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Silver-Catalyzed Benzylation and Allylation of Tertiary Alkyl Bromides with Organozinc Reagents

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Abstract: Silver salts catalyze the benzylation and allylation of tertiary alkyl bromides with organozinc reagents. The reactions create quaternary carbon centers efficiently. Treatment of *gem*-dibromoalkanes with benzylic or allylic zinc reagents under silver catalysis leads to dibenzylation or diallylation. The functional-group compatibility of the present reactions is wider than that of the previous reactions with Grignard reagents.

Keywords: alkyl halides · allylation · benzylation · organozinc reagents · silver

Introduction

Creating quaternary carbon centers[1] poses a significant challenge in organic synthesis,[2] and new synthetic approaches have to be developed. The most popular ionic process that generates quaternary carbon atoms has been the reactions of tertiary alkyl metals with carbon electrophiles. On the other hand, examples of the polarity-inversed process, nucleophilic substitution reactions at tertiary carbon atoms bearing a suitable leaving group with organometallic reagents, are relatively rare because β-elimination usually competes.

Classical nucleophilic substitution reactions of tertiary alkyl halides with organometallic reagents utilizes stoichiometric amounts of Lewis acidic organometallic reagents, such as organoaluminums and organotitaniums.[3] Recently, a Group 13 metal was proven to catalyze the reaction of tertiary alkyl halides with organosilicon reagents.[3c,4] Another approach to quaternary carbon atoms from tertiary alkyl halides and organometallic reagents employs a single-electron transfer process to generate the corresponding tertiary alkyl radical and halide anion.[5,6] The radicals are trapped by organometallic species directly[5] or after undergoing radical addition to alkenes.[6]

We have been interested in the catalytic activities of silver[7,8] and copper[9,10] salts in the reactions of tertiary alkyl halides with Grignard reagents. Notably, silver salts have been proven to catalyze the benzylation and allylation of tertiary alkyl halides with benzylic and allylic Grignard reagents.[7a,c] The reactions offer a highly efficient access to quaternary carbon centers. However, the use of Grignard reagents leads to poor functional-group compatibility. Here we report that benzylic and allylic zinc reagents are also effective for the silver-catalyzed reaction with better functional-group compatibility.

Results and Discussion

Benzylation of tertiary alkyl bromides: The reaction of *tert*-butyl bromide with benzylzinc chloride·lithium chloride complex[11] was performed, and the effects of solvents and silver salts were surveyed (Table 1). In the absence of a silver salt, the reaction in acetonitrile did not proceed (Table 1, entry 1). Silver halides promoted the benzylation sluggishly (entries 2 and 3). Highly cationic silver salts were effective to yield neopentylbenzene in good yields (entries 4–7). Among them, silver trifluoromethanesulfonate showed the highest catalytic activity. Although the choice of solvent was not critical, acetonitrile proved to be the best (entries 7–11).

The use of the zinc reagent complexed with lithium chloride was essential (Table 2). The reaction of 2-methyl-2-bromodecane (**1a**) with benzylzinc bromide, conventionally pre-

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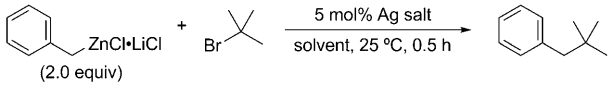
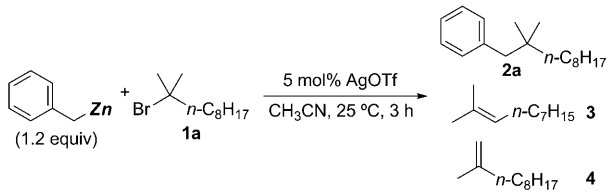
Table 1. Benzylation.



Entry	Ag salt	Solvent	Yield [%]
1	none	CH_3CN	0
2	AgBr	CH_3CN	11
3	AgCl	CH_3CN	24
4	AgOAc	CH_3CN	44
5	$AgNO_3$	CH_3CN	59
6	$AgBF_4$	CH_3CN	58
7	AgOTf	CH_3CN	64
8	AgOTf	CH_3CH_2CN	50
9	AgOTf	THF	37
10	AgOTf	1,4-dioxane	33
11	AgOTf	DMF	47

Table 2. Choice of benzylzinc reagent.

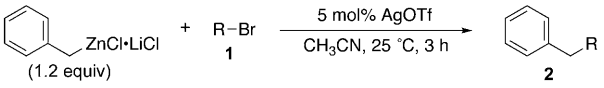


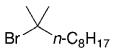
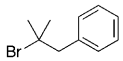
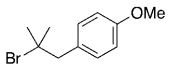
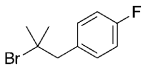
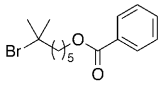
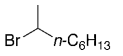
Entry	Benzylzinc	Yield **2a** [%]	Yield **3** [%]	Yield **4** [%]
1	ZnBr	0	63	26
2	ZnBr + LiCl	25	17	9
3	ZnBr • LiCl	48	12	8
4	ZnCl • LiCl	81	0	0

pared from benzyl bromide and zinc powder in the absence of lithium chloride, failed to afford the corresponding product **2a** (Table 2, entry 1). Dehydrobromination took place to yield 2-methyl-2-decene (**3**) and 2-methyl-1-decene (**4**). We confirmed that the dehydrobromination also occurred in the absence of AgOTf. These results indicate that the conventional benzylzinc bromide is too basic to coexist with **1a**. Interestingly, an addition of lithium chloride to a solution of benzylzinc bromide prior to the benzylation changed the reactivity of the benzylzinc reagent and **2a** was obtained in 25% yield (entry 2). When benzylzinc bromide·lithium chloride complex was prepared from benzyl bromide, zinc powder, and lithium chloride according to Knochel's procedure,[11] the yield of **2a** was improved up to 48% (entry 3). Benzylzinc chloride·lithium chloride complex showed the highest reactivity affording **2a** in 81% yield without forming **3** and **4** (entry 4). It is worth noting that the benzylzinc chloride·lithium chloride complex is less basic than the conventional benzylzinc bromide and did not react with **1a** in the absence of AgOTf.

