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# Dynamic Kinetic Asymmetric Ring-Opening/Reductive Amination Sequence of Racemic Nitroepoxides with Chiral Amines: Enantioselective Synthesis of Chiral Vicinal Diamines

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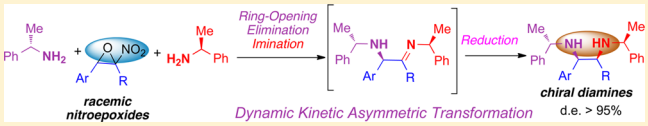
Supporting Information

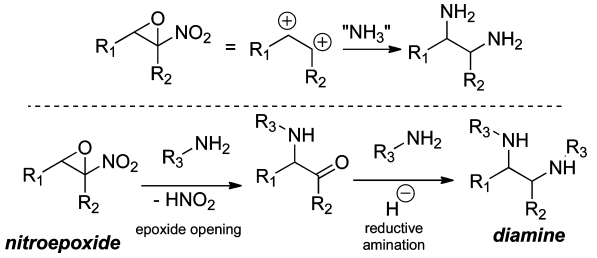
**ABSTRACT:** We report a highly diastereoselective synthesis of vicinal diamines by the treatment of nitroepoxides with primary amines and then a reducing agent. When using a chiral primary amine, racemic nitroepoxides are transformed into chiral diamines as a single enantiomers (>95:5 er) through a dynamic kinetic asymmetric transformation (DYKAT). The overall process is a one-pot procedure combining the exposure of nitroepoxides to chiral amines to afford diastereomeric mixtures of aminoimines and subsequent stereoselective imine reduction.




Dynamic kinetic asymmetric transformations (DYKAT) have emerged as an important synthetic tool to convert a racemate into a single enantiomer in some stereoselective transformations.[1−5] These transformations are particularly important when applied to the synthesis of highly interesting compounds such as natural products,[6−10] allenes,[11] Baylis−Hillman adducts.[12]

Chiral vicinal diamines are important building blocks found in many chiral catalysts and intermediates in the synthesis of biologically active small molecules and therapeutics.[13−15] In contrast, nitroepoxides have been rarely used in synthesis and represent unique opportunities due to their unusual reactivity.[16−19] These strained systems display two highly oxidized vicinal positions by nature of their chemical connectivity and hence are potentially exploitable as synthons with vicinal electrophilic centers (Scheme 1). Given our interest in this

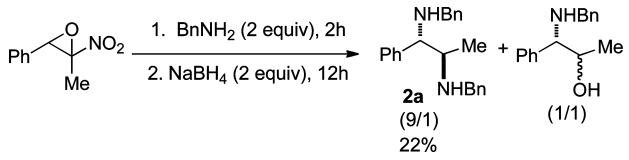
**Scheme 1. Nitroepoxides as Precursors of Vicinal Diamines**




reactivity epoxide class, we envisioned vicinal diamines might be prepared by treating nitroepoxides with 2 equiv of an amine (Scheme 1): the first equivalent of amine would undergo nucleophilic addition to the $\beta$-position of the epoxide, thereby giving rise to a transient aminoketone.[16−19] This intermediate could then form an imine with the second equivalent of amine, which, upon reduction with a suitable hydride reagent, could afford a diamine. Although there is no reported asymmetric synthesis of nitroepoxides, we envisioned preparing chiral diamines by performing a resolution of the starting racemic nitroepoxides using a chiral amine. Essentially, the initial SN2 epoxide ring-opening could be influenced by a specific enantiomer of the chiral primary amine.

Nitroepoxides **1a−i** were easily prepared through epoxidation of the corresponding nitroalkenes. Nitroepoxides resulted to be very stable compounds. We began our studies of the preparation of vicinal diamines by combining nitroepoxide **1a** with benzylamine (2 equiv) in dichloromethane for 2 h and then sodium borohydride (2 equiv) for 12 h. We were pleased to see that the reaction afforded diamine **2a** as a 9:1 mixture of stereoisomers (Scheme 2). A side product of the reaction was the corresponding aminoalcohol (Scheme 2).

**Scheme 2. Preparation of Diamine 2a**




A higher yield was obtained when the reaction was performed for longer time and the number of equivalents of the amine was increased to four (Table 1, entry 1). In addition, improved diastereoselectivities and yields were obtained with sodium triacetoxyborohydride as the reducing agent employing a nonextractive workup (Table 1, entry 2).[20] The use of sodium triacetoxyborohydride as a reducing agent required 3 equiv of reductant for the reaction to be completed. To study the scope of the reaction various nitroepoxide electrophiles were subjected to the optimal reaction conditions. Nitroepoxides having an aryl group and an alkyl group gave high selectivity (Table 1, entries 1−9), while compounds with alkyl groups in

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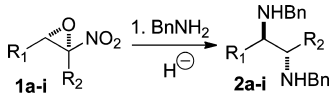
**Table 1. Optimization of Conditions for the Synthesis of Diamines**[a]



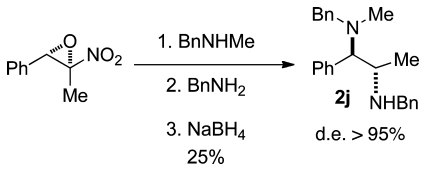

| entry | $R_1$, $R_2$ | prod | exp[b] | dr (*anti*:*syn*)[c] | yield [%][d] |
|---|---|---|---|---|---|
| 1 | Ph, Me | **2a** | A | 90:10 | 60 |
| 2 | Ph, Me | **2a** | B | 97:3 | 65 |
| 3 | Ph, *i*-Pr | **2b** | B | 97:3 | 65 |
| 4 | Ph, *n*-Bu | **2c** | B | 97:3 | 65 |
| 5 | *p*F-Ph, Me | **2d** | A | 83:17 | 63 |
| 6 | *p*F-Ph, Me | **2d** | B | 94:6 | 70 |
| 7 | *p*Me-Ph, Me | **2e** | B | 90:10 | 58 |
| 8 | *p*F-Ph, Et | **2f** | A | >99:1 | 43 |
| 9 | *p*F-Ph, Et | **2f** | B | >99:1 | 73 |
| 10 | *i*-Bu, Me | **2g** | A | 62:38 | 61 |
| 11 | *i*-Bu, Me | **2g** | B | 54:46 | 52 |
| 12 | *n*-Pr, Me | **2h** | B | 64:36 | 59 |
| 13 | *n*-Pr, Et | **2i** | B | 65:35 | 45 |

