

## 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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## Instrumentation and Materials

NMR spectra were recorded on **Bruker Avance I<sup>TM</sup> 400** (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C) spectrometer in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub>. Chemical shifts were reported as δ scale in ppm relative to SiMe<sub>4</sub> (δ = 0) as an internal standard for <sup>1</sup>H NMR and to CDCl<sub>3</sub> (δ = 77.16) or C<sub>6</sub>D<sub>6</sub> (δ = 128.06) for <sup>13</sup>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.

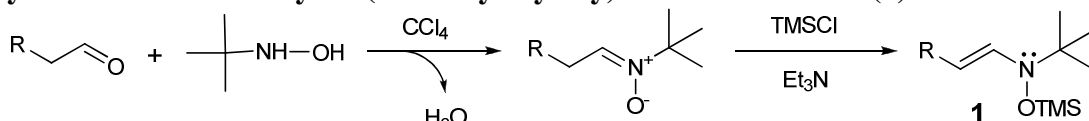
Syntheses of the products **1** and **2** were carried out in the atmosphere of dry argon in glassware dried by heat-gun under vacuum shortly before the experiments. The following solvents were refluxed and distilled over drying reagents before use: CH<sub>2</sub>Cl<sub>2</sub> over CaH<sub>2</sub>, CCl<sub>4</sub> and hexane over P<sub>2</sub>O<sub>5</sub>, 1,2-dimethoxyethane over Na/K alloy with Ph<sub>2</sub>C=O added to form a deep-blue ketyl solution. MeOH was dried by distilling from Mg(OMe)<sub>2</sub> 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 acetals and ketals were obtained from commercial suppliers and distilled before use. Dimethyl acetals and ketals were prepared according to the literature procedure<sup>[1]</sup>. Trimethylsilyl trifluoromethanesulfonate (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<sup>[2]</sup> and isolated by saponification of its benzoyl derivative followed by filtration, saturation of the aqueous phase with NaCl, extraction with ether, drying (Na<sub>2</sub>SO<sub>4</sub>), filtration and removal of Et<sub>2</sub>O at 400 mbar to give Me<sub>3</sub>CNHOH (68% yield) as white crystalline solid. Trimethyl orthoformate, triethylamine, *tert*-butyl methyl ether, benzyl peroxide (75%, remainder H<sub>2</sub>O), K<sub>3</sub>PO<sub>4</sub>·H<sub>2</sub>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<sub>3</sub>N in hexane prior to the chromatographic purifications.

## General Procedures (GP)

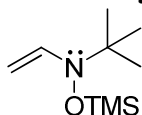
### GP1: Synthesis of *N-tert-butyl-N-(trimethylsilyloxy)alk-1-en-1-amines (1)*



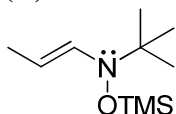
- 1a:** R = H  
**1b:** R = Me  
**1c:** R = *n*-C<sub>5</sub>H<sub>11</sub>  
**1d:** R = Ph  
**1e:** R = *rac*-Ph(Me)CH

An aldehyde (1.2–1.3 equiv.) was added to an ice-cooled solution of Me<sub>3</sub>CNHOH (1 equiv.) in CCl<sub>4</sub> (1 mL per 2 mmol Me<sub>3</sub>CNHOH). The mixture was stirred at room temperature for 1 h, whereupon anhydrous MgSO<sub>4</sub> was added, and stirring was continued for another 15–20 min before MgSO<sub>4</sub> was filtered off and rinsed with a small portion of CCl<sub>4</sub>. The combined filtrate containing the intermediate aldonitronium<sup>[3]</sup> was cooled to 0°C under argon atmosphere, whereupon TMSCl (1.5 equiv.) and Et<sub>3</sub>N (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 (Na<sub>2</sub>SO<sub>4</sub>), 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 CH<sub>2</sub>Cl<sub>2</sub> with equal efficiency.

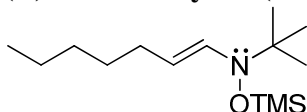
### *N-tert-butyl-N-(trimethylsilyloxy)ethenamine (1a)*



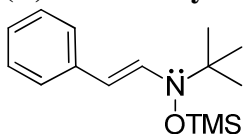
The titled compound was prepared from 5.3 g (60 mmol) of Me<sub>3</sub>CNHOH according to the **GP1**. Silylation reaction time was 80 min at r.t. Distillation at 65–67°C (30 mbar) afforded **1a** as a Colourless liquid (10.4 g, 94% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.30 (1H, dd, <sup>3</sup>J = 14.7 and 8.8 Hz, =CHN), 4.42 (1H, dd, <sup>3</sup>J = 14.7 Hz, <sup>2</sup>J = 0.6 Hz, CH<sub>2</sub>=), 4.20 (1H, dd, <sup>3</sup>J = 8.8 Hz, <sup>2</sup>J = 0.6 Hz, CH<sub>2</sub>=), 1.13 (9H, s, CMe<sub>3</sub>), 0.16 (9H, s, SiMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>[4]</sup>.

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

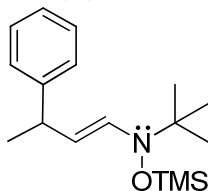
The titled compound was prepared from 3 g (33.6 mmol) of Me<sub>3</sub>CNHOH according to the **GP1**. Silylation reaction time was 5 h at r.t. Distillation at 73–75°C (20 mbar) afforded **1b** as a Colourless liquid (6.4 g, 95% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.96 (1H, dq, <sup>3</sup>J = 13.2 Hz, <sup>4</sup>J = 1.4 Hz, =CHN), 5.01 (1H, dq, <sup>3</sup>J = 13.2 and 6.7 Hz, MeCH=), 1.64 (3H, dd, <sup>3</sup>J = 6.7 Hz, <sup>4</sup>J = 1.4 Hz, MeCH=), 1.09 (9H, s, CMe<sub>3</sub>), 0.13 (9H, s, SiMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 136.94, 108.04, 59.84, 26.29, 15.13, 0.28. 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 C<sub>10</sub>H<sub>23</sub>NOSi [M<sup>+</sup>] 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 Me<sub>3</sub>CNHOH 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). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.96 (1H, d, <sup>3</sup>J = 13.2 Hz, =CHN), 5.02 (1H, dt, <sup>3</sup>J = 13.2 and 7.3 Hz, CH<sub>2</sub>CH=), 1.99 (2H, q, *J* = 7.2 Hz, CH<sub>2</sub>CH=), 1.41–1.25 (6H, m, 3 CH<sub>2</sub>), 1.11 (9H, s, CMe<sub>3</sub>), 0.90 (3H, t, *J* = 6.9 Hz, Me), 0.15 (9H, s, SiMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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 C<sub>14</sub>H<sub>31</sub>NOSi [M<sup>+</sup>] 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 Me<sub>3</sub>CNHOH according to the **GP1** except that TMSCl (2 equiv.) and Et<sub>3</sub>N (3 equiv.) were employed in order to achieve complete conversion of the intermediate nitron. 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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 (5H, s, Ph), 6.84 (1H, d, <sup>3</sup>J = 13.5 Hz, PhCH=), 5.95 (1H, d, <sup>3</sup>J = 13.5 Hz, =CHN), 1.20 (9H, s, CMe<sub>3</sub>), 0.20 (9H, s, SiMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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 C<sub>15</sub>H<sub>25</sub>NOSi [M<sup>+</sup>] 263.1705, found 263.1695.

***rac*-(*E*)-*N*-*tert*-butyl-*N*-(trimethylsilyloxy)-3-phenylbut-1-en-1-amine (**1e**)**

The titled compound was prepared from 2 g (22.4 mmol) of Me<sub>3</sub>CNHOH 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). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>H<sub>6</sub>) δ 7.23–7.15 (4H, m, CH<sub>o,m</sub>) and 7.06 (1H, m<sub>c</sub>, CH<sub>p</sub>), 6.02 (1H, d, <sup>3</sup>J = 13.2 Hz, =CHN), 5.45 (1H, dd, <sup>3</sup>J = 13.2 and 7.5 Hz, CH=), 3.39 (1H, quint, <sup>3</sup>J = 7.1 Hz) 1.33 (3H, d, J = 7.0 Hz), 1.09 (9H, s, CMe<sub>3</sub>), 0.18 (9H, s, SiMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>H<sub>6</sub>) 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 C<sub>17</sub>H<sub>29</sub>NOSi [M<sup>+</sup>] 291.2018, found 291.2090.

**Synthesis and attempted reactions with dibenzyl acetals and ketals**

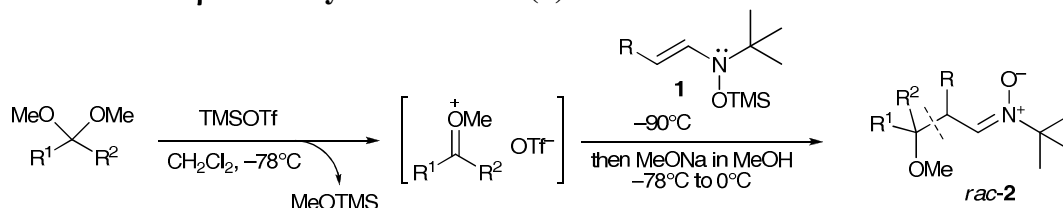
2,2-dibenzylxypropane was prepared by combining dimethoxypropane (16 g, 150 mmol), benzyl alcohol (45.6 g, 430 mmol), and TsOH·H<sub>2</sub>O (10 mg) in benzene (50 mL) followed by slow distillation at atmospheric pressure until the temperature of the distillate rose to 64°C and bath temperature to 122°C. 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 Me<sub>2</sub>(OCH<sub>2</sub>Ph)<sub>2</sub> 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·H<sub>2</sub>O (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(CH<sub>2</sub>)<sub>5</sub>CH(OCH<sub>2</sub>Ph)<sub>2</sub> was obtained by distillation (193°C / 0.28 mbar) as colourless liquid (9.6 g, 97%).

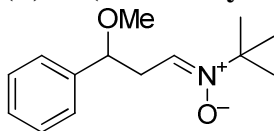
Attempts to prepare propiophenone dibenzyl ketal from propiophenone dimethyl ketal and benzyl alcohol as described above were unsuccessful, resulting in the parent propiophenone. Room-temperature stirring of PhC(OMe)<sub>2</sub>Et with PhCH<sub>2</sub>OH and catalytic TsOH (7 mbar, overnight) led to a mixture of the desired PhC(OCH<sub>2</sub>Ph)<sub>2</sub>Et and propiophenone (1.2:1).

