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Supporting Information

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Convenient Transformation of Optically Active Nitroalkanes to Chiral Aldoximes and Nitriles

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Experimental

All reactions were carried out in dried glassware under an atmosphere of argon. Tetrahydrofuran was dried by passage over A-2 alumina (8 x 14 mesh, Macherey & Nagel; activated at 300 °C under nitrogen atmosphere for 12 h).

Chemicals were purchased from Aldrich, Fluka, or Acros and used as is unless mentioned otherwise.

Evaporation of organic solutions was achieved by rotary evaporation with a water bath temperature below 40 °C. Product purification by flash column chromatography was accomplished using silica gel 60 (32-63 µm particle size from Fluka or Brunschwig) at 0.1 – 0.3 bar pressure. Technical grade solvents were used for chromatography and distilled prior to use. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} glass plates. Visualization was achieved by either fluorescence quenching or by staining with aqueous potassium permanganate solution.

Melting points were measured using a Büchi 510 melting point apparatus in open glass capillaries and are uncorrected.

NMR spectra were recorded at room temperature on a Varian Mercury operating at 300 MHz (^{1}H) and 75 MHz (^{13}C) respectively. Residual solvent signals are internally referenced. Chemical shift δ is referred in terms of ppm, coupling constants are given in Hz. Following abbreviations classify the multiplicity: s = singlet, d =

doublet, t = triplet, q = quartett, m = multiplet or unresolved, br = broad signal.

Infrared spectra were recorded on a Perkin-Elmer Spektrum RX I FT-IR System and reported in cm^{-1}. Samples were prepared in thin film technique.

Combustion analysis was performed by the Mikroelementaranalytisches Laboratorium at ETH Zurich. Mass spectra were obtained from the MS Service of the ETH Zurich or the MS service of the University of Fribourg/Switzerland. MALDI-mass spectra were recorded using an Ion Spec Ultima HR FT-ICR MS MALDI-FT-ICR MS using the DHB-tl (2,5-dihydroxy-benzoic acid-two layers) method at 4.7 Tesla. High resolution EI mass spectra were performed on a Micromass AutoSpec Ultima and were calibrated with perfluorotributylamine (PFTBA) prior to data acquisition.

Enantiomeric ratios were determined with a Merck Hitachi LaChrom D-7000 HPLC using a Chiracel OD-H column, a Knauer differential refractometer, and hexane/isopropanol as eluents.

General procedure for the transformation of nitroalkanes to oximes

In a 25 ml round-bottom-flask, the nitroalkane (1.00 mmol) was dissolved in THF (5 mL) and tetrabutylammonium iodide (18.5 mg, 50.0 µmol) added. Benzyl bromide (188 mg, 132 µL, 1.10 mmol) and potassium hydroxide (58.9 mg, 1.05 mmol) were added. The mixture was stirred for 3 h. Water (15 mL) was added and the solution extracted with diethyl ether (2 x 30 mL). The combined organic layers were dried over Na_2SO_4 and the solvent evaporated. The product was purified by flash column chromatography (silica gel, hexane/EtOAc) and the product isolated as a colorless oil or a colorless solid.

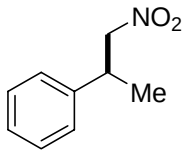
General procedure for the one-pot transformation of nitroalkanes to nitriles using trifluoroacetic anhydride

In a 25 ml round-bottom-flask, the nitroalkane (0.500 mmol) was dissolved in THF (5 mL) and tetrabutylammonium iodide (9.2 mg, 25 µmol) added. Benzyl bromide (94.0 mg, 61.0 µL, 0.550 mmol) and potassium hydroxide (24.4 mg, 0.525 mmol) were added. The mixture was stirred for 3 h. The mixture was cooled to – 20 °C and triethylamine (459 mg, 632 µL, 4.50 mmol) and trifluoroacetic anhydride (472 mg, 318 µL, 2.25 mmol) added. The mixture was stored at – 20 °C for 12 h. Water (15 mL) was added and the solution extracted with diethyl ether (2 x 30 mL). The combined organic layers were dried over Na_2SO_4 and the solvent evaporated. The product was purified by flash column chromatography (silica gel, hexane/EtOAc) and isolated as a colorless oil.

General procedure for the one-pot transformation of nitroalkanes to nitriles using thionyl chloride

In a 25 ml round-bottom-flask, the nitroalkane (0.500 mmol) was dissolved in THF (5 mL) and tetrabutylammonium iodide (9.2 mg, 25 µmol) added. Benzyl bromide (94.0 mg, 61.0 µL, 0.550 mmol) and potassium hydroxide (24.4 mg, 0.525 mmol) were added. The mixture was stirred for 3 h. The mixture was cooled to – 20 °C and triethylamine (459 mg, 632 µL, 4.50 mmol) and thionyl chloride (268 mg, 164 µL, 2.25 mmol) added. The mixture was stored at – 20 °C for 12 h. Water (15 mL) was added and the solution extracted with diethyl ether (2 x 30 mL). The combined organic layers were dried

over Na_2SO_4 and the solvent evaporated. The product was purified by flash column chromatography (silica gel, hexane/EtOAc) and isolated as a colorless oil.



