Electronic Supporting Information

N-Trimethylsilyloxy-enamines as New Aldehyde Enolate Synthons: General, Efficient and Diastereoselective Aldol Reaction with Ketals and Acetals Induced by Trimethylsilyl Trifluoromethanesulfonate.

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TABLE OF CONTENT

Instrumentation and Materials S2

General procedures and characterization data of the products 1–3 S3–S18

Synthesis of N-tert-butyl-N-(trimethylsilyloxy)alk-1-en-1-amines (1) S3–S5

Synthesis and attempted reactions with dibenzyl acetals and ketals S5

Synthesis of β-methoxy aldonitrone (2) S6–S16

Synthesis of β-methoxy aldehydes (3) S16–S19

X-ray Crystal-Structure Determination S20–S32

1H and 13C NMR spectra of the new products S33–S73
Instrumentation and Materials

NMR spectra were recorded on Bruker Avance I™ 400 (400 MHz for $^1$H, 100 MHz for $^{13}$C) spectrometer in CDCl$_3$ or C$_6$D$_6$. Chemical shifts were reported as δ scale in ppm relative to SiMe$_4$ (δ = 0) as an internal standard for $^1$H NMR and to CDCl$_3$ (δ = 77.16) or C$_6$D$_6$ (δ = 128.06) for $^{13}$C NMR. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet), qd (quartet of doublet). GC–MS spectra were recorded on an Agilent 7890A gas chromatograph coupled with a 5975C quadrupole mass-selective electron impact (EI) detector (70 eV). High-resolution mass spectra (HRMS) were recorded on a LTQ Orbitrap XL instrument using electrospray ionization (ESI). Elemental analyses were obtained using a Perkin–Elmer PE 2400 Series II CHNS analyzer. Infrared spectra were measured on a FTIR instrument as a net compound. Melting points were measured with a Hund Wetzlar melting point apparatus and are uncorrected.

Syntheses of the products 1 and 2 were carried out in the atmosphere of dry argon in glassware dried by heat-gun under vacuum shortly before the experiments. The following solvents were refluxed and distilled over drying reagents before use: CH$_2$Cl$_2$ over CaH$_2$, CCl$_4$ and hexane over P$_2$O$_5$, 1,2-dimethoxyethane over Na/K alloy with Ph$_2$C=O added to form a deep-blue ketyl solution. MeOH was dried by distilling from Mg(OMe)$_2$ prepared by dissolving Mg turnings in crude MeOH. 2M solution of MeONa was prepared by dissolving Na in the dry MeOH.

2,2-Dimethoxypropane and all the aldehydes and ketones used for synthesis of N-silyloxy enamines 1 or acetics and ketals were obtained from commercial suppliers and distilled before use. Dimethyl acetics and ketals were prepared according to the literature procedure$^{[1]}$. Timethylsilyl trifluoromethanesulfonylate (TMSOTf) was used as purchased from FLUKA or obtained by us according to the equation: HOTf + TMSCl = TMSOTf + HCl followed by distillation at 64–66°C (60 mbar). The latter gave cleaner reactions with higher yields of the products 2. N-tert-butylhydroxylamine was prepared as described by us earlier$^{[2]}$ and isolated by saponification of its benzoyl derivative followed by filtration, saturation of the aqueous phase with NaCl, extraction with ether, drying (Na$_2$SO$_4$), filtration and removal of Et$_3$O at 400 mbar to give Me$_3$CNHOH (68% yield) as white crystalline solid. Trimethyl orthoformate, triethylamine, tert-butyl methyl ether, benzyl peroxide (75%, remainder H$_2$O), K$_3$PO$_4$·H$_2$O and TMSCl were used as purchased from commercial suppliers.

Thin-layer chromatography was performed with Silica on Alu foils FLUKA Product No. 60778. Fluka Silica gel 60 (230–400 mesh, Product No. 12479, enriched with approx. ~0.1% Ca to protect acid-labile protection groups) was used for flash chromatography. To prevent elimination of MeOH from the products 2, the silica gel in the column was washed with 15% Et$_3$N in hexane prior to the chromatographic purifications.
General Procedures (GP)

GP1: Synthesis of N-tert-buty1-N-(trimethylsilyloxy)alk-1-en-1-amines (1)

An aldehyde (1.2–1.3 equiv.) was added to an ice-cooled solution of Me₃CNHOH (1 equiv.) in CCl₄ (1 mL per 2 mmol Me₃CNHOH). The mixture was stirred at room temperature for 1 h, whereupon anhydrous MgSO₄ was added, and stirring was continued for another 15–20 min before MgSO₄ was filtered off and rinsed with a small portion of CCl₄. The combined filtrate containing the intermediate aldonitrone[3] was cooled to 0°C under argon atmosphere, whereupon TMSCl (1.5 equiv.) and Et₃N (1.7 equiv.) were added dropwise, and the reaction mixture was allowed to warm up to r.t. The silylation reaction time is given for each individual entry (see below). Upon completion, the reaction mixture was added to the two-phase mixture of hexane / ice–water. Organic phase was separated, and the aqueous phase was extracted with hexane. The combined organic phase was dried (Na₂SO₄), volatiles were removed in vacuum, and the residue was distilled in vacuum to give the pure enamine 1. Enamines 1a, 1b or 1d were also prepared in hexane, benzene or CH₂Cl₂ with equal efficiency.

N-tert-buty1-N-(trimethylsilyloxy)ethenamine (1a)

The titled compound was prepared from 5.3 g (60 mmol) of Me₃CNHOH according to the GP1. Silylation reaction time was 80 min at r.t. Distillation at 65–67°C (30 mbar) afforded 1a as a Colourless liquid (10.4 g, 94% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.30 (1H, dd, J = 14.7 and 8.8 Hz, =CHN), 4.42 (1H, dd, ³J = 14.7 Hz, ²J = 0.6 Hz, CH₂=), 4.20 (1H, dd, ³J = 8.8 Hz, ²J = 0.6 Hz, CH₂=), 1.13 (9H, s, CMe₃), 0.16 (9H, s, SiMe₃). ¹³C NMR (100 MHz, CDCl₃) δ 140.89, 92.74, 60.02, 26.52, 0.25. MS (EI mode) m/z %: 187 (21), 172 (8), 131 (45), 116 (100), 100 (5), 89 (15), 75 (48), 73 (42), 57 (83), 41 (25), 27 (9). Physical and spectral data are in a good consistency with those reported earlier[4].

-S3-
(E)-N-tert-butyl-N-((trimethylsilyloxy)prop-1-en-1-amine (1b)

The titled compound was prepared from 3 g (33.6 mmol) of Me₂CNHOH according to the GP1. Silylation reaction time was 5 h at r.t. Distillation at 73–75°C (20 mbar) afforded 1b as a Colourless liquid (6.4 g, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.96 (1H, dq, ³J = 13.2 Hz, ⁴J = 1.4 Hz, =CHN), 5.01 (1H, dq, ³J = 13.2 and 6.7 Hz, MeCH=), 1.64 (3H, dd, ³J = 6.7 Hz, ⁴J = 1.4 Hz, MeCH=), 1.09 (9H, s, CMe₃), 0.13 (9H, s, SiMe₃). ¹³C NMR (100 MHz, CDCl₃) δ 136.94, 108.04, 59.84, 59.87, 31.57, 30.34, 30.25, 26.31, 22.69, 14.23, 0.34. MS (EI mode) m/z %: 201 (37), 186 (8), 145 (100), 130 (46), 112 (10), 102 (9), 87 (22), 75 (85), 73 (47), 57 (81), 41 (27), 27 (11). HRMS (ESI) calcd for C₁₀H₁₄NOSi [M⁺] 201.1549, found 201.1582.

(E)-N-tert-butyl-N-((trimethylsilyloxy)hept-1-en-1-amine (1c)

The titled compound was prepared from 2 g (22.4 mmol) of Me₂CNHOH according to the GP1. Silylation reaction time was 6 h at r.t. Distillation at 113–115°C (2 mbar) afforded 1c as a Colourless liquid (5.2 g, 91% yield). ¹H NMR (400 MHz, CDCl₃) δ 5.96 (1H, dq, ³J = 13.2 Hz, =CHN), 5.02 (1H, dt, ³J = 13.2 and 7.3 Hz, CH₂CH=), 1.99 (2H, q, J = 7.2 Hz, CH₂CH=), 1.41–1.25 (6H, m, 3 CH₃), 1.11 (9H, s, CMe₃), 0.90 (3H, t, J = 6.9 Hz, Me), 0.15 (9H, s, SiMe₃). ¹³C NMR (100 MHz, CDCl₃) δ 135.36, 113.62, 59.87, 31.57, 30.34, 30.25, 26.31, 22.69, 14.23, 0.34. MS (EI mode) m/z %: 257 (26), 242 (49), 201 (35), 186 (16), 158 (21), 144 (100), 128 (41), 96 (11), 75(35), 57 (46), 41 (17), 27 (7). HRMS (ESI) calcd for C₁₄H₃₁NOSi [M⁺] 257.2175, found 257.2197.

(E)-N-tert-butyl-N-((trimethylsilyloxy)-2-phenylethen-1-amine (1d)

The titled compound was prepared from 3 g (33.6 mmol) of Me₂CNHOH according to the GP1 except that TMSCl (2 equiv.) and Et₃N (3 equiv.) were employed in order to achieve complete conversion of the intermediate nitrore. Silylation reaction time was 2 h at r.t. Distillation at 138–140°C (2 mbar) afforded 1d as a faint yellow oil (7.8 g, 89% yield) which solidified upon standing at r.t. ¹H NMR (400 MHz, CDCl₃) δ 7.25 (5H, s, Ph), 6.84 (1H, d, ³J = 13.5 Hz, PhCH=), 5.95 (1H, d, ³J = 13.5 Hz, =CHN), 1.20 (9H, s, CMe₃), 0.20 (9H, s, SiMe₃). ¹³C NMR (100 MHz, CDCl₃) δ 138.46, 135.89, 128.64, 125.19, 110.53, 61.10, 26.78, 0.31. MS (EI mode) m/z %: 263 (42), 248 (6), 217 (100), 179 (22), 163 (36), 149 (62), 118 (46), 117 (89), 91 (24), 75 (45), 57 (68), 41 (21), 27 (9). HRMS (ESI) calcd for C₁₅H₂₃NOSi [M⁺] 263.1705, found 263.1695.
The titled compound was prepared from 2 g (22.4 mmol) of Me₂CNHOH according to the GP1. Silylation reaction time was 14 h at r.t. Distillation at 147–149°C (2 mbar) afforded 1e as a Colourless liquid (5.9 g, 91% yield). ¹H NMR (400 MHz, C₆H₆) δ 7.23–7.15 (4H, m, CH₉,m) and 7.06 (1H, m, CH₉), 6.02 (1H, d, 3J = 13.2 Hz, =CHN), 5.45 (1H, dd, 3J = 13.2 and 7.5 Hz, CH=), 3.39 (1H, quint, 3J = 7.1 Hz) 1.33 (3H, d, J = 7.0 Hz), 1.09 (9H, s, CMe₂), 0.18 (9H, s, SiMe₃). ¹³C NMR (100 MHz, C₆H₆) δ 146.91, 131.47, 129.08, 127.48, 126.89, 69.00, 37.34, 35.70, 28.21, 22.88, 2.39. MS (EI mode) m/z %: 291 (37), 276 (13), 235 (28), 220 (100), 186 (5), 144 (35), 129 (11), 118 (21), 105 (31), 75 (34), 57 (36), 41 (12), 27 (6). HRMS (ESI) calcd for C₁₇H₂₉NOSi [M⁺] 291.2018, found 291.2090.

