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Asymmetric Synthesis of Functionalized Tetrahydronaphthalenes *via* an Organocatalytic Nitroalkane-Michael/Henry Domino Reaction

Dieter Enders,[a,*] Robert Hahn,[a] and Iuliana Atodiresei[a]

[a] Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany
Fax: (+49)-241-809-2127; e-mail: enders@rwth-aachen.de

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Abstract: An organocatalytic nitroalkane-Michael/Henry reaction sequence to functionalized 1,2,3,4-tetrahydronaphthalen-1-ols is described. Starting from 2-(nitromethyl)benzaldehyde and nitroalkenes a bifunctional quinine-based squaramide organocatalyst is used to afford the title compounds in moderate to very good yields (25–84%), high diastereomeric ratios ($dr > 95:5$) after crystallization and good to excellent enantioselectivities of 63–99% *ee*. Starting from γ-nitro aldehydes and ketones secondary and tertiary cyclohexanols bearing four stereogenic centers can also be prepared with this Michael/Henry domino reaction.

Keywords: cyclohexanes; domino reactions; organocatalysis; squaramides; tetrahydronaphthalenes

Introduction

The trio of general concepts of asymmetric catalysis, namely biocatalysis, metal catalysis and organocatalysis,[1] constitutes a basic platform of modern synthetic chemistry. Especially the latter field, the catalysis with small organic molecules, has grown with enormous speed since about the turn of the millennium. Among the various subfields of organocatalysis, domino or cascade reactions[2] have been intensively investigated during the past few years, which open up efficient direct entries to complex molecules from simple precursors in a single one-pot operation.

The 1,2,3,4-tetrahydronaphthalene moiety is present as a characteristic structural feature in the class of second generation rodenticides, like difenacoum, brodifacoum and flocoumafen,[3a,b] in MT_2 melatonin receptor antagonists,[3c] and can also inhibit the growth of human tumor cells lines.[3d] Therefore diastereo- and enantioselective syntheses of these compounds and of cyclohexanes in general are of great interest.[4,5] In recent years several different strategies for the catalytic asymmetric synthesis of polysubstituted cyclohexanes bearing contiguous stereocenters have been developed, including covalent enamine/iminium activation modes as well as hydrogen-bonding concepts.[6]

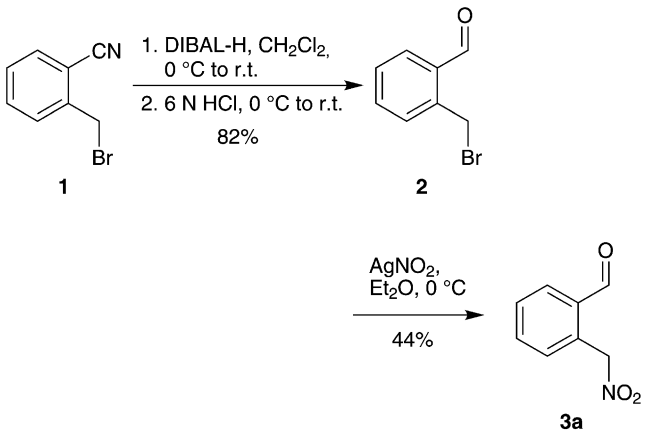
We now would like to report the asymmetric synthesis of polyfunctionalized 1,2,3,4-tetrahydronaphthalen-1-ols *via* a nitroalkane-Michael/Henry reaction sequence using a hydrogen-bonding squaramide organocatalyst.

Results and Discussion

To access the title tetrahydronaphthalenes we envisaged the reaction of 2-(nitromethyl)benzaldehyde (**3a**) with β-nitrostyrenes **4** based on a related nitroalkane-Michael/aldol reaction sequence, that was developed in our group.[7] The cascade starts with a nucleophilic attack of the γ-nitro aldehyde to the nitroalkene, which becomes the nitronate donor for a subsequent ring closure to the cyclohexane through an intramolecular Henry reaction.

Firstly, a shorter and more efficient route to aldehyde **3a** as compared to the known procedure has been worked out (Scheme 1).[7] The benzaldehyde **2** was obtained by reduction of the nitrile group of commercially available 2-(bromomethyl)benzonitrile (**1**) with DIBAL-H and followed by acidic hydrolysis.[8a] Subsequently treatment with silver nitrite[8b] at 0 °C yielded the desired γ-nitroaldehyde **3a**.[9]

We investigated the reaction of 2-(nitromethyl)benzaldehyde (**3a**) and nitrostyrene (**4a**) with different hydrogen-bonding thiourea and squaramide organocatalysts. All of them are reported to facilitate the conversion of α-acidic nitro compounds to



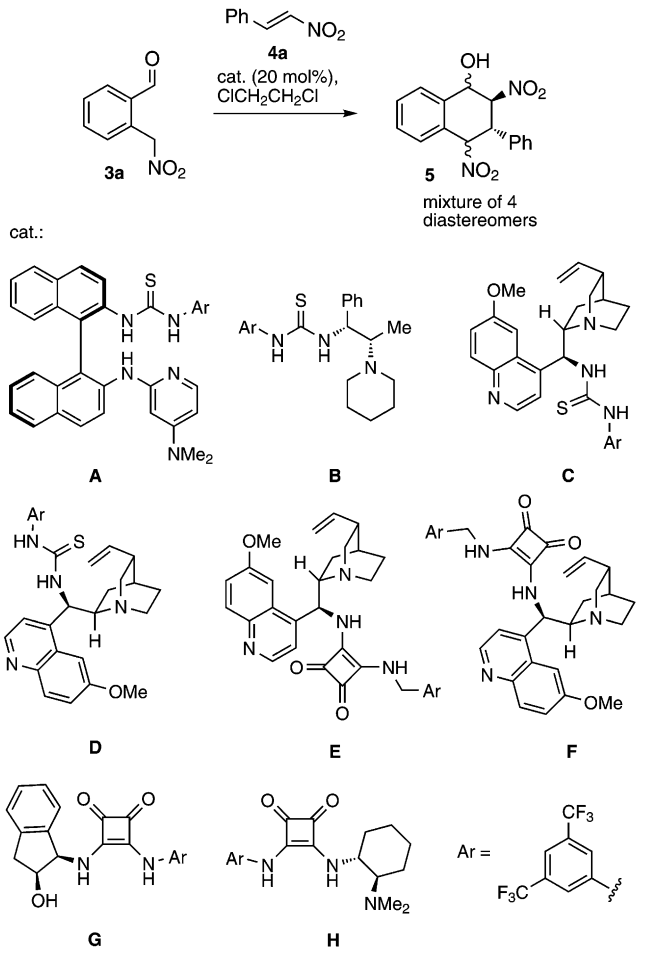
Scheme 1. Improved two-step protocol for the synthesis of 2-(nitromethyl)benzaldehyde (**3a**).

various Michael-acceptors.[10] Due to their bifunctional character, the organocatalysts can activate both the acceptor and the donor in which the nitro group can serve as a directing moiety.

Nearly all tested catalysts **A**–**H** promoted the anticipated domino reaction, which resulted in a mixture of four diastereomers **5** with respect to the stereocenters in the 1- and 4-positions. All have in common their *trans*-relationship at the 2,3-positions. The organocatalyst **A** with its binaphthyl backbone gave a yield of 43% with a low diastereoselectivity and a modest enantiomeric excess of 46% of the major diastereomer (Table 1, entry 1). After 5.5 days 83% yield of **5** in 27% *ee* (Table 1, entry 2) could be obtained with the norephedrine-derived catalyst **B** that was recently developed in our group.[11] No satisfying improvement was achieved after applying the quinine-based catalyst **C** (49% yield, 59% *ee*) and its *pseudo*-enantiomer **D** (61% yield, 13% *ee*) in the domino reaction (Table 1, entries 3 and 4). Switching from thiourea-based catalysts to the more efficient hydrogen-bonding squaramides led to an overall improvement. With catalyst **E** an excellent enantioselectivity with good diastereselectivity of the major isomer was achieved in a short reaction time (Table 1, entry 5). Compared to **E**, a decrease of enantioselectivity (93% to 58%) was observed with the quinidine-derived catalyst **F** (Table 1, entry 6). No conversion was detected with catalyst **G**, probably because a more basic moiety is needed than a hydrogen bond directing group (Table 1, entry 7). The squaramide catalyst **H** also gave a low enantioselectivity (Table 1, entry 8).

With the suitable catalyst **E** in hand, further screening of catalyst loading, solvent and temperature was conducted (Table 2). The catalyst loading could be reduced to 5 mol% while still providing good results (Table 2, entries 1–3). After testing different chlorinated solvents (Table 2, entry 4 and 5), $CHCl_3$ proved

Table 1. Catalyst screening for the nitroalkane-Michael/Henry sequence of 2-(nitromethyl)benzaldehyde (**3a**) and nitrostyrene (**4a**) yielding diastereomeric mixtures of the 1,2,3,4-tetrahydronaphthalen-1-ols **5**.



Entry[a]	Cat.	*t* [d]	Yield [%][b]	**5**, *dr*[c]	*ee* [%][d]
1	**A**	9	43	1:1:6:3	46[e]
2	**B**	5.5	83	1:2:15:7	27
3	**C**	6	49	n.d.[f]	59
4	**D**	7	61	n.d.[f]	13[e]
5	**E**	0.5	59	1:2:22:3	93
6	**F**	0.5	72	1:1:40:3	58[e]
7	**G**	21	0	–	–
8	**H**	1	62	1:2:14:4	28[e]

[a] Reactions were performed on a 0.5 mmol scale at −20 °C.
[b] Combined yield of isolated product **5** as a mixture of diastereomers after flash chromatography.
[c] Determined by ^{1}H NMR spectroscopy.
[d] Determined by HPLC analysis on a chiral stationary phase for the major (1*R*,2*S*,3*R*,4*R*)-**5** diastereomer.
[e] The opposite enantiomer of the major diastereomer was obtained.
[f] Not determined.

to be the best choice with excellent 94% *ee*. Common solvents in organocatalytic reactions like toluene and

Table 2. Screening for the optimized conditions including catalyst loading, solvent and temperature for the nitroalkane-Michael/Henry reaction sequence.

