Alkylpotassium-Catalyzed Benzylic C–H Alkylation of Alkylarenes with Alkenes

Io Sato
Yasuhiro Yamashita*
Shū Kobayashi*
0000-0002-8235-4368
Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan
shu_kobayashi@chem.s.u-tokyo.ac.jp
yyamashita@chem.s.u-tokyo.ac.jp

Abstract Catalytic benzylic C–H alkylation reactions of alkylarenes with alkenes such as β-substituted styrenes and vinylsilanes have been achieved by utilizing alkylpotassium as a catalyst. Various substituted toluene derivatives can be alkylated under mild reaction conditions to afford the desired functionalized hydrocarbons in moderate to high yields.

Key words strong base, alkylarene, alkylation, alkylpotassium, alkene

Catalytic benzylic C–H functionalization of alkylarenes, such as toluene and xylene, toward C–C bond formation is among the most simple and efficient methods for the introduction of a benzyl moiety into complex organic molecules, such as pharmaceuticals and natural products, because alkylarenes are abundant, inexpensive, and easy-to-handle starting materials.1 In the past several decades, chemists have developed these types of reactions, and one general approach is benzylic C–H activation of alkylarenes to produce benzylic radical intermediates (Scheme 1a, top panel).1,2 Although many types of transition-metal-catalyzed reactions have been achieved, there are several disadvantages, such as harsh reaction conditions and the use of excess amounts of oxidants (e.g., tert-butyl hydroperoxide). Alternative reactions (carbene insertion,3 photocatalysis,4 Ru-catalyzed condensation5) were also reported, but precious and toxic transition metals were required as catalysts. Therefore, much milder, atom-economical, and efficient reactions are in high demand.6 Brønsted base catalyzed C–C bond formation is one of the most ideal methods for the construction of carbon frameworks because of the high efficiency and atom-economy of the approach.7 Although there are thousands of Brønsted base-catalyzed C–C bond forming reactions reported, there is a severe limitation with respect to the acidity of the hydrogen of pro-nucleophiles (pKₐ <25). As for toluene (pKₐ value of benzylic hydrogen ca. 43),8 stoichiometric amounts of strong base species such as Schlosser’s base9 are required for the functionalization of toluene via benzylic anionic species (Scheme 1a, bottom panel).

Recently, our group has made an effort to break this limitation by focusing on the basicity of reaction intermediates.10,11 By using this strategy, we have reported the strong Brønsted base-catalyzed addition reactions of esters,11a,b amides,11c nitriles,11d alkylaza-arenes,11e and so on. Quite recently, we have developed potassium tert-butoxide/lithium tetramethylpiperidide (KOT-Bu/LiTMP) mixed base-catalyzed addition reactions of alkylarenes with N-alkylamines (Scheme 1b).12 In this reaction, a highly basic reaction intermediate (N-dialkylamide) functions as a base to deprotonate...
a benzylic hydrogen of the alkylarene (or a conjugate acid of KOt-Bu/LiTMP mixed base) to promote a catalytic turnover. We next turned our attention to alkenes, especially styrene derivatives as electrophiles, by which formal alkylation of the benzylic positions of alkylarenes might be achieved.

As pioneering work, Pines et al. reported sodium or potassium metal-catalyzed addition reactions of alkylarenes with styrene derivatives. These reactions required elevated temperature, and poor-to-moderate yields of the desired mono-adducts were obtained due to production of polymeric by-products. Screttes et al. reported Li/K/Mg mixed base-catalyzed alkylation of alkylarenes with ethylene under high-pressure conditions. However, substrates were limited to methylated benzenes such as toluene derivatives and xylenes. Herein, we describe strong Brønsted base catalyzed addition reactions of alkylarenes with alkenes under mild reaction conditions to afford the desired functionalized hydrocarbons (Scheme 1c).

