

Arene-Catalysed Lithiation of Triflates and Triflamides under Barbier-Type Conditions: An Indirect Transformation of Alcohols and Amines into Organolithium Compounds

Emma Alonso, Diego J. Ramón and Miguel Yus*

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, E-03080-Alicante, Spain

Abstract: The reaction of alkyl triflates **1** or allyl or benzyl triflamides **3** with an excess of lithium powder and a catalytic amount of naphthalene (4 mol %) in the presence of different electrophiles [Me_3SiCl , Pr^iCHO , Bu^tCHO , PhCHO , $4\text{-MeOC}_6\text{H}_4\text{CHO}$, $\text{CH}_3(\text{CH}_2)_6\text{CHO}$, Et_2CO , $(\text{CH}_2)_5\text{CO}$, $(c\text{-C}_3\text{H}_5)_2\text{CO}$, PhCOMe , $4\text{-MeC}_6\text{H}_4\text{COPh}$, PhCH=NPh , $n\text{-C}_8\text{H}_7\text{CON}(\text{CH}_2)_4$] in THF at temperature ranging between -78 and 0°C leads, after hydrolysis with water, to the corresponding condensation products **2**. When α,β -unsaturated carbonyl compounds are used as electrophilic compounds 1,2- (2-cyclohexenone) or 1,4-addition (cinnamaldehyde or benzylideneacetone) takes places depending on the electrophile used. Copyright © 1996 Elsevier Science Ltd

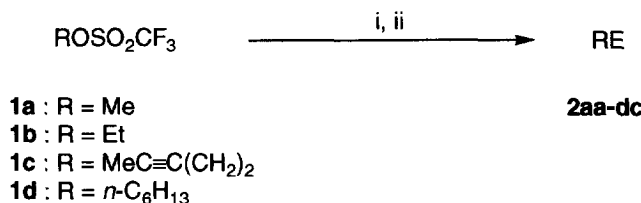
INTRODUCTION

Organolithium compounds are in general prepared from the corresponding halogenated material,¹ other methodologies (deprotonation,^{2a} transmetallation,^{2b} reductive cleavage of ethers or thioethers^{2c} or the Shapiro reaction^{2d}), being of limited application. Concerning our continuous interest in the development of new methods to prepare organolithium compounds, we have recently applied the arene-catalysed lithiation³ to the transformation of allyl or benzyl mesylates into the corresponding organolithium intermediates, this procedure being an indirect way to convert this type of alcohols into organolithiums.^{4,5} However, this procedure failed for alkyl derivatives, for which is necessary to use the corresponding sulfates⁶ or phosphates.⁷ In this paper we report for the first time the *in situ* transformation of alkyl triflates or allyl or benzyl triflamides into organolithium compounds, which are trapped with different electrophiles, using a combination of the mentioned arene-catalysed lithiation and Barbier-type reaction conditions.⁸

RESULTS AND DISCUSSION

The reaction of commercially available methyl or ethyl triflates (**1a** or **1b**, respectively) with an excess of lithium powder (1:14 molar ratio) and a catalytic amount of naphthalene (1:0.08 molar ratio; 4 mol %) in the

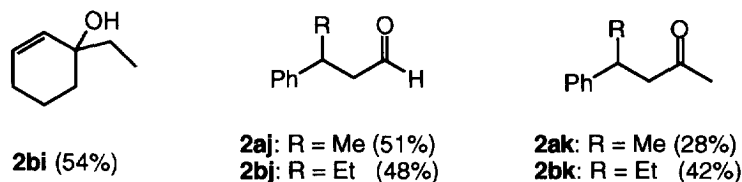
presence of an electrophile [PhCHO, 4-MeOC₆H₄CHO, Me(CH₂)₆CHO, (CH₂)₅CO, (*c*-C₃H₅)₂CO, PhCOMe, 4-MeC₆H₄COPh, PhCH=NPh, *n*-C₈H₁₇CON(CH₂)₄] in THF at temperatures ranging between -78 and 0°C gave after 2 h stirring, and final hydrolysis with water the corresponding products **2aa-2bh** (Scheme 1 and Table 1, entries 1-14).



