DOI: 10.1002/adsc.200700039

Metal Triflate-Catalyzed Regio- and Stereoselective Friedel–Crafts Alkenylation of Arenes with Alkynes in an Ionic Liquid: Scope and Mechanism

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Received: January 23, 2007

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

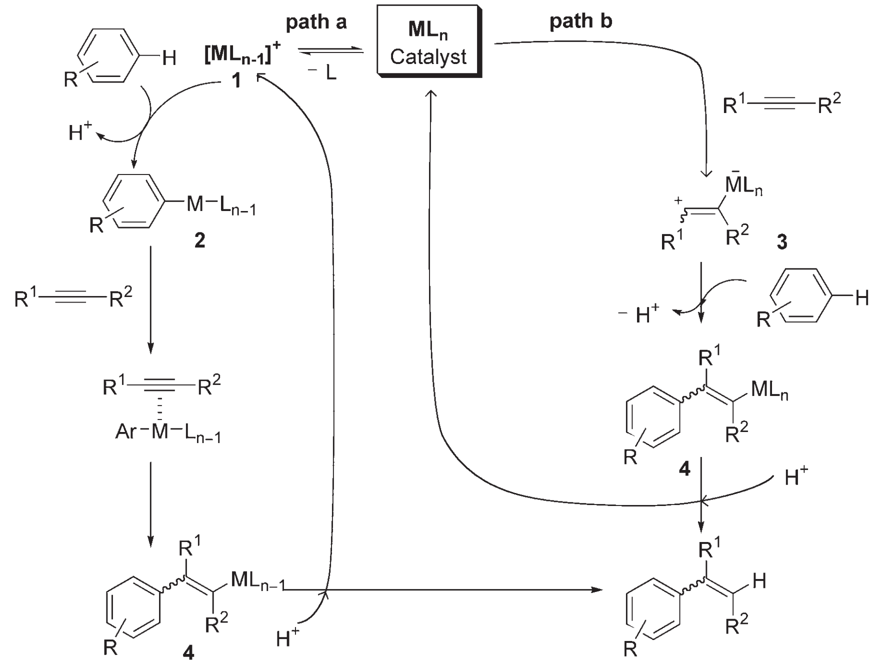
Abstract: In the metal triflate-catalyzed hydroarylation of alkynes, employing an ionic liquid dramatically enhanced the catalytic activities, resulting in broadening the scope of substrates (arenes and alkynes). In some cases, even reactions that were not possible in conventional organic solvents proceeded smoothly in ionic liquids. Moreover, the ionic liquid phase containing catalyst could be readily recovered by simple decantation of the organic layer after reaction and reused for the following runs without any significant loss of activity. Mechanistic studies including ^{13}C NMR analysis of reaction intermediates and isotope experiments confirmed for the first time that this type of reaction proceeds via vinyl cationic intermediates.

Keywords: enhanced Lewis acidity; Friedel–Crafts alkenylation; hydroarylation; ionic liquids containing non-coordinating anions; vinyl cation intermediates

Introduction

The hydroarylation of alkynes (also known as alkenylation of arenes)[1] catalyzed by transition metal complexes, thereby affording styrene derivatives, has received much attention because this approach is, in principle, simpler than those based on Heck reactions,[2] cross-coupling reactions[3] and olefin cross-metathesis reactions.[4] Intramolecular hydroarylation is also of particular interest, since valuable carbo- and heterocycles can be readily obtained.[1] Depending on the type of interaction between the metal and the arene or the triple bond, the hydroarylation of alkynes proceeds either *via* σ-aryl-metal species (see **2** in Scheme 1 below) generated through electrophilic metallation of arenes with metal cationic species **1** (path a in Scheme 1) or *via* alkenyl cation intermediates **3** formed by Lewis acid activation of alkynes (path b in Scheme 1).[1]

For example, in the hydroarylation of alkynes catalyzed by cationic complexes of Pd(II) and Pt(II), σ-aryl-metal species **2** were proposed as intermediates by Fujiwara et al.[5,6] Related mechanistic results with Au(III) catalysts were also reported by He.[7a] Although this type of hydroarylation of alkynes proceed in a highly regio- and stereoselective manner, the use of expensive metals [Pd(II), Pt(II), Au(III)] and the limited scope of the substrates have restricted their widespread use. Yields vary widely according to the nature of the arene and alkynes. Acceptable yields are obtained only with highly electron-rich arenes (usually having more than two electron-donating substituents), due to the characteristics of electrophilic metallation of aromatic C−H bond. Less activated arenes than xylene generally gave very poor yields.[5,7] Moreover, internal alkynes showed almost no reactivity with an Au catalyst.[7b] On the other hand, the Friedel–Crafts-type hydroarylation of alkynes (i.e., alkenylations of arenes with alkynes) which proceeds *via* alkenyl cation intermediate **3** followed by electrophilic attack to the arene can be promoted by Lewis acids. However, the major drawback of this Friedel–Crafts alkenylation is the oligomerization of the alkyne due to the instability of vinyl cationic intermediates **3**.[8] The well known Lewis acid metal chlorides such as $ZrCl_4$ and $AlCl_3$ produced the desired alkenylated products, but with extremely low yields [e.g., 1% and 6% yields of 1-phenyl-1-(*p*-xylyl)ethene



Scheme 1. Two possible mechanisms for metal-catalyzed hydroarylation of alkynes.

for the reaction of *p*-xylene with phenylacetylene using $ZrCl_4$ and $AlCl_3$ at 85 °C, respectively].[9] In contrast to the well established Friedel–Crafts alkylations of arenes with olefins,[10] the corresponding alkenylations with alkynes therefore still remained to be solved. In 2000, Tsuchimoto et al. made a breakthrough in this type of reaction with the discovery that some metal triflates [$M(OTf)_n$; M = Sc, Zr, In] can catalyze the alkenylation of arenes with internal alkynes as well as terminal alkynes through an alkenyl cationic intermediate.[9] However, the catalytic activity of these metal triflates is far too low for preparative use, which narrows the scope of the reaction. For example, the reaction of benzene and phenylacetylene in the presence of 10 mol% of $Sc(OTf)_3$ at 85 °C requires 186 h to give a 73% yield of 1,1-diphenylethene.[9] Moreover, $Sc(OTf)_3$ was totally inactive for electron-deficient alkynes such as *p*-CF_3-phenylacetylene and *p*-Cl-phenylacetylene. Therefore, a practical and more efficient catalyst system for the hydroarylation of alkynes is highly desirable.

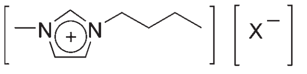
Room temperature ionic liquids (RTILs) are now regarded as eco-friendly alternatives to volatile organic solvents in chemical processes.[11] During our extensive investigations[12] on the utilization of RTILs in various catalytic reactions, we found that switching from an organic solvent to an ionic liquid for some $Sc(OTf)_3$-catalyzed reactions markedly improved the catalytic performance (e.g., increased reaction rates, selectivity improvements, etc.) as well as facile catalyst recycling. For example, in our earlier study we found that the $Sc(OTf)_3$-catalyzed Friedel–Crafts alkylation of aromatic compounds with alkenes is dramatically accelerated in the presence of ionic liquids containing very weakly coordinating anions such as [bmim][SbF_6] (**5a**) or [bmim][PF_6] (**5b**) (bmim = 1-butyl-3-methylimidazolium).[12a] We also found that the catalytic activity in $Sc(OTf)_3$-catalyzed Diels–Alder reactions was up to 100 times higher in the presence of ionic liquids such as **5a** or **5b** than that observed in conventional organic solvents.[12c] These results encouraged us to investigate the metal triflate-catalyzed Friedel–Crafts alkenylation of aromatics with alkynes in ionic liquids. Quite recently, we reported our preliminary results that ionic liquids such as **5a** or **5b** also enhanced catalytic activity dramatically in this reaction.[12h] Therefore, the aim of the present study was to optimize our protocol, investigate the substrate scope, and elucidate the plausible reaction mechanism.

