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Graphical Abstract

Silver-Catalyzed Coupling Reactions of Alkyl Halides with Indenyllithiums

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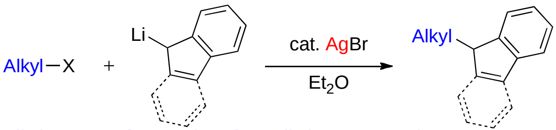

Alkyl = **secondary** and **tertiary** alkyl; X = I, Br, Cl

TETRAHEDRON

Silver-Catalyzed Coupling Reactions of Alkyl Halides with Indenyllithiums

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Abstract—Coupling reactions of tertiary and secondary alkyl halides with indenyllithiums proceeded effectively in the presence of a catalytic amount of silver bromide to provide tertiary- and secondary-alkyl-substituted indene derivatives in good yields.

1. Introduction

Owing to the high nucleophilicity and the ready availability of organolithiums, coupling reactions of alkyl halides with organolithiums have been widely used for carbon-carbon bond formations in organic synthesis.[1] The reaction of primary alkyl halides can proceed smoothly without any catalyst. However, the use of sterically bulky secondary alkyl halides as substrates in the coupling reactions often results in affording the corresponding coupling products in low yields, which is due to competitive side reactions such as elimination to alkenes and reduction to alkanes.

Recent progress of transition-metal-catalyzed coupling reactions of alkyl halides enables us to use secondary alkyl halides as well as primary ones as substrates in the coupling reactions.[2] While there are many reports in which Mg,[3] Zn,[4] Sn,[5] B,[6] or Si[7] is used as the metal of organometallic reagent, the use of organolithium is less investigated.[8] Moreover, the reactions of tertiary alkyl halides are still rare and have to be established.[3a,3b,9]

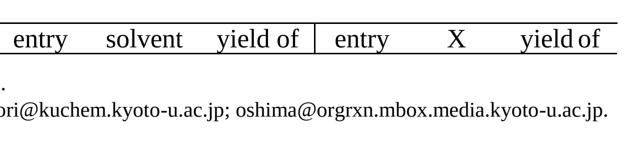
Recently, we have reported silver-catalyzed coupling reactions of alkyl halides with Grignard reagents.[9,10] In these reactions, tertiary and secondary alkyl halides can be employed as substrates. Here, we report silver-catalyzed coupling reactions of tertiary and secondary alkyl halides with indenyllithium derivatives. Indene framework can be found both in a large number of drug candidates[11] and in various metallocene complexes.[12] The new efficient route to modified indenes would thus be important.

2. Results and discussion

2.1. Optimization and scope of alkyl halides

Treatment of 3-bromo-3-methyl-1-phenylbutane (**1a**) with two equivalents of indenyllithium in the presence of 5 mol% AgBr in Et_2O afforded the corresponding alkylated indene **2a** in 90% yield (Table 1, entry 1).[13] The reaction afforded 1-alkylindenes selectively, and no isomerization to 3-alkylindene occurred despite the presence of basic indenyllithium. Indenyllithium was prepared through deprotonative lithiation of indene with *sec*-butyllithium in Et_2O at 0 °C for 30 min.[14] When AgBr was not added, only a trace amount of **2a** was detected.[15,16] The reactions performed in other ethereal solvents, such as THF and cyclopentyl methyl ether (CPME), resulted in lower yields (entries 2 and 3). The reaction in hexane, which was the solvent of *sec*-butyllithium, resulted in moderate yield (entry 4).[17] Other silver halides, such as AgI and AgCl, were not effective (entries 5 and 6). When we used $AgNO_3$ instead of AgBr, the reaction was sluggish (entry 7).[18] The reaction with AgOTf resulted in slightly lower yield than that with AgBr (entry 8).

Table 1. Effects of solvents and silver salts



entry	solvent	yield of	entry	X	yield of

Keywords: Coupling reaction, Silver, Carbon-Carbon bond formation, alkyl halide.

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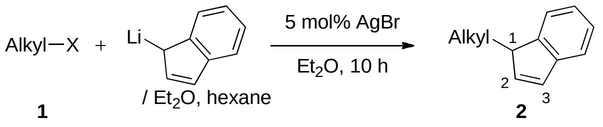
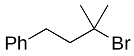
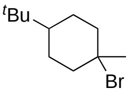
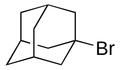
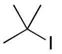
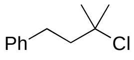
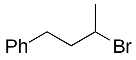
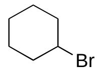
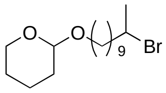
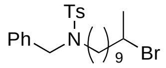
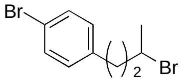
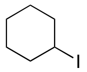
		2a /%[b]			**2a** /%[b]
1[a]	Et_2O	90	5[d]	I	2[e]
2[a]	THF	10	6[d]	Cl	30[f]
3[a]	CPME	56	7[d]	NO_3	26[g]
4[a,c]	hexane	64	8[d]	OTf	74

[a] Performed with 2.0 eq of indenyllithium in the presence of 5 mol% AgBr. [b] Based on NMR analysis. [c] Indenyllithium was prepared in hexane. [d] Performed in Et_2O. [e] **1a** was recovered in 88% yield. [f] **1a** was recovered in 62% yield. [g] **1a** was recovered in 40% yield.

The silver-catalyzed coupling reactions of various alkyl halides are summarized in Table 2. Cyclic tertiary alkyl bromide **1b** also underwent the reaction smoothly (entry 2). It should be noted that the reaction of **1b** was not stereospecific, which is highly suggestive of the existence of an intermediate having an sp^2-hybridized carbon center.[9a] Since the reaction of 1-bromoadamantane (**1c**) was slow, CPME was used as a cosolvent and the reaction was performed under refluxing conditions (entry 3). Tertiary alkyl iodides **1d** was too reactive under the reaction conditions (entry 4). The reaction of tertiary alkyl chloride **1e** required a prolonged reaction time and a high temperature in CPME/Et_2O, and the coupling product was a 88/12 mixture of 1-alkyl- and 3-alkylindene derivatives through deprotonation of **2a** by indenyllithium under the reaction conditions (entry 5). Both cyclic and acyclic secondary alkyl bromides reacted smoothly in refluxing Et_2O (entries 6 and 7).[19] The substrates having functional groups such as THP ether and sulfonamide could be also employed (entries 8 and 9). The coupling reaction of dibromide **1j** proceeded selectively at the sp^3-hybridized brominated carbon, although palladium-catalyzed coupling reactions of aryl halides with organolithiums can proceed smoothly (entry 10).[8a] Secondary alkyl iodides **1k** can be employed (entry 11). However, cyclohexyl chloride resisted the reaction, being converted to **2f** in only 17% yield.

