A Practical Synthesis of 1,2-Nitroamines by Michael Addition of N-Nucleophiles to Nitroalkenes

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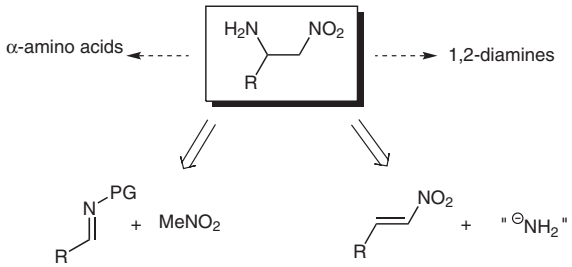
Abstract: A practical method for the synthesis of α-nitroamines by Michael addition of azide to nitroalkene has been developed. This reaction proceeds in high yields under very mild conditions (phase-transfer catalysis) and is found to be general; good yields are obtained with both aryl and alkyl derivatives as well as with 1,1-disubstituted ones.

Key words: azides, amines, Michael addition, nitroalkenes, nitroamines

Nitroamines are versatile intermediates in organic synthesis as they can lead to both α-amino acids, after Nef oxidation, and 1,2-diamines, upon reductive conditions.[1–3] Two strategies can be envisaged for their preparation (Scheme 1). The most developed method consists in the addition of nitro compounds to activated imines, the aza-Henry reaction.[4,5] This method has, however, some limitations: (1) it is restricted, with only few exceptions, to non-enolizable imines and (2) examples of addition of nitro compounds to ketimines are very limited.[6] An alternative route is the addition of amines to nitroalkenes. However, although addition of carbon nucleophiles to nitroalkenes is well documented,[7] surprisingly there are only a few reports on the Michael addition of N-nucleophiles onto these activated olefins.[8] We report herein our results on the development of the synthesis of 1,2-nitroamines by Michael addition of azide onto nitroalkene under very mild conditions.



Scheme 1 Strategies toward 1,2-diamines

If the development of a general synthesis of 1,2-nitroamines is desired, it is important for the obtained Michael adducts to be easily deprotectable to provide the corresponding primary amines. Enders and co-workers nicely addressed this issue and showed that (–)-(2*S*,3*R*,4*R*,5*S*)-1-amino-3,4-dimethoxy-2,5-bis(methoxymethyl)pyrrolidine (ADMP) could act as a chiral equivalent of ammonia.[8g] This hydrazine adds onto nitroalkenes and subsequent reduction furnishes corresponding vicinal diamines in moderate yields and diastereoselectivities. The drawback of this method is that this ammonia equivalent must be synthesized in seven steps.

Mioskowski and co-workers reported that addition of oxazolidinone derivatives onto nitroalkenes gives corresponding Michael adducts in high yield (and diastereoselectivity).[8f] Cleavage of the oxazolidinone by Li/NH_3 reduction allows access to the primary amine. However, Michael addition of oxazolidinone derivatives (as well as their cleavage) involves harsh conditions, which limit their use in the synthesis of complex molecules. Indeed, due to the low nucleophilicity of oxazolidinone derivatives, their addition necessitates prior activation by quantitative deprotonation using a strong base (*n*-BuLi, NaH, *t*-BuOK, etc.). In order to avoid the harsh conditions for the addition, good N-nucleophiles (not necessitating prior deprotonation) are needed, keeping in mind that the adduct formed must also be easily cleavable to lead to the corresponding primary amine.

We began our search for such a suitable nitrogen nucleophile by considering the addition of benzotriazole to nitroalkenes **1a** and **1b** (Scheme 2).[9] It has been shown that benzotriazole reacts via both N1 and N2 with a regioselectivity depending on the reaction conditions, N2-regioisomer being usually the thermodynamic product. However, none of the reaction conditions tested for the addition of benzotriazole to **1a** and **1b** gave N2-regioisomer **3** as the major product.[10,11] Further, all attempts to isomerize N1-adduct **2** into its N2-isomer **3** (expected to be more stable[12]) led to no significant change in **2/3** ratio. This is unfortunate since, for our purpose, a high regioselectivity for N2-adduct **3** was required. Indeed, only the N2-regioisomer **3a** allows obtaining the primary amine quantitatively after hydrogenation (see Scheme 2). Although not very efficient in this particular case due to a low regioselectivity in the addition, this method constitutes, to the best of our knowledge, the first example of the use of benzotriazole as ammonia equivalent.

