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Imino Ene Reaction Catalyzed by Ytterbium(III) Triflate and TMSCl or TMSOTf

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A novel combined system of $Yb(OTf)_3$ with TMSCl or TMSOTf catalyzed an imino ene reaction. The reaction of *N*-tosylbenzaldimine (**1**) with α-methylstyrene (**2**) proceeded smoothly to give homoallylic amine **3** in the presence of a catalytic amount of $Yb(OTf)_3$ and TMSCl. This catalytic system was successfully applied to the imino ene reactions of various aldimines with alkenes. This new imino ene reaction provides a unique method for the three-component coupling reaction of an aldehyde, tosylamide, and α-methylstyrene in the presence of $Yb(OTf)_3$ and TMSOTf, to give the corresponding homoallylic amine.

Introduction

The development of new methods for the synthesis of amines is one of the most important and attractive subjects in synthetic organic chemistry, especially for the synthesis of alkaloids and biologically active nitrogen-containing compounds. Moreover, homoallylic amines are frequently found in many naturally occurring nitrogen-containing compounds, pharmaceuticals, and agrochemicals and in substances with important biological activities. In addition, homoallylic amines are also a useful building block for synthetic intermediates. Although several methods exist for the synthesis of homoallylic amines, two direct methods are the most well-known. One of the most general procedures is the nucleophilic addition of allylmetal reagents to imines, which is a powerful method for selective C−C bond formation.[1] As part of our ongoing project along these lines, we previously reported the diastereo- and enantioselective addition of alkyllithium to chiral imines.[2] The other method is an imino ene reaction that involves a concerted addition reaction of imines with alkenes to form a homoallylic amine (Scheme 1).[3]

Several recent reports have shown that imino ene reactions are limited to either intramolecular reactions or those of reactive imines such as glyoxalate imines.[3] Moreover, although a few excellent catalytic asymmetric imino ene reactions have recently been reported, the substrates were also limited to glyoxalate imine.[4] Therefore, we focused our attention on the use of Lewis acid catalysts to increase the reactivities of the imine groups in the imino ene reactions. For this purpose, we selected lanthanide metals as a catalyst, since they have been reported to have excellent catalytic activities as Lewis acids for a variety of reactions, including catalytic enantioselective reactions.[5] In addition, lanthanide Lewis acids have been shown to effectively activate imino groups.[6] Therefore, we envisioned that lanthanide metal Lewis acids may be able to catalyze an imino ene reaction. In fact, we recently found an imino ene reaction catalyzed by a novel catalytic system: $Yb(OTf)_3$ with

SCHEME 1. Imino Ene Reaction

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(1) (a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207−2293. (b) Bloch, R. *Chem. Rev.* **1998**, *98*, 1407−1438. (c) Kobayashi, S.; Busujima, T.; Nagayama, S. *Chem. Commun.* **1998**, 19−20. (d) Nakamura, H.; Nakamura, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4242−4243. (e) Yamasaki, S.; Fujii, K.; Wada, R.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2002**, *124*, 6536−6537.

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SCHEME 2

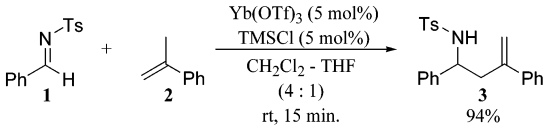
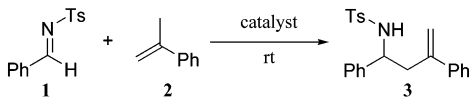


TABLE 1. Lewis Acid-Catalyzed Imino Ene Reaction



entry	catalyst (mol %)	time	**3** (%)
1[a]	$BF_3{\cdot}OEt_2$(25)	24 h	0
2[a]	$AlCl_3$ (25)	2 h	0
3[a]	$TiCl_4$ (25)	2 h	0
4[b]	$Yb(OTf)_3$ (25)	48 h	58
5[b]	$Yb(OTf)_3$ (5) and TMSCl (120)	15 min	90
6[b]	$Yb(OTf)_3$ (5) and TMSCl (5)	15 min	94

[a] CH_2Cl_2 was used as a solvent. [b] CH_2Cl_2−THF (4:1) was used as a solvent.

TMSCl (Scheme 2).[7] In this report, we describe in detail $Yb(OTf)_3$-catalyzed imino ene reactions in the presence of TMSCl or TMSOTf.

Results and Discussion

We initiated the reaction of *N*-tosylbenzaldimine (**1**) with α-methylstyrene (**2**) under various conditions. Typical Lewis acids such as $BF_3{\cdot}OEt_2$, $AlCl_3$, and $TiCl_4$ did not catalyze the reaction, even though unidentified products were formed with $AlCl_3$ and $TiCl_4$ (Table 1, entries 1−3). On the other hand, to our delight, 25 mol % $Yb(OTf)_3$ was found to catalyze the imino ene reaction of **1** with **2**, and after 48 h of stirring at room temperature, the expected homoallylic amine **3** was obtained in 58% yield (entry 4). We anticipated that under this condition, $Yb(OTf)_3$ may coordinate with the amine produced, which required a prolonged reaction time. Therefore, it was assumed that the reaction would proceed much faster if this coordination of the amine with $Yb(OTf)_3$ could be prevented. Accordingly, we examined the effect of a stoichiometric amount of TMSCl on the reaction.[8] As expected, the reaction of **1** and **2** was indeed accelerated and **3** was obtained in 90% yield after 15 min of stirring at room temperature (entry 5). To our surprise, a catalytic amount of TMSCl was sufficient to accelerate the reaction. Even 5 mol % $Yb(OTf)_3$ and 5 mol % TMSCl gave almost a quantitative isolated yield (94%) of imino ene product **3** in only 15 min (entry 6).

We next turned our attention to the effect of a silyl reagent in this reaction (Table 2). TMSOTf, triethylsilyl chloride (TESCl), and TESOTf were found to be as effective as TMSCl (entries 2, 4, and 5). However, the reaction did not take place with 1-(trimethylsilyl)imidazole (TMSImd) (entry 3). Other silyl reagents with bulky alkyl groups such as TBDMSCl or TBDMSOTf also catalyzed the imino ene reaction to give **3** in moderate yield. These results suggested that the cationic nature of the silyl group was an important factor in catalyzing the reaction.

TABLE 2. Effects of Silyl Reagents on the Imino Ene Reaction between 1 and 2[a]

entry	silyl reagent	time (min)	**3** (%)
1	TMSCl	15	94
2	TMSOTf	15	92
3	TMSImd	240	0
4	TESCl	15	94
5	TESOTf	15	89
6	TBDMSCl	240	53
7	TBDMSOTf	60	79

[a] All reactions were carried out under 5 mol% $Yb(OTf)_3$ and 5 mol% silyl reagent at room temperature.

To shed light on the mechanism for the formation of **3** and on the nature of the reaction, we screened the catalytic activities of other combinations of lanthanide metal triflates [$Ln(OTf)_3$] with TMSCl in the imino ene reaction of **1** with **2**. The catalytic activity profile of $Ln(OTf)_3$ and TMSCl is shown with an oxophilicity scale (Figure 1). As illustrated, all of the $Ln(OTf)_3$ with TMSCl catalyzed the reaction with low to excellent yields. On the other hand, without TMSCl, the reaction either did not occur or only gave **3** in lower yields. Remarkably, $Yb(OTf)_3$-TMSCl and $Sc(OTf)_3$-TMSCl each gave **3** in higher yield and proved to be the catalysts of choice. These results agreed well with the oxophilicity of lanthanide elements using tandem mass spectroscopy, as reported by Yamaguchi and Imamoto, who concluded that this oxophilicity reflects the relative Lewis acidity of lanthanide elements.[9] These observations suggest that the oxophilicity, i.e., the Lewis acidity, of the lanthanide metal may play an important role in the imino ene reaction.

To explore the generality of this imino ene reaction, we next applied $Yb(OTf)_3$-TMSX catalyst in the reaction of various aldimines with α-methylstyrene **2** under optimized conditions. As shown in Table 3, homoallylic amines were exclusively formed in the reaction of **2** with benzaldimine with an electron-withdrawing group at the benzene ring (entries 1 and 2), whereas an electron-donating substituent reduced the yield (entry 3). 2-Furylaldimine **10** also reacted with **2** to give **11** in moderate yield, but only if the reaction temperature was kept at −15 °C due to its high reactivity (entry 4). The nature of the substituents on the nitrogen had a profound effect. The reaction of *N*-benzenesulfonyl and *N*-4-nitrobenzenesulfonyl (*p*-Ns) derivatives, **12** and **14** respectively, with **2** proceeded as smoothly as that of **1** (entries 5 and 6). However, an *N*-methoxycarbonyl group deactivated the imino ene reaction with **2**. A combination of $Yb(OTf)_3$ with TMSCl (10 mol %) in the reaction of **16** gave **17** in moderate yield (entry 7). TMSOTf was more effective than TMSCl with a less-reactive substrate like **16**. The yield of **17** increased up to 74% when TMSOTf (10 mol %) was used instead of TMSCl (entry 8). Phosphinoyl imine **18** also gave the corresponding homoallylic amine **19**, but in low yield, even when 25 mol % $Yb(OTf)_3$ and TMSOTf were used (entry 9). Interestingly, when

(7) Yamanaka, M.; Nishida, A.; Nakagawa, M. *Org. Lett.* **2000**, *2*, 159−161.