The scope of the alkyl halides is summarized in Table 3. Cyclic tertiary alkyl bromide **1b** underwent benzylation efficiently (Table 3, entry 2). Functional groups, such as methoxy, fluoro, and benzoyloxy groups were compatible under the reaction conditions (entries 4–6). Unfortunately, 1-bromoadamantane (**1g**) failed to undergo the benzylation (entry 7). Secondary alkyl bromide was less reactive, and the reaction of 2-bromooctane (**1h**) with 2.0 equivalents of the benzylzinc reagent required 24 h to complete (entry 8). Tertiary alkyl chlorides were completely unreactive. Tertiary alkyl iodides were smoothly converted to the corresponding alkenes by dehydroiodination.

Table 3. Scope of alkyl halides in the benzylation reaction.



Entry	R–X	**1**	**2**	Yield [%]
1		**1a**	**2a**	81
2		**1b**	**2b**	78
3		**1c**	**2c**	79
4		**1d**	**2d**	68
5		**1e**	**2e**	90
6[a]		**1f**	**2f**	82
7[b]		**1g**	**2g**	3
8[c]		**1h**	**2h**	57

[a] AgOAc was used instead of AgOTf. [b] Performed for 1.5 h. [c] Performed with 2.0 equiv of the benzylzinc reagent for 24 h.

Other benzylic zinc reagents were applicable to the reaction (Table 4). Sterically demanding benzylic zinc reagents showed moderate reactivities, requiring a longer reaction time (Table 4, entries 2 and 3). Vinyl, methoxy, and bromo

Abstract in Japanese:

銀塩が有機亜鉛反応剤を用いる第三級臭化アルキルのベンジル化ならびにアリル化反応を触媒することを見いだした。本反応により第四級炭素を効率よく構築することができる。銀触媒存在下 *gem*-ジブロモアルカンに対してベンジルもしくはアリル亜鉛反応剤を作用させると、ジベンジル化やジアリル化が起こる。以前に我々が報告したグリニャール反応剤を利用する同様の反応と比較して、本反応の官能基許容性は広い。

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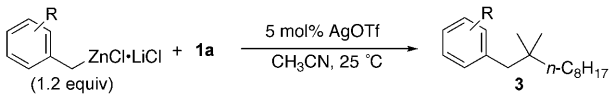
Table 4. Benzylic zinc reagents.



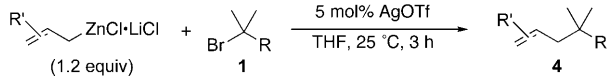
Entry	R	*t* [h]	**3**	Yield [%]
1	4-Me	3	**3a**	81
2	2-Me	6	**3b**	57
3	(1-naphthyl)	6	**3c**	60
4	4-vinyl	3	**3d**	61
5	3-MeO	3	**3e**	68
6	3-Br	6	**3f**	64
7	4-F	6	**3g**	23[a]
8	3-COOEt	3	**3h**	4
9	3-CN	3	**3i**	5

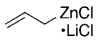
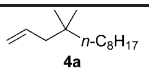
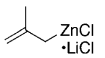
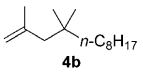
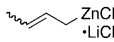
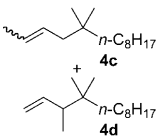
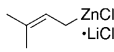
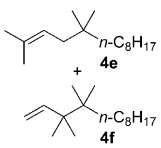
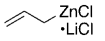
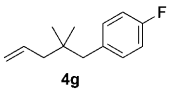
[a] Performed with 2.0 equiv of the benzylic zinc reagent.

groups were compatible under the reaction conditions (entries 4–6). However, benzylic zinc reagents bearing an electron-withdrawing group were much less reactive (entries 7–9).

Allylation of tertiary alkyl bromides: We next exploited the silver-catalyzed allylation reaction with allylic zinc reagents. However, an attempted silver-catalyzed allylation in acetonitrile failed to afford the corresponding allylated product. After some investigation, we found that the desired allylation reaction proceeded smoothly in THF (Table 5, entry 1). The conditions are applicable to methallylation, crotylation, and prenylation (entries 2–4). Unfortunately, the crotylation and prenylation afforded mixtures of regioisomers in moderate yields. Because of the high reactivity of allylic zinc reagents, functional-group compatibility is narrow. For instance, an ester group reacted smoothly with allylzinc chloride·lithium chloride complex.

Table 5. Tertiary alkyl bromides with allylic zinc reagents.

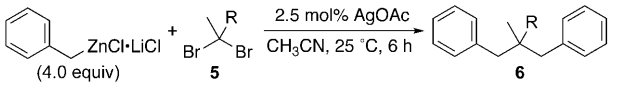


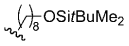
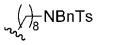
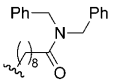
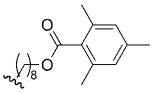
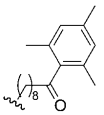
Entry	**1**	Allylic zinc reagent	**4**	Yield [%]
1	**1a**		 **4a**	96
2	**1a**		 **4b**	90
3	**1a**		 **4c** + **4d**	66 **4c**/**4d** 63:37
4	**1a**		 **4e** + **4f**	42 **4e**/**4f** 71:29
5	**1e**		 **4g**	86

Dibenzylation and diallylation of *gem*-dibromoalkanes: Geminal dihaloalkanes are readily available, easy to handle, and reactive under proper reaction conditions, and hence represent a useful class of compounds in organic synthesis.[12] According to our previous report,[7c] we expected that *gem*-dibromoalkanes would undergo successive silver-catalyzed dibenzylation or diallylation with organozinc reagents to create quaternary carbon centers. The reactions indeed occurred with 2.5 mol% of silver acetate and 4.0 equivalents of organozinc reagents.

