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Synthesis of Substituted 2-Arylindanes from *E*-(2-Stilbenyl)methanols via Lewis Acid-Mediated Cyclization and Nucleophililc Transfer from Trialkylsilyl Reagents

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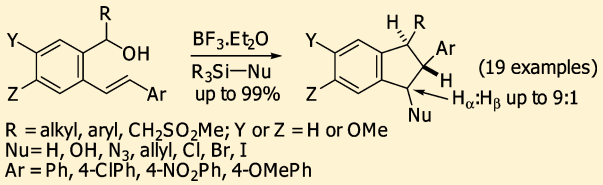
Supporting Information

ABSTRACT: A preparative method for the synthesis of functionalized 2-arylindanes has been developed via the Lewis acid-mediated ring closure of stilbenyl methanols followed by nucleophilic transfer from trialkylsilyl reagents. The reactions gave the corresponding products in moderate to high yields and diastereoselectivity. The solvent as well as the nucleophile played an important role in determining the type(s) of product arising either from nucleophilic addition (indanes) or loss of a proton β to the indanyl-type carbocations (indenes). Electron-donating groups on the fused aromatic ring (Y and Z = OMe) or the presence of electron-withdrawing groups (NO_2) on the nonfused Ar ring facilitate the cyclization. In contrast, the presence of electron-donating groups (OMe) on the nonfused Ar ring impedes the process. In the case of Cl on the nonfused Ar ring, temperature modulates the resonance versus inductive field effects on the overall reaction pathways involving cyclization to form the indanyl-type cation. Quantum chemical calculations supported the intermediacy of the carbocation species and the transfer of hydride from triethylsilane (Nu = H) to the indanyl-type cations to form the *trans*-1,2-disubstituted indane as the single diastereomer product.



INTRODUCTION

Indane constitutes an important core of natural products such as those shown in Figure 1, including quadrangularin A (**1**)[1,2] as well as paucifloral F (**2**),[3,4] α-amino acid derivatives (**3**),[5] and medicinal agents[6] such as the anticancer indane carbocyclic nucleosides (**4**).[7] It should be noted that both quadrangularin A and paucifloral F feature the 2,3-*trans*-2-arylindane as their core structure. A number of useful preparative methods, including the reactions mediated by metal salt complexes, have been developed for various substituted indanes such as mutisianthol (**5**),[8,9] trikentrins,[10−15] herbindoles,[10−15] and taiwaniaquinoids[16,17] (e.g., (+)-*trans*-trikentrin A (**6**), herbindole A (**7**), and taiwaniaquinol A (**8**)).

In recent years, the work in our group has involved the use of Lewis or Brønsted acids for a number of organic transformations.[18,19] Herein, we wish to report a facile synthetic method for an efficient preparation of substituted 2-arylindanes with a range of substitutions around the indane core. Our strategy has focused on the formation of the cyclopentane ring via a Lewis acid-mediated ring closure of the olefin to form the indanyl cation which can be further reacted by a number of nucleophiles (see Scheme 1).[20−22]

RESULTS AND DISCUSSION

The requisite starting material, benzyl alcohol **11**, was readily available in two steps from 2-bromobenzaldehyde **9** via the Heck reaction[23,24] to generate the stilbene **10** that reacted with phenyllithium to furnish the product, as shown in Scheme 2. Both steps proceeded smoothly in 78−84% and 98% yields, respectively.

Optimization of the Reaction Conditions. First, as shown in Scheme 3, in the absence of a nucleophile, with $BF_3{\cdot}Et_2O$ as a Lewis acid, the reaction gave only the corresponding indene products **12** (1−10%) and **13** (5−9%) among unidentifiable byproducts, suggesting that, for compound **11**, the ensuing loss of a benzylic proton β to the indanyl-type carbocation to give **12** or 1,2-hydride shift followed by loss of proton to produce **13** was not a major pathway. It should be noted that similar results were obtained with both stoichiometric and catalytic amounts of $BF_3{\cdot}Et_2O$.

Next, in order to minimize the structural complexity of the product(s), hydride was selected as a nucleophile. The effects of different Lewis and Brønsted acids, hydride sources, and

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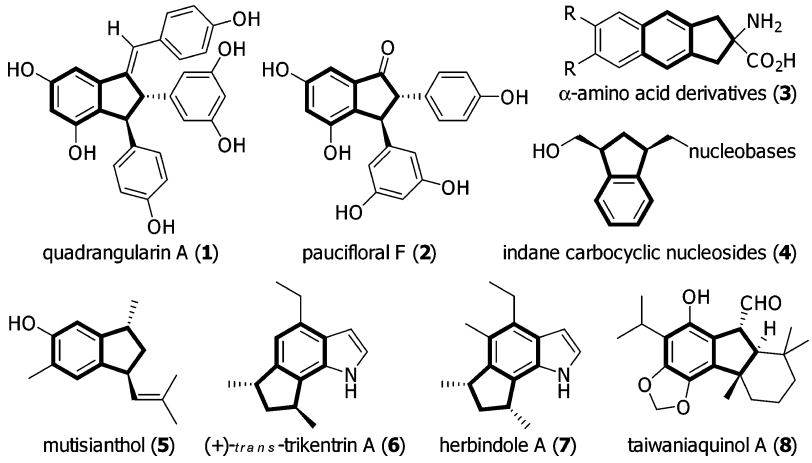
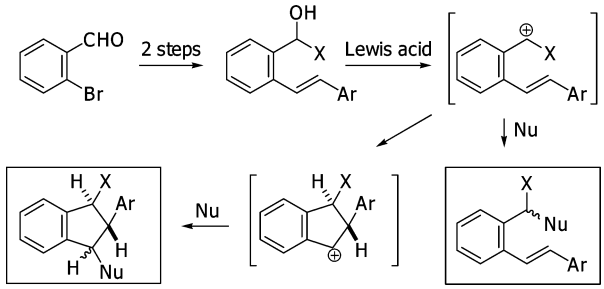
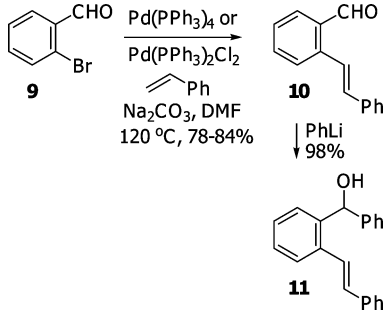


Figure 1. Natural and synthetic substituted indanes.

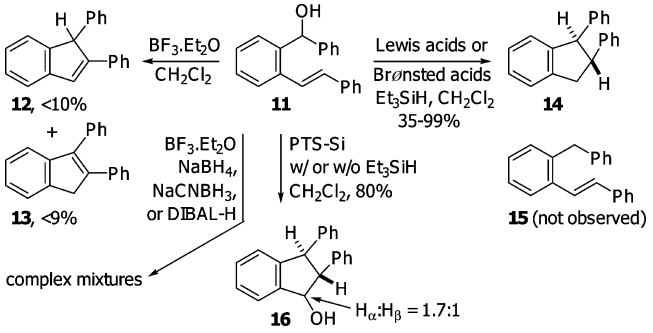
Scheme 1. A Strategy Toward the Substituted 2-Arylindanes



Scheme 2. Preparation of Benzyl Alcohol 10

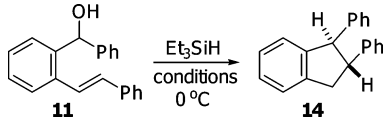


Scheme 3. Products from Different Reaction Conditions



solvents were investigated, and the results are summarized in Table 1. After some experimentation, it was found that the use of Et_3SiH as a hydride source gave the best results, while other sources of hydride such as $NaBH_4$, $NaCNBH_3$, and diisobutylaluminium hydride (DIBAL-H) gave no desired

Table 1. Screening the Conditions for 14[a]



entry	acid[b]	solvent	time (h)	yield (%)[c]
1	$BF_3{\cdot}Et_2O$	CH_2Cl_2	0.1	90
2[d]	$BF_3{\cdot}Et_2O$	CH_2Cl_2	1.0	54
3[e]	$BF_3{\cdot}Et_2O$	PhMe	0.1	60
4[f]	$BF_3{\cdot}Et_2O$	THF	240	0
5	TFA	CH_2Cl_2	1.5	35
6[e]	CF_3SO_3H	CH_2Cl_2	1.5	60
7[g]	PTS-Si	CH_2Cl_2	1.5	0
8	$InCl_3$	CH_2Cl_2	4	83
9	$ZnCl_2$	CH_2Cl_2	25	99

[a]Unless noted otherwise, the reactions were performed at 0 °C using 1.5 equiv of Lewis or Brønsted acid and 1.5 equiv of Et_3SiH. [b]Other Lewis acids such as $PdCl_2$, $PtCl_4$, $SnCl_4$, $TiCl_3$, and $AlCl_3$ gave no desired indane product. [c]Isolated yield. [d]Catalytic amount (15 mol %) of $BF_3{\cdot}Et_2O$ was employed. [e]The product was obtained with trace amount of unidentified impurities. [f]An unidentifiable mixture of compounds was obtained. [g]The corresponding indanol **16** was obtained.

product; only complex mixtures of unidentifiable byproducts were observed in those cases. $InCl_3$, $BF_3{\cdot}Et_2O$, and $ZnCl_2$ gave the best yields (83–99%; entries 1, 8, and 9) of the 1,2-*trans*-diphenylindane **14** as a single diastereomer, while other Lewis acids including $PdCl_2$, $PtCl_4$, $TiCl_3$, $AlCl_3$, and $SnCl_4$ gave no desired product. Use of Brønsted acids (entries 5 and 6) such as trifluoroacetic acid (TFA)[25] or trifluoromethanesulfonic acid (TfOH) gave the corresponding indane **14**, albeit in lower yields (35 and 60%, respectively). It should be noted that the use of $BF_3{\cdot}Et_2O$ and Et_3SiH is typically expected to yield the deoxygenated product **15** which, under these conditions, was not observed.[26] A stoichiometric amount of $BF_3{\cdot}Et_2O$ was required, giving the product in much higher yield than the catalytic amount (90 vs 54% yields; entries 1 and 2). The effect of different solvents can be observed when $BF_3{\cdot}Et_2O$ was used (entries 1–4). Dichloromethane (CH_2Cl_2) gave the best result, providing **14** in 90% yield compared with 60% when toluene was used. It should be noted that the reaction performed in tetrahydrofuran (THF) did not furnish the product; decomposition of **11** into a mixture of unidentifiable compounds was

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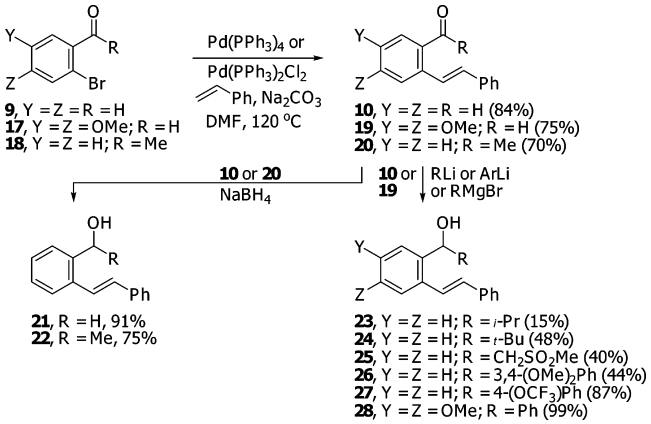
observed instead when the reaction was allowed to reach room temperature and stirred for 240 h. Interestingly, when *p*-toluenesulfonic acid on the surface of silica (PTS-Si) was employed (entry 7), the reaction furnished the corresponding indanol **16** as a 1.7:1 inseparable mixture of epimers at the C1 position in 80% yield, slightly favoring the trans relationship between the two adjacent stereocenters.[27] Similar mixtures of the epimers were obtained from the reactions both in the presence and absence of Et_3SiH, suggesting that water, presumably from the protonation of the hydroxy group by the immobilized PTS-Si or from solvent, rather than the hydride, acts as a nucleophile (see the discussion on the plausible mechanism in a subsequent section).

Scope of Substrates. Because it was easier to handle and gave yields comparable to $ZnCl_2$ with much shorter reaction time, $BF_3{\cdot}Et_2O$ was selected for the subsequent studies. We next investigated the effects of a different group at the benzylic position (X = alkyl or aryl). Starting from the aldehydes **9** and **17** or acetophenone **18**, the corresponding Heck products **10**, **19**, and **20** could be prepared in good yields (70–99%). Subsequently, either (1) nucleophilic addition to the aldehyde **10** or **19** or (2) borohydride reduction of the aldehyde **10** or acetophenone **20** furnished the corresponding benzyl alcohols **21**–**28** in moderate to good yields (15–91%), as shown in Scheme 4. It should be noted that low yield (15%) was

Scheme 4. Preparation of Benzyl Alcohols 21–28

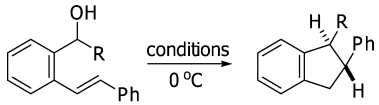


obtained from the addition of *i*-Pr group to the aldehyde **10** because of the competing "hydride" transfer from *i*-PrMgBr to the aldehyde, yielding the reduced product **21**.

The results of $BF_3{\cdot}Et_2O$-mediated cyclization of **21**–**27** followed by hydride addition from Et_3SiH are summarized in Table 2. Except for the primary benzyl alcohol **21**, all the secondary benzyl alcohols containing alkyl or aryl substituents (**11** and **22**–**27**) gave the corresponding substituted *trans*-2-phenylindanes **14** and **30**–**35** in moderate to excellent yields (50–99%). When compound **21** was subjected to the reaction conditions, only a complex mixture was obtained without any trace of the indane **29**. Presumably, the corresponding initial primary benzylic carbocation generated from **21** was unstable under the reaction conditions and underwent decomposition prior to cyclization to the subsequent indanyl-type carbocation and hydride addition. It should be noted that the product **33** was obtained as a 2:1 mixture of unassignable cis and trans diastereomers.

The effects of substituents on the fused benzene ring were also investigated. As summarized in Table 3, the presence of

Table 2. Scope of Substrates Containing Different R Groups[a]

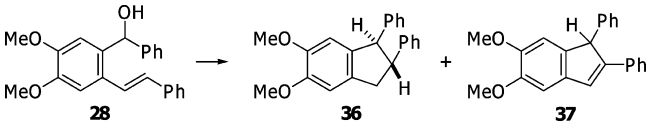


11 and **21**-**27** → **14** and **30**-**35**

entry	compound	R	product	yield (%)[b]
1	**21**	H	**29**	0
2	**22**	Me	**30**	99
3	**23**	*i*-Pr	**31**	50
4	**24**	*tert*-Bu	**32**	85
5[c]	**25**	CH_2SO_2Me	**33**	50
6	**11**	Ph	**14**	90
7	**26**	3,4-diOMePh	**34**	60
8	**27**	4-OCF_3Ph	**35**	75

[a]Unless noted otherwise, the reactions were performed in CH_2Cl_2 at 0 °C using 1.5 equiv of $BF_3{\cdot}Et_2O$ and 1.5 equiv of Et_3SiH. [b]Isolated yield. [c]A 2:1 mixture of unassignable cis and trans isomers was obtained.

