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Aromatic alkenylation using electrophilic organogallium reagent generated from allenylsilane and $GaCl_3$

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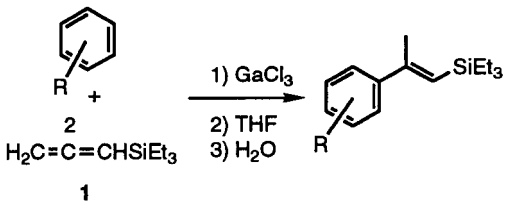
Abstract—Aromatic hydrocarbons are alkenylated with silylallene in the presence of $GaCl_3$ at −90°C. Organometallic electrophiles generated from the allene and $GaCl_3$ are the active species in this reaction. A modest level of *ortho*-selectivity is observed. While the silylallene reacts exclusively at the 2-position, 1,2-alkadiene reacts at the 1-position predominantly.

Alkyne and halogenated alkene are common reagents for the electrophilic alkenylation of aromatic compounds.[1,2] Although allene potentially is another attractive alkenylating reagent, their use has been quite limited.[3,4] It may be caused by the instability of the allene and/or alkenylated product under acidic conditions. Previously, we reported the Friedel–Crafts β-silylethenylation reaction using organogallium cationic species derived from silylethyne **3** and $GaCl_3$.[2] The reaction of silylated 1,3-butadiyne **2** was also studied, which exhibited unusually high *ortho*-selectivity.[5] It therefore appeared interesting to see if $GaCl_3$ could be used for the aromatic alkenylation of silylallene **1**, and to compare the behavior of **1** with that of **2** and **3** (Scheme 1). Described here is the electrophilic aromatic C–C bond formation using allenes promoted by $GaCl_3$. Reactions of several alkenes are also conducted.

Arene (3 mol. equivalents) and 1-triethylsilyl-1,2-propadiene (**1**) (1 mol. equivalent) were reacted with $GaCl_3$ (1 mol equivalent) in dichloromethane at −90°C for 2–3 h. Then THF was added, and an aqueous workup gave (*E*)-1-silyl-1-propen-2-ylated arene (Fig. 1). The C–C bond formation takes place at the 2-position of **1**, and no product at the 1- or 3-positions was detected. β-Cation stabilization by the silicon substituent probably was playing an important role on the regioselectivity. As in the reaction of silylethyne **3**,[2] the alkenylation is likely to proceed via organogallium electrophiles rather than vinyl cations generated by protonation of **1**. Treatment of an excess *p*-xylene and **1** with HCl and $GaCl_3$ gave a complex mixture of products, and not the alkenylated arene. Sulfuric acid and trifluoromethanesulfonic acid were also not effective.

The orientation of the aromatic substitution indicates an electrophilic mechanism. It exhibits a modest tendency to alkenylate the *o*-position of alkyl substituents: the reaction of **1** and toluene gives a ca. 1:1 mixture of the *o*- and *p*-products (Fig. 2). Reaction of silylethyne **3** and disilyl-1,3,5,7-octatetrayne **4** takes place at the *p*-position predominantly,[2,5] while disilylated 1,3-butadiyne **2** reacts at the *o*-position selectively.[5] This order of unsaturated compounds must be reflecting some property of their $GaCl_3$ complex, although the origin is not clear at present. The following examples also show such tendencies: reactions of *o*-xylene or 1,2,3,4-tetrahydronaphthalene with **1** give mixtures of comparable amounts of two regioisomers. In contrast, **3** reacts at the less hindered sites predominantly for both substrates,[2] and **2** at the more hindered sites.[5] In addition, while **3** does not react with 1,3,5-trimethylbenzene, **1** and **2** smoothly react at the hindered position between two methyl groups.

The complex formed from **1** and $GaCl_3$ can be detected by low temperature NMR studies (Scheme 2). When an equimolar amount of the compounds was mixed at −85°C, a low field shift and broadening of the 1-H of **1** was observed. The use of 2 mol. eq. of $GaCl_3$ resulted in a further low field shift



Scheme 1.

Keywords: gallium trichloride; organometallic electrophile; aromatic alkenylation; allenylsilane.

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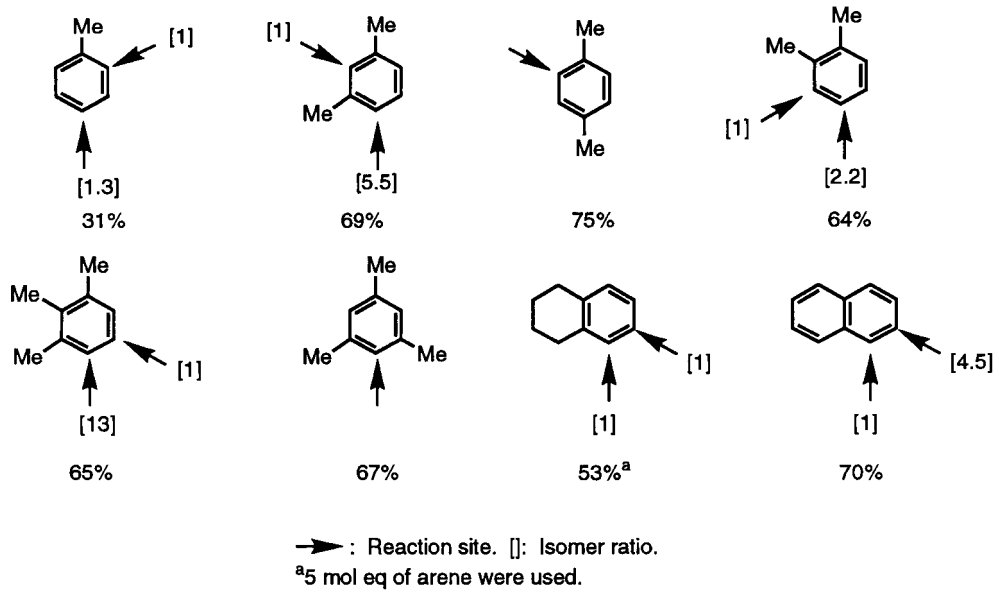


