Straightforward heterogeneous palladium catalyzed synthesis of aryl ethers and aryl amines \textit{via} a solvent free dehydrogenative arylation

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SUPPORTING INFORMATION

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Experimental

General

All reagents were used as received from the chemical company. Alcohols and cyclohexanone derivatives were supplied by Acros, Sigma-Aldrich, Alfa Aesar and TCI. Glycerol, 99%, Reagentplus® was purchased from Sigma-Aldrich, Diglycerol 80% from TCI, Pd/C (5%) on activated carbon, reduced and dry (Escaf 1431) from Strem Chemicals.

$^1$H NMR and $^{13}$C NMR spectra were recorded on a BRUKER DRX 300 or BRUKER ALS 300 ($^1$H 300 MHz, $^{13}$C 75 MHz) in CDCl$_3$ (except when mentioned) and chemical shifts are given in ppm. $J$ values are given in Hertz (Hz). Abbreviations are defined as follows: br = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quadruplet, m = multiplet.

IR spectra were recorded on a Spectro Nicolet IS10 Smart ITR with an ATR diamond.

The HRMS-ESI mass spectra were recorded in positive-ion mode on a hybrid quadrupole time-of-flight mass spectrometer (MicroTOFQ-II, Bruker Daltonics, Bremen) with an Electrospray Ionization (ESI) ion source. The flow of spray gas was at 0.6 bar and the capillary voltage was 4.5kV. The solutions were infused at 180µL/h in a mixture of solvents (methanol / dichloromethane / water 45/40/15). The mass range of the analysis was 50-1000m/z and the calibration was done with sodium formate. The HRMS-CI mass spectra were recorded on a double-focusing mass spectrometer (ThermoFinnigan MAT95XL, Bremen, Germany) equipped with a chemical ionization (CI) source. The reagent gas was isobutene and the calibrations for high resolution mass spectra were done with perfluorotrybutylamine (FC43).

The GC-MS analysis were performed on a Focus GC (Thermo Electron Corporation, Bremen, Germany) equipped with a DB-5MS capillary column (30m, 0.25mm i.d, 0.25µm film thickness) and a DSQ mass spectrometer as a detector (Thermo Electron corporation, Bremen, Germany). The carrier gas was helium, at a flow rate of 1 mL/min. Column temperature was initially 70°C for 2 min, then gradually increased to 310°C at 15°C/min and finally kept at 310°C for 10min. The injector temperature was 220°C and the transfer line temperature was 280°C. For GC-MS detection an electron ionization system was used with electron energy of 70 eV, and the mass analyzer was a simple quadrupole.

General procedure for dehydrogenative alkylation of a cyclohexanone derivative and an alcohol as solvent and reagent in open reactor (table 2, entries 1-5, table 3, entries 1-3):

In a round-bottom flask equipped with a condenser fitted with a CaCl$_2$ guard, 3 mmol of cyclohexanone derivative was added to 15 mmol of alcohol. Next, 64 mg of Pd/C (5%) (0.03 mmol, 1 mol%) was added to the mixture, under an inert argon atmosphere. The medium was stirred at 130°C during 24h at 800 rpm. After the reaction, the crude was dissolved in CH$_2$Cl$_2$ and filtered off (Millipore Durapore filter 0.01 µm).
The solvent was evaporated under reduced pressure and the crude product was finally purified by silica column chromatography to afford the desired aromatic ether (eluent: cyclohexane/ethyl acetate = 100:0~1:1).

**Dehydrogenative alkylation of cyclohexanone with glycerol in open reactor (table 2, entry 6):**

In a round-bottom flask equipped with a condenser fitted with a CaCl$_2$ guard, 0.30 ml of cyclohexanone 2a (0.29 g, 3 mmol) was added to 5.53 g of glycerol 1f (60 mmol). Next, 128 mg of Pd/C (5%) (0.06 mmol, 2 mol%) was added to the mixture, under an inert argon atmosphere. The medium was stirred at 130°C during 60h at 800 rpm. After the reaction, the crude was dissolved in a mixture of MeOH/CH$_2$Cl$_2$ and filtered off (Millipore Durapore filter 0.01 µm). The solvents were evaporated under reduced pressure and the crude was extracted three times with CH$_2$Cl$_2$ and the organic layer was washed with H$_2$O and finally dried other MgSO$_4$. After evaporation of the solvents under reduced pressure, the crude product was finally purified by silica column chromatography to afford the desired aromatic ether 3f in 67% isolated yield (eluent: cyclohexane/ethyl acetate = 6:1~1:2).

