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Supporting Information

69451 Weinheim, Germany

Mild Cobalt-catalyzed Hydrocyanation of Olefins with Tosyl Cyanide

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General. All reactions were carried out under an atmosphere of argon or nitrogen. For flash chromatography technical grade solvents were used, which were distilled prior to use. Solvents for reactions were analytical grade purchased from Merck or Baker and used without further purifications. Co-complexes **3** and **4** were prepared according to previously reported procedures.[1]

Chromatographic purification was performed as flash chromatography using Brunschwig silica 32-63, 60Å, using hexanes/diethylether or hexanes/ethyl acetate as eluent with 0.3-0.5 bar pressure. TLC was performed on Merck silica gel 60 F_{254} TLC glass plates and visualized with UV light and permanganate stain.

Melting points were measured on a Büchi 510 melting point apparatus using open glass capillaries, the data is uncorrected. Optical rotation measurements were carried out on a Jasco DIP-1000 Polarimeter

^{1}H-NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration, interpretation). ^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a VARIAN Mercury 75 MHz spectrometer in chloroform-d, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm as standard.

Infrared spectra were recorded on a Perkin Elmer Spectrum RX-I FT-IR spectrophotometer as thin films unless stated otherwise and are reported as cm^{-1} (w=weak, m=medium, s=strong, sh=shoulder).

Mass spectrometric measurements were performed by the mass spectrometry service of the LOC at the ETHZ on a Finnigan TSQ 7000 ESI spectrometer for low resolution measurements and High resolution mass spectra were obtained on a VG-TRIBRID for electron impact ionization (EI) and Ion spec Ultima 4.7 spectrometer for MALDI. Elemental analysis was performed by the Mikroelementaranalytisches Laboratorium der ETHZ.

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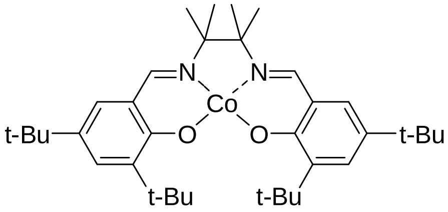
[1] J. Waser, B. Gaspar, H. Nambu, E. M. Carreira, *J. Am. Chem. Soc.* **2006**, *128*, 11693-11712.

1,1,2,2-Tetramethyl-1,2-ethanediamino-*N,N*`-bis(3,5-di-*tert*-butylsalicylidene)-cobalt(II) (6a)



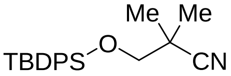
Ligand (**8**)[2] (500 mg, 0.911 mmol, 1.0 equiv.) in EtOH (20 ml) was heated to reflux under argon. After 10 minutes $Co(OAc)_2$ (obtained by drying its hydrate under vacuum at 70 °C for 3 hours, 227 mg, 0.911 mmol, 1.0 equiv.) was added and the mixture became purple. The reaction mixture was refluxed for 2 hours, cooled to RT and the precipitate filtered. The purple solid was washed with cold EtOH (10 ml) and dried under high vacuum to give 443 mg (80%) of the cobalt(II) complex **6a**.

HRMS (MALDI): calcd for $C_{36}H_{54}CoN_2O_2^+$ (M) 605.3512 Found 605.3523.

IR ν 2950 (s), 2907 (m), 2359 (w), 1578 (s), 1522 (s), 1461 (m), 1422 (m), 1381 (s), 1323 (m), 1249 (s), 1204 (m), 1176 (m), 1141 (s), 1027 (w), 934 (w), 904 (w), 864 (w), 829 (w), 785 (w), 748 (w), 699 (w), 634 (w);

Anal. calcd for $C_{36}H_{54}CoN_2O_2$: C 71.38, H 8.98, N 4.62 Found: C 71.09, H 9.01, N 4.63

3-(*tert*-butyldiphenylsilyloxy)-2,2-dimethylpropanenitrile (2)



General Procedure A:

Catalyst **5a**[3] (3.3 mg, 0.005 mmol, 1 mol%) was dissolved in EtOH (2 ml) at RT under argon. After 2 min, *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane[4] (156 mg, 0.5 mmol, 1.0 equiv.) was added followed by *p*-TsCN (95% Aldrich, 144 mg, 0.75 mmol, 1.5 equiv.). TBHP (5.5 M solution in decane, 25 μl, 0.14 mmol, 0.28 equiv) was added to the brown solution followed by $PhSiH_3$ (98% ACROS, 62 μl, 0.5 mmol, 1.0 equiv.) and another portion of EtOH (1 ml). The resulting pale yellow, homogeneous solution was stirred at RT and the reaction was monitored by TLC (hexane:Et_2O=20:1). After completion (2 hours) the solvent was evaporated and the crude mixture purified by flash chromatography (hexane:EtOAc=20:1) to afford 3-(*tert*-butyldiphenylsilyloxy)-2,2-dimethylpropanenitrile (**2**) (148 mg, 88%) as a colorless oil.

