Unexpected Reactivity of 3-(Phenylethynyl)-1*H*-indenes towards Nucleophiles: Noncatalytic Addition to Triple Bond with or without Double Bond Migration

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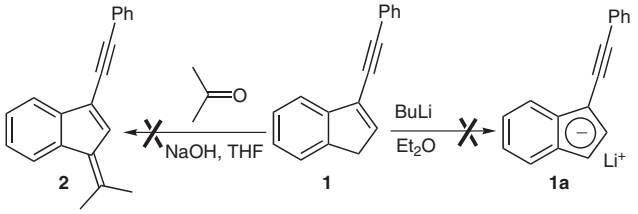
Abstract: When studying the chemical properties of (3-phenylethynyl)-1*H*-indenes, a new reaction was discovered, namely, nucleophilic addition to conjugated enynes accompanied in some cases by migration. The reaction takes place under mild conditions and is not catalyzed by transition metal complexes. A putative reaction mechanism via an allene intermediate is discussed.

Key words: alkynes, allenes, enynes, nucleophilic additions, rearrangements

Substituted indenes are widely used both in organic synthesis and as ligands for the preparation of organometallic compounds.[1] Thousands of alkyl-,[2] alkenyl-,[3] and arylindenes[4] and diverse indenes containing heteroatom(s) in the side chain[3,5] have now been prepared. However, alkynylindenes remain barely described,[6] which accounts for our interest in these compounds.

During our work on the synthesis and study of acetylenylindenes, we prepared (3-phenylethynyl)-1*H*-indene (**1**) and attempted to convert it into the corresponding dimethylfulvene **2**. First, we investigated the two most popular approaches to this synthesis: the transformation of indene into the lithium salt followed by treatment with acetone and the base-catalyzed reaction of indene with acetone (Scheme 1).

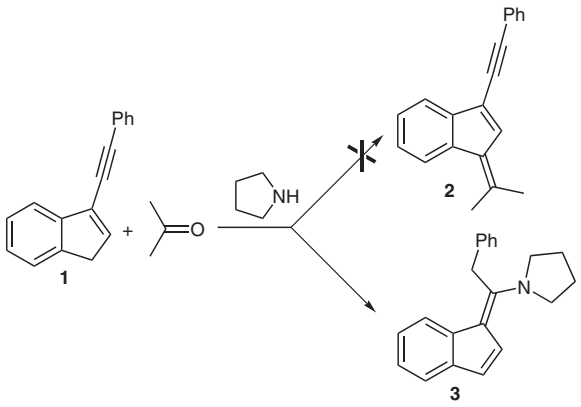


Scheme 1

Unexpectedly, neither of these reactions gave the desired product; moreover, it was impossible to isolate the lithium derivative **1a** (Scheme 1). The reaction of **1** with *n*-butyllithium gave unidentified products, presumably polymers.

This fact is surprising, because, to our knowledge, all 3-substituted indenes known to date are able to form lithium salts which are quite stable under inert atmosphere.

Therefore, we resorted to a substantially milder method for the synthesis of fulvenes,[7] which involves the reaction of **1** with acetone in the presence of pyrrolidine. This did not give the desired fulvene either; however, compound **3**, which can be regarded as resulting from the addition of pyrrolidine to the indene **1** triple bond followed by isomerization, was isolated quantitatively (Scheme 2).



Scheme 2

The molecular structure of **3** was determined by X-ray diffraction (Figure 1). The molecule has an *E*-configuration; no significant deviations of the bond lengths and angles from the normal values were detected.

To the best of our knowledge, no data on the addition of secondary amines to acetylenes and enynes *not catalyzed by transition metals* has been reported previously; hence, the formation of **3** is a new outcome in this area. This article describes the study of the reaction of (3-phenylethynyl)-1*H*-indene (**1**) and some of its analogues with amines and other nucleophilic reagents in order to determine the synthetic potential and to elucidate the most likely mechanism of this reaction.

We prepared 3-(phenylethynyl)-1*H*-indene (**1**) by the reaction of PhC≡CMgBr with indan-1-one followed by hydrolysis and dehydration. Substituted indanones, 2-methylindan-1-one, 4,7-dimethylindan-1-one, and 2,4,7-

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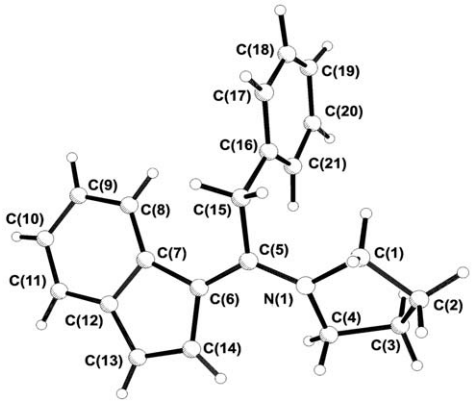
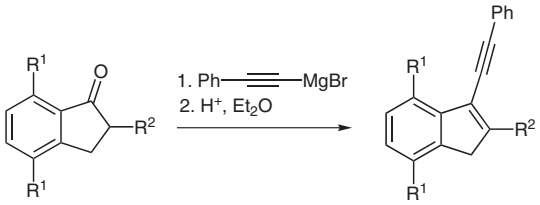


Figure 1 Molecular structure of **3**

trimethylindan-1-one, react similarly (Table 1). The newly prepared 3-(phenylethynyl)-1*H*-indenes **1**, **4**, **5**, and **6** are quite air-stable crystalline materials.

Table 1 3-(Phenylethynyl)-1*H*-indenes **1**, **4**–**6**



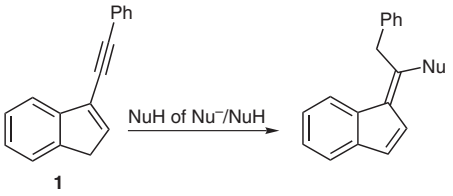
Product	R^1	R^2	Yield (%)
1	H	H	57
4	H	Me	67
5	Me	H	71
6	Me	Me	85

The reaction of indene **1** with an equivalent amount of pyrrolidine gives adduct **3** in a nearly quantitative yield. Compound **1** was also found to react with dimethylamine, sodium ethoxide in ethanol, *t*-BuSNa/THF, and $(EtO)_2PONa$/THF to give products **7**–**10** with structures similar to **3** (Table 2). All of the reactions give products in high yields (88–94%). In the cases of potassium *tert*-butyl thiolate and sodium diethyl phosphonate high product yields were attained only upon the presence of substantial amounts of *tert*-butyl mercaptan and diethyl phosphite.

However, the reaction of **1** with amines is not always stereo- and regioselective giving only one product, as in the case of **3** and **7**. Some other amines react to give adduct mixtures. For example, *tert*-butylamine forms a mixture of two isomeric fulvenes **11** and **12**, and piperidine yields three reaction products, two of which are isomeric fulvenes **13** and **14**, while the third one is vinylindene **15** (Table 3). Arylamines and hydrazines do not react with **1**.

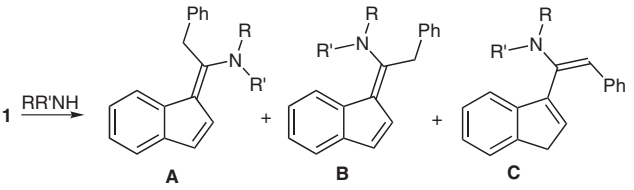
Substituents in positions 2 and/or 4 (7) of the indenyl ring are known to hamper the formation of substituted fulvenes.[8] Therefore, it was pertinent to find out whether fulvenes similar to **A** and **B** would arise upon the reaction of indenes **4**–**6** with nucleophiles. We studied the reactions of **4**–**6** with a standard set of N-, O-, S- and P-nucleophiles and found that only vinylindene products of type **C** are formed in each case. Yields are generally high (Scheme 3, Table 4). Thus, the lack of possibility for the formation of type **A** and **B** fulvenes does not preclude the reaction giving products of type **C**.