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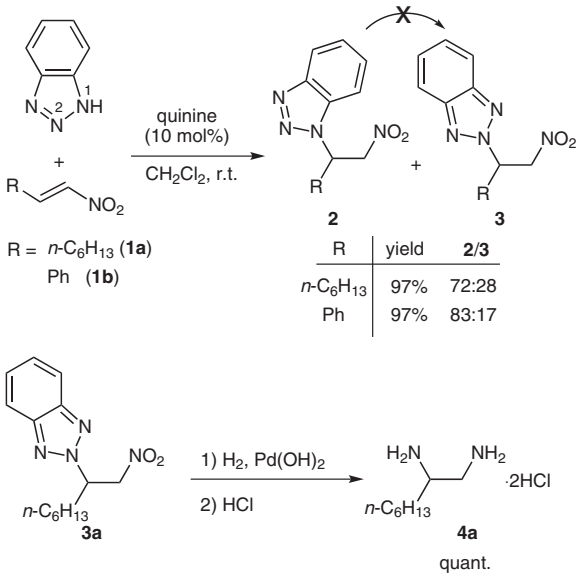
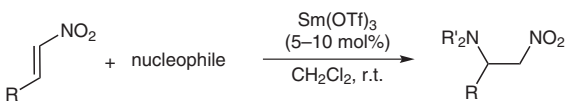
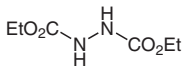


Scheme 2 Addition of benzotriazole to nitroalkenes

We then turned our attention to other nitrogen nucleophiles. Since Yadav and co-workers reported that $Sm(OTf)_3$ efficiently catalyzes the addition of N-nucleophiles to activated olefins under smooth conditions,[13] these conditions were applied. Benzylamine and 1,2-dicarbethoxyhydrazine were found to be unreactive toward nitroalkenes **1a** and **1b** under these conditions (Table 1, entries 1–4). A more nucleophilic amine such as methylhydrazine leads to corresponding Michael adducts but in low yield (Table 1, entries 5 and 6).[14]

Table 1 Addition of Amine Nucleophiles to Nitroalkenes

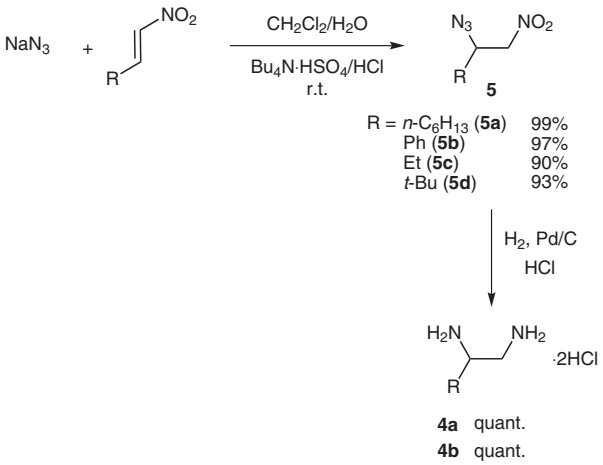


Entry	Nucleophile	R	Yield (%)[a]
1	$BnNH_2$	*n*-C_6H_{13}	NR
2		Ph	NR
3		*n*-C_6H_{13}	NR
4		Ph	NR
5	$MeNHNH_2$	*n*-C_6H_{13}	38
6		Ph	32
7	$BnONH_2$	*n*-C_6H_{13}	76 (91)[b]
8		Ph	81 (96)[b]

[a] Isolated yield.
[b] Yields in parentheses correspond to reactions carried out by stirring at reflux a solution of nitroalkene (1 equiv) and hydroxylamine (1 equiv) in the presence of SiO_2 (10 equiv) in MeCN for 4 h.

The best yields were obtained with *O*-benzylhydroxylamine (Table 1, entries 7,8).[15] The reaction proceeds smoothly (6 h) in the presence of 5 mol% of $Sm(OTf)_3$ at room temperature (76–81%).[13] We found that even SiO_2 was an efficient catalyst for this reaction.[16] All our attempts of deprotection and cleavage of the O–N bond led however to complex mixtures.

The use of sodium azide as N-nucleophile was then considered. Zard and co-workers have shown that, in hot DMSO, sodium azide reacts with nitroalkenes to give the corresponding 1,2,3-triazoles.[17] However, we found that, at room temperature and under phase-transfer conditions, the azide anion adds smoothly to nitroalkenes to give the corresponding Michael adducts **5** (Scheme 3).[18,19] These are obtained in excellent yields (88–99%), even in the case of sterically hindered substrates (see **5d**).



