Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Towards a General and Straightforward Synthesis of Ethers from Esters: A Convenient Iron-catalyzed Hydrosilylation of Esters

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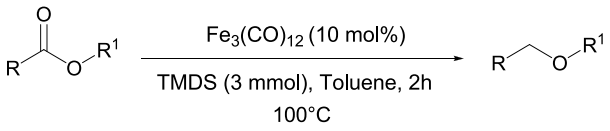
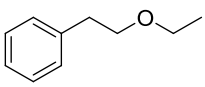
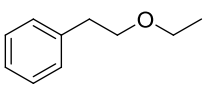
General information: Unless otherwise stated, reactions were run under an argon atmosphere with exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds. THF, toluene, 1,2-dimethoxyethane, 1,4-dioxane, diglyme and di-n-butyl ether were distilled from sodium and dichloromethane was distitlled from calcium hydride. NMR spectra were recorded on Bruker AV 300. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively. All measurements were carried out at room temperature unless otherwise stated. Infrared spectra were recorded on a Nicolet Magna-IR-Serie 550 spectrometer using the ATR method. Wave numbers (ν) are reported in cm-1. Mass spectra were recorded on an AMD 402/3 or a HP 5989A mass selective detector. Gas chromatography was performed on a HP 6890 chromatograph with a HP5 column.



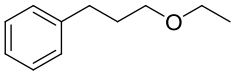
General procedure for the reduction of esters: A 25 mL oven dried schlenk tube containing a stirr bar was charged with $Fe_3(CO)_{12}$ (10 mol%), and the corresponding ester (1 mmol). Dry toluene (3 mL) and tetramethyldisiloxane (TMDS) (3 mmol) were added respectively after purging the schlenk tube with argon and vacuum for three times. The resulting mixture was stirred at 100 °C until the substrates completely goes away. After complete disappearance of the substrates, the reaction mixture was vigorously stirred with 3 mL 2(M) NaOH solution in 50 mL conical flask for 3 h and then extracted with excess ethylacetate (3 x 20 mL).The combined organic layer dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by silica gel column chromatography using ethylacetate / hexane to afford the pure desired product.



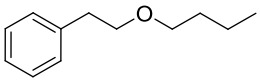
(2-Ethoxyethyl)benzene[1] (1): yield 85%, colourless liquid. **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ 7.24 (m, 2H), 7.20 (m, 3H), 3.59 (t, J = 7.52 Hz , 2H), 3.48 (q, J = 7.52 Hz, 2H), 2.88 (t, J = 7.53 Hz, 2H), 1.17 (t, J = 7.52 Hz, 3H). **^{13}C NMR** δ 138.8, 127.9, 126.2, 125.8, 70.6, 65.8, 35.8, 14.9. **MS (EI):** *m/z* 150(M^+). **HRMS** (EI, m/z) calcd. for $C_{10}H_{14}O$, 150.21756; found 150.21759.



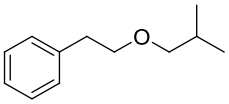
(2-Ethoxyethyl)benzene[1] (2): yield 85%, colourless liquid. **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ 7.24 (m, 2H), 7.20 (m, 3H), 3.59 (t, J = 7.52 Hz , 2H), 3.48 (q, J = 7.52 Hz, 2H), 2.88 (t, J = 7.53 Hz, 2H), 1.17 (t, J = 7.52 Hz, 3H). **^{13}C NMR** δ 138.8, 127.9, 126.2, 125.8, 70.6, 65.8, 35.8, 14.9. **MS (EI):** *m/z* 150(M^+). **HRMS** (EI, m/z) calcd. for $C_{10}H_{14}O$, 150.21756; found 150.21759.



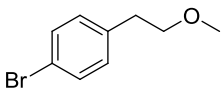
(3-Ethoxypropyl)benzene[1] (3): yield 78%, colourless liquid; **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.24 (m, 2H), 7.13 (m, 3H), 3.40 (q, 2H, *J* = 6.92 Hz), 3.38 (t, 2H, *J* = 6.93 Hz), 2.63 (t, 2H, *J* = 6.92 Hz), 1.85 (m, 2H), 1.18 (t, 3H, *J* = 6.89 Hz); **^{13}C NMR** (300.1 MHz, $CDCl_3$) δ 141.5, 128.0, 127.9, 125.0, 68.8, 65.8, 32.0, 30.9, 15.0; **MS (EI):** *m/z* 164 (M+) **HRMS** (EI, m/z) calcd. for $C_{11}H_{16}O$, 164.24414; found 164.24410.



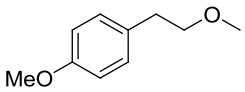
(2-Butoxyethyl)benzene[1] (4): yield 70%, colourless liquid; **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ 7.20 (m, 2H), 7.15 (m, 3H), 3.56 (t, 2H, *J* = 6.92 Hz), 3.40 (t, 2H, *J* = 6.95 Hz), 2.83(t, 2H, *J* = 6.95 Hz), 1.51 (q, 2H, *J*= 6.94 Hz), 1.35 (m, 2H), 0.85 (t, 3H, *J* = 6.95 Hz); **^{13}C** NMR (300.1 MHz, $CDCl_3$) δ 138.5, 127.3, 127.0, 125.8, 70.9, 70.3, 35.8, 30.8, 18.5, 12.8; MS (EI): *m/z* 178.