Table 2. Silver-catalyzed coupling reactions of various alkyl halides[a]

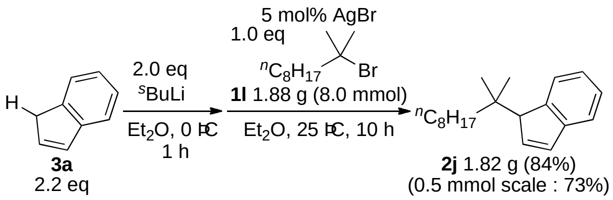


entry	Alkyl-X	**1**	temp.	**2**	yield /%[b]
1		**1a**	0 °C	**2a**	86
2		**1b**[c]	reflux	**2b**	74[d,e]
3		**1c**	reflux	**2c**	61[f,g,h]
4		**1d**	0 °C	**2d**	31
5		**1e**	reflux	**2a**	38[f,h,i,j]
6		**1f**	reflux	**2e**	85[k]
7		**1g**	reflux	**2f**	65
8		**1h**	reflux	**2g**	72[k]
9		**1i**	reflux	**2h**	86[k]
10		**1j**	reflux	**2i**	79[k]
11		**1k**	reflux	**2f**	70

[a] Conditions: **1** (0.50 mmol), indenyllithium (1.0 mmol) in Et_2O (3.0 mL). [b] Isolated yields. [c] *cis*/*trans* = 84:16. [d] *cis*/*trans* = 35:65. [e] Performed for 12 h. [f] Temperature of oil bath was 90 °C. [g] Performed with 3.0 eq of indenyllithium for 20 h. [h] Performed in CPME/Et_2O (1/1). [i] **2a**/3-alkylindene = 88/12. [j] Performed for 40 h. [k] ~1/1 mixtures of diastereomers.

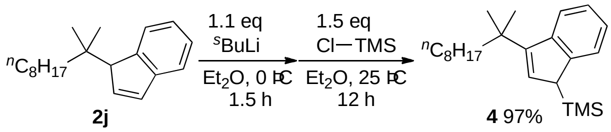
2.2. Application

The silver-catalyzed coupling reaction could proceed effectively in a gram-scale (Scheme 1). Treatment of 1.88 g of tertiary alkyl bromide **1l** (8.0 mmol) with indenyllithium (16 mmol) under the silver-catalyzed conditions afforded 1.82 g of **2j** (84% yield). The same reaction in a 0.5 mmol-scale afforded **2j** in 73% yield.



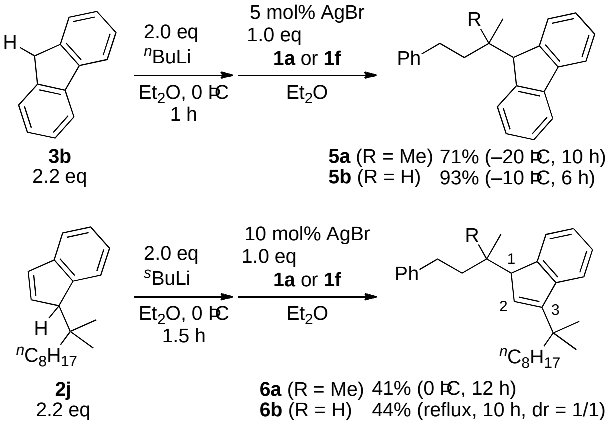
Scheme 1. Gram-scale coupling reaction

Treatment of **2j** with *sec*-butyllithium followed by the addition of chlorotrimethylsilane afforded the corresponding indenylsilane derivative **4** in high yield (Scheme 2). Indenylsilanes are known to be converted into the corresponding indenyltitanium trichlorides, which are the precursors of syndiospecific catalysts for Ziegler-Natta polymerization of styrene.[12a]



Scheme 2. Synthesis of indenylsilane derivative

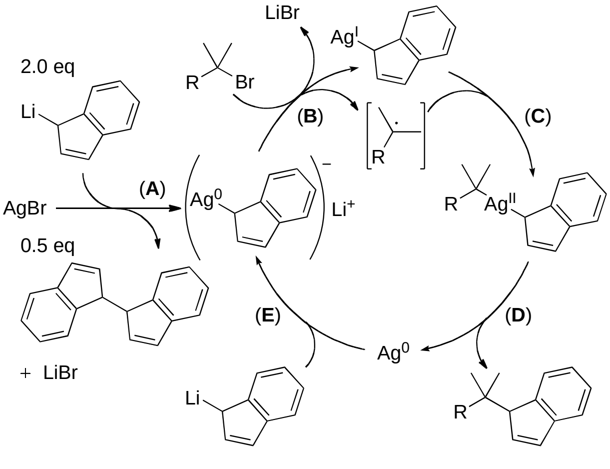
The silver-catalyzed conditions were applicable to other stabilized organolithiums (Scheme 3). The reactions of both tertiary and secondary alkyl bromides with fluorenyllithium provided the corresponding 9-alkylfluorenes in good yields. The coupling reactions can be a useful tool because fluorene frameworks are known to have attractive optical properties.[20] The regiocontrolled synthesis of 1,3-dialkylindene could be achieved by the silver-catalyzed coupling reaction with organolithium derived from **2j**. The alkyl moiety which resulted from the alkyl halide was substituted at the 1-position of the 1,3-dialkylated indenes and the regioisomer was not detected.[21]



Scheme 3. Silver-catalyzed coupling reactions with other organolithiums

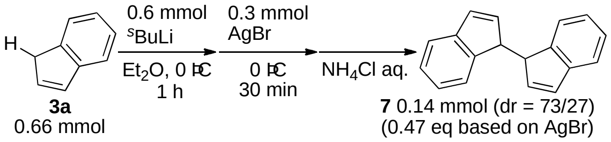
2.3. Mechanistic consideration

We propose a draft mechanism shown in Scheme 4. Formation of electron-rich silver(0)-ate complex[9,22] initially takes place through the reaction of AgBr with two equivalents of indenyllithium (**A**). The ate complex effects single electron transfer to alkyl halide to form the corresponding alkyl radical as cobalt- and manganese-ate complexes do (**B**).[23] The radical is trapped by indenylsilver(I) to yield oxidative adduct (**C**). Reductive elimination gives the coupling product (**D**), and the initial silver-ate complex is regenerated by the action of the remaining indenyllithium (**E**).[24]