[a]Reactions were carried out using nitroepoxide (1.0 equiv), amine (4.0 equiv) in DCM at room temperature for 6 h, and then reducing agent (2.0 or 3.0 equiv) was added and stirred for 16 h. [b]Experimental procedure: (A) $NaBH_4$ (2.0 equiv) in DCM and then extractive workup; (B) NaBH(OAc)3 (3.0 equiv) in DCE and then nonextractive workup. [c]Ratio measured by $^1H$ NMR of the crude reaction mixtures. [d]Yield of isolated product (see ref note 21 for comments about byproducts). DCM = dichloromethane; DCE = dichloroethane.

both $\alpha$- and $\beta$-positions provided lower stereoselectivity (Table 1, entries 10−13).[21] Nitroepoxides with aryl groups in both $\alpha$- and $\beta$-positions did not afford diamine, and other compounds were isolated instead.[21]

Other potential parameters of the reaction were explored. For example, if a secondary amine was used (*N*-benzylmethylamine), then the corresponding diamine was obtained in a very low yield (3%). Aminoketone or an equimolecular mixture of aminoalcohols were obtained as the main products. Interestingly, an *N*,*N*-disubstituted diamine **2j** could be prepared when benzylamine was added after the secondary amine addition,[22] followed by the final reducing step (Scheme 3).

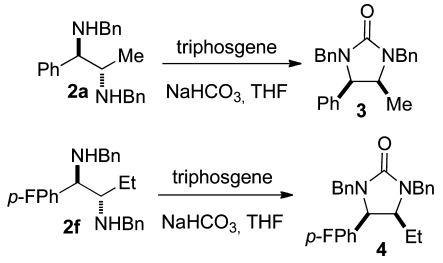
**Scheme 3. Synthesis of Diamine 2j**




Diamines **2a** and **2f** were transformed into cyclic ureas **3** and **4**, respectively. The stereochemistry of the diamines **2a** and **2f** was assigned by NMR experiments over the cyclic ureas (Scheme 4).[23] Also the crystal structure of the dihydrochloride of diamine **2k** was determined (see Supporting Information).[24]

Since $\alpha$-amino imines tautomerize easily,[25] isotopic experiments were performed to provide information as to which carbon atom of the amino imine underwent addition by the hydride during the reduction step (Scheme 5). When nitroepoxide **1a** was treated with benzylamine and sodium deuteroborohydride is used as a reducing agent, the labeled diamine **5** was obtained in 68% yield as a 9:1 mixture of

**Scheme 4. Stereochemistry Assignment through Cyclic Ureas**

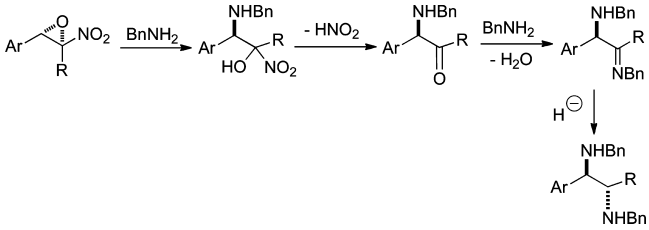



**Scheme 5. Deuterium Labeling Experiments**


diastereomers (Scheme 5). These results indicated not only that the imine located on the C1 position was undergoing reduction, but also that the process proceeded with a high level of dr, most likely due to either a chelation model or alternatively described through a Felkin−Anh model if the aromatic group is considered the "large" substituent. In the case of 1,2-dialkyl diamines **2g**−**2i**, the alkyl group did not determine the selectivity of the attack, and thus, no preferential attack of the hydride ion occurred, affording diamines in low stereoselectivity.

Diamines would be formed through reductive amination of the corresponding aminoketone already formed by reaction between nitroepoxide and 1 equiv of the amine (Scheme 6). The reaction between aminoketone and a second equivalent of amine would yield the $\alpha$-aminoimine, which can epimerize. Reduction would afford the corresponding diamine.

**Scheme 6. Mechanism of the Diamine Synthesis**




Chiral diamines were prepared in high diastereoselectivity when nitroepoxides **1a**−**d** and inexpensive L-$\alpha$-methyl benzylamine were used (Table 2).[21] For all cases, the obtained diamine displayed a (1*R*,2*S*) stereochemistry.

On the basis of our earlier studies (see above), our current understanding of this interesting process is as follows. In the case of using a chiral amine, the process constitutes a DYKAT. The reaction between aminoketone and a second equivalent of the amine would yield an isomeric mixture of $\alpha$-aminoimines (Scheme 7). These intermediates would go into a DYKAT: isomeric $\alpha$-aminoimines can interconvert to furnish the *R* isomer as the main product, which upon reduction would furnish the final diamine. The overall process is a one-pot procedure combining the treatment of nitroepoxides with a chiral amine to give a diastereomeric mixture of aminoimines and then stereoselective reduction that proceeds through a dynamic kinetic asymmetric transformation.


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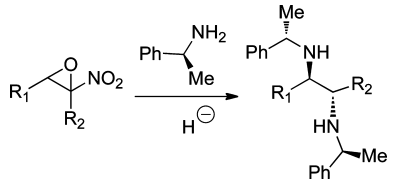
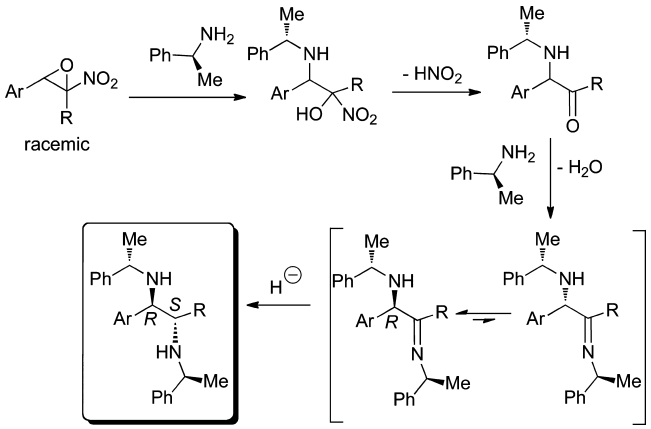
**Table 2. Preparation of Chiral Diamines**[a]



| entry | $R_1$, $R_2$ | prod | exp[b] | dr (*a1*:*a2*:*s1*:*s2*)[c] | yield [%][d] |
|---|---|---|---|---|---|
| 1 | Ph, Me | **2k** | A | 80:16:4:0 | 70 |
| 2 | Ph, Me | **2k** | B | 94:5:1:0 | 72 |
| 3 | *p*F-Ph, Me | **2l** | B | >99:1:0:0 | 66 |
| 4 | *p*F-Ph, Et | **2m** | B | >99:1:0:0 | 55 |