**General procedure for dehydrogenative alkylation of a tetralone derivative and an alcohol as solvent and reagent in a sealed tube (table 3, entries 4-6, table 4, entries 1-4):**

In a sealed tube under an inert atmosphere of argon, 3 mmol of tetralone derivative was added to 15 mmol of alcohol. Next, 64 mg of Pd/C (5%) (0.03 mmol, 1 mol%) was added to the mixture. The tube was sealed and the medium was stirred at 150°C during 16h at 800 rpm. After the reaction, the crude was dissolved in CH$_2$Cl$_2$ and filtered off (Millipore Durapore filter 0.01 µm). The solvent was evaporated under reduced pressure and the crude product was finally purified by silica column chromatography to afford the desired aromatic ether (eluent: cyclohexane/ethyl acetate = 100:0~1:1). Products 3n and 3p were purified by using a mixture of cyclohexane/ethyl acetate in a ratio 4:1~0:100 and products 3o and 3q were purified by using a mixture of CH$_2$Cl$_2$/MeOH as eluent in a ratio 98/2~9:1.

**Dehydrogenative alkylation of cyclohexanone and hexylamine in open reactor (scheme 3):**

In a round-bottom flask equipped with a condenser fitted with a CaCl$_2$ guard, 0.30 ml of cyclohexanone (0.29 g, 3 mmol) was added to 0.40 ml of hexylamine (0.31 g, 3 mmol). Next, 64 mg of Pd/C (5%) (0.03 mmol, 1 mol%) was added to the mixture, under an inert argon atmosphere. The medium was stirred at 100°C during 60h at 800 rpm. After the reaction, the crude was dissolved in CH$_2$Cl$_2$ and filtered off (Millipore Durapore filter 0.01 µm). The solvent was evaporated under reduced pressure and the crude product was finally purified by silica column chromatography to afford the desired arylamine 11a in 71% yield (eluent: cyclohexane/ethyl acetate = 100:0~95:5).
Dehydrogenative alkylation of α-tetralone and hexylamine in sealed tube (scheme 3):

In a sealed tube under an inert atmosphere of argon, 0.67 ml of α-tetralone (0.73 g, 5 mmol) was added to 0.67 ml of hexylamine (0.51 g, 5 mmol). Next, 106 mg of Pd/C (5%) (0.05 mmol, 1 mol%) was added to the mixture, under an inert argon atmosphere. The tube was sealed and the medium was stirred at 100°C during 16h at 800 rpm. After the reaction, the crude was dissolved in CH₂Cl₂ and filtered off (Millipore Durapore filter 0.01 µm). The solvent was evaporated under reduced pressure and the crude product was finally purified by silica column chromatography to afford the desired arylamine 11b in 78 % isolated yield (eluent: cyclohexane/ethyl acetate = 100:0~95:5).

(hexyloxy)benzene [1132-66-7] (3a)

Colorless oil; ¹H NMR: δ = 0.95 (t, J = 7 Hz, 3H, CH₃), 1.35-1.43 (m, 4H, CH₂), 1.43-1.53 (m, 2H, CH₂), 3.98 (t, J = 6.5 Hz, 2H, CH₂), 6.92-6.96 (m, 3H, CH⁺arom); ¹³C NMR: δ = 14.2 (CH₃), 22.7 (CH₂), 25.9 (CH₂), 29.4 (CH₂), 31.7 (CH₂), 67.9 (CH₂), 114.6 (CH⁺arom), 120.5 (CH⁺arom), 129.5 (CH⁺arom), 159.3 (Cq); IR (ATR): νmax = 2930, 2858, 1600, 1586, 1497, , 1243, 1036, 751; 690 cm⁻¹; HRMS-ESI: m/z [MH⁺] calcd for C₁₂H₁₉O: 179.1430 found: 179.1432.

