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$RuCl_2(DMSO)_4$ catalyzes the β-alkylation of secondary alcohols with primary alcohols through a hydrogen autotransfer process

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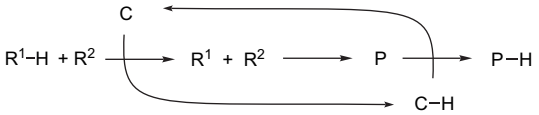
Abstract—The electrophilic β-alkylation of secondary alcohols with primary alcohols is accomplished by a hydrogen autotransfer process catalyzed by $RuCl_2(DMSO)_4$. The reaction can produce either simple alkylated secondary alcohols or α,β-unsaturated ketones with good to excellent results just by choosing the appropriate starting secondary alcohol (methyl or longer chain secondary alcohol, respectively), as well as quinolines (by using 2-aminobenzyl alcohol).

1. Introduction

Alcohols are one of the most important classes of organic compounds owing to their wide variety of uses in industrial and laboratory chemistry. Although a plethora of methods for the synthesis of alcohols are known,[1] their simple creation by carbon–carbon bond manipulation is very unusual. In this approach, the usual protocol involves the oxidation of alcohol to ketone, followed by alkylation, and final reduction of the carbonyl moiety to the alcohol. Therefore, any new strategy for simple alkylation of alcohols would be welcome, more if it is environmentally benign and supports the sustainable chemical industry.[2]

The hydrogen autotransfer process, which can be considered as a new type of domino reaction,[3] involves an initial removal of hydrogen from at least one of the initial reagents (R^1-H) by a catalyst (C), followed by reaction of the new reagents (R^1 and R^2) to form a new compound (P), which is in turn the hydrogen acceptor of the previously formed hydrogenated catalyst (C-H), renewing the catalyst (Scheme 1). This strategy has been used in the alkylation of different carbonyl derivatives using primary alcohols as electrophiles.[4] The reaction starts with the oxidation of the primary alcohol to give the corresponding aldehyde and the hydride metal derivative, followed by condensation with the carbonyl derivative to render the corresponding α,β-unsaturated carbonyl derivative, which is finally reduced with the hydride metal derivative to give the corresponding carbonyl compound.[5] In the case of using methyl ketones as starting materials, the presence and extra equivalent of primary alcohol forced the process to yield the related secondary alkylated alcohol[6] after a final Meerwein–Ponndorf–Verley reduction.[7]



$$\text{Atom Efficiency (\%)} = \text{Yield (\%)} \times \frac{\text{Mw of Final Product}}{\sum_i (\text{Equiv.} \times \text{Mw of all reagents})_i}$$

Scheme 1. General scheme for a hydrogen autotransfer process.

Despite the high atom efficiency obtained in the α-alkylation of methyl ketone derivatives with alcohols through a hydrogen autotransfer process, the related process using 2-alkanol derivatives, as masked ketones, has been scarcely reported. In fact, there are only two examples of this process.[8] The first one uses the air sensitive $RuCl_2(PPh_3)_3$ as catalyst, a double amount of primary alcohol, and a large excess of 1-dodecene as sacrificial additive.[9] The second one uses the very expensive catalyst $[Cp^*IrCl_2]_2$, sodium *tert*-butoxide, and a slight excess of the primary alcohol.[10] The yields in both cases are comparable, in the range of 70–80%.

Here we report an alternative protocol for the β-alkylation of secondary alcohols with primary alcohols catalyzed by $RuCl_2(DMSO)_4$.[11]

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2. Results and discussion

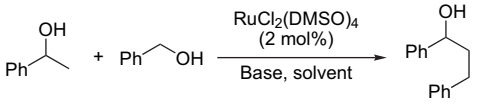
2.1. β-Alkylation of 2-alkanol derivatives using primary alcohols as electrophiles

The alkylation of equimolecular amounts of 1-phenylethanol (**1a**) with benzylic alcohol to give the corresponding alcohol **3a** was chosen as the reaction model in order to optimize all different parameters, with the solvent being the first one (Table 1). The reaction in toluene gave the expected product with modest yield after seven days, while the reaction failed using other more polar solvents, such as water, MeCN or DMSO (entries 1–4).