Scheme 1. *Reagents and conditions:* i, Li powder, C₁₀H₈ cat. (4 mol%), E⁺ = Bu^tCHO, PhCHO, 4-MeOC₆H₄CHO, Me(CH₂)₆CHO, (CH₂)₅CO, (*c*-C₃H₅)₂CO, PhCOMe, 4-MeC₆H₄COPh, PhCH=NPh, *n*-C₈H₁₇CON(CH₂)₄, THF, -78 to 0°C; ii, H₂O.

The reaction shown in Scheme 1 can be applied to other alcohol derivatives. Thus, we prepared the starting triflates **1c** and **1d** (by reaction of the corresponding alcohol with triflic anhydride) and submitted them to the same reaction described above for compounds **1a** and **1b**, so the corresponding compounds **2ca-dc** were isolated (Scheme 1 and Table 1, entries 15-20).

We studied also the reaction with α,β-unsaturated carbonyl compounds, finding different results depending on the substrate used. Thus, applying the reaction shown in Scheme 1 to 2-cyclohexenone as electrophile and starting triflate **1b**, the corresponding 1,2-addition product **2bi** was the only one isolated, after work-up. However, when cinnamaldehyde or benzylideneacetone were used as electrophilic olefines, starting triflates **1a** or **1b** yielded compounds **2aj**, **2bj** and **2ak**, **2bk**, respectively, resulting from a 1,4-addition.



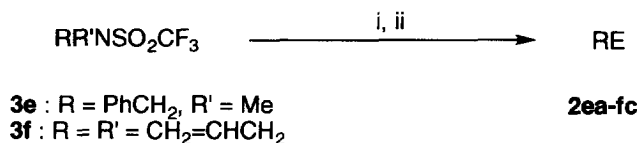
In an attempt to have a look on the scope of the reaction shown in Scheme 1 we tried the same process with phenyl triflate and benzaldehyde as electrophile, in the presence of BF₃; after work-up the expected diphenylmethanol was obtained in poor isolated yield (17%). This result is a clear demonstration that C_{sp}²-O bond is more difficult to cleave than the corresponding C_{sp}³-O one.

Table 1. Preparation of Compounds **2** from Alkyl Triflates **1**

Entry	Starting triflate	Electrophile (E ⁺)	Product ^a		
			No.	E	Yield (%) ^b
1	1a	PhCHO	2aa	PhCHOH	67
2	1a	4-MeOC ₆ H ₄ CHO	2ab	4-MeOC ₆ H ₄ CHOH	42
3	1a	(CH ₂) ₅ CO	2ac	(CH ₂) ₅ COH	47
4	1a	PhCOMe	2ad	PhC(OH)Me	33
5	1a	4-MeC ₆ H ₄ COPh	2ae	4-MeC ₆ H ₄ C(OH)Ph	28
6	1a	(PhCH ₂ S) ₂	2af	PhCH ₂ S	15
7	1b	PhCHO	2ba	PhCHOH	61
8	1b	4-MeOC ₆ H ₄ CHO	2bb	4-MeOC ₆ H ₄ CHOH	78
9	1b	(CH ₂) ₅ CO	2bc	(CH ₂) ₅ COH	75
10	1b	PhCOMe	2bd	PhC(OH)Me	46
11	1b	Me(CH ₂) ₆ CHO	2be	Me(CH ₂) ₆ CHOH	24
12	1b	(<i>c</i> -C ₃ H ₅) ₂ CO	2bf	(<i>c</i> -C ₃ H ₅) ₂ COH	36
13	1b	PhCH=NPh	2bg	PhCHNPh	50
14	1b	<i>n</i> -C ₈ H ₁₇ CON(CH ₂) ₄	2bh	<i>n</i> -C ₈ H ₁₇ CO	41
15	1c	PhCHO	2ca	PhCHOH	54
16	1c	4-MeOC ₆ H ₄ CHO	2cb	4-MeOC ₆ H ₄ CHOH	22
17	1c	(CH ₂) ₅ CO	2cc	(CH ₂) ₅ COH	45
18	1d	Bu ^t CHO	2da	Bu ^t CHOH	91
19	1d	PhCHO	2db	PhCHOH	74
20	1d	(CH ₂) ₅ CO	2dc	(CH ₂) ₅ COH	61

^a All products **2** were >95% pure (GLC and/or 300 MHz ¹H NMR). ^b Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting triflate **1**.

