Ammonia–Borane-Mediated Reduction of Nitroalkenes

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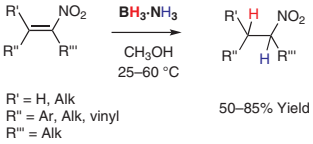

Highly chemoselective with alkyl and aryl nitro alkenes

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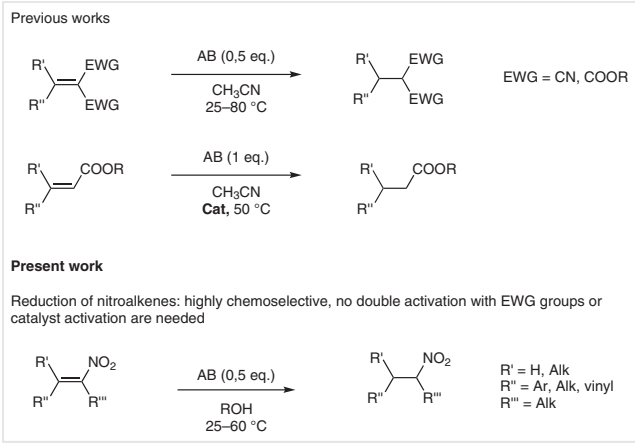
Abstract Ammonia borane (AB) has been successfully employed in the reduction of nitroalkenes. A variety of nitrostyrenes and alkyl-substituted nitroalkenes were chemoselectively reduced to the corresponding nitroalkanes, in short reaction time, with an atom-economic, simple experimental procedure that also works with α- and β-substituted nitroolefins.

Key words reduction, ammonia borane, nitroalkenes, atom economy



Scheme 1 Chemoselective AB-mediated reduction of nitroalkenes

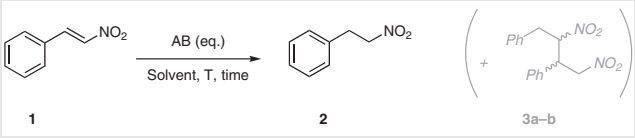
Ammonia borane (AB) is attracting considerable attention as a convenient material for hydrogen storage and release.[1,2] However, considering atom economy principles, it is also a relatively inexpensive and useful reduction reagent for developing new green synthetic transformations.

Ammonia borane could act as a convenient replacement for the well-known metal hydrides (sodium borohydride and derivatives), and as a safer and greener replacement[3] of Hantzsch esters, which generate a significant amount of waste (the oxidized pyridine needs to be removed and separated from the reaction product). Reduction with ammonia borane of carbonyl derivatives, imines and amides has been described in detail.[4] One the other hand, the AB-mediated reduction of alkenes is less developed[5] and only highly electron-deficient alkenes bearing two electron-withdrawing groups (esters or nitriles) have been successfully reduced (Scheme 1).[6] The presence of a catalytic additive is required to accomplish the reduction of unsaturated esters.[7]

Herein, we wish to report, for the first time, the use of ammonia borane in the reduction of nitroalkenes. A variety of nitrostyrenes and alkyl-substituted nitroalkenes can be chemoselectively reduced to the corresponding nitroalkanes, without need for catalyst or additive, in a short time and with a straightforward experimental procedure that is applicable to both α- and β-substituted nitroalkenes. After a simple aqueous work up, the reaction product can be obtained by evaporation of the organic solvent, in many cases as the sole or major product (see the Supporting Information).

We decided to investigate the reaction of ammonia borane with β-nitrostyrene as a model reaction (Scheme 2) in which experimental parameters, such as solvent, temperature, stoichiometry, and reaction time, were studied.

A detailed optimization work was performed to obtain the best yields under the most convenient experimental conditions, and to minimize the formation of the dimeric



Scheme 2 AB-mediated reduction of β-nitrostyrene

by-products **3a** and **3b**, thus simplifying the isolation procedure of the nitroalkane;[8] selected data are collected in Table 1.

