Benzotriazole-Assisted Aromatic Ring Annulation: Efficient and General Syntheses of Polysubstituted Naphthalenes and Phenanthrenes

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(Benzotriazol-1-ylmethyl)benzenes and -naphthalenes **1a**−**f**, easily accessible from benzyl bromides and benzotriazole, readily undergo lithiation and subsequent 1,4-addition to α,*β*-unsaturated aldehydes and ketones. Intramolecular cyclization of the products, induced by acetic acid−hydrobromic acid or polyphosphoric acid (PPA), followed by simultaneous dehydration and debenzotriazolylation furnishes a wide range of polysubstituted naphthalenes **7a**−**f** and of phenanthrenes **9** and **11** in moderate to good yields in one-pot procedures. If compounds **1** are first lithiated and reacted with electrophiles, the resulting alkylation products undergo similar annulation reactions with α,*β*-unsaturated carbonyl compounds to provide the more highly substituted naphthalenes **6a**,**b** and phenanthrenes **10a**,**b** in moderate overall yields.

Introduction

Highly substituted naphthalenes and phenanthrenes are common features of numerous biologically significant natural products and pharmaceuticals,[1] and improved methods for their construction are highly desired.[2] The most important reported annulation routes to naphthalenes include the following: (i) Diels−Alder reactions of benzynes,[2d,f,3−5] *o*-quinodimethanes,[2ah,6] isobenzofurans,[7] and isoquinolinium salts;[8] however, in many cases either the diene or the dienophile must be symmetrical in order to control the regiochemistry; (ii) Michael addition of α-carbanions of benzene derivatives followed by intramolecular cyclization with an ester group at the *ortho* position,[9−11] which is most useful for the preparation of naphthols with electron-withdrawing substituents, especially COR and CO_2R groups; (iii) condensations of *β*-metallo derivatives of protected propanals [MCH_2CH_2-$CH(OR)_2$] with aromatic aldehydes followed by cyclization with dilute sulfuric acid,[2g,12] which are limited by the availability of annulating reagents; (iv) other annulation methods, which include an elegant tandem conjugate addition−aldol reaction, followed by an acid-catalyzed construction of the naphthalene ring,[2e] and an anionic annulation *via o*-allylbenzamides.[13]

The most important routes to phenanthrenes include (i) Diels−Alder reactions of naphthynes,[2i,k] (ii) palladium-catalyzed cyclocarbonylation of 3-naphthylallyl acetates,[2l] and (iii) intramolecular C−C coupling of 2,2′-dialkoxystilbenes with low-valent titanium.[2j] All require the synthesis of functionalized substrates to facilitate the annulation step.

Benzotriazole-assisted syntheses of a wide range of useful organic compounds have blossomed in our laboratory due to the unique properties of the benzotriazolyl group as both a good anion-stabilizing group and a good leaving group.[14] Recently, we have demonstrated that 1-benzylbenzotriazoles **1** can undergo lithiation and the resulting anions react with aldehydes and ketones followed by $ZnBr_2$-assisted rearrangement to furnish one-carbon chain-extended or ring-expanded α-aryl alkyl ketones.[15] We now report that 1-benzylbenzotriazoles and 1-(naphthylmethyl)benzotriazoles **1** can function as 1,3-dipole synthons in Michael addition−cyclization routes to provide a wide range of polysubstituted naphthalenes (**6** and **7**) and phenanthrenes (**9**−**11**).

Results and Discussion

Preparation of 1-Benzylbenzotriazoles and 1-(Naphthylmethyl)benzotriazoles 1 and *in Situ* Preparation and Reactions with α,*β*-Unsaturated Carbonyl Compounds of Their Lithio Derivatives. 1-(4-Methylbenzyl)benzotriazole (**1a**),[16] 1-benzylbenzotriazole

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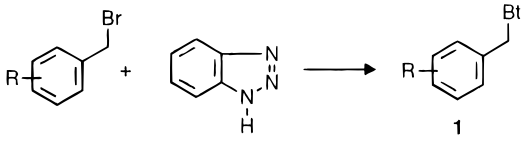
Scheme 1



1	a	b	c	d	e	f
R	*p*-Me	H	*p*-MeO	*m*-MeO	C_4H_4[a]	C_4H_4[b]

[a] 1-(Naphth-1-ylmethyl)benzotriazole

[b] 1-(Naphth-2-ylmethyl)benzotriazole

(**1b**),[16] and 1-(4-methoxybenzyl)benzotriazole (**1c**)[17] were synthesized according to previously reported procedures. 1-(3-Methoxybenzyl)benzotriazole (**1d**), 1-(naphth-1-ylmethyl)benzotriazole (**1e**), and 1-(naphth-2-ylmethyl)benzotriazole (**1f**) were prepared in good yields from the reaction of the corresponding benzyl and naphthylmethyl halides with benzotriazole (Scheme 1). All of these benzotriazole derivatives can be easily prepared on a large scale.