(8) Reaction rate in the nucleophilic addition of diethyl zinc to imine was accelerated by R_3SiCl: Jimeno, C.; Vidal-Ferran, A.; Moyano, A.; Pericàs, M. A.; Riera, A. *Tetrahedron Lett.* **1999**, *40*, 777−780.

(9) Tsuruta, H.; Yamaguchi, K.; Imamoto, T. *Chem. Commun.* **1999**, 1703−1704.

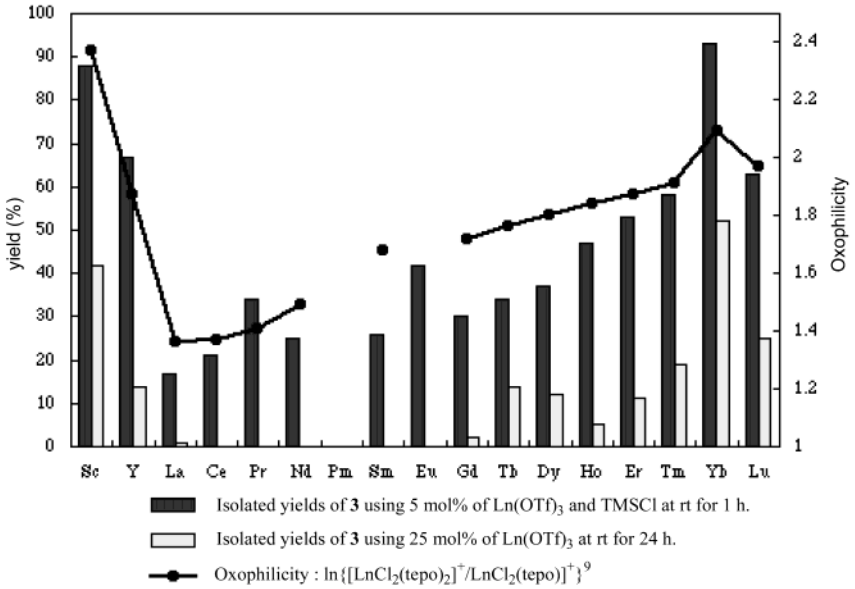
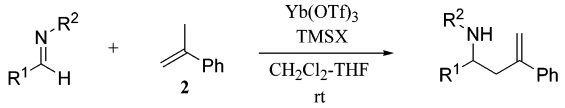


FIGURE 1. Lanthanide metal effects.

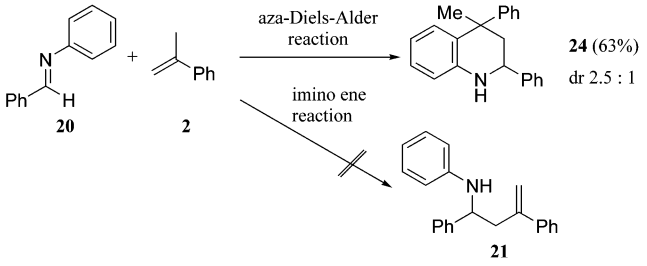
TABLE 3. Imino Ene Reactions of Various Aldimines Catalyzed by Yb(OTf)$_3$-TMSX



	aldimine						
entry		R1	R2	X	catalyst (mol%)	time (h)	yield (%)
1	**4**	*o*-ClC_6H_4	Ts	Cl	5	0.5	**5** (92)
2	**6**	*p*-$NO_2C_6H_4$	Ts	OTf	10	1	**7** (86)
3	**8**	*p*-$MeOC_6H_4$	Ts	Cl	5	2	**9** (54)
4[a]	**10**	2-furyl	Ts	Cl	5	3	**11** (66)
5	**12**	Ph	SO_2Ph	Cl	5	0.5	**13** (91)
6	**14**	Ph	SO_2*p*-$NO_2C_6H_4$	OTf	5	2	**15** (81)
7	**16**	Ph	CO_2Me	Cl	10	1	**17** (44)
8	**16**	Ph	CO_2Me	OTf	10	1	**17** (74)
9	**18**	Ph	$P(O)Ph_2$	OTf	25	1.5	**19** (38)
10	**20**	Ph	Ph	Cl	25	5	**21** (0)[b]
11	**22**	Ph	Bn	OTf	25	48	**23** (0)

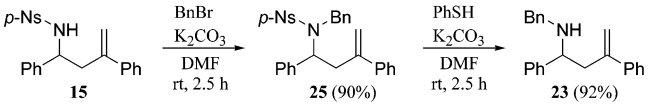
[a] Reaction was carried out at −15 °C. [b] Aza-Diels−Alder adduct (**24**) was obtained in 63% yield.

SCHEME 3



N-phenylaldimine **20** was subjected to similar reaction conditions, the aza Diels−Alder reaction proceeded exclusively to give **24**, and no imino ene product **21** was obtained (entry 10 and Scheme 3).[10] On the other hand, an *N*-alkylaldimine such as **22** was inert in a similar reaction with **2** (entry 11). These results indicate that the electron-withdrawing nature of the *N*-substituent is necessary for a successful imino ene reaction. Although a direct imino ene reaction of an *N*-alkylaldimine such as **22** did not take place, *N*-alkylated homoallylic amines were readily accessible by using Fukuyama's *p*-Ns protecting group.[11] Thus, benzylation of **15** with benzyl bromide under usual conditions gave *N*-benzyl derivative **25**, which was in turn treated with PhSH in the presence

SCHEME 4

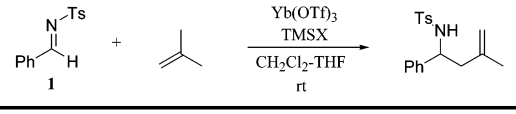


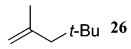
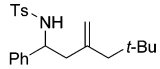
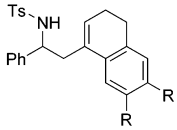
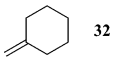
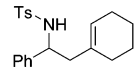
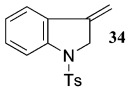
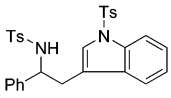
p-Ns : SO_2*p*-$NO_2C_6H_4$

(10) Aza Diels−Alder reaction of *N*-arylaldimine with alkene: (a) Makioka, Y.; Shindo, T.; Taniguchi, Y.; Takaki, K.; Fujiwara, Y. *Synthesis* **1995**, 801−804. (b) Kobayashi, S.; Ishitani, H.; Nagayama, S. *Synthesis* **1995**, 1195−1202. (c) Batey, R. A.; Simoncic, P. D.; Lin, D.; Smyj, R. P.; Lough, A. J. *Chem. Commun.* **1999**, 651−652.

(11) (a) Fukuyama, T.; Jow, C.-K.; Cheung, M. *Tetrahedron Lett.* **1995**, *36*, 6373−6374. (b) Fukuyama, T.; Cheung, M.; Jow, C.-K.; Hidai, Y.; Kan, T. *Tetrahedron Lett.* **1997**, *38*, 5831−5834.

TABLE 4. Imino Ene Reactions of Various Alkenes Catalyzed by Yb(OTf)$_3$-TMSX



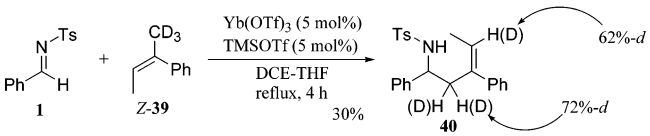
entry	Alkene	X	catalysts (mol%)	time (h)	product	yield (%)
1	 **26**	OTf	10	4		**27** (68)
2	**28** : R = H	Cl	5	1		**29** (59)
3	**30** : R = OMe	Cl	5	0.25		**31** (82)
4	 **32**	OTf	10	20		**33** (24)
5	 **34**	Cl	5	0.5		**35** (73)

of K_2CO_3 to deprotect the *p*-Ns group to give **23** in high yield (Scheme 4).