Table 2 Addition of Nucleophiles to 3-(Phenylethynyl)-1*H*-indene (**1**)

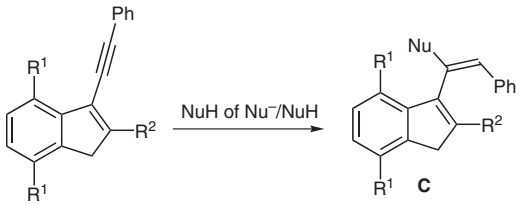


Product	Nu	Yield (%)
3		93
7	NMe_2	93
8	OEt	88
9	$SCMe_3$	96
10	$P(O)(OEt)_2$	94

Table 3 Reaction of *t*-$BuNH_2$ and Piperidine with 3-(Phenylethynyl)-1*H*-indene (**1**)



R	R′	Product type A; Yield (%)	Product type B; Yield (%)	Product type C; Yield (%)
t-Bu	H	**11**; 12	**12**; 69	0
	$-(CH_2)_4-$	**13**; 10	**14**; 15	**15**; 59



Scheme 3

Considering the experimental data, the reaction mechanism shown in Scheme 4 appears most likely. For simplicity, the reaction of **1** with pyrrolidine is presented. In the first stage, 3-(phenylethynyl)-1*H*-indene (**1**) partially

Table 4 Interaction of Substituted 3-(Phenylethynyl)-1*H*-indenes with Nucleophiles[a]

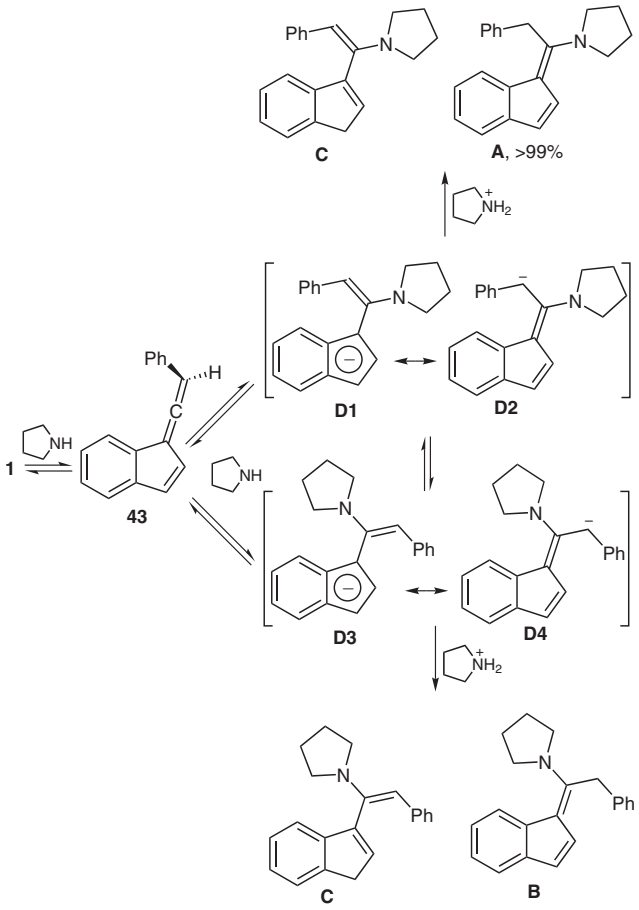
Nucleophilic reagent	Solvent	Product, yield (%)		
		4	**5**	**6**
$NHMe_2$	Et_2O	**16**, 95	**17**, 98	**18**, 82
$NHEt_2$	Et_2O	**19**, 93	**20**, 89	**21**, 85
n-$BuNH_2$	Et_2O	**22**, 81	**23**, 76	**24**, 90
	Et_2O	**25**, 81	**26**, 92	**27**, 98
	Et_2O	**28**, 95	**29**, 94	**30**, 92
	Et_2O	**31**, 85	**32**, 98	**33**, 96
EtONa/EtOH	EtOH	**34**, 95	**35**, 89	**36**, 90
t-BuSNa/*t*-BuSH	THF	**37**, 86	**38**, 90	**39**, 71
$(EtO)_2PONa$/ $(EtO)_2POH$	THF	**40**, 81	**41**, 96	**42**, 84

[a] Reactions conducted at 20 °C.

isomerizes into allene **43**. This process is highly probable in view of the fact that the reactions of **1** with pyrrolidine or other nucleophiles take place in basic media. Compound **43** reacts with a pyrrole molecule to give anion **D**. Anion **D** can be represented as two resonance structures, **D1** and **D2**, illustrating two ways of the protonation of **D** leading both fulvenes and vinylindenes.[9]

Note that the attack by the nucleophile on fulvene **43** should occur stereoselectively as the *anti*-addition with respect to the phenyl group in order to minimize the steric strain in the transition state. Hence isomers **C** of compounds **16**–**42** are formed. It is also noteworthy that the attack by the nucleophile on allene **43** should be immediately followed by rotation of the PhHC= group about the C–C bond giving rise to anion **D** (Scheme 4). In this rotation, the pyrrolidine group may move either toward the indene six-membered ring or in the opposite direction. The latter option is more likely, as in this case, the steric repulsion between the pyrrolidine group and the indenyl fragment would be minimal. Hence, the reaction of **1** with pyrrolidine gives *E*-isomer of **3** rather than *Z*-isomer. Then the protonation of conformer **D3**-**4** appears to be the obvious route to the *Z*-isomer (Scheme 4).

If our assumption concerning the mechanism is valid, compounds structurally related to 3-(phenylethynyl)-1*H*-indene (**1**) but incapable of isomerization to allene would not react with nucleophiles to give addition products. To verify this hypothesis, we prepared compounds **44**–**46** (Figure 2) and allowed them to react with pyrrolidine. In none of the cases, did the reaction occur, not even under drastic conditions.



Scheme 4

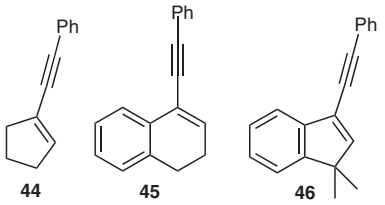


Figure 2

When studying the chemical properties of (3-phenylethynyl)-1*H*-indene (**1**), a new reaction was discovered – nucleophilic addition to conjugated enynes under mild conditions accompanied by migration of the multiple bonds locations. It was shown that the most probable reaction mechanism includes a 2,4-enyne to 1,3,4-triene rearrangement. The high synthetic potential of the reaction was demonstrated by the preparation of a number of functionalized indenes.

All manipulations were carried out under argon. The solvents were commercially available, purified by conventional means and distilled immediately prior to use. 2-Methylindanone,[10] 4,7-dimethylindanone,[11] 2,4,7-trimethylindanone,[11] and 3,3-dimethylindanone[12] were prepared according to published procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded at 20 °C on a Varian XR-400 spectrometer. The assignments in braces in the NMR data represent collective allotments for the preceding peaks.

3-(Phenylethynyl)-1*H*-indene (1); Typical Procedure

A solution of EtBr (12.7 mL, 0.17 mol) in Et_2O (200 mL) was added dropwise to Mg turnings (4.13 g, 0.17 mol). After stirring for 1 h of, phenylacetylene (20 mL, 0.18 mol) was added within 30 min at r.t. The resulting mixture was stirred for 1 h, refluxed for 2 h, cooled to 0 °C, and indan-1-one (15 g, 113 mmol) in Et_2O (50 mL) was added dropwise. After stirring overnight at r.t., the mixture was cooled to 0 °C, and 10% aq NH_4Cl was added until transparency. The pale yellow organic layer was separated, and the aqueous phase was extracted with Et_2O (4 × 50 mL). The combined organic phase was dried ($MgSO_4$) and evaporated at 80 °C/20 Torr. The residue was dissolved in Et_2O (150 mL), PTSA (0.2 g) was added, and the mixture was refluxed for 1 h. The resulting red-brown solution was cooled, washed with H_2O (200 mL) and aq Na_2CO_3 (5%, 20 mL), dried ($MgSO_4$), evaporated, and dried in vacuo. Hexane (40 mL) was added, and the mixture was refluxed until most of the brown oil had dissolved. The resulting clear solution was separated and cooled to 2 °C. After 1 d, the precipitate was filtered off, washed with pentane, and dried in vacuo, giving 13.9 g (57%) of the product; orange powder.

^{1}H NMR ($CDCl_3$): δ = 7.72 (d, ^3J = 7.3 Hz, 1 H), 7.66 (m, 2 H), 7.55 (d, ^3J = 7.2 Hz, 1 H), 7.46 (m, 4 H), 7.35 (t, ^3J = 7.3 Hz, 1 H) {H_{arom}}, 6.94 (t, ^3J = 2.2 Hz, 1 H, CH=), 3.57 (d, ^3J = 2.35 Hz, 2 H, CH_2).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 143.6, 142.5, 126.2, 123.0 (C=), 138.1, 131.6, 128.2, 126.4, 125.4, 123.5, 120.1 (CH=), 92.7, 83.4 (C≡), 38.5 (CH_2).

Anal. Calcd for $C_{17}H_{12}$ (216.28): C, 94.41; H, 5.59. Found: C, 94.35; H, 5.65.

