Palladium-Promoted Arylation of Functionalised Organolithium Compounds via Their Zinc Derivatives

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Dedicated to Professor E. Negishi for his outstanding contributions to main-group metal organometallic chemistry

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The reaction of different functionalised organolithium compounds **2**, **5**, **8**, and **13** [easily prepared by DTBB-catalysed lithiation of isochromane (**1**), phthalane (**4**), 2,3-dihydrobenzofuran (**7**) and 1-chloro-3,3-diethoxypropane (**12**), respectively] with an equimolecular amount of zinc bromide, followed by reaction with an aryl or an alkenyl bromide in the presence of a catalytic amount of $[Pd(PPh_3)_4]$ or $[Pd(PPh_3)_2(OAc)_2]$ (5 mol %) under THF reflux overnight gives the expected cross-coupling products **3**, **6**, **9** and **14**, respectively. This arylation or alkenylation process, which also works with the corresponding iodinated derivatives, is not possible in the absence of both the zinc and palladium compounds, under the same reaction conditions.

Introduction

Organolithium compounds are versatile carbanionic intermediates in synthetic organic chemistry, especially in carbon-carbon bond formation reactions.[1] When organolithium reagents bear a functional group, their utility in synthesis is strongly increased as they are able to transfer the functionality to the electrophilic reagent, so polyfunctionalised molecules can be prepared directly in only one reaction step.[2] In general, whereas alkylation of organolithiums works nicely, especially with primary alkyl halides, the reaction of these intermediates with vinylic or aromatic halides works only in special cases, mainly through the in situ generation of the corresponding arynes.[3] In fact, a useful methodology to prepare aryllithium compounds is halogen (mainly iodine or bromine)-lithium exchange using an alkyllithium reagent for that purpose.[3,4] In the last few years, we have been preparing functionalised organolithium compounds[2] by an arene-catalysed lithiation[5–7] starting from (a) functionalised chlorinated materials, or (b) from heterocyclic compounds[8] by chlorine-lithium exchange or reductive ring opening, respectively. As expected, these intermediates react with different electrophiles, such as H_2O, D_2O, RCHO, RR′CO, CO_2 or Me_3SiCl, and in some cases alkyl halides,[9] although they are resistant to arylation or alkenylation, with the corresponding bromides or iodides. In this paper we describe a solution to this problem by using a lithium–zinc transmetallation[10] followed by a palladium-catalysed cross-coupling arylation or alkenylation (Negishi-type reaction)[11] with the corresponding bromides.[12] This process is essentially an sp^3-sp^2-carbon hybridised cross-coupling reaction, generating a new type of functionalised organic molecules.

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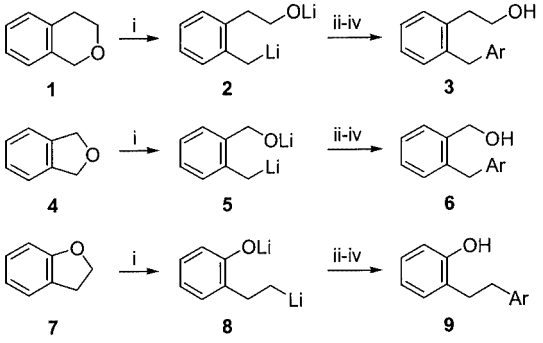
Results and Discussion

The 4,4′-di-*tert*-butylbiphenyl (DTBB)-catalysed lithiation[5] of isochromane (**1**)[13] in THF at 20 °C led to a suspension which, after filtration of the excess of lithium, gave a solution of the corresponding functionalised organolithium compound **2**. This intermediate was treated with zinc bromide (1:1 molar ratio) and then successively with the corresponding aryl bromide (1:1.1 molar ratio) and a catalytic amount of a palladium compound {$[Pd(PPh_3)_4]$ (Method A) or $[Pd(PPh_3)_2(OAc)_2]$ (Method B); 5 mol %} and refluxed overnight. Final hydrolysis with hydrochloric acid afforded the expected products **3a–3l** (Scheme 1 and Table 1, entries 1–13). This Negishi cross-coupling reaction also worked nicely with aryl iodides, as was shown with iodobenzene (Table 1, entry 1 and footnote [d]), although the reaction failed with chlorobenzene. In addition, aryl bromides containing electron-withdrawing (F, CF_3, MeCO, CN, CO_2Et) or -donating (MeO, Me_2N) groups can be used for the coupling reaction, as well as naphthyl or heterocyclic derivatives. Concerning the catalyst, both methods A and B, gave comparable results (see, for instance, Table 1, entries 1 and 2).

Table 1. Preparation of compounds **3**, **6** and **9**

Entry	Starting material	Organolithium intermediate	Aryl bromide	Method[a]	Product[b]	Yield (%)[c]
1	**1**	**2**	PhBr	A	**3a**	77 (83)[d]
2				B	**3a**	74
3	**1**	**2**	4-FC_6H_4Br	B	**3b**	69
4	**1**	**2**	4-$CF_3C_6H_4Br$	A	**3c**	67
5	**1**	**2**	4-$MeOC_6H_4Br$	A	**3d**	63
6	**1**	**2**	4-$Me_2NC_6H_4Br$	B	**3e**	38[e]
7	**1**	**2**	4-$MeCOC_6H_4Br$	A	**3f**	33
8	**1**	**2**	4-NCC_6H_4Br	B	**3g**	78[e]
9	**1**	**2**	4-$EtO_2CC_6H_4Br$	B	**3h**	49[e]
10	**1**	**2**	1-bromonaphthalene	A	**3i**	56
11	**1**	**2**	4-bromopyridine	A	**3j**	29[e]
12	**1**	**2**	2-bromothiophene	A	**3k**	59
13	**1**	**2**	3-bromofuran	B	**3l**	30
14	**4**	**5**	PhBr	B	**6a**	43
15	**4**	**5**	4-*t*BuC_6H_4Br	B	**6b**	41
16	**4**	**5**	4-$MeOC_6H_4Br$	B	**6c**	26
17	**7**	**8**	PhBr	B	**9**	49