Scheme 4. Plausible mechanism

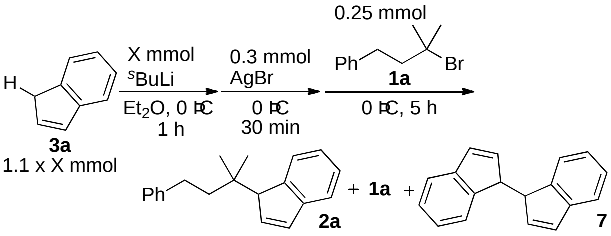
The initial reduction of silver(I) salt to silver(0) is justified as follows. Treatment of AgBr (0.30 mmol) with indenyllithium (0.60 mmol) in Et_2O at 0 ˚C for 30 min afforded 1*H*,1’*H*-1,1’-biindene (**7**) (0.14 mmol, dr = 73/27) (Scheme 5). The formation of **7**, the amount of which is roughly equal to a half of AgBr used, indicates that Ag(I) would be reduced to Ag(0).



Scheme 5. A mechanistic consideration

The following experiments revealed that monoindenylsilver(0)-ate complex[25,26] is reactive enough to effect the coupling reaction (Table 3). A reaction mixture prepared from equimolar amounts of AgBr and indenyllithium failed to promote the reaction of **1a** (entry 1). In contrast, a 1/2 mixture of AgBr and indenyllithium was highly reactive to yield **2a** in 90% yield (entry 2). Three equivalents of the indenyllithium based on AgBr did not improve the efficiency significantly (entry 3). Although the exact feature of the catalytically active species is not clear, these results support our proposed mechanism shown in Scheme 4.

Table 3. Reactions with stoichiometric silver bromide



entry	X /mmol	yield of **2a** /%[a]	recovery of **1a** /%[a]	yield of **7** /mmol[a]
1	0.3	<5	96	0.14
2	0.6	90	0	0.15
3	0.9	93	0	0.14

[a] Based on NMR analysis.

3. Conclusion

We have developed silver-catalyzed coupling reactions of alkyl halides with indenyllithiums. The silver-catalyzed coupling reactions can afford tertiary- and secondary-alkyl-substituted indenes and fluorenes in good yields.

4. Experimental

4.1. General

4.1.1. Instrumentation

^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were recorded in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^1H and relative to $CDCl_3$ at 77.23 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Florisil (75–150 µm, 100–200 mesh) was used for filtration. Silica gel (Wakogel 200 mesh) was used for column chromatography. Mass (EI) were determined on a JASCO IR-810 spectrometer. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

4.1.2. Materials

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Silver bromide, silver chloride, silver nitrate, 1*H*-indene, and cyclopentyl methyl ether were purchased from Wako Pure Chemicals. Silver iodide, butyllithium (1.6 M in hexane solution), 9*H*-fluorene, and hexane were purchased from Nacalai Tesque. Diethyl ether and tetrahydrofuran were purchased from Kanto Chemical Co., stored under nitrogen, and used as it is. Secondary butyllithium (1.0 M in cyclohexane/hexane solution) was also purchased from Kanto Chemical Co. Silver trifluoromethanesulfonate was purchased from Aldrich. All reactions were carried out under argon atmosphere.

4.2. Experimental Procedures

4.2.1. Synthesis of 3-bromo-3-methyl-1-phenylbutane (1a)

2-Methyl-4-phenyl-2-butanol (4.1 g, 25 mmol) was placed in a 100-mL reaction flask. Then hydrobromic acid (47% solution, 12.9 g, 75 mmol) was added dropwise to the reaction mixture. After being stirred for 1 d at 25 ˚C, the reaction mixture was poured into ethylene glycol (20 mL). The products were extracted with hexane (30 mL × 2). The combined organic layer was dried over Na_2SO_4 and concentrated. Distillation of the crude oil (1 Torr, 110 ˚C) afforded tertiary alkyl bromide **1a** (4.2g 18.4 mmol) in 74% isolated yield.

4.2.2. Synthesis of 3-chloro-3-methyl-1-phenylbutane (1e)

2-Methyl-4-phenyl-2-butanol (4.9 g, 30 mmol) was placed in a 100-mL reaction flask. Hydrochloric acid (11 M solution, 11 mL, 121 mmol) was then added dropwise to the reaction mixture. After being stirred for 1 d at 25 ˚C, the reaction mixture was poured into ethylene glycol (20 mL). The products were extracted with hexane (30 mL × 2). The combined organic layer was dried over Na_2SO_4 and concentrated. Silica gel column purification (hexane) of the crude oil afforded tertiary alkyl chloride **1e** (3.3 g, 17.8 mmol) in 93% isolated yield.

4.2.3. Synthesis of 3-bromo-1-(4-bromophenyl)butane (1j)

Magnesium (turnings, 0.36 g, 15 mmol) and Et_2O (5 mL) were placed in a 100-mL reaction flask. 4-Bromobenzyl bromide (2.5 g, 10 mmol) in Et_2O (10 mL) was added dropwise to the reaction mixture at 0 ˚C. After the mixture was stirred for 2 h, THF (10 mL) and 1,2-epoxypropane (1.4 mL, 20 mmol) were successively added at 0 ˚C. The reaction mixture was stirred for 2 h at room temperature. Then, the reaction mixture was poured into a saturated ammonium chloride solution. The products were extracted with ethyl acetate (20 mL × 2). The combined organic layer was dried over Na_2SO_4 and concentrated. Silica gel column purification (hexane/ethyl acetate = 2/1) of the crude oil afforded 4-(4-bromophenyl)-2-butanol (0.84 g, 3.7 mmol) in 37% isolated yield. This alcohol and dichloromethane (4 mL) were placed in a 30-mL reaction flask. Then, triethylamine (1.0 mL, 7.4 mmol), methanesulfonyl chloride (0.43 mL, 5.6 mmol), and 4-(dimethylamino)pyridine (0.01 mmol, 1.2 mg) were successively added to the reaction mixture. After being stirred for 4 h at room temperature, the reaction mixture was poured into a saturated ammonium chloride solution. The products were extracted with ethyl acetate (20 mL × 2). The combined organic layer was dried over Na_2SO_4 and concentrated. The crude oil in acetone (4 mL) was placed in a 30-mL reaction flask. Lithium bromide (0.96 g, 11 mmol) was then added to the reaction mixture. After being stirred for 12 h in refluxing acetone, the reaction mixture was poured into water. The products were extracted with hexane (20 mL × 2). The combined organic layer was dried over Na_2SO_4 and concentrated. Silica gel column purification (hexane) of the crude oil afforded **1j** (0.66 g, 2.3 mmol) in 61% isolated yield.