General procedure B:

Catalyst **6a** (3 mg, 0.005 mmol, 1 mol%) was dissolved in EtOH (2 ml) at RT under argon. After 2 min, *tert*-butyl-(2-methyl-allyloxy)-diphenyl-silane[4] (156 mg, 0.5 mmol, 1.0 equiv.) was added to the red solution followed by *p*-TsCN (95% Aldrich, 115 mg, 0.6 mmol, 1.2 equiv.). Finally $PhSiH_3$ (98% ACROS, 62 μl, 0.5 mmol, 1.0 equiv.) was added and another portion of EtOH (0.5 ml). The resulting red homogeneous mixture was stirred at RT and the reaction was monitored by TLC (hexane:Et_2O=20:1). After completion (1.5 hours) the solvent was evaporated and the crude mixture purified by flash chromatography (hexane:EtOAc=20:1) to afford 3-(*tert*-butyldiphenylsilyloxy)-2,2-dimethylpropanenitrile (**2**) (168 mg, 99%) as a colorless oil.

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[2] For the preparation of ligand **8** see: G. A. Morris, H. Zhou, C. L. Stern, S. T. Nguyen, *Inorg. Chem.* **2001**, *40*, 3222-3227.

[3] For the preparation of catalyst **5a** see: S. E. Schaus, B. D. Brandes, J. F. Larrow, M. Tokunaga, K. B. Hansen, A. E. Gould, M. E. Furrow, E. N. Jacobsen, *J. Am. Chem. Soc.* **2002**, *124*, 7, 1307-1315.

[4] For the preparation of starting materials see: J. Waser, H. Nambu, E. M. Carreira, *J. Am. Chem. Soc.* **2005**, *127*, 23, 8294-8295.

R_f (Hexane/EtOAc=20:1) 0.36;

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.70-7.67 (m, 4H), 7.48-7.38 (m, 6H), 3.54 (s, 2H, OCH_2), 1.35 (s, 6H, 2xCH_3), 1.10 (s, 9H, $C(CH_3)_3$);

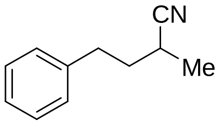
^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.49, 132.54, 129.79, 127.70, 124.06, 69.68, 35.20, 26.79, 23.31, 19.43;

IR ν 3072 (s), 2933 (s), 2859 (s), 2239 (m), 2176 (m), 1590 (m), 1472 (s), 1428 (s), 1393 (s), 1365 (s), 1294 (w), 1225 (w), 1188 (m), 1111 (s), 1030 (m), 999 (s), 939 (m), 824 (s), 741 (s), 701 (s), 615 (s), 594 (s), 503 (s), 445 (m);

HRMS (EI): calcd for $C_{21}H_{27}NOSi^+$ (M-C_4H_9) 280.1152 Found 280.1153;

MS (ESI) 360.2 (M+Na)

2-methyl-4-phenylbutanentrile (9)[5]



Nitrile **9** (79 mg, 99%) was obtained as a colorless oil following the General procedure A with 4-phenylbutene (99% Aldrich, 75 µl, 0.5 mmol, 1.0 equiv.) in 1.5 hours after purification by flash chromatography (Hexane:EtOAc=20:1).

Nitrile **9** (79 mg, 99%) was obtained as a colorless oil following the General procedure B with 4-phenylbutene (99% Aldrich, 75 µl, 0.5 mmol, 1.0 equiv.) in 1 hour after purification by flash chromatography (Hexane:EtOAc=20:1).

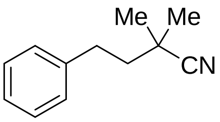
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34-7.19 (m, 5H), 2.93-2.70 (m, 2H), 2.64-2.52 (m, 1H), 2.05-1.78 (m, 2H), 1.34 (d, ^3J=6.6 Hz, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.99, 128.51, 128.28, 126.27, 122.65, 35.80, 33.25, 24.93, 18.10;

IR ν 3735 (w), 3649 (m), 3029 (m), 2940 (m), 2360 (m), 2340 (m), 2239 (m), 1734 (w), 1684 (m), 1558 (m), 1497 (m), 1456 (s), 1386 (m), 1338 (w), 1124 (m), 1031 (w), 849 (w), 742 (m), 699 (m), 558 (w), 472 (w);

HRMS (EI): calcd for $C_{11}H_{13}N^+$ (M) 159.1042 Found 159.1043

2,2-dimethyl-4-phenylbutanenitrile (10)[6]



Nitrile **10** (83 mg, 95%) was obtained as a colorless oil following the General procedure A with 3-methylbut-3-enylbenzene[4] (73 mg, 0.5 mmol, 1.0 equiv.) in 2 hours after purification by flash chromatography (Hexane:EtOAc=20:1).

Nitrile **10** (87 mg, 99%) was obtained as a colorless oil following the General procedure B with 3-methylbut-3-enylbenzene (73 mg, 0.5 mmol, 1.0 equiv.) in 1 hour after purification by flash chromatography (Hexane:EtOAc=20:1).

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[5] T. Funabiki, Y. Yamazaki, Y. Sato, S. Yoshida, *J. Chem. Soc. Perkin Trans II* **1983**, *12*, 1915-1918.

[6] A. L. Rodriguez, T. Bunlaksananusorn, P. Knochel, *Org. Lett.* **2000**, *2*, 21, 3285-3287.