Initially, in the presence of 30 mol% KOt-Bu/LiTMP, the addition reaction of toluene (1a) with styrene (2) was conducted (Table 1, entry 1). It was found that only a trace amount of the desired product was obtained, and oligomers derived from styrenes were observed. To suppress the oligomerization, trans-stilbene (2a) was used as an electrophile, and then the desired product (3aa) was obtained in 47% yield, while the by-product 3′ was obtained in 12% yield (entry 2). To increase the reactivity and the selectivity between the product and the by-product, further optimization was conducted. First, N,N,N′,N′-tetramethylethylenediamine (TMEDA) was added to the reaction as a ligand to obtain the desired product in 86% yield (entry 3). The catalyst loading could be reduced to 10 mol% without any reduction in the yield (entry 4). N,N,N′,N′-Pentamethyldiethylenetriamine (PMDTA) as a ligand gave a slightly increased yield compared with TMEDA (entry 5). Next, several solvents were tested for the reaction; the reaction in cyclopentyl methyl ether (CPME) showed the best selectivity.

Biographical Sketches

Io Sato is a graduate student in the Department of Chemistry, Graduate School of Science, the University of Tokyo, Japan. He obtained his B.Sc. and M.Sc. degrees under the supervision of Prof. Shū Kobayashi in 2014 and 2016, respectively. Now he is working as a Ph.D. course student in the same group. His research focuses on C–C bond forming reactions using inert compounds catalyzed by strong Brønsted bases.

Yasuhiro Yamashita studied chemistry at the Graduate School of Pharmaceutical Sciences, The University of Tokyo, and received his Master degree in 1998 (supervisor, the late Professor Kenji Koga) and his Ph.D. degree in 2001 (supervisor, Professor Shū Kobayashi). He started his academic career as an assistant professor in 2001 in the Graduate School of Pharmaceutical Sciences, the University of Tokyo. He then joined Professor John F. Hartwig’s group at Yale University as a postdoctoral fellow (2005-2006). He returned to the University of Tokyo and was promoted to an associate professor in the Department of Chemistry, School of Science (2007).

Shū Kobayashi studied at the University of Tokyo, receiving his Ph.D. degree in 1988 working under the direction of Professor Teruaki Mukaiyama. Following an initial period as assistant professor, he was promoted to lecturer then associate professor at the Science University of Tokyo. In 1998, he moved to the Graduate School of Pharmaceutical Sciences, The University of Tokyo, as full professor. In April 2007, he was appointed to his current position as professor of organic chemistry in the Department of Chemistry, within the Faculty of Science of The University of Tokyo.
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Feature

Table 1  Optimization of the Reaction Conditionsa

<table>
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<th>Entry</th>
<th>R</th>
<th>A (equiv)</th>
<th>x (mol%)</th>
<th>Additive</th>
<th>Solvent</th>
<th>Yield (%) of 3aa</th>
<th>Yield (%) of 3’a</th>
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<td>PMDTA</td>
<td>CPME</td>
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*a The reaction of 1a with 2 (0.3 mmol) was conducted in the presence of KOt-Bu, LiTMP, and an additive at r.t. for 24 h, unless otherwise noted.

b NMR yield.
c Time: 18 h.
d Time: 13 h.
e Conditions: 20 mol% of PMDTA, 0.8 M, 0 °C.

toward the product (entry 8). Finally, a higher ligand loading (20 mol%), higher concentration, and lower reaction temperature gave the desired product in 98% yield (entry 9). To check the effect of substituents on the aromatic ring of the nucleophile, the addition reaction of p-methoxy-substituted toluene, p-methylanisole (1b), as a nucleophile was conducted under the optimal reaction conditions. However, although the electrophile was completely consumed, the desired product 3ba was obtained in only 32% yield and the reaction system became complex (Table 2, entry 1). Analysis of the by-products revealed that the aryl-exchanged products 3ba’ and 3aa were produced.