Figure 1. Aromatic alkenylation using silylallene **1** promoted by $GaCl_3$.

and sharpening of 1-H, while the shift was subtle at 3-H. 2-C also shifted to a low field, and 3-C a high field. It is likely that $GaCl_3$ and **1** form complex **5**, where $GaCl_3$ interacts with the double bond close to the silyl group. *p*-Xylene then attacks at the 2-position of **5**, generating an arenium species **6**. When the reaction of *p*-xylene and **1** was quenched with D_2O, no deuteration of the product **7** took place. It may be because of the proton transfer of the allylgallium **6** giving **7** in the reaction mixture. Although this mechanism suggests the catalysis by $GaCl_3$, 10 mol% of $GaCl_3$ fails to give the product under these reaction conditions. Related proton transfer is considered to occur in the reaction of **2** as well.[5]

An alkylallene shows different behavior from the silylallene **1**. When 1,2-undecadiene (**8**) was reacted with *p*-xylene at −78°C in the presence of $GaCl_3$, an isomeric mixture of allylated product (*E*)- and (*Z*)-**9** (X=H) and alkenylated product (*E*)-**10** was obtained with the former predominating (Scheme 3). The alkyl substituent of **8** appears to stabilize the allyl cation rather than the vinyl cation. Notably, workup with D_2O gives monodeuterated **9** (X=D) and non-deuterated **10**. The mixture of **9** (X=D) and **10** is subjected to ozonolysis, followed by reductive workup, giving 2-arylethanol, 1-arylethanol, and 1-nonanol. Deuterium is incorporated only in the 2-arylethanol at the 1-position, as indicated by D-NMR. The compound **9** therefore should be formed from the vinylgallium **11** by a similar mechanism with the reaction of **3**.[2] Formation of non-deuterated **10**

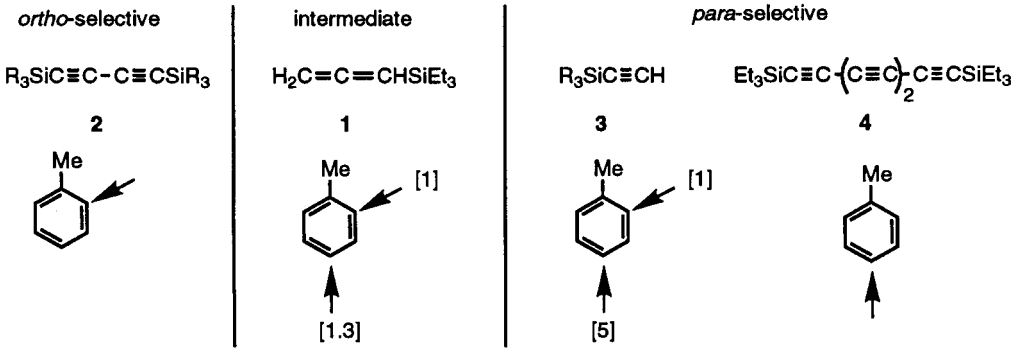
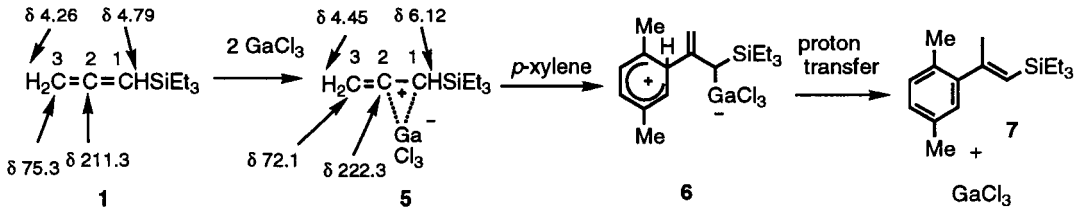
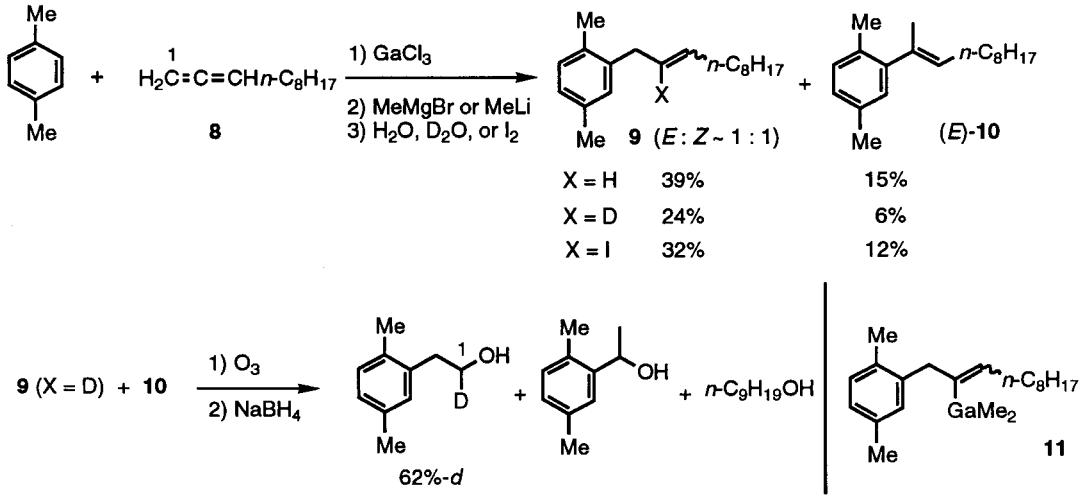


Figure 2. *Ortho*/*para*-selectivity in the aromatic substitution promoted by $GaCl_3$.



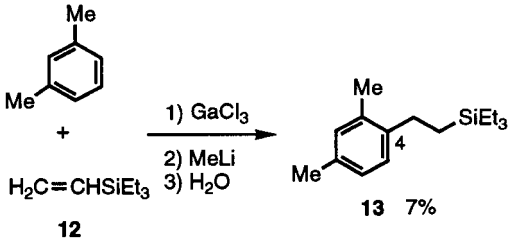
Scheme 2.