2-Methyl-3-(phenylethynyl)-1*H*-indene (4)

In the same manner as described above, compound **4** (21.5 g) was obtained in 67% yield by the reaction of PhC≡CMgBr (0.30 mol) with 2-methylindan-1-one (20.1 g, 0.14 mol); orange crystals; mp 62 °C.

^{1}H NMR ($CDCl_3$): δ = 7.65 (m, 2 H), 7.57 (d, ^3J = 7.4 Hz, 1 H), 7.45–7.40 (group of m, 4 H), 7.39 (d, ^3J = 7.4 Hz, 1 H), 7.25 (t, ^3J = 7.4 Hz, 1 H) {H_{arom}}, 3.49 (s, 2,H, CH_2), 2.40 (s, 3 H, CH_3).

Anal. Calcd for $C_{18}H_{14}$ (230.30): C, 93.87; H, 6.13. Found: C, 93.80; H, 6.20.

4,7-Dimethyl-3-(phenylethynyl)-1*H*-indene (5)

In the same manner as described above, compound **5** (31.3 g) was obtained in 71% yield by the reaction of PhC≡CMgBr (0.27 mol) with 4,7-dimethylindan-1-one (28.8 g, 0.18 mol); yellow crystals; mp 84 °C.

^{1}H NMR ($CDCl_3$): δ = 7.62 (m, 2 H), 7.42 (m, 3 H), 7.09 (d, ^3J = 7.8 Hz, 1 H), 7.03 (d, ^3J = 7.8 Hz, 1 H) {H_{arom}}, 6.95 (t, ^3J = 2.4 Hz, 1 H, CH=), 3.41 (d, ^3J = 2.4 Hz, 2 H, CH_2), 2.89 (s, 3 H), 2.40 (s, 3 H) {CH_3}.

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 142.0, 140.2, 130.4, 129.6, 126.7, 123.5 (C=), 139.5, 131.2, 129.1, 128.3, 128.2, 126.6 (=CH), 92.0, 86.7 (C≡), 37.4 (CH_2), 18.6, 18.2 (CH_3).

Anal. Calcd for $C_{19}H_{16}$ (244.33): C, 93.40; H, 6.60. Found: C, 93.33; H, 6.47.

2,4,7-Trimethyl-3-(phenylethynyl)-1*H*-indene (6)

In the same manner as described above, compound **6** (10 g) was obtained in 85% yield by the reaction of PhC≡CMgBr (72 mmol) with 2,4,7-trimethylindan-1-one (7.9 g, 45 mmol); yellow crystals; mp 88 °C.

^{1}H NMR ($CDCl_3$): δ = 7.63 (m, 2 H), 7.41 (m, 3 H), 7.07 (d, ^3J = 7.6 Hz, 1 H), 6.96 (d, ^3J = 7.6 Hz, 1 H) {H_{arom}, =CH}, 3.31 (s, 2 H, CH_2), 2.87 (s, 3 H), 2.41 (s, 3 H), 2.36 (s, 3 H) {CH_3}.

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 151.4, 141.0, 140.3, 129.8, 128.4, 123.9, 121.4 (C=), 130.9, 129.0, 128.2, 127.8, 125.5 (=CH), 94.8, 86.1(C≡), 41.4 (CH_2), 18.5, 18.1, 15.9 (CH_3).

Anal. Calcd for $C_{20}H_{18}$ (258.36): C, 92.98; H, 7.02. Found: C, 92.90; H, 7.10.

1-[(1*E*)-1-(1*H*-Inden-1-ylidene)-2-phenylethyl]pyrrolidine (3)

Pyrrolidine (0.41 mL, 7 mmol) was added with stirring to a solution of **1** (1.08 g, 5 mmol) in Et_2O (10 mL). The mixture became green-brown. After stirring for 20 min, 10% aq NH_4Cl (20 mL) and Et_2O (20 mL) were added. The organic phase was separated, washed with aq NH_4Cl (10%, 5 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue (green-brown solid) was dried in vacuo to give 1.34 g (93%) of product.

^{1}H NMR ($CDCl_3$): δ = 7.58 (d, ^3J = 7.6 Hz, 1 H), 7.51 (d, ^3J = 7.8 Hz, 1 H), 7.43–7.27 (m, 5 H), 7.28 (d, ^3J = 5.2 Hz, 1 H), 7.16 (dd, ^3J = 7.6, 6.8 Hz, 1 H), 7.03 (dd, ^3J = 7.8, 6.8 Hz, 1 H), 6.84 (d, ^3J = 5.2 Hz, 1 H) {H_{arom}, CH=}, 4.52 (br s, 2 H, CH_2), 3.73 (m, 4 H, NCH_2), 1.90 (m, 4 H, NCH_2CH_2).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 153.2, 139.5, 136.4, 135.6, 113.2 (C=), 128.9, 127.9, 126.5, 125.9, 121.8, 121.7, 120.5, 120.1, 117.9 (CH=), 51.8 (NCH_2CH_2), 39.2 (CH_2), 25.1 (NCH_3CH_2).

Anal. Calcd for $C_{21}H_{21}N$ (287.40): C, 87.76; H, 7.37. Found: C, 87.71; H, 7.44.

(1*E*)-1-(1*H*-Inden-1-ylidene)-*N*,*N*-dimethyl-2-phenylethanamine (7)

In the same manner as described for **3**, adduct **7** (0.34 g) was obtained in 85% yield by the reaction of **1** (303 mg, 1.4 mmol) with 40% aq Me_2NH (0.18 mL, 1.6 mmol) in Et_2O (10 mL); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.48–7.36 (m, 6 H), 7.29–6.99 (m, 3 H), 6.93 (d, ^3J = 5.2 Hz, 1 H), 6.83 (d, ^3J = 5.2 Hz, 1 H) {H_{arom}, CH=}, 4.36 (s, 2 H, CH_2), 2.78 (s, 6 H, NCH_3).

Anal. Calcd for $C_{19}H_{19}N$ (261.36): C, 87.31; H, 7.33. Found: C, 87.26; H, 7.40.

(1*E*)-1-(1-Ethoxy-2-phenylethylidene)-1*H*-indene (8)

Compound **1** (2.16 g, 10 mmol) was added to a vigorously stirred solution of EtONa [obtained from Na (0.23 g, 10 mmol)] in EtOH (30 mL). After 4 h, 10% aq NH_4Cl (20 mL) and Et_2O (100 mL) were added. The organic phase was separated, washed with aq NH_4Cl (2 × 20 mL) and H_2O (2 × 20 mL), and dried ($MgSO_4$). The solvents were removed, and the residue was purified by column chromatography (hexane–CH_2Cl_2, 1:1; R_f = 0.5) to afford 2.18 g (88%) of the product; viscous red oil.

^{1}H NMR ($CDCl_3$): δ = 8.21 (m, 1 H), 7.45–7.25 (group of m, 8 H) {H_{arom}}, 6.84, 6.82 (AB, ^3J = 5.5 Hz, 2 H, CH=), 4.22 (s, 2 H, CH_2), 4.17 (q, ^3J = 7.1 Hz, 2 H, CH_2), 1.45 (t, ^3J = 7.1 Hz, 3 H, CH_3).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 159.7, 142.1, 136.7, 134.3, 122.0 (C=), 128.8, 128.1, 126.9, 126.6, 125.9, 125.3, 124.3, 124.0, 120.4 (CH=), 64.0 (OCH_2), 35.4 (CH_2), 15.2 (CH_3).

Anal. Calcd for $C_{19}H_{18}O$ (262.35): C, 86.99; H, 6.92. Found: C, 86.90; H, 7.01.

(1*E*)-1-[1-(*tert*-Butylsulfanyl)-2-phenylethylidene]-1*H*-indene (9)

tert-Butylmercaptan (1.24 mL, 11 mmol) was added to a suspension of NaH (0.24 g, 10 mmol) in a mixture of Et_2O (25 mL) and THF (3 mL). The resulting mixture was refluxed for 2 h and cooled to r.t., and **1** (2.16 g, 10 mmol) in Et_2O (10 mL) was added dropwise. After stirring for 4 h, the mixture was cooled, and 10% aq NH_4Cl (10 mL) was added. The organic phase was separated, dried ($MgSO_4$), evaporated, and finally dried in vacuo giving a dark red oily product (2.94 g, 96%).