Table 3. Product Distribution as a Result of Acid and Solvent Effects on the Reactions of 28[a]



28 → **36** + **37**

entry	acid	solvent	**36**:**37**	yield (%)[b]
1	$BF_3{\cdot}Et_2O$	CH_2Cl_2	100:0	12[c]
2[d]		CH_2Cl_2	100:0	86
3		MeCN	11:1	83
4		PhMe	10:1	67
5		DME[e]	1.3:1	86
6[e]		1,4-dioxane	0.3:1	95
7[e]		Et_2O	0:100	68
8[e]		THF	0:100	72
9	$InCl_3$	CH_2Cl_2	100:0	63
10	TFA	CH_2Cl_2	100:0	99

[a]Unless noted otherwise, the reactions were performed at 0 °C using 1.5 equiv of $BF_3{\cdot}Et_2O$ and 1.5 equiv of Et_3SiH. [b]Isolated yield. [c]Besides the desired product, only unidentified baseline materials were obtained. [d]Catalytic amount (15 mol %) of $BF_3{\cdot}Et_2O$ was used. [e]The reactions took 15 h to complete.

two methoxy groups in **28** directed the reactions to provide the corresponding indane **36** (from nucleophilic addition of hydride to the indanyl cation) as well as the indene **37** (from the loss of proton at the 2-position), depending on the solvent. The indane was obtained in 86% yield exclusively from the reaction in CH_2Cl_2 (entries 1–2) while those in THF and Et_2O (entries 7 and 8) furnished the indene exclusively in good yields (68 and 72%, respectively). When CH_2Cl_2 was used as solvent, the reaction employing catalytic amount of $BF_3{\cdot}Et_2O$ (15 mol %) proceeded more cleanly and gave **36** in much higher yield than that with 1.5 equiv of the Lewis acid. Interestingly, other solvents gave both products in different ratios (entries 3–6). It is evident that the more coordinating oxygen-containing solvents (1,2-dimethoxyethane (DME), 1,4-dioxane, Et_2O, and THF) furnished the indene more preferentially than other solvents. Thus, the different ratios of products **36** and **37** neither depend on nor reflect the relative polarity of solvents. As shown in Scheme 5, the mechanism for

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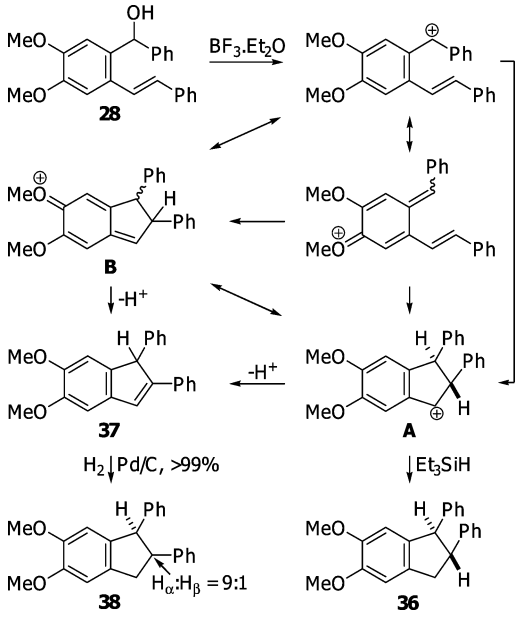
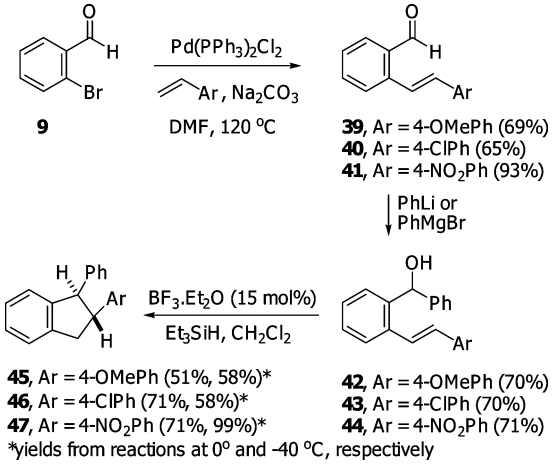
Scheme 5. A Proposed Mechanism for the Formation of 36 and 37



the formation of indene **37** may proceed via the carbocation and involve *p*-quinone methide and the participation of either one or both of the methoxy groups (both intermediates **A** and **B**). The structure of indene **37** was confirmed by hydrogenation, which gave the corresponding indane **38** as a 9:1 mixture of diastereomers favoring the addition of hydrogen to the olefin from the face opposite the phenyl group. Use of $InCl_3$ and TFA in CH_2Cl_2 as solvent gave only the indane **36** in 63 and 99% yields, respectively (entries 10 and 11).

The electronic effects from the nonfused aromatic (Ar) group were also investigated. When 4-methoxystyrene, 4-chlorostyrene, and 4-nitrostyrene were employed in the Heck reactions, the corresponding benzaldehydes **39**–**41** were obtained in moderate to good yields (65–93%), as shown in Scheme 6.[28] Subsequent PhLi or PhMgBr addition gave the requisite benzyl alcohol **42**–**44** in good yields (70–71%); these alcohols were then subjected to $BF_3{\cdot}Et_2O$-mediated cyclization followed by hydride transfer from Et_3SiH.

Scheme 6. Preparation of 2-Arylindanes 45–47 with Different Ar Groups via Heck Reactions



After some experimentation by varying temperature and the amount of $BF_3{\cdot}Et_2O$, the desired products **45**–**47** could be obtained in moderate to excellent yields (51–99%). Because 1.5 equiv of $BF_3{\cdot}Et_2O$ led to the complete consumption of the starting material **42** without any indane product, it was necessary to lower the amount of the Lewis acid in the final step to 15 mol % for **42** (this is similar to the reaction of **28** to form indane **36**), and thus $BF_3{\cdot}Et_2O$ was employed with **43** and then with **44** for comparison.[29] At 0 °C, both **43** and **44** gave the products **46** and **47** in good yield (71%); **42** gave the product **45** in much lower yield (51%). When lowering the temperature to −40 °C,[30] only **44** gave **47** in virtually quantitative yield (99%) while both **42** and **43** gave the corresponding indane products **45** and **46** in moderate yields (58%). For comparison, compound **11**, without any substituent on the Ar group (Ar = Ph), gave the product **14** in 54% yield (Table 1, entry 2) when 15 mol % of $BF_3{\cdot}Et_2O$ was used at 0 °C. It is apparent that changing the reaction temperature had little effect on the yield of this reaction for **42**. In the cases of **43** and **44**, lowering the temperature affected the yields of the reactions in the opposite direction—lower in the case of **43** but higher in that of **44**.

To account for these results, the electronic nature of these substituents was considered. In the cases of **42** and **44**, the methoxy (OMe) and the nitro (NO_2) groups are clearly electron-donating (EDG) and electron-withdrawing (EWG) groups, respectively, via resonance effects, which modulate the electron density in the stibenyl olefin moiety (increased with OMe and decreased with NO_2 with reference to H). However, in the case of Cl in **43**, it appears that both resonance and inductive field effects govern the overall effects of the Cl substituent; the extent and contribution of each effect may vary under different reaction conditions.[31] By resonance, the Cl substituent on an aromatic system is normally considered to be an EDG; however, inductively, Cl deactivates the aromatic ring and can be considered to be an EWG.[31] In our case, the effects from Cl appeared to be temperature-dependent. At 0 °C, the inductive field effect of Cl seemed to predominate as the yields of **46** and **47** were similar (71%). In other words, Cl behaves as an EWG at 0 °C. At −40 °C, the resonance effect of Cl through the aromatic system appeared to contribute more significantly as the yield of **46** decreased to be similar to that of **45** (58%); Cl is an EDG under this reaction condition. These results suggested that the presence of the EWG on this aromatic ring facilitates the cyclization step of the initial carbocations to the indanyl-type cations. In contrast, the presence of the EDG on the same ring appears to encumber such cyclization (see Plausible Mechanisms for the Formation of the Products in a subsequent section).

Scope of Nucleophiles. With the developed condition ($BF_3{\cdot}Et_2O$ in CH_2Cl_2) in hand, we then investigated the scope of nucleophilic transfer from the trialkylsilyl reagents as summarized in Table 4. The azide, allyl, chloride, bromide, and iodide groups were transferred smoothly from the corresponding trimethylsilyl (TMS)-containing reagents to the indanyl-type cation, yielding the corresponding products **48**–**54** in 33–75% yields without any additive (entries 1–3 and 7–9). The azidoindane **48** was obtained in a 9:1 diastereomeric ratio while the allyl indane **49** and the haloindanes **50**–**52** were obtained in 1:1–3:1 ratios, with slight preference for the 1,2-*trans* relationship. Both alcohols **42** and **43**, upon reacting with TMS-N_3, gave the corresponding azidoindanes **53** and **54** in 61 and 65% yields, respectively, with slight preference for the 1,2-

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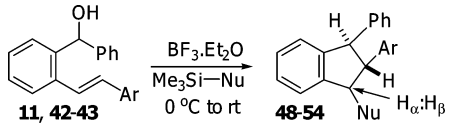
Table 4. Scope of Nucleophilic Transfer from Trialkylsilyl Reagents[a]



entry	Ar	Nu	equiv of $BF_3{\cdot}Et_2O$	additive	equiv of additive	Prod	H_α:H_β	yield (%)[b]
1	Ph	N_3	1.5	none	0.0	**48**	9:1	75
2		allyl	1.5	none	0.0	**49**	1:1	<79[c]
3		allyl	0.15	none	0.0	**49**	1:1	68
4		allyl	0.15	TBAF[d]	1.5	**49**	N/A	0[e]
5		allyl	2.0	TBAF	1.5	**49**	1:1	23[f]
6		allyl	3.5	TBAF	3.0	**49**	1:2	27[f]
7[g,h]		Cl	0.15	none	0.0	**50**	3:1	48
8[h]		Br	0.15	none	0.0	**51**	2:1	72
9[g,h]		I	0.15	none	0.0	**52**	3:1	33
10		F	2.0	none	0.0	**12**	N/A	32
11[i]	4-OMePh	N_3	0.15	none	0.0	**53**	2:1	61
12[i]	4-ClPh	N_3	0.15	none	0.0	**54**	3:1	65

[a]Unless noted otherwise, the reactions were performed at 0 °C and 1.5 equiv of Me_3Si—Nu. [b]Isolated yield. [c]The product was obtained with some unknown and inseparable impurities. [d]TBAF was added as a solution in CH_2Cl_2 pretreated with excess Na_2SO_4 to remove any trace amount of water. [e]No reaction occurred; starting material recovered. [f]Significant amount of indene **12** (55–63%) was also isolated. [g]The reaction was performed at −30 °C. [h]The reactions were purified by passing the crude reaction mixture through a plug of silica. [i]The ratios reported for H_α:H_β of the crude and the isolated diastereomers were comparable.

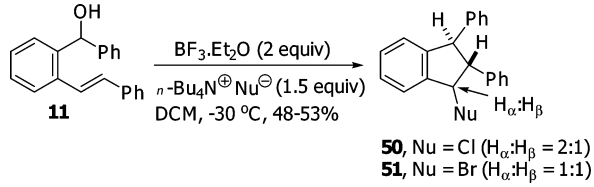
trans relationship. It should be noted that the 1,2,3-*trans* and 1,2-*cis*-2,3-*trans* indane products **53** and **54**, unlike other indane products **48**–**52**, were separable by chromatography. The presence of tetrabutylammonium fluoride (TBAF) in excess as additive did not furnish the corresponding fluoroindane (entries 4–6). When only a catalytic amount of $BF_3{\cdot}Et_2O$ was employed, the formation of the tetrabutylammonium tetrafluoroborate ($Bu_4N^+BF_4^-$) presumably occurred more readily while resulting in complete recovery of the starting material **11** (entry 4). However, in the presence of a slight excess of $BF_3{\cdot}Et_2O$ relative to TBAF (entries 5–6), the corresponding product allylindane **49** was obtained, albeit in low yields (23–27%), with significant amount of indene **12** (55–63%). In the presence of TBAF alone (entry 10), only the indene **12** was obtained in 32% yield, suggesting that the fluoride ion from TBAF did not act as a nucleophile or effectively facilitate the transfer of the allyl group from allyltrimethylsilane by mediating the cleavage of the allyl group from the silicon atom.

It should be noted that temperature plays an important role for the transfer of the chloride and iodide to form chloroindane **50** and iodoindane **52**, respectively. When these reactions were performed either at 0 °C or from 0 °C to room temperature, a significant amount of indene **12** was observed. At lower temperature (−30 °C), the reaction gave the desired products **50** and **52** cleanly in moderate yields of 48 and 33%, respectively. It was also observed that purification of these haloindanes **50**–**52** by column chromatography on silica led to significant or complete decomposition of the products to mixtures of indenes **12** and **13**, among other unidentified products. Thus, following the complete consumption of **11**, these reactions were passed through a plug of silica to remove any baseline materials. This procedure gave the homogeneous products shown by both ^1H and ^{13}C NMR spectra (see the Supporting Information); the mass of each reaction following the procedure was then used to calculate the percent yield (entries 7–9). While both chloroindane **50** and bromoindane **51** were chemically robust even at room temperature either neat or as solutions in $CDCl_3$, the iodoindane **52** was found to be unstable as a solution in $CDCl_3$ at room temperature and readily decomposed to the indene **13**. After some experimentation, **52** could be kept refrigerated (at ca. −20 °C) either neat or as a solution in $CDCl_3$ without detectable decomposition.

It was anticipated that water, even in trace amounts, may compete with halides during these reactions. Thus, excess Na_2SO_4 was added to the reaction using TMSBr.[32] No detrimental effects or significant differences were observed with added Na_2SO_4; the corresponding bromoindane **51** was obtained in 69% yield as a 2:1 mixture of diastereomers.

