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Transition-metal chloride mediated addition reaction of diorganomagnesium to easily enolizable ketones

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ABSTRACT

An alkylation to an easily enolizable ketone, such as β-tetralone, is difficult to perform with Grignard reagent (RMgX) or with diorganomagnesium (R_2Mg), because a deprotonation to form a magnesium enolate occurs predominantly. To avoid the prior enolization, a complex reagent of a transition-metal salt and R_2Mg was examined: A combination of R_2Mg with iron(II) chloride ($FeCl_2$) or ytterbium(III) chloride ($YbCl_3$) gave a complex reagent that can realize a nucleophilic reaction to β-tetralone prior to the enolization. A combination of RMgX with these metal salts is inferior to a combination of R_2Mg with them to obtain *the nucleophilic complex reagent*.

1. Introduction

Organomagnesium reagents have frequently been used for C–C bond forming reactions; examples include their nucleophilic addition to carbonyl compounds.[1] While they show high potential as carbon nucleophiles, they also work as bases to some carbonyl compounds, which are classified as easily enolizable ketones. In the reactions with these ketones, a deprotonation occurs preferentially to give magnesium enolates. To suppress this undesired side reaction, a complex reagent, which consists of Grignard reagent and a metal halide, has been developed.[2,3] For example, it was reported by Imamoto that the complex reagent, which was prepared from cerium(III) chloride ($CeCl_3$) and Grignard reagent (RMgX), was used as an efficient nucleophile for the addition to an easily enolizable ketone, such as β-tetralone (**1a**).[3] In this $CeCl_3$-mediated reaction, we had shown that diorganomagnesium (R_2Mg) was superior to RMgX from the viewpoint of efficiency in the preparation of the complex reagent.[4] Such efficiency, coming from use of R_2Mg instead of RMgX, would also enable another transition-metal salt to form the corresponding complex reagent, so treatment of some transition-metal salts with R_2Mg was examined to obtain the reagent that can perform the addition to β-tetralone prior to enolization. Among them, treatment of ytterbium(III) chloride ($YbCl_3$)[4] or iron(II) chloride ($FeCl_2$)[5] with R_2Mg gave the reagents, which were effective for the nucleophilic addition to β-tetralone (**1a**). The ketone **1a** is one of the most difficult substrates for organomagnesium and organolithium reagent to perform a nucleophilic addition owing to their high acidity. Therefore, the reagent, which can attack β-tetralone smoothly, would perform an efficient nucleophilic addition with versatile easily enolizable ketones. We wish to discuss about these complex reagents prepared from R_2Mg and transition-metal salts (Fig. 1).

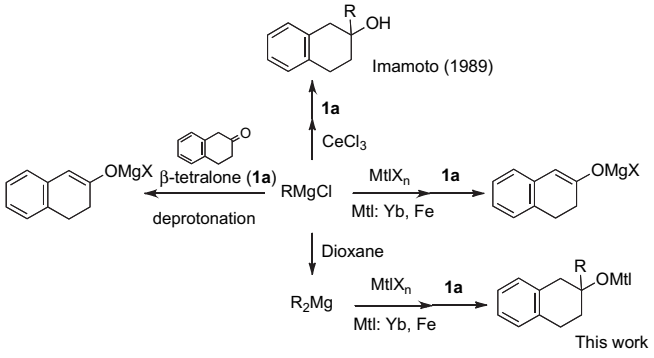

Fig. 1. Enolization and addition in reactions of β-tetralone (**1a**) with the reagent from organomagnesium and transition-metal salts.

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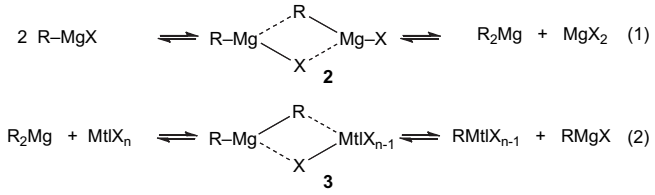
2. Results and discussion

It is well known that Grignard reagent from an organic halide and magnesium metal exists under Schlenk equilibrium between RMgX and R_2Mg in a solution (Eq. 1, Scheme 1).[6] Analogously, it can be surmised that another equilibrium would be induced by treatment of a metal halide with a R_2Mg as a hetero-Schlenk equilibrium (Eq. 2 Scheme 1). The following experiments were performed based on this assumption.