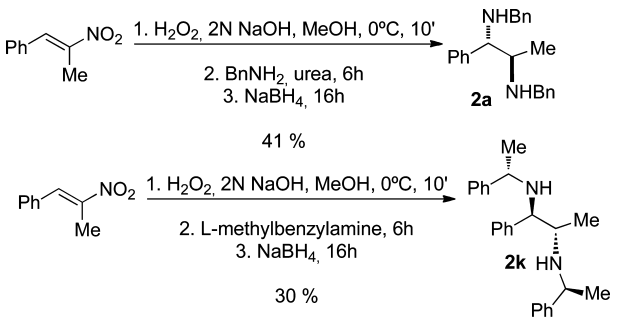
[a]Reactions were carried out using nitroepoxide (1.0 equiv), amine (4.0 equiv) in DCM at room temperature for 6 h, and then reducing agent (2.0 or 3.0 equiv) was added and stirred for 16 h. [b]Experimental procedure: (A) $NaBH_4$ (2.0 equiv) in DCM and then extractive workup; (B) NaBH(OAc)3 (3.0 equiv) in DCE and then nonextractive workup. [c]*a1*:*a2*:*s1*:*s2* refers to *anti* 1:*anti* 2:*syn* 1:*syn* 2 stereoisomers, respectively. Ratio measured by $^1$H NMR of the crude reaction mixtures. [d]Yield of isolated product. DCM = dichloromethane; DCE = dichloroethane.

**Scheme 7. Mechanism of the Diamine Synthesis through a DYKAT**



The entire sequence can be performed as a one-pot procedure for the preparation of diamines **2a** and **2k** starting from nitroalkene. For example, *β*-methyl nitrostyrene was directly converted into diamine **2a** and **2k** through a sequential epoxidation, amination and reduction process (Scheme 8).[21] If urea was added with the amine, then higher yields were obtained.[26]

**Scheme 8. One-Pot Procedure**



In summary, *anti*-vicinal diamines can be prepared in a highly diastereoselective fashion when nitroepoxides are first treated with benzylamine and then with a reducing agent. This procedure represents a convenient method to prepare vicinal diamines from easily accessible starting compounds. When chiral *α*-methyl benzylamine is utilized in this process, a new DYKAT is operative, which subsequently affords a facile and highly selective method for the preparation of enantio- and diastereomerically pure *anti*-1,2-diamines. This method represents a one-pot procedure that starts with formation of amino imines as a diastereomeric mixture from a racemic mixture of nitroepoxides and concludes with a reduction to furnish a single enantiomer through a dynamic kinetic asymmetric transformation. In terms of ease of preparation, this protocol to access diamines can be accessed directly from nitroalkenes in a one-pot sequence. This process provides a convenient method for the generation of important 1,2-diamines and highlights the synthetic versatility of racemic nitroepoxides as useful synthons.

## EXPERIMENTAL SECTION

**General Experimental Methods.** Unless otherwise specified, all reactions were carried out under nitrogen atmosphere with magnetic stirring. All solvents and reagents were obtained from commercial sources and were purified according to standard procedures before use. $^1$H NMR spectra and $^{13}$C NMR spectra were measured in $CDCl_3$ ($^1$H, 7.24 ppm; $^{13}$C 77.0 ppm) solution at 30 °C on a 300 MHz or a 500 MHz NMR spectrometer. Mass spectra were measured in a QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface. EM Science Silica Gel 60 was used for column chromatography while TLC was performed with precoated plates (Kieselgel 60, $F_{254}$, 0.25 mm).

**General Experimental Procedure for the Preparation of Nitroalkenes.**[27] To a stirred solution of aldehyde (30 mmol) in nitroethane (11 mL, 150 mmol) at rt was added dropwise triethylamine (420 μL, 3 mmol). The resulting mixture was stirred under $N_2$ for 16 h. Excess solvent was evaporated in vacuo, and the crude nitroaldol was dissolved in $CH_2Cl_2$ (12 mL), cooled with an ice bath, and then methanesulfonylchloride (2.9 mL, 36 mmol) and ethyldiisopropylamine (11.1 mL, 63 mmol) were added. The solution was allowed to warm up to room temperature and stirred until TLC analysis indicated consumption of nitroaldol. Water and $CH_2Cl_2$ were added, and the organic phase was separated, washed with 2 M HCl, brine, dried ($MgSO_4$) and concentrated to yield an orange oil, which was purified by silica-gel chromatography (9:1 to 7:3, hexane:ethyl acetate) to give the pure product as a yellow solid.

**(*E*)-(2-Nitropent-1-en-1-yl)benzene.** Yellowish oil (yield 2.98 g, 52%): $^1$H NMR (300 MHz, $CDCl_3$) *δ* 8.04 (s, 1H), 7.55 7.37 (m, 5H), 2.85 2.80 (m, 2H), 1.75 1.64 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) *δ* 133.33, 132.43, 129.86, 129.59, 128.94, 127.54, 29.02, 21.31, 13.82 ppm; HRMS (EI) calcd for $C_{11}H_{13}NO_2$ (M) 191.0946, found 191.0947; IR (KBr) *δ* 3042, 2887, 1530, 1313, 1248, 1188, 816 cm$^{-1}$.

**(*E*)-(2-Nitrohex-1-en-1-yl)benzene.** Yellowish oil (yield 3.26 g, 53%): $^1$H NMR (300 MHz, $CDCl_3$) *δ* 8.01 (s, 1H), 7.59 7.32 (m, 5H), 2.99 2.72 (m, 2H), 1.77 1.52 (m, 2H), 1.54 1.30 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) *δ* 152.49, 133.14, 132.45, 129.86, 129.58, 128.94, 29.94, 26.91, 22.53, 13.64 ppm; HRMS (EI) calcd for $C_{12}H_{15}NO_2$ (M) 205.1103, found 205.1105; IR (KBr) *δ* 3056, 2922, 1528, 1312, 1250, 1189, 812 cm$^{-1}$.