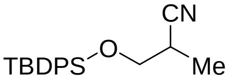
^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.33-7.19 (m, 5H), 2.84-2.78 (m, 2H, PhCH$_2$), 1.86-1.80 (m, 2H, CH$_2$), 1.42 (s, 6H, C(CH$_3$)$_2$);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 140.67, 128.45, 128.18, 126.11, 124.71, 43.13, 32.53, 31.88, 26.79;

IR ν 3064 (w), 3028 (m), 1970 (s), 2936 (s), 2864 (w), 2234 (m), 1603 (w), 1498 (s), 1455 (s), 1392 (w), 1371 (m), 1237 (w), 1208 (w), 1129 (m), 1074 (m), 1030 (w), 849 (m), 753 (s), 703 (s), 506 (m);

HRMS (EI): calcd for $C_{12}H_{15}N^+$ (M) 173.1199 Found 173.1197

3-(*tert*-butyldiphenylsilyloxy)-2-methylpropanenitrile (11)



Nitrile **11** (136 mg, 84%) was obtained as a colorless oil following the General procedure A with prop-2-enyloxy(*tert*-butyl)diphenylsilane[4] (148 mg, 0.5 mmol, 1.0 equiv.) in 2.5 hours after purification by flash chromatography (Hexane:EtOAc=20:1).

Nitrile **11** (154 mg, 95%) was obtained as a colorless oil following the General procedure B with prop-2-enyloxy(*tert*-butyl)diphenylsilane (148 mg, 0.5 mmol, 1.0 equiv.) in 3.5 hours after purification by flash chromatography (Hexane:EtOAc=20:1).

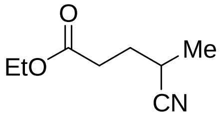
^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.69-7.66 (m, 4H), 7.48-7.38 (m, 6H), 3.73 (dd, ^3J=6.6 Hz, ^2J=9.9 Hz, 1H, OCH$_A$), 3.68 (dd, ^3J=5.7 Hz, ^2J=9.9 Hz, 1H, OCH$_B$), 2.85-2.74 (m, 1H, CHCN), 1.31 (d, ^3J=7.2 Hz, 3H, CH$_3$), 1.09 (s, 9H, C(CH$_3$)$_3$);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 135.43, 132.55, 129.85, 127.74, 121.44, 64.78, 28.87, 26.80, 19.34, 14.49;

IR ν 3072 (m), 3051 (m), 2932 (s), 2859 (s), 2246 (w), 1590 (w), 1472 (s), 1428 (s), 1392 (s), 1362 (m), 1329 (w), 1258 (w), 1188 (m), 1112 (s), 1021 (s), 939 (w), 830 (s), 741 (s), 702 (s), 641 (m), 607 (s), 505 (s), 490 (s);

HRMS (EI): calcd for $C_{20}H_{25}NOSi^+$ (M) 323.1700 Found 323.1698

Ethyl 4-cyanopentanoate (12)[7]



Nitrile **12** (64 mg, 82%) was obtained as a colorless oil following the General procedure A with ethyl pent-4-enoate[8] (64 mg, 0.5 mmol, 1.0 equiv.) in 1.5 hours after purification by flash chromatography (Hexane:EtOAc=4:1).

Nitrile **12** (69 mg, 89%) was obtained as a colorless oil following the General procedure B with ethyl pent-4-enoate (64 mg, 0.5 mmol, 1.0 equiv.) in 1.5 hours after purification by flash chromatography (Hexane:EtOAc=4:1).

^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.15 (q, ^3J=7.2 Hz, 2H, OCH$_2$), 2.81-2.69 (m, 1H, CHCN), 2.60-2.42 (m, 2H, CH$_2$C=O), 1.99-1.81 (m, 2H, CH$_2$), 1.34 (d, ^3J=6.9 Hz, 3H, CHCH_3), 1.27 (t, ^3J=7.2 Hz, 3H, OCH$_2$CH_3);

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[7] R. Yoneda, S. Harusawa, T. Kurihara, *J. Org. Chem.* **1991**, *56*, 5, 1827-1832.

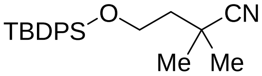
[8] Ethyl pent-4-enoate was prepared according to: S. R. Berryhill, T. Price, M. Rosenblum, *J. Org. Chem.* **1983**, *48*, 2, 158-162 using a Dean-Stark trap.

^{13}C NMR (CDCl$_3$, 75 MHz) δ 172.15, 122.21, 60.73, 31.37, 29.02, 24.88, 17.89, 14.13;

IR ν 3647 (w), 3552 (w), 2985 (m), 2942 (m), 2883 (w), 2240 (m), 1732 (s), 1459 (m), 1420 (w), 1377 (m), 1320 (m), 1266 (m), 1185 (s), 1126 (m), 1096 (m), 1034 (m), 975 (w), 933 (w), 885 (w), 856 (w), 794 (w), 751 (w), 706 (w);

HRMS (EI): calcd for $C_8H_{13}NO_2^+$ (M-C_2H_5O) 110.0600 Found 110.0599

4-(*tert*-butyldiphenylsilyloxy-2,2-dimethylbutanenitrile (13)



Nitrile **13** (84 mg, 48%) was obtained as a colorless oil following the General procedure A with *tert*-butyl-(3-methylbut-2-enyloxy)-diphenylsilane[4] (162 mg, 0.5 mmol, 1.0 equiv.) in 3 hours after purification by flash chromatography (Hexane:EtOAc=20:1).