Scheme 1. Schlenk equilibrium of Grignard reagent and hetero-Schlenk equilibrium.

In general, depending on the metal salt, the preparation of a complex reagent with RMgX does not always work well. For example, while the treatment of $CeCl_3$ with RMgX was reported to give a nucleophilic reagent, that of $YbCl_3$ did not afford the reagent efficiently.[7,8] Considering the equations in Scheme 1, we supposed that the use of R_2Mg instead of RMgX should be advantageous to a formation of the initial complex **3**, which can lead to transmetalation. So, it should be possible to prepare the reagent more efficiently by treatment of a transition-metal salt with R_2Mg, rather than with RMgX.[9]

The complex reagents, which were obtained from treatment of $YbCl_3$ with RMgX or R_2Mg for various aging periods (T [min]) at −78 °C, were treated with β-tetralone. In Fig. 2, the yield of the adduct **5ab** in each reaction was plotted. The detailed procedure was as follows. The commercially available $YbCl_3 \cdot 6H_2O$ (3.0 mmol with **4a**; 2.0 mmol with **4b**) was dried in vacuo at 140 °C for 2 h. To the dried salt, 5 mL of anhydrous THF was added under Ar atmosphere, and the mixture was sonicated for 0.5 h using an ultrasonic cleaner. The obtained suspension was cooled at −78 °C, and *n*-butylmagnesium reagent (*n*-BuMgBr (**4a**): 1.2 M in ether, 2.0 mmol; *n*-Bu_2Mg (**4b**): 0.5 M in ether, 1.0 mmol) was added. After the mixture was stirred for the various aging periods (T [min]) at −78 °C, β-tetralone (**1a**, 1.0 mmol) in THF (1.0 mL) was added to the mixture. The mixture was stirred for 5 min at −78 °C, and quenched with 1 M aqueous HCl. As ketone **1a** is easily enolized by RMgX or R_2Mg, the formation of the complex reagent can be monitored by the yield of the adduct **5ab**. The period for the preparation of the complex reagent from $YbCl_3$–*n*-Bu_2Mg, which gave the best yield of **5ab**, was 5 min, while that of $YbCl_3$–*n*-BuMgBr was 20 min. From these observations, we could conclude that the formation of the complex reagent, which performed the nucleophilic addition preferentially, was accomplished more efficiently with the use of *n*-Bu_2Mg.

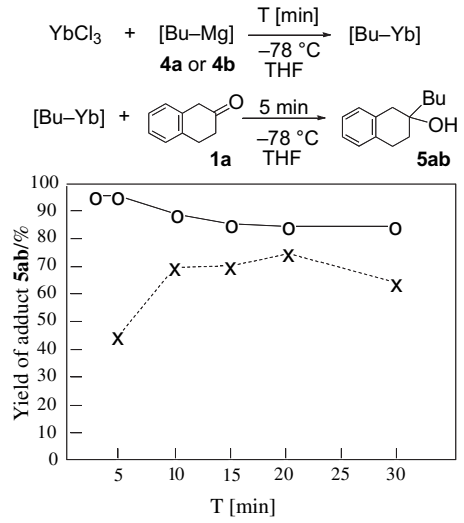
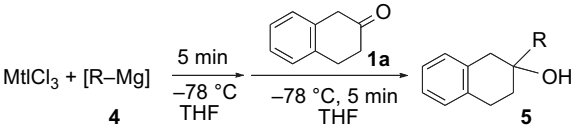


Fig. 2. The yields of the butylation reaction of β-tetralone (**1a**) with the complex reagent prepared from butylmagnesium and ytterbium(III) chloride (–o–: *n*-Bu_2Mg+$YbCl_3$; –x–: *n*-BuMgBr+$YbCl_3$) under various aging periods (T [min]).