Due to the electron-withdrawing ability of the benzotriazolyl group, compounds **1** can be easily lithiated. Accordingly, lithio derivatives of **1a**−**f** were prepared *in situ* as deep green solutions in THF under argon by stirring compounds **1** with *n*-butyllithium at −78 °C for *ca.* 30 min, which readily underwent 1,4-addition with a variety of α,*β*-unsaturated aldehydes and ketones. As an example, treatment of the lithio derivative of **1a** with chalcone at −78 °C for 2 h and then 20 °C overnight provided the expected 1,4-addition product **4a** in 62% yield (Scheme 2), accompanied by the formation of the corresponding 1,2-addition product (25%). Both the 1,4-addition product **4a** and the 1,2-addition product, 1,3-diphenyl-3-hydroxy-4-(benzotriazol-1-yl)-4-(4-methylphenyl)butene-1, were isolated and characterized.

Synthesis of Polysubstituted Naphthalenes 6 and 7. For the preparation of naphthalenes, it is not necessary to separate the intermediates **4**, and the transformation can be accomplished in one pot. Accordingly, the intermediates **4** thus produced were shown in each case to be capable of *in situ* cyclization assisted by acetic acid and hydrobromic acid (for **7a**−**d)** or polyphosphoric acid (for **7e** and **7f**) to provide a wide variety of polysubstituted naphthalenes **7** regiospecifically in moderate to good yields. The reason for the use of PPA instead of acetic acid and hydrobromic acid in the cases of **7e** and **7f** is to avoid the demethylation of the methyl ether moiety present in the molecules by hydrobromic acid. The formation of naphthalenes **7** is envisaged to proceed *via* Michael addition of the anions of **1** to α,*β*-unsaturated carbonyl compounds to form intermediates **2**, which are then protonated to the ketones **4**. Acid-promoted cyclization of **4** followed by concurrent dehydration and debenzotriazolylation afforded the desired products **7**.

Significantly, additional substituents can be readily introduced into the 4-positions of the products (Scheme 2). Thus, as examples, the lithio derivative of **1a** was first reacted with alkyl halides. The intermediates **3** thus produced, without separation, were treated with butyllithium followed by α,*β*-unsaturated carbonyl compounds. The resulting addition products upon exposure to acetic acid and hydrobromic acid cyclized and aromatized to

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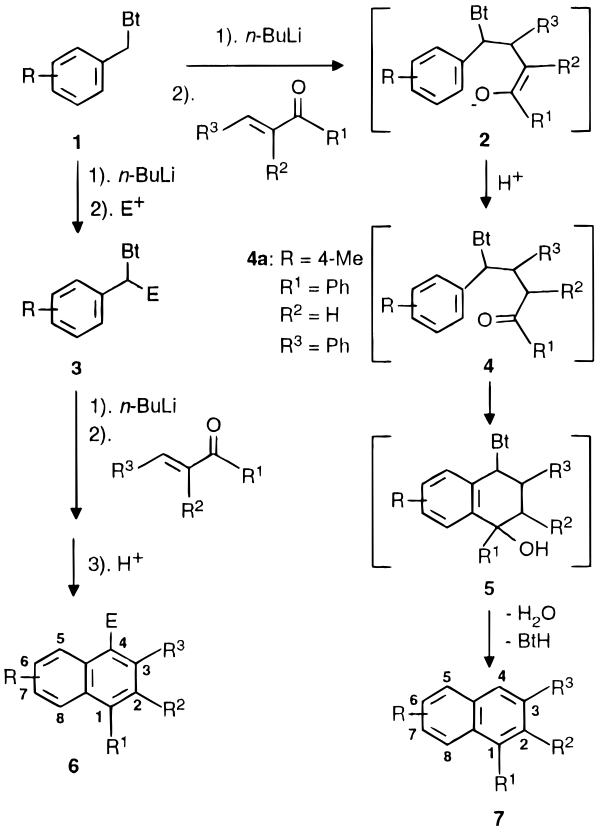
Scheme 2

