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Double nitro-Mannich reaction utilizing in situ generated *N*-trimethylsilylaldimines: novel four-component one-pot synthesis of nitroimines

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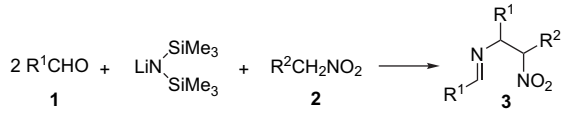
Abstract

Four-component synthesis of nitroimine derivatives (**3**) via double nitro-Mannich reaction was carried out in which nitroalkane, two moles of aldehyde, and lithium hexamethyldisilazide (LHMDS) were coupled in one-pot. In situ generated *N*-trimethylsilylaldimine was reacted with nitroalkane dianion followed by the second addition of the resulting nitrogen anion to the aldimine and the subsequent elimination of bistrimethylsilylamine furnished nitoroimine. The reaction was proceeded with *erythro* selectivity.

1. Introduction

Aldimines are versatile synthetic reagents and numerous examples of addition reactions of electrophiles to them have been reported,[1] generally known as the Mannich type reaction.[2] One of the characteristics of Mannich type reaction is the feasibility of one-pot synthesis, where three components: amines, carbonyl compounds, and electrophiles, can be coupled in one-pot.[3] It is intriguing and synthetically useful if further numbers of components are coupled together in one-pot with some modification of the reaction. Recently, much attention has been paid to such a four-component one-pot synthesis.[4] In some cases, the reactions were carried out in solvent-free conditions as an environmentally benign synthesis.[5]

During the course of our study of regioselective aldol addition reaction of nitroalkanes,[6] we found a novel four-component coupling reaction in one-pot affording nitroimines. When lithium hexamethyldisilazide (LHMDS) was used as a base instead of *n*-BuLi or LDA in the reaction of nitroalkanes and aldehydes, nitroimines were obtained instead of aldol products. The four components, nitroalkane, LHMDS, and two molecules of aldehydes were coupled to form nitroimines (Scheme 1). The reaction can be interpreted in terms of the double nitro-Mannich reaction which involves the initial nitro-Mannich[7] process, the addition of a nitroalkane dianion to *N*-trimethylsilylaldimine,[8] followed by the second Mannich reaction, and further addition of the resulting anion to *N*-trimethylsilylaldimine. The involvement of *N*-trimethylsilylaldimine as the intermediacy of the reaction was confirmed by the reaction of independently prepared *N*-trimethylsilylaldimine with the nitroalkane dianion. In this stepwise way, nitroimines were also obtained in good yields. Herein, we report on the details of this novel double nitro-Mannich reaction.



1 2 3

Scheme 1.

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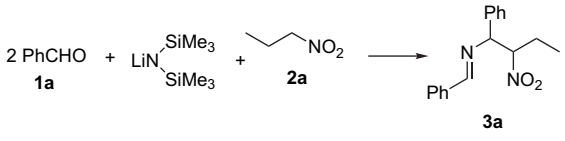
2. Results and discussion

2.1. Optimization of reaction conditions

The order of addition of reagents was important in our double nitro-Mannich reaction. Two ways of the addition of reagents, the methods A and B were investigated. In the method A, nitroalkane was added to a solution of LHMDS and then aromatic aldehyde was added to the resulting mixture. On the contrary, an addition of reagent was carried out in the sequence of aromatic aldehyde and then nitroalkane to a solution of LHMDS in the method B. For both methods, effects of the amount of LHMDS and of the presence of DMPU (*N*,*N*′-dimethylpropylurea), a dipolar aprotic solvent,[9] were examined. A typical reaction was carried out in the following way to optimize the reaction conditions. To a solution of LHMDS in THF was added either 1-nitropropane (method A) or benzaldehyde (method B) at −90 °C in the presence or absence of DMPU. The resulting mixture was stirred for 1 h at −60 °C (method A) or at room temperature (method B). After cooling to −90 °C, benzaldehyde (method A) or 1-nitropropane (method B) was added to this mixture and the solution was stirred for additional 3 h at −40 °C. The reaction was quenched by adding acetic acid at −90 °C in both methods. The product nitroimine **3a** was purified by column chromatography on silica gel. The structure of **3a** was confirmed from its spectral and physical data. Its structure was also supported by its reduction by hydrogenation to the reported amine[10] and also by its hydrolysis to benzaldehyde and the corresponding amine. Isolated yields and diastereomeric (*erythro*/*threo*) ratios are presented in Table 1. From these data, it is clear that the addition of DMPU does not affect neither the product yields nor the diastereomeric ratios. The best result was obtained by method B when 3 equiv amounts of LHMDS to nitroalkane were added (entry 7). Quenching temperature affected the diastereomeric ratio. *erythro* Diastereomer was obtained predominantly when quenching was carried out at −90 °C. The *erythro*/*threo* ratio was decreased from 5/1 at −90 °C (entry 7) to 2/1 at 0 °C (entry 8). For further study of the double nitro-Mannich reaction of nitroalkanes, method B (conditions described in entry 7) was employed.

Table 1
Double nitro-Mannich reaction of 1-nitropropane with benzaldehyde affording nitroimine **3a**



Entry	LHMDS[c] (mmol)	**1a**[c] (mmol)	**2a**[c] (mmol)	DMPU[c] (mmol)	**3a** (%)	*erythro*/*threo*
1[a]	22	20	10	0	31	2.5/1[c]
2[a]	22	15	7.5	0	56	5/1[c]
3[a]	22	15	7.5	44	39	2/1[c]
4[a]	22	20	10	44	38	3/1[c]
5[b]	30	15	7.5	0	13	2/1[d]
6[b]	15	15	7.5	0	49	2/1[d]
7[b]	22	15	7.5	0	62	5/1[c]
8[b]	22	15	7.5	0	61	2/1[d]

[a] Method A: 1-nitropropane was added to a solution of LHMDS and then benzaldehyde was added to the resulting mixture.
[b] Method B; benzaldehyde was added to a solution of LHMDS and then 1-nitropropane was added to the resulting mixture.
[c] Quenched at −90 °C.
[d] Quenched at 0 °C.

2.2. Preparation of nitroimines from nitroalkanes and aromatic aldehydes

In order to demonstrate the usefulness of this double nitro-Mannich reaction, additional 19 nitroimines were prepared by method B from 3 nitroalkanes with 8 aromatic aldehydes. The results are summarized in Table 2. The higher yields were obtained with electron donating substituents. Poor yield was obtained for **3h** in the reaction with 9-anthryl aldehyde probably due to steric hindrance. Diastereomeric ratios were determined based on integrals in their ^{1}H NMR spectra or by HPLC analysis. A single diastereomer (*erythro*) was obtained for **3e**, **3h**, and **3m**.

