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Sequential acylation/silylation/hetero-Claisen rearrangement of nitroalkanes for the synthesis of protected hydroxyoxime derivatives

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Dedicated to the memory of Prof. Yu. I. Smushkevich (1935-2021)

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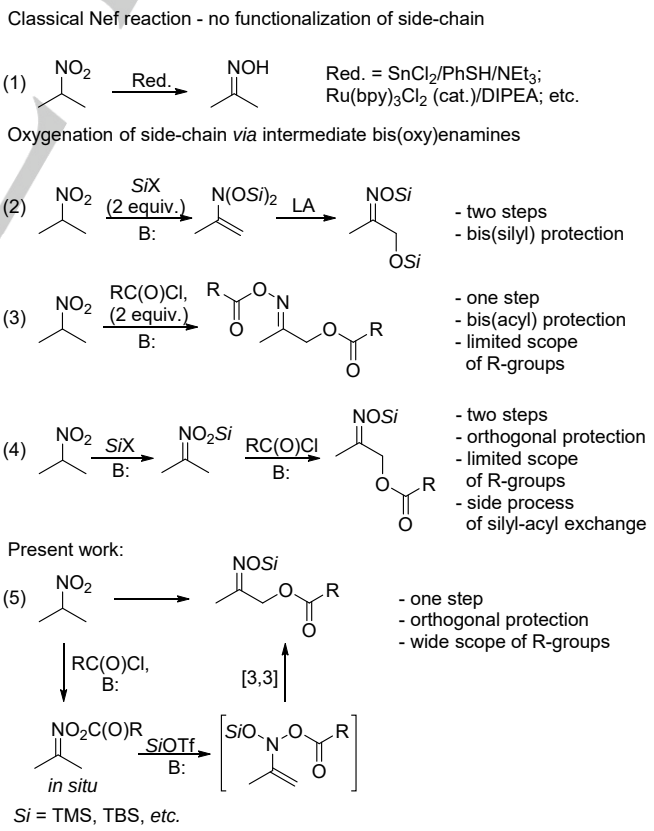
Abstract: Sequential acylation/silylation of nitroalkanes leads to *O*-silylated α-acyloxyoximes in high yields. First step of reaction involves deprotonation of nitro compound with sodium hydride promoted by DBU or alcohol/15-crown-5 system followed by treatment with acyl chloride. *In situ* generated acyl nitronate is further silylated by silyl triflate that triggers hetero-Claisen [3,3]-rearrangement within *N*-acyloxyenamine moiety furnishing orthogonally protected oxime derivatives. The procedure has large substrate scope for both nitroalkanes and acylating agents (acyl chlorides, chloroformates) and allows tuning of reaction conditions depending on the particular type of substrate. Application of obtained oxime derivatives in organic synthesis is demonstrated.

Introduction

Oximes and their *O*-substituted derivatives play an important role in modern organic synthesis.[1] They are valuable precursors for the synthesis of amines, hydroxylamines and various heterocycles, such as isoxazolines, pyridines and pyrroles. Coordination chemistry of oximes is employed in numerous transition metal-catalyzed transformations. One of the methods toward the synthesis of oximes is the reductive variant of the Nef reaction starting from aliphatic nitro compounds (Scheme 1, eq. 1).[2,3] Here reduction is achieved by the external reagent. Interesting alternative to the described variant is the redox-neutral conversion of nitro-group into the oxime. In this case carbon skeleton of the substrate acts as a reductant thus allowing its oxygenation. Overall this would allow synthesis of polyfunctionalized molecules from simple available starting materials such as aliphatic nitro compounds.[4] Recently several approaches for the conversion of nitro compounds into hydroxyoxime derivatives were described. They are based on the intermediate formation of *N*-oxyenamine C=C–N–O moiety and its rearrangement.[5] Double silylation (eq. 2),[6] double acylation (eq. 3)[7] and sequential silylation/acylation (eq. 4)[8] has already been demonstrated. Each of them has its own *pro et contra*. Particularly, synthesis of silylated hydroxyoximes *via* double silylation is usually performed in a two-step variant requiring isolation of labile bis(silyloxy)enamines for subsequent Lewis acid promoted [1,3]-shift of silyloxy group. Bis-acylation approach (eq. 3) has wide substrate scope with respect to nitro compounds, albeit is limited to active acylating reagents possessing no α-protons (pivaloyl chloride, benzoyl chloride). Finally, silylation-acylation approach involves isolation of rather

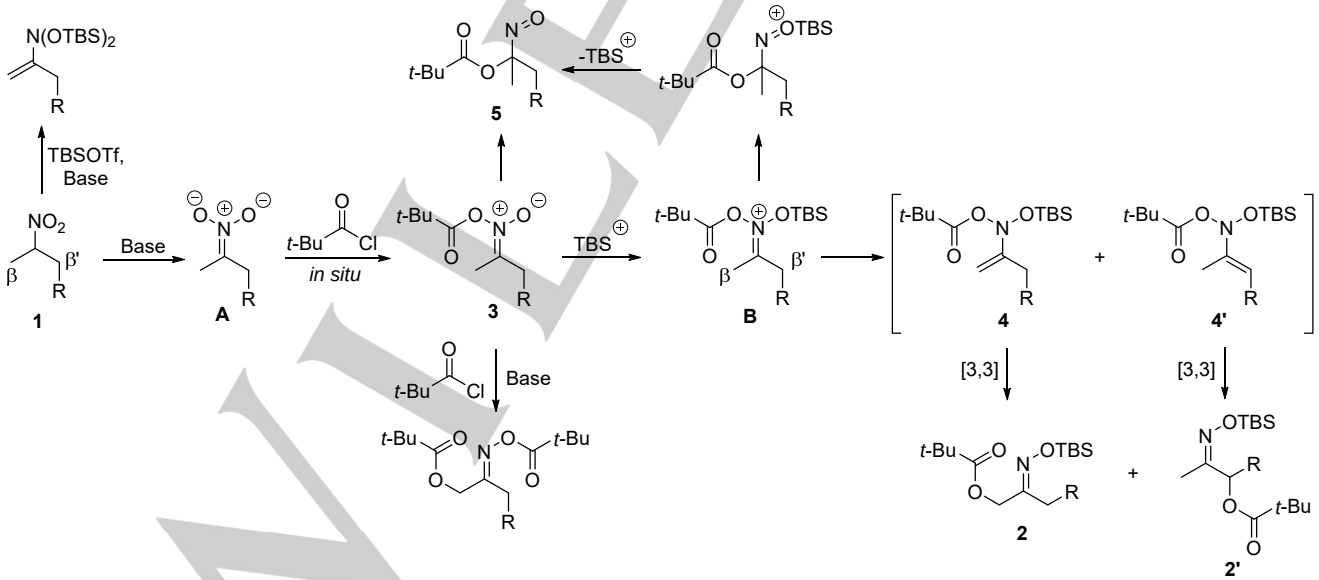


Scheme 1. Classical Nef reaction and nitro-to-oxime conversion with concomitant carbon chain functionalization.

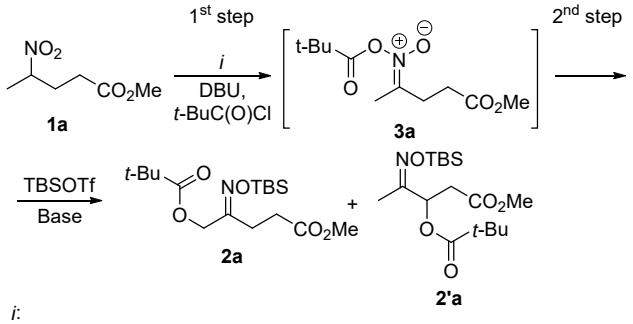
labile silyl nitronates (eq. 4). It also suffers from side reaction of silyl-acyl exchange at the second (acylation) step. Overall, this makes desirable development of the new approaches. Herein we report an acylation-silylation procedure for the conversion of aliphatic nitro compounds into protected α-hydroxyoxime derivatives (eq. 5).

Results and Discussion

Proposed reaction pathway as well as possible side-processes for the target acylation-silylation sequence is presented in Scheme 2. According to it generation of acyl nitronate **3** should be performed at first step with its subsequent silylation at the second step. The latter was envisaged to proceed *via* formation of *N*-acyloxyenamine **4** that undergo hetero-Claisen rearrangement. Several issues had to be addressed. The first one was to achieve the complete conversion of substrate **1** at first step **1**→**3**, since unreacted nitro compound **1** could undergo side process of double silylation at the second step.[6a,9] Also acylation conditions for the first step should not facilitate acylation of nitronate **3** itself.[7] Next, for unsymmetric nitro compounds **1**, possessing differently substituted β and β'-positions, formation of two constitutional isomers **2** and **2'** (*via* respective enamines **4** and **4'**) should be taken into account. Instability of acyl nitronates **3**[10] prevented the use of higher reaction temperatures for both reaction steps due to possible acyloxy-group migration in nitronate **3** as well as in cation **B**.[8,10] Indeed, green-blue color characteristic for nitroso compounds of type **5** was observed while performing reaction at r.t.. We also tried to avoid isolation of pure nitronate salts **A** due to their explosive nature.[11] Therefore, all the sequence **1**→**2** should have been optimized in a *one pot* variant. We started the investigation with the model reaction of methyl 4-nitropentanoate **1a** (Scheme 3, Table 1). This substrate possessing CH_3 and CH_2-groups in β-positions would also reveal the influence of reaction conditions on the regioselectivity (**2a**:**2'a** ratio). Firstly, we chose DBU for the first reaction step, as this base is known to deprotonate nitro compounds to a sufficient extent, that is used in the synthesis of silyl nitronates and nitro-Michael additions.[12] Thus, substrate **1a** was treated with 1.5 equiv. of DBU, followed by cooling to −78°C and addition of pivaloyl chloride (*t*-BuC(O)Cl). Expecting complete conversion to acyl nitronate after 1 h exposure, triethylamine and TBSOTf were added for the second reaction step. Fortunately, such primary procedure resulted in 75% yield of target oxime ethers **2a/2'a** (Entry 1) indicating the feasibility of desired reaction sequence. Further variations revealed DIPEA and CH_2Cl_2 as an optimum combination of solvent and base (Entry 2). Toluene and THF (Entries 3-4) led to incomplete consumption of substrate **1a** and lower yields of target products **2a/2'a**. Tertiary amines (triethylamine, DIPEA, *N*-methylmorpholine (NMM), Entries 1,2,5) gave higher yields compared to aromatic amines (Entries 6,7) and DBU (Entry 8), that is in accordance with previous results on the silylation/acylation of silyl or alkyl nitronates.[6a,b,7-9] While tertiary amines gave similar yields, their nature was decisive on the regiochemical outcome with bulky DIPEA producing the better **2a**/**2'a** ratio (Entry 2) that can be attributed to steric accessibility of primary CH_3-group compared to secondary CH_2-site. We should also note that some excess of TBSOTf (Cf. Entries 2 and 9) is required as some amount of TBSOTf is deactivated by OTf/Cl exchange with $DBUH^+Cl^-$ presenting in reaction mixture.



Scheme 2. General reaction scheme and possible side-processes.



Scheme 3. Screening of the reaction conditions: optimization of the silylation step.

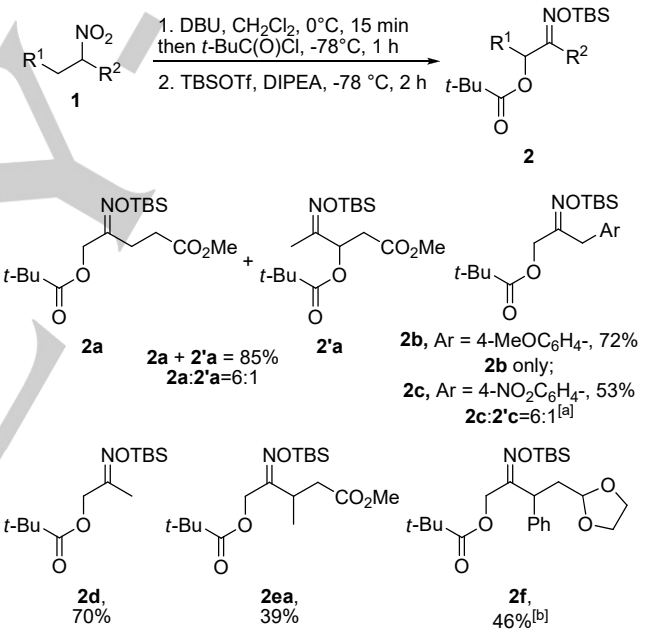
Table 1. Optimization of the reaction conditions (see Scheme 3 for reaction).[a]

Entry	*Si*OTf, equiv.	Base	Solvent	Total yield **2a**+**2'a**, %	**2a**/**2'a**
1	2.5	NEt_3	CH_2Cl_2	75	64:36
2	**2.5**	**DIPEA**	**CH_2Cl_2**	**87**	**83:17**
3	2.5	DIPEA	PhMe	52[b]	77:23
4	2.5	DIPEA	THF	23[c]	78:22
5	2.5	NMM	CH_2Cl_2	77	56:44
6	2.5	Pyridine	CH_2Cl_2	0	n.a.
7	2.5	2,6-lutidine	CH_2Cl_2	56	70:30
8	2.5	DBU	CH_2Cl_2	26	55:45
9	2.0	DIPEA	CH_2Cl_2	58	86:14

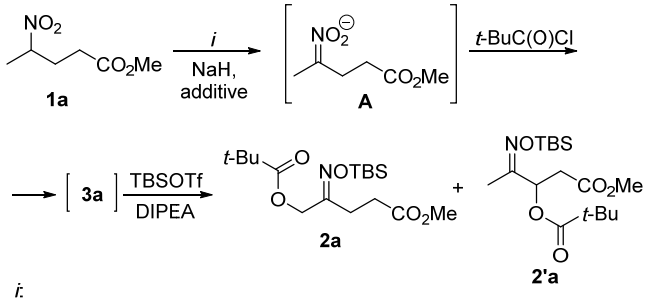
[a] Procedure: 0.5 M Solution of **1a** was treated with DBU (1.5 equiv.) at r.t. for 15 min, cooled to -78°C, then *t*-BuC(O)Cl (1.5 equiv.) was added and reaction mixture was stirred at -78°C for 1 h. Then base (3 equiv.) and TBSOTf were successively added. After 2 h at -78°C the reaction mixture was worked up and analyzed by ^{1}H NMR with internal standard (dimethyl terephtalate). [b] recovery of **1a** - 9%. [c] recovery of **1a** - 48%.

Then we proceeded to evaluation of substrate scope (Scheme 4). In such a manner products **2a-2d** were obtained in high yields. Notably, product **2b** was prepared regioselectively, that can be explained by relative bulkiness of benzyl group as compared to methyl group. However, for **2c** some amount of isomer **2'c** was observed when more electron-withdrawing *p*-nitrophenyl group was used, that can be attributed to higher acidity of neighbouring CH_2-group. A drop in yield and poorer conversion of starting materials was observed with some increase of steric bulk of substrate. Thus, product **2ea** possessing methyl group in side chain was obtained in moderate 39% yield, while increased bulkiness of phenyl substituent (product **2f**) resulted in incomplete conversion of substrate. Considering these facts as indicative for insufficient deprotonation of starting nitro compounds we pursued for additional optimization of the first reaction step, namely, acyl nitronate **3** formation.[13]

Aiming at complete deprotonation of nitro compound we forwarded to the use of cheap sodium hydride (Scheme 5, Table 2). Its insolubility in CH_2Cl_2 suggested the need of a base that could act as a mediator. This base should be able to deprotonate starting nitro compound and then be regenerated *via* reaction with NaH. Here 0.1 equiv. of DBU worked well (Entry 1), while triethylamine, 4-dimethylaminopyridine and tetramethylguanidine gave inferior results, as nearly no hydrogen evolution was observed together with incomplete conversion of substrate **1a**. Another positive result was obtained with the use of *tert*-butyl alcohol (*t*-BuONa as a mediating base). However, it required the addition of 15-crown-5 to increase its solubility (Entry 4). Indeed while mixing **1a**/*t*-BuOH/NaH in CH_2Cl_2 at 0 °C showed little reaction, gas evolution was observed when adding the crown ether indicating the formation of nitronate **A**. Comparable results were also achieved with increased amount of crown ether in the absence of *t*-BuOH (Entry 6). However, we preferred alcohol-mediated protocol due to high price of crown ether. At this step we also managed to diminish the amount of TBSOTf to 1.7 equiv. without substantial drop in yield (Entries 1-3). Attempt to increase reaction temperature did not result in better **2a**/**2'a** ratio, albeit lower yield was observed (Entry 8).



Scheme 4. Synthesis of oximes **2** *via* acylation/silylation sequence with use of stoichiometric amounts of DBU at the first step. [a] measured by ^{1}H NMR of crude product. Minor isomer **2'c** was not separated from side-products. [b] determined by ^{1}H NMR, 42% recovery of **1f**.



i:
1. NaH, Additive (0.1 equiv.), CH_2Cl_2, 0 °C, 1 h,
then *t*-BuC(O)Cl, -78 °C, 0.5 h
2. TBSOTf, DIPEA, -78 °C, 2 h

Scheme 5. Screening of reaction conditions: variation of additive for the deprotonation of nitro compound with NaH.

