Insertion of Polar and Nonpolar Unsaturated Molecules into Carbon−Rhenium Bonds Generated by C−H Bond Activation: Synthesis of Phthalimidine and Indene Derivatives

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Abstract: A rhenium complex, [ReBr(CO)$_3$(thf)]$_2$, catalyzes the reaction of an aromatic aldimine with an isocyanate and an acetylene to give a phthalimidine and an indene derivative in a quantitative yield, respectively. The reactions proceed via C−H bond activation, insertion of the isocyanate or the acetylene, intramolecular nucleophilic cyclization to the aldimine of the generated amido− or alkenyl−rhenium species, and reductive elimination. In contrast to ruthenium and rhodium catalysts, which are usually employed in this type of reaction, the rhenium catalyst promotes the insertion of a polar unsaturated molecule. This occurs more easily than the insertion of a nonpolar unsaturated molecule.

Introduction

Transition-metal-catalyzed chemical transformations via C−H bond activation are an important and challenging theme because the introduction of functional groups can be achieved in short reaction steps and byproducts such as metal halides are not formed. Although there have been many examples of the insertion of unsaturated bonds, such as olefins and acetylenes to aromatic C−H bonds using ruthenium or rhodium complexes as a catalyst,[1] most have been limited to nonpolar unsaturated bonds. Insertion of polar unsaturated bonds into carbon−metal bonds generated by C−H bond activation could enlarge the scope of the C−H bond activation; however, only a few examples have been reported.[2]

As one of the applications of C−H bond activation chemistry, there have been several reports on the construction of cyclic compounds.[3] However, these reactions are limited to intramolecular cyclizations and need special starting materials to afford the cyclic products. In contrast, we have recently succeeded in the rhenium-catalyzed intermolecular annulation of aromatic aldimines with internal acetylenes via C−H bond activation to give indene derivatives.[4] The annulation method requires only a catalytic amount of a rhenium complex, and compares favorably with the manganese-mediated[5a] synthesis of indene

derivatives via *ortho*-manganated aryl ketones generated by treatment of aryl ketones with a stoichiometric amount of a manganese complex.[5] Only a few reports have appeared on the rhenium-catalyzed C−H bond activation.[6,7] This is the first rhenium-catalyzed insertion of an unsaturated molecule into a C−H bond, and it is also the first intramolecular nucleophilic addition of an organometallic species derived from C−H bond activation to an imine moiety.

We disclose here the rhenium-catalyzed insertion of a nonpolar molecule, acetylene, and more interestingly, a polar molecule, isocyanate, into a carbon−rhenium bond at the *ortho*-position of an aldimine, derived from catalytic C−H bond activation, proceeds smoothly and that an indene[8−11] or a

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phthalimidine derivative[12,13] is produced by successive intramolecular cyclization. A comparison between the reactivity of an acetylene and an isocyanate toward the aromatic aldimine shows that the isocyanate is more reactive than the acetylene.
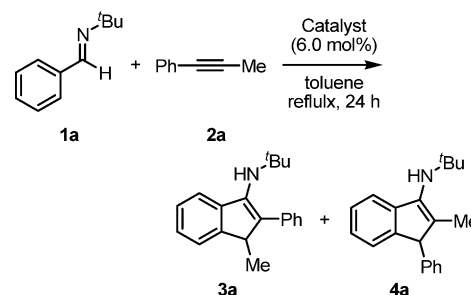
Results and Discussion

Reaction of Aromatic Aldimines with Internal Acetylenes. The treatment of aromatic aldimine **1a** (0.50 mmol) with acetylene **2a** (0.50 mmol) in toluene (1.0 mL) in the presence of a possible catalyst (6.0 mol %) under reflux conditions for 24 h gave indene derivatives (eq 1).[14,15]
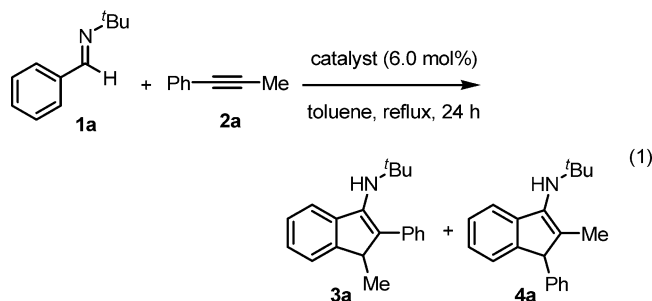
We screened several catalysts in the reaction of aldimine **1a** with 1-phenyl-1-propyne **2a** (Table 1). First, we examined a popular rhodium(I) complex, RhCl(PPh$_3$)$_3$, and a ruthenium complex, Ru$_3$(CO)$_{12}$, but the reactions did not occur and aldimine **1a** remained unchanged in both cases (Table 1, entries 1 and 2). Although the ruthenium complex has been reported to catalyze C−H bond activation of aldimine and successive insertion of the 1-trimethylsilyl-1-propyne,[16] the process stops at the insertion stage, and further intramolecular cyclization does not occur. The reaction did not proceed when a dinuclear rhenium(0) complex, Re$_2$(CO)$_{10}$, was used (Table 1, entry 3). Among the catalysts examined, a rhenium(I) complex, ReCl-(CO)$_5$, was found to catalyze the desired reaction and gave two isomeric indene derivatives, **3a** and **4a**, though the yields were low (both 20% yields) (Table 1, entry 4). This result suggests that the rhenium complex has a similar ability for C−H bond activation as Ru$_3$(CO)$_{12}$ and that the formed alkenyl−rhenium part has sufficient nucleophilicity to add to the aldimine moiety. The yields and selectivity were improved by changing the ligand of the rhenium complex from chloride to bromide (Table 1, entry 5). For the purpose of accelerating the reaction rate by promoting ligand dissociation, ReBr(CO)$_3$(CH$_3$CN)$_2$ or [ReBr-

(12) Phthalimidine (isoindolinone, benzo-γ-lactam) has a five-membered ring with one nitrogen atom and is a part of the structure of bioactive compounds: (a) Fajardo, V.; Elango, V.; Cassels, B. K.; Shamma, M. *Tetrahedron Lett.* **1982**, *23*, 39. (b) Valencia, E.; Freyer, A. J.; Shamma, M. *Tetrahedron Lett.* **1984**, *25*, 599. (c) Valencia, E.; Fajardo, V.; Freyer, A. J.; Shamma, M. *Tetrahedron Lett.* **1985**, *26*, 993. (d) Takahashi, I.; Kawakami, T.; Hirano, E.; Yokota, H.; Kitajima, H. *Synlett* **1996**, 353 and references therein. (e) Moreau, A.; Couture, A.; Deniau, E.; Grandclaudon, P. *J. Org. Chem.* **2004**, *69*, 4527.
(13) Several synthetic methods of phthalimidine derivatives using transition metal compounds have been reported: (a) Uozumi, Y.; Kawasaki, N.; Mori, E.; Mori, M.; Shibasaki, M. *J. Am. Chem. Soc.* **1989**, *111*, 3725. (b) Duckworth, D. M.; Lee-Wong, S.; Slawin, A. M. Z.; Smith, E. H.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 1* **1996**, 815. (c) Couty, S.; Liegault, B.; Meyer, C.; Cossy, J. *Org. Lett.* **2004**, *6*, 2511. (d) Orito, K.; Horibata, A.; Nakamura, T.; Ushito, H.; Nagasaki, H.; Yuguchi, M.; Yamashita, S.; Tokuda, M. *J. Am. Chem. Soc.* **2004**, *126*, 14342.
(14) The ^{1}H NMR yields were determined by using 1,1,2,2-tetrachloroethane as an internal standard.
(15) Heat and/or a rhenium catalyst promote interconversion of substituents at 1,2-position of the indene framework. The elucidation of the mechanism is now under consideration.
(16) Kakiuchi, F.; Sato, T.; Tsujimoto, T.; Yamauchi, M.; Chatani, N.; Murai, S. *Chem. Lett.* **1998**, 1053.