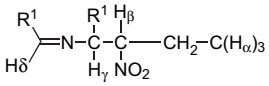
2.3. Determination of the stereochemistry of nitroimines

Stereochemistry of nitroimines was determined based on the comparison of the coupling constants $J_{\beta\gamma}$ of both diastereomers (Tables 3 and 4). The assumption was made on the basis that vicinal coupling constants of *threo* diastereomers were larger than those of *erythro* diastereomers as reported for β-nitroalcohols (ca. 4 Hz for *erythro* and ca. 8 Hz for *threo*).[11] However, the differences in coupling constants between some of our diastereomers (nitroimies derived from 1-nitropropane) are very small, which makes the assignment of the stereochemistry of diastereomers difficult. The confirmation of the

Table 2
Product yields of double nitro-Mannich reaction of nitroalkanes with various aldehydes

Product	R^1	R^2	Yield (%)	*erythro*/*threo* ratio
3b	4-$CH_3OC_6H_4$	C_2H_5	72	2/1
3c	4-$CH_3C_6H_4$	C_2H_5	60	2/1
3d	4-$NO_2C_6H_4$	C_2H_5	43	2.5/1
3e	1-Naphthyl	C_2H_5	66	*erythro* only
3f	2-Naphthyl	C_2H_5	75	4/1
3g	1-Furfuryl	C_2H_5	60	2/1
3h	9-Anthryl	C_2H_5	29	*erythro* only
3i	C_6H_5	CH_3	66	4.5/1
3j	4-$CH_3OC_6H_4$	CH_3	81	2.5/1
3k	4-$CH_3C_6H_4$	CH_3	87	3/1
3l	4-$NO_2C_6H_4$	CH_3	40	2.5/1
3m	1-Naphthyl	CH_3	58	*erythro* only
3n	2-Naphthyl	CH_3	67	2/1
3o	C_6H_5	H	72	—
3p	4-$CH_3OC_6H_4$	H	96	—
3q	4-$CH_3C_6H_4$	H	91	—
3r	4-$NO_2C_6H_4$	H	40	—
3s	1-Naphthyl	H	85	—
3t	2-Naphthyl	H	76	—

Table 3
^{1}H NMR chemical shifts and coupling constants of nitroimines **3** derived from 1-nitropropane

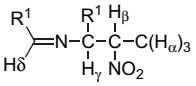


Compd	R		H_α	H_β	H_γ	H_δ	$J_{\beta\gamma}$
3a	C_6H_5	*threo*	0.82	4.95	4.65	8.18	9.8
		erythro	0.94	4.93	4.71	8.29	8.3
3b	4-$CH_3OC_6H_4$	*threo*	0.88	4.89	4.65	8.11	9.9
		erythro	0.95	4.88	4.62	8.22	8.4
3c	4-$CH_3C_6H_4$	*threo*	0.88	4.93	4.60	8.15	9.7
		erythro	0.95	4.91	4.65	8.26	8.4
3d	4-$NO_2C_6H_4$	*threo*	0.95	4.96	4.92	8.35	9.8
		erythro	1.00	5.01	4.96	8.53	8.0
3e	1-Naphthyl	*threo*	—	—	—	—	—
		erythro	0.91	5.25	5.69	9.01	5.5
3f	2-Naphthyl	*threo*	0.85	5.11	4.87	8.35	10.1
		erythro	0.96	5.11	4.92	8.42	8.3
3g	1-Furfuryl	*threo*	0.95	5.10	4.83	8.00	10.0
		erythro	0.99	5.09	4.88	8.11	8.8
3h	9-Anthryl	*threo*	—	—	—	—	—
		erythro	0.91	5.25	5.69	9.01	5.5

stereochemistry of nitoroimine was carried out by single crystal X-ray diffraction analysis of *erythro*-**3b** (Fig. 1).

Its stereochemistry was unequivocally determined to be *erythro*. The molecule has an *anti* conformation. The torsion angle (H_β–C–C–H_γ) measured in its single crystal X-ray structure is 176°, which supports the observed value of $J_{\beta\gamma}$ (8.4 Hz). Therefore, the other diastereomer ($J_{\beta\gamma}$=9.9 Hz) was assigned to be *threo*. In some cases, single diastereomers were obtained. In the case of nitroimine **3m**, its stereochemistry was determined to be *erythro* from its single crystal X-ray diffraction analysis (Fig. 2). The *syn* conformation with the torsion angle (H_β–C–C–H_γ) of 66° attests the observed coupling constant of 4.0 Hz. Nitroimine **3e** with the same substituent (R=1-naphthyl) as **3m** was assigned to be *erythro* from its $J_{\beta\gamma}$. As we observed, the coupling constants of *erythro*-**3b** and **3m** were very different due to their conformational

Table 4
^{1}H NMR chemical shifts and coupling constants of nitroimines **3** derived from 1-nitroethane



Compd	R		H_α	H_β	H_γ	H_δ	$J_{\beta\gamma}$
3i	C_6H_5	*threo*	1.40	5.00	4.66	8.23	9.8
		erythro	1.59	5.11	4.90	8.29	6.7
3j	4-$CH_3OC_6H_4$	*threo*	1.39	5.05	4.58	8.14	9.7
		erythro	1.58	4.96	4.77	8.22	6.7
3k	4-$CH_3C_6H_4$	*threo*	1.39	5.07	4.60	8.17	9.8
		erythro	1.57	4.98	4.81	8.26	6.7
3l	4-$NO_2C_6H_4$	*threo*	1.39	5.04	5.02	8.30	9.2
		erythro	1.54	4.96	4.80	8.39	6.6
3m	1-Naphthyl	*threo*	—	—	—	—	—
		erythro	1.69	5.30	5.95	9.09	4.0
3n	2-Naphthyl	*threo*	1.43	5.26	4.89	8.41	9.8
		erythro	1.65	5.14	5.11	8.47	6.4

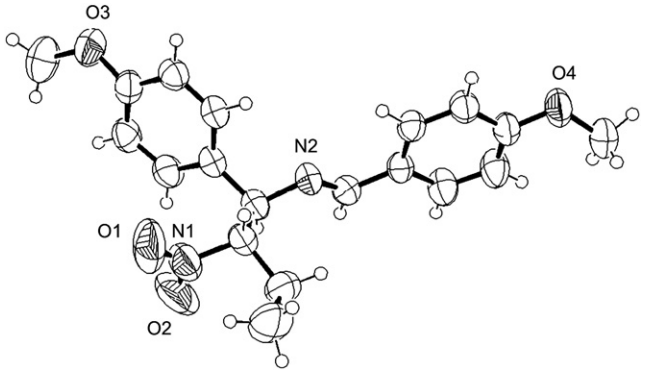


Figure 1. ORTEP diagram of *erythro*-**3b**.

difference even though they had the same *erythro* configuration. Their conformational stabilities were examined by the AM1 calculations. The results showed that *anti-erythro*-**3b** was 0.2 kcal/mol (the difference in heat of formation between the two diastereomers) more stable than that of the *syn* conformation of *erythro*-**3b**, while *syn*-**3m** was 2.3 kcal/mol more stable than that of *anti*-**3m**. The configuration of **3h** was difficult to determine from its $J_{\beta\gamma}$. Unlike 1-naphthyl derivatives (**3e** and **3m**), **3h** had a large value (10.7 Hz) of $J_{\beta\gamma}$. Since **3h** have a large value of $J_{\beta\gamma}$, it should have an *anti* conformation. Except a few nitroimines, **3i** and **3l**, the protons H_β of *threo* diastereomers appeared at slightly lower field than those of *erythro* diastereomers and H_γ of *threo* diastereomers have the chemical shifts of slightly up-field than those of *erythro* diastereomers. There was a tendency that the methyl protons and the vinylic protons H_δ of *threo* diastereomers appeared at higher field than those of *erythro* diastereomers (Tables 3 and 4).