Despite these disappointing results, we found that the reaction using 1,4-dioxane gave the expected compound **3a** with an excellent yield (Table 1, entry 5). The reaction can also be performed in solvent-free conditions[12] giving slightly lower results but in only three days (entry 6). After finding dioxane as the best solvent, we studied the influence of the amount of base (KOH), the decrease or increase from 2 equiv being detrimental (Table 1, entries 5 and 7–9). The increase of the temperature also renders lower results (entries 10 and 11). Finally the nature of base was also tested at different temperatures, giving in all cases worse results (entries 12–14).

On the basis of the above results, we next examined the reactions of various 2-alkanols with primary alcohols under optimized conditions (Table 2). The standard reaction to give compound **3a** permitted us to compare our results with those of literature. Thus, the reaction using the catalyst $RuCl_2(PPh_3)_3$ gave 82% yield,[9] while using $[Cp^*IrCl_2]_2$ gave 75% yield,[10] both yields being lower than those in our case (Table 2, entry 1). Our protocol gave not only better chemical yield for compound **3a** but also better atom efficiency (see Scheme 1: in our case 57% and in the literature 12[9] and 43%[10]) than the reported procedures.

Table 1. Optimization of β-alkylation of alcohols[a]

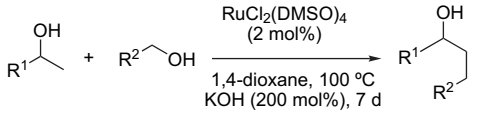


1a **2a** **3a**

Entry	Solvent	Base (%)	T (°C)	t (day)	Yield (%)[b]
1	PhMe	KOH (200)	100	7	56[c]
2	H_2O	KOH (200)	100	3	0[d]
3	MeCN	KOH (200)	100	3	0[d]
4	DMSO	KOH (200)	100	3	0[d]
5	Dioxane	KOH (200)	100	7	98
6	—[e]	KOH (200)	100	3	91
7	Dioxane	KOH (100)	100	7	38
8	Dioxane	KOH (300)	100	7	87
9	Dioxane	KOH (600)	100	7	56
10	Dioxane[f]	KOH (200)	120	3	92
11	THF[f]	KOH (200)	120	3	73
12	Dioxane	KOBu^t (200)	100	3	85
13	Dioxane[f]	KOBu^t (200)	120	2	73
14	Dioxane	$NaNH_2$ (200)	100	3	76

[a] All reactions were performed using 5 mmol (100 mol %) of each alcohol.
[b] Yields determined by ^{1}H NMR using *N*,*N*-diphenyl formamide as internal standard.
[c] Forty-three percent of corresponding ketone was detected.
[d] Initial reagents were recovered unchanged.
[e] The reaction was performed under solvent-free conditions.
[f] The reaction was performed in a pressure tube.

Table 2. β-Alkylation of 2-alkanol derivatives **1** with primary alcohols **2**[a]



