rare-earth alkyl complexes were synthesised and structurally characterised by X-ray diffraction and NMR analyses. The cationic imidazolin-2-iminato scandium(III) alkyl complex was eventually identified as an efficient catalyst for highly regioselective C–H alkylation of anisole with *ortho*-Csp²-H and 2-methylanisole with Csp³-H (0.5–10 mol% catalyst loading, 56 examples, 16–99% yield). Notably, in comparison with cationic half-sandwich rare earth alkyl catalyst, a different catalytic performance was observed with these newly designed rare-earth metal complexes obtained from the reaction of 2-methylanisoles with styrenes.^{3a} In addition, a possible catalytic cycle has been provided to understand the reaction mechanism based on deuterium-labelling experiments, reaction kinetic studies, and DFT calculations.

Results and discussion

To validate the feasibility of the hypothesis, we first prepared a set of imidazolin-2-iminato rare-earth alkyl complexes by acid–base reaction of homoleptic tris(aminobenzyl) rare-earth complex RE(CH₂C₆H₄NMe₂-*o*)₃ and 1 equivalent of imidazolin-2-imine¹⁶ in THF at room temperature for 12 h (Scheme 2b). The molecular structure of **Sc-1**, **Sc-2**, **Y-1**, and **Gd-1** were established by single crystal X-ray diffraction analysis. As shown in single crystal structures, extremely short metal–nitrogen bonds [Sc–N: 1.956(4) Å, 1.971(3) Å, Y–N: 2.104(2) Å, Gd–N: 2.147(2) Å] and almost linear M–N–C angles (178.1–178.9°) were observed.¹⁷ To better understand the nature of the Sc–N bond, the bond order, localised molecular orbitals, and canonical molecular orbitals analysis were performed with Multiwfn software (see ESI† for more details). As depicted in Fig. 1a, the calculated Wiberg bond order of Sc–N is 1.36,¹⁸ indicating a strong interaction between the N atom of NHI and the scandium(III) ion. The decomposing Mayer bond order (MBO) analysis shows that one σ and two π orbitals contribute to the Sc–N bond. The molecule orbital analysis of **Sc-1** also disclosed that except for the existence of one σ-bond, two p orbitals of the N atom in NHI form two π bonds with two d orbitals of the Sc ion, respectively, providing further evidence for their capability of acting as 2σ,4π-electron donors (Fig. 1b–d). The calculated ADCH charges suggested the charge donation from the NHI to the scandium(III) centre is –0.91 (for more details, see ESI†).

To investigate the catalytic activity of the newly designed imidazolin-2-iminato rare earth alkyl complexes, we conducted anisole Csp²-H alkylation and 2-methylanisole benzyl Csp³-H