The dibenzylation proceeded in acetonitrile with moderate efficiency (Table 6). Major byproducts could not be fully identified. However, the byproducts seemed to result from a failure in the second benzylation reaction according to

Table 6. Dibenzylation of *gem*-dibromoalkanes with a benzylzinc reagent.

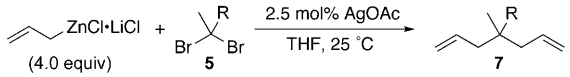


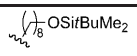
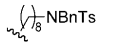
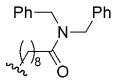
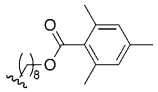
Entry	R	**5**	**6**	Yield [%]
1		**5a**	**6a**	46
2		**5b**	**6b**	51
3		**5c**	**6c**	36
4		**5d**	**6d**	50
5		**5e**	**6e**	46
6		**5f**	**6f**	47

NMR spectroscopic and mass spectrometric analyses of the crude reaction mixture.[13] Functional-group compatibility is as high as expected: siloxy, ester, amide, bulky ketone, and cyano moieties survived under the reaction conditions. The scope of the dibenzylation with the zinc reagent is wider than that of the dibenzylation with benzylmagnesium, although the yields are lower.[7c]

The diallylation in THF afforded the corresponding 1,6-heptadienes in higher yields (Table 7) than the dibenzylation. The allylzinc reagent may be more reactive than the benzylzinc reagent, thus undergoing the second allylation more efficiently. On the other hand, the carbonyl group of **5e** and the cyano group of **5f** reacted with the allylzinc reagent, which shows the lower functional-group compatibility. The products will be able to undergo ring-closing metathe-

Table 7. Diallylation of *gem*-dibromoalkanes with an allylzinc reagent.



Entry	R	5	*t* [h]	7	Yield [%]
1		**5a**	5	**7a**	58
2		**5b**	6	**7b**	66
3		**5c**	4	**7c**	62
4		**5d**	4	**7d**	69
5[a]		**5g**	3	**7e**	72
6[a]		**5h**	3	**7f**	66

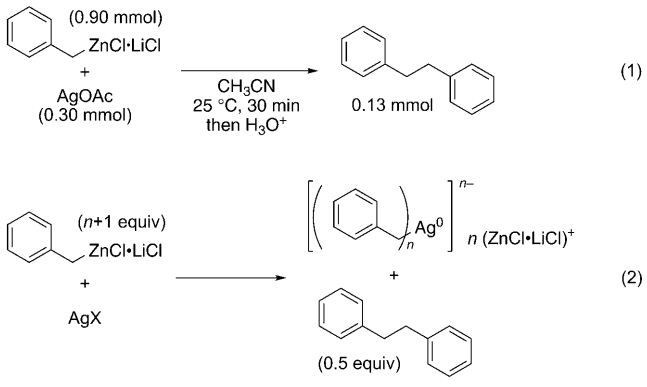
[a] AgOTf was used.

sis[14] to form cyclopentene derivatives and hence serve as useful intermediates in organic synthesis.

Possible reaction mechanisms: In general, a nucleophilic substitution reaction of tertiary alkyl halide proceeds through an S_N1 process. In the present reactions, a cooperative Lewis acid catalysis of silver and zinc can promote the formation of the corresponding tertiary carbocation, which reacts with a benzylic or allylic metal. Similar mechanisms are proposed in the literature.[4]

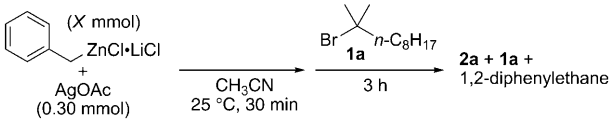
Alternatively, we can consider that the zinc reagents would initially reduce the silver salt to an electron-rich silver species, which can play an important role in the reaction. Treatment of AgOAc (0.30 mmol) with benzylzinc chloride·lithium chloride complex (0.90 mmol) in acetonitrile at 25 °C for 30 min afforded 1,2-diphenylethane (0.13 mmol) [Eq. (1)]. The formation of diphenylethane, the amount of which is roughly equal to a half of AgOAc used, indicates that Ag^I would be reduced to Ag^0. In addition, a silver mirror did not appear inside the reaction flask. We are thus tempted to propose the formation of a benzylic silver(0)–ate complex[15] [Eq. (2)].

Although the number of the benzyl groups on the silver atom of the benzylic silver is not clear, the following experiments revealed that monobenzylsilver is reactive enough to



effect benzylation (Table 8). A reaction mixture prepared from equimolar amounts of AgOAc and benzylzinc chloride·lithium chloride failed to promote the benzylation reaction of **1a** and afforded considerable amounts of dehydrobromination products **3** and **4** (Table 8, entry 1). In contrast, a 1:2 mixture of AgOAc and the benzylzinc reagent was highly reactive to yield **2a** in an 84% yield (entry 2). Three or four equivalents of the benzylzinc reagent did not improve the efficiency significantly (entries 3 and 4).