For the mechanism of by-product formation, it was assumed that the substituted stilbene and the benzyl anion of toluene were produced through a deprotonation/elimination pathway of the product, and then the substituted stilbene was attacked by a second nucleophilic benzyl anion of 1b to form by-product 3ba’, and the benzyl anion of toluene attacked another stilbene to form by-product 3aa (Scheme 2). Similar phenomena were also observed in the reactions of other nucleophiles. To suppress this by-product formation, screening of strong base catalysts was conducted, and it was found that, in the presence of catalytic amounts of (trimethylsilyl)methylpotassium (KCH2TMS) and PMDTA as a strong base catalyst and a ligand, respectively, by-product formation was suppressed, and the desired product was obtained in 79% yield (Table 2, entry 2). Potassium amide generated in situ as a catalyst gave almost the same result (entry 3). On the other hand, in the presence of lithium cations, the yield of the desired product decreased, and by-

Table 2  Screening of Base Catalysts4

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield (%) of 3ba</th>
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<tr>
<td>1</td>
<td>KOt-Bu (10 mol%) PMDTA (20 mol%)</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>KCH2TMS (10 mol%) PMDTA (20 mol%)</td>
<td>79</td>
</tr>
<tr>
<td>3</td>
<td>KCH2TMS (10 mol%) H–TMP (10 mol%) PMDTA (10 mol%)</td>
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</tr>
<tr>
<td>4</td>
<td>KCH2TMS (10 mol%) LiTMP (10 mol%) PMDTA (20 mol%)</td>
<td>26</td>
</tr>
<tr>
<td>5</td>
<td>KCH2TMS (10 mol%) LiOt-Bu (10 mol%) PMDTA (20 mol%)</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>KCH2TMS (2 mol%) PMDTA (2 mol%)</td>
<td>86 (78)c</td>
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*a The reaction of 1b (4.0 equiv) with 2 (0.3 mmol) in CPME (0.8 M) was conducted in the presence of a catalyst at 0 °C for 18 h, unless otherwise noted.

b NMR yield.
c Isolated yield.

(continued)
product formation was accelerated (entries 4 and 5). These results implied that the presence of lithium cations facilitated by-product formation, probably because altering the aggregation states of the reaction intermediates enhanced their basicity and facilitated a deprotonation/elimination pathway leading to by-product formation.20 Finally, the catalyst loading could be reduced to 2 mol% KCH2TMS and PMDTA to afford the desired product in 78% isolated yield (entry 6).

Scheme 2  Assumed pathway for by-product formation

The catalytic addition reactions of various substituted alkylarenes with stilbenes were then investigated (Scheme 3). Under the neat Condition A, the product 3aa was obtained in high yield with only 1 mol% catalyst. The reactions of methoxy- or fluoro-substituted toluene derivatives were conducted in CPME as solvent (Condition B). Both o- and m-methoxy-substituted toluenes gave the desired products 3ba and 3ca, respectively, in high yields. Unfortunately, p-methoxytoluene showed lower reactivity and selectivity toward the desired product, and the desired product was obtained in up to ca. 30% yield under several modified reaction conditions, probably because of the low acidity of the benzylic hydrogen. Disubstituted toluene was also subjected to the reaction conditions. The reaction of 3,5-dimethylanisole was conducted to afford the product 3da in moderate yield. The low nucleophilicity and low durability of fluoro-substituted toluene under strongly basic reaction conditions meant that higher catalyst loading and a slightly lower reaction temperature were required for their reactions to afford the desired products 3ea and 3fa in moderate-to-good yields. For the reactions of xylenes, neat conditions (Condition A) were adopted. The reaction of o- and m-xylene proceeded smoothly to afford the desired compounds 3ga and 3ha in high yields with 1 or 2 mol% catalyst.

p-Xylene showed lower reactivity; in this case, elevated temperature and prolonged reaction time gave the desired compound 3ia in moderate yield. The reaction with p-isopropyltoluene was sluggish, and 5 mol% catalyst was required to obtain the desired compound 3ja in moderate yield. The reaction of ethylbenzene in the presence of 10 mol% catalyst afforded almost quantitative amounts of the product 3ka with moderate diastereoselectivity.

