

Highly Enantioselective Organocatalytic Cyclopropanation of Enals using Benzyl Chlorides

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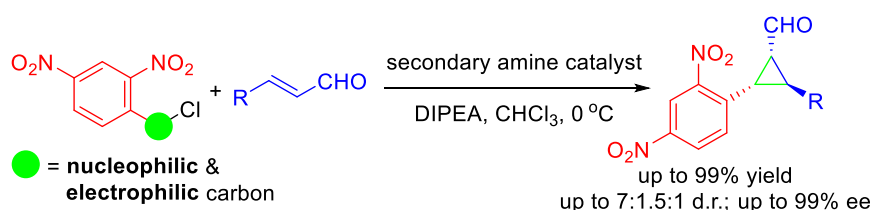
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Abstract

Herein we describe the first enantioselective cyclopropanation of enals using benzyl chlorides as bifunctional (nucleophilic and electrophilic) reagents. The reaction is simply catalyzed by chiral secondary amines to afford the formyl cyclopropane derivatives in good yields and with moderate to excellent stereoselectivities.



■ INTRODUCTION

Cyclopropane subunits have always fascinated organic chemists because of their unusual structural properties and their wide presence in natural products and pharmaceuticals. The cyclopropane skeletal structure is often found in terpenes, pheromones, fatty acid metabolites, and unnatural amino acids; moreover, its derivatives present a plethora of biological activities such as insecticidal, antibiotic, antifungal, antitumor, and antiviral properties. For these reasons, many scientists are interested in developing new enantioselective methods for the construction of cyclopropanes.

Since the seminal report of Simmons and Smith on the reaction of alkenes with diiodomethane in the presence of zinc dust to afford cyclopropanes in high yields,¹ several asymmetric versions of cyclopropanations were reported. These methodologies rely either on the use of stoichiometric amounts of chiral auxiliaries or promoters with allylic alcohols (or amines), α,β -

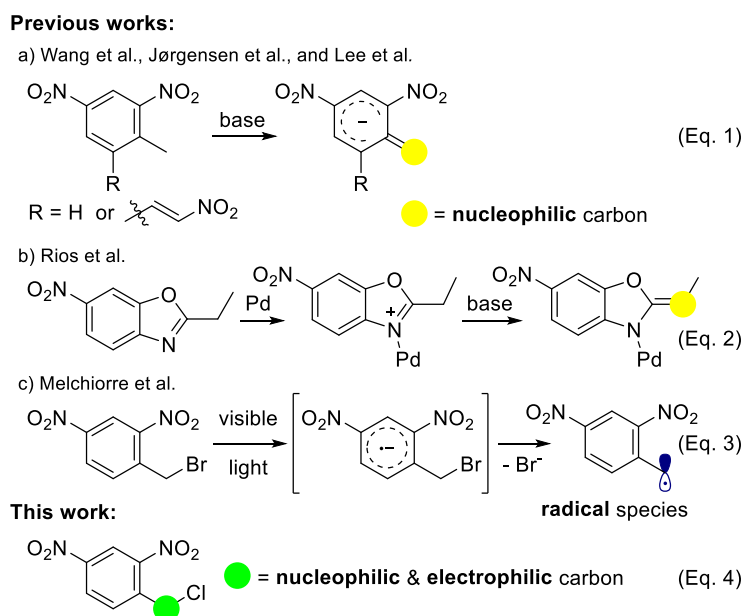
unsaturated carbonyls, allenic alcohols, homoallylic ethers, or unfunctionalized alkenes, or on catalytic amounts of chiral transition-metal complexes with electron-deficient diazo compounds. Among these, the most common approach employs transition-metals (e.g., copper, rhodium, ruthenium and cobalt) to catalyze the reaction of diazoacetates with alkenes, rendering the final cyclopropanes in excellent results.²

During the past few years, organocatalysis has emerged as the third pillar of asymmetric organic catalysis, complementing the previous organometallic and enzymatic catalysis. Since the pioneering works of List and MacMillan in 2000,³ many great accomplishments, including the design of new organocatalysts, strategies, and methodologies, have been achieved.

Recognizing the value of cyclopropanes, several research groups (e.g., Gaunt,⁴ Connon,⁵ MacMillan,⁶ Córdova,⁷ and Wang⁸) reported various organocatalytic methodologies. Most of them are based on the Michael-initiated ring-closing (MIRC) reaction of pre-enolized or readily enolizable nucleophilic species, such as α -brominated malonates, bromonitromethanes and sulfur ylides, with unsaturated derivatives (e.g., enals, enones, and nitrostyrenes). In 2011, Lattanzi's group reported the asymmetric cyclopropanation via a domino Michael-alkylation reaction of alkenes bearing electron-withdrawing groups (EWGs), such as 2-arylidene-1,3-indandiones, for the synthesis of spirocyclopropanes.⁹ Despite the impressive advances in this field, pre-enolized or enolizable compounds are still considered the most effective reactants.

Very recently, aryl methanes and their derivatives, usually considered as poor nucleophiles, have been independently reported by the groups of Wang,¹⁰ Jørgensen¹¹ and Lee¹² as suitable nucleophilic reagents in the organocatalytic Michael addition to α,β -unsaturated aldehydes (Scheme 1, Eq. 1). Their nucleophilicity is dramatically enhanced by the introduction of nitro groups at the *ortho*- and/or *para*-positions of the aromatic ring, as a result of strong inductive and resonance effects.

Moreover, our group investigated the enantioselective addition of alkylbenzoxazoles, acting as pseudo-benzylic functionalities, to enals, via a synergistic catalysis between organocatalysis and transition-metal catalysis (Scheme 1, Eq. 2);¹³ the coordination of palladium with the nitrogen atom of the benzoxazole moiety enhanced the nucleophilicity of the pseudo-benzylic position of α -azaarenes. Recently, Melchiorre and co-workers reported the use of 2,4-dinitrobenzyl bromide as a radical source for alkylation reactions (Scheme 1, Eq. 3).¹⁴

Scheme 1. Aryl Methane Derivatives Serving as Pseudo-Benzylic Functionalities

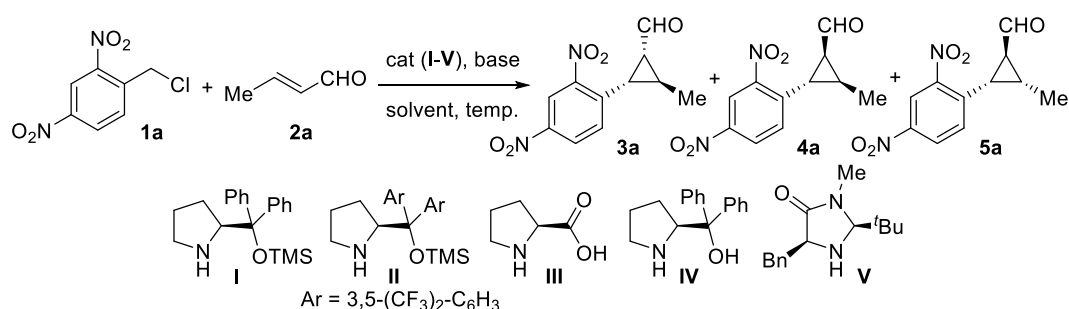
On the basis of these previous reports and our experience with pseudo-benzylic functionalized molecules, we envisioned an easy access to cyclopropanes via an asymmetric organocatalytic Michael addition- α -alkylation cascade of benzyl halides with enals.^[15] In general, benzyl halides are considered electrophilic species; however, when decorated with strong electron-withdrawing group (EWG), such as $-\text{NO}_2$ group, on the aromatic rings and in the presence of a weak base, they could act as nucleophiles [Scheme 1, Eq. (4)]. The in-situ generation of a carbanion at the α -position of the benzyl halide could initiate the organocascade reaction,^[16] in which the α,β -unsaturated aldehyde, activated by an aminocatalyst, would act as electrophilic counterpart; the following irreversible intramolecular alkylation would give the benzylic cyclopropanated products by iminium and enamine activation.

■ RESULTS AND DISCUSSION

In order to assess the feasibility of the proposed transformation, we commenced our studies by testing the reaction of 2,4-dinitrobenzyl chloride **1a** and crotonaldehyde **2a** and by evaluating the effect of parameters such as catalysts, solvents, bases, and temperature. As shown in Table 1, the desired cyclopropane was initially obtained in 29% conversion with reasonable diastereo-

and excellent enantioselectivity under illustrated reaction conditions [20 mol% of diphenylprolinol silyl ether catalyst **I**, 1.1 equiv. of 2,6-lutidine, toluene at room temperature] (Table 1, entry 1). The use of other solvents such as acetonitrile and chloroform results in a slight increase in the cyclopropane yield (Table 1, entries 2 and 4), and no reaction occurred when DMSO was used as the solvent (Table 1, entries 3). Next, we focused on the screening of bases, such as K_2CO_3 , Et_3N and DIPEA (*N,N*-diisopropylethylamine; Hunig's base); the presence of a base is crucial for trapping HCl released, thereby enhancing the reaction rate and reducing the formation of side products. Among various bases examined, DIPEA gave the full conversion when the reaction was performed with 20 mol% of catalyst **I** in $CHCl_3$ at room temperature (Table 1, entry 7). Next, several organocatalysts (**II-V**) were tested: di(trifluoromethyl)-substituted prolinol silyl ether **II** gave excellent enantioselectivity but low conversion, whereas proline **III** gave full conversion but low enantioselectivity (Table 1, entries 8-9).

Table 1. Optimization of the Asymmetric Cyclopropanation^a



entry	catalyst	solvent	base	temp. (°C)	conv. (%) ^b	dr of 3a:4a:5a ^b	ee of 3a:4a:5a ^c
1	I	Toluene	2,6-Lutidine	rt	29	7:8:1	94:87:40
2	I	CH_3CN	2,6-Lutidine	rt	36	2:2:1	93:74:76
3	I	DMSO	2,6-Lutidine	rt	-	-	-
4	I	$CHCl_3$	2,6-Lutidine	rt	47	4:2:1	98:77:67
5	I	$CHCl_3$	Et_3N	rt	71	3:2:1	98:92:69
6	I	$CHCl_3$	K_2CO_3	rt	72	2.6:2:1	98:91:71
7	I	$CHCl_3$	DIPEA	rt	>99	4:3:1	98:77:71
8	II	$CHCl_3$	DIPEA	rt	27	2.4:2.2:1	98:71:31
9	III	$CHCl_3$	DIPEA	rt	>99	2:2:1	59:44:21
10	IV	$CHCl_3$	DIPEA	rt	trace	-	-
11	V	$CHCl_3$	DIPEA	rt	trace	-	-
12	I	$CHCl_3$	DIPEA	0	>99	3:2.5:1	98:81:66

13 I CHCl₃ DIPEA -20 >99 3:2.5:1 98:82:40

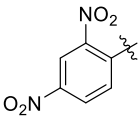
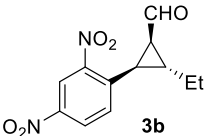
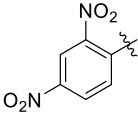
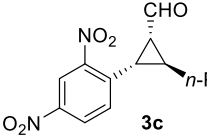
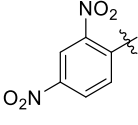
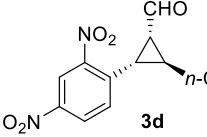
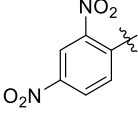
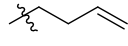
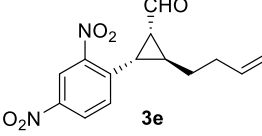
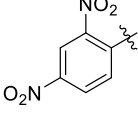
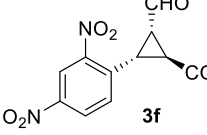
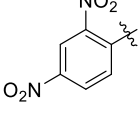
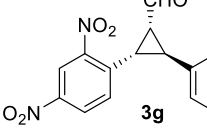
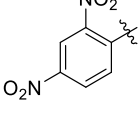
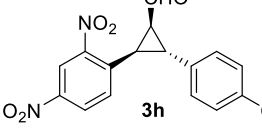
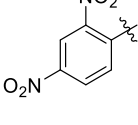
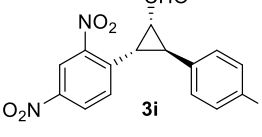
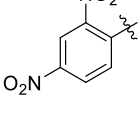
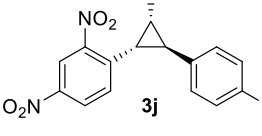
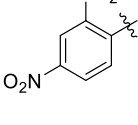
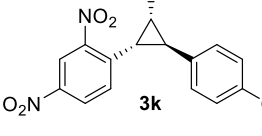
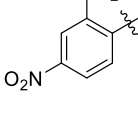
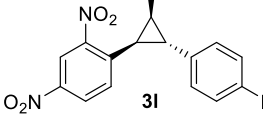
^a General reaction conditions: **1a** (1 equiv), **2a** (2 equiv), catalysts **I-V** (20 mol%), base (1.1 mmol), solvent, temperature (0 or rt). ^b Determined by ¹H NMR of the crude reaction. ^c Determined by HPLC analysis using a chiral column.

Surprisingly, diphenyl prolinol **IV** and MacMillan's second-generation imidazolidinone catalyst **V**, which has been previously used by Lattanzi and co-workers in similar MIRC reactions with excellent results, did not catalyze the reaction to any significant extent, yielding only a trace amount of product (Table 1, entries 10-11). We also investigated the effect of the reaction temperature on the yield and selectivity. When the reaction was performed at 0 °C, the stereoselectivity slightly increased without any loss of catalytic activity (Table 1, entry 12). A similar result was achieved when the reaction was carried out at -20 °C (Table 1, entry 13). Thus, the best conditions for the asymmetric cyclopropanation reaction are as follows: 20 mol% of chiral organocatalyst **I**, 1.1 equiv. of DIPEA, CHCl₃ at 0 °C.

With the optimal conditions in hands, we extended the reaction scope to various benzyl chlorides **1** bearing strong electron-withdrawing groups (EWGs) with both aliphatic and aromatic α,β -unsaturated aldehydes **2** (Table 2). In the reaction of aliphatic α,β -unsaturated aldehydes with benzyl chloride **1a**, the corresponding products were produced in high yields with excellent diastereo- and enantioselectivities of major products **3** (Table 2, entries 1-5).