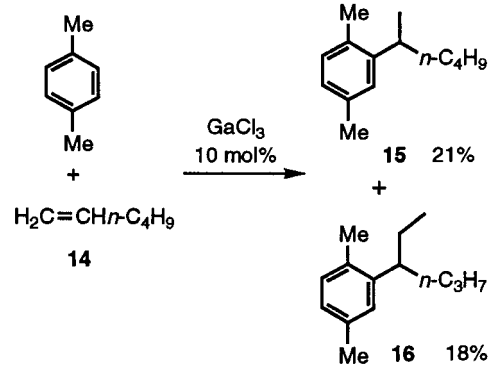
Scheme 3.

probably involves the proton transfer as described for **1** in Scheme 2. It may be reasonable that the allylgallium is more reactive towards protonation than the vinylgallium species. When the reaction was quenched with iodine, vinyl iodides (*E*)-**9** (X=I), (*Z*)-**9** (X=I), and allylarene (*E*)-**10** were obtained. The iodides (*E*)-**9** (X=I) and (*Z*)-**9** (X=I) can be converted stereospecifically to (*Z*)-**9** (X=H) and (*E*)-**9** (X=H), respectively, by lithiation and aqueous treatments.

It turned out that monoolefins also react with aromatic hydrocarbons in the presence of $GaCl_3$, although their reactions are generally less effective than allenes. Treatment of vinylsilane **12** with *m*-xylene gives a very low yield of the 4-silylethylated product **13** (Scheme 4). Polymerization of **12** under the reaction conditions competes with the alkylation. Electrophiles generated from **12** appear to be less stable than those from **1** or **3**.



Scheme 4.



Scheme 5.

Reaction of 1-alkene is sensitive to the substrate structure. 3,3-Dimethyl-1-butene and styrene do not give the aromatic alkylated product. In the case of 1-hexene (**14**), a mixture of two isomers, 2-hexyl derivative **15** and 3-hexyl derivative **16**, is obtained. Apparently, **16** is formed via the rearrangement of the electrophile first generated from **14**. Notably, this reaction proceeds catalytically concerning $GaCl_3$, and **15** and **16** are obtained in 21 and 18% yields, respectively, using 10 mol% of $GaCl_3$ at −50°C (Scheme 5).

1. Experimental

IR spectra were measured on a JASCO FT/IR-400 spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Mercury NMR (400 MHz) with Me_4Si as an internal standard. Mass spectra were recorded on a JEOL JMS-DX-303 or JMS-AX-500 spectrometer. Gel permeation chromatography (GPC) was conducted with Recycling Preparative HPLC LC-908 (Japan Analytical Industry Co. Ltd).

1.1. (*E*)-1-(1-Triethylsilyl-1-propen-2-yl)-2,5-dimethylbenzene

Under an argon atmosphere, to a solution of *p*-xylene (0.38 ml, 3.0 mmol) in CH_2Cl_2 (8 ml) was added a solution of $GaCl_3$ (1.0 M in methylcyclohexane, 2.0 mL) at −90°C. Then, **1** (154 mg, 1.0 mmol) in CH_2Cl_2 (2.0 mL) was added, and the mixture was stirred at this temperature for 2 h. THF (5.0 mL) was added, and stirring was continued for a further 30 min. The reaction was quenched by the addition of water. The organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography (silica gel, *n*-hexane) to give (*E*)-1-(1-triethylsilyl-1-propen-2-yl)-2,5-dimethylbenzene (195 mg, 75%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.69 (6H, q, J=7.6 Hz), 1.00 (9H, t, J=8.0 Hz), 2.05 (3H, d, J=0.8 Hz), 2.24 (3H, s), 2.29 (3H, s), 5.26 (1H, q, J=0.8 Hz), 6.89 (1H, br s), 6.93 (1H, d, J=7.6 Hz), 7.03 (1H, d, J=7.6 Hz).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 4.89, 7.81, 19.42, 21.02, 23.86, 125.21, 127.02, 127.67, 129.88, 130.15, 134.71, 147.52, 155.59. IR (neat) 2952, 2911, 2873, 1604, 1457, 1239, 1015, 808, 768, 731 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 260 (2, M^+), 231 (100), 203 (14), 163 (21), 135 (16), 87 (14), 59 (14). HRMS (EI, 70 eV) Calcd. for $C_{17}H_{28}Si$: 260.1959. Found: 260.1957 (M^+). The stereochemistry was determined by NOE.

1.2. (*E*)-1-(1-Triethylsilyl-1-propen-2-yl)-2-methylbenzene and (*E*)-1-(1-triethylsilyl-1-propen-2-yl)-4-methylbenzene

^{1}H-NMR (400 MHz, $CDCl_3$) δ *2-methyl isomer*: 0.69 (6H, q, *J*=7.9 Hz), 1.00 (9H, t, *J*=7.9 Hz), 2.07 (3H, s), 2.29 (3H, s), 5.28 (1H, s), 7.05–7.10 (1H, m), 7.12–7.17 (3H, m); *4-methyl isomer*: 0.68 (6H, q, *J*=7.9 Hz), 0.98 (9H, t, *J*=7.7 Hz), 2.19 (3H, s), 2.34 (3H, s), 5.82 (1H, s), 7.13 (2H, d, *J*=6.3 Hz), 7.36 (2H, d, *J*=8.1 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ *2-methyl isomer*: 4.69, 7.70, 19.81, 23.74, 125.44, 125.59, 126.37, 127.13, 130.00, 133.44, 147.76, 155.46; *4-methyl isomer*: 4.79, 7.68, 21.07, 21.36, 122.82, 125.35, 128.70, 136.95, 141.61, 152.28. IR (neat, mixture of isomers) 2952, 2910, 2873, 1598, 1457, 1237, 1015, 805, 768, 736 cm^{-1}. MS (EI, 70 eV, mixture of isomers) *m/z* (%) 246 (5, M^+), 217 (100), 189 (18), 177 (21), 149 (27), 121 (21). HRMS (EI, 70 eV, mixture of isomers) Calcd for $C_{16}H_{26}Si$: 246.1802. Found: 246.1797 (M^+).

