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Metal-Free and Recyclable Route to Synthesize Polysubstituted Olefins *via* C−C Bond Construction from Direct Dehydrative Coupling of Alcohols or Alkenes with Alcohols Catalyzed by Sulfonic Acid-Functionalized Ionic Liquids

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Abstract: A direct synthesis of polysubstituted olefins *via* construction of C−C bonds, which involves the direct dehydrative coupling of alcohols or alkenes with alcohols, was realized using a series of alkanesulfonic acid group-functionalized ionic liquids (SO_3H-functionlization ILs) without additives. The metal-free and recyclable catalyst system avoided the disposal and neutralization of acidic catalysts after reaction and tolerated a broad range of substrates, including benzylic, allyl, propargylic, aliphatic and aromatic or aliphatic olefins. Additionally, the catalytic system was suitable for a gram-scale preparation. Preliminary mechanistic studies indicated that the C−H bond cleavage in this reaction might be involved in the rate-determining step.

Keywords: alcohols; alkenes; C−C bond construction; direct dehydrative coupling; sulfonic acid-functionalized ionic liquids

Introduction

Nucleophilic substitution reactions of electrophiles with activated nucleophiles, such as thiols, amines, and indoles, are among the most powerful tools for the formation of carbon-carbon and carbon-heteroatom bonds.[1] Traditionally, activated electrophilic reagents (C−X, X = halide, tosylate, triflate, mesylate, etc.) with good leaving groups are usually used as the partner in this type of reaction.[2] However, the additional steps for synthesis of these reagents and the potential generation of stoichiometric amounts of wastes make such a protocol fairly unattractive. Apparently, the direct coupling of alcohols with various nucleophiles would be preferable because of its environmentally benign and atom-efficient features, since only H_2O is formed as a by-product.[3] In this context, the acid- or transition-metal-catalyzed Friedel–Crafts-type alkylation of alcohols with allyl, aryl, and alkynyl partners has been widely investigated and developed.[4] However, few examples for the direct dehydrative coupling of alcohols with simple alkenes to generate substituted alkenes, which possess biological activities or provide an opportunity for further functionalization, have been developed to date.

A seminal work on the direct coupling of alcohols and simple alkenes was reported by Muzart and coworkers, in which 2,3-dihydro-1-styryl-1*H*-indene was generated in low yield and the selectivity from 1-indanol and styrene was achieved by using $H_6P_2W_{18}O_{62}$ as the catalyst.[5] Yamamoto et al. developed the Pd(II)-catalyzed direct coupling of benzylic alcohols with styrenes by using PPh_3 as the ligand and $(CF_3CO)_2O$ as the additive.[6] Subsequently, Liu et al. developed $FeCl_3·6H_2O$-catalyzed direct dehydrative coupling of alcohols with aromatic olefins or alcohols in the presence of stoichiometric amounts of TsOH.[7] Liu et al. established a novel protocol for producing 4*H*-chromene derivatives *via* dehydrative coupling of the corresponding 2-(hydroxymethyl)phenols with ketene dithioacetals using $CuBr_2$ as the catalyst.[8] Yi and co-workers reported the selective coupling of alkenes with aliphatic alcohols *via* the vinyl C−H activation pathway with the cationic ruthenium complex $[(C_6H_6)(PCy_3)(CO)RuH]^+BF_4^-$ (Cy = cyclohexyl) as the sole catalyst.[9] Wang et al. reported the use of a $FeCl_3$-catalyzed propargylic substitution reaction to synthesize diarylalkenyl propargylic compounds directly from propargylic alcohols with 1,1-diarylalkenes.[10] Subsequently, Zhang, Pan and co-workers discovered that the propargylic substitution reaction could be extended to other terminal aromatic alkenes in the presence of catalytic amounts of $Cu(OTf)_2$.[11] More recently, two novel protocols for the direct coupling of various alcohols with alkenes have also been achieved by employing simple TfOH and $NaHSO_4/SiO_2$ as catalyst and promoter, respectively.[12] Despite these important achievements, the reported methods for the direct coupling of alcohols with alkenes suffered from difficult catalyst reusability, narrow substrate scope, transition metal utilization, and disposal of strong acidic catalysts after the reaction leading to the necessity of performing additional procedures.

Inspired by our previous research on the sulfonic acid-functionalized ionic liquids-catalyzed direct amination of alcohols[13] and previous reports on carbocation chemistry,[4c] we envisioned that the formed carbocation intermediate from an alcohol under the action of SO_3H-functionalized ionic liquids could participate in a nucleophilic addition of olefins to afford new carbon-carbon bonds with water as the only byproduct. In addition, the olefin coupling partner can be obtained *in situ* by the dehydration of the corresponding inexpensive and often easily available alcohols bearing H at the β position.

Based on the above mentioned hypothesis, a series of alkanesulfonic acid group-functionalized ionic liquids derived from pyrrolidine, imidazole, pyridine and guanidine was used as metal-free and recyclable catalysts to synthesize polysubstituted olefins from alcohols or alkenes with alcohols (Figure 1). Among the ionic liquid catalysts tested, [BsOdP][OTf] exhibited the best activity and could be reused at least six times without significant loss of activity, effectively avoiding the disposal and neutralization of the acidic catalysts after the reaction. Notably, the catalytic system has a wide substrate scope and various alcohols and alkenes including benzylic, allyl, propargylic, aliphatic alcohols, and aromatic, aliphatic alkenes could participate in the transformation. Moreover, it was found that C–H bond cleavage might be involved in the rate-determining step as indicated by intermolecular competing kinetic isotope effect (KIE) experiments.

Results and Discussion

Initially, we chose the direct dehydrative coupling between **1a** and **2a** as the model reaction and various reaction parameters have been screened, as shown in Table 1. A variety of ionic liquids derived from 1-methylimidazolium, guanidine, pyridine, pyrrolidine was first screened. The results indicated that [Bmim][BF_4] and [Bmim][PF_6] had no catalytic activities toward the reaction (entries 1 and 2). Interestingly, a 31% yield of the desired product was obtained on employing [BsMim][HSO_4] as the catalyst and this yield could be improved up to 55% by adjusting the anion from $[HSO_4]^-$ to $[OTf]^-$ (entry 3 *vs.* entry 4). Additionally, a series of ionic liquids based on 1-menthylimidazolium, guanidinium, pyridinium and pyrrolidinium as the cations and OTf^- as the anion was then tested (entries 5–12). To our delight, [BsOdP][OTf] exhibited the best activity in the reaction and an 80% yield of the desired **3aa** was obtained. The acidities of the above mentioned pyrrolidinium-based SO_3H-functionalized ionic liquids were evaluated from the Hammett acidity function using UV-visible spectroscopy with 2-nitroanline as the indicator in dichloromethane (DCM)[14] (see the Supporting Information, Table S1 and Figure S1). Interestingly, it was found that the acidities of the SO_3H-functionalized ionic liquids decreased with increasing carbon atom number in the side chain of the pyrrolidine ring, whereas the catalyst activities increased until a maximum was reached. The effects of reaction temperature and catalyst loading on the reaction were also screened. We found that 80 °C is the best reaction temperature and 10 mol% of [BsOdP][OTf] is the best catalyst loading (entries 13–20). The yield remarkably increased when the temperature increased from 40 °C to 80 °C (entries 12, 14 and 15) and no significant change was observed with further increase in temperature (entries 16 and 17). Catalyst loading also substantially affected yield with variation of loading

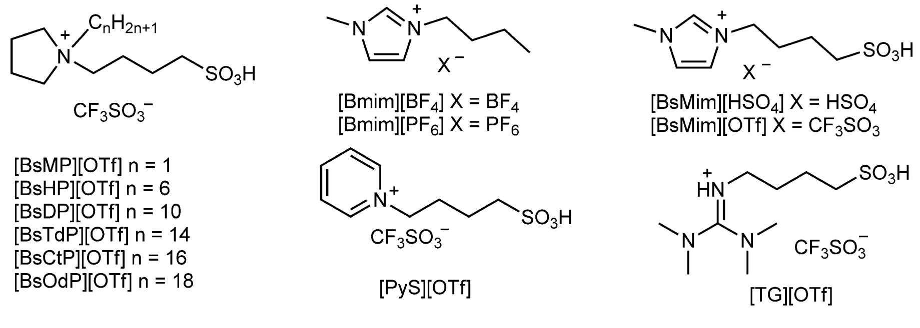
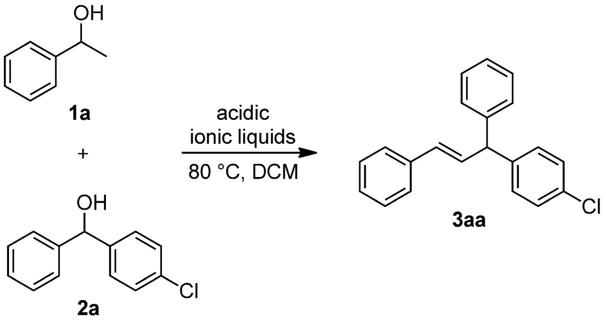


Figure 1. Functionalized ionic liquids used in the direct dehydrative coupling reactions.