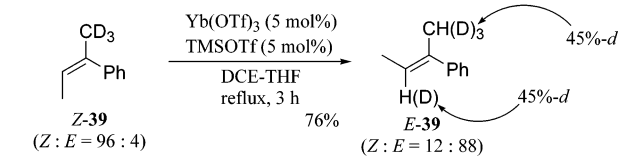
Next, we examined the similar reaction of **1** with various 1,1-disubstituted alkenes (Table 4). Sterically hindered alkene **26** reacted somewhat more slowly to give **27** in 68% yield when TMSOTf was used (entry 1). Tetrahydro-1-naphthylidene **28** also reacted with **1** to give **29** in 59% yield (entry 2). The effect of a dimethoxy group was remarkable. The reaction of **30**, in contrast to **28**, was complete within 15 min, and the yield increased to 82% (entry 3), implying that the nucleophilic nature of the alkene favors the imino ene reaction. Tryptamine derivative **35** was obtained by the reaction of **1** with indolidene **34**, which was readily prepared by selective allylic bromination with Yb(OTf)$_3$-TMSCl followed by cyclization (entry 5).[12]

We encountered an unexpected phenomenon in the reaction with trisubstituted olefin (**36**). The reaction of **1** with (*Z*)-**36** using Yb(OTf)$_3$-TMSCl or TMSOTf at room temperature gave a mixture of imino ene product **37** and unexpected product **38** in a ratio of 3:2 or 1:1, respectively

SCHEME 5



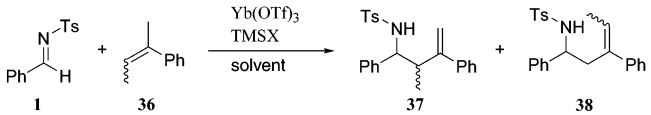
SCHEME 6



(Table 5, entries 1 and 2). Furthermore, **38** was a mixture of (*E*)- and (*Z*)-isomers (nearly 9:1) as determined by ^{1}H NMR spectroscopy ((*E*)-isomer, δ_{CH3} 1.56 ppm; (*Z*)-isomer, δ_{CH3} 1.50 ppm). Remarkably, raising the temperature to reflux improved the product yield to 60% and **38** became the major product (entry 4), whereas lowering the temperature to −10 °C hampered the reaction (entry 3). When 1,2-dichloroethane (DCE)−THF was used, the reaction occurred more rapidly and **38** was obtained as almost a single product (entries 5 and 6). The reaction of (*E*)-**36** with **1** under identical conditions gave results quite similar to those with (*Z*)-**36** and produced **38** as the major product along with minor amounts of **37** (entry 7).

To examine the fate of the C−H at the methyl group of **36**, we carried out the reaction of deuterated alkene (*Z*)-**39** (D content = 96%) with **1**. Subjecting (*Z*)-**39** to similar conditions led to a uniquely labeled product **40**, although the reaction was sluggish and gave a low yield (30%). The ^{1}H NMR spectra of **40** showed that deuterium was incorporated into the allylic and olefinic positions, as shown in Scheme 5, suggesting that isomerization of the double bond in **36** occurred prior to the imino ene reaction. In fact, when (*Z*)-**39** was treated with Yb(OTf)$_3$ and TMSOTf in the absence of **1**, isomerization of (*Z*)-**39** to the (*E*)-isomer was observed along with an imbalance of deuterium (Scheme 6). These results suggested that Yb(OTf)$_3$-TMSX catalyzed the isomerization of the double bond more rapidly than the imino ene reaction, and 1,1-disubstituted isomer **41** generated in situ reacted with **1** more rapidly than other isomers such as (*E*)- or (*Z*)-**36** to give **38**. Supporting evidence was obtained by the reaction of α-ethylstyrene **41** with **1**, which produced the

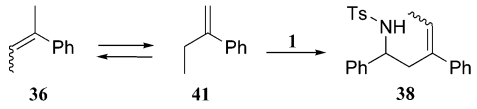
TABLE 5. Reaction of 1 with Trisubstituted Olefin (36)



entry	**36**[a]	X	catalyst (mol %)	solvent[b]	temp	time (h)	yield of **37** + **38** (%)	**37**[c]:**38**	*E*:*Z* (**38**)
1	(*Z*)-**36**	Cl	5	CH_2Cl_2-THF	rt	30	31	3:2	90:10
2	(*Z*)-**36**	OTf	5	CH_2Cl_2-THF	rt	30	41	1:1	88:12
3	(*Z*)-**36**	Cl	10	CH_2Cl_2-THF	−10 °C	7 days	0		
4	(*Z*)-**36**	Cl	10	CH_2Cl_2-THF	reflux	6	60	1:7	91:9
5	(*Z*)-**36**	Cl	5	DCE-THF	reflux	2	55	<1:10	82:18
6	(*Z*)-**36**	OTf	5	DCE-THF	reflux	3	73	<1:10	82:18
7	(*E*)-**36**	OTf	5	DCE-THF	reflux	2	76	<1:10	84:16

[a] (*Z*)-**36** = 96% *Z*; (*E*)-**36** = 85% *E*. [b] DCE = 1,2-dichloroethane. [c] About 1:1 mixture of syn and anti adducts.

SCHEME 7



SCHEME 8

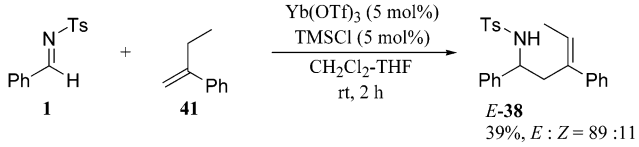
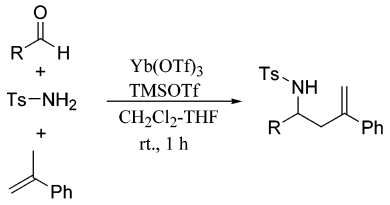


TABLE 6. Yb(OTf)$_3$-TMSOTf-Catalyzed Three-Component Reaction of Aldehyde, Tosylamide, and α-Methylstyrene[a]



entry	R	yield (%)
1	Ph	**3** (92)
2[b]	CH_3	**42** (79)
3	*i*Pr	**43** (71)
4	*t*-Bu	**44** (45)
5	*c*-C_3H_5	**45** (76)
6	*c*-C_6H_{11}	**46** (85)
7	CO_2Et	**47** (66)

[a] All reactions were carried out with 5 mol% Yb(OTf)$_3$ and 120 mol% TMSOTf at room temperature. [b] Used 2 equiv of acetaldehyde. [c] Carbonyl ene product (13%) was also obtained.

expected compound **38** (Scheme 7).[13] The geometric isomer ratio of the trisubstituted olefin of **38** was 89:11 (*E*:*Z*), as determined by the ^{1}H NMR spectrum. Interestingly, the ratio of (*E*)- and (*Z*)-isomers of **38** obtained from **41** was quite similar to that in the reaction of **36** with **1** (Scheme 8).

Having developed a unique imino ene reaction, we next examined the three-component coupling reaction[14] of aldehyde, amine, and alkene, since the direct isolation and purification of some imines can be difficult due to their instability. First, we investigated the reaction between benzaldehyde, tosylamide, and α-methylstyrene under various conditions.[7] In three-component coupling reactions, the addition of TMSOTf was found to give better results. Accordingly, when 5 mol % Yb(OTf)$_3$ was used along with 120 mol % TMSOTf, the reaction proceeded rapidly to give **3** in 92% yield (Table 6, entry 1). These conditions were applied to various aldehydes, and in all cases the corresponding imino ene products (**42**−**46**) were obtained in moderate to good yields (entries 2−6). The anticipated carbonyl ene products were not observed, except with glyoxalate. When glyoxalate was used, the reaction gave imino ene product **47** in 66% yield, together with homoallylic alcohol derived from the carbonyl ene reaction in 13% yield (entry 7).

In summary, we have demonstrated for the first time the utility of a Yb(OTf)$_3$-TMSX catalyst, which is experimentally simple and inexpensive, for the imino ene reaction of aldimines with 1,1-disubstituted alkenes. This process proceeds under mild conditions and provides efficient access to synthetically useful homoallylic amines. These procedures can now be conducted in a single preparative coupling step. Further application of these reactions to the synthesis of heterocyclic natural products is now in progress.

Experimental Section

General Experimental. All reactions were carried out under an argon atmosphere. Tetrahydrofuran was distilled from sodium/benzophenone prior to use. Dichloromethane was distilled from P_2O_5 and redistilled from CaH_2 prior to use. Dimethylformamide and 1,2-dichloroethane were distilled from CaH_2. ^{1}H NMR spectra were recorded at 400 MHz. ^{13}C NMR spectra were recorded at 100 MHz.