(*R*)-2-Phenyl-1-nitro-propane:

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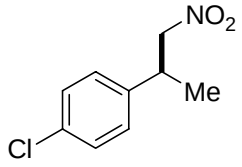
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.34 (m, 2H, arom. *H*), 7.25 (m, 3H, arom. *H*), 4.58 (dd, *J* = 12.1, 7.5 Hz, 1H, C1-*H*^{1}), 4.49 (dd, *J* = 12.1, 8.1 Hz, 1H, C1-*H*^{2}), 3.64 (m, 1H, C2-*H*), 1.39 (d, *J* = 6.8 Hz, 3H, Me).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 140.7, 128.8, 127.4, 126.8, 81.8, 38.7, 18.8.

IR (film): ν = 3032, 2974, 2934, 1604, 1556, 1496, 1454, 1432, 1384, 1332, 1204, 1211, 1022, 765, 701 cm^{-1}.



(*R*)-2-(4-Chloro-phenyl)-1-nitro-propane:

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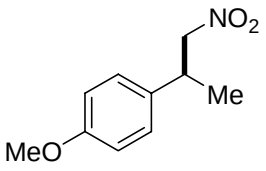
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.31 (m, 2H, arom. *H*), 7.16 (m, 2H, arom. *H*), 4.52 (dd, *J* = 15.8, 7.8 Hz, 1H, C1-*H*^{1}), 4.48 (dd, *J* = 15.8, 7.8 Hz, 1H, C1-*H*^{2}), 3.62 (m, 1H, C2-*H*), 1.36 (d, *J* = 7.2 Hz, 3H, Me).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 139.2, 133.2, 129.0, 128.2, 81.5, 38.1, 18.8.

IR (film): ν = 2974, 1553, 1495, 1381, 1094, 1014, 829, 738 cm^{-1}.

Anal. Calcd for $C_9H_{10}NO_2Cl$: C, 54.15, H, 5.05, N, 7.02. Found: C, 54.35, H, 5.09, N, 6.85.



(*R*)-2-(4-Methoxy-phenyl)-1-nitro-propane:

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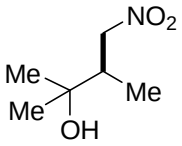
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.15 (m, 2H, arom. *H*), 6.87 (m, 2H, arom. *H*), 4.51 (dd, *J* = 11.8, 7.5 Hz, 1H, C1-*H*^{1}), 4.45 (dd, *J* = 11.8, 8.1 Hz, 1H, C1-*H*^{2}), 3.79 (s, 3H, OMe), 3.59 (m, 1H, C2-*H*), 1.36 (d, 3H, *J* = 7.2 Hz, Me).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 158.7, 132.7, 127.8, 114.2, 82.1, 55.3, 38.0, 18.9.

IR (film): ν = 2968, 1613, 1551, 1515, 1459, 1382, 1300, 1250, 1181, 1123, 1025, 832, 772 cm^{-1}.



(*R*)-3-Hydroxy-2,3-dimethyl-1-nitro-butane:

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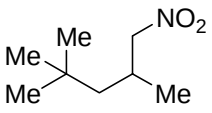
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.77 (dd, *J* = 12.1, 4.4 Hz, 1H, C1-*H*^{1}), 4.17 (dd, *J* = 12.1, 9.7 Hz, 1H, C1-*H*^{2}), 2.44 (m, 1H, C2-*H*), 1.31 (s, 3H, C3-*Me*^{1}), 1.25 (s, 1H, O*H*), 1.17 (s, 3H, C3-*Me*^{2}), 1.03 (d, *J* = 6.9 Hz, 3H, C2-*Me*).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 78.6, 43.3, 29.3, 25.0, 13.7.

IR (film): ν = 3402, 2977, 2924, 2855, 1552, 1463, 1435, 1379, 1227, 1154, 1095, 952, 899 cm^{-1}.

HRMS (ESI, MeOH/KOAc) *m/e*: Calcd for (M+K$^+$) $C_6H_{13}NO_3K$ 186.05270, Found: 186.05278.

Anal. Calcd for $C_6H_{13}NO_3$: C, 48.97; H, 8.90; N, 9.52. Found: C, 49.12; H, 8.83; N, 9.44.



(*R*)-2,4,4-Trimethyl-1-nitro-pentane:[1]

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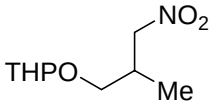
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.30 (dd, ***J*** = 11.5, 6.2 Hz, 1H, C1-***H***^{1}), 4.14 (dd, ***J*** = 11.5, 8.3 Hz, 1H, C1-***H***^{2}), 2.39 (m, 1H, C2-***H***), 1.26 (dd, ***J*** = 14.3, 4.4 Hz, 1H, C3-***H***^{1}), 1.17 (dd, ***J*** = 14.3, 6.2 Hz, 1H, C3-***H***^{2}), 1.05 (d, ***J*** = 6.9 Hz, 3H, C2-***Me***), 0.94 (s, 9H, ***t***-Bu).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 82.9, 47.4, 31.0, 29.8, 29.5, 20.2.

IR (film): ν = 2960, 2871, 1553, 1470, 1434, 1384, 1367, 1248, 1228, 1097, 973, 758 cm^{-1}.



(*S*)-*O*-Tetrahydropyranyl-2-methyl-3-nitro-propan-1-ol (mixture of diastereomers):

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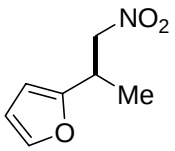
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.56 (m, 4H), 4.29 (dd, ***J*** = 12.1, 7.8 Hz, 1H), 4.25 (dd, ***J*** = 12.1, 7.8 Hz, 1H), 3.80 (m, 3H), 3.62 (dd, ***J*** = 10.0, 7.5 Hz, 1H), 3.52 (m, 2H), 3.41 (dd, ***J*** = 10.0, 4.7 Hz, 1H), 3.24 (dd, ***J*** = 10.0, 7.5 Hz, 1H), 2.65 (m, 2H), 1.62-1.86 (m, 4H), 1.46-1.62 (m, 8 H), 1.06 (d, ***J*** = 6.8 Hz, 3H), 1.05 (d, ***J*** = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 99.2, 98.6, 79.0, 69.4, 68.9, 62.2, 62.2, 34.5, 33.3, 33.2, 30.4, 25.3, 19.3, 19.2, 14.5, 14.5.

