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Lewis acid-promoted conjugate addition of functionalised organolithium compounds to electrophilic olefins

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This paper is dedicated to Professor Ron Grigg, University of Leeds, on the occasion of his 65th birthday

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Abstract—The reaction of several functionalised organolithium compounds **1**–**3** with different α,β-unsaturated ketones or esters **4**–**12** in the presence of a Lewis acid [ZnX_2 (X=Cl, Br, I), $AlCl_3$, $FeCl_3$, BF_3] leads, after hydrolysis, mainly to 1,4-addition products **13**–**31**.

1. Introduction

As it is well documented in the literature, organolithium compounds add to the carbonyl group of α,β-unsaturated carbonyl compounds, rather than giving 1,4 (Michael) addition.[1] Probably the best procedure to get this last reaction is the use of organocuprates,[2] which can be easily generated in situ from the corresponding lithium derivatives.[3] An interesting version of this reaction consists in the use of a catalytic amount of a copper salt and stoichiometric amounts of an organometallic compound derived from magnesium,[4] zinc[5,6] or aluminium.[7] In a different way, conjugate addition of organozinc compounds can be effectively promoted by using a cosolvent (e.g. *N*-methylpyrrolidinone[8]) or a coreagent (e.g. chlorotrimethylsilane[9]). Concerning organolithium intermediates, in the last few years we have been studying the preparation and synthetic applications of functionalised organolithium compounds.[10] This type of intermediates are interesting because in the reaction with an electrophile they are able to transfer the functionality to the reagent and consequently to generate polyfunctionalised molecules in only one reaction step. Concerning the generation of functionalised organolithium compounds, a versatile methodology consists in performing

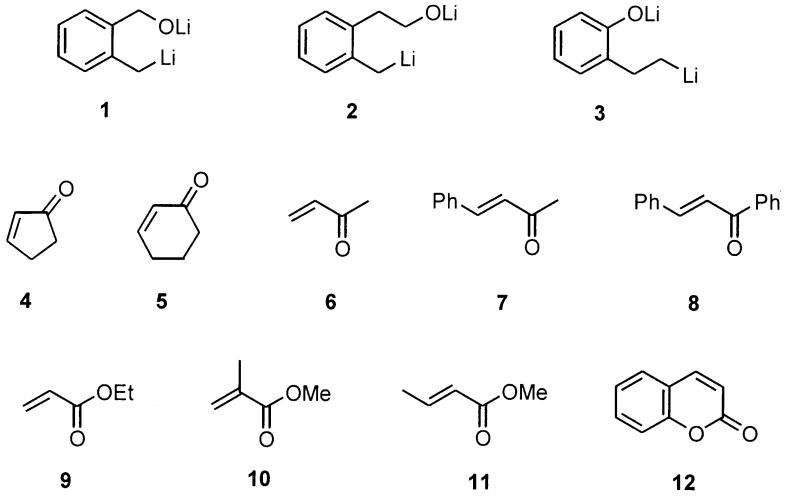

Chart 1. Functionalised organolithium compounds (**1**–**3**) and electrophilic olefins (**4**–**12**) used.

Keywords: functionalised organolithiums; conjugate addition; α,β-unsaturated ketones and esters; Lewis acids.
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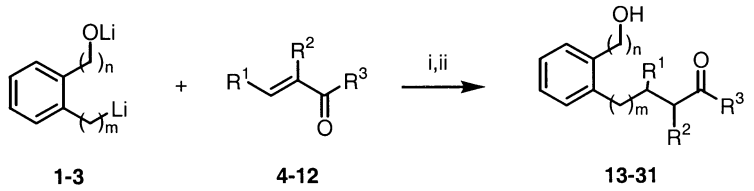


Scheme 1. *Reagents and conditions*: i, 2 $ZnBr_2$, THF, −78°C; ii, NH_4Cl–H_2O, −78–20°C.