Nitrile **13** (162 mg, 92%) was obtained as a colorless oil following the General procedure B with *tert*-butyl-(3-methylbut-2-enyloxy)-diphenylsilane (162 mg, 0.5 mmol, 1.0 equiv.) in 2.5 hours after purification by flash chromatography (Hexane:EtOAc=20:1).

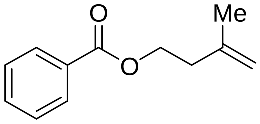
^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.70-7.66 (m, 4H), 7.48-7.37 (m, 6H), 3.86 (t, ^3J=6.6 Hz, 2H, OCH$_2$), 1.81 (t, ^3J=6.6 Hz, 2H, CH$_2$), 1.36 (s, 6H, C(CH$_3$)$_2$), 1.06 (s. 9H, C(CH$_3$)$_3$);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 135.52, 133.31, 129.72, 127.71, 124.87, 60.68, 42.77, 30.85, 27.21, 26.75, 19.08;

IR ν 3072 (m), 3051 (m), 2933 (s), 2858 (s), 2235 (m), 2173 (w), 1964 (w), 1892 (w), 1828 (w), 1472 (s), 1428 (m), 1391 (m), 1370 (m), 1307 (w), 1264 (w), 1210 (w), 1188 (m), 1147 (s), 1107 (s), 1054 (s), 1029 (m), 998 (s), 938 (m), 898 (m), 824 (s), 799 (m), 740 (s), 703 (s), 615 (s), 507 (m);

HRMS (EI): calcd for $C_{22}H_{29}NOSi^+$ (M-C_4H_9) 294.1309 Found 294.1311

3-methylbut-3-enyl benzoate (14)[9]



Benzoyl chloride (700 μl, 6 mmol, 1.0 equiv) was added to a solution of 3-methylbut-3-en-1-ol (608 μl, 6 mmol, 1.0 equiv) in dry CH$_2$Cl$_2$ (8 ml) at 0-5 °C (ice-bath) under argon. Et$_3$N (1.69 ml, 12 mmol, 2.0 equiv) was added and the reaction mixture was stirred 15 min. CH$_2$Cl$_2$ (2 ml) was added and reaction mixture was stirred at RT 3.5 hours. CH$_2$Cl$_2$ (10 ml) was added and washed with 10% HCl (2x15 ml) then sat. NaHCO$_3$ (15 ml) and brine (15 ml). The solvent was evaporated and the crude product purified by flash chromatography (Hexane:CH$_2$Cl$_2$=1:4) to give **14** (1.03 g, 90%) as a colorless oil.

^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.05-8.02 (m, 2H), 7.58-7.53 (m, 1H), 7.46-7.41 (m, 2H), 4.84 (bs, 1H, C=CH), 4,82 (bs, 1H, C=CH), 4.40 (t, 2H, ^3J=6.9 Hz, OCH$_2$), 2.49 (t, 2H, ^3J=6.9 Hz, CH$_2$), 1.82 (s, 3H, CH$_3$)

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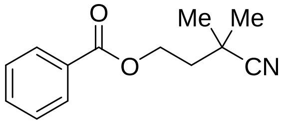
[9] T. Tokuyasu, S. Kunikawa, K. J. McCullough, A. Masayuma, M. Nojima, *J. Org. Chem.* **2005**, *70*, 251-260.

3-cyano-3-methylbutyl benzoate (15)



Nitrile **15** (108 mg, 99%) was obtained as a colorless oil following the General procedure A with 3-methylbut-3-enyl benzoate (**14**) (95 mg, 0.5 mmol, 1.0 equiv.) in 2.5 hours after purification by flash chromatography (Hexane:EtOAc=4:1).

Nitrile **15** (105 mg, 96%) was obtained as a colorless oil following the General procedure B with 3-methylbut-3-enyl benzoate (**14**) (95 mg, 0.5 mmol, 1.0 equiv.) in 1.5 hours after purification by flash chromatography (Hexane:EtOAc=4:1).

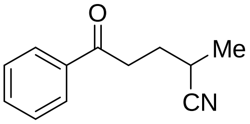
^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.08-8.05 (m, 2H), 7.60-7.54 (m, 1H), 7.47-7.42 (m, 2H), 4.53 (t, ^3J=6.6 Hz, 2H, OCH$_2$), 2.06 (t, ^3J=6.6 Hz, 2H, CH$_2$), 1.46 (s, 6H, C(CH$_3$)$_2$);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 166.36, 133.10, 129.75, 129.65, 128.40, 124.43, 61.25, 39.24, 30.68, 26.95;

IR ν 3071 (w), 2979 (s), 2940 (m), 2879 (w), 2236 (m), 2177 (w), 1715 (s), 1602 (m), 1585 (m), 1453 (s), 1430 (m), 1392 (m), 1371 (m), 1353 (m), 1316 (s), 1275 (s), 1213 (m), 1178 (s), 1114 (s), 1071 (s), 1027 (s), 981 (m), 933 (w), 848 (m), 713 (s), 688 (m), 479 (w);

HRMS (EI): calcd for $C_{13}H_{15}NO_2$ (M) 217.1097 Found 217.1096

2-methyl-5-oxo-5-phenylpantanenitrile (16)[10]



Nitrile **16** (37 mg, 40%) was obtained as a colorless oil following the General procedure A with 1-phenylpent-4-en-1-one[3] (80 mg, 0.5 mmol, 1.0 equiv.) in 3 hours after purification by flash chromatography (Hexane:EtOAc=4:1).