1.3. (*E*)-1-(1-Triethylsilyl-1-propen-2-yl)-2,4-dimethylbenzene and (*E*)-1-(1-triethylsilyl-1-propen-2-yl)-2,6-dimethylbenzene

^{1}H-NMR (400 MHz, $CDCl_3$) δ *2,4-dimethyl isomer*: 0.68 (6H, q, *J*=7.8 Hz), 0.99 (9H, t, *J*=7.8 Hz), 2.05 (3H, d, *J*=1.1 Hz), 2.25 (3H, s), 2.30 (3H, s), 5.26 (1H, q, *J*=1.1 Hz), 6.89 (1H, br s), 6.94 (1H, d, *J*= 7.6 Hz), 6.97 (1H, m), 6.98 (1H, d, *J*=7.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ *2,4-dimethyl isomer*: 4.85, 7.80, 19.88, 21.09, 23.95, 125.42, 126.01, 127.01, 130.69, 133.21, 135.77, 144.87, 155.28. IR (neat, mixture of isomers) 2952, 2911, 2873, 1605, 1457, 1236, 1015, 816, 768, 738 cm^{-1}. MS (EI, 70 eV, mixture of isomers) *m/z* (%) 260 (6, M^+), 231 (100), 203 (16), 191 (21), 163 (28), 135 (21), 87 (15), 59 (14). HRMS (EI, 70 eV, mixture of isomers) Calcd for $C_{17}H_{28}Si$: 260.1959. Found: 260.1960 (M^+). Treatment of the isomeric mixture (6:1) with *m*-chloroperbenzoic acid (CH_2Cl_2; 0°C, 3 h) gave (*E*)-1-triethylsilyl-2-methyl-2-(2,4-dimethylphenyl)oxirane (66%) and recovered (*E*)-1-(1-triethylsilyl-1-propen-2-yl)-2,6-dimethylbenzene (12%). **(*E*)-1-Triethylsilyl-2-methyl-2-(2,4-dimethylphenyl)oxirane.** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.74 (3H, q, *J*=8.1 Hz), 0.75 (3H, q, *J*=7.7 Hz), 1.06 (9H, t, *J*=7.7 Hz), 1.56 (3H, s), 2.28 (1H, s), 2.29 (3H, s), 2.36 (3H, s), 6.94 (1H, m), 6.97 (1H, d, *J*=7.7 Hz), 7.25 (1H, d, *J*=7.7 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 3.41, 7.51, 19.26, 21.10, 23.00, 57.37, 61.93, 125.95, 126.26, 130.55, 134.24, 136.56, 140.04. IR (neat) 2954, 2876, 1615, 1456, 1365, 1237, 1016, 857, 822, 754, 719 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 276 (70, M^+), 261 (28), 247 (100), 219 (34), 160 (58), 115 (52), 103 (30), 87 (62), 75 (40), 59 (39). HRMS (EI, 70 eV) Calcd for $C_{17}H_{28}OSi$: 276.1908. Found: 276.1915 (M^+). **(*E*)-1-(1-Triethylsilyl-1-propen-2-yl)-2,6-dimethylbenzene:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.69 (6H, q, *J*=8.1 Hz), 1.01 (9H, t, *J*=8.1 Hz), 2.00 (3H, s), 2.24 (6H, s), 2.29 (3H, s), 5.23 (1H, q, *J*= 1.1 Hz), 6.99–7.05 (3H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 4.88, 7.80, 19.82, 23.02, 125.26, 125.83, 127.11, 133.41, 147.10, 155.57. FT-IR (neat) 2952, 2910, 2873, 1614, 1462, 1236, 1015, 796, 768, 738 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 260 (10, M^+), 231 (100), 203 (37), 101 (25). HRMS (EI, 70 eV) Calcd. for $C_{17}H_{28}Si$: 260.1959. Found 260.1950 (M^+). The epoxide was converted to methyl 2-(2,4-dimethylphenyl)propionate in three steps. (i) CH_3SO_3H, THF-H_2O; 0°C, 5 h.[6] (ii) $NaClO_2$, NaH_2PO_4, 2-methyl-2-butene, *t*-BuOH-H_2O, rt, 4 h. (iii) Me_3SiCHN_2. **Methyl 2-(2,4-Dimethylphenyl)propionate:** ^{1}H-NMR (400 MHz, $CDCl_3$) d 1.45 (3H, d, *J*=7.2 Hz), 2.29 (3H, s), 2.32 (3H, s), 3.64 (3H, s), 3.91 (1H, q, *J*=7.2 Hz), 6.98 (1H, s), 6.99 (1H, br d, *J*=7.0 Hz), 7.13 (1H, d, *J*=8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 18.14, 19.61, 21.05, 41.02, 52.00, 126.31, 126.97, 131.17, 135.29, 135.99, 136.36, 175.20. IR (neat) 2951, 1739, 1505, 1456, 1209, 1193, 855, 824 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 192 (21, M^+), 133 (100), 117 (6), 105 (7), 91 (7). HRMS (EI, 70 eV) Calcd for $C_{12}H_{16}O_2$: 192.1149. Found: 192.1161 (M^+).

1.4. (*E*)-1-(1-Triethylsilyl-1-propen-2-yl)-2,3-dimethylbenzene and (*E*)-1-(1-triethylsilyl-1-propen-2-yl)-3,4-dimethylbenzene

^{1}H-NMR (400 MHz, $CDCl_3$) δ *2,3-dimethyl isomer*: 0.69 (6H, q, *J*=8.0 Hz), 1.00 (9H, t, *J*=7.6 Hz), 2.06 (1H, m), 2.19 (3H, s), 2.27 (3H, s), 5.26 (1H, d, *J*=0.8 Hz), 6.91–6.96 (1H, m), 7.01–7.04 (2H, m); *3,4-dimethyl isomer*: 0.69 (6H, q, *J*=8.0 Hz), 0.98 (9H, t, *J*=7.6 Hz), 2.18 (3H, s), 2.25 (3H, s), 2.27 (3H, s), 5.79 (1H, s), 7.07 (1H, d, *J*=7.8 Hz), 7.20 (1H, dd, *J*=7.8, 2.0 Hz), 7.03 (1H, br s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ *2,3-dimethyl isomer*: 4.87, 7.82, 16.47, 20.60, 24.25, 125.05, 125.21, 124.89, 127.86, 131.83, 136.70, 148.01, 156.18; *3,4-dimethyl isomer*: 4.95, 7.82, 19.50, 20.01, 21.51, 122.56, 122.84, 126.67, 129.22, 135.52, 135.89, 142.12, 152.39. IR (neat, mixture of isomers) 2952, 2911, 2873, 1595, 1456, 1239, 1015, 811, 767, 733 cm^{-1}. MS (EI, 70 eV, mixture of isomers) *m/z* (%) 260 (6, M^+), 231 (100), 191 (19), 163 (23), 135 (19). HRMS (EI, 70 eV, mixture) Calcd for $C_{17}H_{28}Si$: 260.1959. Found: 260.1964 (M^+).