Table 1. Preparation of compounds **13**–**19**, **23**, **25** and **31** in a one-pot reaction

Entry	Organolithium intermediate	Electrophilic olefin	Product[a]	
			No.	Yield (%)[b]
1	**1**	**4**	**13**	70
2	**1**	**5**	**14**	74 (52)[c]
3	**1**	**6**	**15**	51
4	**1**	**7**	**16**	50
5	**1**	**8**	**17**	62
6	**1**	**9**	**18**	35
7	**1**	**10**	**19**	28
8	**2**	**5**	**23**	72
9	**2**	**7**	**25**	56
10	**3**	**5**	**31**	43

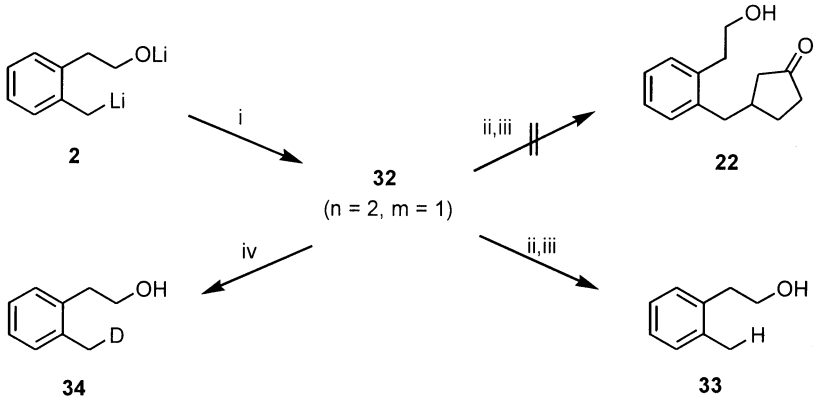
[a] All compounds **13**–**19**, **23**, **25** and **31** were ≥95% pure (GLC and/or 300 MHz ^{1}H NMR).
[b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate), based on the heterocyclic precursor of the starting organolithium compound **1**–**3**.
[c] Yield of the corresponding reaction carried out at 0°C.

an arene-catalysed lithiation[11] from the adequate functionalised chlorinated material[12a] or heterocyclic intermediates.[12b] Since, as expected, functionalised organolithium compounds react usually at the carbonyl group of α,β-unsaturated carbonyl compounds,[13] methodologies involving catalytic[14] or stoichiometric[15] amounts of a copper(I) salt have been developed in order to achieve conjugate additions. In this paper we report the last reaction (1,4-addition) of some functionalised organolithium compounds to α,β-unsaturated carbonyl compounds mediated by a Lewis acid.

2. Results and discussion

When functionalised organolithium compounds **1**, **2** and **3** (easily prepared by an arene-catalysed lithiation of phthalan,[16] isochroman[17] and 2,3-benzodihydrofuran,[18] respectively, following the reported procedures; see Chart 1) reacted with a mixture of zinc bromide (1:2 molar ratio) and different electrophilic olefins **4**–**12** (Chart 1) in THF at −78°C, the corresponding conjugate addition products **13**–**31** were isolated after 0.5 h and final hydrolysis with a saturated solution of ammonium chloride at temperatures ranging between −78°C and room temperature (Scheme 1 and Table 1). From the results included in Table 1 it can be deduced that, as expected, the process worked better with α,β-unsaturated ketones **4**–**8** (Table 1, entries 1–5 and 8–10) than with α,β-unsaturated esters **9**, **10** (Table 1, entries 6 and 7).

Regarding a possible mechanism for the reaction shown in Scheme 1, we think that an organozinc reagent of type **32** (either having an acyclic or a cyclic structure) could be



Scheme 2. *Reagents and conditions*: i, $ZnBr_2$, THF, −78°C; ii, cyclopent-2-enone (**4**), −78, 0, or 65°C; iii, H_2O; iv, D_2O.