We report herein that, in the metal triflate-catalyzed Friedel–Crafts alkenylation of arenes with alkynes, employing an ionic liquid can not only facilitate catalyst recycling but also dramatically enhance the catalytic activities, resulting in a broadening the scope of substrates. Moreover, it was confirmed for the first time by mechanistic studies that this type of reaction proceeds *via* vinyl cationic intermediates (path b in Scheme 1).

Results and Discussion

Effects of Ionic Liquids on Catalytic Activity

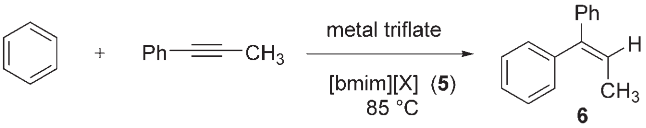
To investigate the effects of ionic liquids (Figure 1) on the catalytic activity of metal triflate in the Friedel–Crafts alkenylation reaction, we first examined the reaction between benzene and 1-phenyl-1-propyne under various conditions. The results are summarized in Table 1. The alkenylation of benzene with 1-phenyl-1-propyne in the presence of 10 mol% of $Sc(OTf)_3$ without an ionic liquid proceeded very slowly, with a product yield of only 27% after 96 h (entry 1 in Table 1). Moreover, this long reaction time resulted in increased undesired side product formation. On the other hand, when the reaction was carried out in the imidazolium salts **5a**, **b**, which contain very weakly coordinating anions such as SbF_6^- or PF_6^-, the catalytic activity of $Sc(OTf)_3$ was dramatically enhanced, and thus, the reaction was completed within 4 h and afforded the desired product, 1,1-diphenyl-1-propene (**6**), in excellent yields (91 or 90%, respectively, entries 2 and 3).[14] In sharp contrast to these results, however, in the hydrophilic ionic liquids, [bmim][BF_4] (**5c**) or [bmim][OTf] (**5d**), only tiny amounts of the alkenylated product were obtained after 4 h (<5% yield) (entries 4 and 5 in Table 1). A similar anion effect of ionic liquids on catalyst activity was observed by us in the $Sc(OTf)_3$-catalyzed Friedel–Crafts alkylation reactions.[12a] The origin of this significant effect of ILs, in particular the strong influence of anion-type on catalytic activity, might be attributed by anion exchange of metal triflate with weakly coordinating anions such as PF_6^- or SbF_6^- of ILs. By anion exchange, ILs having very weakly coordinating anions such as PF_6^- or SbF_6^- may activate the metal triflate catalyst, generating *in situ* a more Lewis acidic catalyst.[15]



[bmim][X]
(X = SbF_6 (**5a**), PF_6 (**5b**), BF_4 (**5c**), OTf (**5d**))

Figure 1. The ionic liquids used in this study.[13]

Table 1. Friedel–Crafts alkenylation of benzene with 1-phenyl-1-propyne.[a]



Entry	Catalyst (equivs.)	Ionic Liquid	Time [h]	Yield [%][b]
1	$Sc(OTf)_3$ (0.1)	none	96	27
2	$Sc(OTf)_3$ (0.1)	**5a**	4	91
3	$Sc(OTf)_3$ (0.1)	**5b**	4	90
4	$Sc(OTf)_3$ (0.1)	**5c**	4	<5
5	$Sc(OTf)_3$ (0.1)	**5d**	4	<5
6[9]	$In(OTf)_3$ (0.1)	none	16	63
7	$In(OTf)_3$ (0.1)	**5a**	2.5	81
8	$In(OTf)_3$ (0.05)	**5a**	6	94
9	$In(OTf)_3$ (0.025)	**5a**	24	91
10	$Hf(OTf)_4$ (0.1)	**5a**	1	90
11	$Hf(OTf)_4$ (0.05)	**5a**	5	91
12	$Hf(OTf)_4$ (0.025)	**5a**	9	85
13	$Y(OTf)_3$ (0.1)	**5a**	2	80
14	$Yb(OTf)_3$ (0.1)	**5a**	4	81
15	$Lu(OTf)_3$ (0.1)	**5a**	4	94

[a] All reactions were carried out at 85 °C using 1-phenyl-1-propyne (1 mmol), benzene (6 mL) and ionic liquid **5** (1 mL) in the presence of the metal triflate as a catalyst.

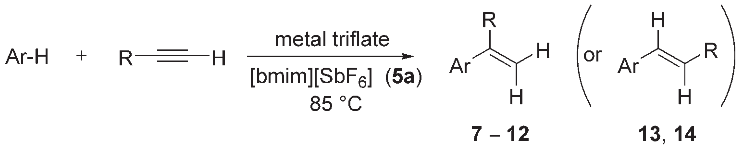
[b] Isolated yield based on 1-phenyl-1-propyne.

Next, we examined the catalytic activity of various metal triflates in the presence of **5a**. Among the various metal triflates investigated, indium triflate, hafnium triflate and yttrium triflate, in particular, were found to exhibit higher activity than scandium triflate, and thus, the reaction was completed within 2.5 h, 1 h and 2 h, respectively (entries 7, 10 and 13 in Table 1). Even in the presence of reduced amounts of these metal triflates (5 mol% and 2.5 mol%), the reactions proceeded smoothly with excellent yields (entries 8, 9, 11 and 12). Ytterbium triflate and lutetium triflate also exhibited similar catalytic activity to that of scandium triflate (entries 14 and 15). However, the catalytic activities of other metal triflates investigated in this study [Ag(OTf) (4%), $Cu(OTf)_2$ (27%), $Mg(OTf)_2$ (21%), $Zn(OTf)_2$ (2%), $Sn(OTf)_2$ (69%), $La(OTf)_3$ (62%), $Pr(OTf)_3$ (19%), $Nd(OTf)_3$ (37%), $Sm(OTf)_3$ (15%), $Eu(OTf)_3$ (16%), $Gd(OTf)_3$ (23%), $Tb(OTf)_3$ (34%), $Dy(OTf)_3$ (28%), $Ho(OTf)_3$ (30%), $Er(OTf)_3$ (40%), $Tm(OTf)_3$ (22%)] were much lower than those of $Sc(OTf)_3$, $In(OTf)_3$, $Hf(OTf)_4$, $Y(OTf)_3$, $Yb(OTf)_3$ and $Lu(OTf)_3$. This catalytic effect profile of various metal triflates is nearly consistent with the relative Lewis acidity scale evaluated by the use of tandem mass spectrometry[16] and observed in other metal triflate-catalyzed reactions.[17] The difference of catalytic activity between various metal triflates can be attributed to their charge density, i.e., the ionic radii of the metal cations, M^{n+}.[18]

Hydroarylation of Terminal Aryl-substituted Alkynes

To survey the scope and generality of our method, we first carried out a series of Friedel–Crafts alkenylations of arenes with several terminal alkynes in ionic liquid **5a**. As shown from the results in Table 2, all re-

Table 2. Metal triflate-catalyzed Friedel–Crafts alkenylation of arenes with terminal alkynes in **5a**.[a]



