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铑(III)催化的非活化烯烃与 α-重氮羰基化合物的对映选择性烯丙位 C—H 键烷基化反应

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摘要 报道了铑(III)催化的非活化烯烃与 α-重氮羰基化合物的对映选择性烯丙位 C—H 键烷基化反应, 能够高效地获得相应手性产物, 其产率达到 77%, 对映选择性为 92%, B/L(分支/线性)选择性为＞10∶1. 该反应具有原子经济性与步骤经济性等优点, 能在温和条件下实现非活化烯烃向高附加值手性产物的直接转化, 为不对称烯丙位 C—H 键官能化提供了有效策略.

关键词 C—H 键活化; 烯丙位不对称烷基化; 铑(III)催化; 重氮化合物

Rhodium(III)-Catalyzed Enantioselective Allylic C—H Alkylation of Unactivated Alkenes with α-Diazocarbonyl Compounds

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Abstract Direct enantioselective allylic C—H functionalization has emerged as a powerful strategy for the asymmetric synthesis of highly valuable chiral products. Herein, a Rh(III)-catalyzed enantioselective allylic C—H alkylation of unactivated alkenes with α-diazo carbonyl compounds is described, enabling direct access to chiral products with high efficiency (up to 77% yield, 92% *ee*, and ＞10∶1 B/L (branched/linear) selectivity). This atom- and step-economical protocol directly converts simple, unactivated substrates into valuable enantioenriched products under mild conditions, providing an efficient catalytic system for asymmetric allylic C—H functionalization.

Keywords C—H bond activation; asymmetric allylic alkylation; Rh(III)-catalysis; diazo compounds

1 Introduction

Transition metal-catalyzed asymmetric allylic alkylation (AAA) has emerged as a versatile and efficient method for the enantioselective construction of allylic stereocenters, which are pivotal motifs in bioactive molecules and chiral synthons.[1] The past two decades have seen transformative advances in transition metal-catalyzed asymmetric allylic alkylation, where palladium, rhodium and iridium have emerged as the dominant catalytic platforms, enabling precise stereocontrol in the construction of challenging allylic stereocenters.[2] In these transformations, the choice of ally-

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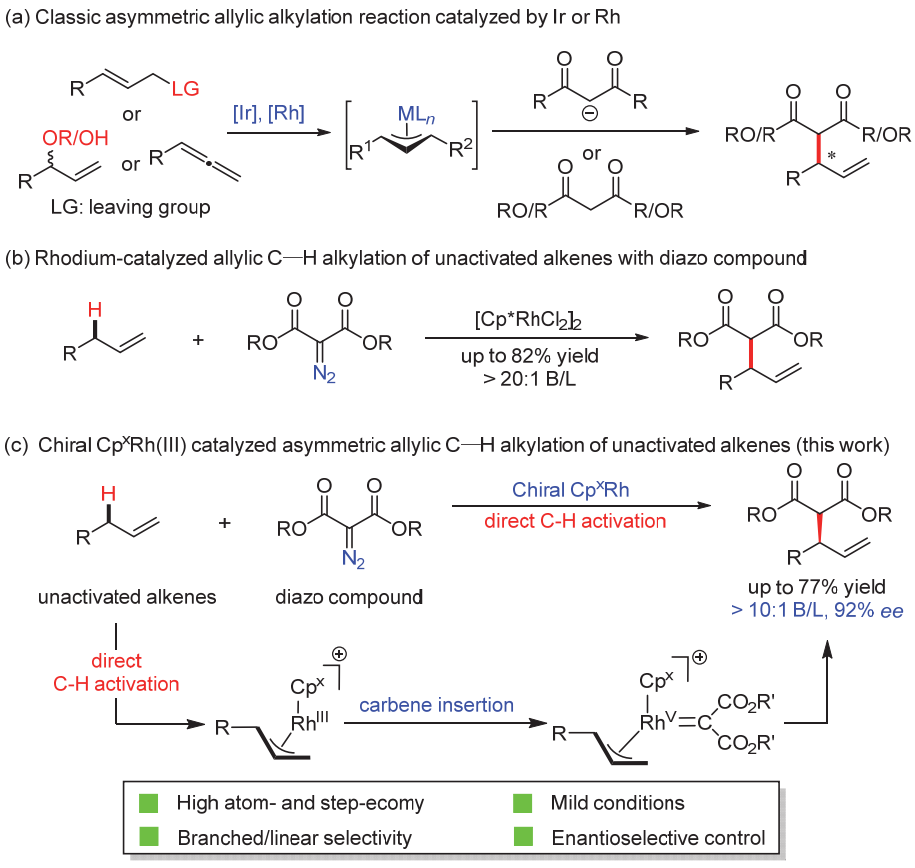
lic electrophiles is critical for achieving optimal reactivity and selectivity. Early studies on rhodium- and iridium-catalyzed systems predominantly employed linear allylic esters as substrates. However, recent efforts have shifted toward the use of more sustainable branched allylic alcohols, offering both environmental and synthetic advantages.[3] Notably, allenes have been successfully employed as versatile substrates in asymmetric allylic alkylation reactions (Scheme 1a).[4] Recent breakthroughs include Carreira's work in 2018,[5] where they developed an Ir-catalyzed allylation of branched allylic carbonates using trimethyl orthoacetate as an enolate surrogate. Around the same time, the You's group[6] reported an asymmetric Rh-catalyzed allylic alkylation of branched alcohols with 1,3-diketones, employing readily available allylic alcohols as starting materials while achieving high *regio*- and *enantio*-selectivity for both aryl and aliphatic allylic alcohols. More recently, Yang and coworkers demonstrated an iridium-catalyzed allylic alkylation of racemic branched alkyl-substituted allylic acetates or alcohols with malonates (Scheme 1a).[7]

The development of sustainable and atom-economical methodologies for C—C bond formation is a significant challenge in synthetic chemistry. The ability to convert inert C—H bonds into C—C bonds has driven the development of various atom- and step-efficient strategies.[8] Among these, transition metal-catalyzed allylic C—H bond functionalization has emerged as a particularly promising approach for accessing complex molecular structures and enabling efficient late-stage functionalization.[9] Recently, Jeganmohan and coworkers reported a Rh(III)-catalyzed allylic C—H alkylation of unactivated alkenes using diazo compounds, proceeding via a migratory insertion mechanism (Scheme 1b).[10] Notably, this approach selectively suppresses competing pathways such as cyclopropanation, allylic olefination, and carbene dimerization, thereby enabling efficient and direct C—C bond formation at the allylic position. While remarkable progress has been achieved in transition metal-catalyzed asymmetric allylic functionalization, the direct enantioselective allylic C—H alkylation of unactivated alkenes remains an unsolved challenge. The formidable obstacles stem from two fundamental limitations: (i) the pronounced thermodynamic stability of allylic C—H bonds in simple alkenes, and (ii) the intricate stereoelectronic requirements for simultaneous *regio*- and enantiocontrol in C—H activation processes. Inspired by Jeganmohan's study, we propose that chiral cyclopentadienyl rhodium(III) Cp^xRh^{III} catalysts would provide an efficient and selective approach for achieving asymmetric allylic C—H alkylation of unactivated alkenes. This approach harnesses three key design elements: (1) the inherent electrophilicity of Rh^{III} centers for efficient C—H bond cleavage, (2) the rigid, well-defined chiral environment of the Cp^x ligand provides optimal steric control for enantio-



Scheme 1 Transition-metal-catalyzed asymmetric allylic alkylation reactions

selectivity; and (3) the tunable nature of the catalyst system allows for the regulation of regiochemical outcomes (Scheme 1c).

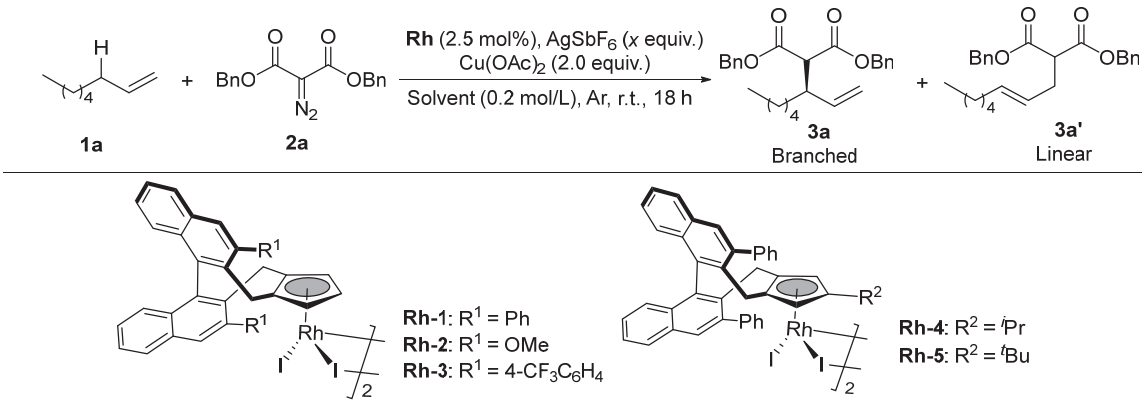
2 Results and discussion

Our investigation began with the enantioselective C—H allylation of unactivated 1-octene (**1a**) using dibenzyl 2-diazomalonate (**2a**) under Rh(III) catalysis.[11] Initial conditions employing chiral Cp^{x}Rh(III) complex **Rh-1** with $AgSbF_6$/$Cu(OAc)_2$ additives in 2,2,2-trifluoroethanol (TFE) at 25 ℃ under N_2 afforded the branched product **3a** with modest efficiency (42% yield, 56% *ee*, B/L (branched/linear)=1.5∶1; Table 1, Entry 1). Screening of BINOL-derived Cp^{x}Rh(III) catalysts (**Rh-2** to **Rh-5**) proved unsatisfactory, yielding **3a** with poor to moderate results (20%～35% yield, 15%～51% *ee*, B∶L=1.2∶1～2.3∶1; Entries 2～5). Solvent evaluation revealed that TFE was the optimal solvent (Entries 6～8). Control experiments established the essential role of $AgSbF_6$, as no reaction occurred in its absence (Entry 9). Optimal performance was achieved with 2.0 equiv. of $AgSbF_6$, providing **3a** with good yield, high enantioselectivity and B/L ratio (Entry 11, 71% yield, 87% *ee*, B∶L=3.1∶1). $AgSbF_6$ served as a critical additive for the generation of the active cationic Rh(III) catalyst, thereby increasing the system's reactivity and chiral induction. Notably, alternative silver or copper additives consistently diminished both yield and enantioselectivity.

