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Versatile Intramolecular Aza-Prins and Prins Cyclization of Aryl Epoxides: A Facile Synthesis of Diaza-, Oxa-aza-, and Dioxa-bicycles

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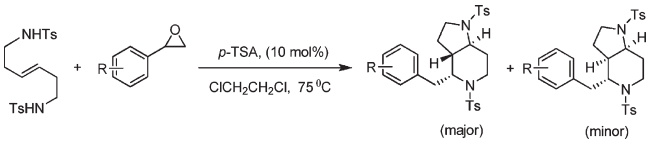

Aryl epoxides undergo coupling smoothly with (*E*)-hex-3-ene-1,6-ditosylamide in the presence of 10 mol % *p*-TSA in 1,2-dichloroethane at 75 °C to produce the corresponding 1,5-ditosyl-octahydro-1*H*-pyrrolidino-[3,2-*c*]pyridines in good yields with high *trans*-selectivity, whereas the coupling of (*Z*)-hex-3-ene-1,6-ditosylamide gave *cis*-fused octahydro-1*H*-pyrrolidino[3,2-*c*]pyridines predominantly. The use of readily available *p*-TSA makes this method simple, convenient, and practical.

Epoxides are versatile intermediates in organic synthesis due to their easy availability.[1] The inherent polarity and strain of these three-membered rings make them susceptible to ring-opening with a large number of reagents. Thus, they are well-known carbon electrophiles capable of reacting with various nucleophiles, and their ability to undergo regioselective ring-opening reactions contribute largely to their synthetic value.[1] One of the most frequently used atom economical reaction of epoxides is their rearrangement to carbonyl compounds, which provides an easy access for unstable aldehydes. Thus, in situ formed carbonyl compounds are very useful precursors for many organic transformations.[2] The octahydro-1*H*-pyrrolidino[3,2-*c*]pyridine moiety is a core structure in some biologically active natural products such as martinellic acid **1a** and martinelline **1b** (Figure 1).[3] They are the first nonpeptide natural product bradykinin receptor antagonists.[3] These compounds also exhibits potent antibiotic activities against both Gram-positive and Gram-negative bacteria and also has affinity for several G-protein coupled receptors.[4]

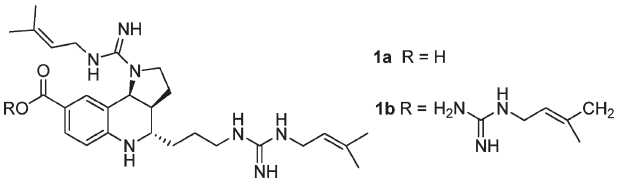

FIGURE 1. Examples of natural products bearing pyrrolidino[3,2-*c*]-pyridine skeleton.

The hetero-Diels−Alder reaction is a simple and most powerful method for the synthesis of hexahydropyrroloquinolines.[5] On the other hand, aza-Prins cyclization is one of the most elegant approaches for the synthesis of piperidine derivatives, usually with net addition of an external nucleophile to the resulting carbenium ion.[6] Besides aldehydes, epoxides have also been found to be effective in the Prins and aza-Prins cyclizations in the presence of Lewis acids.[7] Recently, an intramolecular Prins cyclization has also been reported for the synthesis of angularly fused furo[3,2-*c*]-pyrans.[8] However, to the best of our knowledge, intramolecular Prins and aza-Prins cyclizations of epoxides have not been explored with homoallylic alcohols bearing terminal hydroxyl group and bishomoallylic amides, respectively. Recently, *p*-TSA has received attention as a cost-effective, nontoxic, readily available, and selective reagent for various organic transformations.[9] The mild Brønsted acidity associated with *p*-TSA enhances its use at levels from stoichiometric to catalytic, as a powerful reagent for various organic transformations.[10]

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SCHEME 1. Reaction of *E*-Olefin with *p*-Chlorostyrene Oxide