Entry	Ar-H	Alkynes (R)	Catalyst	Time	Product	Yield[b]	(*E*)/(*Z*)[c]
1	benzene	Ph	$Sc(OTf)_3$	4 h	**7**	70 %	-
2	*p*-xylene	Ph	$Sc(OTf)_3$	4 h	**8**	70 %	-
3	*p*-xylene	Ph	$In(OTf)_3$	3 h	**8**	80 %	-
4	*p*-xylene	Ph	$Hf(OTf)_4$	3 h	**8**	85 %	-
5	mesitylene	ferrocenyl	$Hf(OTf)_4$	5 min	**9**	78 %	-
6[d]	pentamethylbenzene	ferrocenyl	$Hf(OTf)_4$	5 min	**10**	65 %	-
7	*p*-xylene	*p*-CF_3-C_6H_4	$Sc(OTf)_3$	22 h	**11**	73 %	-
8	*p*-xylene	*p*-CF_3-C_6H_4	$In(OTf)_3$	5 h	**11**	78 %	-
9	*p*-xylene	*p*-CF_3-C_6H_4	$Hf(OTf)_4$	5 h	**11**	68 %	-
10	*p*-xylene	*p*-Cl-C_6H_4	$Sc(OTf)_3$	12 h	**12**	63 %	-
11	*p*-xylene	*p*-Cl-C_6H_4	$Hf(OTf)_4$	4 h	**12**	70 %	-
12	mesitylene	COMe	$Hf(OTf)_4$	10 min	**13**	73 %	> 99/1
13[d]	pentamethylbenzene	COMe	$Hf(OTf)_4$	15 min	**14**	76 %	> 99/1

[a] Unless otherwise indicated, all reactions were carried out using alkyne (1 mmol), arene (6 mL) and ionic liquid **5a** (1 mL) in the presence of metal triflate (10 mol % based on alkyne) as a catalyst at 85 °C.

[b] Isolated yields based on the alkyne.

[c] (*E*)/(*Z*) ratios were determined by ^{1}H NMR spectroscopy.

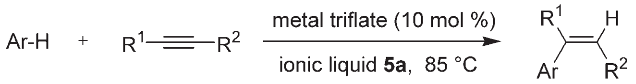
[d] One equivalent of solid arene based on alkyne (1 mmol) and 4 mL of 1,2-dichloroethane as a co-solvent were used.

actions with aryl-substituted alkynes proceeded much faster than those without using an ionic liquid[9] and, thus, were completed within a few minutes to a few hours, affording the corresponding alkenylated products in good to excellent yields with perfect regioselectivity in favor of the Markovnikov-type 1,1-product (entries 1–11). For example, in the presence of ionic liquid **5a**, the reaction of benzene with phenylacetylene was completed within 4 h affording the desired product, 1,1-diphenylethene (entry 1). On the other hand, in a common organic solvent such as CH_3NO_2, a much longer reaction time (186 h) was required to complete the reaction.[9] Under strict anaerobic conditions, ferrocenylacetylene could be also hydroarylated within 5 min, affording **9** and **10** in good yields (entries 5 and 6). In all cases of entries 1–11, no other regioisomer was observed by analysis of the reaction mixture with GC-MS and ^{1}H NMR. The perfect regiochemistry can be attributed to the conjugative stabilizing effect of the α-aryl group on the vinyl cation intermediate **3**. Notably, $Sc(OTf)_3$, $In(OTf)_3$ and $Hf(OTf)_4$ effectively catalyzed the alkenylation of the electron-deficient alkynes such as *p*-CF_3-phenylacetylene and *p*-Cl-phenylacetylene, which were totally inactive without ionic liquid (entries 7–11).[9] In these reactions, $In(OTf)_3$ and $Hf(OTf)_4$ exhibited higher catalytic activities than those of $Sc(OTf)_3$ (entries 7 and 10 *vs.* entries 8, 9 and 11). We also tested the reactions of the terminal alkynes conjugated to an electron-withdrawing group such as COMe. The reaction of arenes with an alkynone, 3-butyn-2-one, was completed within 15 min, giving exclusively β-aryl-substituted *trans*-alkenes, (*E*)-4-aryl-3-buten-2-ones **13** and **14** (entries 12 and 13 in Table 1). No other regio- or stereoisomers were observed in the reaction mixture. The regiochemistry of this reaction is dominated by the electronic effect in a type of Lewis acid-catalyzed Michael addition. The possible reasons for the (*E*)-selectivity of the reaction will be discussed in the latter part of this paper.

Hydroarylation of Internal Alkynes

The scope of our method was further explored by the reactions of electron-rich and electron-poor arenes with various internal alkynes using 10 mol % of $Sc(OTf)_3$, $In(OTf)_3$ or $Hf(OTf)_4$ in the presence of **5a**. As shown in Table 3, in the presence of an ionic liquid, all reactions proceeded much faster than those without using an ionic liquid, and were highly regio- and stereoselective, giving the corresponding alkenylation products in good to excellent yields with high (*Z*)-selectivity. The regio- and stereochemistries of all products were assigned by comparison with ^{1}H NMR spectroscopic data from the literature.[5,7,19] It should be here noted that, as mentioned previously, when using cationic Pd and Pt catalysts, only the electron-

Table 3. Metal triflate-catalyzed Friedel–Crafts alkenylation of arenes with internal alkynes in **5a**.[a]



Entry	Ar-H	Alkyne		Catalyst	Time	Product	Yield[b]	(*E*)/(*Z*)[c]
		R^1	R^2					
1	benzene	Ph	Me	$Sc(OTf)_3$	4 h	**6**	91%	-
2	benzene	Ph	Ph	$Sc(OTf)_3$	2 h	**15**	79%	-
3	benzene	Ph	Ph	$In(OTf)_3$	2 h	**15**	82%	-
4	benzene	Ph	Ph	$Hf(OTf)_4$	1 h	**15**	92%	-
5	benzene	Ph	CO_2Et	$Hf(OTf)_4$	22 h	**16**	89%	-
6	*p*-xylene	Ph	Me	$Sc(OTf)_3$	4 h	**17**	96%	4/96
7	*p*-xylene	Ph	Ph	$Sc(OTf)_3$	4 h	**18**	80%	12/88
8	*p*-xylene	Ph	CO_2Et	$Hf(OTf)_4$	10 h	**19**	70%	13/87
9	mesitylene	Ph	Me	$Hf(OTf)_4$	1 h	**20**	92%	1/99
10	mesitylene	Ph	Ph	$Hf(OTf)_4$	1.5 h	**21**	90%	1/99
11	mesitylene	Ph	COMe	$Hf(OTf)_4$	30 min	**22**	72%	1/99
12	mesitylene	Ph	CO_2Et	$Hf(OTf)_4$	13 h	**23**	72%	1/99
13[d]	pentamethylbenzene	Ph	Me	$Hf(OTf)_4$	15 min	**24**	81%	1/99
14[d]	pentamethylbenzene	Ph	Ph	$Hf(OTf)_4$	1 h	**25**	77%	1/99
15[d]	pentamethylbenzene	Ph	COMe	$Hf(OTf)_4$	12 h	**26**	67%	1/99
16[d]	pentamethylbenzene	Ph	CO_2Et	$Hf(OTf)_4$	29 h	**27**	70%	10/90
17[d]	naphthalene	Ph	Me	$Hf(OTf)_4$	10 min	**28**	92%[e]	n.d.
18	chlorobenzene	Ph	Me	$In(OTf)_3$	1 h	**29**	38%[f]	n.d.
19	chlorobenzene	Ph	Ph	$Sc(OTf)_3$	6 h	**30**	44%[f]	n.d.

[a] Unless otherwise indicated, all reactions were carried out using alkyne (1 mmol), arene (6 mL) and ionic liquid **5a** (1 mL) in the presence of 10 mol% metal triflates as catalyst at 85 °C.

[b] Isolated yield based on the alkyne.

[c] (*E*)/(*Z*) ratios were determined by ^{1}H NMR spectroscopy.