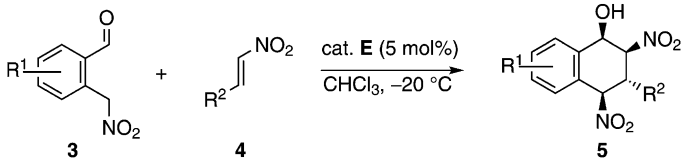
Entry[a]	**E** [mol%]	Solvent	T [°C]	Time [h]	Yield [%][b]	**5**, *dr*[c]	*ee* [%][d]
1	10	$ClCH_2CH_2Cl$	−20	15	61	1:2:20:2	88
2	5	$ClCH_2CH_2Cl$	−20	15	60	1:2:16:2	88
3	1	$ClCH_2CH_2Cl$	−20	–[e]	–	–	–
4	5	$CHCl_3$	−20	18	81	1:3:30:3	94 (>99)[f]
5	5	CH_2Cl_2	−20	15	69	1:2:21:3	85
6	5	toluene	−20	18	68	1:3:31:3	87
7	5	Et_2O	−20	96	64	1:2:19:3	91
8	5	EtOAc	−20	110	80	1:2:14:2	94
9	5	$CHCl_3$	0	6	57	1:2:24:4	89
10	5	$CHCl_3$	r.t.	6	55	1:2:20:4	74

[a] The reactions were performed on a 0.5 mmol scale.
[b] Combined yield of isolated product **5** as a mixture of diastereomers after flash chromatography.
[c] Determined by ^1H NMR spectroscopy.
[d] Determined by HPLC analysis on a chiral stationary phase for the major (1*R*,2*S*,3*R*,4*R*)-**5** diastereomer.
[e] Stopped after four weeks.
[f] After one recrystallization.

diethyl ether (Table 2, entry 6 and 7) could not compete with chloroform. Ethyl acetate gave the same induction but with lack of a good diastereoselectivity (Table 2, entry 8). Increasing the temperature resulted in a drop of enantioselectivity (Table 2, entries 9 and 10).

After the optimization of the conditions, we investigated the scope of this reaction (Table 3). The reactions between 2-(nitromethyl)benzaldehyde (**3a**) and various aromatic nitroalkenes **4** were examined. After column chromatography, the diastereomeric mixtures were recrystallized and afforded the (1*R*,2*S*,3*R*,4*R*)-1,2,3,4-tetrahydronaphthalen-1-ols **5a–o** (*dr* > 95:5).

Table 3. Scope of the nitroalkane-Michael/Henry reaction sequence to form the 1,2,3,4-tetrahydronaphthalen-1-ols **5a–o**.



5[a]	R^1	R^2	Time [d]	Yield [%][b,c]	*ee* [%][d]
a	H	Ph	1	70	94 (>99)
b	H	4-MeC_6H_4	5	81	83
c	H	4-$MeOC_6H_4$	3.5	40	95
d	H	3,4,5-$(MeO)_3C_6H_2$	4	71	78
e	H	3-$NO_2C_6H_4$	5	48	97
f	H	4-$NO_2C_6H_4$	7	50	78 (91)
g	H	3-ClC_6H_4	1	78	87 (97)
h	H	4-ClC_6H_4	1	84	80 (82)
i	H	3,4-$OCH_2OC_6H_3$	5	51	67 (87)
j	H	2-naphthyl	3	68	92
k	H	2-furyl	17	62	64
l[e]	3-OMe	Ph	6	41	63 (70)
m	4-Br	Ph	6	35	81 (97)
n	5-F	Ph	4	45	77
o	H	Ph (*Z*)	6.5	42	86

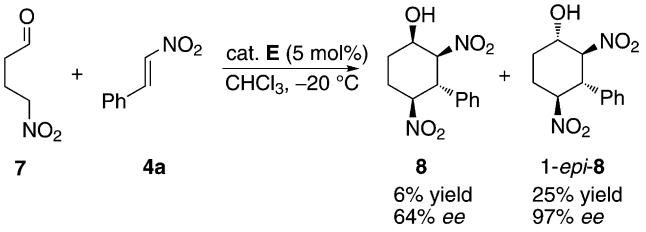
[a] The reactions were performed on a 0.5 mmol scale at −20 °C.
[b] Combined yield of isolated product **5** as a mixture of diastereomers after flash chromatography.
[c] After one recrystallization, *dr* > 95:5 (major *vs.* the minor diastereomers).
[d] Determined by HPLC analysis on a chiral stationary phase; value in bracket after one recrystallization.
[e] The 4-*epimer* was obtained as major diastereomer.

Electron-donating substituents of the aromatic group R^2 like methyl or methoxy groups (Table 3, **5b–d**) generated the corresponding 1,2,3,4-tetrahydronaphthalen-1-ols in moderate to good yields (40–81%) and very good enantioselectivities (78–95% *ee*). The position of the substituents had a strong influence on the stereoselectivity. Nitroolefins with a substituent in *meta*-position delivered much better enantiomeric excesses than their *para*-counterparts (97% *vs.* 78% *ee* for the nitro group and 87% *vs.* 80% *ee* for chloro group, respectively, Table 3, **5e–h**). Changing the phenyl for a naphthyl group led to a good yield (68%) and a high enantioselectivity (92% *ee*) of **5j**.[12] As a representative for heterocyclic compounds, the furyl group was introduced, but only moderate results were obtained after a long reaction time (62% yield, 64% *ee*, **5k**). It should be mentioned that 1,2-disubstituted nitroalkenes **4** cannot be used as Michael-acceptors in our protocol.

A few functionalized 2-(nitromethyl)benzaldehydes **3l–n** were also synthesized and applied in the cascade protocol (Table 3). They gave moderate yields (35–45%) and good enantioselectivities (63–81% *ee*). Interestingly, the major diastereomer was different as compared to the previous ones (Table 3, **5l**). Propably due to the steric interference of the *ortho*-substituted methoxy group 4-*epi*-**5l** was formed. To determine the influence of the nitroalkene configuration the synthesis of **5a** was repeated using the corresponding (*Z*)-configured isomer (Table 3, **5o**). Expecting a 3,4-*cis*-relationship as the stereochemical outcome, surprisingly the same product **5a** was obtained, but in a moderate yield of 42% and almost the same enantioselectivity (86% *ee*). We assume that under the reaction conditions a slow (*E*/*Z*) isomerization of nitrostyrene can occur, which may explain the long reaction time and lower yield.

A further experiment was conducted on a gram scale to prove the scalability of the model reaction for compound **5a**. As expected, the reaction proceeded in the determined way with similar yield (1.36 g, 60%) and enantioselectivity (85% *ee*). It is notable that the amount of catalyst could be reduced to 1 mol% with no drop of enantioselectivity.

In addition, we extended our domino protocol to an aliphatic γ-nitro aldehyde, which should undergo the same cascade reaction like the aromatic counterpart **3a** (Scheme 2). To prove this, 4-nitrobutanal (**7**) was reacted with (*E*)-nitrostyrene (**4a**) and furnished the secondary cyclohexanols **8** and 1-*epi*-**8**.[13] Interestingly, the absolute configuration of the secondary cyclohexanol **8** matches with the configuration of the tetrahydronaphthalenes **5a–o**, however, only a poor yield (6%) and moderate enantioselectivity (64% *ee*) was obtained. In contrast, the 1-*epimer* of **8** gave a 25% yield with excellent enantioselectivity (97% *ee*). This stereochemical outcome may be explained

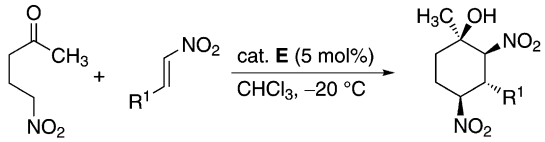


Scheme 2. Asymmetric organocatalytic domino reaction to form the secondary cyclohexanols **8** and 1-*epi*-**8**.

by the fact that the 1-epimeric cyclohexanol **8** has each substituent in its thermodynamically more stable equatorial conformation. In the case of the tetrahydronaphthalen-1-ols, after the first bond is generated from the substrates **3** and **4**, they form a conformationally more rigid intermediate, whose configuration determines the final stereochemical outcome. The relatively low combined yield can be explained with the tendency of the γ-nitro aldehyde **7** to undergo an intermolecular Henry reaction.

By expanding the scope of our asymmetric organocatalytic domino reaction to the aliphatic γ-nitro ketone substrate **10** we were able to generate a tertiary alcohol function with the final Henry ring closure. The polysubstitued tertiary cyclohexanols **11a–d** (Table 4) were synthesized in moderate to good yields (47–68%), very good diastereomeric ratios ($dr > 95:5$) and with very good enantioselectivities (87–94% *ee*). The relative configuration of the tertiary cyclohexanols **11** could be assigned by NOE measurements (Figure 1, **11a**). The absolute configuration of the tet-

Table 4. Scope of the nitroalkane-Michael/Henry reaction sequence to form tertiary cyclohexanols **11a–d**.