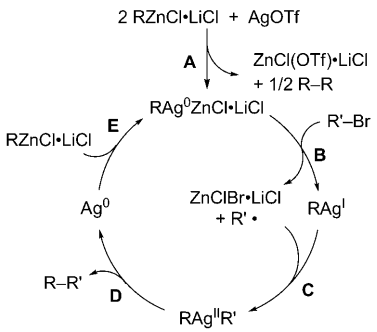
Table 8. Reaction of **1a** with benzylsilver reagents.



Entry	*X* [mmol]	**2a** [%]	**1a** [%]	Diphenylethane [mmol]
1	0.30	6	40	0.13
2	0.60	84	0	0.14
3	0.90	93	0	0.15
4	1.20	96	0	0.15

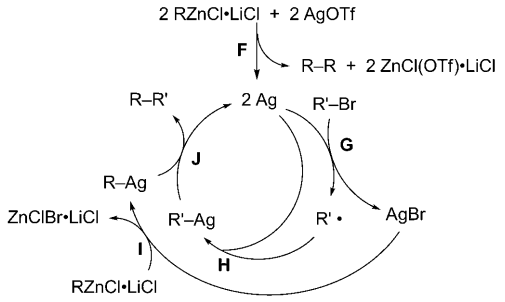
We propose a draft mechanism as shown in Scheme 1, for which an electron-rich silver–ate complex promotes single-electron transfer to the tertiary alkyl halide as cobalt- and manganese–ate complexes do.[16] Formation of the silver(0)–ate complex initially takes place (Scheme 1, step A). The ate complex effects single-electron transfer to the tertiary alkyl halide to form the corresponding tertiary alkyl radical (step B). The radical is trapped by benzyl- or allylsilver(I) to yield the oxidative adduct (step C). Reductive elimination gives the coupling product (step D), and the initial silver–ate complex is regenerated by the action of the remaining organozinc reagent (step E).

The mechanistic study on silver-catalyzed reactions by Tamura and Kochi is also worth noting (Scheme 2).[8a,17] According to their study, organozinc initially reduces monovalent silver to zerovalent silver (Scheme 2, step F). Single-electron transfer from the naked silver to tertiary alkyl bromide takes place to form the corresponding alkyl radical R′ and silver bromide (step G). The radical is trapped by another zerovalent silver to form alkylsilver R′Ag (step H). The silver bromide reacts with organozinc RZnCl·LiCl to yield benzyl- or allylsilver RAg (step I). Reductive coupling



Scheme 1. On the basis of our study. (R = benzyl or allyl, R′ = tertiary alkyl).

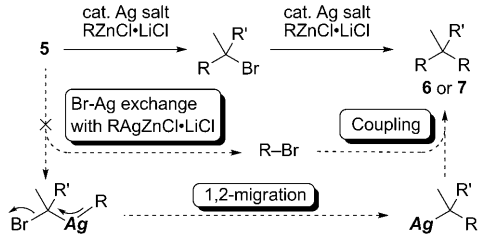
CHEMISTRY
AN ASIAN JOURNAL



Scheme 2. On the basis of the study by Tamura and Kochi. (R = benzyl or allyl, R′ = tertiary alkyl).

of the benzyl- or allylsilver with the alkyl silver affords the product R,R′ and regenerates zerovalent silver (step J), although the exact mechanism of the reductive coupling is not clear.

The mechanism of the reaction of *gem*-dibromoalkane is also unclear. However, we confirmed that the dibenzylation consists of a couple of nucleophilic benzylation steps (Scheme 3) as we observed the corresponding monobenzylated tertiary alkyl bromides as intermediates. The reaction course is totally different from that of the typical reactions of *gem*-dihaloalkanes with organometallic reagents, which includes sequential halogen metal exchange, 1,2-migration of a ligand on the metal, and trapping with various electrophiles.[18,19]



Scheme 3. The reaction of *gem*-dibromoalkane. (R = benzyl or allyl).

Conclusions

Silver catalysis allows the coupling reaction of tertiary alkyl bromides with benzylic and allylic zinc reagents. Dibenzylation and diallylation proceed in the reaction of *gem*-dibromoalkanes. Although the exact mechanism is not clear at this stage, the method is useful for constructing quaternary carbon centers with moderate functional-group compatibility.

Experimental Section

General: ^{1}H (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck Silica gel 60F_{254}. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. AgOTf and AgOAc were purchased from Aldrich and were handled under argon. Benzylic and allylic zinc reagents were prepared according to the literature.[11] Acetonitrile was dried over molecular sieves 3 Å. THF was purchased from Kanto Chemical, stored under nitrogen, and used as it is. All reactions were carried out under an argon atmosphere. Tertiary alkyl bromides were prepared by bromination of the corresponding tertiary alcohols with phosphorus tribromide in ether at −20 °C. *gem*-Dibromoalkanes were prepared from ketones via the hydrazones.[20]

Typical procedure for the benzylation or allylation of tertiary alkyl bromide: The reaction of 2-bromo-2-methyldecane (**1a**) is representative (Table 3, entry 1). AgOTf (13 mg, 0.050 mmol) was placed in a 20 mL reaction flask under argon and then acetonitrile (2.0 mL) and benzylzinc chloride·lithium chloride complex (0.79 M in THF, 1.52 mL, 1.2 mmol) were sequentially added. The resulting mixture was stirred for 5 min and then alkyl bromide **1a** (0.24 g, 1.0 mmol) was added. The whole mixture was stirred for 3 h at 25 °C. The reaction was quenched with saturated ammonium chloride solution. Organic compounds were extracted with ether (10 mL × 3). The combined organic phase was dried over anhydrous sodium sulfate and concentrated. Silica-gel column purification (hexane) afforded 2,2-dimethyl-1-phenyldecane (**2a**, 0.20 g, 0.81 mmol, 81 %).