[d] 1 equivalent of solid arene based on alkyne (1 mmol) and 4 mL of 1,2-dichloroethane as a co-solvent were used.

[e] The reaction gave an inseparable mixture of 1-naphthyl (major isomer) and 2-naphthyl regioisomers, including the corresponding (*E*)/(*Z*) isomers. The isomer ratio determined by GC-MS analysis was 75/19/4/1 (entry 17).

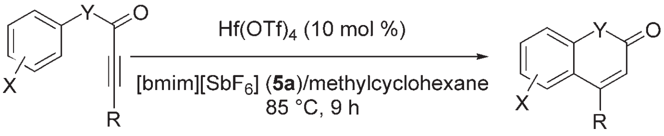
[f] The reaction gave an inseparable mixture of *ortho* and *para* regioisomers, including the corresponding (*E*)/(*Z*) isomers. The isomer ratios determined by GC-MS analysis are as follows: 11/15/31/39 (entry 18) and 8/18/34/40 (entry 19).

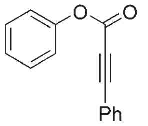
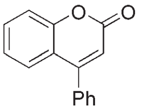
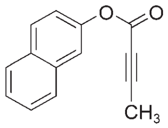
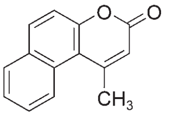
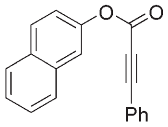
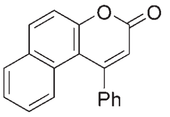
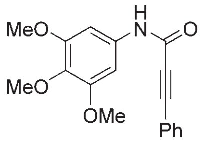
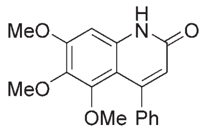
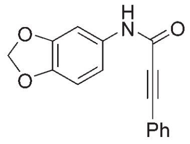
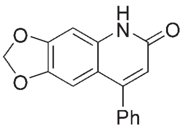
rich arenes (usually having more than two electron-donating substituents) underwent the reactions with internal alkynes.[5] Moreover, Au catalysts cannot catalyze the reaction with internal alkynes.[7b] In contrast to these results, our reaction recipe could be more widely applicable even for arenes having electron-withdrawing groups. For example, the reactions of chlorobenzene with 1-phenyl-1-propyne or diphenylacetylene using $Sc(OTf)_3$ (10 mol%) in [bmim][SbF_6] proceeded smoothly and, thus, were completed within a few hours, affording the corresponding products as a mixture of *o*-, *m*- and *p*-regioisomers in moderate yields (entries 18 and 19). The reaction of arenes with the alkynes conjugated to an electron-withdrawing group such as COMe and CO_2Et in the presence of $Hf(OTf)_4$ also proceeded smoothly in ionic liquid **5a** (entries 5, 8, 11, 12. 15 and 16), whereas only <5% conversion was observed without [bmim][SbF_6] (**5a**).

Intramolecular Hydroarylation

Finally, our protocol has been further extended to intramolecular hydroarylation (Table 4). The intramolecular reaction of aryl phenylpropiolates **31** or **35** catalyzed by $Hf(OTf)_4$ (10 mol%) in a mixture of **5a** and methylcyclohexane at 85 °C for 9–10 h proceeded regioselectively, affording the 4-phenylcoumarins **32** or **36**, respectively, in good yields. Surprisingly, the reaction of aryl 2-butynoate **33** was also successfully performed to afford the corresponding coumarin **34** in excellent yield. Due to the lower stabilizing effect of the alkyl group compared to the phenyl group on the vinyl cation intermediate, alkyl-substituted alkynes usually underwent self-oligomerization rather than the desired alkenylation reaction. The intramolecular alkenylation allowed us also to synthesize 2(1*H*)-quinolinones **38** or **40** from the corresponding arylamides of phenylpropiolic acid **37** or **39** in good yields.

Table 4. Metal triflate-catalyzed intramolecular Friedel–Crafts alkenylation in **5a**.[a]



Entry	Substrate		Product		Yield (%)[b]
1		**31**		**32**	51
2		**33**		**34**	89
3		**35**		**36**	55
4		**37**		**38**	72
5		**39**		**40**	72

[a] All reactions were carried out at 85 °C using the substrate (1 mmol), methylcyclohexane (6 mL) and ionic liquid **5a** (1 mL) in the presence of 10 mol% of Hf(OTf)$_4$ as a catalyst.

[b] Isolated yield.

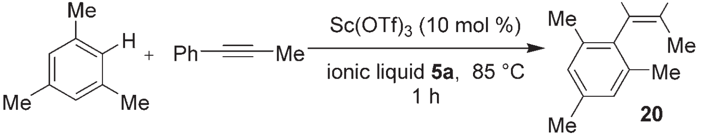
Catalyst Recycling Experiment

In order to test the immobilization effect of ionic liquid on the catalyst, we also performed the following recycling experiments. After completion of the reaction of mesitylene with 1-phenyl-1-propyne, when the reaction mixture was cooled to −40 °C, the ionic liquid phase (lower layer) containing the Sc catalyst remained as a solid. The product phase (upper layer) was then simply separated by decantation (i.e., by "pouring off" the organic products). Interestingly, the recovered ionic liquid phase containing the Sc catalyst exhibited nearly indefinite stability under the reaction conditions which allowed for its repeated recycling. Thus, the catalyst was reused eight times without any significant loss of activity (Table 5).

Computational Calculation of the Relative Energies of the (*E*)/(*Z*) Stereoisomers

In their previous study,[5] Fujiwara et al. assigned the (*Z*)-isomers of trisubstituted alkenes obtained in this work as the kinetic product. Without consideration for structural details, one may expect the (*Z*)-configuration to be energetically more disfavored than the (*E*)-configuration because of the bulkier groups on the same side of the double bond. However, our and Tsuchimoto's[9] experimental data signify that the (*Z*)-isomers are the thermodynamically rather than the kinetically controlled products. In agreement with the observation of Tsuchimoto et al.,[9] we also observed that at the initial stage of the reaction both stereoisomers exist in the reaction mixture, whereas (*Z*)-isomers were obtained predominantly as the main products at the end of the reaction. To elucidate the aforementioned conflict, we carried out *ab initio* calculations for (*E*)/(*Z*)-isomers of 1-phenyl-1-(*p*-xylyl)propene (**17**), 1,2-diphenyl-1-(*p*-xylyl)ethene (**18**), 1-pentamethylphenyl-1-phenylpropene (**24**) and 1-pentamethylphenyl-1,2-diphenylpropene (**25**) as representatives at the levels of density functional theory (DFT) and Möller-Plesset second order perturbation (MP2) theory with the 6-31G* basis set using a suite of the Gaussian 03 program.[20] It should be noted from the calculated structures that the steric effect would be negligible even in the case of highly bulky compounds **24** and **25** because it was found that for all the compounds calculated the (*Z*)-isomers are more stable than the (*E*)-isomers. The relative energies of the (*E*)-isomers with respect to the corresponding (*Z*)-isomers are 1.12, 1.27, 2.19 and 2.97 kcal

Table 5. Catalyst recycling experiment.