11[a]	R^1	*t* [d]	Yield [%][b,c]	*ee* [%][d]
a	Ph	1	61	89 (94)
b	4-ClC_6H_4	5	77	89
c	3-$NO_2C_6H_4$	3.5	68	91
d	2-BrC_6H_4	4	47	87

[a] The reactions were performed on a 0.5 mmol scale at −20 °C.
[b] Combined yield of isolated product **11** as a mixture of diastereomers after flash chromatography.
[c] After one recrystallization, $dr > 95:5$ (major *vs.* the minor diastereomers).
[d] Determined by HPLC analysis on a chiral stationary phase; value in brackets after one recrystallization.

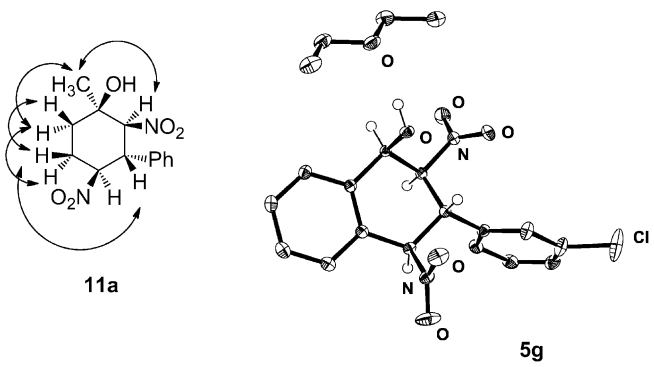


Figure 1. Determination of the relative and absolute configuration by NOE (**11a**) and X-ray crystal structure analysis (**5g**).[14]

rahydronaphthalenes was determined by single crystal X-ray analysis of compound **5g**[14] (Figure 1).

Conclusions

In summary, we have developed an organocatalytic nitroalkane-Michael/Henry domino reaction starting drom different γ-nitro aldehydes or ketones and nitroalkenes. Using a hydrogen-bonding organocatalyst on a squaramide basis, polysubstituted 1,2,3,4-tetrahydronaphthalen-1-ols or secondary/tertiary cyclohexanols bearing four contiguous stereocenters were obtained in moderate to good yields (25–84%), after crystallization in high diasteriomeric ratios ($dr > 95:5$) and very good to excellent enantiomeric excesses (63–99% *ee*).

Experimental Section

Flash column chromatography: SIL G-25 UV_{254} (size 0.040–0.063 mm) Machery&Nagel. TLC: silica gel 60 F254 plates, Merck, Darmstadt. Visualization of the developed TLC plates was performed with UV radiation (254 nm) or by staining with a potassium permanganate solution. Elemental analyses were carried out with a Vario EL element analyzer. Melting points were determined with a Büchi Melting Point B-540 apparatus. Optical rotation values were taken on a Perkin–Elmer P241 polarimeter. The *ee* values were determined by analytical HPLC with a Hewlett–Packard 1100 Series instrument using chiral stationary phases. IR spectra were recorded on a Perkin–Elmer FT-IR Spectrum 100 spectrometer. ^{1}H and ^{13}C NMR spectra were measured at ambient temperature with Varian Gemini 300, Varian Mercury 300 or Varian Innova 600 spectrometers using TMS as internal standard. Mass spectra were recorded on a Finnigan SSQ7000 (EI 70 eV) spectrometer, high resolution mass spectra on a Finnigan MAT 95 and high resolution ESI spectra on a ThermoFisher Scientific LTQ-Orbitrap XL.

General Procedure for the Asymmetric Synthesis of 1,2,3,4-Tetrahydronaphthalen-1-ol Derivatives 5a–o and the Cyclohexanols 1-*epi*-8 and 11a–d

In a glass vial equipped with a magnetic stirring bar the γ-nitro carbonyl compound **3**, **7** or **10** (1.0 equiv,. 0.5 mmol), nitroalkene **4** (1.1 equiv., 0.5–0.6 mmol) and catalyst **E** (5 mol%) were dissolved in chloroform (1 mL). After stirring at −20 °C for the appropriate time the crude solution was directly purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 8:1 to 2:1) to afford the compounds **5a–o**, **8** and **11a–d** as colorless to yellow solids.

(1*R*,2*S*,3*R*,4*R*)-2,4-Dinitro-3-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol (5a): Synthesized according to the general procedure by using 2-(nitromethyl)benzaldehyde (**3a**) (80 mg, 0.48 mmol) and (*E*)-(2-nitrovinyl)benzene (**4a**) (85 mg, 0.57 mmol); colorless solid; yield: 106 mg (70%); $[\alpha]_D^{25}$: +60.4 (*c* 0.28, $CHCl_3$); 99% *ee*; $R_f = 0.71$ (*n*-hexane/ethyl acetate = 1:1); mp 164 °C. IR (film): $\nu = 3511$, 2044, 1996, 1613, 1552, 1493, 1451, 1367, 1291, 1230, 1118, 1048, 911, 851, 775, 700 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD): $\delta =$ 4.67 (dd, $J = 10.3$, 12.4 Hz, 1H, C*H*Ph), 5.31 (d, $J = 3.6$ Hz, 1H, C*H*OH), 5.62 (dd, $J = 3.6$, 12.4 Hz, 1H, C*H*NO_2), 6.08 (d, $J = 10.3$ Hz, 1H, C*H*NO_2), 7.26 (d, $J = 7.8$ Hz, 1H, CH_{arom}), 7.29–7.39 (m, 5H, CH_{arom}), 7.43 (ddd, $J = 1.7$, 7.2, 7.7 Hz, 1H, CH_{arom}), 7.48–7.52 (m, 1H, CH_{arom}), 7.54 (dd, $J = 1.7$, 7.7 Hz, 1H, CH_{arom}), the OH proton could not be observed; ^{13}C NMR (100 MHz CD_3OD): $\delta = 42.0$ (*C*HPh), 68.3 (*C*HOH), 87.1 (*C*HNO_2), 92.5 (*C*HNO_2), 125.6 (*C*H$_{arom}$), 127.7 (2*C*H$_{arom}$), 127.9 (*C*$_{arom}$), 128.6 (2*C*H$_{arom}$), 128.8 (*C*$_{arom}$), 129.4 (*C*H$_{arom}$), 129.7 (*C*H$_{arom}$), 130.4 (*C*H$_{arom}$), 135.8 (*C*$_{arom}$), 137.1 (*C*$_{arom}$); MS (EI, 70 eV): *m/z* (%) = 222 (21), 221 [$M^+ - HNO_2 - NO_2$] (100), 204 (21), 203 (20); anal. calcd. for $C_{16}H_{14}N_2O_5$: C 61.14, H 4.49, N 8.91; found: C 61.00, H 4.50, N 8.66.

(1*R*,2*S*,3*R*,4*R*)-2,4-Dinitro-3-*p*-tolyl-1,2,3,4-tetrahydronaphthalen-1-ol (5b): Synthesized according to the general procedure by using 2-(nitromethyl)benzaldehyde (**3a**) (80 mg, 0.48 mmol) and (*E*)-1-methyl-4-(2-nitrovinyl)benzene (**4b**) (80 mg, 0.49 mmol); colorless solid; yield: 127 mg (81%); $[\alpha]_D^{25}$: +52.4 (*c* 1.04, $CHCl_3$); 83% *ee*; $R_f = 0.69$ (*n*-hexane/ethyl acetate = 1:1); mp 165 °C. IR (film): $\nu = 3825$, 3560, 3438, 2919, 2707, 2480, 2273, 2225, 2174, 2109, 2036, 1980, 1910, 1554, 1454, 1367, 1293, 1229, 1120, 1049, 926, 809, 773, 725 cm^{-1}; ^{1}H NMR (600 MHz, CD_3OD): $\delta = 2.32$ (s, 3H, CH_3), 4.64 (dd, $J = 10.4$, 12.4 Hz, 1H, C*H*Ar), 5.31 (d, $J = 3.6$ Hz, 1H, C*H*OH), 5.59 (dd, $J = 3.6$, 12.4 Hz, 1H, C*H*NO_2), 6.06 (d, $J = 10.4$ Hz, 1H, C*H*NO_2), 7.17 (d, $J =$ 7.9 Hz, 2H, 2CH_{arom}), 7.25–7.26 (m, 3H, 3CH_{arom}), 7.44 (ddd, $J = 1.4$, 7.5, 7.7 Hz, 1H, CH_{arom}), 7.49–7.51 (m, 1H, CH_{arom}), 7.55 (dd, $J = 1.1$, 7.7 Hz, 1H, CH_{arom}), the OH proton could not be observed; ^{13}C NMR (150 MHz CD_3OD): $\delta = 19.7$ (*C*H_3), 41.6 (*C*HAr), 68.3 (*C*HOH), 87.2 (*C*HNO_2), 92.6 (*C*HNO_2), 125.6 (*C*H$_{arom}$), 127.6 (2*C*H$_{arom}$), 128.8 (*C*$_{arom}$), 129.2 (2x*C*H$_{arom}$), 129.4 (*C*H$_{arom}$), 129.7 (*C*H$_{arom}$), 130.4 (*C*H$_{arom}$), 134.0 (*C*$_{arom}$), 135.8 (*C*$_{arom}$), 137.9 (*C*$_{arom}$); MS (EI, 70 eV): *m/z* (%) = 236 (24), 235 [$M^+ - HNO_2 - NO_2$] (100), 218 (19), 202 (18), 143 (16), 115 (26); anal. calcd. for $C_{17}H_{16}N_2O_5$: C 62.19, H 4.91, N 8.53; found: C 61.84, H 4.79, N 8.54.