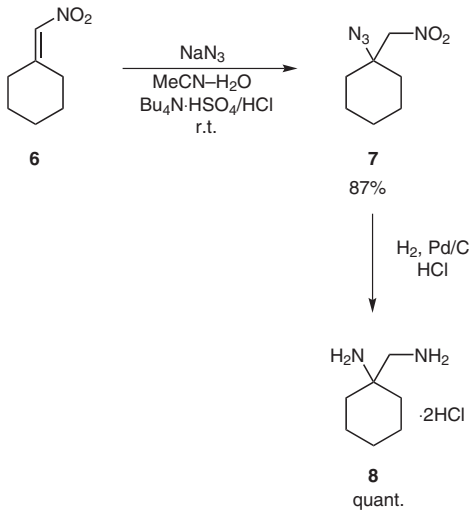
Scheme 3 Addition of azide to nitroalkenes and reduction

Next, the transformation of the azide function into the corresponding primary amine was investigated. Several conditions [$BHCl_2$,[20] PPh_3/H_2O,[21] $HS(CH_2)_3SH/Et_3N$[22]] were tested and palladium-catalyzed hydrogenation was found to give the corresponding diamines in quantitative yield (see Scheme 3).

As mentioned above, one limitation of the aza-Henry strategy (see Scheme 1) is that examples of addition of nitro compounds to ketimines are very limited.[6] Accordingly, we tested our methodology on a 2,2-disubstituted nitroalkene **6** and found that it allows the formation of the corresponding 1,1-disubstituted vicinal diamine **8** in excellent yield (Scheme 4).

In summary, we have developed a practical and general methodology for the synthesis of α-nitroamines. The first step of this method is the addition of azide to nitroalkene. This reaction proceeds in high yields under very mild conditions (phase-transfer catalysis). The obtained Michael adducts can then undergo reduction to furnish the corresponding 1,2-diamines in good yields. This method works not only with alkyl derivatives but also with aromatic and 1,1-disubstituted derivatives. The application of this methodology to the synthesis of biologically active compounds is underway in our laboratory.

Nitroalkenes were prepared according to reported procedures.[23,24] Flash chromatography was performed on silica gel (230–400 mesh). TLC was performed on aluminum-backed silica plates, which were



Scheme 4 Reaction with 2,2-disubstituted nitroolefins

developed using standard visualizing agents: UV fluorescence (254 and 366 nm), $KMnO_4$, *p*-anisaldehyde. NMR spectra were recorded on Bruker AC-300 Avance II and Bruker DRX 500 spectrometers. Chemical shifts (NMR) are quoted in parts per million (ppm), referenced to TMS (for ^1H and ^{13}C) and NH_3 (for ^{15}N). IR spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer. Mass spectra (MS) were recorded on a Finnigan MAT LCQ apparatus. HRMS were measured at the University College of London.

Addition of Benzotriazole to Nitroalkenes; General Procedure

A solution of the nitroalkene **1** (3.0 mmol) in CH_2Cl_2 (5 mL) was added to a solution of benzotriazole (357 mg, 3.0 mmol) and quinine (97 mg, 0.3 mmol) in CH_2Cl_2 (30 mL) at –40 °C. The reaction mixture was allowed to warm to r.t. and stirred for 3 days. The solution was concentrated under vacuum to give a mixture of regioisomers, which were purified (and separated) by column chromatography (hexanes–EtOAc, 70:30).

1-(1-Nitrooctan-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (2a; R = *n*-C_6H_{13})

Liquid; yield: 580 mg (70%).

IR (neat): 2954.7, 2927.7, 2858.3, 1556.4, 1452.3, 1377.1, 1163.0 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.1–1.35 (m, 11 H, *n*-C_6H_{13}), 1.95–2.4 (m, 2 H, *n*-C_6H_{13}), 4.93 (dd, *J* = 4.2, 14.0 Hz, 1 H, H_aCHNO$_2$), 5.29 (dd, *J* = 9.4, 14.0 Hz, 1 H, H_bCHNO$_2$), 5.51 (m, 1 H, CHN), 7.40 (m, 1 H_{arom}), 7.5–7.65 (m, 2 H_{arom}), 8.08 (d, *J* = 8.4 Hz, 1 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 21.3, 25.8, 28.8, 31.6, 33.0, 56.9, 78.1, 109.8, 121.1, 125.3, 128.9, 134.4, 146.8.