Ammonia borane was typically added to a solution of nitroalkene at 25 °C and then the reaction was stirred for 4–24 hours, depending on the experimental conditions. Initially, the reduction was carried out at 25 °C, in methanol at 0.01–0.1 M substrate concentration. After 18 hours, product **2** was isolated in 61% yield (Table 1, entry 1) with minor amounts of the dimer **3**, as mixture of isomers (less than 15%). To accelerate the reaction and suppress by-product formation, the reaction was performed at 60 °C in methanol. After only 4 hours the product was obtained in 53% yield after chromatographic purification (entry 4). Lower yields were observed other alcohol solvents such as ethanol or *n*-butanol, whereas in solvents such as THF, DCM or acetonitrile, the reduction was inefficient. When the reduction was performed in more concentrated solutions, similar yields of nitroalkane were observed, but with increased amounts of the dimeric product. The use of excess of ammonia borane did not bring any significant improvement to the yield or the selectivity of the reaction. Ultimately, the best compromise was found using 0.05 M substrate concentration, with 1 mol equiv of AB for 4 hours at 60 °C; under these conditions the product **2** was isolated in 60% yield, with minor amounts of by-product **3**.

Finally, the use of urea and thiourea derivatives was investigated, especially with the aim to suppress the formation of dimeric material. By employing urea as additive in methanol, low yields were observed, while somewhat better results were observed in THF. More interesting results were achieved by using Schreiner thiourea (1,3-bis(3,5-bis(trifluoromethyl)phenyl)thiourea). In this case, the reaction afforded **2** in good yield with very minor amounts of dimers **3**. The use of (thio)urea derivatives opens the way towards the development of chiral catalysts that can be used to promote the enantioselective reduction of β-substituted β-nitrostyrenes to the corresponding nitroalkanes, which are valuable precursors of chiral amines (see below).

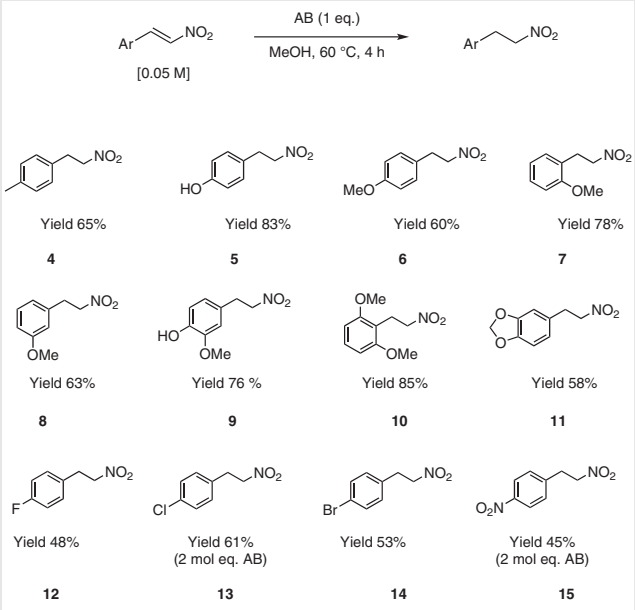
The scope of the reaction was then investigated with differently substituted aryl and alkyl nitroalkenes (for experimental details on nitroalkene preparation see the Supporting Information), reacting with 1 mol equiv of ammonia borane in methanol for 4 hours at 60 °C. The results obtained on the reduction of a range functionalized nitrostyrenes are summarized in Scheme 3.

The reaction was successfully performed with a range of nitrostyrenes. Electron-rich nitroalkenes were reduced in fair to very good yields, up to 85% (see products **4**–**11** in Scheme 3). The reduction of substrates bearing electron-withdrawing groups afforded the corresponding nitroalkanes **12**–**15** in yields typically ranging from 45 to 60%. The methodology was also extended to aliphatic nitroalkenes (Scheme 4).