The source of halides was also investigated. Because of its more labile nature, iodoindane **52** was more difficult to handle when compared with chloroindane **50** and bromoindane **51**, so we decided to focus on the use of tetrabutylammonium chloride (TBACl) and tetrabutylammonium bromide (TBAB) as nucleophiles for these reactions (see Scheme 7). Because of

Scheme 7. Tetrabutylammonium Halides as Nucleophiles



their hygroscopic nature, we anticipated that adding these ammonium salts directly to the reactions would introduce significant amounts of water which would act as a nucleophile and compete with the halides during these reactions. Thus, it is crucial that the solutions of these tetrabutylammonium halides in CH_2Cl_2 are treated with excess Na_2SO_4 to remove any water prior to their addition.[32] The results showed that the TBACl gave the product **50** in identical yield (48%) with a slightly lower diastereoselectivity (2:1) when compared with the reaction employing TMSCl (48% yield and 3:1 diastereomeric

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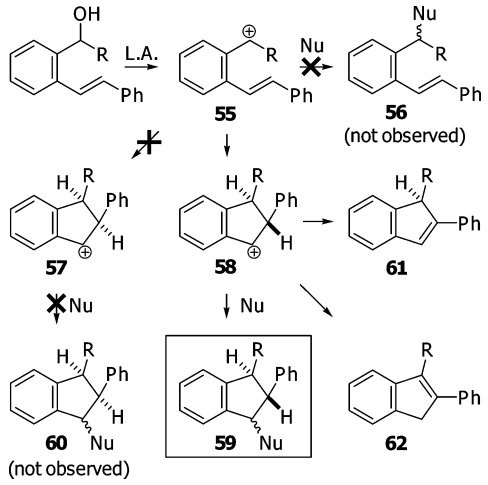
ratio). However, TBAB furnished the bromoindane **51** in lower yield (53%) with a slightly lower diastereoselectivity (1:1) when compared with the reaction using TMSBr (72% yield and 2:1 diastereomeric ratio).

Plausible Mechanisms for the Formation of the Products. A plausible mechanism for the formation of indane is depicted in Scheme 8, proposing that the carbocation **55** is expected to form from the initial complexation by Lewis acid or protonation by Brønsted acid at the hydroxy group. Subsequent direct nucleophilic addition to this carbocation to form the corresponding product **56** was not observed. Instead, the carbocation **55** underwent cyclization with a stilbenyl olefin moiety to form either the *cis*- or *trans*-indanyl-type cations **57** or **58**, indicating that the intramolecular cyclization occurred more readily than the direct intermolecular nucleophilic addition to the carbocation **55**.[33] Our observation of the product **59** was consistent with the formation of the corresponding *trans*-indanyl cation **58** without any detectable *cis*-diastereomer **60**. The *trans*-indanyl cation **58** may also undergo (1) direct loss of β-proton to produce the indene **61** or (2) 1,2-hydride shift followed by loss of β-proton to furnish the indene **62**.[20]

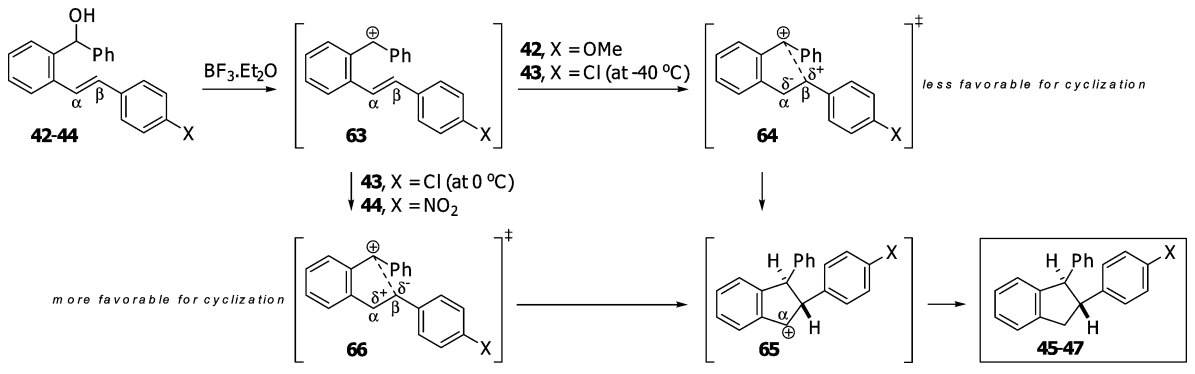
The electronic effects from the substituents on the fused (**28**) or nonfused (**42**–**44**) aromatic ring to form the corresponding indane products (**36** and **45**–**47**) provided important mechanistic insights which supported and signified the cyclization process to form the subsequent indanyl-type cation such as **58**. From Table 3 and Scheme 5, the reactions of benzyl alcohol **28**, with two methoxy groups on the fused aromatic ring, gave indane **36** via a series of stabilized carbocations. The results implied that, on the fused aromatic ring, these EDGs which can stabilize the initially-formed carbocation (a species similar to **55**) as well as others along the reaction pathway may facilitate the cyclization to form the subsequent indanyl-type carbocation (**A** in Scheme 5 which is similar to **58** in Scheme 8), ultimately leading to the formation of the indane product.[34]

On the other hand, the electronic effects from the nonfused Ar group of **42**–**44** indicated that the presence of EDGs on the nonfused aromatic ring hampered the cyclization while that of EWG facilitated it. As shown in Scheme 9, by resonance, following the formation of the initial carbocation **63**, the EDG (X = OMe) in **42** increased the electron density (δ^-) at the α-carbon of the stilbenyl olefin system, as shown in transition state **64**, rendering the cyclization to form the indanyl-type cation **65** less favorable because of the increasing carbocationic character (δ^+) on the β-carbon which, in turn, was required to cyclize with the carbocation. Contrary to the EDGs, by resonance and inductive field effect, the strongly electron-withdrawing nitro group at the same position in **44** decreased the electron density of the aromatic ring, thereby providing stabilization for the developing anionic character (δ^-) on the β-carbon for the subsequent cyclization to form **65** via the transition state **66**. Consequently, the EWG on the nonfused aromatic ring would also increase the carbocationic character (δ^+) on the α-carbon, favoring the formation of the indanyl-type cation **65**. For Cl as a substituent on the aromatic ring, depending on reaction conditions, the transition state similar to **64** (X = Cl) may predominate at low temperature (−40 °C), while at higher temperature (0 °C) the other transition state like **66** (X = Cl) may predominate instead. These results clearly delineated the significance of both carbocationic character developing on the α-carbon and anionic character on the β-carbon of the stilbenyl olefin moiety for the successful cyclization to form the indanyl-type cation. Taken together, the results from the reactions of **28** and **42**–**44** unequivocally indicated the importance of carbocation stability as well as the parameters which affect it both for the initially formed carbocation like **55** (or **63**) and the indanyl-type cation **65** during this Lewis or Brønsted acid-mediated cyclization prior to the nucleophilic transfer from the trialkylsilyl reagents.[34]

Scheme 8. A Proposed Mechanism for the Formation of Indane 59 and Indenes 61 and 62



Scheme 9. Further Mechanistic Insights for Cyclization of 42–44 and the Importance of the Indanyl-Type Cationic Intermediates 65



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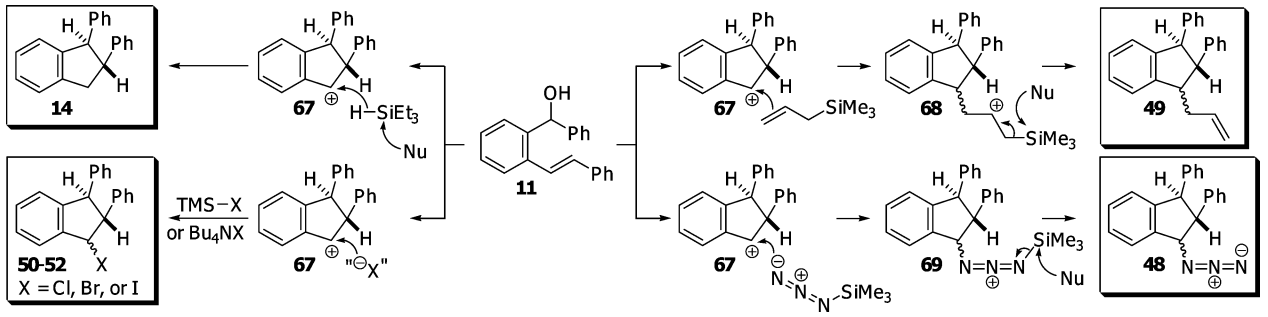
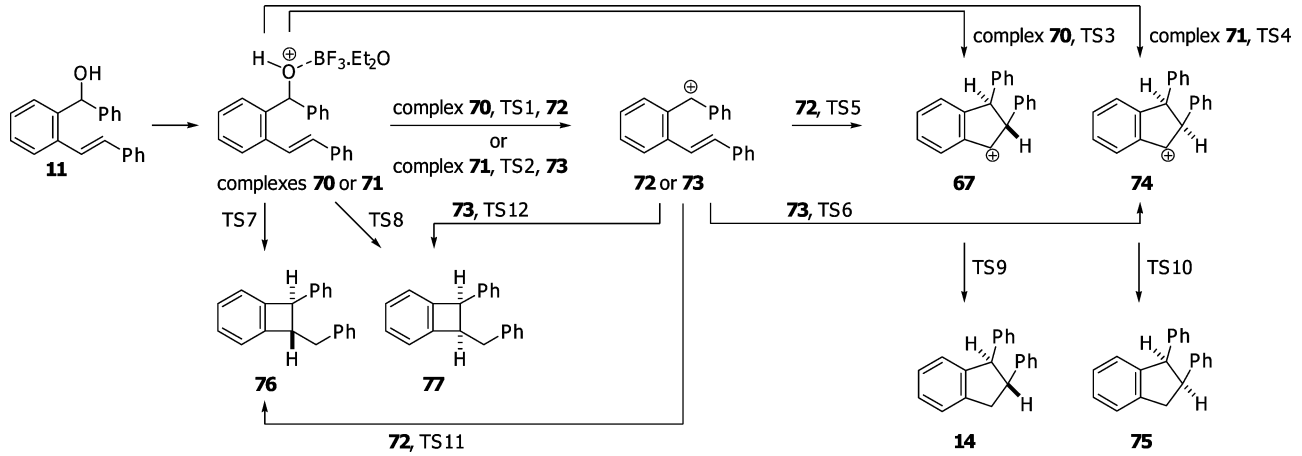
Scheme 10. A Plausible Mechanism for the Transfer of Nucleophiles



Scheme 11. Concerted versus Stepwise Reaction Mechanisms for Quantum Chemical Calculations



It should be noted that the hydride addition required activation of the Si–H bond which could be mediated by the fluoride ion from $BF_3{\cdot}Et_2O$.[35−37] In the case of the Brønsted acids (TFA and TfOH), the weak conjugate base could activate the Si–H bond albeit less effectively as evident by lower yields. $InCl_3$-promoted reaction may proceed via a different mechanism.[38] For PTS-Si, because the conjugate base *p*-toluenesulfonyl anion was immobilized on silica, Et_3SiH was not activated to deliver the hydride, and similar results arising from nucleophilic addition by water were obtained both in the presence and absence of Et_3SiH.

Unlike the hydride transfer, the allyl and azide groups are likely to undergo direct nucleophilic addition to the indanyl-type cation **67** generated from **11** via the terminal olefin of the allyl group[39,40] or the nitrogen atom of the azide group,[41,42] as shown in Scheme 10. The positive charge on the carbocation **68**[40] or nitrogen **69** can be stabilized by the *β*-Si atom.[43] Subsequent nucleophilic attack (presumably by fluoride ion from $BF_3{\cdot}Et_2O$) on Si then led directly to the products. In the case of chloride, bromide, or iodide transfer from the corresponding trimethylsilyl halides, greater ionic character of the Si-halogen bond when compared to that of either the Si-allyl or the Si–N_3 bond may have led, under the reaction conditions, to generation of the corresponding halide ions which then reacted with the indanyl-type cation to furnish the haloindane products. Similar results using different sources of halides (TMS-halides versus TBACl or TBAB) supported this proposed mechanism for the transfer of halides.

Quantum Chemical Calculations. To gain further insight into the reaction and to account for our experimental observations, quantum chemical calculations were employed to study the reaction in detail. Theoretically, the reaction of compound **11**, $BF_3{\cdot}Et_2O$, and Et_3SiH can give rise to four distinct cyclic products. The trans-stereochemical selectivity observed here therefore suggests that the mechanism leading to the preferred product is (a) stereochemically distinct and (b) significantly lower in energy than the mechanisms leading to the other products.

In principle, the chemical reaction could occur in a stepwise fashion, involving the formation of a discrete carbocation, followed by ring closure, and finally hydride transfer. Alternatively, the reaction could proceed in a concerted fashion, with the formation of the carbocation ion occurring alongside the ring closure and hydride transfer (see Scheme 11).

The relative energetics associated with the different mechanisms, and the relative energies of the different products, are reported in Figure 2 and Table 5. The reaction to form the cyclic products may commence from the initial nonbonded complex formed by **11**, $BF_3{\cdot}Et_2O$, and Et_3SiH, resulting in the formation of two possible distinct conformations, complexes **70** and **71**, as shown in Figure 3. The two complexes differ in the orientation of the two substituents that are ortho to each other on the phenyl ring.

Structures of complexes **70** and **71** correspond to the chemisorbed complex formed between **11** and BF_3 via the formation of a B–O bond (∼1.6 Å). Both complexes can form the corresponding discrete carbocations, **72** or **73**, by the loss of BF_3OH^- via the transition states TS1 (17.4 kcal/mol) or TS2 (19.9 kcal/mol), respectively. Both carbocations, **72** and **73**, can undergo cyclization to form the corresponding five-membered ring indanyl-type cations, resulting in a 5-*trans*

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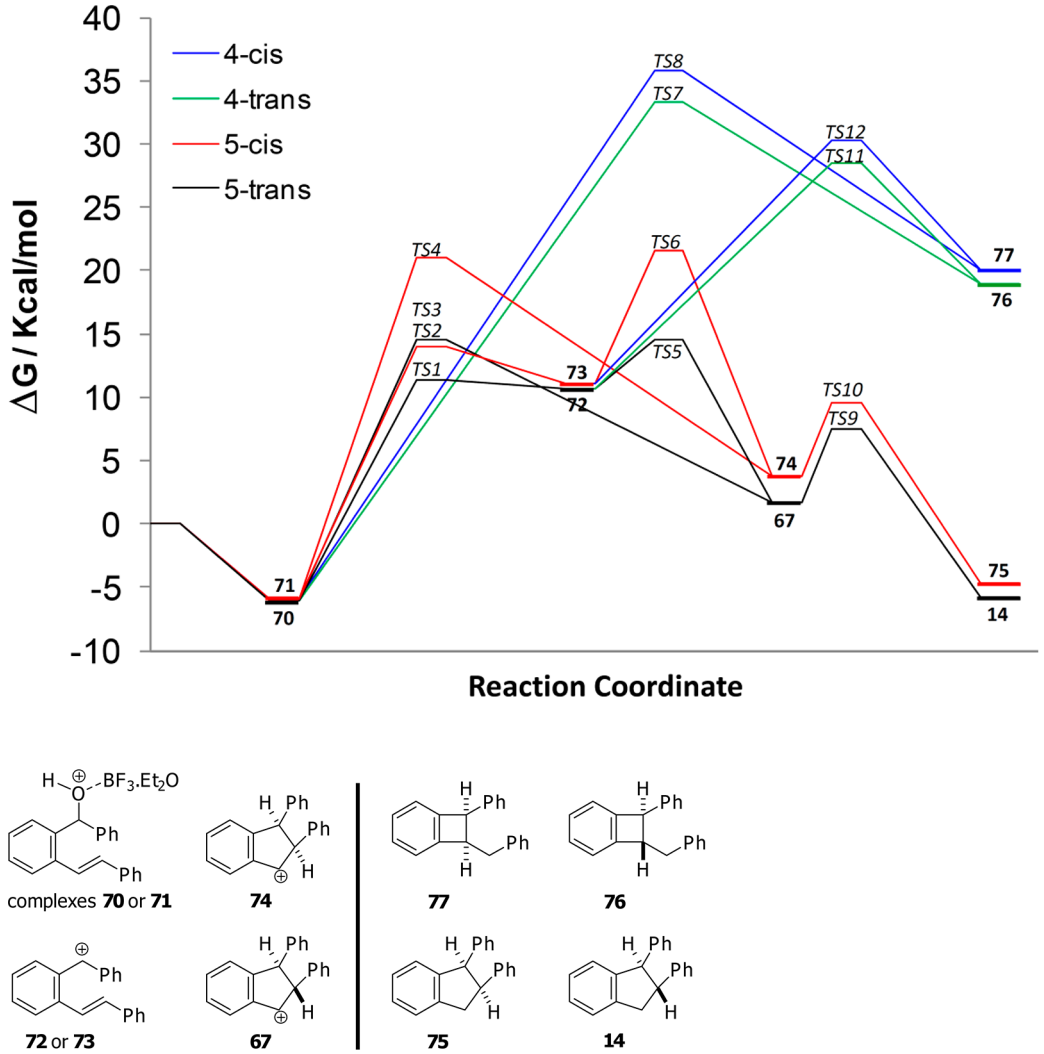