Synthesis and attempted reactions with dibenzyl acetals and ketals

2,2-dibenzxylopropane was prepared by combining dimethoxypropane (16 g, 150 mmol), benzyl alcohol (45.6 g, 430 mmol), and TsOH-H₂O (10 mg) in benzene (50 mL) followed by slow distillation at atmospheric pressure until the temperature of the distillate rose to 64°C and bath temperature to 122°C. It was then cooled down and treated with hexane / mixture of ice with diluted NaOH and washed twice with water. Drying (KOH pellets), removal of volatiles in vacuum followed by distillation (153–155°C / 0.3 mbar) afforded pure Me₂(OCH₂Ph)₂ as colourless liquid (37 g, 94%).

Heptaldehyde dibenzyl acetal was prepared by combining heptaldehyde dimethyl acetal (5.1 g, 32.1 mmol) with benzyl alcohol (16.7 g, 154 mmol) and TsOH-H₂O (2 mol%) followed by heating with vigorous stirring at 75°C (7 mbar) for 3 h. After aqueous workup as described above, the product Me(CH₂)₅CH(OCH₂Ph)₂ was obtained by distillation (193°C / 0.28 mbar) as colourless liquid (9.6 g, 97%).

Attempts to prepare propiophenone dibenzyl ketal from propiophenone dimethyl ketal and benzyl alcohol as described above were unsuccessful, resulting in the parent propiophenone. Room-temperature stirring of PhC(OMe)₂Et with PhCH₂OH and catalytic TsOH (7 mbar, overnight) led to a mixture of the desired PhC(OCH₂Ph)₂Et and propiophenone (1:2:1).

Reaction of 2,2-dibenzxylopropane with the enamine 1b was carried out according to the GP2, see also product 2h below.

Attempts to react heptaldehyde dibenzyl acetal with the enamines 1b or 1d under the standard conditions (GP2) yielded mixtures of the essentially intact dibenzyl acetal with the parent N-tert-butyl nitrones.
GP2: Synthesis of rac-β-methoxy aldonitrones (2)

TMSOTf (0.53 g, 2.4 mmol, 1.2 equiv.) was added dropwise to a solution of acetal or ketal (2.0 mmol, 1.0 equiv.) in CH₂Cl₂ (8 mL) at −78°C (bath temperature), and the resulting mixture was stirred for 30 min. It was then cooled down to −90°C, and enamine 1 (2.4 mmol, 1.2 equiv.) was added neat (except 1d which was diluted with 1 mL hexane) dropwise within a minute. The reaction mixture was allowed to warm up to −78°C and stirred for additional 45 min (TLC control) while maintaining the temperature at −78°C. After quenching by dropwise addition of MeONa (2.0 mmol, 1.1 equiv.) in MeOH (2 M) and stirring for 2–3 min, the cold solution was poured into the two-phase hexane / ice–water mixture. The aqueous phase was extracted with hexane (2 × 5 mL). The combined organic phase was dried (Na₂SO₄), filtered, the volatiles were removed in vacuum and the residue was purified by column chromatography to afford the pure product 2. Most of the β-methoxy aldonitrones 2 are bench stable compounds. However all the samples were routinely stored in a fridge at 4°C. For the diastereomeric ratios of 2, see Table 1.

(Z)-N-(3-methoxy-3-phenylpropylidene)-2-methylpropan-2-amine oxide (2a)

\[
\begin{align*}
\text{The titled compound was prepared according to the GP2. 2a, colourless oil, yield 0.451 g (96%).} & \quad ^1H \text{ NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 7.33 (5H, m, Ph), 6.90 (1H, t, } J = 5.5 \text{ Hz, CH=NN), 4.52 (1H, t, } J = 6.6 \\
\text{Hz, CHOme), 3.25 (3H, s, OMe), 2.88 (2H, t, } J = 5.7 \text{ Hz, CH}_2\text{), 1.46 (9H, s, CMe}_3\text{).} & \quad ^13C \text{ NMR (100 MHz, CDCl}_3\text{) } \delta \text{ 141.31, 131.62, 128.62, 127.96, 126.42, 79.91, 69.30, 56.85, 35.69, 28.09.} \\
\text{HRMS (ESI) Calcd for (C}_{14}\text{H}_{21}\text{NO}_2 + Na}^+ : 258.1470 \text{ found 258.1465.} \\
\text{Elemental analysis calcd (% for C}_{14}\text{H}_{21}\text{NO}_2 : C 71.46, H 8.99, N 5.95; found: C 71.30, H 9.04, N 5.80.} & \quad \text{FTIR (neat, cm}^{-1}\text{): } \nu_{\text{C-O}} 1096, \\
\text{v}_{\text{N-O}} 1454, \text{v}_{\text{C-N}} 1583. 
\end{align*}
\]

(Z)-N-[3-methoxy-3-(4-methoxyphenyl)propylidene]-2-methylpropan-2-amine oxide (2b)

\[
\begin{align*}
\text{The titled compound was prepared according to the GP2. 2b, colourless oil, yield 0.450 g (85%).} & \quad ^1H \text{ NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 7.24 (2H, d, } J = 8.6 \text{ Hz, CH}_3\text{Ar), 6.89 (3H, m, CH}_3\text{Ar + CH=NN), 4.46 (1H, } t, J = 6.4 \text{ Hz, CHOme), 3.80 (3H, s, CArOMe), 3.22 (3H, s, CHOME), 2.87 (2H, } m, \text{ CH}_2\text{), 1.46 (9H, } s, \text{ CMe}_3\text{).} & \quad ^13C \text{ NMR (100 MHz, CDCl}_3\text{) } \delta \text{ 159.38, 133.29, 131.17, 127.65, 113.98, 79.44, 69.22, 56.56, 55.62, 35.63, 28.08.} \\
\text{HRMS (ESI) Calcd for (C}_{14}\text{H}_{21}\text{NO}_2 + Na}^+ : 288.1576 \text{ found 288.1571.} 
\end{align*}
\]
Elemental analysis calcd (%) for C_{15}H_{22}NO_{2}: C 67.90, H 8.74, N 5.28; found: C 67.47, H 8.53, N 5.17. FTIR (neat, cm\(^{-1}\)): \(\nu_{C-O} \) 1167, \(\nu_{N-O} \) 1508, \(\nu_{C=N} \) 1669.

(Z)-N-[(E)-3-methoxy-5-phenylpent-4-enylidene]-2-methylpropan-2-amine oxide (2c)

![Chemical Structure](image)

The compound was prepared according to the GP2. Yellow oil, yield 0.511 g (98%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.35 (5H, m, Ph), 6.97 (1H, t, \(^3\)J = 5.5 Hz, CH=), 6.62 (1H, d, \(^3\)J = 15.9 Hz, PhCH=), 6.10 (1H, dd, \(^3\)J = 15.9 and 7.5 Hz, =CH), 4.10 (1H, s, CHOME), 3.36 (3H, s, OMe), 2.85 (1H, dt, \(^3\)J = 16.9 Hz, \(^3\)J = 5.6 Hz, CH\(_3\)CH\(_2\)), 2.80 (1H, ddd, \(^3\)J = 16.9 Hz, \(^3\)J = 7.3 and 5.4 Hz, CH\(_2\)CH\(_3\)), 1.51 (9H, s, CMe\(_3\)). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 136.40, 132.73, 130.75, 129.11, 128.70, 127.98, 126.64, 78.73, 69.35, 56.51, 33.35, 28.15. HRMS (ESI) Calcd for (C\(_{16}\)H\(_{23}\)NO\(_2\) + Na\(^+\)): 284.1626 found 284.1621. Elemental analysis calcd (%) for C\(_{16}\)H\(_{23}\)NO\(_2\): C 73.53, H 8.87, N 5.36; found: C 73.20, H 8.51, N 5.31. FTIR (neat, cm\(^{-1}\)): \(\nu_{C-O} \) 1093, \(\nu_{N-O} \) 1448, \(\nu_{C=N} \) 1615.

(Z)-N-(3-methoxy-3-phenylbutylidene)-2-methylpropan-2-amine oxide (2d)

![Chemical Structure](image)

The compound was prepared according to the GP2. Colourless oil, yield 0.453 g (91%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.36 (4H, m, CH\(_{2,3m}\)), 7.24 (1H, m, CH\(_p\)), 6.89 (1H, t, \(^3\)J = 5.3 Hz, CH=), 3.12 (3H, s, OMe), 3.03 (2H, dd, \(^3\)J = 5.7 and 4.7 Hz), 1.57 (3H, s, Me), 1.44 (9H, s, CMe\(_3\)). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 144.44, 131.26, 128.46, 127.29, 125.81, 77.94, 69.33, 50.60, 38.34, 28.09, 25.23. HRMS (ESI) Calcd for (C\(_{15}\)H\(_{23}\)NO\(_2\) + Na\(^+\)): 272.1626 found 272.1621. Elemental analysis calcd (%) for C\(_{15}\)H\(_{23}\)NO\(_2\): C 72.25, H 9.30, N 5.62; found: C 72.13, H 9.09, N 5.31. FTIR (neat, cm\(^{-1}\)): \(\nu_{C-O} \) 1106, \(\nu_{N-O} \) 1360, \(\nu_{C=N} \) 1592.