IR (film): ν = 2944, 2875, 1552, 1456, 1436, 1383, 1354, 1202, 1124, 1078, 1065, 1035, 975, 904, 870, 815 cm^{-1}.

Anal. Calcd for $C_9H_{17}NO_4$: C, 53.19; H, 8.43; N, 6.89. Found: C, 53.35; H, 8.39; N, 6.87.

[1] Larkin, J.M.; Kreuz, K.L. *J. Org. Chem.* **1971**, *36*, 2574-2575.



(*R*)-2-(Furan-2-yl)-1-nitro-propane:

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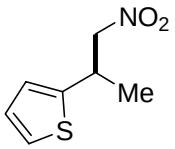
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.35 (dd, *J* = 1.9, 0.6 Hz, 1H, arom. *H*), 6.31 (dd, *J* = 3.4, 1.9 Hz, 1H, arom. *H*), 6.13 (m, 1H, arom. *H*), 4.67 (dd, *J* = 12.1, 6.5 Hz, 1H, C1–H^1), 4.43 (dd, *J* = 12.1, 8.1 Hz, 1H, C1–H^2), 3.74 (m, 1H, C2–*H*), 1.38 (d, *J* = 7.2 Hz, 3H, *Me*).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.7, 141.9, 110.2, 105.9, 79.5, 32.5, 16.2.

IR (film): ν = 2982, 1555, 1508, 1433, 1378, 1150, 1013, 739 cm^{-1}.

Anal. Calcd for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.30; H, 6.12; N, 8.77.



(*R*)-2-(Thiophen-2-yl)-1-nitro-propane:

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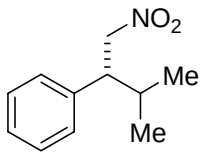
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.22 (dd, *J* = 5.3, 1.2 Hz, 1H, arom. *H*), 6.96 (dd, *J* = 5.3, 3.4, 1H, arom. *H*), 6.90 (m, 1H, arom. *H*), 4.58 (dd, *J* = 12.1, 7.2 Hz, 1H, C1–H^1), 4.48 (dd, *J* = 12.1, 8.1 Hz, 1H, C1–H^2), 3.97 (m, 1H, C2–*H*), 1.47 (d, *J* = 6.9 Hz, 3H, *Me*).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 143.8, 126.9, 124.4, 124.2, 82.1, 34.2, 19.8.

IR (film): ν = 2973, 1552, 1455, 1430, 1384, 1240, 1113, 1040, 850, 772, 702 cm^{-1}.

Anal. Calcd for $C_7H_9NO_2S$: C, 49.10; H, 5.30; N, 8.18. Found: C, 49.28; H, 5.37; N, 8.30.



(*S*)-3-Methyl-2-phenyl-1-nitro-butane:

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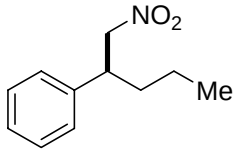
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.22–7.34 (m, 3H, arom. *H*), 7.12–7.17 (m, 2H, arom. *H*), 4.77 (dd, *J* = 12.5, 5.9 Hz, 1H, C1–*H*^{1}), 4.64 (dd, *J* = 12.1, 10.0 Hz, 1H, C1–*H*^{2}), 3.23 (m, 1H, C2–*H*), 1.96 (m, 1H, C3–*H*), 1.01 (d, *J* = 6.9 Hz, 3H, C3*Me*^{1}), 0.81 (d, *J* = 6.9 Hz, 3H, C3*Me*^{2}).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 138.5, 128.5, 128.0, 127.3, 79.1, 51.1, 31.4, 20.7, 20.3.

IR (film): ν =. 3032, 2965, 1556, 1496, 1455, 1435, 1381, 755, 702 cm^{-1}.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.40; H, 7.72; N, 7.23.



(*R*)-2-Phenyl-1-nitro-pentane:

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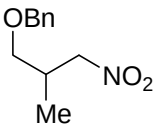
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.23–7.37 (m, 3H, arom. *H*), 7.17–7.22 (m, 2H, arom. *H*), 4.58 (dd, *J* = 12.1, 7.8 Hz, 1H, C1–*H*^{1}), 4.53 (dd, *J* = 12.1, 8.1 Hz, 1H, C1–*H*^{2}), 3.47 (m, 2H, C2–*H*), 1.67 (m, 2H, C3–H_2), 1.22 (m, 2H, C4–H_2), 0.88 (t, *J* = 7.2 Hz, 3H, *Me*).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 139.4, 128.8, 127.4, 127.4, 81.0, 44.2, 35.2, 20.2, 13.9.

IR (film): ν =. 3032, 2961, 2934, 2874, 1553, 1496, 1455, 1431, 1380, 763, 701 cm^{-1}.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.22; H, 7.77; N, 7.21.