Typical procedure for the benzylation or allylation of *gem*-dibromoalkanes: The reaction of **5d** is representative (Table 6, entry 4). AgOAc (2.1 mg, 0.013 mmol) was placed in a 20 mL reaction flask under argon and then acetonitrile (2.0 mL) and benzylzinc chloride·lithium chloride complex (0.86 M in THF, 2.33 mL, 2.0 mmol) were sequentially added. The resulting mixture was stirred for 5 min and then *gem*-Dibromoalkane **5d** (0.23 g, 0.50 mmol) was added. The whole mixture was stirred for 6 h at 25 °C. The reaction was quenched with saturated ammonium chloride solution. Organic compounds were extracted with hexane (10 mL × 3). The combined organic phase was dried over anhydrous sodium sulfate and concentrated. Silica-gel column purification (hexane/ethyl acetate 20:1) of the crude product provided the corresponding dibenzylated product **6d** (0.12 g, 0.25 mmol, 50 %).

Characterization data of products: Compounds **2a**,[7a] **2c**,[21] **2h**,[7a] **3b**,[7a] **3e**,[7a] **3g**,[7a] **4a–f**,[7a,16a,b] and **7e**[7c] produced spectra that were identical to those shown in the literature. Other compounds were characterized as shown below.

1-Methyl-1-benzylcyclohexane (2b): IR (neat): $\tilde{\nu}$ = 3062, 3028, 2849, 1601, 1496, 1452, 1376, 1031, 758, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.83 (s, 3H), 1.22–1.33 (m, 4H), 1.41–1.51 (m, 4H), 1.52–1.56 (m, 2H), 2.53 (s, 2H), 7.11–7.14 (m, 2H), 7.17–7.21 (m, 1H), 7.24–7.27 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 22.34, 24.76, 26.66, 34.24, 37.82, 49.00, 125.82, 127.71, 130.90, 139.38 ppm; elemental analysis calcd (%) for $C_{14}H_{20}$: C 89.29, H 10.71; found: C 84.49, H 10.96.

4-(2,2-Dimethyl-3-phenylpropyl)-1-methoxybenzene (2d): IR (neat): $\tilde{\nu}$ = 2912, 2834, 1610, 1497, 1441, 1384, 1364, 1301, 1177, 1039, 809, 774, 757, 731, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.81 (s, 6H), 2.52 (s, 2H), 2.56 (s, 2H), 3.79 (s, 3H), 6.80–6.83 (m, 2H), 7.03–7.06 (m, 2H), 7.12–7.14 (m, 2H), 7.19–7.22 (m, 1H), 7.25–7.28 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 26.18, 35.59, 48.64, 49.39, 55.38, 113.25, 125.97, 127.81, 130.93, 131.34, 131.79, 139.39, 158.04 ppm; elemental analysis calcd (%) for $C_{18}H_{22}O$: C 84.99, H 8.72; found: C 84.81, H 8.85.

4-(2,2-Dimethyl-3-phenylpropyl)-1-fluorobenzene (2e): IR (neat): $\tilde{\nu}$ = 3028, 2929, 2851, 1604, 1497, 1470, 1452, 1385, 1366, 1223, 1158, 829, 759, 733, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.81 (s, 6H), 2.55 (s, 2H), 2.56 (s, 2H), 6.94–6.98 (m, 2H), 7.05–7.09 (m, 2H), 7.12–7.14 (m, 2H), 7.20–7.23 (m, 1H), 7.25–7.29 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 26.14, 35.51, 48.56, 49.46, 114.62 (d, J = 21.2 Hz), 126.09, 127.88, 130.91, 132.14 (d, J = 7.8 Hz), 134.86 (d, J = 2.9 Hz), 139.12, 161.66 ppm (d, J = 244 Hz); elemental analysis calcd (%) for $C_{17}H_{19}F$: C 84.26, H 7.90; found: C 84.40, H 8.08.

6,6-Dimethyl-7-phenylheptyl benzoate (2f): IR (neat): $\tilde{\nu}$ = 2932, 2862, 1720, 1605, 1450, 1389, 1273, 1111, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.85 (s, 6H), 1.18–1.26 (m, 2H), 1.36–1.49 (m, 4H), 1.79 (tt, J = 7.5, 2.0 Hz, 2H), 2.45 (s, 2H), 4.33 (t, J = 7.0 Hz, 2H), 7.10–7.12 (m, 2H), 7.19 (tt, J = 7.5, 2.0 Hz, 1H), 7.23–7.27 (m, 2H), 7.44 (tt, J = 7.5, 1.5 Hz, 2H), 7.56 (tt, J = 7.5, 1.5 Hz, 1H), 8.03–8.07 ppm (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 24.15, 27.01, 27.18, 29.06, 34.37, 42.25, 48.65, 65.35, 125.93, 127.83, 128.55, 129.76, 130.75, 130.80, 133.02, 139.65, 166.92 ppm; HRMS (EI): m/z: calcd for $C_{22}H_{28}O_2$: 324.2089; found: 324.2093.

2,2-Dimethyl-1-(4-methylphenyl)decane (3a): IR (neat): $\tilde{\nu}$ = 2927, 2854, 1513, 1468, 1384, 1364, 1022, 813 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.82 (s, 6H), 0.89 (t, J = 7.0 Hz, 3H), 1.15–1.18 (m, 2H), 1.22–1.32 (m, 12H), 2.32 (s, 3H), 2.45 (s, 2H), 7.00 (d, J = 7.5 Hz, 2H), 7.07 ppm (d, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 14.33, 21.20, 22.88, 24.37, 27.01, 29.57, 29.93, 30.78, 32.12, 34.28, 42.31, 48.11, 128.47, 130.66, 135.22, 136.66 ppm; elemental analysis calcd (%) for $C_{19}H_{32}$: C 87.62, H 12.38; found: C 87.32, H 12.61.

