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

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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-$MeOC_6H_4CHO$, $CH_3(CH_2)_6CHO$, Et_2CO, $(CH_2)_5CO$, (c-$C_3H_5)_2CO$, PhCOMe, 4-MeC_6H_4COPh, PhCH=NPh, n-$C_8H_7CON(CH_2)_4$] 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 lithiation[3] 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 sulfates[6] 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-$MeOC_6H_4CHO$, $Me(CH_2)_6CHO$, $(CH_2)_5CO$, (c-$C_3H_5)_2CO$, PhCOMe, 4-MeC_6H_4COPh, PhCH=NPh, n-$C_8H_{17}CON(CH_2)_4$] 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).

$$ROSO_2CF_3 \xrightarrow{i, ii} RE$$

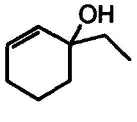
2aa-dc

1a : R = Me
1b : R = Et
1c : R = $MeC{\equiv}C(CH_2)_2$
1d : R = n-C_6H_{13}

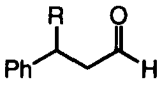
Scheme 1. *Reagents and conditions*: i, Li powder, $C_{10}H_8$ cat. (4 mol%), E^+ = Bu^tCHO, PhCHO, 4-$MeOC_6H_4CHO$, $Me(CH_2)_6CHO$, $(CH_2)_5CO$, (c-$C_3H_5)_2CO$, PhCOMe, 4-MeC_6H_4COPh, PhCH=NPh, n-$C_8H_{17}CON(CH_2)_4$, THF, -78 to 0°C; ii, H_2O.

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).

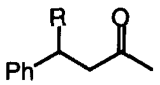
We studied also the reaction with α,β-unsaturated carbonyl compounds, finding different results depending on the sustrated used. Thus, applying the reaction shown in Scheme 1 to 2-cyclohexenone as electrophile and starting triflate **1b**, the corresponding 1,2-addition product **2bi** was the only one 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.



2bl (54%)



2aj: R = Me (51%)
2bj: R = Et (48%)



2ak: R = Me (28%)
2bk: R = Et (42%)

In an attempt to have a look on the scope of the reaction shown in Scheme 1 we tried the same proccess with phenyl triflate and benzaldehyde as electrophile, in the presence of BF_3; 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**	$4\text{-MeOC}_6\text{H}_4\text{CHO}$	**2ab**	$4\text{-MeOC}_6\text{H}_4\text{CHOH}$	42
3	**1a**	$(\text{CH}_2)_5\text{CO}$	**2ac**	$(\text{CH}_2)_5\text{COH}$	47
4	**1a**	PhCOMe	**2ad**	PhC(OH)Me	33
5	**1a**	$4\text{-MeC}_6\text{H}_4\text{COPh}$	**2ae**	$4\text{-MeC}_6\text{H}_4\text{C(OH)Ph}$	28
6	**1a**	$(\text{PhCH}_2\text{S})_2$	**2af**	PhCH_2S	15
7	**1b**	PhCHO	**2ba**	PhCHOH	61
8	**1b**	$4\text{-MeOC}_6\text{H}_4\text{CHO}$	**2bb**	$4\text{-MeOC}_6\text{H}_4\text{CHOH}$	78
9	**1b**	$(\text{CH}_2)_5\text{CO}$	**2bc**	$(\text{CH}_2)_5\text{COH}$	75
10	**1b**	PhCOMe	**2bd**	PhC(OH)Me	46
11	**1b**	$\text{Me(CH}_2)_6\text{CHO}$	**2be**	$\text{Me(CH}_2)_6\text{CHOH}$	24
12	**1b**	$(c\text{-C}_3\text{H}_5)_2\text{CO}$	**2bf**	$(c\text{-C}_3\text{H}_5)_2\text{COH}$	36
13	**1b**	PhCH=NPh	**2bg**	PhCHNHPh	50
14	**1b**	$n\text{-C}_8\text{H}_{17}\text{CON(CH}_2)_4$	**2bh**	$n\text{-C}_8\text{H}_{17}\text{CO}$	41
15	**1c**	PhCHO	**2ca**	PhCHOH	54
16	**1c**	$4\text{-MeOC}_6\text{H}_4\text{CHO}$	**2cb**	$4\text{-MeOC}_6\text{H}_4\text{CHOH}$	22
17	**1c**	$(\text{CH}_2)_5\text{CO}$	**2cc**	$(\text{CH}_2)_5\text{COH}$	45
18	**1d**	Bu^tCHO	**2da**	Bu^tCHOH	91
19	**1d**	PhCHO	**2db**	PhCHOH	74
20	**1d**	$(\text{CH}_2)_5\text{CO}$	**2dc**	$(\text{CH}_2)_5\text{COH}$	61