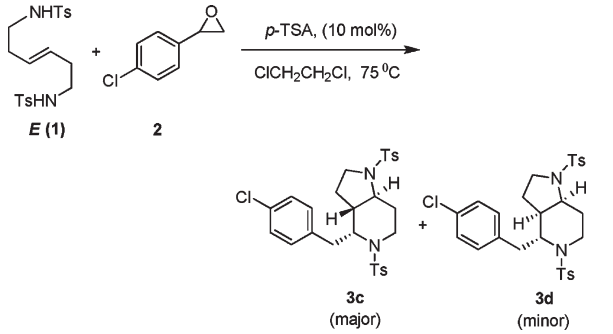
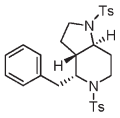
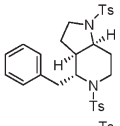
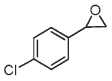
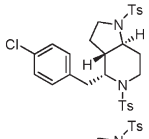
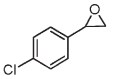
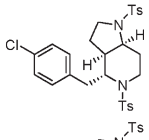
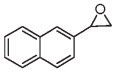
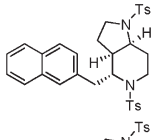
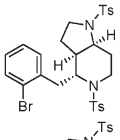
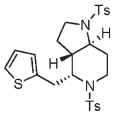


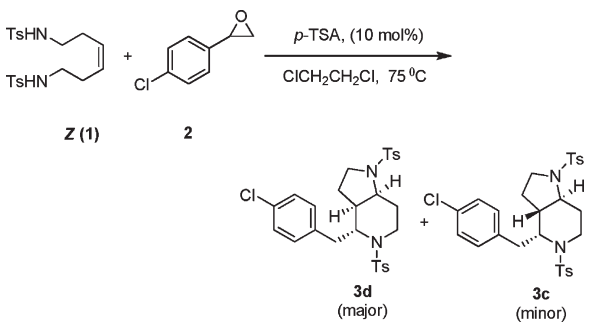
TABLE 1. *p*-TSA-Catalyzed Synthesis of 2-Substituted Octahydro *N*,*N*-Ditosyl Pyrrolidinopyridine[a]

Entry	Olefin (**1**)	Epoxide (**2**)	Product (**3**)[b]	Time (h)	Yield (%)[c]	*Trans*:*cis* Ratio[d]
a	*E*			08	67	96:04
b	*Z*			09	70	05:95
c	*E*			07	71	95:05
d	*Z*			07	73	10:90
e	*Z*			06	74	05:95
f	*Z*			08	70	04:96
g	*E*			06	65	95:05

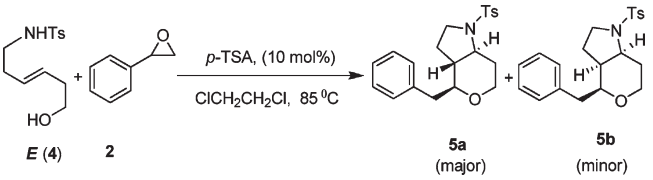
[a]Reaction was performed with 0.5 mmol olefin, 0.75 mmol epoxide, and 10 mol % *p*-TSA. [b]All the products were characterized by ^{1}H and ^{13}C NMR, IR, and mass spectroscopy. [c]Yield refers to pure product after column chromatography. [d]*Trans*/*cis* ratio was determined by ^{1}H NMR spectra of crude product.

In continuation of our interest on Prins-type cyclization and its applications in the total synthesis of natural products,[11] we herein report a versatile method for the synthesis of diaza-, oxa-aza-, and dioxa-bicycles by means of intramolecular aza-Prins and Prins cyclizations of epoxides. Initially, we have attempted the coupling of 4-chlorostyrene oxide (**2**) with (*E*)-hex-3-ene-1,6-ditosylamide (**1**) in the presence of 10 mol % of *p*-TSA in 1,2-dichloroethane. The reaction was found to be sluggish at room temperature. Interestingly, the reaction proceeded smoothly at 75 °C to afford the product **3c** in 71% yield with high *trans*-selectivity (96:4, Scheme 1, Table 1).

SCHEME 2. Reaction of *Z*-Olefin with *p*-Chlorostyrene Oxide



SCHEME 3. Synthesis of *trans*-Fused Oxa-aza-bicyles via Intramolecular Prins Cyclization



The coupling of (*Z*)-hex-3-ene-1,6-ditosylamide with *p*-chlorostyrene oxide (**2**) in the presence of 10 mol % of *p*-TSA in 1,2-dichloroethane at 75 °C gave the product **3d** in 73% yield with high *cis*-selectivity (Scheme 2).