^{1}H NMR ($CDCl_3$): δ = 7.57 (m, 1 H), 7.40 (m, 2 H), 7.29–7.24 (m, 1 H), 7.20–7.16 (m, 1 H), 6.69 (t, ^3J = 2.4 Hz, 1 H) {H_{arom}, CH=}, 4.52 (br s, 2 H, CH_2), 1.38 [s, 9 H, $C(CH_3)_3$].

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 144.5, 143.6, 142.9, 136.6, 129.8 (C=), 138.0, 133.7, 128.7, 127.8, 127.1, 125.7, 124.6, 123.5, 121.5 (CH=), 46.6 [$C(CH_3)_3$], 38.0 (CH_2), 31.3 [$C(CH_3)_3$].

Anal. Calcd for $C_{21}H_{22}S$ (306.46): C, 82.31; H, 7.24. Found: C, 82.25; H, 7.17.

Diethyl (1*E*)-1-(1*H*-Inden-1-ylidene)-2-phenylethylphosphonate (10)

Diethyl phosphite (0.76 mL, 5.5 mmol) was added to a suspension of NaH (0.12 g, 5 mmol) in Et_2O (20 mL). The resulting mixture was stirred for 2 h, cooled to –20 °C, and a solution of **1** (1.08 g, 5 mmol) in Et_2O (5 mL) was added. After 2 h, the mixture was treated with 10% aq NH_4Cl (20 mL). The organic phase was separated, dried ($MgSO_4$), evaporated, and finally dried in vacuo to give a pale brown oily product (1.67 g, 94%).

^{1}H NMR ($CDCl_3$): δ = 7.90 (d, ^3J = 16.8 Hz, 1 H), 7.58 (d, ^3J = 8.0 Hz, 1 H), 7.39 (m, 2 H), 7.28–7.15 (m, 5 H), 7.09 (d, ^3J = 8.0 Hz, 1 H), 6.72 (m, 1 H) {H_{arom}, CH=}, 4.20 (qd, J = 7.4, 2.2 Hz, 4 H, OCH_2CH_3), 3.63 (dd, J = 5.7, 2.1 Hz, 2 H, CH_2), 1.33 (t, ^3J = 7.4 Hz, 6 H, OCH_2CH_3).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 142.4, 138.6 (d), 134.7 (d), 124.9, 123.1 (C=), 144.5 (d), 132.9, 129.8, 128.9, 127.9, 125.6, 124.6, 123.5, 120.3 (CH=), 81.8 (OCH_2), 38.4 (CH_2), 16.0 (CH_3).

^{31}P NMR ($CDCl_3$): δ = 15.86.

Anal. Calcd for $C_{21}H_{23}O_3P$ (354.38): C, 71.17; H, 6.54. Found: C, 71.28; H, 6.66.

Reaction of 1 with *tert*-Butylamine; *N*-[(1*E*)-1-(1*H*-Inden-1-ylidene)-2-phenylethyl]-2-methyl-2-propanamine (11) and *N*-[(1*Z*)-1-(1*H*-Inden-1-ylidene)-2-phenylethyl]-2-methyl-2-propanamine (12)

In the same manner as described for **3**, the adduct with *tert*-butylamine was obtained in 81% yield (0.33 g) by the reaction of **1** (303 mg, 1.4 mmol) with *tert*-$BuNH_2$ (117 mg, 1.6 mmol) in Et_2O (10 mL); brown oil. A mixture of two inseparable *E*- and *Z*-isomers (1:6) was obtained.

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^{1}H NMR ($CDCl_3$): δ = 7.60 (d, ^3J = 7.4 Hz, 1 H), 7.54 (d, ^3J = 7.0 Hz, 1 H), 7.42–6.72 (group of m, 9 H) {H_{arom}, CH=}, 4.52 (s, 2 H, CH_2), 1.41 [s, 9 H, $C(CH_3)_3$].

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^{1}H NMR ($CDCl_3$): δ = 7.69 (d, ^3J = 7.2 Hz, 1 H), 7.54 (d, ^3J = 7.0 Hz, 1 H), 7.42–6.72 (group of m, 7 H), 6.83 (d, ^3J = 5.4 Hz, 1 H), 6.62 (d, ^3J = 5.4 Hz, 1 H) {H_{arom}, CH=}, 4.37 (s, 2 H, CH_2), 1.49 [s, 9 H, $C(CH_3)_3$].

Anal. Calcd for $C_{21}H_{23}N$ (289.41): C, 87.15; H, 8.01. Found: C, 87.22; H, 7.95.

Reaction of 1 with Piperidine 1-[(1*E*)-1-(1*H*-Inden-1-ylidene)-2-phenylethyl]piperidine (13), 1-[(1*Z*)-1-(1*H*-Inden-1-ylidene)-2-phenylethyl]piperidine (14), and 1-[(*E*)-1-(1*H*-Inden-3-yl)-2-phenylethenyl]piperidine (15)

In the same manner as described for **3**, the adduct with piperidine was obtained in 84% yield (0.36 g) by the reaction of **1** (303 mg, 1.4 mmol) with piperidine (136 mg, 1.6 mmol) in Et_2O (10 mL); brown oil. A mixture of three inseparable *E*- and *Z*-fulvene isomers **13**, **14** and enamine **15** was obtained in the ratio of 2:3:12.

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^{1}H NMR ($CDCl_3$): δ = 7.70–6.95 (group of m, 8 H), 6.85 (d, ^3J = 5.0 Hz, 1 H) {H_{arom}, CH=}, 4.58 (s, 2 H, CH_2), 3.70 (m, 4 H, NCH_2), 1.51 (m, 6 H, CH_2).

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^{1}H NMR ($CDCl_3$): δ = 7.70–6.95 (group of m, 8 H), 6.83 (d, ^3J = 5.0 Hz, 1 H) {H_{arom}, CH=}, 4.28 (s, 2 H, CH_2), 3.52 (m, 4 H, NCH_2), 1.51 (m, 6 H, CH_2).

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^{1}H NMR ($CDCl_3$): δ = 7.66 (d, ^3J = 7.0 Hz, 1 H), 7.58 (d, ^3J = 6.8 Hz, 1 H), 7.36–7.31 (m, 3 H), 7.13–7.05 (m, 4 H), 6.49 (t, ^3J = 2.0 Hz, 1 H) {H_{arom}, =CH}, 5.79 (s, 1 H, =C*H*Ph), 3.44 (d, ^3J = 2.0 Hz, 2 H, CH_2), 3.09 (br s, 4 H, NCH_2), 1.68 (m, 6 H, CH_2).

Anal. Calcd for $C_{22}H_{23}N$ (301.43): C, 87.66; H, 7.69. Found: C, 87.71; H, 7.59.

(*E*)-*N*,*N*-Dimethyl-1-(2-methyl-1*H*-inden-3-yl)-2-phenylethenamine (16)

In the same manner as described for **3**, adduct **16** (0.34 g) was obtained in 95% yield by the reaction of **4** (300 mg, 1.3 mmol) with 40% aq Me_2NH (0.17 mL, 1.5 mmol) in Et_2O (10 mL); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.48 (d, ^3J = 7.4 Hz, 1 H), 7.44 (d, ^3J = 7.6 Hz, 1 H), 7.32 (t, ^3J = 7.6 Hz, 1 H), 7.22 (t, ^3J = 7.4 Hz, 1 H), 7.10–6.91 (group of m, 5 H) {H_{arom}}, 5.66 (s, 1 H, =CH), 3.35 (AB, ^2J = 22.8 Hz, 2 H, CH_2), 2.81 (s, 6 H, NCH_3), 1.80 (s, 3 H, CH_3).

Anal. Calcd for $C_{20}H_{21}N$ (275.39): C, 87.23; H, 7.69. Found: C, 87.30; H, 7.77.

(*E*)-1-(4,7-Dimethyl-1*H*-inden-3-yl)-*N*,*N*-dimethyl-2-phenylethenamine (17)

In the same manner as described for **3**, adduct **17** (0.34 g) was obtained in 98% yield by the reaction of **5** (293 mg, 1.2 mmol) with 40% aq Me_2NH (0.17 mL, 1.5 mmol) in Et_2O (10 mL); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.24 (m, 1 H), 7.12–7.01 (m, 3 H), 6.96 (d, ^3J = 7.6 Hz, 2 H), 6.89 (t, ^3J = 7.2 Hz, 1 H), 6.44 (s, 1 H) {H_{arom}, =CH}, 5.57 (s, 1 H, =C*H*Ph), 3.25 (AB, ^2J = 24.4 Hz, 2 H, CH_2), 2.86 (s, 6 H, NCH_3), 2.52 (s, 3 H), 2.43 (s, 3 H) {CH_3}.