(1*R*,2*S*,3*R*,4*R*)-3-(4′-Methoxyphenyl)-2,4-dinitro-1,2,3,4-tetrahydronaphthalen-1-ol (5c): Synthesized according to

the general procedure by using 2-(nitromethyl)benzaldehyde (**3a**) (83 mg, 0.50 mmol) and (*E*)-1-methoxy-4-(2-nitrovinyl)-benzene (**4c**) (95 mg, 0.53 mmol); colorless solid; yield: 69 mg (40%); $[\alpha]_D^{25}$: +71.4 (*c* 0.28, $CHCl_3$); 95% *ee*; R_f = 0.64 (*n*-hexane/ethyl acetate = 1:1); mp 173 °C. IR (film): ν = 3562, 2983, 2907, 1610, 1549, 1512, 1457, 1360, 1249, 1181, 1119, 1095, 1049, 1024, 913, 827, 779, 725 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ = 3.77 (s, 3H, OCH_3), 4.56 (br s, 1H, O*H*), 4.60 (dd, *J* = 10.4, 12.4 Hz, 1H, C*H*Ar), 5.28 (d, *J* = 3.6 Hz, 1H, C*H*OH), 5.55 (dd, *J* = 3.6, 12.4 Hz, 1H, $CHNO_2$), 6.05 (d, *J* = 10.4 Hz, 1H, $CHNO_2$), 6.89 (dd, *J* = 2.1, 6.7 Hz, 2H, 2 CH_{arom}), 7.24 (d, *J* = 7.8 Hz, 1H, CH_{arom}), 7.29 (dd, *J* = 2.1, 6.7 Hz, 2H, 2 CH_{arom}), 7.43 (ddd, *J* = 1.7, 7.3, 7.7 Hz, 1H, CH_{arom}), 7.47–7.51 (m, 1H, CH_{arom}), 7.53 (dd, *J* = 1.6, 7.7 Hz, 1H, CH_{arom}); ^{13}C NMR (125 MHz CD_3OD): δ = 41.3 (*C*HAr), 54.3 (OCH_3), 68.2 (*C*HOH), 87.3 ($CHNO_2$), 92.7 ($CHNO_2$), 114.0 (2 CH_{arom}), 125.5 (CH_{arom}), 128.7 (C_{arom}), 128.8 (2 CH_{arom}), 129.4 (CH_{arom}), 129.7 (CH_{arom}), 130.4 (CH_{arom}), 135.6 (C_{arom}), 135.7 (C_{arom}), 159.6 (C_{arom}); MS (EI, 70 eV): *m/z* (%) = 344 [M^+] (4), 280 (21), 251 (100), 234 (39), 219 (19), 218 (16), 190 (16), 189 (33), 165 (18), 143 (26), 121 (68), 115 (48), 77 (20); anal. calcd. for $C_{17}H_{16}N_2O_6$: C 59.30, H 4.68, N 8.14; found: C 59.00, H 4.50, N 8.00.

(1*R*,2*S*,3*R*,4*R*)-3-(3′,4′,5′-Trimethoxyphenyl)-2,4-dinitro-1,2,3,4-tetrahydronaphthalen-1-ol (5d): Synthesized according to the general procedure by using 2-(nitromethyl)benzaldehyde (**3a**) (80 mg, 0.48 mmol) and (*E*)-1,2,3-trimethoxy-5-(2-nitrovinyl)benzene (**4d**) (122 mg, 0.51 mmol); colorless solid; yield: 139 mg (71%); $[\alpha]_D^{25}$: +82.1 (*c* 0.75, $CHCl_3$); 78% *ee*; R_f = 0.45 (*n*-hexane/ethyl acetate = 1:1); mp 167 °C. IR (film): ν = 3379, 3005, 2942, 2900, 2844, 1595, 1554, 1511, 1459, 1428, 1362, 1245, 1187, 1127, 1062, 993, 932, 893, 834, 782, 758, 711 725 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ = 3.74 (s, 3H, OCH_3), 3.80 (s, 6H, 2 OCH_3), 4.62 (dd, *J* = 10.4, 12.3 Hz, 1H, C*H*Ar), 5.31 (d, *J* = 3.6 Hz, 1H, C*H*OH), 5.65 (dd, *J* = 3.6, 12.4 Hz, 1H, $CHNO_2$), 6.10 (d, *J* = 10.3 Hz, 1H, $CHNO_2$), 6.68 (s, 2H, 2x CH_{arom}), 7.26 (d, *J* = 7.5 Hz, 1H, CH_{Ar}), 7.44 (ddd, *J* = 1.7, 7.2, 7.8, 1H, CH_{arom}), 7.48–7.52 (m, 1H, CH_{arom}), 7.54 (dd, *J* = 1.7, 7.7 Hz, 1H, CH_{arom}), the OH proton could not be observed; ^{13}C NMR (100 MHz CD_3OD): δ = 42.4 (*C*HAr), 55.3 (2 OCH_3), 59.6 (OCH_3), 68.3 (*C*HOH), 86.9 ($CHNO_2$), 92.5 ($CHNO_2$), 105.0 (2 CH_{arom}), 125.6 (CH_{arom}), 128.7 (C_{arom}), 129.4 (CH_{arom}), 129.8 (CH_{arom}), 130.4 (CH_{arom}), 133.0 (C_{arom}), 135.7 (C_{arom}), 137.5 (C_{arom}), 153.5 (2 C_{arom}); MS (EI, 70 eV): *m/z* (%) = 404 [M^+] (29), 340 (19), 312 (77), 311 (100), 281 (24), 280 (25), 181 (44), 168 (25), 165 (21); HR-MS (ESI): *m/z* = 427.1112, calcd. for $C_{19}H_{20}N_2O_8Na$ [M^+ + Na]: 427.1107.

(1*R*,2*S*,3*R*,4*R*)-2,4-Dinitro-3-(3′-nitrophenyl)-1,2,3,4-tetrahydronaphthalen-1-ol (5e): Synthesized according to the general procedure by using 2-(nitromethyl)benzaldehyde (**3a**) (81 mg, 0.49 mmol) and (*E*)-1-nitro-3-(2-nitrovinyl)benzene (**4e**) (99 mg, 0.51 mmol); colorless solid; yield: 85 mg (48%); $[\alpha]_D^{25}$: +52.6 (*c* 0.68, $CHCl_3$); 97% *ee*; R_f = 0.62 (*n*-hexane/ethyl acetate = 1:1); mp 156 °C. IR (film): ν = 3491, 2924, 2858, 1698, 1666, 1530, 1350, 1112, 1055, 909, 812, 749 cm^{-1}; ^1H NMR (600 MHz, CD_3OD): δ = 4.87 (dd, *J* = 10.4, 12.3 Hz, 1H, C*H*Ar), 5.38 (d, *J* = 3.6 Hz, 1H, C*H*OH), 5.76 (dd, *J* = 3.6, 12.3 Hz, 1H, $CHNO_2$), 6.20 (d, *J* = 10.3 Hz, 1H, $CHNO_2$), 7.31 (d, *J* = 7.9 Hz, 1H, CH_{arom}), 7.48 (ddd, *J* = 1.5, 7.5, 7.7 Hz, 1H, CH_{arom}), 7.53–7.57 (m, 1H, CH_{arom}), 7.58 (dd, *J* = 1.0, 7.8 Hz, 1H, CH_{arom}), 7.65 (dd, *J* = 7.9, 8.0 Hz, 1H, CH_{arom}), 7.86 (d, *J* = 7.7 Hz, 1H, CH_{arom}), 8.22 (dd, *J* = 2.1, 8.3 Hz, 1H, CH_{arom}), 8.36 (dd, *J* = 1.9, 1.9 Hz, 1H, CH_{arom}); ^{13}C NMR (150 MHz CD_3OD): δ = 41.9 (*C*HAr), 68.3 (*C*HOH), 86.8 ($CHNO_2$), 91.9 ($CHNO_2$), 122.6 (CH_{arom}), 122.9 (CH_{arom}), 125.8 (CH_{arom}), 128.2 (C_{arom}), 129.5 (CH_{arom}), 130.0 (CH_{arom}), 130.0 (CH_{arom}), 130.4 (CH_{arom}), 134.4 (CH_{arom}), 135.7 (C_{arom}), 139.6 (C_{arom}), 148.6 (C_{arom}); MS (EI, 70 eV): *m/z* (%) = 295 [M^+-H_2O, $-NO_2$] (80), 266 (48), 262 (17), 249 (59), 232 (18), 202 (100), 200 (21), 189 (27), 176 (20), 127 (19), 101 (17), 76 (16); HR-MS (ESI): *m/z* = 313.0820, calcd. for $C_{16}H_{13}N_2O_5$ [M^+-NO_2]: 313.0819.