1 **2** **3**

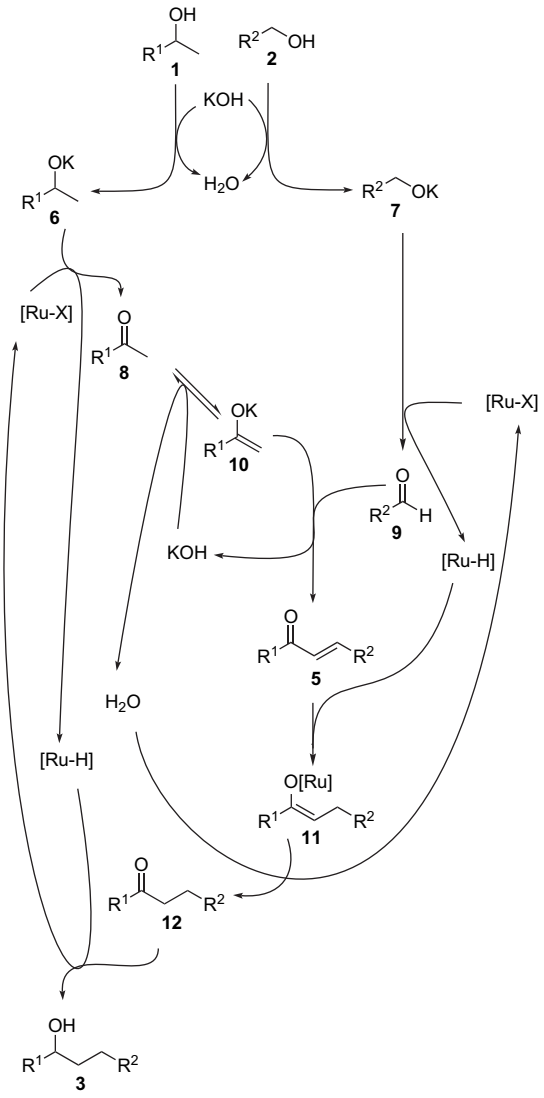
Entry	R^1	R^2	Compd no.	Yield (%)[b]
1	Ph	Ph	**3a**	95
2	Ph	4-ClC_6H_4	**3b**	69
3	Ph	3-ClC_6H_4	**3c**	98[c]
4	Ph	4-$MeOC_6H_4$	**3d**	98[c]
5	Ph	1-Naphthyl	**3e**	85
6	Ph	2-Furyl	**3f**	98[c]
7	Ph	Pr^i	**3g**	42 (47)
8	4-$F_3CC_6H_4$	Ph	**3h**	80
9	4-MeC_6H_4	Ph	**3i**	98[c]
10	4-MeC_6H_4	4-ClC_6H_4	**3j**	76
11	4-MeC_6H_4	3,4-$(MeO)_2C_6H_3$	**3k**	71
12	Bu^t	Ph	**3l**	48 (58)
13	n-C_5H_{11}	Ph	**3m**	<5

[a] All reactions were performed using 5 mmol (100 mol %) of each alcohol.
[b] Isolated yield after column chromatography (silica gel: hexane/ethyl acetate); in parenthesis: yields obtained under solvent-free conditions after three days.
[c] Compound obtained pure after work-up.

The reaction gave homogeneous results for primary aromatic alcohols, independent of the nature of the substituent on the aromatic ring, even using heteroaromatic derivatives (Table 2, entries 1–6). However, the reaction with aliphatic primary alcohols gave lower chemical yield, also under solvent-free conditions (entry 7). The reaction gave good results when different aromatic secondary ethanol derivatives **1** were tested (entries 8–11), with the yield being lower for substituted aliphatic alcohols or null for non-substituted reagents (entries 12 and 13, respectively).

Concerning a possible mechanism, and considering the previously proposed catalytic cycle for the related α-alkylation of ketones[4n] (deduced by detecting different by-products such as aldehydes and α,β-unsaturated ketones, as well as by isotopic labelling experiments), we propose the catalytic cycle shown in Scheme 2 which contains an extra oxidation–reduction step.

Probably, in the reaction medium the initial ruthenium complex evolves to form the real catalyst, which could be a polymetallic species, even bearing hydroxy groups,[13] although the permanence of chlorine ligands cannot be ruled out. In turn, this intermediate reacts with alkoxide derivatives to form the corresponding mono- or dihydride ruthenium catalytic active species.[14] The necessary use of stoichiometric amounts of base can indicate that its role is not only in the deprotonation of the in situ formed ketone **8** but also in the deprotonation of the alcohols **1** and **2**. The corresponding oxidized carbonyl compounds **8** and **9** suffer a classical basic aldol condensation to render the α,β-unsaturated ketone **5**. The last steps are the reduction of carbon–carbon double bond through a Michael-type addition to form the α-alkylated ketone **12** and final reduction of the carbonyl group to the alcohol **3**,[15] renewing the catalyst.



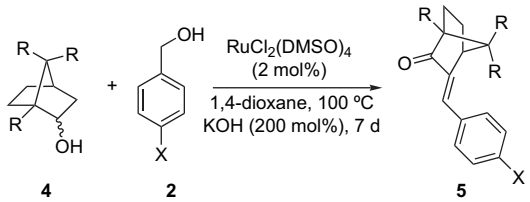
Scheme 2. Proposed catalytic cycle for the β-alkylation of 2-alkanols with primary alcohols.