[a] All products **2** 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 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 ocurred 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^+ = Me_3SiCl, Pr^iCHO, PhCHO, Et_2CO, $(\text{CH}_2)_5\text{CO}$] 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, Et_2CO, $(\text{CH}_2)_5\text{CO}$] to yield two equivalents of the final allylic product **3fa-fc** (Scheme 2 and Table 2, entries 6-8).

$$\mathrm{RR'NSO_2CF_3} \xrightarrow{\text{i, ii}} \mathrm{RE}$$

3e : R = $PhCH_2$, R' = Me
3f : R = R' = $CH_2{=}CHCH_2$

2ea-fc

Scheme 2. *Reagents and conditions*: i, Li powder, $C_{10}H_8$ cat. (4 mol%), E^+ = Me_3SiCl, Pr^iCHO, PhCHO, Et_2CO, $(CH_2)_5CO$, THF, -78 to 0°C; ii, H_2O.

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

Entry	Starting Triflamide	Electrophile (E^+)	Product[a]			
			No.	R	E	Yield (%)[b]
1	**3e**	Me_3SiCl	**2ea**	$PhCH_2$	Me_3Si	60
2	**3e**	Pr^iCHO	**2eb**	$PhCH_2$	Pr^iCHOH	56
3	**3e**	PhCHO	**2ec**	$PhCH_2$	PhCHOH	50
4	**3e**	Et_2CO	**2ed**	$PhCH_2$	Et_2COH	94
5	**3e**	$(CH_2)_5CO$	**2ee**	$PhCH_2$	$(CH_2)_5COH$	54
6	**3f**	PhCHO	**2fa**	$CH_2{=}CHCH_2$	PhCHOH	71[c]
7	**3f**	Et_2CO	**2fb**	$CH_2{=}CHCH_2$	Et_2COH	45[c]
8	**3f**	$(CH_2)_5CO$	**2fc**	$CH_2{=}CHCH_2$	$(CH_2)_5COH$	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** → 2 **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 triflate[12] 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; ν (film) 3090, 1645 (HC=C), 1389, 1227, 1189 cm^{-1} (SO_2CF_3); δ_H 3.96 (4H, d, J=6.4, $2xCH_2N$), 5.28, 5.33 (2 and 2H, 2dd, J=1.2, 17.1 and 1.2, 12.2, respectively, $2xCH_2{=}C$), 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 ($2xCH_2{=}C$); *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 Na_2SO_4 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 diphenylmethanol[17] which have been previously fully described by us, were characterized by comparation of their spectroscopic (IR, ^{1}H and ^{13}C 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; ν (film) 3385 (OH), 1612, 1513 (HC=C), 1247, 1176, 1036 cm^{-1} (C-O); δ_H 1.45 (3H, d, *J*=6.4, CH_3CH), 2.16 (1H, br s, OH), 3.78 (3H, s, CH$_3$O), 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 (CH$_3$C), 55.2 (CH$_3$O), 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; ν (film) 3360 cm^{-1} (OH); δ_H 1.10 (3H, s, CH$_3$), 1.20-1.60 (10H, m, 5xCH$_2$), 1.75 (1H, s, OH); δ_C 22.7, 25.65 (4xCH$_2$), 29.55 (CH$_3$), 39.5 (CH$_2$), 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; ν (film) 3020, 1494 (HC=C), 1724 cm^{-1} (C=O); δ_H 1.32 (3H, d, *J*=7.0, CH$_3$), 2.66, 2.76 (1 and 1H, respectively, ddd, *J*=2.1, 7.6, 16.6 and 1.8, 6.9, 16.6, respectively, CH$_2$), 3.30-3.40 (1H, m, CHPh), 7.15-7.35 (5H, m, Ph), 9.73 (1H, s, CHO); δ_C 22.15 (CH$_3$), 34.3 (CHPh), 51.7 (CH$_2$), 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; ν (film) 3091, 3062, 3027, 1602, 1494 (HC=C), 1716 cm^{-1} (C=O); δ_H 1.26 (3H, d, *J*=6.7, CH_3CH), 2.06 (3H, s, CH_3CO), 2.65, 2.75 (1 and 1H, respectively, dd, *J*=7.9, 16.2 and 6.4, 16.2, respectively, CH$_2$), 3.25-3.35 (1H, m, CHPh), 7.15-7.30 (5H, m, Ph); δ_C 21.95 (CH$_3$CH), 