HETEROCYCLES, Vol. 103, No. 2, 2021, pp. 1078 - 1098. © 2021 The Japan Institute of Heterocyclic Chemistry
Received, 30th November, 2020, Accepted, 8th January, 2021, Published online, 17th February, 2021
DOI: 10.3987/COM-20-S(K)61

DIASTEREO- AND ENANTIOSELECTIVE INTRAMOLECULAR 1,6-C–H INSERTION REACTION OF DIARYLDIAZOMETHANES CATALYZED BY CHIRAL DIRHODIUM(II) CARBOXYLATES†

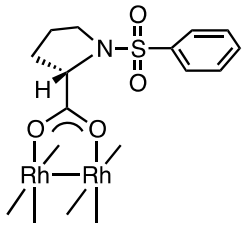
Motoki Ito,[1] Yuji Kondo,[1] Ryosuke Namie,[1] Yoshihiro Natori,[1] Koji Takeda,[1] Hisanori Nambu,[1] Masahiro Anada,[1,2]* Yasunori Yamamoto,[3] and Shunichi Hashimoto[1,4]*

[1]Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan [2]Research Institute of Pharmaceutical Sciences, Musashino University, Nishitokyo, Tokyo 202-8585, Japan [3]Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan [4]Research Organization of Science and Technology, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan
e-mail: m_anada@musashino-u.ac.jp, hsmt@pharm.hokudai.ac.jp

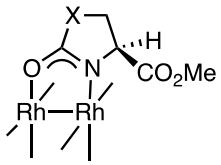
Abstract – A highly diastereo- and enantioselective intramolecular 1,6-C–H insertion reaction of diaryldiazomethanes possessing an ether group has been achieved with the use of dirhodium(II) tetrakis[*N*-phthaloyl-(*S*)-*tert*-leucinate] as a catalyst, providing exclusively 3-substituted *cis*-3,4-dihydro-4-phenyl-1*H*-isochromans in up to 99% ee with no evidence of tandem ylide formation–rearrangement.

Chiral dirhodium(II) complex-catalyzed intramolecular C–H insertion reaction of diazo compounds represents one of the most powerful methods for the construction of both optically active carbocycles and heterocycles, featuring C–C bond formation at an unactivated carbon atom with simultaneous creation of new stereogenic centers.[1–3] McKervey et al. were the first to demonstrate asymmetric induction (up to 12% ee) in intramolecular C–H insertion reactions when cyclization of α-diazo-β-ketosulfones was explored by devising dirhodium(II) tetrakis[*N*-benzenesulfonyl-(*S*)-prolinate], Rh_2(*S*-BSP)$_4$ (**1**).[4] Significant progress was made by Doyle et al. in intramolecular C–H insertion reactions of α-diazoacetates and α-diazoacetamides by the development of chiral dirhodium(II) carboxamidates such as Rh_2(5*S*-MEPY)$_4$ (**2a**), Rh_2(4*S*-MEOX)$_4$ (**2b**), and Rh_2(4*S*-MPPIM)$_4$ (**2c**).[5] In this area, we have developed chiral dirhodium(II) carboxylate complexes that incorporate *N*-phthaloyl-(*S*)-amino acids as

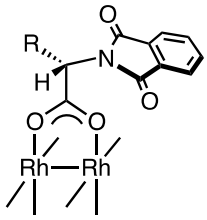
†Dedicated to Professor Dr. Yasuyuki Kita on the occasion of his 77th birthday



Rh_2(*S*-BSP)$_4$ (**1**)



X = CH_2: Rh_2(5S-MEPY)$_4$ (**2a**)
X = O: Rh_2(4S-MEOX)$_4$ (**2b**)
X = $PhCH_2CH_2CON$: Rh_2(4S-MPPIM)$_4$ (**2c**)

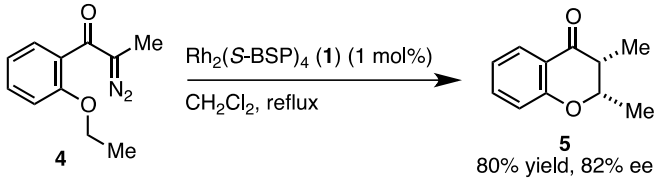


R = ^{t}Bu: Rh_2(*S*-PTTL)$_4$ (**3a**)
R = Bn: Rh_2(*S*-PTPA)$_4$ (**3b**)
R = Me: Rh_2(*S*-PTA)$_4$ (**3c**)

bridging ligands, such as Rh_2(*S*-PTTL)$_4$ (**3a**), Rh_2(*S*-PTPA)$_4$ (**3b**), and Rh_2(*S*-PTA)$_4$ (**3c**). These catalysts mediate intramolecular C–H insertion reactions of α-diazo-β-ketoesters,[6] α-diazoketones,[7] and α-methoxycarbonyl-α-diazoacetamides[8] to give optically active cyclopentanone,[6] 2-indanone,[7] 2-pyrrolidinone,[8a] and 2-azetidinone[8b] derivatives with high levels of enantioselectivity and diastereoselectivity. Of these catalysts, Rh_2(*S*-PTTL)$_4$ (**3a**) with a bulky *tert*-butyl group has proven to be the most generally effective catalyst for a range of diazo substrates.[9–13]

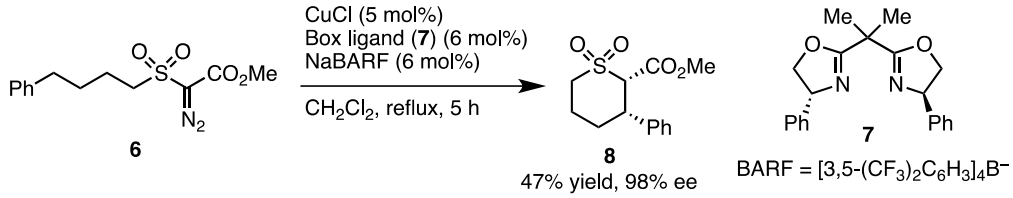
While intramolecular C–H insertion to form five-membered rings is the preferred process, there are few examples of the synthesis of six-membered heterocycles via a 1,6-C–H insertion reaction.[14–16] McKervey et al. demonstrated the first example of enantioselective intramolecular 1,6-C–H insertion of α-diazocarbonyl compounds, in which Rh_2(*S*-BSP)$_4$ (**1**)-catalyzed reaction of α-diazoketone (**4**) gave 2,3-*cis*-disubstituted 4-chromanone (**5**) with 82% ee (Scheme 1a).[17] Maguire et al. reported the intramolecular 1,6-C–H insertion of α-diazo-β-sulfonyl ester (**6**) using CuCl/chiral bis(oxazoline) (**7**)/NaBARF as a catalyst, in which excellent enantioselectivity (98% ee) and perfect *cis* selectivity were achieved (Scheme 1b).[18] The preference for the formation of a six-membered ring in this reaction is attributed to the geometry surrounding the sulfonyl fragment.[15,18a] Recently, we have demonstrated the first asymmetric intramolecular 1,6-C–H insertion reaction of α-diazo esters (Scheme 2a).[19]

a) Enantioselective intramolecular 1,6-C–H insertion reaction of α-diazoketone (**4**)



4 → **5**
80% yield, 82% ee

b) Enantioselective intramolecular 1,6-C–H insertion reaction of α-diazo-β-sulfonyl ester (**6**)

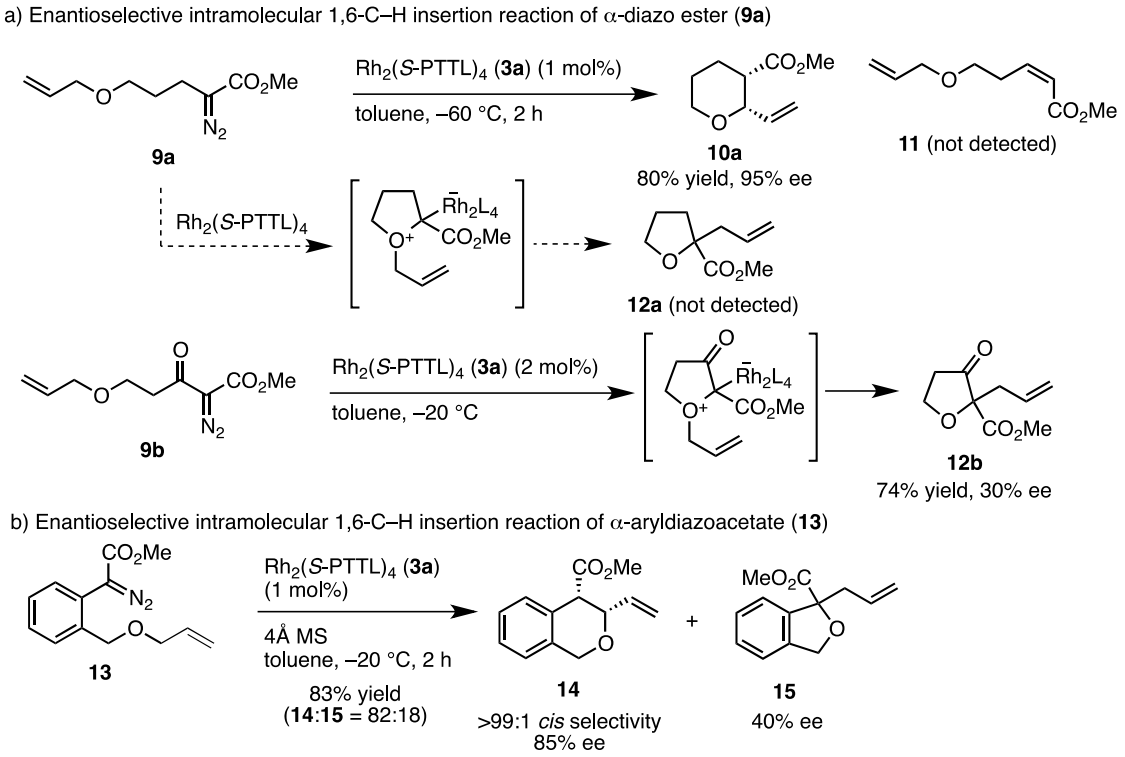


6 → **8**
47% yield, 98% ee

7
BARF = $[3,5\text{-}(CF_3)_2C_6H_3]_4B^-$

Scheme 1

The reaction of 5-allyloxy-2-diazopentanoate (**9a**) under the influence of Rh_2(*S*-PTTL)$_4$ (**3a**) provided exclusively 2,3-*cis*-disubstituted tetrahydropyran (**10**) in up to 95% ee with no evidence of tandem oxonium ylide formation/[2,3]-sigmatropic rearrangement[20,21] that is observed in the case of α-diazo-β-ketoester (**9b**)[21d] or formation of (*Z*)-alkene (**11**) via a 1,2-hydride shift of the dirhodium(II) carbene intermediate.[22] However, the reaction of aryldiazoacetate (**13**) was found to give an 82:18 mixture of C–H insertion product (**14**) (>99:1 *cis* selectivity, 85% ee) and ylide formation-rearrangement product (**15**) (40% ee) (Scheme 2b).[19] This result suggested that the donor/acceptor dirhodium(II) carbene intermediate derived from **13** might be more electrophilic than that derived from **9a**. In this regard, we envisioned that ylide formation could be prevented by using diaryldiazomethanes,[23–25] which have recently been intensively investigated as precursors of less electrophilic donor-donor rhodium(II) carbene intermediates with no pendant electron-withdrawing groups.[23]