2.4. Mechanism of the double nitro-Mannich reaction and stereoselectivity

From the fact that even by method A nitroimines were obtained in reasonable yields, the formation of *N*-trimethylsilylaldimines should be faster than nitro-aldol (Henry) reaction.[12]

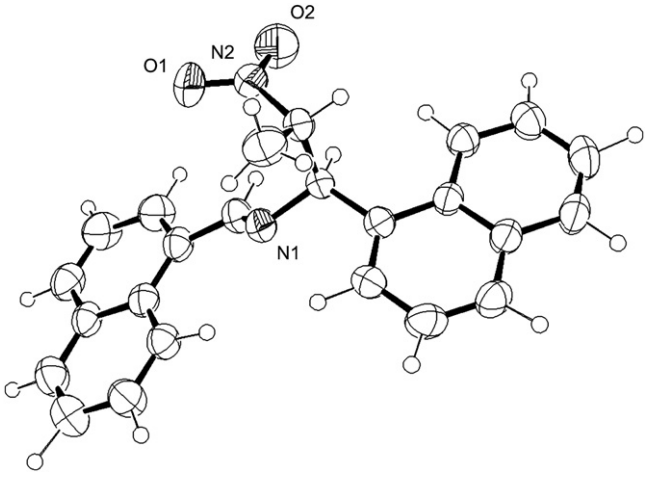
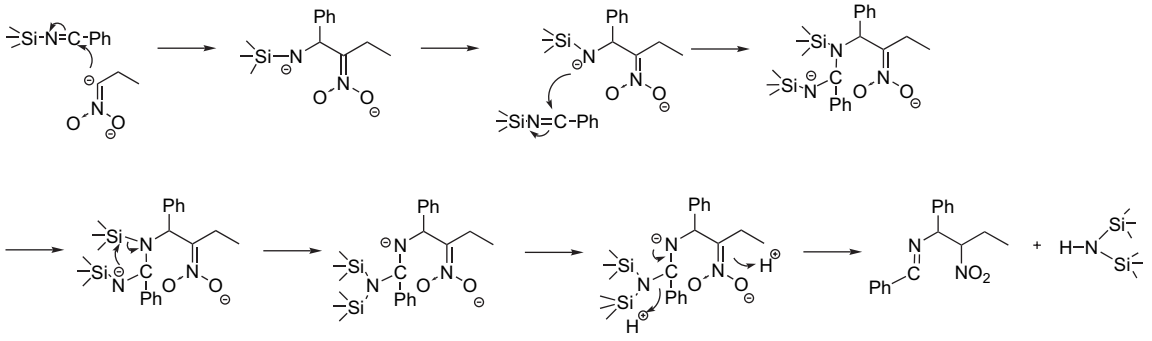


Figure 2. ORTEP diagram of *erythro*-**3m**.



Scheme 2. Proposed mechanism of the double nitro-Mannich reaction.

The proposed mechanism of the double nitro-Mannich reaction is shown in Scheme 2. The reaction involves LHMDS, one molecule of nitoralkane, and two molecules of aromatic aldehydes. Prior to the nitro-Mannich reaction, *N*-trimethylsilylaldimine is formed by the condensation of LHMDS and aromatic aldehyde followed by the nucleophilic addition of nitoalkane dianion to the aldimine. The second addition of the resulting nitrogen anion to the aldimine and the subsequent elimination of bistrimethylsilylamine furnish nitoroimine. An involvement of *N*-trimethylsilylaldimine was confirmed by the nitro-Mannich reaction of independently prepared *N*-trimethylsilylbenzaldimine with dianions of 1-nitoropropane and nitroethane. Nitroimines **3a** (*erythro*/*threo*=5/1) and **3i** (*erythro*/*threo*=3/1) were obtained in 65% and 91% yields, respectively. *erythro* Selectivity[13] of the reaction can be explained by the chelation model. An electrophile should approach from the side where a small group locates. The protonation in this transition state affords the *erythro* isomer (Fig. 3). This *erythro* selectivity is strongly depended on the bulkiness of the aldehyde and the quenching (protonation) temperature. 1-Naphthylaldehyde afforded the corresponding single diastereomers **3e** and **3m** with 1-nitropropane and nitroethane, respectively. However, 2-naphthyl derivatives gave poor *erythro* selectivity for **3f** and **3m**. This difference might be caused by the sterical ease due to the difference in the substitution position of the naphthyl group. Rigidity of the six-membered-ring lithium chelation complex could be improved at low temperature, which regulated the protonation process more efficiently leading preferentially to *erythro* with sterical control. This was confirmed by the epimerization experiment. Nitroimine **3a** (*erythro*/*threo*=1/1) was treated with LDA and then quenched at 0 °C or −90 °C. The ratio of *erythro*/*threo* was unchanged at 0 °C. However, the epimerization from the *threo* to the *erythro* diastereomer was favorable at −90 °C and the *erythro*/*threo* ratio was increased to 5/1.

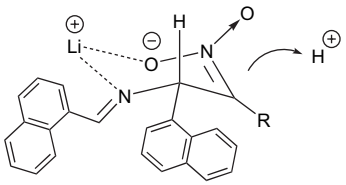


Figure 3. Chelation model for *erythro* selectivity.

3. Conclusions

The double nitro-Mannich reaction of nitroalkanes with in situ generated trimethylsilylaldimies was studied. The coupling of four components: nitroalkane, two molecules of aromatic aldehydes, and LHMDS can be carried out in a one-pot affording nitroimines with *erythro* selectivity. The present reaction gives a new type in the family of nitro-Mannich reaction which is one of the most useful C–C–N bond formation reactions.

4. Experimental

4.1. General

All reactions were performed under an argon atmosphere. All solvents were distilled prior to use according to the standard procedures. All melting points were taken with Yanaco MP-S3 melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 500 MHZ (or 400 MHZ) and 125 MHZ with JEOL GSX500 or LA-400 spectrometer. The chemical shifts were reported in parts per million using TMS as an internal standard. Mass spectra were recorded on a JMS-HX110 instrument. The X-ray crystallographic analysis was performed on Rigaku AFC7S four-circle diffractometer. For refinement of the structures, structural analysis, and production of crystallographic illustration, the program packages TEXSAN (SIR 97) were used. Column chromatography was performed on Merk Silica gel 60. HPLC analysis was performed on HITACHI L-6050, L-4000, and L-3350 apparatus with MERK column Si-60.

Crystallographic data for the structural analysis of compounds reported herein have been deposited at the Cambridge Crystallographic Data Center, CCDC nos. 6634773 (*erythro*-**3m**) and 663474 (*erythro*-**3b**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1233 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

4.2. Synthetic procedure

4.2.1. Method A (preparation of *3a*)

To a stirred solution of 3.55 g (22 mmol) of 1,1,1,3,3,3-hexamethyldisilazane in 30 ml of tetrahydrofuran was added

a hexane solution of 1.6 M *n*-butyllithium (14 ml, 22 mmol) at −78 °C. The resulting solution was stirred for 1 h followed by addition of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (5.3 ml, 44 mmol). The solution was stirred for 0.5 h at −90 °C followed by the addition of a THF solution (5 ml) of 1-nitropropane (0.7 ml, 7.5 mmol) at a rate that the temperature of the solution did not exceed −90 °C. The resulting solution of nitronate dianion was stirred for additional 1 h at −60 °C and then a THF solution (5 ml) of benzaldehyde (1.5 ml, 15 mmol) was added. The resulting mixture was allowed to warm up to −40 °C and stirred for 3 h. The resulting mixture was again cooled down to −90 °C. The reaction was quenched by the addition of a THF solution (5 ml) of acetic acid (2.5 ml) at −90 °C. The mixture was stirred at room temperature for 30 min, poured into 100 ml of saturated NaCl solution, and extracted three times with diethyl ether (100 ml× 3). The combined extracts were dried over anhydrous Na_2SO_4 and the organic layer was concentrated in vacuum. The residual oil was flash-chromatographed on silica gel eluted with hexane/ethyl acetate (2/1) to give 829 mg (yield 39%) of imine derivative **3a** (*erythro*/*threo* ratio; 2/1), with trace amounts of 1-phenyl-2-nitro-1-butanol,[9a,14] and benzaldehyde.