In the last part of this work we studied the naphthalene-catalysed lithiation of *N*-substituted triflamides, finding that the expected transformation into the corresponding organolithium intermediates occurred only for benzylic or allylic derivatives and under Barbier-type reaction conditions. Thus, *N*-benzyl-*N*-methyl triflamide **3e** reacted under the reaction conditions shown in Scheme 1 [E⁺ = Me₃SiCl, PrⁱCHO, PhCHO, Et₂CO, (CH₂)₅CO] to give the expected benzylic derivative **2ea-ee** (Scheme 2 and Table 2, entries 1-5); in the case of the diallyl derivative **3f** the reaction was carried out in the presence of two equivalents of the electrophile [E⁺ = PhCHO, Et₂CO, (CH₂)₅CO] to yield two equivalents of the final allylic product **3fa-fc** (Scheme 2 and Table 2, entries 6-8).



Scheme 2. Reagents and conditions: i, Li powder, C₁₀H₈ cat. (4 mol%), E⁺ = Me₃SiCl, PriCHO, PhCHO, Et₂CO, (CH₂)₅CO, THF, -78 to 0°C; ii, H₂O.

Table 2. Preparation of Compounds **2** from Benzylic or Allylic Triflamides **3**

Entry	Starting Triflamide	Electrophile (E ⁺)	Product ^a			Yield (%) ^b
			No.	R	E	
1	3e	Me ₃ SiCl	2ea	PhCH ₂	Me ₃ Si	60
2	3e	PriCHO	2eb	PhCH ₂	PriCHOH	56
3	3e	PhCHO	2ec	PhCH ₂	PhCHOH	50
4	3e	Et ₂ CO	2ed	PhCH ₂	Et ₂ COH	94
5	3e	(CH ₂) ₅ CO	2ee	PhCH ₂	(CH ₂) ₅ COH	54
6	3f	PhCHO	2fa	CH ₂ =CHCH ₂	PhCHOH	71 ^c
7	3f	Et ₂ CO	2fb	CH ₂ =CHCH ₂	Et ₂ COH	45 ^c
8	3f	(CH ₂) ₅ CO	2fc	CH ₂ =CHCH ₂	(CH ₂) ₅ COH	25 ^c

^a All products **2** were >95% pure (GLC and/or 300 MHz ¹H NMR). ^b Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting triflamide **3**. ^c Yield based on the starting material **3f** and corresponding to the transformation **3f** → **2f**.

As a conclusion, we have shown in this paper that alkylic triflates or allylic or benzylic triflamides can be transformed into the corresponding organolithium compound by a naphthalene-catalysed lithiation; the process has to be performed in the presence of the electrophile (Barbier-type reaction conditions) in order to avoid by-products, mainly Wurtz-type coupling of the *in situ* formed alkyllithium in the case of the starting alkyl triflate.

EXPERIMENTAL PART

General.- For general information, see reference 9. Starting triflates **1a** and **1b** were commercially available (Aldrich) and used as received. The other triflates **1c**,¹⁰ **1d**,¹¹ phenyl triflate¹² and the triflamides **3e**,¹³ and **3f** were prepared according to the literature procedures:^{14,15} *N,N*-Diallyl trifluoromethanesulfonamide (**3f**): *R*_f 0.38 (Hexane/ethyl acetate: 4/1); *t*_r 5.38; *v* (film) 3090, 1645 (HC=C), 1389, 1227, 1189 cm⁻¹ (SO₂CF₃); δ_H 3.96 (4H, d, *J*=6.4, 2xCH₂N), 5.28, 5.33 (2 and 2H, ddd, *J*=1.2, 17.1 and 1.2, 12.2, respectively, 2xCH₂=C), 5.65-5.85 (2H, m, 2xCH=C); δ_C 49.7 (2xCN), 119.85 (q, *J*=322.5, CF), 120.6 (2xCH=C), 132.0 (2xCH₂=C); *m/z* 229 (M⁺, <1%), 200 (31), 188 (16), 160 (12), 96 (29), 94 (20), 80 (16),

69 (54), 68 (43), 67 (27), 56 (38), 55 (24), 54 (42), 42 (53), 41 (100).