1.5. (*E*)-1-(1-Triethylsilyl-1-propen-2-yl)-2,3,4-trimethylbenzene and (*E*)-1-(1-triethylsilyl-1-propen-2-yl)-3,4,5-trimethylbenzene

^{1}H-NMR (400 MHz, $CDCl_3$) δ *2,3,4-trimethyl isomer*: 0.68 (6H, q, *J*=7.9 Hz), 1.00 (9H, t, *J*= 7.9 Hz), 2.05 (3H, d, *J*=0.9 Hz), 2.19 (3H, s), 2.22 (3H, s), 2.28 (3H, s), 5.25 (1H, q, *J*=0.9 Hz), 6.85 (1H, d, *J*= 7.7 Hz), 6.95 (1H, d, *J*=7.7 Hz); *3,4,5-trimethyl isomer*: 0.69 (6H, q, *J*=7.9 Hz), 0.98 (9H, t, *J*=7.9 Hz), 2.16 (3H, s), 2.17 (3H, d, *J*=0.9 Hz), 2.30 (6H, s), 5.77 (1H, q, *J*= 0.7 Hz), 7.11 (2H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ *2,3,4-trimethyl isomer*: 4.75, 7.69, 15.78, 17.00, 20.65, 24.31, 124.21, 125.06, 126.78, 131.66, 134.33, 135.07, 146.03, 156.54; *3,4,5-trimethyl isomer*: 4.75, 7.69, 15.16, 20.66, 21.39, 122.33, 124.62, 134.03, 135.81, 141.50, 152.54. IR (neat, mixture of

isomers) 2952, 2910, 2873, 1609, 1457, 1239, 1015, 815, 768, 735 cm^{-1}. MS (EI, 70 eV, mixture of isomers) *m/z* (%) 274 (6, M^+), 245 (100), 205 (17), 177 (24), 149 (20), 87 (21), 59 (13). HRMS (EI, 70 eV, mixture of isomers) Calcd for $C_{18}H_{30}Si$: 274.2115. Found: 274.2117 (M^+).

1.6. (*E*)-1-(1-Triethylsilyl-1-propen-2-yl)-2,4,6-trimethylbenzene

^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.68 (6H, q, J= 7.9 Hz), 1.00 (9H, t, J=7.9 Hz), 1.98 (3H, d, J=0.9 Hz), 2.21 (6H, s), 2.26 (3H, s), 5.21 (1H, q, J=0.9 Hz), 6.84 (2H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 4.92, 7.80, 19.72, 21.02, 23.20, 125.40, 127.88, 133.33, 135.23, 144.37, 154.68. IR (neat) 2952, 2911, 2873, 1615, 1457, 1236, 1015, 849, 776, 737 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 274 (15, M^+), 245 (100), 217 (26), 177 (17), 149 (15), 101 (30), 87 (29), 73 (20), 59 (23). HRMS (EI, 70 eV) Calcd for $C_{18}H_{30}Si$: 274.2115. Found: 274.2122 (M^+).

1.7. (*E*)-5-(1-Triethylsilyl-1-propen-2-yl)-1,2,3,4-tetrahydronaphthalene and (*E*)-6-(1-triethylsilyl-1-propen-2-yl)-1,2,3,4-tetrahydronaphthalene

^{1}H-NMR (400 MHz, $CDCl_3$, mixture of isomers) δ 0.68 (6H, q, J=7.9 Hz), 0.69 (6H, q, J=7.9 Hz), 0.98 (9H, t, J=7.7 Hz), 1.00 (9H, t, J=7.9 Hz), 1.74–1.81 (4H, m), 2.05 (3H, d, J=0.9 Hz), 2.18 (3H, d, J=0.7 Hz), 2.67–2.82 (4H, m), 5.26 (1H, d, J= 0.9 Hz), 5.79 (1H, d, J=0.7 Hz), 6.88 (1H, br d, J=7.5 Hz), 6.95 (1H, br d, J=7.5 Hz), 7.01 (1H, d, J=8.1 Hz), 7.05 (1H, t, J=7.5 Hz), 7.16 (1H, br s), 7.20 (1H, dd, J=7.9, 2.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$, mixture of isomers) δ 4.85, 4.94, 7.82, 21.49, 23.20, 23.43, 23.46, 23.61, 23.91, 27.18, 29.24, 29.70, 30.07, 122.54, 122.65, 124.36, 124.99, 125.08, 125.97, 127.39, 128.69, 132.58, 136.21, 136.46, 137.02, 141.71, 147.87, 152.46, 155.62. IR (neat, mixture of isomers) 2951, 2873, 1595, 1458, 1239, 1015, 806, 758 cm^{-1}. MS (EI, 70 eV, mixture of isomers) *m/z* (%) 286 (15, M^+), 257 (100), 189 (16), 169 (22), 115 (27), 101 (22), 87 (35), 59 (26). HRMS (EI, 70 eV, mixture of isomers) Calcd for $C_{19}H_{30}Si$: 286.2115. Found: 286.2112 (M^+). Treatment of the isomeric mixture (1:1) with $RuCl_3$ (4 mol%) and $NaIO_4$ (CCl_4, CH_3CN and H_2O; rt, 2 h)[7] gave 5-acetyl-1,2,3,4-tetrahydronaphthalene (43%) and 6-acetyl-1,2,3,4-tetrahydronaphthalene (42%). **5-Acetyl-1,2,3,4-tetrahydronaphthalene:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.74–1.80 (4H, m), 2.55 (3H, s), 2.79–2.84 (2H, m), 2.92–2.98 (2H, m), 7.15 (1H, t, J=7.4 Hz), 7.19 (1H, d, J=7.8 Hz), 7.43 (1H, dd, J=7.8, 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 22.57, 23.24, 27.81, 30.26, 30.31, 124.81, 126.12, 132.41, 136.59, 138.46, 138.51, 202.67. IR (neat) 2929, 2857, 1683, 1450, 1354, 1259, 1122, 776 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 174 (62, M^+), 159 (100), 131 (71), 91 (44). HRMS (EI, 70 eV) Calcd for $C_{12}H_{14}O$: 174.1044. Found: 174.1049 (M^+). **6-Acetyl-1,2,3,4-tetrahydronaphthalene:** ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.79–1.84 (4H, m), 2.57 (3H, s), 2.78–2.84 (4H, m), 7.14 (1H, d, J=8.4 Hz), 7.64–7.69 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 22.94, 23.08, 26.65, 29.47, 29.73, 125.27, 129.06, 129.15, 134.54, 137.24, 143.00, 197.88. IR (neat) *n*/cm^{-1} 2930, 2857, 1682, 1605, 1416, 1357, 1270, 830 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 174 (43, M^+), 159 (100), 131 (26), 91 (29). HRMS (EI, 70 eV) Calcd for $C_{12}H_{14}O$: 174.1044. Found: 174.1037 (M^+).