(Z)-N-(3-methoxy-3-phenylpentylidene)-2-methylpropan-2-amine oxide (2e)

![Chemical Structure](image)

The compound was prepared according to the GP2. Colourless oil, yield 0.415 g (79%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.35 (4H, m, CH\(_{2,3m}\)), 7.25 (1H, m, CH\(_p\)), 6.79 (1H, t, \(^3\)J = 5.2 Hz, CH=), 3.20 (1H, dd, \(^3\)J = 18.6 Hz, \(^3\)J = 5.2 Hz, CH\(_3\)CH\(_2\)CH=), 3.15 (3H, s, OMe), 3.06 (1H, dd, \(^3\)J = 18.6 Hz, \(^3\)J = 5.3 Hz, CH\(_3\)CH\(_2\)CH=), 1.94 (1H, dq, \(^3\)J = 14.3 Hz, \(^3\)J = 7.0 Hz, CH\(_3\)CH\(_2\)Me), 1.82 (1H, dq, \(^3\)J = 14.3 Hz, \(^3\)J = 7.0 Hz, CH\(_3\)CH\(_2\)Me), 1.42 (9H, s, CMe\(_3\)). 0.69 (3H, t, \(^3\)J = 7.3 Hz). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 131.23, 128.25, 127.06, 126.23, 80.35, 69.27, 49.48, 33.21, 31.67, 28.07, 7.85. HRMS (ESI) Calcd for (C\(_{16}\)H\(_{25}\)NO\(_2\) + Na\(^+\)): 286.1783 found 286.1778. Elemental analysis calcd (%) for C\(_{16}\)H\(_{25}\)NO\(_2\): C 72.96, H 9.57, N 5.32; found: C 72.61, H 9.23, N 5.18. FTIR (neat, cm\(^{-1}\)): \(\nu_{C-O} \) 1110, \(\nu_{N-O} \) 1493, \(\nu_{C=N} \) 1668.
The compound was prepared according to the GP2. Yellow oil, yield 0.274 g (73%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.97 (1H, t, $J = 5.4$ Hz, CH=N), 3.20 (1H, s, OMe). 2.71 (2H, d, $J = 5.4$ Hz, CH$_2$), 1.51 (9H, s, CMe$_3$), 1.23 (6H, s, CMe$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 131.60, 73.77, 69.31, 39.54, 37.29, 28.17, 25.47. HRMS (ESI) Calcd for (C$_{10}$H$_{21}$NO$_2$ + Na)$^+$: 210.1470 found 210.1465. Elemental analysis calcd (%) for C$_{10}$H$_{21}$NO$_2$: C 64.13, H 11.30, N 7.48; found: C 63.95, H 11.40, N 7.28. FTIR (neat, cm$^{-1}$): $\nu_{C=O}$ 1110, $\nu_{\text{N-O}}$ 1441, $\nu_{\text{C= N}}$ 1672.

The compound was prepared according to the GP2. Colourless oil, yield 0.280 g (65%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.97 (1H, t, $J = 5.5$ Hz, CH=N), 3.23 (3H, s, OMe), 2.87 (1H, dd, $^2J = 18.5$ Hz, $J = 5.6$ Hz, CH$_3$H$_B$), 2.70 (1H, dd, $^2J = 18.5$ Hz, $^3J = 5.4$ Hz, CH$_A$H$_B$), 1.49 (9H, s, NCH$_3$), 1.18 (3H, s, Me), 0.94 (9H, s, CMe$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 133.30, 80.23, 69.05, 51.03, 39.12, 28.09, 32.43, 26.15, 18.47. HRMS (ESI) Calcd for (C$_{13}$H$_{27}$NO$_2$ + Na)$^+$: 252.1936 found 252.1931. Elemental analysis calcd (%) for C$_{13}$H$_{27}$NO$_2$: C 68.08, H 11.87, N 6.11; found: C 68.12, H 11.67, N 6.19. FTIR (neat, cm$^{-1}$): $\nu_{C=O}$ 1104, $\nu_{\text{N-O}}$ 1465, $\nu_{\text{C= N}}$ 1574.

The compound was prepared according to the GP2. Colourless oil, yield 0.305 g (76%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.85 (1H, d, $J = 7.7$ Hz, CH=N), 3.37 (1H, m, CHMe), 3.18 (3H, s, OMe), 1.49 (9H, s, CMe$_3$), 1.18 (3H, s, Me), 1.15 (3H, s, Me), 1.05 (3H, d, $J = 6.9$ Hz, CHMe). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.75, 75.99, 69.17, 49.25, 39.37, 28.12, 23.26, 22.72, 11.20. HRMS (ESI) Calcd for (C$_{11}$H$_{23}$NO$_2$ + Na)$^+$: 224.1626 found 224.1621. Elemental analysis calcd (%) for C$_{11}$H$_{23}$NO$_2$: C 65.63, H 11.52, N 6.96; found: C 65.28, H 11.21, N 6.50. FTIR (neat, cm$^{-1}$): $\nu_{\text{C=O}}$ 1102, $\nu_{\text{N-O}}$ 1457, $\nu_{\text{C= N}}$ 1640.
(Z)-N-[3-(1-benzyloxy)-2,3-dimethylbutylidene]-2-methylpropan-2-amine oxide (2h')

The compound was prepared according to the GP2. Drying at 45°C in high vacuum (0.02 mbar) with vigorous magnetic stirring afforded 2h' (0.538 g, 97% yield) as a slightly yellowish oil (contains trace amount of benzyl alcohol); decomposes on silica gel. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.16 (1H, s, Ph), 6.79 (1H, d, \(J = 7.7\) Hz, CH=N), 4.30 (1H, d, \(^2J = 11.5\) Hz, PhCH\(_2\)O), 4.28 (1H, d, \(^2J = 11.5\) Hz, PhCH\(_2\)O), 3.30 (1H, quint, \(J = 7\) Hz, CH\(_3\)C), 1.32 (9H, s, CMe\(_3\)), 1.14 (3H, s, Me), 1.11 (3H, s, Me), 0.98 (3H, d, \(J = 7.0\) Hz, CH\(_2\)CH\(_2\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 139.85, 136.99, 128.30, 127.15, 127.08, 76.68, 69.25, 63.60, 40.05, 28.16, 24.15, 23.11, 11.44. LRMS (ESI): 278 [M+H]\(^+\), 222 [(M+H) – CH\(_2\)=CMe\(_2\)]\(^+\), 170 [(M+H) – PhCH\(_2\)OH]\(^+\). Elemental analysis calcld (%) for C\(_{17}\)H\(_{27}\)NO\(_2\): C 73.61, H 9.81, N 5.05; found: C 73.40, H 9.81, N 4.90. FTIR (near, cm\(^{-1}\)): \(\nu\)\(_{C=O}\) 1083, \(\nu\)\(_{N-O}\) 1450, \(\nu\)\(_{C=N}\) 1576.

(Z)-N-[2-(1-methoxycyclopentyl)propylidene]-2-methylpropan-2-amine oxide (2i)

The compound was prepared according to the GP2. Colourless oil, yield 0.404 g (89%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.79 (1H, d, \(J = 7.7\) Hz, CH=N), 3.61 (1H, m, CHMe), 3.17 (3H, s, OMe), 1.89–1.65 (4H, m, 2CH\(_2\)=C), 1.63–1.44 (4H, m, 2CH\(_2\)CH\(_2\)) (9H, s, CMe\(_3\)), 1.08 (3H, d, \(J = 6.9\) Hz, CHMe). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 136.74, 88.59, 69.22, 49.61, 36.16, 33.41, 32.86, 28.12, 24.75, 24.44, 11.99. HRMS (ESI) Calcd for (C\(_{13}\)H\(_{25}\)NO\(_2\) + Na\(^+\)): 250.1783 found 250.1778. Elemental analysis calcld (%) for C\(_{13}\)H\(_{25}\)NO\(_2\): C 68.68, H 11.08, N 6.16; found: C 68.35, H 11.02, N 6.04. FTIR (near, cm\(^{-1}\)): \(\nu\)\(_{C=O}\) 1074, \(\nu\)\(_{N-O}\) 1458, \(\nu\)\(_{C=N}\) 1573.

(Z)-N-[2-(1-methoxycyclopentyl)heptylidene]-2-methylpropan-2-amine oxide (2j)

The compound was prepared according to the GP2. Waxy solid, yield 0.532 g (94%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.67 (1H, d, \(J = 8.4\) Hz, CH=N), 3.66 (1H, dt, \(J = 8.6\) and 3.1 Hz, CH\(_C\)), 3.19 (3H, s, OMe), 1.92–1.51 (8H, m, 4=CH\(_{2}\)(cyclic)), 1.50 (9H, s, CMe\(_3\)), 1.45–1.15 (8H, m, CH\(_3\)(CH\(_2\))\(_x\)=), 0.86 (3H, t, \(J = 6.9\) Hz, Me\(_t\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 136.25, 89.16, 69.42, 49.70, 41.15, 34.05, 33.05, 32.14, 28.79, 28.27, 27.79, 24.53, 24.21, 22.55, 14.03. HRMS (ESI) Calcd for (C\(_{17}\)H\(_{33}\)NO\(_2\) + Na\(^+\)): 306.2409 found 306.2404. Elemental analysis calcld (%) for C\(_{17}\)H\(_{33}\)NO\(_2\): C 72.03, H 11.73, N 4.94; found: C 72.20, H 11.68, N 4.82. FTIR (near, cm\(^{-1}\)): \(\nu\)\(_{C=O}\) 1111, \(\nu\)\(_{N-O}\) 1455, \(\nu\)\(_{C=N}\) 1571.
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(Z)-N-(3-methoxy-3-methyl-2-phenylbutylidene)-2-methylpropan-2-amine oxide (2k)

\[
\text{OMe} \quad \text{N} \quad \text{O}^{-}
\]

The compound was prepared according to the GP2. White solid (mp. 99°C), yield 0.378 g (72%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38 (1H, d, \(J = 7.6\) Hz, CH=N), 7.32–7.20 (5H, m, Ph), 4.32 (1H, d, \(J = 7.6\) Hz, CHPh), 3.20 (3H, s, OMe), 1.47 (9H, s, CMe\(_3\)), 1.22 (3H, s, CH\(_3\)C), 1.04 (3H, s, CH\(_3\)C). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.81, 134.78, 130.03, 128.11, 126.83, 76.93, 69.48, 52.20, 49.59, 28.23, 23.93, 23.36. HRMS (ESI) Calcd for (C\(_{16}\)H\(_{25}\)NO\(_2\) + Na\(^+\))\(^\ast\): 286.1783 found 286.1778. Elemental analysis calcd (%) for C\(_{16}\)H\(_{25}\)NO\(_2\): C 72.96, H 9.57, N 5.32; found: C 72.83, H 9.60, N 5.21. FTIR (near, cm\(^{-1}\)): \(v_{\text{C-O}} \) 1064, \(v_{\text{N-O}} \) 1454, \(v_{\text{C=N}} \) 1567.