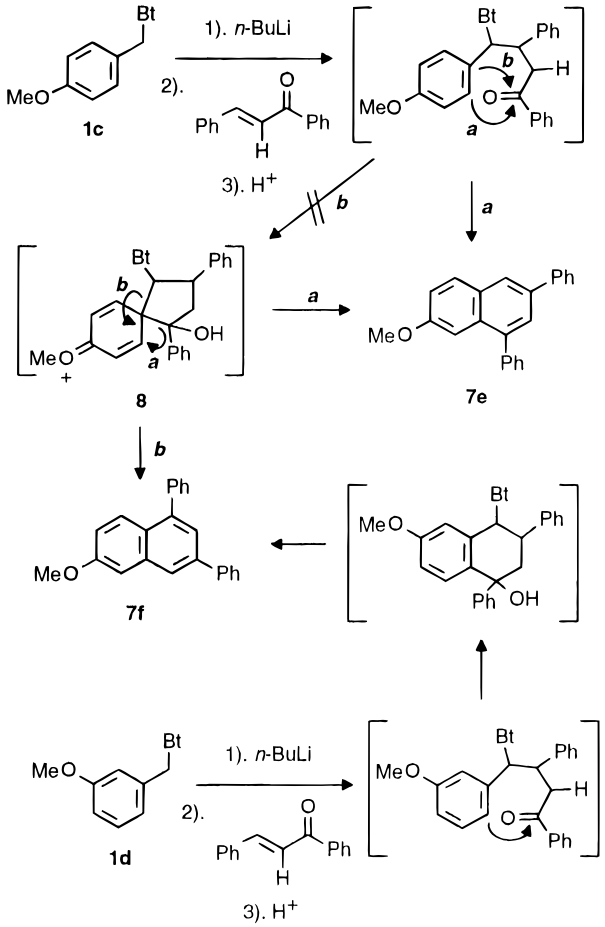


6,7	E	R	R^1	R^2	R^3
7a	-	7-Me	Me	H	Ph
7b	-	7-Me	Ph	H	Ph
7c	-	H	Me	H	Ph
7d	-	7-Me	H	Ph	Et
7e	-	7-MeO	Ph	H	Ph
7f	-	6-MeO	Ph	H	Ph
6a	Me	7-Me	Ph	H	Ph
6b	Et	7-Me	Ph	H	Ph

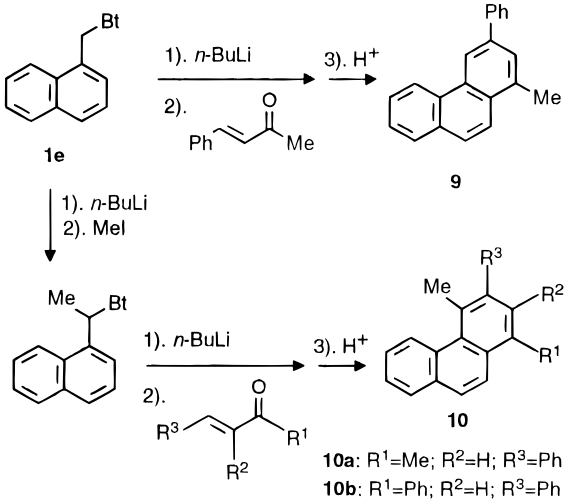
naphthalenes **6a** and **6b** in 40% and 33% overall yields starting from **1a**.

When (benzotriazol-1-ylmethyl)benzenes with *para*-electron-donating substituents such as **1a** and **1c** are used as substrates, two possible cyclization pathways exist. As exemplified by the reaction of **1c** with chalcone (Scheme 3), the ring closure of the resulting ketone could have occurred directly at the 2-position to give naphthalene **7e** or first at the more reactive 1-position to give the corresponding spiro intermediate cation **8**, followed by the migration of either the ***a*** or ***b*** bond to give two regioisomers **7e** and **7f**. However, the single isomer **7e** was obtained. The other expected regioisomer **7f** was not detected, indicating that the direct C2 ring closure might be operative under the present reaction conditions. However, while we view the spiro intermediate **8** as unlikely, it cannot be ruled out as an intermediate to **7e** from the available information. Discrimination between structures **7e** and **7f** was accomplished by the successful preparation of **7f** from the reaction of 1-(3-methoxybenzyl)benzotriazole (**1d**) with chalcone (Scheme 3). In this case, the methoxy group caused the 2-position to be more reactive than the 1-position, leading unambiguously to the directly cyclized product **7f**.