4.2.4. General procedure for silver-catalyzed coupling reactions of alkyl halides with indenyllithiums

The reaction of **1a** with indenyllithium is representative (Table 2, entry 1). Silver bromide (4.7 mg, 0.025 mmol) in Et_2O (1 mL) was placed in a 30-mL reaction flask. Indenyllithium, which was prepared by treatment of 1*H*-indene (0.13 mL, 1.1 mmol) with *sec*-butyllithium (1.0 M in cyclohexane/hexane solution, 1.0 mL, 1.0 mmol) in Et_2O (3 mL) at 0 ˚C for 1 h, was added to the reaction mixture at 0 ˚C. Then, substrate **1a** (113.6 mg, 0.50 mmol) in Et_2O (2 mL) was added. After being stirred vigorously for 10 h at 0 ˚C, the reaction mixture was poured into a saturated ammonium chloride solution (30 mL). The products were extracted with ethyl acetate (30 mL × 3). The combined organic layer was passed through Florisil, dried over Na_2SO_4 and concentrated. Silica gel column purification (hexane/ethyl acetate = 80/1) of the crude product provided the corresponding coupling product **2a** (112.8 mg, 0.43 mmol) in 86% isolated yield.

4.2.5. Silver-catalyzed coupling reaction in gram-scale

Silver bromide (75.1 mg, 0.40 mmol) in Et_2O (8 mL) was placed in a 100-mL reaction flask. Indenyllithium prepared by treatment of 1*H*-indene (2.1 mL, 17.6 mmol) with *sec*-butyllithium (1.0 M in cyclohexane/hexane solution, 16 mL, 16 mmol) in Et$_2$O (16 mL) at 0 ˚C for 1 h, was added to the mixture at room temperature. Substrate **1l** (1.88 g, 8.0 mmol) in Et$_2$O (16 mL) was then added to the reaction mixture. After being stirred vigorously for 10 h at room temperature, the reaction mixture was poured into a saturated ammonium chloride solution (30 mL). The products were extracted with ethyl acetate (30 mL × 3). The combined organic layer was passed through Florisil, dried over Na$_2$SO$_4$ and concentrated. Silica gel column purification (hexane) of the crude product provided the corresponding coupling product **2j** (1.82 g, 6.7 mmol) in 84% isolated yield.

4.2.6. Synthesis of 3-(1,1-dimethylnonyl)-1-trimethylsilyl-1*H*-indene (4)

Indene derivative **2j** (0.41 g, 1.5 mmol) in Et$_2$O (1.5 mL) was placed in a 30-mL reaction flask. Then, *sec*-butyllithium (1.0 M in cyclohexane/hexane solution, 1.65 mL, 1.65 mmol) was added dropwise to the mixture at 0 ˚C. After the mixture was stirred at 0 ˚C for 1.5 h, chlorotrimethylsilane (0.29 mL, 2.25 mmol) was added to the reaction mixture at 0 ˚C. The reaction mixture was stirred at room temperature for 12 h. Then, the reaction mixture was poured into water (20 mL). The products were extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over Na$_2$SO$_4$ and concentrated. Silica gel column purification (hexane) of the crude product provided the corresponding indenylsilane derivative **4** (0.50 g, 1.45 mmol) in 97% isolated yield. (Silica Gel 60 N (spherical, neutral) 40–100 μm, which was purchased from Kanto Chemical Co., was used for column chromatography in this case.)

4.2.7. General procedure for silver-catalyzed coupling reactions of alkyl halides with fluorenyllithiums

The synthesis of **5a** is representative (Scheme 3). Silver bromide (4.7 mg, 0.025 mmol) in Et$_2$O (1 mL) was placed in a 30-mL reaction flask. Fluorenyllithium, which was prepared through treatment of 9*H*-fluorene (182.8 mg, 1.1 mmol) with butyllithium (1.6 M in cyclohexane/hexane solution, 0.63 mL, 1.0 mmol) in Et$_2$O (3 mL) at 0 ˚C for 1 h, was added to the reaction mixture at –20 ˚C. Then, substrate **1a** (113.6 mg, 0.50 mmol) in Et$_2$O (2 mL) was added at the same temperature. After being stirred vigorously for 10 h at –20 ˚C, the reaction mixture was poured into a saturated ammonium chloride solution (30 mL). The products were extracted with ethyl acetate (30 mL × 3). The combined organic layer was passed through Florisil, dried over Na$_2$SO$_4$ and concentrated. Silica gel column purification (hexane/ethyl acetate = 50/1) of the crude product provided the corresponding coupling product **5a** (110.4 mg, 0.35 mmol) in 71% isolated yield.

4.2.8. General procedure for synthesis of 1,3-dialkylindenes

The synthesis of **6a** is representative (Scheme 3). Silver bromide (4.7 mg, 0.025 mmol) in Et$_2$O (1 mL) was placed in a 30-mL reaction flask. Indenyllithium derivative, which was prepared through treatment of **2j** (297.5 mg, 1.1 mmol) with *sec*-butyllithium (1.0 M in cyclohexane/hexane solution, 1.0 mL, 1.0 mmol) in Et$_2$O (3 mL) at 0 ˚C for 1.5 h, was added to the reaction mixture at 0 ˚C. Then, substrate **1a** (113.6 mg, 0.50 mmol) in Et$_2$O (2 mL) was added at the same temperature. After being stirred vigorously for 12 h at 0 ˚C, the reaction mixture was poured into a saturated ammonium chloride solution (30 mL). The products were extracted with ethyl acetate (30 mL × 3). The combined organic layer was passed through Florisil, dried over Na$_2$SO$_4$ and concentrated. Purification by silica gel column chromatography (hexane/ethyl acetate = 80/1), which was followed by gel permeation chromatography, of the crude product provided the corresponding coupling product **6a** (84.6 mg, 0.20mmol) in 41% isolated yield.