4.2.2. Method B (preparation of *3a*)

To a stirred THF solution of lithium hexamethyldisilazide (22 mmol) was added a THF solution (5 ml) of benzaldehyde (1.5 ml, 15 mmol) at −90 °C. The resulting solution was stirred for 1 h at room temperature and then cooled down to −90 °C followed by the addition of a THF solution (5 ml) of 1-nitropropane (0.7 ml, 7.5 mmol). The resulting mixture was allowed to warm up to −40 °C and stirred for 3 h. The resulting mixture was again cooled down to −90 °C. The reaction was quenched by the addition of a THF solution (5 ml) of acetic acid (2.5 ml) at −90 °C. The mixture was stirred at room temperature for 30 min, poured into 100 ml of saturated NaCl solution, and extracted three times with diethyl ether (100 ml×3). The combined extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residual oil was flash-chromatographed on silica gel eluted with hexane/ethyl acetate (2/1) to give 1380 mg (yield 65%) of imine derivative **3a** (*erythro*/*threo* ratio; 5/1).

4.3. Nitroimines

4.3.1. erythro-(1E)-2-Aza-4-nitro-1,3-diphenylhex-1-ene (*erythro-3a*)

Mp 64–65 °C; IR ν (KBr) 2970, 2880, 1955, 1640, 1550, 1500, 1455, 1385, 1300, 1255, 1215, 1080, 1025, 970 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.94 (t, J=7.4 Hz, 3H), 1.88–1.96 (m, 1H), 1.99–2.09 (m, 1H), 4.71 (d, J=8.3, 8.3 Hz, 1H), 4.93 (ddd, J=10.1, 8.3, 3.1 Hz, 1H), 7.23–7.42 (m, 8H), 7.74 (d, J=1.9 Hz, 1H), 7.76 (d, J=1.3 Hz, 1H), 8.29 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.3 (q), 24.0 (t), 76.5 (d), 95.1 (d), 127.5 (d), 128.1 (d), 128.3 (d), 128.47 (d), 128.54 (d), 128.6 (d), 128.8 (d), 129.0 (d), 131.4 (d), 139.3 (s), 135.6 (s), 163.3 (d); HRMS (FAB): calcd for $C_{17}H_{19}N_2O_2$ (M+1): 283.1447, found: 283.1428. Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.25; H, 6.27; N, 9.98.

4.3.2. threo-(1E)-2-Aza-4-nitro-1,3-diphenylhex-1-ene (*threo-3a*)

^1H NMR (500 MHz, $CDCl_3$) δ 0.82 (t, J=7.3 Hz, 3H), 1.46–1.51 (m, 2H), 4.65 (d, J=9.8 Hz, 1H), 4.91–4.99 (m, 1H), 7.20–7.50 (m, 8H), 7.76–7.80 (m, 2H), 8.18 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.0 (q), 24.0 (t), 77.0 (d), 95.2 (d), 127.3 (d), 127.9 (d), 128.1 (d), 128.35 (d), 128.39 (d), 128.76 (d), 128.82 (d), 129.5 (d, 9C), 131.0 (d), 134.2 (s), 138.3 (s), 162.6 (s).

4.3.3. erythro-(1E)-2-Aza-1,3-bis(4-methoxyphenyl)-4-nitrohex-1-ene (*erythro-3b*)

Mp 85–86 °C; IR ν (KBr) 2971, 2936, 2838, 1639, 1606, 1578, 1549, 1511, 1461, 1441, 1422, 1373, 1304, 1250, 1166, 1109, 1031, 832 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, J=7.4 Hz, 3H), 1.92–2.05 (m, 2H), 3.77 (s, 3H), 3.84 (s, 3H), 4.62 (d, J=8.3 Hz, 1H), 4.88 (ddd, J=10.2, 8.5, 3.4 Hz, 1H), 6.85 (d, J=8.9 Hz, 2H), 6.91 (d, J=8.8 Hz, 2H), 7.32 (d, J=8.9 Hz, 2H), 7.69 (d, J=8.8 Hz, 2H), 8.22 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.3 (q), 24.2 (t), 55.2 (q), 55.4 (q), 76.0 (d), 95.3 (d), 113.9 (d), 114.0 (d), 114.1 (d), 114.4 (d), 128.6 (d), 128.7 (d), 130.2 (s), 130.2 (d), 131.7 (s), 132.0 (d), 159.4 (s), 162.2 (d), 164.6 (s); HRMS (FAB): calcd for $C_{19}H_{23}N_2O_4$ (M+1): 343.1658, found: 343.1652. Anal. Calcd for $C_{19}H_{22}N_2O_4$: C, 66.65; H, 6.48; N, 8.18. Found: C, 66.37; H, 6.51; N, 8.15.

4.3.4. threo-(1E)-2-Aza-1,3-bis(4-methoxyphenyl)-4-nitrohex-1-ene (*threo-3b*)

^1H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, J=7.4 Hz, 3H), 1.51–1.56 (m, 1H), 1.84–1.91 (m, 1H), 3.79 (s, 3H), 3.81 (s, 3H), 4.57 (d, J=9.8 Hz, 1H), 4.89 (ddd, J=10.9, 9.8, 3.2 Hz, 1H), 6.86 (d, J=8.9 Hz, 2H), 6.90 (d, J=8.9 Hz, 2H), 7.35 (d, J=8.9 Hz, 2H), 7.64 (d, J=8.9 Hz, 2H), 8.11 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.4 (q), 24.3 (t), 55.31 (q), 55.35 (q), 76.7 (d), 95.7 (d), 113.9 (d), 114.0 (d), 114.12 (d), 114.36 (d), 128.73 (d), 129.11 (d), 130.15 (s), 130.23 (d), 130.84 (s), 159.6 (s), 161.6 (d), 164.6 (s).

4.3.5. erythro-(1E)-2-Aza-1,3-bis(4-methylphenyl)-4-nitrohex-1-ene (*erythro-3c*)

IR ν (NaCl) 3026, 2975, 2937, 2922, 2878, 1643, 1609, 1573, 1549, 1512, 1457, 1372, 1307, 1174, 1037, 1021, 814 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, J=7.4 Hz, 3H), 1.83–2.07 (m, 2H), 2.30 (s, 3H), 2.37 (s, 3H), 4.65 (d, J=8.3 Hz, 1H), 4.91 (ddd, J=10.7, 8.3, 3.3 Hz, 1H), 7.13 (d, J=7.9 Hz, 2H), 7.20 (d, J=7.7 Hz, 2H), 7.29 (d, J=8.3 Hz, 2H), 7.64 (d, J=8.3 Hz, 2H), 8.26 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.3 (q), 21.1 (q), 21.5 (q), 24.1 (t), 76.4 (d), 95.2 (d), 127.4 (d), 128.5 (d), 129.3 (d), 129.5 (d), 133.2 (s), 136.5 (s), 138.0 (s), 141.7 (s), 163.0 (d); HRMS (FAB): calcd for $C_{19}H_{23}N_2O_2$ (M+1): 311.1760, found: 311.1763.