**(*E*)-1-Fluoro-4-(2-nitrobut-1-en-1-yl)benzene.** Yellow crystals, mp 63−70 °C (yield 4.10 g, 70%): $^1$H NMR (300 MHz, $CDCl_3$) *δ* 7.93 (s, 1H), 7.45−7.35 (m, 2H), 7.11 (t, *J* = 8.6 Hz, 2H), 2.81 (q, *J* = 7.4 Hz, 2H), 1.23 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) *δ* 163.4 (d, *J* = 250.5 Hz), 153.1, 131.9, 131.7 (d, *J* = 9 Hz), 128.5, 116.2 (d, *J* = 21.8 Hz), 20.6, 12.3 ppm; HRMS (EI) calcd for $C_{10}H_{10}FNO_2$ (M) 195.0696, found 195.0697; IR (KBr) *δ* 3052, 2976, 1520, 1328, 1232, 1159, 836 cm$^{-1}$.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**(*E*)-5-Methyl-2-nitrohex-2-ene.** Yellowish oil (yield 3.43 g, 80%): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.04 (t, $J$ = 8.0 Hz, 1H), 2.10−1.99 (m, 5H), 1.84−1.66 (m, 1H), 0.87 (d, $J$ = 6.6 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 148.0, 135.1, 36.9, 31.5, 28.2, 22.2, 12.4 ppm; HRMS calcd for $C_7H_{14}NO_2$ (M + H$^+$) 144.1025, found 144.1031; HRMS (EI) calcd for $C_7H_{13}NO_2$ (M) 143.0946, found 143.0949; IR (KBr) $\delta$ 1668, 1556 cm$^{-1}$.

**(*E*)-2-Nitrohex-2-ene.** Yellowish oil (yield 2.52 g, 65%): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.02 (t, $J$ = 7.9 Hz, 1H), 2.14 (q, $J$ = 7.4 Hz, 2H), 2.07 (s, 3H), 1.64−1.25 (m, 2H), 0.88 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 147.6, 136.0, 30.0, 21.5, 13.5, 12.2 ppm; HRMS (EI) calcd for $C_6H_{11}NO_2$ (M) 129.0790, found 129.0791; IR (KBr) $\delta$ 3056, 2961, 1671, 1512, 1389, 1330 cm$^{-1}$.

**(*E*)-3-Nitrohept-3-ene.** Yellowish oil (yield 2.57 g, 60%): $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.02 (t, $J$ = 8.0 Hz, 1H), 2.58 (q, $J$ = 7.6 Hz, 2H), 2.19 (q, $J$ = 7.6 Hz, 2H), 1.52 (m, 2H), 1.08 (t, $J$ = 7.5 Hz, 3H), 0.95 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 153.2, 135.6, 29.6, 21.8, 19.8, 13.6, 12.5 ppm; HRMS (EI) calcd for $C_7H_{13}NO_2$ (M) 143.0946, found 143.0948; IR (KBr) $\delta$ 2920, 2850, 1713, 1455 cm$^{-1}$.

**General Experimental Procedure for the Epoxidation of Nitroalkenes.**[28] To a stirred ice-bath suspension of nitroalkene (0.852 mmol) in methanol (2.0 mL) containing hydrogen peroxide (50%) (728 $\mu$L, 12.80 mmol) was added NaOH 2 M (213 $\mu$L, 0.43 mmol). After 10 min ice water was added, and the colorless solid collected was filtered, washed with water and air-dried to obtain a yellow pale solid, which was further purified through a silica-gel chromatography (hexane:ethyl acetate, 9:1).

**2-Methyl-2-nitro-3-phenyloxirane 1a.** Yellowish oil (yield 125 mg, 82%): $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.41 (m, 3H), 7.30 (m, 2H), 4.56 (s, 1H), 1.78 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 131.0, 129.3, 128.7, 126.3, 88.8, 62.6, 12.2 ppm; HRMS (EI) calcd for $C_9H_9NO_3$ (M) 179.0582, found 179.0587; IR (KBr) $\delta$ 3062, 3028, 2948, 1555, 1495, 1448, 1354, 1158, 1105, 982, 899 cm$^{-1}$.

**2-Nitro-3-phenyl-2-propyloxirane 1b.** Yellowish oil (yield 176 mg, 79%): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.45−7.37 (m, 3H), 7.33−7.26 (m, 2H), 4.45 (s, $J$ = 0.4 Hz, 1H), 2.55−2.35 (m, 2H), 1.73−1.36 (m, 2H), 0.91 (dt, $J$ = 7.3, 5.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 131.2, 129.4, 128.7, 126.3, 91.9, 62.7, 27.5, 17.0, 13.6 ppm; HRMS (EI) calcd for $C_{11}H_{13}NO_3$ (M) 207.0895, found 207.0899 IR (KBr) $\delta$ 3082, 3014, 2981, 1497, 1476, 1314, 1151, 987, 885 cm$^{-1}$.

**2-Butyl-2-nitro-3-phenyloxirane 1c.** Yellowish oil (yield 188 mg, 92%): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.62 7.06 (m, 5H), 4.46 (s, 1H), 2.66 2.31 (m, 2H), 1.73 1.19 (m, 4H), 0.85 (td, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 131.2, 129.4, 128.7, 126.3, 92.0, 62.8, 25.5, 25.3, 22.1, 13.6 ppm; HRMS (EI) calcd for $C_{12}H_{15}NO_3$ (M) 221.1052, found 221.1054; IR (KBr) $\delta$ 3086, 3020, 2992, 1506, 1495, 1328, 1160, 992, 891 cm$^{-1}$.

**3-(4-Fluorophenyl)-2-methyl-2-nitrooxirane 1d.** Colorless oil (yield 104 mg, 62%): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.33−7.26 (m, 2H), 7.13−7.05 (m, 2H), 4.51 (s, 1H), 1.76 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 163.2 (d, $J$ = 247.8 Hz), 128.3 (d, $J$ = 8.4 Hz), 126.8 (d, $J$ = 4.0 Hz), 115.8 (d, $J$ = 22.0 Hz), 88.8, 62.1, 12.1 ppm; HRMS (EI) calcd for $C_9H_8N\,FO_3$ (M) 197.0488, found 197.0492 IR (KBr) $\delta$ 3059, 3024, 2944, 1546, 1490, 1452, 1205, 896, 830 cm$^{-1}$.

**2-Methyl-2-nitro-3-(*p*-tolyl)oxirane 1e.** Yellowish oil (yield 97 mg, 59%): $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.26−7.17 (m, 4H), 4.50 (s, 1H), 2.38 (s, 3H), 1.80 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 139.6, 129.5, 128.0, 126.4, 89.1, 62.8, 21.1, 12.4 ppm; HRMS (EI) calcd for $C_{10}H_{11}NO_3$ (M) 193.0739, found 193.0745; IR (KBr) $\delta$ 3062, 3025, 2948, 1552, 1449, 1346, 1158, 899, 768 cm$^{-1}$.