Table 2. Optimization of the reaction conditions (see Scheme 5 for reaction).[a]

Entry	TBSOTf, equiv.	Additive	Total yield **2a+2'a**, %	**2a**/**2'a**
1	2.5	DBU	78	74:26
2	**1.7**	**DBU**	**74**	**77:23**
3	1.2	DBU	68	79:21
4	**1.7**	***t*-BuOH/ 15-crown-5**	**62**	**81:19**
5	1.7	Diethylene glycol monoethyl ether	54	80:20
6	1.7	15-crown-5 (0.5 equiv.)	68	80:20
7	1.7	*t*-BuOH/ 18-crown-6	49	80:20
8[b]	1.7	*t*-BuOH/ 15-crown-5	42	83:17

[a] Procedure: 0.25 M solution of **1a** in CH_2Cl_2 was treated with NaH (1.2 equiv.) and additive (0.1 equiv.) at 0 °C for 1 h, cooled to −78°C, then *t*-BuC(O)Cl (1.2 equiv.) was added and the reaction mixture was stirred at -78°C for 0.5 h. Then DIPEA and TBSOTf were successively added. After 2 h at −78°C the reaction mixture was worked up and analyzed by ^{1}H NMR with internal standard (dimethyl terephtalate). [b] Treatment with DIPEA/TBSOTf and subsequrent reaction was performed at 0 °C

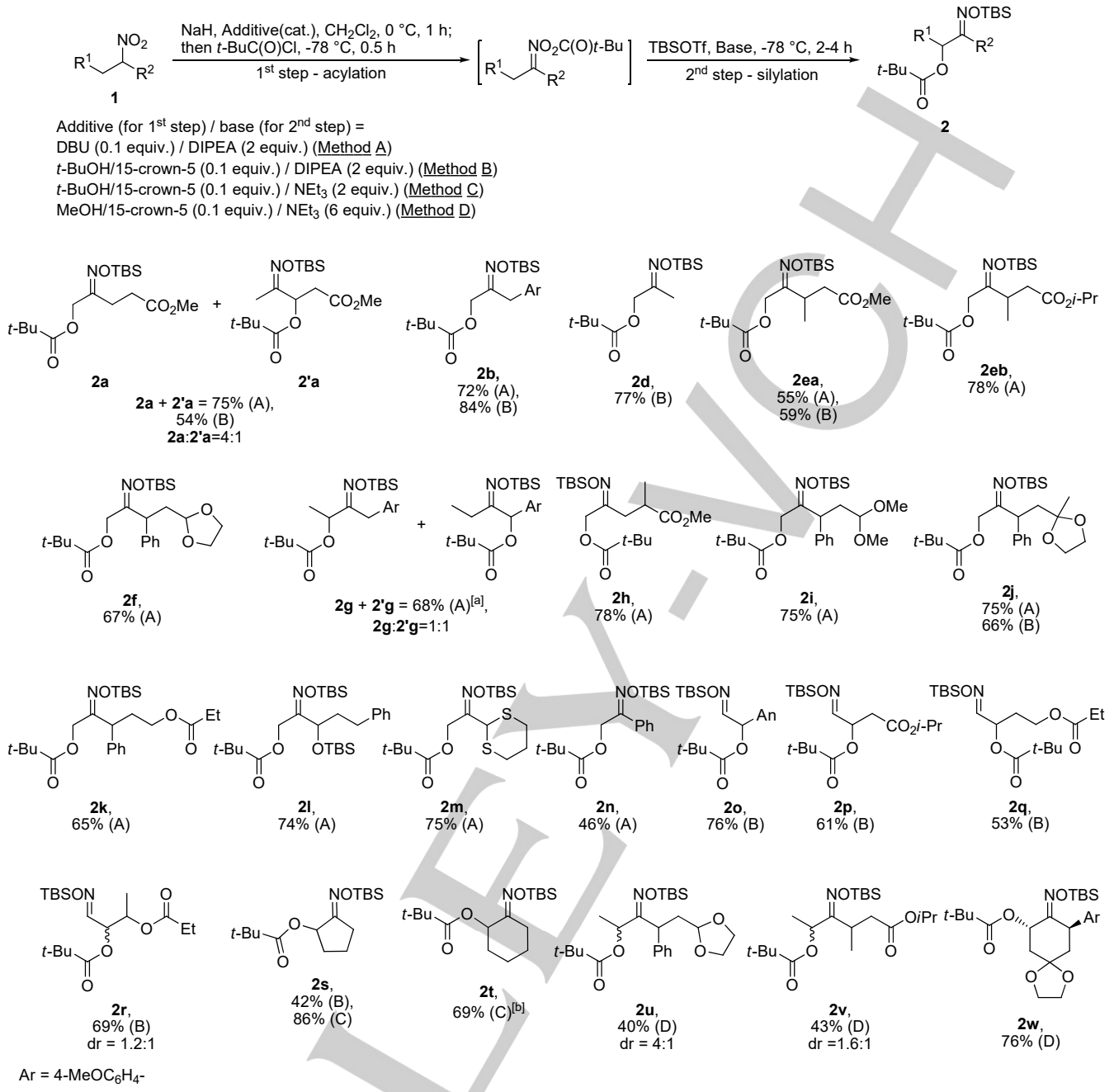
For evaluation of the substrate scope for these optimized conditions utilizing NaH/mediating base a wide range of nitro compounds **1** was used (Scheme 6). As can be seen good yields of target products were achieved for substrates possessing ester (*e.g.* **2a,ea,eb,h**), acetal (**2f,i,j**), thioacetal (**2m**), protected alcohols (esters **2k,q,r**; silyl ether **2l**). However, methyl ester should be considered as somewhat labile as isopropyl esters provided higher yields at average (cf. **2ea** and **2eb**). Choice of the deprotonation protocol was determined by relative steric hindrance of the substrate. DBU as a mediating base (Method A) worked well for secondary nitro compounds possessing unsubstituted β-carbon $CH_3CH(NO_2)R$ allowing oxygenation of the methyl group (products **2a,b,d-n**).

For relatively non-bulky substrates (primary nitro compounds, 2-nitropropane) use of DBU (cat.)/NaH gave inferior results. As no significant hydrogen evolution was observed at the first deprotonation step, we could attribute it to relatively strong hydrogen bonding between $DBUH^+$ and nitronate anion,[14] that prevents turnover of the mediator. For these cases *t*-BuOH/15-crown-5 worked pretty well giving products **2d,o-r** in good yields (Method B). For several substrates both Methods A and B were successfully employed demonstrating variability in choice of the protocol (products **2a,b,ea,j**). Importantly, advantage of the presented procedure is emphasized by successful functionalization of primary nitro compounds (products **2o-r**), that was not possible for previously reported double acylation protocol.[7]

An increase in steric hindrance also prevented the use of DBU and required stronger alcoholate base. This accounts to nitro compounds possessing β-CH_2 and β'-CH/CH_2 groups, including cyclic nitro compounds – derivatives of cyclopentane and cyclohexane. Moreover, for these substrates use of DIPEA at the silylation step gave poor yields of products **2** that was accompanied by blue color of reaction mixture at the 2nd step (see, *e.g.* yields of product **2s**). We attributed it to the steric hindrance of substrates that hampered proton abstraction by DIPEA and made rearrangement within intermediate bis(oxy)iminium cation[8] (see **B**→**5**, Scheme 2) a dominant side-process. To facilitate the deprotonation, NEt_3 was employed as a base. As was mentioned earlier, NEt_3 and DIPEA gave comparable yields of target oxime ethers while were different in regioselectivity for model substrate **1a** (see Table 1). Since there are no regioselectivity issues in case of symmetrical substrates **1s,t**, high yields of target products **2s,t** were observed using *t*-BuOH at 1st step and NEt_3 at the 2nd step (Method C).

Finally, the most encumbered substrates **1u-w** were slowly deprotonated by sodium *tert*-butoxide. For these cases less sterically demanding base was required. Use of MeONa as a mediator together with excess of NEt_3 allowed the preparation of products **2u-w** in moderate yields (Method D). Despite using NEt_3 as a base, regiochemical outcome was found to be governed mostly by substrate structure resulting in formation of products **2u-w**. Unfortunately, in these cases poor diastereoinduction was observed for both acyclic substrates **1u,v** (dr = 4:1 and 1.6:1 respectively). However, for cyclic substrate **1w** stereoselectivity can be attributed to chair-like transition state with bulky aryl substituent occupying an equatorial position (Figure 1).

Regiochemical regularities were similar to those observed for double acylation protocol, that can be explained by steric reasons.[7] Thus, functionalization of methyl group was preferable competitively to the methylene group (**2a,b,h**), while complete methyl group reactivity was observed for substrates possessing methyl and methyne moieties (**2ea,eb,f,i-m**). As was mentioned above, for sterically hindered nitro compounds, possessing CH_2 at β-position and CH at β'-position, complete preference for CH_2-functionalization was also observed.



Scheme 6. Synthesis of oxime ethers **2**. Scope of nitro compounds **1**. [a] NEt_3 was used instead of DIPEA; [b] 6 equiv. of NEt_3.

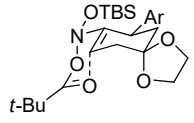
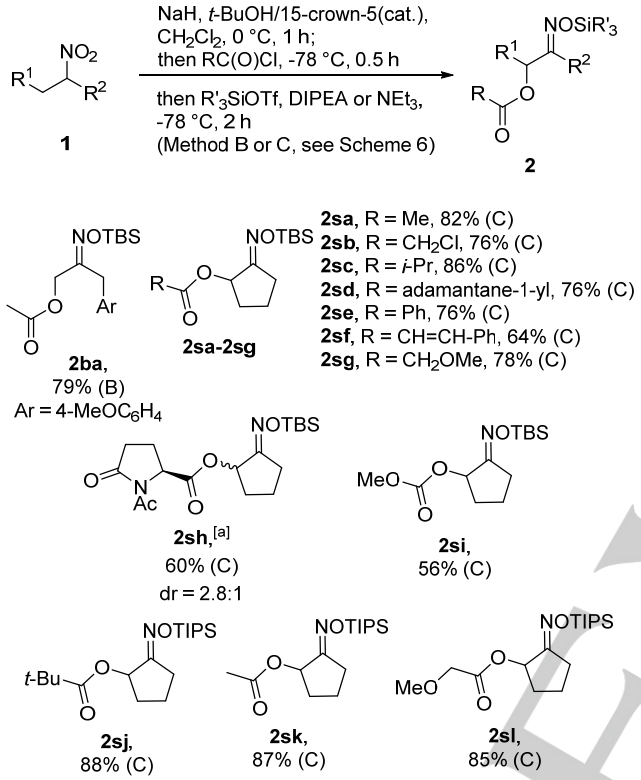


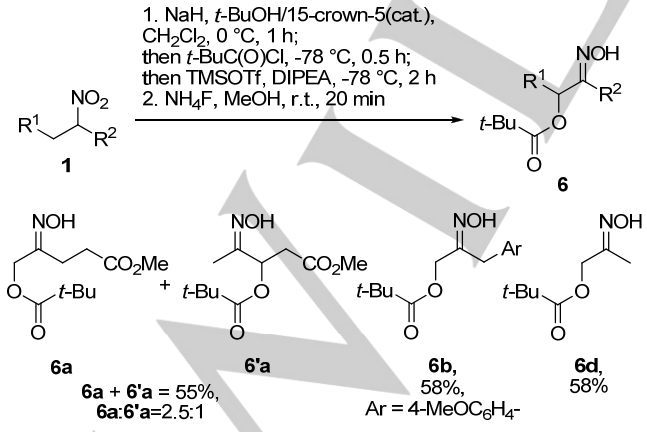
Figure 1. Rationale for the stereoselectivity of formation of **2w**.

As described previously, one of the limitations for reported protocols for acylation-[3,3]-rearrangement of nitronates was rather narrow scope of acylating agents. One of the reasons was ascribed to competitive elimination of HCl from α-CH possessing acyl chlorides in the presence of bases.[7,8] This resulted in the dominant employment of pivaloyl chloride. However, obvious disadvantage of the pivaloyl group is in its bulkiness that often hampers its deprotection. In the presented acylation-silylation protocol introduction of acyl group to the reacting molecule is accomplished at the early stage, *via* interaction with preformed nitronate anion **A** (see Schemes 2,5), that avoids simultaneous presence of equivalent amounts of acyl chloride and the base in the reaction mixture. Thus, a wider range of acyloxy-groups could be introduced (Scheme 7). Acetyl (**2ba,sa**), chloroacetyl (**2sb**), isobutyryl (**2sc**), 1-adamantane-carbonyl (**2sd**), benzoyl (**2se**), cinnamoyl (**2sf**) and methoxyacetyl-substituted (**2sg**) products were obtained in good yields. Pyroglutamate-derivative **2sh** was also successfully obtained with moderate stereoinduction observed. Another advantage was the possibility to introduce a carbonate moiety (**2si**), that was not possible for

other acylation protocols as chloroformates were unreactive toward alkyl nitronates[8] and required excess of reagent during acylation of nitrones.[15] Presented method also allowed variation of the silyl group at oxime moiety. Thus, bulky TIPS-protection was successfully introduced providing products **2sj,sk,sl**. In contrast, use of labile TMS-group resulted in its partial cleavage during purification of products. Therefore, NOH-unprotected oximes **6** were prepared in *one-pot* fashion after treatment with methanolic ammonium fluoride (Scheme 8).

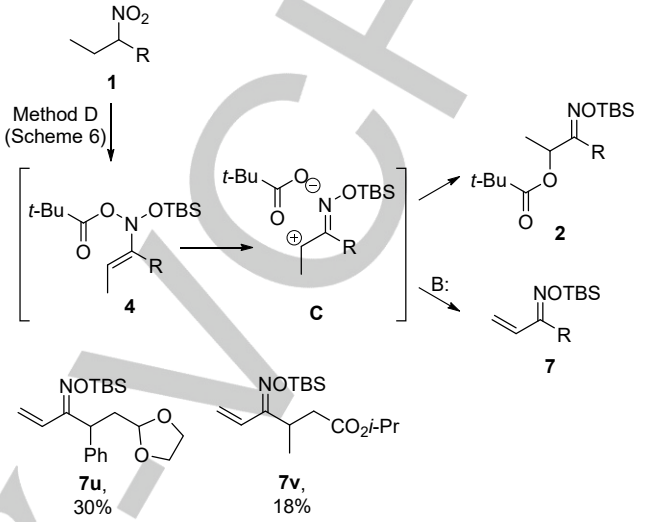


Scheme 7. Synthesis of oxime ethers **2**. Scope of acylating and silylating agents. [a] – reaction time for treatment with RC(O)Cl - 2.5 h instead of 0.5 h.



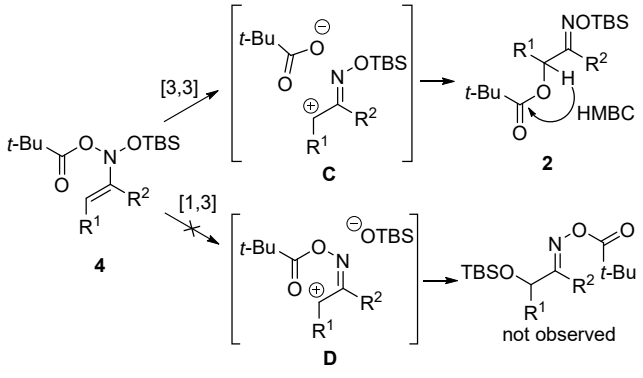
Scheme 8. Synthesis of NOH-unprotected oximes **6**.

One of the major observed side-products were enoximes **7** (Scheme 9). When nitro compounds possessing alkyl side-chain were subjected to the described protocol enoximes **7** were obtained in the yields up to 30 %. When isolated oxime ether **2u** was subjected to the reaction conditions (TBSOTf/NEt_3) no enoxime formation was detected by ^{1}H NMR. Therefore enoximes **7** should be directly formed from intermediate enamine **4** possibly *via* cation **C**.



Scheme 9. Formation of enoximes **7** during acylation-silylation sequence.

Structures of obtained products were confirmed by ^{1}H and ^{13}C NMR including 2D-spectroscopy as well as by HRMS data. For major isomer of product **2sh** single crystal X-ray analysis was performed (Figure 2). ^{1}H-^{13}C HMBC spectra of products **2** revealed that β-oxygen atom of target oximes **2** carries acyloxy-group and not the silyloxy-group (Scheme 10) thus underlying the preference of [3,3]-migration over the [1,3]-shift. Indeed [3,3]-rearrangement of **4** should be preferable regardless of concerted or ionic pathway. If concerted, uncatalyzed [1,3]-sigmatropic rearrangement should have high barrier due to the orbital symmetry rules.[16] If ionic, cation **C** possessing *O*-silyl group should be more stable than cation **D** possessing more accepting *O*-acyl group, as well as carboxylate anion (formed simultaneously with **C**) is more stable than silanolate anion. These also makes [3,3]-rearrangement a preferable route (Scheme 10).



Scheme 10. Possible migrations in bis(oxy)enamines **4** and characteristic HMBC interactions in products **2**.

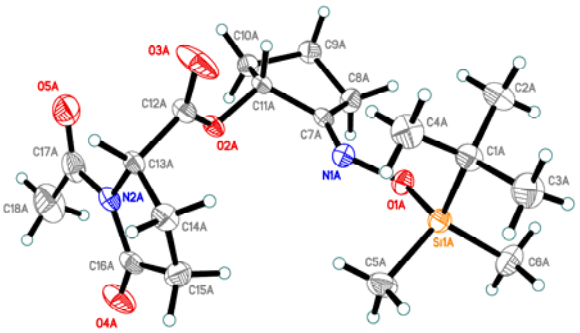
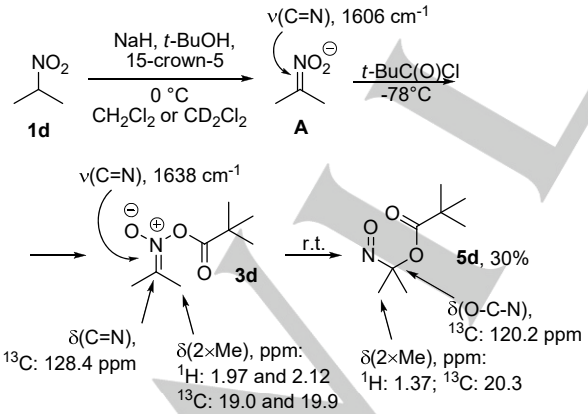


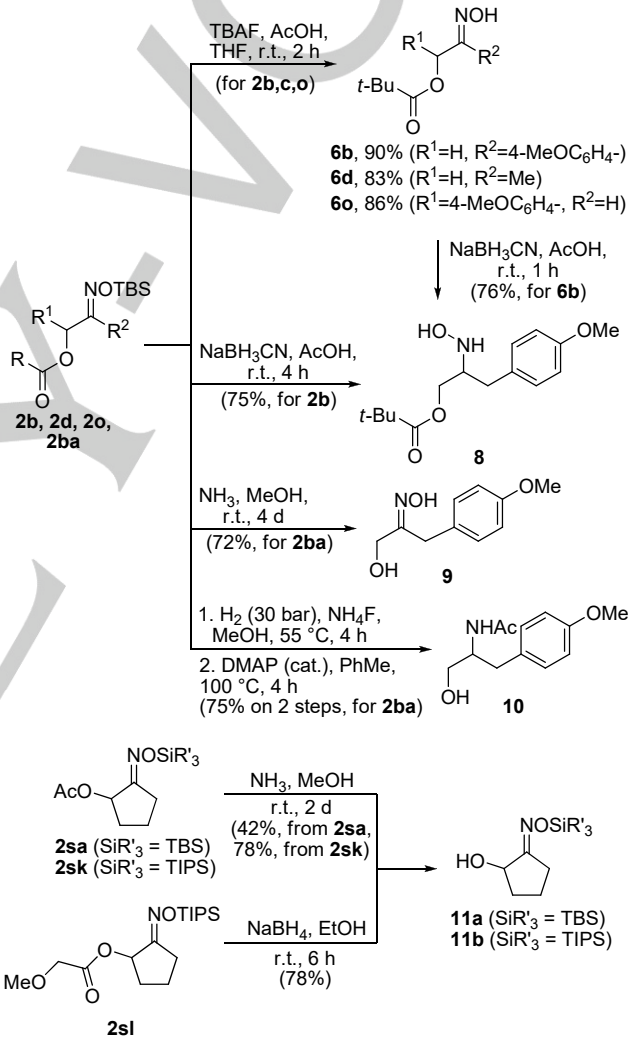
Figure 2. General view of the compound **2sh** (major diastereomer) in representation of atoms *via* thermal ellipsoids at 50% probability level. One of several symmetry-independent molecules is shown. [17]

To verify the intermediacy of acyl nitronates **3** low temperature spectroscopic investigations were performed. For this aim 2-nitropropane **1d** was sequentially treated with NaH/*t*-BuOH/15-crown-5 and pivaloyl chloride in CD_2Cl_2 (Scheme 11, cf. Method B, Scheme 6). At -70°C both proton and carbon NMR spectra showed expected signals of **3d**. Thus, two distinct methyl groups were observed indicating of C=N double bond. These two methyl groups showed ^{1}H-^{13}C HMBC cross-peak to ^{13}C peak at 128 ppm, that is in accordance with literature data for nitronic esters.[18] Warming up the reaction to r.t. resulted in change in spectra and decomposition of acyl nitronate. Major observable signals are in accordance with the formation of *gem*-acyloxynitroso compound **5d**. [8,19] The most characteristic was the upfield shift of methyl groups in ^{1}H spectra. Importantly, both methyl groups appeared as a single peak indicative of absence of C=N double bond. Fortunately, nitroso compound **5d** was isolated in individual state, while drop in yield can be attributed to it's volatility and instability due to dimerization and hydrolysis.[19a-d] IR data corroborates NMR data featuring C=N nitronate bands in anion **A** and acyl nitronate **3d** at 1606 and 1638 cm^{-1}, respectively.



Scheme 11. Detection of acyl nitronate **3d**.

To demonstrate the synthetic utility of obtained products several further transformations were performed (Scheme 12).[7,20] Firstly, oxime *O*-silyl group was selectively cleaved under treatment with TBAF/AcOH in THF producing oximes **6** in excellent yields. Several possibilities were demonstrated for selective deprotection of ester moiety producing free alcohol. Thus, acetate-group could be hydrolitically cleaved by methanolic ammonia. However, moderate yield was observed in the case of TBS-protected oxime **11a**, that could be ascribed to concomitant silyl cleavage. Higher yield and selectivity was obtained using bulkier TIPS-protection at oxime (product **11b**). Another possibility for selective ester deprotection was demonstrated for substrate **2sl**. Here reductive conditions resulted in cleavage of methoxyacetyl ester giving rise to good yield of alcohol **11b**. Complete deprotection was demonstrated for ester **2ba** where both silyl and acetate groups were cleaved after prolonged exposure to methanolic ammonia (product **9**).