*4.3.6. threo-(1E)-2-Aza-1,3-bis(4-methylphenyl)-4-nitrohex-1-ene (threo-**3c**)*

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J=7.5 Hz, 3H), 1.50–1.57 (m, 1H), 1.82–1.93 (m, 1H), 2.33 (s, 3H), 2.34 (s, 3H), 4.60 (d, J=9.8 Hz, 1H), 4.93 (ddd, J=11.3, 9.8, 3.1 Hz, 1H), 7.15 (d, J=7.9 Hz, 2H), 7.18 (d, J=7.7 Hz, 2H), 7.32 (d, J=8.2 Hz, 2H), 7.59 (d, J=7.9 Hz, 2H), 8.15 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.2 (q), 21.0 (q), 21.5 (q), 24.4 (t), 76.8 (d), 95.5 (d), 127.9 (d), 128.5 (d), 129.1 (d), 129.6 (d), 133.1 (s), 135.6 (s), 138.2 (s), 141.4 (s), 162.4 (d).

*4.3.7. erythro-(1E)-2-Aza-1,3-bis(4-nitrophenyl)-4-nitrohex-1-ene (erythro-**3d**)*

IR ν (NaCl) 3078, 2979, 2941, 2884, 1640, 1600, 1550, 1523, 1376, 1345, 1314, 1105, 1013, 855 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (t, J=7.3 Hz, 3H), 1.91–2.01 (m, 1H), 2.05–2.15 (m, 1H), 4.96 (d, J=8.0 Hz, 1H), 5.01 (ddd, J=10.0, 8.0, 3.3 Hz, 1H), 7.67 (d, J=8.9 Hz, 2H), 8.02 (d, J=8.9 Hz, 2H), 8.21 (d, J=8.9 Hz, 2H), 8.29 (d, J=8.9 Hz, 2H), 8.53 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.0 (q), 23.8 (t), 75.5 (d), 94.2 (d), 123.8 (d), 124.0 (d), 128.4 (d), 129.3 (d), 140.2 (s), 145.4 (s), 147.7 (s), 149.5 (s), 161.7 (d).

*4.3.8. threo-(1E)-2-Aza-1,3-bis(4-nitrophenyl)-4-nitrohex-1-ene (threo-**3d**)*

Mp 162–164 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (t, J=7.3 Hz, 3H), 1.49–1.57 (m, 1H), 1.90–2.00 (m, 1H), 4.86 (d, J=9.8 Hz, 1H), 4.96 (ddd, J=10.2, 9.8, 3.0 Hz, 1H), 7.70 (d, J=8.6 Hz, 2H), 7.91 (d, J=8.6 Hz, 2H), 8.25 (d, J=8.6 Hz, 2H), 8.28 (d, J=8.6 Hz, 2H), 8.35 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.1 (q), 24.1 (t), 76.5 (d), 94.5 (d), 123.8 (d), 124.3 (d), 129.0 (d), 129.4 (d), 140.2 (s), 144.5 (s), 148.1 (s), 149.6 (s), 161.7 (d); HRMS (FAB): calcd for $C_{17}H_{17}N_4O_6$ (M+1): 373.1148, found: 373.1115. Anal. Calcd for $C_{17}H_{16}N_4O_6$: C, 54.84; H, 4.33; N, 15.05. Found: C, 54.61; H, 4.49; N, 14.91.

*4.3.9. erythro-(1E)-2-Aza-1,3-dinaphthyl-4-nitrohex-1-ene (erythro-**3e**)*

IR ν (NaCl) 3051, 2974, 2936, 2879, 1640, 1617, 1547, 1509, 1459, 1369, 1215, 1168, 802, 775 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (t, J=7.3 Hz, 3H), 2.03–2.11 (m, 1H), 2.36–2.45 (m, 1H), 5.25 (ddd, J=11.8, 5.5, 2.5 Hz, 1H), 5.69 (d, J=5.5 Hz, 1H), 7.44–7.88 (m, 12H), 8.47 (d, J=8.6 Hz, 1H), 8.92 (s, 1H), 9.01 (d, J=8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.7 (q), 22.4 (t), 74.5 (d), 94.0 (d), 123.1 (d), 124.5 (d), 125.1 (d), 125.4 (d), 125.9 (d), 126.2 (d), 126.6 (d), 126.8 (d), 127.5 (d), 128.7 (d), 129.0 (d), 129.30 (d), 130.4 (s), 130.5 (d), 130.9 (d), 131.3 (s), 131.9 (s), 133.8 (s), 134.1 (s), 134.9 (s), 163.6 (d); HRMS (FAB): calcd for $C_{25}H_{23}N_2O_2$ (M+1): 383.1760, found: 387.1789.

*4.3.10. erythro-(1E)-2-Aza-1,3-di(2-naphthyl)-4-nitrohex-1-ene (erythro-**3f**)*

IR ν (NaCl) 3056, 2970, 2929, 2854, 1637, 1547, 1369, 1346, 1121, 895, 858, 819, 746 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (t, J=7.3 Hz, 3H), 1.98–2.06 (m, 1H), 2.07–2.17 (m, 1H), 4.92 (d, J=8.3 Hz, 1H), 5.07–5.14 (m, 1H), 7.38–8.05 (m, 14H), 8.42 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.3 (q), 24.0 (t), 76.6 (d), 95.0 (d), 123.7 (d), 124.9 (d), 126.27 (d), 126.31 (d), 126.6 (d), 126.9 (d), 126.5 (d), 126.7 (d), 127.9 (d), 128.5 (d), 128.7 (d), 129.7 (d), 130.9 (d), 132.9 (s), 133.21 (s), 133.28 (s), 135.0 (s), 136.7 (s), 163.7 (d); HRMS (FAB): calcd for $C_{25}H_{23}N_2O_2$ (M+1): 383.1760, found: 383.1789.

*4.3.11. threo-(1E)-2-Aza-1,3-di(2-naphthyl)-4-nitrohex-1-ene (threo-**3f**)*

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, J=7.3 Hz, 3H), 1.47–1.55 (m, 1H), 1.89–1.98 (m, 1H), 4.87 (d, J=10.1 Hz, 1H), 5.07–5.14 (m, 1H), 7.38–8.00 (m, 14H), 8.35 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.3 (q), 24.4 (t), 76.6 (d), 95.4 (d), 123.9 (d), 126.45 (d), 126.53 (d), 127.4 (d), 127.8 (d), 128.0 (d), 128.1 (d), 128.4 (d), 129.0 (d), 132.9 (s), 133.2 (s), 133.3 (s), 135.0 (s), 135.7 (s), 163.0 (d).

*4.3.12. erythro-(1E)-2-Aza-1,3-di(2-furyl)-4-nitrohex-1-ene (erythro-**3g**)*

IR ν (NaCl) 3124, 2975, 2938, 2882, 1644, 1550, 1482, 1373, 1277, 1150, 1078, 1014, 933, 884, 810, 748 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (t, J=7.3 Hz, 3H), 1.95–2.17 (m, 2H), 4.88 (d, J=8.8 Hz, 1H), 5.09 (ddd, J=10.8, 8.8, 3.7 Hz, 1H), 6.31–6.34 (m, 2H), 6.50 (dd, J=3.4, 1.8 Hz, 1H), 6.86 (d, J=3.7 Hz, 1H), 7.37 (dd, J=1.7, 0.6 Hz, 1H), 7.55 (d, J=1.8 Hz, 1H), 8.11 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.1 (q), 24.4 (t), 69.1 (d), 91.6 (d), 108.3 (d), 110.5 (d), 112.0 (d), 116.5 (d), 143.0 (d), 145.7 (d), 150.7 (s), 150.8 (s), 152.7 (d); HRMS (FAB): calcd for $C_{13}H_{15}N_2O_4$ (M+1): 163.1032, found: 163.1026.