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

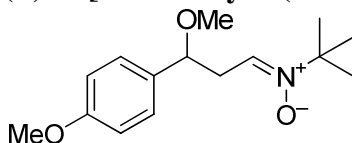
Attempts to react heptaldehyde dibenzyl acetal with the enamines **1b** or **1d** under the standard conditions (**GP2**) yielded mixtures of the essentially intact dibenzyl acetal with the parent *N*-*tert*-butyl nitrones.

**GP2: Synthesis of *rac*- $\beta$ -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 CH<sub>2</sub>Cl<sub>2</sub> (8 mL) at  $-78^{\circ}\text{C}$  (bath temperature), and the resulting mixture was stirred for 30 min. It was then cooled down to  $-90^{\circ}\text{C}$ , 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  $-78^{\circ}\text{C}$  and stirred for additional 45 min (TLC control) while maintaining the temperature at  $-78^{\circ}\text{C}$ . After quenching by dropwise addition of MeONa (2.0 mmol, 1.1 equiv.) in MeOH (2M) 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 (Na<sub>2</sub>SO<sub>4</sub>), filtered, the volatiles were removed in vacuum and the residue was purified by column chromatography to afford the pure product **2**. Most of the  $\beta$ -methoxy aldonitrones **2** are bench stable compounds. However all the samples were routinely stored in a fridge at  $4^{\circ}\text{C}$ . For the diastereomeric ratios of **2**, see Table 1.

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

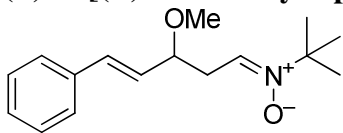
The titled compound was prepared according to the **GP2**. **2a**, colourless oil, yield 0.451 g (96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 (5H, m, Ph), 6.90 (1H, t,  $J = 5.5$  Hz, CH=N), 4.52 (1H, t,  $J = 6.6$  Hz, CHOMe), 3.25 (3H, s, OMe), 2.88 (2H, t,  $J = 5.7$  Hz, CH<sub>2</sub>), 1.46 (9H, s, CMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.31, 131.62, 128.62, 127.96, 126.42, 79.91, 69.30, 56.86, 35.69, 28.09. HRMS (ESI) Calcd for (C<sub>14</sub>H<sub>21</sub>NO<sub>2</sub> + Na)<sup>+</sup>: 258.1470 found 258.1465. Elemental analysis calcd (%) for C<sub>14</sub>H<sub>21</sub>NO<sub>2</sub>: C 71.46, H 8.99, N 5.95; found: C 71.30, H 9.04, N 5.80. FTIR (neat, cm<sup>-1</sup>):  $\nu_{\text{C-O}}$  1096,  $\nu_{\text{N-O}}$  1454,  $\nu_{\text{C=N}}$  1583.

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

The titled compound was prepared according to the **GP2**. **2b**, colourless oil, yield 0.450 g (85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 (2H, d,  $J = 8.6$  Hz, CH<sub>Arl</sub>), 6.89 (3H, m, CH<sub>Arl</sub> + CH=N), 4.46 (1H, t,  $J = 6.4$  Hz, CHOMe), 3.80 (3H, s, C<sub>Arl</sub>OMe), 3.22 (3H, s, CHOMe), 2.87 (2H, m, CH<sub>2</sub>), 1.46 (9H, s, CMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.38, 133.29, 131.17, 127.65, 113.98, 79.44, 69.22, 56.56, 55.62, 35.63, 28.08. HRMS (ESI) Calcd for (C<sub>14</sub>H<sub>21</sub>NO<sub>2</sub> + Na)<sup>+</sup>: 288.1576 found 288.1571.

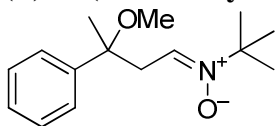
Elemental analysis calcd (%) for  $C_{15}H_{23}NO_2$ : C 67.90, H 8.74, N 5.28; found: C 67.47, H 8.53, N 5.17. FTIR (neat,  $cm^{-1}$ ):  $\nu_{C-O}$  1167,  $\nu_{N-O}$  1508,  $\nu_{C=N}$  1669.

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



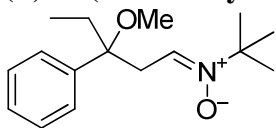
The compound was prepared according to the **GP2**. Yellow oil, yield 0.511 g (98%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.35 (5H, m, Ph), 6.97 (1H, t,  $^3J = 5.5$  Hz,  $CH=N$ ), 6.62 (1H, d,  $^3J = 15.9$  Hz,  $PhCH=$ ), 6.10 (1H, dd,  $^3J = 15.9$  and  $7.5$  Hz,  $=CH$ ), 4.10 (1H, m<sub>c</sub>,  $CHOMe$ ), 3.36 (3H, s, OMe), 2.85 (1H, dt,  $^2J = 16.9$  Hz,  $^3J_t = 5.6$  Hz,  $CH_AH_B$ ), 2.80 (1H, ddd,  $^2J = 16.9$  Hz,  $^3J = 7.3$  and  $5.4$  Hz,  $CH_AH_B$ ), 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)**

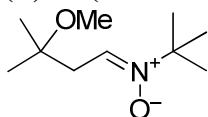


The compound was prepared according to the **GP2**. Colourless oil, yield 0.453 g (91%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.36 (4H, m,  $CH_{o,m}$ ), 7.24 (1H, m<sub>c</sub>,  $CH_p$ ), 6.89 (1H, t,  $J = 5.3$  Hz,  $CH=N$ ), 3.12 (3H, s, OMe), 3.03 (2H, dd,  $J = 5.7$  and  $4.7$  Hz), 1.57 (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.

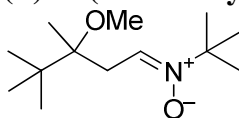
**(Z)-N-(3-methoxy-3-phenylpentylidene)-2-methylpropan-2-amine oxide (2e)**



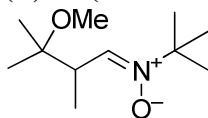
The compound was prepared according to the **GP2**. Colourless oil, yield 0.415 g (79%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.35 (4H, m,  $CH_{o,m}$ ), 7.25 (1H, m<sub>c</sub>,  $CH_p$ ), 6.79 (1H, t,  $J = 5.2$  Hz,  $CH=N$ ), 3.20 (1H, dd,  $^2J = 18.6$  Hz,  $^3J = 5.2$  Hz,  $CH_AH_BCH=N$ ), 3.15 (3H, s, OMe), 3.06 (1H, dd,  $^2J = 18.6$  Hz,  $J = 5.3$  Hz,  $CH_AH_BCH=N$ ), 1.94 (1H, dq,  $^2J = 14.3$  Hz,  $J = 7.0$  Hz,  $CH_AH_BMe$ ), 1.82 (1H, dq,  $^2J = 14.3$  Hz,  $^3J = 7.0$  Hz,  $CH_AH_BMe$ ), 1.42 (9H, s,  $CMe_3$ ), 0.69 (3H, t,  $J = 7.3$  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.

**(Z)-N-(3-methoxy-3-methylbutylidene)-2-methylpropan-2-amine oxide (2f)**

The compound was prepared according to the **GP2**. Yellow oil, yield 0.274 g (73%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.97 (1H, t,  $J = 5.4$  Hz,  $\text{CH}=\text{N}$ ), 3.20 (1H, s, OMe), 2.71 (2H, d,  $J = 5.4$  Hz,  $\text{CH}_2$ ), 1.51 (9H, s,  $\text{CMe}_3$ ), 1.23 (6H, s,  $\text{CMe}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  131.60, 73.77, 69.31, 39.54, 37.29, 28.17, 25.47. HRMS (ESI) Calcd for  $(\text{C}_{10}\text{H}_{21}\text{NO}_2 + \text{Na})^+$ : 210.1470 found 210.1465. Elemental analysis calcd (%) for  $\text{C}_{10}\text{H}_{21}\text{NO}_2$ : C 64.13, H 11.30, N 7.48; found: C 63.95, H 11.40, N 7.28. FTIR (neat,  $\text{cm}^{-1}$ ):  $\nu_{\text{C-O}}$  1110,  $\nu_{\text{N-O}}$  1441,  $\nu_{\text{C=N}}$  1672.

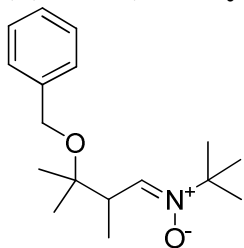
**(Z)-N-(3-methoxy-3,4,4-trimethylpentylidene)-2-methylpropan-2-amine oxide (2g)**

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

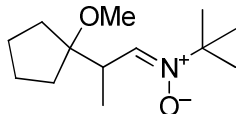
**(Z)-N-(3-methoxy-2,3-dimethylbutylidene)-2-methylpropan-2-amine oxide (2h)**

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

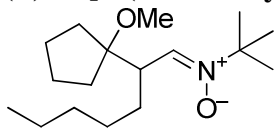


**(Z)-N-[3-(1-benzyloxy)-2,3dimethylbutylidene]-2-methylpropan-2-amine oxide (2h')**

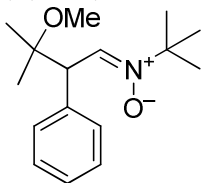
The compound was prepared according to the **GP2**. Drying at 45°C in high vacuum (0.02 mbar) with vigorous magnetic stirring afforded **2h'** (0.538 g, 97% yield) as a slightly yellowish oil (contains trace amount of benzyl alcohol); decomposes on silica gel. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.16 (1H, s, Ph), 6.79 (1H, d, *J* = 7.7 Hz, CH=N), 4.30 (1H, d, <sup>2</sup>*J* = 11.5 Hz, PhCH<sub>2</sub>O), 4.28 (1H, d, <sup>2</sup>*J* = 11.5 Hz, PhCH<sub>2</sub>O), 3.30 (1H, quint, *J* = 7 Hz, CHCH<sub>3</sub>), 1.32 (9H, s, CMe<sub>3</sub>), 1.14 (3H, s, Me), 1.11 (3H, s, Me), 0.98 (3H, d, *J* = 7.0 Hz, CHCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 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]<sup>+</sup>, 222 [(M+H) – CH<sub>2</sub>=CMe<sub>2</sub>]<sup>+</sup>, 170 [(M+H) – PhCH<sub>2</sub>OH]<sup>+</sup>. Elemental analysis calcd (%) for C<sub>17</sub>H<sub>27</sub>NO<sub>2</sub>: C 73.61, H 9.81, N 5.05; found: C 73.40, H 9.81, N 4.90. FTIR (neat, cm<sup>-1</sup>): ν<sub>C-O</sub> 1083, ν<sub>N-O</sub> 1450, ν<sub>C=N</sub> 1576.