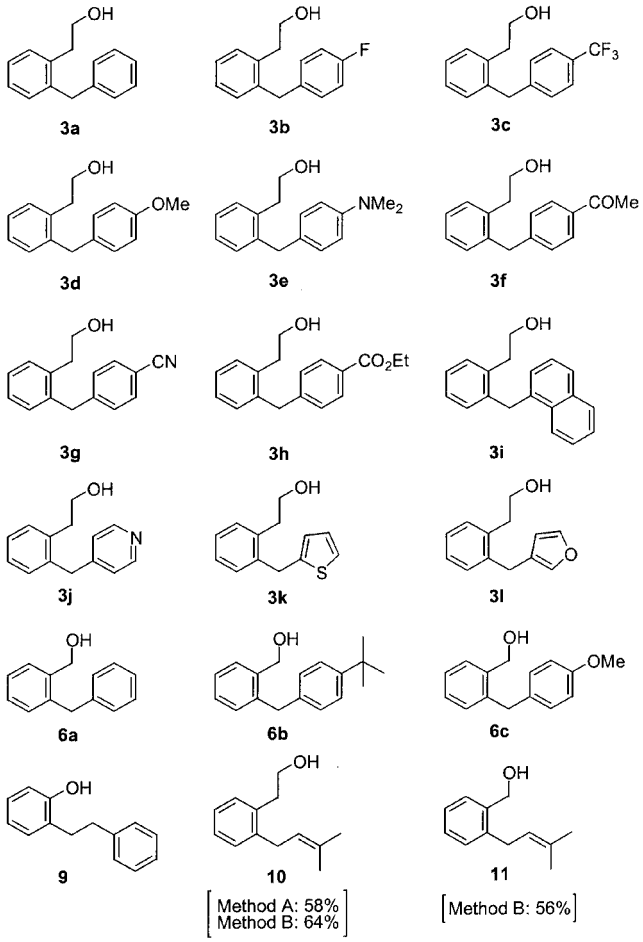
[a] Method A: $[Pd(PPh_3)_4]$; Method B: $[Pd(PPh_3)_2(OAc)_2]$. [b] All products **3**, **6** or **9** were ≥ 95% pure (300 MHz ^1H NMR and/or GC). [c] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the heterocyclic precursors **1**, **4** or **7**, respectively. [d] Iodobenzene was used instead of bromobenzene. [e] Water was used in the final hydrolysis.



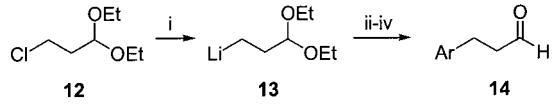
Scheme 1. Preparation of compounds **3**, **6** and **9**: (i) Li, DTBB (5 mol %), THF, 0 or 20 °C, then filter off the excess of lithium; (ii) $ZnBr_2$, THF, 20 °C; (iii) ArBr (1:1.1 molar ratio), $[Pd(PPh_3)_4]$ (Method A) or $[Pd(PPh_3)_2(OAc)_2]$ (Method B) (5 mol %), THF, 70 °C; (iv) HCl/H_2O

The reaction with isochromane (**1**) shown in Scheme 1 is applicable to other functionalised organolithium compounds prepared by ring opening of different heterocycles. Thus, starting from phthalane (**4**)[14] or 2,3-dihydrobenzofuran (**7**),[15] and by using the same procedure, intermediates **5** and **8** were prepared, which, after lithium−zinc transmetallation and palladium-catalysed cross-coupling reaction, gave products **6a−6c** and **9**, respectively (Scheme 1 and Table 1, entries 14−16 and 17, respectively).

The cross-coupling reaction with sp^3- or sp-hybridised bromides failed. For instance, when the same protocol (methods A or B) was applied to the intermediate **2** and cyclohexyl bromide or 1-bromo-2-phenylacetylene, only the "reduced" product, 2-(2-methylphenyl)ethanol (> 90%), resulting from a metal-hydrogen exchange, was isolated without any detectable coupling product. However, the reaction worked nicely with olefinic bromides, such as 1-bromo-2-methylpropene, giving the expected products **10** (from isochromane **1**) or **11** (from phthalane **4**) using either method A or B.



Finally, we studied the application of the Negishi-type cross-coupling reaction shown in Scheme 1 to different functionalised organolithium compounds, generated by chlorine-lithium exchange under arene-catalysis conditions.[16] For instance, the reaction of the chloroacetal **12** with lithium and a catalytic amount of DTBB (5 mol %) in THF at −78 °C led, after filtration of the excess of lithium, to a solution of the corresponding organolithium intermediate **13**.[17,18] This reagent was submitted to a lithium−zinc transmetallation and final palladium-catalysed cross-coupling reaction with different aryl bromides under the reaction conditions shown in Scheme 1, to give the expected products **14**, after hydrolysis under acidic conditions (Scheme 2 and Table 2). The reaction, which was studied employing the method B, seems to be sensitive to steric hindrance, since 2-chlorobromobenzene gave a much lower yield than the 4-substituted analogue (Table 2, entries 2 and 3). The mentioned acidic workup with concomitant hydrolysis of the acetal moiety is more convenient than the isolation of the corresponding acetal intermediates **15** due to difficulties found during their purification by column chromatography, in which partial deprotection occurred.



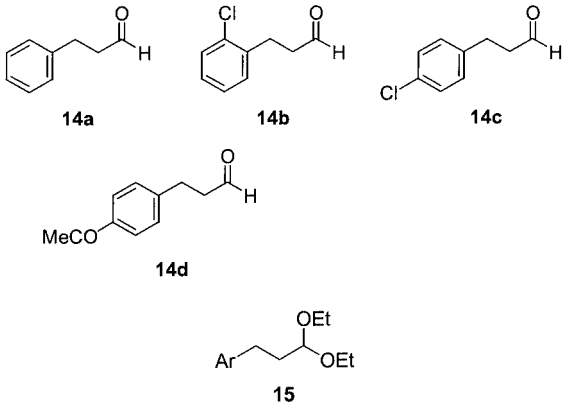
12 **13** **14**

Scheme 2. Preparation of compounds **14**: (i) Li, DTBB (5 mol %), THF, −78 °C, then filter off the excess of lithium; (ii) $ZnBr_2$, THF, −78 to 20 °C; (iii) ArBr (1:1.1 molar ratio), $[Pd(PPh_3)_2(OAc)_2]$ (Method B) (5 mol %), THF, 70 °C; (iv) NH_4Cl/H_2O, then HCl/H_2O

Table 2. Preparation of compounds **14**

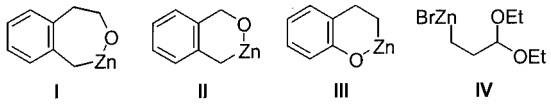
Entry	Aryl bromide	Method[a]	Product[b]	Yield (%)[c]
1	PhBr	B	**14a**	51
2	2-ClC_6H_4Br	B	**14b**	10 (19)[d]
3	4-ClC_6H_4Br	B	**14c**	48
4	4-$MeCOC_6H_4Br$	B	**14d**	50

[a] See footnote [a] in Table 1. [b] All products **14** were ≥ 93% pure (300 MHz ^{1}H NMR and/or GC). [c] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting chloroacetal **12**. [d] Yield after refluxing for 1 day.