1-((2-Methyl-3-nitropropoxy)methyl)benzene:

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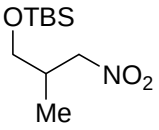
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.25–7.40 (m, 5H, arom. *H*), 4.58 (dd, *J* = 12.1, 6.2 Hz, 1H, C*H*^{1}NO_2), 4.51 (s, 2H, PhC*H*$_2$), 4.28 (dd, *J* = 12.1, 7.8 Hz, 1H, PhC*H*^{2}NO_2), 3.51 (dd, *J* = 9.3, 4.7 Hz, 1H, PhC*H*^{1}), 3.35 (dd, *J* = 9.3, 7.2 Hz, 1H, PhC*H*^{2}), 2.65 (m, 1H, C(2)*H*), 1.05 (d, *J* = 6.6 Hz, 3H, *Me*).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 137.8, 128.4, 127.7, 127.5, 78.9, 73.2, 71.7, 33.3, 14.4.

IR (film): ν = 3065, 3031, 2970, 2864, 1551, 1496, 1454, 1383, 1208, 1103, 739, 699, 608 cm^{-1}.

HRMS (EI) *m/e*: Calcd for ($M+H^+$) $C_{11}H_{16}NO_3$: 210.1130 Found: 210.1124.

Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14, H, 7.23, N, 6.69. Found: C, 63.02, H, 7.39, N, 6.48.



(2-Methyl-3-nitropropoxy)(*tert*-butyl)dimethyl-silane:

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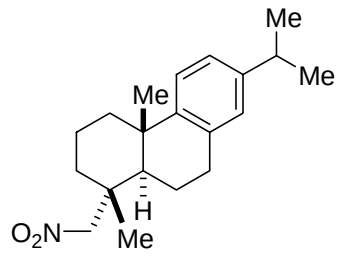
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.56 (dd, *J* = 12.1, 6.0 Hz, 1H, C*H*^{1}NO_2), 4.22 (dd, *J* = 12.1, 7.7 Hz, 1H, C*H*^{2}NO_2), 3.64 (dd, *J* = 10.2, 4.4 Hz, 1H, C*H*^{1}O), 3.45 (dd, *J* = 10.2, 6.9 Hz, 1H, C*H*^{2}O), 2.51 (m, 1H, C(2)*H*), 1.00 (d, *J* = 6.9 Hz, 3H, *Me*), 0.89 (s, 9H, *tBu*), 0.05 (s, 6H, *Me*$_2$Si).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 78.7, 64.8, 35.4, 25.8, 18.3, 14.2, -5.5, -5.5.

IR (film): ν = 2956, 2939, 2885, 2859, 1554, 1472, 1382, 1258, 1106, 1038, 1007, 838, 814, 778, 735, 669 cm^{-1}.

Anal. Calcd for $C_9H_{17}NO_3$: C, 51.46, H, 9.93, N, 6.00. Found: C, 51.65, H, 9.98, N, 5.95.



(1*R*,4*aS*)-1,2,3,4,4*a*,9,10,10*a*-Octahydro-7-isopropyl-1,4*a*-dimethyl-1-(nitromethyl) phenanthrene:

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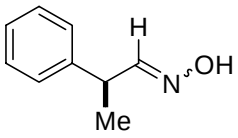
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.20 (d, *J* = 8.1 Hz, 1H, arom. *H*), 7.03 (dd, *J* = 8.1, 1.6 Hz, arom. *H*), 6.93 (m, 1H, arom. *H*), 4.41 (d, *J* = 10.0 Hz, 1H, C*H*^{1}NO2), 4.28 (d, *J* = 10.0 Hz, 1H, C*H*^{2}NO2), 2.78-3.02 (m, 3H), 2.34 (m, 1H), 1.37-1.94 (m, 9H), 1.28 (s, 3H, *Me*), 1.26 (d, *J* = 7.2 Hz, 6H, *iPr*), 1.15 (s, 3H, *Me*).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 146.3, 145.7, 134.1, 126.7, 124.0, 123.9, 86.8, 45.8, 39.2, 37.9, 37.8, 35.8, 33.5, 29.9, 25.4, 24.0, 19.6, 18.5, 18.4.

IR (film): ν = 2958, 2870, 1725, 1612, 1547, 1498, 1455, 1380, 1248, 907, 822, 772, 734, 648, 628 cm^{-1}.

HRMS (EI) *m/e*: Calcd for (M^+) $C_{20}H_{29}NO_2$: 315.2198. Found 315.2190.



2-Phenylpropanal oxime:

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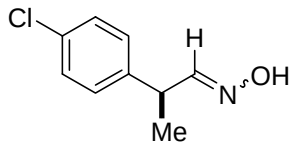
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.06 (s, 1H, O*H*), 7.58 (d, *J* = 6.2 Hz, 0.71 H, C_{major}(1)*H*), 7.25-7.42 (m, 5H, arom. *H*), 6.88 (d, *J* = 7.5 Hz, 0.29H, C_{minor}(1)*H*), 4.52 (m, 0.29H, C_{minor}(2)*H*), 3.73 (m, 0.71H, C_{major}(2)*H*), 1.51 (d, *J* = 6.9 Hz, 2.13H, Me_{major}), 1.49 (d, *J* = 7.5 Hz, 0.87H, Me_{minor}).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.9, 154.5, 141.9, 141.6, 128.6, 128.5, 127.2, 127.1, 126.8, 126.6, 40.4, 35.0, 18.8, 18.3.

IR (film): ν = 3271, 3086, 3029, 2973, 2932, 2876, 1654, 1602, 1494, 1453, 1375, 1303, 1017, 939, 762, 699, 581, 538 cm^{-1}.