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

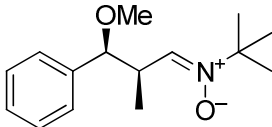
The compound was prepared according to the **GP2**. Colourless oil, yield 0.404 g (89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.79 (1H, d, *J* = 7.7 Hz, CH=N), 3.61 (1H, m, CHMe), 3.17 (3H, s, OMe), 1.89–1.65 (4H, m, 2CH<sub>2</sub>=C), 1.63–1.44 (4H, m, 2CH<sub>2</sub>CH<sub>2</sub>) (9H, s, CMe<sub>3</sub>), 1.08 (3H, d, *J* = 6.9 Hz, CHMe). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 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<sub>13</sub>H<sub>25</sub>NO<sub>2</sub> + Na)<sup>+</sup>: 250.1783 found 250.1778. Elemental analysis calcd (%) for C<sub>13</sub>H<sub>25</sub>NO<sub>2</sub>: C 68.68, H 11.08, N 6.16; found: C 68.35, H 11.02, N 6.04. FTIR (neat, cm<sup>-1</sup>): ν<sub>C-O</sub> 1074, ν<sub>N-O</sub> 1458, ν<sub>C=N</sub> 1573.

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

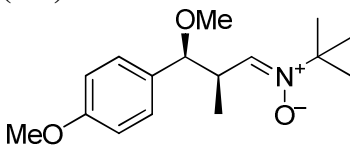
The compound was prepared according to the **GP2**. Waxy solid, yield 0.532 g (94%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.67 (1H, d, *J* = 8.4 Hz, CH=N), 3.66 (1H, dt, *J* = 8.6 and 3.1 Hz, CH<sub>C</sub>), 3.19 (3H, s, OMe), 1.92–1.51 (8H, m, 4=CH<sub>2</sub>cyclic), 1.50 (9H, s, CMe<sub>3</sub>), 1.45–1.15 (8H, m, CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>=), 0.86 (3H, t, *J* = 6.9 Hz, Me). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 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<sub>17</sub>H<sub>33</sub>NO<sub>2</sub> + Na)<sup>+</sup>: 306.2409 found 306.2404. Elemental analysis calcd (%) for C<sub>17</sub>H<sub>33</sub>NO<sub>2</sub>: C 72.03, H 11.73, N 4.94; found: C 72.20, H 11.68, N 4.82. FTIR (neat, cm<sup>-1</sup>): ν<sub>C-O</sub> 1111, ν<sub>N-O</sub> 1455, ν<sub>C=N</sub> 1571.

**(Z)-N-(3-methoxy-3-methyl-2-phenylbutylidene)-2-methylpropan-2-amine oxide (2k)**

The compound was prepared according to the **GP2**. White solid (mp. 99°C), yield 0.378 g (72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 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<sub>3</sub>), 1.22 (3H, s, CH<sub>3</sub>C), 1.04 (3H, s, CH<sub>3</sub>C). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 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<sub>16</sub>H<sub>25</sub>NO<sub>2</sub> + Na)<sup>+</sup>: 286.1783 found 286.1778. Elemental analysis calcd (%) for C<sub>16</sub>H<sub>25</sub>NO<sub>2</sub>: C 72.96, H 9.57, N 5.32; found: C 72.83, H 9.60, N 5.21. FTIR (neat, cm<sup>-1</sup>): ν<sub>C-O</sub> 1064, ν<sub>N-O</sub> 1454, ν<sub>C=N</sub> 1567.

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

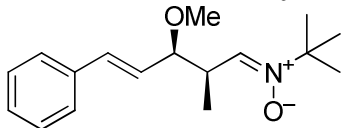
The compound was prepared according to the **GP2**. Waxy solid, yield 0.473 g (95%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ Major *syn*-diastereomer (shown) 7.33 (5H, m, Ph), 6.77 (1H, d, *J* = 7 Hz, CH=N), 4.55 (1H, dd, *J* = 4.5 and 0.9 Hz, =CHOMe), 3.34 (1H, m, CH<sub>3</sub>CH=), 3.26 (3H, s, OMe), 1.44 (9H, s, CMe<sub>3</sub>), 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<sub>3</sub>CH=), 3.27 (3H, s, OMe), 1.05 (3H, d, *J* = 6.1 Hz, Me). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 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 <sup>1</sup>H and <sup>13</sup>C NMR peaks of minor diastereomer are not observed due to overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C<sub>15</sub>H<sub>23</sub>NO<sub>2</sub> + Na)<sup>+</sup>: 272.1626 found 272.1621. Elemental analysis calcd (%) for C<sub>15</sub>H<sub>23</sub>NO<sub>2</sub>: C 72.25, H 9.30, N 5.62; found: C 72.00, H 9.37, N 5.51. FTIR (neat, cm<sup>-1</sup>): ν<sub>C-O</sub> 1099, ν<sub>N-O</sub> 1453, ν<sub>C=N</sub> 1575.

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

The compound was prepared according to the **GP2**. White solid (mp. 98°C), yield 0.546 g (98%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ Major *syn*-diastereomer (shown) 7.25 (2H, d, *J* = 8.5 Hz, CH<sub>Arl</sub>), 6.88 (2H, d, *J* = 8.5 Hz, CH<sub>Arl</sub>), 6.74 (1H, d, *J* = 7.1 Hz, CH=N), 4.46 (1H, d, *J* = 4.8 Hz, =CHOMe), 3.80 (3H, s, C<sub>Arl</sub>OMe), 3.33 (1H, m, =CHCH<sub>3</sub>), 3.23 (3H, s, CHOMe), 1.43 (9H, s, CMe<sub>3</sub>), 1.03 (3H, d, *J* = 7 Hz, Me). Minor *anti*-diastereomer 7.15 (2H, d, *J* = 8.5 Hz, CH<sub>Arl</sub>), 4.28 (1H, d, *J* = 6.2 Hz, =CHOMe), 3.44 (1H, m, =CHCH<sub>3</sub>), 1.45 (9H, s, CMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 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,

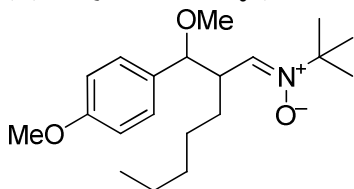
11.17. Minor *anti*-diastereomer 159.18, 128.16, 83.90, 56.82, 38.10, 28.05, 12.37. Other  $^1\text{H}$  and  $^{13}\text{C}$  NMR peaks of minor diastereomer are not observed due to overlap with those of the major diastereomer. HRMS (ESI) Calcd for  $(\text{C}_{16}\text{H}_{25}\text{NO}_2 + \text{Na})^+$ : 302.1732 found 302.1727. Elemental analysis calcd (%) for  $\text{C}_{16}\text{H}_{25}\text{NO}_2$ : C 68.79, H 9.02, N 5.01; found: C 68.75, H 9.07, N 4.93. FTIR (neat,  $\text{cm}^{-1}$ ):  $\nu_{\text{C-O}}$  1094,  $\nu_{\text{N-O}}$  1509,  $\nu_{\text{C=N}}$  1608.

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

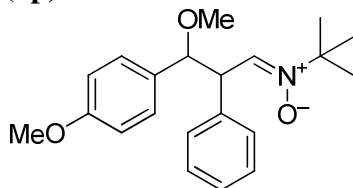


The compound was prepared according to the **GP2**. Yellow oil, yield 0.539 g (98%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  Major *syn*-diastereomer (shown) 7.31 (5H, m, Ph), 6.78 (1H, d,  $J = 7.1$  Hz,  $\text{CH=N}$ ), 6.60 (1H, d,  $J = 15.9$  Hz,  $\text{PhCH=}$ ), 6.15 (1H, dd,  $J = 15.9$  and 7.5 Hz,  $=\text{CH}$ ), 4.00 (1H, ddd,  $^3J = 7.4$  and 4.9 Hz,  $^4J = 0.9$  Hz,  $\text{CHOMe}$ ), 3.35 (1H, m,  $=\text{CHCH}_3$ ), 3.31 (3H, s,  $\text{OMe}$ ), 1.46 (9H, s,  $\text{CMe}_3$ ), 1.16 (3H, d,  $J = 7$  Hz,  $\text{Me}$ ). 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,  $^3J = 7.6$  and 5.2 Hz,  $^4J = 0.8$  Hz,  $\text{CHOMe}$ ), 3.44 (1H, m,  $=\text{CHCH}_3$ ), 1.47 (9H, s,  $\text{CMe}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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, 126.67, 82.97, 56.86, 36.39, 28.11, 12.52. Other  $^1\text{H}$  and  $^{13}\text{C}$  NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer. HRMS (ESI) Calcd for  $(\text{C}_{17}\text{H}_{25}\text{NO}_2 + \text{Na})^+$ : 298.1783 found 298.1778. Elemental analysis calcd (%) for  $\text{C}_{17}\text{H}_{25}\text{NO}_2$ : C 74.14, H 9.15, N 5.09; found: C 73.95, H 9.16, N 5.00. FTIR (neat,  $\text{cm}^{-1}$ ):  $\nu_{\text{C-O}}$  1096,  $\nu_{\text{N-O}}$  1494,  $\nu_{\text{C=N}}$  1670.