Table 1. Screening the activities of SO_3H-functionalized ionic liquids.[a]



Entry	Catalyst	Cat. amount [mol%]	*T* [°C]	Yield [%][b]
1	[Bmim][BF_4]	10	80	NR[c]
2	[Bmim][PF_6]	10	80	NR[c]
3	[BsMim][HSO_4]	10	80	31
4	[BsMim][OTf]	10	80	55
5	[TG][OTf]	10	80	63
6	[PyS][OTf]	10	80	67
7	[BsMP][OTf]	10	80	58
8	[BsHP][OTf]	10	80	65
9	[BsDP][OTf]	10	80	69
10	[BsCtP][OTf]	10	80	74
11	[BsTdP][OTf]	10	80	77
12	[BsOdP][OTf]	10	80	80
13	[BsOdP][OTf]	10	25	NR[c]
14	[BsOdP][OTf]	10	40	59
15	[BsTdP][OTf]	10	60	71
16	[BsOdP][OTf]	10	100	82
17	[BsOdP][OTf]	10	120	83
18	[BsTdP][OTf]	1	80	39
19	[BsOdP][OTf]	5	80	68
20	[BsOdP][OTf]	20	80	82
21	[BsOdP][OTf]	30	80	83
22	[BsOdP][OTf]	10	80	78[d]
23	[BsOdP][OTf]	10	80	75[e]
24	[BsOdP][OTf]	10	80	70[f]
25	[BsOdP][OTf]	10	80	67[g]
26	[BsOdP][OTf]	10	80	61[h]
27	TfOH	10	80	63
28	TsOH	10	80	trace

[a] *Reaction conditions:* **1a**: 1.0 mmol, **2a**: 0.50 mmol, catalyst: 10 mol%, reaction temperature: 80 °C, solvent: DCM, 2.0 mL, reaction time: 12 h.

[b] Isolated yield.

[c] NR = no reaction.

[d] **1a**: 0.75 mmol, **2a**: 0.50 mmol.

[e] **1a**: 0.60 mmol, **2a**: 0.50 mmol.

[f] **1a**: 0.50 mmol, **2a**: 0.60 mmol.

[g] **1a**: 0.50 mmol, **2a**: 0.75 mmol.

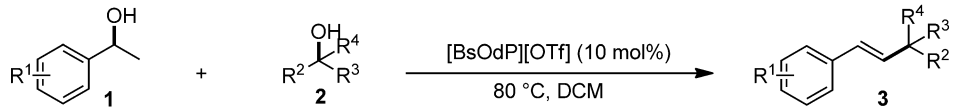
[h] **1a**: 0.50 mmol, **2a**: 1.0 mmol.

from 1 mol% to 10 mol% (entries 18, 19 and 12). However, the yield slightly changed when the catalyst loading was in the range of 10 mol% to 30 mol% (entry 13 *vs.* entries 20 and 21). Meanwhile, material ratios of the two alcohols were also investigated. It was found that an excess of olefin-generating benzylic alcohol can promote the coupling reaction (entries 22–26). Additionally, some control experiments were also conducted to compare the catalytic activities between traditional Brønsted acids catalysis and SO_3H-functionalized ionic liquids catalysis. As expected, only 63% yield of the desired product was obtained with TfOH catalyst. Additionally, the reaction became very sluggish when using TsOH as the catalyst, and only trace amounts of the desired product was detected under the same reaction conditions (entries 27 and 28).

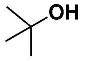
With the optimized reaction conditions in hand, we next surveyed the substrate scope of this protocol for the formation of polysubstituted olefins *via* direct dehydrative coupling of two different alcohols (Table 2). Initially, a series of diphenylmethanol and derivatives was studied employing 1-phenylethanol *in situ* generating styrene as the coupling partner. Interestingly, the reactivities of diphenylmethanol derivatives with one substituent on one of the aryl rings had a slight relationship with the electronic properties and steric hindrance. The substrates with *meta-* or *ortho-*substituent produced relatively lower yields compared with *para-*substituted ones (**3ab**, **3ac** and **3ad** *vs.* **3aa**). An electron-donating group such as methyl was beneficial for the reaction, giving 87% yield of the desired product (**3ae**). Interestingly, bis(4-chlorophenyl)methanol and bis(4-fluorophenyl)methanol also afforded the desired products **3ag** and **3ah** in 89% and 83% yields, respectively. The effect of the electronic properties and steric hindrance of 1-phenylethanol derivatives was then investigated with (4-chlorophenyl)-(phenyl)methanol as the coupling partner (**3ba–3ea**). Yields of 75% to 79% of the desired products were obtained on employing **1d** or **1e** with an *ortho-*substituent as the olefin source (**3da** and **3ea**). Additionally, homo-coupling of 1-phenylethanol derivatives also gave 1,3-diarylbut-1-ene derivatives in moderate yields (**3aa′–3dd′**). Interestingly, direct dehydrative coupling of **1b** and **2i** selectively generated **3bi** as the product. To our delight, *tert-*butyl alcohol (**1f**) was also compatible with the reaction conditions and the desired product **3ff** was obtained in 81% yield.

Subsequent studies showed that olefins could be directly used as the direct dehydrative coupling partner under the optimized reaction conditions. Various olefins can participate in the coupling reaction, and the results are summarized in Table 3. The coupling reactions of styrene with a series of alcohols were initially investigated. Obviously, benzhydrol and its derivatives, which contain electron-donating and electron-withdrawing groups on the aryl rings, were suitable substrates for this protocol, and the corresponding products were obtained in 35–82% yields (**3aa–3ah**, **3ja–3ka**). In these cases, a significant steric effect was

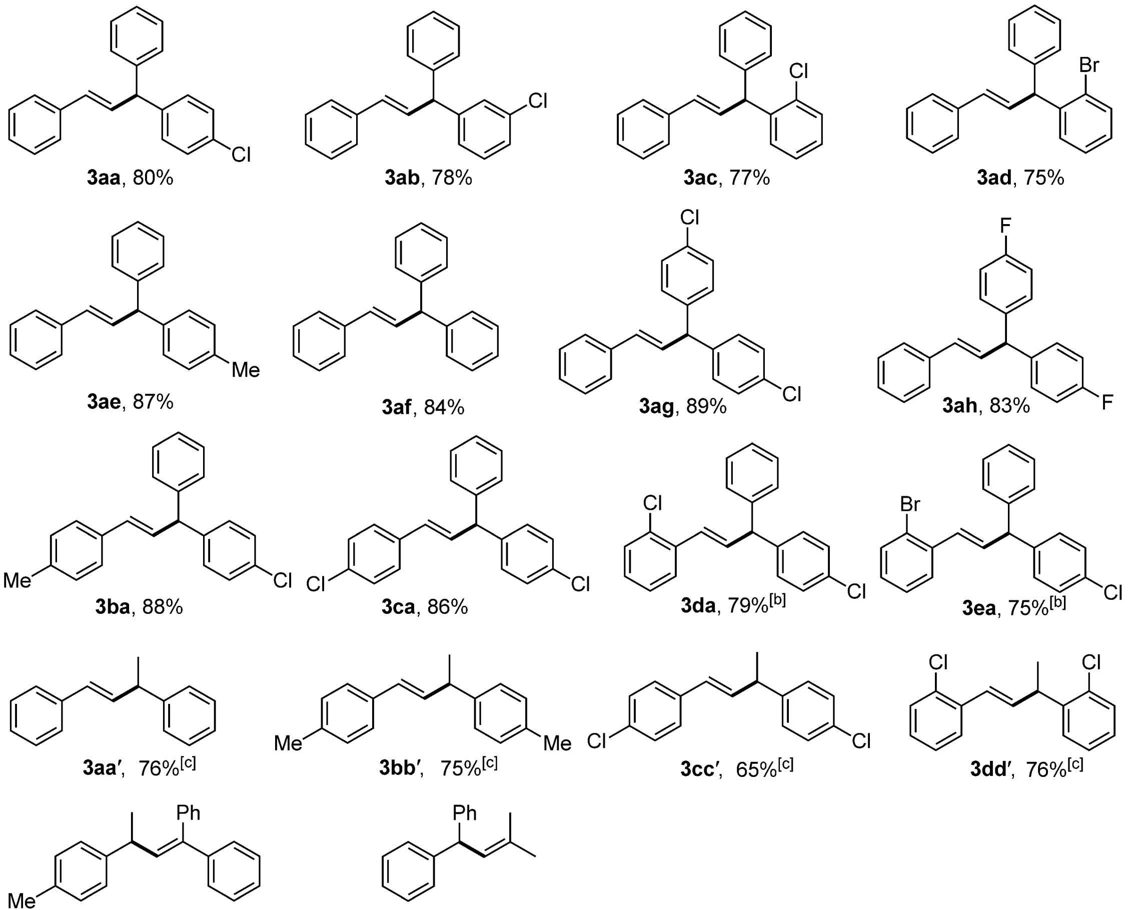
Table 2. Direct dehydrative coupling of benzylic alcohols with alcohols.[a]