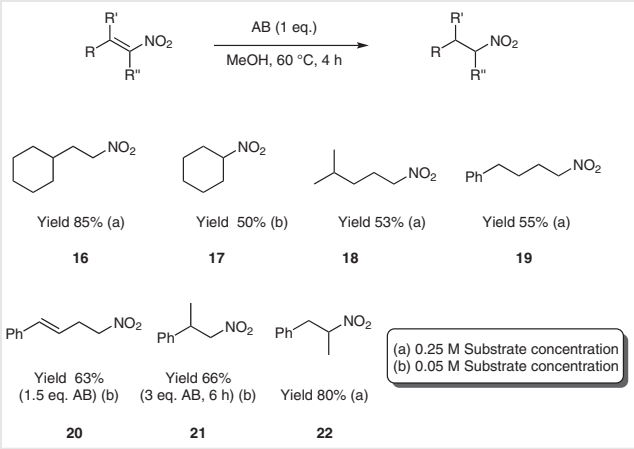
Table 1 Nitrostyrene Reduction: Optimization Studies[a] (Scheme 2)

Entry	Solvent	*T* (°C)	Time (h)	Concn (M)	Yield **2** (%)[b]
1	MeOH	25	18	0.01	61
2	MeOH	25	18	0.1	40
3	CH_3CN	25	18	0.01	12
4	MeOH	60	4	0.1	53
5	EtOH	60	4	0.1	33
6	*n*-BuOH	60	4	0.1	41
7[c]	MeOH	60	4	0.1	43
8[d]	MeOH	60	4	0.1	55
9	MeOH	60	4	0.05	60
10[e]	THF	60	4	0.1	40
11[f]	MeOH	60	4	0.1	47

[a] Typical reaction conditions: AB (1 mol equiv), no additive. For the general procedure and work-up see the experimental section.
[b] Isolated yield after chromatographic purification.
[c] 2 mol equiv of AB were used.
[d] 4 mol equiv of AB were used.
[e] 0.2 mol equiv of urea was added.
[f] 0.2 mol equiv of Schreiner thiourea were added.



Scheme 3 AB-mediated reduction of functionalized β-nitrostyrenes



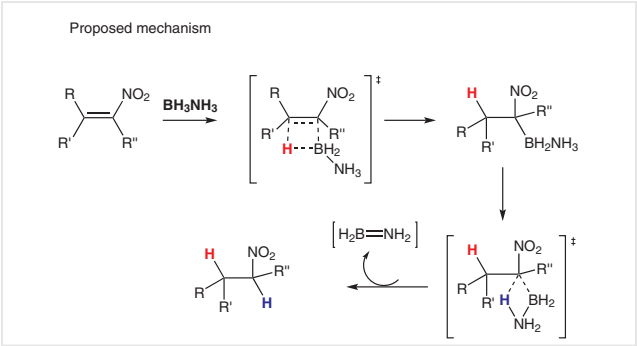
Scheme 4 AB-mediated reduction of β-nitroalkenes

Ammonia borane proved to be an efficient reagent for the reduction of both linear and branched aliphatic nitroalkenes, affording the expected products in fair to excellent yields. Notably, the nitro derivative **20** was isolated in 63% yield, with complete chemoselectivity, by reduction of the corresponding nitrobutadiene.[9]

The reaction worked very well with either α- or β-substituted nitrostyrenes and improved yields for product **21** were obtained when 3 mol equiv of AB were employed; thus affording **21** in 66% yield after 6 hours. This result opens the way towards the development of new catalytic, asymmetric, atom-economical and convenient strategies for the synthesis of chiral nitroalkanes, which are valuable precursors of chiral amines.[10]

α-Substituted nitroalkane **22** was isolated in 80% yield and the reaction was conducted on a gram scale, without significant difference in yield (76%). It is worth noting that, for both compounds **21** and **22**, after a simple aqueous work up, NMR analysis of the crude reaction mixture showed only the desired nitroalkane, without the need for chromatographic purification (see NMR spectra in the Supporting Information).

Based on previous reports,[11] a proposed reaction mechanism is shown in Scheme 5. The first step is the transfer of a hydride from BH_3 to the β-position of the nitroalkene, together with the hydroboration of the C–C double bond. The intermediate is then proposed to convert slowly into the product by intramolecular transfer of a H atom from the NH_3 residue, thus realizing a BH_2=NH_2 species that might be involved in the reduction of another equivalent of the olefin.[12]



Scheme 5 Proposed mechanism for the AB-mediated reduction of β-nitroalkenes

In conclusion, we have developed a chemoselective reduction of nitroalkenes to nitroalkanes, using ammonia borane in methanol. The methodology works with aryl- and alkyl-substituted nitroolefins, it affords the products after a simple aqueous work up, and relies on the use of the atom-economical, very convenient and inexpensive reagent $BH_3{\cdot}NH_3$. The reaction proceeds smoothly with α- and β-substituted nitroalkenes, thus paving the way for development of enantioselective catalytic reduction of nitroalkenes, which are valuable precursors of chiral amines.