4.3. Characterization data of new compounds

Compounds **1c**, **1d**, **1g**, **1k**, **3a**, and **3b** were commercially available. Compound **1b**,[27] **1f**,[28] **1h**,[9b] **1i**,[9b] and **1l**[3b] were found in the literature.

4.3.1. 3-Bromo-3-methyl-1-phenylbutane (1a).

colorless oil. IR (neat) 3024, 2932, 1604, 1497, 1450, 1103, 740, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.82 (s, 6H), 2.09 (ddd, *J* = 8.0, 4.5, 3.5 Hz, 2H), 2.84–2.87 (m, 2H), 7.18–7.22 (m, 3H), 7.27–7.31 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 33.11, 34.49, 49.66, 67.69, 126.19, 128.63, 128.70, 141.81; Found: C, 58.33; H, 6.68%. Calcd for C$_{11}$H$_{15}$Br: C, 58.17; H, 6.66%.

4.3.2. 3-Chloro-3-methyl-1-phenylbutane (1e).

colorless oil. IR (neat) 2932, 2893, 1604, 1458, 1373, 1110, 748, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.64 (s, 6H), 2.04 (ddd, *J* = 8.0, 5.0, 4.5 Hz, 2H), 2.82 (dt, *J* = 8.0, 4.5 Hz, 2H), 7.18–7.22 (m, 3H), 7.27–7.31 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 31.87, 32.69, 48.17, 70.76, 126.15, 128.61, 128.68, 141.99; Found: C, 72.41; H, 8.19%. Calcd for C$_{11}$H$_{15}$Cl: C, 72.32; H, 8.28%.

4.3.3. 3-Bromo-1-(4-bromophenyl)butane (1j).

yellow oil. IR (neat) 2924, 2862, 1489, 1450, 1072, 1001, 826 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.72 (d, *J* = 6.5 Hz, 3H), 2.00 (m, 1H), 2.10 (m, 1H), 2.71 (m, 1H), 2.82 (m, 1H), 4.04 (m, 1H), 7.09 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.41 (dt, *J* = 8.5, 2.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 26.74, 33.59, 42.62, 50.73, 120.08, 130.51, 131.76, 140.06; Found: C, 41.20; H, 4.19%. Calcd for C$_{10}$H$_{12}$Br$_2$: C, 41.13; H, 4.14%.

4.3.4. 1-(1,1-Dimethyl-3-phenylpropyl)-1*H*-indene (2a).

yellow oil. IR (neat) 3024, 2963, 2862, 1605, 1458, 1366, 763, 702 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.05 (s, 3H), 1.07 (s, 3H), 1.66–1.77 (m, 2H), 2.69 (t, *J* = 8.5 Hz, 2H), 3.46 (t, *J* = 2.0 Hz, 1H), 6.57 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.83 (dd, *J* = 6.0, 2.0 Hz, 1H), 7.13–7.19 (m, 4H), 7.22–7.29 (m, 3H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 26.22, 26.28, 31.10, 37.07, 43.96, 59.64, 121.24, 124.52, 124.98, 125.89, 126.65, 128.56, 128.62, 132.00, 137.74, 143.30, 145.69, 145.72,; Found: C, 91.67; H, 8.51%. Calcd for C$_{20}$H$_{22}$: C, 91.55; H, 8.45%.

4.3.5. 1-(1-Methyl-4-(1,1-dimethylethyl)cyclohexyl)-1*H*-indene (2b) (cis/trans = 35/65 mixture of diastereomers).[29]

white solid. IR (Nujol) 3063, 2939, 2862, 1458, 1366, 1227, 1150, 1103, 1026, 926, 756, 725 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.34 (s, 0.35×3H), 0.68 (s, 0.65×3H), 0.85 (s, 0.65×9H), 0.92 (s, 0.35×9H), 0.95 (m, 0.65×1H), 1.12–1.32 (m, 0.35×1H+2H), 1.47–1.81 (m, 0.65×1H+4H), 1.99 (m, 1H), 2.37 (m, 0.35×1H), 3.20 (br-s, 0.65×1H), 3.85 (br-s, 0.35×1H), 6.53 (dd, *J* = 5.5, 2.0 Hz, 0.35×1H), 6.58 (dd, *J* = 5.5, 2.0 Hz, 0.65×1H), 6.81(m, 1H), 7.13 (m, 1H), 7.23 (m, 1H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 0.35×1H), 7.54 (d, *J* = 7.5 Hz, 0.65×1H); ^{13}C NMR (CDCl$_3$) δ 18.62, 22.84, 22.97, 23.09, 23.18, 23.96, 27.76, 27.87, 32.60, 32.80, 36.51, 37.06, 37.75, 38.15, 38.38, 40.20, 48.30, 48.32, 52.22, 63.58, 121.04, 121.17, 124.26, 124.30, 124.95, 125.41, 126.44, 126.55, 131.61, 131.77, 137.56, 138.10, 145.60, 145.78, 145.80, 146.06; Found: C, 89.20; H, 10.72%. Calcd for C$_{20}$H$_{28}$: C, 89.49; H, 10.51%. m.p. 54–55 ˚C.

4.3.6. 1-(1-Adamantyl)-1*H*-indene (2c).

white solid. IR (Nujol) 2854, 1450, 1366, 1096, 756, 716 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.58–1.64 (m, 6H), 1.66–1.71 (dm, 3H), 1.82 (dm, 3H), 1.95 (br-s, 3H), 3.14 (s, 1H), 6.60 (d, *J* = 5.5 Hz, 1H), 6.80 (d, *J* = 5.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 29.03, 37.03, 37.28, 41.01, 62.02, 121.03, 124.17, 125.53, 126.53, 131.77, 137.09, 145.00, 145.72; Found: C, 91.22; H, 8.60%. Calcd for C$_{19}$H$_{22}$: C, 91.14; H, 8.86%. m.p. 64–65 ˚C.