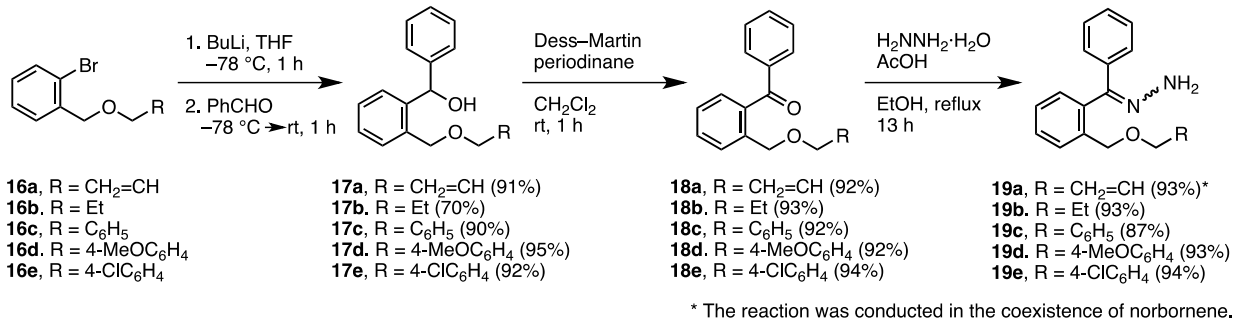


Scheme 2

In continuation of our studies on dirhodium(II)-catalyzed asymmetric reactions,[25] we herein report a chemo-, enantio- and diastereoselective intramolecular 1,6-C–H insertion of diaryldiazomethanes possessing an ether group.[26]

According to the procedure in our previous work,[25] the requisite diarylketone hydrazones (**19a-e**) were prepared from the known aryl bromides (**16a-e**) as shown in Scheme 3. Lithiation of **16a-e** with 1 equiv of butyllithium in THF at –78 °C followed by treatment with benzaldehyde and Dess–Martin periodinane provided diarylketones (**18a-e**) in good to high yields. Treatment of **18a-e** with hydrazine monohydrate in the presence of acetic acid gave hydrazone (**19a-e**) in high yields. In the case of preparation of **19a** from

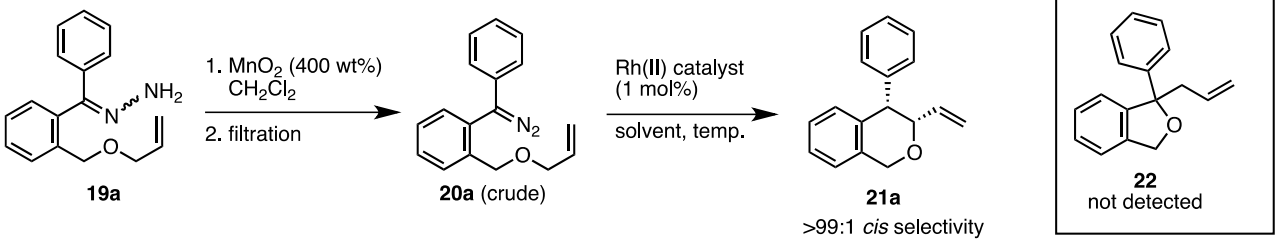
18a, the reaction was conducted in the coexistence of norbornene (bicyclo[2.2.1]hept-2-ene) to prevent reduction of the double bond of the allyl group by diimide arising from the hydrazine.[27]



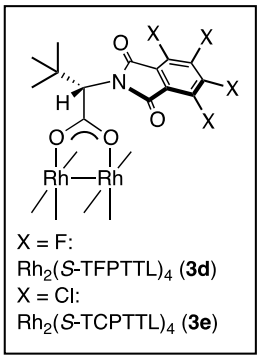
Scheme 3

At the outset, we explored the intramolecular C–H insertion of diaryldiazomethane (**20a**), which was prepared from hydrazone (**19a**) by oxidation with MnO_2 followed by filtration and evaporation. The reaction in dichloromethane at −40 °C using 1 mol% of Rh_2(*S*-PTTL)$_4$ (**3a**) proceeded smoothly to completion within 0.5 h to give the expected *cis*-3,4-dihydro-1*H*-isochroman derivative (**21a**) as the sole product in 92% yield (Table 1, entry 1). As expected, no signs of tandem ylide formation–rearrangement

Table 1. Enantioselective Intramolecular C–H Insertion Reaction of Diaryldiazomethane (**20a**) Catalyzed by Dirhodium(II) Carboxylates[a]



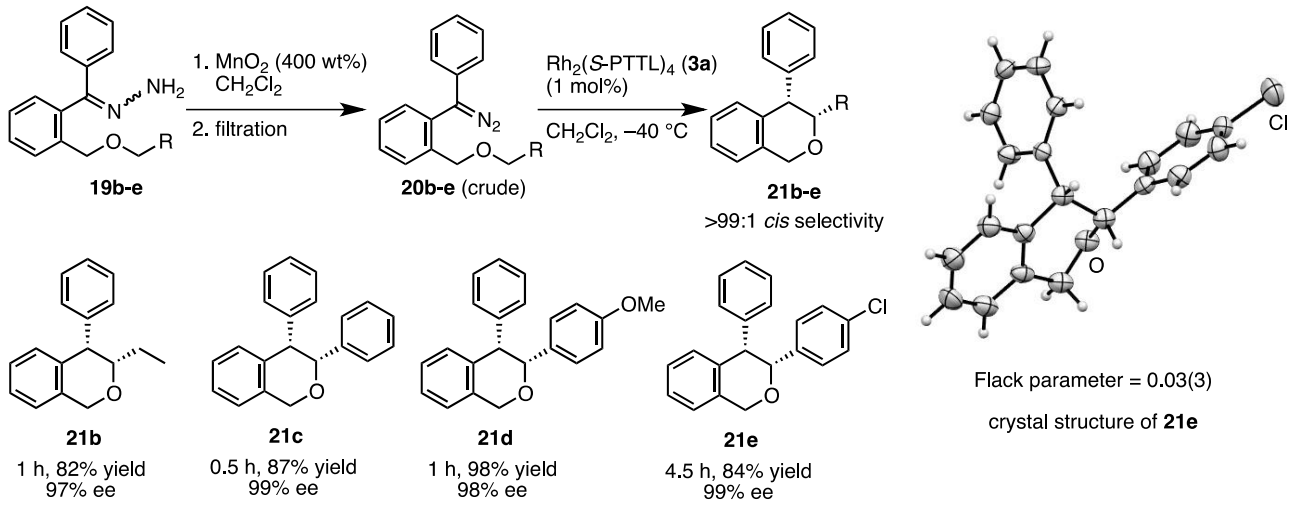
entry	Rh(II) catalyst	solvent	temp, °C	time h	**21a** % yield[b]	**21a** % ee[c]
1	Rh_2(*S*-PTTL)$_4$ (**3a**)	CH_2Cl_2	–40	0.5	92	97
2	Rh_2(*S*-PTTL)$_4$ (**3a**)	toluene	–40	0.5	99	94
3	Rh_2(*S*-PTTL)$_4$ (**3a**)	Et_2O	–40	6	85	95
4	Rh_2(*S*-PTTL)$_4$ (**3a**)	CH_2Cl_2	–60	8	94	98
5	Rh_2(*S*-PTTL)$_4$ (**3a**)	CH_2Cl_2	0	0.5	94	94
6	Rh_2(*S*-TFPTTL)$_4$ (**3d**)	CH_2Cl_2	–40	7	91	95
7	Rh_2(*S*-TCPTTL)$_4$ (**3e**)	CH_2Cl_2	–40	6	94	94



[a]All reactions were carried out as follows: MnO_2 (400 wt%) was added to a solution of **19a** (0.2 mmol) in CH_2Cl_2 (2 mL) at 0 °C and stirred at room temperature for 0.5 h. After filtration through a Celite pad and evaporation, Rh(II) catalyst (1 mol%) was added to a solution of crude **20a** in the indicated solvent (2 mL) at the indicated temperature. [b]Isolated yield based on hydrazone (**19a**). [c]Determined by HPLC (Chiralpak IB).

product (**22**) were detected in the crude reaction mixture by NMR spectroscopy. The enantioselectivity of this reaction was determined to be 97% by chiral HPLC analysis (Daicel ChiralPak IB). A survey of solvents at –40 °C revealed that dichloromethane was the optimal solvent for this transformation (Entries 1 vs 2 and 3). Although toluene exhibited essentially the same rate and product yield as those found in dichloromethane, a slight drop in enantioselectivity was observed (Entry 2). Ether retarded the reaction and diminished the product yield (Entry 3). An examination of the temperature profile demonstrated that –40 °C was the temperature limit. Not unexpectedly, increasing the reaction temperature to 0 °C was accompanied by a slight decrease in enantioselectivity (Entry 4). Using dichloromethane as the solvent, we then evaluated the performance of other chiral dirhodium(II) carboxylates, Rh_2(*S*-TFPTTL)$_4$ (**3d**),[28,29] and Rh_2(*S*-TCPTTL)$_4$ (**3e**),[30,31] fluorinated and chlorinated analogues of Rh_2(*S*-PTTL)$_4$ (Entries 6 and 7). While the use of these catalysts had little impact on the product yield and enantioselectivity, significantly longer reaction times were required to complete the reaction.