Table 2. Substrate Scope for the Asymmetric Cyclopropanation^a

entry	Ar	R	product (major)	yield (%) ^b	dr of 3:4:5 ^c	ee of 3:4:5 ^d
1		Me		61	8:3:1	98:73:60

2 ^e		Et		68	9:2:1	99:93:n.d.
3		<i>n</i> -Pr		82	7:1:1	99:93:54
4		<i>n</i> -C ₇ H ₁₅		99	7:1.5:1	99:92:54
5				66	4:1:1	99:92:n.d.
6		CO ₂ Et		68	1:1:1	73:40:80
7		Ph		78	3:2:1	97:91:96
8 ^e		4-CN-C ₆ H ₄		80	2:1.5:1	99:99:n.d.
9		4-NO ₂ -C ₆ H ₄		67	2:2:1	98:n.d.:n.d.
10		4-F-C ₆ H ₄		78	1.5:1.5:1	98:91:90
11		4-Cl-C ₆ H ₄		86	2.5:1.5:1	99:94:97
12 ^e		4-Br-C ₆ H ₄		71	2:2:1	99:95:98

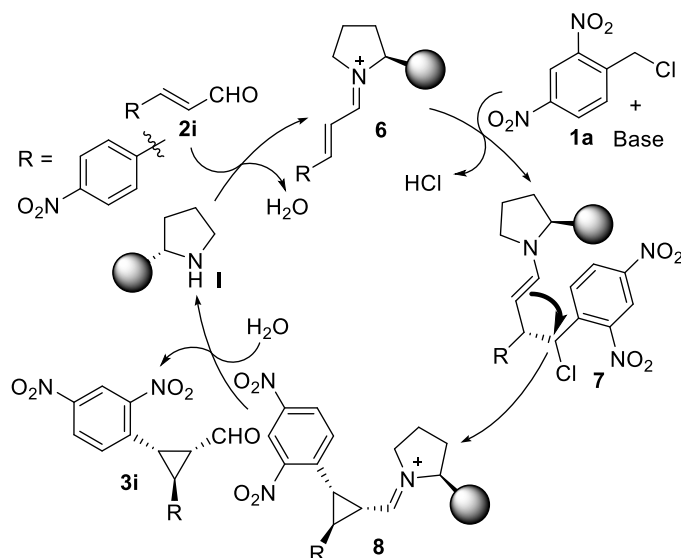
13 ^e		4-Me-C ₆ H ₄		80	3:2:1	98:85:96
14		4-MeO-C ₆ H ₄		79	1.5:1:1	98:90:94
15 ^f		Ph		47	1.5:1:1	99:90:90
16 ^{e,f}		4-NO ₂ -C ₆ H ₄		52	1.5:1:1	85:n.d.:79

^a Reaction conditions: **1** (1 equiv), **2** (2 equiv), catalysts **I** (20 mol%), DIPEA (1.1 equiv), C HCl₃, temperature (0 °C), 3-5 h. ^b Isolated yield (sum of diastereomers). ^c Determined by ¹H N MR of the crudereaction. ^d Determined by HPLC analysis using a chiral column. ^e Using *ent*-**I** [(*R*)-configuration] ^f Run at 60 °C. [n.d. = not determined].

The reaction with glyoxylate derivatives gave a 1:1:1 mixture of diastereomers with moderate enantioselectivities (Table 2, entry 6). Next, we studied the reaction with aromatic enals, and investigated the influence of the electronic properties of the aromatic substituents on the reactivity and selectivity. In almost all cases, the final products were obtained in excellent enantioselectivities with moderate diastereoselectivities (Table 2, entries 7-16). Aromatic α,β -unsaturated aldehydes bearing electron-donating groups (EDGs), such as –OMe or –Me group, gave yields and stereoselectivities similar to those obtained for enals with relatively stronger EWGs, such as –CN and –NO₂ group (Table 2, entries 8-9 and 13-14). In the presence of halogen substituents on the aromatic ring of the α,β -unsaturated aldehyde, similar yields and stereoselectivities are observed for all compounds studied, and the desired products are obtained in very good yields, with moderate diastereoselectivities and excellent enantioselectivities (Table 2, entries 10-12). Finally, we tested the reaction of substrates bearing other aromatic substituents and it was found that the cyclopropanation reaction requires two strong EWGs on the aromatic ring of the benzylic chloride in order to enhance the acidity and nucleophilicity of the benzylic position. 4-Trifluoromethyl-2-nitrobenzyl chloride reacted with enals to give the corresponding chiral cyclopropanes in moderate yields and

diastereoselectivities and good enantioselectivities (Table 2, entries 15-16). However, this reaction requires higher reaction temperatures (60 °C), which could be responsible for the lower stereoselectivities obtained as compared with those observed for dinitrobenzyl derivatives. A plausible catalytic cycle for the asymmetric cyclopropanation is depicted in Scheme 2.

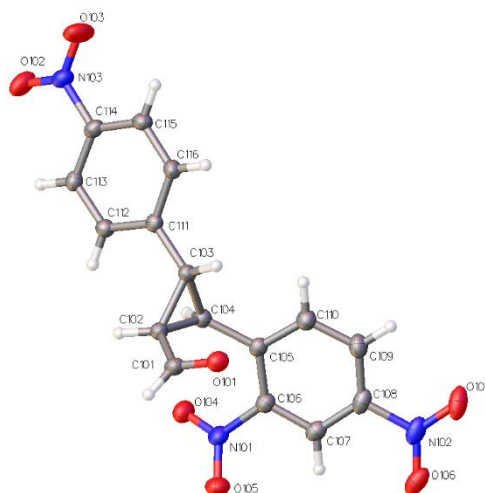
Scheme 2. Plausible Catalytic Cycle for the Enantioselective Intermolecular Cyclopropanation



α,β -unsaturated iminium ion **6** was initially formed by the reaction of diphenyl prolinol silyl ether catalyst **I** with α,β -unsaturated aldehyde **2i**. At this stage, the bulky group of catalyst **I** shields the *Si*-face of α,β -unsaturated iminium ion **6**. Intermediate **8** was therefore formed by nucleophilic attack of **1a** predominantly on the *Re*-face of iminium ion **6** via Michael addition, followed by intramolecular ring-closing reaction between the enamine and the secondary alkyl chloride. Iminium ion **8** is hydrolyzed to the desired product **3i** and catalyst **I** is regenerated.

Absolute stereochemistry of product *ent*-**3i**, which is derived from (*R*)-configured catalyst (*ent*-**I**), was unambiguously determined by single crystal X-ray diffraction analysis (Figure 1).

Figure 1. X-ray Structure of Cyclopropanation Product *ent*-**3i**

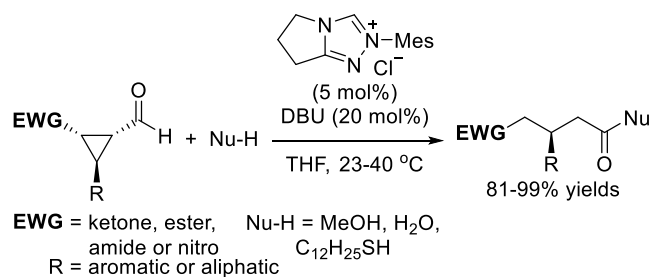


Ellipsoids are shown at the 50% probability level.

The relative configuration of compounds **3**, **4**, and **5** was determined by NMR analysis and the absolute configuration was established by circular dichroism (CD) spectroscopy (see Supporting Information). In order to confirm the absolute configuration of compound **4**, we envisioned the ring-opening of cyclopropanes **3g** and **4g** via *N*-heterocyclic carbene (NHC) catalysis.

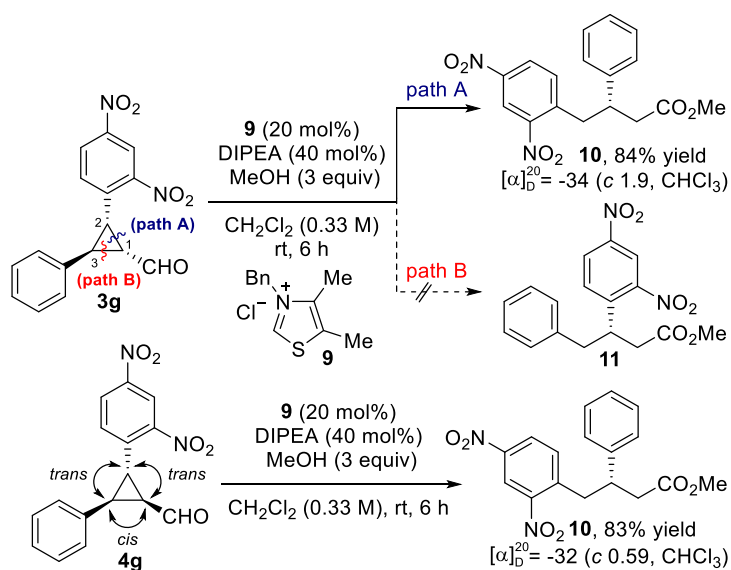
Selective ring-opening of cyclopropane derivatives is an important issue in organic synthesis because it is always associated with inherent regiochemical preferences, which are highly dependent on the nature of the functional groups on the cyclopropanes. In general, exceptionally regioselective outcomes are observed when strong EWGs (i.e., ketones, esters, and amides) are located in a vicinal position to EDGs. In 2006, Bode and co-workers reported the redox-esterification of formylcyclopropanes with alcohol, thiol or water, using NHC catalysis (Scheme 3).¹⁷ In all cases, stronger EWGs such as ketones, esters, amides, or nitro groups are essential to obtain regioselective ring-opened products with high yields.

Scheme 3. NHC-Catalyzed Ring-Opening of Cyclopropanes Bearing Strong Electron-Withdrawing Groups



Based on these results, we became interested in the ring-opening reaction of cyclopropane bearing two aryls (**3g**), instead of two electronically different functional groups, on the cyclopropane ring through NHC catalysis. As a result, only a single product **10** was obtained under our experimental conditions [cyclopropanated product **3g**, MeOH (3 equiv.), thiazolium precatalyst **9** (20 mol%), DIPEA (40 mol%), CH₂Cl₂ (0.33 M), rt.] (Scheme 4).

Scheme 4. Regioselective Ring-Opening of Cyclopropanes **3g** and **4g**.

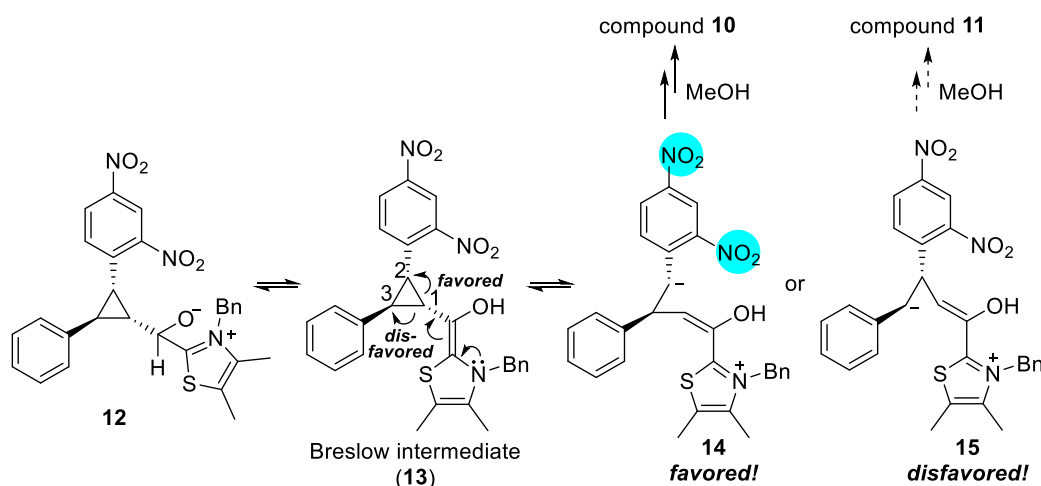


Moreover, we performed the reaction with the second major diastereomer **4g** under the same conditions, and the same configuration of product **10** was observed, as confirmed by comparison of the optical rotation with that of the product derived from **3g**. Thus, the absolute configuration of compound **4g** was ultimately determined on the basis of optical rotation

measurements and NMR analysis.

Finally, we propose a plausible mechanism, to elucidate the origin of the regioselectivity of this process (Scheme 5). At first, the nucleophilic addition of the NHC to the aldehyde produced enaminol **13**, the so-called Breslow intermediate. At this stage, two competitive pathways for the ring-opening reaction are possible, and control could be achieved by fine-tuning the electronic properties of the substituents on two aromatic rings. When the C2 position is relatively more electron-deficient, this C-C bond is preferentially cleaved because two nitro groups on the aromatic ring can stabilize the resultant carbanion **14**. Thus, compound **10** was regioselectively formed instead of compound **11**.

Scheme 5. Rationale for the Origin of the Regioselectivity



To the best of our knowledge, this is the first example of regioselective ring-opening reaction of cyclopropanes containing two aromatic rings. This approach is a formal benzyl addition to unsaturated esters, which can be achieved in good yields and excellent enantioselectivities. This two-step procedure is particularly advantageous for the synthesis of aliphatic derivatives that can only be obtained in low yields using Wang and Jørgensen's methodologies.^{10,11}

■ CONCLUSION

In summary, we reported the first cyclopropanation reaction of benzyl chlorides with enals.

The final products were obtained in good yields and enantioselectivities and with moderate to excellent diastereoselectivities. Moreover, we also demonstrated the ring-opening of diaryl-substituted cyclopropanes furnished the desired products with complete regioselective fashion through N-heterocyclic carbene catalysis.

■ EXPERIMENTAL SECTION

Thin layer chromatography (TLC) was performed on Merck TLC Silicagel 60 F₂₅₄. Product spots were visualized by UV-light at 254 nm. Column chromatography was effectuated using silica gel (Geduran Si60, 40-63 μm). Infra-red spectra were recorded on a Nicolet 280 FT-IR; the IR analyses were performed as a liquid IR with the compounds dissolved in CHCl_3 . ^1H NMR, ^{13}C NMR, ^{19}F NMR were recorded with a Bruker DPX400 NMR. High resolution mass spectra were recorded using a MaXis (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Time of Flight (TOF) analyzer.

General procedure for asymmetric cyclopropanation using 2,4-dinitrobenzyl chloride (A): In a vial, (*S*)- α,α -diphenylprolinol trimethylsilyl ether (20 mol%) and 2,4-dinitrobenzyl chloride (1 equiv., 100 mg, 0.4617 mmol) were dissolved in chloroform (1 mL). The vial was covered with aluminum foil and the resulting solution was cooled to 0 °C. After 15 minutes, α,β -unsaturated aldehyde (2 equiv.) and *N,N*-diisopropylethylamine (DIPEA, 1.1 equiv.) were added to the reaction mixtures. The resulting solution was stirred at 0 °C for 3-5 hours. After the reaction was completed, the crude product was purified by flash column chromatography (hexane/EtOAc) to obtain the desired cyclopropane.