30.5 (CH$_2$), 35.45 (CH$_3$CO), 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; ν (film) 3395 (OH), 1612, 1513 (HC=C), 1248 cm^{-1} (C-O); δ_H 0.88 (3H, t, *J*=7.3, CH_3C), 1.60-1.90 (2H, m, CH$_2$), 2.06 (1H, s, OH), 3.78 (3H, s, CH$_3$O), 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 (CH$_3$C), 31.7 (CH$_2$), 55.2 (CH$_3$O), 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; ν (film) 3418 (OH), 3059, 3026, 1494 cm^{-1} (HC=C); δ_H 0.79 (3H, t, *J*=7.5, CH_3CH$_2$), 1.54 (3H, s, CH_3C), 1.75-1.95 (3H, m, CH$_2$, OH), 7.15-7.25, 7.30-7.35, 7.40-7.45 (1, 2 and 2H, respectively, 3m, Ph); δ_C 8.25 (CH$_3$CH$_2$), 29.55 (CH$_3$C), 36.6 (CH_2), 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; ν (film) 3356 cm^{-1} (OH); δ_H 0.88, 0.94 (3 and 3H, respectively, 2t, *J*=6.9 and 7.5, respectively, 2xCH_3), 1.25-1.55 (15H, m, 7xCH_2, OH), 3.50-3.60 (1H, m, CH); δ_C 9.85, 14.05 (2xCH_3), 22.65, 25.65, 29.3, 29.65, 30.1, 31.8, 36.95 (7xCH_2), 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; ν (film) 3489 cm^{-1} (OH); δ_H 0.25-0.45 (8H, m, 4xCH_2CH), 0.75-0.90 (3H, m, 2xCH, OH), 1.00 (3H, t, *J*=7.6, CH_3), 1.59 (2H, q, *J*=7.6, CH_2CO); δ_C -0.85, 0.60 (4xCH_2CH), 8.25 (CH_3), 18.0 (2xCH), 35.0 (CH_2CO), 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; ν (film) 3414 (NH), 3086, 3053, 3024, 1603, 1504 cm^{-1} (HC=C); δ_H 0.93 (3H, t, *J*=7.6, CH_3), 1.70-1.90 (2H, m, CH_2), 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 (CH_3), 31.6 (CH_2), 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; ν (film) 1718 cm^{-1} (C=O); δ_H 0.90, 1.07 (3 and 3H, 2t;, *J*=6.2 and 7.3, respectively, 2xCH_3), 1.20-1.65 [12H, m, $(CH_2)_6CH_3$], 2.35-2.50 (4H, m, 2xCH_2CO); δ_C 7.65, 13.9 (2xCH_3), 22.5, 23.8, 29.0, 29.15, 29.25, 31.7, 35.65, 42.25, (8xCH_2), 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; ν (film) 3381 (OH), 3018, 1647 cm^{-1} (HC=C); δ_H 0.91 (3H, t, *J*=7.5, CH_3), 1.50-1.75 (9H, m, 4xCH_2, 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 (CH_3), 18.95, 25.2, 34.65, 34.75 (4xCH_2), 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; ν (film) 3028, 1494, 1453 (HC=C), 1724 cm^{-1} (C-O); δ_H 0.81 (3H, t, *J*=7.3, CH_3), 1.55-1.80 (2H, m, CH_2CH_3), 2.72 (2H, d, *J*=7.3, CH_2CH), 3.00-3.15 (1H, m, CHPh), 7.05-7.35 (5H, m, Ph), 9.66 (1H, s, CHO); δ_C 11.85 (CH_3), 29.45 (CCH_3), 41.75 (CPh), 50.2 (CH_2CO), 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; ν (film) 3061, 3027, 1602, 1494, 1453 (HC=C), 1718 cm^{-1} (C=O); δ_H 0.77 (3H, t, *J*=7.3, CH_3CH_2), 1.45-1.75 (2H, m, CH_2CH_3), 2.01 (3H, s, CH_3CO), 2.72 (2H, d, *J*=7.3, CH_2CH), 3.03 (1H, m, $CHCH_2$), 7.15-7.30 (5H, m, Ph); δ_C 11.9 (CH_3CH_2), 29.3 (CH_3CO), 30.6 (CH_2CH_3), 42.95 (CH_2CO), 50.5 ($CHCH_2$), 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; ν (film) 3386 (OH), 3085, 3062, 3030, 1603, 1493 (HC=C), 2245 cm^{-1} (C≡C); δ_H 1.79 (3H, s, CH_3), 1.80-2.05, 2.10-2.35 (1 and 3H, respectively, 2m, 2xCH_2), 4.82 (1H, t, *J*=6.4, CHO), 7.25-7.35 (5H, m, Ph); δ_C 3.45 (CH_3), 15.4, 37.9 (2xCH_2), 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; ν (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,