With optimized conditions established, the substrate scope using various unactivated aliphatic alkenes was explored. As shown in Table 2, the reaction delivered products **3b**～**3f** in 45%～77% yields, 85%～92% *ee*, and 1.1∶1～4.8∶1 B/L ratios. Allylbenzene-type substrates afforded product **3g** in good yield and *ee*, but with low B/L selectivity. Other aromatic ring-substituted alkenes also provided the corresponding products **3h**～**3j** in moderate yields, enantioselectivity and B/L ratios. The reaction demonstrated excellent tolerance toward terminal alkenes bearing halogen, hydroxyl and ester groups, yielding the desired products **3k**～**3q** (47%～72% yields, 71%～89% *ee*, 2∶1～>10∶1 B/L). The heterocyclic ester-substituted alkene was suitable for asymmetric allylic alkylation, yielding product **3r** with 38% yield, 75% *ee* enantioselectivity and 2∶1 B/L ratio. Electron-withdrawing groups (OTs, *N*-Ts) afforded products **3s**～**3t** in 66%～70% yields with moderate *ee* and B/L ratios.

Next, we tested diazo compounds with 1-octene **1a**. As shown in Table 3, benzyl- and phenyl-substituted diazo compounds reacted smoothly, yielding products **3a** and **3u**

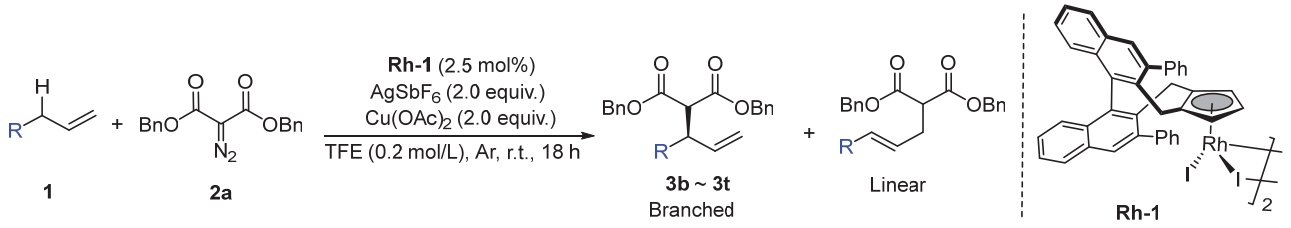
Table 1 Reaction optimization of asymmetric alkylation[a]

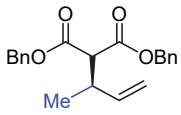


Entry	Rh	Solvent	$AgSbF_6$ (equiv.)	Yield/%	*ee*/%	B/L
1	**Rh-1**	TFE	0.1	42	56	1.5∶1
2	**Rh-2**	TFE	0.1	25	15	1.1∶1
3	**Rh-3**	TFE	0.1	20	35	1.3∶1
4	**Rh-4**	TFE	0.1	35	49	2.4∶1
5	**Rh-5**	TFE	0.1	32	51	2.1∶1
6	**Rh-1**	HFIP	0.1	43	40	2.8∶1
7	**Rh-1**	DCE	0.1	48	37	2.2∶1
8	**Rh-1**	MeOH	0.1	48	54	1.2∶1
9	**Rh-1**	TFE	—	NR	—	—
10	**Rh-1**	TFE	1.0	60	70	3.2∶1
11	**Rh-1**	TFE	2.0	71	87	3.3∶1
12	**Rh-1**	TFE	2.5	68	87	3.2∶1

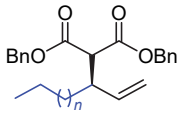
[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.1 mmol), **Rh** cat (2.5 mol%), $AgSbF_6$ (*x* eqiuv.), $Cu(OAc)_2$ (2.0 equiv.), solvent (0.2 mol/L), r.t., 18 h. Isolated yields (branched and linear). Determined by HPLC analysis on a chiral stationary phase. The radiometric ratio (branched/linear) was obtained by analysis of the ^{1}H NMR spectra of the crude reaction mixtures.

Table 2 Substrate scope of unactivated terminal alkenes

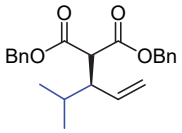




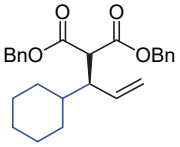
3b, 65% yield
85% *ee*, 3:1 B/L



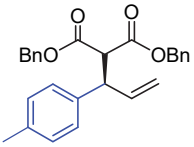
3c, *n* = 1, 72% yield
88% *ee*, 4.8:1 B/L
3d, *n* = 4, 77% yield
87% *ee*, 4:1 B/L



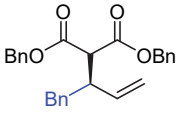
3e, 65% yield
86% *ee*, 1.1:1 B/L



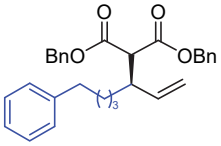
3f, 45% yield
92% *ee*, 1:1.5 B/L



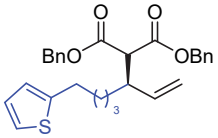
3g, 61% yield
76% *ee*, 1:1 B/L



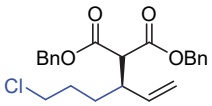
3h, 32% yield
80% *ee*, 5:1 B/L



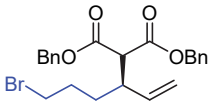
3i, 65% yield[b]
73% *ee*, 1.5:1 B/L



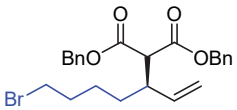
3j, 52% yield
73% *ee*, 2.5:1 B/L



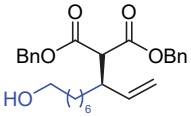
3k, 47% yield
77% *ee*, 2:1 B/L



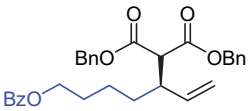
3l, 67% yield[b]
72% *ee*, 6.7:1 B/L



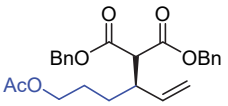
3m, 49% yield[b]
71% *ee*, > 10:1 B/L



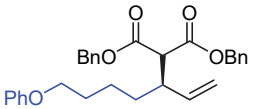
3n, 66% yield
73% *ee*, 2.5:1 B/L



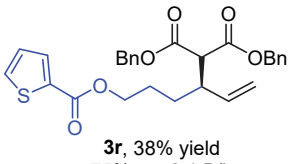
3o, 65% yield
89% *ee*, 2.5:1 B/L



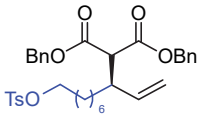
3p, 72% yield
87% *ee*, 2.5:1 B/L



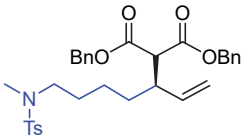
3q, 56% yield
75% *ee*, 2.5:1 B/L



3r, 38% yield
75% *ee*, 2:1 B/L



3s, 66% yield
80% *ee*, 2:1 B/L



3t, 70% yield
55% *ee*, 5:1 B/L

[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.1 mmol), **Rh-1** (2.5 mol%), $AgSbF_6$ (2.0 equiv.), $Cu(OAc)_2$ (2.0 equiv.), TFE (0.2 mol/L), r.t., 18 h. Isolated yields (branched and linear). Enantiomeric excess was determined by HPLC analysis. Regiomeric ratio (branched/linear) was determined by analysis of the ^1H NMR spectra of the crude reaction mixtures. [b] 40 ℃, 48 h.

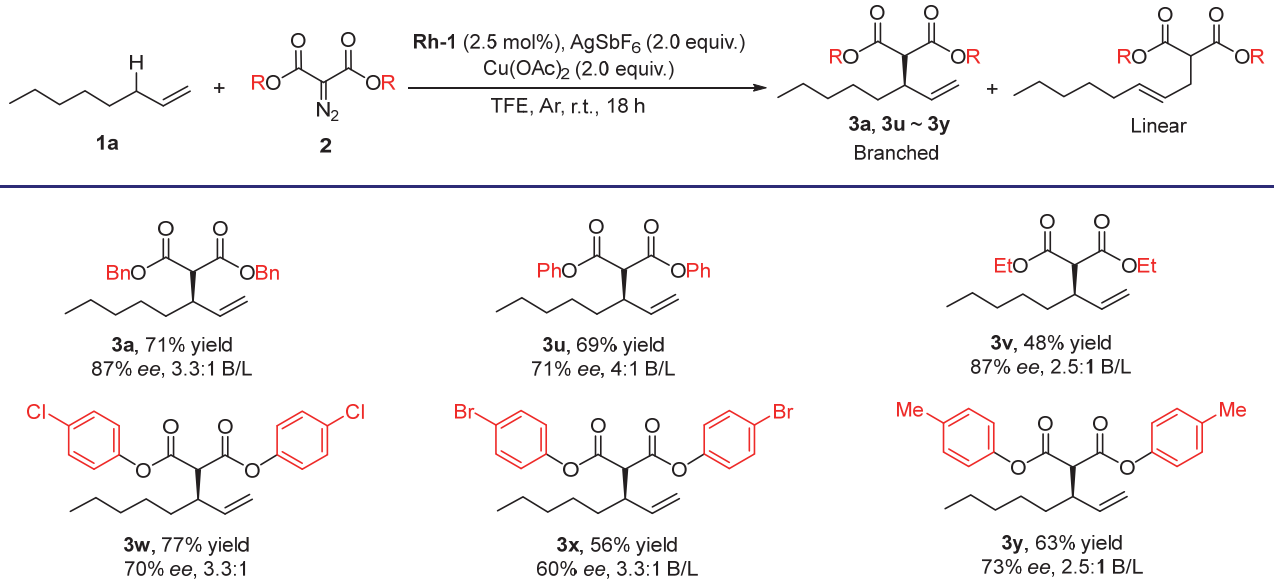
with good yields, enantioselectivity, and B/L ratios. Ethyl-substituted diazo ester derivatives were also compatible, yielding product **3v** in 48% yield with 82% *ee* and 2.5∶1 B/L ratio. Subsequent evaluation of diazo substrates bearing substituted aryl groups revealed that chloro-, bromo- and methyl-substituted derivatives were well tolerated, providing products **3w**～**3y** in moderate to good yields with 60%～73% *ee* and 2.5∶1～3.3∶1 B/L ratios.

To demonstrate the synthetic utility of this methodology, a 1.0 mmol scale reaction to afford **3a** without loss of enantiomeric excess was performed (Scheme 2a). The versatility of **3a** was further demonstrated by its derivatization, affording allylation product **4** and hydrolysis product **5** (Scheme 2b).