(isopentyloxy)benzene [1129-64-2] (3b)

Colorless oil; ¹H NMR: δ = 0.96 (d, J = 6.6 Hz, 6H, CH₃), 1.54-1.71 (m, 2H, CH₂), 1.82-1.87 (m, 1H, CH), 3.99 (t, J = 6.7 Hz, 2H, CH₂), 6.88-6.93 (m, 3H, CH⁺arom), 7.25-7.28 (m, 2H, CH⁺arom); ¹³C NMR: δ = 22.7 (CH₃), 25.2 (CH), 38.2 (CH₂), 66.3 (CH₂), 114.6 (CH⁺arom), 120.6 (CH⁺arom), 129.5 (CH⁺arom), 159.3 (Cq); IR (ATR): νmax = 3018, 2956, 2929, 2871, 1600, 1586, 1496, 1242, 1171, 750, 690 cm⁻¹; HRMS-CI: m/z [MH⁺] calcd for C₁₁H₁₇O: 165.1274 found: 165.1275.

(hexan-2-yloxy)benzene [23170-95-8] (3c)

Colorless oil; ¹H NMR: δ = 0.93 (t, J = 6.9 Hz, 3H, CH₃), 1.29 (d, J = 6 Hz, 3H, CH₃), 1.30-1.81 (m, 6H, CH₂), 4.33-4.40 (m, 1H, CH), 6.89-6.96 (m, 3H, CH⁺arom), 7.26-7.31 (m, 2H, CH⁺arom); ¹³C NMR: δ = 14.2 (CH₃), 19.9 (CH₃), 22.8 (CH₂), 27.9 (CH₂), 36.4 (CH₂), 73.8 (CH), 116.0 (CH⁺arom), 120.5 (CH⁺arom), 129.6
(CHₐrom), 158.4 (Cₗq); IR (ATR): νₘₐₓ = 2957, 2932, 2861, 1598, 1586, 1493, 1239, 1173, 1116, 749, 691 cm⁻¹; HRMS-ESI: m/z [MH]^+ calcd for C₁₂H₁₉O: 178.1430 found: 178.1428.

2-phenoxyethanol [122-99-6] (3d)

HO–O–CH₂–CH₃

Colorless oil; ¹H NMR: δ = 1.94 (br, 1H, OH), 3.95-3.98 (m, 2H, CH₂), 4.07-4.11 (m, 2H, CH₂), 6.91-7.00 (m, 3H, CHₐrom), 7.26-7.33 (m, 2H, CHₐrom); ¹³C NMR: δ = 61.7 (CH₂), 69.2 (CH₂), 114.7 (CHₐrom), 121.3 (CHₐrom), 129.7 (CHₐrom), 158.7 (Cₗq); IR (ATR): νₘₐₓ = 3361, 3063, 2930, 2874, 1598, 1587, 1495, 1455, 1241, 1172, 1079, 1041, 915, 893, 751, 690 cm⁻¹; HRMS-ESI: m/z [MNa]^+ calcd for C₈H₁₀NaO₂: 161.0573 found: 161.0572.

1-phenoxypropan-2-ol [770-35-4] (3e)

HO–O–CH₂–CH₂–CH₃

Colorless oil; ¹H NMR (400 MHz): δ = 1.29 (d, J = 6.3 Hz, 3H, CH₃), 2.12 (br, 1H, OH), 3.75-3.82 (m, 1H, CH₂), 3.93-3.97 (m, 1H, CH₂), 4.16-4.24 (m, 1H, CH), 6.90-6.99 (m, 3H, CHₐrom), 7.26-7.35 (m, 2H, CHₐrom); ¹³C NMR (100 MHz): δ = 18.9 (CH₃), 66.4 (CH), 73.3 (CH₂), 114.7 (CHₐrom), 121.3 (CHₐrom), 129.7 (CHₐrom), 158.7 (Cₗq); IR (ATR): νₘₐₓ = 3376, 2973, 2928, 2875, 1598, 1587, 1493, 1239, 1173, 1041, 750, 690 cm⁻¹; HRMS-ESI: m/z [MNa]^+ calcd for C₉H₁₂NaO₂: 175.0730 found: 175.0722.