Commercial grade reagents and solvents were used without further purification. *trans*-β-Nitrostyrene [CAS Reg. No. 5153-67-3], *trans*-β-methyl-β-nitrostyrene [CAS Reg. No. 705-60-2] and 1-nitro-1-cyclohexene [CAS Reg. No. 2562-37-0] were purchased from Sigma Aldrich and were used without further purification. Ammonia borane [CAS Reg. No. 13774-81-7] was purchased by Sigma Aldrich and was used without further purification.

^1H, ^{19}F, and ^{13}C NMR spectra were recorded at 300 MHz with a Bruker AV 300 instrument. The chemical shifts are reported in ppm (δ) referenced to tetramethylsilane (TMS). Mass spectrometric and accurate mass analyses were carried out with a VG AUTOSPEC-M246 spectrometer (double-focusing magnetic sector instrument with EBE

geometry) equipped with an EI source. Reactions and chromatographic purifications were monitored by analytical thin-layer chromatography (TLC) using silica gel 60 F254 pre-coated glass plates and visualized using UV light, vanillin or $KMnO_4$. Purification of the products was performed by flash column chromatography using silica gel 230–400 mesh. Dry solvents used were commercially available and they were stored under nitrogen over molecular sieves. Microwave reactions were conducted with a CEM Discover SP microwave with an irradiation power of 200 W and reaction temperature of 90 °C for 1 hour.

Aryl-substituted and alkyl-substituted nitroalkenes were prepared from the corresponding aldehydes and nitromethane according to published procedures and purified by crystallization from EtOH (see the Supporting Information).

Reduction of Nitroalkenes; General Procedure

Caution: Readily reduced, flammable compounds (e.g., acetone) may combust upon contact with ammonia borane.

A solution of nitroalkene (0.4 mmol) in anhydrous MeOH (8 mL) was prepared in a 25 mL two-necked round-bottom flask fitted with a condenser. Ammonia borane (12 mg, 0.4 mmol) was added to the solution at r.t. and the reaction flask was placed in an oil bath (previously heated to 60 °C). After 4 hours, the reaction mixture was cooled to r.t. and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (8 mL) and washed with water (5 mL). The aqueous phase was extracted once with dichloromethane (5 mL) and the combined organic phases were dried over Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. If necessary, the crude product was purified by rapid filtration through silica.

2-Phenylnitroethane (2)

The crude product was purified by column chromatography on silica gel, eluting with hexane/EtOAc 95:5 to afford the title product as a colorless oil. All analytical data are in agreement with the literature.[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.19 (m, 5 H), 4.61 (t, *J* = 7.4 Hz, 2 H), 3.32 (t, *J* = 7.4 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.78, 129.00, 128.63, 127.47, 76.30, 33.46.

((2*R*,3*S*)-2,4-Dinitrobutane-1,3-diyl)dibenzene (3a)

Isolated as a pale-yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.38 (m, 3 H), 7.29– 7.24 (m, 5 H), 7.00 (dd, *J* = 7.1, 2.6 Hz, 2 H), 4.99 (td, *J* = 10.3, 3.5 Hz, 1 H), 4.83 (dd, *J* = 13.1, 10.2 Hz, 1 H), 4.64 (dd, *J* = 13.1, 4.3 Hz, 1 H), 4.08 (td, *J* = 10.1, 4.3 Hz, 1 H), 3.14 (dd, *J* = 14.6, 10.7 Hz, 1 H), 2.86 (dd, *J* = 14.6, 3.5 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.59, 134.11, 129.95, 129.46, 129.11, 128.67, 128.14, 127.95, 91.82, 77.00, 47.30, 38.32.

MS(EI+): *m*/*z* calcd for $C_{16}H_{16}N_2O_4$: 300.111007; found: 300.102000.