Anal. Calcd for $C_{21}H_{23}N$ (289.41): C, 87.15; H, 8.01. Found: C, 87.22; H, 7.95.

(*E*)-*N*,*N*-Dimethyl-2-phenyl-1-(2,4,7-trimethyl-1*H*-inden-3-yl)ethenamine (18)

In the same manner as described for **3**, adduct **18** (0.30 g) was obtained in 82% yield by the reaction of **6** (310 mg, 1.2 mmol) with 40% aq Me_2NH (0.17 mL, 1.5 mmol) in Et_2O (10 mL); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.11–6.92 (group of m, 7 H, H_{arom}), 5.58 (br s, 1 H, =CH), 3.26 (AB, ^2J = 22.8 Hz, 2 H, CH_2), 2.85 (s, 6 H, NCH_3), 2.47 (s, 3 H), 2.42 (s, 3 H), 1.90 (s, 3 H) {CH_3}.

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 145.6, 143.5, 142.4, 141.4, 140.0, 135.4, 129.7, 128.6 (C=), 129.1, 127.8, 126.5, 125.2, 122.9, 102.1 (=CH), 41.4 (CH_2), 39.5, 18.3, 17.7, 14.5 (CH_3).

Anal. Calcd for $C_{22}H_{25}N$ (303.44): C, 87.08; H, 8.30. Found: C, 87.15; H, 8.33.

(*E*)-*N*,*N*-Diethyl-1-(2-methyl-1*H*-inden-3-yl)-2-phenylethenamine (19)

In the same manner as described for **3**, adduct **19** (0.37 g) was obtained in 93% yield by the reaction of **4** (300 mg, 1.3 mmol) with diethylamine (110 mg, 1.5 mmol) in Et_2O (10 mL); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.50 (d, ^3J = 7.2 Hz, 2 H), 7.34 (t, ^3J = 7.5 Hz, 1 H), 7.24 (t, ^3J = 7.5 Hz, 1 H), 7.08 (m, 2 H), 6.97 (m, 3 H) {H_{arom}}, 5.70 (s, 1 H, =CH), 3.35 (AB, ^2J = 22.6 Hz, 2 H, CH_2), 3.25

(m, 4 H, CH_2CH_3), 1.84 (s, 3 H, CH_3), 1.21 (t, ^3J = 7.2 Hz, CH_2CH_3).

Anal. Calcd for $C_{22}H_{25}N$ (303.44): C, 87.08; H, 8.30. Found: C, 87.18; H, 8.38.

(*E*)-1-(4,7-Dimethyl-1*H*-inden-3-yl)-*N*,*N*-diethyl-2-phenylethenamine (20)

In the same manner as described for **3**, adduct **20** (0.37 g) was obtained in 89% yield by the reaction of **5** (293 mg, 1.2 mmol) with diethylamine (110 mg, 1.5 mmol) in Et_2O (10 mL); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.10–7.02 (group of m, 4 H), 6.96 (d, ^3J = 7.6 Hz, 2 H), 6.89 (t, ^3J = 7.3 Hz, 1 H), 6.40 (br s, 1 H), 5.54 (br s, 1 H) {H_{arom}, =CH}, 3.31 (AB, ^2J = 24.0 Hz, 2 H, CH_2), 3.25 (m, 4 H, CH_2CH_3), 2.50 (s, 3 H), 2.44 (s, 3 H) {CH_3}, 1.17 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 145.0, 143.0, 142.6, 141.9, 140.3, 130.3, 129.7 (C=), 133.6, 129.0, 127.7, 126.9, 126.3, 122.5, 100.1 (=CH), 43.0, 37.0 (CH_2), 18.4, 18.1, 12.7 (CH_3).

Anal.Calcd for $C_{23}H_{27}N$ (317.47): C, 87.02; H, 8.57. Found: C, 87.10; H, 8.67.

(*E*)-*N*,*N*-Diethyl-2-phenyl-1-(2,4,7-trimethyl-1*H*-inden-3-yl)ethenamine (21)

In the same manner as described for **3**, adduct **21** (0.37 g) was obtained in 85% yield by the reaction of **6** (310 mg, 1.2 mmol) with diethylamine (110 mg, 1.5 mmol) in Et_2O (10 mL); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.08–6.87 (group of m, 7 H) {H_{arom}}, 5.58 (s, 1 H, =CH), 3.24 (AB, ^2J = 23.0 Hz, 2 H, CH_2), 3.35–3.19 (group of m, 4 H, CH_2CH_3), 2.49 (s, 3 H), 2.41 (s, 3 H), 1.91 (s, 3 H) {CH_3}, 1.17 (br t, 6 H, CH_2CH_3).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 143.8, 143.7, 142.3, 141.2, 140.5, 135.5, 129.6, 128.6 (C=), 129.1, 127.7, 126.4, 125.2, 122.4, 99.8 (=CH), 43.0, 41.4 (CH_2), 18.3, 18.0, 14.6, 13.0 (CH_3).

Anal. Calcd for $C_{24}H_{29}N$ (331.49): C, 86.96; H, 8.82. Found: C, 87.04; H, 8.88.

(*E*)-*N*-Butyl-1-(2-methyl-1*H*-inden-3-yl)-2-phenylethenamine (22)

In the same manner as described for **3**, adduct **22** (0.32 g) was obtained in 81% yield by the reaction of **4** (300 mg, 1.3 mmol) with *n*-butylamine (110 mg, 1.5 mmol) in Et_2O (10 mL); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.45–7.36 (m, 2 H), 7.27–7.15 (group of m, 5 H), 7.05–6.97 (m, 2 H) {H_{arom}}, 5.61 (s, 1 H, =CH), 3.85 (AB, ^2J = 26.0 Hz, 2 H, CH_2), 3.23 (q, ^3J = 7.0 Hz, 2 H, NCH_2), 1.63 (m, 2 H), 1.35 (m, 2 H) {$CH_2CH_2CH_3$}, 1.52 (s, 3 H, CH_3), 0.87 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3).

Anal. Calcd for $C_{22}H_{25}N$ (303.44): C, 87.08; H, 8.30. Found: C, 82.25; H, 11.68; N, 5.99.

(*E*)-*N*-Butyl-1-(4,7-dimethyl-1*H*-inden-3-yl)-2-phenylethenamine (23)

In the same manner as described for **3**, adduct **23** (0.29 g) was obtained in 76% yield by the reaction of **5** (293 mg, 1.2 mmol) with *n*-butylamine (110 mg, 1.5 mmol) in Et_2O (10 mL); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.35–7.03 (group of m, 8 H) {H_{arom}, =CH}, 5.67 (s, 1 H, =C*H*Ph), 4.09 and 3.77 (AB, ^2J = 13.8 Hz, 2 H, CH_2), 3.26 (q, ^3J = 7.4 Hz, 2 H, NCH_2), 2.38 (s, 3 H), 2.36 (s, 3 H) {CH_3}, 1.50 (m, 2 H), 1.35 (m, 2 H) {$CH_2CH_2CH_3$}, 0.93 (t, ^3J = 6.8 Hz, 3 H, CH_2CH_3).

Anal. Calcd for $C_{23}H_{27}N$ (317.47): C, 87.02; H, 8.57. Found: C, 87.00; H, 8.66.

(*E*)-*N*-Butyl-2-phenyl-1-(2,4,7-trimethyl-1*H*-inden-3-yl)ethenamine (24)

In the same manner as described for **3**, adduct **24** (0.36 g) was obtained in 90% yield by the reaction of **6** (310 mg, 1.2 mmol) with *n*-butylamine (110 mg, 1.5 mmol) in Et_2O (10 mL); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.51 (t, ^3J = 7.4 Hz, 2 H), 7.31 (t, ^3J = 7.4 Hz, 1 H), 7.25–7.20 (m, 2 H), 7.09 (d, ^3J = 7.4 Hz, 1 H), 6.94 (d, ^3J = 7.4 Hz, 2 H) {H_{arom}, =CH}, 3.26 (m, 2 H, NCH_2), 3.11 (AB, ^2J = 14.2 Hz, 2 H, CH_2), 2.31 (s, 3 H), 2.25 (s, 3 H), 2.05 (s, 3 H) {CH_3}, 1.60–1.31 (m, 4 H, $CH_2CH_2CH_3$), 0.97 (t, ^3J = 6.8 Hz, 3 H, CH_2CH_3).

Anal. Calcd for $C_{24}H_{29}N$ (331.49): C, 86.96; H, 8.82. Found: C, 87.00; H, 8.90.