General procedure for asymmetric cyclopropanation using 2-nitro-4-(trifluoromethyl)benzyl chloride (B): In a vial, (*S*)- α,α -diphenylprolinol trimethylsilyl ether (20 mol%) and 2-nitro-4-(trifluoromethyl)-benzyl chloride (1 equiv., 100 mg, 0.417 mmol) were dissolved in chloroform (1 mL). The vial was covered with aluminum foil and α,β -unsaturated aldehyde (2 equiv.) and *N,N*-diisopropylethylamine (DIPEA, 1.1 equiv.) were added to the reaction mixtures. The resulting solution was stirred at 60 °C for 24 hours. After the reaction was completed, the crude was purified by flash column chromatography (hexane/EtOAc) to obtain the desired cyclopropane.

2-(2,4-Dinitrophenyl)-3-methylcyclopropane-1-carbaldehyde (3a, 4a and 5a): The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 10:1), affording the title compound as a yellow oil; Diastereomeric ratios of **3a:4a:5a** = 8:3:1; Enantiomeric excesses of **3a:4a:5a** = 98:73:60; Total yield of **3a:4a:5a** = 61% (71 mg).

(1R,2S,3S)-2-(2,4-Dinitrophenyl)-3-methylcyclopropane-1-carbaldehyde (3a). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 21.4 min, t_R = 24.6 min; $[\alpha]_D^{26}$ = -90.8° (*c* 0.6, CHCl₃) (**S catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.43 (d, *J* = 2.8, 1H), 8.71 (d, *J* = 2.3, 1H), 8.36 (dd, *J* = 8.6, 2.3, 1H), 7.66 (d, *J* = 8.6, 1H), 2.86 (dd, *J* = 8.1, 8.0, 1H), 2.46 (ddd, *J* = 8.0, 4.8, 2.8, 1H), 2.18 (m, 1H), 1.38 (d, *J* = 6.0, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 198.1 (CHO), 150.1 (Cq), 146.8 (Cq), 138.8 (Cq), 133.6 (CH), 126.7 (CH), 119.9 (CH), 38.0 (CH), 34.2 (CH), 24.2 (CH), 17.5 (CH₃); IR ν_{max} (KBr, cm⁻¹): 3105, 2966, 2866, 2009, 1702, 1604, 1530 (aromatic NO₂), 1461, 1346 (aromatic NO₂), 1152, 1087, 1044, 938, 909, 854, 835, 737; HRMS (ESI) calcd for C₁₁H₁₀N₂O₅ [M+Na]⁺ 273.0482, found 273.0480.

(1S,2S,3S)-2-(2,4-Dinitrophenyl)-3-methylcyclopropane-1-carbaldehyde (4a) and (1S,2S,3R)-2-(2,4-dinitrophenyl)-3-methylcyclopropane-1-carbaldehyde (5a).

[inseparable mixture of diastereoisomers]: Yellow oil; The enantiomeric excess of product **4a** was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 29.7 min, t_R = 27.3 min; The enantiomeric excess of product **5a** was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 43.4 min, t_R = 37.0 min; ¹H NMR (400 MHz, CDCl₃) [diastereomer – H' (**4a**); diastereomer – H (**5a**)] δ = 9.69 (d, *J* = 3.9, 1H'), 9.45 (d, *J* = 4.2, 1H), 8.82 (d, *J* = 2.3, 1H), 8.76 (d, *J* = 2.3, 1H'), 8.41 (dd, *J* = 8.5, 2.3, 1H), 8.36 (dd, *J* = 8.6, 2.3, 1H'), 7.59 (d, *J* = 8.5, 1H), 7.40 (d, *J* = 8.6, 1H'), 3.28 (dd, *J* = 9.8, 5.5, 1H), 3.18 (dd, *J* = 6.2, 5.9, 1H'), 2.36 (ddd, *J* = 9.2, 4.9, 4.1, 1H), 2.20 – 2.14 (m, 1H), 2.11 (ddd, *J* = 8.6, 6.0, 3.9, 1H'), 1.96 – 1.84 (m, 1H'), 1.43 (d, *J* = 6.3, 3H'), 0.88 (d, *J* = 6.2, 3H); ¹³C NMR (101 MHz, CDCl₃) [diastereomer (**4a**) – C'; diastereomer (**5a**) – C] δ = 198.3 (CHO), 197.9 (C'HO), 150.1 (Cq), 146.6 (Cq'), 141.3 (Cq'), 138.2 (Cq'), 134.7 (Cq), 133.2 (CH), 131.2 (Cq), 130.0 (C'H), 127.2 (C'H), 127.0 (CH), 120.3 (CH), 120.3 (C'H), 37.2 (CH), 36.4 (C'H), 29.8 (C'H), 29.6 (CH), 27.5 (C'H), 23.8 (CH), 12.9 (CH₃), 12.7 (C'H₃); IR ν_{max} (KBr, cm⁻¹): 3105, 2966, 2866, 2009, 1702, 1604, 1530 (aromatic NO₂), 1461, 1346 (aromatic NO₂), 1152, 1087, 1044, 938,

909, 854, 835, 737; HRMS (ESI) calcd for C₁₁H₁₀N₂O₅ [M+Na]⁺ 273.0482, found 273.0476.

2-(2,4-Dinitrophenyl)-3-ethylcyclopropane-1-carbaldehyde (3b, 4b and 5b): The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 10:1), affording the title compound as a yellow oil; Diastereomeric ratios of **3b:4b:5b** = 9:2:1; Enantiomeric excesses of **3b:4b:5b** = 99:93:n.d.; Total yield of **3b:4b:5b** = 68% (83.3 mg).

(1*S*,2*R*,3*R*)-2-(2,4-Dinitrophenyl)-3-ethylcyclopropane-1-carbaldehyde (3b). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 18.1 min, t_R = 19.6 min; $[\alpha]_D^{21}$ = -61.9° (*c* 1.2, CHCl₃) (**S catalyst**), $[\alpha]_D^{21}$ = +58.9° (*c* 1.3, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.45 (d, *J* = 2.7, 1H), 8.72 (d, *J* = 2.3, 1H), 8.37 (dd, *J* = 8.6, 2.3, 1H), 7.68 (d, *J* = 8.6, 1H), 2.88 (dd, *J* = 8.2, 8.0, 1H), 2.49 (ddd, *J* = 8.1, 4.9, 2.7, 1H), 2.19 – 2.11 (m, 1H), 1.72 – 1.54 (m, 1H), 1.09 (t, *J* = 7.4, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 198.0 (CHO), 150.1 (Cq), 146.8 (Cq), 139.0 (Cq), 133.6 (CH), 126.8 (CH), 119.9 (CH), 36.8 (CH), 33.1 (CH), 31.6 (CH), 25.6 (CH₂), 13.0 (CH₃); IR ν_{max} (KBr, cm⁻¹): 3099, 2963, 2927, 2853, 2022, 1701, 1605, 1530 (aromatic NO₂), 1463, 1346 (aromatic NO₂), 1150, 1067, 991, 907, 835, 738; HRMS (ESI) calcd for C₁₂H₁₂N₂O₅ [M+Na]⁺ 287.0638, found 287.0634.

(1*R*,2*R*,3*R*)-2-(2,4-Dinitrophenyl)-3-ethylcyclopropane-1-carbaldehyde (4b). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 33.5 min, t_R = 19.3 min; $[\alpha]_D^{21}$ = -27.6° (*c* 0.5, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.66 (d, *J* = 4.0, 1H), 8.75 (d, *J* = 2.3, 1H), 8.36 (dd, *J* = 8.6, 2.3, 1H), 7.39 (d, *J* = 8.6, 1H), 3.24 (dd, *J* = 5.9, 5.8, 1H), 2.33 (ddd, *J* = 9.1, 4.9, 4.2, 1H), 1.87 (ddt, *J* = 13.7, 8.9, 6.8, 2H), 1.72 – 1.62 (m, 1H), 1.02 (t, *J* = 7.2, 3H); ¹³C NMR (101 MHz, CDCl₃) δ = 197.6 (CHO), 150.1 (Cq), 146.5 (Cq), 141.4 (Cq), 129.9 (CH), 127.2 (CH), 120.3 (CH), 36.4 (CH), 35.3 (CH), 29.0 (CH), 20.9 (CH₂), 13.9 (CH₃); IR ν_{max} (KBr, cm⁻¹): 3099, 2963, 2927, 2853, 2022, 1701, 1605, 1530 (aromatic NO₂), 1463, 1346 (aromatic NO₂), 1150, 1067, 991, 907, 835, 738; HRMS (ESI) calcd for C₁₂H₁₂N₂O₅ [M+Na]⁺ 287.0638, found 287.0640.

(1*R*,2*R*,3*S*)-2-(2,4-Dinitrophenyl)-3-ethylcyclopropane-1-carbaldehyde (5b). The title compound was unable to characterize because of extremely low yield, which is attributed to high diastereoselectivity of the major diastereomers.

2-(2,4-Dinitrophenyl)-3-propylcyclopropane-1-carbaldehyde (3c, 4c and 5c): The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 7:1), affording the title compound as a yellow oil; Diastereomeric ratios of **3c:4c:5c** = 7:1:1; Enantiomeric excesses of **3c:4c:5c** = 99:93:54; Total yield of **3c:4c:5c** = 82% (105 mg).

(1R,2S,3S)-2-(2,4-Dinitrophenyl)-3-propylcyclopropane-1-carbaldehyde (3c). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 15.1 min, t_R = 16.2 min; $[\alpha]_D^{21}$ = -106.5° (*c* 0.9, CHCl₃) (**S catalyst**), $[\alpha]_D^{21}$ = +104.3° (*c* 0.9, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.44 (d, *J* = 2.7, 1H), 8.71 (d, *J* = 2.2, 1H), 8.37 (dd, *J* = 8.6, 2.1, 1H), 7.68 (d, *J* = 8.6, 1H), 2.88 (dd, *J* = 8.1, 8.0, 1H), 2.48 (ddd, *J* = 7.9, 4.9, 2.9 1H), 2.22 – 2.14 (m, 1H), 1.62 – 1.48 (m, 4H), 0.97 (t, *J* = 7.1, 3H); ¹³C NMR (101 MHz, CDCl₃) δ = 198.0 (CHO), 150.1 (Cq), 146.8 (Cq), 139 (Cq), 133.5 (CH), 126.8 (CH), 119.9 (CH), 37.0 (CH), 34.4 (CH₂), 33.2 (CH), 29.7 (CH), 22.1 (CH₂), 13.8 (CH₃); IR ν_{max} (KBr, cm⁻¹): 2960, 2930, 2873, 1701, 1604, 1530 (aromatic NO₂), 1465, 1346 (aromatic NO₂), 1151, 1067, 1001, 912, 835, 738; HRMS (ESI) calcd for C₁₃H₁₄N₂O₅ [M+Na]⁺ 301.0795, found 301.0792.

(1S,2S,3S)-2-(2,4-Dinitrophenyl)-3-propylcyclopropane-1-carbaldehyde (4c). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 30.6 min, t_R = 22.4 min; $[\alpha]_D^{21}$ = +83.4° (*c* 0.7, CHCl₃) (**S catalyst**), $[\alpha]_D^{21}$ = -77.8° (*c* 0.6, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.65 (d, *J* = 4.1, 1H), 8.75 (d, *J* = 2.2, 1H), 8.36 (dd, *J* = 8.6, 2.2, 1H), 7.38 (d, *J* = 8.6, 1H), 3.23 (dd, *J* = 5.9, 5.8, 1H), 2.33 (ddd, *J* = 9.2, 4.9, 4.2, 1H), 1.94-1.77 (m, 2H), 1.69 – 1.57 (m, 1H), 1.51 – 1.33 (m, 2H), 0.93 (t, *J* = 7.3, 3H); ¹³C NMR (101 MHz, CDCl₃) δ = 197.7 (CHO), 150.1 (Cq), 146.5 (Cq), 141.4 (Cq), 129.8 (CH), 127.2 (CH), 120.3 (CH), 36.4 (CH), 33.3 (CH), 29.4 (CH₂), 28.9 (CH), 22.8 (CH₂), 13.7 (CH₃); IR ν_{max} (KBr, cm⁻¹): 2960, 2930, 2873, 1701, 1604, 1530 (aromatic NO₂), 1465, 1346 (aromatic NO₂), 1151, 1067, 1001, 912, 835, 738; HRMS (ESI) calcd for C₁₃H₁₄N₂O₅ [M+Na]⁺ 301.0795, found 301.0792.

(1S,2R,3R)-2-(2,4-Dinitrophenyl)-3-propylcyclopropane-1-carbaldehyde (5c). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 18.4 min, t_R = 31.1 min, $[\alpha]_D^{21}$ = -116.5° (*c* 0.2, CHCl₃) (**S catalyst**), $[\alpha]_D^{21}$ = +130.8° (*c* 0.2, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.43 (d, *J* = 4.4, 1H), 8.82 (d, *J* = 2.1, 1H), 8.40 (dd, *J* = 8.5, 2.1, 1H), 7.57 (d, *J* = 8.5, 1H), 3.33 (dd, *J* = 9.4, 4.6, 1H), 2.24 - 2.20 (m, 1H), 2.11-2.04 (m, 1H), 1.39 – 1.26

(m, 4H), 0.80 (t, $J = 7.1$, 3H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 198.2$ (CHO), 150.7 (Cq), 147 (Cq), 138.4 (Cq), 132.8 (CH), 127 (CH), 120.4 (CH), 36.3 (CH), 29.9 (CH_2), 29.5 (CH), 29.1 (CH), 22.0 (CH_2), 13.6 (CH_3); IR ν_{max} (KBr, cm^{-1}): 2960, 2930, 2873, 1701, 1604, 1530 (aromatic NO_2), 1465, 1346 (aromatic NO_2), 1151, 1067, 1001, 912, 835, 738; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_5$ $[\text{M}+\text{Na}]^+$ 301.0795, found 301.0796.

2-(2,4-Dinitrophenyl)-3-heptylcyclopropane-1-carbaldehyde (3d, 4d and 5d): The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 7:1), affording the title compound as a yellow oil; Diastereomeric ratios of **3d:4d:5d** = 7:1:1; Enantiomeric excesses of **3d:4d:5d** = 99:92:54; Total yield of **3c:4c:5c** = 99% (153 mg).