Reactions of toluene with disubstituted symmetrical stilbene derivatives 2 were then conducted (Scheme 4). 4-tert-Butyl- and 3-methoxy-substituted stilbenes were good substrates and afforded the products 3ab and 3ac in high

Scheme 3  Substrate scope of the reaction with respect to nucleophiles
yields. For the reaction of 4-methoxy-substituted stilbene, a higher reaction temperature was required because of the low electrophilicity of the substrate; the use of KOT-Bu/LiTMP as catalyst also gave a higher yield compared with the reactions with KCH₂TMS, affording the product 3ad in excellent yield. The latter result probably stems from the higher stability of the catalytic species derived from KOT-Bu/LiTMP at high temperature. 1-Naphthyl-substituted alkene exhibited lower reactivity; nevertheless, conducting the reaction for longer time gave compound 3ae in good yield. The addition reactions of alkylarenes with unsymmetrical stilbenes were also examined. For the unsymmetrical stilbenes, two regioisomers, α- and β-adducts, are possible.

The reactions of toluene with 4-methoxy-substituted stilbene gave the β-adduct 3af in high yield and with high regioselectivity. The selectivity could be attributed to the lower stability of the α-adduct reaction intermediate compared with that of the β-adduct because of the electron-donating 4-methoxy group. Both o- and m-methoxytoluene derivatives were good substrates, affording the desired hydrocarbons 3bf and 3cf, respectively, in high yields and with high selectivities. On the other hand, the use of 2-methoxy-substituted stilbene resulted in lower regioselectivity (ratio of α-adduct 3ba to β-adduct 3ag, 2.2:1), probably because of steric hindrance and the coordination ability of the 2-methoxy group. The reaction of β-naphthyl-substituted styrene was sluggish; in this case, prolonging the...
reaction time gave adduct 3ah in high yield with excellent regioselectivity for the α-adduct. In addition to stilbene derivatives, the use of β-alkyl-substituted styrenes was also examined. Due to the lower electrophilicity and the presence of allylic hydrogen atoms that can be deprotonated, higher reaction temperature and KOt-Bu/LiTMP were applied to afford the β-adducts 3ai and 3aj in poor-to-good yields with complete regioselectivities.

Vinylsilanes were also suitable electrophiles for the catalytic addition reaction, because the α-silyl anion, which is a reaction intermediate formed upon nucleophilic addition to vinylsilane, could deprotonate a benzyl hydrogen of alkylarene to produce a nucleophilic benzyl anion. The addition reaction of toluene with triphenyl- and phenyldimethylvinylsilanes proceeded smoothly in the presence of 10 mol% KCH₂TMS and PMDTA to give alkylsilanes 5aa and 5ab, respectively, in high yields. The reaction of m-methoxytoluene with phenyldimethylvinylsilane also proceeded to afford the product 5cb in good yield (Scheme 5). To gain insight into the mechanism of the reaction, the kinetic isotope effect was measured with toluene and toluene-d₈ (Scheme 6). The observed primary KIE value (5.3) indicated that deprotonation of a benzyl hydrogen from toluene was the rate-determining step.

The assumed reaction mechanism is shown in Scheme 7. First, KCH₂TMS ligated with PMDTA deprotonates a benzyl hydrogen of the alkylarene to form a potassiumbenzyl species. Nucleophilic addition to the alkene occurs to produce an alkylpotassium species, which possess relatively strong basicity. This reaction intermediate then deprotonates another benzyl hydrogen of a second alkylarene to afford the products and the next nucleophilic species. Thereby, the addition reaction proceeds with only a catalytic amount of KCH₂TMS and the ligand.

In summary, we have achieved alkylpotassium-catalyzed addition reactions of alkylarenes with several alkenes. KCH₂TMS with PMDTA as a catalytic species showed suitable reactivity and selectivity for the reaction, and allowed much milder reaction conditions and a broader substrate scope. Further investigations of alkylpotassium-catalyzed reactions are under way in our laboratory.