Table 1. Catalytic Activities of Transition Metal Complexes

entry	catalyst	yield^a [%]	
		3a	**4a**
1	RhCl(PPh$_3$)$_3$	0	0
2	Ru$_3$(CO)$_{12}$^{b}	0	0
3	Re$_2$(CO)$_{10}$^{c}	0	0
4	ReCl(CO)$_5$	20	20
5	ReBr(CO)$_5$	74	22
6	ReBr(CO)$_3$(CH$_3$CN)$_2$	0	0
7	[ReBr(CO)$_3$(thf)]$_2$^{c}	>99	0
8	Re(CH$_3$)(CO)$_5$	2	0
9	ReCp*(CO)$_3$	0	0
10	ReCl$_3$(PMe$_2$Ph)$_3$	0	0
11	MnBr(CO)$_5$	0	0

^{a} The yield was detemined by ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard. ^{b} 2.0 mol %. ^{c} 3.0 mol %.
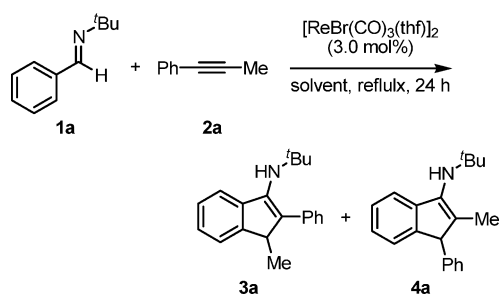
(CO)$_3$(thf)]$_2$ was used as the catalyst (Table 1, entries 6 and 7). Although ReBr(CO)$_3$(CH$_3$CN)$_2$ did not afford the product at all, indene derivative **3a** was obtained quantitatively by using [ReBr(CO)$_3$(thf)]$_2$. Methyl−rhenium complex, Re(CH$_3$)(CO)$_5$, facilitated the reaction, but the yield of **3a** was very low (Table 1, entry 8). The formation reaction of indene derivatives did not occur with rhenium(I) complex, ReCp*(CO)$_3$, rhenium(III) complex, ReCl$_3$(PMe$_2$Ph)$_3$, or manganese(I) complex, MnBr-(CO)$_5$ (Table 1, entries 9−11).

The highest yield and selectivity could be obtained by using toluene as a solvent in the reaction of aromatic aldimine **1a** with acetylene **2a** (Table 2, entry 1). In octane, the reaction proceeded quantitatively, but the selectivity of the products was low (Table 2, entry 2). In polar solvents such as THF and methylene chloride, the indene derivatives were obtained in low yields (Table 2, entries 3 and 4). When more polar solvents were used, such as 1,3-dimethyl-2-imidazolidinone (DMI) and dimethylformamide (DMF), the yields were very low (Table 2, entries 5 and 6).

Although the reaction of aromatic aldimine **1a** with acetylene **2a** proceeded in quantitative yields at both 115 °C and 80 °C, the selectivity of indene derivatives **3a** and **4a** was low at 80 °C (**3a**:**4a** = 54:46). Even at 25 °C, the indene derivative **4a** could be obtained catalytically (21%).

Then, we varied the substituents of aldimines and alkynes (Table 3). By the reaction of 1-phenyl-1-propyne (**2a**) with aldimine **1b** instead of **1a**, the selectivity reversed and the indene derivative **4b** was obtained selectively (entry 2). The reaction did not proceed with the oxime or hydrazone of an aldehyde instead of the aldimine. Treatment of diphenylacetylene (**2b**) and aldimine **1a** with [ReBr(CO)$_3$(thf)]$_2$ afforded the indene derivative quantitatively (entry 3). Aldimines bearing electron-donating groups, such as methoxy and methyl groups at the *para*-position of the aldimine, gave the corresponding indene derivatives in excellent yields (entries 4 and 5). A reaction of
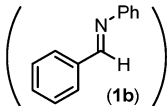
Table 2. Investigation of the Solvent

| entry	solvent	yield[a] [%]	
		3a	**4a**
1	toluene	>99	0
2	Octane	89	11
3	THF	0	17
4	CH_2Cl_2	6	29
5	DMI[b]	7	10
6	DMF[c]	0	0

[a] The yield was detemined by ^1H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [b] 1,3-Dimethyl-2-imidazolidinone. [c] Dimethylformamide.

Table 3. Rhenium-Catalyzed Reaction of an Aromatic Aldimine with an Acetylene
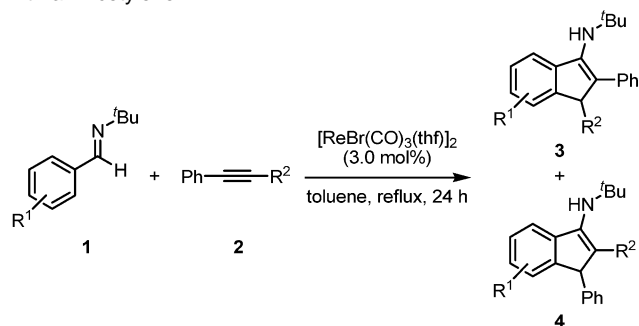
entry	imine (R^1)	acetylene (R^2)	% yield[a]	3:4[b]
1	**1a**: R^1 = H	**2a**: R^2 = Me	**3a**: 95 (>99)	>99:<1
2[c]	(**1b**)	**2a**	**4b**: 89 (>99)	<1:>99
3	**1a**	**2b**: R^2 = Ph	**3c**: 96 (>99)	
4	**1c**: R^1 = *p*-MeO	**2b**	**3d**: 89 (96)	
5	**1d**: R^1 = *p*-Me	**2b**	**3e**: 95 (>99)	
6	**1e**: R^1 = *p*-Ph	**2b**	**3f**: 83 (93)	
7	**1f**: R^1 = *p*-CF$_3$	**2b**	**3g**: 14 (16)	
8	**1g**: R^1 = *o*-Me	**2b**	**3h**: 40 (52)	
9	**1h**: R^1 = *o*-MeO	**2b**	**3i**: 0 (0)	
10[d]	**1a**	**2c**: R^2 = *n*-C$_6$H$_{13}$	**3j**: 64 (68)	>99:<1
11	**1a**	**2d**: R^2 = SiMe$_3$	**4k**: 81 (87)	<1:>99

[a] Isolated yield. The yield determined by ^1H NMR is reported in parentheses. [b] The ratios of indene derivatives **3** and **4**. [c] 1-Phenyl-1-propyne (1.1 equiv), 135 °C. [d] 135 °C.

an aldimine possessing a *para*-phenyl group with **2b** gave the indene derivative **3b** in good yield (entry 6). However, an aldimine bearing an electron-withdrawing trifluoromethyl group at the *para*-position gave the corresponding indene derivative in low yield (entry 7). In contrast to the *para* substituents, the
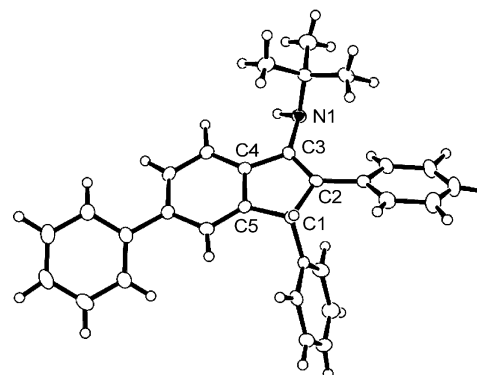
**Figure 1.** X-ray crystal structure of indene derivative **3f**.

yields decreased when substituents were attached to the *ortho*-position of the aldimines. For example, the indene derivative was obtained in 40% yield by the reaction of an aldimine bearing *ortho*-methyl group with **2b** (entry 8), and an aldimine with an *ortho*-methoxy group did not afford the corresponding indene derivative (entry 9). The reaction of **2b** with benzaldehyde or acetophenone did not proceed at all. The imine nitrogen atom could coordinate more strongly to the rhenium center than the oxygen atoms and promoted the C−H bond activation. The reaction of **2b** with an *N,N*-dimethylhydrazone of benzaldehyde did not proceed at all, and the starting materials were recovered completely. In contrast, the reaction of **2b** with an *N,N*-dimethylhydrazone of acetophenone produced the insertion product of the acetylene after C−H bond activation in 21% yield, although most of the starting materials were recovered unchanged (both in 75% yields).