Naphthalene-Catalysed Lithiation of Triflates 1 or Triflamides 3 in the Presence of Electrophiles. Isolation of Compounds 2. General Procedure.- To a green suspension of lithium powder (100 mg, 14 mmol) and naphthalene (10 mg, 0.08 mmol) in THF (5 ml) was slowly added (ca. 10 min) a solution of the corresponding triflate **1** or triflamide **3** (1 mmol) and the electrophile [1.2 mmol; 2.4 mmol for compounds **3f** (see text)] in THF (2 ml) at -78°C under an argon atmosphere. Stirring was continued for 2 h allowing the temperature to rise to 0°C.¹⁶ This resulting mixture was then hydrolysed with water (5 ml) and extracted with diethyl ether (2x20 ml). The organic layer was dried over anhydrous Na₂SO₄ and the solvents were evaporated (15 Torr) to give a residue, which was purified by column chromatography (silica gel, hexane/ethyl acetate) affording the pure title compounds **2**. Yields are included in Tables 1 and 2 and in the text. Compounds **2aa**,^{6c} **2ad**,¹⁷ **2ae**,¹⁸ **2af**,^{6c} **2ba**,^{6c} **2bc**,^{6c} **2ea**,⁵ **2eb**,¹⁹ **2ec**,⁵ **2ed**,⁵ **2ee**,⁵ **2fa**,⁵ **2fb**,⁵ **2fc**,¹⁹ and diphenylmethanol¹⁷ which have been previously fully described by us, were characterized by comparison of their spectroscopic (IR, ¹H and ¹³C NMR, and mass spectra) and chromatographic data with those of the reported products. In other cases, physical and spectroscopic data as well as literature references for known compounds follow.

*1-(4-Methoxyphenyl)ethanol (2ab):*²⁰ *R*_f 0.48 (Hexane/ethyl acetate: 2/1); *t*_r 9.00; *v* (film) 3385 (OH), 1612, 1513 (HC=C), 1247, 1176, 1036 cm⁻¹ (C-O); δ_{H} 1.45 (3H, d, *J*=6.4, CH₃CH), 2.16 (1H, br s, OH), 3.78 (3H, s, CH₃O), 4.82 (1H, q, *J*=6.4, CHO), 6.86, 7.27 (2 and 2H, 2d, *J*=8.2, 8.2, respectively, Ph); δ_{C} 24.95 (CH₃C), 55.2 (CH₃O), 69.8 (CHO), 113.75, 126.6, 138.0, 158.85 (Ph); *m/z* 153 (M⁺⁺¹, 1%), 152 (M⁺, 17), 137 (66), 136 (12), 135 (27), 134 (100), 119 (50), 109 (28), 94 (18), 91 (48), 77 (31), 65 (36), 63 (18), 51 (19), 50 (12), 43 (44), 40 (26).

1-Methylcyclohexanol (2ac):^{3a} *R*_f 0.43 (Hexane/ethyl acetate: 4/1); *t*_r 3.93; *v* (film) 3360 cm⁻¹ (OH); δ_{H} 1.10 (3H, s, CH₃), 1.20-1.60 (10H, m, 5xCH₂), 1.75 (1H, s, OH); δ_{C} 22.7, 25.65 (4xCH₂), 29.55 (CH₃), 39.5 (CH₂), 69.85 (CO); *m/z* 115 (M⁺⁺¹, 1%), 114 (M⁺, 18), 99 (40), 85 (12), 81 (39), 79 (11), 72 (17), 71 (100), 58 (41), 57 (14), 55 (17), 53 (11), 43 (90), 42 (12), 41 (24).