Scheme 12. Synthetic transformations of products **2**.

Finally, reductive transformation of oxime moiety were explored. Treatment with $NaBH_3CN$ in glacial acetic acid for NOH-substrate **6b** gave good yield of hydroxylamine **8**. The same result was obtained directly from silyl-protected oxime **2b** using slightly prolonged reaction times aiming in both silyl cleavage and reduction of C=N double bond. Exhaustive reduction was attempted using catalytic hydrogenation. However, TBS-protected substrate **2ba** remained intact under 30 atm of H_2 over

Raney nickel at 25 °C for 6 h. Target transformation was achieved using NH_4F as an additive that could promote silyl cleavage. Oxygen-to-nitrogen migration of acetyl moiety furnished amide **10** in good yield.

Conclusion

In conclusion, sequential acylation-silylation of aliphatic nitro compounds was developed as an efficient method for the synthesis of silylated α-acyloxy oxime derivatives. Use of stoichiometric amounts of NaH mediated by DBU or alcohol/15-crown-5 represents a useful procedure for the deprotonation of nitro compounds. Presented protocol has advantages as compared to previously described similar functionalizations *via* double acylation or silylation-acylation sequences. Independent variation of reaction conditions for the acylation and silylation steps allows functionalization of a wide range of substrates, including sterically hindered nitro compounds possessing secondary and tertiary β-carbons. Presented protocol tolerates primary nitro compounds, has wide scope with respect to acylating agents (*e.g.*, those possessing α-protons) and allows introduction of carbonate moiety. Mechanistic scheme for the reaction was proposed and key acyl nitronate intermediate was verified by NMR and IR spectra. Further selective synthetic transformations were performed to demonstrate the synthetic utility of obtained protected oxime derivatives.

Experimental Section

All reactions were performed in oven-dried (150 °C) glassware. Most of the chemicals were acquired from commercial sources and used as received. Petroleum ether (PE) and ethyl acetate for column chromatography were distilled. CH_2Cl_2 was distilled from CaH_2 prior to use. Triethylamine, diisopropylethylamine (DIPEA) and commercial acyl chlorides were distilled from CaH_2. Brine refers to saturated aqueous solution of NaCl. TLC were performed on silica coated on aluminium with UV254 indicator. Visualization was accomplished with UV and/or anisaldehyde/H_2SO_4/EtOH stain. Column chromatography was performed on silica (0.04–0.063 mm, 60 Å). NMR spectra were recorded at 300K (unless otherwise mentioned) on Bruker AM300, Fourier 300HD, Avance NEO and AV 600 spectrometers. *E/Z*-configuration of oxime C=N double bond was assigned on the basis of ^{13}C chemical shifts as reported previously.[7,21] Multiplicities are assigned as s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintet), sext (sextet), m (multiplet), br (broad), app (apparent). Low temperature FT-IR monitoring was conducted on Simex FT-801 infrared spectrometer equipped with MCT detector and ATR-P-Ge-G30-150/50 probe with PIR 900/1000 fiber. High resolution mass spectra were acquired on Bruker micrOTOF spectrometer using electrospray ionization (ESI). Melting points were determined on a Koffler melting point apparatus and are uncorrected. Optical rotations were measured on JASCO P-2000 polarimeter. Concentrations *c* in optical rotation angles are given in g/100 mL.

Starting nitro compounds **1** were prepared by standard protocols. See Supporting information for detailed procedures.

General procedure for the synthesis of oximes ethers 2a,b,c,d,ea GP-1.
(equivalent amount of DBU). To a stirring solution of nitro compound **1** in CH_2Cl_2 (2 mL / 1 mmol of nitro compound **1**) DBU (1.5 equiv) was added at r.t. under an argon atmosphere. After 15 min the reaction mixture was cooled to -78 °C (dry ice/isopropanol bath), and then pivaloyl chloride (1.5 equiv) was added. The solution was stirred for 1 h and then DIPEA (3.0 equiv) and TBSOTf (2.5 equiv) were consequently added. The reaction mixture was maintained at -78 °C for 2 h and transferred into EtOAc (25 mL) / H_2O (20 mL). The organic layer was washed with $NaHSO_4$ (20 mL, 0.5 M aq. solution), brine (20 mL), dried (Na_2SO_4) and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel to give target oxime ethers **2**.

General procedure for the synthesis of oximes ethers 2a,b,ea,eb,f-n GP-2 (Scheme 6, Method A, NaH, DBU-mediated deprotonation, DIPEA at silylation step). A solution of nitro compound **1** in CH_2Cl_2 (4 mL / 1 mmol of nitro compound **1**) was cooled to 0 °C (ice/water bath) under an argon atmosphere and NaH (1.2 equiv) and DBU (0.1 equiv) were consequently added with stirring. The reaction mixture was maintained for 1 h and cooled to -78 °C (dry ice/isopropanol bath), then pivaloyl chloride (1.2 equiv) was added and the mixture was stirred for 0.5 h. After that DIPEA (2.0 equiv) and TBSOTf (1.7 equiv) were consequently added, the reaction mixture was stirred for 2 h at the same temperature and NEt_3 (5 equiv) and MeOH (10 equiv) were added. After that the mixture was warmed to r.t., stirred for 0.5 h and transferred into EtOAc (25 mL) / H_2O (20 mL). The organic layer was washed with $NaHSO_4$ (20 mL, 0.5 M aq. solution), brine (20 mL), dried (Na_2SO_4) and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel to give target oxime ethers **2**.

General procedure for the synthesis of oximes ethers 2a,b,d,ea,j,o-s,ba GP-3 (Scheme 6, Method B, NaH, 15-crown-5/*t*-BuOH-mediated deprotonation, DIPEA at silylation step). A solution of nitro compound **1** in CH_2Cl_2 (4 mL / 1 mmol of nitro compound **1**) was cooled to 0 °C (ice/water bath) under an argon atmosphere and NaH (1.2 equiv), 15-crown-5 (0.1 equiv) and *t*-BuOH (0.1 equiv) were consequently added with stirring. The reaction mixture was maintained for 1 h and cooled to -78 °C (dry ice/isopropanol bath), then acyl chloride (1.2 equiv) was added and the mixture was stirred for 0.5 h. After that DIPEA (2.0 equiv) and TBSOTf (1.7 equiv) were consequently added, the reaction mixture was stirred for 2 h at the same temperature and NEt_3 (5 equiv) and MeOH (10 equiv) were added. After that the mixture was warmed to r.t., stirred for 0.5 h and transferred into EtOAc (25 mL) / H_2O (20 mL). The organic layer was washed with $NaHSO_4$ (20 mL, 0.5 M aq. solution), brine (20 mL), dried (Na_2SO_4) and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel to give target oxime ethers **2**.

General procedure for the synthesis of oximes ethers 2s,t,sa-sl GP-4 (Scheme 6, Method C, NaH, 15-crown-5/*t*-BuOH-mediated deprotonation, NEt_3 at silylation step). A solution of nitro compound **1** in CH_2Cl_2 (4 mL / 1 mmol of nitro compound **1**) was cooled to 0 °C (ice/water bath) under an argon atmosphere and NaH (1.2 equiv), 15-crown-5 (0.1 equiv) and *t*-BuOH (0.1 equiv) were consequently added with stirring. The reaction mixture was maintained for 1 h and cooled to -78 °C (dry ice/isopropanol bath), then acyl chloride (1.2 equiv) was added and the mixture was stirred for 0.5 h. After that NEt_3 (2.0 equiv) and silyl triflate (1.7 equiv) were consequently added, the reaction mixture was stirred for 2 h at the same temperature and NEt_3 (5 equiv) and MeOH (10 equiv) were added. After that the mixture was warmed to r.t., stirred for 0.5 h and transferred into EtOAc (25 mL) / H_2O (20 mL). The organic layer was washed with $NaHSO_4$ (20 mL, 0.5 M aq. solution), brine (20 mL), dried (Na_2SO_4) and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel to give target oxime ethers **2**.

General procedure for the synthesis of oximes ethers 2u-w GP-5 (Scheme 6, Method D, NaH, 15-crown-5/MeOH-mediated deprotonation, NEt_3 at silylation step). A solution of nitro compound **1** in CH_2Cl_2 (4 mL / 1 mmol of nitro compound **1**) was cooled to 0 °C (ice/water bath) under an argon atmosphere and NaH (1.2 equiv), 15-crown-5 (0.1 equiv) and MeOH (0.1 equiv) were consequently added

with stirring. The reaction mixture was maintained for 1 h and cooled to -78 °C (dry ice/isopropanol bath), then pivaloyl chloride (1.2 equiv) was added and the mixture was stirred for 0.5 h. After that NEt_3 (6.0 equiv) and TBSOTf (1.7 equiv) were consequently added, the reaction mixture was stirred for 2 h at the same temperature and NEt_3 (5 equiv) and MeOH (10 equiv) were added. After that the mixture was warmed to r.t., stirred for 0.5 h and transferred into EtOAc (25 mL) / H_2O (20 mL). The organic layer was washed with $NaHSO_4$ (20 mL, 0.5 M aq. solution), brine (20 mL), dried (Na_2SO_4) and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel to give target oxime ethers **2**.

General procedure for the synthesis of oximes 6a,b,d, GP-6. A solution of nitro compound **1** in CH_2Cl_2 (4 mL / 1 mmol of nitro compound **1**) was cooled to 0 °C (ice/water bath) under an argon atmosphere and NaH (1.2 equiv), 15-crown-5 (0.1 equiv) and *t*-BuOH (0.1 equiv) were consequently added with stirring. The reaction mixture was maintained for 1 h and cooled to -78 °C (dry ice/isopropanol bath), then pivaloyl chloride (1.2 equiv) was added and the mixture was stirred for 0.5 h. After that DIPEA (2.0 equiv) and TMSOTf (1.7 equiv) were consequently added, the reaction mixture was stirred for 2 h at the same temperature and NEt_3 (5 equiv) and MeOH (10 equiv) were added. After that the mixture was warmed to r.t., stirred for 0.5 h and transferred into EtOAc (25 mL) / H_2O (20 mL). The organic layer was washed with $NaHSO_4$ (20 mL, 0.5 M aq. solution), brine (20 mL), dried (Na_2SO_4) and evaporated. Crude product was dissolved in MeOH (2 mL / 1 mmol of starting nitro compound **1**), NH_4F (2 equiv) was added and the reaction mixture was stirred for 20 min at r.t. After that the mixture was diluted with EtOAc (2 mL) and evaporated. The residue was preadsorbed on Celite® and subjected to column chromatography on silica gel to give target oximes **5**.

Methyl 4-(*tert*-butyldimethylsilyloxyimino)-5-(pivaloyloxy)pentanoate 2a and Methyl 4-(*tert*-butyldimethylsilyloxyimino)-3-(pivaloyloxy)pentanoate 2'a.

1. Oxime ethers **2a** and **2'a** were obtained from nitro compound **1a** (56 mg, 0.35 mmol), pivaloyl chloride (65 µL, 63 mg, 0.52 mmol) and TBSOTf (0.20 mL, 0.23 g, 0.88 mmol) according to GP-1. Column chromatography (eluent: PE/EtOAc, 30:1) afforded 97 mg of a mixture of **2a** and **2'a** (ratio **2a**/**2'a** = 5:1, ^{1}H NMR) and 9 mg of pure oxime ether **2a**. R_f = 0.67 (PE/EtOAc, 20:1, anisaldehyde). Total yield of **2a**: 90 mg (72%). Total yield of **2'a**: 16 mg (13%).

2. Oxime ethers **2a** and **2'a** were obtained from nitro compound **1a** (142 mg, 0.88 mmol), pivaloyl chloride (0.13 mL, 0.13 g, 1.06 mmol) and TBSOTf (0.34 mL, 0.40 g, 1.50 mmol) according to GP-2. Column chromatography (eluent: PE/EtOAc, 40:1, then 30:1) afforded isomeric mixtures: 40 mg (ratio **2a**/**2'a** = 1:4, ^{1}H NMR), 23 mg (ratio **2a**/**2'a** = 5:1, ^{1}H NMR) and 172 mg (ratio **2a**/**2'a** = 11:1, ^{1}H NMR), – as colorless oils. Total yield of **2a**: 185 mg (59%). Total yield of **2'a**: 50 mg (16%).

3. Oxime ether **2a** was obtained from nitro compound **1a** (44 mg, 0.27 mmol), pivaloyl chloride (40 µL, 39 mg, 0.32 mmol) and TBSOTf (0.11 mL, 0.13 g, 0.48 mmol) according to GP-3. Column chromatography (eluent: PE/EtOAc, 40:1, then 30:1) afforded 52 mg (54%, **2a**/**2'a**= 4:1, ^{1}H NMR) of target oxime ether as colorless oil. NMR matched previously reported data.[8]

2-(((*tert*-Butyldimethylsilyl)oxy)imino)-3-(4-methoxyphenyl)propyl pivalate 2b

1. Oxime ether **2b** was obtained from nitro compound **1b** (73 mg, 0.37 mmol), pivaloyl chloride (70 µL, 67 mg, 0.56 mmol) and TBSOTf (0.21 mL, 0.24 g, 0.93 mmol) according to GP-1. Column chromatography (eluent: PE/EtOAc, 50:1) afforded 105 mg (72%) of target oxime ether as slightly yellow oil.

2. Oxime ether **2b** was obtained from nitro compound **1b** (110 mg, 0.56 mmol), pivaloyl chloride (83 µL, 81 mg, 0.67 mmol) and TBSOTf (0.22 mL, 0.25 g, 0.95 mmol) according to GP-2. Column chromatography (eluent: PE/EtOAc, 100:1, then 30:1) afforded 153 mg (72%) of target oxime ether as slightly yellow oil.

3. Oxime ether **2b** was obtained from nitro compound **1b** (60 mg, 0.31 mmol), pivaloyl chloride (46 µL, 45 mg, 0.37 mmol) and TBSOTf (0.12 mL, 0.14 g, 0.52 mmol) according to GP-3. Column chromatography (eluent: PE/EtOAc, 40:1) afforded 102 mg (84%) of target oxime ether as slightly yellow oil.

R_f = 0.53 (PE/EtOAc, 9:1, UV, anisaldehyde). *E*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.22 (s, 6H, Me_2Si), 0.97 (s, 9H, *t*-BuSi), 1.20 (s, 9H, *t*-Bu), 3.75 (s, 2H, CH_2−Ar), 3.80 (s, 3H, OCH_3), 4.58 (s, 2H, CH_2−O), 6.83 (d, *J* = 8.6 Hz, 2H, CH_{Ar}), 7.13 (d, *J* = 8.6 Hz, CH_{Ar}). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.2 ($\underline{Me}_2Si$), 18.1 ($Me_3\underline{C}$−Si), 26.1 ($\underline{Me}_3CSi$), 27.2 ($\underline{Me}_3CC(O)$), 31.1 (CH_2), 38.8 ($Me_3\underline{C}$), 55.3 (MeO), 63.8 (CH_2−O), 114.0 (CH_{Ar}), 128.2 (C_{Ar}), 130.0 (CH_{Ar}), 158.3 and 158.5 ($\underline{C}_{Ar}$–OMe and C=N), 177.8 (C=O). *Z*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.21 (s, 6H, Me_2Si), 0.97 (s, 9H, *t*-BuSi), 1.18 (s, 9H, *t*-Bu), 3.59 (s, 2H, CH_2−Ar), 3.80 (s, 3H, OCH_3), 4.91 (s, 2H, CH_2−O), 6.85 (d, *J* = 8.6 Hz, 2H, CH_{Ar}), 7.14 (d, *J* = 8.6 Hz, CH_{Ar}). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$, characteristic signals): δ -5.3 ($\underline{Me}_2Si$), 26.1 ($\underline{Me}_3CSi$), 27.2 ($\underline{Me}_3CC(O)$), 36.3 (CH_2), 38.8 ($Me_3\underline{C}$), 55.3 (MeO), 58.9 (CH_2−O), 113.9 (CH_{Ar}), 129.6 (CH_{Ar}), 159.9 (C=N), 177.8 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{21}H_{35}NO_4Si$ + H^+]: 394.2411, found: 394.2408.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)-3-(4-nitrophenyl)propyl pivalate 2c. Oxime ether **2c** was obtained from nitro compound **1c** (56 mg, 0.27 mmol), pivaloyl chloride (50 µL, 49 mg, 0.40 mmol) and TBSOTf (0.15 mL, 0.17 g, 0.65 mmol) according to GP-1. **2c**:**2'c** = 6:1 (^{1}H NMR). Column chromatography (eluent: PE, then PE/EtOAc, 80:1) afforded 58 mg (53%) of target oxime ether as colorless oil. R_f = 0.72 (PE/EtOAc, 3:1, UV, anisaldehyde). Minor isomer **2'c** could not be separated from side product (1-nitro-4-(prop-1-en-1-yl)benzene).[22] **2c**: *E*-isomer, ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.20 (s, 6H, Me_2Si), 0.91 (s, 9H, *t*-BuSi), 1.16 (s, 9H, *t*-Bu), 3.87 (s, 2H, CH_2−Ar), 4.67 (s, 2H, CH_2−O), 7.39 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 8.17 (d, *J* = 8.7 Hz, CH_{Ar}). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.2 ($\underline{Me}_2Si$), 18.0 ($Me_3\underline{C}$−Si), 25.9 ($\underline{Me}_3CSi$), 27.1 ($\underline{Me}_3CC(O)$), 32.3 (CH_2), 38.8 ($Me_3\underline{C}$), 64.2 (CH_2−O), 123.7 (CH_{Ar}), 129.6 (CH_{Ar}), 144.1 (C_{Ar}), 146.7 (C–NO_2), 156.7 (C=N), 177.9 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{20}H_{32}N_2O_5Si$ + H^+]: 409.2153, found: 409.2149. **2'c** (characteristic signals) ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 9H, *t*-Bu), 1.83 (s, 3H, ON=C−Me), 6.42 (s, 1H, CH−O), 7.52 (d, *J* = 8.8 Hz, 2H, CH_{Ar}), 8.24 (d, *J* = 8.8 Hz, CH_{Ar}). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 10.5 (ON=C−$\underline{Me}$), 75.5 (CH−O), 127.1 (CH_{Ar}), 158.5 (C=N).

2-(((*tert*-Butyldimethylsilyl)oxy)imino)propyl pivalate 2d.

1. Oxime ether **2d** was obtained from nitro compound **1d** (0.18 mL, 0.18 g, 2.0 mmol), pivaloyl chloride (0.37 mL, 0.36 g, 3.0 mmol) and TBSOTf (1.15 mL, 1.32 g, 5.0 mmol) according to GP-1. Column chromatography (eluent: PE/EtOAc, 50:1) afforded 403 mg (70%) of target oxime ether as colorless oil.

2. Oxime ether **2d** was obtained from nitro compound **1d** (45 µL, 45 mg, 0.50 mmol), pivaloyl chloride (75 µL, 72 mg, 0.60 mmol) and TBSOTf (0.19 mL, 0.22 g, 0.83 mmol) according to GP-3 Column chromatography (eluent: PE/EtOAc, 50:1) afforded 110 mg (77%) of target oxime ether as colorless oil. NMR matches previously reported data.[8]

Methyl 4-(((*tert*-butyldimethylsilyl)oxy)imino)-3-methyl-5-(pivaloyloxy)pentanoate 2ea.

1. Oxime ether **2ea** was obtained from nitro compound **1ea** (98 mg, 0.56 mmol), pivaloyl chloride (0.10 mL, 97 mg, 0.80 mmol) and TBSOTf (0.32 mL, 0.37 g, 1.40 mmol) according to GP-1. Column chromatography (eluent: PE/EtOAc, 25:1) afforded 82 mg (39%) of target oxime ether as colorless oil.