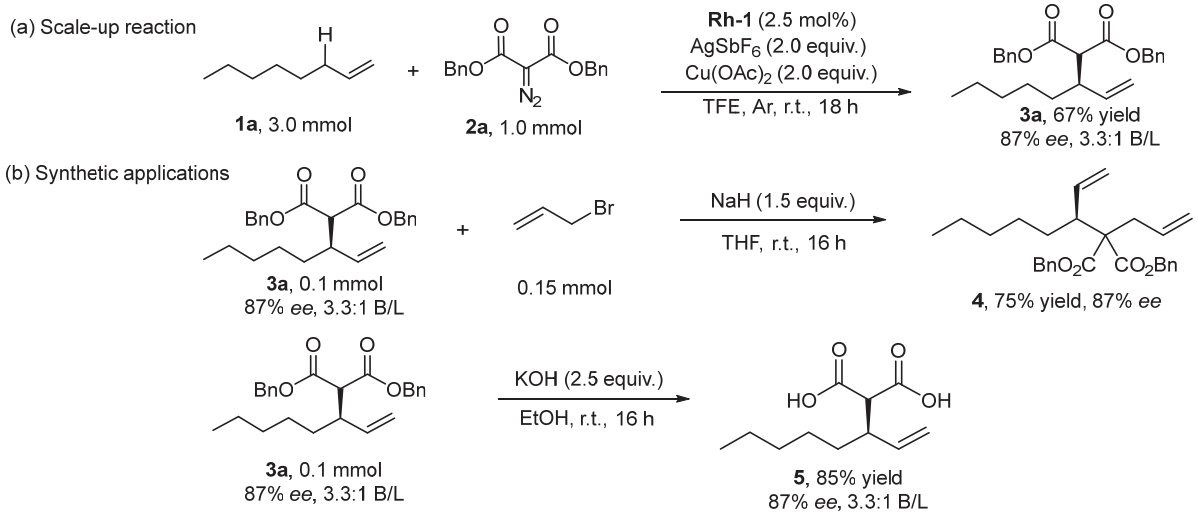
To probe the mechanism, competitive and parallel kinetic isotope effect (KIE) experiments were performed (Schemes 3a, 3b). The observed competitive KIE (k_H/k_D=6.7) and parallel KIE (k_H/k_D=2.9) values strongly suggest that allylic C—H bond cleavage represents the rate-determining step in the catalytic cycle.[12]

Based on these results, the mechanism outlined in Scheme 4 was proposed. The active cationic Rh(III) catalyst **I** forms upon treatment of the chiral $Cp^xRh(III)$ complex with $AgSbF_6$ in the presence of pivalate. Coordination of alkene **1** to complex **I** generates intermediate **II**, which undergoes rate- and enantio-determining allylic C—H activation to form the π-allyl Rh(III) complex **III**.[13] Subsequent reaction with diazo compound **2** leads to carbene formation, yielding the key Rh(V)-carbene intermediate **IV**.[10] Reductive elimination from **IV** affords complex **V**, which undergoes protonolysis to release product **3** while regenerating the active catalyst.

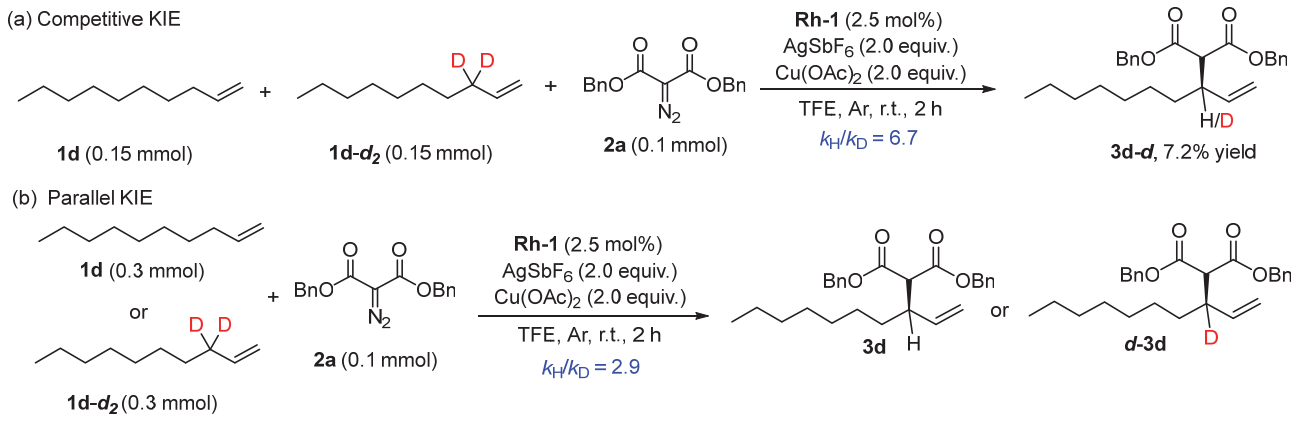
Table 3 Substrate scope of substituted diazo compounds



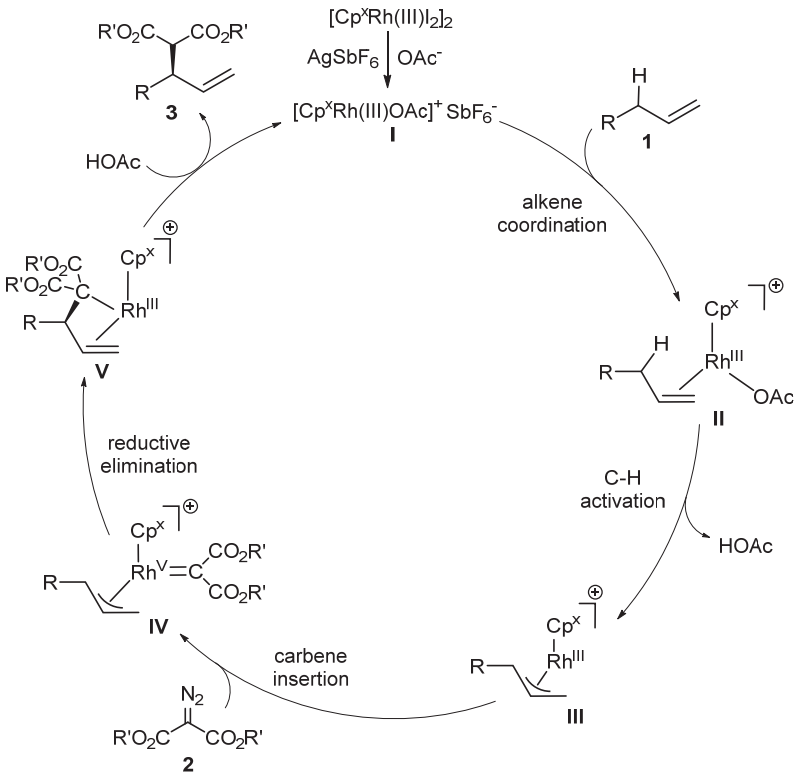
[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.1 mmol), **Rh-1** (2.5 mol%), $AgSbF_6$ (2.0 equiv.), $Cu(OAc)_2$ (2.0 equiv.), TFE (0.2 mol/L), r.t., 18 h. Isolated yields (branched and linear). Enantiomeric excess was determined by HPLC analysis. Regiomeric ratio (branched/linear) was determined by analysis of the ^1H NMR spectra of the crude reaction mixtures.



Scheme 2 Scale-up reaction and synthetic applications



Scheme 3 Mechanistic investigation



Scheme 4 Proposed catalytic cycle

3 Conclusions

In summary, we report a chiral Cp^{x}Rh(III)-catalyzed enantioselective allylic C—H alkylation of unactivated alkenes with *α*-diazocarbonyl compounds. This method features high atom economy, broad substrate scope, and excellent functional group tolerance. Mechanistic investigations, including kinetic isotope effect studies, support a proposed pathway involving allylic C—H activation followed by carbene insertion. This methodology provides a strategic approach to asymmetric allylic C—H functionalization and advances the frontier of C—H activation catalysis. Novel investigations into the asymmetric activation of allylic C—H bonds are currently ongoing in our laboratory.

4 Experimental section

4.1 General information

Commercially available chemicals were obtained from Adamas, Bide Pharmatech Co., Energy Chemical, and TCI and used as received unless otherwise stated. Anhydrous solvent, purchased from Adamas and J&K Scientific, were used as received. All reactions were carried out under the N_2 atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with nitrogen prior to use (three times). Thin-layer chromatography (TLC) was performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max}=254 nm). Flash chromatography was carried out on SiO_2 (silica gel 60, 200～300 mesh). Melting points were corrected and recorded using digital Büchi Melting Point Apparatus B540.

^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance II-400/500 MHz spectrometer. Solvent used for spectra was chloroform-*d*. ^{1}H NMR chemical shifts were reported relative to trimethylsilane (TMS) (*δ* 0.00), chloroform-*d* (*δ* 7.26), and ^{13}C NMR are reported relative to chloroform-*d* (*δ* 77.16). ESI-HRMS data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. Enantiomeric excess (*ee*) value was determined by high-performance liquid chromatography (HPLC) analysis using a chiral stationary phase on Waters B2695 instrument in comparison with the authentic racemates. All the chiral stationary phases including Chiral IG-3, IB N-5, IC, MD (2), MQ (2) and MX (2) used were purchased from Daicel Chiral Technologies (China) Co., Ltd. and Guangzhou FLM Scientific Instrument Co. Ltd. Optical rotations were measured using a Rudolph Autopol I polarimeter.

4.2 General procedure for Rh(III)-catalyzed allylation of olefins with diazo compounds

A 10 mL Schlenk tube with septum containing **Rh-1** (2.5 mol%), $Cu(OAc)_2$ (2.0 equiv.) and $AgSbF_6$ (2.0 equiv.) were evacuated and purged with nitrogen gas three times. Followed by this, alkene **1** (3.0 equiv.) and diazo compound **2** (1.0 equiv.) were dissolved in 2,2,2-trifluoroethanol (TFE, 0.5 mL), and the resulting solution was added into the reaction mixture via syringe. Then, rubber septum was taken out and screw cap was used to cover the tube. The reaction mixture was allowed to stir at 25 ℃ for 18 h. The reaction

mixture was allowed to reach ambient temperature and diluted with CH_2Cl_2, followed by filtration through celite and the filtrate was concentrated. The crude residue was purified through a silica gel column chromatography using hexane and ethyl acetate as eluent to give **3** and **3'**.

Dibenzyl (*R*)-2-(oct-1-en-3-yl)malonate (**3a**) and dibenzyl (*E*)-2-(oct-2-en-1-yl)malonate (**3a'**): Yellow oil (28.1 mg, 71% yield, B∶L=3.3∶1, 87% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ −1.04 (*c* 0.3, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38～7.26 (m, 13H), 5.68～5.57 (m, 1H), 5.53～5.46 (m, 0.33H), 5.37～5.31 (m, 0.30H), 5.15 (d, *J*=1.5 Hz, 3H), 5.10 (s, 2H), 5.05～4.98 (m, 2H), 3.52～3.49 (m, 0.36H), 3.47 (d, *J*=8.8 Hz, 1H), 2.79 (dd *J*=9.3, 3.7 Hz, 1H), 2.65～2.59 (m, 0.61H), 1.91 (q, *J*=7.0 Hz, 0.63H), 1.44～1.15 (m, 10H), 0.86 (dt, *J*=14.1, 7.0 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.89, 168.25, 168.08, 138.14, 135.55, 135.52, 134.44, 128.66, 128.62, 128.46, 128.44, 128.42, 128.29, 125.02, 117.60, 67.18, 67.16, 67.07, 57.15, 52.46, 44.36, 32.35, 31.64, 26.73, 22.61, 14.15. HRMS (ESI-TOF) calcd for $C_{25}H_{31}O_4$ $[M+H]^+$ 395.2222, found 395.2229. HPLC analysis: chiral IG-3 (250 mm×4.6 mm, 3 μm, *V*(hexane)∶*V*(*i*-PrOH)=98∶2, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=32.02 min, t_R(major)=33.29 min.