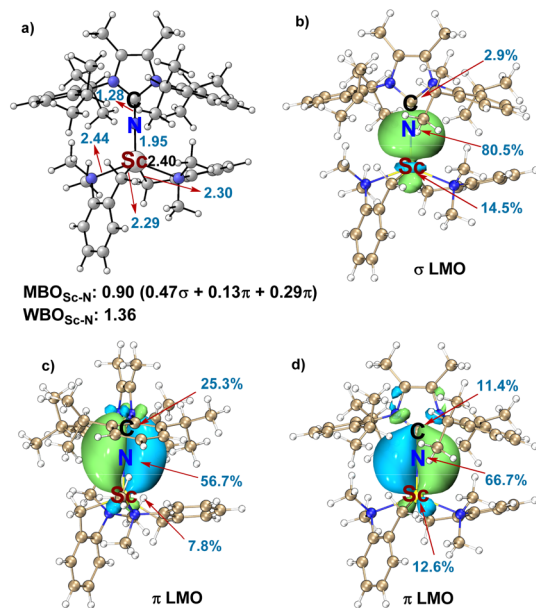


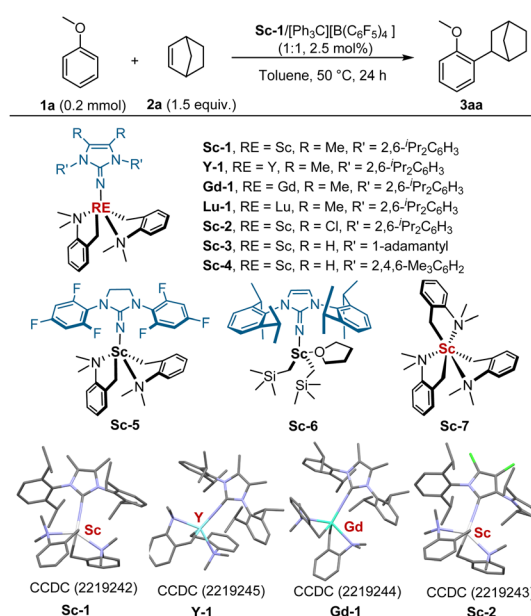
Fig. 1 The Mayer bond order (MBO), Wiberg bond order (WBO), and the localised molecular orbitals of σ and π bond between the Sc and N atoms in the catalyst **Sc-1** (isovalue = 0.02).

alkylation with alkenes. Initially, the reaction of methyl phenyl ether (**1a**) with norbornene (**2a**) was selected as the model reaction for optimisation. As summarised in Table 1, the rare-earth ions displayed a significant effect on the activity of catalysts. With 2.5 mol% imidazolin-2-iminato scandium bis(aminobenzyl) complex **Sc-1** as the catalyst, the reaction of **1a** and **2a** underwent well in toluene at 50 °C for 24 h, affording the corresponding *ortho*-alkylation product **3aa** in 99% yield (Table 1, entry 1). In stark contrast, no reaction was detected for its analogues, such as yttrium (**Y-1**), gadolinium (**Gd-1**), or lutetium (**Lu-1**) (entry 2). The effect of ligand structure on catalytic activity was examined. Changing 4,5-dimethyl groups on the skeleton of the imidazolin-2-imine ring to 4,5-dichloride presented comparable activity (entry 3, 99% yield). Decreasing the steric hindrance of the aromatic group on nitrogen atoms from 2,6-*i*-Pr₂ to 2,4,6-Me₃ or replacing 2,6-*i*-Pr₂C₆H₃ with 1-adamantyl substitution led to no product. No reaction was observed with 1,3-bis(2,4,6-trifluorophenyl)imidazolidin-2-imine-derived **Sc-5** (entry 4). **Sc-6** with bis(noesityl) [CH₂Si(CH₃)₃] basic ligand also performed well with 99% yield (entry 5).¹⁹ Switching **Sc-1** to tris(aminobenzyl) scandium(III) **Sc-7** resulted in an obvious decrease in yield (entry 6). Performing the reaction without [Ph₃C][B(C₆F₅)₄] led to a full loss of activity (entry 7). Running the reaction without **Sc-1** resulted in an obvious decrease in yield (entry 8). These results suggested that the cationic imidazolin-2-iminato scandium(III) alkyl complex was probably the real catalytic active species, and the presence of imidazolin-2-iminato ligand was crucial for the high activity observed. Next, other reaction parameters were studied (for more details, see ESI†). It was found that the reaction took place well in *n*-hexane, and 86% yield was obtained (entry 9). The coordinative solvents, for example, THF, inhibited the reaction (entry 10). When the

reaction was carried out at a higher temperature (70 °C), an excellent yield was obtained (entry 11). A further decrease in temperature to 40 °C led to reduced yield (entry 12, 88% yield). Performing the reaction with 2 mol% of catalyst provided a slightly lower yield (91% vs. 99%). Further decrease in the catalyst loading to 1 mol% led to severe erosion in yield (entries 13, 47% yield).

With the optimum reaction conditions in hand, we assessed the reactions of norbornene with various anisoles in the presence of **Sc-1** (Scheme 3). Anisoles with different substituents at the *para*- and *meta*-position of the phenyl ring were all compatible in the current system, yielding the related *ortho*-alkylation products **3aa-3ia** in 86–99% yields. Halide atoms (F, Cl, Br, I) at the *para*-position of the phenyl ring were retained