1a, R^1 = H
1b, R^1 = *p*-Me
1c, R^1 = *p*-Cl
1d, R^1 = *o*-Cl
1e, R^1 = *o*-Br
1f,



2a, R^2 = *p*-Cl-phenyl, R^3 = Ph, R^4 = H
2b, R^2 = *m*-Cl-phenyl, R^3 = Ph, R^4 = H
2c, R^2 = *o*-Cl-phenyl, R^3 = Ph, R^4 = H
2d, R^2 = *o*-Br-phenyl, R^3 = Ph, R^4 = H
2e, R^2 = *p*-Me-phenyl, R^3 = Ph, R^4 = H
2f, R^2 = R^3 = Ph, R^4 = H
2g, R^2 = R^3 = *p*-Cl-phenyl, R^4 = H
2h, R^2 = R^3 = *p*-F-phenyl, R^4 = H
2i, R^2 = R^3 = Ph, R^4 = Me



3aa, 80% **3ab**, 78% **3ac**, 77% **3ad**, 75%

3ae, 87% **3af**, 84% **3ag**, 89% **3ah**, 83%

3ba, 88% **3ca**, 86% **3da**, 79%[b] **3ea**, 75%[b]

3aa′, 76%[c] **3bb′**, 75%[c] **3cc′**, 65%[c] **3dd′**, 76%[c]

3bi, 67% **3ff**, 81%[d]

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[a] *Reaction conditions:* alcohol **1**: 1.0 mmol, alcohol **2**: 0.50 mmol; catalyst: [BsOdP][OTf], 10 mol% (referred to alcohol **2**), solvent: DCM, 2.0 mL, reaction temperature: 80 °C, reaction time: 12 h. Isolated yields are shown. Only the *E* isomer was observed in all cases.

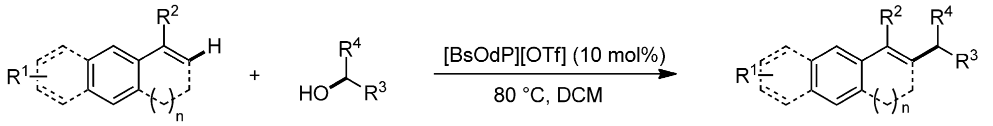
[b] $t = 24$ h.

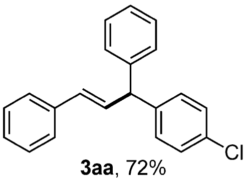
[c] Alcohol **1**: 1.0 mmol.

[d] *tert*-Butyl alcohol (**1f**) as alcohol **1**, 2.0 mmol, diphenylmethanol (**2f**) as alcohol **2**.

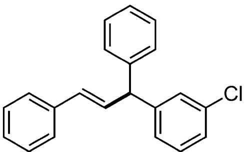
observed (**3ac** and **3ad**). In addition, the reactions of allyl alcohol and propargyl alcohol were also tested and 72% yield of dialkene **5la** and 67% yield of enyne **5ma** were obtained. Aromatic primary alcohols were also investigated (Supporting Information, Table S4). However, only benzylic alcohols with electron-donating groups on the aryl ring could result in a satisfactory reaction (**5na**). Then, the reactivities of

Table 3. Direct dehydrative coupling of alcohols with alkenes.[a]

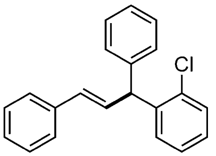




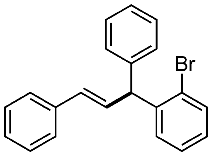
3aa, 72%



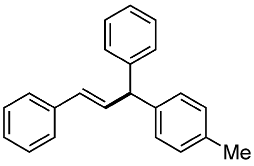
3ab, 63%



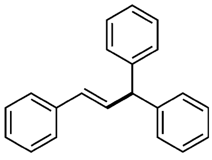
3ac, 43%[b]



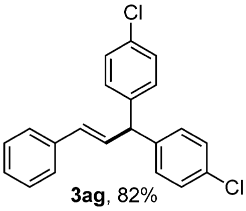
3ad, 35%[c]



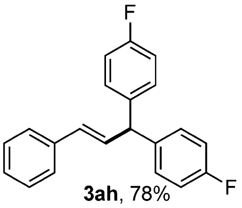
3ae, 75%



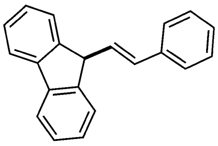
3af, 68%



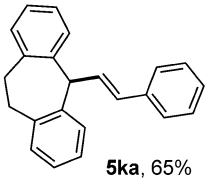
3ag, 82%



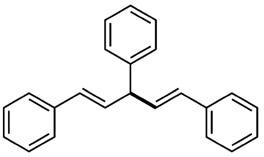
3ah, 78%



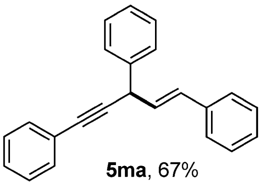
5ja, 63%



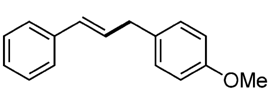
5ka, 65%



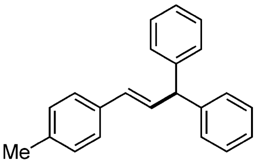
5la, 72%



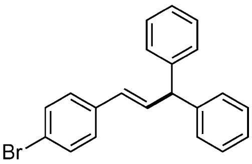
5ma, 67%



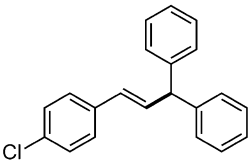
5na, 83%



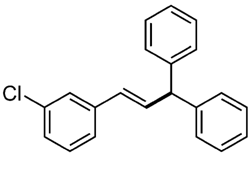
5fb, 73%



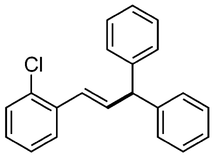
5fc, 88%



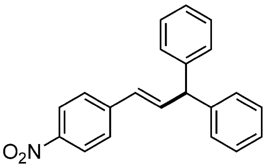
5fd, 89%



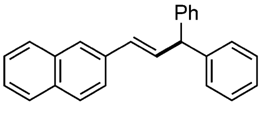
5fe, 92%



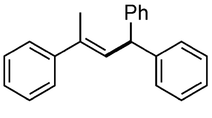
5ff, 95%



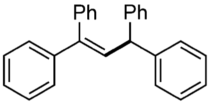
5fg, 84%



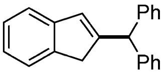
5fh, 89%



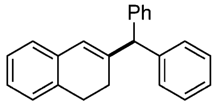
5fi, 85%[d]



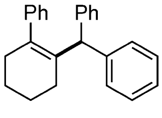
5fj, 98%[d]



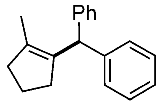
5fk, 83%



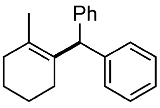
5fl, 74%



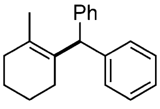
5fm, 91%



5fn, 92%[e]



5fo, 95%[e,f]



5fo, 86%[e,g]

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[a] *Reaction conditions:* alcohol: 0.50 mmol, olefin: 1.0 mmol, catalyst: [BsOdP]OTf, 10 mol% (referred to alcohol), solvent: DCM, 2.0 mL, temperature: 80 °C, reaction time: 12 h. Isolated yields are shown. Only the *E* isomer was observed in all cases.