(1*R*,2*S*,3*R*,4*R*)-2,4-Dinitro-3-(4′-nitrophenyl)-1,2,3,4-tetrahydronaphthalen-1-ol (5f): Synthesized according to the general procedure by using 2-(nitromethyl)benzaldehyde (**3a**) (86 mg, 0.52 mmol) and (*E*)-1-nitro-4-(2-nitrovinyl)benzene (**4f**) (106 mg, 0.55 mmol); colorless solid; yield: 94 mg (50%); $[\alpha]_D^{25}$: +27.4 (*c* 0.65, $CHCl_3$); 91% *ee*; R_f = 0.60 (*n*-hexane/ethyl acetate = 1:1); mp 156 °C. IR (film): ν = 3511, 1603, 1553, 1514, 1349, 1115, 1057, 957, 913, 856, 766, 701 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ = 4.87 (dd, *J* = 10.3, 12.3 Hz, 1H, C*H*Ar), 5.37 (d, *J* = 3.5 Hz, 1H, C*H*OH), 5.70 (dd, *J* = 3.5, 12.2 Hz, 1H, $CHNO_2$), 6.15 (d, *J* = 10.2 Hz, 1H, $CHNO_2$), 7.29 (d, *J* = 7.7 Hz, 1H, CH_{arom}), 7.46 (ddd, *J* = 1.8, 7.1, 7.8 Hz, 1H, CH_{arom}), 7.50–7.54 (m, 1H, CH_{arom}), 7.56 (dd, *J* = 1.7, 7.7 Hz, 1H, CH_{arom}), 7.67 (dd, *J* = 2.0, 6.8 Hz, 2H, 2 CH_{arom}), 8.24 (dd, *J* = 2.0, 6.8 Hz, 2H, 2 CH_{arom}), the OH proton could not be observed; ^{13}C NMR (100 MHz CD_3OD): δ = 41.9 (*C*HAr), 68.3 (*C*HOH), 86.8 ($CHNO_2$), 91.8 ($CHNO_2$), 123.6 (2 CH_{arom}), 125.8 (CH_{arom}), 128.2 (C_{arom}), 129.1 (2 CH_{arom}), 129.5 (CH_{arom}), 130.0 (CH_{arom}), 130.4 (CH_{arom}), 135.7 (C_{Ar}), 144.8 (C_{arom}), 147.8 (C_{arom}); MS (EI, 70 eV): *m/z* (%) = 295 [M^+-H_2O, $-NO_2$] (54), 294 (61), 266 (50), 249 (49), 218 (21), 202 (100), 200 (37), 191 (15), 189 (34), 165 (16); HR-MS (ESI): *m/z* = 313.0819, calcd. for $C_{16}H_{13}N_2O_5$ [M^+-NO_2]: 313.0819.

(1*R*,2*S*,3*R*,4*R*)-3-(3′-Chlorophenyl)-2,4-dinitro-1,2,3,4-tetrahydronaphthalen-1-ol (5g): Synthesized according to the general procedure by using 2-(nitromethyl)benzaldehyde (**3a**) (80 mg, 0.48 mmol) and (*E*)-1-chloro-3-(2-nitrovinyl)-benzene (**4g**) (92 mg, 0.50 mmol); colorless solid; yield: 132 mg (78%); $[\alpha]_D^{25}$: +64.6 (*c* 0.84, $CHCl_3$); 97% *ee*; R_f = 0.67 (*n*-hexane/ethyl acetate = 1:1); mp 163 °C. IR (film): ν = 3544, 1597, 1551, 1480, 1434, 1362, 1286, 1229, 1197, 1101, 1056, 938, 886, 780, 725 cm^{-1}; ^1H NMR (600 MHz, CD_3OD): δ = 4.69 (dd, *J* = 10.3, 12.3 Hz, 1H, C*H*Ar), 5.34 (d, *J* = 3.6 Hz, 1H, C*H*OH), 5.64 (dd, *J* = 3.6, 12.4 Hz, 1H, $CHNO_2$), 6.10 (d, *J* = 10.4 Hz, 1H, $CHNO_2$), 7.28 (d, *J* = 7.8 Hz, 1H, CH_{arom}), 7.32–7.37 (m, 3H, 3 CH_{arom}), 7.44–7.47 (m, 2H, 2 CH_{arom}), 7.51–7.53 (m, 1H, CH_{arom}), 7.56 (dd, *J* = 1.3, 7.7 Hz, 1H, CH_{arom}), the OH proton could not be observed; ^{13}C NMR (150 MHz CD_3OD): δ = 41.8 (*C*HAr), 68.3 (*C*HOH), 86.9 ($CHNO_2$), 92.2 ($CHNO_2$), 125.7 (CH_{arom}), 126.3 (CH_{arom}), 127.9 (CH_{arom}), 128.1 (CH_{arom}), 128.5 (C_{arom}), 129.5 (CH_{arom}), 129.9 (CH_{arom}), 130.2 (CH_{arom}), 130.4 (CH_{arom}), 134.5 (C_{arom}), 135.7 (C_{arom}), 139.5 (C_{arom}); MS (EI, 70 eV): *m/z* (%) = 284 (18), 257 (24), 256 (22), 255 [M^+-HNO_2, $-NO_2$] (100), 238 (28), 220 (30), 202 (47), 191 (15), 115 (15); HR-MS (ESI): *m/z* = 371.0405, calcd. for $C_{16}H_{13}N_2O_5ClNa$ [M^+ + Na]: 371.0405.

(1*R*,2*S*,3*R*,4*R*)-3-(4′-Chlorophenyl)-2,4-dinitro-1,2,3,4-tetrahydronaphthalen-1-ol (5h): Synthesized according to the general procedure by using 2-(nitromethyl)benzaldehyde (**3a**) (88 mg, 0.53 mmol) and (*E*)-1-chloro-4-(2-nitrovinyl)-benzene (**4h**) (100 mg, 0.55 mmol); colorless solid; yield: 156 mg (84%); $[\alpha]_D^{25}$: +58.1 (*c* 1.00, $CHCl_3$); 82% *ee*; R_f = 0.71 (*n*-hexane/ethyl acetate = 1:1); mp 164 °C. IR (film): ν = 3554, 1553, 1491, 1365, 1289, 1228, 1118, 1093, 1055, 1015, 948, 909, 821, 774, 709 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ = 4.70 (dd, *J* = 10.4, 12.3 Hz, 1H, C*H*Ar), 5.33 (d, *J* = 3.5 Hz, 1H, C*H*OH), 5.62 (dd, *J* = 3.6, 12.3 Hz, 1H, C*H*NO_2), 6.09 (d, *J* = 10.3 Hz, 1H, C*H*NO_2), 7.28 (d, *J* = 7.9 Hz, 1H, CH_{arom}), 7.37 (dd, *J* = 2.0, 6.5 Hz, 2H, 2xCH_{arom}), 7.40 (dd, *J* = 2.1, 6.5 Hz, 2H, 2CH_{arom}), 7.45 (ddd, *J* = 1.2, 7.5, 7.6 Hz, 1H, CH_{arom}), 7.50–7.53 (m, 1H, CH_{arom}), 7.56 (dd, *J* = 0.8, 7.7 Hz, 1H, CH_{arom}), the OH proton could not be observed; ^{13}C NMR (100 MHz CD_3OD): δ = 41.5 (*C*HAr), 68.3 (*C*HOH), 87.0 (*C*HNO_2), 92.3 (*C*HNO_2), 125.6 (*C*H_{arom}), 128.5 (*C*$_{arom}$), 128.7 (2*C*H_{arom}), 129.4 (2*C*H_{arom}), 129.4 (*C*H_{arom}), 129.8 (*C*H_{arom}), 130.4 (*C*H_{arom}), 133.8 (*C*$_{arom}$), 135.7 (*C*$_{arom}$), 136.0 (*C*$_{arom}$); MS (EI, 70 eV): *m/z* (%) = 257 (33), 256 (20), 255 [M^+−HNO_2, −NO_2] (100), 238 (26), 220 (30), 202 (36), 131 (16), 115 (25), 101 (21); HR-MS (ESI): *m/z* = 348.0507, calcd. for $C_{16}H_{13}N_2O_5Cl$ [M^+]: 348.0508.

(1*R*,2*S*,3*R*,4*R*)-3-(3′,4′-Methylenedioxyphenyl)-2,4-dinitro-1,2,3,4-tetrahydronaphthalen-1-ol (5i): Synthesized according to the general procedure by using 2-(nitromethyl)-benzaldehyde (**3a**) (80 mg, 0.48 mmol) and (*E*)-1,2-methylendioxy-4-(2-nitrovinyl)benzene (**4i**) (97 mg, 0.50 mmol); colorless solid; yield: 88 mg (51%); $[\alpha]_D^{25}$: +38.4 (*c* 0.88, $CHCl_3$); 87% *ee*; R_f = 0.64 (*n*-hexane/ethyl acetate = 1:1); mp 161 °C. IR (film) ν = 3532, 2905, 1697, 1551, 1493, 1448, 1363, 1242, 1113, 1035, 925, 859, 810, 755 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ = 4.58 (dd, *J* = 10.4, 12.4 Hz, 1H, C*H*Ar), 5.29 (d, *J* = 3.6 Hz, 1H, C*H*OH), 5.55 (dd, *J* = 3.6, 12.4 Hz, 1H, C*H*NO_2), 5.93 (d, *J* = 1.2 Hz, 1H, C*H*H), 5.94 (d, *J* = 1.2 Hz, 1H, C*H*H), 6.04 (d, *J* = 10.4 Hz, 1H, C*H*NO_2), 6.77 (d, *J* = 8.0 Hz, 1H, CH_{arom}), 6.84 (dd, *J* = 1.8, 8.0 Hz, 1H, CH_{arom}), 6.88 (d, *J* = 1.8 Hz, 1H, CH_{arom}), 7.24 (d, *J* = 7.7 Hz, 1H, CH_{arom}), 7.42 (ddd, *J* = 1.8, 7.2, 7.8 Hz, 1H, CH_{arom}), 7.47–7.51 (m, 1H, CH_{arom}), 7.53 (dd, *J* = 1.8, 7.7 Hz, 1H, CH_{arom}), the OH proton could not be observed; ^{13}C NMR (100 MHz CD_3OD): δ = 41.2 (*C*HAr), 68.2 (*C*HOH), 87.1 (*C*HNO_2), 92.6 (*C*HNO_2), 101.3 (*C*H_2), 107.7 (*C*H_{arom}), 108.1 (*C*H_{arom}), 121.5 (*C*H_{arom}), 125.5 (*C*H_{arom}), 128.8 (*C*$_{arom}$), 129.4 (*C*H_{arom}), 129.7 (*C*H_{arom}), 130.4 (*C*H_{arom}), 130.5 (*C*$_{arom}$), 135.7 (*C*$_{arom}$), 147.6 (*C*$_{arom}$), 148.2 (*C*$_{arom}$); MS (EI, 70 eV): *m/z* (%) = 358 [M^+] (18), 294 (27), 266 (26), 265 (100), 248 (50), 235 (29), 207 (24), 190 (15), 189 (55), 178 (23), 165 (16), 148 (37), 135 (49), 124 (22), 121 (20), 119 (22), 118 (16), 115 (21), 94 (17), 91 (33), 89 (27), 65 (23), 63 (17); HR-MS (ESI): *m/z* = 381.0692, calcd. for $C_{17}H_{14}N_2O_7Na$ [M^++Na]: 381.0693.