Preparation of Imines. The *N*-sulfonyl imines were prepared by known methods.[15] For example, in preparation of **1**, benzaldehyde (2.0 mL, 20 mmol), *p*-toluenesulfonamide (3.42 g, 20 mmol), and Si(OEt)$_4$ (4.7 mL, 21 mmol) were placed in a flask and heated at 160 °C for 5 h. On cooling, the reaction mixture was crystallized with EtOAc and *n*-pentane. The resulting crystals were collected by filtration and gave pure **1** (3.67 g, 71%). The other compounds, **4**, **6**, **8**, **10**, **12**, and **14**,[16] were prepared using a similar procedure. *N*-Methoxycarbonyl imine (**16**),[17] *N*-phosphynoyl imine (**18**),[18] *N*-phenyl imine (**20**),[19] and *N*-benzyl imine (**22**)[20] were also synthesized by known procedures.

Preparation of Alkenes. 2, **26**, and **32** were purchased from commercial sources and used without purification. **28**,[21] **30**,[22] and **41** were prepared from the corresponding ketones by Wittig methylenation. **34** was synthesized by Mizoroki−Heck reaction[23] or allylic bromination and cyclization.[12] **36** was prepared by the ethylenation of acetophenone.[24]

General Procedure for the Imino Ene Reaction. A dichloromethane (4 mL) solution of imine (0.5 mmol) was added to a tetrahydrofuran (1 mL) solution of Yb(OTf)$_3$. TMSX and alkene (1.0 mmol) were then added successively. The reaction mixture was stirred at room temperature for the specified time. The mixture was diluted with H_2O and extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over $MgSO_4$. Concentration under reduced pressure gave a crude residue, which was chromatographed on silica gel.

***N*-(1,3-Diphenylbut-3-enyl)-4-methylbenzenesulfonamide (3).** According to the general procedure, imine **1** (130 mg, 0.5 mmol) and **2** (0.13 mL, 1.0 mmol) were reacted in the

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(13) However, **36** could not be detected in the reaction mixture of **41** and **1**.
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presence of $Yb(OTf)_3$ (16 mg, 0.025 mmol) and TMSCl (2.7 mg, 0.025 mmol) at room temperature for 15 min. Column chromatography on silica gel (*n*-hexane/acetone = 8/1) gave rise to pure **3** (177 mg, 94%) as a pale yellow oil: IR (neat) 3278, 2925, 1599, 1495, 1443, 1323, 1158, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.33 (3H, s), 2.89 (2H, m), 4.23 (1H, dd, J = 7.0, 13.0 Hz), 4.94 (1H, d, J = 1.0 Hz), 5.17 (1H, brs), 5.22 (1H, d, J = 1.0 Hz), 7.02−7.05 (4H, m), 7.13−7.26 (8H, m), 7.44 (2H, d, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 21.4, 44.1, 56.4, 111.3, 126.1, 126.6, 127.0, 127.4, 127.7, 128.3, 128.4, 129.2, 136.9, 139.3, 140.7, 142.9, 143.7; LRMS (FAB) m/z 376 [5, M^+ − H], 260 [100]; HRMS ($C_{23}H_{22}NO_2S$) found 376.1371, calcd 376.1371.

Yield of 3 (Figure 1). Reactions were carried out in the presence of 5 mol % $Ln(OTf)_3$ and 5 mol % TMSCl at room temperature for 1 h. $Sc(OTf)_3$, 88%; $Y(OTf)_3$, 67%; $La(OTf)_3$, 17%; $Ce(OTf)_3$, 21%; $Pr(OTf)_3$, 34%; $Nd(OTf)_3$, 25%; $Sm(OTf)_3$, 26%; $Eu(OTf)_3$, 42%; $Gd(OTf)_3$, 30%; $Tb(OTf)_3$, 34%; $Dy(OTf)_3$, 37%; $Ho(OTf)_3$, 47%; $Er(OTf)_3$, 53%; $Tm(OTf)_3$, 58%; $Yb(OTf)_3$, 93%; $Lu(OTf)_3$, 63%. Reactions were carried out in the presence of 25 mol % $Ln(OTf)_3$ at room temperature for 24 h. $Sc(OTf)_3$, 42%; $Y(OTf)_3$, 14%; $La(OTf)_3$, 1%; $Ce(OTf)_3$, 0%; $Pr(OTf)_3$, 0%; $Nd(OTf)_3$, 0%; $Sm(OTf)_3$, 0%; $Eu(OTf)_3$, 0%; $Gd(OTf)_3$, 2%; $Tb(OTf)_3$, 14%; $Dy(OTf)_3$, 12%; $Ho(OTf)_3$, 5%; $Er(OTf)_3$, 11%; $Tm(OTf)_3$, 19%; $Yb(OTf)_3$, 52%; $Lu(OTf)_3$, 25%.

***N*-[1-(2-Chlorophenyl)-3-phenylbut-3-enyl]-4-methylbenzenesulfonamide (5).** According to the general procedure, imine **4** (147 mg, 0.5 mmol) and **2** (0.13 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (16 mg, 0.025 mmol) and TMSCl (2.7 mg, 0.025 mmol) at room temperature for 30 min. Column chromatography on silica gel (*n*-hexane/acetone = 8/1) gave rise to pure **5** (190 mg, 92%) as a colorless oil: IR (neat) 3280, 2924, 1598, 1444, 1325, 1160, 759 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.32 (3H, s), 2.64 (1H, dd, J = 10.0, 14.0 Hz), 3.07 (1H, dd, J = 5.0, 14.0 Hz), 4.64 (1H, ddd, 5.0, 5.0, 10.0 Hz), 4.92 (1H, brs), 5.06 (1H, s), 5.34 (1H, s), 7.01 (2H, d, J = 8.0 Hz), 7.10−7.24 (9H, m), 7.42 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.4. 42.1, 53.3, 116.7, 126.0, 126.9, 127.0, 127.7, 128.3, 128.4, 128.8, 129.2, 129.4, 131.9, 136.0, 138.4, 138.5, 143.0, 143.5; (FAB) m/z 410 [20, M^+ − H], 294 [100]; HRMS ($C_{23}H_{21}ClNO_2S$) found 410.1001, calcd 410.0981.

4-Methyl-*N*-[1-(4-nitrophenyl)-3-phenylbut-3-enyl]-benzenesulfonamide (7). According to the general procedure, imine **6** (152 mg, 0.5 mmol) and **2** (0.13 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (16 mg, 0.025 mmol) and TMSCl (2.7 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography on silica gel (*n*-hexane/acetone = 6/1) gave rise to pure **7** (181 mg, 86%) as a pale green solid: mp = 154−156 °C (*n*-hexane/EtOAc); IR (KBr) 3248, 2910, 1597, 1514, 1346, 1157, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36 (3H, s), 2.83−2.86 (2H, m), 4.31 (1H, ddd, J = 2.5, 7.5, 15.0 Hz), 4.97 (1H, d, J = 1.0 Hz), 5.28 (1H, d, J = 1.0 Hz), 5.29 (1H, brs), 7.08 (2H, d, J = 8.0 Hz), 7.12 (2H, dd, J = 1.5, 8.0 Hz), 7.24−7.27 (5H, m), 7.44 (2H, d, J = 8.5 Hz), 8.02 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.4, 43.8, 55.6, 117.2, 123.5, 126.0, 127.0, 127.6, 128.0, 128.6, 129.4, 136.3, 138.5, 142.9, 143.6, 147.1, 148.3; LRMS (FAB) m/z 423 [3, M^+ − H], 154 [100]; Anal. Calcd for $C_{23}H_{22}N_2O_4S$: C, 65.39; H, 5.25; N, 6.63. Found: C, 65.49; H, 5.30; N, 6.43.

***N*-[1-(4-Methoxyphenyl)-3-phenylbut-3-enyl]-4-methylbenzenesulfonamide (9).** According to the general procedure, imine **8** (145 mg, 0.5 mmol) and **2** (0.13 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and TMSOTf (11 mg, 0.05 mmol) at room temperature for 1 h. Column chromatography on silica gel (*n*-hexane/acetone = 5/1) gave rise to pure **9** (111 mg, 54%) as a colorless oil: IR (neat) 3276, 2933, 1612, 1512, 1442, 1321, 1250, 1159, 1034, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.34 (3H, s), 2.85 (1H, dd, J = 7.0, 14.5 Hz), 2.92 (1H, dd, J = 8.0, 14.5 Hz), 3.74 (3H, s), 4.17 (1H, ddd, 5.0, 7.0, 8.0 Hz), 4.95 (2H, brs), 5.23 (1H, d, J = 1.0 Hz), 6.69 (2H, d, J = 9.0 Hz), 6.94 (2H, d, J = 8.5 Hz), 7.06 (2H, d, J = 8.0 Hz), 7.18−7.20 (2H, m), 7.25−7.27 (3H, m), 7.44 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.4, 44.1, 55.2, 55.8, 113.7, 116.3, 126.1, 127.1, 127.7, 127.8, 128.4, 129.2, 132.6, 133.7, 136.9, 139.3, 142.8, 143.9; LRMS (FAB) m/z 406 [2, M^+ − H], 260 [100]; HRMS ($C_{24}H_{24}NO_3S$) found 406.1446, calcd 406.1477.