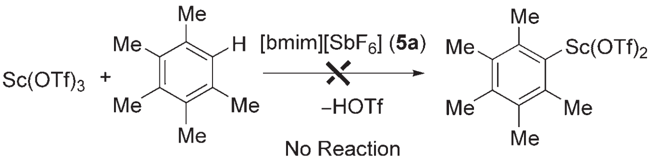
Run	1	2	3	4	5	6	7	8
Yield [%]	91	90	92	90	90	94	93	90

mol^{-1} for **17**, **18**, **24** and **25**, respectively, at the MP2/6-31G* level with zero-point-energy (ZPE) corrections using the vibrational frequencies calculated at the B3LYP/6-31G* level [for the MP2/6-31G* optimized structures of (*Z*)- and (*E*)-isomers of **17**, **18**, **24** and **25**, see the Supporting Information]. These relative energies give theoretical (*E*)/(*Z*) ratios [for example, (*E*)/(*Z*) = 13:87, 11:89, 2:98 and 1:99 for **17**, **18**, **24** and **25**, respectively], considering the Boltzmann distribution at 300 K, that are in excellent agreement with the experimental (*E*)/(*Z*) ratios [for example, (*E*)/(*Z*) = 4/96, 12/88, 1/99 and 1:99 for **17**, **18**, **24** and **25**, respectively]. The (*E*)/(*Z*) ratio can be explained from the C–H•••••π interactions between the methyl (or phenyl) and aryl groups (*p*-xylyl or pentamethylphenyl). The C–H•••••π interactions have been found in a number of complexes involving aromatic moiety.[21] For example, in **17**, the hydrogen atoms of vinyl-CH_3 interact with the π-electron cloud of the *p*-xylyl group in the (*Z*)-conformer, while they interacts with the phenyl group in the (*E*)-isomer. Obviously, an electron-donating substituent at the phenyl strengthens the C–H•••••π interactions by increasing the π-electron density of the aryl group. Thus, the intramolecular C–H•••••π interactions are responsible for the preference for the (*Z*)-isomer over the corresponding (*E*)-isomer because the steric effect seems to be negligible as noted in the optimized structures. This preference for (*Z*)-isomer over (*E*)-isomer can also be explained in **18**, **24** and **25** by a similar reasoning. For **18**, the aromatic-aromatic interactions are working between two phenyl groups. The preference for the (*Z*)-isomer is much more pronounced in compounds **24** and **25** than in **17** and **18** because five electron-donating methyl groups at the phenyl moiety enhance the π-electron density significantly. The distance between hydrogen atoms of the methyl (or phenyl) group and the nearest carbon atom of the *p*-xylyl (or pentamethylphenyl) group is about 2.66–2.75 Å, which is in the range of typical π-hydrogen interactions.[21] The induction energy should be larger in (*Z*)-conformers than in their corresponding (*E*)-isomers, as revealed from the natural bond orbital (NBO) population analysis. The NBO charges of the hydrogen atom of the methyl (or phenyl) of (*Z*)-isomers are less positive than those of (*E*)-isomers, indicating that more charge is transferred from π-electron cloud to the methyl hydrogen in the (*Z*)-isomer than in the (*E*)-isomer. Therefore, the C–H•••••π interactions are stronger in the (*Z*)-isomer than in the (*E*)-isomer, consistent with the relative stability. Our computational results clearly explain that the product ratio of the (*E*)- and (*Z*)-isomers is thermodynamically rather than kinetically determined.

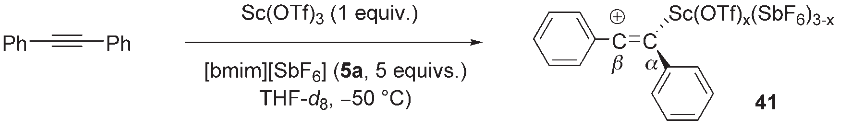
Mechanistic Considerations

Studies on the Reaction Pathway

As mentioned in the Introduction, metal triflates have been believed to promote a Friedel–Crafts type hydroarylation (path b in Scheme 1).[9,12h] Nevertheless, to examine the possible involvement of σ-aryl-metal complex **2** (path a in Scheme 1), we mixed stoichiometric amounts of $Sc(OTf)_3$ with pentamethylbenzene in [bmim][SbF_6] (**5a**). After stirring this mixture at 85 °C for 1 h, the reaction mixture was analyzed by ^1H NMR. No change of the aromatic proton signal in the ^1H NMR spectrum was observed (Scheme 2). On the other hand, it has been reported that the aryl proton immediately disappeared when mixing the Pd(II)[5] or Au(III)[7a] catalyst with pentamethylbenzene at room temperature. Thus, the possible involvement of σ-aryl-metal species **2** in our reaction can be excluded. Rather, as proposed by Tsuchimoto et al.,[9] it is more likely that vinyl cationic intermediates **3** may be involved in our reaction. The ratio of *o*-, *m*- and *p*-regioisomers in the reactions with chlorobenzene (entries 18 and 19 in Table 3) is typical for Friedel–Crafts electrophilic aromatic substitution and this is indirect evidence for the reaction pathway. To gain more direct evidence for the involvement of the vinyl cationic intermediates **3** in our reaction, we next tried to detect the vinyl cationic species **3** in the mixture of diphenylacetylene with $Sc(OTf)_3$ and [bmim][SbF_6] (**5a**) by ^{13}C NMR spectroscopy (Scheme 3). In many reports,[22] vinyl cations,



Scheme 2.



Scheme 3.

i.e., dicoordinated carbocations in which the positive charge is located at an *sp*-hybridized carbon of a double bond, have been established as reaction intermediates in the protonation reactions of alkynes.[23] Some vinyl cations generated by protonation of alkynes in superacidic media at temperatures below −100 °C have been characterized by NMR spectroscopy.[24] In our case, fortunately, the lifetime of vinyl cation **41** generated from diphenylacetylene with 1 equiv. of $Sc(OTf)_3$ in the presence of ionic liquid **5a** (5 equivs.) was sufficient to obtain a ^{13}C NMR spectrum at −50 °C. As shown from the ^{13}C NMR spectrum (125 MHz) in Figure 2 (a), three characteristic signals for vinyl cationic carbons in **41** (225.6, 218.8 and 176.4 ppm) were observed initially, indicating that at least three vinyl cationic species were present. However, the two peaks at 225.6 and 218.8 ppm disappeared after 1 min, while the cation peak at 176.4 ppm could be observed even after 1 h at −50 °C although its intensity did decrease with time.[25] The possible reason for the existence of several vinyl cationic species can be attributed to the formation of several Sc species by the anionic exchange reaction of $Sc(OTf)_3$ and ionic liquid **5a**. This result provides clear evidence that the reaction proceeds through the Friedel–Crafts alkenylation reaction pathway (path b in Scheme 1).