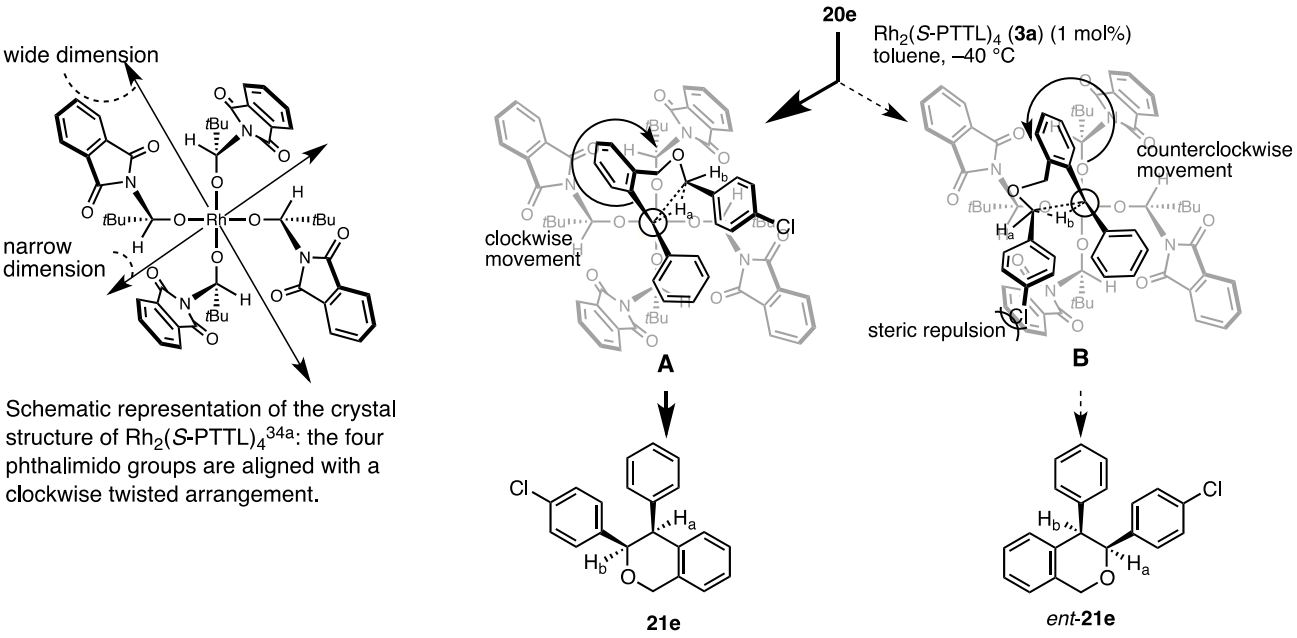
We then investigated the scope of this catalytic process with respect to substituents at the insertion site (Scheme 4). Aside from complete *cis* selectivity, excellent enantioselectivities (97–99% ee) were maintained with alkyl and phenyl groups at the insertion site. It is also notable that no trace of oxonium ylide formation/Stevens rearrangement products were observed when using benzyl ethers (**20c-e**).[26,32] The preferred absolute configuration of **21e** {$[\alpha]_D^{22}$ +428.6 (*c* 1.08, $CHCl_3$) for 99% ee} was determined to be (3*R*,4*S*) by single-crystal X-ray analysis.[33]



Scheme 4

The stereochemical outcome of the C–H insertion of diaryldiazomethane (**21e**) can be explained on the basis of the crystal structure of Rh_2(*S*-PTTL)$_4$, which was determined by Fox et al.,[34] coupled with Doyle–Taber's mechanistic hypothesis (Scheme 5).[35,36] Provided that the chiral crown structure of Rh_2(*S*-PTTL)$_4$ is available in solution,[34,37,38] there are two competing transition states, (**A**) and (**B**), in

which the phenyl group on the carbene carbon is accommodated in the wide dimension of the chiral cavity[34a] in either case, and the oxygen-containing chain undergoing C–H insertion approaches the rhodium-bound carbene through a clockwise or counterclockwise movement, respectively. Transition state (**A**) is favored over transition state (**B**) because of the steric repulsion between the 4-chlorophenyl moiety and the phthalimido group in **B**, directing the cyclization toward C–H_a bond in accord with the observed sense of asymmetric induction.



Scheme 5

In summary, we have reported a chemo-, diastereo- and enantioselective intramolecular 1,6-C–H insertion reaction of diaryldiazomethane derivatives possessing an ether group. With the use of Rh_2(S-PTTL)$_4$ as a catalyst, the reaction proceeded in a fully chemoselective manner to give 3-substituted *cis*-3,4-dihydro-4-phenyl-1*H*-isochromans with enantioselectivities of up to 99% ee and perfect diastereoselectivity. Application of this method to the asymmetric synthesis of pharmacologically active compounds containing an isochroman skeleton is currently underway.

EXPERIMENTAL

General. Melting points were determined on a Büchi 535 digital melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer and absorbance bands are reported in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on JEOL JNM-ECX400P spectrometer or JEOL JNM-ECS400 spectrometer. Optical rotations were measured on a JASCO P-1030 digital polarimeter at the sodium D line (589 nm). ESI-MS and APCI-MS spectra were obtained on a Thermo Scientific Exactive spectrometer. Analytical high performance liquid chromatography (HPLC) was performed on a

JASCO PU-1580 intelligent HPLC pump with JASCO UV-1575 intelligent UV/vis detector. Detection was performed at 254 nm. Chiralpak IA (0.46 cm × 25 cm) or Chiralpak IB (0.46 cm × 25 cm) from Daicel were used. Retention times (t_R) and peak ratios were determined with JASCO-ChromNAV analysis system. Single crystal X-ray analysis was performed on a Rigaku XtaLAB Mini II. All non-aqueous reactions were carried out in flame-dried glassware under an argon atmosphere unless otherwise noted. Reagents and solvents were purified by standard means. Dehydrated stabilizer-free CH_2Cl_2, toluene, Et_2O and THF were purchased from Kanto Chemical Co., Inc and purified by a solvent dispensing system supplied by Glass Contour (Nikko Hansen & Co. Ltd.).

1-Bromo-2-propyloxymethylbenzene (16b). 1-Propanol (180 mg, 3.0 mmol) was added to a suspension of NaH (120 mg, 3.0 mmol) in THF (4.5 mL) at 0 °C. After stirring at the same temperature for 1 h, a solution of 1-bromo-2-bromomethylbenzene (500 mg, 2.0 mmol) in THF (2.0 mL) was added, and the mixture was allowed to warm to room temperature. After stirring for 1.5 h, the mixture was poured into a two-layer mixture of Et_2O (10 mL) and saturated aqueous NH_4Cl (10 mL) at 0 °C, and the aqueous layer was extracted with EtOAc (50 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL) and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, hexane/EtOAc 25:1) to give **16b** (448 mg, 99%) as a colorless oil; R_f = 0.68 (4:1 hexane/EtOAc); IR (film) ν 2961, 2874, 1439, 1102, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.99 (t, *J* = 7.4 Hz, 3H, C*H*$_3$), 1.62–1.74 (m, 2H, OCH$_2$C*H*$_2$CH$_3$), 3,53 (t, *J* = 6.8 Hz, 2H, OC*H*$_2$CH$_2$CH$_3$), 4.57 (s, 2H, ArC*H*$_2$O), 7.14 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.32 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.50 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.54 (d, *J* = 7.7 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.7 (CH_3), 22.9 (CH_2), 72.0 (CH_2), 72.6 (CH_2), 122.5 (C), 127.3 (CH), 128.7 (CH), 128.8 (CH), 132.4 (CH), 138.0 (C); HRMS (EI) calcd for $C_{10}H_{13}BrO$ (M^+) 228.0150, found 228.0144.

1-Bromo-2-(4-chlorophenylmethoxymethyl)benzene (16e). 2-Bromobenzyl alcohol (500 mg, 2.67 mmol) was added to a suspension of NaH (208 mg, 2.94 mmol) in DMF (2.7 mL) at 0 °C. After stirring at the same temperature for 1 h, a solution of *p*-chlorobenzyl bromide (660 mg, 3.20 mmol) in DMF (1 mL) was added and the mixture was stirred at room temperature for 2 h. The reaction mixture was then poured into 10% aqueous HCl (5 mL) and the whole was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with water (2 × 20 mL) and brine (2 × 20 mL) and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, hexane/EtOAc 20:1) to give **16e** (626 mg, 75%) as a colorless oil; R_f = 0.68 (4:1 hexane/EtOAc); IR (film) ν 3063, 2857, 1491, 1090, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.60 (s, 2H, ArC*H*$_2$O), 4.62 (s, 2H, ArC*H*$_2$O), 7.16 (dt, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.29–7.37 (m, 5H, Ar*H*),

7.49–7.56 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 71.6 (CH_2), 71.9 (CH_2), 122.8 (C), 127.4 (CH), 128.6 (CH), 129.01 (CH), 129.02 (CH), 129.2 (CH), 132.6 (CH), 133.4 (C), 136.5 (C), 137.3 (C); HRMS (EI) calcd for $C_{14}H_{12}BrClO$ (M^+) 309.9760, found 309.9757.

Typical Procedure for Preparation of Diarylmethanol: 1-[(2-Allyloxymethy)phenyl]-1-phenylmethanol (17a). Butyllithium (1.6 M in hexane, 0.3 mL, 0.44 mmol) was added to a solution of 1-allyloxymethyl-2-bromobenzene (**16a**)[39] (100 mg, 0.44 mmol) in THF (1.5 mL) at –78 °C. The mixture was stirred at –78 °C for 1 h, and benzaldehyde (51 mg, 0.05 mL, 0.48 mmol) was added. After stirring at –78 °C for 30 min, the mixture was allowed to warm to room temperature. After stirring at room temperature for 1 h, the mixture was poured into a two-layer mixture of Et_2O (5 mL) and saturated aqueous NH_4Cl (5 mL) at 0 °C. The aqueous layer was extracted with EtOAc (2 × 30 mL), and the combined organic layers were washed with water (15 mL) and brine (15 mL) and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product which was purified by column chromatography (silica gel, hexane/EtOAc 10:1 → 6:1) to provide **17a** (100 mg, 91%) as a colorless oil; R_f = 0.44 (4:1 hexane/EtOAc); IR (film) ν 3407, 3063, 3027, 2860, 1451 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.95–3.99 (m, 3H, ArCH(O*H*)Ar + OC*H*$_2$CH=CH$_2$), 4.34 (d, *J* = 11.4 Hz, 1H, ArCH*H*O), 4.54 (d, *J* = 11.4 Hz, 1H, ArCH*H*O), 5.22 (dd, *J* = 10.2, 1.3 Hz, 1H, *cis*-OCH$_2$CH=CH*H*), 5.29 (ddd, *J* = 17.2, 3.2, 1.3 Hz Hz, 1H, *trans*-OCH$_2$CH=CH*H*), 5.87–5.96 (m, 1H, OCH$_2$C*H*=CHH), (d. *J* = 5.2 Hz, 1H, ArC*H*(OH)Ar), 7.25–7.39 (m, 9H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 71.2 (CH_2), 73.89 (CH), 73.91 (CH_2), 118.0 (CH_2), 126.4 (CH), 127.1 (CH), 127.8 (CH), 128.1 (CH), 128.8 (CH), 129.1 (CH), 130.7 (CH), 133.8 (CH), 135.1 (C), 142.8 (C), 143.5 (C); HRMS (ESI) calcd for $C_{17}H_{18}O_2Na$ (M+Na$^+$) 277.1204, found 277.1203.