**2-Ethyl-3-(4-fluorophenyl)-2-nitrooxirane 1f.** Yellowish oil (yield 153 mg, 85%): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.37−7.19 (m, 2H), 7.10 (t, $J$ = 8.6 Hz, 2H), 4.49 (s, 1H), 2.45 (dq, $J$ = 15.1, 7.4 Hz, 1H), 1.67 (dq, $J$ = 14.8, 7.3 Hz, 1H), 1.05 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 163.2 (d, $J$ = 247.5 Hz), 128.2 (d, $J$ = 8.3 Hz), 127.0 (d, $J$ = 2.3 Hz), 115.9 (d, $J$ = 21.8 Hz), 92.37, 62.62, 19.44, 7.53 ppm; HRMS (EI) calcd for $C_{10}H_{10}FNO_3$ (M) 211.0645, found 211.0651; IR (KBr) $\delta$ 3052, 2979, 1710, 1606, 1552, 1510, 1347, 1227, 1156 cm$^{-1}$.

**3-Isobutyl-2-methyl-2-nitrooxirane 1g.** Yellowish oil (yield 75 mg, 55%): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.33 (dd, $J$ = 6.8, 5.3 Hz, 1H), 1.80 (s, 3H), 1.72−1−85 (m, 1H), 1.52−1.31 (m, 2H), 0.90 (d, $J$ = 6.7 Hz, 3H), 0.89 (d, $J$ = 6.6 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 87.6, 62.0, 36.1, 26.0, 22.3, 22.2, 13.4 ppm; HRMS (EI) calcd for $C_7H_{13}NO_3$ (M) 159.0895, found 159.0901; IR (KBr) $\delta$ 2940, 1561, 1167 cm$^{-1}$.

**2-Methyl-2-nitro-3-propyloxirane 1h.** Yellowish oil (yield 85 mg, 68%): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.39 (t, $J$ = 5.7 Hz, 1H), 1.89 (s, 3H), 1.66−1.43 (m, 4H), 0.96 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 87.9, 62.9, 29.7, 19.1, 13.6 ppm; HRMS (EI) calcd for $C_6H_{11}NO_3$ (M) 145.0739, found 145.0741; IR (KBr) $\delta$ 3028, 1555, 1029 cm$^{-1}$.

**2-Ethyl-2-nitro-3-propyloxirane 1i.** Yellowish oil (yield 87 mg, 64%): $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 3.37 (m, 1H), 2.62 (dq, $J$ = 14.8, 7.4 Hz, 1H), 1.84 (dq, $J$ = 14.8, 7.4 Hz, 1H), 1.68−1.46 (m, 4H), 1.11 (t, $J$ = 7.3 Hz, 3H), 0.98 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 91.9, 63.6, 29.7, 20.7, 19.4, 13.6, 7.8 ppm; HRMS (EI) calcd for $C_7H_{13}NO_3$ (M) 159.0895, found 159.0896; IR (KBr) $\delta$ 3028, 1555, 1029 cm$^{-1}$.

**General Experimental Procedures for the Preparation of Diamines.** *Method A.* To a solution of nitroepoxide (2.8 mmol, 500 mg) in $CH_2Cl_2$ (11 mL) was added benzylamine dropwise, and the mixture was stirred at rt under $N_2$ atmosphere for 6 h. After that, $NaBH_4$ (8.4 mmol, 324 mg) was added in one portion and kept stirring for additional 16 h. The reaction was then stopped, and ether and water were added. The aqueous layer was extracted with ether (3 × 15 mL), and the collected organic layers were washed with brine, dried over $Na_2SO_4$ and concentrated to obtain a yellow crude oil, which was purified by passing it through a chromatography column with 99:1 ($CH_2Cl_2$:MeOH) as eluent.

*Method B.* To a solution of nitroepoxide (2 mmol, 360 mg) in dichloroethane (11 mL) was added benzylamine (8 mmol, 883 $\mu$L) dropwise, and the resulting mixture was stirred during 6 h at rt over $N_2$ atmosphere. After that, $NaBH(OAc)_3$ (6 mmol, 1311 mg) was added, and the resulting mixture was stirred for 16 h. Then, NaOH 50% (12 mmol, 1520 $\mu$L) and the mixture was stirred during 2 h. Finally, $MgSO_4$ (644 mg, 5.35 mmol) was added, and the mixture was stirred for additional 1.5 h and filtered. The filtrate was concentrated to yield a yellow crude oil, which was purified by passing it through a chromatography column with 99:1 ($CH_2Cl_2$:MeOH) as eluent. A colorless oil was obtained.

**One-Pot Procedure.** To a solution of nitroalkene (3 mmol, 495 mg) in methanol (7.2 mL) containing hydrogen peroxide 50% (4.5 mmol, 250 $\mu$L) was added NaOH 2 M (1.5 mmol, 760 $\mu$L). After 30 min urea (3 mmol, 180 mg) and benzylamine (18 mmol, 1987 $\mu$L) were added, and the reaction was stirred at rt under $N_2$ atmosphere during 6 h. Then, the solution was cooled (ice bath), and $NaBH_4$ (9 mmol, 347 mg) was added in portions. After the effervescence had ceased, the reaction mixture was stirred 1 h at rt, carefully acidified (4 mL HCl 1M) and extracted four times with the same volume of ethyl acetate. To the acidic aqueous phase and a double volume of diethyl ether, 5 M NaOH (2 mL) was added carefully until pH = 9−14. After separation the aqueous phase was extracted additionally three times with the same volume of diethyl ether, and the combined organic phases were dried ($MgSO_4$), filtered and concentrated under reduced pressure providing the corresponding diamine as a yellow oil, which was further purified by passing it through a flash chromatography column with 99:1 ($CH_2Cl_2$:MeOH) as eluent. A colorless oil was obtained.

**$N^1$,$N^2$-Dibenzyl-1-phenylpropane-1,2-diamine 2a.** Yellowish oil: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.52−7.32 (m, 15H), 3.93−3.79 (m, 4H), 3.59 (d, $J$ = 13.4 Hz, 1H), 3.03 (dq, $J$ = 6.4, 4.7 Hz, 1H), 1.91 (br s, 2H), 1.11 (d, $J$ = 6.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 141.3, 140.7, 140.6, 128.2, 128.1, 128.0, 127.9, 127.8, 126.7, 126.6, 64.1, 57.4, 53.0, 51,3, 15.6 ppm; HRMS (ESI) calcd for $C_{23}H_{27}N_2$ (M + H$^+$) 331.2174, found 331.2171; IR (KBr) $\delta$ 3291, 3024, 2822, 1600, 1492, 1449, 1363, 1108, 1026, 759 cm$^{-1}$.