Figure 2. The energetic profile associated with the formation of four possible products from the reaction of **11** in the presence of $BF_3{\cdot}Et_2O$ and Et_3SiH.

configuration for **72** via the transition state TS5 and a 5-*cis* configuration for **73** via the transition state TS6. The barrier associated with this step is considerably lower for the 5-*trans* carbocation **67** (3.4 kcal/mol) than for the 5-*cis* carbocation **74** (10.0 kcal/mol). In the final step of the hydride transfer from Et_3SiH, the 5-*trans* carbocation **67** and the 5-*cis* carbocation **74** subsequently gave the corresponding 5-*trans* indane **14** and 5-*cis* indane **75** via the transition states TS9 and TS10, respectively (Figure 4). It should be noted that while the barriers associated with the final step are equivalent at 5.7 kcal/mol, the 5-*trans* indane **14** is 1.0 kcal/mol lower in energy.

Alternatively, both the 5-*trans* carbocation **67** and 5-*cis* carbocation **74** may be formed directly from the chemisorbed complex via the simultaneous C−O bond breakage and the intramolecular C−C bond formation and cyclization via the transition states TS3 and TS4, respectively, without the explicit carbocations **72** or **73** (see Figure 3). However, the barriers for both cases (20.6 kcal/mol for 5-*trans* carbocation **67** via TS3 and 26.9 kcal/mol for 5-*cis* carbocation **74** via TS4) are higher than those leading to the formation of the discrete carbocations **72** (17.4 kcal/mol) and **73** (19.9 kcal/mol), suggesting that these alternative pathways are less important. In addition, a concerted process involving the simultaneous C−O bond breakage, intramolecular C−C bond formation and cyclization, and hydride transfer can be completely ruled out for the five-membered ring products due to steric constraints.

Theoretically, the corresponding four-membered ring benzocyclobutene (BCB) products are also possible outcomes of the reaction. However, analysis of the results presented in Figure 2 shows that these BCB products are considerably higher in energy (24.7 kcal/mol) compared to the five-membered ring indanes. The BCB products can be formed by two distinct pathways. First, complexes **70** and **71** can directly cyclize to form the four-membered ring products via the simultaneous C−O bond breakage, C−C bond formation and cyclization, and hydride transfer (transition states TS7 and TS8, respectively). As shown in Figure 4, both transition states TS7 (39.4 kcal/mol) and TS8 (41.7 kcal/mol) are extremely high in energy for the corresponding *trans*- and *cis*-BCB products **76** and **77**, respectively. Alternatively, both *trans*- and *cis*-BCB products can arise by stepwise processes of lower energy pathways involving either **72** or **73** and transition states TS11 (barrier of 17.5 kcal/mol) or TS12 (barrier of 18.7 kcal/mol), respectively. While these barriers are considerably lower than those for the concerted processes, they are still remarkably higher than the equivalent barriers (TS5, which is 3.4 kcal/mol,

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Table 5. Energies of the Different Structures

intermediate	energy (kcal/mol)
complex **70**	−6.11
complex **71**	−5.91
TS1	11.34
TS2	13.99
TS3	14.53
TS4	20.95
72	11.09
73	11.53
TS5	14.50
TS6	21.57
74	3.81
67	1.70
TS9	7.44
TS10	9.51
75	−4.69
14	−5.74
TS7	33.31
TS8	35.79
TS11	28.54
TS12	30.26
77	20.05
76	18.95

or TS6, which is 10.0 kcal/mol) leading to the five-membered indane products. Thus, the quantum chemical calculations clearly showed that the formation of the BCBs is much less favorable than the corresponding indanes.

The quantum chemical calculations undertaken to study the BF_3-mediated cyclization of compound **11** followed by hydride transfer from Et_3SiH showed that the formation of the observed indane product **14** is likely to proceed via discrete albeit short-lived carbocations (e.g., **72**) and not via a concerted process. The energetic profile and calculated energies of transition states also supported the observation that the *trans*-indane is the exclusive product from these reactions.

CONCLUSIONS

In summary, a novel synthetic method for the synthesis of 2-arylindane derivatives has been developed based on the Lewis acid-mediated cyclization of *E*-(2-stilbenyl)methanols followed by the nucleophililc transfer from trialkylsilyl reagents. The reaction has been found to be suitable for a relatively wide range of substrates and nucleophiles, providing various substituted and functionalized 2-arylindanes in good to excellent yields (up to 99%). Among the Lewis and Brønsted acids screened, $BF_3{\cdot}Et_2O$ was found to be most effective for this reaction as evident by good to excellent yields of the products and short reaction time. Solvents play an important role in determining the types of products generated from the reactions. In general, CH_2Cl_2 was found to be the solvent of choice for these reactions. In addition to the transfer of hydride from Et_3SiH, transfer of azide, allyl, chloride, bromide, and iodide from the corresponding trimethylsilyl reagents to the indanyl-type carbocation furnished the corresponding products in moderate to good yields. Cyclization to form the indanyl-type carbocation proceeded with high stereoselectivity to give the *trans*-indanyl-type cation as the only observed intermediate; however, the nucleophilic transfer from the trialkylsilyl reagents to the indanyl-type cation proceeded only in moderate to good diastereoselectivity. Electron-donating groups on the fused

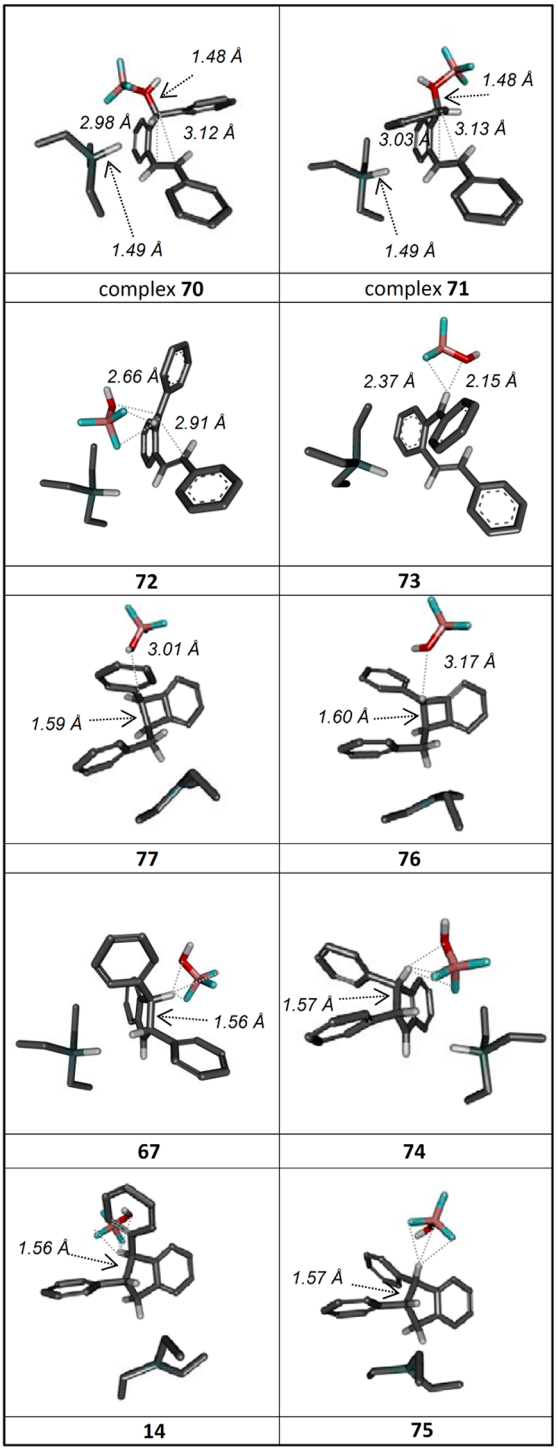

Figure 3. Predicted minima from quantum chemical calculations.

aromatic ring are beneficial as they stabilize the carbocations along the reaction pathways; the presence of electron-withdrawing groups on the nonfused aromatic ring directs the reaction toward cyclization to form the indanyl-type cation by stabilizing the developing anionic characters on the 2-position of the newly formed indane systems. Quantum chemical calculations of the energetic profile of the plausible complexes as well as intermediates and transition states along the distinct pathways further supported and confirmed that the most likely mechanism of this reaction commenced with the complexation between the Lewis acid ($BF_3{\cdot}Et_2O$) and the hydroxyl group of

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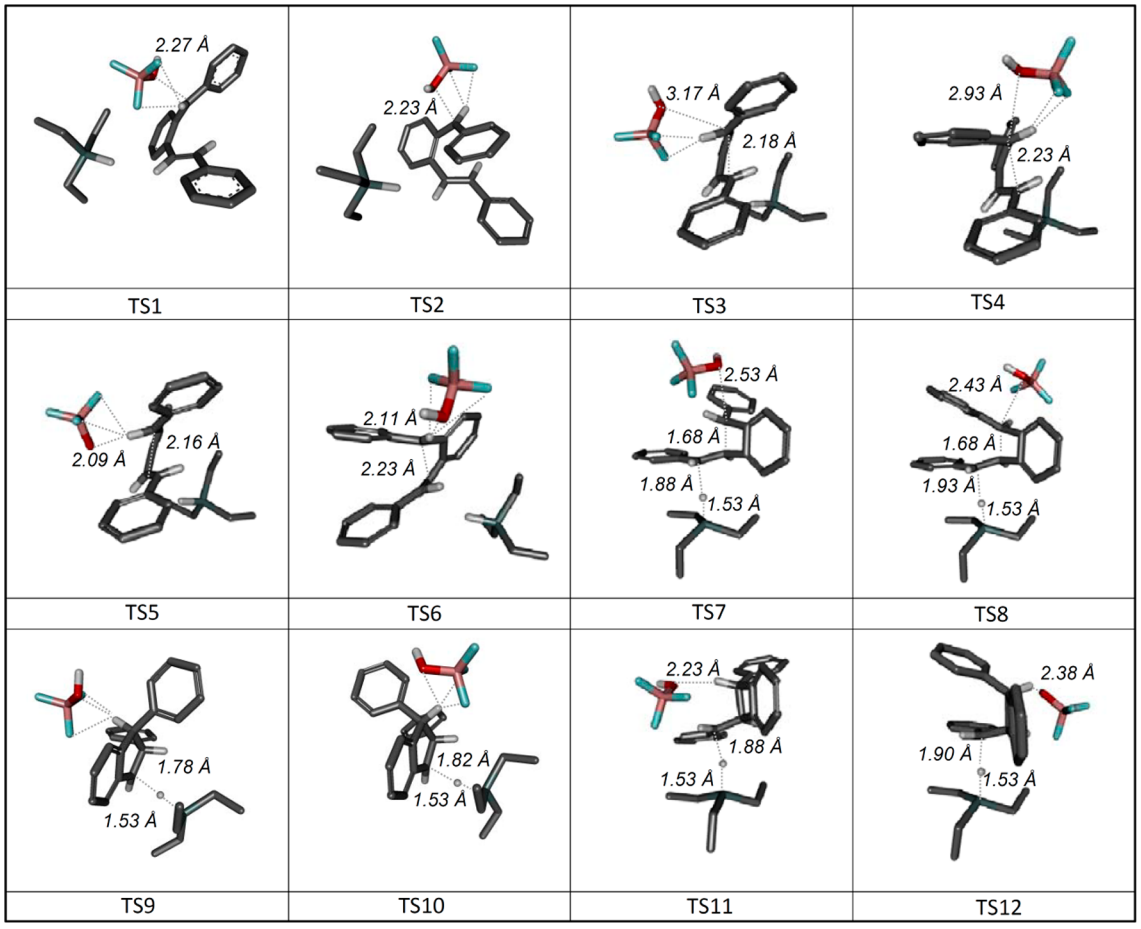

Figure 4. Predicted transition states from quantum chemical calculations.

the starting material *E*-(2-stilbenyl)methanol followed by the generation of the corresponding discrete carbocation which readily underwent the intramolecular cyclization to yield the C1−C2 substituted *trans*-indanyl-type carbocation. Subsequent nucleophilic transfer from the trialkylsilyl agents to such *trans*-indanyl-type carbocation then furnished the C1−C2 *trans*-indane product exclusively. Applications of the developed method toward the synthesis of biologically active compounds as well as natural products are under way and will be reported in due course.

EXPERIMENTAL SECTION

General Experimental Methods. Unless otherwise noted, reactions were run in oven-dried round-bottomed flasks. THF was distilled from sodium benzophenone ketyl or purified by the solvent purification system, while CH_2Cl_2 was also purified by the solvent purification system prior to use. All other compounds were used as received from the suppliers; PTS-Si (*p*-TsOH immobilized on silica) employed in these experiments possessed the surface area of 500 m^2/g as indicated by the supplier. The crude reaction mixtures were concentrated by a rotary evaporator that removed organic solvents under reduced pressure. Column chromatography was performed using silica gel 60 (particle size 0.06−0.2 mm; 70−230 mesh ASTM). Analytical thin-layer chromatography (TLC) was performed with silica gel 60 F_{254} aluminum sheets. Chemical shifts for ^1H nuclear magnetic resonance (NMR) spectra were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br), and doublet of doublet (dd). Resonances for infrared (IR) spectra were reported in wavenumbers (cm^{-1}). Low resolution (LRMS) mass spectra were obtained either using electron ionization (EI) or time-of-flight (TOF), while high resolution (HRMS) mass spectra were obtained using time-of-flight (TOF) via atmospheric pressure chemical ionization (APCI) or electrospray ionization (ESI). Melting points were uncorrected.