Dibenzyl (*R*)-2-(but-3-en-2-yl)malonate (**3b**) and dibenzyl (*E*)-2-(but-2-en-1-yl)malonate (**3b'**): Yellow oil (19.2 mg, 65% yield, B∶L=3∶1, 85% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +4.32 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38～7.27 (m, 13H), 5.83～5.71 (m, 1H), 5.55～5.44 (m, 0.32H), 5.39～5.32 (m, 0.38H), 5.15 (s, 3H), 5.11 (s, 2H), 5.04 (dt, *J*=17.1, 1.3 Hz, 1H), 4.97 (dt, *J*=10.4, 1.1 Hz, 1H), 3.49 (t, *J*=7.6 Hz, 0.32H), 3.41 (d, *J*=8.8 Hz, 1H), 3.06～2.94 (m, 1H), 2.61 (td, *J*=7.2, 1.3 Hz, 0.64H), 1.58 (dt, *J*=2.8, 1.29 Hz, 1H), 1.08 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.9, 168.1, 168.1, 139.7, 135.5, 135.5, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 126.3, 115.7, 67.2, 67.1, 57.8, 52.4, 38.2, 32.0, 18.1, 18.0. HRMS (ESI-TOF) calcd for $C_{21}H_{23}O_4Na$ $[M+Na]^+$ 361.1416, found 361.1415. HPLC analysis: chiral IC (250 mm×4.6 mm, 5 μm, *V*(hexane)∶*V*(*i*-PrOH)=99∶1, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=34.19 min, t_R(major)=34.10 min.

Dibenzyl (*R*)-2-(hex-1-en-3-yl)malonate (**3c**) and dibenzyl (*E*)-2-(hex-2-en-1-yl)malonate (**3c'**): Yellow oil (25.4 mg, 72% yield, B∶L=4.8∶1, 88% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10; $[\alpha]_D^{20}$ −1.37 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.27 (m, 12H), 5.69～5.56 (m, 1H), 5.54～5.44 (m, 0.25H), 5.39～5.27 (m, 0.25H), 5.20～5.13 (m, 3H), 5.10 (s, 2H), 5.05～4.98 (m, 2H), 3.50 (t, *J*=7.6 Hz, 0.22H), 3.46 (d, *J*=8.8 Hz, 1H), 2.81 (d, *J*=1.3 Hz, 1H), 2.66～2.59 (m, 0.41H), 1.90 (q, *J*=7.2, 9.2 Hz, 0.45H), 1.42～1.14 (m, 5H), 0.86 (d, *J*=7.4 Hz, 0.60H), 0.84～0.79 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.9, 168.2, 168.1, 138.1, 135.5, 135.5, 134.2, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 125.3, 117.6, 67.2, 67.1, 57.1, 52.5, 44.1, 34.6, 34.5, 32.0, 22.5, 20.2, 13.9, 13.7. HRMS (ESI-TOF) calcd for $C_{23}H_{27}O_4$ $[M+H]^+$ 367.1909, found 367.1912. HPLC analysis: chiral IC (250 mm×4.6 mm, 5 μm, *V*(hexane)∶*V*(*i*-PrOH)=99∶1, 1.0 mL/min, 25 ℃, 210 nm), t_R(minor)=13.33 min, t_R(major)=14.67 min.

Dibenzyl (*R*)-2-(dec-1-en-3-yl)malonate (**3d**) and dibenzyl (*E*)-2-(dec-2-en-1-yl)malonate (**3d'**): Yellow oil (27.3 mg, 77% yield, B∶L=4∶1, 87% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ −17.32 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.27 (m, 12H), 5.69～5.57 (m, 1H), 5.53～5.45 (m, 0.29H), 5.37～5.28 (m, 0.33H), 5.15 (d, *J*=2.0 Hz, 3H), 5.10 (s, 2H), 5.05～5.01 (m, 1H), 5.00 (s, 1H), 3.51 (d, *J*=7.6 Hz, 0.18H), 3.47 (d, *J*=8.7 Hz, 1H), 2.79 (q, *J*=9.2 , 1H), 2.65～2.58 (m, 0.51H), 1.91 (q, *J*=5.2 Hz, 0.58H), 1.46～1.36 (m, 1H), 1.32～1.14 (m, 14H), 0.87 (t, *J*=7.0 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.9, 168.2, 168.1, 138.1, 135.5, 135.5, 134.4, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 125.0, 117.6, 67.2, 67.2, 67.1, 57.1, 52.5, 44.4, 32.6, 32.4, 32.0, 31.9, 29.4, 29.3, 29.2, 27.1, 22.8, 22.8, 14.2. HRMS (ESI-TOF) calcd for $C_{27}H_{33}O_4$ $[M-H]^+$ 421.2386, found 421.2384. HPLC analysis: chiral IG-3 (250 mm×4.6 mm, 3 μm, *V*(he- xane)∶*V*(*i*-PrOH)=99∶1, 1.0 mL/min, 25 ℃, 210 nm), t_R(minor) = 29.27 min, t_R(major)=34.27 min.

Dibenzyl (*R*)-2-(4-methylpent-1-en-3-yl)malonate (**3e**) and dibenzyl (*E*)-2-(4-methylpent-2-en-1-yl)malonate (**3e'**): Yellow oil (21.1 mg, 65% yield, B∶L=1.1∶1, 86% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ −7.12 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38～7.26 (m, 21H), 5.69 (dt, *J*=17.0, 10.1 Hz, 1H), 5.53～5.43 (m, 1H), 5.35～5.25 (m, 1H), 5.15 (s, 6H), 5.10 (s, 2H), 5.08～4.97 (m, 2H), 3.67 (d, *J*=9.5 Hz, 1H), 3.51 (t, *J*=7.6 Hz, 1H), 2.70 (td, *J*=9.7, 5.1 Hz, 1H), 2.62 (td, *J*=7.2, 1.0 Hz, 2.26H), 2.24～2.13 (m, 1.13H), 1.73 (pd, *J*=6.8, 5.0 Hz, 1.05H), 0.91 (d, *J*=6.8 Hz, 7H), 0.88 (d, *J*=6.7 Hz, 3H), 0.82 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.9, 168.4, 168.1, 141.3, 135.6, 134.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 122.1, 118.9, 67.2, 67.1, 67.1, 55.1, 52.5, 50.5, 31.9, 31.0, 29.1, 22.4, 21.3, 17.7. HRMS (ESI-TOF) calcd for $C_{23}H_{26}NO_4$ $[M+NH_4]^+$ 384.2175, found 384.2170. HPLC analysis: chiral MQ (250 mm×4.6 mm, 5 μm, *V*(hexane)∶*V*(*i*-PrOH)=95∶5, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=29.35 min, t_R(major)=34.14 min.

Dibenzyl (*R*)-2-(1-cyclohexylallyl)malonate (**3f**) and dibenzyl (*E*)-2-(3-cyclohexylallyl)malonate (**3f'**): Yellow oil (18.7 mg, 45% yield, B∶L=1∶1.5, 92% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ −8.19 (*c* 0.3, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34～7.28 (m, 25H), 5.72 (dt, *J*=17.0, 10.1 Hz, 1H), 5.50～5.41 (m, 1.51H), 5.35～5.25 (m, 1.64H), 5.15 (s, 8H), 5.11 (d, *J*=3.8 Hz, 2H), 5.03～4.93 (m, 2H), 3.71 (d, *J*=9.2 Hz, 1H), 3.50 (t, *J*=7.6 Hz, 1.47H), 2.67 (td, *J*=9.5, 5.5 Hz, 1H), 2.61 (t, *J*=7.2 Hz, 3H), 1.88～1.79 (m, 1.55H), 1.71～1.61 (m, 11H), 1.28～0.82 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.9, 168.6, 168.2, 140.2, 135.8, 135.6, 128.7,

128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 122.6, 118.5, 67.2, 67.1, 67.0, 54.5, 52.6, 50.3, 40.6, 39.1, 33.0, 32.1, 31.6, 28.6, 26.4, 26.3, 26.2, 26.1. HRMS (ESI-TOF) calcd for $C_{26}H_{31}O_4$ $[M+H]^+$ 407.2222, found 407.2230. HPLC analysis: chiral MX (2) (250 mm×4.6 mm, 5 μm, *V*(hexane)∶*V*(*i*-Pr- OH)=95∶5 , 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=13.74 min, t_R(major)=15.70 min.

Dibenzyl (*R*)-2-(1-phenylallyl)malonate (**3g**) and dibenzyl 2-cinnamylmalonate (**3g'**): Yellow oil (24.2 mg, 61% yield, B∶L=1∶1, 75% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10; $[\alpha]_D^{20}$ −7.17 (*c* 0.3, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.38～7.20 (m, 20 H), 7.16 (d, *J*=8.0 Hz, 2H), 7.12～7.02 (m, 8H), 6.41 (d, *J*=15.8 Hz, 1H), 6.12～6.01 (m, 1H), 6.02～5.93 (m, 1H), 5.16 (d, *J*=3.5 Hz, 6H), 5.09～4.98 (m, 2H), 4.91 (s, 2H), 4.14～4.05 (m, 1H), 3.94 (d, *J*=11.0 Hz, 1H), 3.61 (t, *J*=7.5 Hz, 1H), 2.87～2.77 (m, 2H), 2.32 (d, *J*=14.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ*: 168.8, 167.7, 167.4, 138.0, 137.3, 137.0, 136.8, 135.5, 135.4, 135.3, 134.3, 133.0, 129.5, 129.3, 128.7, 128.7, 128.5, 128.5, 128.4, 128.3, 128.2, 127.9, 126.3, 124.3, 116.6, 67.4, 67.3, 67.2, 57.6, 52.3, 49.5, 32.4, 21.3, 21.2. HRMS (ESI-TOF) calcd for $C_{26}H_{25}O_4$ $[M+H]^+$ 401.1753, found 401.1759. HPLC analysis: chiral IC (250 mm×4.6 mm, 5 μm, *V*(hexane)∶*V*(*i*-PrOH)=99∶1, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=40.52 min, t_R(major)=42.91 min.