1-[(*E*)-1-(2-Methyl-1*H*-inden-3-yl)-2-phenylethenyl]pyrrolidine (25)

In the same manner as described for **3**, adduct **25** (0.34 g) was obtained in 81% yield by the reaction of **4** (300 mg, 1.3 mmol) with pyrrolidine (107 mg, 1.5 mmol) in Et_2O (10 mL); yellow oil.

^{1}H NMR ($CDCl_3$): δ = 7.50 (d, ^3J = 7.3 Hz, 1 H), 7.39 (d, ^3J = 7.2 Hz, 1 H), 7.33 (dd, ^3J = 7.2, 8.2 Hz, 1 H), 7.24 (dd, ^3J = 7.3, 8.2 Hz, 1 H), 7.08–6.98 (group of m, 4 H), 6.90 (t, ^3J = 7.0 Hz, 1 H) {H_{arom}}, 5.54 (s, 1 H, =CH), 3.41 (AB, ^2J = 22.8 Hz, 2 H, CH_2), 3.25 (m, 4 H, NCH_2CH_2), 1.95 (m, 4 H, NCH_2CH_2), 1.92 (s, 3 H, CH_3).

Anal. Calcd for $C_{22}H_{23}N$ (301.43): C, 87.66; H, 7.69. Found: C, 87.58; H, 7.77.

1-[(*E*)-1-(4,7-Dimethyl-1*H*-inden-3-yl)-2-phenylethenyl]pyrrolidine (26)

In the same manner as described for **3**, adduct **26** (0.35 g) was obtained in 92% yield by the reaction of **5** (293 mg, 1.2 mmol) with pyrrolidine (107 mg, 1.5 mmol) in Et_2O (10 mL); yellow-brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.11–7.01 (m, 6 H), 6.91 (t, ^3J = 7.2 Hz, 1 H) {H_{arom}}, 6.43 (t, ^3J = 2.0 Hz, 1 H), 5.39 (s, 1 H) {=CH}, 3.35 (AB, ^2J = 24.0 Hz, 2 H, CH_2), 3.27 (m, 4 H, NCH_2CH_2), 2.48 (s, 3 H), 2.47 (s, 3 H) {CH_3}, 1.96 (m, 4 H, NCH_2CH_2).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 144.1, 143.1, 142.5, 142.0, 140.2, 130.4, 129.3 (C=), 132.2, 129.0, 127.8, 126.4, 126.26, 122.2, 98.6 (=CH), 47.8, 37.0, 25.3 (CH_2), 18.3, 17.4 (CH_3).

Anal. Calcd for $C_{23}H_{25}N$ (315.45): C, 87.57; H, 7.99. Found: C, 87.50; H, 8.05.

1-[(*E*)-2-Phenyl-1-(2,4,7-trimethyl-1*H*-inden-3-yl)ethenyl]pyrrolidine (27)

In the same manner as described for **3**, adduct **27** (0.38 g) was obtained in 98% yield by the reaction of **6** (310 mg, 1.2 mmol) with pyrrolidine (107 mg, 1.5 mmol) in Et_2O (10 mL); colorless crystals, mp 82 °C.

^{1}H NMR ($CDCl_3$): δ = 7.05–6.92 (m, 6 H), 6.84 (m, 1 H) {H_{arom}}, 5.35 (s, 1 H, =C*H*Ph), 3.24 (AB, ^2J = 24.0 Hz, 2 H, CH_2), 3.24–3.15 (m, 4 H, NCH_2), 2.38 (s, 6 H), 1.92 (s, 3 H) {CH_3}, 1.91 (m, 4 H, NCH_2CH_2).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 143.0, 142.9, 141.3, 141.1, 140.3, 136.2, 129.7, 128.2 (C=), 128.9, 127.8, 125.8, 125.1, 122.1, 98.9 (=CH), 47.5, 41.3, 25.3 (CH_2), 18.3, 17.3, 14.3 {CH_3}.

Anal. Calcd for $C_{24}H_{27}N$ (329.48): C, 87.49; H, 8.26. Found: C, 87.44; H, 8.33.

1-[(*E*)-1-(2-Methyl-1*H*-inden-3-yl)-2-phenylethenyl]piperidine (28)

In the same manner as described for **3**, adduct **28** (0.39 g) was obtained in 95% yield by the reaction of **4** (300 mg, 1.3 mmol) with piperidine (128 mg, 1.5 mmol) in Et_2O (10 mL); yellow-brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.57 (d, ^3J = 7.5 Hz, 1 H), 7.45 (d, ^3J = 7.2 Hz, 1 H), 7.31 (dd, ^3J = 7.5, 8.4 Hz, 1 H), 7.20 (dd, ^3J = 7.2, 8.4 Hz, 1 H), 7.10–6.97 (group of m, 5 H) {H_{arom}}, 5.77 (s, 1 H, =CH), 3.31 (AB, ^2J = 23.0 Hz, 2 H, CH_2), 3.06 (m, 4 H, NCH_2), 1.75 (s, 3 H, CH_3), 1.63 (m, 6 H, $NCH_2CH_2CH_2$).

Anal. Calcd for $C_{23}H_{25}N$ (315.45): C, 87.57; H, 7.99. Found: C, 87.64; H, 7.91.

1-[(*E*)-1-(4,7-Dimethyl-1*H*-inden-3-yl)-2-phenylethenyl]piperidine (29)

In the same manner as described for **3**, adduct **29** (0.37 g) was obtained in 94% yield by the reaction of **5** (293 mg, 1.2 mmol) with piperidine (128 mg, 1.5 mmol) in Et_2O (10 mL); yellow-brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.11–7.03 (m, 6 H), 6.96 (t, ^3J = 7.2 Hz, 1 H) {H_{arom}}, 6.37 (t, ^3J = 2.0 Hz, 1 H) 5.72 (s, 1 H) {=CH}, 3.30 (AB, ^2J = 23.6 Hz, 2 H, CH_2), 3.11 (m, 4 H, NCH_2CH_2), 2.59 (s, 3 H), 2.45 (s, 3 H) {CH_3}, 1.63 (m, 6 H, $NCH_2CH_2CH_3$).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 147.7, 143.3, 142.5, 142.2, 139.7, 130.1, 129.9 (C=), 134.3, 129.1, 127.7, 127.4, 126.1, 123.4, 104.4 (=CH), 48.6, 36.9, 25.9, 24.5 (CH_2), 18.5, 18.31 (CH_3).

Anal. Calcd for $C_{24}H_{27}N$ (329.48): C, 87.49; H, 8.26. Found: C, 87.42; H, 8.32.

1-[(*E*)-2-Phenyl-1-(2,4,7-trimethyl-1*H*-inden-3-yl)ethenyl]piperidine (30)

In the same manner as described for **3**, adduct **30** (0.38 g) was obtained in 92% yield by the reaction of **6** (310 mg, 1.2 mmol) with piperidine (128 mg, 1.5 mmol) in Et_2O (10 mL); yellow-brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.09–7.03 (m, 2 H), 7.01–6.94 (m, 4 H), 6.87 (d, ^3J = 7.4 Hz, 1 H) {H_{arom}}, 5.59 (s, 1 H, =CH), 3.34–3.17 (m, 4 H, NCH_2), 3.05 (AB, ^2J = 23.8 Hz, 2 H, CH_2), 2.35 (s, 3 H), 2.27 (s, 3 H), 2.02 (s, 3 H) {CH_3}, 1.69 (m, 6 H).

Anal. Calcd for $C_{25}H_{29}N$ (343.50): C, 87.41; H, 8.51. Found: C, 87.49; H, 8.44.

4-[(*E*)-1-(2-Methyl-1*H*-inden-3-yl)-2-phenylethenyl]morpholine (31)

In the same manner as described for **3**, adduct **31** (0.35 g) was obtained in 85% yield by the reaction of **4** (300 mg, 1.3 mmol) with morpholine (131 mg, 1.5 mmol) in Et_2O (10 mL); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.11–7.01 (m, 6 H), 6.91 (d, ^3J = 7.2 Hz, 1 H) {H_{arom}}, 6.43 (t, ^3J = 2.0 Hz, 1 H) 5.39 (s, 1 H) {=CH}, 3.35 (AB, ^2J = 24.0 Hz, 2 H, CH_2), 3.27 (m, 4 H, NCH_2CH_2), 2.48 (s, 3 H), 2.47 (s, 3 H) {CH_3}, 1.96 (m, 4 H, NCH_2CH_2).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 144.1, 143.1, 142.5, 142.0, 140.2, 130.4, 129.3 (C=), 132.2, 129.0, 127.8, 126.4, 126.26, 122.2, 98.6 (=CH), 47.8, 37.0, 25.3 (CH_2), 18.3, 17.4 (CH_3).