Scheme 3

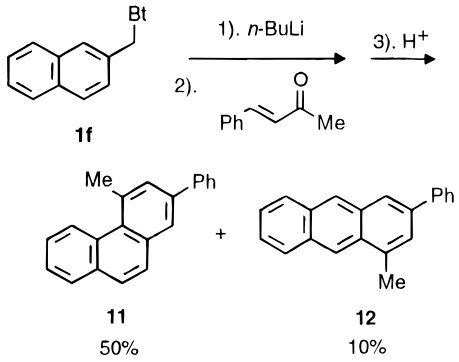


Scheme 4



Synthesis of Polysubstituted Phenanthrenes. Following a similar protocol, polysubstituted phenanthrenes can be readily accessed by the annulation of (benzotriazol-1-ylmethyl)naphthalenes with α,β-unsaturated aldehydes and ketones. Accordingly, as an example, reaction of the anion of **1e** with 4-phenyl-3-buten-2-one, followed by HOAc−HBr-induced cyclization and subsequent aromatization, furnished disubstituted phenanthrene **9** in 41% yield (Scheme 4). If **1e** is first lithiated and alkylated, the alkylation products can undergo similar annulation reactions with α,β-unsaturated carbonyl compounds to afford trisubstituted phenanthrenes **10a** and **10b** in *ca.* 40% overall yields starting from **1e**.

Scheme 5



Substituted phenanthrenes can also be prepared from 2-(benzotriazol-1-ylmethyl)naphthalene (**1f**) as exemplified by the annulation of **1f** with 4-phenyl-3-buten-2-one (Scheme 5). However, in this case, cyclization could occur at both 1- and 3-positions, leading to a mixture of two possible products 1-methyl-3-phenylphenanthrene (**11**) and 1-methyl-3-phenylanthracene (**12**) with phenanthrene **11** largely predominant. Compounds **11** and **12** were separated in 50% and 10% yields, respectively, and identified by their NMR spectra and elemental analyses. A 1H doublet at 8.9 ppm (5-proton) in the ^{1}H NMR spectrum of compound **11** is characteristic of the phenanthrene system.

Conclusion

The aromatic ring annulation of (benzotriazol-1-ylmethyl)benzenes and (benzotriazol-1-ylmethyl)naphthalenes **1** with α,β-unsaturated carbonyl compounds *via* Michael addition−acidic cyclization sequences thus presents a general, simple and efficient protocol for the construction of polysubstituted naphthalenes and phenanthrenes. An attractive feature of this methodology is that by appropriate choice of α,β-unsaturated aldehydes and ketones, as well as benzyl halides, it makes readily available a wide range of polysubstituted naphthalenes and phenanthrenes. Naphthalenes (**6a**,**b** and **7a**−**f**) and phenanthrenes (**9**, **10a**,**b**, and **11**) prepared in the present work are novel except **7a** and **7f**. Compounds **7a** and **7f** were prepared previously *via* the acidic rearrangement of the suitably substituted 4*H*-pyran derivatives,[18] which themselves were available only by multistep synthesis.

Experimental Section

General Methods. Melting points were determined with a hot-stage apparatus and are uncorrected. NMR spectra were taken in $CDCl_3$ with tetramethylsilane as the internal standard for ^{1}H (300 MHz) or solvent as the internal standard for ^{13}C (75 MHz). Tetrahydrofuran was distilled under nitrogen immediately prior to use from sodium/benzophenone. All reactions with air-sensitive compounds were carried out under an argon atmosphere. Column chromatography was conducted with silica gel 230−400 mesh. 1-(4-Methylbenzyl)benzotriazole (**1a**),[16] 1-benzylbenzotriazole (**1b**),[16] and 1-(4-methoxybenzyl)benzotriazole (**1c**)[17] were prepared according to previously reported procedures.

Preparation of 1-Benzylbenzotriazole 1d and 1-(Naphthylmethyl)benzotriazoles 1e and 1f. General Procedure. To a solution of an appropriate benzyl chloride or naphthylmethyl chloride (50 mmol) in toluene (100 mL) was added benzotriazole (55 mmol). The mixture was refluxed for 48 h and then washed with sodium hydroxide (2 N, 60 mL) to

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remove the excess benzotriazole. To the organic layer was added hydrochloric acid (25%) until no product remained in the organic layer based on TLC. The aqueous layer was neutralized with NaOH (10 N) until pH ≈ 5. The solid was filtered and dissolved in CH_2Cl_2 (60 mL). The solution was washed with water (50 mL) and dried over $MgSO_4$. Removal of the solvent gave pure compound **1**.

1-(3-Methoxybenzyl)benzotriazole (1d): yield 81%; mp 54−55 °C; ^{1}H NMR δ 8.06 (d, J = 8.1 Hz, 1H), 7.41−7.22 (m, 4H), 6.88−6.80 (m, 3H), 5.81 (s, 2H), 3.74 (s, 3H); ^{13}C NMR δ 160.0, 146.3, 136.2, 132.8, 130.0, 127.3, 123.8, 120.0, 119.7, 113.8, 113.2, 109.7, 55.2, 52.1. Anal. Calcd for $C_{14}H_{13}N_3O$: C, 70.28; H, 5.48; N, 17.56. Found: C, 70.65; H, 5.51; N, 17.65.