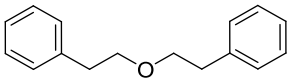
(2-Isobutoxyethyl)benzene[1] (5): yield 70%, colourless liquid; **^{1}H NMR** (300.1 MHz, $CDCl_3$) δ7.24 (m, 2H), 7.15 (m, 3H), 3.58 (t, 2H, *J* = 6.92 Hz), 3.15 (d, 2H, *J* = 6.32 Hz), 2.80 (t, 2H, *J* = 6.98 Hz), 1.80 (m, 1H), 0.85 (d, 6H, *J* = 6.95 Hz); **^{13}C NMR** (300.1 MHz, $CDCl_3$) δ 138.8, 127.8, 127.9, 126.0, 75.9, 70.8, 35.8, 27.9 18.8; **MS (EI):** *m/z* 178 (M+).



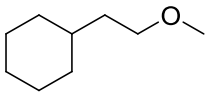
1-Bromo-4-(2-ethoxyethyl)benzene[1] (6): yield 75%, colourless liquid. **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 3.50 (t, *J* = 6.90 Hz, 2H,), 3.28 (s, 3H), 2.76 (t, *J* = 7.0 Hz, 2H) **^{13}C NMR** δ 138.8, 132.0, 131.5, 121.5, 76.0, 59.2, 36.2 **MS (EI):** *m/z* 213 (M^+).



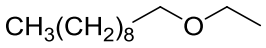
1-(2-Ethoxyethyl)-4-methoxybenzene[2] (7): yield 70%, colourless liquid. **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 3.70 (s, 3H), 3.52 (t, *J* = 7.2 Hz, 2H), 3.31 (s, 3H), 2.78 (t, *J* = 6.8 Hz, 2H). **^{13}C NMR** δ 157.8, 129.7, 128.8, 112.9, 73.2, 56.5, 54.8, 34.8. **MS (EI):** *m/z* 166(M^+).



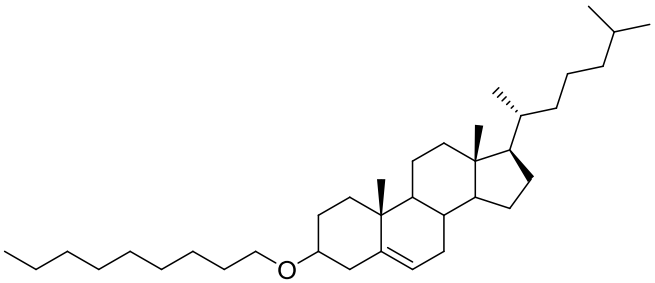
2,2'-Oxybis(ethane-2,1-diyl)dibenzene[3] (9): yield 85%, colourless liquid. **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ 7.43-7.32 (m, 4H), 7.30-7.25 (m, 6H), 3.63 (t, J= 6.93Hz, 4H), 2.80 (t, J= 6.95Hz, 4H) **^{13}C NMR** δ 140.2, 135.3, 132.1, 130.3, 76.2, 36.5 **MS (EI):** *m/z* 226(M^+).



(2-Ethoxyethyl)cyclohexane[4] (10): yield 65%, colourless liquid. **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ 3.50-3.46 (m, 2H), 3.35 (s, 3H), 0.82-1.92 (m, 13H); **^{13}C NMR** δ 74.2, 60.3, 35.2, 35.0, 34.9, 34.0, 26.2, 25.8. **MS (EI):** *m/z* 142(M^+).



1-Ethoxydecane[1] (18): yield 70%, colourless liquid. **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ 3.52 (q, 2H, J = 6.93 Hz), 3.36 (t, 2H, J = 6.95 Hz), 1.53 (m, 2H, J = 6.98 Hz), 1.38-1.20 (m, 14H), 1.15 (t, 3H, J = 6.98 Hz), 0.80 (t, 3H, J = 6.95 Hz); ^{13}C NMR (300.1 MHz, $CDCl_3$) δ 70.0, 65.6, 31.0, 29.2, 28.8, 28.6, 28.4, 28.0, 25.8, 21.9, 14.8, 13.6. **MS (EI):** *m/z* 186 (M+).



(10R,13R,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-3-(nonyloxy)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene (19): Yield: 70%, colourless liquid. **^{1}H NMR** (300.1 MHz, $CDCl_3$): δ 5.26 (s, br, 1H), 3.36 (t, J= 7.25 Hz, 2H), 3.10-2.98 (m, 1H), 2.32-2.23(m, 1H), 2.17-2.09 (m, 1H), 1.98-1.89 (m, 2H), 1.84-1.71 (m, 4H), 1.53-1.37 (m, 8H), 1.32-1.14 (m, 17H), 1.097-0.98 (m, 4H), 0.97-0.88 (m, 6H), 0.86-0.75 (m, 13H), 0.60(s, 4H) **^{13}C NMR** δ 140.1, 120.3, 67.1, 55.7, 55.1, 49.1, 41.2, 38.7, 38.4, 38.1, 36.2, 35.8, 35.1, 34.7, 30.8, 29.1, 28.8, 28.5, 28.4, 28.2, 27.9, 27.4, 27.0, 26.9, 25.1, 23.2, 21.6, 20.0, 18.6, 17.8, 13.1, 10.9. **MS (EI):** m/z 512(M^+). HRMS (EI,m/z) calcd. for $C_{36}H_{64}O$, 512.89276; found 512.89280.

References:

1. N. Sakai, T. Moriya, T. Konakahara, *J. Org. Chem.* **2007**, *72*, 5920.

2. O. Vechorkin, V. Proust, X. Hu, *J. Am. Chem. Soc*. **2009**, *131*, 9756.

3. J. S. Yadav, B. V. Subba Reddy, K. Shiva Shankar, T. Swamy, *Tetrahedron Lett.* **2010**, *51*, 46.

4. L. A. Paquette, G. Zon, *J. Am. Chem. Soc.* **1974**, *96*, 203.