Table 2. Influence of temperature and stoichiometry in the preparation of compound **22** with $ZnBr_2$ in the one-pot procedure

Entry	$ZnBr_2$ (equiv.)	Temperature (°C)	Yield (%)[a]
1	2	−78	40
2	2	0	15
3	0.5	−78	28
4	1.1	−78	54

[a] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on isochroman, the precursor of intermediate **2**.

Table 3. Influence of the Lewis acid in the formation of compound **22**

Entry	Lewis acid	Yield (%)[a]
1	$ZnCl_2$	45
2	$ZnBr_2$	54
3	ZnI_2	23
4	$AlCl_3$	35
5	$FeCl_3$	70
6	BF_3	55

For the reaction of **2**+**4** at −78°C and using 1.1 equiv. of the corresponding Lewis acid.
[a] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on isochroman, the precursor of intermediate **2**.

Table 4. Reaction of intermediate **1** with compounds **4**–**12** and a Lewis acid

Entry	Electrophilic olefin	Lewis acid[a]	Product	
			No.	Yield (%)[b]
1	**4**	$ZnBr_2$	**13**	73 (3)
2		$FeCl_3$		47 (24)
3		BF_3		67 (8)
4	**5**	$ZnBr_2$	**14**	75 (8)
5		$FeCl_3$		52 (23)
6		BF_3		37 (27)
7	**6**	$ZnBr_2$	**15**	53 (21)
8		$FeCl_3$		28 (18)
9		BF_3		25 (16)
10	**7**	$ZnBr_2$	**16**	54 (25)
11		$FeCl_3$		33 (20)
12		BF_3		38 (–)
13	**8**	$ZnBr_2$	**17**	51 (30)
14		$FeCl_3$		44 (14)
15		BF_3		79 (3)
16	**9**	$ZnBr_2$	**18**	35
17		$FeCl_3$		25
18		BF_3		26
19	**10**	$ZnBr_2$	**19**	26
20		$FeCl_3$		12
21		BF_3		10
22	**11**	$ZnBr_2$	**20**	48
23		$FeCl_3$		17
24		BF_3		29
25	**12**	$ZnBr_2$	**21**	67
26		$FeCl_3$		52
27		BF_3		63

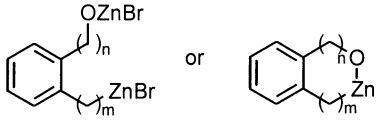
[a] BF_3 was used as the corresponding etherate complex; in all cases 1.1 equiv. of the Lewis acid was used.
[b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on phthalan, the heterocyclic precursor of the intermediate **1**; in parenthesis yield corresponding to the 1,2-addition product **35**–**39**, deduced by GLC after column chromatography isolation.

Table 5. Reaction of intermediate **2** with compounds **4**–**12** and a Lewis acid

Entry	Electrophilic olefin	Lewis acid[a]	Product	
			No.	Yield (%)[b]
1	**4**	$ZnBr_2$	**22**	54 (–)
2		$FeCl_3$		70 (8)
3		BF_3		55 (10)
4	**5**	$ZnBr_2$	**23**	72 (20)
5		$FeCl_3$		52 (13)
6		BF_3		40 (8)
7	**6**	$ZnBr_2$	**24**	10 (12)
8		$FeCl_3$		38 (15)
9		BF_3		14 (16)
10	**7**	$ZnBr_2$	**25**	56 (5)
11		$FeCl_3$		42 (26)
12		BF_3		44 (28)
13	**8**	$ZnBr_2$	**26**	32 (4)
14		$FeCl_3$		56 (3)
15		BF_3		64 (3)
16	**9**	$ZnBr_2$	**27**	46
17		$FeCl_3$		29
18		BF_3		35
19	**10**	$ZnBr_2$	**28**	15
20		$FeCl_3$		23
21		BF_3		22
22	**11**	$ZnBr_2$	**29**	36
23		$FeCl_3$		29
24		BF_3		30
25	**12**	$ZnBr_2$	**30**	48
26		$FeCl_3$		47
27		BF_3		56

[a] BF_3 was used as the corresponding etherate complex; in all cases 1.1 equiv. of the Lewis acid was used.
[b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on isochroman, the heterocyclic precursor of the intermediate **2**; in parenthesis yield corresponding to the 1,2-addition product **40**–**44**, deduced by GLC after column chromatography isolation.

involved in the reaction, which after a Michael-type addition would give the final reaction product **13**–**31**.