Nitrile **16** (86 mg, 91%) was obtained as a colorless oil following the General procedure B with 1-phenylpent-4-en-1-one (80 mg, 0.5 mmol, 1.0 equiv.) in 8 hours after purification by flash chromatography (Hexane:EtOAc=4:1).

^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.99-7,95 (m 2H), 7.61-7.56 (m, 1H), 7.50-7.45 (m, 2H), 3.24-3.18 (m, 2H, COCH$_2$), 2.89-2.77 (m, 1H, CNCH), 2.17-2.06 (m, 1H), 2.02-1.94 (m, 1H), 1.39 (d, ^3J=7.2 Hz, 3H, CH$_3$);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 198.03, 136.27, 133.27, 128.57, 127.84, 122.48, 35.54, 28.24, 25.13, 18.28;

IR ν 2347 (w), 3064 (m), 2983 (m), 2940 (m), 2239 (m), 1976 (w), 1732 (w), 1682 (s), 1456 (m), 1414 (w), 1369 (m), 1323 (m), 1272 (m), 1240 (m), 1211 (s), 1183 (m), 1159 (w), 1126 (w), 1076 (w), 1017 (w), 972 (m), 929 (m), 844 (w), 794 (w), 753 (s), 692 (s), 655 (m);

HRMS (EI): calcd for $C_{12}H_{13}NO^+$ (M) 187.0992 Found 187.0993

3-methyl-*N*-phenylbut-3-enamide (17)

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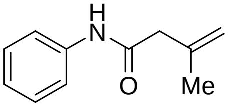
[10] A. R. Forester, H. Irikawa, R. H. Thomson, S. O. Woo, T. J. King, *J. Chem. Soc. Perkin Trans. 1*, **1981**, 1712-1720.



3-methylbut-3-enoic acid (250 mg, 2.5 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (3 ml) at RT under argon. Dimethylaminopyridine (8 mg, 0.063 mmol, 0.025 equiv) and aniline (458 µl, 5 mmol, 2.0 equiv) were added, the mixture was cooled to 0-5 °C (ice-bath) and DCC (516 mg, 2.5 mmol, 1.0 equiv) was added. The mixture was stirred 15 min. at this temperature and then 4 hours at RT. CH_2Cl_2 (8 ml) was added and the precipitate filtered off. The resulting homogeneous solution was washed with 10% HCl (10 ml) and sat. $NaHCO_3$ (10 ml). The solvent was evaporated and the crude product purified by flash chromatography (Hexane:EtOAc=2:1) to give **17** (348 mg, 79%) as a white solid.

R_f (Hexane:EtOAc=2:1) 0.5;

Mp 72-75 °C;

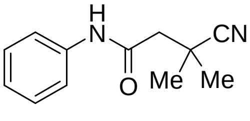
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52-7.49 (m, 2H), 7.47 (br s, 1H, NH), 7.35-7.29 (m, 2H), 7.13-7.08 (m, 1H), 5.08 (m, 1H, C=CH), 5.02 (br s, 1H, C=CH), 3.14 (s, 2H, CH_2), 1.87 (s, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.55, 140.24, 137.72, 128.89, 124.27, 119.72, 115.99, 47.30, 22.40;

IR ν 3297 (m), 3199 (m), 3140 (m), (3082 (w), 2971 (w), 2934 (w), 1654 (s), 1618 (m), 1599 (s), 1544 (s), 1498 (s), 1443 (s), 1420 (m), 1353 (m), 1309 (m), 1251 (m), 1210 (w), 1183 (w), 956 (w), 898 (m), 754 (m), 734 (w), 692 (w);

HRMS (EI) calcd for $C_{11}H_{13}NO^+$ (M) 175.0992 Found 175.0991

3-cyano-3-methyl-*N*-phenylbutanamide (18)



Nitrile **18** (87 mg, 86%) was obtained as a colorless solid following the General procedure A with 3-methyl-*N*-phenylbut-3-enamide (**17**) (88 mg, 0.5 mmol, 1.0 equiv.) in 2 hours after purification by flash chromatography (Hexane:EtOAc=2:3).

Nitrile **18** (30 mg, 87%) was obtained as a colorless solid following the General procedure B with 3-methyl-*N*-phenylbut-3-enamide (**17**) (30 mg, 0.17 mmol, 1.0 equiv.) in 3 hours after purification by flash chromatography (Hexane:EtOAc=2:3).