14a **14b** **14c** **14d** **15**

In order to shed some light on the mechanism of the whole process shown in Schemes 1 and 2, we carried out three blank experiments: (1) in the absence of both the zinc bromide and the palladium catalyst, the reaction of intermediate **2** with bromobenzene gave only the "reduced" product, 2-(2-methylphenyl)ethanol (> 90%), and bromobenzene (≈ 90%); (2) in the absence of zinc bromide, and using method A for the same process, only 2-(2-methylphenyl)ethanol (> 90%), and biphenyl (91%) were isolated; (3) in the absence of the palladium catalyst the only reaction products obtained almost quantitatively were 2-(2-methylphenyl)ethanol and bromobenzene. With this information in hand, we assume that after the lithium−zinc transmetallation, and considering the stoichiometry used (1:1), intermediates of the type **I−III** (for starting materials **1**, **4**, and **7**, respectively) or **IV** (for the precursor **12**) should be involved in the process.[19] These in situ generated functionalised organozinc compounds[2d] take part in the catalytic cycle generally accepted for the Negishi cross-coupling reaction.[11]



I **II** **III** **IV**

Conclusions

In conclusion, the palladium-catalysed Negishi cross-coupling reaction can be applied successfully to in situ generated functionalised organozinc reagents (easily prepared from the corresponding functionalised organolithium compounds by a lithium−zinc transmetallation process); this reaction is not possible without the help of both the zinc and palladium components. Finally, the process works well for arylic and vinylic bromides, as well as with iodides.

Experimental Section

General: FT-IR spectra were obtained on a Nicolet Impact 400D spectrophotometer. NMR spectra were recorded on a Bruker AC-300 spectrometer with $CDCl_3$ as solvent and TMS as internal standard; chemical shifts are given in ppm and coupling constants (*J*) are given in Hz. ^{13}C NMR assignments were made on the basis of DEPT experiments. Mass spectra (EI) were obtained at 70 eV on a Shimadzu QP-5000 spectrometer, fragment ions in *m*/*z* with relative intensities (%) in parentheses. High resolution mass spectra were obtained by the corresponding service at the University of Alicante using a Finnigan MAT 95 S apparatus. The purity of volatile products and the chromatographic analyses (GLC) were determined with a Hewlett−Packard HP−4890 instrument equipped with a flame ionisation detector and a 30-m capillary column (0.25 mm diameter, 0.25 μm film thickness), nitrogen (2 mL/min) as carrier gas, $T_{injector}$ = 275 °C, T_{column} = 80 °C (3 min) and 80−270 °C (15 °C/min); retention times (t_R) are given under these conditions. Thin layer chromatography (TLC) was carried out on Merck plastic sheets coated with silica gel 60 F_{254}. All starting materials were commercially available (Acros, Aldrich, Fluka) of the

best grade and were used without further purification. Lithium powder was prepared from commercially available lithium granules (99%, high sodium content, Aldrich) as already reported by us.[20] THF was dried over benzophenone ketyl under a nitrogen atmosphere and distilled before use. Zinc bromide was dried by heating at 120 °C under reduced pressure (0.1 Torr) for 2 hours before use.

DTBB-Catalysed Lithiation of Isochromane (1), Phthalane (4) and 2,3-Dihydrobenzofuran (7), and the Palladium-Catalysed Cross-Coupling Reaction with Aryl and Vinyl Bromides. Isolation of Compounds 3, 6 and 9−11. General Procedure: Isochromane (**1**), phthalane (**4**) or 2,3-dihydrobenzofuran (**7**) (2 mmol) was added dropwise at room temperature (for **1** and **7**) or 0 °C (for **4**) under an argon atmosphere to a stirred green suspension of lithium powder (70 mg, 10 mmol) and DTBB (53 mg, 0.2 mmol) in THF (10 mL). The colour disappeared after the addition, and after 45 min (for **1** and **4**) or 2 h (for **7**) stirring the green colour appeared again. The excess of lithium was then filtered off under an inert atmosphere and the filtrate was added to a solution of dry zinc bromide (450 mg, 2 mmol) in THF (5 mL). After 30 min stirring, a solution of the corresponding aryl bromide (2.2 mmol) and the palladium catalyst (0.1 mmol for both Methods A and B) in THF (10 mL) was added to the resulting solution and refluxed overnight. After cooling to room temperature, the mixture was successively treated with 3 M hydrochloric acid (4 mL) (see Table 1, footnote e) and water (10 mL), and extracted with ether (3 × 10 mL). The organic layer was washed with brine (10 mL), dried (Na_2SO_4) and the solvents evaporated (15 Torr) to give a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) to give pure compounds **3**, **6**, and **9−11**. Yields are included in Table 1. Physical, analytical and spectroscopic data follow.

2-(2-Benzylphenyl)ethanol (3a):[21] R_f = 0.38 (hexane/ethyl acetate, 2:1), t_R = 15.79 min. IR (film): $\tilde{\nu}$ = 3670−3118 (OH), 3060, 3024, 1494, 1452 (C=CH), 1044 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.75 (br. s, 1 H, OH), 2.85 (t, J = 6.9 Hz, 2 H, $ArCH_2CH_2$), 3.68 (t, J = 6.9 Hz, 2 H, CH_2OH), 4.05 (s, 2 H, $ArCH_2Ar$), 7.10−7.21 (m, 7 H, ArH), 7.26 (t, J = 7.3 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.9, 39.9 (2 × CH_2Ar), 62.9 (CH_2OH), 126.0, 126.6, 128.4, 128.6, 130.0, 130.7, 136.7, 138.9, 140.7 (12 C, ArC) ppm. GC-LRMS: m/z (%) = 212 (21) [M^+], 195 (15), 194 (100), 193 (92), 181 (22), 180 (18), 179 (99), 178 (57), 167 (47), 166 (61), 165 (94), 153 (10), 152 (17), 117 (18), 116 (49), 115 (36), 104 (13), 103 (13), 91 (65), 89 (24), 82 (17), 77 (26), 76 (13), 65 (20), 63 (14), 51 (21). HRMS for $C_{15}H_{16}O$: calcd. 212.1201; found 212.1207 [M^+].