The ratio of *cis*/*trans* isomers was determined by ^{1}H NMR spectra of the crude product, and the results are given in Table 1. The two isomers could be easily separated by silica gel column chromatography. This result provided the incentive to extend this process for various aryl epoxides. Interestingly, other epoxides such as styrene oxide, 2-naphthalen-2-yl oxirane, 2-bromostyrene oxide, and 2-(thiophen-2-yl)-oxirane also participated well in this reaction to produce diaza-bicyles (entries **a**, **b**, **e**, **f**, and **g**, Table 1).

Next, we attempted the coupling of (*E*)-*N*-(6-hydroxyhex-3-enyl)-4-methylbenzenesulfonamide (**4**) with aryl oxiranes. In those cases, *trans*-fused octahydropyrano[4,3-*b*]pyrrole **5a**, **5d**, **5f**, and **5g** were obtained as major products from the Prins cyclization (Scheme 3). It is worth mentioning that higher temperature (85−90 °C) favors Prins cyclization. At low temperatures (below 65 °C), the competitive aza-Prins cyclization was also observed.

The *cis* and *trans* isomers were easily separated by column chromatography. The ratio of *cis*/*trans* isomers was determined by ^{1}H NMR spectra of the crude product (Table 2). However, the Prins cyclization of aryl epoxides with *Z*-*N*-(6-hydroxyhex-3-enyl)-4-methylbenzenesulfonamide under similar conditions gave *cis*-fused products exclusively (Scheme 4).

The scope of the reaction is illustrated with respect to various epoxides, and the results are summarized in Table 2. Besides styrene oxide, *p*-chlorostyrene oxide, stilbene oxide, indene oxide, and 2-methyl-3-phenyloxirane were also effective for this conversion (entries **c**−**g**, Table 2). In the case of

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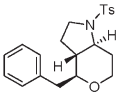
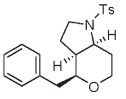
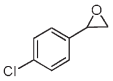
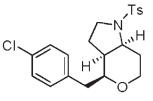
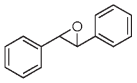
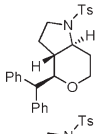
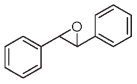
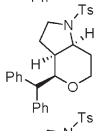
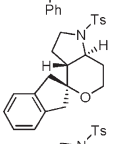
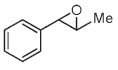
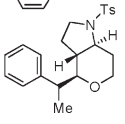
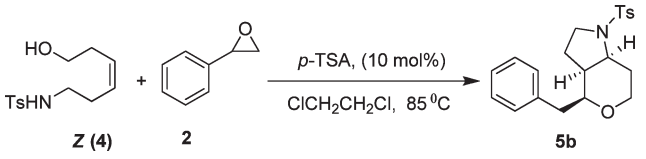
TABLE 2. *p*-TSA-Catalyzed Synthesis of 2-Substituted Octahydro *N*-Tosyl Pyranopyrrole[a]

Entry	Olefin (**4**)	Epoxide (**2**)	Product (**5**)[b]	Time (h)	Yield (%)[c]	*Trans:cis* Ratio[d]
a	*E*			09	70	95:05
b	*Z*			10	68	
c	*Z*			08	67	
d	*E*			07	73	95:05
e	*Z*			07	71	
f	*E*			18	62[e]	95:05
g	*E*			09	70	85:15

[a]Reaction was performed with 0.5 mmol olefin, 0.75 mmol epoxide, and 10 mol % *p*-TSA. [b]All the products were characterized by ^{1}H and ^{13}C NMR, IR, and mass spectroscopy. [c]Yield refers to pure product after column chromatography. [d]*Trans*−*cis* ratio was determined by ^{1}H NMR spectra of crude product. [e]Epoxide (1 mmol) was used.

SCHEME 4. Synthesis of *cis*-Fused Oxa-aza-bicyles via Intramolecular Prins Cyclization



indene oxide, the corresponding spiro-oxa-aza-bicycle was formed under the reaction conditions (entry **f**, Table 2).