*4.3.13. threo-(1E)-2-Aza-1,3-di(2-furyl)-4-nitrohex-1-ene (threo-**3g**)*

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, J=7.3 Hz, 3H), 1.63–1.95 (m, 2H), 4.83 (d, J=10.1 Hz, 1H), 5.10 (ddd, J=10.2, 10.1, 3.4 Hz, 1H), 6.36–6.38 (m, 2H), 6.45 (dd, J=3.4, 1.8 Hz, 1H), 6.80 (d, J=3.4 Hz, 1H), 7.42 (dd, J=1.7, 0.7 Hz, 1H), 7.50 (d, J=1.5 Hz, 1H), 8.00 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.1 (q), 24.5 (t), 69.8 (d), 92.8 (d), 109.1 (d), 110.5 (d), 111.8 (d), 116.3 (d), 143.1 (d), 145.6 (d), 150.2 (s), 150.7 (s), 152.2 (d).

*4.3.14. erythro-(1E)-1,3-Di(9-anthryl)-2-aza-4-nitrohex-1-ene (erythro-**3h**)*

Mp 206–207 °C; IR ν (KBr) 3051, 2967, 2931, 2853, 1635, 1549, 1521, 1446, 1371, 891, 728 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.79 (t, J=7.3 Hz, 3H), 1.18–1.26 (m, 1H), 2.00–2.10 (m, 1H), 5.98 (ddd, J=3.0, 10.9, 10.9 Hz, 1H), 6.79 (d, J=10.7 Hz, 1H), 7.23–8.17 (m, 14H), 8.36 (s, 1H), 8.56 (s, 1H), 8.76 (d, J=9.2 Hz, 1H), 9.18 (d, J=8.3 Hz, 1H), 9.49 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.4 (q), 25.0 (t), 72.1 (d), 94.6 (d), 120.9 (d), 121.9 (d), 123.2 (d), 124.7 (d), 124.7 (d), 125.1 (d), 125.2 (d), 125.3 (d), 125.4 (d), 126.4 (s), 126.8 (s), 127.0 (d), 127.7 (d), 127.9 (d), 128.3 (d), 129.0 (d), 129.4 (s), 129.5 (d), 129.6 (s), 129.7 (d), 129.9 (d), 130.1 (s), 131.2

(s), 131.6 (s), 132.2 (s), 163.3 (d); HRMS (FAB): calcd for $C_{33}H_{26}N_2O_4$ (M+1): 483.2073, found: 483.2029.

*4.3.15. erythro-(1E)-2-Aza-4-nitro-1,3-diphenylpent-1-ene (erythro-**3i**)*

IR ν (NaCl) 3050, 2890, 1710, 1645, 1550, 1495, 1460, 1390, 1360, 1220, 1050 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.59 (d, J=6.5 Hz, 3H), 4.89 (d, J=6.5 Hz, 1H), 5.00 (q, J=6.5 Hz, 1H), 7.32–7.45 (m, 8H), 7.78 (d, J=1.5 Hz, 2H), 8.31 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.7 (q), 76.2 (d), 88.1 (d), 127.3 (d), 128.0 (d), 128.1 (d), 128.5 (d), 128.56 (d), 128.58 (d), 128.7 (d), 129.0 (d), 131.3 (d), 135.6 (s), 138.4 (s), 163.6 (d); HRMS (FAB): calcd for $C_{16}H_{17}N_2O_2$ (M+1): 269.1290, found: 269.1282. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.4. Found: C, 70.69; H, 6.11; N, 10.13.

*4.3.16. threo-(1E)-2-Aza-4-nitro-1,3-diphenylpent-1-ene (threo-**3i**)*

^1H NMR (500 MHz, $CDCl_3$) δ 1.40 (d, J=6.7 Hz, 3H), 4.66 (d, J=9.8 Hz, 1H), 5.11 (dq, J=9.8, 6.7 Hz, 1H), 7.27–7.45 (m, 8H), 7.76 (d, J=1.9 Hz, 2H), 8.23 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.8 (q), 77.8 (d), 88.5 (d), 127.3 (d), 128.0 (d), 128.1 (d), 128.46 (d), 128.56 (d), 128.58 (d), 128.7 (d), 1289.0 (d), 131.2 (d), 135.6 (s), 138.2 (s), 162.9 (d).

*4.3.17. erythro-(1E)-2-Aza-1,3-bis(4-methoxyphenyl)-4-nitropent-1-ene (erythro-**3j**)*

IR ν (NaCl) 2933, 2838, 1642, 1606, 1578, 1548, 1511, 1462, 1423, 1388, 1359, 1250, 1166, 1030, 831 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.58 (d, J=6.8 Hz, 3H), 3.78 (s, 3H), 3.83 (s, 3H), 4.77 (d, J=6.8 Hz, 1H), 4.96 (quint, J=6.8 Hz, 1H), 6.87 (d, J=8.9 Hz, 2H), 6.92 (d, J=8.6 Hz, 2H), 7.34 (d, J=8.6 Hz, 2H), 7.71 (d, J=8.9 Hz, 2H), 8.22 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.1 (q), 55.3 (q), 55.4 (q), 75.9 (d), 88.4 (d), 114.0 (d), 114.1 (d), 114.3 (d), 128.5 (d), 128.8 (d), 129.1 (d), 130.0 (d), 130.2 (d), 131.7 (s), 132.0 (d), 159.4 (s), 162.2 (s), 162.5 (s); HRMS (FAB): calcd for $C_{18}H_{21}N_2O_4$ (M+1): 329.1501, found: 329.1498.

*4.3.18. threo-(1E)-2-Aza-1,3-bis(4-methoxyphenyl)-4-nitropent-1-ene (threo-**3j**)*

^1H NMR (500 MHz, $CDCl_3$) δ 1.40 (d, J=6.7 Hz, 3H), 3.80 (s, 3H), 3.82 (s, 3H), 4.58 (d, J=9.5 Hz, 1H), 5.05 (dq, J=9.5, 6.7 Hz, 1H), 6.87 (d, J=8.9 Hz, 2H), 6.91 (d, J=8.9 Hz, 2H), 7.36 (d, J=8.5 Hz, 2H), 7.65 (d, J=8.9 Hz, 2H), 8.14 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.9 (q), 55.3 (q), 55.4 (q), 76.8 (d), 88.8 (d), 113.9 (d), 114.1 (d), 114.2 (d), 114.4 (d), 128.5 (d), 128.7 (d), 129.2 (d), 130.3 (d), 130.6 (s), 132.1 (d), 159.6 (s), 161.9 (s), 162.1 (d).

*4.3.19. erythro-(1E)-2-Aza-1,3-bis(4-methylphenyl)-4-nitropent-1-ene (erythro-**3k**)*

IR ν (NaCl) 3026, 2922, 2865, 1644, 1607, 1574, 1549, 1512, 1450, 1389, 1359, 1174, 1020, 813 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.57 (d, J=6.7 Hz, 3H), 2.31 (s, 3H), 2.37 (s, 3H), 4.81 (d, J=6.7 Hz, 1H), 4.98 (quint, J=6.7 Hz, 1H), 7.13–7.31 (m, 6H), 7.65 (d, J=7.9 Hz, 2H), 8.25 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.0 (q), 21.1 (q, 2C), 76.2 (d), 88.3 (d), 127.3 (d), 128.6 (d), 129.3 (d), 129.4 (d), 133.2 (s), 136.6 (s), 137.9 (s), 141.7 (s), 163.2 (d); HRMS (FAB): calcd for $C_{18}H_{21}N_2O_2$ (M+1): 297.1603, found: 297.1578. Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.79; H, 6.80; N, 9.30.

