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Asymmetric Synthesis of Multifunctionalized 2,3-Benzodiazepines by a One-pot N-Heterocyclic Carbene/Chiral Palladium Sequential Catalysis

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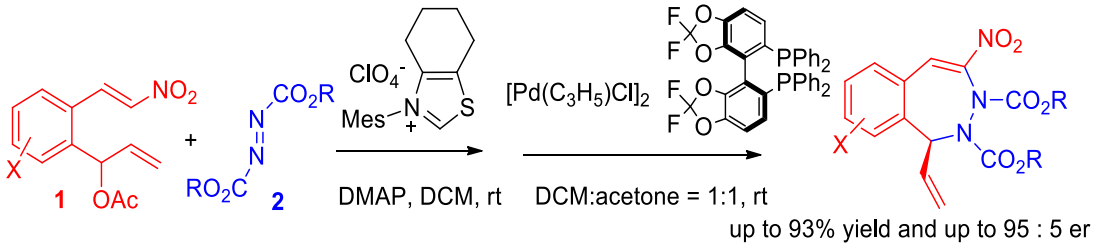


ABSTRACT:

We report the first example of the construction of chiral 2,3-benzodiazepine compounds which are of biologic and pharmaceutical relevance by asymmetric catalysis. Catalyzed by a thiazolium derived carbene and a palladium-chiral bidentate phosphine complex in sequence, one-pot reaction between 1-(2-(2-nitrovinyl)aryl)allyl esters **1** with azodicarboxylates **2** took place efficiently at ambient temperature to produce 4-nitro-1-vinyl-1*H*-2,3-benzodiazepine-2,3-dicarboxylates **5** in good to excellent yields with an enantiomeric ratio up to 95 : 5.

INTRODUCTION

2,3-Benzodiazepine and hydrogenated 2,3-benzodiazepines constitute the core

skeletons of a large number of biological active compounds. For example, a number of 7,8-methylenedioxy-2,3-benzodiazepine derivatives **A-E** including dihydrobenzodiazepines and dihydrobenzodiazepinones have been demonstrated to be noncompetitive AMPA receptor antagonists,[1] with compound **A** (LY 300164, Talampanel) being clinically studied as an anticonvulsant agent.[2] On the other hand, a series of 1-aryl-4,5-dihydro-2,3-benzodiazepines **F** were prepared as bromodomain inhibitors (BET protein-inhibiting and BRD4-inhibiting) useful in the pharmaceutical agents for hyperproliferative diseases and tumor diseases.[3] In addition, various synthetic 5-acylamino-2,3-benzodiazepin-4-ones **G** and 5-acylamino-2,3-benzodiazepin-1,4-diones **H** have shown inhibition to β-amyloidogenic peptide (β-AP) production and have potential application in the treatment of Alzheimer's Disease.[4]

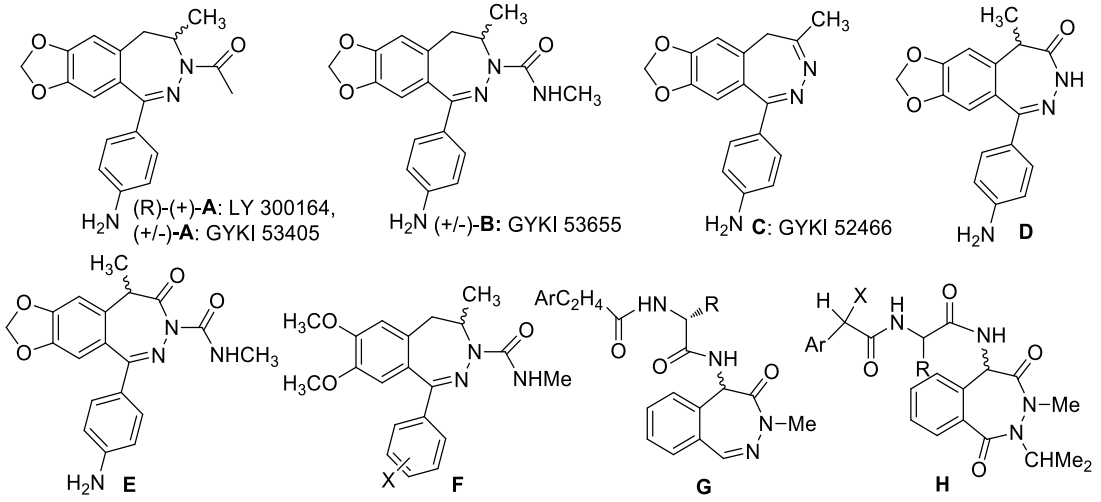


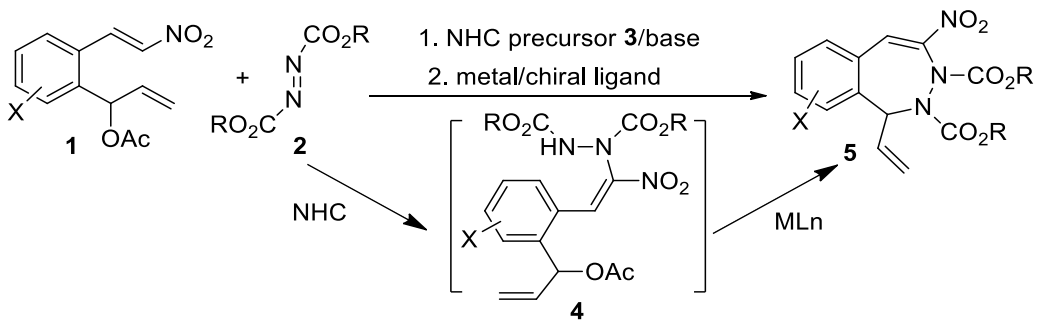
Figure 1. Biological active 2,3-benzodiazepine derivatives.

Due to their broad and powerful pharmacologic activities, the syntheses of 2,3-benzodiazepine derivatives have attracted continuous interests from both organic and medicinal chemists. One of the most frequently used strategies to synthesize 2,3-

benzodiazepine, dihydro- and tetrahydro-2,3-benzodiazepine, 2,3-benzodiazepin-4-one and 2,3-benzodiazepin-1,4-dione compounds is to construct the 2,3-benzodiazepine ring by means of the condensation reaction between a hydrazine or substituted hydrazines with the carbonyl compound including 1-(*o*-acyl)aryl-2-ketones,[3a, 5] 2-(*o*-acyl)arylacetic acids and esters,[1c,4b] and 2-(*o*-carboxy)arylacetic acid anhydride.[4a] Other methods such as the Rh-catalyzed coupling reaction between *N*-boc hydrazones and diazoketoesters followed by intramolecular condensation,[6] the ring expansion reaction of tetrahydrodiazirino[3,1-a]isoquinoline with sulfonyl chlorides,[7] and the reaction of hydrazine with 2-benzopyrylium or 2-benzoselenopyrylium salts[8] have also been reported. Although most of the bioactive 2,3-benzodiazepine derivatives contain a stereogenic center, and different enantiomers have considerably different bioactivities on the physiologic system,[1b-1d] surprisingly, the asymmetric synthesis of chiral 2,3-benzodiazepine derivatives remains largely unexplored. Enantiomerically pure 3,5-dihydro- and 1,2,3,5-tetrahydro-2,3-benzodiazepin-4-ones were obtained by the resolution of racemates using chiral HPLC.[1b-1d] Enantioselective synthesis of 3,5-dihydro-2,3-benzodiazepines was reported once by asymmetric reduction of a C=N bond of 2,3-benzodiazepines.[9] The other examples involved the synthesis of chiral 2,3-benzodiazepines used optically active 1-arylpropan-2-ols as reactants which were prepared from the asymmetric reduction of 1-arylpropan-2-ones.[10] To the best of our knowledge, the asymmetric synthesis of dihydro- and tetrahydro-2,3-benzodiazepines by chiral catalysis has not been reported so far. The development of efficient and

enantioselective reactions for the synthesis of highly enantiomercally pure 2,3-benzodiazepine compounds is therefore of great importance.

We have been interested in developing new synthetic methods by means of N-heterocyclic carbene (NHC) and transition metal cascade catalysis for many years. Recently, we reported novel and efficient NHC/Pd cascade catalytic method for the synthesis of 2,2-disubstituted benzofuran-3-ones[11a] and NHC/Cu(II) cascade catalytic method for the synthesis of 2-amido-3-benzylidene-1-indanones.[11b] In 2013, Ye and co-workers reported a NHC-catalyzed Morita–Baylis–Hillman (MBH) reaction of β-arylnitroalkenes with azodicarboxylates, which produced 1-(2-aryl-1-nitrovinyl)hydrazine-1,2-dicarboxylates in excellent yields.[12] We envisioned that the NHC-catalyzed reaction of 1-(2-(2-nitrovinyl)aryl)allyl esters **1** with azodicarboxylates **2** followed by the transition metal-catalyzed intramolecular *N*-allylation would provide a new route to 1*H*-2,3-benzodiazepine derivatives (Scheme 1). Herein we report the first asymmetrical synthesis of multifunctionalized 1*H*-2,3-benzodiazepines by a catalytic cascade reaction.



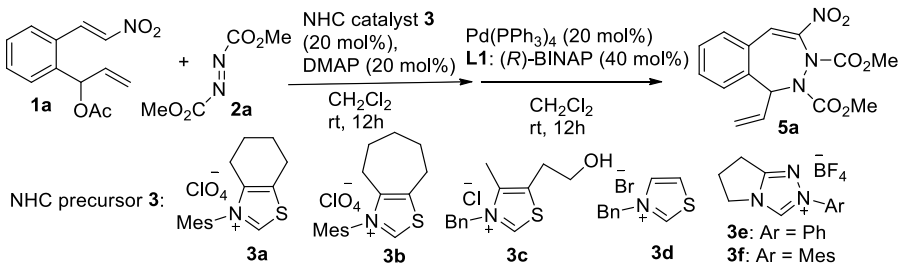
Scheme 1. Strategy for NHC/Transition Metal Catalyzed Construction of Substituted 2,3-Benzodiazepines.