From our experiments, it was found that acetylenes bearing at least one aryl group gave the corresponding indene derivatives (entries 10 and 11). Indene derivatives could not be obtained by the reaction of aldimine with 6-dodecyne, 1-trimethylsilyl-1-propyne, bis(trimethylsilyl)acetylene.

The detailed structure of the indene framework was determined by X-ray crystal structure analysis (Figure 1). By the reaction of *N*-phenyl aldimine (R^1 = Ph) with diphenylacetylene, indene derivative **3f** could be obtained in 93% yield (Table 1, entry 6). After isolation by silica gel column chromatography and recrystalization from toluene/hexane, yellow single crystals of indene derivative **3f** could be obtained.
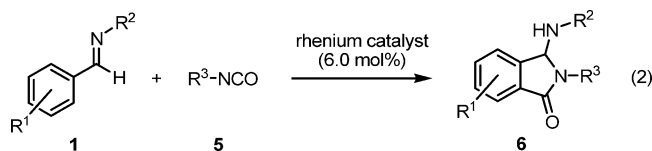
The X-ray crystal structure analysis showed that the indene derivative **3f** has an aminoindene framework (Figure 1). The bond length of C2−C3 is shorter than that of C1−C2, C3−C4, and C5−C1, and is suitable for that of the C=C double bond. The bond length of C3−N1 is also appropriate for that of the C−N single bond. The results that C2, C3, C4, and N1 are located on almost the same plane and C1 is a sp^3 carbon atom also indicate that **3f** has an aminoindene framework.

When the proposed reaction was carried out with ReBr(CO)$_5$ under an atmosphere of carbon monoxide (1.0 atm), an indene derivative was not obtained and the starting materials **1a** and **2a** were recovered quantitatively. This result and the fact that the catalytic activity of [ReBr(CO)$_3$(thf)]$_2$ is higher than that of ReBr(CO)$_5$ indicated that the formation step of one or more vacant coordination sites as a result of the carbonyl ligand(s) leaving the rhenium center is important to promote the reaction. The proposed reaction mechanism is as follows (Scheme 1): (1) Coordination of a nitrogen atom of an imine to a rhenium

Scheme 1. Proposed Mechanism of the Formation of Indene Derivatives
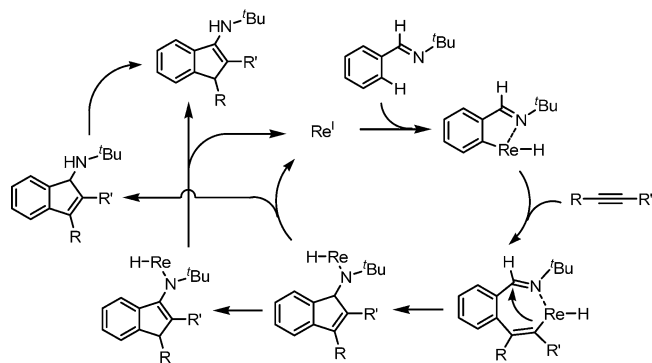
center.[17] (2) C−H bond activation at the *ortho*-position of the imine moiety. Although electrophilic metalation of the acetylene is another possibility, we are tempted to assume that the rhenium-catalyzed reactions proceed via C−H bond activation based on the following two experimental results. First, the orientation of the two substituents on the products derived from acetylenes is *cis*-form. If the reactions proceed via electrophilic metalation, the orientation must be *trans*-form and thus it must be difficult to promote further intramolecular cyclization. The second experimental evidence is that these reactions proceed in the presence of a base (K_2CO_3 or tributylamine) without decreasing the yield. The electrophilic metalation must be inhibited by the addition of the base because a proton is formed during the reaction step.[18,19] (3) Insertion of an acetylene to the rhenium−carbon bond of the aryl−rhenium intermediate. (4) Intramolecular nucleophilic attack of the formed alkenylrhenium moiety to a carbon atom of the imine. (5) Reductive elimination and 1,3-rearrangement of hydrogen atoms (or vice versa).

Reaction of Aromatic Aldimines with Isocyanates. Because rhenium has a lower electronegativity than rhodium or ruthenium, a carbon−rhenium bond is expected to be more polarized than a carbon−rhodium or a carbon−ruthenium bond. Therefore, we thought that it might be possible to promote the insertion of polar unsaturated molecules into a C−H bond by using a rhenium catalyst. As a result of our investigations on the insertion of polar unsaturated molecules, the rhenium-catalyzed insertion reactions of isocyanates **5** (0.50 mmol) into the C−H bond of aldimines **1** (R^1 = H; R^2 = ^tBu, 0.50 mmol) proceeded at 90 °C to give phthalimidine derivatives (eq 2).[20]

Among the catalysts examined,[21] the rhenium(I) complex $ReBr(CO)_5$ proved to have a catalytic activity; phthalimidine

6a (R^1 = H; R^2 = ^tBu; R^3 = Ph) was obtained in 73% yield and **1a** was recovered in 23% yield. To improve the catalytic activity of the rhenium complex, $[ReBr(CO)_3(thf)]_2$ was used, and **6a** was formed in quantitative yield (Table 4, entry 1).[22,23] In this reaction, a functionalized compound at two *ortho*-positions did not form.[24] The rhenium complex $Re(CH_3)(CO)_5$ showed low reactivity (4% yield of **6a**). The reaction did not proceed with other potential catalysts such as $Ru_3(CO)_{12}$, $RuH_2(CO)(PPh_3)_3$, and $RhCl(PPh_3)_3$.

The phthalimidine synthesis proceeded in THF (bath temperature = 115 °C), hexane (bath temperature = 80 °C), and toluene as a solvent, and **6a** was obtained in 59%, 69%, and 90% yields, respectively; however, it did not proceed in dichloromethane, *N,N*-dimethylformamide (DMF), or dimethylimidazolidinone (DMI) under reflux conditions.

A primary alkyl isocyanate, 2-phenylethylisocyanate, and a secondary alkyl isocyanate, cyclohexylisocyanate, did not react with aldimine **1a**.[25] In contrast, the reactions of arylisocyanates possessing both electron-donating (*p*-OMe, **5b**) and electron-withdrawing groups (*p*-CF$_3$, **5c**) and aldimine **1a** gave the corresponding phthalimidine derivatives **6b** and **6c** in 85% and quantitative yields, respectively (Table 4, entries 2 and 3). However, allylisothiocyanate and phenylisothiocyanate did not react with aldimine **1a**.

By the reactions of aldimines bearing an electron-donating group at the *para*-position (**1c** and **1d**) with phenylisocyanate **5a**, the corresponding phthalimidine derivatives **6d** and **6e** could be obtained in good yields (Table 4, entries 4 and 5). The reaction of aldimines having an electron-withdrawing group (**1e** and **1f**) and **5a** gave phthalimidine derivatives **6f** and **6g** in quantitative yields (Table 4, entries 6 and 7).[26] The yields decreased when forming phthalimidine derivatives bearing substituents at the *ortho*-position (Table 4, entries 8 and 9). *N*-Benzyl aldimine **1i** gave a phthalimidine derivative **6j** in moderate yield (Table 4, entry 10). However, the reactions of *N*-phenyl aldimine or *N*-methoxy aldimine with **5a** did not occur.

(17) There is another possible pathway: C−H bond activation is reversible and can occur at all positions on the aromatic ring. After C−H bond activation, the coordinating group acts to trap the *ortho*-C−H bond addition product and stable chelated intermediate. See: Zhang, X.; Kanzelberger, M.; Emge, T. J.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13192.

(18) There have been some reports on the synthesis of *ortho*-rhenated complexes. *Ortho*-rhenation of aromatic imines with Re(CH$_2$Ph)(CO)$_5$: (a) Böhm, A.; Sünkel, K.; Polborn, K.; Beck, W. *J. Organomet. Chem.* **1998**, *552*, 237. *Ortho*-rhenation of phenylpyridine derivatives with Re(CH$_2$Ph)(CO)$_5$: (b) Djukic, J.-P.; Maisse, A.; Pfeffer, M.; Dötz, K. H.; Nieger, M. *Organometallics* **1999**, *18*, 2786.