(1R,2S,3S)-2-(2,4-Dinitrophenyl)-3-heptylcyclopropane-1-carbaldehyde (3d). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $\lambda = 210$ nm): $t_{\text{R}} = 11.7$ min, $t_{\text{R}} = 12.9$ min; $[\alpha]_{\text{D}}^{22} = -62.4^\circ$ (c 0.9, CHCl_3) (**S catalyst**). $[\alpha]_{\text{D}}^{22} = +77.5^\circ$ (c 1.1, CHCl_3) (**R catalyst**); ^1H NMR (400 MHz, CDCl_3) $\delta = 9.41$ (d, $J = 2.7$, 1H), 8.70 (d, $J = 2.1$, 1H), 8.36 (dd, $J = 8.6$, 2.3, 1H), 7.67 (d, $J = 8.6$, 1H), 2.87 (dd, $J = 8.2$, 8.1, 1H), 2.47 (ddd, $J = 8.0$, 4.9, 2.8, 1H), 2.20 – 2.12 (m, 1H), 1.62–1.54 (m, 2H), 1.36 – 1.18 (m, 10H), 0.85 (t, $J = 6.7$, 3H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 198.1$ (CHO), 150.0 (Cq), 146.8 (Cq), 139.1 (Cq), 133.6 (CH), 126.8 (CH), 119.9 (CH), 37.1 (CH), 33.3 (CH), 32.4 (CH_2), 31.7 (CH_2), 29.9 (CH), 29.2 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 22.6 (CH_2), 14.1 (CH_3); IR ν_{max} (KBr, cm^{-1}): 2925, 2854, 1699, 1603, 1530 (aromatic NO_2), 1465, 1343 (aromatic NO_2), 1150, 1066, 909, 834, 738, 689, 642, 508; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_5$ $[\text{M}+\text{Na}]^+$ 357.1421, found 357.1421.

(1S,2S,3S)-2-(2,4-Dinitrophenyl)-3-heptylcyclopropane-1-carbaldehyde (4d). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, $\lambda = 230$ nm): $t_{\text{R}} = 24.4$ min, $t_{\text{R}} = 18.9$ min; $[\alpha]_{\text{D}}^{22} = +46.8^\circ$ (c 0.4, CHCl_3) (**S catalyst**), $[\alpha]_{\text{D}}^{22} = -53.1^\circ$ (c 1.0, CHCl_3) (**R catalyst**); ^1H NMR (400 MHz, CDCl_3) $\delta = 9.64$ (d, $J = 4.1$, 1H), 8.74 (d, $J = 2.3$, 1H), 8.36 (dd, $J = 8.6$, 2.3, 1H), 7.38 (d, $J = 8.6$, 1H), 3.23 (dd, $J = 5.9$, 5.7, 1H), 2.32 (ddd, $J = 9.1$, 4.9, 4.4, 1H), 1.93 – 1.80 (m, 2H), 1.69 – 1.54 (m, 1H), 1.34 – 1.18 (m, 10H), 0.85 (t, $J = 6.8$, 3H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 197.7$ (CHO), 150.1 (Cq), 146.5 (Cq), 141.4 (Cq), 129.8 (CH), 127.2 (CH), 120.3 (CH), 36.5 (CH), 33.6 (CH), 31.7 (CH_2), 29.6 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.9 (CH), 27.5 (CH_2), 22.6 (CH_2), 14.1 (CH_3); IR ν_{max} (KBr, cm^{-1}): 2925, 2854, 1699, 1603, 1530 (aromatic

NO₂), 1465, 1343 (aromatic NO₂), 1150, 1066, 909, 834, 738, 689, 642, 508; HRMS (ESI) calcd for C₁₇H₂₂N₂O₅ [M+Na]⁺ 357.1421, found 357.1416.

(1*S*,2*R*,3*R*)-2-(2,4-Dinitrophenyl)-3-heptylcyclopropane-1-carbaldehyde (5d). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 15.6 min, t_R = 22.7 min; [α]_D²² = -71.5° (c 0.3, CHCl₃) (**S catalyst**), [α]_D²² = +132.6° (c 0.61, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.42 (d, *J* = 4.4, 1H), 8.82 (d, *J* = 2.3, 1H), 8.40 (dd, *J* = 8.5, 2.3, 1H), 7.57 (d, *J* = 8.5, 1H), 3.33 (dd, *J* = 9.9, 5.4, 1H), 2.23 – 2.20 (m, 1H), 2.12 – 2.00 (m, 1H), 1.32 – 1.18 (m, 12H), 0.82 (t, *J* = 7.0, 3H); ¹³C NMR (101 MHz, CDCl₃) δ = 198.3 (CHO), 150.7 (Cq), 146.9 (Cq), 138.4 (Cq), 132.8 (CH), 127.0 (CH), 120.4 (CH), 36.3 (CH), 33.4 (CH), 31.6 (CH₂), 29.7 (CH), 29.2 (CH), 29.0 (CH₂), 28.8 (CH₂), 28.0 (CH₂), 22.5 (CH₂), 14.0 (CH₃); IR ν_{max} (KBr, cm⁻¹): 2925, 2854, 1699, 1603, 1530 (aromatic NO₂), 1465, 1343 (aromatic NO₂), 1150, 1066, 909, 834, 738, 689, 642, 508; HRMS (ESI) calcd for C₁₇H₂₂N₂O₅ [M+Na]⁺ 357.1421, found 357.1423.

2-(But-3-en-1-yl)-3-(2,4-dinitrophenyl)cyclopropane-1-carbaldehyde (3e, 4e and 5e): The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 7:1), affording the title compound as a yellow oil; Diastereomeric ratios of **3e:4e:5e** = 4:1:1; Enantiomeric excesses of **3e:4e:5e** = 99:92:n.d.; Total yield of **3e:4e:5e** = 66% (89 mg).

(1*R*,2*S*,3*S*)-2-(But-3-en-1-yl)-3-(2,4-dinitrophenyl)cyclopropane-1-carbaldehyde (3e). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 75:25, flow rate 1.0 mL/min, λ = 210 nm): t_R = 14.4 min, t_R = 16.4 min; [α]_D²³ = -119.1° (c 1.3, CHCl₃) (**S catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.44 (d, *J* = 2.7, 1H), 8.73 (d, *J* = 2.4, 1H), 8.37 (dd, *J* = 8.6, 2.4, 1H), 7.68 (d, *J* = 8.6, 1H), 5.90 – 5.74 (m, 1H), 5.12 – 4.98 (m, 2H), 2.89 (dd, *J* = 8.2, 8.1, 1H), 2.51 (ddd, *J* = 8.8, 5.0, 2.7, 1H), 2.29 – 2.24 (m, 2H), 2.23 – 2.16 (m, 1H), 1.80 – 1.62 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ = 197.9 (CHO), 150.0 (Cq), 146.9 (Cq), 138.8 (Cq), 137.1 (CH), 133.6 (CH), 126.8 (CH), 119.9 (CH), 116.1 (CH₂), 37.0 (CH), 33.3 (CH), 33.1 (CH₂), 31.6 (CH₂), 29.2 (CH); IR ν_{max} (KBr, cm⁻¹): 3079, 2924, 2849, 2211, 2133, 1702, 1640, 1603, 1530 (aromatic NO₂), 1437, 1346 (aromatic NO₂), 1150, 1066, 995, 911, 835, 738; HRMS (ESI) calcd for C₁₄H₁₄N₂O₅ [M+Na]⁺ 313.0795, found 313.0797.

(1*S*,2*S*,3*S*)-2-(But-3-en-1-yl)-3-(2,4-dinitrophenyl)cyclopropane-1-carbaldehyde (4e).

Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 75:25, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 25.2 min, t_R = 19.6 min; $[\alpha]_D^{23}$ = +49.0° (*c* 0.4, CHCl₃) (**S catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.68 (d, *J* = 3.9, 1H), 8.76 (d, *J* = 2.4, 1H), 8.36 (dd, *J* = 8.6, 2.4, 1H), 7.39 (d, *J* = 8.6, 1H), 5.77 (ddt, *J* = 17.0, 10.2, 6.7, 1H), 5.08 – 4.96 (m, 2H), 3.24 (dd, *J* = 6.1, 5.9 1H), 2.34 (ddd, *J* = 9.1, 5.3, 3.9, 1H), 2.22 – 2.12 (m, 2H), 2.02 – 1.85 (m, 2H), 1.82 – 1.72 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 197.5 (CHO), 150.1 (Cq), 146.6 (Cq), 141.3 (Cq), 137.0 (CH), 129.9 (CH), 127.2 (CH), 120.3 (CH), 116.1 (CH₂), 36.3 (CH), 33.5 (CH₂), 32.8 (CH), 28.9 (CH), 26.5 (CH₂); IR ν_{max} (KBr, cm⁻¹): 3079, 2924, 2849, 2211, 2133, 1702, 1640, 1603, 1530 (aromatic NO₂), 1437, 1346 (aromatic NO₂), 1150, 1066, 995, 911, 835, 738; HRMS (ESI) calcd for C₁₄H₁₄N₂O₅ [M+Na]⁺ 313.0795, found 313.0795.

(1*R*,2*S*,3*R*)-2-(But-3-en-1-yl)-3-(2,4-dinitrophenyl)cyclopropane-1-carbaldehyde (5e).

Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ = 9.43 (d, *J* = 4.3, 1H), 8.82 (d, *J* = 2.4, 1H), 8.40 (dd, *J* = 8.5, 2.4, 1H), 7.57 (d, *J* = 8.5, 1H), 5.70 – 5.57 (m, 1H), 4.98 – 4.85 (m, 2H), 3.33 (dd, *J* = 10.0, 5.5, 1H), 2.25 – 2.22 (m, 1H), 2.12 – 2.02 (m, 3H), 1.51 – 1.43 (m, 1H), 0.80 – 0.68 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 198.1 (CHO), 147.0 (Cq), 138.2 (Cq), 136.5 (CH), 132.8 (CH), 127.0 (CH), 120.4 (CH), 120.3 (Cq), 116.1 (CH₂), 36.2 (CH), 32.9 (CH₂), 29.2 (CH), 29.1 (CH), 27.3 (CH₂); IR ν_{max} (KBr, cm⁻¹): 3079, 2924, 2849, 2211, 2133, 1702, 1640, 1603, 1530 (aromatic NO₂), 1437, 1346 (aromatic NO₂), 1150, 1066, 995, 911, 835, 738; HRMS (ESI) calcd for C₁₄H₁₄N₂O₅ [M+Na]⁺ 313.0795, found 313.0801.

Ethyl 2-(2,4-dinitrophenyl)-3-formylcyclopropane-1-carboxylate (3f, 4f and 5f): The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 7:1), affording the title compound as a yellow oil; Diastereomeric ratios of **3f:4f:5f** = 1:1:1; Enantiomeric excesses of **3f:4f:5f** = 73:40:80; Total yield of **3f:4f:5f** = 68% (97 mg).

Ethyl (1*S*,2*R*,3*S*)-2-(2,4-dinitrophenyl)-3-formylcyclopropane-1-carboxylate (3f). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 65:35, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 22.0 min, t_R = 42.2 min; $[\alpha]_D^{23}$ = +1.4° (*c* 0.4, CHCl₃) (**S catalyst**), $[\alpha]_D^{23}$ = - 0.25° (*c* = 1.2, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.60 (d, *J* = 1.7, 1H), 8.81 (d, *J* = 2.3, 1H), 8.42 (dd, *J* = 8.5, 2.3, 1H), 7.70 (d, *J* = 8.5, 1H), 4.25 (q, *J* = 7.1, 2H), 3.51 (dd, *J* = 9.5, 6.8, 1H), 3.21 (ddd, *J* = 9.6, 4.8, 1.7, 1H), 2.92 (dd, *J* = 6.7, 4.8, 1H), 1.33 (t, *J* = 7.1, 1H); ¹³C NMR (101 MHz, CDCl₃) δ

= 195.5 (CHO), 169.6 (Cq), 149.8 (Cq), 147.4 (Cq), 136.2 (Cq), 133.7 (CH), 127.1 (CH), 120.3 (CH), 62.1 (CH₂), 36.1 (CH), 32.4 (CH), 28.6 (CH), 14.2 (CH₃); IR ν_{\max} (KBr, cm⁻¹): 2922, 2852, 2248, 2209, 2190, 2182, 2158, 2150, 1727, 1705, 1604, 1530 (aromatic NO₂), 1466, 1444, 1392, 1344 (aromatic NO₂), 1286, 1183, 1095, 1050, 1030, 985, 910, 835, 739; HRMS (ESI) calcd for C₁₃H₁₂N₂O₇ [M+Na]⁺ 331.0537, found 331.0535.

Ethyl (1S,2R,3R)-2-(2,4-dinitrophenyl)-3-formylcyclopropane-1-carboxylate (4f). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 65:35, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 36.8 min, t_R = 29.3 min; $[\alpha]_D^{23}$ = - 9.7° (*c* 0.5, CHCl₃) (**S catalyst**), $[\alpha]_D^{23}$ = +10.3° (*c* 1.4, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.62 (d, *J* = 5.8, 1H), 8.90 (d, *J* = 2.3, 1H), 8.43 (dd, *J* = 8.5, 2.4, 1H), 7.50 (d, *J* = 8.6, 1H), 4.31 – 4.21 (m, 2H), 3.95 (dd, *J* = 6.6, 6.6, 1H), 2.55 (dd, *J* = 9.3, 6.5, 1H), 2.40 (ddd, *J* = 9.3, 6.6, 5.8, 1H), 1.32 (t, *J* = 7.1, 3H); ¹³C NMR (101 MHz, CDCl₃) δ = 196.5 (CHO), 168.6 (Cq), 138.3 (Cq), 130.7 (CH), 127.7 (CH), 120.8 (CH), 120.0 (Cq), 93.1 (Cq), 62.3 (CH₂), 37.0 (CH), 30.4 (CH), 28.5 (CH), 14.1 (CH₃); IR ν_{\max} (KBr, cm⁻¹): 2922, 2852, 2248, 2209, 2190, 2182, 2158, 2150, 1727, 1705, 1604, 1530 (aromatic NO₂), 1466, 1444, 1392, 1344 (aromatic NO₂), 1286, 1183, 1095, 1050, 1030, 985, 910, 835, 739; HRMS (ESI) calcd for C₁₃H₁₂N₂O₇ [M+Na]⁺ 331.0537, found 331.0539.