***N*-(1-Furan-2-yl-3-phenylbut-3-enyl)-4-methylbenzenesulfonamide (11).** According to the general procedure, imine **10** (125 mg, 0.5 mmol) and **2** (0.13 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (16 mg, 0.025 mmol) and TMSCl (2.7 mg, 0.025 mmol) at −15 °C for 3 h. Column chromatography on silica gel (*n*-hexane/acetone = 5/1) gave rise to pure **11** (121 mg, 66%) as a brown oil: IR (neat) 3276, 2926, 1599, 1496, 1444, 1328, 1160, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.16 (3H, s), 2.96 (1H, dd, J = 7.5, 14.0 Hz), 3.02 (1H, dd, J = 7.0, 14.0 Hz), 4.43 (1H, ddd, J = 7.0, 7.5, 7.5 Hz), 4.98 (1H, d, J = 1.0 Hz), 5.05 (1H, d, J = 7.5 Hz), 5.24 (1H, d, J = 1.0 Hz), 5.86 (1H, d, J = 3.0 Hz), 6.08 (1H, dd, J = 2.0, 3.0 Hz), 7.08−7.15 (4H, m), 7.20−7.29 (4H, m), 7.53 (2H, d, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 21.4, 40.9, 50.3, 107.5, 109.9, 116.3, 126.1, 127.0, 127.7, 128.4, 129.3, 137.3, 139.4, 141.8, 143.0, 143.3, 152.2; LRMS (EI) m/z 367 [1, M^+], 91 [100]; HRMS ($C_{21}H_{22}NO_3S$) found 368.1303, calcd 368.1320.

***N*-(1,3-Diphenylbut-3-enyl)-benzenesulfonamide (13).** According to the general procedure, imine **12** (123 mg, 0.5 mmol) and **2** (0.13 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (16 mg, 0.025 mmol) and TMSCl (2.7 mg, 0.025 mmol) at room temperature for 15 min. Column chromatography on silica gel (*n*-hexane/EtOAc = 4/1) gave rise to pure **13** (165 mg, 91%) as a colorless oil: IR (neat) 3278, 2938, 1600, 1495, 1447, 1323, 1159, 754, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.90 (2H, m), 4.28 (1H, dd, J = 7.5, 13.0 Hz), 4.95 (1H, s), 5.16 (1H, brs), 5.23 (1H, s), 6.99−7.01 (2H, m), 7.12−7.42 (11H, m), 7.55 (2H, dd, J = 1.0, 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 44.1, 56.5, 116.4, 126.1, 126.6, 127.0, 127.5, 127.8, 128.3, 128.5, 128.6, 132.2, 139.4, 140.0, 140.4, 143.8; LRMS (FAB) m/z 363 [5, M^+], 246 [100]; HRMS ($C_{22}H_{21}NO_2S$) found 363.1306, calcd 363.1293.

***N*-(1,3-Diphenylbut-3-enyl)-4-nitrobenzenesulfonamide (15).** According to the general procedure, imine **14** (290 mg, 1.0 mmol) and **2** (0.26 mL, 2.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and TMSOTf (11 mg, 0.05 mmol) at room temperature for 2 h. Column chromatography on silica gel (*n*-hexane/acetone = 6/1) gave rise to pure **15** (329 mg, 81%) as a pale green solid: mp = 147−148 °C (*n*-hexane/EtOAc); IR (KBr) 3251, 1604, 1523, 1350, 1312, 1161, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.83 (1H, dd, J = 9.5, 14.5 Hz), 2.99 (1H, ddd, J = 1.0, 5.5, 14.5 Hz), 4.34 (1H, ddd, J = 5.0, 5.5, 9.5 Hz), 4.97 (1H, d, J = 5.0 Hz), 5.07 (1H, d, J = 1.0 Hz), 5.35 (1H, d, J = 1.0 Hz), 7.04−7.06 (2H, m), 7.15−7.18 (3H, m), 7.23−7.30 (5H, m), 7.60 (2H, d, J = 9.0 Hz), 8.01 (2H, d, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 44.1, 56.6, 116.8, 123.7, 126.0, 126.6, 127.9, 128.2, 128.5, 128.7, 129.4, 131.7, 138.7, 139.9, 143.5, 145.7; LRMS (FAB, negative) m/z 407 [100, M − H^-]. Anal. Calcd for $C_{22}H_{20}N_2O_4S$: C, 64.69; H, 4.93; N, 6.86. Found: C, 64.44; H, 4.92; N, 6.99.

***N*-(1,3-Diphenylbut-3-enyl)-carbamic Acid Methyl Ester (17).** According to the general procedure, imine **16** (82 mg, 0.5 mmol) and **2** (0.13 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and TMSOTf (11 mg, 0.05 mmol) at room temperature for 1 h. Column chromatography on silica gel (*n*-hexane/EtOAc = 6/1) gave rise to pure **17** (103 mg, 74%) as a colorless oil: IR (neat) 3328, 1718, 1701, 1543, 1509, 1458, 1363, 1193, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.95 (2H, d, J = 7.0 Hz), 3.57 (3H, s), 4.72 (1H, brs), 4.94 (1H, brs), 5.00 (1H, d, J = 1.0 Hz), 5.27 (1H, d, J = 1.0 Hz), 7.18−7.37 (10H, m); ^{13}C NMR ($CDCl_3$) δ 43.2, 51.9, 54.2, 115.6, 126.3, 127.3, 127.7, 128.4, 128.5, 140.5, 142.4, 144.9, 156.2; LRMS (FAB) m/z 282 [7, M^+ + H], 164 [100]; HRMS ($C_{18}H_{20}NO_2$) found 282.1504, calcd 282.1494.

***N*-(1,3-Diphenylbut-3-enyl)-*P*,*P*-diphenylphosphinic-amide (19).** According to the general procedure, imine **18** (306 mg, 1.0 mmol) and **2** (0.26 mL, 2.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (155 mg, 0.25 mmol) and TMSOTf (56 mg, 0.25 mmol) at room temperature for 1.5 h. Column

chromatography on silica gel (*n*-hexane/EtOAc = 2/1) gave rise to pure **19** (163 mg, 38%) as a white powder. IR (KBr) 3446, 2918, 1437, 1187, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.99 (1H, dd, J = 8.0, 14.0 Hz), 3.24 (1H, dd, J = 6.5, 14.0 Hz), 3.35 (1H, brs), 4.27 (1H, dd, J = 6.5, 8.5 Hz), 4.87 (1H, d, J = 1.0 Hz), 5.21 (1H, d, J = 1.0 Hz), 7.06 (2H, d, J = 6.5 Hz), 7.16−7.75 (18H, m); ^{13}C NMR ($CDCl_3$) δ 45.5, 54.8, 116.0, 126.2, 126.6, 127.2, 127.5, 128.3, 128.4, 128.5, 131.8, 131.9, 132.0, 132.2, 132.3, 140.0, 142.9, 144.4; LRMS (FAB) m/z 424 [20, M^+ + H], 306 [100]; HRMS ($C_{28}H_{27}NOP$) found 424.1817, calcd 424.1830.