1-Phenyl-1-[(2-propyloxymethyl)phenyl]methanol (17b). According to the typical procedure for preparation of diarylmethanol, **17b** was prepared from **16b** (350 mg, 1.53 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 10:1 → 6:1) furnished **17b** (269 mg, 70%) as a colorless oil; R_f = 0.47 (4:1 hexane/EtOAc); IR (film) ν 3398, 2963, 2874, 1452, 761, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, *J* = 7.4 Hz, 3H, C*H*$_3$), 1.57–1.66 (m, 2H, OCH$_2$C*H*$_2$CH$_3$), 3.35–3.44 (m, 2H, OC*H*$_2$CH$_2$CH$_3$), 4.28–4.31 (m, 2H, ArCH(O*H*)Ar + ArCH*H*O), 4.49 (d, *J* = 11.6 Hz, 1H, ArCH*H*O), 5.99 (d. *J* = 5.6 Hz, 1H, ArC*H*(OH)Ar), 7.23–7.38 (m, 9H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.5 (CH_3), 22.7 (CH_2), 72.1 (CH_2), 72.3 (CH_2), 74.0 (CH), 126.3 (CH), 127.0 (CH), 127.7 (CH), 128.1 (CH), 128.6 (CH), 129.1 (CH), 130.7 (CH), 135.4 (C), 142.9 (C), 143.5 (C); HRMS (ESI) calcd for $C_{17}H_{20}O_2Na$ (M+Na$^+$) 279.1356, found 279.1354.

1-[(2-Benzyloxymethyl)phenyl]-1-phenylmethanol (17c). According to the typical procedure for preparation of diarylmethanol, **17c** was prepared from 1-benzyloxymethyl-2-bromobenzene (**16c**)[40] (600 mg, 2.16 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 10:1 → 5:1) furnished **17c** (583 mg, 90%) as a colorless oil; R_f = 0.39 (4:1 hexane/EtOAc); IR (film) ν 3405, 3062, 3029, 2863, 1452 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.82 (d, *J* = 5.6 Hz, 1H, ArCH(O*H*)Ar), 4.38 (d, *J* = 11.2 Hz, 1H, ArCH*H*O), 4.51 (s, 2H, PhCH_2O), 4.56 (d, *J* = 11.2 Hz, 1H, ArCH*H*O), 6.02 (d. *J* = 5.6 Hz, 1H, ArC*H*(OH)Ar), 7.24–7.37 (m, 14H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 71.1 (CH_2), 72.5 (CH_2), 73.8 (CH), 126.4 (CH), 127.1 (CH), 127.8 (CH), 127.9 (CH), 128.1 (CH), 128.2 (CH), 128.5 (CH), 128.8 (CH), 129.0 (CH), 130.7 (CH), 135.1 (C), 137.2 (C), 142.9 (C), 143.4 (C); HRMS (ESI) calcd for $C_{21}H_{20}O_2Na$ ($M+Na^+$) 327.1356, found 327.1356.

1-[[2-(4-Methoxyphenyl)methoxymethyl]phenyl]-1-phenylmethanol (17d). According to the typical procedure for preparation of diarylmethanol, **17d** was prepared from 1-bromo-2-(4-methoxybenzyloxymethyl)benzene (**16d**)[41] (600 mg, 1.95 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 10:1 → 5:1) furnished **17d** (615 mg, 95%) as a colorless oil; R_f = 0.30 (4:1 hexane/EtOAc); IR (film) ν 3407, 3028, 2862, 1612, 1513, 1248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 3H, OCH_3), 3.95 (d, *J* = 5.6 Hz, 1H, ArCH(O*H*)Ar), 4.33 (d, *J* = 11.6 Hz, 1H, ArCH*H*O), 4.43 (s, 2H, ArCH_2O), 4.53 (d, *J* = 11.6 Hz, 1H, ArCH*H*O), 6.00 (d. *J* = 5.6 Hz, 1H, ArC*H*(OH)Ar), 6.89 (dt, *J* = 8.8, 2.6 Hz, 2H, ArH), 7.23–7.35 (m, 11H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2 (CH_3), 70.9 (CH_2), 72.1 (CH_2), 73.8 (CH), 113.9 (CH), 126.4 (CH), 127.0 (CH), 127.7 (CH), 128.1 (CH), 128.7 (CH), 129.0 (CH), 129.3 (C), 129.7 (CH), 130.7 (CH), 135.2 (C), 142.9 (C), 143.5 (C), 159.4 (C); HRMS (ESI) calcd for $C_{22}H_{22}O_3Na$ ($M+Na^+$) 357.1461, found 357.1461.

1-[[2-(4-Chlorophenyl)methoxymethyl]phenyl]-1-phenylmethanol (17e). According to the typical procedure for preparation of diarylmethanol, **17e** was prepared from **16e** (600 mg, 1.93 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 10:1 → 5:1) furnished **17e** (599 mg, 92%) as a colorless oil; R_f = 0.37 (4:1 hexane/EtOAc); IR (film) ν 3407, 3028, 2863, 1598, 1491, 1087, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.70 (d, *J* = 5.6 Hz, 1H, ArCH(O*H*)Ar), 4.37 (d, *J* = 11.2 Hz, 1H, ArCH*H*O), 4.44 (s, 2H, ArCH_2O), 4.53 (d, *J* = 11.2 Hz, 1H, ArCH*H*O), 6.00 (d. *J* = 5.6 Hz, 1H, ArC*H*(OH)Ar), 7.21–7.33 (m, 13H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 71.1 (CH_2), 71.5 (CH_2), 73.7 (CH), 126.4 (CH), 127.2 (CH), 127.8 (CH), 128.2 (CH), 128.6 (CH), 128.8 (CH), 128.9 (CH), 129.3 (CH), 130.5 (CH), 133.6 (C), 134.9 (C), 135.8 (C), 142.8 (C), 143.2 (C); HRMS (ESI) calcd for $C_{21}H_{19}ClO_2Na$ ($M+Na^+$) 361.0966, found 361.0966.

Typical Procedure for Preparation of Diarylketone: 1-[(2-Allyloxymethy)phenyl]-1-phenylmethanone (18a). Dess–Martin periodinane (1.47 g, 3.46 mmol) was added to a solution of alcohol **17a** (800 mg, 3.15 mmol) in CH_2Cl_2 (32 mL) at 0 °C. After stirring at room temperature for 1 h, the reaction was quenched by saturated aqueous $Na_2S_2O_3$ (10 mL) and saturated aqueous $NaHCO_3$ (10 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL) and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, hexane/EtOAc 15:1) to provide **18a** (700 mg, 92%) as a colorless oil; R_f = 0.57 (4:1 hexane/EtOAc); IR (film) ν 3064, 3025, 2856, 1666, 1579, 1448, 1270 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.88 (dt, *J* = 5.2, 1.4 Hz, 2H, OC*H*$_2$CH=CH$_2$), 4.60 (s, 2H, ArC*H*$_2$O), 5.07 (ddd, *J* = 10.6, 3.3, 1.6 Hz, 1H, *cis*-OCH$_2$CH=CH*H*), 5.15 (ddd, *J* = 17.5, 3.3 1.6 Hz Hz, 1H, *trans*-OCH$_2$CH=CH*H*), 5.70–5.80 (m, 1H, OCH$_2$C*H*=CHH), 7.35–7.38 (m, 2H, Ar*H*), 7.43–7.51 (m, 3H, Ar*H*), 7.56–7.60 (m, 2H, Ar*H*), 7.79–7.81 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.7 (CH_2), 71.5 (CH_2), 117.0 (CH_2), 126.9 (CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 130.0 (CH), 130.4 (CH), 133.0 (CH), 134.2 (CH), 137.6 (C), 137.7 (C), 138.0 (C), 197.9 (C=O); HRMS (ESI) calcd for $C_{17}H_{16}O_2Na$ ($M+Na^+$) 275.1048, found 275.1047.

1-Phenyl-1-[(2-propyloxymethyl)phenyl]methanone (18b). According to the typical procedure for preparation of diarylketone, **18b** was prepared from **17b** (220 mg, 0.86 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 15:1) furnished **18b** (202 mg, 93%) as a colorless oil; R_f = 0.55 (4:1 hexane/EtOAc); IR (film) ν 2963, 2873, 1667, 1270, 926, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.77 (t, *J* = 7.6 Hz, 3H, C*H*$_3$), 1.39–1.48 (m, 2H, OCH$_2$C*H*$_2$CH$_3$), 3.28 (t, *J* = 6.8 Hz, 2H, OC*H*$_2$CH$_2$CH$_3$), 4.58 (s, 2H, ArC*H*$_2$O), 7.26–7.36 (m, 2H, Ar*H*), 7.42–7.50 (m, 3H, Ar*H*), 7.54–7.58 (m, 2H, Ar*H*), 7.79–7.82 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.4 (CH_3), 22.6 (CH_2), 70.3 (CH_2), 72.5 (CH_2), 126.8 (CH), 128.18 (CH), 128.22 (CH), 128.6 (CH), 130.0 (CH), 130.3 (CH), 132.9 (CH), 137.5 (C), 137.7 (C), 138.3 (C), 197.8 (C=O); HRMS (ESI) calcd for $C_{17}H_{18}O_2Na$ ($M+Na^+$) 277.1199, found 277.1199.

1-[(2-Benzyloxymethyl)phenyl]-1-phenylmethanone (18c). According to the typical procedure for preparation of diarylketone, **18c** was prepared from **17c** (80 mg, 0.26 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 15:1) furnished **18c** (73 mg, 92%) as a colorless oil; R_f = 0.52 (4:1 hexane/EtOAc); IR (film) ν 3062, 3028, 2859, 1664, 1270 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.41 (s, 2H, ArC*H*$_2$O), 4.66 (s, 2H, ArC*H*$_2$O), 7.15–7.17 (m, 2H, Ar*H*), 7.21–7.26 (m, 3H, Ar*H*), 7.33–7.38 (m, 2H, Ar*H*), 7.42–7.45 (m, 2H, Ar*H*), 7.49 (td, *J* = 7.4, 2.5 Hz, 1H, ArH),

7.55–7.60 (m, 2H, Ar*H*), 7.79–7.81 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.0 (CH_2), 72.8 (CH_2), 127.0 (CH), 127.5 (CH), 127.6 (CH), 128.2 (CH), 128.3 (CH), 128.6 (CH), 128.7 (CH), 130.1 (CH), 130.4 (CH), 133.0 (CH), 137.6 (C), 137.82 (C), 137.85 (C), 137.9 (C), 197.9 (C=O); HRMS (ESI) calcd for $C_{21}H_{18}O_2Na$ ($M+Na^+$) 325.1199 found 325.1198.