[b] $t = 24$ h.

[c] $t = 48$ h.

[d] $t = 2$ h.

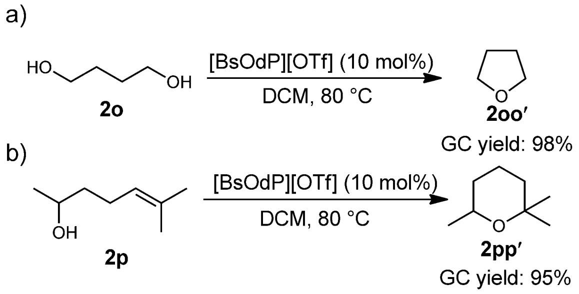
[e] Olefin, 2.0 mmol, $t = 6$ h.

[f] 1-Methylcyclohex-1-ene as substrate.

[g] Methylenecyclohexane as substrate.

several kinds of olefins were examined employing benzhydrol as the alcohol partner. Styrene derivatives bearing electron-withdrawing groups provided the corresponding product in good to excellent yields (**5fc**–**5fg**), while an electron-donating group was not beneficial for the reaction (**5fb)**. Interestingly, olefins with larger steric hindrance, such as naphthalene ethylene and styrene derivatives with α substitutents, showed better activities than styrene (**5fh**–**5fj**). Notably, up to a 98% yield of **5fj** was obtained *via* direct coupling of stilbene and benzhydrol. Additionally, cyclic internal olefins also exhibited excellent activities (**5fk**–**5fo**). It is worth mentioning that 1-methylcyclohex-1-ene and methylenecyclohexane reacted with diphenylmethanol to offer the same desired product **5fo**. Furthermore, SO_3H-functionalized ionic liquids also promoted the intramolecular cyclization reactions of an aliphatic diol **2o** and an alkenyl alcohol **2p** to form furan ring **2oo′** and pyranoid ring **2pp′** in excellent conversions (Scheme 1).

The present synthetic protocol for the synthesis of olefins *via* direct dehydrative coupling of alcohol and olefin can be carried out as a gram-scale preparation, which is significant from the standpoint of practical applications (Scheme 2). Starting with 10 mmol of (4-chlorophenyl)(phenyl)methanol and 20 mmol of styrene as substrates, the corresponding product **3aa** could be isolated in 72% yield under the typical conditions. Moreover, the gram-scale reaction was also successfully demonstrated by using 1,1-diphenylethylene and diphenylmethanol as substrates. After stirring at 80 °C in DCM for 3 h, the desired product **5fj** could be isolated in 91% yield through simple recrystallization with petroleum ether as the solvent.



Scheme 1. Intramolecular cyclization reactions of **2o** and **2p** catalyzed by [BsOdP]OTf.

Another practical feature of the current catalyst system is the facile separation of the product and the recyclability of the catalyst. To test the catalyst's reusability, the reaction was carried out in the presence of catalytic amounts of [BsOdP][OTf] under the optimal reaction conditions using **1a** and **2a** as substrates. After each cycle, the catalyst and the product were separated by petroleum ether and water. Subsequently, the water layer containing the catalyst was concentrated and dried under reduced pressure at 80 °C for 24 h in order to be reused directly. The results shown in Figure 2 indicate that the isolated yield of the product is almost consistent after six runs and [BsOdP][OTf] can be reused at least six times without significant loss of activity.

To gain insights into the mechanism of the present reaction, some control experiments were conducted (Scheme 3). Under the typical conditions for 5 min, employing styrene **4a** and diphenylmethanol **2f** as the

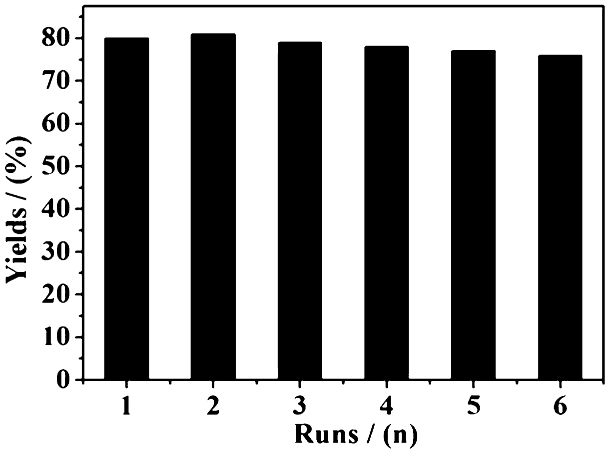
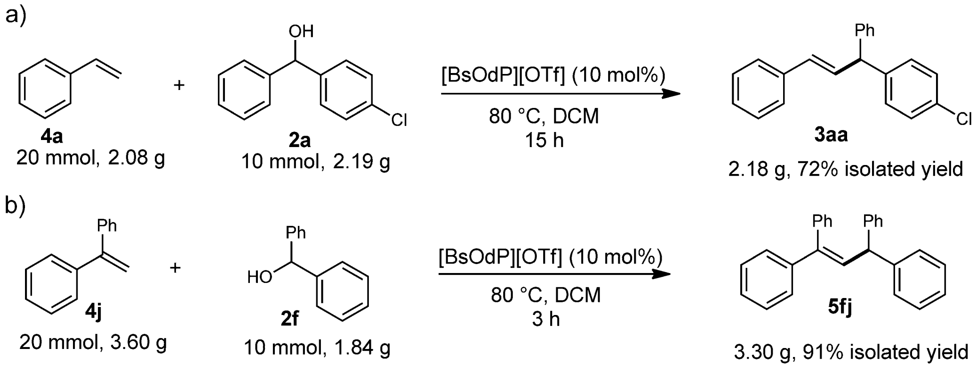
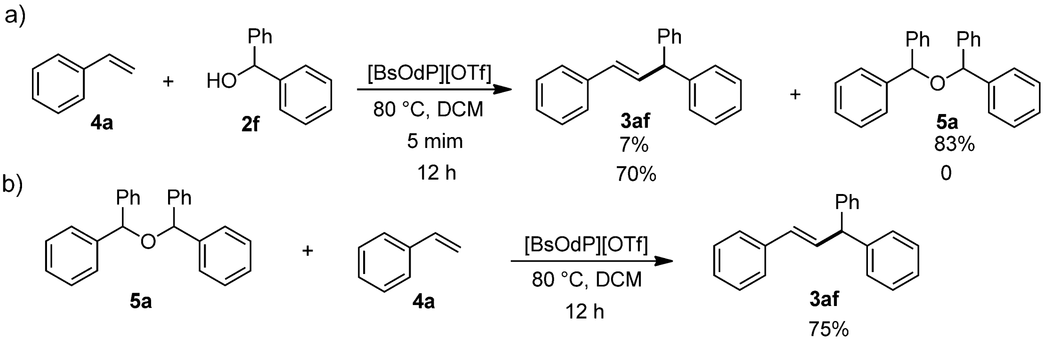


Figure 2. Recyclability of [BsOdP][OTf] in direct dehydrative coupling of **1a** and **2a**.



Scheme 2. Gram-scale synthesis of polysubstituted olefins.



Scheme 3. Control experiments.

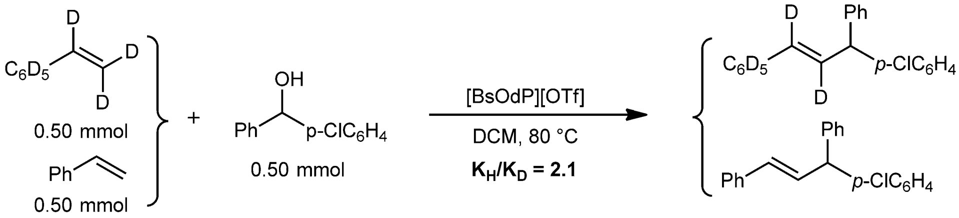
substrates gave the desired product **3af** along with the dimeric ether **5a** in yields of 7% and 83%, respectively. By contrast, after a prolonged reaction time (12 h), a 70% yield of **3af** was obtained, and **5a** disappeared. Similarly, when employing **4a** and **5a** as the substrate also the desired product **3af** was also furnished in 75% yield. These results suggested that dimeric ether **5a** might be an intermediate in the reaction.