General Procedure for the Heck Reaction. To a stirred solution under argon atmosphere of 2-bromobenzaldehyde (**9** or **17**) or 2-bromoacetophenone (**18**) (1 equiv) in *N*,*N*-dimethylformamide (DMF) was added styrene (5 equiv), sodium carbonate (Na_2CO_3, 2 equiv), and tetrakis-triphenylphosphine palladium(0) or bis-(triphenylphosphine)palladium(II) (0.01 equiv). The reaction mixture was heated to 120 °C for 18 h. Then, the reaction was allowed to cool to room temperature. Water and ethyl acetate (EtOAc) were added; the two phases were separated. The aqueous layer was extracted twice with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product which was further purified by column chromatography on silica (EtOAc/hexanes) to furnish the desired products (**10**, **19**, **20**, **39**−**41**).

(*E*)-2-Styrylbenzaldehyde (10). The product was obtained as a yellow oil (5% EtOAc/hexanes as an eluent, 1.48 g, 84%). IR (neat): $\overline{\nu}_{max}$ 3061, 3025, 2839, 2739, 1690, 1595, 1196 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.06 (d, 1H, J = 16.2 Hz), 7.25−7.46 (m, 4H), 7.59 (d, 3H, J = 7.8 Hz), 7.72 (d, 1H, J = 7.8 Hz), 7.84 (d, 1H, J = 7.8 Hz), 8.05 (d, 1H, J = 15.9 Hz), 10.3 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.8, 127.0, 127.2, 128.3, 128.8, 132.3, 132.9, 133.7, 134.0, 136.7, 139.9, 192.7. LRMS−EI m/z (relative intensity) 208 (100, M^+), 207 (41), 179 (51), 178 (65), 165 (31), 152 (17), 130 (18), 89 (29), 77 (21), 76 (28). TOF−HRMS calcd for $C_{15}H_{13}O$ $(M + H)^+$ 209.0961, found 209.0954.

(*E*)-4,5-Dimethoxy-2-styrylbenzaldehyde (19). The product was obtained as a yellow solid (30% EtOAc/hexanes, 2.48 g, 75%). mp

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(EtOAc/hexanes) 148−150 °C. IR (neat): $\bar{\nu}_{max}$ 3002, 2936, 2835, 1669, 1591, 1508, 1273, 1102 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.96 (s, 3H), 4.03 (s, 3H), 6.97 (d, 1H, J = 16.2 Hz), 7.10 (s, 1H), 7.27−7.35 (m, 1H), 7.36−7.43 (m, 3H), 7.52−7.58 (m, 2H), 7.89 (d, 1H, J = 16.2 Hz), 10.33 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.1, 56.2, 108.8, 111.0, 123.6, 126.5, 126.8, 128.3, 128.8, 133.3, 135.6, 136.8, 148.9, 153.7, 190.0. LRMS−EI m/z (relative intensity) 268 (100, M^+), 237 (23), 209 (20), 191 (20), 165 (51), 153 (30), 152 (41), 91 (18), 69 (37), 57 (49). TOF−HRMS calcd for $C_{17}H_{17}O_3$ $(M + H)^+$ 269.1172, found 269.1170.

(*E*)-1-(2-Stilbenyl)ethanone (20). The product was obtained as a yellow-brown oil (10% EtOAc/hexanes, 0.30 g, 70%). IR (neat): $\bar{\nu}_{max}$ 3060, 3024, 1678, 1354, 1267, 1241 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.61 (s, 3H), 6.99 (d, 1H, J = 16.2 Hz), 7.22−7.39 (m, 4H), 7.45−7.55 (m, 3H), 7.63−7.72 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.9, 126.8, 127.2, 127.3, 127.4, 127.9, 128.6, 129.0, 131.6, 137.2, 137.3, 137.4, 202.2. LRMS−EI m/z (relative intensity) 222 (100, M^+), 221 (41), 207 (47), 179 (52), 178 (86), 152 (20), 145 (62), 89 (31), 76 (22). TOF−HRMS calcd for $C_{16}H_{15}O$ $(M + H)^+$ 223.1117, found 223.1111.

(*E*)-2-(4-Methoxystyryl)benzaldehyde (39). The product was obtained as an orange oil (10% EtOAc/hexanes, 0.43 g, 70%). IR (neat): $\bar{\nu}_{max}$ 3004, 1693, 1606, 1595, 1250, 1175 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3H), 6.90 (d, 2H, J = 8.1 Hz), 6.99 (d, 1H, J = 16.2 Hz), 7.38 (t, 1H, J = 7.5 Hz), 7.49 (d, 2H, J = 8.7 Hz), 7.55 (d, 1H, J = 7.2 Hz), 7.68 (d, 1H, J = 7.8 Hz), 7.80 (d, 1H, J = 7.8 Hz), 7.90 (d, 1H, J = 16.2 Hz), 10.30 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 114.1, 122.3, 126.9, 127.1, 128.2, 129.7, 132.1, 133.5, 133.6, 140.3, 159.8, 192.6. LRMS−EI m/z (relative intensity) 238 (1, M^+), 195 (95), 194 (58), 178 (33), 167 (28), 165 (22), 149 (100), 105 (27), 91 (17), 77 (28). TOF−HRMS calcd for $C_{16}H_{14}O_2Na$ $(M + Na)^+$ 261.0886, found 261.0879.

(*E*)-2-(4-Chlorostyryl)benzaldehyde (40). The product was obtained as a yellow oil (10% EtOAc/hexanes, 47.1 mg, 65%). IR (neat): $\bar{\nu}_{max}$ 3036, 3023, 2841, 2739, 1693 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.00 (d, 1H, J = 18.0 Hz), 7.26−7.36 (m, 2H), 7.43−7.56 (m, 3H), 7.58−7.61 (m, 1H), 7.71 (d, 1H, J = 6.0 Hz), 7.83 (dd, 1H, J = 1.5, 9.0 Hz), 8.05 (d, 1H, J = 18.0 Hz), 10.28 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 125.6, 127.1, 127.9, 128.2, 129.0, 132.4, 132.95, 132.97, 133.8, 133.9, 135.5, 139.4, 192.8. LRMS−EI m/z (relative intensity) 244 (23, M+2), 242 (73, M^+), 207 (52), 179 (52), 178 (100), 176 (33), 149 (54), 111 (10), 77 (16). TOF−HRMS calcd for $C_{15}H_{11}ClONa$ $(M + Na)^+$ 265.0391, found 265.0378.

(*E*)-2-(4-Nitrostyryl)benzaldehyde (41). The product was obtained as a brown solid (10% EtOAc/hexanes, 115.0 mg, 93%). mp (EtOAc/hexanes) 122−123 °C. IR (neat): $\bar{\nu}_{max}$ 3063, 2923, 2852, 1693, 1595, 1531, 1340 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.11 (d, 1H, J = 15.0 Hz), 7.52−7.57 (m, 1H), 7.62−7.78 (m, 4H), 7.86 (d, 1H, J = 6.0 Hz), 8.23−8.34 (m, 3H), 10.26 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.15, 127.25, 127.43, 128.7, 130.1, 130.9, 133.8, 134.0, 193.0. LRMS−EI m/z (relative intensity) 253 (46, M^+), 178 (63), 167 (27), 149 (100), 111 (21), 97 (40), 83 (30), 77 (19), 69 (60). TOF−HRMS calcd for $C_{15}H_{11}NO_3Na$ $(M + Na)^+$ 276.0631, found 276.0621.

General Procedure for the Synthesis of 11, 23, 24, 28, and 42−44. To a stirred solution (1 equiv) of **10** or **19** in dry THF at −78 °C under argon atmosphere was added phenyllithium or phenylmagnesium bromide (for **11**, **28**, **42**−**44**), *i*-propylmagnesium chloride (for **23**), *t*-butyllithium (for **24**) (1.5 equiv). The reaction mixture was stirred at −78 °C for 30 min, then warmed to room temperature and stirred until all of the starting material was consumed as monitored by TLC. Water and EtOAc were added, and the two phases were separated. The aqueous layer was extracted twice with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product which was further purified by column chromatography on silica (EtOAc/hexanes) to furnish the desired products.

(*E*)-Phenyl(2-stilbenyl)methanol (11). The product was obtained as a yellowish white solid (30% EtOAc/hexanes, 1.24 g, 98%). mp (EtOAc/hexanes) 113−115 °C. IR (neat): $\bar{\nu}_{max}$ 3353 (br), 3027, 1597, 1494, 1450, 1177, 1017 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.28 (d, 1H, J = 3.3 Hz), 6.18 (d, 1H, J = 2.4 Hz), 6.92 (d, 1H, J = 16.2 Hz), 7.25−7.40 (m, 13H), 7.46−7.51 (m, 1H), 7.57−7.62 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 73.4, 125.9, 126.3, 126.6, 126.8, 127.1, 127.6, 127.7, 127.8, 128.5, 128.7, 131.2, 135.8, 137.3, 140.7, 143.0. LRMS−EI m/z (relative intensity) 286 (4, M^+), 196 (15), 195 (100), 194 (59), 178 (27), 165 (21), 105 (22), 91 (24), 77 (24). TOF−HRMS calcd for $C_{21}H_{17}O$ $(M - H)^+$ 285.1274, found 285.1270.

(*E*)-2-Methyl-1-(2-stilbenyl)propan-1-ol (23). The product was obtained as a light yellow oil (20% EtOAc/hexanes, 43.6 mg, 15%). IR (neat): $\bar{\nu}_{max}$ 3428 (br), 3026, 2959, 1599, 1494, 1468, 1448, 1003 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.83 (d, 3H, J = 6.9 Hz), 1.01 (d, 3H, J = 6.6 Hz), 1.89 (br s, 1H), 1.97−2.10 (m, 1H), 4.78 (d, 1H, J = 6.6 Hz), 6.94 (d, 1H, J = 15.9 Hz), 7.22−7.30 (m, 3H), 7.30−7.42 (m, 2H), 7.42−7.55 (m, 4H), 7.55−7.61 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.8, 19.6, 34.8, 76.4, 126.1, 126.14, 126.5, 126.7, 127.4, 127.6, 127.7, 128.7, 130.8, 135.6, 137.5, 141.3. LRMS−EI m/z (relative intensity) 252 (10, M^+), 210 (16), 209 (100), 178 (18), 165 (19), 131 (83), 103 (70), 91 (28), 77 (18). TOF−HRMS calcd for $C_{18}H_{20}O$ (M^+) 252.1509, found 252.1516.

(*E*)-2,2-Dimethyl-1-(2-stilbenyl)propan-1-ol (24). The product was obtained as a colorless oil (20% EtOAc/hexanes, 61.9 mg, 48%). IR (neat): $\bar{\nu}_{max}$ 3451 (br), 3026, 2954, 1599, 1495, 1479, 1448, 1363, 1176, 1043, 1004 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.96 (s, 9H), 1.85 (br s, 1H), 4.96 (s, 1H), 6.91 (d, 1H, J = 15.9 Hz), 7.23−7.32 (m, 3H), 7.33−7.41 (m, 2H), 7.44−7.59 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.3, 37.0, 76.9, 126.0, 126.5, 127.0, 127.2, 127.4, 127.6, 127.9, 128.7, 130.6, 136.5, 137.6, 140.1. LRMS−EI m/z (relative intensity) 266 (5, M^+), 210 (17), 209 (100), 178 (18), 165 (16), 31 (85), 103 (66), 91 (25), 77 (15), 57 (13). TOF−HRMS calcd for $C_{19}H_{22}O$ (M^+) 266.1665, found 266.1668.

(*E*)-(4,5-Dimethoxy-2-Stilbenyl)(phenyl)methanol (28). The product was obtained as a yellow sticky gum (30% EtOAc/hexanes, 0.65 g, 99%). IR (neat): $\bar{\nu}_{max}$ 3499 (br), 3026, 2934, 1602, 1509, 1449, 1274, 1202, 1097 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 1H), 3.88 (s, 3H), 3.97 (s, 3H), 6.22 (s, 1H), 6.88 (d, 2H, J = 16.2 Hz), 7.05 (s, 1H), 7.12 (s, 1H), 7.24−7.50 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.8, 55.9, 72.3, 108.7, 110.0, 125.4, 126.4, 126.6, 127.5, 128.1, 128.5, 128.6, 129.4, 133.8, 137.4, 143.3, 148.4, 148.9. LRMS−EI m/z (relative intensity) 346 (23, M^+), 328 (13), 256 (18), 255 (100), 254 (31), 224 (46), 223 (24), 165 (26), 149 (23), 105 (28), 91 (29), 77 (33), 57 (23). TOF−HRMS calcd for $C_{23}H_{22}O_3$ (M^+) 346.1563, found 346.1557.

(*E*)-(2-(4-Methoxystyryl)phenyl)methanol (42). The product was obtained as a yellow oil (10% EtOAc/hexanes, 0.20 g, 70%). IR (neat): $\bar{\nu}_{max}$ 3421 (br), 3058, 3030, 1606, 1249, 1175 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.23 (s, 1H) 3.82 (s, 3H), 6.19 (s, 1H), 6.86−6.90 (m, 3H), 7.22−7.39 (m, 10H), 7.54 (d, 1H, J = 6.0 Hz), 7.58 (d, 1H, J = 6.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.3, 73.3, 114.1, 123.7, 126.1, 126.8, 127.1, 127.4, 127.8, 127.9, 128.5, 130.2, 130.7, 136.1, 140.5, 143.1, 159.3. LRMS−EI m/z (relative intensity) 316 (2, M^+), 167 (26), 149 (100), 121 (25), 91 (5), 77 (7), 71 (37), 69 (38), 57 (37). TOF−HRMS calcd for $C_{22}H_{20}O_2Na$ $(M + Na)^+$ 339.1356, found 339.1357.

(*E*)-(2-(4-Chlorostyryl)phenyl)methanol (43). The product was obtained as a white solid (10% EtOAc/hexanes, 61.6 mg, 70%). mp (EtOAc/hexanes) 66−68 °C. IR (neat): $\bar{\nu}_{max}$ 3421 (br), 3058, 3029, 2924, 2854, 1492 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 1H), 6.12 (s, 1H), 6.83 (d, 1H, J = 18.0 Hz), 7.28−7.36 (m, 12H), 7.44−7.50 (m, 1H), 7.53−7.59 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 73.5, 126.3, 126.6, 126.5, 126.2, 127.6, 127.7, 127.9, 128.0, 128.5, 128.8, 129.7, 133.3, 135.5, 135.8, 140.7, 143.0. LRMS−EI m/z (relative intensity) 322 (2, M+2), 320 (6, M^+), 195, (100), 177 (33), 149 (53), 125 (21), 97 (24), 91 (32), 77 (28), 69 (54). TOF−HRMS calcd for $C_{21}H_{17}ClO$ (M^+) 320.0962, found 320.0963.