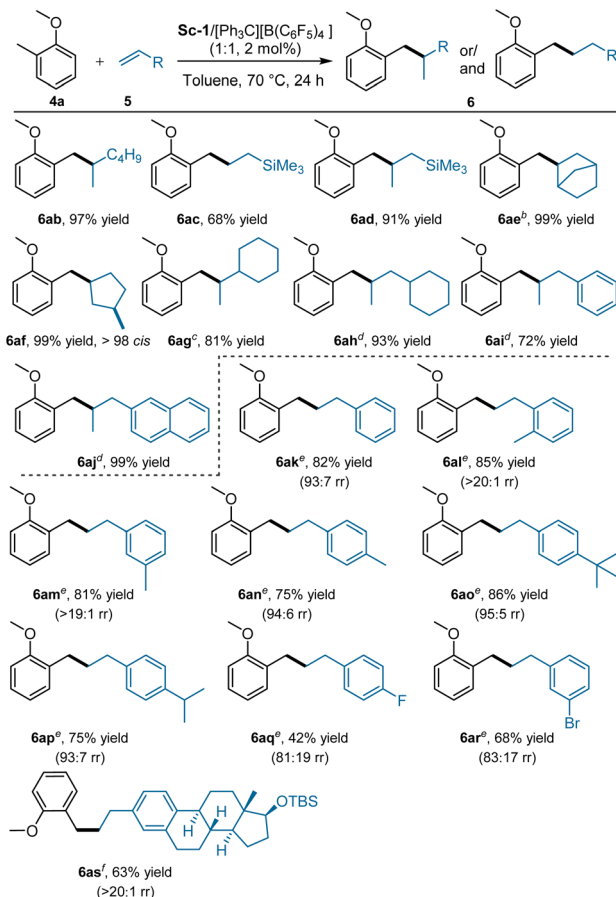
Table 1 Screening of the reaction conditions of anisole **1a** with norbornene **2a**^a



Entry	Deviations	Yield (%) ^b
1	None	99 (99)
2	10 mol% Y-1 , Gd-1 or Lu-1	NR
3	10 mol% Sc-2	99
4	10 mol% Sc-3 , Sc-4 or Sc-5	NR
5	10 mol% Sc-6	99
6	10 mol% Sc-7	37
7	No [Ph ₃ C][B(C ₆ F ₅) ₄]	NR
8	No Sc-1	30
9	<i>n</i> -hexane	86
10	THF	NR
11	70 °C	94 (94)
12	40 °C	88
13	2 mol% Sc-1	91 (90)
14	1 mol% Sc-1	47 (45)

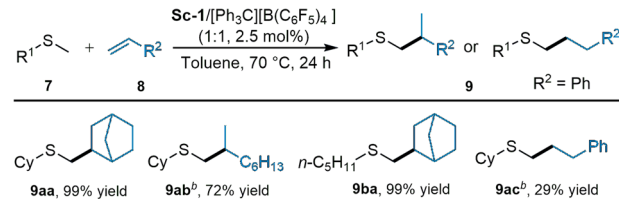
^a Standard conditions: **Sc-1**/[Ph₃C][B(C₆F₅)₄] (1 : 1, 2.5 mol%), **1a** (0.20 mmol), **2a** (0.30 mmol) in toluene at 50 °C for 24 h. ^b Yield was determined by ¹H NMR with C₂H₂Br₄ as an internal standard. Yield in brackets refers to isolated yield.



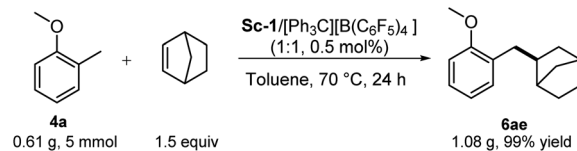


Scheme 5 Substrate scope of alkenes. ^aUnless otherwise noted, all reactions were performed with Sc-1/[Ph₃C][B(C₆F₅)₄] (1 : 1, 2 mol%), 4a (0.20 mmol), 5 (0.60 mmol) in toluene (0.5 mL) at 70 °C for 24 h. The yield of isolated product. ^b0.5 mol% catalyst. ^c5 mol% catalyst. ^d10 mol% catalyst. ^eRun with 10 mol% catalyst, 4a (0.10 mmol), 5 (0.15 mmol). Yield of isolated linear product. ^fCarried out with 10 mol% catalyst, 4a (0.15 mmol), 5 (0.10 mmol).