**$N^1$,$N^2$-Dibenzyl-1-phenylpentane-1,2-diamine 2b.** Yellowish oil: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.49 7.10 (m, 15H), 3.87 (d, $J$ =


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4.5 Hz, 1H), 3.78 (d, $J$ = 13.4 Hz, 1H), 3.73 (s, 1H), 3.47 (d, $J$ = 13.4 Hz, 1H), 2.74 (dt, $J$ = 7.5, 4.1 Hz, 1H), 1.91 (s, 2H), 1.41 1.25 (m, 3H), 1.15 (dd, $J$ = 13.3, 6.5 Hz, 1H), 0.78 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 141.26, 140.86, 128.33, 128.27, 128.22, 128.17, 128.14, 128.08, 126.85, 126.75, 62.76, 62.37, 52.11, 51.54, 31.65, 19.78, 14.08 ppm; HRMS (ESI) calcd for $C_{25}H_{31}N_2$ (M + H$^+$) 359.2487, found 359.2490; IR (KBr) $\delta$ 3288, 3022, 2956, 2899, 2824, 1519, 1485, 1227, 903 cm$^{-1}$.

**$N^1$,$N^2$-Dibenzyl-1-phenylhexane-1,2-diamine 2c.** Yellowish oil: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.60−7.15 (m, 15H), 3.88 (d, $J$ = 4.2 Hz, 1H), 3.78 (d, $J$ = 13.4 Hz, 1H), 3.73 (s, 2H), 3.48 (d, $J$ = 13.4 Hz, 1H), 2.73 (dt, $J$ = 8.2, 4.2 Hz, 1H), 2.12 (s, 2H), 1.40−1.25 (m, 2H), 1.25−1.05 (m, 4H), 0.80 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 141.23, 140.81, 128.35, 128.29, 128.26, 128.20, 128.17, 128.11, 126.88, 126.79, 62.74, 62.51, 52.11, 51.53, 29.06, 28.79, 22.72, 13.97 ppm; HRMS (ESI) calcd for $C_{26}H_{33}N_2$ (M + H$^+$) 373.2644, found 373.2646; IR (KBr) $\delta$ 3294, 3028, 2948, 2916, 2866, 1507, 1489, 1206, 791 cm$^{-1}$.

**$N^1$,$N^2$-Dibenzyl-1-(4-fluorophenyl)propane-1,2-diamine 2d.** Yellowish oil: $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.45−7.22 (m, 12H), 7.07 (t, $J$ = 8.7 Hz, 2H), 3.85−3.70 (m, 4H), 3.47 (d, $J$ = 13.4 Hz, 1H), 2.91 (dq, $J$ = 6.5, 4.5 Hz, 1H), 1.98 (br s, 2H), 1.00 (d, $J$ = 6.5 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 162.0 (d, $J$ = 238.8 Hz), 140.7, 140.6, 136.9 (d, $J$ = 3.0 Hz), 129.6 (d, $J$ = 7.5 Hz), 128.5, 128.4, 128.2, 128.0, 127.0, 126.9, 115.0 (d, $J$ = 20.3 Hz), 63.5, 57.3, 52.9, 51.6, 15.8 ppm; HRMS (ESI) calcd for $C_{23}H_{26}FN_2$ (M + H$^+$) 349.2080, found 349.2084; IR (KBr) $\delta$ 3295, 3026, 2962, 2922, 2827, 1602, 1506, 1452, 1219, 832 cm$^{-1}$.

**$N^1$,$N^2$-Dibenzyl-1-(*p*-tolyl)propane-1,2-diamine 2e.** Yellowish oil: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.37−7.18 (m, 14H), 3.82−3.68 (m, 4H), 3.49 (d, $J$ = 13.4 Hz, 1H), 2.91 (dq, $J$ = 6.5, 4.5 Hz, 1H), 2.39 (s, 3H), 1.87 (br s, 2H), 1.01 (d, $J$ = 6.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 141.0, 140.7, 138.2, 136.5, 129.0, 128.3, 128.2, 128.0, 126.8, 126.7, 64.3, 57.4, 51.5, 21.0, 15.7 ppm; HRMS (ESI) calcd for $C_{24}H_{29}N_2$ (M + H$^+$) 345.2331, found 345.2333; IR (KBr) $\delta$ 3291, 3023, 2957, 2921, 2849, 1492, 1452, 1111, 1026, 820 cm$^{-1}$.

**$N^1$,$N^2$-Dibenzyl-1-(4-fluorophenyl)butane-1,2-diamine 2f.** Yellowish oil: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.45−7.22 (m, 12H), 7.07 (t, $J$ = 6.0 Hz, 2H), 3.87 (d, $J$ = 4.2 Hz, 1H), 3.81−3.72 (m, 3H), 3.47 (d, $J$ = 13.4 Hz, 1H), 2.66 (m, 1H), 1.84 (s, 2H), 1.41 (m, 2H), 0.86 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 161.9 (d, $J$ = 252.8 Hz), 140.8, 140.7, 136.9 (d, $J$ = 3.0 Hz), 129.5 (d, $J$ = 7.5 Hz), 128.4, 128.3, 128.2, 128.1, 126.9, 126.8, 115.0 (d, $J$ = 20.3 Hz), 64.3, 62.0, 52.1, 51.4, 22.0, 11.0 ppm; HRMS (ESI) calcd for $C_{24}H_{28}FN_2$ (M + H$^+$) 363.2237, found 363.2241; IR (KBr) 3291, 3060, 3023, 2922, 2852, 1601, 1507, 1452, 1217, 1117, 830 cm$^{-1}$.

**$N^2$,$N^3$-Dibenzyl-5-methylhexane-2,3-diamine 2g.** Yellowish oil: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.35−7.21 (m, 10H), 3.84−3.61 (m, 4H), 2.91−2.46 (m, 4H), 1.71−1.54 (m, 1H), 1.44−1.12 (m, 2H), 1.07 (d, $J$ = 6.6 Hz, 3H), 0.89 (d, $J$ = 6.5 Hz, 3H), 0.85 (d, $J$ = 6.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 140.0, 140.3, 128.5, 128.2, 128.4, 127.0, 126.9, 58.3 (minor), 57.3 (major), 54.8 (minor), 52.3 (major), 51.7 (major), 51.3 (minor), 51.2 (minor), 51.1 (major), 40.2 (minor), 38.9 (major), 25.3 (minor), 25.0 (major), 23.7 (minor), 23.11 (major), 22.6 (major), 22.3 (minor), 16.2 (minor), 15.2 (major) ppm; HRMS (ESI) calcd for $C_{21}H_{31}N_2$ (M + H$^+$) 311.2487, found 311.2492; IR (KBr) $\delta$ 3291, 3025, 2955, 1453 cm$^{-1}$.