Ethyl (1R,2S,3R)-2-(2,4-dinitrophenyl)-3-formylcyclopropane-1-carboxylate (5f). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*PrOH = 65:35, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 20.3 min, t_R = 41.8 min; $[\alpha]_D^{23}$ = - 58.0° (*c* 0.5, CHCl₃) (**S catalyst**), $[\alpha]_D^{23}$ = +44.1° (*c* 0.7, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.68 (d, *J* = 3.2, 1H), 8.81 (d, *J* = 2.3, 1H), 8.41 (dd, *J* = 8.5, 2.3, 1H), 7.67 (d, *J* = 8.5, 1H), 4.02 – 3.93 (m, 2H), 3.50 (dd, *J* = 9.6, 6.8, 1H), 3.02 (ddd, *J* = 6.7, 4.6, 3.2, 1H), 2.87 (dd, *J* = 9.6, 4.6, 1H), 1.14 (t, *J* = 7.1, 3H); ¹³C NMR (101 MHz, CDCl₃) δ = 195.9 (CHO), 168.1 (Cq), 150.0 (Cq), 147.3 (Cq), 136.7 (Cq), 133.6 (CH), 127.0 (CH), 120.2 (CH), 62.0 (CH₂), 35.3 (CH), 30.1 (CH), 29.4 (CH), 13.9 (CH₃); IR ν_{\max} (KBr, cm⁻¹): 2922, 2852, 2248, 2209, 2190, 2182, 2158, 2150, 1727, 1705, 1604, 1530 (aromatic NO₂), 1466, 1444, 1392, 1344 (aromatic NO₂), 1286, 1183, 1095, 1050, 1030, 985, 910, 835, 739; HRMS (ESI) calcd for C₁₃H₁₂N₂O₇ [M+Na]⁺ 331.0537, found 331.0531.

2-(2,4-Dinitrophenyl)-3-phenylcyclopropane-1-carbaldehyde (3g, 4g and 5g): The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 5:1), affording the title compound as a yellow oil;

Diastereomeric ratios of **3g:4g:5g** = 3:2:1; Enantiomeric excesses of **3g:4g:5g** = 97:91:96; Total yield of **3g:4g:5g** = 78% (112 mg).

(1R,2S,3S)-2-(2,4-Dinitrophenyl)-3-phenylcyclopropane-1-carbaldehyde (3g). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 46.0 min, t_R = 52.3 min; $[\alpha]_D^{26}$ = +8.9° (*c* 0.7, CHCl₃) (**S catalyst**), $[\alpha]_D^{26}$ = -7.8° (*c* 1.4, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.60 (d, *J* = 1.9, 1H), 8.74 (d, *J* = 2.0, 1H), 8.39 (dd, *J* = 8.5, 2.0, 1H), 7.80 (d, *J* = 8.6, 1H), 7.33 (t, *J* = 7.3, 2H), 7.27 (d, *J* = 7.1, 1H), 7.22 (d, *J* = 8.0, 2H), 3.40 (dd, *J* = 8.6, 8.0, 1H), 3.27 (dd, *J* = 7.2, 5.4, 1H), 2.93 (ddd, *J* = 7.3, 5.2, 2.1, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 197 (CHO), 149.9 (Cq), 147.1 (Cq), 138.3 (Cq), 137.1 (Cq), 133.8 (CH), 129.0 (2 CH), 127.8 (CH), 127.1 (CH), 126.6 (2 CH), 120.1 (CH), 39.1 (CH), 34.1 (CH), 33.4 (CH); IR ν_{max} (KBr, cm⁻¹): 3099, 2924, 2853, 2025, 1702, 1603, 1529 (aromatic NO₂), 1458, 1345 (aromatic NO₂), 1151, 1127, 1065, 1031, 1010, 964, 919, 835, 752, 738, 698, 520; HRMS (ESI) calcd for C₁₆H₁₂N₂O₅ [M+Na]⁺ 335.0638, found 335.0644.

(1S,2S,3S)-2-(2,4-Dinitrophenyl)-3-phenylcyclopropane-1-carbaldehyde (4g). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 75.3 min, t_R = 66.7 min; $[\alpha]_D^{26}$ = -70.8° (*c* 0.2, CHCl₃) (**S catalyst**), $[\alpha]_D^{26}$ = +37.8° (*c* 1.3, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.02 (d, *J* = 5.6, 1H), 8.82 (d, *J* = 2.1, 1H), 8.42 (dd, *J* = 8.6, 2.1, 1H), 7.55 (d, *J* = 8.6, 1H), 7.42 – 7.32 (m, 4H), 7.28 (d, *J* = 6.9, 1H), 3.97 (dd, *J* = 6.7, 5.6, 1H), 3.23 (dd, *J* = 8.8, 7.8, 1H), 2.55 (ddd, *J* = 10.7, 9.6, 5.4, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 197.2 (CHO), 150.2 (Cq), 146.8 (Cq), 140.5 (Cq), 133.4 (Cq), 130.1 (CH), 128.9 (2 CH), 128.9 (2 CH), 128.1 (CH), 127.5 (CH), 120.5 (CH), 38.3 (CH), 34.9 (CH), 26.2 (CH); IR ν_{max} (KBr, cm⁻¹): 3099, 2924, 2853, 2025, 1702, 1603, 1529 (aromatic NO₂), 1458, 1345 (aromatic NO₂), 1151, 1127, 1065, 1031, 1010, 964, 919, 835, 752, 738, 698, 520; HRMS (ESI) calcd for C₁₆H₁₂N₂O₅ [M+Na]⁺ 335.0638, found 335.0630.

(1S,2R,3R)-2-(2,4-Dinitrophenyl)-3-phenylcyclopropane-1-carbaldehyde (5g). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 31.0 min, t_R = 41.3 min; $[\alpha]_D^{26}$ = -73.9° (*c* 0.8, CHCl₃) (**S catalyst**), $[\alpha]_D^{26}$ = +70.8° (*c* 1.4, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.69 (d, *J* = 3.7, 1H), 8.61 (d, *J* = 2.1, 1H), 8.25 (dd, *J* = 8.5, 2.1, 1H), 7.43 (d, *J* = 8.6, 1H), 7.13 – 7.06 (m, 3H), 6.82 – 6.77 (m, 2H), 3.63 (dd, *J* = 10.2, 5.7, 1H), 3.32 (dd, *J* = 10.2, 5.1, 1H), 3.03 – 2.99 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 197.6 (CHO),

150.5 (Cq), 146.8 (Cq), 137.5 (Cq), 133.0 (CH), 132.8 (Cq), 128.6 (2 CH), 127.6 (3 CH), 126.7 (CH), 120.2 (CH), 35.4 (CH), 33.1 (CH), 31.4 (CH); IR ν_{\max} (KBr, cm^{-1}): 3099, 2924, 2853, 2025, 1702, 1603, 1529 (aromatic NO_2), 1458, 1345 (aromatic NO_2), 1151, 1127, 1065, 1031, 1010, 964, 919, 835, 752, 738, 698, 520; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_5$ $[\text{M}+\text{Na}]^+$ 335.0638, found 335.0641.

4-(2-(2,4-Dinitrophenyl)-3-formylcyclopropyl)benzotrile (3h, 4h and 5h): The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 6:1 to 4:1), affording the title compound as a yellow oil; Diastereomeric ratios of **3h:4h:5h** = 2:1.5:1; Enantiomeric excesses of **3h:4h:5h** = 99:99:n.d.; Total yield of **3h:4h:5h** = 80% (125 mg).

4-((1R,2R,3S)-2-(2,4-Dinitrophenyl)-3-formylcyclopropyl)benzotrile (3h). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 55:45, flow rate = 1.0 mL/min, λ = 230 nm): t_{R} = 37.1 min, t_{R} = 43.6 min; $[\alpha]_{\text{D}}^{23}$ = -13.9° (*c* 0.6, CHCl_3) (**R catalyst**); ^1H NMR (400 MHz, CDCl_3) δ = 9.68 (d, J = 1.8, 1H), 8.82 (d, J = 2.3, 1H), 8.44 (dd, J = 8.5, 2.3, 1H), 7.79 (d, J = 8.5, 1H), 7.67 (d, J = 8.2, 2H), 7.37 (d, J = 8.3, 2H), 3.47 (dd, J = 8.0, 7.6, 1H), 3.33 (dd, J = 7.3, 5.3, 1H), 3.07 (ddd, J = 9.2, 5.2, 1.8, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ = 196.1 (CHO), 149.9 (Cq), 147.3 (Cq), 142.6 (Cq), 137.2 (Cq), 133.7 (CH), 132.8 (CH), 132.6 (CH), 127.3 (CH), 127.2 (CH), 126.7 (CH), 120.3 (CH), 118.3 (Cq), 111.7 (Cq), 38.9 (CH), 34.4 (CH), 32.6 (CH); IR ν_{\max} (KBr, cm^{-1}): 3051, 2921, 1702, 1672, 1628, 1576, 1538, 1499, 1450, 1354, 1327 (aromatic NO_2), 1134, 1091, 973, 908; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_5$ $[\text{M}+\text{Na}]^+$ 360.0591, found 360.0586.

4-((1R,2R,3R)-2-(2,4-Dinitrophenyl)-3-formylcyclopropyl)benzotrile (4h) and 4-((1S,2S,3R)-2-(2,4-dinitrophenyl)-3-formylcyclopropyl)benzotrile (5h). [inseparable mixture of diastereoisomers]: Yellow oil; The enantiomeric excess of product **4h** was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 65:35, flow rate = 1.0 mL/min, λ = 230 nm): t_{R} = 48.2 min, t_{R} = 45.2 min; ^1H NMR (400 MHz, CDCl_3) [diastereomer (**4h**) – H'; diastereomer (**5h**) – H] δ = 9.76 (d, J = 3.4, 1H'), 9.25 (d, J = 4.2, 1H), 8.85 (d, J = 2.3, 1H), 8.66 (d, J = 2.3, 1H'), 8.45 (dd, J = 8.6, 2.4, 1H), 8.33 (dd, J = 8.5, 2.4, 1H'), 7.65 (d, J = 8.4, 2H), 7.57 (d, J = 8.6, 1H), 7.51 (d, J = 8.6, 1H'), 7.42 – 7.37 (m, 2H' and 2H), 6.92 (d, J = 8.2, 2H'), 4.01 (dd, J = 7.2, 5.7, 1H), 3.70 (dd, J = 10.2, 6.0, 1H'), 3.35 (dd, J = 10.3, 5.2, 1H'), 3.18 (dd, J = 9.3, 7.4, 1H), 3.14 (dd, J = 5.5, 3.4, 1H'), 2.77 (ddd, J = 9.6, 5.5, 4.2, 1H); ^{13}C NMR (101 MHz, CDCl_3) [diastereomer (**4h**) – C'; diastereomer (**5h**) – C] δ =

196.7 (C'HO), 195.7 (CHO), 150.3 (C'q), 150.1 (Cq), 147.2 (C'q), 147.1 (Cq), 139.6 (Cq), 138.8 (Cq), 138.6 (C'q), 136.3 (C'q), 133.0 (C'H), 132.5 (2 CH), 132.3 (2 C'H), 130.5 (CH), 129.8 (2 CH), 128.3 (2 C'H), 127.6 (CH), 127.2 (C'H), 120.7 (CH), 120.5 (C'H), 118.3 (Cq), 118.1 (C'q), 111.9 (Cq), 111.7 (C'q), 37.7 (CH), 35.2 (C'H), 35.1 (CH), 32.8 (C'H), 32.1 (C'H), 26.7 (CH); HRMS (ESI) calcd for C₁₇H₁₁N₃O₅ [M+Na]⁺ 360.0591, found 360.0584.

2-(2,4-Dinitrophenyl)-3-(4-nitrophenyl)cyclopropane-1-carbaldehyde (3i, 4i and 5i): The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 6:1), affording the title compound as a yellow solid; Diastereomeric ratios of **3i:4i:5i** = 2:2:1; Enantiomeric excesses of **3i:4i:5i** = 98:n.d.:n.d.; Total yield of **3i:4i:5i** = 67% (110.5 mg).

(1R,2S,3S)-2-(2,4-Dinitrophenyl)-3-(4-nitrophenyl)cyclopropane-1-carbaldehyde (3i).

Yellow solid; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 45:55, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 42.2 min, t_R = 51.3 min; [α]_D²³ = +26.3° (c 0.5, CHCl₃) (**S catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.70 (d, *J* = 1.8, 1H), 8.83 (d, *J* = 2.3, 1H), 8.46 (dd, *J* = 8.5, 2.3, 1H), 8.24 (d, *J* = 8.8, 2H), 7.80 (d, *J* = 8.6, 1H), 7.42 (d, *J* = 8.7, 2H), 3.51 (dd, *J* = 8.7, 7.9, 1H), 3.38 (dd, *J* = 7.4, 5.2, 1H), 3.12 (ddd, *J* = 9.2, 5.2, 1.9, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 196.0 (CHO), 149.9 (Cq), 147.4 (Cq), 147.4 (Cq), 144.6 (Cq), 137.1 (Cq), 133.7 (CH), 127.4 (2 CH), 127.2 (CH), 124.3 (2 CH), 120.3 (CH), 39.0 (CH), 34.6 (CH), 32.4 (CH); IR ν_{max} (KBr, cm⁻¹): 2922, 2852, 2159, 2054, 1703, 1602, 1518 (aromatic NO₂), 1345 (aromatic NO₂), 1151, 1111, 1065, 1012, 960, 919, 854, 835, 749, 694; HRMS (ESI) calcd for C₁₆H₁₁N₃O₇ [M+Na]⁺ 380.0489, found 380.0480.

(1S,2S,3S)-2-(2,4-Dinitrophenyl)-3-(4-nitrophenyl)cyclopropane-1-carbaldehyde (4i) and (1S,2R,3R)-2-(2,4-dinitrophenyl)-3-(4-nitrophenyl)cyclopropane-1-carbaldehyde (5i).