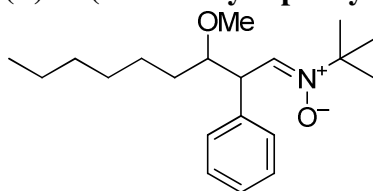
**(Z)-N-{2-[methoxy(4-methoxyphenyl)methyl]heptylidene}-2-methylpropan-2-amine oxide (2o)**



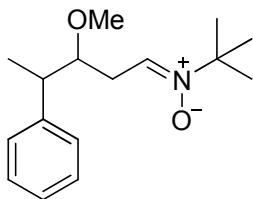
The compound was prepared according to the **GP2**. Waxy solid, yield 0.643 g (96%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  Major diastereomer 7.15 (2H, d,  $J = 8.6$  Hz,  $\text{CH}_{\text{Arl}}$ ), 6.87 (2H, d,  $J = 8.6$  Hz,  $\text{CH}_{\text{Arl}}$ ), 6.68 (1H, d,  $J = 7.1$  Hz,  $\text{CH=N}$ ), 4.41 (1H, d,  $J = 5$  Hz,  $=\text{CHOMe}$ ), 3.81 (3H, s,  $\text{C}_{\text{Arl}}\text{OMe}$ ), 3.31 (1H, m,  $=\text{CHCH}_2$ ), 3.22 (3H, s,  $\text{CHOMe}$ ), 1.52 (2H, m,  $\text{CHCH}_2=$ ), 1.43 (9H, s,  $\text{CMe}_3$ ), 1.30–1.10 (6H, m,  $\text{CH}_3(\text{CH}_2)_3=$ ), 0.82 (3H, t,  $J = 6.9$  Hz,  $\text{Me}$ ). Minor diastereomer 7.27 (2H, d,  $J = 8.6$  Hz,  $\text{CH}_{\text{Arl}}$ ), 6.69 (1H, d,  $J = 7.3$  Hz,  $\text{CH=N}$ ), 4.52 (1H, d,  $J = 5.2$  Hz,  $=\text{CHOMe}$ ), 3.80 (3H, s,  $\text{C}_{\text{Arl}}\text{OMe}$ ), 3.26 (3H, s,  $\text{CHOMe}$ ), 1.44 (9H, s,  $\text{CMe}_3$ ), 0.87 (3H, t,  $J = 7.2$  Hz,  $\text{Me}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $^1\text{H}$  and  $^{13}\text{C}$  NMR peaks of minor diastereomer are not observed due to overlap with those of the major diastereomer. HRMS (ESI) Calcd for  $(\text{C}_{20}\text{H}_{33}\text{NO}_2 + \text{Na})^+$ : 358.2358 found 358.2353. Elemental analysis calcd (%) for  $\text{C}_{20}\text{H}_{33}\text{NO}_2$ : C 71.60, H 9.91, N 4.18; found: C 71.50, H 10.00, N 4.20. FTIR (neat,  $\text{cm}^{-1}$ ):  $\nu_{\text{C-O}}$  1091,  $\nu_{\text{N-O}}$  1510,  $\nu_{\text{C=N}}$  1610.

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

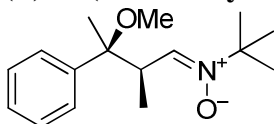
The compound was prepared according to the **GP2**. White solid (mp.134°C), yield 0.552 g (81%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ Major diastereomer 7.21 (3H, m, CH<sub>m,p</sub>), 7.14 (2H, m, CH<sub>o</sub>), 7.08 (1H, d, *J* = 7.2 Hz, CH<sub>Arl</sub>), 7.01 (2H, d, *J* = 8.4 Hz, CH<sub>Arl</sub>), 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, C<sub>Arl</sub>OMe), 3.18 (3H, s, CHOMe), 1.41 (9H, s, CMe<sub>3</sub>). Minor diastereomer 3.77 (3H, s, C<sub>Arl</sub>OMe), 3.22 (3H, s, CHOMe), 1.44 (9H, s, CMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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 <sup>1</sup>H and <sup>13</sup>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<sub>21</sub>H<sub>27</sub>NO<sub>2</sub> + Na)<sup>+</sup>: 364.1889 found 364.1884. Elemental analysis calcd (%) for C<sub>21</sub>H<sub>27</sub>NO<sub>2</sub>: C 73.87, H 7.97, N 4.10; found: C 73.85, H 7.92, N 4.15. FTIR (neat, cm<sup>-1</sup>): ν<sub>C=O</sub> 1094, ν<sub>N-O</sub> 1455, ν<sub>C=N</sub> 1598.

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

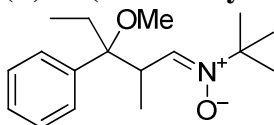
The compound was prepared according to the **GP2**. Colourless oil, yield 0.503 g (79%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ Major diastereomer 7.37 (5H, m), 7.16 (1H, d, *J* = 6.8 Hz, CH=N), 4.39 (1H, dd, *J* = 6.8 and 4.0 Hz, PhCH), 3.82 (1H, m, CHOMe), 3.36 (3H, s, OMe), 1.50 (9H, s, CMe<sub>3</sub>), 1.38 (2H, m, CH<sub>2</sub>CH), 1.21(8H, m, CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>), 0.84 (3H, t, *J* = 6.9 Hz, Me). Minor diastereomer 7.11 (1H, d, *J* = 6.8 Hz, CH=N), 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, CMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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 <sup>1</sup>H and <sup>13</sup>C NMR peaks of minor diastereomer are not observed due to overlap with those of the major diastereomer. HRMS (ESI) Calcd for (C<sub>20</sub>H<sub>33</sub>NO<sub>2</sub> + Na)<sup>+</sup>: 342.2409 found 342.2404. Elemental analysis calcd (%) for C<sub>20</sub>H<sub>33</sub>NO<sub>2</sub>: C 75.19, H 10.41, N 4.38; found: C 74.92, H 10.11, N 4.40. FTIR (neat, cm<sup>-1</sup>): ν<sub>C=O</sub> 1089, ν<sub>N-O</sub> 1496, ν<sub>C=N</sub> 1685.

**(Z)-N-(3-methoxy-4-phenylpentylidene)-2-methylpropan-2-amine oxide (2r)**

The compound was prepared according to the **GP2**. Colourless oil, yield 0.441 g (84%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  Major diastereomer 7.28 (5H, m, Ph), 6.67 (1H, t,  $J = 5.4$  Hz,  $\text{CH}=\text{N}$ ), 3.66 (1H, dt,  $J = 6.5$  Hz and 5.3 Hz,  $\text{CHOMe}$ ), 3.31 (3H, s,  $\text{OMe}$ ), 2.98 (1H, m,  $\text{CHCH}_3$ ), 2.74–2.54 (2H, m), 1.39 (9H, s,  $\text{CMe}_3$ ), 1.31 (3H, d,  $J = 7.1$  Hz,  $\text{Me}$ ). Minor diastereomer 7.20 (5H, m, Ph), 6.44 (1H, t,  $J = 5.6$  Hz,  $\text{CH}=\text{N}$ ), 3.57 (1H, dt,  $J = 7.3$  Hz and 5.8 Hz,  $\text{CHOMe}$ ), 3.43 (3H, s,  $\text{OMe}$ ), 2.88 (1H, m,  $\text{CHCH}_3$ ), 1.35 (9H, s,  $\text{CMe}_3$ ), 1.31 (3H, d,  $J = 7.1$  Hz,  $\text{Me}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $^1\text{H}$  NMR peaks of minor diastereomer are not observed due to overlap with those of the major diastereomer. HRMS (ESI) Calcd for  $(\text{C}_{16}\text{H}_{25}\text{NO}_2 + \text{Na})^+$ : 286.1783 found 286.1778. Elemental analysis calcd (%) for  $\text{C}_{16}\text{H}_{25}\text{NO}_2$ : C 72.96, H 9.57, N 5.32; found: C 72.62, H 9.42, N 5.16. FTIR (neat,  $\text{cm}^{-1}$ ):  $\nu_{\text{C-O}}$  1088,  $\nu_{\text{N-O}}$  1480,  $\nu_{\text{C=N}}$  1579.

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

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

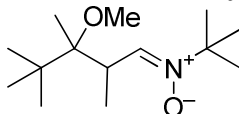
**(Z)-N-(3-methoxy-2-methyl-3-phenylpentylidene)-2-methylpropan-2-amine oxide (2t)**

The compound was prepared according to the **GP2**. Colourless oil, yield 0.509 g (92%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  Major diastereomer 7.37 (4H, m,  $\text{CH}_{o,m}$ ), 7.27 (1H, m,  $\text{CH}_p$ ), 6.70 (1H, d,  $J = 7.8$  Hz,  $\text{CH}=\text{N}$ ), 3.75 (1H, dq,  $J = 7.6$  and 7.1 Hz,  $\text{CH}_3\text{CH}$ ), 3.22 (3H, s,  $\text{OMe}$ ), 2.07 (2H, dq,  $^2J =$

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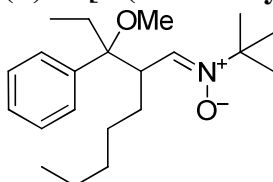
17.8,  $^3J = 7.5$  Hz,  $\text{CH}_3\text{CH}_A\text{H}_B$ ), 1.45 (9H, s,  $\text{CMe}_3$ ), 0.88 (3H, d,  $J = 7$  Hz,  $\text{CH}_3\text{CH}$ ), 0.84 (3H, t,  $J = 7.3$  Hz,  $\text{CH}_3\text{CH}_2$ ). Minor diastereomer 6.85 (1H, d,  $J = 7.7$  Hz,  $\text{CH}=\text{N}$ ), 3.91 (1H, dq,  $J = 8.2$  and 6.9 Hz,  $\text{CH}_3\text{CH}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $^1\text{H}$  and  $^{13}\text{C}$  NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer. HRMS (ESI) Calcd for  $(\text{C}_{17}\text{H}_{27}\text{NO}_2 + \text{Na})^+$ : 300.1939 found 300.1934. Elemental analysis calcd (%) for  $\text{C}_{17}\text{H}_{27}\text{NO}_2$ : C 73.61, H 9.81, N 5.05; found: C 73.41, H 9.752, N 4.85. FTIR (neat,  $\text{cm}^{-1}$ ):  $\nu_{\text{C-O}}$  1074,  $\nu_{\text{N-O}}$  1446,  $\nu_{\text{C=N}}$  1577.