*3-Phenylbutanal (2aj):*²¹ *R*_f 0.86 (Hexane/ethyl acetate: 2/1); *t*_r 7.87; *v* (film) 3020, 1494 (HC=C), 1724 cm⁻¹ (C=O); δ_{H} 1.32 (3H, d, *J*=7.0, CH₃), 2.66, 2.76 (1 and 1H, respectively, ddd, *J*=2.1, 7.6, 16.6 and 1.8, 6.9, 16.6, respectively, CH₂), 3.30-3.40 (1H, m, CHPh), 7.15-7.35 (5H, m, Ph), 9.73 (1H, s, CHO); δ_{C} 22.15 (CH₃), 34.3 (CHPh), 51.7 (CH₂), 126.5, 126.75, 128.65, 145.45 (Ph), 210.8 (CO); *m/z* 149 (M⁺⁺¹, 5%), 148 (M⁺, 47), 133 (36), 130 (12), 106 (32), 105 (100), 103 (20), 91 (55), 79 (32), 78 (27), 77 (40), 55 (11), 51 (31), 50 (10), 41 (25).

*4-Phenyl-2-pentanone (2ak):*²² *R*_f 0.44 (Hexane/ethyl acetate: 6/1); *t*_r 8.65; *v* (film) 3091, 3062, 3027, 1602, 1494 (HC=C), 1716 cm⁻¹ (C=O); δ_{H} 1.26 (3H, d, *J*=6.7, CH₃CH), 2.06 (3H, s, CH₃CO), 2.65, 2.75 (1 and 1H, respectively, dd, *J*=7.9, 16.2 and 6.4, 16.2, respectively, CH₂), 3.25-3.35 (1H, m, CHPh), 7.15-7.30 (5H, m, Ph); δ_{C} 21.95 (CH₃CH), 30.5 (CH₂), 35.45 (CH₃CO), 51.95 (CHPh), 126.3, 126.75, 128.5, 146.15 (Ph), 207.8 (CO); *m/z* 163 (M⁺⁺¹, 5%), 162 (M⁺, 44), 147 (76), 129 (13), 119 (20), 106 (11), 105 (100), 104 (35), 103 (16), 91 (58), 79 (25), 78 (15), 77 (32), 51 (24), 44 (11), 43 (92), 41 (29).

*1-(4-Methoxyphenyl)propanol (2bb):*²³ *R*_f 0.30 (Hexane/ethyl acetate: 4/1); *t*_r 8.92; *v* (film) 3395 (OH), 1612, 1513 (HC=C), 1248 cm⁻¹ (C-O); δ_{H} 0.88 (3H, t, *J*=7.3, CH₃C), 1.60-1.90 (2H, m, CH₂), 2.06 (1H, s, OH), 3.78 (3H, s, CH₃O), 4.50 (1H, t, *J*=6.6, CHO), 6.86, 7.24 (2 and 2H, respectively, 2d, *J*=8.7, Ph); δ_{C} 10.15 (CH₃C), 31.7 (CH₂), 55.2 (CH₃O), 75.55 (CHO), 113.7, 127.15, 136.75, 158.9 (Ph); *m/z* 167 (M⁺⁺¹, 1%), 166 (M⁺, 8), 148 (56), 147 (32), 137 (100), 133 (13), 121 (12), 17 (20), 115 (12), 109 (30), 105 (15), 103 (10), 94 (27), 91 (18), 79 (18), 78 (14), 77 (48), 66 (11), 65 (17), 63 (15), 55 (13), 51 (26), 49 (13).

*2-Phenyl-2-butanol (2bd):*²⁴ *R*_f 0.42 (Hexane/ethyl acetate: 6/1); *t*_r 7.42; *v* (film) 3418 (OH), 3059, 3026, 1494 cm⁻¹ (HC=C); δ_{H} 0.79 (3H, t, *J*=7.5, CH₃CH₂), 1.54 (3H, s, CH₃C), 1.75-1.95 (3H, m, CH₂, OH), 7.15-7.25, 7.30-7.35, 7.40-7.45 (1, 2 and 2H, respectively, 3m, Ph); δ_{C} 8.25 (CH₃CH₂), 29.55 (CH₃C),

36.6 (CH₂), 74.85 (CO), 124.85, 126.45, 128.05, 147.7 (Ph); *m/z* 150 (M⁺, <1%), 121 (33), 57 (11), 43 (100).