RESULTS AND DISCUSSION

We commenced our study with the investigation of the reaction of (*E*)-1-(2-(2-nitrovinyl)phenyl)allyl acetate **1a** with dimethyl azodicarboxylate **2a** in the presence of an NHC and a palladium catalyst. Initially, a mixture of substrates **1a** and **2a**, thiazolium salt **3a** as the NHC precursor, DMAP as a base, $Pd(PPh_3)_4$ and BINAP was stirred in dichloromethane for 24h. Disappointedly, however, only compound **4a** that was derived from the NHC-catalyzed reaction of **1a** with **2a** was observed. Obviously, the palladium catalyst did not participate in the reaction under the conditions examined**.** We then attempted the cascade reaction of nitroalkene **1a** with azodicarboxylate **2a** by means of one-pot sequential catalysis. Thus, a mixture of substrates **1a** and **2a** (**1a** : **2a** = 1 : 1.8), the NHC precursor **3** (20 mol %) and DMAP (20 mol %) in dry solvent was first stirred for 12 h at room temperature. The palladium catalyst and ligand were then added, and the resulting mixture was kept stirring for another 12 h. This sequential catalytic method enabled the formation of desired 4-nitro-1-vinyl-1*H*-2,3-benzodiazepine-2,3-dicarboxylate **5a**. To established an efficient and highly enantioselective synthesis of **5a**, the reaction conditions were then optimized by varying NHCs, palladium catalysts, ligands, solvents and temperature. To trigger the addition of nitroalkene **1a** to azodicarboxylate **2a** and to examine the compatibility of N-heterocyclic carbenes with palladium catalyst, we first surveyed a series of heterocyclic azolium salts such as thiazolium salts **3a-3d**, triazolium salts **3e** and **3f** as NHC precatalysts. As illustrated in Table 1, under the conditions using $Pd(PPh_3)_4$/(*R*)-BINAP as a chiral transition metal catalyst, the reaction of **1a** with **2a** proceeded smoothly at room temperature in DCM to afford **5a** in 35-83% yields when a thiazole or a triazole carbene was used (entries 1-

6). Clearly, the reaction promoted by the triazole carbene **3a'** followed by $Pd(PPh_3)_4$/(*R*)-BINAP catalysis gave the highest chemical yield of **5a** (83%) albeit with low enantioselectivity (63:37 er) (Table 1, entry 1). On the contrary, the combination of triazole carbene **3c'** with $Pd(PPh_3)_4$/BINAP led to the formation of product **5a** in a low yield (41%) but with the highest enantioselectivity (85:15 er) (Table 1, entry 3).

Table 1. Screening of NHC Catalysts.



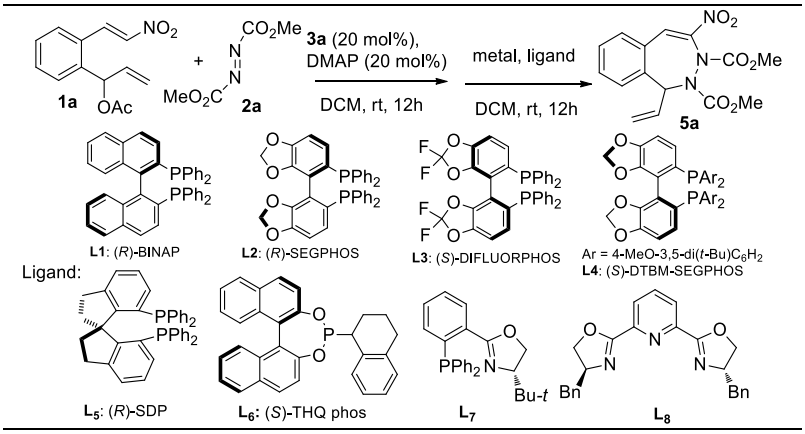
Entry	NHC catalyst	Yield of **5a** (%)[a]	er of **5a**[b]	Entry	NHC catalyst	Yield of **5a** (%)[a]	er of **5a**[b]
1	**3a**	83	63:37	4	**3d**	74	68:32
2	**3b**	57	66:34	5	**3e**	58	57:43
3	**3c**	41	85:15	6	**3f**	35	65:35

[a]Isolated yields. [b]Determined by chiral HPLC.

Since the stereogenic center is generated in the second transition metal catalyzed *N*-allylation step, we set to optimize the chiral palladium catalysts with the use of thiazolium salt **3a** as an NHC precatalyst. As summarized in Table 2, while using (*R*)-BINAP as the chiral ligand, the replacement of $Pd(PPh_3)_4$ with $Pd_2(dba)_3CHCl_3$, $Pd_2(dba)_3$ and $[Pd(C_3H_5)Cl]_2$ improved the enantioselectivity, albeit the chemical yield were decreased slightly (entries 1-3). It was notable that $Pd(TFA)_2$ was inactive in this reaction. The reducing of the loading of $[Pd(C_3H_5)Cl]_2$ from 20 mol% to 15 mol% and 10 mol% led to the drastic decrease of both the yield and er value of product (entries 5 and 6). Since $[Pd(C_3H_5)Cl]_2$/BINAP gave higher enantioselectivity than $Pd(PPh_3)_4$/BINAP with comparable chemical yields, the reaction was further optimized

by varying the ligands with $[Pd(C_3H_5)Cl]_2$ as palladium source. It was found that, among the chiral bidentate phosphine ligands **L1-L5,** the (*S*)-DIFLUORPHOS (**L3**) stood out as the best chiral ligand, which resulted in the formation of **5a** in 80% yield and 87:13 er (Table 2, entry 8). The use of (*R*)-SEGPHOS (**L2**) as a ligand gave product **5a** in 57% yield with 85:15 er (entry 7). On the contrary, the sterically bulky ligand (*S*)-DTBM-SEGPHOS (**L4**) and 1,1'-spirobiindane ligand (*R*)-SDP (**L5**) appeared as less efficient and enantioselective (entries 9 and 10). It should be noted that the unidentate phosphine ligand (*S*)-THQ phos (**L6**) led to the formation of high yield of product but displayed no enantiocontrol at all, and the N, P-ligand (**L7**) and N, N-ligand (**L8**) were entirely ineffective ligands (entries 11-13).

Table 2. Screening of Palladium Catalysts and Chiral Ligands.



Entry	Metal (mol %)	Ligand (mol %)	Yield of **5a** (%)[a]	er of **5a**[b]
1	$Pd_2(dba)_3CHCl_3$ (20)	**L1** (40)	67	70:30
2	$Pd_2(dba)_3$ (20)	**L1** (40)	70	75:25
3	$[Pd(C_3H_5)Cl]_2$ (20)	**L1** (40)	76	79:21
4	$Pd(TFA)_2$ (20)	**L1** (40)	–	
5	$[Pd(C_3H_5)Cl]_2$ (15)	**L1** (30)	45	71:29
6	$[Pd(C_3H_5)Cl]_2$ (10)	**L1** (20)	37	76:24
7	$[Pd(C_3H_5)Cl]_2$ (20)	**L2** (40)	57	85:15
8	**$[Pd(C_3H_5)Cl]_2$ (20)**	**L3 (40)**	**80**	**87:13**
9	$[Pd(C_3H_5)Cl]_2$ (20)	**L4** (40)	30	76:24
10	$[Pd(C_3H_5)Cl]_2$ (20)	**L5** (40)	37	58:42

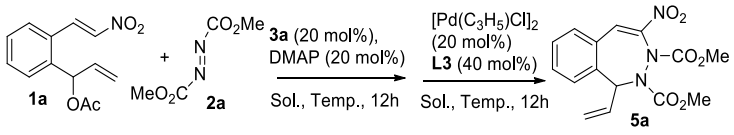
11	$[Pd(C_3H_5)Cl]_2$ (20)	**L6** (80)	78	50:50
12	$[Pd(C_3H_5)Cl]_2$ (20)	**L7** (40)	–	
13	$[Pd(C_3H_5)Cl]_2$ (20)	**L8** (40)	–	

[a]Isolated yields. [b]Determined by chiral HPLC.

With thiazole **3a'** and $[Pd(C_3H_5)Cl]_2$/(*S*)-DIFLUORPHOS (**L3**) as NHC and the chiral palladium catalyst, respectively, the solvent effect was studied (Table 3). Under the otherwise identical conditions, the reactions in dichloroethane, acetonitrile, acetone THF and toluene gave similar enantioselectivity as that in dichloromethane but with lower yields (Table 3, entries 1-5). Other solvents such as chloroform and 1,4-dioxane led to both lower yields and lower enantioselectivity (entries 6, 7). To improve enantioselectivity, different solvents were used in NHC- and palladium-catalyzed reaction steps. For example, DCM was employed as the solvent for the reaction of **1a** with **2a** catalyzed by thiazolium salt **3a**/DMAP. After the NHC-catalyzed reaction, the $[Pd(C_3H_5)Cl]_2$/DIFLUORPHOS (**L3**) complex and another solvent including acetonitrile, acetone and THF were added to the reaction mixture. It was found that, although the use of a mixture of solvents did not significantly improve the enantioselectivity, the chemical yield of **5a** was increased dramatically to 90% with er value remaining as 88:12 when the second step was conducted in DCM/acetone (1:1) (entries 8-10). Finally, the examination of the influence of temperature on the reaction indicated either a higher (60 ^{o} C) or a lower temperature (0 ^{o}C) greatly decreased the chemical yield of product, although the enantioselectivity was only slightly affected (entries 11 and 12). Thus, the sequential catalytic reaction conducted using thiazolium **3a** (20 mol%)/DMAP (20 mol%.) in DCM followed by $[Pd(C_3H_5)Cl]_2$ (20 mol%)/(*S*)-DIFLUORPHOS (**L3**, 40 mol%) in a mixture of DCM and acetone (1:1) at room

temperature appeared optimal for the asymmetric synthesis of 1*H*-2,3-benzodiazepine derivative **5** from the 1-(2-(2-nitrovinyl)phenyl)allyl acetate **1** with azodicarboxylate **2**.

Table 3. Optimization of Reaction Solvent and Temperature.