(19) Although we tried to prepare or isolate the rhenium−hydride intermediate by the quantitative reaction of [ReBr(CO)$_3$(thf)]$_2$ with aldimine, we could not observe the formation of the intermediate.

(20) The ^{1}H NMR yields of **6** were determined based on dibromomethane as an internal standard.

(21) Rhenium complexes Re$_2$(CO)$_{10}$, ReCp*(CO)$_3$, and ReCl$_3$(PMe$_2$Ph)$_3$ and the manganese complex MnBr(CO)$_5$ did not promote the formation reaction of **6a**.

(22) Under reflux conditions, **6a** was obtained irregularly as time passed. That is, yields of **6a** were 3% (1 h), 18% (3 h), 95% (8 h), and >99% (24 h), respectively. These results indicate the existence of an induction time to form active species to catalyze the formation reaction of phthalimidine derivatives. However, the structure of the active species is still not clear.

(23) Though phthalimidine **6a** was obtained with [ReBr(CO)$_3$(thf)]$_2$ in 1,2-dichloroethane in quantitative yield under reflux conditions, the yield decreased to 27% at 70 °C, and the reaction did not proceed at all at 50 °C.

(24) In the following reports, compounds derived from double C−H bond activation and insertion of unsaturated molecules at two *ortho*-positions were obtained as side products: (a) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529. (b) Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N.; Murai, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62. (c) Kakiuchi, F.; Tsujimoto, T.; Sonoda, M.; Chatani, N.; Murai, S. *Synlett* **2001**, 948. (d) Lim, Y.-G.; Han, J.-S.; Yang, S.-S.; Chun, J. H. *Tetrahedron Lett.* **2001**, *42*, 4853. (e) Lim, Y.-G.; Lee, K.-H.; Koo, B. T.; Kang, J.-B. *Tetrahedron Lett.* **2001**, *42*, 7609. (f) Lim, Y.-G.; Han, J.-S.; Koo, B. T.; Kang, J.-B. *J. Mol. Catal. A:* **2004**, *209*, 41.

(25) To investigate the reason phthalimidine derivatives were not formed using alkyl isocyanate, we carried out the reaction without aldimine. In 1,2-dichloroethane in the presence of [ReBr(CO)$_3$(thf)]$_2$ under reflux conditions, 2-phenylethylisocyanate was recovered quantitatively. Though this result shows that the problems are not in the stability of alkyl isocyanate, the reason is not clear.

(26) The reactivities of aldimines bearing an electron-donating or an electron-withdrawing group toward acetylenes or isocyanates are opposite. The reason for these results is not clear yet.

Table 4. Formation of Phthalimidine Derivatives by the Reaction of Aldimines with Isocyanates

| entry	aldimine	isocyanate	yield / %[a]
1	**1a**: R^1 = H	**5a**: R^3 = Ph	**6a**: 97 (>99)
2	**1a**	**5b**: R^3 = p-MeOC$_6$H$_4$	**6b**: 81 (85)
3	**1a**	**5c**: R^3 = p-CF$_3$C$_6$H$_4$	**6c**: 94 (>99)
4	**1c**: R^1 = p-MeO	**5a**	**6d**: 80 (83)
5	**1d**: R^1 = p-Me	**5a**	**6e**: 92 (96)
6	**1e**: R^1 = p-Ph	**5a**	**6f**: 92 (>99)
7	**1f**: R^1 = p-CF$_3$	**5a**	**6g**: 87 (>99)
8	**1g**: R^1 = o-Me	**5a**	**6h**: 51 (55)
9	**1h**: R^1 = o-MeO	**5a**	**6i**: 32 (34)
10	**1i**	**5a**	**6j**: 40 (42)

[a] Isolated yield. The yield determined by ^{1}H NMR is reported in parentheses.

Scheme 2. Proposed Mechanism for the Formation of Phthalimidine Derivatives
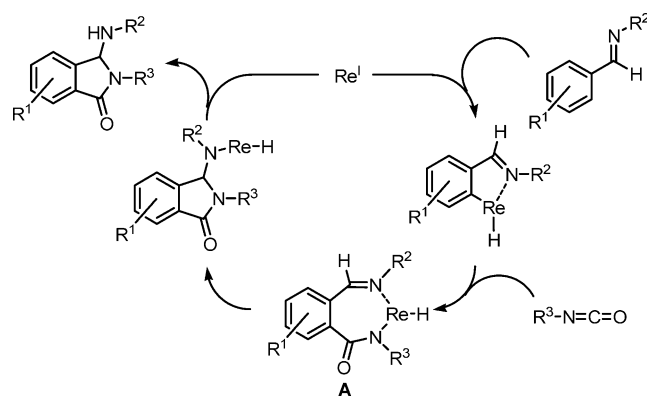
The proposed mechanism for the formation of phthalimidine derivatives is shown in Scheme 2. Owing to the coordination of a nitrogen atom of aldimine **1** to a rhenium center, the rhenium atom approaches close to the aromatic C–H bond at the *ortho*-position of the imine moiety.[4,17] After C–H bond activation, isocyanate **5** inserts into the aromatic carbon–rhenium bond. This step is unique because it has been difficult for the previous transition metal-catalyzed transformations via C–H bond activation to promote the insertion of polar unsaturated molecules. Intramolecular nucleophilic addition of the amido–rhenium moiety to an imine group of an intermediate **A** gives a phthalimidine framework. Though rhenium-catalyzed intramolecular nucleophilic cyclizations via C–H bond activation have been reported,[4] nucleophilic attack of the rhenium–nitrogen moiety to C=N bond is new. After the reductive elimination occurs, the active rhenium(I) species is regenerated and the phthalimidine derivative **6** can be obtained.

Comparison of the Reactivity between an Acetylene and an Isocyanate. We compared the reactivity between nonpolar

and polar molecules (eq 3). The investigations were performed

solvent	3c	6a
toluene	12%	62%
CH$_2$ClCH$_2$Cl	14%	57%
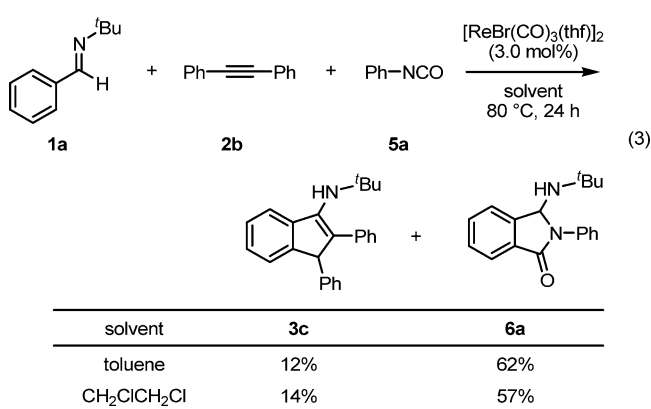
by the reaction of aldimine **1a** (1.0 equiv), diphenylacetylene **2b** (1.0 equiv), and phenylisocyanate **5a** (1.0 equiv) in the presence of a rhenium catalyst, [ReBr(CO)$_3$(thf)]$_2$.[19] In both toluene and 1,2-dichloroethane, isocyanate **5a** reacted with aldimine **1a** more efficiently than diphenylacetylene **2b** and gave the corresponding phthalimidine derivative **6a** in 62% and 57% yields, respectively. This result shows that a polar unsaturated molecule is more reactive than a nonpolar one. The tendency with the rhenium catalyst is opposite to that reported with ruthenium and rhodium catalysts.[27,28]

Conclusion

We have succeeded in the quantitative synthesis of indene and phthalimidine derivatives via C–H bond activation by the reactions of aromatic aldimines with phenyl acetylenes and aromatic isocyanates catalyzed by a rhenium complex, [ReBr-(CO)$_3$(thf)]$_2$. There are only a few precedents for the rhenium-catalyzed C(sp^2)–H bond activation.[5,6] In addition, to our knowledge, the intramolecular nucleophilic addition of organometallic species derived from C–H bond activation to an imine moiety has not been reported. These reactions need only a catalytic amount of the metal reagent and a few reaction steps compared with the reported synthetic methods of indene and phthalimidine derivatives. Therefore, it will become a useful method to synthesize indene and phthalimidine derivatives. Since examples of the insertion of a polarized unsaturated molecule via C–H bond activation are still rare, the results obtained in this paper will help the development of synthetic strategies via C–H bond activation. We are currently working to develop new rhenium-catalyzed synthetic methods via C–H bond activation.