2-[2-(4-Fluorobenzyl)phenyl]ethanol (3b): R_f = 0.32 (hexane/ethyl acetate, 2:1), t_R = 15.67 min. IR (film): $\tilde{\nu}$ = 3683−3118 (OH), 3063, 3019, 1508 (C=CH), 1223 (CF), 1044 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.46 (br. s, 1 H, OH), 2.85 (t, J = 7.0 Hz, 2 H, $ArCH_2CH_2$), 3.73 (t, J = 7.0 Hz, 2 H, CH_2OH), 4.02 (s, 2 H, $ArCH_2Ar$), 6.92−7.25 (m, 8 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.8, 38.0 (2 × CH_2Ar), 62.9 (CH_2OH), 115.1 (d, $J_{C,F}$ = 20.8 Hz), 126.7, 126.8, 129.9, 130.0 (d, $J_{C,F}$ = 6.1 Hz), 130.5, 136.2 (d, $J_{C,F}$ = 3.7 Hz), 136.6, 138.8, 161.3 (d, $J_{C,F}$ = 244.1 Hz) (12 C, ArC) ppm. GC-LRMS: m/z (%) = 230 (20) [M^+], 213 (15), 212 (100), 199 (14), 198 (14), 197 (78), 196 (45), 185 (35), 184 (37), 183 (60), 179 (72), 178 (20), 177 (12), 165 (18), 133 (16), 117 (14), 116 (25), 115 (18), 109 (36), 105 (13), 104 (10), 91 (30), 89 (11), 82 (17), 77 (19), 63 (12), 51 (16). HRMS for $C_{15}H_{15}FO$: calcd. 230.1107; found 230.1105 [M^+].

2-[2-(4-Trifluoromethylbenzyl)phenyl]ethanol (3c): R_f = 0.27 (hexane/ethyl acetate, 2:1), t_R = 15.52 min. IR (film): $\tilde{\nu}$ = 3715−3112 (OH), 3066, 3019, 1618, 1418 (C=CH), 1121 (CF_3), 1067 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.90 (br. s, 1 H, OH), 2.84 (t, J = 7.0 Hz, 2 H, $ArCH_2CH_2$), 3.75 (t, J = 7.0 Hz, 2 H, CH_2OH), 4.11 (s, 2 H, $ArCH_2Ar$), 7.10−7.27 (m, 6 H, ArH), 7.51 (d, J = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.8, 38.6 (2 × CH_2Ar), 62.8 (CH_2OH), 124.2 (q, $J_{C,F}$ = 271.8 Hz, CF_3), 125.2 (q, $J_{C,F}$ = 3.7 Hz, $ArCCF_3$), 126.8, 127.0, 128.8, 130.1, 130.6, 136.8, 137.9, 144.9 (11 C, ArC) ppm. GC-LRMS: m/z (%) = 280 (6) [M^+], 263 (16), 262 (97), 261 (49), 249 (14), 247 (28), 235 (15), 234 (12), 233 (11), 229 (13), 214 (12), 194 (17), 193 (100), 183 (12), 180 (18), 179 (33), 178 (66), 166 (14), 165 (62), 159 (13), 117 (24), 116 (18), 115 (27), 91 (64), 89 (16), 77 (20), 63 (11), 51 (15). HRMS for $C_{16}H_{15}F_3O$: calcd. 280.1075; found 280.1093 [M^+].

2-[2-(4-Methoxybenzyl)phenyl]ethanol (3d): R_f = 0.25 (hexane/ethyl acetate, 2:1), t_R = 17.91 min. IR (film): $\tilde{\nu}$ = 3670−3125 (OH), 3059, 3013, 1508, 1458 (C=CH), 1029 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.20 (br. s, 1 H, OH), 2.85 (t, J = 7.0 Hz, 2 H, $ArCH_2CH_2$), 3.68 (t, J = 7.0 Hz, 2 H, CH_2OH), 3.73 (s, 3 H, CH_3O), 3.98 (s, 2 H, $ArCH_2Ar$), 6.80, 7.02 (2d, J = 8.6 Hz, 2 H and 2 H, ArH), 7.11−7.21 (m, 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.8, 37.8 (2 × CH_2Ar), 55.0 (CH_3O), 62.7 (CH_2OH), 114, 126.3, 126.4, 129.4, 129.9, 130.3, 132.6, 136.6, 139.2, 157.7 (12 C, ArC) ppm. GC-LRMS: m/z (%) = 243 (18) [M^+ + 1], 242 (100) [M^+], 224 (17), 223 (41), 209 (32), 198 (13), 197 (88), 195 (10), 194 (23), 193 (55), 181 (12), 179 (32), 178 (43), 166 (16), 165 (40), 153 (15), 152 (21), 133 (12), 121 (32), 116 (30), 115 (35), 106 (12), 105 (80), 104 (23), 91 (27), 89 (14), 78 (14), 77 (25), 65 (11), 63 (11), 51 (14), 45 (11). HRMS for $C_{16}H_{18}O_2$: calcd. 242.1307; found 242.1310 [M^+].