1H and 13C NMR spectra were recorded with JEOL JNM-ECA500 and JNM-ECX600 spectrometers in CDCl₃, unless otherwise noted. TMS served as internal standard (δ = 0) for 1H NMR, and CDCl₃ served as internal standard (δ = 77.0) for 13C NMR. Benzotrifluoride (BTF)
served as internal standard (δ = -63.72) for 19F NMR. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer. Preparative TLC (PTLC) was carried out with Wakogel B-5F. KOR-Bu was purchased from Wako Pure Chemical Industries, Ltd. Lithium 2,2,6,6-tetramethylpiperidizide (LiTMP) was purchased from Aldrich Co., Ltd. Trimethylisilylmethylpotassium ([KCH₂TMS]) was prepared according to a reported procedure. TMEDA and PMDTA were purchased from Tokyo Chemical Industry Co., Ltd. Heptane was purchased from Aldrich Co., Ltd, and distilled just before use in the presence of benzophenone and Na. Alkylarenes were purchased from Tokyo Chemical Industry Co., Ltd., and distilled with CaH. Electrofries were prepared according to reported methods. Detailed information is provided in the Supporting Information.

Catalytic Addition Reaction of Alkylarenes 1 with Alkenes 2 (Condition A); Propene-1,2,3-triylibenzene (3aa); Typical Procedure (Scheme 3)

KCH₂TMS (3.8 mg, 3.0 × 10⁻² mmol) and alkene 2a (540.4 mg, 3.0 mmol) were placed in a flame-dried 20 mL flask inside a glove box filled with argon, and alkylarene 1a (7.5 mL) and PMDTA (6.3 µL, 3.0 × 10⁻² mmol) were subsequently added at -78 °C using a well-dried syringe, and the mixture was stirred for 24 h at 0 °C. The reaction was quenched by adding H₂O (2 mL) and the aqueous phase was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layers were dried (anhyd Na₂SO₄). After filtration and concentration under reduced pressure, the crude product was obtained by flash column chromatography on silica gel (hexane/CH₂Cl₂ 20:1) to afford the desired product 3aa: yield: 710.1 mg (2.61 mmol, 87%)

[3-(2-Methoxyphenyl)propane-1,2-diyl]dibenzene (3ba); Typical Procedure (Scheme 3)

KCH₂TMS (3.8 mg, 3.0 × 10⁻² mmol) and alkene 2a (271.0 mg, 1.5 mmol) were placed in a flame-dried 10 mL flask inside a glove box filled with argon, and PMDTA (0.75 mL, 1.2 × 10 mmol, 4.0 equiv) and PMDTA (6.2 µL, 3.0 × 10⁻² mmol) were subsequently added at -78 °C using a well-dried syringe, and the mixture was stirred for 18 h at 0 °C. The reaction was quenched by adding H₂O (2 mL) and the aqueous phase was extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layers were dried (anhyd Na₂SO₄). After filtration and concentration under reduced pressure, the crude product was obtained by PTLC (hexane/CH₂Cl₂ 8:1 × 3) to afford the desired product 3ba: yield: 351.6 mg (1.16 mmol, 78%)

Propane-1,2,3-triylibenzene (3aa)
Condition A; scale: 3.0 mmol; catalyst loading: 1 mmol; temperature: 0 °C; time: 24 h; colorless oil; yield: 710.1 mg (87%); Rf = 0.2 (hexane/CH₂Cl₂ 20:1)
IR (neat): 3061, 3027, 2924, 2853, 1601, 1495, 1449, 1075, 1031 cm⁻¹
¹H NMR (CDCl₃, 600 MHz): δ = 7.14–7.11 (6 H, m), 7.06–7.03 (3 H, m), 6.97 (2 H, d, J = 8.25 Hz), 6.92 (4 H, d, J = 8.25 Hz), 3.08–3.03 (1 H, m), 2.92 (2 H, dd, J = 13.74, 6.18 Hz), 2.83 (2 H, dd, J = 13.75, 8.25 Hz)
¹³C NMR (CDCl₃, 150 MHz): δ = 144.22, 140.45, 129.11, 128.08, 128.03, 127.88, 126.10, 125.79, 49.87, 42.44
HRMS (Dart): m/z [M + H⁺] calcd for C₂₃H₂₅O: 317.19489; found: 317.19370