((2*R*,3*R*)-2,4-Dinitrobutane-1,3-diyl)dibenzene (3b)

Isolated as a pale-yellow solid.

^{1}H NMR spectrum is in agreement with the literature, but the ^{13}C NMR spectrum differs for some signals with respect to the literature.[14]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.35 (m, 3 H), 7.33–7.28 (m, 3 H), 7.20–7.13 (m, 4 H), 5.14 (dt, *J* = 9.5, 5.5 Hz, 1 H), 4.99 (dd, *J* = 13.8, 6.6 Hz, 1 H), 4.83 (dd, *J* = 13.8, 7.9 Hz, 1 H), 4.11–4.05 (m, 1 H), 3.26 (dd, *J* = 14.5, 9.5 Hz, 1 H), 3.11 (dd, *J* = 14.5, 5.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.66, 133.31, 129.50, 129.41, 129.21, 128.94, 128.22, 127.93, 90.22, 76.36, 46.50, 36.99.

2-*p*-Tolylnitroethane (4)

The crude product was purified by column chromatography on silica gel, eluting with hexane/EtOAc 95:5 to afford the title product as a pale-yellow oil (64% yield). All analytical data are in agreement with the literature.[15]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 8.2 Hz, 2 H), 7.12 (d, *J* = 8.2 Hz, 2 H), 4.61 (t, *J* = 7.4 Hz, 2 H), 3.30 (t, *J* = 7.4 Hz, 2 H), 2.36 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.17, 132.68, 129.71, 128.52, 76.51, 33.16, 21.11.

2-(4-Hydroxyphenyl)-1-nitroethane (5)

The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 6:4 to afford the title product as a pale-orange oil (83% yield). All analytical data are in agreement with the literature.[16]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05 (d, *J* = 8.5 Hz, 2 H), 6.78 (d, *J* = 8.5 Hz, 2 H), 5.90 (brs, 1 H), 4.56 (t, *J* = 7.3 Hz, 2 H), 3.22 (t, *J* = 7.3 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.10, 129.89, 127.67, 115.92, 76.74, 32.74.

1-Methoxy-4-(2-nitroethyl)-benzene (6)

The crude product was purified by column chromatography on silica gel, eluting with hexane/EtOAc 8:2 to afford the title product as a yellow oil (58% yield). All analytical data are in agreement with the literature.[17]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 8.6 Hz, 2 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 4.56 (t, *J* = 7.3 Hz, 2 H), 3.78 (s, 3 H), 3.24 (t, *J* = 7.3 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.01, 129.71, 127.72, 114.44, 76.67, 55.36, 32.77.

1-Methoxy-2-(2-nitroethyl)benzene (7)

The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 85: 15 to afford the title product as a pale-yellow oil (78% yield). All analytical data are in agreement with the literature.[18]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (td, *J* = 7.8, 1.8 Hz, 1 H), 7.15 (dd, *J* = 7.4, 1.8 Hz, 1 H), 6.97–6.82 (m, 2 H), 4.61 (t, *J* = 7.3 Hz, 2 H), 3.85 (s, 3 H), 3.32 (t, *J* = 7.4 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.57, 130.78, 128.96, 123.97, 120.83, 110.50, 74.82, 55.33, 29.22.

1-Methoxy-3-(2-nitroethyl)benzene (8)

The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 8:2 to afford the title product as a pale-yellow oil (60% yield). All analytical data are in agreement with the literature.[19]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25 (t, *J* = 7.9 Hz, 1 H), 6.83–6.74 (m, 3 H), 4.60 (t, *J* = 7.4 Hz, 2 H), 3.80 (s, 3 H), 3.29 (t, *J* = 7.4 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.10, 137.29, 130.09, 120.86, 114.54, 112.79, 76.25, 55.31, 33.52.

2-Methoxy-4-(2-nitroethyl)phenol (9)

The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 65:35 to afford the title product as a yellow oil (76% yield). All analytical data are in agreement with the literature.[20]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.85 (d, *J* = 8.5 Hz, 1 H), 6.71–6.67 (m, 2 H), 5.64 (s, 1 H), 4.57 (t, *J* = 7.3 Hz, 2 H), 3.86 (s, 3 H), 3.23 (t, *J* = 7.3 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.84, 145.02, 127.57, 121.40, 114.84, 111.23, 76.73, 56.02, 33.29.