The difference of the efficiency between RMgX and R_2Mg in the preparation of the Yb-complex reagents was also examined in various organomagnesium reagents (Table 1). The complex reagent was prepared by treatment of $YbCl_3$ with organomagnesium **4** in THF at −78 °C for 5 min and then reacted with β-tetralone (**1a**). As shown in Table 1, use of R_2Mg for a preparation of Yb-complex reagents gave better yields than that of RMgX in all cases. Especially in the case of Ph_2Mg, the efficiency was remarkable (entries 5 and 6), and treatment of $YbCl_3$ with vinylmagnesium showed slight difference between RMgX and R_2Mg (entries 7 and 8). It should be also noted that the efficiency of using R_2Mg was also observed in the combination with $CeCl_3$ (entries 9 and 10).

Table 1
The addition of organomagnesium–$YbCl_3$ or $CeCl_3$ to β-tetralone (**1a**)[a]



Entry	$MtlCl_3$	[R–Mg][b]	**5** (%)
1	—	*n*-BuMgBr **4a**	9 (**5ab**)
2	—	*n*-Bu_2Mg**4b**	7 (**5ab**)
3	$YbCl_3$	*n*-BuMgBr **4a**	44 (**5ab**)
4	$YbCl_3$	*n*-Bu_2Mg **4b**	98 (**5ab**)
5	$YbCl_3$	PhMgBr **4c**[c]	9 (**5cd**)
6	$YbCl_3$	Ph_2Mg **4d**[d]	74 (**5cd**)
7	$YbCl_3$	CH_2=CHMgBr **4e**	89 (**5ef**)
8	$YbCl_3$	$(CH_2CH)_2Mg$ **4f**	94 (**5ef**)
9	$CeCl_3$	*n*-BuMgBr **4a**	66 (**5ab**)
10	$CeCl_3$	*n*-Bu_2Mg **4b**	81 (**5ab**)

[a] $YbCl_3$ (3.0 mmol), RMgBr (2.0 mmol), β-tetralone (1.0 mmol), and THF (6 mL) were used; $YbCl_3$ (2.0 mmol), R_2Mg (1.0 mmol), β-tetralone (1.0 mmol), and THF (6 mL) were used.

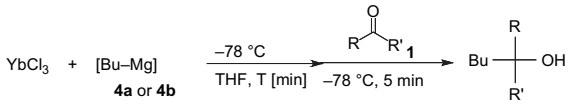
[b] RMgX was prepared in ether except vinylmagnesium bromide (**4e**). The reagent **4e** was prepared in THF. R_2Mg was prepared by addition of 1,4-dioxane to an ethereal solution of RMgX.[6,10]

[c] When the complex reagent was prepared from PhMgBr and $YbCl_3$ for 15 min at −78 °C, the yield of **5cd** was 28%.

[d] When the complex reagent was prepared from Ph_2Mg and $YbCl_3$ for 15 min at −78 °C, the yield of **5cd** was 98%.

We did the following experiments in order to get any information about the reagent as shown in Table 2. The complex reagent was treated with an excess amount of a ketone. Treatment of β-tetralone (**1a**, 3.0 mmol) with the complex reagent, prepared from $YbCl_3$ (2.0 mmol)–*n*-Bu_2Mg (1.0 mmol), afforded 0.98 mmol of the adduct **5** (entry 1). In other words, only one butyl group of *n*-Bu_2Mg could react as a nucleophile in the reaction of the complex reagent. As shown in entry 2, treatment of 2-heptanone (**1b**, 3.0 mmol) with the same reagent gave 1.66 mmol of the corresponding adduct. The result showed that both butyl groups in *n*-Bu_2Mg could act as nucleophile in the reaction with 2-heptanone (**1b**). In entries 3 and 4, the results using $YbCl_3$ (4.0 mmol)–*n*-BuMgBr (2.0 mmol) are shown. Less than half (45%) of Grignard reagent could work as nucleophile to β-tetralone (**1a**), while 79% of the initially added Grignard reagent reacted with 2-heptanone (**1b**).

Table 2
Treatment of the reagent with excess amount of a ketone[a]



Entry	**4a** or **4b**/[mmol]	$YbCl_3$ [mmol]	*T* [min]	**1**/[mmol]	Adduct [mmol]
1	*n*-Bu_2Mg/1.0	2.0	5	β-Tetralone/3.0	0.98
2	*n*-Bu_2Mg/1.0	2.0	5	2-Heptanone/3.0	1.66
3	*n*-BuMgBr/2.0	4.0	20	β-Tetralone/3.0	0.89
4	*n*-BuMgBr/2.0	4.0	20	2-Heptanone/3.0	1.58

[a] $YbCl_3$ (4.0 mmol), *n*-BuMgBr (2.0 mmol), ketone (3.0 mmol), and THF (10 mL) were used; $YbCl_3$ (2.0 mmol), *n*-Bu_2Mg (1.0 mmol), ketone (3.0 mmol), and THF (6 mL) were used.