Encouraged by the results obtained from hex-3-ene-1,6-ditosylamide (**1**) and *N*-(6-hydroxyhex-3-enyl)-4-methylbenzenesulfonamide (**4**), we turned our attention to study the Prins cyclization with hex-3-ene-1,6-diol. Accordingly, styrene oxide was treated with (*E*)-hex-3-ene-1,6-diol (**6**) in the presence of 10 mol % *p*-TSA in 1,2-dichloroethane. The reaction proceeded smoothly at 75 °C to afford the corresponding *trans*-fused hexahydrofuro[3,2-*c*]pyran **7a** as a major product (Scheme 5).

The *cis* and *trans* isomers **7b**/**7a** are inseparable on silica gel column chromatography. Yet *cis*/*trans* ratio was determined by ^{1}H NMR spectra of the crude product (Table 3).

However, the coupling of (*Z*)-hex-3-ene-1,6-diol with styrene oxide gave *cis*-fused furo[3,2-*c*]pyran **7b** exclusively (Scheme 6).

Similarly, other epoxides such as *p*-chlorostyrene oxide, 2-naphthalen-2-yl oxirane, *trans*-stilbene oxide, 2-bromostyrene oxide, and 2-methyl-3-phenyloxirane also underwent

SCHEME 5. Synthesis of *trans*-Fused Furo[3,2-*c*]pyrans via Intramolecular Prins Cyclization

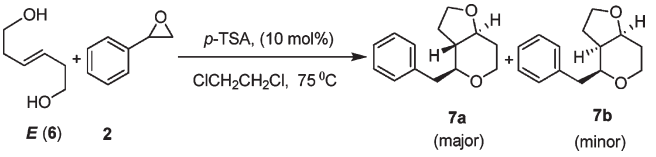
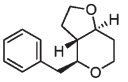
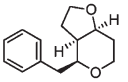
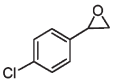
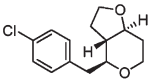
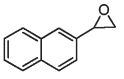
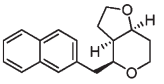
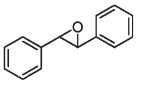
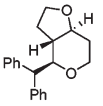
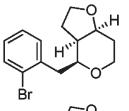
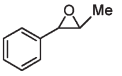
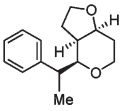
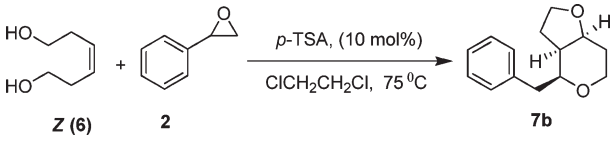


TABLE 3. *p*-TSA-Catalyzed Synthesis of 2-Substituted Furanopyrans[a]

Entry	Olefin (**6**)	Epoxide (**2**)	Product (**7**)[b]	Time (h)	Yield (%)[c]	*Trans:cis* Ratio[d]
a	*E*			10	68	95:05
b	*Z*			11	69	
c	*E*			09	72	95:05
d	*Z*			09	74	
e	*E*			08	79	95:05
f	*Z*			10	70	
g	*Z*			09	71	

[a]Reaction was performed with 0.5 mmol olefin, 0.75 mmol epoxide, and 10 mol % *p*-TSA. [b]All the products were characterized by ^{1}H and ^{13}C NMR, IR, and mass spectroscopy. [c]Yield refers to pure product after column chromatography. [d]Trans−cis ratio was determined by ^{1}H NMR spectra of crude product.

SCHEME 6. Synthesis of *cis*-Fused Furo[3,2-*c*]pyrans via Intramolecular Prins Cyclization



smooth intramolecular Prins cyclization to afford the respective furo[3,2-*c*]pyrans in good yields (entries **c**−**g**, Table 3). The structures of **3c**, **5a**, and **5e** were established by X-ray crystallography.