*4.3.20. threo-(1E)-2-Aza-1,3-bis(4-methylphenyl)-4-nitropent-1-ene (threo-**3k**)*

^1H NMR (500 MHz, $CDCl_3$) δ 1.39 (d, J=7.0 Hz, 3H), 2.33 (s, 3H), 2.33 (s, 3H), 4.60 (d, J=9.8 Hz, 1H), 5.05–5.11 (m, 1H), 7.15–7.32 (m, 6H), 7.59 (d, J=7.9 Hz, 2H), 8.17 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.9 (q), 21.50 (q), 21.53 (q), 77.6 (d), 88.6 (d), 127.9 (d), 129.1 (d), 129.2 (d), 129.7 (d), 129.8 (d), 133.1 (s), 135.4 (s), 138.2 (s), 141.5 (s), 162.6 (d).

*4.3.21. erythro-(1E)-2-Aza-1,3-bis(4-nitrophenyl)-4-nitropent-1-ene (erythro-**3l**)*

IR ν (NaCl) 3109, 3080, 2942, 2858, 1731, 1708, 1644, 1602, 1555, 1493, 1453, 1390, 1347, 1295, 1107, 1014 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.54 (d, J=6.4 Hz, 3H), 4.96 (quint, J=6.4 Hz, 1H), 5.03 (d, J=6.4 Hz, 1H), 7.58 (d, J=8.9 Hz, 2H), 7.91 (d, J=8.9 Hz, 2H), 8.15–8.23 (m, 4H), 8.39 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5 (q), 75.5 (d), 87.4 (d), 124.0 (d), 124.1 (d), 128.3 (d), 130.4 (d), 140.2 (s), 145.5 (s), 149.9 (s), 149.7 (s), 162.7 (d); HRMS (FAB): calcd for $C_{16}H_{15}N_4O_6$ (M+1): 359.0992, found: 359.1019.

*4.3.22. threo-(1E)-2-Aza-1,3-bis(4-nitrophenyl)-4-nitropent-1-ene (threo-**3l**)*

^1H NMR (500 MHz, $CDCl_3$) δ 1.39 (d, J=7.1 Hz, 3H), 4.80 (d, J=9.2 Hz, 1H), 5.02–5.07 (m, 1H), 7.62 (d, J=8.5 Hz, 2H), 7.84 (d, J=8.5 Hz, 2H), 8.16–8.21 (m, 4H), 8.30 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6 (q), 77.0 (d), 87.7 (d), 123.8 (d), 124.5 (d), 129.0 (d), 129.4 (d), 140.2 (s), 144.3 (s), 148.1 (s), 149.6 (s), 161.9 (d).

*4.3.23. erythro-(1E)-(3RS,4SR)-2-Aza-1,3-dinaphthyl-4-nitropent-1-ene (erythro-**3m**)*

Mp 127.5–129 °C; IR ν (KBr) 3051, 1734, 1685, 1636, 1615, 1590, 1546, 1508, 1443, 1383, 1361, 1162, 1049, 970 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.69 (d, J=6.4 Hz, 3H), 5.30 (dq, J=6.4, 4.0 Hz, 1H), 5.95 (d, J=4.0 Hz, 1H), 7.45–7.95 (m, 12H), 8.42 (d, J=8.5 Hz, 1H), 8.98 (s, 1H), 9.09 (d, J=7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.2 (q), 73.7 (d), 86.4 (d), 122.5 (d), 124.6 (d), 125.1 (d), 125.5 (d), 125.9 (d), 126.2 (d), 126.3 (d), 127.0 (d), 127.6 (d), 128.7 (d), 128.8 (d), 129.4 (d), 130.1 (s), 130.7 (d), 131.0 (s), 131.3 (s), 132.0 (d), 133.9 (s), 134.0 (s), 134.9 (s), 164.1 (d); HRMS (FAB): calcd for $C_{24}H_{21}N_2O_2$ (M+1): 369.1603, found: 369.1584. Anal. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60. Found: C, 77.96; H, 5.48; N, 7.53.

*4.3.24. erythro-(1E)-2-Aza-1,3-di(2-naphtyl)-4-nitropent-1-ene (erythro-**3n**)*

IR ν (NaCl) 3058, 2867, 1734, 1638, 1548, 1450, 1387, 1359, 1243, 1122, 1048, 1638 cm^{-1}; ^1H NMR (500 MHz,

$CDCl_3$) δ 1.65 (d, J=6.4 Hz, 3H), 5.11 (d, J=6.4 Hz, 1H), 5.14 (quint, J=6.4 Hz, 1H), 7.44–8.09 (m, 14H), 8.47 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.9 (q), 76.4 (d), 88.1 (d), 123.8 (d), 124.9 (d), 126.3 (d), 126.4 (d), 126.6 (d), 126.7 (d), 127.5 (d), 127.7 (d), 127.9 (d), 128.1 (d), 128.5 (d), 128.7 (d), 131.0 (d), 132.9 (s), 133.1 (s), 133.3 (s), 135.0 (s), 136.8 (s), 163.9 (d); HRMS (FAB): calcd for $C_{24}H_{21}N_2O_2$ (M+1): 369.1603, found: 369.1595.

*4.3.25. threo-(1E)-2-Aza-1,3-di(2-naphtyl)-4-nitropent-1-ene (threo-**3n**)*

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43 (d, J=6.7 Hz, 3H), 4.89 (d, J=9.8 Hz, 3H), 5.26 (dq, J=9.8, 6.7 Hz, 1H), 7.43–8.10 (m, 14H), 8.41 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.0 (q), 78.0 (d), 88.5 (d), 123.9 (d), 125.3 (d), 126.4 (d), 126.5 (d), 127.4 (d), 127.76 (d), 127.83 (d), 128.0 (d), 128.4 (d), 128.7 (d), 129.0 (d), 130.9 (d), 132.9 (s), 133.1 (s), 133.3 (s), 134.9 (s), 135.6 (s), 163.2 (d).

*4.3.26. (1E)-2-Aza-4-nitro-1,3-diphenylbut-1-ene (**3o**)*

IR ν (NaCl) 3062, 3030, 2873, 1643, 1601, 1579, 1555, 1519, 1493, 1453, 1418, 1376, 1343, 1218, 1027, 969 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.56 (dd, J=12.7, 3.8 Hz, 1H), 4.82 (dd, J=12.7, 9.9 Hz, 1H), 5.04 (dd, J=9.9, 3.8 Hz, 1H), 7.21–7.34 (m, 6H), 7.39 (d, J=7.4 Hz, 2H), 7.70 (d, J=7.9 Hz, 2H), 8.25 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 71.3 (d), 80.9 (t), 127.1 (d), 128.3 (d), 128.5 (d), 128.6 (d), 128.9 (d), 129.2 (d), 131.3 (d), 135.4 (s), 138.4 (s), 163.2 (d); HRMS (FAB): calcd for $C_{15}H_{15}N_2O_2$ (M+1): 255.1134, found: 255.1151.