1-(Naphth-1-ylmethyl)benzotriazole (1e): yield 80%; mp 149−150 °C; ^{1}H NMR δ 8.19 (d, J = 8.1 Hz, 1H), 8.05−8.02 (m, 1H), 7.87−7.82 (m, 2H), 7.54−7.46 (m, 2H), 7.43−7.38 (m, 1H), 7.30−7.25 (m, 4H), 6.28 (s, 2H); ^{13}C NMR δ 146.3, 133.8, 133.1, 131.1, 129.9, 129.5, 128.8, 127.3, 127.0, 126.7, 126.2, 125.1, 123.8, 122.9, 120.0, 110.0, 50.8. Anal. Calcd for $C_{17}H_{13}N_3$: C, 78.74; H, 5.05; N, 16.20. Found: C, 78.51; H, 5.03; N, 16.25.

1-(Naphth-2-ylmethyl)benzotriazole (1f): yield 75%; mp 150−151 °C; ^{1}H NMR δ 8.06 (d, J = 6.9 Hz, 1H), 7.76−7.72 (m, 4H), 7.47−7.43 (m, 2H), 7.33−7.28 (m, 4H), 5.94 (s, 2H); ^{13}C NMR δ 146.2, 133.0, 132.9, 132.7, 132.0, 128.9, 127.7, 127.6, 127.3, 126.6, 126.5, 126.4, 124.9, 123.8, 119.9, 109.7, 52.3. Anal. Calcd for $C_{17}H_{13}N_3$: C, 78.74; H, 5.05; N, 16.20. Found: C, 78.36; H, 5.10; N, 16.32.

Reaction of 1-(4-Methylbenzyl)benzotriazole (1a) with Chalcone. Preparation of 1,3-Diphenyl-4-benzotriazol-1-yl-4-(4-methylphenyl)butan-1-one (4a) and 1,3-Diphenyl-3-hydroxy-4-benzotriazol-1-yl-4-(4-methylphenyl)-butene-1. To a solution of 1-(4-methylbenzyl)benzotriazole (**1a**) (1.12 g, 5 mmol) in THF (80 mL) at −78 °C under argon was added *n*-BuLi (2.2 mL, 2.5 M in hexane, 5.5 mmol). After 1 h, chalcone (1.1 g, 5.5 mmol) in THF (10 mL) was added. The reaction mixture was stirred at −78 °C for an additional 2 h and then allowed to warm to room temperature overnight. Water (60 mL) and Et_2O (80 mL) were added to the mixture, and the organic layer was separated. The aqueous layer was extracted with Et_2O (2×50 mL) and the combined organic extracts were dried over $MgSO_4$. After the solvent was removed, the crude mixture was separated by column chromatography (ethyl acetate:hexanes = 1:5) to give pure **4a** and 1,3-diphenyl-3-hydroxy-4-benzotriazol-1-yl-4-(4-methylphenyl)-butene-1.

1,3-Diphenyl-4-benzotriazol-1-yl-4-(4-methylphenyl)-butan-1-one (4a): yield 62%; mp 187−188 °C; ^{1}H NMR δ 8.02 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 7.1 Hz, 2H), 7.53−7.40 (m, 3H), 7.38−7.28 (m, 3H), 7.25−7.03 (m, 7H), 6.94 (d, J = 7.9 Hz, 2H), 6.19 (d, J = 10.1 Hz, 1H), 4.91 (dt, J = 10.1 and 3.5 Hz, 1H), 3.61 (dd, J = 16.8 and 10.1 Hz, 1H), 3.31 (dd, J = 16.8 and 3.5 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR δ 197.9, 145.9, 139.9, 137.8, 136.8, 134.1, 133.3, 132.9, 129.1 (2C), 128.4 (4C), 128.3 (2C), 128.0 (2C), 127.6 (2C), 127.4, 127.0, 124.0, 119.9, 109.8, 67.3, 46.0, 41.6, 21.0. Anal. Calcd for $C_{29}H_{25}N_3O$: C, 80.72; H, 5.84; N, 9.74. Found: C, 80.66; H, 5.89; N, 9.78.