1-[[2-(4-Methoxyphenyl)methoxymethyl]phenyl]-1-phenylmethanone (18d). According to the typical procedure for preparation of diarylketone, **18d** was prepared from **17d** (500 mg, 1.50 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 10:1) furnished **18d** (450 mg, 92%) as a colorless oil; R_f = 0.41 (4:1 hexane/EtOAc); IR (film) ν 3061, 2857, 1664, 1513, 1248 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H, OC*H*$_3$), 4.33 (s, 2H, ArC*H*$_2$O), 4.62 (s, 2H, ArC*H*$_2$O), 6.76 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.08 (d. *J* = 8.8 Hz, 2H, Ar*H*), 7.32–7.38 (m, 2H, Ar*H*), 7.42–7.50 (m, 3H, Ar*H*), 7.56–7.59 (m, 2H, Ar*H*), 7.80 (d, *J* = 7.2 Hz, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2 (CH_3), 69.6 (CH_2), 72.4 (CH_2), 113.6 (CH), 126.9 (CH), 128.3 (CH), 128.6 (CH), 128.7 (CH), 129.3 (CH), 130.0 (C), 130.1 (CH), 130.4 (CH), 133.0 (CH), 137.6 (C), 137.9 (C), 138.0 (C), 159.0 (C), 197.9 (C=O); HRMS (ESI) calcd for $C_{22}H_{20}O_3Na$ ($M+Na^+$) 355.1305, found 355.1303.

1-[[2-(4-Chlorophenyl)methoxymethyl]phenyl]-1-phenylmethanone (18e). According to the typical procedure for preparation of diarylketone, **18e** was prepared from **17e** (400 mg, 1.18 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 15:1) furnished **18e** (366 mg, 94%) as a colorless oil; R_f = 0.52 (4:1 hexane/EtOAc); IR (film) ν 3062 2859, 1665, 1271 1087 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.36 (s, 2H, ArC*H*$_2$O), 4.65 (s, 2H, ArC*H*$_2$O), 7.05 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.17 (d. *J* = 8.4 Hz, 2H, Ar*H*), 7.33–7.38 (m, 2H, Ar*H*), 7.41–7.44 (m, 2H, Ar*H*), 7.46–7.50 (m, 1H, Ar*H*), 7.54–7.59 (m, 2H, Ar*H*), 7.77–7.79 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.1 (CH_2), 71.9 (CH_2), 127.1 (CH), 128.27 (CH), 127.30 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 130.1 (CH), 130.3 (CH), 133.10 (CH), 133.12 (C), 136.3 (C), 137.5 (C), 137.6 (C), 137.9 (C), 197.8 (C=O); HRMS (ESI) calcd for $C_{21}H_{17}ClO_2Na$ ($M+Na^+$) 359.0809, found 359.0809.

Typical Procedure for Preparation of Hydrazone: [1-[(2-Benzyloxymethyl)phenyl]-1-phenylmethylene]hydrazine (19c). Hydrazine monohydrate (730 mg, 14.6 mmol) was added to a solution of **18c** (440 mg, 1.46 mmol) and acetic acid (870 mg, 14.6 mmol) in EtOH (15 mL), and the mixture was stirred under reflux for 13 h. After cooling to room temperature, the reaction was quenched by water (5 mL), and the whole was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with water (40 mL) and brine (50 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product, which was purified

by column chromatography (silica gel, hexane/EtOAc 5:1) to give hydrazone **19c** (400 mg, 87%, *E*/*Z* = 91:9) as a yellow solid; R_f = 0.27 (minor isomer), 0.33 (major isomer) (4:1 hexane/EtOAc). Recrystallization of **19c** (127 mg, *E*/*Z* = 91:9) from hexane/EtOAc (100:1) provided a major geometrical isomer (72.4 mg) in analytically pure form; mp 53.0–54.5 °C; IR (KBr) ν 3395, 3276, 3052, 2833, 1600, 1441, 1121 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.35 (d, *J* = 12.2 Hz, 1H, ArC*H*HO), 4.40 (d, *J* = 12.2 Hz, 1H, ArC*H*HO), 4.43 (d, *J* = 12.0 Hz, 1H, ArC*H*HO), 4.46 (d, *J* = 12.0 Hz, 1H, ArC*H*HO), 5.34 (br-s, 2H, C=NNH_2), 7.17 (dd, *J* = 7.6, 1.7 Hz, 1H, Ar*H*), 7.22–7.34 (m, 8H, Ar*H*), 7.43–7.51 (m, 4H, Ar*H*), 7.68–7.70 (m, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.0 (CH_2), 72.9 (CH_2), 125.9 (CH), 127.5 (CH), 127.7 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 128.7 (CH), 128.8 (CH), 129.2 (CH), 129.3 (CH), 132.0 (C), 137.2 (C), 137.9 (C), 138.0 (C), 148.3 (C=N); HRMS (ESI) calcd for $C_{21}H_{20}N_2ONa$ ($M+Na^+$) 339.1468, found 339.1471.

[1-Phenyl-1-[(2-propyloxymethyl)phenyl]methylene]hydrazine (19b). According to the typical procedure for preparation of hydrazone, **19b** was prepared from **18b** (150 mg, 0.59 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 5:1) furnished **19b** (147 mg, 93%, *E*/*Z* = 91:9) as a yellow solid; R_f = 0.37 (4:1 hexane/EtOAc). Recrystallization of **19b** from hexane/EtOAc (10:1) provided a major geometrical isomer in analytically pure form; mp 70.5–71.5 °C; IR (film) ν 3392, 2851, 1441, 1124, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.2 Hz, 3H, CH_3), 1.48–1.55 (m, 2H, $OCH_2CH_2CH_3$), 3.33 (t, *J* = 6.8 Hz, 2H, $OCH_2CH_2CH_3$), 4.27 (d, *J* = 12.0 Hz, 1H,ArCH*H*O), 4.33 (d, *J* = 12.0 Hz, 1H,ArCH*H*O), 5.37 (br-s, 2H, C=NNH_2), 7.15–7.17 (m, 1H, Ar*H*), 7.26–7.30 (m, 3H, Ar*H*), 7.42–7.50 (m, 4H, Ar*H*), 7.65–7.67 (m, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.5 (CH_3), 22.8 (CH_2), 70.2 (CH_2), 72.7 (CH_2), 125.9 (CH), 128.0 (CH), 128.2 (CH), 128.5 (CH), 128.7 (CH), 128.8 (CH), 129.3 (CH), 131.8 (C), 137.6 (C), 137.9 (C), 148.4 (C=N); HRMS (ESI) calcd for $C_{17}H_{20}N_2ONa$ ($M+Na^+$) 291.1468, found 291.1467.

[1-[[2-(4-Methoxyphenyl)methoxymethyl]phenyl]-1-phenylmethylene]hydrazine (19d). According to the typical procedure for preparation of hydrazone, **19d** was prepared from **18d** (400 mg, 1.20 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 4:1) furnished **19d** (388 mg, 93%, *E*/*Z* = 90:10) as a yellow solid; R_f = 0.23 (minor isomer), 0.30 (major isomer) (4:1 hexane/EtOAc). Recrystallization of **19d** (270 mg) from hexane/EtOAc (2.5:1) provided a major geometrical isomer (205 mg) in analytically pure form; mp 106.0–107.0 °C; IR (film) ν 3392, 3273, 2834, 1615, 1517, 1357, 1253 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 3H, OCH_3), 4.30–4.40 (m, 4H, ArCH_2O + ArCH_2O), 5.34 (br-s, 2H, C=NNH_2), 6.80–6.84 (m, 4H, Ar*H*), 7.13–7.19 (m, 3H, Ar*H*), 7.29–7.30 (m, 3H, Ar*H*), 7.43–7.50 (m, 4H, Ar*H*), 7.66–7.68 (m, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ

55.2 (CH_3), 69.7 (CH_2), 72.6 (CH_2), 113.7 (CH), 125.9 (CH), 128.1 (CH), 128.2 (CH), 128.7 (CH), 128.8 (CH), 129.2 (C), 129.28 (CH), 129.34 (CH), 130.1 (C), 132.1 (C), 137.3 (C), 137.9 (C), 148.4 (C=N), 159.1 (C); HRMS (ESI) calcd for $C_{22}H_{22}O_2N_2Na$ ($M+Na^+$) 369.1574, found 369.1571.

[1-[[2-(4-Chlorophenyl)methoxymethyl]phenyl]-1-phenylmethylene]hydrazine (19e). According to the typical procedure for preparation of hydrazone, **19e** was prepared from **18e** (300 mg, 0.89 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 15:1) furnished **19e** (309 mg, 94%, *E*/*Z* = 90:10) as a yellow solid; R_f = 0.24 (minor isomer), 0.34 (major isomer) (4:1 hexane/EtOAc). Recrystallization of **19e** (180 mg) from hexane/EtOAc (2.5:1) provided a major geometrical isomer (134 mg) in analytically pure form; mp 124.5–125.5 °C; IR (film) ν 3407, 3283, 3053, 2841, 1560, 1493, 1158 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.32–4.39 (m, 4H, ArC*H*$_2$O + ArC*H*$_2$O), 5.34 (br-s, 2H, C=NN*H*$_2$), 7.12 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.18 (d. *J* = 8.8 Hz, 1H, Ar*H*), 7.22–7.24 (m, 2H, Ar*H*), 7.27–7.30 (m, 3H, Ar*H*), 7.42–7.45 (m, 2H, Ar*H*), 7.46–7.52 (m, 2H, Ar*H*), 7.65–7.68 (m, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.1 (CH_2), 72.0 (CH_2), 125.9 (CH), 128.1 (CH), 128.2 (CH), 128.4 (CH), 128.8 (CH), 128.9 (CH), 129.2 (CH), 129.3 (CH), 132.1 (C), 133.2 (C), 136.4 (C), 136.7 (C), 137.8 (C), 148.2 (C=N) (one carbon is missing due to overlapping signals); HRMS (ESI) calcd for $C_{21}H_{19}ClN_2ONa$ ($M+Na^+$) 373.1078, found 373.1078.