Finally, kinetic isotope effect (KIE) experiments were also performed (Scheme 4). The observed significant isotopic effects ($k_H/k_D = 2.1$) indicated that the C–H bond cleavage reaction might be involved in the rate-determining step.[15]

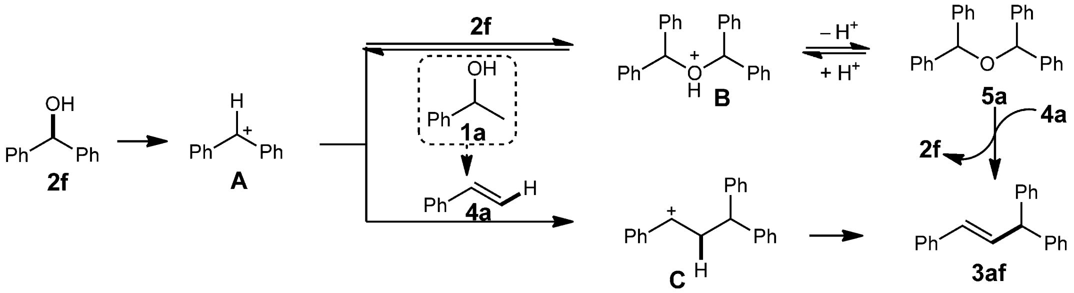
Although the exact reaction mechanism is not known at this stage, on the basis of the experimental results and previous work by others,[4d,12,16] two plausible pathways for this dehydrative coupling reaction are proposed as shown in Scheme 5. One possible pathway involves ether **5a** as an intermediate of the reaction.[11,12a,16a] Diphenylmethanol **2f** initially activated by [BsOdP][OTf] would generate a carbocation intermediate **A**,[7,13] which in turn reacts with **2f** to form oxonium salt **B** and etheric compound **5a**. The ether **5a** then reacts with styrene **4a** to produce the desired product **3af**. Another probable pathway could be a direct alkylation of styrene **4a** and alcohol **2f** to produce carbocation intermediate **C**, which would be followed by deprotonation to give the corresponding product **3af**. In both pathways, styrene **4a** could be generated *in situ* from benzylic alcohol **1a** *via* dehydration under the reaction conditions.

Conclusions

In summary, we have successfully developed a convenient and efficient method for C–C bond formation by direct dehydrative coupling of various alcohols with alcohols and alkenes using SO_3H-functionlized ionic liquids as metal-free, highly efficient and reusable cat-



Scheme 4. Competing KIE experiments.



Scheme 5. Proposed mechanisms for the direct dehydrative coupling.

alysts under mild reaction conditions. The present protocol provides an effective approach to synthesize a diverse range of polysubstituted olefins in good to excellent yields. The kinetic competition experiment shows that the C−H bond cleavage might be involved in the rate-determining step. Further investigations on the detailed mechanism and its application are ongoing in our laboratory.

Experimental Section

General Remarks

NMR spectra were recorded on Bruker Avance™ III spectrometers. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained as solutions in $CDCl_3$, D_2O or $(CD_3)_2SO$. Chemical shifts are reported in parts per million (ppm, δ) and referenced to $CHCl_3$ ($\delta = 7.26$), D_2O ($\delta = 4.88$) or $(CD_3)_2SO$ ($\delta = 2.50$); GC-MS analyses were performed using an Agilent 6850 system (FID) and ion source of the mass spectrometer is EI. Mass spectra (MS) were recorded on Waters ZQ4000 mass instrument (ESI). UV-vis spectra were recorded on Agilent Cary 60. Silica gel (200–300 microns) was used for all chromatographic separations. IR spectra were recorded FT-IR spectroscopy Nexus 870. Anhydrous organic solvents were dried and stored under nitrogen. All other chemicals used for synthetic procedures were reagent grade or better. Solutions were concentrated under vacuum with a rotary evaporator and the residue was purified using a silica gel column unless specified otherwise. All reactions were monitored by TLC with silica gel coated plates and detection was conducted by UV absorption (254 nm).

Experimental Procedure for Ionic Liquid *N*-Octadecyl-[*N*-(4-butanesulfonyl)pyrrolidine] Trifluoromethanesulfonate ([BsOdP][OTf])

N-Octadecylpyrrolidine (6.46 g, 0.020 mol) and 1,4-butanesultone (2.25 mL, 0.022 mol) were charged into a 100-mL round-bottom flask. Then the mixtures were stirred at 40 °C for 10 h. The white solid zwitterion was washed repeatedly with ether to remove non-ionic residues and dried under vacuum. After washing the salt with ether and toluene to remove any unreacted starting materials, the solid was dried under vacuum. Then, a stoichiometric amount of trifluoromethanesulfonic acid (1.80 mL, 0.020 mol) was added dropwise and the mixture stirred for 12 h at 80 °C, which resulted in the formation of *N*-octadecyl-[*N*-(4-sulfonbutyl)pyrrolidine] trifluoromethanesulfonate ([BsOdP][OTf]). The ionic liquid phase was then washed repeatedly with toluene and ether to remove non-ionic residues, and dried under vacuum. The product (11.9 g, 98% yield) was formed quantitatively and in high purity as assessed by NMR, IR and mass spectroscopy. ^{1}H NMR (400 MHz, D_2O): $\delta = 0.73$ (t, $J = 4.8$ Hz, 3 H), 1.15–1.22 (m, 30 H), 1.55–1.74 (m, 6 H), 2.00–2.07 (m, 4 H), 2.77 (t, $J = 7.2$ Hz, 2 H), 3.09–3.19 (m, 4 H), 3.38–3.42 (m, 4 H); ^{13}C NMR (100 MHz, D_2O): $\delta =$ 13.8, 21.5, 21.6, 21.8, 22.5, 22.7, 22.8, 23.0, 26.3, 28.8, 29.1, 29.6, 29.8, 29.9, 30.0, 30.1, 30.2, 32.0, 50.1, 59.4, 59.7, 62.7, 119.9 (q, $J_{C,F} = 316.4$ Hz, CF_3); IR: 3327, 2950, 1621, 1589, 1458, 1406, 1290, 1227, 1167, 1067, 1030, 897, 761, 719, 638, 573, 574, 476; MS (ESI): $[m/z]^+ = 460.2$, $[m/z]^- = 148.9$.

Typical Procedure for the Direct Dehydrative Coupling of Alcohols with Alcohols and Reuse of [BsOdP][OTf]

[BsOdP]OTf (30.5 mg, 10 mol%), 1-phenylethanol **1a** (122 mg, 1.0 mmol), (4-chlorophenyl)(phenyl)methanol **2a** (109 mg, 0.5 mmol), and dry dichloromethane (2.0 mL) were added into the screw-cap vial. Then the mixture was stirred continuously at 80 °C for 12 h and monitored by TLC. At the end of the reaction, the catalyst and the product were separated using petroleum ether and water. The combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated under vacuum. Flash column chromatography (petroleum ether) on silica gel of the residue gave (*E*)-(3-(4-chlorophenyl)prop-1-ene-1,3-diyl)dibenzene (**3aa**) as a colorless oil in high purity as assessed by NMR and GC-mass spectroscopy; yield: 121.6 mg (80%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.86$ (d, $J = 7.2$ Hz, 1 H), 6.33 (d, $J = 16.0$ Hz, 1 H), 6.62 (dd, $J = 7.6$, 16.0 Hz, 1 H), 7.15–7.18 (m, 2 H), 7.20–7.38 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 53.5$, 126.3, 126.7, 127.5, 128.6, 128.6, 128.6, 130.0, 131.8, 132.0, 132.3, 137.1, 142.0, 143.0; GC-MS (EI): $[m/z]^+ = 304.1$

The ionic liquid ([BsOdP]OTf) obtained by concentrating the water layer and drying under vacuum at 80 °C for 24 h could be reused for another five runs without significant decreases in catalytic activity as shown in Figure 2.

Typical Procedure for Direct Dehydrative Coupling of Alcohols with Alkenes

A mixture of alcohol (0.50 mmol), olefin (1.0 mmol), [BsOdP]OTf (10 mol%), and dry dichloromethane (2.0 mL) was heated at 80 °C for the indicated time until complete consumption of alcohol as monitored by TLC. After the reaction had finished, the mixture was extracted by petroleum ether and water. Then the water layer containing the catalyst was concentrated and dried under reduced pressure at 80 °C for 24 h in order to be reused directly. The petroleum ether layer was evaporated under vacuum and purified by flash column chromatography (petroleum ether) to afford the desired product.