*4.3.27. (1E)-2-Aza-1,3-bis(4-methoxyphenyl)-4-nitrobut-1-ene (**3p**)*

IR ν (NaCl) 3107, 2928, 1685, 1632, 1605, 1498, 1414, 1333, 1264, 1186, 964, 809 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.78 (s, 1H), 3.82 (s, 1H), 4.64 (dd, J=12.4, 4.0 Hz, 1H), 4.86 (dd, J=12.4, 9.9 Hz, 1H), 5.03 (dd, J=9.9, 4.0 Hz, 1H), 6.89 (d, J=8.9 Hz, 2H), 6.90 (d, J=8.9 Hz, 2H), 7.37 (d, J=8.9 Hz, 2H), 7.69 (d, J=8.9 Hz, 2H), 8.24 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3 (q), 55.4 (q), 71.0 (d), 81.2 (t), 114.0 (d), 114.4 (d), 128.3 (d), 128.6 (s), 130.3 (d), 130.8 (s), 132.0 (d), 159.5 (s), 162.1 (s), 162.5 (d); HRMS (FAB): calcd for $C_{17}H_{19}N_2O_4$ (M+1): 315.1345, found: 315.1367.

*4.3.28. (1E)-2-Aza-1,3-bis(4-methylphenyl)-4-nitrobut-1-ene (**3q**)*

IR ν (NaCl) 3026, 2920, 2869, 1686, 1642, 1610, 1554, 1512, 1375, 1338, 1175, 969, 813 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 1H), 2.36 (s, 1H), 4.65 (dd, J=12.3, 3.6 Hz, 1H), 4.89 (dd, J=12.3, 9.9 Hz, 1H), 5.06 (dd, J=9.9, 3.6 Hz, 1H), 7.16–7.20 (m, 4H), 7.34 (d, J=7.8 Hz, 2H), 7.64 (d, J=7.8 Hz, 2H), 8.28 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1 (q), 21.5 (q), 71.3 (d), 81.1 (t), 127.1 (d), 128.6 (d), 129.2 (d), 129.3 (d), 129.7 (d), 130.2 (d), 133.0 (s), 135.7 (s), 136.3 (d), 138.2 (s), 139.2 (d), 141.7 (s), 163.3 (d); HRMS (FAB): calcd for $C_{17}H_{19}N_2O_2$ (M+1): 283.1447, found: 283.1466.

*4.3.29. (1E)-2-Aza-1,3-bis(4-nitrophenyl)-4-nitrobut-1-ene (**3r**)*

IR ν (NaCl) 3106, 2915, 1687, 1641, 1600, 1555, 1523, 1415, 1376, 1347, 1315, 1217, 1108, 1072, 857 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.75 (dd, J=12.9, 3.9 Hz, 1H), 4.94 (dd, J=12.9, 9.8 Hz, 1H), 5.32 (dd, J=9.8, 3.9 Hz, 1H), 7.72 (d, J=8.6 Hz, 2H), 7.98 (d, J=8.6 Hz, 2H), 8.26–8.29 (m, 4H), 8.50 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.8 (d), 80.0 (t), 123.9 (d), 124.4 (d), 128.2 (d), 129.5 (d), 140.1 (s), 144.5 (s), 148.1 (s), 149.7 (s), 162.7 (d); HRMS (FAB): calcd for $C_{15}H_{13}N_4O_6$ (M+1): 345.0835, found: 345.0824.

*4.3.30. (1E)-2-Aza-1,3-dinaphthyl-4-nitrobut-1-ene (**3s**)*

IR ν (NaCl) 3058, 2913, 1732, 1687, 1637, 1618, 1555, 1509, 1375, 1340, 1228, 1167, 802 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.91 (dd, J=12.8, 3.1 Hz, 1H), 5.11 (dd, J=12.8, 10.1 Hz, 1H), 6.01 (dd, J=10.1, 3.1 Hz, 1H), 7.48–7.56 (m, 4H), 7.60–7.66 (m, 2H), 7.83–7.88 (m, 2H), 7.91–7.95 (m, 4H), 8.36 (d, J=8.5 Hz, 1H), 8.99 (d, J=8.5 Hz, 1H), 9.06 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.4 (d), 80.5 (t), 122.4 (d), 124.5 (d) 125.1 (d), 125.7 (d), 125.9 (d), 126.0 (d), 126.2 (d), 127.0 (d), 127.5 (d), 128.7 (d), 129.0 (d), 129.4 (d), 130.1 (s), 130.3 (d), 130.9 (s), 131.3 (s), 132.0 (d), 133.8 (s), 134.1 (s), 134.1 (s), 164.1 (d); HRMS (FAB): calcd for $C_{23}H_{19}N_2O_2$ (M+1): 355.1447, found: 355.1472.

*4.3.31. (1E)-2-Aza-1,3-di(2-naphthyl)-4-nitrobut-1-ene (**3t**)*

IR ν (NaCl) 3056, 2970, 2872, 1692, 1632, 1598, 1547, 1508, 1467, 1419, 1374, 1271, 1215, 1122, 1063, 828 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77 (dd, J=12.5, 4.0 Hz, 1H), 5.03 (dd, J=12.5, 10.0 Hz, 1H), 5.32 (dd, J=4.0, 10.0 Hz, 1H), 7.4–8.1 (m, 12H), 7.59 (d, J=7.3 Hz, 1H), 8.06 (d, J=8.6 Hz, 1H), 8.50 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 71.7 (d), 81.0 (t), 123.8 (d), 124.7 (d), 126.4 (d), 126.5 (d), 127.5 (d), 127.7 (d), 127.9 (d), 128.0 (d), 128.5 (d), 128.7 (d), 128.9 (d), 131.0 (d), 132.9 (s), 133.2 (s), 133.4 (s), 135.0 (s), 135.8 (s), 163.9 (d); HRMS (FAB): calcd for $C_{23}H_{19}N_2O_2$ (M+1): 355.1447, found: 355.1429.

*4.4. Hydrogenation of imine derivative **3a***

A suspension of **3a** (1300 mg) and 10 wt % Pd–C (300 mg) in ethanol (15 ml) was stirred under hydrogen atmosphere for 5 h at room temperature. Ethanol (10 ml) was added and after the catalyst had settled the supernatant liquid was carefully decanted. The solvent was then distilled off in a rotary evaporator to obtain the crude product which was chromatographed on silica gel to give 617 mg (47%) of (2-nitro-1-phenylbutyl)-benzylamine (*erythro*/*threo* ratio; 1/10).

threo-(2-Nitro-1-phenylbutyl)benzylamine: IR ν (NaCl) 3328, 3061, 3027, 2972, 2935, 1551, 1494, 1454, 1374, 1258, 1108, 1078, 1027, 806, 735, 735, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (t, J=7.4 Hz, 3H), 1.32–1.40 (m, 1H), 1.75–1.83 (m, 1H), 1.74 (br s, 1H), 3.45 (d, J=13.3 Hz, 1H), 3.64 (d, J=13.3 Hz, 1H), 3.99 (d, J=10.1 Hz, 1H), 4.55 (ddd, J=3.4, 10.1, 10.7 Hz, 1H), 7.17–7.42 (m, 10H); ^{13}C NMR (125 Hz, $CDCl_3$) δ 10.3 (q), 24.8 (t), 50.8 (t), 64.5 (d),

95.3 (d), 127.1 (d), 127.7 (d), 128.0 (d), 128.2 (d), 128.29 (d), 128.32 (d), 128.5 (d), 128.6 (d), 129.0 (d), 129.1 (d), 138.5 (s), 139.4 (s); HRMS (FAB): calcd for $C_{17}H_{21}N_2O_2$ (M+1): 285.1603, found: 285.1606.

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