2-[2-(4-Dimethylaminobenzyl)phenyl]ethanol (3e): R_f = 0.19 (hexane/ethyl acetate, 2:1), t_R = 19.71 min. IR (film): $\tilde{\nu}$ = 3702−3118 (OH), 3061, 3015, 1615, 1519 (C=CH), 1045 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.65 (br. s, 1 H, OH), 2.84−2.88 (m, 8 H, $ArCH_2CH_2$ and $(CH_3)_2N$), 3.70 (t, J = 7.0 Hz, 2 H, CH_2OH), 3.94 (s, 2 H, $ArCH_2Ar$), 6.66, 6.97 (2d, J = 8.6 Hz, 2 H and 2 H, ArH), 7.15−7.22 (m, 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.9, 37.9 (2 × CH_2Ar), 40.8 (2 C, 2 × CH_3), 63.0 (CH_2OH), 113.0, 126.3, 126.5, 128.8, 129.2, 129.9, 130.6, 136.6, 139.8, 149.0 (12 C, ArC) ppm. GC-LRMS: m/z (%) = 255 (52) [M^+], 210 (11), 178 (12), 165 (11), 134 (27), 122 (14), 121 (100), 120 (21), 118 (16), 105 (11), 104 (12), 91 (12). HRMS for $C_{17}H_{21}NO$: calcd. 255.1623; found 255.1622 [M^+].

4′-[2-(2-Hydroxyethyl)benzyl]acetophenone (3f): R_f = 0.13 (hexane/ethyl acetate, 2:1), t_R = 19.92 min. IR (film): $\tilde{\nu}$ = 3638−3131 (OH), 3059, 3020, 1604, 1450 (C=CH), 1677 (C=O), 1046 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.50 (br. s, 1 H, OH), 2.57 (s, 3 H, CH_3), 2.84 (t, J = 6.7 Hz, 2 H, $ArCH_2CH_2$), 3.74 (t, J = 6.7 Hz, 2 H, CH_2OH), 4.11 (s, 2 H, $ArCH_2Ar$), 7.11−7.26 (m, 6 H, ArH), 7.87 (d, J = 7.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.5 (CH_3), 35.9, 38.9 (2 × CH_2Ar), 63.0 (CH_2OH), 126.9, 127.0, 128.6, 128.8, 130.1, 130.7, 135.2, 136.8, 138.0, 146.5 (12 C, ArC), 197.8 (CO) ppm. GC-LRMS: m/z (%) = 254 (6) [M^+], 193 (14), 179 (10), 178 (17), 121 (25), 44 (11), 43 (100), 40 (14). HRMS for $C_{17}H_{18}O_2$: calcd. 254.1307; found 254.1311 [M^+].

4-[2-(2-Hydroxyethyl)benzyl]benzonitrile (3g): R_f = 0.20 (hexane/ethyl acetate, 2:1), t_R = 19.22 min. IR (film): $\tilde{\nu}$ = 3702−3118 (OH), 3062, 3019, 1607, 1503 (C=CH), 2227 (CN), 1045 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.25 (br. s, 1 H, OH), 2.80 (t, J = 7.0 Hz, 2 H, $ArCH_2CH_2$), 3.71 (t, J = 7.0 Hz, 2 H, CH_2OH), 4.11 (s, 2 H, $ArCH_2Ar$), 7.08−7.53 (m, 8 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.7, 38.8 (2 × CH_2Ar), 62.7 (CH_2OH),

118.8 (CN), 109.6, 126.7, 127.1, 129.2, 130.1, 130.5, 132.0, 136.8, 137.2, 146.4 (12 C, ArC) ppm. GC-LRMS: *m/z* (%) = 237 (5) [M^+], 220 (12), 219 (72), 218 (100), 206 (14), 205 (16), 204 (65), 203 (23), 192 (13), 191 (22), 190 (32), 179 (22), 178 (19), 165 (10), 117 (13), 116 (17), 91 (36), 89 (18), 77 (16), 63 (11), 51 (14). HRMS for $C_{16}H_{15}NO$: calcd. 237.1154; found 237.1146 [M^+].

Ethyl 4-[2-(2-Hydroxyethyl)benzyl]benzoate (3h): R_f = 0.18 (hexane/ethyl acetate, 2:1), t_R = 21.05 min. IR (film): $\tilde{\nu}$ = 3676−3118 (OH), 3060, 3023, 1610, 1415 (C=CH), 1718 (CO_2), 1046, 1021 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.37 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.70 (br. s, 1 H, OH), 2.83 (t, *J* = 6.7 Hz, 2 H, ArC$H_2$$CH_2$), 3.71 (t, *J* = 6.7 Hz, 2 H, CH_2OH), 4.10 (s, 2 H, Ar-CH_2Ar), 4.34 (q, *J* = 7.0 Hz, 2 H, OC$H_2$$CH_3$), 7.10−7.25 (m, 6 H, ArH), 7.94 (d, *J* = 7.9 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 (CH_3), 35.9, 38.9 (2 × CH_2Ar), 60.8, 62.9 (2 × CH_2O), 126.8, 126.9, 128.4, 128.6, 129.7, 130.1, 130.7, 136.8, 138.1, 146.1 (12 C, ArC), 166.5 (CO_2) ppm. GC-LRMS: *m/z* (%) = 284 (26) [M^+], 254 (18), 239 (24), 238 (18), 237 (42), 225 (10), 207 (10), 194 (17), 193 (100), 181 (28), 180 (14), 179 (44), 178 (76), 166 (26), 165 (49), 152 (12), 135 (13), 117 (16), 116 (13), 115 (31), 105 (28), 104 (12), 103 (12), 91 (40), 89 (26), 77 (21), 76 (15), 65 (10), 51 (11), 44 (20), 40 (17). HRMS for $C_{18}H_{20}O_3$: calcd. 284.1412; found 284.1417 [M^+].

2-[2-(1-Naphthylmethyl)phenyl]ethanol (3i): R_f = 0.36 (hexane/ethyl acetate, 2:1), t_R = 21.51 min. IR (film): $\tilde{\nu}$ = 3689−3125 (OH), 3059, 3016, 1597, 1509 (C=CH), 1044 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.79 (br. s, 1 H, OH), 2.84 (t, *J* = 6.9 Hz, 2 H, ArC$H_2$$CH_2$), 3.76 (t, *J* = 6.9 Hz, 2 H, CH_2OH), 4.42 (s, 2 H, $ArCH_2Ar$), 6.91−7.95 (m, 11 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.6, 35.9 (2 × CH_2Ar), 62.8 (CH_2OH), 123.7, 125.5, 125.6, 126.0, 126.4, 126.5, 126.7, 126.9, 128.6, 129.8, 130.3, 13.0, 133.6, 136.3, 136.8, 138.4 (ArC) ppm. GC-LRMS: *m/z* (%) = 263 (18) [M^+ + 1], 262 (89) [M^+], 244 (24), 243 (38), 231 (11), 230 (18), 229 (88), 228 (48), 227 (11), 226 (14), 217 (33), 216 (38), 215 (84), 202 (23), 153 (10), 141 (23), 129 (28), 128 (27), 122 (10), 121 (11), 117 (17), 116 (100), 115 (70), 114 (20), 113 (12), 107 (42), 105 (28), 104 (18), 103 (10), 101 (18), 94 (12), 91 (23), 77 (17), 51 (10). HRMS for $C_{14}H_{18}O$: calcd. 262.1358; found 262.1342 [M^+].