2. Oxime ether **2ea** was obtained from nitro compound **1ea** (90 mg, 0.51 mmol), pivaloyl chloride (76 µL, 74 mg, 0.61 mmol) and TBSOTf (0.20 mL, 0.23 g, 0.87 mmol) according to GP-2. Column chromatography (eluent: PE/EtOAc, 30:1) afforded 104 mg (55%) of target oxime ether as colorless oil.

3. Oxime ether **2ea** was obtained from nitro compound **1ea** (74 mg, 0.42 mmol), pivaloyl chloride (63 µL, 61 mg, 0.50 mmol) and TBSOTf (0.16 mL, 0.19 g, 0.71 mmol) according to GP-3. Column chromatography (eluent: PE/EtOAc, 30:1) afforded 93 mg (59%) of target oxime ether as colorless oil. R_f = 0.35 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.16 (s, 6H, Me_2Si), 0.94 (s, 9H, *t*-BuSi), 1.20 (d, *J* = 7.1 Hz, 1H, CHMe), 1.23 (s, 9H, *t*-BuCO), 2.48 (dd, *J* = 15.9, 8.2 Hz, 1H, $CH_{2a}CO$), 2.77 (dd, *J* = 15.9, 6.7 Hz, 1H, $CH_{2b}CO$), 3.41-3.53 (m, 1H, CHMe), 3.67 (s, 3H, OMe), 4.63 (d, *J* = 12.7 Hz, 1H, CH_{2a}–O), 4.69 (d, *J* = 12.7 Hz, 1H, CH_{2b}–O). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.4 (Me_2Si), 16.2 (CHMe), 18.0 (Si–CMe_3), 26.0 (Si–CMe_3), 27.2 (Me_3CCO), 29.6 (CHMe), 37.6 (CH_2CO), 38.8 (Me_3CCO), 51.6 (OMe), 64.3 (CH_2–O), 161.3 (C=N), 172.5 (CO_2Me), 177.8 (*t*-BuC=O). HRMS (ESI): *m/z* calcd. for $[C_{18}H_{35}NO_5Si + Na^+]$: 396.2179, found: 396.2177.

Isopropyl 4-(((*tert*-butyldimethylsilyl)oxy)imino)-3-methyl-5-(pivaloyloxy)pentanoate 2eb. Oxime ether **2eb** was obtained from nitro compound **1eb** (62 mg, 0.31 mmol), pivaloyl chloride (45 µL, 44 mg, 0.36 mmol) and TBSOTf (0.12 mL, 0.14 g, 0.52 mmol) according to GP-2. Column chromatography (eluent: PE, PE/EtOAc, 50:1) afforded 95 mg (78%) of target oxime ether as colorless oil. R_f = 0.50 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.15 (s, 6H, Me_2Si), 0.94 (s, 9H, *t*-BuSi), 1.18-1.25 (m, 18H, *t*-Bu, $(CH_3)_2CH$ and CH_3CH), 2.41 (dd, *J* = 15.7, 8.2 Hz, 1H, CH_{2a}), 2.73 (dd, *J* = 15.7, 6.7 Hz, 1H, CH_{2b}), 3.47 (app sext, *J* = 7.2 Hz, 1H, CHC=N), 4.62 (d, *J* = 12.6 Hz, 1H, CH_{2a}−O), 4.69 (d, *J* = 12.6 Hz, 1H, CH_{2b}−O), 5.00 (hept, *J* = 6.3 Hz, 1H, $OCH(CH_3)_2$). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.4 (Me_2Si), 16.1 (Me), 18.0 (Me_3C−Si), 21.75 and 21.77 ($CHMe_2$), 26.0 (Me_3CSi), 27.2 ($Me_3CC(O)$), 29.6 (CHMe), 38.2 (CH_2CO), 38.8 (Me_3C), 64.3 (CH−O), 67.7 (Me_2CH−O), 161.4 (C=N), 171.5 (CO_2i-Pr), 177.7 (C=O). HRMS (ESI): *m/z* calcd. for $[C_{20}H_{39}NO_5Si + Na^+]$: 424.2490, found: 424.2482.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)-4-(1,3-dioxolan-2-yl)-3-phenylbutyl pivalate 2f. Oxime ether **2f** was obtained from nitro compound **1f** (77 mg, 0.31 mmol), pivaloyl chloride (46 µL, 45 mg, 0.37 mmol) and TBSOTf (0.12 mL, 0.14 g, 0.52 mmol) according to GP-2. Column chromatography (eluent: PE/EtOAc, 50:1, then 30:1) afforded 93 mg (67%) of target oxime ether as colorless oil. R_f = 0.32 (PE/EtOAc, 9:1, UV, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 6H, Me_2Si), 0.95 (s, 9H, *t*-BuSi), 1.17 (s, 9H, *t*-Bu), 2.27-2.46 (m, 2H, CH_2), 3.78-3.85 and 3.91-4.00 (m, total 4H, OCH_2CH_2O), 4.56 (d, *J* = 12.8 Hz, 1H, CH_{2a}–O), 4.62 (d, *J* = 12.8 Hz, 1H, CH_{2b}–O), 4.79-4.87 (m, 2H, CHPh and $CH(OCH_2)_2$), 7.21-7.33 (m, 5H, Ph). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.3 (Me_2Si), 18.0 (Me_3C−Si), 26.0 (Me_3CSi), 27.1 ($Me_3CC(O)$), 35.1 (CH_2), 38.5 (CHPh), 38.7 (Me_3C), 63.6 (CH_2–O), 64.81 and 64.84 (OCH_2CH_2O), 102.9 ($CH(OCH_2)_2$), 126.7 (CH_{Ph}), 128.1 (CH_{Ph}), 128.4 (CH_{Ph}), 139.6 (C_{Ph}), 159.8 (C=N), 177.8 (C=O). HRMS (ESI): *m/z* calcd. for $[C_{24}H_{39}NO_5Si + H^+]$: 450.2662, found: 450.2670.

3-(((*tert*-Butyldimethylsilyl)oxy)imino)-4-(4-methoxyphenyl)butan-2-yl pivalate 2g and **2-(((*tert*-Butyldimethylsilyl)oxy)imino)-1-(4-methoxyphenyl)butyl pivalate 2'g.** Oxime ethers **2g** and **2'g** were obtained from nitro compound **1g** (64 mg, 0.31 mmol), pivaloyl chloride (46 µL, 45 mg, 0.37 mmol) and TBSOTf (0.12 mL, 0.14 g, 0.53 mmol) according to GP-2 with following change: NEt_3 was used instead of DIPEA at the silylation stage. Column chromatography (eluent: PE, then PE/EtOAc, 60:1) afforded 86 mg of a mixture of **2g** and **2'g** (ratio **2g**/**2'g** ≈ 1:1). Total yield of **2g**: 43 mg (34%). Total yield of **2'g**: 43 mg (34%). R_f = 0.52 (PE/EtOAc, 9:1, UV, anisaldehyde).**2g:** ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.20 (s, 6H, Me_2Si), 0.95 (s, 9H, *t*-BuSi), 1.16 (s, 9H, *t*-BuC(O)), 1.31 (d, *J* = 6.5 Hz, 3H, CHMe), 3.54 (d, *J* = 13.9 Hz, 1H, $CH_{2a}Ar$), 3.79 (s, 3H, OMe), 3.91 (d, *J* = 13.9 Hz, 1H, $CH_{2b}Ar$), 5.46 (q, *J* = 6.5 Hz, 1H, CH–O), 6.82 (d, *J* = 8.6 Hz, 2H, CH_{Ar}), 7.13 (d, *J* = 8.6 Hz, 2H, CH_{Ar}).^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.2 (Me_2Si), 17.7 (CHMe), 18.1 (Me_3CSi), 26.1 (Me_3CSi), 27.0 ($Me_3CC(O)$), 30.6 (CH_2), 38.7 ($Me_3CC(O)$), 55.2 (OMe), 70.3 (CH–O), 113.9 (CH_{Ar}), 128.7 (C_{Ar}), 129.9 (CH_{Ar}), 158.1 (C_{Ar}–OMe), 161.3 (C=N), 177.5 (C=O). **2'g:** *E*/*Z* = 1.4:1. *E*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.18 (s, 3H, MeSi), 0.19 (s, 3H, MeSi), 0.95 (s, 9H, *t*-BuSi), 0.92-0.99 (m, 3H, CH_2Me), 1.28 (s, 9H, *t*-BuC(O)), 2.22-2.32 (m, 2H, CH_2Me), 3.82 (s, 3H, OMe), 6.27 (s, 1H, CH–O), 6.90 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.32 (d, *J* = 8.7 Hz, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.2 (Me_2Si), 10.6 (CH_2Me), 18.1 (Me_3CSi), 19.5 (CH_2), 26.1 (Me_3CSi), 27.2 ($Me_3CC(O)$), 38.9 ($Me_3CC(O)$), 55.2 (OMe), 75.6 (CH–O), 113.9 (CH_{Ar}), 128.0 (CH_{Ar}), 129.4 (C_{Ar}), 159.5 (C_{Ar}–OMe), 163.4 (C=N), 176.9 (C=O). *Z*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.15 (s, 3H, MeSi), 0.16 (s, 3H, MeSi), 0.95 (s, 9H, *t*-BuSi), 1.09 (t, *J* = 7.4 Hz, 1H, CH_2Me), 1.28 (s, 9H, *t*-BuC(O)), 2.29-2.40 (m, 2H, CH_2Me), 3.81 (s, 3H, OMe), 6.88 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.12 (s, 1H, CH–O), 7.31 (d, *J* = 8.7 Hz, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.2 (Me_2Si), 10.5 (CH_2Me), 18.1 (Me_3CSi), 22.8 (CH_2), 26.1 (Me_3CSi), 27.2 ($Me_3CC(O)$), 38.9 ($Me_3CC(O)$), 55.2 (OMe), 70.2 (CH–O), 113.7 (CH_{Ar}), 127.8 (CH_{Ar}), 129.7 (C_{Ar}), 159.1 (C_{Ar}–OMe), 162.3 (C=N), 176.9 (C=O). HRMS (ESI): *m/z* calcd. for $[C_{22}H_{37}NO_4Si + Na^+]$: 430.2384, found: 430.2379.

Methyl 4-(((*tert*-butyldimethylsilyl)oxy)imino)-2-methyl-5-(pivaloyloxy)pentanoate 2h. Oxime ether **2h** was obtained from nitro compound **1h** (69 mg, 0.39 mmol), pivaloyl chloride (58 µL, 56 mg, 0.47 mmol) and TBSOTf (0.15 mL, 0.17 g, 0.65 mmol) according to GP-2. Column chromatography (eluent: PE/EtOAc, 70:1, then 50:1) afforded 113 mg (78%) of target oxime ether as colorless oil. Maintaining NMR sample of (*E*)-**2h**/(*Z*)-**2h** mixture (ratio (*E*)-**2h**/(*Z*)-**2h**= 20:1) in $CDCl_3$ at 50 °C (oil bath) for 6 h resulted in ratio (*E*)-**2h**/(*Z*)-**2h** = 6:1. R_f = 0.45 (PE/EtOAc, 9:1, anisaldehyde). *E*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.15 (s, 6H, Me_2Si), 0.93 (s, 9H, *t*-BuSi), 1.18 (d, *J* = 7.1 Hz, 3H, $CHCH_3$), 1.22 (s, 9H, *t*-Bu), 2.57 (dd, *J* = 11.0, 5.2 Hz, 1H, CH_{2a}), 2.64 (dd, *J* = 11.0, 5.2 Hz, 1H, CH_{2b}), 2.90 (app sext, *J* = 7.2 Hz, 1H, CHMe), 3.67 (s, 3H, OCH_3), 4.60 (d, *J* = 13.1 Hz, CH_{2a}−O), 4.66 (d, *J* = 13.1 Hz, 1H, CH_{2b}−O). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.3 (Me_2Si), 17.1 (Me), 18.0 (Me_3C−Si), 26.0 (Me_3CSi), 27.1 ($Me_3CC(O)$), 29.8 (CH_2), 36.2 (CH), 38.8 (Me_3C), 51.7 (OMe), 64.5 (CH−O), 157.9 (C=N), 175.9 (CO_2Me), 177.8 ($COOCH_2$). *Z*-isomer (characteristic signals): ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.29 (dd, *J* = 16.3, 5.9 Hz, CH_{2a}), 3.65 (s, 3H, OCH_3), 4.89 (d, *J* = 16.3 Hz, CH_{2a}−O), 5.00 (d, *J* = 16.3 Hz, 1H, CH_{2b}−O). ^{13}C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 60.0 (CH_2−O). HRMS (ESI): *m/z* calcd. for $[C_{18}H_{35}NO_5Si + K^+]$: 412.1916, found: 412.1908.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)-5,5-dimethoxy-3-phenylpentyl pivalate 2i. Oxime ether **2i** was obtained from nitro compound **1i** (66 mg, 0.26 mmol), pivaloyl chloride (39 µL, 38 mg, 0.31 mmol) and TBSOTf (0.10 mL, 0.12 g, 0.44 mmol) according to GP-2. Column chromatography (eluent: PE/EtOAc, 50:1) afforded 88 mg (75%) of target oxime ether as colorless oil. R_f = 0.31 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.19 (s, 6H, Me_2Si), 0.96 (s, 9H, *t*-BuSi), 1.17 (s, 9H, *t*-Bu), 2.20-2.40 (m, 2H, CH_2), 3.32 and 3.33 (both s, both 3H, OCH_3), 4.33 (t, *J* = 5.7 Hz, 1H, $CH(OCH_3)_2$), 4.56 (s, 2H, CH_2–O), 4.70 (t, *J* = 8.0 Hz, 1H, CHPh), 7.19-7.33 (m, 5H, Ph). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.2 (Me_2Si), 18.1 (Me_3C−Si), 26.0 (Me_3CSi), 27.1 ($Me_3CC(O)$), 33.8 (CH_2), 38.7 (Me_3C), 38.9 (CHPh), 52.5 (OMe), 53.1 (OMe), 63.4 (CH_2–O), 102.7 ($CH(OMe)_2$), 126.8 (CH_{Ph}), 128.1 (CH_{Ph}), 128.5 (CH_{Ph}), 139.5 (C_{Ph}), 159.5 (C=N), 177.7 (C=O). HRMS (ESI): *m/z* calcd. for $[C_{24}H_{41}NO_5Si + H^+]$: 452.2827, found: 452.2827.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)-4-(2-methyl-1,3-dioxolan-2-yl)-3-phenylbutyl pivalate 2j.

1. Oxime ether **2j** was obtained from nitro compound **1j** (92 mg, 0.35 mmol), pivaloyl chloride (52 µL, 51 mg, 0.42 mmol) and TBSOTf (0.14 mL, 0.16 g, 0.60 mmol) according to GP-2. Column chromatography (eluent: PE/EtOAc, 40:1) afforded 120 mg (75%) of target oxime ether as slightly yellow oil.

2. Oxime ether **2j** was obtained from nitro compound **1j** (84 mg, 0.32 mmol), pivaloyl chloride (47 µL, 46 mg, 0.38 mmol) and TBSOTf (0.12 mL, 0.14 g, 0.52 mmol) according to GP-3. Column chromatography (eluent: PE/EtOAc, 30:1) afforded 96 mg (66%) of target oxime ether as

slightly yellow oil. R_f = 0.24 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 6H, Me_2Si), 0.96 (s, 9H, *t*-BuSi), 1.10 (s, 9H, *t*-Bu), 1.34 (s, 3H, C–CH_3), 2.32 (dd, *J* = 14.6, 5.1 Hz, 1H, CH_{2a}), 2.49 (dd, *J* = 14.6, 9.2 Hz, 1H, CH_{2b}), 3.85-3.95 (m, 4H, OCH_2CH_2O), 4.66 (d, *J* = 12.9 Hz, 1H, CH_{2a}–O), 4.75 (d, *J* = 12.9 Hz, 1H, CH_{2b}–O), 4.95 (dd, *J* = 9.2, 5.1 Hz, 1H, CHPh), 7.16-7.35 (m, 5H, Ph). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.2 ($\underline{Me}_2Si$), 18.0 ($Me_3\underline{C}$−Si), 24.6 (CH_3), 26.0 ($\underline{Me}_3CSi$), 27.1 ($\underline{Me}_3CC(O)$), 37.2 (CHPh), 38.7 ($Me_3\underline{C}$), 39.5 (CH_2), 63.2 (CH_2–O), 64.5 and 64.7 (OCH_2CH_2O), 109.4 ($\underline{C}(OCH_2)_2$)), 126.4 (CH_{Ph}), 128.0 (CH_{Ph}), 128.3 (CH_{Ph}), 140.6 (C_{Ph}), 160.5 (C=N), 177.8 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{25}H_{41}NO_5Si$ + H^+]: 464.2824, found: 464.2827.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)-3-phenyl-4-(propionyloxy)-butyl pivalate 2k. Oxime ether **2k** was obtained from nitro compound **1k** (98 mg, 0.37 mmol), pivaloyl chloride (55 µL, 54 mg, 0.44 mmol) and TBSOTf (0.14 mL, 0.17 g, 0.63 mmol) according to GP-2. Column chromatography (eluent: PE/EtOAc, 70:1, then 40:1) afforded 112 mg (65%) of target oxime ether as colorless oil. R_f = 0.31 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.20 (s, 6H, Me_2Si), 0.97 (s, 9H, *t*-BuSi), 1.14 (t, *J* = 7.7 Hz, 3H, $C\underline{H}_3CH_2$), 1.17 (s, 9H, *t*-Bu), 2.31 (q, *J* = 7.6 Hz, 2H, $C\underline{H}_2Me$), 2.31-2.37 (m, 2H, CH_2), 4.03-4.19 (m, 2H, $C\underline{H}_2OC(O)Et$), 4.47-4.55 (m, 2H, $C\underline{H}_2$–OC(O)*t*-Bu), 4.80 (app t, *J* = 8.0 Hz ,1H, CHPh), 7.21-7.34 (m, 5H, Ph). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.3 ($\underline{Me}_2Si$), 9.1 ($\underline{Me}CH_2$), 18.0 ($Me_3\underline{C}$−Si), 26.0 ($\underline{Me}_3CSi$), 27.1 ($\underline{Me}_3CC(O)$), 27.5 ($\underline{C}H_2Me$), 29.7 (CH_2), 38.7 ($Me_3\underline{C}$), 39.1 (CHPh), 62.5 ($\underline{C}H_2OC(O)Et$), 63.1 ($\underline{C}H_2$–OC(O)*t*-Bu), 127.0 (CH_{Ph}), 128.1 (CH_{Ph}), 128.4 (CH_{Ph}), 139.0 (C_{Ph}), 159.3 (C=N), 174.3 (C=O), 177.7 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{25}H_{41}NO_5Si$ + H^+]: 464.2827, found: 464.2815.