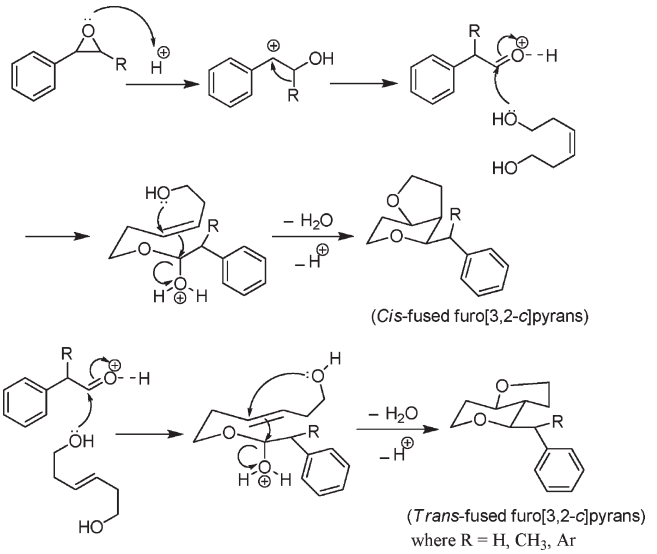
Furthermore, we have performed the reactions with both epoxide and its corresponding aldehyde so as to compare the yields in the same reactions. For example, styreneoxide and phenyl acetaldehyde were used to perform intramolecular Prins and aza-Prins cyclizations, and the results are presented in Table 4. It is observed that slightly higher yields were obtained with aldehydethan epoxide.

However, aliphatic epoxides such as 1-octene oxide, and cyclohexene oxide underwent simple ring-opening

TABLE 4. Comparative Study of Prins and Aza-Prins Cyclizations with Styrene Oxide and Phenyl Acetaldehyde

			yield (%)	
entry	olefin	product	styrene oxide	phenyl acetaldehyde
a	*E*-**1**	**3a**	67	70
b	*Z*-**4**	**5b**	68	71
c	*Z*-**6**	**7b**	69	73

SCHEME 7. Plausible Intramolecular Prins Cyclization Mechanism



with homoallyl alcohols and homoallylic amides instead of expected intramolecular Prins and aza-Prins cyclizations, respectively. The effects of various acid catalysts such as camphorsulfonic acid (CSA), phosphomolybdic acid (PMA), and Amberlyst-15 were studied for this conversion. Of these, *p*-TSA was found to give the best results in terms of yields. The reaction was performed in various solvents such as 1,2-dichloroethane, toluene, and acetonitrile. Among these, 1,2-dichloroethane was found to give the highest yield. This method utilizes easily accessible precursors and inexpensive *p*-TSA. This protocol is simple and convenient and also provides the desired products in good yields with high stereoselectivity. Mechanistically, the reaction proceeds via the rearrangement of epoxide to the corresponding aldehyde, which subsequently reacts with homoallylic alcohol to give the hemiacetal. The latter intermediate may undergo cyclization with olefin followed by the trapping of the resulting carbenium ion by terminal hydroxyl group affording furopyrans (Scheme 7).

In conclusion, we have developed a novel protocol for the synthesis of octahydro-1*H*-pyrrolidino[3,2-*c*]pyridines, octahydropyrano[4,3-*b*]pyrroles, and hexahydro-2*H*-furo[3,2-*c*]-pyrans by means of intramolecular aza-Prins and Prins cyclization, respectively. This is an efficient and highly diastereoselective method to accomplish the synthesis of a series of diaza-, oxa-aza-, and dioxa-bicycles in a single-step operation. The use of *p*-toluenesulfonic acid makes this method simple, convenient and economically viable for large-scale synthesis.

Experimental Section

Typical Procedure for the Intramolecular Aza-Prins Cyclization. To a stirred solution of (*E*)-hex-3-ene-1,6-ditosylamide (**1**; 211 mg, 0.50 mmol) and *p*-chlorostyrene oxide (**2**; 116 mg, 0.75 mmol) in anhydrous 1,2-dichloroethane (4 mL) was added *p*-TSA (9.5 mg, 10 mol %) and was heated at 75 °C for 7 h. After completion of the reaction, as indicated by TLC, the mixture was quenched with saturated $NaHCO_3$ solution (0.5 mL) and extracted with dichloromethane (2 × 10 mL). The combined organic layers were washed with brine (3 × 2 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The resulting crude product was purified by column chromatography (silica gel, Merck, 100−200 mesh). Elution starts with 50 mL of 10% EtOAc in *n*-hexane, then with 50 mL (2 drops of triethylamine) of 16% EtOAc in *n*-hexane, followed by 100 mL (5 drops of triethylamine) of 19% EtOAc in *n*-hexane to afford pure product **3c** (198 mg, 71% yield).