(Z)-N-(3-methoxy-2-methyl-3-phenylpropylidene)-2-methylpropan-2-amine oxide (2l)

\[
\text{OMe} \quad \text{N} \quad \text{O}^{-}
\]

The compound was prepared according to the GP2. Waxy solid, yield 0.473 g (95%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) Major syn-diastereomer (shown) 7.33 (5H, m, Ph), 6.77 (1H, d, \(J = 7\) Hz, CH=N), 4.55 (1H, dd, \(J = 4.5\) and 0.9 Hz, =CHOme), 3.34 (1H, m, CH\(_3\)CH=), 3.26 (3H, s, OMe), 1.44 (9H, s, CMe\(_3\)), 1.02 (3H, d, \(J = 7\) Hz, Me). Minor anti-diastereomer 7.24 (5H, m, Ph), 6.72 (1H, d, \(J = 6.9\) Hz, CH=N), 4.35 (1H, d, \(J = 5.8\) Hz, =CHOme), 3.47 (1H, m, CH\(_3\)CH=), 3.27 (3H, s, OMe), 1.05 (3H, d, \(J = 6.1\) Hz, Me). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) Major syn-diastereomer 140.07, 136.62, 128.24, 127.48, 126.89, 83.23, 69.17, 57.54, 38.46, 28.10, 11.09. Minor anti-diastereomer 135.81, 128.28, 127.78, 127.05, 84.32, 69.21, 57.13, 38.12, 12.49. Other \(^1\)H and \(^{13}\)C NMR peaks of minor diastereomer are not observed due to overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C\(_{15}\)H\(_{23}\)N\(_2\)O\(_2\) + Na\(^+\))\(^\ast\): 272.1626 found 272.1621. Elemental analysis calcd (%) for C\(_{15}\)H\(_{23}\)N\(_2\)O\(_2\): C 72.25, H 9.30, N 5.62; found: C 72.00, H 9.37, N 5.51. FTIR (near, cm\(^{-1}\)): \(v_{\text{C-O}} \) 1099, \(v_{\text{N-O}} \) 1453, \(v_{\text{C=N}} \) 1575.

(Z)-N-[3-methoxy-3-(4-methoxyphenyl)-2-methylpropylidene]-2-methylpropan-2-amine oxide (2m)

\[
\text{OMe} \quad \text{N} \quad \text{O}^{-}
\]

The compound was prepared according to the GP2. White solid (mp. 98°C), yield 0.546 g (98%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) Major syn-diastereomer (shown) 7.25 (2H, d, \(J = 8.5\) Hz, CH\(_{\text{Ar}}\)), 6.88 (2H, d, \(J = 8.5\) Hz, CH\(_{\text{Ar}}\)), 6.74 (1H, d, \(J = 7.1\) Hz, CH=N), 4.46 (1H, d, \(J = 4.8\) Hz, =CHOMe), 3.80 (3H, s, C\(_{\text{Ar}}\)OMe), 3.33 (1H, m, =CHCH\(_3\)), 3.23 (3H, s, CHOMe), 1.43 (9H, s, CMe\(_3\)), 1.03 (3H, d, \(J = 7\) Hz, Me). Minor anti-diastereomer 7.15 (2H, d, \(J = 8.5\) Hz, CH\(_{\text{Ar}}\)), 4.28 (1H, d, \(J = 6.2\) Hz, =CHOMe), 3.44 (1H, m, =CHCH\(_3\)), 1.45 (9H, s, CMe\(_3\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) Major syn-diastereomer 159.01, 136.57, 131.96, 127.98, 113.60, 82.94, 69.05, 57.22, 55.25, 38.35, 28.02,
11.17. Minor anti-diastereomer 159.18, 128.16, 83.90, 56.82, 38.10, 28.05, 12.37. Other $^1$H and $^{13}$C NMR peaks of minor diastereomer are not observed due to overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C$_{18}$H$_{25}$NO$_2$ + Na)$^+$: 302.1732 found 302.1727. Elemental analysis calcd (%) for C$_{18}$H$_{25}$NO$_2$: C 68.79, H 9.02, N 5.01; found: C 68.75, H 9.07, N 4.93. FTIR (neat, cm$^{-1}$): $\nu_{C-O}$ 1094, $\nu_{N-O}$ 1509, $\nu_{C=N}$ 1608.

(Z)-N-[(E)-3-methoxy-2-methyl-5-phenylpent-4-enylidene]-2-methylpropan-2-amine oxide (2n)

The compound was prepared according to the GP2. Yellow oil, yield 0.539 g (98%). $^1$H NMR (400 MHz, CDCl$_3$) δ Major syn-diastereomer (shown) 7.31 (5H, m, Ph), 6.78 (1H, d, J = 7.1 Hz, CH=N), 6.60 (1H, d, J = 15.9 Hz, PhCH=), 6.15 (1H, dd, J = 15.9 and 7.5 Hz, =CH), 4.00 (1H, ddd, $^3$J = 7.4 and 4.9 Hz, $^4$J = 0.9 Hz, CHOMe), 3.35 (1H, m, =CHCH$_3$), 3.31 (3H, s, OMe), 1.46 (9H, s, CMe$_3$), 1.16 (3H, d, J = 7 Hz, Me). Minor anti-diastereomer 6.53 (1H, d, J = 16 Hz), 6.04 (1H, dd, J = 15.9 and 7.6 Hz), 3.95 (1H, ddd, $^3$J = 7.6 and 5.2 Hz, $^4$J = 0.8 Hz, CHOMe), 3.44 (1H, m, =CHCH$_3$), 1.47 (9H, s, CMe$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ Major syn-diastereomer 136.59, 136.25, 132.92, 128.64, 127.95, 127.80, 126.60, 82.94, 69.26, 57.00, 36.73, 28.13, 11.61. Minor anti-diastereomer 136.50, 135.80, 128.71, 128.01, 127.86, 82.97, 56.86, 36.39, 28.11, 12.52. Other $^1$H and $^{13}$C NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C$_{17}$H$_{25}$NO$_2$ + Na)$^+$: 298.1783 found 298.1778. Elemental analysis calcd (%) for C$_{17}$H$_{25}$NO$_2$: C 74.14, H 9.15, N 5.09; found: C 73.95, H 9.16, N 5.00. FTIR (neat, cm$^{-1}$): $\nu_{C-O}$ 1096, $\nu_{N-O}$ 1494, $\nu_{C=N}$ 1670.

(Z)-N-{2-[methoxy(4-methoxyphenyl)methyl]heptylidene]-2-methylpropan-2-amine oxide (2o)

The compound was prepared according to the GP2. Waxy solid, yield 0.643 g (96%). $^1$H NMR (400 MHz, CDCl$_3$) δ Major diastereomer 7.15 (2H, d, J = 8.6 Hz, CH$_{2}$Ar), 6.87 (2H, d, J = 8.6 Hz, CH$_{2}$Ar), 6.68 (1H, d, J = 7.1 Hz, CH=), 4.41 (1H, d, J = 5 Hz, =CHOMe), 3.81 (3H, s, CH$_{2}$ArOMe), 3.31 (1H, m, =CHCH$_3$), 3.22 (3H, s, CHOMe), 1.52 (2H, m, CHCH$_3$=), 1.43 (9H, s, CMe$_3$), 1.30–1.10 (6H, m, CH$_3$(CH$_2$)$_2$=), 0.82 (3H, t, J = 6.9 Hz, Me). Minor diastereomer 7.27 (2H, d, J = 8.6 Hz, CH$_{2}$Ar), 6.69 (1H, d, J = 7.3 Hz, CH=), 4.52 (1H, d, J = 5.2 Hz, =CHOMe), 3.80 (3H, s, CH$_{2}$ArOMe), 3.26 (3H, s, CHOMe), 1.44 (9H, s, CMe$_3$), 0.87 (3H, t, J = 7.2 Hz, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) δ Major diastereomer 159.09, 136.08, 132.31, 128.07, 113.67, 82.80, 69.27, 57.38, 55.36, 43.79, 32.05, 28.21, 27.45, 27.03, 22.60, 14.09. Minor diastereomer 159.18, 135.38, 132.44, 113.72, 82.17, 69.29, 57.01, 43.49, 32.08, 29.34, 27.77, 27.24, 22.65, 14.11. Other $^1$H and $^{13}$C NMR peaks of minor diastereomer are not observed due to overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C$_{20}$H$_{33}$NO$_2$ + Na)$^+$: 358.2358 found 358.2353. Elemental analysis calcd (%) for C$_{20}$H$_{33}$NO$_2$: C 71.60, H 9.91, N 4.18; found: C 71.50, H 10.00, N 4.20. FTIR (neat, cm$^{-1}$): $\nu_{C-O}$ 1091, $\nu_{N-O}$ 1510, $\nu_{C=N}$ 1610.
(Z)-N-[3-methoxy-3-(4-methoxyphenyl)-2-phenylpropylene]-2-methylpropan-2-amine oxide (2p)

The compound was prepared according to the GP2. White solid (mp.134°C), yield 0.552 g (81%). ¹H NMR (400 MHz, CDCl₃) δ Major diastereomer 7.21 (3H, m, CH₃p), 7.14 (2H, m, CH₃o), 7.08 (1H, d, J = 7.2 Hz, CH₃r), 7.01 (2H, d, J = 8.4 Hz, CH₃Ar), 6.75 (H, d, J = 8.7 Hz, CH=N), 4.80 (1H, d, J = 5.6 Hz, =CHOme), 4.49 (1H, dd, J = 7.2 and 5.6 Hz, PhCH=), 3.76 (3H, s, CArOMe), 3.18 (3H, s, CHOMe), 1.41 (9H, s, CMes). Minor diastereomer 3.77 (3H, s, CArOMe), 3.22 (3H, s, CHOMe), 1.44 (9H, s, CMes). ¹³C NMR (100 MHz, CDCl₃) δ Major diastereomer 159.23, 137.69, 134.44, 131.54, 129.58, 128.42, 128.17, 126.96, 113.46, 83.34, 69.49, 57.20, 55.34, 50.15, 28.09. Minor diastereomer 137.73, 134.49, 131.60, 128.92, 128.31, 113.67, 69.53, 28.17. Other ¹H and ¹³C NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C₂₁H₂₇NO₂ + Na⁺): 364.1889 found 364.1884. Elemental analysis calcd (%) for C₂₁H₂₇NO₂: C 73.87, H 7.97, N 4.10; found: C 73.85, H 7.92, N 4.15. FTIR (neat, cm⁻¹): ν C=O 1094, ν N=O 1455, ν C=N 1598.