Dibenzyl (*R*)-2-(1-phenylbut-3-en-2-yl)malonate (**3h**) and dibenzyl (*E*)-2-(4-phenylbut-2-en-1-yl) malonate (**3h'**): Yellow oil (13.2 mg, 32% yield, B∶L=5∶1, 80% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +11.43 (*c* 0.3, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.35～7.28 (m, 12H), 7.25～7.14 (m, 5H), 7.09～7.02 (m, 2H), 5.80～5.69 (m, 1H), 5.67～5.61 (m, 0.21H), 5.47～5.19 (m, 0.19H), 5.15～5.09 (m, 5H), 4.98～4.81 (m, 2H), 3.52 (d, *J*=7.8 Hz, 1H), 3.17～3.16 (m, 0.07 H) 3.15～3.05 (m, 1H), 2.87～2.79 (m, 1H), 2.70～2.59 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ*: 168.3, 168.0, 139.0, 137.2, 129.5, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.3, 128.3, 126.4, 117.8, 67.3, 67.2, 55.9, 45.7, 38.9. HRMS (ESI-TOF) calcd for $C_{27}H_{25}O_4$ $[M-H]^+$ 413.1758, found 413.156. HPLC analysis: chiral IG-3 (250 mm×4.6 mm, 3 μm, *V*(hexane)∶*V*(*i*-PrOH)=95∶5, 1.0 mL/min, 25 ℃, 210 nm), t_R(minor) = 10.45 min, t_R(major)=11.38 min.

Dibenzyl (*R*)-2-(7-phenylhept-1-en-3-yl)malonate (**3i**) and dibenzyl (*E*)-2-(4-phenylhept-2-en-1-yl)malonate (**3i'**): Yellow oil (26.2 mg, 65% yield, B∶L=1.5∶1, 73% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +12.76 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.36～7.22 (m, 20H), 7.21～7.10 (m, 5H), 5.67～5.55 (m, 1H), 5.52～5.42 (m, 0.69H), 5.36～5.29 (m, 0.69H), 5.14 (d, *J*=1.3 Hz, 2H), 5.12 (d, *J*=3.0 Hz, 2H), 5.09 (s, 2H), 5.04～4.99 (m, 1H), 4.98 (s, 1H), 3.49 (t, *J*=7.7 Hz, 0.65H), 3.46 (d, *J*=8.8 Hz, 1H), 2.78 (q, *J*=9.2, 1H), 2.59 (dt, *J*=15.6, 7.8 Hz, 3H), 2.54～2.49 (m, 1.49H), 1.94 (q, *J*=7.1 Hz, 1.30H), 1.57～1.48 (m, 3H), 1.47～1.40 (m, 1H), 1.39～1.28 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 168.9, 168.2, 168.0, 142.7, 138.0, 135.5, 135.5, 135.5, 134.1, 128.7, 128.6, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 125.7, 125.3, 117.7, 67.2, 67.2, 67.1, 57.1, 52.4, 44.2, 35.9, 35.9, 32.4, 32.2, 32.0, 31.2, 31.0, 29.0, 26.7. HRMS (ESI-TOF) calcd for $C_{30}H_{31}O_4$ $[M+H]^+$ 455.2227, found 455.2229. HPLC analysis: chiral IC (250 mm×4.6 mm, 5 μm, *V*(hexane)∶*V*(*i*-PrOH)=99∶1, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=41.17 min, t_R(major)=43.73 min.

Dibenzyl (*R*)-2-(7-(thiophen-2-yl)hept-1-en-3-yl)-malonate (**3j**) and dibenzyl (*E*)-2-(7-(thiophen-2-yl)hept-2-en-1-yl)malonate (**3j'**): Yellow oil (23.7 mg, 52% yield, B∶L=3∶1, 72% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +6.02 (*c* 0.3, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.37～7.26 (m, 17H), 7.14～7.05 (m, 2H), 6.97～6.88 (m, 2H), 6.82～6.71 (m, 2H), 5.69～5.58 (m, 1H), 5.51～5.42 (m, 0.35H), 5.38～5.31 (m, 0.49H), 5.17～5.10 (m, 6H), 5.07～4.99 (m, 2H), 3.51 (t, J=7.6 Hz, 0.38H), 3.47 (d, *J*=8.7 Hz, 1H), 2.84～2.72 (m, 4H), 2.63 (t, *J*=7.2 Hz, 1H), 2.00～1.92 (m, 1H), 1.65～1.57 (m, 3H), 1.50～1.20 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 168.8, 168.2, 168.0, 145.5, 137.9, 135.5, 135.5, 135.5, 133.9, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.1, 126.8, 126.8, 125.4, 124.1, 124.1, 122.9, 117.8, 67.2, 67.2, 67.1, 57.1, 52.4, 44.2, 32.2, 32.0, 32.0, 31.5, 31.3, 29.9, 29.8, 29.8, 28.7, 26.5. HRMS (ESI-TOF) calcd for $C_{28}H_{31}O_4S$ $[M+H]^+$ 463.1943, found 463.1944. HPLC analysis: chiral IC (250 mm×4.6 mm, 5 μm, *V*(hexane)∶*V*(*i*-PrOH)=99∶1, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor) = 50.17 min, t_R(major)=53.21 min.

Dibenzyl (*R*)-2-(6-chlorohex-1-en-3-yl)malonate (**3k**) and dibenzyl (*E*)-2-(6-chlorohex-2-en-1-yl)malonate (**3k'**): Yellow oil (18.9 mg, 47% yield, B∶L=2∶1, 77% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +6.82 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.38～7.27 (m, 14H), 5.62 (dt, *J*=17.4, 9.5 Hz, 1H), 5.42 (q, *J*=5.5 Hz, 1H), 5.16 (s, 2H), 5.15 (d, *J*=1.2 Hz, 2H), 5.11 (s, 2H), 5.08～5.00 (m, 2H), 3.54～3.36 (m, 4.41H), 2.80 (q, *J*=9.2, 1H), 2.67～2.59 (m, 1H), 2.07 (q, *J*=6.4, 1H), 1.84～1.72 (m, 2H), 1.70～1.63 (m, 1H), 1.59～1.53 (m, 1H), 1.47～1.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 168.7, 168.0, 167.8, 137.4, 135.5, 135.4, 132.1, 128.7, 128.6, 128.5, 128.5, 128.5, 128.3, 126.8, 118.4, 67.3, 67.2, 67.2, 57.0, 52.2, 44.7, 44.3, 43.8, 31.9, 31.9, 30.3, 29.6, 29.5. HRMS (ESI-TOF) calcd for $C_{23}H_{24}ClO_4$ $[M-H]^+$ 399.1368, found 399.1370. HPLC analysis: chiral IG-3 (250 mm×4.6 mm, 3 μm, *V*(hexane)∶*V*(*i*-PrOH)=98∶2, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor) = 20.54 min, t_R(major)=21.86 min.

Dibenzyl (*R*)-2-(6-bromohex-1-en-3-yl)malonate (**3l**) and dibenzyl (*E*)-2-(6-bromohex-2-en-1-yl)malonate (**3l'**): Yellow oil (26.3 mg, 67% yield, B∶L=6.7∶1, 72% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +19.70 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.36～7.30 (m, 15H), 5.62 (dt, *J*=17.4, 9.6 Hz, 1H), 5.44～5.38 (m, 1H), 5.15 (d, *J*=4.3 Hz, 3H), 5.11 (s, 2H), 5.04 (q, *J*=13.6, 2H), 3.51 (d, *J*=7.6 Hz, 0.25H), 3.49～

3.45 (m, 1H), 3.37～3.23 (m, 3H), 3.00 (d, J=5.3 Hz, 0.46H), 2.80 (q, J=9.3, 1H), 2.65～2.60 (m, 0.48H), 2.12～2.03 (m, 1H), 1.91～1.80 (m, 2H), 1.79～1.70 (m, 1H), 1.59～1.52 (m, 1H), 1.48～1.36 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.96, 167.81, 137.37, 135.40, 128.71, 128.65, 128.56, 128.51, 128.35, 118.42, 67.35, 67.23, 56.98, 43.73, 33.33, 30.89, 30.52. HRMS (ESI-TOF) calcd for $C_{23}H_{26}BrO_4$ $[M+H]^+$ 443.0863, found 443.0865. HPLC analysis: chiral IC (250 mm×4.6 mm, 5 μm, V(hexane)∶V(*i*-PrOH)=99∶1, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=57.07 min, t_R(major)=57.68 min.

Dibenzyl (*R*)-2-(7-bromohept-1-en-3-yl)malonate (**3m**) and dibenzyl (*E*)-2-(7-bromohept-2-en-1-yl) malonate (**3m'**): Yellow oil (22.9 mg, 49% yield, B∶L=20∶1, 71% *ee*). Eluent: V(petroleum ether)∶V(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ −4.11 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.25 (m, 11H), 5.68～5.54 (m, 1H), 5.21～5.17 (m, 0.22H), 5.15 (d, J=1.2 Hz, 2H), 5.11 (s, 2H), 5.09～5.02 (m, 1H), 5.02 (s, 1H), 3.51 (d, J=7.3 Hz, 0.06H), 3.46 (d, J=8.7 Hz, 1H), 3.37 (d, J=6.8 Hz, 0.20H), 3.32 (td, J=6.8, 1.3 Hz, 2H), 2.85～2.73 (m, 1H), 2.62 (t, J=7.0 Hz, 0.10H), 1.95 (q, J=7.0 Hz, 0.11H), 1.85～1.67 (m, 2H), 1.48～1.38 (m, 2H), 1.30 (q, J=2.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.1, 167.9, 137.6, 135.4, 135.4, 128.7, 128.7, 128.6, 128.5, 128.5, 128.5, 128.5, 118.1, 67.2, 67.1, 57.0, 44.1, 33.6, 32.4, 31.3, 25.6. HRMS (ESI-TOF) calcd for $C_{24}H_{26}BrO_4$ $[M-H]^+$ 457.1020, found 457.1021. HPLC analysis: chiral IC (250 mm×4.6 mm, 5 μm, V(hexane)∶V(*i*-PrOH)=99∶1, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=32.87 min, t_R(major)=35.33 min.

Dibenzyl (*R*)-2-(10-hydroxydec-1-en-3-yl)malonate (**3n**) and dibenzyl (*E*)-2-(10-hydroxydec-2-en-1-yl)malonate (**3n'**): Yellow oil (26.5 mg, 66% yield, B∶L=2.5∶1, 73% *ee*). Eluent: V(petroleum ether)∶V(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +30.35 (*c* 0.3, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35～7.27 (m, 14H), 5.67～5.57 (m, 1H), 5.52～5.45 (m, 0.42H), 5.37～5.30 (m, 0.45H), 5.14 (dd, J=3.1, 1.5 Hz, 3H), 5.10 (s, 2H), 5.05～5.01 (m, 1H), 5.00 (s, 1H), 3.62 (td, J=6.6, 2.6 Hz, 2.82H), 3.50 (t, J=7.6 Hz, 0.42H), 3.46 (d, J=8.8 Hz, 1H), 2.78 (q, J=9.3 Hz, 1H), 2.62 (t, J=7.2 Hz, 0.80H), 1.91 (q, J=6.7 Hz, 0.87H), 1.58～1.51 (m, 4H), 1.35～1.21 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 168.9, 168.2, 168.0, 138.1, 135.5, 135.5, 135.5, 134.3, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 125.1, 117.6, 67.2, 67.1, 67.1, 63.1, 63.1, 57.1, 52.4, 44.3, 32.9, 32.8, 32.5, 32.3, 32.0, 29.3, 29.3, 29.2, 29.1, 27.0, 25.8, 25.7. HRMS (ESI-TOF) calcd for $C_{27}H_{34}O_5Na$ $[M+Na]^+$ 461.2304, found 461.2308. HPLC analysis: chiral MD (2) (250 mm×4.6 mm, 5 μm, V(hexane)∶V(*i*-PrOH)=90∶10, 1.0 mL/min, 25 ℃, 210 nm), t_R(minor)=20.29 min, t_R(major)=21.57 min.