2-phenoxypropan-1-ol [4169-04-4] (3e’)

HO–O–CH₂–CH₂–CH₂–OH

Colorless oil; ¹H NMR (400 MHz): δ = 1.28 (d, J = 6.1 Hz, 3H, CH₃), 2.12 (br, 1H, OH), 3.69-3.83 (m, 2H, CH₂), 4.49-4.53 (m, 1H, CH), 6.90-6.99 (m, 3H, CHₐrom), 7.26-7.35 (m, 2H, CHₐrom); ¹³C NMR (100 MHz): δ = 15.9 (CH₃), 66.5 (CH₂), 76.9 (CH), 116.3 (CHₐrom), 121.4 (CHₐrom), 129.7 (CHₐrom), 157.8 (Cₗq); IR (ATR): νₘₐₓ = 3376, 2973, 2928, 2875, 1598, 1587, 1493, 1239, 1173, 1041, 750, 690 cm⁻¹; HRMS-ESI: m/z [MNa]^+ calcd for C₉H₁₂NaO₂: 175.0730 found: 175.0722.

3-phenoxypropane-1,2-diol [538-43-2] (3f)

HO–O–CH₂–CH₂–O–OH

Beige solid; Mp = 57 °C; ¹H NMR: δ = 2.41 (br, 2H, OH), 3.72-3.87 (m, 2H, CH₂), 4.03-4.06 (m, 2H, CH₂), 4.08-4.14 (m, 1H, CH), 6.89-7.00 (m, 3H, CHₐrom), 7.26-7.33 (m, 2H, CHₐrom); ¹³C NMR: δ = 63.8
(CH₂), 69.0 (CH₂), 70.7 (CH), 114.6 (CH₃), 121.3 (CH₂), 129.6 (CH₂), 158.4 (Cq); IR (ATR): ν_{max} = 3446, 3101, 3039, 2982, 2934, 2915, 2875, 1598, 1586, 1495, 1472, 1456, 1245, 1171, 1044, 1021, 745, 684 cm⁻¹; HRMS-ESI: m/z [MNa⁺]calcd for C₉H₁₂NaO₃: 191.0679 found: 191.0675.

1-(hexyloxy)-3-methylbenzene [57792-36-6] (3g)

Colorless oil; ¹H NMR: δ = 0.91 (t, J = 6.2 Hz, 3H, CH₃), 1.31-1.38 (m, 4H, CH₂), 1.40-1.48 (m, 2H, CH₂), 1.72-1.82 (m, 2H, CH₂), 2.33 (s, 3H, CH₃), 3.94 (t, J = 6.6 Hz, 2H, CH₂), 6.69-6.76 (m, 3H, CH₂), 7.13-7.18 (m, 1H, CH₃); ¹³C NMR: δ = 13.7 (CH₃), 21.6 (CH₂), 22.8 (CH₂), 25.9 (CH₂), 29.4 (CH₂), 31.9 (CH₂), 67.8 (CH₂), 111.5 (CH₃), 115.5 (CH₃), 121.4 (CH₃), 129.3 (CH₃), 139.5 (Cq), 159.3 (Cq); IR (ATR): ν_{max} = 2974, 2928, 2859, 1601, 1584, 1489, 1258, 1157, 1048, 1035, 767, 689 cm⁻¹; HRMS-ESI: m/z [MNa⁺]calcd for C₁₃H₂₀NaO: 215.1406 found: 215.1405.

3-(hexyloxy)thiophene [63285-85-8] (3i)

Colorless oil; ¹H NMR (400 MHz): δ = 0.90 (t, J = 7.0 Hz, 3H, CH₃), 1.31-1.35 (m, 4H, CH₂), 1.42-1.47 (m, 2H, CH₂), 1.68-1.80 (m, 2H, CH₂), 3.94 (t, J = 6.5 Hz, 2H, CH₂), 6.21-6.23 (m, 1H, CH₃), 6.74-6.76 (m, 1H, CH₃); ¹³C NMR (100 MHz): δ = 14.2 (CH₃), 22.8 (CH₂), 25.9 (CH₂), 29.4 (CH₂), 31.7 (CH₂), 70.4 (CH₂), 97.1 (CH₃), 119.7 (CH₃), 124.7 (CH₃), 158.2 (Cq); IR (ATR): ν_{max} = 2922, 2851, 1545, 1377, 1370, 1234, 1175, 1071, 1028, 749, 625 cm⁻¹; HRMS-Cl: m/z [MH]⁺ calcd for C₁₀H₁₇OS: 185.1000 found: 185.1002.