R_f (Hexane:EtOAc=2:3) 0.51;

Mp 117-122 °C;

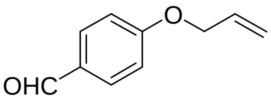
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57 (br s, 1H, NH), 7.51 (d, ^3J=7.5 Hz, 2H), 7.31 (t, ^3J=7.8 Hz, 2H), 7.12 (t, ^3J=7.5 Hz, 1H), 2.59 (s, 2H, CH_2), 1.52 (s, 6H, $(CH_3)_2$);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.15, 137.13, 128.89, 124.68, 124.37, 120.09, 47.48, 30.89, 26.74;

IR ν 3318 (m), 3060 (w), 2979 (m), 2237 (w), 1670 (s), 1600 (s), 1542 (s), 1500 (s), 1444 (s), 1369 (m), 1310 (m), 1251 (m), 1156 (w), 1079 (w), 1029 (w), 906 (w), 756 (m), 693 (m), 540 (w), 504 (m);

HRMS (EI) calcd for $C_{12}H_{14}N_2O^+$ (M) 202.1101 Found 202.1101

4-(allyloxy)benzaldehyde (19)[11]



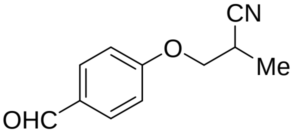
To the solution of 4-hydroxybenzaldehyde (1 g, 8.1 mmol, 1.0 equiv.) in acetone (20 ml), K_2CO_3 (3.36 g, 24.3 mmol, 3.0 equiv.) was added at RT under argon. Allyl bromide (1.06 ml, 12.2 mmol, 1.5 equiv.) was added at RT and the mixture was stirred 2 hours. The reaction mixture was then heated to reflux and stirred another 2 hours. After cooling to RT the mixture was filtered, washed with acetone and the solvent evaporated. Purification by flash chromatography (Hexane:EtOAc=5:1) afforded 4-(allyloxy)benzaldehyde (**19**) (84%, 1.1 g) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.88 (s, 1H, CHO), 7.85-7.81 (m, 2H), 7.04-6.99 (m, 2H), 6.12-5.99 (m, 1H), 5.47-5.31 (m, 2H), 4.64-4.61 (m, 2H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 190.53, 163.37, 132.12, 131.82, 129.88, 118.25, 114.88, 68.98;

IR ν 3079 (w), 3022 (w), 2987 (w), 2925 (w), 2830 (m), 2740 (m), 1694 (s), 1682 (s), 1652 (m), 1601 (s), 1576 (s), 1507 (s), 1456 (m), 1426 (m), 1393 (m), 1365 (w), 1313 (s), 1258 (s), 1162 (s), 1112 (m), 996 (s), 933 (m), 859 (m), 833 (s), 761 (w), 657 (m).

3-(4-formylphenoxy)-2-methylpropanenitrile (20)



Nitrile **20** (61 mg, 64%) was obtained as a colorless solid following the General procedure A with 4-(allyloxy)benzaldehyde (**19**) (81 mg, 0.5 mmol, 1.0 equiv.) in 2 hours after purification by flash chromatography (Hexane:EtOAc=3:2).

Nitrile **20** (77 mg, 81%) was obtained as a colorless solid following the General procedure B with 4-(allyloxy)benzaldehyde (**19**) (81 mg, 0.5 mmol, 1.0 equiv.) in 2.5 hours after purification by flash chromatography (Hexane:EtOAc=3:2).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.90 (s, 1H, CHO), 7.88-7.83 (m, 2H), 7.04-7.00 (m, 2H), 4.19-4.09 (m, 2H, OCH_2), 3.20-3.09 (m, 1H, CNCH), 1.49 (d, ^3J=7.2 Hz, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 190.64, 162.60, 131.98, 130.67, 120.29, 114.79, 68.44, 26.18, 14.65;

IR ν 3627 (w), 3366 (w), 3076 (m), 2990 (m), 2945 (m), 2885 (m), 2834 (m), 2746 (m), 2247 (m), 1694 (s), 1682 (s), 1601 (s), 1506 (s), 1471 (s), 1428 (m), 1395 (s), 1312 (s), 1258 (s), 1161 (s), 1111 (m), 1065 (m), 1033 (m), 995 (m), 969 (w), 929 (w), 833 (s), 776 (w), 675 (m), 651 (m), 619 (s), 588 (s);

HRMS (EI): calcd for $C_{11}H_{11}NO_2^+$ (M-H) 188.0706 Found 188.0705

2-((1*S*,2*R*,4*R*)-2-hydroxy-4-methylcyclohexyl)-2-methylpropanenitrile (21)

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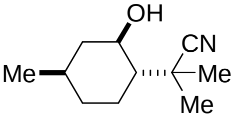
[11] W. Gu, R. B. Silverman, *Org. Lett.* **2003**, *5*, 415-418.



Nitrile **21** (66 mg, 73%) was obtained as a colorless solid following the General procedure A with (-)-isopulegol (Fluka, 85 µl, 0.5 mmol, 1.0 equiv) in 2 hours after purification by flash chromatography (Hexane:EtOAc=3:1).

Nitrile **21** (65 mg, 71%) was obtained as a colorless solid following the General procedure B with (-)-isopulegol (Fluka, 85 µl, 0.5 mmol, 1.0 equiv) in 1 hour after purification by flash chromatography (Hexane:EtOAc=3:1).