MS (APCI): *m*/*z* = 277.2, 120.2.

HRMS-APCI: *m*/*z* calcd for $C_{14}H_{21}N_4O_2$: 277.1671; found: 277.1665.

2-(1-Nitrooctan-2-yl)-2*H*-benzo[*d*][1,2,3]triazole (3a; R = *n*-C_6H_{13})

Liquid; yield: 224 mg (27%).

IR (neat): 2954.7, 2927.7, 3858.3, 1556.4, 1450.4, 1375.2, 1326.9, 1271.0, 1197.7 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.1–1.4 (m, 11 H), 1.9–2.3 (m, 2 H), 4.85 (dd, *J* = 9.2, 13.9 Hz, 1 H, H_bCHNO$_2$), 5.31 (dd, *J* = 4.4, 13.9 Hz, 1 H, H_aCHNO$_2$), 5.66 (m, 1 H, CHN), 7.40 (AA′XX′ system, *J* = 1.0, 6.7, 8.7 Hz, 2 H_{arom}), 7.85 (AA′XX′ system, *J* = 0.8, 1.0, 8.7 Hz, 2 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 22.4, 25.3, 28.4, 31.3, 33.0, 63.9, 77.2, 118.2, 126.8, 144.2.

^{15}N NMR (50 MHz, $CDCl_3$): δ = 253.3, 308.5, 371.9.

MS (APCI): *m*/*z* = 277.3, 120.2.

HRMS (APCI): *m*/*z* calcd for $C_{14}H_{21}N_4O_2$: 277.1670; found: 277.1665.

1-(2-Nitro-1-phenylethyl)-1*H*-benzo[*d*][1,2,3]triazole (2b; R = Ph)

White crystals; yield: 546 mg (70%); mp 88–89 °C.

IR (KBr): 3068.5, 3035.8, 2925.8, 2252.7, 1562.2, 1496.7, 1454.2, 1375.1, 1163.0 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.14 (dd, *J* = 4.9, 14.6 Hz, 1 H, H_aCHNO$_2$), 5.94 (dd, *J* = 9.6, 14.6 Hz, 1 H, H_bCHNO$_2$), 6.57 (dd, *J* = 4.9, 9.6 Hz, 1 H, CHN), 7.3–7.5 (m, 8 H_{arom}), 8.08 (d, *J* = 8.0 Hz, 1 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 59.9, 76.7, 109.5, 120.4, 124.7, 127.0, 128.2, 129.6, 130.0, 132.8, 134.1, 146.4.

MS (ESI): *m*/*z* = 269.1, 120.1.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{13}N_4O_2$: 269.1027; found: 269.1039.

2-(2-Nitro-1-phenylethyl)-2*H*-benzo[*d*][1,2,3]triazole (3b; R = Ph)

White crystals; yield: 133 mg (16%); mp 92–93 °C.

IR (KBr): 3037.7, 2922.0, 2852.5, 2358.8, 1550.7, 1496.7, 1456.2, 1415.7, 1373.2, 1323.1, 1271.0, 970.1 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.06 (dd, *J* = 4.4, 14.8 Hz, 1 H, H_aCHNO$_2$), 5.89 (dd, *J* = 10.3, 14.8 Hz, 1 H, H_bCHNO$_2$), 6.80 (dd, *J* = 4.4, 10.3 Hz, 1 H, CHN), 7.35–7.45 (m, 8 H_{arom}), 7.86 (m, 1 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 66.7, 76.6, 118.5, 127.1, 129.6, 129.9, 134.1, 144.1.

MS (ESI): *m*/*z* = 269.1, 120.0.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{12}N_4O_2$: 268.09547; found: 268.09489.

Octane-1,2-diamine Dihydrochloride (4a)[25]

A solution of **3a** (200 mg, 1.05 mmol, 1 equiv), concd HCl (0.86 mL, ~10 equiv), 10% Pd/C (1 mg) in EtOH (20 mL) was stirred overnight under a H_2 atmosphere (3 atm). The reaction mixture was filtered on Celite and concentrated under reduced pressure.

White solid; yield: 225 mg (quant.); mp 153–155 °C.

^1H NMR (300 MHz, DMSO-d_6): δ = 0.90 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.0–1.5 (m, 8 H, CH_2), 1.63 (m, 2 H, CH_2), 3.05 (m, 1 H, CHN), 3.40 (m, 2 H, CH_2N), 8.36 (br s, 6 H, NH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 14.9, 22.9, 25.4, 29.3, 31.2, 31.9, 41.9, 50.3.