2.2. Reaction of secondary bicyclic alcohols with primary alcohols

When the same above protocol was followed using bicyclic alcohols **4** as secondary alcohol partners, ketone derivatives **5** were isolated instead of the expected alcohol of type **3** (Table 3). The reason for this fact is not yet very clear but it would be related with the higher stability of trisubstituted carbon–carbon double bond, as well as the higher instability of ruthenium bicyclic enolate of type **11**, which would make more difficult the corresponding Michael-type addition of the ruthenium hydride intermediate, the reoxidation of this hydride complex being accomplished either by the molecular oxygen[16] or by direct generation of hydrogen.[17]

The reaction worked nicely for different substituted benzylic alcohols **2**, giving similar results for the protocol using dioxane as solvent as well as for solvent-free conditions (entry 4). The use of borneol or isoborneol did not have any important difference, obtaining similar results (Table 3, entries 5 and 6). The *Z*-configuration of the double bond

Table 3. Reaction of secondary bicyclic alcohols **4** with benzylic alcohols **2**[a]



Entry	R	Alcohol **4**	X	Compd no.	Yield (%)[b]
1	H	Mixture[c]	H	**5a**	85
2	H	Mixture[c]	MeO	**5b**	96
3	Me	*endo*	H	**5c**	71
4	Me	*endo*	Me	**5d**	47 (34)
5	Me	*endo*	MeO	**5e**	62
6	Me	*exo*	MeO	**5e**	73

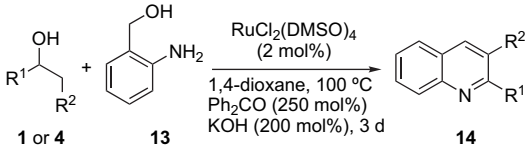
[a] All reactions were performed using 5 mmol (100 mol %) of each alcohol.
[b] Isolated yield after column chromatography (silica gel: hexane/ethyl acetate); in parenthesis: yields obtained under solvent-free conditions after three days.
[c] Mixture of isomer *endo*:*exo*=83:17.

was unambiguously determined by the X-ray of compound **5e** and by NOESY experiments of compounds **5a** and **e**.[4n]

2.3. Synthesis of quinolines

Finally, it should be pointed out that the above reaction with 2-aminobenzyl alcohol **13** gave the corresponding quinolines **14** (Table 4).[18] The tentative mechanism pathway would involve the oxidation of both alcohols to the corresponding carbonyl compounds of type **8** and **9**, followed by either the ketone-imine formation and final aldol condensation process, or by an aldol reaction to give the corresponding α,β-unsaturated ketone of type **5** and final ring closing imine formation. Benzophenone was used as hydride scavenger, in order to reoxidize the ruthenium hydride intermediate and renewing the starting ruthenium catalyst. The reaction worked nicely for aromatic and heteroaromatic substituted ethanol derivatives, giving pure quinoline derivative **14** in practically quantitative yield after acidic/basic

Table 4. Synthesis of quinolines[a]



Entry	Compd no.	R^1	R^2	Yield (%)[b]
1	**14a**	Ph	H	98[c] (98)[c]
2	**14b**	4-MeC_6H_4	H	98[c]
3	**14c**	2-Furyl	H	98[c]
4	**14d**	Et	Me	98[c,d]
5	**14e**	$-(CH_2)_4-$		71[d] (89)
6	**14f**			41[d,e]

[a] All reactions were performed using 5 mmol (100 mol %) of each alcohol.
[b] Isolated yield after acidic/basic aqueous extraction; in parenthesis: yields obtained under solvent-free conditions after three days.
[c] Compound obtained pure after work-up.
[d] Yield after seven days' reaction time.
[e] Purified by column chromatography (silica gel: hexane/ethyl acetate).

aqueous extraction (entries 1–3). Surprisingly, the reaction gave excellent results also for non-substituted secondary alcohols, which could indicate that prior to the aldol reaction, the formation of imine derivative takes place. Finally, it should be pointed out that the reaction performed under solvent-free conditions gave in some cases better chemical yields in shorter reaction times.