1,3-Diphenyl-3-hydroxy-4-benzotriazol-1-yl-4-(4-methylphenyl)butene-1: yield 25%; mp 229−230 °C; ^{1}H NMR δ 7.92 (d, J = 8.5 Hz, 1H), 7.54 (d, J = 7.4 Hz, 2H), 7.42−7.37 (m, 4H), 7.29−7.04 (m, 11H), 6.47 (s, 2H), 6.33 (s, 1H), 5.57 (s, 1H), 2.27 (s, 3H); ^{13}C NMR δ 144.7, 143.7, 138.3, 136.7, 133.3, 131.9, 131.7, 130.8, 129.0 (2C), 128.8 (2C), 128.4 (2C), 128.3 (2C), 127.8, 127.6, 127.1, 126.6 (2C), 124.9 (2C), 124.2, 120.0, 109.2, 80.2, 69.3, 21.1. Anal. Calcd for $C_{29}H_{25}N_3O$: C, 80.72; H, 5.84; N, 9.74. Found: C, 80.49; H, 5.56; N, 9.41.

General Procedure for the Preparation of Naphthalenes 7a−f, Phenanthrenes 9 and 11, and Anthracene 12. To a solution of an appropriate 1-benzylbenzotriazole or 1-(naphthylmethyl)benzotriazole **1** (5 mmol) in THF (80 mL) at −78 °C under argon was added *n*-BuLi (2.2 mL, 2.5 *M* in hexane, 5.5 mmol). After 1 h, the appropriate α,β-unsaturated aldehyde or ketone (5.5 mmol) in THF (10 mL) was added. The reaction mixture was stirred at −78 °C for an additional 2 h and then allowed to warm to room temperature overnight. After the THF was distilled off under argon, (*i*) *glacial acetic acid (30 mL) and hydrobromic acid (48% in water, 30 mL) were added. The mixture was refluxed under argon overnight. On cooling, the mixture was extracted with CH_2Cl_2 (4 × 50 mL). The extract was washed subsequently with NaOH (2 N, 60 mL) and H_2O (60 mL) and dried over $MgSO_4$ (for **7a**-**d**, **9**, **11** and **12**); (ii) PPA (15 g) was added. The mixture was heated at 70 °C overnight and poured into ice−water (30 mL). The mixture then was extracted with $CHCl_3$ (4 × 40 mL). The combined organic layer was washed subsequently with H_2O (60 mL), NaOH (2 N, 60 mL), and H_2O (60 mL) and dried over $MgSO_4$ (for **7e** and **7f**).* After the solvent was evaporated, the residue was purified by column chromatography to give the pure product.

1,7-Dimethyl-3-phenylnaphthalene (7a). Hexane was used as the eluent to give the pure compound: yield 54%; mp 40−41 °C; ^{1}H NMR δ 7.84 (s, 1H), 7.78−7.74 (m, 2H), 7.69 (d, J = 7.1 Hz, 2H), 7.55 (s, 1H), 7.47−7.42 (m, 2H), 7.35−7.30 (m, 2H), 2.70 (s, 3H), 2.54 (s, 3H); ^{13}C NMR δ 141.3, 137.3, 135.4, 134.1, 132.1, 132.0, 128.7 (2C), 128.6, 128.2, 127.3 (2C), 127.1, 126.4, 124.0, 123.1, 22.1, 19.5. Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.84; H, 7.09.

1,3-Diphenyl-7-methylnaphthalene (7b). Hexane was used as the eluent to give the pure compound: yield 49%; mp 100−101 °C; ^{1}H NMR δ 7.97 (s, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.67−7.65 (m, 4H), 7.53−7.36 (m, 7H), 7.31−7.25 (m, 2H), 2.38 (s, 3H); ^{13}C NMR δ 141.0 (2C), 140.1, 137.1, 135.8, 132.4, 131.0, 130.1 (2C), 128.8 (2C), 128.5 (2C), 128.3 (2C), 127.3 (2C), 127.2 (2C), 126.8, 125.2, 124.7, 21.9. Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 94.31; H, 6.36.

1-Methyl-3-phenylnaphthalene (7c). Hexane was used as the eluent to give the pure compound: yield 41%; mp 62−63 °C (lit.[18] mp 67−68 °C); ^{1}H NMR δ 8.00−7.97 (m, 1H), 7.89−7.86 (m, 2H), 7.71 (d, J = 7.1 Hz, 2H), 7.58 (s, 1H), 7.51−7.43 (m, 4H), 7.38−7.32 (m, 1H), 2.73 (s, 3H); ^{13}C NMR δ 141.2, 138.2, 134.8, 133.9, 131.8, 128.8 (3C), 127.4 (2C), 127.2, 126.3, 126.0, 125.8, 124.2, 124.0, 19.5.