[inseparable mixture of diastereoisomers]: Yellow oil; ¹H NMR (400 MHz, CDCl₃) [diastereomer (**4i**) – H'; diastereomer (**5i**) – H] δ = 9.79 (d, *J* = 3.3, 1H'), 9.29 (d, *J* = 4.0, 1H), 8.86 (d, *J* = 2.3, 1H), 8.65 (d, *J* = 2.3, 1H'), 8.46 (dd, *J* = 8.6, 2.4, 1H), 8.34 (dd, *J* = 8.5, 2.3, 1H'), 8.20 (d, *J* = 8.8, 2H), 7.96 (d, *J* = 8.8, 2H'), 7.58 (t, *J* = 9.1 Hz, 3H), 7.54 (d, *J* = 8.6 Hz, 1H'), 6.98 (d, *J* = 8.7, 2H'), 4.04 (dd, *J* = 7.3, 5.7, 1H), 3.72 (dd, *J* = 10.2, 6.0, 1H'), 3.40 (dd, *J* = 10.3, 5.2, 1H'), 3.22 (dd, *J* = 9.4, 7.5, 1H), 3.14 (ddd, *J* = 8.8, 5.5, 3.3, 1H'), 2.82 (ddd, *J* = 9.5, 5.5, 4.0, 1H); ¹³C NMR (101 MHz, CDCl₃) [diastereomer (**4i**) – C'; diastereomer (**5i**) – C] δ = 196.6 (C'HO), 195.5 (CHO), 150.3 (Cq), 150.1 (Cq), 147.5 (C'q), 147.3 (C'q), 147.2 (C'q),

140.8 (Cq), 140.7 (C'q), 139.5 (Cq), 136.2 (C'q), 133.0 (C'H), 130.5 (C'H), 129.9 (2 CH), 128.4 (2 C'H), 127.7 (CH), 127.2 (C'H), 126.4 (Cq), 124.0 (2 CH), 123.8 (2 C'H), 120.7 (CH), 120.5 (CH), 37.7 (CH), 35.4 (C'H), 34. (CH), 32.7 (C'H), 32.3 (C'H), 27.0 (CH); IR ν_{\max} (KBr, cm^{-1}): 2922, 2852, 2159, 2054, 1703, 1602, 1518 (aromatic NO_2), 1345 (aromatic NO_2), 1151, 1111, 1065, 1012, 960, 919, 854, 835, 749, 694; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_7$ $[\text{M}+\text{Na}]^+$ 380.0489, found 380.0486.

2-(2,4-Dinitrophenyl)-3-(4-fluorophenyl)cyclopropane-1-carbaldehyde (3j, 4j and 5j):

The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 7:1), affording the title compound as an orange oil; Diastereomeric ratios of **3j:4j:5j** = 1.5:1.5:1; Enantiomeric excesses of **3j:4j:5j** = 98:91:90; Total yield of **3j:4j:5j** = 78% (119 mg).

(1R,2S,3S)-2-(2,4-Dinitrophenyl)-3-(4-fluorophenyl)cyclopropane-1-carbaldehyde (3j).

Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 245 nm): t_{R} = 25.2 min, t_{R} = 33.0 min; $[\alpha]_{\text{D}}^{20}$ = +7.3° (*c* 1.0, CHCl_3) (*S* catalyst); ^1H NMR (500 MHz, CDCl_3) δ = 9.67 (d, J = 2, 1H), 8.82 (d, J = 2, 1H), 8.46 (dd, J = 8.5, 2.5, 1H), 7.85 (d, J = 8.5, 1H), 7.25 (m, 2H), 7.08 (m, 2H), 3.43 (t, J = 8.3, 1H), 3.33 (dd, J = 7.5, 5.5, 1H), 3.00 (ddd, J = 9.3, 5.3, 2.3, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ = 197.0 (CHO), 162.1 (d, J =247.7Hz, Cq), 149.9 (Cq), 147.2 (Cq), 138.2 (Cq), 133.9 (CH), 132.9 (CH), 128.5 (d, J =8.1Hz, CH), 127.2 (CH), 120.3 (CH), 116.1 (d, J =21.7Hz, CH), 39.1 (CH), 34.2 (CH), 32.7 (CH); IR ν_{\max} (KBr, cm^{-1}): 2957, 2921, 2855, 2803, 2368, 2356, 1703, 1605, 1535 (aromatic NO_2), 1515, 1349 (aromatic NO_2), 1229, 1161, 912, 836, 822, 737, 670, 636; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{FN}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 331.0725, found 331.0726.

(1S,2S,3S)-2-(2,4-Dinitrophenyl)-3-(4-fluorophenyl)cyclopropane-1-carbaldehyde (4j).

Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 245 nm): t_{R} = 15.4 min, t_{R} = 20.6 min; $[\alpha]_{\text{D}}^{20}$ = - 49.4° (*c* 0.56, CHCl_3) (*S* catalyst); ^1H NMR (500 MHz, CDCl_3) δ = 9.12 (d, J = 5, 1H), 8.85 (d, J = 2.5, 1H), 8.45 (dd, J = 8.7, 2.3, 1H), 7.57 (d, J = 8.5, 1H), 7.39 (dd, J = 8.5, 5.5, 2H), 7.07 (t, J = 8.7, 2H), 3.96 (dd, J = 6.5, 5.5, 1H), 3.20 (t, J = 8.3, 1H), 2.62 (dt, J = 9.5, 5, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ = 196.9 (CHO), 162.1 (d, J =247.5Hz, Cq), 150.1 (Cq), 146.9 (Cq), 140.3 (Cq), 130.6 (d, J =8.2Hz, CH), 130.2 (CH), 129.4 (d, J =8.1Hz, CH), 127.5 (CH), 120.6 (CH), 115.8 (d, J =21.7Hz, CH), 37.9 (CH), 34.4 (CH), 26.6 (CH); IR ν_{\max}

(KBr, cm^{-1}): 2957, 2921, 2855, 2803, 2368, 2356, 1703, 1605, 1535 (aromatic NO_2), 1515, 1349 (aromatic NO_2), 1229, 1161, 912, 836, 822, 737, 670, 636; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{FN}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 331.0725, found 331.0726.

(1*S*,2*R*,3*R*)-2-(2,4-Dinitrophenyl)-3-(4-fluorophenyl)cyclopropane-1-carbaldehyde (5j).

Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, λ = 245 nm): $t_{\text{R}} = 27.8$ min, $t_{\text{R}} = 36.8$; $[\alpha]_{\text{D}}^{20} = -52.8^\circ$ (*c* 0.51, CHCl_3) (**S catalyst**); ^1H NMR (500 MHz, CDCl_3) $\delta = 9.72$ (d, $J = 3.5$, 1H), 8.67 (d, $J = 2.5$, 1H), 8.30 (dd, $J = 8.7, 2.3$, 1H), 7.45 (d, $J = 8.5$, 1H), 6.84-6.78 (m, 4H), 3.63 (dd, $J = 10.3, 5.8$, 1H), 3.33 (dd, $J = 10.5, 5$, 1H), 3.01 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) $\delta = 197.6$ (CHO), 162.1 (d, $J=247.7\text{Hz}$, Cq), 150.5 (Cq), 147.0 (Cq), 137.3 (Cq), 133.0 (CH), 129.4 (CH), 128.6 (CH), 126.9 (CH), 120.4 (CH), 115.8 (d, $J=21.7\text{Hz}$, CH), 35.5 (CH), 32.5 (CH), 31.5 (CH); IR ν_{max} (KBr, cm^{-1}): 2957, 2921, 2855, 2803, 2368, 2356, 1703, 1605, 1535 (aromatic NO_2), 1515, 1349 (aromatic NO_2), 1229, 1161, 912, 836, 822, 737, 670, 636; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{FN}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 331.0725, found 331.0728.

2-(4-Chlorophenyl)-3-(2,4-dinitrophenyl)cyclopropane-1-carbaldehyde (3k, 4k and 5k):

The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 5:1), affording the title compound as a yellow oil; Diastereomeric ratios of **3k:4k:5k** = 2.5:1.5:1; Enantiomeric excesses of **3k:4k:5k** = 99:94:97; Total yield of **3k:4k:5k** = 86% (137 mg).

(1*R*,2*S*,3*S*)-2-(4-Chlorophenyl)-3-(2,4-dinitrophenyl)cyclopropane-1-carbaldehyde (3k).

Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 55:45, flow rate = 1.0 mL/min, λ = 230 nm): $t_{\text{R}} = 24.4$ min, $t_{\text{R}} = 31.8$ min; $[\alpha]_{\text{D}}^{23} = +21.1^\circ$ (*c* 0.7, CHCl_3) (**S catalyst**); ^1H NMR (400 MHz, CDCl_3) $\delta = 9.64$ (d, $J = 2.0$, 1H), 8.79 (d, $J = 2.3$, 1H), 8.43 (dd, $J = 8.5, 2.3$, 1H), 7.81 (d, $J = 8.5$, 1H), 7.33 (d, $J = 8.5$, 2H), 7.19 (d, $J = 8.4$, 2H), 3.40 (dd, $J = 8.5, 8.2$, 1H), 3.28 (dd, $J = 7.4, 5.2$, 1H), 2.98 (ddd, $J = 9.1, 5.1, 2.1$, 1H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 196.6$ (CHO), 149.9 (Cq), 147.2 (Cq), 137.9 (Cq), 135.6 (Cq), 133.7 (CH), 133.7 (Cq), 129.2 (2 CH), 127.9 (2 CH), 127.1 (CH), 120.1 (CH), 38.9 (CH), 34.1 (CH), 32.5 (CH); IR ν_{max} (KBr, cm^{-1}): 3099, 2925, 2854, 1702, 1603, 1529 (aromatic NO_2), 1496, 1435, 1397, 1345 (aromatic NO_2), 1214, 1151, 1126, 1092, 1066, 1038, 1013, 964, 918, 835, 811, 759, 739, 668; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{ClN}_2\text{O}_5$ $[\text{M}+\text{Na}]^+$ 369.0249, found 369.0247.

(1*S*,2*S*,3*S*)-2-(4-Chlorophenyl)-3-(2,4-dinitrophenyl)cyclopropane-1-carbaldehyde (4k).

Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 55:45, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 43.8 min, t_R = 39.4 min; $[\alpha]_D^{22}$ = - 75.7° (*c* 0.9, CHCl₃) (**S catalyst**), $[\alpha]_D^{22}$ = +72.2° (*c* 0.8, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.10 (d, *J* = 5.0, 1H), 8.81 (d, *J* = 2.3, 1H), 8.42 (dd, *J* = 8.6, 2.3, 1H), 7.54 (d, *J* = 8.6, 1H), 7.35 – 7.27 (m, 4H), 3.93 (dd, *J* = 7.0, 5.6, 1H), 3.15 (dd, *J* = 9.4, 7.2, 1H), 2.61 (ddd, *J* = 10.0, 9.8, 5.2, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 196.6 (CHO), 150.1 (Cq), 146.9 (Cq), 140.1 (Cq), 134 (Cq), 131.9 (Cq), 130.3 (3 CH), 129.1 (2 CH), 127.5 (CH), 120.5 (CH), 37.9 (CH), 34.5 (CH), 26.5 (CH); IR ν_{max} (KBr, cm⁻¹): 3099, 2925, 2854, 1702, 1603, 1529 (aromatic NO₂), 1496, 1435, 1397, 1345 (aromatic NO₂), 1214, 1151, 1126, 1092, 1066, 1038, 1013, 964, 918, 835, 811, 759, 739, 668; HRMS (ESI) calcd for C₁₆H₁₁ClN₂O₅ [M+Na]⁺ 369.0249, found 369.0240.

(1*S*,2*R*,3*R*)-2-(4-Chlorophenyl)-3-(2,4-dinitrophenyl)cyclopropane-1-carbaldehyde (5k).

Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 60:40, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 29.1 min, t_R = 32.6 min; $[\alpha]_D^{22}$ = - 56.1° (*c* 0.6, CHCl₃) (**S catalyst**), $[\alpha]_D^{22}$ = +56.2° (*c* 0.7, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.71 (d, *J* = 3.6, 1H), 8.66 (d, *J* = 2.3, 1H), 8.29 (dd, *J* = 8.5, 2.3, 1H), 7.42 (d, *J* = 8.6, 1H), 7.08 (d, *J* = 8.5, 2H), 6.75 (d, *J* = 8.5, 2H), 3.62 (dd, *J* = 10.2, 5.8, 1H), 3.29 (dd, *J* = 10.2, 5.2, 1H), 3.01 – 2.97 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 197.2 (CHO), 150.4 (Cq), 147 (Cq), 137 (Cq), 133.7 (Cq), 132.8 (CH), 131.4 (Cq), 128.9 (2 CH), 128.9 (2 CH), 126.7 (CH), 120.4 (CH), 35.2 (CH), 32.5 (CH), 31.4 (CH); IR ν_{max} (KBr, cm⁻¹): 3099, 2925, 2854, 1702, 1603, 1529 (aromatic NO₂), 1496, 1435, 1397, 1345 (aromatic NO₂), 1214, 1151, 1126, 1092, 1066, 1038, 1013, 964, 918, 835, 811, 759, 739, 668; HRMS (ESI) calcd for C₁₆H₁₁ClN₂O₅ [M+Na]⁺ 369.0249, found 369.0249.

2-(4-Bromophenyl)-3-(2,4-dinitrophenyl)cyclopropane-1-carbaldehyde (3l, 4l and 5l):

The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 5:1), affording the title compound as a yellow solid; Diastereomeric ratios of **3l:4l:5l** = 2:2:1; Enantiomeric excesses of **3l:4l:5l** = 99:95:98; Total yield of **3l:4l:5l** = 71% (129 mg).

(1*S*,2*R*,3*R*)-2-(4-Bromophenyl)-3-(2,4-dinitrophenyl)cyclopropane-1-carbaldehyde (3l).

Yellow solid; M.p.:117 °C; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 40.6 min, t_R = 56.2 min; $[\alpha]_D^{22}$ = - 2.4° (*c* 0.5, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃)

$\delta = 9.65$ (d, $J = 2.0$, 1H), 8.80 (d, $J = 2.3$, 1H), 8.44 (dd, $J = 8.5$, 2.3, 1H), 7.81 (d, $J = 8.6$, 1H), 7.49 (d, $J = 8.5$, 2H), 7.13 (d, $J = 8.4$, 2H), 3.41 (dd, $J = 8.5$, 8.2, 1H), 3.26 (dd, $J = 7.5$, 5.2, 1H), 2.99 (ddd, $J = 9.1$, 5.1, 2.1, 1H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 196.7$ (CHO), 149.9 (Cq), 147.2 (Cq), 137.9 (Cq), 136.1 (Cq), 133.7 (CH), 132.1 (2 CH), 128.3 (2 CH), 127.1 (CH), 121.6 (Cq), 120.2 (CH), 38.9 (CH), 34.1 (CH), 32.6 (CH); IR ν_{max} (KBr, cm^{-1}): 2998, 2925, 1712, 1673, 1622, 1576, 1538, 1499, 1450, 1354, 1327 (aromatic NO_2), 1134, 1091, 973, 908; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{BrN}_2\text{O}_5$ $[\text{M}+\text{Na}]^+$ 412.9744, found 412.9750.