[3-(2-Methoxyphenyl)propane-1,2,3-diyl]dibenzene (3ba)
Condition B; scale: 1.5 mmol; catalyst loading: 2 mmol; temperature: 0 °C; time: 18 h; colorless oil; yield: 124.8 mg (66%); Rf = 0.1 (hexane/CH₂Cl₂ 3:1)
IR (neat): 3061, 3027, 2924, 2853, 1601, 1495, 1449, 1075, 1031 cm⁻¹
¹H NMR (CDCl₃, 600 MHz): δ = 7.14–7.08 (4 H, m), 7.06–7.00 (3 H, m), 6.97 (2 H, d, J = 7.56 Hz), 6.92 (2 H, d, J = 7.56 Hz), 6.45 (2 H, d, J = 7.56 Hz), 6.43 (1 H, s), 3.59 (3 H, s), 3.08–3.03 (1 H, m), 2.91–2.79 (4 H, m)
¹³C NMR (CDCl₃, 150 MHz): δ = 159.29, 144.23, 142.04, 140.41, 129.11, 128.95, 128.08, 128.02, 127.88, 126.11, 125.79, 121.55, 114.74, 111.27, 55.01, 49.72, 42.45, 42.42
HRMS (Dart): m/z [M + H⁺] calcd for C₂₃H₂₅O: 303.17489; found: 303.17370
[3-(3-Fluorophenyl)propane-1,2-diyl]dibenzone (3fa)

Condition A; scale: 1.0 mmol; catalyst loading: 2 mol%; temperature: –10 °C; time: 24 h; colorless oil; yield: 257.2 mg (90%);

IR (neat): 564, 696, 739, 778, 881, 909, 936, 959, 1031, 1072, 1249, 1452, 1486, 1588, 1602, 1615 cm⁻¹.

1H NMR (CDCl3, 500 MHz): δ = 7.21–7.09 (7 H, m), 7.04–7.00 (4 H, m), 6.80 (1 H, d, J = 8.50, 2.27 Hz), 6.74 (1 H, d, J = 6.67 Hz), 6.67 (1 H, d, J = 9.64 Hz), 3.13–3.10 (1 H, m), 2.95–2.90 (4 H, m).

13C NMR (CDCl3, 125 MHz): 149.30, 141.00, 138.12, 136.16, 130.06, 129.19, 129.11, 128.09, 128.04, 127.78, 126.12, 125.90, 125.80, 125.46, 48.63, 48.24, 38.39, 19.28.


[3-(p-Toly)propane-1,2-diyl]dibenzone (3ca)

Condition A; scale: 1.0 mmol; catalyst loading: 0.5 mol%; temperature: 0 °C; time: 24 h; colorless oil; yield: 257.2 mg (90%); Rf = 0.3 (hexane/CH2Cl2 9:1).

IR (neat): 564, 696, 739, 778, 881, 909, 936, 959, 1031, 1072, 1249, 1452, 1486, 1588, 1602, 1615 cm⁻¹.

1H NMR (CDCl3, 500 MHz): δ = 7.21–7.10 (6 H, m), 7.07–6.97 (7 H, m), 6.86 (1 H, d, J = 7.37 Hz), 3.08–2.94 (4 H, m), 2.84 (1 H, dd, J = 13.89, 8.22 Hz), 2.09 (3 H, s).

13C NMR (CDCl3, 125 MHz): 149.30, 141.00, 138.12, 136.16, 130.06, 129.19, 129.11, 128.09, 128.04, 127.78, 126.12, 125.90, 125.80, 125.46, 48.63, 48.24, 38.39, 19.28.


4,4′-(3-Phenylpropane-1,2-diyl)bis(tert-butylbenzene) (3ab)
Condition A; scale: 0.3 mmol; catalyst loading: 10 mol%; temperature: 0 °C; time: 18 h; white solid; yield: 115.7 mg (85%); mp 82–84 °C; R₆ = 0.5 (hexane/CH₂Cl₂ 4:1).
IR (neat): 599, 698, 746, 774, 789, 1395, 1453, 1495, 1509, 1596 cm⁻¹.
1H NMR (CDCl₃, 500 MHz): δ = 7.15–7.12 (4 H, m), 7.08–7.06 (2 H, m), 7.03–7.00 (1 H, m), 6.94–6.88 (6 H, m), 3.08–3.03 (1 H, m), 2.87–2.75 (4 H, m), 1.20 (9 H, s), 1.20 (9 H, s).