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

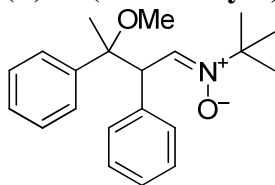


The compound was prepared according to the **GP2**. Colourless oil, yield 0.320 g (70%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  Major diastereomer 6.73 (1H, d,  $J = 8.5$  Hz,  $\text{CH}=\text{N}$ ), 3.73 (1H, dq,  $J = 8.5$  and 6.9 Hz,  $\text{CH}_3\text{CH}$ ), 3.30 (3H, s,  $\text{OMe}$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

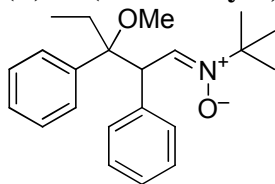
**(Z)-N-[2-(1-methoxy-1-phenylpropyl)heptylidene]-2-methylpropan-2-amine oxide (2v)**



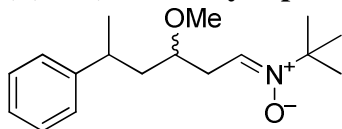
The compound was prepared according to the **GP2**. Colourless oil, yield 0.593 g (89%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  Major diastereomer 7.36 (4H, m,  $\text{CH}_{o,m}$ ), 7.25 (1H, m,  $\text{CH}_p$ ), 6.53 (1H, d,  $J = 8.1$  Hz,  $\text{CH}=\text{N}$ ), 3.82 (1H, dt,  $J = 8.8$  and 8.1 Hz,  $\text{CH}_2\text{CH}$ ), 3.24 (3H, s,  $\text{OMe}$ ), 2.09 (2H, q,  $J = 7.3$  Hz,  $\text{CH}_3\text{CH}_2$ ), 1.48 (9H, s,  $\text{CMe}_3$ ), 1.18–0.99 (8H, m,  $\text{CH}_3(\text{CH}_2)_4$ ), 0.80 (3H, t,  $J = 7.2$  Hz,  $\text{CH}_2\text{Me}$ ), 0.79 (3H, t,  $J = 5.4$  Hz,  $\text{Me}$ ). Minor diastereomer 6.16 (1H, d,  $J = 8.6$  Hz,  $\text{CH}=\text{N}$ ), 4.11 (1H, q,  $J = 7.1$  Hz,  $\text{CH}_2\text{CH}$ ), 3.28 (3H, s,  $\text{OMe}$ ), 1.87 (2H, q,  $J = 7.4$  Hz,  $\text{CH}_3\text{CH}_2$ ), 1.45 (9H, s,  $\text{CMe}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $^1\text{H}$  and  $^{13}\text{C}$  NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer. HRMS (ESI) Calcd for  $(\text{C}_{21}\text{H}_{35}\text{NO}_2 + \text{Na})^+$ : 356.2565 found 356.2560. Elemental analysis calcd (%) for  $\text{C}_{21}\text{H}_{35}\text{NO}_2$ : C 75.63, H 10.58, N 4.20; found: C 75.61, H 10.70, N 4.18. FTIR (neat,  $\text{cm}^{-1}$ ):  $\nu_{\text{C-O}}$  1106,  $\nu_{\text{N-O}}$  1459,  $\nu_{\text{C=N}}$  1573.

**(Z)-N-(3-methoxy-2,3-diphenylbutylidene)-2-methylpropan-2-amine oxide (2w)**

The compound was prepared according to the **GP2**. White solid (mp.136°C), yield 0.611 g (94%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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<sub>3</sub>C), 1.44 (9H, s, CMe<sub>3</sub>). Minor diastereomer 4.34 (1H, d, *J* = 7.5 Hz, PhCH), 3.19 (3H, s, OMe), 1.26 (9H, s, CMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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 <sup>13</sup>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<sub>21</sub>H<sub>27</sub>NO<sub>2</sub> + Na)<sup>+</sup>: 348.1939 found 348.1934. Elemental analysis calcd (%) for C<sub>21</sub>H<sub>27</sub>NO<sub>2</sub>: C 77.50, H 8.36, N 4.30; found: C 77.39, H 8.50, N 4.20. FTIR (neat, cm<sup>-1</sup>): ν<sub>C-O</sub> 1112, ν<sub>N-O</sub> 1450, ν<sub>C=N</sub> 1623.

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

The compound was prepared according to the **GP2**. White solid (mp.102°C), yield 0.630 g (93%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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, <sup>2</sup>*J* = 15.0 Hz, <sup>3</sup>*J* = 7.3 Hz, CH<sub>A</sub>H<sub>B</sub>Me), 1.95 (1H, dq, <sup>2</sup>*J* = 15.0 Hz, <sup>3</sup>*J* = 7.4 Hz, CH<sub>A</sub>H<sub>B</sub>Me), 1.43 (9H, s, CMe<sub>3</sub>), 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<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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 <sup>13</sup>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<sub>22</sub>H<sub>29</sub>NO<sub>2</sub> + Na)<sup>+</sup>: 362.2096 found 362.2091. Elemental analysis calcd (%) for C<sub>22</sub>H<sub>29</sub>NO<sub>2</sub>: C 77.84, H 8.61, N 4.13; found: C 77.70, H 8.81, N 4.19. FTIR (neat, cm<sup>-1</sup>): ν<sub>C-O</sub> 1076, ν<sub>N-O</sub> 1452, ν<sub>C=N</sub> 1572.

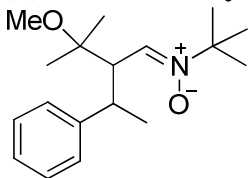
**(Z)-N-(3-methoxy-5-phenylhexylidene)-2-methylpropan-2-amine oxide (2y)**

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 <sup>1</sup>H and <sup>13</sup>C NMR signals are listed for the both together: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31–7.26 (4H, m) and 7.24–7.17 (6H, m) (2 Ph), 6.89 (1H, t, *J* = 5.4 Hz,

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$CH=N$ ), 6.85 (1H, t,  $J = 5.4$  Hz,  $CH=N$ ), 3.40 (1H, m<sub>c</sub>,  $CHOMe$ ), 3.27 (6H, s, 2  $OMe$ ), 3.21 (1H, m<sub>c</sub>,  $CHOMe$ ), 2.96–2.92 (1H, m), 2.88 (1H, m<sub>c</sub>), 2.73 (2H, m<sub>c</sub>) and 2.66 (2H, m<sub>c</sub>) (2  $CHPh$  + 2  $CH_2CH=N$ ), 2.00–1.94 (1H, m), 1.86–1.81 (1H, m) and 1.68–1.52 (2H, m) (2  $CHCH_2CH$ ), 1.49 (9H, s,  $CMe_3$ ), 1.48 (9H, s,  $CMe_3$ ), 1.26 (6H, d,  $J \approx 7$  Hz, 2  $CHMe$ ).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  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  $(C_{17}H_{27}NO_2 + Na)^+$ : 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 73.28, H 9.87, N 4.83. FTIR (neat,  $cm^{-1}$ ):  $\nu_{C-O}$  1091,  $\nu_{N-O}$  1452,  $\nu_{C=N}$  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,  $CDCl_3$ )  $\delta$  Major diastereomer 7.42 (2H, m,  $CH_m$ ), 7.29–7.22 (3H, m,  $CH_{o,p}$ ), 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,  $CMe_3$ ), 1.17 (3H, d,  $J = 7.2$  Hz,  $CHMe$ ), 1.03 (3H, s,  $CMe$ ), 1.02 (3H, s,  $CMe$ ), 1.54 (9H, s,  $CMe_3$ ). Minor diastereomer 7.21 (2H, m,  $CH_m$ ), 7.14 (3H, m,  $CH_{o,p}$ ), 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,  $CMe_3$ ).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  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  $(C_{18}H_{29}NO_2 + Na)^+$ : 314.2096 found 314.2091. Elemental analysis calcd (%) for  $C_{18}H_{29}NO_2$ : C 74.18, H 10.03, N 4.81; found: C 74.21, H 10.13, N 4.85. FTIR (neat,  $cm^{-1}$ ):  $\nu_{C-O}$  1068,  $\nu_{N-O}$  1453,  $\nu_{C=N}$  1571.

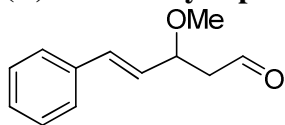
**GP3: Synthesis of *rac*- $\beta$ -methoxy aldehydes (3)**

*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  $H_3PO_4$  (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 nitron (TLC control). The phases were separated, the organic phase was dried ( $Na_2SO_4$ ), and evaporated in vacuum to afford a pure aldehyde **3**.

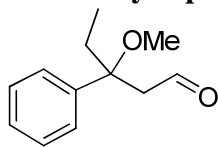
*ii*: For the aldonitrones **2** resistant to the hydrolysis under the above two-phase conditions, homogeneous conditions (1.5 mL MeOH, 0.15–0.2 mmol HCl in 1 mL  $H_2O$ ) were applied as specified in the Table 2 of the article. The workup (hexane / water) was as described above.

Syntheses of the aldehydes **3l**, **3m**, **3s** were carried out starting from the respective enamines **1** without isolation of the corresponding nitron **2** with the other conditions as specified in the **GP2** and **GP3**.

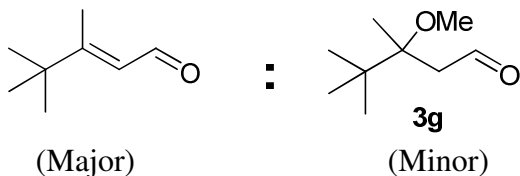


**(E)-3-methoxy-5-phenylpent-4-enal (3c)**

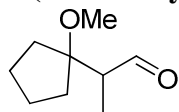
The compound was prepared according to the general procedure **3i**. Colourless liquid (97% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.80 (1H, t, *J* = 1.8 Hz, CH=O), 7.33 (5H, m, Ph), 6.63 (1H, d, *J* = 15.9 Hz, PhCH=), 6.08 (1H, dd, *J* = 15.9 and 7.8 Hz, =CH), 4.28 (1H, m, CHOMe), 3.33 (3H, s, OMe), 2.78 (1H, ddd, <sup>2</sup>*J* = 16.3, <sup>3</sup>*J* = 4.7 and 1.7 Hz, CHCH<sub>A</sub>CH<sub>B</sub>), 2.62 (1H, ddd, <sup>2</sup>*J* = 16.3, <sup>3</sup>*J* = 4.7 and 1.7 Hz, CHCH<sub>A</sub>CH<sub>B</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.6 (1H, t, *J* = 2.8 Hz, CH=O), 7.37 (4H, d, *J* = 4.3 Hz, CH<sub>o,m</sub>), 7.28 (1H, m, CH<sub>p</sub>), 3.18 (3H, s, OMe), 2.89 (2H, dd, *J* = 15.4 and 3.2 Hz, CCH<sub>2</sub>), 2.04 (1H, dq, <sup>2</sup>*J* = 14.5 and <sup>3</sup>*J* = 7.2 Hz, CH<sub>3</sub>CH<sub>A</sub>CH<sub>B</sub>), 1.94 (1H, dq, <sup>2</sup>*J* = 14.5 and <sup>3</sup>*J* = 7.2 Hz, CH<sub>3</sub>CH<sub>A</sub>CH<sub>B</sub>), 0.77 (3H, t, *J* = 7.3 Hz, CH<sub>2</sub>Me). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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)**

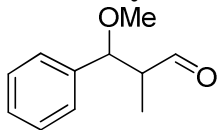
The compound was prepared according to the general procedure **3i**. Colourless liquid (95:5% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ Major product 10.06 (1H, d, *J* = 7.8 Hz, CH=O), 5.96 (1H, dq, *J* = 7.8 and 1.1 Hz, =CH), 2.18 (3H, d, *J* = 1.1 Hz, Me), 1.14 (9H, s, CMe<sub>3</sub>). 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, CCH<sub>A</sub>CH<sub>B</sub>), 2.46 (1H, dd, *J* = 15.2 and 3.0 Hz, CCH<sub>A</sub>CH<sub>B</sub>), 2.04 (3H, s, Me), 0.94 (9H, s, CMe<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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)**

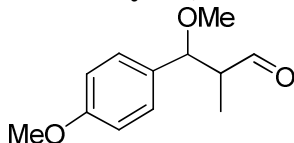
The compound was prepared according to the general procedure **3ii**. Colourless liquid (89% yield).