**$N^2$,$N^3$-Dibenzylhexane-2,3-diamine 2h.** Yellowish oil: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.38−7.22 (m, 10H), 3.89 (d, $J$ = 13.2 Hz, 1H), 3.78 (d, $J$ = 13.0 Hz, 1H), 3.68 (d, $J$ = 12.7 Hz, 1H), 3.66 (d, $J$ = 13.1 Hz, 1H), 2.63 (dq, $J$ = 6.5, 6.7 Hz, 1H), 2.43 (m, 1H), 2.09 (br s, 1H), 1.36 (m, 4H), 1.09 (d, $J$ = 6.3 Hz, 3H), 0.92 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 140.1, 140.0, 128.1, 127.0, 61.2, 54.8, 51.4, 32.3, 18.8, 16.9, 14.1 ppm; HRMS (ESI) calcd for $C_{20}H_{29}N_2$ (M + H$^+$) 297.2331, found 297.2329; IR (KBr) $\delta$ 3433, 3291, 3024, 2955, 2863, 1667, 1451 cm$^{-1}$.

**$N^3$,$N^4$-Dibenzylheptane-3,4-diamine 2i.** Yellowish oil: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.42−7.24 (m, 8H), 7.12−7.03 (m, 2H), 3.82−3.61 (m, 4H), 2.66−2.45 (m, 2H), 1.77−1.21 (m, 8H), 0.89 (m, 6H); $^{13}$C NMR (300 MHz, $CDCl_3$) $\delta$ 141.7, 141.6, 128.8, 128.7, 128.6, 127.2, 61.0, 60.0, 58.8, 57.8, 53.6, 52.5, 52.4, 52.3, 33.3, 32.4, 23.3, 23.0, 20.5, 20.0, 15.0, 14.8, 11.8, 10.6 ppm; HRMS (ESI) calcd for $C_{21}H_{30}N_2$ (M + H$^+$) 311.2487, found 311.2484; IR (KBr) 3325, 3004, 2896, 1512 cm$^{-1}$.

**(1*S*,2*R*)-$N^1$,$N^2$-Dibenzyl-$N^1$-methyl-1-phenylpropane-1,2-diamine 2j.** Yellowish oil: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.37−7.11 (m, 15H), 4.10 (d, $J$ = 13.2 Hz, 1H), 3.78 (d, $J$ = 13.2 Hz, 1H), 3.60 (d, $J$ = 10.5 Hz, 1H), 3.47−3.23 (m, 3H), 1.87 (s, 3H), 0.94 (d, $J$ = 6.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 139.2, 139.2, 134.3, 129.7, 128.7, 128.6, 128.4, 128.0, 127.6, 127.4, 127.0, 73.0, 58.4, 51.0, 36.5, 29.7, 17.0 ppm; HRMS (ESI) calcd for $C_{24}H_{29}N_2$ (M + H$^+$) 345.2331, found 345.2339; IR (KBr) $\delta$ 3351, 3004, 2982, 2929, 2872, 1678, 1492, 1439, 1357, 1113, 1021, 870 cm$^{-1}$.

**(1*R*,2*S*)-1-Phenyl-$N^1$,$N^2$-bis((*S*)-1-phenylethyl)propane-1,2-diamine 2k.** Pale yellow oil: $\alpha^{21}_D$ −136.2 ($c$ 0.9, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.44−7.12 (m, 15H), 3.64−3.60 (m, 2H), 3.35 (q, $J$ = 6.4 Hz, 1H), 2.55 (dq, $J$ = 3.7, 6.7 Hz, 1H), 1.89 (br s, 2H), 1.48 (d, $J$ = 6.7 Hz, 3H), 1.26 (d, $J$ = 6.5 Hz, 3H), 0.83 (d, $J$ = 6.6 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 146.0, 145.8, 142.4, 128.3, 128.2, 128.1, 127.5, 127.0, 126.9, 126.7, 126.4, 60.0, 55.2, 55.0, 54.5, 24.7, 24.5, 15.6 ppm; HRMS (ESI) calcd for $C_{25}H_{30}FN_2$ (M + H$^+$) 377.2393, found 377.2390; IR (KBr) 3291, 3062, 3023, 2962, 2923, 2861, 1491, 1451, 1120 cm$^{-1}$.

**(1*R*,2*S*)-1-(4-Fluorophenyl)-$N^1$,$N^2$-bis((*S*)-1-phenylethyl)-propane-1,2-diamine 2l.** Yellowish oil: $\alpha^{21}_D$ −60.6 ($c$ 0.7, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.39−7.17 (m, 8H), 7.06−6.92 (m, 6H), 3.50 (m, 2H), 3.25 (q, J = 6.6 Hz,1H), 2.44 (dq, $J$ = 3.8, 6.3 Hz, 1H), 1.93 (br s, 2H), 1.41 (d, $J$ = 6.7 Hz, 3H), 1.21 (d, $J$ = 6.6 Hz, 3H), 0.75 (d, $J$ = 6.6 Hz, 3H); $^{13}$C NMR (75 MHz, cdcl$_3$) $\delta$ 161.6 (d, $J$ = 244.0 Hz), 145.8, 137.8 (d, $J$ = 3.0 Hz), 128.9 (d, $J$ = 7.8 Hz), 128.3, 128.2, 126.9, 126.8, 126.7, 126.3, 114.8 (d, $J$ = 21.1 Hz), 59.1, 55.1, 54.9, 54.4, 24.6, 24.3, 15.5 ppm; HRMS (ESI) calcd for $C_{25}H_{30}FN_2$ (M + H$^+$) 377.2393, found 377.2390; IR (KBr) $\delta$ 3441, 3303, 2970, 2931, 2860, 1680, 1609, 1507, 1450, 1365, 1262, 1223, 1127, 823 cm$^{-1}$.