Dibenzyl (*R*)-2-(7-(benzoyloxy)hept-1-en-3-yl)malonate (**3o**) and dibenzyl (*E*)-2-(7-(benzoyloxy)hept-2-en-1-yl)-malonate (**3o'**): Yellow oil (31.7 mg, 65% yield, B∶L=2.5∶1, 89% *ee*). Eluent: V(petroleum ether)∶V(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +30.35 (*c* 0.3, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09～8.02 (m, 2.84H), 7.58～7.52 (m, 1.43H), 7.47～7.41 (m, 2.94H), 7.34～7.29 (m, 14H), 5.68～5.57 (m, 1H), 5.52～5.45 (m, 0.44H), 5.37～5.31 (m, 0.43H), 5.15 (dd, J=3.6, 1.7 Hz, 3H), 5.10 (s, 2H), 5.05～4.97 (m, 2H), 4.31 (td, J=6.7, 3.2 Hz, 2.83H), 3.50 (t, J=7.6 Hz, 0.39H), 3.47 (d, J=8.8 Hz, 1H), 2.79 (q, J=9.3 Hz, 1H), 2.65～2.60 (m, 0.80H), 1.92 (q, J=6.7 Hz, 0.85H), 1.78～1.71 (m, 2.80H), 1.45～1.39 (m, 2.97H), 1.24～1.15 (m, 2.33H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 168.8, 168.2, 168.0, 166.8, 165.2, 138.0, 135.5, 135.5, 135.5, 134.2, 132.9, 130.6, 129.6, 128.8, 128.8, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 125.1, 117.7, 68.1, 67.2, 67.1, 67.1, 65.2, 57.1, 52.4, 44.3, 32.3, 29.3, 29.3, 29.2, 29.2, 29.1, 28.8, 28.8, 27.0, 26.1, 26.1. HRMS (ESI-TOF) calcd for $C_{31}H_{32}O_6Na$ $[M+Na]^+$ 523.2097, found 523.2099. HPLC analysis: chiral IC (250 mm×4.6 mm, 5 μm, V(hexane)∶V(*i*-PrOH)=98∶2, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=27.81 min, t_R(major)=30.70 min.

Dibenzyl (*R*)-2-(6-acetoxyhex-1-en-3-yl)malonate (**3p**) and dibenzyl (*E*)-2-(6-acetoxyhex-2-en-1-yl)malonate (**3p'**): Yellow oil (30.5 mg, 72% yield, B∶L=2.5∶1, 87% *ee*). Eluent: V(petroleum ether)∶V(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ −27.06 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34～7.27 (m, 14H), 5.68～5.55 (m, 1H), 5.51～5.43 (m, 0.46H), 5.38 (dd, J=14.5, 7.5 Hz, 0.56H), 5.14 (s, 3.44H), 5.10 (s, 2H), 5.04 (dd, J=13.8, 2.4 Hz, 2H), 4.05～3.91 (m, 2.87H), 3.48 (dd, J=14.4, 8.0 Hz, 1.39H), 2.79 (td, J=9.0, 6.2 Hz, 1H), 2.62 (t, J=7.1 Hz, 0.86H), 2.02 (d, J=11.3 Hz, 5.34H), 1.60 (s, 1H), 1.50 (td, J=11.9, 4.1 Hz, 2H), 1.37～1.29 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.22, 168.78, 168.01, 167.85, 137.43, 135.52, 135.42, 132.74, 128.75, 128.69, 128.67, 128.64, 128.54, 128.47, 128.44, 128.32, 126.22, 118.34, 67.28, 67.21, 67.18, 64.25, 57.01, 44.04, 28.70, 28.22, 26.37, 21.08. HRMS (ESI-TOF) calcd for $C_{25}H_{27}O_6$ $[M-H]^+$ 423.1713, found 423.1714. HPLC analysis: chiral IG-3 (250 mm×4.6 mm, 3 μm, V(hexane)∶V(*i*-PrOH)=95∶5, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=46.70 min, t_R(major)=54.66 min.

Dibenzyl (*R*)-2-(7-phenoxyhept-1-en-3-yl)malonate (**3q**) and dibenzyl (*E*)-2-(7-phenoxyhept-2-en-1-yl)malonate (**3q'**): Yellow oil (19.2 mg, 56% yield, B∶L=2.5∶1, 75% *ee*). Eluent: V(petroleum ether)∶V(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +47.68 (*c* 0.3, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.38～7.24 (m, 18H), 6.95～6.90 (m, 1H), 6.90～6.84 (m, 2H), 5.68～5.58 (m, 1H), 5.53～5.46 (m, 0.42H), 5.40～5.33 (m, 0.45H), 5.14 (d, J=1.3 Hz, 3H), 5.10 (s, 2H), 5.06～5.00 (m, 2H), 3.90 (dt, J=17.4, 6.4 Hz, 2.80H), 3.48 (q, J=8.4 Hz, 1.40H), 2.85～2.76 (m, 1H), 2.65～2.59 (m, 0.76H), 1.99 (q, J=7.1 Hz, 0.80H), 1.77～1.62 (m, 3H), 1.53～1.42 (m, 3H), 1.37～1.30 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.9, 168.2, 168.0, 159.1, 137.8, 135.5, 135.5, 133.8, 129.5, 129.5, 128.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.3, 125.7, 120.6, 118.0, 114.6, 114.6, 67.7, 67.6, 67.2, 67.2, 67.1, 57.1, 52.4, 44.3, 32.2, 32.1, 29.1, 28.8, 25.8, 23.7. HRMS (ESI-TOF) calcd for $C_{30}H_{33}O_5$ $[M+H]^+$ 473.2328, found 473.2325. HPLC analysis: chiral MX (2) (250 mm×4.6 mm, 5 μm,

V(hexane)∶*V*(*i*-PrOH)=98∶2, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=33.32 min, t_R(major)=43.37 min.

Dibenzyl (*R*)-2-(6-((thiophene-2-carbonyl)oxy)hex-1-en-3-yl)malonate (**3r**) and dibenzyl (*Z*)-2-(6-((thiophene-2-carbonyl)oxy)hex-2-en-1-yl)malonate (**3r'**): Yellow oil (14.7 mg, 38% yield, B∶L=2∶1, 75% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +30.35 (*c* 0.3, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.80 (dd, *J*=3.7, 1.3 Hz, 0.54H), 7.78 (dd, *J*=3.7, 1.3 Hz, 2H), 7.55～7.53 (m, 0.55H), 7.53～7.51 (m, 2H), 7.33～7.28 (m, 15H), 7.15～7.03 (m, 2H), 5.71～5.60 (m, 1H), 5.54～5.48 (m, 0.51H), 5.44～5.36 (m, 0.53H), 5.17～5.11 (m, 6H), 5.11～5.03 (m, 2H), 4.28～4.15 (m, 3H), 3.52 (t, *J*=8.9 Hz, 0.46H), 3.50 (d, *J*=8.9 Hz, 1H), 2.90～2.82 (m, 1H), 2.67～2.60 (m, 1H), 2.22 (s, 1H), 2.11～2.03 (m, 1H), 1.83～1.70 (m, 3H), 1.66～1.55 (m, 2H), 1.48～1.40 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ*: 168.7, 167.9, 167.8, 164.3, 162.3, 162.3, 137.4, 133.4, 132.4, 128.7, 128.7, 128.6, 128.6, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 127.8, 127.0, 118.3, 68.2, 67.2, 67.1, 67.1, 64.8, 57.0, 44.0, 28.7, 26.4. HRMS (ESI-TOF) calcd for $C_{28}H_{29}O_6S$ $[M+H]^+$ 493.1685, found 493.1680. HPLC analysis: chiral IC (250 mm×4.6 mm, 5 μm, *V*(hexane)∶*V*(*i*-PrOH)=90∶10, 1.0 mL/min, 25 ℃, 210 nm), t_R(minor)=33.32 min, t_R(major)=24.32 min.

Dibenzyl (*R*)-2-(10-(tosyloxy)dec-1-en-3-yl)malonate (**3s**) and dibenzyl (*E*)-2-(10-(tosyloxy)dec-2-en-1-yl)-malonate (**3s'**): Yellow oil (37.1 mg, 66% yield, B∶L=2∶1, 80% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +3.71 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.78 (d, *J*=8.3 Hz, 3H), 7.53～7.15 (m, 17H), 5.60 (dt, *J*=17.5, 9.5 Hz, 1H), 5.45 (dt, *J*=13.9, 6.6 Hz, 1H), 5.36～5.27 (m, 1H), 5.14 (d, *J*=1.5 Hz, 3H), 5.09 (s, 2H), 5.05～4.99 (m, 1H), 4.98 (d, *J*=2.0 Hz, 1H), 4.00 (td, *J*=6.5, 2.9 Hz, 3H), 3.50 (d, *J*=7.6 Hz, 1H), 3.44 (d, *J*=8.8 Hz, 1H), 2.75 (q, *J*=9.3 Hz, 1H), 2.61 (t, *J*=7.2 Hz, 1H), 2.44 (s, 4H), 1.88 (q, *J*=6.8 Hz, 1H), 1.62 (d, *J*=7.0 Hz, 1H), 1.57 (d, *J*=6.6 Hz, 2H), 1.33～1.05 (m, 14H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 168.9, 168.2, 168.0, 144.8, 138.0, 135.5, 129.9, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 128.0, 117.7, 70.8, 67.2, 67.1, 57.1, 44.3, 32.4, 32.3, 29.2, 28.9, 28.9, 26.9, 25.4, 21.8. HRMS (ESI-TOF) calcd for $C_{34}H_{41}O_7S$ $[M+H]^+$ 593.2573, found 593.2579. HPLC analysis: chiral MX (2) (250 mm×4.6 mm, 5 μm, *V*(hexane)∶*V*(*i*-PrOH)=90∶10, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=64.95 min, t_R(major)=68.88 min.