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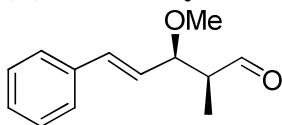
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.7 (1H, d,  $J = 2.41$  Hz,  $\text{CH}=\text{O}$ ), 3.18 (3H, s,  $\text{OMe}$ ), 2.76–2.71 (1H, dq,  $J = 6.9$  and  $2.4$  Hz,  $\text{CHMe}$ ), 1.89 (2H, m,  $\text{CH}_{2\text{cyclic}}$ ), 1.80–1.52 (6H, m,  $\text{CH}_{2\text{cyclic}}$ ), 1.1 (3H, d,  $J = 6.9$  Hz,  $\text{Me}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  204.86, 87.86, 51.18, 49.70, 33.69, 33.22, 24.20, 24.12, 9.77.

**3-methoxy-2-methyl-3-phenylpropanal (3l)**

The compound was prepared according to the general procedure **3i**. Colourless liquid (86% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  Major *syn*-diastereomer 9.74 (1H, d,  $J = 1.2$  Hz,  $\text{CH}=\text{O}$ ), 7.40–7.25 (5H, m, Ph), 4.61 (1H, d,  $J = 4.8$  Hz,  $\text{CHOMe}$ ), 3.26 (3H, s,  $\text{OMe}$ ), 2.64 (1H, m,  $\text{CHMe}$ ), 1.06 (3H, d,  $J = 7.0$  Hz,  $\text{CHMe}$ ). Minor diastereomer 9.81 (1H, d,  $J = 2.8$  Hz,  $\text{CH}=\text{O}$ ), 7.40–7.25 (5H, m, Ph) 4.27 (1H, d,  $J = 9.0$  Hz,  $\text{CHOMe}$ ), 3.18 (3H, s,  $\text{OMe}$ ), 2.7 (1H, m,  $\text{CHMe}$ ), 0.83 (3H, d,  $J = 7.1$  Hz,  $\text{CHMe}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  Major diastereomer 203.61, 139.12, 128.62, 127.99, 126.99, 83.03, 57.26, 53.19, 8.59. Minor diastereomer 204.00, 138.96, 128.70, 128.42, 127.53, 85.07, 56.88, 52.82, 11.04. The  $^1\text{H}$  NMR data are in good consistency with those given in literature<sup>[5]</sup>.

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

The compound was prepared according to the general procedure **3i**. Colourless liquid (83% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  Major diastereomer 9.7 (1H, d,  $J = 1.3$  Hz,  $\text{CH}=\text{O}$ ), 7.20 (2H, d,  $J = 8.4$  Hz,  $\text{CH}_{\text{Arl}}$ ), 6.9 (2H, d,  $J = 8.7$  Hz,  $\text{CH}_{\text{Arl}}$ ), 4.5 (1H, d,  $J = 5.2$  Hz,  $\text{CHOMe}$ ), 3.81 (3H, s,  $\text{C}_{\text{Arl}}\text{OMe}$ ), 3.24 (3H, s,  $\text{CHOMe}$ ), 2.64 (1H, m,  $\text{CHMe}$ ), 1.0 (3H, d,  $J = 7$  Hz,  $\text{Me}$ ). Minor diastereomer 9.8 (1H, d,  $J = 2.9$  Hz,  $\text{CH}=\text{O}$ ), 7.22 (2H, d,  $J = 8.4$  Hz,  $\text{CH}_{\text{Arl}}$ ), 6.91 (2H, d,  $J = 8.7$  Hz,  $\text{CH}_{\text{Arl}}$ ), 4.22 (1H, d,  $J = 9.1$  Hz,  $\text{CHOMe}$ ), 3.82 (3H, s,  $\text{C}_{\text{Arl}}\text{OMe}$ ), 3.16 (3H, s,  $\text{CHOMe}$ ), 2.71 (1H, m,  $\text{CHMe}$ ), 0.82 (3H, d,  $J = 7$  Hz,  $\text{Me}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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.

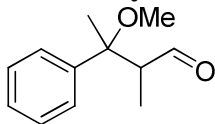
**(E)-3-methoxy-2-methyl-5-phenylpent-4-enal (3n)**

The compound was prepared according to the general procedure **3i**. Colourless liquid (98% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  Major *syn*-diastereomer (shown, *cf.* ref.<sup>[6]</sup>) 9.79 (1H, d,  $J = 1.2$  Hz,  $\text{CH}=\text{O}$ ), 7.32 (5H, m, Ph), 6.62 (1H, d,  $J = 15.9$  Hz,  $\text{PhCH}=\text{}$ ), 6.09 (1H, dd,  $J = 15.9$  and  $7.9$  Hz,  $=\text{CH}$ ), 4.12 (1H, ddd,  $^3J = 7.9$  and  $4.6$  Hz,  $^4J = 0.8$  Hz,  $\text{CHOMe}$ ), 3.32 (3H, s,  $\text{OMe}$ ), 2.63 (1H, ddq,  $^3J_{\text{q}} = 7.1$  Hz,  $^3J_{\text{d}} = 4.6$  and  $1.2$  Hz,  $\text{CHMe}$ ), 1.15 (3H, d,  $J = 7.1$  Hz,  $\text{CHMe}$ ). Minor diastereomer 9.76 (1H, d,  $J = 2.5$  Hz,  $\text{CH}=\text{O}$ ), 6.60 (1H, d,  $J = 15.8$  Hz,  $\text{PhCH}=\text{}$ ), 6.16 (1H, dd,  $J = 15.9$  and  $7.5$  Hz,  $=\text{CH}$ ), 4.00 (1H, ddd,  $^3J = 7.4$  and  $4.9$  Hz,  $^4J = 0.9$  Hz,  $\text{CHOMe}$ ), 3.31 (3H, s,  $\text{OMe}$ ), 2.62 (1H, m,  $\text{CHMe}$ ), 1.05 (3H, d,  $J = 7.1$  Hz,  $\text{CHMe}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  Major diastereomer

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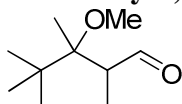
203.71, 136.17, 134.04, 128.72, 128.13, 126.64, 82.19, 56.81, 51.35, 28.12, 8.91. Minor diastereomer 136.60, 132.90, 128.64, 127.80, 126.68, 82.72, 57.00, 51.09, 36.74, 11.62. Other  $^{13}\text{C}$  NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer.

### 3-methoxy-2-methyl-3-phenylbutanal (3s)



The compound was prepared according to the general procedure **3ii**. Colourless liquid (85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  Major diastereomer 9.65 (1H, d,  $J = 2.6$  Hz,  $\text{CH}=\text{O}$ ), 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,  $\text{CH}=\text{O}$ ), 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  $^1\text{H}$  NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  Major diastereomer 204.71, 142.05, 128.48, 127.64, 126.88, 80.39, 57.74, 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.

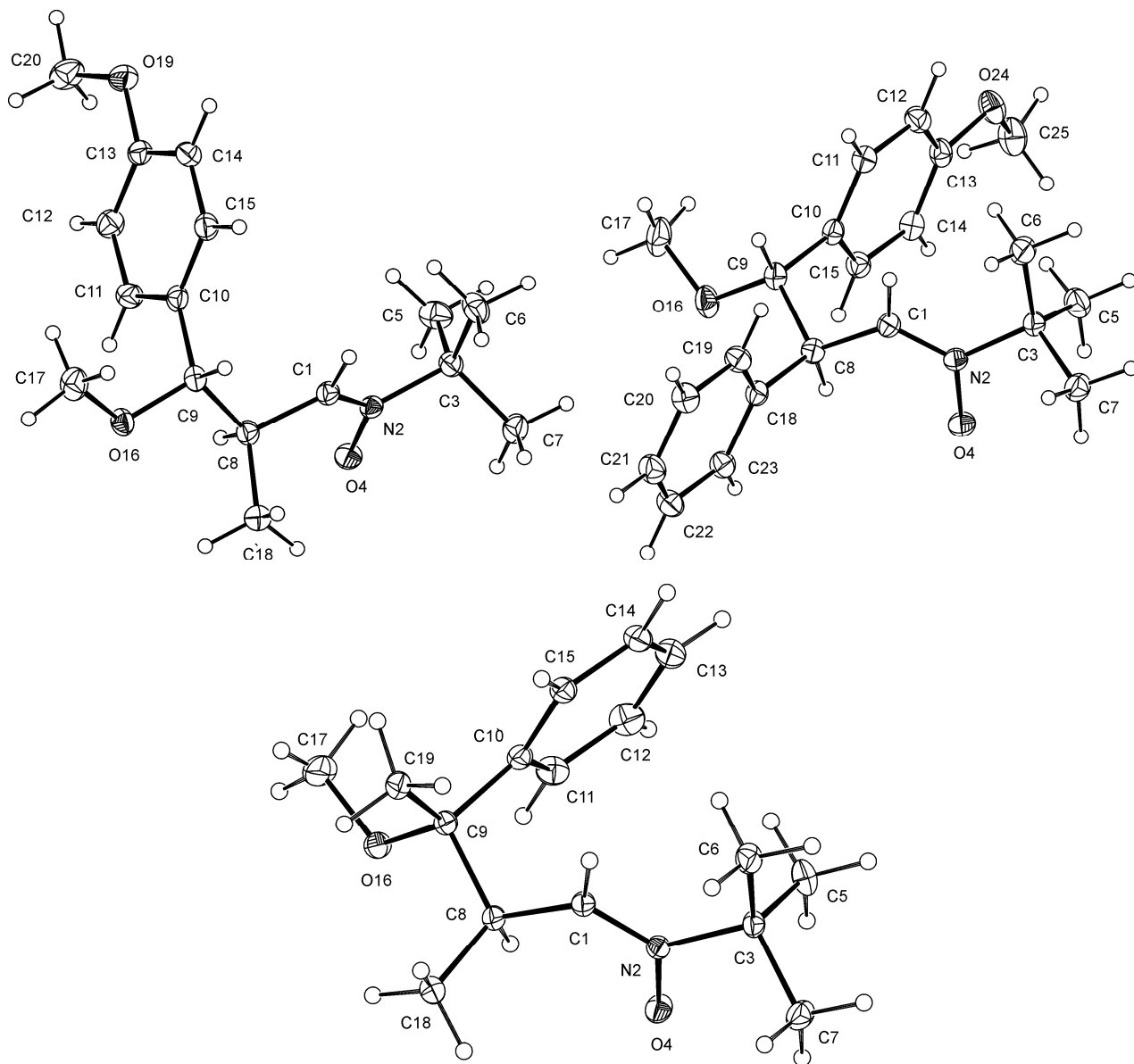
### 3-methoxy-2,3,4,4-tetramethylpentanal (3u)