(Z)-N-(3-methoxy-2-phenylisoxazoline)-2-methylpropan-2-amine oxide (2q)

The compound was prepared according to the GP2. Colourless oil, yield 0.503 g (79%). ¹H NMR (400 MHz, CDCl₃) δ Major diastereomer 7.37 (5H, m), 7.16 (1H, d, J = 6.8 Hz, CH=NH), 4.39 (1H, dd, J = 6.8 and 4.0 Hz, PhCH), 3.82 (1H, m, CHOMe), 3.36 (3H, s, OMe), 1.50 (9H, s, CMes), 1.38 (2H, m, CH₂CH), 1.21(8H, m, CH₃(CH₂)₄), 0.84 (3H, t, J = 6.9 Hz, Me). Minor diastereomer 7.11 (1H, d, J = 6.8 Hz, CH=NH), 4.44 (1H, dd, J = 7.3 and 4.4 Hz, PhCH), 3.56 (1H, m, CHOMe), 3.27 (3H, s, OMe), 1.49 (9H, s, CMes). ¹³C NMR (100 MHz, CDCl₃) δ Major diastereomer 138.00, 135.19, 129.39, 128.41, 126.93, 81.60, 69.42, 58.54, 47.12, 32.07, 31.75, 29.36, 28.05, 25.88, 22.54, 14.05. Minor diastereomer 139.56, 133.66, 129.39, 128.48, 126.75, 83.43, 69.50, 57.63, 46.31, 32.56, 29.71, 28.12, 25.49, 22.59, 14.12. Other ¹H and ¹³C NMR peaks of minor diastereomer are not observed due to overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C₂₀H₃₃NO₂ + Na⁺): 342.2409 found 342.2404. Elemental analysis calcd (%) for C₂₀H₃₃NO₂: C 75.19, H 10.41, N 4.38; found: C 74.92, H 10.11, N 4.40. FTIR (neat, cm⁻¹): ν C=O 1089, ν N=O 1496, ν C=N 1685.
The compound was prepared according to the GP2. Colourless oil, yield 0.441 g (84%). $^1$H NMR (400 MHz, CDCl$_3$) δ Major diastereomer 7.28 (5H, m, Ph), 6.67 (1H, t, $J = 5.4$ Hz, CH=N), 3.66 (1H, dt, $J = 6.5$ Hz and 5.3 Hz, CHOme), 3.31 (3H, s, OMe), 2.98 (1H, m, CHCH$_3$), 2.74–2.54 (2H, m), 1.39 (9H, s, Me$_3$), 1.31 (3H, d, $J = 7.1$ Hz, Me). Minor diastereomer 7.20 (5H, m, Ph), 6.44 (1H, t, $J = 5.6$ Hz, CH=N), 3.57 (1H, dt, $J = 7.3$ Hz and 5.8 Hz, CHOme), 3.43 (3H, s, OMe), 2.88 (1H, m, CHCH$_3$), 1.35 (9H, s, Me$_3$), 1.31 (3H, d, $J = 7.1$ Hz, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) δ Major diastereomer 143.37, 131.81, 128.44, 128.40, 126.57, 82.31, 69.07, 58.05, 43.69, 29.45, 28.03, 16.37. Minor diastereomer 143.53, 131.47, 128.65, 128.19, 126.79, 82.56, 68.97, 57.61, 44.73, 30.27, 28.19, 17.87. Other $^1$H NMR peaks of minor diastereomer are not observed due to overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C$_{16}$H$_{25}$NO$_2$ + Na)$^+$: 286.1783 found 286.1778. Elemental analysis calcld (%) for C$_{16}$H$_{25}$NO$_2$: C 72.96, H 9.57, N 5.32; found: C 72.62, H 9.42, N 5.16. FTIR (neat, cm$^{-1}$): $\nu$$_{C=O}$ 1088, $\nu$$_{N=O}$ 1480, $\nu$$_{C=\equiv N}$ 1579.

(Z)-N-(3-methoxy-2-methyl-3-phenylbutyldiene)-2-methylpropan-2-amine oxide (2s)

The compound was prepared according to the GP2. White solid (mp.100°C), yield 0.489 g (93%). $^1$H NMR (400 MHz, CDCl$_3$) δ Major diastereomer 7.33 (5H, s, Ph), 6.85 (1H, d, $J = 7.9$ Hz, CH=N), 3.49 (1H, dq, $J = 7.8$ and 7.0 Hz, CH$_2$CH), 3.17 (3H, s, OMe), 1.59 (3H, s, Me$_3$), 1.45 (9H, s, Me$_3$), 0.88 (3H, d, $J = 7.0$ Hz, Me). Minor diastereomer 7.33 (5H, s, Ph), 6.85 (1H, d, $J = 7.7$ Hz, CH=N), 3.18 (3H, s, OMe), 1.61 (3H, s, Me$_3$), 1.32 (9H, s, Me$_3$), 1.05 (3H, d, $J = 6.9$ Hz, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) δ Major diastereomer 143.09, 136.65, 128.17, 127.09, 126.07, 80.75, 69.33, 50.92, 42.69, 28.21, 21.70, 11.49. $^{13}$C NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C$_{16}$H$_{25}$NO$_2$ + Na)$^+$: 286.1783 found 286.1778. Elemental analysis calcld (%) for C$_{16}$H$_{25}$NO$_2$: C 72.96, H 9.57, N 5.32; found: C 72.87, H 9.67, N 5.27. FTIR (neat, cm$^{-1}$): $\nu$$_{C=O}$ 1112, $\nu$$_{N=O}$ 1443, $\nu$$_{C=\equiv N}$ 1621.

(Z)-N-(3-methoxy-2-methyl-3-phenylpentylidene)-2-methylpropan-2-amine oxide (2t)

The compound was prepared according to the GP2. Colourless oil, yield 0.509 g (92%). $^1$H NMR (400 MHz, CDCl$_3$) δ Major diastereomer 7.37 (4H, m, CH$_{o,m}$), 7.27 (1H, m, CH$_p$), 6.70 (1H, d, $J = 7.8$ Hz, CH=N), 3.75 (1H, dq, $J = 7.6$ and 7.1 Hz, CH$_2$CH), 3.22 (3H, s, OMe), 2.07 (2H, dq, $^2J =$
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17.8, $^3J = 7.5$ Hz, CH$_3$CH$_3$H$_B$, 1.45 (9H, s, CMe$_3$), 0.88 (3H, d, $J = 7$ Hz, CH$_3$CH), 0.84 (3H, t, $J = 7.3$ Hz, CH$_3$CH$_2$). Minor diastereomer 6.85 (1H, d, $J = 7.7$ Hz, CH=N), 3.91 (1H, dq, $J = 8.2$ and 6.9 Hz, CH$_3$CH). $^{13}$C NMR (100 MHz, CDCl$_3$) δ Major diastereomer 141.39, 136.60, 127.93, 127.26, 126.91, 83.19, 69.17, 65.89, 50.29, 37.99, 28.06, 25.64, 12.27, 7.47. Minor diastereomer 127.11, 65.89, 28.18. Other $^1$H and $^{13}$C NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C$_{17}$H$_{27}$NO$_2$ + Na)$^+$: 300.1939 found 300.1934. Elemental analysis calcd (%) for C$_{17}$H$_{27}$NO$_2$: C 73.61, H 9.81, N 5.05; found: C 73.41, H 9.752, N 4.85. FTIR (neat, cm$^{-1}$): $\nu_{C-O}$ 1074, $\nu_{N-O}$ 1446, $\nu_{C=N}$ 1577.

(Z)-N-(3-methoxy-2,3,4,4-tetramethylpentylidene)-2-methylpropan-2-amine oxide (2u)

The compound was prepared according to the GP2. Colourless oil, yield 0.320 g (70%). $^1$H NMR (400 MHz, CDCl$_3$) δ Major diastereomer 6.73 (1H, d, $J = 8.5$ Hz, CH=N), 3.73 (1H, dq, $J = 8.5$ and 6.9 Hz, CH$_3$CH), 3.30 (3H, s, OMe), 1.47 (9H, s, NCMe$_3$), 1.16 (3H, s, CCH$_3$), 1.08 (3H, d, $J = 7$ Hz, CH$_3$CH), 0.96 (9H, s, CMe$_3$). Minor diastereomer 7.12 (1H, d, $J = 7.6$ Hz, CH=N), 3.81 (1H, m, CH$_3$CH), 3.35 (3H, s, OMe), 1.46 (9H, s, NCMe$_3$), 1.20 (3H, s, CCH$_3$), 0.89 (9H, s, CMe$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ Major diastereomer 137.99, 82.08, 69.06, 52.82, 40.44, 36.16, 27.82, 26.59, 15.52, 13.86. Minor diastereomer 139.61, 81.52, 69.47, 52.90, 40.25, 36.64, 27.97, 26.66, 14.05, 13.55. Other $^1$H and $^{13}$C NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C$_{14}$H$_{29}$NO$_2$ + Na)$^+$: 266.2096 found 266.2091. Elemental analysis calcd (%) for C$_{14}$H$_{29}$NO$_2$: C 69.09, H 12.01, N 5.75; found: C 68.88, H 11.90, N 5.71. FTIR (neat, cm$^{-1}$): $\nu_{C-O}$ 1102, $\nu_{N-O}$ 1456, $\nu_{C=N}$ 1569.