Experimental Section

General. All reactions were carried out in a dry solvent under an argon atmosphere. 1,2-Dichloroethane and toluene were purchased from Wako Pure Chemical Industries and were dried, distilled, and degassed before use. [ReBr(CO)$_3$(thf)]$_2$ was prepared by heating a THF solution of ReBr(CO)$_5$ at reflux temperature for 16 h as reported.[29] The resulting solution was concentrated in vacuo and was recrystallized from THF/

(27) Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N.; Murai, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 62.
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hexane to give [ReBr(CO)$_3$(thf)]$_2$ as a white solid in 75% yield.[30] Aldimines were prepared by condensation of the corresponding aldehydes with the corresponding amines in the presence of molecular sieves (4 Å) in hexane at 50 °C for 10 h and were used after distillation. The structures of **1a**,[31] **1b**,[32] **1c**,[33] **1d**,[33] **1g**,[34] **1h**,[35] and **1i**[36] were determined by the comparison with the data, which were already reported. The spectral data of **1e** and **1f** are reported in the Supporting Information. Acetylenes and isocyanates were purchased from Wako Pure Chemical Industries, Tokyo Kasei Kogyo Co., and Aldrich Co. and used after distillation.

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are reported relative to Me$_4$Si (CDCl$_3$) at δ 0.00 ppm or residual solvent peak (CDCl$_3$ at δ 7.26 ppm). Carbon chemical shifts are reported relative to CDCl$_3$ at δ 77.00 ppm. IR spectra were recorded on Nicolet Protégé 460. The crystal was mounted on a Rigaku RAXIS-IV Imaging Plate diffractometer for data collection using MoKα (graphite monochromated, λ = 0.7107 Å) radiation.

General Procedure for the Reaction of Aldimines with Acetylenes. The mixture of aldimine (0.500 mmol), acetylene (0.500 mmol), and [ReBr(CO)$_3$(thf)]$_2$ (12.7 mg, 0.0150 mmol) in toluene (1.0 mL) was refluxed for 24 h. After the solvent was removed in vacuo, the products were isolated by silica gel column chromatography.

***N*-tert-Butyl-3-methyl-2-phenyl-3*H*-inden-1-amine (3a).** ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.05 (s, 9H), 1.18 (d, J = 7.5 Hz, 3H), 3.28 (brs, 1H), 3.86 (q, J = 7.5 Hz, 1H), 7.21−7.28 (m, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.38−7.46 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 16.68 (1C), 30.74 (3C), 44.02 (1C), 54.66 (1C), 119.74 (1C), 122.45 (1C), 124.72 (1C), 126.10 (1C), 126.25 (1C), 128.20 (2C), 128.86 (2C), 137.06 (1C), 138.95 (1C), 140.86 (1C), 144.33 (1C), 147.55 (1C); IR (Nujol, ν/ cm^{-1}) 3056 (w), 3021 (w), 2962 (m), 1602 (m), 1494 (m), 1389 (m), 1221 (m), 1200 (w), 1153 (w), 1135 (w), 1074 (m), 1019 (w), 933 (w), 912 (w), 869 (w), 843 (w), 768 (w), 757 (s), 738 (w), 698 (s). Anal.Calcd for C$_{20}$H$_{23}$N: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.70; H, 8.38; N, 4.92.

***N*-tert-Butyl-2-methyl-3-phenyl-3*H*-inden-1-amine (4a).** ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.02 (s, 9H), 2.03 (s, 3H), 4.69 (s, 1H), 7.19−7.33 (m, 6H), 7.39 (t, J = 7.3 Hz, 2H), 7.55 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 11.19 (1C), 30.81 (3C), 50.66 (1C), 62.78 (1C), 119.01 (1C), 123.41 (1C), 125.45 (1C), 126.88 (1C), 127.21 (1C), 127.92 (2C), 129.74 (2C), 134.21 (1C), 136.35 (1C), 144.90 (1C), 145.61 (1C), 147.91 (1C); IR (Nujol, ν/cm^{-1}) 3057 (w), 3024 (w), 2961 (m), 1905 (w), 1601 (m), 1493 (w), 1441 (w), 1387 (m), 1290 (w), 1227 (w), 1153 (w), 1097 (w), 1020 (w), 792 (w), 757 (s), 735 (m), 700 (s), 665 (w). Anal.Calcd for C$_{20}$H$_{23}$N: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.59; H, 8.35; N, 5.00.

2-Methyl-*N*,3-diphenyl-3*H*-inden-1-amine (4b). ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.27 (d, J = 1.8 Hz, 3H), 5.47 (s, 1H), 6.61 (d, J = 8.1 Hz, 2H), 6.67 (t, J = 7.6 Hz, 1H), 7.11−7.19 (m, 3H), 7.25−7.28 (m, 1H), 7.35−7.41 (m, 6H), 7.48 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 11.90 (1C), 62.04 (1C), 113.67 (1C), 117.50 (1C), 119.34 (1C), 122.90 (1C), 125.85 (2C), 126.90 (2C), 127.90 (1C), 128.25 (1C), 129.05 (2C), 129.14 (2C), 135.13 (1C), 135.57 (1C), 142.22 (1C), 144.73 (1C), 145.11 (1C), 147.71 (1C); IR (Nujol, ν/cm^{-1}) 3095 (m), 3049 (w), 1907 (w), 1599 (m), 1502 (w), 1430 (w), 1378 (m), 1340 (w), 1315 (m), 1244 (s), 1174 (w), 1153 (s), 1131 (m), 1092 (w), 1075 (w), 1039 (m), 1020 (m), 991 (m), 972 (w), 960 (w), 937 (m), 908 (s), 876 (m), 850 (m), 773 (s), 744 (w), 692 (s), 623 (m), 584

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(w). Anal.Calcd for C$_{22}$H$_{19}$N: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.65; H, 6.65; N, 4.65.

***N*-tert-Butyl-2,3-diphenyl-3*H*-inden-1-amine (3c).** ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.12 (s, 9H), 4.87 (s, 1H), 7.04 (d, J = 7.6 Hz, 2H), 7.09−7.17 (m, 6H), 7.22 (t, J = 7.7 Hz, 2H), 7.28−7.31 (m, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 6.9 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 31.03 (3C), 54.88 (1C), 56.66 (1C), 119.90 (2C), 123.77 (1C), 125.41 (1C), 126.35 (1C), 126.45 (2C), 128.12 (1C), 128.17 (2C), 128.34 (1C), 128.46 (2C), 128.86 (1C), 136.68 (1C), 137.03 (1C), 140.41 (1C), 143.21 (1C), 144.33 (1C), 147.39 (1C); IR (Nujol, ν/cm^{-1}) 3061 (w), 3022 (w), 1951 (w), 1653 (w), 1601 (m), 1493 (m), 1430 (m), 1389 (w), 1378 (w), 1284 (w), 1218 (w), 1199 (m), 1121 (w), 1095 (w), 1071 (m), 1026 (m), 938 (w), 918 (w), 815 (w), 783 (m), 759 (s), 736 (m), 696 (s), 675 (w), 666 (m), 651 (m), 621 (m). Anal.Calcd for C$_{25}$H$_{25}$N: C, 88.45; H, 7.42; N, 4.13. Found: C, 88.57; H, 7.41; N, 4.03.