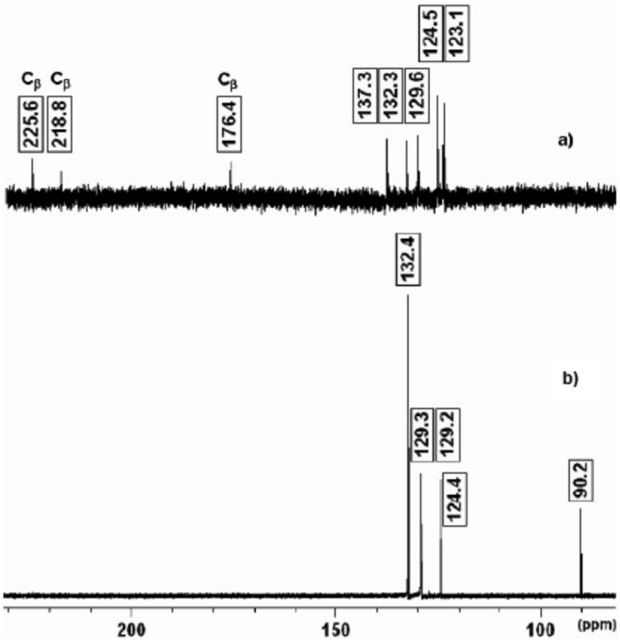
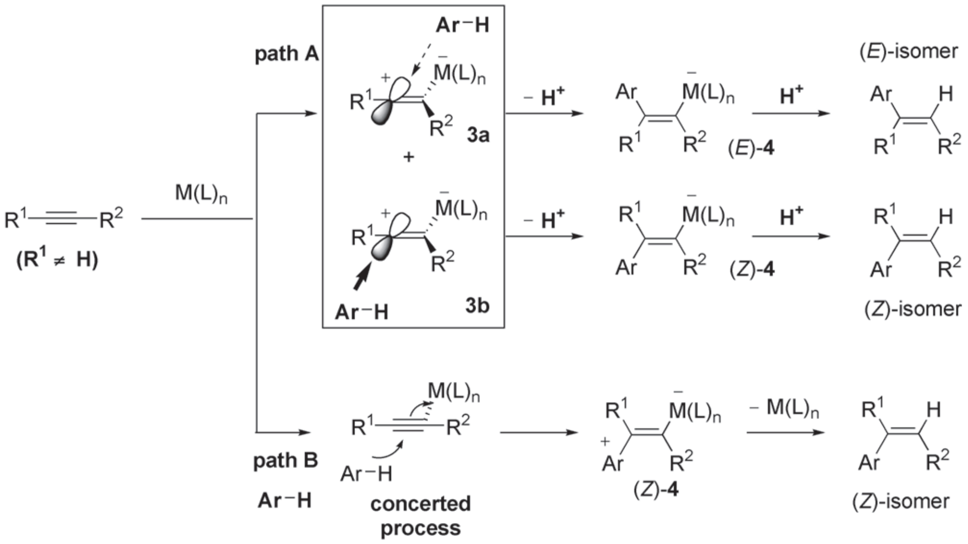


Figure 2. (**a**) Part of ^{13}C NMR spectrum of cation **41** at −50 °C in [D$_8$]THF (after 15 seconds); (**b**) Part of ^{13}C NMR spectrum of diphenylacethylene.

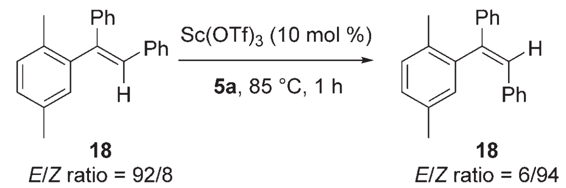
Generally, two routes (paths A and B in Scheme 4) may be possible for the Friedel–Crafts alkenylation reaction pathway (path b in Scheme 1). Similarly to that observed in the metal triflate-catalyzed reaction without using ionic liquids,[9] both (*Z*)/(*E*)-stereoisomers were also observed at the early stage of the reaction of arenes with internal alkynes in the presence of ionic liquids. This result, together with the aforementioned ^{13}C NMR analysis of the carbocation **41**, strongly indicates that the reaction proceeds not through a concerted process (path B in Scheme 4) but *via* vinyl cationic intermediates **3** (path A in Scheme 4). As already proposed by Tsuchimoto et al.,[9] if the reaction proceeds through a concerted mechanism (i.e., the simultaneous activation of an



Scheme 4. The possible two routes (paths A and B) for the Friedel–Crafts alkenylation reaction with $Sc(OTf)_3$ and [bmim][SbF_6] (**5a**).

alkyne by a metal triflate and the attack of an arene to the activated alkyne), an arene attacks the alkyne stereoselectively from the side opposite to the metal triflate, consequently giving the (*Z*)-isomer as the sole product. On the other hand, in path A, the arene attack, which initially formed vinyl cationic intermediates **3a** and **3b** (in Scheme 4) from both sides, affords a mixture of (*E*)-vinyl-M complex (*E*)-**4** and (*Z*)-vinyl-M complex (*Z*)-**4**, which are subsequently transformed by protonation to (*E*)-isomer and (*Z*)-isomer, respectively. This reaction pathway (path A in Scheme 4) is strongly supported by the existence of both stereoisomers at the initial stage of the reaction and the predominance of the (*Z*)-isomer at the end of the reaction. That is, as proposed by Tsuchimoto et al.,[9] the reaction at the initial stage proceeds *via* (*E*)-vinyl metal intermediate (*E*)-**4** which gives the corresponding (*E*)-isomer which is then transformed to the thermodynamically favored (*Z*)-isomer by Lewis acid-catalyzed isomerization (Scheme 5). To prove this, compound **18** with an (*E*)/(*Z*)-ratio of 92/8[26] was heated to 85 °C in the presence of Sc(OTf)$_3$ and **5a** (Scheme 6). As expected, the initial (*E*)/(*Z*) ratio of 92/8 of **18** was changed to 6/94 after 1 h.

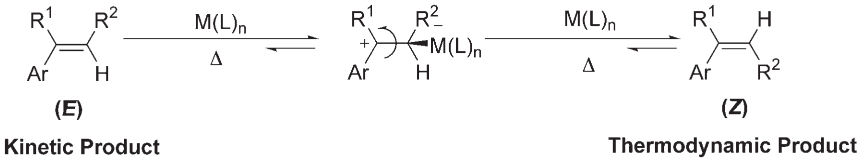
In the case of the reactions of arenes with the terminal alkynes conjugated with a carbonyl group such as 3-butyne-2-one, (*E*)-isomers were obtained as sole products at the end of the reaction (entries 12 and 13 in Table 2). Rather than being due to a change in mechanism, this (*E*)-selectivity is likely to be due to the isomerization of the initially formed (*Z*)-isomers under the conditions to the thermodynamically favorable (*E*)-isomers.



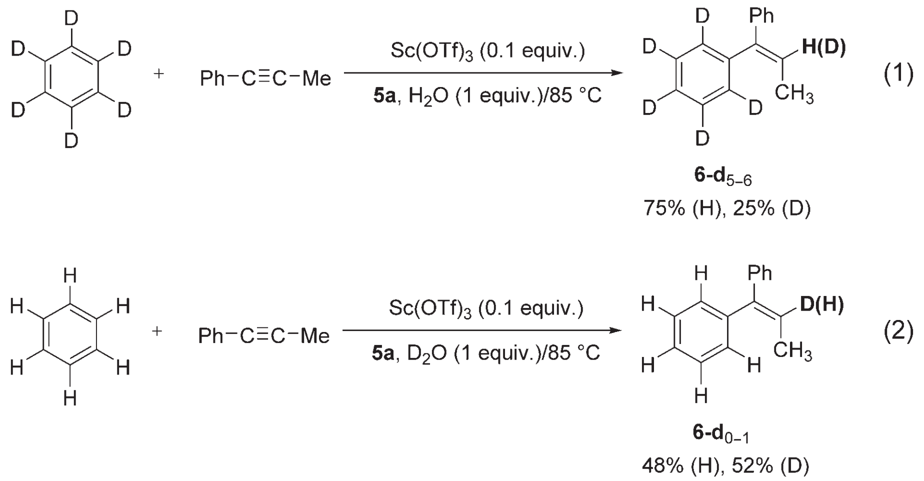
Scheme 6. Isomerization experiment of **18**.

Formation of Vinyl-M Species

To gain further insights of the mechanism, an isotope experiment was carried out on the reaction of benzene-d_6 with an internal alkyne (1-phenyl-1-propyne) in the presence of H_2O (1 equiv.) and [bmim][SbF$_6$] (**5a**) [Eq. (1) in Scheme 7] using Sc(OTf)$_3$ as catalyst. The ^{1}H NMR spectrum of **6-d$_{5-6}$** [Figure 3 (a)] showed that around 25 % of deuterium atoms and 75 % of protons were incorporated into the vinyl part of product **6-d$_{5-6}$**. The GC/MS confirmed the predominant formation of the five-deuterium-incorporated adduct **6-d$_5$** (*m*/*z* M$^+$ for **6-d$_5$** = 199.1, 200.1). Benzene was also reacted with 1-phenyl-1-propyne in the presence of D_2O (1 equiv.) and [bmim][SbF$_6$] (**5a**) [Eq. (2) in Scheme 7]. The incorporation of D (52 %) from D_2O



Scheme 5. Lewis acid-catalyzed isomerization to the thermodynamically favored (*Z*)-isomer.