(1*R*,2*S*,3*R*,4*R*)-3-(2′-Naphthyl)-2,4-dinitro-1,2,3,4-tetrahydronaphthalen-1-ol (5j): Synthesized according to the general procedure by using 2-(nitromethyl)benzaldehyde (**3a**) (82 mg, 0.50 mmol) and (*E*)-2-(2-nitrovinyl)naphthalene (**4j**) (105 mg, 0.53 mmol); colorless solid; yield: 123 mg (68%); $[\alpha]_D^{25}$: +71.0 (*c* 1.01, $CHCl_3$); 92% *ee*; R_f = 0.68 (*n*-hexane/ethyl acetate = 1:1); mp 168 °C. IR (film): ν = 3853, 3061, 2913, 2653, 2290, 2108, 2065, 1984, 1912, 1550, 1454, 1364, 1364, 1125, 1060, 964, 902, 862, 817, 751 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ = 4.86 (dd, *J* = 10.3, 12.3 Hz, 1H, C*H*Ar), 5.37 (d, *J* = 3.6 Hz, 1H, C*H*OH), 5.75 (dd, *J* = 3.6, 12.3 Hz, 1H, C*H*NO_2), 6.21 (d, *J* = 10.3 Hz, 1H, C*H*NO_2), 7.28 (d, *J* = 7.9 Hz, 1H, CH_{arom}), 7.42–7.54 (m, 5H, 5CH_{arom}), 7.57 (dd, *J* = 1.5, 7.7 Hz, 1H, CH_{arom}), 7.81–7.86 (m, 3H, 3CH_{arom}), 7.88 (d, *J* = 1.6 Hz, 1H, CH_{arom}), the OH proton could not be observed; ^{13}C NMR (100 MHz CD_3OD): δ = 42.2 (*C*HAr), 68.4 (*C*HOH), 87.2 (*C*HNO_2), 92.5 (*C*HNO_2), 125.0 (*C*H_{arom}), 125.7 (*C*H_{arom}), 126.0 (*C*H_{arom}), 126.1 (*C*H_{arom}), 127.1 (*C*H_{arom}), 127.3 (*C*H_{arom}), 127.5 (*C*H_{arom}), 128.5 (*C*H_{arom}), 128.8 (*C*$_{arom}$), 129.4 (*C*H_{arom}), 129.8 (*C*H_{arom}), 130.4 (*C*H_{arom}), 133.1 (*C*$_{arom}$), 133.4 (*C*$_{arom}$), 134.5 (*C*$_{arom}$), 135.8 (*C*$_{arom}$); MS (EI, 70 eV): *m/z* (%) = 364 [M^+−H] (8), 272 (26), 271 (100), 254 (38), 253 (34), 252 (29), 143 (25), 141 (21), 128 (22), 127 (36), 126 (30), 115 (36); HR-MS (ESI): *m/z* = 387.0951, calcd. for $C_{20}H_{16}N_2O_5Na$ [M^++Na]: 387.0951.

(1*R*,2*S*,3*R*,4*R*)-3-(2′-Furyl)-2,4-dinitro-1,2,3,4-tetrahydronaphthalen-1-ol (5k): Synthesized according to the general procedure by using 2-(nitromethyl)benzaldehyde (**3a**) (85 mg, 0.52 mmol) and (*E*)-(2-nitrovinyl)furyl (**4k**) (76 mg, 0.55 mmol); brownish solid; yield: 97 mg (62%); $[\alpha]_D^{25}$: +16.3 (*c* 1.02, $CHCl_3$); 64% *ee*; R_f = 0.70 (*n*-hexane/ethyl acetate = 1:1); mp 158 °C. IR (film) ν = 3464, 2918, 2566, 2062, 1738, 1548, 1453, 1360, 1287, 1194, 1144, 1096, 1061, 1013, 935, 886, 819, 773, 741 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ = 4.93 (dd, *J* = 9.5, 11.8 Hz, 1H, C*H*Ar), 5.28 (d, *J* = 3.3 Hz, 1H, C*H*OH), 5.41 (dd, *J* = 3.4, 11.9 Hz, 1H, C*H*NO_2), 6.05 (d, *J* = 9.4 Hz, 1H, C*H*NO_2), 6.29 (d, *J* = 3.1 Hz, 1H, CH_{arom}), 6.33–6.34 (m, 1H, CH_{arom}), 7.27 (d, *J* = 7.8 Hz, 1H, CH_{arom}), 7.38–7.49 (m, 4H, 4xCH_{arom}), the OH proton could not be observed; ^{13}C NMR (100 MHz CD_3OD): δ = 36.1 (*C*HAr), 68.2 (*C*HOH), 85.3 (*C*HNO_2), 89.5 (*C*HNO_2), 108.3 (*C*H_{arom}), 110.3 (*C*H_{arom}), 126.4 (*C*H_{arom}), 128.1 (*C*$_{arom}$), 129.4 (*C*H_{arom}), 129.9 (*C*H_{arom}), 130.0 (*C*H_{arom}), 135.7 (*C*$_{arom}$), 142.7 (*C*H_{arom}), 150.0 (*C*$_{arom}$); MS (EI, 70 eV): *m/z* (%) = 257 [M^+−HNO_2] (4), 212 (19), 211 (100), 194 (30), 183 (17), 165 (51), 155 (18), 153 (19), 152 (16), 128 (15), 115 (31); anal. calcd. for $C_{14}H_{12}N_2O_6$: C 55.27 H 3.98, N 9.21; found: C 54.84, H 4.29, N 8.82.

(1*R*,2*S*,3*R*,4*S*)-5-Methoxy-2,4-dinitro-3-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol (5l): Synthesized according to the general procedure by using 3-methoxy-2-(nitromethyl)benzaldehyde (**3l**) (104 mg, 0.53 mmol) and (*E*)-(2-nitrovinyl)-benzene (**4a**) (85 mg, 0.57 mmol); colorless solid; yield: 75 mg (41%); $[\alpha]_D^{25}$: −167.3 (*c* 0.89, $CHCl_3$); 70% *ee*; R_f = 0.47 (*n*-hexane/ethyl acetate = 1:1); mp 199 °C. IR (film): ν = 3571, 3472, 3006, 2936, 1696, 1596, 1547, 1472, 1363, 1331, 1268, 1188, 1088, 1053, 1011, 974, 925, 853, 810, 784, 747 741 cm^{-1}; ^1H NMR (600 MHz, CD_3OD): δ = 3.80 (s, 3H, OCH_3), 4.49 (dd, *J* = 6.1, 12.8 Hz, 1H, C*H*Ph), 5.43 (d, *J* = 4.0 Hz, 1H, C*H*OH), 6.01 (dd, *J* = 4.0, 12.8 Hz, 1H, C*H*NO_2), 6.15 (d, *J* = 6.1 Hz, 1H, C*H*NO_2), 7.05 (d, *J* = 8.3 Hz, 1H, CH_{arom}), 7.17 (d, *J* = 7.7 Hz, 1H, CH_{arom}), 7.27–7.35 (m, 5H, 5CH_{arom}), 7.54 (dd, *J* = 8.1, 8.1 Hz, 1H, CH_{arom}), the OH proton could not be observed; ^{13}C NMR (150 MHz CD_3OD): δ = 39.7 (*C*HPh), 54.9 (*C*H_3), 68.0 (*C*HOH), 84.1 (*C*HNO_2), 86.7 (*C*HNO_2), 110.5 (*C*H_{arom}), 117.0 (*C*$_{arom}$), 122.1 (*C*H_{arom}), 126.6 (2*C*H_{Ar}), 127.7 (*C*H_{Ar}), 128.6 (2*C*H_{arom}), 131.8 (*C*H_{arom}), 135.9 (*C*$_{arom}$), 138.3 (*C*$_{arom}$), 157.4 (*C*$_{arom}$); MS (EI, 70 eV): *m/z* (%) = 298 [M^+−NO_2] (3),

251 (100), 236 (17); HR-MS (ESI): m/z = 298.1074, calcd. for $C_{17}H_{16}N_1O_4$ [M^+-NO_2]: 298.1074.