***N*-tert-Butyl-5-methoxy-2,3-diphenyl-3*H*-inden-1-amine (3d).** ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.34 (s, 9H), 3.75 (s, 3H), 4.84 (s, 1H), 6.72 (d, J = 2.1 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 7.05 (d, J = 7.5 Hz, 2H), 7.09−7.19 (m, 4H), 7.21−7.26 (m, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.39 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 30.99 (3C), 55.33 (1C), 56.39 (1C), 58.80 (1C), 110.10 (1C), 111.94 (2C), 120.54 (2C), 126.05 (1C), 126.39 (1C), 128.08 (1C), 128.12 (1C), 128.45 (2C), 128.68 (2C), 134.55 (1C), 137.10 (1C), 137.13 (1C), 140.55 (1C), 142.90 (1C), 149.21 (1C), 158.28 (1C); IR (Nujol, ν/cm^{-1}) 3322 (w), 3087 (w), 3042 (w), 3024 (w), 1653 (w), 1600 (s), 1494 (m), 1433 (w), 1388 (w), 1367 (w), 1280 (s), 1255 (w), 1218 (m), 1181 (w), 1136 (m), 1102 (m), 1071 (m), 1027 (m), 876 (m), 850 (m), 809 (m), 795 (w), 756 (s), 740 (s), 729 (w), 696 (s), 681 (w), 650 (w), 616 (w). Anal.Calcd for C$_{26}$H$_{27}$NO: C, 84.51; H, 7.37; N, 3.79. Found: C, 84.74; H, 7.51; N, 3.76.

***N*-tert-Butyl-5-methyl-2,3-diphenyl-3*H*-inden-1-amine (3e).** ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.13 (s, 9H), 2.27 (s, 3H), 3.40 (br, 1H), 4.84 (s, 1H), 6.96 (s, 1H), 7.04−7.10 (m, 5H), 7.12−7.16 (m, 2H), 7.20 (t, J = 8.1 Hz, 2H), 7.33−7.38 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.32 (1C), 30.95 (3C), 54.77 (1C), 56.33 (1C), 119.59 (1C), 124.59 (1C), 126.12 (1C), 126.32 (2C), 127.14 (1C), 128.03 (2C), 128.12 (2C), 128.39 (1C), 128.72 (2C), 135.10 (1C), 135.57 (1C), 137.06 (1C), 140.59 (1C), 141.61 (1C), 143.13 (1C), 147.59 (1C); IR (Nujol, ν/cm^{-1}) 3308 (w), 3081 (w), 3055 (w), 3023 (w), 2950 (w), 1937 (w), 1885 (w), 1599 (s), 1494 (m), 1439 (m), 1388 (w), 1323 (w), 1225 (m), 1200 (m), 1130 (m), 1097 (w), 1069 (m), 1049 (w), 1026 (w), 939 (w), 912 (w), 885 (w), 857 (m), 822 (m), 809 (m), 797 (m), 751 (m), 731 (m), 694 (s), 647 (m), 633 (m), 615 (m). Anal. Calcd. for C$_{26}$H$_{27}$N: C, 88.34; H, 7.70; N, 3.96. Found: C, 88.13; H, 7.69; N, 3.85.

***N*-tert-Butyl-2,3,5-triphenyl-3*H*-inden-1-amine (3f).** ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.14 (s, 9H), 3.46 (br, 1H), 4.92 (s, 1H), 7.06−7.16 (m, 6H), 7.20−7.26 (m, 3H), 7.32−7.39 (m, 5H), 7.52 (d, J = 9.6 Hz, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 31.04 (3C), 54.90 (1C), 56.71 (1C), 120.23 (1C), 122.65 (1C), 125.57 (1C), 126.41 (1C), 126.50 (1C), 126.86 (1C), 127.06 (2C), 127.34 (1C), 128.15 (2C), 128.25 (2C), 128.52 (2C), 128.59 (2C), 128.83 (2C), 136.97 (1C), 138.50 (1C), 140.24 (1C), 141.37 (1C), 143.06 (1C), 143.64 (1C), 148.08 (1C); IR (Nujol, ν/ cm^{-1}) 3022 (w), 1951 (w), 1653 (m), 1601 (m), 1439 (m), 1430 (m), 1389 (w), 1378 (w), 1284 (w), 1218 (w), 1199 (m), 1121 (w), 1095 (w), 1071 (m), 1026 (m), 938 (w), 918 (w), 815 (w), 783 (m), 759 (s), 736 (m), 696 (s), 675 (w), 666 (w), 651 (m), 621 (m). Anal.Calcd for C$_{31}$H$_{29}$N: C, 89.60; H, 7.03; N, 3.37. Found: C, 89.45; H, 7.07; N, 3.30.

***N*-tert-Butyl-5-(trifluoromethyl)-2,3-diphenyl-3*H*-inden-1-amine (3g).** ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.12 (s, 9H), 3.44 (br, 1H), 4.92 (s, 1H), 7.03 (d, J = 6.9 Hz, 2H), 7.14−7.19 (m, 4H), 7.26 (t, J = 7.3 Hz, 2H), 7.31 (d, J = 7.5 Hz, 2H), 7.37 (s, 1H), 7.58 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 30.88 (3C), 55.22 (1C), 56.64 (1C), 120.12 (1C), 120.56 (1C), 120.59 (1C), 123.94 (1C), 123.97 (1C),

126.90 (1C), 126.94 (1C), 127.12 (1C), 127.45 (1C), 128.14 (2C), 128.30 (2C), 128.70 (2C), 128.74 (2C), 136.13 (1C), 138.84 (1C), 147.51 (1C), 147.86 (1C); IR (Nujol, ν/cm^{-1}) 3316 (w), 1616 (m), 1601 (w), 1493 (w), 1392 (w), 1377 (m), 1328 (s), 1275 (m), 1235 (w), 1160 (s), 1120 (w), 1109 (w), 1071 (w), 1060 (m), 929 (m), 913 (m), 850 (w), 816 (m), 753 (m), 698 (w), 691 (w), 681 (m), 637 (w). Anal.Calcd for C$_{26}$H$_{24}$F$_3$N: C, 76.64; H, 5.94; N, 3.44. Found: C, 76.54; H, 6.00; N, 3.31.

N-tert-Butyl-7-methyl-2,3-diphenyl-3H-inden-1-amine (3h). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.75 (s, 9H), 2.66 (s, 3H), 5.14 (s, 1H), 6.99 (t, J = 6.9 Hz, 2H), 7.14−7.25 (m, 6H), 7.27−7.38 (m, 5H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 18.76 (1C), 31.23 (3C), 52.71 (1C), 64.33 (1C), 118.17 (1C), 126.45 (1C), 127.19 (1C), 127.45 (1C), 127.75 (1C), 128.03 (2C), 128.52 (2C), 129.17 (2C), 129.66 (2C), 134.90 (1C), 135.70 (1C), 135.93 (1C), 138.77 (1C), 143.61 (1C), 143.90 (1C), 146.35 (1C); IR (Nujol, ν/cm^{-1}) 3050 (w), 3029 (w), 2960 (w), 1954 (w), 1888 (w), 1597 (m), 1499 (w), 1443 (m), 1385 (w), 1377 (w), 1226 (w), 1213 (w), 1156 (w), 1104 (w), 1089 (w), 1074 (m), 1049 (w), 1029 (m), 959 (w), 917 (m), 847 (w), 797 (w), 776 (m), 755 (s), 725 (w), 700 (s), 632 (m), 603 (w). Anal.Calcd for C$_{26}$H$_{27}$N: C, 88.34; H, 7.70; N, 3.96. Found: C, 88.29; H, 7.71; N, 3.91.