HRMS (ESI) *m/e*: Calcd for ($M+Na^+$) $C_9H_{11}NONa$: 172.0738. Found: 172.0729.

Anal. Calcd for $C_9H_{11}NO$: C, 72.46, H, 7.43, N, 9.39. Found: C, 72.30, H, 7.49, N, 9.51.



2-(4-Chlorophenyl)propanal oxime:

Mp: 53–57 °C

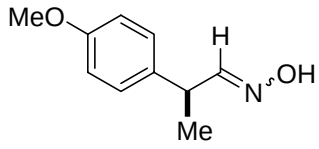
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.48 (d, *J* = 5.9 Hz, 0.71H, $C_{major}(1)H$), 7.13–7.33 (m, 4H, arom. *H*), 6.80 (br m, 0.29H, $C_{minor}(1)H$), 4.41 (br m, 0.29H, $C_{minor}(2)H$), 3.66 (m, 0.71H, $C_{major}(2)H$), 1.44 (d, *J* = 7.2 Hz, 2.13H, Me_{major}), 1.42 (d, *J* = 7.2 Hz, 0.87H, Me_{minor}).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.6, 154.1, 140.4, 140.1, 132.7, 132.4, 128.8, 128.7, 128.6, 128.5, 39.8, 34.5, 18.8, 18.4.

IR (film): ν = 3292, 3096, 2974, 1595, 1492, 1455, 1302, 1133, 1093, 1013, 934, 827, 785, 727, 700 cm^{-1}.

HRMS (ESI) *m/e*: Calcd for ($M+H^+$) $C_9H_{11}NOCl$: 184.0529. Found 184.0524.

Anal. Calcd for $C_9H_{10}NOCl$: C, 58.87, H, 5.49, N, 7.63. Found: C, 59.02, H, 5.43, N, 7.70.



2-(4-Methoxyphenyl)propanal oxime:

Mp: 96–99 °C

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.20 (br s, 1H, O*H*), 7.51 (d, *J* = 6.2 Hz, 0.64H, $C_{major}(1)H$), 7.22 (d, *J* = 8.7 Hz, 0.72H, arom. H_{minor}), 7.16 (d, *J* = 8.7 Hz, 1.28H, arom. H_{major}), 6.89 (d, *J* = 8.1 Hz, 2H, arom. *H*), 6.80 (d, *J* = 6.2 Hz, 0.36H, $C_{minor}(1)H$), 4.43 (m, 0.36H,

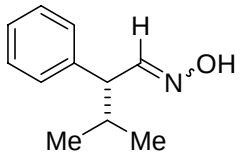
$C_{minor}(2)H$), 3.81 (s, 3H, O*Me*), 3.65 (m, 0.65H, $C_{major}(2)H$), 1.45 (d, *J* = 6.2 Hz, 1.95H, Me_{major}), 1.43 (d, *J* = 6.2 Hz, 1.05H, Me_{minor}).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 158.3, 154.7, 134.0, 133.7, 128.2, 128.0, 114.0, 114.0, 55.3, 39.5, 34.1, 18.9, 18.4.

IR (film): ν = 3273, 2970, 2935, 2837, 1612, 1584, 1553, 1513, 1457, 1375, 1304, 1247, 1180, 1114, 1036, 937, 831 cm^{-1}.

HRMS (ESI) *m/e*: Calcd for $(M+H^+)$ $C_{10}H_{15}NO_2$: 180.1025. Found 180.1019.

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02, H, 7.31, N, 7.82. Found: C, 66.92, H, 7.39, N, 7.75.



3-Methyl-2-phenylbutanal oxime:

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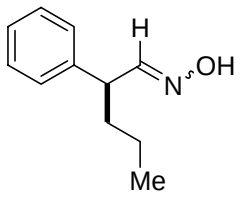
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.72 (br s, 1H, O*H*), 7.61 (d, *J* = 8.7 Hz, 0.65 H, $C_{major}(1)H$), 7.16–7.37 (m, 5H, arom. *H*), 6.94 (br s, 0.35H, $C_{minor}(1)H$), 4.01 (t, *J* = 8.4 Hz, 0.35H, $C_{minor}(2)H$), 3.15 (t, *J* = 9.3 Hz, 0.65H, $C_{major}(2)H$), 2.02–2.20 (m, 1H, C(3)*H*), 1.05 (d, *J* = 6.5 Hz, 1.05H, Me_{minor}), 1.04 (d, *J* = 6.5Hz, 1.95H, Me_{major}), 0.84 (d, *J* = 6.2 Hz, 1.05H, Me_{minor}), 0.82 (d, *J* = 5.9 Hz, 1.95H, Me_{major}).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.8, 140.2, 140.1, 128.5, 128.4, 128.1, 128.0, 126.6, 126.5, 53.8, 48.2, 31.9, 31.7, 20.9, 20.7, 20.6, 20.5.

IR (film): ν = 3249, 3088, 3030, 2962, 2926, 1654, 1600, 1492, 1457, 1388, 1302, 1140, 1076, 954, 925, 824, 757, 700, 611 cm^{-1}.

HRMS (ESI) *m/e*: Calcd for $(M+Na^+)$ $C_{10}H_{15}NONa$: 200.1051. Found 200.1042.

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54, H, 8.53, N, 7.90. Found: C, 74.60, H, 8.57, N, 7.77.