The results in Table 2 can be explained as follows. As shown in Fig. 3, *n*-Bu_2Mg and $YbCl_3$ form a complex **3a**. A reaction of **3a** with β-tetralone will afford not only the adduct but also *n*-BuMgCl; the latter works as a base for the highly enolizable β-tetralone (**1a**) to form an enolate. On the other hand, the complex reagent **3a** also reacts with 2-heptanone (**1b**) to afford the corresponding adduct and *n*-BuMgCl; the latter can undergo a butylation to 2-heptanone (**1b**). These results implied that the nucleophilic reagent may be the complex **3a**. We cannot omit the formation of *n*-$BuYbCl_2$ from **3a**. In this case, however, it accompanies the equimolar amount *n*-BuMgCl, which interrupts the butylation of β-tetralone. The use of *n*-BuMgBr showed the same tendency as that of *n*-Bu_2Mg (entries 3 and 4 in Table 2). Considering the Schlenk equilibrium of Grignard reagent (Eq. 1, Scheme 1), it is plausible that the complexation of *n*-BuMgBr with $YbCl_3$ would also proceed via *n*-Bu_2Mg.

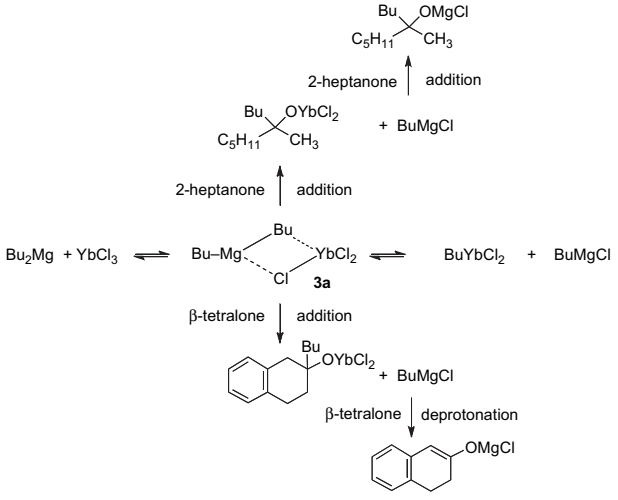
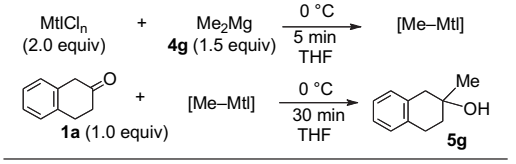


Fig. 3. Plausible pathway of the addition reaction of the complex reagent **3a** with ketones.

To explore a nucleophilic complex reagent made from Me_2Mg (**4g**) and some other metal salts, we examined the fourth periodical transition-metal salts in the same addition reaction. As shown in Scheme 2, $FeCl_2$–Me_2Mg gave the best result among them.[11] A combination with β-titanium(III) chloride (β-$TiCl_3$)[12,13] showed a compatible result. Except for these two metal salts, the others did not show any improvement of the yield of the adduct **5g**, compared with the yield of the reaction using Me_2Mg solely.[14]

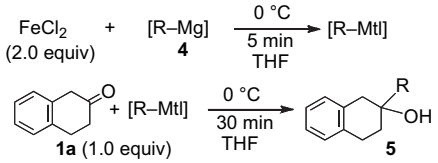
The detailed studies for the formation of $FeCl_2$–methylmagnesium reagent are summarized in Table 3. Reaction of **1a** with MeMgI (**4h**) or Me_2Mg (**4g**) did not afford the adduct **5g** in a reasonable yield,



$CaCl_2$	$TiCl_3$	VCl_3	$CrCl_3$	$MnCl_2$	$FeCl_2$
33%	68%	34%	4%	10%	70%
$CoCl_2$	$NiCl_2$	CuCl	$ZnCl_2$	$GaCl_3$	–
nd	nd	6%	nd	nd	34%

Scheme 2. The yields of **5g** in the reaction of **1a** and the reagents prepared from Me_2Mg and the fourth periodical transition-metal salts (nd: not detected).