3-((*tert*-Butyldimethylsilyl)oxy)-2-(((*tert*-butyldimethylsilyl)oxy)-imino)-5-phenylpentyl pivalate 2l. Oxime ether **2l** was obtained from nitro compound **1l** (101 mg, 0.31 mmol), pivaloyl chloride (47 µL, 45 mg, 0.38 mmol) and TBSOTf (0.12 mL, 0.14 g, 0.53 mmol) according to GP-2. Column chromatography (eluent: PE/EtOAc, 50:1) afforded 120 mg (74%) of target oxime ether as slightly yellow oil. R_f = 0.60 (PE/EtOAc, 9:1, UV, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.07 (s, 3H, MeSi), 0.10 (s, 3H, MeSi), 0.19 (s, 6H, Me_2Si), 0.95 (s, 9H, *t*-BuSi), 0.97 (s, 9H, *t*-BuSi), 1.25 (s, 9H, *t*-Bu), 1.91-2.09 (m, 2H, $C\underline{H}_2CH$–O), 2.63 (ddd, *J* = 13.7, 10.6, 6.4 Hz, 1H, $C\underline{H}_{2a}Ph$), 2.81 (ddd, *J* = 13.7, 10.9, 5.6 Hz, 1H, $C\underline{H}_{2b}Ph$), 4.67 (d, *J* = 13.6 Hz, 1H, CH_{2a}–O), 4.96 (d, *J* = 13.6 Hz, 1H, CH_{2b}–O), 5.28 (dd, *J* = 7.5, 5.3 Hz, 1H, CH–O), 7.18-7.33 (m, 5H, Ph). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.29 (MeSi), -5.24 (MeSi), -5.09 (MeSi), -5.06 (MeSi), 18.0 ($Me_3\underline{C}$−Si), 18.1 ($Me_3\underline{C}$−Si), 25.8 ($\underline{Me}_3CSi$), 26.0 ($\underline{Me}_3CSi$), 27.3 ($\underline{Me}_3CC(O)$), 31.7 ($\underline{C}H_2Ph$), 36.8 ($\underline{C}H_2CH$–O), 38.7 ($Me_3\underline{C}$), 61.3 (CH_2−O), 66.8 (CH−O), 125.8 (CH_{Ph}), 128.3 (CH_{Ph}), 128.4 (CH_{Ph}), 142.0 (C_{Ph}), 161.8 (C=N), 177.8 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{28}H_{51}NO_4Si_2$ + H^+]: 522.3429, found: 522.3428.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)-2-(1,3-dithian-2-yl)ethyl pivalate 2m. Oxime ether **2m** was obtained from nitro compound **1m** (65 mg, 0.34 mmol), pivaloyl chloride (51 µL, 49 mg, 0.41 mmol) and TBSOTf (0.13 mL, 0.15 g, 0.58 mmol) according to GP-2. Column chromatography (eluent: PE/EtOAc, 50:1) afforded 100 mg (75%) of target oxime ether as slightly yellow oil. R_f = 0.49 (PE/EtOAc, 9:1, UV, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.21 (s, 6H, Me_2Si), 0.96 (s, 9H, *t*-BuSi), 1.26 (s, 9H, *t*-Bu), 1.87-2.01 (m, 1H, CH_{2a}), 2.06-2.17 (m, 1H, CH_{2b}), 2.87 (ddd, *J* = 15.1, 7.9, 5.3 Hz, 2H, CH_{2a}−S), 3.00 (ddd, *J* = 15.1, 11.7, 2.7 Hz, 2H, CH_{2b}−S), 4.81 (s, 2H, CH_2−O), 5.86 (s, 1H, CH–S). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.3 ($\underline{Me}_2Si$), 18.2 ($Me_3\underline{C}$−Si), 25.3 (CH_2), 26.0 ($\underline{Me}_3CSi$), 27.2 ($\underline{Me}_3CC(O)$), 30.8 (CH_2), 38.8 ($Me_3\underline{C}$), 41.7 (CH–S), 62.2 (CH−O), 154.5 (C=N), 177.7 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{17}H_{33}NO_3S_2Si$ + H^+]: 392.1749, found: 392.1744.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)-2-phenylethyl pivalate 2n. Oxime ether **2n** was obtained from nitro compound **1n** (63 mg, 0.42 mmol), pivaloyl chloride (62 µL, 60 mg, 0.37 mmol) and TBSOTf (0.12 mL, 0.14 g, 0.36 mmol) according to GP-2. Column chromatography (eluent: PE/EtOAc, 50:1) afforded 67 mg (46%) of target oxime ether as colorless oil. *E*/*Z* = 2.3:1. *E*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.21 (s, 6H, Me_2Si), 0.92 (s, 9H, *t*-BuSi), 1.11 (s, 9H, *t*-BuC), 5.02 (s, 2H, CH_2−O), 7.34-7.43 (m, 3H, CH_{Ph}), 7.54-7.60 (m, 2H, CH_{Ph}). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.3 ($\underline{Me}_2Si$), 18.0 ($Me_3\underline{C}$Si), 26.0 ($\underline{Me}_3CSi$), 27.0 ($\underline{Me}_3CC(O)$), 38.7 ($Me_3\underline{C}$), 64.6 (CH_2–O), 127.8 (CH_{Ph}), 128.6 (CH_{Ph}), 129.1 (CH_{Ph}), 131.3 (C_{Ph}), 156.3 (C=N), 177.8 (C=O). *Z*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.27 (s, 6H, Me_2Si), 1.01 (s, 9H, *t*-BuSi), 1.09 (s, 9H, *t*-BuC), 5.33 (s, 2H, CH_2−O), 7.34-7.43 (m, 3H, CH_{Ph}), 7.54-7.60 (m, 2H, CH_{Ph}). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.2 ($\underline{Me}_2Si$), 18.2 ($Me_3\underline{C}$Si), 26.1 ($\underline{Me}_3CSi$), 27.0 ($\underline{Me}_3CC(O)$), 38.7 ($Me_3\underline{C}$), 56.7 (CH_2–O), 127.1 (CH_{Ph}), 128.2 (CH_{Ph}), 129.2 (CH_{Ph}), 133.9 (C_{Ph}), 158.6 (C=N), 177.9 (C=O). NMR matched previously reported data.[8]

2-(((*tert*-Butyldimethylsilyl)oxy)imino)-1-(4-methoxyphenyl)ethyl pivalate 2o. Oxime ether **2o** was obtained from nitro compound **1o** (65 mg, 0.36 mmol), pivaloyl chloride (54 µL, 52 mg, 0.43 mmol) and TBSOTf (0.14 mL, 0.16 g, 0.61 mmol) according to GP-3. Column chromatography (eluent: PE, then PE/EtOAc 80:1) afforded 103 mg (76%) of target oxime ether as colorless oil. R_f = 0.47 (PE/EtOAc, 9:1, UV, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.17 (s, 3H, MeSi), 0.19 (s, 3H, MeSi), 0.94 (s, 9H, *t*-BuSi), 1.25 (s, 9H, *t*-Bu), 3.82 (s, 3H, OMe), 6.32 (d, *J* = 6.2 Hz, 1H, CH−O), 6.92 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.31 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.62 (d, *J* = 6.2 Hz, 1H, CH=N). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.3 (Me_2Si), 18.2 ($Me_3\underline{C}$−Si), 26.1 ($\underline{Me}_3CSi$), 27.1 ($\underline{Me}_3CC(O)$), 38.9 ($Me_3\underline{C}$), 55.3 (MeO), 72.3 (CH−O), 114.1 (CH_{Ar}), 128.3 (CH_{Ar}), 129.2 (C_{Ar}), 152.5 (CH=N), 159.7 (C_{Ar}), 176.9 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{20}H_{33}NO_4Si$ + Na^+]: 402.2071, found: 402.2061.

Isopropyl 4-(((*tert*-butyldimethylsilyl)oxy)imino)-3-(pivaloyloxy)-butanoate 2p. Oxime ether **2p** was obtained from nitro compound **1p** (60 mg, 0.34 mmol), pivaloyl chloride (51 µL, 49 mg, 0.41 mmol) and TBSOTf (0.13 mL, 0.15 g, 0.58 mmol) according to GP-3. Column chromatography (eluent: PE, then PE/EtOAc, 70:1) afforded 77 mg (61%) of target oxime ether as colorless oil. R_f = 0.62 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.15 (s, 6H, Me_2Si), 0.93 (s, 9H, *t*-BuSi), 1.20 (s, 9H, *t*-Bu), 1.24 (d, *J* = 6.3 Hz, 6H, $(C\underline{H}_3)_2CH$), 2.73 (dd, *J* = 16.1, 8.2 Hz, 1H, CH_{2a}), 2.86 (dd, *J* = 16.1, 5.3 Hz, 1H, CH_{2b}), 5.01 (hept, *J* = 6.2 Hz, 1H, $(CH_3)_2C\underline{H}$), 5.72 (app dt, *J* = 8.2, 4.7 Hz, 1H, CH−O), 7.53 (d, *J* = 3.9 Hz, 1H, H−C=N). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): -5.4 ($\underline{Me}_2Si$), 18.2 ($Me_3\underline{C}$−Si), 21.7 and 21.8 (($\underline{C}H_3)_2CH$), 26.0 ($\underline{Me}_3CSi$), 27.0 ($\underline{Me}_3CC(O)$), 37.2 (CH_2), 38.7 ($Me_3\underline{C}$), 67.4 and 68.3 ($\underline{C}H$−OPiv and $(CH_3)_2\underline{C}H$−O), 151.6 (CH=N), 169.0 ($\underline{C}OOi$-Pr), 177.1 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{18}H_{35}NO_5Si$ + Na^+]: 396.2177, found: 396.2175.

2,2,3,3-Tetramethyl-11-oxo-4,10-dioxa-5-aza-3-silatridec-5-en-7-yl pivalate 2q. Oxime ether **2q** was obtained from nitro compound **1q** (58 mg, 0.33 mmol), pivaloyl chloride (51 µL, 49 mg, 0.41 mmol) and TBSOTf (0.13 mL, 0.15 g, 0.58 mmol) according to GP-3. Column chromatography (eluent: PE/EtOAc, 70:1, then 50:1) afforded 65 mg (53%) of target oxime ether as colorless oil. R_f = 0.44 (PE/EtOAc, 9:1, anisaldehyde).^{1}H NMR (300 MHz, $CDCl_3$): δ 0.16 (s, 6H, Me_2Si), 0.93 (s, 9H, *t*-BuSi), 1.14 (t, *J* = 7.6 Hz, 3H, CH_3), 1.22 (s, 9H, *t*-Bu), 2.04-2.22 (m, 2H, $C\underline{H}_2$−CH), 2.32 (q, *J* = 7.6 Hz, 2H, CH_2−C=O), 4.17 (t, *J* = 6.4 Hz, 2H, CH_2−O), 5.45 (app dt, *J* = 7.6, 5.3 Hz, 1H, CH−O), 7.49 (d, *J* = 4.8 Hz, 1H, H−C=N). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): -5.4 ($\underline{Me}_2Si$), 9.1 ($\underline{Me}CH_2$), 18.2 ($Me_3\underline{C}$−Si), 26.0 ($\underline{Me}_3CSi$), 27.0 ($\underline{Me}_3CC(O)$), 27.5 ($\underline{C}H_2$−C=O), 31.2 ($\underline{C}H_2$−CH), 38.8 ($Me_3\underline{C}$), 59.8 (CH_2–O), 67.8 (CH−O), 152.2 (CH=N), 174.2 (C=O), 177.3 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{18}H_{35}NO_5Si$ + H^+]: 374.2357, found: 374.2353.

2,2,3,3,8-Pentamethyl-10-oxo-4,9-dioxa-5-aza-3-siladodec-5-en-7-yl pivalate 2r. Oxime ether **2r** was obtained from nitro compound **1r** (57 mg, 0.33 mmol), pivaloyl chloride (49 µL, 47 mg, 0.39 mmol) and TBSOTf (0.13 mL, 0.15 g, 0.55 mmol) according to GP-3. Column

chromatography (eluent: PE, then PE/EtOAc 50:1) afforded 84 mg (69%) of target oxime ether as colorless oil. dr ≈ 1.2:1. Relative configuration of diastereomers was not determined. R_f = 0.38 (PE/EtOAc, 9:1, anisaldehyde). Major isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.16 (s, 3H, MeSi), 0.17 (s, 3H, MeSi), 0.93 (s, 9H, *t*-BuSi), 1.14 (t, *J* = 7.6 Hz, CH_2CH_3), 1.22 (s, 9H, *t*-Bu), 1.27 (d, *J* = 5.9 Hz, 3H, CH_3–CH), 2.32 (q, *J* = 7.6 Hz, 2H, CH_2–C=O), 5.23 (app quint, *J* = 6.3 Hz, 1H, CH_3CH–O), 5.41-5.47 (m, CH–OPiv), 7.43 (d, *J* = 5.5 Hz, 1H, CH=N). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): -5.4 (Me_2Si), 9.0 ($MeCH_2$), 16.1 (MeCH), 18.2 (Me_3C–Si), 26.0 (Me_3CSi), 27.1 ($Me_3CC(O)$), 27.6 (CH_2–C=O), 38.9 (Me_3C), 69.2 (CH_2–O), 71.7 (CH–OPiv), 149.9 (CH=N), 173.3 (C=O), 176.9 (C=O). Minor isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.16 (s, 3H, MeSi), 0.17 (s, 3H, MeSi), 0.94 (s, 9H, *t*-BuSi), 1.14 (t, *J* = 7.6 Hz, CH_2CH_3), 1.21 (s, 9H, *t*-Bu), 1.27 (d, *J* = 5.9 Hz, 3H, CH_3–CH), 2.32 (q, *J* = 7.6 Hz, 2H, CH_2–C=O), 5.29 (qd, *J* = 6.5, 3.7 Hz, 1H, CH_3CH–O), 5.41-5.47 (m, CH–OPiv), 7.47 (d, *J* = 5.9 Hz, 1H, CH=N). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): -5.4 (Me_2Si), 9.1 ($MeCH_2$), 15.4 (MeCH), 18.2 (Me_3C–Si), 26.0 (Me_3CSi), 27.1 ($Me_3CC(O)$), 27.6 (CH_2–C=O), 38.9 (Me_3C), 69.5 (CH_2–O), 72.0 (CH–OPiv), 149.7 (CH=N), 173.4 (C=O), 176.9 (C=O). HRMS (ESI): *m/z* calcd. for $[C_{18}H_{35}NO_5Si + Na^+]$: 396.2177, found: 396.2168.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)cyclopentyl pivalate 2s.
1. Oxime ether **2s** was obtained from nitro compound **1s** (57 mg, 0.49 mmol), pivaloyl chloride (73 µL, 71 mg, 0.59 mmol) and TBSOTf (0.19 mL, 0.22 g, 0.83 mmol) according to GP-3. Column chromatography (eluent: PE/EtOAc, 50:1) afforded 64 mg (42%) of target oxime ether as slightly yellow oil.
2. Oxime ether **2s** was obtained from nitro compound **1s** (52 mg, 0.45 mmol), pivaloyl chloride (67 µL, 65 mg, 0.54 mmol) and TBSOTf (0.17 mL, 0.20 g, 0.76 mmol) according to GP-4. Column chromatography (eluent: PE/EtOAc, 50:1) afforded 120 mg (86%) of target oxime ether as slightly yellow oil. R_f = 0.52 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.15 (s, 6H, Me_2Si), 0.92 (s, 9H, *t*-BuSi), 1.19 (s, 9H, *t*-Bu), 1.69-1.93 (m, 3H) and 1.97-2.06 (m, 1H) (2×CH_2), 2.41-2.65 (m, 2H, CH_2), 5.52 (t, *J* = 5.3 Hz, 1H, CH–O). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.3 and -5.2 (Me_2Si), 18.2 (Si–CMe_3), 20.6 (CH_2), 26.1 (Si–CMe_3), 27.1 (Me_3CCO), 26.3 (CH_2), 32.1 (CH_2), 38.7 (Me_3C), 73.4 (CH–O), 166.5 (C=N), 177.5 (C=O). HRMS (ESI): *m/z* calcd. for $[C_{16}H_{31}NO_3Si + H^+]$: 314.2146, found: 314.2146.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)cyclohexyl pivalate 2t. Oxime ether **2t** was obtained from nitro compound **1t** (47 mg, 0.36 mmol), pivaloyl chloride (54 µL, 52 mg, 0.43 mmol) and TBSOTf (0.14 mL, 0.16 g, 0.61 mmol) according to GP-4 with following change: an excess of NEt_3 (0.31 mL, 0.22 g, 2.2 mmol) was used at the silylation stage. Column chromatography (eluent: PE, then PE/EtOAc, 70:1) afforded 82 mg (69%) of target oxime ether as colorless oil, which solidified upon storage in a fridge. R_f = 0.58 (PE/EtOAc, 9:1, anisaldehyde). mp = 62-64 °C (PE/EtOAc, 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.17 (s, 6H, Me_2Si), 0.93 (s, 9H, *t*-BuSi), 1.23 (s, 9H, *t*-Bu), 1.44-1.64 (m, 2H) and 1.67-1.80 (m, 3H) and 1.91-2.03 (m, 1H) (3×CH_2), 2.41 (ddd, J = 14.2, 10.3, 5.0, 1H, CH_{2a}–C=N), 2.85 (app dt, *J* = 13.9, 4.9 Hz, 1H, CH_{2b}–C=N), 5.32 (dd, *J* = 5.7, 2.8 Hz, 1H, CH–O). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.3 (Me_2Si), 18.2 (Me_3C–Si), 21.5 (CH_2), 22.7 (CH_2), 25.2 (CH_2), 26.1 (*t*-BuSi), 27.2 (Me_3CCO), 32.2 (CH_2), 38.9 (Me_3C), 71.5 (CH–O), 160.8 (C=N), 177.0 (C=O). HRMS (ESI): *m/z* calcd. for $[C_{17}H_{33}NO_3Si + H^+]$: 328.2302, found: 328.2299.

3-(((*tert*-Butyldimethylsilyl)oxy)imino)-5-(1,3-dioxolan-2-yl)-4-phenylpentan-2-yl pivalate 2u. Oxime ether **2u** was obtained from nitro compound **1u** (77 mg, 0.29 mmol), pivaloyl chloride (43 µL, 42 mg, 0.35 mmol) and TBSOTf (0.11 mL, 0.13 g, 0.49 mmol) according to GP-5 with following change: DBU (13 µL, 13 mg, 0.09 mmol, 0.3 equiv.) was added before TBSOTf at the silylation stage. Column chromatography (eluent: PE/EtOAc, 70:1, then 50:1) afforded 29 mg of enoxime **7u** as orange oil, 43 mg of target oxime ether **2u** (ratio major/minor = 7:1) as yellow oil and 13 mg of enoxime/major isomer of **2u**/minor isomer of **2u** mixture (ratio enoxime/major/minor = 1:1.6:1.3) as yellow oil. Relative configuration of diastereomers was not determined. Total yield of major isomer of **2u**: 42 mg (32%). Total yield of minor isomer of **2u**: 11 mg (8%). Total yield of enoxime **7u**: 32 mg (30%). Major isomer: R_f = 0.35 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.18 (s, 3H, MeSi), 0.19 (s, 3H, MeSi), 0.96 (s, 9H, *t*-BuSi), 1.19 (s, 9H, *t*-BuC), 1.17-1.20 (m, 3H, CH_3–CHOPiv), 2.32 (ddd, *J* = 13.5, 7.4, 5.3 Hz, 1H, CH_{2a}), 2.45 (ddd, *J* = 13.5, 8.0, 4.0 Hz, 1H, CH_{2b}), 3.78-3.84 and 3.91-3.98 (m, 4H, OCH_2CH_2O), 4.60 (app t, *J* = 7.8 Hz, 1H, CHPh), 4.82 (app t, *J* = 5.1 Hz, 1H, $CH(OCH_2)_2$), 5.43 (q, *J* = 6.4 Hz, 1H, CH–OPiv), 7.18-7.35 (m, 5H, Ph). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.2 (Me_2Si), 18.0 (Me_3C–Si), 18.2 (MeCH), 26.0 (Me_3CSi), 27.0 ($Me_3CC(O)$), 35.4 (CH_2), 38.7 (Me_3C), 39.6 (CHPh), 64.7 and 64.8 (OCH_2CH_2O), 69.6 (CH–O), 103.0 ($CH(OCH_2)_2$), 126.6 (CH_{Ph}), 128.2 (CH_{Ph}), 128.4 (CH_{Ph}), 139.8 (C_{Ph}), 161.9 (C=N), 177.4 (C=O). HRMS (ESI): *m/z* calcd. for $[C_{25}H_{41}NO_5Si + Na^+]$: 486.2646, found: 486.2638. Minor isomer (characteristic signals): ^{1}H NMR (300 MHz, COSY, $CDCl_3$): 1.33 (d, *J* = 6.5 Hz, 3H, CH_3–CHOPiv), 4.41 (app t, *J* = 7.8 Hz, 1H, CHPh), 5.57 (q, *J* = 6.5 Hz, 1H, CH–OPiv). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 17.8 (Me–CHOPiv), 39.6 (CHPh), 69.8 (CH–O).