3-Decanol (2be):²⁵ *R_f* 0.58 (Hexane/ethyl acetate: 6/1); *t_r* 7.82; *v* (film) 3356 cm⁻¹ (OH); δ_{H} 0.88, 0.94 (3 and 3H, respectively, 2t, *J*=6.9 and 7.5, respectively, 2xCH₃), 1.25-1.55 (15H, m, 7xCH₂, OH), 3.50-3.60 (1H, m, CH); δ_{C} 9.85, 14.05 (2xCH₃), 22.65, 25.65, 29.3, 29.65, 30.1, 31.8, 36.95 (7xCH₂), 73.35 (CO); *m/z* 140 (M⁺-18, 1%), 69 (65), 59 (100), 58 (22), 57 (22), 55 (43), 43 (32), 42 (10), 41 (53).

1,1-Dicyclopropylpropanol (2bf):²⁶ *R_f* 0.58 (Hexane/ethyl acetate: 6/1); *t_r* 6.44; *v* (film) 3489 cm⁻¹ (OH); δ_{H} 0.25-0.45 (8H, m, 4xCH₂CH), 0.75-0.90 (3H, m, 2xCH, OH), 1.00 (3H, t, *J*=7.6, CH₃), 1.59 (2H, q, *J*=7.6, CH₂CO); δ_{C} -0.85, 0.60 (4xCH₂CH), 8.25 (CH₃), 18.0 (2xCH), 35.0 (CH₂CO), 70.9 (CO); *m/z* 122 (M⁺-18, 4%), 111 (60), 91 (14), 83 (25), 79 (25), 77 (15), 69 (100), 57 (43), 55 (38), 43 (23), 41 (96).

N,1-Diphenylpropamine (2bg):²⁷ *R_f* 0.62 (Hexane/ethyl acetate: 2/1); *t_r* 12.98; *v* (film) 3414 (NH), 3086, 3053, 3024, 1603, 1504 cm⁻¹ (HC=C); δ_{H} 0.93 (3H, t, *J*=7.6, CH₃), 1.70-1.90 (2H, m, CH₂), 4.01 (1H, br s, NH), 4.20 (1H, t, *J*=6.7, CHN), 6.50-7.35 (10H, m, 2xPh); δ_{C} 10.8 (CH₃), 31.6 (CH₂), 59.65 (CN), 113.2, 117.05, 126.4, 126.8, 128.4, 129.0, 143.85, 147.45 (2xPh); *m/z* 212 (M⁺+1, 3%), 211 (M⁺, 17), 183 (27), 182 (100), 104 (31), 93 (19), 91 (75), 78 (10), 77 (47), 51 (24), 41 (16).

3-Undecanone (2bh):²⁸ *R_f* 0.56 (Hexane); *t_r* 8.79; *v* (film) 1718 cm⁻¹ (C=O); δ_{H} 0.90, 1.07 (3 and 3H, 2t, *J*=6.2 and 7.3, respectively, 2xCH₃), 1.20-1.65 [12H, m, (CH₂)₆CH₃], 2.35-2.50 (4H, m, 2xCH₂CO); δ_{C} 7.65, 13.9 (2xCH₃), 22.5, 23.8, 29.0, 29.15, 29.25, 31.7, 35.65, 42.25, (8xCH₂), 211.65 (CO); *m/z* 171 (M⁺+1, 1%), 170 (M⁺, 4), 141 (82), 85 (50), 81 (26), 73 (59), 72 (95), 71 (71), 67 (19), 58 (17), 57 (100), 56 (25), 55 (54), 44 (23), 43 (92), 42 (91), 41 (74), 40 (26).

1-Ethyl-2-cyclohexen-1-ol (2bi):²⁹ *R_f* 0.49 (Hexane/ethyl acetate: 6/1); *t_r* 5.15; *v* (film) 3381 (OH), 3018, 1647 cm⁻¹ (HC=C); δ_{H} 0.91 (3H, t, *J*=7.5, CH₃), 1.50-1.75 (9H, m, 4xCH₂, OH), 5.61 (1H, d, *J*=9.9, CHCO), 5.81 (1H, ddd, *J*=2.8, 4.6, 9.9, CH=CCO); δ_{C} 7.75 (CH₃), 18.95, 25.2, 34.65, 34.75 (4xCH₂), 69.8 (CO), 129.9, 132.5 (2xCH=C); *m/z* 126 (M⁺, <1%), 98 (15), 97 (100), 93 (11), 79 (43), 77 (19), 69 (34), 67 (16), 55 (35), 49 (29), 41 (39).