CH_3C, 2xCH_2, OH), 3.80 (3H, s, CH_3O), 6.88, 7.27 (2 and 2H, respectively, 2d, *J*=8.3, Ph); δ_C 3.45 (CH_3C), 15.45, 37.8 (2xCH_2), 55.25 (CH_3O), 73.1 (CHO), 76.35, 78.45 ($C\equiv C$), 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} ($C\equiv C$); δ_H 1.25-1.70 [13H, m, CH_2CO, $(CH_2)_5$, OH], 1.77 (3H, t, *J*=2.6, CH_3), 2.20-2.35 (2H, m, $CH_2C\equiv C$); δ_C 3.4 (CH_3), 12.65, 22.15, 25.8, 37.25, 40.55 (7xCH_2), 71.3 (CO), 76.15, 79.5 ($C\equiv C$); *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, 4xCH_3), 1.25-1.60 (11H, m, 5xCH_2, OH), 3.15-3.20 (1H, m, CH); δ_C 14.05 (CH_3CH_2), 25.7 (3xCH_3C), 22.65, 27.05, 29.4, 31.5, 31.9 (5xCH_2), 34.9 (*C*CHO), 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, CH_3) 1.20-1.85 (11H, m, 5xCH_2, OH), 4.65 (1H, t, *J*=6.7, CHO), 7.25-7.35 (5H, m, Ph); δ_C 14.05 (CH_3), 22.6, 25.8, 29.2, 31.75, 39.1 (5xCH_2), 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, CH_3), 1.25-1.60 (21H, m, 10xCH_2, OH); δ_C 14.05 (CH_3), 22.3, 22.6, 22.85, 25.85, 29.95, 31.9, 37.45, 42.45 (10xCH_2), 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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