N-tert-Butyl-3-hexyl-2-phenyl-3H-inden-1-amine (3j). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.75 (t, J = 7.1 Hz, 3H), 1.04 (s, 9H), 0.87−1.12 (m, 8H), 1.55−1.62 (m, 1H), 1.81−1.89 (m, 1H), 3.94 (t, J = 4.9 Hz, 1H), 7.19−7.32 (m, 3H), 7.38−7.47 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.07 (1C), 22.43 (1C), 23.76 (1C), 29.39 (1C), 30.32 (1C), 30.88 (3C), 31.46 (1C), 49.02 (1C), 54.68 (1C), 119.90 (1C), 122.61 (1C), 124.57 (1C), 126.03 (1C), 126.32 (1C), 128.37 (2C), 128.86 (2C), 137.32 (1C), 137.48 (1C), 141.72 (1C), 145.13 (1C), 146.10 (1C); IR (Nujol, ν/ cm^{-1}) 3059 (w), 3020 (w), 2956 (w), 1602 (m), 1493 (w), 1389 (m), 1222 (m), 1201 (w), 1072 (w), 1024 (w), 935 (w), 912 (w), 783 (w), 758 (s), 698 (s), 666 (w). HR-MS Calcd for C$_{25}$H$_{33}$N: 347.2613; Found: 347.2613.

N-tert-Butyl-2-(trimethylsilyl)-3-phenyl-3H-inden-1-amine (4k). ^{1}H NMR (400 MHz, CDCl$_3$) δ −0.34 (s, 9H), 1.01 (s, 9H), 3.91 (s, 1H), 7.16 (t, J = 5.2 Hz, 1H), 7.20−7.29 (m, 2H), 7.37 (d, 4.4 Hz, 4H), 7.41 (d, J = 7.2 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ −2.48 (3C), 30.92 (3C), 45.71 (1C), 54.68 (1C), 120.56 (1C), 122.88 (1C), 123.45 (1C), 124.45 (1C), 126.52 (1C), 128.39 (2C), 129.14 (2C), 136.17 (1C), 138.73 (1C), 140.10 (1C), 143.42 (1C), 144.02 (1C); IR (Nujol, ν/cm^{-1}) 3025 (w), 1975 (w), 1955 (w), 1935 (w), 1903 (w), 1599 (m), 1580 (w), 1558 (w), 1491 (w), 1377 (w), 1307 (w), 1249 (m), 1222 (w), 1202 (w), 1155 (w), 1140 (w), 1125 (m), 1099 (m), 1072 (m), 1047 (m), 1024 (s), 968 (w), 941 (m), 916 (w), 892 (m), 839 (s), 781 (s), 761 (m), 740 (w), 705 (s), 632 (m), 615 (m), 599 (m). HR-MS Calcd for C$_{22}$H$_{29}$NSi: 335.2069; Found: 335.2068.

General Procedure for the Reaction of Aldimines with Isocyanates. A mixture of aldimine (0.500 mmol), isocyanate (0.500 mmol), and [ReBr(CO)$_3$(thf)]$_2$ (12.7 mg, 0.0150 mmol) in 1,2-dichloroethane (1.0 mL) was refluxed for 24 h. After the solvent was removed in vacuo, the products were isolated by silica gel column chromatography.

3-tert-Butylimino-2-phenyl-2,3-dihydro-isoindol-1-one (6a). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.93 (s, 9H, ^{t}Bu), 1.72 (s, 1H, NH), 5.88 (s, 1H, CH−NH), 7.28−7.31 (m, 1H, Ar), 7.39−7.46 (m, 4H, Ar), 7.48−7.52 (m, 1H, Ar), 7.57−7.60 (m, 2H, Ar), 7.87 (d, 1H, Ar, J = 7.5 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 31.95 (3C), 50.44 (1C), 73.18 (1C), 123.25 (1C), 123.56 (1C), 126.74 (1C), 127.46 (2C), 128.75 (2C), 128.94 (1C), 131.95 (1C), 132.01 (1C), 136.79 (1C), 145.66 (1C), 166.49 (1C); IR (Nujol, ν/cm^{-1}) 3367 (w), 1675 (m), 1595 (m), 1501 (m), 1489 (m), 1244 (w), 1218 (w), 1108 (m), 1035 (w), 1019 (w), 754 (m), 692 (m), 664 (w), 636 (w); EI-MS (+) m/z = 280 (M$^+$). Anal.Calcd for C$_{18}$H$_{20}$N$_2$O: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.03; H, 7.11; N, 9.96.

3-tert-Butylimino-2-(4-methoxy-phenyl)-2,3-dihydro-isoindol-1-one (6b). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.96 (s, 9H, ^{t}Bu), 1.63 (s, 1H, NH), 3.83 (s, 3H, MeO), 5.73 (s, 1H, CH−NH), 6.96 (d, 2H, Ar, J = 8.7 Hz), 7.28 (d, 2H, J = 8.7 Hz), 7.49 (t, 1H, J = 6.8 Hz), 7.55−7.60 (m, 2H, Ar), 7.86 (d, 1H, Ar, J = 7.5 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 30.88 (3C), 50.33 (1C), 55.33 (1C), 73.29 (1C), 114.03 (2C), 123.03 (1C), 123.54 (1C), 128.88 (1C), 129.37 (2C), 129.52 (1C), 131.94 (1C), 132.10 (1C), 145.91 (1C), 158.46 (1C), 166.75 (1C); IR (Nujol, ν/cm^{-1}) 3367 (w), 2042 (m), 1980 (m), 1965 (m), 1699 (m), 1607 (w), 1514 (m), 1298 (w), 1249 (m), 1123 (w), 1103 (w), 1026 (w); EI-MS (+) m/z = 310 (M$^+$). Anal.Calcd for C$_{19}$H$_{22}$N$_2$O$_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.33; H, 7.05; N, 9.04.

3-tert-Butylimino-2-(4-trifluoromethyl-phenyl)-2,3-dihydro-isoindol-1-one (6c). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.94 (s, 9H, ^{t}Bu), 1.83 (s, 1H, NH), 5.98 (s, 1H, CH−NH), 7.50−7.54 (m, 1H, Ar), 7.59−7.63 (m, 4H, Ar), 7.70 (d, 2H, Ar, J = 8.4 Hz), 7.87 (d, 2H, Ar, J = 7.5 Hz); ^{13}C NMR (100 MHz, CDCl3) δ 31.03 (3C), 50.55 (1C), 73.16 (1C), 117.92 (1C), 123.50 (2C), 125.28 (1C), 125.65 (1C), 126.48 (2C), 127.85 (1C), 129.05 (1C), 131.32 (1C), 132.37 (1C), 140.26 (1C), 145.33 (1C), 166.44 (1C); IR (Nujol, ν/cm-1) 2042 (m), 1981 (m), 1966 (m), 1683 (m), 1653 (w), 1612 (w), 1330 (w), 1165 (w), 1137 (w), 1121 (w), 1070 (w); EI-MS (+) m/z = 348 (M$^+$). Anal.Calcd for C$_{19}$H$_{19}$F$_3$N$_2$O: C, 65.51; H, 5.50; N, 8.04. Found: C, 65.24; H, 5.52; N, 8.00.

3-tert-Butylimino-2-phenyl-6-methoxy-2,3-dihydro-isoindol-1-one (6d). ^{1}H NMR (400 MHz, CDCl3) δ 0.92 (s, 9H, ^{t}Bu), 1.68 (s, 1H, NH), 3.89 (s, 3H, OMe), 5.83 (s, 1H, CH−NH), 7.14 (d, 1H, Ar, J = 8.4 Hz), 7.28−7.32 (m, 1H, Ar), 7.37 (m, 1H, Ar), 7.39−7.49 (m, 5H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 31.08 (3C), 50.44 (1C), 55.75 (1C), 73.02 (1C), 106.29 (1C), 120.23 (1C), 124.26 (1C), 126.74 (1C), 127.41 (2C), 128.83 (2C), 133.57 (1C), 136.97 (1C), 137.75 (1C), 160.64 (1C), 166.49 (1C); IR (Nujol, ν/cm^{-1}) 3351 (w), 2015 (w), 1916 (w), 1861 (w), 1675 (s), 1595 (w), 1497 (m), 1291 (m), 1246 (m), 1100 (w), 1040 (w); EI-MS (+) m/z = 310 (M$^+$). HR-MS Calcd for C$_{19}$H$_{22}$N$_2$O$_2$: 310.1681; Found: 310.1682.