5-(1,3-Dioxolan-2-yl)-4-phenylpent-1-en-3-one O-(*tert*-butyldimethylsilyl) oxime 7u. Obtained during the synthesis of oxime ether **2u**. Orange oil. R_f = 0.42 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.16 (s, 3H, MeSi), 0.18 (s, 3H, MeSi), 0.93 (s, 9H, *t*-BuSi), 2.36 (dt, *J* = 13.7, 5.9 Hz, CH_{2a}), 2.53 (ddd, *J* = 13.7, 9.3, 4.2 Hz, 1H, CH_{2b}), 3.80-3.88 (m) and 3.90-4.02 (m) (total 4H, OCH_2CH_2O), 4.80-4.87 (m, 2H, CHPh and $CH(OCH_2)_2$), 5.31 (d, *J* = 11.2 Hz, 1H, $=CH_{2cis}$), 5.68 (d, 1H, *J* = 17.7 Hz, $=CH_{2trans}$), 6.31 (dd, *J* = 17.7, 11.2 Hz, 1H, =CH), 7.17-7.31 (m, 5H, Ph). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.3 (MeSi), -5.2 (MeSi), 18.0 (Me_3C–Si), 26.0 (Me_3C), 35.0 (CH_2), 37.3 (CHPh), 64.8 (2×CH_2–O), 103.2 ($CH(OCH_2)_2$), 119.0 (=CH_2), 126.3 (CH_{Ph}), 127.7 (CH_{Ph}), 128.2 (CH_{Ph}), 132.5 (=CH), 140.5 (C_{Ph}), 162.1 (C=N). HRMS (ESI): *m/z* calcd. for $[C_{20}H_{31}NO_3Si + H^+]$: 362.2146, found: 362.2139.

Isopropyl 4-(((*tert*-butyldimethylsilyl)oxy)imino)-3-methyl-5-(pivaloyloxy)hexanoate 2v. Oxime ether **2v** was obtained from nitro compound **1v** (73 mg, 0.34 mmol), pivaloyl chloride (51 µL, 49 mg, 0.41 mmol) and TBSOTf (0.13 mL, 0.13 g, 0.58 mmol) according to GP-5. Column chromatography (eluent: PE/EtOAc, 70:1, then 50:1) afforded 141 mg (43%) of target oxime ester **2v** (diastereomeric mixture, dr ≈ 1.6:1, relative configuration was not determined) and 20 mg (18%) of enoxime **7v**.**2v**: Colorless oil. R_f = 0.50 (PE/EtOAc, 9:1, anisaldehyde). Major isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.16 (s, 6H, Me_2Si), 0.95 (s, 9H, *t*-BuSi), 1.21-1.27 (m, 18H, *t*-Bu, Me_2CH and CH_3CH), 1.36 (d, *J* = 6.4 Hz, 3H, CH_3–CHOPiv), 2.55 (dd, *J* = 16.0, 8.9 Hz, 1H, CH_{2a}), 2.79 (dd, *J* = 16.0, 6.0 Hz, 1H, CH_{2b}), 3.09 (app sext, *J* = 6.8 Hz, 1H, CH–CH_3), 5.00 (hept, *J* = 6.3 Hz, 1H, $OCH(CH_3)_2$), 5.51 (q, *J* = 6.4 Hz, 1H, CH–OPiv). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.4 (Me_2Si), 16.1 (CHMe), 17.2 (Me–CHOPiv), 18.0 (Me_3C–Si), 21.78 and 21.81 (2×CH_3), 26.0 (Me_3CSi), 27.0 ($Me_3CC(O)$), 30.9 (CHC=N), 38.2 (CH_2), 38.8 (Me_3C), 67.6 (Me_2CH–O), 71.3 (CH–O), 163.5 (C=N), 171.9 (CO_2i-Pr), 177.5 (C=O). Minor isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.16 (s, 6H, Me_2Si), 0.95 (s, 9H, *t*-BuSi), 1.21-1.27 (m, 18H, *t*-Bu, Me_2CH and CH_3CH), 1.36 (d, *J* = 6.4 Hz, 3H, CH_3–CHOPiv), 2.60-2.63 (m, 2H, CH_2), 3.23 (app sext, *J* = 7.1 Hz, 1H, CH–CH_3), 5.00 (hept, *J* = 6.3 Hz, 1H, $OCH(CH_3)_2$), 5.47 (q, *J* = 6.3 Hz, 1H, CH–OPiv). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.4 (Me_2Si), 16.3 (CHMe), 17.5 (Me–CHOPiv), 18.0 (Me_3C–Si), 21.78 and 21.81 (2×CH_3), 26.0 (Me_3CSi), 27.0 ($Me_3CC(O)$), 30.2 (CHC=N), 38.0 (CH_2), 38.8 (Me_3C), 67.7 (Me_2CH–O), 70.4 (CH–O), 163.4 (C=N), 171.8 (CO_2i-Pr), 177.4 (C=O). HRMS (ESI): *m/z* calcd. for $[C_{21}H_{41}NO_5Si + Na^+]$: 438.2646, found: 438.2652.

Isopropyl 4-(((*tert*-butyldimethylsilyl)oxy)imino)-3-methylhex-5-enoate 7v. Obtained during the synthesis of oxime ether **2v**. Slightly yellow oil. R_f = 0.54 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz,

$CDCl_3$): δ 0.19 (s, 6H, Me_2Si), 0.97 (s, 9H, *t*-BuSi), 1.20-1.25 (m, 9H, 3×CH_3), 2.56 (dd, *J* = 15.7, 7.6 Hz, 1H, CH_{2a}), 2.83 (dd, *J* = 15.7, 7.3 Hz, 1H, CH_{2b}), 3.48 (app sext, *J* = 7.3 Hz, 1H, C<u>H</u>Me), 4.99 (hept, *J* = 6.3 Hz, 1H, OC<u>H</u>$(CH_3)_2$), 5.35 (d, *J* = 11.2 Hz, 1H, =CH_{2cis}), 5.68 (d, 1H, *J* = 17.7 Hz, =CH_{2trans}), 6.33 (dd, *J* = 17.7, 11.2 Hz, 1H, =CH). ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ -5.3 (<u>Me</u>$_2$Si), 16.5 (CH<u>Me</u>), 18.0 (Me_3<u>C</u>−Si), 21.8 (2×CH_3), 26.1 ($\underline{Me}_3$C), 28.8 (<u>C</u>HMe_2), 38.3 (CH_2), 67.6 (Me_2<u>C</u>H−O), 118.0 (=CH_2), 133.0 (=CH), 163.6 (C=N), 171.9 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{16}H_{31}NO_3Si$ + H^+]: 314.2146, found: 314.2154.

***rel*-(7*S*,9*R*)-8-(((*tert*-Butyldimethylsilyl)oxy)imino)-9-(4-methoxyphenyl)-1,4-dioxaspiro[4.5]decan-7-yl pivalate 2w.** Oxime ether **2w** was obtained from nitro compound **1w** (89 mg, 0.30 mmol), pivaloyl chloride (45 µL, 43 mg, 0.36 mmol) and TBSOTf (0.12 mL, 0.14 g, 0.52 mmol) according to GP-5 with following change: silylation stage was prolonged to 4 h. Column chromatography (eluent: PE/EtOAc, 9:1) afforded 115 mg (76%) of target oxime ether as slightly yellow oil. Relative configuration was assigned based on coupling constants for CH(7) and CH(9) and NOESY specta assuming a chair-like conformation. R_f = 0.51 (PE/EtOAc, 3:1, UV, anisaldehyde). Two conformers in a ratio 4:1.Major conformer: ^{1}H NMR (300 MHz, COSY, NOESY, $CDCl_3$): δ 0.00 (s, 3H, MeSi), 0.07 (s, 3H, MeSi), 0.71 (s, 9H, *t*-BuSi), 1.21 (s, 9H, *t*-Bu), 2.10 (dd, *J* = 13.5, 6.2 Hz, 1H, CH_{2ax}(10)), 2.26-2.37 (m, 3H, CH_{2eq}(10) and CH_2(6)), 3.78 (s, 3H, OMe), 3.86-3.97 (m, 4H, OCH_2CH_2O), 4.29 (dd, *J* = 12.1, 6.5 Hz, 1H, $CH(9)_{ax}$Ar), 5.65 (dd, *J* = 4.7, 2.6 Hz, 1H, CH_{eq}(7)−OPiv), 6.80 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.19 (d, *J* = 8.7 Hz, 2H, CH_{Ar}). ^{1}H NMR (300 MHz, CD_3CN): δ 0.00 (s, 3H, MeSi), 0.07 (s, 3H, MeSi), 0.71 (s, 9H, *t*-BuSi), 1.15 (s, 9H, *t*-Bu), 2.16-2.35 (m, *4*H, CH_2(6) and CH_2(10)), 3.73 (s, 3H, OMe), 3.82-3.98 (m, 4H, OCH_2CH_2O), 4.26 (dd, *J* = 11.1, 7.7 Hz, 1H, CH_{ax}(9)Ar), 5.56 (dd, *J* = 5.8, 1.9 Hz, 1H, CH_{eq}(7)−OPiv), 6.81 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.17 (d, *J* = 8.7 Hz, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.4 ($\underline{Me}_2$Si), 17.8 (Me_3<u>C</u>−Si), 25.7 ($\underline{Me}_3$CSi), 27.1 ($\underline{Me}_3$CC(O)), 38.6 (CH(9)−Ar), 38.8 (Me_3<u>C</u>), 39.2 (CH_2(10)), 41.4 (CH_2(6)), 55.3 (OMe), 64.1 and 64.4 (OCH_2CH_2O), 71.7 (CH(7)–O), 107.5 (<u>C</u>H$(OCH_2)_2$), 113.6 (CH_{Ar}), 128.0 (CH_{Ar}), 134.2 (C_{Ar}), 157.9 (C_{Ar}), 159.8 (C=N), 177.0 (C=O). Minor conformer: ^{1}H NMR (300 MHz, COSY, NOESY, $CDCl_3$): δ 0.03 (s, 3H, MeSi), 0.12 (s, 3H, MeSi), 0.78 (s, 9H, *t*-BuSi), 1.28 (s, 9H, *t*-Bu), 2.06-2.17 (m, 2H) and 2.24-2.37 (m, 2H) (CH_2(6) and CH_2(10)), 3.78 (s, 3H, OMe), 3.86-3.97 (m, 4H, OCH_2CH_2O), 4.79 (app t, *J* = 5.9 Hz, 1H, $CH(9)_{eq}$Ar), 5.68 (dd, *J* = 12.2, 6.2 Hz, 1H, CH_{ax}(7)−OPiv), 6.84 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.22 (d, *J* = 8.7 Hz, 2H, CH_{Ar}). Characteristic NOESY interactions: CH(7)−O / CH_{Ar}. ^{1}H NMR (300 MHz, CD_3CN): δ 0.01 (s, 3H, MeSi), 0.09 (s, 3H, MeSi), 0.77 (s, 9H, *t*-BuSi), 1.23 (s, 9H, *t*-Bu), 2.01-2.35 (m, 4H, CH_2(6) and CH_2(10)), 3.75 (s, 3H, OMe), 3.82-3.98 (m, 4H, OCH_2CH_2O), 4.67 (app t, *J* = 6.5 Hz, 1H, CH_{eq}(9)Ar), 5.62 (dd, *J* = 11.8, 6.6 Hz, 1H, CH_{ax}(7)−OPiv), 6.84 (d, *J* = 8.8 Hz, 2H, CH_{Ar}), 7.23 (d, *J* = 8.8 Hz, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$, characteristic signals): δ -5.3 (MeSi), 17.9 (Me_3<u>C</u>−Si), 25.9 ($\underline{Me}_3$CSi), 27.3 ($\underline{Me}_3$CC(O)), 36.1 (CH(9)−Ar), 38.1 and 40.8 (CH_2(6) and CH_2(10)), 55.2 (OMe), 64.2 and 64.5 (OCH_2CH_2O), 68.0 (CH(7)–O), 107.8 (<u>C</u>H$(OCH_2)_2$), 113.7 (CH_{Ar}), 128.0 (CH_{Ar}). HRMS (ESI): *m/z* calcd. for [$C_{26}H_{41}NO_6Si$ + H^+]: 492.2776, found: 492.2779.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)-3-(4-methoxyphenyl)propyl acetate 2ba. Oxime ether **2ba** was obtained from nitro compound **1b** (168 mg, 0.86 mmol), acetyl chloride (74 µL, 81 mg, 1.04 mmol) and TBSOTf (0.34 mL, 0.39 g, 1.48 mmol) according to GP-3. Column chromatography (eluent: PE/EtOAc, 20:1) afforded 238 mg (79%) of target oxime ether as slightly yellow oil. R_f = 0.44 (PE/EtOAc, 9:1, UV, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.21 (s, 6H, Me_2Si), 0.97 (s, 9H, *t*-BuSi), 2.04 (s, 3H, MeC(O)), 3.74 (s, 2H, CH_2−Ar), 3.80 (s, 3H, OCH_3), 4.60 (s, 2H, CH_2−O), 6.83 (d, *J* = 8.6 Hz, 2H, CH_{Ar}), 7.14 (d, *J* = 8.6 Hz, CH_{Ar}). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.2 ($\underline{Me}_2$Si), 18.1 (Me_3<u>C</u>−Si), 20.7 (<u>Me</u>C(O)), 26.0 ($\underline{Me}_3$CSi), 31.1 (CH_2), 55.2 (MeO), 63.9 (CH−O), 114.0 (CH_{Ar}), 128.2 (C_{Ar}), 130.1 (CH_{Ar}), 158.2 and 158.3 ($\underline{C}_{Ar}$–OMe and C=N), 170.3 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{18}H_{29}NO_4Si$ + H^+]: 352.1938, found: 352.1939.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)cyclopentyl acetate 2sa. Oxime ether **2sa** was obtained from nitro compound **1s** (41 mg, 0.36 mmol), acetyl chloride (30 µL, 34 mg, 0.43 mmol) and TBSOTf (0.14 mL, 0.16 g, 0.61 mmol) according to GP-4. Column chromatography (eluent: PE, then PE/EtOAc, 50:1) afforded 80 mg (82%) of target oxime ether as colorless oil. R_f = 0.44 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.16 (s, 3H, MeSi), 0.17 (s, 3H, MeSi), 0.93 (s, 9H, *t*-BuSi), 1.72-2.06 (m, 4H, 2×CH_2), 2.06 (s, 3H, CH_3CO), 2.47 (ddd, *J* = 19.2, 8.1, 6.3 Hz, 1H, CH_{2a}), 2.54-2.65 (m, 1H, CH_{2b}), 5.54 (t, *J* = 5.0 Hz, 1H, CH−O). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.29 (MeSi), -5.27 (MeSi), 18.1 (Me_3<u>C</u>Si), 20.6 (CH_2), 21.1 (<u>Me</u>CO), 26.0 ($\underline{Me}_3$C), 26.3 (CH_2), 32.2 (CH_2), 73.8 (CH−O), 166.6 (C=N), 170.1 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{13}H_{25}NO_3Si$ + H^+]: 272.1680, found: 272.1676.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)cyclopentyl 2-chloroacetate 2sb. Oxime ether **2sb** was obtained from nitro compound **1s** (40 mg, 0.35 mmol), chloroacetyl chloride (33 µL, 47 mg, 0.42 mmol) and TBSOTf (0.13 mL, 0.15 g, 0.57 mmol) according to GP-4. Column chromatography (eluent: PE, then PE/EtOAc, 50:1) afforded 80 mg (76%) of target oxime ether as slightly yellow oil. R_f = 0.41 (PE/EtOAc, 9:1, UV, anisaldehyde). *E*/*Z* ≈ 1:1. *E*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.15 (s, 3H, MeSi), 0.16 (s, 3H, MeSi), 0.93 (s, 9H, *t*-BuSi), 1.69-2.16 (m, 4H, 2×CH_2), 2.37-2.67 (m, 2H, CH_2), 4.06 (s, 2H, CH_2Cl), 5.62 (t, *J* = 4.5 Hz, 1H, CH−O).^{13}C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ -5.3 ($\underline{Me}_2$Si), 18.0 (Me_3<u>C</u>Si), 20.7 (CH_2), 26.0 ($\underline{Me}_3$C), 26.2 ($\underline{C}H_2$–C=N), 32.1 (CH_2), 40.9 (CH_2Cl), 75.6 (CH−O), 165.8 and 166.0 (C=N and C=O). *Z*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$,): δ 0.15 (s, 3H, MeSi), 0.17 (s, 3H, MeSi), 0.91 (s, 9H, t-BuSi), 1.69-2.16 (m, 4H, 2×CH_2), 2.37-2.67 (m, 2H, CH_2), 4.02 (s, 2H, CH_2Cl), 5.98 (dd, *J* = 6.7, 3.9 Hz 1H, CH−O). ^{13}C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ -5.3 ($\underline{Me}_2$Si), 18.1 (Me_3<u>C</u>Si), 22.2 (CH_2), 25.9 ($\underline{Me}_3$C), 29.5 ($\underline{C}H_2$–C=N), 32.3 (CH_2), 40.8 (CH_2Cl), 70.2 (CH−O), 165.0 and 166.4 (C=N and C=O). HRMS (ESI): *m/z* calcd. for [$C_{13}H_{24}ClNO_3Si$ + H^+]: 306.1287, found: 306.1290.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)cyclopentyl isobutyrate 2sc. Oxime ether **2sc** was obtained from nitro compound **1s** (43 mg, 0.37 mmol), isobutyryl chloride (47 µL, 47 mg, 0.45 mmol) and TBSOTf (0.14 mL, 0.17 g, 0.63 mmol) according to GP-4. Column chromatography (eluent: PE, then PE/EtOAc, 50:1) afforded 95 mg (86%) of target oxime ether as colorless oil. R_f = 0.49 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.148 (s, 3H, MeSi), 0.154 (s, 3H, MeSi), 0.92 (s, 9H, *t*-BuSi), 1.16 (d, *J* = 7.0 Hz, 6H, C<u>H</u>$\underline{Me}_2$), 1.69-1.94 (m, 3H) and 1.98-2.06 (m, 1H) (2×CH_2), 2.41-2.65 (m, 3H, CH_2 and C<u>H</u>Me_2), 5.55 (t, *J* = 5.4 Hz, 1H, CH−O). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.32 (MeSi), -5.28 (MeSi), 18.1 (Me_3<u>C</u>−Si), 18.8 and 18.9 ($\underline{Me}_2$CH), 20.6 (CH_2), 26.0 ($\underline{Me}_3$C), 26.3 (CH_2), 32.2 (CH_2), 34.0 (Me_2<u>C</u>H), 73.4 (CH−O), 166.5 (C=N), 176.1 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{15}H_{29}NO_3Si$ + Na^+]: 322.1806, found: 322.1809.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)cyclopentyl (3r,5r,7r)-adamantane-1-carboxylate 2sd. Oxime ether **2sd** was obtained from nitro compound **1s** (53 mg, 0.46 mmol), adamantanecarbonyl chloride (110 mg, 0.55 mmol) and TBSOTf (0.18 mL, 0.21 g, 0.78 mmol) according to GP-4. Column chromatography (eluent: PE, then PE/EtOAc 90:1) afforded 137 mg (76%) of target oxime ether as colorless oil, which solidified upon storage in a fridge. R_f = 0.53 (PE/EtOAc, 9:1, anisaldehyde).mp = 54-56 °C (PE). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.16 (s, 3H, MeSi), 0.17 (s, 3H, MeSi), 0.94 (s, 9H, *t*-BuSi), 1.67-2.06 (m, 19 H, all CH_{2Ad}, all CH_{Ad}, 2×CH_2), 2.42-2.66 (m, 2H, CH_2), 5.53 (t, *J* = 5.3 Hz, 1H, CH−O). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.3 (MeSi), -5.2 (MeSi), 18.2 (Me_3<u>C</u>−Si), 20.7 (CH_2), 26.1 ($\underline{Me}_3$C), 26.3 (CH_2), 28.0 (CH_{Ad}), 32.2 (CH_2), 36.5 and 38.8 (CH_{2Ad}), 40.7 (C_{Ad}), 73.2 (CH−O), 166.6 (C=N), 176.6 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{22}H_{37}NO_3Si$ + Na^+]: 414.2435, found: 414.2429.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)cyclopentyl benzoate 2se. Oxime ether **2se** was obtained from nitro compound **1s** (44 mg, 0.38 mmol), benzoyl chloride (53 µL, 64 mg, 0.46 mmol) and TBSOTf (0.15