Sm(OTf)$_3$-Catalyzed Michael Addition of Amine Nucleophiles to Nitroalkenes; General Procedure

Sm(OTf)$_3$ (60 mg, 1 mmol) was added to a solution of amine nucleophile (1.2 mmol) listed in Table 1 and nitroalkene (1 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 6 h at r.t.. The mixture was washed with H_2O (3 mL) and brine (3 mL). The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. Products were purified by flash chromatography over silica gel. The data of the products obtained from *O*-benzylhydroxylamine as the amine nucleophile are described below.

***O*-Benzyl-*N*-(1-nitrooctan-2-yl)hydroxylamine (R = *n*-C_6H_{13}, Nu = $PhCH_2ONH_2$)**
Liquid; yield: 213 mg (76%).

IR (neat): 2954.7, 2927.7, 2954.7, 2858.3, 2360.7, 2343.3, 1552.6, 1454.2, 1380.9, 1209.3 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 5.7 Hz, 3 H, CH_3), 1.25–1.60 (m, 10 H), 3.49–3.55 (m, 1 H, C*H*NH), 4.44 (dd, *J* = 4.3, 12.4 Hz, 1 H, H_aCHNO_2), 4.59 (dd, *J* = 7.1, 12.4 Hz, 1 H, H_bCHNO_2), 4.69 (s, 2 H, CH_2O), 7.2–7.40 (m, 5 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2, 22.7, 26.0, 29.2, 29.3, 31.7, 59.3, 76.7, 76.9, 128.2, 128.6, 128.7, 137.4.

MS (ESI): *m*/*z* = 281.2, 91.0.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{25}N_2O_3$: 281.18651; found: 281.18691.

***O*-Benzyl-*N*-(2-nitro-1-phenylethyl)hydroxylamine (R = Ph, Nu = $PhCH_2ONH_2$)**
Liquid; yield: 220 mg (81%).

IR (neat): 3249.8, 3062.7, 3031.9, 2918.1, 2869.9, 2387.7, 2289.3, 1552.6, 1494.7, 1454.2, 1379.0 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.57 (dd, *J* = 4.8, 11.9 Hz, 1 H, C*H*NH), 4.62–4.91 (m, 3 H, CH_2NO_2 and CH_2O), 7.25–7.40 (m, 10 H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 63.2, 77.2, 78.0, 127.8, 128.3, 128.6, 128.8, 129.1, 129.2, 135.8, 137.1.

MS (ES): *m*/*z* = 273.2, 90.9.

HRMS (ES): *m*/*z* calcd for $C_{15}H_{17}N_2O_3$: 273.1236; found: 273.1239.

Addition of Sodium Azide to Nitroalkenes; General Procedure
A solution of NaN_3 (1 g, 15 mmol) and Bu_4NHSO_4 (50 mg, 5 mol%) in H_2O (30 mL) was added to a solution of the nitroalkene (3 mmol) in CH_2Cl_2 (30 mL). The acidity of the solution was adjusted to pH 1–2 with aq 1 N HCl. The reaction mixture was stirred vigorously overnight. The two phases were separated and the organic layer was washed with H_2O (until the pH of the aqueous phase was equal to 7). The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure.

2-Azido-1-nitrooctane (5a; R = *n*-C_6H_{13})
Liquid; yield: 595 mg (99%).

IR (neat): 2956.7, 2929.7, 2860.2, 2127.3, 1560.3, 1465.8, 1380.9, 1263.3 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (m, 3 H, CH_3), 1.2–1.7 (m, 10 H, CH_2), 4.13 (m, 1 H, HCN_3), 4.37 (m, 2 H, CH_2NO_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 25.7, 28.9, 31.6, 31.9, 59.6, 77.8.

MS (CI): *m*/*z* = 201.0, 112.0, 69.8.

HRMS (CI): *m*/*z* calcd for $C_8H_{17}N_4O_2$: 201.13514; found: 201.13531.

(1-Azido-2-nitroethyl)benzene (5b; R = Ph)[26]
Liquid; yield: 559 mg (97%).