2-Ethyl-3-phenyl-6-methylnaphthalene (7d). Hexane was used as the eluent to give the pure compound: yield 55%; mp 52−53 °C; ^{1}H NMR δ 7.72 (d, J = 8.5 Hz, 1H), 7.69 (s, 1H), 7.58 (s, 1H), 7.55 (s, 1H), 7.43−7.36 (m, 5H), 7.29 (d, J = 8.5 Hz, 1H), 2.74 (q, J = 7.5 Hz, 2H), 2.49 (s, 3H), 1.13 (t, J = 8.5 Hz, 3H); ^{13}C NMR δ 142.0, 140.7, 139.1, 134.9, 132.0, 131.3, 129.4 (2C), 128.1, 128.0 (3C), 126.9, 126.8, 126.5, 126.2, 26.5, 21.7, 15.2. Anal. Calcd for $C_{19}H_{18}$: C, 92.64; H, 7.36. Found: C, 92.30; H, 7.52.

1,3-Diphenyl-7-methoxynaphthalene (7e). Hexane:methylene chloride (6:1) was used as the eluent to give the pure compound: yield 75%; mp 117−118 °C (lit.[18] mp 117−118 °C); ^{1}H NMR δ 7.98 (s, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.73−7.67 (m, 3H), 7.57−7.41 (m, 7H), 7.36−7.31 (m, 1H), 7.23−7.16 (m, 2H), 3.75 (s, 3H); ^{13}C NMR δ 157.9, 141.0 (2C), 139.6, 135.9, 132.0, 130.1, 129.9 (2C), 129.7, 128.8 (2C), 128.4 (2C), 127.3 (2C), 127.2 (2C), 127.1, 125.2, 118.7, 104.5, 55.2. Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 89.08; H, 5.87.

1,3-Diphenyl-6-methoxynaphthalene (7f). Hexane:methylene chloride (6:1) was used as the eluent to give the pure compound: yield 69%; oil; ^{1}H NMR δ 7.78 (s, 1H), 7.66 (d, J = 9.3 Hz, 1H), 7.56 (d, J = 7.1 Hz, 2H), 7.41−7.14 (m, 9H), 7.06 (d, J = 2.5 Hz, 1H), 6.92 (dd, J = 9.3, 2.5 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR δ 157.8, 141.0, 140.8 (2C), 138.6, 135.5, 130.0 (2C), 128.8 (2C), 128.3 (2C), 127.5, 127.4 (2C), 127.3 (2C), 126.3, 124.5, 124.3, 118.7, 106.4, 55.2. Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 89.20; H, 5.91.

1-Methyl-3-phenylphenanthrene (9). Hexane was used as the eluent to give the pure compound: yield 41%; mp 124−125 °C; ^{1}H NMR δ 8.69 (s, 1H), 8.67 (d, J = 9.4 Hz, 1H), 7.83−7.77 (m, 2H), 7.72−7.70 (m, 2H), 7.66−7.58 (m, 2H), 7.55−7.49 (m, 2H), 7.47−7.41 (m, 2H), 7.35−7.30 (m, 1H), 2.67 (s, 3H); ^{13}C NMR δ 141.6, 138.7, 135.2, 131.9, 130.7, 130.6, 129.9, 128.8 (2C), 128.5, 127.5 (2C), 127.2, 127.1, 126.7, 126.5, 126.4, 122.9, 122.6, 119.2, 20.0. Anal. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 93.83; H, 6.05.

2-Phenyl-4-methylphenanthrene (11). Hexane was used as the eluent to give the pure compound: yield 50%; mp 143−144 °C; ^{1}H NMR δ 8.91 (d, J = 7.9 Hz, 1H), 7.97 (d, J = 2.2 Hz, 1H), 7.91 (dd, J = 7.9 and 2.2 Hz, 1H), 7.78−7.73 (m, 5H),

7.65−7.56 (m, 2H), 7.52−7.47 (m, 2H), 7.41−7.21 (m, 1H), 3.20 (s, 3H); ^{13}C NMR δ 140.5, 138.2, 136.1, 134.2, 133.5, 131.5, 130.3, 129.2, 128.9 (2C), 128.8, 128.2, 127.5, 127.4, 127.3 (3C), 125.8, 125.7, 125.4, 27.5. Anal. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01. Found: C, 93.95; H, 6.03.

1-Methyl-3-phenylanthracene (12). Hexane was used as the eluent to give the pure compound: yield 10%; mp 102−103 °C; ^{1}H NMR δ 7.77 (d, J = 9.0 Hz, 1H), 7.67 (s, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.64−7.34 (m, 6H), 7.28 (s, 1H), 7.07 (t, J = 7.8 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR δ 145.3, 140.4, 135.2, 133.8, 133.1, 132.5, 130.4, 129.0 (2C), 128.9 (2C), 128.3, 128.1, 127.9, 127.6, 127.2, 127.0, 126.4, 125.5, 124.8, 21.1; HRMS calcd for $C_{21}H_{16}$ 268.1252 (M^+), found 268.1249.