1-(hexyloxy)naphthalene [60951-03-3] (3j)

Colorless oil; ¹H NMR: δ = 0.92 (t, J = 7.0 Hz, 3H, CH₃), 1.37-1.43 (m, 4H, CH₂), 1.54-1.61 (m, 2H, CH₂), 1.88-1.96 (m, 2H, CH₂), 4.14 (t, J = 6.4 Hz, 2H, CH₂), 6.79-6.82 (m, 1H, CH₃), 7.33-7.41 (m, 2H, CH₃), 7.45-7.49 (m, 2H, CH₃), 7.77-7.81 (m, 1H, CH₃), 8.27-8.31 (m, 1H, CH₃); ¹³C NMR: δ = 14.2 (CH₃), 22.8 (CH₂), 26.1 (CH₂), 29.4 (CH₂), 31.8 (CH₂), 68.2 (CH₂), 104.6 (CH₃), 120.0 (CH₃), 122.2 (CH₃), 125.2 (CH₃), 125.9 (Cq), 126.0 (CH₃), 126.4 (CH₃), 127.5 (CH₃), 134.6 (Cq), 155.0 (Cq); IR (ATR): ν_{max} = 3052, 2928, 2857, 1580, 1508, 1460, 1267, 1239, 1099, 789, 767 cm⁻¹; HRMS-Cl: m/z [MH]⁺ calcd for C₁₆H₁₂O: 229.1587 found: 229.1587.
2-(hexyloxy)naphthalene [31059-20-8] (3k)

Colorless oil; $^1$H NMR: $\delta = 0.92$ (t, $J = 7.0$ Hz, 3H, CH$_3$), 1.33-1.40 (m, 4H, CH$_2$), 1.46-1.54 (m, 2H, CH$_2$), 1.80-1.90 (m, 2H, CH$_2$), 4.08 (t, $J = 6.6$ Hz, 2H, CH$_2$), 7.13-7.17 (m, 2H, CH$_{arom}$), 7.29-7.35 (m, 1H, CH$_{arom}$), 7.40-7.46 (m, 1H, CH$_{arom}$), 7.70-7.77 (m, 3H, CH$_{arom}$); $^{13}$C NMR: $\delta = 14.2$ (CH$_3$), 22.8 (CH$_2$), 25.9 (CH$_2$), 29.4 (CH$_2$), 31.8 (CH$_2$), 68.1 (CH$_2$), 106.6 (CH$_{arom}$), 119.2 (CH$_{arom}$), 123.6 (CH$_{arom}$), 126.4 (CH$_{arom}$), 126.8 (CH$_{arom}$), 127.8 (CH$_{arom}$), 129.0 (C$_q$), 129.4 (CH$_{arom}$), 134.8 (C$_q$), 157.3 (C$_q$); IR (ATR): $\nu_{max} = 3057$, 2928, 2857, 1628, 1600, 1584, 1440, 1430, 1371, 1222, 835, 743, 622 cm$^{-1}$; HRMS-ESI: $m/z$ [MH]$^+$ calcd for C$_{16}$H$_{20}$O: 229.1587 found: 229.1580.

1-(hexyloxy)-6-methoxynaphthalene [No CAS Number] (3l)

White solid; Mp = 67 °C; $^1$H NMR: $\delta = 0.92$ (t, $J = 7.0$ Hz, 3H, CH$_3$), 1.34-1.44 (m, 4H, CH$_2$), 1.47-1.59 (m, 2H, CH$_2$), 1.87-1.95 (m, 2H, CH$_2$), 3.92 (s, 3H, CH$_3$), 4.12 (t, $J = 6.4$ Hz, 2H, CH$_2$), 5.68-5.89 (m, 1H, CH$_{arom}$), 7.10-7.14 (m, 2H, CH$_{arom}$), 7.26-7.33 (m, 2H, CH$_{arom}$), 8.18-8.21 (m, 1H, CH$_{arom}$); $^{13}$C NMR: $\delta = 14.2$ (CH$_3$), 22.8 (CH$_2$), 26.1 (CH$_2$), 29.4 (CH$_2$), 31.8 (CH$_2$), 55.3 (CH$_3$), 68.2 (CH$_2$), 102.9 (CH$_{arom}$), 105.7 (CH$_{arom}$), 117.5 (CH$_{arom}$), 119.1 (CH$_{arom}$), 121.1 (C$_q$), 124.0 (CH$_{arom}$), 126.8 (CH$_{arom}$), 136.0 (C$_q$), 155.3 (C$_q$), 158.2 (C$_q$); IR (ATR): $\nu_{max} = 2980, 2939, 2854, 1627, 1600, 1584, 1440, 1430, 1371, 1222, 1144, 1097, 1028, 841, 831, 781, 744, 732$ cm$^{-1}$; HRMS-ESI: $m/z$ [MH]$^+$ calcd for C$_{17}$H$_{23}$O$_2$: 259.1693 found: 259.1692.