Dibenzyl (*R*)-2-(7-((*N*,4-dimethylphenyl)sulfonamido)-hept-1-en-3-yl)malonate (**3t**) and dibenzyl (*E*)-2-(7-((*N*,4-dimethylphenyl)sulfonamido)hept-2-en-1-yl)malonate (**3t'**): Yellow oil (39.1 mg, 70% yield, B∶L=5∶1, 55% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ 41.27 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.69～7.62 (m, 3H), 7.34～7.28 (m, 16H), 5.67～5.52 (m, 1H), 5.47～5.42 (m, 0.49H), 5.37～5.32 (m, 0.50H), 5.19～5.06 (m, 5H), 5.01 (q, *J*=13.9 Hz, 2H), 3.47 (d, *J*=8.2 Hz, 0.41H), 3.45 (d, *J*=8.8 Hz, 1H), 2.97～2.88 (m, 3H), 2.76 (dd, *J*=9.2, 3.4 Hz, 1H), 2.66 (d, *J*=8.2 Hz, 4H), 2.64～2.57 (m, 1H), 2.42 (d, *J*=2.5 Hz, 5H), 2.11～2.00 (m, 1H), 1.93 (q, *J*=7.1 Hz, 1H), 1.56～1.25 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 168.13, 167.96, 143.31, 137.72, 135.47, 134.71, 129.74, 128.68, 128.63, 128.50, 128.48, 128.47, 128.30, 127.55, 118.03, 67.24, 67.14, 57.05, 49.95, 44.15, 34.68, 31.79, 27.33, 24.01, 21.62. HRMS (ESI-TOF) calcd for $C_{32}H_{36}NO_6S$ $[M-H]^+$ 564.2268, found 562.2266. HPLC analysis: chiral MX (2) (250 mm×4.6 mm, 5 μm, *V*(hexane)∶*V*(*i*-PrOH)=80∶20, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=37.43 min, t_R(major)=41.27 min.

Diphenyl (*R*)-2-(oct-1-en-3-yl)malonate (**3u**) and diphenyl (*E*)-2-(oct-2-en-1-yl)malonate (**3u'**): Yellow oil (25.2 mg, 69% yield, B∶L=4∶1, 67% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +3.28 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.45～7.34 (m, 5H), 7.29～7.21 (m, 3H), 7.17～7.08 (m, 5H), 5.88 (dt, *J*=17.1, 9.8 Hz, 1H), 5.75～5.67 (m, 0.27H), 5.60～5.51 (m, 0.22H), 5.31～5.21 (m, 2H), 3.88 (t, *J*=7.6 Hz, 0.25H), 3.85 (d, *J*=8.2 Hz, 1H), 3.02 (q, *J*=9.6 Hz, 1H), 2.88～2.82 (m, 0.47H), 2.05 (q, *J*=7.0 Hz, 0.56H), 1.75～1.66 (m, 1H), 1.59～1.50 (m, 1H), 1.43～1.27 (m, 7H), 0.93～0.86 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 167.44, 166.88, 166.63, 150.62, 150.58, 137.91, 135.09, 129.69, 129.67, 129.63, 126.37, 126.36, 126.32, 124.69, 121.50, 121.46, 118.31, 56.81, 52.41, 44.48, 32.65, 32.60, 32.08, 31.66, 31.47, 29.12, 26.84, 22.66, 14.15. HRMS (ESI-TOF) calcd for $C_{23}H_{27}O_4$ $[M+H]^+$ 367.1909, found 367.1904. HPLC analysis: chiral MD (2) (250 mm×4.6 mm, 5 μm, *V*(hexane)∶*V*(*i*-PrOH)=98∶2, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=33.32 min, t_R(major)=35.16 min.

Diethyl (*R*)-2-(oct-1-en-3-yl)malonate (**3v**) and diethyl (*E*)-2-(oct-2-en-1-yl)malonate (**3v'**): Yellow oil (13.2 mg, 48% yield, B∶L=2.5∶1, 82% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +3.28 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 5.68～5.57 (m, 1H), 5.55～5.47 (m, 0.44H), 5.38～5.29 (m, 0.40H), 5.10～5.02 (m, 2H), 4.21～4.10 (m, 5.64H), 3.39～3.27 (m, 1.36H), 2.74 (q, *J*=9.3 Hz, 1H), 2.59～2.53 (m, 0.89H), 1.98～1.90 (m, 0.80H), 1.47～1.39 (m, 1H), 1.25 (d, *J*=6.6 Hz, 16H), 0.85 (td, *J*=6.9, 2.7 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ*: 169.20, 168.56, 168.37, 138.34, 134.12, 125.31, 117.37, 61.39, 61.24, 57.17, 52.44, 44.22, 32.54, 32.37, 31.99, 31.65, 31.39, 29.09, 26.73, 22.61, 14.22, 14.12. HRMS (ESI-TOF) calcd for $C_{15}H_{27}O_4$ $[M+H]^+$ 271.1909, found 271.1905. HPLC analysis: chiral IG-3 (250 mm×4.6 mm, 3 μm, *V*(hexane)∶*V*(*i*-PrOH)=98∶2, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor) = 21.50 min, t_R(major)=25.15 min.

Bis(4-chlorobenzyl) (*R*)-2-(oct-1-en-3-yl)malonate (**3w**) and bis(4-chlorobenzyl) (*E*)-2-(oct-2-en-1-yl)malonate (**3w'**): Yellow oil (35.2 mg, 77% yield, B∶L=3.3∶1, 71% *ee*). Eluent: *V*(petroleum ether)∶*V*(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ +9.59 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.33～7.27 (m, 5H), 7.22 (dd, *J*=8.6, 6.8 Hz, 5H), 5.66～5.54 (m, 1H), 5.52～5.43 (m, 0.31H), 5.35～5.27 (m, 0.33H), 5.14～5.07 (m, 3H), 5.05 (s, 2H), 5.04～

4.97 (m, 2H), 3.48 (t, J=7.6 Hz, 0.30H), 3.44 (d, J=8.8 Hz, 1H), 2.76 (q, J=9.2 Hz, 1H), 2.63～2.55 (m, 0.60H), 1.90 (q, J=6.8 Hz, 0.63H), 1.36～1.12 (m, 10H), 0.86 (dt, J=9.2, 6.9 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.66, 168.03, 167.85, 137.95, 134.58, 134.48, 134.40, 133.95, 133.92, 129.87, 129.70, 128.86, 128.80, 124.79, 117.70, 66.32, 66.30, 66.21, 57.01, 52.32, 44.34, 32.50, 32.32, 31.96, 31.61, 31.41, 29.01, 26.69, 22.60, 22.58, 14.17, 14.12. HRMS (ESI-TOF) calcd for $C_{25}H_{29}Cl_2O_4$ $[M+H]^+$ 463.1443, found 463.1440. HPLC analysis: chiral MD (2) (250 mm×4.6 mm, 5 μm, V(hexane)∶V(*i*-PrOH)=98∶2, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=19.88 min, t_R(major)=21.78 min.

Bis(4-bromobenzyl) (*R*)-2-(oct-1-en-3-yl)malonate (**3x**) and bis(4-bromobenzyl) (*E*)-2-(oct-2-en-1-yl)malonate (**3x'**): Yellow oil (20.8 mg, 56% yield, B∶L=3.3∶1, 73% *ee*). Eluent: V(petroleum ether)∶V(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ −10.88 (*c* 0.3, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48～7.43 (m, 5H), 7.15 (t, J=8.5 Hz, 5H), 5.60 (dt, J=17.5, 9.5 Hz, 1H), 5.50～5.44 (m, 0.36H), 5.33～5.28 (m, 0.37H), 5.12～5.06 (m, 3H), 5.03 (s, 2H), 5.03～4.98 (m, 2H), 3.48 (d, J=7.6 Hz, 0.30H), 3.44 (d, J=8.8 Hz, 1H), 2.75 (q, J=9.3 Hz, 1H), 2.62～2.57 (m, 0.65H), 1.90 (q, J=6.9 Hz, 0.68H), 1.40～1.16 (m, 10H), 0.86 (dt, J=11.0, 7.0 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 168.65, 168.02, 167.84, 137.96, 134.61, 134.46, 134.43, 131.84, 131.79, 130.16, 129.99, 124.78, 122.65, 122.59, 122.57, 117.73, 66.37, 66.34, 66.25, 57.02, 52.32, 44.35, 32.52, 32.34, 31.97, 31.62, 31.43, 29.03, 26.71, 22.63, 22.60, 14.19, 14.15. HRMS (ESI-TOF) calcd for $C_{25}H_{29}Br_2O_4$ $[M+H]^+$ 551.0433, found 551.0430. HPLC analysis: chiral MD (2) (250 mm×4.6 mm, 5 μm, V(hexane)∶V(*i*-PrOH)=95∶5, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=50.71 min, t_R(major)=53.21 min.

Bis(4-methylbenzyl) (*R*)-2-(oct-1-en-3-yl)malonate (**3y**) and bis(4-methylbenzyl) (*E*)-2-(oct-2-en-1-yl)malonate (**3y'**): Yellow oil (26.5 mg, 63% yield, B∶L=2.5∶1, 77% *ee*). Eluent: V(petroleum ether)∶V(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ −17.22 (*c* 0.3, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.23～7.17 (m, 5.66H), 7.14 (d, J=7.6 Hz, 5.68H), 5.68～5.57 (m, 1H), 5.52～5.45 (m, 0.41H), 5.36～5.29 (m, 0.45H), 5.13～5.10 (m, 3H), 5.06 (s, 2H), 5.05～4.98 (m, 2H), 3.50～3.42 (m, 1.31H), 2.82～2.74 (m, 1H), 2.61 (t, J=7.2 Hz, 0.73H), 2.36 (s, 8.54H), 1.91 (q, J=5.5 Hz, 0.86H), 1.42～1.36 (m, 1H), 1.30～1.15 (m, 9H), 0.86 (q, J=7.9 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$). HRMS (ESI-TOF) calcd for $C_{27}H_{35}O_4$ $[M+H]^+$ 423.2535, found 423.2538. HPLC analysis: chiral IC (250 mm×4.6 mm, 5 μm, V(hexane)∶V(*i*-PrOH)=99∶1, 0.5 mL/min, 25 ℃, 210 nm), t_R(minor)=20.54 min, t_R(major)=21.56 min.