3-Phenylpentanal (2bj):³⁰ *R_f* 0.63 (Hexane/ethyl acetate: 6/1); *t_r* 8.64; *v* (film) 3028, 1494, 1453 (HC=C), 1724 cm⁻¹ (C-O); δ_{H} 0.81 (3H, t, *J*=7.3, CH₃), 1.55-1.80 (2H, m, CH₂CH₃), 2.72 (2H, d, *J*=7.3, CH₂CH), 3.00-3.15 (1H, m, CHPh), 7.05-7.35 (5H, m, Ph), 9.66 (1H, s, CHO); δ_{C} 11.85 (CH₃), 29.45 (CCH₃), 41.75 (CPh), 50.2 (CH₂CO), 126.55, 127.5, 128.55, 143.6 (Ph), 202.05 (CO); *m/z* 163 (M⁺+1, 4%), 162 (M⁺, 33), 133 (75), 115 (13), 105 (67), 103 (14), 92 (11), 91 (97), 79 (18), 78 (22), 77 (29), 65 (10), 55 (15), 51 (20), 44 (26), 41 (20), 40 (100).

4-Phenyl-2-hexanone (2bk):³¹ *R_f* 0.54 (Hexane/ethyl acetate: 6/1); *t_r* 9.35; *v* (film) 3061, 3027, 1602, 1494, 1453 (HC=C), 1718 cm⁻¹ (C=O); δ_{H} 0.77 (3H, t, *J*=7.3, CH₃CH₂), 1.45-1.75 (2H, m, CH₂CH₃), 2.01 (3H, s, CH₃CO), 2.72 (2H, d, *J*=7.3, CH₂CH), 3.03 (1H, m, CHCH₂), 7.15-7.30 (5H, m, Ph); δ_{C} 11.9 (CH₃CH₂), 29.3 (CH₃CO), 30.6 (CH₂CH₃), 42.95 (CH₂CO), 50.5 (CHCH₂), 126.3, 127.5, 128.4, 144.25 (Ph), 208.0 (CO); *m/z* 177 (M⁺+1, 1%), 176 (M⁺, 5), 147 (42), 119 (19), 118 (81), 117 (21), 91 (64), 77 (14), 55 (11), 51 (14), 44 (12), 43 (100), 41 (15).

1-Phenyl-4-hexyn-1-ol (2ca):³² *R_f* 0.39 (Hexane/ethyl acetate: 6/1); *t_r* 10.95; *v* (film) 3386 (OH), 3085, 3062, 3030, 1603, 1493 (HC=C), 2245 cm⁻¹ (C≡C); δ_{H} 1.79 (3H, s, CH₃), 1.80-2.05, 2.10-2.35 (1 and 3H, respectively, 2m, 2xCH₂), 4.82 (1H, t, *J*=6.4, CHO), 7.25-7.35 (5H, m, Ph); δ_{C} 3.45 (CH₃), 15.4, 37.9 (2xCH₂), 73.45 (CO), 76.45, 78.4 (C≡C), 125.8, 127.55, 128.4, 144.2 (Ph); *m/z* 174 (M⁺, 2%), 159 (44), 145 (14), 141 (19), 120 (18), 115 (13), 106 (100), 105 (83), 104 (16), 97 (31), 91 (19), 79 (84), 78 (40), 77 (80), 67 (19), 65 (15), 63 (10), 53 (31), 52 (16), 51 (52), 50 (19), 43 (23), 41 (38), 40 (21).