(3a*S*,4*R*,7a*S*)-4-(4-Chlorobenzyl)-octahydro-1,5-ditosyl-1*H*-pyrrolidino[3,2-*c*]pyridine (3c; Table 1). Solid, mp 203−204 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 7.4 Hz, 2H), 7.15−7.05 (m, 4H), 6.87 (d, J = 8.3 Hz, 2H), 4.62−4.51 (m, 1H), 3.94−3.83 (m, 1H), 3.43 (t, J = 10.0 Hz, 1H), 3.34−3.20 (m, 1H), 3.15−2.91 (m, 2H), 2.57 (d, J = 7.7 Hz, 2H), 2.46 (s, 3H), 2.40 (s, 3H), 2.14−1.97 (m, 1H), 1.81−1.51 (m, 3H), 1.27−1.08 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 143.2, 136.9, 135.8, 133.8, 132.3, 130.1, 129.8, 129.5, 128.5, 127.4, 126.7, 58.1, 57.1, 47.9, 46.9, 39.4, 32.8, 31.4, 26.0, 21.6, 21.5; IR (KBr) ν_{max} 2925, 1305, 1156, 1089, 810, 661 cm^{-1}; ESI-MS (m/z) 559 (M^+ + H); HRMS calcd for $C_{28}H_{31}N_2O_4NaS_2Cl$, 581.1311; found, 581.1295.

(3a*R*,4*S*,7a*S*)-4-Benzyl-octahydro-1-tosylpyrano[4,3-*b*]pyrrole (5a; Table 2). Yield, 130 mg, 70%;solid, mp 187−188 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.30−7.13 (m, 5H), 4.07 (dd, J = 3.2, 12.0 Hz, 1H), 3.47−3.18 (m, 4H), 2.77 (d, J = 6.0 Hz, 2H), 2.59−2.33 (m, 4H), 1.91−1.54 (m, 4H), 1.13−0.94 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 137.9, 133.1, 129.7, 129.2, 128.2, 127.7, 126.3, 81.1, 65.8, 63.4, 48.7, 47.9, 40.7, 33.4, 25.3, 21.5; IR (KBr) ν_{max} 2928, 2834, 1342, 1163, 1076, 747, 702, 664 cm^{-1}; ESI-MS (m/z) 372 (M^+ + H); HRMS calcd for $C_{21}H_{25}NO_3NaS$, 394.1452; found, 394.1445.

(3a*R*,4*S*,7a*S*)-4-Benzyl-hexahydro-2*H*-furo[3,2-*c*]pyran (7b; Table 3). Yield, 75 mg, 69%; colorless viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34−7.19 (m, 5H), 4.15−4.08 (m, 1H), 4.07−4.01 (m, 1H), 3.97−3.90 (m, 1H), 3.89−3.80 (m, 2H), 3.29 (dt, J = 2.4, 12.1 Hz, 1H), 2.98−2.90 (m, 1H), 2.74−2.65 (m, 1H), 2.21−2.07 (m, 2H), 1.97−1.86 (m, 1H), 1.73−1.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 128.9, 128.3, 126.3, 77.0, 74.9, 66.3, 65.4, 41.8, 40.7, 28.3, 23.1; IR (neat) ν_{max} 2950, 2848, 1092, 752, 702 cm^{-1}; MS (APCI) m/z 219 (M^+ + H); HRMS (APCI) calcd for $C_{14}H_{19}O_2$, 219.1385; found, 219.1379.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds (**3a**−**3g**, **5a**−**5g**, and **7a**−**7g**), general experimental procedure for reactions, catalyst screening results, ^{1}H NMR, and NOE studies of selected compounds, and X-ray data of compounds (**3c**, **5a**, and **5e**) are provided in the CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.