(1*R*,2*S*,3*R*,4*R*)-6-Bromo-2,4-dinitro-3-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol (5m): Synthesized according to the general procedure by using 4-bromo-2-(nitromethyl)benzaldehyde (**3m**) (130 mg, 0.53 mmol) and (*E*)-(2-nitrovinyl)benzene (**4a**) (83 mg, 0.56 mmol); colorless solid; yield: 73 mg (35%); $[\alpha]_D^{25}$: +19.1 (*c* 0.90, $CHCl_3$); 97% *ee*; R_f = 0.74 (*n*-hexane/ethyl acetate = 1:1); mp 116 °C. IR (film): ν = 3499, 2922, 2855, 1703, 1553, 1486, 1362, 1287, 1189, 1117, 1053, 922, 874, 824, 761 cm^{-1}; ^1H NMR (600 MHz, CD_3OD): δ = 4.69 (dd, J = 10.1, 12.2 Hz, 1H, C*H*Ph), 5.30 (d, J = 3.5 Hz, 1H, C*H*OH), 5.59 (dd, J = 3.6, 12.3 Hz, 1H, C*H*NO_2), 6.07 (d, J = 10.4 Hz, 1H, C*H*NO_2), 7.30–7.39 (m, 5H, 5CH_{arom}), 7.43 (s, 1H, CH_{arom}), 7.48 (d, J = 8.3 Hz, 1H, CH_{arom}), 7.68 (dd, J = 1.9, 8.3 Hz, 1H, CH_{arom}), the OH proton could not be observed; ^{13}C NMR (150 MHz CD_3OD): δ = 39.6 (*C*HPh), 67.8 (*C*HOH), 87.0 (*C*HNO_2), 91.6 (*C*HNO_2), 122.9 (C_{arom}), 127.7 (2CH_{arom}), 128.0 (CH_{arom}), 128.7 (2CH_{arom}), 128.7 (CH_{arom}), 130.8 (C_{arom}), 132.1 (CH_{arom}), 133.0 (CH_{arom}), 135.2 (C_{arom}), 136.9 (C_{arom}); MS (EI, 70 eV): m/z (%) = 330, 328 [M^+-H_2O, $-NO_2$] (47, 50), 301 (63), 299 (57), 284 (15), 283 (23), 282 (36), 249 (17), 220 (100), 203 (24), 202 (82), 191 (19), 126 (15), 115 (17), 91 (15), 77 (18); HR-MS (ESI): m/z = 414.9901, calcd. for $C_{16}H_{13}N_2O_5BrNa$ [M^+ + Na]: 414.9900.

(1*R*,2*S*,3*R*,4*R*)-7-Fluoro-2,4-dinitro-3-phenyl-1,2,3,4-tetrahydronaphthalen-1-ol (5n): Synthesized according to the general procedure by using 5-fluoro-2-(nitromethyl)benzaldehyde (**3n**) (90 mg, 0.49 mmol) and (*E*)-(2-nitrovinyl)benzene (**4a**) (84 mg, 0.51 mmol); brownish oil; yield: 73 mg (45%); $[\alpha]_D^{25}$: +8.0 (*c* 0.20, $CHCl_3$); 77% *ee*; R_f = 0.76 (*n*-hexane/ethyl acetate = 1:1). IR (film): ν = 3480, 2922, 2286, 2110, 2070, 1990, 1922, 1740, 1607, 1553, 1500, 1446, 1362, 1250, 1151, 1110, 1056, 877, 821, 758 cm^{-1}; ^1H NMR (600 MHz, CD_3OD): δ = 4.69 (dd, J = 10.1, 12.3 Hz, 1H, C*H*Ph), 5.31 (d, J = 3.6 Hz, 1H, C*H*OH), 5.62 (dd, J = 3.6, 12.2 Hz, 1H, C*H*NO_2), 6.05 (d, J = 10.0 Hz, 1H, C*H*NO_2), 7.22 (ddd, J = 2.8, 8.5, 8.6 Hz, 1H, CH_{arom}), 7.29–7.39 (m, 7H, 7CH_{arom}), the OH proton could not be observed; ^{13}C NMR (150 MHz CD_3OD): δ = 42.0 (*C*HPh), 67.9 (*C*HOH), 87.0 (*C*HNO_2), 91.8 (*C*HNO_2), 116.3 (d, $^2J_{C,F}$ = 22.3 Hz, *C*H$_{arom}$), 116.6 (d, $^2J_{C,F}$ = 22.3 Hz, *C*H$_{arom}$), 126.9 (C_{arom}), 127.7 (2CH_{arom}), 127.9 (CH_{arom}), 128.4 (d, $^3J_{C,F}$ = 8.7 Hz, CH_{arom}), 128.7 (2CH_{arom}, C_{arom}), 137.1 (C_{arom}), 163.2 (d, $^1J_{C,F}$ = 248.3 Hz, *C*F); ^{19}F NMR (565 MHz, CD_3OD): δ = −113.1; MS (EI, 70 eV): m/z (%) = 286 [M^+-NO_2] (1), 239 (100), 220 (19); HR-MS (ESI): m/z = 355.0700, calcd. for $C_{16}H_{13}N_2O_5FNa$ [M^+ + Na]: 355.0701.

(1*S*,2*S*,3*R*,4*S*)-2,4-Dinitro-3-phenylcyclohexan-1-ol (1-*epi*-8): Synthesized according to the general procedure by using 4-nitrobutanal (**7**) (60 mg, 0.51 mmol) and (*E*)-(2-nitrovinyl)benzene (**4a**) (85 mg, 0.57 mmol); colorless solid; yield: 34 mg (25%); $[\alpha]_D^{25}$: −24.1 (*c* 1.00, $CHCl_3$); 97% *ee*; mp 145 °C. IR (film): ν = 2924, 2855, 1736, 1547, 1494, 1453, 1372, 1284, 1214, 1068, 1014, 981, 861, 760 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ = 1.70–1.82 (m, 1H, C*H*H), 2.17–2.24 (m, 2H, 2C*H*H), 2.36–2.42 (m, 1H, C*H*H), 3.73 (dd, J = 11.7, 11.7 Hz, 1H, C*H*Ph), 4.20 (ddd, J = 4.5, 9.7, 14.0 Hz, C*H*OH), 4.76 (dd, J = 9.7, 11.9 Hz, 1H, C*H*NO_2), 5.06 (ddd, J = 4.3, 11.7, 11.7 Hz, 1H, C*H*NO_2), 7.22–7.34 (m, 5H, 5CH_{arom}), the OH proton could not be observed; ^{13}C NMR (100 MHz CD_3OD): δ = 29.0 (*C*H_2), 27.8 (*C*H_2), 50.1 (*C*HPh), 70.6 (*C*HOH), 87.3 (*C*HNO_2), 94.3 (*C*HNO_2), 127.9 (*C*H$_{arom}$), 128.3 (2*C*H$_{arom}$), 128.5 (2*C*H$_{arom}$), 134.1 (C_{arom}); MS (EI, 70 eV): m/z (%) = 266 [M^+] (28), 189 (24), 174 (16), 173 (100), 172 (22), 171 (15), 155 (33), 146 (16), 145 (57), 143 (30), 131 (22), 130 (15), 129 (59), 128 (37), 117 (34), 116 (15), 115 (56), 105 (43), 103 (16), 91 (96), 77 (24), 67 (17), 55 (15); HR-MS (ESI): m/z = 266.0900, calcd. for $C_{12}H_{14}N_2O_5$ [M^+]: 266.0897.

(1*R*,2*S*,3*R*,4*S*)-1-Methyl-2,4-dinitro-3-phenylcyclohexan-1-ol (11a): Synthesized according to the general procedure by using 5-nitropentan-2-one (**10**) (71 mg, 0.54 mmol) and (*E*)-(2-nitrovinyl)benzene (**4a**) (85 mg, 0.57 mmol); colorless solid; yield: 93 mg (61%); $[\alpha]_D^{25}$: −15.1 (*c* 1.00, $CHCl_3$); 94% *ee*; R_f = 0.65 (*n*-hexane/ethyl acetate = 1:1); mp 182 °C. IR (film): ν = 3559, 2939, 1737, 1548, 1495, 1451, 1373, 1327, 1290, 1137, 1089, 1031, 949, 917, 887, 825, 761, 729, 701 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ = 1.32 (s. 3H, CH_3), 1.85 (ddd, J = 4.0, 13.9, 14.2 Hz, 1H, C*H*H), 1.96 (ddd, J = 3.1, 4.3, 14.3 Hz, 1H, C*H*H), 2.14 (dddd, J = 3.1, 4.0, 4.0, 12.4 Hz, 1H, C*H*H), 2.47 (dddd, J = 4.3, 12.5, 12.5, 13.7, 1H, C*H*H), 4.18 (dd, J = 11.8, 11.8 Hz, 1H, C*H*Ph), 4.95 (ddd, J = 4.3 Hz, 11.9, 11.9 Hz, 1H, C*H*NO_2), 5.02 (d, J = 12.0 Hz, 1H, C*H*NO_2), 7.23–7.32 (m, 5H, 5CH_{arom},) the OH proton could not be observed; ^{13}C NMR (100 MHz CD_3OD): δ = 25.4 (*C*H_3), 26.3 (*C*H_2), 35.6 (*C*H_2), 45.8 (*C*HPh), 68.9 (*C*CH_3OH), 88.7 (*C*HNO_2), 94.1 (*C*HNO_2), 127.9 (*C*H$_{arom}$), 128.3 (4*C*H$_{arom}$), 135.4 (C_{arom}); MS (EI, 70 eV): m/z (%) = 280 [M^+] (61), 187 (75), 186 (42), 185 (15), 173 (17), 171 (16), 169 (35), 158 (39), 157 (25), 156 (16), 149 (18), 145 (39), 144 (17), 143 (90), 131 (21), 130 (22), 129 (69), 128 (58), 127 (20), 117 (61), 116 (19), 115 (68), 105 (86), 103 (22), 91 (100), 77 (35), 71 (29), 65 (17), 55 (16); anal. calcd. for $C_{13}H_{16}N_2O_5$: C 55.71 H 5.75, N 9.99; found: C 55.46, H 5.24, N 9.69.