2-Phenylpentanal oxime:

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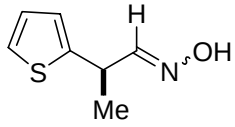
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.51 (d, *J* = 7.2 Hz, 0.66H, $C_{major}(1)H$), 7.91-7.36 (m, 5H, arom. *H*), 6.84 (br d, *J* = 7.2 Hz, 0.34H, $C_{minor}(1)H$), 4.33 (m, 0.34H, $C_{minor}(2)H$), 3.50 (m, 0.66H, $C_{major}(2)H$), 1.71-1.92 (m, 2H, $C(3)H_2$), 1.22-1.41 (m, 2H, $C(4)H_2$), 0.94 (t, *J* = 7.2 Hz, 1.02H, Me_{minor}), 0.92 (t, *J* = 7.5 Hz, 1.98H, Me_{major}).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.5, 154.2, 140.9, 140.7, 128.6, 127.7, 127.6, 126.8, 126.6, 46.0, 40.7, 35.8, 35.6, 20.5, 20.5, 14.0.

IR (film): ν = 3255, 3087, 2959, 2932, 2873, 1659, 1602, 1494, 1454, 1380, 1308, 1076, 1030, 930, 744, 699, 627, 583, 544 cm^{-1}.

HRMS (ESI) *m/e*: Calcd for $(M+H^+)$ $C_{11}H_{16}NO$: 178.1232. Found 178.1226.

Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54, H, 8.53, N, 7.90. Found: C, 74.34, H, 8.49, N, 7.87.



2-(Thiophen-2-yl)propanal oxime:

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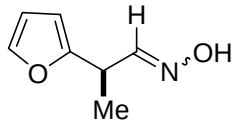
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.68 (br s, 1H, O*H*), 7.53 (d, *J* = 6.5 Hz, 0.69H, $C_{major}(1)H$), 7.21 (m, 1H, arom. *H*), 6.99 (m, 1H, arom. *H*), 6.89-6.94 (m, 1H, arom. *H*), 6.83 (br d, *J* = 4.7 Hz, 0.31H, $C_{minor}(1)H$), 4.75 (m, 0.31 H, $C_{minor}(2)H$), 3.99 (m, 0.69H, $C_{major}(2)H$), 1.55 (d, *J* = 7.2 Hz, 2.07H, Me_{major}), 1.53 (d, *J* = 6.9 Hz, 0.93H, Me_{minor}).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 153.1, 153.8, 145.0, 126.8, 126.7, 124.0, 124.0, 123.8, 123.7, 35.8, 30.7, 19.7, 19.0.

IR (film): ν = 3269, 3104, 2974, 2932, 1654, 1452, 1376, 1297, 1235, 937, 850, 772, 698 cm^{-1}.

HRMS (ESI) *m/e*: Calcd for ($M+Na^+$) C_7H_9NOSNa: 178.0303. Found: 178.0294.



2-(Furan-2-yl)propanal oxime:

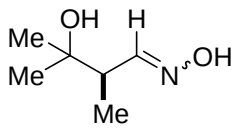
Mp: 93-96 °C

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.48 (d, ***J*** = 6.5 Hz, 0.69H, $C_{major}(1)$***H***), 7.36 (m, 1H, arom. ***H***), 6.66 (br d, ***J*** = 5.9 Hz, 0.31H, $C_{minor}(1)$***H***), 6.32 (m, 1H, arom. ***H***), 6.11 (m, 1H, arom. ***H***), 4.52 (m, 0.31H, $C_{minor}(2)$***H***), 3.76 (m, 0.69H, $C_{major}(2)$***H***), 1.45 (d, ***J*** = 7.2 Hz, 2.07H, ***Me***$_{major}$), 1.42 (d, ***J*** = 7.2 H, 0.93H, ***Me***$_{minor}$).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.6, 152.2, 141.8, 141.6, 110.2, 110.1, 105.3, 105.0, 34.4, 29.6, 16.4, 15.9.

IR (film): ν = 3275, 3121, 2981, 2937, 1663, 1649, 1592, 1505, 1454, 1377, 1300, 1231, 1184, 1148, 1081, 1048, 1081, 1011, 937, 884, 806, 736, 598 cm^{-1}.

HRMS (ESI) *m/e*: Calcd for (M^+) $C_7H_9NO_2$: 139.0633. Found 139.0629.



3-Hydroxy-2,3-dimethylbutanal oxime:

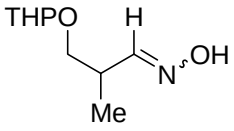
Mp: 75-78 °C

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.42 (d, ***J*** = 7.7 Hz, 0.68H, $C_{major}(1)$***H***), 6.77 (br d, ***J*** = 7.1 Hz, 0.32H, $C_{minor}(1)$***H***), 5.79 (br s, 1H, O***H***), 3.22 (m, 0.32H, $C_{minor}(2)$***H***), 2.42 (m, 0.68H, $C_{major}(2)$***H***), 1.22 (d, ***J*** = 6.6 Hz, 1.92H, ***Me***$_{2minor}$), 1.20 (d, ***J*** = 9.3 Hz, 4.08H, ***Me***$_{2major}$), 1.09 (d, ***J*** = 7.1 Hz, 2.04H, ***Me***$_{major}$), 1.06 (d, ***J*** = 6.9 Hz, 0.96H, ***Me***$_{minor}$).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.6, 154.3, 72.4, 45.0, 40.0, 28.1, 27.8, 26.3, 13.4, 12.7.

IR (film): ν = 3327, 2977, 1655, 1458, 1376, 1315, 1170, 1033, 933, 868, 772 cm^{-1}.