4.3 Synthesis of **4**

To a solution of **3a** (0.2 mmol) in tetrahydrofuran (THF) (0.4 mL), NaH (1.5 equiv.) was added portion wise at 0 ℃. This solution was allowed to stir for 30 min and allyl bromide (1.5 equiv.) was added to the solution slowly. Followed by the stirring of the reaction mixture at room temperature for next 12 h. The progress of the reaction was monitored by the TLC analysis. After completion of the reaction, the mixture was filtered through the celite and washed with ethyl acetate (10 mL×2). The organic layer was extracted with ethyl acetate, concentrated under reduced pressure and subjected to column chromatographic purification, resulting into **4**[10] as a yellow oil (32.5 mg, 75% yield, 87% *ee*). Eluent: V(petroleum ether)∶V(ethyl acetate)=90∶10. $[\alpha]_D^{20}$ −24.52 (*c* 0.3, acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.26 (m, 10H), 5.82～5.68 (m, 1H), 5.51 (dt, J=17.0, 10.1 Hz, 1H), 5.20～5.10 (m, 4H), 5.10～5.06 (m, 1H), 5.06～4.94 (m, 3H), 2.66 (d, J=7.3 Hz, 2H), 2.59 (td, J=10.2, 2.3 Hz, 1H), 1.60 (dt, J=10.4, 3.9 Hz, 2H), 1.32～1.18 (m, 4H), 1.14～1.07 (m, 2H), 0.84 (t, J=7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.17, 169.91, 136.81, 135.29, 135.25, 132.91, 128.28, 128.19, 128.05, 118.40, 118.33, 66.67, 61.36, 48.56, 38.70, 31.34, 30.28, 27.28, 22.35, 13.86. HRMS (ESI-TOF) calcd for $C_{28}H_{33}O_4$ $[M-H]^+$ 433.2384, found 433.2380. HPLC analysis: chiral IC (250 mm×4.6 mm, 5 μm, V(hexane)∶V(*i*-PrOH) = 99∶1, 1.0 mL/min, 25 ℃, 210 nm), t_R(minor)=15.28 min, t_R(major)=16.07 min.

4.4 Synthesis of **5**

To a flame-dried RB charged with a stir bar were added **3a** (1.0 equiv.) and 0.5 mL of ethanol. To the vial was added 0.5 mL of an ethanolic solution of KOH (14 mg, 2.5 equiv.). The reaction mixture was stirred for 18 h at room temperature under nitrogen. The reaction mixture was then concentrated to dryness and acidified with 1 mol/L HCl until precipitate stopped appearing. The resulting mixture was diluted with water and then extracted with EtOAc (10 mL×3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to afford **5** as a yellow oil (14.2 mg, 85% yield, B∶L=3.3∶1, 87% *ee*). Eluent: DCM/MeOH=80∶20. $[\alpha]_D^{20}$ +4.32 (*c* 0.3, acetone; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (s, 3H), 5.64 (dt, J=17.1, 8.4 Hz, 1H), 5.59～5.50 (m, 0.21H), 5.36 (dt, J=9.2, 5.8 Hz, 0.28H), 5.18～5.06 (m, 2H), 3.43 (d, J=8.0 Hz, 1H), 2.80～2.68 (m, 1H), 2.60 (s, 0.34H), 1.98 (p, J=7.0 Hz, 0.60H), 1.43～1.18 (m, 10H), 0.87 (t, J=6.6 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ: 173.84, 137.49, 118.23, 56.89, 44.58, 32.28, 31.61, 26.82, 22.65, 14.16, 14.14. HRMS (ESI-TOF) calcd for $C_{11}H_{17}O_4$ $[M-H]^+$ 213.1132, found 213.1128. HPLC analysis: chiral IB N-5 (250 mm×4.6 mm, 5 μm, V(hexane)∶V(*i*-PrOH)=80∶20, 1.0 mL/min, 25 ℃, 210 nm), t_R(minor)=65.97 min, t_R(major)=72.67 min).

Supporting Information Experimental procedures, characterization data and NMR spectra. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

References

[1] (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Cheng, Q.; Tu, H.-F.; Zheng, C.; Qu, J.-P.; Helmchen G.; You,

S.-L. *Chem. Rev*. **2019**, *119*, 1855.
(c) Trost, B. M.; Crawley, M. L. *Chem. Rev*. **2003**, *103*, 2921.
(d) Harutyunyan, S. R.; den Hartog, T.; Geurts, K.; Minnaard, A. J.; Feringa, B. L. *Chem. Rev*. **2008**, *108*, 2824.
(e) Butt, N. A.; Zhang, W. *Chem. Soc. Rev*. **2015**, *44*, 7929.
[2] (a) Süsse, L.; Stoltz, B. M. *Chem. Rev*. **2021**, *121*, 4084.
(b) Kalita, S. J.; Huang Y.-Y.; Schneider, U. *Sci. Bull*. **2020**, *65*, 1865.
(c) Sempere, Y.; Alfke, J. L.; Rössler S. L.; Carreira, E. M. *Angew. Chem. Int. Ed*. **2019**, *58*, 9537.
(d) Chang, X.; Che, C.; Wang Z.-F.; Wang, C.-J. *CCS Chem*. **2022**, *4*, 1414.
(e) Huo, X.; Zhao, L.; Luo, Y.; Wu, Y.; Sun, Y.; Li, G.; Gridneva, T.; Zhang, J.; Ye Y.; Zhang, W. *CCS Chem*. **2022**, *4*, 1720.
(f) Pal, D.; Veeranna, K. D.; Wong, Y. F.; Evans, P. A. *Sci. China Chem*. **2024**, *67*, 3791.
(g) Jiang, R.; Zhao, Q.-R.; Zheng, C.; You, S.-L. *Nat. Catal.* **2022**, *5*, 1089.
(h) Wang, T.-C.; Fan, L.-F.; Shen, Y.; Wang P.-S.; Gong, L.-Z. *J. Am. Chem. Soc*. **2019**, *141*, 10616.
(i) Fan, L.-F.; Luo, S.-W.; Chen, S.-S.; Wang, T.-C.; Wang, P.-S.; Gong, L. Z. *Angew. Chem. Int. Ed*. **2019**, *58*, 16806.
(j) Stanley, L. M.; Bai, C.; Ueda, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 8918.
(k) Richard, F.; Clark, P.; Hannam, A.; Keenan, T.; Jean, A.; Arseniyadis, S. *Chem. Soc. Rev.* **2024,** *53*, 1936.
(l) Bartels, B.; García-Yebra, C.; Rominger, F.; Helmchen, G. *Eur. J. Inorg. Chem*. **2002**, 2569.
[3] (a) Janssen J. P.; Helmchen, G. *Tetrahedron Lett*. **1997**, *38*, 8025.
(b) Alonso, D. A.; Maciá, B.; Pastor, I. M.; Baeza, A. *ACS Org. Inorg. Au* **2024**, *4*, 269.
(c) Bartels, B.; Helmchen, G. *Chem. Commun.* **1999**, 741.
(d) Moghadam, F. A.; Hicks, E. F.; Sercel, Z. P.; Cusumano, A. Q.; Bartberger M. D.; Stoltz, B. M. *J. Am. Chem. Soc.* **2022**, *144*, 7983.
(e) Hayashi, T.; Okada, A.; Suzuka T.; Kawatsura, M. *Org. Lett.* **2003**, *5*, 1713.
[4] (a) Trost, B. M.; Fandrick, D. R.; Dinh, D. C. *J. Am. Chem. Soc.* **2005**, *127*, 14186.
(b) Koschker, P.; Breit, B. *Acc. Chem. Res.* **2016**, *49*, 1524.
(c) Wang, W.; Hu, Y.; Li, K.; Xu, J.; Zhang, C.; Zhou, L.; Zhu, L.; Guo, H. *ACS Catal.* **2024**, *14*, 9940.
[5] Sempere, Y.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2018**, *57*, 7654.
[6] Tang, S.-B.; Zhang, X.; Tu, H.-F.; You, S.-L. *J. Am. Chem. Soc.* **2018**, *140*, 7737.
[7] (a) Meng, C.-Y.; Liang, X.; Wei K.; Yang, Y.-R. *Org. Lett.* **2019**, *21*, 840.
(b) Zhang, T.-Y.; Deng, Y.; Wei, K.; Yang, Y.-R. *Org. Lett.* **2021**, 23, 1086.
[8] (a) Newton, C. G.; Wang, S.-G.; Oliveira, C. C.; Cramer, N. *Chem. Rev*. **2017**, *117*, 8908.
(b) Chen, Z.; Rong, M.-Y.; Nie, J.; Zhu, X.-F.; Shi, B.-F.; Ma, J.-A. *Chem. Soc. Rev*. **2019**, *48*, 4921.
(c) Gandeepan, P.; Müller, T.; Zell, D.; Cera, G.; Warratz, S.; Ackermann, L. *Chem. Rev*. **2018**, *119*, 2192.
(d) Liu, C.-X.; Yin, S.-Y.; Zhao, F.; Yang, H.; Feng, Z.; Gu, Q.; You, S.-L. *Chem. Rev*. **2023**, *123*, 10079.
(e) Rej, S.; Ano, Y.; Chatani, N. *Chem. Rev*. **2020**, *120*, 1788.
(f) Chu, J. C.; Rovis, T. *Angew. Chem. Int. Ed.* **2018**, *57*, 62.
(g) Wang, R.; Luan, Y.; Ye, M. *Chin. J. Chem*. **2019**, *37*, 720.
[9] (a) Castellino, N. J.; Montgomery, A. P.; Danon, J. J.; Kassiou, M. *Chem. Rev.* **2023**, *123*, 8127.
(b) Burman, J. S.; Blakey, S. B. *Angew. Chem. Int. Ed*. **2017**, *56*, 13666.
(c) Knecht, T.; Mondal, S.; Ye, J.-H.; Das, M.; Glorius, F. *Angew. Chem. Int. Ed*. **2019**, *58*, 7117.
(d) Sihag, P.; Jeganmohan, M. *Chem. Commun*. **2021**, *57*, 6428.
(e) Lei, H.; Rovis, T. *J. Am. Chem. Soc*. **2019**, *141*, 2268.
(f) Guillemard, L.; Kaplaneris, N.; Ackermann, L.; Johansson, M. J. *Nat. Rev. Chem.* **2021**, *5*, 522.
(g) Lerchen, A.; Knecht, T.; Koy, M.; Ernst, J. B.; Bergander, K.; Daniliuc, C. G.; Glorius, F. *Angew. Chem. Int. Ed*. **2018**, *57*, 15248.
(h) Fernandes, R. A.; Nallasivam, J. L. *Org. Biomol. Chem*. **2019**, *17*, 8647.
(i) Manoharan, R.; Jeganmohan, M. *Eur. J. Org. Chem.* **2020**, 7304.
(j) Jana, R.; Begam, H. M.; Dinda, E. *Chem. Commun.* **2021**, *57*, 10842.
[10] Sihag, P.; Chakraborty, T.; Jeganmohan, M. *Org. Lett.* **2023**, *25*, 1257.
[11] Ye, B.; Cramer, N. *J. Am. Chem. Soc.* **2013**, *135*, 636.
[12] Baik, M. H.; Blakey, S. B. *J. Am. Chem. Soc.* **2020**, *142*, 5842.
[13] Farr, C. M. B.; Kazerouni, A. M.; Park, B.; Poff, C. D.; Won, J.; Sharp, K. R.; Baik, M. H.; Blakey, S. B. *J. Am. Chem. Soc.* **2020**, *142*, 13996.

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