2,2-Dimethyl-1-(4-vinylphenyl)decane (3d): IR (neat): $\tilde{\nu}$ = 2853, 1631, 1609, 1469, 1437, 1406, 1385, 1170, 1017, 988, 902, 829, 762 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.83 (s, 6H), 0.89 (t, J = 7.0 Hz, 3H), 1.15–1.18 (m, 2H), 1.22–1.32 (m, 12H), 2.48 (s, 2H), 5.19 (dd, J = 11.0, 1.0 Hz, 1H), 5.71 (dd, J = 17.5, 1.0 Hz, 1H), 6.70 (dd, J = 17.5, 11.0 Hz, 1H) 7.07 (d, J = 8.0 Hz, 2H), 7.31 ppm (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 14.33, 22.89, 24.37, 27.03, 29.57, 29.93, 30.76, 32.12, 34.46, 42.34, 48.28, 113.02, 125.65, 130.93, 135.22, 136.95, 139.65 ppm; elemental analysis calcd (%) for $C_{20}H_{32}$: C 88.16, H 11.84; found: C 88.09, H 12.09.

2,2-Dimethyl-1-(3-bromophenyl)decane (3f): IR (neat): $\tilde{\nu}$ = 2927, 2854, 1685, 1594, 1566, 1560, 1507, 1473, 1458, 1424, 1073, 889, 785, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.83 (s, 6H), 0.89 (t, J = 7.0 Hz, 3H), 1.15–1.17 (m, 2H), 1.22–1.32 (m, 12H), 2.45 (s, 2H), 7.02–7.05 (m, 1H), 7.11–7.14 (m, 1H), 7.26–7.27 (m, 1H), 7.31–7.34 ppm (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 14.33, 22.88, 24.32, 26.95, 29.56, 29.90, 30.70, 32.10, 34.42, 42.31, 48.12, 121.93, 128.97, 129.31, 129.38, 133.58, 142.18 ppm; elemental analysis calcd (%) for $C_{18}H_{29}Br$: C 66.45, H 8.98; found: C 66.50, H 9.10.

4-(2,2-Dimethyl-4-pentenyl)-1-fluorobenzene (4g): IR (neat): $\tilde{\nu}$ = 2962, 2915, 2855, 1640, 1471, 1437, 1416, 1385, 1366, 1158, 1095, 1016, 995, 915, 892, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.84 (s, 6H), 1.96–1.98 (m, 2H), 2.48 (s, 2H), 5.00–5.05 (m, 1H), 5.06–5.08 (m, 1H), 5.83–5.92 (m, 1H), 6.92–7.00 (m, 2H), 7.05–7.09 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 26.67, 34.58, 46.73, 47.63, 114.59 (d, J = 21.2 Hz), 117.41, 132.03 (d, J = 7.67 Hz), 134.98 (d, J = 3.91 Hz), 135.66, 161.61 ppm (d, J = 244 Hz); elemental analysis calcd (%) for $C_{13}H_{17}F$: C, 81.21; H, 8.91; found: C 81.33, H 9.07.

1-(*tert*-Butyldimethylsilyloxy)-9,9-dibenzyldecane (6a): IR (neat): $\tilde{\nu}$ = 2932, 2855, 1466, 1250, 1103, 841, 779, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.05 (s, 6H), 0.78 (s, 3H), 0.90 (s, 9H), 1.13–1.18 (m, 2H), 1.21–1.35 (m, 8H), 1.37–1.44 (m, 2H), 1.52 (tt, J = 6.5, 6.5 Hz, 2H), 2.58 (td, J = 17.0, 4.0 Hz, 4H), 3.60 (t, J = 6.5 Hz, 2H), 7.10–7.13 (m, 4H), 7.20 (tt, J = 7.0, 2.0 Hz, 2H), 7.26 ppm (tt, J = 7.5, 2.0 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = −5.11, 18.62, 24.20, 24.48, 26.06, 26.22, 29.72, 30.00, 30.59, 33.12, 38.06, 38.32, 46.46, 63.58, 126.00, 127.88, 131.01, 139.39 ppm; elemental analysis calcd (%) for $C_{30}H_{48}OSi$: C 79.58, H 10.69; found: C 79.55, H 10.87.

***N*-Benzyl-*N*-(9,9-dibenzyldecyl)-4-methylphenylsulfonamide (6b)**: IR (neat): $\tilde{\nu}$ = 2932, 2855, 1597, 1458, 1342, 1157, 910, 733, 656 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.78 (s, 3H), 1.02–1.18 (m, 10H), 1.25–1.38 (m, 4H), 2.43 (s, 3H), 2.57 (td, J = 16.0, 3.0 Hz, 4H), 3.07 (t, J = 7.5 Hz, 2H), 4.31 (s, 2H), 7.08–7.13 (m, 4H), 7.20 (tt, J = 7.5, 2.5 Hz, 2H), 7.26 (tt, J = 7.5, 2.0 Hz, 6H), 7.28–7.32 (m, 5H), 7.73 ppm (dt, J = 4.0, 2.0 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.73, 24.13, 24.46, 26.83, 28.14, 29.30, 29.74, 30.45, 38.03, 38.30, 46.46, 48.31, 52.08, 126.02, 127.42, 127.89, 128.49, 128.72, 129.87, 130.99, 136.85, 137.43, 139.34, 143.31, 231.99 ppm; HRMS (FAB): m/z: calcd for $C_{38}H_{46}NO_2S$: 580.3249; found: 580.3264 $[M-H]^-$.