HRMS (ESI) *m/e*: Calcd for ($M+Na^+$) $C_6H_{13}NO_2Na$: 154.0844. Found 154.0839.



2-Methyl-3-(tetrahydro-2*H*-pyran-2-yloxy)propanal oxime:

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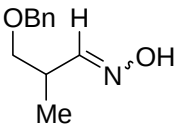
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.26 (br s, 1H, O***H***), 7.40 (dd, ***J*** = 6.5, 1.3 Hz, 0.72 H, C_{major}(1)***H***), 6.66 (m, 0.28 H, C_{minor}(1)***H***), 4.59 (m, 1H, C(2)'***H***), 3.74-3.86 (m, 1H, C(3)H^1), 3.65-3.73 (m, 1H, C(3)H^2), 3.45-3.53 (m, 1H, C(6)'H^1), 3.33-3.41 (m, 1.28 H, C(6)'H^2, C_{minor}(3)***H***), 2.67 (m, 0.72 H, C_{major}(3)***H***), 1.43-1.86 (m, 6H, THP), 1.10 (d, ***J*** = 6.9 Hz, 2.16 H, ***Me***$_{major}$), 1.08 (d, ***J*** = 6.9 Hz, 0.84 H, ***Me***$_{minor}$).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.3, 154.2, 153.7, 153.6, 98.7, 98.6, 98.4, 98.3, 70.1, 69.9, 69.4, 69.4, 62.0, 61.9, 35.1, 34.9, 30.7, 30.4, 30.3, 25.4, 19.2, 19.2, 14.8, 14.7, 14.2, 14.1.

IR (film): ν = 3350, 3116, 2943, 2874, 1652, 1455, 1378, 1353, 1324, 1263, 1202, 1185, 1122, 1077, 1062, 1034, 974, 945, 905, 868, 810, 702 cm^{-1}.

HRMS (ESI) *m/e*: Calcd for ($M+Na^+$) $C_9H_{17}NO_3Na$: 210.1106. Found: 210.1101.

Anal. Calcd for $C_9H_{17}NO_3$: C, 57.73, H, 9.15, N, 7.48. Found: C, 57.64, H, 9.13, N, 7.30.



3-(Benzyloxy)-2-methylpropanal oxime:

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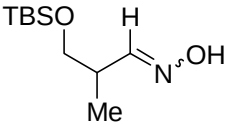
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.90 (br s, 1H, O*H*), 7.45 (d, *J* = 6.2 Hz, 0.68H, $C_{major}(1)H$), 7.26–7.38 (m, 5H, arom. *H*), 6.72 (br m, 0.32H, $C_{minor}(1)H$), 4.54 (s, 0.64H, $PhC_{minor}H_2$), 4.53 (s, 1.36H, $PhC_{major}H_2$), 3.41–3.53 (m, 2H, CH_2O), 2.74 (m, 0.68H, $C_{major}(2)H$), 1.14 (d, *J* = 6.9 Hz, 2.04H, Me_{major}), 1.13 (d, *J* = 6.5 Hz, 0.96H, Me_{minor}).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.4, 153.8, 138.0, 137.9, 128.2, 127.5, 73.0, 72.9, 72.7, 72.2, 35.1, 30.6, 14.7, 14.1.

IR (film): ν = 3325, 3031, 2968, 2936, 2871, 1649, 1496, 1454, 1361, 1307, 1205, 1099, 1028, 938, 739, 699, 611 cm^{-1}.

HRMS (ESI) *m/e*: Calcd for $(M+Na^+)$ $C_{11}H_{15}NO_2Na$: 216.1000. Found: 216.0992.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37, H, 7.82, N, 7.25. Found: C, 68.20, H, 7.71, N, 7.21.



3-(*tert*-Butyldimethylsilyloxy)-2-methylpropanal oxime:

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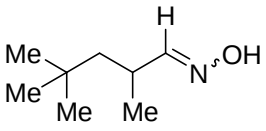
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.40 (d, *J* = 6.2 Hz, 0.72H, $C_{major}(1)H$), 6.67 (d, *J* = 7.2 Hz, 0.28H, $C_{minor}(1)H$), 3.60 (m, 1.44H, $C_{major}H_2O$), 3.60 (m, 0.56H, $C_{minor}H_2O$), 3.25 (m, 0.28H, $C_{minor}(2)H$), 2.56 (m, 0.72H, $C_{major}(2)H$), 1.08 (d, *J* = 6.9 Hz, 3H, *Me*), 0.89 (s, 9H, *tBu*), 0.04 (s, 6H, Me_2Si).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 154.6, 154.1, 66.0, 65.1, 37.4, 32.8, 25.9, 18.4, 14.3, 13.9, -5.3.

IR (film): ν = 3297, 3121, 2956, 2932, 2859, 1655, 1470, 1389, 1363, 1256, 1104, 1032, 940, 838, 777, 670 cm^{-1}.