Scheme 7. Isotope experiments.

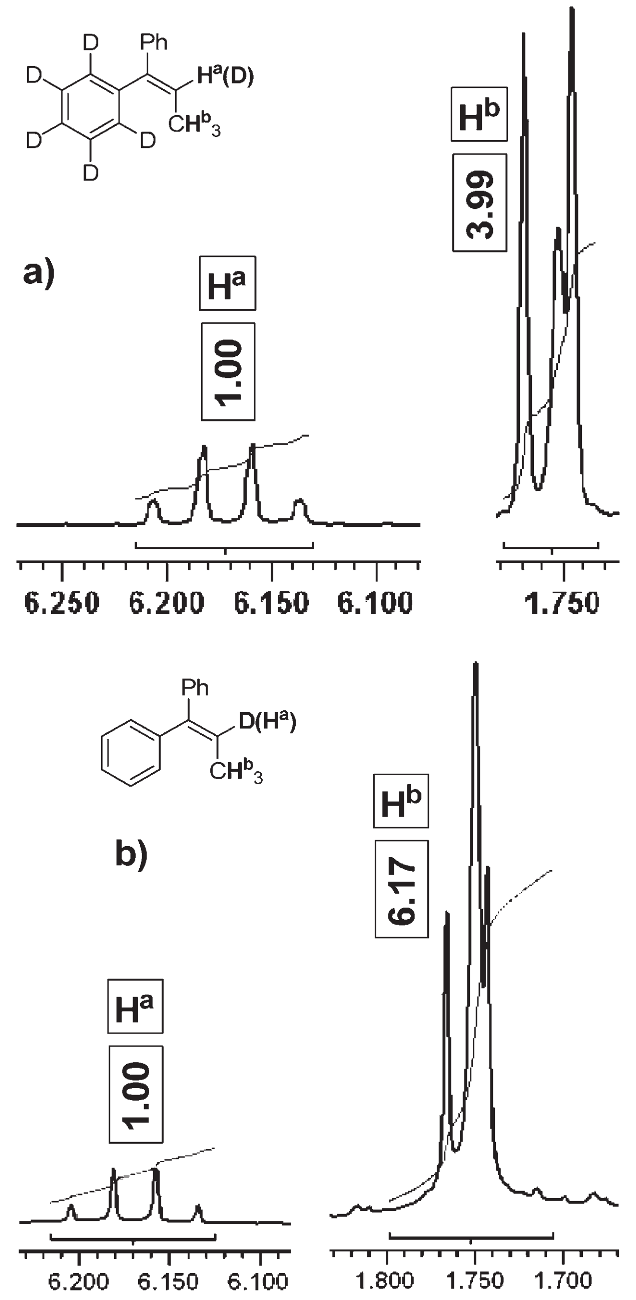


Figure 3. Part of ^1H NMR spectrum of **a)** **6-d_{5-6}** and **b)** **6-d_{0-1}**.

and H (48%) from aromatic substrate into the vinyl part of adduct **6-d_{0-1}** was observed on the basis of ^1H NMR [Figure 3 (b)] and GC/MS (*m*/*z* M^+ for **6-d_1** = 195.1, 196.1) analysis. All these results strongly suggest that the deuterium cation [Eq. (1) in Scheme 7] or proton [Eq. (2) in Scheme 7] originated from the aromatic substrate during the reaction is liberated into the solution before it is incorporated into the final product. These results in combination provide strong evidence for formation of the vinyl-metal complexes **4**.

Conclusions

In summary, by employing an ionic liquid, a simple and highly regio- and/or stereoselective method for metal triflate-catalyzed, inter- and intramolecular Friedel–Crafts alkenylation of a broad spectrum of arenes and alkynes was realized. In some cases, moreover, even those reactions that were not possible in conventional organic solvents proceeded smoothly in ionic liquids. To our knowledge, the protocol described here is the most broad-scoped alkenylation method presented in the literature so far. Moreover, the ionic liquid phase containing catalyst could be readily recovered by simple decantation of the organic layer after reaction and reused for subsequent runs without any significant loss of activity. Mechanistic studies including ^{13}C NMR analysis of vinyl cations and isotope experiments confirmed for the first time that this type of reaction proceeds *via* vinyl cationic intermediates.

Experimental Section

General Remarks

All reactions were performed in an argon atmosphere using standard Schlenk techniques An inert atmosphere is advisable in order to minimize ketone formation and catalyst deactivation.

Chromatographic purification of products was carried out by flash chromatography using Merck silica gel 60 (230–400 mesh). Thin layer chromatography was carried out on Merck silica gel 60F plates. ^1H and ^{13}C NMR spectra were recorded on Varian 300 and Varian 500 spectrometers using Me_4Si as an internal standard. GC-MS analysis was performed using GC/MSD; Varian 4000. The molecular mechanics calculations were made by using a suite of the Gaussian 03 program.[20]

All metal triflates used in this study were purchased from Aldrich. Ionic liquids **5a–e** were purchased from C-Tri Co., Ltd., Korea, http://www.c-tri.co.kr/) and used without further purification. They were spectrometrically pure, nearly chloride-free (<10 ppm) and their water content was <200 ppm (determined by Karl-Fisher titration). Other organic solvents were dried (CaH_2 or Na) and distilled under an argon atmosphere prior to use. All other chemicals were obtained from commercial sources and used without further purification.

Isolated compounds were fully characterized by ^1H, ^{13}C NMR and GC/MS (For ^1H and ^{13}C NMR data, see the Supporting Information). The stereochemistry of all adducts was assigned by comparison with literature NMR spectroscopic data.[5,7,19].

Typical Procedure for Intermolecular Friedel–Crafts Alkenylations in Ionic Liquid

Liquid Arenes (benzene): Under an argon atmosphere, 1-phenyl-1-propyne (116.1 mg, 1 mmol) was added to a mixture of $Sc(OTf)_3$ (49.2 mg, 0.1 mmol), benzene (6 mL) and [bmim][SbF_6] (1 mL). Two phases were formed and the mixture was stirred at 85 °C until the disappearance of alkyne, as monitored by TLC or GC-MS (4 h). After cooling to room temperature, the reaction mixture was poured into a saturated aqueous NaCl solution and extracted with ethyl acetate. The organic layer was washed with water, and dried over anhydrous Mg_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica (hexane) to give pure 1,1-diphenyl-1-propene (**6**) as a pale yellow viscous liquid; yield: 177 mg (91 %).

Solid Arenes (pentamethylbenzene): Under an argon atmosphere, 1-phenyl-1-propyne (116.1 mg, 1 mmol) was added to a mixture of $Sc(OTf)_3$ (49.2 mg, 0.1 mmol), pentamethylbenzene (148.2 mg, 1 mmol) in dichloroethane (4 mL) and [bmim][SbF_6] (1 mL). The reaction mixture was stirred at 35 °C until the disappearance of alkyne, as monitored by TLC or GC-MS (15 min). After cooling to room temperature, the reaction mixture was poured into a saturated aqueous NaCl solution and extracted with ethyl acetate. The organic layer was washed with water, and dried over anhydrous Mg_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica (hexane) to give pure 1-pentamethylphenyl-1-diphenyl-1-propene (**24**) as a pale yellow solid; yield: 214.1 mg (81 %).