Next, diverse alkenes were evaluated with 2-methyl substituted anisole (4a). Alkyl-substituted alkenes, such as 1-hexene, allyltrimethylsilane, and norbornene, were all suitable, affording branched benzyl Csp³-H alkylation products (6ab, 6ad, and 6ae) in 91–99% yields (Scheme 5). Notably, the use of vinyltrimethylsilane generated the linear product 6ac in 68% yield due to the ability of silicon to aid the stabilisation of negative charge.²¹ In the case of 1,5-hexadiene, continuous 2,1-insertion resulted in hydroalkylation and cyclisation product 6af in 99% yield with >98 *cis*. Vinyl cyclohexane was subjected to the reaction, branched product 6ag was produced in 81% yield. The present reaction was applicable for allyl cyclohexane, allylbenzene, and 2-allylnaphthalene as well, giving the corresponding products 6ah–6aj in 72–99% yields. In Hou's work,^{3a} no reaction of 2-methylanisole with styrene occurred in the presence of a half-sandwich rare-earth complex. To our delight, styrene and its derivatives were feasible in the current reaction system, and linear products were generated as the major products with a variable amount of branched adducts.²¹ As shown in Scheme 5, the bottom part, *ortho*-, and *meta*-methyl



Scheme 6 Substrate scope of sulfides. ^aUnless otherwise noted, all reactions were performed with Sc-1/[Ph₃C][B(C₆F₅)₄] (1 : 1, 2.5 mol%), 7 (0.20 mmol), 8 (0.60 mmol) in toluene (0.5 mL) at 70 °C for 24 h. The yield of isolated product. ^b10 mol% catalyst, 7a (1.0 mmol), 8 (0.20 mmol).



Scheme 7 Gram-scale synthesis of 6ae.

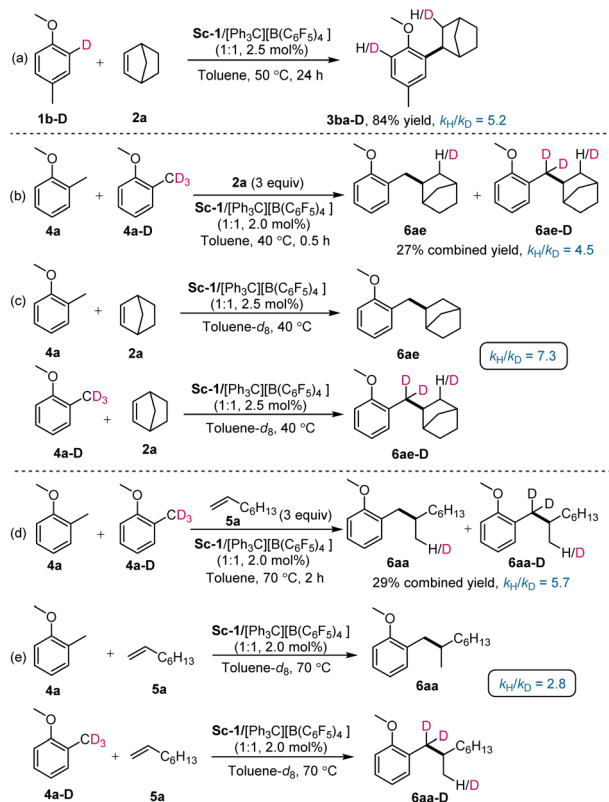
substituted styrenes provided higher yield than *para*-substituted ones due to the formation of less amount of branched by-products (85 and 81% yield vs. 75% yield). Relatively lower yields (6aq: 42% yield; 6ar: 68% yield) were afforded for the reaction of styrenes with fluoro or bromine groups than those of other alkyl groups. Olefins derived from estradiol also transformed into the related product 6as in moderate yield (63%).

In addition, sulfides were feasible as well in the current reaction system.²² As shown in Scheme 6, high yields (9aa: 99% yield; 9ba: 99% yield) were obtained for the reaction of cyclohexyl(methyl)sulfane and methyl(pentyl)sulfane with norbornene. Vinyl cyclohexane converted into the related branched product 9ab with 72% yield. The reaction of styrene afforded the linear product 9ac in low yield (29%).