4-Methyl-2,4-diphenyl-1,2,3,4-tetrahydroquinoline (24).[25] According to the general procedure of imino ene reaction, imine **20** (91 mg, 0.5 mmol) and **2** (0.13 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (77 mg, 0.13 mmol) and TMSCl (14 mg, 0.13 mmol) at room temperature for 5 h. Column chromatography on silica gel (*n*-hexane/EtOAc = 10/1) gave rise to aza Diels−Alder cycloadduct **24** (95 mg, 63%) as a mixture of two diastereomers. Further purification with flash column chromatography on silica gel (*n*-hexane/EtOAc = 10/1) could separate these two isomers. Major diastereomer: yellow solid; IR (KBr) 3383, 2966, 1602, 1495, 1474, 1345, 1311, 1256, 1113, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.82 (3H, s), 1.95 (1H, dd, J = 2.5, 13.0 Hz), 2.26 (1H, dd, J = 12.0, 13.0 Hz), 4.01 (1H, dd, J = 2.5, 12.0 Hz), 6.58 (1H, d, J = 8.5 Hz), 7.00 (1H, ddd, J = 1.5, 7.5, 7.5 hz), 7.14−7.37 (10H, m), 7.44 (2H, d, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 29.7, 42.3, 48.3, 54.0, 114.5, 117.6, 125.8, 126.7, 126.9, 127.2, 127.3, 127.5, 127.6, 128.0, 128.6, 143.9, 144.7, 150.2; LRMS (FAB) m/z 299 [100, M^+]; HRMS ($C_{22}H_{21}N$) found 299.1659, calcd 299.1674. Minor diastereomer: yellow solid; IR (KBr) 3385, 2958, 1602, 1482, 1444, 1338, 1312, 1259, 1119, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (3H, s), 2.14 (1H, dd, J = 11.5, 13.0 Hz), 2.26 (1H, dd, J = 3.0, 13.0 Hz), 4.01 (1H, dd, J = 3.0, 11.5 Hz), 6.60 (1H, dd, J = 1.0, 8.5 Hz), 6.75 (1H, ddd, J = 1.0, 7.5, 8.0 Hz), 7.09−7.13 (3H, m), 7.16−7.32 (9H, m); ^{13}C NMR ($CDCl_3$) δ 29.6, 41.6, 47.9, 53.1, 114.2, 117.3, 125.8, 126.4, 126.6, 127.1, 127.5, 127.6, 128.2, 128.5, 144.3, 144.6, 150.4; LRMS (FAB) m/z 299 [100, M^+]; HRMS ($C_{22}H_{21}N$) found 299.1672, calcd 299.1674.

***N*-Benzyl-*N*-(1,3-diphenylbut-3-enyl)-4-nitrobenzenesulfonamide (25).** To a solution of **15** (327 mg, 0.8 mmol) in DMF (8 mL) were added K_2CO_3 (553 mg, 4.0 mmol) and BnBr (0.14 mL, 1.2 mmol) in sequence. The reaction mixture was stirred for 2.5 h at ambient temperature, and the disappearance of **15** was monitored by TLC analysis. Then, the mixture was diluted with H_2O and extracted with Et_2O. Combined organic layers were washed with brine and dried over $MgSO_4$. Concentration in vacuo afforded a yellow crude residue. Column chromatography on silica gel (*n*-hexane/acetone = 7/1) gave rise to pure **25** (357 mg, 90%) as a yellow caramel: IR (neat) 3100, 2932, 1605, 1528, 1496, 1455, 1348, 1161, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.17 (1H, dd, J = 9.5, 14.0 Hz), 3.22 (1H, dd, J = 6.0, 14.0 Hz), 4.19 (1H, d, J = 15.5 Hz), 4.54 (1H, d, J = 15.5 Hz), 4.92 (1H, s), 4.98 (1H, dd, J = 6.0, 9.5 Hz), 5.16 (1H, s), 6.91 (2H, d, J = 7.0 Hz), 7.07−7.29 (11H, m), 7.54 (2H, d, J = 9.0 Hz), 7.91 (1H, d, J = 9.0 Hz), 8.09 (2H, d, J = 9.0 Hz), 8.27 (1H, d, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 49.7, 50.7, 60.8, 116.2, 123.8, 124.2, 126.3, 127.7, 127.9, 128.2, 128.4, 128.5, 128.6, 129.0, 134.8, 140.0, 144.3, 146.9, 149.4; LRMS (FAB) m/z 499 [5, M^+ + H], 291 [100]; HRMS ($C_{29}H_{27}N_2O_4S$) found 499.1707, calcd 499.1691.

***N*-Benzyl-(1,3-diphenylbut-3-enyl)-amine (23).** To a solution of **25** (150 mg, 0.3 mmol) in DMF (3 mL) were added K_2CO_3 (124 mg, 0.9 mmol) and PhSH (0.04 mL, 0.4 mmol) in sequence. The reaction mixture was stirred for 2.5 h at ambient temperature, and the disappearance of **25** was monitored by TLC analysis. Then, the mixture was quenched with 1 N NaOH and extracted with Et_2O. Combined organic layers were washed with brine and dried over $MgSO_4$. Concentration in vacuo afforded a yellow crude residue. Column chromatography on silica gel (*n*-hexane/acetone = 6/1) gave rise to pure **23** (86 mg, 92%) as a yellow oil: IR (neat) 3325, 2924, 1626, 1601, 1493, 1453, 1116, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72 (1H, brs), 2.76 (1H, dd, J = 9.5, 14.0 Hz), 2.89 (1H, dd, J = 5.0, 14.0 Hz), 3.37 (1H, d, J = 13.5 Hz), 3.60 (1H, d, J = 13.5 Hz), 3.68 (1H, dd, J = 5.0, 9.5 Hz), 5.07 (1H, s), 5.29 (1H, s), 7.11−7.37 (15H, m); ^{13}C NMR ($CDCl_3$) δ 45.2, 51.4, 60.0, 115.4, 126.3, 126.7, 127.0, 127.2, 127.6, 127.9, 128.2, 128.4, 140.5, 144.0, 145.7; LRMS (EI) m/z 313 [6, M^+], 197 [100]; HRMS ($C_{23}H_{24}N$) found 314.1917, calcd 314.1909.

***N*-[3-(2,2-Dimethylpropyl)-1-phenylbut-3-enyl]-4-methylbenzenesulfonamide (27).** According to the general procedure, imine **1** (130 mg, 0.5 mmol) and **26** (0.16 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and TMSOTf (11 mg, 0.05 mmol) at room temperature for 4 h. Column chromatography on silica gel (*n*-hexane/ EtOAc = 8/1) gave rise to pure **27** (125 mg, 68%) as a pale yellow solid: mp = 70−73 °C (*n*-hexane/EtOAc); IR (KBr) 3278, 2952, 1599, 1456, 1327, 1159, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (9H, s), 1.54 (1H, d, J = 13.5 Hz), 1.60 (1H, d, J = 13.5 Hz), 2.33 (1H, dd, J = 9.5, 14.0 Hz), 2.36 (3H, s), 2.44 (1H, dd, J = 5.5, 14.0 Hz), 4.33 (1H, ddd, 5.0, 5.5, 9.5 Hz), 4.77 (1H, s), 4.85 (1H, s), 5.00 (1H, d, J = 5.0 Hz), 7.11−7.19 (7H, m), 7.54 (2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.4, 29.8, 30.8, 46.8, 47.8, 56.0, 117.9, 126.6, 127.2, 127.3, 128.1, 128.2, 129.2, 137.1, 141.1, 143.0; LRMS (FAB) m/z 370 [3, M^+ − H], 260 [100]. Anal. Calcd for $C_{22}H_{29}NO_2S$: C, 71.12; H, 7.87; N, 3.77. Found: C, 71.19; H, 7.94; N, 3.72.

***N*-[2-(3,4-Dihydronaphthalen-1-yl)-1-phenylethyl]-4-methylbenzenesulfonamide (29).** According to the general procedure, imine **1** (130 mg, 0.5 mmol) and **28** (144 mg, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (16 mg, 0.025 mmol) and TMSCl (2.7 mg, 0.025 mmol) at room temperature for 1 h. Column chromatography on silica gel (*n*-hexane/acetone = 8/1) gave rise to pure **29** (238 mg, 59%) as a pale yellow solid: mp = 49−51 °C (*n*-hexane/acetone); IR (KBr) 3282, 2931, 1599, 1491, 1448, 1323, 1157, 1093, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.05−2.21 (2H, m), 2.28 (3H, s), 2.55 (1H, d, J = 8.0 Hz), 2.57 (1H, d, J = 8.0 Hz), 2.66 (1H, dd, J = 9.5, 14.0 Hz), 2.83 (1H, dd, J = 6.0, 14.0 Hz), 4.31 (1H, ddd, J = 4.5, 5.5, 9.0 Hz), 4.97 (1H, d, J = 4.0 Hz), 5.73 (1H, t, J = 4.5 Hz), 6.96 (2H, d, J = 8.5 Hz), 7.05−7.12 (4H, m), 7.16−7.26 (5H, m), 7.43 (2H, d, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 21.4, 23.0, 28.0, 42.2, 56.0, 122.4, 126.4, 126.5, 126.8, 126.9, 127.4, 127.7, 128.3, 129.1, 129.5, 132.1, 133.0, 136.4, 136.6, 141.5, 142.9; LRMS (FAB) m/z 404 [10, M^+ + H], 260 [100]; HRMS ($C_{25}H_{25}NO_2S$) found 403.1579, calcd 403.1606.