[1-[(2-Allyloxymethy)phenyl]-1-phenylmethylene]hydrazine (19a). Hydrazine monohydrate (790 mg, 15.9 mmol) was added to a solution of **18a** (400 mg, 1.59 mmol), acetic acid (950 mg, 15.9 mmol) and norbornene (745 mg, 7.93 mmol) in EtOH (16 mL), and the mixture was stirred under reflux for 13 h. After cooling to room temperature, the reaction was quenched by water (5 mL), and the whole was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with water (40 mL) and brine (50 mL), and dried over anhydrous Na_2SO_4. Filtration and evaporation in vacuo furnished the crude product, which was purified by column chromatography (silica gel, hexane/EtOAc 5:1) to give hydrazone **19a** (390 mg, 93%, *E*/*Z* = 92:8) as a yellow solid; ; Rf = 0.27 (minor isomer), 0.33 (major isomer) (4:1 hexane/EtOAc). Recrystallization of **19a** (390 mg, *E*/*Z* = 92:8) from hexane/EtOAc (15:1) provided a major geometrical isomer (253 mg) in analytically pure form; mp 83.0–84.0 °C; IR (KBr) ν 3388, 3271, 2859, 2836, 1629, 1441, 1346 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.92 (d, *J* = 4.0 Hz, 2H, OC*H*$_2$CH=CH$_2$), 4.30 (d, *J* = 12.4 Hz, 2H, ArC*H*H), 4.35 (d, *J* = 12.4 Hz, 2H, ArC*H*H), 5.11 (d, *J* = 10.2 Hz, 1H, *cis*-OCH$_2$CH=CH*H*), 5.19 (d, *J* = 17.5 Hz, 1H, *trans*-OCH$_2$CH=CH*H*), 5.37 (br-s, 2H, C=NN*H*$_2$), 5.78–5.85 (m, 1H, OCH$_2$C*H*=CHH), 7.16 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.27–7.30 (m, 3H, Ar*H*), 7.43–7.48 (m, 4H, Ar*H*), 7.69 (d, *J* = 7.2 Hz, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.7 (CH_2), 71.7 (CH_2), 117.0 (CH_2), 125.9 (CH), 128.1 (CH), 128.2 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 129.3 (CH),

131.6 (C), 134.4 (CH), 137.2 (C), 137.8 (C), 148.3 (C=N); HRMS (ESI) calcd for $C_{17}H_{18}N_2O$ (M^+) 266.1419, found 266.1418.

Typical Procedure for Intramolecular C–H Insertion Reaction of Diaryldiazomethane: *cis*-3,4-Dihydro-4-phenyl-3-vinyl-1*H*-isochroman (21a). MnO_2 (213 mg, 400 wt%) was added to a solution of hydrazone **19a** (53.2 mg, 0.20 mmol) in CH_2Cl_2 (2.0 mL) at 0 °C. After stirring at room temperature for 30 min, the reaction mixture was filtered through a Celite pad. The filtrate was evaporated in vacuo to furnish the crude diaryldiazomethane **20a** (54.4 mg), which was used without further purification.

Rh_2(*S*-PTTL)$_4$·2EtOAc (2.8 mg, 0.002 mmol, 1 mol%) was added to a solution of the crude diaryldiazomethane **20a** in CH_2Cl_2 (2.0 mL) at –40 °C under argon atmosphere. After stirring for 30 min at the same temperature, the reaction mixture was concentrated in vacuo and the residue was purified by column chromatography (silica gel, hexane/EtOAc 15:1) to provide **21a** (43.4 mg, 92% for 2 steps) as a white solid; R_f = 0.62 (hexane/EtOAc 4:1); mp 91.0–92.5 °C; $[\alpha]_D^{20}$ +312.8 (*c* 1.00, $CHCl_3$) for 97% ee; IR (KBr) ν 3076, 3025, 2855, 2830, 1491, 1449, 1426, 1086 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.92 (d, *J* = 3.2 Hz, 1H, C4-*H*), 4.45 (m, 1H, C3-*H*), 4.96–5.11 (m, 3H, C1-*H* and *cis*-OCH_2CH=C*H*H), 5.23 (dt, *J* = 17.6, 1.5 Hz, 1H, *trans*-OCH_2CH=C*H*H), 5.48 (m, 1H, OCH_2C*H*=CHH), 7.01 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.08–7.24 (m, 8H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.5 (CH), 68.3 (CH_2), 79.1 (CH), 116.3 (CH_2), 124.0 (CH), 126.4 (CH), 126.5 (CH), 126.8 (CH), 127.8 (CH), 129.9 (CH), 130.1 (C), 133.9 (C), 136.8 (C), 136.9 (CH), 141.5 (C); HRMS (ESI) calcd for $C_{17}H_{16}ONa$ ($M+Na^+$) 259.1099, found 259.1101. The enantiomeric excess of **21a** was determined to be 97% by HPLC with a Chiralpak IB column, eluent: 200:1 hexane/*i*-PrOH; flow rate: 1.0 mL/min; t_R (major enantiomer) = 6.4 min; t_R (minor enantiomer) = 8.1 min. The preferred absolute configuration of **21a** was not determined.

***cis*-3-Ethyl-3,4-dihydro-4-phenyl-1*H*-isochroman (21b).** According to the typical procedure for intramolecular C–H insertion reaction of diaryldiazomethane, **21b** was prepared from **19b** (53.6 mg, 0.20 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 15:1) furnished **21b** (43.8 mg, 92% for 2 steps) as a colorless oil; R_f = 0.75 (hexane/EtOAc 4:1); $[\alpha]_D^{20}$ +261.9 (*c* 0.96, $CHCl_3$) for 97% ee; IR (film) ν 3062, 2963, 2837, 1492, 1451, 1372, 742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (t, *J* = 7.2 Hz, 3H, C*H*$_3$$CH_2$), 1.16–1.35 (m, 2H, CH_3C*H*$_2$), 3.76 (m, 1H, C3-*H*), 3.84 (d, *J* = 3.2 Hz, 1H, C4-*H*), 7.01 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.07–7.12 (m, 2H, Ar*H*), 7.15–7.19 (m, 4H, Ar*H*), 7.21–7.25 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.4 (CH_3), 26.6 (CH_2), 47.6 (CH), 68.8 (CH_2), 79.8 (CH), 124.0 (CH), 126.25 (CH), 126.3 (CH), 126.7 (CH), 127.9 (CH), 129.7 (CH), 130.3 (CH), 134.2 (C), 137.5 (C), 142.1 (C); HRMS (ESI) calcd for $C_{17}H_{19}O$ ($M+H^+$) 239.1430, found

239.1433. The enantiomeric excess of **21b** was determined to be 97% by HPLC with a Chiralpak IB column, eluent: 200:1 hexane/*i*-PrOH; flow rate: 1.0 mL/min; t_R (major enantiomer) = 5.8 min; t_R (minor enantiomer) = 6.5 min. The preferred absolute configuration of **21b** was not determined.

***cis*-3,4-Dihydro-3,4-diphenyl-1*H*-isochroman (21c).** According to the typical procedure for intramolecular C–H insertion reaction of diaryldiazomethane, **21c** was prepared from **19c** (63.2 mg, 0.20 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 30:1) furnished **19c** (49.7 mg, 87% for 2 steps) as a white solid; R_f = 0.62 (hexane/EtOAc 4:1); mp 123.5–125.0 °C; $[\alpha]_D^{20}$ +462.6 (*c* 1.12, $CHCl_3$) for 99% ee; IR (KBr) ν 3024, 2744, 1602, 1581, 1492, 1450, 1089, 1071, 1030 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.14 (d, *J* = 2.4 Hz, 1H, C4-*H*), 5.11–5.15 (m, 2H, C1-*H* and C3-*H*), 5.25 (d, *J* = 12.4 Hz, 1H, C1-*H*), 6.76 (dd, *J* = 5.8, 1.4 Hz, 2H, Ar*H*), 6.96–6.98 (m, 2H, Ar*H*), 7.01–7.07 (m, 4H, Ar*H*), 7.13–7.19 (m, 5H, ArH), 7.25–7.28 (m, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.2 (CH), 69.1 (CH_2), 80.0 (CH), 124.0 (CH), 125.9 (CH), 126.1 (CH), 126.6 (CH), 126.8 (CH), 126.9 (CH), 127.2 (CH), 127.6 (CH), 130.1 (CH), 130.2 (CH), 134.2 (C), 137.1 (C), 140.2 (C), 140.7 (C); HRMS (ESI) calcd for $C_{21}H_{18}ONa$ ($M+Na^+$) 309.1250, found 309.1253. The enantiomeric excess of **19c** was determined to be 99% by HPLC with a Chiralpak IA column, eluent: 500:1 hexane/*i*-PrOH; flow rate: 1.0 mL/min; t_R (minor enantiomer) = 7.5 min; t_R (major enantiomer) = 9.1 min. The preferred absolute configuration of **19c** was not determined.

***cis*-3,4-Dihydro-3-(4-methoxyphenyl)-4-phenyl-1*H*-isochroman (21d).** According to the typical procedure for intramolecular C–H insertion reaction of diaryldiazomethane, **21d** was prepared from **19d** (50.0 mg, 0.14 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 20:1) furnished **21d** (49.8 mg, 98% for 2 steps) as a white solid; R_f = 0.59 (hexane/EtOAc 4:1); mp 188.0–190.0 °C; $[\alpha]_D^{20}$ +332.4 (*c* 1.19, $CHCl_3$) for 98% ee; IR (KBr) ν 3027, 2841, 1611, 1584, 1513, 1491, 1246, 1084 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.72 (s, 3H, OCH_3), 4.08 (d, *J* = 3.0 Hz, 1H, C4-*H*), 5.04 (d, *J* = 3.0 Hz, 1H, C3-*H*), 5.09–5.28 (m, 2H, C1-*H*), 6.60 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.68–6.70 (m, 2H, Ar*H*), 6.77 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.96–6.98 (m, 4H, Ar*H*), 7.07–7.10 (m, 2H, Ar*H*), 7.17 (t, *J* = 6.8 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.4 (CH), 55.1 (CH_3), 69.1 (CH_2), 79.7 (CH), 113.0 (CH), 124.0 (CH), 126.0 (CH), 126.6 (CH), 126.8 (CH), 127.1 (CH), 127.3 (CH), 130.1 (CH), 130.2 (CH), 132.4 (C), 134.2 (C), 137.2 (C), 140.8 (C), 158.4 (C); HRMS (ESI) calcd for $C_{22}H_{20}O_2Na$ ($M+Na^+$) 339.1356, found 339.1358. The enantiomeric excess of **21d** was determined to be 98% by HPLC with a Chiralpak IA column, eluent: 500:1 hexane/*i*-PrOH; flow rate: 1.0 mL/min; t_R (minor enantiomer) = 17.0 min; t_R (major enantiomer) = 23.8 min. The preferred absolute configuration of **21d** was not determined.