To further demonstrate the synthetic utility of this protocol, a gram-scale reaction was conducted. As shown in Scheme 7, the reaction of 5 mmol of 4a with 1.5 equivalents of 2a in the presence of 0.5 mol% of Sc-1 proceeded smoothly, furnishing the corresponding benzyl Csp³-H alkylation product 6ae in 99% isolated yield (1.08 g) (Scheme 7).

To gain further insights into the mechanism of Csp²-H alkylation of anisole and benzyl Csp³-H alkylation of 2-methylanisole, a series of deuterium-labelling and kinetic studies were carried out. Intramolecular KIE experiment of deuterium-labelled 4-methyl[2-D]anisole (1b-D) with norbornene (2a) showed a significant kinetic isotope effect (KIE) value of 5.2 (Scheme 8a), indicating that Csp²-H cleavage of anisole might be involved in the turnover limiting step. In Hou's work, an intramolecular kinetic isotopic effect was not observed ($k_{\text{H}}/k_{\text{D}} = 1$) in the reaction with styrene.^{3a} Two sets of intermolecular KIE experiments of 2-methylanisole and 1-methoxy-2-(methyl-*d*₃)benzene react with norbornene or 1-octene mixed in 1:1:3 molar ratio showed a significant kinetic isotope effect (KIE) value of 4.5 and 5.7, respectively (Scheme 8b and 8d). Two sets



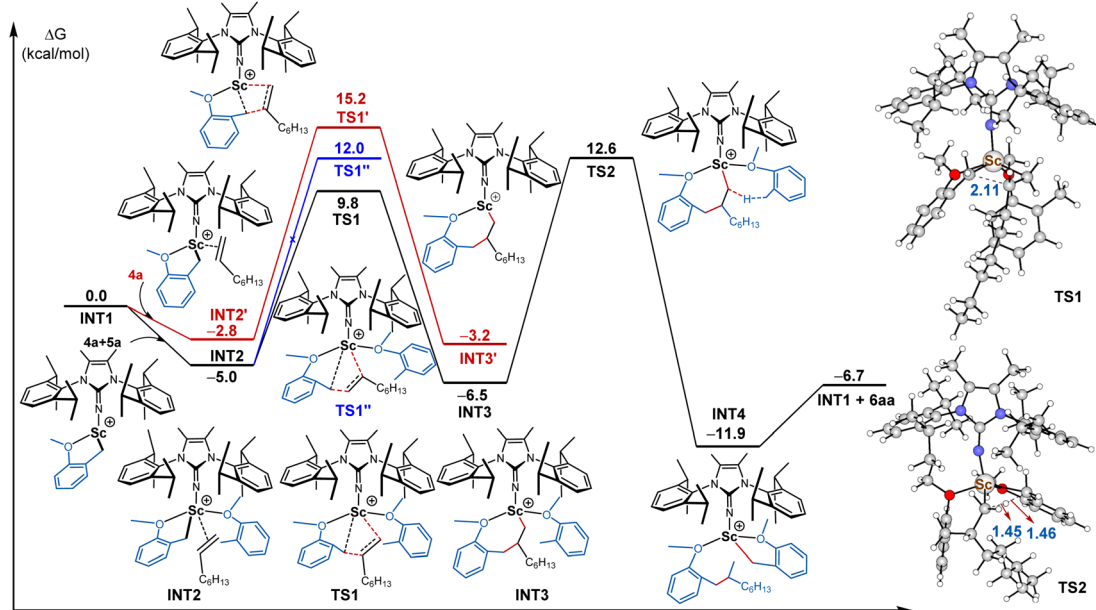


Scheme 8 Deuterium-labelling experiments.

of parallel reactions were conducted and KIE values of 7.3 and 2.8 were observed (Scheme 8c and 8e). The above outcomes suggested that benzyl Csp³-H cleavage of 2-methylanisole might be involved in the turnover-limiting step as well. In addition, we measured the rate concentration dependences of 2-

methylanisole (**4a**), 1-octene (**5a**), and catalyst precursor **Sc-1**. It was found that the reaction showed a first-order rate dependence on the concentration of **4a** and the catalyst. Interestingly, the concentration of **5a** also affected the reaction rate, an approximate first-order rate (0.75) dependence on the **5a** concentration was observed. Overall, the reaction rate was affected by the concentration of 2-methylanisole (**4a**), 1-octene (**5a**), and the catalyst precursor **Sc-1**.