(*E*)-(2-(4-Nitrostyryl)phenyl)methanol (44). The product was obtained as a yellow oil (10% EtOAc/hexanes, 47.4 mg, 71%). IR (neat): $\bar{\nu}_{max}$ 3544, 3393 (br), 3062, 3030, 2926, 1593, 1513, 1494, 1339 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$):δ 2.30 (br s, 1H), 6.17 (s, 1H), 6.94 (d, 1H, J = 16.1 Hz), 7.26−7.36 (m, 6H), 7.38−7.52 (m,

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3H), 7.54−7.62 (m, 3H), 8.18 (d, 2H, J = 8.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 73.6, 124.0, 126.4, 126.6, 126.9, 127.6, 128.1, 128.2, 128.4, 128.5, 126.7, 130.7, 134.7, 141.7, 142.9, 143.8, 146.7. LRMS−EI m/z (relative intensity) 331 (0.3, M^+), 227 (12), 167 (28), 149 (100), 97 (22), 83 (19), 77 (6), 71 (43), 69 (53), 57 (42). TOF−HRMS calcd for $C_{21}H_{17}NO_3$ (M^+) 331.1203, found 331.1207.

(*E*)-(2-Stilbenyl)methanol (21). To a stirred solution of **10** (0.43 g, 2.07 mmol) in absolute MeOH (10 mL) was added $NaBH_4$ (0.09 g, 2.27 mmol). This was stirred at room temperature for 30 min and then concentrated. Water (10 mL) and EtOAc (10 mL) were added, and the two phases were separated. The aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the product **21** as a white solid (0.39 g, 91%) which was recrystallized from EtOAc/hexanes. mp (EtOAc/hexanes) 89−91 °C. IR (neat): $\bar{\nu}_{max}$ 3332 (br), 3247, 3030, 2920, 2866, 1738, 1596, 1578, 1490, 1479, 1452, 1371, 1042 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (br s, 1H), 4.84 (d, 2H, J = 5.4 Hz), 7.05 (d, 1H, J = 15.9 Hz), 7.25−7.37 (m, 6H), 7.46 (d, 1H, J = 16.2 Hz), 7.53 (d, 2H, J = 7.5 Hz), 7.66 (d, 1H, J = 8.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 63.6, 125.3, 126.0, 126.7, 127.7, 127.8, 128.3, 128.6, 131.2, 136.3, 137.3, 137.8. TOF−HRMS calcd for $C_{15}H_{13}O$ ($M - H$)$^+$ 209.0972, found 209.0969.

(*E*)-1-(2-Stilbenyl)ethanol (22). To a stirred solution of **20** (0.16 g, 0.697 mmol) in absolute EtOH (10 mL) was added $NaBH_4$ (0.04 g, 1.05 mmol). This was stirred at room temperature for 30 min and then concentrated. Water (10 mL) and EtOAc (10 mL) were added, and the two phases were separated. The aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product which was further purified by column chromatography on silica (10% EtOAc/hexanes) to furnish **22** as a light yellow oil (0.12 g, 75%). IR (neat): $\bar{\nu}_{max}$ 3357 (br), 3026, 2973, 1599, 1493, 1448, 1369, 1259, 1071 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.52 (d, 3H, J = 6.3 Hz), 5.31 (q, 1H, J = 6.5 Hz), 6.97 (d, 1H, J = 15.9 Hz), 7.24−7.45 (m, 6H), 7.47−7.61 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.4, 67.2, 125.0, 125.6, 126.2, 126.6, 127.6, 127.8, 128.0, 128.7, 131.3, 135.0, 137.4, 143.0. LRMS−EI m/z (relative intensity) 224 (20, M^+), 209 (80), 178 (25), 165 (18), 133 (58), 131 (20), 115 (15), 105 (29), 103 (31), 91 (100), 77 (24). TOF−HRMS calcd for $C_{16}H_{16}O$ (M^+) 224.1196, found 224.1203.

(*E*)-2-(Methylsulfonyl)-1-(2-stilbenyl)ethanol (25). To a stirred solution of dimethyl sulfone (0.21 g, 2.18 mmol) in THF (15 mL) at −78 °C was added *n*-butyllithium (1.2 M in hexanes, 1.82 mL, 2.18 mmol) via syringe. After 1 h, a solution of (*E*)-2-styrylbenzaldehyde **10** (0.30 g, 1.45 mmol) in THF (5 mL) was added via syringe. The resulting mixture was warmed up to room temperature and stirred until the starting material was consumed as indicated by TLC. Then, the reaction was cooled to 0 °C. Water (15 mL) and EtOAc (15 mL) were added, and the two phases were separated. The aqueous layer was extracted with EtOAc (2 × 15 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude product which was further purified by column chromatography on silica (50% EtOAc/hexanes) to furnish **25** as a light yellow oil (0.18 g, 40%). IR (neat): $\bar{\nu}_{max}$ 3473 (br), 3027, 2928, 1599, 1495, 1292, 1127, 1056 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.00 (s, 3H), 3.10−3.25 (m, 2H), 3.38 (dd, 1H, J = 9.9, 14.7 Hz), 5.75 (d, 1H, J = 9.9 Hz), 6.97 (d, 1H, J = 15.9 Hz), 7.24−7.42 (m, 6H), 7.50−7.61 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.6, 61.5, 66.2, 124.0, 125.5, 125.5, 126.7, 128.1, 128.2, 128.6, 128.8, 132.6, 134.8, 136.8, 138.1. LRMS−EI m/z (relative intensity) 302 (11, M^+), 222 (20), 205 (20), 178 (27), 165 (14), 145 (20), 131 (100), 115 (21), 103 (26), 91 (53), 77 (18). TOF−HRMS calcd for $C_{17}H_{18}NaO_3S$ ($M + Na$)$^+$ 325.0869, found 325.0865.

(*E*)-(3,4-Dimethoxyphenyl)(2-stilbenyl)methanol (26). To a solution of 4-bromoveratrole (0.15 mL, 1.05 mmol) in THF (10 mL) was added *t*-butyllithium (1.7 M in pentane, 1.23 mL, 2.09 mmol) via syringe, and the reaction mixture was stirred for 30 min at −78 °C. At that time, a solution of (*E*)-2-styrylbenzaldehyde **10** (0.22 g, 1.05 mmol) in THF (5 mL) was added via syringe. The resulting mixture was warmed up to room temperature and stirred until the starting material was consumed as indicated by TLC. Water (10 mL) and EtOAc (10 mL) were added, and the two phases were separated. The aqueous layer was extracted with EtOAc (2 × 15 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product which was further purified by column chromatography on silica (15% EtOAc/hexanes) to furnish the desired product **26** as a light yellow oil (0.16 g, 44%). IR (neat): $\bar{\nu}_{max}$ 3503 (br), 3001, 2925, 2852, 1596, 1512, 1463, 1450, 1417, 1258, 1234, 1137, 1026 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.66 (br s, 1H), 3.74 (s, 3H), 3.78 (s, 3H), 6.04 (s, 1H), 6.71−6.92 (m, 4H), 7.18−7.41 (m, 8H), 7.46−7.51 (m, 1H), 7.53−7.56 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.8, 55.9, 73.3, 110.2, 111.1, 120.2, 126.1, 126.4, 126.6, 126.8, 127.8, 127.9, 128.7, 131.2, 135.8, 137.4, 140.1. LRMS−EI m/z (relative intensity) 346 (2, M^+), 269 (19), 268 (100), 253 (8), 240 (12), 225 (21), 209 (29), 193 (18), 181 (19), 165 (50), 152 (34), 126 (15), 91 (14), 82 (15), 76 (27), 57 (20). TOF−HRMS calcd for $C_{23}H_{22}O_3$ (M^+) 346.1563, found 346.1560.

(*E*)-(2-Stilbenyl)(4-(trifluoromethoxy)phenyl)methanol (27). A solution (1.50 M) of the Grignard solution was prepared by mixing 1-bromo-4-(trifluoromethoxy)benzene (0.67 mL, 4.51 mmol) and magnesium (0.37 g, 1.54 mmol) in Et_2O (3 mL). To this mixture was added iodine as catalyst, and the mixture was stirred for 15 min at room temperature. After bubbles disappeared, the Grignard solution (0.51 mL, 0.77 mmol) was transferred to the solution of (*E*)-2-styrylbenzaldehyde **10** (0.80 g, 0.38 mmol) in Et_2O (3 mL). The reaction mixture was stirred for 1 h at 0 °C. Then the resulting mixture was warmed up to room temperature. Water (5 mL) and EtOAc (5 mL) were added, and the two phases were separated. The aqueous layer was extracted with EtOAc (2 × 10 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product which was further purified by preparative TLC (10% EtOAc/hexanes) to furnish the desired product **27** as a colorless oil (0.12 g, 87%). IR (neat): $\bar{\nu}_{max}$ 3356, 3028, 1506, 1450, 1254, 1220, 1162, 1017 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.21 (s, 1H), 6.94 (d, 1H, J = 16.2 Hz), 7.18 (d, 2H, J = 8.1 Hz), 7.23−7.47 (m, 12H), 7.60−7.64 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 72.7, 120.5 (q, J_{C-F} = 255.8 Hz), 120.9, 125.6, 126.6, 126.62, 127.2, 127.9, 127.94, 128.1, 128.3, 131.7, 136.0, 137.2, 140.4, 141.8, 148.5. LRMS−EI m/z (relative intensity) 370 (6, M^+), 352 (5), 280 (15), 279 (92), 278 (60), 195 (24), 194 (30), 178 (38), 165 (44), 152 (17), 105 (43), 91 (100), 77 (36). TOF−HRMS calcd for $C_{22}H_{17}F_3O_2$ (M^+) 370.1175, found 370.1170.

General Procedure for the Synthesis of Indane via Lewis Acid-Mediated Cyclization Followed by Nucleophilic Transfer from the Silyl Reagents. To a stirred solution of the *E*-(2-stilbenyl)methanols (0.02−0.03 g, 1 equiv) **11**, **21**−**28**, and **42**−**44** in solvents (CH_2Cl_2, PhMe, THF, MeCN, cyclohexane, 1,2-dimethoxyethane (DME), 1,4-dioxane, Et_2O) at 0 °C was added trialkylsilyl reagent (type and equivalent as indicated in each Table or Scheme). Then, a Lewis or Brønsted acid (type and equivalent as indicated in each Table or Scheme) was added, and the resulting mixture was stirred at 0 °C until the starting material was consumed as monitored on TLC. The reaction mixture was concentrated and purified by preparative TLC (EtOAc/hexanes) to furnish the desired product.

1,2-Diphenyl-1*H*-indene (12). The product was obtained as a light yellow oil (2% EtOAc/hexanes, 2.30 mg, 8%). IR (neat): $\bar{\nu}_{max}$ 2923, 2847, 1710, 1599, 1491, 1456 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.97 (s, 1H), 7.07−7.27 (m, 10H), 7.36−7.42 (m, 3H), 7.50 (d, 2H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.2, 121.1, 123.8, 125.4, 126.6, 126.7, 127.0, 127.3, 127.8, 128.0, 135.0, 140.0, 143.2, 149.1, 149.9. TOF−HRMS calcd for $C_{21}H_{16}$ (M^+) 268.1247, found 268.1255.

2,3-Diphenyl-1*H*-indene (13). The product was obtained as a light yellow oil (2% EtOAc/hexanes, 2.80 mg, 10%). IR (neat): $\bar{\nu}_{max}$ 3053, 3025, 2924, 2853, 1710, 1603, 1488, 1459, 1443, 1391 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93 (s, 2H), 7.19−7.29 (m, 8H), 7.35−7.42 (m, 5H), 7.54 (d, 1H, J = 6.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$):

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δ 41.2, 120.4, 123.6, 125.0, 126.0, 126.5, 126.9, 127.4, 127.8, 128.2, 128.3, 128.4, 128.8, 129.1, 129.4, 136.1, 136.6, 139.9, 141.1, 142.4, 146.9. TOF−HRMS calcd for $C_{21}H_{16}$ (M^+) 268.1247, found 268.1254.

***trans*-1,2-Diphenyl-2,3-dihydro-1*H*-indene (14).** The product was obtained as a light yellow oil (10% EtOAc/hexanes, 86.6 mg, 73%). IR (neat): $\bar{\nu}_{max}$ 3060, 3027, 1602, 1495, 1453 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.23 (dd, 1H, *J* = 10.0, 15.6 Hz), 3.41 (dd, 1H, *J* = 8.0, 15.7 Hz), 3.56−3.65 (m, 1H), 4.41 (d, 1H, *J* = 9.6 Hz), 6.91 (d, 1H, *J* = 7.5 Hz), 7.05−7.09 (m, 2H), 7.13−7.31 (m, 11H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.2, 56.7, 59.7, 124.1, 125.0, 126.4, 126.5, 126.7, 127.0, 127.5, 128.3, 128.34, 128.5, 142.6, 143.2, 143.4, 145.9. LRMS−EI *m*/*z* (relative intensity) 270 (55, M^+), 192 (56), 191 (27), 179 (93), 178 (100), 165 (16), 115 (9), 91 (13). TOF−HRMS calcd for $C_{21}H_{18}$ (M^+) 270.1403, found 270.1409.

***trans*-2,3-Diphenyl-2,3-dihydro-1*H*-inden-1-ol (16).** The product was obtained as a 1.7:1 mixture of diastereomer at C1 as colorless oil (10% EtOAc/hexanes, 17.6 mg, 80%). IR (neat): $\bar{\nu}_{max}$ 2258, 3028, 2899, 1601, 1495, 1476, 1453, 1266, 1208, 1108, 1050 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.31 (br s, 1H), 3.34 (dd, 1H, *J* = 8.6, 10.1 Hz), 3.70 (dd, 1H, *J* = 5.6, 9.2 Hz, minor), 4.33 (d, 1H, *J* = 9.9 Hz), 4.86 (d, 1H, *J* = 9.3 Hz, minor), 5.26 (d, 1H, *J* = 5.4 Hz, minor), 5.37 (d, 1H, *J* = 8.4 Hz), 6.93 (d, 1H, *J* = 7.5 Hz), 6.98−7.02 (m, 1H, minor), 7.06−7.19 (m, 3H), 7.19−7.39 (m, 20H), 7.46−7.53 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.4 (minor), 55.8, 61.5 (minor), 67.4, 76.8 (minor), 81.1, 123.5, 124.9, 125.2, 125.3, 126.6, 126.7, 127.2, 127.5, 127.53, 128.1, 128.3, 128.4, 128.5, 128.53, 128.56, 128.6, 129.1, 129.3, 137.7, 140.1, 132.2, 142.3, 143.0, 143.5, 143.9, 147.1. LRMS−EI *m*/*z* (relative intensity) 286 (14, M^+), 268 (11), 195 (100), 194 (25), 179 (15), 178 (19), 177 (16), 165 (26), 152 (12), 126 (6), 105 (10), 91 (12), 77 (9). TOF−HRMS calcd for $C_{21}H_{18}O$ (M^+) 286.1352, found 286.1351.