(3*R*,4*S*)-*cis*-3,4-Dihydro-3-(4-chlorophenyl)-4-phenyl-1*H*-isochroman (21e). According to the typical procedure for intramolecular C–H insertion reaction of diaryldiazomethane, **21e** was prepared from **19e** (50.0 mg, 0.14 mmol), MnO_2 (200 mg, 400 wt%) and Rh_2(*S*-PTTL)$_4$·2EtOAc (2.0 mg, 0.0014 mmol, 1 mol%). The crude product was purified by column chromatography (silica gel, hexane/EtOAc 20:1) furnished **21e** (37.8 mg, 84% for 2 steps) as a white solid; R_f = 0.63 (hexane/EtOAc 4:1); mp 152.5–154.0 °C; $[\alpha]_D^{20}$ +428.6 (*c* 1.08, $CHCl_3$) for 99% ee; IR (KBr) ν 3027, 2842, 1490, 1081 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.09 (d, *J* = 3.0 Hz, 1H, C4-*H*), 5.06 (d, *J* = 3.0 Hz, 1H, C3-*H*), 5.10 (d, *J* = 15.6 Hz, 1H, C1-*H*), 5.20 (d, *J* = 15.6 Hz, 1H, C1-*H*), 6.74–6.76 (m, 2H, Ar*H*), 6.89 (d, *J* = 6.8 Hz, 2H, Ar*H*), 7.01–7.05 (m, 4H, Ar*H*), 7.09–7.12 (m, 2H, Ar*H*), 7.16 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.23–7.27 (m, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.1 (CH), 69.0 (CH_2), 79.3 (CH), 124.0 (CH), 126.3 (CH), 126.7 (CH), 126.9 (CH), 127.3 (CH), 127.4 (CH), 127.8 (CH), 130.0 (CH), 130.2 (CH), 132.5 (C), 133.9 (C), 136.8 (C), 138.8 (C), 140.3 (C); HRMS (ESI) calcd for $C_{21}H_{17}ClONa$ ($M+Na^+$) 343.0866, found 343.0876. The enantiomeric excess of **21e** was determined to be 99% by HPLC with a Chiralpak IA column; eluent: 500:1 hexane/*i*-PrOH; flow rate: 1.0 mL/min; t_R (minor enantiomer) = 9.1 min; t_R (major enantiomer) = 9.7 min.

ACKNOWLEDGEMENTS

This research was supported in part by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture, Japan. We are grateful to Prof. Shigeki Matsunaga at Hokkaido University for fruitful discussion. We also thank S. Oka and T. Hirose of the Instrumental Analysis Division, Global Facility Center, Creative Research Institution at Hokkaido University for MS measurements.

REFERENCES AND NOTES

1. For books and reviews, see: (a) M. P. Doyle, M. A. McKervey, and T. Ye, '*Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*,' Wiley-Interscience, New York, 1998; (b) H. M. L. Davies and R. E. J. Beckwith, *Chem. Rev.*, 2003, **103**, 2861; (c) H. M. L. Davies and J. R. Manning, *Nature*, 2008, **451**, 417; (d) H. M. L. Davies and J. Hansen, '*Catalytic Asymmetric Synthesis*,' ed. by I. Ojima, John Wiley & Sons, Hoboken, 2010, Chapter 4; (e) C. N. Slattery, A. Ford, and A. R. Maguire, *Tetrahedron*, 2010, **66**, 6681; (f) M. P. Doyle, R. Duffy, M. Ratnikov, and L. Zhou, *Chem. Rev.*, 2010, **110**, 704; (g) H. M. L. Davies and D. Morton, *Chem. Soc. Rev.*, 2011, **40**, 1857; (h) J. Yamaguchi, A. D. Yamaguchi, and K. Itami, *Angew. Chem. Int. Ed.*, 2012, **51**, 8960; (i) M. P. Doyle, Y. Liu, and M. Ratnikov, *Org. React.*, 2013, **80**, 1; (j) A. Ford, H. Miel, A. Ring, C. N. Slattery, A. R. Maguire, and M. A. McKervey, *Chem. Rev.*, 2015, **115**, 9981; (k) T. Yakura and H. Nambu, *Tetrahedron Lett.*, 2018, **59**, 188; (l) T. Begum, R. Prakash, G. Duarah, and S. Gogoi, '*Studies in Natural Products Chemistry*,' ed. by Atta-ur-Rahman, Elsevier, Amsterdam, 2020, **65**,

349.

2. For characterization of a reactive dirhodium carbene complex, see: (a) K. P. Kornecki, J. F. Briones, V. Boyarskikh, F. Fullilove, J. Autschbach, K. E. Schrote, K. M. Lancaster, H. M. L. Davies, and J. F. Berry, *Science*, 2013, **342**, 351; (b) C. Werlé, R. Goddard, and A. Fürstner, *Angew. Chem. Int. Ed.*, 2015, **54**, 15452; (c) C. Werlé, R. Goddard, P. Philipps, C. Farés, and A. Fürstner, *J. Am. Chem. Soc.*, 2016, **138**, 3797.
3. For the theoretical study of an exceptional reactivity of a dirhodium carbene complex generated from a diazo compound with a dirhodium(II) tetracarboxylate complex, see: (a) S. M. Sheehan, A. Padwa, and J. P. Snyder, *Tetrahedron Lett.*, 1998, **39**, 949; (b) E. Nakamura, N. Yoshikai, and M. Yamanaka, *J. Am. Chem. Soc.*, 2002, **124**, 7181; (c) J. F. Berry, *Dalton Trans.*, 2012, **41**, 700.
4. M. Kennedy, M. A. McKervey, A. R. Maguire, and G. H. P. Roos, *J. Chem. Soc., Chem. Commun.*, 1990, 361.
5. (a) M. P. Doyle, A. van Oeveren, L. J. Westrum, M. N. Protopopova, and T. W. Clayton, Jr., *J. Am. Chem. Soc.*, 1991, **113**, 8982; (b) M. P. Doyle, M. N. Protopopova, W. R. Winchester, and K. L. Daniel, *Tetrahedron Lett.*, 1992, **33**, 7819; (c) M. P. Doyle, A. B. Dyatkin, G. H. P. Roos, F. Cañas, D. A. Pierson, A. van Basten, P. Müller, and P. Polleux, *J. Am. Chem. Soc.*, 1994, **116**, 4507; (d) M. P. Doyle, W. Hu, and M. V. Valenzuela, *J. Org. Chem.*, 2002, **67**, 2954; (e) M. P. Doyle, *J. Org. Chem.*, 2006, **71**, 9253. and references cited therein.
6. (a) S. Hashimoto, N. Watanabe, T. Sato, M. Shiro, and S. Ikegami, *Tetrahedron Lett.*, 1993, **34**, 5109; (b) T. Takahashi, H. Tsutsui, M. Tamura, S. Kitagaki, M. Nakajima, and S. Hashimoto, *Chem. Commun.*, 2001, 1604.
7. N. Watanabe, T. Ogawa, Y. Ohtake, S. Ikegami, and S. Hashimoto, *Synlett*, 1996, 85.
8. (a) M. Anada and S. Hashimoto, *Tetrahedron Lett.*, 1998, **39**, 79; (b) M. Anada, N. Watanabe, and S. Hashimoto, *Chem. Commun.*, 1998, 1517.
9. (a) H. Saito, H. Oishi, S. Kitagaki, S. Nakamura, M. Anada, and S. Hashimoto, *Org. Lett.*, 2002, **4**, 3887; (b) Y. Natori, H. Tsutsui, N. Sato, S. Nakamura, H. Nambu, M. Shiro, and S. Hashimoto, *J. Org. Chem.*, 2009, **74**, 4418; (c) M. Ito, R. Namie, J. Krishnamurthi, H. Miyamae, K. Takeda, H. Nambu, and S. Hashimoto, *Synlett*, 2014, **25**, 288.
10. (a) K. Minami, H. Saito, H. Tsutsui, H. Nambu, M. Anada, and S. Hashimoto, *Adv. Synth. Catal.*, 2005, **347**, 1483; (b) T. Miyazawa, K. Minami, M. Ito, M. Anada, S. Matsunaga, and S. Hashimoto, *Tetrahedron*, 2016, **72**, 3939; (c) T. Miyazawa, K. Imai, M. Ito, K. Takeda, M. Anada, S. Matsunaga, and S. Hashimoto, *Heterocycles*, 2017, **95**, 1211.
11. For a practical synthesis of Rh_2(*S*-PTTL)$_4$, see: H. Tsutsui, T. Abe, S. Nakamura, M. Anada, and S. Hashimoto, *Chem. Pharm. Bull.*, 2005, **53**, 1366.

12. For the effective use of an immobilized catalyst based on Rh_2(*S*-PTTL)$_4$, see: K. Takeda, T. Oohara, M. Anada, H. Nambu, and S. Hashimoto, *Angew. Chem. Int. Ed.*, 2010, **49**, 6979.
13. Davies et al. reported that dirhodium(II) tetrakis[*N*-phthaloyl-(*S*)-1-adamantylglycinate], Rh_2(*S*-PTAD)$_4$, is a highly effective catalyst for intra- and intermolecular C–H insertion reactions: (a) R. P. Reddy, G. H. Lee, and H. M. L. Davies, *Org. Lett.*, 2006, **8**, 3437; (b) J. R. Denton and H. M. L. Davies, *Org. Lett.*, 2009, **11**, 787; (c) D. L. Ventura, Z. Li, M. G. Coleman, and H. M. L. Davies, *Tetrahedron*, 2009, **65**, 3052.
14. (a) D. E. Cane and P. J. Thomas, *J. Am. Chem. Soc.*, 1984, **106**, 5295; (b) E. Lee, I. Choi, and S. Y. Song, *J. Chem. Soc., Chem. Commun.*, 1995, 321; (c) M. P. Doyle and A. B. Dyatkin, *J. Org. Chem.*, 1995, **60**, 3035; (d) A. Rosales, I. Rodríguez-García, C. López-Sánchez, M. Álvarez-Corrál, and M. Muñoz-Dorado, *Tetrahedron*, 2011, **67**, 3071; (e) A. Archambeau, F. Miege, C. Meyer, and J. Cossy, *Angew. Chem. Int. Ed.*, 2012, **51**, 11540.
15. (a) J. P. John and A. V. Novikov, *Org. Lett.*, 2007, **9**, 61; (b) S. A. Wolckenhauer, A. S. Devlin, and J. Du Bois, *Org. Lett.*, 2007, **9**, 4363; (c) C. S. Jungong and A. V. Novikov, *Tetrahedron:* 2013, **24**, 151.
16. For a synthesis of cyclohexanones via a 1,6-C–H insertion reaction of α-aryl-α-diazoketones catalyzed by Rh_2(esp)$_4$, see: D. F. Taber, C. M. Paquette, P. Gu, and W. Tian, *J. Org. Chem.*, 2013, **78**, 9772.
17. (a) M. A. McKervey and T. Ye, *J. Chem. Soc., Chem. Commun.*, 1992, 823; (b) T. Ye, C. F. García, and M. A. McKervey, *J. Chem. Soc., Perkin Trans. 1*, 1995, 1373.
18. (a) C. J. Flynn, C. J. Elcoate, S. E. Lawrence, and A. R. Maguire, *J. Am. Chem. Soc.*, 2010, **132**, 1184; (b) A. E. Shiely, L.-A. Clarke, C. J. Flynn, A. M. Buckley, A. Ford, S. E. Lawrence, and A. R. Maguire, *Eur. J. Org. Chem.*, 2018, 2277; (c) T. A. Brouder, C. N. Slattery, A. Ford, U. B. R. Khandavilli, E. Skořepová, K. S. Eccles, M. Lusi, S. E. Lawrence, and A. R. Maguire, *J. Org. Chem.*, 2019, **84**, 7543.
19. M. Ito, Y. Kondo, H. Nambu, M. Anada, K. Takeda, and S. Hashimoto, *Tetrahdron Lett.*, 2015, **56**, 1397.
20. For a recent review on Rh(II)-catalyzed tandem oxonium ylide formation-rearrangement, see: G. K. Murphy, C. Stewart, and F. G. West, *Tetrahedron*, 2013, **69**, 2667.
21. (a) M. C. Pirrung and J. A. Werner, *J. Am. Chem. Soc.*, 1986, **108**, 6060; (b) E. J. Roskamp and C. R. Johnson, *J. Am. Chem. Soc.*, 1986, **108**, 6062; (c) N. McCarthy, M. A. McKervey, T. Ye, M. McCann, E. Murphy, and M. P. Doyle, *Tetrahedron Lett.*, 1992, **33**, 5983; (d) S. Kitagaki, Y. Yanamoto, H. Tsutsui, M. Anada, M. Nakajima, and S. Hashimoto, *Tetrahedron Lett.*, 2001, **42**, 6361; (e) H. Tsutsui, M. Matsuura, K. Makino, S. Nakamura, M. Nakajima, S. Kitagaki, and S.