(1*R*,2*S*,3*R*,4*S*)-3-(4′-Chlorophenyl)-1-methyl-2,4-dinitrocyclohexan-1-ol (11b): Synthesized according to the general procedure by using 5-nitropentan-2-one (**10**) (63 mg, 0.48 mmol) and (*E*)-1-chloro-4-(2-nitrovinyl)benzene **4** (R^1 = 4-ClC_6H_4) (89 mg, 0.48 mmol); colorless solid; yield: 100 mg (77%); $[\alpha]_D^{25}$: −21.6 (*c* 0.70, $CHCl_3$); 89% *ee*; R_f = 0.61 (*n*-hexane/ethyl acetate = 1:1); mp 110 °C. IR (film): ν = 3554, 2968, 1549, 1493, 1451, 1371, 1285, 1179, 1132, 1093, 1029, 918, 891, 822, 755 cm^{-1}; ^1H NMR (600 MHz, CD_3OD): δ = 1.32 (s, 3H, CH_3), 1.84 (ddd, J = 4.0, 14.0, 14.1 Hz, 1H, C*H*H), 1.96 (ddd, J = 3.1, 4.2, 14.3 Hz, C*H*H), 2.15 (dddd, J = 3.1, 4.0, 4.0, 12.4 Hz, 1H, C*H*H), 2.47 (dddd, J = 4.2, 12.4, 12.4, 13.8 Hz, 1H, C*H*H), 4.19 (dd, J = 11.8, 11.8 Hz, 1H, C*H*Ar), 4.93 (ddd, J = 4.4, 11.8, 11.9 Hz, 1H, C*H*NO_2), 5.01 (d, J = 12.0 Hz, 1H, C*H*NO_2), 7.27–7.32 (m, 4H, 4CH_{arom}), the OH proton could not be observed; ^{13}C NMR (150 MHz CD_3OD): δ = 25.4 (*C*H_3), 26.3 (*C*H_2), 35.6 (*C*H_2), 45.3 (*C*HAr), 68.9 (*C*CH_3OH), 88.5 (*C*HNO_2), 93.9 (*C*HNO_2), 128.4 (2*C*H$_{arom}$), 129.9 (2*C*H$_{arom}$), 133.9 (C_{arom}), 134.3 (C_{arom}); MS (EI, 70 eV): m/z (%) = 316, 314 [M^+] (31, 97), 237 (20), 223 (31), 222 (38), 221 (93), 220 (96), 207 (22), 206 (18), 205 (15), 204 (35), 203 (44), 194 (23), 193 (25), 192 (68), 191 (42), 190 (22), 179 (53), 177 (73), 168 (15), 167 (33), 165 (39), 163 (30), 153 (27), 152 (22), 151 (47), 149 (16), 143 (16), 142 (25), 141 (73), 139 (100), 129 (44), 128 (64), 127 (71), 125 (75), 116 (30), 115 (84), 102 (19), 101 (27), 99 (27), 91 (16), 83 (29), 81 (22), 77 (30), 75 (17), 71

(44); HR-MS (ESI): $m/z = 314.0663$, calcd. for $C_{13}H_{15}N_2O_5Cl$ $[M^+]$: 314.0664.

(1*R*,2*S*,3*R*,4*S*)-1-Methyl-2,4-dinitro-3-(3′-nitrophenyl)cyclohexan-1-ol (11c): Synthesized according to the general procedure by using 5-nitropentan-2-one (10) (71 mg, 0.54 mmol) and (*E*)-1-nitro-3-(2-nitrovinyl)benzene **4** (R^1 = 3-$NO_2C_6H_4$) (107 mg, 0.55 mmol); colorless solid; yield: 120 mg (68%); $[\alpha]_D^{25}$: −9.6 (*c* 0.57, CH_3OH); 91% *ee*; R_f = 0.58 (*n*-hexane/ethyl acetate = 1:1); mp 188 °C. IR (film) ν = 3582, 3082, 2935, 2646, 1536, 1454, 1352, 1122, 1032, 913, 868, 815, 730 cm^{-1}; ^1H NMR (600 MHz, CD_3OD): $\delta = 1.37$ (s, 3H, CH_3), 1.91 (ddd, $J = 4.0, 14.0, 14.2$ Hz, 1H, C*H*H), 2.01 (ddd, $J = 3.4, 3.9, 14.4$ Hz, 1H, C*H*H), 2.22 (dddd, $J = 3.1, 4.0, 4.0, 12.5$ Hz, 1H, C*H*H), 2.52 (dddd, $J = 4.2, 12.5, 12.5, 13.8$ Hz, 1H, C*H*H), 4.39 (dd, $J = 11.7, 11.7$ Hz, 1H, C*H*Ar), 5.07 (ddd, $J = 4.3, 11.8, 11.8$ Hz, 1H, C*H*NO_2), 5.17 (d, $J = 11.9$ Hz, 1H, C*H*NO_2), 7.58 (dd, $J = 8.0, 8.0$ Hz, 1H, CH_{arom}), 7.77 (d, $J = 7.5$ Hz, 1H, CH_{arom}), 8.17 (ddd, $J = 1.0, 2.2, 8.3$ Hz, 1H, CH_{arom}), 8.31 (s, 1H, CH_{arom}), the OH proton could not be observed; ^{13}C NMR (150 MHz CD_3OD): $\delta = 25.4$ (*C*H_3), 26.3 (*C*H_2), 35.6 (*C*H_2), 45.7 (*C*HAr), 68.9 (*C*CH_3OH), 88.2 (*C*HNO_2), 93.7 (*C*HNO_2), 122.9 (*C*H_{arom}), 123.0 (*C*H_{arom}), 129.7 (*C*H_{arom}), 135.0 (*C*H_{arom}), 137.9 (C_{arom}), 148.4 (C_{arom}); MS (EI, 70 eV): *m/z* (%) = 325 $[M^+]$ (27), 232 (100), 218 (58), 215 (20), 214 (45), 207 (27), 203 (25), 202 (50), 190 (69), 188 (31), 184 (16), 172 (16), 171 (18), 168 (24), 167 (24), 154 (16), 152 (22), 150 (33); HR-MS (ESI) $m/z = 348.0803$, calcd. for $C_{13}H_{15}N_3O_7Na$ $[M^+ + Na]$: 348.0802.

(1*R*,2*S*,3*R*,4*S*)-3-(2′-Bromophenyl)-1-methyl-2,4-dinitrocyclohexan-1-ol (11d): Synthesized according to the general procedure by using 5-nitropentan-2-one (**10**) (73 mg, 0.56 mmol) and (*E*)-1-bromo-2-(2-nitrovinyl)benzene **4** (R^1 = 2-BrC_6H_4) (130 mg, 0.57 mmol); colorless solid; yield: 94 mg (47%); $[\alpha]_D^{25}$: −10.3 (*c* 0.84, $CHCl_3$); 87% *ee*; mp 151 °C. IR (film): ν = 3579, 3292, 2918, 2852, 2008, 1731, 1547, 1471, 1367, 1285, 1248, 1177, 1129, 1031, 949, 916, 889, 820, 768, 722 cm^{-1}; ^1H NMR (600 MHz, CD_3OD): $\delta = 1.33$ (s, 3H, CH_3), 1.84 (ddd, $J = 4.1, 14.0, 14.1$ Hz, 1H, C*H*H), 1.97 (ddd, $J = 3.1, 4.3, 14.3$ Hz, 1H, C*H*H), 2.13 (dddd, $J = 3.0, 4.0, 4.0, 12.7$ Hz, 1H, C*H*H), 2.55 (dddd, $J = 4.4, 12.0, 12.6, 13.8$ Hz, 1H, C*H*H), 4.85–4.92 (m, 1H, C*H*NO_2), 4.98–5.00 (m, 2H, C*H*NO_2, C*H*Ar), 7.13 (ddd, $J = 1.7, 7.4, 8.1$ Hz, 1H, CH_{arom}), 7.35 (ddd, $J = 1.3, 7.5, 7.7$ Hz, 1H, CH_{arom}), 7.51 (dd, $J = 1.3, 8.1$, 1H, CH_{arom}), 7.64 (dd, $J = 1.6, 7.9$ Hz, 1H, CH_{arom}), the OH proton could not be observed; ^{13}C NMR (150 MHz CD_3OD): $\delta = 25.4$ (*C*H_3), 26.1 (*C*H_2), 35.5 (*C*H_2), 43.7 (*C*HAr), 69.0 (*C*CH_3OH), 88.3 (*C*HNO_2), 94.2 (*C*HNO_2), 126.0 (C_{arom}), 127.7 (*C*H_{arom}), 128.0 (*C*H_{arom}), 129.3 (*C*H_{arom}), 133.4 (*C*H_{arom}), 135.1 (C_{arom}); MS (EI, 70 eV): *m/z* (%) = 360, 358 $[M^+]$ (58, 62), 279 (91), 266 (33), 265 (32), 249 (23), 247 (16), 223 (28), 221 (25), 202 (68), 185 (36), 183 (23), 171 (40), 169 (33), 168 (61), 159 (20), 154 (16), 152 (15), 145 (18), 144 (23), 143 (23), 142 (41), 141 (35), 131 (17), 130 (19), 129 (44), 128 (100), 127 (15), 116 (53), 115 (87), 102 (25), 101 (15), 99 (15), 91 (19), 89 (16), 83 (21), 77 (24), 71 (31); HR-MS (ESI): $m/z = 358.0159$, calcd. for $C_{13}H_{15}N_2O_5Br$ $[M^+]$: 358.0159.

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