Anal. Calcd for $C_{22}H_{23}NO$ (317.42): C, 83.24; H, 7.30. Found: C, 83.30; H, 11.73.

4-[(*E*)-1-(4,7-Dimethyl-1*H*-inden-3-yl)-2-phenylethenyl]morpholine (32)

In the same manner as described for **3**, adduct **32** (0.39 g) was obtained in 98% yield by the reaction of **5** (293 mg, 1.2 mmol) with morpholine (131 mg, 1.5 mmol) in Et_2O (10 mL); yellow crystals; mp 112 °C.

^{1}H NMR ($CDCl_3$): δ = 7.09–6.94 (m, 7 H) {H_{arom}}, 6.33 (t, ^3J = 2.0 Hz, 1 H) 5.71 (s, 1 H) {=CH}, 3.73 (m, 4 H, CH_2O), 3.27 (AB, ^2J = 23.4 Hz, ^3J = 2.0 Hz, 2 H, CH_2), 3.13–2.98 (m, 4 H, NCH_2), 2.55 (s, 3 H), 2.39 (s, 3 H) {CH_3}.

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 148.1, 143.3, 142.2, 141.4, 138.9, 130.4, 129.8 (C=), 134.9, 127.9, 127.6, 126.4, 124.1, 105.5 (=CH), 67.0, 48.2, 37.0 (CH_2), 18.5, 18.4 (CH_3).

Anal. Calcd for $C_{23}H_{25}NO$ (331.45): C, 83.34; H, 7.60. Found: C, 83.26; H, 11.74.

4-[(*E*)-2-Phenyl-1-(2,4,7-trimethyl-1*H*-inden-3-yl)ethenyl]morpholine (33)

In the same manner as described for **3**, adduct **33** (0.40 g) was obtained in 96% yield by the reaction of **6** (336 mg, 1.3 mmol) with morpholine (131 mg, 1.5 mmol) in Et_2O (10 mL); yellow crystals; mp 134 °C.

^{1}H NMR ($CDCl_3$): δ = 7.14–7.07 (m, 5 H), 7.02 (m, 2 H) {H_{arom}}, 5.84 (s, 1 H, =CH), 3.78 (m, 4 H, OCH_2), 3.28 (AB, ^2J = 23.1 Hz, 2 H, CH_2), 3.19–3.03 (m, 4 H, NCH_2), 2.61 (s, 3 H), 2.42 (s, 3 H), 1.88 (s, 3 H) {CH_3}.

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 145.7, 143.5, 143.3, 141.3, 138.9, 134.4, 129.6, 128.6 (C=), 129.2, 127.8, 127.1, 125.3, 124.0, 106.3 (=CH), 66.9, 47.7, 41.4 (CH_2), 18.4, 18.3, 14.6 (CH_3).

Anal. Calcd for $C_{24}H_{27}NO$ (345.48): C, 83.44; H, 7.88. Found: C, 83.40; H, 7.95.

3-[(*E*)-1-Ethoxy-2-phenylethenyl]-2-methyl-1*H*-indene (34)

In the same manner as described for **8**, adduct **34** (0.34 g) was obtained in 95% yield by the reaction of **4** (300 mg, 1.3 mmol) with EtONa (102 mg, 1.5 mmol) in EtOH (10 mL); dark brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.44 (d, ^3J = 7.4 Hz, 1 H), 7.37 (d, ^3J = 7.6 Hz, 1 H), 7.30 (dd, ^3J = 7.6, 8.6 Hz, 1 H), 7.20 (dd, ^3J = 7.4, 8.6 Hz, 1 H), 7.18–7.04 (group of m, 5 H) {H_{arom}}, 6.13 (s, 1 H, =CH), 4.07 (q, ^3J = 7.1 Hz, 2 H, OCH_2), 3.36 (AB, 2 H, CH_2), 1.81 (s, 3 H, CH_3), 1.45 (t, ^3J = 7.1 Hz, 3 H, CH_2CH_3).

Anal. Calcd for $C_{20}H_{20}O$ (276.37): C, 86.92; H, 7.29. Found: C, 86.85; H, 7.36.

3-[(*E*)-1-Ethoxy-2-phenylethenyl]-4,7-dimethyl-1*H*-indene (35)

In the same manner as described for **8**, adduct **35** (0.41 g) was obtained in 89% yield by the reaction of **5** (318 mg, 1.3 mmol) with EtONa (102 mg, 1.5 mmol) in EtOH (10 mL); dark brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.85 (d, ^3J = 7.6 Hz, 1 H), 7.45–7.03 (group of m, 6 H) {H_{arom}}, 6.51 (br s, 1 H), 6.01 (s, 1 H) {=CH}, 3.90 (q, ^3J = 7.0 Hz, 2 H, OCH_2), 3.36 (AB, br, 2 H, CH_2), 2.57 (s, 3 H), 2.44 (s, 3 H) {CH_3}, 1.49 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3).

Anal. Calcd for $C_{21}H_{22}O$ (290.40): C, 86.85; H, 7.64. Found: C, 86.80; H, 7.71.

3-[(*E*)-1-Ethoxy-2-phenylethenyl]-2,4,7-trimethyl-1*H*-indene (36)

In the same manner as described for **8**, adduct **36** (0.30 g) was obtained in 71% yield by the reaction of **6** (362 mg, 1.4 mmol) with EtONa (109 mg, 1.6 mmol) in EtOH (10 mL); red-brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.26–7.10 (group of m, 5 H), 7.06 (d, ^3J = 7.5 Hz, 1 H), 6.97 (d, ^3J = 7.5 Hz, 1 H) {H_{arom}}, 6.05 (s, 1 H, =CH), 4.15–3.95 (group of m, 2 H, OCH_2), 3.25 (AB, ^2J = 23.0 Hz, 2 H, CH_2), 2.51 (s, 3 H), 2.38 (s, 3 H), 1.87 (s, 3 H) {CH_3}, 1.45 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3).

Anal. Calcd for $C_{22}H_{24}O$ (304.43): C, 86.80; H, 7.95. Found: C, 86.79; H, 8.04.

3-[(*E*)-1-(*tert*-Butylsulfanyl)-2-phenylethenyl]-2-methyl-1*H*-indene (37)

In the same manner as described for **9**, adduct **37** (0.36 g) was obtained in 86% yield by the reaction of **4** (322 mg, 1.4 mmol) with *t*-BuSNa (168 mg, 1.5 mmol) in Et_2O (10 mL) and THF (2 mL); red-brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.62–7.13 (group of m, 10 H) {H_{arom}, =CH}, 3.33 (AB, 2 H, CH_2), 1.88 (s, 3 H, CH_3), 1.36 [s, 9 H, $C(CH_3)_3$].

Anal. Calcd for $C_{22}H_{24}S$ (320.49): C, 82.45; H, 7.55. Found: C, 82.55; H, 7.47.

3-[(*E*)-1-(*tert*-Butylsulfanyl)-2-phenylethenyl]-4,7-dimethyl-1*H*-indene (38)

In the same manner as described for **9**, adduct **38** (0.36 g) was obtained in 77% yield by the reaction of **5** (342 mg, 1.4 mmol) with *t*-BuSNa (168 mg, 1.5 mmol) in Et_2O (10 mL) and THF (2 mL); brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.27–7.14 (group of m, 6 H), 7.04 (m, 2 H), 6.35 (t, ^3J = 2.2 Hz, 1 H) {H_{arom}, =CH}, 3.31 (AB, ^2J = 24.2 Hz, 2 H, CH_2), 2.58 (s, 3 H), 2.41 (s, 3 H) {CH_3}, 1.41 [s, 9 H, $C(CH_3)_3$].

Anal. Calcd for $C_{23}H_{26}S$ (334.52): C, 82.58; H, 7.83. Found: C, 82.66; H, 7.77.

3-[(*E*)-1-(*tert*-Butylsulfanyl)-2-phenylethenyl]-2,4,7-trimethyl-1*H*-indene (39)

In the same manner as described for **9**, adduct **39** (0.30 g) was obtained in 71% yield by the reaction of **6** (362 mg, 1.4 mmol) with *t*-BuSNa (168 mg, 1.5 mmol) in Et_2O (10 mL) and THF (2 mL) brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.27–7.14 (group of m, 5 H), 7.07 (s, 1 H), 7.04 (d, ^3J = 7.7 Hz, 1 H), 6.96 (d, ^3J = 7.7 Hz, 1 H) {H_{arom}, =CH}, 3.23 (AB, ^2J = 22.9 Hz, 2 H, CH_2), 2.63 (s, 3 H), 2.37 (s, 3 H), 1.94 (s, 3 H) {CH_3}, 1.44 [s, 9 H, $C(CH_3)_3$].