Hashimoto, *Isr. J. Chem.*, 2001, **41**, 283; (f) N. Shimada, S. Nakamura, M. Anada, M. Shiro, and S. Hashimoto, *Chem. Lett.*, 2009, **38**, 488; (g) J. S. Clark and K. E. Hansen, *Chem. Eur. J.*, 2014, **20**, 5454, and references cited therein.

22. (a) N. Ikota, N. Takamura, S. D. Young, and B. Ganem, *Tetrahedron Lett.*, 1981, **22**, 4163; (b) D. F. Taber, R. J. Herr, S. K. Pack, and J. M. Geremia, *J. Org. Chem.*, 1996, **61**, 2908; (c) C. F. Garcia, M. A. McKervey, and T. Ye, *Chem. Commun.*, 1996, 1465; (d) D. F. Taber and P. V. Joshi, *J. Org. Chem.*, 2004, **69**, 4276.
23. For reviews, see: (a) J. T. Shaw, *Synlett*, 2020, **31**, 838; (b) D. Zhu, L. Chen, H. Fan, Q. Yao, and S. Zhu, *Chem. Soc. Rev.*, 2020, **49**, 908; (c) B. D. Bergstrom, L. A. Nickerson, J. T. Shaw, and L. W. Souza, *Angew. Chem. Int. Ed.*, 2021, **60**, 6864.
24. (a) C. Soldi, K. N. Lamb, R. A. Squitieri, M. González-López, M. J. Di Maso, and J. T. Shaw, *J. Am. Chem. Soc.*, 2014, **136**, 15142; (b) K. N. Lamb, R. A. Squitieri, S. R. Chintala, A. J. Kwong, E. I. Balmond, C. Soldi, O. Dmitrenko, M. C. Reis, R. Chung, J. B. Addison, J. C. Fettinger, J. E. Hein, D. J. Tantillo, J. M. Fox, and J. T. Shaw, *Chem. Eur. J.*, 2017, **23**, 11843; (c) L. W. Souza, R. A. Squitieri, C. A. Dimirjian, B. M. Hodur, L. A. Nickerson, C. N. Penrod, J. Cordova, J. C. Fettinger, and J. T. Shaw, *Angew. Chem. Int. Ed.*, 2018, **57**, 15213; (d) J. R. Jagannathan, J. C. Fettinger, J. T. Shaw, and A. K. Franz, *J. Am. Chem. Soc.*, 2020, **142**, 11674; (e) L.-L. Yang, D. Evans, B. Xu, W.-T. Li, M.-L. Li, S.-F. Zhu, K. N. Houk, and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2020, **142**, 12394; (f) M. Lee, Z. Ren, D. G. Musaev, and H. M. L. Davies, *ACS Catal.*, 2020, **10**, 6240.
25. Y. Natori, M. Ito, M. Anada, H. Nambu, and S. Hashimoto, *Tetrahedron Lett.*, 2015, **56**, 4324.
26. Recently, Shaw et al. reported the first example of enantioselective intramolecular 1,6-C–H insertion reaction of diaryldiazomethanes, in which catalysis with the use of Rh_2(*R*-PTAD)$_4$ at room temperature proceeded in a chemoselective manner to give *cis*-3,4-disubstituted isochromans with complete diastereoselectivity and excellent enantioselectivities (up to 99% ee). See: L. A. Nickerson, B. D. Bergstrom, M. Gao, Y.-S. Shiue, C. J. Laconsay, M. R. Culberson, W. A. Knauss, J. C. Fettinger, D. J. Tantillo, and J. T. Shaw, *Chem. Sci.*, 2020, **11**, 494.
27. (a) B. E. Marysnoff, M. N. Greco, H.-C. Zhang, P. Andrade-Gordon, J. A. Kauffman, K. C. Nicolaou, A. Liu, and P. H. Brungs, *J. Am. Chem. Soc.*, 1995, **117**, 1225. The use of a diimide scavenger was essential for the preparation of **19a** since the separation of **19a** from **19b** by column chromatography was quite difficult. We found that norbornene, a highly strained cycloalkene, acts as a good diimide scavenger for this transformation. For the reactivity of alkenes toward diimide, see: (b) E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *J. Am. Chem. Soc.*, 1965, **87**, 2932.
28. (a) H. Tsutsui, Y. Yamaguchi, S. Kitagaki, S. Nakamura, M. Anada, and S. Hashimoto,

Tetrahedron: Asymmetry, 2003, **14**, 817; (b) M. Anada, M. Tanaka, T. Washio, M. Yamawaki, T. Abe, and S. Hashimoto, *Org. Lett*., 2007, **9**, 4559; (c) N. Shimada, S. Nakamura, M. Anada, M. Shiro, and S. Hashimoto, *Chem. Lett*., 2009, **38**, 488.

29. Y. Liu, Y. Deng, P. Y. Zavalij, R. Liu, and M. P. Doyle, *Chem. Commun*., 2015, **51**, 565.
30. (a) M. Yamawaki, H. Tsutsui, S. Kitagaki, M. Anada, and S. Hashimoto, *Tetrahedron Lett*., 2002, **43**, 9561; (b) N. Shimada, M. Anada, S. Nakamura, H. Nambu, H. Tsutsui, and S. Hashimoto, *Org. Lett*., 2008, **10**, 3603; (c) N. Shimada, T. Oohara, J. Krishnamurthi, H. Nambu, and S. Hashimoto, *Org. Lett*., 2011, **13**, 6284; (d) J. Krishnamurthi, H. Nambu, K. Takeda, M. Anada, A. Yamano, and S. Hashimoto, *Org. Biomol. Chem*., 2013, **11**, 5374; (e) T. Hanari, N. Shimada, Y. Kurosaki, N. Thrimurtulu, H. Nambu, M. Anada, and S. Hashimoto, *Chem. Eur. J*., 2015, **21**, 11671.
31. (a) V. N. G. Lindsay, W. Lin, and A. B. Charette, *J. Am. Chem. Soc*., 2009, **131**, 16383; (b) V. N. G. Lindsay and A. B. Charette, *ACS Catal*., 2012, **2**, 1221.
32. (a) H. Nozaki, S. Moriuti, H. Takaya, and R. Noyori, *Tetrahedron Lett*., 1966, 5239; (b) E. J. Roskamp and C. R. Johnson, *J. Am. Chem. Soc*., 1986, **108**, 6062; (c) T. H. Eberlein, F. G. West, and R. W. Tester, *J. Org. Chem*., 1992, **57**, 3479; (d) K. Ito, M. Yoshitake, and T. Katsuki, *Heterocycles*, 1996, **42**, 305.
33. The crystal structure of **21e** has been deposited at the Cambridge Crystallographic Data Centre, and the deposition number CCDC 2038908 has been allocated. Its absolute configuration was confirmed with a Flack parameter of 0.03 (3).
34. (a) A. DeAngelis, O. Dmitrenko, G. P. A. Yap, and J. M. Fox, *J. Am. Chem. Soc*., 2009, **131**, 7230; (b) A. DeAngelis, D. T. Boruta, J.-B. Lubin, J. N. Plampin, III., G. P. A. Yap, and J. M. Fox, *Chem. Commun*., 2010, **46**, 4541; (c) D. T. Boruta, O. Dmitrenko, G. P. A. Yap, and J. M. Fox, *Chem. Sci*., 2012, **3**, 1589; (d) Ref. 17e; (e) R. A. Panish, S. R. Chintala, and J. M. Fox, *Angew. Chem. Int. Ed*., 2016, **55**, 4983.
35. (a) M. P. Doyle, L. J. Westrum, W. N. E. Wolthuis, M. M. See, W. P. Boone, V. Bagheri, and M. M Pearson, *J. Am. Chem. Soc*., 1993, **115**, 958; (b) D. F. Taber, K. K. You, and A. L. Rheingold, *J. Am. Chem. Soc*., 1996, **118**, 547. For a mechanism of dirhodium(II) carboxylate-catalyzed C–H insertion reaction based on DFT calculations, see: (c) Ref. 3b; (d) N. Yoshikai and E. Nakamura, *Adv. Synth. Catal*., 2003, **345**, 1159; (e) J. Hansen, J. Autschbach, and H. M. L. Davies, *J. Org. Chem*., 2009, **74**, 6555.
36. Shaw proposed a stepwise mechanism involving an ylide intermediate in dirhodium(II) carboxylate-catalyzed intramolecular C–H insertion reaction of diaryldiazomethanes. See: Ref. 24b.
37. (a) A. Ghanem, M. G. Gardiner, R. M. Williamson, and P. Müller, *Chem. Eur. J*., 2010, **16**, 3291; (b) F. G. Adly, M. G. Gardiner, and A. Ghanem, *Chem. Eur. J*., 2016, **22**, 3447.

38. C. Werlé, R. Goddard, P. Phillips, C. Farés, and A. Fürstner, *Angew. Chem. Int. Ed.*, 2016, **55**, 10760.
39. A. Padwa, S. F. Hornbuckle, G. E. Flyxell, and P. D. Stull, *J. Org. Chem.*, 1989, **54**, 817.
40. J. D. Majmudar, H. B. Hodges-Loaiza, K. Hahne, J. L. Donelson, J. Song, L. Shrestha, M. L. Harrison, C. A. Hrycyna, and R. A. Gibbs, *Bioorg. Med. Chem.*, 2012, **20**, 283.
41. B. Martín-Matute, C. Nevado, D. J. Cárdenas, and A. M. Echavarren, *J. Am. Chem. Soc.*, 2003, **125**, 5757.