***N*-[2-(6,7-Dimethoxy-3,4-dihydronaphthalen-1-yl)-1-phenylethyl]-4-methylbenzenesulfonamide (31).** According to the general procedure, imine **1** (259 mg, 1.0 mmol) and **30** (409 mg, 2.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and TMSCl (5 mg, 0.05 mmol) at room temperature for 15 min. Column chromatography on silica gel (*n*-hexane/acetone = 5/1) gave rise to pure **31** (379 mg, 82%) as an orange powder: mp = 62−63 °C (*n*-hexane/CH_2Cl_2); IR (KBr) 3284, 2935, 1603, 1510, 1458, 1327, 1267, 1159, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.07−2.19 (2H, m), 2.30 (3H, s), 2.49−2.55 (2H, m), 2.73 (1H, dd, J = 8.5, 14.5 Hz), 2.80 (1H, dd, J = 6.5, 14.5 Hz), 3.85 (3H, s), 3.91 (3H, s), 4.28 (1H, ddd, J = 4.0, 6.5, 8.5 Hz), 4.89 (1H, brs), 5.62 (1H, t, J = 4.5 Hz), 6.63 (1H, s), 6.66 (1H, s), 6.98 (2H, d, J = 7.5 Hz), 7.13 (2H, dd, J = 2.0, 7.5 Hz), 7.21−7.24 (3H, m), 7.41 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.3, 23.1, 27.8, 42.6, 55.8, 56.0, 56.2, 106.9, 111.3, 125.8, 126.4, 126.8, 127.3, 127.4, 128.4, 129.1, 129.3, 131.6, 136.2, 141.2, 143.0, 147.1, 147.8; LRMS (EI) m/z 463 [13, M^+], 260 [100]. Anal. Calcd for $C_{27}H_{29}NO_4S$: C, 69.95; H, 6.30; N, 3.02. Found: C, 69.74; H, 6.07; N, 2.75.

***N*-[2-(Cyclohex-1-enyl)-1-phenylethyl]-4-methylbenzenesulfonamide (33).** According to the general procedure, imine **1** (259 mg, 1.0 mmol) and **32** (0.24 mL, 2.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (62 mg, 0.10 mmol) and TMSOTf (22 mg, 0.10 mmol) at room temperature for 20 h. Column

(25) Hesse, K.-D. *Liebigs Ann. Chem.* **1970**, *741*, 117−123.

chromatography on silica gel (*n*-hexane/acetone = 8/1) gave rise to pure **33** (86 mg, 24%) as a pale yellow solid: IR (KBr) 3271, 2941, 1458, 1323, 1161, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23−1.40 (2H, m), 1.47 (2H, s like), 1.58−1.66 (2H, m), 1.95 (2H, brs like), 2.30−2.37 (6H, m), 4.67−4.69 (2H, m), 5.67 (1H, m), 7.05−7.14 (7H, m), 7.50 (2H, d, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.9, 21.2, 21.4, 23.2, 25.3, 45.7, 58.1, 111.9, 126.7, 127.2, 127.3, 127.7, 128.3, 129.1, 132.6, 137.0, 139.4, 143.1; LRMS (FAB) m/z 356 [5, M^+ + H], 260 [100]; HRMS ($C_{21}H_{26}NO_2S$) found 356.1662, calcd 356.1684.

4-Methyl-*N*-{1-phenyl-2-[1-(toluene-4-sulfonyl)-1*H*-indol-3-yl]ethyl}-benzenesulfonamide (35). According to the general procedure, imine **1** (130 mg, 0.5 mmol) and **34** (285 mg, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (16 mg, 0.025 mmol) and TMSCl (2.7 mg, 0.025 mmol) at room temperature for 30 min. Column chromatography on silica gel (*n*-hexane/acetone = 4/1) gave rise to pure **35** (198 mg, 73%) as an orange powder: mp = 176 °C (Et_2O); IR (KBr) 3278, 2924, 1599, 1495, 1448, 1365, 1325, 1173, 1122, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30 (6H, s), 3.03 (1H, dd, J = 6.5, 14.5 Hz), 3.09 (1H, dd, J = 7.5, 14.5 Hz), 4.50 (1H, ddd, J = 6.5, 7.0, 7.5 Hz), 5.23 (1H, d, J = 6.5 Hz), 6.94 (2H, d, J = 8.0 Hz), 7.06−7.28 (11H, m), 7.36 (2H, d, J = 8.0 Hz), 7.63 (2H, d, J = 8.5 Hz), 7.89 (1H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.4, 21.5, 33.6, 57.4, 113.6, 117.5, 119,1, 123.1, 124.6, 126.5, 126.7, 127.6, 128.5, 129.2, 129.8, 130.3, 134.9, 135.0, 136.6, 140.6, 143.1, 144.9; LRMS (FAB) m/z 545 [7, M^+ + H], 260 [100]. Anal. Calcd for $C_{30}H_{28}N_2O_4S_2$: C, 66.15; H, 5.18; N, 5.14. Found: C, 65.89; H, 5.18; N, 5.04.

***N*-(1,3-Diphenylpent-(3*E*)-enyl)-4-methylbenzenesulfonamide ((*E*)-38).** Dichloroethane (4 mL) solution of imine **1** (130 mg, 0.5 mmol) was added to the tetrahydrofuran (1 mL) solution of $Yb(OTf)_3$ (16 mg, 0.025 mmol). Then, TMSOTf (6 mg, 0.025 mmol) and (*Z*)-**36** (132 mg, 1.0 mmol) were added successively. The reaction mixture was refluxed for 3 h. After cooling to room temperature, the reaction mixture was diluted with H_2O and extracted with CH_2Cl_2. Combined organic layers were washed with brine and dried over $MgSO_4$. Concentration under reduced pressure afforded a crude residure. The residure was chromatographed on silica gel (*n*-hexane/EtOAc = 7/1) to give a mixture of **37** and **38** (143 mg, 73%). Further purification with flash column chromatography on silica gel (*n*-hexane/EtOAc = 8/1) gave rise to pure (*E*)-**38** as a pale yellow oil: IR (neat) 3277, 2924, 1599, 1495, 1454, 1325, 1159, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56 (3H, d, J = 7.0 Hz), 2.35 (3H, s), 2.87 (1H, dd, J = 7.5, 14.0 Hz), 3.01 (1H, dd, J = 7.5, 14.0 Hz), 4.13 (1H, m), 4.74 (1H, d, J = 4.5 Hz), 5.71 (1H, q, J = 7.0 Hz), 6.99−7.01 (2H, m), 7.07 (2H, d, J = 8.0 Hz), 7.10−7.28 (9H, m), 7.42 (2H, d, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.2, 21.4, 37.7, 56.9, 126.4, 126.6, 126.9, 127.1, 127.5, 127.9, 128.2, 128.7, 129.2, 129.7, 136.1, 140.6, 141.8, 143.0; LRMS (FAB, negative) m/z 390 [100, M − H^-]; HRMS ($C_{24}H_{24}NO_2S$) found 390.1532, calcd 390.1527.

General Procedure for the Three-Component Coupling. Aldehyde (1.0 mmol) was added to the dichloromethane (8 mL) and tetrahydrofuran (2 mL) solution of $Yb(OTf)_3$ (0.05 mmol) and $TsNH_2$ (1.0 mmol). Then, TMSOTf (1.2 mmol) and **2** (2.0 mmol) were added successively. The reaction mixture was stirred at room temperature for 1 h. The mixture was diluted with H_2O and extracted with CH_2Cl_2. Combined organic layers were washed with brine and dried over $MgSO_4$. Concentration under reduced pressure afforded a crude residue. The residue was chromatographed on silica gel.

***N*-(1,3-Diphenylbut-3-enyl)-4-methylbenzenesulfonamide (3).** According to the general procedure, PhCHO (0.1 mL, 1.0 mmol), $TsNH_2$ (171 mg, 1.0 mmol), and **2** (0.26 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and TMSOTf (0.22 mL, 1.2 mmol). Column chromatography on silica gel (*n*-hexane/acetone = 8/1) gave rise to pure **3** (347 mg, 92%) as a pale yellow oil.

4-Methyl-*N*-(1-methyl-3-phenylbut-3-enyl)-benzenesulfonamide (42). According to the general procedure, CH_3CHO (0.12 mL, 2.0 mmol), $TsNH_2$ (171 mg, 1.0 mmol), and **2** (0.26 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and TMSOTf (0.22 mL, 1.2 mmol). Column chromatography on silica gel (*n*-hexane/acetone = 6/1) gave rise to pure **42** (248 mg, 79%) as a pale yellow oil: IR (neat) 3278, 2973, 1599, 1495, 1426, 1323, 1161, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (3H, d, J = 6.5 Hz), 2.31 (3H, s), 2.40 (1H, dd, J = 7.5, 14.0 Hz), 2.65 (1H, dd, J = 6.5, 14.0 Hz), 3.18 (1H, ddq, J = 6.5, 6.5, 7.0 Hz), 4.66 (1H, brs), 4.95 (1H, s), 5.20 (1H, s), 7.08−7.17 (7H, m), 7.56−7.58 (2H, m); ^{13}C NMR ($CDCl_3$) δ 21.2, 21.4, 43.4, 48.1, 115.7, 126.0, 127.0, 127.6, 128.3, 129.5, 137.5, 139.4, 143.1, 144.3; LRMS (FAB) m/z 315 [40, M^+], 198 [100]; HRMS ($C_{18}H_{21}NO_2S$) found 315.1301, calcd 315.1293.