1-(4-Methoxyphenyl)-4-hexyn-1-ol (2cb): *R_f* 0.29 (Hexane/ethyl acetate: 4/1); *t_r* 13.14; *v* (film) 3422 (OH), 3001, 1611, 1513 (HC=C), 2246 (C≡C), 1248, 1175, 1035 cm⁻¹ (C-O); δ_{H} 1.70-2.30 (8H, m with s at 1.79,

CH₃C, 2xCH₂, OH), 3.80 (3H, s, CH₃O), 6.88, 7.27 (2 and 2H, respectively, 2d, *J*=8.3, Ph); δ_C 3.45 (CH₃C), 15.45, 37.8 (2xCH₂), 55.25 (CH₃O), 73.1 (CHO), 76.35, 78.45 (C≡C), 113.8, 127.05, 136.35, 159.05 (Ph); *m/z* 205 (M⁺+1, 2%), 204 (M⁺, 12), 189 (13), 187 (14), 186 (46), 174 (14), 171 (49), 161 (16), 155 (10), 153 (10), 141 (11), 138 (11), 137 (100), 135 (34), 129 (12), 128 (34), 127 (10), 121 (22), 119 (20), 115 (22), 109 (47), 105 (12), 94 (27), 91 (26), 78 (14), 77 (54), 66 (12), 65 (25), 63 (18), 53 (16), 51 (27), 41 (13), 40 (16).

3-Pentyn-1-yl-1-cyclohexanol (2cc): *R_f* 0.35 (Hexane/ethyl acetate: 6/1); *t_r* 9.64; ν (film) 3431 (OH), 1280 (C-O), 2244 cm⁻¹ (C≡C); δ_H 1.25-1.70 [13H, m, CH₂CO, (CH₂)₅, OH], 1.77 (3H, t, *J*=2.6, CH₃), 2.20-2.35 (2H, m, CH₂C≡C); δ_C 3.4 (CH₃), 12.65, 22.15, 25.8, 37.25, 40.55 (7xCH₂), 71.3 (CO), 76.15, 79.5 (C≡C); *m/z* 166 (M⁺, 1%), 133 (13), 110 (17), 109 (22), 105 (11), 99 (82), 98 (21), 95 (37), 94 (21), 91 (17), 81 (74), 79 (25), 67 (49), 65 (14), 57 (25), 55 (100), 53 (37), 51 (11), 43 (63), 42 (20), 41 (73), 40 (12).

2,2-Dimethyl-3-nonanol (2da):³³ *R_f* 0.59 (Hexane); *t_r* 7.58; ν (film) 3403 cm⁻¹ (OH); δ_H 0.85-0.95 (12H, m, 4xCH₃), 1.25-1.60 (11H, m, 5xCH₂, OH), 3.15-3.20 (1H, m, CH); δ_C 14.05 (CH₃CH₂), 25.7 (3xCH₃C), 22.65, 27.05, 29.4, 31.5, 31.9 (5xCH₂), 34.9 (CCHO), 80.0 (CH); *m/z* 157 (M⁺-15, 1%), 115 (15), 97 (70), 87 (23), 69 (37), 57 (58), 56 (27), 55 (100), 45 (17), 44 (11), 43 (51).

1-Phenylheptanol (2db):³⁴ *R_f* 0.33 (Hexane/ethyl acetate: 6/1); *t_r* 11.36; ν (film) 3372 (OH), 3090, 3065, 3026, 1600, 1466 cm⁻¹ (HC=C); δ_H 0.86 (3H, t, *J*=6.9, CH₃) 1.20-1.85 (11H, m, 5xCH₂, OH), 4.65 (1H, t, *J*=6.7, CHO), 7.25-7.35 (5H, m, Ph); δ_C 14.05 (CH₃), 22.6, 25.8, 29.2, 31.75, 39.1 (5xCH₂), 74.7 (CO), 125.9, 127.45, 128.4, 144.95 (Ph); *m/z* 192 (M⁺, 2%), 107 (100), 79 (38), 77 (18), 43 (16).

1-Hexylcyclohexanol (2dc):³⁵ *R_f* 0.43 (Hexane/ethyl acetate: 6/1); *t_r* 9.64; ν (film) 3421 cm⁻¹ (OH); δ_H 0.88 (3H, t, *J*=6.4, CH₃), 1.25-1.60 (21H, m, 10xCH₂, OH); δ_C 14.05 (CH₃), 22.3, 22.6, 22.85, 25.85, 29.95, 31.9, 37.45, 42.45 (10xCH₂), 71.45 (CO); *m/z* 166 (M⁺-18, 2%), 113 (13), 100 (10), 99 (100), 96 (11), 82 (10), 81 (66), 71 (15), 67 (27), 59 (13), 58 (30), 57 (37), 54 (45), 43 (54), 42 (11).

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