Entry	Solvent	Temp. (°C)	Yield of **5a** (%)	er of **5a**
1	DCE	rt	70	84:16
2	CH_3CN	rt	73	86:14
3	acetone	rt	61	87:13
4	THF	rt	51	87:13
5	toluene	rt	27	85:15
6	$CHCl_3$	rt	58	77:23
7	1,4-dioxane	rt	39	79:21
8	DCM/(DCM and CH_3CN, 1:1)[a]	rt	70	89:11
9	DCM/(DCM and acetone, 1:1)[a]	**rt**	**90**	**88:12**
10	DCM/(DCM and THF, 1:1)[a]	rt	78	86:14
11	DCM/(DCM and acetone, 1:1)[a]	rt /0 °C[b]	60	88:12
12	DCM/(DCM and acetone, 1:1)[a]	rt /60 °C[b]	67	85:15

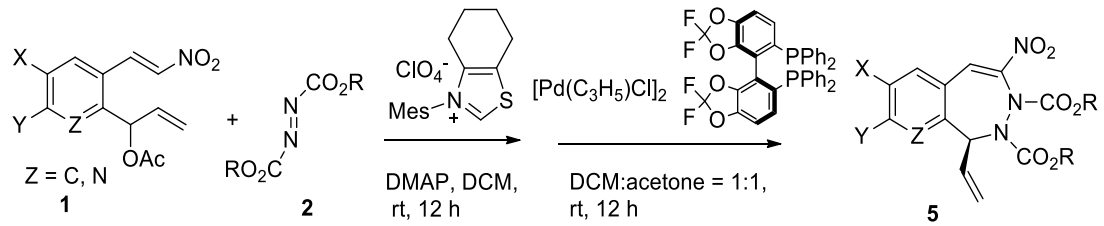
[a]In these reactions, the NHC-catalyzed reaction was carried out in DCM, followed by the addition of Pd catalyst and another solvent. [b]The NHC- and Pd-catalyzed reactions were performed at different temperature.

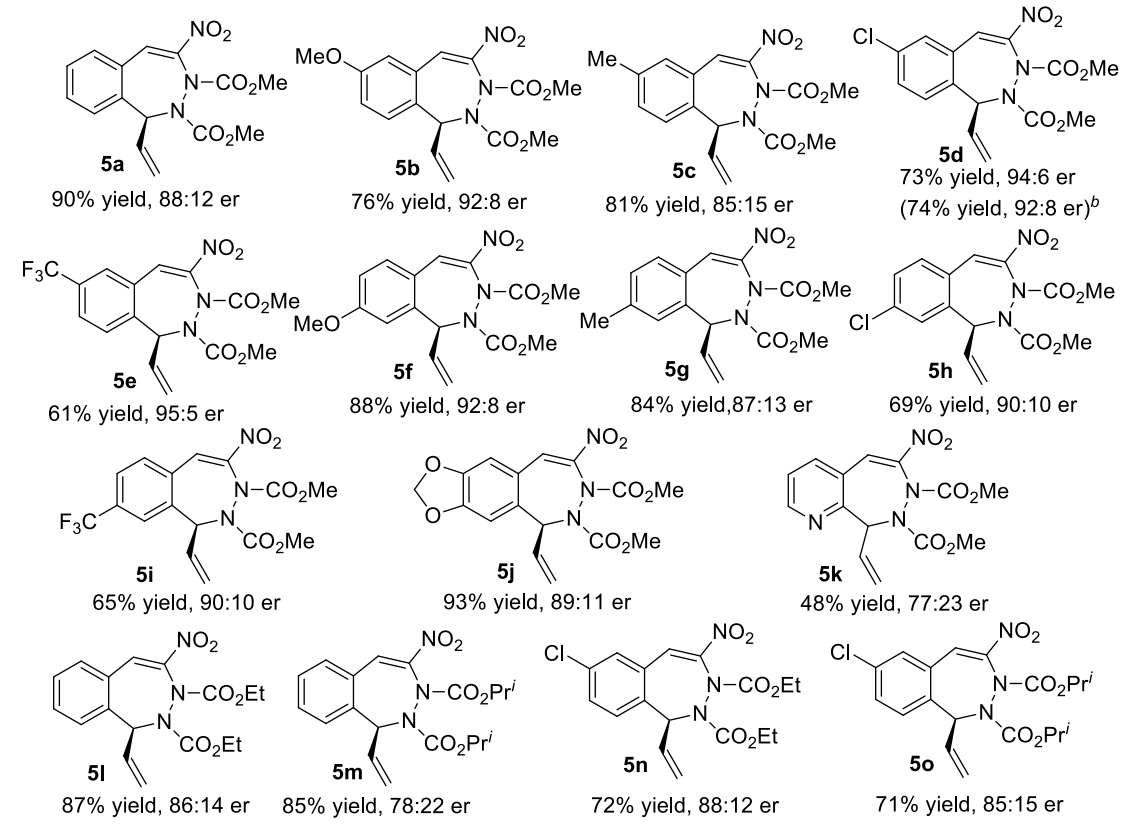
With the optimized conditions established, we examined the substrate scope for the synthesis of 4-nitro-1-vinyl-1*H*-2,3-benzodiazepine-2,3-dicarboxylates **5** by employing various 1-(2-(2-nitrovinyl)phenyl)allyl acetates **1** and azodicarboxylates **2**. Under nitrogen atmosphere and at room temperature, the mixture of allyl acetates **1** (0.2 mmol), NHC catalyst **3a** (20 mol%), DMAP (20 mol%) and azodicarboxylates **2** (0.36 mmol) in DCM was stirred for 12h. Then the chiral palladium catalyst prepared from

$[Pd(C_3H_5)Cl]_2$ (20 mol%) and (*S*)-DIFLUORPHOS (40 mol%) in DCM was added to the reaction mixture, followed by the addition of another solvent acetone in a glove box. The mixture was stirred for another 12 h at room temperature. Pleasingly, as compiled in Table 4, the sequential catalytic reaction was found to tolerate both electron-donating and electron-withdrawing groups on the substrates **1**. The electronic nature and substitution pattern of substituents attached to the benzene ring of **1** have marginal influence on the reaction efficiency and enantioselectivity. For example, 1-(2-(2-nitrovinyl)phenyl)allyl acetates **1b-1e** bearing an electron-donating methoxy and methyl, or an electron-withdrawing chloro and trifluoromethyl on the *para*-position of allyl acetate underwent efficient reaction with dimethyl azodicarboxylate **2a**, affording the corresponding products **5b-5e** in 61-81% yields with 85:15-95:5% er. On the other hand, the substrates **1f-1i** substituted by an MeO, Me, Cl or CF_3 group on the *meta*-position of allyl acetate reacted with **2a** to produce products **5f-5i** in 65-88% yields with 87:13-92:8 er. The [1,3]dioxolo[4',5':4,5]benzo[1,2-*d*][1,2]diazepine product **5j** that resembled the key structure of many bioactive 2,3-benzodiazepine derivatives has also been prepared in 93% yield with 89:11 er from the reaction of 1-(6-(2-nitrovinyl)benzo[*d*][1,3]dioxol-5-yl)allyl acetate **1j** with **2a**. In addition to the 1-(2-(2-nitrovinyl)phenyl)allyl acetates **1b-1j**, heterocyclic aryl substituted allyl acetate analogues were also included in the study. 1-(3-(2-Nitrovinyl)pyridinyl)allyl acetate and 1-(3-(2-nitrovinyl)thiophenyl)allyl acetate were prepared readily using the similar procedures for the synthesis of 1-(2-(2-nitrovinyl)phenyl)allyl acetates. However, the 1-(3-(2-nitrovinyl)furanyl)allyl acetate was not obtained, because furanyl carbaldehyde

substrate was unstable under the reaction conditions. It was found that, the reaction of 1-(3-(2-nitrovinyl)pyridin-2-yl)allyl acetate **1k** with **2a** proceeded equally well to give the 7*H*-2,3-pyrido[2,3-*d*]diazepine-7,8-dicarboxylate **5k** in a moderated yield and enantioselectivity (48% yield, 77:23 er). Unfortunately, no expected thieno[2,3-*d*]diazepine product was observed from the reaction of 1-(3-(2-nitrovinyl)thiophen-2-yl)allyl acetate with **2a**. This is most probably due to the fact that the product derived from the first step of NHC-catalyzed reaction did not undergo the palladium-catalyzed intramolecular cyclization because of the poisoning effect of thiophene imposed on palladium catalyst. Other azodicarboxylateas **2** were also accepted as the substrates in the synthesis of 1*H*-2,3-benzodiazepine-2,3-dicarboxylates **5**. For instance, under the identical catalytic conditions, diethyl and diisopropyl azodicarboxylate **2b** and **2c** reacted analogously with **1a** and **1d** to furnish products **5l-5o** in comparable yields. The enantioselectivity decreased slightly, probably owing to the increase of steric hindrance of alkyl group from methyl to ethyl and isopropyl. Finally, the reaction of **1d** with **2a** was repeated in 1 mmol scale, which provided product **5d** in 74% yield with 92:8 er.

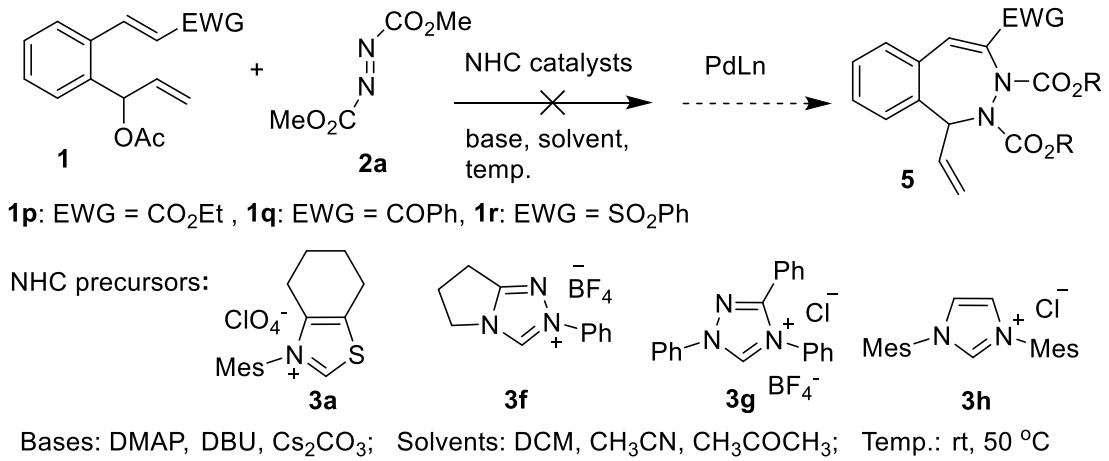
Table 4. Scope of the NHC and $[Pd(C_3H_5)Cl]_2$/DIFLUORPHOS Sequentially Catalyzed Reaction of 1-(*o*-(2-Nitrovinyl)aryl)allyl Acetates **1** with Azodicarboxylateas **2**.[a]





[a] Reaction conditions: allyl acetates **1** (0.2 mmol), NHC catalyst **3a** (20 mol%), DMAP (20 mol%) and azodicarboxylates **2** (0.36 mmol) in DCM (0.5 mL) reacted at RT for 12h. Then chiral palladium catalyst prepared from $[Pd(C_3H_5)Cl]_2$ (20 mol%) and (*S*)-DIFLUORPHOS (40 mol%) in DCM (0.75 mL) and acetone (1.25 mL) were added, and the reaction mixture was stirred for another 12 h at RT. [b]The yield and er value in the parenthesis were obtained from the reaction of **1d** (1 mmol) with **2a** (1.8 mmol).