2-[2-(4-Pyridylmethyl)phenyl]ethanol (3j): R_f = 0.23 (ethyl acetate), t_R = 16.67 min. IR (film): $\tilde{\nu}$ = 3657−3120 (OH), 3065, 3023, 1491 (C=CH), 1049 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.82 (t, *J* = 7.0 Hz, 2 H, ArC$H_2$$CH_2$), 3.32 (br. s, 1 H, OH), 3.75 (t, *J* = 7.0 Hz, 2 H, CH_2OH), 4.05 (s, 2 H, $ArCH_2Ar$), 7.02−7.28 (m, 6 H, ArH), 8.37 (d, *J* = 4.9 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.9, 38.2 (2 × CH_2Ar), 62.6 (CH_2OH), 121.4, 124.0, 126.7, 127.2, 130.2, 130.6, 136.6, 137.2, 149.3 (11 C, ArC) ppm. GC-LRMS: *m/z* (%) = 213 (39) [M^+], 195 (12), 194 (39), 183 (11), 182 (27), 181 (18), 180 (100), 168 (13), 167 (21), 152 (14), 121 (13), 117 (13), 115 (12), 91 (34), 80 (14), 77 (12), 65 (10), 51 (15). HRMS for $C_{14}H_{15}NO$: calcd. 213.1154; found 213.1159 [M^+].

2-[2-(2-Thienylmethyl)phenyl]ethanol (3k): R_f = 0.32 (hexane/ethyl acetate, 2:1), t_R = 15.74 min. IR (film): $\tilde{\nu}$ = 3626−3131 (OH), 3055, 3017, 1491, 1458 (C=CH), 1041 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.72 (br. s, 1 H, OH), 2.88 (t, *J* = 7.0 Hz, 2 H, ArC$H_2$$CH_2$), 3.71 (t, *J* = 6.7 Hz, 2 H, CH_2OH), 4.18 (s, 2 H, $ArCH_2Ar$), 6.69, 6.88, 7.12, 7.20 (4m, 1 H, 1 H, 1 H and 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.3, 35.8 (2 × CH_2Ar), 63.1 (CH_2OH), 123.8, 124.9, 126.8, 127.0, 130.1, 130.2, 136.5, 138.6, 144.1 (10 C, ArC) ppm. GC-LRMS: *m/z* (%) = 218 (69) [M^+], 201 (13), 200 (63), 199 (100), 187 (13), 186 (12), 185 (69), 184 (37), 173 (52), 172 (13), 171 (18), 167 (48), 166 (12), 165 (19), 154 (24), 153 (44), 152 (34), 141 (26), 134 (11), 129 (13), 128 (29), 127 (11), 116 (32), 115 (50), 105 (34), 104 (16), 103 (12), 97 (45), 91 (22), 85 (30), 77 (24), 65 (14), 63 (18), 53 (16), 51 (20), 45 (48). HRMS for $C_{13}H_{14}OS$: calcd. 218.0765; found 218.0766 [M^+].

2-[2-(3-Furylmethyl)phenyl]ethanol (3l): R_f = 0.31 (hexane/ethyl acetate, 2:1), t_R = 14.23 min. IR (film): $\tilde{\nu}$ = 3657−3144 (OH), 3061, 3019, 1491, 1452 (C=CH), 1043 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.60 (br. s, 1 H, OH), 2.90 (t, *J* = 7.0 Hz, 2 H, ArC$H_2$$CH_2$), 3.76−3.84 (m, 4 H, C$H_2$OH and $ArCH_2Ar$), 6.21, 7.08, 7.15−7.24, 7.34 (4m, 1 H, 1 H, 4 H and 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.5, 35.8 (2 × CH_2Ar), 63.1 (CH_2OH), 111.1, 124.2, 126.6, 126.7, 129.9, 130.0, 136.3, 138.5, 139.6, 143.0 (ArC) ppm. GC-LRMS: *m/z* (%) = 202 (25) [M^+], 183 (12), 171 (12), 169 (12), 157 (23), 155 (37), 153 (30), 152 (31), 143 (18), 142 (18), 141 (65), 134 (11), 129 (34), 128 (100), 127 (16), 116 (23), 115 (64), 106 (94), 105 (25), 104 (15), 103 (11), 98 (10), 97 (34), 91 (34), 89 (13), 81 (22), 78 (13), 77 (30), 76 (13), 69 (96), 65 (21), 63 (27), 55 (69), 53 (24), 52 (11), 51 (41), 50 (16), 44 (14), 43 (12), 41 (14). HRMS for $C_{13}H_{14}O_2$: calcd. 202.0994; found 202.0997 [M^+].

2-Benzylphenylmethanol (6a):[22] R_f = 0.48 (hexane/ethyl acetate, 2:1), t_R = 15.05 min. IR (film): $\tilde{\nu}$ = 3676−3106 (OH), 3062, 3025, 1494, 1452 (C=CH), 1038 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.26 (br. s, 1 H, OH), 4.01 (s, 2 H, $ArCH_2Ar$), 4.54 (s, 2 H, CH_2OH), 7.07−7.36 (m, 9 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.3 ($ArCH_2Ar$), 62.8 (CH_2OH), 126.0, 126.6, 127.8, 128.1, 128.4, 128.6, 130.4, 138.4, 138.7, 140.4 (12 C, ArC) ppm. GC-LRMS: *m/z* (%) = 181 (14) [M^+ − OH], 180 (89), 179 (100), 178 (37), 165 (42), 91 (27), 89 (31), 77 (16), 76 (13), 65 (17), 51 (15), 40 (12). HRMS for $C_{14}H_{12}$: calcd. 180.0939; found 180.0931 [M^+ − H_2O].