32

In order to prove this hypothesis we performed the corresponding reaction in a two-step process generating in situ the expected organozinc intermediate. Thus, when intermediate **2** was treated successively with zinc bromide and after 15 min stirring with cyclopent-2-enone (**4**) at −78°C (as well as at 0 or 65°C) the expected product **22** was not obtained after hydrolysis with aqueous ammonium chloride. Instead, compound **33** resulting from a metal–hydrogen exchange, was the only reaction product obtained (Scheme 2). It seems that either (a) after a lithium–zinc transmetallation reaction the intermediate of type **32** is not reactive enough to add to cyclopenten-2-one conjugatively or (b) the transmetallation did not take place. The last possibility was ruled out because without zinc bromide the reaction of intermediate **2** with cyclopenten-2-one gave a very different mixture of compound **33** together with 1,2- and 1,4-addition products, the first one being the most abundant one.[19] Thus,

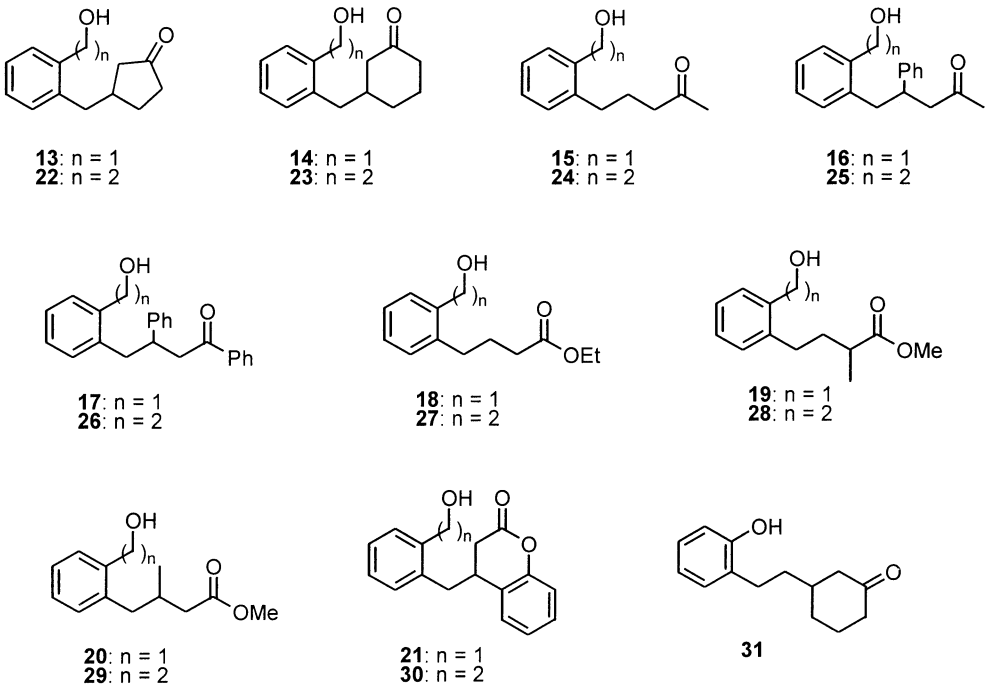


Chart 2. Compounds **13**–**31** prepared.

admitting that the transmetallation took place first we performed the corresponding deuterolysis with deuterium oxide after treating the starting material **2** with zinc bromide, so the expected labelled compound **34** was isolated (ca. 70% deuterium incorporation from mass spectrometry). After these experiments (Scheme 2), we conclude that once an organozinc reagent of type **32** was generated it did not react with the unsaturated carbonyl compound under different reaction conditions (from −78 to 65°C), due probably to its low reactivity.