Table 3
Reaction of organoiron species with β-tetralone (**1a**)[a]



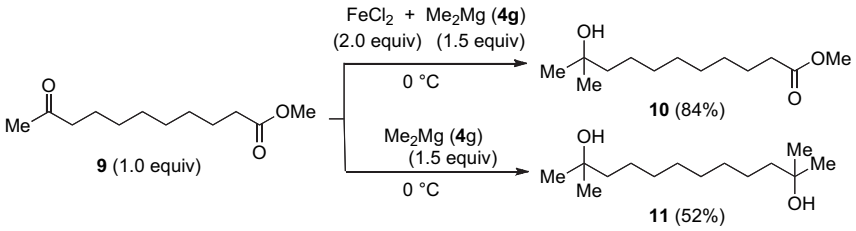
Entry	[Me−Mg]/equiv	$FeCl_2$/equiv	**5** (%)	**1a** (%)
1	MeMgI (**4h**)/1.5	—	24	70
2	Me_2Mg (**4g**)/1.5	—	34	65
3	MeMgI (**4h**)/1.5	2.0	12	84
4	MeMgI (**4h**)/3.0	2.0	41	54
5	Me_2Mg (**4g**)/1.5[b,c]	2.0	70	30
6	*n*-Bu_2Mg (**4b**)/1.5	2.0	<5[d]	20
7	Ph_2Mg (**4d**)/1.5	2.0	46	51

[a] Anhydrous $FeCl_2$ (2.0 mmol), organomagnesium (1.5, or 3.0 mmol), and β-tetralone (**1a**, 1.0 mmol) were used. The preparation of the reagent was performed at 0 °C for 5 min. The yield of the product was determined by ^1H NMR after aqueous work-up using bromoform as an internal standard.
[b] The preparation of the reagent was examined at −20 °C for 5 min. The adduct **5g** was obtained in 57% yield with 43% recovery.
[c] The preparation of the reagent was examined at 0 °C for 10 min. The adduct **5g** was obtained in 56% yield with 37% recovery.
[d] Reduced product (R=H) was obtained in 62% yield.

as an enolization occurred predominantly to give a recovery of the substrate (entries 1, 2). Treatment of **1a** with the mixture of $FeCl_2$ and MeMgI did not improve the yield of **5g** (entries 3 and 4). On the contrary, a reagent from $FeCl_2$ and Me_2Mg gave the adduct **5g** in 70% yield (entry 5). From these observations, we can conclude that the formation of iron−organomagnesium complex reagent proceeds more efficiently with Me_2Mg. Analogously, *n*-Bu_2Mg (**4b**) was used instead of Me_2Mg (**4g**). The main product was an adduct of hydride. The use of Ph_2Mg gave the corresponding adduct in 46% yield.

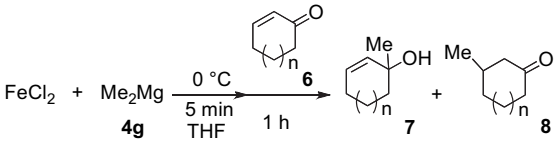
$FeCl_2$–Me_2Mg was also examined in the reaction of cycloalkenone (**6**).[15] While a reaction of cyclohexenone (**6a**) with Me_2Mg gave the corresponding 1,2-adduct **7a** predominantly, it was shown that treatment of **6a** with $FeCl_2$–Me_2Mg reagent gave the 1,4-adduct **8a** selectively (entries 2 and 3). The reaction with cycloheptenone **6b** also gave 1,4-adduct **8b** (entry 4). The different reactivities clearly show the formation of the complex reagent.

The nucleophilicity of $FeCl_2$–Me_2Mg reagent was examined by a reaction with ketoester **9**. A reaction of **9** with $FeCl_2$–Me_2Mg gave the corresponding hydroxy ester **10**, while that with Me_2Mg gave the diol **11**. These results mean that the reactivity of $FeCl_2$–Me_2Mg is weaker than that of Me_2Mg (Scheme 3).[16] The efficient addition of iron reagent to the highly enolizable ketone **1a** in Table 3 was owing to the suppressed basicity (Table 4).