1.8. (*E*)-1-(1-Triethylsilyl-1-propen-2-yl)naphthalene and (*E*)-2-(1-triethylsilyl-1-propen-2-yl)naphthalene

^{1}H-NMR (400 MHz, $CDCl_3$, mixture of isomers) δ 0.72 (q, J= 7.7 Hz), 0.73 (q, J=7.7 Hz), 1.02 (t, J=7.7 Hz), 1.04 (t, J=7.7 Hz), 2.25 (d, J=0.9 Hz), 2.32 (d, J=0.7 Hz), 5.52 (t, J=0.9 Hz), 6.01 (s), 7.16 (s), 7.256 (d, J=7.0 Hz), 7.36–7.47 (m), 7.65 (dd, J=8.6, 1.9 Hz), 7.70 (d, J= 8.1 Hz), 7.74 (d, J=8.4 Hz), 7.79 (t, J=6.6 Hz), 7.84 (br s), 8.00 (dd, J=7.3, 1.9 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$, mixture of isomers) δ 4.77, 4.83, 7.77, 21.45, 24.64, 123.70, 123.98, 124.17, 124.67, 125.30, 125.48, 125.56, 125.67, 125.70, 125.99, 126.69, 127.40, 127.47, 128.21, 130.26, 132.69, 133.28, 133.73, 141.50, 146.05, 152.20, 154.14. IR (neat, mixture of isomers) 3056, 2952, 2872, 1590, 1457, 1378, 1236, 1015, 813, 763, 733 cm^{-1}. MS (EI, 70 eV, mixture of isomers) *m/z* (%) 282 (2, M^+), 253 (11), 168 (36), 153 (45), 128 (100). HRMS (EI, 70 eV, mixture of isomers) Calcd for $C_{19}H_{26}Si$: 282.1802. Found: 282.1795 (M^+). Treatment of the isomeric mixture (4:1) with $RuCl_3$ (4 mol%) and $NaIO_4$ (CCl_4, CH_3CN and H_2O; rt, 2 h)[7] gave a mixture of 2-acetylnaphthalene (59%) and 1-acetylnaphthalene (15%), the structures of which were confirmed by comparison with authentic samples.

1.9. Reaction of 1,2-undecadiene (8) and *p*-xylene

Under an argon atmosphere, to a stirred solution of *p*-xylene (0.32 ml, 2.5 mmol) in CH_2Cl_2 (3.75 mL) was added a solution of $GaCl_3$ (1.0 M in methylcyclohexane, 0.75 ml) at −78°C. Then, **8** (76 mg, 0.50 mmol) in CH_2Cl_2 (0.5 mL) was added, and after 5 min methymagnesium bromide (0.94 M in THF, 2.7 mL) was added. The mixture was warmed to 0°C, and stirring was continued for another 30 min at this temperature. The reaction was quenched by adding aqueous NH_4Cl. The organic layer was separated, dried over $MgSO_4$, and concentrated. The residue was purified by GPC to give a mixture of products (70 mg, 54%) containing (*E*)-**9** (X=H) (21%), (*Z*)-**9** (X=H) (18%), and (*E*)-**10** (15%). The yields were determined by ^{1}H-NMR. The stereochemistry was determined by NOE. (*E*)-**9** (X=H): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J=7.0 Hz), 1.24–1.44 (12H, m), 2.00 (2H, q, J=7.0 Hz), 2.24 (3H, s), 2.29 (3H, s), 3.26 (2H, d, J=6.4 Hz), 5.37–5.55 (2H, m), 6.92 (1H, br d, J= 7.9 Hz), 6.94 (1H, br s), 7.01 (1H, d, J=7.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.26, 18.99, 21.08, 22.81, 29.33, 29.42, 29.59, 29.62, 31.99, 32.67, 36.70, 126.54, 127.79, 129.59, 129.82, 131.72, 132.91, 135.14, 138.78. IR (neat) 2955, 2925, 2854, 1615, 1504, 1458, 1377, 968, 807 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 258 (31, M^+), 159 (11), 145 (100), 132 (61), 119 (68), 105 (23), 91 (22). HRMS (EI, 70 eV) Calcd for $C_{19}H_{30}$: 258.2346. Found: 258.2342 (M^+). (*Z*)-**9** (X=H): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J= 7.0 Hz), 1.24–1.44 (12H, m), 2.14 (2H, q, J=7.2 Hz), 2.25 (3H, s), 2.29 (3H, s), 3.32 (2H, d, J=5.9 Hz), 5.41–5.54 (2H, m), 6.92 (1H, br d, J=7.5 Hz), 6.96 (1H, br s), 7.02 (1H, d, J=7.7 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.26, 19.11, 21.10, 22.82, 27.47, 29.44, 29.50, 29.65, 29.77, 31.34, 32.01, 126.48, 127.35, 129.26, 129.81,