mL, 0.17 g, 0.65 mmol) according to GP-4. Column chromatography (eluent: PE, then PE/EtOAc, 50:1) afforded 98 mg (76%) of target oxime ether as colorless oil. R_f = 0.51 (PE/EtOAc, 9:1, UV, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 3H, MeSi), 0.19 (s, 3H, MeSi), 0.95 (s, 9H, *t*-BuSi), 1.77-1.88 (m, 1H), 1.93-2.08 (m, 2H) and 2.12-2.24 (m, 1H) (2×CH_2), 2.56 (ddd, *J* = 19.3, 8.2, 6.5 Hz, 1H, CH_{2a}), 2.68 (ddd, *J* = 19.3, 8.5, 6.1 Hz, 1H, CH_{2b}), 5.79 (t, *J* = 5.0 Hz, 1H, CH−O) 7.44 (t, *J* = 7.6 Hz, 2H, CH_{Ph}), 7.57 (t, *J* = 7.4 Hz, 1H, CH_{Ph}), 8.06 (d, *J* = 7.1 Hz, 2H, CH_{Ph}). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.3 and -5.2 ($\underline{Me}_2$Si), 18.2 ($Me_3\underline{C}$−Si), 20.8 (CH_2), 26.1 ($\underline{Me}_3$C), 26.4 (CH_2), 32.5 (CH_2), 74.5 (CH−O), 128.3 (CH_{Ph}), 129.7 (CH_{Ph}), 130.4 (C_{Ph}), 132.9 (CH_{Ph}), 165.8 and 166.6 (C=O and C=N). HRMS (ESI): *m/z* calcd. for [$C_{18}H_{27}NO_3Si$ + Na^+]: 356.1652, found: 356.1657.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)cyclopentyl cinnamate 2sf. Oxime ether **2sf** was obtained from nitro compound **1s** (50 mg, 0.43 mmol), cinnamoyl chloride (86 mg, 0.52 mmol) and TBSOTf (0.17 mL, 0.19 g, 0.73 mmol) according to GP-4. Column chromatography (eluent: PE, then PE/EtOAc, 70:1) afforded 98 mg (64%) of target oxime ether as colorless oil. R_f = 0.40 (PE/EtOAc, 9:1, UV, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.17 (s, 3H, MeSi), 0.19 (s, 3H, MeSi), 0.94 (s, 9H, *t*-BuSi), 1.76-2.01 (m, 1H, CH_2), 1.96-2.16 (m, 2H, CH_2), 2.46-2.72 (m, 2H, CH_2), 5.67 (t, *J* = 4.7 Hz, 1H, CH−O), 6.44 (d, *J* = 16.0 Hz, =CH–CO), 7.38-7.40 (m, 3H, CH_{Ph}), 7.51-7.55 (m, 2H, CH_{Ph}), 7.70 (d, *J* = 16.0 Hz, 1H, =C$\underline{H}$–Ph). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ -5.2 (Me_2Si), 18.2 ($Me_3\underline{C}$Si), 20.8 (CH_2), 26.1 ($\underline{Me}_3$C), 26.4 (CH_2), 32.4 (CH_2), 74.1 (CH−O), 118.2 (=$\underline{C}$H–CO), 128.1 (CH_{Ph}), 128.9 (CH_{Ph}), 130.3 (CH_{Ph}), 134.5 (C_{Ph}), 144.9 (=$\underline{C}$H–Ph), 166.1 and 166.8 (C=O and C=N). HRMS (ESI): *m/z* calcd. for [$C_{20}H_{29}NO_3Si$ + H^+]: 360.1989, found: 360.1990.

2-(((*tert*-Butyldimethylsilyl)oxy)imino)cyclopentyl 2-methoxyacetate 2sg. Oxime ether **2sg** was obtained from nitro compound **1s** (72 mg, 0.63 mmol), methoxyacetyl chloride (86 mg, 0.79 mmol) and TBSOTf (0.25 mL, 0.29 g, 1.09 mmol) according to GP-4. Column chromatography (eluent: PE/EtOAc, 20:1, then PE/EtOAc, 10:1) afforded 148 mg (78%) of target oxime ether as colorless oil. R_f = 0.27 (PE/EtOAc, 9:1, anisaldehyde). *E*:*Z*=3:1. *E*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.15 (s, 3H, MeSi), 0.16 (s, 3H, MeSi), 0.92 (s, 9H, *t*-BuSi), 1.69-2.14 (m, 4H, 2×CH_2), 2.36-2.66 (m, 2H, CH_2(5)), 3.46 (s, 3H, OMe), 4.04 (s, 2H, CH_2–O), 5.66 (t, *J* = 4.9 Hz, 1H, CH–O). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.3 (SiMe), 18.1 (Si–$\underline{C}Me_3$), 20.6 (CH_2), 26.0 (Si–C$\underline{Me}_3$), 26.2 ($\underline{C}H_2$–C=N), 32.1 (CH_2), 59.3 (OMe), 69.8 (CH_2–O), 74.2 (CH–O), 166.1 (C=N), 169.5 (C=O). *Z*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.15 (s, 3H, MeSi), 0.16 (s, 3H, MeSi), 0.91 (s, 9H, *t*-BuSi), 1.69-2.14 (m, 4H, 2×CH_2), 2.36-2.66 (m, 2H, CH_2(5)), 3.44 (s, 3H, OMe), 4.00 (s, 2H, CH_2–O), 5.66 (dd, *J* = 6.3, 3.8 Hz, 1H, CH–O). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.3 (SiMe), 18.0 (Si–$\underline{C}Me_3$), 22.2 (CH_2), 25.9 (Si–C$\underline{Me}_3$), 29.6 ($\underline{C}H_2$–C=N), 32.5 (CH_2), 59.3 (OMe), 68.9 (CH–O), 69.7 (CH_2–O), 165.5 (C=N), 169.0 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{14}H_{27}NO_4Si$ + H^+]: 302.1782, found: 302.1776.

(*S*)-((*S*)-2-(*tert*-Butyldimethylsilyloxyimino)cyclopentyl) 1-acetyl-5-oxopyrrolidine-2-carboxylate and (*S*)-((*R*)-2-(*tert*-Butyldimethylsilyloxyimino)cyclopentyl) 1-acetyl-5-oxopyrrolidine-2-carboxylate 2sh. Oxime ether **2sh** was obtained from nitro compound **1s** (45 mg, 0.39 mmol), (*S*)-*N*-acetylpyroglutamoyl chloride (89 mg, 0.47 mmol) and TBSOTf (0.15 mL, 0.18 g, 0.66 mmol) according to GP-4 with the following change: acyl chloride was added in CH_2Cl_2 (0.47 ml) to the mixture of nitrocyclopentane, NaH, *t*-BuOH and 15-crown-5 in CH_2Cl_2 (1.10 mL). Reaction time of acylation step - 2.5 h. Column chromatography (eluent: PE/EtOAc, 7:1, then 4:1) afforded 31 mg (16%) of *S*,*S*-isomer of target oxime ether **2sh** as colorless oil and 83 mg (44%) of *S*,*R*-isomer of target oxime ether **2sh** as white solid. (*S*,*S*)-isomer **2sh**: R_f = 0.16 (PE/EtOAc, 5:1, anisaldehyde). $[a]^{20}_D$ = +6.1 (c = 1.0, MeOH, for *E*/*Z* = 2.5:1). *E*/*Z* = 2.5:1. *E*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.15 (s, 6H, Me_2Si), 0.93 (s, 9H, *t*-BuSi), 1.70-1.82 (m, 1H), 1.88-2.02 (m, 2H), 2.04-2.40 (m, 3H), 2.41-2.67 (m, 3H), 2.55 (s, 3H, MeC(O)), 2.67-2.81 (m, 1H), 4.75 (dd, *J* = 9.4, 2.6 Hz, CH−N), 5.65 (t, *J* = 5.2 Hz, 1H, CH−O). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.2 ($\underline{Me}_2$Si), 18.1 ($Me_3\underline{C}$−Si), 20.4 (CH_2), 21.1 (CH_2), 24.6 (Me), 26.0 ($\underline{Me}_3$C), 26.3 (CH_2), 31.7 (CH_2), 31.8 (CH_2), 57.7 (CH−N), 74.7 (CH−O), 166.2 (C=N), 170.2 ($CH_2-\underline{C}$=O), 171.0 (Me−$\underline{C}$=O), 174.5 (O−C=O). *Z*-isomer (characteristic signals): ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.92 (s, 9H, *t*-BuSi), 4.70 (dd, J= 9.5, 2.7 Hz, CH−N), 5.92 (dd, *J* = 5.4, 2.7 Hz, 1H, CH−O). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.1 ($\underline{Me}_2$Si), 18.1 ($Me_3\underline{C}$−Si), 21.1 (CH_2), 22.2 (CH_2), 26.0 ($\underline{Me}_3$C), 29.5 (CH_2), 31.8 (CH_2), 32.6 (CH_2), 57.8 (CH−N), 69.7 (CH−O), 165.5 (C=N), 170.1 (CH_2−C=O), 171.0 (Me−$\underline{C}$=O), 174.4 (O−C=O). HRMS (ESI): *m/z* calcd. for [$C_{18}H_{30}N_2O_5Si$ + H^+]: 383.1997, found: 383.1995. (*S*,*R*)-isomer **2sh**: R_f = 0.11 (PE/EtOAc, 5:1, anisaldehyde). mp = 74-76°C (PE). $[a]^{20}_D$ = +51.6 (c = 1.0, MeOH, *E*-isomer). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.14 (s, 6H, Me_2Si), 0.91 (s, 9H, *t*-BuSi), 1.68-1.87 (m, 3H), 1.96-2.19 (m, 2H), 2.26-2.60 (m, 3H), 2.51 (s, 3H, CH_3C(O)), 2.63-2.79 (m, 1H), 4.76 (dd, *J* = 9.4, 1.7 Hz, CH−N), 5.53 (t, *J* = 5.1 Hz, 1H, CH−O). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.3 ($\underline{Me}_2$Si), 18.1 ($Me_3\underline{C}$−Si), 20.5 (CH_2), 21.4 (CH_2), 24.5 ($\underline{Me}$C(O)), 26.0 ($\underline{Me}_3$C), 26.2 (CH_2), 31.8 (CH_2), 31.9 (CH_2), 58.2 (CH−N), 75.0 (CH−O), 165.9 (C=N), 169.7 ($CH_2-\underline{C}$=O), 170.8 (Me−$\underline{C}$=O), 174.5 (O−C=O). HRMS (ESI): *m/z* calcd. for [$C_{18}H_{30}N_2O_5Si$ + Na^+]: 405.1816, found: 405.1807. The crystallographic information for compound **2sh** (major isomer) was deposited in the Cambridge Crystallographic Data Centre (CCDC 2061545).

2-(((*tert*-Butyldimethylsilyl)oxy)imino)cyclopentyl methyl carbonate 2si. Oxime ether **2si** was obtained from nitro compound **1s** (51 mg, 0.44 mmol), methyl chloroformate (41 µL, 50 mg, 0.53 mmol) and TBSOTf (0.17 mL, 0.20 g, 0.74 mmol) according to GP-4. Column chromatography (eluent: PE, then PE/EtOAc 50:1) afforded 71 mg (56%) of target oxime ether as colorless oil. R_f = 0.43 (PE/EtOAc, 9:1, anisaldehyde). *E*/*Z* = 1.9:1. *E*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 0.16 (s, 3H, MeSi), 0.17 (s, 3H, MeSi), 0.93 (s, 9H, *t*-BuSi), 1.65-2.12 (m, 4H, CH_2), 2.35-2.66 (m, 2H, CH_2), 3.80 (s, 3H, OMe), 5.43 (t, *J* = 4.4 Hz, 1H, CH−O). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.3 ($\underline{Me}_2$Si), 18.1 ($Me_3\underline{C}$Si), 20.6 (CH_2), 26.1 ($\underline{Me}_3$C), 26.1 ($\underline{C}H_2$–C=N), 32.1 (CH_2), 54.8 (OMe), 77.6 (CH−O), 155.1 (C=O), 166.0 (C=N). *Z*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$,): δ 0.16 (s, 3H, MeSi), 0.17 (s, 3H, MeSi), 0.92 (s, 9H, *t*-BuSi), 1.65-2.12 (m, 4H, CH_2), 2.35-2.66 (m, 2H, CH_2), 3.78 (s, 3H, OMe), 5.82 (dd, *J* =6.8, 3.9 Hz, 1H, CH−O). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ -5.4 ($\underline{Me}_2$Si), 17.9 ($Me_3\underline{C}$Si), 22.0 (CH_2), 25.8 ($\underline{Me}_3$C), 29.4 ($\underline{C}H_2$–C=N), 32.3 (CH_2), 54.7 (OMe), 72.3 (CH−O), 155.0 (C=O), 165.2 (C=N). HRMS (ESI): *m/z* calcd. for [$C_{13}H_{25}NO_4Si$ + Na^+]: 310.1445, found: 310.1439.

2-(((Triisopropylsilyl)oxy)imino)cyclopentyl pivalate 2sj. Oxime ether **2sj** was obtained from nitro compound **1s** (44 mg, 0.38 mmol), pivaloyl chloride (57 µL, 55 mg, 0.46 mmol) and TIPSOTf (0.21 mL, 0.23 g, 0.75 mmol) according to GP-4. Column chromatography (eluent: PE, then PE/EtOAc, 50:1) afforded 120 mg (88%) of target oxime ether as colorless oil. R_f = 0.56 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.08 (d, *J* = 6.8 Hz, 18H, Me_{TIPS}), 1.17-1.24 (m, 3H, CH_{TIPS}), 1.20 (t-Bu), 1.71-1.95 (m, 3H) and 1.98-2.11 (m, 1H) (2×CH_2), 2.44-2.73 (m, 2H, CH_2), 5.53 (t, *J* = 5.2 Hz, 1H, CH−O). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 11.9 ($Me_2\underline{C}$H), 17.9 ($\underline{Me}_2$CH), 20.7 (CH_2), 26.1 (CH_2), 27.1 ($\underline{Me}_3$C), 32.2 (CH_2), 38.7 ($Me_3\underline{C}$), 73.4 (CH−O), 166.3 (C=N), 177.4 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{19}H_{37}NO_3Si$ + H^+]: 356.2615, found: 356.2614.

2-(((Triisopropylsilyl)oxy)imino)cyclopentyl acetate 2sk. Oxime ether **2sk** was obtained from nitro compound **2s** (44 mg, 0.38 mmol), acetyl chloride (32 µL, 35 mg, 0.45 mmol) and TIPSOTf (0.20 mL, 0.22 g, 0.72 mmol) according to GP-4. Column chromatography (eluent: PE, then PE/EtOAc 50:1) afforded 104 mg (87%) of target oxime ether as colorless oil. R_f = 0.51 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07 (d, *J* = 6.7 Hz, 18H, Me_{TIPS}), 1.14-1.26 (m, 3H, CH_{TIPS}), 1.69-2.04 (m, 4H, 2×CH_2), 2.04 (s, 3H, MeCO), 2.42-2.68 (m, 2H, CH_2), 5.56 (t, *J* = 5.1 Hz, 1H, CH−O). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ 11.9 ($Me_2\underline{C}$H), 17.7 ($\underline{Me}_2$CH), 20.6 (CH_2), 21.0 ($\underline{Me}$CO), 26.0

(CH_2), 32.1 (CH_2), 73.7 (CH−O), 166.1 (C=N), 170.1 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{16}H_{31}NO_3Si$ + H^+]: 314.2146, found: 314.2147.

2-(((Triisopropylsilyl)oxy)imino)cyclopentyl 2-methoxyacetate 2sI. Oxime ether **2sI** was obtained from nitro compound **1s** (78 mg, 0.68 mmol), methoxyacetyl chloride (89 mg, 0.82 mmol) and TBSOTf (0.36 mL, 0.39 g, 1.28 mmol) according to GP-4. Column chromatography (eluent: PE/EtOAc, 20:1, then PE/EtOAc, 10:1) afforded 198 mg (85%) of target oxime ether as colorless oil. R_f = 0.31 (PE/EtOAc, 9:1, anisaldehyde). *E*:*Z*=1.2:1. *E*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.03-1.05 (m, 18H, Me_{TIPS}), 1.10-1.24 (m, 3H, CH_{TIPS}), 1.67-2.14 (m, 4H, 2×CH_2), 2.32-2.65 (m, 2H, CH_2), 3.43 (s, 3H, OMe), 4.00 (s, 2H, CH_2–O), 5.66 (t, *J* = 5.4 Hz, 1H, CH–O). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 11.8 (CH_{TIPS}), 17.8 (Me_{TIPS}), 20.6 (CH_2), 26.0 ($\underline{C}H_2$–C=N), 32.0 (CH_2), 59.3 (OMe), 69.8 (CH_2–O), 74.0 (CH–O), 165.7 (C=N), 169.4 (C=O). *Z*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 1.03-1.05 (m, 18H, Me_{TIPS}), 1.10-1.24 (m, 3H, CH_{TIPS}), 1.67-2.14 (m, 4H, 2×CH_2), 2.32-2.65 (m, 2H, CH_2), 3.42 (s, 3H, OMe), 3.98 (s, 2H, CH_2–O), 5.97 (dd, *J* = 6.8, 3.6 Hz, CH–O). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 12.3 (CH_{TIPS}), 17.7 (Me_{TIPS}), 22.2 (CH_2), 29.5 ($\underline{C}H_2$–C=N), 32.6 (CH_2), 59.3 (OMe), 68.8 (CH–O), 69.6 (CH_2–O), 164.7 (C=N), 169.1 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{17}H_{33}NO_4Si$ + H^+]: 344.2252, found: 344.2248.

Detection of nitronate 3d, synthesis of nitroso compound 5d. 2-Nitropropane **1d** was subjected to GP-3 with CD_2Cl_2 as a solvent in the presence of MS 4Å. After addition of pivaloyl chloride reaction mixture was maintained for 0.5 h and then analyzed by NMR. Maintaining sample at r.t. for 3 h showed full decay of nitronate **3d**. ^{1}H NMR (600 MHz, CD_2Cl_2, 203 K): δ 1.30 (s, 9H, *t*-Bu), 1.97 (s, 3H, Me), 2.12 (s, 3H, Me). ^{13}C NMR (150 MHz, HMBC, CD_2Cl_2, 203 K): δ 19.0 ($\underline{Me}$C=N), 19.9 ($\underline{Me}$C=N), 26.8 ($\underline{Me}_3$C), 38.9 ($Me_3\underline{C}$), 128.4 (C=N), 174.3 (C=O).
For IR-monitoring and isolation of nitroso compound **5d**: 2-Nitropropane **1d** (0.45 mL, 5 mmol) was subjected to GP-3 albeit 0.5M soln in CH_2Cl_2 was used. After acylation with pivaloyl chloride the reaction mixture was warmed up to r.t. and maintained for 3 d. Reaction was monitored by *in situ* IR at appropriate times. The reaction mixture was extracted with Et_2O/H_2O (50 mL/30 mL). Organic layer was washed with brine (30 mL), dried over Na_2SO_4 and concentrated (appr. 2 mL) in vacuo. The residue was quickly subjected to column chromatography (eluent: pentane) to give 264 mg (30%) of title compound as a dark blue oil. R_f = 0.73 (PE/CH_2Cl_2, 3:1, UV). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (s, 6H, MeC–N), 1.42 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.6 ($\underline{Me}$C–N), 27.1 ($\underline{Me}_3$C), 39.0 ($Me_3\underline{C}$), 120.2 (O–C–N), 176.6 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{16}H_{30}N_2O_6$ + Na^+] (2M+Na^+): 369.1996, found: 369.1983.