Synthesis of Aryl 3-Substituted Propiolates and Alkynamides

Representative procedure for the synthesis of 3-substituted propiolic acid aryl esters: $Me_3N{\cdot}HCl$ (258 mg, 2.7 mmol) was added to a stirred solution of phenylpropiolic acid (204.6 mg. 1.4 mmol), phenol (131.7 mg, 1.4 mmol), Et_3N (414.9 mg, 4.1 mmol), and DMAP (12,2 mg, 0.1 mmol) in CH_3CN (1.0 mL) at 0–5 °C under an argon atmosphere, and the mixture was stirred for 10 min. To this mixture, a solution of Me_2NSO_2Cl (387.7 mg, 2.7 mmol) in MeCN (1.0 mL) was then added and the mixture was maintained at 0–5 °C while being stirred for 3 h. Water was added to the mixture, which was extracted with ether. The organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated. The obtained crude product was purified by flash column chromatography (hexane:ether = 1:1) to give pure phenyl 3-phenylpropiolate as a white solid; yield: 270 mg (87 %).

Representative procedure for the synthesis of phenylpropiolic acid arylamides: $Me_3N{\cdot}HCl$ (258 mg, 2.7 mmol) was added to a stirred solution of phenylpropiolic acid (204.6 mg, 1.4 mmol), 3,4,5-trimethoxyaniline (256.5 mg, 1.4 mmol), Et_3N (414.9 mg, 4.1 mmol), and DMAP (12.2 mg, 0.1 mmol) in CH_3CN (1.0 mL) at 0–5 °C under an argon atmosphere, and the mixture was stirred for 10 min. To this mixture, a solution of Me_2NSO_2Cl (387.7 mg, 2.7 mmol) in MeCN (1.0 mL) was then added and the mixture was maintained at 0–5 °C while being stirred for 3 h. Water was added to the mixture, which was extracted with ethyl acetate. The organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated. The obtained crude product was purified by flash column chromatography (hexane:ethyl acetate = 1: 2) to give pure phenyl propiolic acid 3,4,5-trimethoxyphenylamide as a yellow solid; yield: 366 mg (84 %).

Typical Procedure for Intramolecular Friedel–Crafts Alkenylations in Ionic Liquid

Under an argon atmosphere, a mixture of $Hf(OTf)_4$ (77.4 mg, 0.1 mmol), phenyl 3-phenylpropiolate (222.1 mg, 1 mmol), methylcyclohexane (6 mL) and [bmim][SbF_6] (1 mL) was refluxed for 9 h. After reaction completion, the reaction mixture was cooled to room temperature, all the volatiles were removed under reduced pressure and then the residue was purified by flash column chromatography on silica (hexane:diethyl ether) to give pure 4-phenylcoumarin as a pale yellow solid; yield: 113 mg (51 %).

Catalyst Recycling Experiment

Under an argon atmosphere, 1-phenyl-1-propyne (116.1 mg, 1 mmol) was added to a mixture of $Sc(OTf)_3$ (49.2 mg, 0.1 mmol), mesitylene (6 mL) and [bmim][SbF_6] (1 mL). Two phases are formed and the mixture was stirred at 85 °C until the disappearence of alkyne as monitored by TLC or GC-MS (1 h). After completion of the reaction, the reaction mixture was cooled to −40 °C. The organic layer (upper phase) was separated simply by decantation to leave the solidified ionic liquid phase containing the catalyst which can be reused for next runs. The further work-up procedure was the same as described above. Yields are given in Table 5.

Preparation of Vinyl Cations 41 and their ^{13}C NMR Analysis

In a 5-mm NMR tube, diphenylacetylene (11.1 mg, 0.062 mmol) and $Sc(OTf)_3$ (30.7 mg, 0.062 mmol) were added under argon atmosphere. To this solid mixture, a solution of [bmim][SbF_6] (**5a**, 117.1 mg, 0.312 mmol) in dried THF-d_8 (0.6 mL) was added dropwise at −78 °C and sealed. At this temperature, the reaction mixture remained undissolved. Warming this mixture to −50 °C led to complete dissolution. Thus, at this temperature ^{13}C NMR spectra of the reaction mixture were measured. Spectra are given in Figure 2.

Isomerization Experiment

A solution of **18** (29.6 mg, 0.104 mmol) with a (*E*)/(*Z*)-ratio of 92/8[26] in 2 mL of 1,2-dichloroethane was heated for 1 h at 85 °C in the presence of $Sc(OTf)_3$ (4.9 mg, 0.01 mmol) and **5a** (0.5 mL). After cooling, the reaction mixture was poured into a saturated aqueous NaCl solution and extracted with ethyl acetate. The organic layer was washed with water, and dried over anhydrous Mg_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica (hexane). According to ^1H NMR analysis, the initial (*E*)/(*Z*) ratio of **18** (92/8) was changed to 6/94.

Typical Procedure for Isotope Experiment

Reaction of benzene-d_6 with 1-phenyl-1-propyne in the presence of H_2O and 5a: Under an argon atmosphere, 1-phenyl-1-propyne (58.0 mg, 0.5 mmol) was added to a mixture of $Sc(OTf)_3$ (24.6 mg, 0.05 mmol), benzene-d_6 (2 mL), H_2O (9 μL, 0.5 mmol) and **5a** (0.5 mL). The mixture was stirred at 85 °C for 4 h. Standard work-up gave **6-d$_{5–6}$** as a colorless solid; yield: 79 mg (79%) of The ^{1}H NMR spectrum of **6-d$_{5–6}$** showed that the intensities of the vinyl proton (at 6.17 ppm as a quartet) and methyl protons (doublet at 1.76 ppm for **6-d$_5$** and singlet at 1.75 ppm for **6-d$_6$**) were in a ratio of 1.00 : 3.99. The GC/MS confirmed the formation of five-deuterium-incorporated adduct **6-d$_5$** (*m/z* [M$^+$] = 199.1, 200.1). These results revealed that 75% of the H from H_2O and 25% of D from the aromatic substrate were incorporated into vinyl part of product **6-d$_{5–6}$**.

Reaction of benzene with 1-phenyl-1-propyne in the presence of D_2O and 5a: Under an argon atmosphere, 1-phenyl-1-propyne (58.0 mg, 0.5 mmol) was added to a mixture of $Sc(OTf)_3$ (24.6 mg, 0.05 mmol), benzene (2 mL), D_2O (9 μL, 0.5 mmol) and **5a** (0.5 mL). The mixture was stirred at 85 °C for 4 h. Standard work-up gave **6-d$_{0–1}$** as a colorless solid; yield: 68 mg (70%). The ^{1}H NMR spectrum of **6-d$_{0–1}$** showed that the intensities of the vinyl proton (at 6.17 ppm as a quartet) and methyl protons (doublet at 1.76 ppm for **6-d$_0$** and singlet at 1.75 ppm for **6-d$_1$**) were in a ratio of 1.00:6.17. The GC/MS confirmed the formation of five-deuterium-incorporated adduct **6-d$_1$** (*m/z* [M$^+$] = 195.1, 196.1). These results revealed that 52% of the D from D_2O and 48% of H from the aromatic substrate were incorporated into vinyl part of product **6-d$_{0–1}$**.

Acknowledgements

This work was supported by a Korea Research Foundation Grant (KRF-2005-005-J11901) funded by MOEHRD, and by grants R01-2006-000-10426-0 (KOSEF) and R11-2005-008-00000-0 (SRC program of MOST/KOSEF).

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[26] Compound **6** in an *E*/*Z* ratio of 92/8 was prepared using superacidic ionic liquids containing multinuclear fluoroantimonate anions, with $[bmim][Sb_nF_{5n+1}]$ as catalysts; manuscript in preparation.