The compound was prepared according to the general procedure **3ii**. Colourless liquid (90% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  Major diastereomer 9.83 (1H, d,  $J = 3.1$  Hz,  $\text{CH}=\text{O}$ ), 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*<sub>3</sub>). Minor diastereomer 9.84 (1H, d,  $J = 2.6$  Hz,  $\text{CH}=\text{O}$ ), 3.27 (3H, s, *OMe*), 1.25 (3H, s, *CMe*), 0.97 (9H, s, *CMe*<sub>3</sub>).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  Major diastereomer 204.79, 82.12, 52.75, 51.94, 40.58, 26.73, 15.93, 11.01. Other  $^1\text{H}$  and  $^{13}\text{C}$  NMR peaks of minor diastereomer are not observed due to low intensity or overlap with those of the major diastereomer.

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**X-Ray Crystal-Structure Determination of the  $\beta$ -methoxy aldonitrones (**2m,p,s**)**

**Figure 1** X-ray crystal structures of the  $\beta$ -methoxy aldonitrones **2m** (top, left) **2p** (top, right) and **2s** (bottom) displaying *syn*-configuration of the C(8)–C(9) stereogenic centres. The displacement ellipsoids are drawn on 30% probability level.

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  $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), 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  $H_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{pivot atom})$  or of  $1.5 U_{\text{eq}}$  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*\*,3*S*\*)-3-methoxy-3-(4-methoxyphenyl)-2-methylpropylidene]-2-methylpropan-2-amine oxide (2m)***Crystal data*

$C_{16}H_{25}NO_3$	$D_x = 1.135 \text{ Mg m}^{-3}$
$M_r = 279.37$	Melting point: 371 K
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
Hall symbol: -P 2ybc	$\lambda = 0.71073 \text{ \AA}$
$a = 5.81100 (10) \text{ \AA}$	Cell parameters from 3912 reflections
$b = 13.6360 (3) \text{ \AA}$	$\theta = 1-27.5^\circ$
$c = 21.0230 (5) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$\beta = 100.9640 (13)^\circ$	$T = 150 (2) \text{ K}$
$V = 1635.43 (6) \text{ \AA}^3$	Cell measurement pressure: ? kPa
$Z = 4$	Bar, colourless
$F_{000} = 608$	$0.3 \times 0.1 \times 0.1 \text{ mm}$

*Data collection*

Nonius KappaCCD area detector diffractometer	3772 independent reflections
Radiation source: fine-focus sealed tube	2980 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.037$
Detector resolution: 9.091 pixels $\text{mm}^{-1}$	$\theta_{\text{max}} = 27.5^\circ$
$T = 150(2) \text{ K}$	$\theta_{\text{min}} = 1.8^\circ$
$P = 101.3 \text{ kPa}$	$h = -7 \rightarrow 7$
$\varphi$ and $\omega$ scans to fill the Ewald sphere	$k = -17 \rightarrow 17$
Absorption correction: none	$l = -27 \rightarrow 27$
25986 measured reflections	

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.102$	$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.2392P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
3772 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
191 parameters	$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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**

C1—N2	1.2951 (13)	C10—C11	1.3859 (15)
C1—C8	1.4899 (14)	C10—C15	1.3927 (15)
C1—H1	0.942 (12)	C11—C12	1.3890 (16)
N2—O4	1.3026 (10)	C11—H11	0.9500
N2—C3	1.5153 (13)	C12—C13	1.3820 (16)
C3—C6	1.5194 (15)	C12—H12	0.9500
C3—C7	1.5209 (16)	C13—O19	1.3736 (14)
C3—C5	1.5258 (17)	C13—C14	1.3892 (18)
C5—H5A	0.9800	C14—C15	1.3838 (17)
C5—H5B	0.9800	C14—H14	0.9500
C5—H5C	0.9800	C15—H15	0.9500
C6—H6A	0.9800	O16—C17	1.4197 (14)
C6—H6B	0.9800	C17—H17A	0.9800
C6—H6C	0.9800	C17—H17B	0.9800
C7—H7A	0.9800	C17—H17C	0.9800
C7—H7B	0.9800	C18—H18A	0.9800
C7—H7C	0.9800	C18—H18B	0.9800
C8—C9	1.5325 (14)	C18—H18C	0.9800
C8—C18	1.5332 (16)	O19—C20	1.4266 (17)
C8—H8	1.0000	C20—H20A	0.9800
C9—O16	1.4308 (12)	C20—H20B	0.9800
C9—C10	1.5138 (15)	C20—H20C	0.9800
C9—H9	1.0000		
N2—C1—C8	121.20 (9)	C10—C9—H9	108.9
N2—C1—H1	117.6 (7)	C8—C9—H9	108.9
C8—C1—H1	121.2 (7)	C11—C10—C15	118.13 (10)

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C1—N2—O4	122.25 (9)	C11—C10—C9	120.30 (9)
C1—N2—C3	123.34 (8)	C15—C10—C9	121.55 (9)
O4—N2—C3	114.35 (8)	C10—C11—C12	121.67 (10)
N2—C3—C6	112.01 (8)	C10—C11—H11	119.2
N2—C3—C7	107.16 (9)	C12—C11—H11	119.2
C6—C3—C7	110.05 (10)	C13—C12—C11	119.38 (11)
N2—C3—C5	105.52 (9)	C13—C12—H12	120.3
C6—C3—C5	109.94 (10)	C11—C12—H12	120.3
C7—C3—C5	112.07 (10)	O19—C13—C12	124.13 (11)
C3—C5—H5A	109.5	O19—C13—C14	115.99 (10)
C3—C5—H5B	109.5	C12—C13—C14	119.87 (11)
H5A—C5—H5B	109.5	C15—C14—C13	120.13 (10)
C3—C5—H5C	109.5	C15—C14—H14	119.9
H5A—C5—H5C	109.5	C13—C14—H14	119.9
H5B—C5—H5C	109.5	C14—C15—C10	120.82 (11)
C3—C6—H6A	109.5	C14—C15—H15	119.6
C3—C6—H6B	109.5	C10—C15—H15	119.6
H6A—C6—H6B	109.5	C17—O16—C9	112.20 (9)
C3—C6—H6C	109.5	O16—C17—H17A	109.5
H6A—C6—H6C	109.5	O16—C17—H17B	109.5
H6B—C6—H6C	109.5	H17A—C17—H17B	109.5
C3—C7—H7A	109.5	O16—C17—H17C	109.5
C3—C7—H7B	109.5	H17A—C17—H17C	109.5
H7A—C7—H7B	109.5	H17B—C17—H17C	109.5
C3—C7—H7C	109.5	C8—C18—H18A	109.5
H7A—C7—H7C	109.5	C8—C18—H18B	109.5
H7B—C7—H7C	109.5	H18A—C18—H18B	109.5
C1—C8—C9	108.15 (8)	C8—C18—H18C	109.5
C1—C8—C18	111.34 (9)	H18A—C18—H18C	109.5
C9—C8—C18	112.28 (9)	H18B—C18—H18C	109.5
C1—C8—H8	108.3	C13—O19—C20	117.08 (10)

C9—C8—H8	108.3	O19—C20—H20A	109.5
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-[(2*R*\*,3*S*\*)-3-methoxy-3-(4-methoxyphenyl)-2-phenylpropylidene]-2-methylpropan-2-amine oxide (2p)**

*Crystal data*

C <sub>21</sub> H <sub>27</sub> NO <sub>3</sub>	$D_x = 1.191 \text{ Mg m}^{-3}$
$M_r = 341.44$	Melting point: 407 K
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
Hall symbol: -P 2ybc'	$\lambda = 0.71073 \text{ \AA}$
$a = 16.1659 (5) \text{ \AA}$	Cell parameters from 4645 reflections
$b = 5.6972 (2) \text{ \AA}$	$\theta = 1-27.5^\circ$
$c = 20.6824 (5) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$\beta = 90.5706 (18)^\circ$	$T = 150 (2) \text{ K}$
$V = 1904.76 (10) \text{ \AA}^3$	Cell measurement pressure: ? kPa
$Z = 4$	Prism, colourless
$F_{000} = 736$	$0.4 \times 0.4 \times 0.35 \text{ mm}$

*Data collection*

Nonius KappaCCD area detector diffractometer	4372 independent reflections
Radiation source: fine-focus sealed tube	2807 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.047$
Detector resolution: $9.091 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 27.5^\circ$
$T = 150(2) \text{ K}$	$\theta_{\text{min}} = 2.0^\circ$
$P = 101.3 \text{ kPa}$	$h = -20 \rightarrow 20$
$\varphi$ and $\omega$ scans to fill the Ewald sphere	$k = -7 \rightarrow 7$
Absorption correction: none	$l = -26 \rightarrow 26$
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

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0682P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL,  
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ 

Extinction coefficient: 0.0090 (13)