4.3.7. 1-(1,1-Dimethylethyl)-1*H*-indene (2d).[15]

colorless oil. IR (neat) 3063, 2963, 2870, 1458, 1366, 1226, 764, 725 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.03 (s, 9H), 3.27 (s, 1H), 6.55 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.81 (dt, *J* = 6.0, 1.0 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 28.77, 34.35, 61.56, 121.06, 124.37, 125.04, 126.57, 131.70, 138.22, 145.61, 145.97; Found: C, 90.45; H, 9.63%. Calcd for C$_{13}$H$_{16}$: C, 90.64; H, 9.36%.

4.3.8. 1-(1-Methyl-3-phenylpropyl)-1*H*-indene (2e) (56/44 mixture of diastereomers).

yellow oil. IR (neat) 2924, 2862, 1605, 1458, 1373, 763, 740 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.56 (d, *J* = 7.0 Hz, 0.44×3H), 1.08 (d, *J* = 7.0 Hz, 0.56×3H), 1.35 (m, 1H), 1.70 (m, 0.44×1H), 1.91 (m, 0.44×1H), 2.26 (m, 1H), 2.42 (m, 0.56×1H), 2.62 (m, 0.56×1H), 2.77 (m, 1H), 3.48 (br-s, 0.56×1H), 3.56 (br-s, 0.44×1H), 6.47 (dd, *J* = 6.0, 2.0 Hz, 0.44×1H), 6.50 (dd, *J* = 5.5, 2.0 Hz, 0.56×1H), 6.81 (dd, *J* = 5.5, 2.5 Hz, 0.56×1H), 6.85 (dd, *J* = 5.5, 2.5 Hz, 0.44×1H), 7.04 (d, *J* = 7.5 Hz, 1H), 7.13–7.19 (m, 0.44×1H+1H), 7.21–7.25 (m, 4H), 7.30–7.36 (m, 0.56×1H+2H); ^{13}C NMR (CDCl$_3$) δ 14.88, 18.27, 34.20, 34.36, 34.39, 34.41, 34.67, 38.27, 55.48, 56.55, 121.12, 122.96, 123.38, 124.73, 124.84, 125.82, 126.00, 126.60, 126.64, 128.34, 128.49, 128.56, 128.62, 128.63, 131.82, 132.39, 136.54, 137.48, 142.66, 142.76, 145.12, 145.34, 146.46, 147.17; Found: C, 91.81; H, 8.15%. Calcd for C$_{19}$H$_{20}$: C, 91.88; H, 8.12%.

4.3.9. 1-Cyclohexyl-1*H*-indene (2f).

colorless oil. IR (neat) 3063, 2924, 2855, 1450, 1366, 772, 718 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.90 (m, *J* = 1H), 1.05–1.18 (m, 2H), 1.20–1.35 (m, 3H), 1.61 (dm, 2H), 1.77 (m, 1H), 1.87–2.02 (m, 2H), 3.40 (t, *J* = 2.0 Hz, 1H), 6.52 (dd, *J* = 5.5, 2.0 Hz, 1H), 6.80 (dd, *J* = 5.5, 2.0 Hz, 1H), 7.17 (td, *J* = 7.5, 1.0 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 26.73, 26.73, 27.12, 28.54, 32.47, 40.53, 56.76, 121.03, 123.29, 124.66, 126.52, 131.53, 137.78, 145.15, 146.90; Found: C, 90.67; H, 9.22%. Calcd for C$_{15}$H$_{18}$: C, 90.85; H, 9.15%.

4.3.10. 2-((10-(1*H*-Inden-1-yl)undecyl)oxy)tetrahydropyran (2g) (53/47 mixture of diastereomers).

yellow oil. IR (neat) 2924, 2855, 1458, 1358, 1072, 1034, 772, 725 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.46 (d, *J* = 6.5 Hz, 0.53×3H), 0.98 (d, *J* = 6.5 Hz, 0.47×3H), 1.03 (m, 1H), 1.09–1.47 (m, 14H), 1.49–1.64 (m, 6H), 1.72 (m, 1H), 1.84 (m, 1H), 2.19 (m, 1H), 3.38 (ddt, *J* = 10.5, 10.0, 6.5 Hz, 1H), 3.49 (m, 1H), 3.73 (ddt, *J* = 10.5, 10.0, 6.5 Hz, 1H), 3.87 (m, 1H), 4.57 (m, 1H), 6.47 (dd, *J* = 6.0, 2.0 Hz, 0.47×1H), 6.49 (dd, *J* = 5.5, 2.0 Hz, 0.53×1H), 6.81 (dd, *J* = 6.0, 2.0 Hz, 0.47×1H), 6.84 (dd, *J* = 5.5, 2.0 Hz, 0.53×1H), 7.17 (m, 1H), 7.24 (m, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.39 (m, 1H); ^{13}C NMR (CDCl$_3$) δ 14.86, 18.21, 19.94 (2C), 25.74 (2C), 26.45, 26.48, 27.97, 28.09, 29.67, 29.72, 29.75 (2C), 29.83, 29.84, 29.87, 29.97, 30.00, 30.08, 31.02 (2C), 32.85, 34.89, 35.13, 36.57, 55.62, 56.61, 62.56, 62.58, 67.91 (2C), 99.07, 99.09, 121.03, 121.05, 122.91, 123.42, 124.63, 124.74, 126.47, 126.53, 131.49, 132.11, 136.83, 137.99, 145.14, 145.42, 146.69, 147.48; Found: C, 80.64; H, 10.30%. Calcd for C$_{25}$H$_{38}$O$_2$: C, 81.03; H, 10.33%.

4.3.11. *N*-(10-(1*H*-Inden-1-yl)undecyl)-*N*-(phenylmethyl)-4-methylbenzenesulfonamide (2h) (54/46 mixture of diastereomers).