3-(naphthalen-1-yl)oxy)propane-1,2-diol [36112-95-5] (3m)

Beige solid; Mp = 95 °C; $^1$H NMR: $\delta = 1.79$ (br, 2H, OH), 3.84-3.99 (m, 2H, CH$_2$), 4.23-4.31 (m, 3H, CH+CH$_2$), 6.85 (d, $J = 6.0$ Hz, 1H, CH$_{arom}$), 7.34-7.40 (m, 1H, CH$_{arom}$), 7.45-7.51 (m, 3H, CH$_{arom}$), 7.80-7.83 (m, 1H, CH$_{arom}$), 8.20-8.23 (m, 1H, CH$_{arom}$); $^{13}$C NMR (CDCl$_3$/MeOD = 9/1): $\delta = 63.6$ (CH$_2$), 69.0 (CH$_2$), 70.5 (CH), 104.8 (CH$_{arom}$), 120.5 (CH$_{arom}$), 121.7 (CH$_{arom}$), 125.1 (CH$_{arom}$), 125.5 (C$_q$), 125.8 (CH$_{arom}$), 126.4 (CH$_{arom}$), 127.4 (CH$_{arom}$), 134.4 (C$_q$), 154.2 (C$_q$); IR (ATR): $\nu_{max} = 3278, 3053, 2938, 2871, 1596, 1577, 1509, 1460, 1392, 1265, 1240, 1103, 1070, 1042, 1018, 987, 892, 790, 767, 734, 625$ cm$^{-1}$; HRMS-ESI: $m/z$ [MNa]$^+$ calcd for C$_{13}$H$_{14}$NaO$_3$: 241.0835 found: 241.0841.
3-(2-hydroxy-3-(naphthalen-1-yloxy)propoxy)propane-1,2-diol [No CAS Number] (3n)

White gel (Mixture of isomers) \(^1\)H NMR (400 MHz): \(\delta = 3.50-3.91\) (m, 10H, CH\(_2\)+CH+OH), 4.05-4.15 (m, 2H, CH\(_2\)), 4.28-4.30 (m, 1H, CH), 6.73 (d, \(J = 7.3\) Hz, 1H, CH\(_{arom}\)), 7.29-7.32 (m, 1H, CH\(_{arom}\)), 7.39-7.46 (m, 3H, CH\(_{arom}\)), 7.75-7.77 (m, 1H, CH\(_{arom}\)), 8.20-8.23 (m, 1H, CH\(_{arom}\)); \(^13\)C NMR (100 MHz): \(\delta = 63.9\) (CH\(_2\)), 63.90 (CH\(_2\)), 69.0 (CH\(_2\)), 69.3 (C\(^*\)H), 69.4 (C\(^*\)H), 71.1 (C\(^*\)H), 71.2 (C\(^*\)H), 73.0 (CH\(_2\)), 73.1 (CH\(_2\)), 105.0 (CH\(_{arom}\)), 120.8 (CH\(_{arom}\)), 121.9 (CH\(_{arom}\)), 125.4 (C\(_q\)), 125.6 (CH\(_{arom}\)), 125.9 (CH\(_{arom}\)), 126.6 (CH\(_{arom}\)), 127.7 (CH\(_{arom}\)), 134.6 (C\(_q\)), 154.2 (C\(_q\)); IR (ATR): \(\nu_{max} = 3349, 2925, 2872, 1595, 1580, 1460, 1396, 1268, 1240, 1100, 1068, 1020, 792, 769, 734, 569\) cm\(^{-1}\); HRMS-ESI: \(m/z\) [MNa]\(^+\) calec for C\(_{16}\)H\(_{20}\)NaO\(_4\): 315.1203 found: 315.1187.