Scheme 3. Reaction of $FeCl_2$–Me_2Mg and Me_2Mg with ketoester **9**.

Table 4
Reaction of cycloalkenone (**6**) with $FeCl_2$–Me_2Mg (**4d**)[a]



Entry	$FeCl_2$ (equiv)	Enone (1.0 equiv)	**4g** (equiv)	**7** (%)	**8** (%)
1	—	**6a** (n=1)	1.5	68 (**7a**)	13 (**8a**)
2	2.0	**6a** (n=1)	1.5	nd (**7a**)	77 (**8a**)
3	1.2	**6a** (n=1)	1.2	nd (**7a**)	80 (**8a**)
4	1.2	**6b** (n=2)	1.2	nd (**7b**)	62 (**8b**)

[a] Anhydrous $FeCl_2$ (2.0 mmol), organomagnesium (1.5, or 3.0 mmol), and cycloalkenone (**6**, 1.0 mmol) were used. The preparation of the reagent was performed at 0 °C for 5 min. The yield of the product was determined by ^{1}H NMR after aqueous work-up using bromoform as an internal standard.

3. Conclusion

The 1,2-addition of Grignard reagent to a highly enolizable ketone prior to enolization is difficult process and has been performed by its mixture with stoichiometric amount of transition-metal salt. In this method, a transformation of Grignard reagent into the corresponding complex reagent should be accomplished efficiently, otherwise remaining Grignard reagent would induce enolization. To facilitate the formation of the complex reagent, we proposed a use of R_2Mg instead of RMgX. We thought that a complexation between Grignard reagent and transition-metal salt proceeds via R_2Mg, which is formed from RMgX through Schlenk equilibrium. Actually, combination of R_2Mg and $YbCl_3$ gave the corresponding complex reagent efficiently, which performed 1,2-addition to a highly enolizable ketone, β-tetralone. It was also shown that treatment of Me_2Mg with $FeCl_2$ gave the reagent, which also added 1,2-manner to β-tetralone. The reagent could not be prepared efficiently from MeMgI and $FeCl_2$.

Thus, the efficient complexation between diorganomagnesium and transition-metal salt will easily give us useful complex organometallic reagents which had difficulty for preparation from organomagnesium halide.

4. Experimental section

4.1. General

Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 (^{1}H, 500 MHz; ^{13}C, 125.7 MHz) spectrometer using tetramethylsilane for ^{1}H NMR as an internal standard (δ=0 ppm), $CDCl_3$ for ^{13}C NMR as an internal standard (δ=77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, quint=quintet, sext=sextet, sept=septet, br=broad, m=multiplet), coupling constants (Hz), and integration. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–100 μm).

Unless otherwise noted, commercially available reagents were used without purification. Tetrahydrofuran, Dehydrated stabilizer free —Super— was purchased from Kanto Chemical Co., stored under argon, and used as it is.

4.2. Reaction of $FeCl_2$–Me_2Mg reagent with ketones

The commercially available anhydrous $FeCl_2$ (2.0 mmol) was charged with 4.0 mL of anhydrous THF, and the mixture was sonicated for 0.5 h using an ultrasonic cleaner. The obtained suspension was cooled at 0 °C, and Me_2Mg (1.0 mmol) was added. After the mixture was stirred for 5 min at 0 °C, ketone (1.0 mmol) in THF (2.0 mL) was added to the mixture. The mixture was stirred at 0 °C, and quenched with 1 M aqueous HCl.

*4.2.1. 2-Butyl-1,2,3,4-tetrahydronaphthalen-2-ol (**5ab**):[17] CAS RN [91671–46–4].* Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15–7.09 (m, 3H), 7.09–7.04 (m, 1H), 3.00 (ddd, J=16.5, 9.5, 6.5 Hz, 1H), 2.87 (d, J=16.5 Hz, 1H), 2.83–2.77 (m, 1H), 2.78 (d, J=16.5 Hz, 1H), 1.90–1.83 (m, 1H), 1.79 (ddd, J=13.0, 9.5, 6.0 Hz, 1H), 1.64–1.53 (m, 2H), 1.50–1.41 (m, 2H, 1H), 1.40–1.31 (m, 2H), 0.94 (t, J=7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 135.6, 134.6, 129.7, 128.7, 125.9, 125.8, 70.9, 42.0, 41.2, 33.7, 26.1,25.3,23.3,14.1. The product was identified with the authentic sample.