***trans*-1-Methyl-2-phenyl-2,3-dihydro-1*H*-indene (30).** The product was obtained as a light yellow oil (10% EtOAc/hexanes, 19.7 mg, 99%). IR (neat): $\bar{\nu}_{max}$ 3028, 2926, 1603, 1494, 1454, 1374, 1255, 1078 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.29 (d, 3H, *J* = 6.9 Hz), 3.05−3.15 (m, 2H), 3.19−3.34 (m, 2H), 7.15−7.26 (m, 5H), 7.31−7.37 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.6, 40.5, 47.1, 55.7, 123.1, 124.1, 126.4, 126.6, 127.7, 128.4, 142.2, 143.4, 147.3. LRMS−EI *m*/*z* (relative intensity) 208 (51, M^+), 207 (69), 193 (39), 191 (24), 179 (36), 178 (62), 165 (28), 133 (54), 115 (66), 105 (78), 91 (100), 77 (81), 57 (40). TOF−HRMS calcd for $C_{16}H_{15}$ ($M - H$)$^+$ 207.1168, found 207.1177.

***trans*-1-Isopropyl-2-phenyl-2,3-dihydro-1*H*-indene (31).** The product was obtained as a light yellow oil (10% EtOAc/hexanes, 15.3 mg, 50%). IR (neat): $\bar{\nu}_{max}$ 3020, 2958, 2927, 1603, 1456, 1261, 1073, 1031 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.85 (d, 6H, *J* = 6.8 Hz), 2.00−2.11 (m, 1H), 2.85−2.94 (m, 1H), 3.15−3.19 (m, 1H), 3.28−3.37 (m, 2H), 7.08−7.20 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 20.3, 22.5, 31.9, 41.4, 46.8, 59.9, 124.1, 124.6, 125.9, 126.2, 126.9, 128.4, 143.1, 145.1, 147.9. LRMS−EI *m*/*z* (relative intensity) 236 (18, M^+), 193 (100), 178 (26), 115 (53), 91 (24), 57 (16). TOF−HRMS calcd for $C_{18}H_{19}$ ($M - H$)$^+$ 235.1481, found 235.1486.

***trans*-1-*tert*-Butyl-2-phenyl-2,3-dihydro-1*H*-indene (32).** The product was obtained as a light yellow oil (10% EtOAc/hexanes, 34.7 mg, 85%). IR (neat): $\bar{\nu}_{max}$ 3025, 1954, 1603, 1477, 1453, 1364, 1227, 1031 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.99 (s, 9H), 2.84−2.93 (m, 2H), 3.43−3.53 (m, 2H), 6.97−7.03 (m, 2H), 7.07−7.29 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.8, 35.36, 40.1, 45.9, 65.8, 124.2, 125.6, 125.8, 126.1, 126.8, 127.1, 128.5, 143.9, 144.4, 149.6. LRMS−EI *m*/*z* (relative intensity) 250 (9, M^+), 194 (44), 193 (100), 178 (22), 116 (13), 115 (54), 91 (19), 57 (16). TOF−HRMS calcd for $C_{19}H_{21}$ ($M - H$)$^+$ 249.1638, found 249.1641.

***trans*-1-(Methylsulfonylmethyl)-2-phenyl-2,3-dihydro-1*H*-indene (33).** The product was obtained as a 2:1 mixture of unassignable cis and trans isomers as light yellow oil (30% EtOAc/hexanes, 28.0 mg, 50%). IR (neat): $\bar{\nu}_{max}$ 3026, 2927, 1459, 1294, 1126 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.65 (s, 3H, minor), 2.88 (s, 3H, major), 2.99−3.17 (m, 2H), 3.25−3.45 (m, 2H), 3.46−3.57 (m, 2H), 3.79−3.86 (m, 1H, minor), 4.57 (d, 1H, *J* = 9.0 Hz), 7.15 (s, 1H), 7.21−7.50 (m, 13H), 7.59 (d, 2H, *J* = 7.5 Hz), 7.95 (d, 1H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.8, 40.9, 41.9, 42.3, 47.4, 52.0, 56.0, 58.9, 121.3, 124.39, 124.41, 125.3, 125.7, 126.8, 127.1, 127.3, 127.4, 127.8, 128.0, 128.3, 128.8, 129.1, 133.8, 142.1, 142.8, 143.5, 145.4, 147.9. LRMS−EI *m*/*z* (relative intensity) 284 (7), 207 (13), 206 (60), 205 (64), 204 (100), 203 (77), 202 (44), 189 (13), 178 (15), 165 (10), 149 (10), 128 (16), 101 (23), 91 (46), 83 (14), 71 (19), 69 (24), 57 (32). TOF−HRMS calcd for $C_{17}H_{19}O_2S$ ($M + H$)$^+$ 287.1100, found 287.1097.

***trans*-1-(3,4-Dimethoxyphenyl)-2-phenyl-2,3-dihydro-1*H*-indene (34).** The product was obtained as a light yellow oil (10% EtOAc/hexanes, 23.2 mg, 60%). IR (neat): $\bar{\nu}_{max}$ 3025, 2934, 2835, 1591, 1516, 1454, 1418, 1257, 1234, 1138, 1028 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.25 (dd, 1H, *J* = 10.4, 15.6 Hz), 3.40 (dd, 1H, *J* = 8.0, 15.4 Hz), 3.51−3.60 (m, 1H), 3.72 (s, 3H), 3.85 (s, 3H), 4.34 (d, 1H, *J* = 9.8 Hz), 6.56 (d, 1H, *J* = 1.9 Hz), 6.63 (dd, 1H, *J* = 1.9, 8.2 Hz), 6.76 (d, 1H, *J* = 8.2 Hz), 6.96 (d, 1H, *J* = 7.4 Hz), 7.16−7.33 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.9, 55.8, 56.8, 59.5, 111.3, 111.6, 120.5, 124.1, 124.9, 126.4, 126.7, 126.9, 127.6, 128.3, 135.8, 142.6, 143.2, 145.9, 147.7, 148.9. LRMS−EI *m*/*z* (relative intensity) 330 (100, M^+), 299 (27), 239 (95), 238 (53), 208 (67), 192 (79), 191 (54), 178 (27), 165 (50), 152 (25), 149 (27), 126 (31), 115 (26), 91 (60), 57 (36). TOF−HRMS calcd for $C_{23}H_{22}O_2$ (M^+) 330.1614, found 330.1620.

***trans*-2-Phenyl-1-(4-(trifluoromethoxy)phenyl)-2,3-dihydro-1*H*-indene (35).** The product was obtained as a yellow oil (10% EtOAc/hexanes, 20.4 mg, 75%). IR (neat): $\bar{\nu}_{max}$ 3029, 2930, 1603, 1508, 1479, 1257, 1222, 1164, 1106, 1019 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.25 (dd, 1H, *J* = 10.1, 15.7 Hz), 3.43 (dd, 1H, *J* = 9.6, 16.5 Hz), 3.50−3.59 (m, 1H), 4.43 (d, 1H, *J* = 9.5 Hz), 6.90 (d, 1H, *J* = 7.4 Hz), 7.09 (s, 4H), 7.17−7.34 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.2, 56.9, 59.1, 116.7, 120.5 (q, J_{C-F} = 191.3 Hz), 120.8, 124.2, 124.8, 126.6, 126.7, 127.2, 127.4, 128.4, 129.6, 142.1, 142.6, 142.8, 145.2, 147.9. LRMS−EI *m*/*z* (relative intensity) 354 (52, M^+), 276 (63), 263 (100), 262 (88), 192 (23), 191 (37), 179 (44), 178 (98), 177 (35), 165 (43), 152 (20), 115 (21), 91 (43), 77 (12), 69 (19). TOF−HRMS calcd for $C_{22}H_{17}F_3O$ (M^+) 354.1226, found 354.1233.

***trans*-5,6-Dimethoxy-1,2-diphenyl-2,3-dihydro-1*H*-indene (36).** The product was obtained as a light yellow oil (10% EtOAc/hexanes, 27.1 mg, 86%). IR (neat): $\bar{\nu}_{max}$ 3027, 2933, 1605, 1502, 1453, 1301, 1216, 1097, 1031 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.17 (dd, 1H, *J* = 9.3, 15.3 Hz), 3.37 (dd, 1H, *J* = 8.1, 13.4 Hz), 3.50−3.60 (m, 1H), 3.73 (s, 3H), 3.91 (s, 3H), 4.37 (d, 1H, *J* = 8.7 Hz), 6.46 (s, 1H), 6.85 (s, 1H), 7.05−7.09 (m, 2H), 7.16−7.30 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.1, 56.0, 57.2, 60.0, 107.2, 108.0, 126.3, 126.4, 127.5, 128.2, 128.3, 128.4, 134.3, 137.1, 143.6, 143.9, 148.4, 148.5. LRMS−EI *m*/*z* (relative intensity) 330 (100, M^+), 315 (12), 299 (26), 253 (16), 252 (19), 239 (53), 238 (31), 208 (36), 165 (38), 149 (35), 126 (22), 115 (21), 91 (42), 57 (38). TOF−HRMS calcd for $C_{23}H_{23}O_2$ ($M + H$)$^+$ 331.1693, found 331.1700.

5,6-Dimethoxy-1,2-diphenyl-1*H*-indene (37). The product was obtained as a light yellow oil (10% EtOAc/hexanes, 26.3 mg, 72%). IR (neat): $\bar{\nu}_{max}$ 2934, 2832, 1577, 1597, 1556, 1459, 1464, 1312, 1215, 1101 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.78 (s, 3H), 3.91 (s, 3H), 4.89 (s, 1H), 6.75 (s, 1H), 6.97 (s, 1H), 7.11−7.26 (m, 9H), 7.45 (d, 2H, *J* = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.0, 56.1, 104.5, 107.8, 126.2, 126.6, 126.8, 127.6, 127.8, 128.4, 128.8, 135.1, 138.7, 140.3, 142.0, 147.7, 148.8, 148.9. LRMS−EI *m*/*z* (relative intensity) 328 (100, M^+), 313 (29), 297 (25), 252 (16), 241 (18), 239 (26), 207 (26), 191 (17), 165 (20), 164 (24), 149 (30), 126 (27), 120 (39), 113 (17), 107 (15), 91 (12), 71 (11), 57 (19). TOF−HRMS calcd for $C_{23}H_{21}O_2$ ($M + H$)$^+$ 329.1536, found 329.1533.

5,6-Dimethoxy-1,2-diphenyl-2,3-dihydro-1*H*-indene (38). To a stirred solution of indene **37** (20.5 mg, 0.062 mmol) in EtOAc under H_2 atmosphere (a H_2 balloon) was added Pd/C (0.05 equiv). The reaction mixture was stirred for 18 h. At that time, the resulting mixture was filtered through Celite, and the filtrate was concentrated and purified by preparative TLC using 20% EtOAc/hexanes to furnish the indane **38** as a yellowish oil (20.5 mg, 0.062 mmol, >99%). IR (neat): $\bar{\nu}_{max}$ 3027, 2932, 1606, 1502, 1453, 1301, 1219, 1098 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.18 (dd, 1H, *J* = 7.6, 15.3 Hz), 3.32 (dd,

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1H, J = 8.7, 15.1 Hz), 3.74 (s, minor), 3.76 (s, 3H), 3.92 (s, minor), 3.94 (s, 3H), 4.04 (dd, 1H, J = 8.1, 16.2 Hz), 4.37 (d, J = 9.0 Hz, minor), 4.60 (d, 1H, J = 8.1 Hz), 6.46 (s, minor), 6.58−6.60 (m, 2H), 6.66 (s, 1H), 6.80−6.82 (m, 2H), 6.94 (s, 1H), 6.96−7.05 (m, 6H), 7.16−7.25 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.9, 52.5, 56.0, 56.03, 56.9, 107.3, 108.4, 125.95, 125.97, 127.5, 127.6, 128.4, 129.0, 135.5, 136.9, 141.1, 141.2, 148.0, 148.5. LRMS−EI m/z (relative intensity) 330 (100, M^+), 315 (11), 299 (24), 252 (17), 239 (47), 238 (28), 208 (31), 165 (33), 126 (20), 115 (18), 91 (37). TOF−HRMS calcd for $C_{23}H_{22}O_2$ (M^+) 330.1614, found 330.1623.

***trans*-2-(4-Methoxyphenyl)-1-phenyl-2,3-dihydro-1*H*-indene (45).** The product was obtained as a yellow oil (2% EtOAc/hexanes, 16.6 mg, 58%). IR (neat): $\bar{\nu}_{max}$ 3058, 3027, 1248, 1179 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.20 (dd, 1H, J = 10.0, 15.6 Hz), 3.38 (dd, 1H, J = 7.9, 15.6 Hz), 3.52−3.61 (m, 1H) 3.77 (s, 3H), 4.35 (d, 1H, J = 6.0 Hz), 6.79 (d, 2H, J = 8.7 Hz), 6.90 (d, 1H, J = 7.3 Hz), 7.07−7.31 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.3, 55.2, 56.0, 59.9, 113.7, 124.1, 125.0, 126.5, 126.7, 126.9, 128.3, 128.4, 128.5, 130.7, 135.2, 142.7, 143.4, 146.0. LRMS−EI m/z (relative intensity) 300 (100, M^+), 192 (63), 179 (74), 165 (37), 139 (41), 121 (43), 97 (49), 77 (21), 71 (60), 69 (89), 57 (61). TOF−HRMS calcd for $C_{22}H_{20}O$ $(M)^+$ 300.1509, found 300.1516.

***trans*-2-(4-Chlorophenyl)-1-phenyl-2,3-dihydro-1*H*-indene (46).** The product was obtained as a yellow oil (2% EtOAc/hexanes, 10.1 mg, 58%). IR (neat): $\bar{\nu}_{max}$ 3063, 3027, 2932, 2851, 1600 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.20 (dd, 1H, J = 10.1, 15.6 Hz), 3.40 (dd, 1H, J = 8.0, 15.7 Hz), 3.53−3.62 (m, 1H), 4.35 (d, 1H, J = 9.0 Hz), 6.91 (d, 1H, J = 9.0 Hz), 7.05−7.32 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.1, 56.2, 59.9, 124.2, 125.0, 126.7, 126.9, 127.1, 128.5, 128.9, 132.1, 141.7, 142.4, 143.0. LRMS−EI m/z (relative intensity) 306 (12, M+2), 304 (37, M^+), 192 (32), 179 (100), 178 (80), 165 (23), 149 (12), 125 (14), 77 (12), 69 (14). TOF−HRMS calcd for $C_{21}H_{16}Cl$ $(M - H)^+$ 303.0935, found 303.0943.