10,10,*N*,*N*-Tetrabenzylundecanamide (6c): IR (neat): $\tilde{\nu}$ = 3032, 2932, 2855, 1651, 1450, 1211, 1080, 949, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.78 (s, 3H), 1.12–1.16 (m, 2H), 1.18–1.35 (m, 8H), 1.35–1.43 (m, 2H), 1.72 (tt, J = 7.0, 7.5 Hz, 2H), 2.42 (t, J = 7.5 Hz, 2H), 2.58 (td, J = 16.5, 3.5 Hz, 4H), 4.45 (s, 2H), 4.61 (s, 2H), 7.10–7.12 (m, 4H), 7.15 (d, J = 3.5 Hz, 2H), 7.17–7.23 (m, 4H), 7.24–7.29 (m, 5H), 7.29–7.34 (m, 3H), 7.37 ppm (t, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 24.19, 24.45, 25.68, 29.66, 29.71, 29.87, 30.58, 33.49, 38.03, 38.30, 46.44, 48.26, 50.11, 125.99, 126.59, 127.55, 127.79, 127.88, 128.51, 128.79, 129.15, 131.00, 136.90, 137.80, 139.36, 173.95 ppm; elemental analysis calcd (%) for $C_{39}H_{47}NO$: C 85.82, H 8.68; found: C 85.52, H 8.80.

9,9-Dibenzyldecyl 2,4,6-trimethylbenzoate (6d): IR (neat): $\tilde{\nu}$ = 2932, 2855, 1720, 1612, 1458, 1265, 1173, 1088, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.79 (s, 3H), 1.13–1.17 (m, 2H), 1.22–1.28 (m, 2H), 1.29–1.36 (m, 4H), 1.37–1.46 (m, 4H), 1.74 (tt, J = 7.0, 7.0 Hz, 2H), 2.28 (s, 3H), 2.30 (s, 6H), 2.58 (td, J = 16.5, 3.0 Hz, 4H), 4.31 (t, J = 7.0 Hz, 2H), 6.85 (s, 2H), 7.10–7.13 (m, 4H), 7.20 (tt, J = 7.5, 1.5 Hz, 2H), 7.26 ppm (tt, J = 7.5, 1.5 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 19.95, 21.33, 24.15, 24.46, 26.30, 28.90, 29.49, 29.86, 30.52, 38.04, 38.31, 46.47, 65.23, 126.01, 127.89, 128.58, 131.00, 131.51, 135.20, 139.35, 170.52, 209.03 ppm; HRMS (EI): m/z: calcd for $C_{34}H_{44}O_2$: 484.3341; found: 484.3336.

10,10-Dibenzyl-1-(2,4,6-trimethylphenyl)-1-undecanone (6e): IR (neat): $\tilde{\nu}$ = 2932, 2855, 1697, 1605, 1458, 1034, 910, 849, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.78 (s, 3H), 1.15 (m, 2H), 1.20–1.28 (m, 2H), 1.30–1.45(m, 8H), 1.70 (tt, J = 7.0, 7.0 Hz, 2H), 2.19 (s, 6H), 2.27 (s, 3H), 2.58 (td, J = 16.5, 3.5 Hz, 4H), 2.69 (t, J = 7.5 Hz, 2H), 6.83 (s, 2H), 7.09–7.13 (m, 4H), 7.20 (tt, J = 7.5, 1.5 Hz, 2H), 7.26 ppm (tt, J = 8.0, 2.5 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 19.34, 21.24, 23.65, 24.18, 24.47, 29.50, 29.75, 29.83, 30.58, 38.06, 38.33, 45.10, 46.48, 126.00, 127.88, 128.68, 131.01, 132.69, 138.39, 139.37, 140.13, 211.17 ppm; HRMS (EI): m/z: calcd for $C_{34}H_{44}O$: 468.3392; found: 468.3376;.

11,11-Dibenzyldodecanenitrile (6f): IR (neat): $\tilde{\nu}$ = 3024, 2932, 2855, 2245, 1605, 1458, 910, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.79 (s, 3H), 1.13–1.18 (m, 2H), 1.22–1.35 (m, 8H), 1.37–1.48 (m, 4H), 1.66 (tt, J = 7.5, 7.5 Hz, 2H), 2.34 (t, J = 7.0 Hz, 2H), 2.58 (td, J = 16.5, 3.25 Hz, 4H), 7.10–7.13 (m, 4H), 7.20 (tt, J = 7.5, 2.5 Hz, 2H), 7.26 ppm (tt, J = 7.5, 1.5 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ = 17.35, 24.16, 24.46, 25.60, 28.88, 28.99, 29.56, 29.83, 30.54, 38.04, 38.31, 46.47, 120.06, 126.01, 127.89, 131.00, 139.35 ppm; elemental analysis calcd (%) for $C_{26}H_{35}N$: C 86.37, H 9.76; found: C 86.59, H 9.71.

1-(*tert*-Butyldimethylsilyloxy)-9-methyl-9-(2-propenyl)-11-dodecene (7a): IR (neat): $\tilde{\nu}$ = 2932, 2855, 1466, 1250, 1103, 995, 910, 841, 779 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.05 (s, 6H), 0.82 (s, 3H), 0.90 (s, 9H), 1.14–1.34 (m, 12H), 1.51 (tt, J = 7.0, 6.5 Hz, 2H), 1.96–2.00 (m, 4H), 3.60 (t, J = 7.0 Hz, 2H), 4.98–5.05 (m, 4H), 5.75–5.84 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = −5.03, 18.61, 23.60, 24.79, 26.03, 26.22, 29.68, 29.87, 30.67, 33.11, 36.04, 39.42, 44.09, 63.57, 117.01, 135.69 ppm; elemental analysis calcd (%) for $C_{22}H_{44}OSi$: C 74.92, H 12.58; found: C 74.80, H 12.86.