1,3-Dimethoxy-2-(2-nitroethyl)benzene (10)

Prepared according a reported procedure.[20] The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 8:2 to afford the title product as a pale-yellow oil (85% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (t, *J* = 8.4 Hz, 1 H), 6.56 (d, *J* = 8.4 Hz, 2 H), 4.51–4.46 (m, 2 H), 3.83 (s, 6 H), 3.43–3.38 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.54, 128.63, 111.82, 103.66, 74.05, 55.74, 21.69.

MS(EI+): *m*/*z* calcd. for $C_{10}H_{13}NO_4$: 211.084458; found: 211.084720.

5-(2-Nitroethyl)benzo[1,3]dioxole (11)

The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 9:1 to afford the title product as a yellow oil (58 % yield). All analytical data are in agreement with the literature.[17]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.75 (d, *J* = 7.8 Hz, 1 H), 6.68–6.63 (m, 2 H), 5.93 (s, 2 H), 4.55 (t, *J* = 7.3 Hz, 2 H), 3.22 (t, *J* = 7.3 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.15, 147.03, 129.36, 121.82, 109.00, 108.73, 101.25, 76.63, 33.31.

1-(4-Fluorophenyl)-2-nitroethane (12)

The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 9:1 to afford the title product as a pale-yellow oil (48% yield). All analytical data are in agreement with the literature.[16]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18 (dd, *J* = 8.7, 5.3 Hz, 2 H), 7.01 (t, *J* = 8.7 Hz, 2 H), 4.59 (t, *J* = 7.2 Hz, 2 H), 3.29 (t, *J* = 7.2 Hz, 2 H).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –115.03 (s, 1 F).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.25 (d, *J* = 245.9 Hz), 131.52 (d, *J* = 3.4 Hz), 130.28 (d, *J* = 8.1 Hz), 115.97 (d, *J* = 21.5 Hz), 76.39, 32.72.

1-(4-Chlorophenyl)-2-nitroethane (13)

Prepared according to the general procedure (two equivalents of ammonia borane were used). The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 95:5 to afford the title product as a yellow oil (61% yield). All analytical data are in agreement with the literature.[21]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.4 Hz, 2 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 4.59 (t, *J* = 7.2 Hz, 2 H), 3.29 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.26, 133.52, 130.05, 129.24, 76.10, 32.81.

1-(4-Bromophenyl)-2-nitroethane (14)

The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 95:5 to afford the title product as a pale-yellow oil (53% yield). All analytical data are in agreement with the literature.[16]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.4 Hz, 2 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 4.59 (t, *J* = 7.2 Hz, 2 H), 3.27 (t, *J* = 7.2 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.77, 132.24, 130.41, 121.61, 76.03, 32.91.

1-Nitro-4-(2-nitroethyl)benzene (15)

Prepared according to the general procedure (two equivalents of ammonia borane were used). The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 8:2 to afford the title product as a yellow solid (44% yield). All analytical data are in agreement with the literature.[22]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.4 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 4.68 (t, *J* = 7.0 Hz, 2 H), 3.43 (t, *J* = 7.0 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.51, 143.34, 129.68, 124.25, 75.35, 32.97.

2-Cyclohexyl-1-nitroethane (16)

Prepared according to the general procedure (using 1.6 mL of anhydrous methanol). The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 95:5 to afford the title product as a pale-yellow oil (85% yield). All analytical data are in agreement with the literature.[23]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.39 (t, *J* = 7.4 Hz, 2 H), 1.89 (q, *J* = 7.4 Hz, 2 H), 1.76–1.59 (m, 5 H), 1.39–1.11 (m, 4 H), 1.01–0.86 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 73.98, 35.07, 34.79, 32.85, 26.35, 26.07.