Mp 65-67°C;

$[\alpha]_D^{22}$ -45.79 (*c* 0.4, $CHCl_3$);

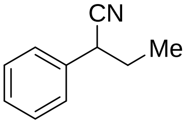
^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.64-3.54 (m, 1H, O-CH), 1.99-1.86 (m, 2H), 1.76-1.64 (m, 1H), 1.48-1.39 (m, 2H), 1.45 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.17-0.82 (m, 3H), 0.92 (d, ^3J=6.6 Hz, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 126.16, 72.21, 50.60, 45.70, 34.74, 34.09, 31.27, 26.34, 25.80, 24.94, 21.75;

IR ν 3446 (m), 2951 (s), 2923 (s), 2871 (m), 2233 (w), 1456 (m), 1391 (w), 1371 (w), 1302 (w), 1269 (w), 1201 (w), 1092 (w), 1058 (w), 1031 (m), 1005 (w), 980 (w), 850 (w), 536 (w);

HRMS (EI) calcd for $C_{11}H_{19}NO^+$ (M) 181.1461 Found 181.1463

2-phenylbutanenitrile (22)[12]



Nitrile **22** (33 mg, 45%) was obtained as a colorless oil following the General procedure A with *trans*-β-methylstyrene (99% Aldrich, 66 µl, 0.5 mmol, 1.0 equiv) in 2 hours after purification by flash chromatography (Hexane:Et_2O=6:1).

Nitrile **22** (40 mg, 55%) was obtained as a colorless oil following the General procedure B with *trans*-β-methylstyrene (99% Aldrich, 66 µl, 0.5 mmol, 1.0 equiv) in 3 hours after purification by flash chromatography (Hexane:Et_2O=6:1).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42-7.29 (m, 5H), 3.74 (t, ^3J=7.2 Hz, 1H, CNCH), 2.00-1.90 (m, 2H, CH_2), 1.08 (t, ^3J=7.5 Hz, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.70, 128.98, 127.98, 127.26, 120.72, 38.90, 29.20, 11.47;

IR ν 3066 (w), 3033 (m), 2972 (s), 2937 (m), 2879 (m), 2241 (m), 1494 (s), 1455 (s), 1384 (m), 1326 (w), 1234 (w), 1190 (w), 1092 (w), 1071 (w), 1030 (w), 932 (w), 912 (w), 890 (w), 831 (w), 798 (w), 760 (s), 699 (s);

HRMS (EI) calcd for $C_{10}H_{11}N^+$ (M) 145.0886 Found 145.0884

2,3-dihydro-1*H*-indene-1-carbonitrile (23)[13]

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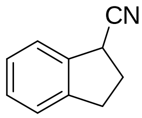
[12] J. You, J. G. Verkade, *J. Org. Chem.* **2003**, *68*, 8003-8007.

[13] L. Crombie, P. Tuchinda, M. J. Powell, *J. Chem. Soc. Perkin Trans. 1* **1982**, 1477-1484.



Nitrile **23** (45 mg, 63%) was obtained as a colorless oil following the General procedure A with indene (Aldrich, 59 µl, 0.5 mmol, 1.0 equiv) in 2 hours after purification by flash chromatography (Hexane:EtOAc=20:1).

Nitrile **23** (46 mg, 64%) was obtained as a colorless oil following the General procedure B with indene (Aldrich, 59 µl, 0.5 mmol, 1.0 equiv) in 1 hour after purification by flash chromatography (Hexane:EtOAc=20:1).

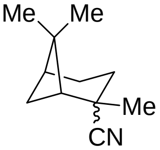
^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.45-7.43 (m, 1H), 7.28-7.25 (m, 3H), 4.11 (t, ^3J=8.4 Hz, 1H, CNCH), 3.10 (ddd, ^3J=4.5 Hz, ^3J=8.4 Hz, ^2J=15.9 Hz, 1H), 3.02-2.91 (m, 1H), 2.64-2.53 (m, 1H), 2.44-2.31 (m, 1H);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 142.72, 137.37, 128.38, 127.11, 124.84, 124.16, 120.98, 34.55, 31.49, 31.24;

IR ν 3072 (m), 3042 (m), 3026 (m), 2952 (m), 2873 (m), 2852 (m), 2239 (m), 1960 (w), 1919 (w), 1813 (w), 1718 (w), 1604 (w), 1480 (s), 1459 (s), 1439 (m), 1319 (w), 1265 (w), 1155 (w), 1140 (w), 1090 (w), 1024 (w), 943 (w), 898 (w), 876 (w), 856 (w), 820 (w), 766 (s), 742 (s);

HRMS (EI) calcd for $C_{10}H_9N^+$ (M) 143.0729 Found 143.0730

2,6,6-trimethylbicyklo[3.1.1]heptane-2-carbonitrile (24)



Nitrile **24** (72 mg, 88%, 90% purity by ^{1}H NMR) was obtained as a colorless oil following the General procedure A with (-)-β-Pinene (Fluka, 78 µl, 0.5 mmol, 1.0 equiv) in 2 hours after purification by flash chromatography (Pentane:Et$_2$O =8:1).