***N*-(1-Isopropyl-3-phenylbut-3-enyl)-4-methylbenzenesulfonamide (43).** According to the general procedure, *i*PrCHO (0.09 mL, 1.0 mmol), $TsNH_2$ (171 mg, 1.0 mmol), and **2** (0.26 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and TMSOTf (0.22 mL, 1.2 mmol). Column chromatography on silica gel (*n*-hexane/acetone = 8/1) gave rise to pure **43** (244 mg, 71%) as a colorless solid: mp = 104−105 °C (*n*-hexane/acetone); IR (KBr) 3290, 2952, 1629, 1602, 1464, 1420, 1319, 1162, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.72 (3H, d, J = 7.0 Hz), 0.82 (3H, d, J = 7.0 Hz), 1.86 (1H, m), 2.40, (3H, s), 2.54 (1H, ddd, J = 1.0, 7.5, 14.5 Hz), 2.60 (1H, ddd, J = 1.0, 7.5, 14.5 Hz), 3.10 (1H, dddd, J = 3.5, 7.5, 7.5, 7.5 Hz), 4.57 (1H, d, J = 7.5 Hz), 5.01 (1H, d, J = 1.5 Hz), 5.22 (1H, d, J = 1.5 Hz), 7.11−7.27 (7H, m), 7.64 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 16.3, 18.3, 21.5, 29.5, 37.8, 56.8, 115.6, 126.1, 127.2, 127.6, 128.3, 129.4, 137.7, 139.4, 143.0, 144.6; LRMS (FAB) m/z 343 [35, M^+], 226 [100]. Anal. Calcd for $C_{20}H_{25}NO_2S$: C, 69.94; H, 7.34; N, 4.08. Found: C, 69.64; H, 7.34; N, 4.00.

***N*-(1-*tert*-Butyl-3-phenylbut-3-enyl)-4-methylbenzenesulfonamide (44).** According to the general procedure, *t*-BuCHO (0.11 mL, 1.0 mmol), $TsNH_2$ (171 mg, 1.0 mmol), and **2** (0.26 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and TMSOTf (0.22 mL, 1.2 mmol). Column chromatography on silica gel (*n*-hexane/acetone = 8/1) gave rise to pure **44** (160 mg, 45%) as a white solid: mp = 132−133 °C (*n*-hexane/EtOAc); IR (KBr) 3288, 2962, 1448, 1369, 1317, 1151, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (9H, s), 2.32 (1H, dd, J = 9.0, 14.5 Hz), 2.39 (3H, s), 2.93 (1H, dd, J = 3.5, 14.5 Hz), 3.25 (1H, ddd, J = 4.0, 9.0, 9.0 Hz), 4.46 (1H, d, J = 9.0 Hz), 4.98 (1H, d, J = 1.0 Hz), 5.10 (1H, d, J = 1.0 Hz), 7.15−7.32 (7H, m), 7.59 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.5, 26.8, 35.6, 38.0, 61.6, 115.9, 126.2, 127.1, 127.5, 128.2, 129.1, 139.1, 139.8, 142.6, 144.6; LRMS (FAB) m/z 357 [4, M^+], 240 [100]. Anal. Calcd for $C_{21}H_{27}NO_2S$: C, 70.55; H, 7.61; N, 3.92. Found: C, 70.69; H, 7.66; N, 4.02.

***N*-(1-Cyclopropyl-3-phenylbut-3-enyl)-4-methylbenzenesulfonamide (45).** According to the general procedure, *c*-C_3H_5CHO (0.07 mL, 1.0 mmol), $TsNH_2$ (171 mg, 1.0 mmol), and **2** (0.26 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and TMSOTf (0.22 mL, 1.2 mmol). Column chromatography on silica gel (*n*-hexane/acetone = 7/1) gave rise to pure **45** (260 mg, 76%) as a colorless oil: IR (neat) 3277, 2925, 1710, 1599, 1495, 1443, 1327, 1160, 708 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.14 (1H, m), 0.01 (1H, m), 0.22 (1H, m), 0.34 (1H, m), 0.69 (1H, m), 2.41 (3H, s), 2.57 (1H, m), 2.68 (1H, ddd, J = 1.0, 7.5, 14.0 Hz), 2.91 (1H, ddd, J = 1.0, 6.0, 14.0 Hz), 4.48 (1H, d, J = 6.0 Hz), 5.09 (1H, d, J = 1.0 Hz), 5.31 (1H, d, J = 1.0 Hz), 7.16−7.30 (7H, m), 7.65 (2H, d, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 3.1, 4.3, 16.3, 21.5, 42.3, 57.1, 116.0, 126.2, 127.2, 127.6, 128.4, 129.4, 137.8, 140.0, 143.1, 144.4; LRMS (FAB) m/z 341 [3, M^+], 224 [100]; HRMS ($C_{20}H_{23}NO_2SNa$) found 364.1317, calcd 364.1347.

***N*-(1-Cyclohexyl-3-phenylbut-3-enyl)-4-methylbenzenesulfonamide (46).** According to the general procedure, *c*-$C_6H_{11}CHO$ (0.12 mL, 1.0 mmol), $TsNH_2$ (171 mg, 1.0 mmol), and **2** (0.26 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and TMSOTf (0.22 mL, 1.2

mmol). Column chromatography on silica gel (*n*-hexane/acetone = 7/1) gave rise to pure **46** (326 mg, 85%) as a white solid: mp = 93 °C (*n*-hexane/Et_2O); IR (KBr) 3338, 2925, 1497, 1409, 1319, 1157, 712 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90−1.08 (5H, m), 1.35 (1H, d, J = 11.0 Hz), 1.45−1.52 (1H, m), 1.62−1.64 (2H, m), 1.73 (1H, d, J = 11.0 Hz), 2.40 (3H, s), 2.51 (1H, dd, J = 7.5, 14.0 Hz), 2.64 (1H, dd, J = 7.5, 14.0 Hz), 3.09 (1H, dddd, J = 3.5, 7.5, 7.5, 7.5 Hz), 4.24 (1H, d, J = 7.5 Hz), 4.98 (1H, d, J = 1.0 Hz), 5.23 (1H, d, J = 1.0 Hz), 7.12−7.15 (2H, m), 7.20 (2H, d, J = 8.5 Hz), 7.25−7.26 (3H, m), 7.61 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.5, 26.2, 26.2, 26.4, 27.1, 28.8, 37.7, 40.0, 56.6, 115.6, 126.1, 127.2, 127.6, 128.3, 129.4, 137.7, 139.5, 143.0, 144.6; LRMS (FAB) m/z 383 [5, M^+], 266 [100]. Anal. Calcd for $C_{23}H_{24}NO_2S$: C, 72.03; H, 7.62; N, 3.65. Found: C, 72.02; H, 7.75; N, 3.63.

4-Phenyl-2-(toluene-4-sulfonylamino)-pent-4-enoic Acid Ethyl Ester (47).[4] According to the general procedure, EtO_2-CCHO (102 mg, 1.0 mmol), $TsNH_2$ (171 mg, 1.0 mmol) and **2** (0.26 mL, 1.0 mmol) were reacted in the presence of $Yb(OTf)_3$ (31 mg, 0.05 mmol) and TMSOTf (0.22 mL, 1.2 mmol). Column chromatography on silica gel (*n*-hexane/EtOAc = 5/1) gave rise to pure **47** (246 mg, 66%) as a colorless solid: mp = 90−91 °C (Et_2O); IR (KBr) 3269, 2981, 1736, 1599, 1495, 1448, 1340, 1213, 1163, 708 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (3H, t, J = 7.0 Hz), 2.38 (3H, s), 2.90 (1H, d, J = 6.5 Hz), 2.92 (1H, d, J = 7.0 Hz), 3.68−3.78 (2H, m), 3.98 (1H, ddd, J = 6.5, 7.0, 9.0 Hz), 5.11 (1H, s), 5.18 (1H, d, J = 9.0 Hz), 5.32 (1H, s), 7.21 (2H, d, J = 8.5 Hz), 7.25−7.31 (5H, m), 7.62 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.7, 21.4, 39.3, 54.5, 61.5, 117.1, 126.3, 127.2, 127.8, 128.3, 129.5, 136.7, 139.4, 142.6, 143.5, 171.0; LRMS (EI) m/z 373 [3, M^+], 218 [100].

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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