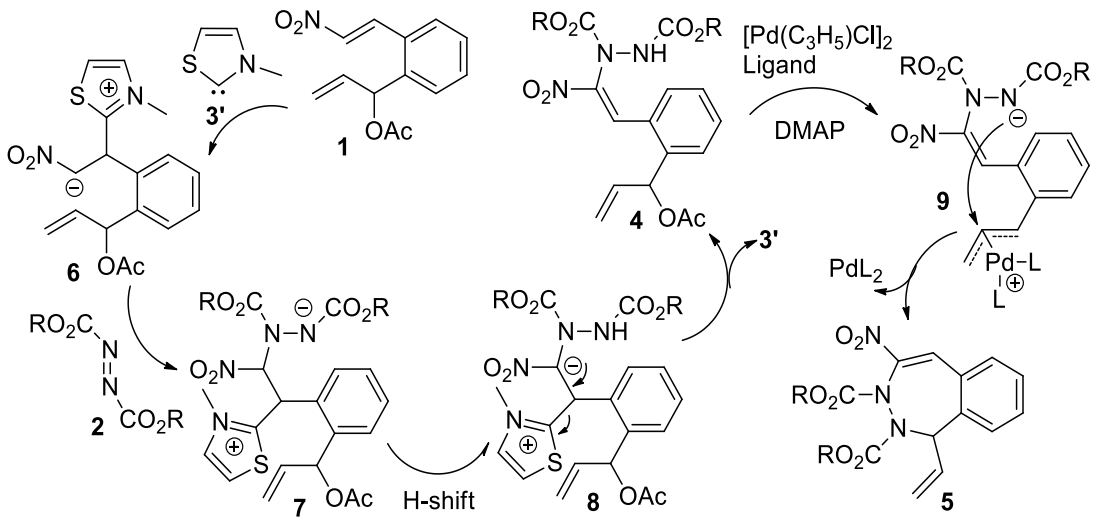
To extend the substrate scope for the synthesis of multifunctionalized 1*H*-2,3-benzodiazepines, we also prepared *o*-allyl ester substituted cinnamate **1p**, chalcone **1q** and sulfonyl styrene **1r** as reactants. The first step of the sequential reaction between electron-deficient styrenes **1p-1r** and azodicarboxylate **2a** was examined in the presence of various N-heterocyclic carbene catalysts. Unfortunately, however, the NHC examined did not triggered the reaction between these electron-deficient styrenes and azodicarboxylate under different conditions (Scheme 2).



Scheme 2. The study on the reactions of *o*-allyl ester substituted sulfonyl styrene, -chalcone and -cinnamate with azodicarboxylate in the presence of N-heterocyclic carbenes.

The structures of products **5** were elucidated on the basis of spectroscopic data and X-ray diffraction analysis. The presence of different conformers led to complicated ^{1}H NMR spectra of **5** at room temperature. Upon heat to 70 °C, due to the rapid interconversion between conformers in relative to ^{1}H NMR time scale, a single set of proton signals was observed. Therefore, all NMR spectra of **5** were recorded at 70 °C in DMSO-d$_6$. X-ray crystallographic analysis of **5d** allowed us to unequivocally confirm the *S*-configuration of stereocenter (See Figure S1 in Supporting Information). The mechanism for the formation of 1*H*-2,3-benzodiazepine derivatives **5** from 1-(2-(2-nitrovinyl)phenyl)allyl acetates **1** and azodicarboxylates **2** was proposed in Scheme 3. The nucleophilic addition of the NHC catalyst to the nitrovinyl group of substrates **1** initiates the first reaction**.** The resulting anion intermediate **6** undergoes nucleophilic addition to azo bond of **2** to form a hydrazine anion **7.** Proton transfer and removal of NHC catalyst result in the formation of intermediates **4.** In the presence of a palladium catalyst, the palladium π-allylic complex is generated,[13] and it undergoes intramolecular reaction with the amide moiety derived from deprotonation of the

hydrazine group of **4** with DMAP to produce the final 2,3-benzodiazepine products **5**.



Scheme 3. Proposed Mechanism for the Formation of 1*H*-2,3-Benzodiazepine Derivatives **5** from the Reaction between 1-(2-(2-Nitrovinyl)phenyl)allyl Acetates **1** and Azodicarboxylates **2.**

Conclusion

In summary, we have developed a novel NHC/Pd sequentially catalytic method for the asymmetric synthesis of multifunctionalized 1*H*-2,3-benzodiazepine derivatives from the reaction of 1-(2-(2-nitrovinyl)phenyl)allyl acetates and azodicarboxylates. Under the catalysis of a thiazole carbene followed by the chiral $[Pd(C_3H_5)Cl]_2$/DIFLUORPHOS catalyst, 1-(2-(2-nitrovinyl)phenyl)allyl acetates and azodicarboxylates undergo a cascade nucleophilic addition and intramolecular N-allylation reaction to produce 4-nitro-1-vinyl-1*H*-2,3-benzodiazepine-2,3-dicarboxylates in good to excellent yields with er up to 95:5. This work represents the first example of catalytic asymmetric construction of 2,3-benzodiazepine core structure, which occurs widely in a large number of biological active compounds.

Experimental Section

1. Preparation of reactants.

(1). Preparation of 1-(*o*-formylaryl)allyl acetates.

A typical experimental procedure for the synthesis of 1-(2-formylphenyl)allyl acetate.[14]

A mixture of 2-bromobenzaldehyde **Ia** (1.85 g, 10 mmol), triethyl orthoformate (2.96 g, 20 mmol) and $TsOH \cdot H_2O$ (38 mg, 0.2 mmol) in anhydrous ethanol (20 mL) was refluxed for 6 h in an oil bath. After removal of the solvent, the residue was chromatographed on a neutral Al_2O_3 column eluting with a mixture of petroleum ether and ethyl acetate (PE : EA = 30 : 1) to give product as a colorless oil. After drying overnight under vacuum, 1-bromo-2-(diethoxymethyl)benzene **IIa** was obtained in 95% yield (2.46 g).

The resulting acetal **IIa** (2.46 g, 9.5 mmol) was dissolved in anhydrous THF (20 mL), and *n*-BuLi (2.5 M in hexane, 4.4 mL, 10.5 mmol) was added dropwise at -78 ˚C under nitrogen atmosphere. After stirring for 30 min at -78 ˚C, anhydrous DMF (1.7g, 23 mmol) was added dropwise to the solution. The resulting mixture was kept stirring at -78 ˚C for another 30 min and then at room temperature for 1 h. The reaction was then quenched by adding a saturated aqueous solution of NH_4Cl (20 mL). The resulting mixture was extracted with ethyl acetate (20 × 3 mL). The combined organic layer was dried over anhydrous $MgSO_4$. After filtration and removal of solvents, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE : EA = 10 : 1) to give the product as a pale yellow oil. 2-(Diethoxymethyl)benzaldehyde **IIIa** was obtained in 92 % yield (1.8 g) after drying overnight under vacuum.

Under nitrogen protection and at 0 °C, to a solution of 2-(diethoxymethyl)benzaldehyde **IIIa** (1.8 g, 8.7 mmol) in anhydrous THF (20 mL) was added dropwise vinylmagnesium bromide (1 M in THF, 13 mL, 13 mmol). The reaction mixture was stirred at 0 ˚C for 12 h. After the reaction was quenched by the addition of water (20 mL), the mixture was extracted with ethyl acetate (20 × 3 mL). The combined organic layer was dried over anhydrous $MgSO_4$. After filtration and removal of solvents, the residue was dissolved in acetic anhydride (3.56 g, 34.8 mmol) and pyridine (2.75 g, 34.8 mmol). The resulting mixture was stirred overnight at ambient temperature. Water (10 mL) was added, and the resulting mixture was extracted with ethyl acetate (20 × 3 mL) and the combined organic layer was washed with water (30 mL) and was dried over anhydrous $MgSO_4$. After filtration and removal of solvents, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE : EA = 10 : 1) to give 1-(2-(diethoxymethyl)phenyl)allyl acetate **IVa** as pale yellow oil (2 g, 84 %). The obtained acetal **IVa** was then hydrolyzed with aqueous hydrochloric acid (3 mol/L, 12 mL, 36 mmol) in THF (50 mL) for 4 h at room temperature. The reaction was terminated by the addition of 30 mL of water and the resulting mixture was extracted with ethyl acetate (10 × 3 mL). The combined organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (30 mL) and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE : EA = 8 : 1) to give 1-(2-formylphenyl)allyl acetate **Va** as a pale yellow oil (1.26 g, 85%).

1-(2-Formylphenyl)allyl acetate Va[14]: pale yellow oil; IR *v* (cm^{-1}) 1746, 1697; ^1H

NMR (400 MHz, $CDCl_3$) δ (ppm) 10.3 (s, 1H), 7.86 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.55-7.57 (m, 2H), 7.48 (td, *J* = 7.6, 1.6 Hz, 1H), 7.03 (dt, *J* = 5.2, 1.2 Hz, 1H), 6.03-6.12 (m, 1H), 5.23 (dt, *J* = 9.6, 1.6 Hz, 1H), 5.22 (dt, *J* = 18.8, 1.6 Hz, 1H), 2.11 (s, 3H).