2-[4-(*tert*-Butyl)benzyl]phenylmethanol (6b): R_f = 0.49 (hexane/ethyl acetate, 2:1), t_R = 17.55 min. IR (film): $\tilde{\nu}$ = 3638−3118 (OH), 3061, 3023, 1514, 1454 (C=CH), 1393, 1363 (*t*Bu), 1039 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.28 [s, 9 H, $C(CH_3)_3$], 1.62 (br. s, 1 H, OH), 4.03 (s, 2 H, $ArCH_2Ar$), 4.61 (s, 2 H, CH_2OH), 7.03−7.40 (m, 8 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.3 (3 C, 3 × CH_3), 34.3 (C), 37.9 ($ArCH_2Ar$), 63.1 (CH_2OH), 125.4, 126.7, 127.9, 128.2, 128.3, 130.5, 137.4, 138.6, 138.8, 148.9 (12 C, ArC) ppm. GC-LRMS: *m/z* (%) = 236 (3) [M^+ − H_2O], 180 (21), 179 (100), 178 (26), 91 (16), 89 (11), 57 (13), 41 (13). HRMS for $C_{18}H_{22}O$: calcd. 254.1671; found 254.1681 [M^+].

2-(4-Methoxybenzyl)phenylmethanol (6c):[23] R_f = 0.34 (hexane/ethyl acetate, 2:1), t_R = 17.09 min. IR (film): $\tilde{\nu}$ = 3638−3118 (OH), 3063, 3024, 1511, 1455 (C=CH), 1035 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.65 (br. s, 1 H, OH), 3.77 (s, 3 H, CH_3O), 4.02 (s, 2 H, $ArCH_2Ar$), 4.64 (s, 2 H, CH_2OH), 6.82, 7.05 (2d, *J* = 8.6 Hz, 2 H and 2 H, ArH), 7.16, 7.26, 7.40 (3m, 1 H, 2 H and 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.6 ($ArCH_2Ar$), 55.2 (CH_3O), 63.2 (CH_2OH), 113.9, 126.7, 128.0, 128.4, 129.6, 130.4, 132.5, 138.7, 139.0, 158.0 (12 C, ArC) ppm. GC-LRMS: *m/z* (%) = 228 (15) [M^+], 211 (16), 210 (100), 209 (95), 195 (15), 194 (31), 180 (16), 179 (94), 178 (37), 167 (14), 166 (10), 165 (29), 152 (19), 121 (12), 120 (26), 118 (31), 105 (12), 91 (38), 89 (13), 82 (12), 77 (18), 65 (14), 51 (14). HRMS for $C_{15}H_{16}O_2$: calcd. 228.1150; found 228.1160 [M^+].

2-Phenethylphenol (9):[24] R_f = 0.61 (hexane/ethyl acetate, 2:1), t_R = 14.89 min. IR (KBr): $\tilde{\nu}$ = 3528 (OH), 3059, 3022, 1590, 1500 (C=CH), 1267 cm^{-1} (C−O). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.91 (s, 4 H, CH_2CH_2), 4.83 (s, 1 H, OH), 6.71 (d, *J* = 8.6 Hz, 1 H,

ArH), 6.85, 7.07 (2t, J = 7.3 Hz, 1 H and 2 H, ArH), 7.18−7.30 (m, 5 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.3, 36.1 (2 × CH_2), 115.3, 120.8, 125.9, 127.3, 127.9, 128.3, 128.4, 130.3, 142.0, 153.5 (12 C, ArC) ppm. GC-LRMS: m/z (%) = 198 (31) [M^+], 107 (100), 91 (34), 77 (27), 65 (14), 51 (10). HRMS for $C_{14}H_{14}O$: calcd. 198.1045; found 198.1041 [M^+].

2-[2-(3-Methyl-2-butenyl)phenyl]ethanol (10): R_f = 0.42 (hexane/ethyl acetate, 2:1), t_R = 13.21 min. IR (film): ṽ = 3632−3125 (OH), 3060, 3017, 1490, 1450 (C=CH), 1044 cm^{-1} (C−O). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.72 (s, 6 H, 2 × CH_3), 1.93 (br. s, 1 H, OH), 2.89 (t, J = 7.0 Hz, 2 H, ArCH_2CH$_2$), 3.35 (d, J = 6.7 Hz, 2 H, ArCH_2CH), 3.80 (t, J = 7.0 Hz, 2 H, CH_2OH), 5.22 (t, J = 7.0 Hz, 1 H, CH=C), 7.15 (m, 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.8, 25.6 (2 × CH_3), 31.6, 35.9 (2 × CH_2Ar), 63.0 (CH_2OH), 123.0, 132.2 (C=C), 126.0, 126.6, 129.3, 129.8, 136.1, 140.1 (ArC) ppm. GC-LRMS: m/z (%) = 190 (24) [M^+], 159 (13), 158 (13), 157 (100), 145 (61), 143 (19), 142 (28), 141 (15), 132 (19), 130 (19), 129 (88), 128 (40), 126 (12), 117 (64), 116 (21), 115 (52), 105 (52), 104 (13), 103 (12), 91 (49), 77 (25), 65 (17), 63 (11), 55 (12), 53 (12), 51 (16), 43 (51), 41 (65). HRMS for $C_{13}H_{18}O$: calcd. 190.1358; found 190.1367 [M^+].

2-[2-(3-Methyl-2-butenyl)phenyl]phenylmethanol (11): R_f = 0.55 (hexane/ethyl acetate, 2:1), t_R = 12.47 min. IR (film): ṽ = 3645−3106 (OH), 3064, 3025, 1449 (C=CH), 1039 cm^{-1} (C−O). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.72 (s, 6 H, 2 × CH_3), 2.22 (br. s, 1 H, OH), 3.36 (d, J = 7.3 Hz, 2 H, ArCH_2CH), 4.62 (s, 2 H, CH_2OH), 5.23 (t, J = 7.3 Hz, 1 H, CH=C), 7.15−7.34 (m, 4 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.8, 25.6 (2 × CH_3), 31.2 (ArCH$_2$CH), 63.0 (CH_2OH), 123.0, 132.6 (C=C), 126.1, 127.8, 128.0, 129.2, 138.4, 139.5 (ArC) ppm. GC-LRMS: m/z (%) = 176 (0.3) [M^+], 158 (29), 144 (12), 143 (100), 129 (14), 128 (44), 127 (10), 120 (31), 119 (40), 116 (14), 115 (24), 91 (35), 77 (24), 65 (19), 63 (10), 53 (11), 51 (21), 43 (23), 41 (44), 40 (11). HRMS for $C_{12}H_{16}O$: calcd. 176.1201; found 176.1201 [M^+].