colorless oil. IR (neat) 3063, 2924, 2855, 1458, 1342, 1157, 733 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.47 (d, *J* = 6.5 Hz, 0.46×3H), 0.98 (d, *J* = 6.5 Hz, 0.54×3H), 0.98–1.57 (m, 16H), 2.18 (m, 1H), 2.43 (s, 0.54×3H), 2.44 (s, 0.46×3H), 3.04–3.09 (m, 2H), 3.46 (br-s, 0.54×1H), 3.50 (br-s, 0.46×1H), 4.30 (s, 0.54×2H), 4.31 (s, 0.46×2H), 6.46 (dd, *J* = 6.0, 2.0 Hz, 0.46×1H), 6.49 (dd, *J* = 6.0, 2.0 Hz, 0.54×1H), 6.81 (dd, *J* = 6.0, 2.0 Hz, 0.54×1H), 6.84 (dd, *J* = 6.0, 2.0 Hz, 0.46×1H), 7.16 (m, 1H), 7.22–7.34 (m, 9H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.72 (dd, *J* = 8.5, 5.0 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 14.91, 18.26, 21.72 (2C), 26.80, 26.84, 27.95, 28.07, 28.09, 28.15, 29.20, 29.27, 29.53, 29.61, 29.62, 29.75, 29.79, 30.03, 32.82, 34.90, 35.14, 36.53, 48.27, 48.32, 52.05, 52.08, 55.63, 56.63, 121.06, 121.07, 122.92, 123.40, 124.64, 124.76, 126.50, 126.55, 127.42, 127.43, 127.90 (2C), 128.49, 128.50, 128.72 (2C), 129.87 (2C), 131.53, 132.14, 136.81, 136.86, 136.88, 137.51 (2C), 137.95, 143.30, 143.31, 145.15, 145.43, 146.70, 147.46; HRMS (m/z) obsd 529.3011 (Δ = –0.6 ppm), calcd for C$_{34}$H$_{43}$O$_2$NS 529.3015.

4.3.12. 1-(3-(4-Bromophenyl)-1-methylpropyl)-1*H*-indene (2i) (54/46 mixture of diastereomers).

yellow oil. IR (neat) 3064, 2924, 2862, 1488, 1373, 1072, 1001, 764 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.56 (d, *J* = 7.0 Hz, 0.46×3H), 1.09 (d, *J* = 7.0 Hz, 0.54×3H), 1.28 (m, 1H), 1.66 (m, 0.46×1H), 1.86 (m, 0.54×1H), 2.22 (m, 1H), 2.35 (dt, *J* = 14.0, 8.0 Hz, 0.54×1H), 2.55 (m, 0.46×1H), 2.72 (m, 1H), 3.46 (t, *J* = 2.0 Hz, 0.46×1H), 3.53 (t, *J* = 2.0 Hz, 0.54×1H), 6.45 (dd, *J* = 5.5, 2.0 Hz, 0.54×1H), 6.49 (dd, *J* = 5.5, 2.0 Hz, 0.46×1H), 6.82 (dd *J* = 5.5, 2.0 Hz, 0.54×1H), 6.85 (dd, *J* = 5.5, 2.0 Hz, 0.46×1H), 6.90 (d, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 7.16 (m, 1H), 7.23–7.36 (m, 4H), 7.42 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.90, 18.45, 33.52, 33.75, 33.98, 34.17, 34.52, 37.96, 55.42, 56.51, 119.50, 119.70, 121.16, 121.17, 122.96, 123.26, 124.79, 124.89, 126.66, 126.71, 130.33, 130.39, 131.44, 131.65, 131.95, 132.49, 136.38, 137.19, 141.54, 141.66, 145.08, 145.26, 146.39, 146.98; Found: C, 69.43; H, 5.83%. Calcd for $C_{19}H_{19}Br$: C, 69.73; H, 5.85%.

4.3.13. 1-(1,1-Dimethylnonyl)-1*H*-indene (2j).

colorless oil. IR (neat) 2924, 2855, 1466, 1366, 763, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 6.5 Hz, 3H), 0.93 (s, 3H), 0.93 (s, 3H), 1.24–1.34 (m, 10H), 1.35–1.46 (m, 4H), 3.39 (br-s, 1H), 6.53 (dd, *J* = 5.5, 2.0 Hz, 1H), 6.80 (dd, *J* = 5.5, 2.0 Hz, 1H), 7.13 (td, *J* = 7.5, 1.0 Hz, 1H), 7.23 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.5 Hz,1H); ^{13}C NMR ($CDCl_3$) δ 14.35, 22.91, 24.41, 26.03, 26.20, 29.59, 29.93, 30.77, 32.14, 36.88, 42.07, 59.52, 121.09, 124.34, 124.98, 126.48, 131.65, 138.17, 145.74, 145.94; Found: C, 88.82; H, 11.28%. Calcd for $C_{20}H_{30}$: C, 88.82; H, 11.18%.

4.3.14. 3-(1,1-Dimethylnonyl)-1-trimethylsilyl-1*H*-indene (4).

yellow oil. IR (neat) 2932, 2855, 1458, 1381, 1249, 1034, 841, 763 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ –0.06 (s, 9H), 0.84 (t, *J* = 7.5 Hz, 3H), 1.09–1.14 (m, 2H), 1.15–1.27 (m, 10H), 1.33 (s, 6H), 1.71–1.82 (m, 2H), 3.33 (d, *J* = 2.0 Hz, 1H), 6.26 (d, *J* = 2.0 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –2.11, 14.30, 22.86, 25.20, 28.44, 28.45, 29.51, 29.78, 30.63, 32.10, 36.72, 41.53, 44.10, 122.12, 123.13, 123.20, 124.26, 129.61, 143.33, 147.51, 149.67; HRMS (m/z) obsd 342.2740 (Δ = –0.8 ppm), calcd for $C_{23}H_{38}Si$ 342.2743.

4.3.15. 9-(1,1-Dimethyl-3-phenylpropyl)-9*H*-fluorene (5a).

white solid. IR (Nujol) 2924, 2854, 1604, 1450, 1381, 1281, 1173, 741 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 6H), 1.73 (dt, *J* = 9.0, 5.0 Hz, 2H), 2.76 (dt, *J* = 9.0, 5.0 Hz, 2H), 3.97 (s, 1H), 7.17–7.24 (m, 5H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.40, 31.02, 37.96, 42.96, 56.29, 119.76, 125.92, 126.24, 126.61, 127.20, 128.54, 128.63, 142.42, 143.11, 145.97; Found: C, 91.97; H, 7.89%. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74%. m.p. 67–68 ˚C.