(2-[4-Methoxyphenyl]-1,3-diyl)dibenzo[248]
Condition A; scale: 0.6 mmol; catalyst loading: 5 mol%; temperature: 0 °C; time: 24 h; colorless oil; yield: 174.9 mg (96%); α: β = 1:12; R₆ = 0.1 (hexane/CH₂Cl₂ 4:1).
IR (neat): 546, 601, 698, 748, 824, 1031, 1105, 1176, 1243, 1300, 1535, 1495, 1510 cm⁻¹.
1H NMR (CDCl₃, 500 MHz): δ = 7.09–7.07 (4 H, m), 7.13–7.11 (2 H, m), 7.00–6.99 (4 H, m), 6.95–6.94 (2 H, m), 6.74–6.73 (2 H, m), 3.74 (3 H, s), 3.10–3.06 (1 H, m), 2.95 (2 H, dd, J = 6.61, 3.31 Hz), 2.86 (2 H, dd, J = 13.32, 8.22 Hz).
13C NMR (CDCl₃, 125 MHz): δ = 157.77, 140.56, 136.24, 129.11, 128.70, 128.01, 129.73, 113.42, 55.10, 48.99, 42.62.

1-Methoxy-2-[2-(4-methoxyphenyl)-3-phenylpropyl]benzene (3bf)
Condition B; scale: 0.6 mmol; catalyst loading: 5 mol%; temperature: 0 °C; time: 18 h; colorless oil; yield: 173.6 mg (87%); R₆ = 0.2 (hexane/CH₂Cl₂ 2:1).
IR (neat): 698, 729, 772, 808, 1029, 1078, 1243, 1355, 1495, 1509, 1596 cm⁻¹.
1H NMR (CDCl₃, 500 MHz): δ = 7.99–7.77 (3 H, m), 7.67 (2 H, d, J = 8.50 Hz), 7.58 (2 H, d, J = 7.94 Hz), 7.40 (4 H, tt, J = 24.37, 10.11 Hz), 7.20–7.02 (8 H, m), 4.34–4.32 (1 H, m), 3.62–3.60 (1 H, m), 3.44–3.42 (1 H, m), 3.16–3.14 (2 H, m).
13C NMR (CDCl₃, 125 MHz): δ = 141.28, 140.33, 136.19, 133.79, 132.04, 129.24, 128.75, 126.85, 126.63, 128.10, 126.96, 126.59, 125.96, 125.70, 125.43, 125.40, 125.24, 125.13, 125.10, 125.07, 123.57, 123.52, 122.62, 42.61, 41.08, 38.78.

1-Methoxy-3-[2-(4-methoxyphenyl)-3-phenylpropyl]benzene (3c)
Condition A; scale: 0.3 mmol; catalyst loading: 10 mol%; temperature: 0 °C; time: 24 h; colorless oil; yield: 174.9 mg (96%); α: β = 1:12; R₆ = 0.1 (hexane/CH₂Cl₂ 4:1).
IR (neat): 598, 696, 746, 772, 821, 908, 1011, 1029, 1109, 1176, 1243, 1290, 1345, 1452, 1495, 1510 cm⁻¹.
1H NMR (CDCl₃, 500 MHz): δ = 7.20–7.16 (4 H, m), 7.13–7.11 (2 H, m), 7.00–6.99 (4 H, m), 6.95–6.94 (2 H, m), 6.74–6.73 (2 H, m), 3.47 (3 H, s), 3.10–3.06 (1 H, m), 2.95 (2 H, dd, J = 6.61, 3.31 Hz), 2.86 (2 H, dd, J = 13.32, 8.22 Hz).
13C NMR (CDCl₃, 125 MHz): δ = 157.77, 140.56, 136.24, 129.11, 128.70, 128.01, 129.73, 113.42, 55.10, 48.99, 42.62.
1492, 1585, 1600 cm$^{-1}$.  
IR (neat): 508, 601, 695, 748, 1029, 1052, 1109, 1241, 1288, 1452, 1492, 1585, 1600 cm$^{-1}$.  