Methyl 4-(hydroxyimino)-5-(pivaloyloxy)pentanoate 6a and **Methyl 4-(hydroxyimino)-3-(pivaloyloxy)pentanoate 6'a.** Oximes **6a** and **6'a** were obtained from nitro compound **1a** (103 mg, 0.64 mmol), pivaloyl chloride (95 µL, 93 mg, 0.76 mmol) and TMSOTf (0.21 mL, 0.24 g, 1.09 mmol) according to GP-6. Crude product was dissolved in MeOH (1.28 mL), NH_4F (49 mg, 1.29 mmol) was added and the reaction mixture was stirred for 20 min at r.t. After that the mixture was diluted with EtOAc (2 mL), evaporated and preadsorbed on Celite®. Column chromatography (eluent: PE/EtOAc, 9:1, then 6:1) afforded 91 mg (55%, **6a/6'a** = 2.5:1 (^{1}H NMR)) of target oximes as colorless oil. R_f = 0.29 (PE/EtOAc, 3:1, UV, anisaldehyde). **6a**: *E*/*Z* = 1.2:1. *E*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 1.21 (s, 9H, *t*-Bu), 2.61-2.71 (m, 4H, CH_2CH_2), 3.69 (s, 3H, OMe), 4.64 (s, 2H, CH_2–O), 9.01 (br s, 1H, OH). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 21.6 ($\underline{C}H_2$C=N), 27.1 ($\underline{Me}_3$C), 29.5 ($\underline{C}H_2CO_2$), 38.9 ($Me_3\underline{C}$), 51.8 (OMe), 64.5 (CH_2–O), 155.3 (C=N), 173.0 ($\underline{C}O_2$Me), 178.0 (C=O). *Z*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$,): δ 1.24 (s, 9H, *t*-Bu), 2.58 (br s, 4H, CH_2CH_2), 3.68 (s, 3H, OMe), 4.98 (s, 2H, CH_2–O), 8.81 (br s, 1H, OH). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 25.7 ($\underline{C}H_2$C=N), 27.1 ($\underline{Me}_3$C), 30.0 ($\underline{C}H_2CO_2$), 38.9 ($Me_3\underline{C}$), 51.8 (OMe), 59.4 (CH_2–O), 155.8 (C=N), 173.1 ($\underline{C}O_2$Me), 177.9 (C=O). **6'a**:*E*/*Z* = 7:1. *E*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 1.19 (s, 9H, *t*-Bu), 1.87 (s, 3H, MeC=N), 2.76-2.79 (m, 2H, CH_2), 3.67 (s, 3H, OMe), 5.70 (t, *J* = 7.0 Hz, 1H, CH–O), 8.81 (br s, 1H, OH). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 10.6 ($\underline{Me}$C=N), 27.0 ($\underline{Me}_3$C), 36.8 ($\underline{C}H_2CO_2$), 38.8 ($Me_3\underline{C}$), 51.9 (OMe), 70.7 (CH–O), 155.0 (C=N), 170.2 ($\underline{C}O_2$Me), 177.2 (C=O). *Z*-isomer (characteristic signals): ^{1}H NMR (300 MHz, COSY, $CDCl_3$,): 1.21 (s, 9H, *t*-Bu), 1.82 (s, 3H, MeC=N), 6.19 (dd, *J* = 9.1, 3.7 Hz, 1H, CH–O). ^{13}C NMR (75 MHz, DEPT, HSQC, HMBC, $CDCl_3$): δ 15.4 ($\underline{Me}$C=N), 66.4 (CH–O). HRMS (ESI): *m/z* calcd. for [$C_{11}H_{19}NO_5$ + H^+]: 246.1336, found: 246.1338.

2-(Hydroxyimino)-3-(4-methoxyphenyl)propyl pivalate 6b.
1. Oxime **6b** was obtained from nitro compound **1b** (77 mg, 0.40 mmol), pivaloyl chloride (59 µL, 57 mg, 0.47 mmol) and TMSOTf (0.13 mL, 0.15 g, 0.67 mmol) according to GP-6. Column chromatography (eluent: PE/EtOAc, 6:1) afforded 64 mg (58%) of target oxime **6b** as white solid.
2. To a stirring solution of *O*-TBS-oxime **2b** (72 mg, 0.18 mmol) in THF (1.83 mL) AcOH (74 µL, 78 mg, 1.30 mmol) and TBAF•$3H_2O$ were added at r.t. under an argon atmosphere. The reaction mixture was stirred for 2 h and transferred into EtOAc (20 mL)/NH_4Cl (sat. aq. solution, 20 mL). The water layer was extracted with EtOAc (10 mL). The combined organic layer was washed with brine (40 mL), dried (Na_2SO_4) and evaporated. Column chromatography (eluent: PE/EtOAc, 4:1) afforded 46 mg (90%) of target oxime **6b** as colorless oil, which solidifies in the fridge. R_f = 0.31 (PE/EtOAc, 5:1, UV, anisaldehyde). mp = 61-63 °C (PE/EtOAc, 20:1). NMR matches previously reported data.[7]

2-(Hydroxyimino)propyl pivalate 6d.
1. Oxime **6d** was obtained from nitro compound **1d** (45 µL mg, 45 mg, 0.50 mmol), pivaloyl chloride (75 µL, 72 mg, 0.60 mmol) and TMSOTf (0.17 mL, 0.20 g, 0.88 mmol) according to GP-6. Column chromatography (eluent: PE/EtOAc, 9:1) afforded 50 mg (58%) of target oxime as colorless oil.
2. Oxime **6d** was obtained from *O*-TBS-oxime **2d** (58 mg, 0.20 mmol) similar to the preparation of **6b** from **2b**. Yield: 29 mg (83%). Colorless oil. R_f = 0.29 (PE/EtOAc, 5:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (s, 9H, *t*-Bu), 1.92 (s, 3H, CH_3), 4.61 (s, 2H, CH−O). ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ 11.5 (CH_3), 27.1 ($\underline{Me}_3$C), 38.9 ($Me_3\underline{C}$), 65.2 (CH−O), 153.9 (C=N), 178.1 (C=O). HRMS (ESI): *m/z* calcd. for [$C_8H_{15}NO_3$ + Na^+]: 196.0944, found: 196.0949.

2-(Hydroxyimino)-1-(4-methoxyphenyl)ethyl pivalate 6o. Oxime **6o** was obtained from *O*-TBS-oxime **2o** (75 mg, 0.20 mmol) similar to the preparation of **6b** from **2b**. Yield: 45 mg (86%). Colorless oil. R_f = 0.27 (PE/EtOAc, 5:1, anisaldehyde). *E*/*Z* = 3:1. *E*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 1.24 (s, 9H, *t*-Bu), 3.83 (s, 3H, OMe), 6.31 (d, *J* = 6.0 Hz, 1H, CH−O), 6.92 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.31 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 7.56 (d, *J* = 6.0 Hz, 1H, CH=N), 8.17 (br s, 1H, N−OH). ^{13}C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 27.1 ($\underline{Me}_3$C), 38.9 ($Me_3\underline{C}$), 55.3 (MeO), 72.2 (CH−O), 114.2 (CH_{Ar}), 128.4 (CH_{Ar}), 128.7 (C_{Ar}), 149.4 (CH=N), 159.8 (C_{Ar}), 177.1 (C=O). *Z*-isomer: ^{1}H NMR (300 MHz, COSY, $CDCl_3$): δ 1.25 (s, 9H, *t*-Bu), 3.83 (s, 3H, OMe), 6.90-6.96 (m, 3H, CH−O and CH_{Ar}), 7.37 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 8.36 (br s, 1H, N−OH). ^{13}C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 27.1 ($\underline{Me}_3$C), 38.8 ($Me_3\underline{C}$), 55.3 (MeO), 68.2 (CH−O), 114.1 (CH_{Ar}), 128.4 (CH_{Ar}), 128.7 (C_{Ar}), 149.8 (CH=N), 159.8 (C_{Ar}), 177.2 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{14}H_{19}NO_4$ + K^+]: 304.0946, found: 304.0932.

2-(Hydroxyamino)-3-(4-methoxyphenyl)propyl pivalate 8.
1. To a stirred solution of **2b** (73 mg, 0.19 mmol) in AcOH (0.93 mL) $NaBH_3CN$ (47 mg, 0.75 mmol) was added at r.t. under an argon atmosphere. The reaction mixture was stirred for 4 h and transferred into EtOAc (25 mL). The organic layer was washed with $NaHCO_3$ (sat. aq. solution, 2×10 mL), brine (10 mL), dried (Na_2SO_4) and evaporated. Column chromatography (eluent: PE/EtOAc, 2:1) afforded 39 mg (75%) of target hydroxylamine as colorless oil.
2. To a stirred solution of **6b** (61 mg, 0.22 mmol) in AcOH (1.09 mL) $NaBH_3CN$ (41 mg, 0.66 mmol) was added at r.t. under an argon atmosphere. The reaction mixture was stirred for 1 h and transferred into EtOAc (25 mL). The organic layer was washed with $NaHCO_3$ (sat. aq.

solution, 2×10 mL), brine (10 mL), dried (Na_2SO_4) and evaporated. Column chromatography (eluent: PE/EtOAc, 2:1) afforded 46 mg (76%) of target hydroxylamine as colorless oil. R_f = 0.33 (PE/EtOAc, 2:1, UV, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (s, 9H, *t*-Bu), 2.69 (dd, *J* = 13.8, 6.5 Hz, 1H, CH_{2a}–Ar), 2.79 (dd, *J* = 13.8, 8.0 Hz, 1H, CH_{2b}–Ar), 3.19-3.27 (m, 1H, CH–N), 3.81 (s, 3H, OMe), 4.11 (dd, *J* = 11.4, 5.7 Hz, 1H, CH_{2a}–O), 4.32 (dd, *J* = 11.4, 3.9 Hz, 1H, CH_{2b}–O), 5.51 (br s, 2H, NHOH), 6.87 (d, *J* = 8.5 Hz, 2H, CH_{Ar}), 7.14 (d, *J* = 8.5 Hz, CH_{Ar}). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ 27.3 ($\underline{Me}_3C$), 33.9 (CH_2Ar), 39.0 ($Me_3\underline{C}$), 55.3 (MeO), 62.4 (CH−N), 62.7 (CH_2−O), 114.2 (CH_{Ar}), 129.6 (C_{Ar}), 130.2 (CH_{Ar}), 158.4 (C_{Ar}), 179.0 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{15}H_{23}NO_4$ + H^+]: 282.1696, found: 282.1700.

1-Hydroxy-3-(4-methoxyphenyl)propan-2-one oxime 9. Oxime ether **2ba** (64 mg, 0.18 mmol) was dissolved in a solution of NH_3 in MeOH (7M, 1.00 mL). The reaction mixture was stirred for 4 d at r.t. and then evaporated. Crystallization of the residue from PE/EtOAc (10:1) afforded 20 mg of target oxime as a white solid. Recrystallization of mother liquor afforded additional 6 mg of product. Total yield: 26 mg (72%). mp = 95-97 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.72 (s, 2H, CH_2Ar), 3.81 (s, 3H, OMe), 4.16 (s, 2H, $C\underline{H}_2OH$), 6.86 (d, *J* = 8.5 Hz, 2H, CH_{Ar}), 7.19 (d, *J* = 8.5 Hz, 2H, CH_{Ar}). ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.59 (s, 2H, CH_2Ar), 3.71 (s, 3H, OMe), 3.84 (s, 2H, $C\underline{H}_2OH$), 6.83 (d, *J* = 8.3 Hz, 2H, CH_{Ar}), 7.15 (d, *J* = 8.3 Hz, 2H, CH_{Ar}), 8.31 (s, 2H, OH and NOH). ^{13}C NMR (75 MHz, DEPT, HSQC, DMSO-d_6): δ 29.8 ($C\underline{H}_2Ar$), 55.4 (OMe), 61.4 (CH_2OH), 114.2 (CH_{Ar}), 129.3 (C_{Ar}), 130.4 (CH_{Ar}), 157.8 and 158.8 (C=N and $\underline{C}_{Ar}$–OMe). HRMS (ESI): *m/z* calcd. for [$C_{10}H_{13}NO_3$ + H^+]: 196.0968, found: 196.0971.

***N*-(1-Hydroxy-3-(4-methoxyphenyl)propan-2-yl)acetamide 10.** To a solution of oxime **2ba** (61 mg, 0.17 mmol) in MeOH (0.43 mL) Raney nickel (ca. 0.06 g, 40% slurry in H_2O, washed with MeOH) in MeOH (0.43 mL) and NH_4F (33 mg, 0.87 mmol) were added. The resulting mixture was placed in a steel autoclave, which was flushed and filled with H_2 to a pressure of 30 bar, and then stirred at 55°C for 4 h. After cooling to r.t., the autoclave was slowly depressurized. The reaction mixture was filtered through SiO_2 and the catalyst was washed with MeOH (10 mL). The filtrate was concentrated under reduced pressure. Then a solution of crude amine and DMAP (2 mg, 0.02 mmol) in toluene (0.35 mL) was heated at 100 °C (oil bath) for 4 h. The reaction mixture was evaporated, preadsorbed on Celite® and subjected to column chromatography on silica gel (eluent: PE/EtOAc, 1:1, then MeOH) to give 28 mg (75%) of target amide as slightly yellow oil. The oil was triturated with PE to give white solid. R_f = 0.67 (MeOH, UV, anisaldehyde). mp = 98-101 °C. (Lit.[23] 98-104 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.99 (s, 3H, MeC(O)), 2.29 (br s, 1H, OH), 2.83 (d, *J* = 7.2 Hz, 2H, CH_2Ar), 3.59-3.73 (m, 2H, CH_2–O), 3.82 (s, 3H, OMe), 4.09-4.17 (m, 1H, CH–N), 5.71 (br s, 1H, NH), 6.87 (d, *J* = 8.5 Hz, 2H, CH_{Ar}), 7.15 (d, *J* = 8.5 Hz, 2H, CH_{Ar}). ^{13}C NMR (75 MHz, DEPT, HMBC, $CDCl_3$): δ 23.4 ($\underline{Me}C(O)$), 36.1 ($\underline{C}H_2Ar$), 53.0 (CH–N), 55.3 (OMe), 64.0 (CH_2–O), 114.1 (CH_{Ar}), 129.6 (C_{Ar}), 130.2 (CH_{Ar}), 158.4 ($\underline{C}_{Ar}$–OMe), 177.0 (C=O). HRMS (ESI): *m/z* calcd. for [$C_{12}H_{17}NO_3$ + H^+]: 224.1281, found: 224.1281.

2-Hydroxycyclopentan-1-one *O*-(*tert*-butyldimethylsilyl) oxime 11a. Oxime ether **2sa** (60 mg, 0.22 mmol) was dissolved in a solution of NH_3 in MeOH (7M, 1.27 mL). Reaction mixture was stirred for 2 d at r.t. and transferred into EtOAc (20 mL)/H_2O (20 mL). The organic layer was washed with $NaHSO_4$ (10 mL, 0.5 M aq. solution), brine (20 mL), dried (Na_2SO_4) and evaporated. Column chromatography (eluent: PE/EtOAc 10:1) afforded 21 mg (42%) of target oxime ether as colorless oil. R_f = 0.22 (PE/EtOAc, 9:1, anisaldehyde). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 6H, Me_2Si), 0.94 (s, 9H, *t*-BuSi), 1.62-1.81 (m, 2H, CH_2), 1.89-2.11 (m, 2H, CH_2), 2.37-2.64 (m, 3H, CH_2 and OH), 4.53 (t, *J* = 6.4 Hz, 1H, CH−O). ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ -5.2 (Me_2Si), 18.1 ($Me_3\underline{C}Si$), 19.9 (CH_2), 25.9 (CH_2), 26.0 ($\underline{Me}_3C$), 33.9 (CH_2), 72.5 (CH−O), 170.5 (C=N). HRMS (ESI): *m/z* calcd. for [$C_{11}H_{23}NO_2Si$ + H^+]: 230.1571, found: 230.1575.

2-Hydroxycyclopentan-1-one *O*-triisopropylsilyl oxime 11b.
1. Oxime ether **2sk** (56 mg, 0.18 mmol) was dissolved in a solution of NH_3 in MeOH (7M, 1.00 mL). The reaction mixture was stirred for 2 d at r.t. and transferred into EtOAc (20 mL)/H_2O (15 mL). The organic layer was washed with $NaHSO_4$ (10 mL, 0.5 M aq. solution), brine (15 mL), dried (Na_2SO_4) and evaporated. Column chromatography (eluent: PE/EtOAc, 15:1) afforded 38 mg (78%) of target oxime ether as colorless oil.
2. To a solution of oxime ester **2sl** (82 mg, 0.24 mmol) in EtOH (2.4 mL) $NaBH_4$ (27 mg, 0.71 mmol) was added. The reaction mixture was stirred at r.t. for 6 h and poured in EtOAc/H_2O (20/25 mL). The organic layer was washed with $NaHSO_4$ (15 mL, 0.5 M aq. solution), brine (20 mL), dried (Na_2SO_4) and evaporated. Column chromatography (eluent: PE/EtOAc, 20:1) afforded 20 mg (31%) of *Z*-isomer and 30 mg (47%) of target oxime ether as colorless oil. R_f = 0.27 (PE/EtOAc, 9:1, anisaldehyde). *E*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (d, *J* = 7.0 Hz, 18H, Me_{TIPS}), 1.17-1.29 (m, 3H, CH_{TIPS}), 1.59-1.77 (m, 2H, CH_2), 1.87-1.97 (m, 2H, CH_2), 2.35 (br s, 1H, OH), 2.40-2.66 (m, 2H, CH_2), 4.52 (t, *J* = 6.4 Hz, 1H, CH–O). ^{13}C NMR (75 MHz, DEPT, $CDCl_3$): δ 11.9 (CH_{TIPS}), 17.9 (Me_{TIPS}), 19.9 (CH_2), 25.7 (CH_2), 34.0 (CH_2), 72.5 (CH–O), 170.0 (C=N). HRMS (ESI): *m/z* calcd. for [$C_{14}H_{29}NO_2Si$ + H^+]: 272.2040, found: 272.2041. *Z*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (d, *J* = 7.2 Hz, 9H, Me_{TIPS}), 1.11 (d, *J* = 7.2 Hz, 9H, Me_{TIPS}), 1.20-1.32 (m, 3H, CH_{TIPS}), 1.58-1.83 (m, 2H), 1.89-2.01 (m, 1H), 2.08-2.19 (m, 1H), 2.33-2.42 (m, 1H) and 2.44-2.55 (m, 1H) (3×CH_2), 3.91 (br s, 1H, OH), 4.87 (t, *J* = 7.1 Hz, 1H, CH–O). ^{13}C NMR (75 MHz, DEPT, HSQC, $CDCl_3$): δ 11.8 (CH_{TIPS}), 17.9 (Me_{TIPS}), 22.0 (CH_2), 29.5 (CH_2), 32.9 (CH_2), 71.0 (CH–O), 169.9 (C=N). HRMS (ESI): *m/z* calcd. for [$C_{14}H_{29}NO_2Si$ + H^+]: 272.2040, found: 272.2043.

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Keywords: Acylation • Nitro compounds • Oxygenation • Protecting groups • Rearrangement

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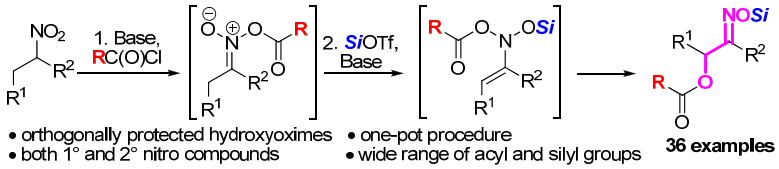

- orthogonally protected hydroxyoximes
- both 1° and 2° nitro compounds
- one-pot procedure
- wide range of acyl and silyl groups

One-pot acylation-silylation sequence was developed for the synthesis of protected hydroxyoximes from aliphatic nitro compounds. Procedure is characterized by wide substrate scope for nitro compounds, acylating and silylating agents.

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