4.3.16. 9-(1-Methyl-3-phenylpropyl)-9*H*-fluorene (5b).

white solid. IR (Nujol) 2924, 2731, 1458, 1373, 740, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.72 (d, *J* = 6.5 Hz, 3H), 1.61 (m, 1H), 1.77 (m, 1H), 2.41 (m, 1H), 2.65 (ddd, *J* = 13.5, 10.0, 6.5 Hz, 1H), 2.75 (ddd, *J* = 13.5, 10.0, 6.0 Hz, 1H), 4.02 (d, *J* = 3.0 Hz, 1H), 7.14–7.20 (m, 3H), 7.24–7.30 (m, 4H), 7.33–7.37 (m, 2H), 7.46–7.48 (m, 2H), 7.74 (dd, *J* = 7.0, 4.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 16.07, 34.37, 36.24, 36.83, 52.69, 119.83, 119.91, 124.66, 125.23, 125.96, 126.84, 126.99, 127.08, 127.14, 128.55, 128.62, 141.77, 142.09, 142.58, 145.82, 146.90; Found: C, 92.60; H, 7.40%. Calcd for $C_{23}H_{22}$: C, 92.57; H, 7.43%. m.p. 72–73 ˚C.

4.3.17. 3-(1,1-Dimethylnonyl)-1-(1,1-dimethyl-3-phenylpropyl)-1*H*-indene (6a).

colorless oil. IR (neat) 2932, 2855, 1605, 1458, 1366, 763 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, *J* = 7.0 Hz, 3H), 1.01 (s, 3H), 1.04 (s, 3H), 1.06–1.25 (m, 12H), 1.30 (s, 3H), 1.31 (s, 3H), 1.62–1.84 (m, 4H), 2.65–2.73 (m, 2H), 3.33 (d, *J* = 2.0 Hz, 1H), 6.18 (d, *J* = 2.0 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.16–7.30 (m, 6H), 7.54 (dd, *J* = 11.5, 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.30, 22.86, 25.15, 26.25, 26.37, 28.21, 28.27, 29.49, 29.68, 30.53, 31.10, 32.08, 36.67, 37.21, 41.11, 44.04, 56.92, 122.10, 123.83, 125.08, 125.85, 126.02, 128.53, 128.60, 131.38, 143.41, 145.02, 147.64, 151.63; Found: C, 89.58; H, 10.49%. Calcd for $C_{31}H_{44}$: C, 89.36; H, 10.64%.

4.3.18. 3-(1,1-Dimethylnonyl)-1-(1-methyl-3-phenylpropyl)-1*H*-indene (6b) (51/49 mixture of diastereomers).

colorless oil. IR (neat) 2924, 2855, 1605, 1458, 1381, 741, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.50 (d, *J* = 7.0 Hz, 0.49×3H), 0.84 (t, *J* = 7.0 Hz, 0.49×3H), 0.84 (t, *J* = 7.0 Hz, 0.51×3H), 1.06 (d, *J* = 7.0 Hz, 0.51×3H), 1.06–1.25 (m, 12H), 1.30–1.35 (m, 7H), 1.64 (m, 1H), 1.71 (m, 0.49×1H), 1.80 (m, 1H), 1.91 (m, 0.51×1H), 2.21 (m, 1H), 2.39 (dt, *J* = 14.0, 8.5 Hz, 0.49×1H), 2.59 (m, 0.51×1H), 2.78 (m, 1H), 3.36 (br-s, 0.51×1H), 3.44 (br-s, 0.49×1H), 6.06 (d, *J* = 2.0 Hz, 0.49×1H), 6.10 (d, *J* = 2.0 Hz, 0.51×1H), 7.03 (d, *J* = 6.5 Hz, 1H), 7.11–7.16 (m, 2H), 7.19–7.24 (m, 3H), 7.32 (dd, *J* = 14.5, 7.0 Hz, 2H), 7.54 (dd, *J* = 7.5, 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.30, 14.31, 14.66, 18.42, 22.86, 22.87, 25.12 (2C), 28.14, 28.15, 28.25 (2C), 29.47, 29.51, 29.67, 29.71, 30.52, 30.53, 32.08 (2C), 34.05, 34.20, 34.45, 34.59, 34.94, 36.69, 36.79, 38.43, 41.08 (2C), 52.95, 54.14, 122.07, 122.09, 123.01, 123.46, 124.11, 124.23, 125.75, 125.97 (2C), 126.02, 128.38, 128.50, 128.59, 128.64, 129.78, 130.88, 142.72, 142.89, 144.51, 144.70, 148.45, 149.19, 151.81, 152.50; Found: C, 89.51; H, 10.79%. Calcd for $C_{30}H_{42}$: C, 89.49; H, 10.51%.

4.3.19. 1*H*,1*H*'-1,1'-biindene (7) (73/27 mixture of diastereomers).

white solid. IR (Nujol) 2924, 2855, 1458, 1373, 964, 802, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.16 (s, 0.27×2H), 4.19 (s, 0.73×2H), 5.85 (dd, *J* = 5.5, 1.0 Hz, 0.73×2H), 6.34 (dd, *J* = 6.0, 1.0 Hz, 0.27×2H), 6.70 (d, *J* = 5.5 Hz, 0.73×2H), 6.73 (d, *J* = 6.0 Hz, 0.27×2H), 6.88 (d, *J* = 7.5 Hz, 0.27×2H), 7.04 (t, *J* = 7.5 Hz, 0.27×2H), 7.21–7.32 (m, 4H), 7.34 (d, *J* = 7.0 Hz, 0.73×2H), 7.62 (d, *J* = 7.0 Hz, 0.73×2H); ^{13}C NMR ($CDCl_3$) δ 50.92, 51.37, 121.27, 121.43, 122.87, 122.99, 124.89, 125.07, 127.08, 127.12, 132.13, 132.31, 136.25, 136.91, 144.72, 144.86, 145.20, 146.02; Found: C, 93.81; H, 6.04%. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13%. m.p. 77–78 °C.

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13. When the catalytic amount of AgBr was reduced from 5 mol%, a prolonged reaction time was needed. Reoptimization of the reaction time should be required.
14. The silver-catalyzed reactions with indenylmagnesium bromide-LiBr complex and with indenyllithium-TMEDA complex afforded **2a** in 37% and 9% yields, respectively.
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16. The coupling reaction of **1a** without AgBr was so slow that alkene rather than the desired coupling product was gradually produced by elimination.
17. In the silver-catalyzed reactions with Grignard reagents (reference 9), Et_2O was also the suitable solvent for the coupling reactions. This fact indicates that silver catalyst coordinated by Et_2O and/or indenyllithium the reactivity of which is controlled by Et_2O are important.
18. In each case, indene was recovered by the protonation of the unreacted indenyllithium after the work-up.
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Supplementary Material

^{1}H and ^{13}C NMR spectra of **1a**, **1e**, **1j**, and the products. Supplementary data associated with this article can be found in the online version.