1-(2-Formylaryl)allyl acetates **Vb-Vk** were synthesized from the substituted 2-bromo aromatic aldehydes **I** using the similar procedures as that for **Va.** The only difference in the preparation of different 1-(2-formylaryl)allyl acetates was that the hydrolysis of 1-(2-(diethoxymethyl)phenyl)allyl acetates **IVa-IVi** (6.1-8.3 mmol) was performed with aqueous hydrochloric acid (3 mol/L, 12 mL, 36 mmol) for 4 h in THF (50 mL) at room temperature, while as the hydrolysis of 1-(6-(diethoxymethyl)benzo[*d*][1,3]dioxol-5-yl)allyl acetate **IVj** (8.5 mmol) and 1-(3-(diethoxymethyl)pyridin-2-yl)allyl acetate **IVk** (7.7 mmol) was conducted with $TsOH{\cdot}H_2O$ (10 mol%) for 3 h in the mixture of THF (50 mL) and H_2O (10 mL) at the refluxing temperature. The reaction scheme for the preparation of 1-(2-formylaryl)allyl acetates **V**, and the chemical yields of all intermediates **II**, **III**, **IV** and products **V** were summarized in Table S1 in Supporting Information.

1-(2-Formyl-4-methoxyphenyl)allyl acetate Vb: pale yellow oil; IR *ν* (cm^{-1}) 1740, 1695; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.3 (s, 1H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.38 (d, *J* = 1.2 Hz, 1H), 7.11 (dd, *J* = 9, 3.6 Hz, 1H), 6.89 (d, *J* = 4.2 Hz, 1H), 6.05-6.10 (m, 1H), 5.24 (d, *J* = 11.4 Hz, 1H), 5.18 (d, *J* = 17.4 Hz, 1H), 3.85 (s, 3H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm) 191.5, 169.7, 159.7, 136.7, 134.8, 133.1, 130.0, 120.4, 117.2, 114.7, 72.4, 55.6, 21.2; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{13}H_{14}O_4Na$: 257.0784, found: 257.0780.

1-(2-Formyl-4-methylphenyl)allyl acetate Vc: pale yellow oil; IR *v* (cm^{-1}) 1746, 1695; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.26 (s, 1H), 7.67 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 5.2 Hz, 1H), 6.02-6.11 (m, 1H), 5.22 (d, *J* = 10.8 Hz, 1H), 5.19 (d, *J* = 16.8 Hz, 1H), 2.41 (s, 3H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 192.3, 169.7, 138.5, 138.1, 136.5, 134.8, 133.3, 132.5, 128.0, 117.1, 72.4, 21.2, 20.9; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{13}H_{14}O_3Na$: 241.0843, found: 241.0838.

1-(4-Chloro-2-formylphenyl)allyl acetate Vd: pale yellow oil; IR *v* (cm^{-1}) 1744, 1695; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.25 (s, 1H), 7.83 (d, *J* = 2.4 Hz, 1H), 7.55 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 5.2 Hz, 1H), 6.01-6.09 (m, 1H), 5.26 (d, *J* = 10.8 Hz, 1H), 5.21 (d, *J* = 17.6 Hz, 1H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 190.5, 169.6, 139.3, 135.9, 134.8, 134.7, 133.9, 131.2, 129.7, 117.8, 72.0, 21.1; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{12}H_{11}ClO_3Na$: 261.0288, found: 261.0291.

1-(2-Formyl-4-(trifluoromethyl)phenyl)allyl acetate Ve: pale yellow oil; IR *v* (cm^{-1}) 1748, 1701; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.3 (s, 1H), 8.12 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 5.4 Hz, 1H), 6.03-6.09 (m, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 5.24 (d, *J* = 17.4 Hz, 1H), 2.12 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 190.6, 169.6, 144.7, 135.5, 133.7, 131.0 (q, *J* = 33.5 Hz), 130.4 (d, *J* = 3.8 Hz), 128.6, 123.4 (q, *J* = 271.2 Hz), 118.2, 72.0, 21.0. HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{13}H_{11}F_3O_3Na$: 295.0552, found: 295.0551.

1-(2-Formyl-5-methoxyphenyl)allyl acetate Vf: pale yellow oil; IR *v* (cm^{-1}) 1736,

1686; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.10 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 4.8 Hz, 1H), 7.05 (d, *J* = 3.0 Hz, 1H), 6.93 (dd, *J* = 7.8, 2.4 Hz, 1H), 6.02-6.07 (m, 1H), 5.24 (d, *J* = 18.6 Hz, 1H), 5.21 (d, *J* = 11.4 Hz, 1H), 3.88 (s, 3H), 2.12 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ (ppm) 190.7, 169.6, 164.1, 143.6, 136.0, 135.5, 126.8, 117.3, 113.6, 112.7, 72.1, 55.7, 21.2; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{13}H_{14}O_4Na$: 257.0784, found: 257.0782.

1-(2-Formyl-5-methylphenyl)allyl acetate Vg: pale yellow oil; IR *v* (cm^{-1}) 1740, 1695; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.2 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.34 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.01 (dt, *J* = 5.2, 1.6 Hz, 1H), 6.02-6.10 (m, 1H), 5.20-5.24 (m, 2H), 2.42 (s, 3H), 2.12 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 191.9, 169.7, 145.2, 140.9, 136.3, 132.6, 131.1, 129.2, 128.4, 117.1, 72.5, 21.9, 21.2; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{13}H_{14}O_3Na$: 241.0835, found: 241.0831.

1-(5-Chloro-2-formylphenyl)allyl acetate Vh: pale yellow oil; IR *v* (cm^{-1}) 1744, 1697; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.22 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.54 (s, 1H), 7.45 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.01 (d, *J* = 6.0 Hz, 1H), 6.0-6.06 (m, 1H), 5.25 (d, *J* = 7.8 Hz, 1H), 5.24 (d, *J* = 16.8 Hz, 1H), 2.13 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 190.8, 169.6, 142.9, 140.6, 135.6, 133.7, 131.6, 128.7, 127.9, 117.8, 71.6, 21.1; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{12}H_{11}ClO_3Na$: 261.0288, found: 261.0290.

1-(2-Formyl-5-(trifluoromethyl)phenyl)allyl acetate Vi: pale yellow oil; IR *v* (cm^{-1}) 1746, 1703; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.35 (s, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.81 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 4.4 Hz, 1H), 6.02-6.10 (m, 1H),

5.29 (d, J = 10.8 Hz, 1H), 5.25 (d, J = 18.4 Hz, 1H), 2.13 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm) 190.9, 169.6, 142.0, 135.8, 135.5, 135.3 (q, J = 33 Hz), 132.2, 125.4, 124.9, 123.3 (q, J = 271.5 Hz), 118.2, 71.8, 21.1; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{13}H_{11}F_3O_3Na$: 295.0552, found: 295.0556.

1-(6-Formylbenzo[*d*][1,3]dioxol-5-yl)allyl acetate Vj: pale yellow oil; IR ν (cm^{-1}) 1742, 1678; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.18 (s, 1H), 7.32 (s, 1H), 6.98 (s, 1H), 6.94 (d, J = 5.4 Hz, 1H), 6.05 (s, 2H), 6.0-6.04 (m, 1H), 5.24 (d, J = 11.4 Hz, 1H), 5.22 (d, J = 18.6 Hz, 1H), 2.11 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 189.4, 169.6, 152.6, 148.0, 138.2, 136.2, 128.4, 117.4, 109.4, 108.0, 102.3, 71.9, 21.1; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{13}H_{12}O_5Na$: 271.0576, found: 271.0580.

1-(3-Formylpyridin-2-yl)allyl acetate Vk: pale yellow oil; IR ν (cm^{-1}) 1742, 1699; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 10.42 (s, 1H), 8.78 (d, J = 5.2, 2 Hz, 1H), 8.17 (d, J = 7.6, 1.6 Hz, 1H), 7.42 (dd, J = 7.6, 4.4 Hz, 1H), 6.89 (dt, J = 6, 1.2 Hz, 1H), 6.14-6.22 (m, 1H), 5.38 (dd, J = 16, 1.2 Hz, 1H), 5.33 (d, J = 10.8 Hz, 1H), 2.13 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 190.6, 170.0, 159.2, 153.4, 138.6, 134.5, 129.3, 123.4, 118.8, 74.4, 21.0; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{11}H_{11}NO_3Na$: 228.0631, found: 228.0628.

(2). Preparation of 1-(*o*-(2-nitrovinyl)aryl)allyl acetates 1.[15]

In a flask, 1-(*o*-formylaryl)allyl acetates **V** (1 mmol) and NH_4OAc (77 mg, 1 mmol) were mixed with CH_3NO_2 (10 mL). The reaction mixture was refluxed for 3h and then the reaction was quenched by the addition of water (10 mL). The resulting mixture was extracted with DCM (10 × 3 mL). The combined organic layer was dried over

anhydrous $MgSO_4$. After filtration and removal of solvents, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE : EA = 8 : 1 – 5:1) to give 1-(2-(2-nitrovinyl)aryl)allyl acetates **1** generally as yellow oils (60-76% yield). The products **1** solidified into yellow solids when kept in refrigerator.

(*E*)-1-(2-(2-Nitrovinyl)phenyl)allyl acetate 1a: yellow solid, 175 mg, 71%, mp 51-52 ^oC (without recrystallization); IR ν (cm^{-1}) 1741; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.49 (d, J = 13.7 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 4.0 Hz, 2H), 7.43 (d, J = 13.6 Hz, 1H), 7.35-7.39 (m, 1H), 6.45 (dt, J = 5.2, 1.2 Hz, 1H), 5.96-6.04 (m, 1H), 5.28 (d, J = 10.4 Hz, 1H), 5.20 (d, J = 17.6 Hz, 1H), 2.11 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 169.8 , 139.2, 138.4, 136.6 , 135.6, 131.9 , 129.0 , 128.7, 127.8, 118.2, 74.1, 21.1; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{13}H_{13}NO_4Na$: 270.0736, found: 270.0740.