At this point, we thought that the role of zinc bromide in the preparation of compounds **13**–**31** could be to act as a Lewis acid activating the carbonyl compound toward the 1,4-addition by preventing the attack to the coordinated carbonyl group.[20] Thus, we performed the reaction shown in Scheme 1 at different temperatures and with different stoichiometry for the preparation of compound **22** using zinc bromide (Table 2) as well as other Lewis acids (Table 3) under the best reaction conditions found in Table 2 (1.1 equiv. of $ZnBr_2$ at −78°C; Table 2, entry 4). As it is shown in Table 3, $ZnBr_2$, $FeCl_3$ and BF_3 were the best Lewis acids for the conjugate addition (Table 3, entries 2, 5 and 6, respectively).

With this information in hand, intermediates **1** and **2** were treated under the mentioned best reaction conditions using the α,β-unsaturated ketones and esters **4**–**12** included in Chart 1. The results are summarised in Tables 4 and 5, respectively, where the corresponding 1,4-addition products **13**–**30** (Chart 2) were the major ones isolated. In the case of ketones **4**–**8** variable amounts (<28%) of the corresponding 1,2-addition compounds **35**–**44** were also isolated (Chart 3, Tables 4 and 5, entries 1–15 and footnote b). Anyhow, even when the amount of 1,2-addition products is significant, the separation of both compounds **13**–**30** and **35**–**44** is very simple by column chromatography due to their different polarity. As already shown above (Table 1) the reaction with α,β-unsaturated esters **9**–**12** gave lower yields than with the α,β-unsaturated ketones **4**–**8**.

A final remark should be done about the low yields observed in some cases: this is due to the formation in some extension of the 'reduced' product (from a metal–hydrogen exchange) of the type **33** (Scheme 2) under the reaction conditions. In addition, when iron trichloride was used as Lewis acid, some dimerisation products were also isolated (<15%).[21]

3. Conclusions

In conclusion, we have demonstrated here that the zinc bromide-promoted 1,4-addition of some functionalised organolithium compounds to α,β-unsaturated ketones and esters does not take place through the corresponding in situ generated functionalised organozinc intermediate but, most

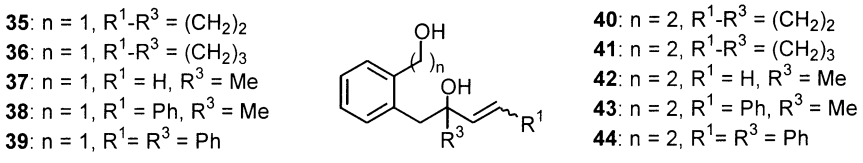


Chart 3. Minor 1,2-addition products **35**–**44** detected.

probably, by acting this salt as a Lewis acid, through a coordination with the carbonyl group of the electrophilic olefin. Other Lewis acids, such as iron, aluminium and boron salts can also be effectively used for the mentioned conjugate addition. In spite of the total conversion, in some cases yields are modest due to partial formation of the corresponding 'reduced' compounds (of type **33**) resulting from a metal–hydrogen exchange during the reaction and/or the work-up.

4. Experimental

4.1. General

For general information see Ref. 22. GLC analyses were performed with a Hewlett Packard HP-5890 instrument equipped with a flame ionisation detector and a 30 m HP-1 capillary column (0.2 mm diameter, 0.33 μm film thickness, OV-1 stationary phase), using nitrogen (2 ml min^{-1}) as carrier gas, $T_{injector}$=275°C, $T_{detector}$=300°C, T_{column}=80°C (3 min) and 80–270°C (15°C min^{-1}), P= 40 kPa; t_r values are given in minutes under these conditions. Starting functionalised intermediates **1**,[16] **2**,[17] and **3**[18] were generated according to the literature procedures.