3-(naphthalen-2-yloxy)propane-1,2-diol [34646-56-5] (3o)

Beige solid; Mp = 109 °C; \(^1\)H NMR: \(\delta = 3.78-3.93\) (m, 2H, CH\(_2\)), 4.10-4.26 (m, 3H, CH+CH\(_2\)), 7.14-7.18 (m, 2H, CH\(_{arom}\)), 7.33-7.38 (m, 1H, CH\(_{arom}\)), 7.42-7.48 (m, 1H, CH\(_{arom}\)), 7.71-7.79 (m, 3H, CH\(_{arom}\)); \(^13\)C NMR (CDCl\(_3\)/MeOD = 4/1): \(\delta = 63.3\) (CH\(_2\)), 68.9 (CH\(_2\)), 70.3 (CH), 106.6 (CH\(_{arom}\)), 118.5 (CH\(_{arom}\)), 123.6 (CH\(_{arom}\)), 126.2 (CH\(_{arom}\)), 126.6 (CH\(_{arom}\)), 127.4 (CH\(_{arom}\)), 129.0 (C\(_q\)), 129.3 (CH\(_{arom}\)), 134.4 (C\(_q\)), 156.5 (C\(_q\)); IR (ATR): \(\nu_{max} = 3292, 2980, 2880, 1627, 1598, 1508, 1454, 1256, 1213, 1182, 1115, 1053, 839, 741\) cm\(^{-1}\); HRMS-ESI: \(m/z\) [MNa]\(^+\) calec for C\(_{13}\)H\(_{14}\)NaO\(_5\): 241.0835 found: 241.0835.

3-(2-hydroxy-3-(naphthalen-2-yloxy)propoxy)propane-1,2-diol [No CAS Number] (3p)

White gel (Mixture of optical isomers); \(^1\)H NMR (400 MHz): \(\delta = 3.53-3.95\) (m, 10H, CH\(_2\)+CH+OH), 4.06-4.11 (m, 2H, CH\(_2\)), 4.20-4.25 (m, 1H, CH), 7.08-7.14 (m, 2H, CH\(_{arom}\)), 7.29-7.34 (m, 1H, CH\(_{arom}\)), 7.38-7.43 (m, 1H, CH\(_{arom}\)), 7.65-7.74 (m, 3H, CH\(_{arom}\)); \(^13\)C NMR (100 MHz): \(\delta = 63.9\) (CH\(_2\)), 69.0 (CH\(_2\)), 69.2 (C\(^*\)H), 69.3 (C\(^*\)H), 71.1 (C\(^*\)H), 71.1 (C\(^*\)H), 72.9 (CH\(_2\)), 73.0 (CH\(_2\)), 73.1 (CH\(_2\)), 107.0 (CH\(_{arom}\)), 118.7 (CH\(_{arom}\)), 124.0 (CH\(_{arom}\)), 126.6 (CH\(_{arom}\)), 126.9 (CH\(_{arom}\)), 127.8 (CH\(_{arom}\)), 129.2 (C\(_q\)), 129.6 (CH\(_{arom}\)), 134.5 (C\(_q\)), 156.5 (C\(_q\)); IR (ATR): \(\nu_{max} = 3348, 2924, 2876, 1628, 1600, 1510, 1464, 1257, 1216, 1181, 1118, 1036, 746, 730, 623\) cm\(^{-1}\); HRMS-ESI: \(m/z\) [MNa]\(^+\) calec for C\(_{16}\)H\(_{20}\)NaO\(_5\): 315.1203 found: 315.1203.
N-hexylaniline [4746-32-1] (11a)

\[
\begin{align*}
\text{Colorless oil; }^1\text{H NMR: } \delta &= 0.89 \ (t, \ J = 6.8 \text{ Hz}, 3\text{H, CH}_3), 1.28-1.43 \ (m, 6\text{H, CH}_2), 1.58-1.66 \ (m, 2\text{H, CH}_2), 3.11 \ (t, \ J = 7.2 \text{ Hz}, 2\text{H, CH}_2), 6.67-6.76 \ (m, 3\text{H, CH}_\text{arom}), 7.16-7.22 \ (m, 2\text{H, CH}_\text{arom}); \\
^{13}\text{C NMR: } \delta &= 14.2 \ (\text{CH}_3), 22.8 \ (\text{CH}_2), 27.0 \ (\text{CH}_2), 29.7 \ (\text{CH}_2), 31.8 \ (\text{CH}_2), 44.1 \ (\text{CH}_2), 112.8 \ (\text{CH}_\text{arom}), 117.2 \ (\text{CH}_\text{arom}), 129.3 \ (\text{CH}_\text{arom}), 148.6 \ (C_q); \\
\text{IR (ATR): } \nu_{\text{max}} &= 3410, 2955, 2925, 2855, 1602, 1505, 1466, 1319, 1254, 1178, 745, 690 \text{ cm}^{-1}; \\
\text{HRMS-ESI: } m/z [\text{M}+\text{H}]^+ \text{ calcld for } C_{12}H_{20}N: 178.1590 \text{ found: 178.1597}. 
\end{align*}
\]