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 142.9, 141.3, 140.4, 137.9, 137.2, 133.3, 129.5, 128.7 (C=), 134.1, 129.4, 128.2, 127.9, 126.7, 125.4 (=CH), 46.8, 41.6 (CH_2 and C), 31.2, 19.0, 18.3, 15.3 (CH_3).

Anal. Calcd for $C_{24}H_{28}S$ (348.55): C, 82.70; H, 8.10. Found: C, 82.77; H, 8.07.

Diethyl (*E*)-1-(2-Methyl-1*H*-inden-3-yl)-2-phenylethenylphosphonate (40)

In the same manner as described for **10**, adduct **40** (0.39 g) was obtained in 81% yield by the reaction of **4** (300 mg, 1.3 mmol) with diethyl phosphite (221 mg, 1.6 mmol) and NaH (34 mg, 1.4 mmol) in Et_2O (20 mL); red-brown oil.

^{1}H NMR ($CDCl_3$): δ = 7.84–7.16 (group of m, 10 H) {H_{arom}, =CH}, 4.16 (qd, ^3J = 17.3 Hz, 4 H, OCH_2CH_3), 3.15 (AB, ^2J = 18.0 Hz, 2 H, CH_2), 2.03 (d, ^3J = 4.0 Hz, 3 H, CH_3), 1.33 (t, ^3J = 6.9 Hz, 3 H, CH_2CH_3), 1.27 (t, ^3J = 6.9 Hz, 3 H, CH_2CH_3).

Anal. Calcd for $C_{22}H_{25}O_3P$ (368.41): C, 71.72; H, 6.84. Found: C, 82.25; H, 11.68.

Diethyl (*E*)-1-(4,7-Dimethyl-1*H*-inden-3-yl)-2-phenylethenylphosphonate (41)

In the same manner as described for **10**, adduct **41** (0.44 g) was obtained in 96% yield by the reaction of **5** (318 mg, 1.3 mmol) with diethyl phosphite (221 mg, 1.6 mmol) and NaH (34 mg, 1.4 mmol) in Et_2O (20 mL); yellow oil.

^{1}H NMR ($CDCl_3$): δ = 7.65 (d, ^3J = 25.8 Hz, 1 H), 7.35 (d, ^3J = 7.6 Hz, 2 H), 7.24–7.18 (m, 3 H), 6.97 (d, ^3J = 7.6 Hz, 1 H), 6.92 (d, ^3J = 7.6 Hz, 1 H), 6.43 (m, 1 H) {H_{arom}, =CH}, 4.24–4.06 (m, 4 H, OCH_2CH_3), 3.40 (m, 2 H, CH_2), 2.41 (s, 3 H), 2.34 (s, 3 H) {C_{ind}-CH_3}, 1.35 (t, ^3J = 7.1 Hz, 3 H), 1.23 (t, ^3J = 7.1 Hz, 3 H) {CH_2CH_3}.

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 142.9, 141.1 (d), 139.7 (d), 135.0 (d), 130.2, 129.5, 128.6 (C=), 143.3 (d), 132.4 (d), 130.0, 129.2, 129.1, 128.4, 126.2 (=CH), 62.2 (d), 62.1 (d) {OCH_2}, 37.3 (CH_2), 18.5, 18.3, 16.2 (d), 16.1 (d) (CH_3).

^{31}P NMR ($CDCl_3$): δ = 7.71.

Anal. Calcd for $C_{23}H_{27}O_3P$ (382.43): C, 72.23; H, 7.12. Found: C, 72.33; H, 11.72.

Diethyl (*E*)-2-Phenyl-1-(2,4,7-trimethyl-1*H*-inden-3-yl)ethenylphosphonate (42)

In the same manner as described for **10**, adduct **42** (0.40 g) was obtained in 84% yield by the reaction of **6** (362 mg, 1.4 mmol) with diethyl phosphite (221 mg, 1.6 mmol) and NaH (36 mg, 1.5 mmol) in Et_2O (20 mL); yellow oil.

^{1}H NMR ($CDCl_3$): δ = 7.70 (d, ^3J = 25.0 Hz, 1 H), 7.45–6.80 (group of m, 7 H) {H_{arom}, =CH}, 4.24–4.06 (m, 4 H, OCH_2CH_3), 3.34 (AB, ^2J = 23.0 Hz, 2 H, CH_2), 2.45 (s, 3 H), 2.39 (s, 3 H), 2.05 (d, ^4J = 4.3 Hz, 3 H) {C_{ind}-CH_3}, 1.34 (t, ^3J = 6.6 Hz, 3 H), 1.28 (t, ^3J = 6.6 Hz, 3 H) {CH_2CH_3}.

Anal. Calcd for $C_{24}H_{29}O_3P$ (396.46): C, 72.71; H, 7.37. Found: C, 72.79; H, 7.44.

(1-Cyclopenten-1-ylethynyl)benzene (44)

In the same manner as described for **1**, compound **44** (22.2 g) was obtained in 66% yield by the reaction of cyclopentanone (16.8 g, 0.20 mol) with PhC≡CMgBr (0.30 mol) in Et_2O (200 mL) with subsequent dehydration (PTSA/Et_2O, 6 h); pale-yellow liquid; bp 56–58 °C/0.1 Torr.

^{1}H NMR ($CDCl_3$): δ = 7.50 (m, 3 H), 7.33 (m, 2 H) {C_6H_5}, 6.20 (m, 1 H, =CH), 2.60 (m, 2 H), 2.52 (m, 2 H), 1.99 (m, 2 H) {CH_2}.

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 137.7, 131.3, 128.1, 127.9 (=CH), 124.4, 123.5 (C=), 90.3, 86.7 (C≡C), 36.3, 33.3, 23.3 (CH_2).

Anal. Calcd for $C_{13}H_{12}$ (168.23): C, 92.81; H, 7.19. Found: C, 92.84; H, 7.16.

4-(Phenylethynyl)-1,2-dihydronaphthalene (45)

In the same manner as described for **1**, compound **45** (0.37 g) was obtained in 78% yield by the reaction of 1-tetralone (29.2 g, 0.20 mmol) with PhC≡CMgBr (0.30 mmol) in Et_2O (200 mL) with subsequent dehydration (PTSA/Et_2O, 2 h); pale-yellow liquid; bp 126–130 °C/0.1 Torr.

^{1}H NMR ($CDCl_3$): δ = 7.90–7.20 (group of m 9 H) {H_{arom}}, 6.66 (t, ^3J = 4.9 Hz, 1 H, =CH), 2.93 (t, ^3J = 8.0 Hz, 4 H, CH_2), 2.93 (tt, ^3J = 8.0, 4.9 Hz, 4 H, CH_2CH=).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 134.8, 132.4, 123.2, 121.5 (C=), 135.2, 131.3, 128.1, 128.0, 127.4, 127.1, 126.3, 124.8 (=CH), 90.0, 87.1 (C≡C), 26.9, 23.4 (CH_2).

Anal. Calcd for $C_{18}H_{14}$ (230.30): C, 93.87; H, 6.13;. Found: C, 82.25; H, 11.68.

1,1-Dimethyl-3-(phenylethynyl)-1*H*-indene (46)

In the same manner as described for **1**, compound **46** (10.3 g) was obtained in 42% yield by the reaction of 3,3-dimethylindan-1-one (16.0 g, 0.1 mol) with PhC≡CMgBr (0.15 mol) in Et_2O (100 mL) with subsequent dehydration (PTSA/Et_2O, 2 h). The product was purified by column chromatography (hexane); pale-yellow crystals; mp 74 °C.

^{1}H NMR ($CDCl_3$): δ = 7.61 (m, 2 H), 7.58 (d, ^3J = 7.4 Hz, 1 H), 7.41–7.30 (group of m, 6 H) {H_{arom}}, 6.72 (s, 1 H, =CH), 1.41 (s, 6 H, CH_3).

^{13}C{^{1}H} NMR ($CDCl_3$): δ = 152.3, 141.5, 123.2, 122.4 (C=), 150.9, 131.7, 128.4, 126.8, 126.0, 121.1, 120.6 (=CH), 92.8, 83.3 (C≡), 49.4 (C), 24.4 (CH_3).

Anal. Calcd for $C_{19}H_{16}$ (244.33): C, 93.40; H, 6.60. Found: C, 93.45; H, 6.55.

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