(Z)-N-[2-(1-methoxy-1-phenylpropyl)heptylidene]-2-methylpropan-2-amine oxide (2v)

The compound was prepared according to the GP2. Colourless oil, yield 0.593 g (89%). $^1$H NMR (400 MHz, CDCl$_3$) δ Major diastereomer 7.36 (4H, m, CH$_{o,m}$), 7.25 (1H, m, CH$_p$), 6.53 (1H, d, $J = 8.1$ Hz, CH=N), 3.82 (1H, dt, $J = 8.8$ and 8.1 Hz, CH$_3$CH), 3.24 (3H, s, OMe), 2.09 (2H, q, $J = 7.3$ Hz, CH$_3$CH$_2$), 1.48 (9H, s, CMe$_3$), 1.18–0.99 (8H, m, CH$_3$(CH$_2$)$_4$), 0.80 (3H, t, $J = 7.2$ Hz, CH$_2$Me), 0.79 (3H, t, $J = 5.4$ Hz, Me). Minor diastereomer 6.16 (1H, d, $J = 8.6$ Hz, CH=N), 4.11 (1H, q, $J = 7.1$ Hz, CH$_3$CH), 3.28 (3H, s, OMe), 1.87 (2H, q, $J = 7.4$ Hz, CH$_3$CH$_2$), 1.45 (9H, s, CMe$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ Major diastereomer 142.07, 135.92, 127.71, 127.02, 126.64, 83.87, 69.32, 50.57, 43.45, 31.96, 29.25, 28.14, 27.15, 25.75, 22.39, 13.91, 7.40. Minor diastereomer 141.56, 127.59, 127.87, 126.70, 83.09, 69.50, 49.22, 41.85, 32.04, 28.11, 27.33, 26.15, 22.53, 14.16, 7.46. Other $^1$H and $^{13}$C NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C$_{21}$H$_{35}$NO$_2$ + Na)$^+$: 356.2565 found 356.2560. Elemental analysis calcd (%) for C$_{21}$H$_{35}$NO$_2$: C 75.63, H 10.58, N 4.20; found: C 75.61, H 10.70, N 4.18. FTIR (neat, cm$^{-1}$): $\nu_{C-O}$ 1106, $\nu_{N-O}$ 1459, $\nu_{C=N}$ 1573.
(Z)-N-(3-methoxy-2,3-diphenylbutylidene)-2-methylpropan-2-amine oxide (2w)

![Chemical structure of 2w](image)

The compound was prepared according to the GP2. White solid (mp.136°C), yield 0.611 g (94%). $^1$H NMR (400 MHz, CDCl$_3$) δ Major diastereomer 7.34 (1H, d, $J = 7.9$ Hz, CH=N), 7.09 (8H, m, Ph), 6.88 (2H, m, Ph), 4.49 (1H, d, $J = 7.9$ Hz, PhCH), 3.15 (3H, s, OMe), 1.65 (3H, s, CH$_3$C), 1.44 (9H, s, CMe$_3$). Minor diastereomer 4.34 (1H, d, $J = 7.5$ Hz, PhCH), 3.19 (3H, s, OMe), 1.26 (9H, s, CMe$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ Major diastereomer 142.23, 137.71, 134.37, 130.31, 127.72, 127.54, 127.07, 127.04, 126.68, 81.57, 69.65, 54.61, 50.80, 28.17, 21.66. All $^{13}$C NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C$_{21}$H$_{27}$NO$_2$ + Na)$^+$: 348.1939 found 348.1934. Elemental analysis calcd (%) for C$_{21}$H$_{27}$NO$_2$: C 77.50, H 8.36, N 4.30; found: C 77.39, H 8.50, N 4.20. FTIR (neat, cm$^{-1}$): $\nu$$_{C=O}$ 1112, $\nu$$_{N=O}$ 1450, $\nu$$_{C=N}$ 1623.

(Z)-N-(3-methoxy-2,3-diphenylpentylidene)-2-methylpropan-2-amine oxide (2x)

![Chemical structure of 2x](image)

The compound was prepared according to the GP2. White solid (mp.102°C), yield 0.630 g (93%). $^1$H NMR (400 MHz, CDCl$_3$) δ Major diastereomer 7.23 (4H, m, Ph), 7.13 (1H, d, $J = 7.1$ Hz, CH=N), 7.08 (2H, m, Ph), 6.99 (2H, m, Ph), 6.68 (2H, m, Ph), 4.80 (1H, d, $J = 7.6$ Hz, PhCH), 3.30 (3H, s, OMe), 2.11 (1H, dq, $^2$$J$ = 15.0 Hz, $^3$$J$ = 7.3 Hz, CH$_2$H$_3$Me), 1.95 (1H, dq, $^2$$J$ = 15.0 Hz, $^3$$J$ = 7.4 Hz, CH$_3$H$_3$Me), 1.43 (9H, s, CMe$_3$), 0.84 (3H, t, $J = 7.3$ Hz, CHMe). Minor diastereomer 4.80 (1H, d, $J = 7.6$ Hz, PhCH), 3.21 (3H, s, OMe), 1.43 (9H, s, CMe$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ Major diastereomer 140.57, 137.64, 134.38, 130.19, 127.89, 127.69, 127.46, 127.10, 126.95, 83.39, 69.43, 50.06, 49.71, 28.09, 25.91, 7.41. All $^{13}$C NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C$_{22}$H$_{29}$NO$_2$ + Na)$^+$: 362.2096 found 362.2091. Elemental analysis calcd (%) for C$_{22}$H$_{29}$NO$_2$: C 77.84, H 8.61, N 4.13; found: C 77.70, H 8.81, N 4.19. FTIR (neat, cm$^{-1}$): $\nu$$_{C=O}$ 1076, $\nu$$_{N=O}$ 1452, $\nu$$_{C=N}$ 1572.

(Z)-N-(3-methoxy-5-phenylhexylidene)-2-methylpropan-2-amine oxide (2y)

![Chemical structure of 2y](image)

The compound was prepared according to the GP2. Colourless oil, yield 0.498 g (90%). Since two diastereomers are found in 1:1 ratio, the $^1$H and $^{13}$C NMR signals are listed for the both together: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31–7.26 (4H, m) and 7.24–7.17 (6H, m) (2 Ph), 6.89 (1H, t, $J = 5.4$ Hz,
CH=N), 6.85 (1H, t, J = 5.4 Hz, CH=N), 3.40 (1H, m, CHOMe), 3.27 (6H, s, 2 OMe), 3.21 (1H, m, CHOMe), 2.96–2.92 (1H, m), 2.88 (1H, m), 2.73 (2H, m) and 2.66 (2H, m) (2 CHPh + 2 CH₂CH=N), 2.00–1.94 (1H, m), 1.86–1.81 (1H, m) and 1.68–1.52 (2H, m) (2 CHCH₂CH), 1.49 (9H, s, CMe₃), 1.48 (9H, s, CMe₃), 1.26 (6H, d, J = 7 Hz, 2 CHMe). ¹³C NMR (100 MHz, CDCl₃) δ 147.15, 146.83, 131.14, 130.89, 128.55 (two), 127.16, 126.94, 126.19, 126.14, 75.81, 75.74, 69.32, 69.31, 56.36, 56.26, 43.70, 42.69, 36.51, 36.19, 31.05, 30.94, 28.12 (two), 22.98, 22.55. HRMS (ESI) Calcd for (C₁₇H₂₇NO₂ + Na)⁺: 300.1939 found 300.1934. Elemental analysis calcd (%) for C₁₇H₂₇NO₂: C 73.61, H 9.81, N 5.05; found: C 73.28, H 9.87, N 4.83. FTIR (neat, cm⁻¹): νC=O 1091, νN-O 1601.

(Z)-N-[3-methoxy-3-methyl-2-(1-phenylethyl)butylidene]-2-methylpropan-2-amine oxide (2z)

The compound was prepared according to the GP2. Waxy solid, yield 0.424 g (73%). ¹H NMR (400 MHz, CDCl₃) δ Major diastereomer 7.42 (2H, m, CH₃), 7.29–7.22 (3H, m, CH₉), 7.02 (1H, d, J = 8.4 Hz, CH=N), 3.87 (1H, dd, J = 8.7 and 7.3 Hz, CCH), 3.17 (1H, m, CHMe), 3.09 (3H, s, OMe), 1.54 (9H, s, CMe₃), 1.17 (3H, d, J = 7.2 Hz, CHMe), 1.03 (3H, s, CMe), 1.02 (3H, s, CMe), 1.54 (9H, s, CMe₃). Minor diastereomer 7.21 (2H, m, CH₃), 7.14 (3H, m, CH₉), 6.37 (1H, d, J = 8.9 Hz, CH=N), 3.72 (1H, dd, J = 8.8 and 6.7 Hz, CCH), 3.27 (3H, s, OMe), 1.48 (3H, d, J = 6.9 Hz, CHMe), 1.40 (3H, s, CMe), 1.27 (3H, s, CMe), 1.14 (9H, s, CMe₃). ¹³C NMR (100 MHz, CDCl₃) δ Major diastereomer 148.79, 135.55, 128.47, 127.73, 125.91, 77.24, 69.56, 49.67, 49.37, 39.98, 28.29, 24.56, 23.84, 21.04. Minor diastereomer 145.78, 136.05, 128.70, 127.79, 126.14, 77.43, 68.87, 49.43, 48.93, 27.77, 23.92, 23.18, 21.25. Other ¹H NMR peaks of minor diastereomer are not observed due to overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C₁₈H₂₉NO₂ + Na)⁺: 314.2096 found 314.2091. Elemental analysis calcd (%) for C₁₈H₂₉NO₂: C 74.18, H 10.03, N 4.81; found: C 74.21, H 10.13, N 4.85. FTIR (neat, cm⁻¹): νC=O 1068, νN-O 1453, νC=N 1571.

GP3: Synthesis of rac-β-methoxy aldehydes (3)

i: A solution of the aldonitrone 2 (0.125 mmol, 1 equiv.) in hexane (0.5 mL) was added to the vigorously stirred two-phase mixture of H₃PO₄ (0.14 mmol, 1.1 equiv.) in water (ca. 1 mL) and hexane (1 mL) at 0°C. It was then allowed to warm up to r.t. and stirred until complete conversion of the starting nitrone (TLC control). The phases were separated, the organic phase was dried (Na₂SO₄), and evaporated in vacuum to afford a pure aldehyde 3.

ii: For the aldonitrone 2 resistant to the hydrolysis under the above two-phase conditions, homogeneous conditions (1.5 mL MeOH, 0.15–0.2 mmol HCl in 1 mL H₂O) were applied as specified in the Table 2 of the article. The workup (hexane / water) was as described above.

Syntheses of the aldehydes 3l, 3m, 3s were carried out starting from the respective enamines 1 without isolation of the corresponding nitrone 2 with the other conditions as specified in the GP2 and GP3.
(E)-3-methoxy-5-phenylpent-4-enal (3c)

The compound was prepared according to the general procedure 3i. Colourless liquid (97% yield).

1H NMR (400 MHz, CDCl₃) δ 9.80 (1H, t, J = 1.8 Hz, CH=O), 7.33 (5H, m, Ph), 6.63 (1H, d, J = 15.9 Hz, PhCH=), 6.08 (1H, dd, J = 15.9 and 7.8 Hz, =CH), 4.28 (1H, m, CHMe), 3.33 (3H, s, OMe), 2.78 (1H, ddd, 1J = 16.3, 2J = 4.7 and 1.7 Hz, CHCH₂CH₃), 2.62 (1H, ddd, 1J = 16.3, 2J = 4.7 and 1.7 Hz, CHCH₂CH₃). 13C NMR (100 MHz, CDCl₃) δ 136.14, 133.29, 128.76, 128.20, 128.15, 126.71, 77.50, 56.56, 49.56.