*4.2.2. 2-Phenyl-1,2,3,4-tetrahydronaphthalen-2-ol (**5cd**):[18] CAS RN [78318–01–1].* Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.52 (m, 2H), 7.40–7.35 (m, 2H), 7.32–7.27 (m, 1H), 7.19–7.15 (m, 3H), 7.15–7.10 (m, 1H), 3.35 (d, J=17.0 Hz, 1H), 3.12 (ddd, J=16.5, 10.0, 6.0 Hz, 1H), 3.04 (dd, J=16.5, 1.5 Hz, 1H), 2.80 (dt, J=17.0, 5.0 Hz, 1H), 2.28 (ddd, J=13.0, 10.5, 6.0 Hz, 1H), 2.15–2.08 (m, 1H), 1.92 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 147.6, 135.3, 134.4, 129.4, 128.8, 128.3, 127.1, 126.1, 126.0, 124.8, 72.5, 43.7, 35.4, 26.3. The product was identified with the authentic sample.

*4.2.3. 2-Vinyl-1,2,3,4-tetrahydronaphthalen-2-ol (**5ef**):[19] CAS RN [102936–18–5].* Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15–7.10 (m, 3H), 7.10–7.05 (m, 1H), 6.07 (dd, J=17.5, 10.5 Hz, 1H), 5.33 (dd, J=17.5, 1.0 Hz, 1H), 5.12 (dd, J=10.5, 1.0 Hz, 1H), 3.04–3.00 (m, 1H), 3.01 (d, J=17.0 Hz, 1H), 2.87–2.79 (m, 1H), 2.84 (d, J=17.0 Hz, 1H), 1.97–1.84 (m, 2H), 1.58 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 144.1, 135.2, 134.0, 129.4, 128.7, 126.0, 125.9, 112.6, 71.2, 41.8, 34.1, 26.1. The product was identified with the authentic sample.

*4.2.4. 2-Methyl-1,2,3,4-tetrahydronaphthalen-2-ol (**5g**):[13] CAS RN [33223–85–7].* Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14–7.09 (m, 3H), 7.08–7.04 (m, 1H), 3.01 (ddd, J=16.5, 9.0, 6.5 Hz, 1H), 2.88 (d, J=17.0 Hz, 1H), 2.87–2.79 (m, 1H), 2.82 (d, J=17.0 Hz, 1H), 1.93–1.86 (m, 1H), 1.84–1.76 (m, 1H), 1.36 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 135.3, 134.8, 123.0, 128.9, 126.2, 126.1, 69.4, 43.8, 36.0, 28.9, 26.6. The product was identified with the authentic sample.

4.2.5. Methyl 10-oxoundecanoate (9):[20] CAS RN [18993–09–4]. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.65 (s, 3H), 2.40 (t, J=8.0 Hz,

2H), 2.28 (t, J=7.5 Hz, 2H), 2.12 (s, 3H), 1.64–1.50 (m, 4H), 1.33–1.20 (m, 8H). ^{13}C NMR ($CDCl_3$) δ 209.3, 174.2, 51.4, 43.7, 34.0, 29.8, 29.1, 29.0, 29.0, 24.9, 23.8. The product was identified with the authentic sample.

*4.2.6. Methyl 10-hydroxy-10-methylundecanoate (**10**):[21] CAS RN [341534–66–5].* Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.30 (t, J=7.5 Hz, 2H), 1.68–1.56 (m, 2H), 1.48–1.42 (m, 2H), 1.35–1.25 (m, 10H), 1.20 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 174.3, 71.0, 51.4, 43.9, 34.1, 30.1, 29.4, 29.2, 29.2, 29.1, 24.9, 24.3. The product was identified with the authentic sample.

*4.2.7. 2,11-Dimethyldodecane-2,11-diol (**11**):[22] CAS RN [22092–59–7].* Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48–1.43 (m, 4H), 1.37–1.23 (m, 12H), 1.21 (s, 12H). ^{13}C NMR ($CDCl_3$) δ 71.0, 43.9, 30.1, 29.5, 29.2, 24.3. The product was identified with the authentic sample.

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