Characterization of the Products

(*E*)-[3-(4-Chlorophenyl)prop-1-ene-1,3-diyl]dibenzene (3aa): Colorless oil, this compound is known.[7,12a,17] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.86$ (d, $J = 7.2$ Hz, 1 H), 6.33 (d, $J = 16.0$ Hz, 1 H), 6.62 (dd, $J = 7.6$, 16.0 Hz, 1 H), 7.15–7.18 (m, 2 H), 7.20–7.38 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 53.5, 126.3, 126.7, 127.5, 128.6, 128.6, 128.6, 130.0, 131.8, 132.0, 132.3, 137.1, 142.0, 143.0; GC-MS (EI): $[m/z]^+ = 304.1$.

(*E*)-[3-(3-Chlorophenyl)prop-1-ene-1,3-diyl)dibenzene (3ab): Colorless oil, this compound was unknown. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.86$ (d, $J = 7.6$ Hz, 1 H), 6.35 (d, $J = 16.0$ Hz, 1 H), 6.62 (dd, $J = 7.6$, 16.0 Hz, 1 H), 7.10–7.13 (m, 1 H), 7.19–7.38 (m, 13 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 53.9, 126.4, 126.7, 126.8, 126.9, 127.6, 128.6, 128.6, 128.7, 129.8, 131.7, 132.0, 134.4, 137.0, 142.8, 145.7; GC-MS (EI): $[m/z]^+ = 304.1$.

(*E*)-[3-(2-Chlorophenyl)prop-1-ene-1,3-diyl]dibenzene (3ac): Colorless oil, this compound was unknown. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 5.40$ (d, $J = 6.8$ Hz, 1 H), 6.28 (dd, $J = 1.2$, 16.0 Hz, 1 H), 6.63 (dd, $J = 6.8$, 15.6 Hz, 1 H), 7.16–7.26 (m, 7 H), 7.27–7.40 (m, 7 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 50.2$, 126.4, 126.6, 126.9, 127.4, 127.8, 128.5, 128.6, 128.8, 129.8, 130.2, 131.3, 132.0, 134.3, 137.2, 141.0, 142.1; GC-MS (EI): [*m/z*]$^+ = 304.1$.

(*E*)-[3-(2-Bromophenyl)prop-1-ene-1,3-diyl]dibenzene (3ad): Colorless oil, this compound was unknown. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 5.39$ (d, $J = 6.8$ Hz, 1 H), 6.27 (dd, $J = 1.2$, 16.0 Hz, 1 H), 6.60 (dd, $J = 6.8$, 15.6 Hz, 1 H), 7.04–7.08 (m, 1 H), 7.16–7.24 (m, 7 H), 7.26–7.29 (m, 3 H), 7.30–7.35 (m, 2 H), 7.56 (d, $J = 7.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 52.9$, 125.3, 126.5, 126.7, 127.6, 127.6, 128.2, 128.6, 128.7, 129.0, 130.6, 131.5, 132.2, 133.3, 137.3, 142.2, 142.7; GC-MS (EI): [*m/z*]$^+ = 348.1$.

(*E*)-(3-*para*-Tolylprop-1-ene-1,3-diyl)dibenzene (3ae): Colorless oil, this compound is known.[7,12a] ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 2.25$ (s, 3 H), 4.78 (d, $J = 7.6$ Hz, 1 H), 6.27 (d, $J = 15.6$ Hz, 1 H), 6.64 (dd, $J = 7.6$, 16.0 Hz, 1 H), 7.05 (s, 4 H), 7.11–7.25 (m, 8 H), 7.28–7.31 (m, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 20.0$, 52.8, 125.2, 125.3, 126.2, 127.4, 127.5, 127.5, 127.6, 128.1, 130.2, 131.8, 134.9, 136.3, 139.5, 142.7; GC-MS (EI): [*m/z*]$^+ = 284.2$.

(*E*)-Prop-2-ene-1,1,3-triyltribenzene (3af): White solid, mp 102–103 °C, this compound is known.[7,12a,17] ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.89$ (d, $J = 7.2$ Hz, 1 H), 6.34 (dd, $J = 1.2$, 15.6 Hz, 1 H), 6.64–6.70 (m, 1 H), 7.18–7.37 (m, 15 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 54.2$, 126.4, 126.5, 127.4, 128.5, 128.6, 128.7, 131.5, 132.6, 137.3, 143.6; GC-MS (EI): [*m/z*]$^+ = 270.1$.

(*E*)-4,4′-(3-Phenylprop-2-ene-1,1-diyl)bis(chlorobenzene) (3ag): Colorless oil, this compound is known.[7,12a] ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.84$ (d, $J = 7.2$ Hz, 1 H), 6.32 (d, $J = 15.6$ Hz, 1 H), 6.54–6.60 (m, 1 H), 7.13–7.15 (m, 4 H), 7.22–7.38 (m, 9 H); ^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 52.8$, 126.3, 127.6, 128.6, 128.7, 129.9, 131.4, 132.1, 132.5, 136.8, 141.5; GC-MS (EI): [*m/z*]$^+ = 339.3$.

(*E*)-4,4′-(3-Phenylprop-2-ene-1,1-diyl)bis(fluorobenzene) (3ah): Colorless oil, this compound was unknown. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.86$ (d, $J = 7.6$ Hz, 1 H), 6.30 (d, $J = 16.0$ Hz, 1 H), 6.59 (dd, $J = 7.2$, 16.0 Hz, 1 H), 6.97–7.03 (m, 4 H), 7.14–7.25 (m, 5 H), 7.28–7.38 (m, 4 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 52.8$, 115.5, 115.7, 126.5, 127.8, 128.8, 130.2, 130.3, 132.0, 132.3, 138.2 ($J_{\text{C–F}} = 206.8$ Hz), 161.8 ($J_{\text{C–F}} = 243.5$ Hz); GC-MS (EI): [*m/z*]$^+ = 306.1$.

(*E*)-1-Chloro-4-(1-phenyl-3-*para*-tolylallyl)benzene (3ba): Colorless oil, this compound is known.[7] ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 2.32$ (s, 3 H), 4.84 (d, $J = 7.6$ Hz, 1 H), 6.29 (d, $J = 15.6$ Hz, 1 H), 6.55 (dd, $J = 7.2$, 15.6 Hz, 1 H), 7.09–7.16 (m, 4 H), 7.19–7.23 (m, 3 H), 7.25–7.33 (m, 6 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 21.1$, 53.5, 126.2, 126.6, 128.3, 128.6, 128.7, 129.2, 130.0, 130.9, 132.6, 133.2, 134.2, 137.3, 142.2, 143.1; GC-MS (EI): [*m/z*]$^+ = 318.1$.

(*E*)-4,4′-(3-Phenylprop-1-ene-1,3-diyl)bis(chlorobenzene) (3ca): Colorless oil, this compound is known.[7] ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.85$ (d, $J = 7.6$ Hz, 1 H), 6.27 (dd, $J = 1.2$, 16.0 Hz, 1 H), 6.59 (dd, $J = 7.6$, 16.0 Hz, 1 H), 7.14–7.34 (m, 13 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 53.5$, 126.8, 127.5, 128.5, 128.6, 128.7, 130.0, 130.6, 132.4, 132.7, 133.1, 135.5, 141.8, 142.7; GC-MS (EI): [*m/z*]$^+ = 338.1$.

(*E*)-1-Chloro-2-[3-(4-chlorophenyl)-3-phenylprop-1-enyl]-benzene (3da): Colorless oil, this compound is known.[7] ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.91$ (d, $J = 7.6$ Hz, 1 H), 6.58 (dd, $J = 7.6$, 15.6 Hz, 1 H), 6.77 (d, $J = 15.6$ Hz, 1 H), 7.14–7.34 (m, 12 H), 7.54 (d, $J = 7.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 53.7$, 126.7, 126.8, 126.9, 128.1, 128.4, 128.5, 128.6, 129.7, 129.9, 132.3, 133.0, 134.7, 135.2, 141.8, 142.7; GC-MS (EI): [*m/z*]$^+ = 339.2$.