3. Conclusion

In summary, we have described here the use of $RuCl_2(DMSO)_4$ for a simple and direct β-alkylation of secondary alcohols with not only high yields but also atom efficiency, using secondary alcohols as the source of nucleophiles and primary alcohols as the electrophilic partners. The final product depends strongly on the alcohol nature, obtaining either the simple alkylation for 2-alkanol derivatives or α,β-unsaturated ketones when methylenic bicyclic alcohols were used as starting materials. In this way, wide variety of quinolines could be prepared with excellent yields just by using 2-aminobenzyl alcohol derivative as alkylating agent. It is worthy to note that this procedure constitutes a good example of very high atom efficiency reaction. Moreover, the waste material of the reactions is water, making them a very interesting process from an environmental and industrial point of view. The catalyst used is very cheap, stable, easy to handle and prepare.[19] All these facts make the $RuCl_2(DMSO)_4$-catalyzed alkylation process very interesting comparing to other protocols using expensive and difficult-to-handle catalysts.

4. Experimental

4.1. Chemicals and instrumentation

Full general statements were described elsewhere.[20] All reagents were commercially available (Acros, Aldrich, Strem) and were used as received.

4.2. General procedure for reaction of secondary alcohols with primary alcohols

To a solution of $RuCl_2(DMSO)_4$ (0.048 g, 0.1 mmol) and KOH (0.660 g, 10 mmol) in 1,4-dioxane (5 mL) was added the corresponding secondary alcohol **1** or **4** (5 mmol), followed by the addition of the corresponding primary alcohol **2** or **13** (5 mmol). In the case of using amino alcohols **13**, benzophenone (2.7 g, 15 mmol) was also added. The mixture was stirred and heated at 80 °C for a period of seven days. Then, the mixture was quenched by addition of a saturated NH_4Cl solution (20 mL) and extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtrated, and removed under reduced pressure. The resulting residue was purified by flash chromatography on silica gel using suitable mixtures of hexane/ethyl acetate to afford the corresponding product **3**, **5** or **14**. Yields are included in Tables 1–4. Compounds **3a**, **3g**, **3h**, **3l**, **5a**, **5b**, **5d**, **5e**, **14a–f**, which have been previously fully described by us,[4n] were characterized by comparison of their spectroscopic (IR, ^1H, and ^{13}C NMR, and mass spectra) and chromatographic data with those of the reported products. Physical and spectroscopic data as well as literature references follow.

4.2.1. 3-(4-Chlorophenyl)-1-phenyl-1-propanol (3b).[10] R_f 0.29 (hexane/ethyl acetate: 4/1); t_R 16.5; ν (film) 3408 (O–H), 3026, 1648 (C=CH), 1063 cm^{-1} (C–O); δ_H 1.84 (1H, s, OH), 1.90–2.15 (2H, m, CH_2CO), 2.55–2.75 (2H, m, CH_2CH_2CO), 4.65–4.70 (1H, m, CHO), 7.11, 7.23, and 7.25–7.40 (2H, 2H, and 5H, respectively, d, d, and m, respectively, J=8.5 and 8.5 Hz, respectively, ArH); δ_C 31.35, 40.30, 73.70, 125.85 (2C), 127.75, 128.45 (2C), 128.55 (2C), 129.75 (2C), 1312.55, 140.20, 144.40; *m/z* 248 (M^++2, 1%), 246 (3), 230 (21), 229 (11), 228 (61), 193 (33), 125 (12), 107 (10), 103 (15), 79 (48), 77 (33).

4.2.2. 3-(3-Chlorophenyl)-1-phenyl-1-propanol (3c). R_f 0.15 (hexane/ethyl acetate: 4/1); t_R 16.4; ν (film) 3381 (O–H), 3069, 1589, 1566 (C=CH), 1078 cm^{-1} (C–O); δ_H 1.97 (1H, s, OH), 1.90–2.15 (2H, m, CH_2CO), 2.55–2.80 (2H, m, CH_2CH_2CO), 4.65 (1H, dd, J=5.5, 7.6 Hz, CHO), 7.05–7.40 (9H, m, ArH); δ_C 31.65, 40.10, 73.65, 125.85, 126.00, 126.60, 127.75 (2C), 128.40, 128.55 (2C), 129.60, 134.05, 143.80, 144.30; *m/z* 248 (M^++2, 8%), 246 (M^+, 23), 228 (14), 126 (10), 107 (100), 103 (11), 91 (11), 79 (41), 77 (29). HRMS: M^+ found 246.0808. $C_{15}H_{15}OCl$ requires 246.0811.