4.2. Reaction of intermediates 1–3 with electrophilic olefins 4–12 and zinc bromide

4.2.1. Isolation of compounds 13–19, 23, 25 and 31: general procedure. Once the corresponding functionalised organolithium reagent **1**–**3** was generated according to the literature procedure,[16–18] the excess of lithium was filtered off. The resulting clear solution (2 mmol scale) was added via cannula to a solution of the corresponding olefin **4**–**10** (2.2 mmol) and zinc bromide (0.92 g, 4 mmol) in THF (8 ml) at ca. −78°C and the mixture was stirred for ca. 25 min at the same temperature. Then it was hydrolysed with a saturated solution of ammonium chloride (10 ml) and extracted with ether (5×8 ml), the organic phase was successively washed with brine (10 ml) and water (10 ml), and dried over anhydrous $MgSO_4$. After evaporation of the solvents (15 Torr), the resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the title compounds, which were characterised by comparison of their chromatographic (GLC) and spectroscopic data (^{1}H NMR and GLC–MS) with those of the same compounds prepared by other procedure in our laboratory and already reported.[15b] Yields are included in Table 2. Retention times (t_r) are as follows: **13** (12.66), **14** (13.44), **15** (10.98), **16** (14.72), **17** (19.35), **18** (11.79), **19** (11.37), **23** (14.30), **25** (15.36) and **31** (13.10).

4.3. Step-by-step reaction of intermediate 2 with zinc bromide and final hydrolysis or deuterolysis

Once the intermediate **2** was generated (see above; 2 mmol scale) it was treated with zinc bromide (0.92 g, 4 mmol) and stirred for ca. 30 min at −78°C, being then hydrolysed with water (1 ml) or deuterolysed with deuterium oxide (0.5 ml) and worked up as described for compounds **13**–**19**. Products **33** and **34** were characterised by comparison of their chromatographic (GLC, TLC) and spectroscopic (GLC–MS) data with those of pure compounds synthesised in our laboratory and already reported.[16]

4.4. Influence of the reaction conditions on the preparation of compound 22

The reactions were carried out following the procedure described above using the intermediate **2** and cyclopenten-2-one (**4**) as reagents, and temperatures, stoichiometries and Lewis acids as indicated in Tables 2 and 3.

4.5. Reaction of intermediates 1 and 2 with electrophilic olefins 4–12 and different Lewis acids

4.5.1. Isolation of compounds 13–21 and 22–30: general procedure. To a mixture of the corresponding Lewis acid (2.2 mmol) and the electrophilic olefin **4**–**12** (2.2 mmol) in THF (5 ml) cooled at −78°C was added a clear solution (ca. 5 ml) of the corresponding intermediate **1** or **2** (see above) and the mixture was stirred for ca. 1 h at the same temperature. Then, it was hydrolysed with water (10 ml) allowing the temperature to rise to room temperature and extracted with ether (3×10 ml). The organic layer was washed with water (10 ml), dried over anhydrous Na_2SO_4 and evaporated (15 Torr) to give a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the expected title compounds **13**–**30**. The characterisation of compounds (t_r) **13**–**19**, **21** (15.99), **28** (12.23) and **30** (16.61) was carried out by comparison of their physical (GLC) and spectroscopic data (^{1}H NMR and GLC–MS) with authentic samples prepared and already described by us.[15b] Yields are included in Tables 4 and 5. For new compounds **20** and **29**, the corresponding analytical, physical and spectroscopic data follow. As by-products, minor compounds **35**–**44**, resulting from a 1,2-addition process, were characterised by their physical (t_r) and some spectroscopic data (GLC-MS and selected ^{1}H NMR data from the crude mixture with major compounds **13**–**17** and **22**–**26**). Their GLC yields are included in Tables 4 and 5 and data for their characterisation follow.