DTBB-Catalysed Lithiation of 1-Chloro-3,3-diethoxypropane (12) and Palladium-Catalysed Cross-Coupling Reaction with Aryl Bromides. Isolation of Compounds 14. General Procedure: 1-Chloro-3,3-diethoxypropane (2 mmol) was added dropwise at −78 °C and under an argon atmosphere to a stirred green suspension of lithium powder (70 mg, 10 mmol) and DTBB (53 mg, 0.2 mmol) in THF (10 mL). The colour disappeared after the addition, and after 1 h stirring the green colour appeared again. The excess of lithium was then filtered off under an inert atmosphere and the filtrate was added to a solution of dry zinc bromide (450 mg, 2 mmol) in THF (5 mL) at −78 °C. After 30 min stirring, the solution was allowed to rise to room temperature, and a solution of the corresponding aryl bromide (2.2 mmol) and the palladium catalyst (0.1 mmol) in THF (10 mL) was added; the resulting solution was refluxed overnight. After cooling to room temperature, the mixture was treated successively with saturated NH_4Cl and water (10 mL) and extracted with ether (3 × 10 mL). The organic layer was washed with brine (10 mL), dried (Na_2SO_4) and the solvents evaporated (15 Torr) to give a residue, which was dissolved in THF (20 mL). HCl (3 M, 8 mL) was then added and the mixture was stirred overnight at room temperature. After the addition of water (10 mL), the mixture was again extracted with ether (3 × 10 mL) and the organic layer was washed with brine (10 mL), dried (Na_2SO_4) and the solvents evaporated (15 Torr) to give a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) to give pure compounds **14**. Yields are included in Table 2. Physical, analytical and spectroscopic data follow.

3-Phenylpropanal (14a):[25] R_f = 0.61 (hexane/ethyl acetate, 2:1), t_R = 8.71 min. IR (film): ṽ = 3062, 3028, 1496, 1451 (C=CH), 1724 (CHO). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.73, 2.93 (2t, J = 7.3 Hz, 2 H and 2 H, CH_2CH_2), 7.19−7.27 (m, 5 H, ArH), 9.76 (s, 1 H, CHO) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.5, 46.5 (2 × CH_2), 125.9, 128.0, 128.2, 140.1 (6 C, ArC), 201.1 (CHO) ppm. GC-LRMS: m/z (%) = 134 (79) [M^+], 133 (14), 105 (37), 103 (16), 92 (87), 91 (100), 79 (32), 78 (66), 77 (43), 65 (30), 63 (11), 55 (10), 51 (41), 50 (17). HRMS for $C_9H_{10}O$: calcd. 134.0732; found 134.0729 [M^+].

3-(2-Chlorophenyl)propanal (14b):[26] R_f = 0.58 (hexane/ethyl acetate, 2:1), t_R = 10.56 min. IR (film): ṽ = 3064, 3022, 1474, 1444 (C=CH), 1724 (CHO). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.79, 3.06 (2t, J = 7.3 Hz, 2 H and 2 H, CH_2CH_2), 7.12−7.36 (m, 4 H, ArH), 9.82 (s, 1 H, CHO) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1, 43.4 (2 × CH_2), 126.9, 127.8, 129.6, 130.4, 133.8, 137.9 (ArC), 201.1 (CHO) ppm. GC-LRMS: m/z (%) = 168 (26) [M^+], 139 (10), 133 (100), 127 (25), 126 (19), 125 (74), 115 (14), 112 (30), 105 (33), 104 (14), 103 (44), 102 (11), 91 (69), 89 (21), 78 (13), 77 (70), 75 (22), 63 (19), 56 (22), 55 (24), 51 (44), 50 (21). HRMS for C_9H_9ClO: calcd. 168.0342; found 168.0340 [M^+].

3-(4-Chlorophenyl)propanal (14c):[27] R_f = 0.52 (hexane/ethyl acetate, 2:1), t_R = 10.98 min. IR (film): ṽ = 3031, 1490 (C=CH), 1723 (CHO). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.76, 2.92 (2t, J = 7.3 Hz, 2 H and 2 H, CH_2CH_2), 7.13, 7.26 (2d, J = 8.5 Hz, 2 H and 2 H, ArH), 9.81 (s, 1 H, CHO) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.4, 45.1 (2 × CH_2), 128.6, 129.6, 132.0, 138.8 (6 C, ArC), 201.0 (CHO) ppm. GC-LRMS: m/z (%) = 170 (12) [M^+ + 2], 168 (40) [M^+], 133 (54), 127 (36), 126 (25), 125 (100), 115 (15), 114 (12), 112 (36), 105 (15), 103 (37), 91 (53), 89 (22), 77 (51), 75 (24), 63 (22), 56 (10), 55 (27), 51 (42), 50 (27). HRMS for C_9H_9ClO: calcd. 168.0342; found 168.0343 [M^+].

3-(4-Acetylphenyl)propanal (14d):[28] R_f = 0.29 (hexane/ethyl acetate, 2:1), t_R = 13.24 min. IR (film): ṽ = 3037, 1606 (C=CH), 1722 (CHO), 1679 (CO). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.59 (s, 3 H, CH_3CO), 2.82, 3.02 (2t, J = 7.3 Hz, 2 H and 2 H, CH_2CH_2), 7.29, 7.89 (2d, J = 7.9 Hz, 2 H and 2 H, ArH), 9.83 (1 H, s, CHO) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.6 (CH_3CO), 27.9, 44.7 (2 × CH_2), 128.5, 128.7, 135.4, 146.0 (6 C, ArC), 197.7 (CO), 200.7 (CHO) ppm. GC-LRMS: m/z (%) = 176 (40) [M^+], 162 (11), 161 (100), 133 (17), 118 (11), 105 (31), 103 (17), 91 (11), 79 (19), 78 (10), 77 (33), 65 (10), 63 (14), 51 (20), 43 (84). HRMS for $C_{11}H_{12}O_2$: calcd. 176.0837; found 176.0826 [M^+].

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