To understand the reaction mechanism, theoretical calculations were performed by using **Sc-1** in the formation **6aa**. The detailed results, including Gibbs free energy profiles and structures, are summarised in Fig. 2. Initially, the catalyst precursor **Sc-1** reacted with [Ph₃C][B(C₆F₅)₄] to generate the corresponding cationic scandium alkyl species, which was confirmed by ¹H NMR analysis.²³ The coordination of the methoxy group of **4a** to scandium(III) provided the cationic scandium species, followed by selective deprotonation at benzylic position afforded the five-membered metallacycle intermediate **INT1** through σ -bond metathesis, which was thought to be the real catalytic active species. According to the energy profile, the pathway involving another 2-methylanisole *via* **TS1** (9.8 kcal mol⁻¹) was more favoured than the other pathway *via* **TS1'** (15.2 kcal mol⁻¹).²⁴ Then, the simultaneous coordination of **INT1** with another **4a** and 1-octene (**5a**) furnished **INT2**, which subsequently underwent 1,2-insertion of **5a** into the Sc-C bond in **INT2** to give rise to intermediate **INT3** *via* the transition state **TS1**. This process needed to overcome an energy barrier of 9.8 kcal mol⁻¹. In contrast, the 2,1-insertion of 1-octene into the Sc-C bond in **INT2** was unfavoured in terms of the energy barrier (12.0 kcal mol⁻¹ *vs.* 9.8 kcal mol⁻¹). In comparison, the DFT calculation suggested that the energy barrier of 1,2-insertion of styrene into the Sc-C bond was slightly higher than that of 2,1-insertion (10.9 kcal mol⁻¹ *vs.*

Fig. 2 Energy profile for the regioselective benzylic Csp³-H alkylation of **4a** with **5a**.

11.6 kcal mol⁻¹, see ESI† for more details). The above results provide a rational explanation for the regioselectivity observed in experimental studies in Schemes 4 and 5. Upon activating the benzylic Csp³-H bond of another molecule **4a**, intermediate **INT4** was generated with an activation barrier of 12.6 kcal mol⁻¹. Finally, **INT4** liberated the desired product **6aa** and regenerated catalytic species **INT1**. Although the turnover limiting step was identified to be the Csp³-H activation step, the activation barriers *via* **TS1** and **TS2** were similar. Therefore, the concentration of alkene substrate had an obvious effect on the reaction rate as well, which was in agreement with kinetic results. In addition, the calculated KIE value (k_H/k_D) was 3.7, which was consistent with the KIE experimental result.

Next, the reaction of 1,4-dimethoxy-2-methylbenzene (**4i**) with 1-octene (**5a**) was studied by DFT calculations to further clarify the regioselectivity (see ESI† for more details). The results indicated that the Csp³-H activation pathway is more favourable than the Csp²-H activation pathway for the 1,4-dimethoxy-2-methylbenzene kinetically and thermodynamically. Therefore, only the Csp³-H alkylation product was obtained in the current reaction system.

Conclusions

A new type of imidazolin-2-iminato rare earth alkyl complexes was prepared and successfully employed as competent catalysts for C-H alkylation of anisoles and 2-methylanisoles with various alkenes. A series of anisole derivatives were obtained under mild conditions with high regioselectivity and yield. The experimental results indicated that the activation of the benzylic Csp³-H bond is preferred to that of *ortho*-Csp²-H in an aromatic ring. Rare-earth ions, ancillary imidazolin-2-iminato ligands, base ligands, and borate play a significant role in the titled transformations. Based on deuterium-labelling experiments, reaction kinetic studies, and DFT calculations, a catalytic cycle along with possible working modes were provided under the reaction mechanism. The development of chiral imidazolin-2-iminato rare earth alkyl complexes and their further utility in other related C-H alkylation reactions are in progress.²⁵

Data availability

The data supporting this article has been uploaded as part of the ESI.†

Author contributions

S. Y. Wang performed experiments and prepared the ESI† and paper. C. H. Zhu repeated some experiments. L. C. Ning carried out the DFT calculations. D. W. Li helped with crystal growth. X. M. Feng and S. X. Dong supervised the project and polished the manuscript and ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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