***trans*-2-(4-Nitrophenyl)-1-phenyl-2,3-dihydro-1*H*-indene (47).** The product was obtained as a yellow oil (2% EtOAc/hexanes, 15.5 mg, 99%). IR (neat): $\bar{\nu}_{max}$ 3063, 3027, 2942, 2853, 1560, 1519, 1345 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.19 (dd, 1H, J = 10.0, 15.1 Hz), 3.39 (dd, 1H, J = 8.0, 15.7 Hz), 3.59−3.68 (m, 1H), 4.33 (d, 1H, J = 9.0 Hz), 6.85 (d, 1H, J = 7.2 Hz), 6.98 (d, 2H, J = 1.6 Hz), 7.00−8.02 (m, 6H), 7.27 (d, 2H, J = 7.2 Hz), 8.05 (d, 2H, J = 1.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.8, 56.5, 59.9, 123.7, 124.2, 125.0, 127.0, 127.1, 128.3, 128.6, 141.8, 142.5, 145.2, 146.7, 151.1. LRMS−EI m/z (relative intensity) 315 (24, M^+), 179 (64), 178 (56), 149 (65), 111 (27), 97 (56), 77 (43), 57 (71). TOF−HRMS calcd for $C_{21}H_{17}NO_2$ (M^+) 315.1254, found 315.1251.

***trans*-1-Azido-2,3-diphenyl-2,3-dihydro-1*H*-indene (48).** The product was obtained as a 9:1 mixture of diastereomers as light yellow oil (10% EtOAc/hexanes, 19.0 mg, 75%). IR (neat): $\bar{\nu}_{max}$ 3029, 2915, 2092, 1601, 1494, 1454, 1314, 1248, 1075, 1029 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.49 (dd, 1H, J = 9.4, 9.5 Hz), 3.79−3.95 (m, minor), 4.39 (d, 1H, J = 9.9 Hz), 4.76−4.86 (m, minor), 5.03 (d, 1H, J = 8.7 Hz), 5.25 (d, J = 7.8 Hz, minor), 6.96 (d, 1H, J = 7.2 Hz), 7.07 (d, 2H, J = 6.6 Hz), 7.16−7.40 (m, 12H), 7.47 (d, 1H, J = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.2 (minor), 56.7, 60.3 (minor), 63.9, 68.8 (minor), 70.9, 123.8, 125.3, 127.0, 127.4, 127.8, 127.9, 128.3, 128.4, 128.5, 128.6, 128.7, 129.0, 129.2, 139.5, 140.1, 141.8, 144.3. LRMS−EI m/z (relative intensity) 283 (44), 282 (69), 269 (12), 206 (89), 192 (50), 191 (29), 179 (73), 178 (100), 165 (51), 152 (19), 91 (32), 77 (21), 69 (14), 57 (17). TOF−HRMS calcd for $C_{21}H_{17}$ $(M - N_3)^+$ 269.1325, found 269.1320, calcd for $C_{21}H_{16}N$ $(M - N_2 - H)^+$ 282.1277, found 282.1275.

***trans*-1-Allyl-2,3-diphenyl-2,3-dihydro-1*H*-indene (49).** The product was obtained as a light yellow solid (2% EtOAc/hexanes, 22.0 mg, 68%). IR (neat): $\bar{\nu}_{max}$ 3062, 3026, 2920, 1639, 1601, 1492, 1475, 1452 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.00−2.02 (m, 1H), 2.43−2.53 (m, 1H), 2.59−2.66 (m, 1H), 3.22 (t, 1H, J = 10.2 Hz), 3.46−3.59 (m, 2H), 3.90 (t, 1H, J = 8.4 Hz), 4.37 (d, 1H, J = 10.2 Hz), 4.73 (d, 1H, J = 9.3 Hz), 4.79 (d, 1H, J = 18.3 Hz), 4.91 (d, 1H, J = 9.9 Hz), 5.01 (d, 1H, J = 9.9 Hz), 5.07 (d, 1H, J = 17.1 Hz), 5.62−5.84 (m, 2H), 6.89−6.96 (m, 2H), 7.02 (d, 2H, J = 6.9 Hz), 7.16−7.29 (m, 21H), 7.33−7.54 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 35.2, 36.2, 48.5, 50.1, 53.5, 59.1, 59.3, 62.6, 116.2, 116.9, 123.5, 124.8, 124.9, 125.1, 126.4, 126.95, 126.99, 128.17, 128.26, 128.3, 128.4, 128.5, 128.6, 128.7, 136.1, 137.0, 140.3, 142.0, 143.3, 145.2, 145.5, 145.9, 146.0. TOF−HRMS calcd for $C_{24}H_{22}$ (M^+) 310.1716, found 310.1714.

***trans*-1-Chloro-2,3-diphenyl-2,3-dihydro-1*H*-indene (50).** The product was obtained as a light orange oil (5% EtOAc/hexanes, 18.9 mg, 59%). IR (neat): $\bar{\nu}_{max}$ 3060, 3028, 2920, 1709, 1601, 1494, 1475, 1453 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.69 (t, 1H, J = 9.3 Hz), 4.00 (dd, 1H, J = 6.0, 9.0 Hz, minor), 4.42 (d, 1H, J = 9.9 Hz), 4.91 (d, 1H, J = 10.2 Hz, minor), 5.49 (d, 1H, J = 8.7 Hz), 5.60 (d, 1H, J = 5.4 Hz, minor), 6.94 (d, 4H, J = 7.2 Hz), 7.02−7.40 (m, 14H), 7.52 (t, 3H, J = 9.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.8 (minor), 57.4, 60.6 (minor), 66.90, 66.92 (minor), 67.5, 124.8, 124.9, 125.4, 126.6, 127.0, 127.2, 127.4, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 129.0, 129.3, 129.4, 137.4, 139.0, 140.8,141.8, 142.3, 143.9, 146.9. TOF−HRMS calcd for $C_{21}H_{17}$ $(M - Cl)^+$ 269.1325, found 269.1327.

***trans*-1-Bromo-2,3-diphenyl-2,3-dihydro-1*H*-indene (51).** The product was obtained as a light yellow oil (5% EtOAc/hexanes, 26.4 mg, 72%). IR (neat): $\bar{\nu}_{max}$ 3060, 3028, 2925, 1724, 1602, 1493, 1453 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.82−3.91 (m, 2H), 4.48 (d, 1H, J = 9.3 Hz), 4.83 (d, 1H, J = 10.2 Hz, minor), 4.91 (d, 1H, J = 10.2 Hz), 5.60 (d, 1H, J = 8.7 Hz), 5.78 (d, 1H, J = 5.1 Hz, minor), 6.90−6.95 (m, 2H), 7.07 (d, 2H, J = 6.6 Hz), 7.24−7.40 (m, 19H), 7.49−7.56 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.6 (minor), 57.7, 58.3, 60.2 (minor), 60.7 (minor), 67.7, 124.7 (minor), 124.9, 125.4 (minor), 125.8, 127.0, 127.1, 127.4, 127.7, 127.8, 128.0, 128.1, 128.50, 128.51, 128.6, 128.7, 129.0, 129.1, 129.3, 138.3, 139.2, 140.4, 141.9, 142.2, 142.7, 144.0, 147.0. TOF−HRMS calcd for $C_{21}H_{17}$ $(M - Br)^+$ 269.1325, found 269.1320.

***trans*-1-Iodo-2,3-diphenyl-2,3-dihydro-1*H*-indene (52).** The product was obtained as a light pink oil (5% EtOAc/hexanes, 13.7 mg, 33%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.23 (dd, 1H, J = 6.0, 12.0 Hz, minor), 3.96 (t, 1H, J = 9.2 Hz), 4.56−4.61 (m, 2H), 5.74 (d, 1H, J = 9.0 Hz), 5.99 (d, 1H, J = 5.4 Hz, minor), 6.84 (d, 1H, J = 7.5 Hz, minor), 6.89 (d, J = 7.2 Hz, 1H), 7.00−7.42 (m, 14H), 7.46−7.55 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 34.9, 43.5 (minor), 52.0 (minor), 59.2, 59.8 (minor), 69.1, 124.3, 124.8, 125.4, 127.0, 127.2, 127.4, 127.6, 127.8, 128.1, 128.2, 128.45, 128.50, 128.6, 128.71, 128.78, 128.81, 129.1, 139.4, 139.9, 142.0, 143.5, 143.8, 144.5. TOF−HRMS calcd for $C_{21}H_{17}$ $(M - I)^+$ 269.1325, found 269.1333.

***trans*-1-Azido-2-(4-methoxyphenyl)-3-phenyl-2,3-dihydro-1*H*-indene (53a).** The product was obtained as a yellow oil (2% EtOAc/hexanes, 16.5 mg, 42%). IR (neat): $\bar{\nu}_{max}$ 3028, 2092, 1248, 1178 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.43 (t, 1H, J = 9.0 Hz), 3.77 (s, 3H), 4.34 (d, 1H, J = 9.0 Hz), 4.98 (d, 1H, J = 12.0 Hz), 6.84 (dd, 2H, J = 3.0, 6.9 Hz), 6.95 (d, 1H, J = 9.0 Hz), 7.05−7.08 (m, 2H), 7.15−7.38 (m, 7H), 7.46 (d, 1H, J = 6.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2, 56.7, 63.3, 70.9, 114.1, 123.8, 125.3, 126.9, 127.7, 128.5, 128.9, 128.9, 131.3, 141.1, 141.8, 144.3, 158.8. LRMS−EI m/z (relative intensity) 314 (23), 313 (100, $(M-N_2)^+$), 312 (79), 206 (86), 179 (95), 178 (95), 165 (45), 121 (90), 91 (20), 77 (30). TOF−HRMS calcd for $C_{22}H_{19}N_3O$ (M^+) 341.1523, found 341.1522.

***cis*-1-Azido-2-(4-methoxyphenyl)-3-phenyl-2,3-dihydro-1*H*-indene (53b).** The product was obtained as a yellow oil (2% EtOAc/hexanes, 7.46 mg, 19%). IR (neat): $\bar{\nu}_{max}$ 3028, 2094, 1247, 1179 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.73−3.78 (m, 4H), 4.77 (d, 1H, J = 12.0 Hz), 5.03 (d, 1H, J = 6.0 Hz), 6.93 (d, 2H, J = 18.0 Hz), 6.99−7.02 (m, 1H), 7.13−7.35 (m, 9H), 7.33−7.35 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2, 59.7, 68.9, 113.7, 124.8, 125.6, 126.9, 127.5, 128.4, 128.6, 129.0, 129.5, 130.2, 139.6, 141.6, 147.1, 158.7. LRMS−EI m/z (relative intensity) 341 (M^+), 314 (23), 313 (100), 312 (73), 206 (62), 179 (65), 178 (90), 165 (47), 149 (54), 121 (830, 97 (36), 77 (35). TOF−HRMS calcd for $C_{22}H_{19}N_3O$ (M^+) 341.1523, found 341.1538.

***trans*-1-Azido-2-(4-chlorophenyl)-3-phenyl-2,3-dihydro-1*H*-indene (54a).** The product was obtained as a yellow oil (2% EtOAc/hexanes, 6.41 mg, 47%). IR (neat): $\bar{\nu}_{max}$ 3328, 2921, 2094, 1600, 1492 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.45 (t, 1H, J = 9.0 Hz), 4.34

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(d, 1H, J = 9.0 Hz), 4.99 (d, 1H, J = 9.0 Hz), 6.96 (d, 1H, J = 9.0 Hz), 7.06 (d, 2H, J = 6.0 Hz), 7.17−7.40 (m, 9H), 7.47 (d, 1H, J = 6.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.8, 63.4, 70.7, 123.9, 125.3, 127.2, 127.9, 128.5, 128.7, 128.9, 129.1, 129.3, 133.2, 137.9, 139.9, 141.4, 144.0. LRMS−EI m/z (relative intensity) 345 (1, M^+), 319 (20), 318 (33), 317 (60), 316 (70), 206 (58), 192 (58), 179 (75), 178 (100), 165 (46), 140 (14), 125 (21), 77 (15). TOF−HRMS calcd for $C_{21}H_{15}ClN$ $(M - N_2 - H)^+$ 316.0888, found 316.0903.

***cis*-1-Azido-2-(4-chlorophenyl)-3-phenyl-2,3-dihydro-1*H*-indene (54b).** The product was obtained as a yellow oil (2% EtOAc/hexanes, 2.45 mg, 18%). IR (neat): $\bar{\nu}_{max}$ 3750, 3610, 3029, 2924, 2100, 1711, 1492 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.75 (t, 1H, J = 9.0 Hz), 4.77 (d, 1H, J = 9.0 Hz), 5.06 (d, 1H, J = 6.0 Hz), 7.00 (s, 1H), 7.13 (d, 1H, J = 9.0 Hz), 7.26−7.36 (m, 10H), 7.475 (d, 1H, J = 3.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.6, 59.8, 68.5, 124.8, 125.7, 127.1, 127.7, 128.4, 128.3, 128.7, 129.7, 130.6. LRMS−EI m/z (relative intensity) 345 (1, M^+), 319 (20), 318 (32), 317 (58), 316 (67), 206 (460, 179 (74), 178 (100), 165 (46), 140 (12), 127 (12), 125 (20), 77 (16). TOF−HRMS calcd for $C_{21}H_{15}ClN$ $(M - N_2 - H)^+$ 316.0888, found 316.0896.

Quantum Chemical Calculations. Quantum chemical calculations were performed using the M062X density functional theory (DFT) method, with the 6-31+G(g,p) basis set, and a polarizable continuum solvent model (PCM) of CH_2Cl_2. All minima and transition states were confirmed from frequency calculations, the former showing all positive frequencies and the latter a single negative frequency. The thermochemically corrected free energies are reported in Figure 2.

■ ASSOCIATED CONTENT

Supporting Information

General information, copies of ^{1}H and ^{13}C NMR spectra of all new compounds, the absolute energies and the vibrational frequencies and intensities of all stationary points obtained on the reaction pathway, and the Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(28) Because of the presence of some unidentifiable byproducts from the reaction which were difficult to separate, only about 30% of the pure compound **41** could be consistently isolated by chromatography on silica when DMF stored over 4 Å molecular sieves was employed as solvent. However, use of the reagent-grade solvent DMF, without additional purification or special storage, gave a better yield of 93%.

(29) At 0 °C, similar yields (70% versus 71%) of **46** were obtained from **43** when 1.5 equiv and 15 mol % of $BF_3{\cdot}Et_2O$ was employed.

(30) The temperature was chosen from the work by Snyder (see ref 20).
(31) It is normally difficult to separate the resonance and field effects of a group or substituent. A chloro substituent on an aromatic ring is denoted to be +*M* for electron-donating ability due to resonance and −*I* for electron-withdrawing ability due to inductive field effect. For groups which are both −*I* and +*M*, it is particularly difficult to predict whether resonance or field effects will predominate in the reaction conditions. For further discussion, see: Smith, , M. B.; March, , J. In *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 6th ed.; John Wiley & Sons, Inc.: NJ, **2007**, pp 19−22, 46−48, 396−397, 485−486, 668, and references cited therein.
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