4.5.2. Methyl 4-(2-hydroxymethylphenyl)-3-methylbutanoate (20). t_r=11.34, R_f=0.32 (hexane/ethyl acetate: 2:1); ν (film) 3689–3118 (OH), 3055, 3017, 1456 (C=CH), 1729 (C=O), 1158, 1031, 1012 cm^{-1} (C–O); δ_H 0.97 (3H, d, J=6.1 Hz, CH_3CH), 2.15–2.42 (4H, m, CH_2CO, CH and OH), 2.54 (1H, dd, J=13.4, 7.3 Hz, CHHCH), 2.74 (1H, dd, J=13.4, 6.4 Hz, CHHCH), 3.59 (3H, s, CH_3O), 4.70 (2H, m, CH_2OH), 7.15–7.26, 7.36 (3H and 1H, respectively, 2m, ArH); δ_C 20.2 (CH_3CH), 31.9 (CH), 39.6, 41.3 (2×CH_2), 51.7 (CH_3O), 63.1 CH_2OH), 126.8, 127.8, 129.0, 130.7, 138.5, 139.2, (ArC), 177.0 (CO_2); m/z 204 (M^+−18, 30%), 172 (15), 145 (25), 131 (26), 130 (100), 129 (27), 115 (12), 105 (11), 104 (12), 93 (13), 91 (45), 77 (28), 74 (14), 65 (10), 59 (19), 43 (15), 41 (16); HRMS: M^+−[H_2O], found 204.1150. $C_{13}H_{16}O_2$ requires 204.1144.

4.5.3. Methyl 4-[2-(2-hydroxyethyl)phenyl]-3-methylbutanoate (29). t_r=12.17, R_f=0.29 (hexane/ethyl acetate: 2:1); ν (film) 3670–3125 (OH), 1736 (C=O), 1456 (C=C), 1045 cm^{-1} (C–O); δ_H 0.96 (3H, d, J=6.4 Hz, CH_3CH), 2.06 (1H, broad s, OH), 2.18–2.37 (3H, m, CH_2CO, CH),

2.49 (1H, dd, J=13.6, 7.7 Hz, ArC*H*HCH), 2.70 (1H, dd, J=13.6, 6.2 Hz, ArCH*H*CH), 2.91 (2H, m, CH_2CH$_2$OH), 3.62 (3H, s, CH$_3$O), 3.82 (2H, t, J=7.0 Hz, CH_2OH), 7.15 (4H, m, ArH); δ_C 19.8 (*C*H$_3$CH), 31.7 (CH), 35.7, 39.8, 41.1 (3×CH$_2$), 51.4 (CH$_3$O), 63.4 (CH_2OH), 126.2, 126.4, 129.9, 130.5, 136.6, 138.6 (ArC), 173.5 (CO$_2$); m/z 218 (M^+-18, 8%), 206 (29), 187 (18), 145 (25), 144 (58), 133 (50), 132 (100), 131 (19), 129 (33), 128 (11), 117 (62), 115 (31), 106 (14), 105 (45), 104 (26), 103 (14), 91 (41), 79 (11), 78 (14), 77 (21), 74 (13), 69 (21), 65 (11), 59 (24), 43 (18); HRMS: $M^+-[H_2O]$, found 218.1309. $C_{14}H_{18}O_2$ requires 218.1307.

4.5.4. 1-[2-(Hydroxymethyl)benzyl]-2-cyclopentenol (35). t_r=9.56; δ_H 5.85 (1H, m, CH=C*H*CH$_2$), 6.06 (1H, m, C*H*=CHCH$_2$); m/z 186 (M^+-18, 2%), 105 (10), 104 (100), 78 (13).

4.5.5. 1-[2-(Hydroxymethyl)benzyl]-2-cyclohexenol (36). t_r=10.74; δ_H 5.62 (1H, m, CH=C*H*CH$_2$), 5.82 (1H, m, C*H*=CHCH$_2$); m/z 200 (M^+-18, 2%), 105 (10), 104 (100), 78 (10).