General Procedure for the Preparation of Naphthalenes 6a,b and Phenanthrenes 10a,b. To a solution of an appropriate 1-benzylbenzotriazole or 1-(naphthylmethyl)benzotriazole **1** (5 mmol) in THF (80 mL) at −78 °C under argon was added *n*-BuLi (2.1 mL, 2.5 M in hexane, 5.5 mmol). After 1 h, methyl iodide (for **6a** and **10a**,**b**) or ethyl iodide (for **6b**) (6.5 mmol) was added, and the mixture was stirred at −78 °C for 2 h. The THF and an excess amount of MeI or EtI were evaporated under vaccum, and the residue was again dissolved in THF (80 mL). To the solution at −78 °C under argon was added *n*-BuLi (2.2 mL, 2.5 M in hexane, 5.5 mmol). After 1 h, the appropriate α,β-unsaturated ketone in THF (10 mL) was added. The reaction mixture was stirred at −78 °C for an additional 2 h and then allowed to warm to room temperature overnight. After the THF was distilled off under argon, glacial acetic acid (30 mL) and hydrobromic acid (48% in water, 30 mL) were added. The mixture was refluxed under argon overnight. On cooling, the mixture was extracted with CH_2Cl_2 (4 × 50 mL). The extract was washed subsequently with NaOH (2 N, 60 mL) and H_2O (60 mL) and dried over $MgSO_4$. After the solvent was evaporated, the residue was purified by column chromatography using hexane as the eluent to give the pure product.

1,6-Dimethyl-2,4-diphenylnaphthalene (6a): yield 46%; mp 140−141 °C; ^{1}H NMR δ 8.06 (d, J = 8.7 Hz, 1H), 7.73 (s, 1H), 7.53−7.34 (m, 12H), 2.64 (s, 3H), 2.44 (s, 3H); ^{13}C NMR δ 142.6, 141.0, 137.8, 137.4, 135.2, 131.5, 131.0, 130.2 (2C), 130.1, 129.9 (2C), 129.5, 128.3, 128.2 (2C), 128.0 (2C), 127.0, 126.7, 125.5, 124.7, 21.7, 16.4. Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.05; H, 6.78.

1-Ethyl-2,4-diphenyl-6-methylnaphthalene (6b): yield 33%; oil; ^{1}H NMR δ 8.08 (d, J = 8.6 Hz, 1H), 7.73 (s, 1H), 7.52−7.33 (m, 11H), 7.27 (s, 1H), 3.04 (q, J = 7.5 Hz, 2H), 2.43 (s, 3H), 1.28 (t, J = 7.5 Hz, 3H); ^{13}C NMR δ 142.8, 141.0, 137.5, 137.3, 136.6, 135.0, 131.6, 130.3, 130.2 (2C), 129.6, 129.4 (2C), 128.2 (3C), 128.0 (2C), 127.0, 126.7, 125.7, 124.8, 22.6, 21.7, 16.0; HRMS calcd for $C_{25}H_{22}$: 322.1721 (M^+), found 322.1735.

1,4-Dimethyl-2-phenylphenanthrene (10a): yield 37%; mp 114−115 °C; ^{1}H NMR δ 8.78 (d, J = 6.3 Hz, 1H), 7.94−7.89 (m, 2H), 7.74 (d, J = 8.9 Hz, 1H), 7.58−7.55 (m, 2H), 7.49−7.36 (m, 6H), 2.88 (s, 3H), 2.74 (s, 3H); ^{13}C NMR δ 143.3, 142.4, 133.5, 131.9, 131.7, 131.6, 131.4, 130.4, 130.0 (2C), 129.7, 128.6, 128.3, 128.2 (2C), 126.9, 126.8, 125.9, 124.8, 123.0, 24.7, 20.0. Anal. Calcd for $C_{22}H_{18}$: C, 93.58; H, 6.42. Found: C, 93.65; H, 6.46.

1-Methyl-2,4-diphenylphenanthrene (10b): yield 40%; mp 126−127 °C; ^{1}H NMR δ 8.82−8.79 (m, 1H), 7.89−7.85 (m, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.62−7.37 (m, 14H), 2.96 (s, 3H); ^{13}C NMR δ 143.0, 142.3, 141.1, 138.4, 133.5, 132.0, 131.9, 131.3, 130.4 (3C), 130.0 (2C), 129.5, 128.6, 128.2 (5C), 127.2, 127.0, 126.8, 126.1, 125.0, 124.9, 24.8. Anal. Calcd for $C_{27}H_{20}$: C, 94.15; H, 5.85. Found: C, 94.17; H, 5.93.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **6b** and **12** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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