2,4,4-Trimethylpentanal oxime:

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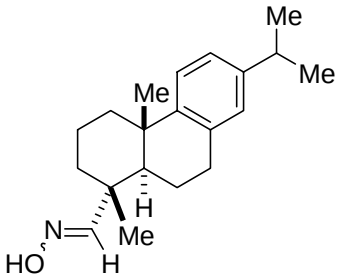
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 9.51 (br s, 0.70 H, O*H*$_{major}$), 9.25 (br s, 0.30 H, O*H*$_{minor}$), 7.25 (d, *J* = 7.8 Hz, 0.30 H, C$_{minor}$(1)*H*), 6.55 (d, *J* = 7.8 Hz, 0.70 H, C$_{major}$(1)*H*), 3.28 (m, 0.70 H, C$_{major}$(2)*H*), 2.54 (m, 0.30 H, C$_{minor}$(2)*H*), 1.43 (dd, *J* = 14.0, 8.7 Hz, 0.60 H, C$_{minor}$(2)*H*), 1.39 (dd, *J* = 14.0, 9.3 Hz, 1.40 H, C$_{major}$(2)*H*), 1.07 (d, *J* = 6.9 Hz, 0.90 H, *Me*$_{minor}$), 1.02 (d, *J* = 6.9 Hz, 2.10 H, *Me*$_{major}$), 0.90 (s, 9H, *tBu*).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 158.6, 157.7, 49.6, 48.9, 31.4, 31.0, 30.0, 29.8, 26.3, 21.1, 19.8.

IR (film): ν = 3248, 3103, 2957, 2903, 2871, 1664, 1469, 1396, 1366, 1340, 1312, 972, 935, 900, 879, 843, 702 cm^{-1}.

HRMS (ESI) *m/e*: Calcd for (M+Na^+) $C_8H_{17}NONa$: 166.1208. Found: 166.1202.

Anal. Calcd for $C_8H_{17}NO$: C, 67.09, H, 11.96, N, 9.78. Found: C, 66.90, H, 11.93, N, 9.60.



(1*R*,4*aS*)-1,2,3,4,4*a*,9,10,10*a*-Octahydro-7-isopropyl-1,4*a*-dimethylphenanthrene-1-carbaldehyde oxime:

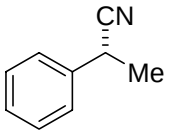
Mp: 114 °C

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.21 (s, 0.31 H, C$_{minor}$*H*N), 7.19 (d, *J* = 8.1 Hz, 1H, arom. *H*), 7.02 (dd, *J* = 8.1, 1.9 Hz, 1H, arom. *H*), 6.91 (m, 1H, arom. *H*), 6.45 (s, 0.69 H, C$_{major}$*H*N), 2.78-2.98 (m, 3H), 2.30 (m, 1H), 1.42-2.14 (m, 9H), 1.41 (2, 3H, *Me*), 1.25 (d, *J* = 6.9 Hz, 6H, *iPr*), 1.25 (s, 3H, *Me*).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 161.2, 159.2, 147.0, 146.7, 145.8, 145.7, 134.6, 126.9, 124.1, 123.9, 46.5, 46.4, 42.6, 40.7, 38.0, 37.9, 37.4, 37.2, 37.0, 34.2, 33.4, 30.3, 29.9, 25.5, 25.4, 24.0, 21.3, 20.3, 18.3, 18.3, 17.9, 16.5.

IR (film): ν = 3306, 2959, 2930, 2869, 1645, 1614, 1498, 1456, 1381, 1363, 1304, 1232, 1058, 945, 910, 822, 733, 629 cm^{-1}.

HRMS (EI) *m/e*: Calcd for (M^+) $C_{20}H_{29}NO$: 299.2249. Found 299.2244.



2-Phenylpropanenitrile:[2]

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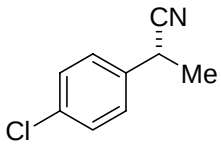
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.30-7.43 (m, 5H, arom. *H*), 3.90 (q, *J* = 7.4 Hz, 1H, C(2)*H*), 1.65 (d, *J* = 7.4, 3H, *Me*).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 137.0, 129.1, 128.0, 126.6, 121.5, 31.2, 21.4.

IR (film): ν = 3032, 2986, 2938, 1684, 1600, 1496, 1452, 1379, 1266, 1091, 1030, 764, 698, 668, 570 cm^{-1}.



2-(4-Chlorophenyl)propanenitrile:[3]

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^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.26-7.39 (m, 4H, arom. *H*), 3.88 (q, *J* = 7.4, 1H, C(2)*H*), 1.62 (dd, *J* = 7.4, 0.6 Hz, 3H, *Me*).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 135.5, 134.0, 129.3, 128.1, 121.1, 30.7, 21.3.

IR (film): ν = 2988, 2939, 2243, 1597, 1493, 1455, 1410, 1380, 1095, 1016, 827, 774, 717, 568, 508 cm^{-1}.

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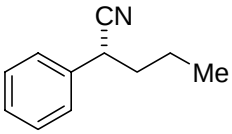
[2] Kharash, M.S.; Sosnovsky, G. *Tetrahedron* **1958**, *3*, 97-104.
[3] Miyamatsu, H.; Ueno, S.; Shimizu, M.; Hosono, J.; Tomari, M.; Seida, K.; Suzuki, T.; Wada, J. *J. Med. Chem.* **1974**, *17*, 491-496.



2-Phenylpentanenitrile:[4]

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^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.28-7.42 (m, 5H, arom. *H*), 3.79 (dd, *J* = 8.5, 6.3 Hz, 1H, C(2)*H*), 1.77-1.99 (m, 2H, C(3)H_2), 1.40-1.59 (m, 2H, C(4)H_2), 0.96 (t, *J* = 7.1 Hz, 3H, *Me*).

^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 136.0, 129.0, 127.9, 127.2, 120.8, 37.8, 37.1, 20.2, 13.4.

IR (film): ν = 3033, 2962, 2934, 2876, 2240, 1602, 1455, 1382, 1030, 757, 699, 668, 574, 510 cm^{-1}.

[4] Rossolymo, A. *Chem. Ber.* **1889**, *22*, 1233-1238.