Nitrocyclohexane (17)

The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 98:2 to afford the title product as a colorless oil (50% yield). All analytical data are in agreement with the literature.[23]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.36 (tt, *J* = 10.6, 4.1 Hz, 1 H), 2.30–2.16 (m, 2 H), 1.97–1.77 (m, 4 H), 1.72–1.62 (m, 1 H), 1.45–1.16 (m, 3 H).

4-Methyl-1-nitropentane (18)

The crude mixture was purified by column chromatography on silica gel, eluting with pentane/diethyl ether 97:3 to afford the title product as a colorless oil (53% yield). All analytical data are in agreement with the literature.[24]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.34 (t, *J* = 7.1 Hz, 2 H), 2.09–1.91 (m, 2 H), 1.58 (dp, *J* = 13.3, 6.6 Hz, 1 H), 1.27–1.19 (m, 2 H), 0.89 (d, *J* = 6.6 Hz, 6 H).

1-Nitro-4-phenylbutane (19)

Prepared according to the general procedure (using 1.6 mL of anhydrous methanol). The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 9:1 to afford the title product as a colorless oil (55% yield). All analytical data are in agreement with the literature.[25]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.17 (m, 5 H), 4.38 (t, *J* = 7.0 Hz, 2 H), 2.69 (t, *J* = 7.5 Hz, 2 H), 2.04 (quint, *J* = 7.2 Hz, 2 H), 1.74 (quint, *J* = 7.7 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.15, 128.61, 128.45, 126.25, 75.59, 35.10, 27.97, 26.94.

(*E*)-(4-Nitrobut-1-en-1-yl)benzene (20)

Prepared according to the general procedure (1.5 equivalents of ammonia borane were used). The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 95:5 to afford the title product as a yellow oil (63% yield). All analytical data are in agreement with the literature.[26]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.21 (m, 5 H), 6.53 (dt, *J* = 15.8, 1.5 Hz, 1 H), 6.12 (dt, *J* = 15.8, 7.0 Hz, 1 H), 4.50 (t, *J* = 7.0 Hz, 2 H), 2.90 (qd, *J* = 7.0, 1.4 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.60, 134.12, 128.72, 127.91, 126.39, 123.06, 75.08, 30.85.

1-Nitro-2-phenylpropane (21)

Prepared according to the general procedure (three equivalents of ammonia borane were used and the reaction was stirred for 6 hours). The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 95:5 to afford the title product as a yellow oil (66% yield). All analytical data are in agreement with the literature.[27]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.22 (m, 5 H), 4.52 (qd, *J* = 12.0, 7.8 Hz, 2 H), 3.64 (h, *J* = 7.2 Hz, 1 H), 1.39 (d, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.04, 129.09, 127.68, 127.03, 81.98, 38.77, 18.85.

2-Nitro-1-phenylpropane (22)

Prepared according to the general procedure (using 1.6 mL of anhydrous methanol). The crude mixture was purified by column chromatography on silica gel, eluting with hexane/EtOAc 95:5 to afford the title product as a pale-yellow oil (80% yield). All analytical data are in agreement with the literature.[19]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (dd, *J* = 9.8, 7.0 Hz, 3 H), 7.18 (d, *J* = 6.6 Hz, 2 H), 4.79 (h, *J* = 6.8 Hz, 1 H), 3.33 (dd, *J* = 14.0, 7.5 Hz, 1 H), 3.02 (dd, *J* = 14.0, 6.8 Hz, 1 H), 1.55 (d, *J* = 6.7 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.66, 129.11, 128.95, 127.54, 84.55, 41.30, 18.92.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1705980.

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(8) The formation of the dimer **3a**,**b** is due to the attack of a molecule of reduced nitroalkane on to a molecule of unreacted nitroalkene still present in solution. The two diastereoisomers are always formed as a 1:1 mixture.
(9) After chromatographic purification, the product was isolated in 63% yield; unreacted starting material (10%), the dimeric adduct (18%) and unidentified decomposition products were also obtained.
(10) Preliminary studies using (thio)urea derivatives of cinchona alkaloid derivatives afforded product **21** in good yields and up to 21% e.e. Further studies and the use of new, '*ad hoc*' designed chiral catalysts are necessary to improve the enantioselectivity of the process, and studies are under way in our group.
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