**(1*R*,2*S*)-1-(4-Fluorophenyl)-$N^1$,$N^2$-bis((*S*)-1-phenylethyl)-butane-1,2-diamine 2m.** Yellowish oil: $\alpha^{20}_D$ −88.5° ($c$ 1.0, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.40−6.94 (m, 14H), 3.62 (d, $J$ = 3.5 Hz, 1H), 3.52 (q, $J$ = 6.8 Hz, 1H), 3.24 (q, $J$ = 6.6 Hz, 1H), 3.03 (br s, 2H), 2.17 (m, 1H), 1.45 (d, $J$ = 6.7 Hz, 3H), 1.39−1.28 (m, 1H), 1.26 (d, $J$ = 6.6 Hz, 3H), 0.96−0.86 (m, 1H), 0.64 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 161.5 (d, $J$ = 249.0 Hz), 145.8, 145.6, 137.7, 129.1, 128.3, 126.8, 126.7, 114.9 (d, $J$ = 28.5 Hz), 61.4, 58.7, 55.0, 54.4, 24.7, 24.2, 21.3, 11.1 ppm; HRMS (ESI) calcd for $C_{26}H_{32}FN_2$ (M + H$^+$) 391.2550, found 391.2543; IR (KBr) $\delta$ 3437, 3309, 2991, 2941, 2891, 1671, 1600, 1503, 1430, 1349, 1251, 1111, 833 cm$^{-1}$.

**Experimental Procedure for the Preparation of Cyclic Ureas.** To a stirred mixture of diamine (70 mg, 0.212 mmol) and sodium carbonate (0.318 mmol, 34 mg) in THF (0.6 mL, freshly distilled) was added a solution of triphosgene (0.255 mmol, 76.3 mg) in THF (0.6 mL) dropwise at rt. After stirring at this temperature overnight, water and ethyl acetate were added. The aqueous layer was extracted with ethyl acetate (3 × 10 mL), and the collected organic layers were washed with brine, dried over $Na_2SO_4$ and concentrated to obtain a red wine crude oil, which was purified by passing it through a silica-gel chromatography column with 9:1 (hexane:ethyl acetate) as eluent to obtain a colorless oil.

**(4*R*,5*S*)-1,3-Dibenzyl-4-methyl-5-phenylimidazolidin-2-one 3.** White solid, mp 65 −70 °C (yield 45 mg, 59%): $^1$H NMR (300 MHz, tol-$d_8$) $\delta$ 7.34−6.93 (m, 15 H), 5.32 (d, $J$ = 14.8 Hz, 1H), 5.02 (d, $J$ = 15.1 Hz, 1H), 4.06 (d, $J$ = 8.8 Hz, 1H), 3.94 (d, $J$ = 15.2 Hz, 1H), 3.58 (d, $J$ = 14.8 Hz, 1H), 3.33 (dq, $J$ = 8.5, 6.5 Hz, 1H), 0.48 (d, $J$ = 6.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 161.2, 137.5, 137.2, 135.7, 128.5, 128.4, 128.2, 128.0, 127.3, 127.2, 60.9, 52.7, 45.6, 14.8 ppm; HRMS calcd for $C_{24}H_{25}N_2O$ (M + H$^+$) 357.1967, found 357.1963; IR (KBr) d 3037, 2984, 2931, 1691, 1439, 1358, 1078, 1028 cm$^{-1}$.

**(4*R*,5*S*)-1,3-Dibenzyl-4-ethyl-5-(4-fluorophenyl)-imidazolidin-2-one 4.** White solid, mp 69 −74 °C (yield 66 mg, 80%): $^1$H NMR (500 MHz, tol-$d_8$) $\delta$ 7.25 (d, $J$ = 7.6 Hz, 2H), 7.14−


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6.51 (m, 10H), 6.61 (t, $J$ = 8.1 Hz, 2H), 5.15 (d, $J$ = 14.9 Hz, 1H), 4.84 (d, $J$ = 15.2 Hz, 1H), 3.99 (d, $J$ = 15.2 Hz, 1H), 3.98 (d, $J$ = 8.2 Hz, 1H), 3.34 (d, $J$ = 14.9 Hz, 1H), 3.10 (m, 1H), 1.29−1.20 (m, 1H), 0.79−0.71 (m, 1H), 0.17 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 162.3 (d, $J$ = 250.8 Hz), 161.4, 137.5, 137.2, 131.3 (d, $J$ = 3.0 Hz), 130.3 (d, $J$ = 7.5 Hz), 128.5, 128.4, 128.3, 128.0, 127.4, 127.3, 115.5 (d, $J$ = 18.5 Hz), 59.8, 59.2, 46.2, 45.4, 21.1, 9.6 ppm; HRMS (ESI) calcd for $C_{25}H_{26}FN_2O$ ($M + H^+$) 389.2020, found 389.2025; calcd for $C_{25}H_{25}FN_2NaO$ ($M + Na^+$) 411.1849, found 411.1844; calcd for $C_{25}H_{25}FN_2KO$ ($M + K^+$) 427.1588, found 427.1582; IR (KBr) d 3038, 2983, 2927, 1687, 1425, 1358, 1102, 1058, 1014 cm$^{-1}$.

**2-Deutero-$N^1$,$N^2$-dibenzyl-1-phenylpropane-1,2-diamine 5.** Yellowish oil: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.48−7.34 (m, 15H), 3.90−3.77 (m, 4H), 3.59 (d, $J$ = 13.4 Hz, 1H), 2.10 (br s, 2H), 1.09 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 141.4, 140.8, 140.6, 128.3, 128.2, 128.1, 128.0, 127.9, 126.8, 126.7, 64.1, 57.0 (t, $J$ = 21 Hz), 51.4, 51,3, 15.5 ppm; HRMS (ESI) calcd for $C_{23}H_{26}DN_2$ ($M + H^+$) 332.2237, found 332.2234; IR (KBr) $\delta$ 3448, 3314, 3091, 3062, 3023, 2970, 2931, 2879, 1602, 1503, 1453, 1376, 1103, 1028 cm$^{-1}$.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Crystallographic data (CIF) of **2k** and graphical NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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(21) Besides the desired diamines, two minor byproducts were isolated: aminoalcohols a in ca. 1:1 mixture of diastereomers resulting from reduction of aminoketone intermediate, amides resulting from carbon−carbon bond breaking such as *N*-benzyl propanamide for reaction in Table 1, entry 9, and *N*-benzyl acetamide in Table 1, entry 12.

(22) The experimental procedure is the same as the procedure A indicated in Table 1, but after addition of the second equivalent of amine, the reaction was stirred for 24 h before addition of the reducing agent.

(23) The cis configuration of compounds **4** and **5** was assigned on the basis of the vicinal H-4/H-5 coupling constants (8.8 and 8.2 Hz, respectively). Published values for cis cyclic ureas range from 7−9 Hz and trans cyclic ureas range from 0−3 Hz ( Li, H.; Song, F.; Widenhoefer, R. A. *Adv. Synth. Catal.* **2011**, *353*, 955−962. ). Also NOE experiments confirmed stereochemical assignment (see Supporting Information).

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