Nitrile **24** (49 mg, 60%, 90% purity by ^{1}H NMR) was obtained as a colorless oil following the General procedure B with (-)-β-Pinene (Fluka, 78 µl, 0.5 mmol, 1.0 equiv) in 1.5 hours after purification by flash chromatography (Hexane:CH$_2$Cl$_2$:3:2).

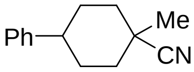
^{1}H NMR (CDCl$_3$, 300 MHz) δ 2.5-2.42 (m, 1H), 2.34-2.26 (m, 1H), 2.07-1.82 (m, 6H), 1.49 (s, 3H, CH$_3$), 1.26 (s, 3H, CH$_3$), 1.03 (s, 3H, CH$_3$);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 127.36, 49.76, 40.28, 38.81, 38.72, 31.75, 28.25, 27.98, 27.24, 25.28, 23.37;

IR ν 2996 (s), 2918 (s), 2872 (s), 2230 (m), 1470 (s), 1387 (m), 1368 (m), 1340 (w), 1288 (w), 1240 (m), 1226 (w), 1186 (w), 1127 (w), 1114 (w), 1083 (w), 1050 (w), 1016 (w), 972 (w), 869 (w);

HRMS (EI) calcd for $C_{11}H_{17}N^+$ (M-H) 162.1277 Found 162.1276

1-methyl-4-phenylcyclohexanecarbonitrile (25)



Nitrile **25** (74 mg, 74%) was obtained as a mixture of two diastereoisomers **25A** and **25B** (dr=17:1) following the General procedure A with (4-methylenecyclohexyl)benzene[14] (86 mg, 0.5 mmol, 1.0 equiv) in 3 hours after purification by flash chromatography (Hexane:CH_2Cl_2=3:2).

Nitrile **25** (81 mg, 81%) was obtained as a mixture of two diastereoisomers **25A** and **25B** (dr=3:1) following the General procedure B with (4-methylenecyclohexyl)benzene (86 mg, 0.5 mmol, 1.0 equiv) in 2.5 hours after purification by flash chromatography (Hexane:CH_2Cl_2=3:2).

Diastereoisomer **25A** (major):

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35-7.18 (m, 5H), 2.53-2.43 (m, 1H, Ph-CH), 2.13-2.08 (m, 2H), 1.96-1.80 (m, 4H), 1.53-1.40 (m, 2H), 1.42 (s, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.81, 128.45, 126.79, 126.32, 124.18, 43.32, 37.56, 34.17, 30.97, 27.36;

IR ν 3084 (m), 3062 (m), 3028 (m), 2973 (s), 2931 (s), 2858 (s), 2232 (m), 1949 (w), 1881 (w), 1807 (w), 1604 (m), 1494 (s), 1453 (s), 1383 (m), 1352 (w), 1302 (w), 1258 (w), 1168 (w), 1150 (m), 1109 (m), 1071 (w), 1029 (m), 969 (m), 934 (m), 894 (w), 856 (w), 758 (s), 701 (s), 647 (w);

HRMS (EI) calcd for $C_{14}H_{17}N^+$ (M) 199.1355 Found 199.1357;

Diastereoisomer **25B** (minor):

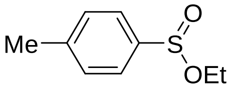
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34-7.19 (m, 5H), 2.68-2.58 (m, 1H, Ph-CH), 2.04-1.83 (m, 6H), 1.80-1.66 (2H), 1.46 (s, 3H, CH_3);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.35, 128.49, 126.70, 126.29, 126.17, 41.82, 35.10, 31.35, 27.68, 21.87;

IR ν 3434 (m), 3028 (w), 2936 (m), 2861 (m), 2232 (w), 1654 (w), 1602 (w), 1494 (w), 1451 (m), 1386 (w), 1164 (w), 1122 (w), 1070 (w), 1030 (w), 986 (w), 848 (w), 758 (m), 788 (s), 546 (m);

HRMS (EI) calcd for $C_{14}H_{17}N^+$ (M) 199.1355 Found 199.1357

Ethyl 4-methylbenzenesulfinate (26)[15]



^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61-7.58 (m, 2H), 7.33 (d, ^3J=8.1 Hz, 2H), 4.15-4.04 (m, 1H), 3.77-3.66 (m, 1H), 2.42 (s, 3H, CH_3), 1.27 (t, ^3J=6.9 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.49, 141.66, 129.55, 125.08, 60.75, 21.60, 15.67;

IR ν 3626 (w), 3564 (w), 3383 (w), 2997 (s), 2171 (m), 1916 (w), 1694 (m), 1651 (w), 1596 (m), 1386 (m), 1130 (s), 1081 (s), 999 (m), 881 (s);

HRMS (EI) calcd for $C_9H_{12}O_2S^+$ (M) 184.0553 Found 184.0551

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[14] (4-methylenecyclohexyl)benzene was prepared according to: A. G. M. Barret, M. J. Betts, A. Fenwick, *J. Org. Chem.* **1985**, *50*, 169-175.

[15] T. Yoshino, S. Imori, H. Togo, *Tetrahedron* **2006**, *62*, 1309-1317.