(1*R*,2*R*,3*R*)-2-(4-Bromophenyl)-3-(2,4-dinitrophenyl)cyclopropane-1-carbaldehyde (4l).

Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*PrOH = 55:45, flow rate = 1.0 mL/min, $\lambda = 210$ nm): $t_{\text{R}} = 50.0$ min, $t_{\text{R}} = 42.9$ min; $[\alpha]_{\text{D}}^{22} = +69.8^\circ$ (c 1.1, CHCl_3) (**R catalyst**); ^1H NMR (400 MHz, CDCl_3) $\delta = 9.11$ (d, $J = 5.0$, 1H), 8.83 (d, $J = 2.3$, 1H), 8.43 (dd, $J = 8.6$, 2.3, 1H), 7.54 (d, $J = 8.6$, 1H), 7.49 – 7.46 (m, 2H), 7.26 (d, $J = 8.3$, 2H), 3.94 (dd, $J = 7.1$, 5.5, 1H), 3.13 (dd, $J = 9.3$, 7.3, 1H), 2.62 (ddd, $J = 9.6$, 5.2, 4.4, 1H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 196.6$ (CHO), 150.1 (Cq), 146.9 (Cq), 140.1 (Cq), 132.4 (Cq), 132.0 (2 CH), 130.6 (2 CH), 130.3 (CH), 127.5 (CH), 122.1 (Cq), 120.6 (CH), 37.9 (CH), 34.5 (CH), 26.4 (CH); HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{BrN}_2\text{O}_5$ $[\text{M}+\text{Na}]^+$ 412.9744, found 412.9748.

(1*R*,2*S*,3*S*)-2-(4-Bromophenyl)-3-(2,4-dinitrophenyl)cyclopropane-1-carbaldehyde (5l).

Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 55:45, flow rate = 1.0 mL/min, $\lambda = 210$ nm): $t_{\text{R}} = 30.6$ min, $t_{\text{R}} = 34.0$ min; $[\alpha]_{\text{D}}^{22} = +46.8^\circ$ (c 0.2, CHCl_3) (**R catalyst**); ^1H NMR (400 MHz, CDCl_3) $\delta = 9.71$ (d, $J = 3.6$, 1H), 8.67 (d, $J = 2.3$, 1H), 8.30 (dd, $J = 8.5$, 2.3, 1H), 7.43 (d, $J = 8.5$, 1H), 7.25 – 7.21 (m, 2H), 6.68 (d, $J = 8.4$, 2H), 3.63 (dd, $J = 10.2$, 5.8, 1H), 3.28 (dd, $J = 10.2$, 5.1, 1H), 3.01 – 2.97 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 197.3$ (CHO), 150.4 (Cq), 147.0 (Cq), 137.0 (Cq), 132.8 (CH), 131.9 (Cq), 131.8 (2 CH), 129.2 (2 CH), 126.9 (CH), 121.7 (Cq), 120.4 (CH), 35.2 (CH), 32.6 (CH), 31.5 (CH); HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{BrN}_2\text{O}_5$ $[\text{M}+\text{Na}]^+$ 412.9744, found 412.9732.

2-(2,4-Dinitrophenyl)-3-(*p*-tolyl)cyclopropane-1-carbaldehyde (3m, 4m and 5m): The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 5:1), affording the title compound as a yellow oil; Diastereomeric ratios of **3m:4m:5m** = 3:2:1; Enantiomeric excesses of **3m:4m:5m** = 98:85:96; Total yield of **3m:4m:5m** = 80% (120 mg).

(1*S*,2*R*,3*R*)-2-(2,4-Dinitrophenyl)-3-(*p*-tolyl)cyclopropane-1-carbaldehyde (3*m*). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 60:40, flow rate = 1.0 mL/min, $\lambda = 230$ nm): $t_R = 29.2$ min, $t_R = 40.1$ min; $[\alpha]_D^{22} = +11.3^\circ$ (*c* 0.6, CHCl₃) (**S catalyst**), $[\alpha]_D^{22} = -11.8^\circ$ (*c* 1.1, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) $\delta = 9.62$ (d, *J* = 2.2, 1H), 8.78 (d, *J* = 2.3, 1H), 8.42 (dd, *J* = 8.5, 2.4, 1H), 7.84 (d, *J* = 8.5, 1H), 7.21 – 7.12 (m, 4H), 3.42 (dd, *J* = 8.2, 7.2, 1H), 3.28 (dd, *J* = 7.5, 5.1, 1H), 2.97 (ddd, *J* = 9.0, 5.1, 2.3, 1H), 2.35 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) $\delta = 197.2$ (CHO), 149.9 (Cq), 147.0 (Cq), 138.5 (Cq), 137.6 (Cq), 134.0 (Cq), 133.8 (CH), 129.7 (2 CH), 127.1 (CH), 126.5 (2 CH), 120.1 (CH), 39.1 (CH), 34.1 (CH), 33.3 (CH), 21.1 (CH₃); IR ν_{\max} (KBr, cm⁻¹): 3020, 2923, 2853, 1699, 1603, 1525 (aromatic NO₂), 1434, 1397, 1342 (aromatic NO₂), 1215, 1150, 1127, 1065, 1038, 1010, 964, 909, 835, 802, 752, 738, 668; HRMS (ESI) calcd for C₁₇H₁₄N₂O₅ [M+Na]⁺ 349.0795, found 349.0797.

(1*R*,2*R*,3*R*)-2-(2,4-Dinitrophenyl)-3-(*p*-tolyl)cyclopropane-1-carbaldehyde (4*m*). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 60:40, flow rate = 1.0 mL/min, $\lambda = 230$ nm): $t_R = 40.6$ min, $t_R = 46.4$ min; $[\alpha]_D^{23} = +50.4^\circ$ (*c* 0.4, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) $\delta = 9.01$ (d, *J* = 5.6, 1H), 8.80 (t, *J* = 2.1, 1H), 8.41 (dd, *J* = 8.6, 2.4, 1H), 7.54 (d, *J* = 8.6, 1H), 7.26 (d, *J* = 8.0, 2H), 7.14 (d, *J* = 7.9, 2H), 3.94 (dd, *J* = 7.0, 5.3, 1H), 3.20 (dd, *J* = 9.0, 7.5, 1H), 2.52 (ddd, *J* = 9.4, 5.4, 4.0, 1H), 2.32 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) $\delta = 197.5$ (CHO), 150.1 (Cq), 146.8 (Cq), 140.7 (Cq), 137.9 (Cq), 130.4 (Cq), 130.2 (CH), 129.6 (2 CH), 128.7 (2 CH), 127.5 (CH), 120.5 (CH), 38.3 (CH), 34.7 (CH), 26.3 (CH), 21.1 (CH₃); IR ν_{\max} (KBr, cm⁻¹): 3020, 2923, 2853, 1699, 1603, 1525 (aromatic NO₂), 1434, 1397, 1342 (aromatic NO₂), 1215, 1150, 1127, 1065, 1038, 1010, 964, 909, 835, 802, 752, 738, 668; HRMS (ESI) calcd for C₁₇H₁₄N₂O₅ [M+Na]⁺ 349.0795, found 349.0803.

(1*R*,2*S*,3*S*)-2-(2,4-Dinitrophenyl)-3-(*p*-tolyl)cyclopropane-1-carbaldehyde (5*m*). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, $\lambda = 230$ nm): $t_R = 33.3$ min, $t_R = 39.2$ min; $[\alpha]_D^{23} = -86.5^\circ$ (*c* 0.1, CHCl₃) (**S catalyst**), $[\alpha]_D^{23} = +83.0^\circ$ (*c* 0.1, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) $\delta = 9.66$ (d, *J* = 3.9, 1H), 8.62 (d, *J* = 2.4, 1H), 8.25 (dd, *J* = 8.5, 2.4, 1H), 7.43 (d, *J* = 8.5, 1H), 6.90 (t, *J* = 8.1, 1H), 6.66 (d, *J* = 8.1, 1H), 3.60 (dd, *J* = 10.2, 5.7, 1H), 3.28 (dd, *J* = 10.2, 5.1, 1H), 2.99 – 2.96 (m, 1H), 2.20 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) $\delta = 197.9$ (CHO), 150.4 (Cq), 146.8 (Cq), 137.7 (Cq), 137.4 (Cq), 133.0 (CH), 129.6 (Cq), 129.3 (2 CH), 127.5 (2 CH), 126.7 (CH), 120.2 (CH), 35.5 (CH), 33.0 (CH), 31.3 (CH),

21.0 (CH₃); IR ν_{\max} (KBr, cm⁻¹): 3020, 2923, 2853, 1699, 1603, 1525 (aromatic NO₂), 1434, 1397, 1342 (aromatic NO₂), 1215, 1150, 1127, 1065, 1038, 1010, 964, 909, 835, 802, 752, 738, 668; HRMS (ESI) calcd for C₁₇H₁₄N₂O₅ [M+Na]⁺ 349.0795, found 349.0799.

2-(2,4-Dinitrophenyl)-3-(4-methoxyphenyl)cyclopropane-1-carbaldehyde (3n, 4n and 5n):

The title compound was synthesized according to general procedure A. The product was purified by column chromatography (hexane/EtOAc = 9:1), affording the title compound as a yellow oil; Diastereomeric ratios of **3n:4n:5n** = 1.5:1:1; Enantiomeric excesses of **3n:4n:5n** = 98:90:94; Total yield of **3n:4n:5n** = 79% (125 mg).

(1R,2S,3S)-2-(2,4-Dinitrophenyl)-3-(4-methoxyphenyl)cyclopropane-1-carbaldehyde

(3n). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 245 nm): t_R = 36.0 min, t_R = 50.7; $[\alpha]_D^{20}$ = +5.2° (*c* 2.5, CHCl₃) (**S catalyst**); ¹H NMR (500 MHz, CDCl₃) δ = 9.66 (d, *J* = 2.0, 1H), 8.81 (d, *J* = 2.0, 1H), 8.45 (dd, *J* = 8.5, 2.5, 1H), 7.85 (d, *J* = 8.5, 1H), 7.19 (d, *J* = 8.5, 2H), 6.91 (d, *J* = 9, 2H), 3.82 (s, 3H), 3.41 (t, *J* = 8.5, 1H), 3.29 (dd, *J* = 7.5, 5.0, 1H), 2.96 (ddd, *J* = 9.0, 5.0, 2.0, 1H); ¹³C NMR (125 MHz, CDCl₃) δ = 197.1, 159.2, 148.9, 147.1, 138.5, 133.8, 128.9, 127.8 (2 C), 127.0, 120.1, 114.4 (2 C), 55.4, 39.1, 34.0, 33.0; IR ν_{\max} (KBr, cm⁻¹): 3321, 2942, 2832, 1701, 1610, 1518 (aromatic NO₂), 1450, 1348, 1249 (aromatic NO₂), 1181, 1113, 1026, 909, 835, 737, 691, 672, 651, 635, 608; HRMS (ESI) calcd for C₁₇H₁₄N₂O₆ [M+H]⁺ 343.0925, found 343.0922.

(1S,2S,3S)-2-(2,4-Dinitrophenyl)-3-(4-methoxyphenyl)cyclopropane-1-carbaldehyde (4n).

Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 245 nm): t_R = 25.5 min, t_R = 31.5 min; $[\alpha]_D^{20}$ = - 21° (*c* 3.2, CHCl₃) (**S catalyst**); ¹H NMR (500 MHz, CDCl₃) δ = 9.06 (d, *J* = 5.5, 1H), 8.84 (d, *J* = 2.5, 1H), 8.44 (dd, *J* = 8.5, 2.0, 1H), 7.54 (d, *J* = 8.5, 1H), 7.32 (d, *J* = 8.5, 2H), 6.90 (d, *J* = 8.5, 2H), 3.94 (dd, *J* = 7.0, 6.0, 1H), 3.81 (s, 3H), 3.19 (dd, *J* = 9.0, 5.0, 1H), 2.54 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ = 197.4, 159.3, 150.1, 146.8, 140.7, 135.2, 130 (2 C), 127.4, 125.3, 120.5, 114.3 (2 C), 55.3, 38.4, 34.5, 26.4; IR ν_{\max} (KBr, cm⁻¹): 3321, 2942, 2832, 1701, 1610, 1518 (aromatic NO₂), 1450, 1348, 1249 (aromatic NO₂), 1181, 1113, 1026, 909, 835, 737, 691, 672, 651, 635, 608; HRMS (ESI) calcd for C₁₇H₁₄N₂O₆ [M+H]⁺ 343.0925, found 343.0927.

(1S,2R,3R)-2-(2,4-Dinitrophenyl)-3-(4-methoxyphenyl)cyclopropane-1-carbaldehyde

(5n). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak AD-H

column (hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, λ = 245 nm): t_R = 45.2 min, t_R = 55.0 min; $[\alpha]_D^{20}$ = - 20.7° (*c* 1.2, CHCl₃) (**S catalyst**); ¹H NMR (500 MHz, CDCl₃) δ = 9.69 (d, *J* = 4.0, 1H), 8.66 (d, *J* = 2.0, 1H), 8.28 (dd, *J* = 8.5, 2.0, 1H), 7.42 (d, *J* = 8.5, 1H), 6.73 (d, *J* = 8.5, 2H), 6.65 (d, *J* = 8.5, 2H), 3.71 (s, 3H), 3.61 (dd, *J* = 10.0, 5.5, 1H), 3.30 (dd, *J* = 10.3, 5.0, 1H), 2.96 (dd, *J* = 9.5, 5.0, 1H); ¹³C NMR (125 MHz, CDCl₃) δ = 197.7, 158.9, 150.5, 146.8, 137.7, 135.2, 132.9, 128.8 (2 C), 126.7, 120.2, 114.1 (2 C), 55.2, 35.5, 32.7, 31.1; IR ν_{max} (KBr, cm⁻¹): 3321, 2942, 2832, 1701, 1610, 1518 (aromatic NO₂), 1450, 1348, 1249 (aromatic NO₂), 1181, 1113, 1026, 909, 835, 737, 691, 672, 651, 635, 608; HRMS (ESI) calcd for C₁₇H₁₄N₂O₆ [M+H]⁺ 343.0925, found 343.0929.