N-hexynaphthalen-1-amine [87619-72-5] (11b)

\[
\begin{align*}
\text{Colorless oil; }^1\text{H NMR: } \delta &= 0.92 \ (t, \ J = 7.1 \text{ Hz}, 3\text{H, CH}_3), 1.35-1.45 \ (m, 4\text{H, CH}_2), 1.47-1.55 \ (m, 2\text{H, CH}_2), 1.74-1.83 \ (m, 2\text{H, CH}_2), 3.28 \ (t, \ J = 7.2 \text{ Hz}, 2\text{H, CH}_2), 6.62 \ (d, \ J = 7.5 \text{ Hz}, 1\text{H, CH}_\text{arom}), 7.22-7.26 \ (m, 1\text{H, CH}_\text{arom}), 7.33-7.38 \ (m, 1\text{H, CH}_\text{arom}), 7.42-7.47 \ (m, 2\text{H, CH}_\text{arom}), 7.78-7.83 \ (m, 2\text{H, CH}_\text{arom}); \\
^{13}\text{C NMR (100 MHz): } \delta &= 14.2 \ (\text{CH}_3), 22.8 \ (\text{CH}_2), 27.2 \ (\text{CH}_2), 29.5 \ (\text{CH}_2), 31.8 \ (\text{CH}_2), 44.4 \ (\text{CH}_2), 104.3 \ (\text{CH}_\text{arom}), 117.2 \ (\text{CH}_\text{arom}), 119.9 \ (\text{CH}_\text{arom}), 123.4 \ (C_q), 124.7 \ (\text{CH}_\text{arom}), 125.7 \ (\text{CH}_\text{arom}), 126.8 \ (\text{CH}_\text{arom}), 128.8 \ (\text{CH}_\text{arom}), 134.4 \ (C_q), 143.8 \ (C_q); \\
\text{IR (ATR): } \nu_{\text{max}} &= 3427, 3052, 2954, 2925, 2854, 1582, 1525, 1476, 1408, 1280, 1132, 1107, 764, 570 \text{ cm}^{-1}; \\
\text{HRMS-ESI: } m/z [\text{M}+\text{H}]^+ \text{ calcld for } C_{16}H_{22}N: 228.1747 \text{ found: 228.1738}. 
\end{align*}
\]
(hexyloxy)benzene [1132-66-7] (3a)
(isopentyloxy)benzene [1129-64-2] (3b)
(hexan-2-yloxy)benzene [23170-95-8] (3c)
1-phenoxyp propane-2-ol [770-35-4] (3e) and 2-phenoxyp propane-1-ol [4169-04-4] (3e')

61% 39%

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1-(hexyloxy)-3-methylbenzene [57792-36-6] (3g)
3-(hexyloxy)thiophene [63285-85-8] (3i)

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1-(hexyloxy)naphthalene [60951-03-3] (3j)
2-(hexyloxy)naphthalene [31059-20-8] (3k)

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1-(hexyloxy)-6-methoxynaphthalene [No CAS Number] (3l)
3-\text{naphthalen-1-ylxy}propane-1,2-diol [36112-95-5] (3m)
3-(2-hydroxy-3-(naphthalen-1-yl)oxy)propoxy)propane-1,2-diol [No CAS Number] (3n).

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3-(naphthalen-2-yloxy)propane-1,2-diol [34646-56-5] (3o)
3-(2-hydroxy-3-(naphthalen-2-yloxy)propoxy)propane-1,2-diol [No CAS Number] (3p)
N-hexylaniline [4746-32-1] (11a)

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**N-hexynaphthalen-1-amine [87619-72-5] (11b)**

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