(*E*)-1-Bromo-2-[3-(4-chlorophenyl)-3-phenylprop-1-enyl]-benzene (3ea): Colorless oil, this compound was unknown. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 4.90$ (d, $J = 7.6$ Hz, 1 H), 6.53 (dd, $J = 7.6$, 15.6 Hz, 1 H), 6.72(d, $J = 15.6$ Hz, 1 H), 7.05–7.34 (m, 10 H), 7.52 (d, $J = 8.0$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 27.0$, 53.6, 123.6, 126.8, 127.1, 127.5, 128.6, 128.7, 128.8, 130.0, 130.8, 132.4, 132.9, 134.9, 137.1, 141.8, 142.7; GC-MS (EI): [*m/z*]$^+ = 382.0$.

(*E*)-But-1-ene-1,3-diyldibenzene (3aa′): Colorless oil, this compound is known.[7,12a,17] ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.39$ (d, $J = 6.8$ Hz, 3 H), 3.53–3.64 (m, 1 H), 6.27–6.36 (m, 2 H), 7.08–7.29 (m, 10 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 20.2$, 41.5, 125.1, 125.2, 126.0, 126.3, 127.4, 134.2, 136.5, 144.6; GC-MS (EI): [*m/z*]$^+ = 208.2$.

(*E*)-4,4′-(But-1-ene-1,3-diyl)bis(methylbenzene) (3bb′): Colorless oil, this compound is known.[7,18] ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.43$ (d, $J = 6.8$ Hz, 3 H), 2.30 (s, 3 H), 2.31 (s, 3 H), 3.55–3.61 (m, 1 H), 6.30 (dd, $J = 6.0$, 16.0 Hz, 1 H), 6.37 (d, $J = 16.0$ Hz, 1 H), 7.07–7.16 (m, 6 H), 7.24 (d, $J = 8.0$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 21.0$, 21.1, 21.3, 42.1, 126.0, 127.2, 128.2, 129.1, 134.4, 134.8, 135.6, 136.7, 142.8; GC-MS (EI): [*m/z*]$^+ = 236.2$.

(*E*)-4,4′-(But-1-ene-1,3-diyl)bis(chlorobenzene) (3cc′): Colorless oil, this compound is known.[7,16b] ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.43$ (d, $J = 7.2$ Hz, 3 H), 3.57–3.63 (m, 1 H), 6.26–6.36 (m, 2 H), 7.16–7.19 (m, 2 H), 7.23–7.30 (m, 6 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 21.1$, 41.9, 127.4, 127.8, 128.6, 128.7, 128.8, 132.0, 132.8, 135.3, 135.8, 143.7; GC-MS (EI): [*m/z*]$^+ = 276.0$.

(*E*)-2,2′-(But-1-ene-1,3-diyl)bis(chlorobenzene) (3dd′): Colorless oil, this compound is known.[7,18] ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.47$ (d, $J = 7.2$ Hz, 3 H), 4.17–4.25 (m, 1 H), 6.34 (dd, $J = 6.4$, 16.0 Hz, 1 H), 6.86 (dd, $J = 1.6$, 16.0 Hz, 1 H), 7.11–7.25 (m, 4 H), 7.28–7.38 (m, 3 H), 7.29 (dd, $J = 2.0$, 7.6 Hz, 1 H); ^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 19.8$, 38.6, 125.6, 126.7, 126.8, 127.1, 127.5, 128.1, 128.2, 129.6, 129.7, 132.9, 133.6, 135.7, 136.3, 142.6; GC-MS (EI): [*m/z*]$^+ = 276.1$.

(*E*)-(3-*para*-Tolylbut-2-ene-1,1-diyl)benzene (3bi): White solid; mp 82–84 °C, this compound is known.[7,19] ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.29$ (d, $J = 6.8$ Hz, 3 H), 2.25 (s, 3 H), 3.45–3.53 (m, 1 H), 6.12 (d, $J = 10.4$ Hz, 1 H), 7.03 (s, 4 H), 7.11–7.19 (m, 7 H), 7.23–7.33 (m, 3 H); ^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 21.0$, 22.4, 38.9, 126.8, 126.9, 127.0, 127.3, 128.1, 128.2, 129.2, 129.8, 134.4, 135.5, 139.9, 140.2, 142.5, 143.2; GC-MS (EI): [*m/z*]$^+ = 298.2$.

(3-Methylbut-2-ene-1,1-diyl)dibenzene (3ff): Colorless oil, this compound is known.[12b] ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.71$ (s, 3 H), 1.78 (s, 3 H), 4.88 (d, $J = 9.6$ Hz, 1 H), 5.61–5.64 (m, 1 H), 7.15–7.29 (m, 10 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 18.1$, 26.0, 49.5, 126.0, 127.4, 128.3, 128.4, 132.5, 145.2; GC-MS (EI): [*m/z*]$^+ = 222.2$.

(*E*)-9-Styryl-9*H*-fluorene (5ja): White solid; mp 99–101 °C, this compound is known.[7] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.65 (d, J = 9.2 Hz, 1H), 6.04 (dd, J = 8.8, 15.6 Hz, 1H), 6.89 (d, J = 16.0 Hz, 1H), 7.21–7.25 (m, 1H), 7.29–7.34 (m, 4H), 7.38–7.42 (m, 4H), 7.51 (d, J = 7.2 Hz, 2H), 7.79 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 52.4, 119.9, 121.5, 122.9, 125.4, 126.3, 127.2, 127.4, 127.5, 128.6, 129.0, 132.5, 146.1; GC-MS (EI): $[m/z]^+$ = 268.2.

(*E*)-5-Styryl-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (5ka): Colorless oil, this compound is known.[7] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.80–2.89 (m, 2H), 3.39–3.48 (m, 2H), 4.78 (dd, J = 2.4, 4.0 Hz, 1H), 5.99 (dd, J = 2.0, 15.6 Hz, 1H), 6.62 (dd, J = 4.4, 16.0 Hz, 1H), 7.11–7.26 (m, 13H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 32.8, 56.5, 126.3, 127.2, 128.5, 130.0, 130.5, 130.7, 134.9, 137.4, 139.9, 140.2; GC-MS (EI): $[m/z]^+$ = 296.2.

(1*E*,4*E*)-Penta-1,4-diene-1,3,5-triyltribenzene (5la): Colorless oil, this compound is known.[12a] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.38–4.41 (m, 1H), 6.44–6.53 (m, 4H), 7.20–7.41 (m, 15H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 51.6, 126.3, 126.6, 127.3, 128.1, 128.5, 128.6, 130.8, 131.8, 137.3, 142.8; GC-MS (EI): $[m/z]^+$ = 296.4.

(*E*)-Pent-1-en-4-yne-1,3,5-triyltribenzene (5ma): Yellow oil, this compound is known.[20] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.76 (d, J = 6.0 Hz, 1H), 6.35 (dd, J = 6.4, 15.6 Hz, 1H), 6.78 (dd, J = 1.2, 15.6 Hz, 1H), 7.21–7.25 (m, 1H), 7.28–7.34 (m, 6H), 7.35–7.41 (m, 4H), 7.48–7.53 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 41.2, 85.4, 88.8, 123.4, 126.5, 127.1, 127.5, 127.7 128.0, 128.2, 128.5, 128.7, 129.6, 130.4, 131.7, 136.8, 140.3; GC-MS (EI): $[m/z]^+$ = 294.1.

1-Cinnamyl-4-methoxybenzene (5na): Colorless oil, this compound is known.[21] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.48 (d, J = 3.2 Hz, 2H), 3.78 (s, 3H), 6.30–6.45 (m, 2H), 6.83–6.87 (m, 2H), 7.14–7.23 (m, 3H), 7.26–7.36 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 38.4, 55.3, 113.9, 126.1, 127.0, 128.5, 129.6, 129.7, 130.7, 132.1, 137.5, 158.0; GC-MS (EI): $[m/z]^+$ = 224.1.

(*E*)-(3-*para*-Tolylprop-2-ene-1,1-diyl)dibenzene (5fb): Colorless oil, this compound is known.[7,12a] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.32 (s, 3H), 4.88 (d, J = 7.6 Hz, 1H), 6.31 (d, J = 15.6 Hz, 1H), 6.61 (dd, J = 7.6, 16.0 Hz, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.17–7.32 (m, 12H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 21.2, 54.2, 126.2, 126.4, 128.5, 128.7, 129.2, 131.3, 131.6, 134.5, 137.1, 143.7; GC-MS (EI): $[m/z]^+$ = 284.2.