130.76, 132.79, 135.22, 139.05. IR (neat) 2955, 2925, 2854, 1615, 1503, 1458, 1377, 807 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 258 (31, M^+), 159 (10), 145 (100), 132 (68), 119 (89), 105 (27), 91 (29). HRMS (EI, 70 eV) Calcd for $C_{19}H_{30}$: 258.2346. Found: 258.2336 (M^+). (*E*)-**10**: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, t, *J*=7.0 Hz), 1.20–1.48 (12H, m), 1.89 (3H, dt, *J*=1.5, 0.7 Hz), 2.14 (2H, q, *J*=6.8 Hz), 2.22 (3H, s), 2.29 (3H, s), 5.26 (1H, tq, *J*=7.1, 1.5 Hz), 6.88 (1H, br s), 6.94 (1H, br d, *J*=7.9 Hz), 7.03 (1H, d, *J*=7.7 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.26, 18.06, 19.50, 21.02, 22.82, 28.37, 29.46 (2 carbons), 29.66, 29.71, 32.02, 126.87, 128.88, 129.49, 129.75, 131.48, 134.69, 135.71, 145.57. IR (neat) 2925, 2854, 1497, 1457, 1376, 808 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 258 (39, M^+), 243 (22), 159 (100), 146 (56), 133 (31), 119 (26). HRMS (EI, 70 eV) Calcd for $C_{19}H_{30}$: 258.2346. Found: 258.2356 (M^+).

1.10. Iodination

Under an argon atmosphere, to a stirred solution of *p*-xylene (0.32 mL, 2.5 mmol) in CH_2Cl_2 (3.75 mL) was added a solution of $GaCl_3$ (1.0 M in methylcyclohexane, 0.75 mL) at −78°C. Then, **8** (76 mg, 0.50 mmol) in CH_2Cl_2 (0.5 mL) was added, and after 5 min methylithium (1.14 M in Et_2O, 2.1 mL) was added. The mixture was stirred for another 30 min at this temperature. Iodine (1.27 g, 5 mmol) in THF (5 mL) was added and, after being warmed to room temperature, stirring was continued for 30 min. The reaction was quenched by adding sat. aqueous Na_2SO_3. The organic layer was separated, dried over $MgSO_4$, and concentrated. The residue was purified by GPC to give a product (77 mg, 45%), which contains (*E*)-**9** (X=I) (13%), (*Z*)-**9** (X=I) (15%), (*E*)-**10** (12%), and **9** (X=H) (5%). The yields were determined by ^{1}H-NMR. The stereochemistry was determined by NOE. The authentic samples were obtained by flash column chromatography on silica gel. (*Z*)-**9** (X=I): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J*=6.8 Hz), 1.20–1.42 (12H, m), 2.12 (2H, q, *J*= 7.2 Hz), 2.22 (3H, s), 2.30 (3H, s), 3.79 (2H, s), 5.32 (1H, tt, *J*=6.8, 1.1 Hz), 6.95 (1H, br s), 6.98 (1H, br d, *J*= 7.9 Hz), 7.04 (1H, d, *J*=7.7 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.26, 19.08, 21.08, 22.80, 28.43, 29.27, 29.35, 29.52, 31.96, 36.56, 49.37, 105.92, 127.45, 130.02, 130.55, 133.37, 135.16, 135.83, 136.78. IR (neat) 2923, 2854, 1503, 1457, 1377, 809 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 384 (21, M^+), 257 (8), 159 (16), 145 (53), 131 (25), 119 (100). HRMS (EI, 70 eV) Calcd for $C_{19}H_{29}I$: 384.1311. Found: 384.1310 (M^+). This compound (*Z*)-**9** (X=I) (15 mg, 40 μmol) was treated with *t*-BuLi (1.5 M in pentane, 0.03 mL) in Et_2O at −90°C followed by water giving (*E*)-**9** (X=H) (7 mg, 67%). (*E*)-**9** (X=I): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J*=6.8 Hz), 1.20–1.44 (12H, m), 2.14 (2H, q, *J*=7.6 Hz), 2.23 (3H, s), 2.31 (3H, s), 3.71 (2H, s), 6.40 (1H, t, *J*=7.2 Hz), 6.95 (1H, br s), 6.98 (1H, br d, *J*=7.6 Hz), 7.04 (1H, d, *J*=7.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.25, 19.31, 21.20, 22.78, 29.13, 29.30, 29.34, 29.50, 31.27, 31.95, 41.51, 99.65, 127.21, 129.25, 129.92, 133.09, 135.20, 136.08, 142.83. IR (neat) 2924, 2854, 1616, 1503, 1457, 1377, 808 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 384 (53, M^+), 257 (8), 159 (15), 145 (42), 131 (18), 119 (100), 106 (85). HRMS (EI, 70 eV) Calcd for $C_{19}H_{29}I$: 384.1311. Found: 384.1306 (M^+). This compound (*E*)-**9** (X=I) was converted to (*Z*)-**9** (X=H) as above.

1.11. Deuteration experiment

Under an argon atmosphere, to a stirred solution of *p*-xylene (0.64 mL, 5.0 mmol) in CH_2Cl_2 (3.0 mL) was added a solution of $GaCl_3$ (1.0 M in methylcyclohexane, 1.0 mL) at −78°C. Then, **8** (152 mg, 1.0 mmol) in CH_2Cl_2 (1.0 mL) was added, and after 5 min methymagnesium bromide (0.94 M in THF, 2.7 mL) was added. The mixture was warmed to 0°C, and stirred for a further 30 min at this temperature. The reaction was quenched by adding D_2O (3 mL). The organic materials were extracted with hexane, dried over $MgSO_4$, and concentrated. The residue was purified by GPC to give a mixture of isomers (77 mg, 30%) containing **9** (X=D) and (*E*)-**10** in a 4:1 ratio. The mixture was treated with excess O_3 in CH_2Cl_2-MeOH (3:2) at −78°C, and $NaBH_4$ (190 mg, 5 mmol) at −78°C to r.t. to give 2-(2,5-dimethylphenyl)ethanol (22 mg, 68 % deuteration at 1-position), 1-(2,5-dimethylphenyl)ethanol (4 mg, no deuteration), and 1-nonanol (26 mg, no deuteration). The deuteration ratio was determined by D-NMR.