(*E*)-1-(4-Methoxy-2-(2-nitrovinyl)phenyl)allyl acetate 1b: yellow solid, 180 mg, 65%, mp 54-55 ^oC (without recrystallization); IR ν (cm^{-1}) 1742; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.46 (d, J = 13.2 Hz, 1H), 7.41 (d, J = 13.2 Hz, 1H), 7.39 (d, J = 7.2 Hz, 1H), 7.00 (d, J = 8.8 Hz, 1H), 6.99 (s, 1H), 6.40 (d, J = 3.6 Hz, 1H), 5.95-6.03 (m, 1H), 5.25 (d, J = 10.8 Hz, 1H), 5.18 (d, J = 17.2 Hz, 1H), 3.82 (s, 3H), 2.08 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 169.8, 159.7, 138.5, 136.6, 136.0, 131.5, 130.7, 130.0, 117.7, 117.4, 112.8, 73.8, 55.6, 21.1; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{14}H_{15}NO_5Na$: 300.0842, found: 300.0839.

(*E*)-1-(4-Methyl-2-(2-nitrovinyl)phenyl)allyl acetate 1c: yellow solid, 172 mg, 66%,

mp 55-56 ºC (without recrystallization); IR *v* (cm^{-1}) 1742; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.47 (d, *J* = 13.6 Hz, 1H), 7.43 (d, *J* = 13.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.33 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.42 (dt, *J* = 5.2, 1.6 Hz, 1H), 5.95-6.04 (m, 1H), 5.26 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.19 (dd, *J* = 18, 0.8 Hz, 1H), 2.37 (s, 3H), 2.09 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 169.8, 139.0, 138.1, 136.8, 136.5, 135.8, 132.8, 129.1, 128.6, 128.3, 117.9, 74.0, 21.1, 21.1; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{14}H_{15}NO_4Na$: 284.0893, found: 284.0890.

(*E*)-1-(4-Chloro-2-(2-nitrovinyl)phenyl)allyl acetate 1d: yellow solid, 197 mg, 70%, mp 61-62 ºC (without recrystallization); *v* (cm^{-1}) 1738; ^1H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.40 (d, *J* = 13.2 Hz, 1H), 7.48 (s, 1H), 7.43-7.45 (m, 2H), 8.41 (d, *J* = 13.8 Hz, 1H), 6.39 (d, *J* = 6.6 Hz, 1H), 5.94-6.0 (m, 1H), 5.30 (d, *J* = 11.4 Hz, 1H), 5.20 (d, *J* = 16.8 Hz, 1H), 2.11 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm) 174.5, 145.6, 143.2, 140.9, 139.5, 138.8, 136.7, 135.7, 135.6, 133.2, 123.1, 77.9, 25.9; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{13}H_{12}ClNO_4Na$: 304.0347, found: 304.0350.

(*E*)-1-(2-(2-Nitrovinyl)-4-(trifluoromethyl)phenyl)allyl acetate 1e: yellow solid, 221 mg, 70%, mp 118-119 ºC (without recrystallization); *v* (cm^{-1}) 1738; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.45 (d, *J* = 13.2 Hz, 1H), 7.73 (s, 1H), 7.72 (d, *J* = 5.2 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 14.0 Hz, 1H), 6.45 (d, *J* = 5.6 Hz, 1H), 5.98 (m, 1H), 5.34 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.23 (dd, *J* = 17.6, 1.2 Hz, 1H), 2.13 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm) 169.6, 142.8, 139.6, 135.0, 134.7, 131.3 (q, *J* = 33 Hz), 129.6, 129.4, 128.1 (d, *J* = 2.9 Hz), 124.7 (d, *J* = 2.9 Hz), 123.4 (q, *J* = 270 Hz), 119.0, 73.4, 20.9; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{14}H_{12}F_3NO_4Na$: 338.0610,

found: 338.0614.

(*E*)-1-(5-methoxy-2-(2-nitrovinyl)phenyl)allyl acetate 1f: yellow solid, 166 mg, 60%, mp 76-77 ºC (without recrystallization); IR *v* (cm^{-1}) 1739; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.41 (d, *J* = 13.2 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.41 (d, *J* = 14.0 Hz, 1H), 6.99 (d, *J* = 2.8 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.44 (dt, *J* = 5.2, 1.6 Hz, 1H), 5.94-6.03 (m, 1H), 5.29 (d, *J* = 10.8 Hz, 1H), 5.22 (d, *J* = 16.4 Hz, 1H), 3.85 (s, 3H), 2.12 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 169.7, 162.7, 141.6, 136.4, 136.1, 135.5, 129.6, 120.7, 118.4, 114.5, 114.4, 73.8, 55.7, 21.1; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{14}H_{15}NO_5Na$: 300.0842, found: 300.0840.

(*E*)-1-(5-methyl-2-(2-nitrovinyl)phenyl)allyl acetate 1g: yellow solid, 180 mg, 69%, mp 75-76 ºC (without recrystallization); IR *v* (cm^{-1}) 1742; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.47 (d, *J* = 14.0 Hz, 1H), 7.45 (s, 1H), 7.43 (d, *J* = 6.0 Hz, 1H), 7.29 (s, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 6.44 (dt, *J* = 5.2, 1.6 Hz, 1H), 5.97-6.05 (m, 1H), 5.29 (dd, *J* = 11.2, 0.8 Hz, 1H), 5.21 (dd, *J* = 18.8, 0.8 Hz, 1H), 2.40 (s, 3H), 2.12 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 169.8 , 142.8, 139.2 , 137.5 , 136.6, 135.7 , 129.8 , 127.8, 125.8, 118.1, 74.2, 21.7 , 21.2; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{14}H_{15}NO_4Na$: 284.0893, found: 284.0890.

(*E*)-1-(5-Chloro-2-(2-nitrovinyl)phenyl)allyl acetate 1h: yellow solid, 206 mg, 73%, mp 60-61 ºC (without recrystallization); IR *v* (cm^{-1}) 1746; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.38 (d, *J* = 13.6 Hz, 1H), 7.47 (s, 1H), 7.46 (d, *J* = 6.8 Hz, 2H), 7.42 (d, *J* = 13.6 Hz, 1H), 7.34 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.40 (dt, *J* = 5.6, 1.2 Hz, 1H), 5.91-6.0 (m, 1H), 5.30 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.23 (dd, *J* = 16.4, 0.8 Hz, 1H), 2.12 (s, 3H);

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 169.7 , 141.0, 138.6, 138.1, 135.2 , 134.9, 129.2, 129.1,128.9,127.1, 118.8, 73.2 , 21.1; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{13}H_{12}ClNO_4Na$: 304.0347, found: 304.0350.

(*E*)-1-(2-(2-Nitrovinyl)-5-(trifluoromethyl)phenyl)allyl acetate 1i: yellow solid, 239 mg, 76%, mp 62-63 ºC (without recrystallization); IR *v* (cm^{-1}) 1746; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.45 (d, *J* = 13.6 Hz, 1H), 7.73 (s, 1H), 7.60-7.65 (m, 2H), 7.44 (d, *J* = 13.6 Hz, 1H), 6.46 (dt, *J* = 4.8, 1.6 Hz, 1H), 5.94-6.02 (m, 1H), 5.34 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.24 (dd, *J* = 17.2, 1.2 Hz, 1H), 2.13 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 169.6, 140.1, 140.0, 135.0, 134.8, 133.4 (q, *J* = 32.5 Hz), 132.3, 128.4, 125.7 (d, *J* = 3.9 Hz), 125.6 (d, *J* = 3.8 Hz), 123.4 (q, *J* = 271.2 Hz), 119.0, 73.3, 21.0; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{14}H_{12}F_3NO_4Na$: 338.0610, found: 338.0613.

(*E*)-1-(6-(2-nitrovinyl)benzo[*d*][1,3]dioxol-5-yl)allyl acetate 1j: yellow solid, 204 mg, 70%, mp 105-106 ºC (without recrystallization); IR *v* (cm^{-1}) 1740; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.42 (d, *J* = 13.2 Hz, 1H), 7.37 (d, *J* = 13.2 Hz, 1H), 6.95 (d, *J* = 4 Hz, 2H), 6.42 (dt, *J* = 5.6, 1.6 Hz, 1H), 6.04 (s, 2H), 5.92-6.0 (m, 1H), 5.28 (dt, *J* = 9.6, 0.8 Hz, 1H), 5.21 (dd, *J* = 17.2, 1.6 Hz, 1H), 2.11 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 169.7 , 151.3, 148.3 , 136.9 , 135.8, 135.7, 135.6 , 122.2, 118.0, 108.9, 106.4, 102.3, 73.2, 21.1; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{14}H_{13}NO_6Na$: 314.0635, found: 314.0632.

(*E*)-1-(3-(2-Nitrovinyl)pyridin-2-yl)allyl acetate 1k: yellow solid, 149 mg, 60%, mp 53-54 ºC (without recrystallization); IR *v* (cm^{-1}) 1744; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.70 (dd, *J* = 5.2, 2 Hz, 1H), 8.50 (d, *J* = 13.6 Hz, 1H), 7.81 (d, *J* = 8, 2 Hz, 1H),

7.43 (d, *J* = 14 Hz, 1H), 7.34 (dd, *J* = 7.6, 4.4 Hz, 1H), 6.46 (d, *J* = 6 Hz, 1H), 6.09-6.17 (m, 1H), 5.33-5.38 (m, 2H), 2.13 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 169.9 , 157.2, 151.9 , 139.5 , 135.6, 134.5 , 134.0 , 124.8, 123.5, 119.0, 75.7, 21.0; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{12}H_{12}N_2O_4Na$: 271.0689, found: 271.0692.

2. General procedure for the enantioselective synthesis of 4-nitro-1-vinyl-*1H*-2,3-benzodiazepine-2,3-dicarboxylates 5 from $[Pd(C_3H_5)Cl]_2$/DIFLUORPHOS catalyzed reaction of 1-(2-(2-nitrovinyl)aryl)allyl acetates and azodicarboxylates.

Under nitrogen atmosphere and at room temperature, 1-(2-(2-nitrovinyl)aryl)allyl acetates **1** (0.2 mmol, 1.0 equiv.), thiazolium **3a** (0.04 mmol, 20 mol%), DMAP (0.04 mmol, 20 mol%) and dry dichlormethane (0.5 mL) were added successively to a dry Schlenk tube. After the mixture was stirred for 5 minutes, azodicarboxylates **2** (0.36 mmol, 1.8 equiv.) were added using a microsyringe. In the sealed Schlenk tube, the reaction mixture was stirred for 12 h at room temperature. On the other hand, the palladium catalyst was prepared in a glove box by mixing $[Pd(C_3H_5)Cl]_2$ (14.6 mg, 0.04 mmol, 20 mol%) and (*S*)-DIFLUORPHOS (54.4 mg, 0.08 mmol, 40 mol%) in dry DCM (0.75 mL) in an oven-dried test tube and was stirred for 2h at room temperature. The Schlenk tube was then moved into the glove box, and pre-prepared palladium-DIFLUORPHOS complex solution was added. The residual palladium catalyst in the test tube was washed with 1.25 mL of dry acetone and was added to the reaction mixture. The resulting reaction mixture in the sealed Schlenk tube was kept stirred for another 12 h at ambient temperature. The reaction was then quenched by removal of the solvents.

The residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE : EA from 5 : 1 to 3 : 1) to give products **5** in 48-93% yields with er from 77:23 to 95:5.

(*S*)-Dimethyl 4-nitro-1-vinyl-1*H*-2,3-benzodiazepine-2,3-dicarboxylate 5a: pale yellow solid, 60 mg, 90%, 88:12 er, $[\alpha]^{20}_{D}$ +397.8 (*c* 0.5, CH_2Cl_2), mp 147-148ºC (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1775, 1736; ^{1}H NMR (600 MHz, DMSO-d_6, 70 ºC) δ (ppm) 7.75 (d, *J* = 7.2 Hz, 1H), 7.55 (s, 1H), 7.48 (td, *J* = 7.8, 1.2 Hz, 1H), 7.44 (td, *J* = 7.8, 1.8 Hz, 1H), 7.41 (d, *J*=7.8, 1H), 6.22 (d, *J* = 4.8 Hz, 1H), 5.95-6.00 (m, 1H), 5.31 (d, *J* = 9.6 Hz, 1H), 4.62 (d, *J* = 16.8 Hz, 1H), 3.72 (s, 3H), 3.62 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6, 70 ºC) δ (ppm) 154.5, 152.6, 145.3, 140.4, 136.5, 134.8, 131.5, 130.7, 128.8, 127.4, 123.0, 121.3, 66.2, 54.9, 54.5; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{15}H_{16}N_3O_6$: 334.1033, found: 334.1031.

(*S*)-Dimethyl 7-methoxy-4-nitro-1-vinyl-1H-2,3-benzodiazepine-2,3-dicarboxylate 5b: yellow solid, 55 mg, 76%, 92:8 er, $[\alpha]^{20}_{D}$ +415.0 (*c* 0.5, CH_2Cl_2), mp 138-139 ºC (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1769, 1713; ^{1}H NMR (400 MHz, DMSO-d_6, 70 ºC) δ (ppm) 7.55 (s, 1H), 7.37 (d, *J* = 2.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.06 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.16 (d, *J* = 5.6 Hz, 1H), 5.91-5.99 (m, 1H), 5.29 (d, *J* = 10 Hz, 1H), 4.62 (d, *J* = 17.6 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.62 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 70 ºC) δ (ppm) 159.2, 154.5, 152.6, 145.5, 135.2, 132.4, 132.0, 128.5, 122.7, 121.4, 120.8, 117.8, 65.7, 56.1, 54.9, 54.5; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{16}H_{18}N_3O_7$: 364.1139, found: 364.1136.

(*S*)-Dimethyl 7-methyl-4-nitro-1-vinyl-1H-2,3-benzodiazepine-2,3-dicarboxylate

5c: yellow solid, 56 mg, 81%, 85:15 er, $[\alpha]^{20}_{D}$ +367.0 (*c* 0.5, CH_2Cl_2), mp 118-119 ºC (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1767, 1738; ^1H NMR (400 MHz, DMSO-d_6, 70 ºC) δ (ppm) 7.56 (s, 1H), 7.49 (s, 1H), 7.27-7.31 (m, 2H), 6.17 (d, *J* = 5.6 Hz, 1H), 5.91-6.00 (m, 1H), 5.29 (d, *J* = 10.4 Hz, 1H), 4.62 (d, *J* = 17.6 Hz, 1H), 3.71 (s, 3H), 3.61 (s, 3H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6, 70 ºC) δ (ppm) 154.5, 152.6, 145.2, 138.3.15, 137.5, 136.8, 135.1, 132.3, 130.7, 127.2, 122.8, 121.5, 65.9, 54.9, 54.5, 20.7; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{16}H_{18}N_3O_6$: 348.1190, found: 348.1187.

(*S*)-Dimethyl 7-chloro-4-nitro-1-vinyl-1H-2,3-benzodiazepine-2,3-dicarboxylate 5d: yellow solid, 54 mg, 73%, 94:6 er, $[\alpha]^{20}_{D}$ +396.4 (*c* 0.59, CH_2Cl_2), mp 149-150 ºC (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1767, 1724; ^1H NMR (400 MHz, DMSO-d_6, 70 ºC) δ (ppm) 7.96 (d, *J* = 2.4 Hz, 1H), 7.60 (s, 1H), 7.57 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 6.28 (d, *J* = 5.2 Hz, 1H), 5.95-6.03 (m, 1H), 5.37 (d, *J* = 10.0 Hz, 1H), 4.67 (d, *J* = 17.6 Hz, 1H), 3.76 (s, 3H), 3.67 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6, 70 ºC) δ (ppm) 154.4, 152.4, 146.1, 139.2, 135.2, 134.4, 133.3, 132.5, 130.9, 129.5, 123.3, 119.6, 65.6, 55.0, 54.6; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{15}H_{15}ClN_3O_6$: 368.0643, found: 368.0644.

(*S*)-Dimethyl 4-nitro-7-trifluoromethyl-1-vinyl-1H-2,3-benzodiazepine-2,3-dicarboxylate 5e: white solid, 49 mg, 61%, 95:5 er, $[\alpha]^{20}_{D}$ +390.6 (*c* 0.5, CH_2Cl_2), mp 129-130 ºC (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1761, 1730; ^1H NMR (400 MHz, DMSO-d_6, 70 ºC) δ (ppm) 8.24 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.72 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 6.35 (d, *J* = 6.0 Hz, 1H), 5.91-5.99 (m, 1H), 5.35 (d,

J = 10.0 Hz, 1H), 4.65 (d, *J* = 17.2 Hz, 1H), 3.74 (s, 3H), 3.63 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6, 70 °C) δ (ppm) 154.4, 152.4, 146.3, 144.6, 134.1, 132.9, 131.8, 129.7 (q, *J* = 33 Hz), 128.6, 127.4, 124.2 (q, *J* = 270 Hz), 123.6, 119.5, 65.9, 55.1, 54.7, HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{16}H_{15}F_3N_3O_6$: 402.0907; found: 402.0905.

(*S*)-Dimethyl 8-methoxy-4-nitro-1-vinyl-1H-2,3-benzodiazepine-2,3-dicarboxylate 5f: yellow solid, 64 mg, 88%, 92:8 er, $[\alpha]^{20}_D$ +397.4 (*c* 0.5, CH_2Cl_2), mp 137-138 °C (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1770, 1732; ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) δ (ppm) 7.71 (d, *J* = 8.4 Hz, 1H), 7.57 (s, 1H), 7.03 (d, *J* = 2.8 Hz, 1H), 7.00 (s, 1H), 6.20 (d, *J* = 5.2 Hz, 1H), 5.91-5.99 (m, 1H), 5.31 (d, *J* = 10.0 Hz, 1H), 4.70 (d, *J* = 16.8 Hz,1H), 3.81 (s, 3H), 3.70 (s, 3H), 3.62 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6, 70 °C) δ (ppm) 162.1, 154.6, 152.7, 143.3, 142.7, 138.8, 134.6, 122.8, 122.0, 120.0, 116.4, 114.6, 66.0, 56.2, 54.7, 54.5; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{16}H_{18}N_3O_7$: 364.1139, found: 364.1141.

(*S*)-Dimethyl 8-methyl-4-nitro-1-vinyl-1H-2,3-benzodiazepine-2,3-dicarboxylate 5g: yellow solid, 58 mg, 84%, 87:13 er, $[\alpha]^{20}_D$ +372.2 (*c* 0.5, CH_2Cl_2), mp 117-118 °C (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1769, 1710; ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) δ (ppm) 7.64 (d, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.23 (s, 1H), 6.16 (d, *J* = 6.0 Hz, 1H), 5.92-6.00 (m, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 4.65 (d, *J* = 16.8 Hz, 1H), 3.71 (s, 3H), 3.62 (s, 3H), 2.33 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6, 70 °C) δ (ppm) 154.6, 152.6, 144.6, 142.1, 140.4, 136.6, 134.7, 131.3, 129.6, 124.7, 122.9, 121.6, 66.1, 54.8, 54.5, 21.3; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{16}H_{18}N_3O_6$: 348.1190, found: 348.1192.

(*S*)-Dimethyl 8-chloro-4-nitro-1-vinyl-1H-2,3-benzodiazepine-2,3-dicarboxylate 5h: pale yellow solid, 51 mg, 69%, 90:10 er, $[\alpha]^{20}_{D}$ +393.8 (*c* 0.5, CH_2Cl_2), mp 114-115 °C (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1751, 1730; ^1H NMR (400 MHz, DMSO-d_6, 70 °C) δ (ppm) 7.80 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 2.4 Hz, 2H), 7.51 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.27 (d, *J* = 5.6 Hz, 1H), 5.90-5.99 (m, 1H) 5.35 (d, *J* = 10.4 Hz, 1H), 4.67 (d, *J* = 16.8 Hz, 1H), 3.72 (s, 3H), 3.63 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6, 70 °C) δ (ppm) 154.4, 152.5, 145.5, 142.5, 138.0, 136.5, 134.3, 130.3, 128.9, 126.5, 123.5, 120.0, 65.5, 55.0, 54.6; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{15}H_{15}ClN_3O_6$: 368.0643, found: 368.0643.