(*E*)-[3-(4-Bromophenyl)prop-2-ene-1,1-diyl]dibenzene (5fc): White solid; mp: 86–87 °C, this compound is known.[12a] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.88 (d, J = 7.2 Hz, 1H), 6.27 (d, J = 15.2 Hz, 1H), 6.66 (dd, J = 7.6, 16.0 Hz, 1H), 7.21–7.41 (m, 14H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 54.2, 121.0, 126.6, 127.9, 128.6, 128.7, 130.3, 131.6, 133.5, 136.2, 143.2; GC-MS (EI): $[m/z]^+$ = 348.1.

(*E*)-[3-(4-Chlorophenyl)prop-2-ene-1,1-diyl]dibenzene (5fd): White solid; mp 72–73 °C, this compound is known.[7,17] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.88 (d, J = 7.6 Hz, 1H), 6.28 (d, J = 16.8 Hz, 1H), 6.65 (dd, J = 7.6, 15.6 Hz, 1H), 7.21–7.33 (m, 14H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 54.2, 126.6, 127.5, 128.5, 128.6, 128.7, 130.3, 132.9, 133.3, 135.8, 143.3; GC-MS (EI): $[m/z]^+$ = 304.1.

(*E*)-[3-(3-Chlorophenyl)prop-2-ene-1,1-diyl]dibenzene (5fe): White solid; mp 75–76 °C, this compound was unknown. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.89 (d, J = 7.6 Hz, 1H), 6.28 (dd, J = 1.2, 15.6 Hz, 1H), 6.69 (dd, J = 7.6, 15.6 Hz, 1H), 7.16–7.36 (m, 14H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 54.1, 124.6, 126.2, 126.6, 127.3, 128.5, 128.6, 129.7, 130.2, 134.2, 134.5, 139.2, 143.2; GC-MS (EI): $[m/z]^+$ = 304.1.

(*E*)-[3-(2-Chlorophenyl)prop-2-ene-1,1-diyl]dibenzene (5ff): White solid; mp 80–81 °C, this compound was unknown. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.94 (d, J = 7.6 Hz, 1H), 6.64 (dd, J = 8.0, 16.0 Hz, 1H), 6.79 (d, J = 16.0 Hz, 1H), 7.14–7.34 (m, 13H), 7.55–7.57 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 54.4, 126.6, 126.8, 126.9, 127.8, 128.4, 128.5, 128.6, 129.7, 133.0, 135.3, 135.5, 143.3; GC-MS (EI): $[m/z]^+$ = 304.1.

(*E*)-[3-(4-Nitrophenyl)prop-2-ene-1,1-diyl]dibenzene (5fg): Yellow solid; mp 128–130 °C, this compound was unknown. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.86 (d, J = 7.2 Hz, 1H), 6.32 (d, J = 15.6 Hz, 1H), 6.80 (dd, J = 7.6, 16.0 Hz, 1H), 7.14–7.19 (m, 6H), 7.24–7.27 (m, 4H), 7.39–7.41 (m, 2H), 8.07 (d, J = 8.8 Hz, 2H); ^{13}C NMR (400 MHz, CDCl$_3$): δ = 53.2, 122.9, 125.7, 127.5, 127.6, 128.5, 131.3, 136.6, 141.5, 142.6, 145.7; GC-MS (EI): $[m/z]^+$ = 315.4.

(*E*)-2-(3,3-Diphenylprop-1-enyl)naphthalene (5fh): White solid; mp 106–107 °C, this compound was unknown. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.96 (d, J = 7.6 Hz, 1H), 6.51 (d, J = 16.0 Hz, 1H), 6.81 (dd, J = 7.6, 16.0 Hz, 1H), 7.22–7.26 (m, 3H), 7.29–7.35 (m, 7H), 7.39–7.46 (m, 2H), 7.62 (dd, J = 1.6, 8.4 Hz, 1H), 7.69 (s, 1H), 7.75–7.79 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 54.3, 123.7, 125.7, 126.1, 126.2, 126.5, 127.7, 127.9, 128.1, 128.5, 128.7, 131.6, 132.9, 133.1, 133.6, 134.7, 143.5; GC-MS (EI): $[m/z]^+$ = 320.4.

(*E*)-But-2-ene-1,1,3-triyltribenzene (5fi): Colorless oil, this compound is known.[7,12a,b] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.12 (s, 3H), 5.07 (d, J = 9.2 Hz, 1H), 6.24 (d, J = 9.6 Hz, 1H), 7.17–7.37 (m, 13H), 7.42 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 16.4, 50.1, 126.0, 126.3, 127.0, 128.3, 128.5, 128.6, 130.8, 135.7, 143.6, 144.7; GC-MS (EI): $[m/z]^+$ = 284.2.

Prop-1-ene-1,1,3,3-tetrayltetrabenzene (5fj): White solid; mp: 131–132 °C, this compound is known.[7,12a,b] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.81 (d, J = 10.8 Hz, 1H), 6.54 (d, J = 10.8 Hz, 1H), 7.15–7.38 (m, 20H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 50.5, 126.3, 127.2, 127.3, 127.5, 128.1, 128.3, 128.4, 128.5, 129.8, 131.0, 139.7, 141.6, 142.2, 144.5; GC-MS (EI): $[m/z]^+$ = 346.3.

2-Benzhydryl-1*H*-indene (5fk): White solid; mp 109–110 °C, this compound was unknown. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 3.28 (s, 2H), 5.15 (s, 1H), 6.24 (s, 1H), 7.01–7.05 (m, 1H), 7.13–7.26 (m, 13H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 41.1, 53.8, 120.6, 123.6, 124.3, 126.4, 126.6, 128.5, 129.0, 130.2, 143.1, 143.5, 144.9, 152.3; GC-MS (EI): $[m/z]^+$ = 282.1.

(*E*)-3-(3,3-Diphenylprop-1-enyl)-1,2-dihydronaphthalene (5fl): White solid; mp 78–80 °C, this compound is known.[7,12b] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.26–2.29 (m, 2H), 2.80–2.85 (m, 2H), 4.90 (s, 1H), 5.97 (s, 1H), 6.91 (d, J = 3.2 Hz, 1H), 7.09 (s, 3H), 7.23–7.32 (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 28.0, 28.4, 58.5, 125.8, 126.1, 126.4, 126.5, 126.6, 127.2, 128.3, 129.4, 134.5, 134.6, 142.0, 143.7; GC-MS (EI): $[m/z]^+$ = 322.2.

[(2-Phenylcyclohex-1-enyl)methylene]dibenzene (5fm): White solid; mp 124–126 °C, this compound is known.[12a] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.69–1.72 (m, 4H), 1.93–1.95 (m, 2H), 2.35–2.36 (m, 2H), 5.01 (s, 1H), 7.06–7.08 (m, 4H), 7.12–7.15 (m, 2H), 7.17–7.29 (m, 9H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 23.0, 23.3, 26.0, 33.2, 53.3, 125.9, 126.3, 127.8, 127.9, 128.2, 129.3, 133.3, 136.3, 143.4, 144.3; GC-MS (EI): $[m/z]^+ = 324.1$.

[(2-Methylcyclopent-1-enyl)methylene]dibenzene (5fn):. Colorless oil, this compound is known.[12a] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.70$ (s, 3H), 1.74–1.80 (m, 2H), 2.20 (brs, 2H), 2.36 (t, $J = 6.8$ Hz, 2H), 5.16 (s, 1H), 7.12–7.19 (m, 6H), 7.25 (t, $J = 7.2$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.3$, 21.9, 34.3, 38.8, 49.9, 126.1, 128.2, 129.1, 134.7, 135.7, 143.5; GC-MS (EI): $[m/z]^+ = 248.2$.

[(2-Methylcyclohex-1-enyl)methylene]dibenzene (5fo): Colorless oil, this compound is known.[12a] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.56$ (brs, 4H), 1.68 (brs, 5H), 2.07 (brs, 2H), 5.34 (s, 1H), 7.11 (d, $J = 8.0$ HZ, 3H), 7.17 (t, $J = 7.20$ Hz, 3H), 7.25 (t, $J = 7.6$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.7$, 23.3, 23.6, 27.7, 32.7, 52.7, 126.0, 128.2, 129.5, 129.6, 130.8, 143.6; GC-MS (EI): $[m/z]^+ = 262.2$.

Oxybis(methanetriyl)tetrabenzene (5a): White solid; mp 113–114 °C, this compound is known.[13] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.39$ (s, 2H), 7.22–7.37 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 79.9$, 127.3, 127.4, 128.4, 142.2; GC-MS (EI): $[m/z]^+ = 350.0$.

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