4.2.3. 3-(4-Methoxyphenyl)-1-phenyl-1-propanol (3d).[10] t_R 16.9; R_f 0.7 (hexane/ethyl acetate: 4/1); ν (film) 3419 (O–H), 3028, 1622, 1513 (C=CH), 1039 cm^{-1} (C–O); δ_H 1.95 (1H, s, OH), 2.00–2.15 (2H, m, CH_2CO), 2.55–2.75 (2H, m, CH_2CH_2CO), 3.76 (3H, s, CH_3), 4.65–4.70 (1H, m, CHO), 6.80–6.85, 7.10–7.15, and 7.25–7.35 (2H, 2H, and 5H, respectively, 3m, ArH); δ_C 31.15, 40.70, 55.30, 73.85, 113.80 (2C), 125.95 (2C), 127.65, 128.55 (2C), 129.35 (2C), 133.80, 144.65, 157.80; *m/z* 242 (M^+, 28%), 225 (17), 224 (100), 223 (20), 209 (15), 193 (19), 135 (16), 133 (11), 122 (22), 121 (51), 108 (14), 107 (32), 105 (12), 91 (13), 79 (29), 78 (11), 77 (26).

4.2.4. 3-(2-Naphthyl)-1-phenyl-1-propanol (3e).[9] t_R 19.4; R_f 0.68 (hexane/ethyl acetate: 4/1); ν (film) 3375 (O–H), 3057, 1596, 1518 (C=CH), 1066 cm^{-1} (C–O); δ_H 1.95 (1H, s, OH), 2.10–2.30 (2H, m, CH_2CO), 3.05–3.15 and 3.20–3.30 (2H, m, CH_2CH_2CO), 4.75–4.80 (1H, m, CHO), 7.25–7.50, 7.70, 7.80–7.85, and 7.95–8.00 (9H, 1H, 1H, and 1H, respectively, m, d, m, and m, respectively, J=8 Hz, ArH); δ_C 29.10, 39.80, 74.15, 123.75, 125.45, 125.55, 125.80, 125.95 (2C), 126.65, 127.70, 128.55 (2C), 128.75, 131.80, 133.90, 137.95, 144.50; *m/z* 262 (M^+, 32%), 244 (24), 155 (17), 154 (11), 153 (38), 152 (14), 143 (12), 142 (100), 141 (40), 133 (11), 128 (13), 115 (22), 107 (20), 79 (22), 77 (18).

4.2.5. 1-Phenyl-3-(2-furyl)-1-propanol (3f).[21] R_f 0.23 (hexane/ethyl acetate: 4/1); t_R 13.4; ν (film) 3394 (O–H), 3021, 1597, 1514 (C=CH), 1065 cm^{-1} (C–O); δ_H 1.95 (1H, s, OH), 2.00–2.15 (2H, m, CH_2CO), 2.65–2.80 (2H, m, CH_2CH_2CO), 4.70–4.75 (1H, m, CHO), 5.95–6.00, 6.25–6.30, and 7.25–7.35 (1H, 1H, and 6H, respectively, 3m, ArH); δ_C 24.35, 37.10, 73.65, 105.00, 110.10, 125.85 (2C), 127.65, 128.50 (2C), 140.95, 144.30, 155.50; *m/z*

202 (M^+, 6%), 185 (14), 184 (100), 183 (13), 155 (27), 141 (12), 120 (12), 107 (30), 105 (17), 104 (10), 91 (12), 81 (22), 79 (40), 77 (31).

4.2.6. 1-(4-Methylphenyl)-3-phenyl-1-propanol (3i).[9] R_f 0.39 (hexane/ethyl acetate: 4/1); t_R 15.7; ν (film) 3377 (O–H), 3023, 1607, 1520 (C=CH), 1066 cm^{-1} (C–O); δ_H 1.86 (1H, s, OH), 1.95–2.20 (2H, m, CH_2CO), 2.34 (3H, s, CH_3), 2.60–2.80 (2H, m, CH_2CH_2CO), 4.60–4.65 (1H, m, CHO), 7.15–7.30 (9H, m, ArH); δ_C 21.10, 32.05, 40.30, 73.70, 125.75, 125.85 (2C), 128.35 (2C), 128.40 (2C), 129.15 (2C), 137.70, 141.55, 141.80; *m/z* 226 (M^+, 16%), 208 (21), 121 (100), 93 (27), 91 (30), 77 (17).