IR (neat): 3111.0, 3064.7, 3033.8, 2922.0, 2110.0, 1633.6, 1556.4, 1519.8, 1377.1, 1344.3, 1261.4, 966.3 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.55 (m, 2 H, CH_2NO_2), 4.32 (dd, *J* = 5.2, 11.9 Hz, 1 H, HCN_3), 7.25–7.65 (m, 5 H, C_6H_5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 62.6, 78.5, 127.1, 129.4, 129.8, 134.2.

MS (CI): *m*/*z* = 193.2, 150.1, 104.0.

HRMS (CI): *m*/*z* calcd for $C_8H_8N_4O_2$: 193.07255; found: 193.07222.

2-Azido-1-nitrobutane (5c; R = Et)
Liquid; yield: 389 mg (90%).

IR (neat): 2974.0, 2939.3, 2881.4, 2131.2, 2106.1, 1556.4, 1380.9, 1267.1 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.06 (t, *J* = 8.6 Hz, 3 H, CH_3), 1.64 (m, 2 H, CH_2), 4.06 (m, 1 H, HCN_3), 4.28–4.45 (m, 2 H, CH_2NO_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.2, 25.2, 60.9, 77.7.

MS (CI): *m*/*z* = 145.0, 71.4, 70.2, 56.2.

HRMS (CI): *m*/*z* calcd for $C_4H_9N_4O_2$: 145.07255; found: 145.07226.

2-Azido-3,3-dimethyl-1-nitrobutane (5d; R = *t*-Bu)[25]
Liquid; yield: 480 mg (93%).

IR (neat): 2970.2, 2873.7, 2133.1, 2094.6, 1380.9, 1269.1 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.02 (s, 9 H, CH_3), 3.91 (dd, *J* = 2.4, 10.6 Hz, 1 H, CHN_3), 4.29 (dd, *J* = 10.6, 13.6 Hz, 1 H, H_aCHNO_2), 4.52 (dd, *J* = 2.4, 13.6 Hz, 1 H, H_bCHNO_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.4, 35.7, 69.5, 75.8.

MS (CI): *m*/*z* = 173.1, 83.8, 56.9.

HRMS (CI): *m*/*z* calcd for $C_6H_{13}N_4O_2$: 173.10385; found: 173.10339.

1-Azido-1-(nitromethyl)cyclohexane (7)
Liquid; yield: 481 mg (87%).

IR (neat): 2939.3, 2862.2, 2106.1, 1552.6, 1450.4, 1429.1, 1379.0, 1326.9, 1294.1, 1251.7 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.85 (m, 10 H, cyclohexyl CH_2), 4.46 (s, 2 H, CH_2NO_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 24.8, 32.8, 61.9, 82.6.

MS (ESI): *m*/*z* = 186.2, 184.2, 142.0, 130.1.

Reduction of the Azide Adducts 5; General Procedure
A solution of **5** (2 mmol, 1 equiv), concd HCl (2 mL, ~10 equiv), and 10% Pd/C (2 mg) in EtOH (40 mL, volume adjusted to reach ~0.05 M of **5**) was stirred overnight under a H_2 atmosphere (3 atm). The reaction mixture was filtered on Celite and concentrated under reduced pressure.[27]

Octane-1,2-diamine Dihydrochloride (4a; R = *n*-C_6H_{13})
White solid; yield: 436 mg (quant.); for analytical and spectral data, see above.

1-Phenylethane-1,2-diamine Dihydrochloride (4b; R = Ph)[28]
White solid; yield: 418 mg (quant.); mp 160 °C (dec.).

^1H NMR (300 MHz, DMSO-d_6): δ = 3.30 (dd, *J* = 6.3, 13.1 Hz, 1 H, $CH_aH_bNH_3$), 3.56 (dd, *J* = 6.8, 13.1, 1 H, $CH_aH_bNH_3$), 4.70 (dd, *J* = 6.3, 6.8 Hz, 1 H, $CHNH_3$), 7.40–7.70 (m, 5 H, C_6H_5), 8.61 (br s, 3 H, NH_3), 9.16 (br s, 3 H, NH_3).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 42.8, 53.0, 128.9, 130.0, 130.4, 135.3.

1-Aminomethylcyclohexylamine Dihydrochloride (8)[29]
White solid; yield: 402 mg (quant.); mp 120 °C (dec.).

^1H NMR (300 MHz, DMSO-d_6): δ = 1.6–2.0 (m, 10 H, cyclohexyl CH_2), 3.23 (s, 2 H, CH_2NH_3), 8.71 (br s, 6 H, NH_3).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 21.2, 25.2, 32.0, 44.4, 55.7.

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