**Triphenyl(3-phenylpropyl)silane (5aa)**  
Condition A; scale: 0.3 mmol; catalyst loading: 10 mol%; temperature: 0 °C; time: 24 h; colorless oil; yield: 88.8 mg (78%); $R_f$ = 0.5 (hexane/CH$_2$Cl$_2$ 4:1).  
IR (neat): 512, 576, 696, 728, 772, 858, 906, 1029, 1028, 1108, 1395, 1426, 1452, 1495, 1509 cm$^{-1}$.  
$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 7.65 (6 H, d, $J$ = 6.80 Hz), 7.55–7.51 (9 H, m), 7.42–7.41 (2 H, m), 7.33 (1 H, t, $J$ = 7.37 Hz), 7.28 (2 H, d, $J$ = 7.37 Hz), 2.83 (2 H, t, $J$ = 7.37 Hz), 2.02–1.95 (2 H, m), 1.59–1.56 (2 H, m).  
$^1$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 141.13, 135.60, 135.10, 129.36, 128.56, 128.21, 127.83, 125.69, 39.71, 25.76, 12.81.  
HRMS (DART): $m/z$ [M + H]$^+$ calcd for C$_{36}$H$_{28}$N$_{3}$: 596.21475; found: 596.21406.  

**Dimethyl(phenyl)(3-phenylpropyl)silane (5ab)**  
Condition B; scale: 0.3 mmol; catalyst loading: 10 mol%; temperature: 0 °C; time: 24 h; colorless oil; yield: 66.6 mg (87%); $R_f$ = 0.4 (hexane).  
$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 7.51–7.49 (2 H, m), 7.35–7.35 (3 H, m), 7.27–7.26 (2 H, m), 7.19–7.15 (3 H, m), 2.62 (2 H, t, $J$ = 7.65 Hz), 1.67–1.63 (2 H, m), 0.82–0.79 (2 H, m), 0.26 (6 H, s).  
$^1$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 142.52, 139.37, 133.54, 128.79, 128.48, 128.19, 127.70, 126.51, 39.79, 25.98, 15.55, -3.08.  
Data are in accordance with the literature.$^{21}$  

**[3-(3-Methoxyphenyl)propyl][dimethyl(phenyl)silane (5cb)**  
Condition B; scale: 0.3 mmol; catalyst loading: 20 mol%; KOR-Bu and LiTMP were used instead of KCH$_2$TMS; temperature: 0 °C; time: 48 h; colorless oil; yield: 52.8 mg (72%); $R_f$ = 1.90.  
IR (neat): 3601, 3027, 2956, 2925, 2868, 1601, 1495, 1452, 1376, 1031 cm$^{-1}$.  
$^1$NMR (CDCl$_3$, 500 MHz): $\delta$ = 7.27–7.25 (4 H, m), 7.18–7.16 (2 H, m), 7.13–7.12 (4 H, m), 2.54 (4 H, d, $J$ = 6.24 Hz), 2.01–1.93 (1 H, m), 1.38–1.34 (2 H, m), 1.23–1.22 (2 H, m), 0.83 (3 H, t, $J$ = 7.37 Hz).  
$^1$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 141.39, 129.18, 128.12, 125.64, 41.65, 40.16, 35.06, 19.68, 14.27.  
HRMS (DART): $m/z$ [M + H]$^+$ calcd for C$_{38}$H$_{38}$N$_{2}$O$_{2}$Si: 525.20598; found: 525.20853.
References


(6) Quite recently, elegant visible light-mediated organocatalytic asymmetric addition reactions of toluene were reported, see: Mazzarella, D.; Cisenza, G. E. M.; Melchiorre, P. J. Am. Chem. Soc. 2018, 140, 8439.


(9) Schlosser, M. Pure Appl. Chem. 1988, 60, 1627.


(15) For preliminary results of catalytic addition reactions of toluene derivatives with β-substituted alkenes, see ref. 12.