3-methoxy-3-phenylpentanal (3e)

The compound was prepared according to the general procedure 3i. Colourless liquid (96% yield).

1H NMR (400 MHz, CDCl₃) δ 9.6 (1H, t, J = 2.8 Hz, CH=O), 7.37 (4H, d, J = 4.3 Hz, CH₃), 7.28 (1H, m, CH₉), 3.18 (3H, s, OMe), 2.89 (2H, m, CH₃CH₂), 2.04 (1H, ddd, 1J = 14.5 and 3J = 7.2 Hz, CH₃CH₂CH₃), 1.94 (1H, dq, 4J = 14.5 and 3J = 7.2 Hz, CH₃CH₂CH₃), 0.77 (3H, t, J = 7.3 Hz, CH₂Me). 13C NMR (100 MHz, CDCl₃) δ 202.02, 142.74, 128.56, 127.46, 126.28, 80.24, 50.02, 49.32, 30.80, 7.57.

(E)-3,4,4-trimethylpent-2-enal and 3-methoxy-3,4,4-trimethylpentanal (3g)

The compound was prepared according to the general procedure 3i. Colourless liquid (95.5% yield).

1H NMR (400 MHz, CDCl₃) δ Major product 10.06 (1H, d, J = 7.8 Hz, CH=O), 5.96 (1H, dq, J = 7.8 and 1.1 Hz, =CH), 2.18 (3H, d, J = 1.1 Hz, Me), 1.14 (9H, s, CH₃). Minor product 9.86 (1H, t, J = 3.1 Hz, CH=O), 3.31 (3H, s, OMe), 2.65 (1H, dd, J = 15.2 and 3.2 Hz, CH₃CH₂CH₃), 2.46 (1H, ddd, J = 15.2 and 3.0 Hz, CH₃CH₂CH₃), 2.04 (3H, s, Me), 0.94 (9H, s, CH₃). 13C NMR (100 MHz, CDCl₃) δ Major product 192.65, 171.10, 124.74, 37.98, 28.51, 13.86. Minor product 203.54, 110.14, 51.41, 48.98, 34.81, 27.05, 18.03.

2-(1-methoxycyclopentyl)propanal (3i)

The compound was prepared according to the general procedure 3ii. Colourless liquid (89% yield).
3-methoxy-2-methyl-3-phenylpropanal (3l)

The compound was prepared according to the general procedure 3i. Colourless liquid (86% yield).

1H NMR (400 MHz, CDCl₃) δ 9.7 (1H, d, J = 2.41 Hz, CH=O), 3.18 (3H, s, OMe), 3.09 (3H, s, O=S18 = 2.41 Hz, CH=O), 3.18 (3H, s, OMe), 2.64 (1H, m, CH₂Me), 1.06 (3H, d, J = 7.0 Hz, CH₂Me). Minor diastereomer 9.81 (1H, d, J = 2.8 Hz, CH=O), 7.40–7.25 (5H, m, Ph). 13C NMR (100 MHz, CDCl₃) δ 203.34, 139.12, 128.62, 127.99, 126.99, 125.81, 123.54, 120.32, 113.64, 84.17, 56.16, 55.07, 52.43, 10.58. The 1H NMR data are in good consistency with those given in literature[5].

3-methoxy-3-(4-methoxyphenyl)-2-methylpropanal (3m)

The compound was prepared according to the general procedure 3i. Colourless liquid (83% yield).

1H NMR (400 MHz, CDCl₃) δ Major diastereomer 9.7 (1H, d, J = 1.3 Hz, CH=O), 7.20 (2H, d, J = 8.4 Hz, CH₃), 6.9 (2H, d, J = 8.7 Hz, CH₃), 4.5 (1H, d, J = 5.2 Hz, CHOMe), 3.82 (3H, s, 31C₅Me), 3.24 (3H, s, CH₂OMe), 2.64 (1H, m, CH₃), 1.0 (3H, d, J = 7 Hz, Me). Minor diastereomer 9.8 (1H, d, J = 2.9 Hz, CH=O), 7.22 (2H, d, J = 8.4 Hz, CH₃), 6.91 (2H, d, J = 8.7 Hz, CH₃), 4.22 (1H, d, J = 9.1 Hz, CHOMe), 3.82 (3H, s, C₅Me), 3.16 (3H, s, CH₂OMe), 2.71 (1H, m, CH₃), 0.82 (3H, d, J = 7 Hz, Me). 13C NMR (100 MHz, CDCl₃) δ Major diastereomer 203.34, 158.99, 130.54, 127.76, 113.61, 82.38, 56.54, 54.92, 52.82, 8.46. Minor diastereomer 203.76, 159.28, 130.43, 128.26, 113.64, 84.17, 56.16, 55.07, 52.43, 10.58.

(E)-3-methoxy-2-methyl-5-phenylpent-4-enal (3n)

The compound was prepared according to the general procedure 3i. Colourless liquid (98% yield).

1H NMR (400 MHz, CDCl₃) δ Major syn-diastereomer (shown, cf. ref.6) 9.79 (1H, d, J = 1.2 Hz, CH=O), 7.32 (5H, m, Ph), 6.62 (1H, d, J = 15.9 Hz, PhCH=), 6.09 (1H, dd, J = 15.9 and 7.9 Hz, =CH), 4.12 (1H, ddd, 3J = 7.9 and 4.6 Hz, 4J = 0.8 Hz, CHOMe), 3.32 (3H, s, OMe), 2.63 (1H, ddq, 3J = 7.1 Hz, 4J = 4.6 and 1.2 Hz, CHMe), 1.15 (3H, d, J = 7.1 Hz, CHMe). Minor diastereomer 9.76 (1H, d, J = 2.5 Hz, CH=O), 6.60 (1H, d, J = 15.8 Hz, PhCH=), 6.16 (1H, dd, J = 15.9 and 7.5 Hz, =CH), 4.00 (1H, ddd, 3J = 7.4 and 4.9 Hz, 4J = 0.9 Hz, CHOMe), 3.31 (3H, s, OMe), 2.62 (1H, m, CHMe), 1.05 (3H, d, J = 7.1 Hz, CHMe). 13C NMR (100 MHz, CDCl₃) δ Major diastereomer
3-methoxy-2-methyl-3-phenylbutanal (3s)

The compound was prepared according to the general procedure 3ii. Colourless liquid (85% yield). 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ Major diastereomer 9.65 (1H, d, $J = 2.6$ Hz, CH=O), 7.32 (5H, m, Ph), 3.14 (3H, s, OMe), 2.65 (1H, dq, $J = 6.9$ and 2.6 Hz, CHMe), 1.63 (3H, s, CMe), 0.97 (3H, d, $J = 6.9$ Hz, CHMe). Minor diastereomer 9.98 (1H, d, $J = 1.7$ Hz, CH=O), 3.09 (3H, s, OMe), 2.74 (1H, dq, $J = 7.0$ and 1.6 Hz, CHMe), 1.57 (3H, s, CMe), 0.79 (3H, d, $J = 7$ Hz, CHMe). Other $^1$H NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ Major diastereomer 204.71, 142.05, 128.48, 127.64, 126.82, 57.19, 50.43, 20.82, 9.62. Minor diastereomer 205.34, 142.84, 128.50, 81.38, 127.60, 126.74, 57.38, 50.58, 17.96, 9.40.

3-methoxy-2,3,4,4-tetramethylpentanal (3u)

The compound was prepared according to the general procedure 3ii. Colourless liquid (90% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ Major diastereomer 9.83 (1H, d, $J = 3.1$ Hz, CH=O), 3.33 (3H, s, OMe), 2.81 (1H, dt, $J = 7.0$ and 3.1 Hz, CHMe), 1.27 (3H, s, CMe), 1.13 (3H, d, $J = 7$ Hz, CHMe), 0.94 (9H, s, CMe$_3$). Minor diastereomer 9.84 (1H, d, $J = 2.6$ Hz, CH=O), 3.27 (3H, s, OMe), 1.25 (3H, s, CMe), 0.97 (9H, s, CMe$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ Major diastereomer 204.79, 82.12, 52.75, 51.94, 40.58, 26.73, 15.93, 11.01. Other $^1$H and $^{13}$C NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer.

References


X-Ray Crystal-Structure Determination of the β-methoxy aldonitrones (2m, p, s)

Crystals suitable for X-ray analysis were obtained by crystallization from the slowly evaporating solutions at r.t.: 2m from hexane, and 2p, s from hexane / AcOEt (1.5:0.5). Data for all colorless crystals were collected at 150 (2)K on a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å), a graphite monochromator. The structures were solved by direct methods (SIR92). All reflections were used in the structure refinement based on $F^2$ by full-matrix least-squares technique (SHELXL97). Hydrogen atoms were mostly localised on a difference Fourier map, however to ensure uniformity of treatment of all crystals, all hydrogen (except hydrogen on C1) were recalculated into idealised positions (riding model) and assigned temperature factors $U_{iso}(H) = 1.2 \times U_{eq}(pivot\ atom)$ or of $1.5U_{eq}$ for the methyl moiety. The hydrogen atom on C1 may be affected by adjacent N-O moiety, therefore its position was not idealized but freely refined with isotropic displacement parameter. Absorption corrections were neglected. Crystallographic data for individual structures are summarized in tables.
**rac-(-Z)-N’-[2(R*,3S*)-3-methoxy-3-(4-methoxyphenyl)-2-methylpropylidene]-2-methylpropan-2-amine oxide (2m)**

**Crystal data**

- **C_{16}H_{25}NO_{3}**
- **M_r = 279.37**
- **Melting point: 371 K**
- **Monoclinic, P2_1/c**
- **Hall symbol: -P 2ybc**
- **λ = 0.71073 Å**
- **θ = 1–27.5°**
- **µ = 0.08 mm⁻¹**
- **T = 150 (2) K**
- **V = 1635.43 (6) Å^3**
- **Z = 4**
- **F_{000} = 608**

**Data collection**

- **Nonius KappaCCD area detector diffractometer**
- **3772 independent reflections**
- **Radiation source: fine-focus sealed tube**
- **2980 reflections with I > 2σ(I)**
- **Monochromator: graphite**
- **θ_{max} = 27.5°**
- **θ_{min} = 1.8°**
- **P = 101.3 kPa**
- **φ and ω scans to fill the Ewald sphere**
- **Absorption correction: none**
- **25986 measured reflections**

**Refinement**

- **Refinement on F^2**
- **Least-squares matrix: full**
- **R(F^2) > 2σ(F^2) = 0.038**
- **wR(F^2) = 0.102**
- **S = 1.05**
- **3772 reflections**
- **191 parameters**

**Secondary atom site location: difference Fourier map**

- **Hydrogen site location: difference Fourier map**
- **H atoms treated by a mixture of independent and constrained refinement**
- **w = 1/[σ^2(F_o^2) + (0.0485P)^2 + 0.2392P]**

where P = (F_o^2 + 2F_c^2)/3

**(Δ/σ)_{max} = 0.001**

**Δρ_{max} = 0.16 e Å⁻³**

**Δρ_{min} = −0.17 e Å⁻³**

**Extinction correction: none**
Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating $R$-factors(gt) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$-factors based on ALL data will be even larger.