4.2.7. 3-(4-Chlorophenyl)-1-(4-methylphenyl)-1-propanol (3j). R_f 0.46 (hexane/ethyl acetate: 8/2); t_R 17.6; ν (film) 3377 (O–H), 3115, 3028, 1500 (C=CH), 1095 (C–O); δ_H 1.82 (1H, s, OH), 1.85–2.15 (2H, m, CH_2CO), 2.55–2.75 (2H, m, CH_2CH_2CO), 2.35 (3H, s, CH_3), 4.62 (1H, t, J=5.7 Hz, CHO), 7.05–7.3 (8H, m, ArH); δ_C 21.00, 31.40, 40.20, 73.50, 125.80, 128.40, 129.2, 129.75, 131.2, 137.2, 140.3, 141.4; *m/z* 260 (M^+, 6%), 242 (23), 121 (100), 93 (25), 91 (19), 77 (16). HRMS: M^+ found 260.0966. $C_{16}H_{17}OCl$ requires 260.0968.

4.2.8. 3-(3,4-Dimethoxyphenyl)-1-(4-methylphenyl)-1-propanol (3k). R_f 0.18 (hexane/ethyl acetate: 8/2); t_R 19.5; ν (film) 3437 (O–H), 3004, 1595 (C=CH), 2839 (MeO), 1033 cm^{-1} (C–O); δ_H 1.90 (1H, s, OH), 1.90–2.15 (2H, m, CH_2CO), 2.35 (3H, s, CH_3), 2.60–2.70 (2H, m, CH_2CH_2CO), 3.85 (6H, s, 2×MeO), 4.65 (1H, t, J=5.1 Hz, CHO), 6.70–6.80, 7.16, and 7.24 (3H, 2H, and 2H, respectively, m, d, and d, respectively, J=7.9 and 8.3 Hz, respectively, ArH); δ_C 21.00, 31.65, 40.50, 55.75, 55.85, 73.70, 111.15, 111.65, 120.15, 125.85, 129.15, 134.40, 137.30, 141.55, 147.10, 148.75; *m/z* 287 (M^++1, 13%), 286 (M^+, 66), 268 (21), 237 (21), 153 (10), 152 (100), 151 (29), 137 (18), 121 (48), 93 (16), 91 (21), 77 (16). HRMS: M^+ found 286.1563. $C_{18}H_{22}O_3$ requires 286.1569.

4.2.9. 1,7,7-Trimethyl-3-[(*E*)-1-phenylmethylidene]bicyclo[2.2.1]heptan-2-one (5c).[22] Mp 73–74 °C; R_f 0.63 (hexane/ethyl acetate: 8/2); $[\alpha]_D^{20}$ −5.2 (*c* 0.8, $CHCl_3$); t_R 15.7; ν (KBr) 3054, 1656 (C=CH), 1728 cm^{-1} (C=O); δ_H 0.80, 0.99, and 1.03 [3H each, 3s, $(CH_3)_2CCCH_3$], 1.45–1.60, 1.75–1.80, and 2.15–2.20 (2H, 1H, and 1H, respectively, 3m, CH_2CH_2), 3.10 (1H, d, J=4.3 Hz, $CHCH_2$), 7.24 (1H, s, C=CHPh), 7.30–7.50 (5H, m, Ph); δ_C 9.20, 18.20, 20.45, 25.85, 30.60, 46.60, 49.10, 57.00, 127.40, 128.55 (2C), 128.60, 129.65 (2C), 135.55, 142.00, 208.10; *m/z* 240 (M^+, 100%), 225 (31), 212 (14), 198 (12), 197 (46), 184 (12), 171 (10), 169 (21), 158 (42), 157 (51), 156 (31), 155 (26), 149 (16), 141 (30), 134 (13), 130 (12), 129 (49), 128 (47), 127 (15), 115 (23), 95 (17), 91 (28), 77 (12), 55 (12).

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