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 ( $\text{\AA}$ ,  $^\circ$ ) for **2p**

C1—N2	1.2919 (15)	C12—C13	1.3816 (18)
C1—C8	1.4962 (17)	C12—H12	0.9500
C1—H1	0.962 (13)	C13—O24	1.3741 (14)
N2—O4	1.3049 (12)	C13—C14	1.3837 (18)
N2—C3	1.5232 (15)	C14—C15	1.3916 (17)
C3—C6	1.5162 (19)	C14—H14	0.9500
C3—C7	1.5215 (17)	C15—H15	0.9500
C3—C5	1.5256 (18)	O16—C17	1.4219 (17)
C5—H5A	0.9800	C17—H17A	0.9800
C5—H5B	0.9800	C17—H17B	0.9800
C5—H5C	0.9800	C17—H17C	0.9800
C6—H6A	0.9800	C18—C23	1.3842 (18)
C6—H6B	0.9800	C18—C19	1.3906 (18)
C6—H6C	0.9800	C19—C20	1.3893 (17)

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C7—H7A	0.9800	C19—H19	0.9500
C7—H7B	0.9800	C20—C21	1.379 (2)
C7—H7C	0.9800	C20—H20	0.9500
C8—C18	1.5210 (16)	C21—C22	1.379 (2)
C8—C9	1.5400 (18)	C21—H21	0.9500
C8—H8	1.0000	C22—C23	1.3917 (18)
C9—O16	1.4253 (15)	C22—H22	0.9500
C9—C10	1.5149 (16)	C23—H23	0.9500
C9—H9	1.0000	O24—C25	1.4318 (17)
C10—C15	1.3862 (18)	C25—H25A	0.9800
C10—C11	1.3888 (18)	C25—H25B	0.9800
C11—C12	1.3860 (17)	C25—H25C	0.9800
C11—H11	0.9500		
N2—C1—C8	122.58 (12)	C12—C11—H11	119.7
N2—C1—H1	117.6 (8)	C10—C11—H11	119.7
C8—C1—H1	119.7 (8)	C13—C12—C11	120.27 (12)
C1—N2—O4	123.11 (11)	C13—C12—H12	119.9
C1—N2—C3	122.37 (10)	C11—C12—H12	119.9
O4—N2—C3	114.38 (9)	O24—C13—C12	115.62 (12)
C6—C3—C7	109.41 (11)	O24—C13—C14	124.20 (12)
C6—C3—N2	111.66 (10)	C12—C13—C14	120.17 (11)
C7—C3—N2	107.63 (10)	C13—C14—C15	118.87 (12)
C6—C3—C5	110.19 (11)	C13—C14—H14	120.6
C7—C3—C5	112.59 (11)	C15—C14—H14	120.6
N2—C3—C5	105.32 (10)	C10—C15—C14	121.84 (12)
C3—C5—H5A	109.5	C10—C15—H15	119.1
C3—C5—H5B	109.5	C14—C15—H15	119.1
H5A—C5—H5B	109.5	C17—O16—C9	112.06 (11)
C3—C5—H5C	109.5	O16—C17—H17A	109.5
H5A—C5—H5C	109.5	O16—C17—H17B	109.5
H5B—C5—H5C	109.5	H17A—C17—H17B	109.5

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C3—C6—H6A	109.5	O16—C17—H17C	109.5
C3—C6—H6B	109.5	H17A—C17—H17C	109.5
H6A—C6—H6B	109.5	H17B—C17—H17C	109.5
C3—C6—H6C	109.5	C23—C18—C19	118.84 (11)
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
H7A—C7—H7B	109.5	C18—C19—H19	119.9
C3—C7—H7C	109.5	C21—C20—C19	120.18 (13)
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)
C10—C9—H9	108.8	O24—C25—H25A	109.5
C8—C9—H9	108.8	O24—C25—H25B	109.5
C15—C10—C11	118.14 (11)	H25A—C25—H25B	109.5
C15—C10—C9	120.79 (11)	O24—C25—H25C	109.5
C11—C10—C9	121.05 (11)	H25A—C25—H25C	109.5
C12—C11—C10	120.69 (12)	H25B—C25—H25C	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-[(2*R*\*,3*S*\*)-3-methoxy-2-methyl-3-phenylbutylidene]-2-methylpropan-2-amine oxide (2s)***Crystal data*

$C_{16}H_{25}NO_2$	$F_{000} = 288$
$M_r = 263.37$	$D_x = 1.152 \text{ Mg m}^{-3}$
Triclinic, $P^-1$	Melting point: 373 K
Hall symbol: -P 1	Mo $K\alpha$ radiation
	$\lambda = 0.71073 \text{ \AA}$
$a = 5.9484 (2) \text{ \AA}$	Cell parameters from 3400 reflections
$b = 8.4271 (3) \text{ \AA}$	$\theta = 1-27.5^\circ$
$c = 15.9289 (5) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$\alpha = 93.4557 (15)^\circ$	$T = 150 (2) \text{ K}$
$\beta = 95.3665 (18)^\circ$	Cell measurement pressure: ? kPa
$\gamma = 106.3773 (17)^\circ$	Prism, colourless
$V = 759.58 (4) \text{ \AA}^3$	$0.4 \times 0.4 \times 0.3 \text{ mm}$
$Z = 2$	

*Data collection*

Nonius KappaCCD area detector diffractometer	3462 independent reflections
Radiation source: fine-focus sealed tube	3032 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.024$
Detector resolution: 9.091 pixels $\text{mm}^{-1}$	$\theta_{\text{max}} = 27.5^\circ$
$T = 150(2) \text{ K}$	$\theta_{\text{min}} = 1.3^\circ$
$P = 101.3 \text{ kPa}$	$h = -7 \rightarrow 7$
$\varphi$ and $\omega$ scans to fill the Ewald sphere	$k = -10 \rightarrow 10$
Absorption correction: none	$l = -20 \rightarrow 20$
15912 measured reflections	

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.037$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.102$	$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.1937P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
3462 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
182 parameters	$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
	Extinction correction: none

Primary atom site location: structure-invariant direct methods

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**

C1—N2	1.2977 (13)	C9—C10	1.5343 (14)
C1—C8	1.4934 (13)	C10—C15	1.3947 (14)
C1—H1	0.963 (13)	C10—C11	1.3973 (15)
N2—O4	1.2990 (10)	C11—C12	1.3882 (17)
N2—C3	1.5160 (12)	C11—H11	0.9500
C3—C6	1.5194 (14)	C12—C13	1.3867 (18)
C3—C7	1.5234 (14)	C12—H12	0.9500
C3—C5	1.5272 (15)	C13—C14	1.3819 (17)
C5—H5A	0.9800	C13—H13	0.9500
C5—H5B	0.9800	C14—C15	1.3936 (15)
C5—H5C	0.9800	C14—H14	0.9500
C6—H6A	0.9800	C15—H15	0.9500
C6—H6B	0.9800	O16—C17	1.4192 (13)
C6—H6C	0.9800	C17—H17A	0.9800
C7—H7A	0.9800	C17—H17B	0.9800
C7—H7B	0.9800	C17—H17C	0.9800
C7—H7C	0.9800	C18—H18A	0.9800
C8—C18	1.5320 (14)	C18—H18B	0.9800
C8—C9	1.5529 (13)	C18—H18C	0.9800
C8—H8	1.0000	C19—H19A	0.9800
C9—O16	1.4393 (11)	C19—H19B	0.9800
C9—C19	1.5232 (15)	C19—H19C	0.9800

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N2—C1—C8	120.37 (9)	C19—C9—C8	112.26 (9)
N2—C1—H1	116.9 (7)	C10—C9—C8	107.09 (8)
C8—C1—H1	122.6 (7)	C15—C10—C11	118.11 (10)
C1—N2—O4	122.92 (8)	C15—C10—C9	122.14 (9)
C1—N2—C3	122.53 (8)	C11—C10—C9	119.43 (9)
O4—N2—C3	114.27 (7)	C12—C11—C10	120.79 (10)
N2—C3—C6	112.25 (8)	C12—C11—H11	119.6
N2—C3—C7	107.56 (8)	C10—C11—H11	119.6
C6—C3—C7	110.08 (9)	C13—C12—C11	120.57 (11)
N2—C3—C5	104.51 (8)	C13—C12—H12	119.7
C6—C3—C5	110.52 (9)	C11—C12—H12	119.7
C7—C3—C5	111.80 (9)	C14—C13—C12	119.24 (11)
C3—C5—H5A	109.5	C14—C13—H13	120.4
C3—C5—H5B	109.5	C12—C13—H13	120.4
H5A—C5—H5B	109.5	C13—C14—C15	120.44 (10)
C3—C5—H5C	109.5	C13—C14—H14	119.8
H5A—C5—H5C	109.5	C15—C14—H14	119.8
H5B—C5—H5C	109.5	C14—C15—C10	120.84 (10)
C3—C6—H6A	109.5	C14—C15—H15	119.6
C3—C6—H6B	109.5	C10—C15—H15	119.6
H6A—C6—H6B	109.5	C17—O16—C9	115.16 (8)
C3—C6—H6C	109.5	O16—C17—H17A	109.5
H6A—C6—H6C	109.5	O16—C17—H17B	109.5
H6B—C6—H6C	109.5	H17A—C17—H17B	109.5
C3—C7—H7A	109.5	O16—C17—H17C	109.5
C3—C7—H7B	109.5	H17A—C17—H17C	109.5
H7A—C7—H7B	109.5	H17B—C17—H17C	109.5
C3—C7—H7C	109.5	C8—C18—H18A	109.5
H7A—C7—H7C	109.5	C8—C18—H18B	109.5
H7B—C7—H7C	109.5	H18A—C18—H18B	109.5
C1—C8—C18	111.30 (8)	C8—C18—H18C	109.5

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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)

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(2s) *SIR92* (Altomare *et al.*, 1994)

Program(s) used to refine structure:

(2m) *SHELXL97* (Sheldrick, 1997)

(2p) *SHELXL97* (Sheldrick, 1997)

(2s) *SHELXL97* (Sheldrick, 1997)

Molecular graphics:

(2m) *Platon* (Speck, 2001)

(2p) *Platon* (Speck, 2001)

(2s) *Platon* (Speck, 2001)

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### Spectral data for new products ( $^1\text{H}$ and $^{13}\text{C}$ in $\text{CDCl}_3 / \text{C}_6\text{H}_6$ )