***N*-Benzyl-*N*-[9-methyl-9-(2-propenyl)-11-dodecenyl]-4-methylphenylsulfonamide (7b)**: IR (neat): $\tilde{\nu}$ = 2924, 2855, 1458, 1342, 1157, 910, 810, 733, 659 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.82 (s, 3H), 1.04–1.20 (m, 12H), 1.24–1.35 (m, 2H), 1.91–1.99 (m, 4H), 2.44 (s, 3H), 3.07 (t, J = 7.5 Hz, 2H), 4.31 (s, 2H), 4.97–5.05 (m, 4H), 5.79 (ddt, J = 8.5, 5.0, 7.0 Hz, 2H), 7.25–7.33 (m, 7H), 7.71–7.74 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 21.73, 23.55, 24.78, 26.82, 28.11, 29.27, 29.63, 30.54, 36.02, 39.38, 44.08, 48.29, 52.05, 117.04, 127.41, 127.89, 128.49, 128.71, 129.87, 135.65, 136.84, 137.45, 143.30 ppm; elemental analysis calcd (%) for $C_{30}H_{43}NO_2S$: C 74.80, H 9.00; found: C 74.62, H 9.04.

***N*,*N*-Dibenzyl-10-methyl-10-(2-propenyl)-12-tridecenamide (7c)**: IR (neat): $\tilde{\nu}$ = 2924, 2855, 1651, 1450, 1358, 1211, 995, 910, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.82 (s, 3H), 1.14–1.34 (m, 12H), 1.71 (tt, J = 7.5, 7.5 Hz, 2H), 1.92–1.99 (m, 4H), 2.41 (t, J = 7.5 Hz, 2H), 4.45 (s, 2H), 4.60 (s, 2H), 4.96–5.05 (m, 4H), 5.79 (ddt, J = 8.5, 5.25, 7.5 Hz, 2H), 7.15 (d, J = 3.5 Hz, 2H), 7.22 (d, J = 3.5 Hz, 2H), 7.25–7.28 (m, 1H), 7.29–7.34 (m, 3H), 7.37 ppm (t, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 23.60, 24.79, 25.69, 29.67, 29.74, 30.67, 33.51, 36.03, 39.41, 44.09, 48.27, 50.13, 109.98, 117.02, 126.61, 127.55, 127.79, 128.52, 128.79, 129.15, 135.69, 136.92, 137.82, 173.97 ppm; elemental analysis calcd (%) for $C_{31}H_{43}NO$: C 83.54, H 9.72; found: C 83.71, H 9.92.

9-Methyl-9-(2-propenyl)-11-dodecenyl 2,4,6-trimethylbenzoate (7d): IR (neat): $\tilde{\nu}$ = 2932, 2855, 1728, 1612, 1458, 1265, 1173, 1088, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.82 (s, 3H), 1.14–1.36 (m, 10H), 1.37–1.44 (m, 2H), 1.73 (tt, J = 7.5, 7.5 Hz, 2H), 1.92–2.00 (m, 4H), 2.28 (s, 3H), 2.29 (s, 6H), 4.30 (t, J = 7.0 Hz, 2H), 4.98–5.05 (m, 4H), 5.78 (ddt, J = 8.5, 5.25, 7.5 Hz, 2H), 6.85 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 19.95, 21.33,

23.57, 24.78, 26.29, 28.90, 29.47, 29.75, 30.61, 36.02, 39.39, 44.08, 65.24, 117.04, 128.58, 131.50, 135.20, 135.66, 139.35, 170.52 ppm; elemental analysis calcd (%) for $C_{26}H_{40}O_2$: C 81.20, H 10.48; found: C 81.28, H 10.66.

4-Methyl-4-(2-phenylethyl)-1,6-heptadiene (7e): IR (neat): $\tilde{\nu}=3074$, 2920, 1638, 1498, 1454, 996, 913, 743, 698 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=$ 0.93 (s, 3H), 1.47–1.52 (m, 2H), 2.02–2.10 (m, 4H), 2.56 (dt, $J=4.5$, 4.5 Hz, 2H), 5.04–5.10 (m, 4H), 5.79–5.90 (m, 2H), 7.14–7.23 (m, 3H), 7.24–7.32 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta=24.79$, 30.35, 36.23, 41.76, 44.02, 117.43, 125.80, 128.53, 128.54, 135.29, 143.53 ppm; elemental analysis calcd (%) for $C_{16}H_{22}$: C 89.65, H 10.35; found: C 89.51, H 10.07.

4-Heptyl-4-methyl-1,6-heptadiene (7f): IR (neat): $\tilde{\nu}=3076$, 2929, 2856, 1639, 1466, 1442, 1377, 995, 912 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta=0.83$ (s, 3H), 0.88 (t, $J=7.0$ Hz, 3H), 1.14–1.34 (m, 12H), 1.92–2.00 (m, 4H), 4.97–5.04 (m, 4H), 5.80 ppm (ddt, $J=8.0$, 2.5, 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): $\delta=$ 14.33, 22.91, 23.64, 24.80, 29.58, 30.71, 32.14, 36.04, 39.44, 44.10, 117.10, 135.71 ppm; elemental analysis calcd (%) for $C_{15}H_{28}$: C 86.46, H 13.54; found: C 86.54, H 13.84.

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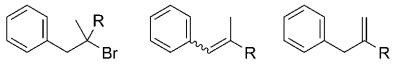

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