**Table 1**
Geometric parameters (Å, °) for 2m

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C18—C8—H8 108.3 O19—C20—H20B 109.5
O16—C9—C10 111.53 (8) H20A—C20—H20B 109.5
O16—C9—C8 106.57 (8) O19—C20—H20C 109.5
C10—C9—C8 111.89 (8) H20A—C20—H20C 109.5
O16—C9—H9 108.9 H20B—C20—H20C 109.5

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**rac-(Z)-N-[(2R*,3S*)-3-methoxy-3-(4-methoxyphenyl)-2-phenylpropylidene]-2-methylpropan-2-amine oxide (2p)**

**Crystal data**

\[ C_{21}H_{27}NO_3 \]  \[ D_\alpha = 1.191 \text{ Mg m}^{-3} \]
\[ M_r = 341.44 \]
Monoclinic, \( P2_1/c \)
Mo \( K\alpha \) radiation \( \lambda = 0.71073 \text{ Å} \)
Hall symbol: \(-P 2ybc'\)
Cell parameters from 4645 reflections
\[ a = 16.1659 \ (5) \text{ Å} \]
\[ b = 5.6972 \ (2) \text{ Å} \]
\[ c = 20.6824 \ (5) \text{ Å} \]
\[ \beta = 90.5706 \ (18) ^\circ \]
\[ V = 1904.76 \ (10) \text{ Å}^3 \]
\[ Z = 4 \]
\[ F_{000} = 736 \]

**Data collection**

Nonius KappaCCD area detector diffractometer
4372 independent reflections
2807 reflections with \( I > 2\sigma(I) \)
Radiation source: fine-focus sealed tube
Monochromator: graphite
Detector resolution: 9.091 pixels mm\(^{-1}\)
\[ \theta_{\text{max}} = 27.5^\circ \]
\[ \theta_{\text{min}} = 2.0^\circ \]
\[ T = 150(2) \text{ K} \]
\[ P = 101.3 \text{ kPa} \]
\[ h = -20 \rightarrow 20 \]
\[ k = -7 \rightarrow 7 \]
\[ l = -26 \rightarrow 26 \]
Absorption correction: none
25374 measured reflections
Refinement

Refinement on \( F^2 \)
Least-squares matrix: full

\[ R[F^2 > 2\sigma(F^2)] = 0.042 \]

\[ wR(F^2) = 0.117 \]
\[ S = 0.98 \]

4372 reflections
236 parameters

Primary atom site location: structure-invariant direct methods

Extinction correction: SHELXL,
\( F_c^* = kF_c[1 + 0.001x\pi F_c^2\lambda^3/\sin(2\theta)]^{1/4} \)

Refinement of \( F^2 \) against ALL reflections. The weighted R-factor \( wR \) and goodness of fit \( S \) are based on \( F^2 \), conventional R-factors \( R \) are based on \( F \), with \( F \) set to zero for negative \( F^2 \). The threshold expression of \( F^2 > 2\sigma(F^2) \) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on \( F^2 \) are statistically about twice as large as those based on \( F \), and R- factors based on ALL data will be even larger.

Table 2
Geometric parameters (Å, °) for 2p

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H6A—C6—H6C 109.5  C23—C18—C8  120.31 (11)
H6B—C6—H6C 109.5  C19—C18—C8  120.83 (11)
C3—C7—H7A 109.5  C20—C19—C18 120.27 (12)
C3—C7—H7B 109.5  C20—C19—H19  119.9
C3—C7—H7C 109.5  C21—C20—C19 120.18 (13)
H7A—C7—H7B 109.5  C18—C19—H19  119.9
C3—C7—H7B 109.5  C20—C19—H19  119.9
H7A—C7—H7C 109.5  C21—C20—H20  119.9
H7B—C7—H7C 109.5  C19—C20—H20  119.9
C1—C8—C18 113.49 (10)  C22—C21—C20 120.20 (12)
C1—C8—C9  106.54 (10)  C22—C21—H21  119.9
C18—C8—C9 111.81 (10)  C20—C21—H21  119.9
C1—C8—H8  108.3  C21—C22—C23  119.53 (13)
C18—C8—H8 108.3  C21—C22—H22  120.2
C9—C8—H8 108.3  C23—C22—H22  120.2
O16—C9—C10 112.39 (10)  C18—C23—C22 120.97 (13)
O16—C9—C8  106.38 (10)  C18—C23—H23  119.5
C10—C9—C8  111.55 (10)  C22—C23—H23  119.5
O16—C9—H9  108.8  C13—O24—C25  117.35 (11)
C8—C9—H9 108.8  O24—C25—H25B 109.5

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
rac-\((Z)\)-N-[(2R*, 3S*)-3-methoxy-2-methyl-3-phenylbutylidene]-2-methylpropan-2-amine oxide (2s)

**Crystal data**

C_{16}H_{25}NO_{2} \quad F_{0(00)} = 288

\( M_r = 263.37 \) \quad \( D_{\chi} = 1.152 \text{ Mg m}^{-3} \)

Triclinic, \( P\bar{1} \) \quad Melting point: 373 K

Hall symbol: -\( P\bar{1} \) \quad Mo K\( \alpha \) radiation

\( \lambda = 0.71073 \) Å

\( a = 5.9484 (2) \) Å \quad Cell parameters from 3400 reflections

\( b = 8.4271 (3) \) Å \quad \( \theta = 1\text{--}27.5^\circ \)

\( c = 15.9289 (5) \) Å \quad \( \mu = 0.08 \text{ mm}^{-1} \)

\( \alpha = 93.4557 (15)^\circ \) \quad \( T = 150 (2) \text{ K} \)

\( \beta = 95.3665 (18)^\circ \) \quad Cell measurement pressure: ? kPa

\( \gamma = 106.3773 (17)^\circ \) \quad Prism, colourless

\( V = 759.58 (4) \) Å

\( Z = 2 \)

**Data collection**

Nonius KappaCCD area detector diffractometer \quad 3462 independent reflections

Radiation source: fine-focus sealed tube \quad 3032 reflections with \( I > 2\sigma(I) \)

Monochromator: graphite \quad \( R_{\text{int}} = 0.024 \)

Detector resolution: 9.091 pixels mm\(^{-1} \) \quad \( \theta_{\text{max}} = 27.5^\circ \)

\( T = 150(2) \) K \quad \( \theta_{\text{min}} = 1.3^\circ \)

\( P = 101.3 \) kPa \quad \( h = -7 \text{--} 7 \)

\( \varphi \) and \( \omega \) scans to fill the Ewald sphere \quad \( k = -10 \text{--} 10 \)

Absorption correction: none \quad \( l = -20 \text{--} 20 \)

15912 measured reflections

**Refinement**

Refinement on \( F^2 \) \quad Secondary atom site location: difference Fourier map

Least-squares matrix: full \quad Hydrogen site location: difference Fourier map

\( R(F^2 > 2\sigma(F^2)) = 0.037 \) \quad H atoms treated by a mixture of independent and constrained refinement

\( wR(F^2) = 0.102 \) \quad \( w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.1937P] \)

\( S = 1.04 \) \quad where \( P = (F_o^2 + 2F_c^2)/3 \)

3462 reflections \quad (\Delta/\sigma)_{\text{max}} < 0.001

182 parameters \quad \Delta\rho_{\text{max}} = 0.27 \text{ e Å}^{-3}

\( \Delta\rho_{\text{min}} = -0.19 \text{ e Å}^{-3} \)

Extinction correction: none
Refinement of $F^2$ against ALL reflections. The weighted R-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional R-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on $F$, and R-factors based on ALL data will be even larger.

**Table 3**

Geometric parameters (Å, °) for 2s

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<thead>
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<th>Bond/Distance</th>
<th>Length (Å)</th>
<th>Bond/Distance</th>
<th>Length (Å)</th>
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C1—C8—C9  110.22 (8)  H18A—C18—H18C  109.5
C18—C8—C9  114.62 (8)  H18B—C18—H18C  109.5
C1—C8—H8  106.7  C9—C19—H19A  109.5
C18—C8—H8  106.7  C9—C19—H19B  109.5
C9—C8—H8  106.7  H19A—C19—H19B  109.5
O16—C9—C19  110.57 (8)  C9—C19—H19C  109.5
O16—C9—C10  110.59 (8)  H19A—C19—H19C  109.5
C19—C9—C10  113.19 (8)  H19B—C19—H19C  109.5
O16—C9—C8  102.59 (7)

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Data collection:
(2m)  COLLECT (Hooft, 1998) and DENZO (Otwinowski & Minor, 1997)
(2p)  COLLECT (Hooft, 1998) and DENZO (Otwinowski & Minor, 1997)
(2s)  COLLECT (Hooft, 1998) and DENZO (Otwinowski & Minor, 1997)

Cell refinement:
(2m)  COLLECT and DENZO
(2p)  COLLECT and DENZO
(2s)  COLLECT and DENZO

Data reduction:
(2m)  COLLECT and DENZO
(2p)  COLLECT and DENZO
(2s)  COLLECT and DENZO

Program(s) used to solve structure:
(2m)  SIR92 (Altomare et al., 1994)
(2p)  SIR92 (Altomare et al., 1994)
SIR92 (Altomare et al., 1994)

Program(s) used to refine structure:

SHELXL97 (Sheldrick, 1997)

Molecular graphics:

Platon (Speck, 2001)

References


Spectral data for new products (\textsuperscript{1}H and \textsuperscript{13}C in CDCl\textsubscript{3} / C\textsubscript{6}H\textsubscript{6})
Supplementary Material (ESI) for Chemical Communications

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- S60 -