2-(2-Nitro-4-(trifluoromethyl)phenyl)-3-phenylcyclopropane-1-carbaldehyde (3o, 4o and 5o): The title compound was synthesized according to general procedure B. The product was purified by column chromatography (hexane/EtOAc = 5:1), affording the title compound as a yellow oil; Diastereomeric ratios of **3o:4o:5o** = 1.5:1:1; Enantiomeric excesses of **3o:4o:5o** = 99:90:90; Total yield of **3o:4o:5o** = 47% (65 mg).

(1R,2S,3S)-2-(2-Nitro-4-(trifluoromethyl)phenyl)-3-phenylcyclopropane-1-carbaldehyde (3o). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 18.1 min, t_R = 13.5 min; $[\alpha]_D^{26}$ = - 37.3° (*c* 0.5, CHCl₃) (**S catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.01 (d, *J* = 5.8, 1H), 8.26 (d, *J* = 1.1, 1H), 7.84 (dd, *J* = 8.3, 1.4, 1H), 7.50 (d, *J* = 7.7, 1H), 7.37 (m, 6H), 6.71 (dd, *J* = 16.0, 7.7, 1H), 3.95 (dd, *J* = 6.7, 5.5, 1H), 3.19 (dd, *J* = 9.3, 7.3, 1H), 2.49 (ddd, *J* = 9.2, 5.5, 3.7, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 197.7 (CHO), 137.6 (Cq), 134.0 (Cq), 133.8 (Cq), 131.3 (CH), 130.8 (Cq), 129.9 (q, *J* = 3.4 Hz, CH), 129.1 (CH), 128.9 (CH), 128.6 (CH), 128.5 (CH), 127.9 (CH), 124.0 (CH), 122.4 (q, *J* = 3.7 Hz, CH), 37.9 (CH), 34.4 (CH), 26.3 (CH); ¹⁹F NMR (376 MHz, CDCl₃) δ -62.9, -62.9, -63.0 ppm; IR ν_{max} (KBr, cm⁻¹): 2923, 2851, 2208, 2146, 2054, 2041, 2030, 2008, 1993, 1965, 1709, 1677, 1628, 1576, 1538, 1499, 1450, 1354, 1327 (aromatic NO₂), 1134, 1091, 973, 908, 845, 813, 787, 751, 699, 644; HRMS (ESI) calcd for C₁₇H₁₂F₃NO₃ [M+H]⁺ 336.0842, found 336.0840.

(1S,2S,3S)-2-(2-Nitro-4-(trifluoromethyl)phenyl)-3-phenylcyclopropane-1-carbaldehyde (4o). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, λ = 230 nm): t_R = 13.5 min, t_R = 11.6 min; $[\alpha]_D^{26}$ = - 52.9° (*c* 0.4, CHCl₃) (**S catalyst**); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.0 ppm; ¹H NMR (400 MHz, CDCl₃) δ = 9.01 (d, *J* = 5.8, 1H), 8.26 (d, *J* = 1.1, 1H), 7.84 (dd, *J* = 8.1,

1.4, 1H), 7.50 (d, $J = 8.2$, 1H), 7.37 (ddd, $J = 12.9$, 7.4, 4.1, 5H), 3.95 (dd, $J = 6.9$, 5.7, 1H), 3.19 (dd, $J = 9.2$, 7.3, 1H), 2.49 (dt, $J = 9.4$, 5.5, 1H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 197.7$ (CHO), 150.2 (Cq), 137.6 (Cq), 133.8 (Cq), 129.9 ((q, $J=3.4\text{Hz}$, CH), 129.8 (CH), 129.5 (q, $J=33.9\text{Hz}$, Cq), 129.2 (Cq), 128.9 (CH), 128.9 (CH), 127.9 (CH), 122.4 (q, $J=3.8\text{Hz}$, CH), 37.9 (CH), 34.4 (CH), 26.3 (CH); IR ν_{max} (KBr, cm^{-1}): 2923, 2851, 2208, 2146, 2054, 2041, 2030, 2008, 1993, 1965, 1709, 1677, 1628, 1576, 1538, 1499, 1450, 1354, 1327 (aromatic NO_2), 1134, 1091, 973, 908, 845, 813, 787, 751, 699, 644; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{F}_3\text{NO}_3$ $[\text{M}+\text{H}]^+$ 336.0842, found: 336.0842.

(1*R*,2*S*,3*S*)-2-(2-Nitro-4-(trifluoromethyl)phenyl)-3-phenylcyclopropane-1-carbaldehyde (5o). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, $\lambda = 230$ nm): $t_{\text{R}} = 10.7$ min, $t_{\text{R}} = 15.0$ min; $[\alpha]_{\text{D}}^{26} = +70.9^\circ$ (c 0.5, CHCl_3) (**R catalyst**); ^{19}F NMR (376 MHz, CDCl_3) $\delta -63.0$ ppm; ^1H NMR (400 MHz, CDCl_3) $\delta = 9.67$ (d, $J = 3.9$, 1H), 8.05 (s, 1H), 7.69 (d, $J = 7.6$, 1H), 7.38 (d, $J = 8.1$, 1H), 7.12 – 7.05 (m, 3H), 6.77 (d, $J = 7.8$, 2H), 3.62 (dd, $J = 10.1$, 5.7, 1H), 3.28 (dd, $J = 10.2$, 5.1, 1H), 2.94 (ddd, $J = 9.5$, 5.3, 3.9, 1H); ^{13}C NMR (101 MHz, CDCl_3) $\delta = 198.0$ (CHO), 150.5 (Cq), 134.5 (Cq), 133.1 (Cq), 132.8 (CH), 130.9 ((q, $J=34.4\text{Hz}$, Cq), 129.2 ((q, $J=3.8\text{Hz}$, CH), 128.5 (CH), 127.6 (CH), 127.4 (CH), 122.5 (q, $J=272$ Hz, CF_3), 122.0 ((q, $J=3.8\text{Hz}$, CH), 35.7 (CH), 32.8 (CH), 31.5 (CH); IR ν_{max} (KBr, cm^{-1}): 2923, 2851, 2208, 2146, 2054, 2041, 2030, 2008, 1993, 1965, 1709, 1677, 1628, 1576, 1538, 1499, 1450, 1354, 1327 (aromatic NO_2), 1134, 1091, 973, 908, 845, 813, 787, 751, 699, 644; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{F}_3\text{NO}_3$ $[\text{M}+\text{Na}]^+$ 358.0661, found 358.0668.

2-(2-Nitro-4-(trifluoromethyl)phenyl)-3-(4-nitrophenyl)cyclopropane-1-carbaldehyde

(3p, 4p and 5p): The title compound was synthesized according to general procedure B. The product was purified by column chromatography (hexane/EtOAc = 7:1), affording the title compound as a yellow oil; Diastereomeric ratios of **3p:4p:5p** = 1.5:1:1; Enantiomeric excesses of **3p:4p:5p** = 85:n.d.:79; Total yield of **3p:4p:5p** = 52% (82 mg).

(1*S*,2*R*,3*R*)-2-(2-nitro-4-(trifluoromethyl)phenyl)-3-(4-nitrophenyl)cyclopropane-1-

carbaldehyde (3p). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 75:25, flow rate = 1.0 mL/min, $\lambda = 230$ nm): $t_{\text{R}} = 20.4$ min, $t_{\text{R}} = 27.7$ min; $[\alpha]_{\text{D}}^{23} = -11.0^\circ$ (c 0.5, CHCl_3) (**R catalyst**); ^1H NMR (400 MHz, CDCl_3) $\delta = 9.61$ (d, $J = 2.2$, 1H), 8.27 – 8.21 (m, 3H), 7.87 (d, $J = 7.1$, 1H), 7.72 (d, $J = 8.1$, 1H), 7.41 (d, $J = 8.7$, 2H), 3.49 (t, $J = 8.3$, 1H), 3.38 (dd, $J = 7.2$, 5.3, 1H), 3.06 (ddd, $J = 9.2$, 5.1, 2.3,

1H); ¹³C NMR (101 MHz, CDCl₃) δ = 196.0 (CHO), 149.9 (Cq), 147.3 (Cq), 145.0 (Cq), 134.1 (Cq), 133.2 (CH), 131.5 (q, J=34.4Hz, Cq), 129.7 (q J=3.4hz, CH) q, 127.4 (CH), 124.2 (CH), 122.2 (q J=3.8Hz, CH), 121.3 (Cq), 39.0 (CH), 34.6 (CH), 31.8 (CH); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.0 ppm; IR ν_{max} (KBr, cm⁻¹): 2922, 2851, 1706, 1629, 1601, 1537 (aromatic NO₂), 1519, 1346, 1325 (aromatic NO₂), 1214, 1180, 1136, 1094, 1013, 960, 853, 746, 668; HRMS (ESI) calcd for C₁₇H₁₁F₃N₂O₅ [M+Na]⁺ 403.0512, found 403.0507.

(1R,2R,3R)-2-(2-Nitro-4-(trifluoromethyl)phenyl)-3-(4-nitrophenyl)cyclopropane-1-carbaldehyde (4p). Yellow oil; [α]_D²³ = 66.3° (c 0.2, CHCl₃) (**R catalyst**); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.0 ppm; ¹H NMR (400 MHz, CDCl₃) δ = 9.27 (d, J = 4.2, 1H), 8.29 (d, J = 1.2, 1H), 8.21 (d, J = 8.8, 2H), 7.87 (dd, J = 8.2, 1.7, 1H), 7.57 (d, J = 8.4, 2H), 7.53 (d, J = 8.1, 1H), 4.05 – 3.99 (m, 1H), 3.16 (dd, J = 9.4, 7.5, 1H), 2.75 (ddd, J = 9.6, 5.5, 4.3, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 196.0 (CHO), 150.1 (Cq), 147.4 (Cq), 141.2 (Cq), 136.6 (Cq), 131.5 (q, J=34.6Hz, Cq), 130.3 (CH), 130.1 (q, J=3.5Hz, CH), 130.0 (CH), 129.9 (CH), 123.9 (CH), 122.6 (q, J=3.8Hz, CH), 121.2 (Cq), 37.5 (CH), 34.6 (CH), 27.1 (CH); IR ν_{max} (KBr, cm⁻¹): 2922, 2851, 1706, 1629, 1601, 1537 (aromatic NO₂), 1519, 1346, 1325 (aromatic NO₂), 1214, 1180, 1136, 1094, 1013, 960, 853, 746, 668; HRMS (ESI) calcd for C₁₇H₁₁F₃N₂O₅ [M+Na]⁺ 403.0512, found 403.0503.

(1R,2S,3S)-2-(2-Nitro-4-(trifluoromethyl)phenyl)-3-(4-nitrophenyl)cyclopropane-1-carbaldehyde (5p). Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, λ = 210 nm): t_R = 24.7 min, t_R = 28.5 min; [α]_D²³ = -18.2° (c 0.5, CHCl₃) (**R catalyst**); ¹H NMR (400 MHz, CDCl₃) δ = 9.75 (d, J = 3.5, 1H), 8.08 (d, J = 1.2, 1H), 7.96 (d, J = 8.8, 2H), 7.76 (dd, J = 8.1, 1.5, 1H), 7.48 (d, J = 8.1, 1H), 6.96 (d, J = 8.7, 2H), 3.70 (dd, J = 10.2, 5.9, 1H), 3.36 (dd, J = 10.2, 5.2, 1H), 3.07 (td, J = 5.5, 3.5, 1H); ¹³C NMR (101 MHz, CDCl₃) δ = 197.0 (CHO), 150.2 (Cq), 147.1 (Cq), 141.2 (Cq), 133.3 (Cq), 132.7 (CH), 131.5 (q, J=35Hz, Cq), 129. (q, J=3.4Hz, CH), 128.4 (CH), 123.7 (CH), 122.4 (q, J=3.7Hz, CH), 121.1 (Cq), 35.7 (CH), 32.4 (CH), 32.4 (CH); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.1 ppm; IR ν_{max} (KBr, cm⁻¹): 2922, 2851, 1706, 1629, 1601, 1537 (aromatic NO₂), 1519, 1346, 1325 (aromatic NO₂), 1214, 1180, 1136, 1094, 1013, 960, 853, 746, 668; HRMS (ESI) calcd for C₁₇H₁₁F₃N₂O₅ [M+Na]⁺ 403.0512, found 403.0515.

General procedure for ring-opening of cyclopropanation product (3g):

To a suspension of thiazolium precatalyst **9** (7.9 mg, 0.033 mmol, 20 mol%) in CH₂Cl₂ (0.5

mL) was added the cyclopropanation product (**3g**; 52 mg, 0.166 mmol), MeOH (20 μ L, 0.5 mmol), and *N,N*-diisopropylethylamine (DIPEA; 11 μ L, 0.06 mmol) at room temperature. The resulting solution was stirred for 6 hours. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc = 6:1) to afford the final ester **10** (48.3 mg, 84%).

Methyl (S)-4-(2,4-dinitrophenyl)-3-phenylbutanoate (10). The title compound was synthesized according to the above-mentioned procedure. Yellow oil; The enantiomeric excess was determined by HPLC using a Chiralpak OD-H column (hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, λ = 245 nm): t_R = 26.6 min, t_R = 37.7 min; $[\alpha]_D^{23}$ = -32° (*c* 0.59, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ = 8.68 (d, *J* = 2.5, 1H), 8.19-8.16 (dd, *J* = 8.5, 2.0, 1H), 7.27-7.19 (m, 4H), 7.05-7.04 (m, 2H), 3.61 (s, 1H), 3.53-3.46 (m, 2H), 3.28-3.23 (m, 1H), 2.80-2.78 (d, *J* = 7, 2H); ¹³C NMR (125 MHz, CDCl₃) δ = 171.9, 149.6, 146.5, 141.7, 141.3, 134.1, 128.9 (2 C), 127.5, 127.5 (2 C), 126.4, 120.3, 51.9, 43.3, 40.7, 39.5; IR ν_{max} (KBr, cm⁻¹): 3708, 3322, 2977, 2946, 2884, 2851, 2363, 2339, 2323, 2059, 1737, 1605, 1539, 1350, 1160, 658; HRMS (ESI) calcd for C₁₇H₁₆N₂O₆ [M+H]⁺ 345.1081, found 345.1070.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Copies of ¹H NMR and ¹³C NMR spectra, HRMS, and HPLC chromatograms of all compounds
X-ray crystallographic file for *ent-3i*

X-ray crystallographic file for *ent-3l*.

Determination of absolute and relative configuration of products [(**3d**, **4d**, **5d**) and (**3k**, **4k**, **5k**)].

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Notes

The authors declare no competing financial interest.

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