3-tert-Butylimino-2-phenyl-6-methyl-2,3-dihydro-isoindol-1-one (6e). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.91 (s, 9H, ^{t}Bu), 1.68 (s, 1H, NH), 2.44 (s, 3H, Me), 5.82 (s, 1H, CH−NH), 7.28−7.29 (m, 1H, Ar), 7.41−7.47 (m, 6H, Ar), 7.67 (s, 1H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.28 (1C), 30.99 (3C), 50.48 (1C), 73.02 (1C), 123.06 (1C), 123.85 (2C), 126.59 (1C), 127.34 (1C), 128.74 (2C), 132.15 (1C), 132.92 (1C), 136.95 (1C), 139.10 (1C), 142.82 (1C), 166.64 (1C); IR (Nujol, ν/cm^{-1}) 3373 (w), 2040 (m), 1980 (m), 1965 (m), 1673 (m), 1594 (w), 1495 (w), 1108 (w); EI-MS (+) m/z = 294 (M$^+$). HR-MS Calcd for C$_{19}$H$_{22}$N$_2$O: 294.1732; Found: 294.1730.

3-tert-Butylimino-2,6-diphenyl-2,3-dihydro-isoindol-1-one (6f). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.95 (s, 9H, ^{t}Bu), 1.72 (s, 1H, NH), 5.90 (s, 1H, CH−NH), 7.31 (t, 1H, Ar, J = 6.8 Hz), 7.37−7.49 (m, 7H, Ar), 7.64−7.66 (m, 3H, Ar), 7.82 (d, 1H, Ar, J = 7.8 Hz), 8.11 (s, 1H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 31.03 (3C), 50.46 (1C), 73.09 (1C), 121.99 (1C), 123.66 (1C), 126.79 (1C), 127.14 (2C), 127.50 (2C), 127.77 (1C), 128.79 (2C), 128.88 (2C), 130.92 (1C), 132.77 (1C), 136.86 (1C), 139.90 (1C), 142.28 (1C), 144.55 (1C), 166.40 (1C); IR (Nujol, ν/ cm^{-1}): 3357 (w), 1682 (s), 1597 (w), 1116 (w), 765 (m), 693 (m); EI-MS (+) m/z = 356 (M$^+$). Anal.Calcd for C$_{24}$H$_{24}$N$_2$O: C, 80.87; H, 6.79; N, 7.86. Found: C, 80.62; H, 6.85; N, 7.93.

3-tert-Butylimino-2-phenyl-6-trifluoromethyl-2,3-dihydro-isoindol-1-one (6g). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.94 (s, 9H, ^{t}Bu), 1.74 (s, 1H, NH), 5.94 (s, 1H, CH−NH), 7.34 (t, 1H, Ar, J = 7.2 Hz), 7.40 (d, 2H, Ar, J = 7.2 Hz), 7.47 (t, 2H, Ar, J = 7.8 Hz), 7.74 (d, 1H, Ar, J = 7.8 Hz), 7.86 (d, 1H, Ar, J = 7.8 Hz), 8.15 (s, 1H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 30.97 (3C), 50.66 (1C), 73.15 (1C), 120.94 (1C), 122.32 (1C), 124.14 (1C), 125.03 (1C), 127.14 (1C), 127.34 (2C), 128.94 (2C), 131.66 (1C), 132.81 (1C), 136.33 (1C), 149.11 (1C), 165.02 (1C); IR (Nujol, ν/cm^{-1}) 3384 (w), 2041 (m), 1979 (m), 1965 (m), 1683 (m), 1595 (m), 1325 (m), 1242 (m), 1167 (m), 1127 (m), 1052 (w), 1037 (w), 1020 (w), 859 (m), 778 (m), 747 (m); EI-MS (+)

m/z = 348 (M$^+$). Anal.Calcd for $C_{19}H_{19}F_3N_2O$: C, 65.51; H, 5.50; N, 8.04. Found: C, 65.22; H, 5.43; N, 8.04.

3-*tert*-Butylimino-2-phenyl-4-methyl-2,3-dihydro-1-isoindol-1-one (6h). ^1H NMR (400 MHz, CDCl$_3$) δ 0.77 (s, 9H, ^{t}Bu), 1.84 (s, 1H, NH), 2.59 (s, 1H, Me), 6.23 (s, 1H, CH−NH), 7.22 (t, 1H, Ar, J = 7.5 Hz), 7.35 (d, 1H, Ar, J = 7.2 Hz), 7.41 (d, 1H, Ar, J = 7.5 Hz), 7.46 (t, 2H, Ar, J = 7.8 Hz), 7.58 (d, 2H, Ar, J = 7.8 Hz); 7.74 (d, 1H, Ar, J = 7.5 Hz); ^{13}C NMR(100 MHz, CDCl$_3$) δ 17.96 (1C), 31.01 (3C), 51.35 (1C), 72.55 (1C), 121.08 (1C), 123.43 (1C), 124.88 (1C) 128.94 (2C), 129.08 (2C), 132.08 (1C), 133.81 (1C), 134.73 (1C), 137.43 (1C), 141.84 (1C), 166.51 (1C); IR (Nujol, ν/cm^{-1}) 3395 (w), 1675 (s), 1597 (s), 1558 (w), 1231 (w), 1119 (m), 1049 (m), 761 (m). HR-MS Calcd for $C_{19}H_{22}N_2O$: 294.1732; Found: 294.1732.

3-*tert*-Butylimino-2-phenyl-4-methoxy-2,3-dihydro-1-isoindol-1-one (6i). ^1H NMR (400 MHz, CDCl$_3$) δ 0.95 (s, 9H, ^{t}Bu), 1.94 (s, 1H, NH), 3.96 (s, 3H, OMe), 6.11 (s, 1H, CH−NH), 7.07 (dd, 1H, Ar, J = 6.6, 2.1 Hz), 7.26 (t, 1H, Ar, J = 6.5 Hz), 7.43−7.52 (m, 6H, Ar); ^{13}C NMR (100 MHz, CDCl$_3$) δ 30.72 (3C), 51.33 (1C), 55.22 (1C), 71.76 (1C), 113.78 (1C), 115.88 (1C), 125.65 (2C), 125.94 (1C), 128.94 (2C), 130.91 (1C), 131.28 (1C), 134.19 (1C), 137.12 (1C), 155.09 (1C), 166.29 (1C); IR (Nujol, ν/cm^{-1}) 3362 (w), 2017 (m), 1902 (m), 1684 (s), 1653 (s), 1559 (m), 1036 (m). HR-MS Calcd for $C_{19}H_{22}N_2O_2$: 310.1681; Found: 310.1682.

3-Benzylamino-2-phenyl-2,3-dihydro-1-isoindol-1-one (6j). ^1H NMR (400 MHz, CDCl$_3$) δ 2.51 (s, 1H, NH), 3.15 (d, 1H, −CH$_2$−, J = 12.9 Hz), 3.32 (d, 1H, −CH$_2$−, J = 12.9 Hz), 6.13 (s, 1H, CH− NH), 7.00 (d, 2H, Ar, J = 7.0 Hz), 7.13−7.27 (m, 4H, Ar), 7.45 (t, 2H, Ar, J = 7.5 Hz), 7.54 (t, 3H, Ar, J = 7.5 Hz), 7.61 (t, 1H, Ar, J = 7.5 Hz), 7.68 (d, 1H, Ar, J = 7.5 Hz), 7.90 (d, 1H, Ar, J = 7.5 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 44.70 (1C), 73.92 (1C), 123.41 (2C), 123.65 (1C), 125.66 (1C), 126.95 (1C), 127.83 (2C), 128.17 (2C), 128.70 (1C), 129.34 (2C), 129.46 (1C), 132.35 (1C), 132.75 (1C), 136.35 (1C), 139.15 (1C), 142.01 (1C), 166.58 (1C); IR (Nujol, ν/cm^{-1}) 3347 (w), 2018 (s), 1901 (s), 1680 (s), 1597 (s), 1112 (m). HR-MS Calcd for $C_{21}H_{18}N_2O$: 314.1420; Found: 314.1417.

Supporting Information Available: X-ray crystallographic data for indene derivative **3f** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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