(*S*)-Dimethyl 4-nitro-8-trifluoromethyl-1-vinyl-1*H*-2,3-benzodiazepine-2,3-dicarboxylate 5i: white solid, 52 mg, 65%, 90:10 er, $[\alpha]^{20}_{D}$ + 317.3 (*c* 0.25, CH_2Cl_2), mp 109-110 °C (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1769, 1732; ^1H NMR (400 MHz, DMSO-d_6, 70 °C) δ (ppm) 7.99 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.61 (s, 1H), 6.41 (d, *J* = 6.0 Hz, 1H), 5.92-6.01 (m, 1H), 5.35 (d, *J* = 10.4 Hz, 1H), 4.63 (d, *J* = 17.6 Hz, 1H), 3.74 (s, 3H), 3.63 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6, 70 °C) δ (ppm) 154.4, 152.4, 146.7, 141.6, 137.1, 134.3, 131.4, 130.9 (q, *J* = 31.7 Hz), 127.2 (d, *J* = 2.9 Hz), 125.3 (d, *J* = 3 Hz), 124.2 (q, *J* = 271.5 Hz), 123.5, 119.1, 65.7, 55.1, 54.7; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{16}H_{15}F_3N_3O_6$: 402.0907, found: 402.0910.

(*S*)-Dimethyl 8-nitro-5-vinyl-5H-1,3-dioxolo[4,5-*h*][2,3]benzodiazepine-6,7-dicarboxylate 5j: yellow solid, 70 mg, 93%, 89:11 er, $[\alpha]^{20}_{D}$ + 426 (*c* 0.25, CH_2Cl_2), mp 135-136 °C (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1771, 1709;

^{1}H NMR (400 MHz, DMSO-d_6, 70 ºC) δ (ppm) 7.71 (s, 1H), 7.32 (s, 1H), 7.01 (s, 1H), 6.14 (d, *J* = 5.2 Hz, 1H), 6.10 (d, *J* = 2 Hz, 2H), 5.86-5.95 (m, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 4.71 (d, *J* = 16.8 Hz, 1H), 3.70 (s, 3H), 3.62 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6, 70 ºC) δ (ppm) 154.5, 152.5, 150.6, 147.8, 143.9, 137.0, 134.6, 122.9, 121.6, 121.2, 114.7, 110.6, 103.0, 66.0, 54.8, 54.5; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{16}H_{15}N_3O_8Na$: 400.0751, found: 400.0749.

Dimethyl 6-nitro-9-vinyl-7H-pyrido[2,3-*d*][1,2]diazepine-7,8-dicarboxylate 5k: white solid, 32 mg, 48%, 77:23 er, $[\alpha]^{20}_D$ + 219 (*c* 0.5, CH_2Cl_2), mp 140-141 ºC (recrystallization from ethyl acetate/*n*-hexane); IR *v* (cm^{-1}) 1757, 1724; ^{1}H NMR (400 MHz, DMSO-d_6, 70 ºC) δ (ppm) 8.60 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.19 (dd, *J* = 8, 1.6 Hz, 1H), 7.59 (s, 1H), 7.48 (dd, *J* = 7.6, 4.4 Hz, 1H), 6.20 (d, *J* = 5.8 Hz, 1H), 5.95-6.03 (m, 1H), 5.34 (d, *J* = 10 Hz, 1H), 4.56 (d, *J* = 17.6 Hz, 1H), 3.74 (s, 3H), 3.64 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 70 ºC) δ (ppm) 158.7, 154.5, 152.5, 150.9, 146.1, 143.7, 133.5, 134.0, 123.8, 123.4, 118.8, 68.4, 55.1, 54.7; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{14}H_{14}N_4O_6Na$: 357.0805, found: 357.0803.

(*S*)-Diethyl 4-nitro-1-vinyl-1H-2,3-benzodiazepine-2,3-dicarboxylate 5l: white solid, 63 mg, 87%, 86:14 er, $[\alpha]^{20}_D$ +329.2 (*c* 0.5, CH_2Cl_2), mp 88-89 ºC (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1757, 1732; ^{1}H NMR (400 MHz, DMSO-d_6, 70 ºC) δ (ppm) 7.75 (d, *J* = 7.6 Hz, 1H), 7.52 (s, 1H), 7.48 (td, *J* = 7.6, 1.6 Hz, 1H), 7.43 (td, *J* = 7.6, 1.8 Hz, 1H), 7.40 (d, *J*=7.6, 1H), 6.22 (d, *J* = 5.6 Hz, 1H), 5.95-6.03 (m, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 4.62 (d, *J* = 16.8 Hz, 1H), 4.17 (q, *J* = 5.6 Hz, 2H), 4.05 (q, *J* = 7.2 Hz, 2H), 1.18 (brs, 3H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H}

NMR (150 MHz, DMSO-d_6, 70 ºC) δ (ppm) 154.1, 151.9, 145.5, 140.4, 136.4, 135.0, 131.4, 130.7, 128.7, 127.5, 122.8, 120.9, 66.1, 64.4, 63.3, 14.5, 14.3; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{17}H_{20}N_3O_6$: 362.1346, found: 362.1349.

(*S*)-Di(isopropyl) 4-nitro-1-vinyl-1H-2,3-benzodiazepine-2,3-dicarboxylate 5m: white solid, 66 mg, 85%, 78:22 er, $[\alpha]^{20}_D$ +370.2 (*c* 0.5, CH_2Cl_2), mp 86-87 ºC (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1750, 1721; ^1H NMR (600 MHz, DMSO-d_6, 70 ºC) δ (ppm) 7.73 (d, *J* = 6.6 Hz, 1H), 7.47 (s, 1H), 7.47 (t, *J* = 6.6 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J*=7.8, 1H), 6.20 (d, *J* = 4.8 Hz, 1H), 5.97-6.01 (m, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 4.84-4.87 (m, 1H), 4.70-4.75 (m, 1H), 4.61 (brs, 1H), 1.18 (brs, 6H), 1.07 (d, *J* = 6 Hz, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6, 70 ºC) δ (ppm) 153.7, 151.2, 145.7, 140.4, 136.3, 135.2, 131.3, 130.7, 128.7, 127.6, 122.7, 120.5, 72.8, 71.2, 65.8, 22.0, 21.5; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{19}H_{24}N_3O_6$: 390.1659, found: 390.1658.

(*S*)-Diethyl 7-chloro-4-nitro-1-vinyl-1H-2,3-benzodiazepine-2,3-dicarboxylate 5n: white solid, 57 mg, 72%, 88:12 er, $[\alpha]^{20}_D$ +362.4 (*c* 0.25, CH_2Cl_2), mp 102-103 ºC (recrystallization from ethyl acetate/*n*-hexane); IR *v* (cm^{-1}) 1759, 1726; ^1H NMR (400 MHz, DMSO-d_6, 70 ºC) δ (ppm) 7.90 (d, *J* = 1.6 Hz, 1H), 7.51 (s, 1H), 7.52 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 6.23 (d, *J* = 5.6 Hz, 1H), 5.93-6.01 (m, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 4.65 (d, *J* = 17.2 Hz, 1H), 4.17 (q, *J* = 6.4 Hz, 2H), 4.05 (q, *J* = 7.2 Hz, 2H), 1.18 (brs, 3H), 1.07 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 70 ºC) δ (ppm) 154.0, 151.7, 146.3, 139.2, 135.1, 134.6, 133.3, 132.5, 130.8, 129.6, 123.1, 119.1, 65.6, 64.5, 63.5, 14.5, 14.3; HRMS (TOF-ESI): $[M + H]^+$ calcd for

$C_{17}H_{19}ClN_3O_6$: 396.0956, found: 396.0961.

(*S*)-Di(isopropyl) 7-chloro-4-nitro-1-vinyl-1H-2,3-benzodiazepine-2,3-dicarboxylate 5o: white solid, 60 mg, 71%, 85:15 er, $[\alpha]^{20}_D$ +252.8 (*c* 0.25, CH_2Cl_2), mp 99-100 ºC (recrystallization from ethyl ether/*n*-hexane); IR *v* (cm^{-1}) 1757, 1719; ^1H NMR (400 MHz, DMSO-d_6, 70 ºC) δ (ppm) 7.89 (d, *J* = 2.4 1H), 7.51 (dd, *J* = 8.4, 2.0, 1H), 7.47 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 6.22 (d, *J* = 6.0 Hz, 1H), 5.93-6.01 (m,1H), 5.30 (d, *J* = 10.0 Hz, 1H), 4.81-4.90 (m, 1H), 4.68-4.78 (m, 1H), 4.63 (d, *J* = 16 Hz, 1H), 1.18 (brs, 6H), 1.08 (d, *J* = 6 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 70 ºC) δ (ppm) 153.5, 151.1, 146.5, 139.2, 135.0, 134.8, 133.2, 132.5, 130.7, 129.7, 123.0, 118.7, 73.1, 71.4, 65.4, 22.0, 21.4; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{19}H_{23}ClN_3O_6$: 424.1269, found: 424.1271.

3. The procedure for the reaction of (*E*)-1-(4-chloro-2-(2-nitrovinyl)phenyl)allyl acetate 1d and azodicarboxylate 2a in 1 mmol scale.

In a glove box, (*E*)-1-(4-chloro-2-(2-nitrovinyl)phenyl)allyl acetate **1d** (281.7 mg, 1 mmol, 1.0 equiv.), thiazolium **3a** (71.5 mg, 0.2 mmol, 20 mol%), DMAP (24.5 mg, 0.2 mmol, 20 mol%) were dissolved in dry dichlormethane (2.5 mL) in a Schlenk tube, and dimethyl azodicarboxylate **2a** (262.8 mg, 1.8 mmol, 1.8 equiv.) was added. The reaction mixture was stirred for 12 h at room temperature. Then the palladium-DIFLUORPHOS complex that was prepared from the reaction of $[Pd(C_3H_5)Cl]_2$ (73 mg, 0.2 mmol, 20 mol%) with (*S*)-DIFLUORPHOS (272 mg, 0.4 mmol, 40 mol%) in dry DCM (3.75 mL) was added, followed by the addition of 6.25 mL of dry acetone. The resulting reaction mixture in the sealed Schlenk tube was kept stirred for another 12 h at ambient

temperature. After removal of solvents, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE : EA from 5 : 1 to 3 : 1) to give product **5d** in 74% yield (271 mg) with 92:8 er.

ASSOCIATED CONTENT

Supporting Information Available. The X-ray structure of **5d**, reaction scheme and results for the preparation of 1-(*o*-formylaryl)allyl acetates **V**; copies of ^{1}H NMR and ^{13}C NMR spectra for 1-(*o*-formylaryl)allyl acetates **V**, 1-(*o*-(2-nitrovinyl)aryl)allyl acetates **1**, benzodiazepine and pyridodiazepine products **5**; copies of HPLC spectra for products **5**; single crystal data of **5d** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest**.**

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