4.5.6. 1-[2-(Hydroxymethyl)phenyl]-2-methyl-3-buten-2-ol (37). t_r=10.15; δ_H 5.00 (1H, d, J=10.4 Hz, CH=C*H*H), 5.13 (1H, d, J=16.5 Hz, CH=CH*H*), 5.96 (1H, dd, J=17.1, 10.4 Hz, C*H*=CH$_2$); m/z 174 (M^+-18, 1%), 105 (10), 104 (100), 91 (12), 78 (10), 77 (11), 71 (21), 43 (39).

4.5.7. (*E*)-1-[2-(Hydroxymethyl)phenyl]-2-methyl-4-phenyl-3-buten-2-ol (38). t_r=13.89; δ_H 6.34 (1H, d, J=16.5 Hz, CH=C*H*Ph), 6.52 (1H, d, J=16.0 Hz, C*H*=CHPh); m/z 250 (M^+-18, 1%), 105 (10), 104 (100), 91 (12), 43 (12).

4.5.8. (*E*)-1-[2-(Hydroxymethyl)phenyl]-2,4-diphenyl-3-buten-2-ol (39). t_r=17.52; δ_H 6.39 (1H, d, J=15.9 Hz, CH=C*H*Ph), 6.53 (1H, d, J=16.5 Hz, C*H*=CHPh); m/z 312 (M^+-18, 3%), 180 (31), 115 (10), 105 (19), 104 (100), 103 (15), 91 (14), 78 (15), 77 (17).

4.5.9. 1-[2-(2-Hydroxyethyl)benzyl]-2-cyclopentenol (40). t_r=10.40; δ_H 5.63 (1H, m, CH=C*H*CH$_2$), 5.78 (1H, m, C*H*=CHCH$_2$); m/z 200 (M^+-18, 5%), 119 (18), 118 (76), 117 (100), 115 (16), 91 (13).

4.5.10. 1-[2-(2-Hydroxyethyl)benzyl]-2-cyclohexenol (41). t_r=11.50; δ_H 5.52 (1H, m, CH=C*H*CH$_2$), 5.72 (1H, m, C*H*=CHCH$_2$); m/z 214 (M^+-18, 3%), 119 (17), 118 (90), 117 (100), 91 (12), 41 (11).

4.5.11. 1-[2-(2-Hydroxyethyl)phenyl]-2-methyl-3-buten-2-ol (42). t_r=10.93; δ_H 5.04 (1H, dd, J=10.4, 1.2 Hz, CH=C*H*H), 5.14 (1H, dd, J=17.1, 1.2 Hz, CH=CH*H*), 6.01 (1H, dd, J=17.1, 10.4 Hz, C*H*=CH$_2$); m/z 188 (M^+-18, 2%), 136 (45), 118 (42), 117 (56), 115 (20), 106 (42), 105 (52), 104 (13), 103 (11), 91 (24), 77 (15), 71 (100), 43 (95), 41 (21).

4.5.12. (*E*)-1-[2-(2-Hydroxyethyl)phenyl]-2-methyl-4-phenyl-3-buten-2-ol (43). t_r=14.57; δ_H 6.31 (1H, d, J=16.0 Hz, CH=C*H*Ph), 6.48 (1H, d, J=16.0 Hz, C*H*=CHPh); m/z 264 (M^+-18, 6%), 119 (11), 118 (95), 117 (100), 91 (19), 77 (10), 43 (17).

4.5.13. (*E*)-1-[2-(2-Hydroxyethyl)phenyl]-2,4-diphenyl-3-buten-2-ol (44). t_r=18.69; δ_H 6.35 (1H, d, J=15.9 Hz, CH=C*H*Ph), 6.52 (1H, d, J=15.9 Hz, C*H*=CHPh); m/z 326 (M^+-18, 1%), 133 (11), 105 (100), 104 (13), 91 (14), 77 (32).

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