1.12. 1-(2-Triethylsilylethyl)-2,4-dimethylbenzene (13)

Under an argon atmosphere, to a stirred solution of *m*-xylene (2.5 mL, 20 mmol) in CH_2Cl_2 (9 mL) was added a 1.0 M solution of $GaCl_3$ in methylcyclohexane (2 mL) at −90°C. Then, triethylsilylethene (**12**) (142 mg, 1.0 mmol) in CH_2Cl_2 (1 mL) was added. After being stirred for 30 min at this temperature, methyllithium (4 mmol) in ether (3.6 mL) was added. Water was added, and the mixture was extracted with hexane. The organic layer was dried over $MgSO_4$, and concentrated. Silica gel flash chromatography gave **13** (18 mg, 7%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.58 (6H, q, *J*=8.0 Hz), 0.78–0.83 (2H, m), 0.98 (9H, t, *J*=8.0 Hz), 2.27 (3H, s), 2.29 (3H, s), 2.52–2.56 (2H, m), 6.95 (1H, d, *J*=6.0 Hz), 6.96 (1H, s), 7.06 (1H, d, *J*=8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 3.45, 7.64, 12.86, 19.17, 20.99, 27.07, 126.51, 127.74, 130.79, 134.80, 134.90, 140.63. IR (neat) 2952, 2875, 1504, 1457, 1416, 1238, 1173, 1015, 824, 784, 731 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 248 (9, M^+), 219 (100), 191 (39), 163 (32), 135 (9), 115 (10), 87 (58), 59 (36). HRMS (EI, 70 eV) Calcd for $C_{16}H_{28}Si$: 248.1959. Found: 248.1966 (M^+).

1.13. Reaction of *p*-xylene and 1-hexene (14)

Under an argon atmosphere, to a stirred solution of *p*-xylene (2.5 mL, 20 mmol) in CH_2Cl_2 (10 mL) was added a 1.0 M solution of $GaCl_3$ in methylcyclohexane (0.1 mL) at −50°C. Then, **14** (0.13 mL, 1.0 mmol) was added, and the mixture was stirred for 1 h at this temperature. THF (4 mL) was added, and stirring was continued for 30 min. Then, water was added, and the organic materials were extracted with hexane. The organic layer was dried over $MgSO_4$, and concentrated. Silica gel chromatography and GPC gave 1-(2-hexyl)-2,5-dimethylbenzene (**15**) (40 mg, 21%) and 1-(3-hexyl)-2,5-dimethylbenzene (**16**) (35 mg, 18%). 15: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.87 (3H, t, *J*=7.2 Hz), 1.18 (3H, d, *J*=6.8 Hz), 1.25 (6H, m), 2.27 (3H, s), 2.31

(3H, s), 2.91 (1H, q, J=6.8 Hz), 6.75 (1H, d, J=7.6 Hz), 6.86 (1H, s), 6.88 (1H, d, J=7.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.22, 19.24, 21.35, 21.68, 23.02, 30.16, 34.48, 37.71, 125.86, 125.92, 129.86, 131.95, 135.19, 145.81. IR (neat) 2958, 2927, 2858, 1503, 1457, 806, 469 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 190 (17, M^+), 133 (100), 119 (13), 105 (5), 57 (12). HRMS (EI, 70 eV) Calcd. for $C_{14}H_{22}$: 190.1720. Found: 190.1730 (M^+). 16: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.78 (3H, t, J=7.4 Hz), 0.85 (3H, t, J=7.4 Hz), 1.11–1.31 (2H, m), 1.47–1.71 (4H, m), 2.26 (3H, s), 2.30 (3H, s), 2.71–2.79 (1H, m), 6.87 (1H, dd, J=7.6, 1.6 Hz), 6.94 (1H, s), 7.00 (1H, d, J=7.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 12.25, 14.51, 19.69, 20.83, 21.36, 29.63, 38.87, 41.57, 125.91, 126.25, 129.85, 132.94, 135.02, 144.07. IR (neat) 2957, 2929, 2871, 1503, 1457, 879, 806 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 190 (28, M^+), 161 (19), 147 (44), 133 (19), 119 (100), 105 (6). HRMS (EI, 70 eV) Calcd for $C_{14}H_{22}$: 190.1720. Found: 190.1719 (M^+).

1.14. NMR experiment

Under an argon atmosphere, a solution of **1** (46 mg, 0.30 mmol) in CD_2Cl_2 (0.3 mL) was cooled to −85°C in an NMR sample tube. A solution of $GaCl_3$ (1.0 M in CD_2Cl_2, 0.3 mL) was then added. The mixture was gently shaken at this temperature until white crystals of $GaCl_3$ disappeared, and the solution turned orange. ^{1}H-NMR (400 MHz, CD_2Cl_2, −85°C)δ 0.6–0.8 (m), 0.9–1.0 (m), 4.52 (2H, br s), 5.5–6.2 (1H, br). ^{13}C-NMR (100 MHz, CD_2Cl_2) δ 2.55, 5.56, 5.99, 74.55. A solution of **1** (31 mg, 0.20 mmol) in CD_2Cl_2 (0.2 mL) was cooled to −85°C in an NMR sample tube. A solution of $GaCl_3$ (1.0 M in CD_2Cl_2, 0.4 mL) was then added. The mixture was gently shaken at this temperature until white crystals of $GaCl_3$ disappeared, and the solution turned orange. ^{1}H-NMR (400 MHz, CD_2Cl_2, −85°C) δ 0.7–1.0 (m), 4.49 (2H, s), 6.12 (1H, s). ^{13}C-NMR (100 MHz, CD_2Cl_2) δ 3.32, 5.53, 5.58, 5.92, 72.15, 222.33.

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